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Metal-free directed C–H bond activation and borylation

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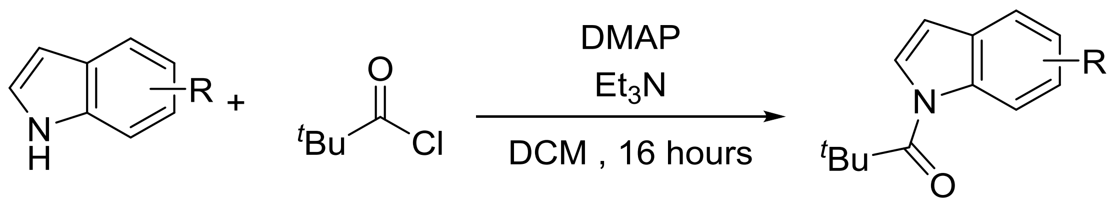
1. General information.

All reactions were carried out in flame-dried 25 mL Schlenk tubes with Teflon screw caps under argon. BBr_3 (1 M in DCM) was purchased from TCI. BBr_3 (99.9%) was purchased from Energy Chemical. Unless otherwise stated, the concentration of BBr_3 used in all experiments was 1M in DCM. Other reagents and solvents were directly used from the supplier without further purification unless noted. All new compounds were fully characterized. NMR-spectra were recorded on Bruker AV-300, ARX-400 MHz or a ARX-600 Associated. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26) if collected in $CDCl_3$. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.00). ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI).

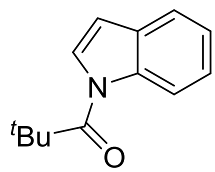
2. Synthesis of substrates

2.1 General procedure for the synthesis of *N*-pivaloyl indoles.



Pivaloyl chloride (1.2 equiv) was added dropwise to a solution of indole (1.0 equiv), DMAP (0.1 equiv) and triethylamine (1.5 equiv) in anhydrous CH_2Cl_2 (0.6 M) at 0 ℃. The solution was stirred for 16 hours at room temperature. After this time, the reaction mixture was evaporated to dryness under reduced pressure. The crude was portioned between Et_2O and saturated aqueous NH_4Cl. The two layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude residue was purified by column chromatography to afford the desired *N*-pivaloyl indoles.

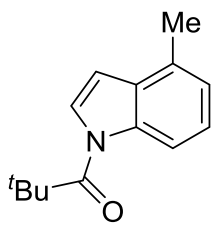
1-(1*H*-Indol-1-yl)-2,2-dimethylpropan-1-one (1a)[1]



1a

Following the general procedure on 10.0 mmol scale, the substrate **1a** was obtained as a white solid in 88.2% yield (1.8 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 3.8 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.39 – 7.35 (m, 1H), 7.32 – 7.24 (m, 1H), 6.63 (dd, *J* = 3.8, 0.8 Hz, 1H), 1.53 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 136.7, 129.3, 125.6, 125.0, 123.5, 120.4, 117.3, 108.2, 41.2, 28.6; **ATR-FTIR (cm^{-1})** 2980, 1692, 1448, 907 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{16}NO^+$ $(M + H)^+$ 202.1226, found 202.1225.

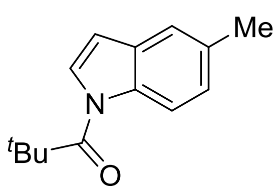
2,2-Dimethyl-1-(4-methyl-1*H*-indol-1-yl)propan-1-one (2a)[1]



2a

Following the general procedure on 3.0 mmol scale, the substrate **2a** was obtained as a white solid in 91.0% yield (586.7 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.42 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 3.9 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 3.9 Hz, 1H), 2.57 (s, 3H), 1.55 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 136.5, 129.8, 128.9, 125.2, 125.1, 123.9, 114.8, 106.5, 41.2, 28.7, 18.5; **ATR-FTIR (cm^{-1})** 2898, 1693, 1459, 1168, 980, 454 cm^{-1}; **HRMS m/z (ESI)** called for $C_{14}H_{18}NO^+$ $(M + H)^+$ 216.1383, found 216.1380.

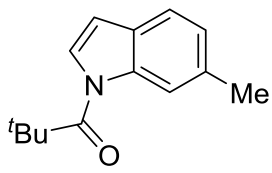
2,2-Dimethyl-1-(5-methyl-1*H*-indol-1-yl)propan-1-one (3a)[2]



3a

Following the general procedure on 3.0 mmol scale, the substrate **3a** was obtained as a white solid in 88.0% yield (568.0 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 3.8 Hz, 1H), 7.35 (dt, *J* = 1.8, 0.9 Hz, 1H), 7.17 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.55 (dd, *J* = 3.8, 0.7 Hz, 1H), 2.45 (s, 3H), 1.52 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.9, 134.9, 133.0, 129.6, 126.4, 125.7, 120.4, 116.9, 108.0, 41.1, 28.7, 21.3; **ATR-FTIR (cm^{-1})** 3019, 1728, 1516, 1128, 993cm^{-1}; **HRMS m/z (ESI)** called for $C_{14}H_{18}NO^+$ $(M + H)^+$ 216.1383, found 216.1378.

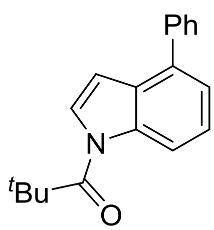
2,2-Dimethyl-1-(6-methyl-1*H*-indol-1-yl)propan-1-one (4a)[3]



4a

Following the general procedure on 3.0 mmol scale, the substrate **4a** was obtained as a white solid in 70.1% yield (451.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.41 – 8.40 (m, 1H), 7.67 (d, *J* = 3.9 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.12 (ddd, *J* = 7.9, 1.5, 0.7 Hz, 1H), 6.58 (dd, *J* = 3.8, 0.8 Hz, 1H), 2.50 (s, 3H), 1.53 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 137.2, 135.2, 127.1, 125.1, 125.0, 120.0, 117.6, 108.2, 41.2, 28.7, 22.0; **ATR-FTIR (cm^{-1})** 3020, 1788, 1546, 1218, 993cm^{-1}; **HRMS m/z (ESI)** called for $C_{14}H_{18}NO^{+}$ $(M + H)^{+}$ 216.1383, found 216.1380.

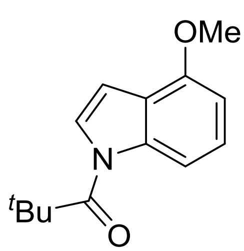
2,2-Dimethyl-1-(4-phenyl-1*H*-indol-1-yl)propan-1-one (5a)



5a

Following the general procedure on 1.0 mmol scale, the substrate **5a** was obtained as a white solid in 80.0% yield (222.4 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.56 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 3.9 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.38 (m, 4H), 7.34 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 1.55 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.1, 140.3, 137.1, 134.4, 128.9, 128.6, 127.5, 127.2, 125.9, 125.4, 123.6, 116.3, 107.4, 41.3, 28.7; **ATR-FTIR (cm^{-1})** 3019, 1718, 1546, 1128, 998cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{20}NO^{+}$ $(M + H)^{+}$ 278.1539, found 278.1539.

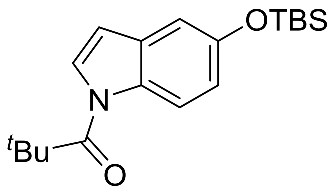
1-(4-Methoxy-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (6a)[1]



6a

Following the general procedure on 5.0 mmol scale, the substrate **6a** was obtained as a white solid in 92.1% yield (1.1 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 3.9 Hz, 1H), 7.28 (t, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 3.8, 0.8 Hz, 1H), 6.72 (dd, *J* = 8.0, 0.6 Hz, 1H), 3.94 (s, 3H), 1.52 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 152.6, 138.0, 126.0, 124.1, 119.6, 110.4, 105.1, 103.9, 55.4, 41.3, 28.7; **ATR-FTIR (cm^{-1})** 2978, 1693, 1362, 1168, 745, 424 cm^{-1}; **HRMS m/z (ESI)** called for $C_{14}H_{18}NO_{2}^{+}$ $(M + H)^{+}$ 232.1332, found 232.1335.

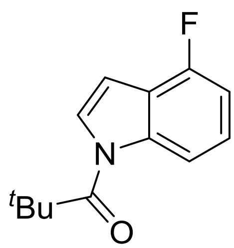
1-(5-((*Tert*-butyldimethylsilyl)oxy)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (7a)



7a

Following the general procedure on 5.0 mmol scale, the substrate **7a** was obtained as a colorless oil in 45.0% yield (747.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.38 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 3.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.52 (d, *J* = 3.8 Hz, 1H), 1.51 (s, 9H), 1.01 (s, 9H), 0.21 (s, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 152.0, 131.9, 130.4, 126.1, 118.3, 117.8, 110.6, 108.0, 41.0, 28.7, 25.7, 18.2, -4.5; **ATR-FTIR (cm^{-1})** 2988, 1703, 1262, 1118, 745, 424 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{30}NO_2Si^+$ $(M + H)^+$ 332.2040, found 332.2045.

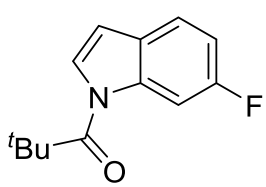
1-(4-Fluoro-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (8a)



8a

Following the general procedure on 3.0 mmol scale, the substrate **8a** was obtained as a white solid in 82.0% yield (541.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 3.9 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.94 – 6.89 (m, 1H), 6.69 (dd, *J* = 3.9, 0.7 Hz, 1H), 1.48 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 155.6 (d, *J* = 247.5 Hz), 138.8 (d, *J* = 9.1 Hz), 125.8 (d, *J* = 7.3 Hz), 125.5, 118.2 (d, *J* = 22.1 Hz), 113.3 (d, *J* = 3.9 Hz), 108.8 (d, *J* = 18.4 Hz), 103.7, 41.2, 28.6; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -122.54; **ATR-FTIR (cm^{-1})** 3735, 2978, 1693, 1362, 1168, 745, 424 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{15}FNO^+$ $(M + H)^+$ 220.1132, found 220.1135.

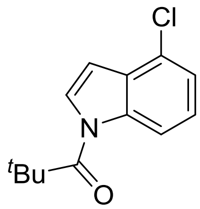
1-(6-Fluoro-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (9a)[2]



9a

Following the general procedure on 3.0 mmol scale, the substrate **9a** was obtained as a colorless oil in 78.0% yield (510.8 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.28 (dd, *J* = 10.9, 2.4 Hz, 1H), 7.72 (d, *J* = 3.9 Hz, 1H), 7.46 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.59 (d, *J* = 3.8 Hz, 1H), 1.52 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 161.3 (d, *J* = 240.1 Hz), 136.9 (d, *J* = 13.1 Hz), 126.0 (d, *J* = 4.0 Hz), 125.6 (d, *J* = 2.0 Hz), 120.8 (d, *J* = 9.9 Hz), 111.7 (d, *J* = 24.4 Hz), 107.9, 104.7 (d, *J* = 29.0 Hz), 41.2, 28.5; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -116.86; **ATR-FTIR (cm^{-1})** 2924, 1697, 1475, 1170, 903 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{15}FNO^+$ $(M + H)^+$ 220.1132, found 220.1133.

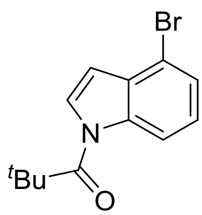
1-(4-Chloro-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (10a)[1]



10a

Following the general procedure on 3.0 mmol scale, the substrate **10a** was obtained as a yellow solid in 75.0% yield (531.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.44 – 8.36 (m, 1H), 7.75 (d, *J* = 3.9 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.73 (dd, *J* = 3.9, 0.7 Hz, 1H), 1.50 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 137.4, 128.1, 126.2, 125.7, 123.3, 115.8, 106.2, 41.3, 28.6; **ATR-FTIR (cm^{-1})** 2983, 1701, 1419, 1305, 1171, 889, 753 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{15}ClNO^+$ $(M + H)^+$ 236.0837, found 236.0835.

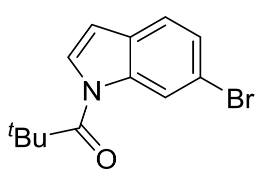
1-(4-Bromo-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (11a)[1]



11a

Following the general procedure on 3.0 mmol scale, the substrate **11a** was obtained as a white solid in 87.0% yield (730.8 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.48 – 8.46 (m, 1H), 7.78 (d, *J* = 3.9 Hz, 1H), 7.43 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 1H), 6.70 (dd, *J* = 3.9, 0.8 Hz, 1H), 1.52 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.1, 137.0, 130.0, 126.4, 126.2, 126.0, 116.3, 114.4, 107.9, 41.3, 28.6; **ATR-FTIR (cm^{-1})** 3029, 1688, 1546, 1138, 990 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{15}BrNO^+$ $(M + H)^+$ 280.0332, found 280.0333.

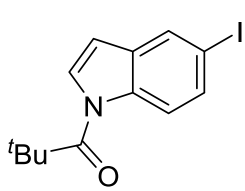
1-(6-Bromo-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (12a)



12a

Following the general procedure on 3.0 mmol scale, the substrate **12a** was obtained as a white solid in 78.0% yield (655.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.74 – 8.75 (m, 1H), 7.71 (d, *J* = 3.9 Hz, 1H), 7.42 – 7.36 (m, 2H), 6.58 (dd, *J* = 3.9, 0.8 Hz, 1H), 1.51 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 137.3, 128.1, 126.7, 126.1, 121.4, 120.4, 118.8, 108.0, 41.2, 28.5; **ATR-FTIR (cm^{-1})** 2924, 1693, 1423, 1315, 1190, 871, 705 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{15}BrNO^+$ $(M + H)^+$ 280.0332, found 280.0337.

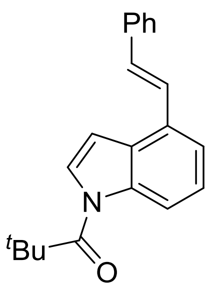
1-(5-Iodo-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (13a)[4]



13a

Following the general procedure on 1.0 mmol scale, the substrate **13a** was obtained as a white solid in 81.0% yield (265.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.28 – 8.26 (m, 1H), 7.89 (d, *J* = 1.7 Hz, 1H), 7.70 (d, *J* = 3.9 Hz, 1H), 7.61 (dd, *J* = 8.8, 1.8 Hz, 1H), 6.54 (dd, *J* = 3.9, 0.7 Hz, 1H), 1.51 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 136.0, 133.5, 131.7, 129.3, 126.3, 119.1, 107.1, 87.6, 41.3, 28.6; **ATR-FTIR (cm^{-1})** 2965, 1699, 1262, 1118, 745, 424 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{15}INO^+$ (M + H)$^+$ 328.0193, found 328.0193.

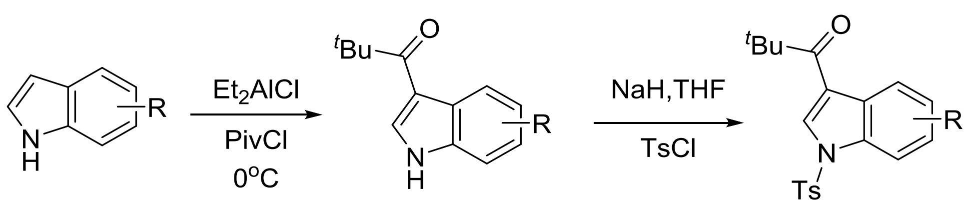
(*E*)-2,2-Dimethyl-1-(4-styryl-1*H*-indol-1-yl)propan-1-one (14a)[5]



14a

Following the general procedure on 3.0 mmol scale, the substrate **14a** was obtained as a white solid in 76.0% yield (693.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.39 – 8.37 (m, 1H), 7.70 (d, *J* = 3.9 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.39 (d, *J* = 16.3 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.23 – 7.11 (m, 2H), 6.81 (dd, *J* = 3.9, 0.8 Hz, 1H), 1.45 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 137.5, 137.1, 130.1, 129.5, 128.7, 127.9, 127.7, 126.5, 125.8, 125.6, 125.3, 120.1, 116.5, 106.2, 41.3, 28.7; **ATR-FTIR (cm^{-1})** 2929, 1696, 1477, 1307, 904, 794 cm^{-1}; **HRMS m/z (ESI)** called for $C_{21}H_{22}NO^+$ (M + H)$^+$ 304.1696, found 304.1691.

2.2 General procedure for the synthesis of 2,2-Dimethyl-1-(1-tosyl-1*H*-indol-3-yl)propan-1-one

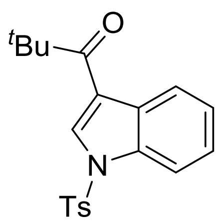


To a solution of indole (5.0 mmol) in 10 mL CH_2Cl_2 was added Et_2AlCl (10.0 mL, 1.0 M in hexane, 10.0 mmol) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 30 minutes. To this solution was added dropwise trimethylacetyl chloride (0.92 mL, 7.5 mmol) at 0 ℃. The resulting solution was stirred at 0 ℃ for another 2 hours and quenched with aqueous $NaHCO_3$. After extraction with EtOAc, the residue was purified by chromatography to give the corresponding C3-pivaloyl *N-H* indole.

An oven-dried flask containing C3-pivaloyl *N-H* indole (4.2 mmol, 1.0 equiv), NaH (60%

dispersed in mineral oil, 5.1 mmol, 1.2 equiv.), and dry THF (20.0 mL), was stirred for 30 minutes at room temperature. To this mixture was added a solution of tosyl chloride (4.2 mmol, 1.0 equiv) in THF (5.0 mL). The solution was stirred at room temperature for another 2 hours. After the reaction, the organic phase was washed with $NaHCO_3$(aq) (1 × 10.0 mL), brine (1 × 10.0 mL), 0.5 mL CH_3OH, and dried over anhydrous $MgSO_4$. The crude solution was concentrated under reduced pressure and purified by chromatography (eluent: PE/EA = 20/1) to afford C3-pivaloyl *N*-Ts indole.

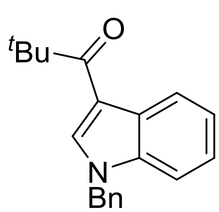
2,2-Dimethyl-1-(1-tosyl-1*H*-indol-3-yl)propan-1-one (15a)[6]



15a

Following the general procedure on 10.0 mmol scale, the substrate **15a** was obtained as a white solid in 60.0% yield (2.1 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.34 – 8.30 (m, 1H), 8.24 (s, 1H), 7.96 – 7.91 (m, 1H), 7.83 – 7.77 (m, 2H), 7.37 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 2.35 (s, 3H), 1.42 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.8, 134.6, 134.1, 130.2, 130.0, 129.5, 127.0, 125.5, 124.7, 123.4, 117.9, 112.9, 44.7, 28.3, 21.6; **ATR-FTIR (cm^{-1})** 2974, 2314, 1667, 1374, 1175, 979, 663 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{22}NO_3S^+$ $(M + H)^+$ 356.1315, found 356.1314.

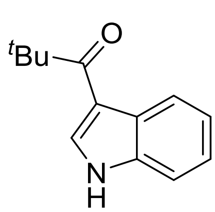
1-(1-Benzyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (16a)[7]



16a

Following the general procedure on 10.0 mmol scale, the substrate **16a** was obtained as a white solid in 66.0% yield (1.9 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.54 – 8.52 (m, 1H), 7.84 (s, 1H), 7.35 – 7.19 (m, 6H), 7.16 – 7.07 (m, 2H), 5.34 (s, 2H), 1.39 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.1, 136.0, 135.9, 133.6, 129.0, 128.4, 128.1, 126.7, 123.4, 123.3, 122.6, 113.2, 109.8, 50.6, 44.1, 28.9; **ATR-FTIR (cm^{-1})** 2970, 1633, 1497, 1476, 1137, 900, 749 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{22}NO^+$ $(M + H)^+$ 292.1696, found 292.1692.

1-(1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (17a)[8]

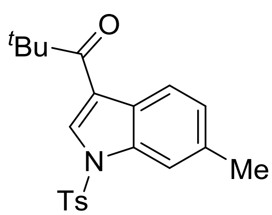


Following the general procedure on 5.0 mmol scale, the substrate **17a** was obtained as a white solid in 81.0% yield (818.1 mg). **^{1}H NMR (400 MHz,**

17a

Chloroform-*d*) δ 9.00 (brs, 1H), 8.51 – 8.43 (m, 1H), 7.86 (d, *J* = 3.1 Hz, 1H), 7.40 – 7.30 (m, 1H), 7.27 – 7.18 (m, 2H), 1.37 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 203.1, 135.4, 130.4, 127.3, 123.5, 124.0, 122.5, 114.1, 111.2, 44.2, 28.9; **ATR-FTIR (cm^{-1})** 2972, 1677, 1241, 1104, 987, 898 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{16}NO^+$ $(M + H)^+$ 202.1226, found 202.1221.

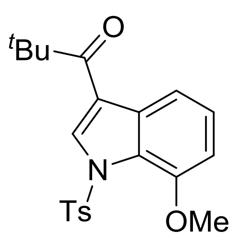
2,2-Dimethyl-1-(6-methyl-1-tosyl-1*H*-indol-3-yl)propan-1-one (18a)



18a

Following the general procedure on 10.0 mmol scale, the substrate **18a** was obtained as a white solid in 69.0% yield (2.2 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.18 – 8.16 (m, 2H), 7.82 – 7.76 (m, 2H), 7.74 – 7.73 (m, 1H), 7.28 – 7.26 (m, 2H), 7.16 – 7.14 (m, 1H), 2.47 (s, 3H), 2.36 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.6, 135.8, 134.7, 134.5, 130.1, 129.5, 127.2, 126.9, 126.2, 123.0, 117.9, 112.8, 44.6, 28.3, 21.9, 21.6; **ATR-FTIR (cm^{-1})** 2809, 1855, 1659, 1430, 1100, 766, 674 cm^{-1}; **HRMS m/z (ESI)** called for $C_{21}H_{24}NO_3S^+$ $(M + H)^+$ 370.1471, found 370.1469.

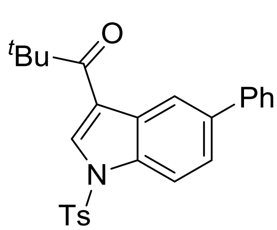
1-(7-Methoxy-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (19a)



19a

Following the general procedure on 5.0 mmol scale, the substrate **19a** was obtained as a white solid in 67.0% yield (1.3 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.53 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 3.67 (s, 3H), 2.41 (s, 3H), 1.45 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.7, 146.5, 144.8, 136.4, 132.6, 132.3, 129.5, 127.4, 125.5, 124.3, 116.1, 115.7, 107.6, 55.4, 44.7, 28.4, 21.6; **ATR-FTIR (cm^{-1})** 1700, 1371, 1176, 923, 742, 457 cm^{-1}; **HRMS m/z (ESI)** $C_{21}H_{24}NO_4S^+$$(M + H)^+$ 386.1421, found 386.1418.

2,2-Dimethyl-1-(5-phenyl-1-tosyl-1*H*-indol-3-yl)propan-1-one (20a)

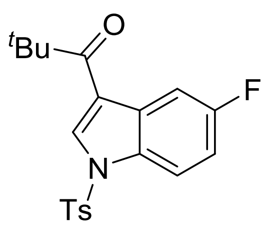


20a

Following the general procedure on 5.0 mmol scale, the substrate **20a** was obtained as a white solid in 70.0% yield (1.5 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.57 (dd, *J* = 1.9, 0.7 Hz, 1H), 8.26 (s, 1H), 7.98 (dd, *J*

= 8.7, 0.7 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.64 – 7.61 (m, 3H), 7.42 (t, J = 7.5 Hz, 2H), 7.36 – 7.27 (m, 3H), 2.37 (s, 3H), 1.43 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.7, 145.9, 140.9, 138.2, 134.5, 133.4, 130.6, 130.2, 130.1, 128.7, 127.4, 127.1, 127.0, 125.1, 121.9, 118.0, 113.1, 44.7, 28.3, 21.6; **ATR-FTIR (cm^{-1})** 2965, 1659, 1539, 1194, 782, 765 cm^{-1}; **HRMS m/z (ESI)** called for $C_{26}H_{26}NO_3S^+$(M + H)$^+$ 432.1628, found 432.1623.

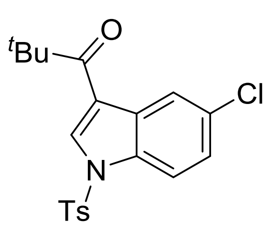
1-(5-Fluoro-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (21a)



21a

Following the general procedure on 5.0 mmol scale, the substrate **21a** was obtained as a white solid in 59.0% yield (1.1 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.26 (s, 1H), 8.03 (dd, J = 9.6, 2.6 Hz, 1H), 7.86 (dd, J = 9.1, 4.4 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.30 – 7.26 (m, 2H), 7.10 – 7.05 (m, 1H), 2.36 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.2, 160.5(d, J = 241.2 Hz), 146.0, 134.3, 131.5, 130.8 (d, J = 11.1 Hz), 130.3, 127.0, 117.5 (d, J = 4.3 Hz), 113.9 (d, J = 4.6 Hz), 113.7 (d, J = 21.1 Hz), 109.3 (d, J = 25.6 Hz), 44.6, 28.2, 21.6; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -117.67; **ATR-FTIR (cm^{-1})** 2975, 1639, 1371, 1141, 960, 855 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{21}FNO_3S^+$(M + H)$^+$ 374.1221, found 374.1218.

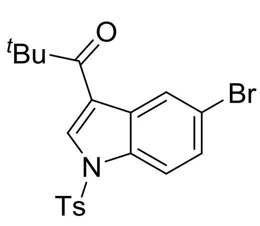
1-(5-Chloro-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (22a)



22a

Following the general procedure on 10.0 mmol scale, the substrate **22a** was obtained as a white solid in 66.0% yield (2.6 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.35 (dd, J = 2.1, 0.6 Hz, 1H), 8.23 (s, 1H), 7.84 (dd, J = 8.9, 0.6 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.33 – 7.26 (m, 3H), 2.37 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.2, 146.1, 134.2, 132.4, 131.1, 130.8, 130.7, 130.3, 127.0, 126.0, 123.3, 117.2, 113.8, 44.6, 28.2, 21.6; **ATR-FTIR (cm^{-1})** 2975, 2315, 1680, 1540, 1475, 1100, 988 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{21}ClNO_3S^+$(M + H)$^+$ 390.0925, found 390.0920.

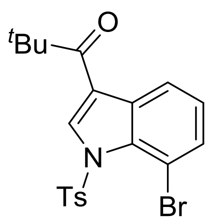
1-(5-Bromo-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (23a)



23a

Following the general procedure on 10.0 mmol scale, the substrate **23a** was obtained as a white solid in 69.0% yield (3.0 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.51 (d, *J* = 1.9 Hz, 1H), 8.21 (s, 1H), 7.78 (dd, *J* = 8.6, 6.9 Hz, 3H), 7.45 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.2, 146.1, 134.2, 132.8, 131.2, 130.8, 130.3, 128.6, 127.0, 126.3, 118.6, 117.1, 114.2, 44.7, 28.2, 21.6; **ATR-FTIR (cm^{-1})** 2922, 1657, 1529, 117, 667, 582 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{21}BrNO_3S^+$ $(M + H)^+$ 434.0420, found 434.0416.

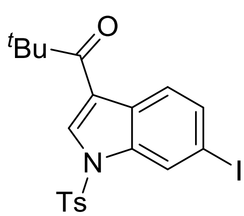
1-(7-Bromo-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (24a)



24a

Following the general procedure on 5.0 mmol scale, the substrate **24a** was obtained as a white solid in 70.0% yield (1.5 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.60 (s, 1H), 8.39 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.49 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 2.42 (s, 3H), 1.45 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.4, 145.3, 136.6, 134.4, 133.5, 133.2, 131.7, 129.9, 127.1, 125.8, 122.5, 116.1, 105.4, 45.0, 28.3, 21.7; **ATR-FTIR (cm^{-1})** 2973, 1659, 1380, 1145, 815, 577 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{21}BrNO_3S^+$ $(M + H)^+$ 434.0420, found 434.0419.

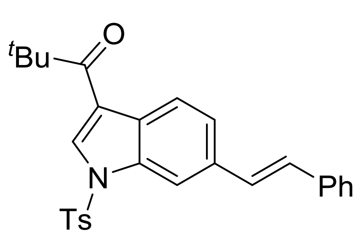
1-(6-Iodo-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (25a)[4]



25a

Following the general procedure on 6.0 mmol scale, the substrate **25a** was obtained as a white solid in 62.0% yield (1.8 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.30 (d, *J* = 1.5 Hz, 1H), 8.14 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.61 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.33 – 7.28 (m, 2H), 2.38 (s, 3H), 1.39 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.2, 146.1, 134.9, 134.3, 133.7, 130.3, 130.0, 129.0, 127.0, 125.0, 121.7, 117.6, 90.1, 44.7, 28.2, 21.6; **ATR-FTIR (cm^{-1})** 2972, 1658, 1377, 1179, 979, 576 cm^{-1}; **HRMS m/z (ESI)** $C_{20}H_{21}INO_3S^+$ $(M + H)^+$ 482.0281, found 482.0279.

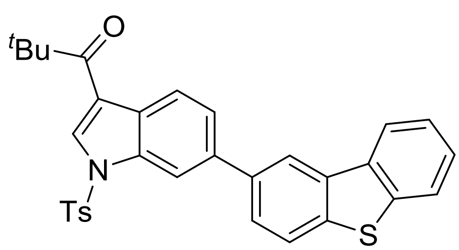
(*E*)-2,2-Dimethyl-1-(6-styryl-1-tosyl-1*H*-indol-3-yl)propan-1-one (26a)[5]



26a

Following the general procedure on 5.0 mmol scale, the substrate **26a** was obtained as a white solid in 71.0% yield (1.6 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.32 (s, 1H), 8.13 (d, J = 1.4 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.67 (d, J = 8.1 Hz, 3H), 7.50 (dd, J = 8.3, 6.8 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.31 (d, J = 5.0 Hz, 2H), 2.47 (s, 3H), 1.53 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.9, 137.1, 135.3, 134.8, 134.6, 130.4, 130.3, 129.2, 129.1, 128.8, 128.6, 127.8, 127.0, 126.6, 123.5, 123.1, 118.1, 111.1, 44.7, 28.3, 21.7; **ATR-FTIR (cm^{-1})** 2971, 1655, 1373, 1179, 988, 933, 541 cm^{-1}; **HRMS m/z (ESI)** called for $C_{28}H_{28}NO_3S^+$ (M + H)$^+$ 458.1784, found 458.1777.

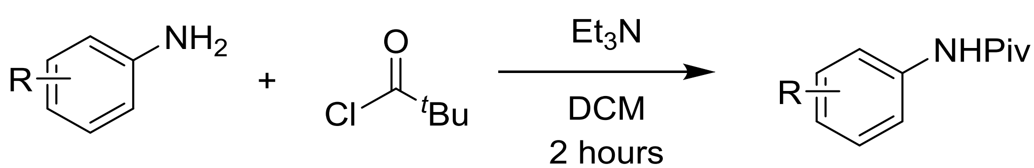
1-(6-(Dibenzo[*b*,*d*]thiophen-2-yl)-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (27a)[9]



27a

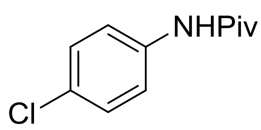
Following the general procedure on 2.0 mmol scale, the substrate **27a** was obtained as a white solid in 53.0% yield (570.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.42 (d, J = 8.4 Hz, 1H), 8.37 (dd, J = 1.8, 0.6 Hz, 1H), 8.29 – 8.23 (m, 3H), 7.95 (dd, J = 8.3, 0.6 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.86 – 7.82 (m, 2H), 7.71 (ddd, J = 13.0, 8.4, 1.7 Hz, 2H), 7.56 – 7.46 (m, 2H), 7.31 – 7.26 (m, 2H), 2.36 (s, 3H), 1.45 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.9, 139.9, 139.1, 137.7, 136.2, 135.4, 134.8, 130.4, 130.3, 128.8, 127.04, 126.98, 126.4, 124.6, 124.5, 123.8, 123.1, 122.9, 121.7, 120.3, 117.9, 111.4, 44.7, 28.3, 21.6 ; **ATR-FTIR (cm^{-1})** 2926, 1657, 1374, 1136, 983, 577 cm^{-1}; **HRMS m/z (ESI)** $C_{32}H_{28}NO_3S_2^+$ (M + H)$^+$ 538.1505, found 538.1506.

2.3 General procedure for the synthesis of *N*-phenylpivalamides.



To a stirred solution of aniline (22.9 mmol, 1.0 equiv.) and triethylamine (3.5 mL, 25.2 mmol, 1.1 equiv.) in 20.0 mL of anhydrous DCM was added dropwise pivaloyl chloride (3.0 mL, 24.4 mmol, 1.05 equiv.) while maintaining the internal temperature below 10 ℃. The mixture was stirred 2 hours at room temperature. 1M HCl solution (20.0 mL) was added. The organic layer was extracted, washed with sat $NaHCO_3$ (30.0 mL), brine (30.0 mL), dried (Na_2SO_4), filtered off and evaporated under reduced pressure. Petroleum ether was added and the residue was allowed to crystallize at 0 ℃. Crystals were filtered off and dried in vacuo to afford the title compound.

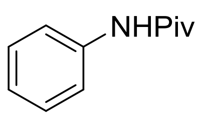
_N_-(4-Chlorophenyl)pivalamide (28a)[10]



28a

Following the general procedure on 5.0 mmol scale, the substrate **28a** was obtained as a white solid in 89.0% yield (943.4 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.50 – 7.45 (m, 2H), 7.37 (brs, 1H), 7.29 – 7.24 (m, 2H), 1.30 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 136.6, 129.1, 128.9, 121.2, 39.6, 27.5; **ATR-FTIR (cm^{-1})** 2794, 1693, 1111, 985, 785 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{15}ClNO^+$ $(M + H)^+$ 212.0837, found 212.0833.

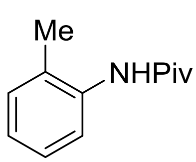
_N_-Phenylpivalamide (29a)[10]



29a

Following the general procedure on 5.0 mmol scale, the substrate **29a** was obtained as a white solid in 89.1% yield (792.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.49 (m, 2H), 7.37 (brs, 1H), 7.34 – 7.27 (m, 2H), 7.13 – 7.06 (m, 1H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.5, 138.0, 128.8, 124.1, 120.0, 39.5, 27.6; **ATR-FTIR (cm^{-1})** 3458, 2871, 1697, 1435, 1148 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{16}NO^+$ $(M + H)^+$ 178.1226, found 178.1223.

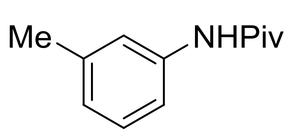
_N_-(_o_-Tolyl)pivalamide (30a)[11]



30a

Following the general procedure on 5.0 mmol scale, the substrate **30a** was obtained as a white solid in 99.0% yield (960.2 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.23 – 7.16 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 2.25 (s, 3H), 1.34 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.4, 135.8, 130.3, 128.7, 126.8, 124.8, 122.8, 39.7, 27.7, 17.6; **ATR-FTIR (cm^{-1})** 3289, 2904, 1683, 1489, 1204, 785, 885 cm^{-1}; **HRMS m/z (ESI)** called for $C_{12}H_{18}NO^+$ $(M + H)^+$ 192.1383, found 192.1380.

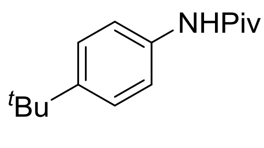
N-(_m_-Tolyl)pivalamide (31a)[11]



31a

Following the general procedure on 5.0 mmol scale, the substrate **31a** was obtained as a white solid in 99.0% yield (960.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.43 (s, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.5, 138.9, 137.9, 128.7, 124.9, 120.6, 116.9, 39.6, 27.6, 21.4; **ATR-FTIR (cm^{-1})** 3303, 2965, 1653, 1591, 1194, 783, 765 cm^{-1}; **HRMS m/z (ESI)** called for $C_{12}H_{18}NO^{+}$ $(M + H)^{+}$ 192.1383, found 192.1379.

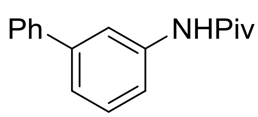
***N*-(4-(*Tert*-butyl)phenyl)pivalamide (32a)[11]**



32a

Following the general procedure on 5.0 mmol scale, the substrate **32a** was obtained as a white solid in 99.0% yield (1.2 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.48 – 7.43 (m, 2H), 7.38 – 7.30 (m, 3H), 1.31 (s, 9H), 1.30 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.4, 147.1, 135.4, 125.7, 119.7, 39.4, 34.3, 31.3, 27.6; **ATR-FTIR (cm^{-1})** 3544, 2768, 1699, 1431, 1151 cm^{-1}; **HRMS m/z (ESI)** called for $C_{15}H_{24}NO^{+}$ $(M + H)^{+}$ 234.1852, found 234.1849.

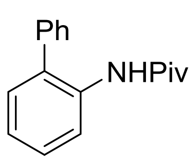
***N*-([1,1'-Biphenyl]-3-yl)pivalamide (33a)[12]**



33a

Following the general procedure on 5.0 mmol scale, the substrate **33a** was obtained as a white solid in 93.0% yield (1.1 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.83 (t, *J* = 1.8 Hz, 1H), 7.61 – 7.53 (m, 3H), 7.47 (dt, *J* = 7.5, 2.0 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.34 – 7.27 (m, 3H), 1.29 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.7, 141.9, 140.6, 138.4, 129.1, 128.6, 127.3, 127.0, 122.8, 118.8, 39.5, 27.5; **ATR-FTIR (cm^{-1})** 2965, 1666, 1599, 1481, 1217, 757, 698 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{20}NO^{+}$ $(M + H)^{+}$ 254.1539, found 254.1536.

***N*-([1,1'-Biphenyl]-2-yl)pivalamide (34a)[10]**

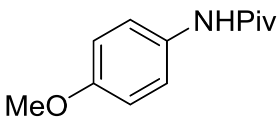


34a

Following the general procedure on 5.0 mmol scale, the substrate **34a** was obtained as a white solid in 91.0% yield (1.1 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.37 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.52 – 7.34 (m, 7H), 7.24 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.15 (td, *J* = 7.5, 1.2 Hz, 1H), 1.09 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.2, 138.0, 135.1, 132.1, 129.7, 129.3, 129.0, 128.4, 128.0, 123.9, 120.8, 39.8, 27.3; **ATR-FTIR (cm^{-1})** 2977, 1696, 1599, 1489, 1217, 767, 698 cm^{-1};

HRMS m/z (ESI) called for $C_{17}H_{20}NO^+$ $(M + H)^+$ 254.1539, found 254.1538.

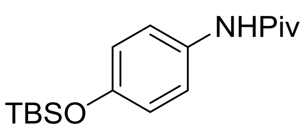
***N*-(4-Methoxyphenyl)pivalamide (35a)**[10]



35a

Following the general procedure on 5.0 mmol scale, the substrate **35a** was obtained as a white solid in 97.0% yield (1.0 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.43 – 7.38 (m, 2H), 7.37 (d, *J* = 3.9 Hz, 1H), 6.84 – 6.79 (m, 2H), 3.76 (s, 3H), 1.28 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.4, 156.2, 131.1, 121.9, 113.9, 55.4, 39.3, 27.5; **ATR-FTIR (cm^{-1})** 3119, 2684, 1699, 1391, 1154, 965, 775 cm^{-1}; **HRMS m/z (ESI)** called for $C_{12}H_{18}NO_2^+$ $(M + H)^+$ 208.1332, found 208.1328.

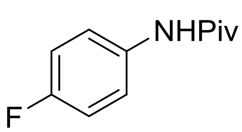
***N*-(4-(*Tert*-butyldimethylsilyl)phenyl)pivalamide (36a)**



36a

Following the general procedure on 10.0 mmol scale, the substrate **36a** was obtained as a yellow solid in 60.0% yield (1.8 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 – 7.33 (m, 2H), 7.25 (brs, 1H), 6.82 – 6.75 (m, 2H), 1.30 (s, 9H), 0.97 (s, 9H), 0.17 (s, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.3, 152.2, 131.6, 121.6, 120.3, 39.4, 27.6, 25.7, 18.2, -4.5; **ATR-FTIR (cm^{-1})** 2957, 1660, 1596, 1382, 1114, 981 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{30}NO_2Si^+$ $(M + H)^+$ 308.2040, found 308.2045.

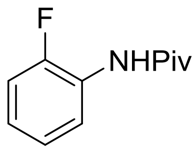
***N*-(4-Fluorophenyl)pivalamide (37a)**[11]



37a

Following the general procedure on 5.0 mmol scale, the substrate **37a** was obtained as a white solid in 89.0% yield (872.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.51 – 7.44 (m, 2H), 7.35 (brs, 1H), 7.03 – 6.95 (m, 2H), 1.30 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 159.3 (d, *J* = 243.3 Hz), 134.0 (d, *J* = 2.9 Hz), 121.9 (d, *J* = 7.8 Hz), 115.5 (d, *J* = 22.4 Hz), 39.5, 27.6; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -118.26; **ATR-FTIR (cm^{-1})** 3103, 2794, 1693, 1451, 1204, 985, 785 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{15}FNO^+$ $(M + H)^+$ 196.1132, found 196.1129.

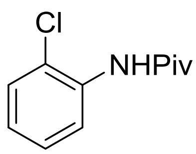
***N*-(2-Fluorophenyl)pivalamide (38a)**[13]



38a

Following the general procedure on 5.0 mmol scale, the substrate **38a** was obtained as a white solid in 87.0% yield (852.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.36 – 8.32 (m, 1H), 7.63 (brs, 1H), 7.16 – 6.97 (m, 3H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 152.5 (d, *J* = 242.2 Hz), 126.6 (d, *J* = 9.6 Hz), 124.5 (d, *J* = 3.7 Hz), 124.0 (d, *J* = 7.7 Hz), 121.6 (d, *J* = 1.1 Hz), 114.6 (d, *J* = 19.3 Hz), 39.9, 27.5; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -132.21; **ATR-FTIR (cm^{-1})** 3103, 2794, 1693, 1451, 1204, 985, 785 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{15}FNO^{+}$ $(M + H)^{+}$ 196.1132, found 196.1128.

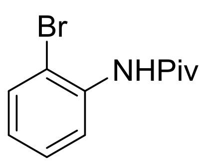
***N*-(2-Chlorophenyl)pivalamide (39a)**[13]



39a

Following the general procedure on 5.0 mmol scale, the substrate **39a** was obtained as a white solid in 89.0% yield (943.4 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.41 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.02 (brs, 1H), 7.36 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.02 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 134.7, 128.8, 127.7, 124.3, 122.8, 121.3, 40.2, 27.6; **ATR-FTIR (cm^{-1})** 3435, 2964, 1692, 1523, 1155, 1034, 568 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{15}ClNO^{+}$ $(M + H)^{+}$ 212.0837, found 212.0833.

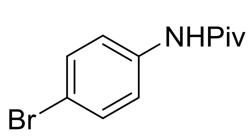
***N*-(2-Bromophenyl)pivalamide (40a)**[13]



40a

Following the general procedure on 5.0 mmol scale, the substrate **40a** was obtained as a white solid in 89.1% yield (1.1 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.40 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.01 (brs, 1H), 7.53 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.31 (td, *J* = 7.9, 1.5 Hz, 1H), 6.96 (td, *J* = 7.7, 1.6 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 135.8, 132.1, 128.4, 124.8, 121.6, 113.6, 40.2, 27.6; **ATR-FTIR (cm^{-1})** 3113, 2864, 1689, 1451, 1324, 985, 785 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{15}BrNO^{+}$ $(M + H)^{+}$ 256.0332, found 256.0329.

***N*-(4-Bromophenyl)pivalamide (41a)**[10]

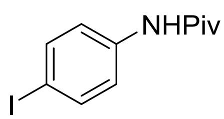


41a

Following the general procedure on 5.0 mmol scale, the substrate **41a** was obtained as a white solid in 82.0% yield (1.0 g). **^{1}H NMR (400 MHz,**

Chloroform-*d*) δ 7.46 – 7.38 (m, 4H), 7.34 (brs, 1H), 1.30 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 137.1, 131.8, 121.5, 116.7, 39.6, 27.5; **ATR-FTIR (cm^{-1})** 3110, 2789, 1688, 1124, 989 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{15}BrNO^+$ $(M + H)^+$ 256.0332, found 256.0332.

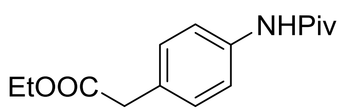
***N*-(4-Iodophenyl)pivalamide (42a)[4]**



42a

Following the general procedure on 5.0 mmol scale, the substrate **42a** was obtained as a white solid in 90.0% yield (1.4 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 – 7.57 (m, 2H), 7.37 – 7.28 (m, 3H), 1.30 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 137.8, 121.8, 87.2, 39.7, 27.5; **ATR-FTIR (cm^{-1})** 3069, 2694, 1699, 1351, 1244, 965, 785 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{15}INO^+$ $(M + H)^+$ 304.0193, found 304.0191.

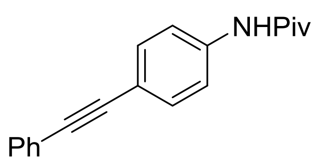
Ethyl 2-(4-pivalamidophenyl)acetate (43a)



43a

Following the general procedure on 5.0 mmol scale, the substrate **43a** was obtained as a white solid in 90.0% yield (1.2 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.51 – 7.45 (m, 2H), 7.40 (brs, 1H), 7.23 – 7.18 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.55 (s, 2H), 1.29 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.5, 171.5, 137.0, 129.8, 129.6, 120.1, 60.8, 40.8, 39.5, 27.5, 14.1; **ATR-FTIR (cm^{-1})** 3039, 1731, 1653, 1519, 1242, 1141 cm^{-1}; **HRMS m/z (ESI)** called for $C_{15}H_{22}NO_3^+$ $(M + H)^+$ 264.1594, found 264.1597.

***N*-(4-(Phenylethynyl)phenyl)pivalamide (44a)[7]**

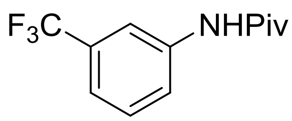


44a

Following the general procedure on 2.0 mmol scale, the substrate **44a** was obtained as a yellow solid in 71.0% yield (394.7 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.57 – 7.47 (m, 6H), 7.40 – 7.30 (m, 4H), 1.32 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 176.5, 138.0, 132.3, 131.5, 128.3, 128.1, 123.3, 119.5, 118.7, 89.1, 89.0, 39.7, 27.6; **ATR-FTIR (cm^{-1})** 3400, 1730, 1240, 989 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{20}NO^+$(M +

H)$^+$ 278.1539, found 278.1538.

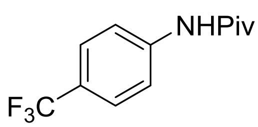
***N*-(3-(Trifluoromethyl)phenyl)pivalamide (45a)**[10]



45a

Following the general procedure on 5.0 mmol scale, the substrate **45a** was obtained as a white solid in 91.0% yield (1.1 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.56 (brs, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 1.32 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 138.5, 131.2 (q, *J* = 32.3 Hz), 129.4, 126.5 (q, *J* = 272.6 Hz), 123.1, 120.7 (q, *J* = 4.0 Hz), 116.8 (q, *J* = 4.0 Hz), 39.7, 27.5; **ATR-FTIR (cm^{-1})** 3010, 1659, 1321, 1116 cm^{-1}; **HRMS m/z (ESI)** called for $C_{12}H_{15}F_3NO^+$ (M + H)$^+$ 246.1100, found 246.1099.

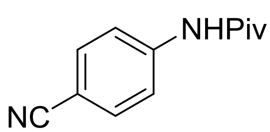
***N*-(4-(Trifluoromethyl)phenyl)pivalamide (46a)**[10]



46a

Following the general procedure on 5.0 mmol scale, the substrate **46a** was obtained as a white solid in 74.0% yield (910.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.45 (brs, 1H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.9, 141.1, 126.2(q, *J* = 3.8 Hz), 125.6 (q, *J* = 34.3 Hz), 122.7, 119.5, 39.8, 27.6; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.10; **ATR-FTIR (cm^{-1})** 3011, 1679, 1431, 1216 cm^{-1}; **HRMS m/z (ESI)** called for $C_{12}H_{15}F_3NO^+$ (M + H)$^+$ 246.1100, found 246.1097.

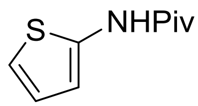
***N*-(4-Cyanophenyl)pivalamide (47a)**



47a

Following the general procedure on 5.0 mmol scale, the substrate **47a** was obtained as a white solid in 95.0% yield (959.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.71 – 7.67 (m, 3H), 7.60 – 7.55 (m, 2H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-d)** δ 177.1, 142.2, 133.1, 119.8, 118.9, 106.7, 39.9, 27.4; **ATR-FTIR (cm^{-1})** 3777, 2226, 1676, 15891, 1308, 918 cm^{-1}; **HRMS m/z (ESI)** called for $C_{12}H_{15}N_2O^+$ (M + H)$^+$ 203.1179, found 203.1174.

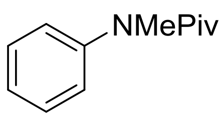
N-(Thiophen-2-yl)pivalamide (48a)[14]



48a

Following the general procedure on 5.0 mmol scale, the substrate **48a** was obtained as a yellow solid in 71.0% yield (986.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.19 (brs, 1H), 6.87 – 6.80 (m, 2H), 6.65 (dd, *J* = 3.6, 1.6 Hz, 1H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.9, 139.2, 123.6, 117.8, 111.3, 38.9, 27.5; **ATR-FTIR (cm^{-1})** 2996, 1635, 1552, 928, 806, 681 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{20}NO^+$(M + H)$^+$ 278.1539, found 278.1538.

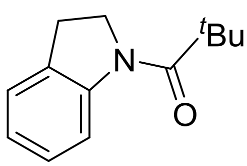
N-Methyl-N-phenylpivalamide (49a)[15]



49a

Following the general procedure on 5.0 mmol scale, the substrate **49a** was obtained as a white solid in 91.0% yield (873.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 – 7.28 (m, 3H), 7.23 – 7.17 (m, 2H), 3.20 (s, 3H), 1.02 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 178.1, 145.2, 129.2, 128.7, 127.7, 41.3, 40.8, 29.3; **ATR-FTIR (cm^{-1})** 2965, 2244, 1636, 1592, 1213, 915, 733 cm^{-1}; **HRMS m/z (ESI)** called for $C_{12}H_{18}NO^+$ (M + H)$^+$ 192.1383, found 192.1385.

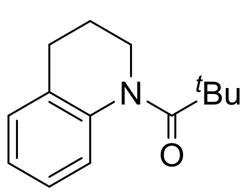
1-(Indolin-1-yl)-2,2-dimethylpropan-1-one (50a)[16]



50a

Following the general procedure on 10.0 mmol scale, the substrate **50a** was obtained as a white solid in 91.0% yield (1.8 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.28 – 8.17 (m, 1H), 7.22 – 7.15 (m, 2H), 7.01 (td, *J* = 7.4, 1.1 Hz, 1H), 4.23 (t, *J* = 8.1 Hz, 2H), 3.14 (t, *J* = 8.1 Hz, 2H), 1.38 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.5, 144.7, 130.7, 127.3, 124.2, 123.6, 118.3, 49.4, 40.2, 29.3, 27.7; **ATR-FTIR (cm^{-1})** 2970, 1645, 1598, 1364, 755 cm^{-1}; **HRMS m/z (ESI)** called for $C_{13}H_{18}NO^+$(M + H)$^+$ 204.1383, found 204.1379.

1-(3,4-Dihydroquinolin-1(2*H*)-yl)-2,2-dimethylpropan-1-one (51a)[16]



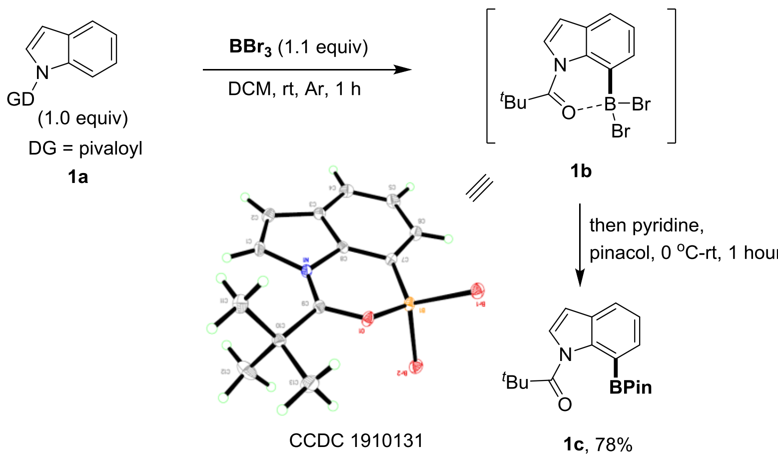
Following the general procedure on 5.0 mmol scale, the substrate **51a** was obtained as a white solid in 92.0% yield (1.0 g). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.04 (m, 3H), 3.78 (t, *J* =

51a

6.3 Hz, 2H), 2.76 (t, J = 7.1 Hz, 2H), 2.02 – 1.95 (m, 2H), 1.29 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 178.3, 140.9, 132.0, 128.5, 125.8, 125.5, 125.0, 45.1, 40.4, 28.9, 26.1, 24.1; **ATR-FTIR (cm^{-1})** 1598, 1401, 1169, 776, 582 cm^{-1}; **HRMS m/z (ESI)** called for $C_{14}H_{20}NO^{+}$(M + H)$^{+}$ 218.1539, found 218.1536.

3. Investigation of reaction conditions

Table S1| Optimization of the reaction conditions.



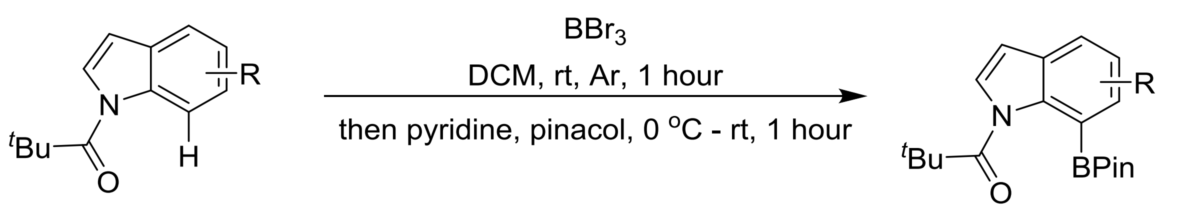
Entry	Variation from the "standard conditions"	Yield of **1c** (%)^{b}
1	none	78 (85)^{c}
2	BF_3 instead of BBr_3	0
3	BCl_3 instead of BBr_3	10
4	ClBcat/ HBpin /9-BBN instead of BBr_3	0
5	DCE instead of DCM	75
6	DG = Ac (**1a-1**)/ Boc (**1a-2**) instead of **1a**	0^{d}

^{a}Standard conditions: **1a** (0.20 mmol), BBr_3 (0.22 mmol) in 1.0 mL DCM at room temperature, 1 hour, under Ar; then, pyridine (1.0 mmol) and pinacol (0.2 mmol) were added to the mixture, and the temperature was increased from 0 ℃ to room temperature over 1 hour. ^{b}Isolated yield. ^{c}Determined by crude ^{1}H NMR. ^{d}The corresponding C7-borylation product.

The reactivity of *N*-pivaloyl indole **1a** in the presence of boron Lewis acids were first explored (Table S1). The reaction of **1a** (1.0 equiv) with BBr_3 (1.1 equiv) in dry DCM without any additive only for 1 hour at room temperature produced the dibromoborane product **1b**, which was confirmed by ^{11}B NMR and X-ray analysis. The structure displays a square planar geometry, and a C-B bond is formed at the indole C7 position chelated by an O atom. The in situ formation of the pinacol boronate ester was facile, and product **1c** was isolated with a 78% yield after reaction with pinacol pyridine. Notably, isomers including indole C2 and C3 borylation products were not detected. Boron halides such as BF_3 failed to yield any borylated product (entry 2), and BCl_3 produced product **1c** only in a very low yield (entry 3). Other boron sources including ClBcat (B-chlorocatecholborane), HBpin (4,4,5,5-tetramethyl-1,3,2-dioxaborolane), and 9-BBN (9-borabicyclo[3.3.1]nonane), which have been previously used for transition metal-catalysed C-H borylation, completely failed in this reaction (entry 4). Changing the solvent to DCE provided a 75% yield of **1c**, and the use of Lewis basic solvents, such as DMF and THF, led to very low yields (entry 5). Further exploration showed that indoles bearing *N*-directing groups, such as Ac (**1a-1**), Boc (**1a-2**) groups, did not provide any of the C7-borylation product, confirming the importance of the *N*-pivaloyl group moiety for achieving both high reactivity and selectivity (entry 6).

4. Experimental procedures and characterization of products

4.1 Genera proceduce A

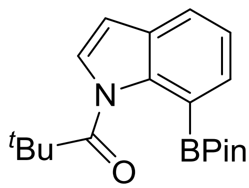


1-14a **1-14c**

To a flame-dried 25 mL Schlenk tube was flushed with argon and charged with *N*-pivaloyl indole **1-14a** (0.2 mmol, 1.0 equiv) and dry DCM (1.0 mL, 0.2 M). A solution of BBr_3 (1 M in DCM, 0.22 mL, 1.1 equiv) was added slowly under argon atmosphere. The reaction mixture was stirred at room temperature for 1 hour (*Note: Many substrates were very fast (~10 minutes). To uniform the reaction time, each reaction was proceeded for 1 hour*) and then quenched with a solution of pinacol (23.6 mg, 0.2 mmol, 1.0 equiv), pyridine (79.1 mg, 1.0 mmol, 5.0 equiv) in dry DCM

(1.0 mL) at 0℃. The resulting mixture was allowed to warm to ambient temperature and continued to stir for another 1 hour. After that, the solvent was removed under vaccum directly and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to get the target product **1-14c**.

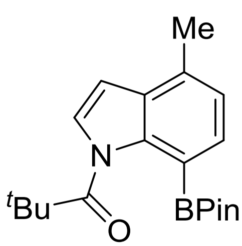
2,2-Dimethyl-1-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)propan-1-one (1c)



1c

The reaction was performed according to the general procedure A with **1a** (40.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 51.6 mg (78%) of **1c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 3.9 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.41 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 3.9 Hz, 1H), 1.47 (s, 9H), 1.41 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.3, 138.0, 129.5, 128.0, 124.5, 124.0, 121.0, 110.1, 83.0, 40.6, 28.6, 25.5; **ATR-FTIR (cm^{-1})** 2975, 1673, 1410, 1187, 860, 792,cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{27}BNO_3^+(M + H)^+$ 328.2079, found 328.2075.

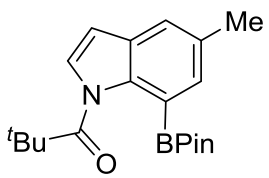
2,2-Dimethyl-1-(4-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)propan-1-one (2c)



2c

The reaction was performed according to the general procedure A with **2a** (43.0 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 55.6 mg (83.0%) of **2c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 (d, *J* = 4.0 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.08 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.66 (d, *J* = 3.9 Hz, 1H), 2.49 (s, 3H), 1.51 (s, 9H), 1.43 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 137.9, 130.4, 129.7, 127.6, 124.6, 124.0, 108.3, 82.9, 40.7, 28.6, 25.5, 18.4; **ATR-FTIR (cm^{-1})** 3000, 1699, 1207, 1126, 974, 780 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{29}BNO_3^+$ $(M + H)^+$ 342.2235, found 342.2239.

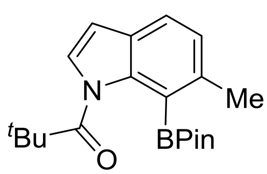
2,2-Dimethyl-1-(5-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)propan-1-one (3c)



3c

The reaction was performed according to the general procedure A with **3a** (43.0 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 52.9 mg (78.0%) of **3c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 3.9 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 6.54 (d, *J* = 3.9 Hz, 1H), 2.42 (s, 3H), 1.50 (s, 9H), 1.45 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 136.2, 133.3, 130.6, 128.31, 124.5, 121.1, 109.8, 82.9, 40.5, 28.6, 25.6, 21.3; **ATR-FTIR (cm^{-1})** 2894, 1703, 1307, 1246, 1123, 974, 780 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{29}BNO_3^+$ $(M + H)^+$ 342.2235, found 342.2239.

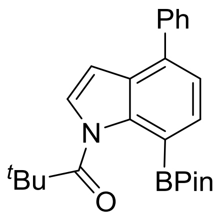
2,2-Dimethyl-1-(6-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)propan-1-one (4c)



4c

The reaction was performed according to the general procedure A with **4a** (43.0 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 57.9 mg (85.0%) of **4c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.56 (d, *J* = 3.9 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.8, 0.7 Hz, 1H), 6.56 (d, *J* = 3.9 Hz, 1H), 2.58 (s, 3H), 1.50 (s, 9H), 1.48 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 139.8, 138.9, 126.5, 126.1, 123.8, 120.5, 110.2, 82.8, 40.5, 28.6, 26.8, 22.0; **ATR-FTIR (cm^{-1})** 2994, 1703, 1317, 1146, 1020, 984, 780 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{29}BNO_3^+$ $(M + H)^+$ 342.2235, found 342.2239.

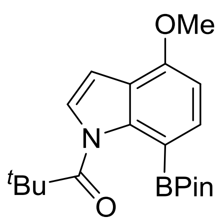
2,2-Dimethyl-1-(4-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)propan-1-one (5c)



5c

The reaction was performed according to the general procedure A with **5a** (55.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 74.0 mg (90.0%) of **5c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.71 (d, *J* = 3.9 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.50 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.44 – 7.36 (m, 2H), 6.82 (d, *J* = 3.9 Hz, 1H), 1.56 (s, 9H), 1.49 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.4, 140.3, 138.5, 134.9, 129.9, 128.9, 128.5, 127.1, 126.2, 124.8, 124.1, 109.4, 83.0, 40.7, 28.6, 25.6; **ATR-FTIR (cm^{-1})** 2975, 1695, 1407, 1197, 904, 826 cm^{-1}; **HRMS m/z (ESI)** called for $C_{25}H_{31}BNO_3^+$(M + H)$^+$ 404.2392, found 404.2387.

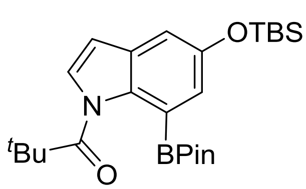
1-(4-Methoxy-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (6c)



6c

The reaction was performed according to the general procedure A with **6a** (46.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 38.9 mg (56.0%) of 6**c** as a white solid. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.55 (d, *J* = 4.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.77 – 6.71 (m, 2H), 3.91 (s, 3H), 1.50 (s, 9H), 1.43 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.3, 153.3, 139.4, 130.9, 123.2, 118.4, 106.6, 104.7, 82.9, 55.3, 40.7, 28.5, 25.5; **ATR-FTIR (cm^{-1})** 3271, 2975, 1674,, 1208, 1008, 895 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{29}BNO_4^+$(M + H)$^+$358.2184, found 358.2182.

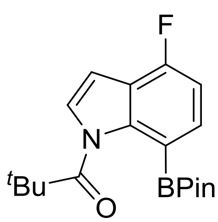
1-(5-((Tert-butyldimethylsilyl)oxy)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (7c)



7c

The reaction was performed according to the general procedure A with **8a** (66.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 56.0 mg (61%) of **7c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.59 (d, *J* = 3.9 Hz, 1H), 6.93 (s, 2H), 6.52 (d, *J* = 3.9 Hz, 1H), 1.49 (s, 9H), 1.42 (s, 12H), 0.99 (s, 9H), 0.18 (s, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.8, 152.4, 133.1, 129.3, 125.0, 122.1, 111.3, 110.0, 82.9, 40.5, 28.6, 25.8, 25.5, 18.3, -4.4; **ATR-FTIR (cm^{-1})** 2974, 1673, 1407, 1146, 1000, 974, 780 cm^{-1}; **HRMS m/z (ESI)** called for $C_{25}H_{41}BNO_4Si^+$ $(M + H)^+$ 458.2892, found 458.2892.

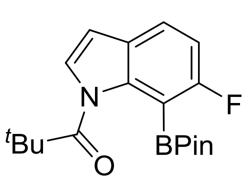
1-(4-Fluoro-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (8c)



8c

The reaction was performed according to the general procedure A with **8a** (44.1 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 61.9 mg (91%) of **8c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (d, *J* = 4.0 Hz, 1H), 7.37 (dd, *J* = 8.1, 5.8 Hz, 1H), 6.97 (dd, *J* = 9.7, 8.1 Hz, 1H), 6.74 (d, *J* = 4.0 Hz, 1H), 1.51 (s, 9H), 1.43 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.4, 156.3 (d, *J* = 248.9 Hz), 140.2 (d, *J* = 9.0 Hz), 130.8 (d, *J* = 6.9 Hz), 124.7, 117.0 (d, *J* = 21.3 Hz), 109.5 (d, *J* = 17.7 Hz), 105.2, 83.2, 40.8, 28.5, 25.5; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -121.91; **ATR-FTIR (cm^{-1})** 1695, 1339, 1088, 909, 848 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{26}BFNO_3^+$$(M + H)^+$ 346.1984, found 346.1984.

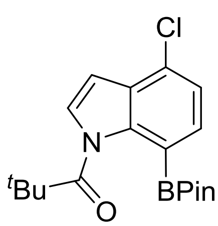
1-(6-Fluoro-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (9c)



9c

The reaction was performed according to the general procedure A with **9a** (44.1 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 53.2 mg (77.0%) of **9c** as a white solid. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 3.9 Hz, 1H), 7.42 (dd, *J* = 8.4, 5.5 Hz, 1H), 6.99 (t, *J* = 8.8 Hz, 1H), 6.58 (d, *J* = 3.9 Hz, 1H), 1.49 (s, 9H), 1.46 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.3, 164.6 (d, *J* = 237.8 Hz), 138.2 (d, *J* = 14.2 Hz), 124.7 (d, *J* = 4.1 Hz), 124.5, 121.7 (d, *J* = 10.5 Hz), 112.1 (d, *J* = 27.2 Hz), 109.7, 83.5, 40.6, 28.5, 25.7; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -108.93; **ATR-FTIR (cm^{-1})** 2977, 1674, 1547, 1333, 1208, 854 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{26}BFNO_3^+$(M + H)$^+$ 346.1984, found 346.1989.

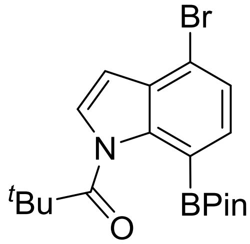
1-(4-Chloro-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (10c)



10c

The reaction was performed according to the general procedure A with **10a** (47.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 52.5 mg (72.0%) of **10c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (d, *J* = 3.9 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 3.9 Hz, 1H), 1.50 (s, 9H), 1.43 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.4, 138.7, 130.4, 127.0, 126.7, 125.2, 123.7, 107.7, 83.3, 40.8, 28.5, 25.5; **ATR-FTIR (cm^{-1})** 2977, 1679, 1591, 1539, 1130, 856 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{25}BClNNaO_3^+$ (M + Na)$^+$ 384.1508, found 384.1512.

1-(4-Bromo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (11c)

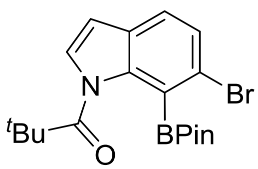


11c

The reaction was performed according to the general procedure A with **11a** (56.0 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 68.5 mg (85.0%) of **11c** as a white solid. **^{1}H NMR (400

MHz, Chloroform-*d*) δ 7.71 (d, *J* = 4.0 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 3.9 Hz, 1H), 1.50 (s, 9H), 1.43 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.5, 138.3, 130.5, 126.8, 125.2, 115.3, 109.5, 83.3, 40.8, 28.5, 25.5; **ATR-FTIR (cm^{-1})** 2975, 1695, 1359, 1288, 909, 848, 669 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{26}BBrNO_3^+$ $(M + H)^+$ 406.1184, found 406.1183.

1-(6-Bromo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (12c)

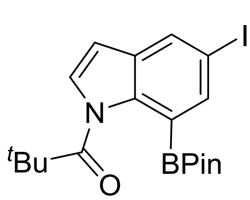


12c

The reaction was performed according to the general procedure A with **12a** (56.0 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 54.2 mg (67%) of **12c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 (d, *J* = 3.9 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 3.9 Hz, 1H), 1.52 (s, 12H), 1.50(s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 138.8, 128.9, 127.3, 124.9, 124.6, 122.0, 109.7, 83.6, 40.6, 28.6, 26.7; .**ATR-FTIR (cm^{-1})** 2975, 1695, 1359, 1288, 909, 848, 669 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{26}BBrNO_3^+$ $(M + H)^+$ 406.1184, found 406.1183.

1-(5-Iodo-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (13c)

The reaction was performed according to the general procedure A with **13a** (55.8 mg, 0.2 mmol),

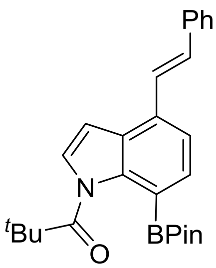


13c

BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 65.3 mg (72.0%) of **13c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (d, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.61 (d, *J* = 3.9 Hz, 1H), 6.54 (d, *J* = 3.9 Hz, 1H), 1.49 (s, 9H), 1.43 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ

177.4, 137.5, 137.2, 130.4, 129.8, 125.3, 108.9, 89.0, 83.3, 40.8, 28.5, 25.5; **ATR-FTIR (cm^{-1})** 2993 1695, 1339, 949, 669 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{26}BINO_3$+$(M + H)^+$ 454.1045, found 454.1030.

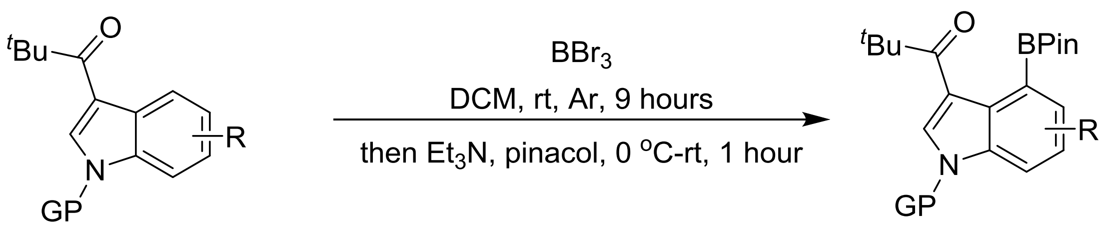
(*E*)-2,2-Dimethyl-1-(4-styryl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl) propan-1-one (14c)



14c

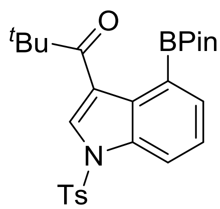
The reaction was performed according to the general procedure A with **14a** (55.8 mg, 0.2mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20) to afford 67.1 mg (78.0%) of **14c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 (d, *J* = 4.0 Hz, 1H), 7.65 – 7.60 (m, 3H), 7.55 – 7.40 (m, 4H), 7.36 – 7.28 (m, 2H), 6.97 (d, *J* = 4.0 Hz, 1H), 1.58 (s, 9H), 1.51 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.4, 138.5, 137.4, 130.0, 129.8, 128.6, 127.6, 126.5, 125.5, 124.6, 120.6, 108.7, 82.9, 40.7, 28.5, 25.5; **ATR-FTIR (cm^{-1})** 2975, 1676, 1601, 1542, 1300, 1114, 904 cm^{-1}; **HRMS m/z (ESI)** called for $C_{27}H_{33}BNO_3^+$ $(M + H)^+$ 430.2548, found 430.2546.

4.2 General procedure B.



Flame-dried 25 mL Schlenk tube was flushed with argon and charged with indole substrates **15-27a** (0.2 mmol, 1.0 equiv) and dry DCM (1.0 mL, 0.2 M). A solution of BBr_3 (1 M in DCM, 0.22 mL, 1.1 equiv) was added slowly under argon atmosphere. The mixture was stirred at room temperature for 9 hours and then quenched with a solution of pinacol (23.6 mg, 0.2 mmol, 1.0 eq), Et_3N (101.0 mg, 1.0 mmol, 5.0 eq) in dry DCM (1.0 mL) at 0℃. The resulting mixture was allowed to warm to room temperature and continued to stirr for another 1 hour. After that, the solvent was removed under vaccum directly and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to get the target product **15-27c**.

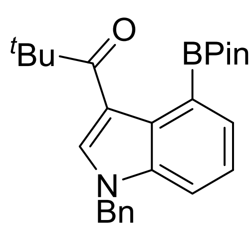
2,2-Dimethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)propan-1-one (15c)



15c

The reaction was performed according to the general procedure B with **15a** (71.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 84.5 mg (88.0%) of **15c** as a light yellow oily liquid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.19 (s, 1H), 7.94 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.46 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.33 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.24 – 7.20 (m, 2H), 2.34 (s, 3H), 1.43 (s, 12H), 1.41(s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.7, 134.4, 133.5, 130.9, 130.0, 129.6, 129.3, 126.8, 125.0, 118.8, 113.8, 83.7, 44.2, 28.1, 25.4, 21.5; **ATR-FTIR (cm^{-1})** 2880, 1705, 1536, 1016, 916 cm^{-1} **HRMS m/z (ESI)** called for $C_{26}H_{33}BNO_5S^+(M + H)^+$ 482.2167, found 482.2163.

1-(1-Benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (16c)

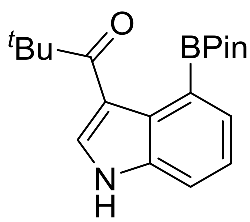


16c

The reaction was performed according to the general procedure B with **16a** (58.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 29.0 mg (34.0%) of **16c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.80 (s, 1H), 7.39 (dd, *J* = 4.5, 3.5 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.24 – 7.18 (m, 2H), 7.05 (dd, *J* = 7.5, 2.1 Hz, 2H), 5.36 (s, 2H), 1.49 (s, 12H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 201.3, 136.2, 135.1, 132.8, 130.0, 128.9, 127.9, 127.2, 126.5, 123.1, 113.4, 110.2, 83.2, 50.6, 43.5, 28.8, 25.7; **ATR-FTIR (cm^{-1})**

2973, 1629, 1526, 1183, 1140, 968, 885 cm^{-1}; **HRMS m/z (ESI)** called for $C_{26}H_{33}BNO_3^+$(M + H)$^+$ 418.2548, found 418.2550.

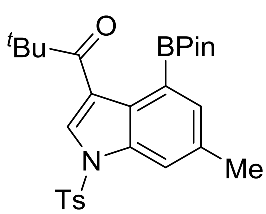
2,2-Dimethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)propan-1-one (17c)



17c

The reaction was performed according to the general procedure B with **17a** (40.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/10 to 1/5) to afford 30.9 mg (48.0%) of **17c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 9.98 (brs, 1H), 7.37 (dd, *J* = 6.9, 1.1 Hz, 1H), 7.17 – 7.06 (m, 3H), 1.49 (s, 12H), 1.15 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.3, 134.1, 131.00, 130.97, 129.1, 126.7, 123.1, 112.7, 111.7, 83.2, 43.1, 28.7, 25.8; **ATR-FTIR (cm^{-1})** 2973, 1612, 1478, 1303, 1194, 1120, 975, 768, 664 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{27}BNO_3^+$(M + H)$^+$ 328.2079, found 328.2079.

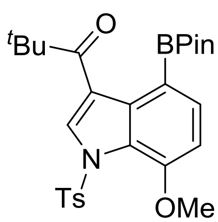
2,2-Dimethyl-1-(6-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)propan-1-one (18c)



18c

The reaction was performed according to the general procedure B with **18a** (74.0 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 84.1 mg (85.0%) of **18c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (s, 1H), 7.76 – 7.69 (m, 3H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.24 – 7.20 (m, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 1.43 (s, 12H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.5, 135.1, 134.6, 134.1, 131.1, 130.0, 128.6, 126.8, 119.0, 113.9, 83.7, 44.2, 28.1, 25.4, 21.8, 21.5; **ATR-FTIR (cm^{-1})** 2975, 1655, 1359, 1188, 909, 848, 669 cm^{-1}; **HRMS m/z (ESI)** called for $C_{27}H_{35}BNO_5S^+$ (M + H)$^+$ 496.2324, found 496.2323.

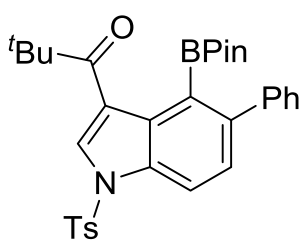
1-(7-Methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (19c)



19c

The reaction was performed according to the general procedure B with **19a** (77.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 86.5 mg (85.0%) of **19c** as a yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.45 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.22 (m, 2H), 6.69 (d, *J* = 8.0 Hz, 1H), 3.63 (s, 3H), 2.39 (s, 3H), 1.45 (s, 9H), 1.41 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.8, 147.8, 144.7, 136.5, 133.9, 131.5, 131.2, 129.5, 127.2, 124.0, 117.5, 107.3, 96.0, 83.5, 55.2, 44.3, 28.2, 25.4, 21.6; **ATR-FTIR (cm^{-1})** 2975, 1657, 1246, 1146, 914, 661 cm^{-1}**; HRMS m/z (ESI)** called for $C_{27}H_{35}BNO_6S^+$ $(M + H)^+$ 512.2273, found 512.2275.

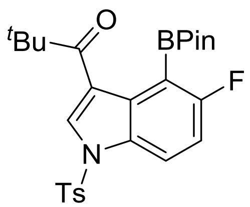
2,2-Dimethyl-1-(5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)propan-1-one (20c)



20c

The reaction was performed according to the general procedure B with **20a** (86.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 79.9 mg (71.0%) of **20c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.30 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.31 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 1H), 2.38 (s, 3H), 1.42 (s, 9H), 1.11 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 201.9, 145.8, 144.7, 143.2, 134.4, 132.7, 130.9, 130.2, 130.1, 127.5, 127.3, 126.8, 126.8, 118.2, 112.7, 83.6, 44.0, 28.5, 26.2, 21.6; **ATR-FTIR (cm^{-1})** 2973, 1655, 1369, 1172, 1012, 662, 581; **HRMS m/z (ESI)** calcd for: $C_{32}H_{37}BNO_5S^+$ $(M + H)^+$ 558.2480, found 558.2486.

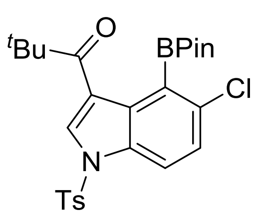
1-(5-Fluoro-1-(phenylsulfonyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (21c)



21c

The reaction was performed according to the general procedure B with **21a** (74.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 92.8 mg (93.0%) of **21c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.26 (s, 1H), 7.87 (dd, *J* = 9.1, 4.6 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.25 – 7.19 (m, 2H), 7.03 (t, *J* = 8.9 Hz, 1H), 2.35 (s, 3H), 1.46 (s, 12H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 201.9, 163.8 (d, *J* = 237.6 Hz), 146.0, 134.2, 132.1 (d, *J* = 12.0 Hz), 131.5, 130.1, 130.0, 126.8, 117.6 (d, *J* = 4.1 Hz), 114.8 (d, *J* = 10.1 Hz), 113.4 (d, *J* = 29.1 Hz), 84.1, 44.0, 28.3, 25.7, 21.6; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -109.73; **ATR-FTIR (cm^{-1})** 2976, 1662, 1535, 1167, 960, 808; **HRMS m/z (ESI)** $C_{26}H_{32}BFNO_5S^+$(M + H)$^+$500.2073, found 500.2070.

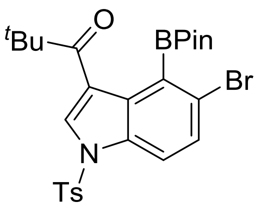
1-(5-Chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (22c)



22c

The reaction was performed according to the general procedure B with **22a** (77.8 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 93.7 mg (90.0%) of **22c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.25 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H), 1.50 (s, 12H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 201.7, 146.1, 135.5, 134.1, 132.3, 131.9, 131.2, 130.2, 126.8, 126.6, 117.4, 114.5, 84.1, 44.0, 28.3, 26.4, 21.5; **ATR-FTIR (cm^{-1})** 2976, 1654, 1535, 1141, 848, 778 cm^{-1}; **HRMS m/z (ESI)** called for $C_{26}H_{32}BClNO_5S^+$ $(M + H)^+$ 516.1777, found 516.1775.

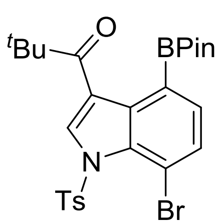
1-(5-Bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (23c)



23c

The reaction was performed according to the general procedure B with **23a** (86.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 85.9 mg (77.0%) of **23c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.23 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H), 1.52 (s, 12H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 201.7, 146.1, 134.1, 132.6, 132.3, 131.0, 130.2, 129.7, 126.8, 124.3, 117.4, 114.8, 84.2, 44.0, 28.4, 26.6, 21.6; **ATR-FTIR (cm^{-1})** 2974, 1654, 1170, 1009, 740, 640 cm^{-1}; **HRMS m/z (ESI)** called for$C_{26}H_{32}BBrNO_5S^+$ $(M + H)^+$ 560.1272, found 560.1273.

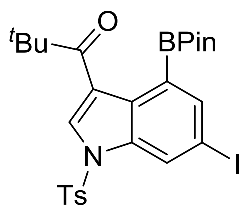
1-(7-Dromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (24c)



24c

The reaction was performed according to the general procedure B with **24a** (86.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 88.1 mg (79.0%) of **24c** as a colourless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.62 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.25 (m, 3H), 2.40 (s, 3H), 1.46 (s, 9H), 1.44 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.3, 136.5, 134.7, 134.4, 132.6, 131.3, 130.6, 129.9, 127.0, 116.3, 106.4, 83.7, 44.4, 28.3, 25.5, 21.7; **ATR-FTIR (cm^{-1})** 2970, 1659, 1170, 999, 577 cm^{-1}**; HRMS m/z (ESI)** called for $C_{26}H_{32}BBrNO_5S^+$ $(M + H)^+$ 560.1272, found 560.1267.

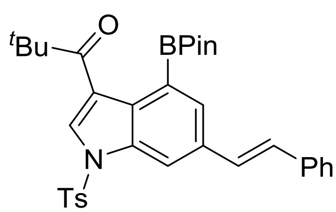
1-(6-Iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (25c)



25c

The reaction was performed according to the general procedure B with **25a** (96.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA / PE=1/20 to 1/10) to afford 65.9 mg (55.2%) of **25c** as a colourless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.32 (d, *J* = 1.5 Hz, 1H), 8.08 (s, 1H), 7.73(s, 1H), 7.72 – 7.68 (m, 2H), 7.28 – 7.24 (m, 2H), 2.38 (s, 3H), 1.42 (s, 12H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.3, 146.1, 138.0, 134.4, 134.2, 130.3, 129.4, 126.8, 122.6, 118.6, 90.4, 84.0, 44.3, 28.1, 25.5, 21.6 ; **ATR-FTIR (cm^{-1})** 2976, 1655, 1378, 1189, 1013, 917, 667, 578 cm^{-1}; **HRMS m/z (ESI)** called for $C_{26}H_{32}BINO_5S^+$ $(M + H)^+$ 608.1133, found 608.1129.

(*E*)-2,2-Dimethyl-1-(6-styryl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*-indol-3-yl)propan-1-one (26c)

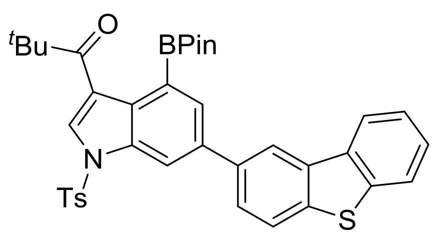


26c

The reaction was performed according to the general procedure B with **29a** (91.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA / PE = 1/20 to 1/10) to afford 69.9 mg (60.2%) of **26c** as a colourless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.14 (s, 1H), 8.06 (d, *J* = 1.5 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.63 (d, *J* = 1.5 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.38 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.26 – 7.22 (m, 2H), 7.19 (d, *J* = 2.1 Hz, 2H), 2.35 (s, 3H), 1.45 (s, 12H), 1.41 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.5, 145.8, 137.2, 134.6, 134.5, 134.4, 130.6, 130.2, 129.5, 129.0, 128.7, 128.6, 128.4, 127.7, 126.8, 126.5, 119.3, 111.8, 96.1, 83.9, 44.3, 28.1, 25.5, 21.6; **ATR-FTIR (cm^{-1})** 2975, 1703, 1362, 1162, 668 cm^{-1}; **HRMS m/z (ESI)** calcd for: $C_{34}H_{39}BNO_5S^+$: 584.2637, found.584.2630.

1-(6-(Dibenzo[*b*,*d*]thiophen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1*H*

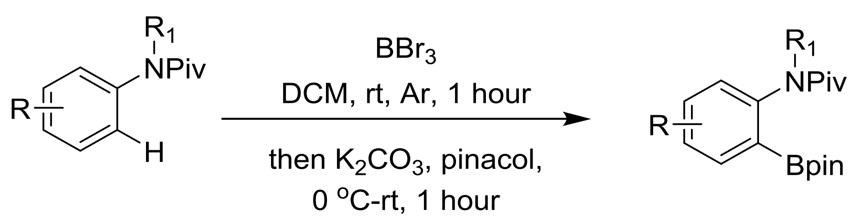
-indol-3-yl)-2,2-dimethylpropan-1-one (27c)



27c

The reaction was performed according to the general procedure B with **27a** (107.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. After quenched the reaction, the solvent was removed directly under vacuum and the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/20 to 1/10) to afford 113.5 mg (87.2%) of **27c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.37 (d, *J* = 1.7 Hz, 1H), 8.31 – 8.21 (m, 3H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.81 – 7.76 (m, 3H), 7.72 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.26 – 7.22 (m, 2H), 2.35 (s, 3H), 1.46 (s, 12H), 1.45(s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.6, 145.8, 139.9, 138.6, 138.5, 137.9, 136.1, 135.4, 134.5, 134.4, 130.2, 129.52, 129.50, 126.9, 126.7, 124.4, 123.0, 122.9, 121.8, 120.5, 119.1, 112.6, 83.9, 44.3, 28.1, 25.5, 21.6; **ATR-FTIR (cm^{-1})** 2970, 1656, 1370, 1176, 1143, 1076, 1020, 916 cm^{-1}; **HRMS m/z (ESI)** called for $C_{38}H_{39}BNO_5S_2^+$ $(M + H)^+$ 664.2357, found 664.2351.

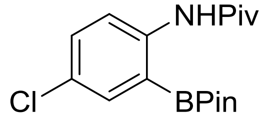
4.3 General procedure C.



28a-51a **28c-51c**

Flame-dried 25 mL Schlenk tube was flushed with argon and charged with *N*-pivaloyl amide substrates **28-51a** (0.2 mmol, 1.0 equiv) and dry DCM (1.0 mL, 0.2 M). A solution of BBr_3 (1 M in DCM, 0.22 mL, 1.1 equiv) was added slowly under argon atmosphere. The mixture was stirred at room temperature for 1.0 hour and then quenched with a solution of 0.5 ml of 1 M K_2CO_3 aq and pinacol (23.6 mg, 0.2 mmol, 1.0 equiv) in 0.5 ml of DCM at 0 ℃. The resulting mixture was allowed to warm to room temperature and continued to stirr for another 1 hour. After that, the excess water was removed by filtration with $MgSO_4$ and then washed with EA. The filtrate was collected and the solvent removed in vacuo and then loaded onto the top of a short column slurry-packed with EA or CH_3OH to get the target product **28-51c**.

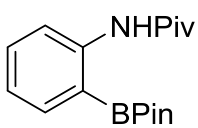
***N*-(4-Chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (28c)**



28c

The reaction was performed according to the general procedure C with **28a** (39.0 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA) to afford 57.3 mg (85.1%) of **28c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.48 (brs, 1H), 8.51 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 2.6 Hz, 1H), 7.38 (dd, *J* = 9.0, 2.7 Hz, 1H), 1.38 (s, 12H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 143.4, 135.5, 132.5, 127.8, 120.6, 84.7, 40.1, 27.5, 24.9; **ATR-FTIR (cm^{-1})** 3396, 2977, 1691, 1406, 1374, 1142, 963, 754 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{26}BClNO_3^+$ (M + H)$^+$ 338.1689, found 338.1687.

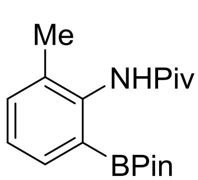
***N*-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (29c)** [18]



29c

The reaction was performed according to the general procedure C with **29a** (35.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA/PE = 1/2 to 1/1) to afford 53.5 mg (88.1%) of **29c** as a white solid. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.54 (brs, 1H), 8.59 – 8.54 (m, 1H), 7.77 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.07 – 7.03 (m, 1H), 1.38 (s, 12H), 1.33 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.1, 145.1, 136.2, 132.8, 122.6, 119.1, 84.3, 40.1, 27.6, 24.9; **ATR-FTIR (cm^{-1})** 3386, 2972, 1688, 1447, 1317, 1145, 761 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{27}BNO_3^+$ (M + H)$^+$ 304.2079, found 304.2079.

***N*-(2-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (30c)**

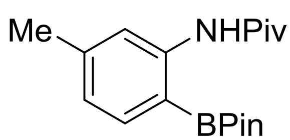


The reaction was performed according to the general procedure C with **30a** (38.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the excess water

30c

was removed by filtration with $MgSO_4$, washed with EA. The filtrate was collected and the solvent removed in vacuum to give a white solid 61.0 mg (96.0%) of **30c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.26 (brs, 1H), 7.58 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 2.22 (s, 3H), 1.37 (s, 9H), 1.33 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.8, 138.9, 132.7, 132.3, 129.3, 125.6, 82.6, 39.1, 27.3, 25.4, 18.0; **ATR-FTIR (cm^{-1})** 2972, 1682, 1505, 1352, 1138, 666 cm^{-1}; **HRMS m/z (ESI)** called for $C_{18}H_{29}BNO_3^+$ (M + H)$^+$ 318.2235, found 318.2238.

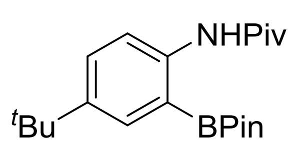
***N*-(5-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (31c)**



31c

The reaction was performed according to the general procedure C with **31a** (38.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA) to afford 54.1 mg (85.2%) of **31c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.54 (brs, 1H), 8.46 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.85 (m, 1H), 2.35 (s, 3H), 1.36 (s, 12H), 1.32 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 145.1, 143.5, 136.2, 123.5, 119.7, 84.1, 40.1, 27.5, 24.8, 22.0; **ATR-FTIR (cm^{-1})** 3388, 2976, 1690, 1188, 963, 672 cm^{-1}; **HRMS m/z (ESI)** called for $C_{18}H_{29}BNO_3^+$ (M + H)$^+$ 318.2235, found 318.2237.

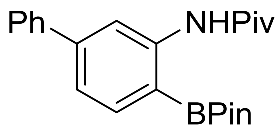
***N*-(4-(*Tert*-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (32c)**



32c

The reaction was performed according to the general procedure C with **32a** (46.8 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA) to afford 67.2 mg (94.0%) of **32c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.54 (s, 1H), 8.49 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 2.5 Hz, 1H), 7.49 (dd, *J* = 8.8, 2.6 Hz, 1H), 1.38 (s, 12H), 1.33 – 1.31 (m, 18H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.9, 145.1, 142.7, 132.6, 129.9, 118.9, 84.2, 40.0, 34.2, 31.3, 27.6, 24.9; **ATR-FTIR (cm^{-1})** 3380, 2966, 1689, 1359, 1139, 845, 684 cm^{-1}; **HRMS m/z (ESI)** called for $C_{21}H_{35}BNO_3^+$ $(M + H)^+$ 360.2705, found 360.2703.

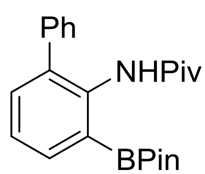
***N*-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-3-yl)pivalamide (33c)**



33c

The reaction was performed according to the general procedure C with **33a** (50.8 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA) to afford 75.1 mg (80.0%) of **33c** as a white solid. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.62 (s, 1H), 8.97 – 8.93 (m, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.31 (m, 2H), 1.40 (s, 12H), 1.36 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 177.3, 145.6, 145.5, 140.6, 136.7, 128.6, 127.7, 127.3, 121.2, 117.8, 84.4, 40.2, 27.6, 24.9; **ATR-FTIR (cm^{-1})** 3408, 2850, 1679, 1453, 1127, 999 cm^{-1};. **HRMS m/z (ESI)** called for $C_{23}H_{31}BNO_3^+$ $(M + H)^+$380.2392, found 380.2395.

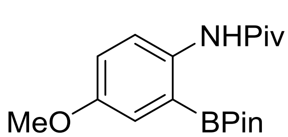
***N*-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-2-yl)pivalamide (34c)**



34c

The reaction was performed according to the general procedure C with **34a** (50.8 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA) to afford 62.9 mg (83.1%) of **34c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.52 (brs, 1H), 7.69 – 7.65 (m, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.34 – 7.26 (m, 3H), 7.18 (dd, *J* = 7.5, 1.5 Hz, 1H), 1.34 (s, 12H), 1.18 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 137.6, 133.6, 132.9, 129.3, 129.6, 129.0, 128.7, 128.1, 126.2, 80.7, 38.6, 26.6, 26.1; **ATR-FTIR (cm^{-1})** 3414, 2970, 1679, 1453, 1127, 1042 cm^{-1}; **HRMS m/z (ESI)** called for $C_{23}H_{31}BNO_3^+$ $(M + H)^+$380.2392, found 380.2395.

***N*-(4-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (35c)**

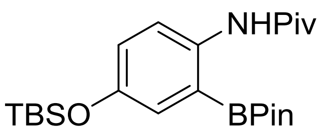


The reaction was performed according to the general procedure C with **35a** (41.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0

35c

mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/2) to afford 39.6 mg (59.1%) of **35c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.37 (brs, 1H), 8.45 (d, *J* = 9.1 Hz, 1H), 7.28 (d, *J* = 3.1 Hz, 1H), 6.99 (dd, *J* = 9.1, 3.2 Hz, 1H), 3.80 (s, 3H), 1.37 (s, 12H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.7, 154.8, 138.6, 120.7, 120.0, 118.6, 84.3, 55.5, 39.9, 27.6, 24.9; **ATR-FTIR (cm^{-1})** 2973, 1690, 1400, 1138, 753 cm^{-1}; **HRMS m/z (ESI)** called for $C_{18}H_{29}BNO_4^+$ (M + H)$^+$ 334.2184, found 334.2185.

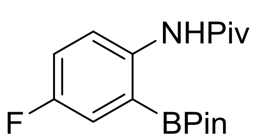
***N*-(4-(*tert*-Butyldimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (36c)**



36c

The reaction was performed according to the general procedure C with **36a** (61.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA) to afford 60.7 mg (70.1%) of **36c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.38 (s, 1H), 8.38 (d, *J* = 9.0 Hz, 1H), 7.21 (d, *J* = 3.0 Hz, 1H), 6.91 (dd, *J* = 9.0, 3.0 Hz, 1H), 1.36 (s, 12H), 1.31 (s, 9H), 0.97 (s, 9H), 0.17 (s, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.6, 150.6, 138.9, 126.8, 124.0, 120.4, 84.2, 39.9, 27.6, 25.7, 24.9, 18.1, -4.5; **ATR-FTIR (cm^{-1})** 3734, 2962, 1687, 1415, 1347, 839 cm^{-1}; **HRMS m/z (ESI)** called for $C_{23}H_{41}BNO_3Si^+$ (M + H)$^+$ 434.2892, found 434.2894.

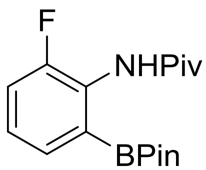
***N*-(4-Fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (37c)**



37c

The reaction was performed according to the general procedure C with **37a** (39.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the excess water was removed by filtration with $MgSO_4$, washed with EA. The filtrate was collected and the solvent removed in vacuum to give a white solid 63.1 mg (95.0%) of **37c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.43 (brs, 1H), 8.45 (dd, *J* = 9.2, 4.8 Hz, 1H), 7.42 (dd, *J* = 8.7, 3.1 Hz, 1H), 7.10 (ddd, *J* = 9.2, 8.0, 3.2 Hz, 1H), 1.37 (s, 12H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 158.1 (d, *J* = 243.2 Hz), 140.7 (d, *J* = 2.3 Hz), 121.6 (d, *J* = 20.8 Hz), 120.8 (d, *J* = 6.8 Hz), 119.0 (d, *J* = 21.9 Hz), 115.4 (d, *J* = 22.3 Hz), 39.9, 27.5, 24.9; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -120.40;.**ATR-FTIR (cm^{-1})** 3390, 2975, 1689, 1477, 1141, 966, 854, 574 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{26}BFNO_3^+$ $(M + H)^+$ 322.1984, found 322.1984.

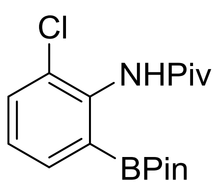
***N*-(2-Fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (38c)**



38c

The reaction was performed according to the general procedure C with **38a** (39.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on acidic alumina (eluent: EA) to afford 45.7 mg (71.0%) of **38c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.33 (brs, 1H), 7.44 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.09 – 7.04 (m, 1H), 1.37 (s, 9H), 1.34 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.5, 152.3 (d, *J* = 247.2 Hz), 129.3 (d, *J* = 3.6 Hz), 126.4 (d, *J* = 6.9 Hz), 115.5 (d, *J* = 18.6 Hz), 82.1, 39.1, 27.1, 25.6; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -130.25; **ATR-FTIR (cm^{-1})** 3120, 1701, 1477, 1141, 976, 854, 574 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{26}BFNO_3^+$ $(M + H)^+$ 322.1984, found 322.1984.

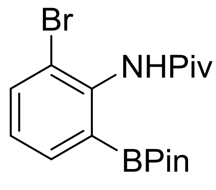
***N*-(2-Chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (39c)**



39c

The reaction was performed according to the general procedure C with **39a** (42.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the excess water was removed by filtration with $MgSO_4$, washed with EA. The filtrate was collected and the solvent removed in vacuum to give a white solid 77 mg (99.0%) **39c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.82 (brs, 1H), 7.52 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.25 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 1.36 (s, 9H), 1.30 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 178.2, 133.2, 132.0, 128.8, 127.9, 127.1, 124.3, 81.0, 39.0, 26.8, 26.0; **ATR-FTIR (cm^{-1})** 3422, 2973, 1690, 1528, 1350, 1148, 867, 783 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{26}BClNO_3^+$ $(M + H)^+$ 338.1689, found 338.1686.

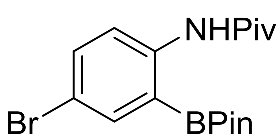
N-(2-Bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (40c)



40c

The reaction was performed according to the general procedure C with **40a** (51.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the excess water was removed by filtration with $MgSO_4$, washed with EA. The filtrate was collected and the solvent removed in vacuum to give a white solid 78 mg (99.0%) **40c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.91 (brs, 1H), 7.57 (dd, J = 7.3, 1.4 Hz, 1H), 7.41 (dd, J = 8.0, 1.4 Hz, 1H), 7.10 – 7.05 (m, 1H), 1.38 (s, 9H), 1.30 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 134.1, 132.6, 130.0, 127.7, 110.9, 81.0, 39.0, 26.8, 26.0; **ATR-FTIR (cm^{-1})** 3412, 2863, 1690, 1148, 887, 783 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{26}BBrNO_3^+$ (M + H)$^+$ 382.1184, found 382.1181.

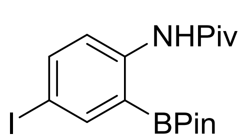
N-(4-Bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (41c)



41c

The reaction was performed according to the general procedure C with **41a** (51.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the excess water was removed by filtration with $MgSO_4$, washed with EA. The filtrate was collected and the solvent removed in vacuum to give a white solid 78.0 mg (99.0%) **41c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.49 (brs, 1H), 8.45 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.51 (dd, J = 9.0, 2.5 Hz, 1H), 1.37 (s, 12H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 143.9, 138.4, 135.4, 121.0, 115.5, 84.7, 40.2, 27.5, 24.9; **ATR-FTIR (cm^{-1})** 3384, 2973, 1690, 1522, 1343, 114, 922, 858 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{26}BBrNO_3^+$ (M + H)$^+$ 382.1184, found 382.1181.

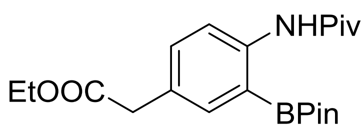
N-(4-Iodo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (42c)



42c

The reaction was performed according to the general procedure C with **42a** (60.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the excess water was removed by filtration with $MgSO_4$, washed with EA. The filtrate was collected and the solvent removed in vacuum to give a white solid 87.1 mg (99.0%) **42c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.49 (brs, 1H), 8.35 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 2.3 Hz, 1H), 7.71 (dd, *J* = 8.8, 2.3 Hz, 1H), 1.38 (s, 12H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 144.5, 144.4, 141.3, 121.2, 86.2, 84.7, 40.1, 27.5, 24.9; **ATR-FTIR (cm^{-1})** 2976, 1690, 1561, 1478, 1142, 961, 922 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{26}BINO_3^+$ $(M + H)^+$ 430.1045, found 430.1044.

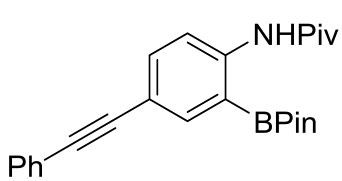
Eyl 2-(4-pivalamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) cetate (43c)



43c

The reaction was performed according to the general procedure C with **43a** (52.8 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 56.2 mg (72.1%) of **43c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.52 (s, 1H), 8.53 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.37 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 2H), 1.37 (s, 12H), 1.31 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.1, 171.7, 144.1, 136.9, 133.7, 128.2, 119.3, 84.4, 60.8, 40.6, 40.1, 27.6, 24.9, 14.2; **ATR-FTIR (cm^{-1})** 2976, 1736, 1592, 1425, 1142, 749 cm^{-1}; **HRMS m/z (ESI)** called for $C_{21}H_{33}BNO_5^+$ $(M + Na)^+$ 390.2446, found 390.2450.

***N*-(4-(Phenylethynyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (44c)**

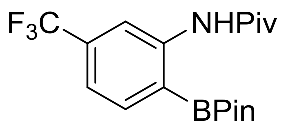


44c

The reaction was performed according to the general procedure C with **44a** (55.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 41.9 mg (52.2%) of **44c** as a yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.60 (brs, 1H), 8.60 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 2.1 Hz, 1H), 7.61 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.53

– 7.49 (m, 2H), 7.37 – 7.27 (m, 3H), 1.39 (s, 12H), 1.34 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 144.8, 139.6, 135.8, 131.4, 128.3, 127.9, 123.5, 119.0, 117.4, 89.3, 88.7, 84.6, 40.2, 27.5, 24.9; **ATR-FTIR (cm^{-1})** 3380, 2973, 1690, 1583, 1405, 1311, 1138, 753 cm^{-1}; **HRMS m/z (ESI)** called for $C_{25}H_{31}BNO_3^+$ (M + H)$^+$ 404.2392, found 404.2388.

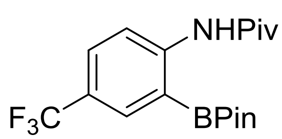
***N*-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl)pivalamide (45c)**



45c

The reaction was performed according to the slightly modified procedure C with **45a** (49.2 mg, 0.2 mmol), BBr_3 (99.9%, 500 mg, 2.0 mmol, 10.0 equiv) in dry DCM (0.1 mL) at room temperature under Ar for 1 hour. The solvent was removed under vaccum directly, diluted with 0.5 mL DCM, and then quenched the reaction. The crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 49.4 mg (66.1%) of **45c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.68 (brs, 1H), 8.70 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.3 Hz, 1H), 1.40 (s, 12H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.5, 147.9, 133.2 (q, *J* = 3.9 Hz), 129.7 (q, *J* = 3.8 Hz), 119.0, 84.9, 40.3, 27.5, 24.9; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.03; **ATR-FTIR (cm^{-1})** 3000, 1689, 1594, 1359, 1309, 1116 cm^{-1}; **HRMS m/z (ESI)** called for $C_{18}H_{26}BF_3NO_3^+$ (M + H)$^+$ 372.1952, found 372.1957.

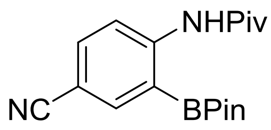
***N*-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)phenyl)pivalamide (46c)**



46c

The reaction was performed according to the slightly modified procedure C with **46a** (49.2 mg, 0.2 mmol), BBr_3 (99.9%, 500 mg, 2.0 mmol, 10.0 equiv) in dry DCM (0.1 mL) at room temperature under Ar for 1 hour. The solvent was removed under vaccum directly, diluted with 0.5 mL DCM, and then quenched the reaction. The crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 42.0 mg (56.2%) of **46c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.64 (brs, 1H), 8.93 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.26 (m, 1H), 1.39 (s, 12H), 1.34 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.5, 145.4, 136.7, 118.9 (q, *J* = 3.8 Hz), 115.7 (q, *J* = 3.9 Hz), 84.9, 40.2, 27.5, 24.9; **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -63.27; **ATR-FTIR (cm^{-1})** 3010, 1699, 1594, 1359, 1219, 986 cm^{-1}; **HRMS m/z (ESI)** called for $C_{18}H_{25}BF_3NNaO_3^+$ $(M + Na)^+$ 394.1772, found 394.1773.

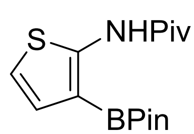
N-(4-Cyano-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (47c)



47c

The reaction was performed according to the slightly modified procedure C with **47a** (40.4 mg, 0.2 mmol), BBr_3 (99.9%, 500 mg, 2.0 mmol, 10.0 equiv) in dry DCM (0.1 mL) at room temperature under Ar for 1 hour. The solvent was removed under vaccum directly, diluted with 0.5 mL DCM, and then quenched the reaction. The crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 32.1 mg (49.1%) of **47c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.70 (brs, 1H), 8.70 (d, J = 8.8 Hz, 1H), 8.06 (d, J = 2.1 Hz, 1H), 7.69 (dd, J = 8.8, 2.2 Hz, 1H), 1.39 (s, 12H), 1.32 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.6, 148.5, 140.5, 136.3, 119.3, 119.0, 105.8, 85.1, 40.4, 27.4, 24.9; **ATR-FTIR (cm^{-1})** 3370, 2225, 1696, 1584, 1356, 1264 cm^{-1}; **HRMS m/z (ESI)** called for $C_{18}H_{26}BN_2O_3^+$ $(M + H)^+$ 329.2031, found 329.2030.

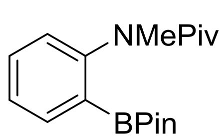
N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pivalamide (48c)



48c

The reaction was performed according to the general procedure C with **48a** (36.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 33.3 mg (54.0%) of **48c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 10.20 (brs, 1H), 7.08 (d, J = 5.5 Hz, 1H), 6.80 (dd, J = 5.5, 0.8 Hz, 1H), 1.36 (s, 12H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.9, 151.6, 127.9, 117.0, 83.9, 39.0, 27.3, 24.9; **ATR-FTIR (cm^{-1})** 2973, 1677, 1552, 1406, 1239, 1139, 677 cm^{-1}; **HRMS m/z (ESI)** called for $C_{15}H_{25}BNO_3S^+$ $(M + H)^+$ 310.1643, found 310.1648.

N-Methyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (49c)

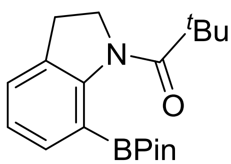


The reaction was performed according to the general procedure C with **49a** (38.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at

49c

room temperature under Ar for 1 hour. After quenched the reaction, the crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 30.0 mg (50%) of **49c** as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.83 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.43 (td, *J* = 7.6, 1.6 Hz, 1H), 7.31 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 3.19 (brs, 3H), 1.31 (s, 12H), 1.00 (brs, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.0, 136.5, 131.6, 129.2, 127.2, 83.8, 41.4, 29.6, 24.9; **ATR-FTIR (cm^{-1})** 2978, 1636, 1598, 1353, 1070, 746 cm^{-1}; **HRMS m/z (ESI)** called for $C_{18}H_{28}BNNaO_3^+$ $(M + Na)^+$ 340.2054, found 340.2055.

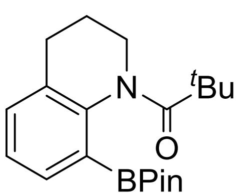
2,2-Dimethyl-1-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-1-yl)propan-1-one (50c)



50c

The reaction was performed according to the general procedure C with **50a** (40.8 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 h. After quenched the reaction, the excess water was removed by filtration with $MgSO_4$. The filtrate was collected and the solvent removed in vacuum to give a white solid 66.1 mg (99.0%) **50c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.42 (d, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 4.27 (t, *J* = 7.9 Hz, 2H), 3.19 (t, *J* = 7.9 Hz, 2H), 1.38 (s, 9H), 1.29 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.5, 143.7, 130.8, 127.0, 123.1, 80.3, 49.2, 39.4, 28.7, 27.2, 25.9; **ATR-FTIR (cm^{-1})** 3629, 2928, 1685, 1367,983 cm^{-1}; **HRMS m/z (ESI)** called for $C_{19}H_{29}BNO_3^+$ $(M + H)^+$ 330.2235, found 330.2238.

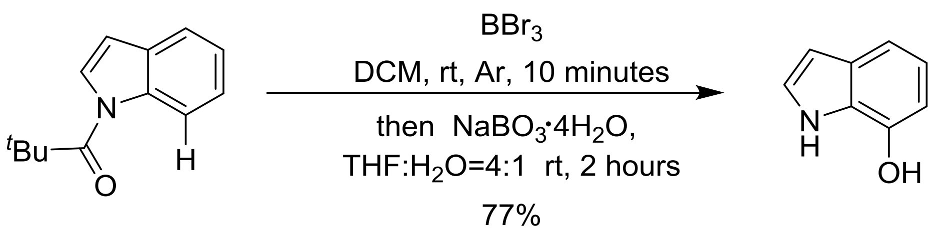
2,2-Dimethyl-1-(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinolin-1(2*H*)-yl)propan-1-one (51c)



51c

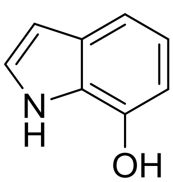
The reaction was performed according to the general procedure C with **51a** (43.6 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. After quenched the reaction, the excess water was removed by filtration with $MgSO_4$. The filtrate was collected and the solvent removed in vacuum to give a white solid 68.8 mg (99.0%) **51c**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.49 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.02 – 6.99 (m, 1H), 4.09 – 3.99 (m, 2H), 2.89 (t, J = 6.7 Hz, 2H), 2.06 – 2.00 (m, 2H), 1.46 (s, 9H), 1.28 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.5, 138.4, 130.3, 128.4, 126.5, 124.8, 79.9, 47.2, 40.2, 28.4, 27.1, 26.0, 22.2; **ATR-FTIR (cm^{-1})** 2926, 2698, 1428, 1129, 1058, 983 cm^{-1}; **HRMS m/z (ESI)** called for $C_{20}H_{31}BNO_3^+$ $(M + H)^+$ 344.2392, found 344.2393.

5. Applications of metal-free directed C-H borylation strategy



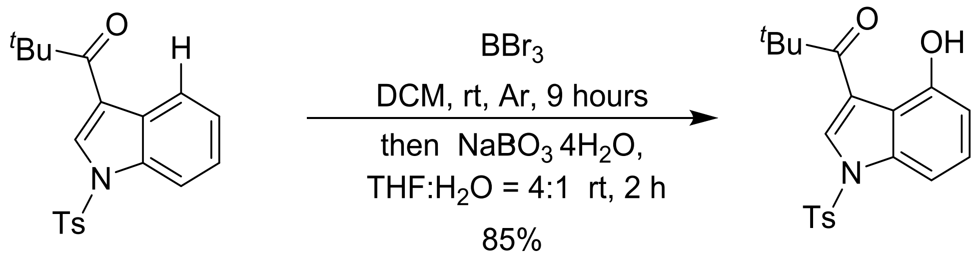
1a **53**

1*H*-Indol-7-ol (53)[19]



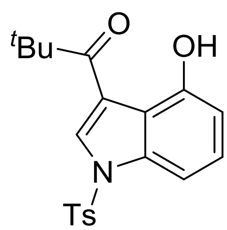
53

The reaction of 1-(1*H*-indol-1-yl)-2,2-dimethylpropan-1-one **1a** (40.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv), in dry DCM (1.0 mL) at room temperature under Ar for 10 minutes. The solvent was removed under vaccum directly. $NaBO_3 \cdot 4H_2O$ (91.0 mg, 0.6 mmol), 2.0 ml THF and 0.5 mL H_2O added to the reaction mixture and stirred at room temperature for another 2 hours. Then after column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 21.0 mg (77.2%) of **53** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.39 (brs, 1H), 7.25 (dt, J = 8.0, 0.9 Hz, 1H), 7.17 (t, J = 2.8 Hz, 1H), 6.94 (t, J = 7.8 Hz, 1H), 6.59 – 6.50 (m, 2H), 5.26 (brs, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 141.4, 130.1, 125.7, 124.2, 120.1, 113.6, 106.4, 102.9; **ATR-FTIR (cm^{-1})** 3855, 2926, 1655, 1583, 1366, 1163, 1132, 898, 451 cm^{-1}; **HRMS m/z (ESI)** called for $C_8H_8NO^+$ $(M + H)^+$ 134.0600, found 134.0595.



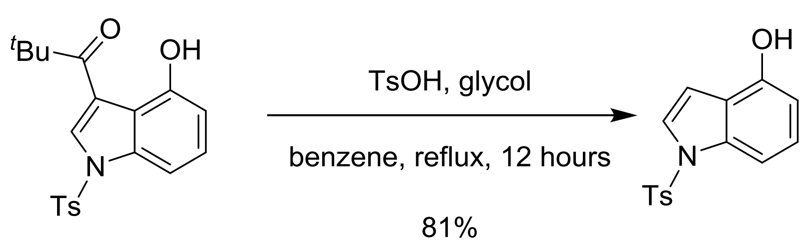
15a **54**

1-(4-Hydroxy-1-tosyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one (54)



54

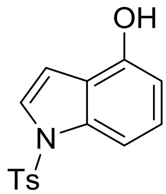
The reaction of 2,2-Dimethyl-1-(1-tosyl-1*H*-indol-3-yl)propan-1-one (**15a**) (71.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv), in dry DCM (1.0 mL) at room temperature under Ar for 9 hours. The solvent was removed under vaccum directly. $NaBO_3{\cdot}4H_2O$ (91.0 mg, 0.6 mmol), 2 mL THF and 0.5mL H_2O added to the reaction mixture and stirred at room temperature for another 2 hours. Then after column chromatography on silica gel (eluent: EA/PE = 1/5) to afford 63.1 mg (85.1%) of **54** as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 11.42 (s, 1H), 8.39 (s, 1H), 7.84 – 7.78 (m, 2H), 7.36 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.23 (t, *J* = 8.1 Hz, 1H), 6.77 (dd, *J* = 8.0, 0.9 Hz, 1H), 2.38 (s, 3H), 1.47 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.0, 152.4, 146.2, 135.7, 134.0, 132.3, 130.3, 128.0, 127.2, 118.4, 116.7, 110.9, 103.7, 44.7, 29.2, 21.7; **ATR-FTIR (cm^{-1})** 3725, 2978, 1697, 1370, 1165, 1080, 660 cm$^{-1;}$ **HRMS m/z (ESI)** called for $C_{20}H_{22}NO_4S^+$ $(M + H)^+$ 372.1264, found 372.1269.



54 **55**

1-Tosyl-1*H*-indol-4-ol (55) [7]

A solution of **54** (0.2 mmol), TsOH (0.3 mmol, 1.5 equiv) and glycol (1.6 mmol, 8.0 equiv) in benzene (1.0 mL) as heated under reflux conditions for 12 hours. The solvent was then removed under reduced pressure. The crude product was purified by column chromatography (eluent:

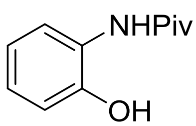


55

EA/PE = 1/20 to 1/10) to afford 49.8 mg (81.2%) of **55** as a white solid. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.79 – 7.72 (m, 2H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 3.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.74 (dd, *J* = 3.7, 0.8 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 5.43 (brs, 1H), 2.33 (s, 3H).; **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 149.0, 145.0, 136.5, 135.1, 129.8, 126.8, 125.5, 125.1, 120.0, 108.2, 106.5, 105.3, 21.5; **ATR-FTIR (cm^{-1})** 3739, 2975, 1289, 1009, 914, 579, 421 cm^{-1}; **HRMS m/z (ESI)** called for $C_{15}H_{14}NO_3S^+$ $(M + H)^+$ 288.0689, found 288.0683.

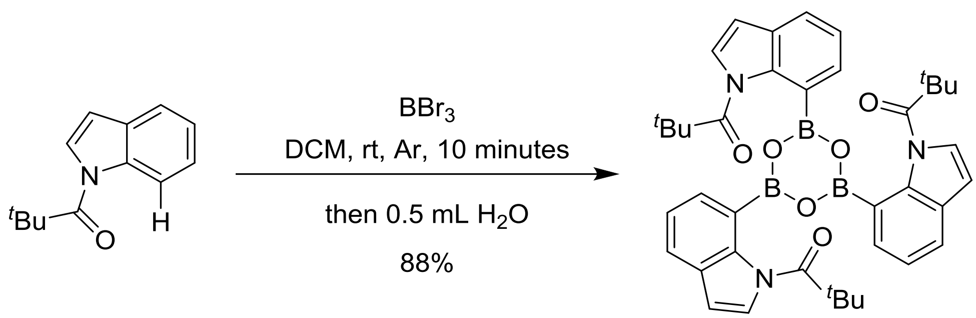
29a **56**

***N*-(2-hydroxyphenyl)pivalamide (56)** [20]



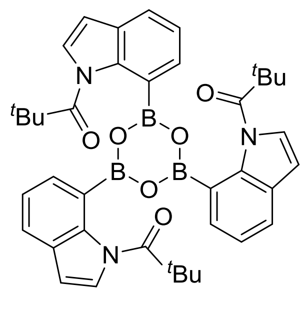
56

The mixture of *N*-phenylpivalamide (**29a**) (35.4 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv) was stirred in dry DCM (1.0 mL) at room temperature under Ar for 1 hour. The solvent was removed under vaccum directly. $NaBO_3{\cdot}4H_2O$ (91.0 mg, 0.6 mmol), 2 mL THF and 0.5 mL H_2O added to the reaction mixture and stirred at room temperature for another 1 hour. Then after column chromatography on silica gel (eluent: EA/PE = 1/10) to afford 31.1 mg (82.1%) of **56** as a white solid: **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.81 (s, 1H), 7.61 (brs, 1H), 7.14 – 7.11 (m, 1H), 7.04 – 7.00 (m, 2H), 6.90 – 6.82 (m, 1H), 1.36 (s, 9H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 178.9, 148.5, 126.8, 125.6, 122.0, 120.4, 119.3, 39.5, 27.6; **ATR-FTIR (cm^{-1})** 3430, 2789, 1688, 1154, 989 cm^{-1}; **HRMS m/z (ESI)** called for $C_{11}H_{16}NO_2^+$ $(M + H)^+$ 194.1176, found 194.1171.



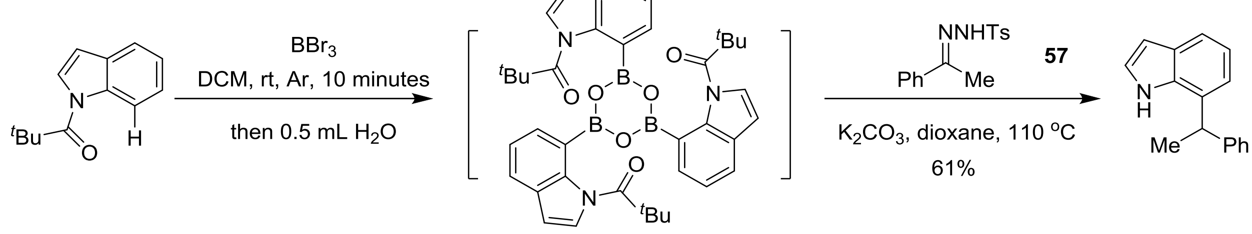
1a **1d**

1,1',1''-((1,3,5,2,4,6-Trioxatriborinane-2,4,6-triyl)tris(1*H*-indole-7,1-diyl))tris(2,2-dimethylpropan-1-one) (1d)



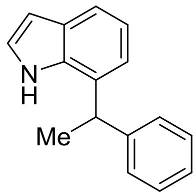
1d

The reaction of 1-(1*H*-indol-1-yl)-2,2-dimethylpropan-1-one **1a** (105.0 mg, 0.50 mmol), BBr_3 (1 M in DCM) (0.55 mL, 0.55 mmol), in dry DCM (1.0 mL) at room temperature under Ar for 10 minutes. The solvent was removed under vaccum directly. 1mL DCM and 0.5 mL H_2O added to the reaction mixture and stirred at room temperature for another 2 h, after that DCM (5 mL) was added. The biphasic mixture was separated and the aqueous phase was extracted with DCM (2 × 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, the dried solution was filtered and the filtrate was concentrated under reduced pressure to give a white solid 99.9 mg (88.1%) **1d**. The product can be used without further purification by flash column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.84 (d, *J* = 7.0 Hz, 3H), 7.58 (d, *J* = 3.9 Hz, 3H), 7.41 (dd, *J* = 7.7, 1.3 Hz, 3H), 7.32 (t, *J* = 7.4 Hz, 3H), 6.62 (d, *J* = 3.9 Hz, 3H), 1.59 (s, 27H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.9, 137.6, 129.5, 126.9, 124.7, 123.8, 119.4, 113.5, 111.6, 40.5, 28.7. **ATR-FTIR (cm^{-1})** 2968, 1690, 1439, 1110, 698 cm^{-1}; **HRMS m/z (ESI)** called for $C_{39}H_{43}B_3N_3O_6+^+$ $(M + H)^+$ 682.3426, found 682.3426.



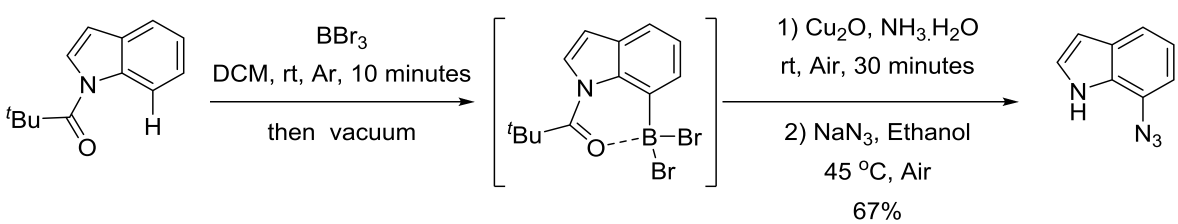
1a **1d** **58**

7-(1-Phenylethyl)-1*H*-indole (58) [21]



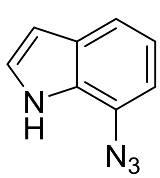
58

A reaction tube was charged with potassium carbonate (41.5 mg, 0.3 mmol), **(1d)** (0.2 mmol), the tosylhydrazone **57** (0.2 mmol, 1.0 equiv) and dioxane (1.0 mL). The system was heated at 110 ℃ with stirring and reflux. The reaction was monitored by GCMS. When the reaction was completed, the crude reaction mixture was allowed to reach room temperature, the solvent was eliminated with a saturated solution of $NaHCO_3$ and dichloromethane were added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with two portions of a saturated solution of $NaHCO_3$, brine, and then dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure. Then after column chromatography on silica gel (eluent: EA/PE = 1/10) to afford 26.5 mg (61.2%) of **58** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.68 (brs, 1H), 7.54 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.30 – 7.19 (m, 6H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.99 (dd, *J* = 3.2, 2.5 Hz, 1H), 6.47 (dd, *J* = 3.2, 2.0 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.7, 134.4, 128.8, 128.1, 128.0, 127.4, 126.5, 123.9, 119.9, 119.8, 119.2, 102.6, 41.3, 21.3; **ATR-FTIR (cm^{-1})** 3451, 2968, 1490, 1339, 910, 698 cm^{-1}; **HRMS m/z (ESI)** called for $C_{16}H_{15}NNa^{+}$ $(M + Na)^{+}$ 244.1097, found 244.1095.



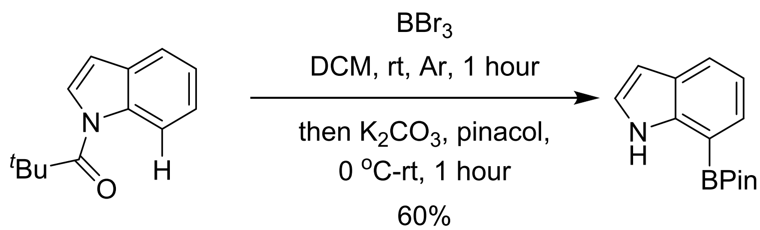
1a 1b 59

7-Azido-1*H*-indole (59) [22]



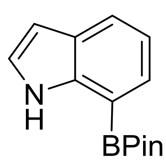
59

The reaction of 1-(1*H*-indol-1-yl)-2,2-dimethylpropan-1-one **1a** (40.2 mg, 0.2 mmol), BBr_3 (0.22 mL, 1.1 equiv), in dry DCM (1.0 mL) at room temperature under Ar for 10 minutes. After the reaction, the solvent was directly removed under vacuum to obtain a yellow solid **1b**. Cu_2O (0.04 mmol, 14.3 mg) and 25% aqueous ammonia (0.19 mL, 2.5 mmol of NH_3) were added to a round-bottom flask charged with a stirrer, and the mixture was stirred for 30 minutes under air at room temperature (~25 ^{o}C). Then, **1b**, ethanol (1.0 mL) and NaN_3 (1.0 mmol) was added to the flask, and the solution was stirred under air at 45 ^{o}C until the reaction was completed (as determined by TLC). The solvent in the resulting solution was removed on a rotary evaporator, water (5.0 mL) was added to the residue, and the target product was extracted with ethyl acetate (3 × 3.0 mL). The combined organic phase was dried over anhydrous Mg_2SO_4, filtered, and concentrated, and the residue was purified by column chromatography on silica gel (eluent: EA/PE = 1/100) give the desired product 20.9 mg (67.1%) as a brown solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.27 (brs, 1H), 7.45 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.21 (dd, *J* = 3.2, 2.4 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.99 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.56 (dd, *J* = 3.2, 2.2 Hz, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 129.5, 128.0, 124.5, 124.31**,** 120.5, 117.4, 110.3, 103.0; **ATR-FTIR (cm^{-1})** 2118, 1577, 1340, 785, 723 cm^{-1}; **HRMS m/z (ESI)** called for $C_8H_7N_4^+$ $(M + H)^+$ 159.0665, found 159.0668.



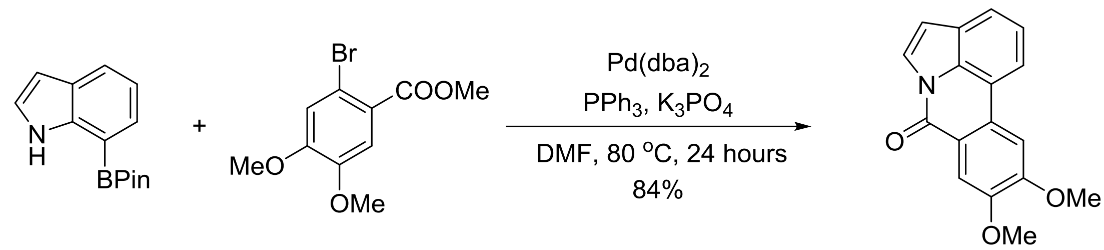
1c **1e**

7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (1e) [23]

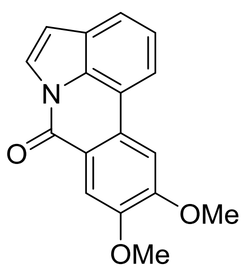


1e

Flame-dried 25 mL Schlenk tube was flushed with argon and charged with **1a** (1.0 g, 5.0 mmol) and dry DCM (5.0 mL, 1.0 M). A solution of BBr_3 (5.5 mL, 1.1 equiv) was added very slowly under argon atmosphere. The reaction mixture was stirred at room temperature for 1 hour and then quenched with a solution of 0.5 mL of saturated K_2CO_3 aq and pinacol (590.0 mg, 5.0 mmol, 1.0 equiv) in 2.0 ml of DCM at 0 ℃. The resulting mixture was allowed to warm to room temperature and continued to stirr for another 1 hour. The excess water was removed by filtration with $MgSO_4$. The filtrate was collected and the solvent removed in vacuo and then loaded onto the top of a short column slurry-packed with eluent (EA/PE = 1/20) to afford 732.1 mg (60.2%) of **1e** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.18 (brs, 1H), 7.70 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.58 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.20 (dd, *J* = 3.2, 2.3 Hz, 1H), 7.06 (dd, *J* = 7.9, 7.0 Hz, 1H), 6.48 (dd, *J* = 3.2, 2.1 Hz, 1H), 1.32 (s, 12H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 140.9, 129.2, 126.8, 124.2, 124.1, 119.2, 101.9, 83.8, 25.0; **ATR-FTIR (cm^{-1})** 3458, 3057, 2978, 1597, 1512, 1430, 1331, 1065, 842 cm^{-1}; **HRMS m/z (ESI)** called for $C_{14}H_{19}BNO_2^+$ $(M + H)^+$ 244.1503, found 244.1503.

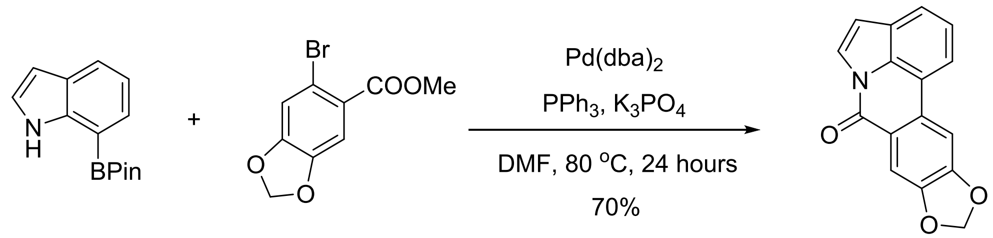


9,10-Dimethoxy-7*H*-pyrrolo[3,2,1-*de*]phenanthridin-7-one (61a) [24]



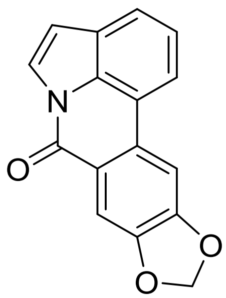
61a

Flame-dried 25 mL Schlenk tube was flushed with argon and charged with **1e** (58.6 mg, 0.24 mmol, 1.0 equiv), $Pd(dba)_2$ (7.2 mg, 0.012 mmol, 0.05 equiv), PPh_3 (12.4 mg, 0.048 mmol, 0.2 equiv), Methyl 6-bromo-1,3-benzodioxole-5-carboxylate **60a** (68.0 mg, 0.26 mmol, 1.1 equiv), K_3PO_4 (153.0 mg, 0.72 mmol, 3.0 equiv), and DMF (1.0 mL) were added to the reaction mixture. The reaction mixture was heated at 80 ℃ for 24 hours. The reaction was filtered through Celite, washed with EtOAc, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (eluent: EA / PE = 1/4) to afford 56.2 mg (84.0%) of **61a** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.06 (d, J = 3.6 Hz, 1H), 8.00 (s, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.75 (dd, J = 7.7, 0.6 Hz, 1H), 7.65 (s, 1H), 7.48 (t, J = 7.7 Hz, 1H), 6.90 (d, J = 3.6 Hz, 1H), 4.12 (s, 3H), 4.07 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.4, 153.7, 149.6, 129.5, 128.5, 123.9, 123.5, 122.4, 120.8, 118.0, 116.7, 110.7, 110.1, 103.7, 56.3, 56.2; **ATR-FTIR (cm^{-1})** 2927, 1792, 1367. 996, 756, 628 cm^{-1}; **HRMS m/z (ESI)** called for $C_{17}H_{14}NO_3^+$ $(M + H)^+$ 280.0968, found 280.0966.



1e 60b Hippadine 61b

7*H*-[1,3]Dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (61b) [24]



61b

Flame-dried 25 mL Schlenk tube was flushed with argon and charged with **1e** (58.6 mg, 0.24 mmol, 1.0 equiv), Pd(dba)$_2$ (7.2 mg, 0.012 mmol, 0.05 equiv), PPh_3 (12.4 mg, 0.05 mmol, 0.2 equiv), Methyl 6-bromobenzo[*d*][1,3]dioxole-5- carboxylate **60b** (66.8 mg, 0.26 mmol, 1.1 equiv), K_3PO_4 (153.0 mg, 0.72 mmol, 3.0 equiv) and DMF (1.0 mL) were added to the reaction mixture. The reaction mixture was heated at 80 ℃ for 24 hours. The reaction was filtered through celite, washed with EtOAc, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (eluent: EA/PE = 1/4) to afford 44.4 mg (70%) of **61b** as a white solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.04 (d, *J* = 3.6 Hz, 1H), 7.98 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.75 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.66 (s, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.17 (s, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.1, 152.6, 148.5, 131.6, 128.4, 124.0, 123.5, 122.6, 118.4, 110.8, 108.0, 102.3, 101.7. **ATR-FTIR (cm^{-1})** 2999, 1671, 1309, 1027, 927, 761 cm^{-1}; **HRMS m/z (ESI)** called for $C_{16}H_{10}NO_3^+$ $(M + H)^+$ 264.0655, found 264.0657.

6. Mechanistic investigations

6.1 DFT calculations for the reaction of 1a with BBr_3

All DFT calculations were performed with the Gaussian 09 package.[25] Geometry optimizations were performed with B3LYP[26-29]/6-31G (d).[30-32] Frequency analysis was conducted at the same level of theory to verify the stationary points to be minima or saddle points and to obtain zero-point vibrational energy (ZPVE) and thermal energy corrections under 298.15 K and 1 atm pressure. All transition states were also confirmed to connect reactants and products by intrinsic reaction coordinate (IRC) calculations. Single-point solvation energies were calculated with M062X[33]/

6-311++G(d,p)[34] by using SMD solvation model (solvent = dichloromethane).[35-36] Unless otherwise noted, the relative energies reported in the text are Gibbs free energies with the solvent effect corrections. Computed structures are illustrated using CYLView.[37]

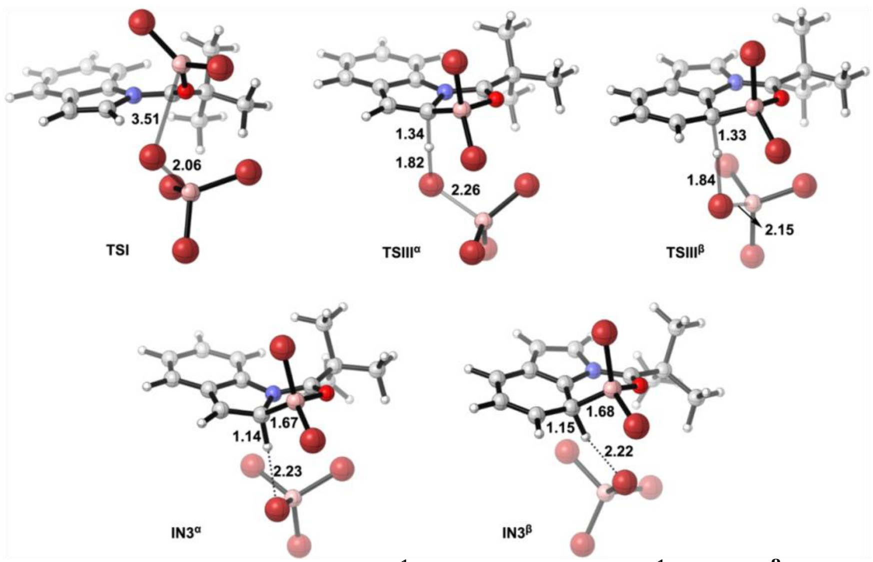


Fig. S1| Optimized structures of **TSI** (19i cm^{-1}), **TSIII$^{\alpha}$** (601i cm^{-1}), **TSIII$^{\beta}$** (388i cm^{-1}), **IN3$^{\alpha}$** and **IN3$^{\beta}$**. Bond lengths are in Å.

Energies, vibrational frequencies and Cartesian coordinates

Table S2| Energies, and vibrational frequencies

filename	E(sol)	ZPVE	TCE	TCH	TCG	Negative Frequency(cm^{-1})
1a	-634.321848	0.253259	0.266821	0.267765	0.213385	
IN1$^{\alpha}$	-8381.810073	0.261212	0.281005	0.281949	0.210942	
IN2$^{\alpha}$	-16129.275348	0.267925	0.294980	0.295924	0.205129	
IN3$^{\alpha}$	-16129.279149	0.267062	0.293513	0.294457	0.205776	
1b$^{\alpha}$	-5807.032765	0.249602	0.266878	0.267822	0.203226	
TSI	-16129.275054	0.267596	0.293877	0.294821	0.206634	-19
TSII$^{\alpha}$	-16129.261981	0.266473	0.292839	0.293784	0.205807	-292
TSIII$^{\alpha}$	-16129.258454	0.261950	0.288369	0.289313	0.200291	-601
IN1$^{\beta}$	-8381.812880	0.261080	0.280853	0.281797	0.211395	
IN2$^{\beta}$	-16129.281001	0.268215	0.295176	0.296120	0.205446	
IN3$^{\beta}$	-16129.276212	0.266281	0.292917	0.293862	0.205016	
1b$^{\beta}$	-5807.037800	0.249693	0.266947	0.267891	0.202814	
TSII$^{\beta}$	-16129.270758	0.266419	0.292948	0.293892	0.204656	-287
TSIII$^{\beta}$	-16129.268444	0.261959	0.288122	0.289067	0.202076	-388

E(sol)= Single-point solvation energies; ZPVE = zero-point vibrational energy; TCE = thermal correction to energy; TCH = thermal correction to enthalpy; TCG = thermal correction to Gibbs free energy.

