

ASIAN JOURNAL
OF ORGANIC CHEMISTRY

Supporting Information

**Asymmetric Disilylation of Spirocyclic Palladacyclopentanes via
Tandem Heck/C–H Activation of Aryl Iodides**

Hang Li⁺, Wei-Sheng Huang⁺, Ke-Fang Yang, Fei Ye, Guan-Wu Yin, Zheng Xu, and Li-Wen Xu*

Table of Contents

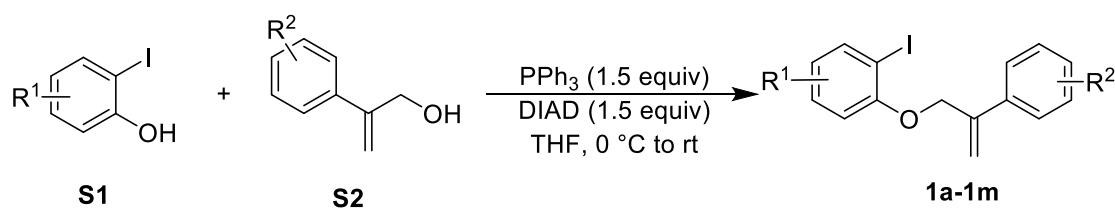
1. General Information	S3
2. Experimental procedures and Compound characterizations	S3
2.1 General procedure for the preparation of 1a-1m.....	S3
2.2 Optimization of Reaction Conditions.....	S10
3. Kinetic Experiment.....	S16
4. General procedure for the preparation of 3a-3m and characterization data.	S17
5. General procedure for the preparation of chiral Ligand and characterization data	S26
6. Possible Mechanism Cycle	S35
7. Reference	S35
8. NMR Spectra.....	S37
9. HPLC Chromatograms	S93

1. General Information

All reagents and solvents were dried and purified before use by the usual procedures. Reactions were monitored by thin-layer chromatography using silica gel. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon. Air and moisture-sensitive liquids and solutions were transferred via a syringe. Reactions were monitored by thin-layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (300 - 400 mesh). Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker 400 MHz spectrometer. ^1H and ^{13}C chemical shifts were reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak (CDCl_3 , $\delta\text{H} = 7.26$ and $\delta\text{C} = 77.16$). Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with a Waters AcQuity HPLC using a chiralcel IA column (Part No 80325) or Waters AcQuity UPLC using a chiralcel INA column (No. FM17000034).

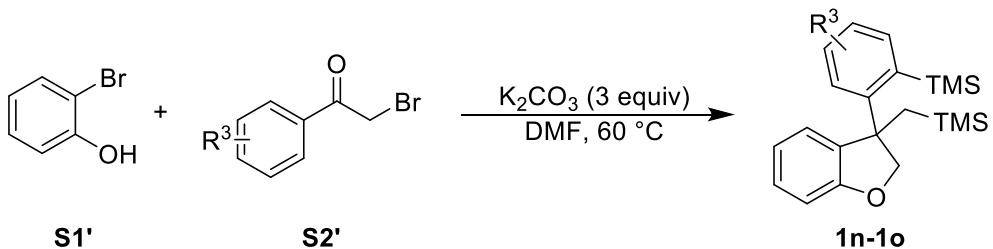
2. Experimental procedures and Compound characterizations

2.1 General procedure for the preparation of **1a-1m**.

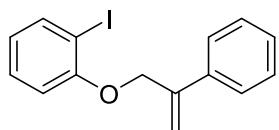


Procedure: synthesis of **1a-m**^[1a]. To a flame-dried flask was added a solution of PPh_3 (15 mmol, 1.5 equiv) and aryl iodide **S1** (10.5 mmol, 1.05 equiv), allylic alcohol **S2** (10 mmol, 1 equiv) in dry THF (40 mL) under N_2 at room temperature. Then, DIAD (15 mmol, 1.5 equiv) in dry THF (10 mL) was added dropwise at 0°C . The reaction

mixture was allowed to warm to room temperature slowly. After the reaction was complete as monitored by TLC, the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford the desired product.

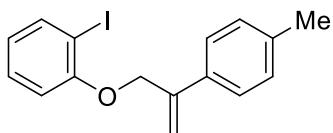


Procedure: synthesis of **1n-1o**^[1b]. In a round bottom flask equipped with a magnetic stirrer, dissolve 2-bromophenol **S1'** (10.0 mmol, 1.0 eq.) and potassium carbonate (30.0 mmol, 3.0 eq.) in DMF (60 mL). Then, the corresponding allyl bromide **S2'** (22.0 mmol, 1.2 eq.) was slowly added to the solution. The reaction mixture was stirred at 60 °C for 16 hours. The reaction mixture was quenched with NH₄Cl and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography (PE/EA = 50/1) to give the pure product.



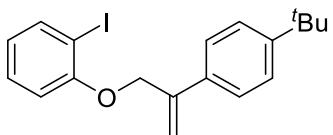
1-iodo-2-((2-phenylallyl)oxy)benzene (1a)

1a was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a colorless oil (2.856g, 85% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.42 – 7.34 (m, 3H), 7.33 – 7.28 (m, 1H), 6.89 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.75 (td, *J* = 7.6, 1.4 Hz, 1H), 5.65 (d, *J* = 3.6 Hz, 2H), 4.96 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 142.5, 139.7, 138.5, 129.5, 128.6, 128.2, 126.3, 122.9, 114.8, 112.7, 86.8, 70.6. HRMS (ESI): m/z calcd for C₁₅H₁₅INaO: 361.0060 [M+Na]⁺; found: 360.9711.



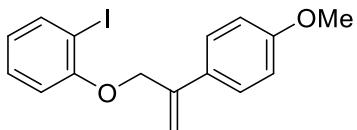
1-iodo-2-((2-(p-tolyl)allyl)oxy)benzene (1b)

1b was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.275g, 65% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (dd, J = 7.8, 1.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 7.0 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 5.50 (s, 2H), 4.83 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.2, 142.2, 139.7, 138.0, 135.5, 129.5, 129.3, 126.1, 122.9, 113.9, 112.6, 86.7, 70.5, 21.3. HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{15}\text{INaO}$: 373.0060 [M+Na]⁺; found: 373.0051.



1-((2-(4-(tert-butyl)phenyl)allyl)oxy)-2-iodobenzene (1c)

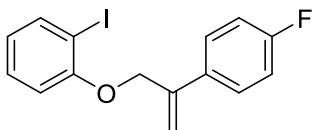
1c was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (3.371g, 86% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, J = 7.8, 1.6 Hz, 1H), 7.33 (q, J = 8.6 Hz, 4H), 7.20 (ddd, J = 8.6, 7.6, 1.6 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.64 (td, J = 7.6, 1.2 Hz, 1H), 5.52 (s, 2H), 4.85 (s, 2H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.2, 151.2, 142.1, 139.7, 135.5, 129.5, 125.9, 125.6, 122.9, 114.0, 112.7, 86.7, 70.5, 34.7, 31.4. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{21}\text{INaO}$: 415.0529 [M+Na]⁺; found: 415.0500.



1-iodo-2-((2-(4-methoxyphenyl)allyl)oxy)benzene (1d)

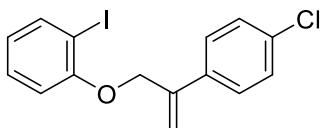
1d was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (1.684 g, 46% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, J = 7.8, 1.6 Hz, 1H), 7.45 (d, J = 8.8 Hz, 2H), 7.34 – 7.27 (m, 1H), 6.91 (d, J = 8.8 Hz, 2H),

6.88 (dd, $J = 8.2, 1.4$ Hz, 1H), 6.73 (td, $J = 7.6, 1.4$ Hz, 1H), 5.55 (d, $J = 5.4$ Hz, 2H), 4.92 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 157.2, 141.8, 139.7, 130.8, 129.5, 127.4, 122.9, 114.0, 113.3, 112.7, 86.8, 70.7, 55.4. HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{15}\text{INaO}_2$: 389.0009 [M+Na]⁺; found: 389.0010.



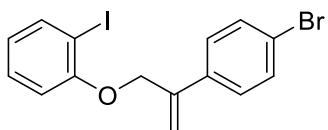
1-((2-(4-fluorophenyl)allyl)oxy)-2-iodobenzene (1e)

1e was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (1.948 g, 55% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.47 (dd, $J = 8.8, 5.4$ Hz, 2H), 7.30 (td, $J = 7.8, 1.6$ Hz, 1H), 7.06 (t, $J = 8.8$ Hz, 2H), 6.90 – 6.85 (m, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 5.60 (d, $J = 11.4$ Hz, 2H), 4.91 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 161.5, 157.1, 141.6, 139.7, 129.5, 128.1, 128.0, 123.0, 115.4, 112.6, 86.7, 70.7. ^{19}F NMR (471 MHz, CDCl_3) δ -118.3, -118.4, -118.4, -118.4. HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{12}\text{FINaO}_2$: 376.9815 [M+Na]⁺; found: 376.9848.



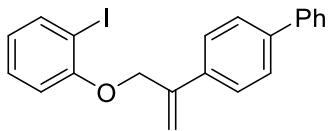
1-((2-(4-chlorophenyl)allyl)oxy)-2-iodobenzene (1f)

1f was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.294 g, 62% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.44 (d, $J = 8.6$ Hz, 2H), 7.35 (d, $J = 8.6$ Hz, 2H), 7.32 – 7.28 (m, 1H), 6.87 (dd, $J = 8.2, 1.4$ Hz, 1H), 6.75 (td, $J = 7.6, 1.4$ Hz, 1H), 5.65 (d, $J = 7.2$ Hz, 2H), 4.90 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 148.1, 146.3, 143.4, 140.6, 136.1, 135.4, 134.2, 129.7, 122.4, 119.3, 93.4, 77.2. HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{12}\text{ClINaO}$: 392.9514 [M+Na]⁺; found: 392.9524.



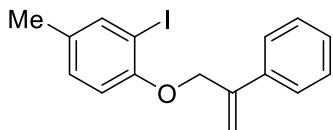
1-((2-(4-bromophenyl)allyl)oxy)-2-iodobenzene (1g)

1g was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.490 g, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 6.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.74 (td, *J* = 7.6, 1.2 Hz, 1H), 5.64 (s, 1H), 5.63 (s, 1H), 4.90 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.0, 141.6, 139.7, 137.2, 131.7, 129.5, 128.0, 123.1, 122.2, 115.8, 112.6, 86.8, 70.5. HRMS (ESI): m/z calcd for C₁₅H₁₂BrINaO: 436.9008 [M+Na]⁺; found: 436.8999.



4-(3-(2-iodophenoxy)prop-1-en-2-yl)-1,1'-biphenyl (1h)

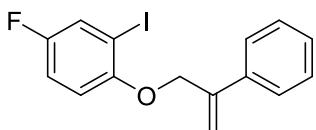
1h was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a White solid (3.625 g, 88% yield). mp 47 - 52 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.79 (m, 1H), 7.66 – 7.56 (m, 6H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.29 (m, 1H), 6.91 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.76 (td, *J* = 7.6, 1.4 Hz, 1H), 5.72 (s, 1H), 5.68 (s, 1H), 4.99 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 142.0, 141.0, 140.7, 139.7, 137.2, 129.5, 128.9, 127.6, 127.3, 127.1, 126.6, 123.0, 114.9, 112.7, 86.8, 70.6. HRMS (ESI): m/z calcd for C₂₁H₁₇INaO: 435.0216 [M+Na]⁺; found: 435.0199.



2-iodo-4-methyl-1-((2-phenylallyl)oxy)benzene (1i)

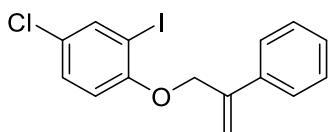
1i was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.870 g, 82% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 2.2 Hz,

1H), 7.53 – 7.48 (m, 2H), 7.40 (d, J = 6.8 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.09 (dd, J = 8.6, 2.0 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 5.63 (s, 2H), 4.92 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.2, 142.6, 140.0, 138.5, 132.5, 129.9, 128.6, 128.1, 126.2, 114.7, 112.5, 86.6, 70.7, 20.1. HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{15}\text{INaO}$: 373.0060 [M+Na]⁺; found: 373.0040.



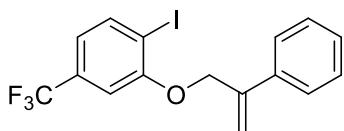
4-fluoro-2-iodo-1-((2-phenylallyl)oxy)benzene (1j)

1j was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.275 g, 65% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (dd, J = 7.6, 3.0 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.47 (d, J = 1.4 Hz, 1H), 7.37 (d, J = 7.2 Hz, 2H), 7.35 – 7.33 (m, 1H), 7.02 (ddd, J = 9.0, 7.8, 3.0 Hz, 1H), 6.80 (dd, J = 9.0, 4.6 Hz, 1H), 5.62 (dd, J = 11.2, 1.2 Hz, 2H), 4.91 (t, J = 1.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 155.8, 142.5, 138.3, 128.7, 128.2, 126.3, 115.8, 115.6, 115.0, 113.0, 86.2, 71.4. ^{19}F NMR (471 MHz, CDCl_3) δ -121.6, -121.6, -121.6, -121.6, -121.6, -121.6. HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{12}\text{FINaO}$: 376.9816 [M+Na]⁺; found: 376.9810.



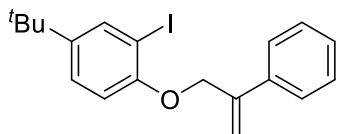
4-chloro-2-iodo-1-((2-phenylallyl)oxy)benzene (1k)

1k was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (3.256 g, 88% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 2.6 Hz, 1H), 7.42 (dd, J = 8.2, 1.6 Hz, 2H), 7.33 (d, J = 6.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.21 (dd, J = 8.8, 2.6 Hz, 1H), 6.72 (d, J = 8.8 Hz, 1H), 5.56 (d, J = 13.0 Hz, 2H), 4.87 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 142.2, 138.8, 138.2, 129.2, 128.7, 128.3, 126.8, 126.2, 115.0, 113.1, 86.9, 71.0. HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{12}\text{ClNaO}$: 392.9514 [M+Na]⁺; found: 392.9514.



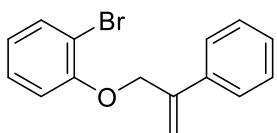
1-iodo-2-((2-phenylallyl)oxy)-4-(trifluoromethyl)benzene (1l)

1l was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a White solid (3.030 g, 75% yield). mp 34 - 37 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.43 – 7.38 (m, 1H), 7.38 – 7.31 (m, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 3.8 Hz, 2H), 4.99 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.5, 142.1, 140.2, 138.1, 128.7, 128.3, 126.3, 119.4, 119.4, 115.4, 108.9, 108.9, 91.3, 71.0. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.5, -62.8, -63.0. HRMS (ESI): m/z calcd for C₁₆H₁₂F₃INaO: 426.9783 [M+Na]⁺; found: 426.9916.



4-(tert-butyl)-2-iodo-1-((2-phenylallyl)oxy)benzene (1m)

1m was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.744 g, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 6.8 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.37 – 7.34 (m, 3H), 7.31 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 5.63 (d, *J* = 1.0 Hz, 2H), 4.93 (s, 2H), 1.30 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 146.0, 142.6, 138.5, 136.8, 128.6, 128.1, 126.4, 126.3, 114.8, 112.1, 86.7, 70.7, 34.2, 31.5. HRMS (ESI): m/z calcd for C₁₉H₂₁INaO: 415.0529 [M+Na]⁺; found: 415.0533.



1-bromo-2-((2-phenylallyl)oxy)benzene (1n)

1n was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.246 g, 78% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, *J* = 8.0,

1.6 Hz, 1H), 7.45 (d, J = 6.8 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.24 – 7.17 (m, 1H), 6.90 (d, J = 8.2 Hz, 1H), 6.80 (dd, J = 8.6, 7.0 Hz, 1H), 5.56 (d, J = 12.2 Hz, 2H), 4.90 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 117.4, 104.9, 100.8, 95.9, 91.0, 90.9, 90.6, 88.6, 84.7, 77.2, 76.3, 75.0, 32.9. HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{13}\text{BrNaO}$: 312.1628 [M+Na]⁺; found: 312.1678.



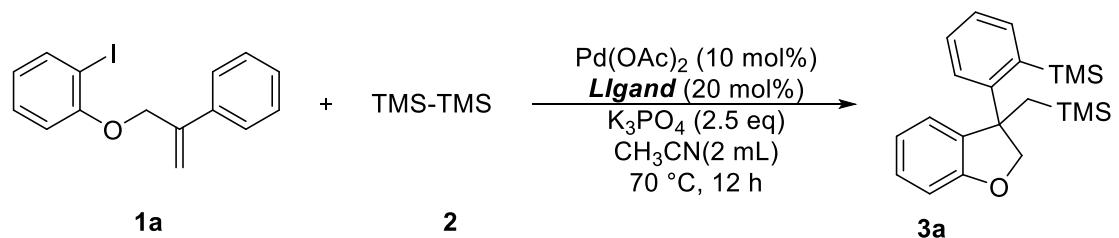
bromo-2-((2-(p-tolyl)allyl)oxy)benzene (**1o**)

1o was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford a Colorless oil (2.121 g, 70% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (dd, J = 8.0, 1.6 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.02 (dd, J = 8.0, 1.6 Hz, 1H), 6.94 (dd, J = 8.2, 1.4 Hz, 1H), 6.84 (t, J = 8.6 Hz, 1H), 5.56 (d, J = 20.2 Hz, 2H), 4.93 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.1, 152.4, 142.3, 138.0, 135.5, 133.5, 132.1, 129.3, 128.5, 126.0, 122.2, 121.9, 116.3, 113.9, 70.6, 21.3. HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{15}\text{BrNaO}$: 325.0204 [M+Na]⁺; found: 325.0454.

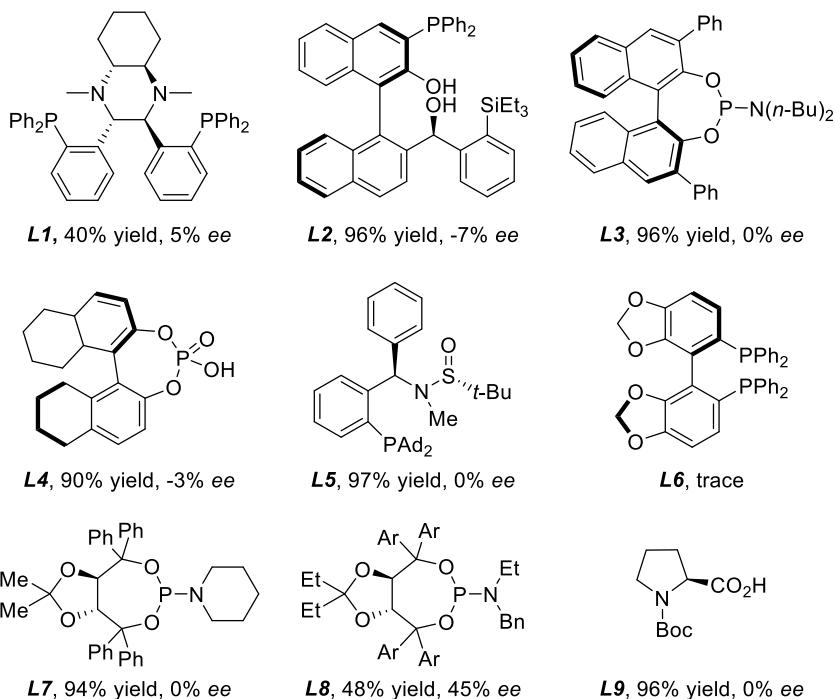
2.2 Optimization of Reaction Conditions

A mixture of $\text{Pd}(\text{OAc})_2$ (0.02 mmol, 10 mol %), Ligand (0.04 mmol, 20 mol %), and K_3PO_4 (0.5 mmol, 2.5 equiv) in CH_3CN (2 mL) was stirred at room temperature under N_2 for 30 min, then **1a** (0.2 mmol) and hexamethyldisilane **2** (1.6 mmol, 8.0 equiv) were added at room temperature under N_2 . The reaction mixture was stirred at 70 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by flash chromatography (PE/EA = 100/1) to provide the desired products **3a**. (Note: Racemic **3a** can be prepared under stander reaction conditions using PPh_3 as the *Ligand*.)

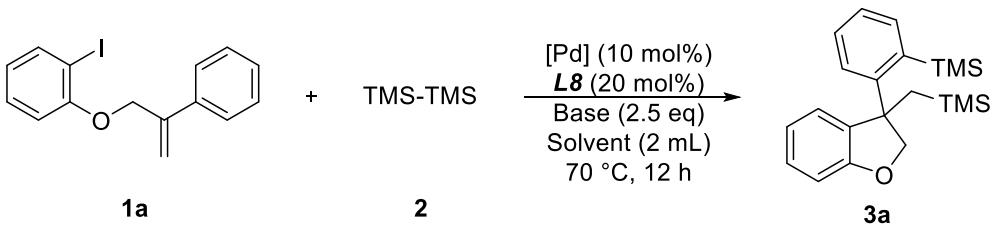
Table 1. The effect of chiral ligand.^[a]



Entry	<i>Ligand</i>	Yield (%) ^[b]	<i>Ee</i> (%) ^[c]
1	<i>PPh</i> ₃	97(95) ^[d]	-
2	L1	40	5
3	L2	96	-7
4	L3	96	0
5	L4	90	-3
6	L5	97	0
7	L6	trace	-
8	L7	68	13
9	L8 ^[e]	48	45
10	L9	96	0
11	L8 ^[f]	63	11



[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2** (1.6 mmol, 8 equiv), Pd(OAc)_2 (0.02 mmol, 10 mol%), Ligand (20 mol%), K_3PO_4 (0.5 mmol, 2.5 equiv), Solvent (2.0 mL), 70°C , 12 h. [b] GC conversion and calibrated by GC yield. [c] Determined by chiral HPLC. [d] Isolated yield. [e] The Ar of **L8** = 3,5-dimethylphenyl. [f] 2 equivalent of TMS-TMS was used.

Table 2. Optimization of chiral conditions^[a]

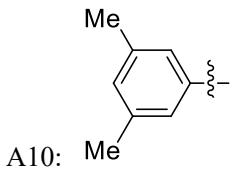
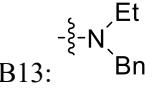
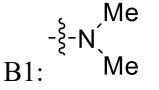
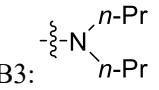
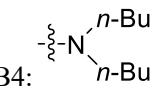
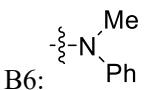
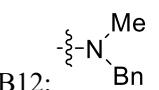
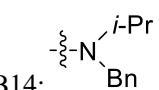
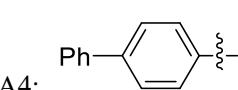
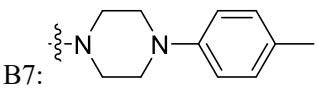
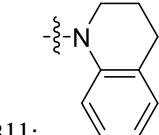
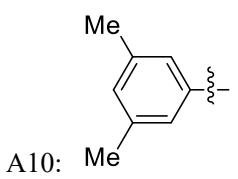
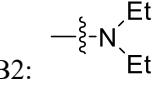
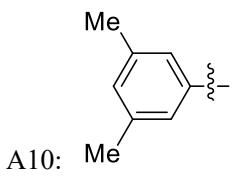
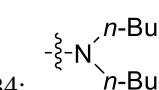
Entry	[Pd]	Base	Solvent	Yield (%) ^[b]	Ee(%) ^[c]
1	Pd(TFA) ₂	K ₃ PO ₄	CH ₃ CN	97	0
2	PdCl ₂	K ₃ PO ₄	CH ₃ CN	91	0
3	Pd(dtbpf)Cl ₂	K ₃ PO ₄	CH ₃ CN	65	57
4	Pd(dtbpf)Cl ₂	Na ₂ CO ₃	CH ₃ CN	18	34
5	Pd(dtbpf)Cl ₂	K ₂ CO ₃	CH ₃ CN	25	25
6	Pd(dtbpf)Cl ₂	Cs ₂ CO ₃	CH ₃ CN	8	7
7	Pd(dtbpf)Cl ₂	CsF	CH ₃ CN	29	25
8	Pd(dtbpf)Cl ₂	TMG	CH ₃ CN	72	0
9	Pd(dtbpf)Cl ₂	DBU	CH ₃ CN	62	0
10	Pd(dtbpf)Cl ₂	DABCO	CH ₃ CN	26	0
11	Pd(dtbpf)Cl ₂	K ₃ PO ₄	DMF	99	3
12	Pd(dtbpf)Cl ₂	K ₃ PO ₄	DMA	99	4
13	Pd(dtbpf)Cl ₂	K ₃ PO ₄	THF	62	11
14	Pd(dtbpf)Cl ₂	K ₃ PO ₄	HMPA	38	16

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2** (1.6 mmol, 8 equiv), [Pd] (0.02 mmol, 10 mol%), **L8** (0.04 mmol, 20 mol%), Base (0.5 mmol, 2.5 equiv), Solvent (2.0 mL), 70 °C, 12 h. [b] GC conversion and calibrated by GC yield. [c] Determined by chiral HPLC.

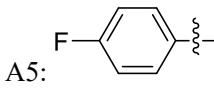
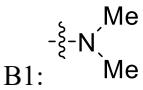
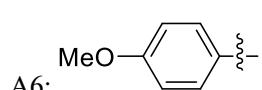
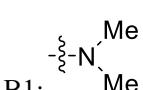
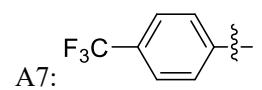
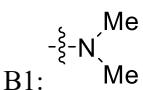
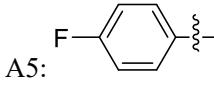
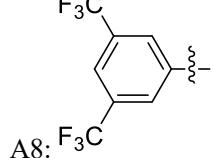
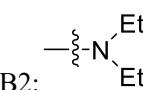
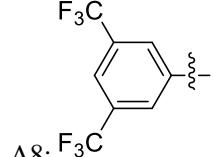
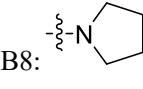
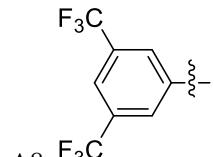
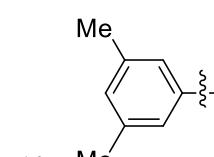
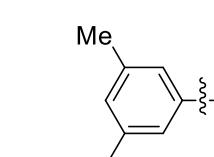
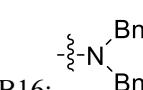
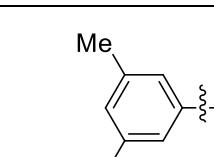
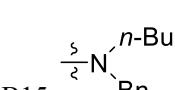
Table 3. Screening of Ligand^a

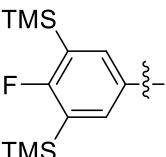
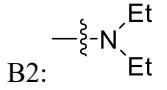
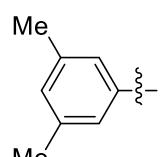
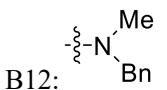
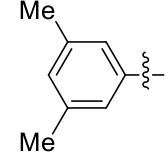
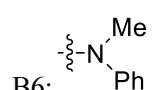
C1: R³ = R⁴ = Me
C2: R³ = R⁴ = Et
C3: R³ = Me, R⁴ = Ph
C4: R³ = Me, R⁴ = t-Bu

Ligand	A (Ar)	B	C	Yield (%) ^b	ee (%) ^c
L7 ^[2]	A1: -Ph	B9: - ξ -N(<i>cyclohexyl</i>) ₂	C1	68	13

L8	A10: 	B13: 	C2	68	45
L10^[3]	A1: -Ph	B1: 	C1	38	0
L11^[4]	A1: -Ph	B3: 	C1	68	2
L12^[5]	A1: -Ph	B4: 	C1	84	2
L13^[6]	A1: -Ph	B6: 	C1	95	4
L14^[3]	A1: -Ph	B12: 	C1	68	13
L15^[7]	A1: -Ph	B14: 	C1	91	0
L16^[8]	A4: 	B7: 	C1	72	8
L17^[2]	A1: -Ph	B11: 	C1	28	38
L18	A10: 	B2: 	C2	56	60
L19	A10: 	B4: 	C1	97	7

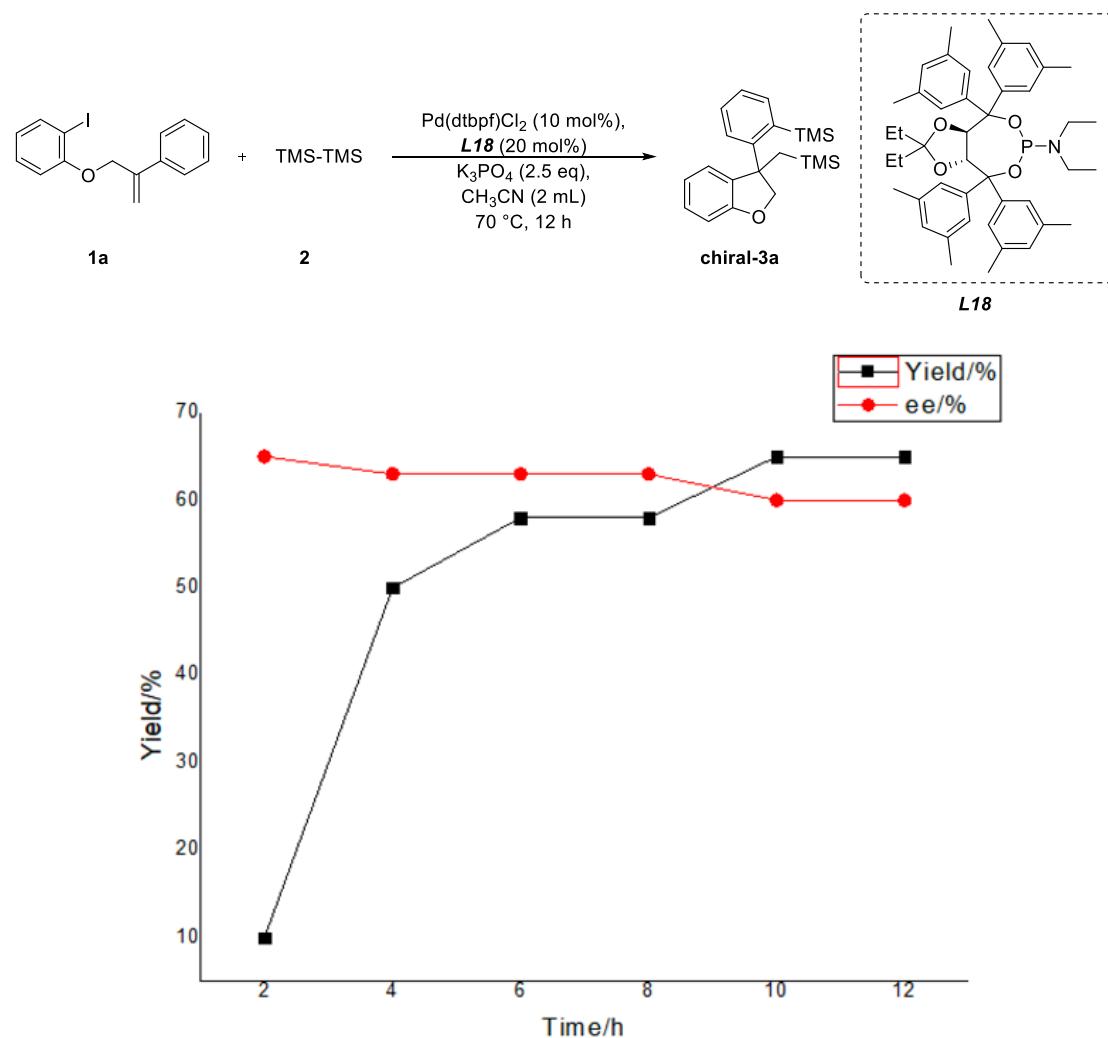
L20	 A10:	 B5:	C1	83	29
L21	 A10:	 B14:	C1	55	2
L22	 A10:	 B4:	C2	97	26
L23	 A10:	 B5:	C2	95	27
L24^[9]	 A10:	 B10:	C2	90	16
L25^[10]	 A10:	 B6:	C4	83	0
L26^[11]	 A2:	 B8:	C1	66	0
L27^[3]	 A3:	 B1:	C1	97	0
L28^[12]	 A9:	 B1:	C1	97	0
L29^[3]	 A4:	 B1:	C1	42	0

L30^[3]	A5: 	B1: 	C1	45	2
L31^[3]	A6: 	B1: 	C1	74	3
L32^[3]	A7: 	B1: 	C1	23	18
L33^[13]	A5: 	B17: —Ph	C1	75	5
L34^[14]	A8: 	B2: 	C1	42	0
L35^[15]	A8: 	B8: 	C1	55	6
L36^[16]	A8: 	B17: —Ph	C1	92	3
L37^[17]	A10: 	B17: —Ph	C2	96	0
L38	A10: 	B16: 	C2	81	15
L39	A10: 	B15: 	C2	82	32

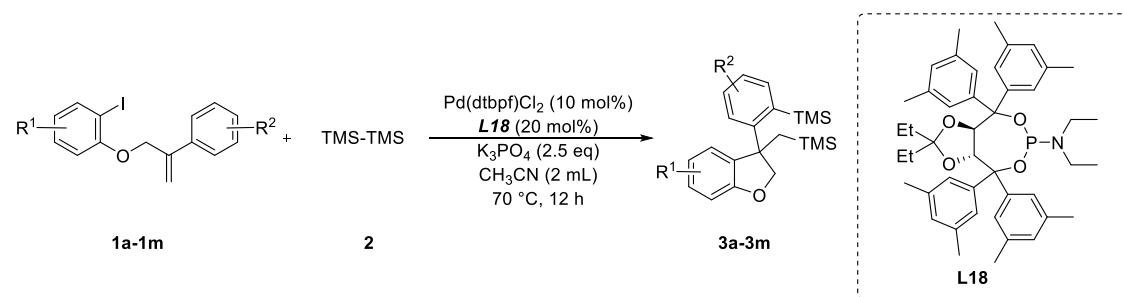
L40	 A11: TMS	 B2:	C2	75	7
L41	 A10: Me	 B12:	C2	22	50
L42^[10]	 A10: Me	 B6:	C3	83	0

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2** (1.6 mmol, 8 equiv), Pd(dtbpf)Cl₂(0.02 mmol, 10 mol%), **Ligand** (0.04 mmol, 20 mol%), K₃PO₄ (0.5 mmol, 2.5 equiv), CH₃CN (2.0 mL), 70 °C, 12 h. [b] GC conversion and calibrated by GC yield. [c] Determined by chiral HPLC.

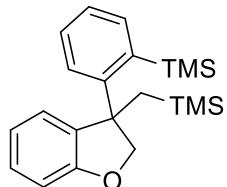
3. Kinetic Experiment



4. General procedure for the preparation of 3a-3m and characterization data

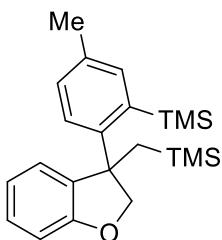


To a 25 mL reaction tube, Pd(dtbpf)Cl₂ (0.02 mmol, 10 mol%), **L18** (0.04 mmol, 20 mol%) and K₃PO₄ (0.5 mmol, 2.5 equiv) were added. Evacuated the reaction tube and refilled it with the N₂ gas mixture through the balloon and then CH₃CN (2 mL) was added. The reaction was stirred at room temperature for half an hour. Then add **1a-1m** (0.2 mmol, 1.0 equiv.) and **2** (1.6 mmol, 8.0 equiv) in sequence. The resulting solution was heated to 70 °C for 12 hours. After the reaction finished, cool down the mixture to room temperature and release the N₂ gas mixture carefully in the fume hood. The resulting solution was heated to 70 °C for 12 hours. After the reaction is complete, cool the mixture to room temperature and carefully release the N₂ gas mixture in a fume hood. The reaction mixture was diluted with EtOAc, filtered through Celite, concentrated in vacuo, and separated by column chromatography (PE/EA = 100/1) to obtain the target product **3a-3m**. The ee value is determined by Waters Technologies HPLC system or Waters AcQuity UPLC on a chiral stationary phase.



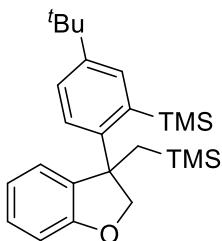
trimethyl(2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (3a).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a Colorless oil (44.9 mg, 62% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.55 (d, *J* = 19.8 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.35 – 7.25 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 5.00 (dd, *J* = 66.0, 8.8 Hz, 2H), 2.28 (d, *J* = 15.0 Hz, 1H), 1.79 (d, *J* = 15.0 Hz, 1H), 0.74 (s, 9H), 0.14 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 155.4, 137.7, 137.4, 134.1, 128.8, 128.6, 127.3, 127.1, 125.5, 120.4, 110.2, 84.7, 55.0, 32.1, 3.4, 0.2. HRMS (ESI): m/z calcd for C₂₁H₃₀NaOSi₂: 377.1726 [M+Na]⁺; found: 377.1769. HPLC: Chiraldpak IA column (hexanes: isopropanol = 100:0, 0.3 mL/min, 230 nm); t_R = 31.0 min (major), t_R = 37.4 min (minor); 80 : 20 er. (60% ee)



trimethyl(5-methyl-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (3b).

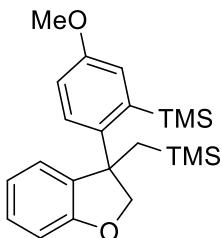
Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (51.5 mg, 70% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (s, 1H), 7.46 – 7.35 (m, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.18 – 7.06 (m, 3H), 7.02 (d, J = 8.0 Hz, 1H), 4.93 (d, J = 8.8 Hz, 1H), 4.76 (d, J = 8.8 Hz, 1H), 2.48 (s, 3H), 2.14 (d, J = 15.0 Hz, 1H), 1.63 (d, J = 15.0 Hz, 1H), 0.60 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 152.5, 138.5, 137.2, 134.6, 134.3, 129.2, 128.7, 127.3, 127.0, 120.4, 110.1, 84.7, 54.6, 32.2, 21.0, 3.4, 0.2. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{32}\text{NaOSi}_2$: 391.1884 [M+Na]⁺; found: 391.1900. UPLC: Chiralpak INA column (hexanes: isopropanol = 100:0, 0.3 mL/min, 230 nm); t_R = 8.8 min (major), t_R = 12.4 min (minor); 71 : 29 er. (42% ee)



(5-(tert-butyl)-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3c).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (67.3 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 2.4 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.13 (d, J = 8.0 Hz, 1H), 5.04 (d, J = 8.8 Hz, 1H), 4.89 (d, J = 8.8 Hz, 1H), 2.26 (d, J = 15.0 Hz, 1H), 1.79 (d, J = 15.0 Hz, 1H), 1.58 (s, 9H), 0.72 (s, 9H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 152.4,

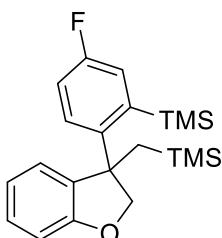
147.4, 136.5, 134.9, 134.4, 128.7, 127.1, 127.0, 125.4, 120.4, 110.1, 84.7, 54.5, 34.5, 32.1, 31.4, 3.5, 0.2. HRMS (ESI): m/z calcd for $C_{25}H_{38}NaOSi_2$: 433.2353 [M+Na]⁺; found: 433.2341. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 254 nm); t_R = 7.3 min (major), t_R = 8.3 min (minor); 68 : 32 er. (36% ee)



(5-methoxy-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3d).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid. (42.3 mg, 55% yield).

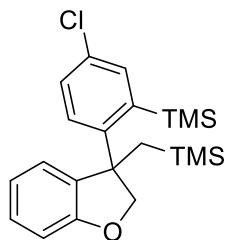
¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 3.0 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.31 (dd, J = 7.6, 1.4 Hz, 1H), 7.15 (dd, J = 8.2, 5.2 Hz, 2H), 7.04 (d, J = 9.0 Hz, 1H), 6.83 (dd, J = 8.8, 3.0 Hz, 1H), 4.93 (d, J = 8.8 Hz, 1H), 4.76 (d, J = 8.8 Hz, 1H), 3.95 (s, 3H), 2.14 (d, J = 15.0 Hz, 1H), 1.65 (d, J = 15.0 Hz, 1H), 0.62 (s, 9H), 0.02 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 156.7, 147.5, 139.1, 134.6, 128.7, 128.6, 126.9, 124.6, 120.4, 111.8, 110.1, 84.8, 55.2, 54.2, 32.2, 3.3, 0.2. HRMS (ESI): m/z calcd for $C_{22}H_{32}NaO_2Si_2$: 407.1845 [M+Na]⁺; found: 407.1845. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_R = 11.4 min (major), t_R = 16.1 min (minor); 81 : 19 er. (62% ee)



(5-fluoro-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3e).

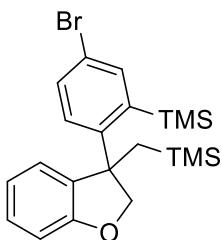
Following the general procedure, the product was isolated by column chromatography

with PE/EA = 100/1 as the eluent to give a White solid (48.4 mg, 65% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.67 (dd, J = 10.2, 3.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 7.07 – 6.97 (m, 1H), 5.01 (d, J = 8.8 Hz, 1H), 4.82 (d, J = 8.8 Hz, 1H), 2.20 (d, J = 15.0 Hz, 1H), 1.73 (d, J = 15.0 Hz, 1H), 0.69 (s, 9H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ ^{13}C NMR (101 MHz, CDCl_3) δ 160.0, 151.0, 140.6, 134.2, 128.9, 126.8, 124.1, 123.9, 120.6, 114.7, 114.5, 110.3, 84.7, 54.4, 32.2, 3.2, 0.2. ^{19}F NMR (471 MHz, CDCl_3) δ -118.4, -118.4, -118.4, -118.4. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{29}\text{FNaOSi}_2$: 395.1639 [M+Na]⁺; found: 395.1634. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_R = 8.2 min (major), t_R = 10.0 min (minor); 75 : 25 er. (50% ee)



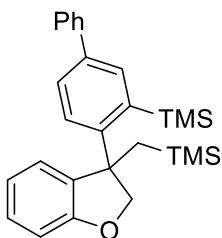
(5-chloro-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3f).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (48.9 mg, 63% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 2.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.19 – 7.11 (m, 2H), 7.07 – 6.96 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 4.81 (d, J = 8.8 Hz, 1H), 4.61 (d, J = 8.8 Hz, 1H), 1.99 (d, J = 15.0 Hz, 1H), 1.47 (d, J = 15.6 Hz, 1H), 0.50 (s, 9H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 146.9, 135.7, 132.6, 128.9, 128.9, 128.1, 124.9, 121.4, 110.6, 85.1, 52.3, 29.5, 1.5, 0.3. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{29}\text{ClNaO}_2\text{Si}_2$: 411.1343 [M+Na]⁺; found: 411.1337. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_R = 8.1 min (major), t_R = 10.1 min (minor); 80 : 20 er. (60% ee)



(5-bromo-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3g).