Cartesiancoordinates

BBr_3

B	-0.000154	0.000168	-0.000077
Br	0.560330	-1.818546	0.000094
Br	-1.855514	0.424149	0.000018
Br	1.295206	1.394373	-0.000101

BBr_4^-

B	0.000000	0.000000	0.000000
Br	1.178178	1.178178	1.178178
Br	-1.178178	-1.178178	1.178178
Br	-1.178178	1.178178	-1.178178
Br	1.178178	-1.178178	-1.178178

HBr

Br	0.000000	0.000000	0.039940
H	0.000000	0.000000	-1.397890

MeOH

C	0.662324	-0.019545	0.000001
H	1.079718	0.991032	-0.000620
H	1.036909	-0.544181	-0.892857
H	1.037007	-0.543133	0.893439
O	-0.749168	0.122497	0.000003
H	-1.134236	-0.766420	0.000010

1a

C	-1.274905	-0.178335	-0.000365
C	-2.098553	0.975016	-0.000202
C	-3.493124	0.840295	0.000389
C	-4.042994	-0.436488	0.000824
C	-3.214343	-1.570773	0.000667
C	-1.824191	-1.464670	0.000055
C	0.049643	1.670010	-0.000954
C	-1.228171	2.123346	-0.000641
H	-4.129012	1.721724	0.000528
H	-5.122575	-0.560100	0.001279
H	-3.663690	-2.560134	0.000986
H	-1.191505	-2.339499	-0.000190
H	0.961315	2.238464	-0.001532
H	-1.528031	3.162846	-0.000789
N	0.074200	0.260820	-0.000718
C	1.186384	-0.605682	-0.001103
O	0.996884	-1.810238	-0.002580
C	2.631601	-0.038456	0.000561
C	2.916487	0.781260	-1.281802
H	2.312686	1.686108	-1.375761
H	3.969881	1.084093	-1.288553
H	2.740117	0.171317	-2.174886
C	2.913921	0.780988	1.283604
H	3.967295	1.083852	1.292461
H	2.309918	1.685799	1.376583
H	2.735863	0.170865	2.176233
C	3.586953	-1.250070	0.001379
H	3.435121	-1.877520	-0.880579
H	4.622782	-0.892438	0.002652
H	3.433117	-1.877858	0.882767

$IN1^{\alpha}$

C	2.834880	-0.103727	0.114646
C	3.353527	-1.369818	0.471182
C	4.658255	-1.718730	0.113858
C	5.418748	-0.815555	-0.625137
C	4.872969	0.409646	-1.026953
C	3.571680	0.775945	-0.675428
C	1.192924	-1.346426	1.150914
C	2.301234	-2.109470	1.134196
H	5.059222	-2.689446	0.390350
H	6.432802	-1.073375	-0.915820
H	5.461863	1.089401	-1.635190
H	3.166499	1.709647	-1.037435
H	0.205394	-1.541384	1.541197
H	2.375426	-3.111711	1.533570
N	1.482488	-0.060871	0.586079
C	0.543441	0.920034	0.619147
C	0.782278	2.432593	0.658212
O	-0.677507	0.574653	0.712409
B	-1.676121	-0.286935	-0.073769
Br	-2.513229	-1.534393	1.252954
Br	-0.730582	-1.261434	-1.555967
Br	-2.976133	1.062538	-0.816065
C	0.672113	2.952493	-0.804113
H	0.747085	4.044989	-0.791862
H	1.451090	2.566339	-1.466079
H	-0.299738	2.675968	-1.225952
C	-0.397544	3.061222	1.452061
H	-1.359301	2.849504	0.982658
H	-0.426392	2.692155	2.482649
H	-0.245897	4.144936	1.482079
C	2.085319	2.850717	1.367701
H	2.102196	2.470209	2.395104
H	2.999638	2.524152	0.875845
H	2.112453	3.943737	1.421916

$IN2^{\alpha}$

C	3.332694	-1.424042	-0.264120
C	3.433071	-1.820403	-1.617089
C	4.539160	-2.542405	-2.062445
C	5.552089	-2.851667	-1.155010
C	5.461687	-2.427478	0.173080
C	4.358975	-1.700559	0.635113
C	1.510035	-0.625193	-1.460945
C	2.268854	-1.323168	-2.320717
H	4.609000	-2.846245	-3.102474
H	6.420402	-3.414339	-1.483877
H	6.258976	-2.661896	0.871462
H	4.338122	-1.388626	1.666708
H	0.510855	-0.226549	-1.580148
H	2.018415	-1.511805	-3.355795
N	2.111893	-0.656337	-0.152231
C	1.507259	-0.048143	0.874040
C	1.706364	-0.245699	2.369421
O	0.653262	0.911788	0.548350
B	0.831004	2.131711	-0.079688
Br	-2.047550	0.104237	-1.891191
Br	2.623633	2.716990	-0.444734
Br	-0.687005	3.150621	-0.457812
C	2.930356	0.622773	2.798633
H	3.044639	0.527911	3.882891
H	3.872415	0.338048	2.328274
H	2.754848	1.677313	2.566371
C	0.467088	0.315463	3.114654
H	0.387990	1.401887	3.027489
H	-0.458121	-0.123416	2.738425
H	0.578818	0.066739	4.174621
C	1.833135	-1.735032	2.762790
H	0.877691	-2.233252	2.581733
H	2.603838	-2.289303	2.229470
H	2.057618	-1.790706	3.832613
B	-2.569753	-0.735700	-0.100358
Br	-1.010959	-1.995105	0.487004
Br	-2.790042	0.705417	1.295969
Br	-4.219383	-1.835659	-0.300183

IN3$^{\alpha}$

C	-1.415039	2.129970	-0.437225
C	-1.633045	1.954338	-1.847111
C	-1.872601	3.069286	-2.686943
C	-1.902136	4.323485	-2.119124
C	-1.685911	4.480790	-0.729128
C	-1.246138	-0.141458	-0.957270
C	-1.550666	0.590625	-2.138631
H	-2.023191	2.922685	-3.751744
H	-2.079756	5.200540	-2.732601
H	-1.695221	5.482522	-0.309502
H	-1.612920	0.140829	-3.122522
N	-1.219317	0.867040	0.107894
C	-1.357470	0.272362	1.333052
C	-1.362409	0.937215	2.686695
O	-1.670348	-0.962560	1.238639
B	-2.090000	-1.363205	-0.195829
Br	-1.558276	-3.183793	-0.641053
Br	-4.075612	-0.982416	-0.280718
C	-2.768169	1.613986	2.786252
H	-2.899247	1.971083	3.812413
H	-2.884545	2.466891	2.113584
H	-3.563357	0.895203	2.562900
C	-1.283503	-0.149781	3.780635
H	-2.140879	-0.826719	3.749370
H	-0.370172	-0.739594	3.672604
H	-1.265917	0.346930	4.755831
C	-0.197822	1.951328	2.865673
H	0.600629	1.499097	3.456037
H	0.274358	2.248663	1.926486
H	-0.554097	2.842876	3.393193
C	-1.443958	3.410964	0.123973
H	-1.254061	3.587293	1.171903
H	-0.206628	-0.599713	-1.084173
B	2.599627	-0.114949	-0.076003
Br	1.841204	-0.607755	1.751358
Br	1.950287	1.750664	-0.598395
Br	4.579684	-0.221549	-0.092984
Br	1.815229	-1.471587	-1.420611

1b$^{\alpha}$

C	-2.265745	-0.509947	0.000248
C	-2.068511	-1.916534	0.000427
C	-3.175404	-2.769667	0.000371
C	-4.456209	-2.220213	0.000141
C	-4.636402	-0.832366	0.000036
C	0.016897	-1.003880	0.000558
C	-0.642825	-2.182467	0.000427
H	-3.032746	-3.846402	0.000463
H	-5.323597	-2.873945	0.000144
H	-5.639935	-0.417684	-0.000023
H	-0.182947	-3.161431	0.000560
N	-0.958515	0.056412	0.000497
C	-0.344185	1.261280	-0.000019
C	-0.977961	2.640253	-0.000091
O	0.933891	1.179608	-0.000107
B	1.434355	-0.302060	0.000145
Br	2.492139	-0.563604	-1.683099
Br	2.493082	-0.563033	1.682735
C	-1.819938	2.816208	1.288612
H	-2.301447	3.799513	1.265408
H	-2.597484	2.060289	1.410825
H	-1.175129	2.777631	2.172820
C	0.137035	3.706961	-0.000105
H	0.774716	3.623233	0.883699
H	0.774709	3.623296	-0.883906
H	-0.327862	4.698449	-0.000053

C	-1.819733	2.816015	-1.289019
H	-1.174740	2.777212	-2.173078
H	-2.597311	2.060124	-1.411182
H	-2.301157	3.799372	-1.266081
C	-3.545093	0.041580	0.000024
H	-3.722687	1.107836	0.000127

TSI

C	3.491929	-1.216715	-0.113383
C	3.643838	-1.710037	-1.428601
C	4.803605	-2.388035	-1.799907
C	5.817858	-2.555334	-0.857081
C	5.675130	-2.034189	0.431117
C	4.517586	-1.349648	0.818437
C	1.646004	-0.633536	-1.397276
C	2.464321	-1.346164	-2.186477
H	4.913269	-2.766874	-2.811493
H	6.727810	-3.081758	-1.128470
H	6.473574	-2.156867	1.156226
H	4.457408	-0.958012	1.820994
H	0.632867	-0.296189	-1.567430
H	2.249901	-1.625829	-3.208940
N	2.218424	-0.526365	-0.079281
C	1.546977	0.085735	0.901575
C	1.725217	-0.030013	2.411826
O	0.615835	0.950675	0.549142
B	0.563637	2.145514	-0.148660
Br	-1.851554	0.195533	-1.782150
Br	2.097614	2.721749	-1.138862
Br	-0.963125	3.206962	0.087834
C	2.862265	0.951242	2.830569
H	2.968020	0.902002	3.918851
H	3.833973	0.737620	2.383309
H	2.596225	1.980107	2.566641
C	0.424291	0.465187	3.099082
H	0.257845	1.534597	2.948041
H	-0.453839	-0.066055	2.727665
H	0.527051	0.282820	4.173400
C	1.950107	-1.487256	2.875285
H	1.047055	-2.067427	2.669850
H	2.790120	-1.997924	2.407503
H	2.120285	-1.481173	3.956450
B	-2.446043	-0.900904	-0.142806
Br	-0.835687	-2.064278	0.478786
Br	-2.949931	0.349169	1.353216
Br	-3.943029	-2.111715	-0.653236

TSII$^{\alpha}$

C	3.021245	-1.357971	-0.707959
C	3.231979	-0.781274	-1.994817
C	4.352377	-1.142301	-2.763219
C	5.251045	-2.057055	-2.240154
C	5.043833	-2.602942	-0.959778
C	1.327886	0.160027	-1.163847
C	2.163119	0.121547	-2.256617
H	4.499991	-0.706116	-3.746341
H	6.122388	-2.355158	-2.814425
H	5.758678	-3.319184	-0.565961
H	0.236768	0.264526	-1.252228
H	1.986473	0.656754	-3.180907
N	1.837171	-0.786190	-0.193621
C	1.336404	-0.597427	1.060952
C	1.416994	-1.484483	2.279497
O	0.838905	0.583135	1.230416
B	1.272414	1.646835	0.305615
Br	0.002205	2.983625	-0.116834
Br	3.155208	2.119580	0.600516
C	2.767326	-1.118746	2.976112
H	2.788262	-1.625700	3.945667
H	3.647945	-1.430200	2.409710
H	2.840705	-0.040603	3.146865
C	0.262083	-1.099029	3.238393
H	0.382759	-0.087895	3.633867
H	-0.702434	-1.153737	2.729325
H	0.271238	-1.804216	4.075555
C	1.313970	-2.989877	1.964531
H	0.286501	-3.242859	1.697470
H	1.957023	-3.322736	1.148208
H	1.589231	-3.553016	2.861932
C	3.943922	-2.262203	-0.175944
H	3.825494	-2.711135	0.798601
Br	-1.365576	-1.959125	-0.075311
B	-2.712930	-0.376537	-0.237251
Br	-2.141096	0.681505	-1.897936
Br	-4.549266	-1.103577	-0.469862
Br	-2.542988	0.769090	1.409141

TSIII$^{\alpha}$

C	-2.617158	1.838074	-0.467151
C	-2.759954	1.562447	-1.863684
C	-3.344648	2.511442	-2.723807
C	-3.781992	3.711174	-2.189869
C	-3.630269	3.973882	-0.815071
C	-1.659409	-0.233097	-0.953030
C	-2.221391	0.275932	-2.124583
H	-3.444033	2.295679	-3.783079
H	-4.236013	4.460279	-2.830528
H	-3.968513	4.926050	-0.417437
H	-2.140332	-0.200548	-3.093841
N	-2.012802	0.705955	0.101979
C	-1.775172	0.147601	1.325770
C	-1.860071	0.808755	2.684844
O	-1.453216	-1.081307	1.251437
B	-1.539634	-1.668014	-0.193343
Br	0.036013	-2.756092	-0.590846
Br	-3.311498	-2.636730	-0.251070

C	-3.343961	1.154138	2.980441
H	-3.396231	1.646211	3.956972
H	-3.798932	1.819223	2.243915
H	-3.948113	0.242334	3.027617
C	-1.375365	-0.192731	3.755366
H	-1.998596	-1.090442	3.781060
H	-0.342999	-0.498225	3.572493
H	-1.427595	0.294626	4.734035
C	-0.932892	2.050245	2.714589
H	0.101415	1.748183	2.526464
H	-1.195779	2.813454	1.979554
H	-0.990660	2.503934	3.709196
C	-3.051183	3.056583	0.059590
H	-2.943321	3.310178	1.103677
H	-0.393652	0.129645	-1.176784
B	2.748809	0.260008	-0.003875
Br	1.897670	-0.335512	1.696510
Br	1.067905	1.212582	-1.182005
Br	3.983691	1.789697	0.213082
Br	3.409466	-1.206472	-1.124900

$IN1^{\beta}$

C	2.347987	-0.073105	0.247773
C	3.616456	0.127325	-0.334585
C	4.602993	-0.854847	-0.215929
C	4.304196	-2.014822	0.495012
C	3.042872	-2.187784	1.080222
C	2.041016	-1.220496	0.970725
C	2.422567	2.016898	-0.718594
C	3.614449	1.433634	-0.958171
H	5.582171	-0.708098	-0.662471
H	5.054427	-2.793580	0.596101
H	2.822653	-3.102782	1.621605
H	1.064508	-1.403932	1.398272
H	2.028888	2.948533	-1.082267
H	4.417003	1.868188	-1.539124
N	1.591031	1.131695	0.025658
C	0.338319	1.399163	0.456592
C	-0.187323	2.824549	0.689233
O	-0.434288	0.429474	0.753728
B	-1.251837	-0.607352	-0.055571
Br	-1.515544	-2.160246	1.174403
Br	-0.260441	-1.082869	-1.735043
Br	-3.011158	0.276536	-0.520241
C	-0.751191	3.357007	-0.658894
H	-1.221648	4.329272	-0.477320
H	0.020749	3.494486	-1.422459
H	-1.510946	2.673488	-1.049655
C	-1.357600	2.736031	1.701490
H	-2.168411	2.110639	1.327223
H	-1.022861	2.332455	2.662829
H	-1.740990	3.747490	1.870449
C	0.872926	3.776052	1.290666
H	1.302542	3.356814	2.207274
H	1.694639	4.023907	0.617902
H	0.377534	4.714900	1.557666

$IN2^{\beta}$

C	-1.928706	2.098844	-0.510156
C	-2.619085	3.326577	-0.480248
C	-2.505644	4.217180	-1.545126
C	-1.669294	3.874174	-2.611136
C	-0.944210	2.680026	-2.591913
C	-1.056221	1.765260	-1.537272
C	-3.019586	2.321907	1.520826
C	-3.292960	3.425051	0.800873
H	-3.033986	5.165715	-1.531391
H	-1.556761	4.558229	-3.446842
H	-0.249594	2.450114	-3.393400
H	-0.422114	0.890507	-1.528253
H	-3.345668	2.042857	2.503933
H	-3.905043	4.250493	1.139677
N	-2.211947	1.428275	0.741932
C	-1.847115	0.202910	1.095092
C	-2.002709	-0.418227	2.490209
O	-1.277299	-0.512868	0.145577
B	-1.670717	-1.565627	-0.654154
Br	2.169941	0.194804	-1.834404
Br	-3.528240	-2.060233	-0.681493
Br	-0.371463	-2.401496	-1.701475
C	-3.504937	-0.632217	2.835858
H	-3.551345	-1.216528	3.759889
H	-4.059666	0.292924	3.006051
H	-4.012851	-1.195926	2.049423
C	-1.311856	-1.801071	2.502268
H	-1.842726	-2.526889	1.877245
H	-0.269586	-1.741406	2.177095
H	-1.333665	-2.180824	3.527845
C	-1.296307	0.467826	3.552718
H	-0.237658	0.580982	3.307338
H	-1.730832	1.465318	3.650064
H	-1.388313	-0.032289	4.521766
B	2.540959	0.096170	0.171431
Br	1.284758	1.434138	1.135108
Br	2.131684	-1.776919	0.848768
Br	4.435673	0.594838	0.556441

$IN3^{\beta}$

C	1.445883	0.158236	1.555760
C	1.583788	0.274602	2.938867
C	1.897113	-0.890389	3.646740
C	2.072553	-2.112659	2.961862
C	1.924772	-2.193646	1.588768
C	1.579067	-1.038647	0.790380
C	1.147403	2.335926	2.099686
C	1.378829	1.675162	3.258287

H	2.011575	-0.861791	4.727014
H	2.321581	-3.001039	3.532890
H	2.039203	-3.141731	1.071779
H	0.600758	-1.242692	0.225154
H	0.970053	3.380882	1.922363
H	1.409255	2.127829	4.239508
N	1.215403	1.415587	1.014877
C	1.216819	1.594678	-0.342477
C	0.712734	2.833675	-1.059192
O	1.723622	0.674484	-1.055683
B	2.449151	-0.605225	-0.577867
Br	2.326829	-1.960163	-2.002516
Br	4.323944	-0.036156	-0.121433
C	1.941593	3.777492	-1.204760
H	1.632579	4.655771	-1.780368
H	2.313645	4.123131	-0.233658
H	2.762084	3.284748	-1.735337
C	0.221243	2.395892	-2.462751
H	1.006031	1.895705	-3.033271
H	-0.637509	1.724370	-2.376321
H	-0.090406	3.292062	-3.007333
C	-0.449112	3.545044	-0.327610
H	-1.201452	2.840419	0.036482
H	-0.112308	4.177076	0.498291
H	-0.941797	4.206857	-1.045438
B	-2.694826	-0.307578	-0.013111
Br	-1.889774	0.396242	1.731898
Br	-1.145733	-1.145229	-1.135226
Br	-4.065610	-1.697743	0.352181
Br	-3.412166	1.233485	-1.093672

$1b^{\beta}$

C	0.584984	1.629594	0.000254
C	1.082154	2.941682	0.000149
C	0.156975	3.988665	-0.000047
C	-1.204391	3.661679	-0.000136
C	-1.648865	2.331930	-0.000093
C	-0.746900	1.256036	0.000097
C	2.870326	1.522298	0.000237
C	2.529912	2.833923	0.000141
H	0.479819	5.025690	-0.000130
H	-1.938350	4.462838	-0.000280
H	-2.714717	2.123393	-0.000234
H	3.844698	1.067409	0.000332
H	3.236985	3.653211	0.000083
N	1.687572	0.730474	0.000331
C	1.490417	-0.603412	0.000080
C	2.616666	-1.639197	-0.000103
O	0.301426	-1.057039	0.000033
B	-1.051534	-0.294564	0.000052
Br	-1.993971	-0.912376	-1.678078
Br	-1.993997	-0.912589	1.678076
C	3.474830	-1.487761	-1.281560
H	3.990545	-0.527203	-1.352493
H	4.234889	-2.275884	-1.289860
H	2.857905	-1.606815	-2.178537
C	1.988106	-3.048763	-0.000308
H	1.363726	-3.210340	0.882095
H	1.363929	-3.210150	-0.882892
H	2.792915	-3.791086	-0.000300
C	3.475062	-1.488280	1.281220
H	4.235453	-2.276081	1.288844
H	3.990332	-0.527537	1.352789
H	2.858359	-1.608202	2.178243

$TSII^{\beta}$

C	1.562136	0.284881	1.540188
C	2.031268	0.674842	2.796063
C	2.563330	-0.310765	3.634618
C	2.613345	-1.638269	3.185606
C	2.080886	-2.001621	1.948775
C	1.527533	-1.035667	1.075847
C	1.282504	2.543648	1.734135
C	1.814259	2.108997	2.896595
H	2.933176	-0.054371	4.623121
H	3.034693	-2.400299	3.833446
H	2.059064	-3.044085	1.647530
H	0.727769	-1.333150	0.384156
H	0.997474	3.532665	1.426707
H	2.033245	2.734955	3.750878
N	1.173014	1.441937	0.827858
C	1.110445	1.463698	-0.514576
C	0.573790	2.602470	-1.360002
O	1.602460	0.457860	-1.159557
B	2.514584	-0.598558	-0.742474
Br	2.316681	-2.207304	-1.781840
Br	4.309088	0.046943	-0.323881
C	1.802183	3.495852	-1.705018
H	1.464490	4.296932	-2.369755
H	2.241333	3.956174	-0.813182
H	2.580845	2.924291	-2.219767
C	-0.003960	2.000857	-2.668879
H	0.739421	1.414323	-3.212436
H	-0.869444	1.368736	-2.455816
H	-0.324023	2.832237	-3.303894
C	-0.535347	3.422256	-0.658406
H	-1.224316	2.787060	-0.095756
H	-0.137540	4.202579	-0.002928
H	-1.119939	3.930280	-1.429708
Br	-1.874214	0.517090	1.744631
B	-2.746572	-0.313995	0.083214
Br	-1.260266	-1.202926	-1.057596
Br	-4.088967	-1.685586	0.616335
Br	-3.560644	1.160096	-1.038064

$TSIII^{\beta}$

C	1.391717	0.475358	1.610509	Br	1.350369	-2.378046	-1.517178
C	1.382461	0.845553	2.958796	Br	4.071231	-0.800001	-0.355753
C	1.527315	-0.171197	3.908971	C	2.559632	3.672848	-1.179909
C	1.697589	-1.500441	3.482541	H	2.563347	4.485334	-1.913302
C	1.698248	-1.829874	2.133199	H	2.567131	4.123897	-0.184245
C	1.458045	-0.847779	1.112499	H	3.485781	3.101081	-1.302865
C	1.226167	2.736063	1.715726	C	1.374115	2.299143	-2.914492
C	1.263173	2.290319	2.993110	H	2.308338	1.775193	-3.132138
H	1.521589	0.060782	4.970295	H	0.543400	1.627177	-3.139550
H	1.831643	-2.279754	4.225981	H	1.304509	3.173763	-3.568547
H	1.799196	-2.864317	1.817148	C	-0.009956	3.556676	-1.238466
H	0.194499	-1.185802	0.897348	H	-0.866999	2.897177	-1.392883
H	1.144595	3.739830	1.340813	H	-0.107405	4.005937	-0.248101
H	1.214542	2.915661	3.873809	H	-0.049437	4.365032	-1.975719
N	1.326009	1.630550	0.826055	B	-2.489673	-0.072592	-0.088517
C	1.405505	1.565137	-0.535503	Br	-2.029649	1.418222	1.185953
C	1.314665	2.780940	-1.449003	Br	-1.519783	-1.823074	0.689954
O	1.630366	0.440885	-1.071819	Br	-4.419070	-0.503233	-0.109932
B	2.042711	-0.899574	-0.406055	Br	-1.718154	0.221630	-1.909927

6.2 Mechanistic investigation of amide 29a

6.2.1 DFT calculations for the reaction of 29a with BBr_3

As shown in Fig. S2, **29a** is easy to complex with BBr_3 to form a stable **IN1_arene** with a reaction free energy of -5.4 kcal/mol. Br^- abstraction from **IN1** by another BBr_3 leads to a borenium cation intermediate **IN2_arene** through **TSI_arene** with a free energy barrier of 19.5 kcal/mol. Then, electrophilic attack by the borenium cation via a six-membered cyclic transition state **TSII_arene** gives an intermediate **IN3_arene** with low barrier of 2.4kcal/mol relative to **IN2_arene**. The subsequent deprotonation by BBr_4^- is 7.6 kcal/mol with respect to **IN3 arene**. Although **TSII_arene** is higher than **IN2_arene** and **IN3_arene** in electronic energy, its free energy at room temperature is 0.5 kcal/mol lower than that of **IN3_arene** after thermal correction. When the electronic energies of a transition state and its corresponding reactant and/or product are very close, the thermal corrections may lead to the free energy of the transition state between the free energies of reactant and product, especially when the transition state has a very large imaginary frequency. Different from the borylation of indole, the deprotonation step is the rate determining step with a total activation free energy of 21.4 kcal/mol.

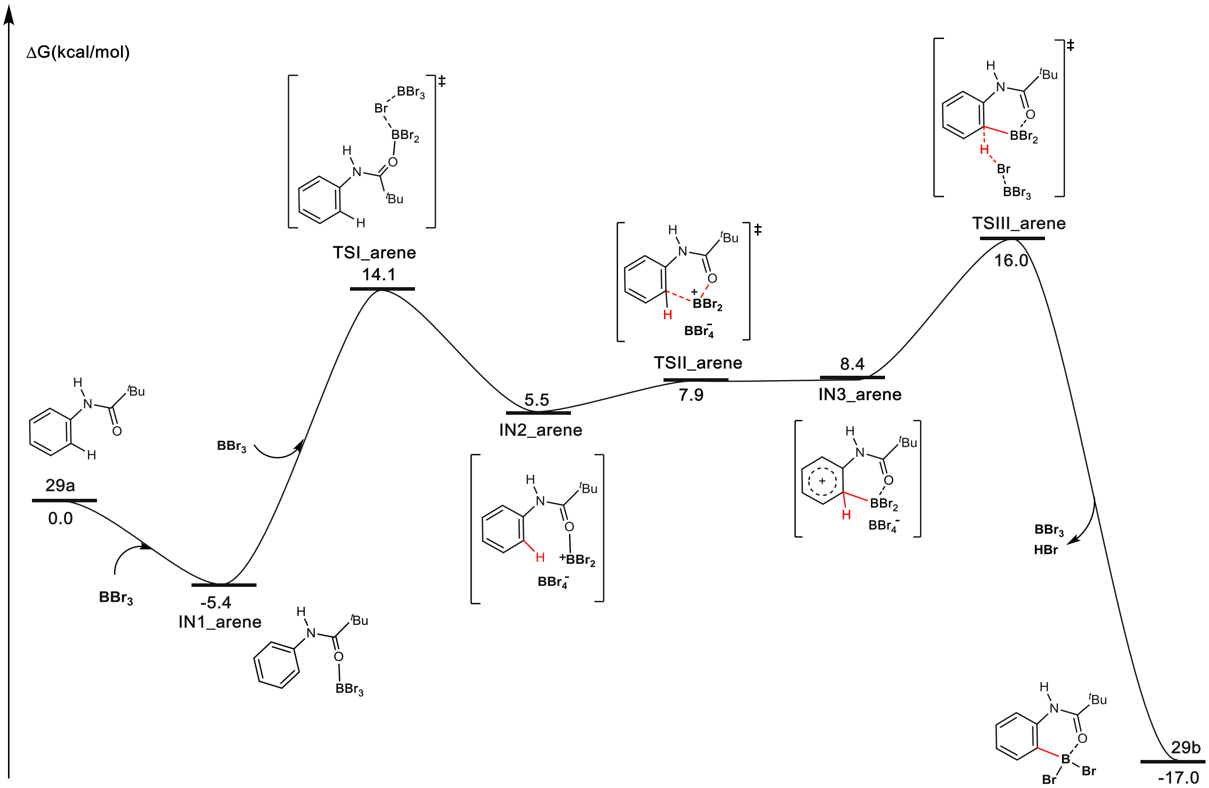


Fig. S2| Free energy profiles for C-H borylation of amide **29a**.

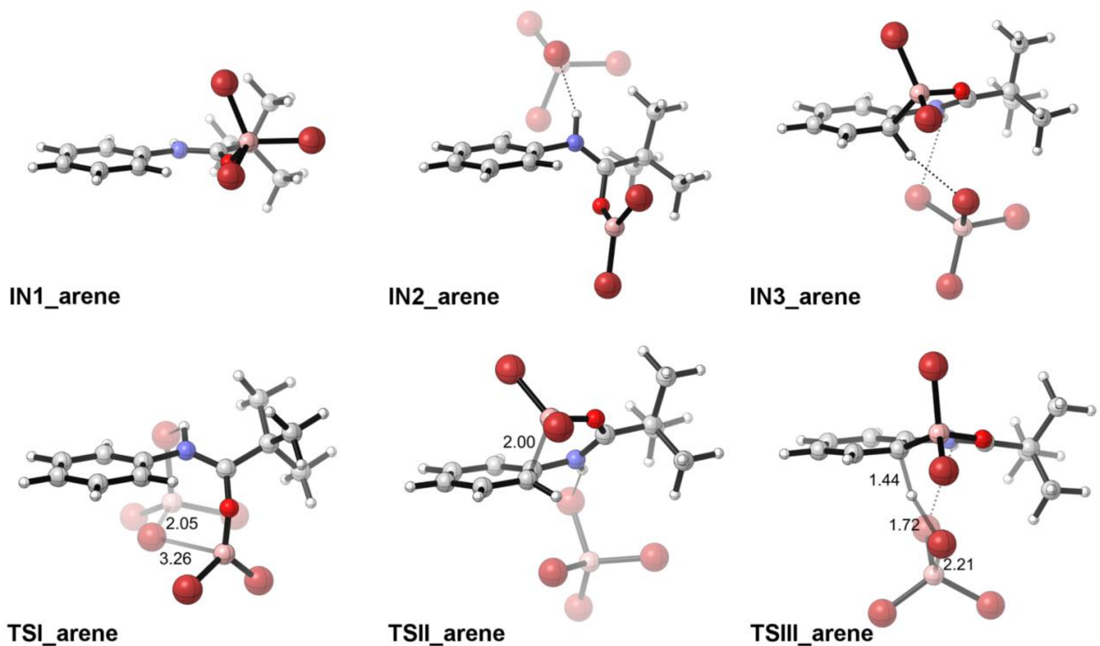


Fig. S3| Optimized structures of **IN1_arene**, **IN2_arene, IN3_arene, TSI_arene** (22i cm^{-1}), **TSII_arene** (199i cm^{-1}) and **TSIII_arene** (683i cm^{-1}). Bond lengths are in Å.

Table S3| Energies, and vibrational frequencies

filename	E(sol)	ZPVE	TCE	TCH	TCG	Negative Frequency(cm^{-1})
29a	-558.131414	0.240875	0.253881	0.254825	0.201002	
29b	-5730.859800	0.237965	0.254414	0.255359	0.191638	
IN1_arene	-8305.634444	0.250027	0.268939	0.269883	0.199929	
IN2_arene	-16053.106670	0.256642	0.282681	0.283625	0.194189	
IN3_arene	-16053.101973	0.255228	0.281005	0.281949	0.194101	
TSI_arene	-16053.096621	0.256589	0.281691	0.282635	0.197829	-22
TSII_arene	-16053.102257	0.255015	0.280488	0.281432	0.193608	-199
TSIII_arene	-16053.086857	0.250490	0.275754	0.276698	0.191123	-683

E(sol)= Single-point solvation energies; ZPVE = zero-point vibrational energy; TCE = thermal correction to energy; TCH = thermal correction to enthalpy; TCG = thermal correction to Gibbs free energy.

Cartesian coordinates

29a_arene

C	-1.303386	-0.187485	-0.000013
C	-2.139171	-1.316348	0.000002
C	-3.523429	-1.172207	0.000011
C	-4.098218	0.100099	0.000006
C	-3.266402	1.220272	-0.000009
C	-1.876920	1.093818	-0.000019
H	-4.152005	-2.058768	0.000024
H	-3.699958	2.217022	-0.000014
H	-1.234619	1.962679	-0.000030
N	0.089442	-0.418446	-0.000025
C	1.127779	0.489346	0.000004
O	0.956956	1.701023	0.000011
C	2.542436	-0.147475	-0.000002
C	2.733764	-1.012144	1.266800
H	2.055219	-1.873106	1.301005
H	3.756860	-1.404700	1.298631
H	2.570780	-0.422297	2.175577
C	2.733906	-1.011963	-1.266908
H	3.757030	-1.404448	-1.298720
H	2.055432	-1.872974	-1.301284
H	2.570951	-0.422008	-2.175620
C	3.577638	0.989074	0.000133
H	3.463846	1.626285	0.881385
H	4.589830	0.568502	0.000153
H	3.463938	1.626412	-0.881040
H	-1.699297	-2.312316	0.000007
H	0.350541	-1.394534	-0.000030
H	-5.178276	0.215263	0.000014

29a_arene_SP

C	1.303386	-0.187485	0.000013
C	2.139171	-1.316348	-0.000002
C	3.523429	-1.172207	-0.000011
C	4.098218	0.100099	-0.000006
C	3.266402	1.220272	0.000009
C	1.876920	1.093818	0.000019
H	4.152005	-2.058768	-0.000024
H	3.699958	2.217022	0.000014
H	1.234619	1.962679	0.000030
N	-0.089442	-0.418446	0.000025
C	-1.127779	0.489346	-0.000004
O	-0.956956	1.701023	-0.000011
C	-2.542436	-0.147475	0.000002
C	-2.733764	-1.012144	-1.266800

H	-2.055219	-1.873106	-1.301005
H	-3.756860	-1.404700	-1.298631
H	-2.570780	-0.422297	-2.175577
C	-2.733906	-1.011963	1.266908
H	-3.757030	-1.404448	1.298720
H	-2.055432	-1.872974	1.301284
H	-2.570951	-0.422008	2.175620
C	-3.577638	0.989074	-0.000133
H	-3.463846	1.626285	-0.881385
H	-4.589830	0.568502	-0.000153
H	-3.463938	1.626412	0.881040
H	1.699297	-2.312316	-0.000007
H	-0.350541	-1.394534	0.000030
H	5.178276	0.215263	-0.000014

29b_arene

C	0.172474	1.997511	-0.006743
C	1.841408	3.719139	0.014990
C	2.827243	2.731629	-0.084953
C	2.470889	1.385005	-0.143633
C	1.131117	0.980445	-0.090559
H	2.116342	4.768927	0.059121
H	3.236092	0.619912	-0.234988
N	-1.203293	1.622870	-0.006191
C	-1.651268	0.401458	-0.264853
C	-3.138181	0.079967	-0.296279
O	-0.846143	-0.570438	-0.473043
B	0.631456	-0.526748	-0.077764
C	-4.017714	1.340293	-0.220187
H	-5.070527	1.046465	-0.267908
H	-3.886882	1.884137	0.724244
H	-3.833937	2.024280	-1.057909
C	-3.415184	-0.832805	0.926318
H	-3.251001	-0.296667	1.867442
H	-4.457450	-1.168109	0.898234
H	-2.760382	-1.707735	0.920666
C	-3.433291	-0.688701	-1.604940
H	-3.255331	-0.060617	-2.485168
H	-2.806909	-1.579641	-1.686178
H	-4.484016	-0.996705	-1.612912
H	-1.888481	2.353240	0.137348
C	0.498407	3.354830	0.046655
H	-0.281202	4.112043	0.105855
Br	0.635901	-1.271425	1.836758
Br	1.623188	-1.728336	-1.342134
H	3.875117	3.016645	-0.118059

29b_arene_SP

C	0.172474	1.997511	-0.006743
C	1.841408	3.719139	0.014990
C	2.827243	2.731629	-0.084953
C	2.470889	1.385005	-0.143633
C	1.131117	0.980445	-0.090559
H	2.116342	4.768927	0.059121
H	3.236092	0.619912	-0.234988
N	-1.203293	1.622870	-0.006191
C	-1.651268	0.401458	-0.264853
C	-3.138181	0.079967	-0.296279
O	-0.846143	-0.570438	-0.473043
B	0.631456	-0.526748	-0.077764
C	-4.017714	1.340293	-0.220187
H	-5.070527	1.046465	-0.267908
H	-3.886882	1.884137	0.724244
H	-3.833937	2.024280	-1.057909
C	-3.415184	-0.832805	0.926318
H	-3.251001	-0.296667	1.867442
H	-4.457450	-1.168109	0.898234
H	-2.760382	-1.707735	0.920666
C	-3.433291	-0.688701	-1.604940
H	-3.255331	-0.060617	-2.485168
H	-2.806909	-1.579641	-1.686178
H	-4.484016	-0.996705	-1.612912
H	-1.888481	2.353240	0.137348
C	0.498407	3.354830	0.046655
H	-0.281202	4.112043	0.105855
Br	0.635901	-1.271425	1.836758
Br	1.623188	-1.728336	-1.342134
H	3.875117	3.016645	-0.118059

BBr_3_arene

B	-0.000154	0.000168	-0.000077
Br	0.560330	-1.818546	0.000094
Br	-1.855514	0.424149	0.000018
Br	1.295206	1.394373	-0.000101

BBr_3_arene_SP

B	-0.000154	-0.000168	0.000077
Br	0.560335	1.818544	-0.000094
Br	-1.855515	-0.424144	-0.000018
Br	1.295202	-1.394377	0.000101

HBr_arene

Br	0.000000	0.000000	0.039940
H	0.000000	0.000000	-1.397890

HBr_arene_SP

Br	0.000000	0.000000	0.039940
H	0.000000	0.000000	-1.397890

IN1_arene

C	-2.766704	0.479936	-0.199640
C	-5.128124	0.064447	0.139294
C	-4.921875	-1.291643	-0.120320
C	-3.637851	-1.747289	-0.419001
C	-2.549787	-0.875308	-0.464021
H	-6.120749	0.437128	0.373809
H	-3.464844	-2.800231	-0.620140
H	-1.569986	-1.265080	-0.698314
N	-1.752963	1.488325	-0.223256
C	-0.439301	1.465472	-0.405198
C	0.324372	2.795358	-0.354889
O	0.136119	0.358465	-0.709515
B	1.078409	-0.613521	-0.021206
Br	0.792189	-2.387264	-0.924066
Br	0.519306	-0.657618	1.926454
Br	3.010705	-0.061167	-0.211192
C	1.165149	2.849586	0.948614
H	1.657612	3.827230	0.996629
H	0.537297	2.731919	1.837267
H	1.933660	2.076404	0.961339
C	1.249675	2.854755	-1.594541
H	1.958490	2.025328	-1.594930
H	0.671677	2.828569	-2.525594
H	1.813541	3.793215	-1.570078
C	-0.620985	4.016016	-0.379909
H	-1.273059	4.025725	-1.262209
H	-1.233723	4.097785	0.528252
H	-0.014538	4.925270	-0.419916
H	-2.127934	2.414658	-0.060520
C	-4.054856	0.948201	0.098293
H	-4.217300	2.004859	0.303679
H	-5.755671	-1.986636	-0.088294

IN1_arene_SP

C	-2.766704	0.479936	-0.199640
C	-5.128124	0.064447	0.139294
C	-4.921875	-1.291643	-0.120320
C	-3.637851	-1.747289	-0.419001
C	-2.549787	-0.875308	-0.464021
H	-6.120749	0.437127	0.373809
H	-3.464844	-2.800231	-0.620140
H	-1.569986	-1.265080	-0.698314
N	-1.752963	1.488325	-0.223256
C	-0.439301	1.465472	-0.405198
C	0.324372	2.795358	-0.354889
O	0.136119	0.358465	-0.709515
B	1.078409	-0.613521	-0.021206
Br	0.792189	-2.387264	-0.924066
Br	0.519306	-0.657618	1.926454
Br	3.010705	-0.061167	-0.211192
C	1.165149	2.849586	0.948614
H	1.657612	3.827230	0.996629
H	0.537297	2.731919	1.837267
H	1.933660	2.076404	0.961339
C	1.249675	2.854755	-1.594541
H	1.958490	2.025328	-1.594930
H	0.671677	2.828569	-2.525594
H	1.813541	3.793215	-1.570078
C	-0.620985	4.016016	-0.379909
H	-1.273059	4.025725	-1.262209
H	-1.233723	4.097785	0.528252

H	-0.014538	4.925270	-0.419916
H	-2.127934	2.414658	-0.060520
C	-4.054856	0.948201	0.098293
H	-4.217300	2.004859	0.303679
H	-5.755671	-1.986637	-0.088294

IN2_arene

C	1.126856	1.818707	-0.280857
C	2.463420	3.745104	-0.799269
C	1.555987	4.549146	-0.106571
C	0.426042	3.980844	0.484638
C	0.195015	2.608843	0.395786
H	3.333232	4.185997	-1.276909
H	-0.287762	4.603736	1.014754
H	-0.678562	2.149581	0.848668
N	0.826840	0.408500	-0.396221
C	1.547746	-0.599276	-0.012091
C	1.060769	-2.039492	-0.043874
O	2.700669	-0.324668	0.619373
B	4.009216	-0.388755	0.235477
Br	5.323123	-0.203682	1.581956
Br	4.465101	-0.622440	-1.609699
C	2.241047	-3.032109	-0.026012
H	1.830039	-4.045081	0.002922
H	2.862775	-2.948955	-0.921576
H	2.872518	-2.913427	0.860485
C	0.231448	-2.223108	1.264424
H	0.881820	-2.157771	2.143746
H	-0.570370	-1.488000	1.366878
H	-0.225953	-3.216639	1.241764
C	0.202244	-2.301647	-1.300743
H	-0.712812	-1.708050	-1.344161
H	0.784940	-2.128753	-2.212817
H	-0.109649	-3.349793	-1.289221
B	-3.397423	-0.137284	0.078627
Br	-2.246520	0.641450	-1.492092
Br	-2.502848	0.418655	1.825404
Br	-5.230084	0.616158	-0.063792
Br	-3.373184	-2.149277	-0.070349
C	2.250535	2.370658	-0.898377
H	2.932319	1.745611	-1.463640
H	-0.141437	0.223475	-0.747618
H	1.724467	5.619855	-0.037483

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IN2_arene_SP

C	1.126856	1.818707	-0.280857
C	2.463420	3.745104	-0.799269
C	1.555987	4.549146	-0.106571
C	0.426042	3.980844	0.484638
C	0.195015	2.608843	0.395786
H	3.333232	4.185997	-1.276909
H	-0.287762	4.603736	1.014754
H	-0.678562	2.149581	0.848668
N	0.826840	0.408500	-0.396221
C	1.547746	-0.599276	-0.012091
C	1.060769	-2.039492	-0.043874
O	2.700669	-0.324668	0.619373
B	4.009216	-0.388755	0.235477
Br	5.323123	-0.203682	1.581956
Br	4.465101	-0.622440	-1.609699
C	2.241047	-3.032109	-0.026012
H	1.830039	-4.045081	0.002922
H	2.862775	-2.948955	-0.921576
H	2.872518	-2.913427	0.860485
C	0.231448	-2.223108	1.264424
H	0.881820	-2.157771	2.143746
H	-0.570370	-1.488000	1.366878
H	-0.225953	-3.216639	1.241764
C	0.202244	-2.301647	-1.300743
H	-0.712812	-1.708050	-1.344161
H	0.784940	-2.128753	-2.212817
H	-0.109649	-3.349793	-1.289221
B	-3.397423	-0.137284	0.078627
Br	-2.246520	0.641450	-1.492092
Br	-2.502848	0.418655	1.825404
Br	-5.230084	0.616158	-0.063792
Br	-3.373184	-2.149277	-0.070349
C	2.250535	2.370658	-0.898377
H	2.932319	1.745611	-1.463640
H	-0.141437	0.223475	-0.747618

H	1.724467	5.619855	-0.037483

IN3_arene_cf1

C	1.004943	-0.905389	0.441807
C	1.157997	-3.171826	1.173312
C	2.076808	-3.486595	0.147317
C	2.439528	-2.513338	-0.749552
C	1.963913	-1.155815	-0.607759
H	0.857893	-3.950495	1.869270
H	3.127330	-2.720079	-1.563472
H	1.694198	-0.686034	-1.558449
N	0.594570	0.423589	0.626397
C	1.369098	1.467531	0.327405
C	0.895541	2.900024	0.458218
O	2.562749	1.286572	-0.121559
B	3.270884	-0.028355	-0.240838
Br	4.488619	0.040453	-1.802594
Br	4.160662	-0.450848	1.492508
C	2.080505	3.770949	0.931807
H	1.743773	4.809930	0.995949
H	2.430168	3.464774	1.923791
H	2.924631	3.722712	0.240392
C	0.457617	3.324449	-0.974970
H	1.277141	3.213948	-1.691925
H	-0.407649	2.744283	-1.309789
H	0.167508	4.379949	-0.943925
C	-0.290906	3.045963	1.430132
H	-1.200452	2.557301	1.071549
H	-0.048990	2.666470	2.429459
H	-0.519847	4.111421	1.529169
B	-3.087051	-0.183137	-0.185101
Br	-2.438405	-0.019839	1.802830
Br	-1.732036	-1.339311	-1.194966
Br	-4.882527	-1.021847	-0.202832
Br	-3.088875	1.672803	-0.978783
C	0.612795	-1.899364	1.328893
H	-0.127582	-1.690599	2.092256
H	-0.337187	0.562035	1.061992
H	2.468527	-4.494787	0.065718

IN3_arene_cf1_SP

C	1.004943	-0.905389	0.441807
C	1.157997	-3.171826	1.173312
C	2.076808	-3.486595	0.147317
C	2.439528	-2.513338	-0.749552
C	1.963913	-1.155815	-0.607759
H	0.857893	-3.950495	1.869270
H	3.127330	-2.720079	-1.563472
H	1.694198	-0.686034	-1.558449
N	0.594570	0.423589	0.626397
C	1.369098	1.467531	0.327405
C	0.895541	2.900024	0.458218
O	2.562749	1.286572	-0.121559
B	3.270884	-0.028355	-0.240838
Br	4.488619	0.040453	-1.802594
Br	4.160662	-0.450848	1.492508
C	2.080505	3.770949	0.931807
H	1.743773	4.809930	0.995949
H	2.430168	3.464774	1.923791
H	2.924631	3.722712	0.240392
C	0.457617	3.324449	-0.974970
H	1.277141	3.213948	-1.691925
H	-0.407649	2.744283	-1.309789
H	0.167508	4.379949	-0.943925
C	-0.290906	3.045963	1.430132
H	-1.200452	2.557301	1.071549
H	-0.048990	2.666470	2.429459
H	-0.519847	4.111421	1.529169
B	-3.087051	-0.183137	-0.185101
Br	-2.438405	-0.019839	1.802830
Br	-1.732036	-1.339311	-1.194966
Br	-4.882527	-1.021847	-0.202832
Br	-3.088875	1.672803	-0.978783
C	0.612795	-1.899364	1.328893
H	-0.127582	-1.690599	2.092256
H	-0.337187	0.562035	1.061992
H	2.468527	-4.494787	0.065718

IN3_arene

C	1.247225	-0.644729	1.527513

C	1.915788	-2.614320	2.693847
C	2.297971	-3.242005	1.490819
C	2.153132	-2.564455	0.302061
C	1.640501	-1.218322	0.269226
H	2.034421	-3.151619	3.630859
H	2.439019	-3.011024	-0.645545
H	0.803448	-1.089242	-0.465848
N	0.777978	0.678423	1.485926
C	1.121170	1.557403	0.536622
C	0.621753	2.988756	0.567718
O	1.986088	1.253057	-0.356932
B	2.680686	-0.071184	-0.505282
Br	2.818024	-0.513074	-2.430191
Br	4.437812	0.052705	0.453624
C	1.879911	3.869985	0.799737
H	1.568911	4.919072	0.818875
H	2.363021	3.640524	1.756382
H	2.613768	3.737712	0.000968
C	-0.012948	3.328944	-0.804316
H	0.675547	3.109552	-1.624469
H	-0.937721	2.769231	-0.958259
H	-0.243279	4.399205	-0.819805
C	-0.400337	3.224628	1.694323
H	-1.310864	2.631184	1.554330
H	0.025232	3.037368	2.688672
H	-0.702934	4.275749	1.674057
B	-2.703423	-0.282190	-0.156114
Br	-2.024157	-0.940934	1.678540
Br	-1.095902	-0.155143	-1.465776
Br	-4.032681	-1.565574	-0.877711
Br	-3.459913	1.571316	0.071024
C	1.390439	-1.320786	2.727781
H	1.105203	-0.861502	3.668516
H	0.006561	0.920753	2.103347
H	2.699756	-4.249447	1.514041

IN3_arene_SP

C	1.247225	-0.644729	1.527513
C	1.915788	-2.614320	2.693847
C	2.297971	-3.242005	1.490819
C	2.153132	-2.564455	0.302061
C	1.640501	-1.218322	0.269226
H	2.034421	-3.151619	3.630859
H	2.439019	-3.011024	-0.645545
H	0.803448	-1.089242	-0.465848
N	0.777978	0.678423	1.485926
C	1.121170	1.557403	0.536622
C	0.621753	2.988756	0.567718
O	1.986088	1.253057	-0.356932
B	2.680686	-0.071184	-0.505282
Br	2.818024	-0.513074	-2.430191
Br	4.437812	0.052705	0.453624
C	1.879911	3.869985	0.799737
H	1.568911	4.919072	0.818875
H	2.363021	3.640524	1.756382
H	2.613768	3.737712	0.000968
C	-0.012948	3.328944	-0.804316
H	0.675547	3.109552	-1.624469
H	-0.937721	2.769231	-0.958259
H	-0.243279	4.399205	-0.819805
C	-0.400337	3.224628	1.694323
H	-1.310864	2.631184	1.554330
H	0.025232	3.037368	2.688672
H	-0.702934	4.275749	1.674057
B	-2.703423	-0.282190	-0.156114
Br	-2.024157	-0.940934	1.678540
Br	-1.095902	-0.155143	-1.465776
Br	-4.032681	-1.565574	-0.877711
Br	-3.459913	1.571316	0.071024
C	1.390439	-1.320786	2.727781
H	1.105203	-0.861502	3.668516
H	0.006561	0.920753	2.103347
H	2.699756	-4.249447	1.514041

TSI_arene

C	-1.569412	2.080784	0.930275
C	-3.416896	3.339409	0.045244
C	-2.541071	4.365644	-0.313263
C	-1.176747	4.243977	-0.041976
C	-0.680439	3.101822	0.580096

H	-4.479923	3.431201	-0.155944
H	-0.488310	5.034503	-0.323838
H	0.380421	2.981924	0.771108
N	-1.051025	0.964060	1.672851
C	-1.414014	-0.293636	1.667725
C	-1.117185	-1.223085	2.832658
O	-2.257855	-0.693285	0.728414
B	-2.169628	-1.132137	-0.594026
Br	0.508823	0.584546	-1.319266
Br	-3.387396	-0.324374	-1.816261
Br	-1.126069	-2.630581	-1.084356
C	-2.503223	-1.450174	3.508825
H	-2.353127	-2.099724	4.376903
H	-2.943939	-0.510303	3.860060
H	-3.207847	-1.940048	2.831332
C	-0.543730	-2.577384	2.368365
H	-1.217687	-3.100185	1.687349
H	0.419449	-2.442188	1.870096
H	-0.400025	-3.205410	3.253551
C	-0.154661	-0.578700	3.847507
H	0.816256	-0.355012	3.394425
H	-0.567391	0.336070	4.290173
H	0.013332	-1.285746	4.664777
B	2.246248	0.140462	-0.325579
Br	2.269920	1.140672	1.511227
Br	2.339484	-1.840574	0.030912
Br	3.799942	0.781319	-1.391867
C	-2.939081	2.190928	0.673139
H	-3.626276	1.405396	0.963082
H	-0.212652	1.165424	2.225069
H	-2.921249	5.257552	-0.802514

TSI_arene_SP

C	-1.569412	2.080784	0.930275
C	-3.416895	3.339410	0.045244
C	-2.541070	4.365644	-0.313263
C	-1.176746	4.243977	-0.041976
C	-0.680438	3.101822	0.580096
H	-4.479922	3.431202	-0.155944
H	-0.488309	5.034503	-0.323838
H	0.380422	2.981924	0.771108
N	-1.051025	0.964060	1.672851
C	-1.414014	-0.293636	1.667725
C	-1.117185	-1.223085	2.832658
O	-2.257855	-0.693285	0.728414
B	-2.169628	-1.132137	-0.594026
Br	0.508823	0.584546	-1.319266
Br	-3.387396	-0.324373	-1.816261
Br	-1.126070	-2.630581	-1.084356
C	-2.503223	-1.450174	3.508825
H	-2.353127	-2.099724	4.376903
H	-2.943939	-0.510302	3.860060
H	-3.207847	-1.940047	2.831332
C	-0.543730	-2.577384	2.368365
H	-1.217688	-3.100185	1.687349
H	0.419449	-2.442188	1.870096
H	-0.400026	-3.205410	3.253551
C	-0.154661	-0.578700	3.847507
H	0.816256	-0.355012	3.394425
H	-0.567391	0.336070	4.290173
H	0.013332	-1.285746	4.664777
B	2.246248	0.140462	-0.325579
Br	2.269920	1.140672	1.511227
Br	2.339484	-1.840574	0.030912
Br	3.799942	0.781318	-1.391867
C	-2.939081	2.190929	0.673139
H	-3.626276	1.405397	0.963082
H	-0.212652	1.165424	2.225069
H	-2.921248	5.257553	-0.802514

TSII_arene

C	-1.020257	-0.911810	-0.356595
C	-1.314985	-3.141380	-1.164303
C	-2.148798	-3.453057	-0.076284
C	-2.393315	-2.496323	0.889677
C	-1.873582	-1.179852	0.746190
H	-1.105592	-3.901908	-1.910991
H	-3.011852	-2.716406	1.753615
H	-1.731641	-0.590794	1.648622
N	-0.582009	0.423524	-0.545303

C	-1.360810	1.466141	-0.324021
C	-0.893818	2.899226	-0.472285
O	-2.581449	1.296421	0.095165
B	-3.349339	0.061505	0.202267
Br	-4.531617	0.100771	1.762047
Br	-4.138598	-0.515567	-1.495462
C	-2.073807	3.759881	-0.975124
H	-1.734753	4.796478	-1.060898
H	-2.416503	3.432560	-1.962861
H	-2.923493	3.731345	-0.289096
C	-0.470310	3.350996	0.956361
H	-1.295063	3.251038	1.669252
H	0.393384	2.778369	1.307798
H	-0.183507	4.406793	0.909846
C	0.301652	3.027579	-1.436262
H	1.208369	2.547480	-1.059999
H	0.069284	2.625003	-2.428569
H	0.529138	4.091370	-1.555178
B	3.108269	-0.194929	0.182048
Br	2.403317	-0.052311	-1.791579
Br	1.814299	-1.387604	1.209874
Br	4.936262	-0.961910	0.150563
Br	3.070359	1.667177	0.975211
C	-0.747011	-1.877027	-1.316989
H	-0.081285	-1.651941	-2.141970
H	0.367578	0.543420	-0.952487
H	-2.573560	-4.447464	0.012088

TSII_arene_SP

C	1.020257	-0.911810	0.356595
C	1.314985	-3.141380	1.164303
C	2.148798	-3.453057	0.076284
C	2.393315	-2.496323	-0.889677
C	1.873582	-1.179852	-0.746190
H	1.105592	-3.901908	1.910991
H	3.011852	-2.716406	-1.753615
H	1.731641	-0.590794	-1.648622
N	0.582009	0.423524	0.545303
C	1.360810	1.466141	0.324021
C	0.893818	2.899226	0.472285
O	2.581449	1.296421	-0.095165
B	3.349339	0.061505	-0.202267
Br	4.531617	0.100771	-1.762047
Br	4.138598	-0.515567	1.495462
C	2.073807	3.759881	0.975124
H	1.734753	4.796478	1.060898
H	2.416503	3.432560	1.962861
H	2.923493	3.731345	0.289096
C	0.470310	3.350996	-0.956361
H	1.295063	3.251038	-1.669252
H	-0.393384	2.778369	-1.307798
H	0.183507	4.406793	-0.909846
C	-0.301652	3.027579	1.436262
H	-1.208369	2.547480	1.059999
H	-0.069284	2.625003	2.428569
H	-0.529138	4.091370	1.555178
B	-3.108269	-0.194929	-0.182048
Br	-2.403317	-0.052311	1.791579
Br	-1.814299	-1.387604	-1.209874
Br	-4.936262	-0.961910	-0.150563
Br	-3.070359	1.667177	-0.975211
C	0.747011	-1.877027	1.316989
H	0.081285	-1.651941	2.141970
H	-0.367578	0.543420	0.952487
H	2.573560	-4.447464	-0.012088

TSIII_arene

C	1.157826	-0.519997	1.713022
C	0.850656	-2.618614	2.817943
C	1.375321	-3.296797	1.707778
C	1.795382	-2.577473	0.600530
C	1.673624	-1.160203	0.551097
H	0.515550	-3.181973	3.683849
H	2.209257	-3.075283	-0.271602
H	0.462469	-1.004223	-0.209009
N	0.969981	0.874772	1.634407
C	1.343471	1.637985	0.600929
C	0.912311	3.091208	0.495020
O	2.096233	1.185996	-0.325440
B	2.624002	-0.242020	-0.389852

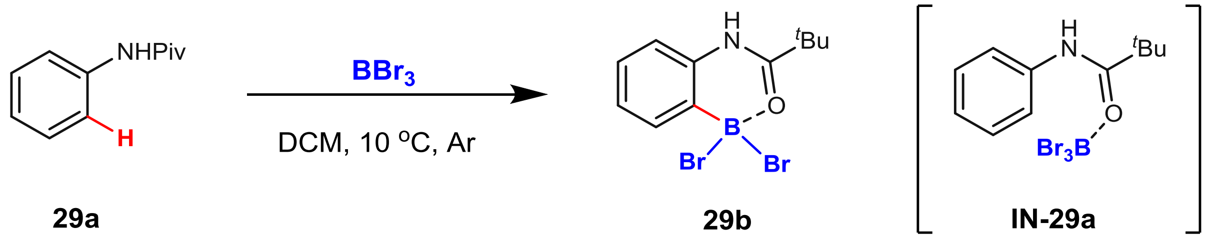
Br	2.591938	-0.816428	-2.306894
Br	4.495083	-0.182159	0.379968
C	2.205328	3.945166	0.495049
H	1.933882	4.999203	0.378689
H	2.757533	3.835889	1.435243
H	2.866666	3.661391	-0.327242
C	0.165134	3.265312	-0.853296
H	0.771108	2.906064	-1.688739
H	-0.790945	2.733743	-0.862376
H	-0.035334	4.331484	-1.002169
C	-0.008727	3.515566	1.653099
H	-0.925431	2.915288	1.684247
H	0.496140	3.465973	2.626791
H	-0.308337	4.556847	1.503469
B	-2.680013	-0.192789	-0.125410
Br	-2.295882	0.270558	1.798293
Br	-0.775670	-0.394284	-1.235643
Br	-3.600579	-1.920536	-0.303848
Br	-3.514152	1.326047	-1.090484
C	0.728881	-1.228370	2.828315
H	0.290794	-0.718701	3.680720
H	0.300338	1.281348	2.277713
H	1.455508	-4.379011	1.723761

TSIII_arene_SP

C	1.157826	-0.519997	1.713022
C	0.850656	-2.618614	2.817943
C	1.375321	-3.296797	1.707778
C	1.795382	-2.577473	0.600530
C	1.673624	-1.160203	0.551097
H	0.515550	-3.181973	3.683849
H	2.209257	-3.075283	-0.271602
H	0.462469	-1.004223	-0.209009
N	0.969981	0.874772	1.634407
C	1.343471	1.637985	0.600929
C	0.912311	3.091208	0.495020
O	2.096233	1.185996	-0.325440
B	2.624002	-0.242020	-0.389852
Br	2.591938	-0.816428	-2.306894
Br	4.495083	-0.182159	0.379968
C	2.205328	3.945166	0.495049
H	1.933882	4.999203	0.378689
H	2.757533	3.835889	1.435243
H	2.866666	3.661391	-0.327242
C	0.165134	3.265312	-0.853296
H	0.771108	2.906064	-1.688739
H	-0.790945	2.733743	-0.862376
H	-0.035334	4.331484	-1.002169
C	-0.008727	3.515566	1.653099
H	-0.925431	2.915288	1.684247
H	0.496140	3.465973	2.626791
H	-0.308337	4.556847	1.503469
B	-2.680013	-0.192789	-0.125410
Br	-2.295882	0.270558	1.798293
Br	-0.775670	-0.394284	-1.235643
Br	-3.600579	-1.920536	-0.303848
Br	-3.514152	1.326047	-1.090484
C	0.728881	-1.228370	2.828315
H	0.290794	-0.718701	3.680720
H	0.300338	1.281348	2.277713
H	1.455508	-4.379011	1.72376

6.2.2 Operando IR experiments of 29a

IR spectra were recorded on a Mettler Toledo React IRTM 15 spectrometer using a diamond comb. In an oven dried self-prepared three-necked micro reactor with a magnetic stirrer, amide **29a** (88.5 mg, 0.5 mmol), DCM (3 mL), dodecane (170.0 mg) as the internal standard were added. The mixture was allowed to stir at 10 ^{o}C and recorded by React IR. Then, the solution of BBr_3 in DCM was added in via a syringe. The course of the reaction can be observed from the characteristic IR band at 1700 cm^{-1} - 1500 cm^{-1}. When the reaction completed, the mixture was quenched by pinacol and K_2CO_3, and the yield was determined by GC analysis.



To establish the mechanism for this metal-free C-H activation process, a series of operando IR experiments were performed by amide **29a** and BBr_3. As shown in Fig. S4 and S5, when BBr_3 was added to the solution of **29a**, **29a** (1681 cm^{-1}) disappeared instantly and a new compound **IN-29a** (1585 cm^{-1} and 1612 cm^{-1}) was formed in the meantime, which was most likely by the complexation of **29a** with BBr_3. **IN-29a** was consumed mildly along with the formation of the desired product **29b** (1556 cm^{-1} and 1630 cm^{-1}). The results indicated that the complexation of **29a** with BBr_3 was a fast step and the process from **IN-29a** to **29b** was involved in the rate-determining step, which matched well with the results from DFT calculations. (Operando IR experiments were performed three times with similar results)

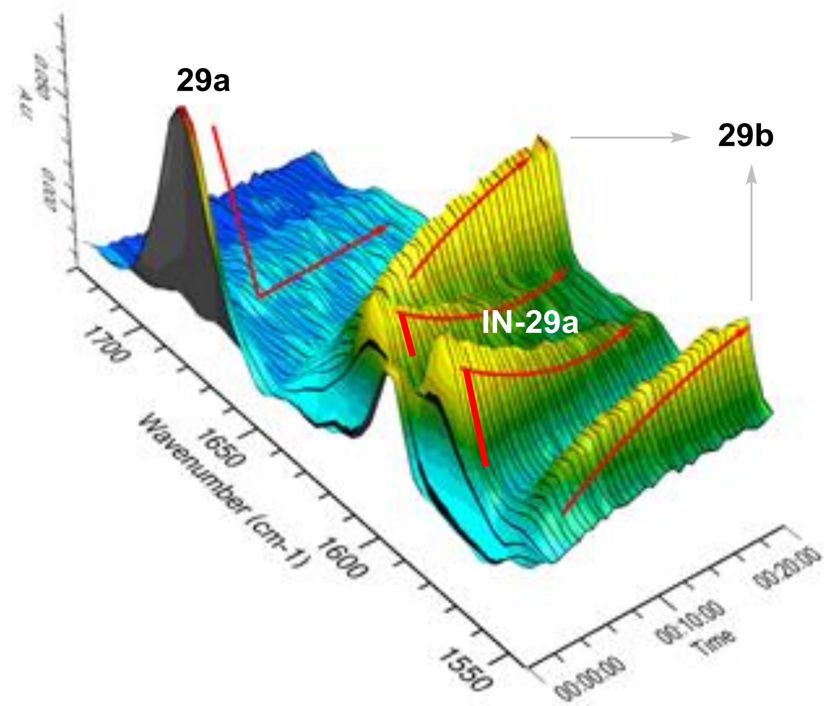


Fig. S4| 3D-profile from Operando IR for the reaction of *N*-pivaloyl amide **29a** with BBr_3.

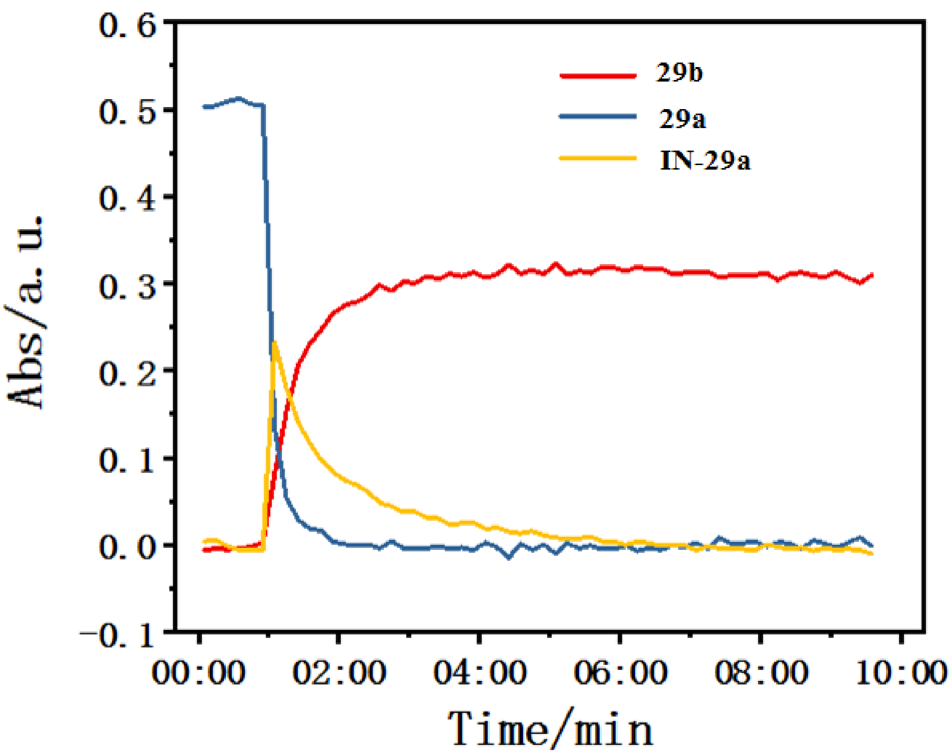
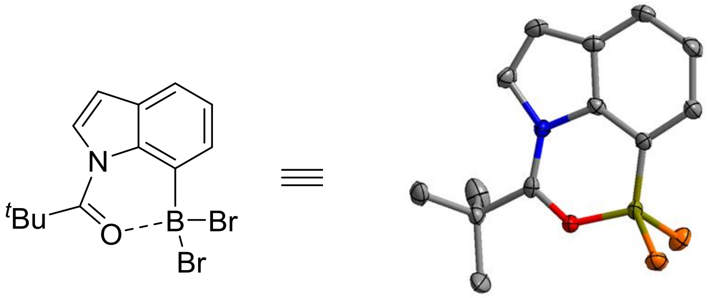


Fig. S5| Absorption intensity change of **29a**, **29b** and **IN-29a** . [**29a**] = 14.23×10^{-2} mol/L, [BBr_3] =18.57×10^{-2} mol/L, 10 °C.

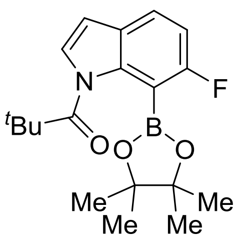
7. Crystallographic data



1b **CCDC 1910131**

Br(1)-B(1)	2.025(4)	C(12)-H(12B)	0.9800
Br(2)-B(1)	2.043(4)	C(12)-H(12C)	0.9800
C(1)-C(2)	1.335(5)	C(13)-H(13A)	0.9800
C(1)-N(1)	1.435(4)	C(13)-H(13B)	0.9800
C(1)-H(1)	0.9500	C(13)-H(13C)	0.9800
C(2)-C(3)	1.456(5)	B(1)-O(1)	1.523(4)
C(2)-H(2)	0.9500		
C(3)-C(4)	1.393(5)	C(2)-C(1)-N(1)	109.4(3)
C(3)-C(8)	1.400(4)	C(2)-C(1)-H(1)	125.3
C(4)-C(5)	1.404(5)	N(1)-C(1)-H(1)	125.3
C(4)-H(4)	0.9500	C(1)-C(2)-C(3)	109.5(3)
C(5)-C(6)	1.393(5)	C(1)-C(2)-H(2)	125.3
C(5)-H(5)	0.9500	C(3)-C(2)-H(2)	125.3
C(6)-C(7)	1.401(4)	C(4)-C(3)-C(8)	117.2(3)
C(6)-H(6)	0.9500	C(4)-C(3)-C(2)	136.5(3)
C(7)-C(8)	1.372(4)	C(8)-C(3)-C(2)	106.3(3)
C(7)-B(1)	1.569(5)	C(3)-C(4)-C(5)	118.0(3)
C(8)-N(1)	1.431(4)	C(3)-C(4)-H(4)	121.0
C(9)-O(1)	1.282(3)	C(5)-C(4)-H(4)	121.0
C(9)-N(1)	1.333(4)	C(6)-C(5)-C(4)	122.1(3)
C(9)-C(10)	1.520(4)	C(6)-C(5)-H(5)	118.9
C(10)-C(11)	1.532(4)	C(4)-C(5)-H(5)	118.9
C(10)-C(13)	1.534(5)	C(5)-C(6)-C(7)	121.3(3)
C(10)-C(12)	1.552(5)	C(5)-C(6)-H(6)	119.4
C(11)-H(11A)	0.9800	C(7)-C(6)-H(6)	119.4
C(11)-H(11B)	0.9800	C(8)-C(7)-C(6)	114.3(3)
C(11)-H(11C)	0.9800	C(8)-C(7)-B(1)	115.2(3)
C(12)-H(12A)	0.9800	C(6)-C(7)-B(1)	130.4(3)

C(7)-C(8)-C(3)	127.1(3)	H(12A)-C(12)-H(12B)	109.5
C(7)-C(8)-N(1)	124.4(3)	C(10)-C(12)-H(12C)	109.5
C(3)-C(8)-N(1)	108.4(3)	H(12A)-C(12)-H(12C)	109.5
O(1)-C(9)-N(1)	119.0(3)	H(12B)-C(12)-H(12C)	109.5
O(1)-C(9)-C(10)	116.4(3)	C(10)-C(13)-H(13A)	109.5
N(1)-C(9)-C(10)	124.5(3)	C(10)-C(13)-H(13B)	109.5
C(9)-C(10)-C(11)	112.1(3)	H(13A)-C(13)-H(13B)	109.5
C(9)-C(10)-C(13)	109.0(3)	C(10)-C(13)-H(13C)	109.5
C(11)-C(10)-C(13)	108.9(3)	H(13A)-C(13)-H(13C)	109.5
C(9)-C(10)-C(12)	106.6(3)	H(13B)-C(13)-H(13C)	109.5
C(11)-C(10)-C(12)	111.2(3)	O(1)-B(1)-C(7)	110.4(2)
C(13)-C(10)-C(12)	108.9(3)	O(1)-B(1)-Br(1)	106.6(2)
C(10)-C(11)-H(11A)	109.5	C(7)-B(1)-Br(1)	114.6(2)
C(10)-C(11)-H(11B)	109.5	O(1)-B(1)-Br(2)	103.4(2)
H(11A)-C(11)-H(11B)	109.5	C(7)-B(1)-Br(2)	111.5(2)
C(10)-C(11)-H(11C)	109.5	Br(1)-B(1)-Br(2)	109.50(16)
H(11A)-C(11)-H(11C)	109.5	C(9)-N(1)-C(8)	121.5(3)
H(11B)-C(11)-H(11C)	109.5	C(9)-N(1)-C(1)	132.0(3)
C(10)-C(12)-H(12A)	109.5	C(8)-N(1)-C(1)	106.4(2)
C(10)-C(12)-H(12B)	109.5	C(9)-O(1)-B(1)	126.9(2)



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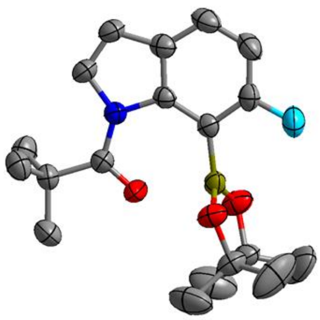
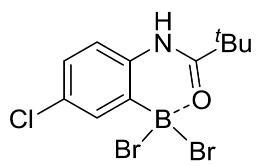


9c **CCDC 1910132**

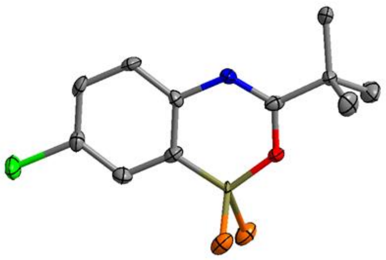
B(1)-O(2)	1.360(4)	C(3)-H(3)	0.9300
B(1)-O(3)	1.360(4)	C(4)-C(5)	1.390(5)
B(1)-C(1)	1.573(5)	C(4)-H(4)	0.9300
C(1)-C(2)	1.381(5)	C(5)-C(6)	1.397(5)
C(1)-C(6)	1.406(4)	C(5)-C(8)	1.446(5)
C(2)-F(1)	1.374(4)	C(6)-N(1)	1.416(4)
C(2)-C(3)	1.378(5)	C(7)-C(8)	1.328(5)
C(3)-C(4)	1.369(5)	C(7)-N(1)	1.405(4)

C(7)-H(7)	0.9300	O(2)-B(1)-C(1)	121.5(3)
C(8)-H(8)	0.9300	O(3)-B(1)-C(1)	122.8(3)
C(9)-O(1)	1.219(4)	C(2)-C(1)-C(6)	112.0(3)
C(9)-N(1)	1.383(4)	C(2)-C(1)-B(1)	119.3(3)
C(9)-C(10)	1.534(4)	C(6)-C(1)-B(1)	128.6(3)
C(10)-C(11)	1.525(5)	F(1)-C(2)-C(3)	116.6(3)
C(10)-C(12)	1.535(5)	F(1)-C(2)-C(1)	116.6(3)
C(10)-C(13)	1.540(5)	C(3)-C(2)-C(1)	126.8(3)
C(11)-H(11A)	0.9600	C(4)-C(3)-C(2)	119.0(3)
C(11)-H(11B)	0.9600	C(4)-C(3)-H(3)	120.5
C(11)-H(11C)	0.9600	C(2)-C(3)-H(3)	120.5
C(12)-H(12A)	0.9600	C(3)-C(4)-C(5)	118.7(4)
C(12)-H(12B)	0.9600	C(3)-C(4)-H(4)	120.7
C(12)-H(12C)	0.9600	C(5)-C(4)-H(4)	120.7
C(13)-H(13A)	0.9600	C(4)-C(5)-C(6)	119.7(3)
C(13)-H(13B)	0.9600	C(4)-C(5)-C(8)	132.8(3)
C(13)-H(13C)	0.9600	C(6)-C(5)-C(8)	107.4(3)
C(14)-O(3)	1.457(4)	C(5)-C(6)-C(1)	123.8(3)
C(14)-C(15)	1.490(6)	C(5)-C(6)-N(1)	107.1(3)
C(14)-C(19)	1.519(7)	C(1)-C(6)-N(1)	129.1(3)
C(14)-C(16)	1.554(5)	C(8)-C(7)-N(1)	110.4(3)
C(15)-H(15A)	0.9600	C(8)-C(7)-H(7)	124.8
C(15)-H(15B)	0.9600	N(1)-C(7)-H(7)	124.8
C(15)-H(15C)	0.9600	C(7)-C(8)-C(5)	107.8(3)
C(16)-O(2)	1.445(4)	C(7)-C(8)-H(8)	126.1
C(16)-C(17)	1.497(6)	C(5)-C(8)-H(8)	126.1
C(16)-C(18)	1.513(6)	O(1)-C(9)-N(1)	117.8(3)
C(17)-H(17A)	0.9600	O(1)-C(9)-C(10)	120.5(3)
C(17)-H(17B)	0.9600	N(1)-C(9)-C(10)	121.7(3)
C(17)-H(17C)	0.9600	C(11)-C(10)-C(9)	107.0(3)
C(18)-H(18A)	0.9600	C(11)-C(10)-C(12)	109.2(3)
C(18)-H(18B)	0.9600	C(9)-C(10)-C(12)	111.5(3)
C(18)-H(18C)	0.9600	C(11)-C(10)-C(13)	107.6(3)
C(19)-H(19A)	0.9600	C(9)-C(10)-C(13)	110.1(3)
C(19)-H(19B)	0.9600	C(12)-C(10)-C(13)	111.3(3)
C(19)-H(19C)	0.9600	C(10)-C(11)-H(11A)	109.5
		C(10)-C(11)-H(11B)	109.5
O(2)-B(1)-O(3)	113.1(3)	H(11A)-C(11)-H(11B)	109.5

C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(3)-C(14)-C(15)	107.1(3)
O(3)-C(14)-C(19)	105.5(4)
C(15)-C(14)-C(19)	109.3(5)
O(3)-C(14)-C(16)	104.2(3)
C(15)-C(14)-C(16)	116.4(4)
C(19)-C(14)-C(16)	113.6(4)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(2)-C(16)-C(17)	107.3(4)
O(2)-C(16)-C(18)	106.5(3)
C(17)-C(16)-C(18)	108.3(4)
O(2)-C(16)-C(14)	104.3(2)
C(17)-C(16)-C(14)	115.1(4)
C(18)-C(16)-C(14)	114.7(4)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(9)-N(1)-C(7)	128.4(3)
C(9)-N(1)-C(6)	124.3(2)
C(7)-N(1)-C(6)	107.2(3)
B(1)-O(2)-C(16)	109.3(3)
B(1)-O(3)-C(14)	108.7(2)



28b



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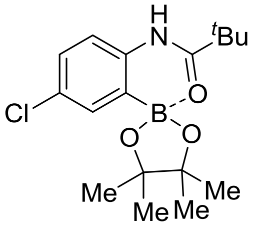
B(1)-O(1)	1.481(8)	C(2)-C(1)-H(1B)	109.5
B(1)-C(11)	1.586(10)	H(1A)-C(1)-H(1B)	109.5
B(1)-Br(2)	2.035(8)	C(2)-C(1)-H(1C)	109.5
B(1)-Br(1)	2.056(8)	H(1A)-C(1)-H(1C)	109.5
C(1)-C(2)	1.523(11)	H(1B)-C(1)-H(1C)	109.5
C(1)-H(1A)	0.9800	C(5)-C(2)-C(3)	105.7(6)
C(1)-H(1B)	0.9800	C(5)-C(2)-C(1)	109.0(6)
C(1)-H(1C)	0.9800	C(3)-C(2)-C(1)	109.7(6)
C(2)-C(5)	1.510(10)	C(5)-C(2)-C(4)	112.1(6)
C(2)-C(3)	1.532(10)	C(3)-C(2)-C(4)	109.6(6)
C(2)-C(4)	1.536(9)	C(1)-C(2)-C(4)	110.5(6)
C(3)-H(3A)	0.9800	C(2)-C(3)-H(3A)	109.5
C(3)-H(3B)	0.9800	C(2)-C(3)-H(3B)	109.5
C(3)-H(3C)	0.9800	H(3A)-C(3)-H(3B)	109.5
C(4)-H(4A)	0.9800	C(2)-C(3)-H(3C)	109.5
C(4)-H(4B)	0.9800	H(3A)-C(3)-H(3C)	109.5
C(4)-H(4C)	0.9800	H(3B)-C(3)-H(3C)	109.5
C(5)-O(1)	1.288(8)	C(2)-C(4)-H(4A)	109.5
C(5)-N(1)	1.305(9)	C(2)-C(4)-H(4B)	109.5
C(6)-C(7)	1.378(10)	H(4A)-C(4)-H(4B)	109.5
C(6)-C(11)	1.401(9)	C(2)-C(4)-H(4C)	109.5
C(6)-N(1)	1.429(9)	H(4A)-C(4)-H(4C)	109.5
C(7)-C(8)	1.412(11)	H(4B)-C(4)-H(4C)	109.5
C(7)-H(7)	0.9500	O(1)-C(5)-N(1)	121.0(7)
C(8)-C(9)	1.381(10)	O(1)-C(5)-C(2)	115.0(6)
C(8)-H(8)	0.9500	N(1)-C(5)-C(2)	124.0(6)
C(9)-C(10)	1.390(10)	C(7)-C(6)-C(11)	123.7(7)
C(9)-Cl(1)	1.752(8)	C(7)-C(6)-N(1)	118.4(6)
C(10)-C(11)	1.392(11)	C(11)-C(6)-N(1)	117.8(6)
C(10)-H(10)	0.9500	C(6)-C(7)-C(8)	118.2(6)
N(1)-H(1)	0.8800	C(6)-C(7)-H(7)	120.9
O(1)-B(1)-C(11)	111.4(6)	C(8)-C(7)-H(7)	120.9
O(1)-B(1)-Br(2)	107.0(5)	C(9)-C(8)-C(7)	118.3(6)
C(11)-B(1)-Br(2)	112.8(5)	C(9)-C(8)-H(8)	120.9
O(1)-B(1)-Br(1)	106.4(5)	C(7)-C(8)-H(8)	120.9
C(11)-B(1)-Br(1)	111.8(5)	C(10)-C(9)-C(8)	123.0(7)
Br(2)-B(1)-Br(1)	107.1(3)		
C(2)-C(1)-H(1A)	109.5	C(10)-C(9)-Cl(1)	119.3(6)

C(8)-C(9)-Cl(1)	117.7(6)	C(10)-C(11)-B(1)	124.2(6)
C(9)-C(10)-C(11)	119.3(7)	C(5)-N(1)-C(6)	125.5(6)
C(9)-C(10)-H(10)	120.3	C(5)-N(1)-H(1)	117.3
C(11)-C(10)-H(10)	120.3	C(6)-N(1)-H(1)	117.3
C(6)-C(11)-C(10)	117.5(6)	C(5)-O(1)-B(1)	125.5(6)
C(6)-C(11)-B(1)	118.3(6)		



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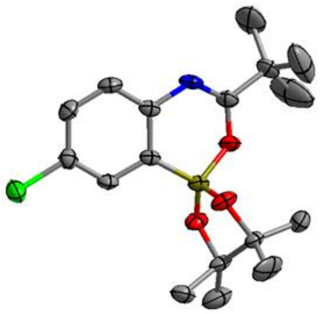


28c **CCDC 1910135**

B(1)-O(2)	1.439(6)	C(7)-C(11)	1.54(3)
B(1)-O(3)	1.441(6)	C(7)-C(8)	1.553(16)
B(1)-O(1)	1.567(6)	C(10)-C(8)	1.488(17)
B(1)-C(5)	1.576(7)	C(10)-H(10A)	0.9600
B(2)-O(6)	1.432(6)	C(10)-H(10B)	0.9600
B(2)-O(5)	1.435(6)	C(10)-H(10C)	0.9600
B(2)-O(4)	1.571(6)	C(8)-O(3)	1.363(13)
B(2)-C(25)	1.587(6)	C(8)-C(9)	1.52(2)
C(1)-C(6)	1.364(7)	C(9)-H(9A)	0.9600
C(1)-C(2)	1.383(7)	C(9)-H(9B)	0.9600
C(1)-Cl(1)	1.745(5)	C(9)-H(9C)	0.9600
C(2)-C(3)	1.374(7)	C(15)-O(1)	1.277(6)
C(2)-H(2A)	0.9300	C(15)-N(1)	1.303(6)
C(3)-C(4)	1.379(6)	C(15)-C(16)	1.511(6)
C(3)-H(3A)	0.9300	C(16)-C(17)	1.507(8)
C(4)-C(5)	1.398(6)	C(16)-C(18)	1.494(8)
C(4)-N(1)	1.417(6)	C(16)-C(19)	1.541(8)
C(5)-C(6)	1.379(6)	C(17)-H(17A)	0.9600
C(6)-H(6A)	0.9300	C(17)-H(17B)	0.9600
C(7)-C(12)	1.501(18)	C(17)-H(17C)	0.9600
C(7)-O(2)	1.523(11)	C(18)-H(18A)	0.9600

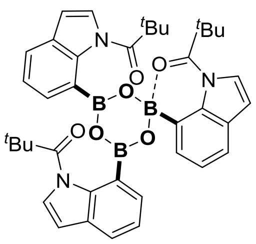
C(18)-H(18B)	0.9600	C(34)-H(34A)	0.9600
C(18)-H(18C)	0.9600	C(34)-H(34B)	0.9600
C(19)-H(19A)	0.9600	C(34)-H(34C)	0.9600
C(19)-H(19B)	0.9600	C(35)-O(6)	1.503(9)
C(19)-H(19C)	0.9600	C(35)-C(36)	1.518(14)
C(20)-C(21)	1.352(6)	C(35)-C(37)	1.528(13)
C(20)-C(25)	1.384(6)	C(36)-H(36A)	0.9600
C(20)-H(20A)	0.9300	C(36)-H(36B)	0.9600
C(21)-C(22)	1.392(7)	C(36)-H(36C)	0.9600
C(21)-Cl(2)	1.740(5)	C(37)-H(37A)	0.9600
C(22)-C(23)	1.379(7)	C(37)-H(37B)	0.9600
C(22)-H(22A)	0.9300	C(37)-H(37C)	0.9600
C(23)-C(24)	1.363(6)	C(11)-H(11A)	0.9600
C(23)-H(23A)	0.9300	C(11)-H(11B)	0.9600
C(24)-C(25)	1.399(6)	C(11)-H(11C)	0.9600
C(24)-N(2)	1.423(6)	C(12)-H(12A)	0.9600
C(27)-O(4)	1.278(6)	C(12)-H(12B)	0.9600
C(27)-N(2)	1.304(6)	C(12)-H(12C)	0.9600
C(27)-C(28)	1.515(7)	C(32')-C(35')	1.52(3)
C(28)-C(30)	1.457(10)	C(32')-C(33')	1.55(3)
C(28)-C(29)	1.524(8)	C(32')-O(5)	1.572(18)
C(28)-C(31)	1.513(10)	C(32')-C(34')	1.76(5)
C(29)-H(29A)	0.9600	C(33')-H(33D)	0.9600
C(29)-H(29B)	0.9600	C(33')-H(33E)	0.9600
C(29)-H(29C)	0.9600	C(33')-H(33F)	0.9600
C(30)-H(30A)	0.9600	C(34')-H(34D)	0.9600
C(30)-H(30B)	0.9600	C(34')-H(34E)	0.9600
C(30)-H(30C)	0.9600	C(34')-H(34F)	0.9600
C(31)-H(31A)	0.9600	C(35')-O(6)	1.32(2)
C(31)-H(31B)	0.9600	C(35')-C(37')	1.51(3)
C(31)-H(31C)	0.9600	C(35')-C(36')	1.55(3)
C(32)-C(34)	1.36(2)	C(36')-H(36D)	0.9600
C(32)-O(5)	1.444(7)	C(36')-H(36E)	0.9600
C(32)-C(33)	1.520(11)	C(36')-H(36F)	0.9600
C(32)-C(35)	1.543(12)	C(37')-H(37D)	0.9600
C(33)-H(33A)	0.9600	C(37')-H(37E)	0.9600
C(33)-H(33B)	0.9600	C(37')-H(37F)	0.9600
C(33)-H(33C)	0.9600	N(1)-H(1A)	0.8600

N(2)-H(2B)	0.8600	C(6)-C(1)-Cl(1)	119.6(4)
O(2)-C(7')	1.432(10)	C(2)-C(1)-Cl(1)	119.2(4)
O(3)-C(8')	1.536(13)	C(3)-C(2)-C(1)	119.0(5)
O(7)-H(7C)	0.8500	C(3)-C(2)-H(2A)	120.5
O(7)-H(7D)	0.8562	C(1)-C(2)-H(2A)	120.5
O(8)-H(8D)	0.8500	C(2)-C(3)-C(4)	119.4(4)
O(8)-H(8A)	0.8501	C(2)-C(3)-H(3A)	120.3
C(12')-C(7')	1.541(16)	C(4)-C(3)-H(3A)	120.3
C(12')-H(12D)	0.9600	C(5)-C(4)-C(3)	122.1(4)
C(12')-H(12E)	0.9600	C(5)-C(4)-N(1)	118.7(4)
C(12')-H(12F)	0.9600	C(3)-C(4)-N(1)	119.1(4)
C(11')-C(7')	1.48(2)	C(4)-C(5)-C(6)	116.9(4)
C(11')-H(11D)	0.9600	C(4)-C(5)-B(1)	119.1(4)
C(11')-H(11E)	0.9600	C(6)-C(5)-B(1)	123.9(4)
C(11')-H(11F)	0.9600	C(1)-C(6)-C(5)	121.3(4)
C(7')-C(8')	1.530(18)	C(1)-C(6)-H(6A)	119.4
C(8')-C(9')	1.52(2)	C(5)-C(6)-H(6A)	119.4
C(8')-C(10')	1.548(19)	C(12)-C(7)-O(2)	111.9(8)
C(9')-H(9'A)	0.9600	C(12)-C(7)-C(11)	109.7(13)
C(9')-H(9'B)	0.9600	O(2)-C(7)-C(11)	105.3(13)
C(9')-H(9'C)	0.9600	C(12)-C(7)-C(8)	113.8(13)
C(10')-H(10D)	0.9600	O(2)-C(7)-C(8)	101.6(8)
C(10')-H(10E)	0.9600	C(11)-C(7)-C(8)	114.0(12)
C(10')-H(10F)	0.9600	C(8)-C(10)-H(10A)	109.5
		C(8)-C(10)-H(10B)	109.5
O(2)-B(1)-O(3)	105.8(4)	H(10A)-C(10)-H(10B)	109.5
O(2)-B(1)-O(1)	107.3(4)	C(8)-C(10)-H(10C)	109.5
O(3)-B(1)-O(1)	105.4(4)	H(10A)-C(10)-H(10C)	109.5
O(2)-B(1)-C(5)	114.5(4)	H(10B)-C(10)-H(10C)	109.5
O(3)-B(1)-C(5)	117.6(4)	O(3)-C(8)-C(10)	114.9(11)
O(1)-B(1)-C(5)	105.5(4)	O(3)-C(8)-C(9)	106.8(10)
O(6)-B(2)-O(5)	106.9(4)	C(10)-C(8)-C(9)	110.7(12)
O(6)-B(2)-O(4)	105.8(4)	O(3)-C(8)-C(7)	97.1(9)
O(5)-B(2)-O(4)	107.5(4)	C(10)-C(8)-C(7)	114.0(11)
O(6)-B(2)-C(25)	117.8(4)	C(9)-C(8)-C(7)	112.5(13)
O(5)-B(2)-C(25)	113.3(4)	C(8)-C(9)-H(9A)	109.5
O(4)-B(2)-C(25)	104.8(3)	C(8)-C(9)-H(9B)	109.5
C(6)-C(1)-C(2)	121.2(4)	H(9A)-C(9)-H(9B)	109.5

C(8)-C(9)-H(9C)	109.5	C(21)-C(22)-H(22A)	120.9
H(9A)-C(9)-H(9C)	109.5	C(24)-C(23)-C(22)	119.8(4)
H(9B)-C(9)-H(9C)	109.5	C(24)-C(23)-H(23A)	120.1
O(1)-C(15)-N(1)	121.1(4)	C(22)-C(23)-H(23A)	120.1
O(1)-C(15)-C(16)	117.0(4)	C(23)-C(24)-C(25)	122.4(4)
N(1)-C(15)-C(16)	121.9(4)	C(23)-C(24)-N(2)	119.5(4)
C(17)-C(16)-C(18)	112.0(5)	C(25)-C(24)-N(2)	118.0(4)
C(17)-C(16)-C(15)	112.0(4)	C(24)-C(25)-C(20)	116.7(4)
C(18)-C(16)-C(15)	107.0(4)	C(24)-C(25)-B(2)	120.1(4)
C(17)-C(16)-C(19)	108.2(5)	C(20)-C(25)-B(2)	123.1(4)
C(18)-C(16)-C(19)	108.4(5)	O(4)-C(27)-N(2)	122.2(4)
C(15)-C(16)-C(19)	109.2(4)	O(4)-C(27)-C(28)	115.8(4)
C(16)-C(17)-H(17A)	109.5	N(2)-C(27)-C(28)	122.0(4)
C(16)-C(17)-H(17B)	109.5	C(30)-C(28)-C(27)	107.8(5)
H(17A)-C(17)-H(17B)	109.5	C(30)-C(28)-C(29)	111.2(6)
C(16)-C(17)-H(17C)	109.5	C(27)-C(28)-C(29)	111.5(5)
H(17A)-C(17)-H(17C)	109.5	C(30)-C(28)-C(31)	110.5(7)
H(17B)-C(17)-H(17C)	109.5	C(27)-C(28)-C(31)	108.8(5)
C(16)-C(18)-H(18A)	109.5	C(29)-C(28)-C(31)	107.0(6)
C(16)-C(18)-H(18B)	109.5	C(28)-C(29)-H(29A)	109.5
H(18A)-C(18)-H(18B)	109.5	C(28)-C(29)-H(29B)	109.5
C(16)-C(18)-H(18C)	109.5	H(29A)-C(29)-H(29B)	109.5
H(18A)-C(18)-H(18C)	109.5	C(28)-C(29)-H(29C)	109.5
H(18B)-C(18)-H(18C)	109.5	H(29A)-C(29)-H(29C)	109.5
C(16)-C(19)-H(19A)	109.5	H(29B)-C(29)-H(29C)	109.5
C(16)-C(19)-H(19B)	109.5	C(28)-C(30)-H(30A)	109.5
H(19A)-C(19)-H(19B)	109.5	C(28)-C(30)-H(30B)	109.5
C(16)-C(19)-H(19C)	109.5	H(30A)-C(30)-H(30B)	109.5
H(19A)-C(19)-H(19C)	109.5	C(28)-C(30)-H(30C)	109.5
H(19B)-C(19)-H(19C)	109.5	H(30A)-C(30)-H(30C)	109.5
C(21)-C(20)-C(25)	121.3(4)	H(30B)-C(30)-H(30C)	109.5
C(21)-C(20)-H(20A)	119.4	C(28)-C(31)-H(31A)	109.5
C(25)-C(20)-H(20A)	119.4	C(28)-C(31)-H(31B)	109.5
C(20)-C(21)-C(22)	121.5(4)	H(31A)-C(31)-H(31B)	109.5
C(20)-C(21)-Cl(2)	119.0(4)	C(28)-C(31)-H(31C)	109.5
C(22)-C(21)-Cl(2)	119.4(4)	H(31A)-C(31)-H(31C)	109.5
C(23)-C(22)-C(21)	118.2(4)	H(31B)-C(31)-H(31C)	109.5
C(23)-C(22)-H(22A)	120.9	C(34)-C(32)-O(5)	112.8(14)

C(34)-C(32)-C(33)	106.4(13)	C(7)-C(11)-H(11C)	109.5
O(5)-C(32)-C(33)	111.4(6)	H(11A)-C(11)-H(11C)	109.5
C(34)-C(32)-C(35)	114.1(15)	H(11B)-C(11)-H(11C)	109.5
O(5)-C(32)-C(35)	98.8(6)	C(7)-C(12)-H(12A)	109.5
C(33)-C(32)-C(35)	113.4(7)	C(7)-C(12)-H(12B)	109.5
C(32)-C(33)-H(33A)	109.5	H(12A)-C(12)-H(12B)	109.5
C(32)-C(33)-H(33B)	109.5	C(7)-C(12)-H(12C)	109.5
H(33A)-C(33)-H(33B)	109.5	H(12A)-C(12)-H(12C)	109.5
C(32)-C(33)-H(33C)	109.5	H(12B)-C(12)-H(12C)	109.5
H(33A)-C(33)-H(33C)	109.5	C(35')-C(32')-C(33')	111(2)
H(33B)-C(33)-H(33C)	109.5	C(35')-C(32')-O(5)	102.7(14)
C(32)-C(34)-H(34A)	109.5	C(33')-C(32')-O(5)	114.8(12)
C(32)-C(34)-H(34B)	109.5	C(35')-C(32')-C(34')	134(2)
H(34A)-C(34)-H(34B)	109.5	C(33')-C(32')-C(34')	95.9(18)
C(32)-C(34)-H(34C)	109.5	O(5)-C(32')-C(34')	97(2)
H(34A)-C(34)-H(34C)	109.5	C(32')-C(33')-H(33D)	109.5
H(34B)-C(34)-H(34C)	109.5	C(32')-C(33')-H(33E)	109.5
O(6)-C(35)-C(36)	109.2(7)	H(33D)-C(33')-H(33E)	109.5
O(6)-C(35)-C(37)	106.7(8)	C(32')-C(33')-H(33F)	109.5
C(36)-C(35)-C(37)	109.5(7)	H(33D)-C(33')-H(33F)	109.5
O(6)-C(35)-C(32)	103.0(6)	H(33E)-C(33')-H(33F)	109.5
C(36)-C(35)-C(32)	112.5(9)	C(32')-C(34')-H(34D)	109.5
C(37)-C(35)-C(32)	115.4(8)	C(32')-C(34')-H(34E)	109.5
C(35)-C(36)-H(36A)	109.5	H(34D)-C(34')-H(34E)	109.5
C(35)-C(36)-H(36B)	109.5	C(32')-C(34')-H(34F)	109.5
H(36A)-C(36)-H(36B)	109.5	H(34D)-C(34')-H(34F)	109.5
C(35)-C(36)-H(36C)	109.5	H(34E)-C(34')-H(34F)	109.5
H(36A)-C(36)-H(36C)	109.5	O(6)-C(35')-C(37')	108.2(17)
H(36B)-C(36)-H(36C)	109.5	O(6)-C(35')-C(32')	96.9(14)
C(35)-C(37)-H(37A)	109.5	C(37')-C(35')-C(32')	114(2)
C(35)-C(37)-H(37B)	109.5	O(6)-C(35')-C(36')	112.2(18)
H(37A)-C(37)-H(37B)	109.5	C(37')-C(35')-C(36')	111.8(19)
C(35)-C(37)-H(37C)	109.5	C(32')-C(35')-C(36')	113.2(17)
H(37A)-C(37)-H(37C)	109.5	C(35')-C(36')-H(36D)	109.5
H(37B)-C(37)-H(37C)	109.5	C(35')-C(36')-H(36E)	109.5
C(7)-C(11)-H(11A)	109.5	H(36D)-C(36')-H(36E)	109.5
C(7)-C(11)-H(11B)	109.5	C(35')-C(36')-H(36F)	109.5
H(11A)-C(11)-H(11B)	109.5	H(36D)-C(36')-H(36F)	109.5

H(36E)-C(36')-H(36F)	109.5	C(7')-C(11')-H(11D)	109.5
C(35')-C(37')-H(37D)	109.5	C(7')-C(11')-H(11E)	109.5
C(35')-C(37')-H(37E)	109.5	H(11D)-C(11')-H(11E)	109.5
H(37D)-C(37')-H(37E)	109.5	C(7')-C(11')-H(11F)	109.5
C(35')-C(37')-H(37F)	109.5	H(11D)-C(11')-H(11F)	109.5
H(37D)-C(37')-H(37F)	109.5	H(11E)-C(11')-H(11F)	109.5
H(37E)-C(37')-H(37F)	109.5	O(2)-C(7')-C(11')	108.1(10)
C(15)-N(1)-C(4)	123.9(4)	O(2)-C(7')-C(12')	113.3(9)
C(15)-N(1)-H(1A)	118.1	C(11')-C(7')-C(12')	109.8(13)
C(4)-N(1)-H(1A)	118.1	O(2)-C(7')-C(8')	97.2(9)
C(27)-N(2)-C(24)	123.5(4)	C(11')-C(7')-C(8')	116.0(14)
C(27)-N(2)-H(2B)	118.3	C(12')-C(7')-C(8')	112.1(10)
C(24)-N(2)-H(2B)	118.3	C(9')-C(8')-C(10')	109.7(11)
C(15)-O(1)-B(1)	124.2(4)	C(9')-C(8')-C(7')	115.2(12)
C(7')-O(2)-B(1)	110.8(5)	C(10')-C(8')-C(7')	111.1(14)
B(1)-O(2)-C(7)	103.3(5)	C(9')-C(8')-O(3)	107.0(11)
C(8)-O(3)-B(1)	110.5(6)	C(10')-C(8')-O(3)	109.4(9)
B(1)-O(3)-C(8')	104.6(6)	C(7')-C(8')-O(3)	104.2(8)
C(27)-O(4)-B(2)	123.8(4)	C(8')-C(9')-H(9'A)	109.5
C(32)-O(5)-B(2)	108.7(4)	C(8')-C(9')-H(9'B)	109.5
B(2)-O(5)-C(32')	99.5(7)	H(9'A)-C(9')-H(9'B)	109.5
C(35')-O(6)-B(2)	112.4(10)	C(8')-C(9')-H(9'C)	109.5
B(2)-O(6)-C(35)	106.2(4)	H(9'A)-C(9')-H(9'C)	109.5
H(7C)-O(7)-H(7D)	109.2	H(9'B)-C(9')-H(9'C)	109.5
H(8D)-O(8)-H(8A)	109.5	C(8')-C(10')-H(10D)	109.5
C(7')-C(12')-H(12D)	109.5	C(8')-C(10')-H(10E)	109.5
C(7')-C(12')-H(12E)	109.5	H(10D)-C(10')-H(10E)	109.5
H(12D)-C(12')-H(12E)	109.5	C(8')-C(10')-H(10F)	109.5
C(7')-C(12')-H(12F)	109.5	H(10D)-C(10')-H(10F)	109.5
H(12D)-C(12')-H(12F)	109.5	H(10E)-C(10')-H(10F)	109.5
H(12E)-C(12')-H(12F)	109.5		



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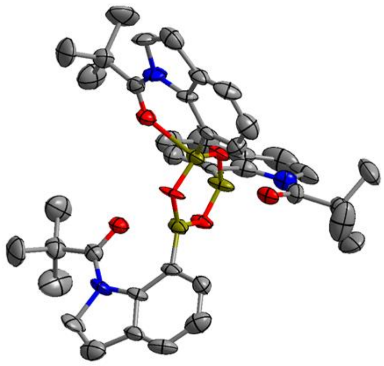

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B(1)-O(2)#1	1.393(13)	C(5)-N(1)	1.331(17)
B(1)-O(2)	1.393(13)	C(6)-C(7)	1.30(2)
B(1)-C(24)	1.58(3)	C(6)-N(1)	1.458(17)
B(1)-O(4)	1.77(3)	C(6)-H(6)	0.9500
B(2)-O(2)	1.362(18)	C(7)-C(8)	1.47(2)
B(2)-O(1)	1.372(16)	C(7)-H(7)	0.9500
B(2)-C(12)	1.56(2)	C(8)-C(9)	1.34(2)
B(3)-O(7)	1.369(17)	C(8)-C(13)	1.450(19)
B(3)-O(6)	1.408(15)	C(9)-C(10)	1.41(2)
B(3)-C(37)	1.561(19)	C(9)-H(9)	0.9500
B(4)-O(7)#1	1.409(13)	C(10)-C(11)	1.37(2)
B(4)-O(7)	1.409(13)	C(10)-H(10)	0.9500
B(4)-O(8)	1.57(3)	C(11)-C(12)	1.405(19)
B(4)-C(49)	1.61(3)	C(11)-H(11)	0.9500
C(1)-C(4)	1.57(2)	C(12)-C(13)	1.395(18)
C(1)-H(1A)	0.9800	C(13)-N(1)	1.397(18)
C(1)-H(1B)	0.9800	C(14)-C(15)	1.54(3)
C(1)-H(1C)	0.9800	C(14)-H(14A)	0.9800
C(2)-C(4)	1.59(2)	C(14)-H(14B)	0.9800
C(2)-H(2A)	0.9800	C(14)-H(14C)	0.9800
C(2)-H(2B)	0.9800	C(14)-H(14A)#1	0.9800
C(2)-H(2C)	0.9800	C(14)-H(14B)#1	0.9800
C(3)-C(4)	1.53(2)	C(14)-H(14C)#1	0.9800
C(3)-H(3A)	0.9800	C(15)-C(17)	1.54(3)
C(3)-H(3B)	0.9800	C(15)-C(16)	1.57(2)
C(3)-H(3C)	0.9800	C(15)-C(16)#1	1.57(2)
C(4)-C(5)	1.48(2)	C(16)-H(16A)	0.9800
C(5)-O(3)	1.259(16)	C(16)-H(16B)	0.9800

C(16)-H(16C)	0.9800	C(33)-C(34)	1.28(2)
C(17)-O(4)	1.29(2)	C(33)-C(38)	1.435(18)
C(17)-N(2)	1.32(3)	C(34)-C(35)	1.40(2)
C(18)-C(19)	1.35(4)	C(34)-H(34)	0.9500
C(18)-N(2)	1.36(3)	C(35)-C(36)	1.39(2)
C(18)-H(18)	0.9500	C(35)-H(35)	0.9500
C(19)-C(20)	1.44(3)	C(36)-C(37)	1.387(19)
C(19)-H(19)	0.9500	C(36)-H(36)	0.9500
C(20)-C(21)	1.35(3)	C(37)-C(38)	1.391(17)
C(20)-C(25)	1.42(3)	C(38)-N(3)	1.423(17)
C(21)-C(22)	1.43(4)	C(39)-C(41)	1.53(3)
C(21)-H(21)	0.9500	C(39)-H(39A)	0.9800
C(22)-C(23)	1.46(3)	C(39)-H(39B)	0.9800
C(22)-H(22)	0.9500	C(39)-H(39C)	0.9800
C(23)-C(24)	1.40(3)	C(39)-H(39A)#1	1.0(4)
C(23)-H(23)	0.9500	C(39)-H(39B)#1	0.98(14)
C(24)-C(25)	1.36(3)	C(39)-H(39C)#1	1.0(2)
C(25)-N(2)	1.44(3)	C(40)-C(41)	1.55(2)
C(26)-C(27)	1.55(2)	C(40)-H(40A)	0.9800
C(26)-H(26A)	0.9800	C(40)-H(40B)	0.9800
C(26)-H(26B)	0.9800	C(40)-H(40C)	0.9800
C(26)-H(26C)	0.9800	C(41)-C(42)	1.54(3)
C(27)-C(28)	1.51(2)	C(42)-N(4)	1.29(3)
C(27)-C(30)	1.53(2)	C(42)-O(8)	1.32(2)
C(27)-C(29)	1.57(2)	C(43)-C(44)	1.23(4)
C(28)-H(28A)	0.9800	C(43)-N(4)	1.44(3)
C(28)-H(28B)	0.9800	C(43)-H(43)	0.9500
C(28)-H(28C)	0.9800	C(44)-C(45)	1.37(4)
C(29)-H(29A)	0.9800	C(44)-H(44)	0.9500
C(29)-H(29B)	0.9800	C(45)-C(46)	1.40(4)
C(29)-H(29C)	0.9800	C(45)-C(50)	1.46(3)
C(30)-O(5)	1.224(15)	C(46)-C(47)	1.46(4)
C(30)-N(3)	1.349(17)	C(46)-H(46)	0.9500
C(31)-C(32)	1.30(2)	C(47)-C(48)	1.41(3)
C(31)-N(3)	1.520(18)	C(47)-H(47)	0.9500
C(31)-H(31)	0.9500	C(48)-C(49)	1.40(3)
C(32)-C(33)	1.53(2)	C(48)-H(48)	0.9500
C(32)-H(32)	0.9500	C(49)-C(50)	1.40(3)

C(50)-N(4)	1.42(3)	C(5)-C(4)-C(3)	111.4(14)
		C(5)-C(4)-C(1)	111.8(14)
O(2)#1-B(1)-O(2)	119.9(17)	C(3)-C(4)-C(1)	108.5(15)
O(2)#1-B(1)-C(24)	117.4(9)	C(5)-C(4)-C(2)	107.0(14)
O(2)-B(1)-C(24)	117.4(9)	C(3)-C(4)-C(2)	102.1(15)
O(2)#1-B(1)-O(4)	97.7(11)	C(1)-C(4)-C(2)	115.6(15)
O(2)-B(1)-O(4)	97.7(11)	O(3)-C(5)-N(1)	117.0(12)
C(24)-B(1)-O(4)	98.0(15)	O(3)-C(5)-C(4)	118.4(14)
O(2)-B(2)-O(1)	118.6(13)	N(1)-C(5)-C(4)	124.6(13)
O(2)-B(2)-C(12)	118.4(12)	C(7)-C(6)-N(1)	112.7(15)
O(1)-B(2)-C(12)	117.9(13)	C(7)-C(6)-H(6)	123.7
O(7)-B(3)-O(6)	119.5(12)	N(1)-C(6)-H(6)	123.7
O(7)-B(3)-C(37)	120.3(12)	C(6)-C(7)-C(8)	107.9(14)
O(6)-B(3)-C(37)	116.5(13)	C(6)-C(7)-H(7)	126.1
O(7)#1-B(4)-O(7)	117.1(16)	C(8)-C(7)-H(7)	126.1
O(7)#1-B(4)-O(8)	103.8(13)	C(9)-C(8)-C(13)	121.4(14)
O(7)-B(4)-O(8)	103.8(13)	C(9)-C(8)-C(7)	133.0(16)
O(7)#1-B(4)-C(49)	113.4(12)	C(13)-C(8)-C(7)	105.6(14)
O(7)-B(4)-C(49)	113.4(12)	C(8)-C(9)-C(10)	117.7(14)
O(8)-B(4)-C(49)	103.0(15)	C(8)-C(9)-H(9)	121.1
C(4)-C(1)-H(1A)	109.5	C(10)-C(9)-H(9)	121.1
C(4)-C(1)-H(1B)	109.5	C(11)-C(10)-C(9)	120.7(15)
H(1A)-C(1)-H(1B)	109.5	C(11)-C(10)-H(10)	119.7
C(4)-C(1)-H(1C)	109.5	C(9)-C(10)-H(10)	119.7
H(1A)-C(1)-H(1C)	109.5	C(10)-C(11)-C(12)	124.2(14)
H(1B)-C(1)-H(1C)	109.5	C(10)-C(11)-H(11)	117.9
C(4)-C(2)-H(2A)	109.5	C(12)-C(11)-H(11)	117.9
C(4)-C(2)-H(2B)	109.5	C(13)-C(12)-C(11)	114.4(13)
H(2A)-C(2)-H(2B)	109.5	C(13)-C(12)-B(2)	127.0(13)
C(4)-C(2)-H(2C)	109.5	C(11)-C(12)-B(2)	118.6(12)
H(2A)-C(2)-H(2C)	109.5	C(12)-C(13)-N(1)	129.6(12)
H(2B)-C(2)-H(2C)	109.5	C(12)-C(13)-C(8)	121.6(14)
C(4)-C(3)-H(3A)	109.5	N(1)-C(13)-C(8)	108.7(12)
C(4)-C(3)-H(3B)	109.5	C(15)-C(14)-H(14A)	109.5
H(3A)-C(3)-H(3B)	109.5	C(15)-C(14)-H(14B)	109.5
C(4)-C(3)-H(3C)	109.5	H(14A)-C(14)-H(14B)	109.5
H(3A)-C(3)-H(3C)	109.5	C(15)-C(14)-H(14C)	109.5
H(3B)-C(3)-H(3C)	109.5	H(14A)-C(14)-H(14C)	109.5

H(14B)-C(14)-H(14C)	109.5	C(21)-C(20)-C(19)	138(3)
C(15)-C(14)-H(14A)#1	109.47(16)	C(25)-C(20)-C(19)	104(2)
H(14A)-C(14)-H(14A)#1	138.9	C(20)-C(21)-C(22)	119(2)
H(14B)-C(14)-H(14A)#1	43.8	C(20)-C(21)-H(21)	120.7
H(14C)-C(14)-H(14A)#1	68.5	C(22)-C(21)-H(21)	120.7
C(15)-C(14)-H(14B)#1	109.5(11)	C(21)-C(22)-C(23)	121(2)
H(14A)-C(14)-H(14B)#1	43.8	C(21)-C(22)-H(22)	119.3
H(14B)-C(14)-H(14B)#1	68.5	C(23)-C(22)-H(22)	119.3
H(14C)-C(14)-H(14B)#1	138.9	C(24)-C(23)-C(22)	119(2)
H(14A)#1-C(14)-H(14B)#1	109.5	C(24)-C(23)-H(23)	120.4
C(15)-C(14)-H(14C)#1	109.5(12)	C(22)-C(23)-H(23)	120.4
H(14A)-C(14)-H(14C)#1	68.5	C(25)-C(24)-C(23)	115(2)
H(14B)-C(14)-H(14C)#1	138.9	C(25)-C(24)-B(1)	126(2)
H(14C)-C(14)-H(14C)#1	43.8	C(23)-C(24)-B(1)	119.0(18)
H(14A)#1-C(14)-H(14C)#1	109.5	C(24)-C(25)-C(20)	128(2)
H(14B)#1-C(14)-H(14C)#1	109.5	C(24)-C(25)-N(2)	124.5(18)
C(14)-C(15)-C(17)	109.7(19)	C(20)-C(25)-N(2)	107(2)
C(14)-C(15)-C(16)	109.6(14)	C(27)-C(26)-H(26A)	109.5
C(17)-C(15)-C(16)	107.8(14)	C(27)-C(26)-H(26B)	109.5
C(14)-C(15)-C(16)#1	109.6(14)	H(26A)-C(26)-H(26B)	109.5
C(17)-C(15)-C(16)#1	107.8(14)	C(27)-C(26)-H(26C)	109.5
C(16)-C(15)-C(16)#1	112(2)	H(26A)-C(26)-H(26C)	109.5
C(15)-C(16)-H(16A)	109.5	H(26B)-C(26)-H(26C)	109.5
C(15)-C(16)-H(16B)	109.5	C(28)-C(27)-C(30)	108.8(13)
H(16A)-C(16)-H(16B)	109.5	C(28)-C(27)-C(26)	112.7(16)
C(15)-C(16)-H(16C)	109.5	C(30)-C(27)-C(26)	111.7(14)
H(16A)-C(16)-H(16C)	109.5	C(28)-C(27)-C(29)	105.4(14)
H(16B)-C(16)-H(16C)	109.5	C(30)-C(27)-C(29)	108.8(13)
O(4)-C(17)-N(2)	120(2)	C(26)-C(27)-C(29)	109.2(15)
O(4)-C(17)-C(15)	116(2)	C(27)-C(28)-H(28A)	109.5
N(2)-C(17)-C(15)	124(2)	C(27)-C(28)-H(28B)	109.5
C(19)-C(18)-N(2)	108(2)	H(28A)-C(28)-H(28B)	109.5
C(19)-C(18)-H(18)	125.8	C(27)-C(28)-H(28C)	109.5
N(2)-C(18)-H(18)	125.8	H(28A)-C(28)-H(28C)	109.5
C(18)-C(19)-C(20)	111(2)	H(28B)-C(28)-H(28C)	109.5
C(18)-C(19)-H(19)	124.4	C(27)-C(29)-H(29A)	109.5
C(20)-C(19)-H(19)	124.4	C(27)-C(29)-H(29B)	109.5
C(21)-C(20)-C(25)	117(2)	H(29A)-C(29)-H(29B)	109.5

C(27)-C(29)-H(29C)	109.5	H(39B)-C(39)-H(39A)#1	127.3
H(29A)-C(29)-H(29C)	109.5	H(39C)-C(39)-H(39A)#1	22.3
H(29B)-C(29)-H(29C)	109.5	C(41)-C(39)-H(39B)#1	109(3)
O(5)-C(30)-N(3)	118.0(12)	H(39A)-C(39)-H(39B)#1	127.3
O(5)-C(30)-C(27)	120.4(13)	H(39B)-C(39)-H(39B)#1	22.3
N(3)-C(30)-C(27)	121.6(12)	H(39C)-C(39)-H(39B)#1	89.2
C(32)-C(31)-N(3)	109.2(14)	H(39A)#1-C(39)-H(39B)#1	109.5
C(32)-C(31)-H(31)	125.4	C(41)-C(39)-H(39C)#1	109(4)
N(3)-C(31)-H(31)	125.4	H(39A)-C(39)-H(39C)#1	22.3
C(31)-C(32)-C(33)	110.2(14)	H(39B)-C(39)-H(39C)#1	89.2
C(31)-C(32)-H(32)	124.9	H(39C)-C(39)-H(39C)#1	127.2
C(33)-C(32)-H(32)	124.9	H(39A)#1-C(39)-H(39C)#1	109.5
C(34)-C(33)-C(38)	121.6(14)	H(39B)#1-C(39)-H(39C)#1	109.5
C(34)-C(33)-C(32)	133.6(14)	C(41)-C(40)-H(40A)	109.5
C(38)-C(33)-C(32)	104.7(14)	C(41)-C(40)-H(40B)	109.5
C(33)-C(34)-C(35)	119.2(15)	H(40A)-C(40)-H(40B)	109.5
C(33)-C(34)-H(34)	120.4	C(41)-C(40)-H(40C)	109.5
C(35)-C(34)-H(34)	120.4	H(40A)-C(40)-H(40C)	109.5
C(36)-C(35)-C(34)	120.6(16)	H(40B)-C(40)-H(40C)	109.5
C(36)-C(35)-H(35)	119.7	C(39)-C(41)-C(42)	111(2)
C(34)-C(35)-H(35)	119.7	C(39)-C(41)-C(40)	110.3(15)
C(35)-C(36)-C(37)	121.8(14)	C(42)-C(41)-C(40)	109.3(15)
C(35)-C(36)-H(36)	119.1	C(39)-C(41)-C(40)#1	110.3(15)
C(37)-C(36)-H(36)	119.1	C(42)-C(41)-C(40)#1	109.3(15)
C(36)-C(37)-C(38)	115.3(12)	C(40)-C(41)-C(40)#1	106.1(19)
C(36)-C(37)-B(3)	118.0(12)	N(4)-C(42)-O(8)	121.0(19)
C(38)-C(37)-B(3)	126.6(13)	N(4)-C(42)-C(41)	122(2)
C(37)-C(38)-N(3)	129.3(12)	O(8)-C(42)-C(41)	117(2)
C(37)-C(38)-C(33)	121.4(13)	C(44)-C(43)-N(4)	114(3)
N(3)-C(38)-C(33)	109.3(11)	C(44)-C(43)-H(43)	123.0
C(41)-C(39)-H(39A)	109.5	N(4)-C(43)-H(43)	123.0
C(41)-C(39)-H(39B)	109.5	C(43)-C(44)-C(45)	111(3)
H(39A)-C(39)-H(39B)	109.5	C(43)-C(44)-H(44)	124.6
C(41)-C(39)-H(39C)	109.5	C(45)-C(44)-H(44)	124.6
H(39A)-C(39)-H(39C)	109.5	C(44)-C(45)-C(46)	139(3)
H(39B)-C(39)-H(39C)	109.5	C(44)-C(45)-C(50)	106(2)
C(41)-C(39)-H(39A)#1	109(7)	C(46)-C(45)-C(50)	115(3)
H(39A)-C(39)-H(39A)#1	89.2	C(45)-C(46)-C(47)	120(3)

C(45)-C(46)-H(46)	120.1	C(13)-N(1)-C(6)	105.0(12)
C(47)-C(46)-H(46)	120.1	C(17)-N(2)-C(18)	130(2)
C(48)-C(47)-C(46)	122(3)	C(17)-N(2)-C(25)	120.9(18)
C(48)-C(47)-H(47)	119.2	C(18)-N(2)-C(25)	108.9(19)
C(46)-C(47)-H(47)	119.2	C(30)-N(3)-C(38)	124.5(11)
C(49)-C(48)-C(47)	121(2)	C(30)-N(3)-C(31)	129.1(12)
C(49)-C(48)-H(48)	119.7	C(38)-N(3)-C(31)	106.2(11)
C(47)-C(48)-H(48)	119.7	C(42)-N(4)-C(50)	118.6(18)
C(48)-C(49)-C(50)	116(2)	C(42)-N(4)-C(43)	139(2)
C(48)-C(49)-B(4)	125(2)	C(50)-N(4)-C(43)	102.8(19)
C(50)-C(49)-B(4)	118(2)	B(2)#1-O(1)-B(2)	122.8(16)
C(49)-C(50)-N(4)	127.0(19)	B(2)-O(2)-B(1)	118.5(13)
C(49)-C(50)-C(45)	127(2)	C(17)-O(4)-B(1)	130.5(16)
N(4)-C(50)-C(45)	106(2)	B(3)#1-O(6)-B(3)	119.2(16)
C(5)-N(1)-C(13)	125.8(11)	B(3)-O(7)-B(4)	121.8(11)
C(5)-N(1)-C(6)	129.1(13)	C(42)-O(8)-B(4)	132.0(15)

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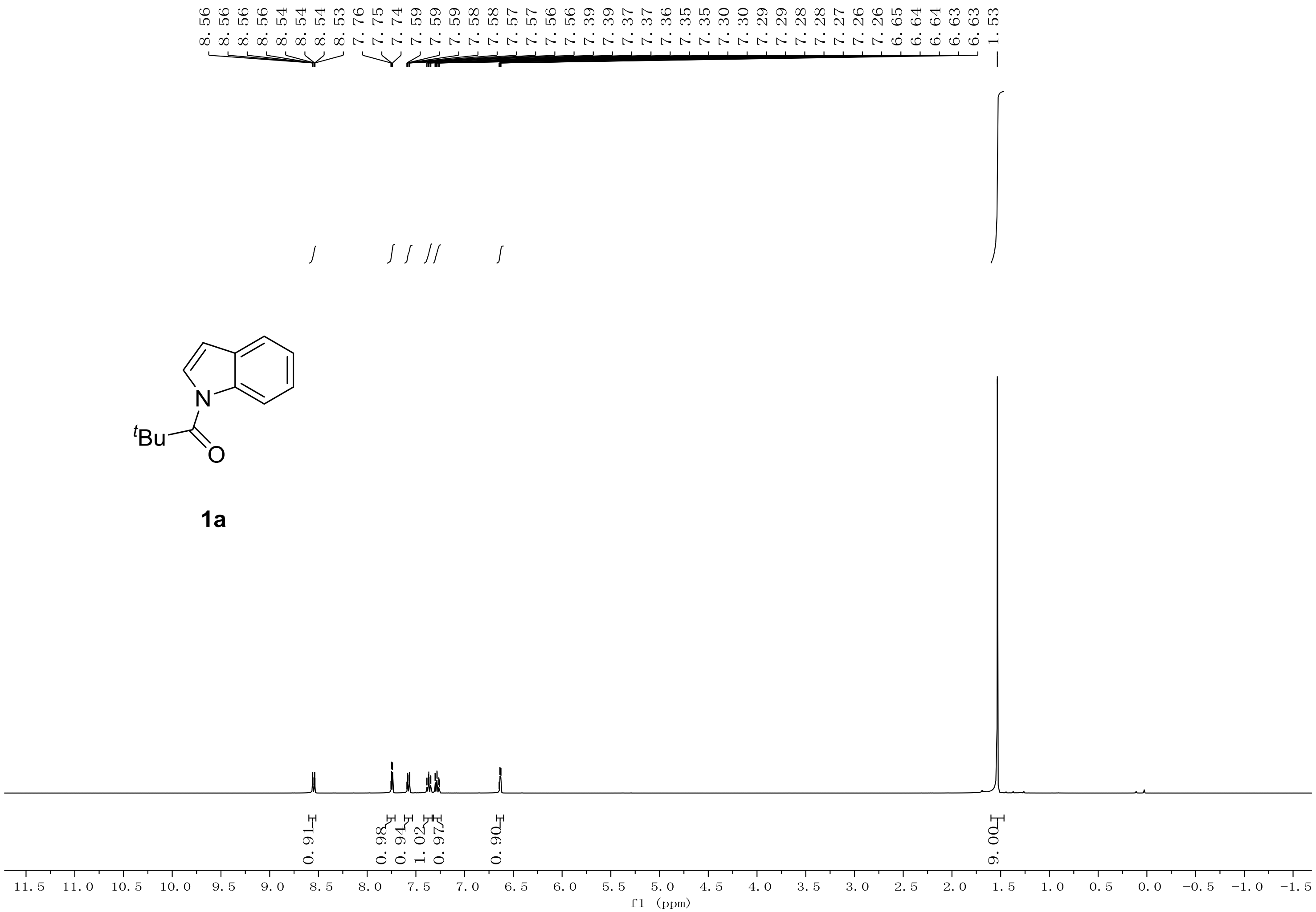

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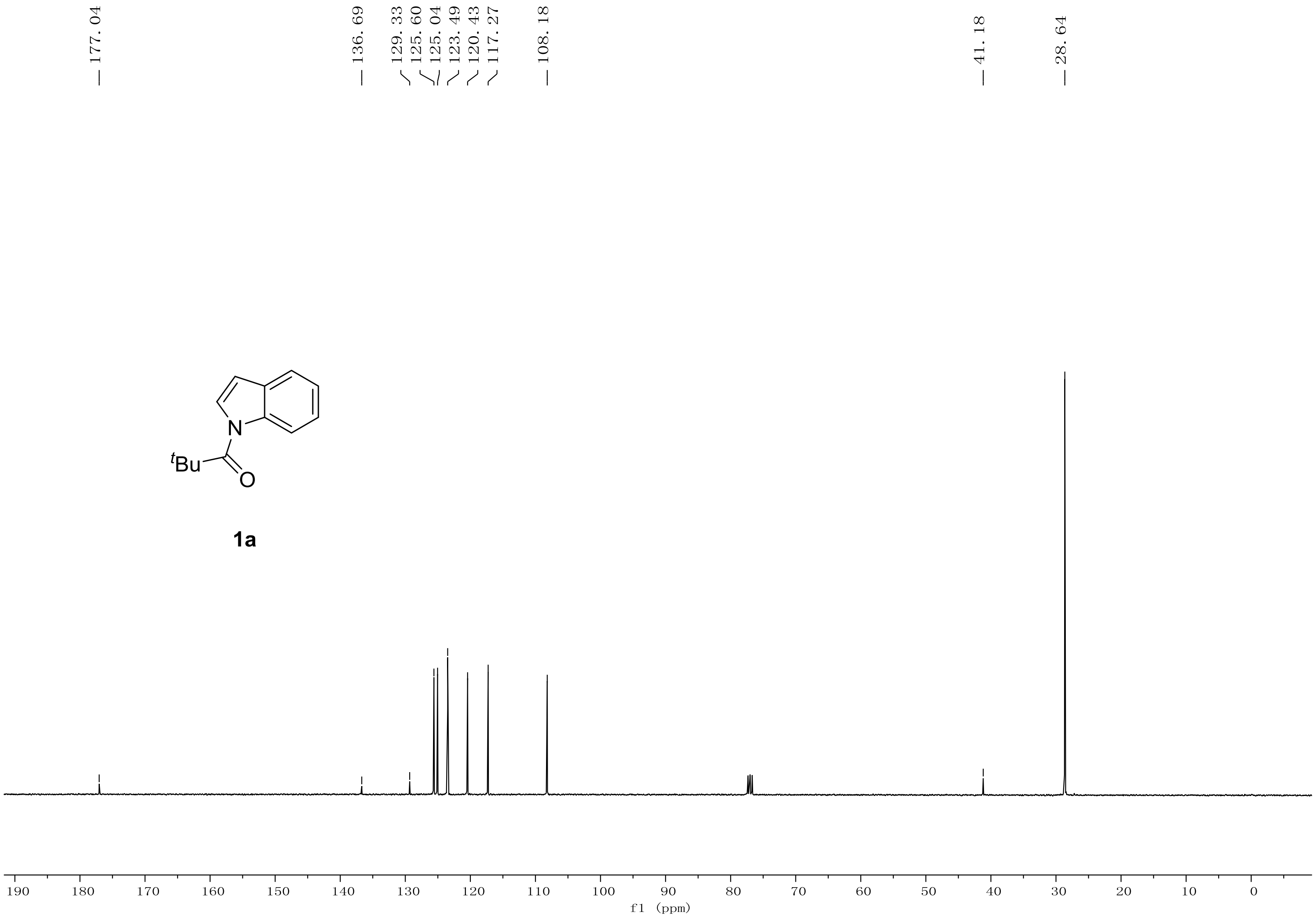
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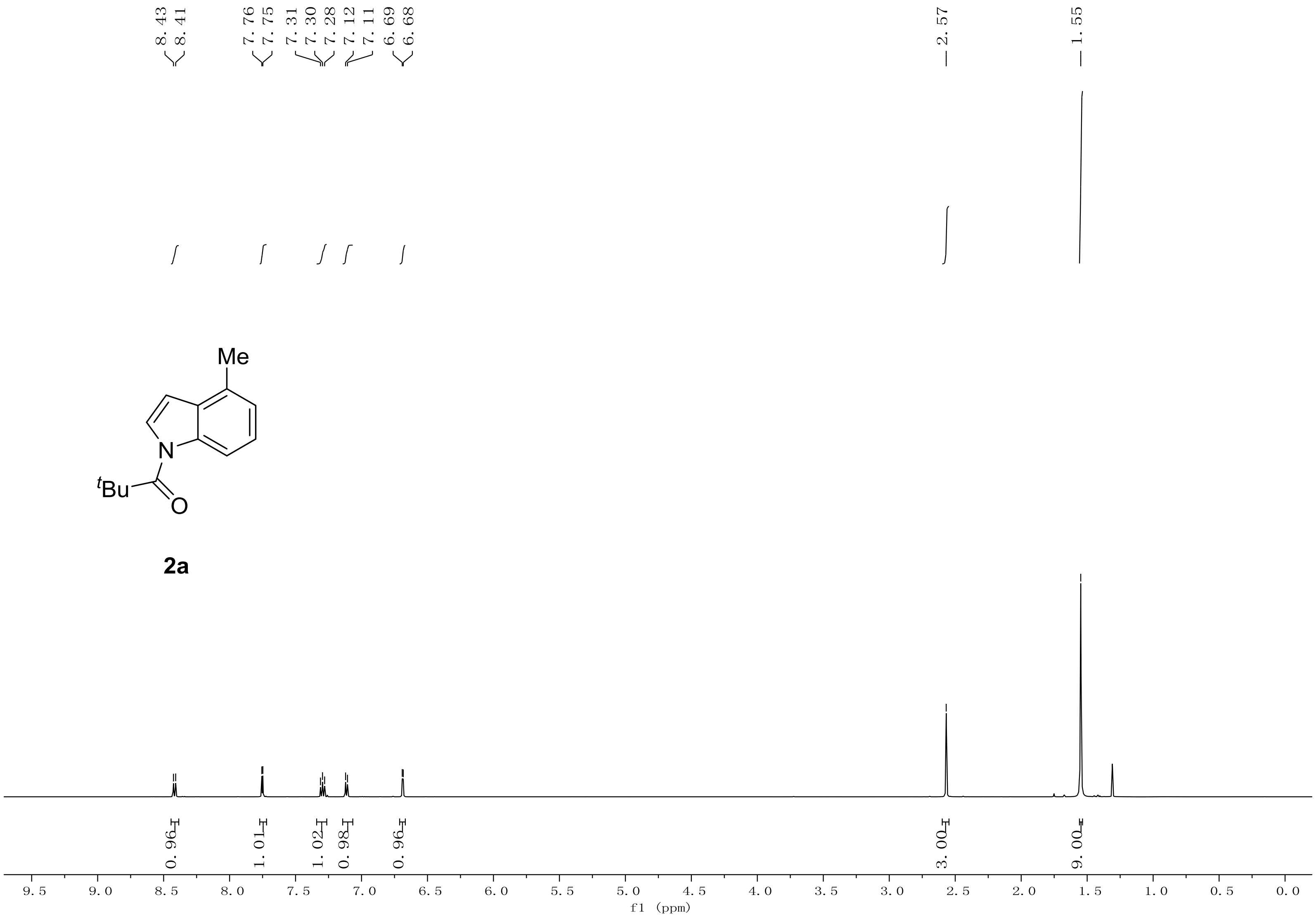
f1 (ppm)
N
tBu
O

1a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6.68
2.57
1.55
0.96
1.01
1.02
0.98
0.96
3.00
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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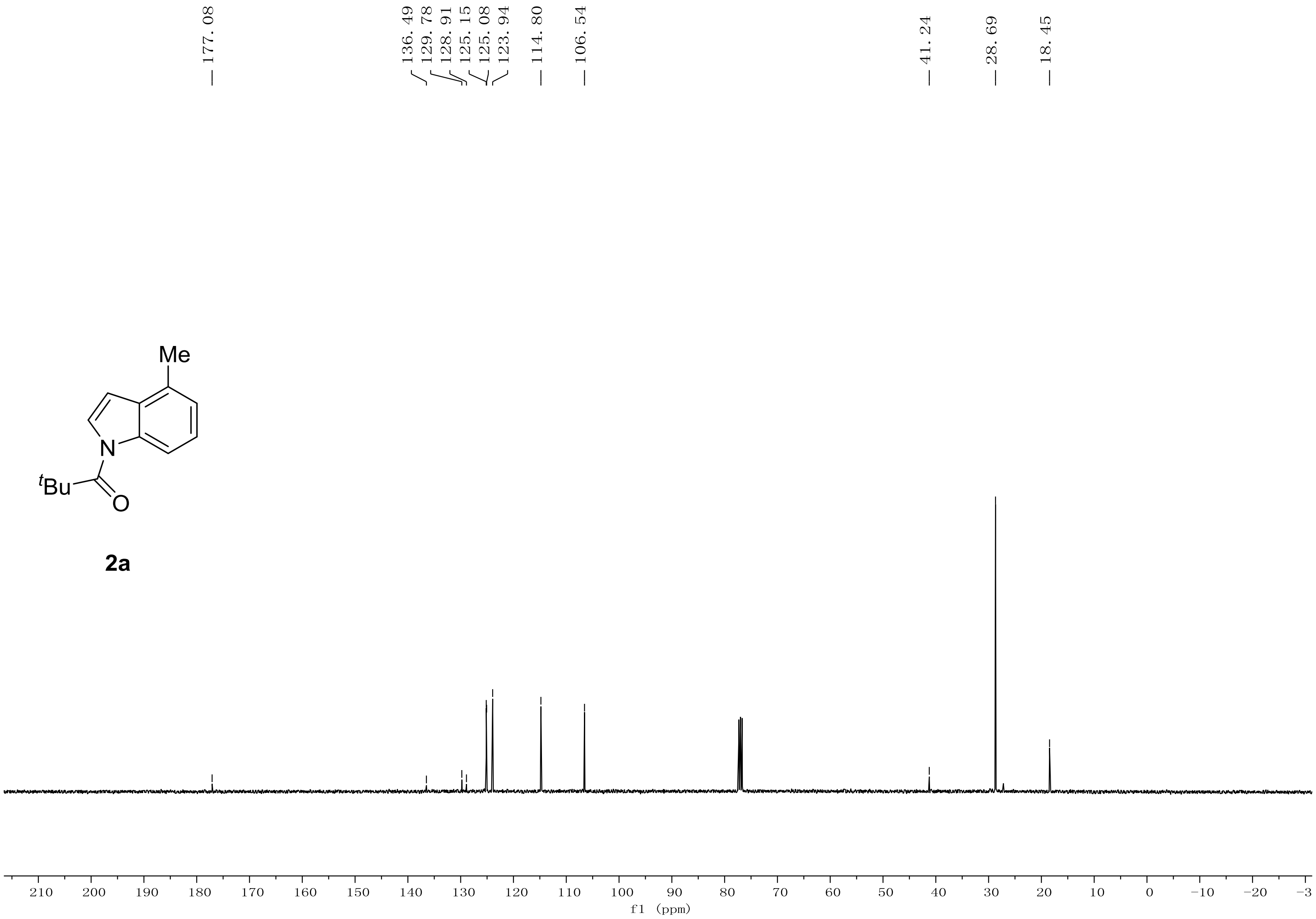
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tBu
O
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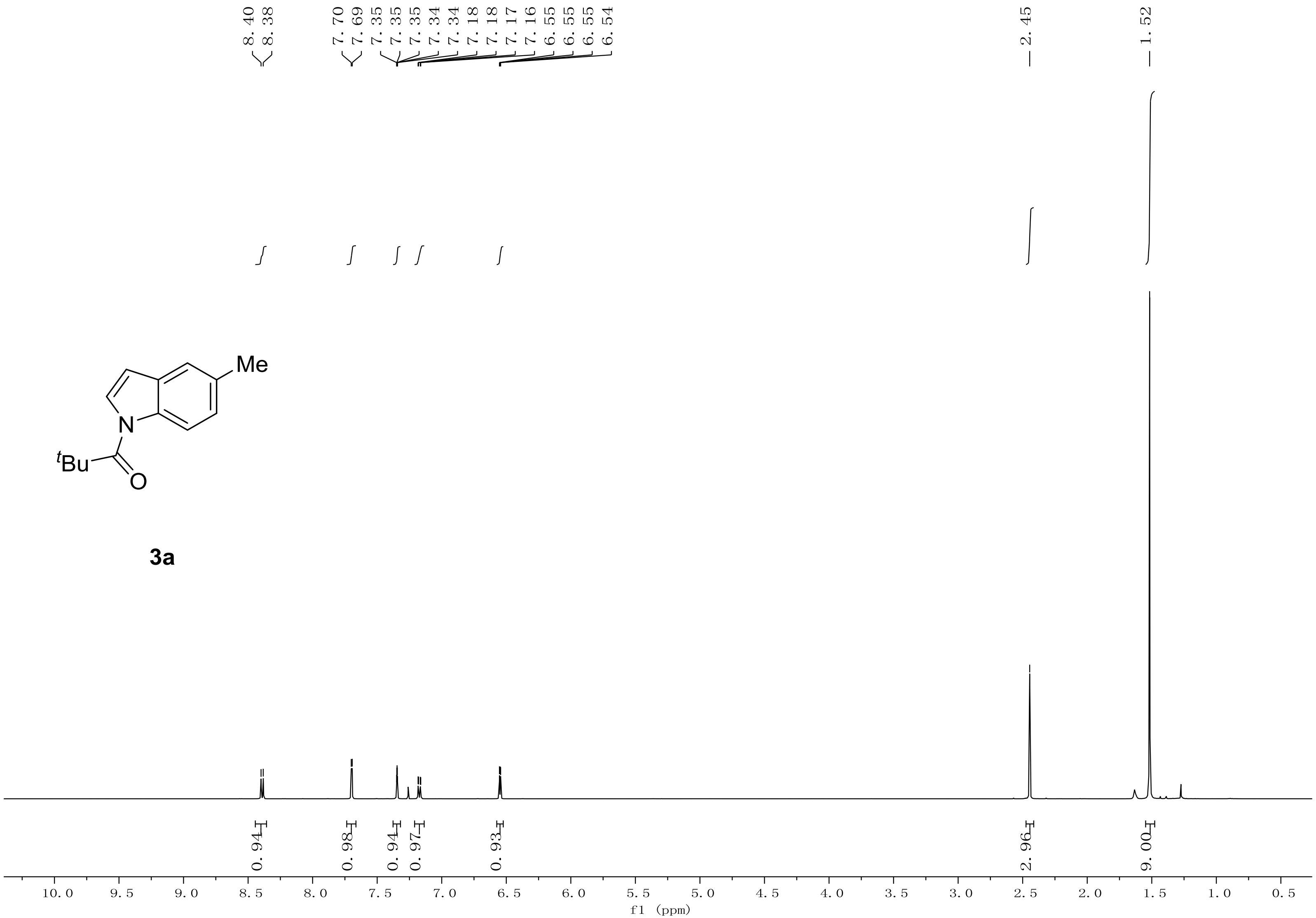
2a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6.55
6.54
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1.52
Me
N
tBu
O
3a
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0.98
0.94
0.97
0.93
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9.00
10.0
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9.0
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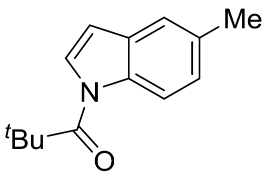

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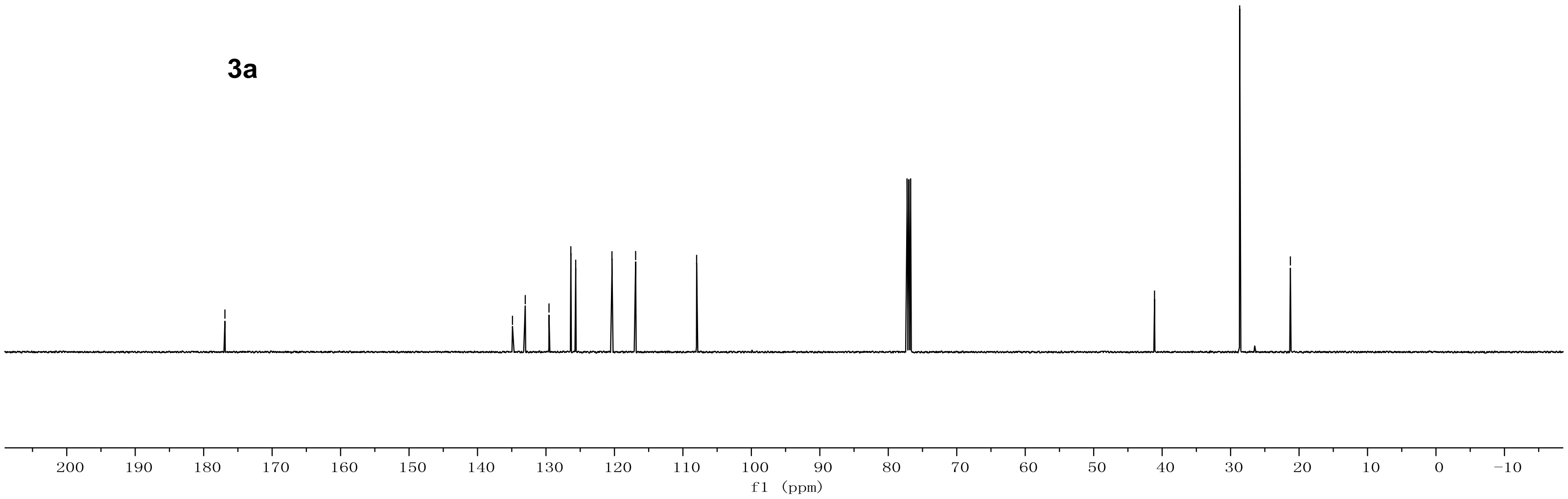
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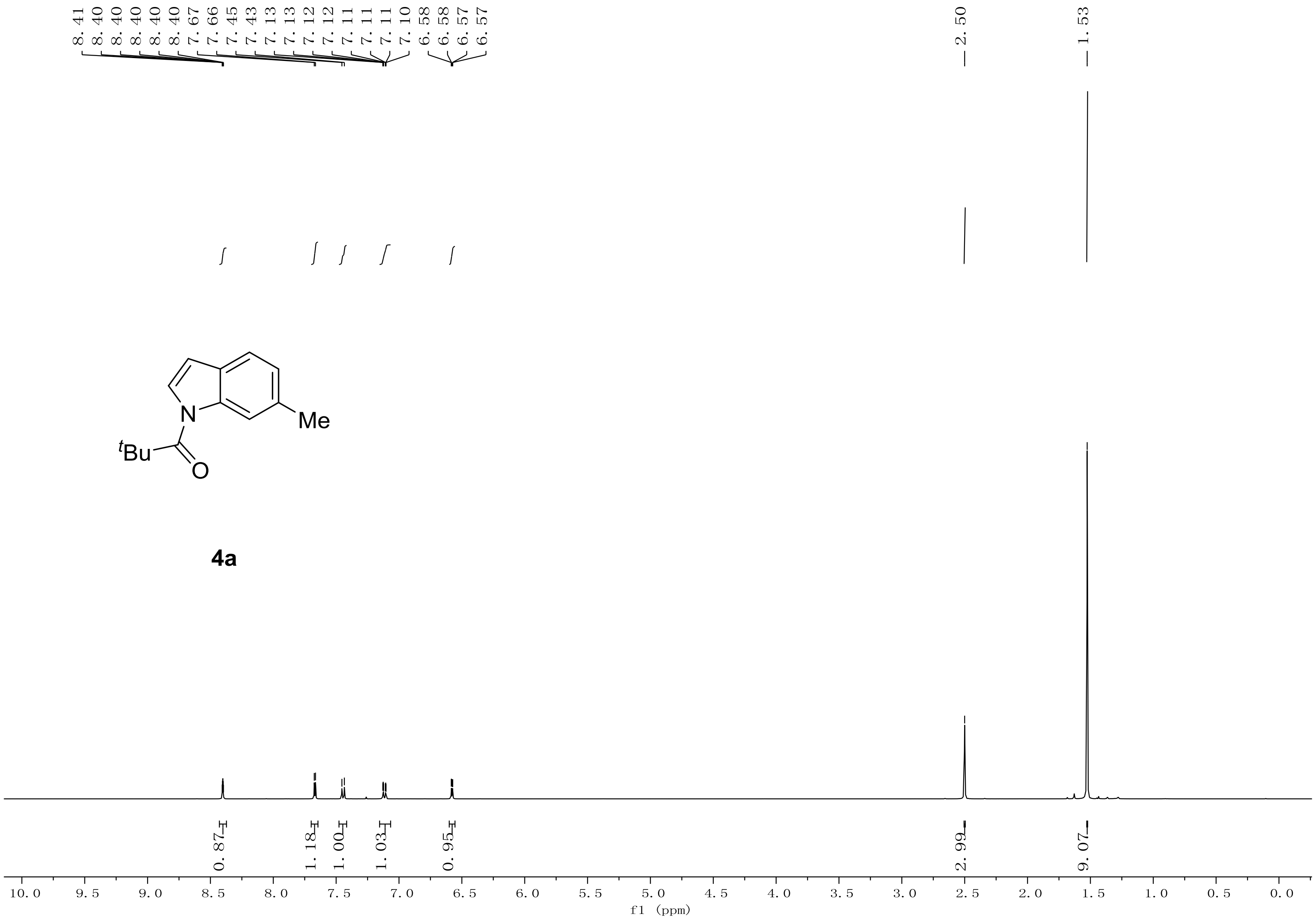
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7.11
7.11
7.10
6.58
6.58
6.57
6.57
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1.53
N
Me
tBu
O
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1.18
1.00
1.03
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2.99
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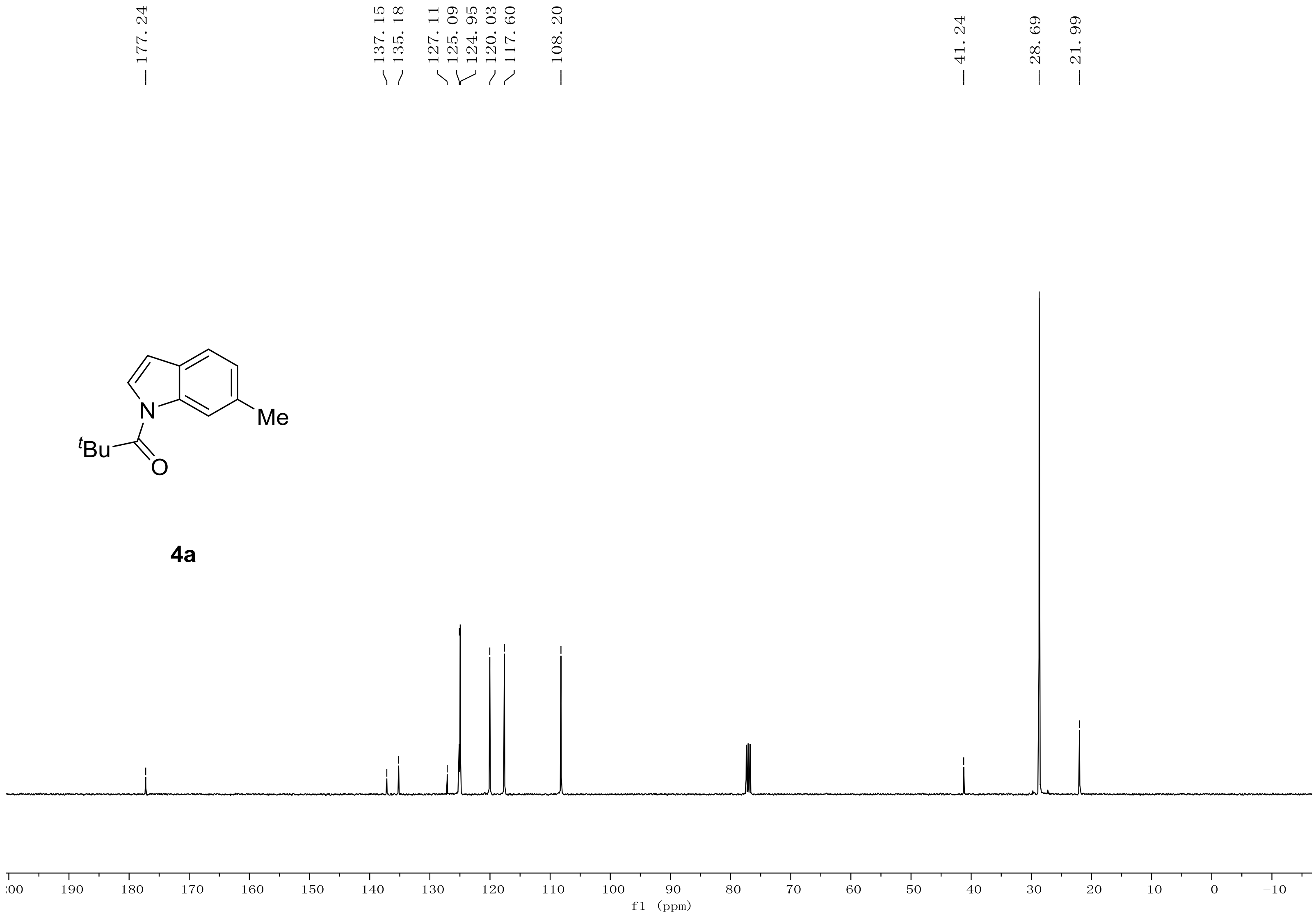
f1 (ppm)

4a



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117.60
108.20
41.24
28.69
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200
190
180
170
160
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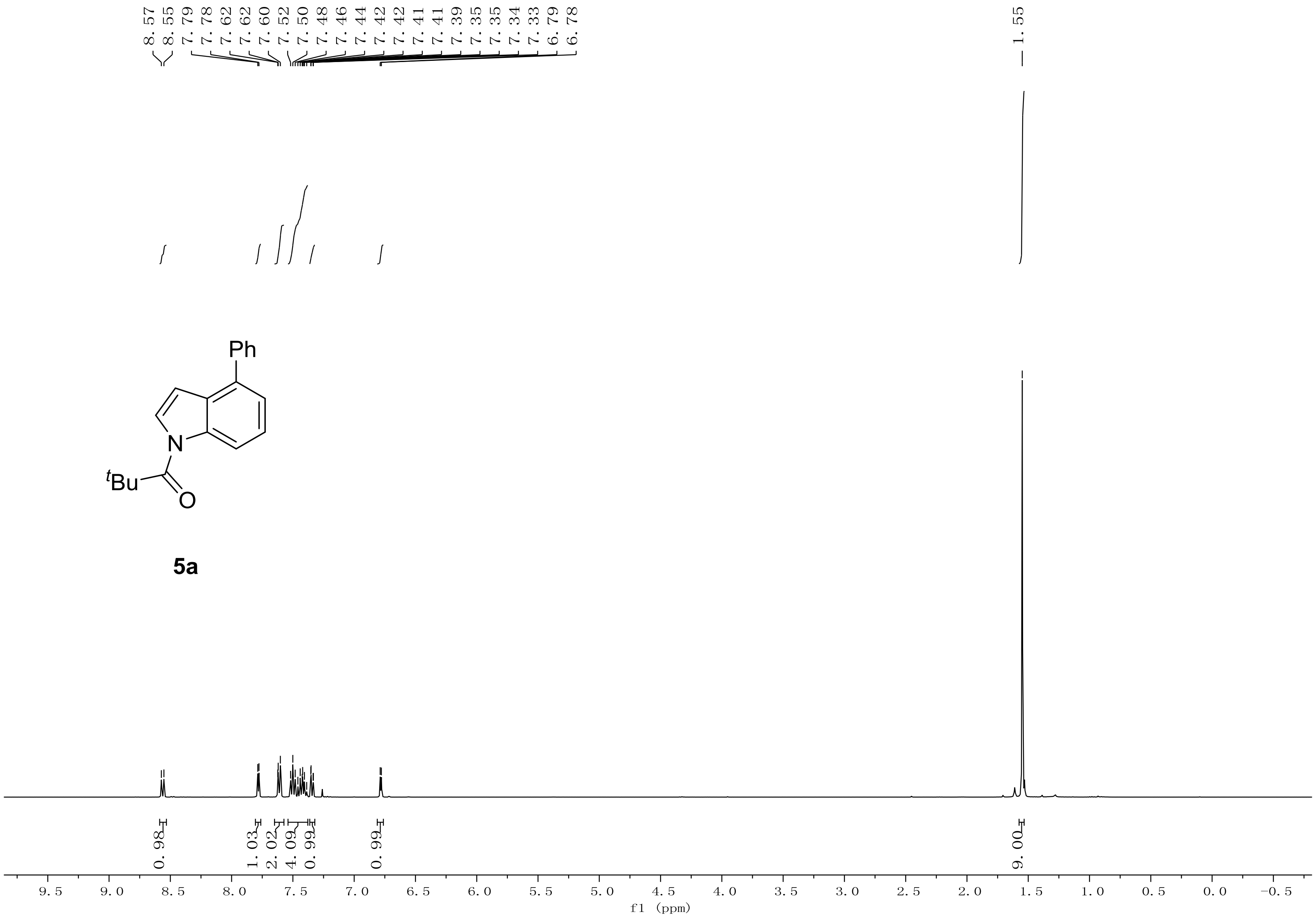
−10
f1 (ppm)

4a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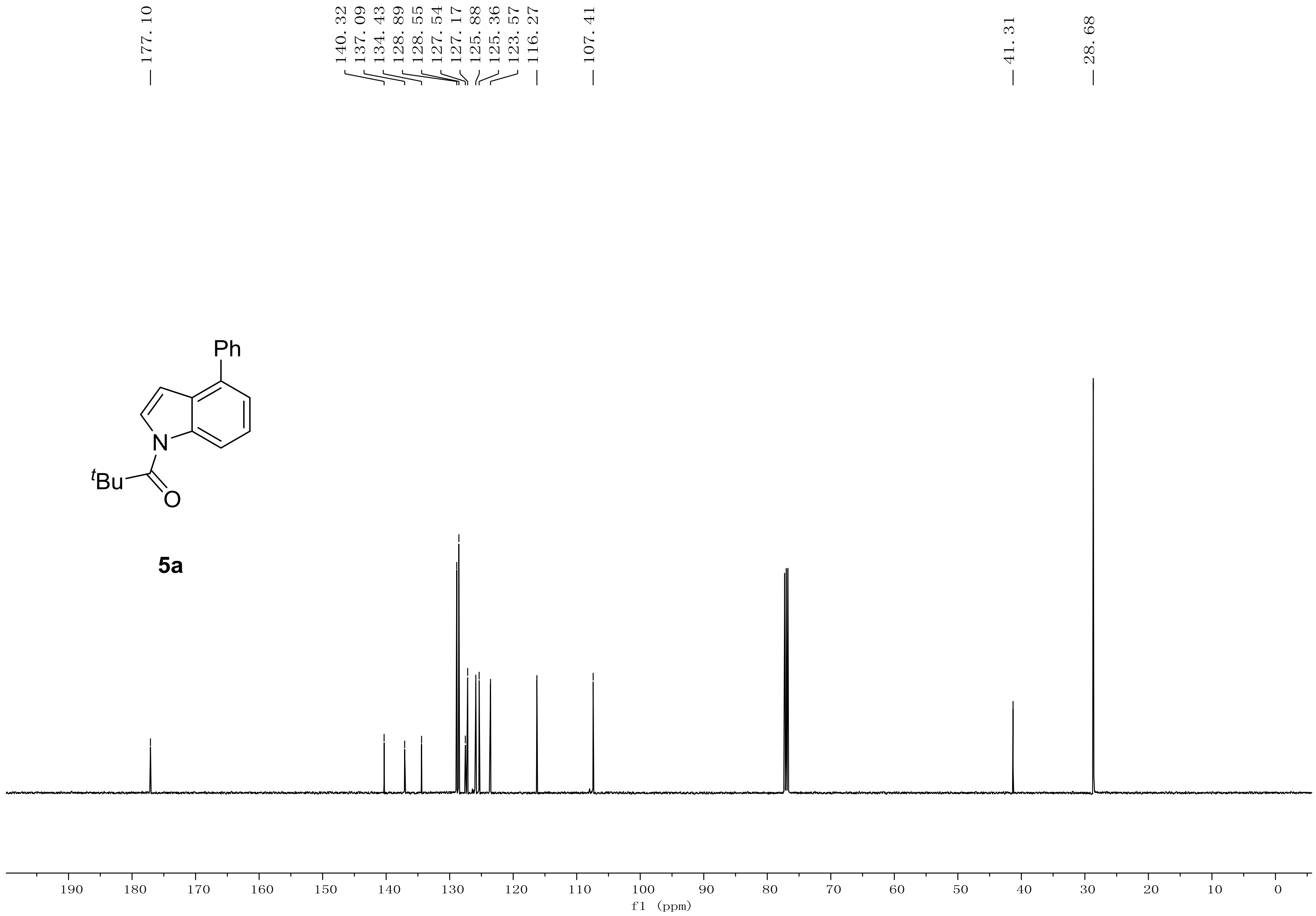
1.55
Ph
N
tBu
O
0.98 1.03 2.02 4.09 0.99 0.99 9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

5a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Ph
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tBu
O
5a
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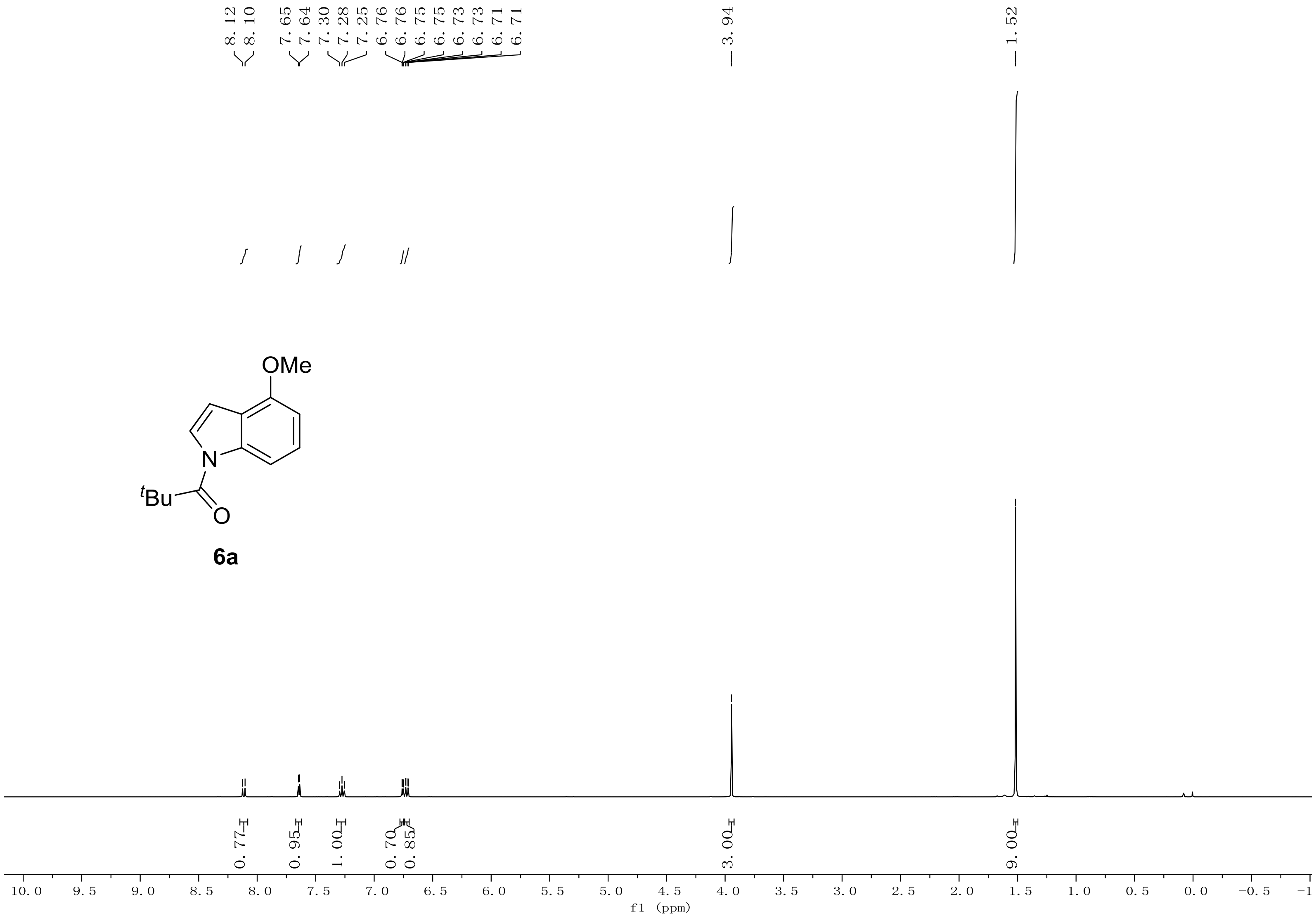
f1 (ppm)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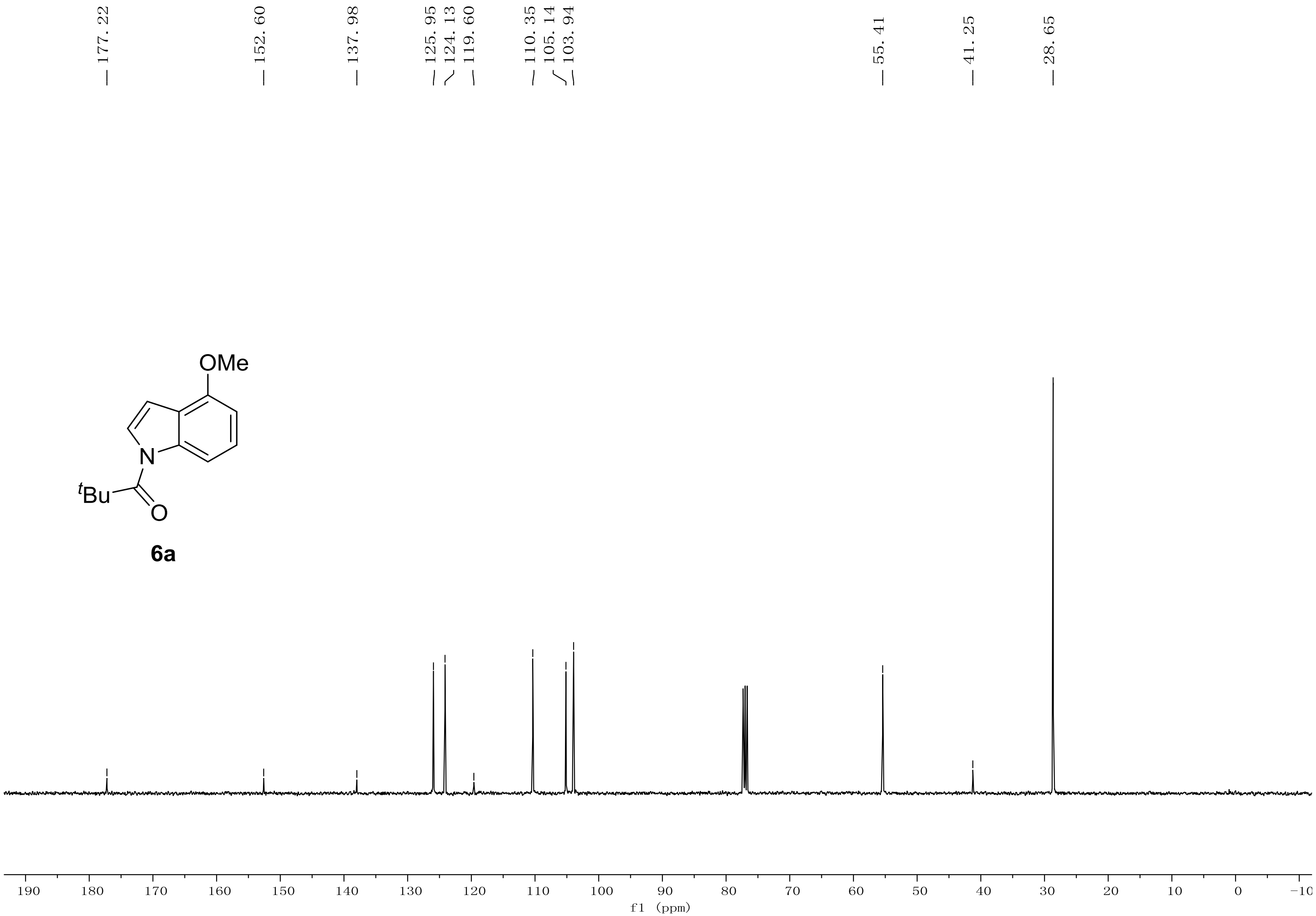
6a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tBu
O
6a
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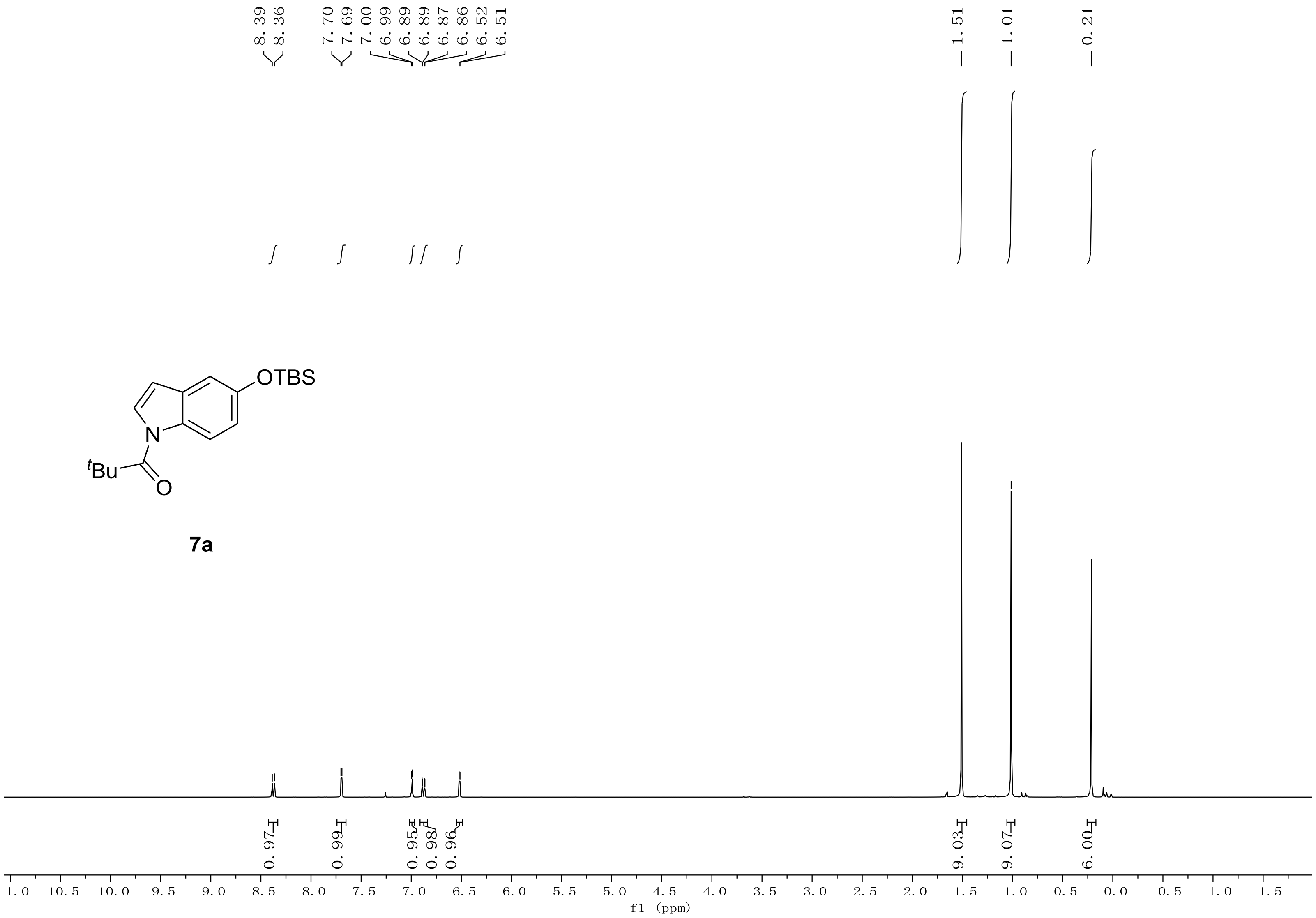
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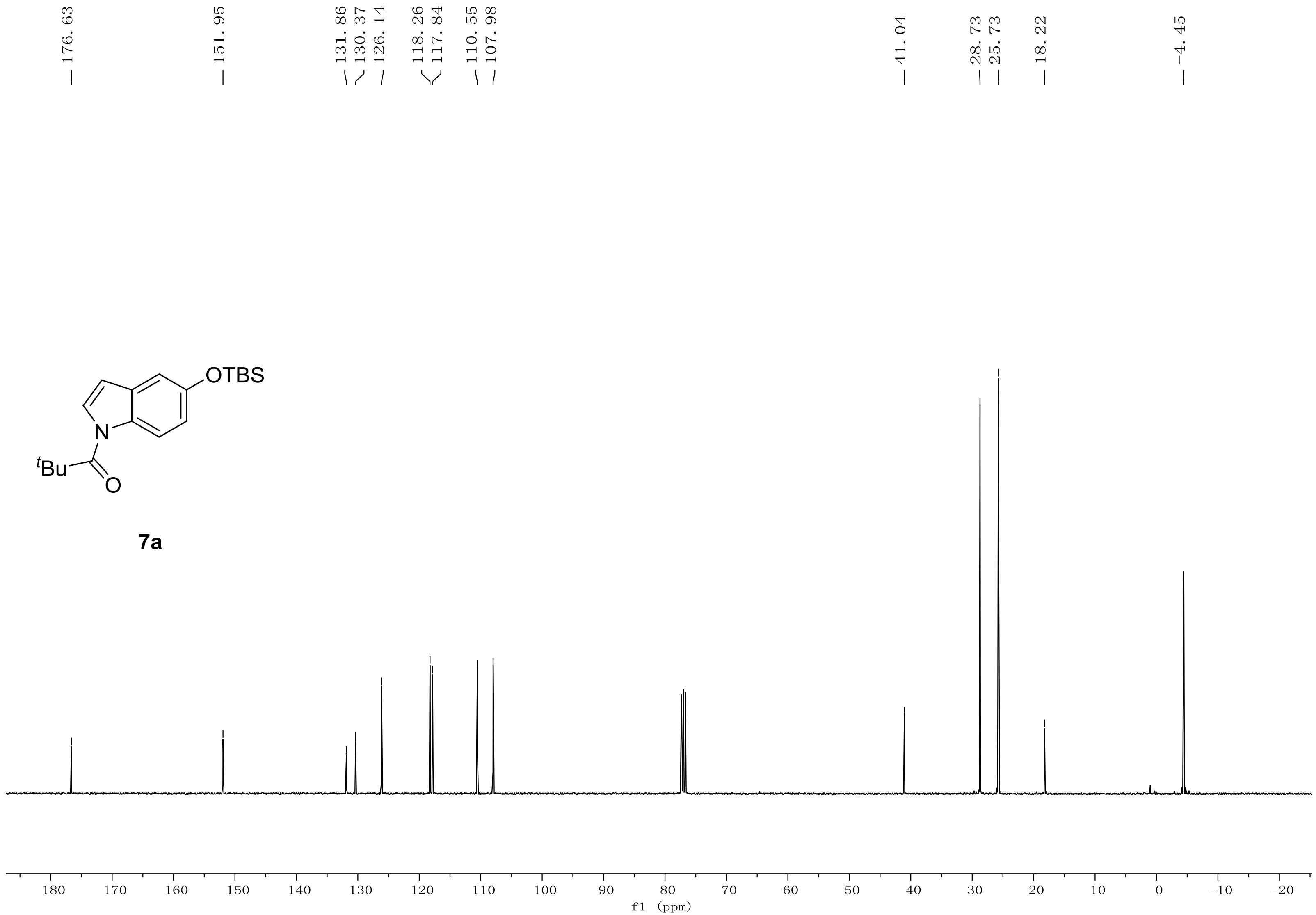
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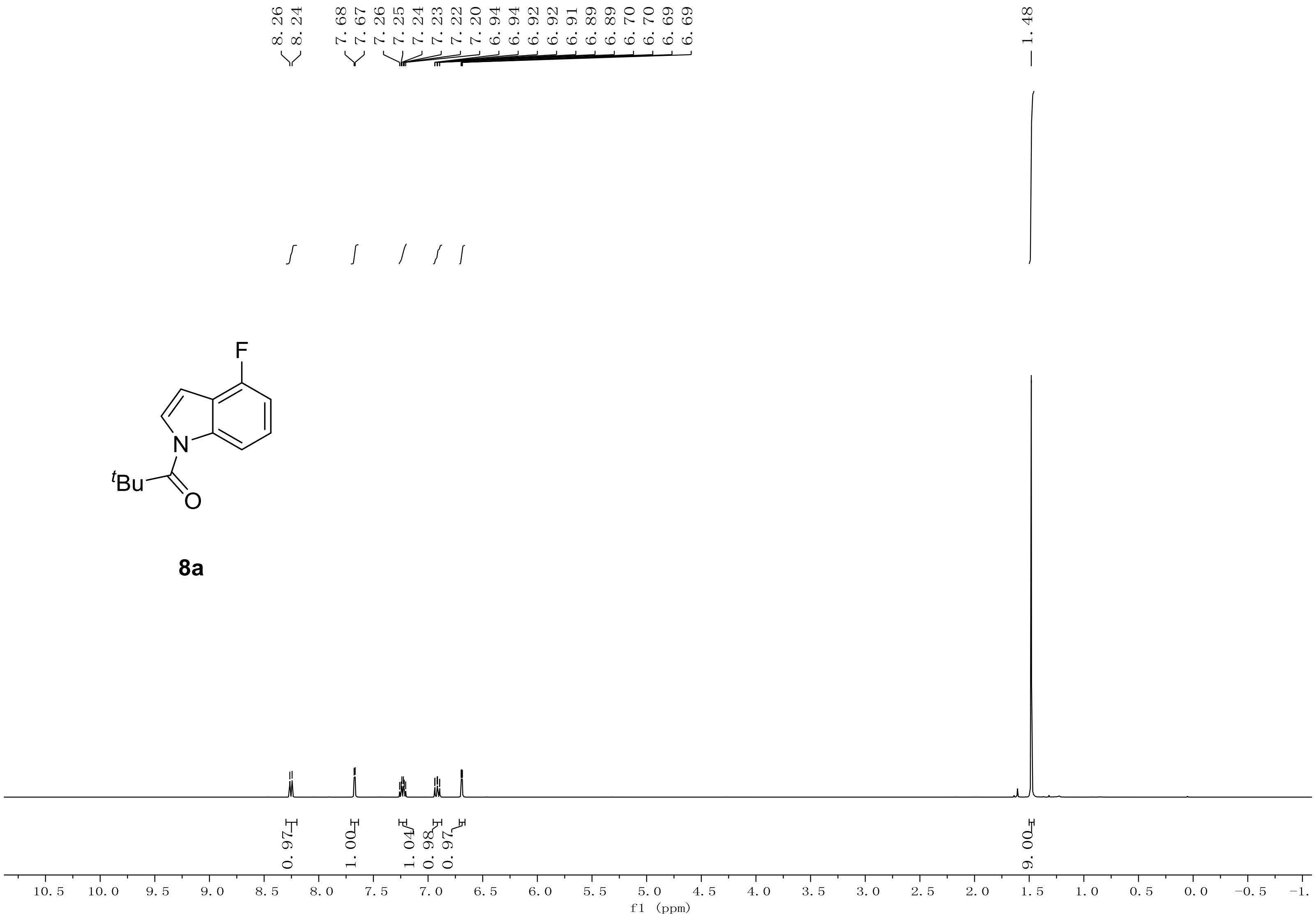

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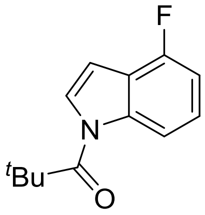
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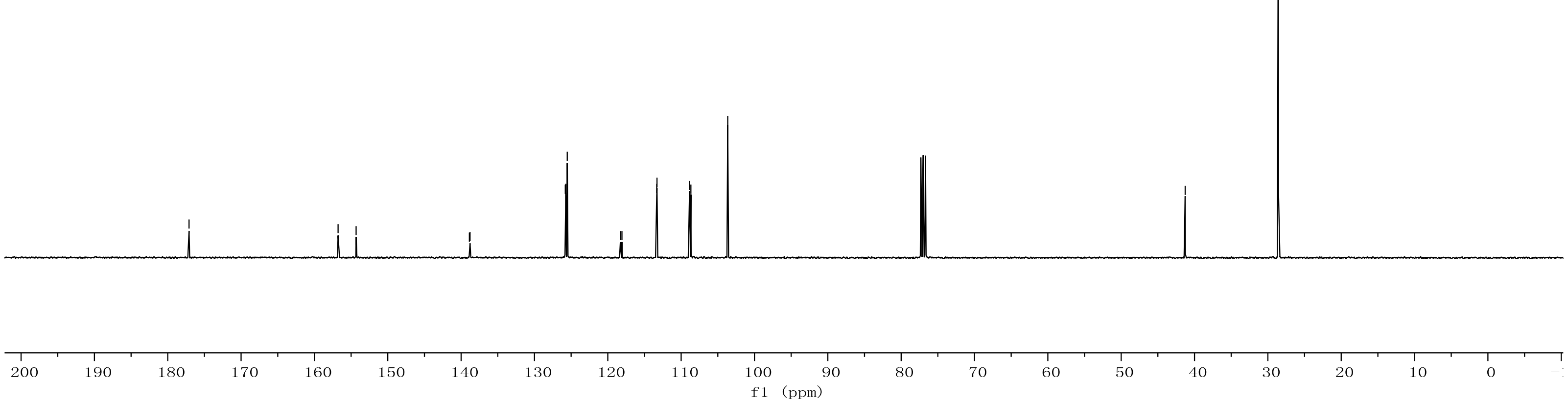
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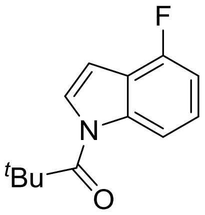

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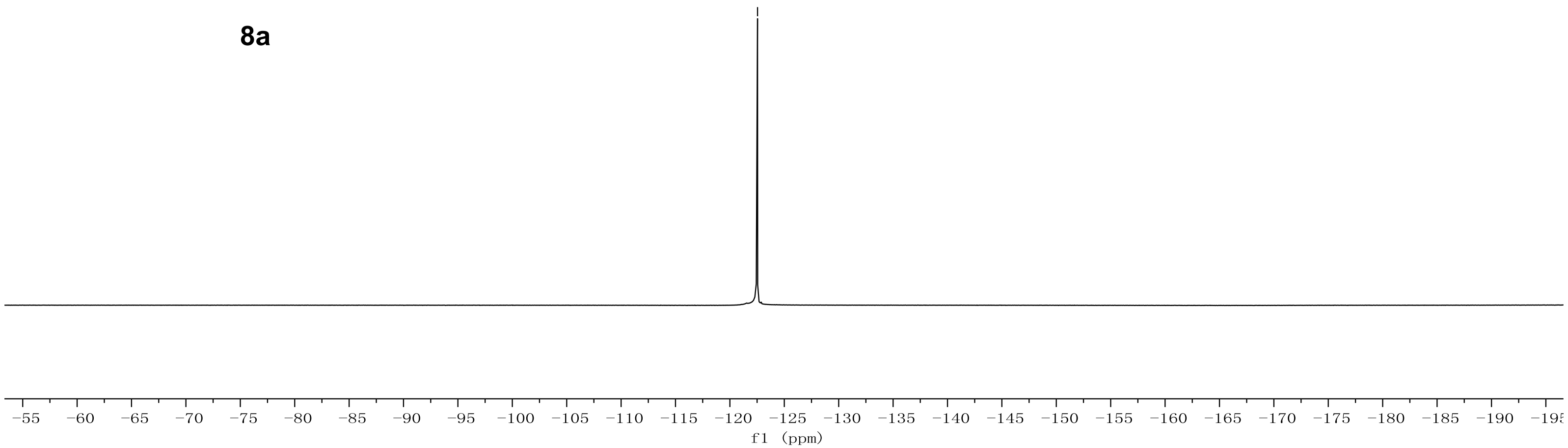

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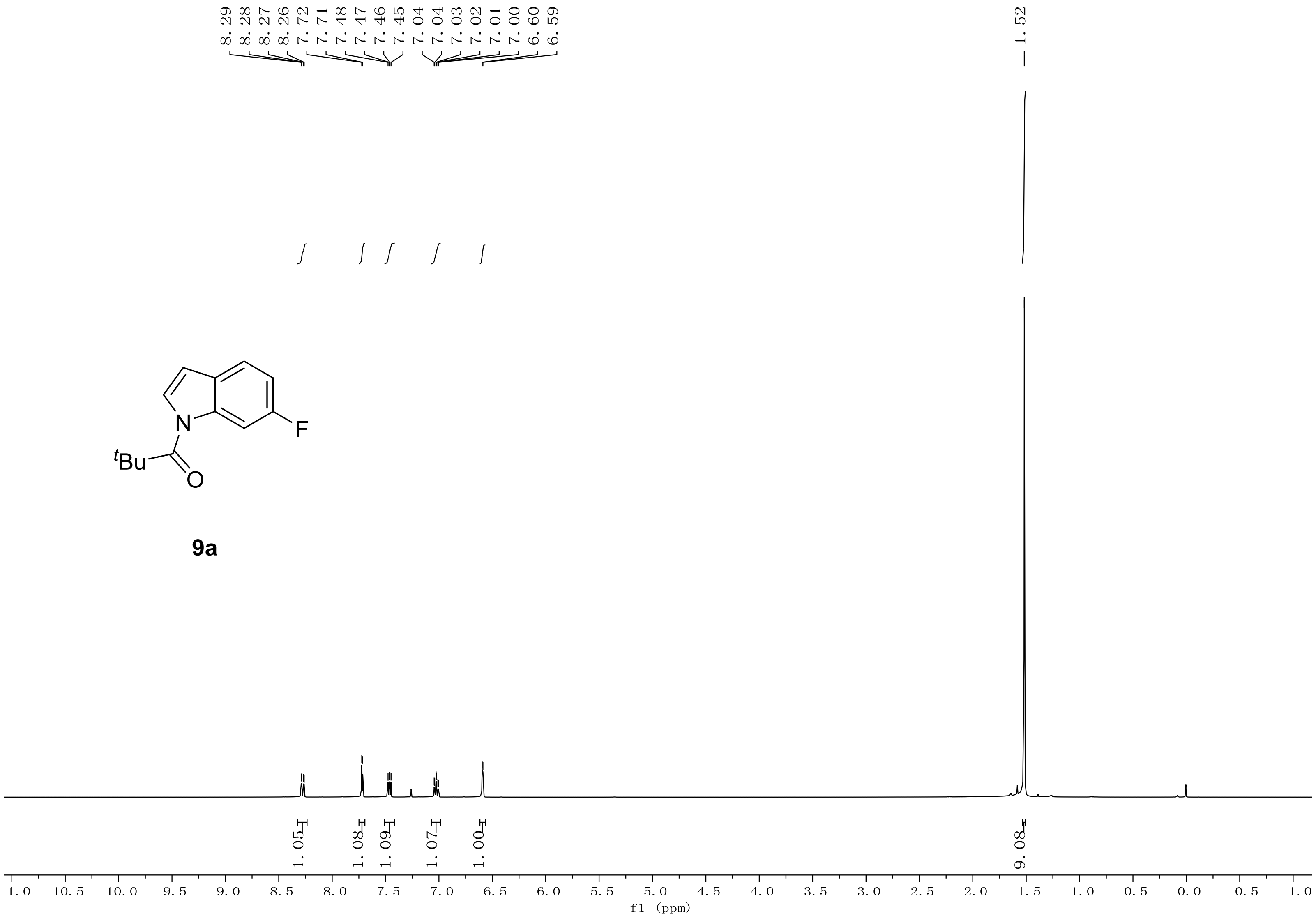
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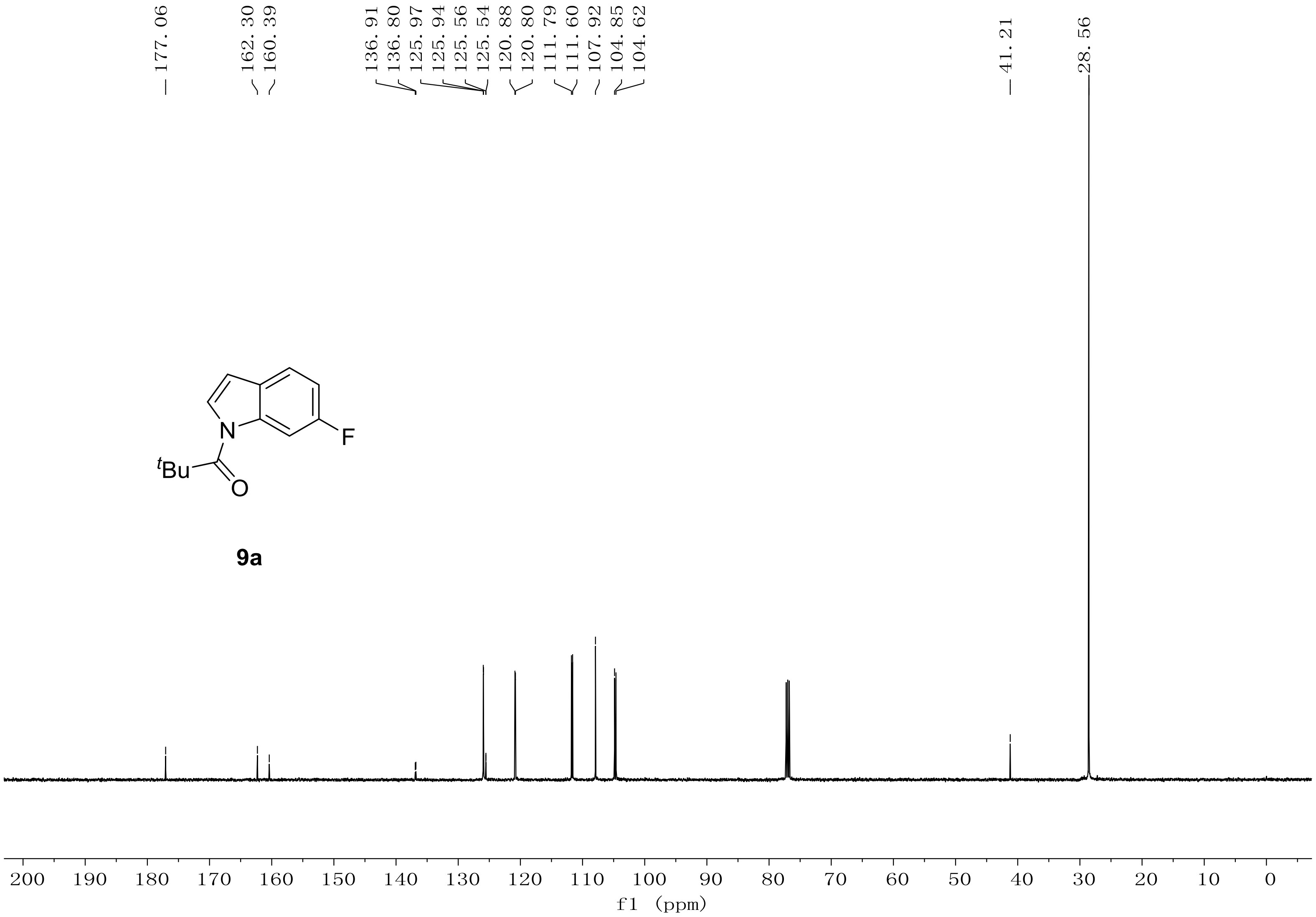
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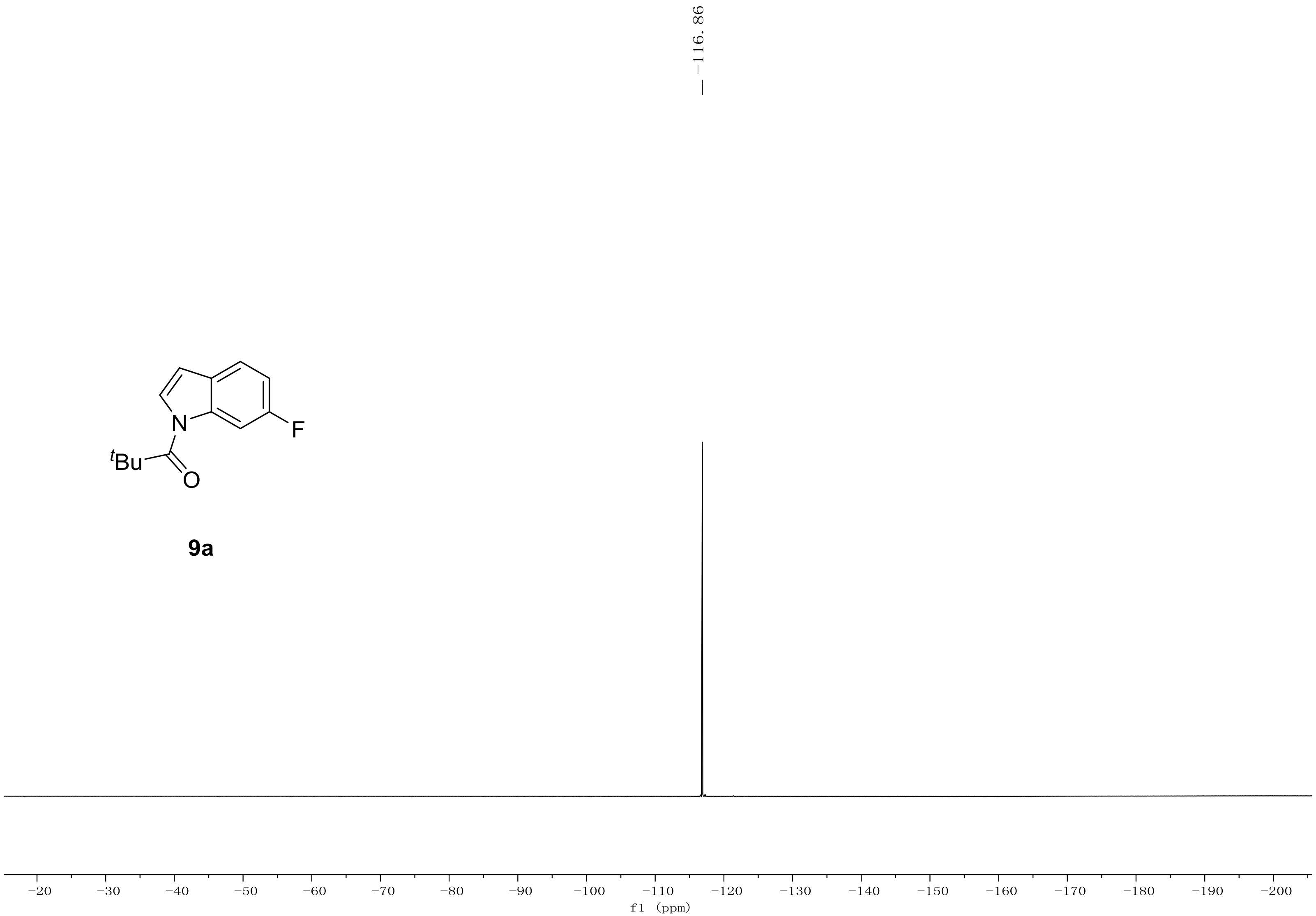

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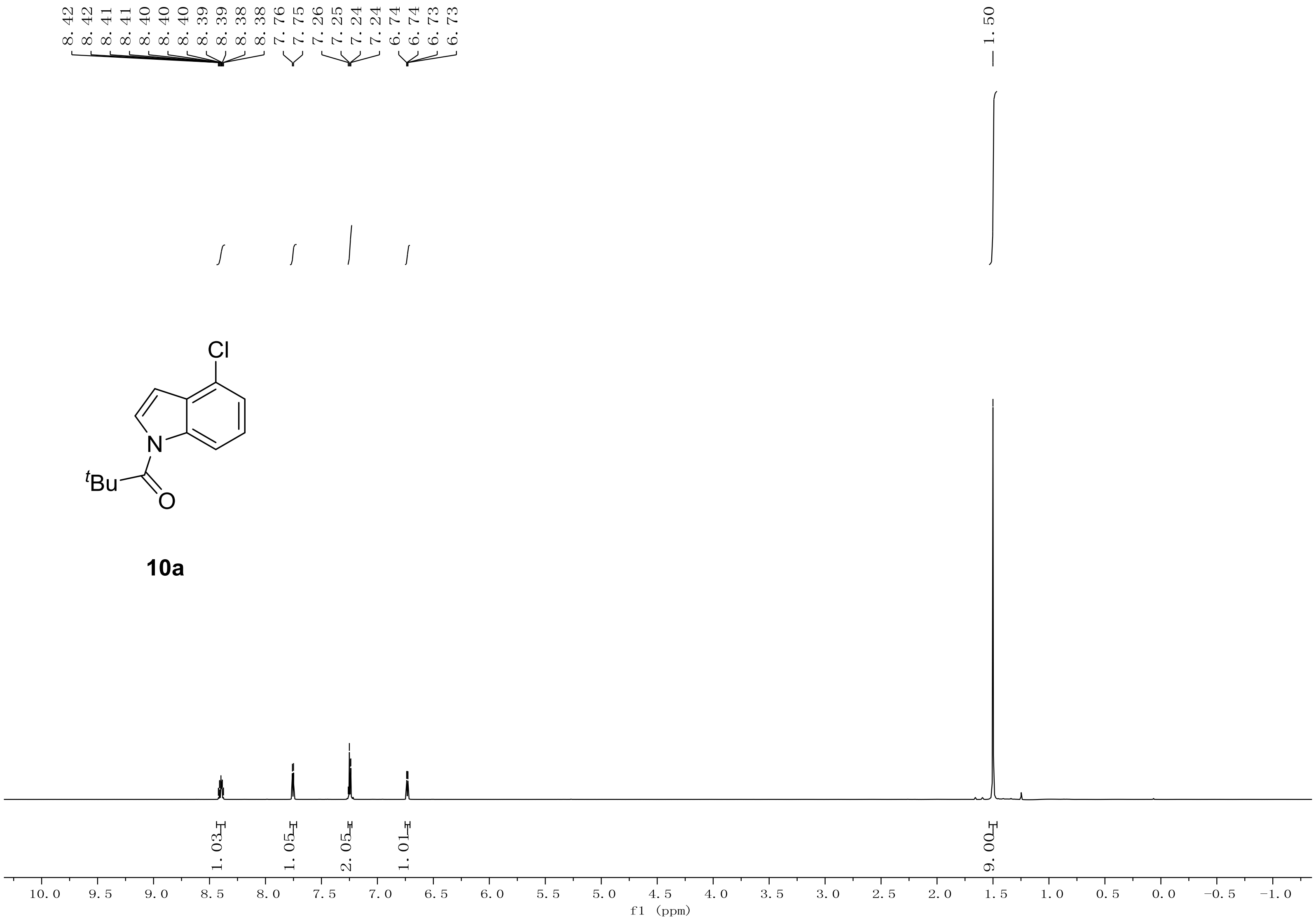
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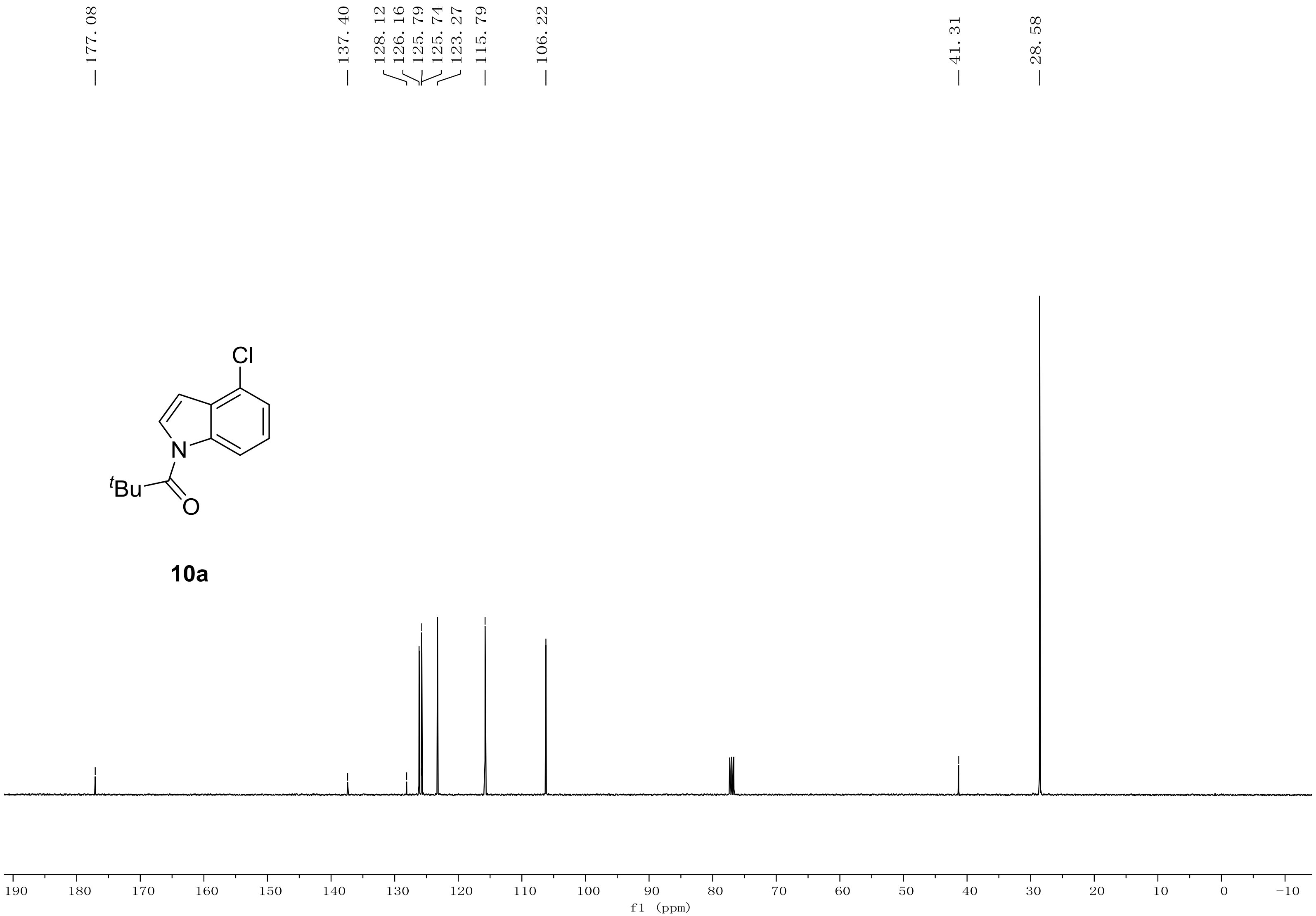
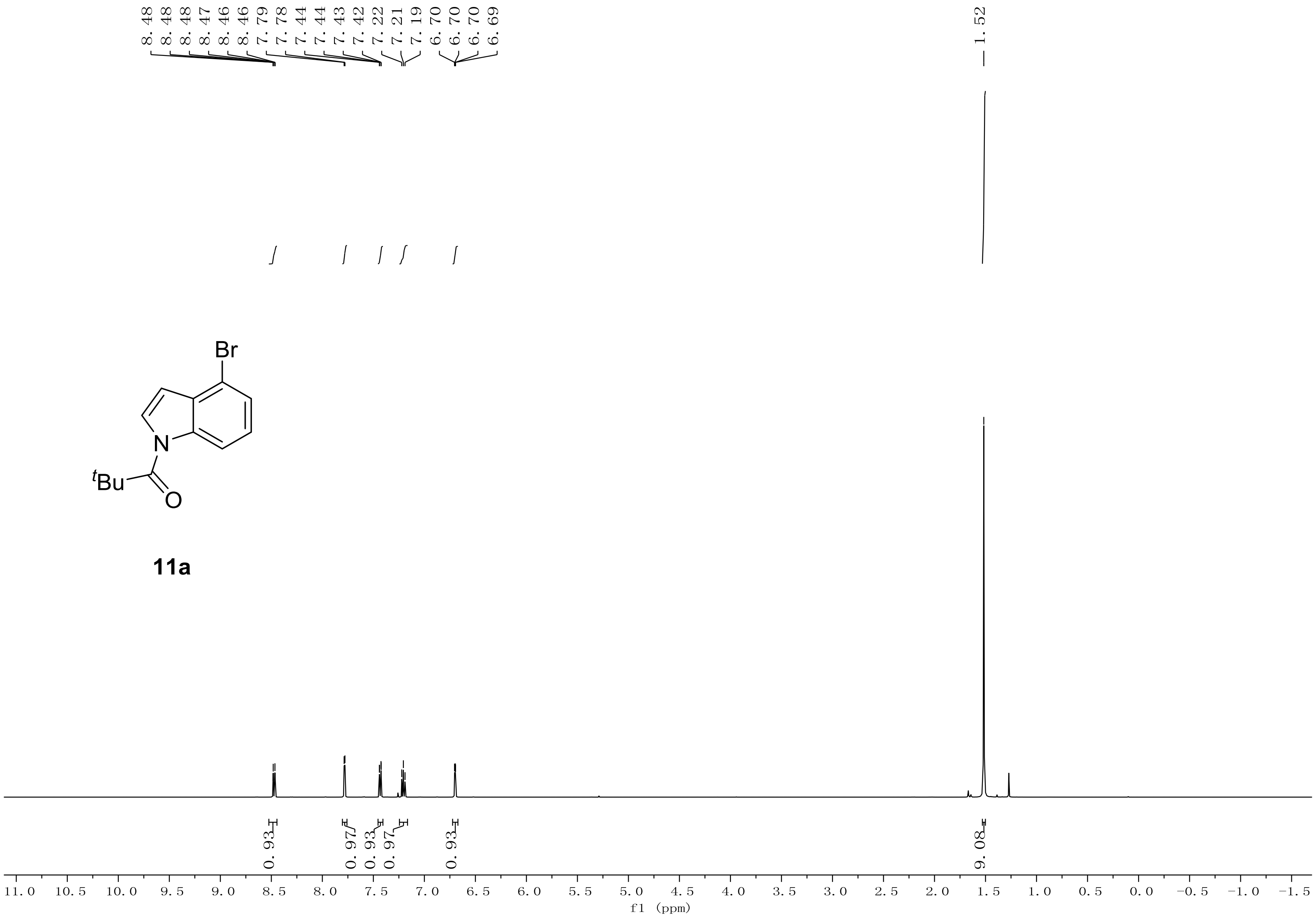
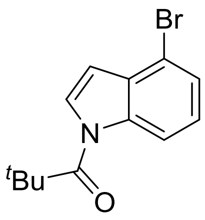
1.01
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

10a

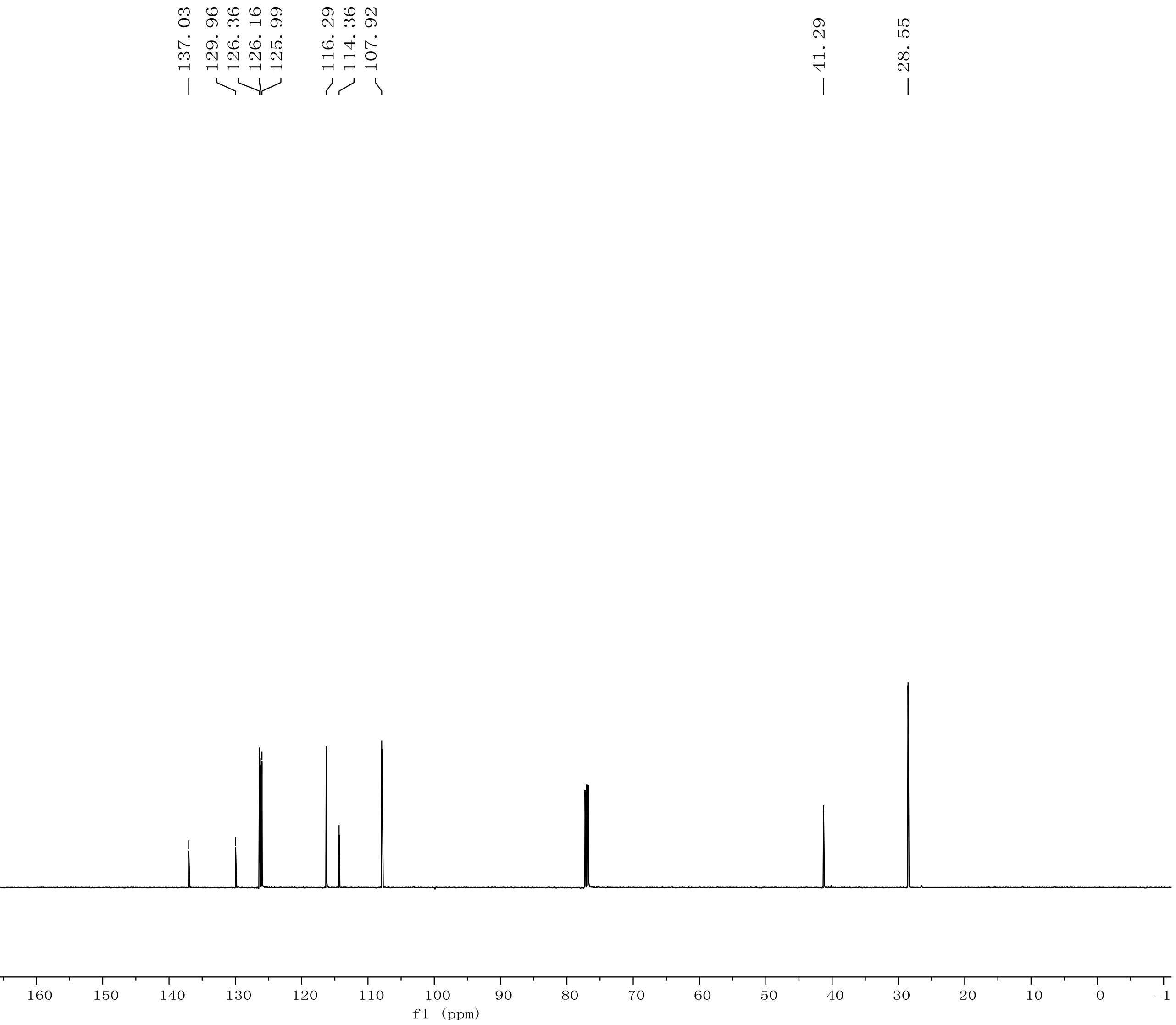

177.08
137.40
128.12
126.16
125.79
125.74
123.27
115.79
106.22
41.31
28.58
Cl
N
tBu
O
10a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


8.48
8.48
8.48
8.47
8.46
8.46
7.79
7.78
7.44
7.44
7.43
7.42
7.22
7.21
7.19
6.70
6.70
6.70
6.69
1.52
0.93
0.97
0.93
0.97
0.93
9.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)
Br
N
tBu
O

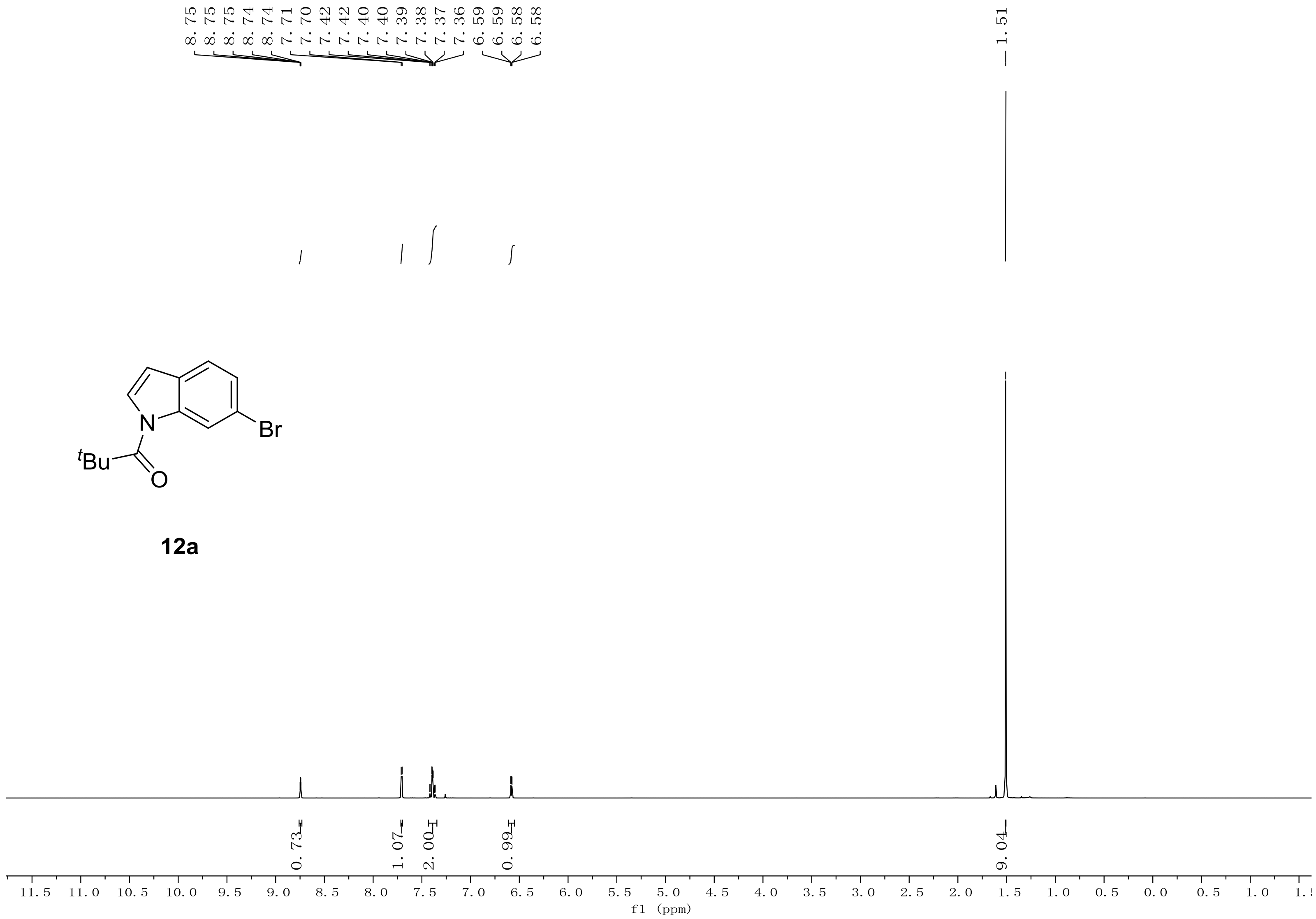
11a



11a

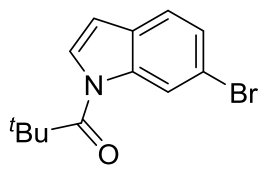


177.08
137.03
129.96
126.36
126.16
125.99
116.29
114.36
107.92
41.29
28.55
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

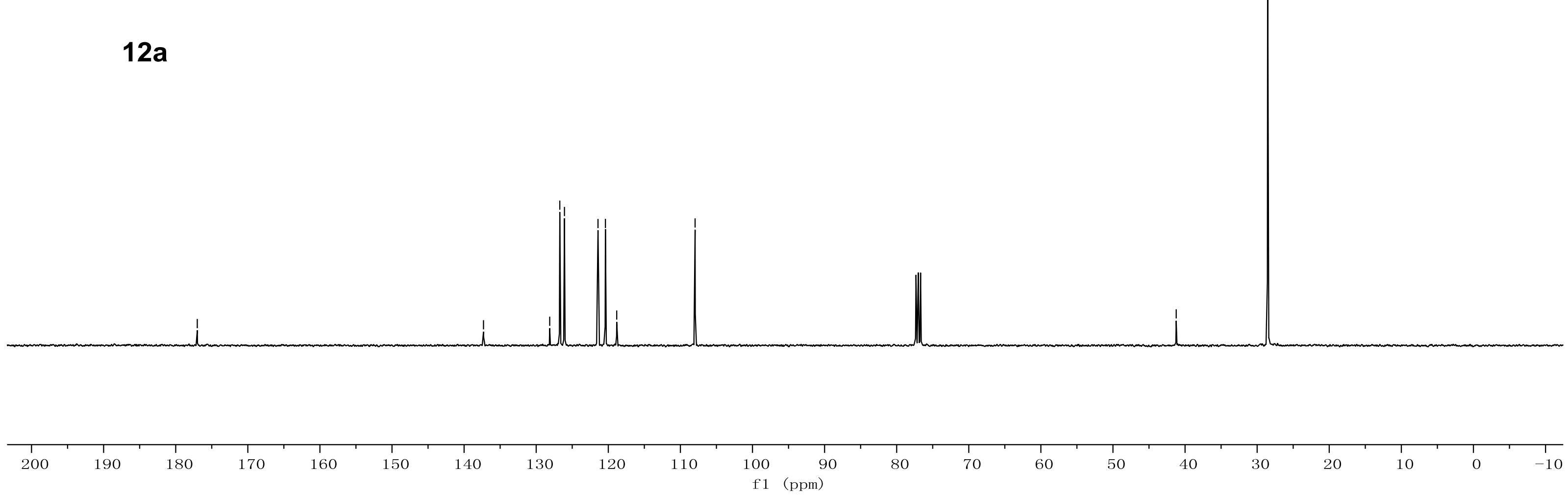


8.75 8.75 8.75 8.74 8.74 7.71 7.70 7.42 7.42 7.40 7.40 7.39 7.38 7.37 7.36 6.59 6.59 6.58 6.58
1.51
N
Br
^{t}Bu
O
0.73
1.07
2.00
0.99
9.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

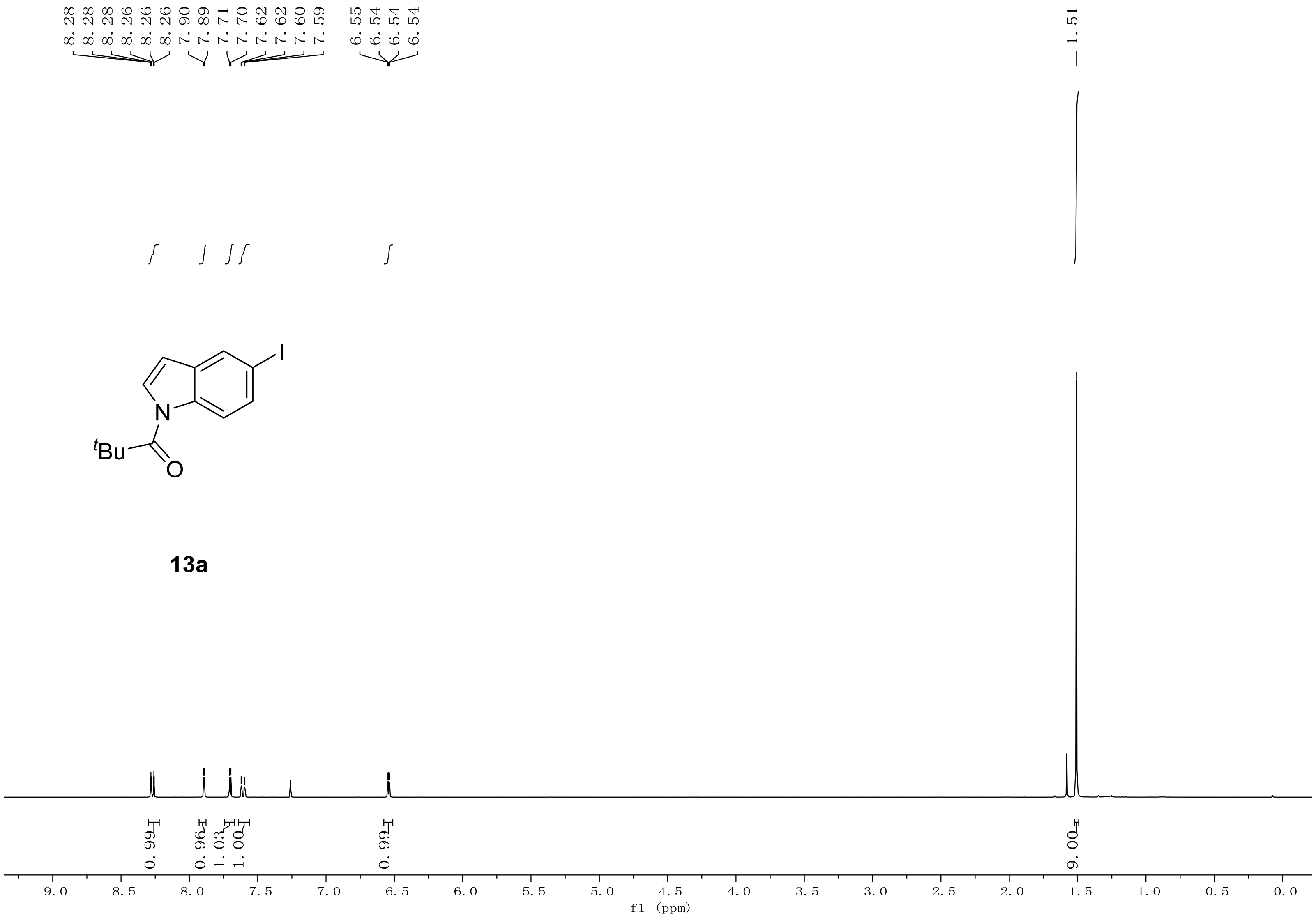
12a



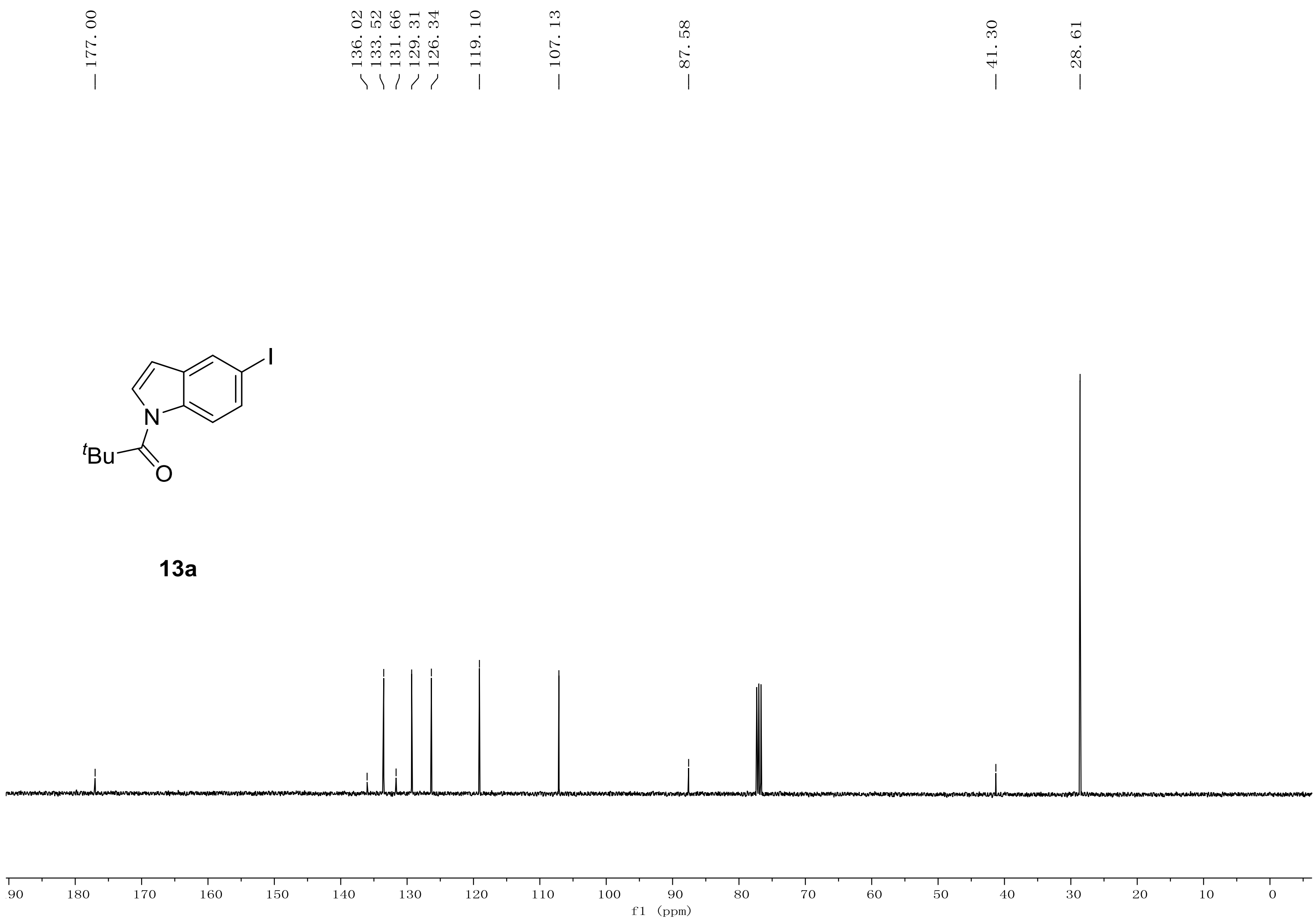
12a



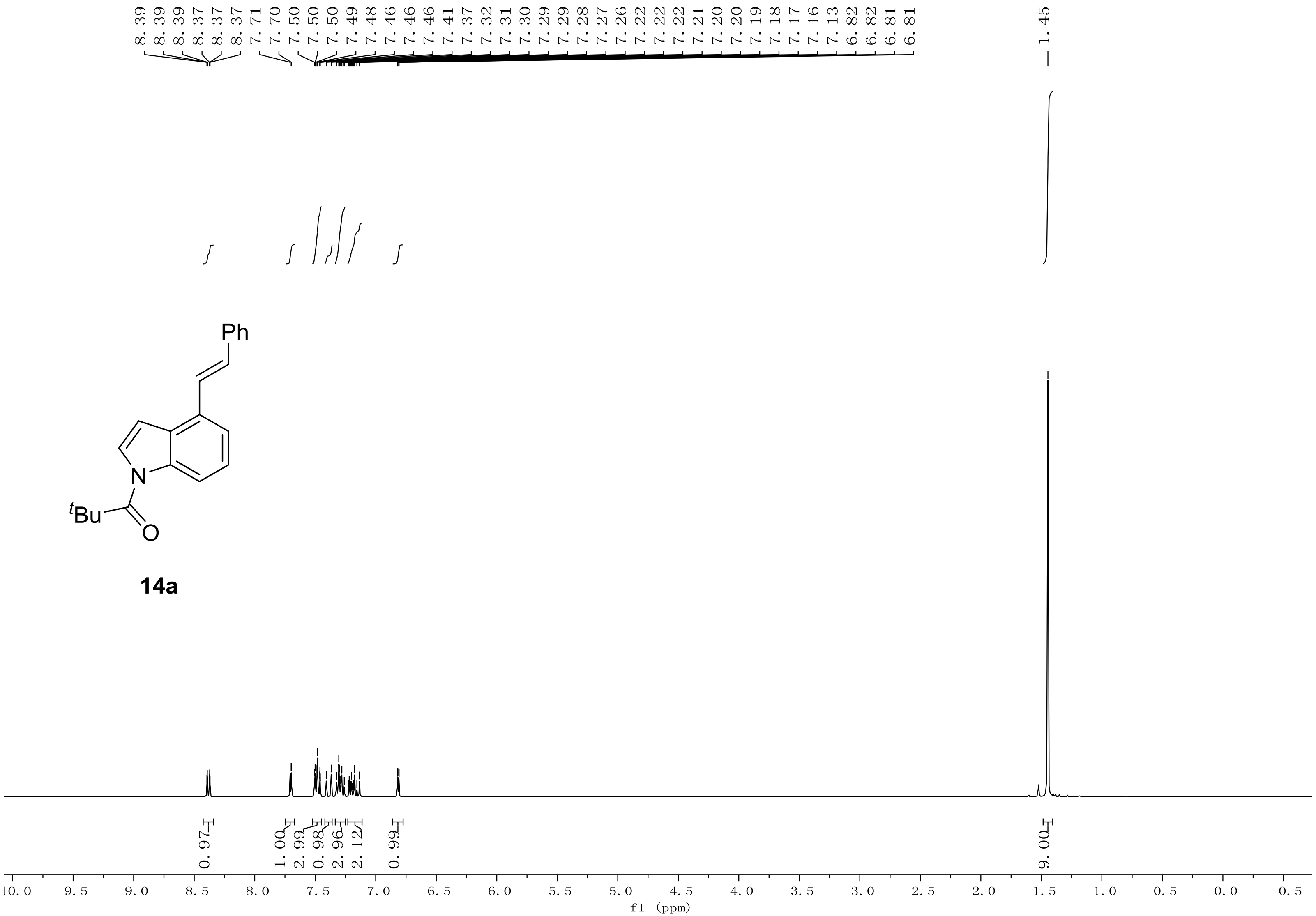
177.01
137.31
128.13
126.73
126.08
121.43
120.40
118.83
107.96
41.23
28.54
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


8.28
8.28
8.28
8.26
8.26
8.26
7.90
7.89
7.71
7.70
7.62
7.62
7.60
7.59
6.55
6.54
6.54
6.54
1.51
I
N
tBu
O
0.99
0.96
1.03
1.00
0.99
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

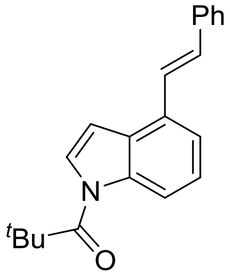
13a



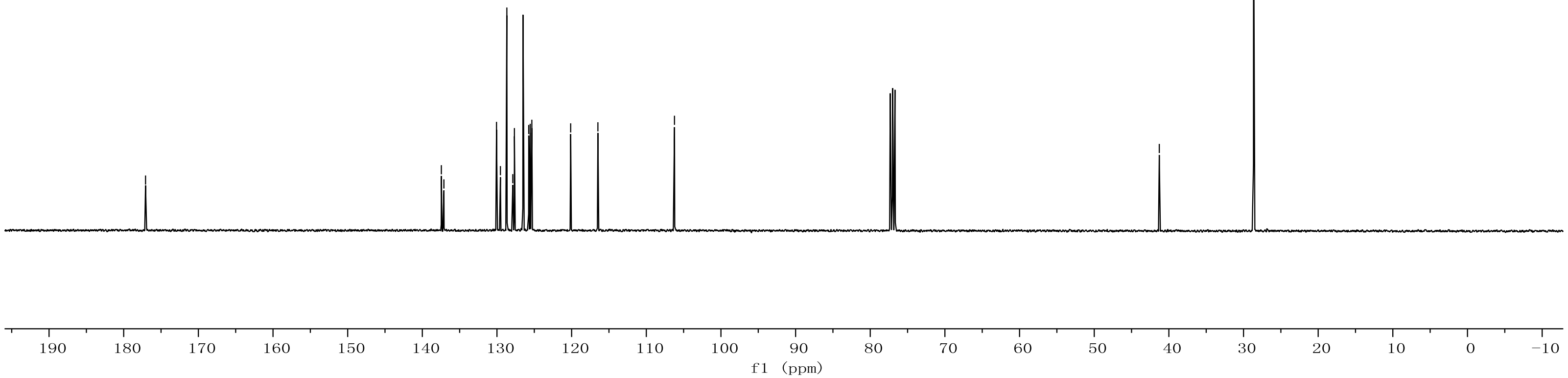
177.00
136.02
133.52
131.66
129.31
126.34
119.10
107.13
87.58
41.30
28.61
I
N
tBu
O
13a
f1 (ppm)


8.39 8.39 8.39 8.37 8.37 8.37 7.71 7.70 7.50 7.50 7.50 7.49 7.48 7.46 7.46 7.46 7.41 7.37 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.26 7.22 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.17 7.16 7.13 6.82 6.82 6.81 6.81
1.45
0.97
1.00
2.99
0.98
2.96
2.12
0.99
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Ph
N
^{t}Bu
O

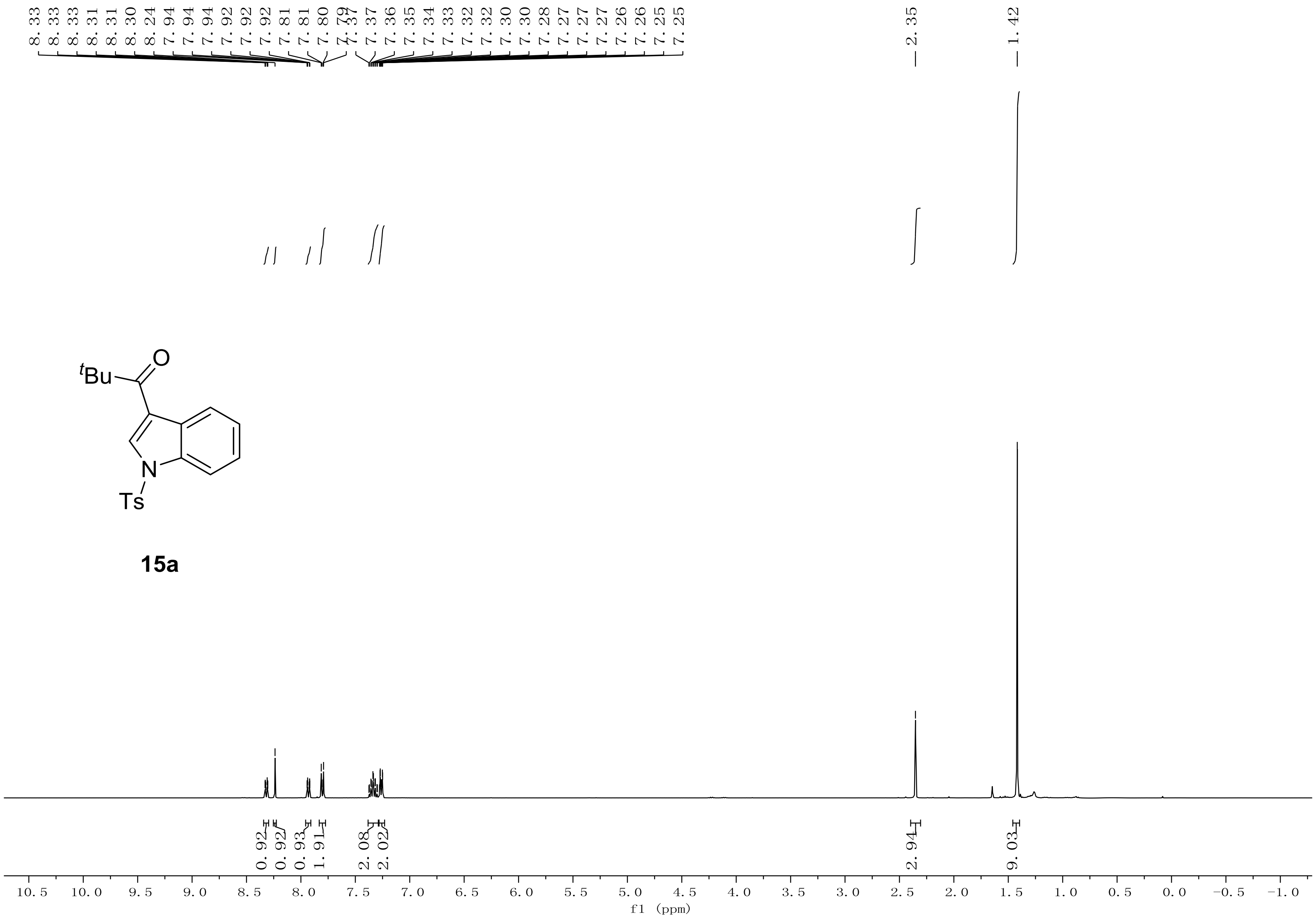
14a



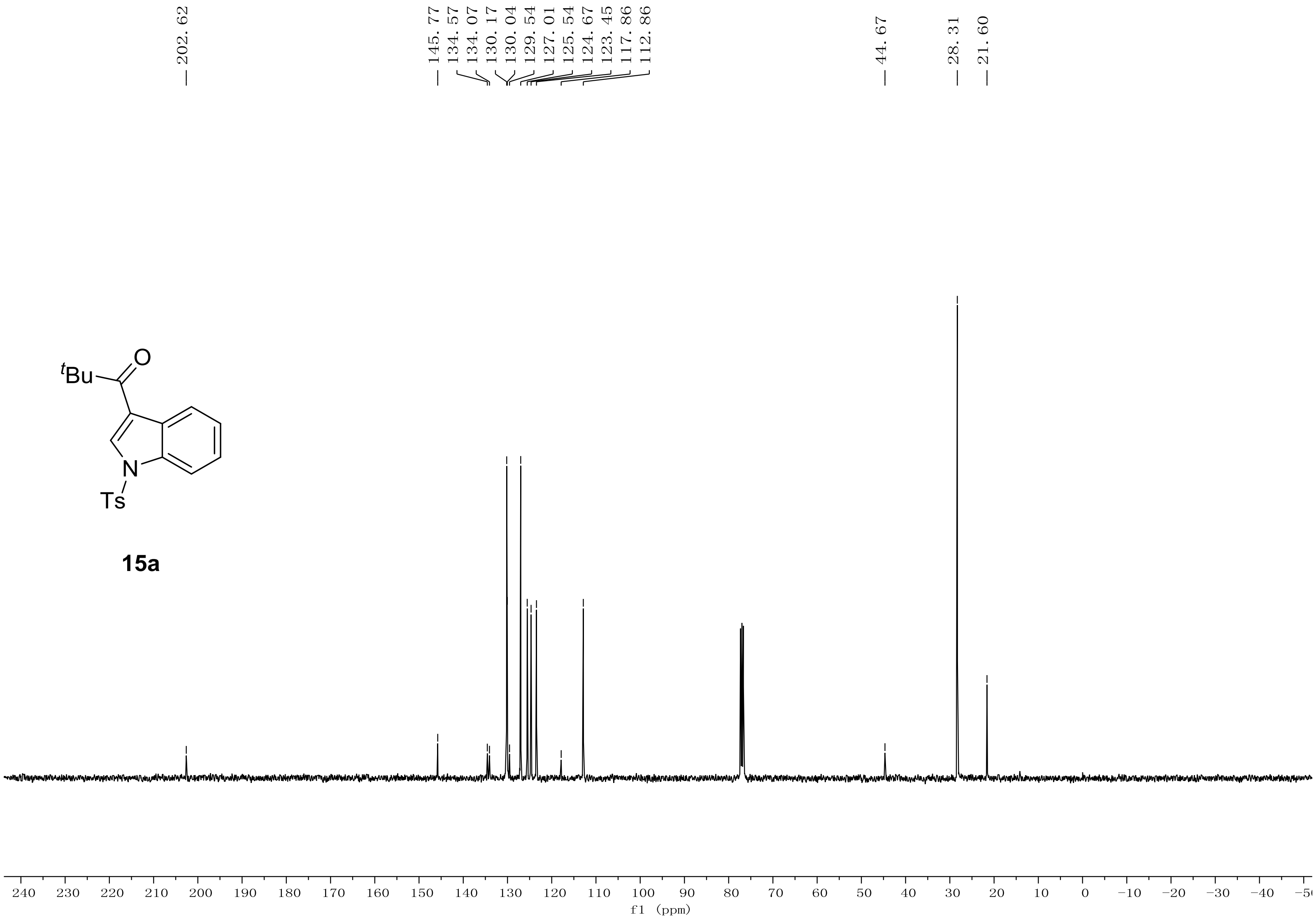
14a



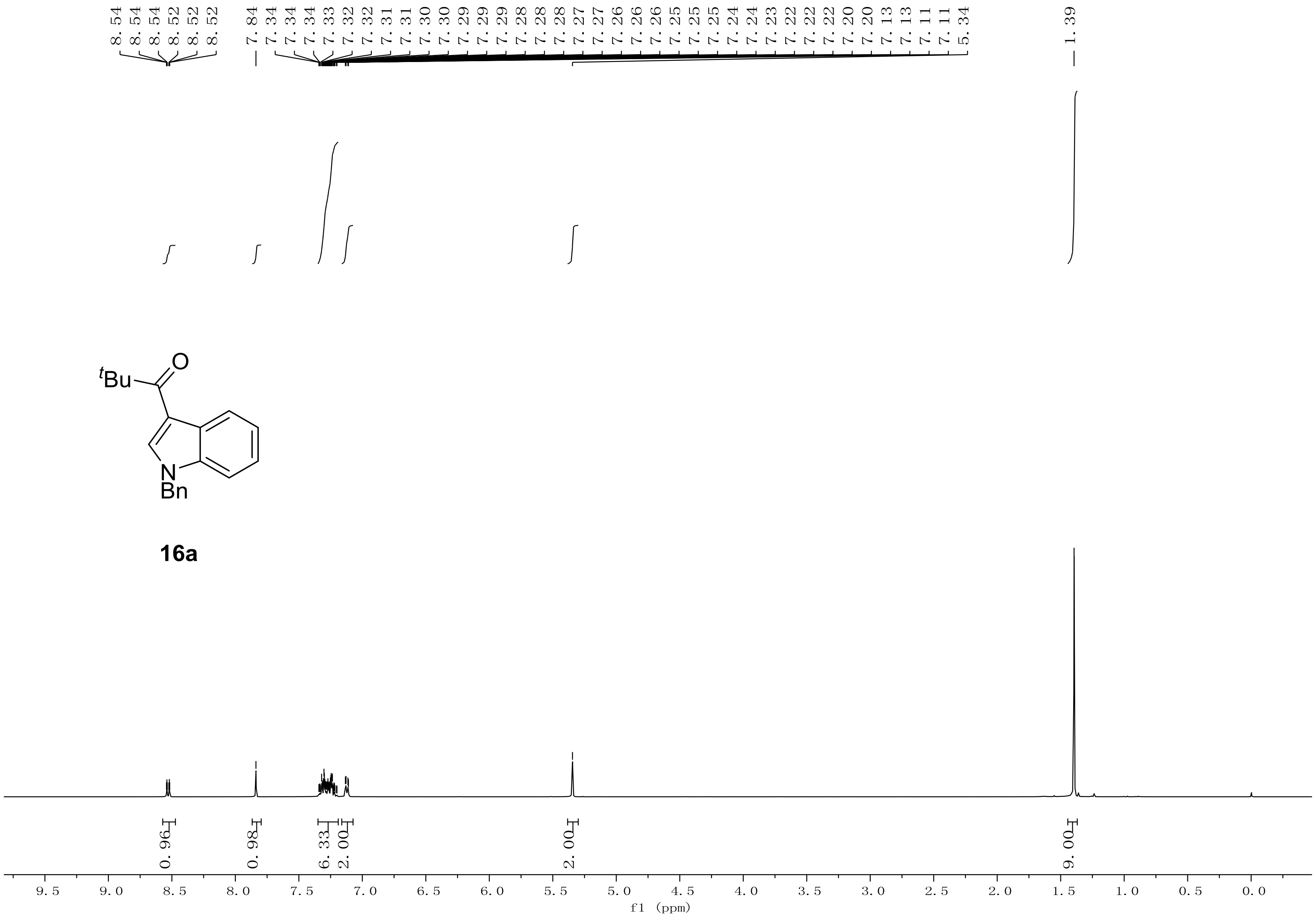
177.08
137.45
137.11
130.06
129.54
128.68
127.88
127.67
126.52
125.75
125.55
125.33
120.13
116.48
106.22
41.28
28.65
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


8.33 8.33 8.33 8.31 8.31 8.30 8.24 7.94 7.94 7.94 7.92 7.92 7.81 7.81 7.80 7.79 7.37 7.37 7.36 7.35 7.34 7.33 7.32 7.32 7.30 7.30 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.25
2.35
1.42
tBu
O
N
Ts
0.92 0.92 0.93 1.91 2.08 2.02
2.94
9.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

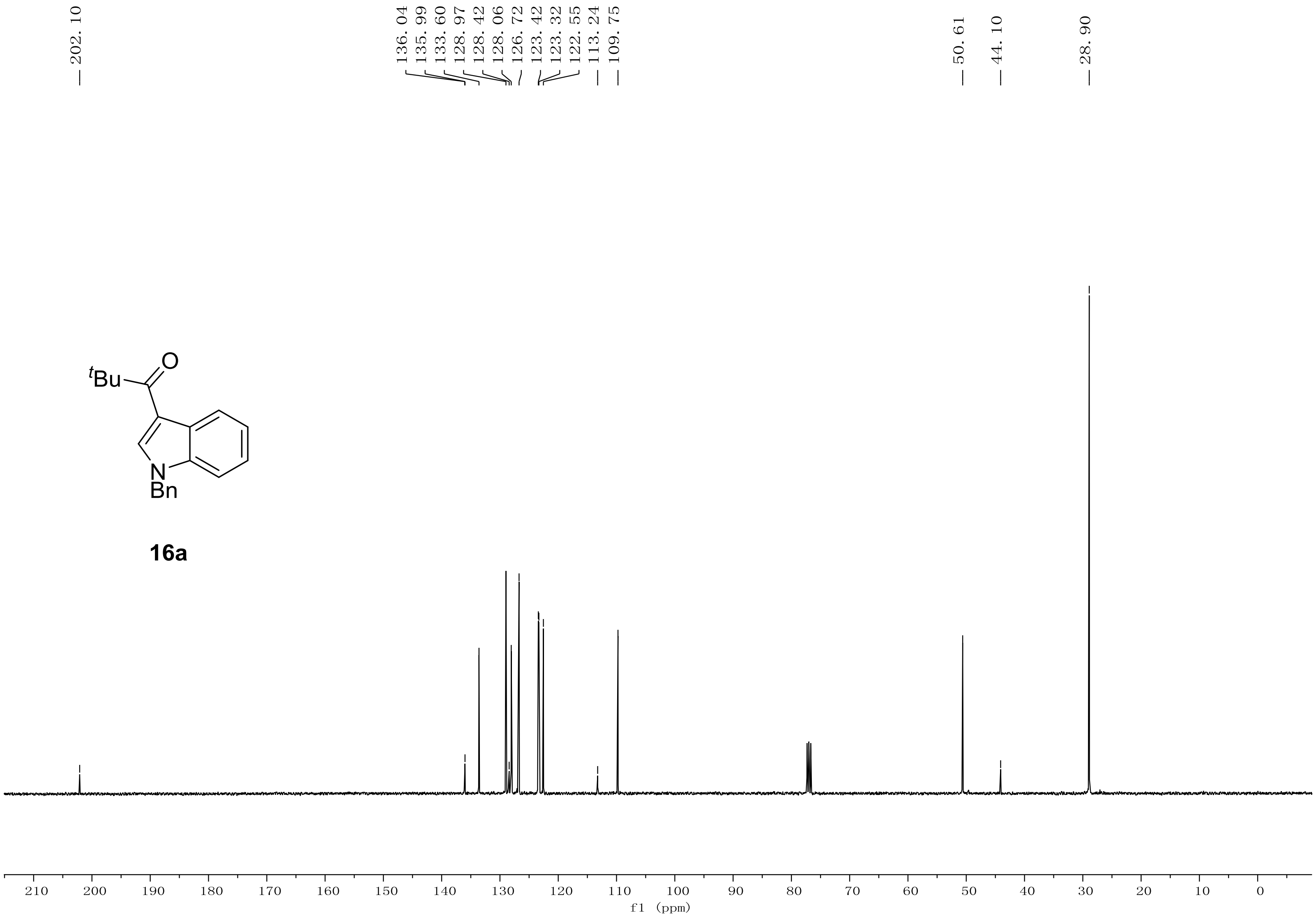
15a



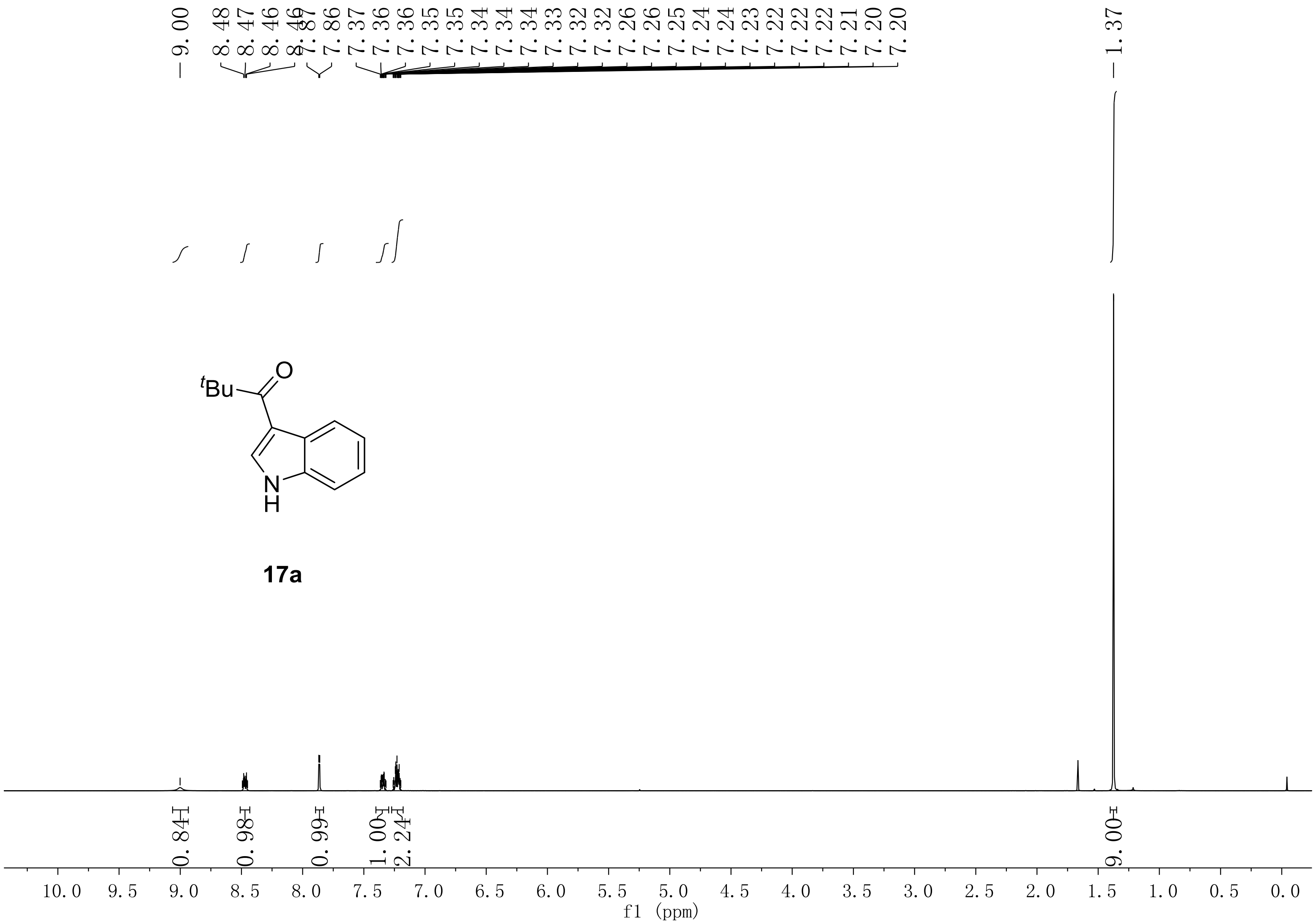
O
^{t}Bu
N
Ts
15a
202.62
145.77
134.57
134.07
130.17
130.04
129.54
127.01
125.54
124.67
123.45
117.86
112.86
44.67
28.31
21.60
f1 (ppm)

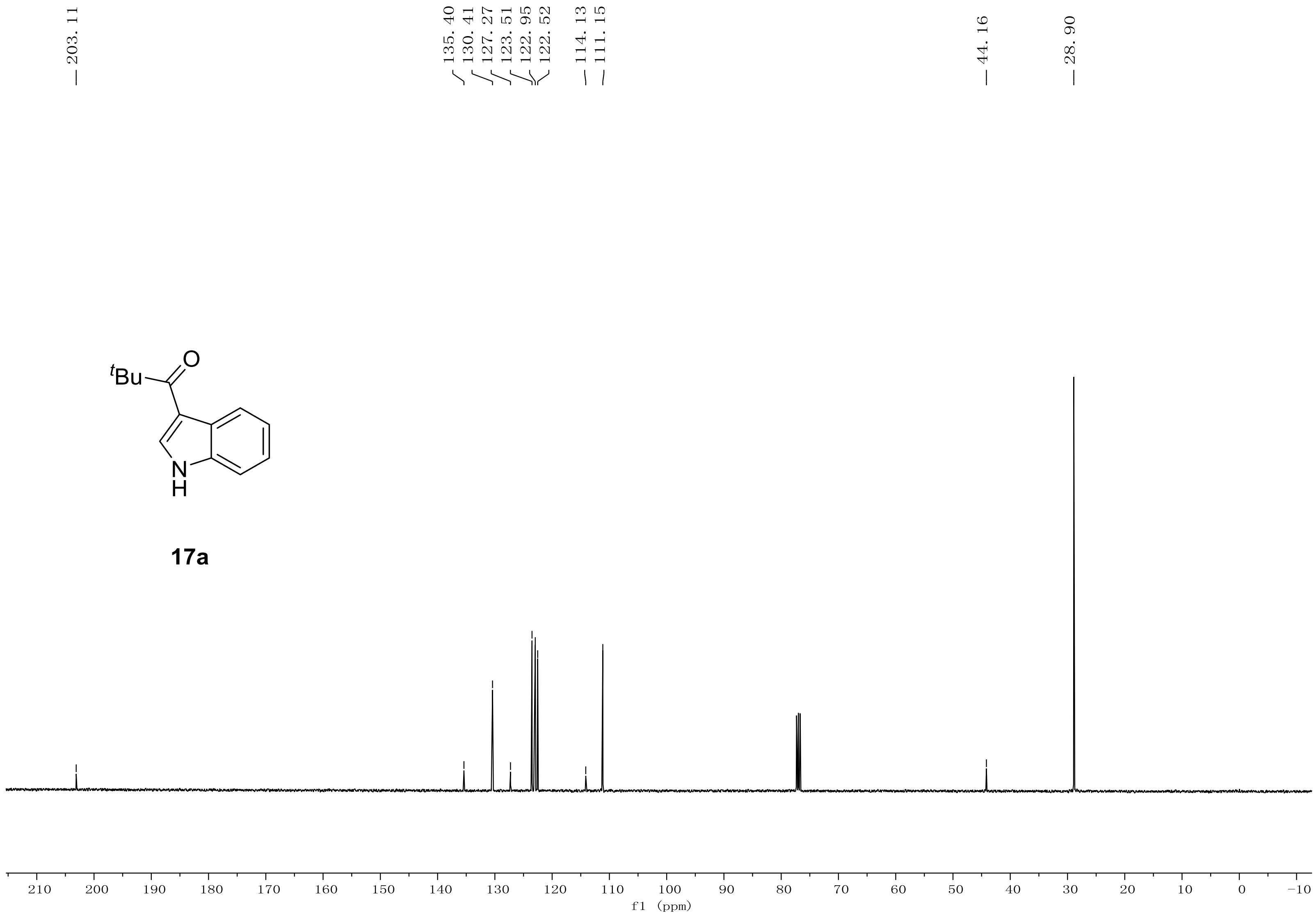

8.54 8.54 8.54 8.52 8.52 8.52
7.84
7.34 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.22 7.20 7.20 7.13 7.13 7.11 7.11
5.34
1.39
^{t}Bu
O
N
Bn
0.96
0.98
6.33
2.00
2.00
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

16a


202.10
136.04
135.99
133.60
128.97
128.42
128.06
126.72
123.42
123.32
122.55
113.24
109.75
50.61
44.10
28.90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

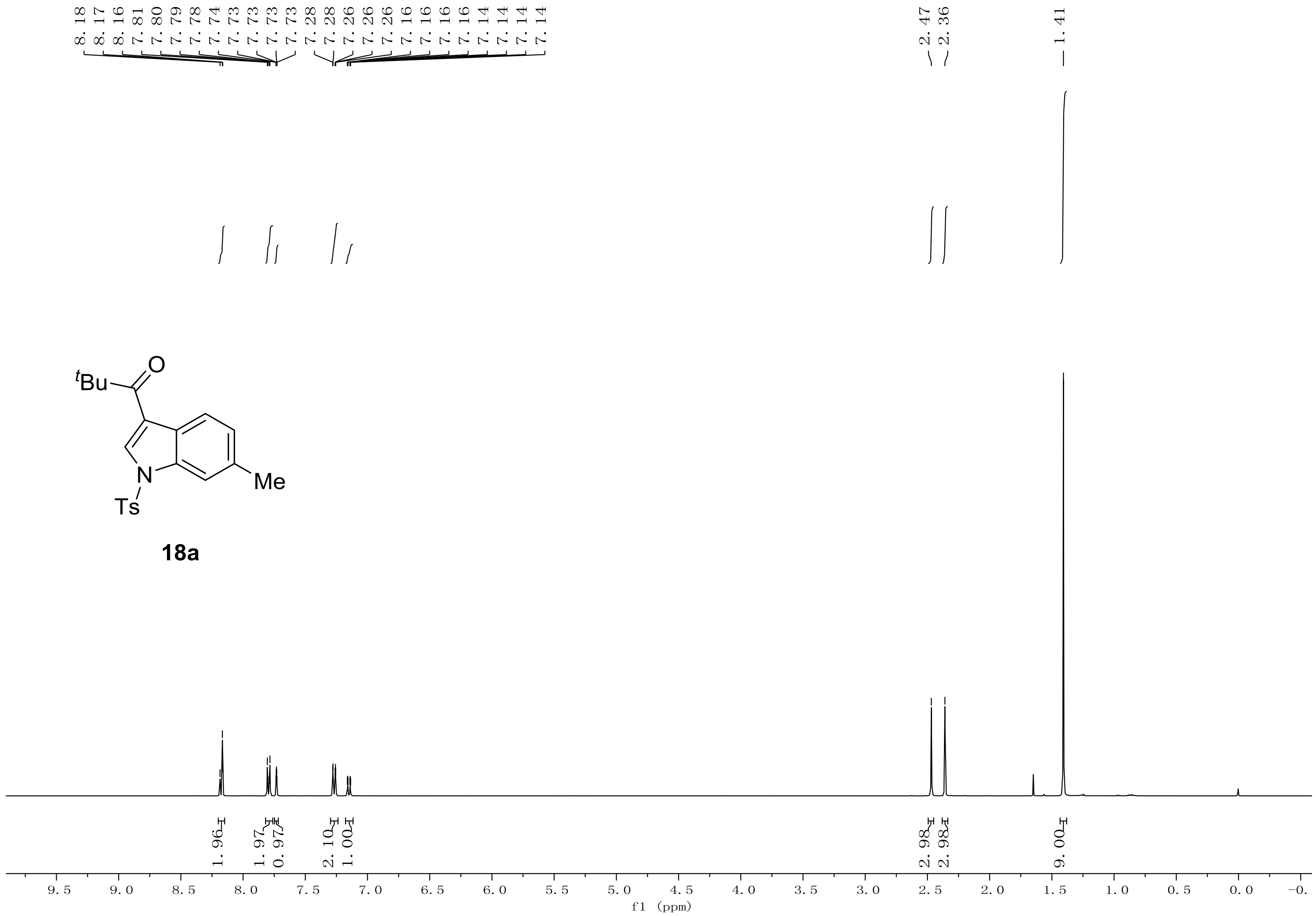
16a

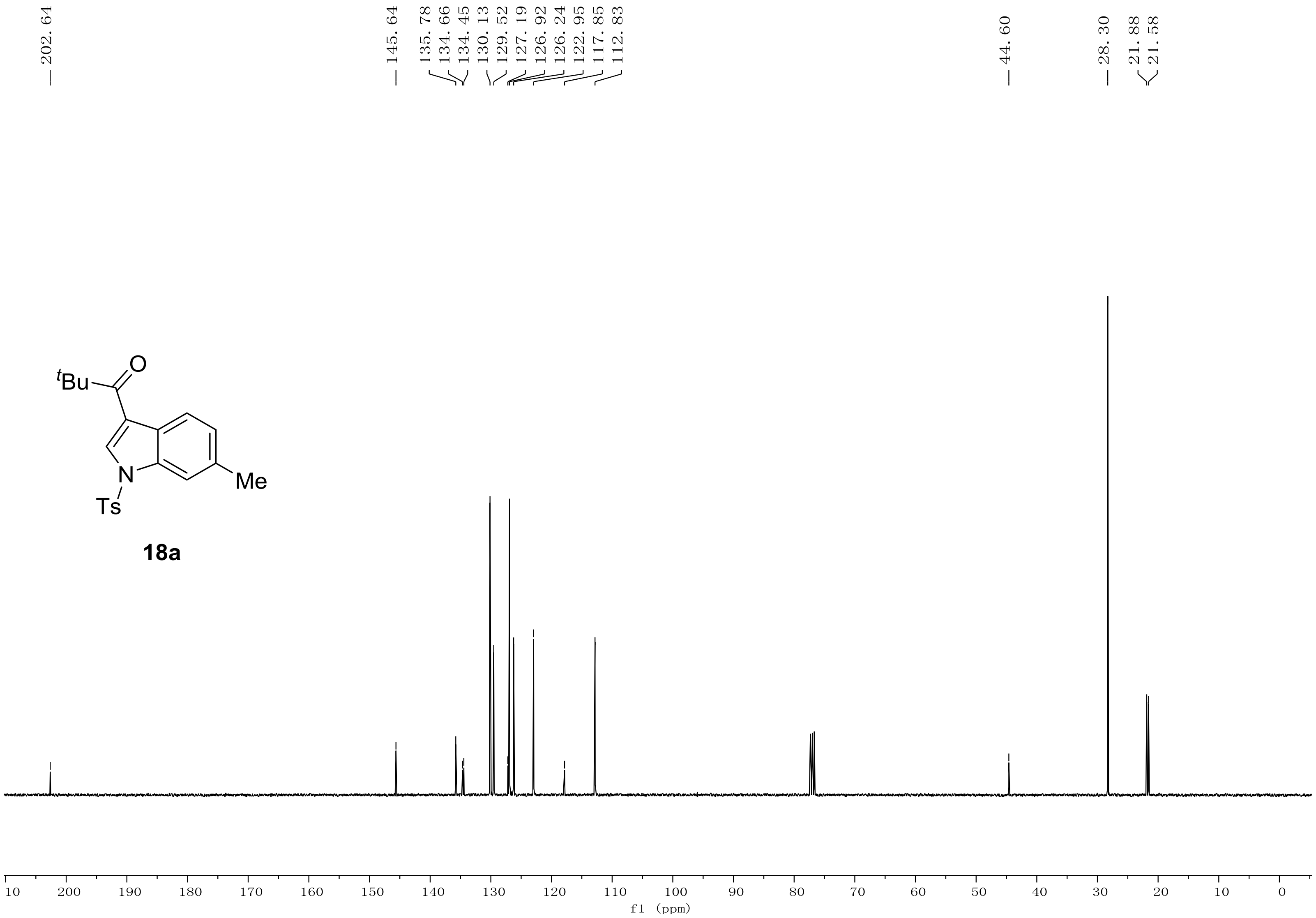

9.00
8.48
8.47
8.46
8.46
7.87
7.86
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.20
1.37
^{t}Bu
O
N
H
17a
0.84
0.98
0.99
1.00
2.24
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



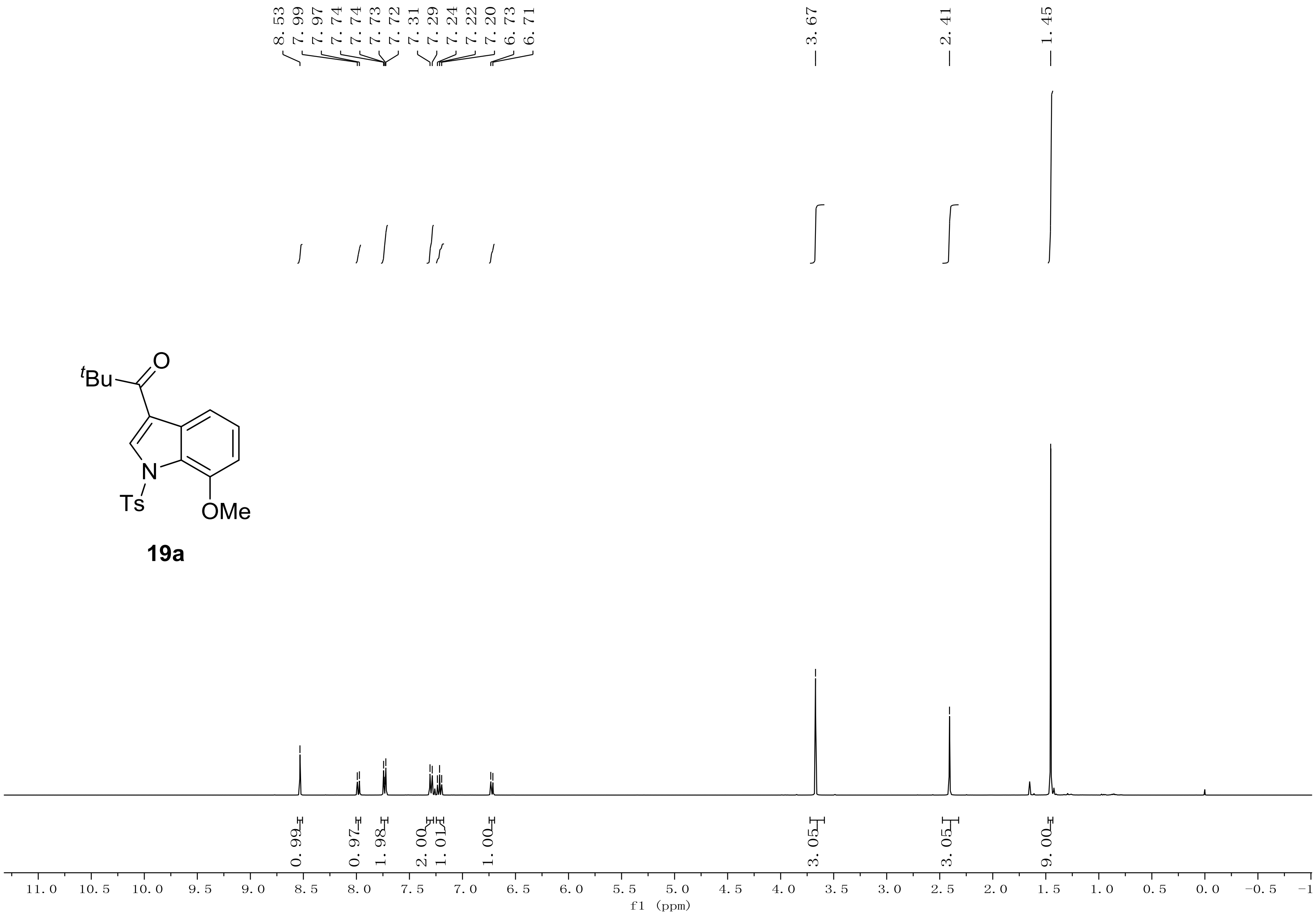
203.11
135.40
130.41
127.27
123.51
122.95
122.52
114.13
111.15
44.16
28.90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

17a


8.18 8.17 8.16 7.81 7.80 7.79 7.78 7.74 7.73 7.73 7.73 7.73 7.28 7.28 7.26 7.26 7.26 7.16 7.16 7.16 7.16 7.14 7.14 7.14 7.14
2.47 2.36
1.41
18a
1.96 1.97 0.97 2.10 1.00 2.98 2.98 9.00
f1 (ppm)

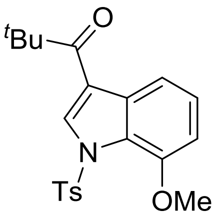


18a

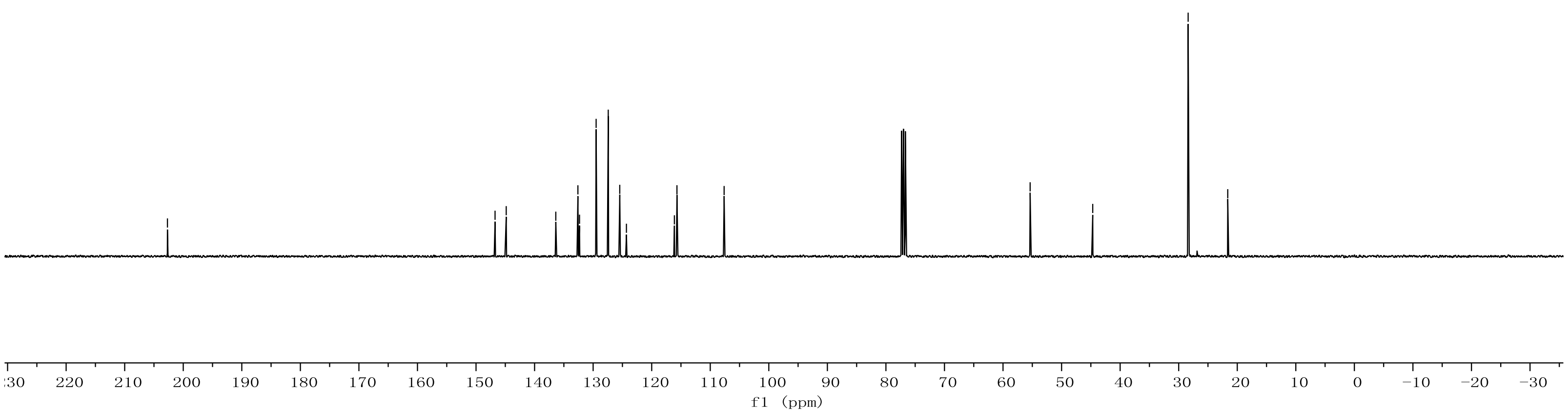


8.53
7.99
7.97
7.74
7.74
7.73
7.72
7.31
7.29
7.24
7.22
7.20
6.73
6.71
3.67
2.41
1.45
0.99
0.97
1.98
2.00
1.01
1.00
3.05
3.05
9.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)
^tBu
O
N
Ts
OMe

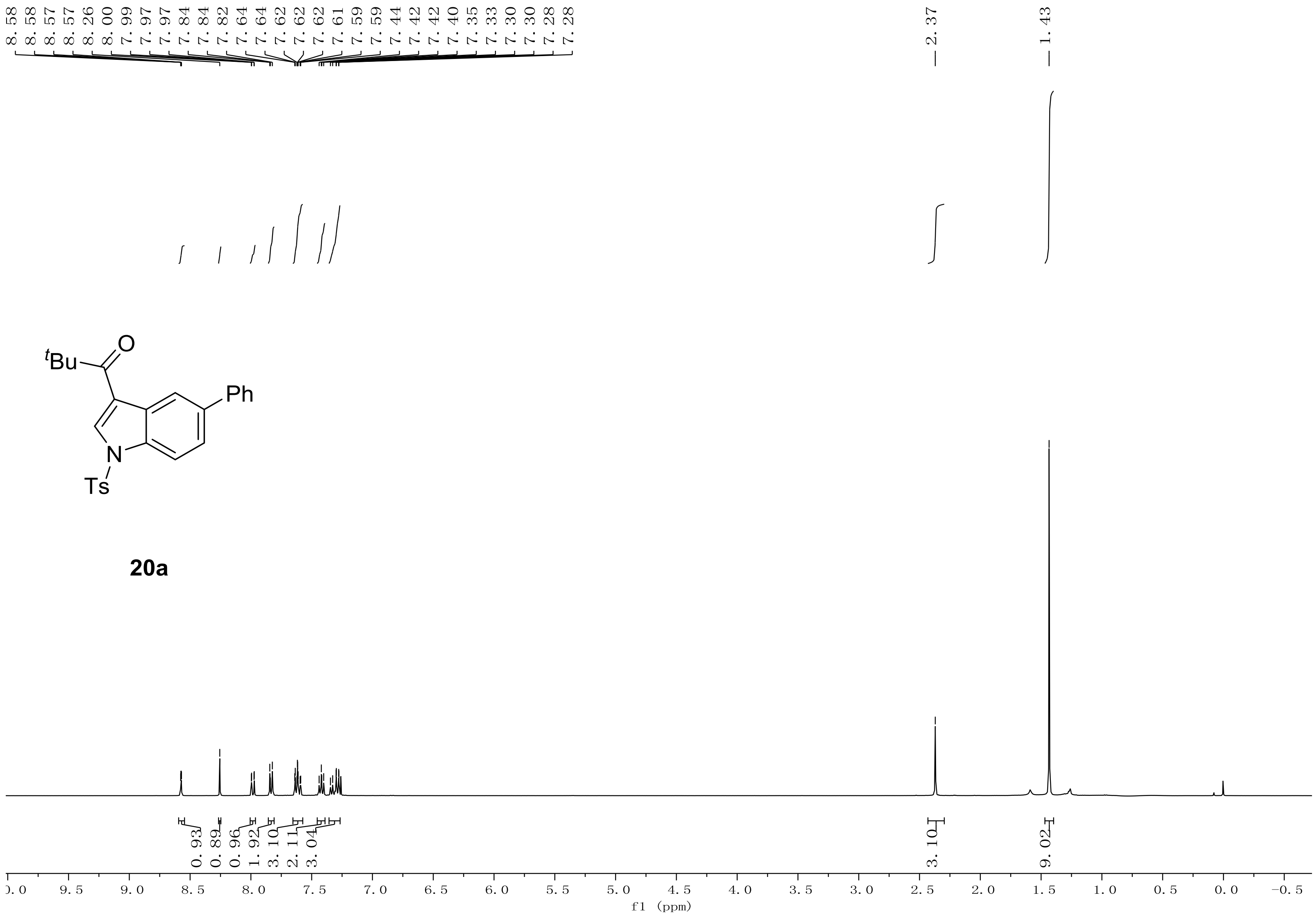
19a



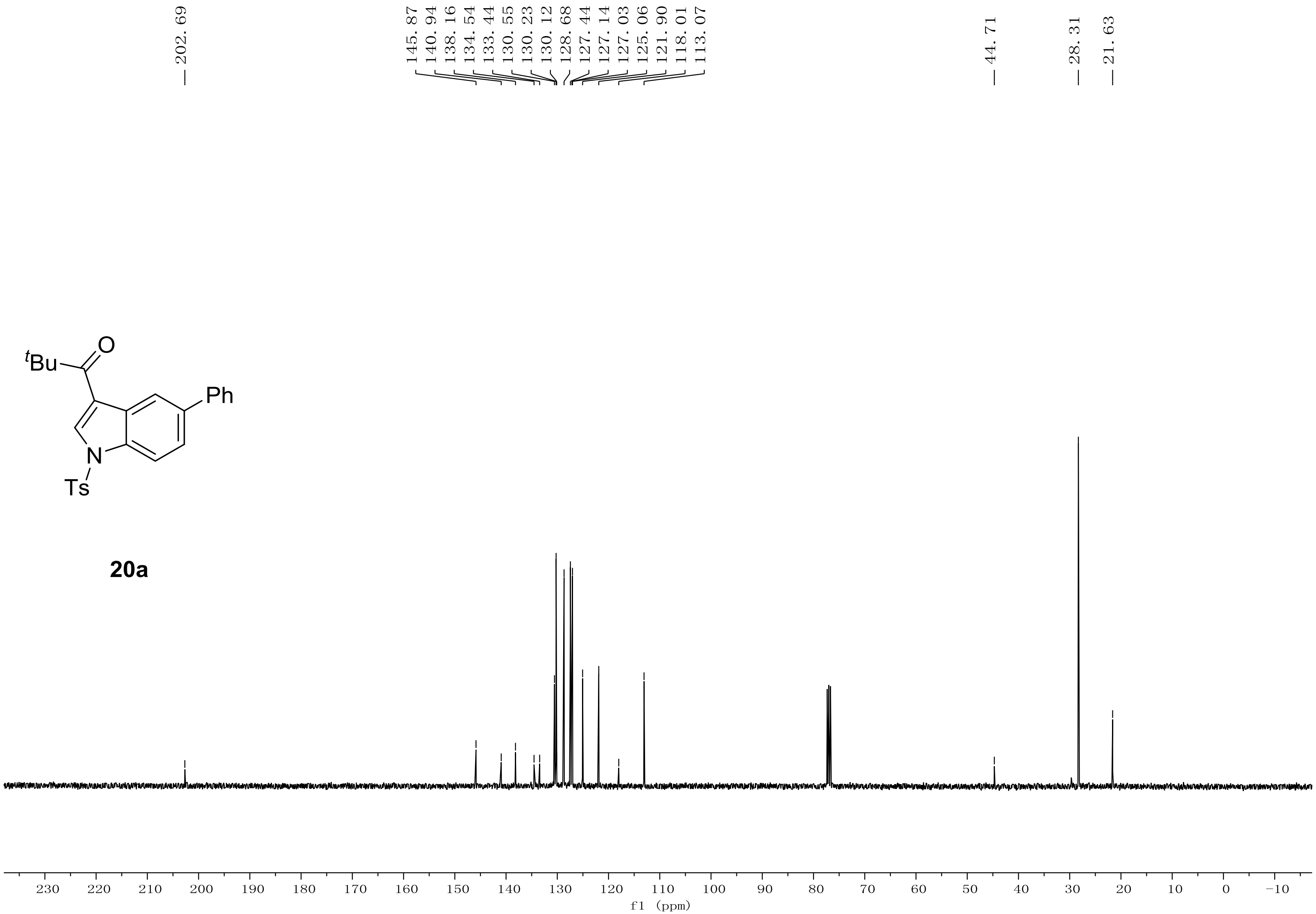
19a



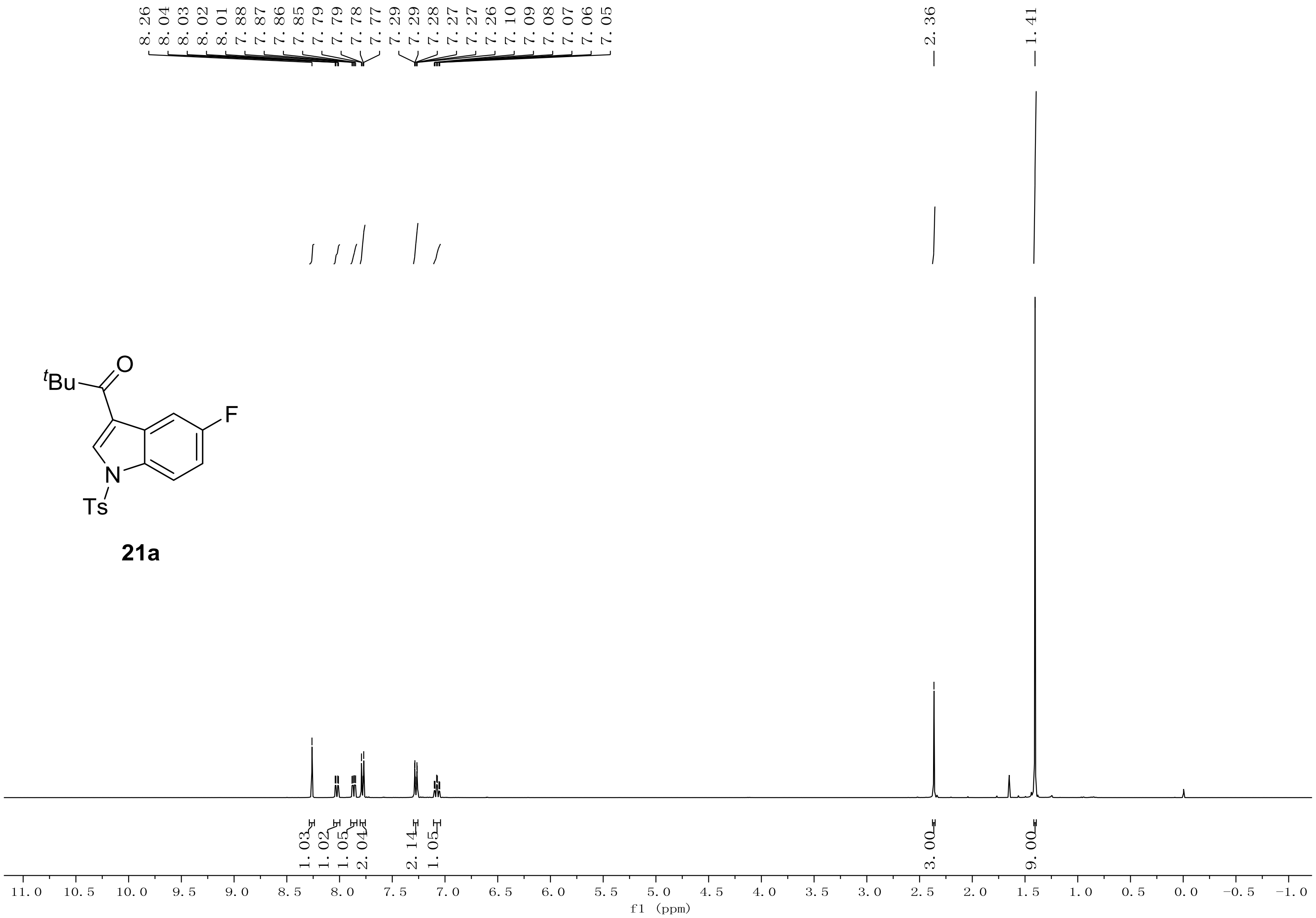
202.70
146.75
144.84
136.37
132.60
132.33
129.49
127.42
125.45
124.31
116.12
115.69
107.63
55.37
44.68
28.39
21.62
f1 (ppm)


8.58
8.58
8.57
8.57
8.26
8.00
7.99
7.97
7.97
7.84
7.84
7.82
7.64
7.64
7.62
7.62
7.62
7.61
7.59
7.59
7.44
7.42
7.42
7.40
7.35
7.33
7.30
7.30
7.28
7.28
2.37
1.43
^{t}Bu
O
Ph
N
Ts
0.93
0.89
0.96
1.92
3.10
2.11
3.04
3.10
9.02
f1 (ppm)

20a

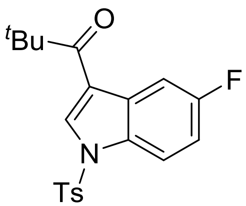


20a
202.69
145.87
140.94
138.16
134.54
133.44
130.55
130.23
130.12
128.68
127.44
127.14
127.03
125.06
121.90
118.01
113.07
44.71
28.31
21.63
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

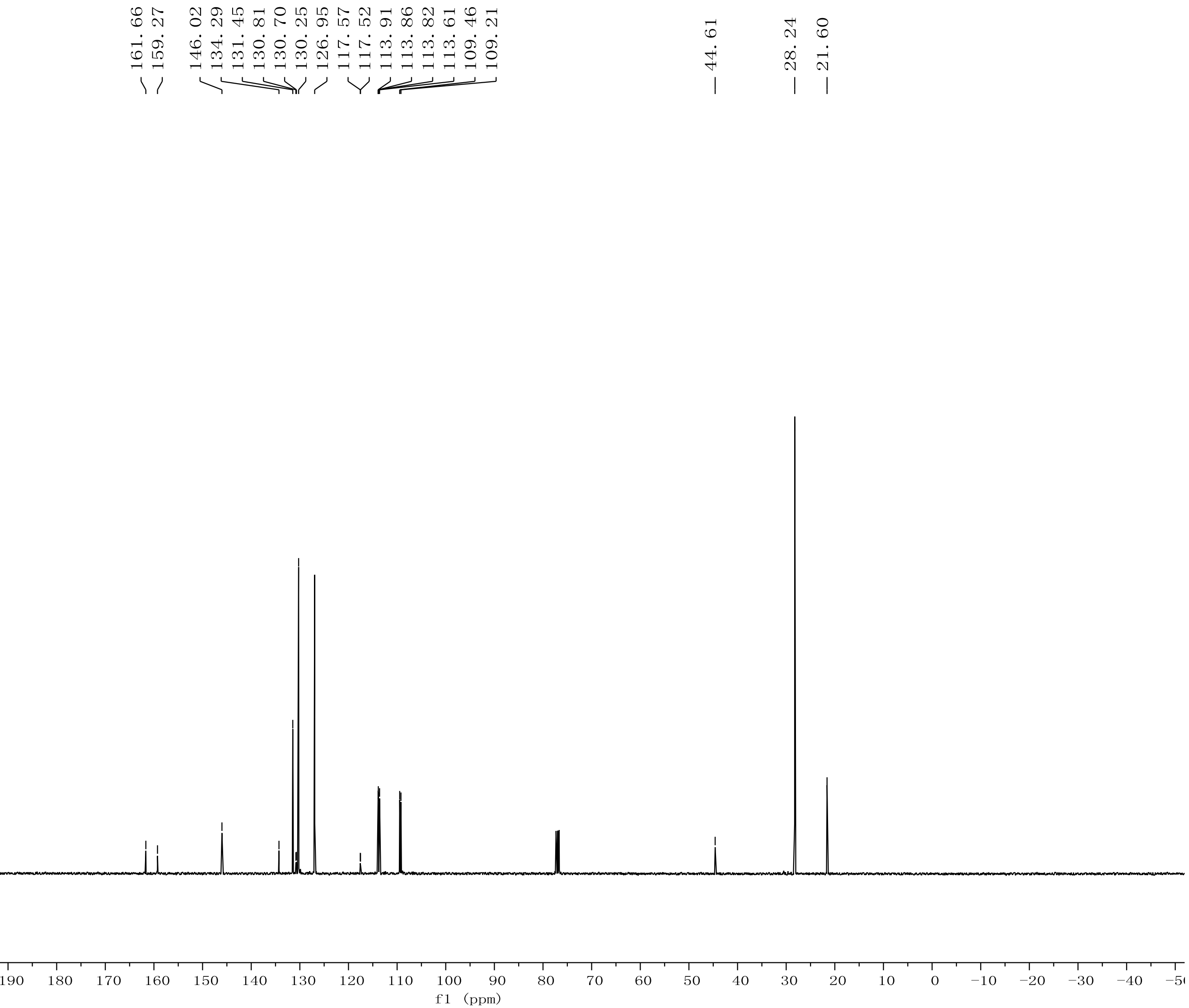


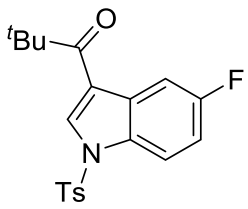
8.26
8.04
8.03
8.02
8.01
7.88
7.87
7.86
7.85
7.79
7.79
7.78
7.77
7.29
7.29
7.28
7.27
7.27
7.26
7.10
7.09
7.08
7.07
7.06
7.05
2.36
1.41
1.03
1.02
1.05
2.04
2.14
1.05
3.00
9.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

21a



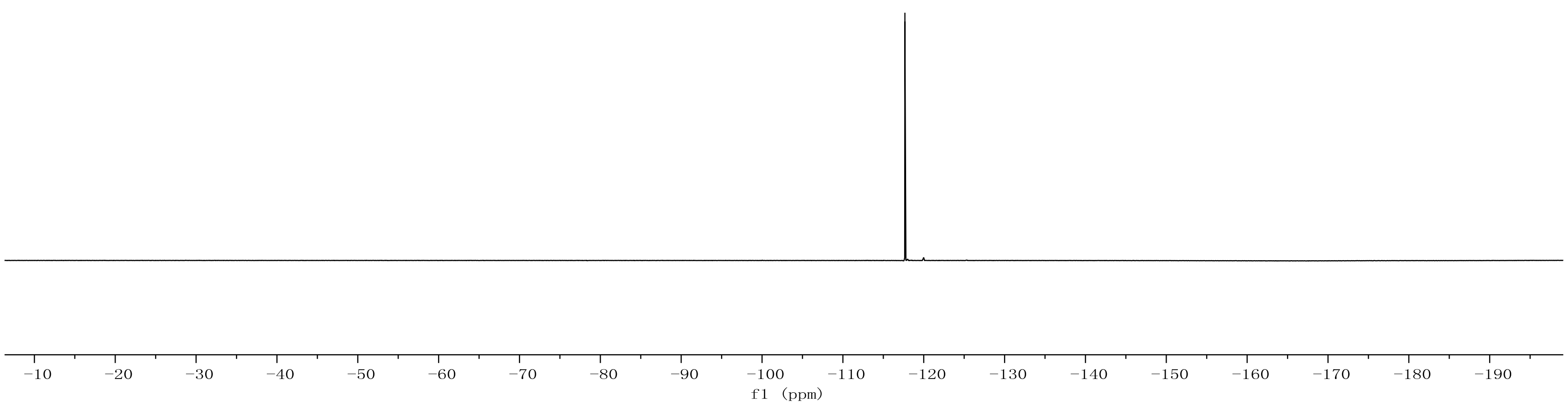
21a


202.19
161.66
159.27
146.02
134.29
131.45
130.81
130.70
130.25
126.95
117.57
117.52
113.91
113.86
113.82
113.61
109.46
109.21
44.61
28.24
21.60
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −5
f1 (ppm)

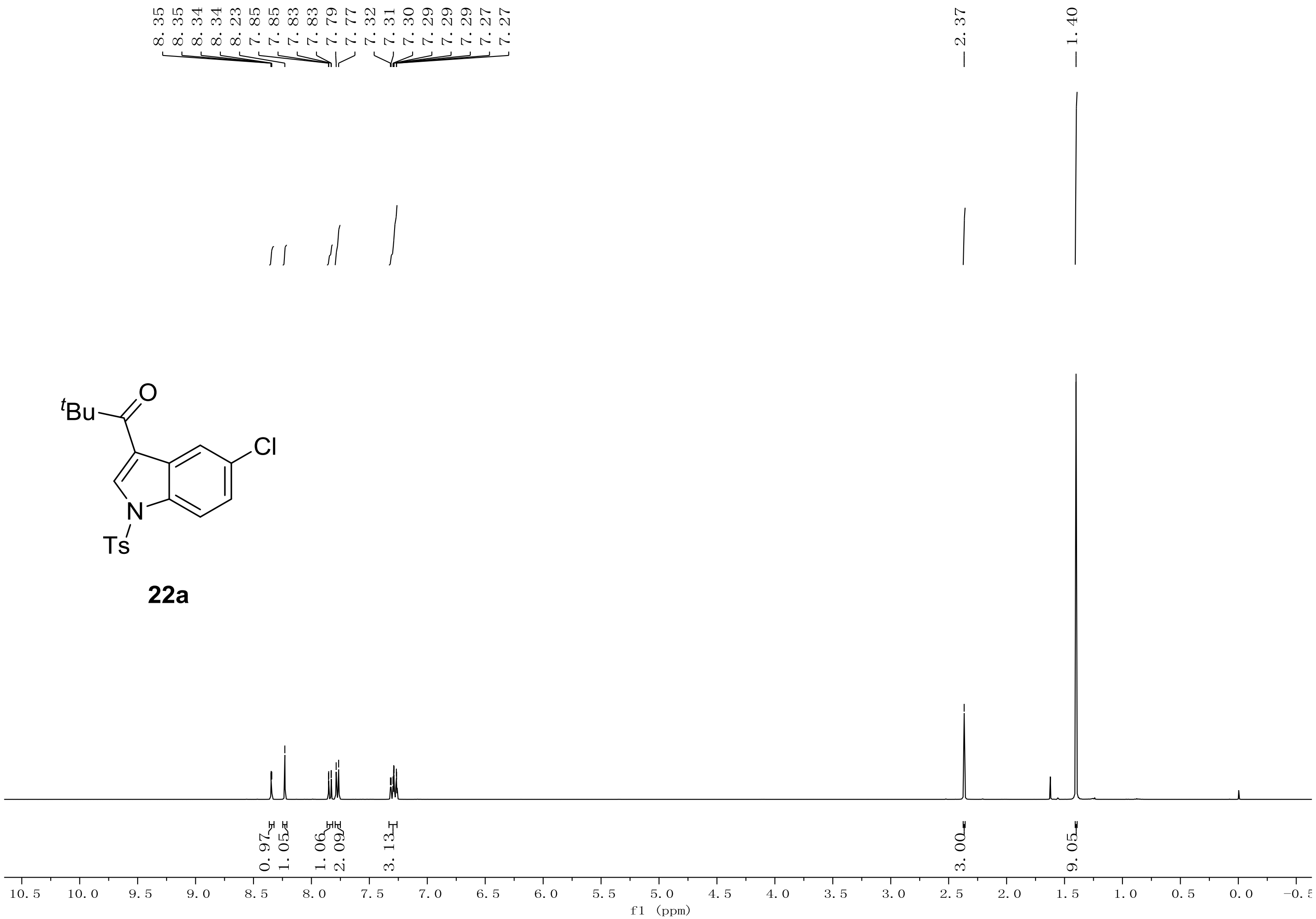


tBu
O
F
N
Ts

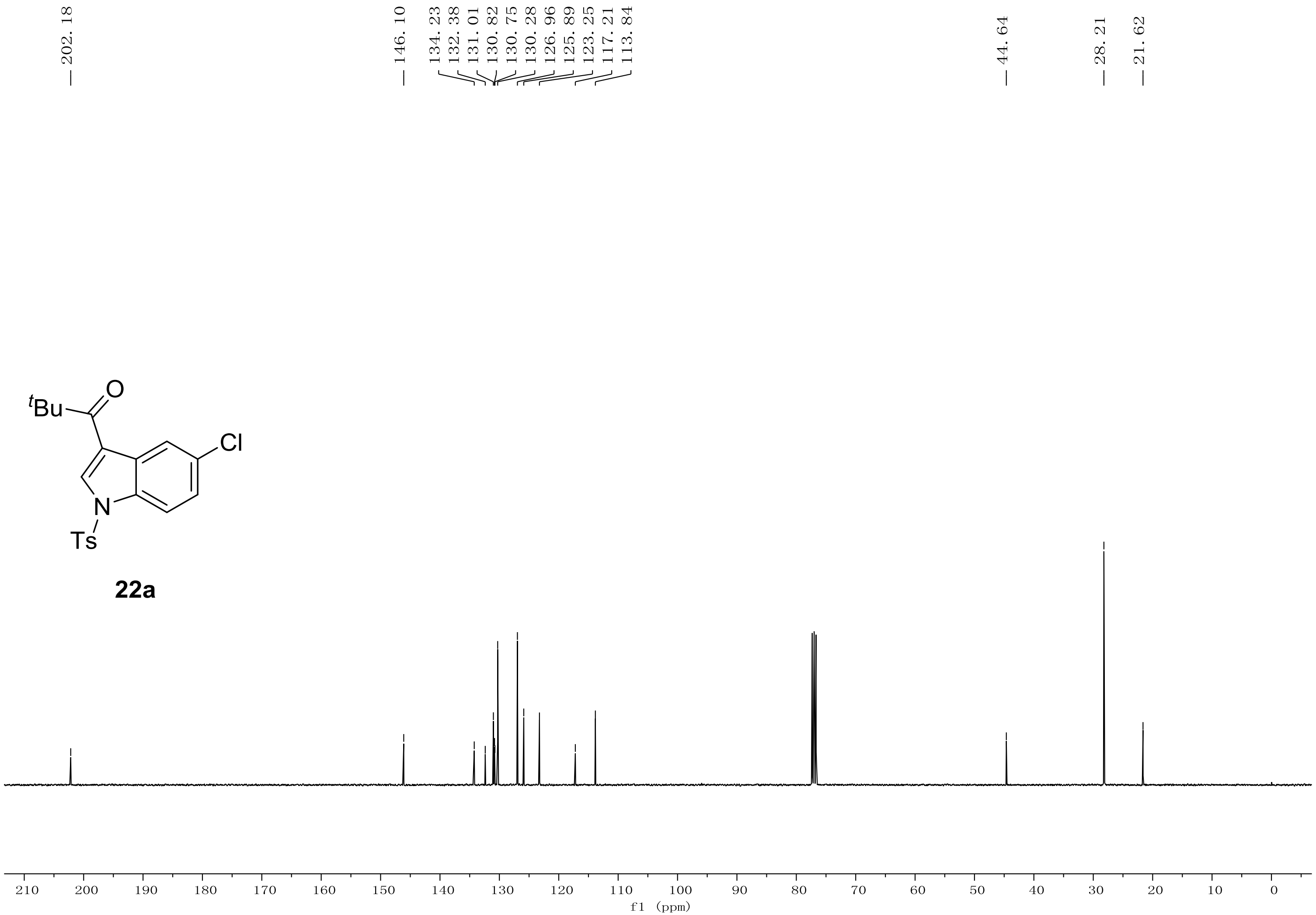
21a



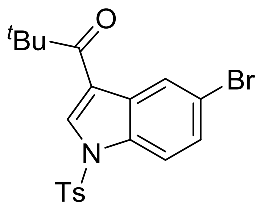
−117.67
−10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)


8.35
8.35
8.34
8.34
8.23
7.85
7.85
7.83
7.83
7.79
7.77
7.32
7.31
7.30
7.29
7.29
7.29
7.27
7.27
2.37
1.40
tBu
O
Cl
N
Ts
0.97
1.05
1.06
2.09
3.13
3.00
9.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