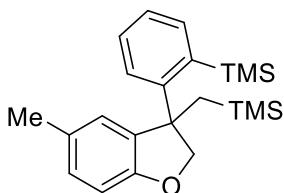
Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (51.9 mg, 60% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 1.6$ Hz, 1H), 7.29 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.21 (td, $J = 7.8, 1.6$ Hz, 1H), 7.12 (dd, $J = 7.4, 1.4$ Hz, 1H), 7.01 – 6.94 (m, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 4.76 (d, $J = 8.8$ Hz, 1H), 4.60 (d, $J = 8.8$ Hz, 1H), 1.97 (d, $J = 15.0$ Hz, 1H), 1.48 (d, $J = 15.0$ Hz, 1H), 0.43 (s, 9H), 0.23 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 152.4, 147.4, 136.5, 134.9, 134.4, 128.7, 127.1, 127.0, 125.4, 120.4, 110.1, 84.7, 54.5, 31.4, 3.5, 1.2. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{29}\text{BrNaOSi}_2$: 455.0836 [M+Na]⁺; found: 455.0998. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_R = 7.2 min (minor), t_R = 7.9 min (major); 12 : 88 er. (76% ee)



trimethyl((3-(3-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)-2,3-dihydrobenzofuran-3-yl)methyl)trimethylsilane (3h).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (83.5 mg, 97% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 2.2$ Hz, 1H), 7.74 (d, $J = 7.0$ Hz, 2H), 7.63 (t, $J = 7.8$ Hz, 2H), 7.57 – 7.52 (m, 2H), 7.44 (d, $J = 8.2$ Hz, 1H), 7.37 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 8.2$ Hz, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 7.8$ Hz, 1H), 5.00 (d, $J = 8.8$ Hz, 1H), 4.84 (d, $J = 8.8$ Hz, 1H), 2.20 (d, $J = 15.0$ Hz, 1H), 1.72 (d, $J =$

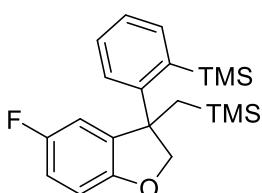
15.0 Hz, 1H), 0.68 (s, 9H), 0.05 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 154.5, 141.1, 138.0, 137.9, 136.6, 134.1, 128.9, 128.8, 127.8, 127.3, 127.2, 127.2, 127.0, 120.5, 110.2, 84.6, 54.7, 32.0, 3.4, 0.2. HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{34}\text{NaOSi}_2$: 453.2040 [M+Na] $^+$; found: 453.2030. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_{R} = 11.7 min (minor), t_{R} = 16.1 min (major); 23 : 77 er. (54% ee)



trimethyl(2-(5-methyl-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (3i).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (72.2 mg, 98% yield).

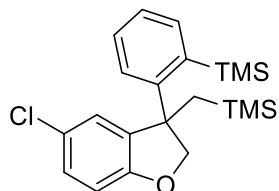
^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, J = 7.0, 2.0 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.26 – 7.16 (m, 2H), 7.10 (s, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.93 (d, J = 8.8 Hz, 1H), 4.77 (d, J = 8.8 Hz, 1H), 2.53 (s, 3H), 2.14 (d, J = 15.0 Hz, 1H), 1.65 (d, J = 15.0 Hz, 1H), 0.61 (s, 9H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.0, 155.4, 137.6, 137.4, 134.0, 129.6, 129.1, 128.6, 127.6, 127.3, 125.4, 109.6, 84.8, 54.9, 32.0, 21.1, 3.4, 0.2. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{32}\text{NaOSi}_2$: 391.1884 [M+Na] $^+$; found: 391.1910. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_{R} = 8.5 min (minor), t_{R} = 10.2 min (major); 38 : 62 er. (24% ee)



(2-(5-fluoro-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3j).

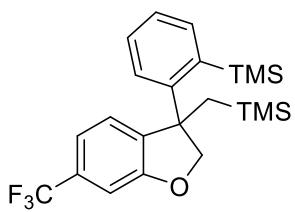
Following the general procedure, the product was isolated by column chromatography

with PE/EA = 100/1 as the eluent to give a White solid (37.2 mg, 50% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, J = 10.2, 3.0 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.22 – 7.16 (m, 3H), 7.08 (d, J = 8.0 Hz, 1H), 7.03 – 6.96 (m, 1H), 4.96 (d, J = 8.8 Hz, 1H), 4.77 (d, J = 8.8 Hz, 1H), 2.16 (d, J = 15.0 Hz, 1H), 1.69 (d, J = 15.0 Hz, 1H), 0.65 (s, 9H), 0.05 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 140.7, 140.6, 134.2, 128.9, 126.8, 124.1, 123.9, 120.6, 114.7, 114.5, 110.2, 84.7, 54.4, 32.2, 3.2, 0.2. ^{19}F NMR (471 MHz, CDCl_3) δ -124.1, -124.1, -124.1, -124.1, -124.2, -124.2. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{29}\text{FNaOSi}_2$: 396.1672 [M+Na]⁺; found : 396.1669. UPLC: Chiralpak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 254 nm); t_{R} = 8.8 min (minor), t_{R} = 9.9 min (major); 36 : 64 er. (28% ee)



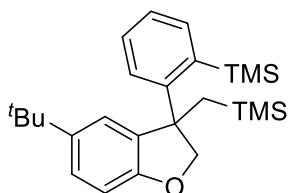
(2-(5-chloro-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3k).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (52.0 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 9.0 Hz, 1H), 7.34 (td, J = 5.0, 2.2 Hz, 3H), 7.23 (d, J = 2.2 Hz, 1H), 7.19 – 7.11 (m, 1H), 6.94 (d, J = 8.6 Hz, 1H), 4.94 (d, J = 8.8 Hz, 1H), 4.78 (d, J = 8.8 Hz, 1H), 2.13 (d, J = 15.0 Hz, 1H), 1.59 (d, J = 15.0 Hz, 1H), 0.58 (s, 9H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 154.4, 137.8, 137.3, 136.3, 128.8, 128.7, 127.1, 127.1, 125.7, 125.2, 111.2, 85.2, 55.2, 32.1, 3.4, 0.2. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{29}\text{ClNaOSi}_2$: 411.1345 [M+Na]⁺; found : 411.1340. UPLC: Chiralpak INA column (hexanes: isopropanol = 100: 0, 0.3 mL/min, 230 nm); t_{R} = 8.5 min (major), t_{R} = 10.0 min (minor); 68 : 32 er. (36% ee)



trimethyl(2-(6-(trifluoromethyl)-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (82.7 mg, 98% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.03 (dd, $J = 7.4, 1.8$ Hz, 1H), 7.54 (s, 2H), 7.45 (ddd, $J = 11.0, 7.4, 1.6$ Hz, 2H), 7.37 (s, 1H), 7.19 (dd, $J = 8.0, 1.4$ Hz, 1H), 5.11 (d, $J = 9.0$ Hz, 1H), 4.94 (d, $J = 8.8$ Hz, 1H), 2.28 (d, $J = 15.0$ Hz, 1H), 1.74 (d, $J = 14.8$ Hz, 1H), 0.70 (s, 9H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 152.5, 138.5, 137.2, 134.6, 134.3, 129.2, 128.7, 127.4, 127.0, 120.4, 110.1, 84.7, 54.6, 32.2, 21.0, 3.4, 0.2. ^{19}F NMR (471 MHz, CDCl_3) δ -62.1. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{29}\text{F}_3\text{NaOSi}_2$: 445.1601 [M+Na]⁺; found : 445.1626. UPLC: Chiraldak INA column (hexanes: isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_{R} = 7.6 min (minor), t_{R} = 8.7 min (major); 34 : 66 er. (32% ee)

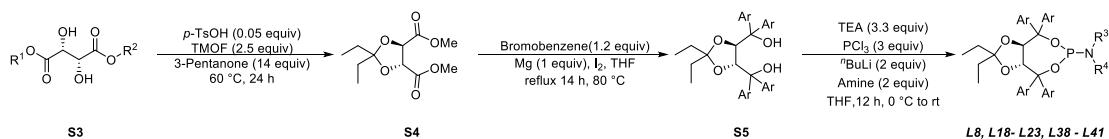


(2-(5-(tert-butyl)-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3m).

Following the general procedure, the product was isolated by column chromatography with PE/EA = 100/1 as the eluent to give a White solid (55.0 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 7.0, 2.0$ Hz, 1H), 7.48 – 7.42 (m, 1H), 7.40 – 7.34 (m, 3H), 7.23 (d, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 4.97 (d, $J = 8.8$ Hz, 1H), 4.79 (d, $J = 8.8$ Hz, 1H), 2.19 (d, $J = 15.0$ Hz, 1H), 1.71 (d, $J = 15.0$ Hz, 1H), 1.53 (s, 9H), 0.64 (s, 9H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 155.5,

143.3, 137.6, 137.5, 133.4, 128.6, 127.3, 125.5, 125.4, 124.0, 109.2, 84.8, 55.1, 34.6, 32.0, 31.9, 3.4, 0.2. HRMS (ESI): m/z calcd for C₂₅H₃₈NaOSi₂: 433.2353 [M+Na]⁺; found : 433.2368. UPLC: Chiralpak INA column (hexanes : isopropanol = 100 : 0, 0.3 mL/min, 230 nm); t_R = 6.9 min (major), t_R = 8.4 min (minor); 73 : 27 er. (46% ee)

5. General procedure for the preparation of chiral Ligand and characterization data

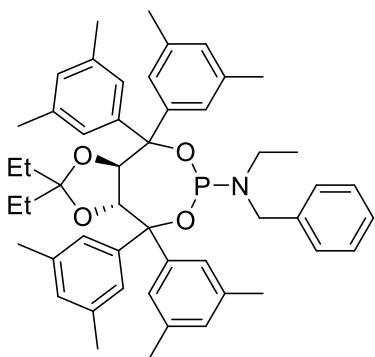


Procedure: synthesis of S4. Dimethyl (2*R*,3*R*)-tartrate (**S3**) (50 mmol, 1 equiv) was dissolved in 3-pentanone (700 mmol, 14 equiv) before trimethyl orthoformate (125 mmol, 2.5 equiv) and p-TsOH (2.5 mmol, 0.05 equiv) were added. The resulting mixture was heated to 60 °C. After stirring for 24 h under argon atmosphere trimethyl orthoformate (41.5 mmol, 0.83 equiv) was admixed and the reaction was stirred for a further 24 h. After cooling to room temperature the reaction mixture was neutralized with NaHCO₃ solution and extracted three times with EtOAc. The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated to obtain title compound as a pure yellowish oil that can be used without further purification.

Procedure: synthesis of S5. To a flame dried 2-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser was added freshly crushed magnesium turnings (45.0 mmol, 4.5 equiv) under N₂. The apparatus was flame-dried three times, a single crystal of I₂ was added and the reaction mixture was diluted with THF. The corresponding bromobenzene (44 mmol, 4.4 equiv) was slowly added to the magnesium mixture at room temperature via a syringe. The reaction was allowed to reflux at 80 °C in an oil bath for 2 h, at which time the reaction was cooled to 0 °C, and a solution of **S4** (10.00 mmol, 1.0 equiv) in THF was added slowly via syringe. The reaction was allowed to reflux for 12 h, after which it was cooled to 0 °C and quenched with NH₄Cl aqueous solution. The organic and aqueous layers were

separated and the aqueous layer was extracted with EtOAc. The combined organics were dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified by silica gel chromatography (PE/EA = 20:1-10:1) to afford the title compound as a white solid.

Procedure: synthesis of **L8, L18 - L23, L38 - L41**. The corresponding amine (2 mmol, 2.0 equiv) was dissolved in THF(2.5 mL), n-butyllithium(0.8 mL, 2.0 equiv, 2.5 M) at 0 °C, and after stirring for half an hour, PCl₃ (3 mmol, 3.0 equiv) was added at 0 °C, and stirred at room temperature for 1 hour. Then the solvent is removed. Then **S5** (1 mmol, 1.0 equiv) and triethylamine (3.3 mmol, 3.3 equiv) dissolved in THF were injected into the reaction system through a syringe at 0 °C, and stirred at room temperature overnight. Quenched with NH₄Cl. The organic and aqueous layers were separated and the aqueous layer was extracted with EtOAc. The combined organics were dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified by silica gel chromatography (PE/EA/Et₃N = 100:1:1) to afford the title compound as a white solid.

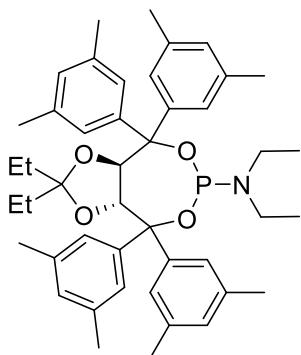


(3aR,8aR)-N-benzyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-N,2,2-triethyltetrahydro-1,3-dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (L8).

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a white solid (662 mg, 86% yield).

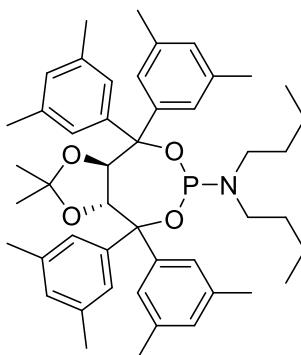
¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.36 – 7.27 (m, 6H), 7.22 (d, *J* = 11.0 Hz, 3H), 7.00 (s, 2H), 6.94 – 6.81 (m, 4H), 5.05 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.82 (d, *J* = 8.6 Hz, 1H), 4.29 (dd, *J* = 7.4, 3.6 Hz, 2H), 3.06 (dq, *J* = 14.0, 7.0 Hz, 2H), 2.33 (s, 6H), 2.28 (s, 12H), 2.22 (s, 6H), 1.43 (dt, *J* = 55.2, 6.8 Hz, 3H), 1.07 (t, *J*

δ = 7.0 Hz, 3H), 0.88 – 0.66 (m, 4H), 0.40 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.2, 136.8, 136.3, 128.3, 125.2, 115.4, 83.3, 81.5, 47.8, 39.6, 29.8, 21.7, 14.6, 8.6. ^{31}P NMR (202 MHz, CDCl_3) δ 138.7. HRMS (ESI): m/z calcd for $\text{C}_{50}\text{H}_{60}\text{NNaO}_4\text{P}$: 792.4158 [M+Na]⁺; found : 792.4168.



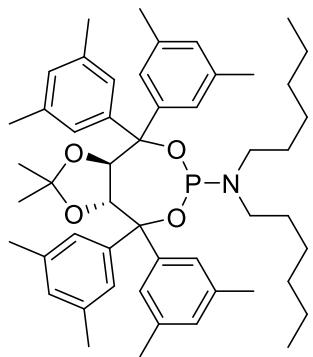
(3*R*,8*R*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-N,N,2,2-tetraethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (L18).

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a white solid (622 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (s, 2H), 7.22 (d, J = 14.6 Hz, 4H), 7.02 (s, 2H), 6.87 (d, J = 20.4 Hz, 4H), 4.97 (dd, J = 8.8, 3.0 Hz, 1H), 4.78 (s, 1H), 3.24 – 3.12 (m, 4H), 2.31 (d, J = 2.8 Hz, 12H), 2.26 (s, 12H), 1.45 (s, 4H), 1.15 (t, J = 7.0 Hz, 6H), 0.72 (t, J = 7.6 Hz, 3H), 0.40 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.2, 136.7, 127.0, 125.1, 115.2, 82.8, 81.4, 39.0, 27.1, 21.8, 15.4, 8.6. ^{31}P NMR (202 MHz, CDCl_3) δ 140.1. HRMS (ESI): m/z calcd for $\text{C}_{45}\text{H}_{58}\text{NNaO}_4\text{P}$: 730.4002 [M+Na]⁺; found : 730.4013.



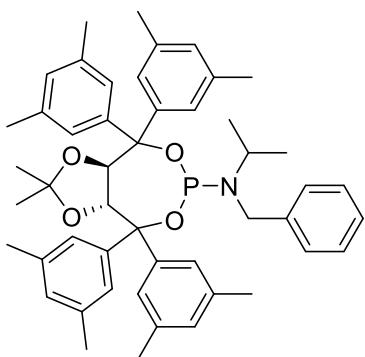
(3a*R*,8a*R*)-N,N-dibutyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-dimethyltetrahydrono-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (L19)

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a White solid (558 mg, 76% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 2H), 7.22 (s, 2H), 7.07 (d, *J* = 14.0 Hz, 4H), 6.91 – 6.80 (m, 4H), 5.11 (dd, *J* = 8.6, 3.6 Hz, 1H), 4.69 (d, *J* = 8.6 Hz, 1H), 3.17 (dd, *J* = 10.0, 6.2 Hz, 4H), 2.29 (d, *J* = 3.2 Hz, 24H), 1.68 – 1.44 (m, 8H), 1.35 (q, *J* = 7.6 Hz, 6H), 0.95 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 137.1, 127.2, 125.3, 111.2, 83.5, 80.9, 45.1, 27.9, 25.5, 21.7, 20.6, 14.2. ³¹P NMR (202 MHz, CDCl₃) δ 140.8. HRMS (ESI): m/z calcd for C₄₇H₆₂NNaO₄P: 758.4313 [M+Na]⁺; found : 758.4305.



(3a*R*,8a*R*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-N,N-dihexyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphhepin-6-amine (L20)

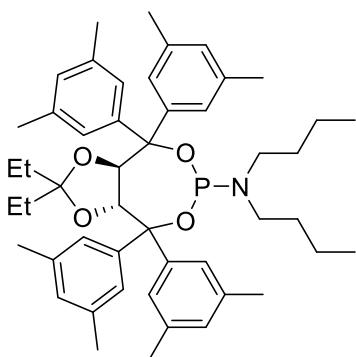
Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a White solid (515 mg, 65% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 2H), 7.23 (s, 2H), 7.08 (d, *J* = 9.0 Hz, 4H), 6.93 – 6.78 (m, 4H), 5.11 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.71 (d, *J* = 8.4 Hz, 1H), 3.28 – 3.03 (m, 4H), 2.30 (s, 24H), 1.54 (d, *J* = 61.6 Hz, 8H), 1.32 (s, 14H), 0.90 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 137.1, 136.2, 127.2, 125.3, 111.3, 82.9, 45.5, 32.0, 27.9, 27.2, 25.5, 22.9, 21.8, 14.2. ³¹P NMR (202 MHz, CDCl₃) δ 140.7. HRMS (ESI): m/z calcd for C₅₁H₇₀NNaO₄P: 814.4939 [M+Na]⁺; found : 815.4923.



(3a*R*,8a*R*)-N-benzyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-N-isopropyl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphhepin-6-amine (L21)

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a White solid (582 mg, 77% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.57 (s, 4H), 7.33 (d, *J* = 14.6 Hz, 5H), 7.09 (d, *J* = 8.6 Hz, 4H), 6.88 (dd, *J* = 21.2, 15.4 Hz, 4H), 5.20 (dd, *J* = 8.6, 3.6 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 2H), 4.50 (d, *J* = 15.6 Hz, 1H), 3.52 (dt, *J* = 14.0, 7.0 Hz, 1H), 2.29 (d, *J* = 31.4 Hz, 24H), 1.54 (s, 3H), 1.15 (dd, *J* = 24.2, 6.8 Hz, 6H), 0.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 136.8, 128.4, 128.3, 125.2, 111.2, 83.5, 81.7, 48.8, 28.0, 25.4, 21.7, 1.2. ³¹P NMR (202 MHz, CDCl₃) δ 137.8. HRMS (ESI): m/z calcd for C₄₉H₅₈NNaO₄P: 778.4002 [M+Na]⁺; found : 778.4028

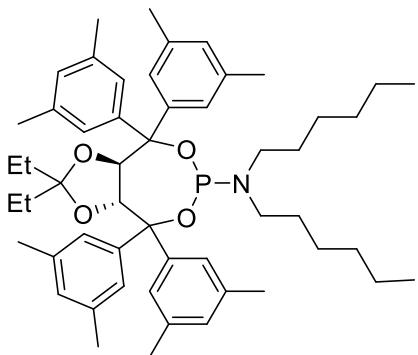


(3*R*,8*R*)-N,N-dibutyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-diethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphhepin-6-amine (L22)

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a white solid (626 mg, 82% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.35 (s, 2H), 7.24 (s, 2H), 7.16 (s, 2H), 7.03 (s, 2H), 6.86 (d, *J* = 17.2 Hz, 4H), 4.99 (dd, *J* = 8.8, 3.0 Hz, 1H), 4.76 (d, *J* = 8.8 Hz, 1H),

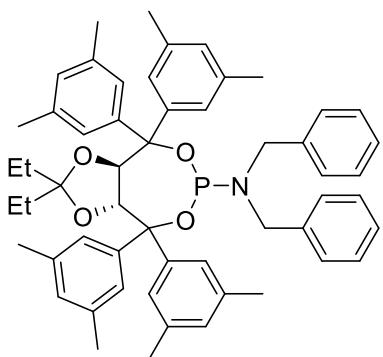
3.20 – 2.97 (m, 4H), 2.29 (d, J = 14.8 Hz, 24H), 1.56 (dt, J = 14.8, 7.1 Hz, 4H), 1.35 – 1.27 (m, 4H), 0.92 (t, J = 7.2 Hz, 6H), 0.75 (t, J = 7.6 Hz, 6H), 0.38 (d, J = 3.0 Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 137.1, 136.7, 125.2, 115.1, 82.3, 81.5, 45.2, 31.8, 29.8, 21.7, 20.5, 14.2, 8.6. ^{31}P NMR (202 MHz, CDCl_3) δ 139.9. HRMS (ESI): m/z calcd for $\text{C}_{49}\text{H}_{66}\text{NNaO}_4\text{P}$: 786.4628 [M+Na]⁺; found : 785.4610



(3*R*,8*R*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-diethyl-N,N-dihexyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphhepin-6-amine (*L*23).

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a white solid (680 mg, 83% yield).

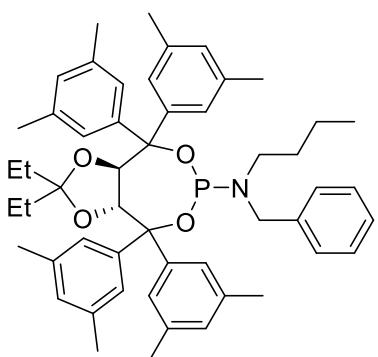
^1H NMR (400 MHz, CDCl_3) δ 7.34 (s, 2H), 7.23 (s, 2H), 7.16 (s, 2H), 7.02 (s, 2H), 6.86 (dd, J = 15.8, 4.8 Hz, 4H), 4.98 (dd, J = 8.8, 3.0 Hz, 1H), 4.77 (d, J = 8.8 Hz, 1H), 3.17 – 2.90 (m, 4H), 2.28 (d, J = 16.0 Hz, 24H), 1.58 – 1.49 (m, 4H), 1.46 – 1.37 (m, 2H), 1.29 (s, 14H), 0.91 – 0.86 (m, 6H), 0.74 (t, J = 7.4 Hz, 3H), 0.38 (d, J = 3.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 137.1, 136.3, 125.2, 115.2, 82.5, 81.9, 45.5, 32.0, 29.8, 28.5, 27.1, 22.9, 21.7, 14.2, 8.6. ^{31}P NMR (202 MHz, CDCl_3) δ 139.9. HRMS (ESI): m/z calcd for $\text{C}_{53}\text{H}_{74}\text{NNaO}_4\text{P}$: 842.5254 [M+Na]⁺; found : 842.5268.



(3*R*,8*R*)-N,N-dibenzyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-diethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (L38).

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a white solid (758 mg, 90% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.41 (s, 2H), 7.32 (s, 2H), 7.29 (d, *J* = 4.2 Hz, 8H), 7.26 – 7.21 (m, 2H), 7.17 (s, 2H), 7.01 (s, 2H), 6.88 (dd, *J* = 28.8, 12.0 Hz, 4H), 5.12 (dd, *J* = 8.6, 3.2 Hz, 1H), 4.85 (d, *J* = 8.6 Hz, 1H), 4.26 – 4.01 (m, 4H), 2.32 (d, *J* = 19.2 Hz, 12H), 2.21 (d, *J* = 14.4 Hz, 12H), 1.69 – 1.45 (m, 2H), 1.36 (dd, *J* = 14.0, 7.2 Hz, 1H), 0.91 – 0.79 (m, 1H), 0.74 (t, *J* = 7.6 Hz, 3H), 0.43 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.2, 136.9, 128.7, 128.3, 125.2, 115.4, 83.7, 81.9, 48.2, 29.8, 21.8, 8.6. ³¹P NMR (202 MHz, CDCl₃) δ 138.7. HRMS (ESI): m/z calcd for C₅₅H₆₂NNaO₄P: 854.4313 [M+Na]⁺; found : 854.4408.

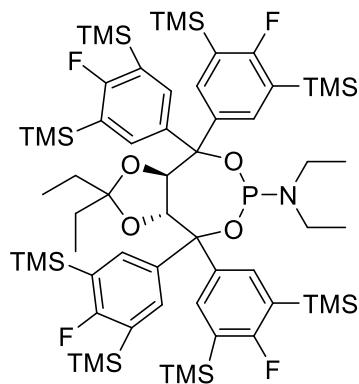


(3a*R*,8a*R*)-N-benzyl-N-butyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-diethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (L39)

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a White solid (447 mg, 56% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.34 (m, 3H), 7.29 (s, 2H), 7.20 (d, *J* = 13.8 Hz,

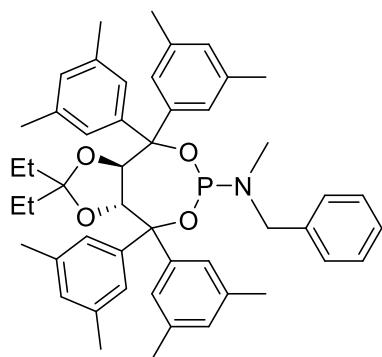
4H), 6.99 (d, $J = 8.0$ Hz, 3H), 6.96 – 6.74 (m, 5H), 5.31 – 4.99 (m, 1H), 4.81 (d, $J = 8.6$ Hz, 1H), 4.42 – 4.12 (m, 1H), 2.96 (dt, $J = 12.8, 6.4$ Hz, 1H), 2.36 – 2.21 (m, 24H), 1.37 (dd, $J = 14.0, 7.2$ Hz, 2H), 1.32 – 1.18 (m, 4H), 0.84 (t, $J = 7.4$ Hz, 4H), 0.73 (t, $J = 7.6$ Hz, 3H), 0.53 – 0.40 (m, 3H), 0.38 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.2, 136.8, 128.3, 125.2, 117.8, 115.3, 88.4, 81.7, 45.2, 29.8, 28.6, 21.7, 20.4, 14.1, 8.6, 7.9. ^{31}P NMR (202 MHz, CDCl_3) δ 138.5. HRMS (ESI): m/z calcd for $\text{C}_{52}\text{H}_{64}\text{NNaO}_4\text{P}$: 820.4472 [M+Na]⁺; found : 821.4489.



(3a*R*,8*aR*)-N,N,2,2-tetraethyl-4,4,8,8-tetrakis(4-fluoro-3,5-bis(trimethylsilyl)phenyl)tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (L40)

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a White solid (635 mg, 51% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 5.4$ Hz, 4H), 7.52 (d, $J = 5.4$ Hz, 2H), 7.43 (d, $J = 5.4$ Hz, 2H), 5.07 (dd, $J = 8.8, 3.0$ Hz, 1H), 4.40 (d, $J = 8.8$ Hz, 1H), 3.57 – 3.41 (m, 2H), 3.31 – 3.13 (m, 2H), 1.66 – 1.08 (m, 12H), 0.29 – 0.24 (m, 72H), 0.16 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 136.3, 125.1, 124.4, 111.1, 84.6, 40.0, 39.8, 28.8, 25.2, 16.5, 0.4. ^{31}P NMR (202 MHz, CDCl_3) δ 141.1. ^{19}F NMR (471 MHz, CDCl_3) δ -89.5, -90.4, -91.4, -91.5. HRMS (ESI): m/z calcd for $\text{C}_{61}\text{H}_{102}\text{F}_4\text{NNaO}_4\text{PSi}_8$: 1266.5545 [M+Na]⁺; found : 1266.5681.

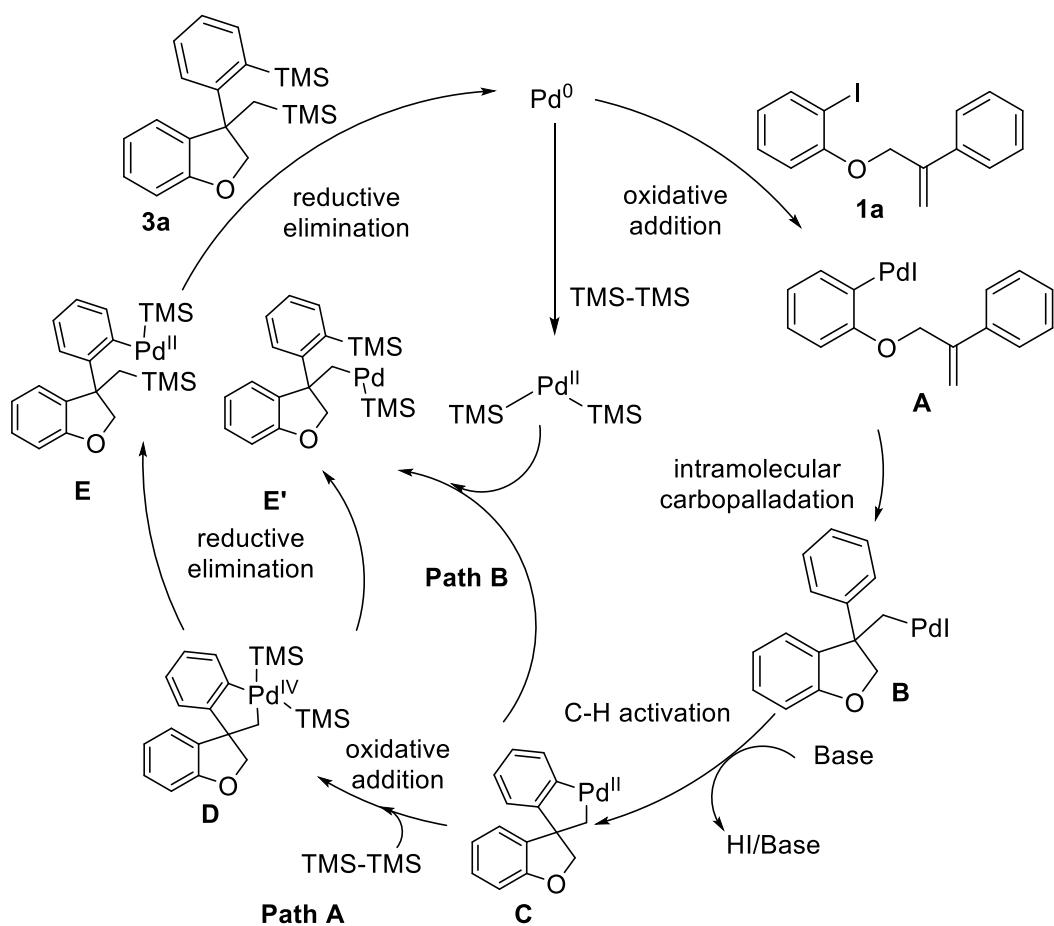


(3*R*,8*R*)-N-benzyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-diethyl-N-methyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (L41)

Following the general procedure, the product was isolated by column chromatography with PE/EA/Et₃N (100/1/1) as the eluent to give a White solid (688 mg, 91% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.26 (m, 8H), 7.22 (s, 3H), 7.00 (s, 2H), 6.88 (dd, *J* = 28.2, 14.8 Hz, 4H), 5.07 (dd, *J* = 8.6, 2.6 Hz, 1H), 4.90 (d, *J* = 8.6 Hz, 1H), 4.18 (dd, *J* = 15.2, 7.8 Hz, 1H), 4.03 (dd, *J* = 15.2, 9.0 Hz, 1H), 2.56 (d, *J* = 9.0 Hz, 3H), 2.33 (d, *J* = 14.4 Hz, 12H), 2.25 (d, *J* = 25.2 Hz, 12H), 1.44 (q, *J* = 7.4, 6.6 Hz, 1H), 1.26 (dd, *J* = 14.0, 7.4 Hz, 1H), 0.87 (dd, *J* = 13.6, 7.3 Hz, 2H), 0.66 (t, *J* = 7.6 Hz, 3H), 0.38 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.2, 139.6, 136.2, 128.4, 125.1, 115.7, 83.7, 81.7, 52.7, 29.7, 28.8, 21.8, 8.4. ³¹P NMR (202 MHz, CDCl₃) δ 135.8. HRMS (ESI): m/z calcd for C₄₉H₅₈NNaO₄P: 778.4002 [M+Na]⁺; found : 778.4395.

6. Possible Mechanism Cycle

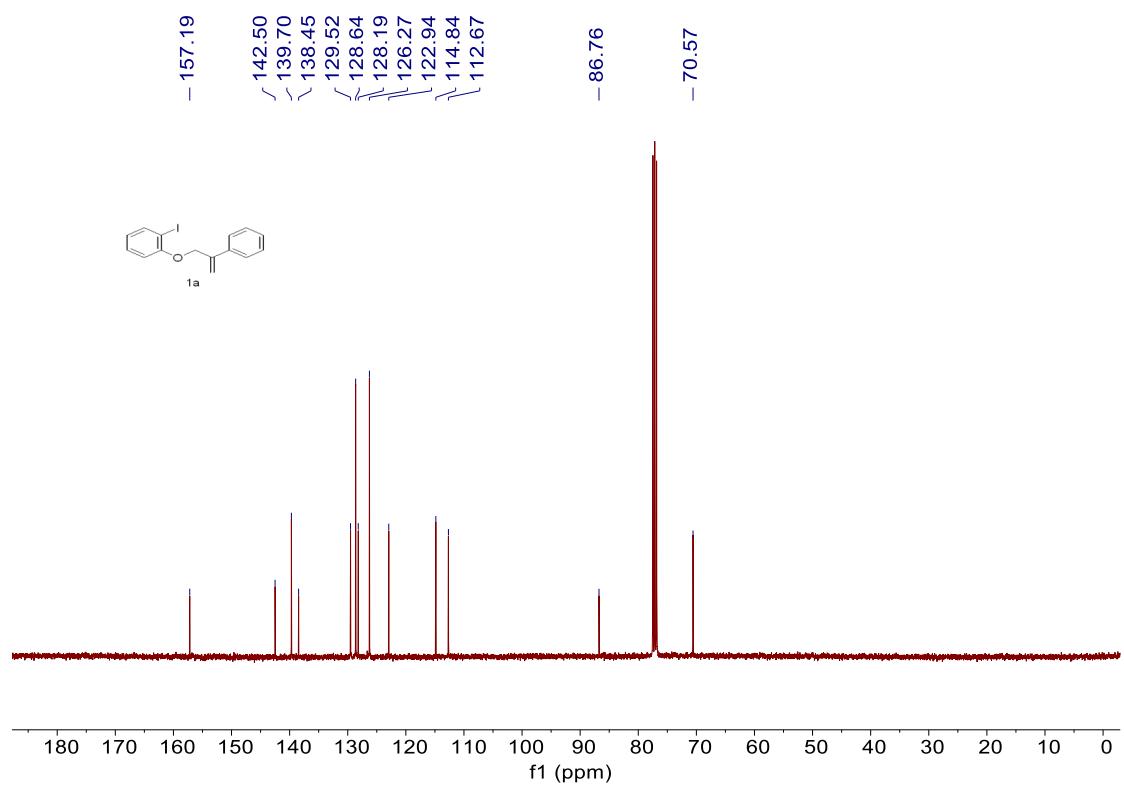
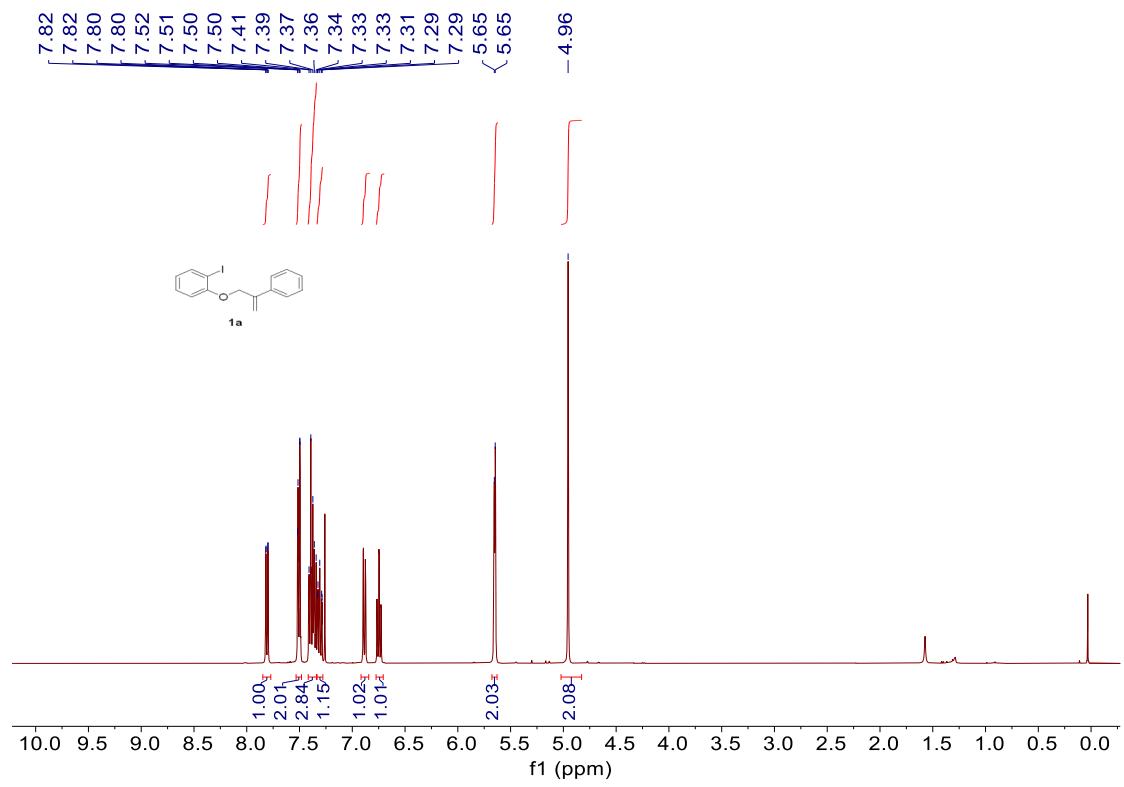


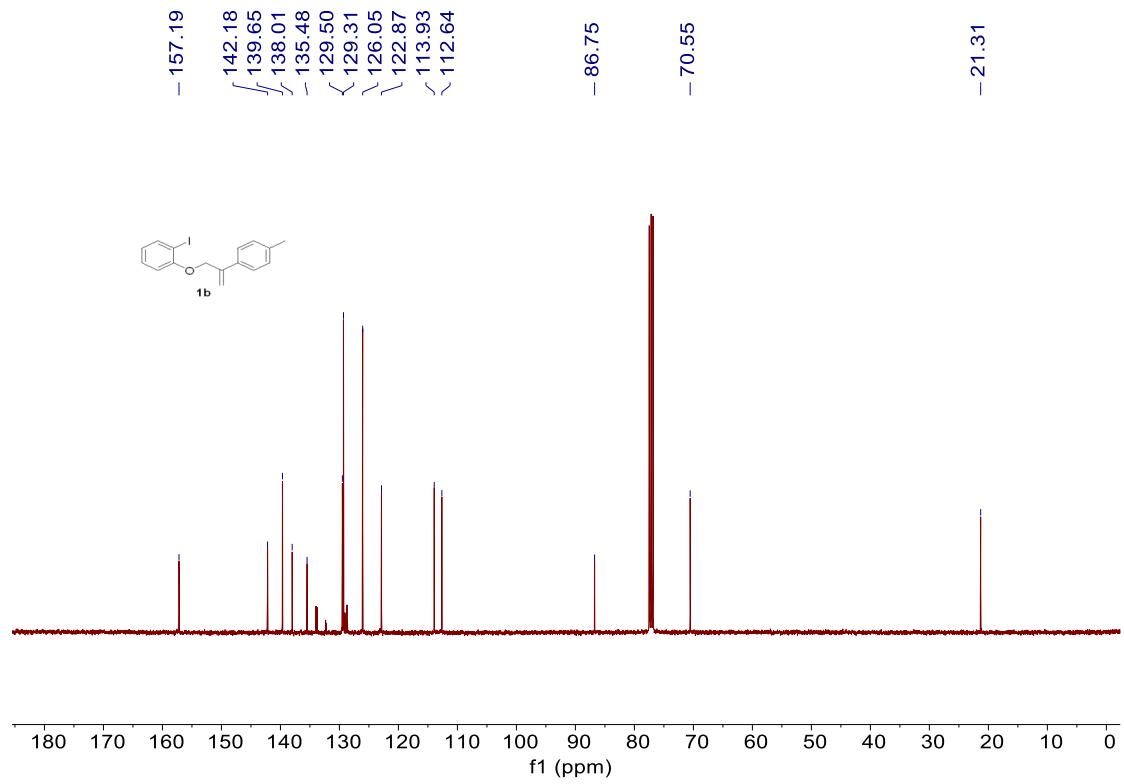
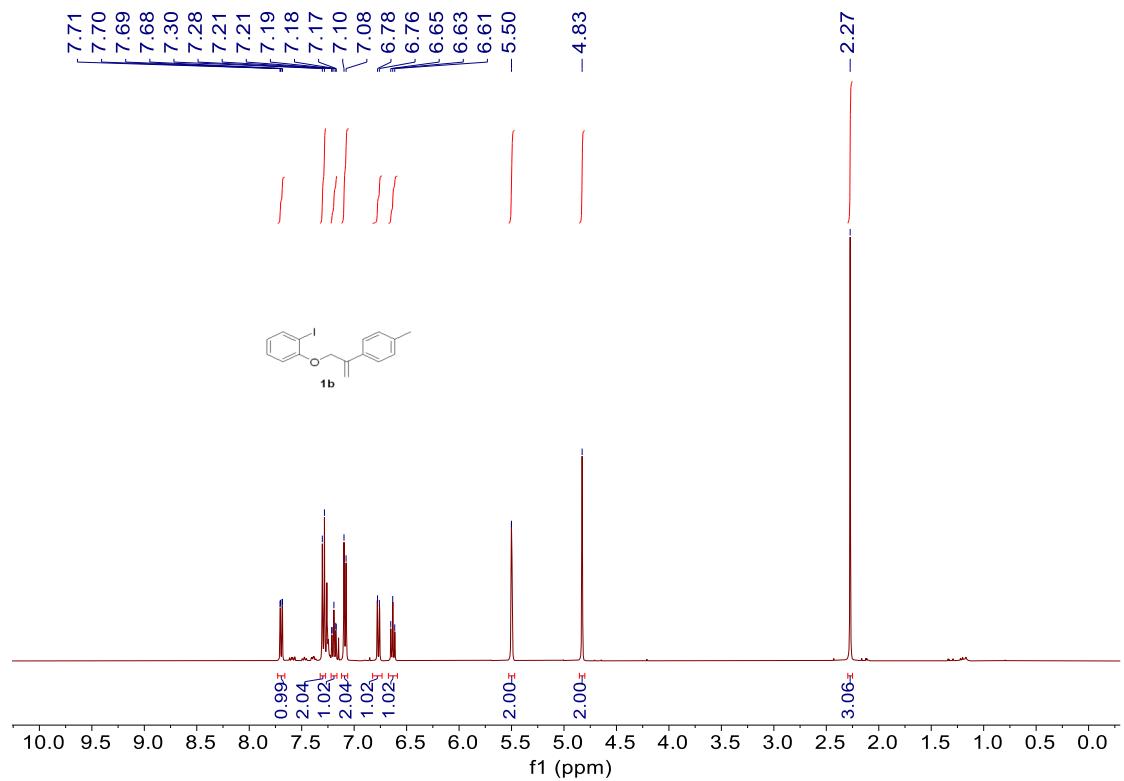
7. Reference