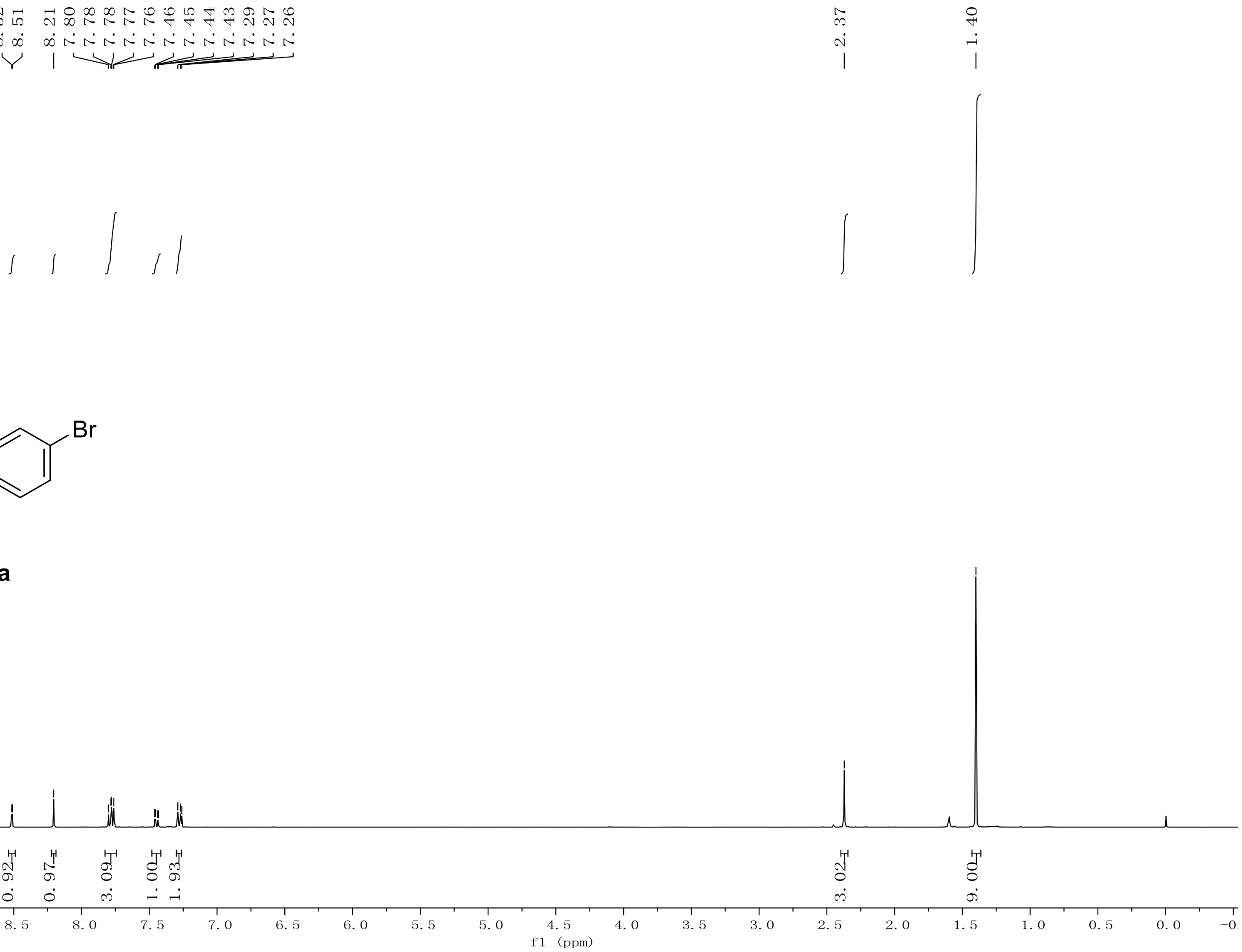
22a


202.18
146.10
134.23
132.38
131.01
130.82
130.75
130.28
126.96
125.89
123.25
117.21
113.84
44.64
28.21
21.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

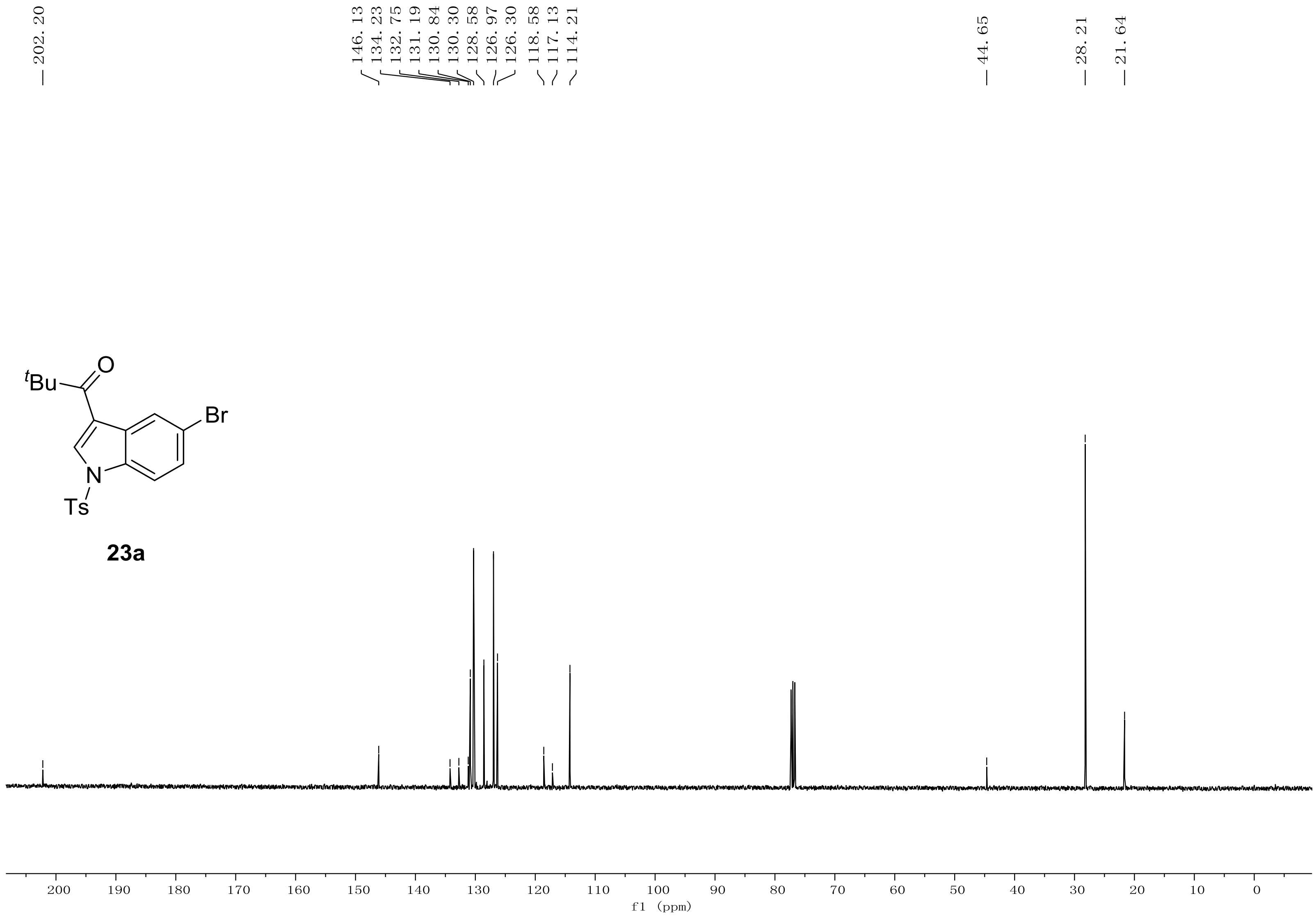
22a

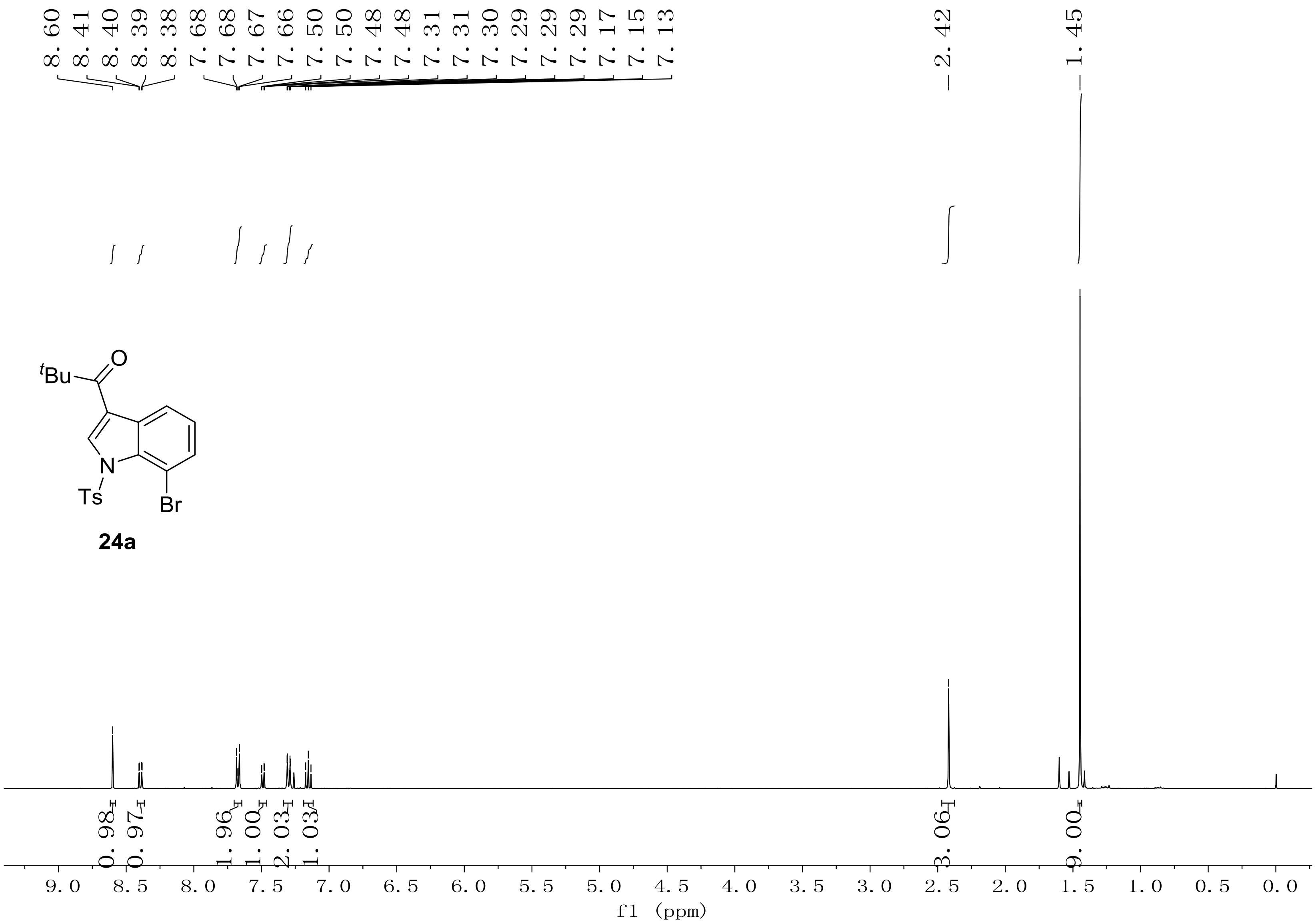


23a

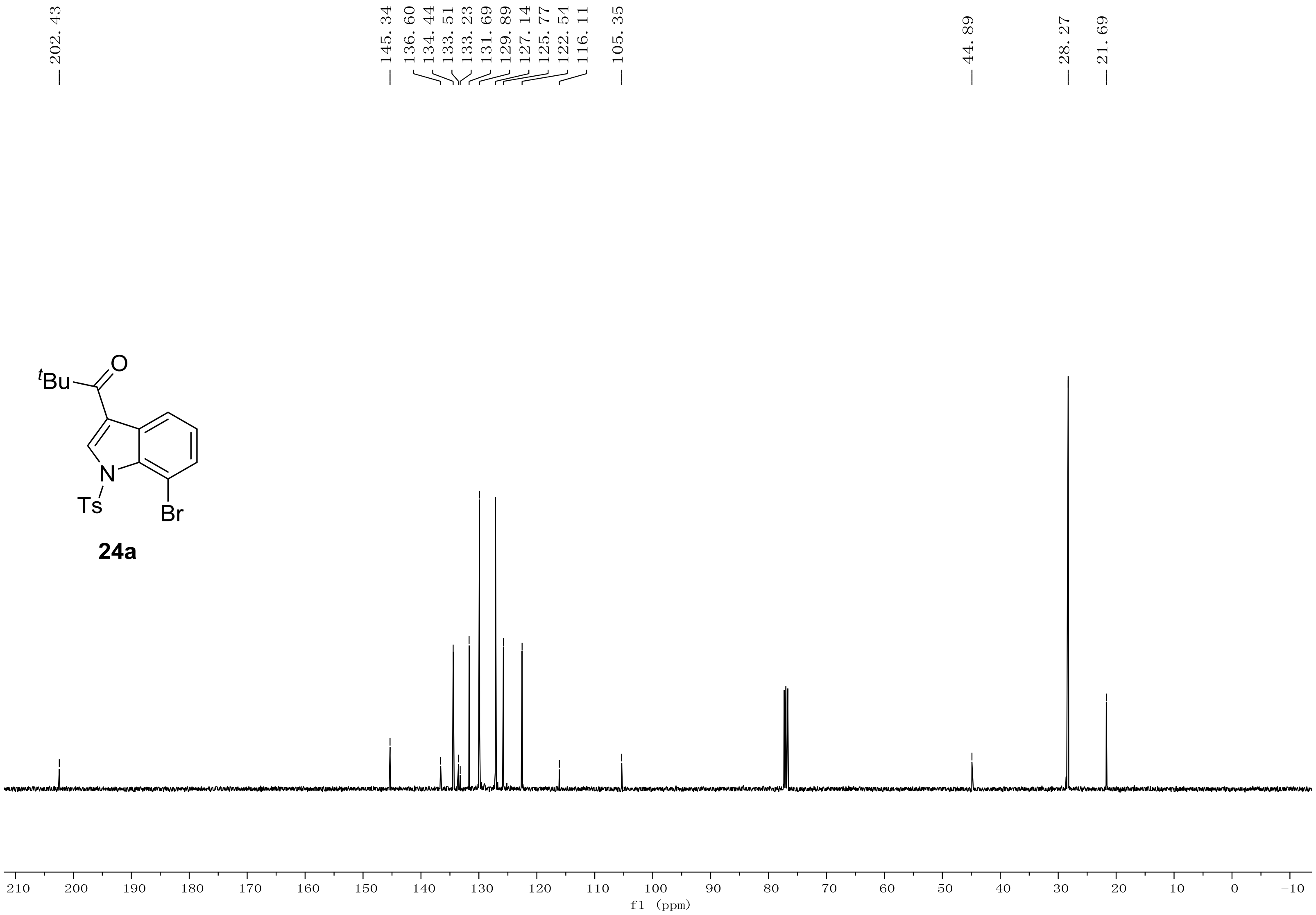


8.52
8.51
8.21
7.80
7.78
7.78
7.77
7.76
7.46
7.45
7.44
7.43
7.29
7.27
7.26
2.37
1.40
0.92
0.97
3.09
1.00
1.93
3.02
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

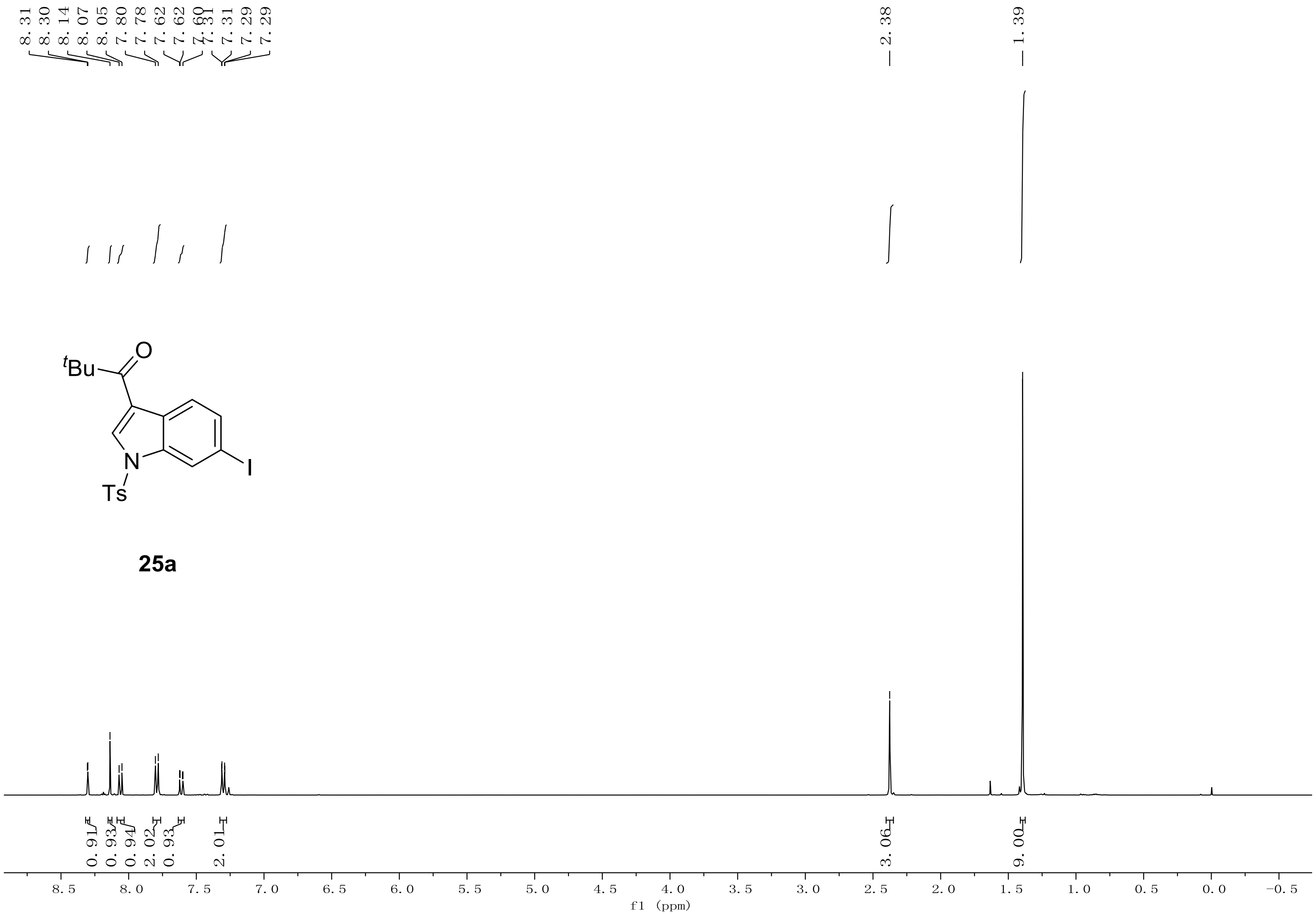

202.20
146.13
134.23
132.75
131.19
130.84
130.30
128.58
126.97
126.30
118.58
117.13
114.21
44.65
28.21
21.64
O
tBu
Br
N
Ts
23a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

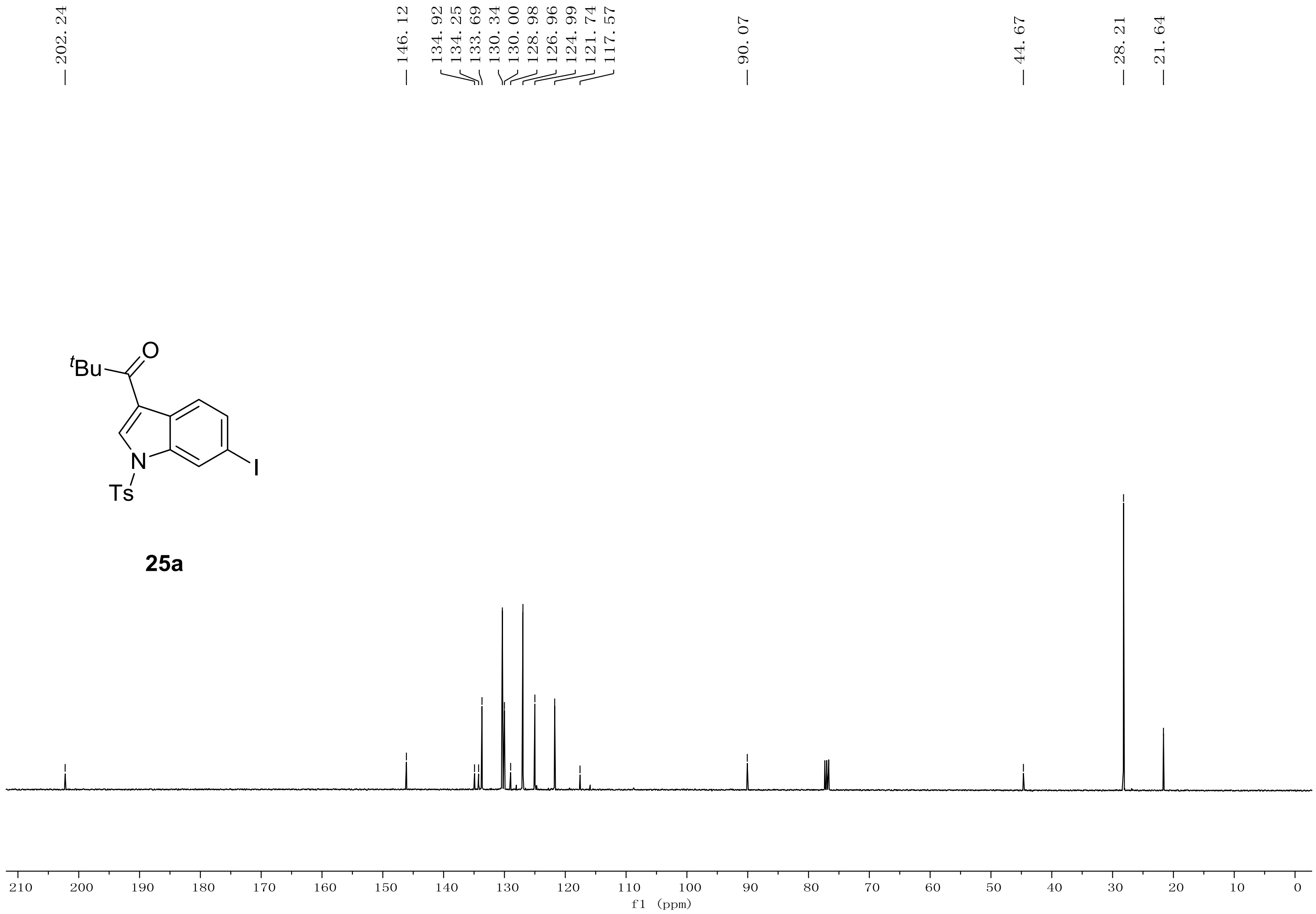

8.60
8.41
8.40
8.39
8.38
7.68
7.68
7.67
7.66
7.50
7.50
7.48
7.48
7.31
7.31
7.30
7.29
7.29
7.29
7.17
7.15
7.13
2.42
1.45
tBu
O
N
Ts
Br
0.98
0.97
1.96
1.00
2.03
1.03
3.06
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

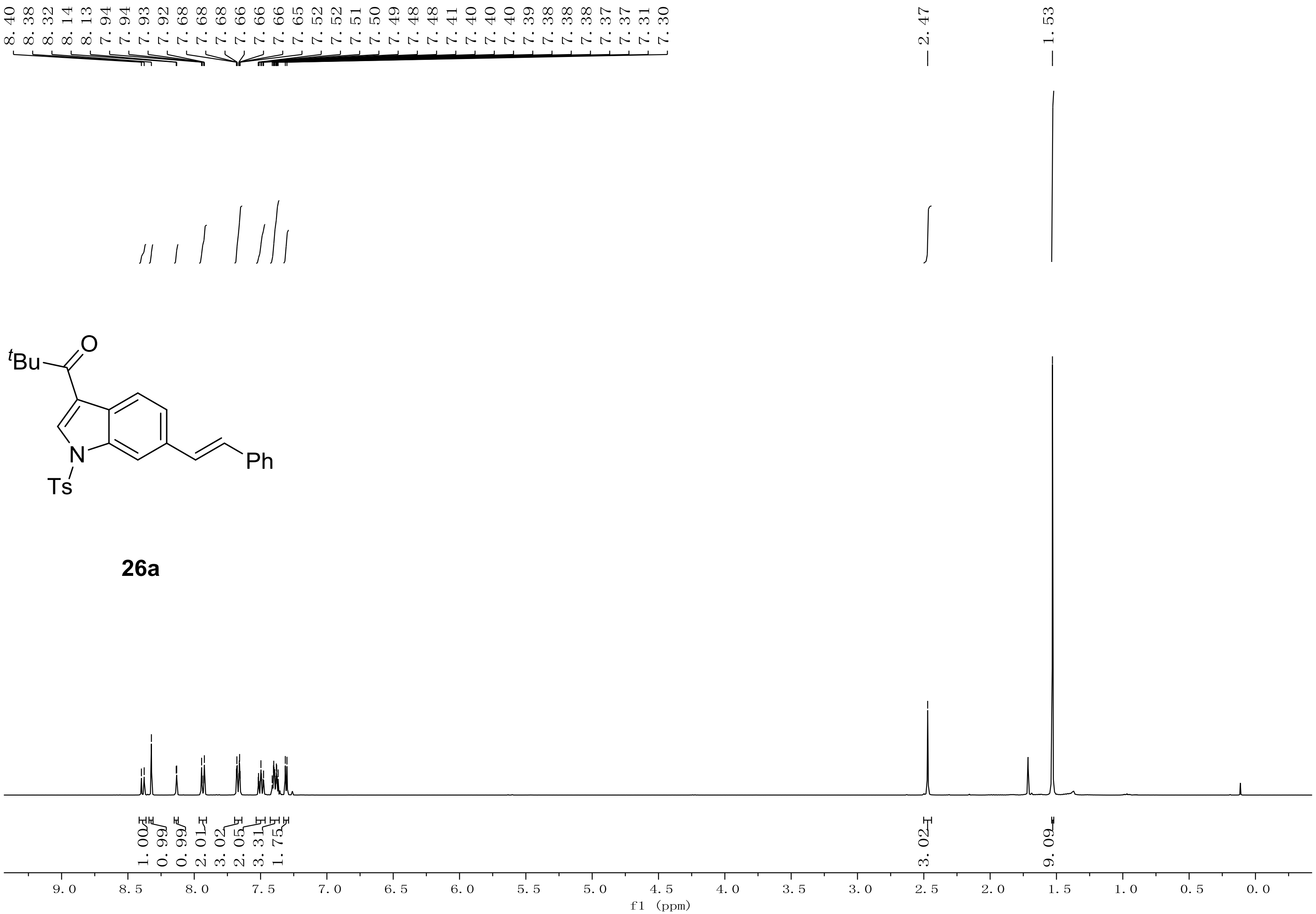
24a


202.43
145.34
136.60
134.44
133.51
133.23
131.69
129.89
127.14
125.77
122.54
116.11
105.35
44.89
28.27
21.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
tBu
O
N
Ts
Br

24a

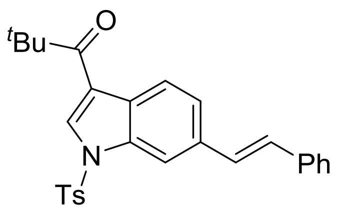

8.31
8.30
8.14
8.07
8.05
7.80
7.78
7.62
7.62
7.60
7.31
7.31
7.29
7.29
2.38
1.39
tBu
O
N
Ts
I
25a
0.91
0.93
0.94
2.02
0.93
2.01
3.06
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


25a
202.24
146.12
134.92
134.25
133.69
130.34
130.00
128.98
126.96
124.99
121.74
117.57
90.07
44.67
28.21
21.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

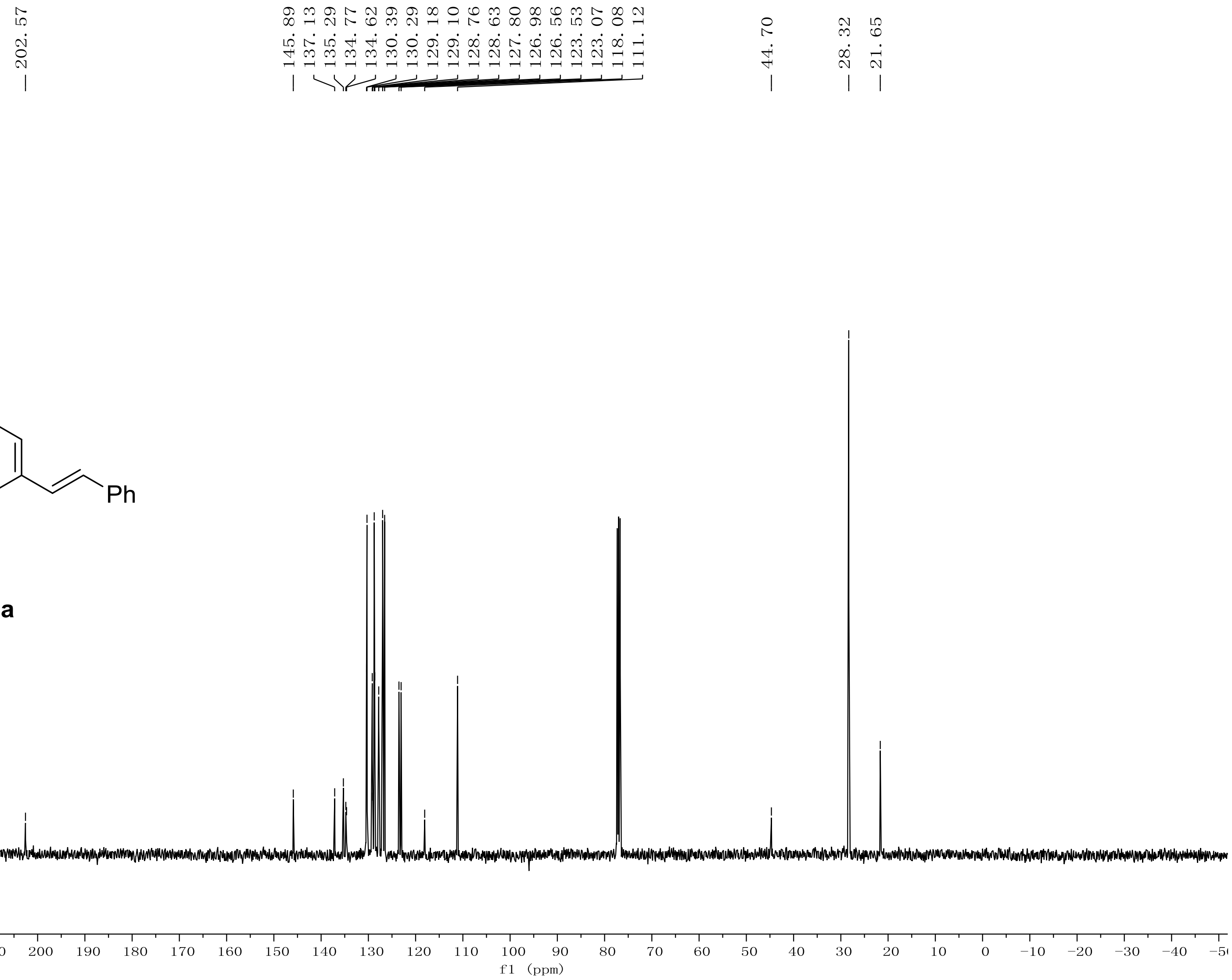


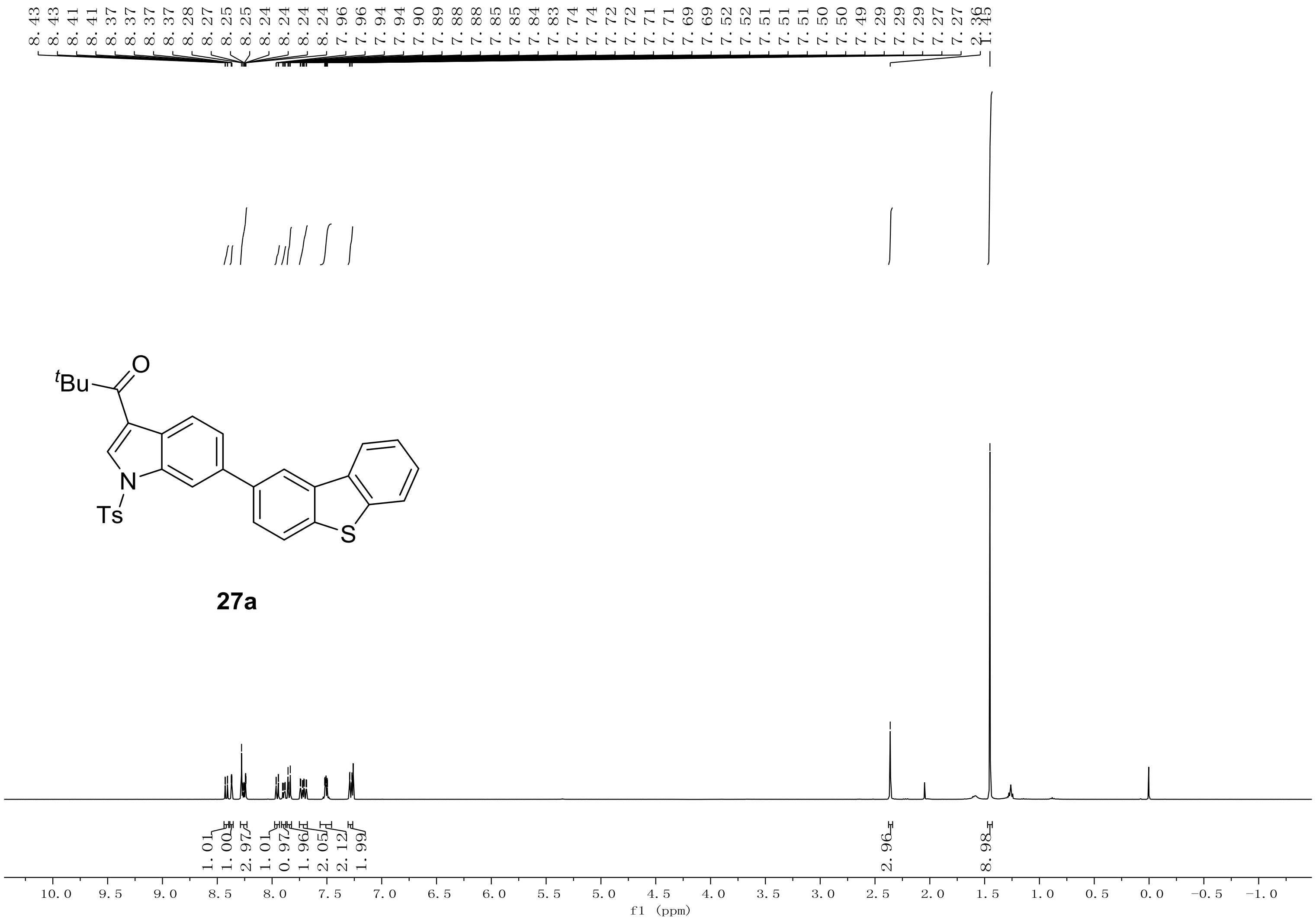
8.40
8.38
8.32
8.14
8.13
7.94
7.94
7.93
7.92
7.68
7.68
7.68
7.66
7.66
7.66
7.65
7.52
7.52
7.51
7.50
7.49
7.48
7.48
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.31
7.30
2.47
1.53
1.00
0.99
0.99
2.01
3.02
2.05
3.31
1.75
3.02
9.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
^{t}Bu
O
N
Ts
Ph

26a

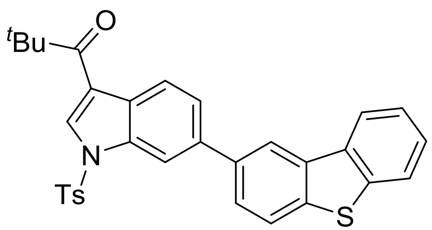

tBu
O
N
Ts
Ph

26a

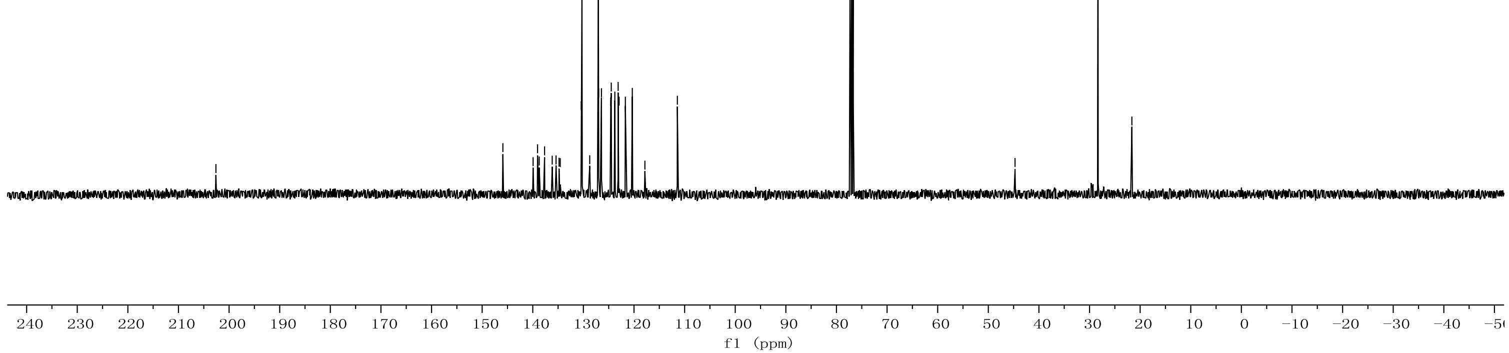

202.57
145.89
137.13
135.29
134.77
134.62
130.39
130.29
129.18
129.10
128.76
128.63
127.80
126.98
126.56
123.53
123.07
118.08
111.12
44.70
28.32
21.65
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)



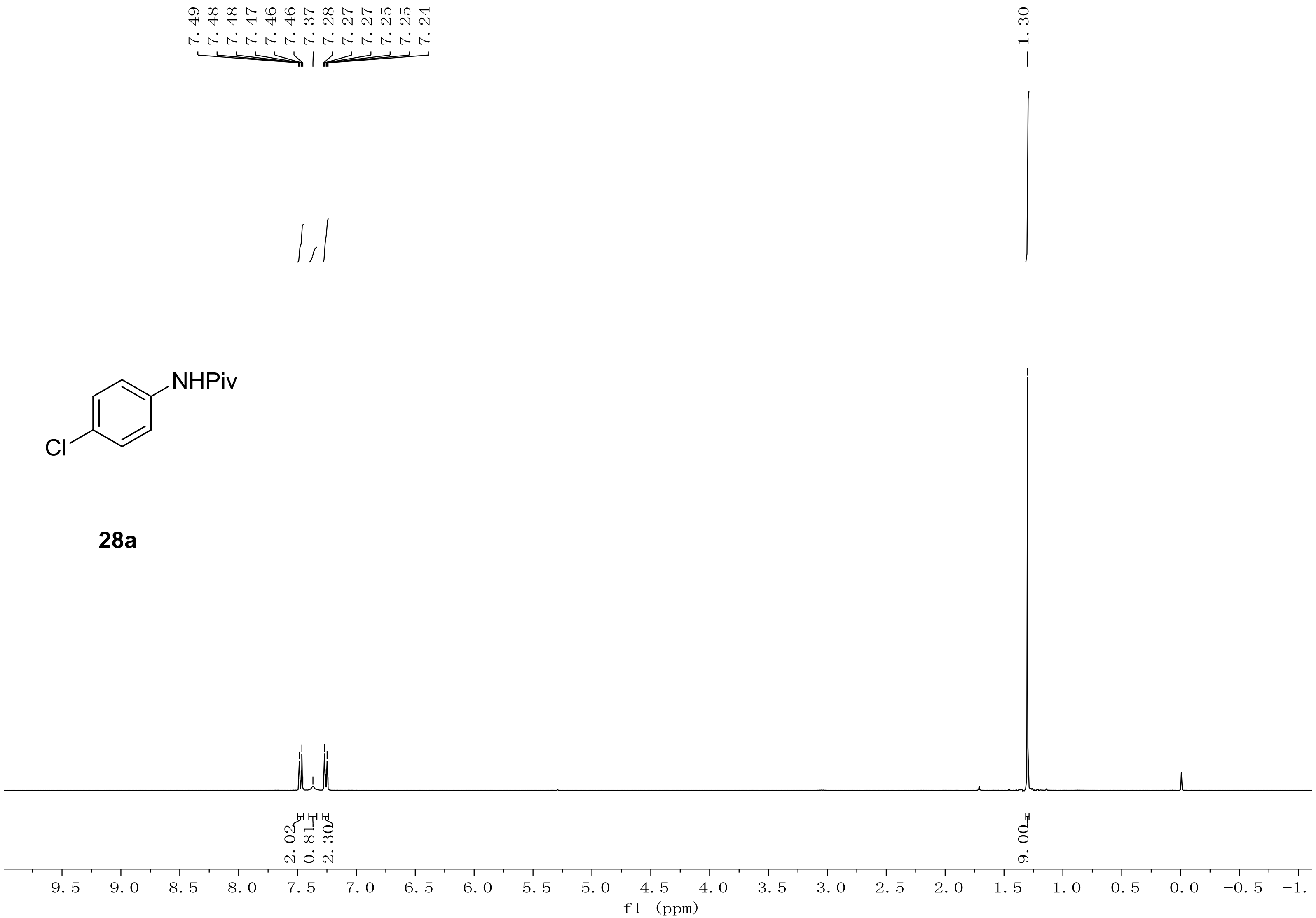
27a



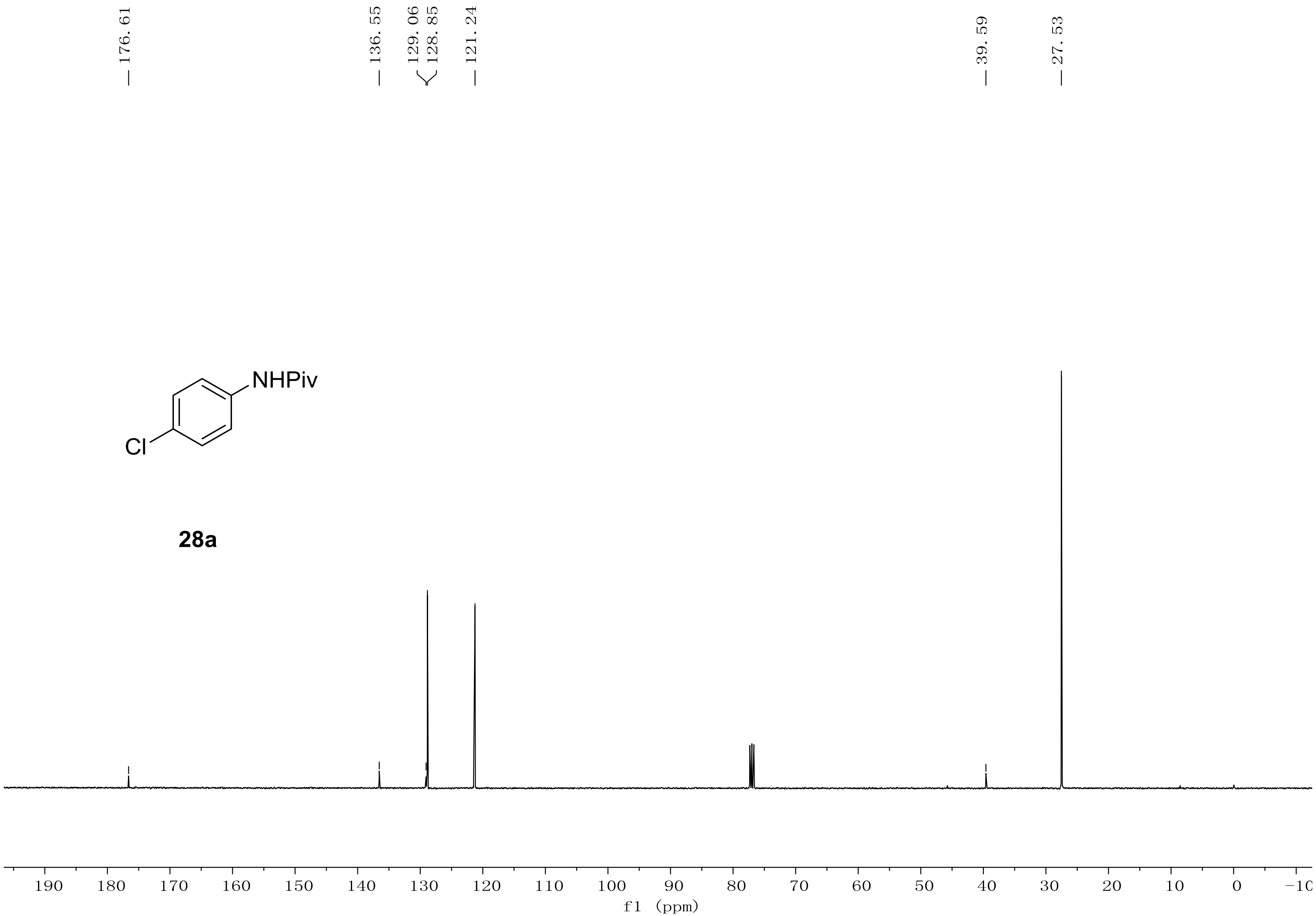
27a



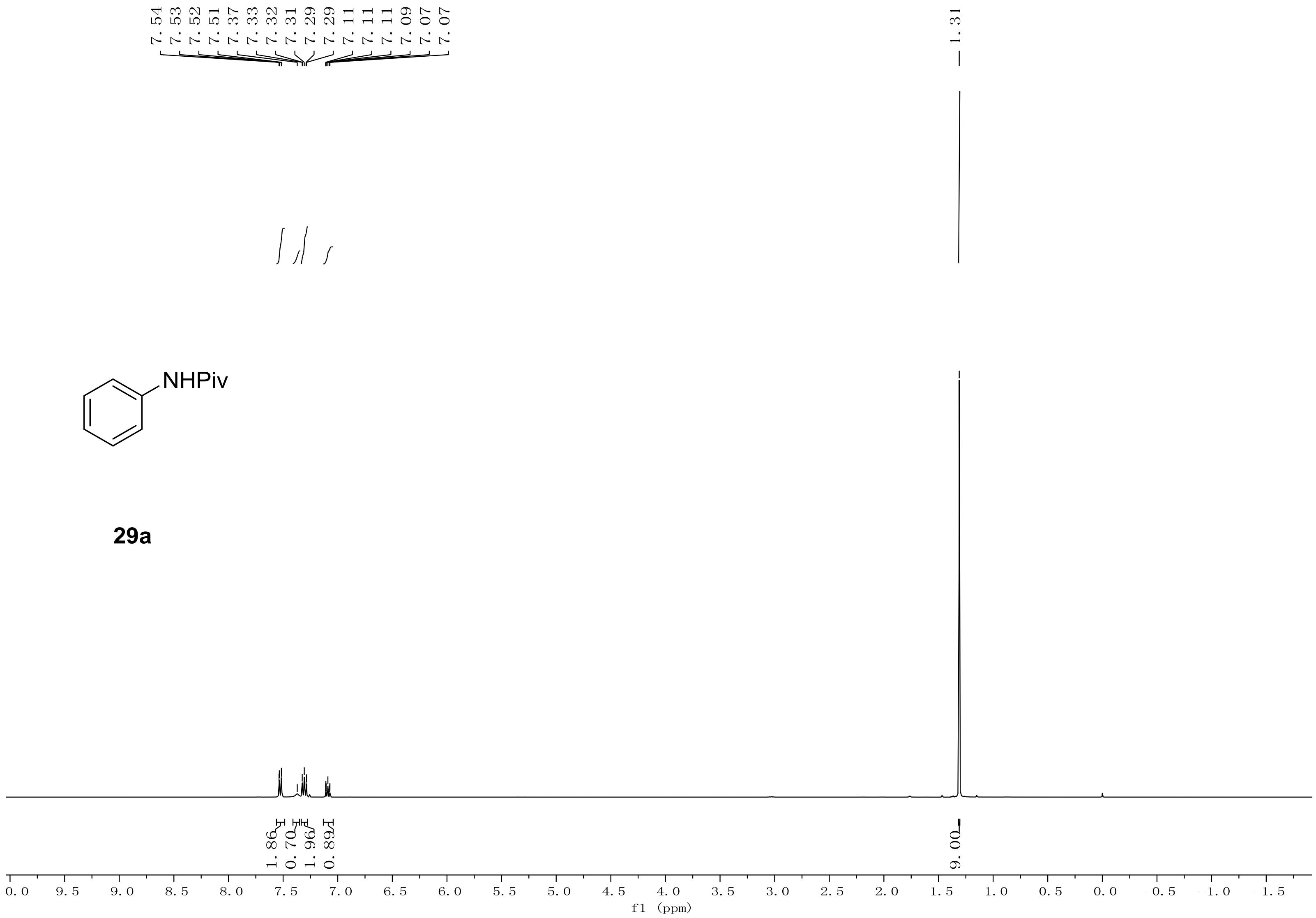
202.60
145.91
139.93
139.05
138.72
137.67
136.16
135.40
134.81
134.57
130.43
130.28
128.75
127.04
126.98
126.43
124.60
124.49
123.79
123.13
122.94
121.71
120.34
117.85
111.43
44.72
28.33
21.63
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50
f1 (ppm)


7.49
7.48
7.48
7.47
7.46
7.46
7.37
7.28
7.27
7.27
7.25
7.25
7.24
1.30
NHPiv
Cl
2.02
0.81
2.30
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

28a

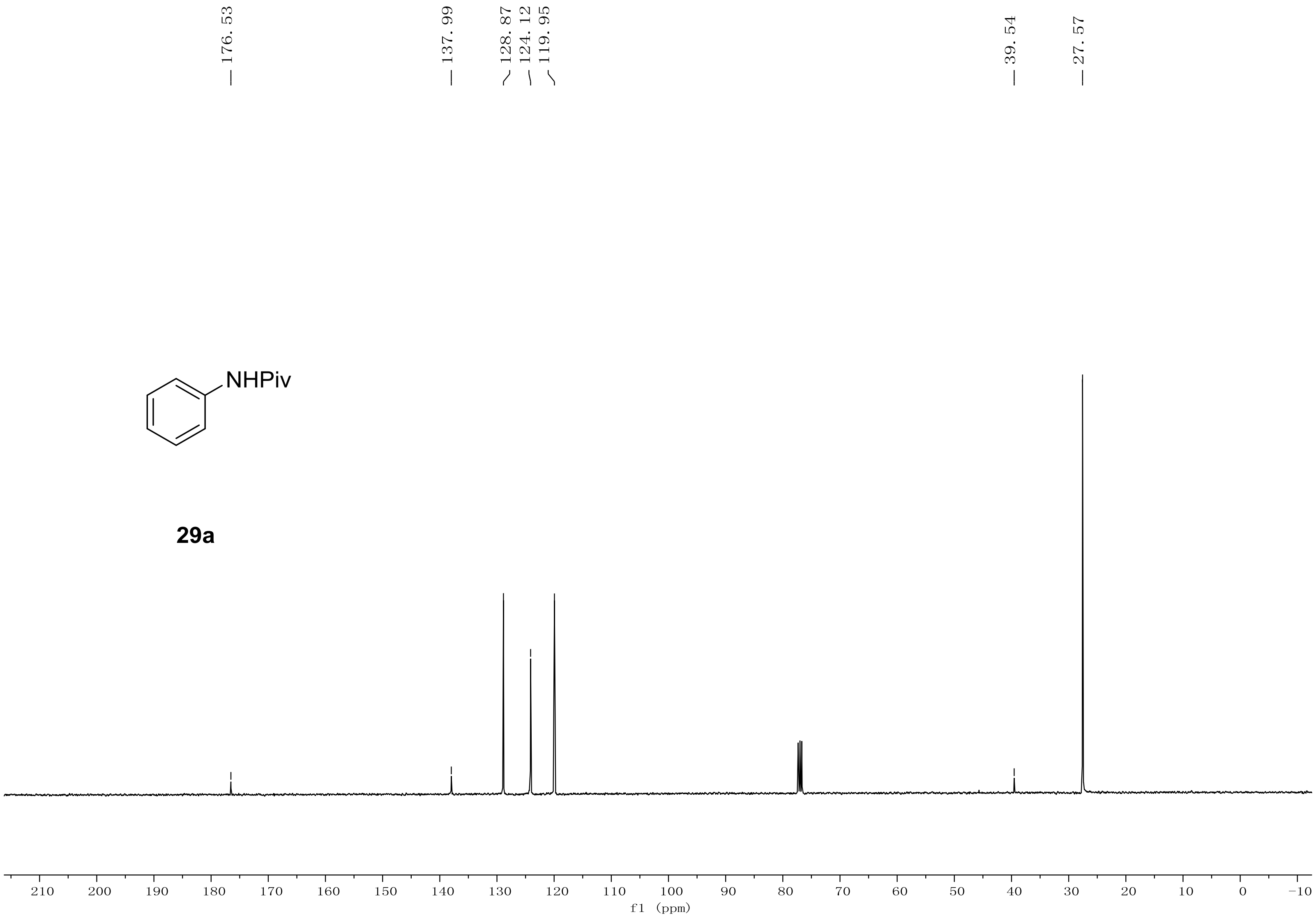

176.61
136.55
129.06
128.85
121.24
39.59
27.53
NHPiv
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

28a



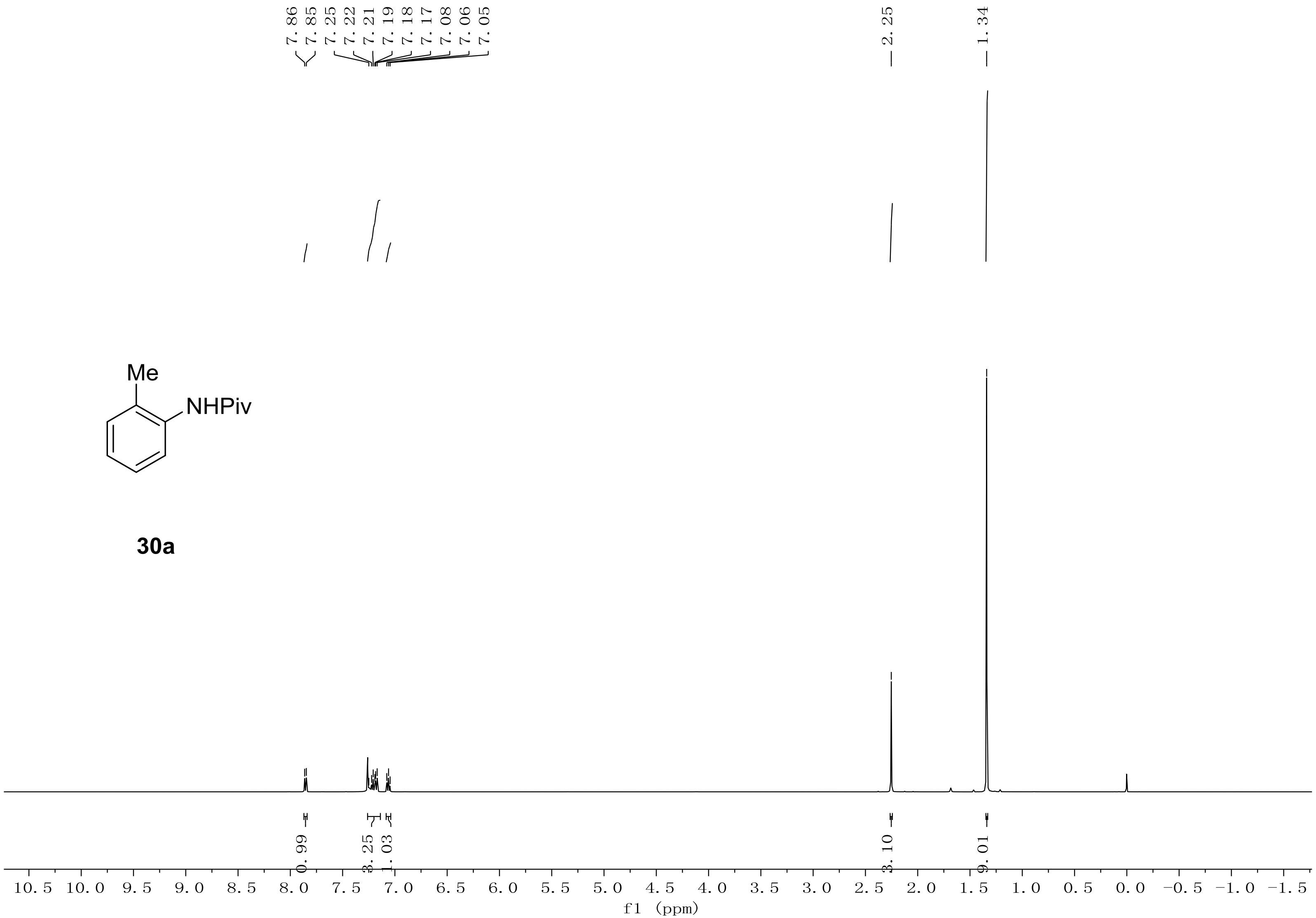
NHPiv
7.54
7.53
7.52
7.51
7.37
7.33
7.32
7.31
7.29
7.29
7.11
7.11
7.11
7.09
7.07
7.07
1.31
1.86
0.70
1.96
0.89
9.00
f1 (ppm)

29a



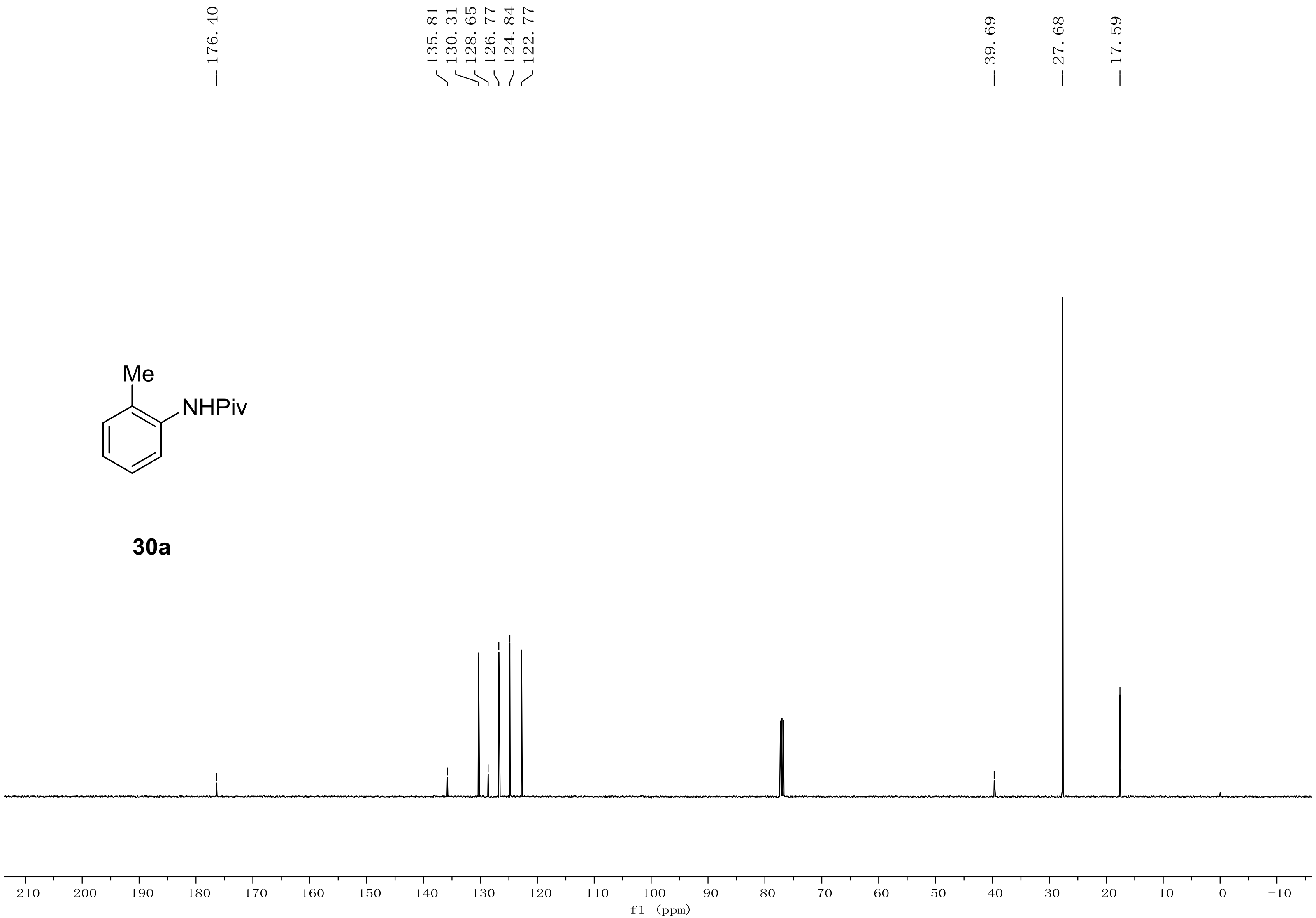
176.53
137.99
128.87
124.12
119.95
39.54
27.57
NHPiv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

29a



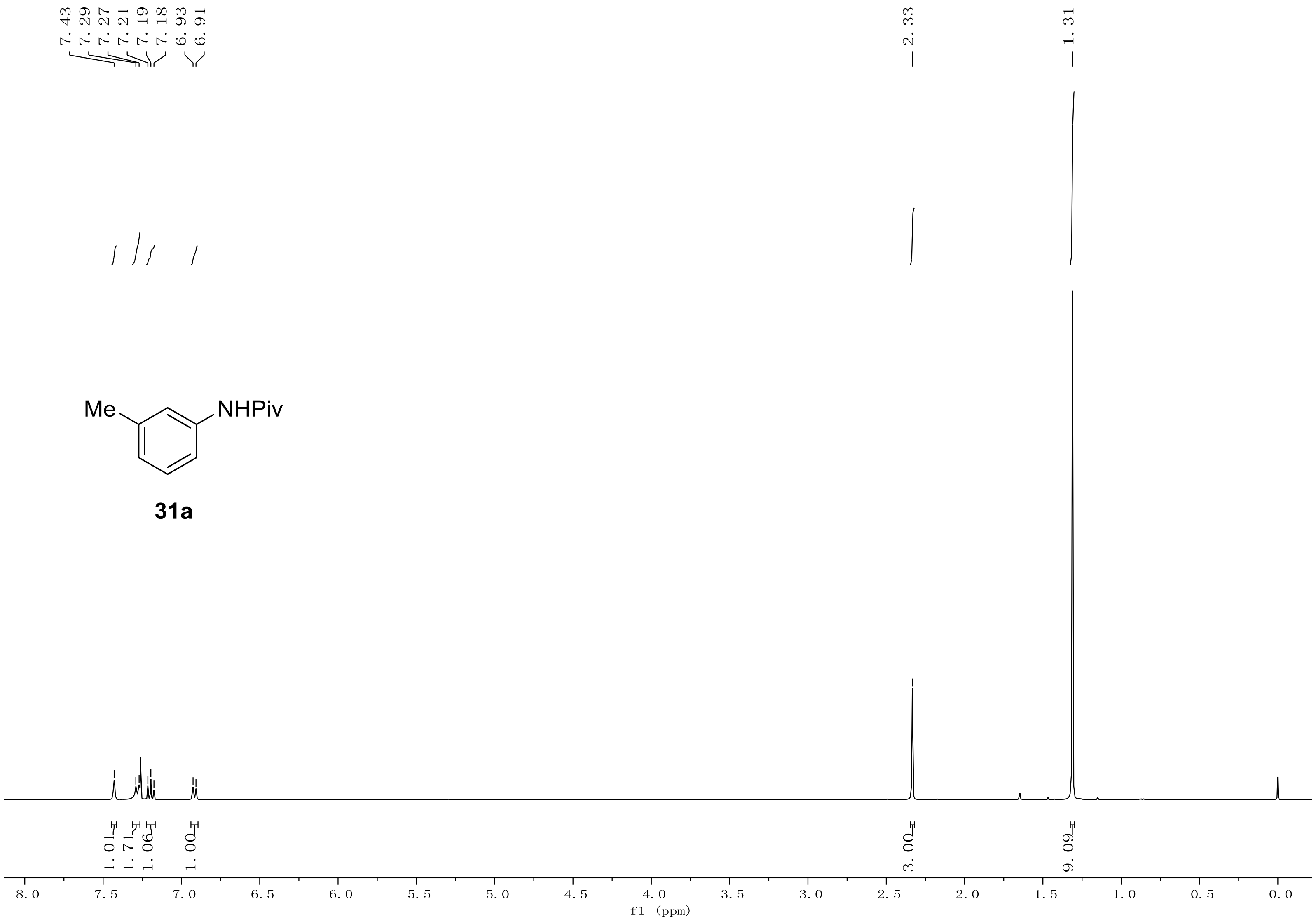
7.86
7.85
7.25
7.22
7.21
7.19
7.18
7.17
7.08
7.06
7.05
2.25
1.34
Me
NHPiv
0.99
3.25
1.03
3.10
9.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

30a

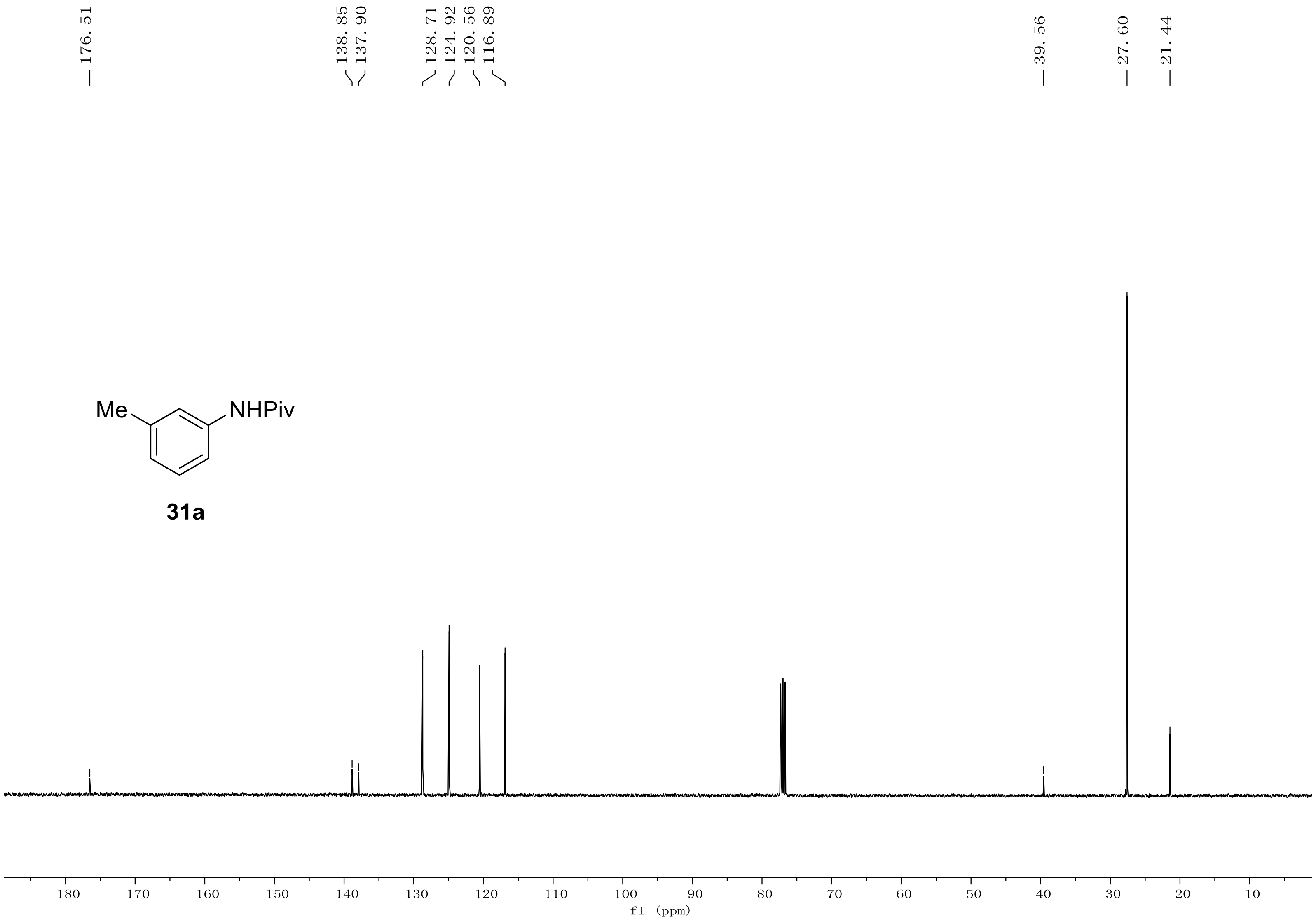


176.40
135.81
130.31
128.65
126.77
124.84
122.77
39.69
27.68
17.59
Me
NHPiv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

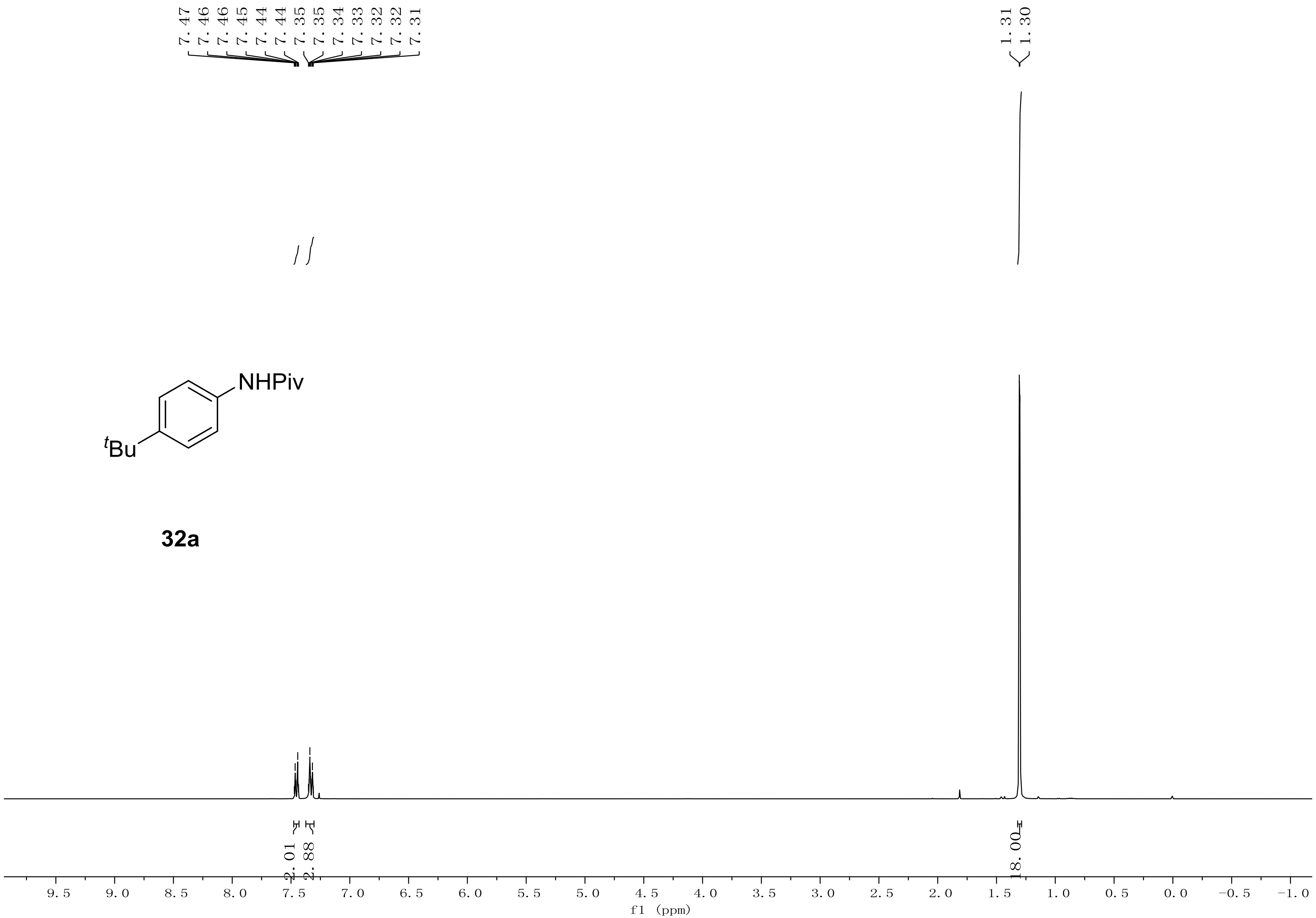
30a


7.43
7.29
7.27
7.21
7.19
7.18
6.93
6.91
2.33
1.31
Me
NHPiv
1.01
1.71
1.06
1.00
3.00
9.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

31a

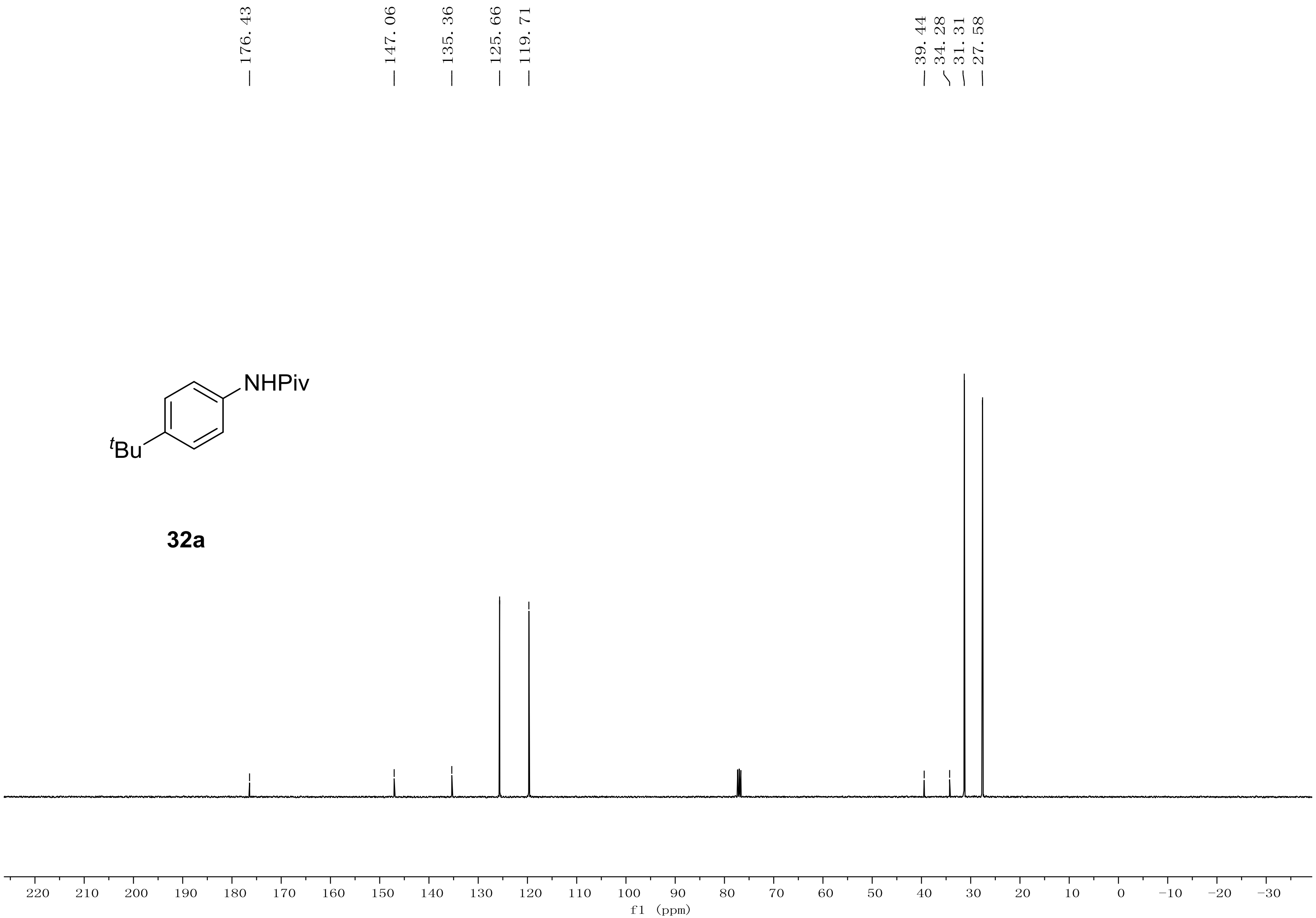

176.51
138.85
137.90
128.71
124.92
120.56
116.89
39.56
27.60
21.44
Me
NHPiv
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

31a

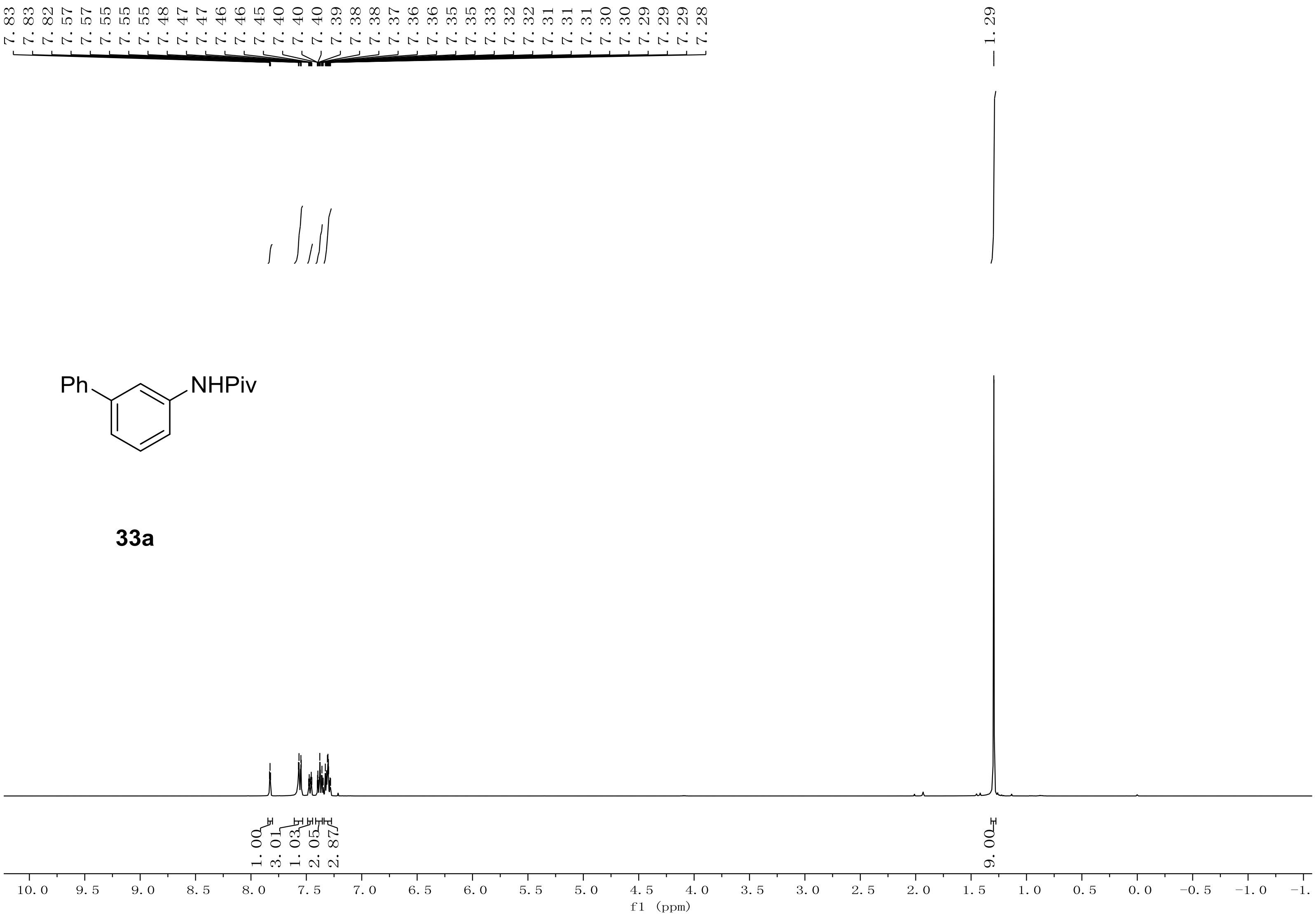


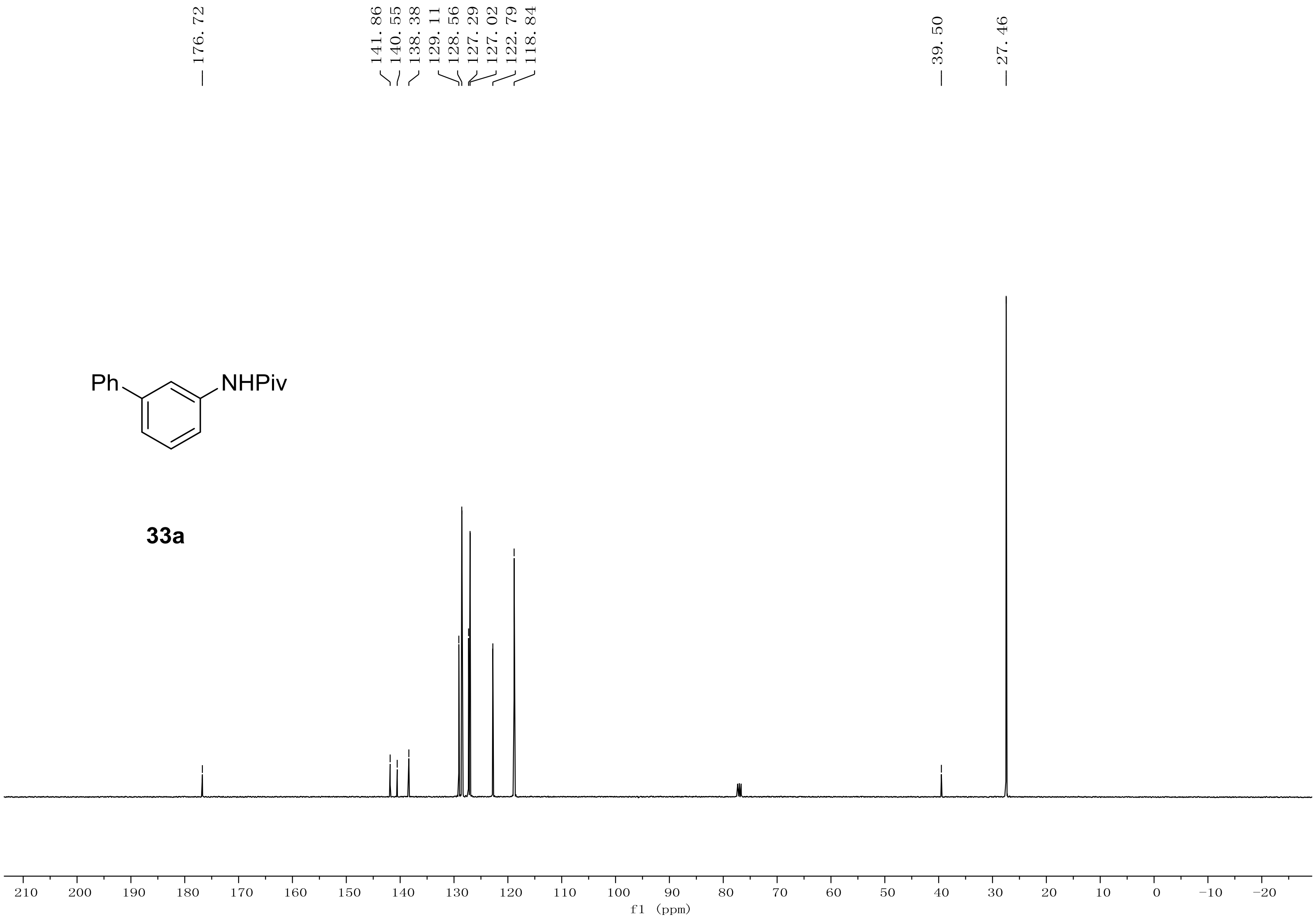
7.47
7.46
7.46
7.45
7.44
7.44
7.35
7.35
7.34
7.33
7.32
7.32
7.31
1.31
1.30
NHPiv
^{t}Bu
2.01
2.88
18.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

32a

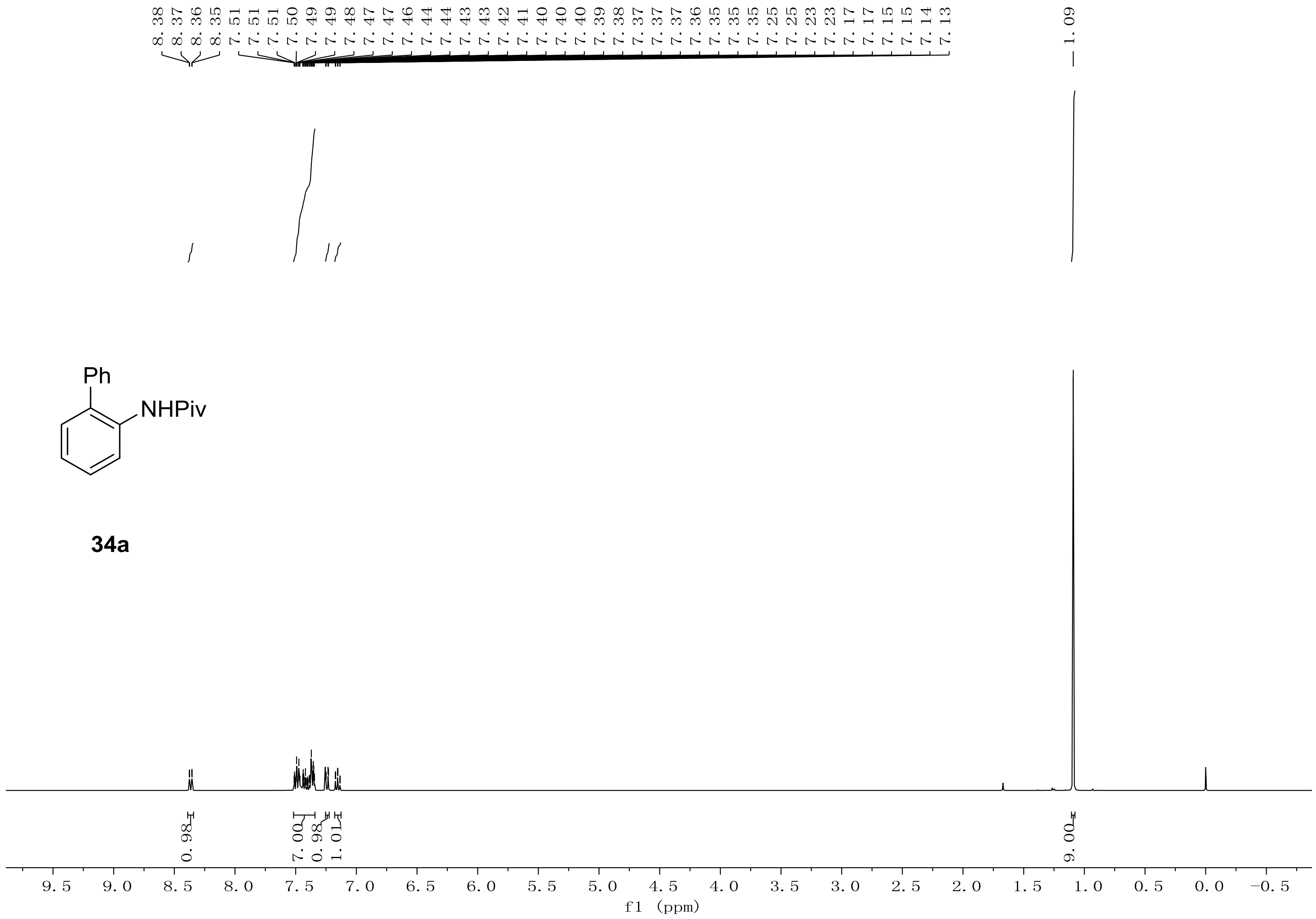

176.43
147.06
135.36
125.66
119.71
39.44
34.28
31.31
27.58
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)
NHPiv
tBu

32a

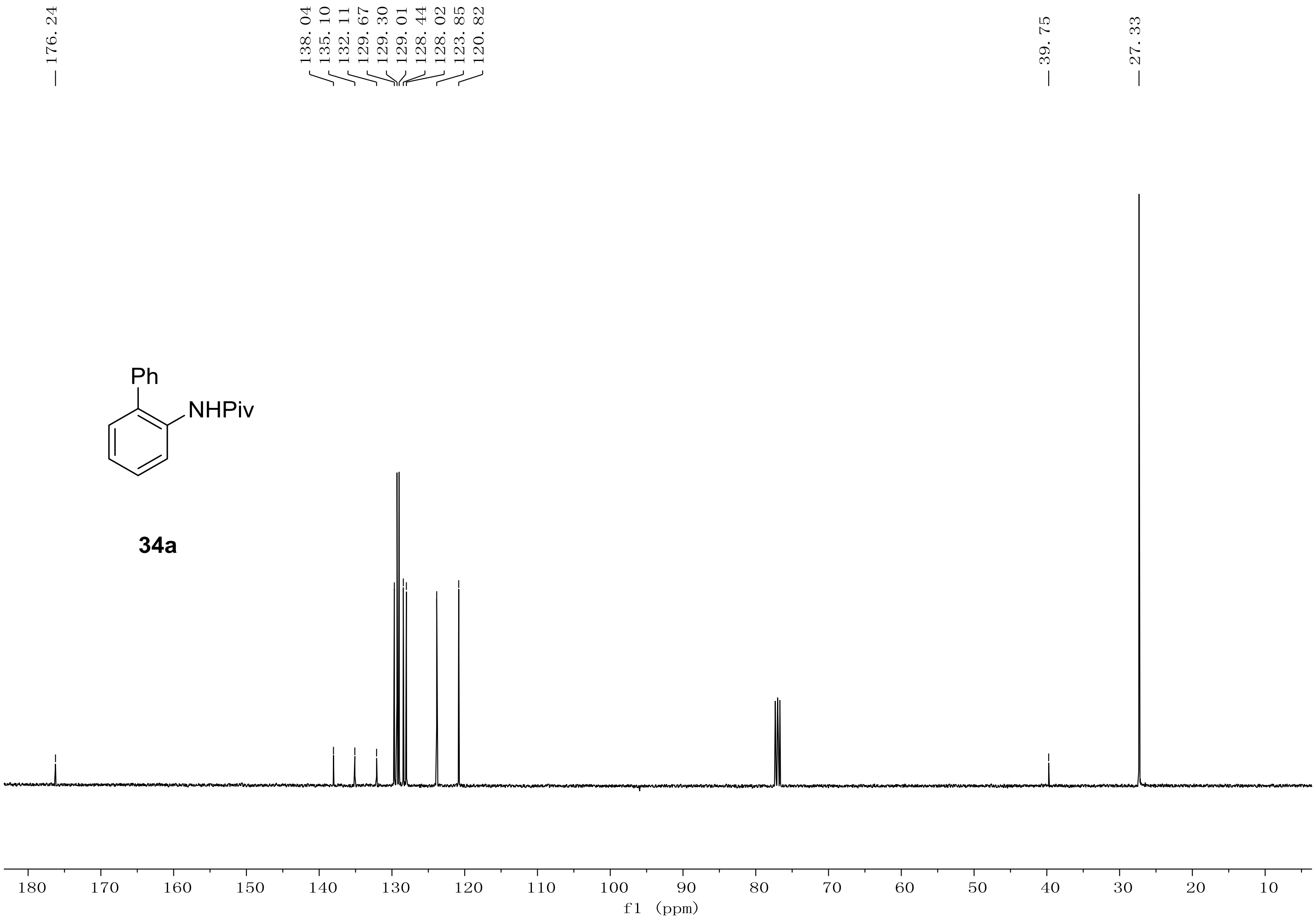

7.83 7.83 7.82 7.57 7.57 7.55 7.55 7.55 7.48 7.47 7.46 7.46 7.45 7.40 7.40 7.40 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28
1.29
Ph
NHPiv
33a
1.00 3.01 1.03 2.05 2.87
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.
f1 (ppm)



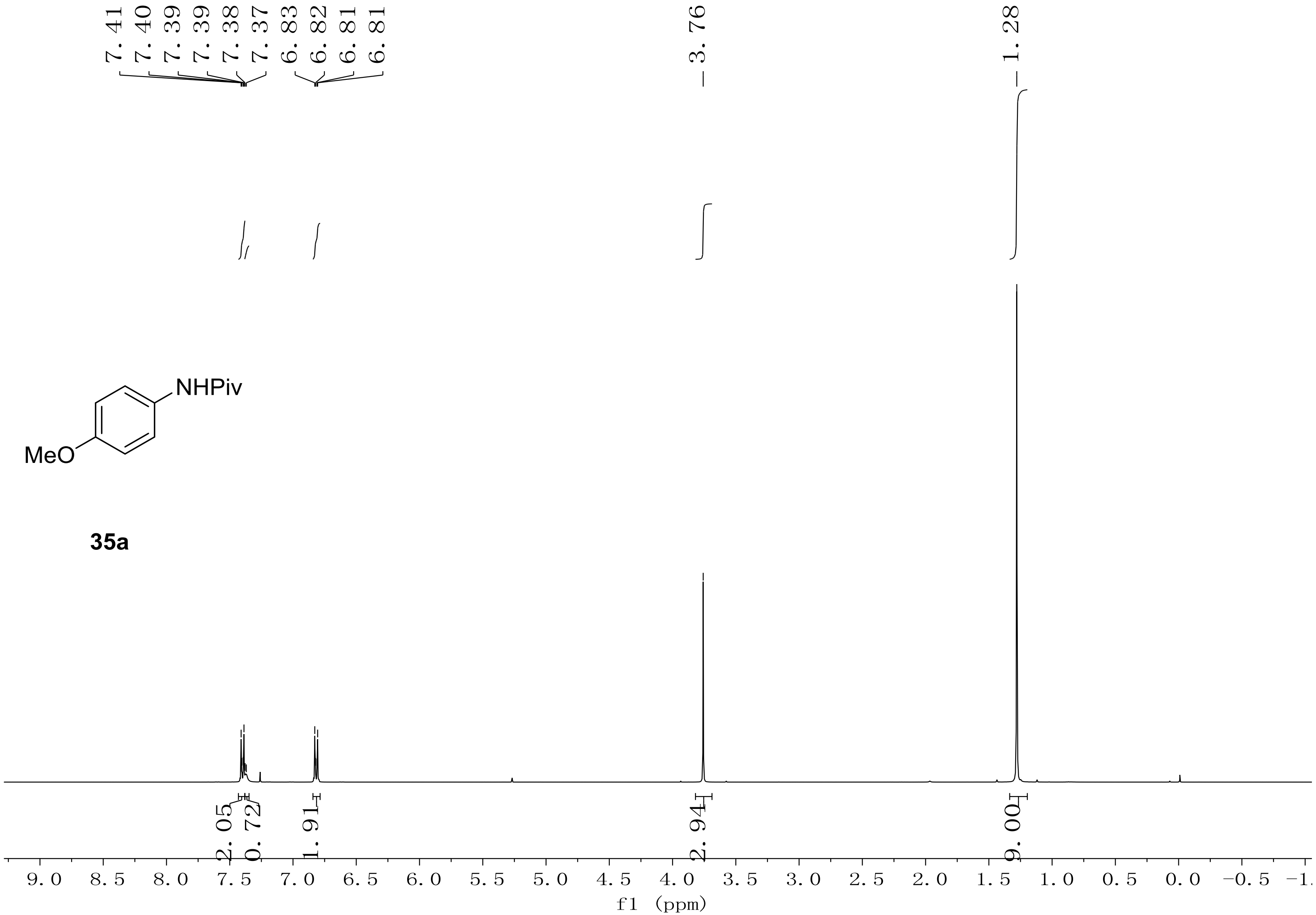
176.72
141.86
140.55
138.38
129.11
128.56
127.29
127.02
122.79
118.84
39.50
27.46
Ph
NHPiv
33a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

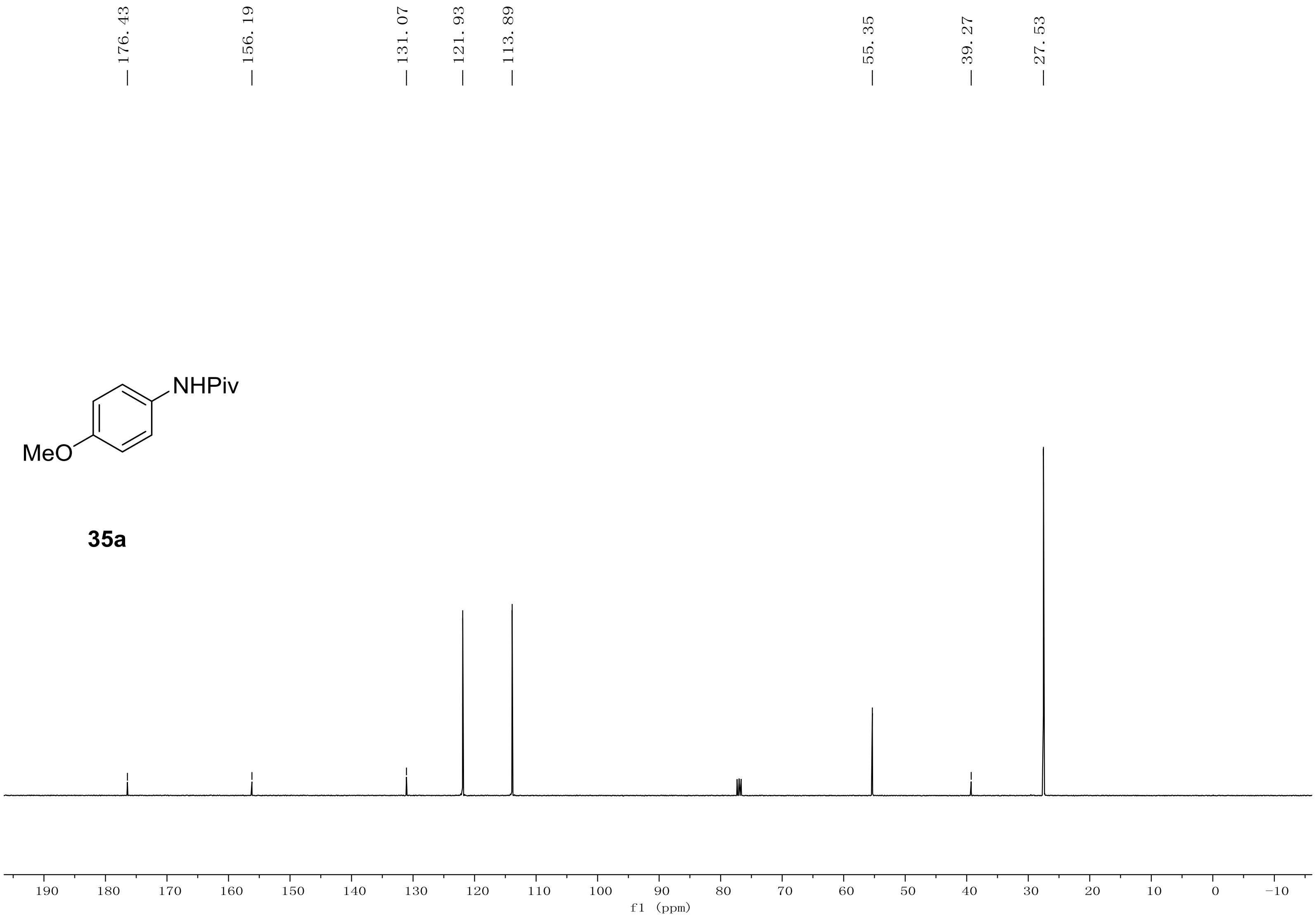

8.38
8.37
8.36
8.35
7.51
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.44
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.40
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.25
7.25
7.23
7.23
7.17
7.17
7.15
7.15
7.14
7.13
1.09
0.98
7.00
0.98
1.01
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)
Ph
NHPiv

34a

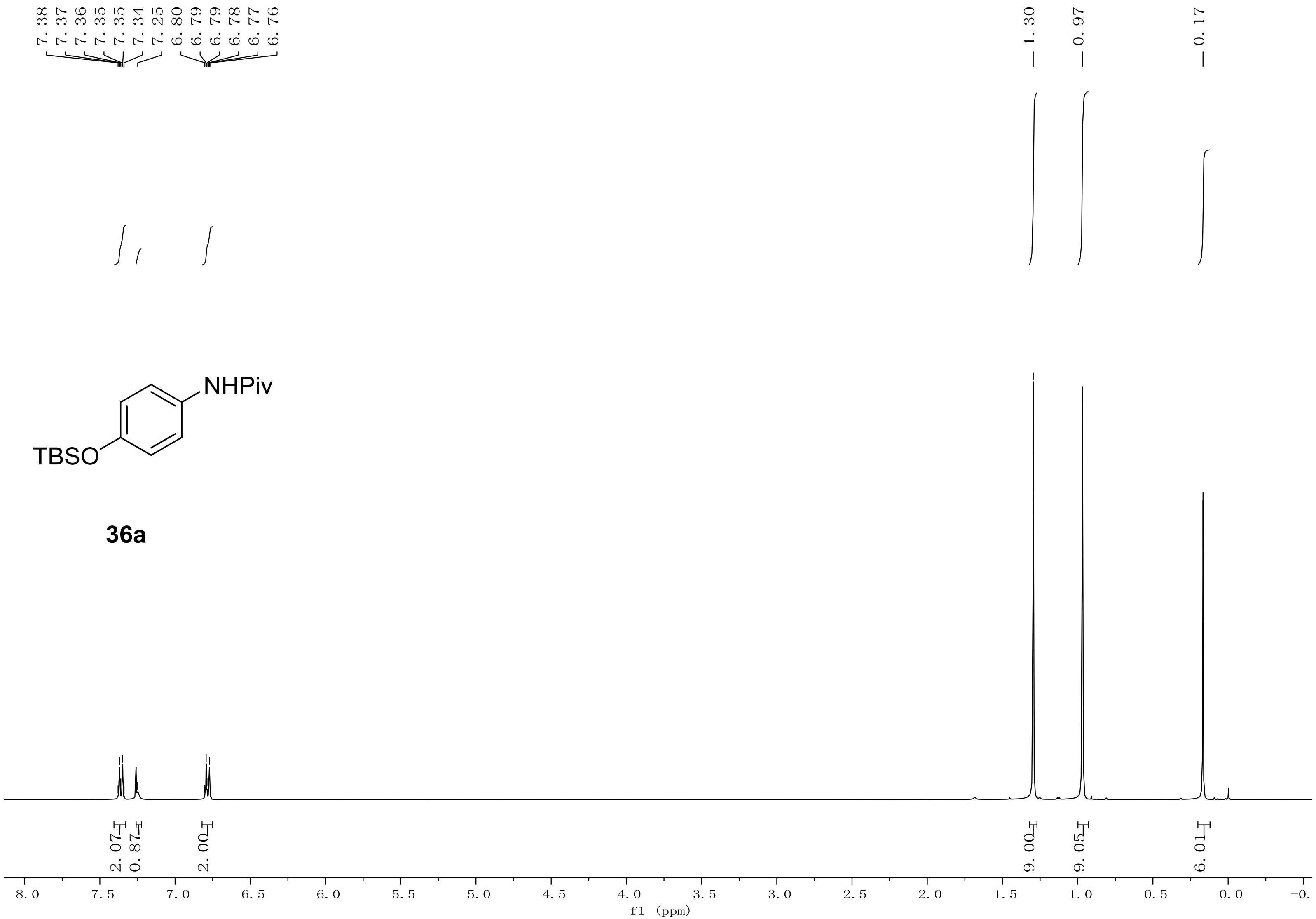

176.24
138.04
135.10
132.11
129.67
129.30
129.01
128.44
128.02
123.85
120.82
39.75
27.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
Ph
NHPiv

34a

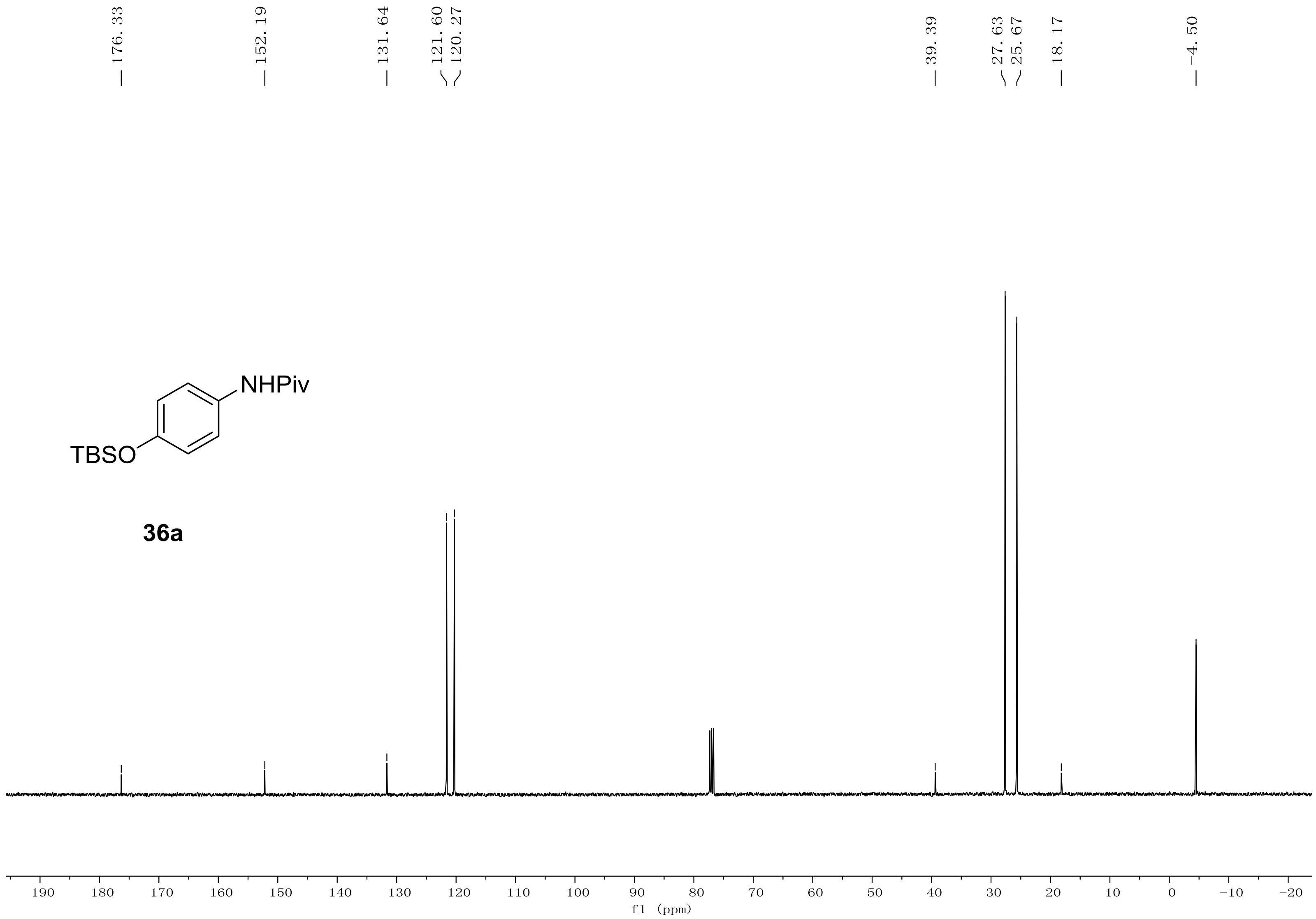

7.41
7.40
7.39
7.39
7.38
7.37
6.83
6.82
6.81
6.81
3.76
1.28
NHPiv
MeO
35a
2.05
0.72
1.91
2.94
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


176.43
156.19
131.07
121.93
113.89
55.35
39.27
27.53
NHPiv
MeO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

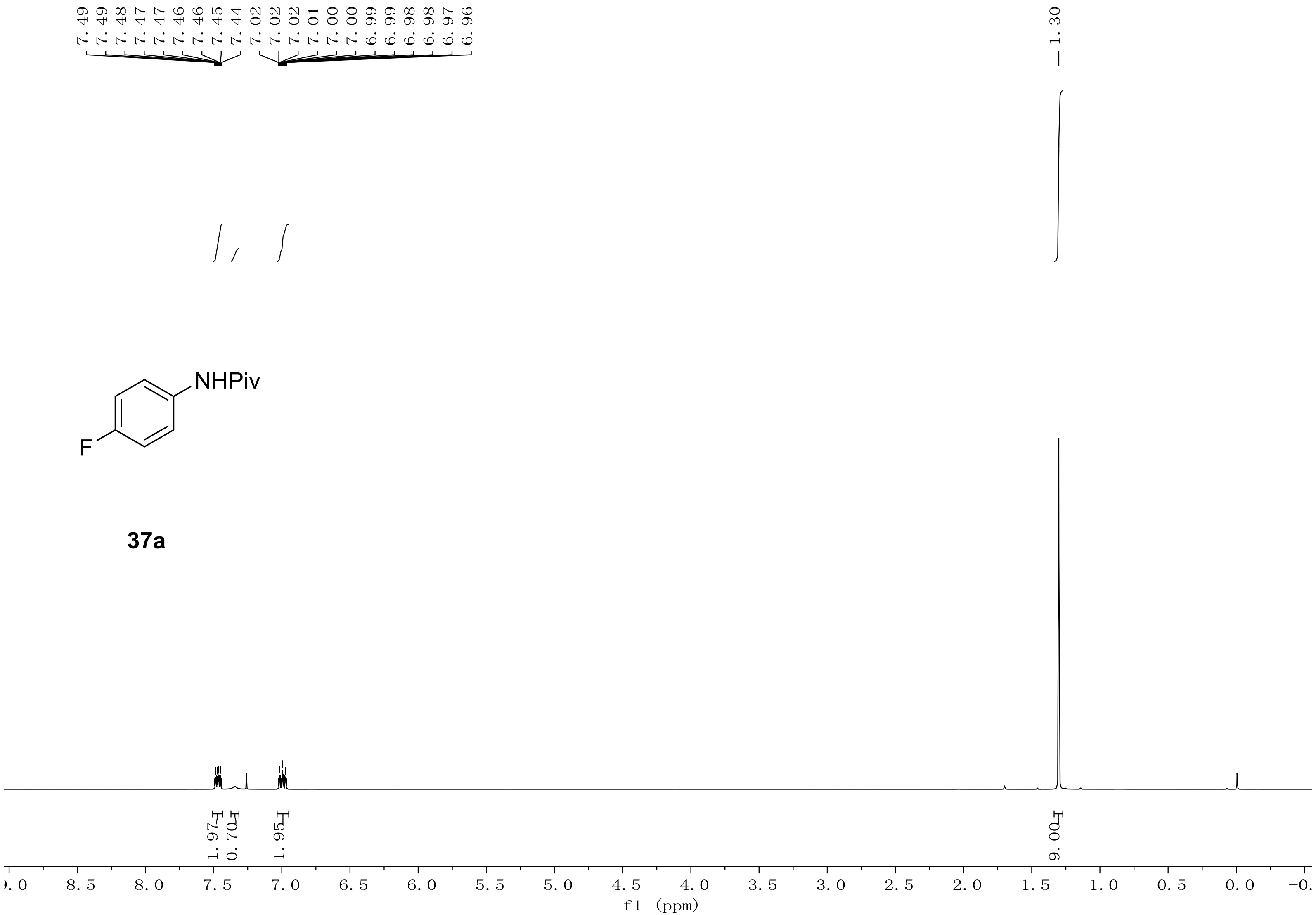
35a


7.38
7.37
7.36
7.35
7.35
7.34
7.25
6.80
6.79
6.79
6.78
6.77
6.76
1.30
0.97
0.17
2.07
0.87
2.00
9.00
9.05
6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)
NHPiv
TBSO

36a

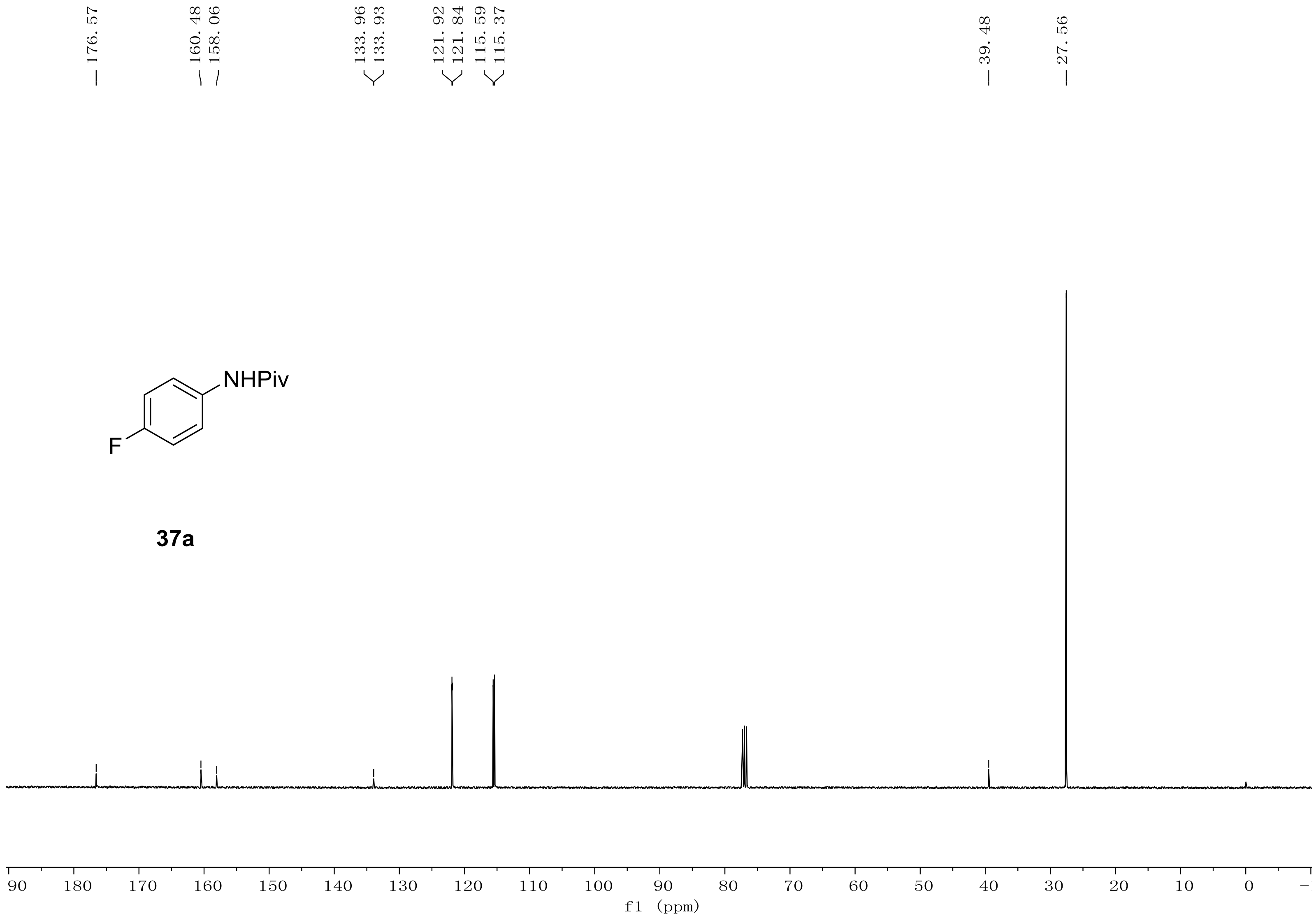


NHPiv
TBSO
36a
176.33
152.19
131.64
121.60
120.27
39.39
27.63
25.67
18.17
−4.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

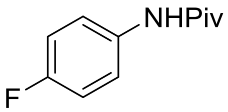


7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.02
7.02
7.02
7.01
7.00
7.00
6.99
6.99
6.98
6.98
6.97
6.96
1.30
1.97
0.70
1.95
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)
NHPiv
F

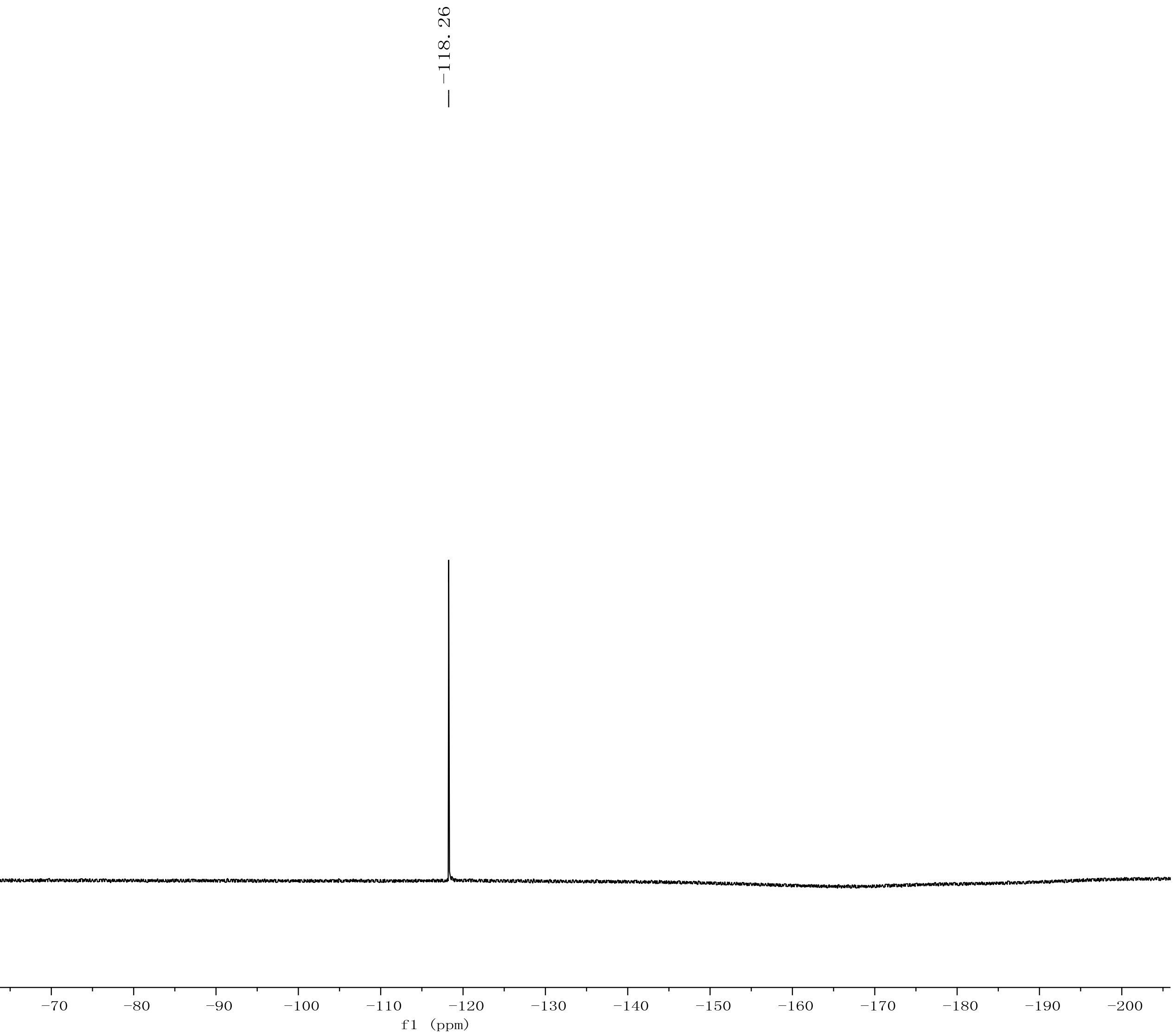
37a


176.57
160.48
158.06
133.96
133.93
121.92
121.84
115.59
115.37
39.48
27.56
NHPiv
F
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

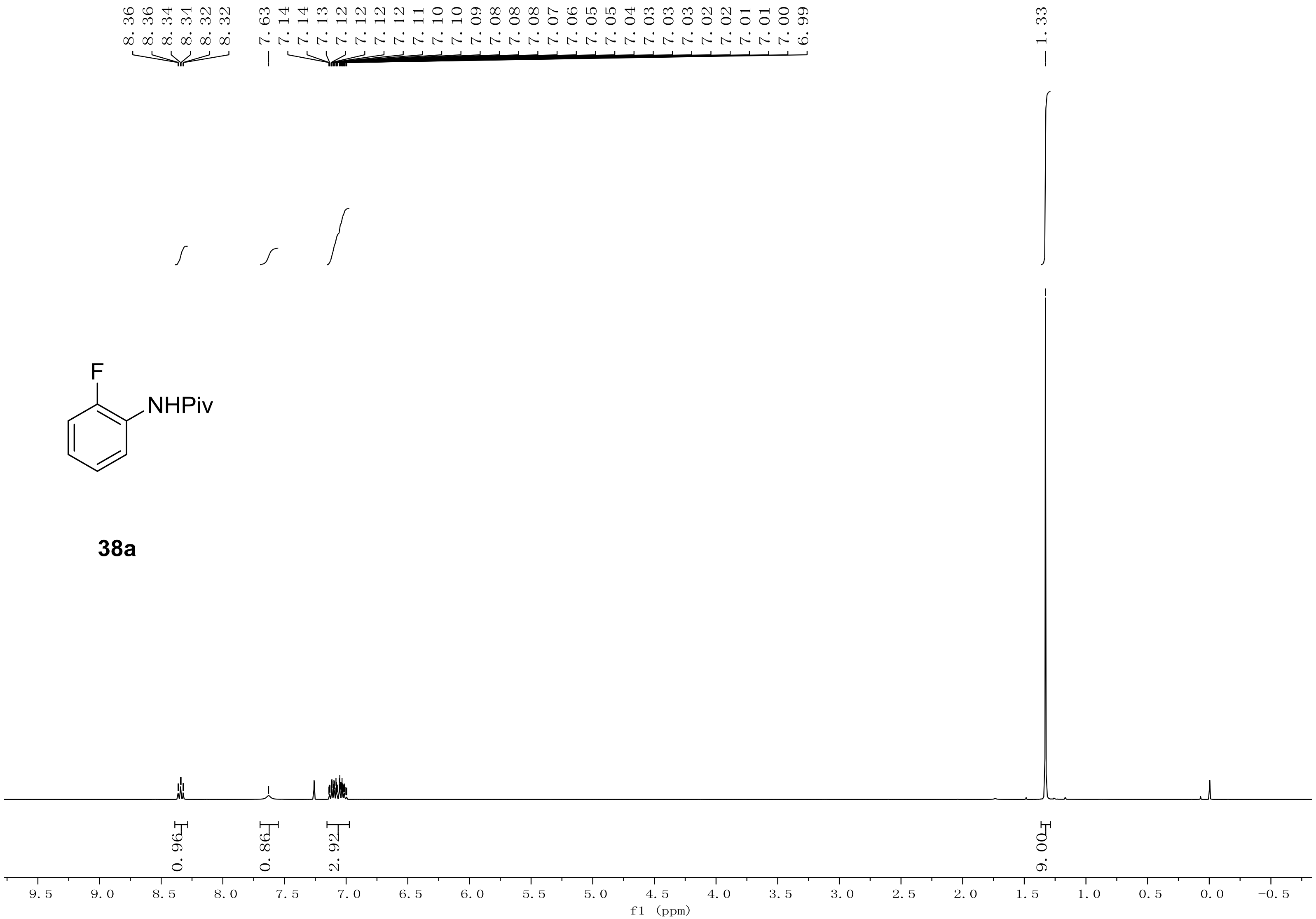
37a



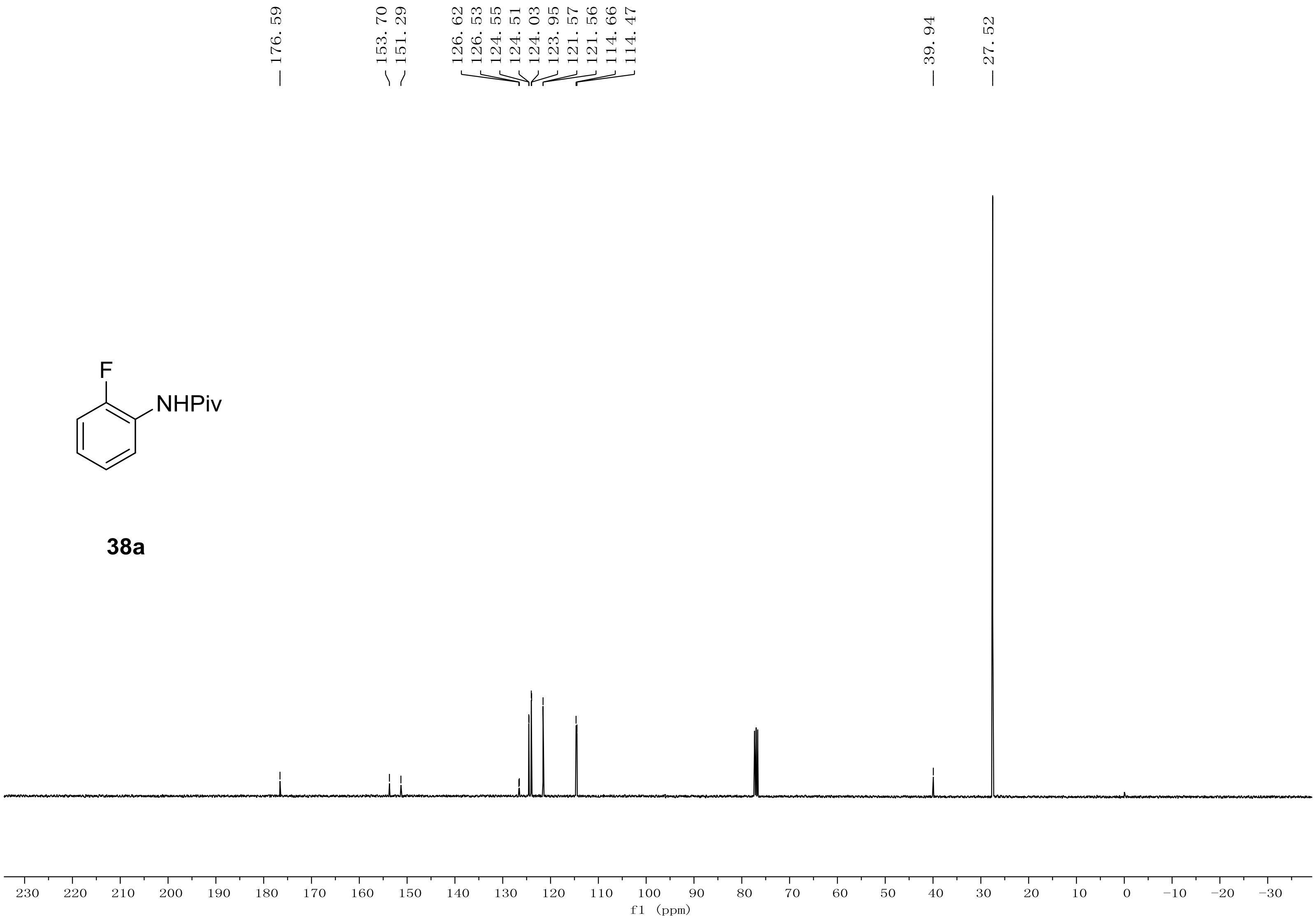
37a



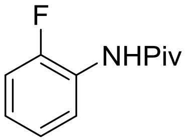
−118.26
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)


8.36
8.36
8.34
8.34
8.32
8.32
7.63
7.14
7.14
7.13
7.12
7.12
7.12
7.12
7.11
7.10
7.10
7.09
7.08
7.08
7.07
7.06
7.05
7.05
7.04
7.03
7.03
7.03
7.02
7.02
7.01
7.01
7.00
6.99
1.33
NHPiv
F
0.96
0.86
2.92
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

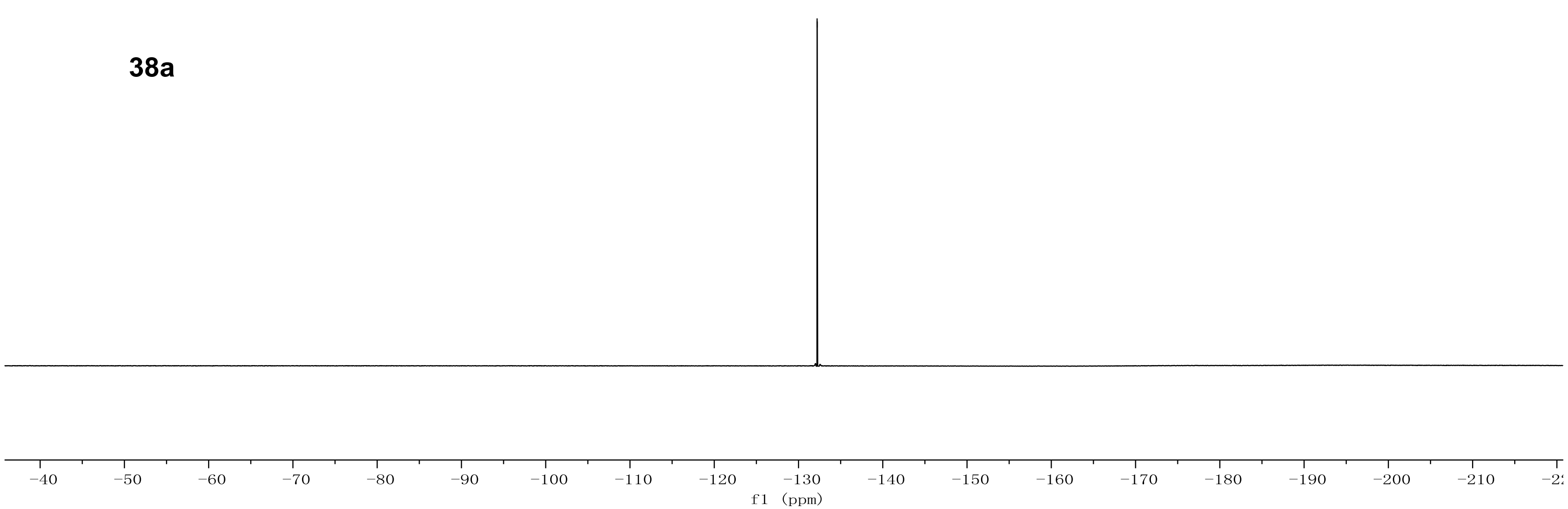
38a

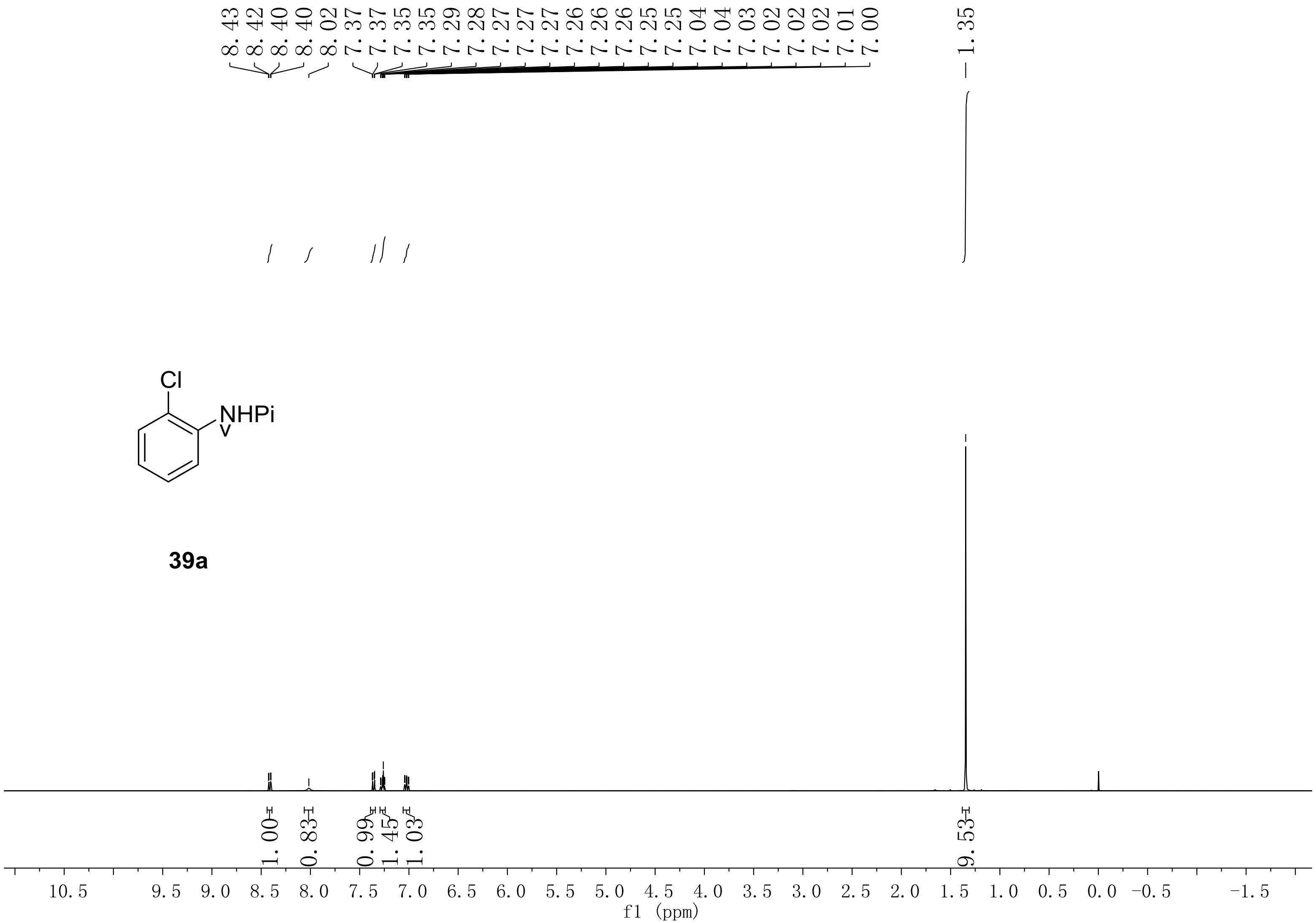

F
NHPiv
176.59
153.70
151.29
126.62
126.53
124.55
124.51
124.03
123.95
121.57
121.56
114.66
114.47
39.94
27.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

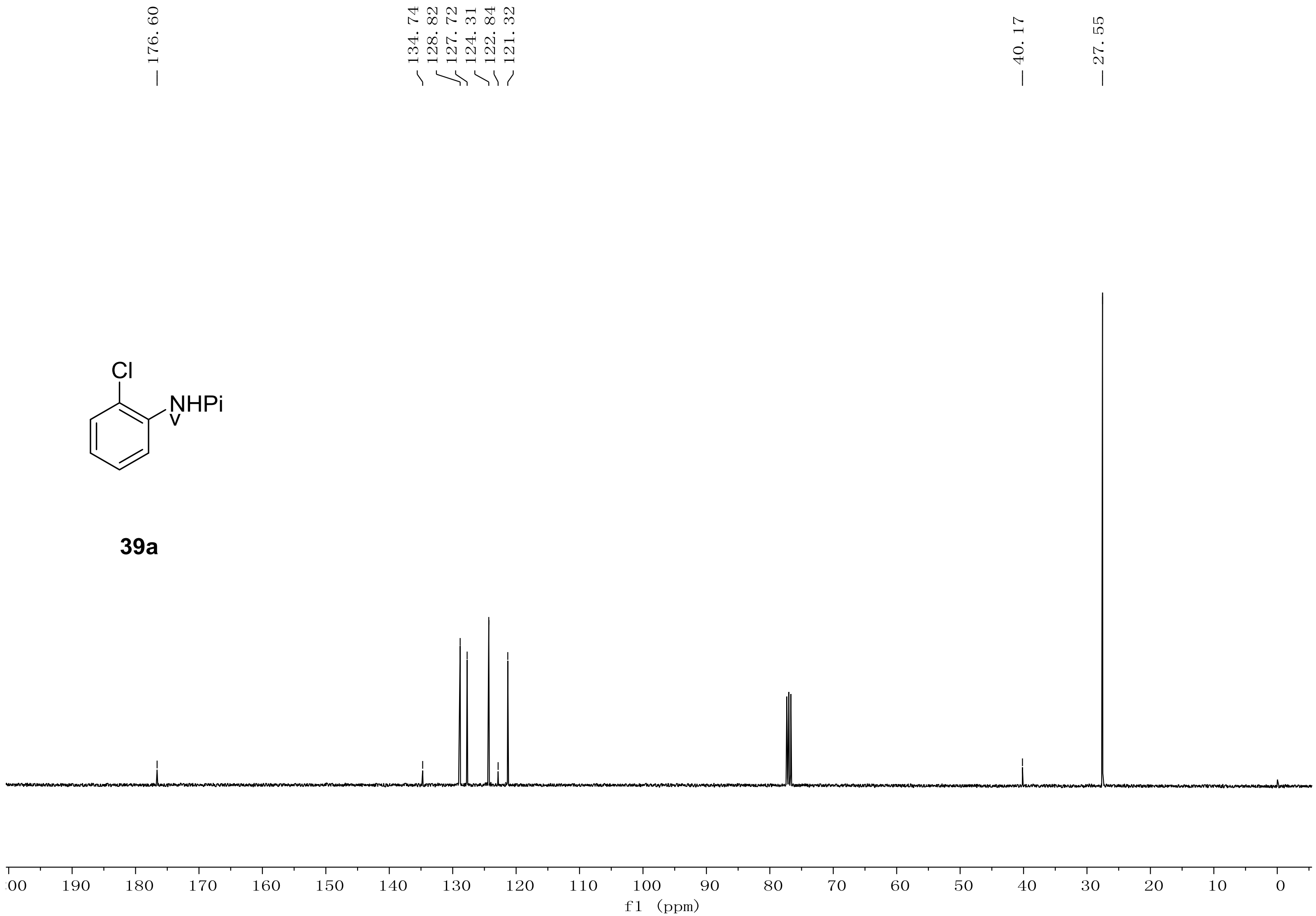
38a


F
NHPiv

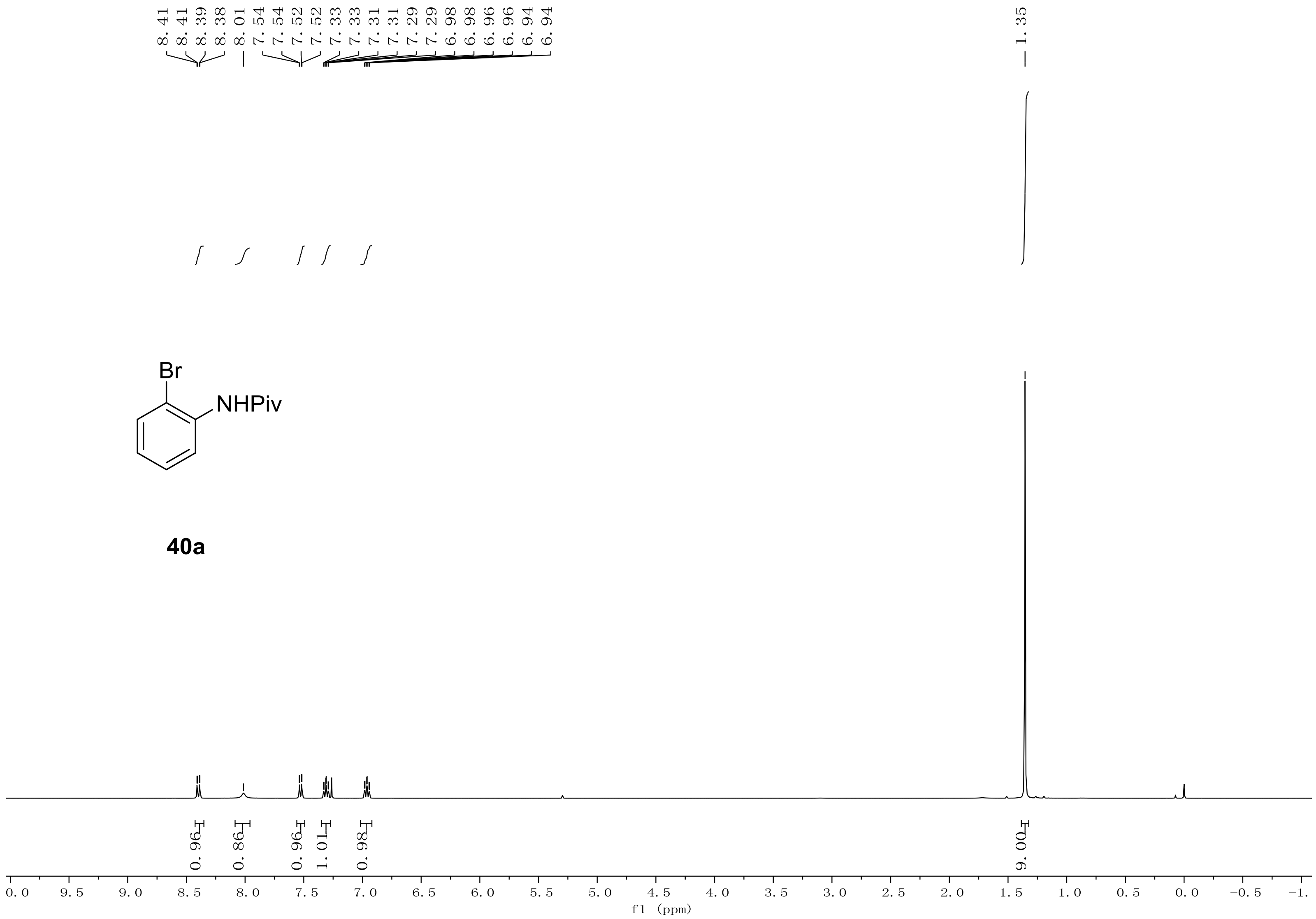
38a


−132.21
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

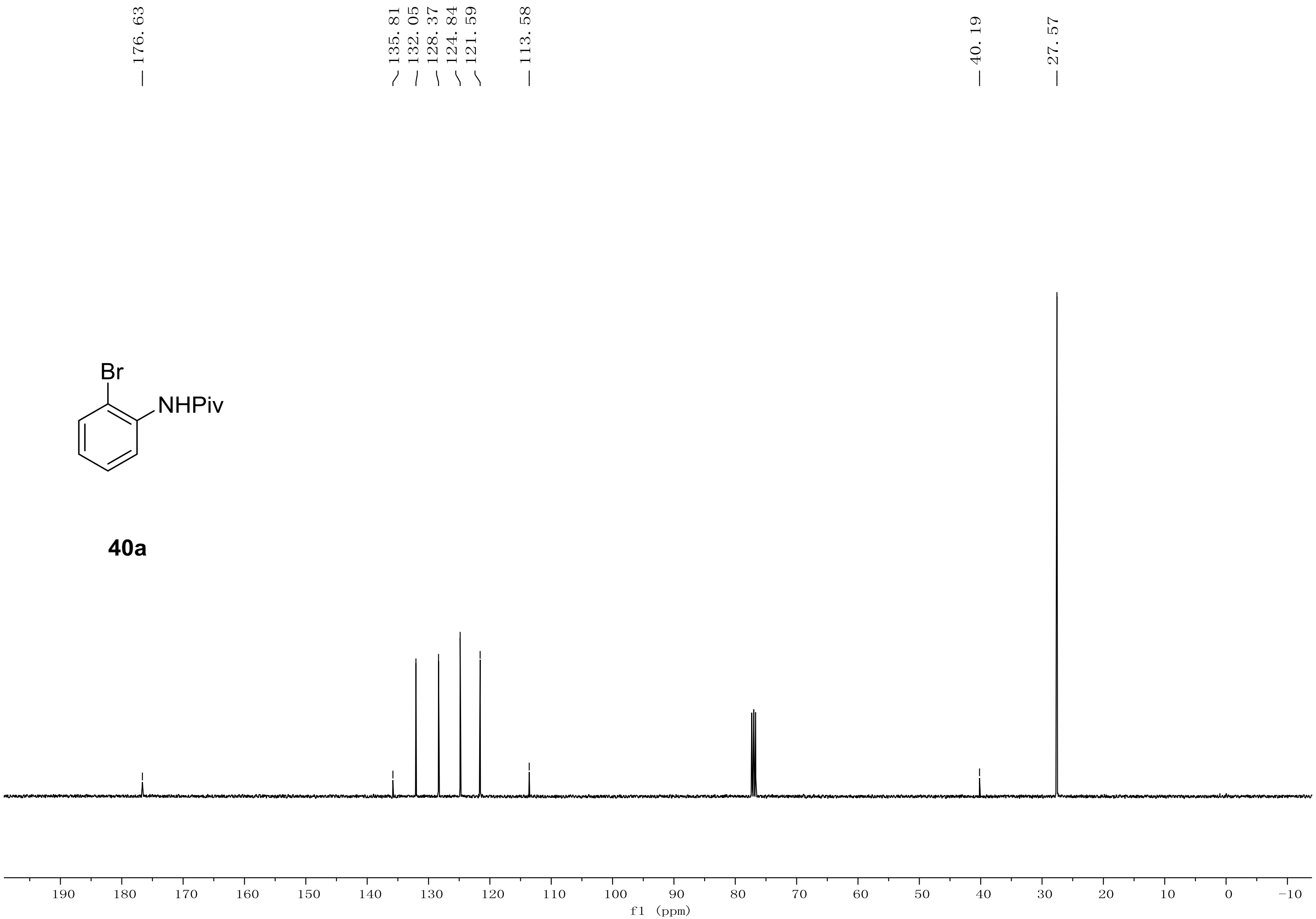

8.43 8.42 8.40 8.40 8.02 7.37 7.37 7.35 7.35 7.29 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.04 7.04 7.03 7.02 7.02 7.02 7.01 7.00
1.35
Cl
NHPiv
39a
1.00
0.83
0.99
1.45
1.03
9.53
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)