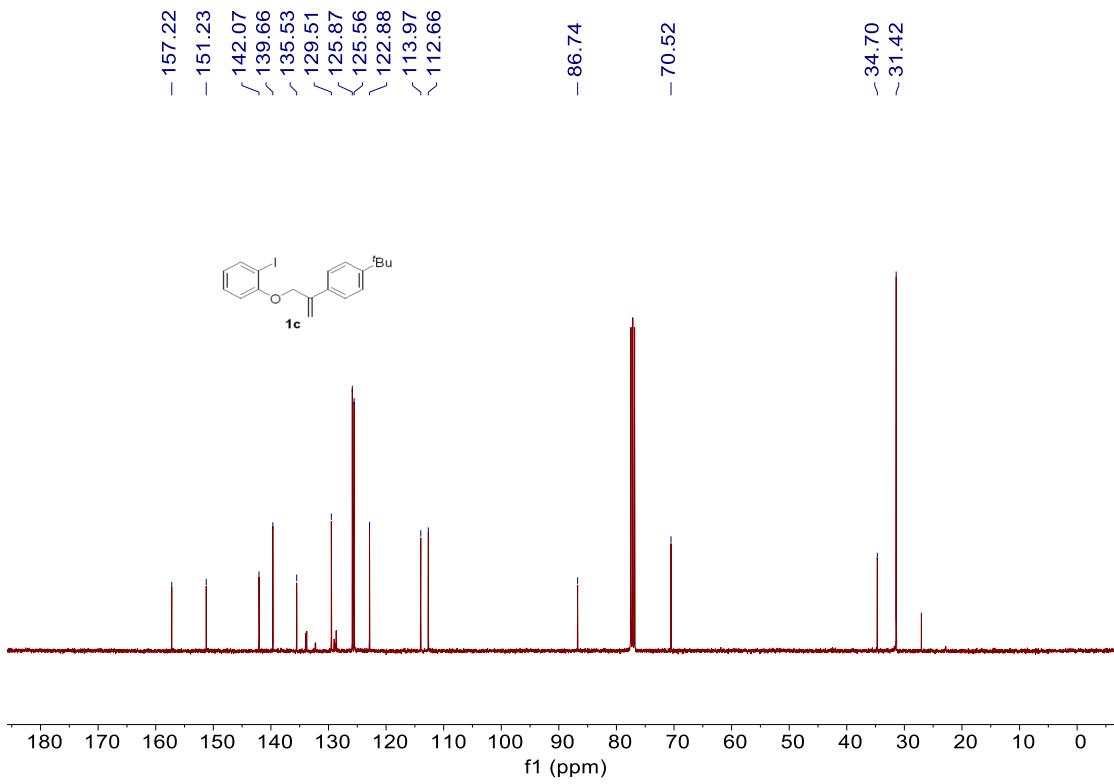
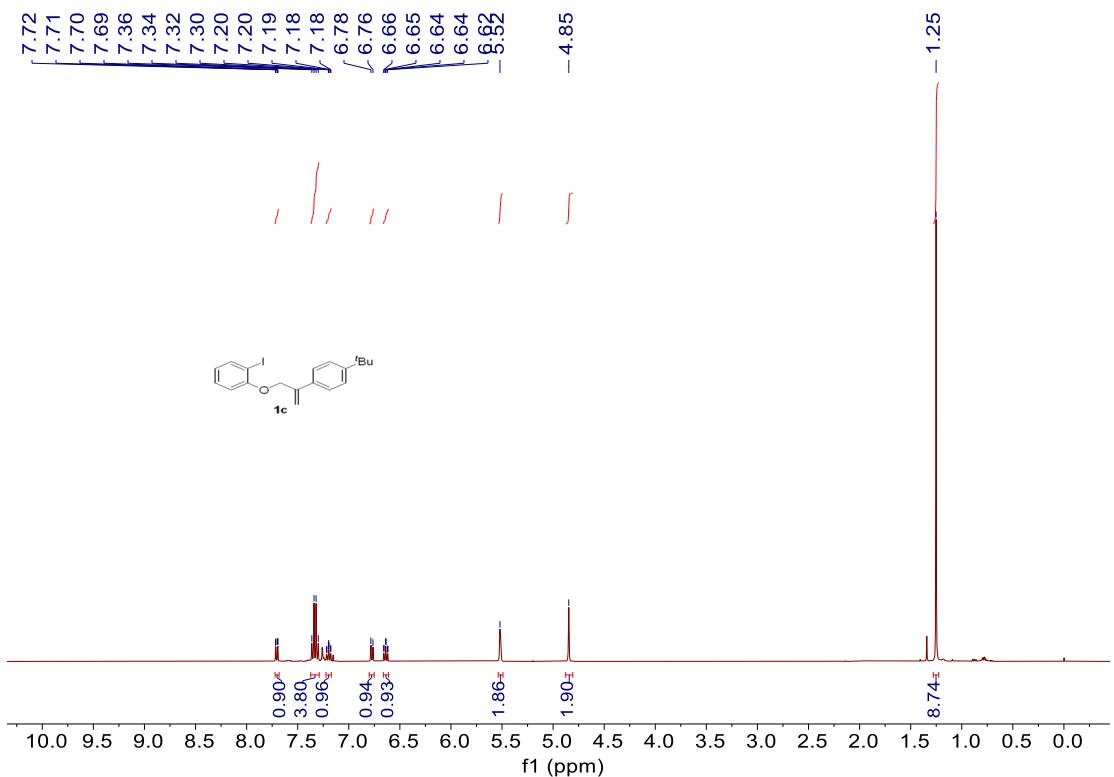
- [1] (a) X.T. Ma, A. L. Lu, X. M. Ji, G. F. Shi, Y. H. Zhang, *Asian J. Org. Chem.* **2018**, 7, 1403 - 1410. (b) C. Liu, Y. K. Li, W. Y. Shi, Y. N. Ding, N. Zheng, H. C. Liu, Y. M. Liang, *Org. Lett.* **2021**, 23, 4311 - 4316.
- [2] C. Schmitz, W. Leitner, G. Franciò, *Chem. Eur. J.* **2015**, 21, 10696 - 10702.
- [3] X. B. Wang, Z. J. Zheng, J. L. Xie, X. W. Gu, Q. C. Mu, G. W. Yin, F. Ye, Z. Xu, L. W. Xu, *Angew. Chem. Int. Ed.* **2020**, 59, 790 - 797; *Angew. Chem.* **2020**, 132, 2 - 807.
- [4] W. C. Yang; X. B. Chen, Ku. L. Song, B. Wu, W. E. Gan, Z. J. Zheng, J. Cao, L. W. Xu, *Org. Lett.* **2021**, 23, 4, 1309 - 1314.
- [5] M. R. Albicker, N. Cramer, *Angew. Chem. Int. Ed.* **2009**, 48, 9139 - 9142.

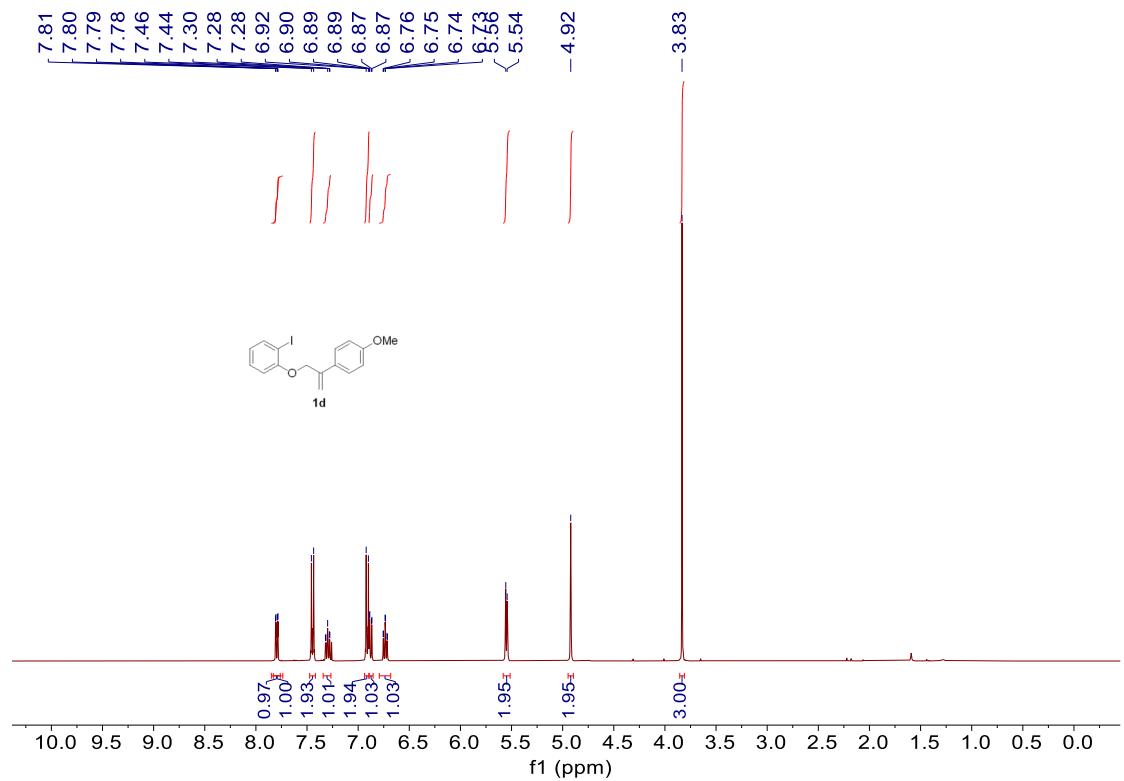
- [6] S. M. Smith, J. M. Takacs, *Org. Lett.* **2010**, 12, 4612 - 4615.
- [7] Y. L. Sun, X. B. Wang, F. N. Sun, Q. Q. Chen, J. Cao, Z. Xu, L. W. Xu, *Angew. Chem. Int. Ed.* **2019**, 58, 6747-6751; *Angew. Chem.* **2019**, 131, 6819 - 6823.
- [8] C. F. He, M. Q. Hou, Z. X. Zhu, Z. H. Gu, *ACS Catal.* **2017**, 7, 8, 5316 - 5320.
- [9] J. Cao, L. Chen, F. N. Sun, Y. L. Sun, K. Z. Jiang, K. F. Yang, Z. Xu, L. W. Xu, *Angew. Chem. Int. Ed.* **2019**, 58, 897 - 901; *Angew. Chem.* **2019**, 131, 907 - 911.
- [10] L. Chen, J. B. Huang, Z. Xu, Z. J. Zheng, K. F. Yang, Y. M. Cui, J. Cao, L. W. Xu, *RSC Adv.* **2016**, 6, 67113 - 67117.
- [11] L. X. Fan, J. J. Liu, L. Bai, Y. Y. Wang, X. J. Luan, *Angew. Chem. Int. Ed.* **2017**, 56, 14257 - 14261; *Angew. Chem.* **2017**, 129, 1 4445 - 14449.
- [12] W. X. Kong, S. J. Xie, C. Y. Z. Cao, C. W. Zhang, C. Y. Wang, W. L. Duan, *Chem. Commun.* **2020**, 56, 2292 - 2295.
- [13] D. Dailler, R. Rocaboy, O. Baudoin, *Angew. Chem. Int. Ed.* **2017**, 56, 7218 - 7222; *Angew. Chem.* **2017**, 129, 7324 - 7328.
- [14] Y. L. Su, Z. Y. Han, Y. H. Li, L. Z. Gong, *ACS Catal.* **2017**, 7, 11, 7917 - 7922.
- [15] D. M. Dalton, A. K. Rappéa, T. Rovis, *Chem. Sci.* **2013**, 4, 2062 - 2070.
- [16] Z. J. Cai, C. X. Liu, Q. Wang, Q. Gu, S. Li. You, *Nat Commun.* **2019**, 10, 4168.
- [17] K. Hong, J. P. Morken, *J. Am. Chem. Soc.* **2013**, 135, 25, 9252 - 9254.

8. NMR Spectra

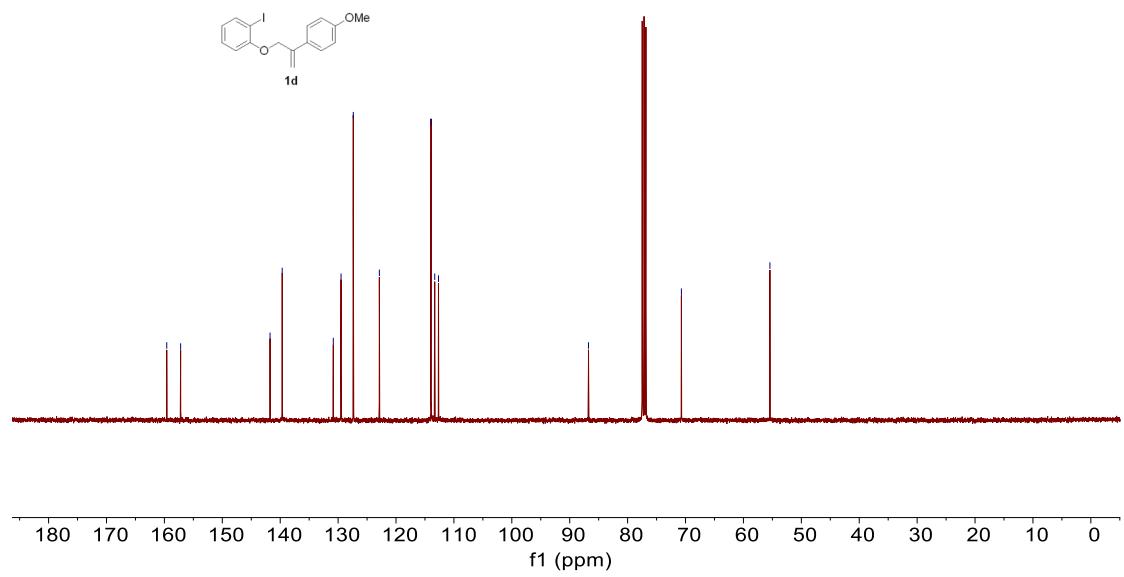


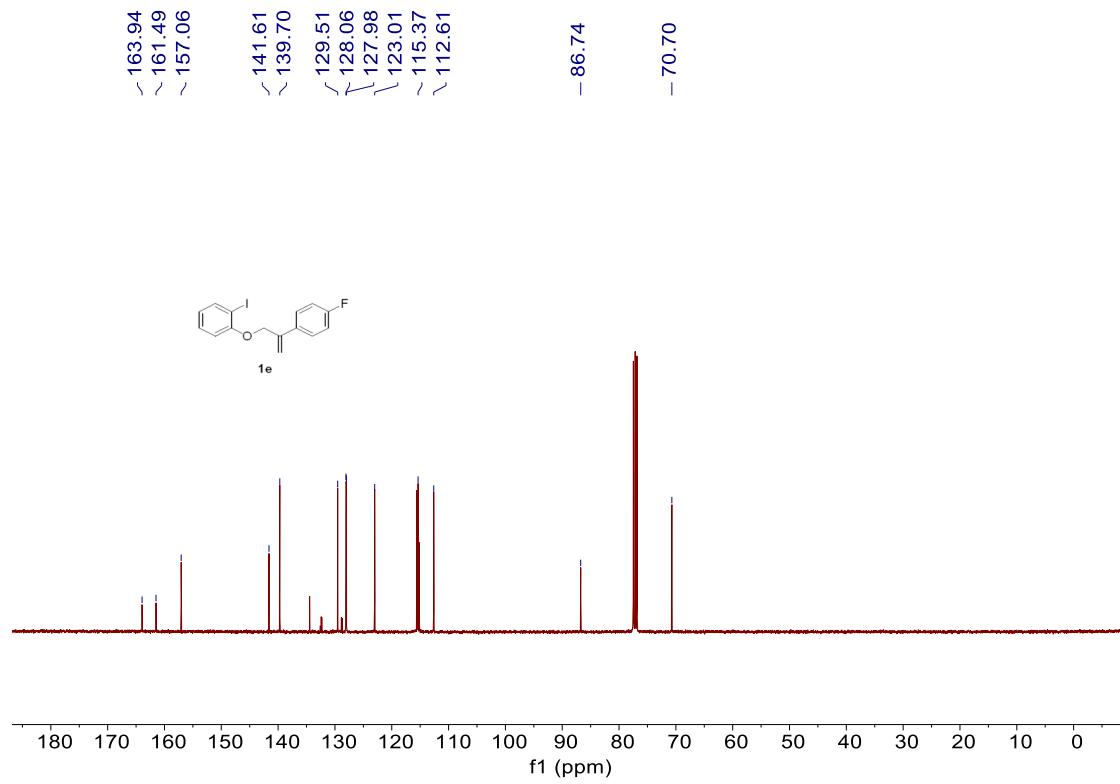
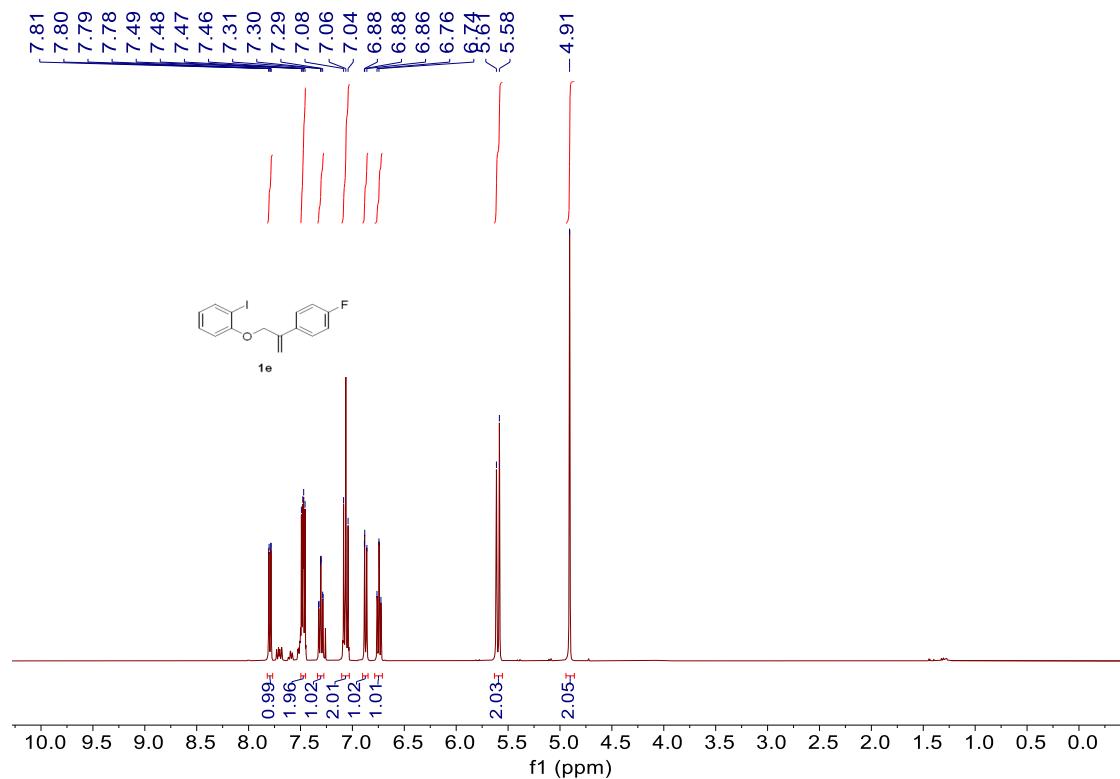


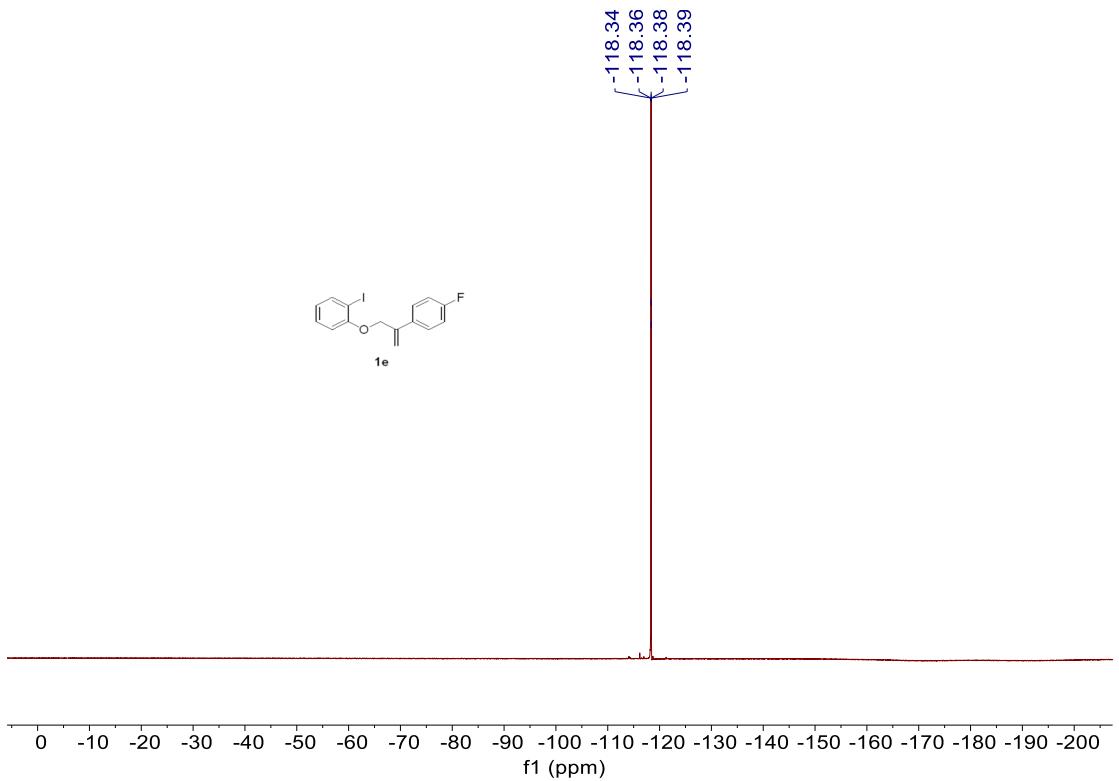


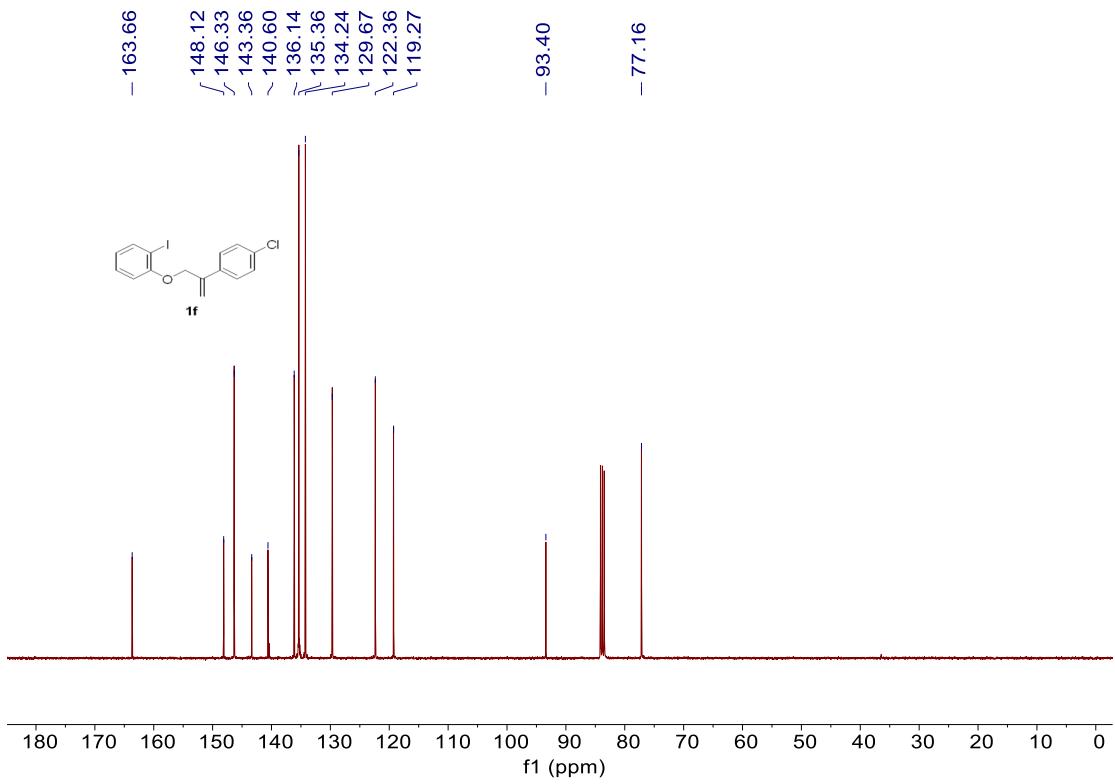
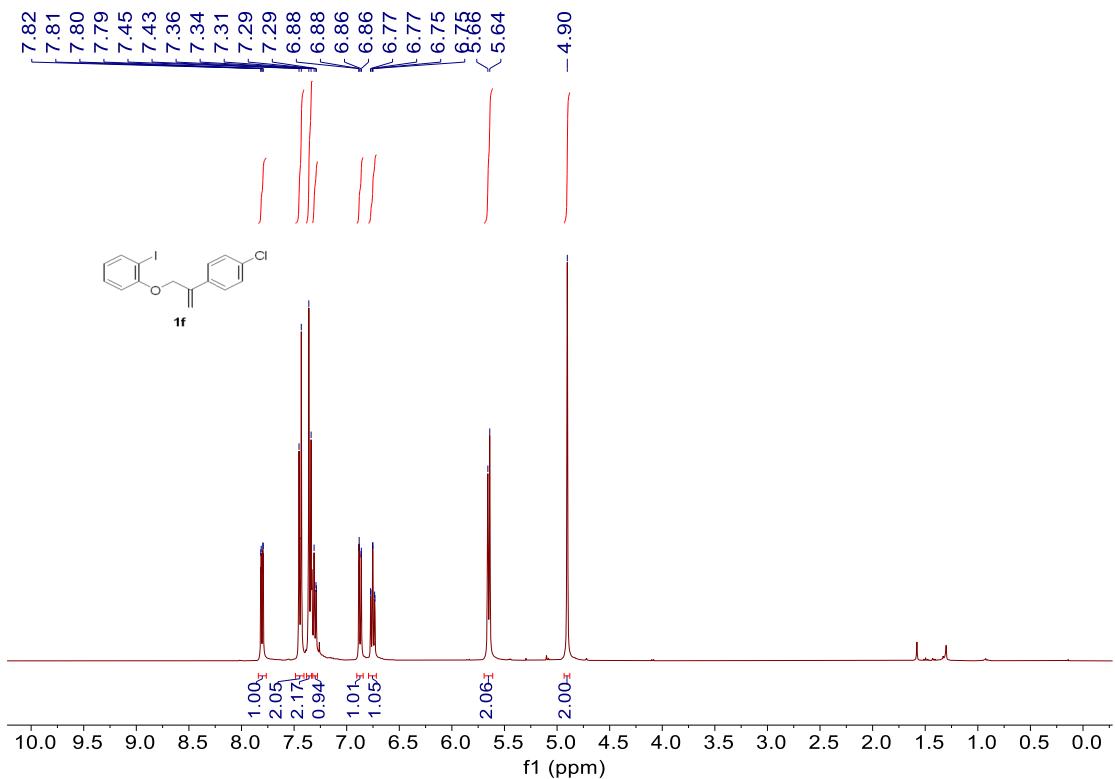


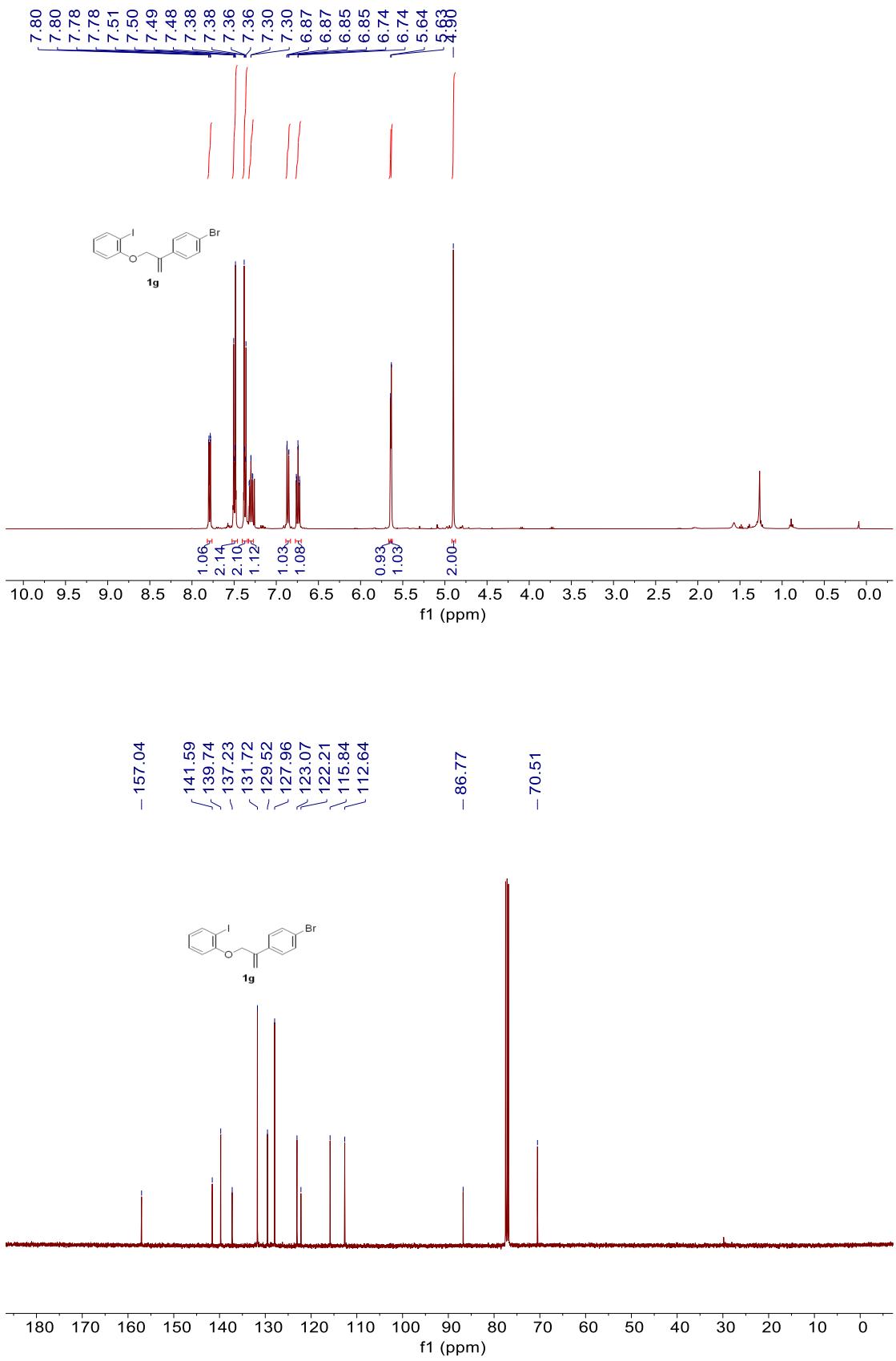
< 159.59
 ~ 157.20
 < 141.75
 ~ 139.65
 130.83
 > 129.49
 > 127.38
 > 122.88
 < 113.95
 < 113.31
 < 112.66

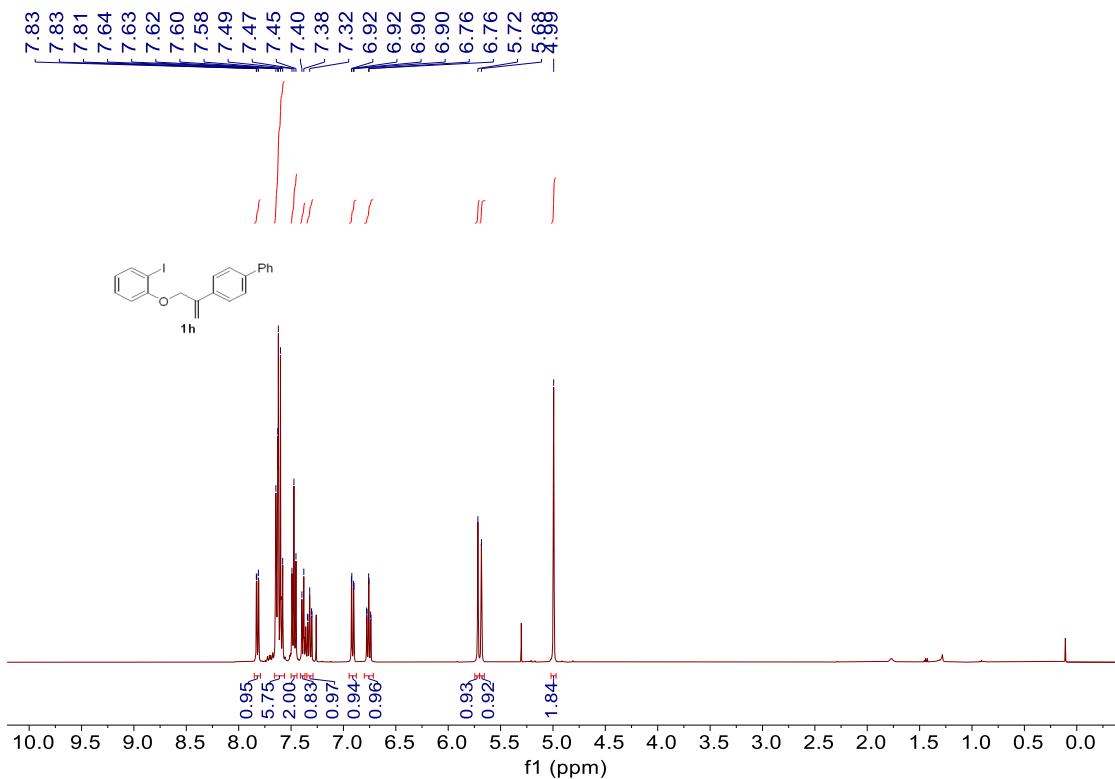




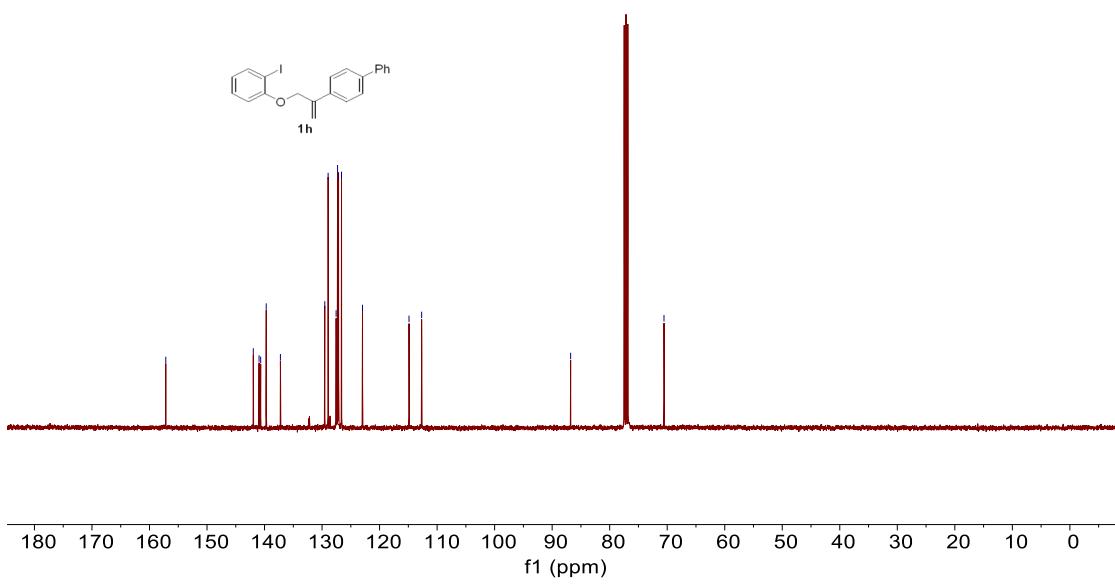


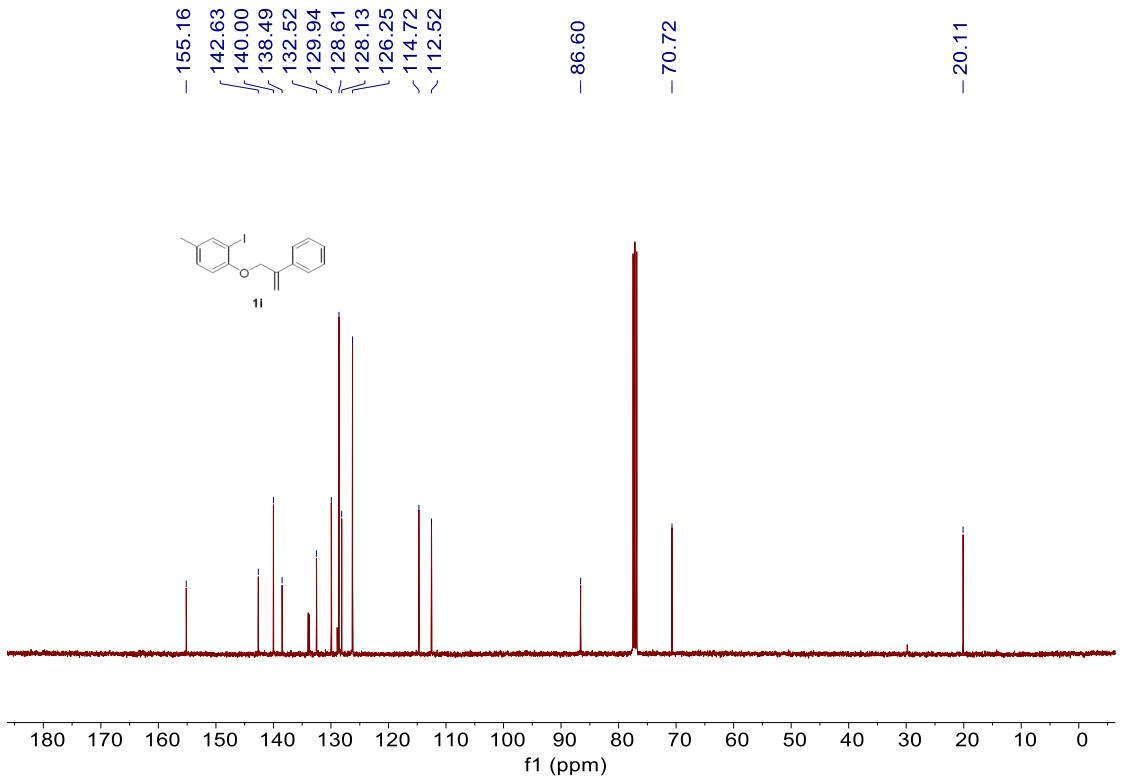
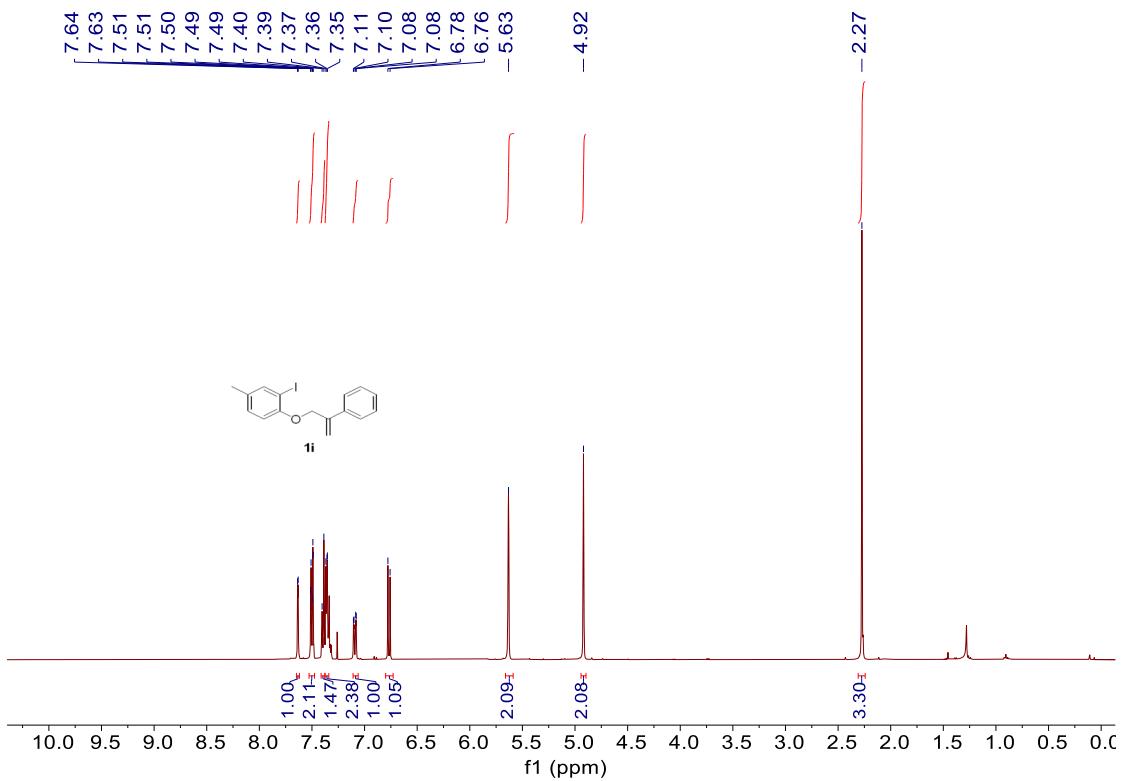