176.60
134.74
128.82
127.72
124.31
122.84
121.32
40.17
27.55
f1 (ppm)
Cl
NHPi

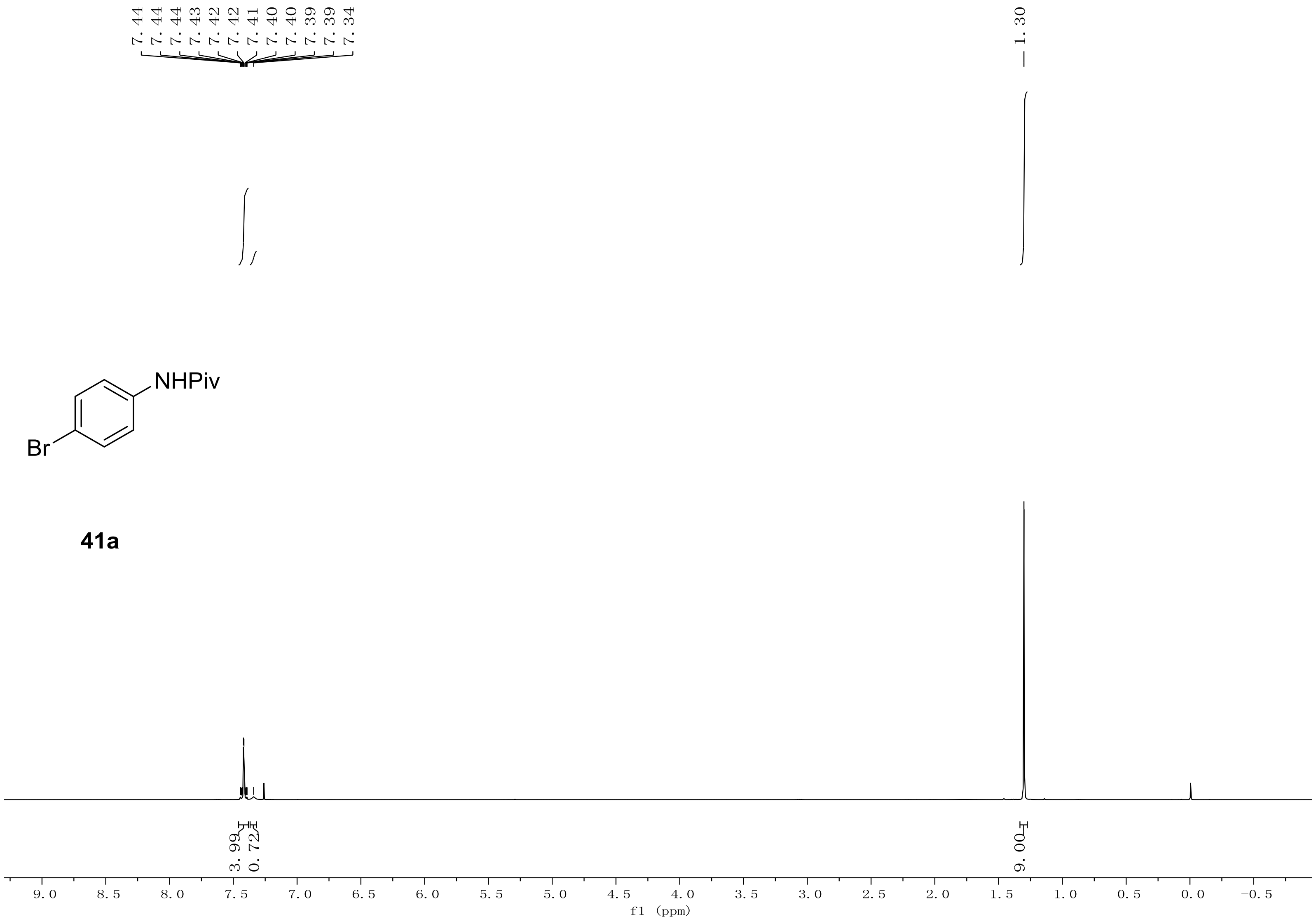
39a


8.41
8.41
8.39
8.38
8.01
7.54
7.54
7.52
7.52
7.33
7.33
7.31
7.31
7.29
7.29
6.98
6.96
6.96
6.94
6.94
1.35
Br
NHPiv
0.96
0.86
0.96
1.01
0.98
9.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

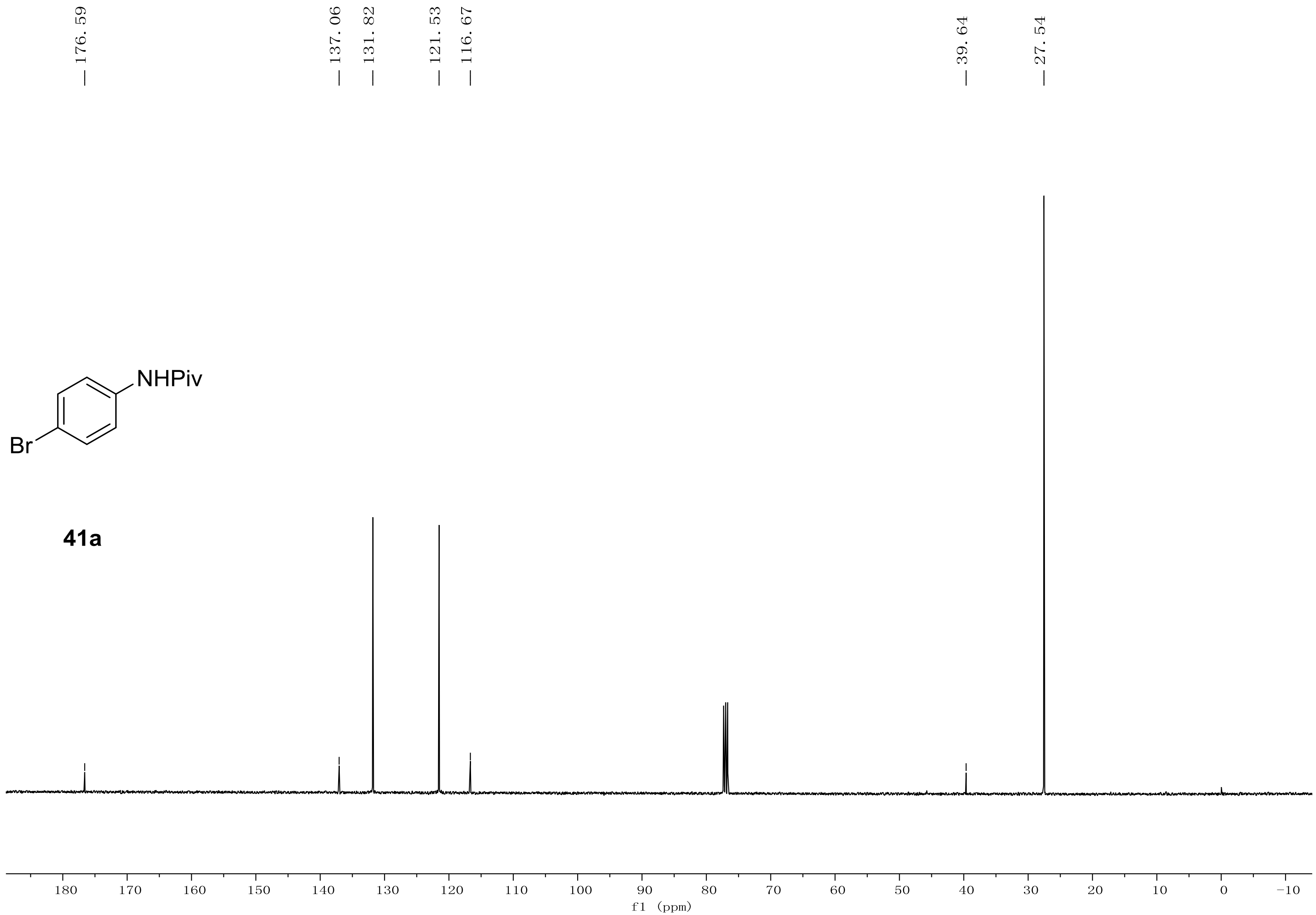
40a


176.63
135.81
132.05
128.37
124.84
121.59
113.58
40.19
27.57
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
Br
NHPiv

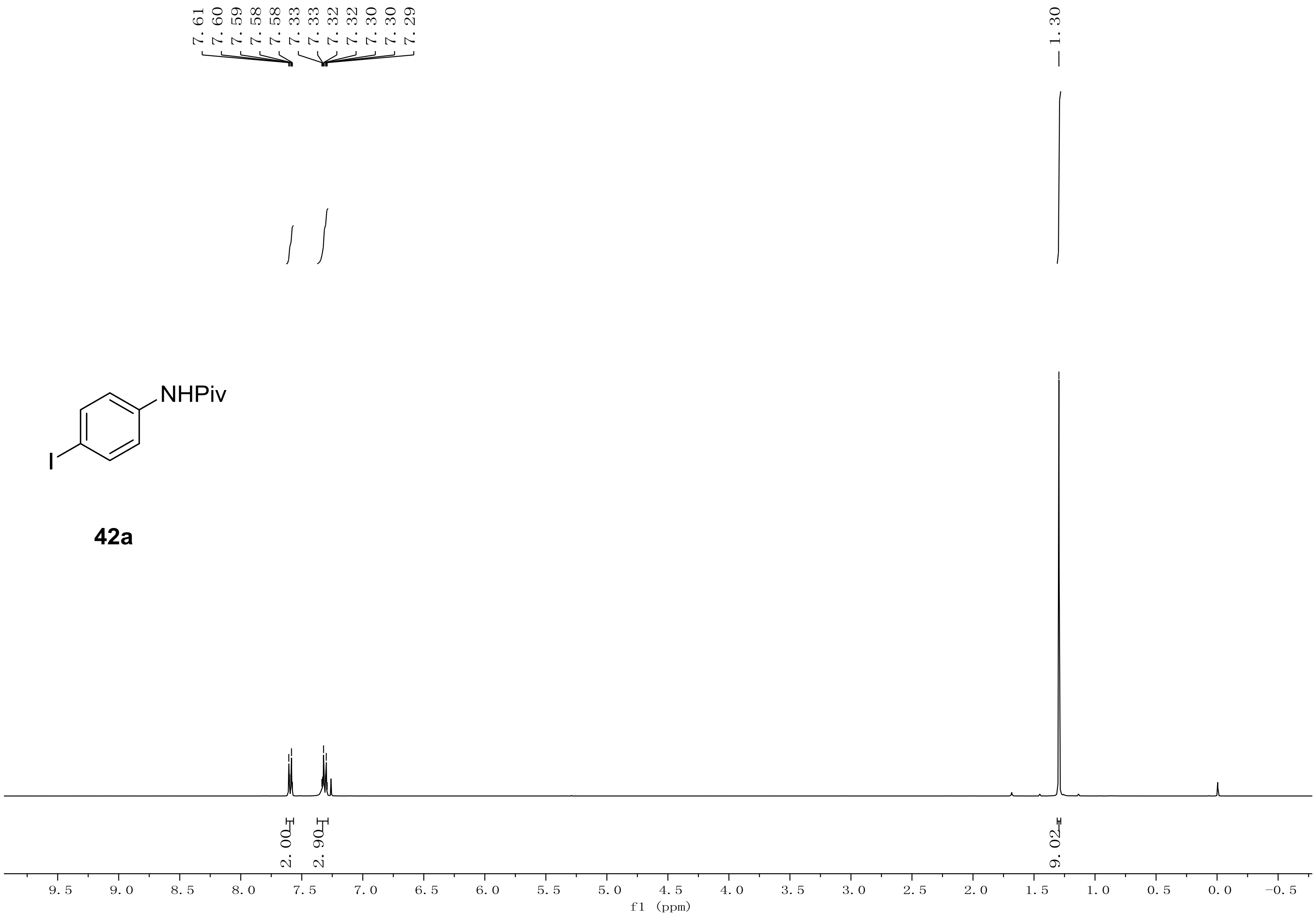
40a


NHPiv
Br
7.44
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.34
1.30
3.99
0.72
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

41a

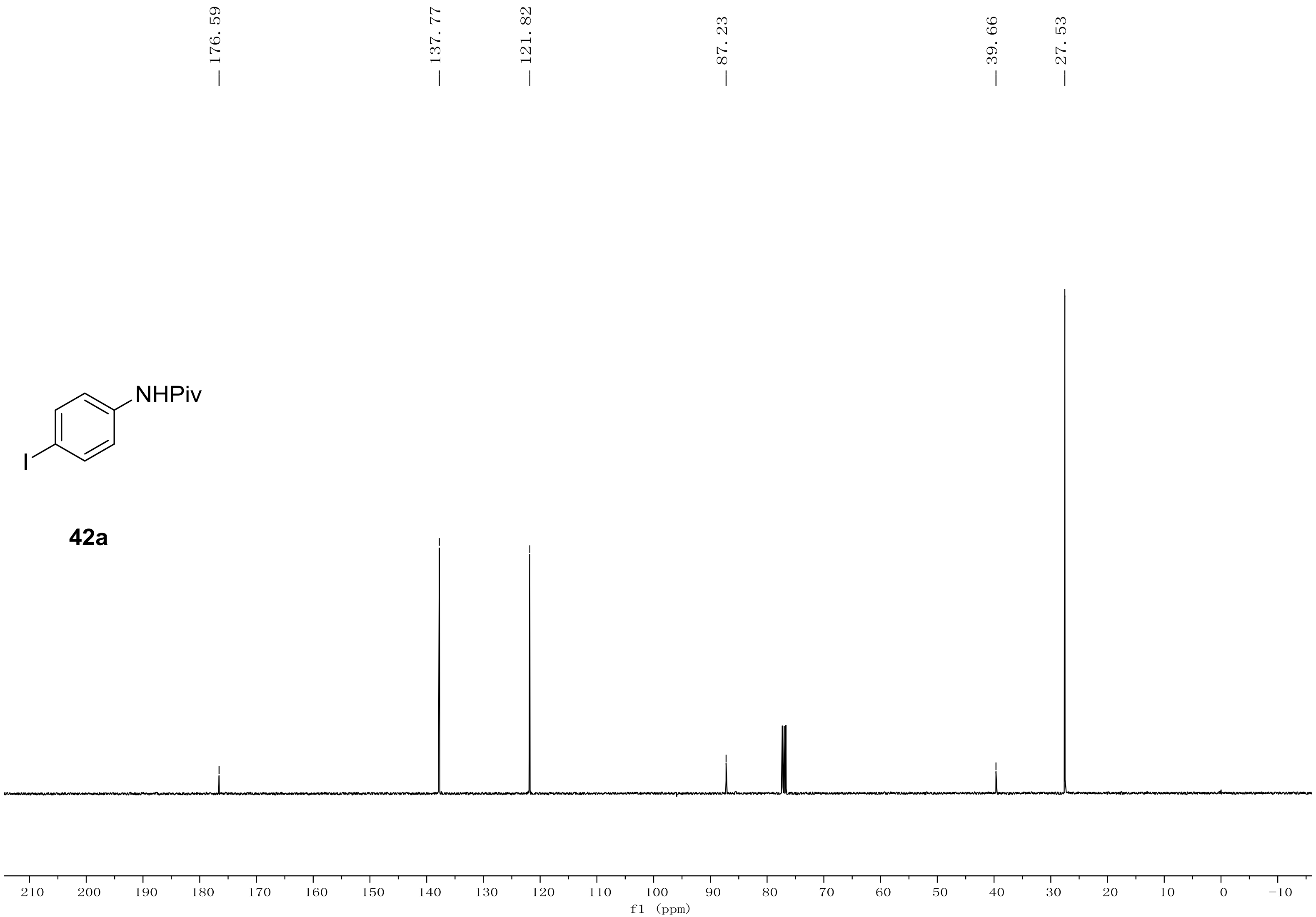

176.59
137.06
131.82
121.53
116.67
39.64
27.54
NHPiv
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

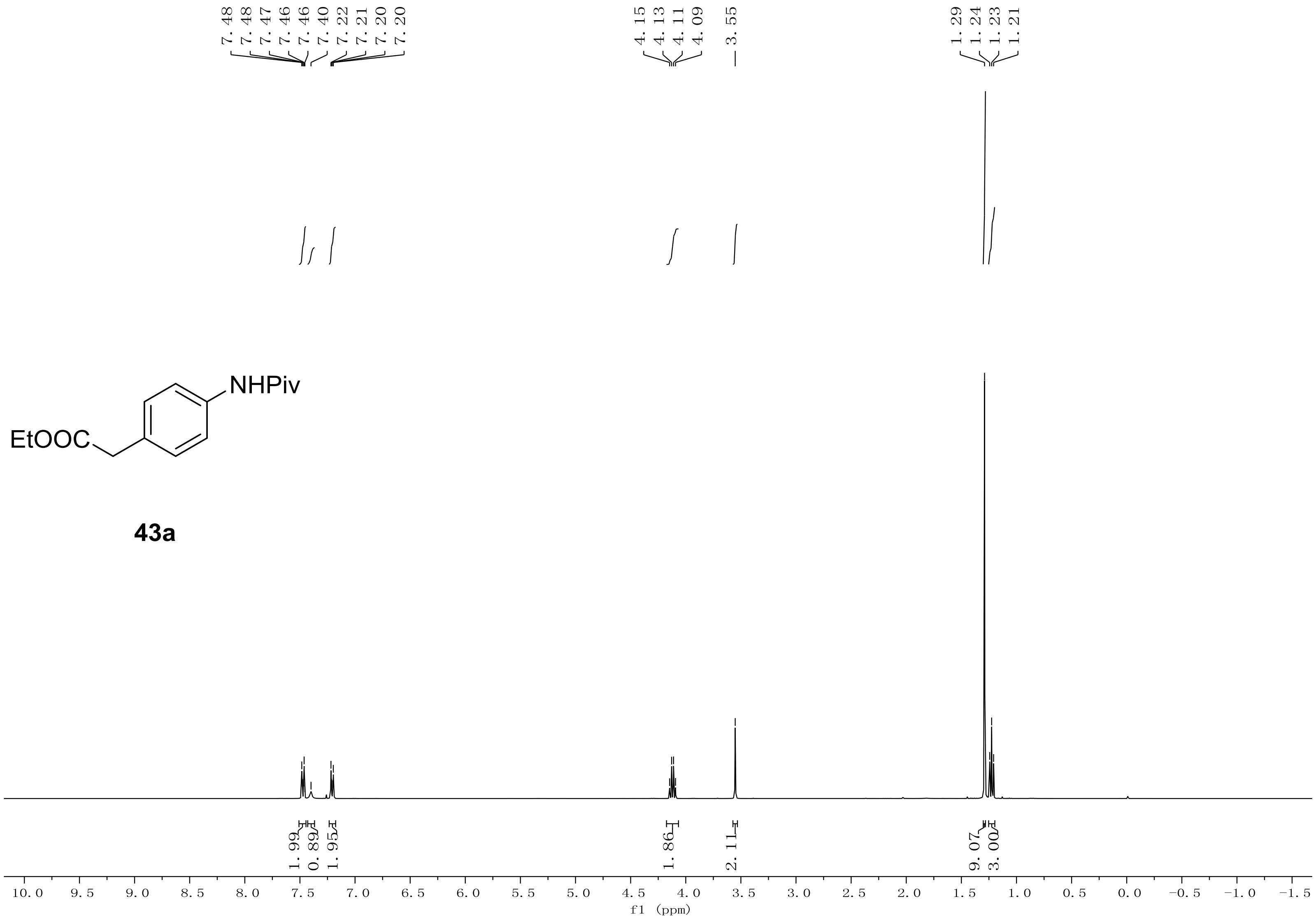
41a



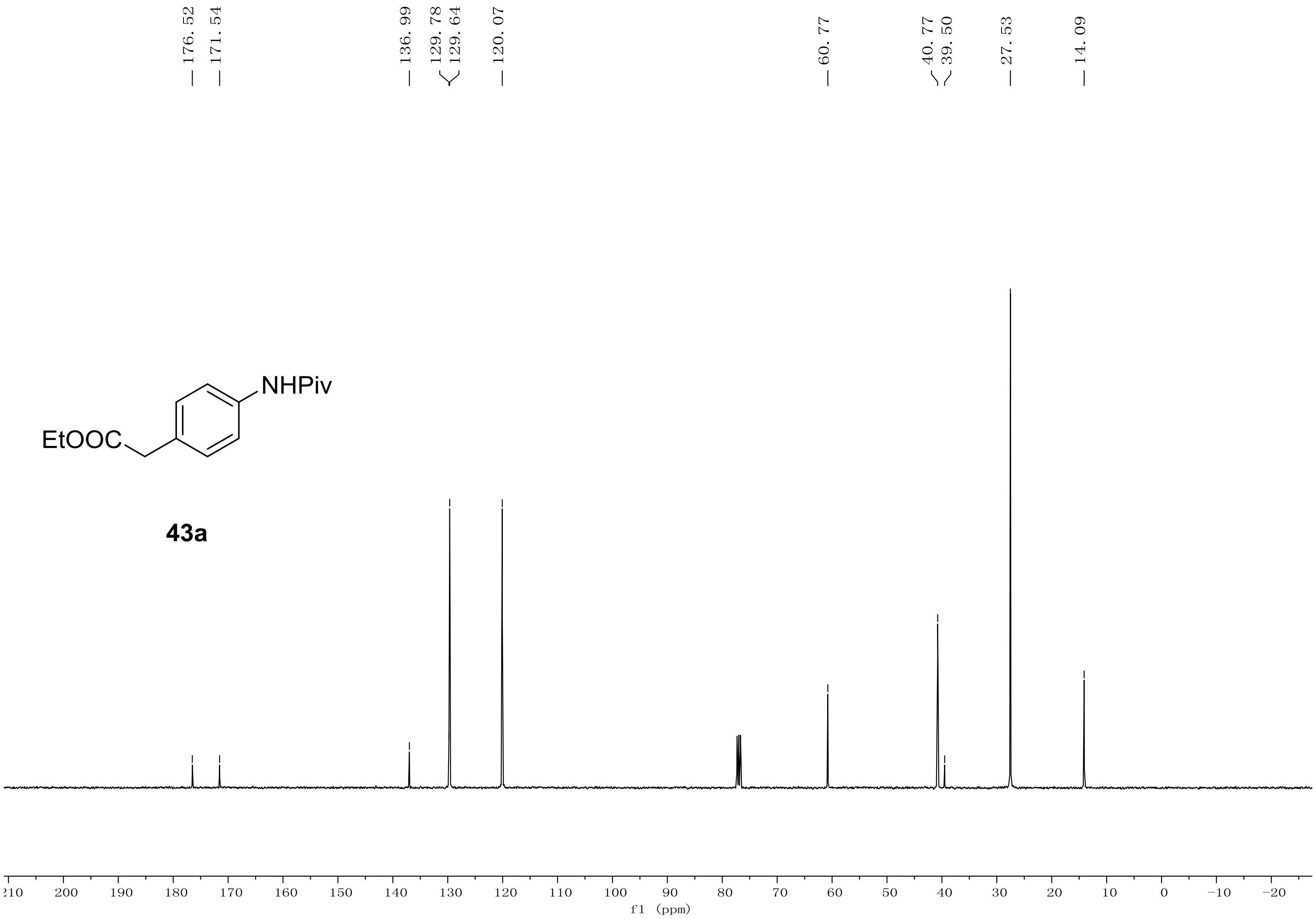
7.61
7.60
7.59
7.58
7.58
7.33
7.33
7.32
7.32
7.30
7.30
7.29
1.30
NHPiv
I
2.00
2.90
9.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

42a

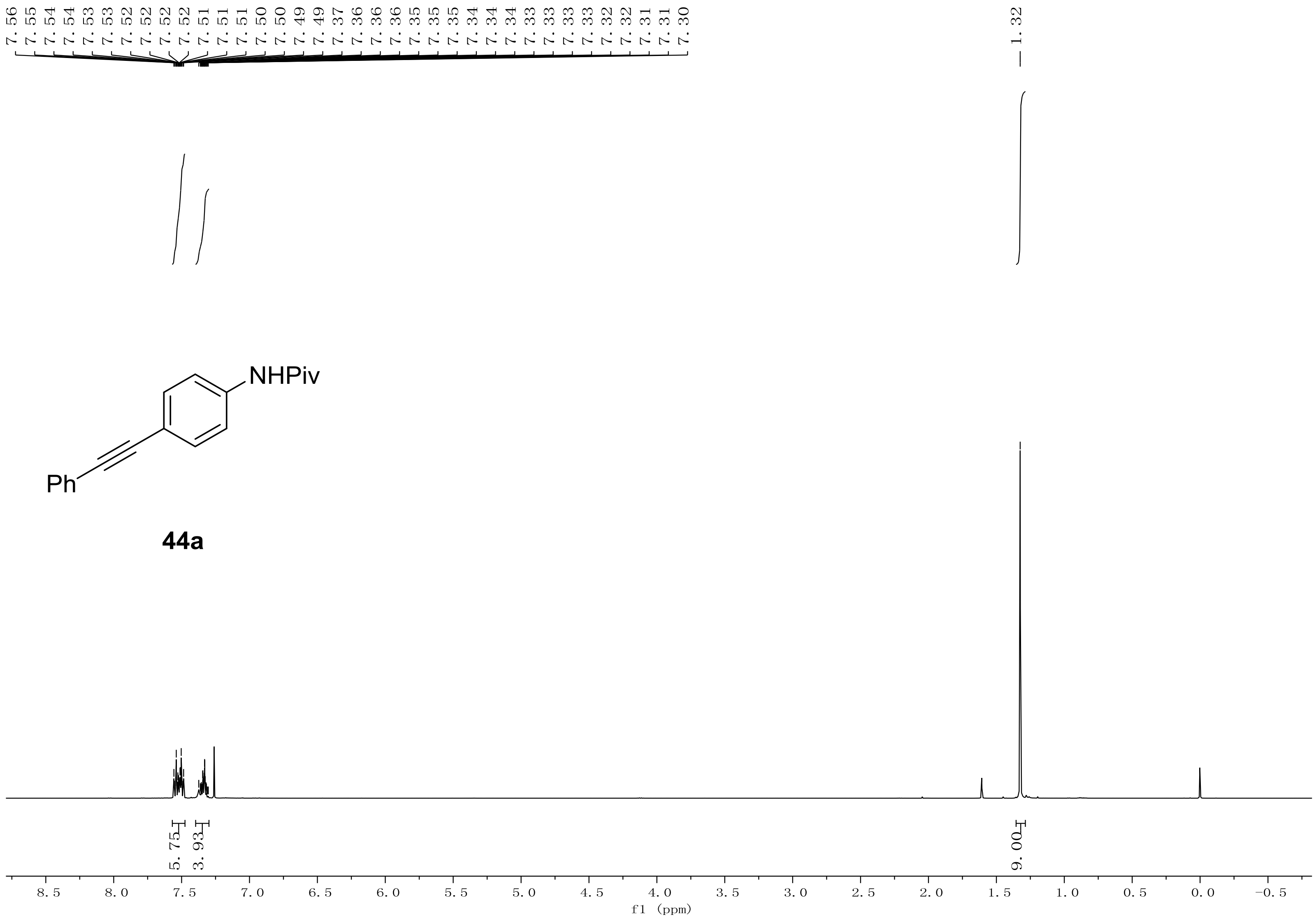

NHPiv
I
42a
176.59
137.77
121.82
87.23
39.66
27.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.48
7.48
7.47
7.46
7.46
7.40
7.22
7.21
7.20
7.20
4.15
4.13
4.11
4.09
3.55
1.29
1.24
1.23
1.21
1.99
0.89
1.95
1.86
2.11
9.07
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

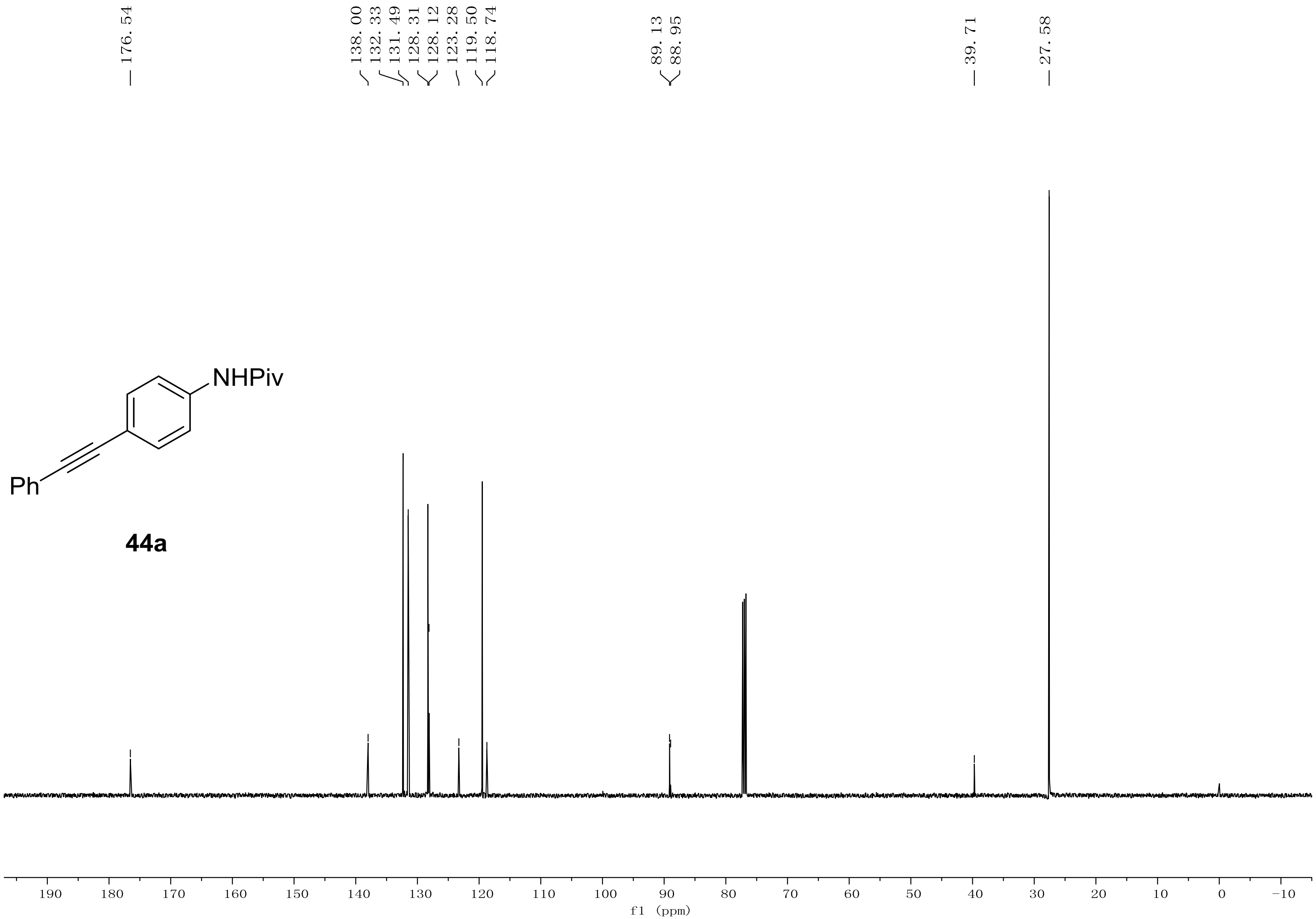
43a


EtOOC
NHPiv
176.52
171.54
136.99
129.78
129.64
120.07
60.77
40.77
39.50
27.53
14.09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

43a

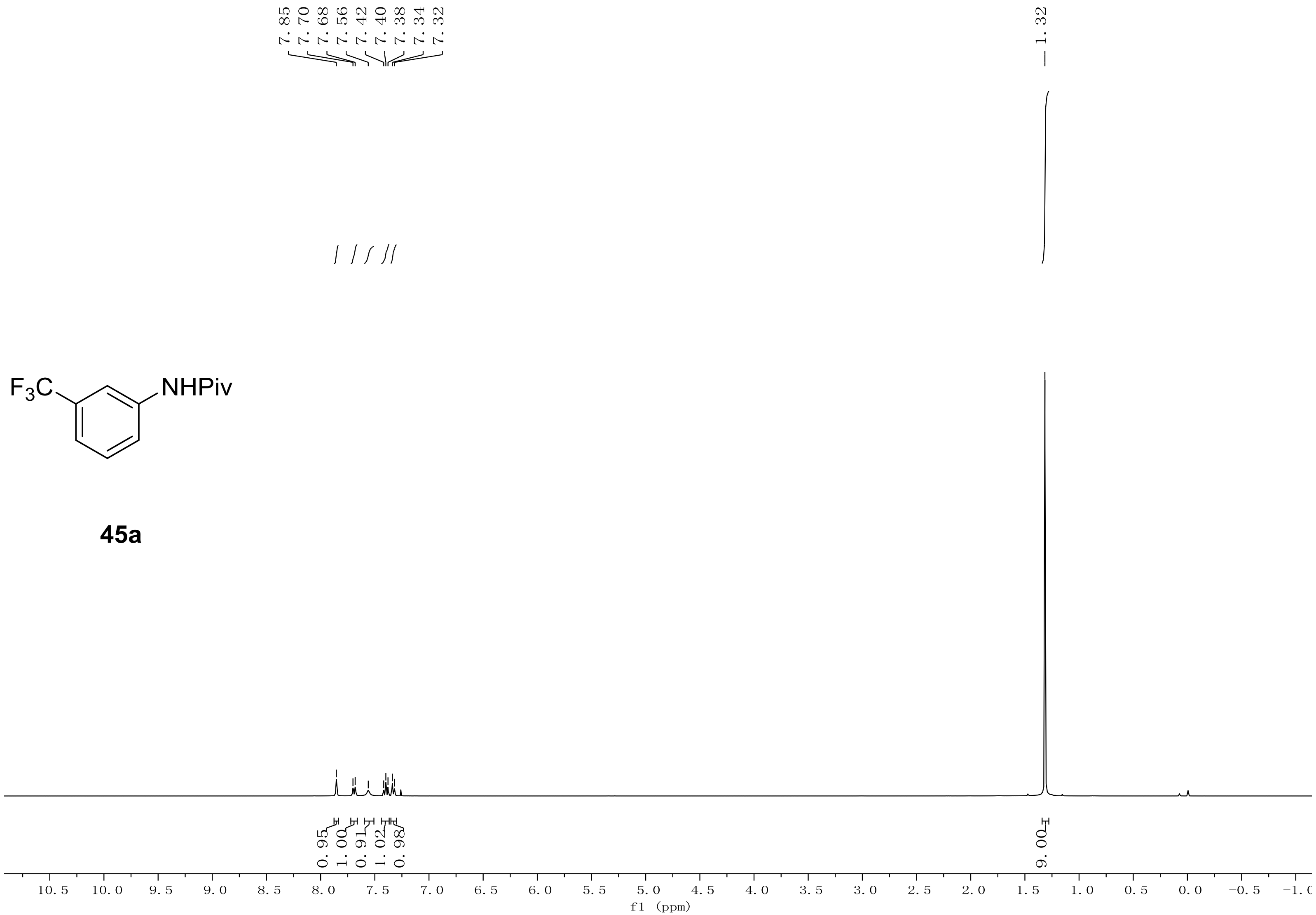

7.56
7.55
7.54
7.53
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
1.32
NHPiv
Ph
5.75
3.93
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

44a

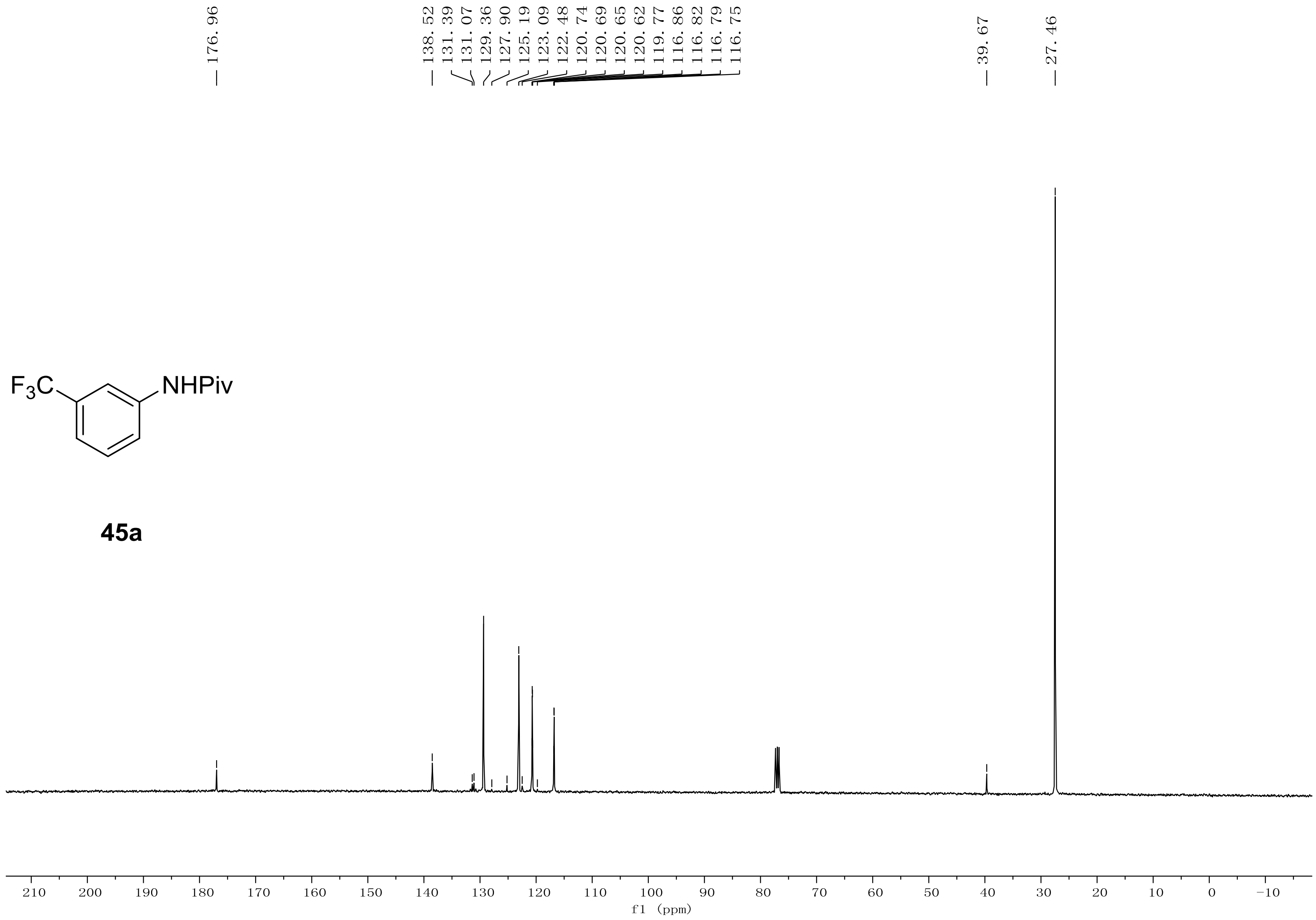


176.54
138.00
132.33
131.49
128.31
128.12
123.28
119.50
118.74
89.13
88.95
39.71
27.58
NHPiv
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

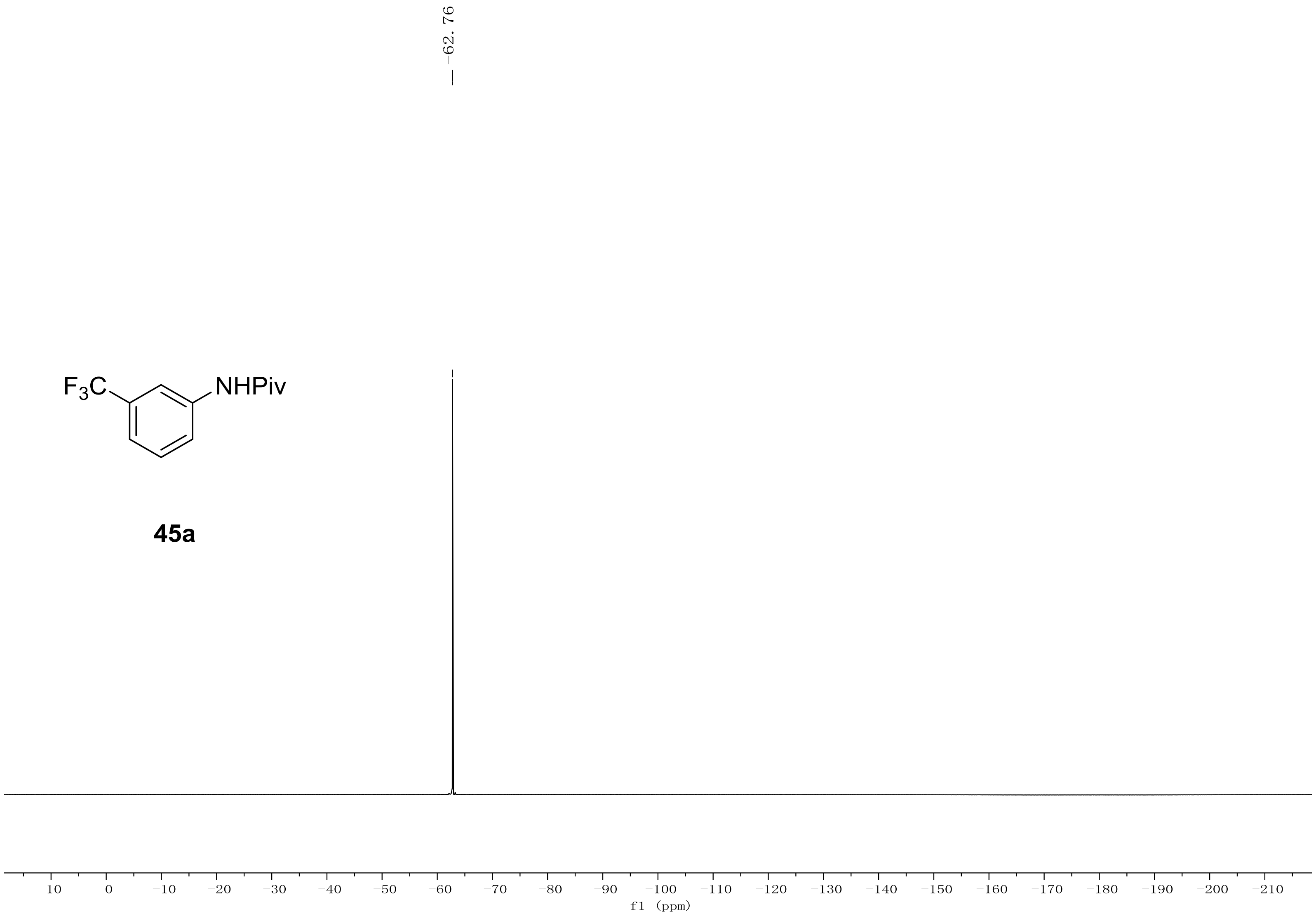
44a



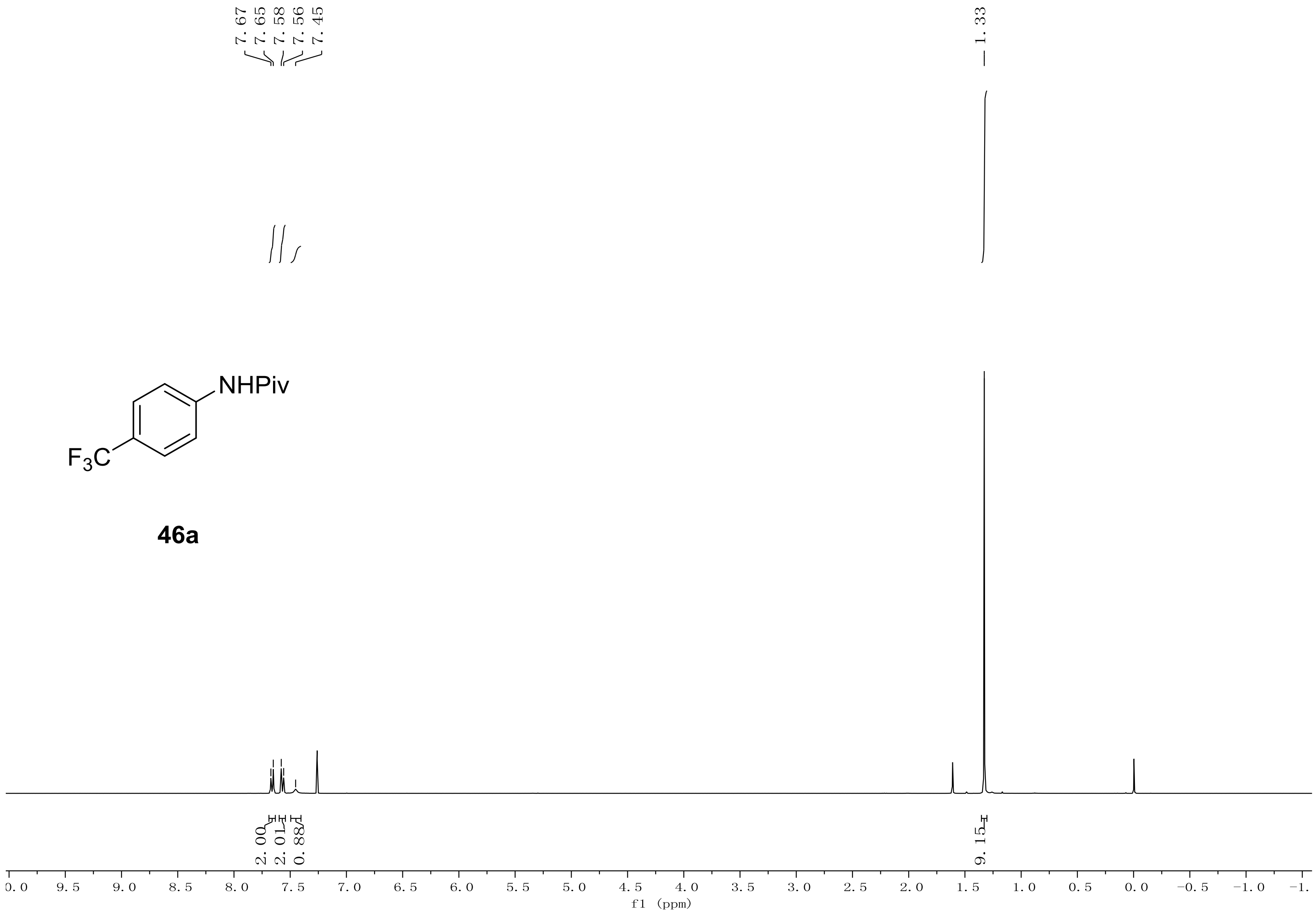
45a


176.96
138.52
131.39
131.07
129.36
127.90
125.19
123.09
122.48
120.74
120.69
120.65
120.62
119.77
116.86
116.82
116.79
116.75
39.67
27.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
F3C
NHPiv

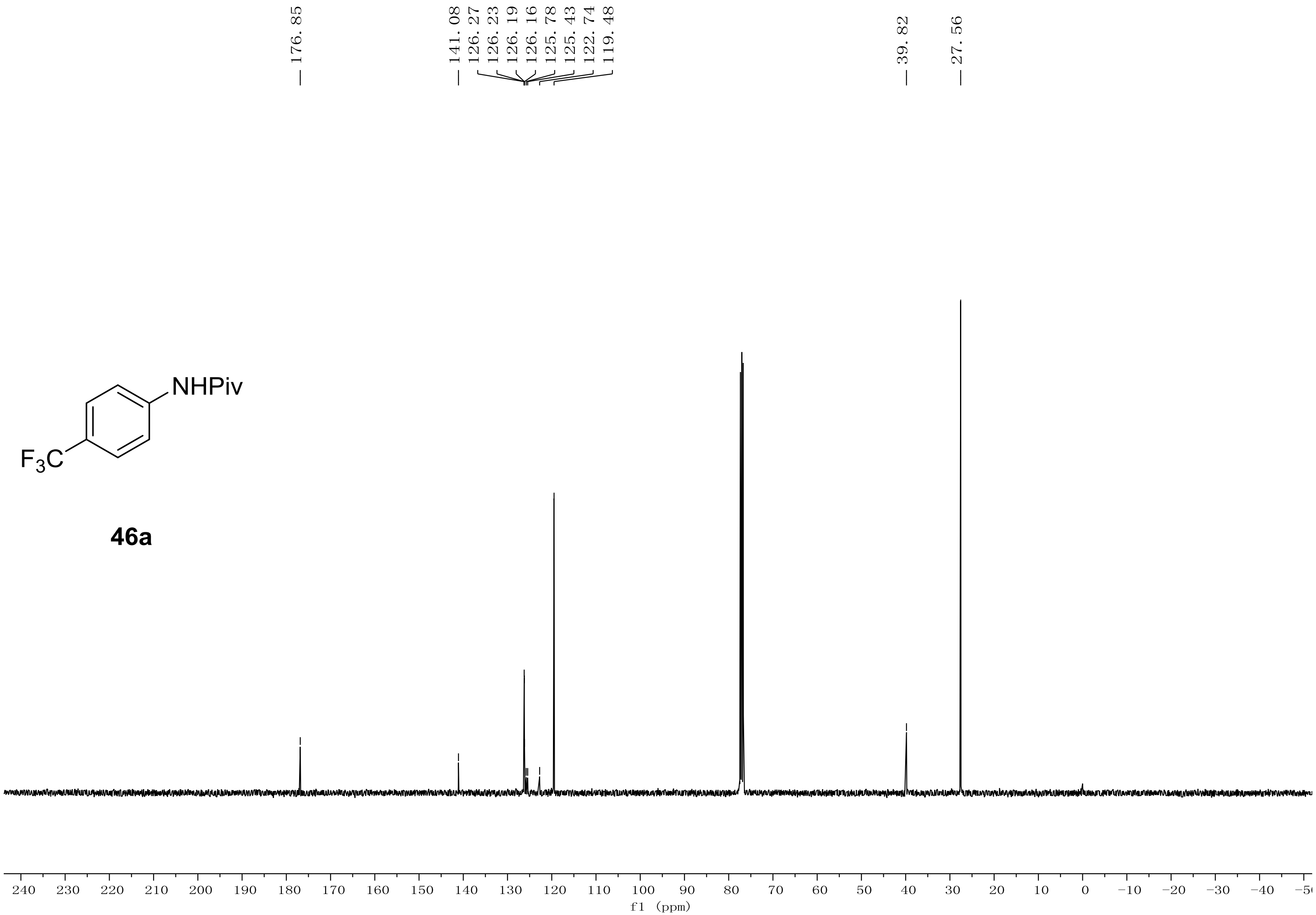
45a



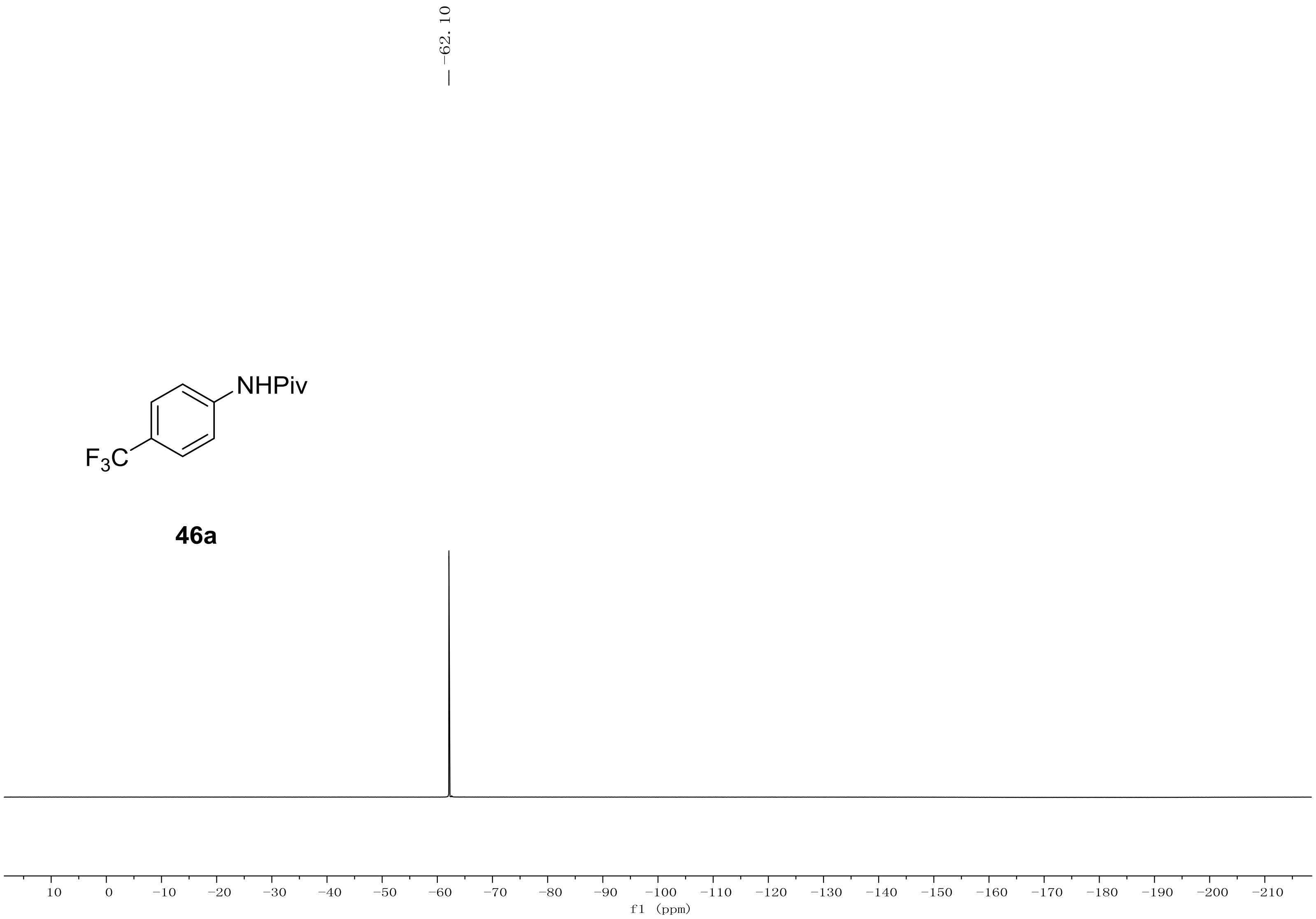
45a

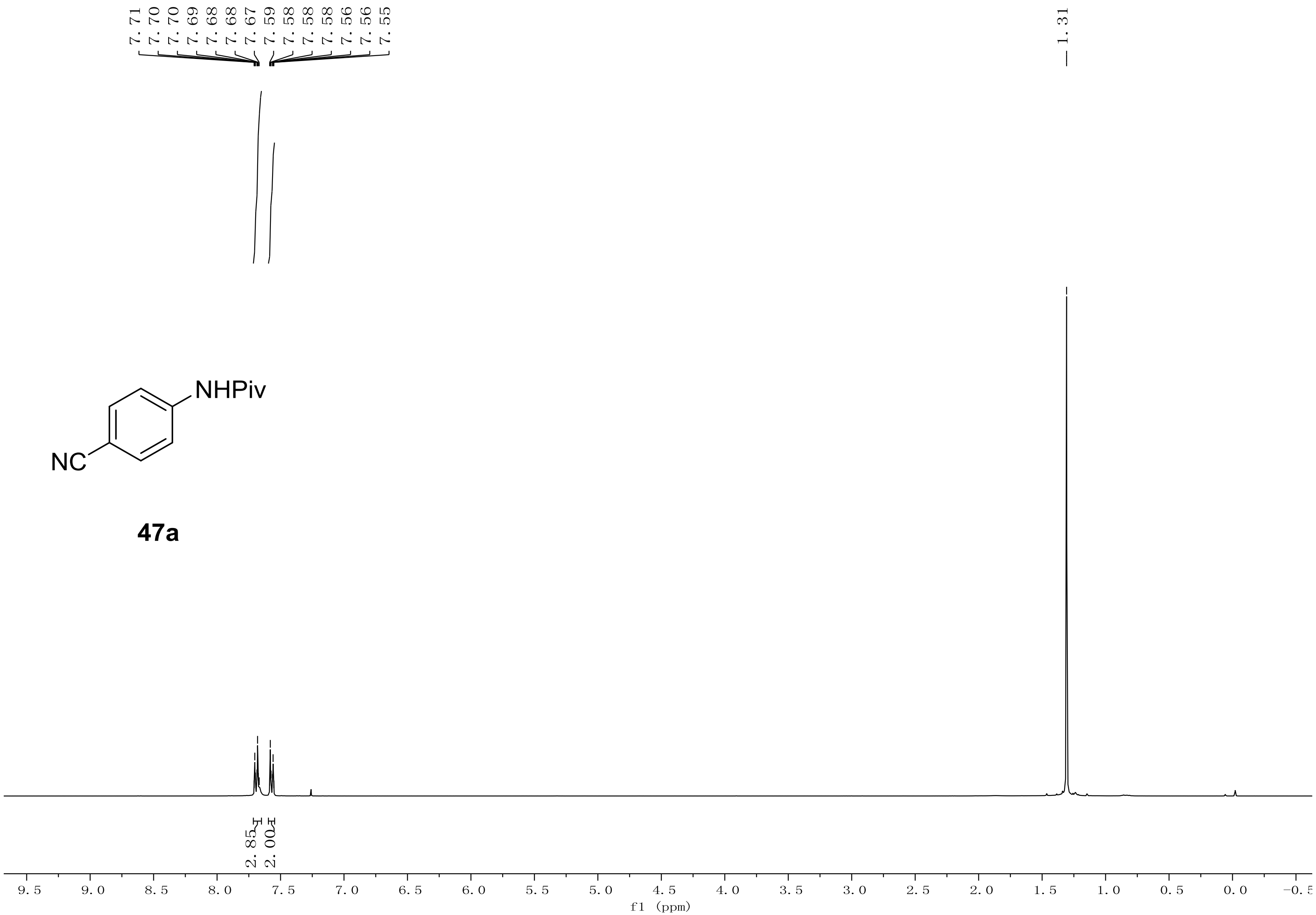


46a

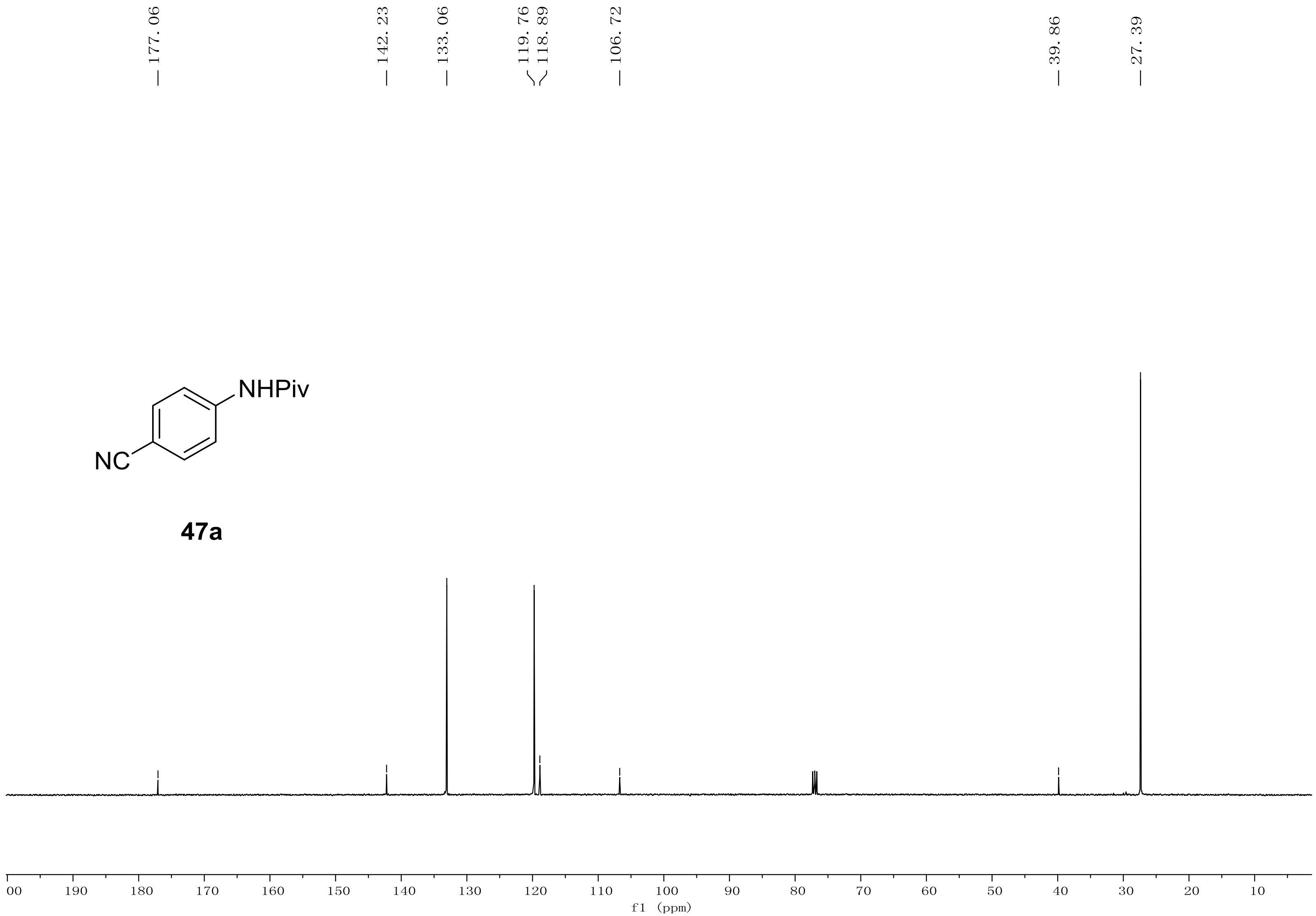


176.85
141.08
126.27
126.23
126.19
126.16
125.78
125.43
122.74
119.48
39.82
27.56
NHPiv
F_3C
46a
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

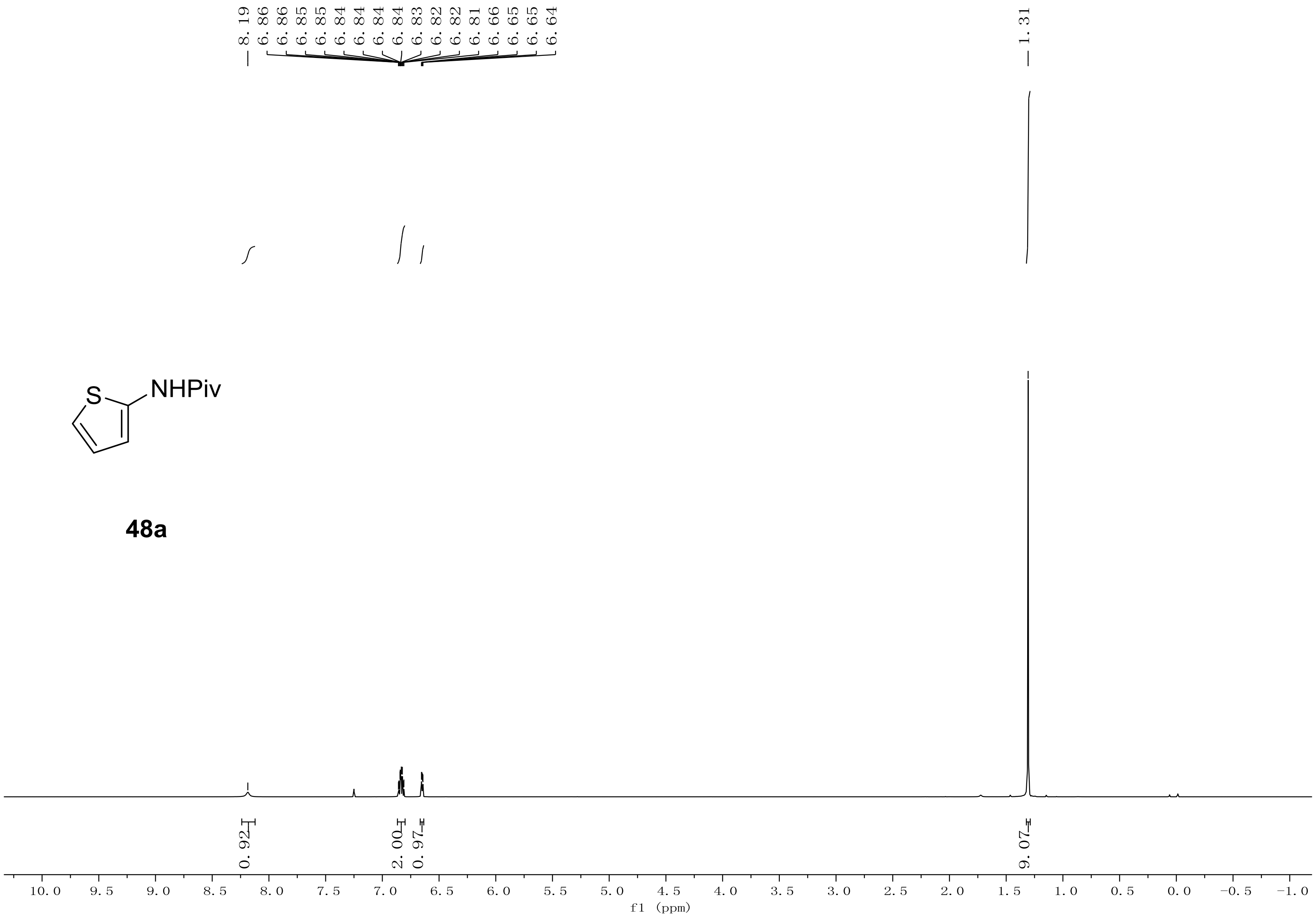

−62.10
NHPiv
F3C
46a
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


7.71
7.70
7.70
7.69
7.68
7.68
7.67
7.59
7.58
7.58
7.58
7.56
7.56
7.55
1.31
NHPiv
NC
2.85
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

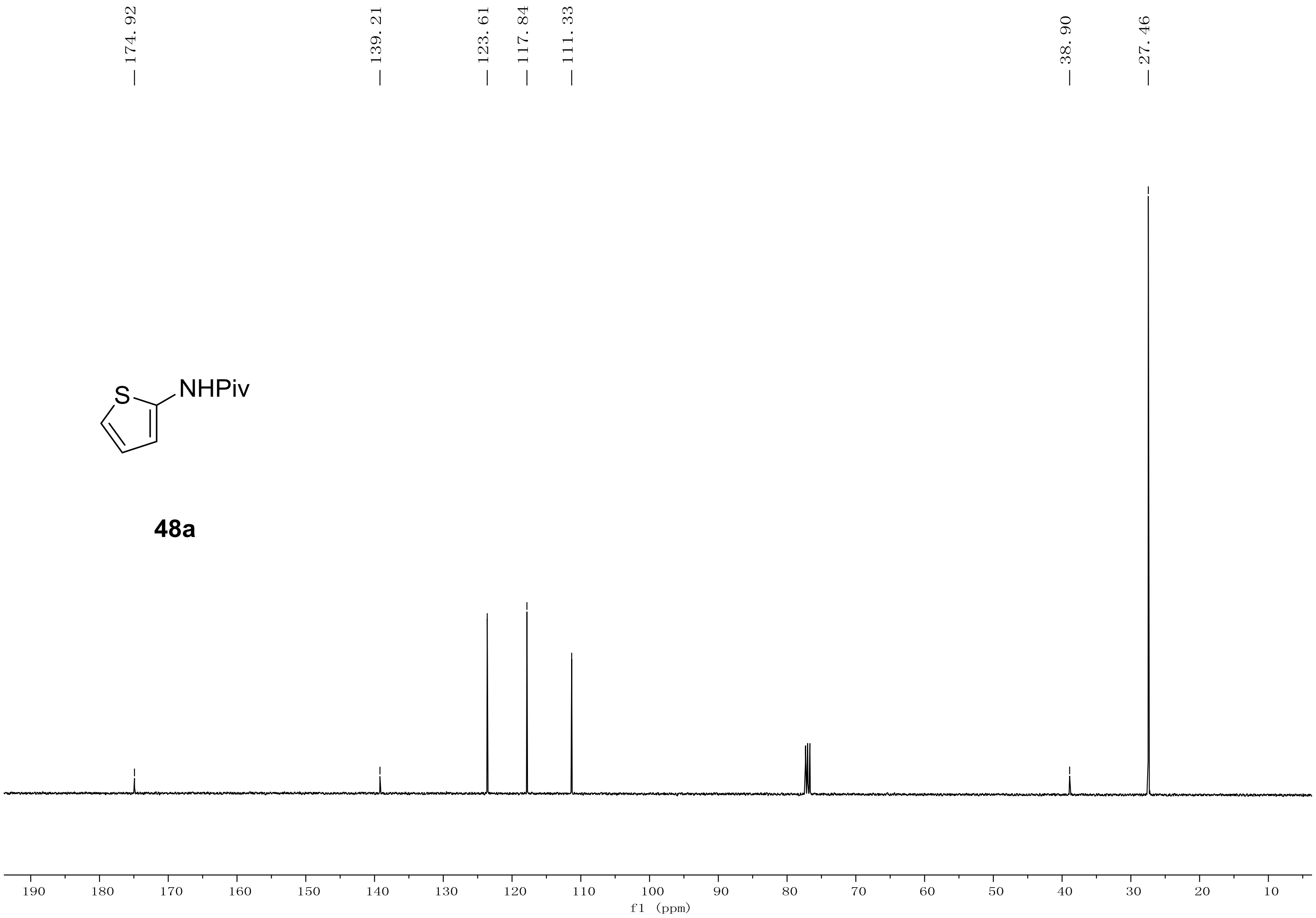
47a



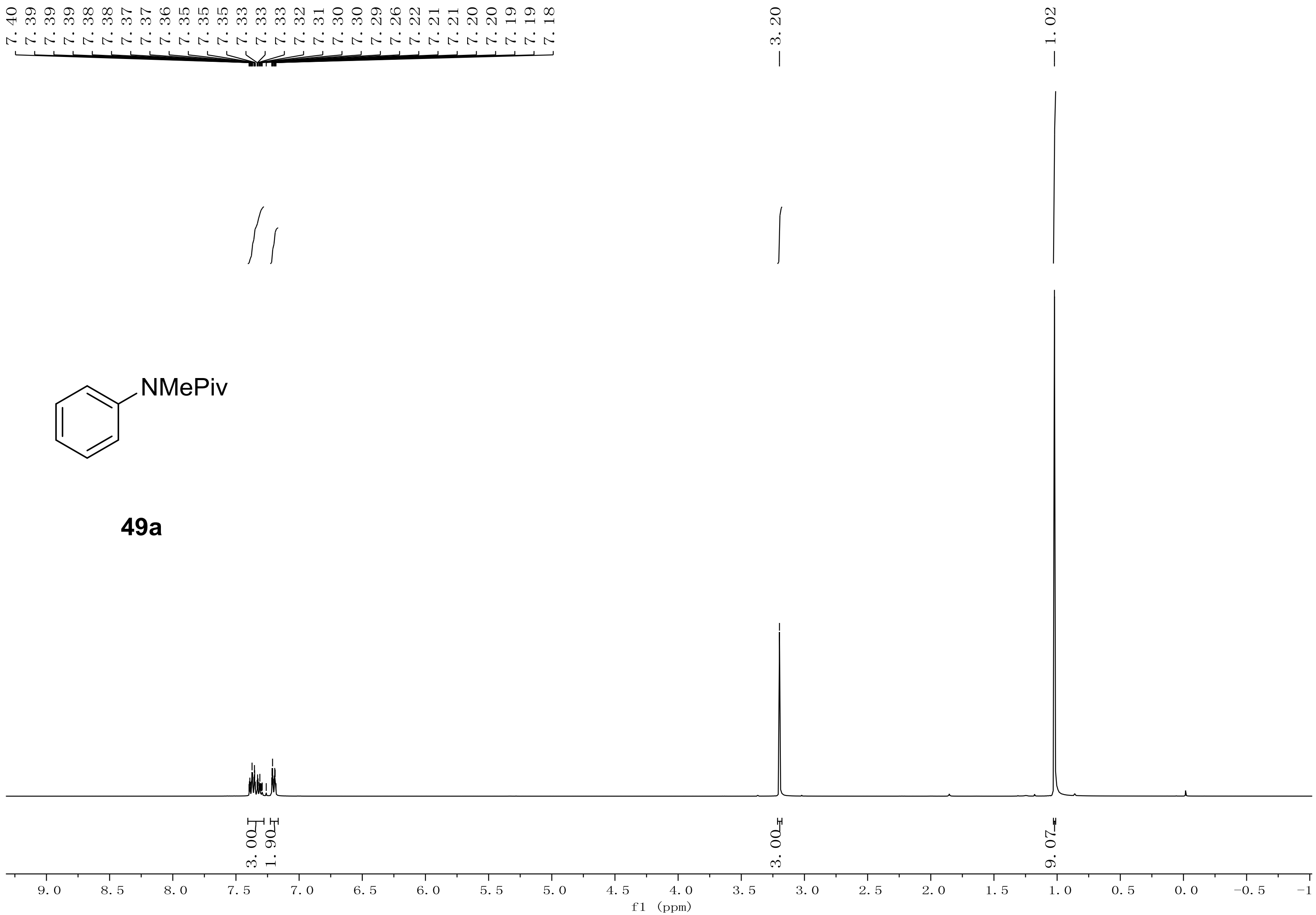
NHPiv
NC
47a
177.06
142.23
133.06
119.76
118.89
106.72
39.86
27.39
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.19
6.86
6.86
6.85
6.85
6.84
6.84
6.84
6.84
6.83
6.82
6.82
6.81
6.66
6.65
6.65
6.64
1.31
0.92
2.00
0.97
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
S
NHPiv

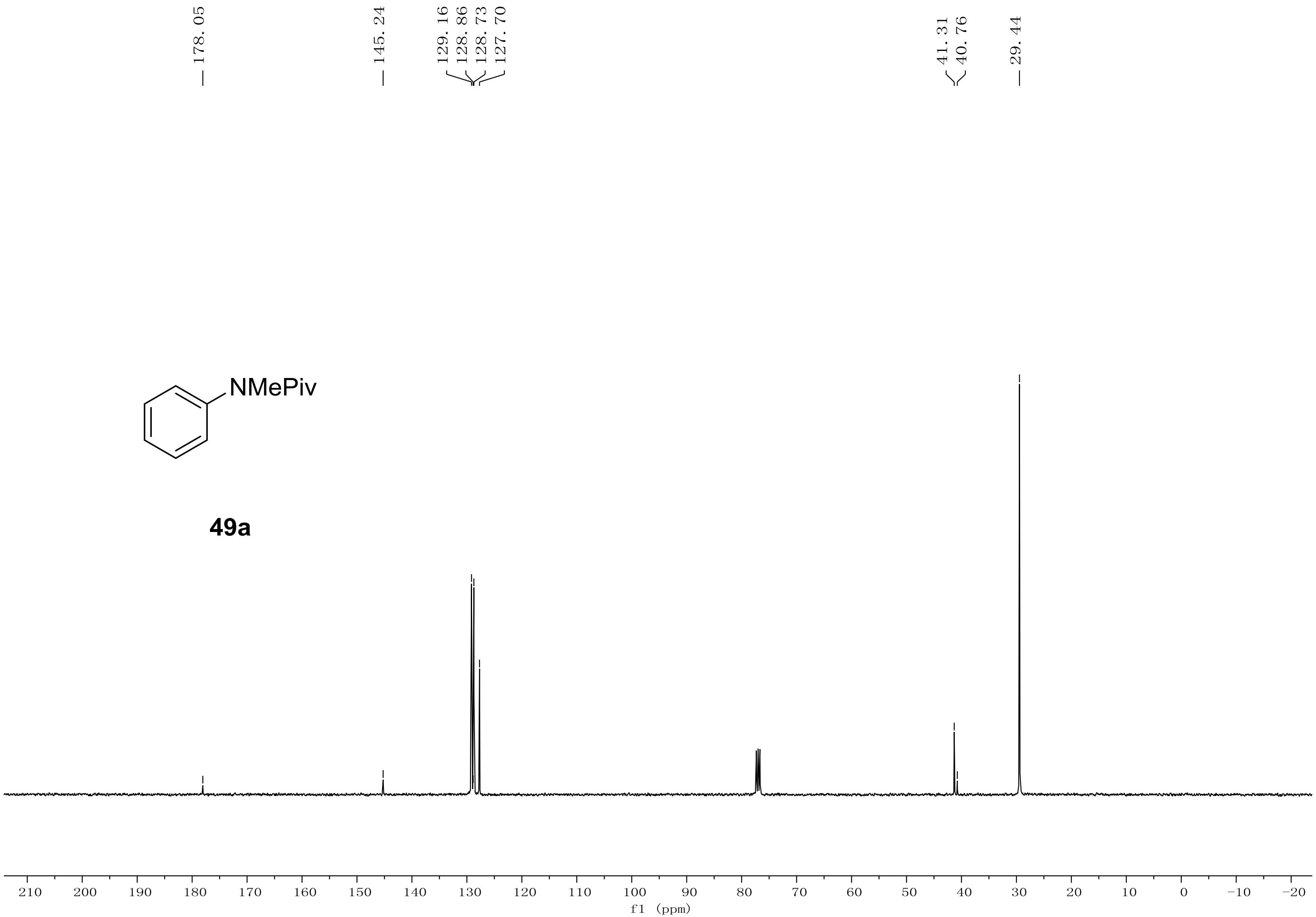
48a


174.92
139.21
123.61
117.84
111.33
38.90
27.46
NHPiv
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

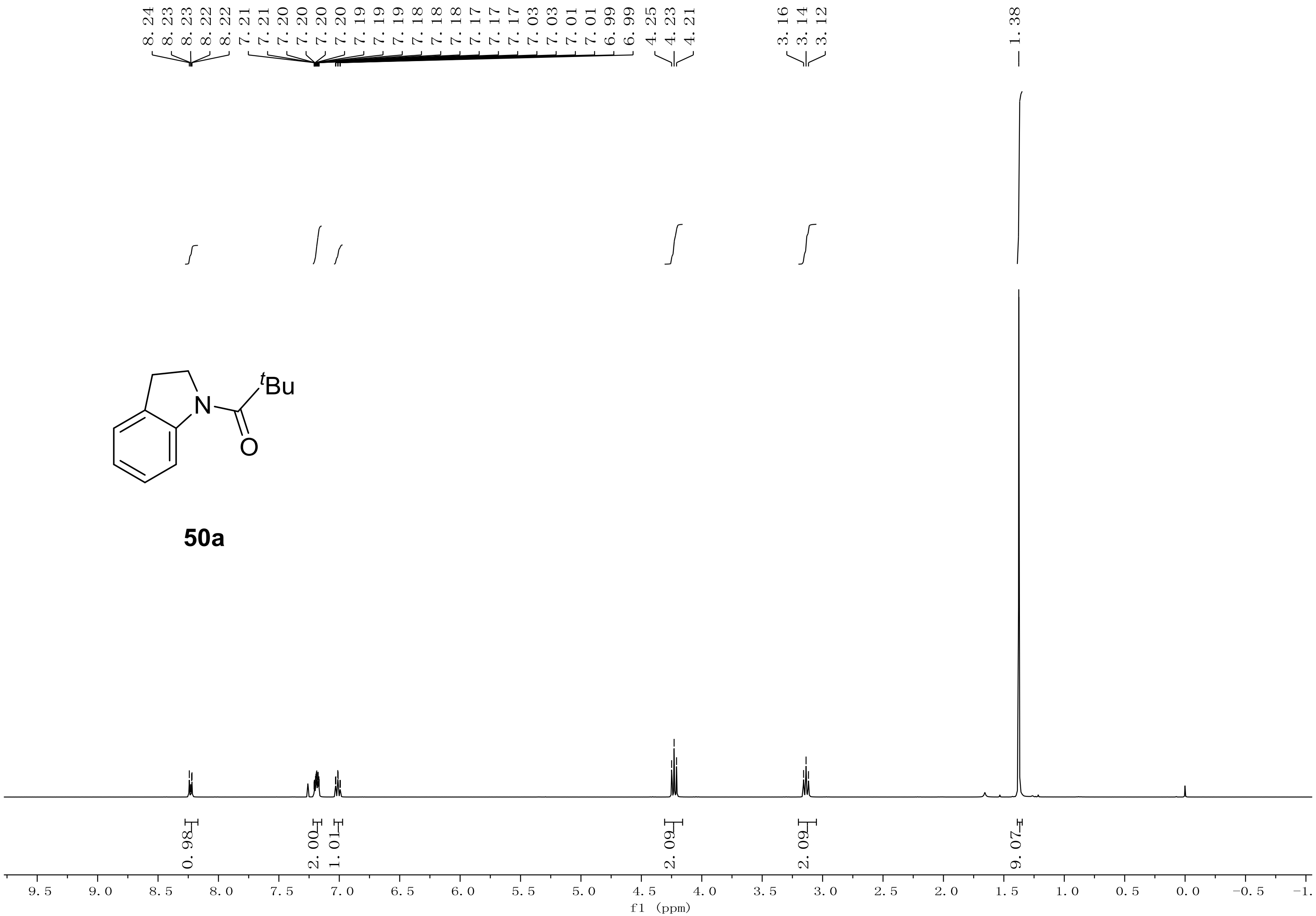
48a


7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.33
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.26
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
3.20
1.02
NMePiv
3.00
1.90
3.00
9.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

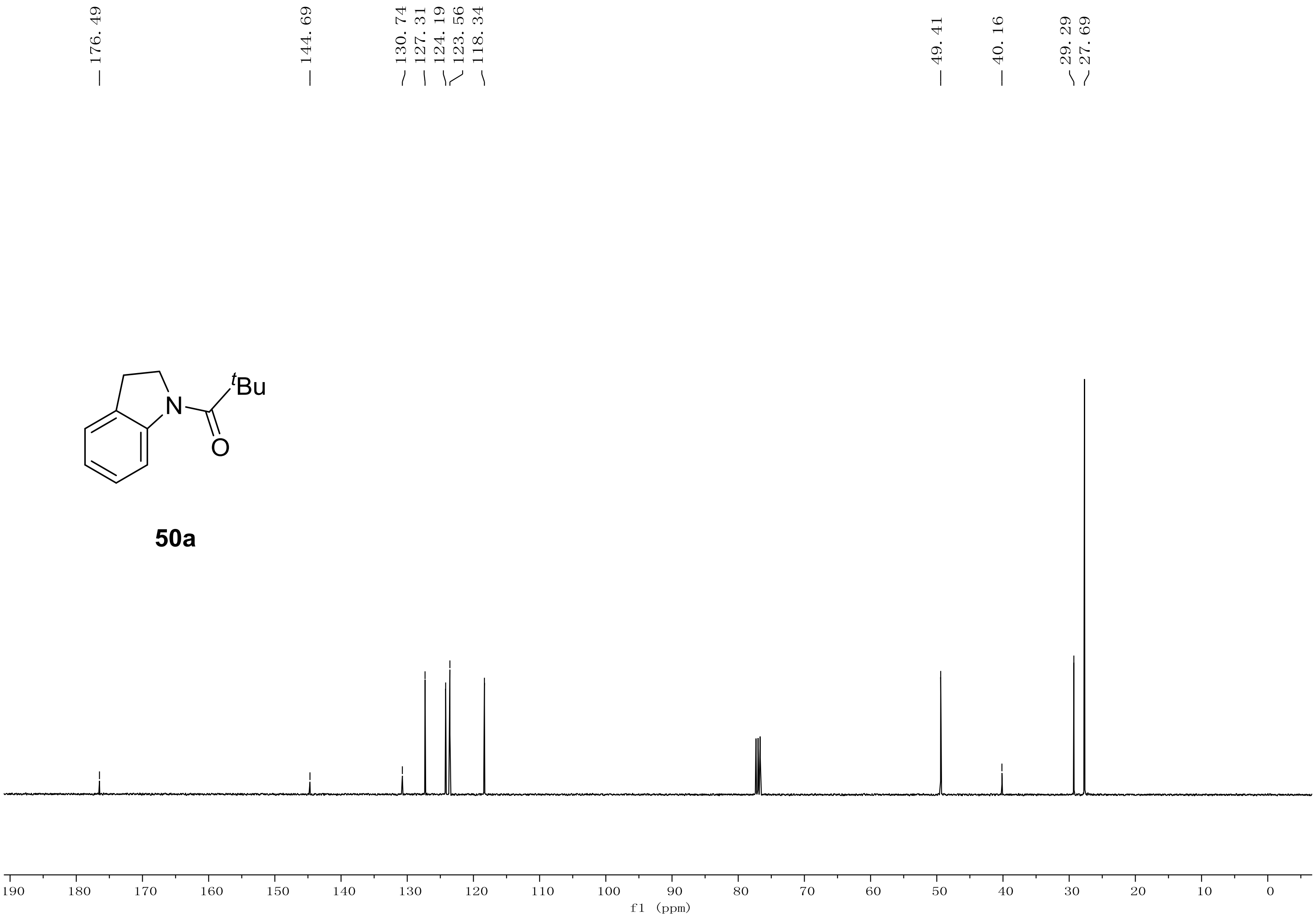
49a


178.05
145.24
129.16
128.86
128.73
127.70
41.31
40.76
29.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
NMePiv

49a

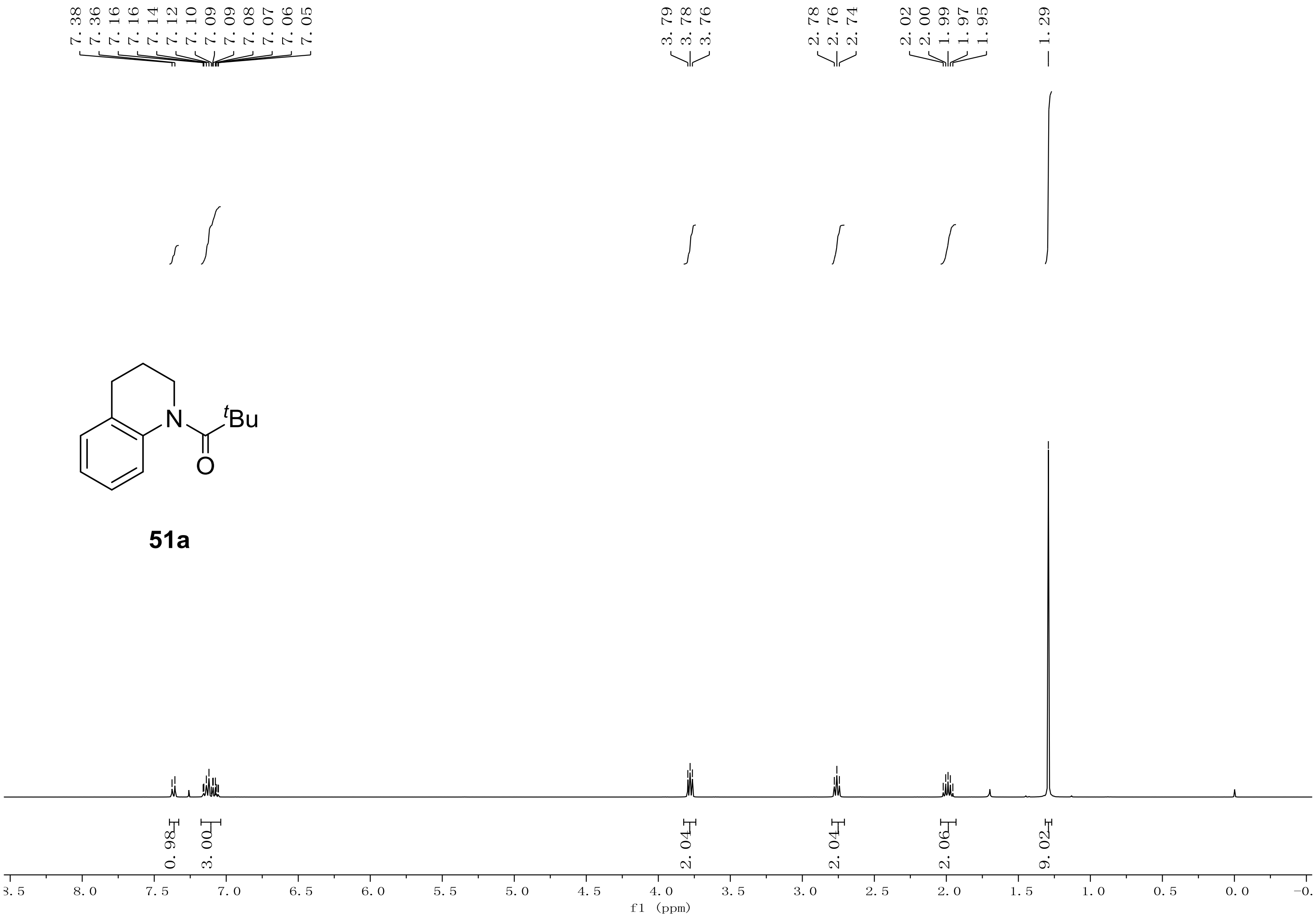

8.24
8.23
8.23
8.22
8.22
7.21
7.21
7.20
7.20
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.17
7.03
7.03
7.01
7.01
6.99
6.99
4.25
4.23
4.21
3.16
3.14
3.12
1.38
^{t}Bu
N
O
0.98
2.00
1.01
2.09
2.09
9.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)

50a

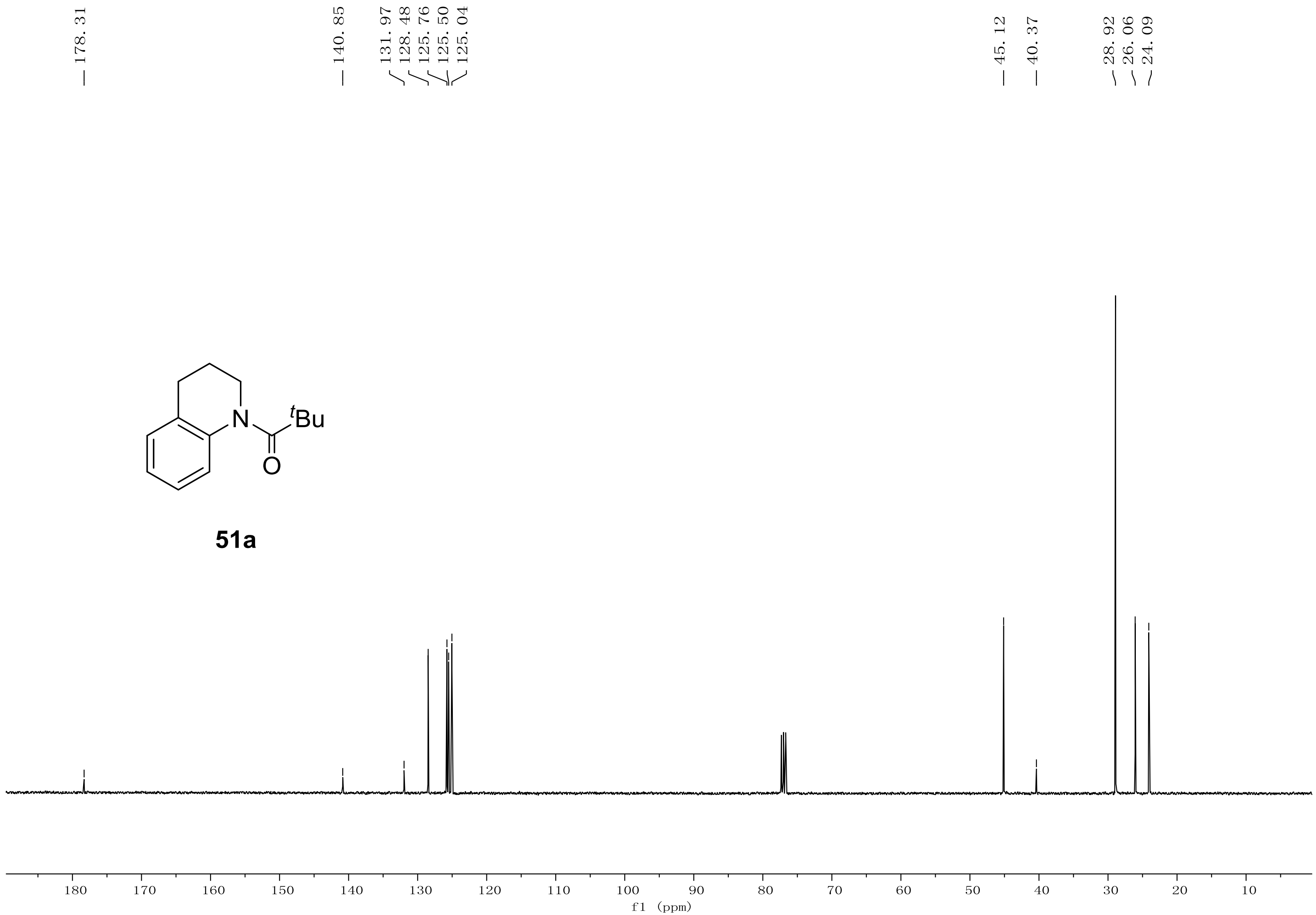


176.49
144.69
130.74
127.31
124.19
123.56
118.34
49.41
40.16
29.29
27.69
tBu
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

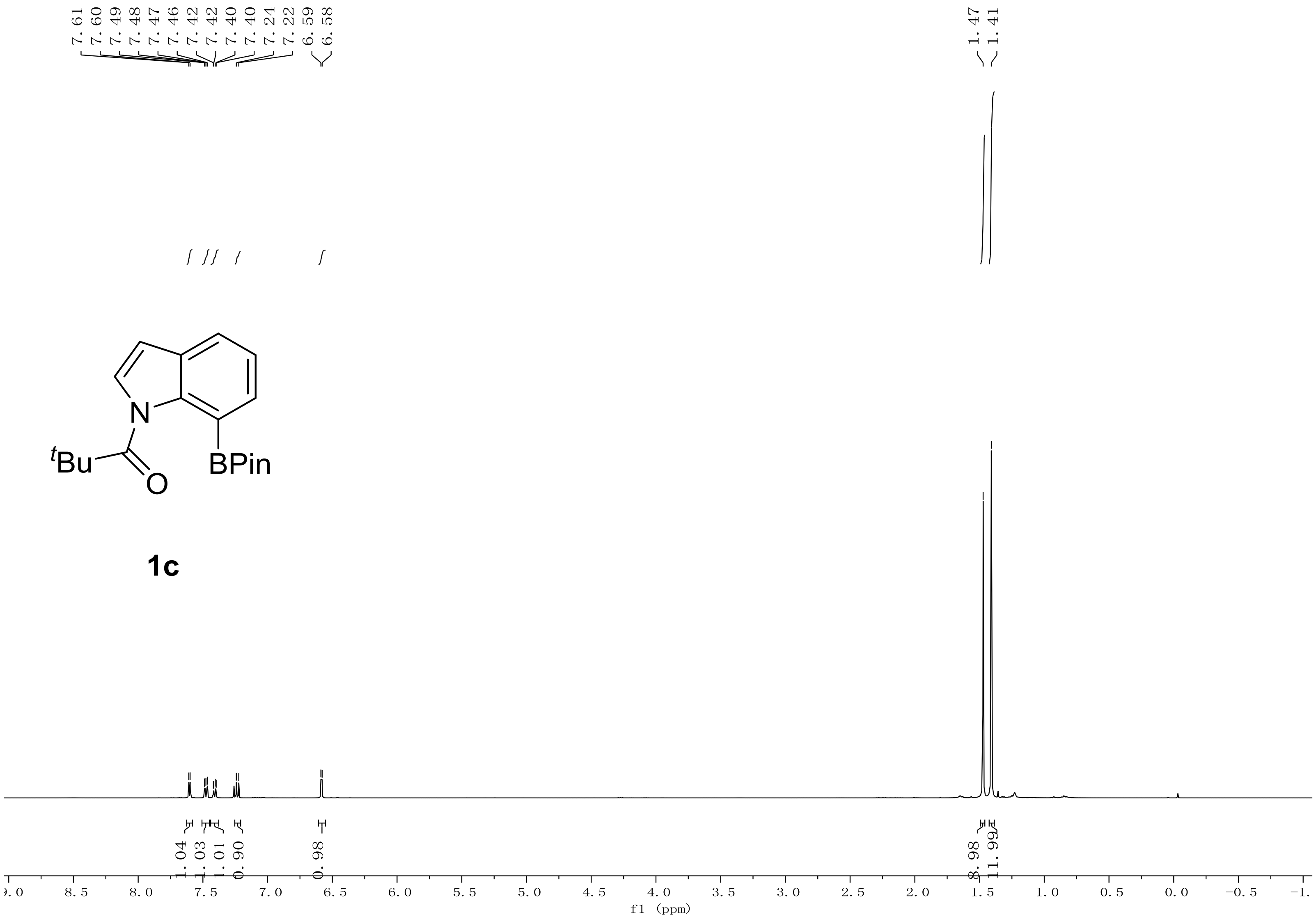
50a


7.38
7.36
7.16
7.16
7.14
7.12
7.10
7.09
7.09
7.08
7.07
7.06
7.05
3.79
3.78
3.76
2.78
2.76
2.74
2.02
2.00
1.99
1.97
1.95
1.29
0.98
3.00
2.04
2.04
2.06
9.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)
N
tBu
O

51a

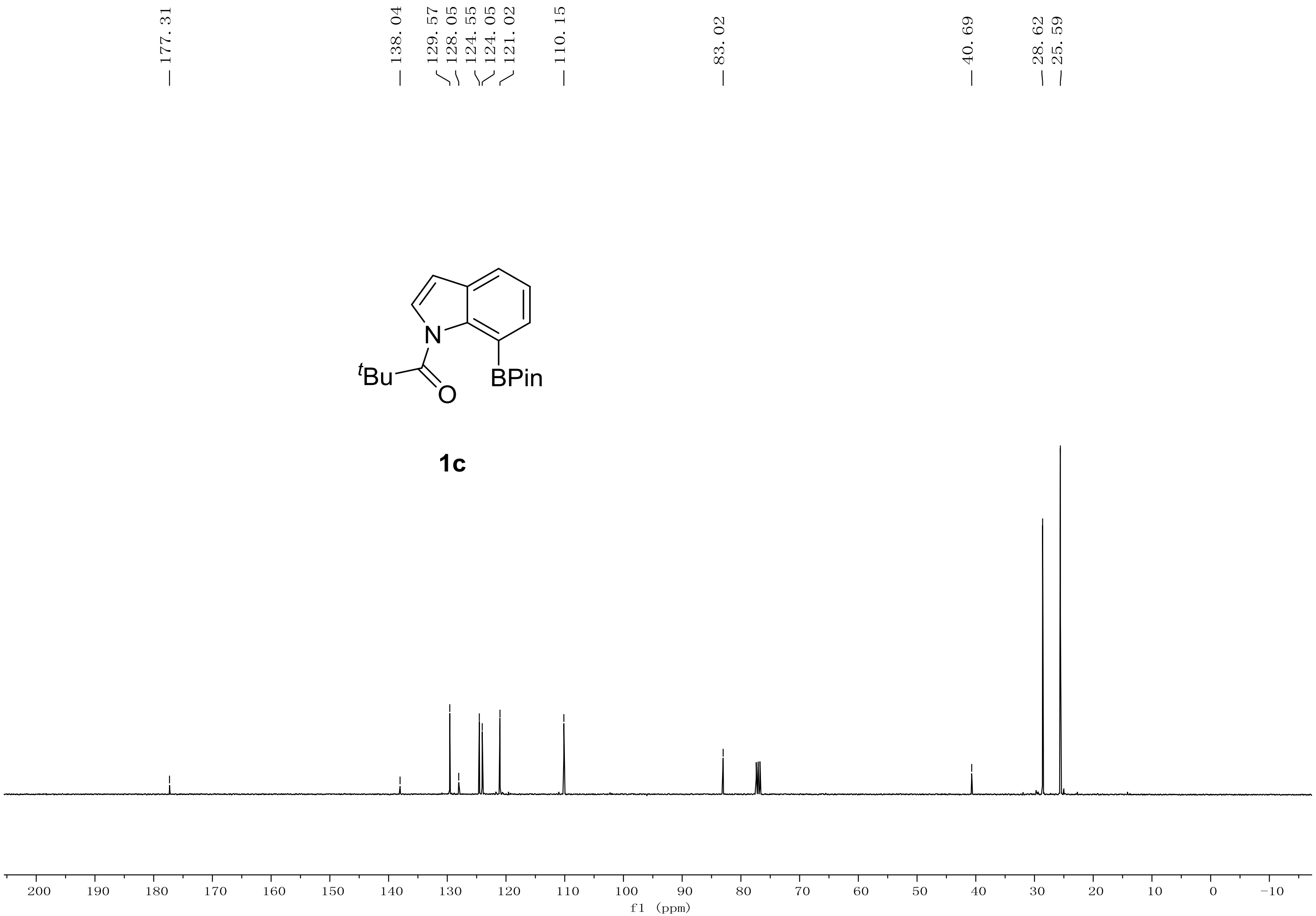

178.31
140.85
131.97
128.48
125.76
125.50
125.04
45.12
40.37
28.92
26.06
24.09
N
^{t}Bu
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

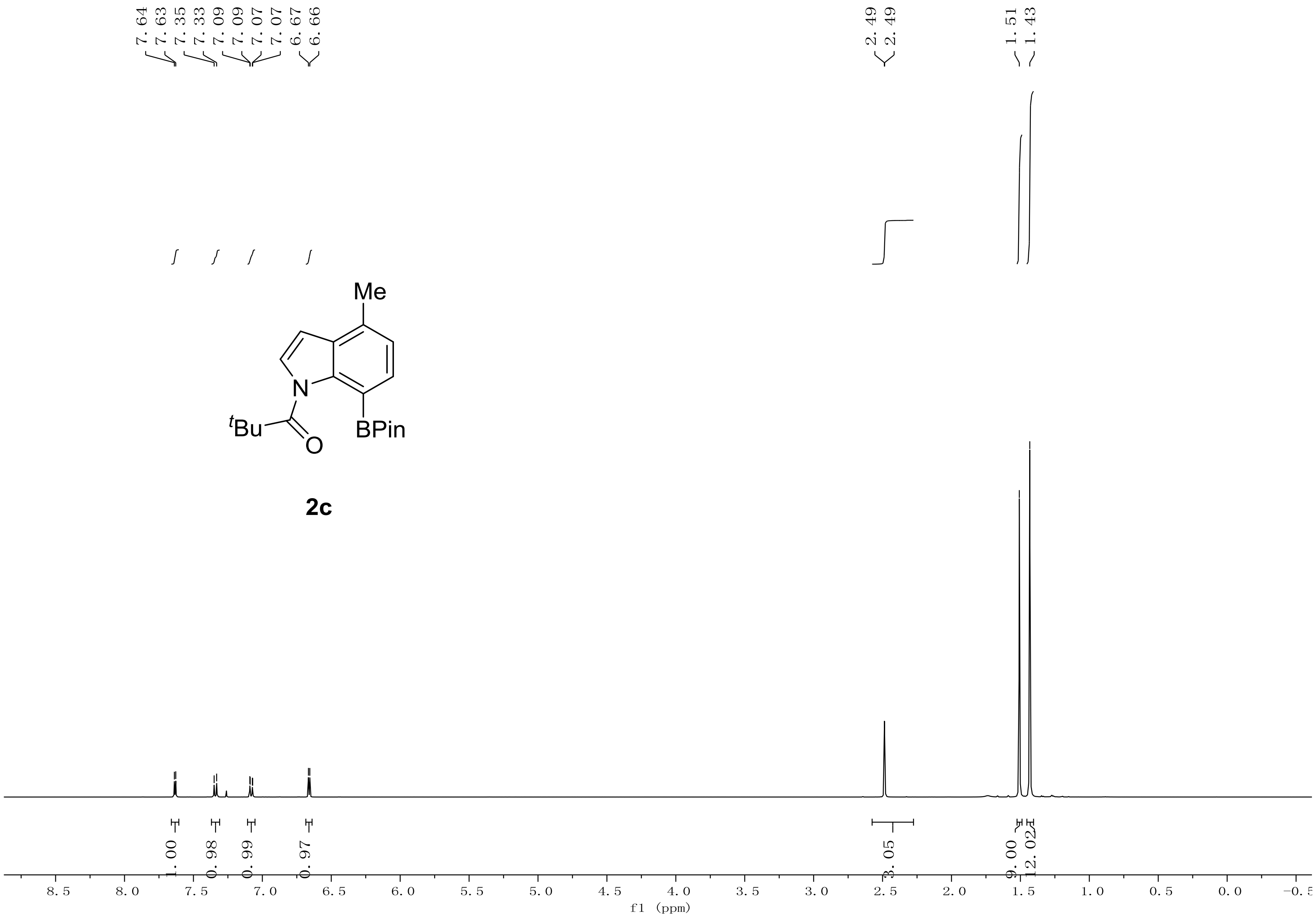
51a

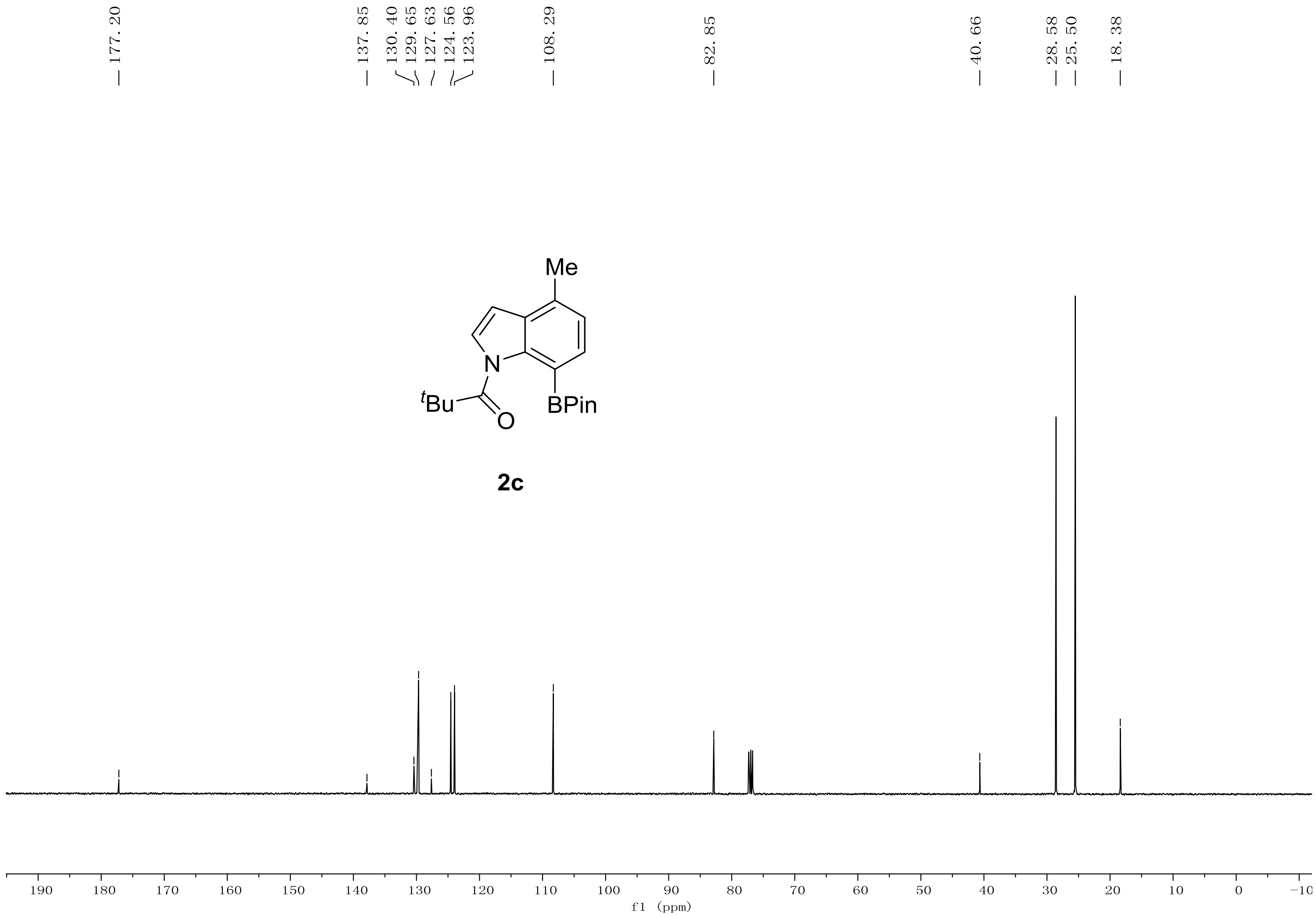


7.61
7.60
7.49
7.48
7.47
7.46
7.42
7.42
7.40
7.40
7.24
7.22
6.59
6.58
1.47
1.41
1.04
1.03
1.01
0.90
0.98
8.98
11.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

1c


177.31
138.04
129.57
128.05
124.55
124.05
121.02
110.15
83.02
40.69
28.62
25.59
N
tBu
O
BPin
1c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.64
7.63
7.35
7.33
7.09
7.09
7.07
7.07
6.67
6.66
2.49
2.49
1.51
1.43
Me
N
tBu
O
BPin
2c
1.00
0.98
0.99
0.97
3.05
9.00
12.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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137.85
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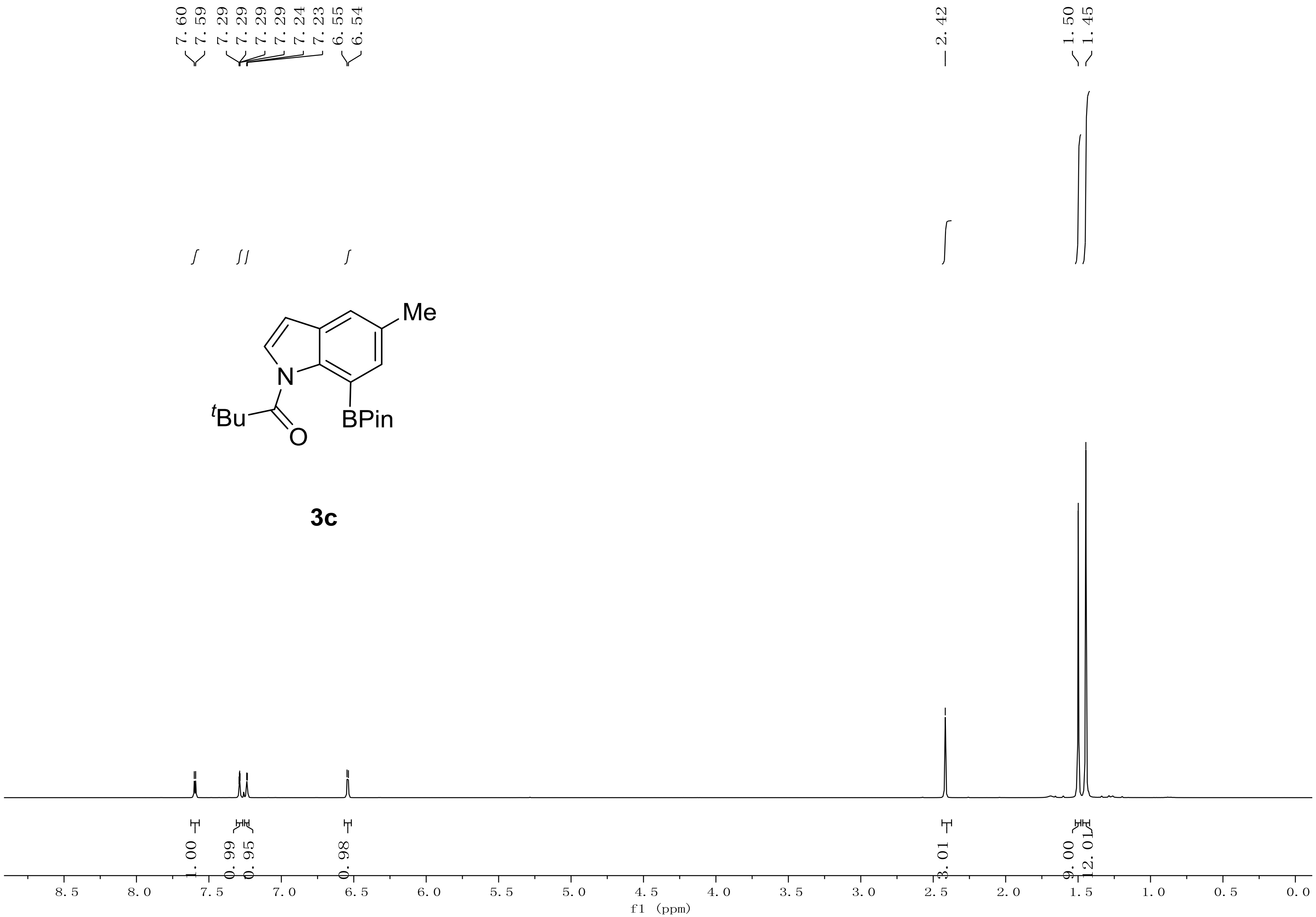
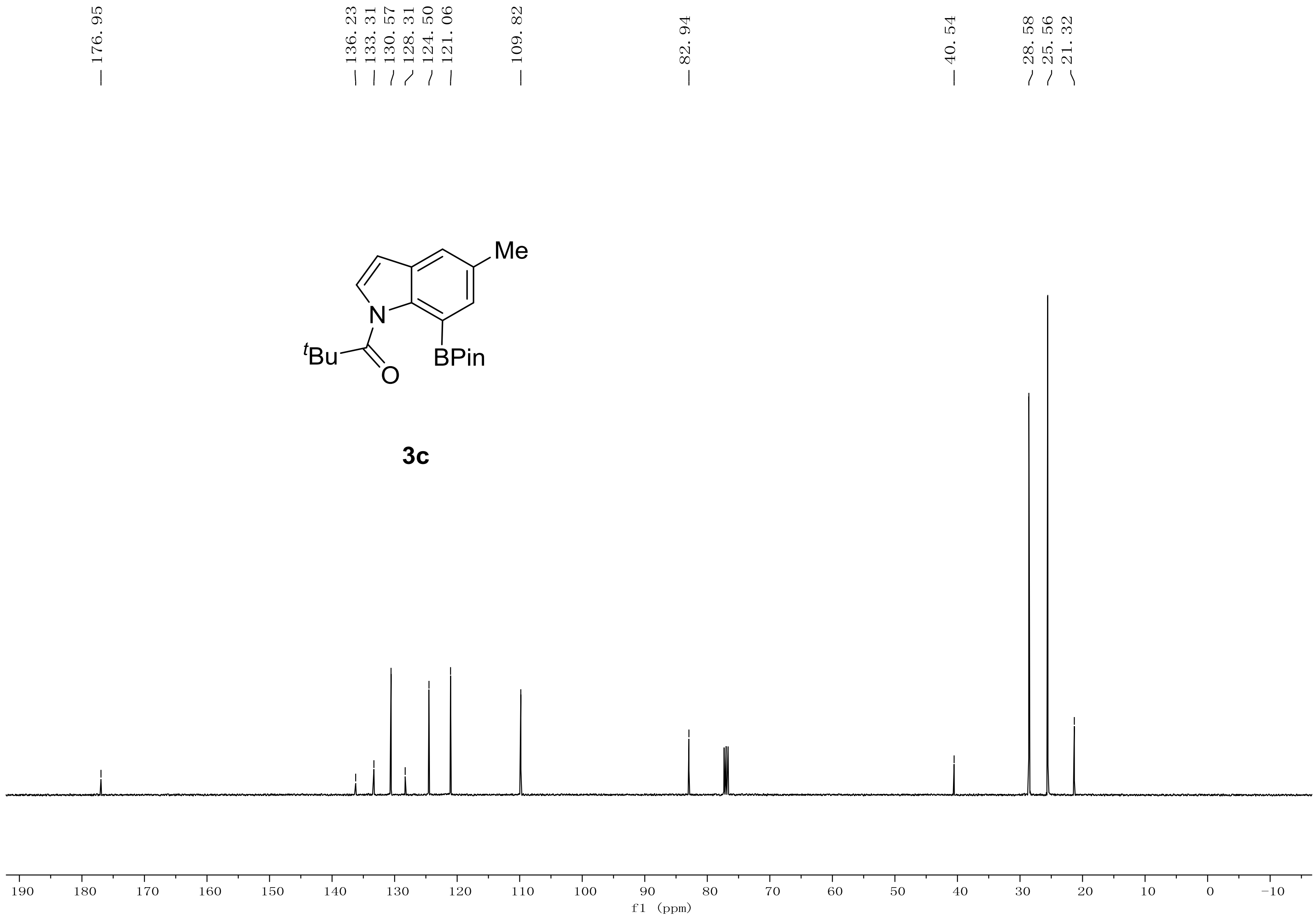
127.63
124.56
123.96
108.29
82.85
40.66
28.58
25.50
18.38
Me
N
BPin
tBu
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

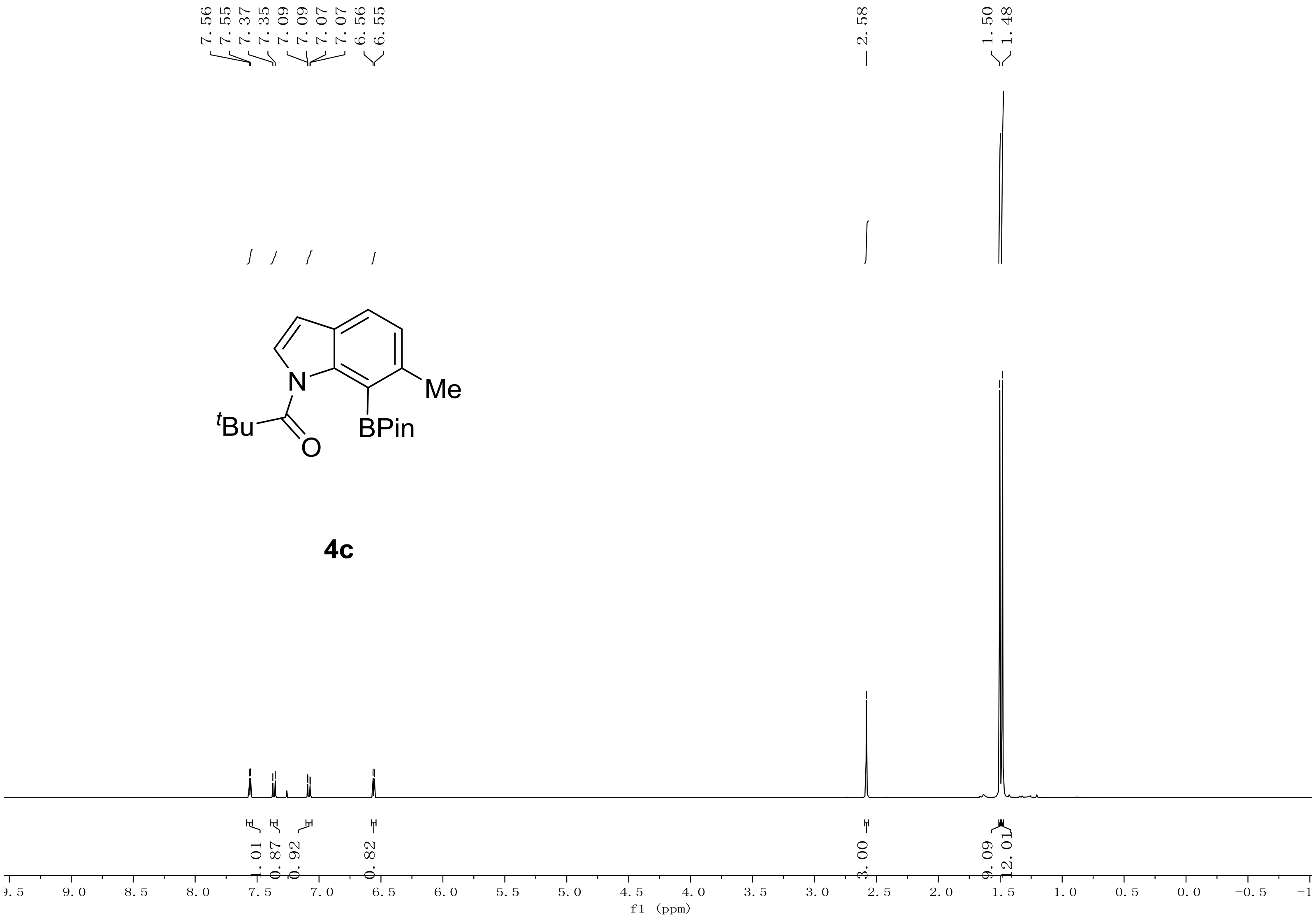
2c


7.60
7.59
7.29
7.29
7.29
7.29
7.24
7.23
6.55
6.54
2.42
1.50
1.45
Me
N
BPin
tBu
O
3c
1.00
0.99
0.95
0.98
3.01
9.00
12.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



176.95
136.23
133.31
130.57
128.31
124.50
121.06
109.82
82.94
40.54
28.58
25.56
21.32
Me
N
tBu
O
BPin
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3c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7.55
7.37
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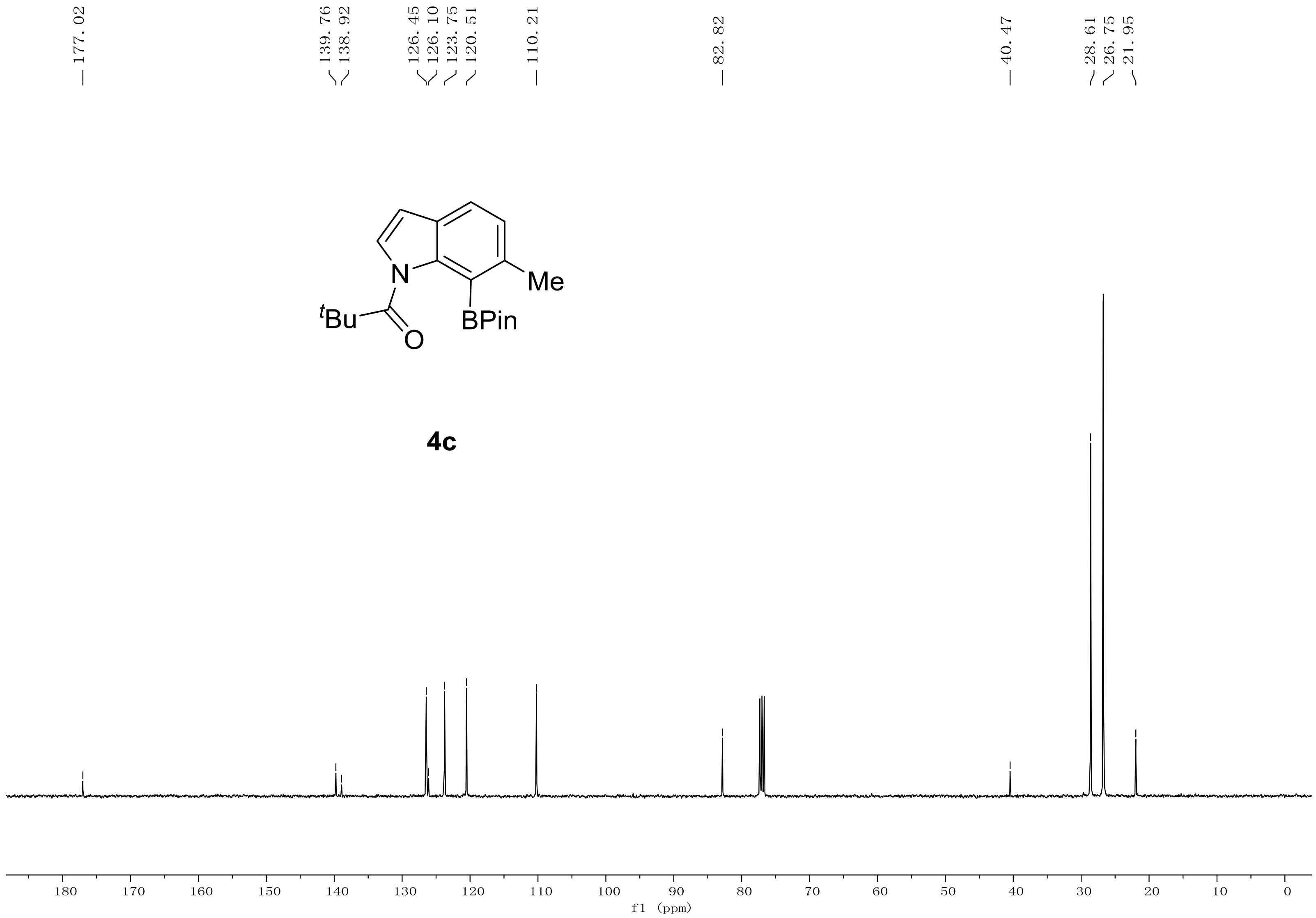
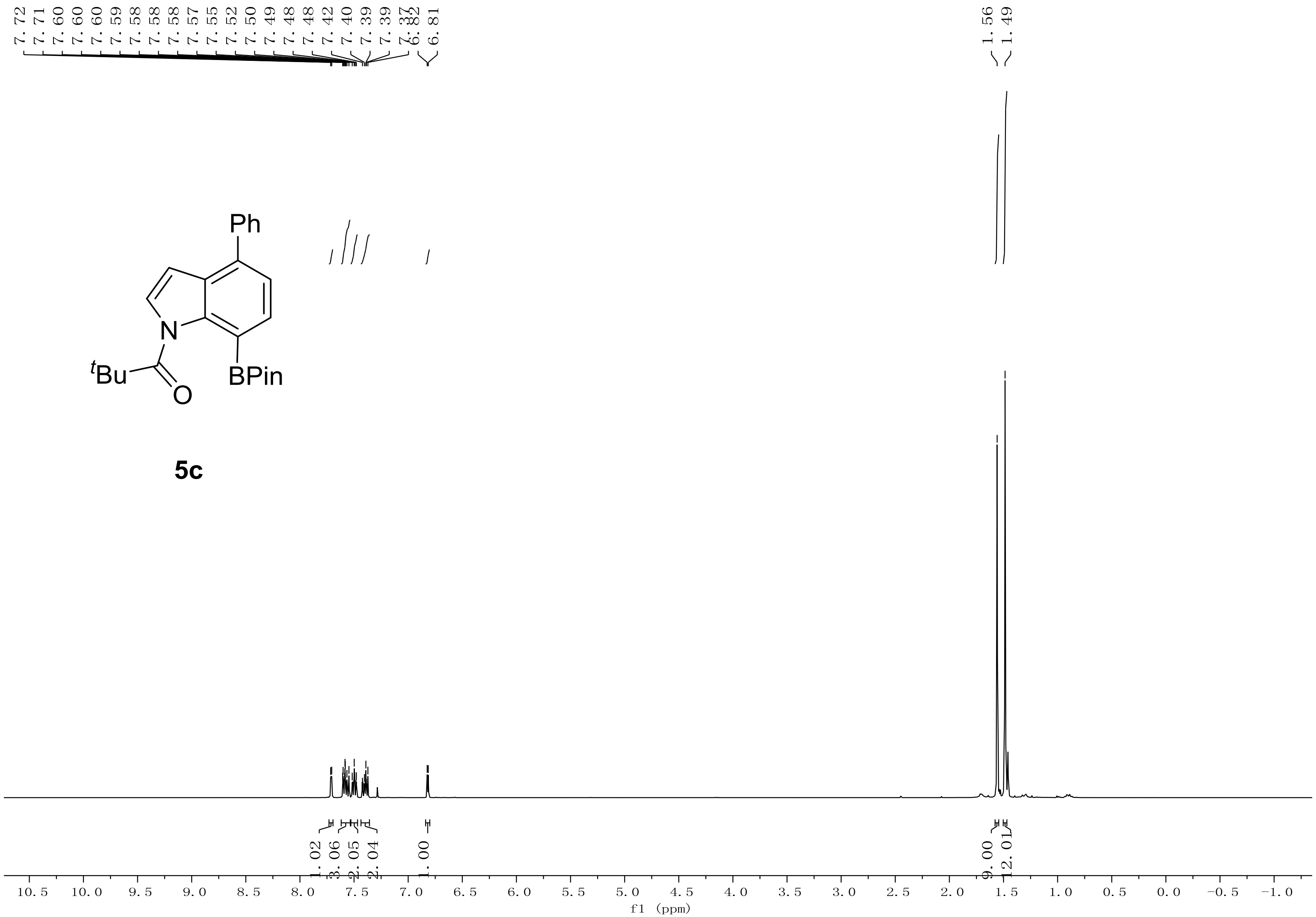
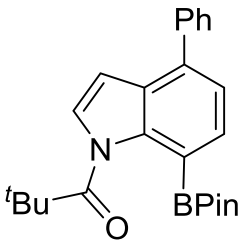
7.09
7.09
7.07
7.07
6.56
6.55
2.58
1.50
1.48
N
Me
tBu
O
BPin
1.01
0.87
0.92
0.82
3.00
9.09
12.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

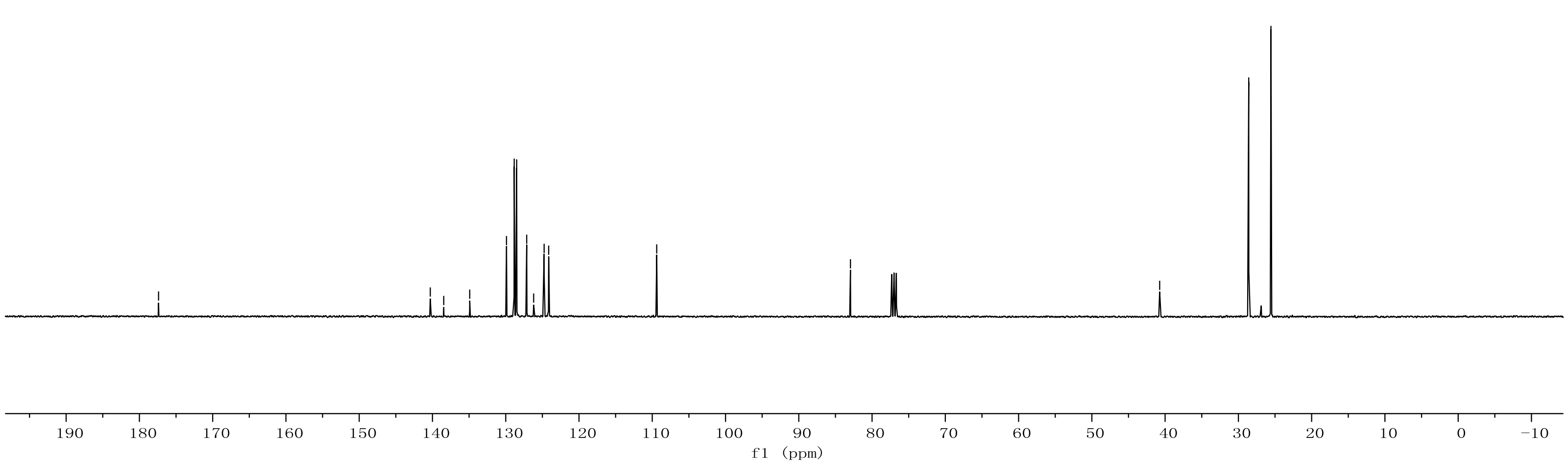
4c

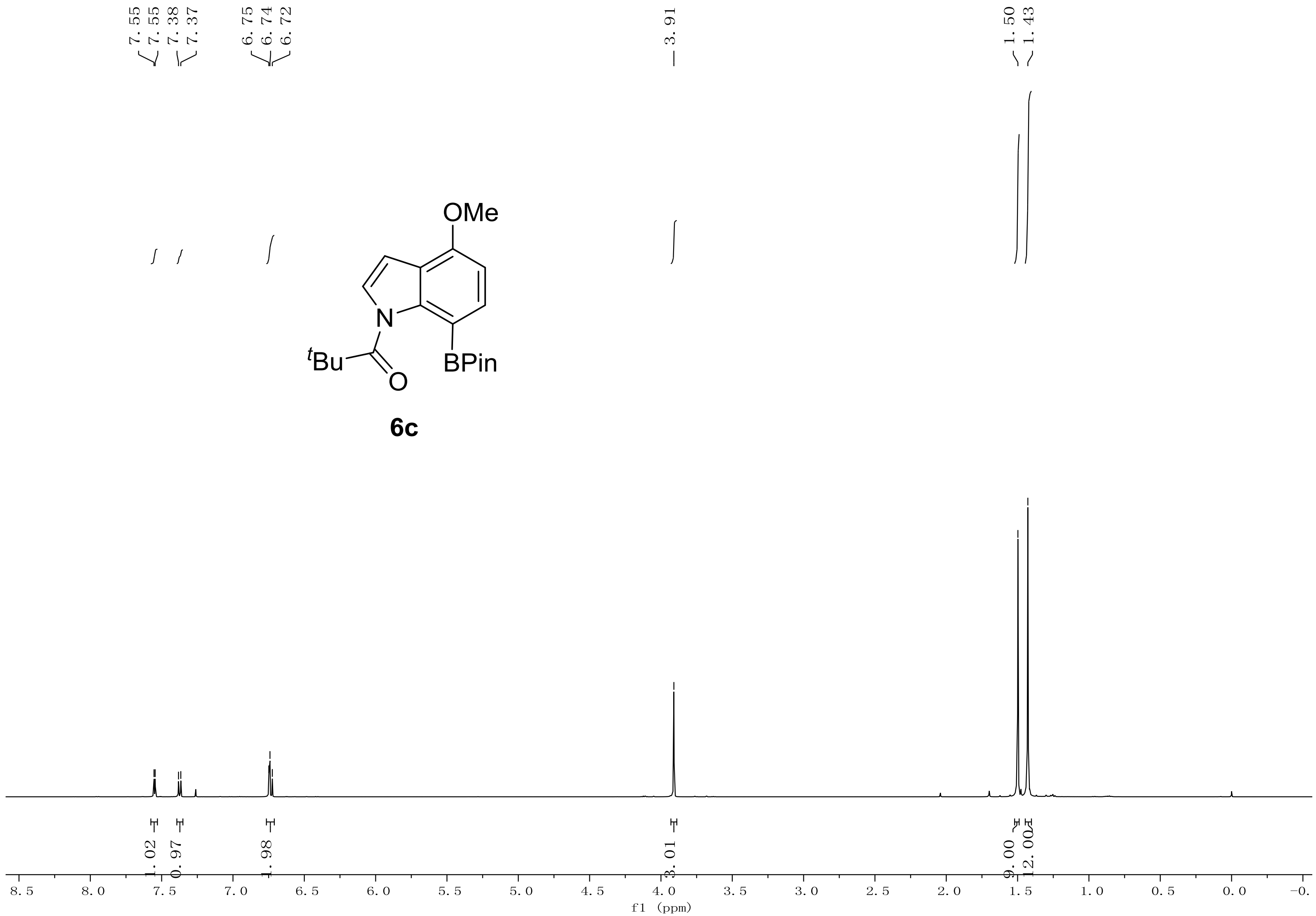

177.02
139.76
138.92
126.45
126.10
123.75
120.51
110.21
82.82
40.47
28.61
26.75
21.95
N
Me
tBu
O
BPin
4c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.72 7.71 7.60 7.60 7.60 7.59 7.58 7.58 7.58 7.57 7.55 7.52 7.50 7.49 7.48 7.48 7.42 7.40 7.39 7.39 7.37 6.82 6.81
1.56 1.49
Ph
N
tBu
O
BPin
5c
1.02 3.06 2.05 2.04 1.00 9.00 12.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

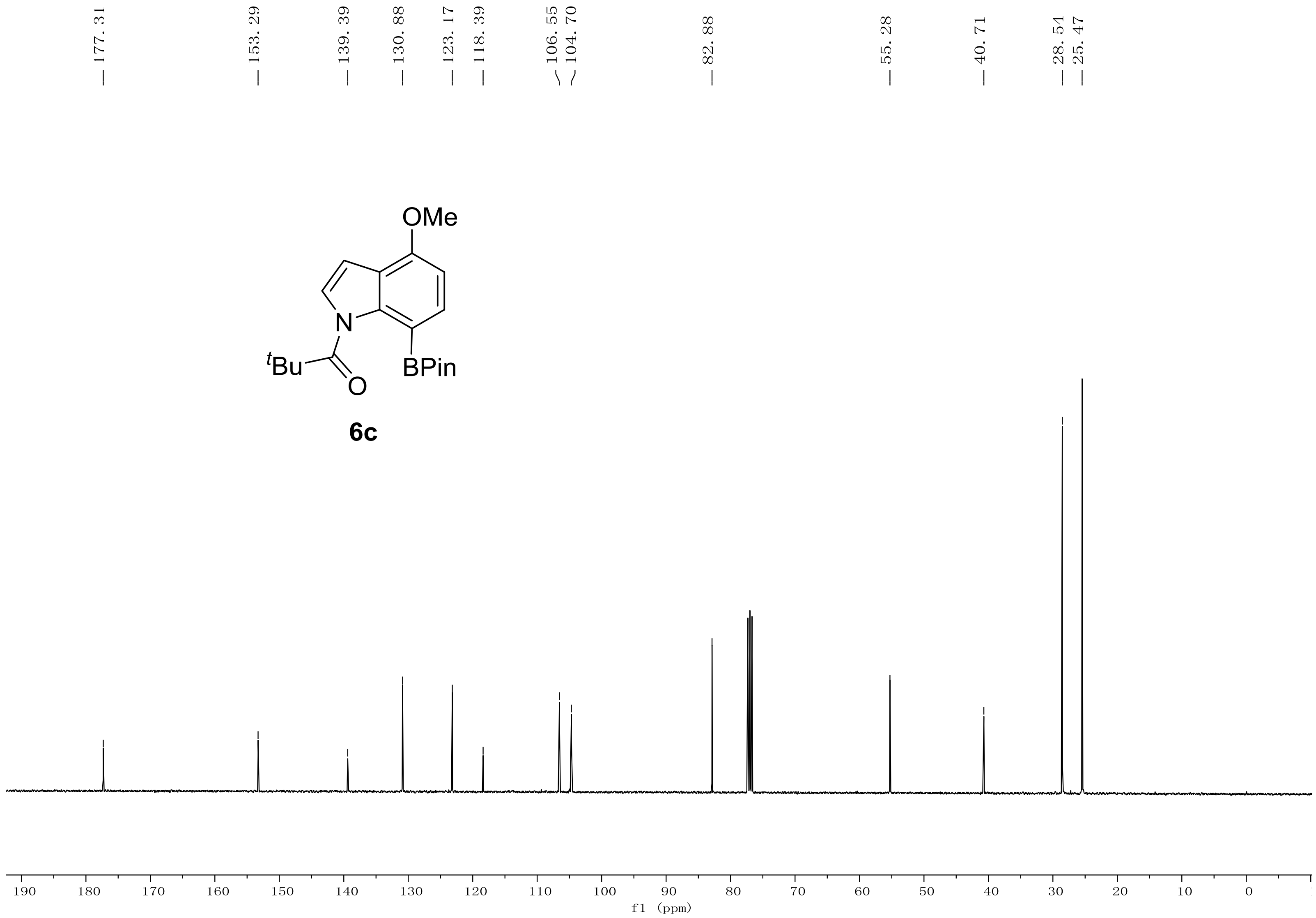

Ph
N
tBu
O
BPin

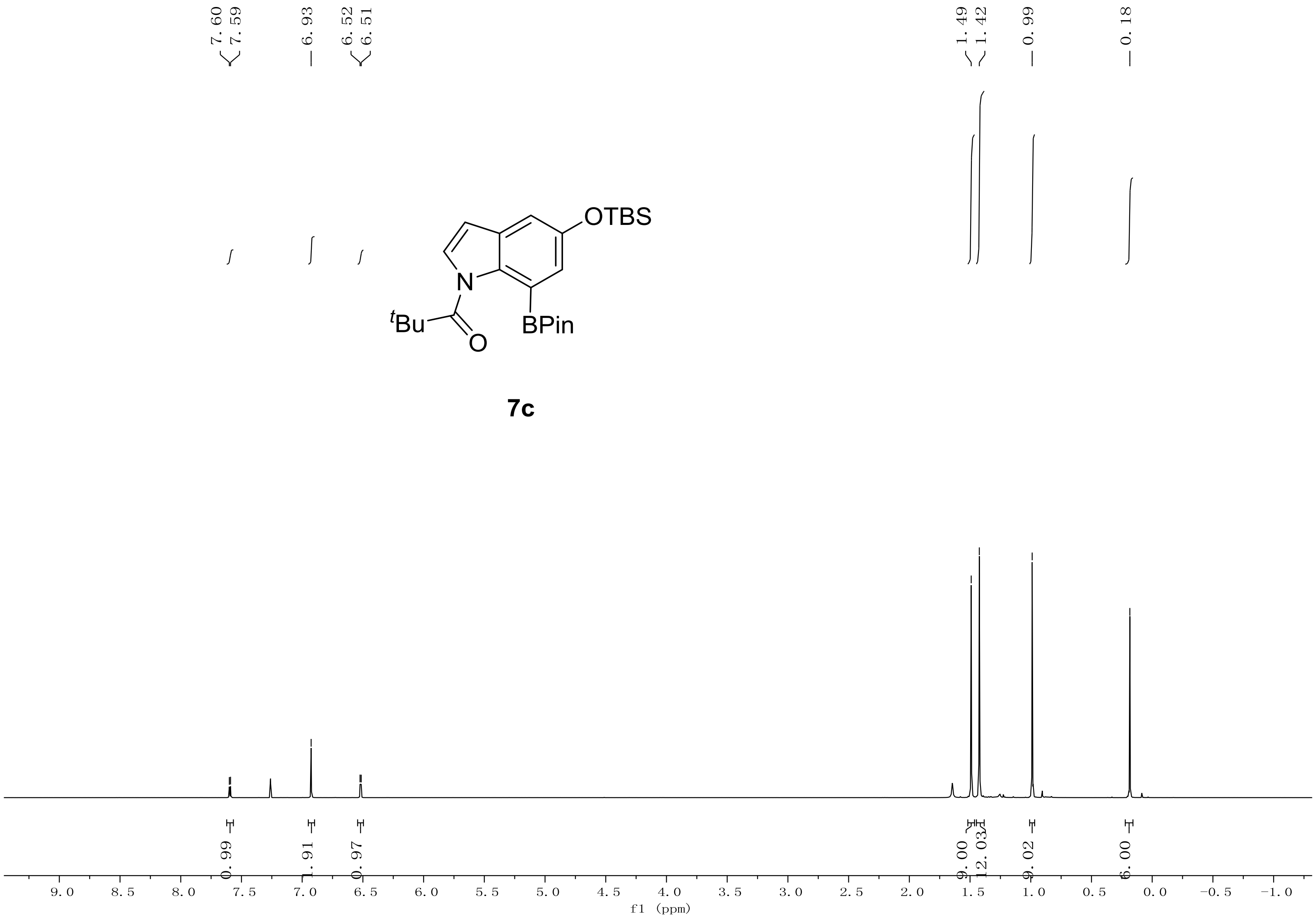
5c

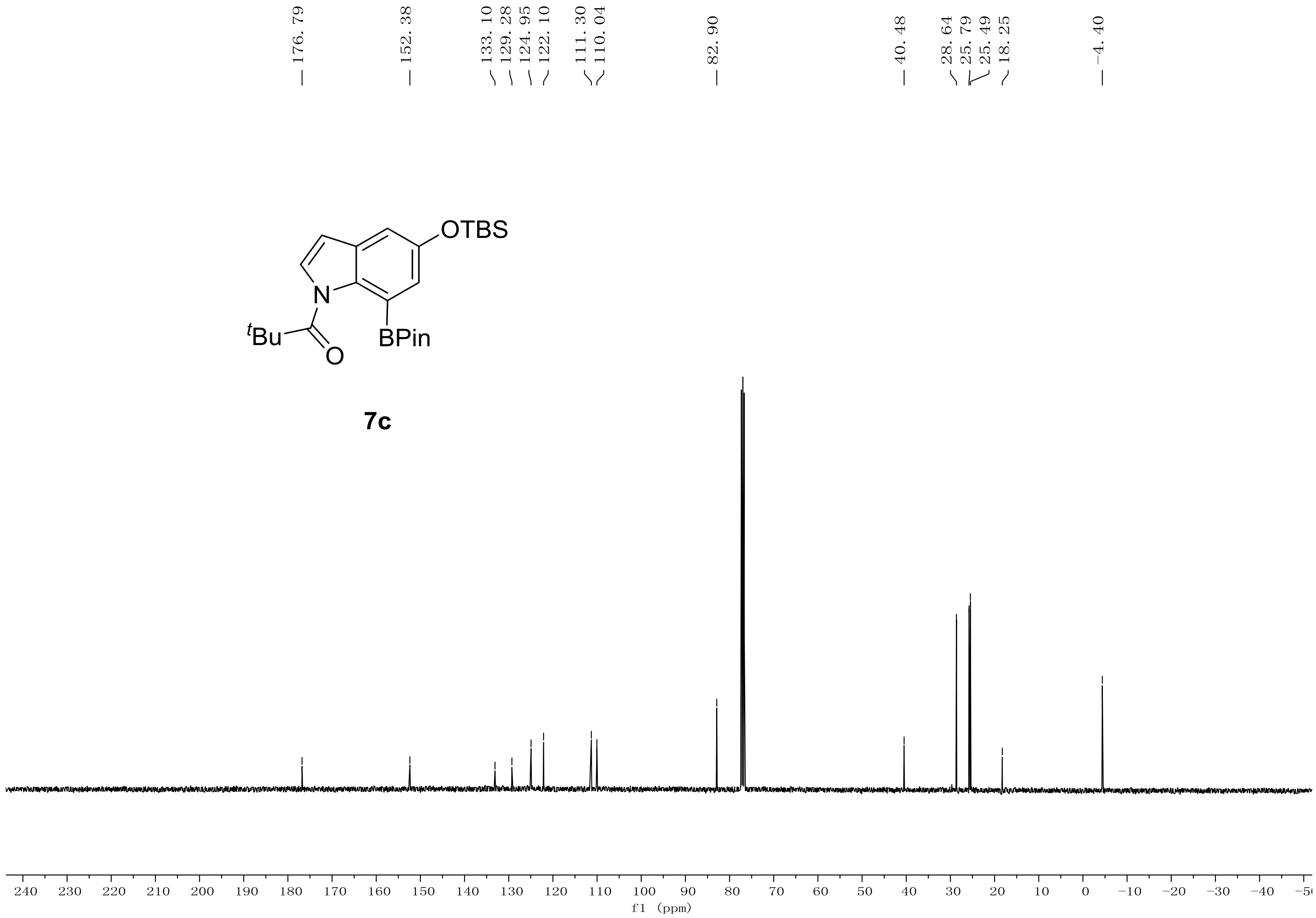

177.39
140.30
138.46
134.91
129.90
128.85
128.51
127.14
126.19
124.76
124.14
109.39
82.95
40.74
28.59
25.55
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