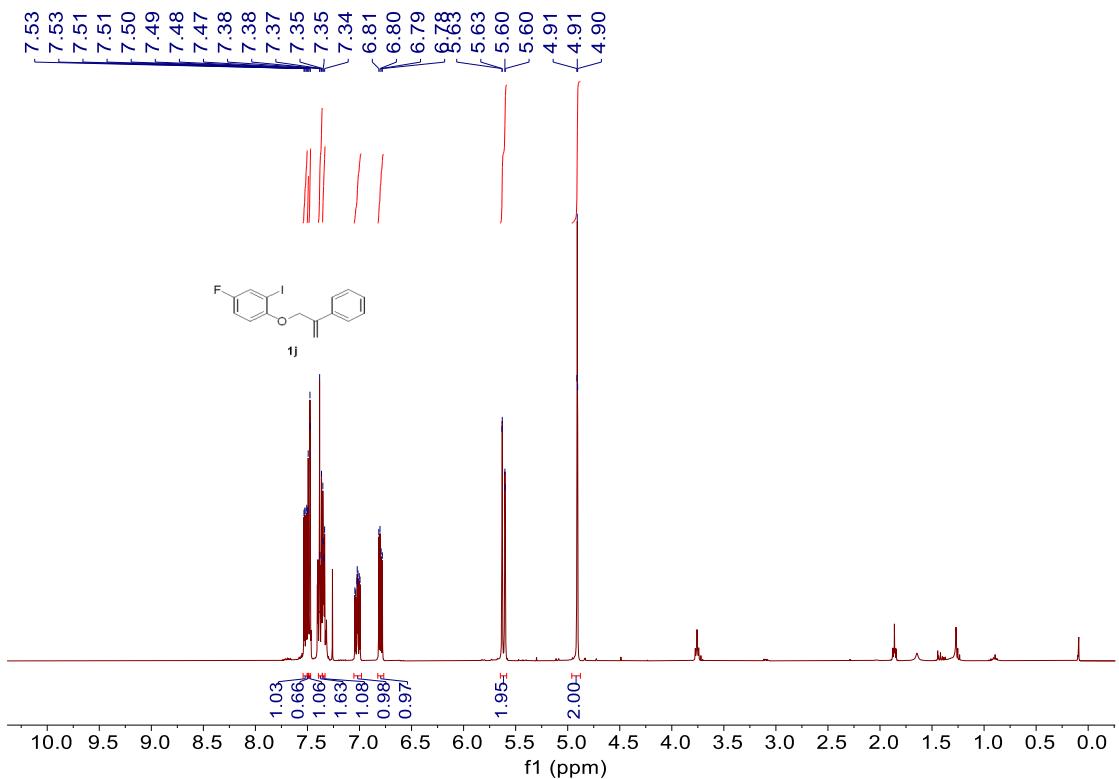




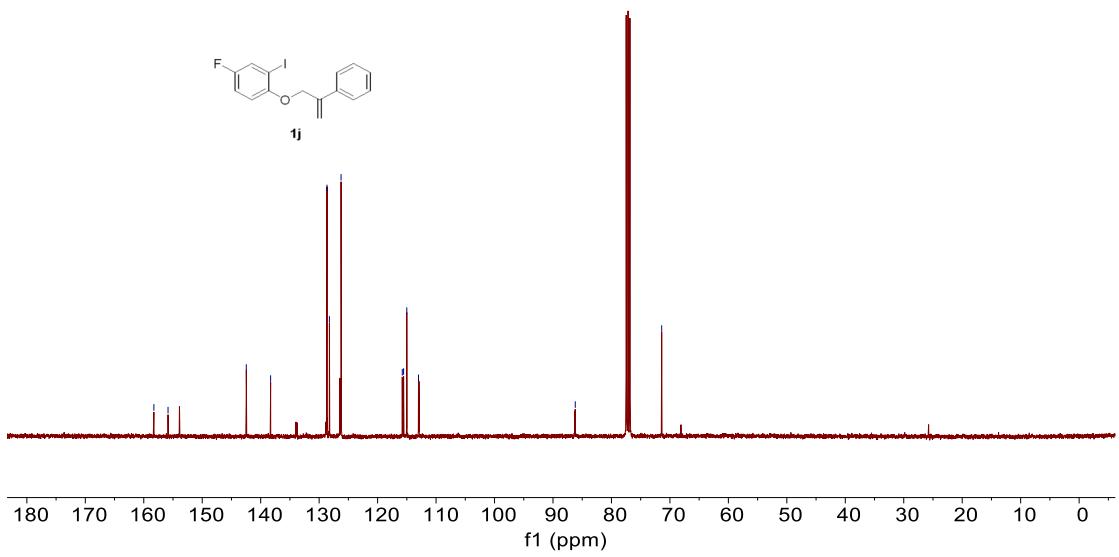
-157.17
-141.95
-140.95
-140.67
-139.70
-137.24
-129.53
-128.95
-127.56
-127.30
-127.13
-126.62
-122.97
-114.88
-112.69
-86.79
-70.56

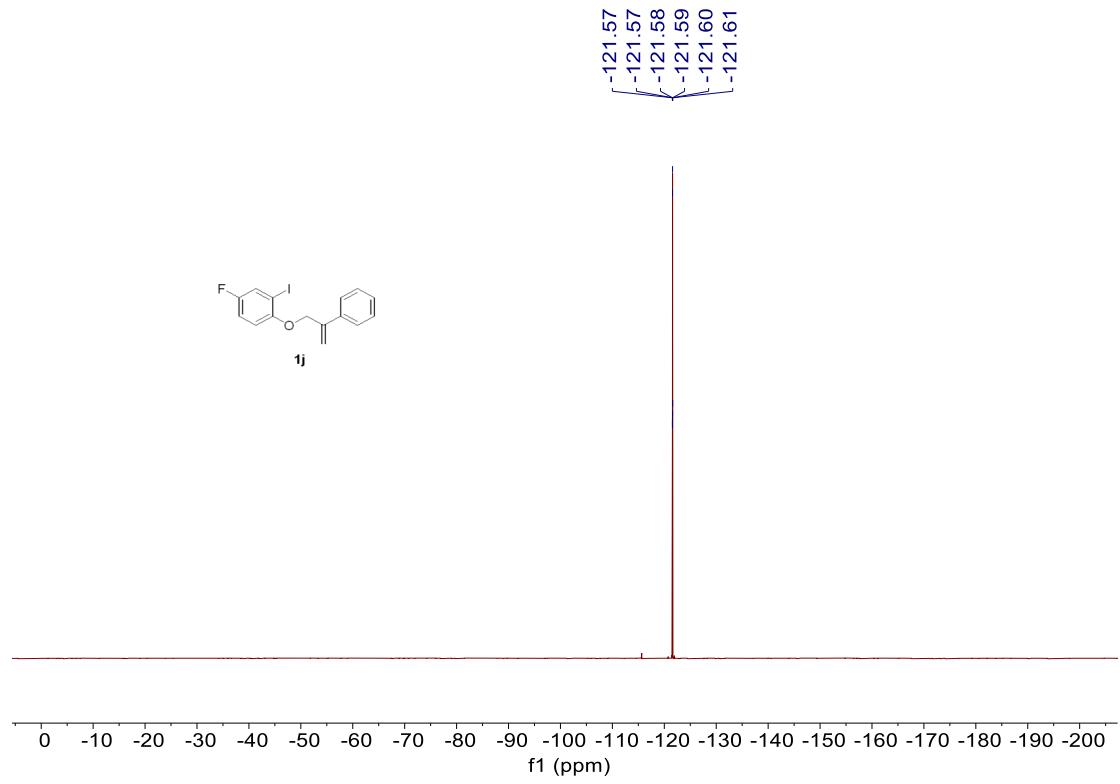


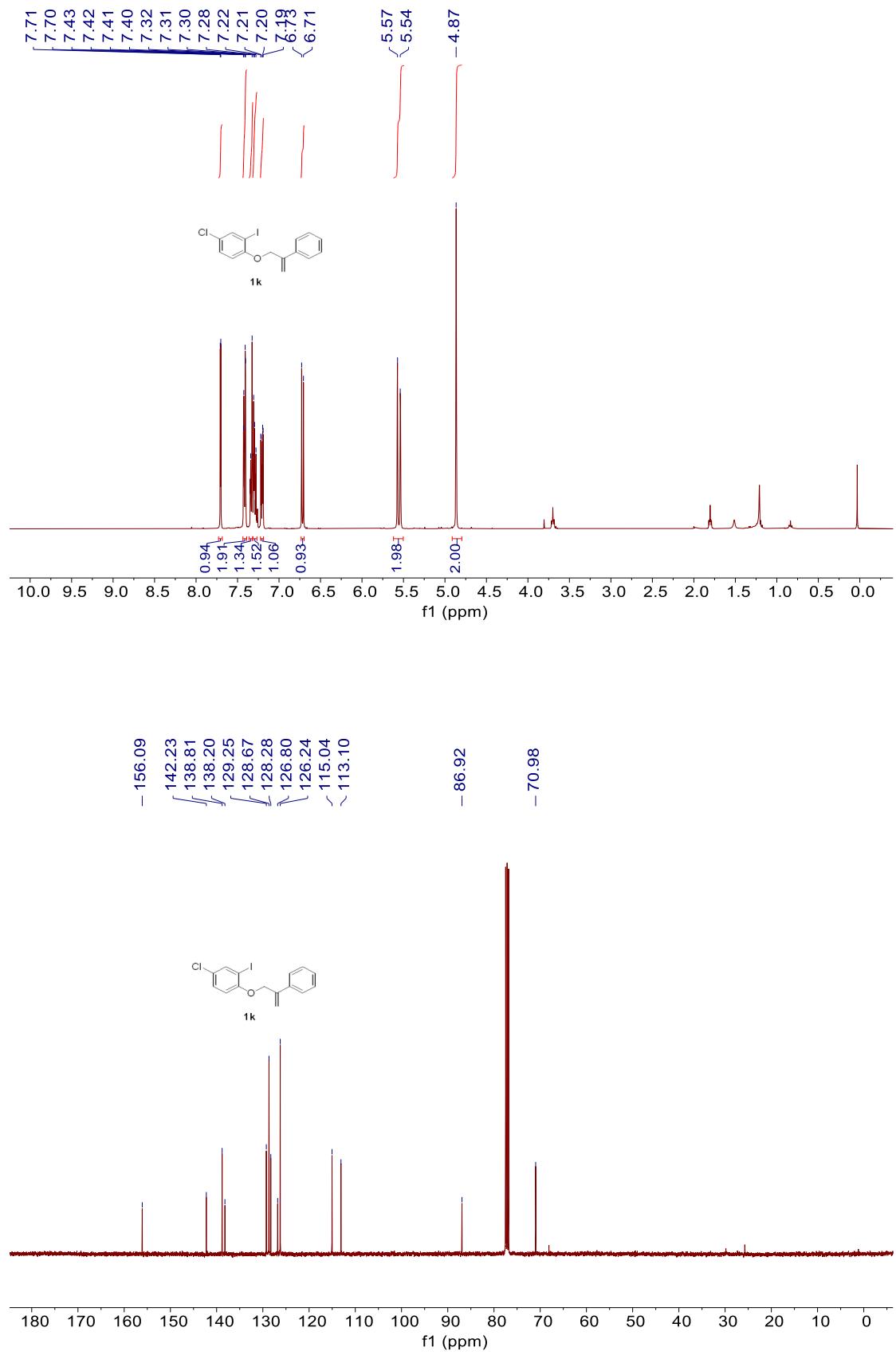


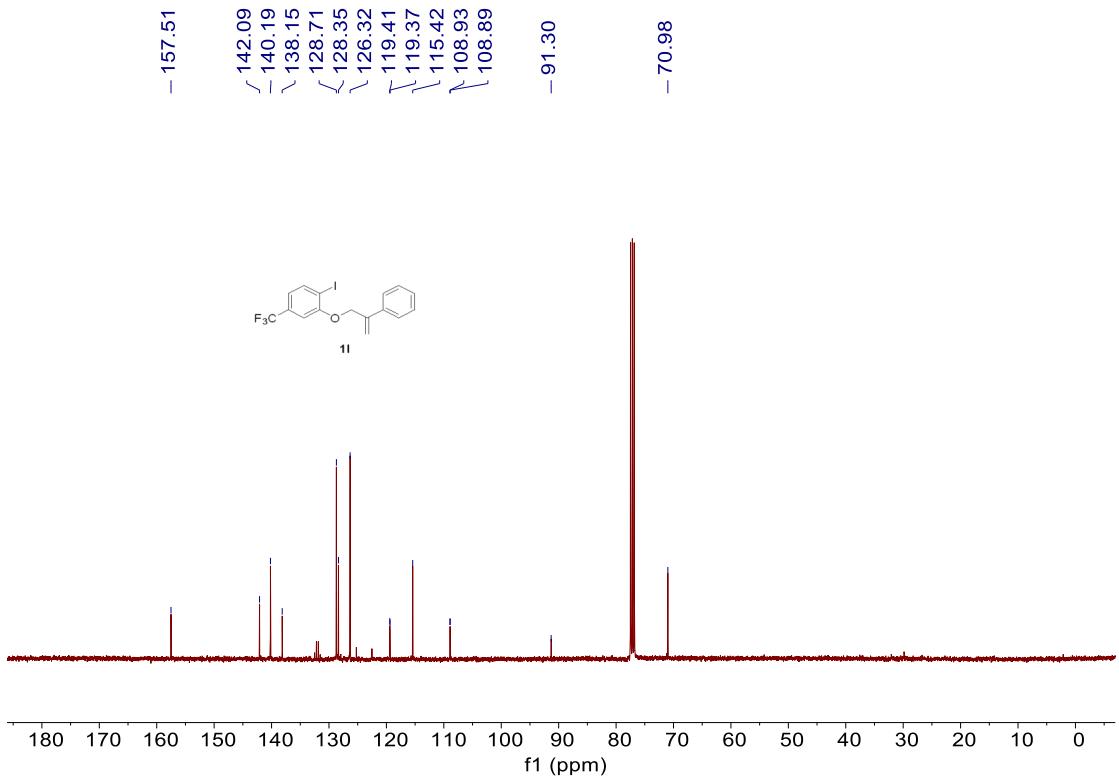
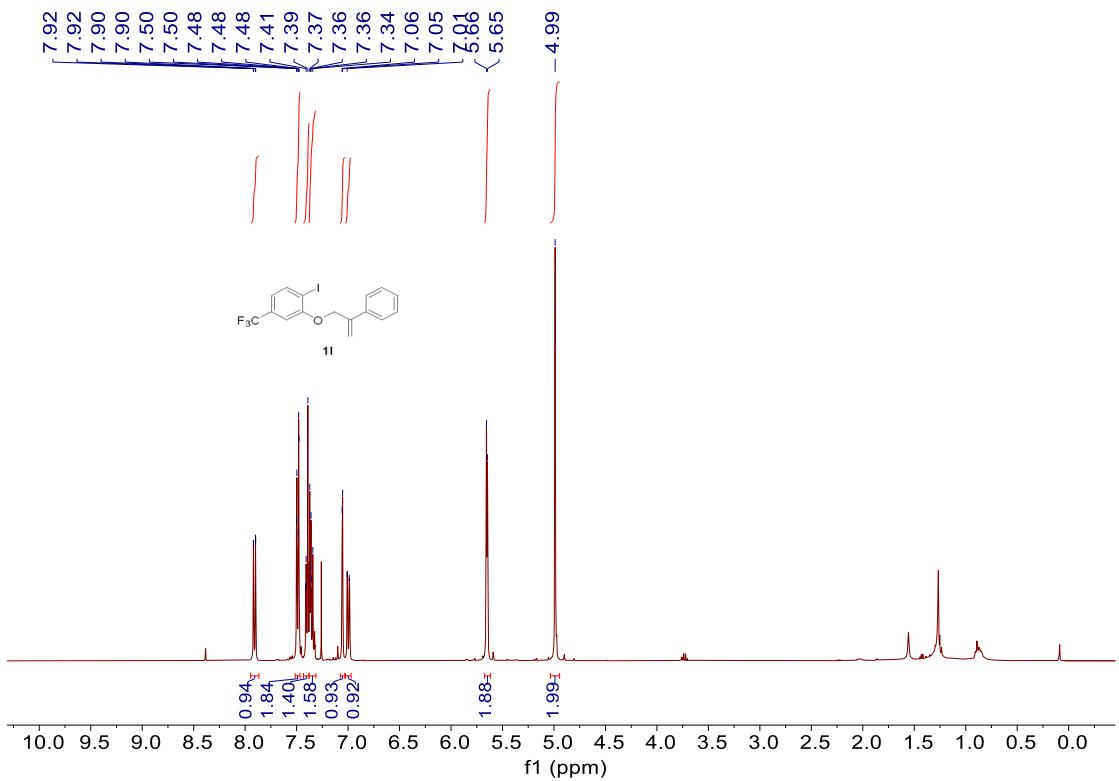


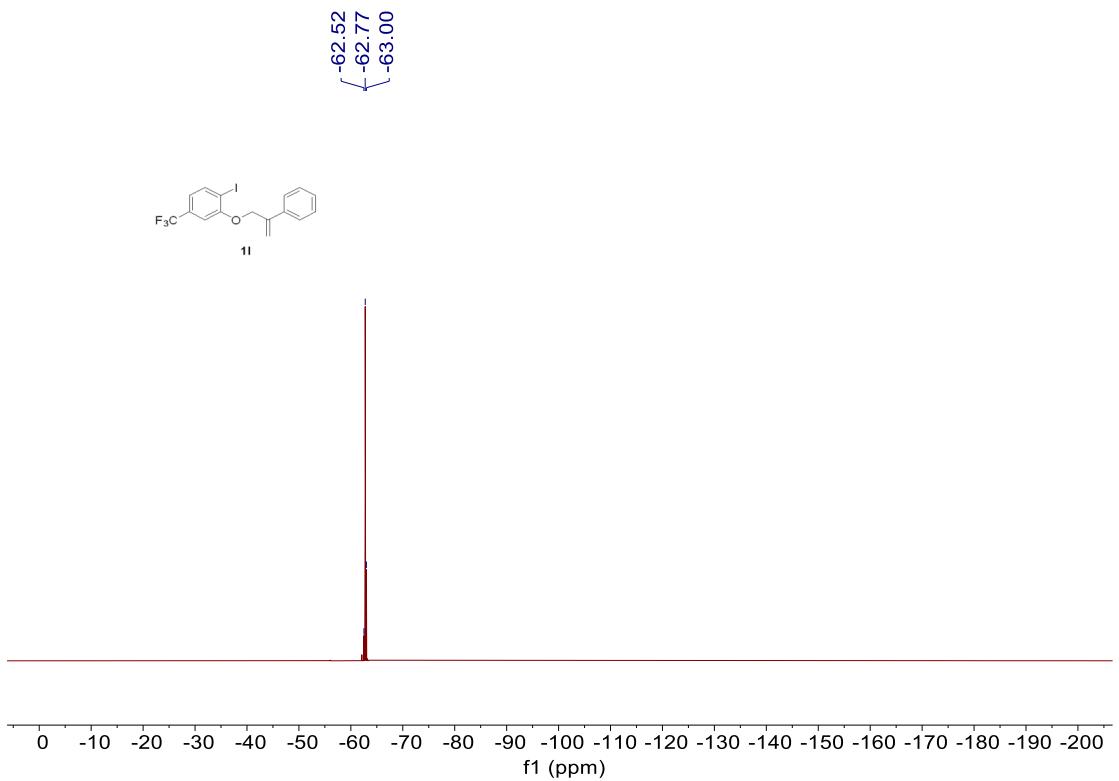
158.27
< 155.85
- 142.46
- 138.30
- 128.66
< 128.24
< 126.25
< 115.78
< 115.56
< 115.01
- 113.01
- 86.19
- 71.41

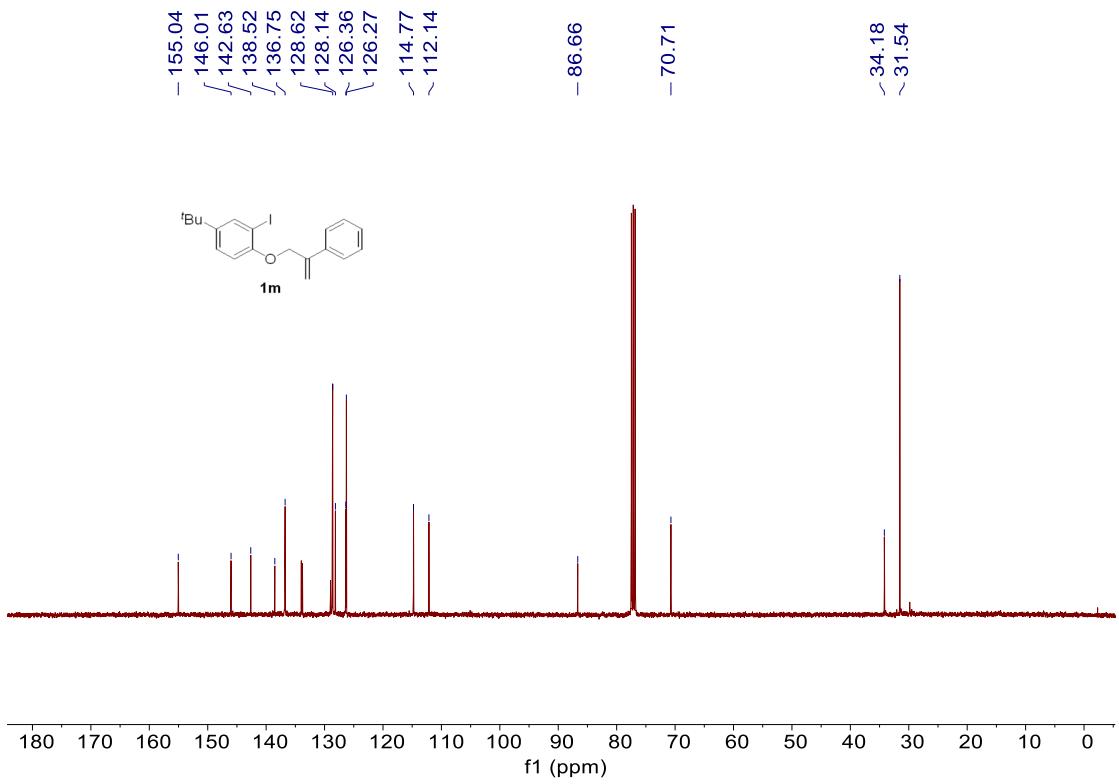
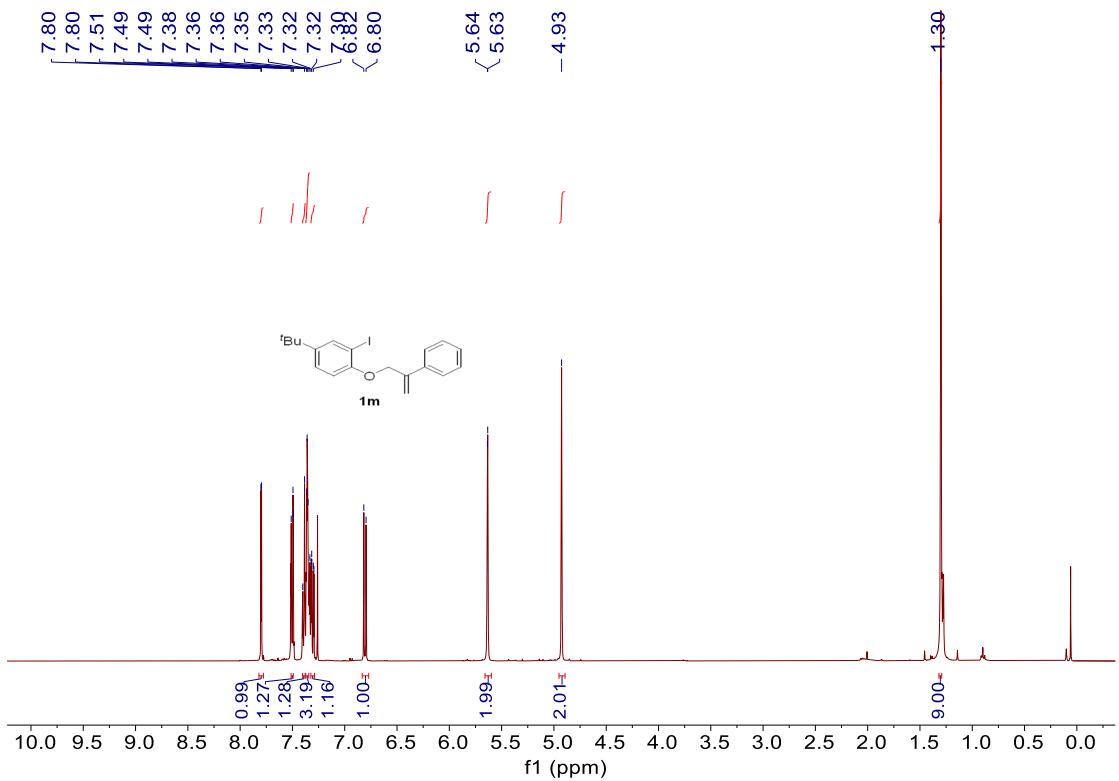


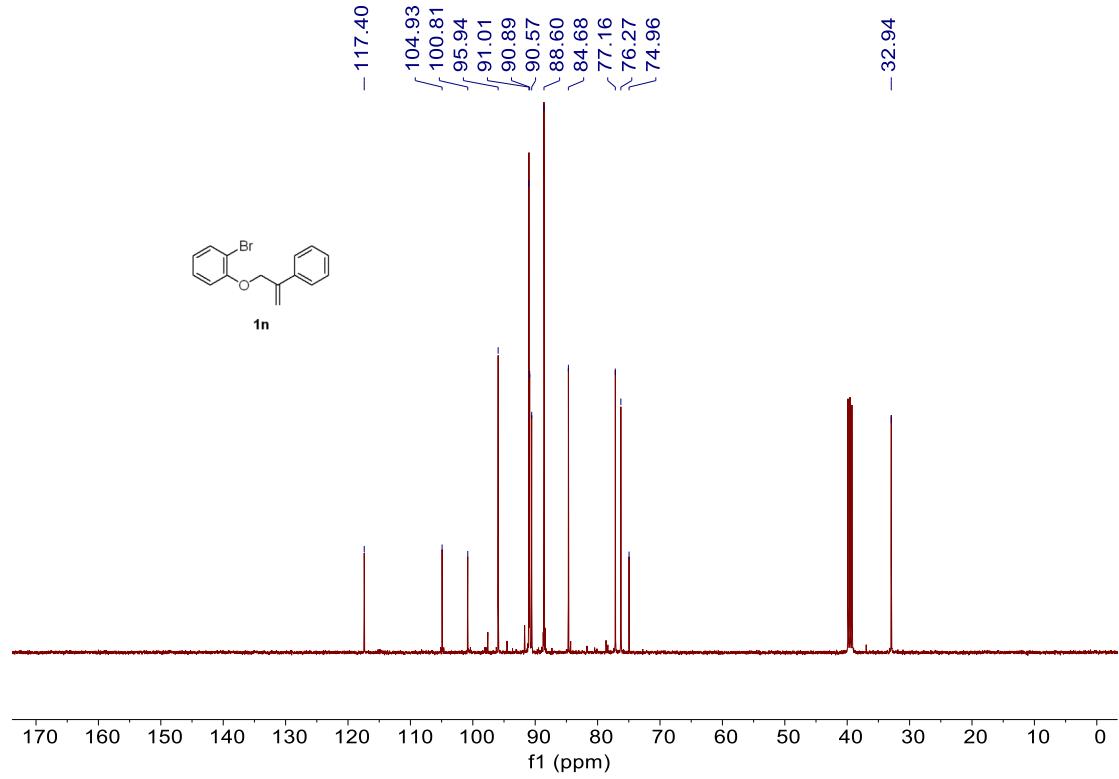
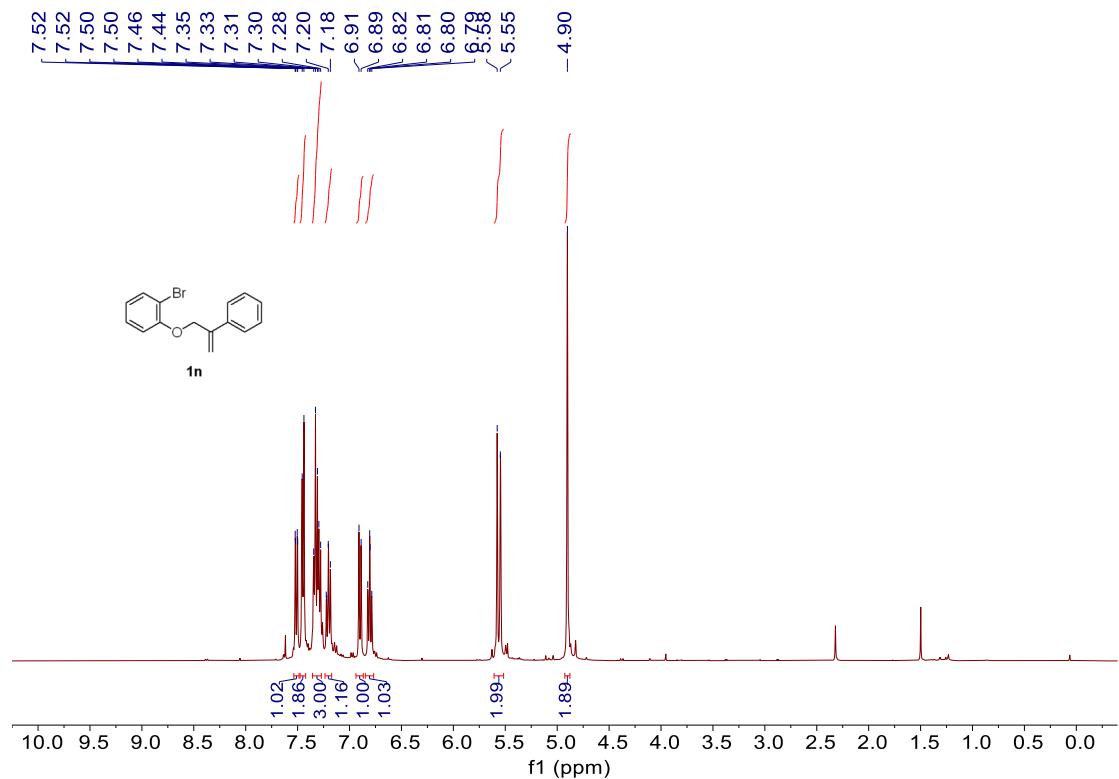


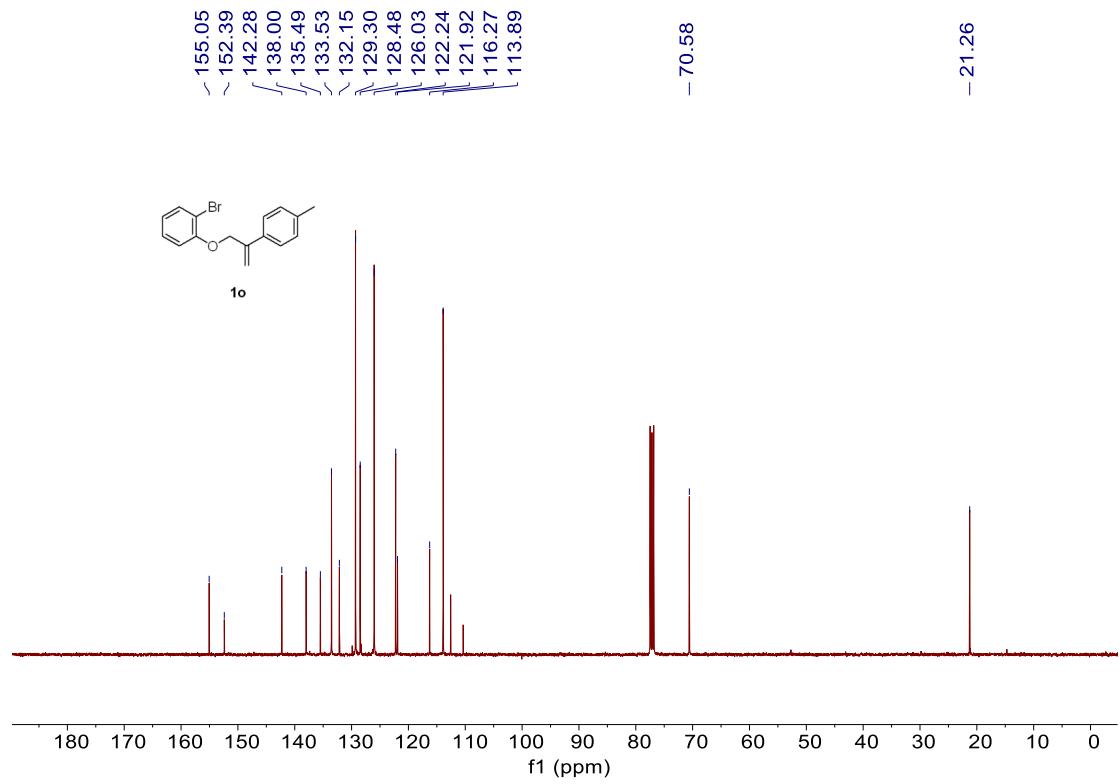
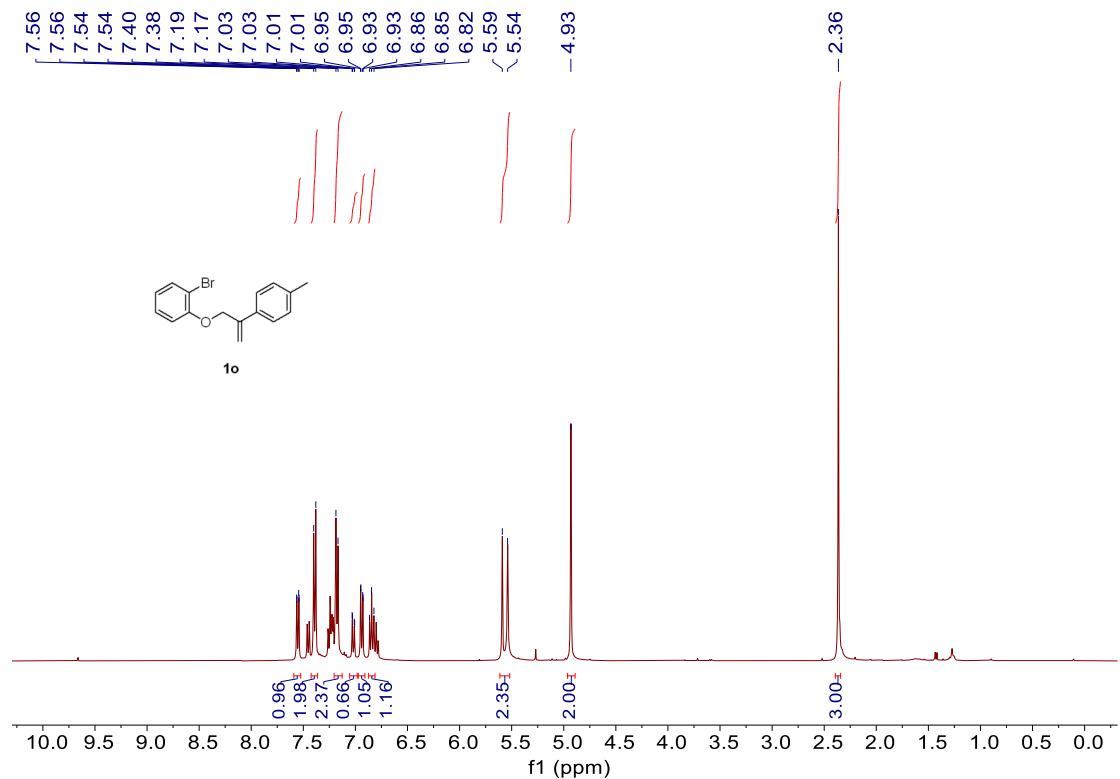