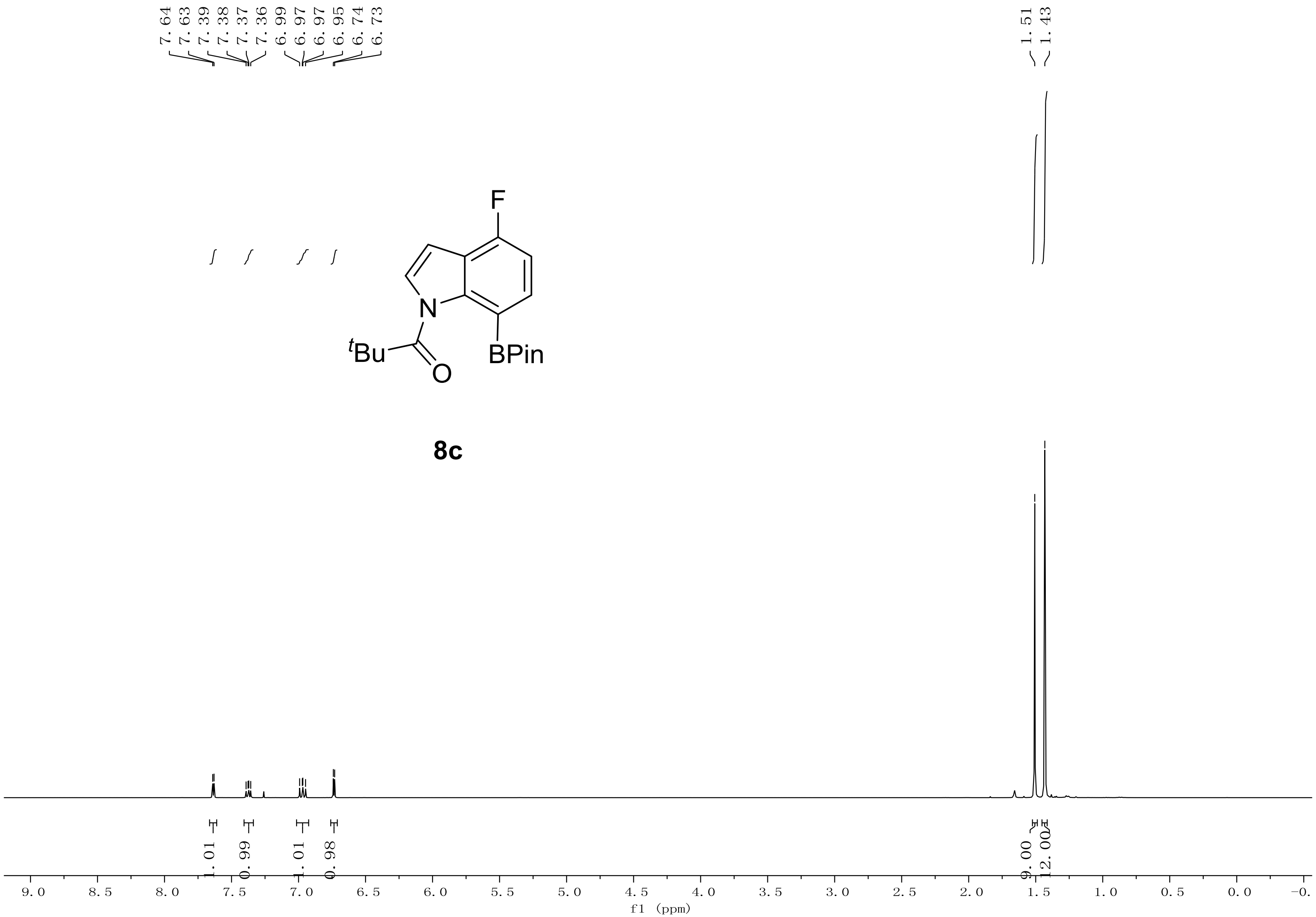

7.55
7.55
7.38
7.37
6.75
6.74
6.72
3.91
1.50
1.43
1.02
0.97
1.98
3.01
9.00
12.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)
OMe
N
^{t}Bu
O
BPin

6c

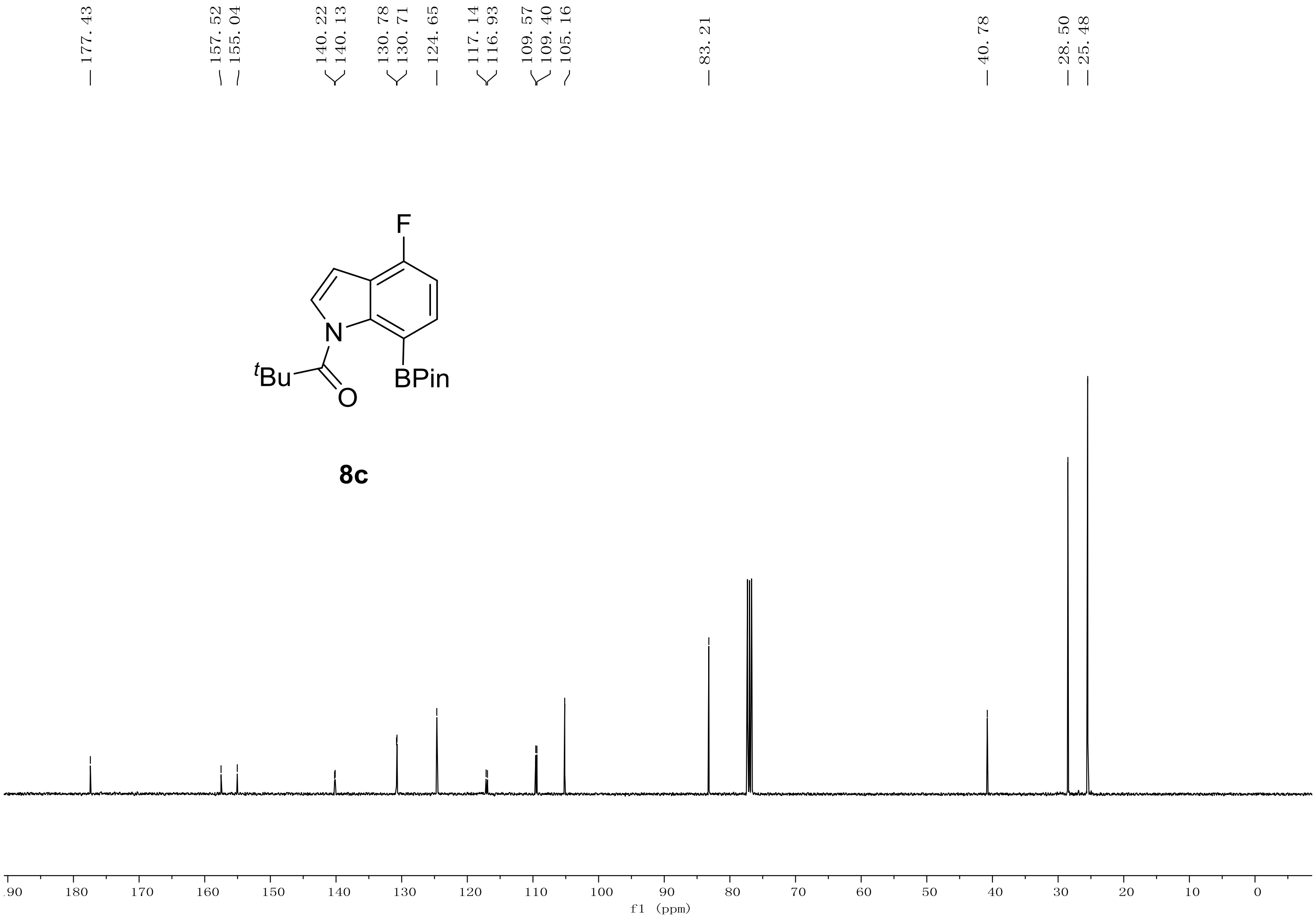

177.31
153.29
139.39
130.88
123.17
118.39
106.55
104.70
82.88
55.28
40.71
28.54
25.47
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
6c


7.60
7.59
6.93
6.52
6.51
1.49
1.42
0.99
0.18
OTBS
N
tBu
O
BPin
7c
0.99
1.91
0.97
9.00
12.03
9.02
6.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

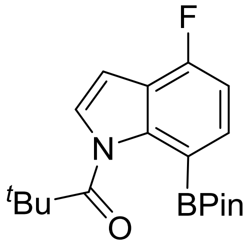

OTBS
N
tBu
O
BPin
7c
176.79
152.38
133.10
129.28
124.95
122.10
111.30
110.04
82.90
40.48
28.64
25.79
25.49
18.25
-4.40
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50
f1 (ppm)


7.64
7.63
7.39
7.38
7.37
7.36
6.99
6.97
6.97
6.95
6.74
6.73
1.51
1.43
F
N
BPin
^{t}Bu
O
1.01
0.99
1.01
0.98
9.00
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

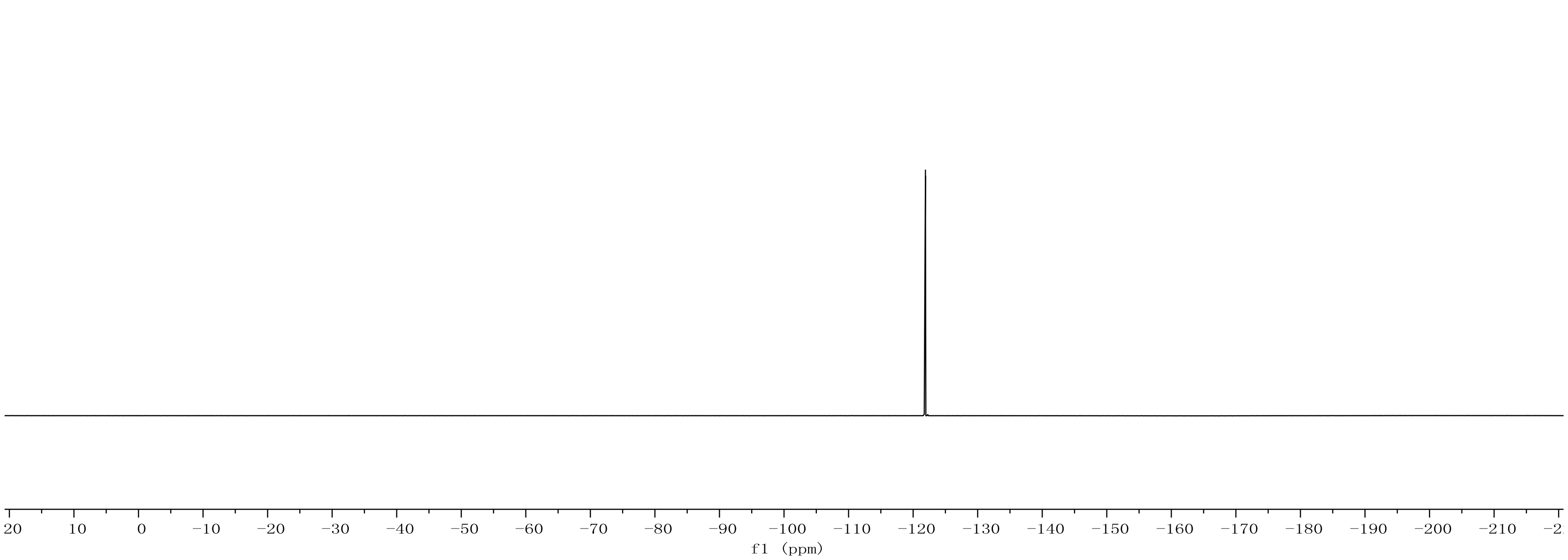
8c

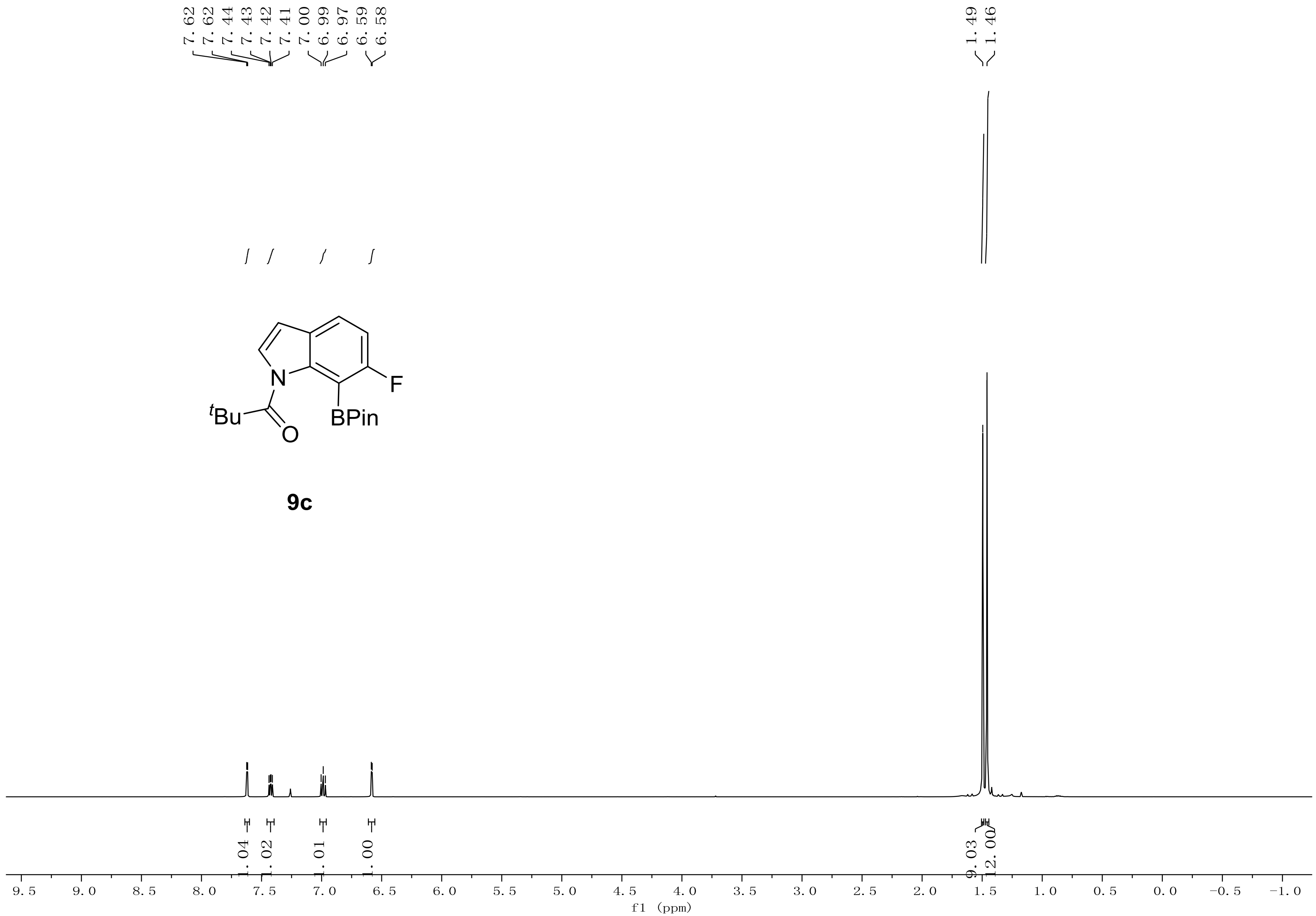

177.43
157.52
155.04
140.22
140.13
130.78
130.71
124.65
117.14
116.93
109.57
109.40
105.16
83.21
40.78
28.50
25.48
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
F
N
^{t}Bu
O
BPin

8c

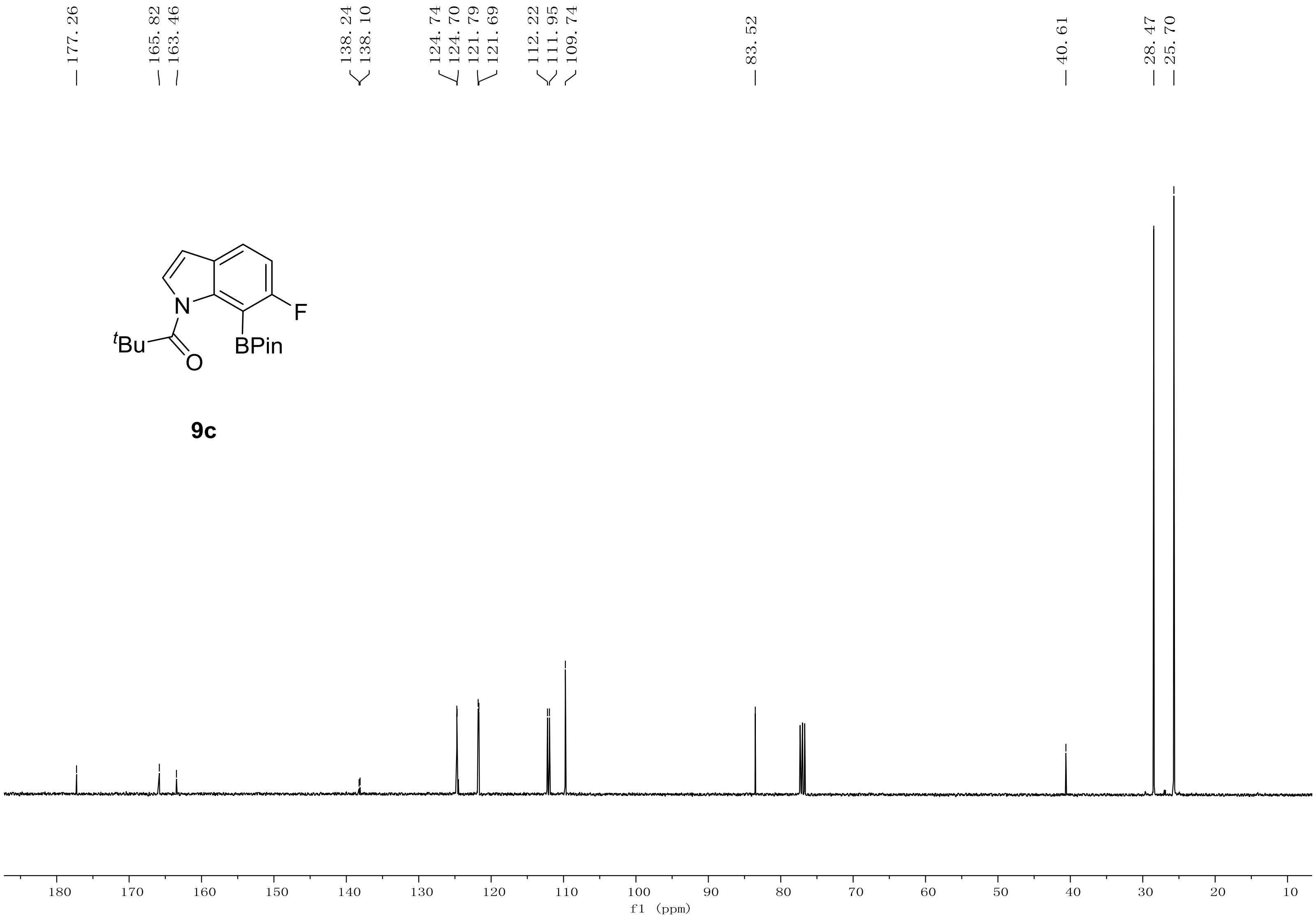

F
N
tBu
O
BPin

8c

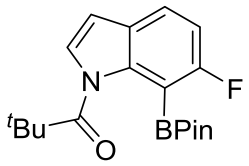

−121.91
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


7.62
7.62
7.44
7.43
7.42
7.41
7.00
6.99
6.97
6.59
6.58
1.49
1.46
F
N
tBu
O
BPin
1.04
1.02
1.01
1.00
9.03
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

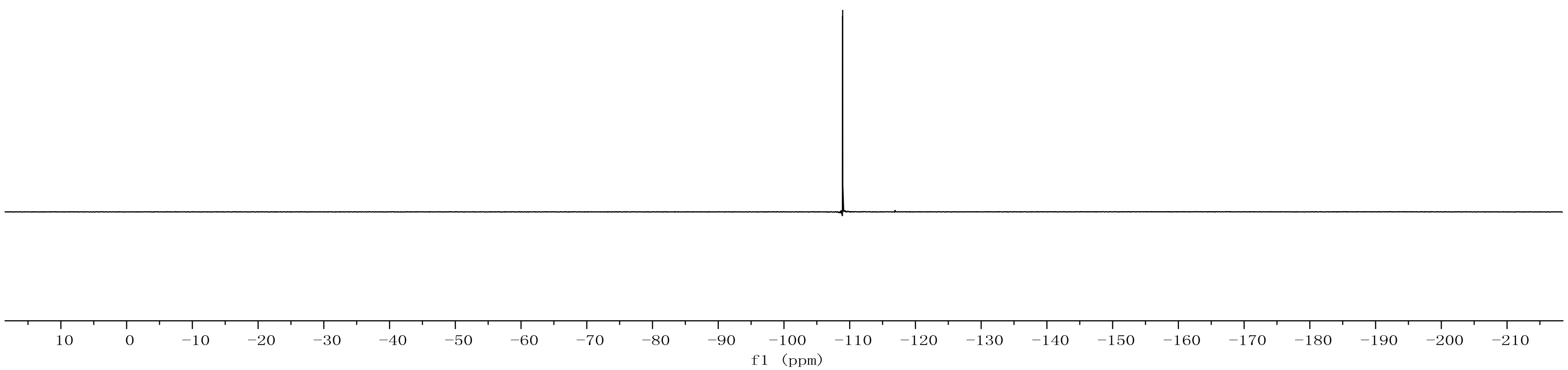
9c


N
F
BPin
tBu
O
177.26
165.82
163.46
138.24
138.10
124.74
124.70
121.79
121.69
112.22
111.95
109.74
83.52
40.61
28.47
25.70
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

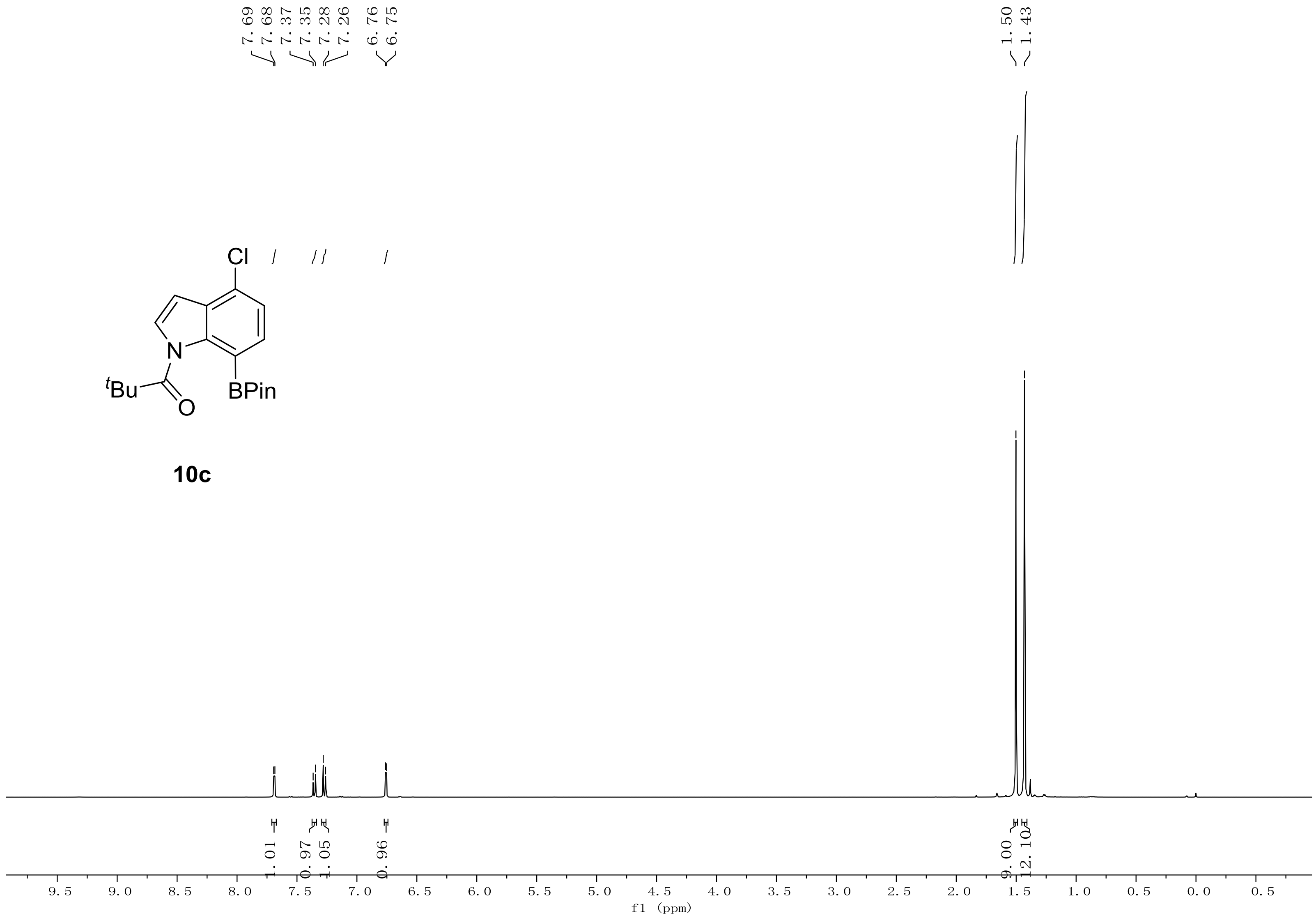
9c



9c



−108.93
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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7.26
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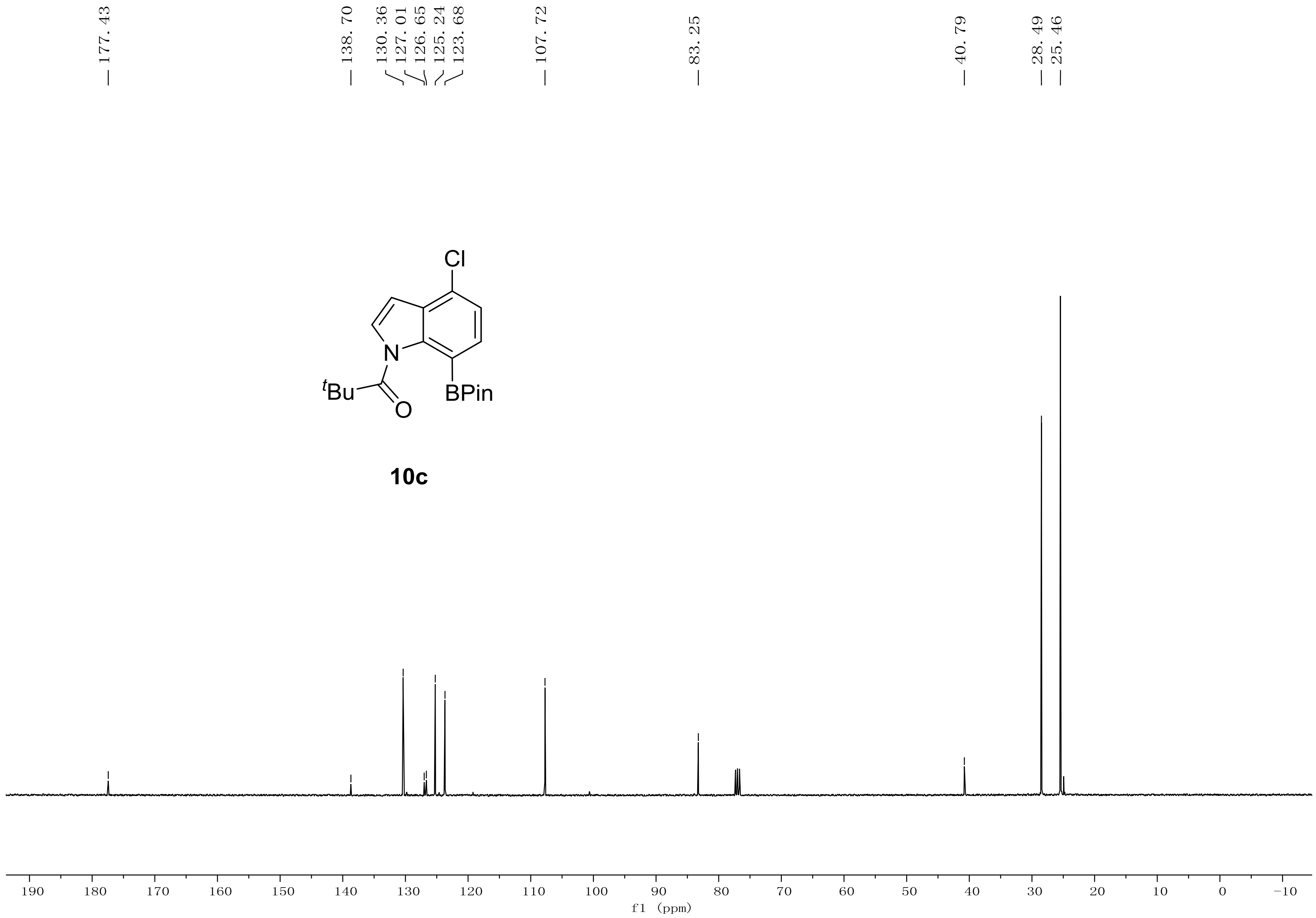
6.75
1.50
1.43
Cl
N
tBu
O
BPin
1.01
0.97
1.05
0.96
9.00
12.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

10c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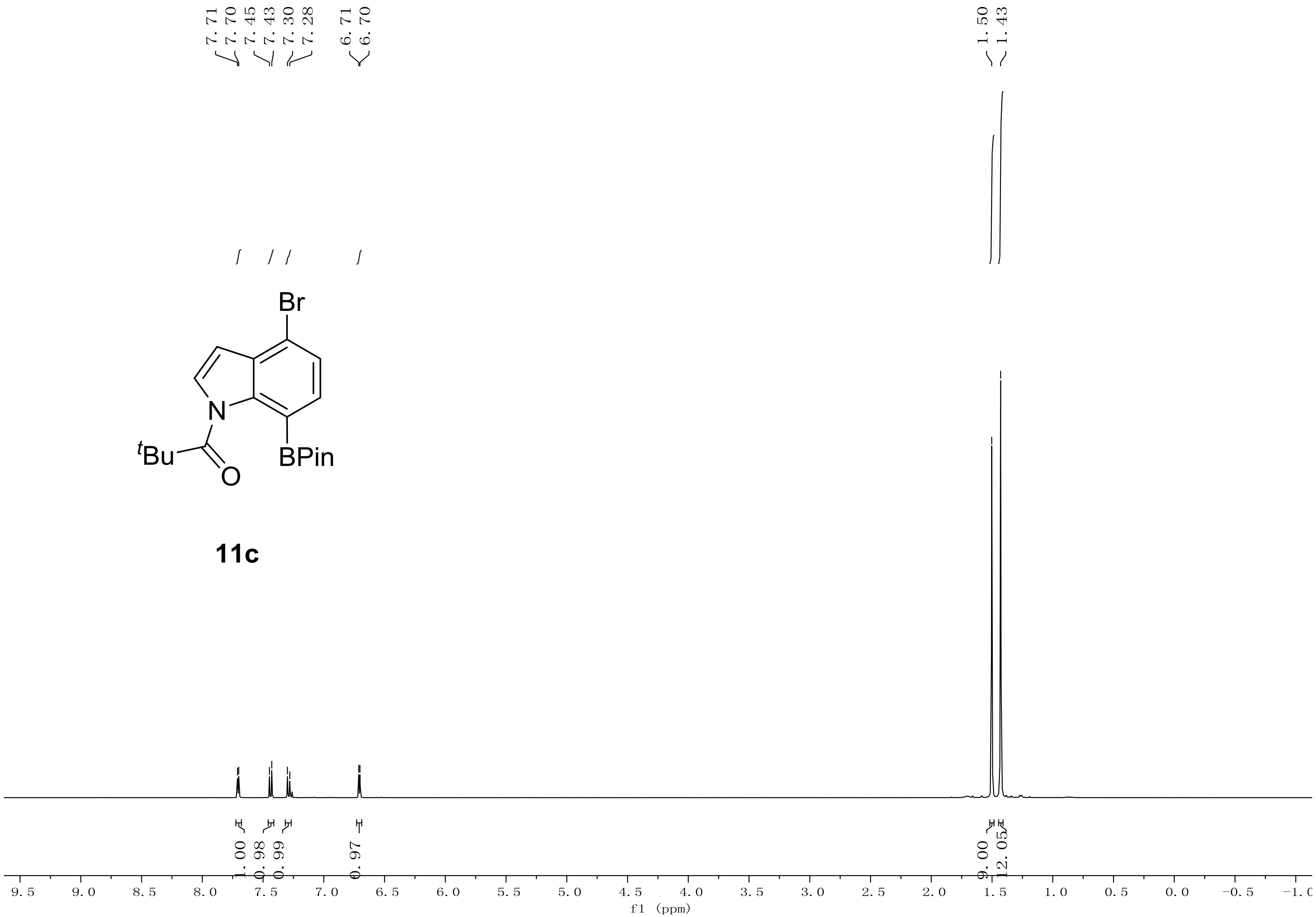
138.70
130.36
127.01
126.65
125.24
123.68
107.72
83.25
40.79
28.49
25.46
Cl
N
tBu
O
BPin
10c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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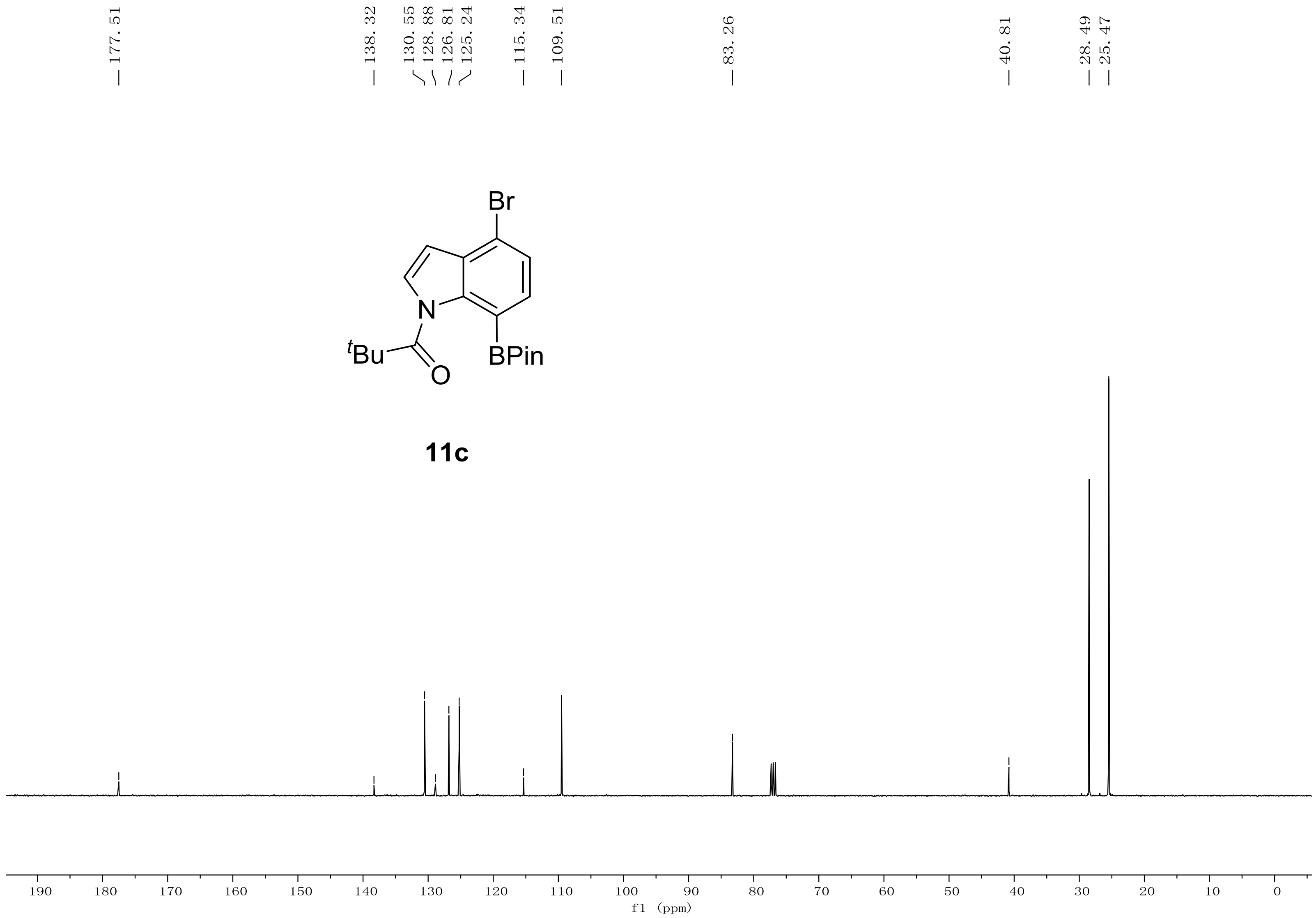
7.70
7.45
7.43
7.30
7.28
6.71
6.70
1.50
1.43
Br
N
BPin
tBu
O
1.00
0.98
0.99
0.97
9.00
12.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

11c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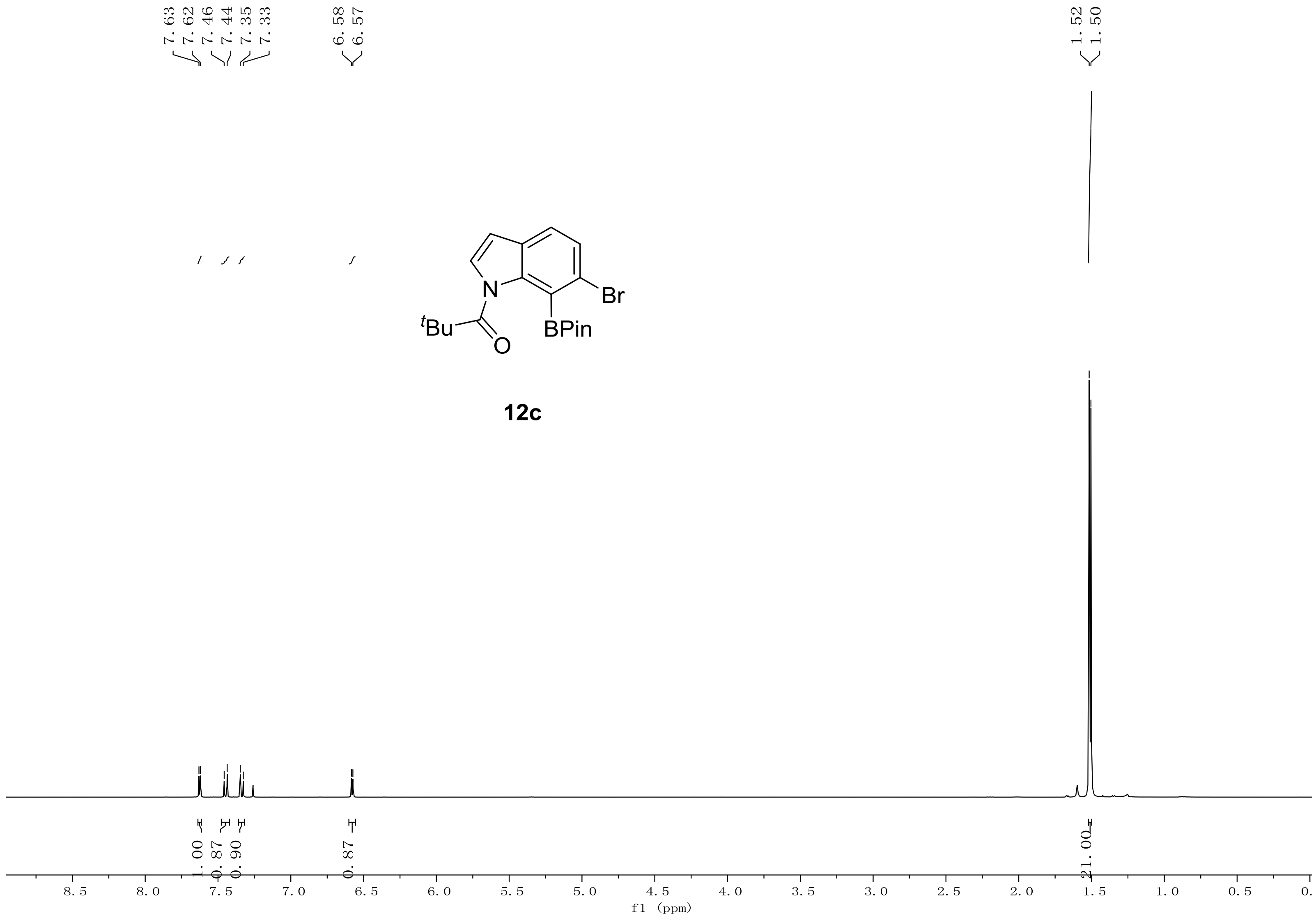
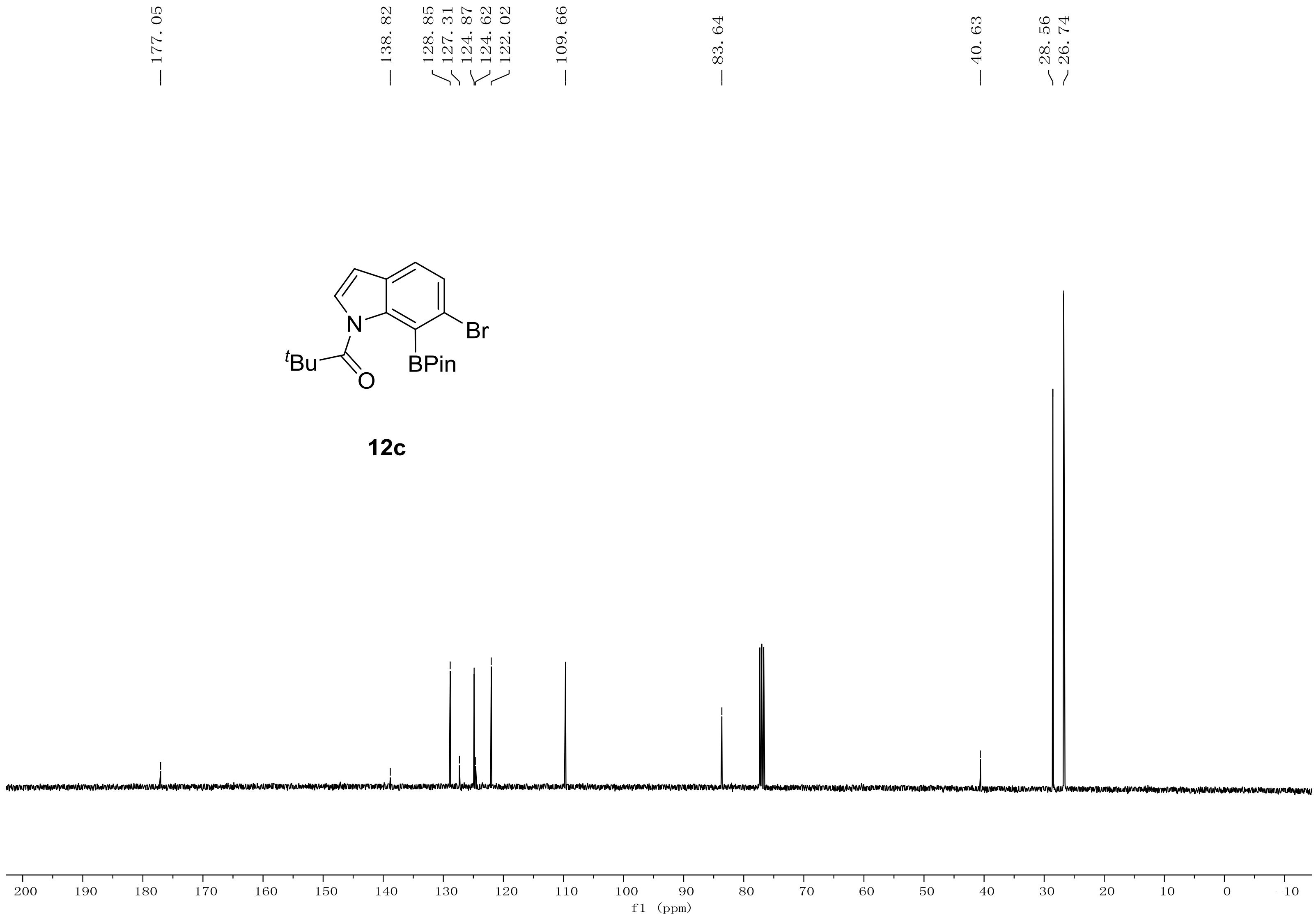
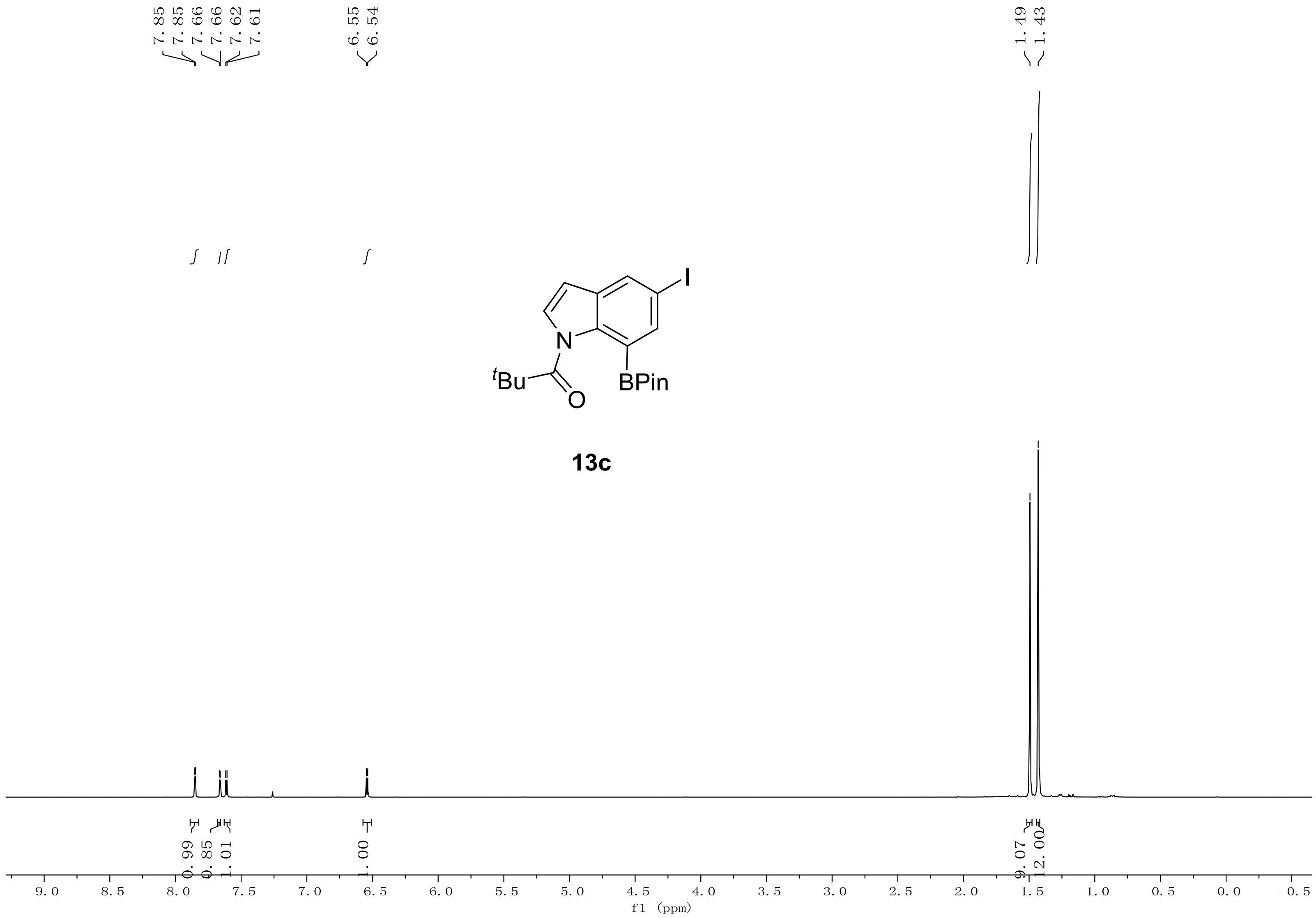
138.32
130.55
128.88
126.81
125.24
115.34
109.51
83.26
40.81
28.49
25.47
Br
N
tBu
O
BPin
11c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.63
7.62
7.46
7.44
7.35
7.33
6.58
6.57
1.52
1.50
N
Br
^{t}Bu
O
BPin
12c
1.00
0.87
0.90
0.87
21.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

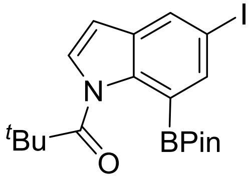

N
Br
^{t}Bu
O
BPin
177.05
138.82
128.85
127.31
124.87
124.62
122.02
109.66
83.64
40.63
28.56
26.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

12c

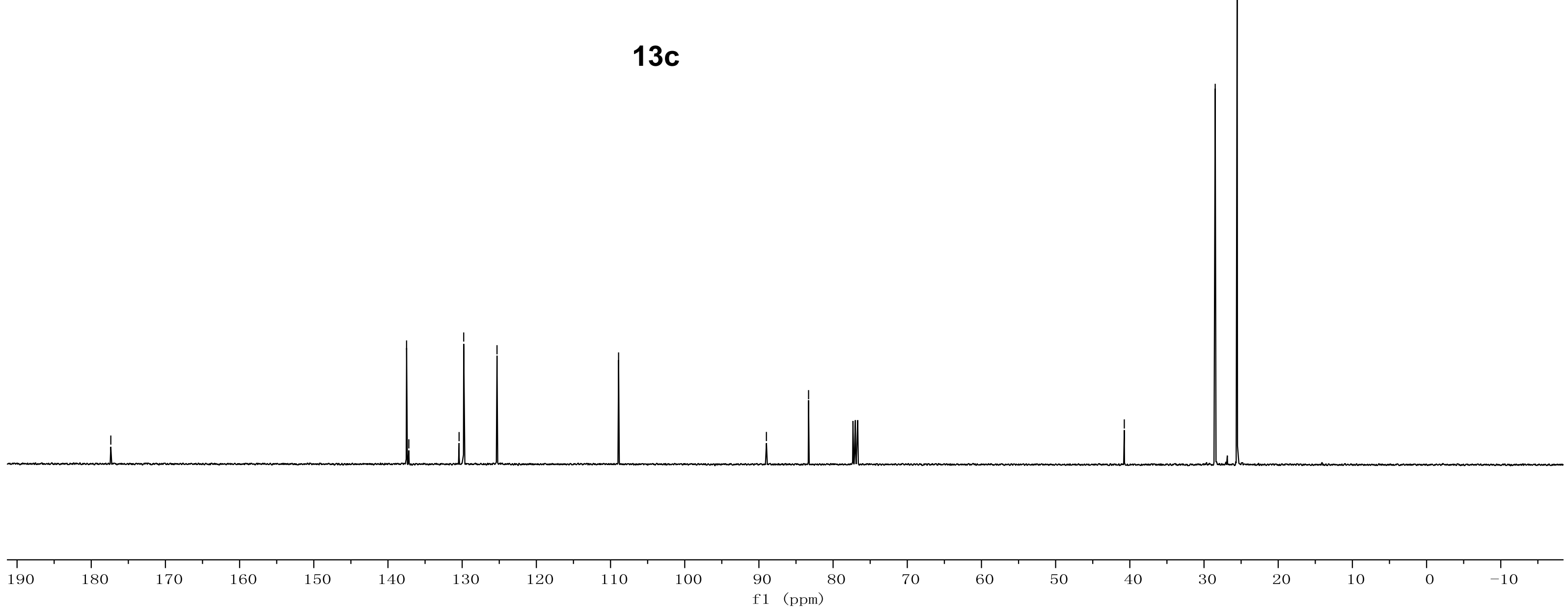


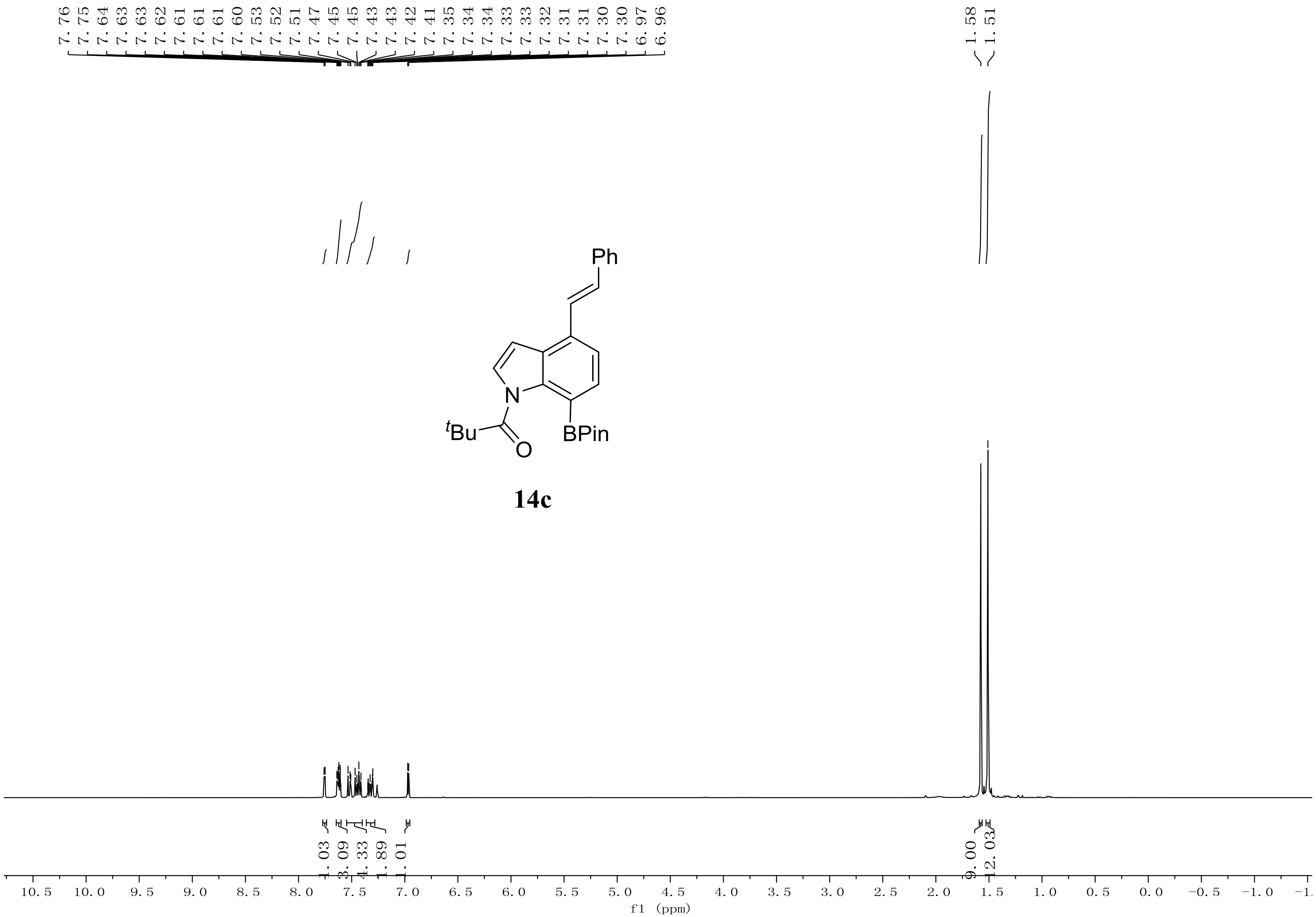
13c

7.85
7.85
7.66
7.66
7.62
7.61
6.55
6.54
1.49
1.43
0.99
0.85
1.01
1.00
9.07
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


I
N
tBu
O
BPin

13c


177.36
137.49
137.19
130.42
129.79
125.30
108.91
88.99
83.31
40.75
28.49
25.53
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.76
7.75
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7.63
7.63
7.62
7.61
7.61
7.61
7.60
7.53
7.52
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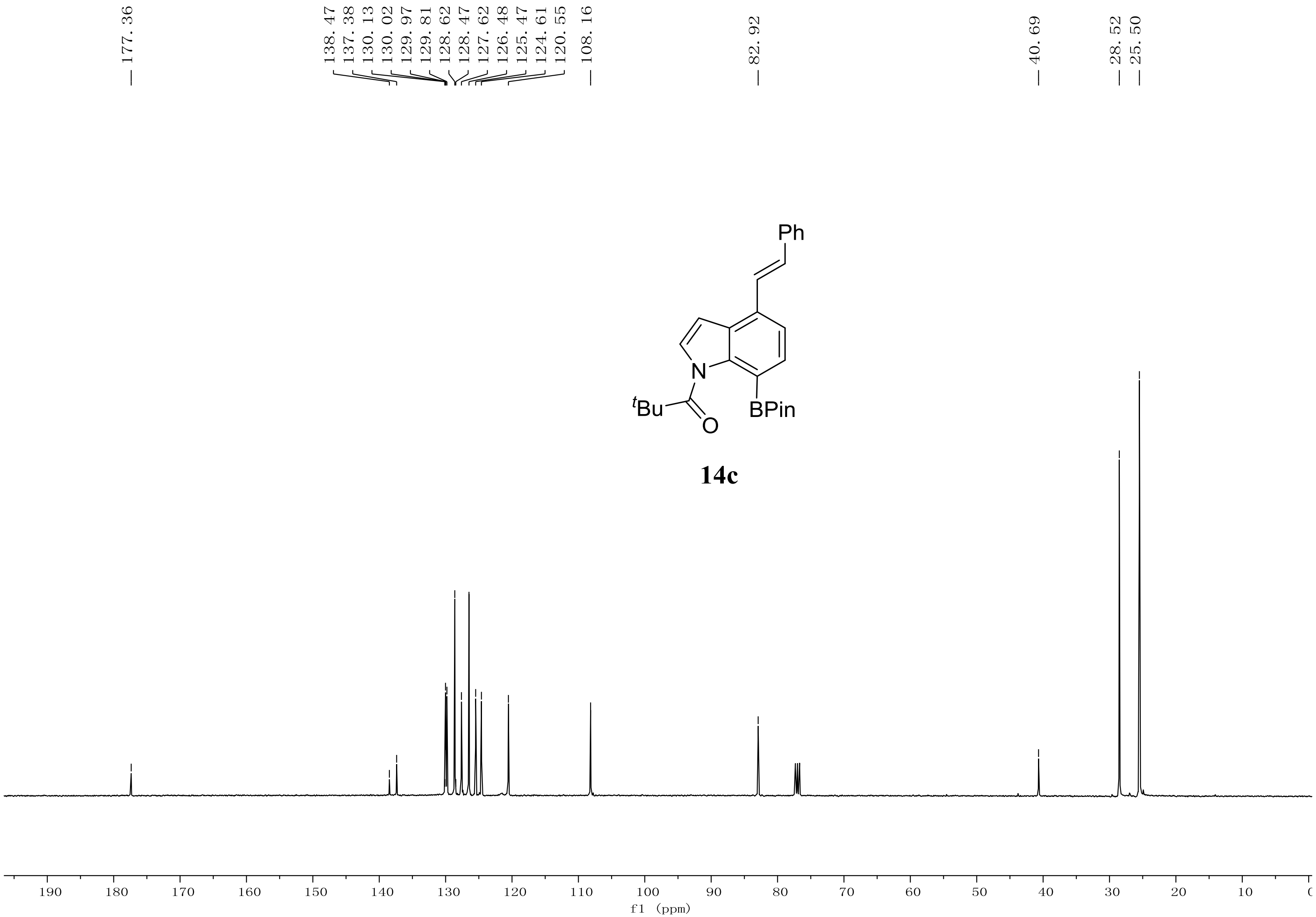
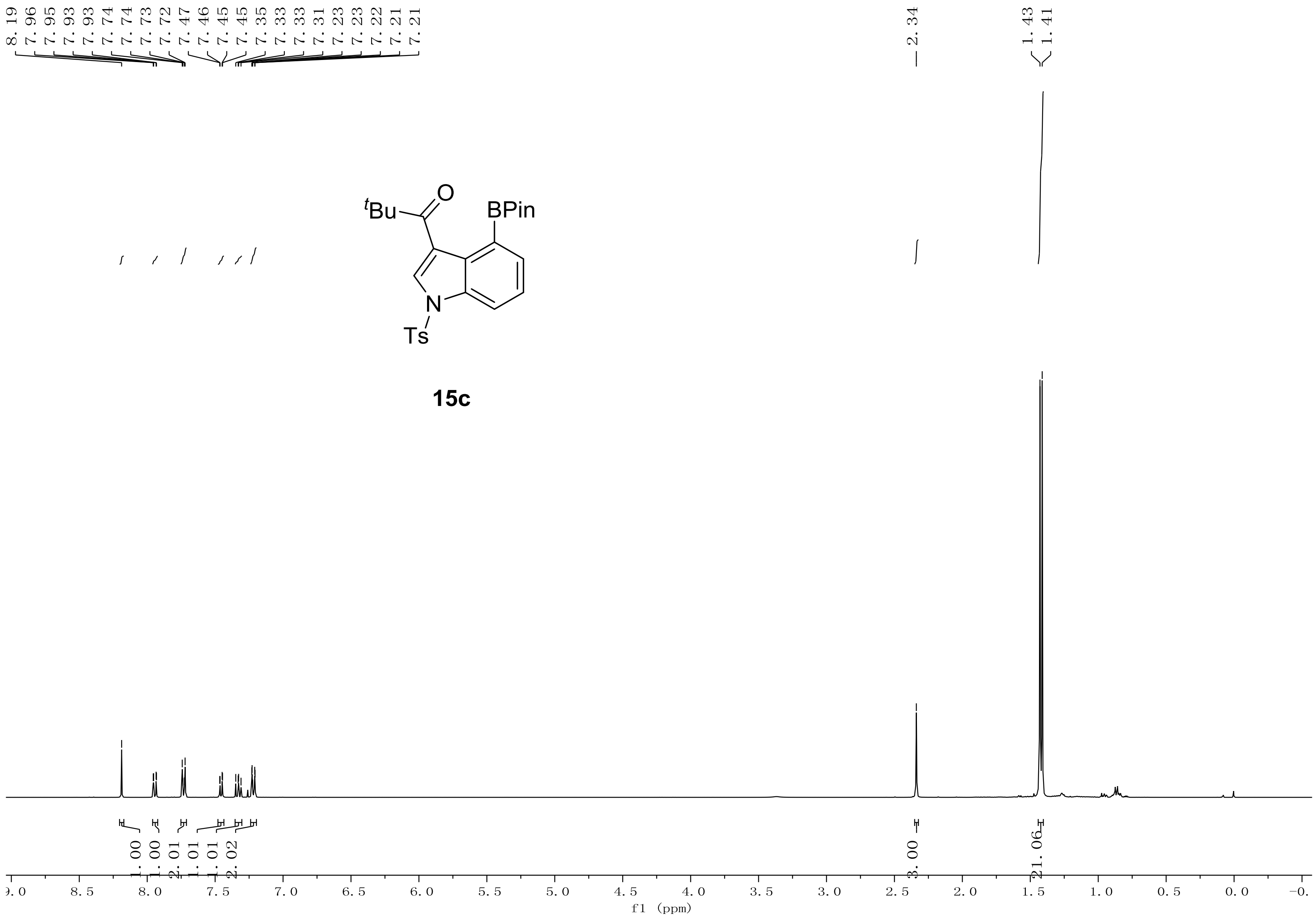
7.47
7.45
7.45
7.43
7.43
7.42
7.41
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.30
6.97
6.96
1.58
1.51
Ph
N
tBu
O
BPin
1.03
3.09
4.33
1.89
1.01
9.00
12.03
f1 (ppm)

14c



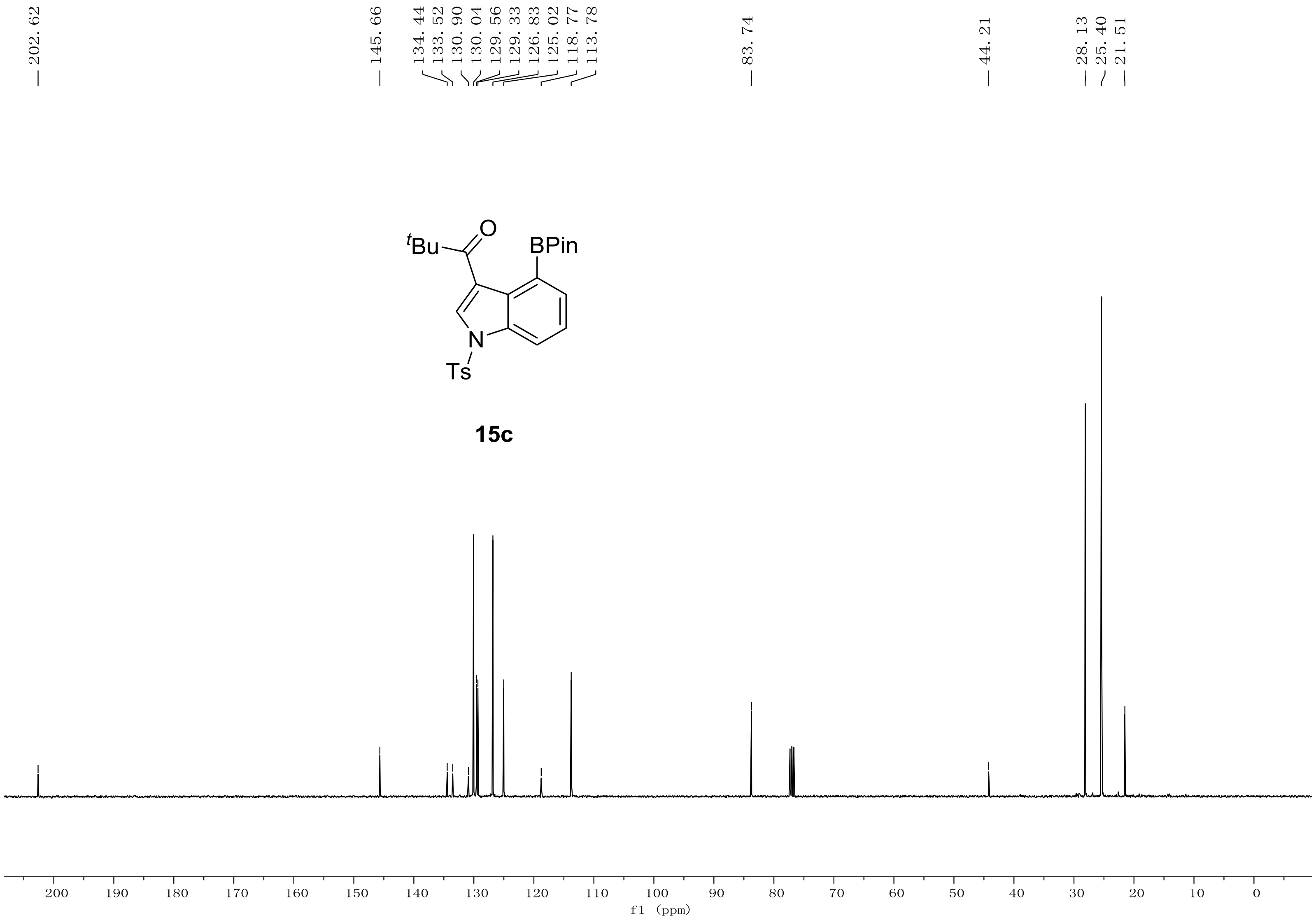
177.36
138.47
137.38
130.13
130.02
129.97
129.81
128.62
128.47
127.62
126.48
125.47
124.61
120.55
108.16
82.92
40.69
28.52
25.50
Ph
N
^{t}Bu
O
BPin
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

14c

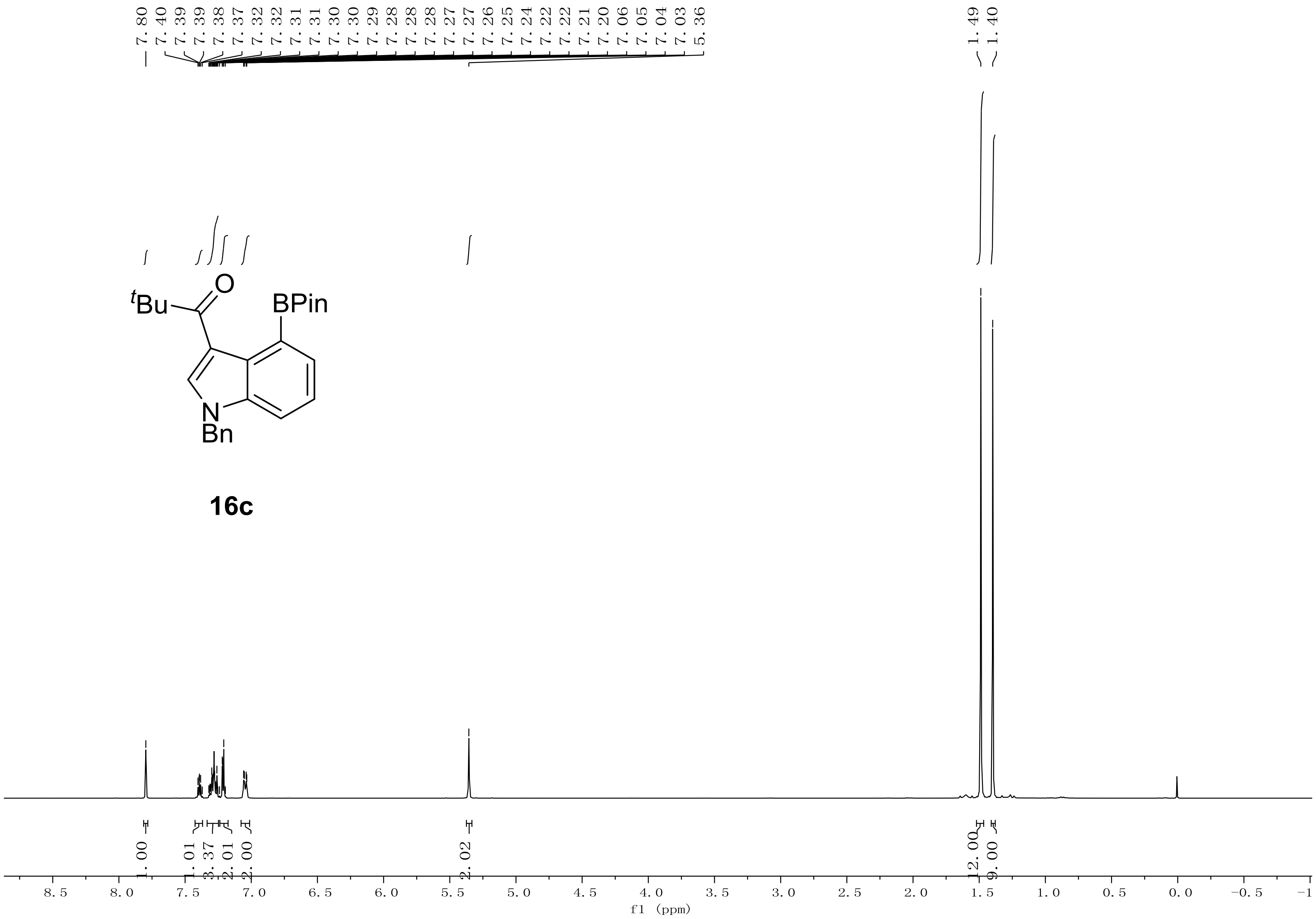


8.19
7.96
7.95
7.93
7.93
7.74
7.74
7.73
7.72
7.47
7.46
7.45
7.45
7.35
7.33
7.33
7.31
7.23
7.23
7.22
7.21
7.21
2.34
1.43
1.41
^{t}Bu
O
BPin
N
Ts
1.00
1.00
2.01
1.01
1.01
2.02
3.00
21.06
f1 (ppm)

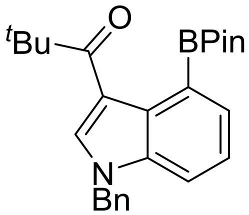
15c


202.62
145.66
134.44
133.52
130.90
130.04
129.56
129.33
126.83
125.02
118.77
113.78
83.74
44.21
28.13
25.40
21.51
tBu
O
BPin
N
Ts
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

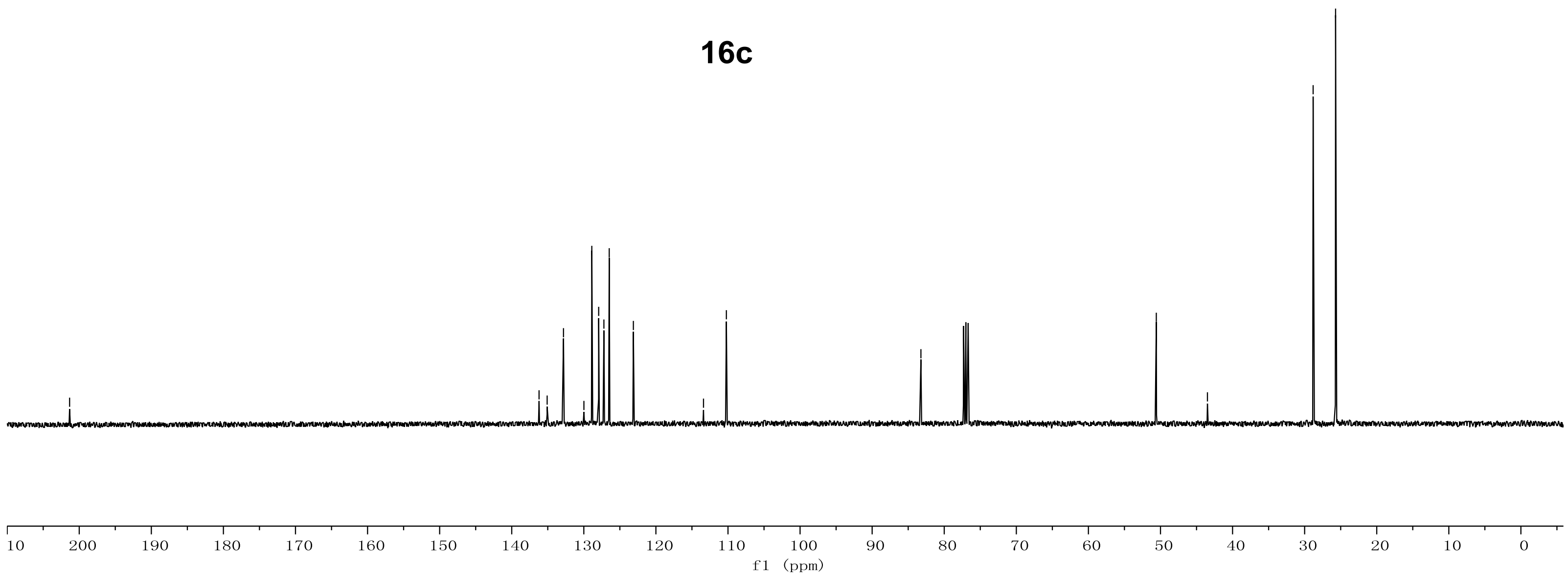
15c

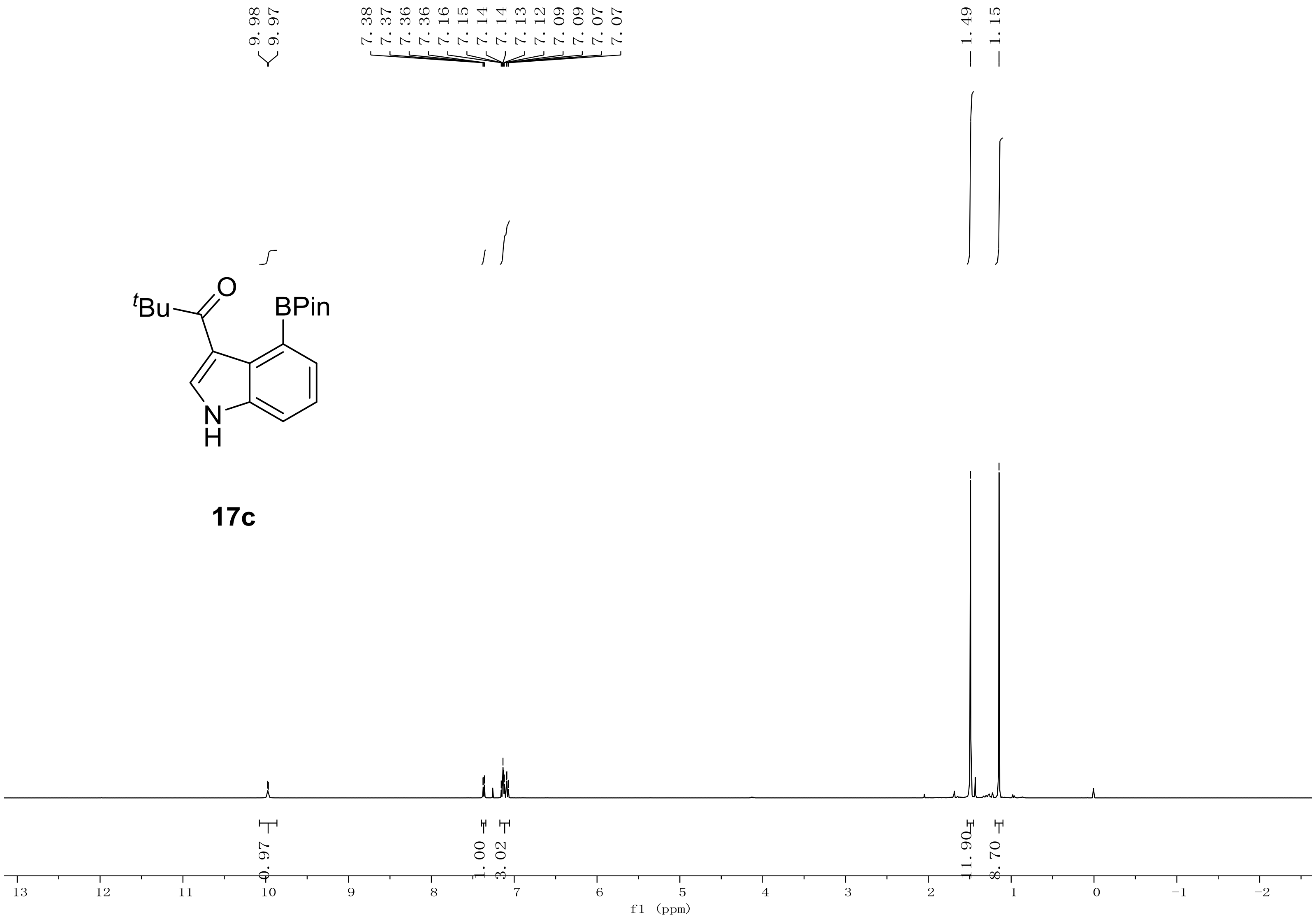


16c



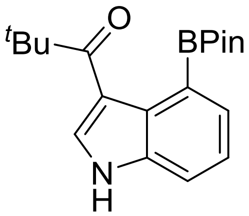
16c


201.34
136.21
135.09
132.82
129.99
128.89
127.94
127.21
126.47
123.13
113.40
110.22
83.23
50.58
43.49
28.82
25.71
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

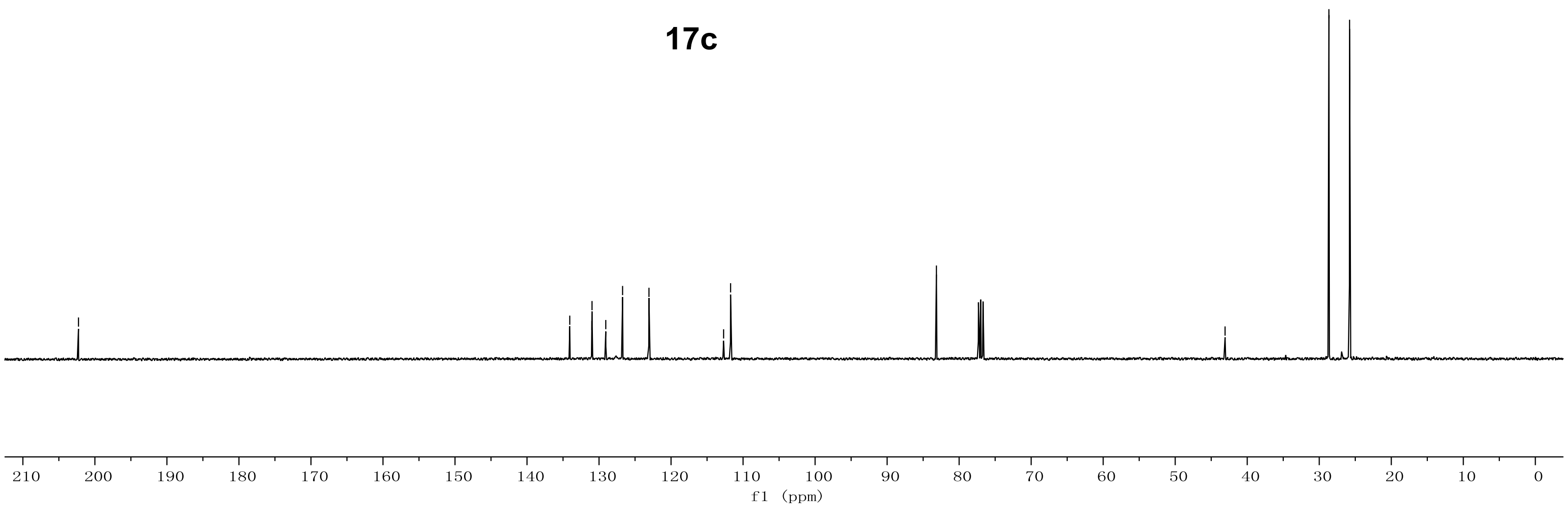


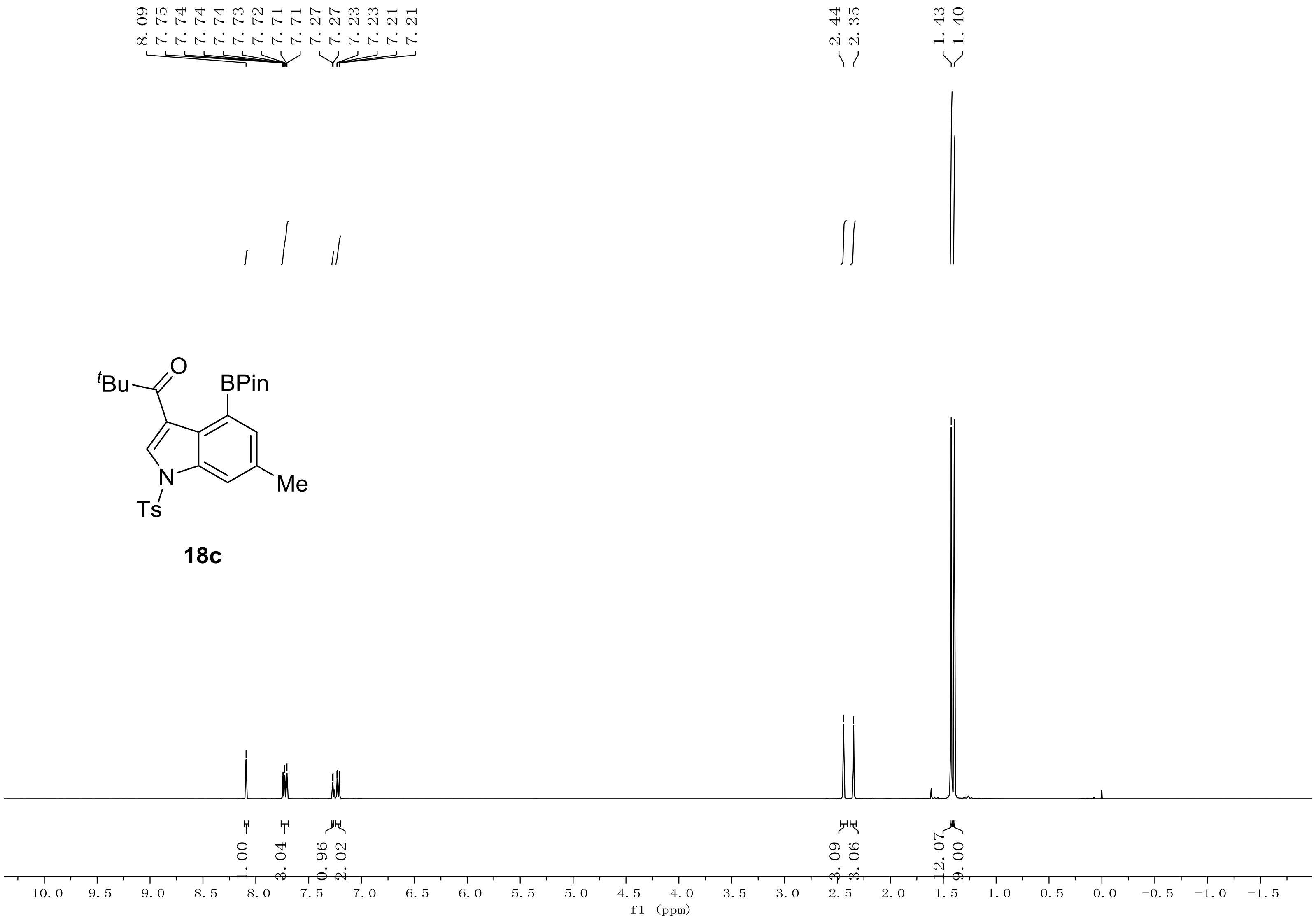
9.98
9.97
7.38
7.37
7.36
7.36
7.16
7.15
7.14
7.14
7.13
7.12
7.09
7.09
7.07
7.07
1.49
1.15
0.97
1.00
3.02
11.90
8.70
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

17c

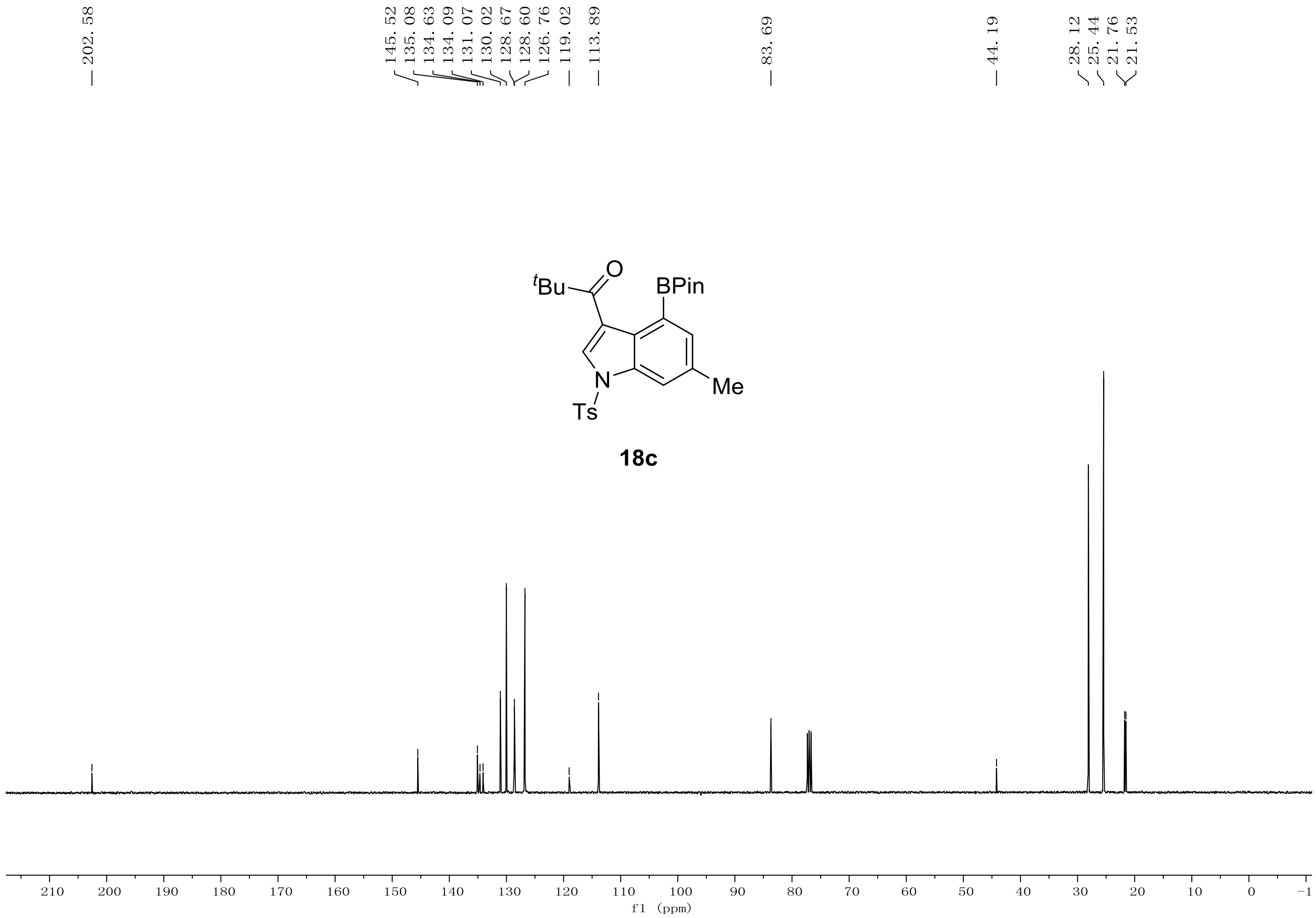

^{t}Bu
O
BPin
N
H

17c

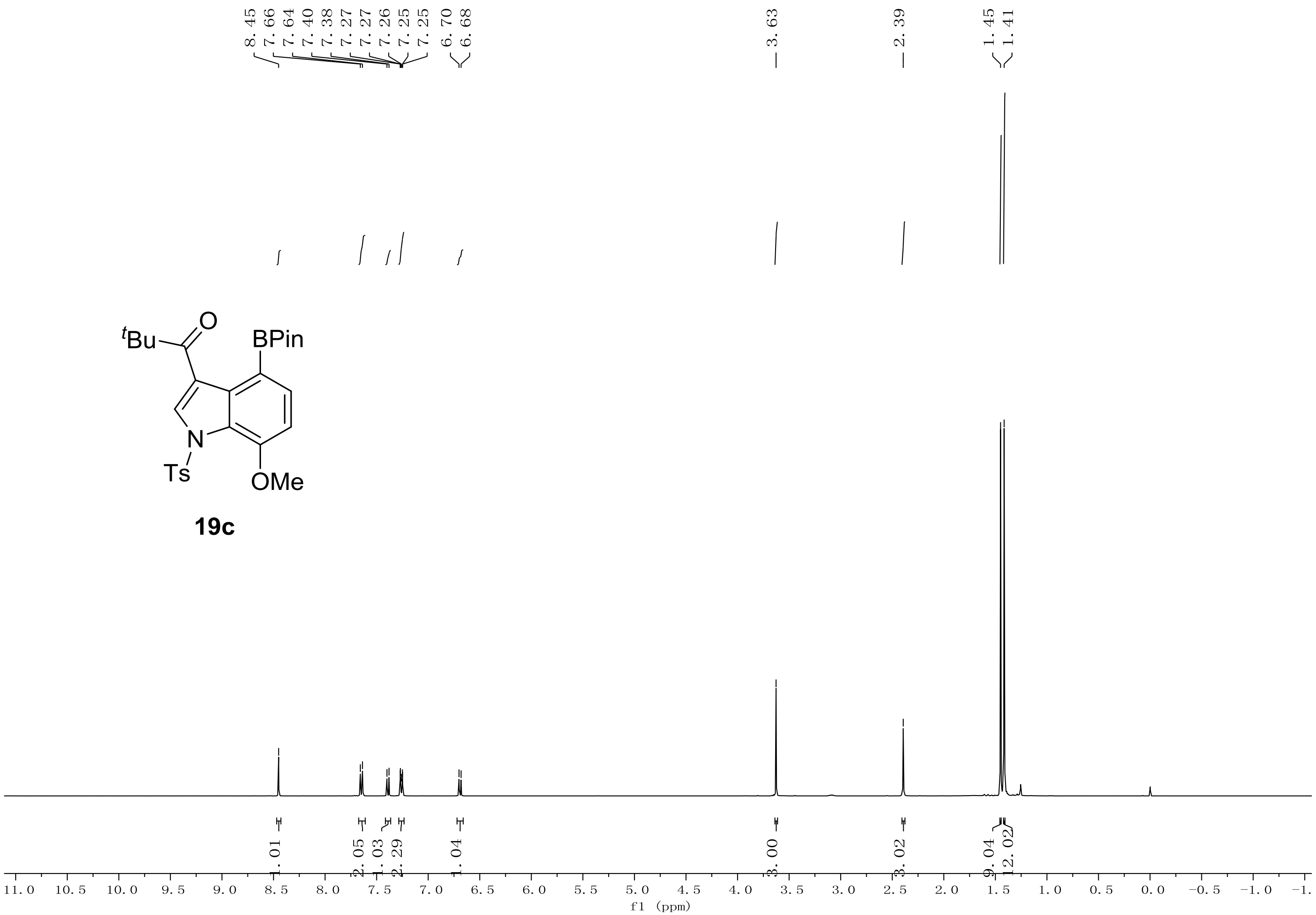

202.28
134.06
131.00
130.97
129.06
126.73
123.07
112.70
111.73
83.16
43.08
28.66
25.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

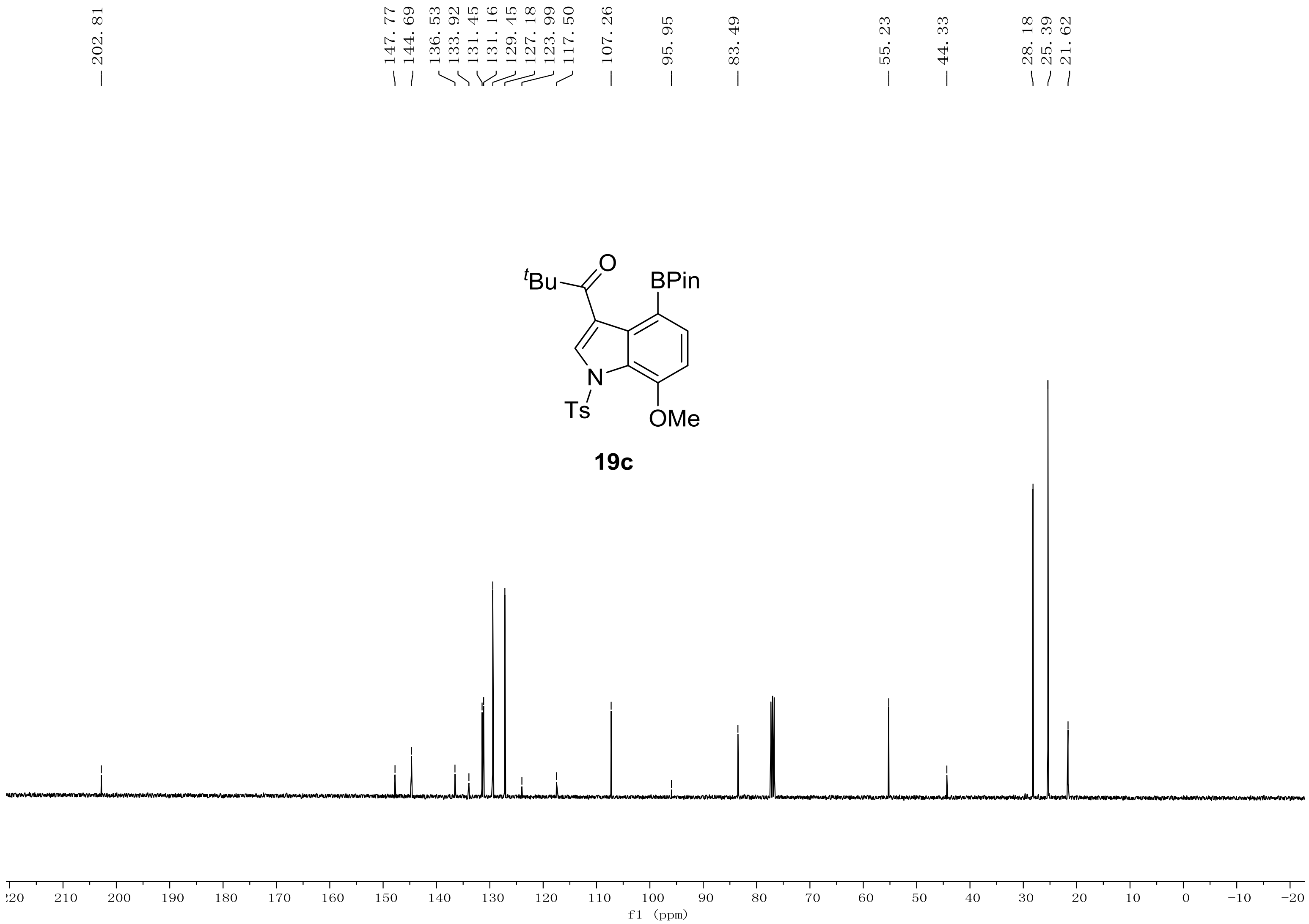

8.09
7.75
7.74
7.74
7.74
7.73
7.72
7.71
7.71
7.27
7.27
7.23
7.23
7.21
7.21
2.44
2.35
1.43
1.40
^{t}Bu
O
BPin
N
Ts
Me
1.00
3.04
0.96
2.02
3.09
3.06
12.07
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)

18c


202.58
145.52
135.08
134.63
134.09
131.07
130.02
128.67
128.60
126.76
119.02
113.89
83.69
44.19
28.12
25.44
21.76
21.53
tBu
O
BPin
N
Ts
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

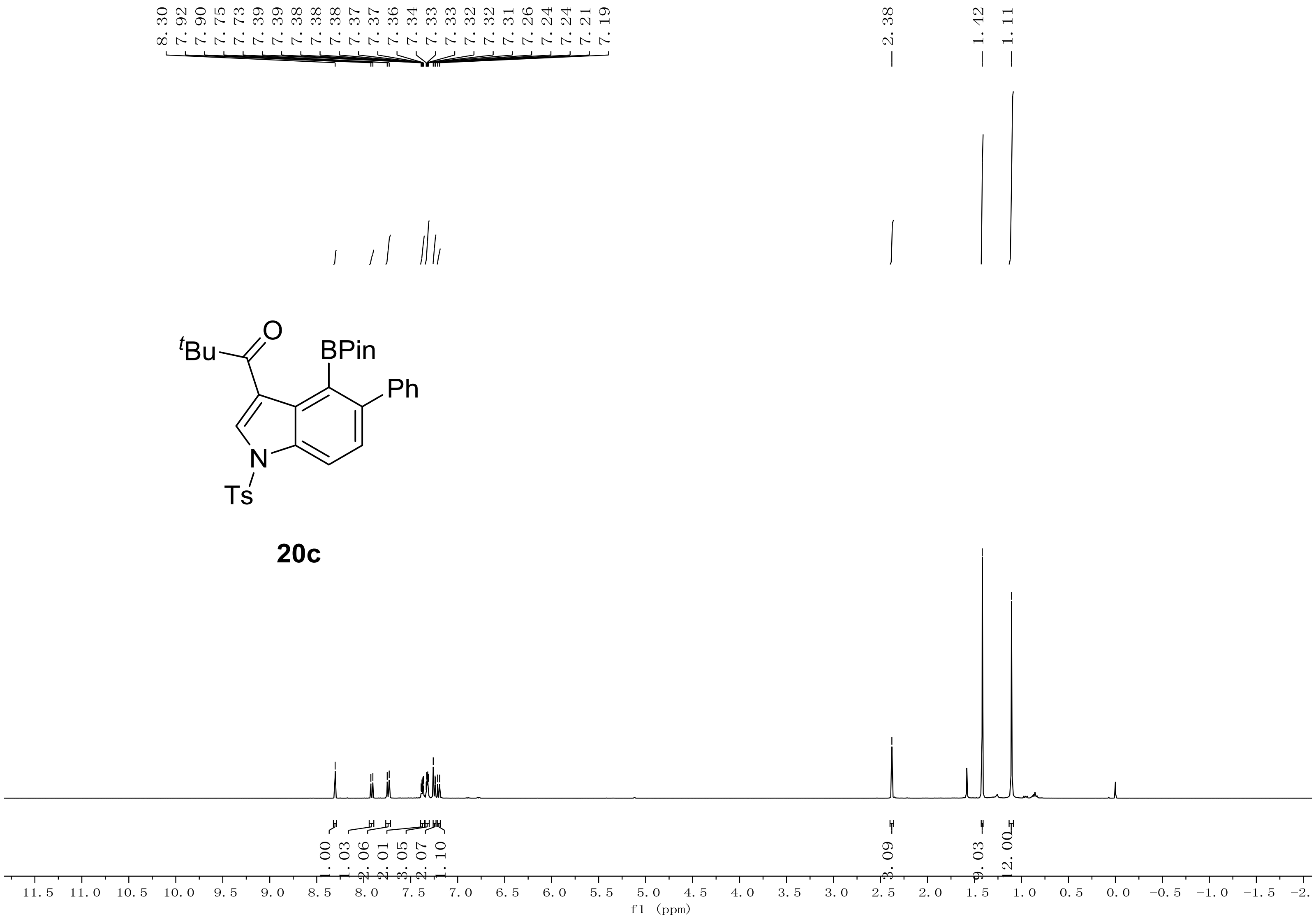
18c


8.45
7.66
7.64
7.40
7.38
7.27
7.27
7.26
7.25
7.25
6.70
6.68
3.63
2.39
1.45
1.41
^{t}Bu
O
BPin
N
Ts
OMe
19c
1.01
2.05
1.03
2.29
1.04
3.00
3.02
9.04
12.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.
f1 (ppm)



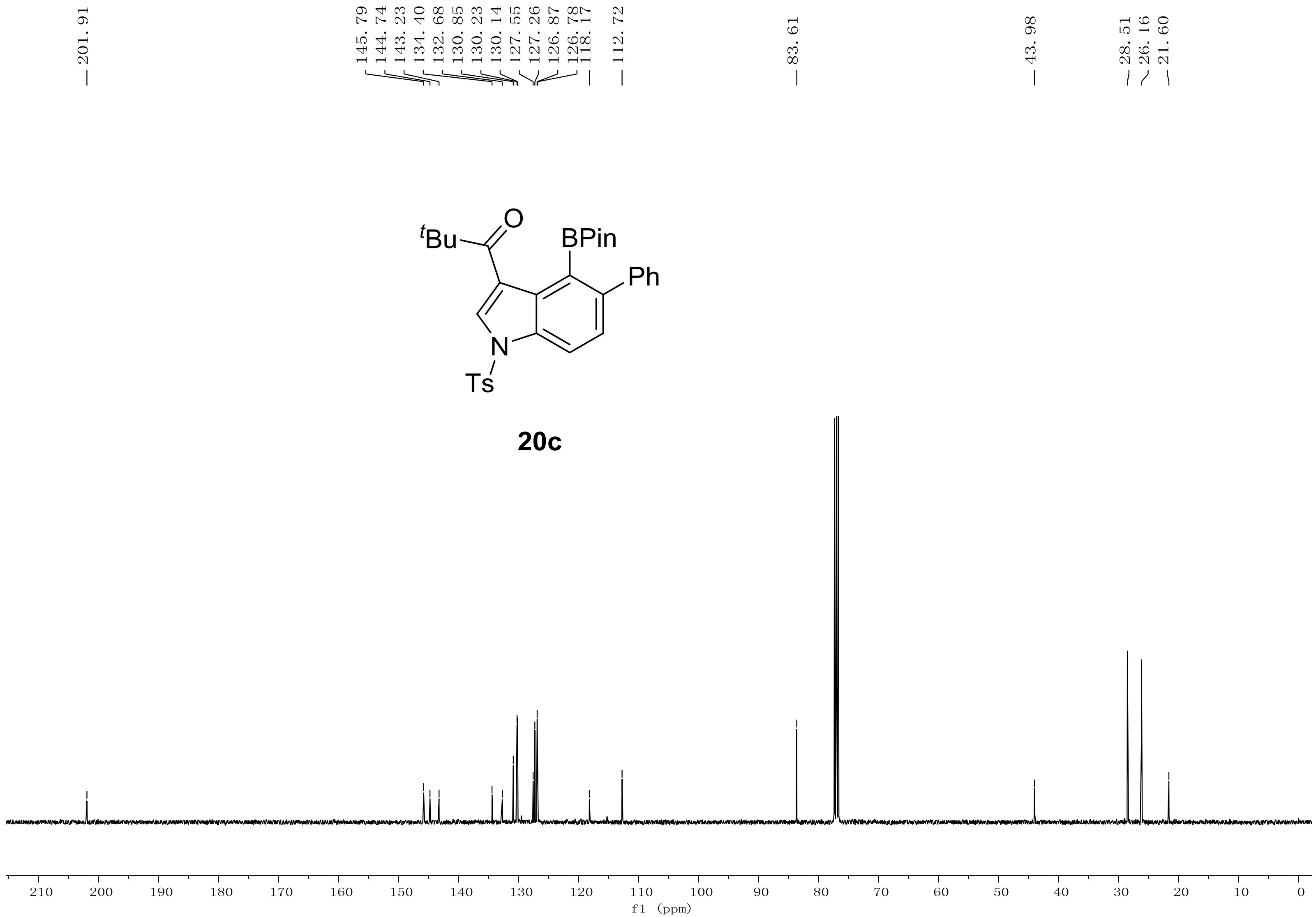
202.81
147.77
144.69
136.53
133.92
131.45
131.16
129.45
127.18
123.99
117.50
107.26
95.95
83.49
55.23
44.33
28.18
25.39
21.62
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
O
tBu
BPin
N
Ts
OMe

19c

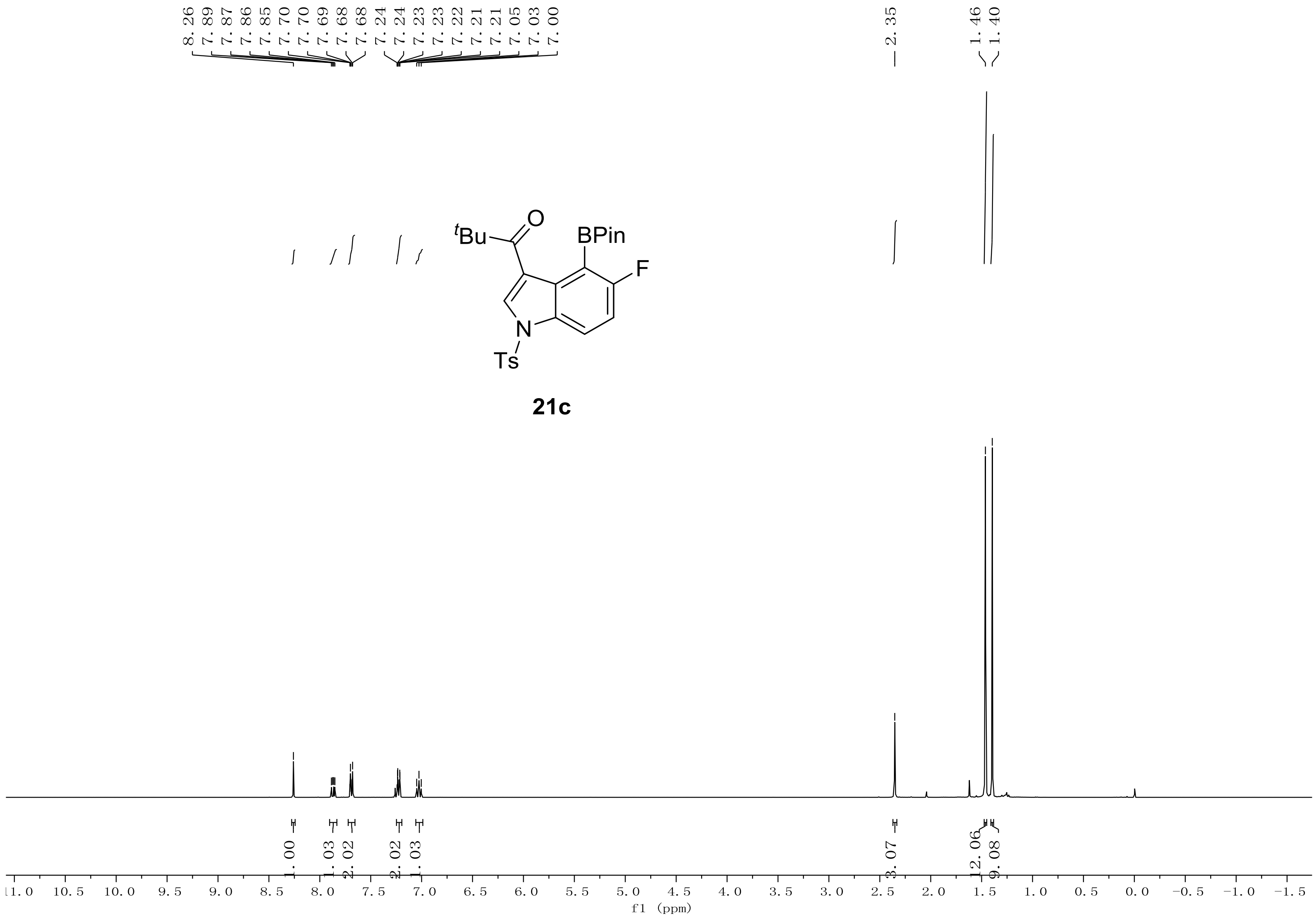


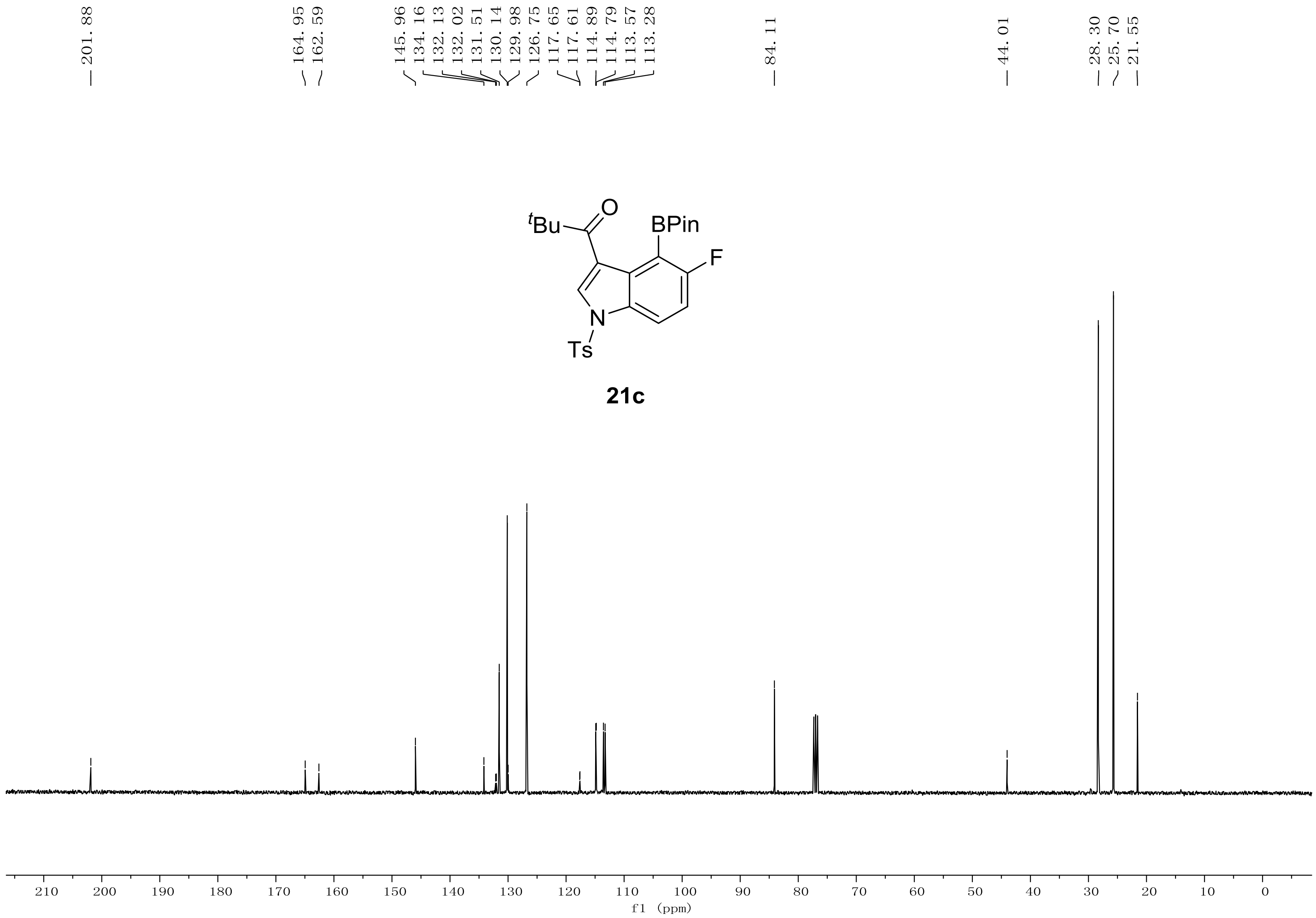
8.30
7.92
7.90
7.75
7.73
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.34
7.33
7.33
7.32
7.32
7.31
7.26
7.24
7.24
7.21
7.19
2.38
1.42
1.11
tBu
O
BPin
Ph
N
Ts
1.00
1.03
2.06
2.01
3.05
2.07
1.10
3.09
9.03
12.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2.
f1 (ppm)

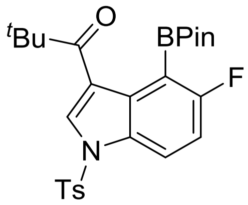
20c


201.91
145.79
144.74
143.23
134.40
132.68
130.85
130.23
130.14
127.55
127.26
126.87
126.78
118.17
112.72
83.61
43.98
28.51
26.16
21.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
tBu
O
BPin
Ph
N
Ts

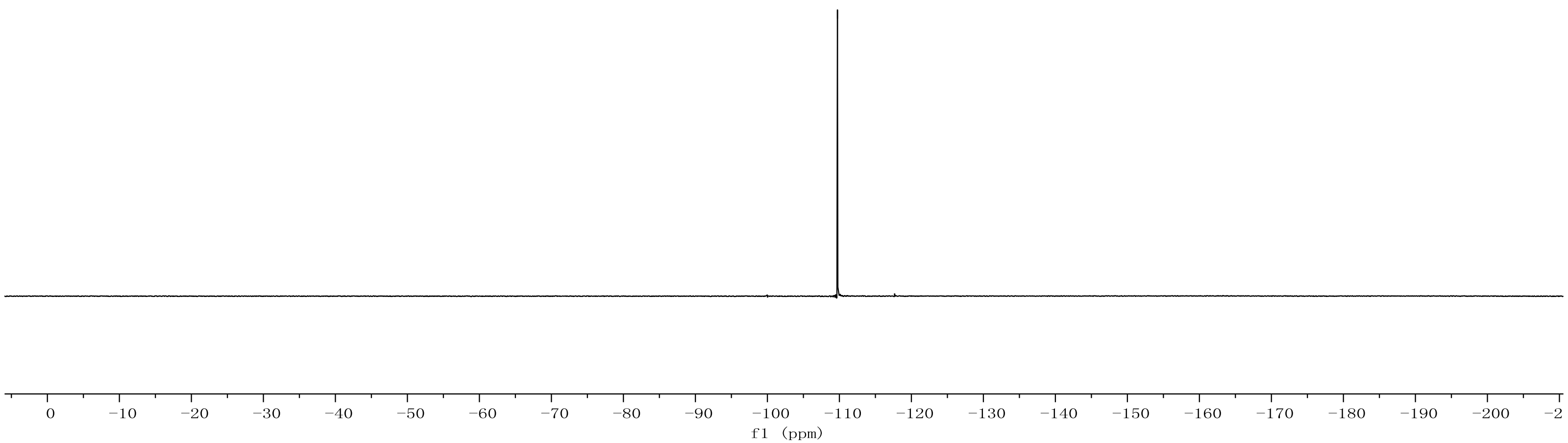
20c


8.26 7.89 7.87 7.86 7.85 7.70 7.70 7.69 7.68 7.68 7.24 7.24 7.23 7.23 7.22 7.21 7.21 7.05 7.03 7.00
2.35
1.46 1.40
tBu
O
BPin
F
N
Ts
21c
1.00 1.03 2.02 2.02 1.03
3.07
12.06 9.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

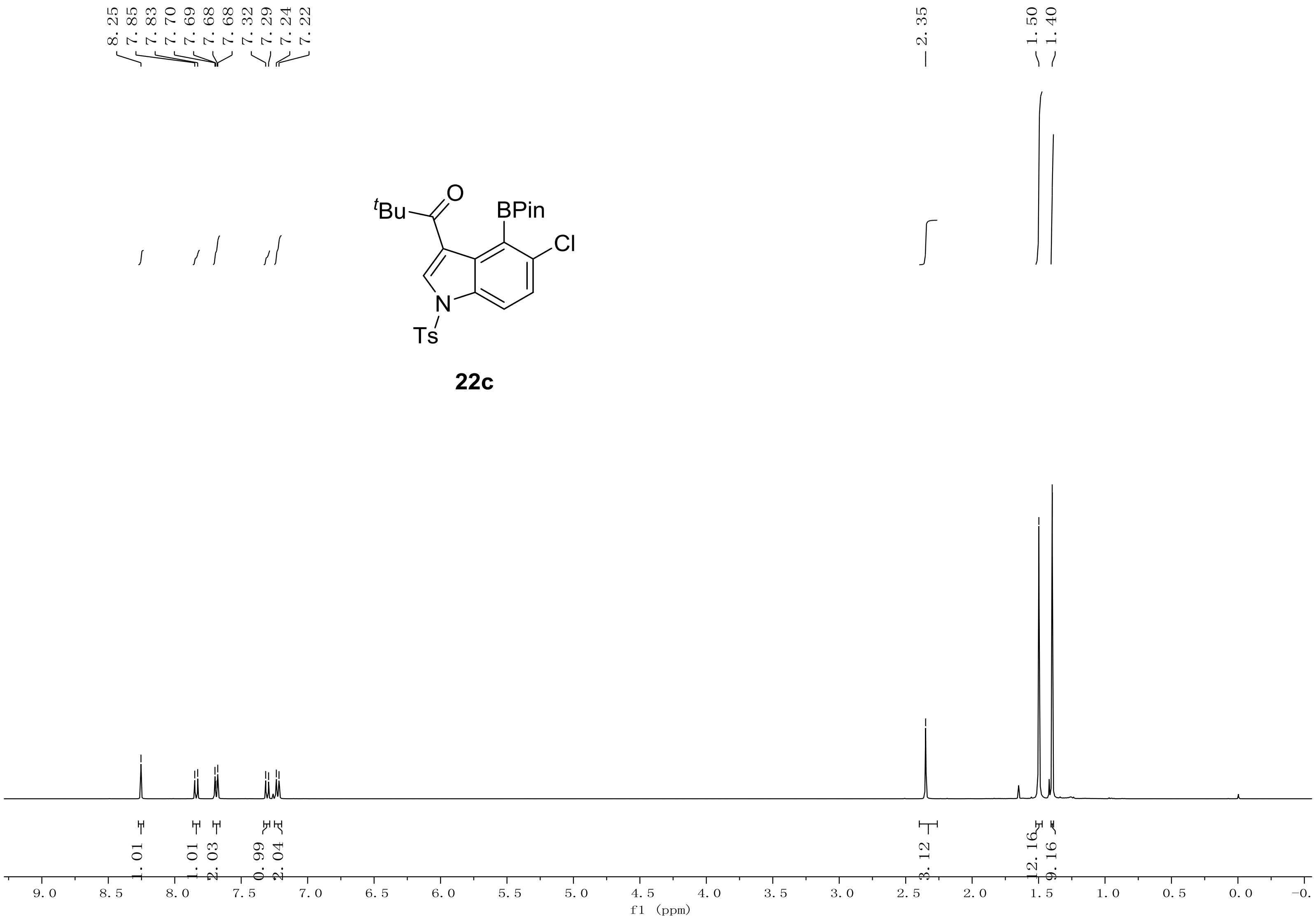

201.88
164.95
162.59
145.96
134.16
132.13
132.02
131.51
130.14
129.98
126.75
117.65
117.61
114.89
114.79
113.57
113.28
84.11
44.01
28.30
25.70
21.55
tBu
O
BPin
F
N
Ts
21c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

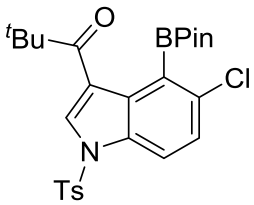


21c

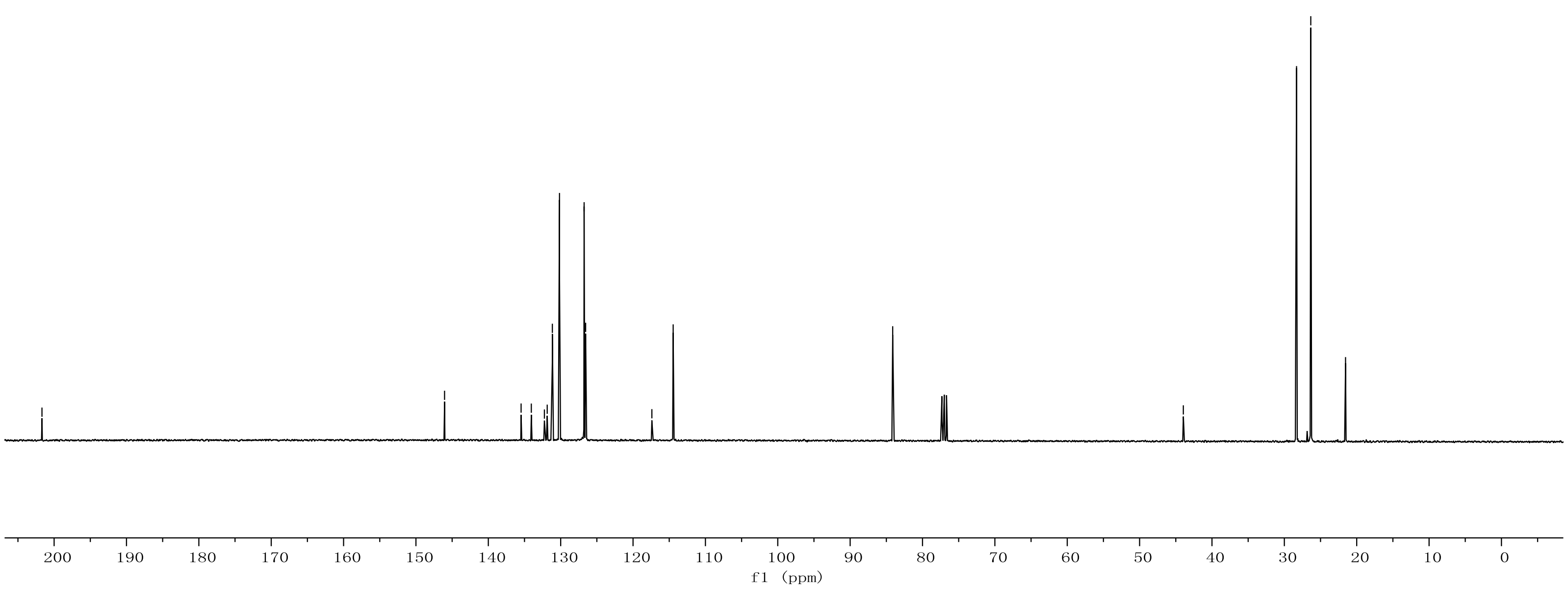


−109.73
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

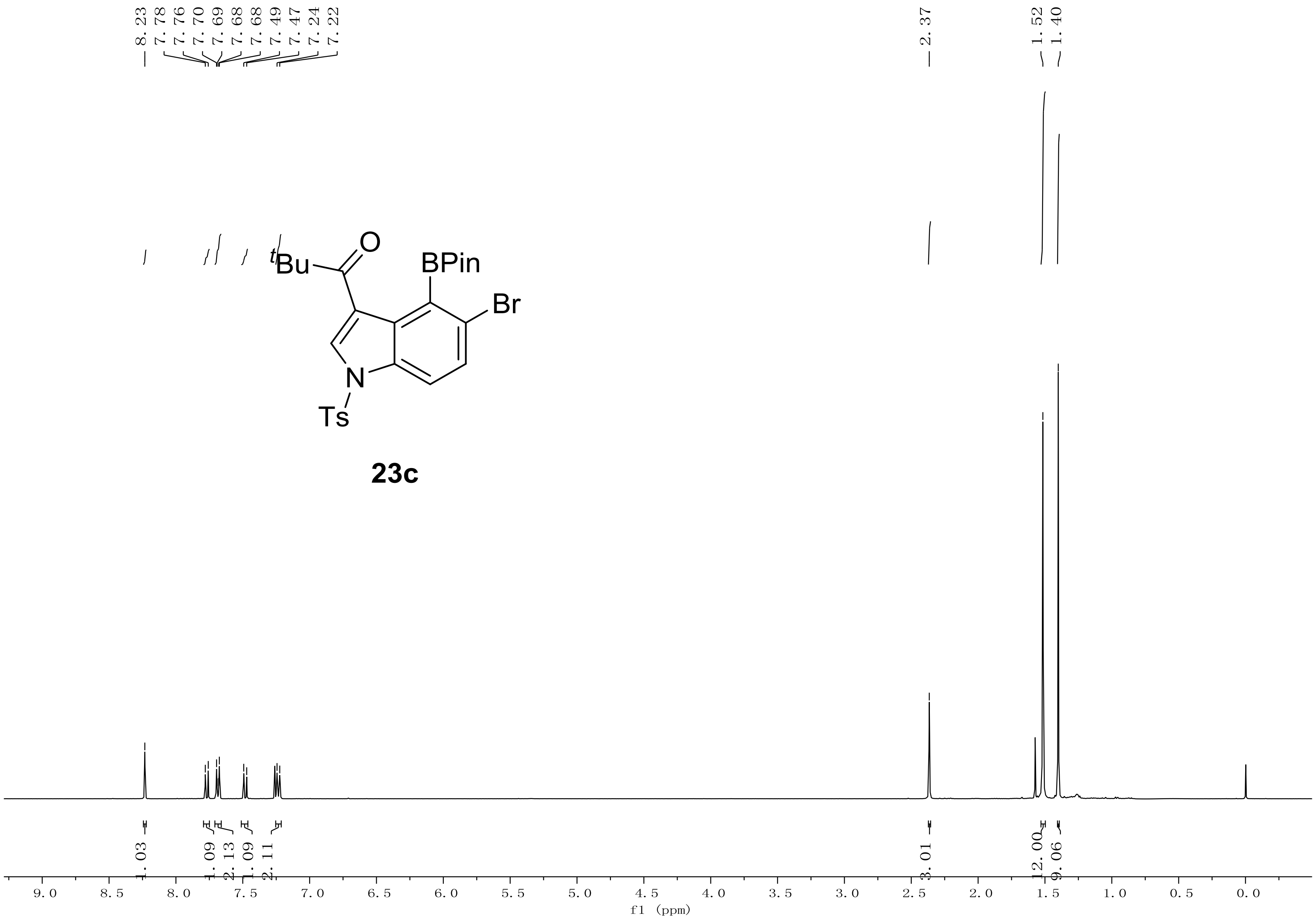

8.25
7.85
7.83
7.70
7.69
7.68
7.68
7.32
7.29
7.24
7.22
2.35
1.50
1.40
tBu
O
BPin
Cl
N
Ts
22c
1.01
1.01
2.03
0.99
2.04
3.12
12.16
9.16
f1 (ppm)



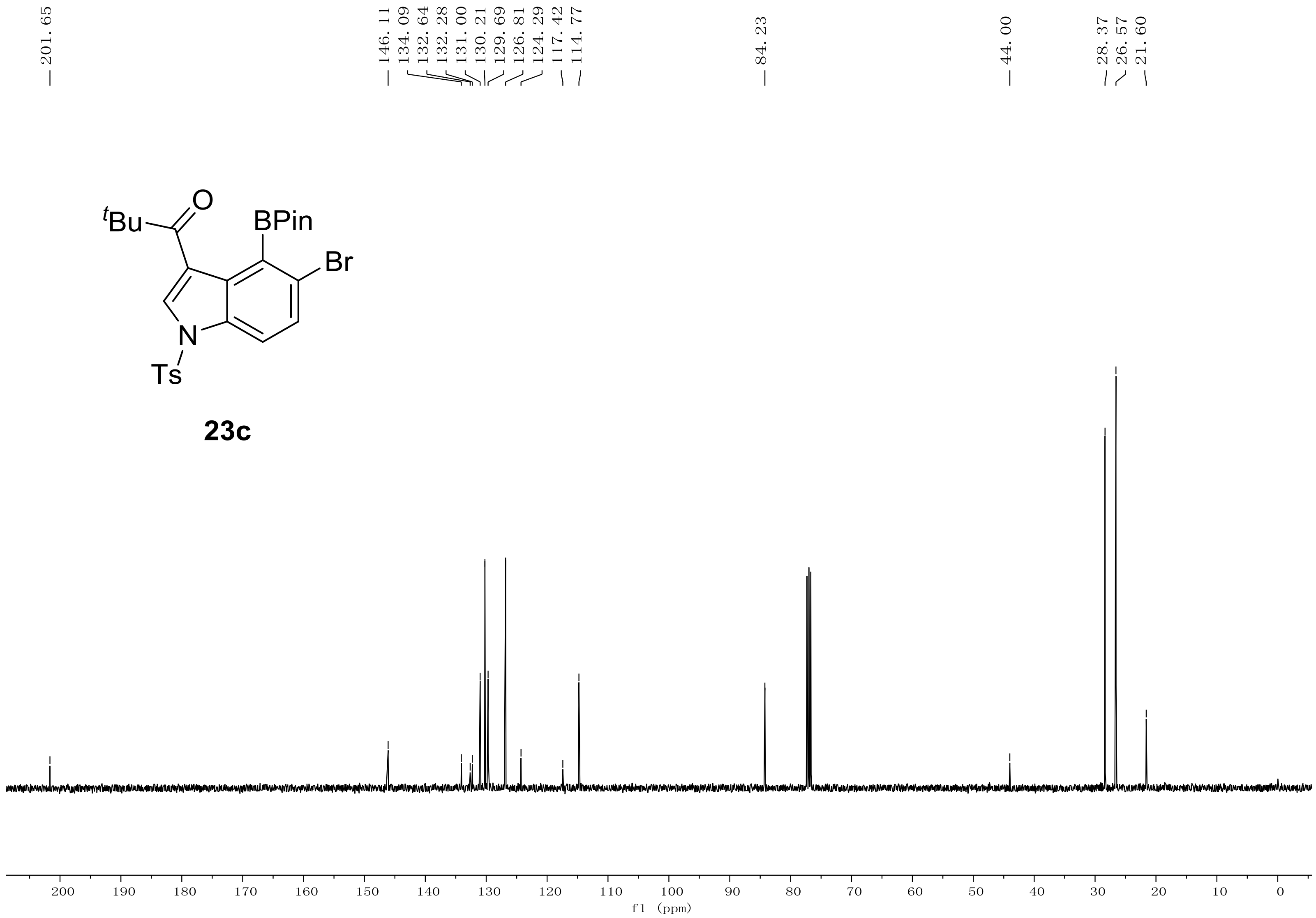
22c



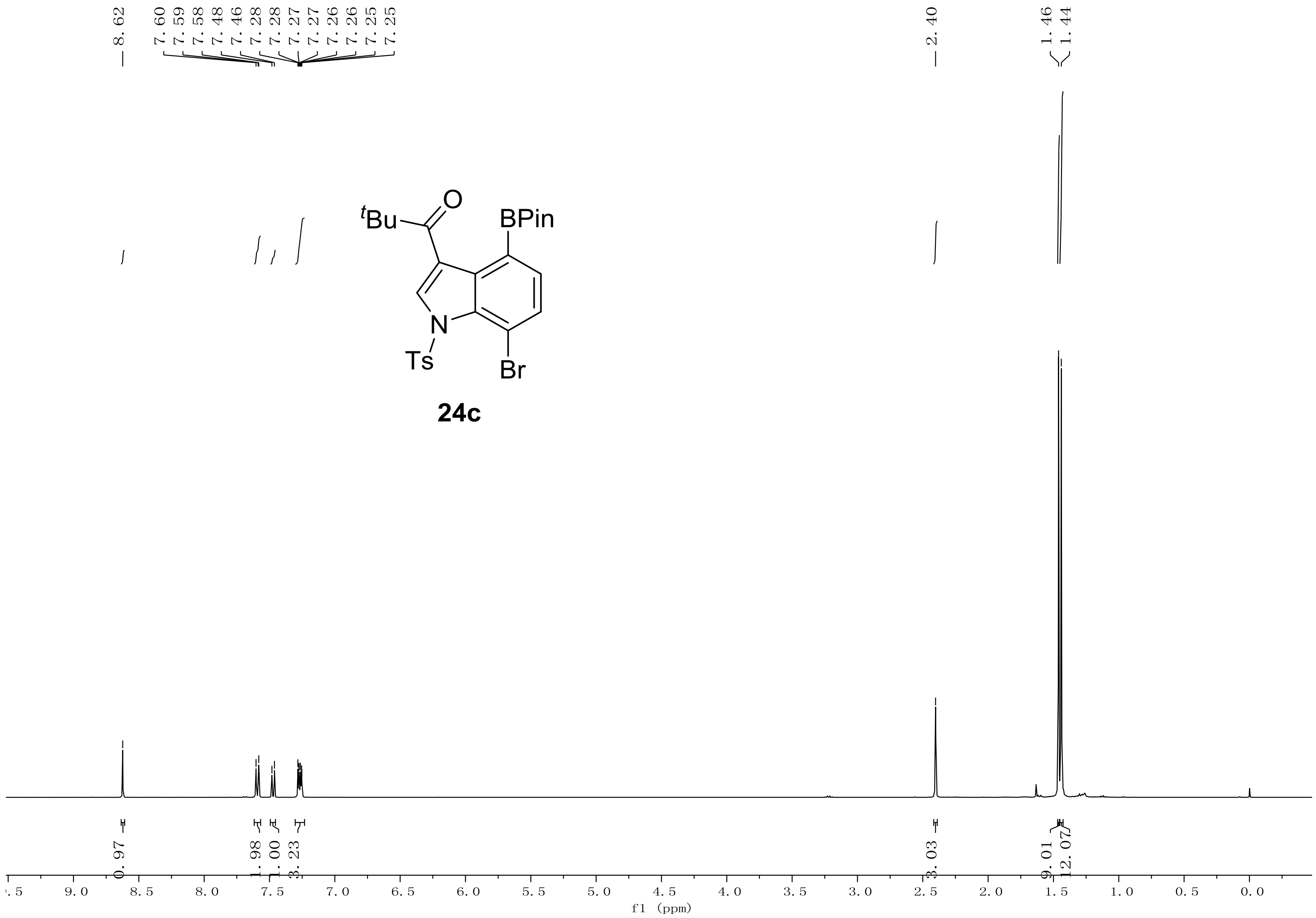
201.68
146.05
135.47
134.06
132.25
131.86
131.15
130.16
126.76
126.55
117.40
114.46
84.12
43.96
28.31
26.35
21.54
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

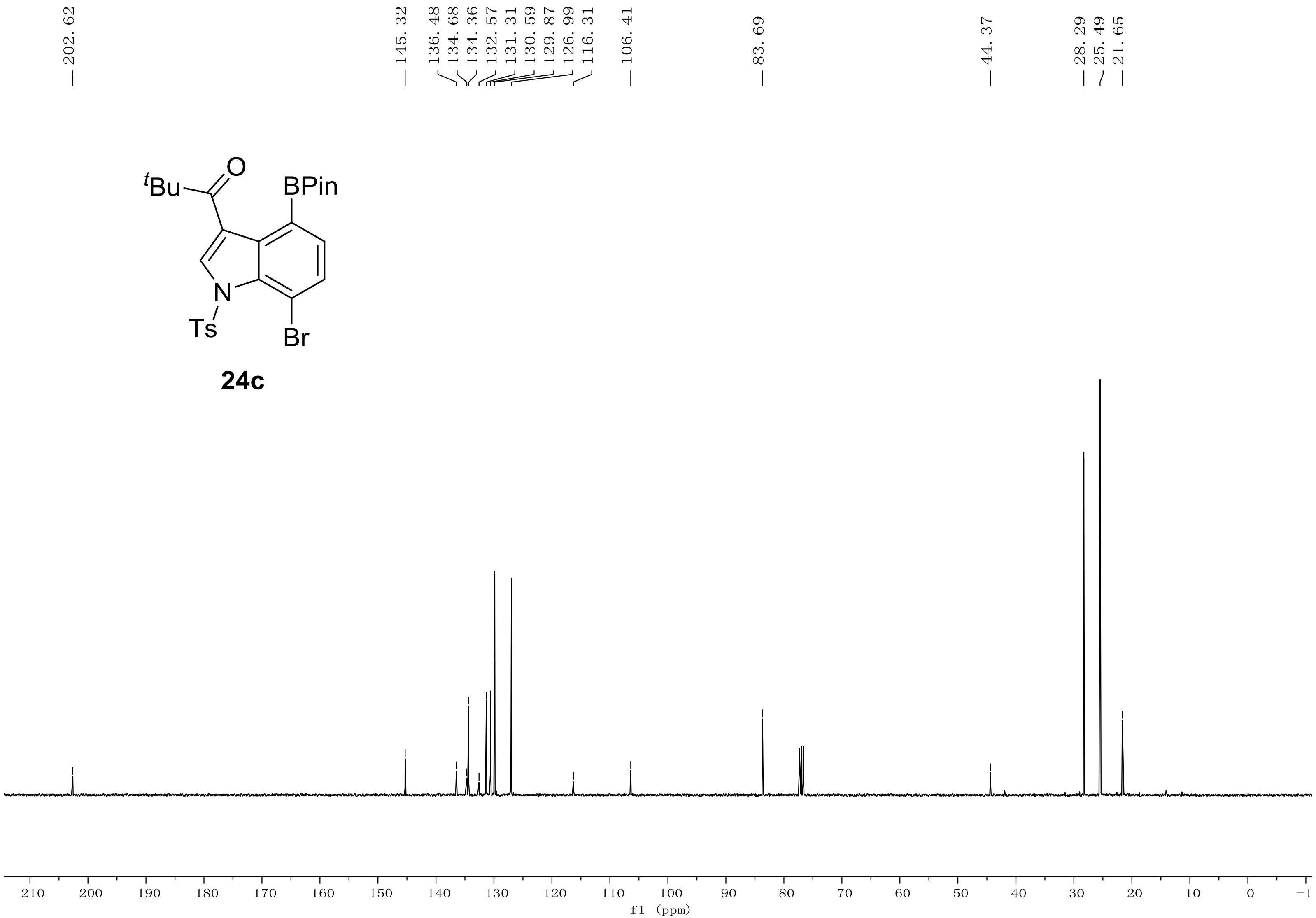

8.23
7.78
7.76
7.70
7.69
7.68
7.68
7.49
7.47
7.24
7.22
2.37
1.52
1.40
tBu
O
BPin
Br
N
Ts
1.03
1.09
2.13
1.09
2.11
3.01
12.00
9.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

23c

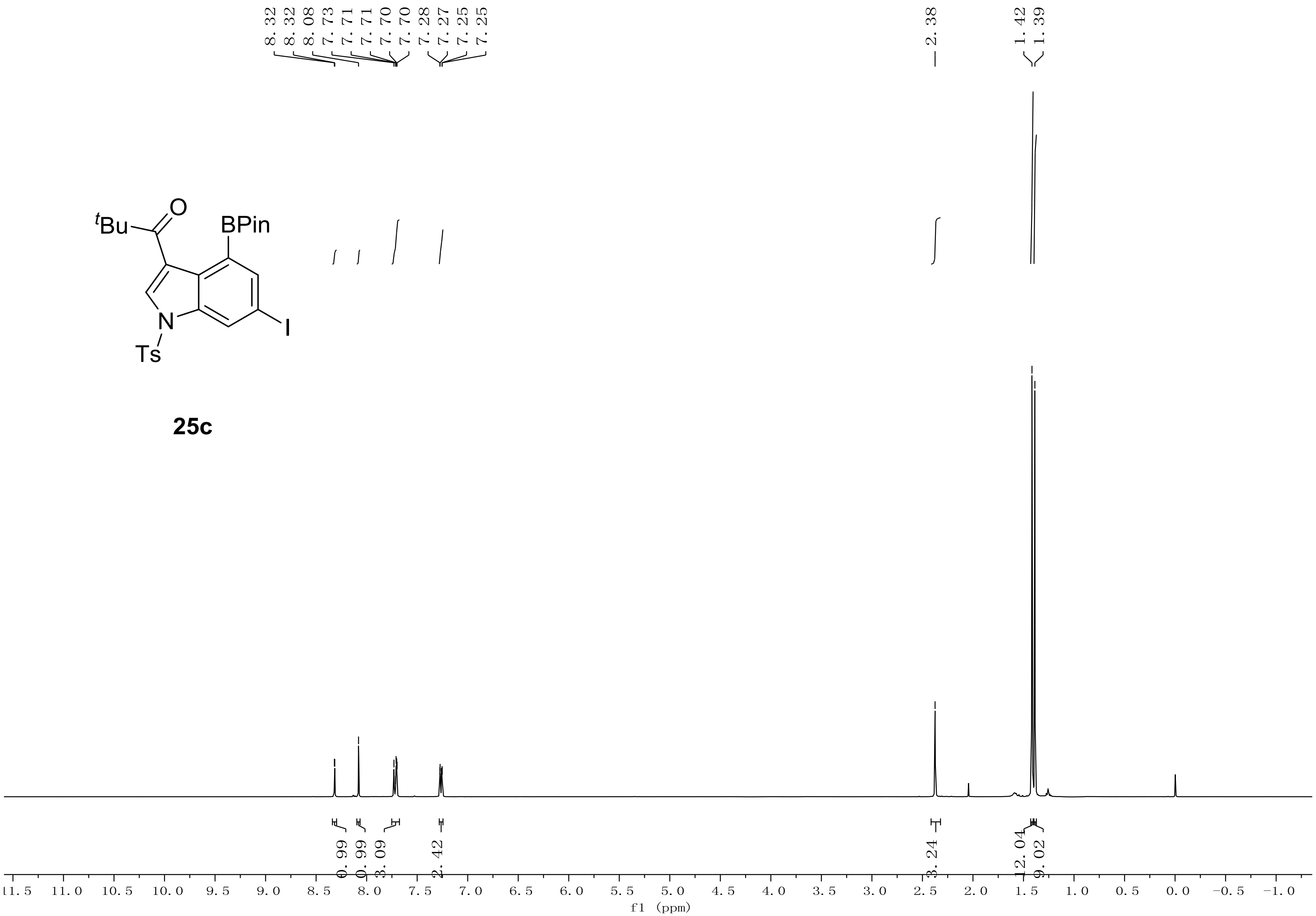


201.65
146.11
134.09
132.64
132.28
131.00
130.21
129.69
126.81
124.29
117.42
114.77
84.23
44.00
28.37
26.57
21.60
tBu
O
BPin
Br
N
Ts
23c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.62
7.60
7.59
7.58
7.48
7.46
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
2.40
1.46
1.44
tBu
O
BPin
N
Ts
Br
24c
0.97
1.98
1.00
3.23
3.03
9.01
12.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

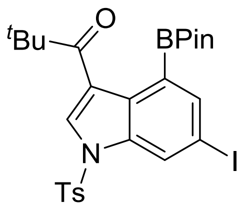


24c
202.62
145.32
136.48
134.68
134.36
132.57
131.31
130.59
129.87
126.99
116.31
106.41
83.69
44.37
28.29
25.49
21.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

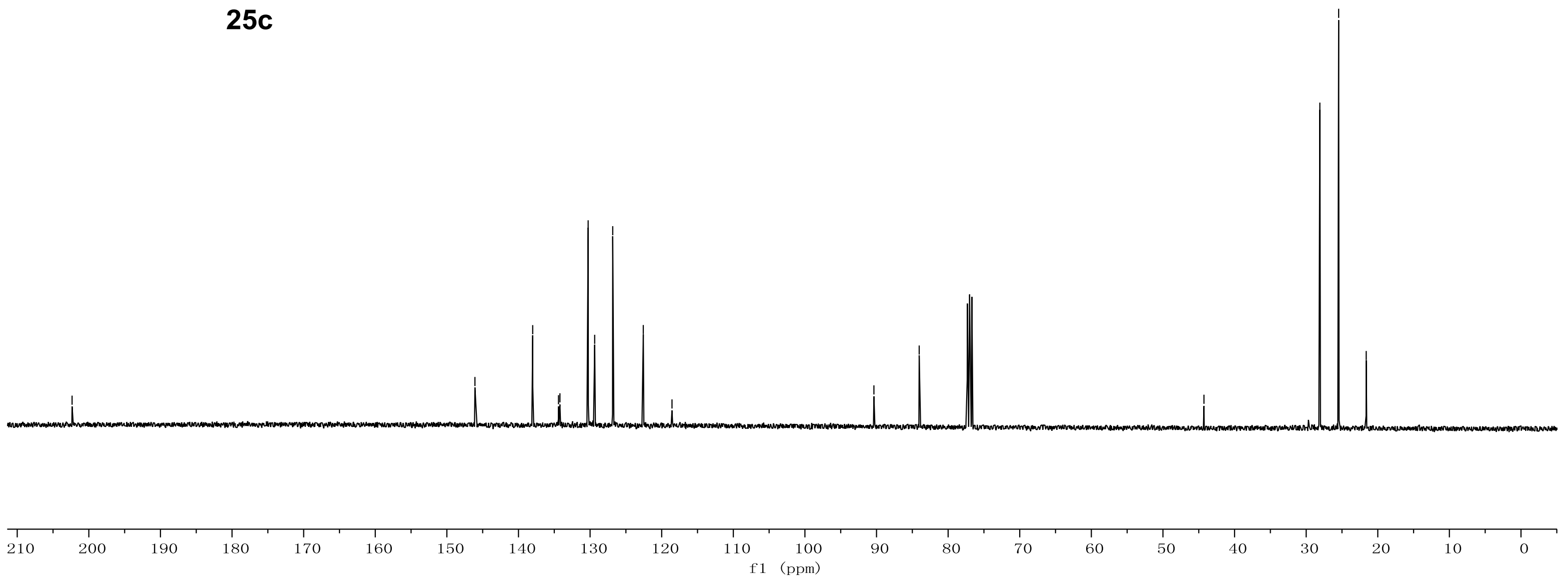


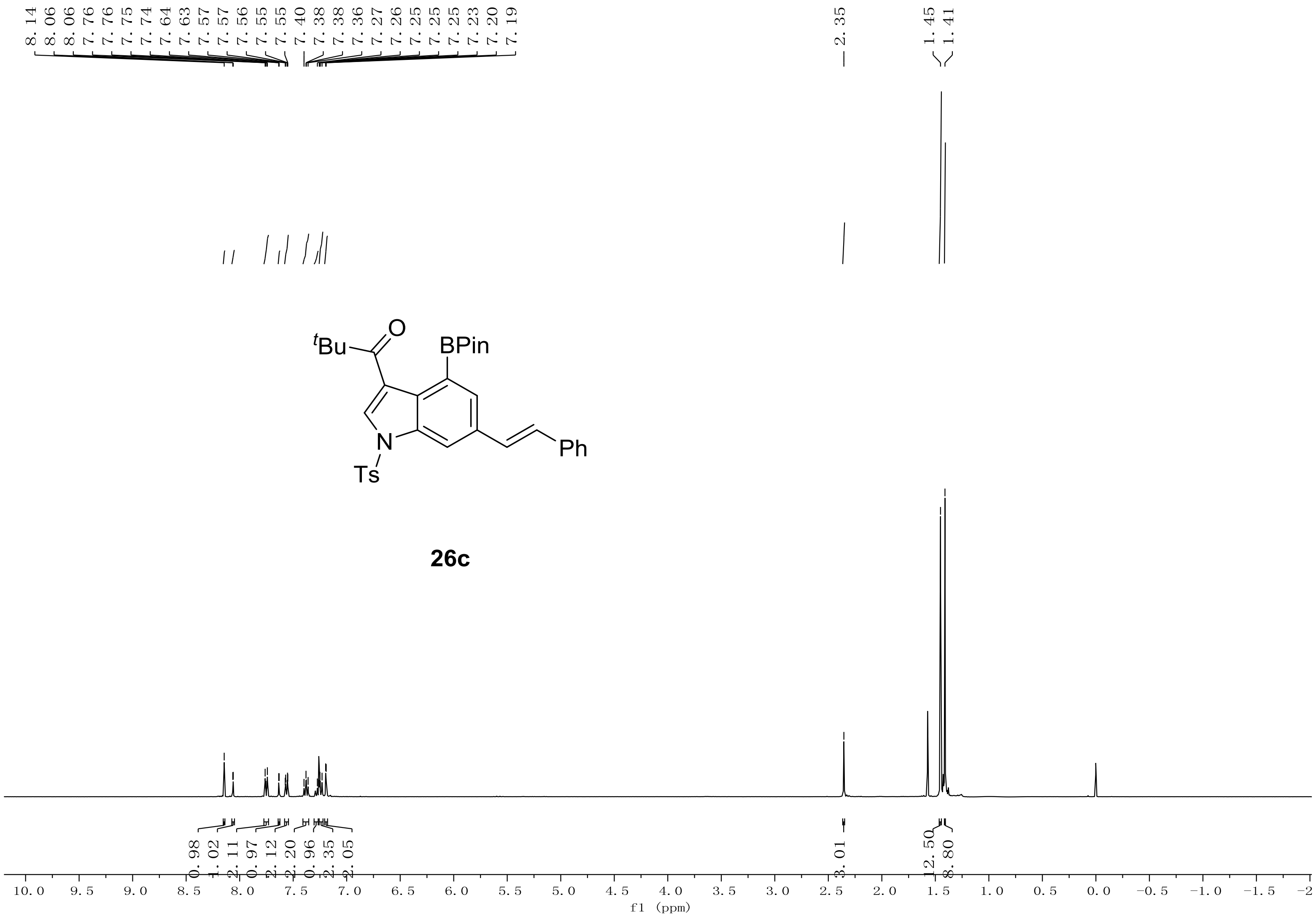
8.32 8.32 8.08 7.73 7.71 7.71 7.70 7.70 7.28 7.27 7.25 7.25
2.38
1.42 1.39
0.99 0.99 3.09 2.42 3.24 12.04 9.02
f1 (ppm)

25c

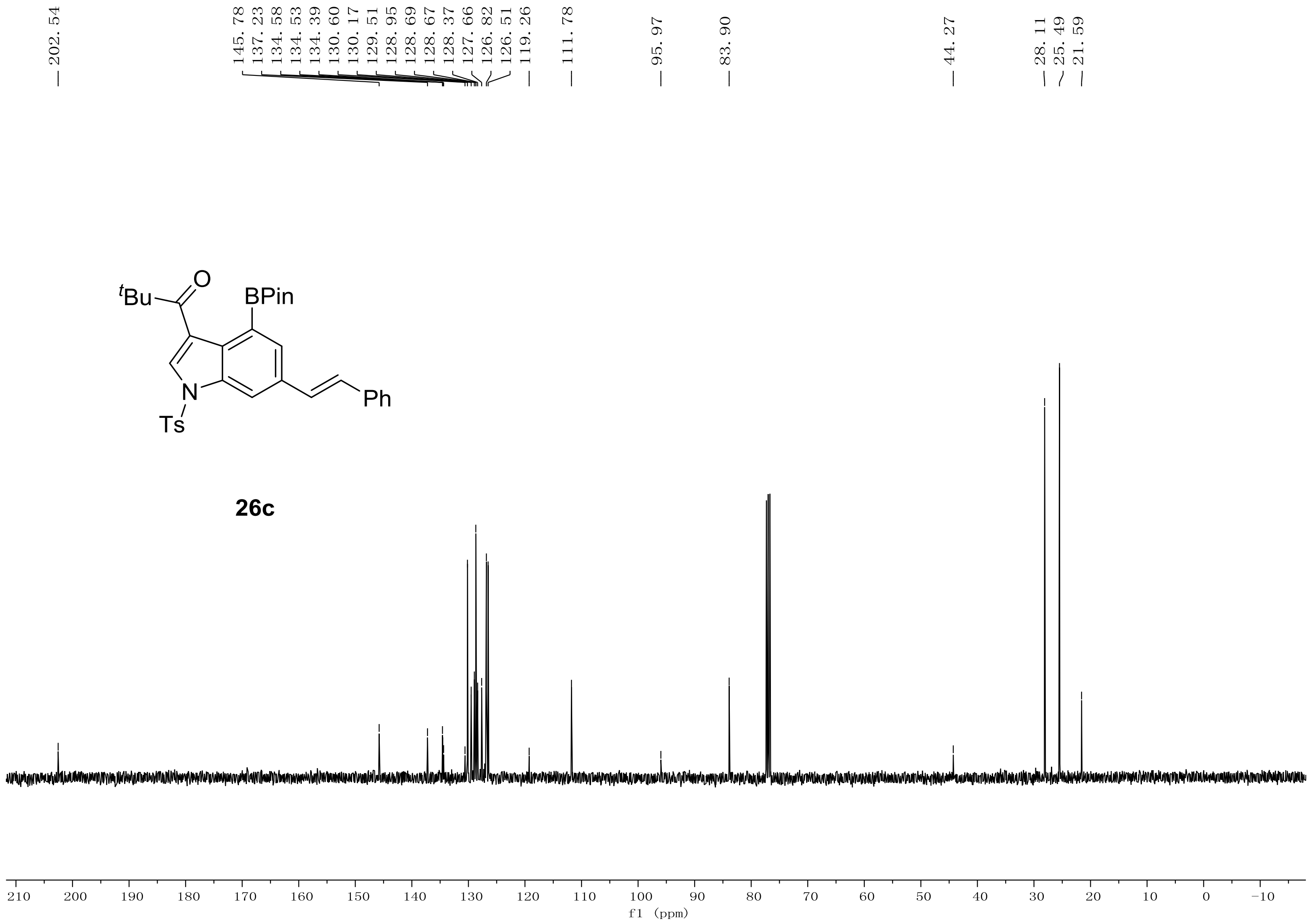

tBu
O
BPin
N
Ts
I

25c


202.34
146.08
138.01
134.41
134.21
130.30
130.27
129.36
126.84
122.57
118.56
90.36
84.04
44.27
28.09
25.46
21.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

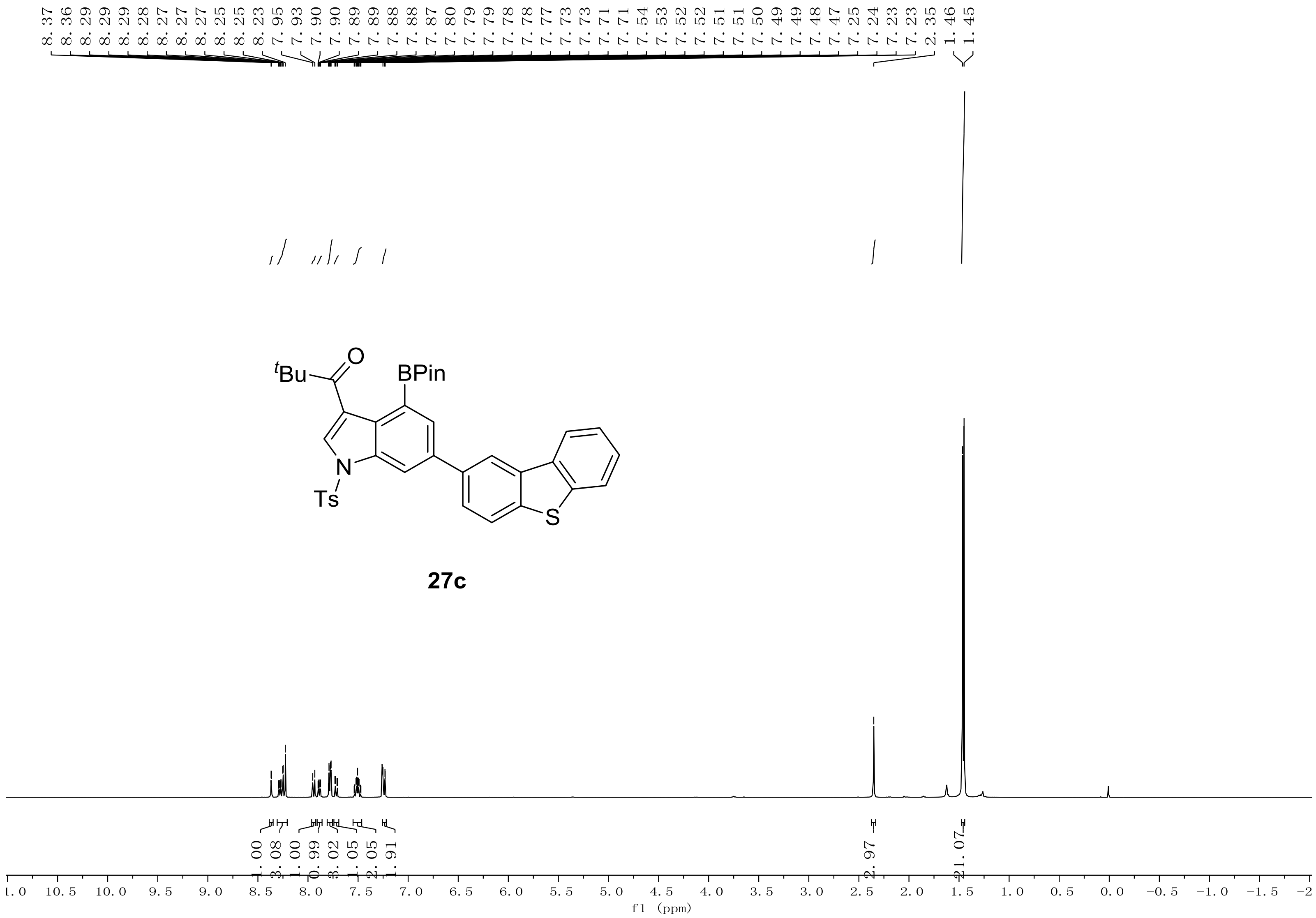

8.14 8.06 8.06 7.76 7.76 7.75 7.74 7.64 7.63 7.57 7.57 7.56 7.55 7.55 7.40 7.38 7.38 7.36 7.27 7.26 7.25 7.25 7.25 7.23 7.20 7.19
2.35
1.45 1.41
tBu
O
BPin
N
Ts
Ph
0.98 1.02 2.11 0.97 2.12 2.20 0.96 2.35 2.05
3.01
12.50 8.80
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2
f1 (ppm)

26c

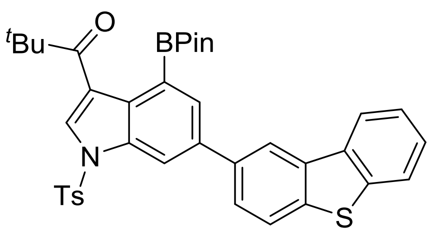


202.54
145.78
137.23
134.58
134.53
134.39
130.60
130.17
129.51
128.95
128.69
128.67
128.37
127.66
126.82
126.51
119.26
111.78
95.97
83.90
44.27
28.11
25.49
21.59
^{t}Bu
O
BPin
N
Ts
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

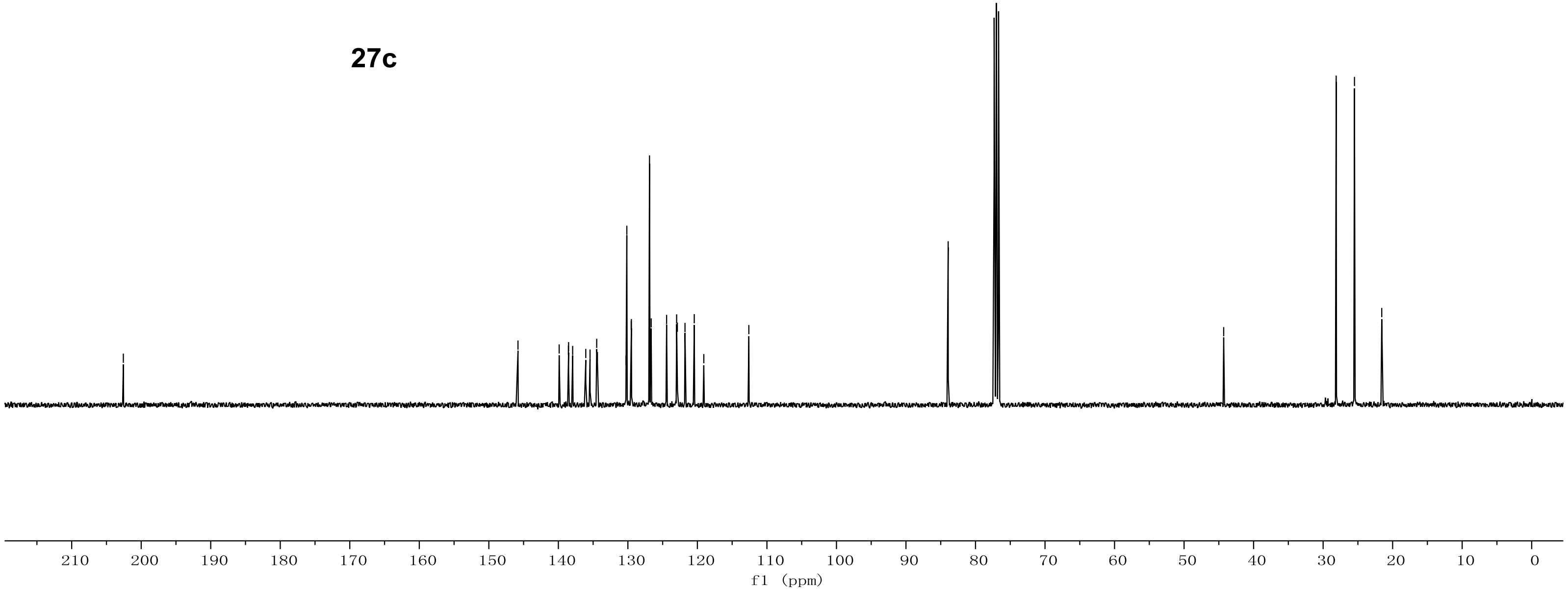
26c



27c

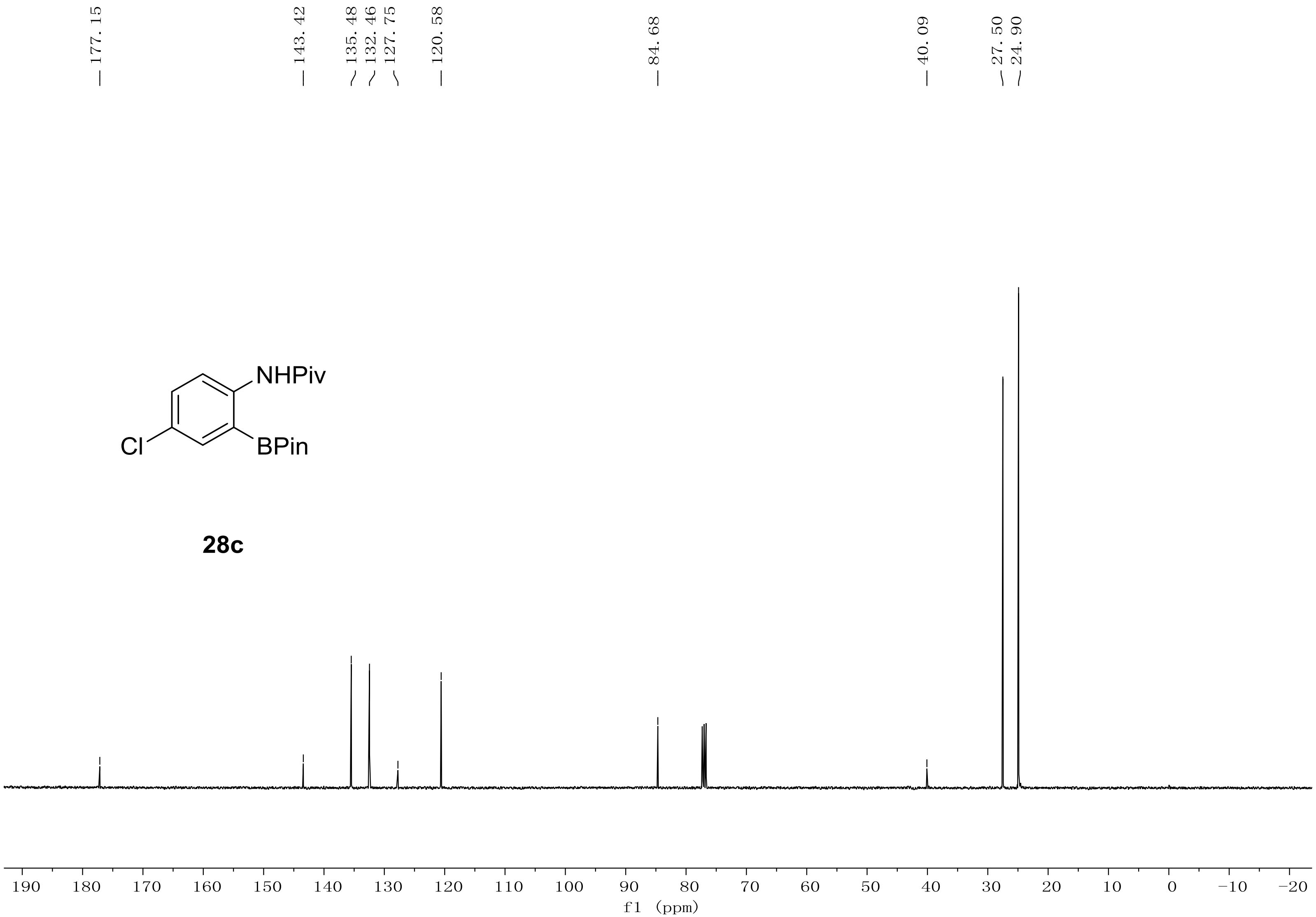

tBu
O
BPin
N
Ts
S

27c

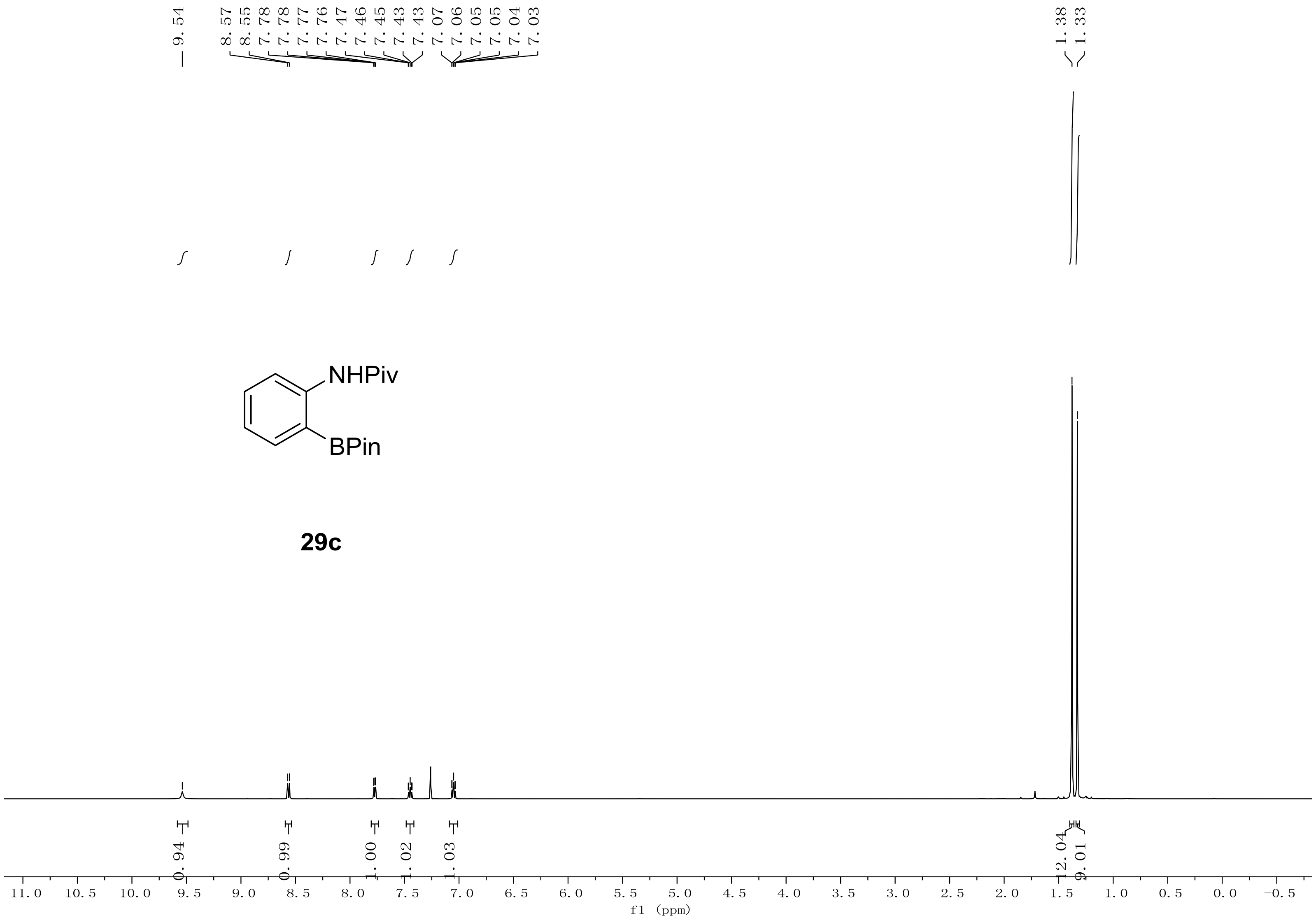

202.57
145.81
139.88
138.56
138.53
137.94
136.06
135.44
134.48
134.38
130.26
130.15
129.52
129.50
126.89
126.65
124.43
122.99
122.88
121.78
120.45
119.08
112.60
83.93
44.30
28.12
25.49
21.57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.48
8.52
8.50
7.71
7.70
7.39
7.38
7.37
7.36
1.38
1.31
0.86
0.99
0.96
0.99
12.08
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
NHPiv
Cl
BPin

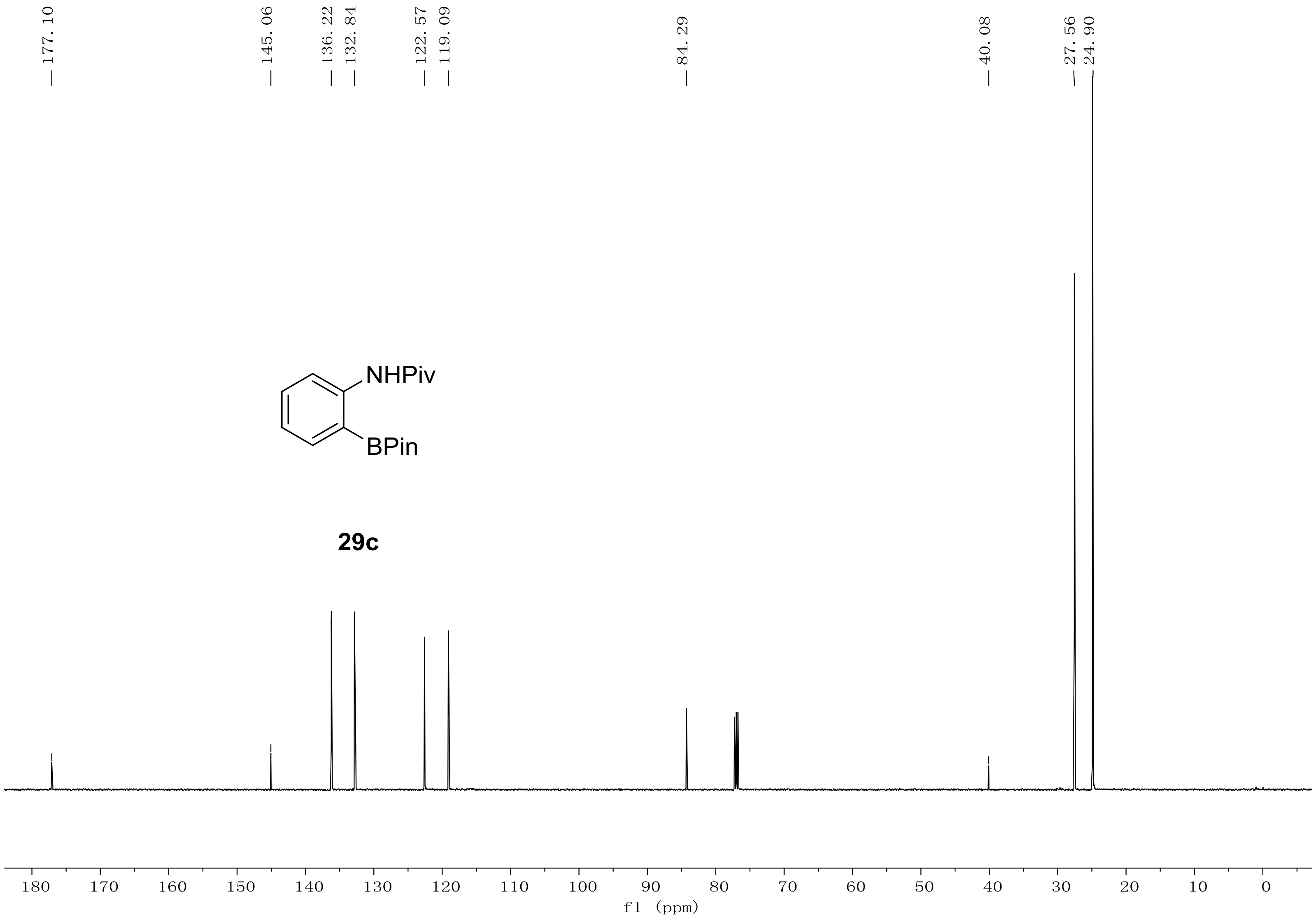
28c


177.15
143.42
135.48
132.46
127.75
120.58
84.68
40.09
27.50
24.90
NHPiv
Cl
BPin
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

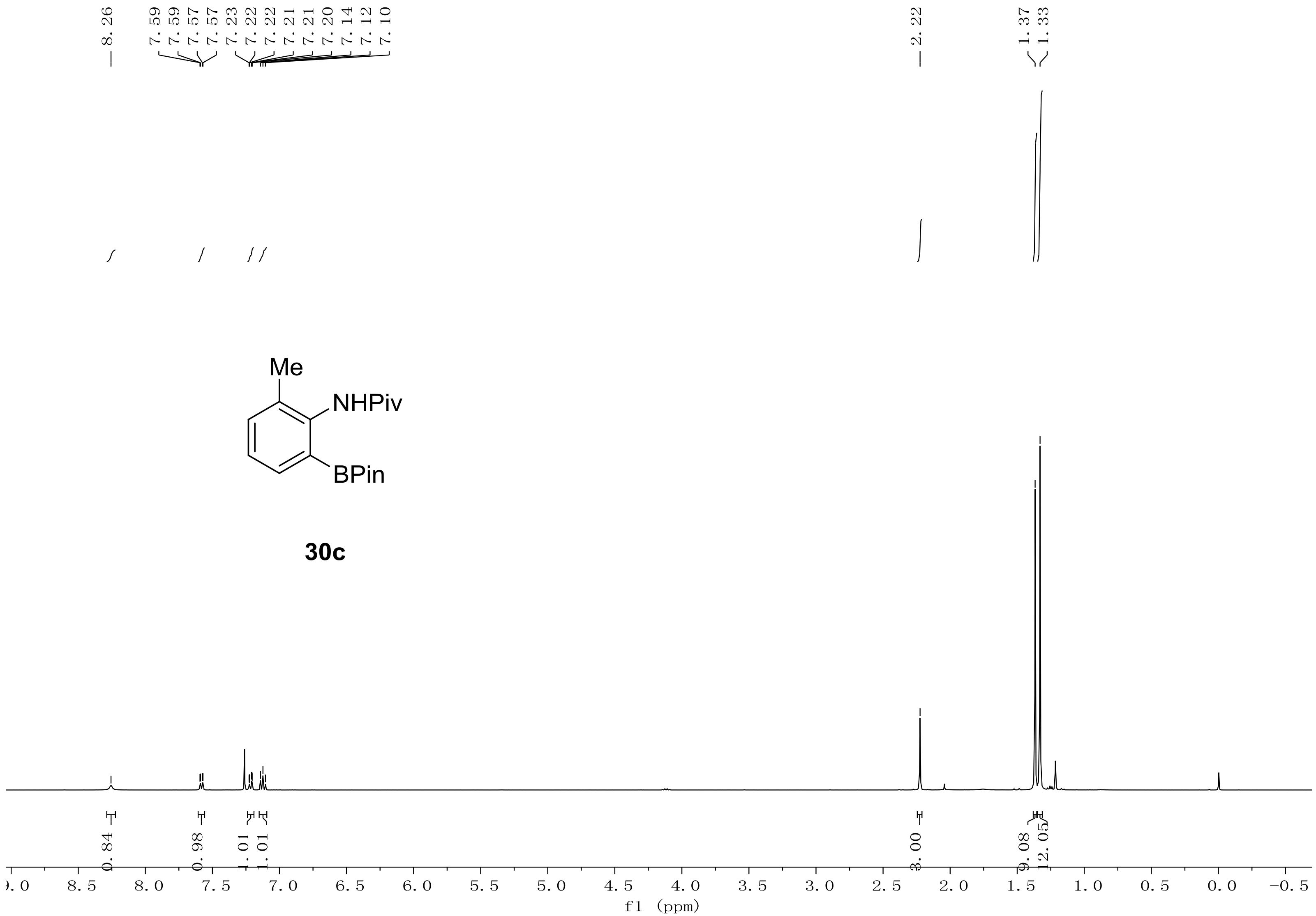
28c


9.54
8.57
8.55
7.78
7.78
7.77
7.76
7.47
7.46
7.45
7.43
7.43
7.07
7.06
7.05
7.05
7.04
7.03
1.38
1.33
NHPiv
BPin
0.94
0.99
1.00
1.02
1.03
12.04
9.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

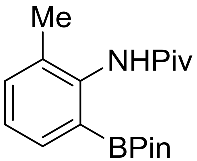
29c


177.10
145.06
136.22
132.84
122.57
119.09
84.29
40.08
27.56
24.90
NHPiv
BPin
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

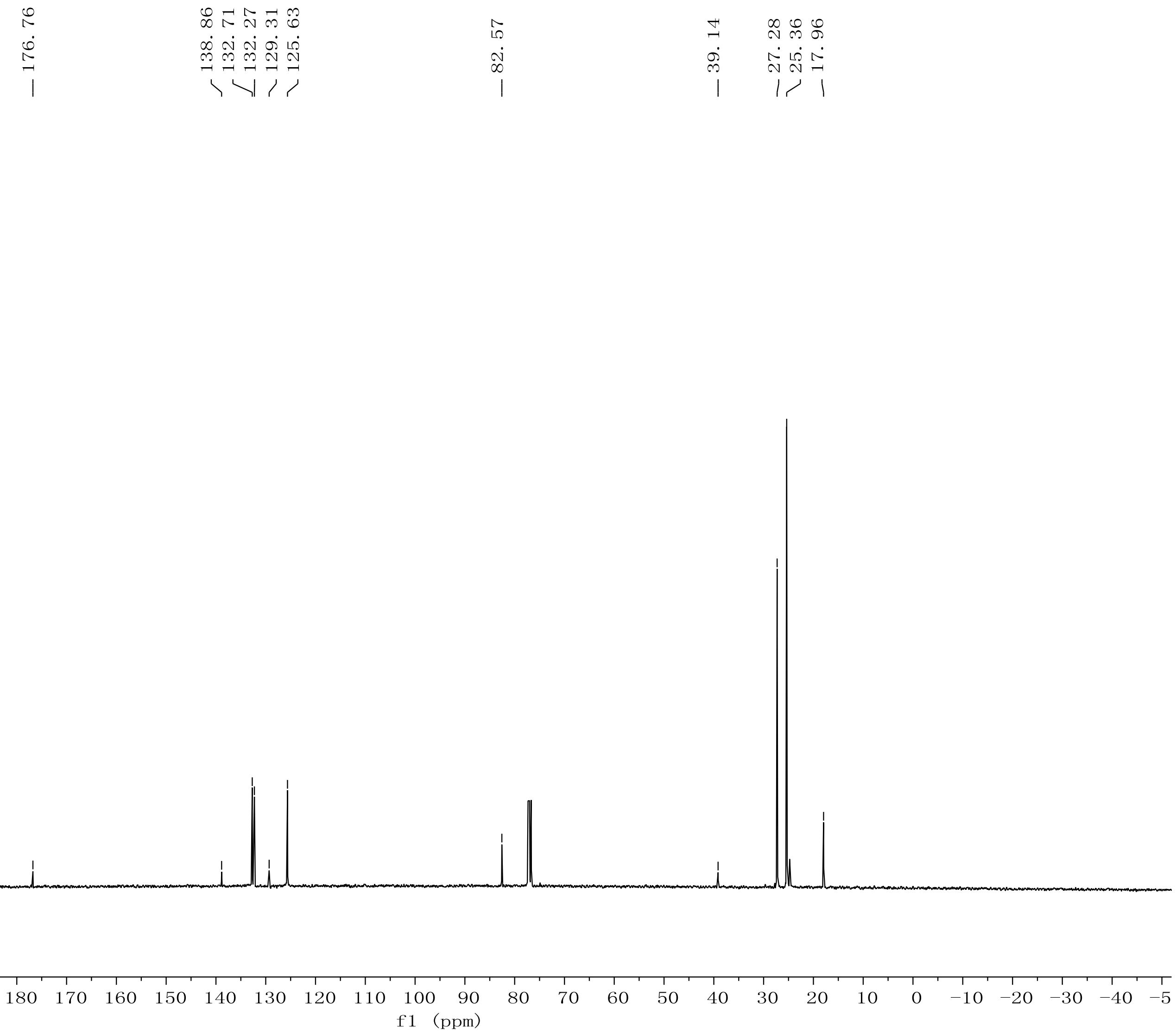
29c

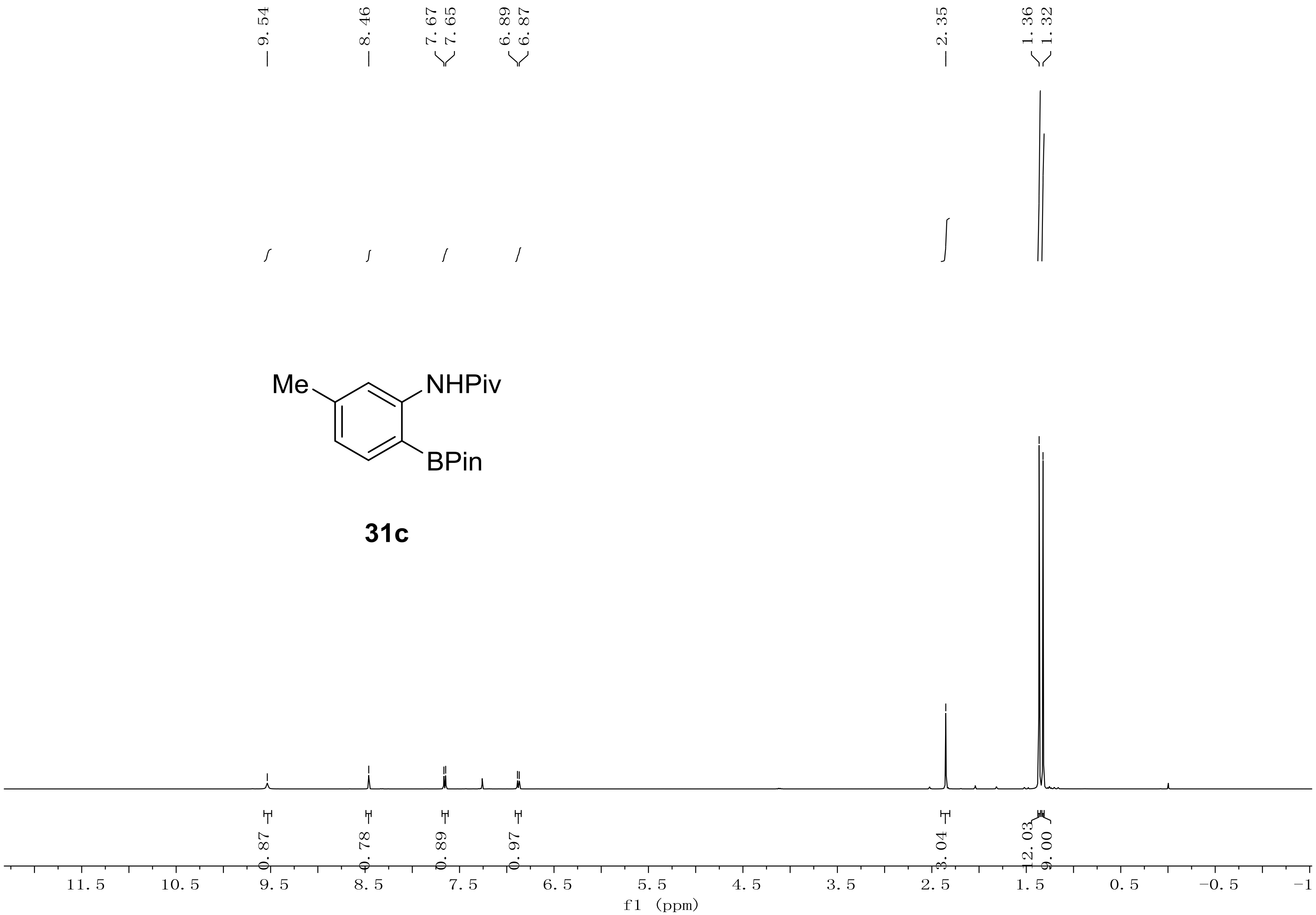

8.26
7.59 7.59 7.57 7.57 7.23 7.22 7.22 7.21 7.21 7.20 7.14 7.12 7.10
2.22
1.37 1.33
0.84
0.98
1.01 1.01
3.00
9.08 12.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
Me
NHPiv
BPin

30c

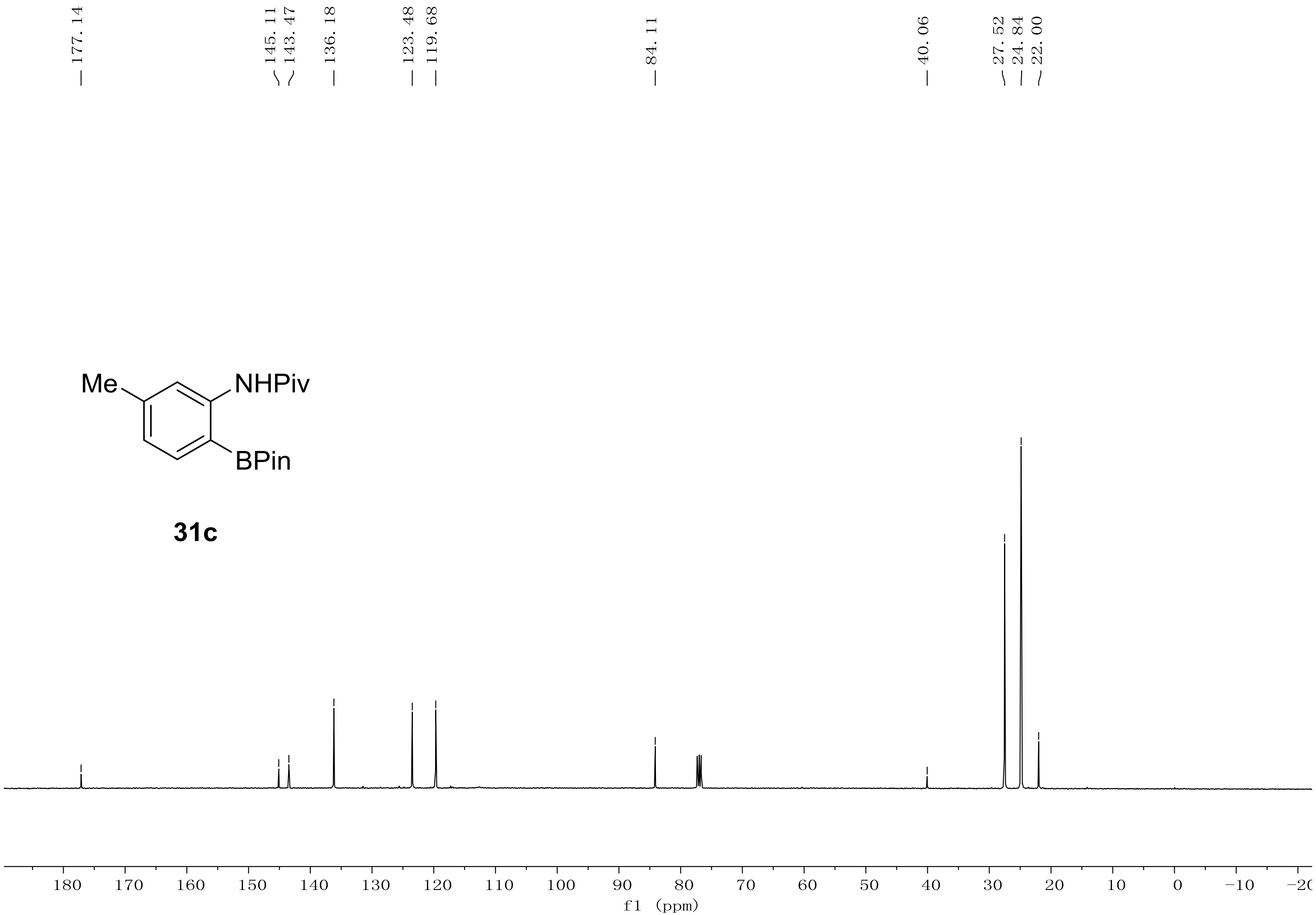


30c

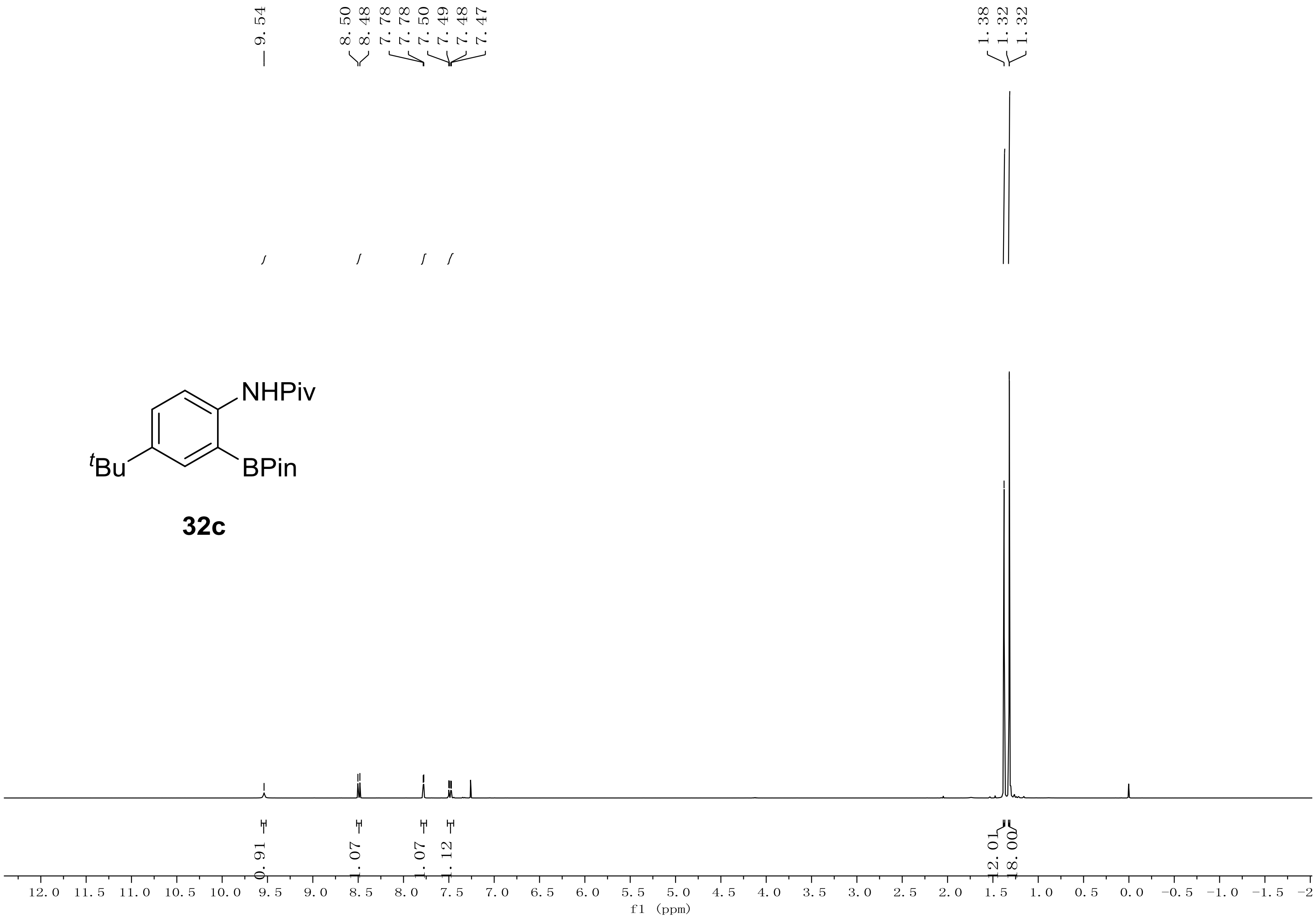

176.76
138.86
132.71
132.27
129.31
125.63
82.57
39.14
27.28
25.36
17.96
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −5
f1 (ppm)

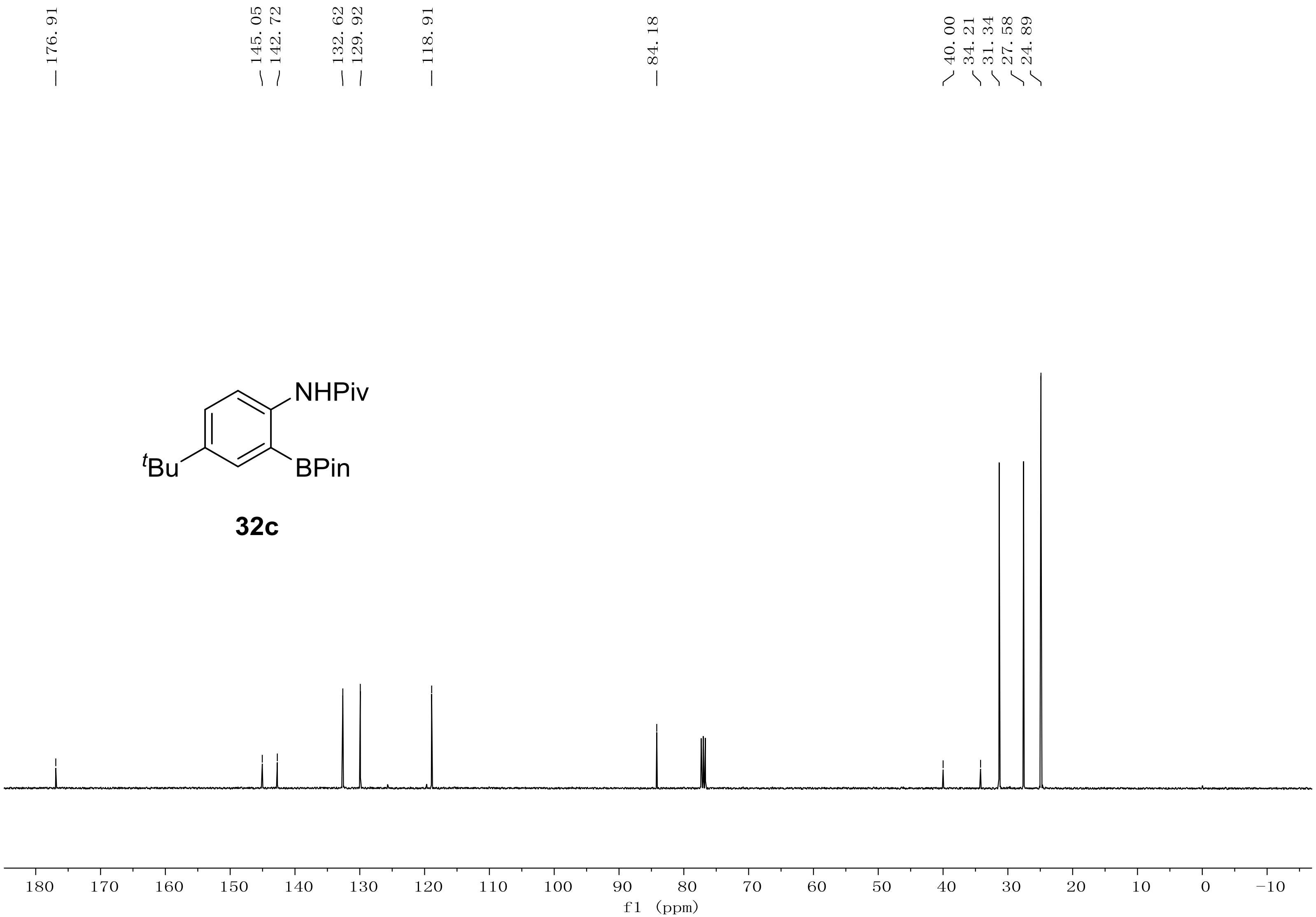


31c


177.14
145.11
143.47
136.18
123.48
119.68
84.11
40.06
27.52
24.84
22.00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −2(
f1 (ppm)
Me
NHPiv
BPin

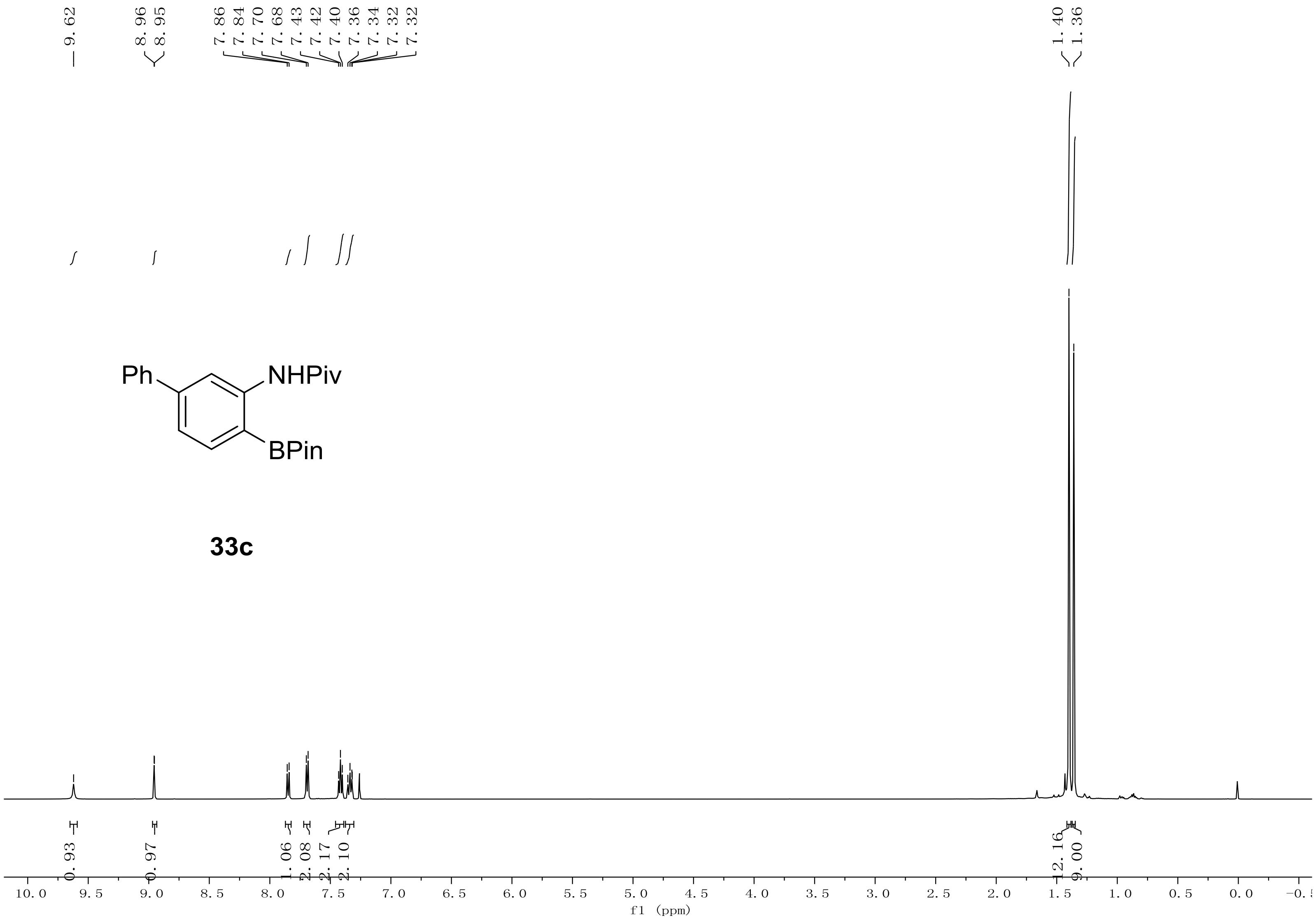
31c

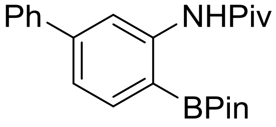

9.54
8.50
8.48
7.78
7.78
7.50
7.49
7.48
7.47
1.38
1.32
1.32
NHPiv
tBu
BPin
32c
0.91
1.07
1.07
1.12
12.01
18.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2
f1 (ppm)



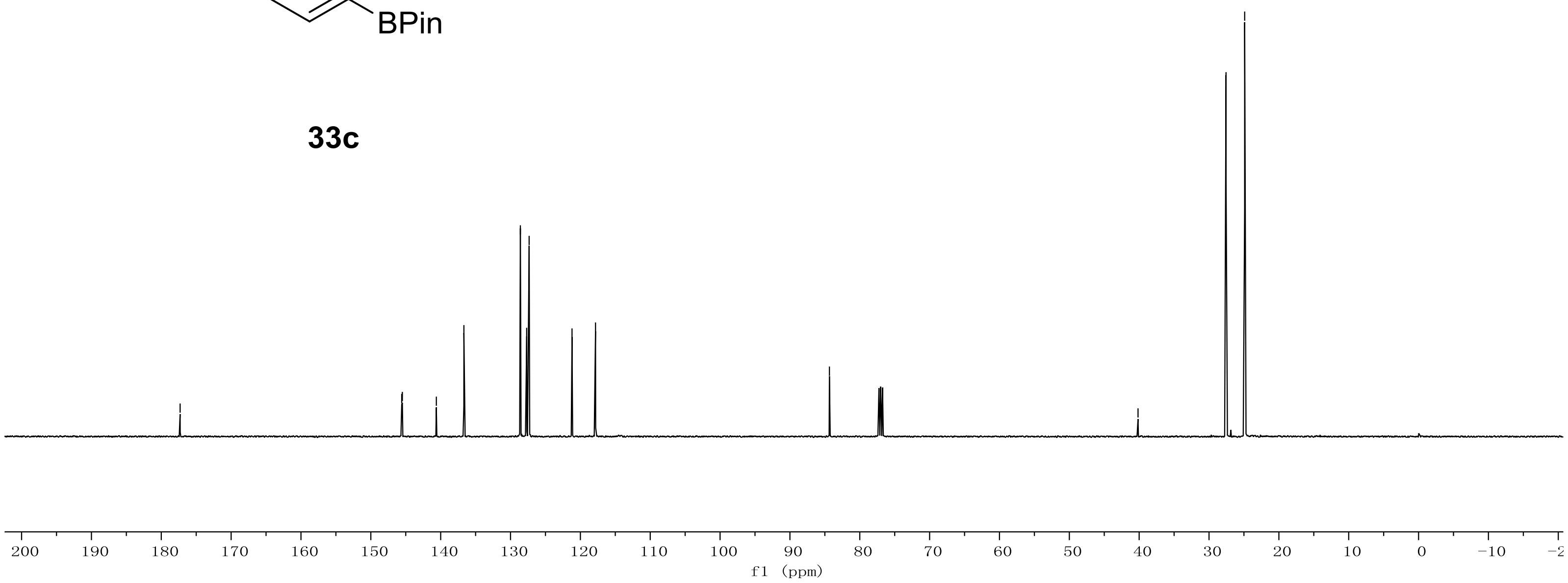
NHPiv
tBu
BPin
176.91
145.05
142.72
132.62
129.92
118.91
84.18
40.00
34.21
31.34
27.58
24.89
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

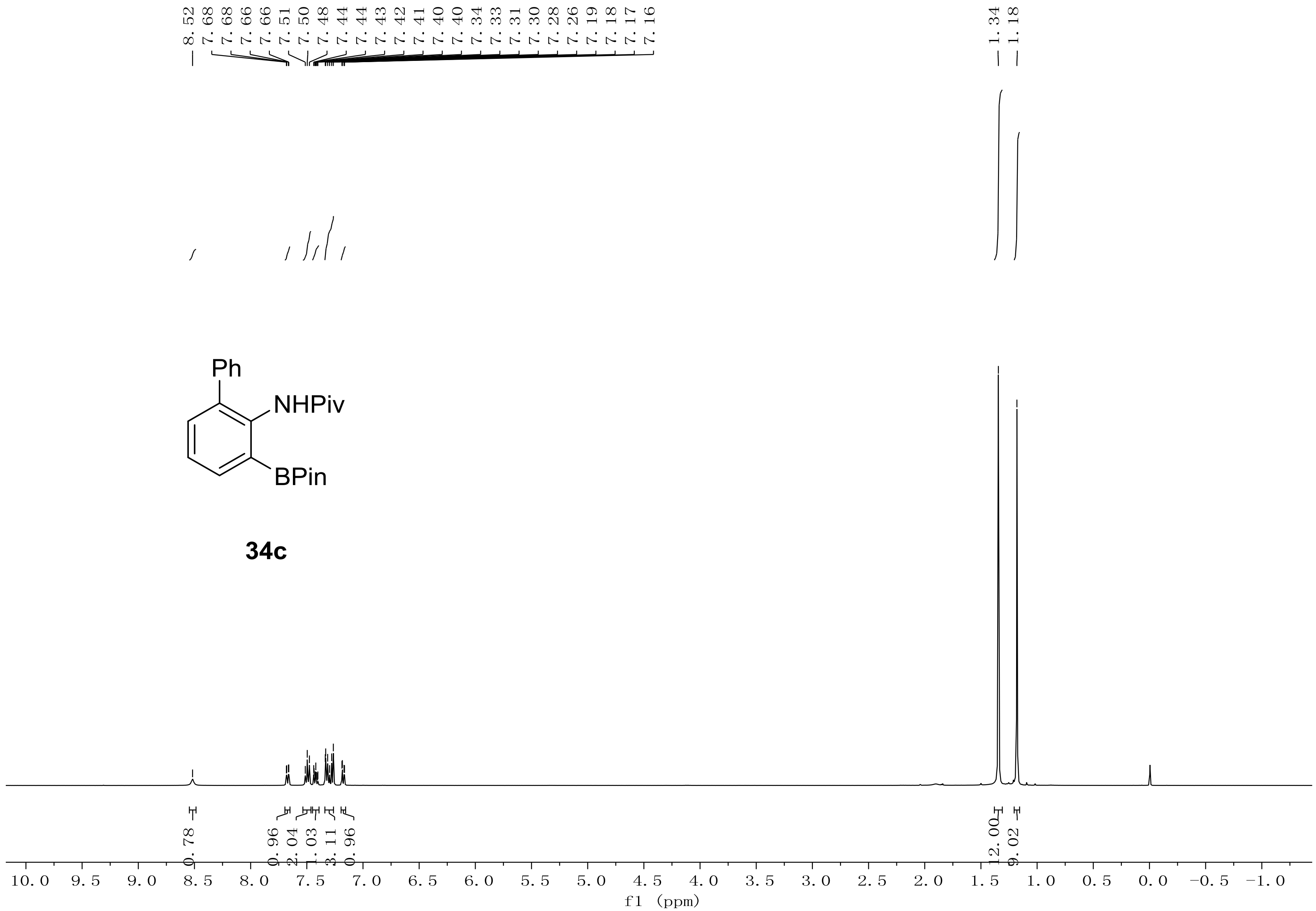
32c


9.62
8.96
8.95
7.86
7.84
7.70
7.68
7.43
7.42
7.40
7.36
7.34
7.32
7.32
1.40
1.36
Ph
NHPiv
BPin
33c
0.93
0.97
1.06
2.08
2.17
2.10
12.16
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

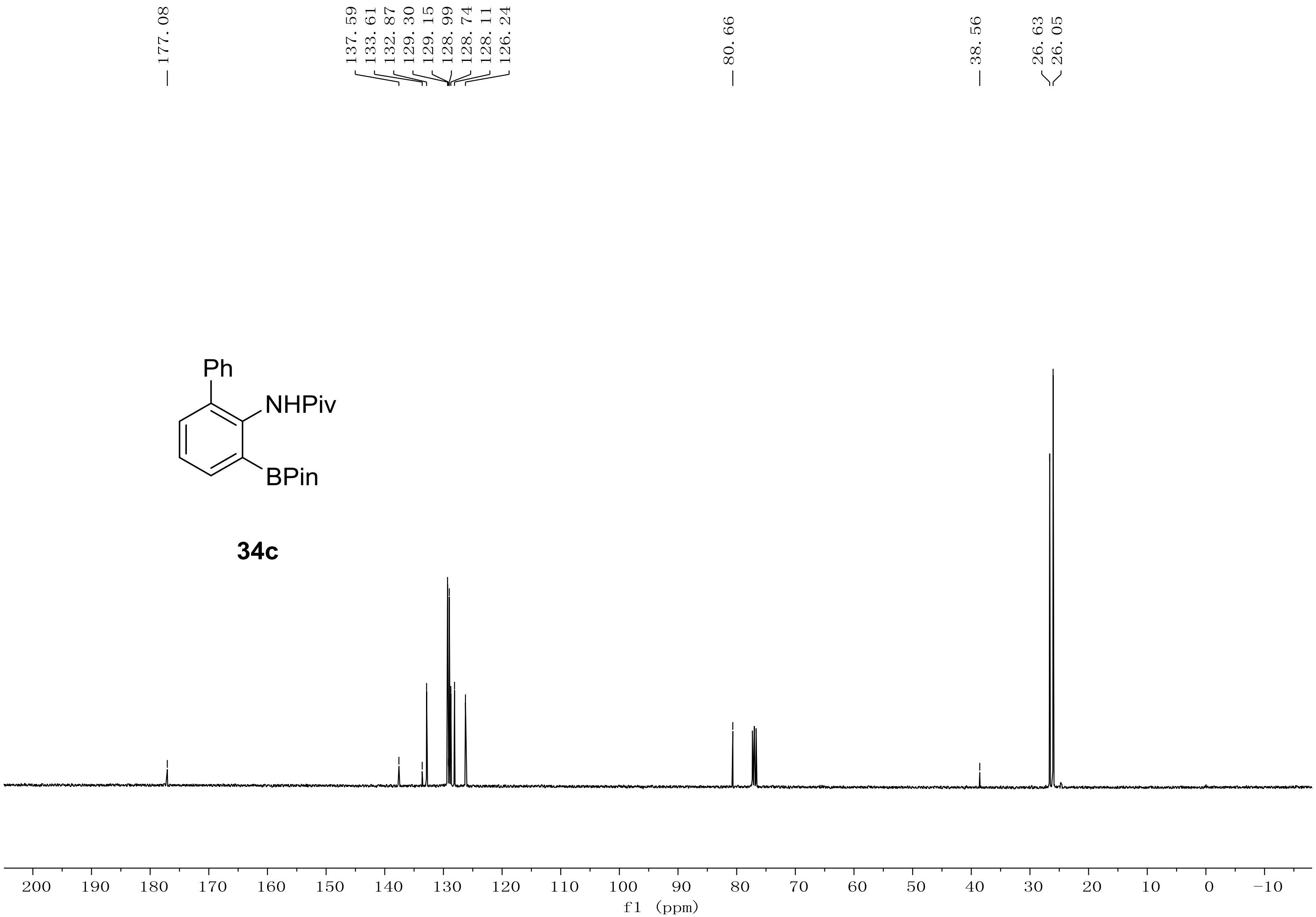

Ph
NHPiv
BPin

33c

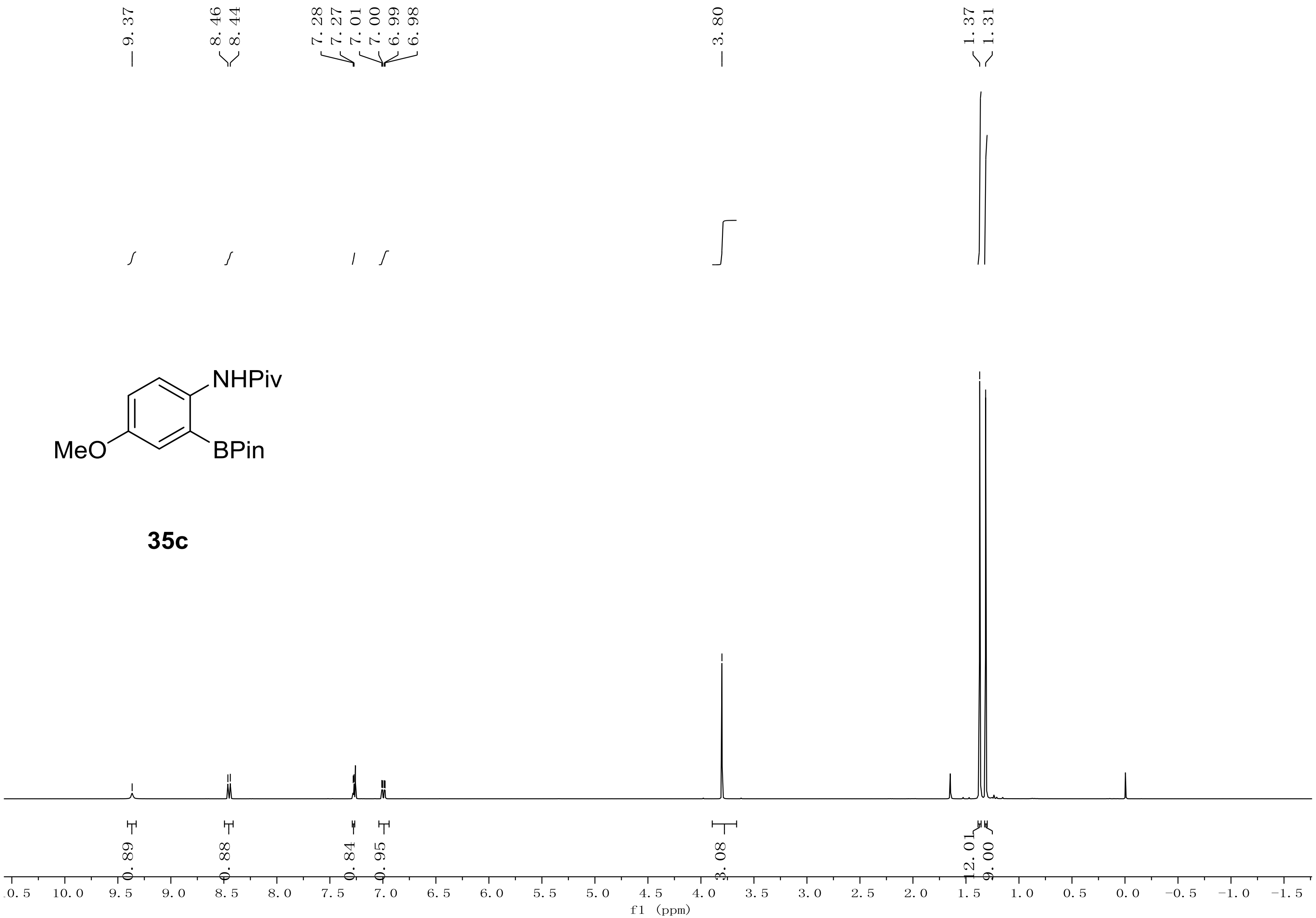

177.30
145.58
145.49
140.62
136.67
128.59
127.69
127.33
121.20
117.83
84.35
40.16
27.57
24.89
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

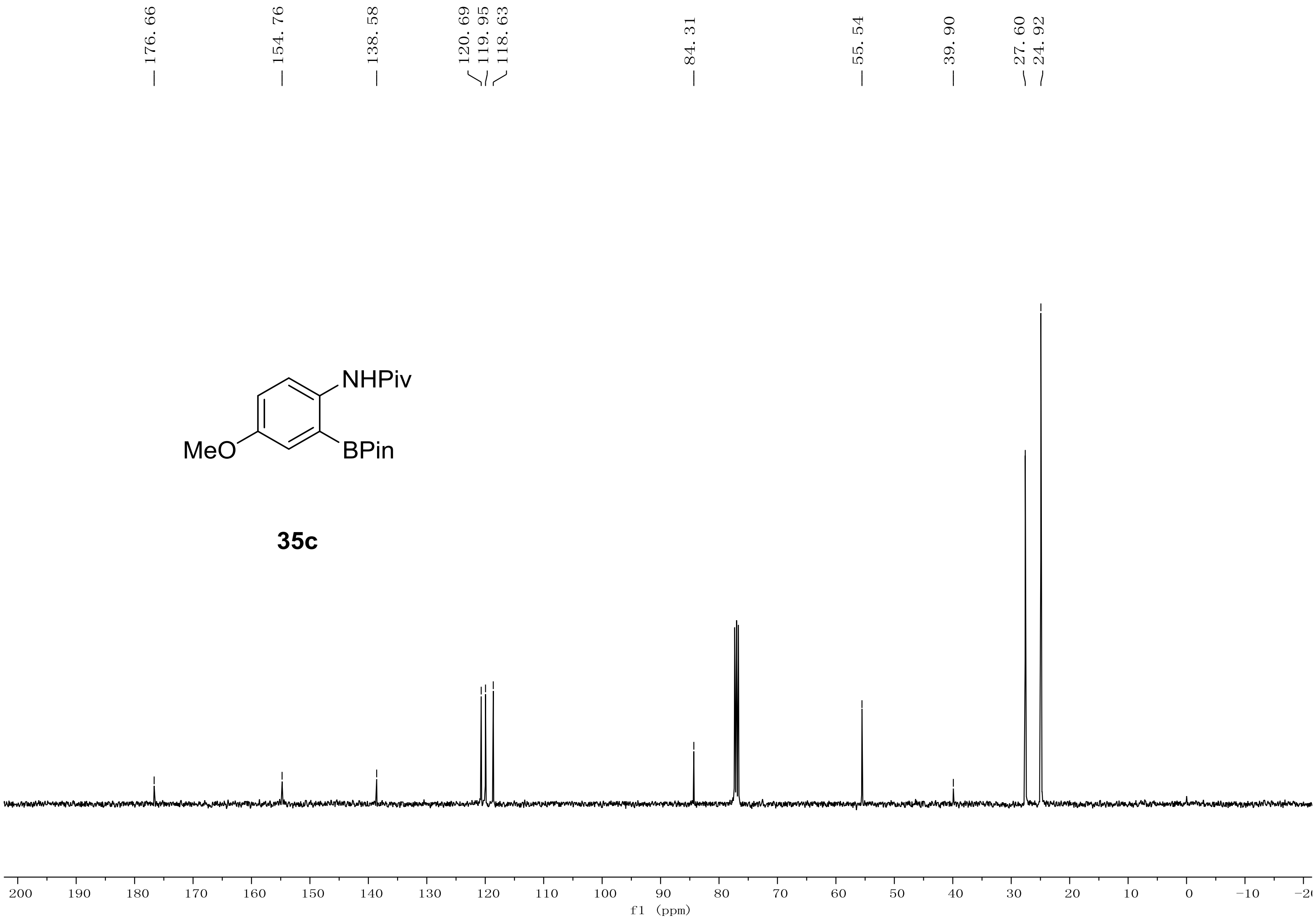


34c

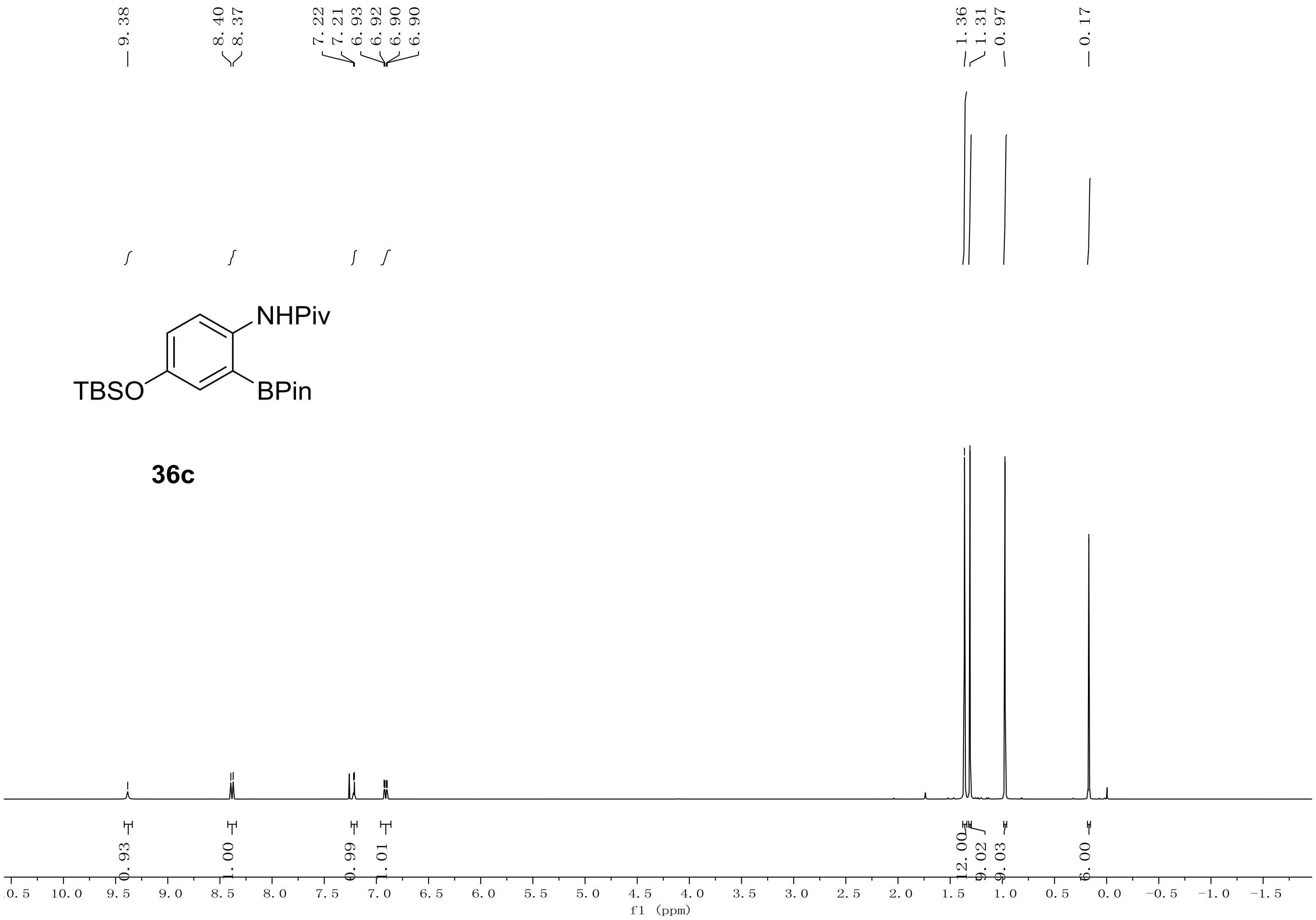

177.08
137.59
133.61
132.87
129.30
129.15
128.99
128.74
128.11
126.24
80.66
38.56
26.63
26.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

34c

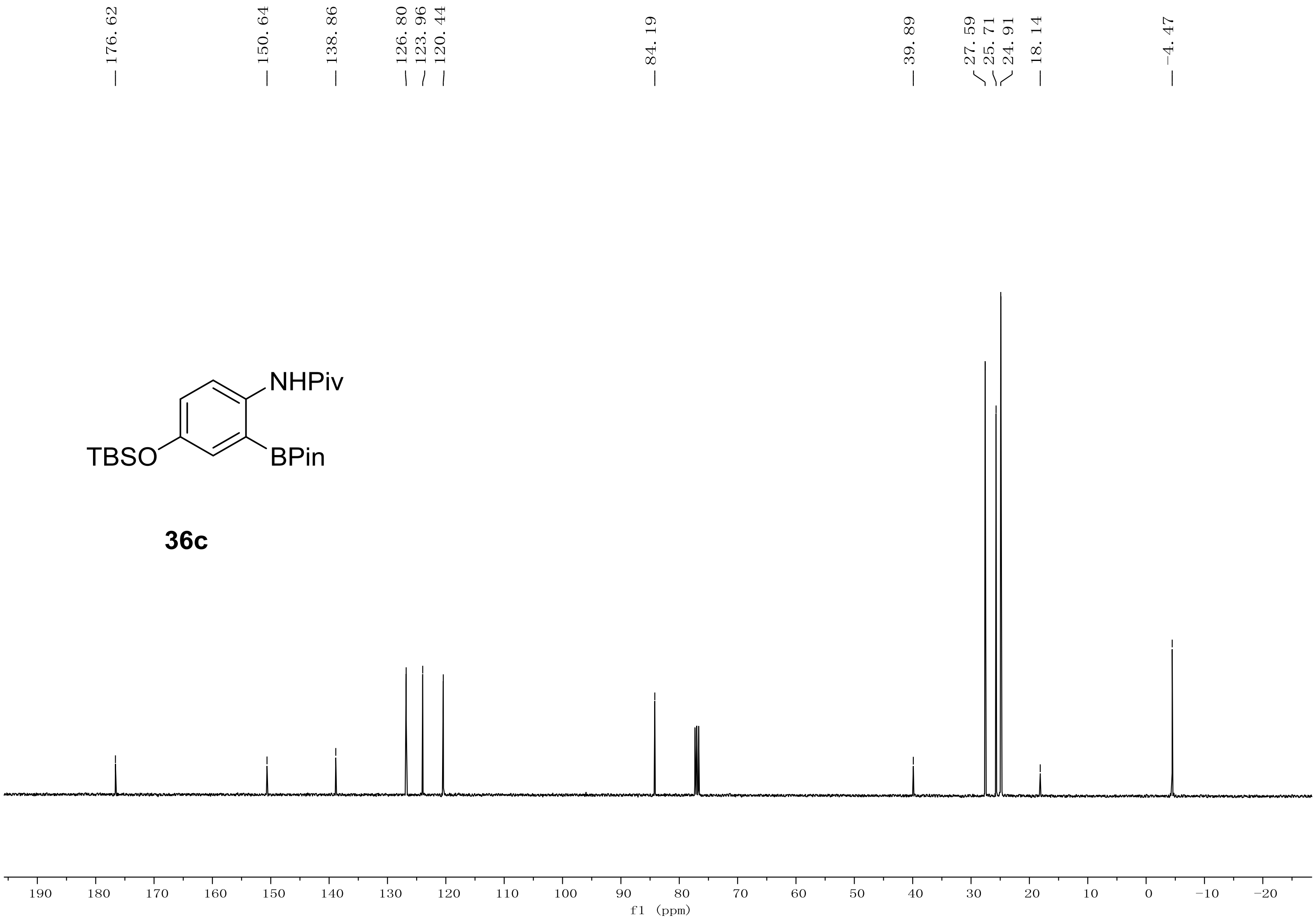

9.37
8.46
8.44
7.28
7.27
7.01
7.00
6.99
6.98
3.80
1.37
1.31
NHPiv
MeO
BPin
35c
0.89
0.88
0.84
0.95
3.08
12.01
9.00
f1 (ppm)


176.66
154.76
138.58
120.69
119.95
118.63
84.31
55.54
39.90
27.60
24.92
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
NHPiv
MeO
BPin

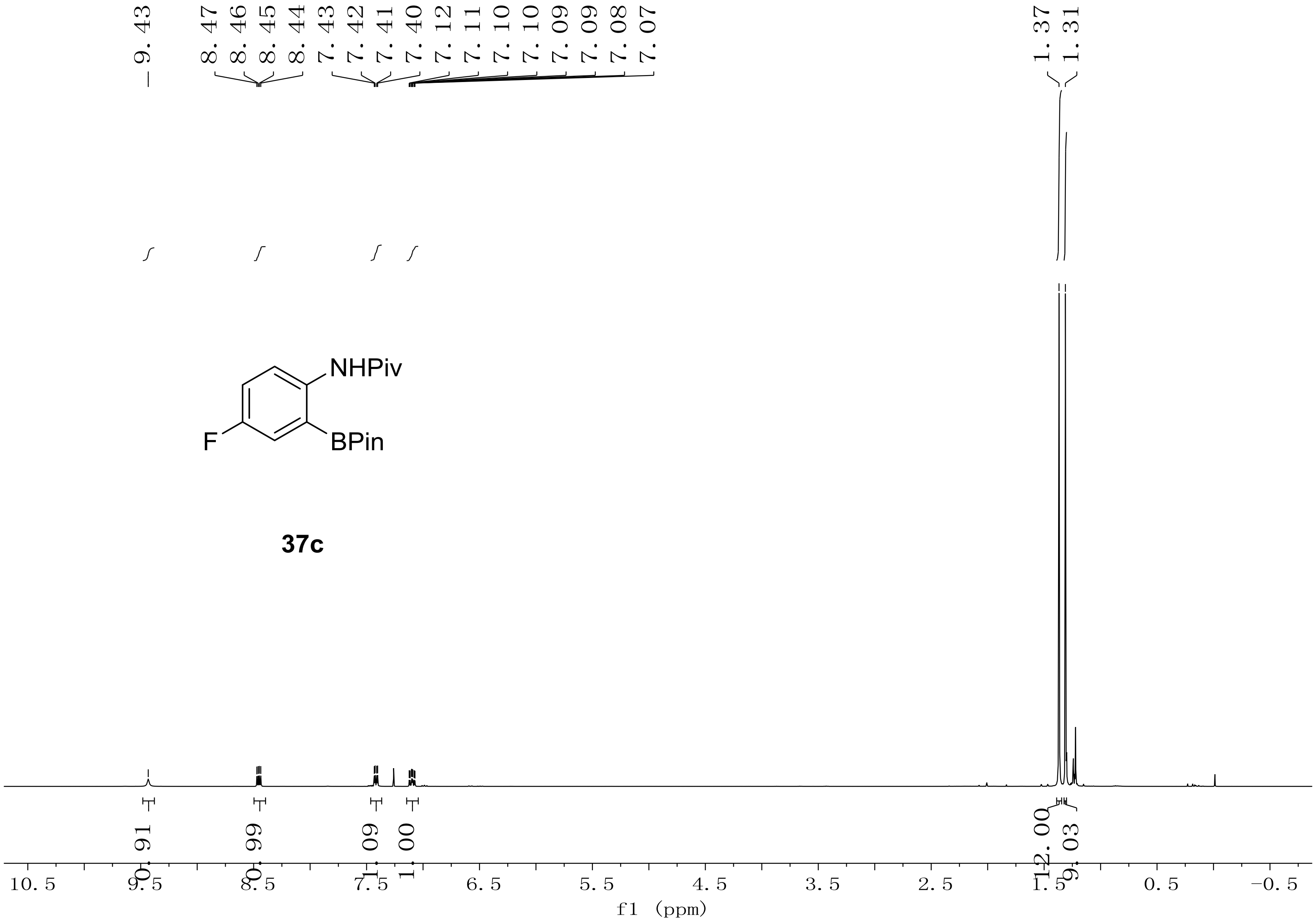
35c


9.38
8.40
8.37
7.22
7.21
6.93
6.92
6.90
6.90
1.36
1.31
0.97
0.17
NHPiv
TBSO
BPin
0.93
1.00
0.99
1.01
12.00
9.02
9.03
6.00
f1 (ppm)

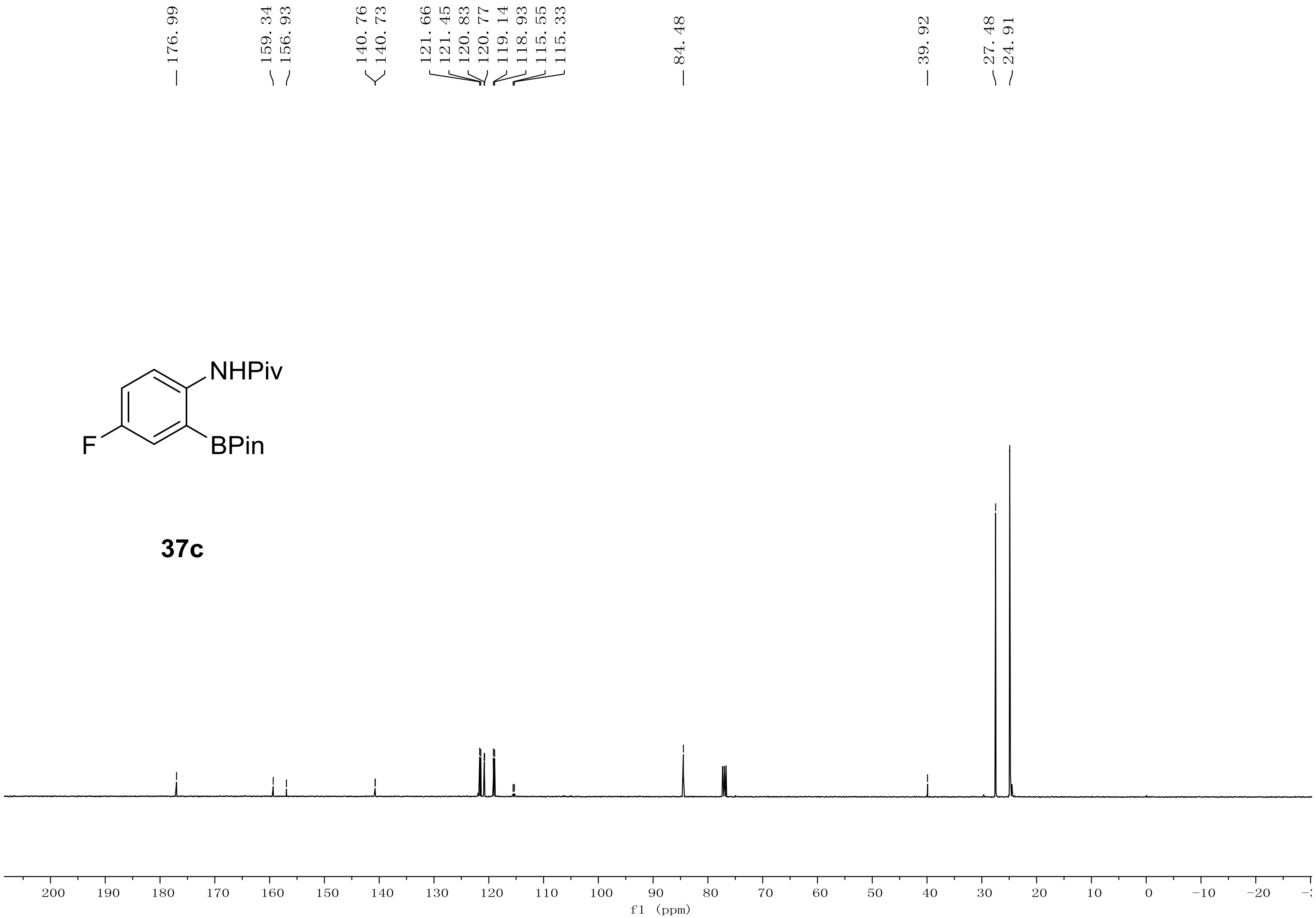
36c


176.62
150.64
138.86
126.80
123.96
120.44
84.19
39.89
27.59
25.71
24.91
18.14
−4.47
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)
NHPiv
TBSO
BPin

36c

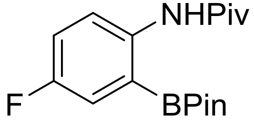

9.43
8.47
8.46
8.45
8.44
7.43
7.42
7.41
7.40
7.12
7.11
7.10
7.10
7.09
7.09
7.08
7.07
1.37
1.31
NHPiv
F
BPin
0.91
0.99
1.09
1.00
12.00
9.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

37c

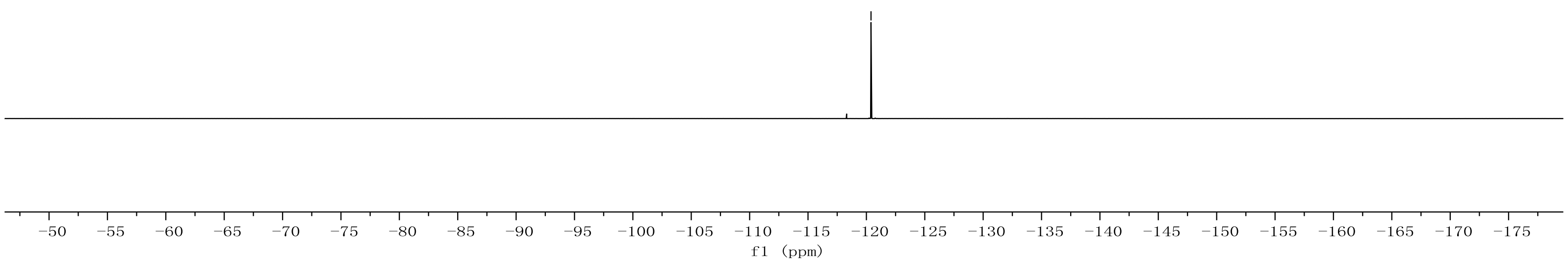


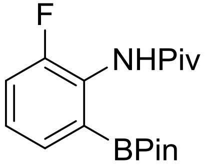
176.99
159.34
156.93
140.76
140.73
121.66
121.45
120.83
120.77
119.14
118.93
115.55
115.33
84.48
39.92
27.48
24.91
NHPiv
F
BPin
f1 (ppm)

37c

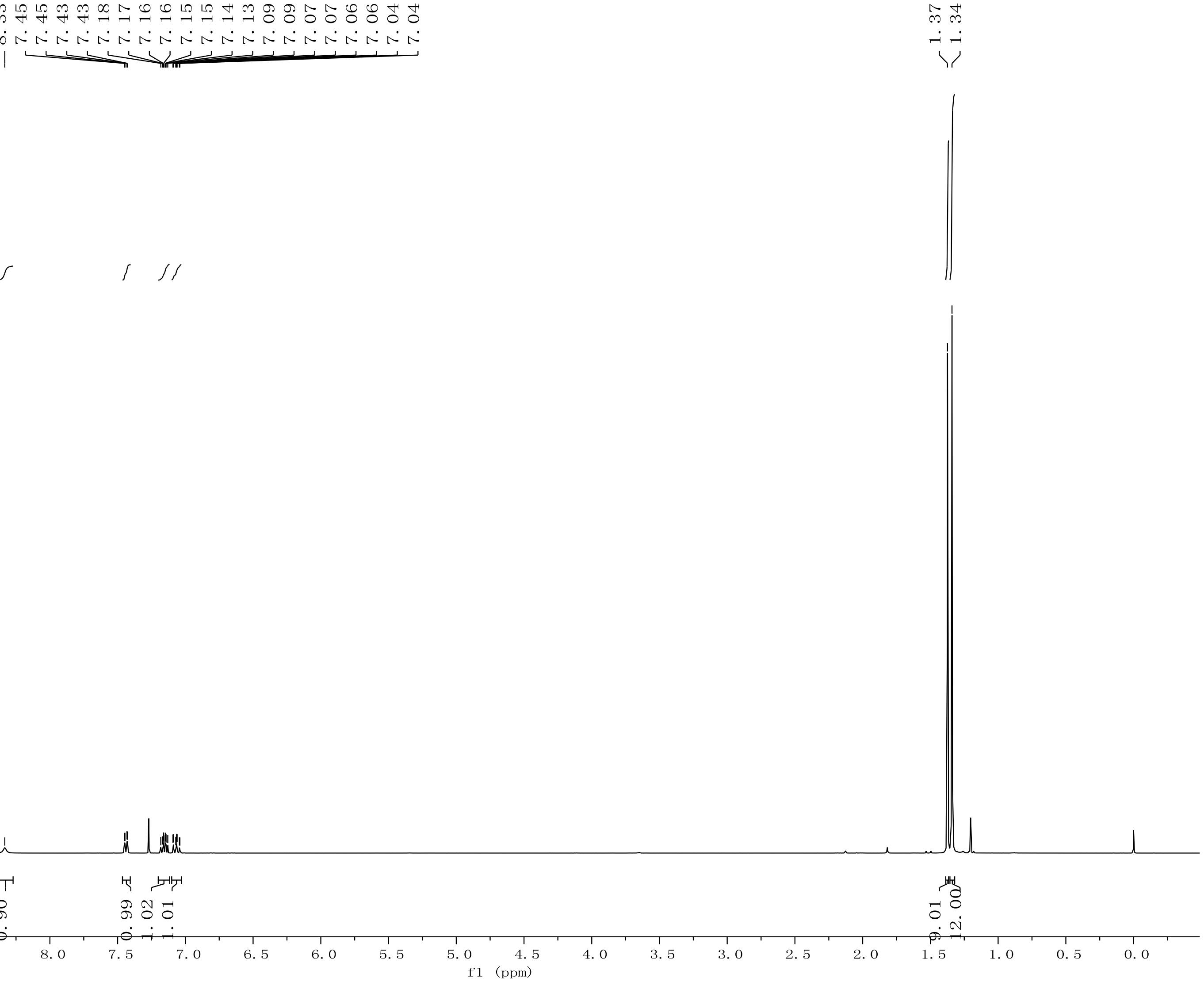

NHPiv
F
BPin

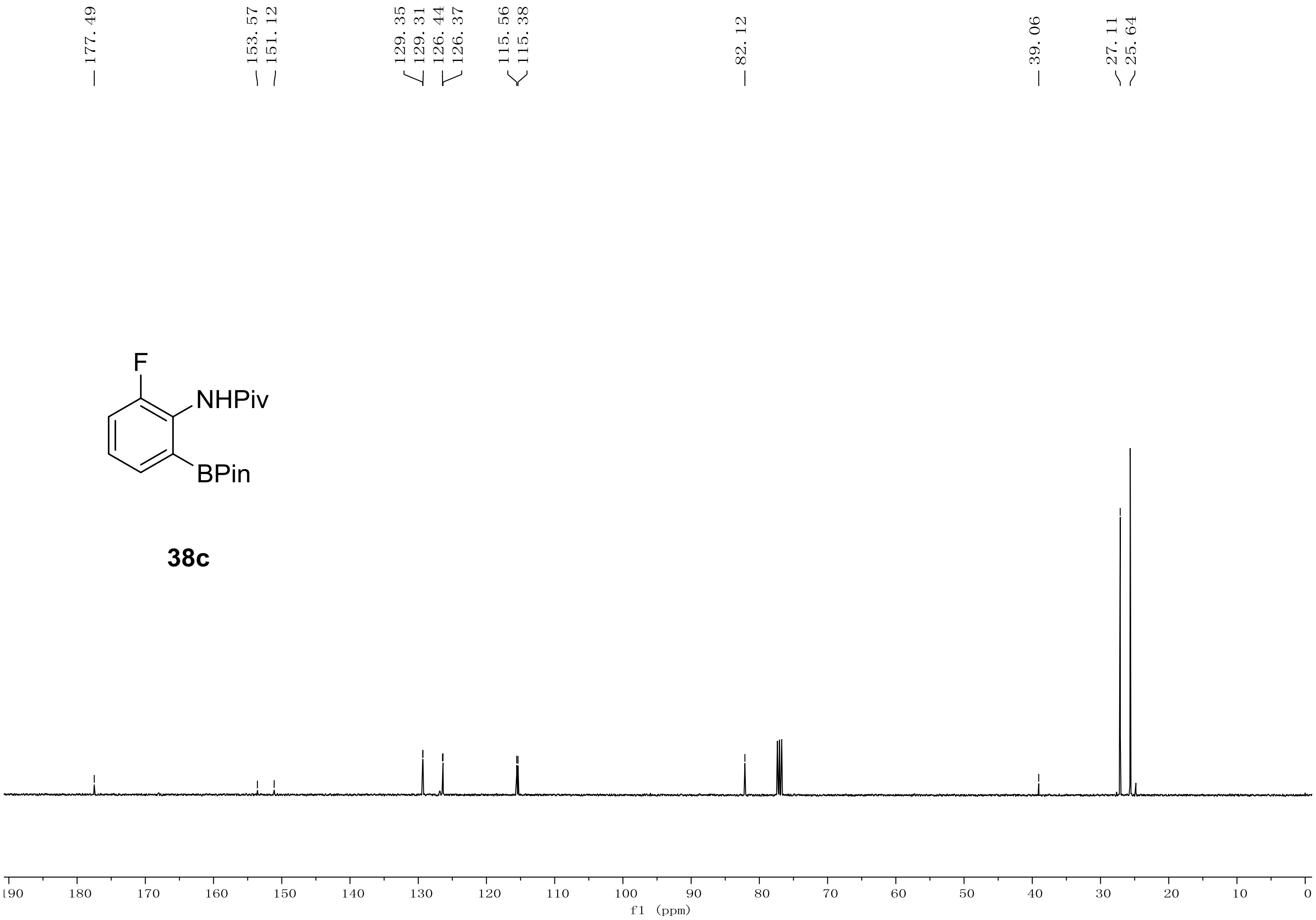
37c

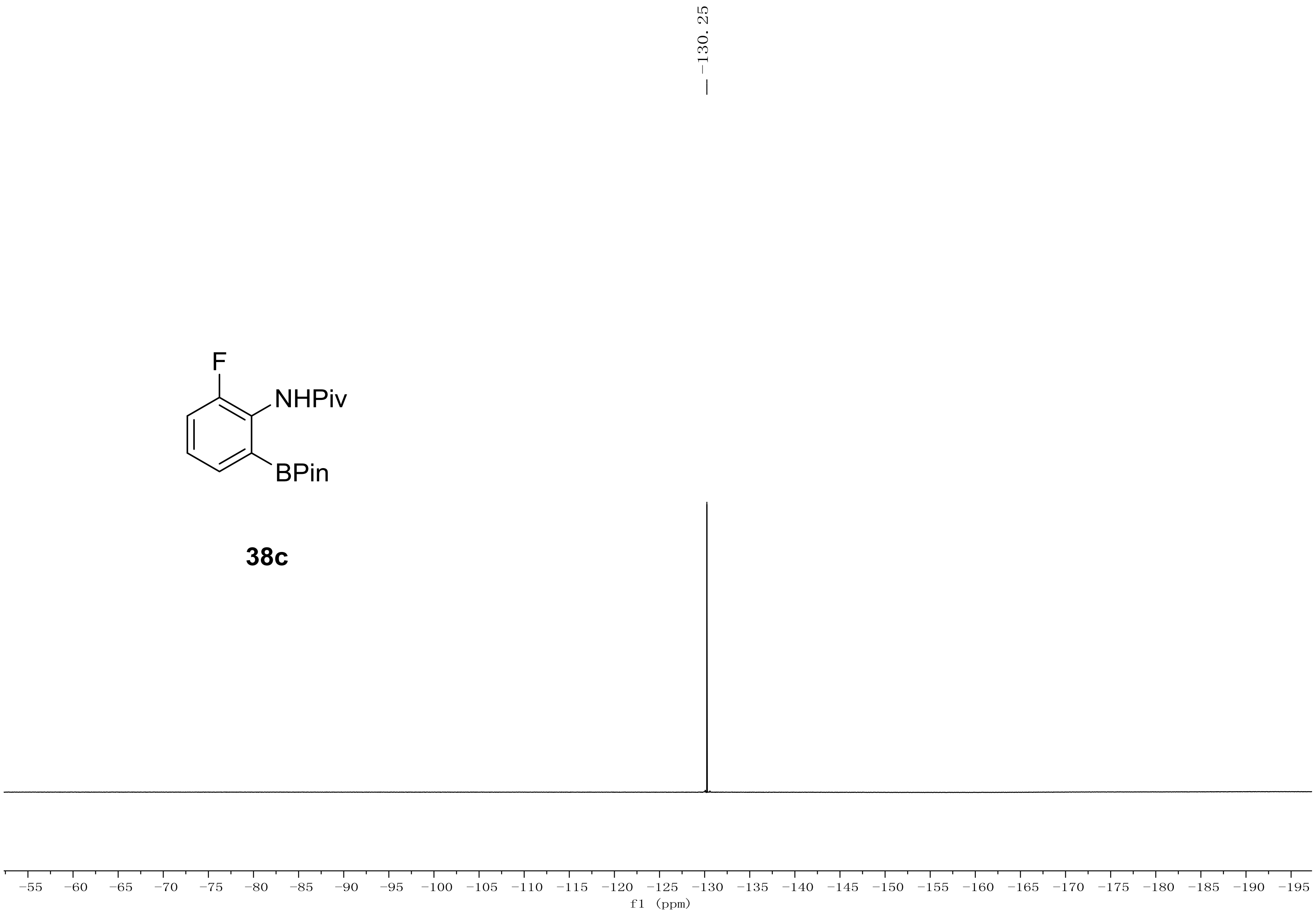

−120.40
−50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170 −175
f1 (ppm)

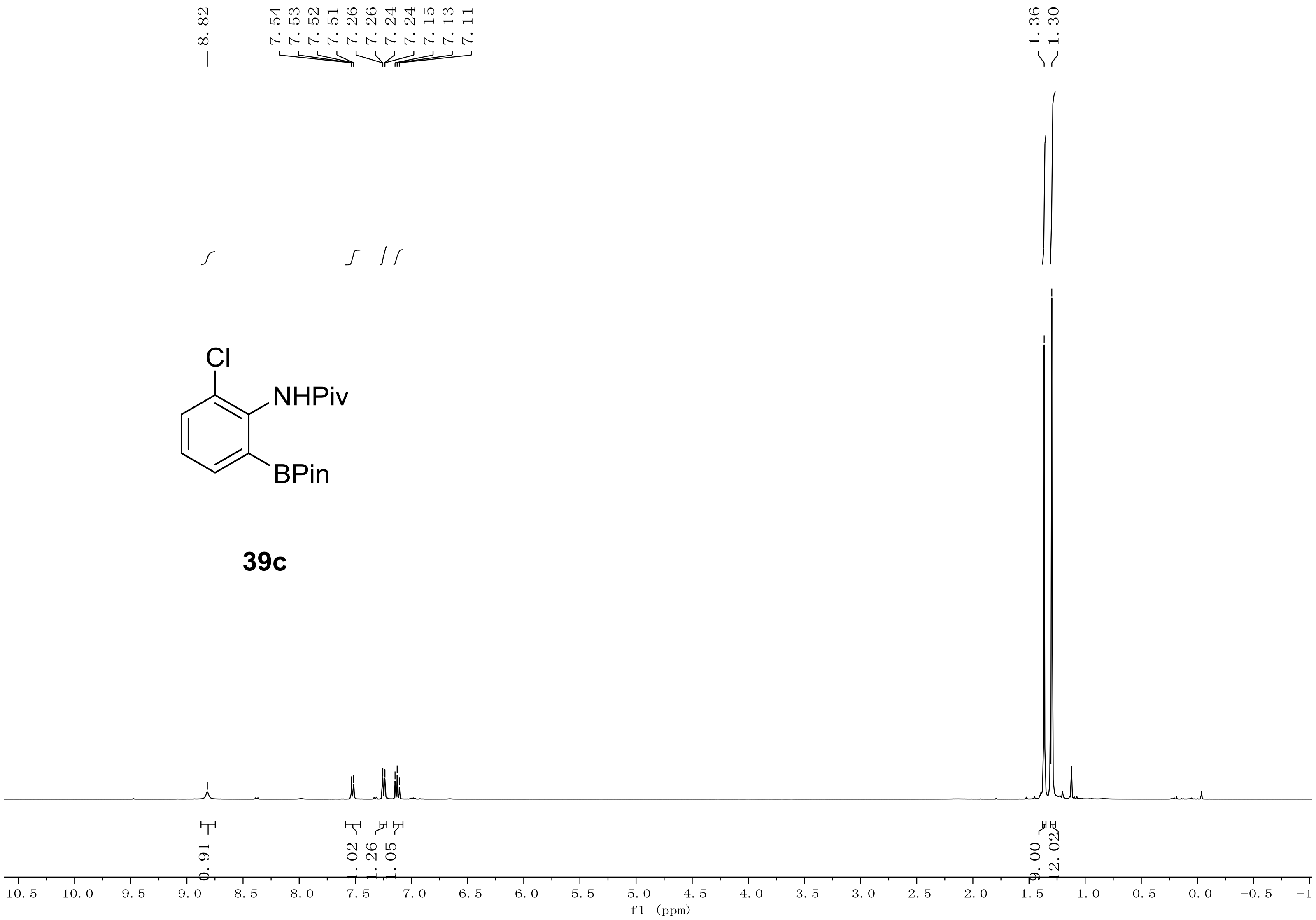

F
NHPiv
BPin

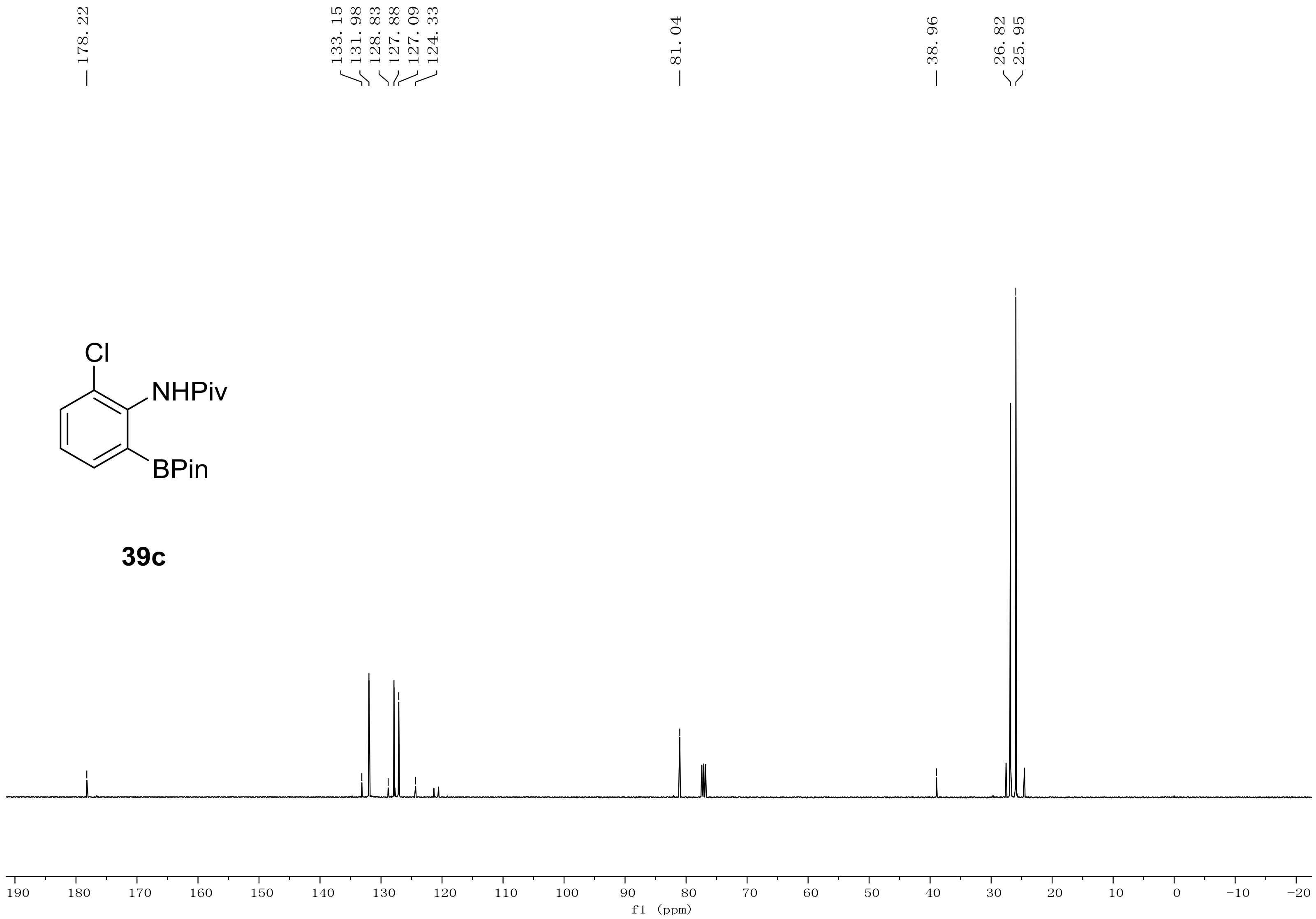
38c


8.33
7.45
7.45
7.43
7.43
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.09
7.09
7.07
7.07
7.06
7.04
7.04
1.37
1.34
0.90
0.99
1.02
1.01
9.01
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

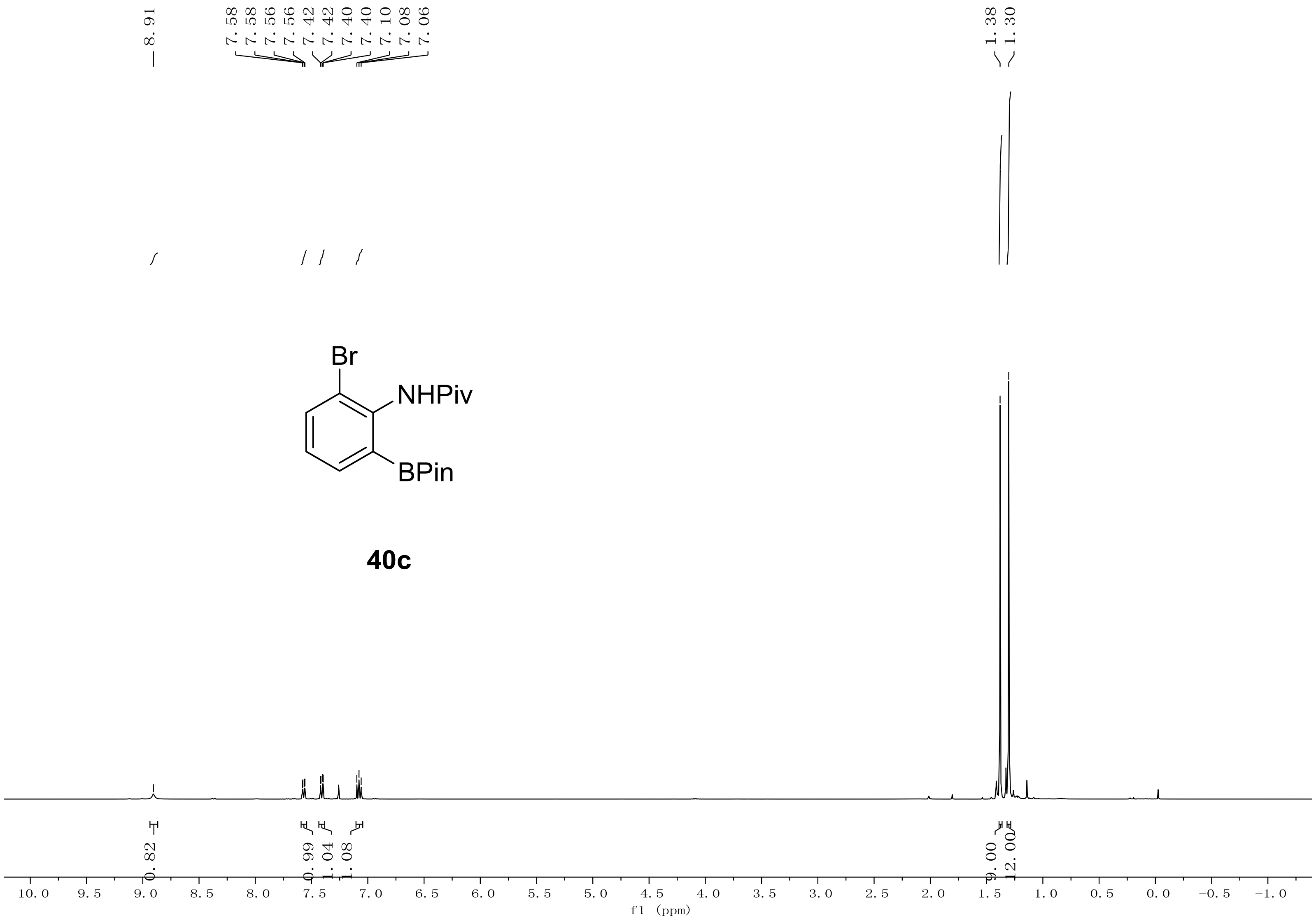

177.49
153.57
151.12
129.35
129.31
126.44
126.37
115.56
115.38
82.12
39.06
27.11
25.64
F
NHPiv
BPin
38c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

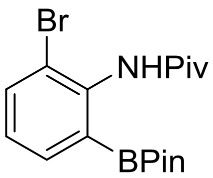

−130.25
F
NHPiv
BPin
38c
−55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170 −175 −180 −185 −190 −195
f1 (ppm)


8.82
7.54
7.53
7.52
7.51
7.26
7.26
7.24
7.24
7.15
7.13
7.11
1.36
1.30
Cl
NHPiv
BPin
39c
0.91
1.02
1.26
1.05
9.00
12.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

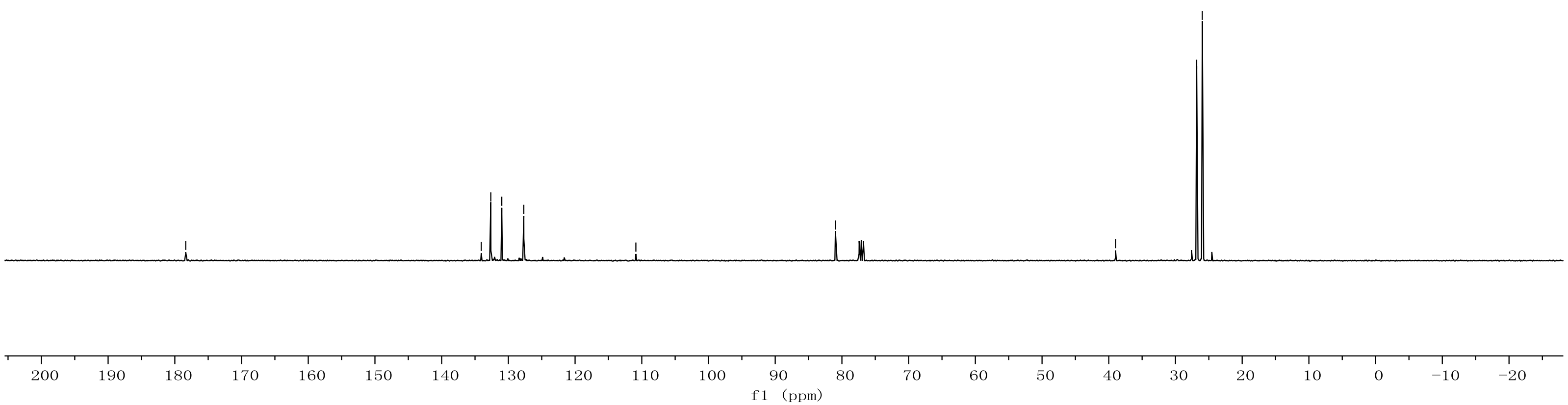

178.22
133.15
131.98
128.83
127.88
127.09
124.33
81.04
38.96
26.82
25.95
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

39c

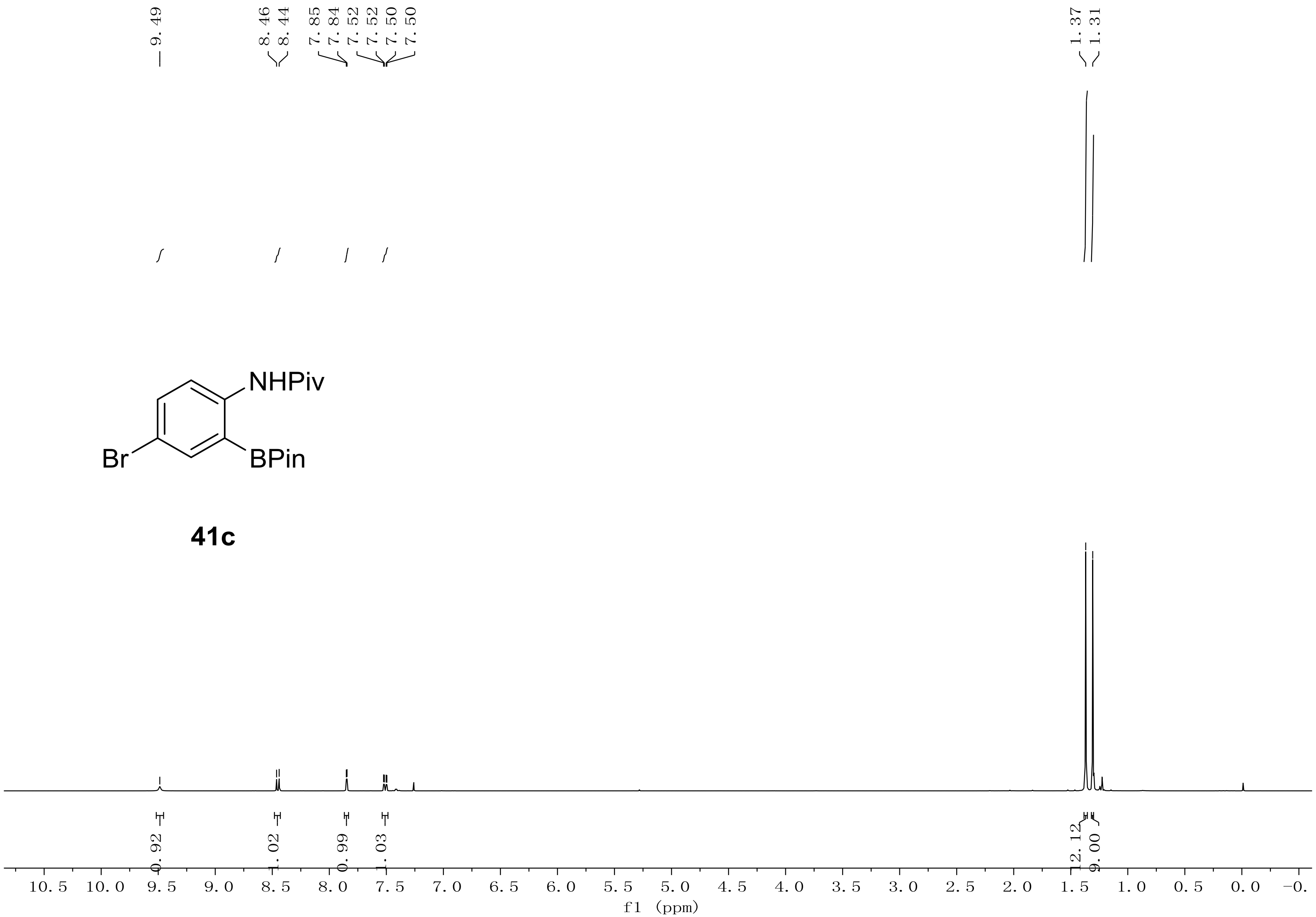

8.91
7.58
7.58
7.56
7.56
7.42
7.42
7.40
7.40
7.10
7.08
7.06
1.38
1.30
Br
NHPiv
BPin
40c
0.82
0.99
1.04
1.08
9.00
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

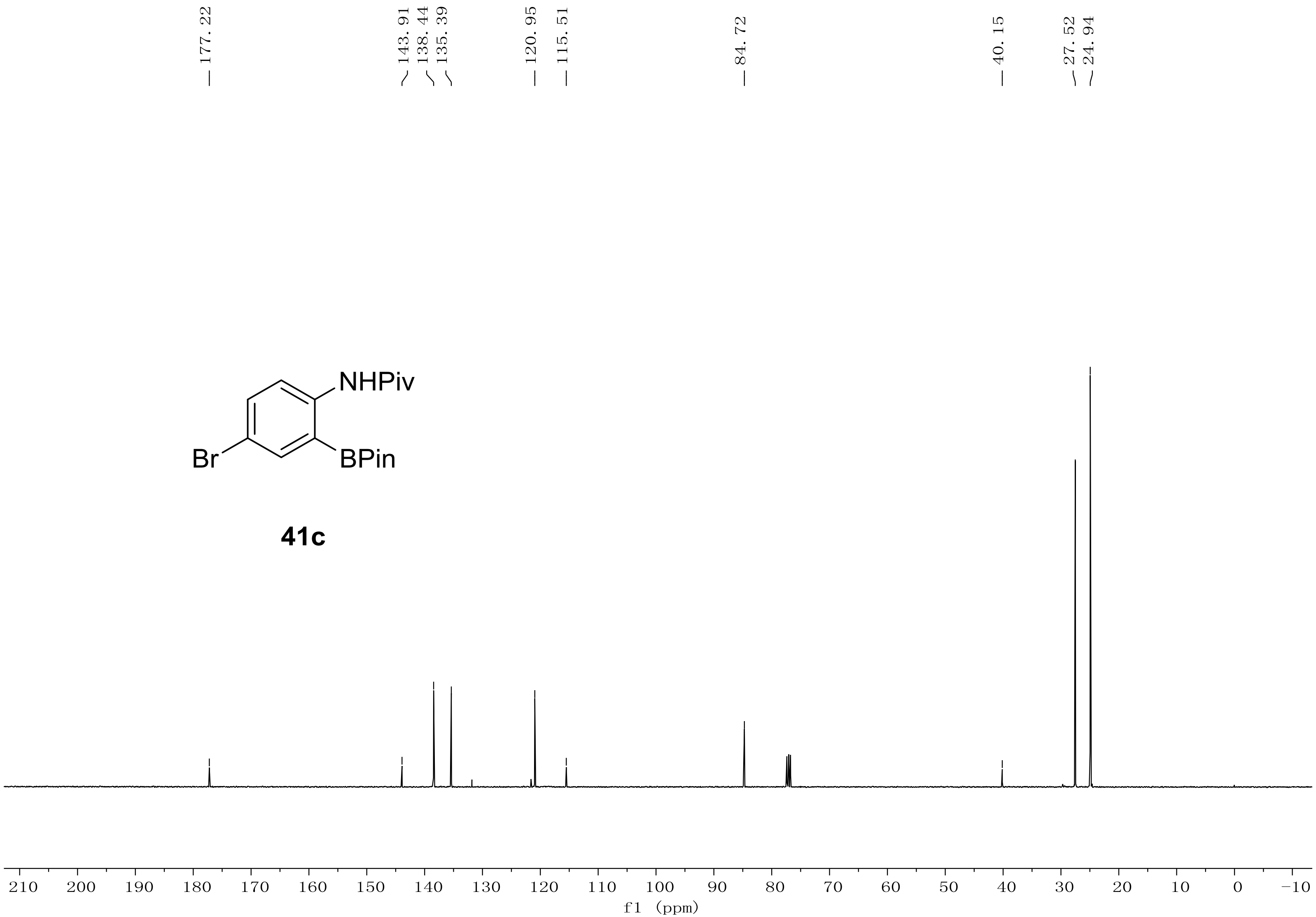


40c

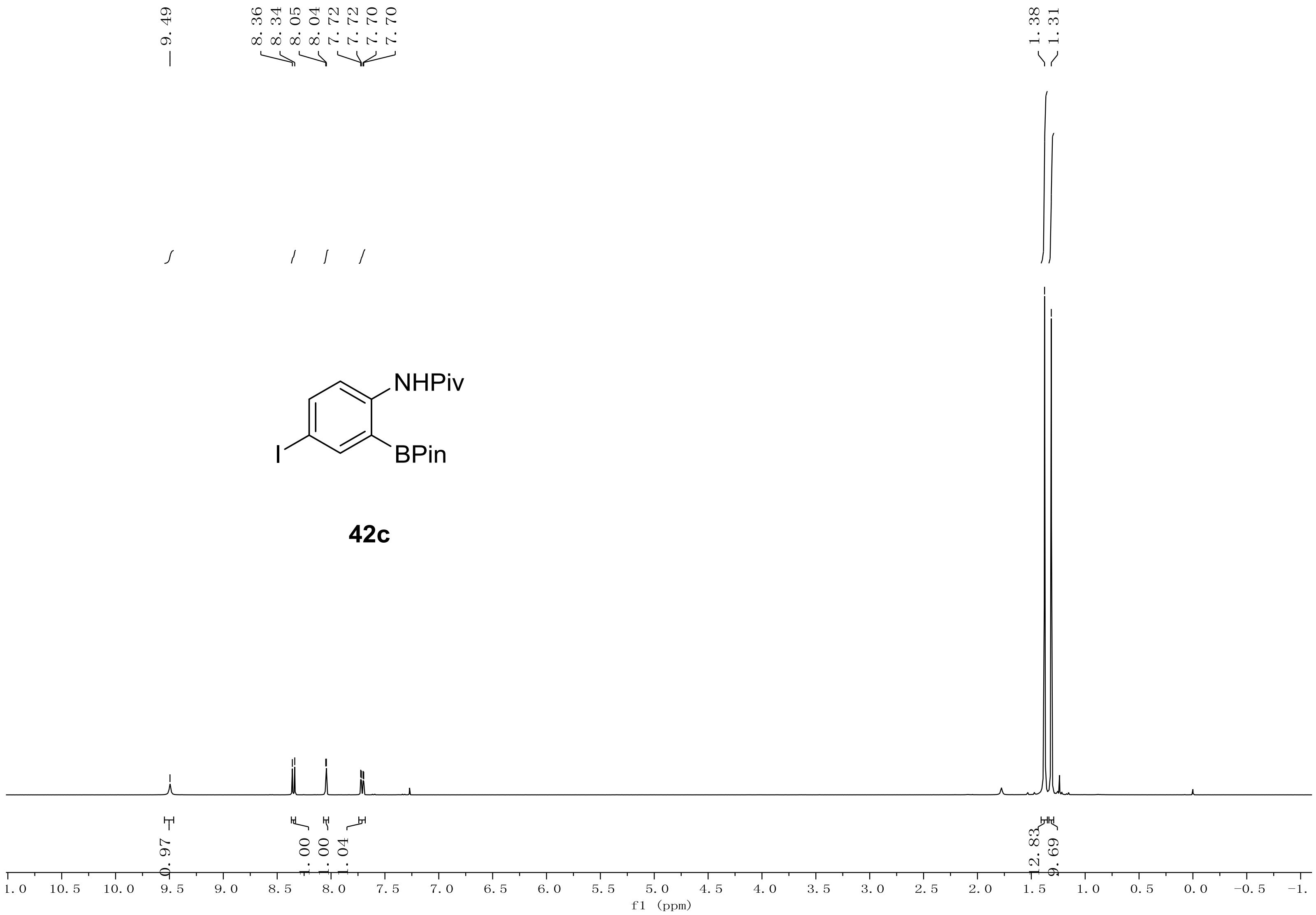


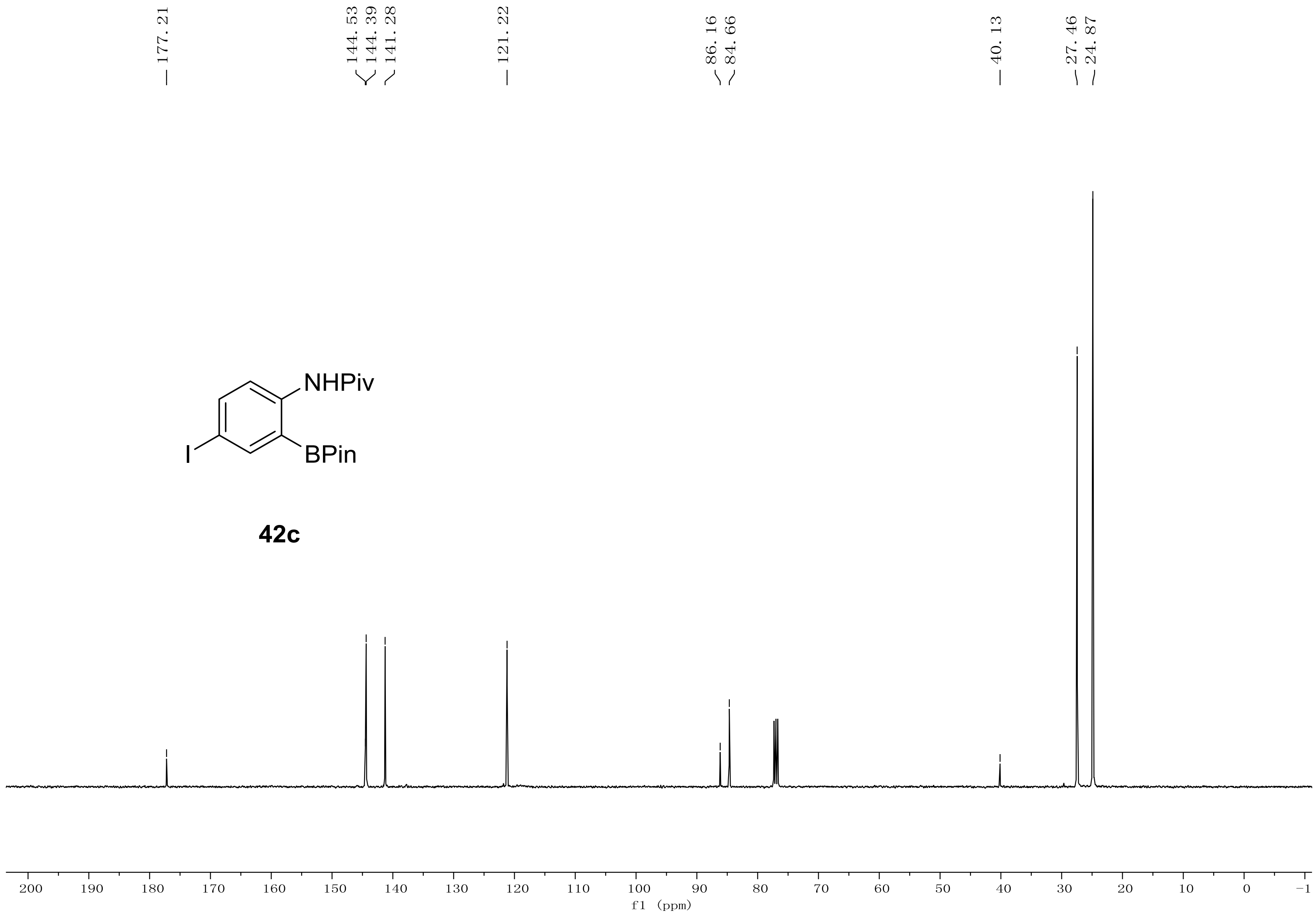
178.36
134.07
132.63
130.99
127.69
110.89
80.98
38.98
26.82
25.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

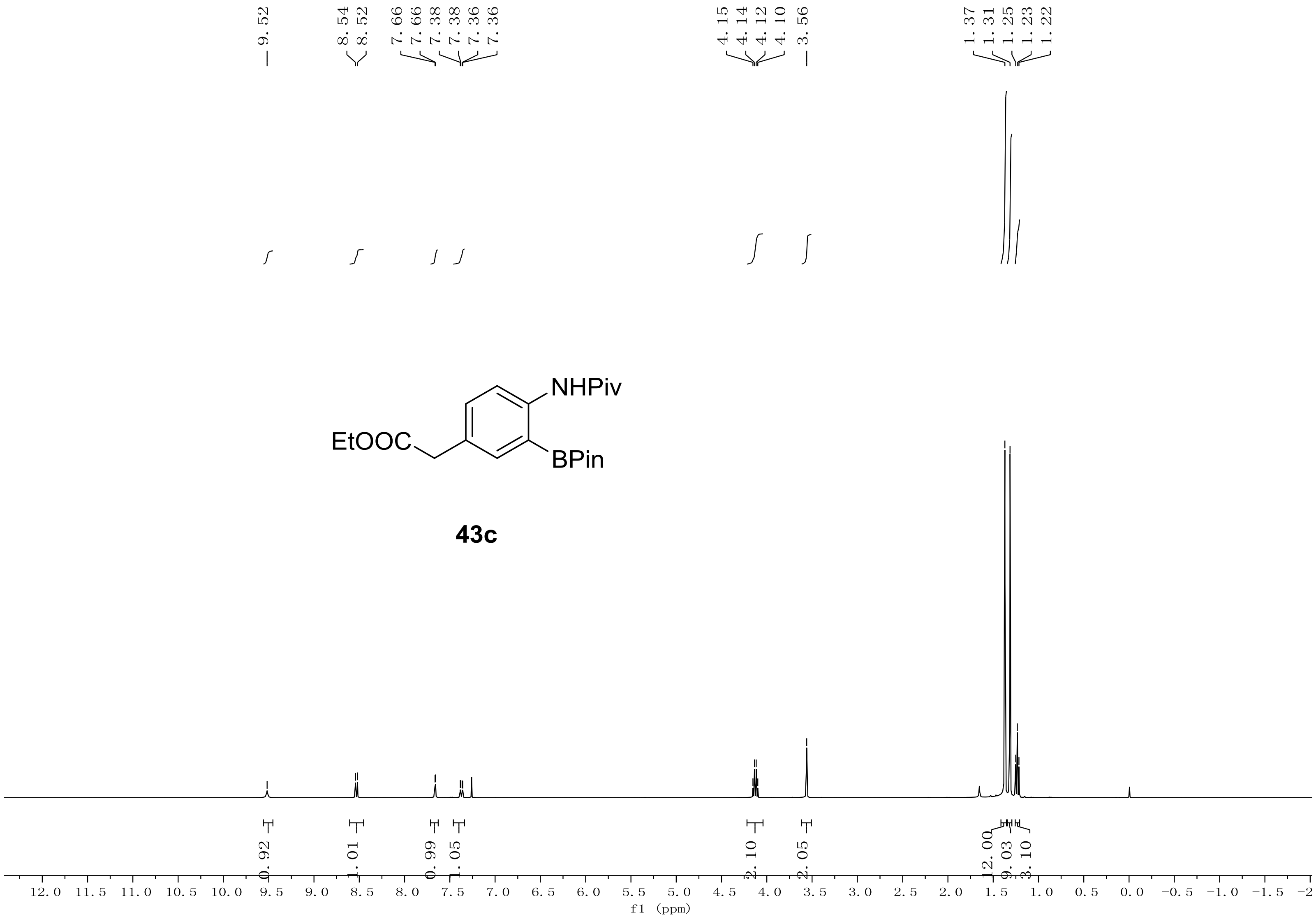

9.49
8.46
8.44
7.85
7.84
7.52
7.52
7.50
7.50
1.37
1.31
NHPiv
Br
BPin
41c
0.92
1.02
0.99
1.03
12.12
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