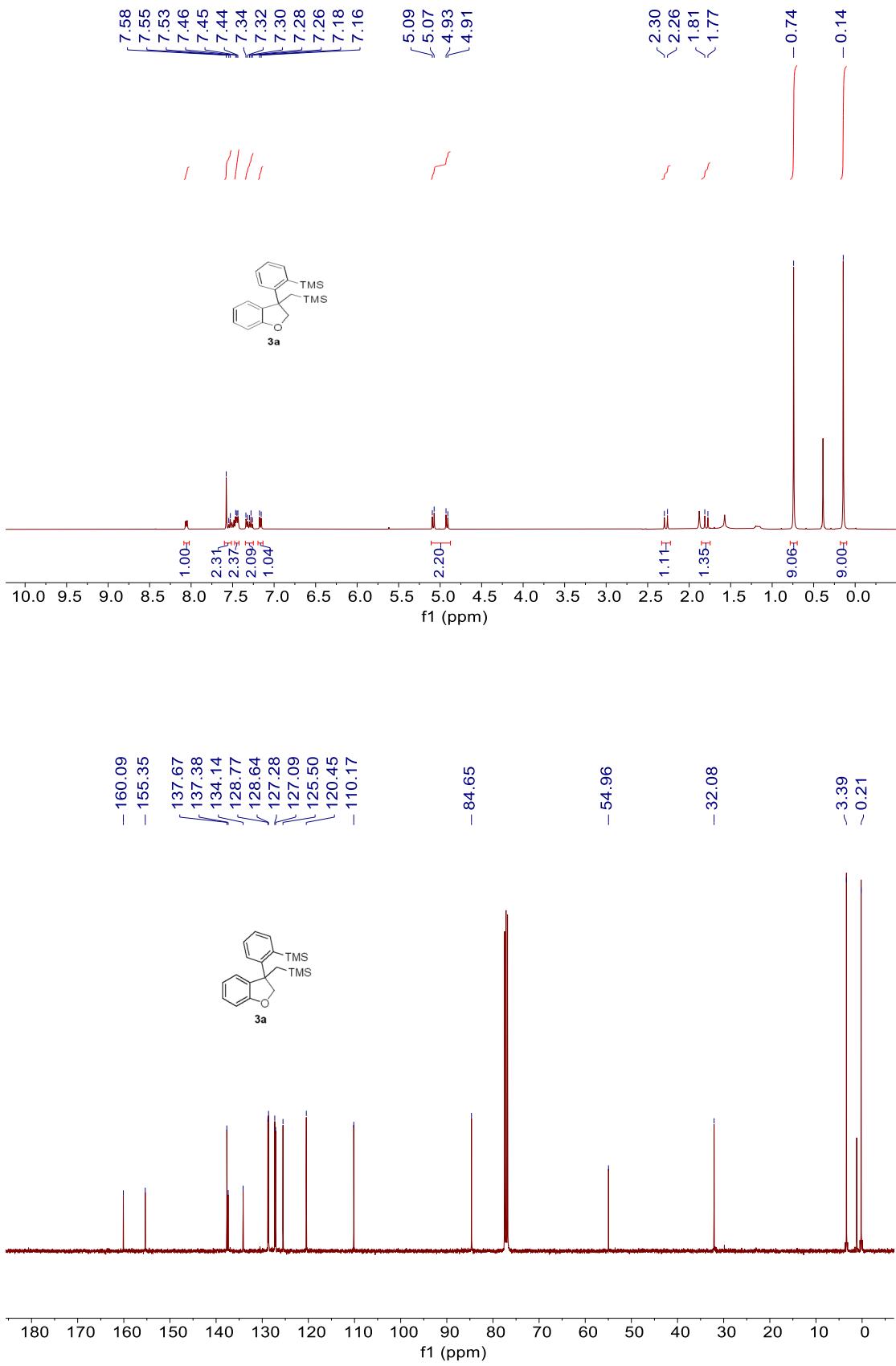


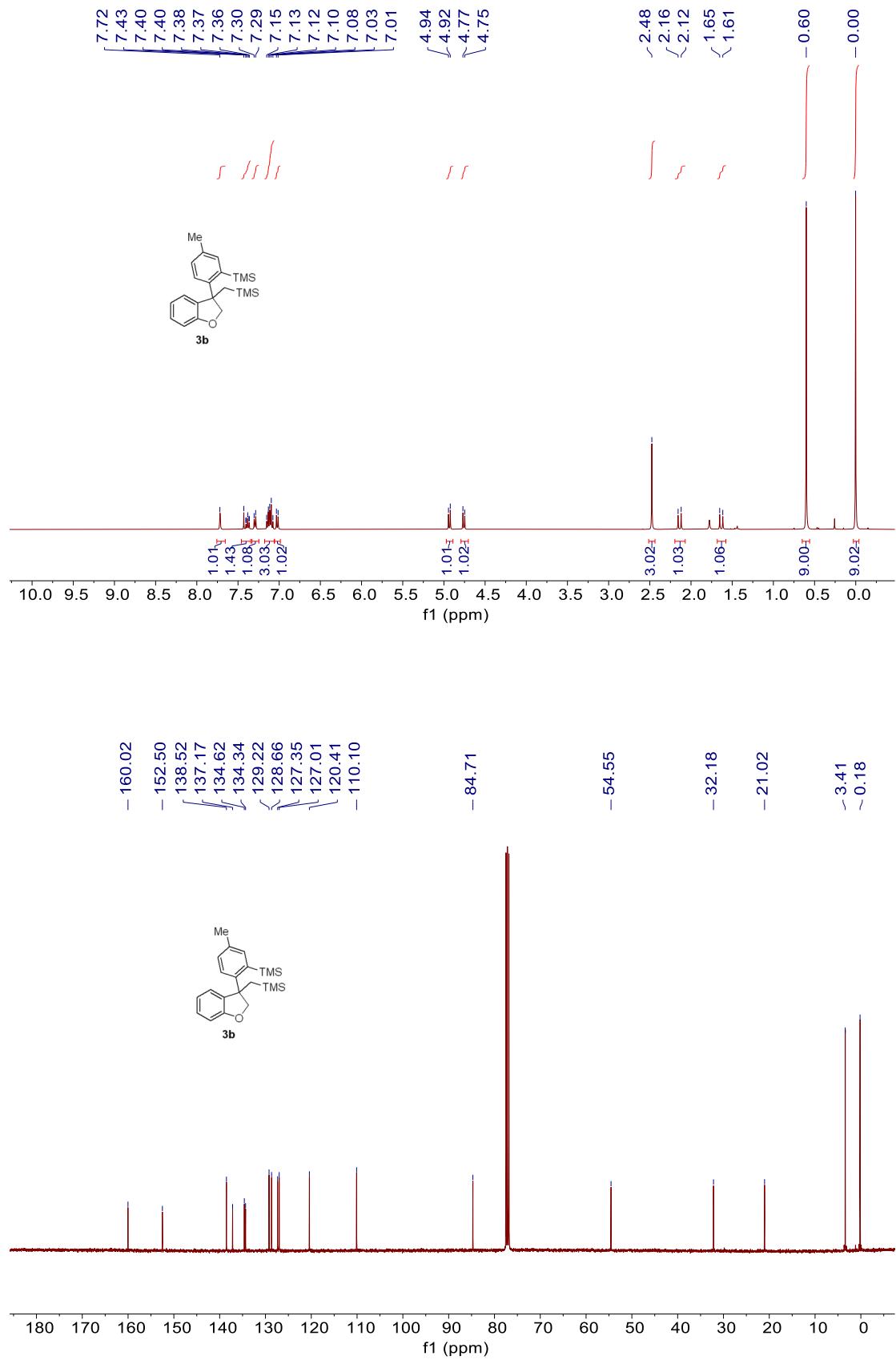


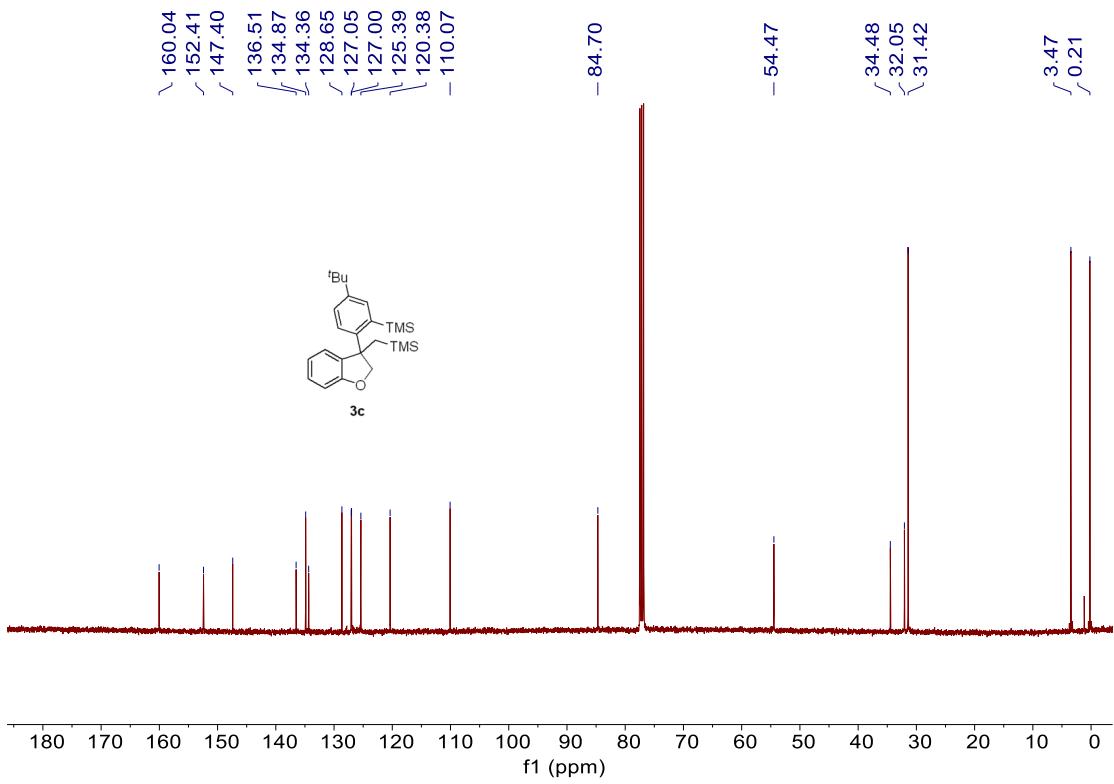
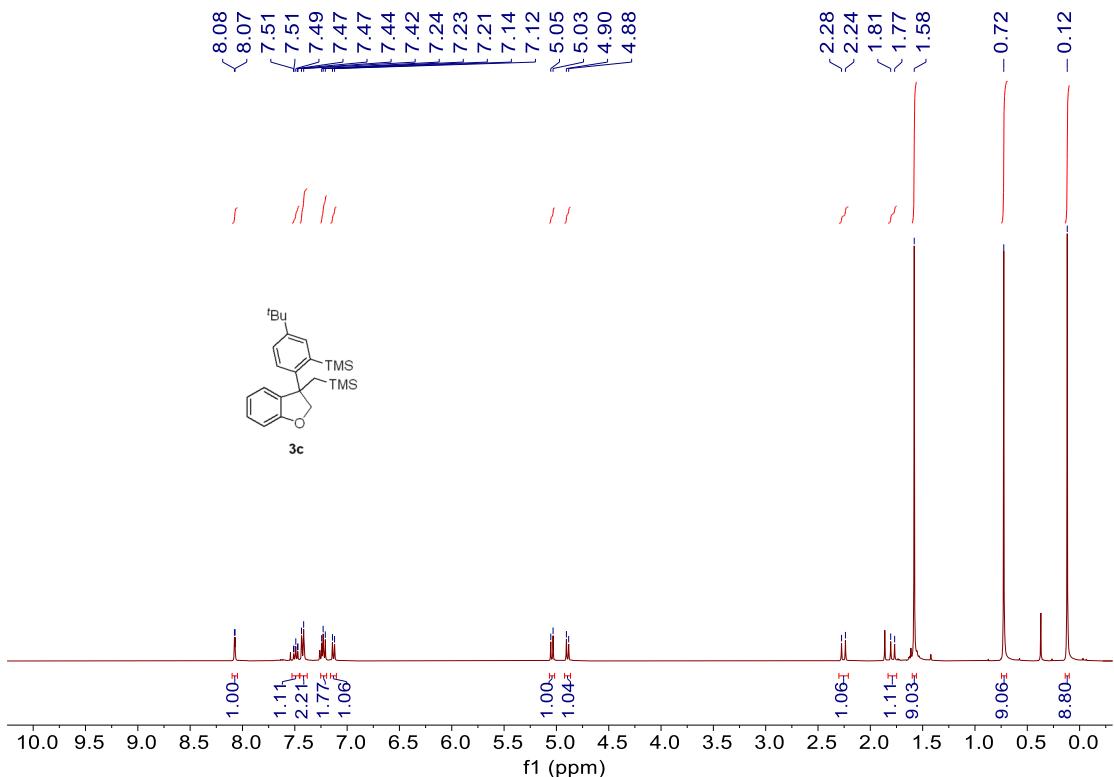


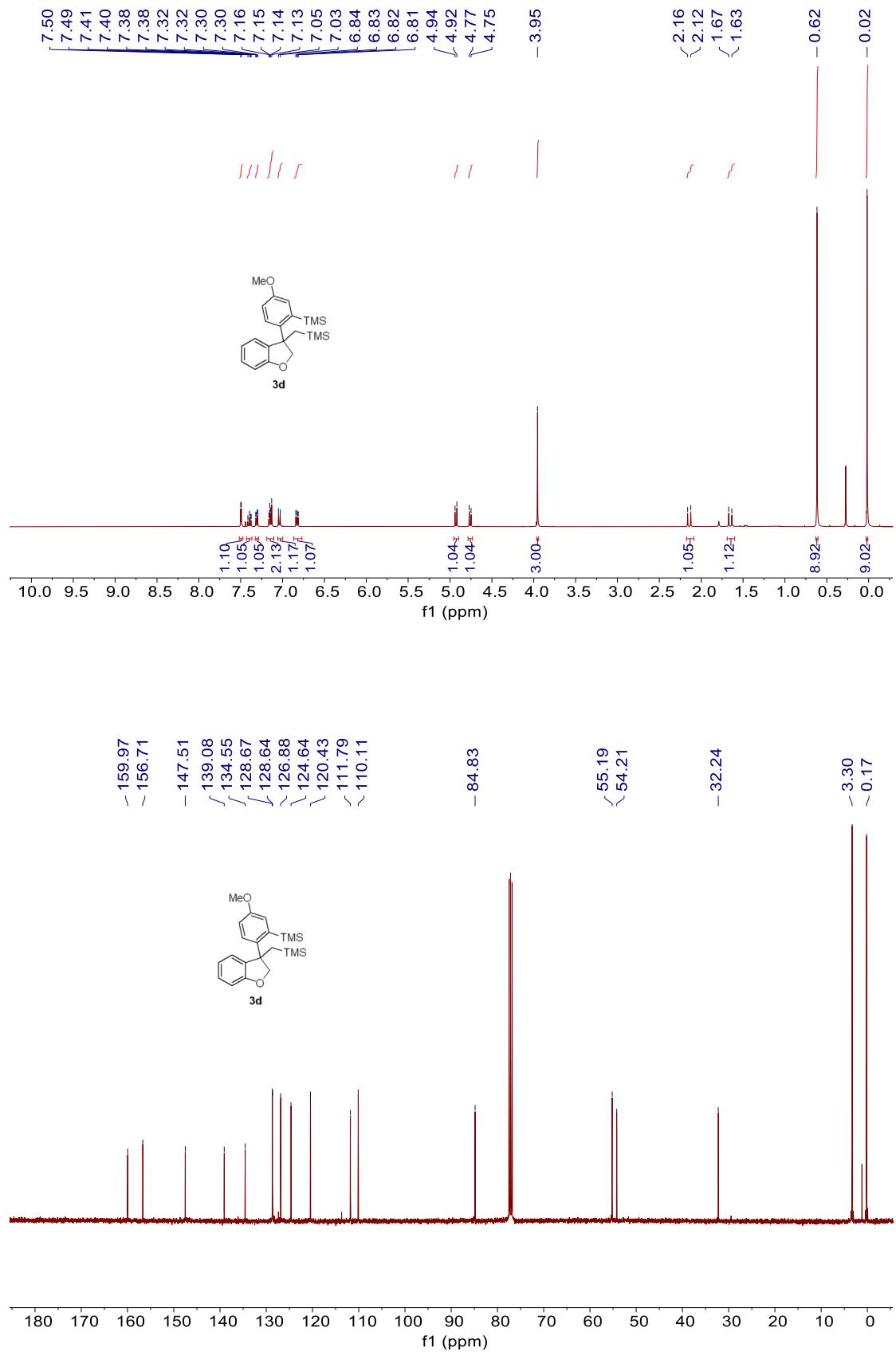


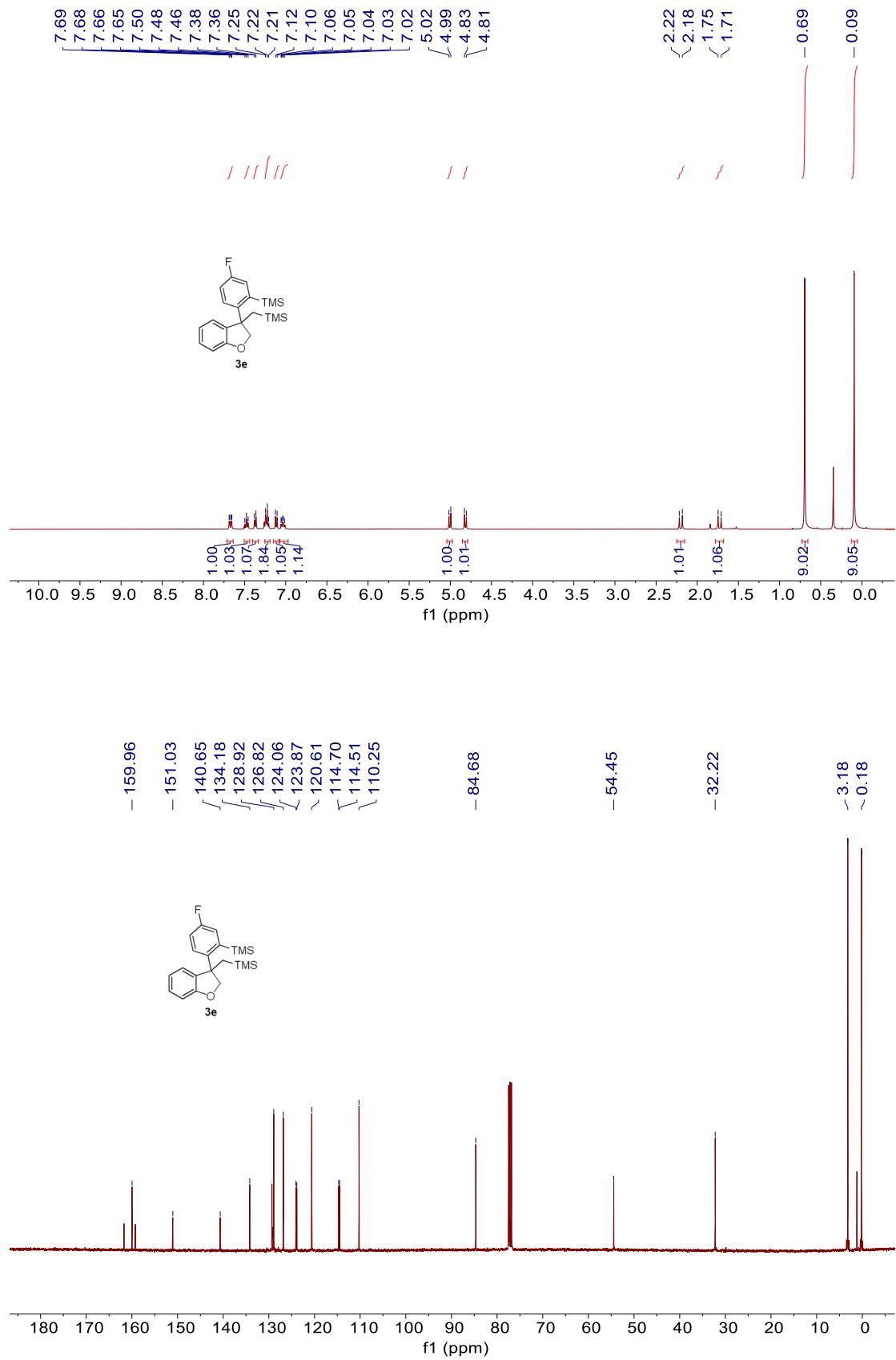


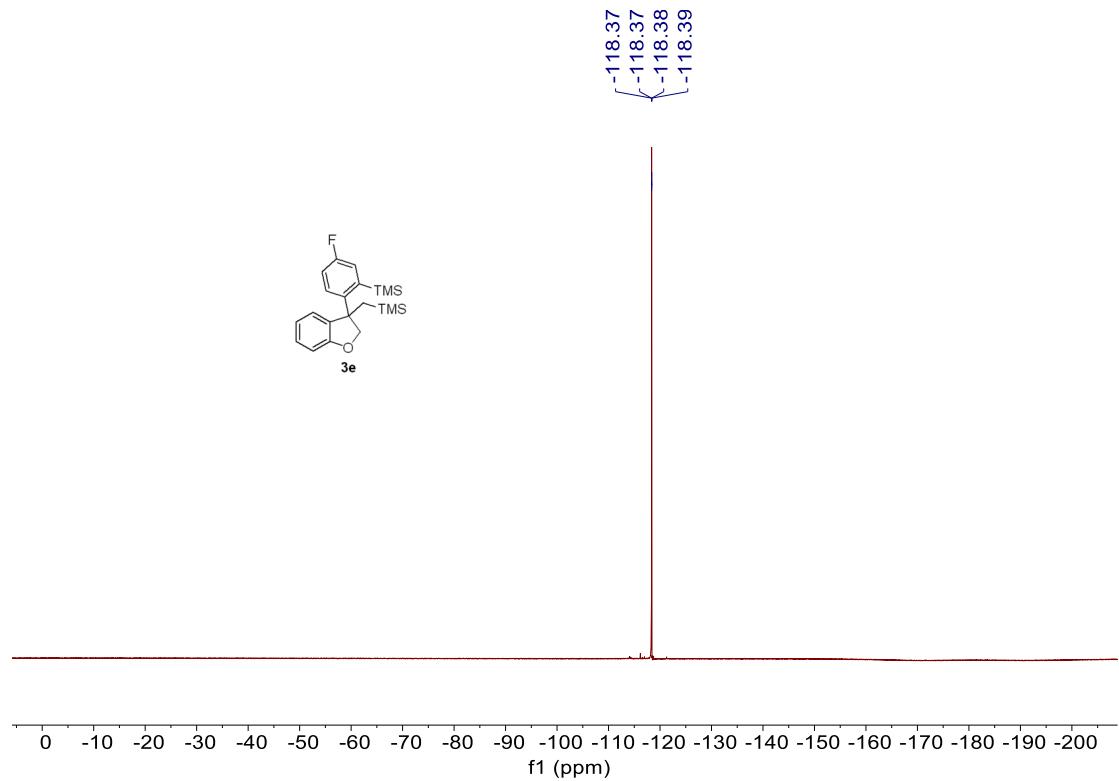


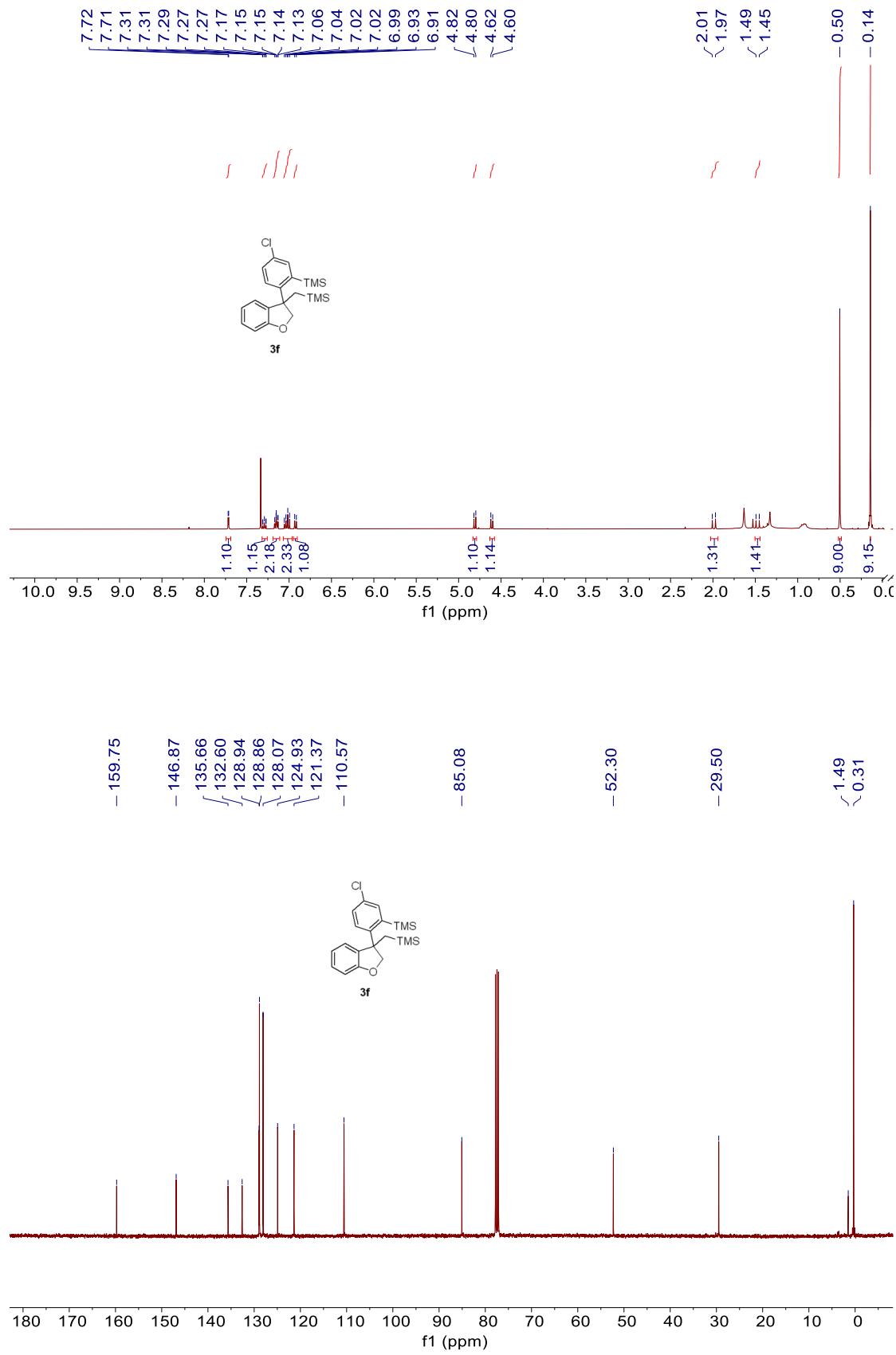


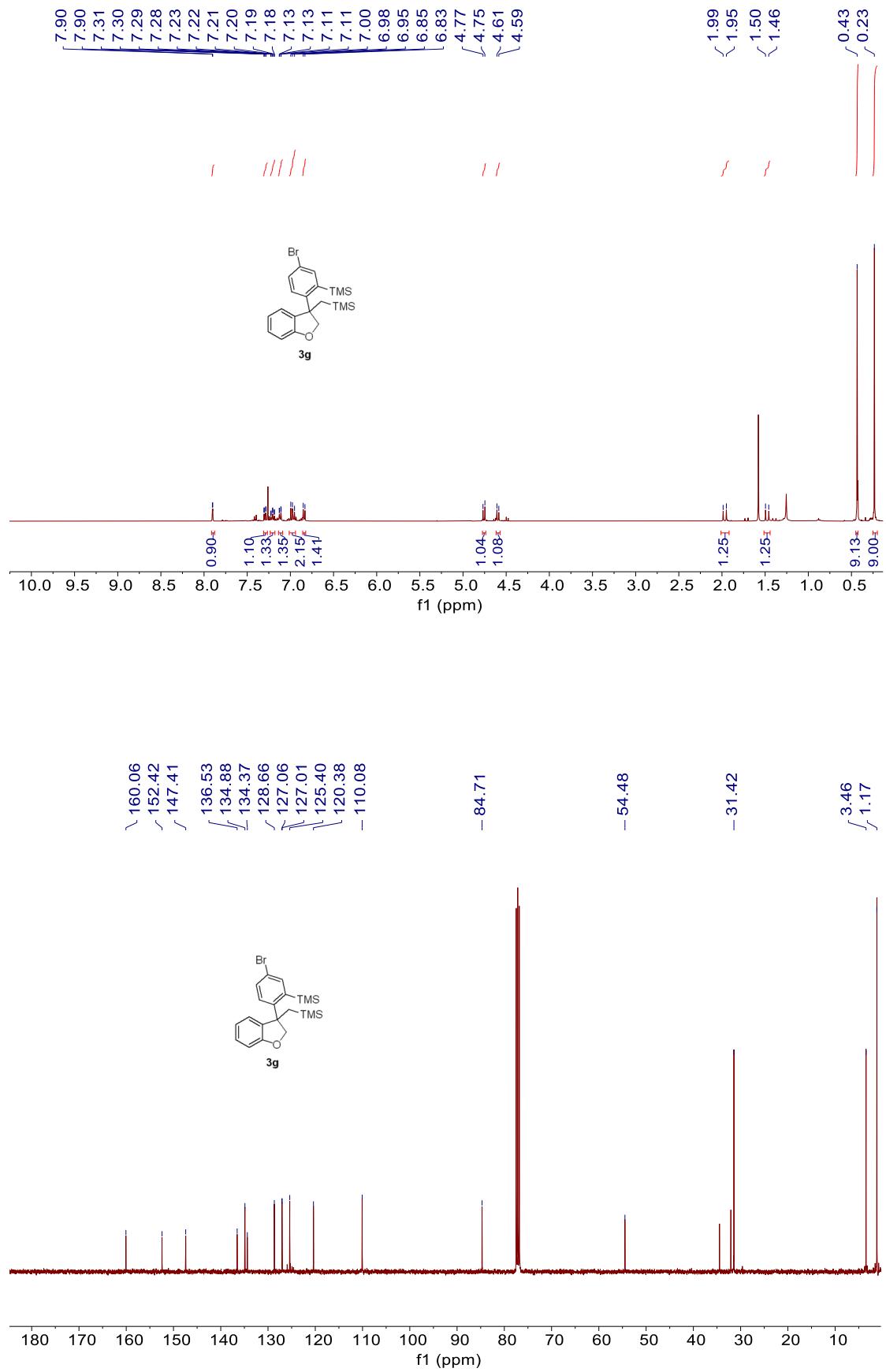


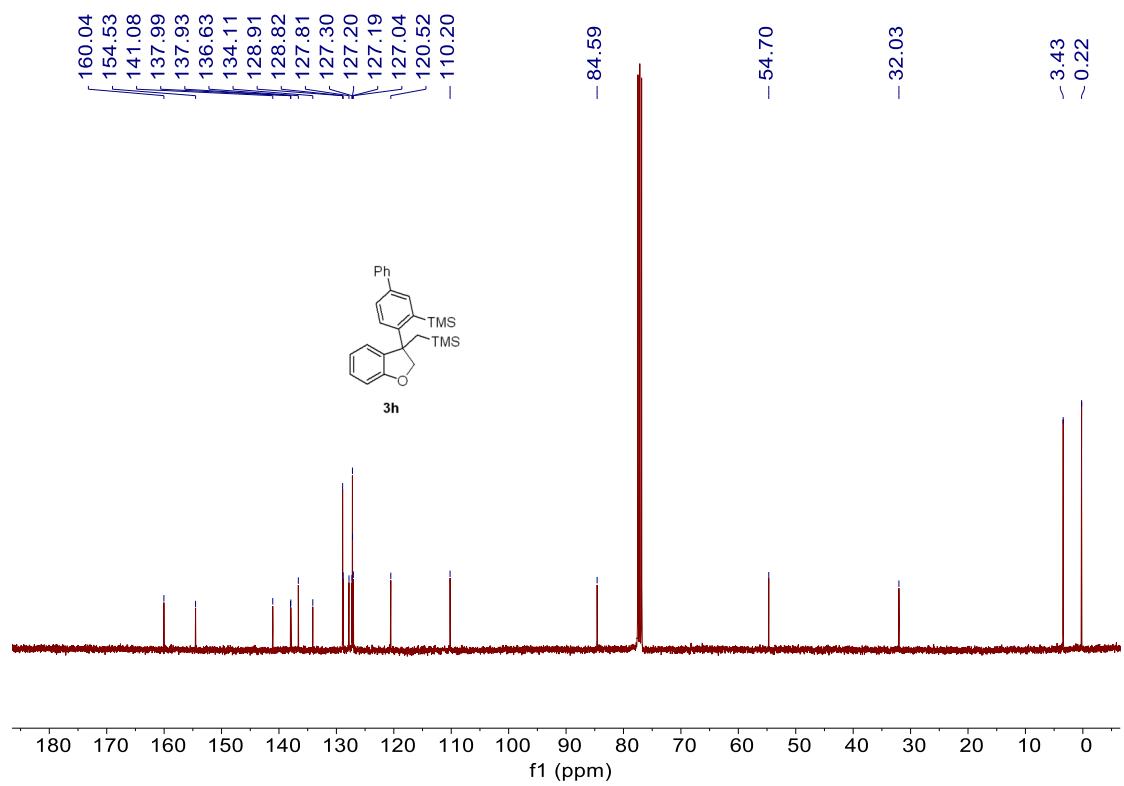
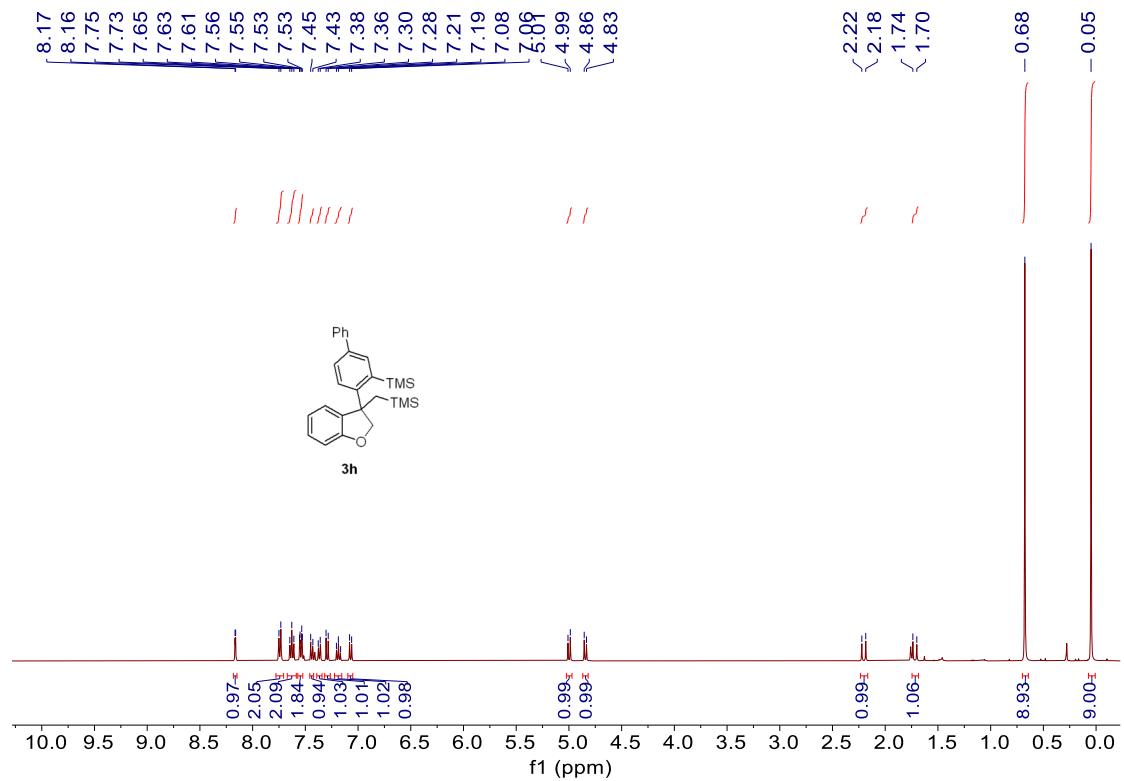


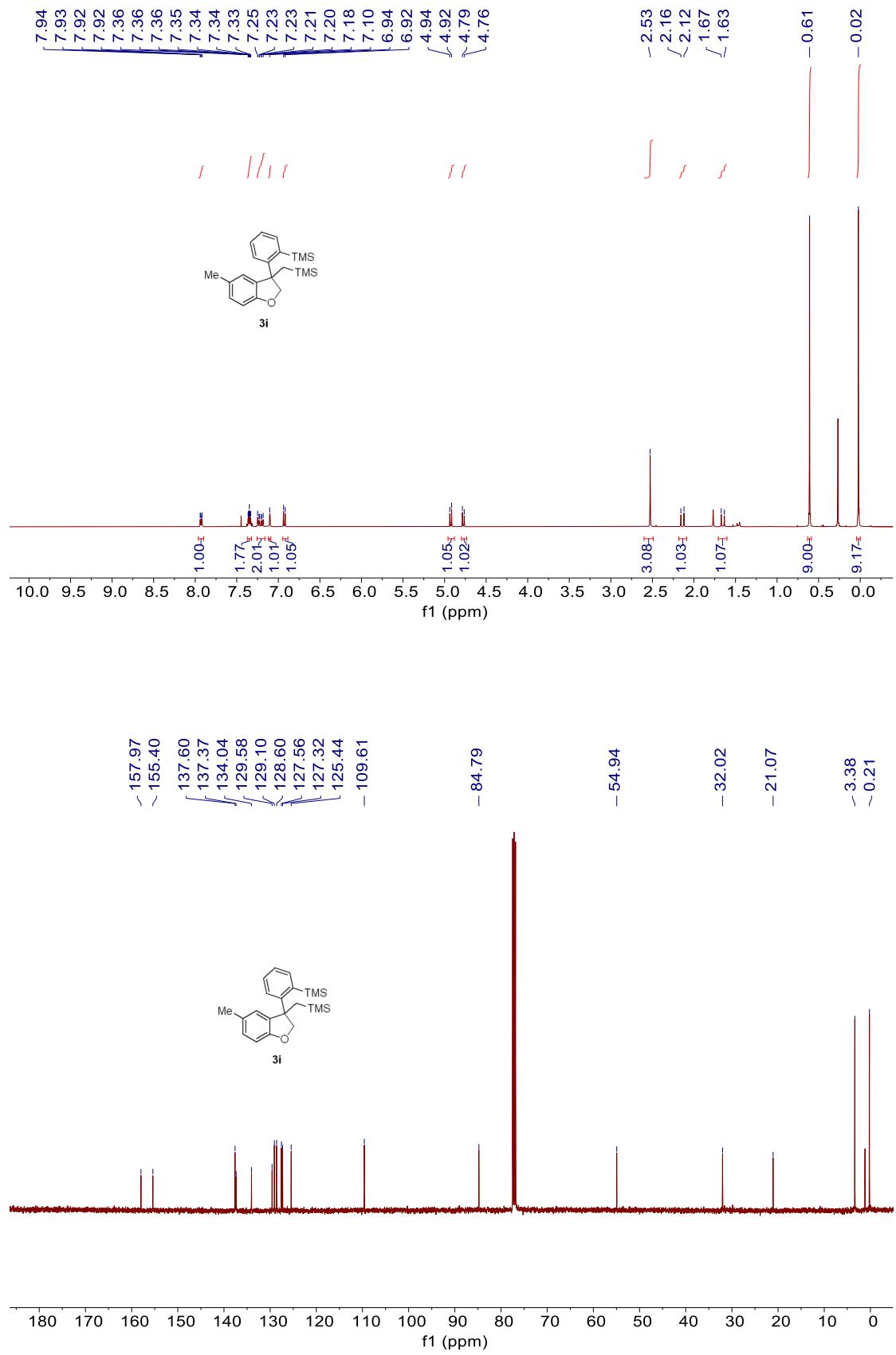


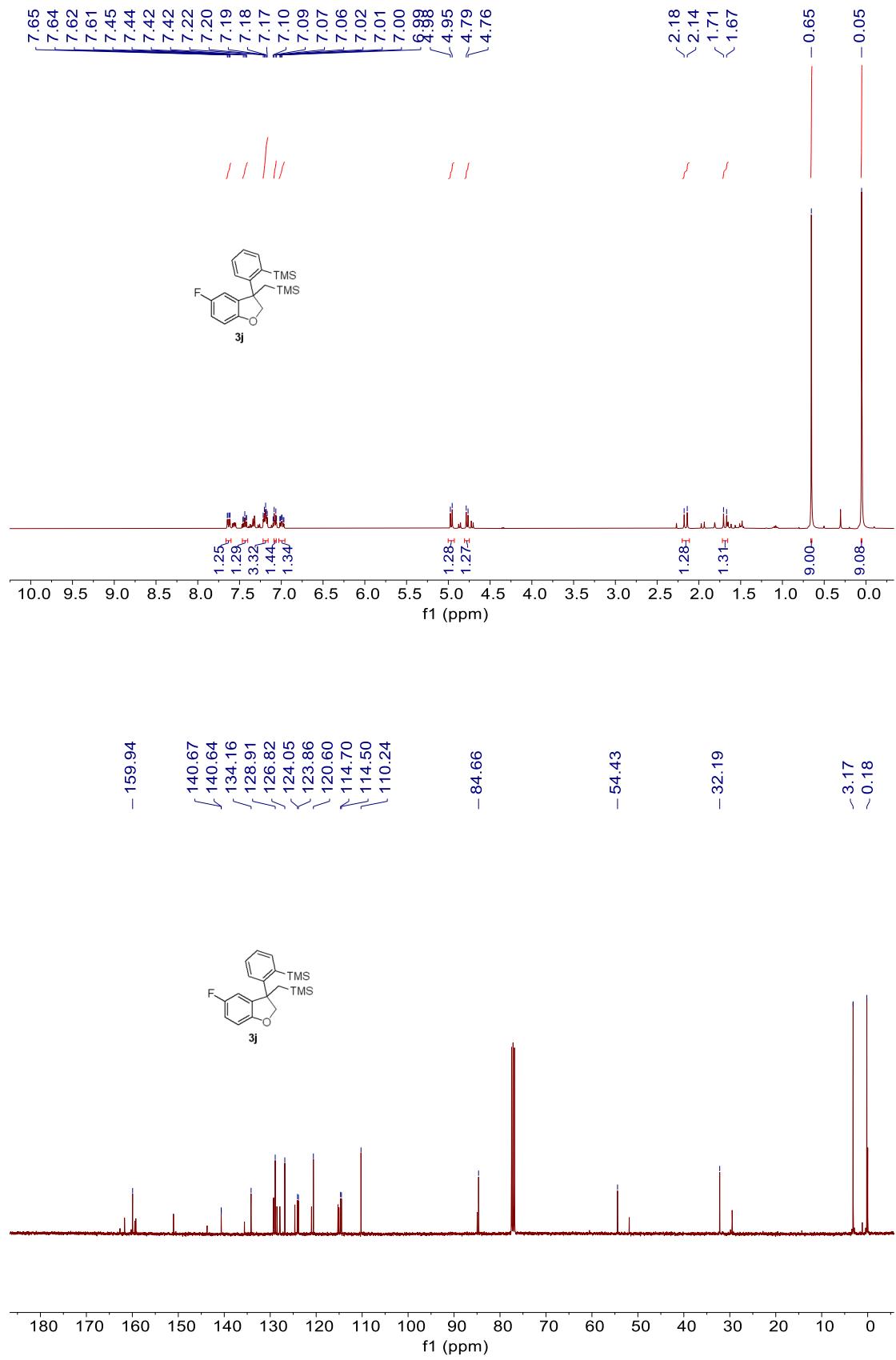


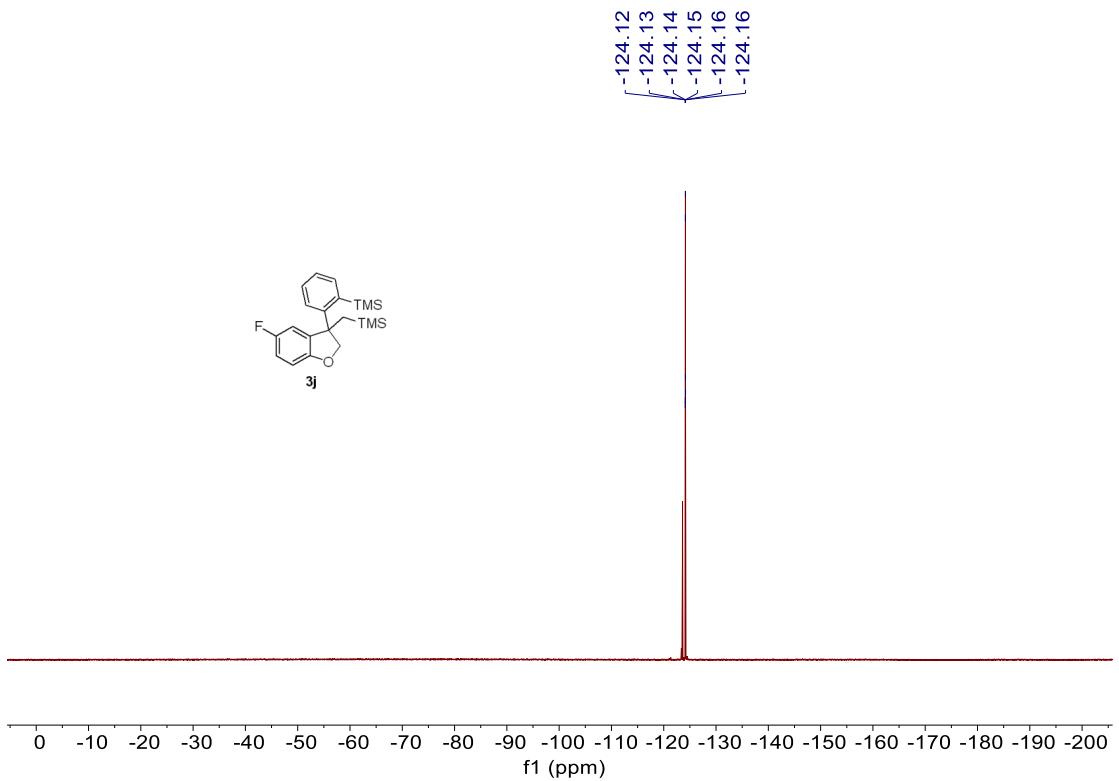


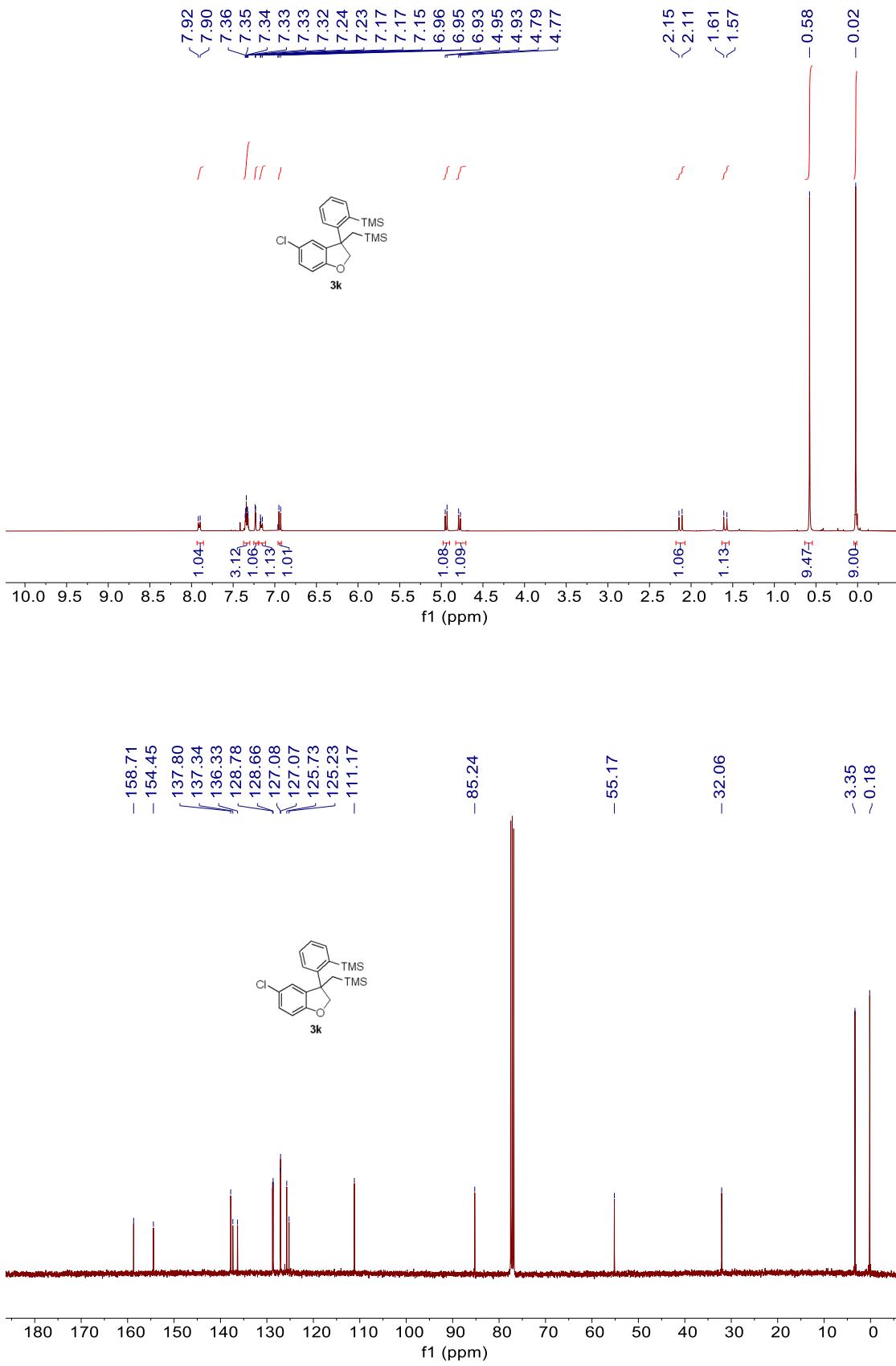


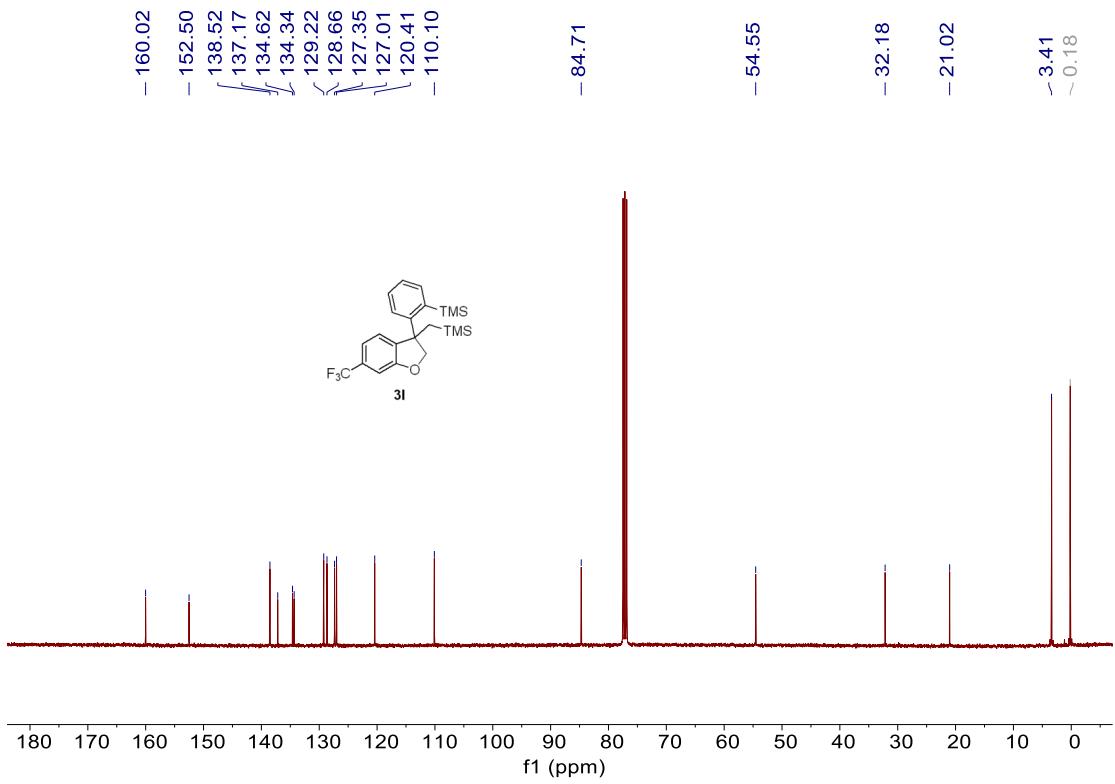
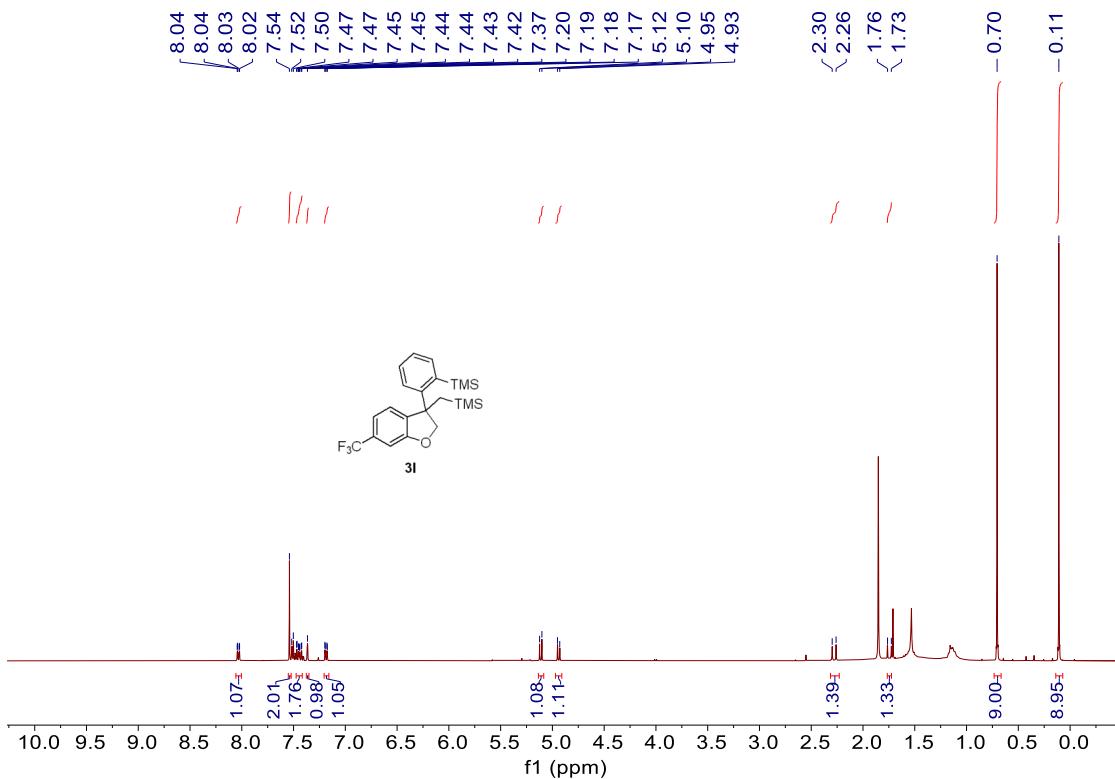


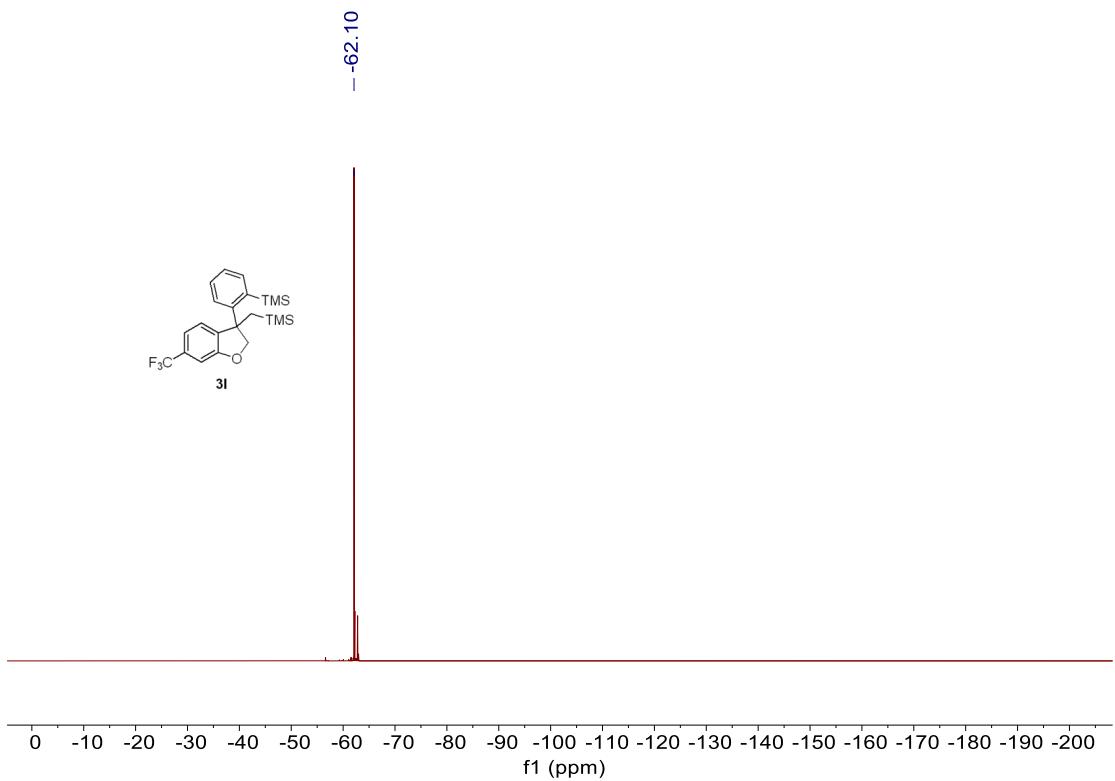


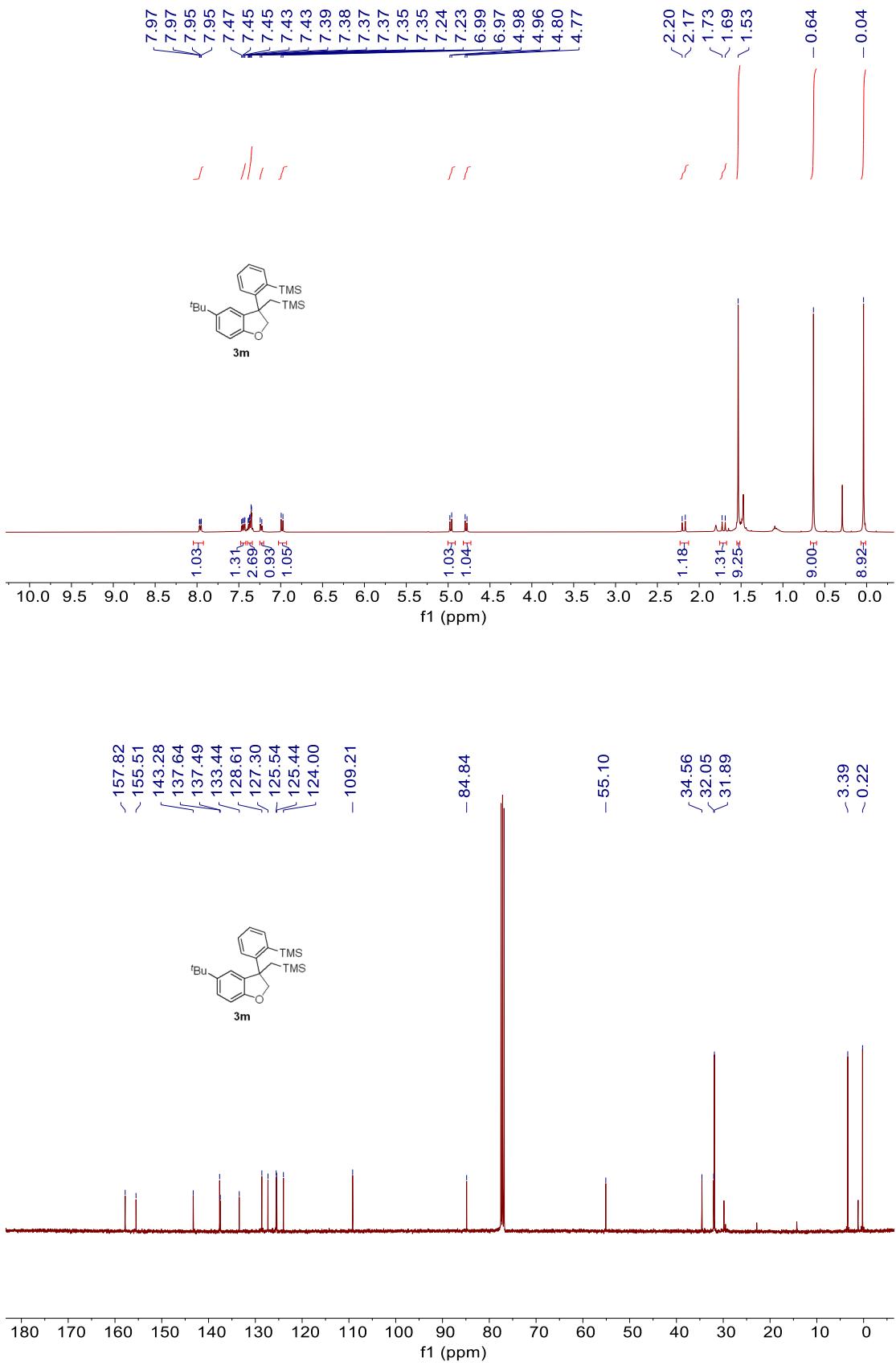


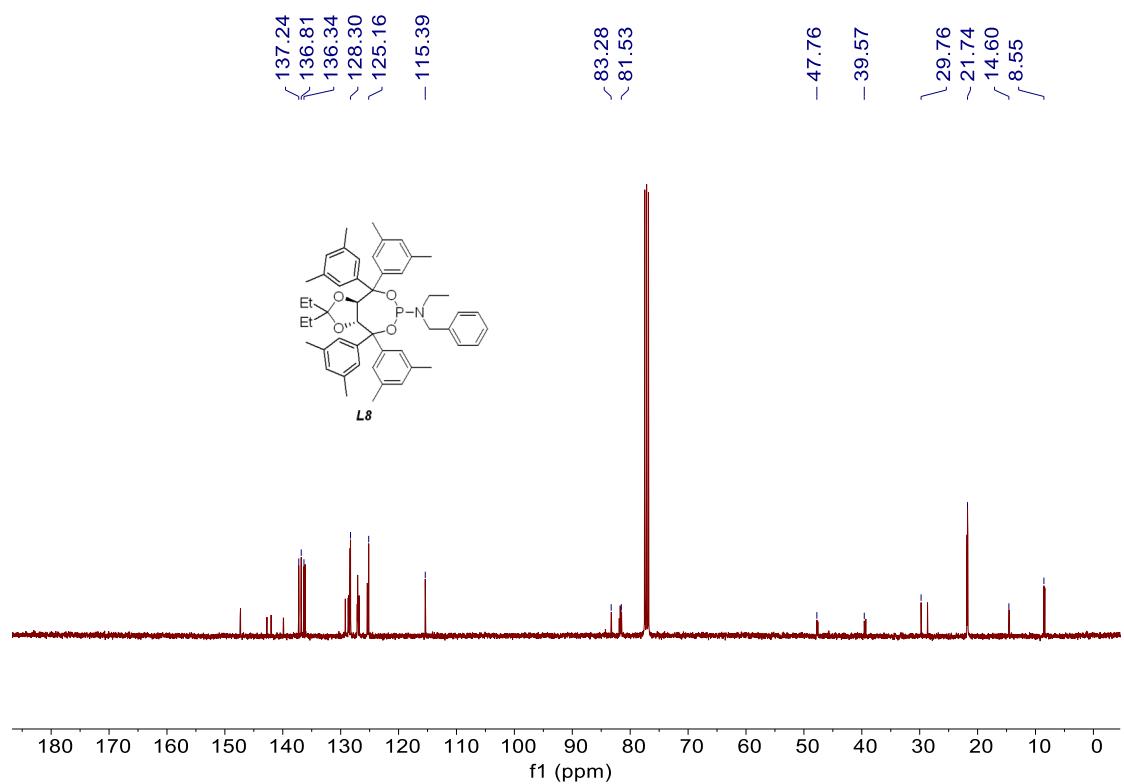
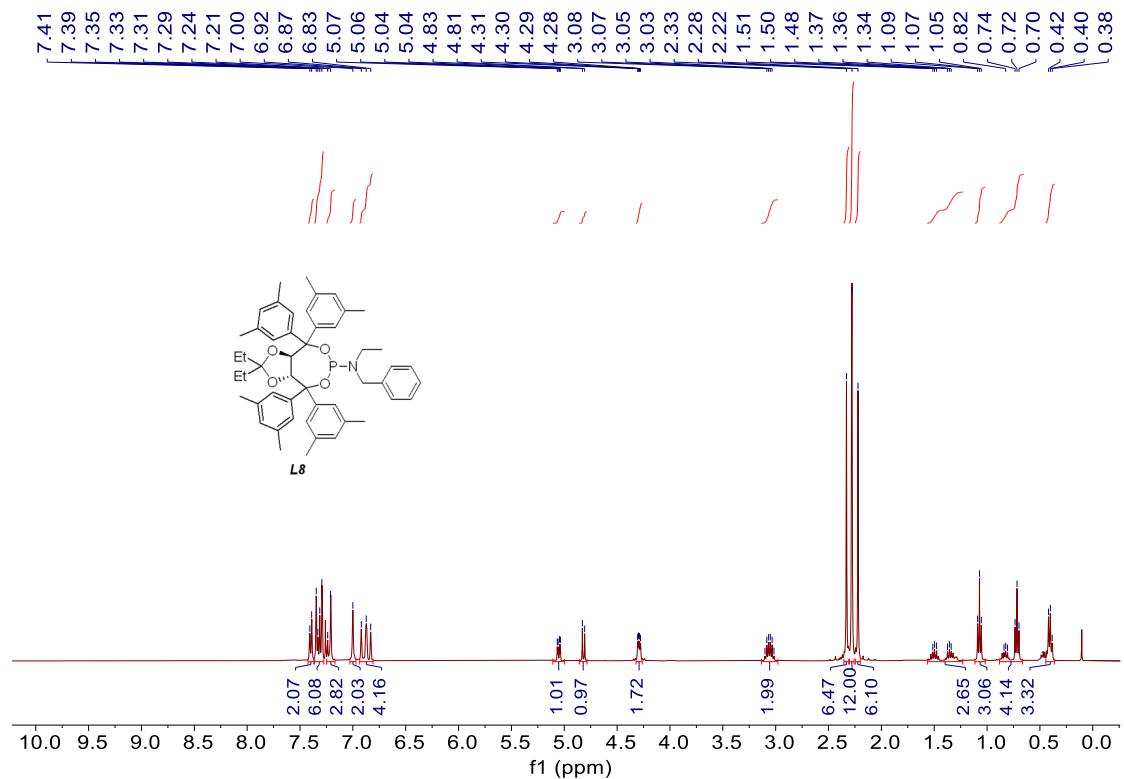




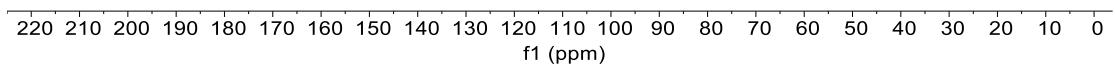
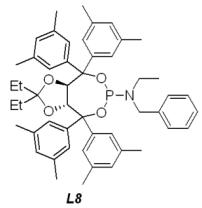


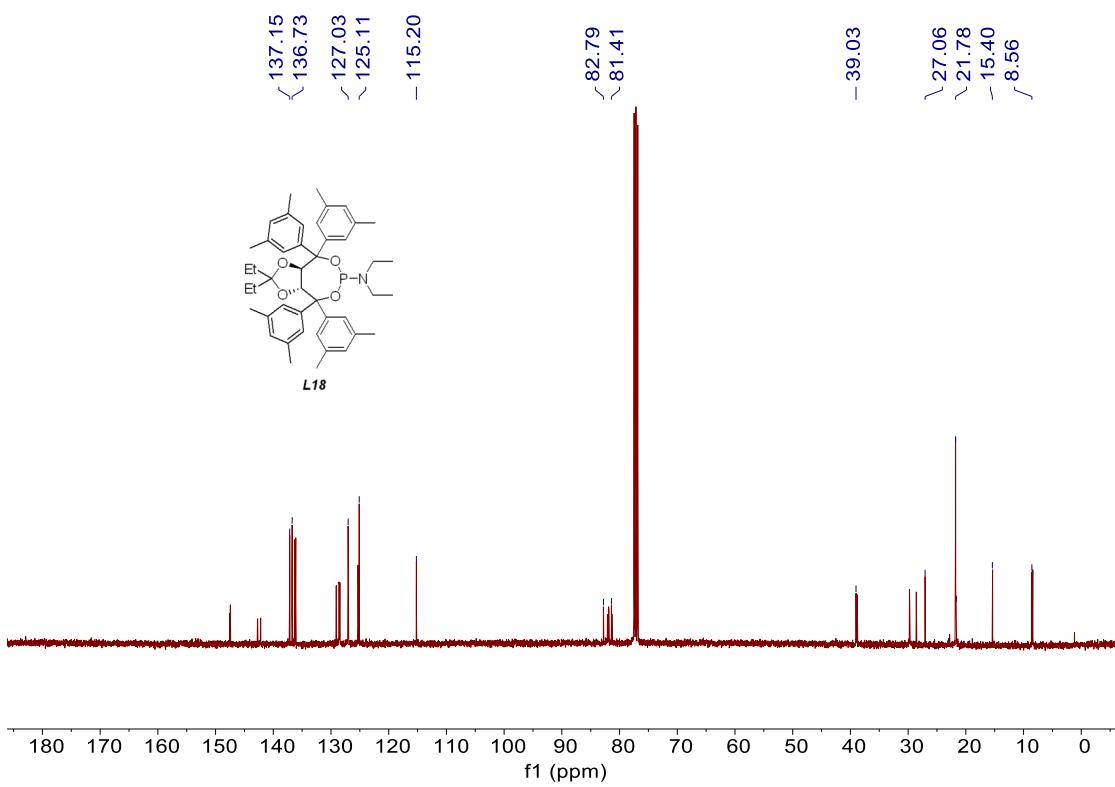
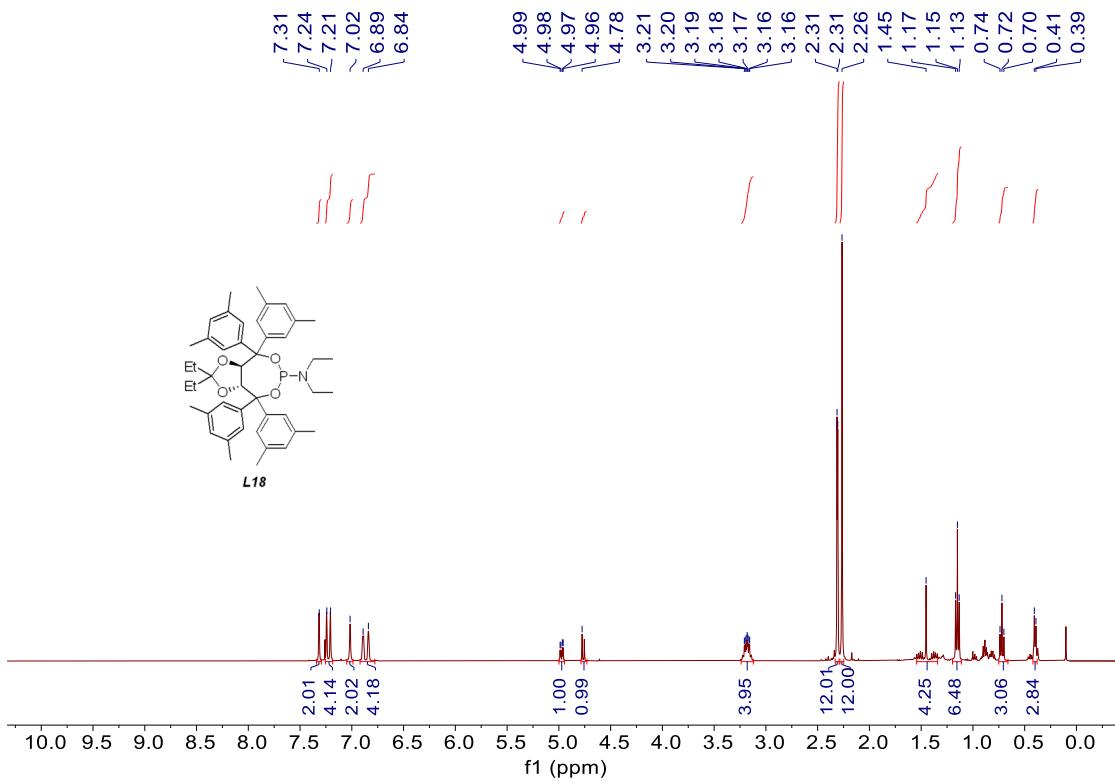




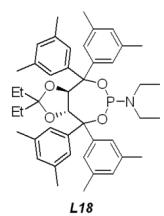


- 138.68

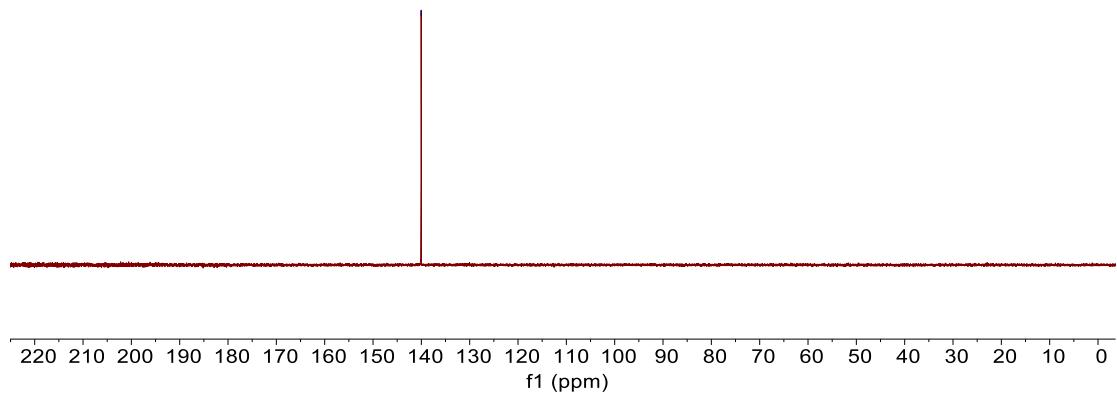


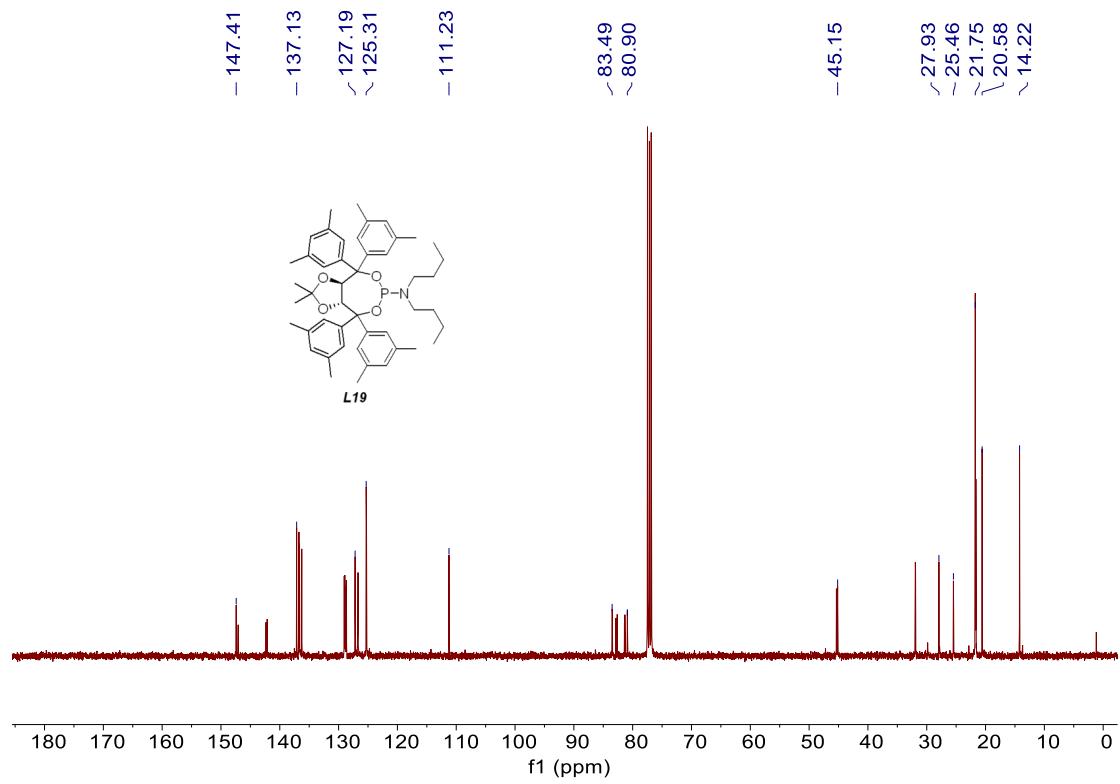
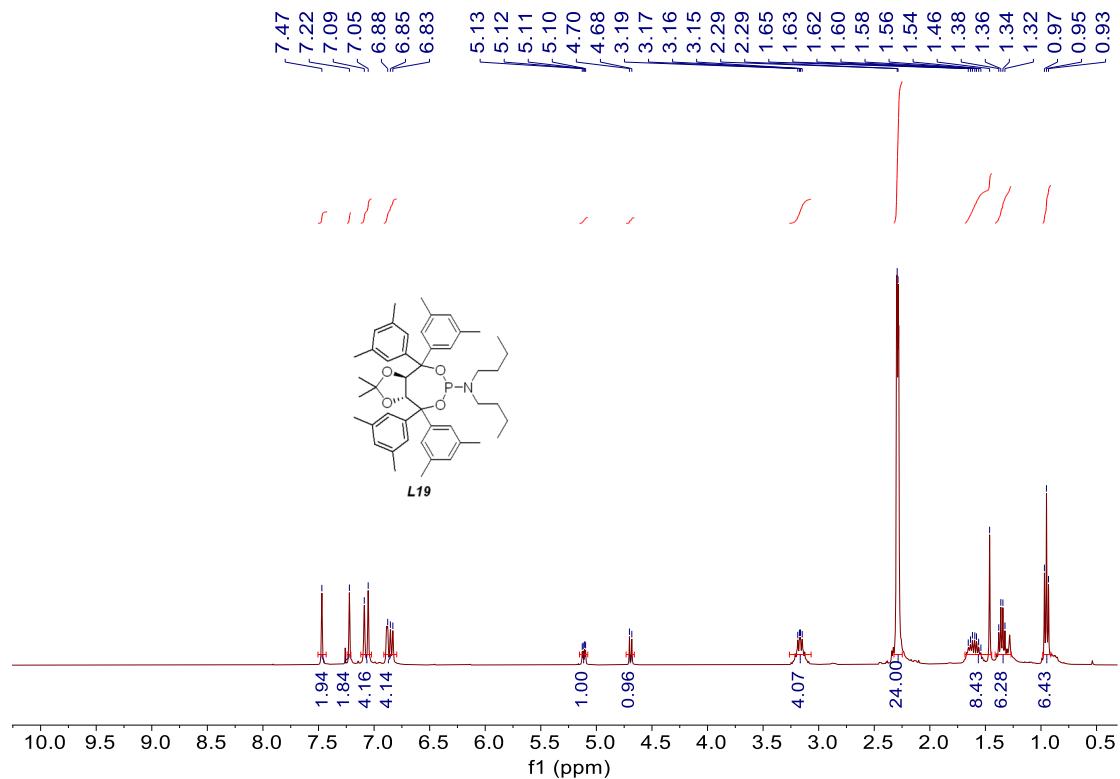


- 140.04

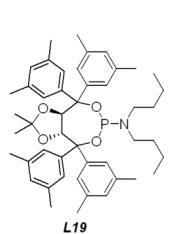


L18

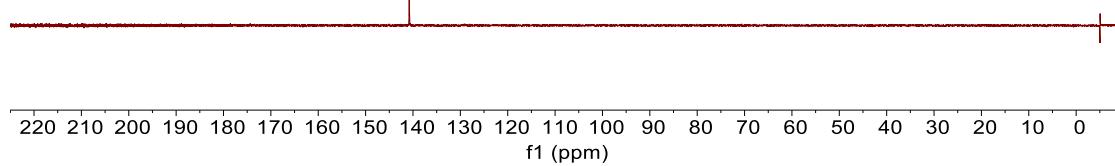


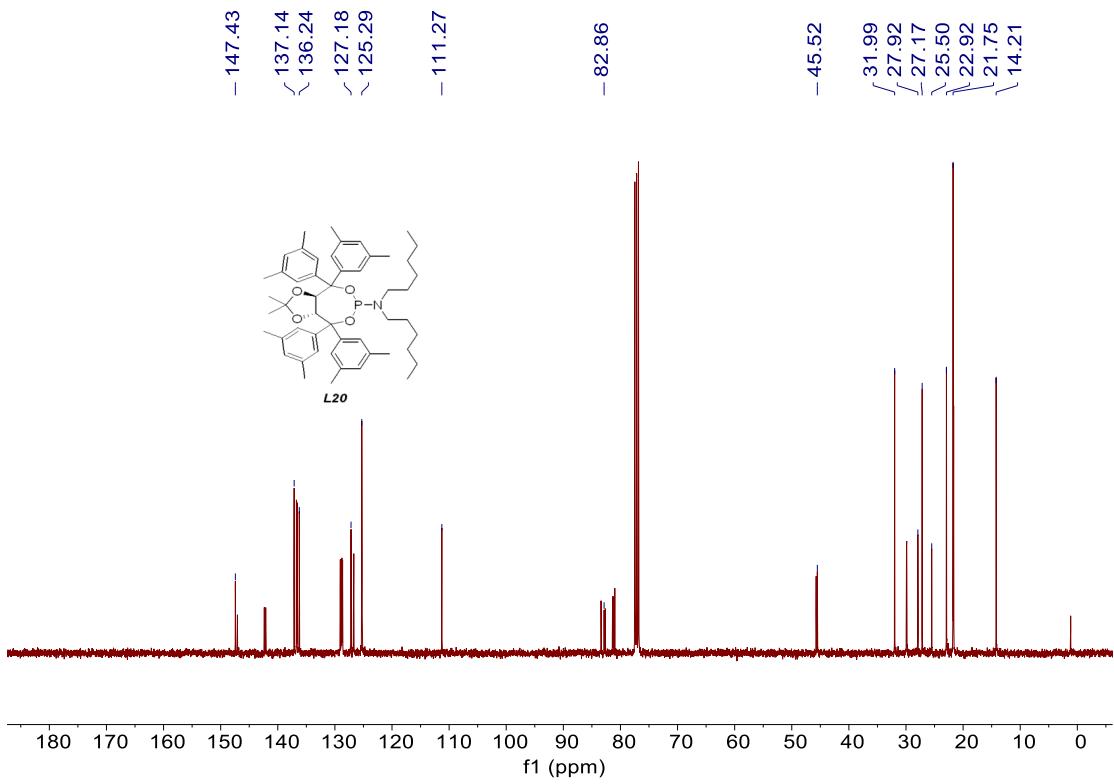
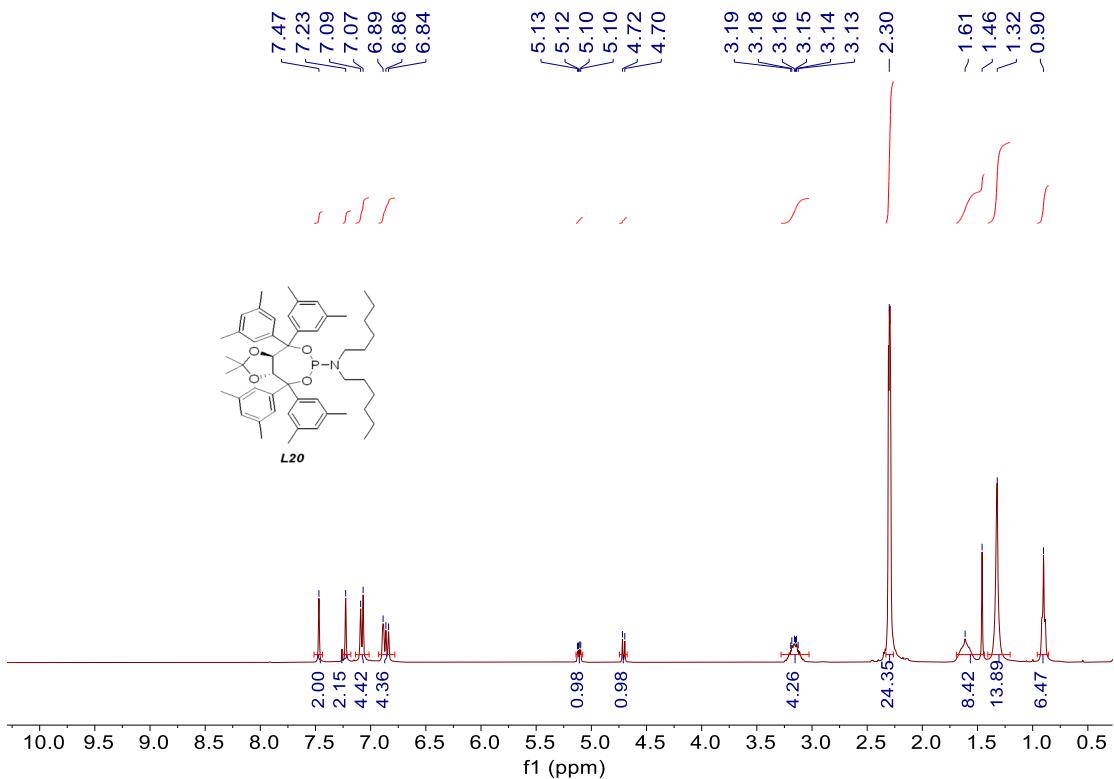