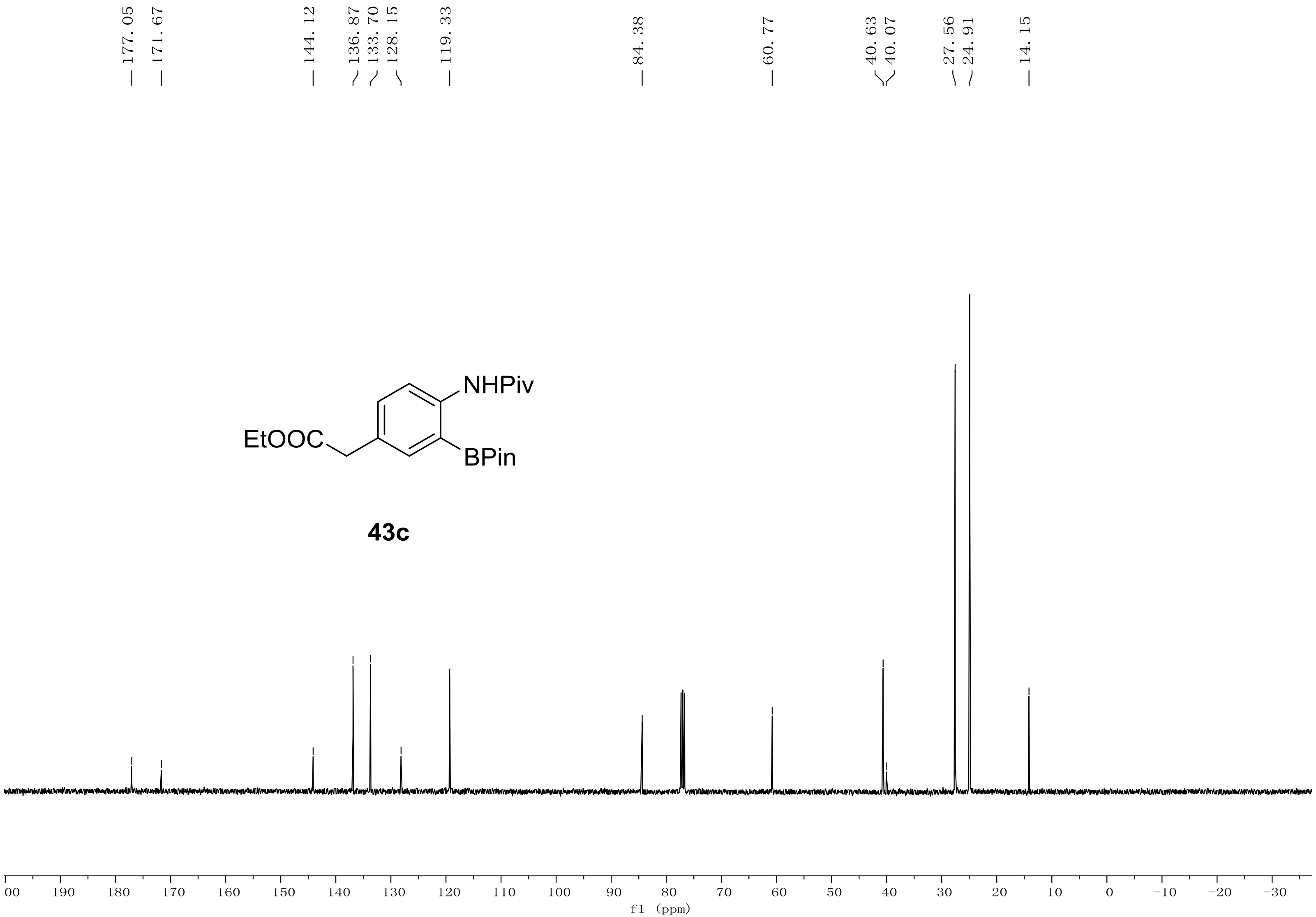

177.22
143.91
138.44
135.39
120.95
115.51
84.72
40.15
27.52
24.94
NHPiv
Br
BPin
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

41c

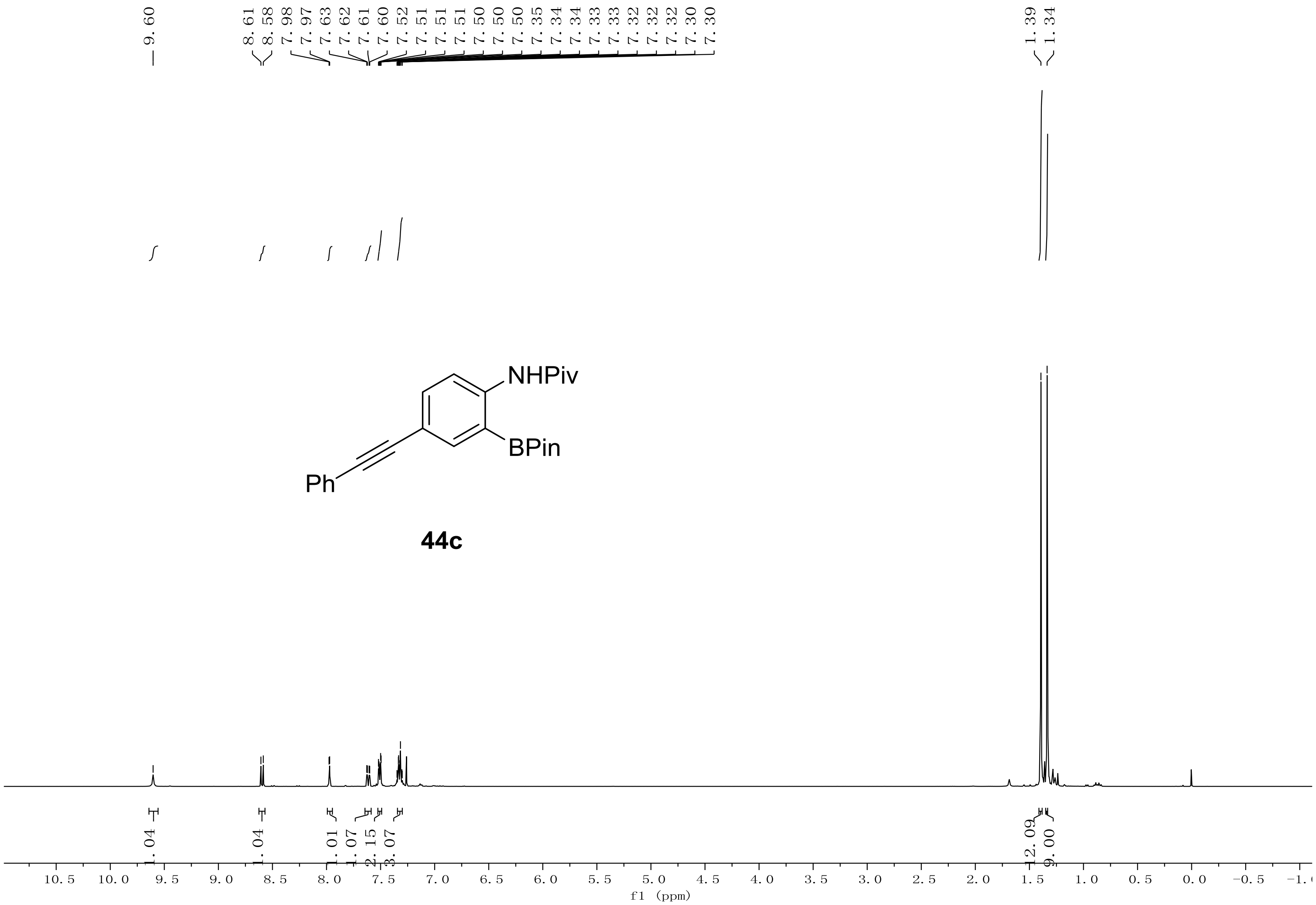

9.49
8.36
8.34
8.05
8.04
7.72
7.72
7.70
7.70
1.38
1.31
NHPiv
BPin
I
42c
0.97
1.00
1.00
1.04
12.83
9.69
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

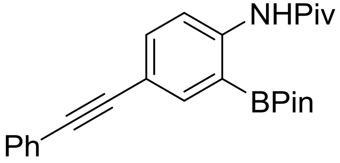

177.21
144.53
144.39
141.28
121.22
86.16
84.66
40.13
27.46
24.87
NHPiv
I
BPin
42c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


9.52
8.54
8.52
7.66
7.66
7.38
7.38
7.36
7.36
4.15
4.14
4.12
4.10
3.56
1.37
1.31
1.25
1.23
1.22
NHPiv
EtOOC
BPin
43c
0.92
1.01
0.99
1.05
2.10
2.05
12.00
9.03
3.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2
f1 (ppm)

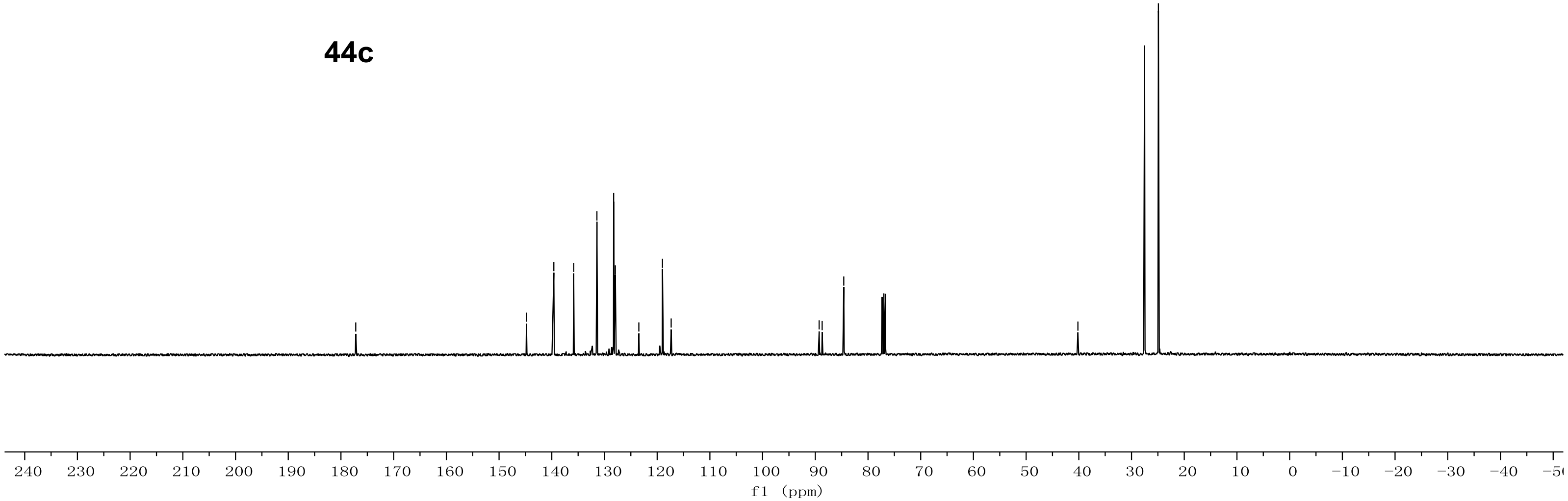


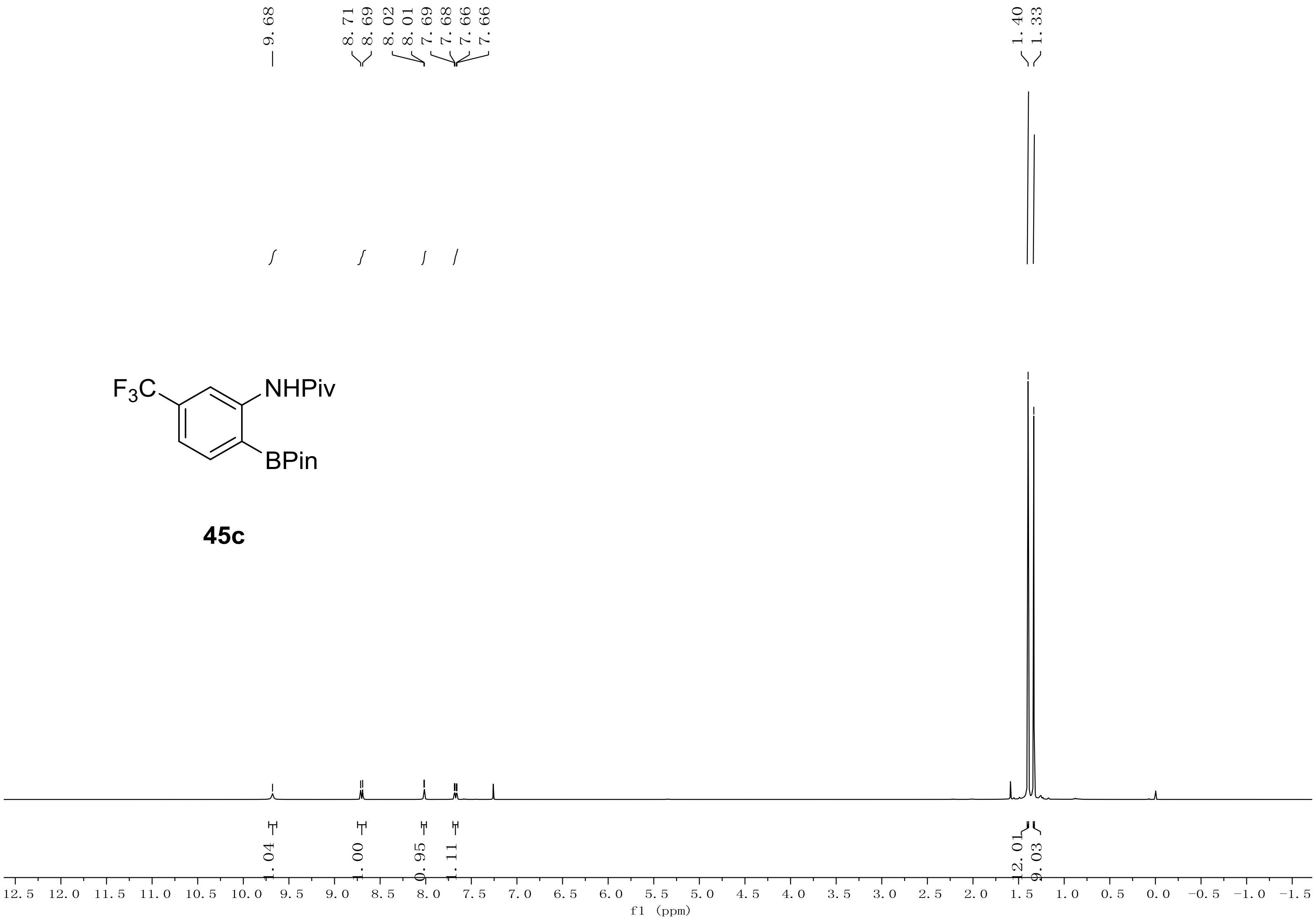
NHPiv
EtOOC
BPin
43c
177.05
171.67
144.12
136.87
133.70
128.15
119.33
84.38
60.77
40.63
40.07
27.56
24.91
14.15
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
f1 (ppm)


9.60
8.61
8.58
7.98
7.97
7.63
7.62
7.61
7.60
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.30
7.30
1.39
1.34
NHPiv
BPin
Ph
44c
1.04
1.04
1.01
1.07
2.15
3.07
12.09
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


NHPiv
BPin
Ph

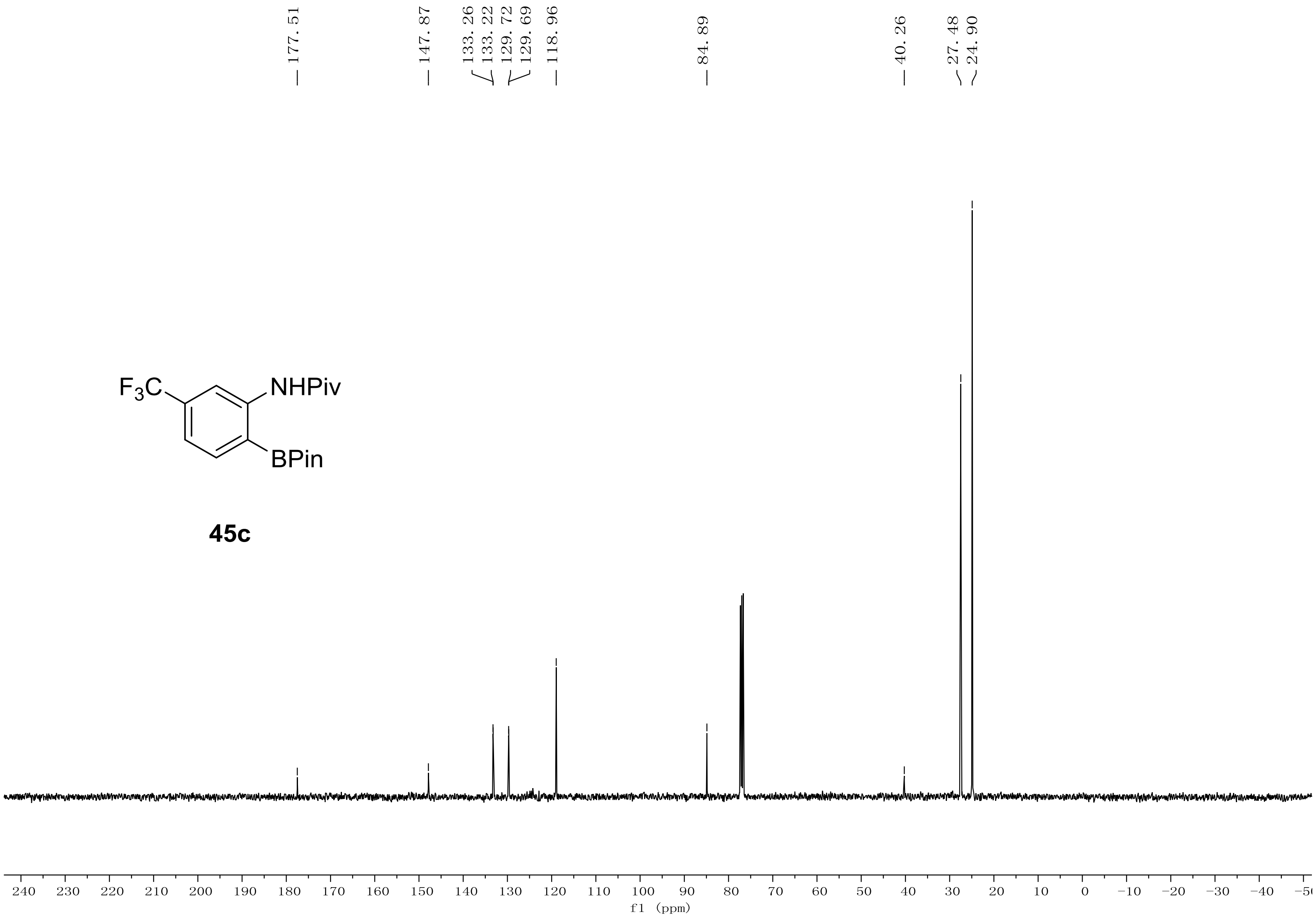
44c


177.19
144.80
139.61
135.84
131.43
128.26
127.94
123.48
119.00
117.35
89.27
88.70
84.60
40.17
27.52
24.90
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

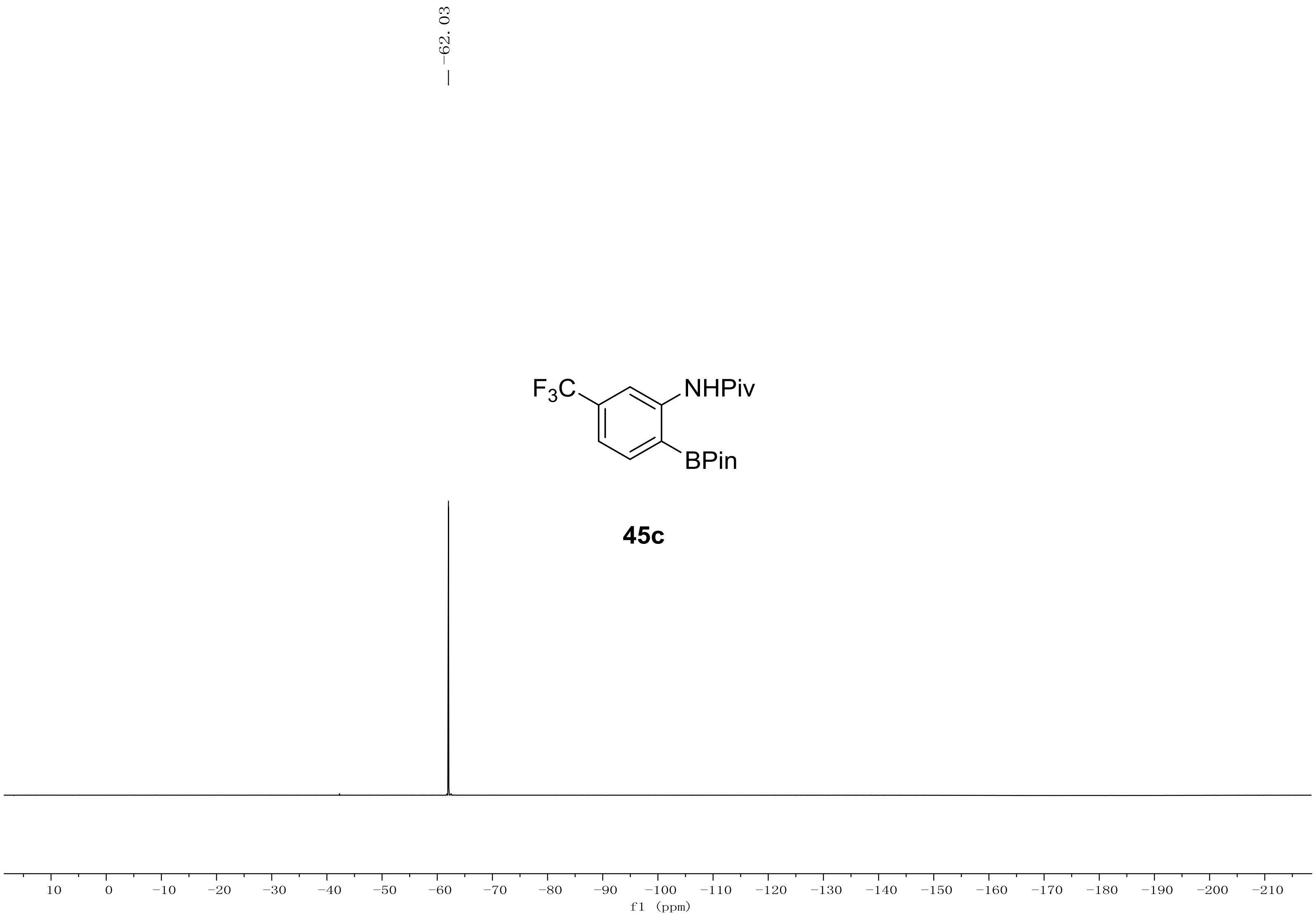

F3C
NHPiv
BPin

45c

9.68
8.71
8.69
8.02
8.01
7.69
7.68
7.66
7.66
1.40
1.33
1.04
1.00
0.95
1.11
12.01
9.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

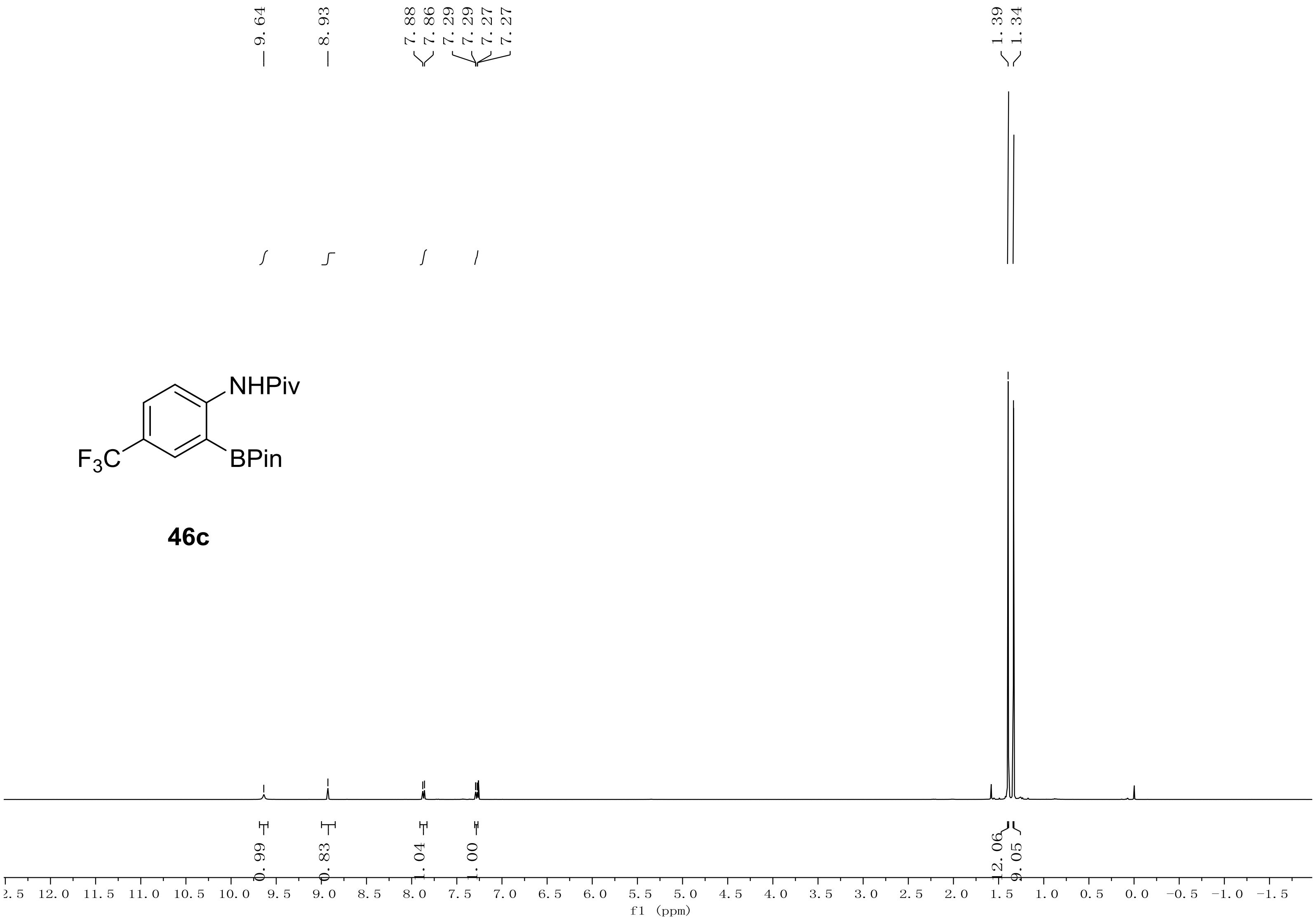

177.51
147.87
133.26
133.22
129.72
129.69
118.96
84.89
40.26
27.48
24.90
F3C
NHPiv
BPin
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

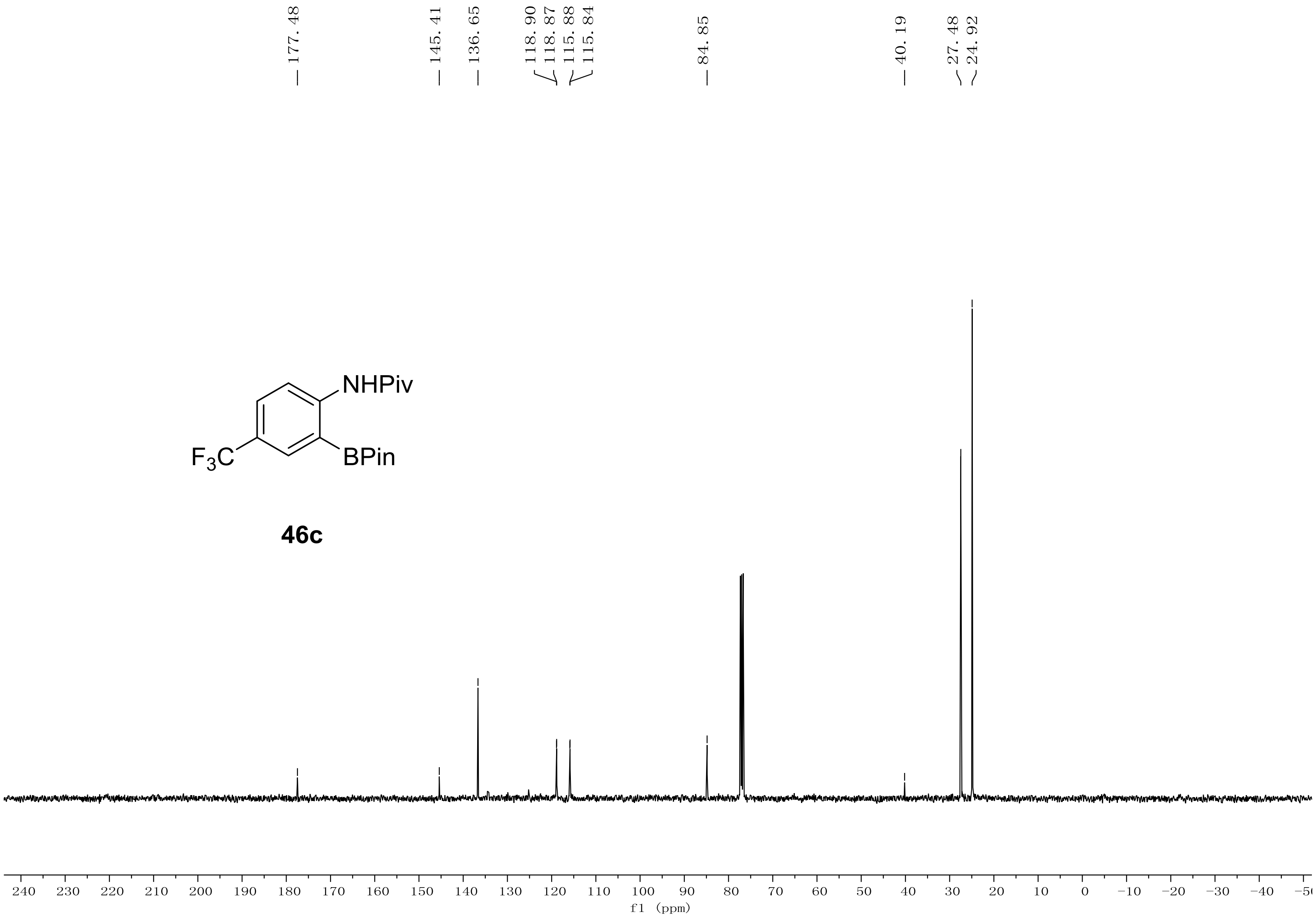
45c



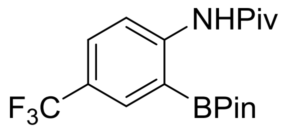
−62.03
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)
F3C
NHPiv
BPin

45c

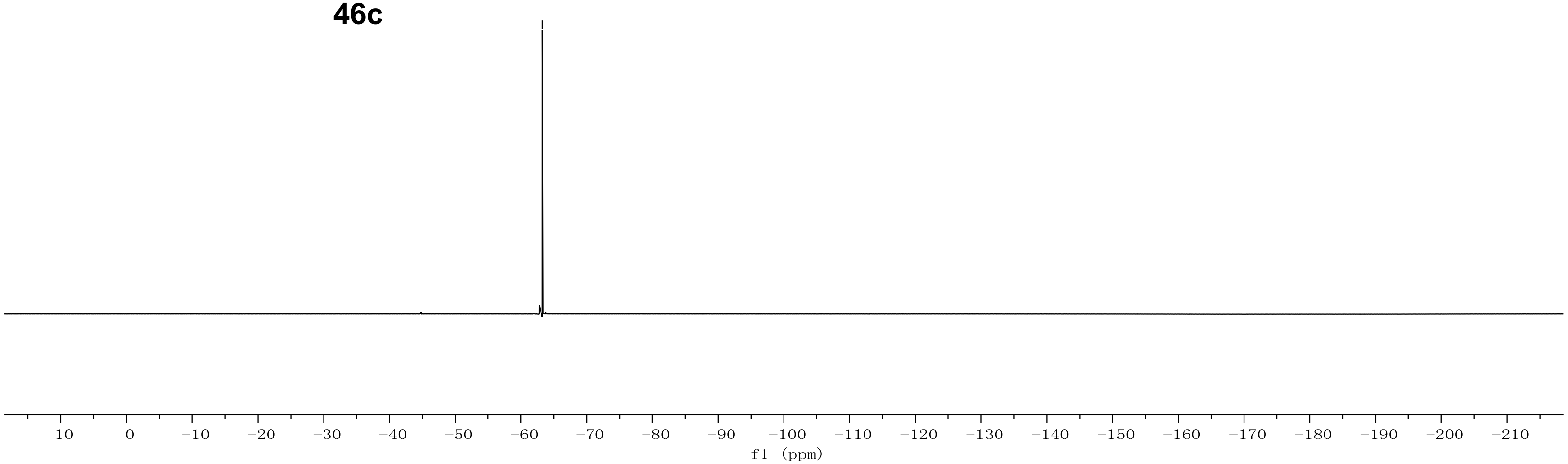

9.64
8.93
7.88
7.86
7.29
7.29
7.27
7.27
1.39
1.34
NHPiv
BPin
F_3C
46c
0.99
0.83
1.04
1.00
12.06
9.05
f1 (ppm)

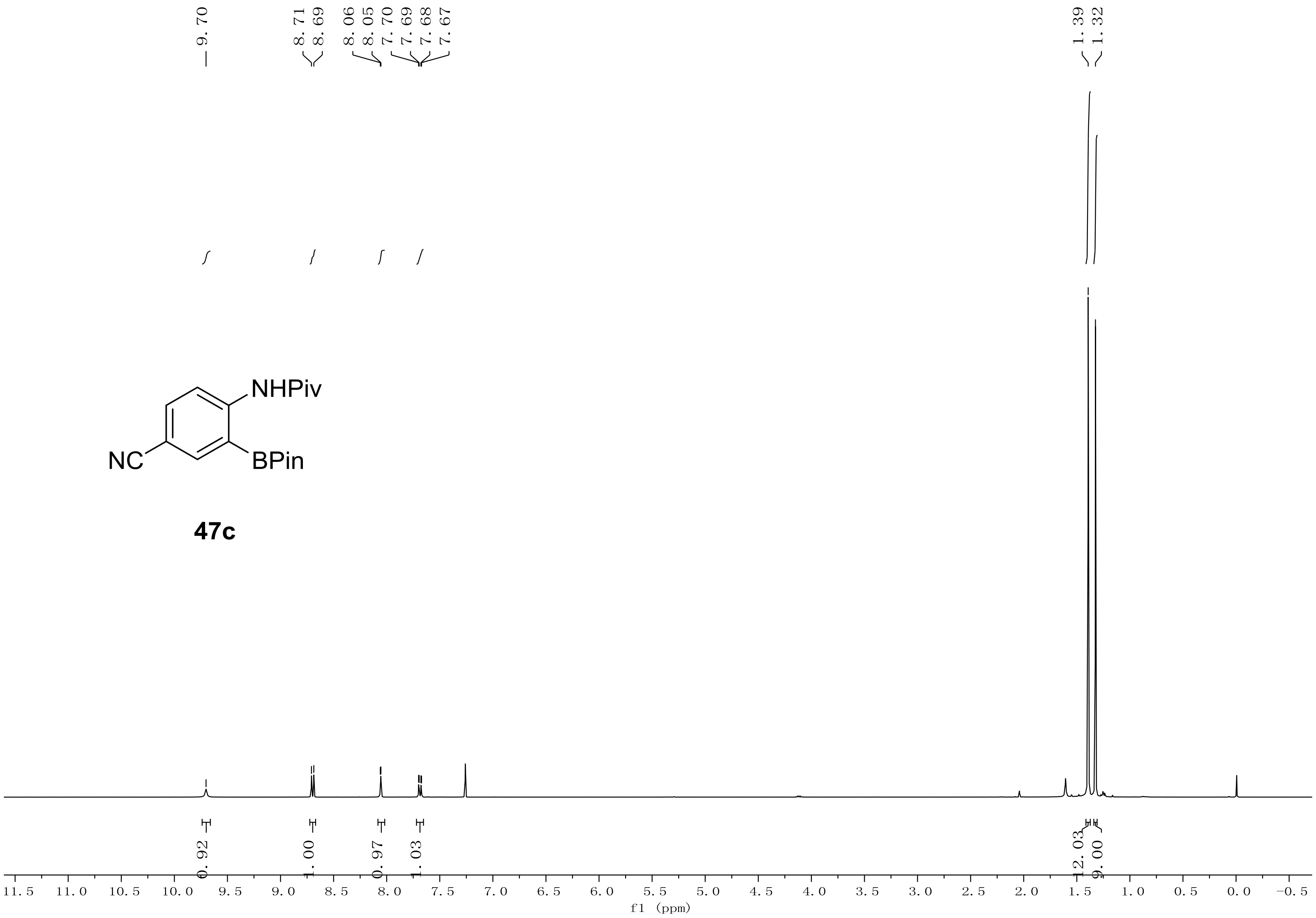

177.48
145.41
136.65
118.90
118.87
115.88
115.84
84.85
40.19
27.48
24.92
f1 (ppm)

46c

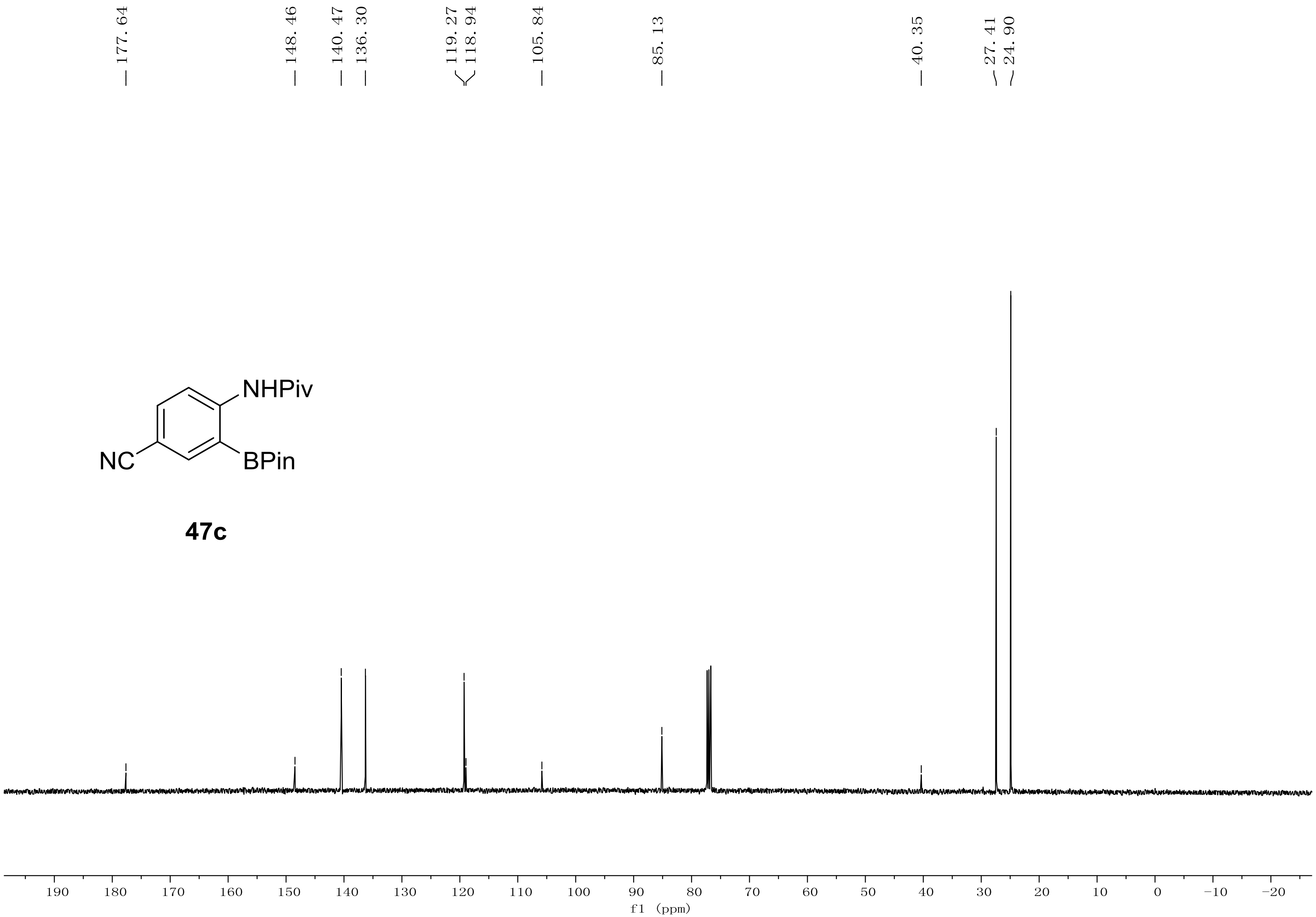

NHPiv
F_3C
BPin

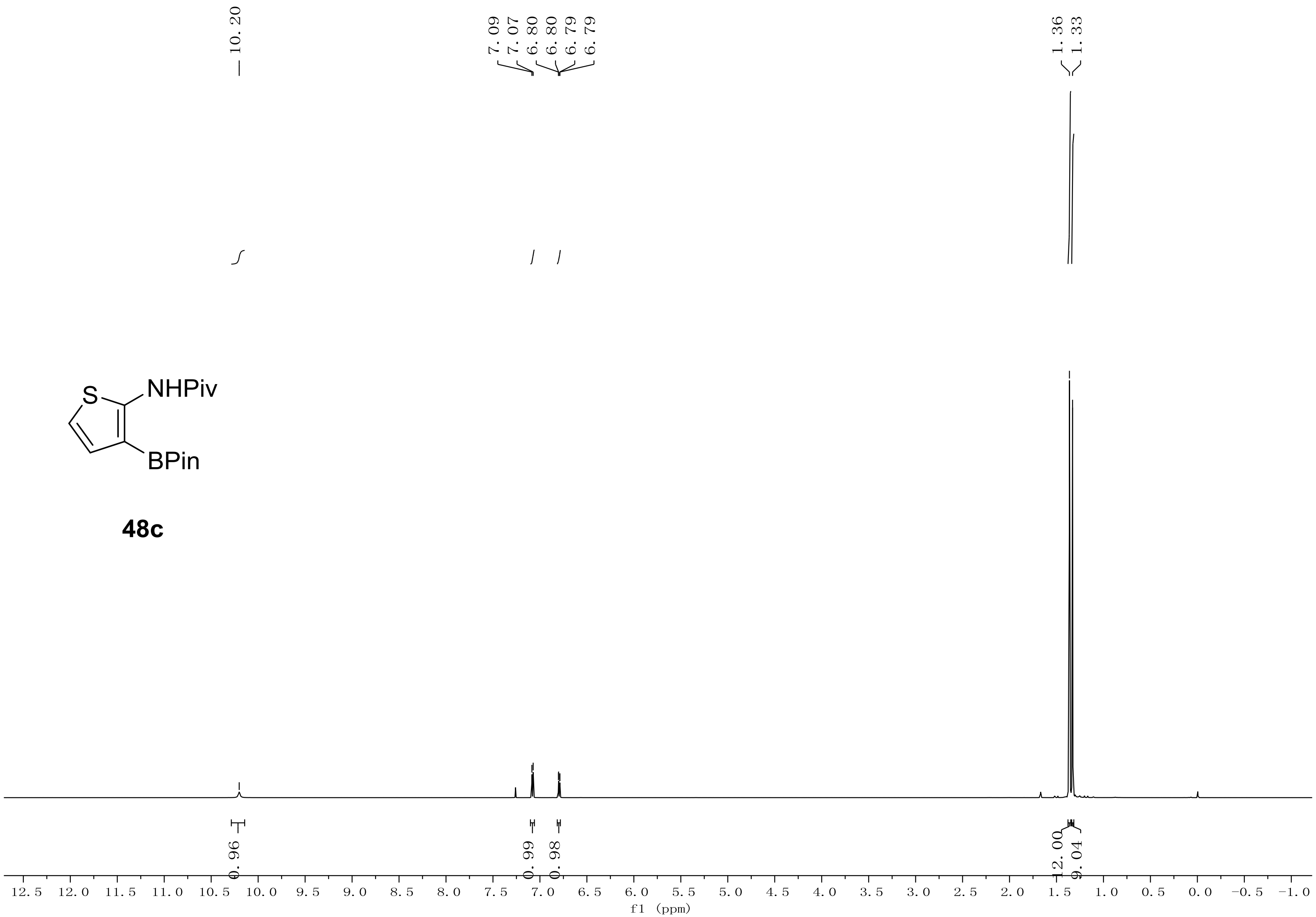
46c


−63.27
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

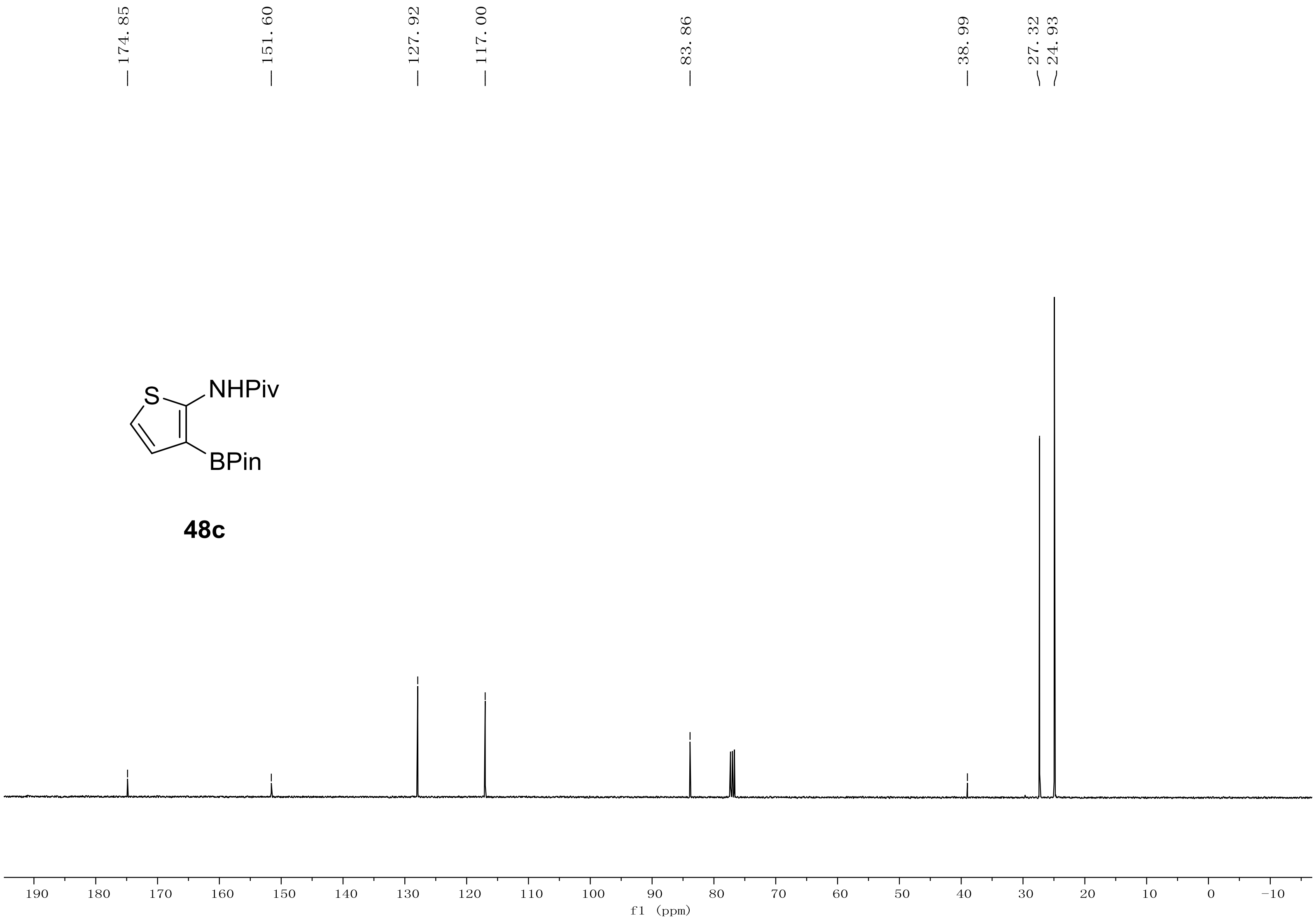


9.70
8.71
8.69
8.06
8.05
7.70
7.69
7.68
7.67
1.39
1.32
NHPiv
NC
BPin
47c
0.92
1.00
0.97
1.03
12.03
9.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

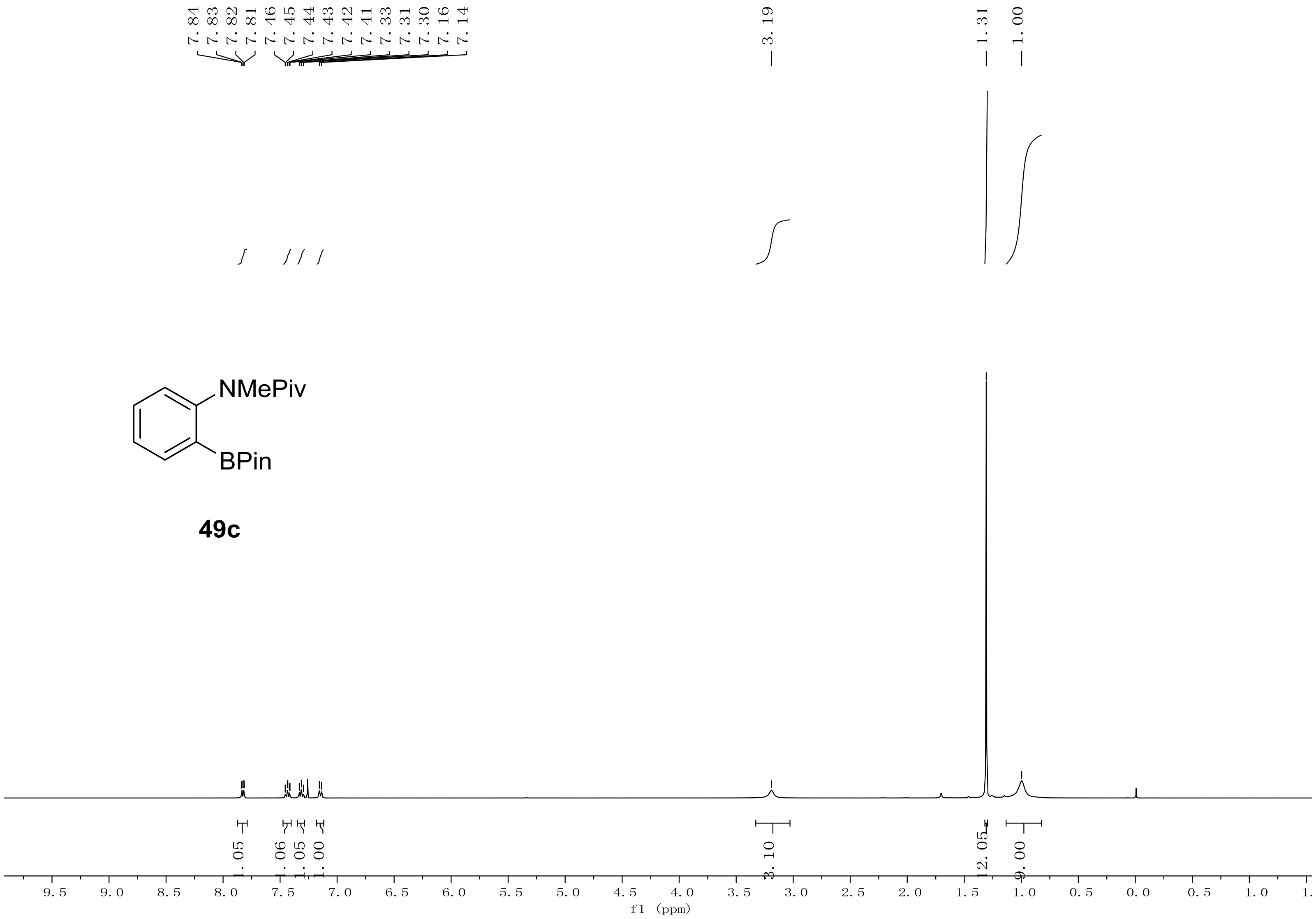

177.64
148.46
140.47
136.30
119.27
118.94
105.84
85.13
40.35
27.41
24.90
NHPiv
NC
BPin
47c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


S
NHPiv
BPin
10.20
7.09
7.07
6.80
6.80
6.79
6.79
1.36
1.33
0.96
0.99
0.98
12.00
9.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

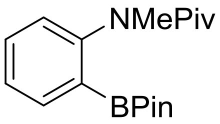
48c



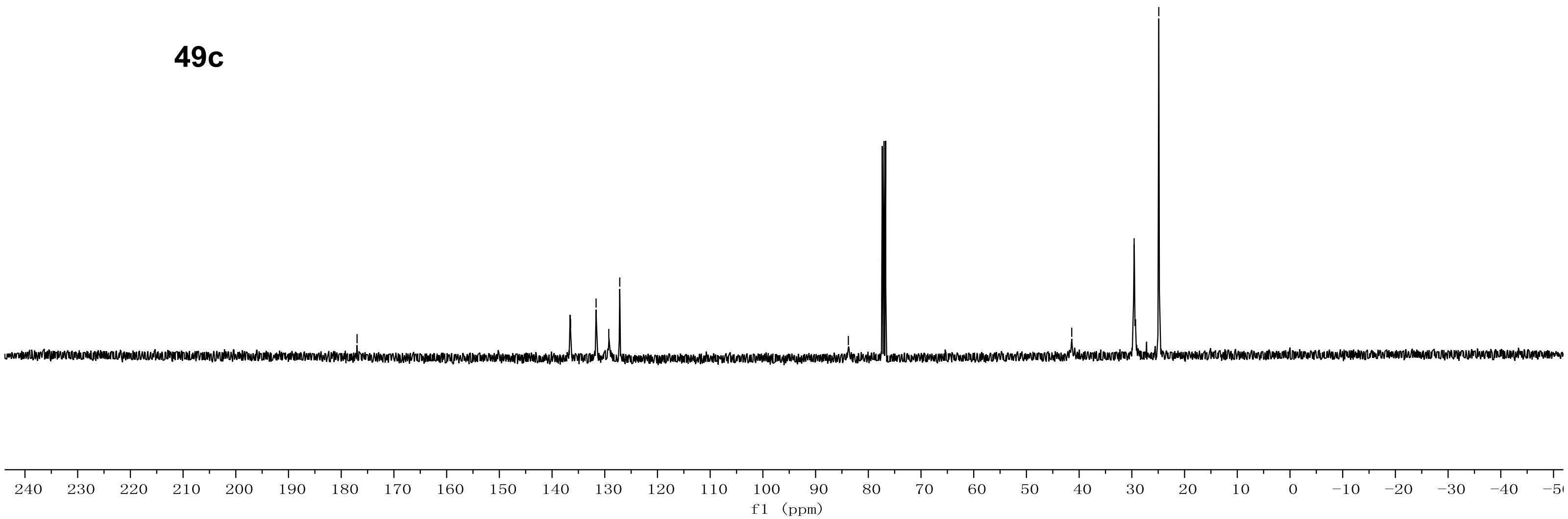
174.85
151.60
127.92
117.00
83.86
38.99
27.32
24.93
NHPiv
S
BPin
48c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

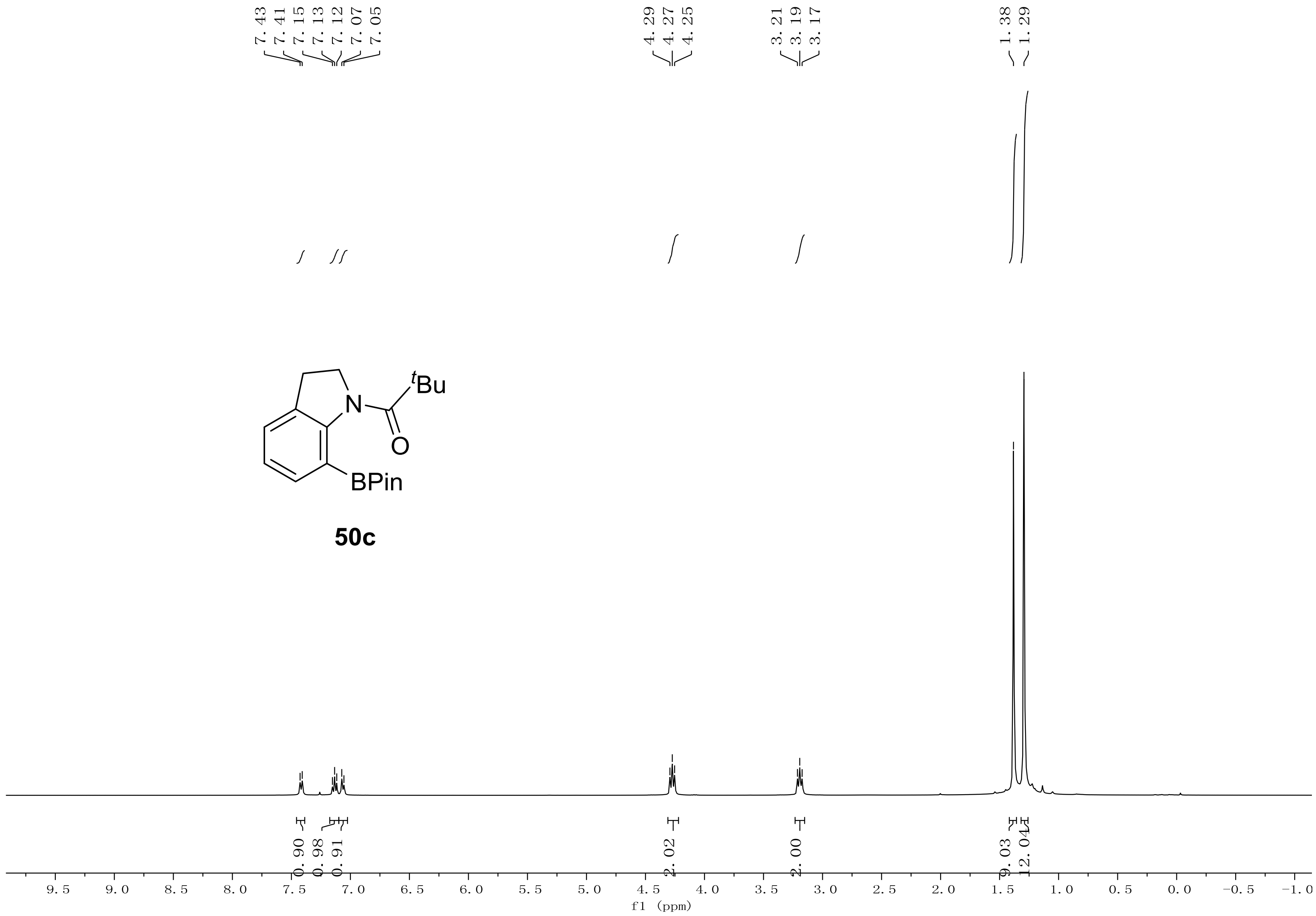


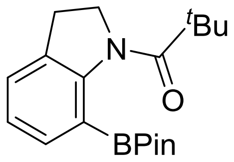
NMePiv
BPin
49c
7.84
7.83
7.82
7.81
7.46
7.45
7.44
7.43
7.42
7.41
7.33
7.31
7.30
7.16
7.14
3.19
1.31
1.00
1.05
1.06
1.05
1.00
3.10
12.05
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)


NMePiv
BPin

49c

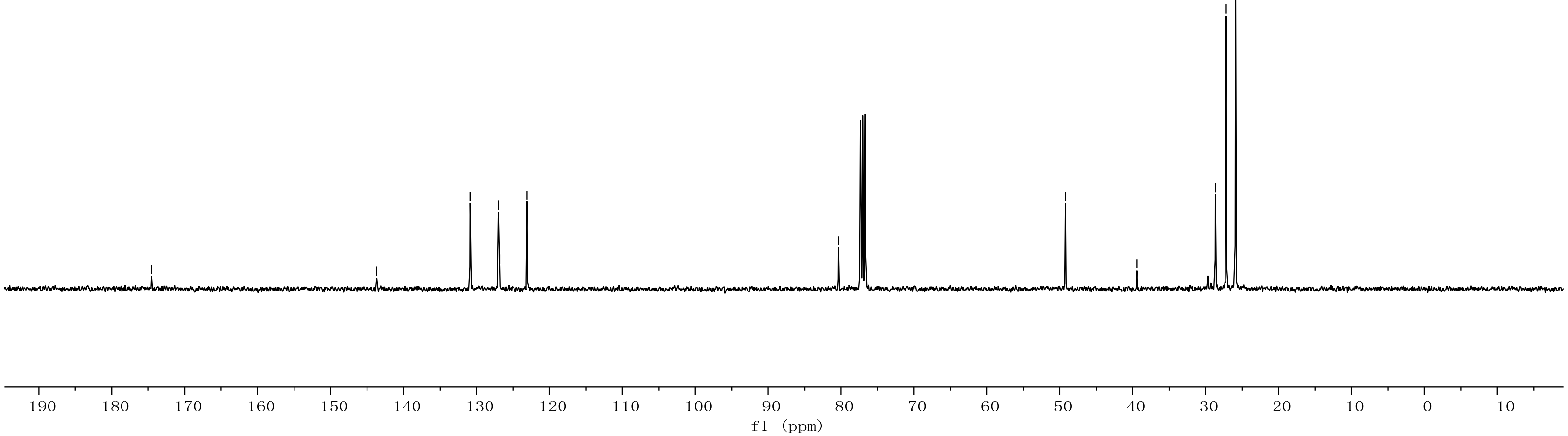

176.99
136.49
131.64
129.24
127.16
83.78
41.40
29.57
24.89
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)


7.43
7.41
7.15
7.13
7.12
7.07
7.05
4.29
4.27
4.25
3.21
3.19
3.17
1.38
1.29
tBu
N
O
BPin
50c
0.90
0.98
0.91
2.02
2.00
9.03
12.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

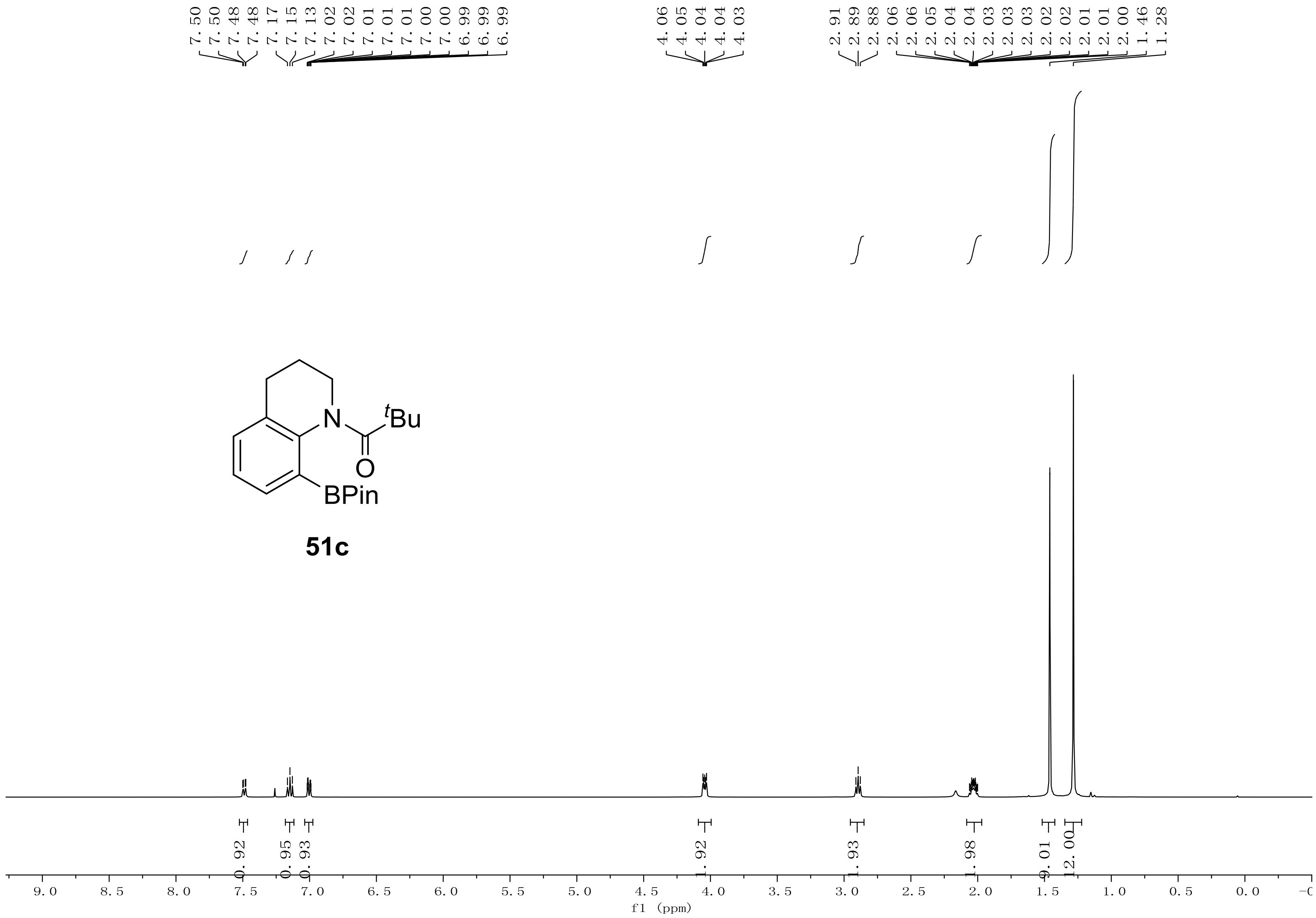


tBu
N
O
BPin

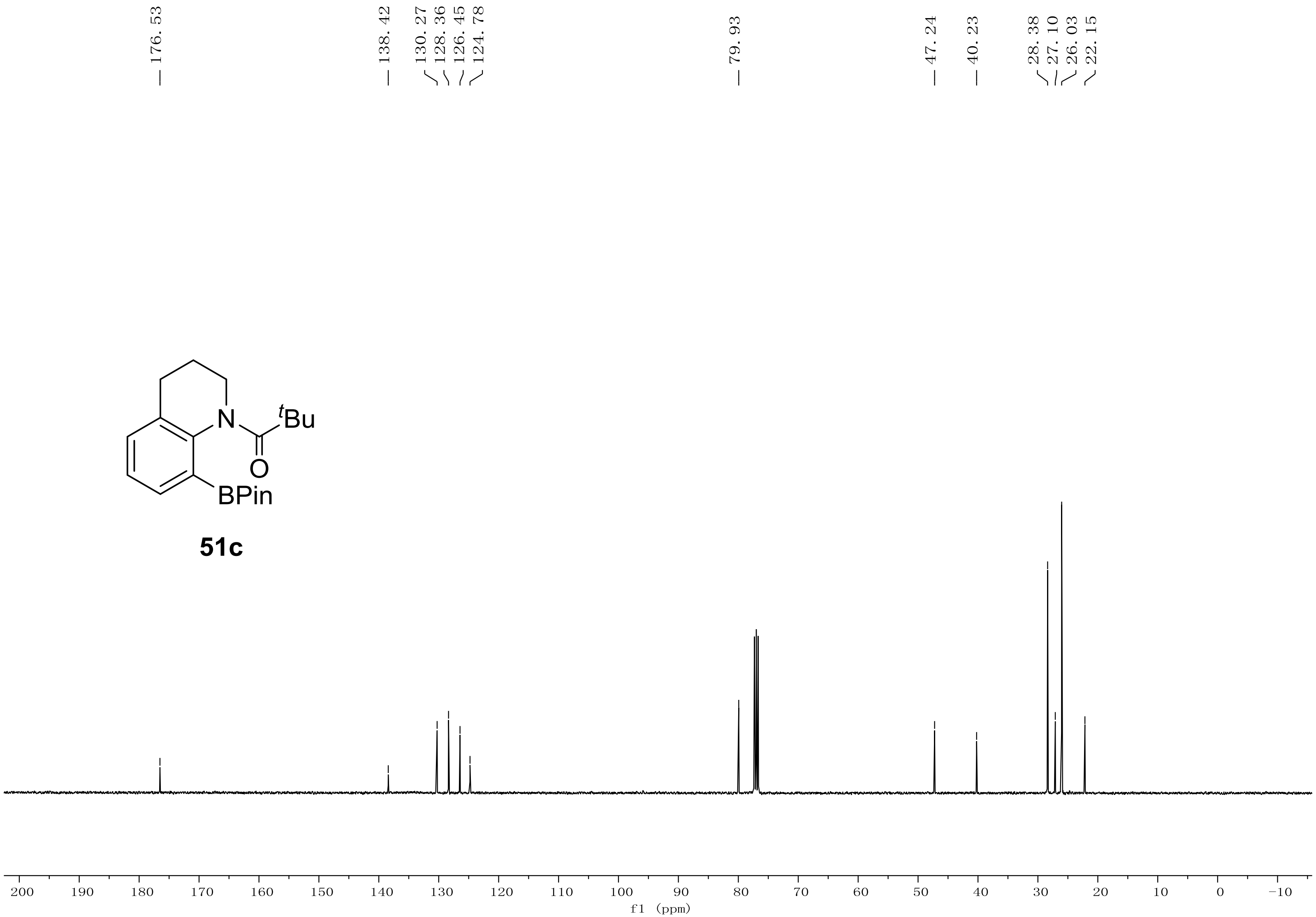
50c

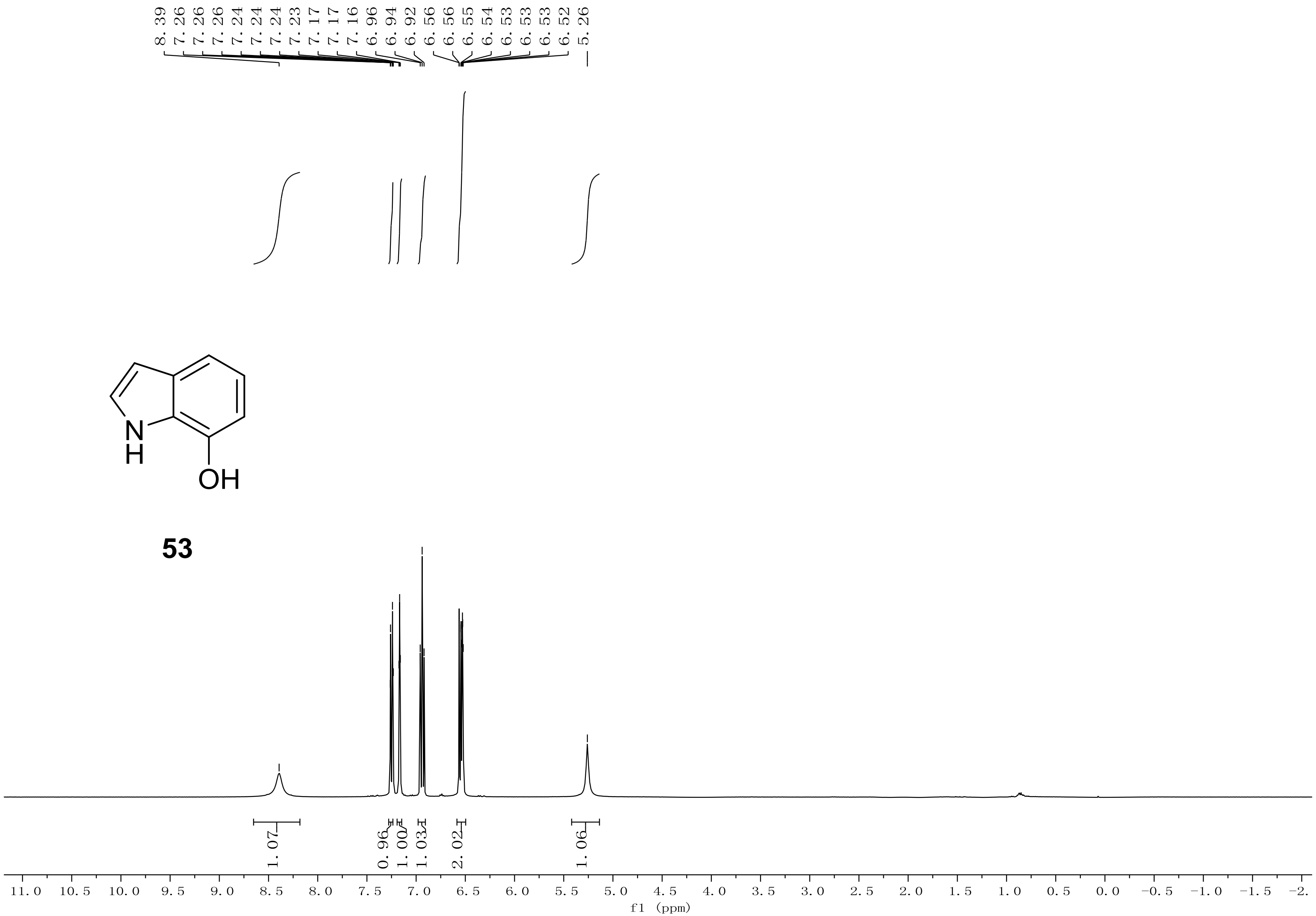


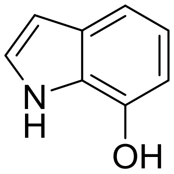
174.54
143.67
130.84
126.97
126.80
123.07
80.34
49.23
39.42
28.68
27.18
25.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.50
7.50
7.48
7.48
7.17
7.15
7.13
7.02
7.02
7.01
7.01
7.01
7.00
7.00
6.99
6.99
4.06
4.05
4.04
4.04
4.03
2.91
2.89
2.88
2.06
2.06
2.05
2.04
2.04
2.03
2.03
2.03
2.02
2.02
2.01
2.01
2.00
1.46
1.28
N
tBu
O
BPin
0.92
0.95
0.93
1.92
1.93
1.98
9.01
12.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

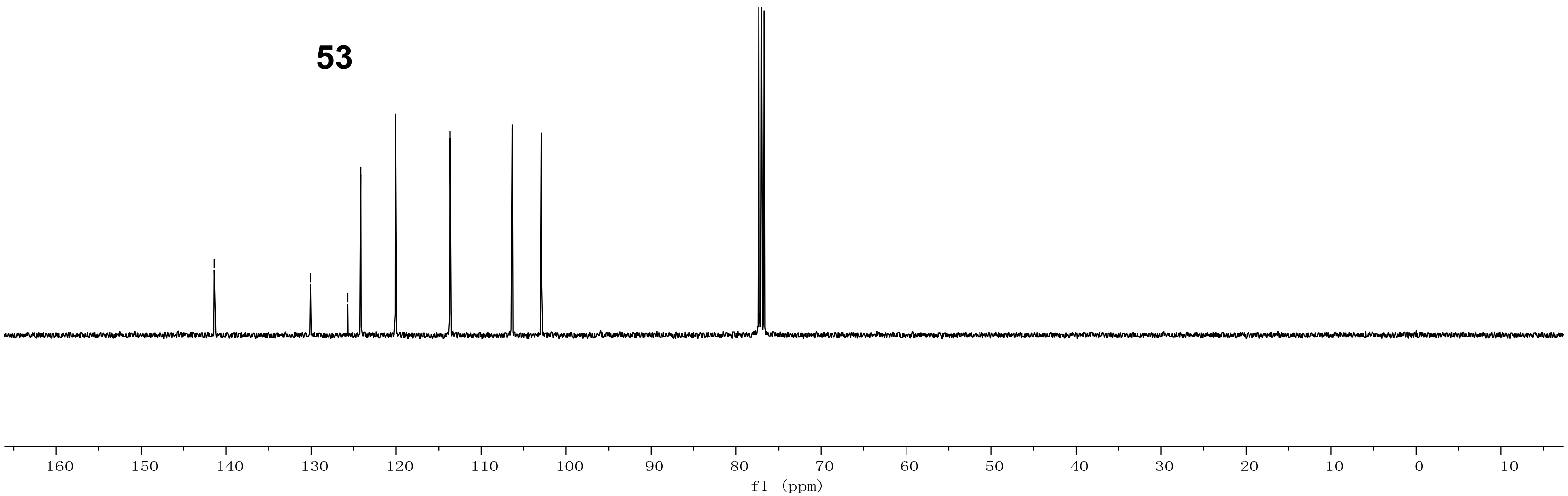
51c

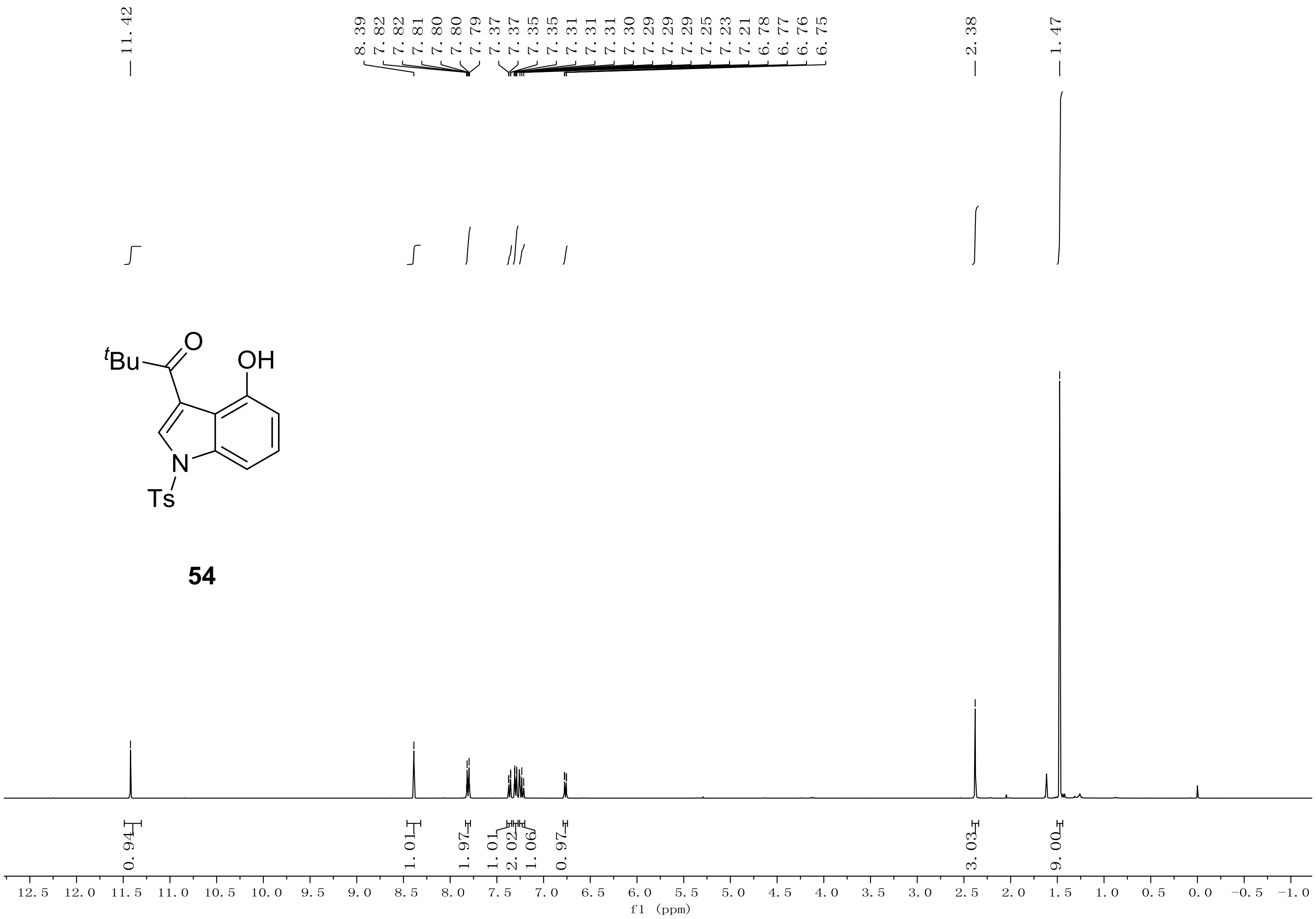

N
tBu
O
BPin
51c
176.53
138.42
130.27
128.36
126.45
124.78
79.93
47.24
40.23
28.38
27.10
26.03
22.15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

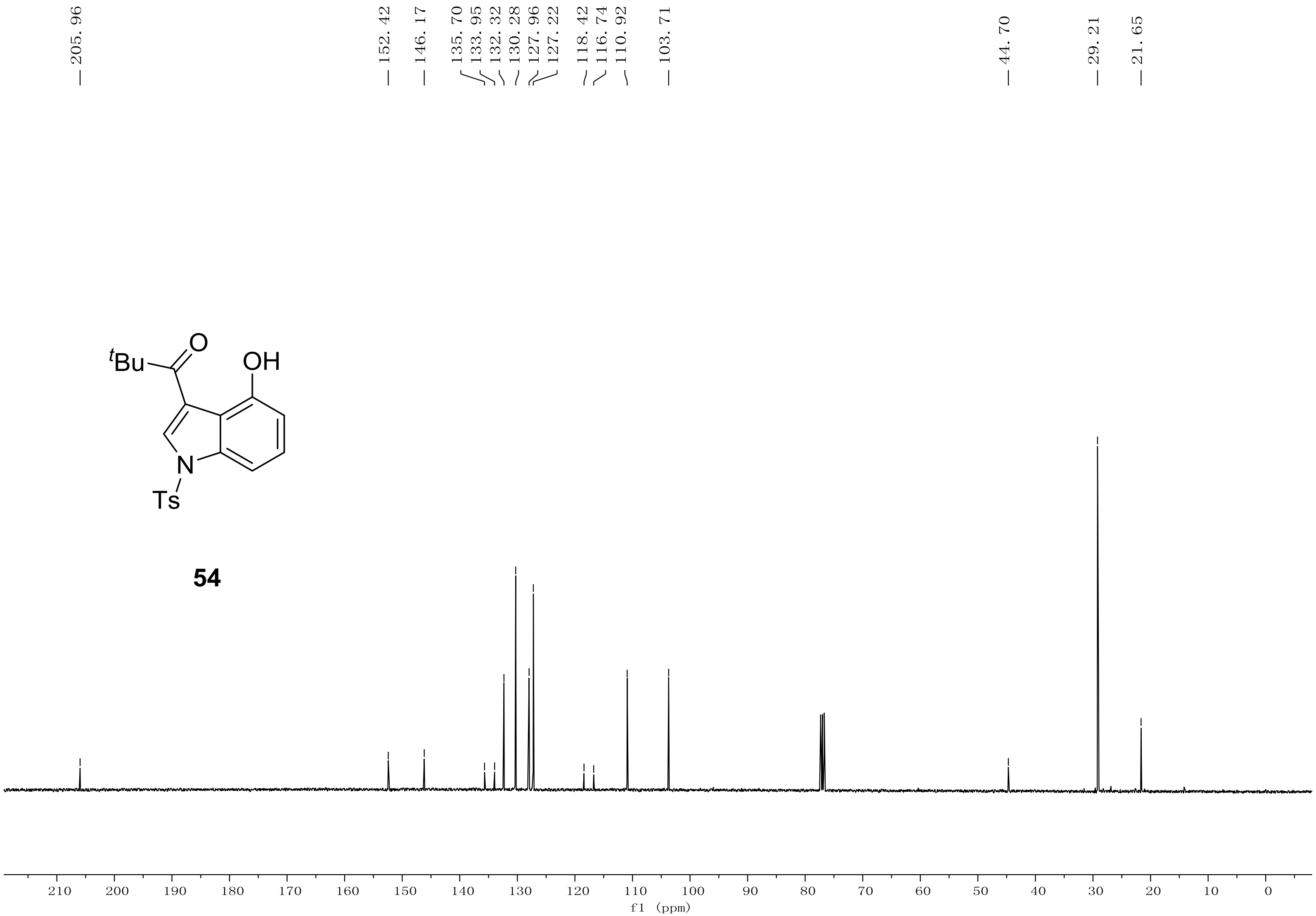

8.39
7.26
7.26
7.26
7.24
7.24
7.24
7.23
7.17
7.17
7.16
6.96
6.94
6.92
6.56
6.56
6.55
6.54
6.53
6.53
6.53
6.52
5.26
1.07
0.96
1.00
1.03
2.02
1.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2.
f1 (ppm)
53



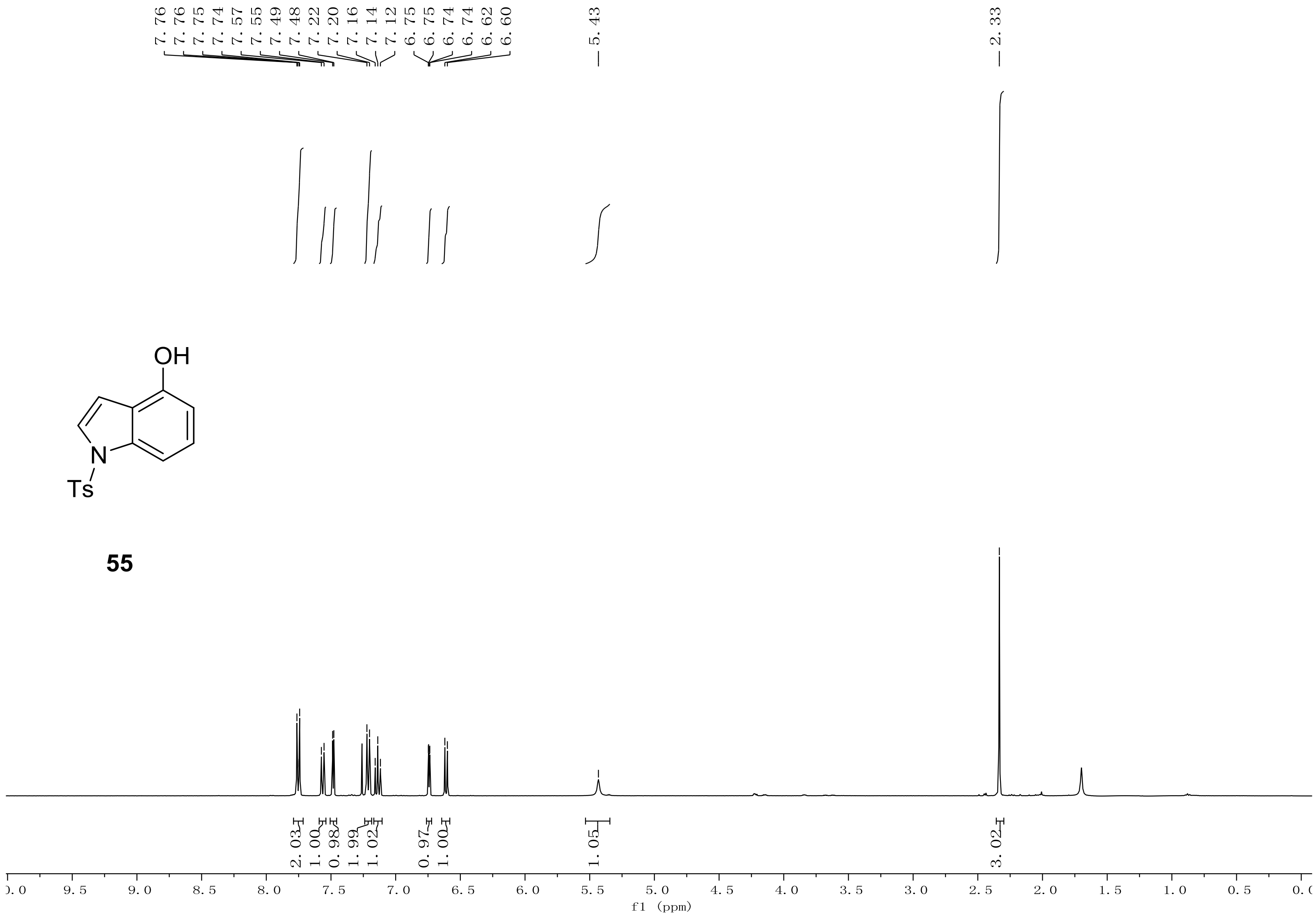
53


141.43
130.08
125.68
124.17
120.06
113.66
106.36
102.90
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

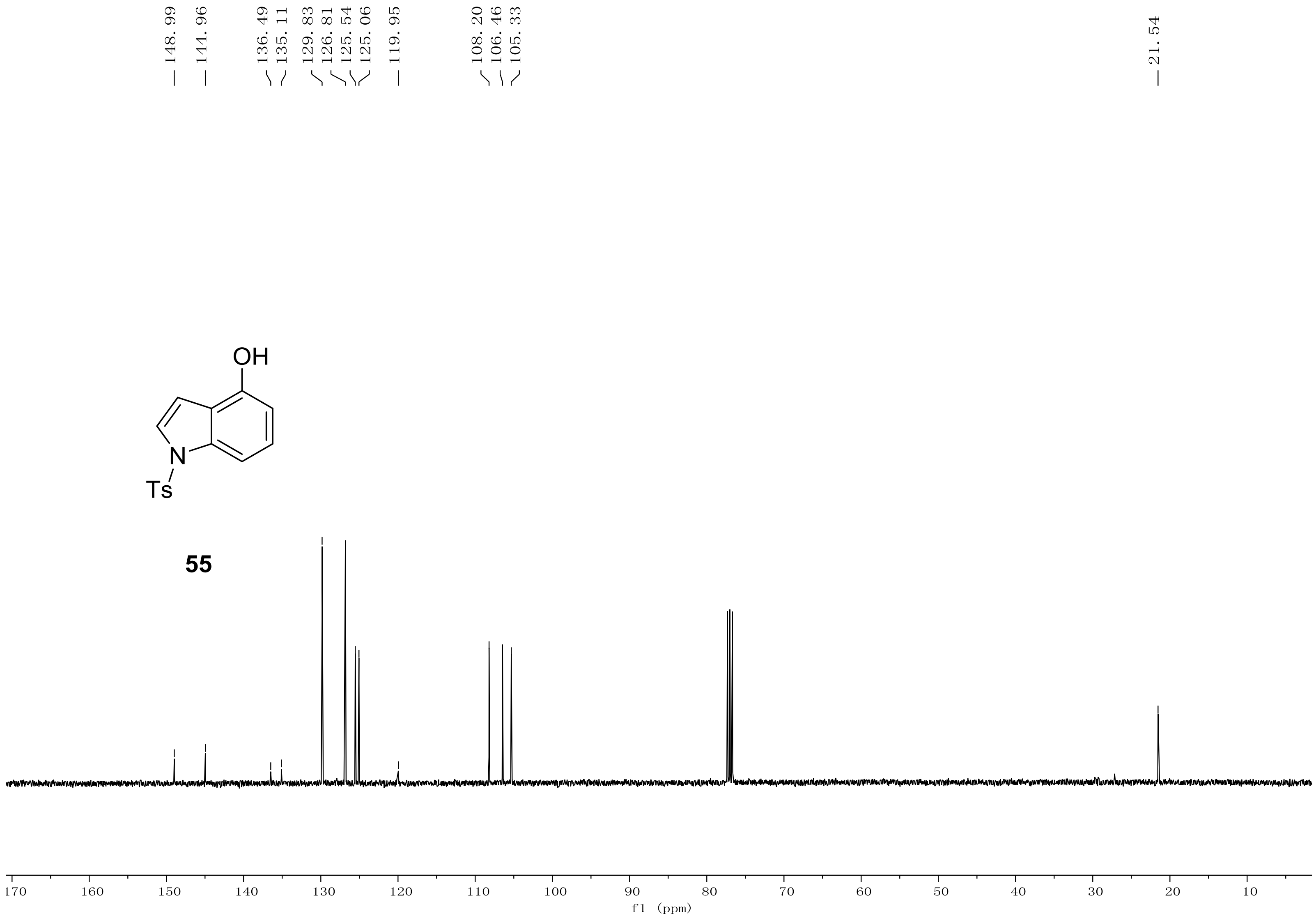

11.42
8.39 7.82 7.82 7.81 7.80 7.80 7.79 7.37 7.37 7.35 7.35 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.25 7.23 7.21 6.78 6.77 6.76 6.75
2.38
1.47
^{t}Bu
O
OH
N
Ts
54
0.94 1.01 1.97 1.01 2.02 1.06 0.97 3.03 9.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

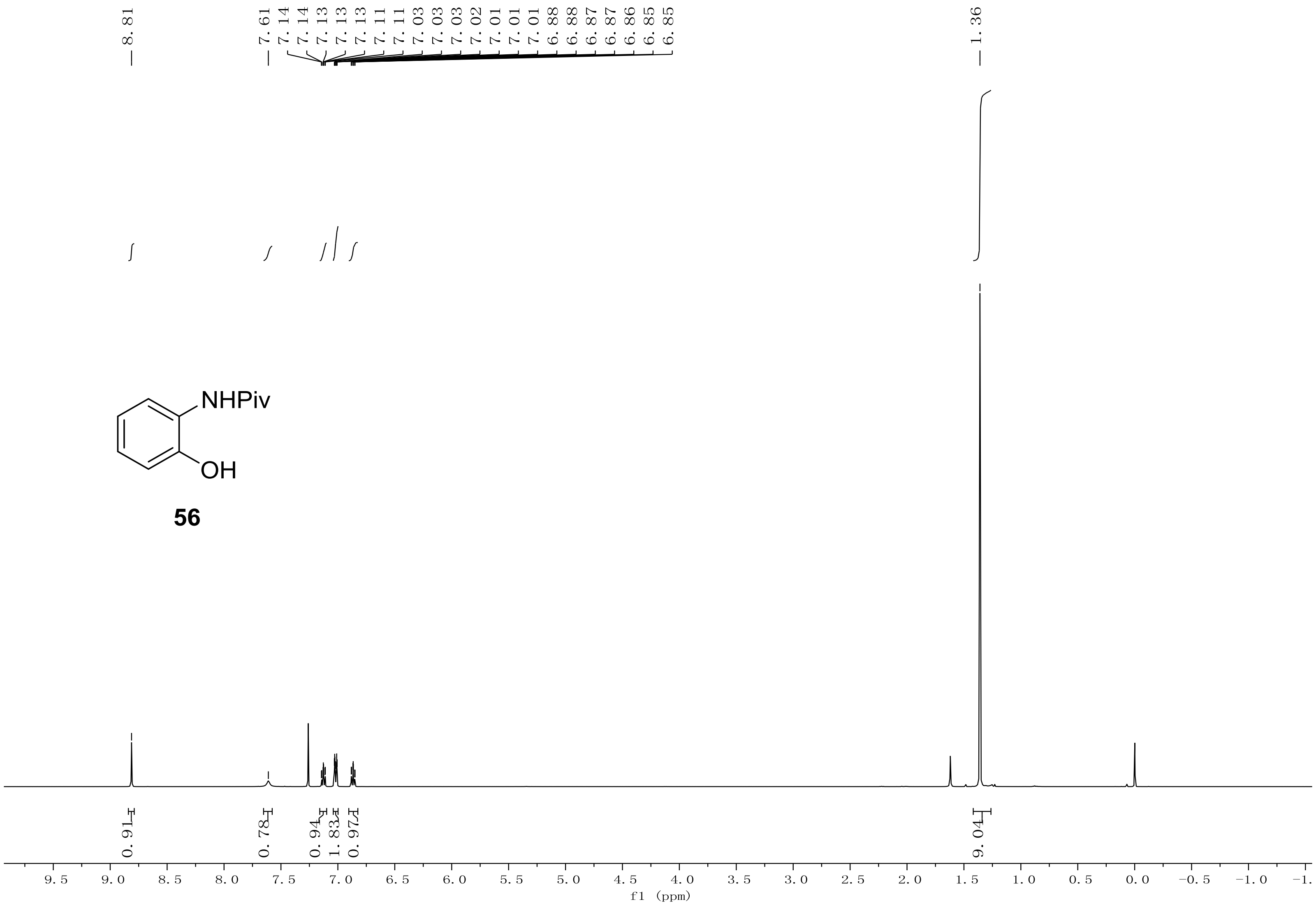


205.96
152.42
146.17
135.70
133.95
132.32
130.28
127.96
127.22
118.42
116.74
110.92
103.71
44.70
29.21
21.65
O
OH
tBu
N
Ts
54
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



55


148.99
144.96
136.49
135.11
129.83
126.81
125.54
125.06
119.95
108.20
106.46
105.33
21.54
OH
N
Ts
55
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.81
7.61
7.14
7.14
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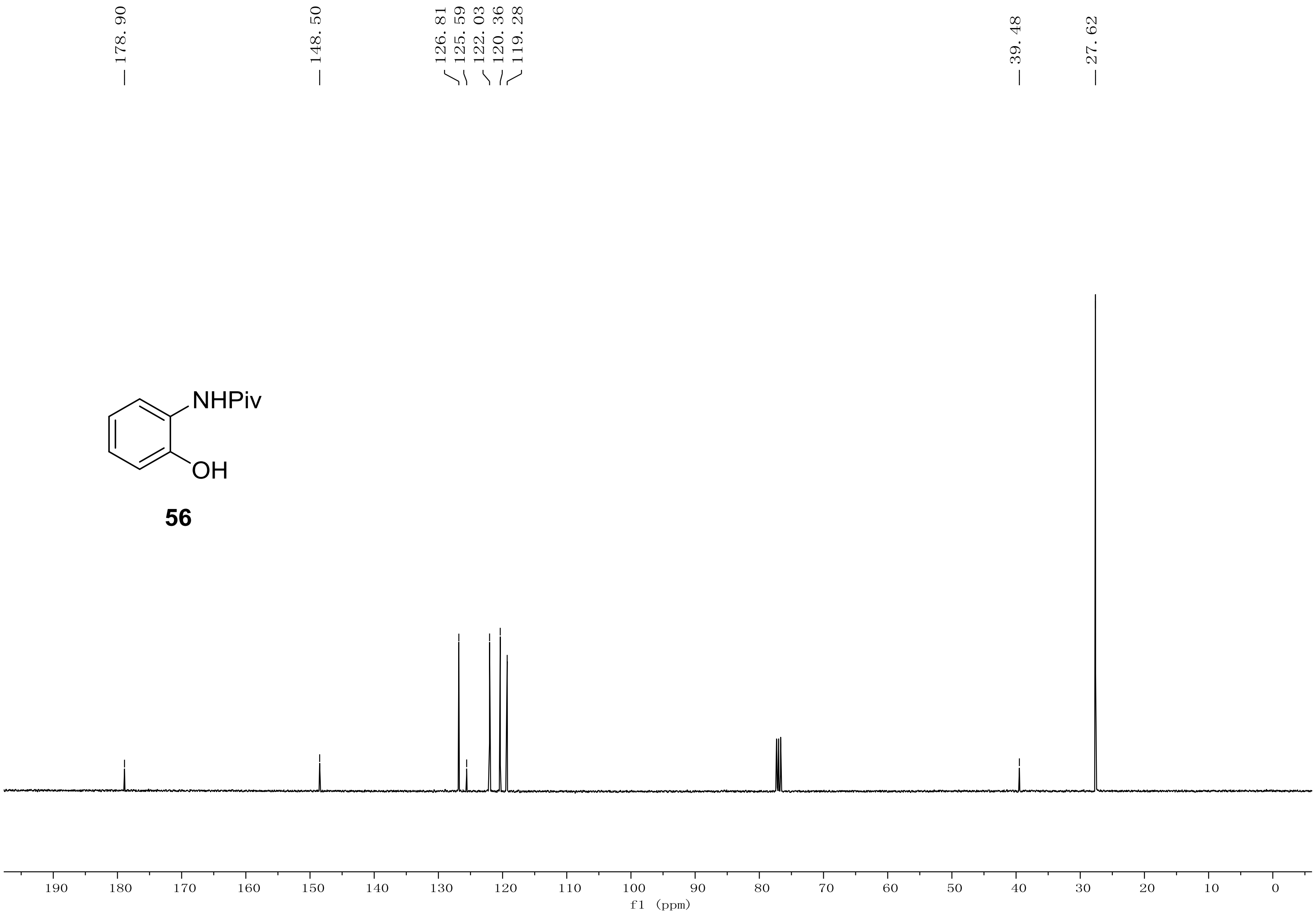
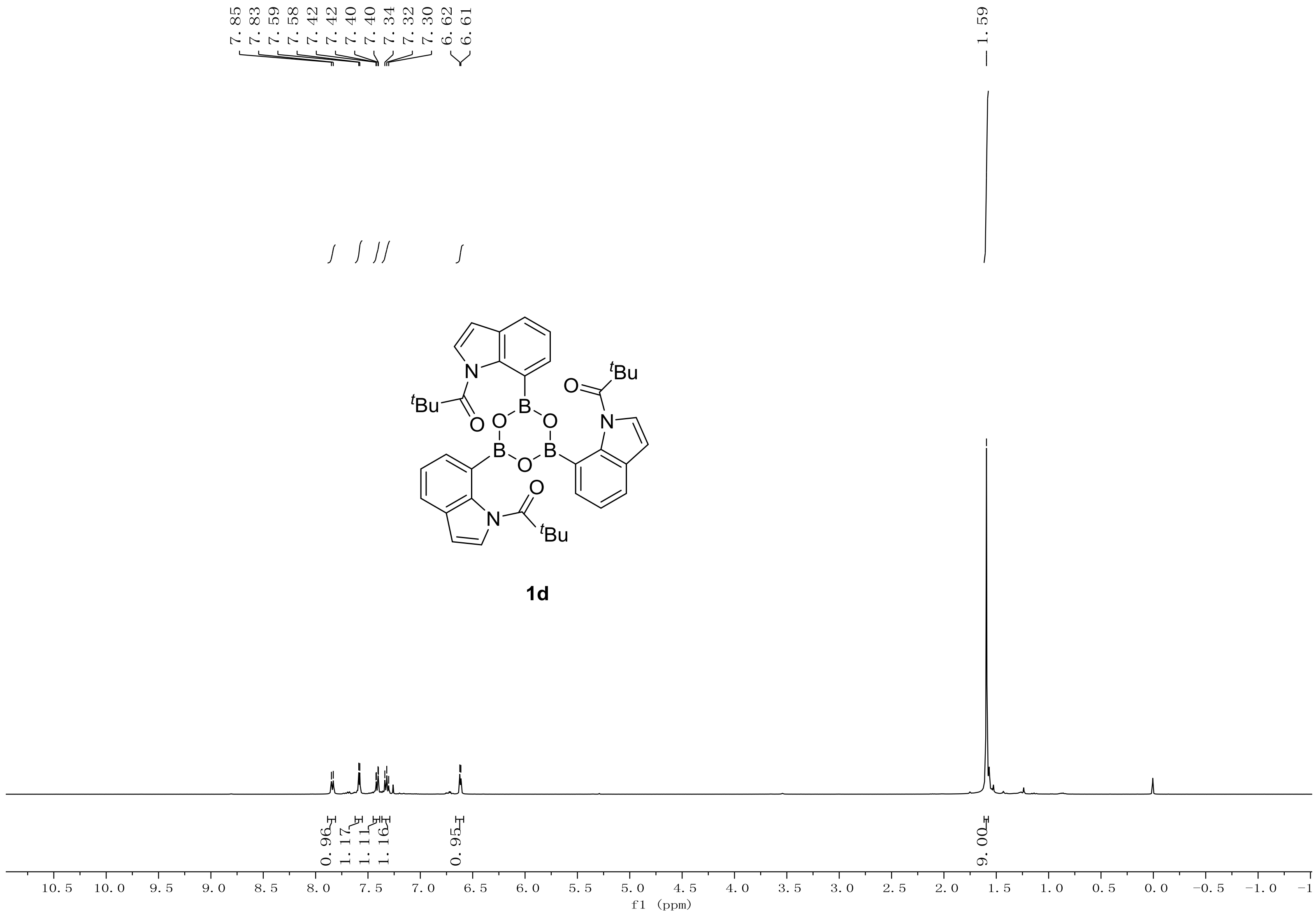
7.13
7.13
7.11
7.11
7.03
7.03
7.03
7.02
7.01
7.01
7.01
6.88
6.88
6.87
6.87
6.86
6.85
6.85
1.36
NHPiv
OH
0.91
0.78
0.94
1.83
0.97
9.04
f1 (ppm)

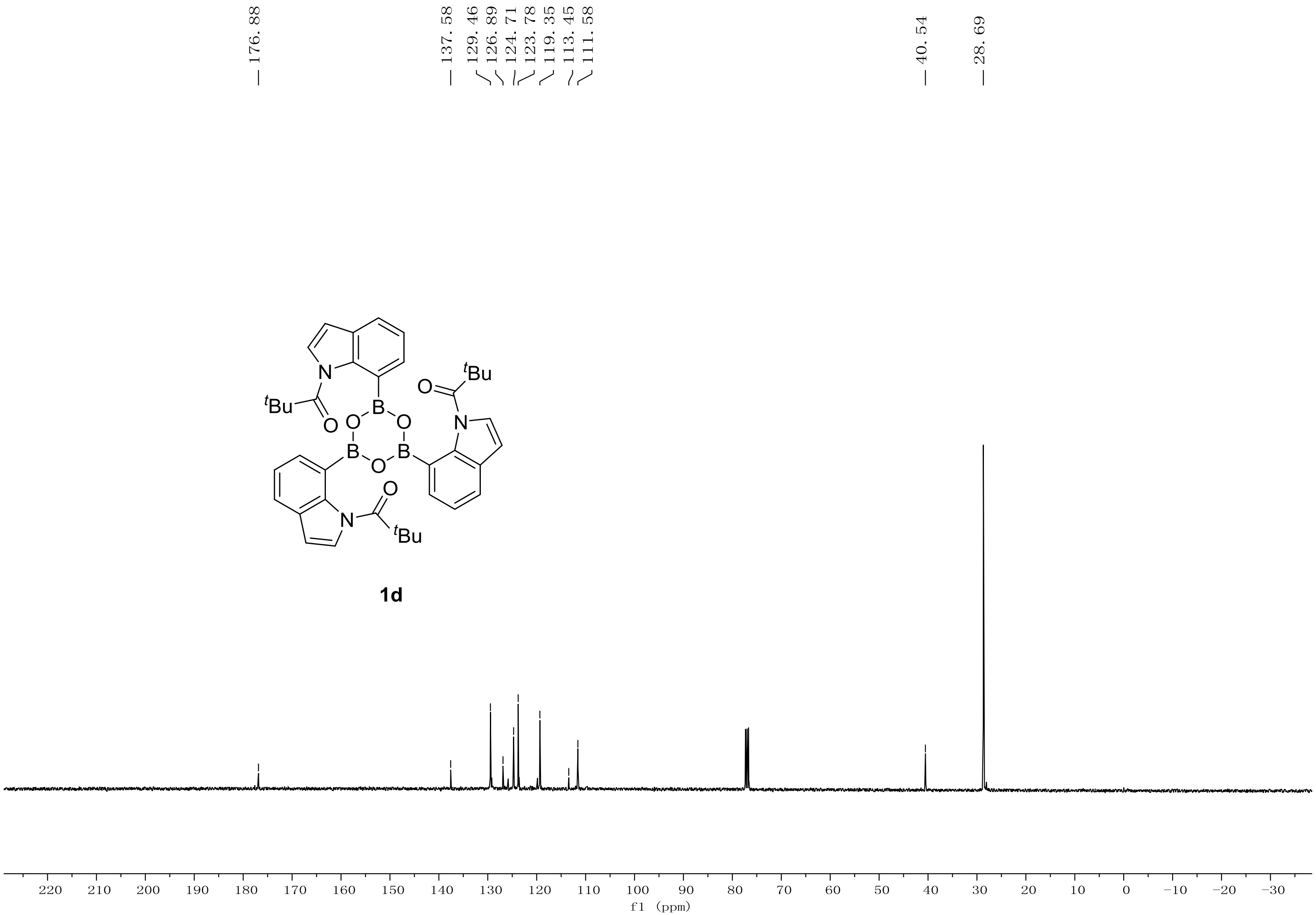
56



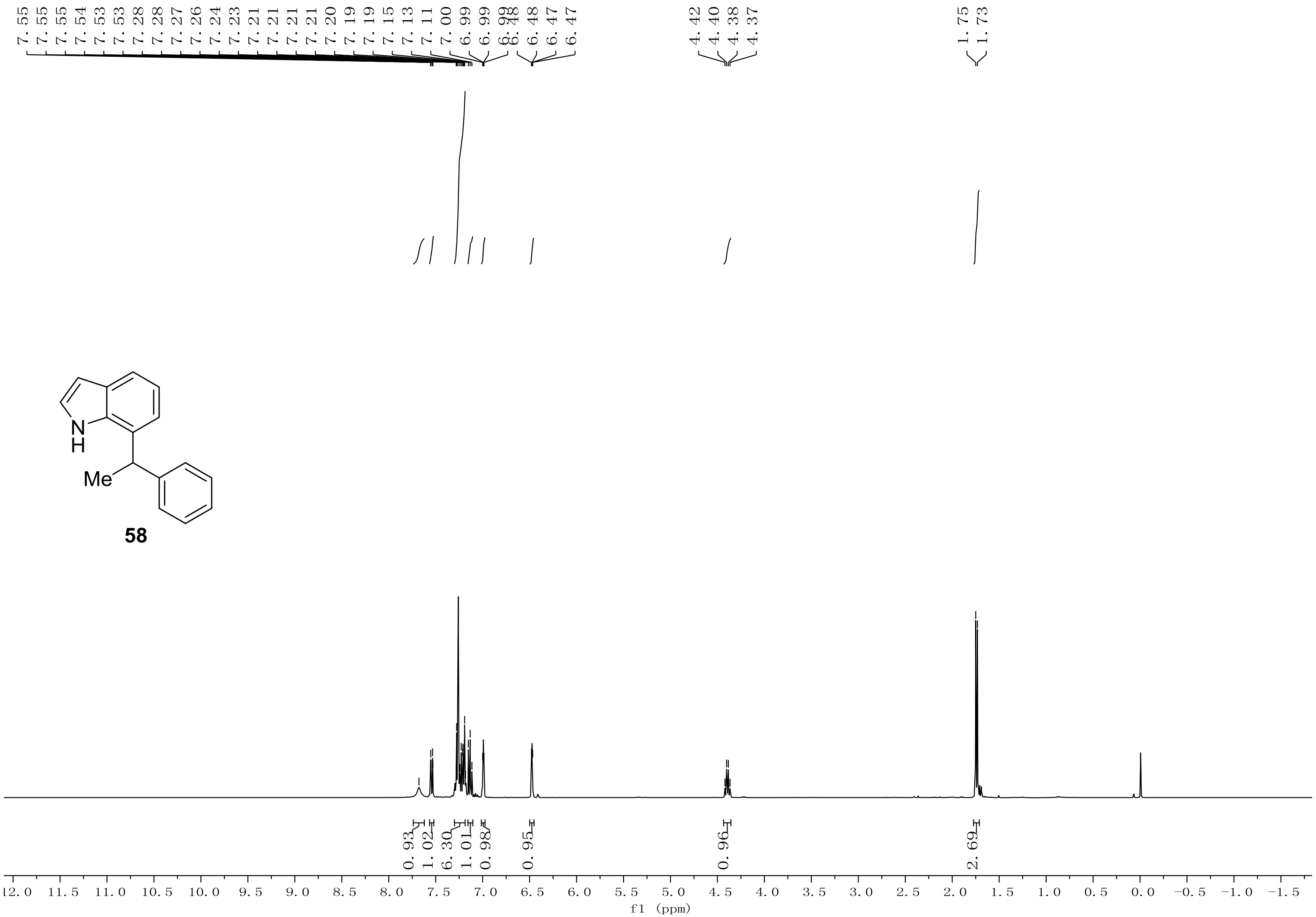
178.90
148.50
126.81
125.59
122.03
120.36
119.28
39.48
27.62
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
NHPiv
OH

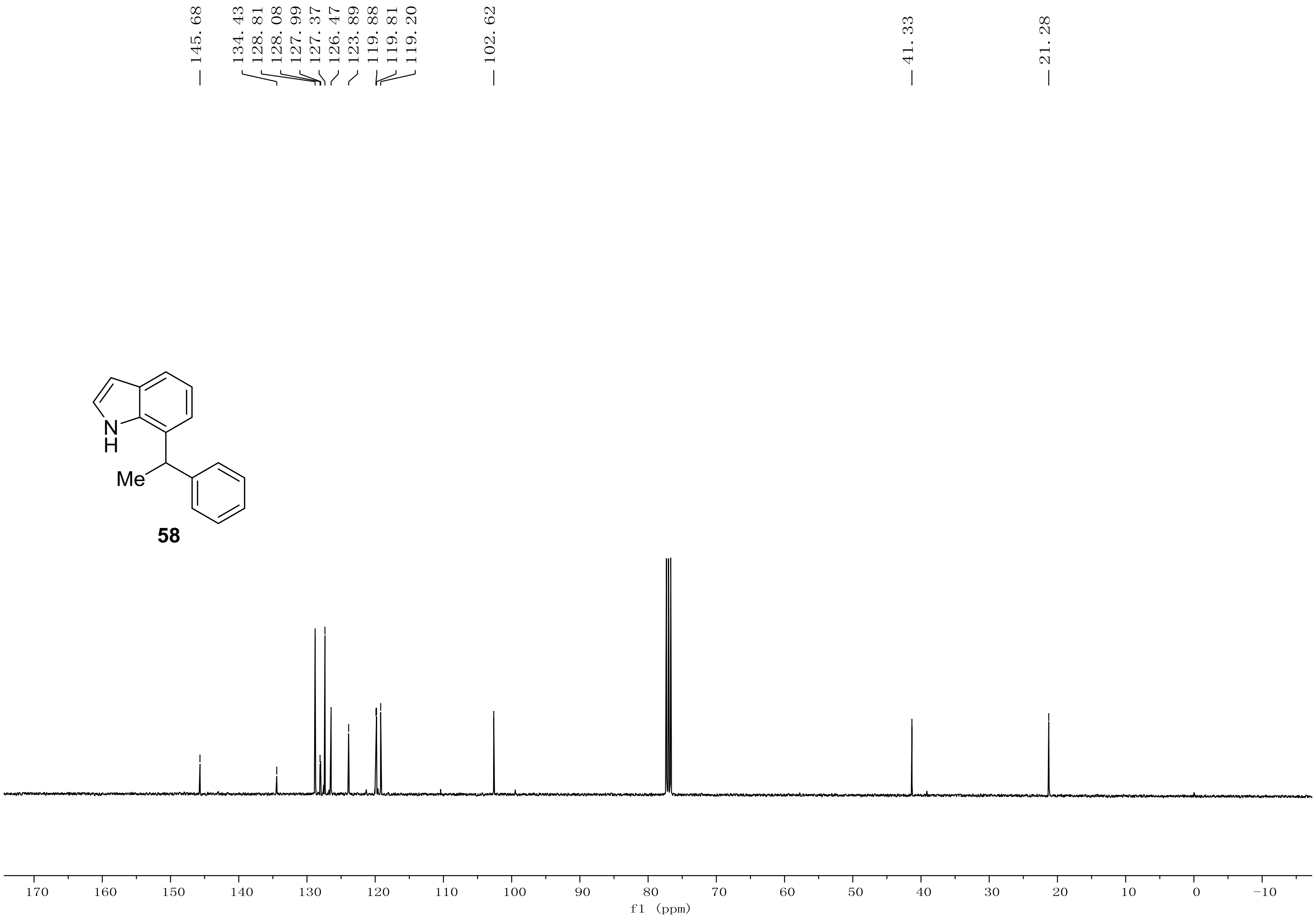
56


7.85
7.83
7.59
7.58
7.42
7.42
7.40
7.40
7.34
7.32
7.30
6.62
6.61
1.59
tBu
O
N
B
1d
0.96
1.17
1.11
1.16
0.95
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1
f1 (ppm)


176.88
137.58
129.46
126.89
124.71
123.78
119.35
113.45
111.58
40.54
28.69
N
O
tBu
B
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

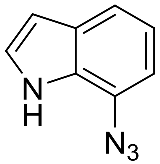
1d


7.55 7.55 7.55 7.54 7.53 7.53 7.28 7.28 7.27 7.26 7.24 7.23 7.21 7.21 7.21 7.21 7.20 7.19 7.19 7.15 7.13 7.11 7.00 6.99 6.99 6.99 6.48 6.48 6.47 6.47
4.42 4.40 4.38 4.37
1.75 1.73
Me
N
H
58
0.93
1.02
6.30
1.01
0.98
0.95
0.96
2.69
f1 (ppm)

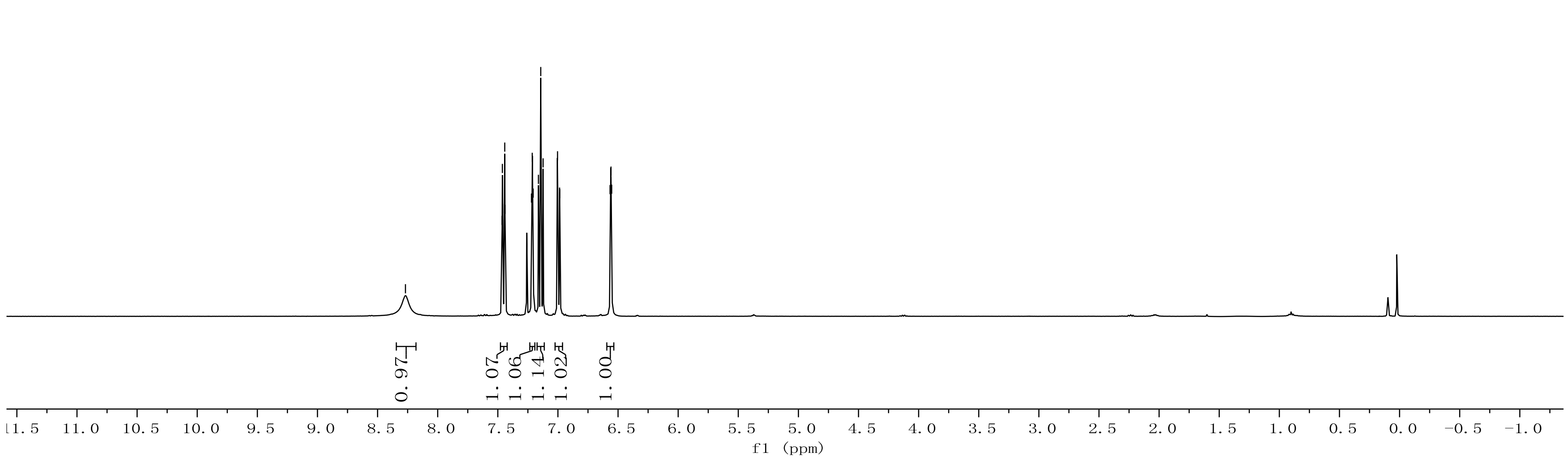


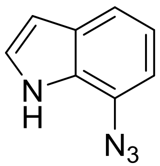
145.68
134.43
128.81
128.08
127.99
127.37
126.47
123.89
119.88
119.81
119.20
102.62
41.33
21.28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

58

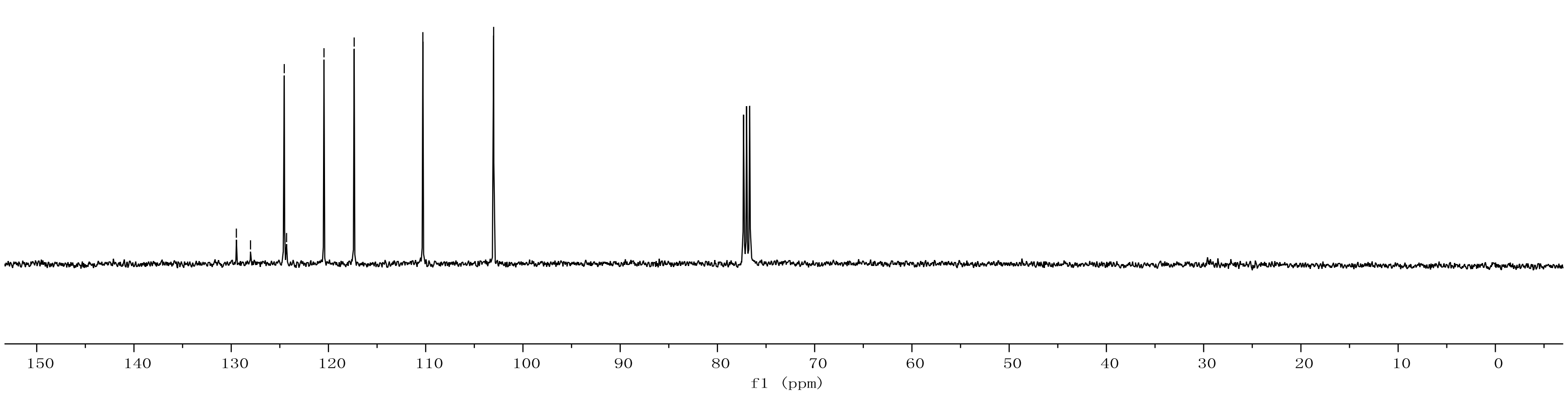

N
H
N3

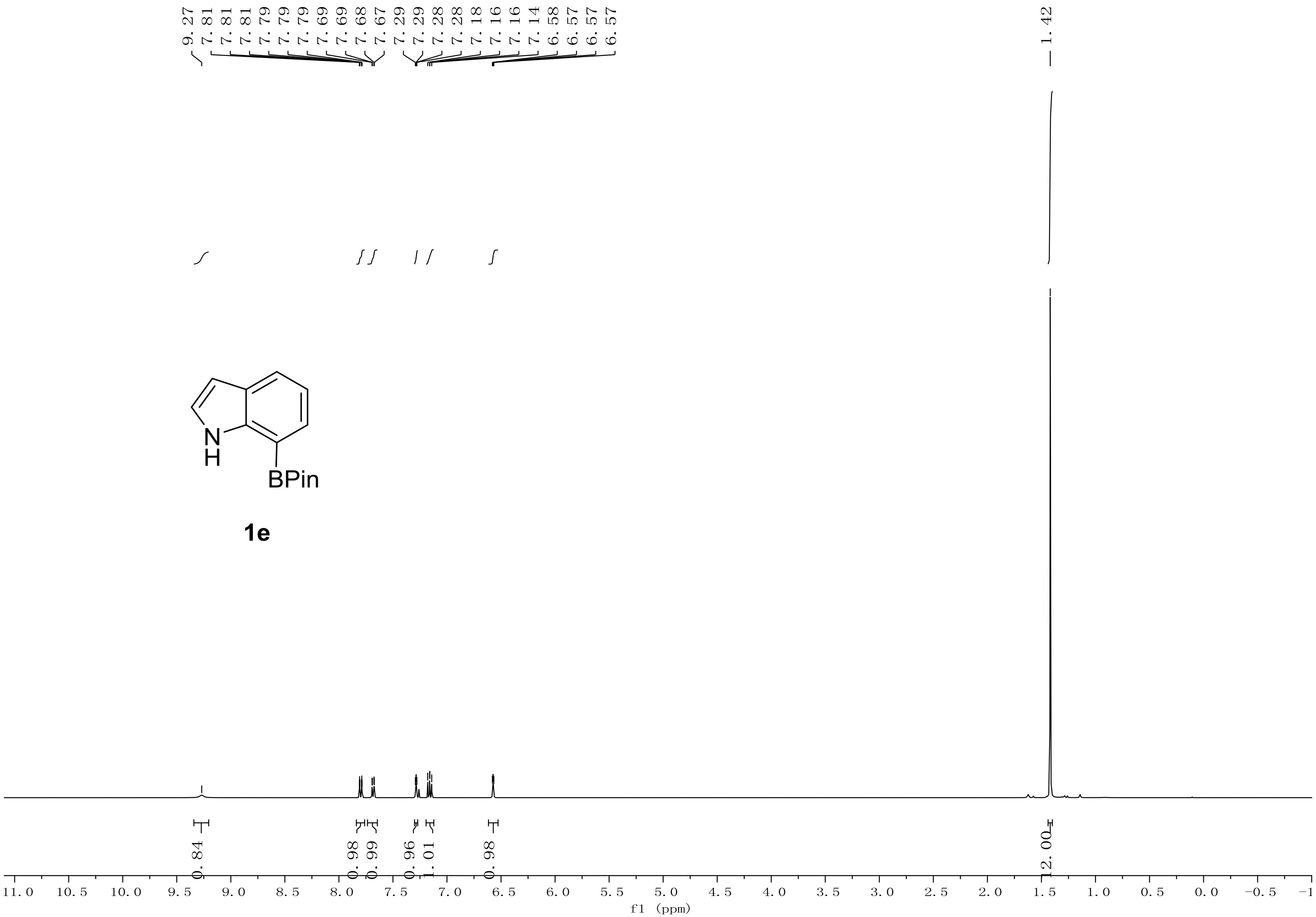
59


8.27
7.46
7.46
7.46
7.44
7.44
7.44
7.22
7.21
7.21
7.21
7.16
7.14
7.12
7.01
7.00
6.99
6.98
6.57
6.56
6.56
6.55
0.97
1.07
1.06
1.14
1.02
1.00
f1 (ppm)



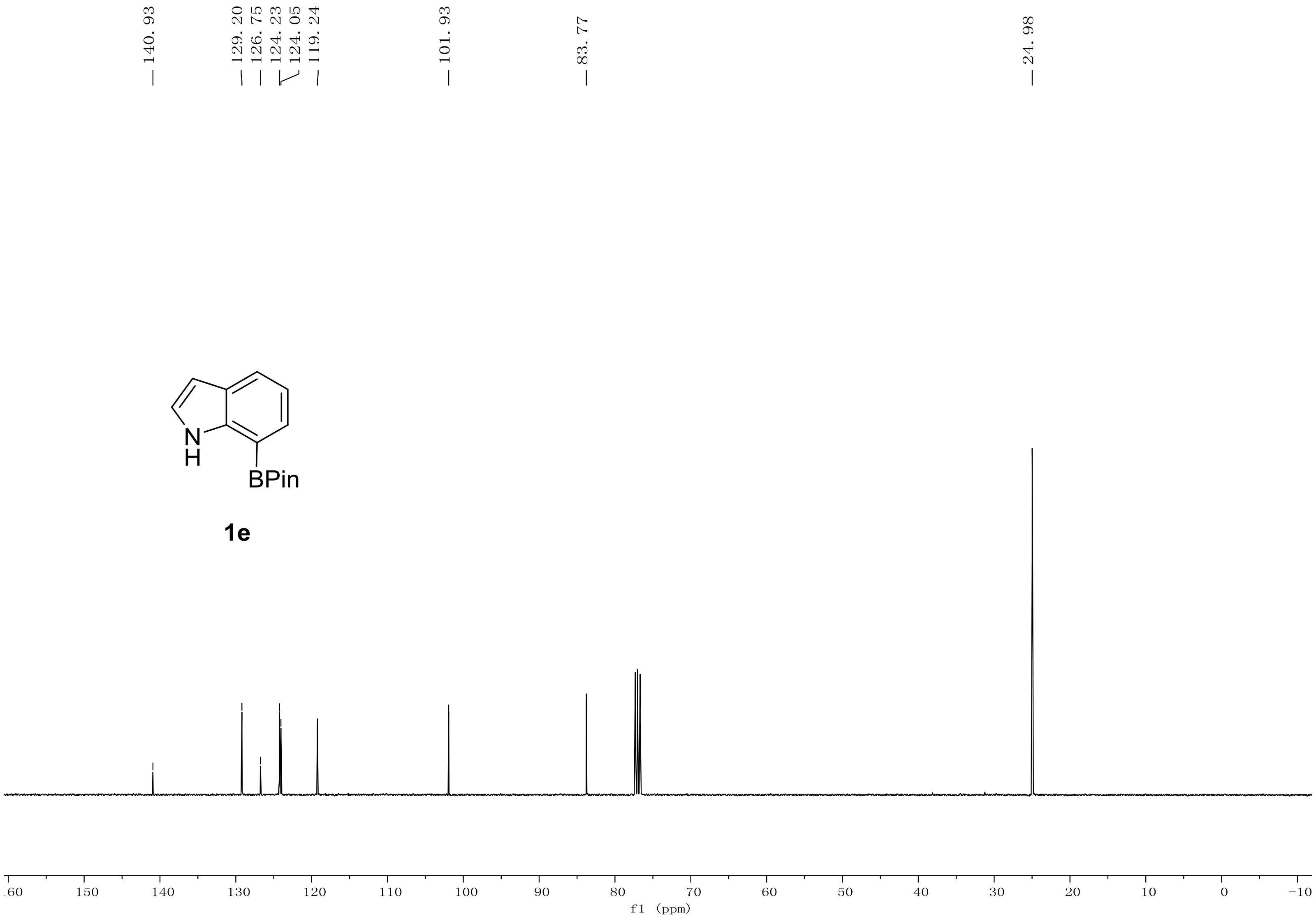
59


129.47
128.01
124.54
124.31
120.46
117.35
110.29
103.01
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

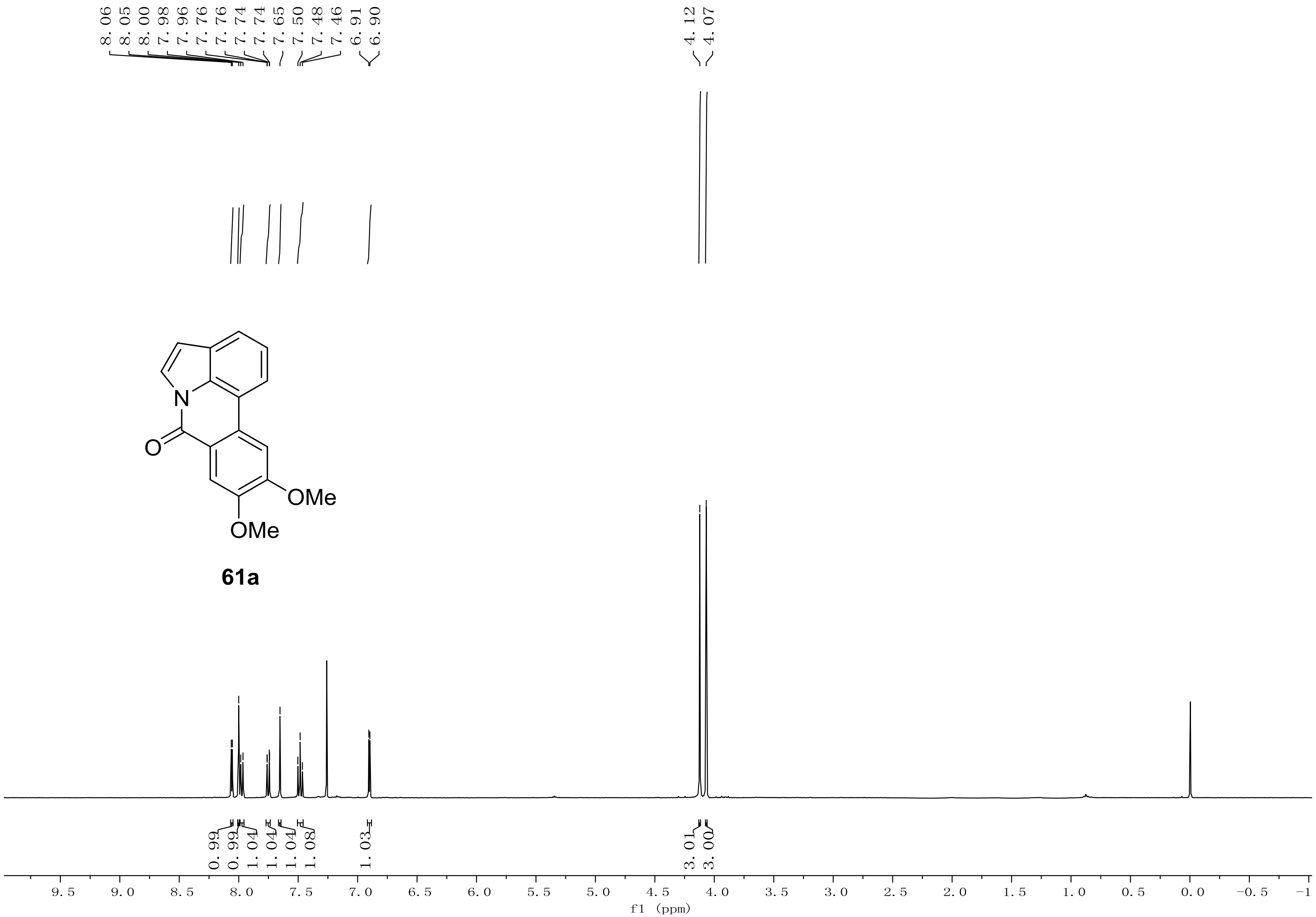


9.27
7.81
7.81
7.79
7.79
7.79
7.69
7.69
7.68
7.67
7.29
7.29
7.28
7.28
7.18
7.16
7.16
7.14
6.58
6.57
6.57
6.57
1.42
N
H
BPin
0.84
0.98
0.99
0.96
1.01
0.98
12.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

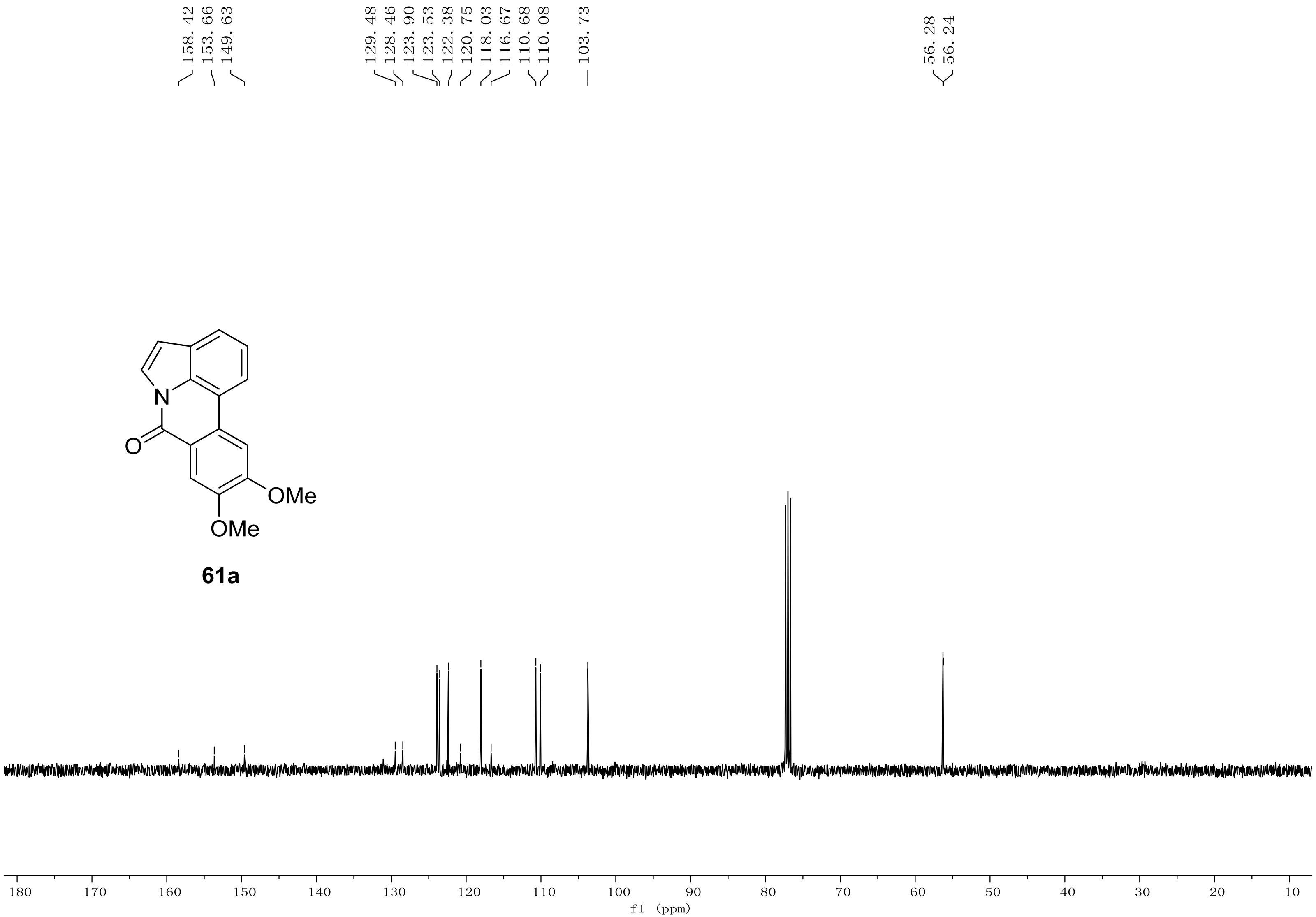
1e


140.93
129.20
126.75
124.23
124.05
119.24
101.93
83.77
24.98
N
H
BPin
f1 (ppm)

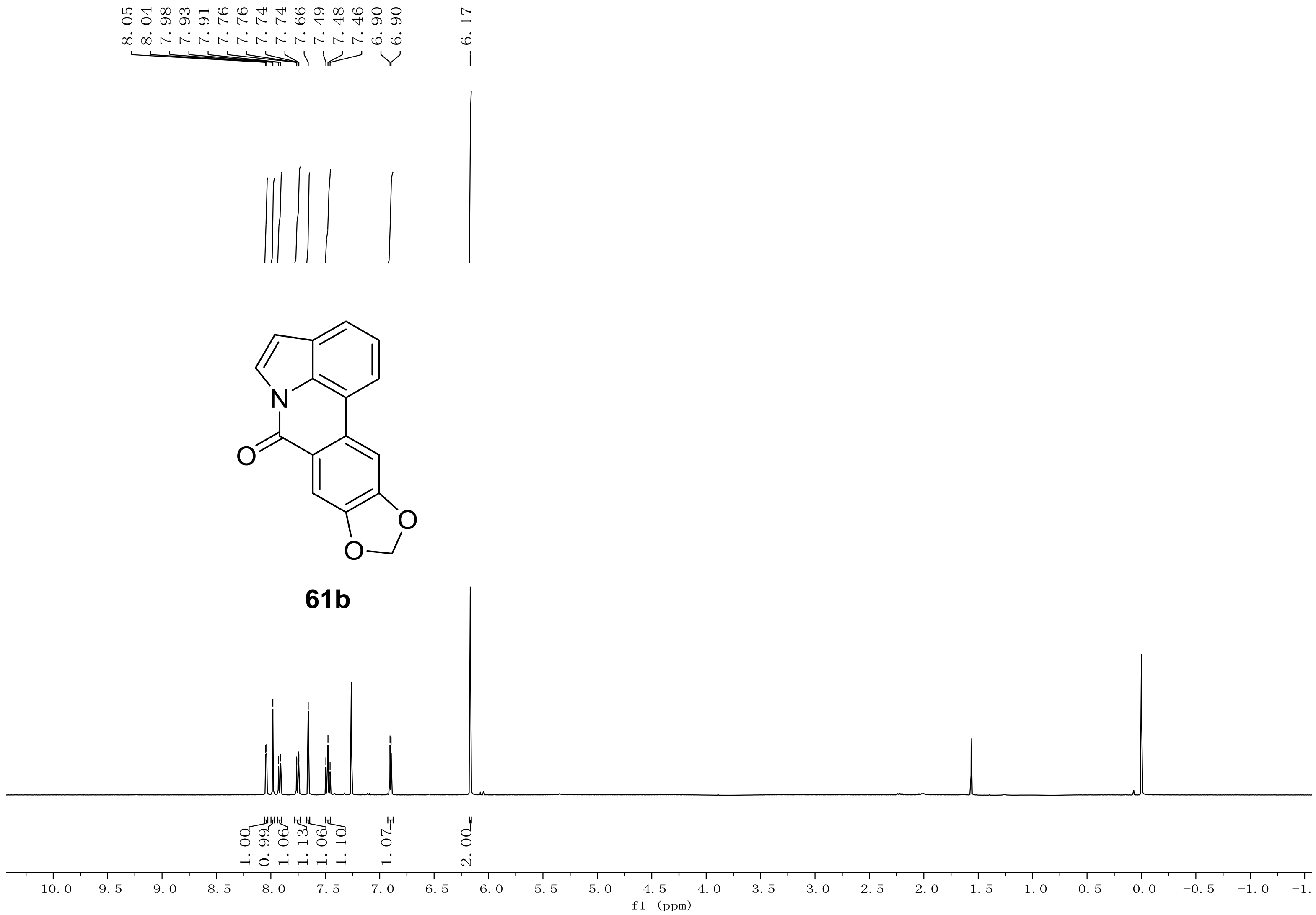
1e



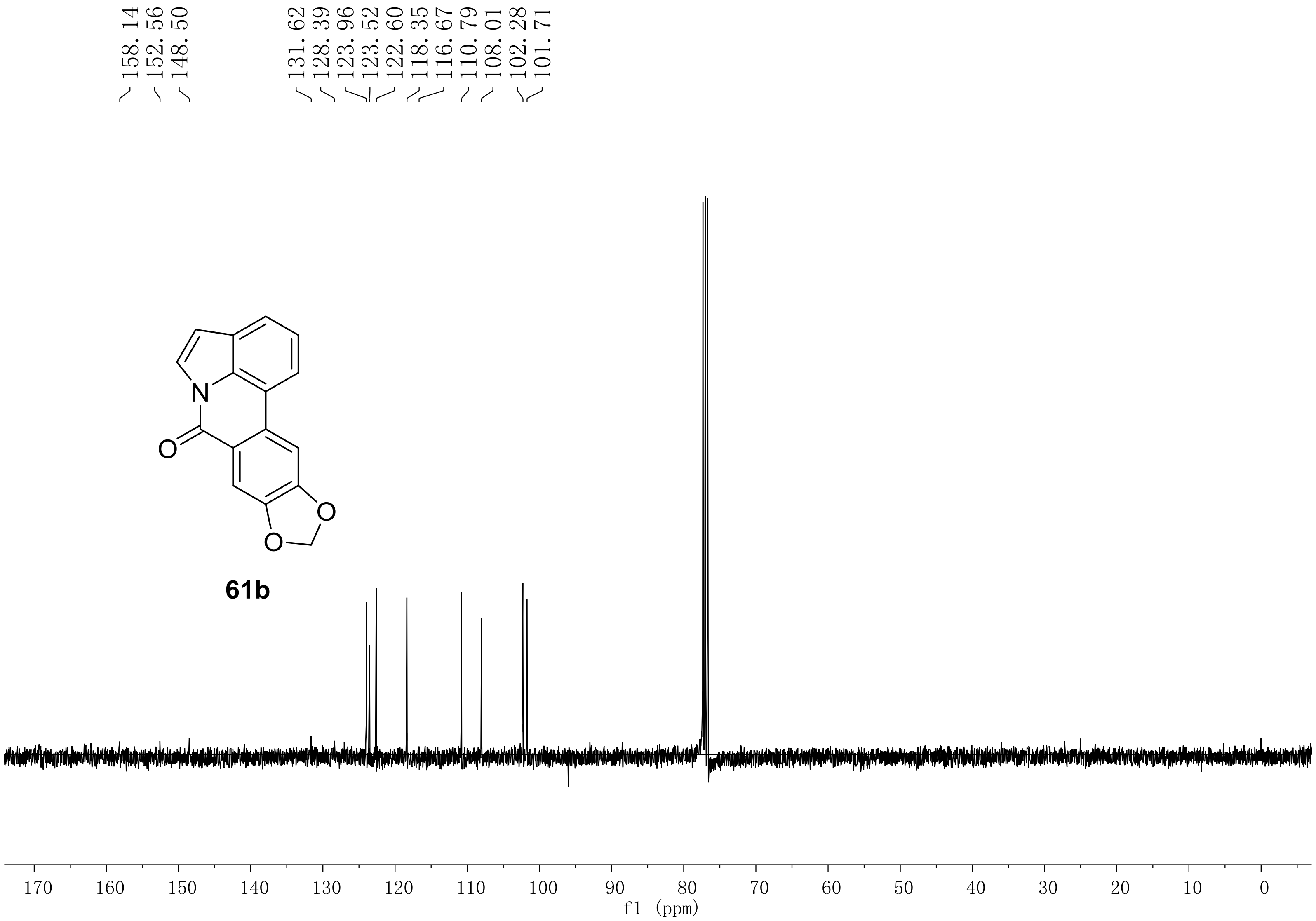
61a


158.42
153.66
149.63
129.48
128.46
123.90
123.53
122.38
120.75
118.03
116.67
110.68
110.08
103.73
56.28
56.24
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

61a



8.05
8.04
7.98
7.93
7.91
7.76
7.76
7.74
7.74
7.66
7.49
7.48
7.46
6.90
6.90
6.17
61b
1.00
0.99
1.06
1.13
1.06
1.10
1.07
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.
f1 (ppm)


158.14
152.56
148.50
131.62
128.39
123.96
123.52
122.60
118.35
116.67
110.79
108.01
102.28
101.71
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

61b