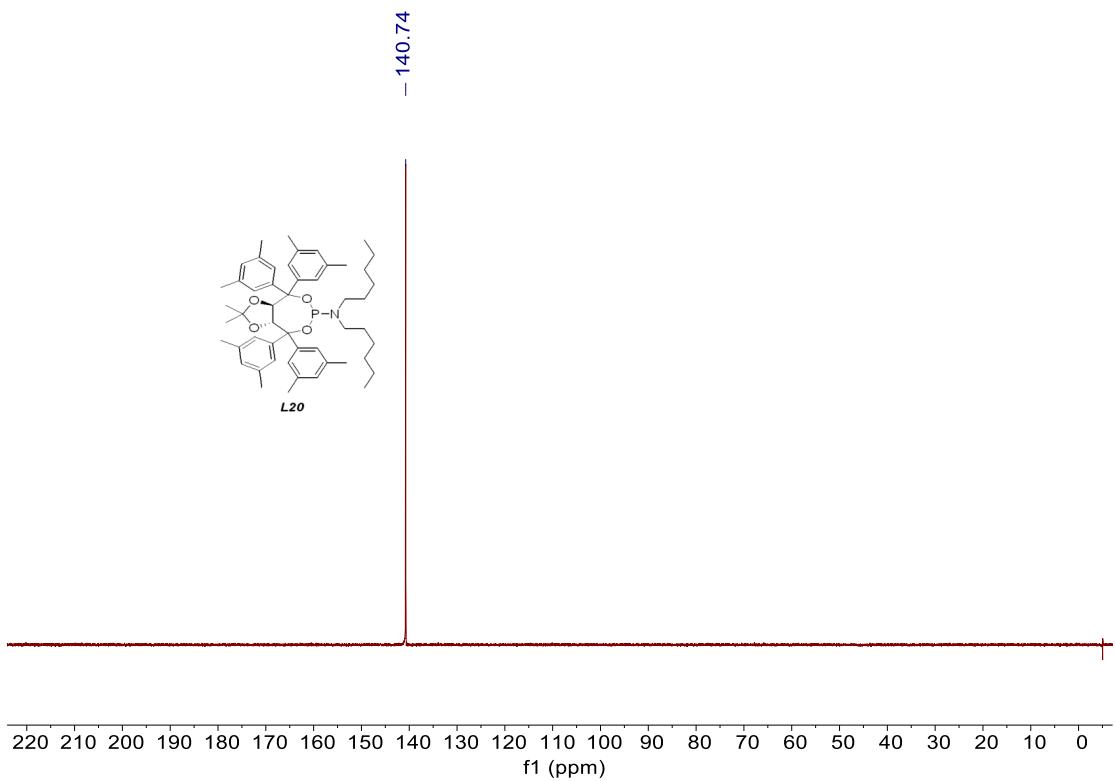
- 140.79

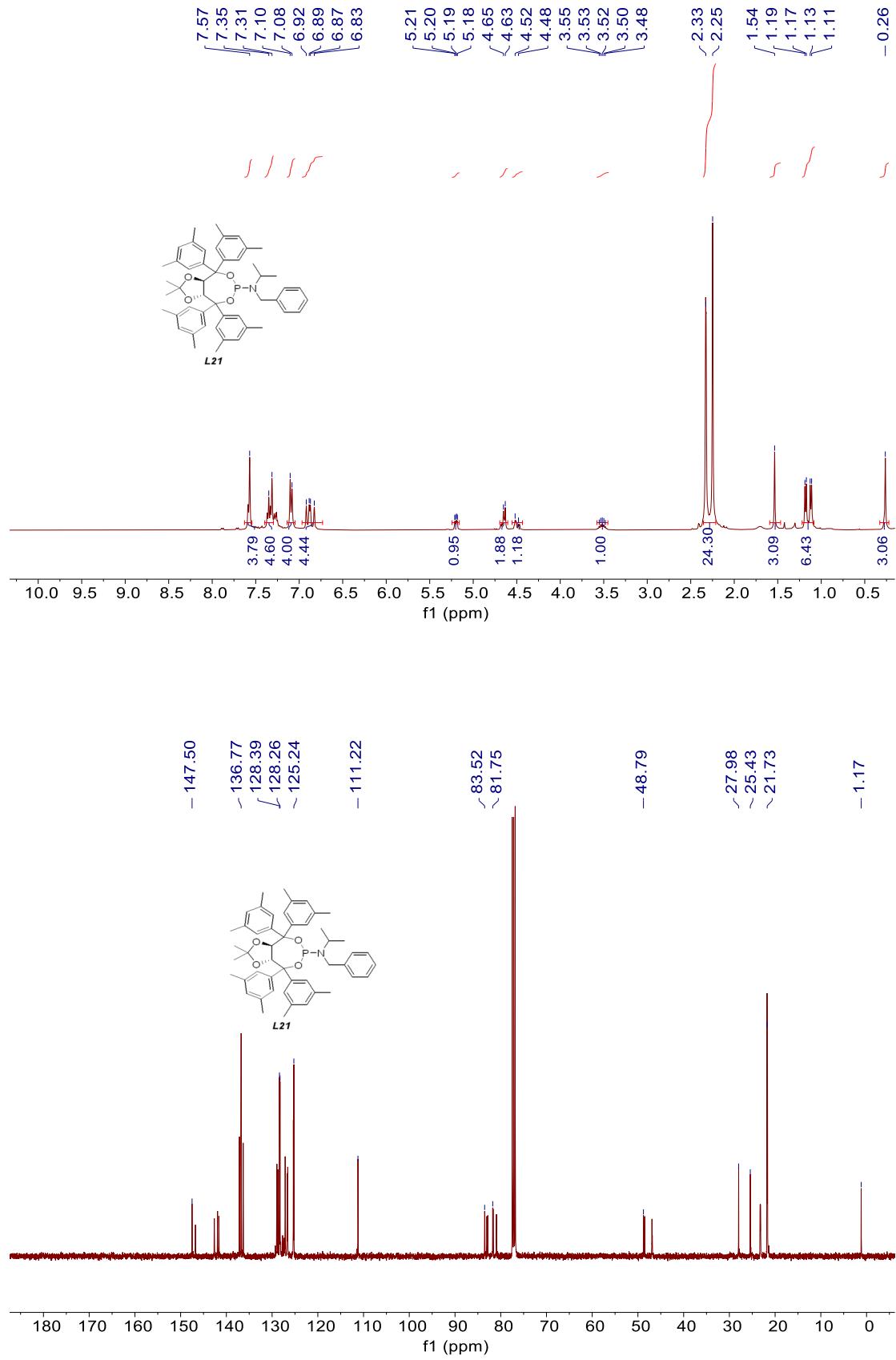


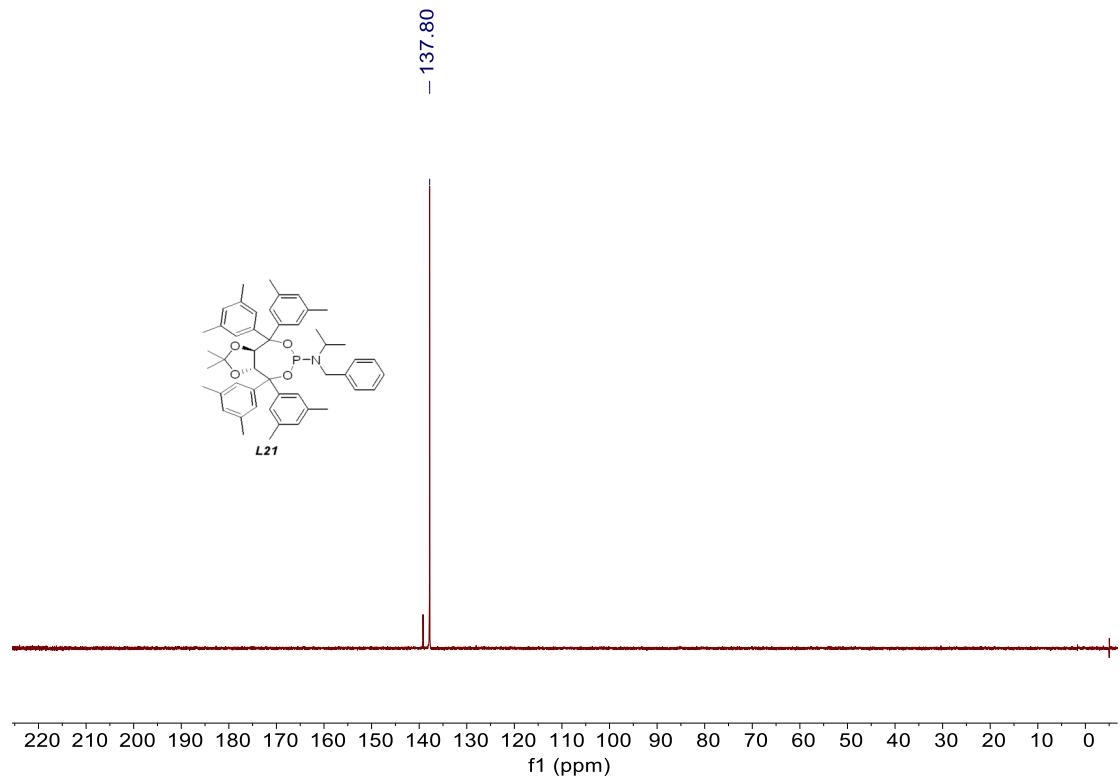
L19

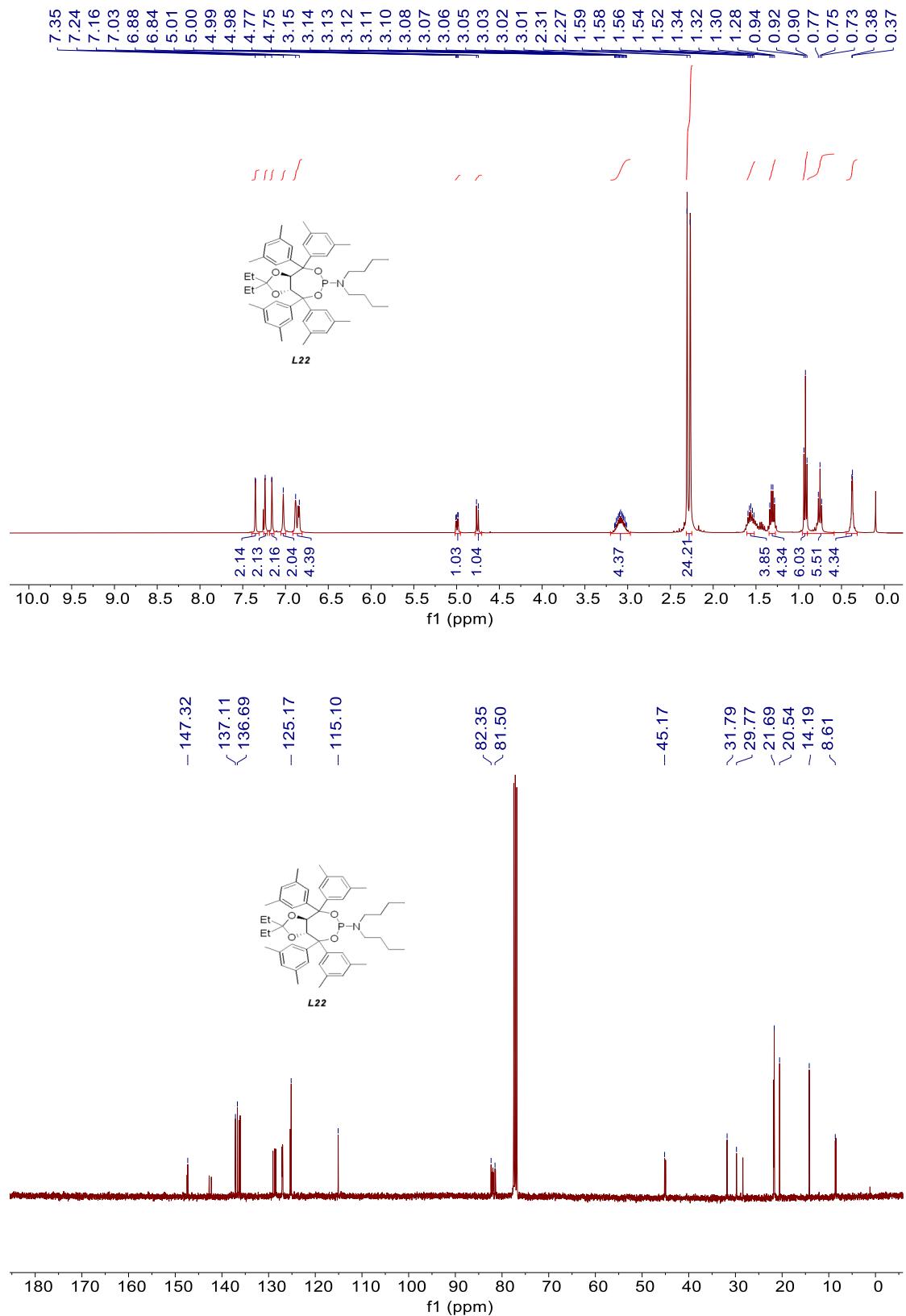


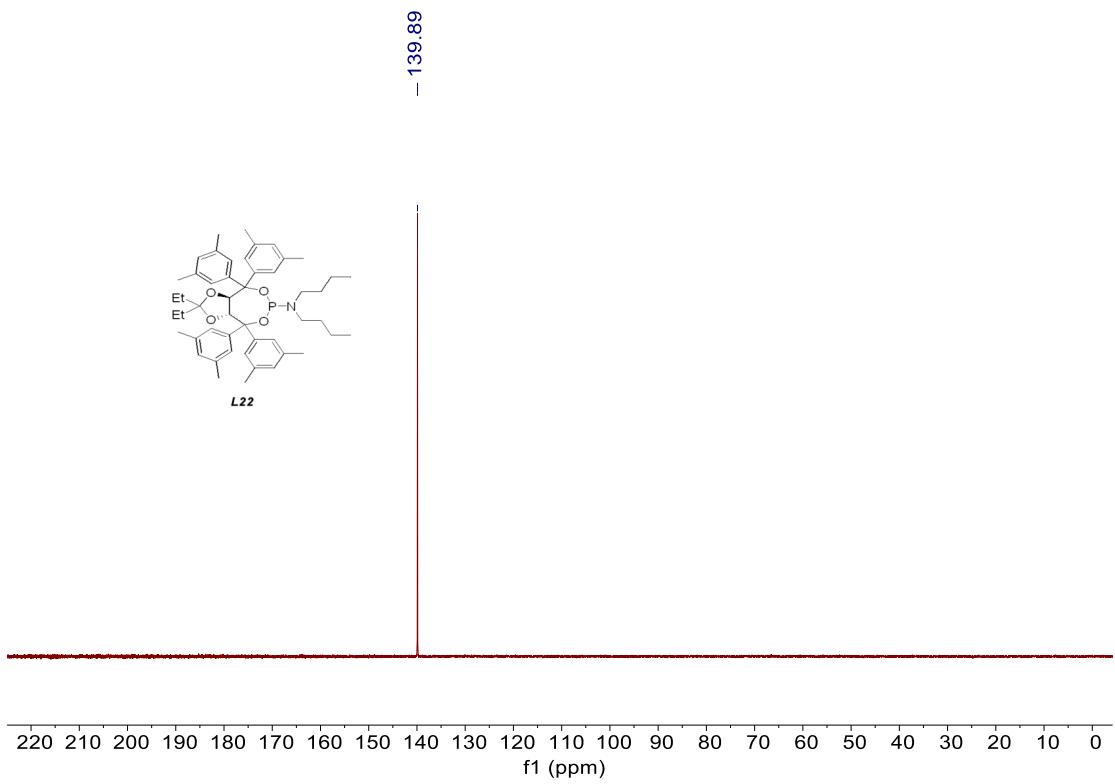


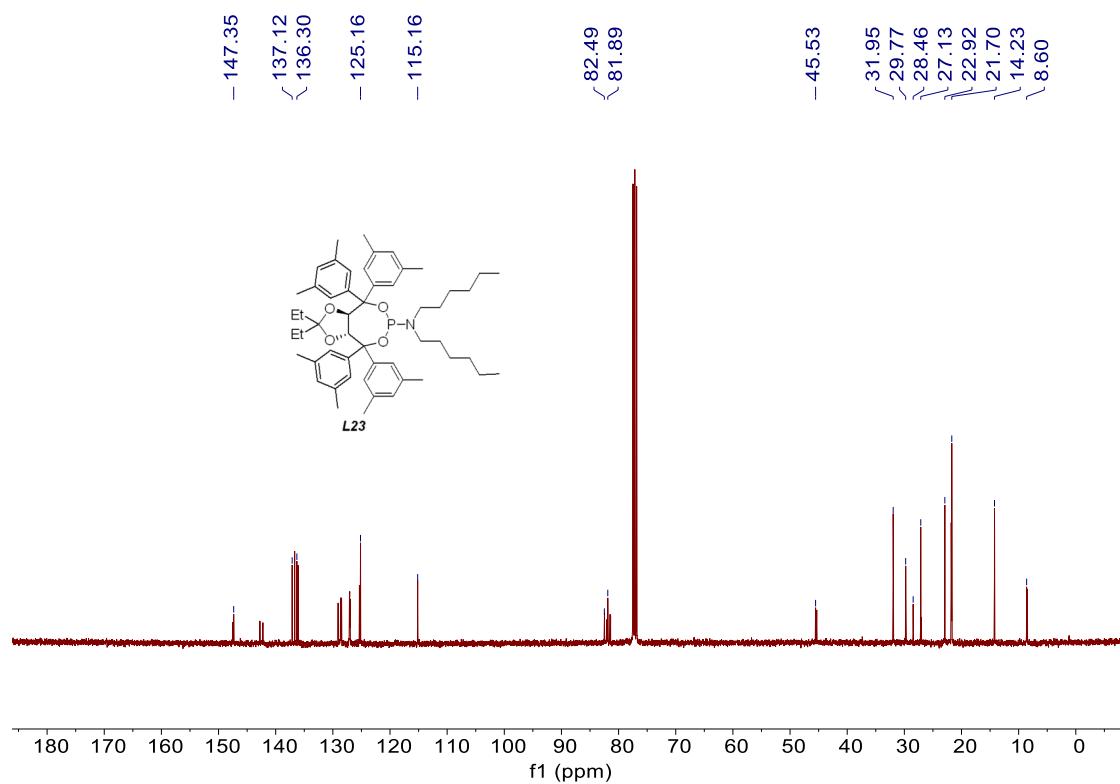
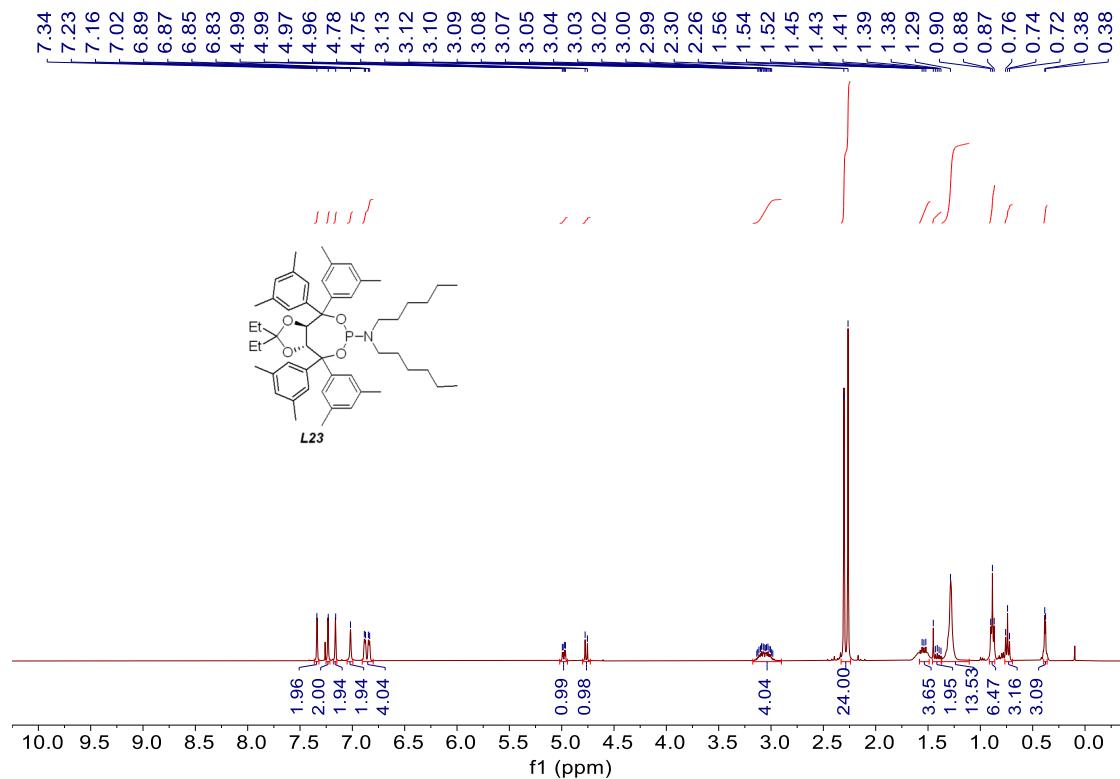


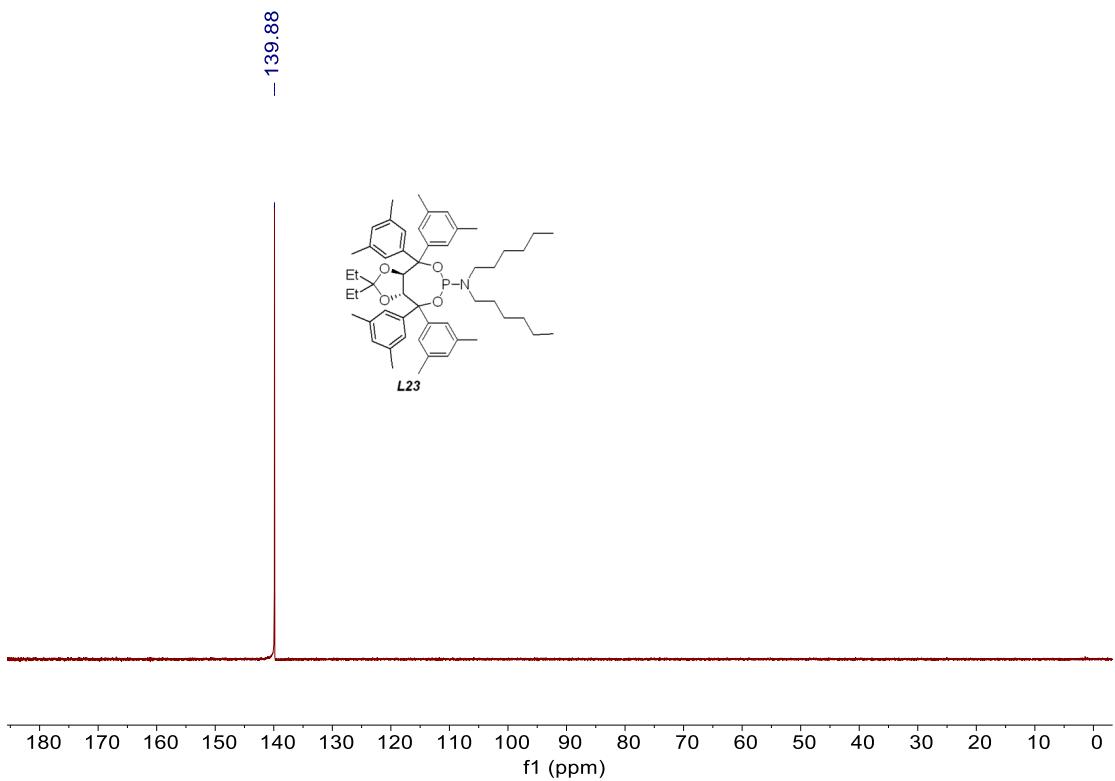


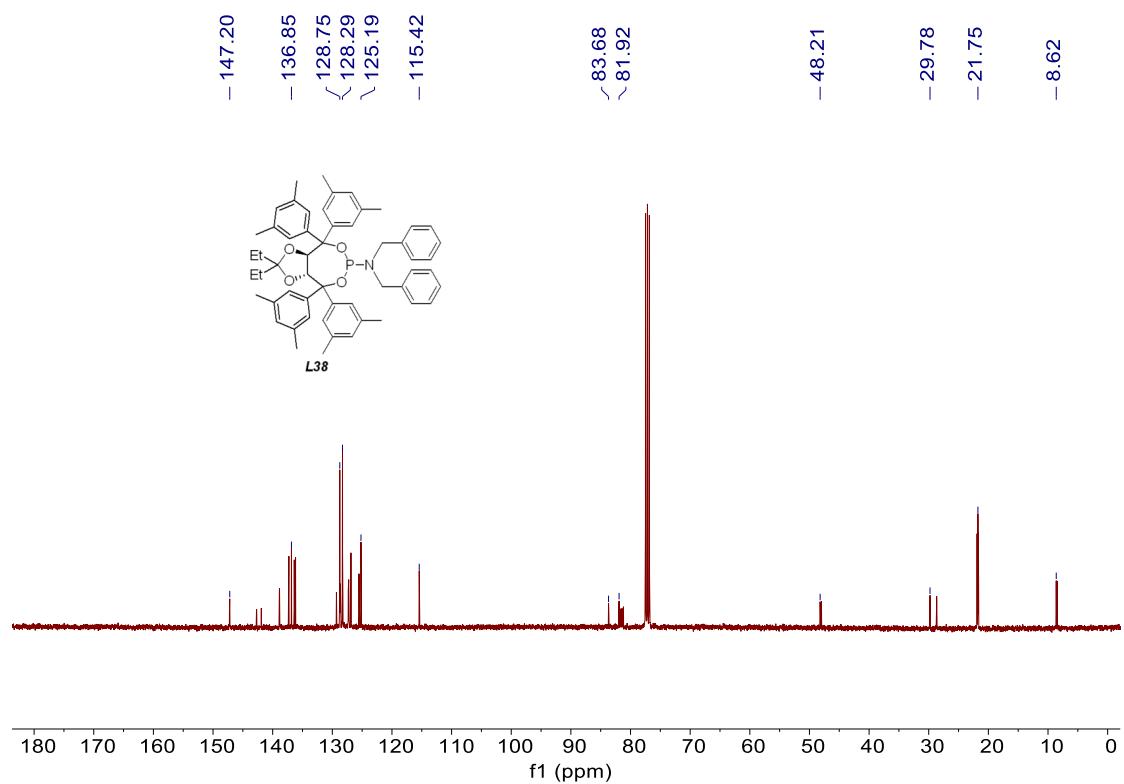
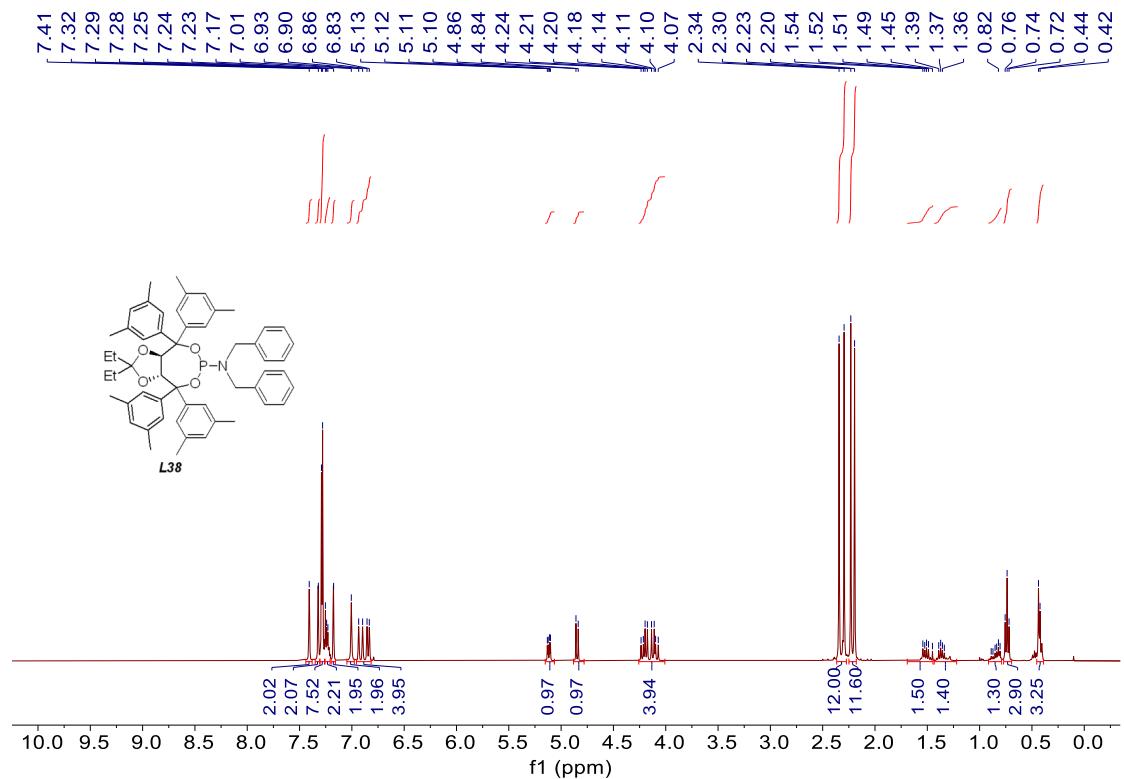




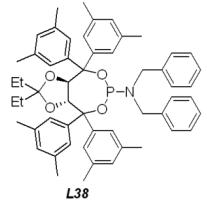




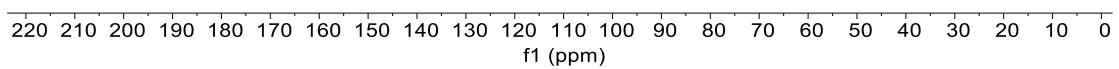


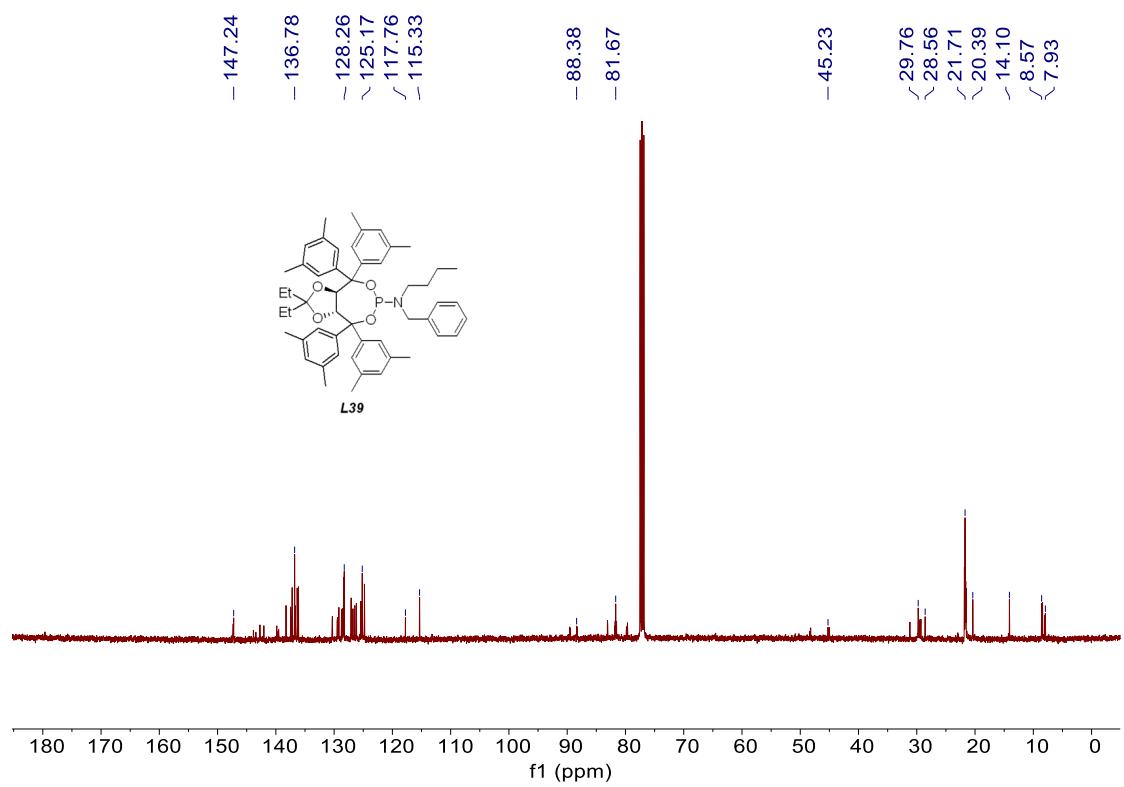
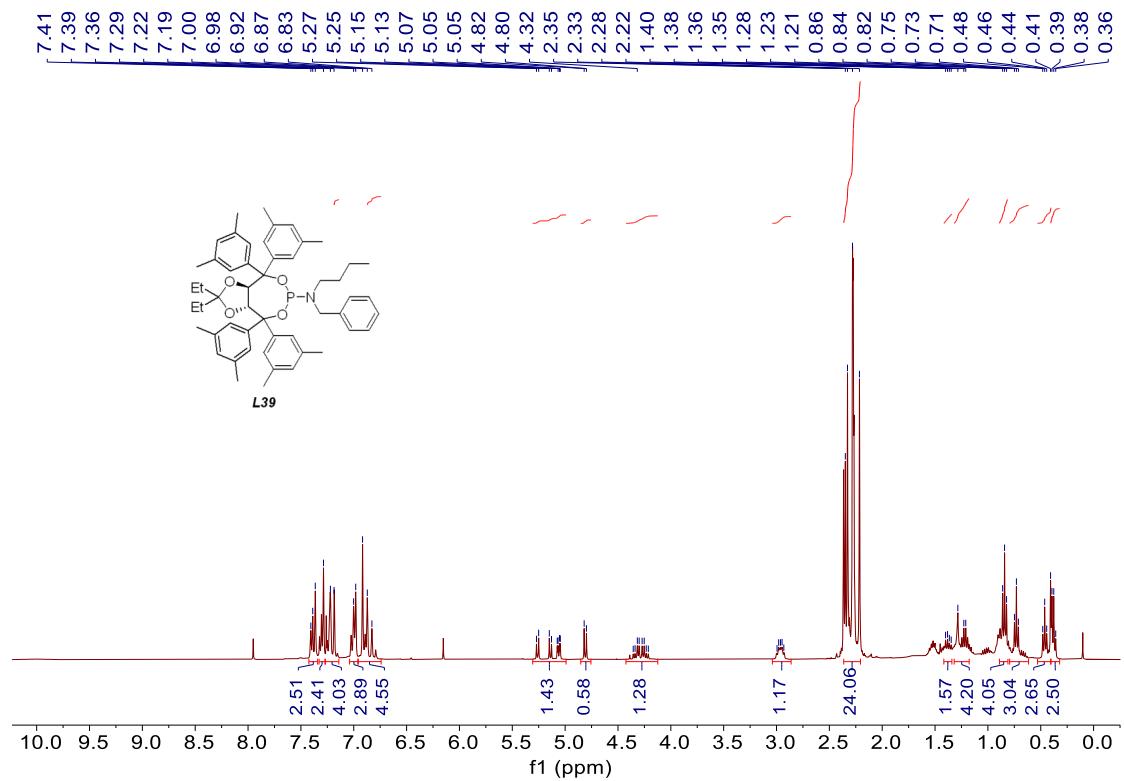


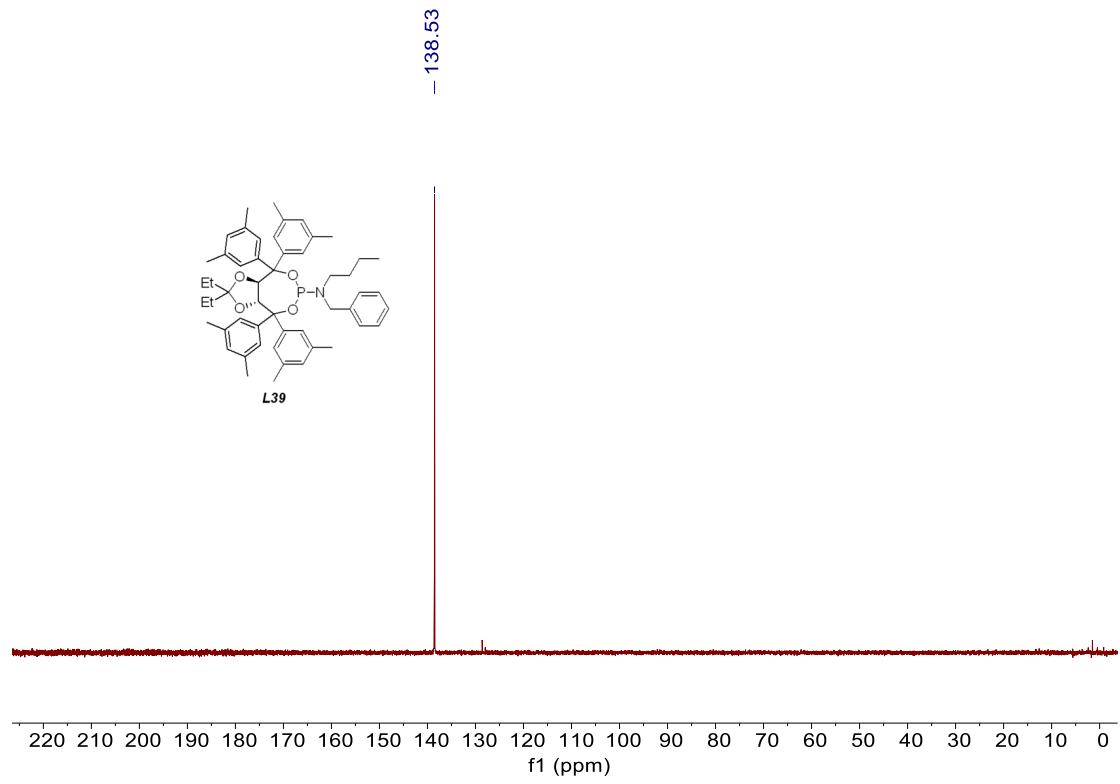
- 138.67

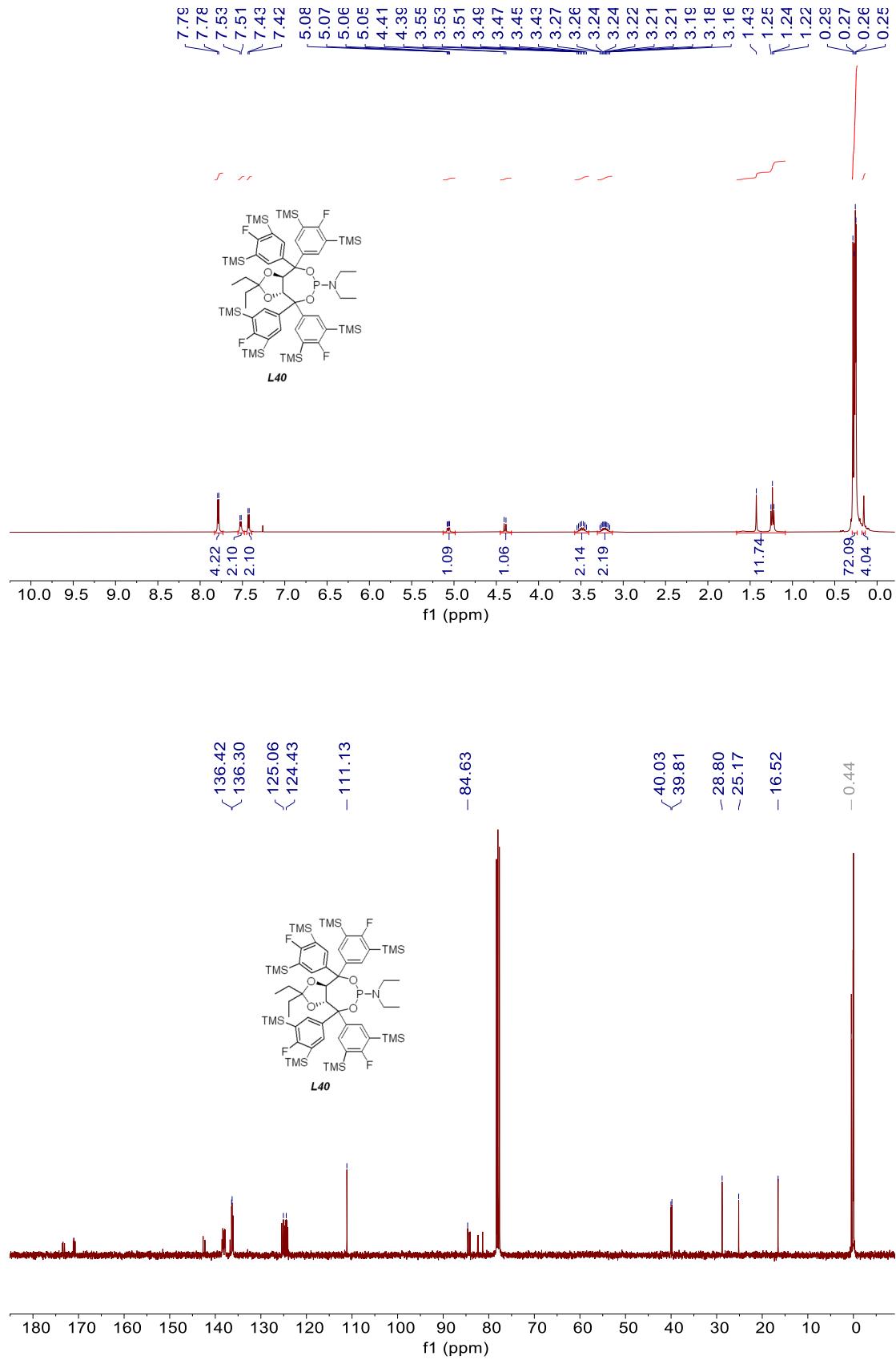


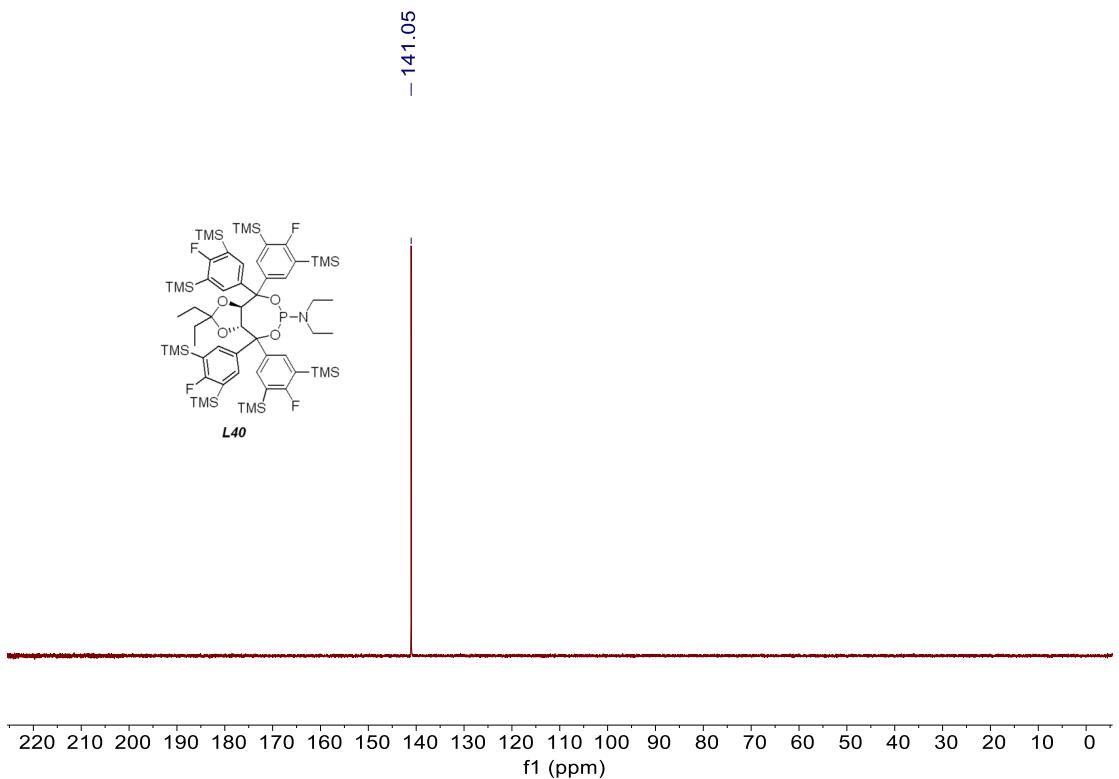
L38



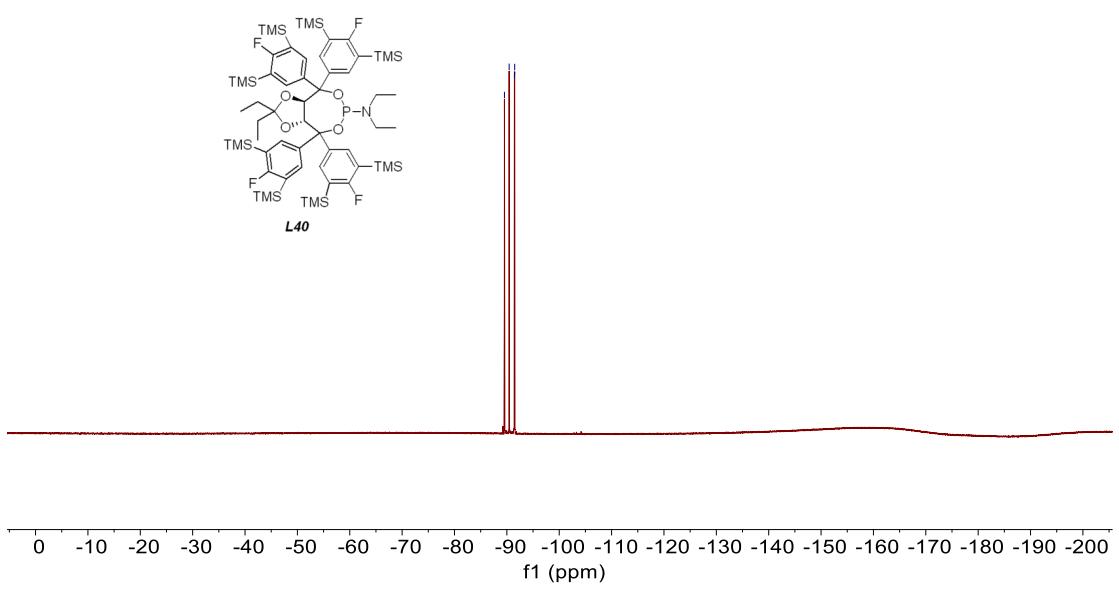


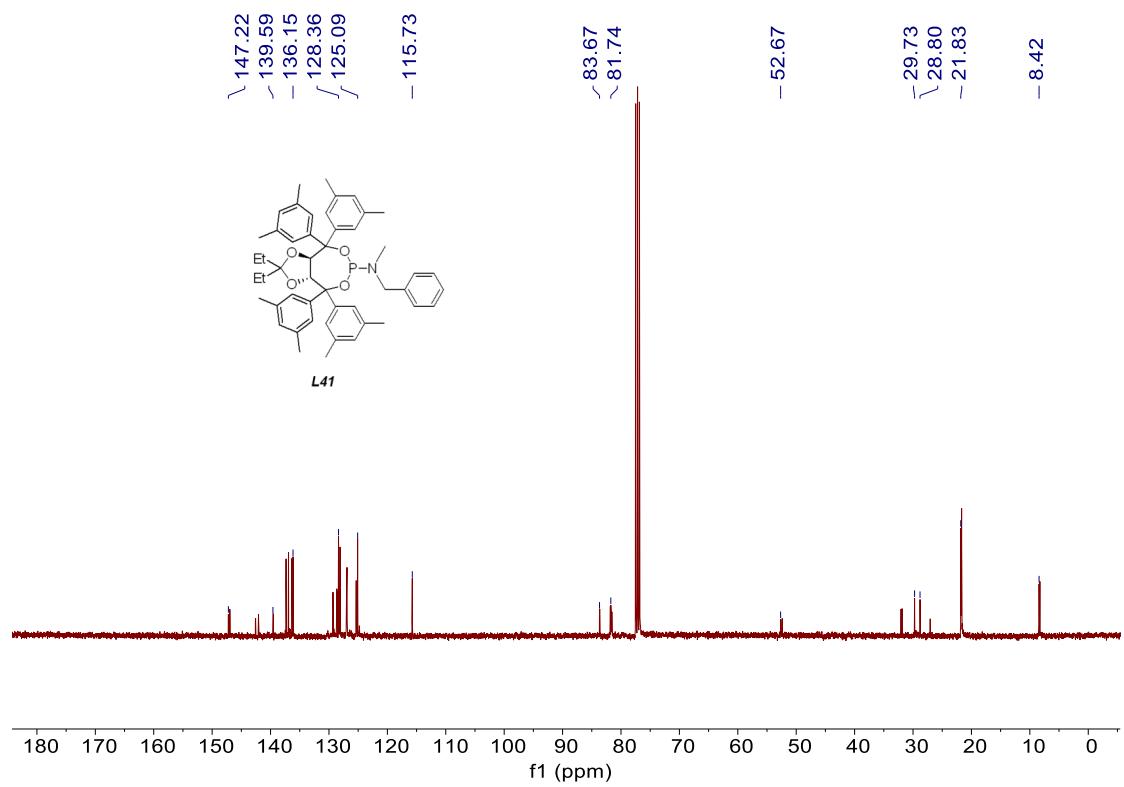
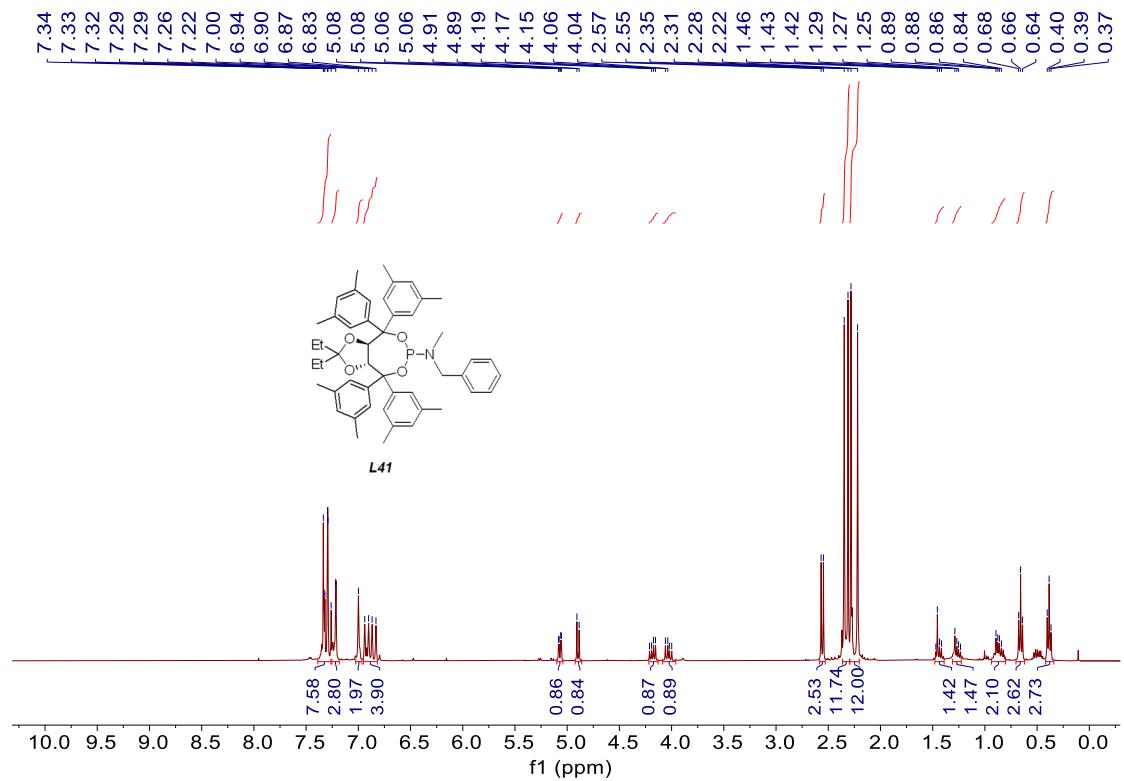


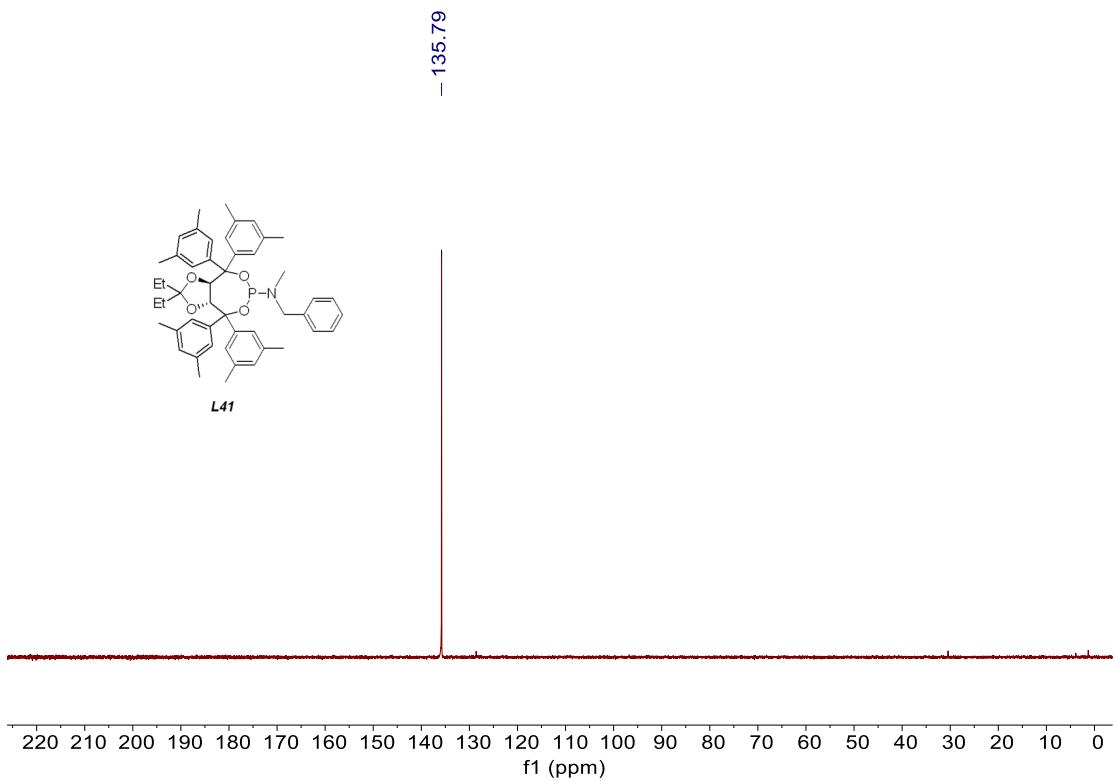




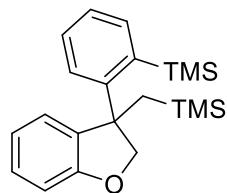
-89.54
-90.44
-91.44
-91.50



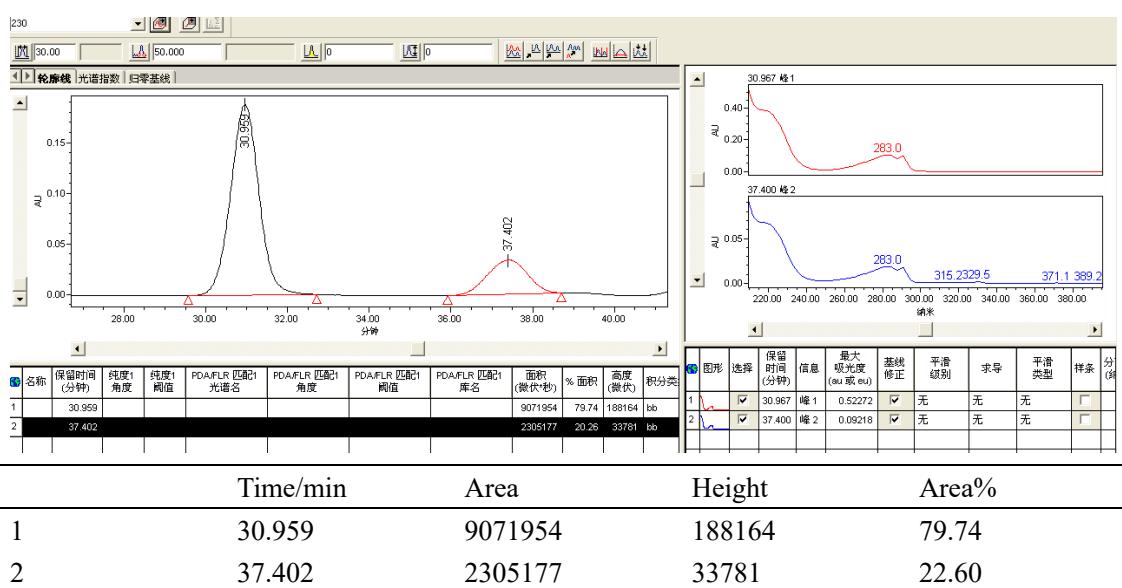
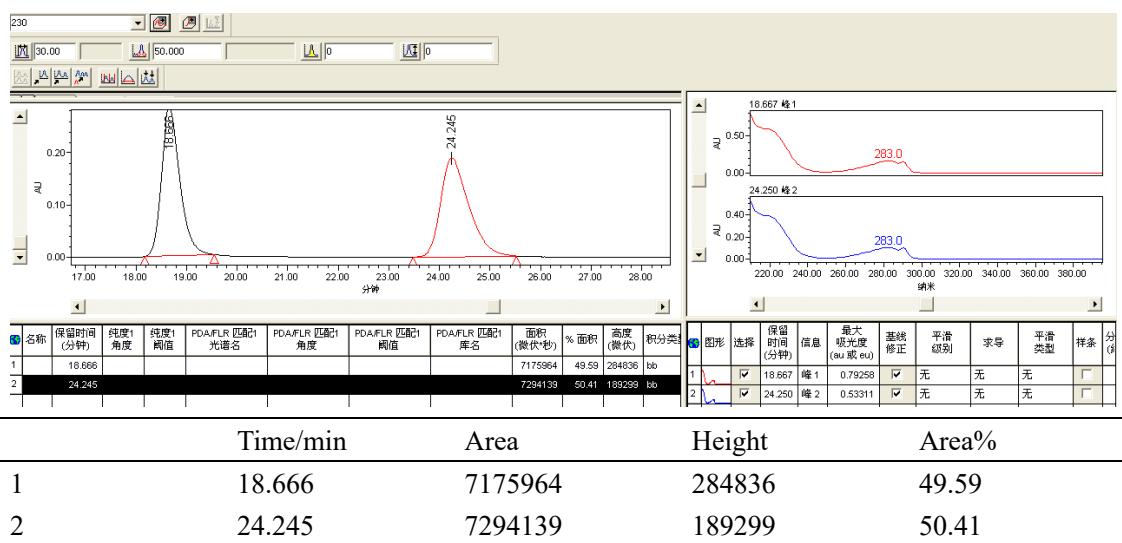


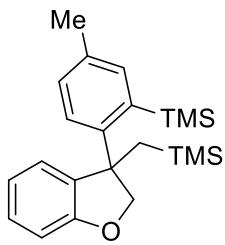


9. HPLC Chromatograms

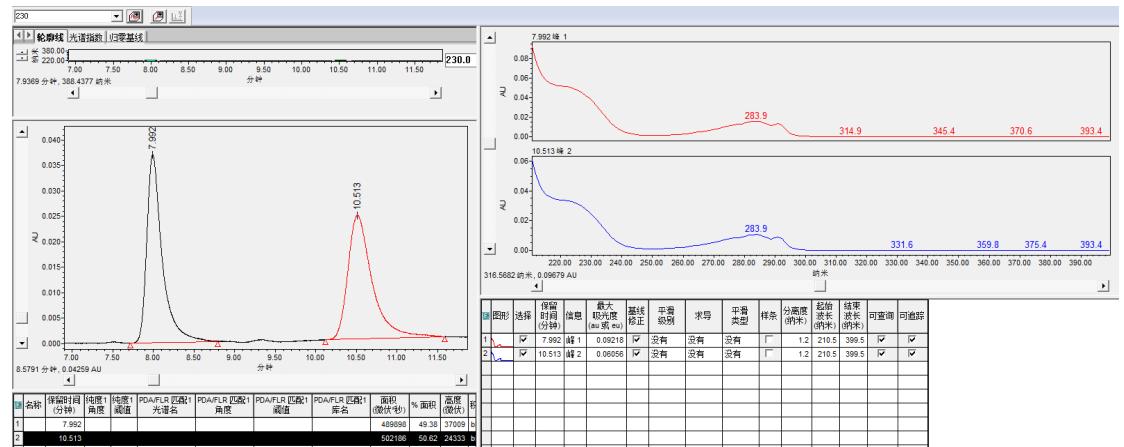


trimethyl(2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (3a)

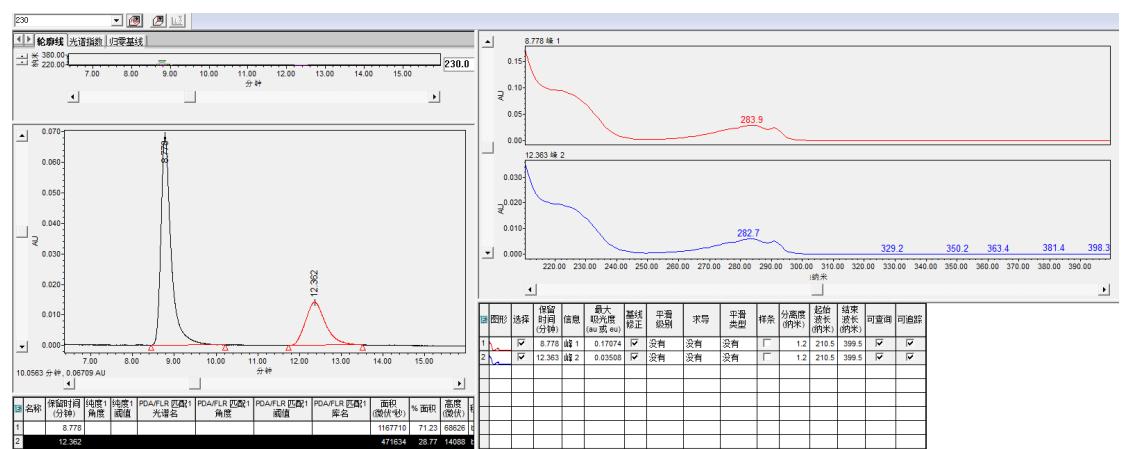


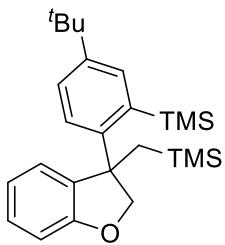


trimethyl(5-methyl-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (3b)

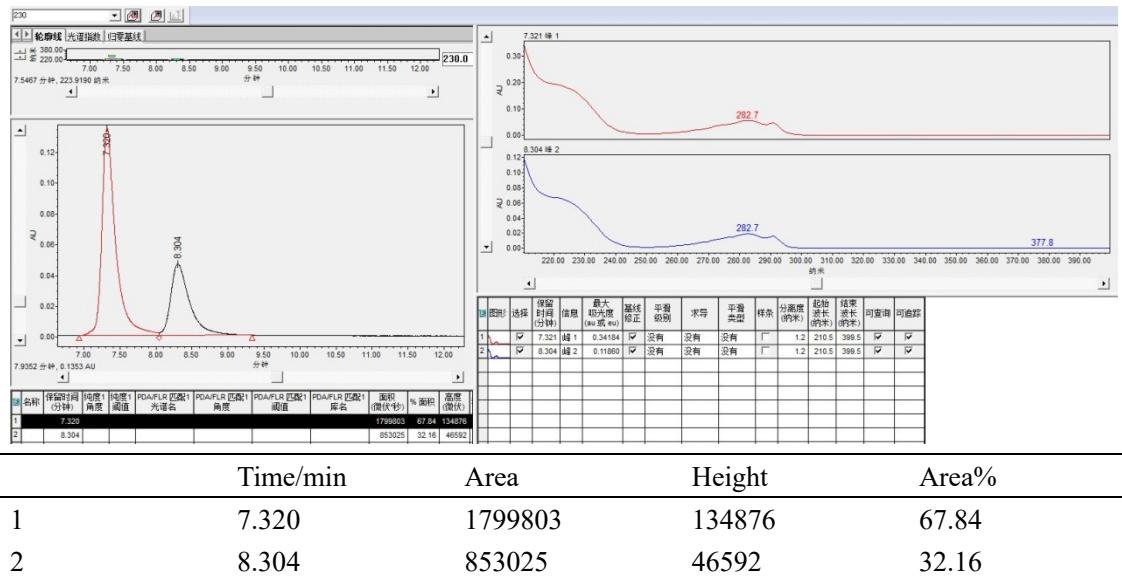
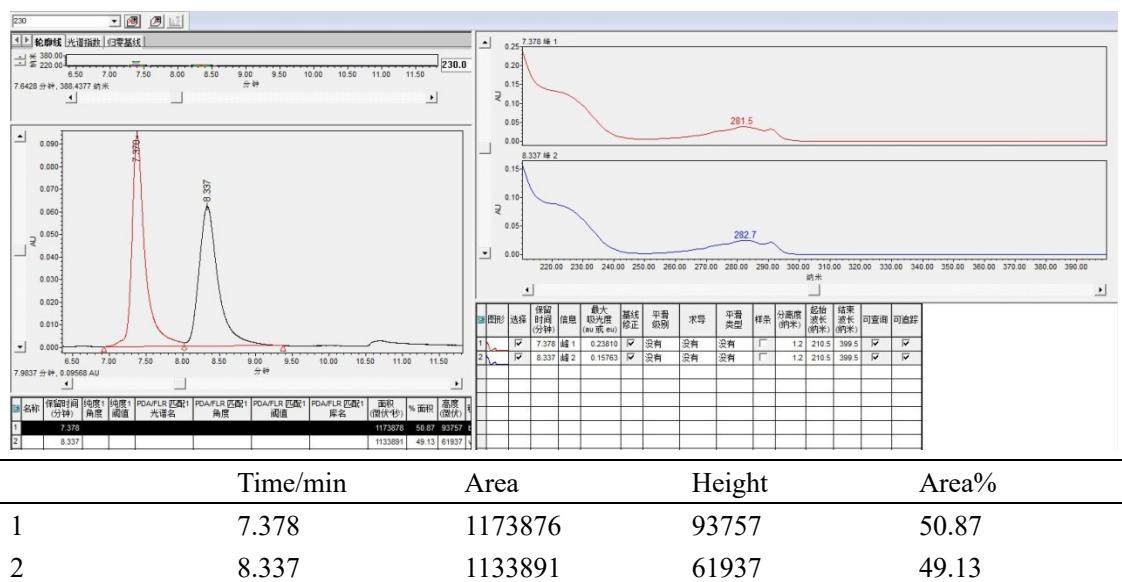


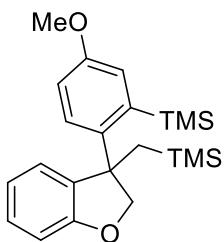
	Time/min	Area	Height	Area%
1	7.992	489898	37009	49.38
2	10.513	502186	24333	50.62



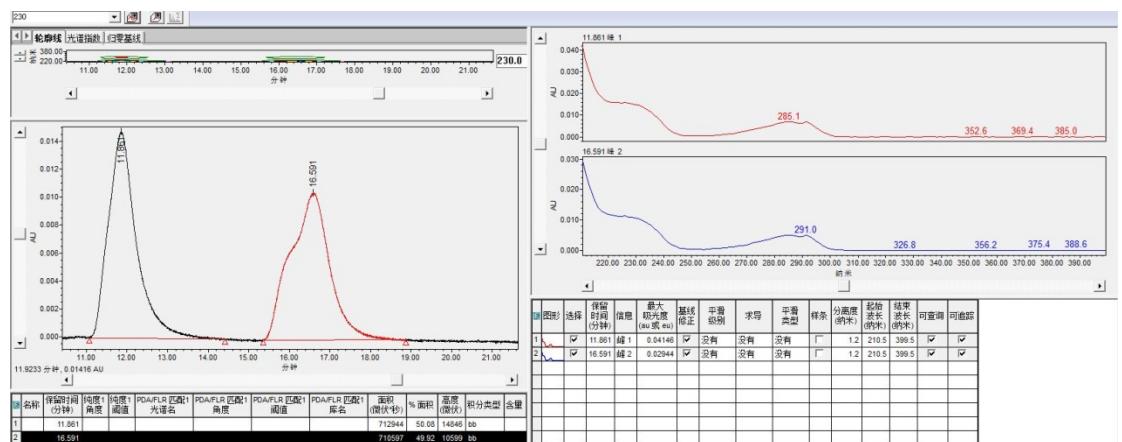


(5-(tert-butyl)-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3c)

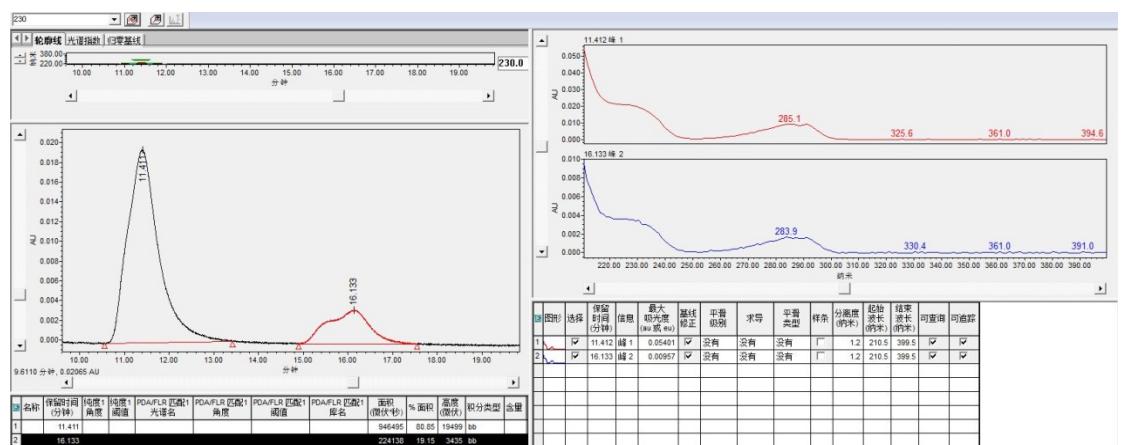




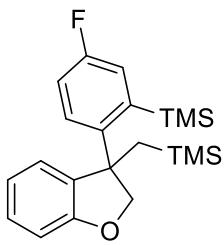
(5-methoxy-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3d)



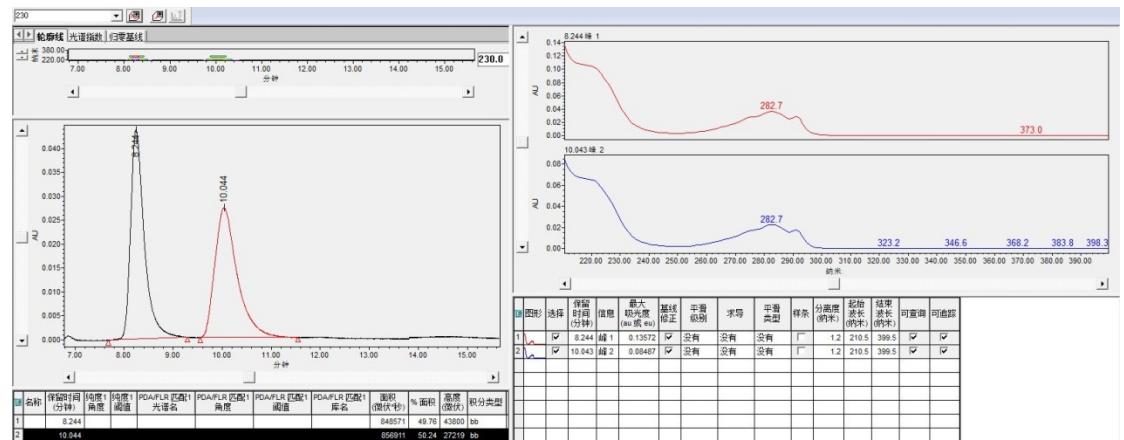
	Time/min	Area	Height	Area%
1	11.861	712944	14846	50.08
2	16.591	710597	10599	49.92



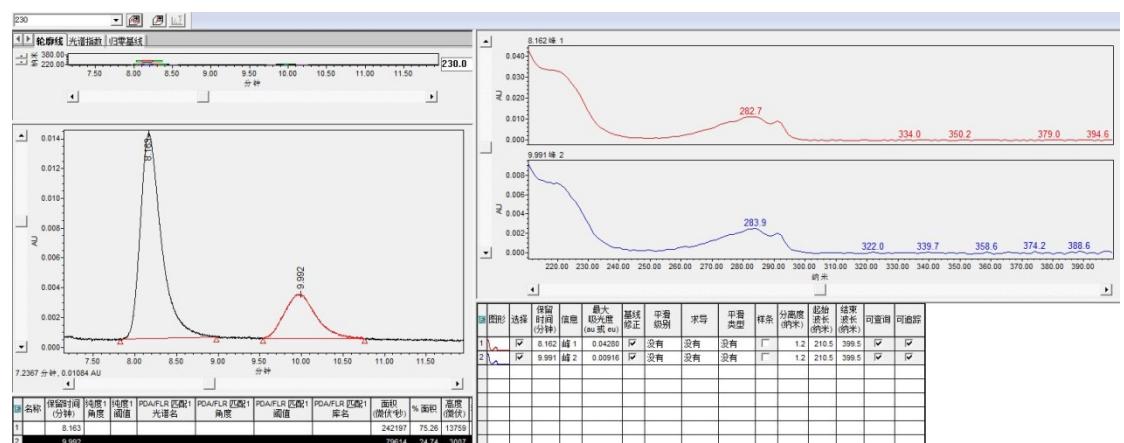
	Time/min	Area	Height	Area%
1	11.411	946495	19499	80.85
2	16.133	224138	3435	19.15



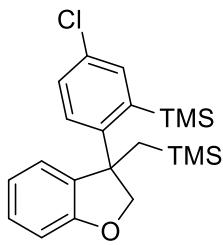
(5-fluoro-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3e)



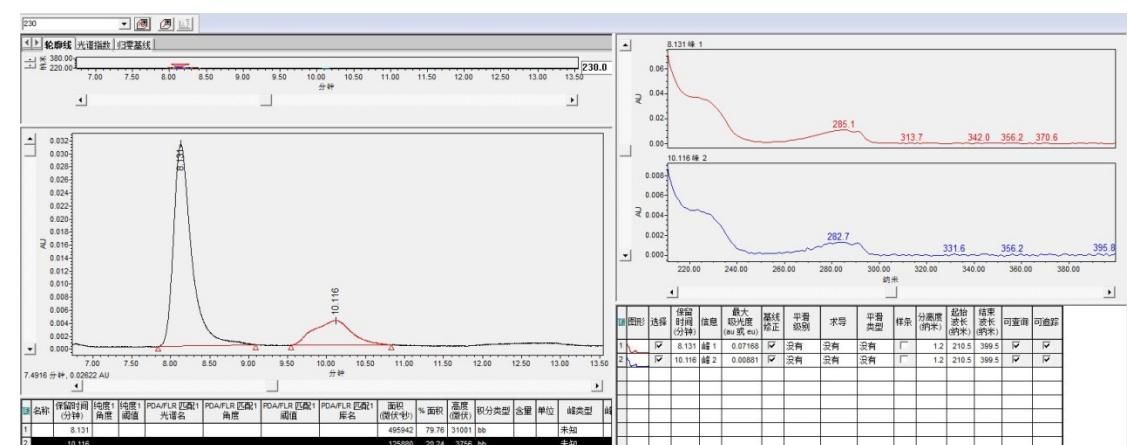
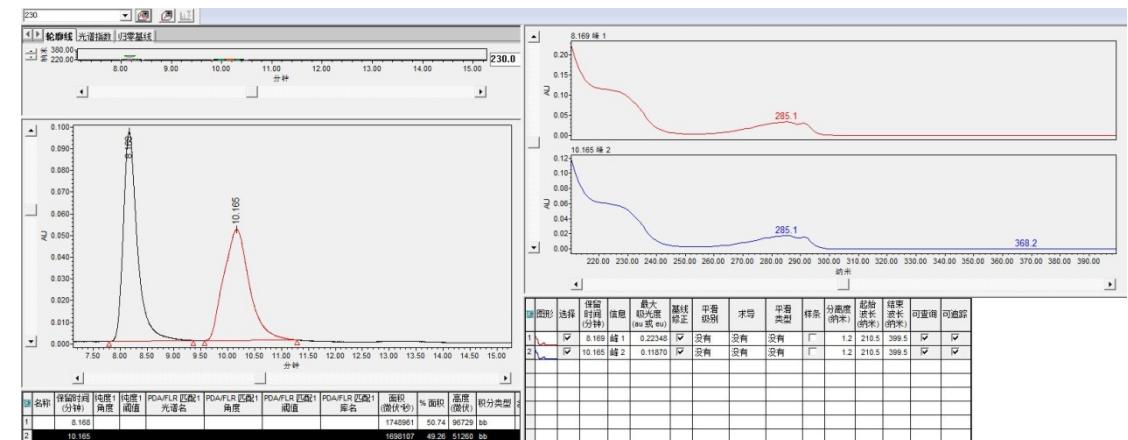
	Time/min	Area	Height	Area%
1	8.244	848571	43800	49.76
2	10.044	856911	27219	50.24

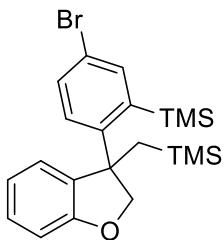


	Time/min	Area	Height	Area%
1	8.163	242197	13759	75.26
2	9.992	79614	3007	24.74

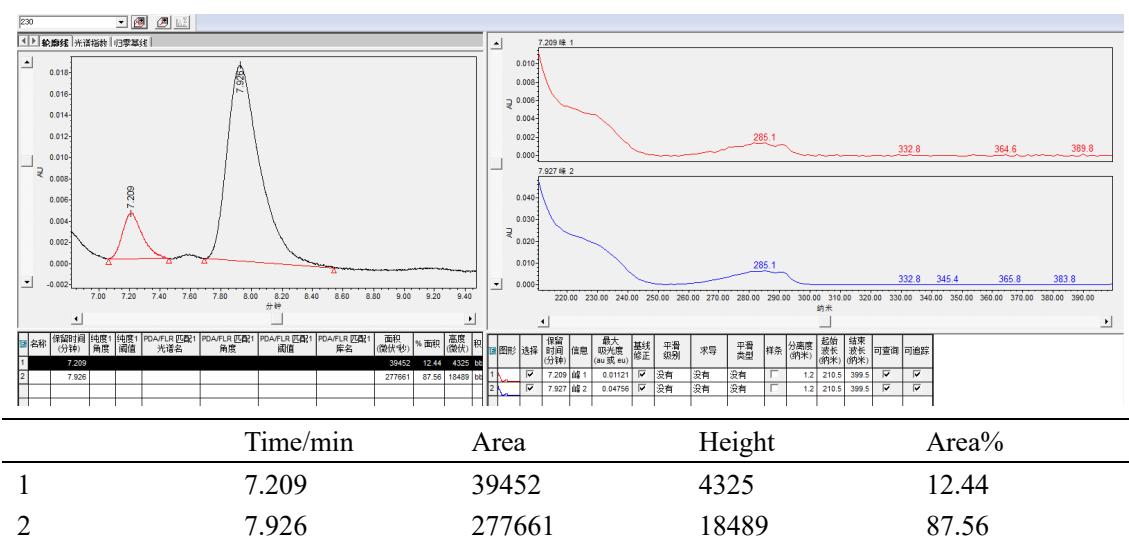
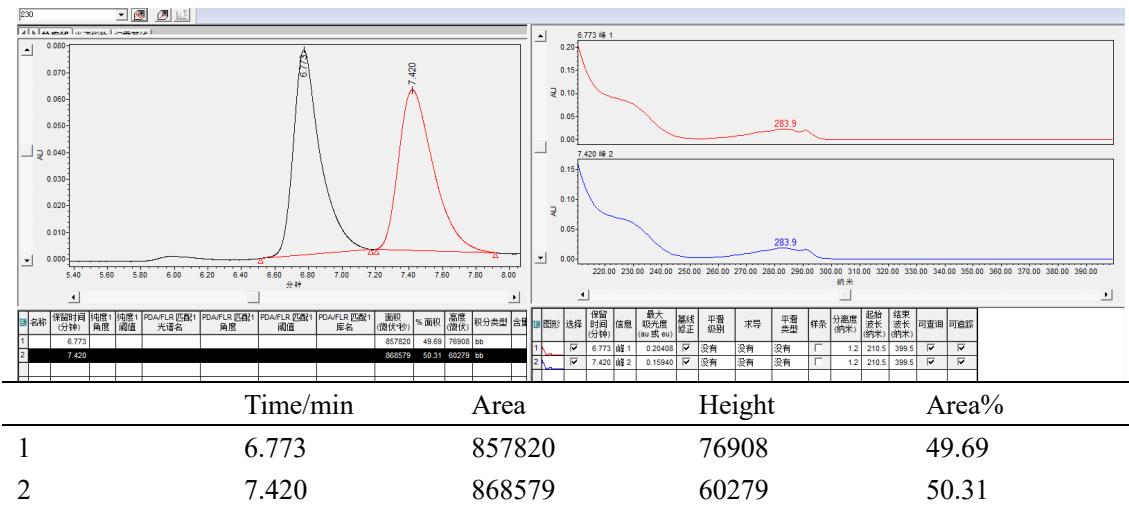


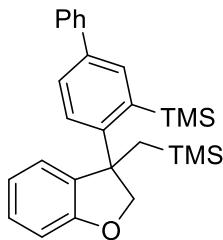
(5-chloro-2-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3f)



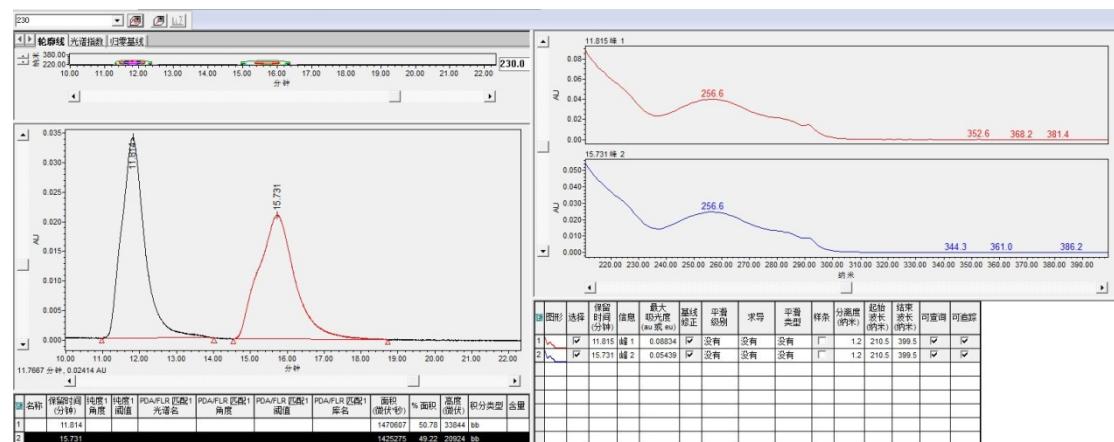


(5-bromo-2-(3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3g)

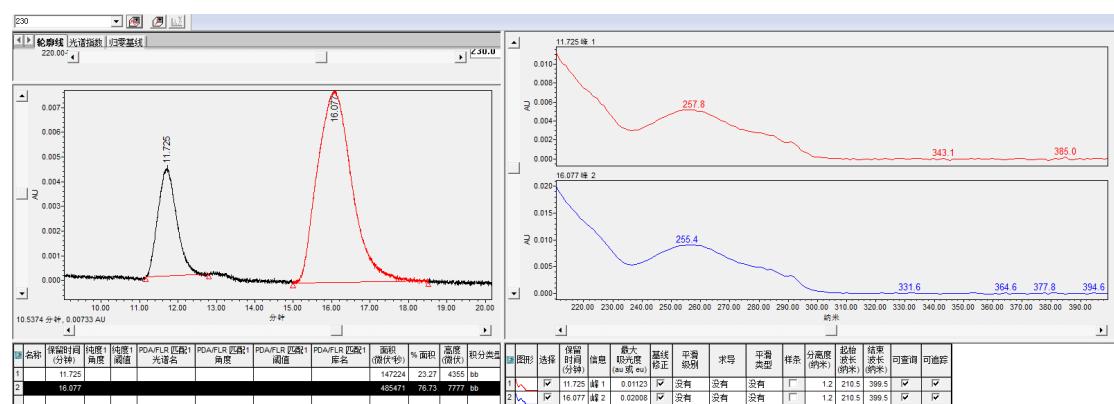




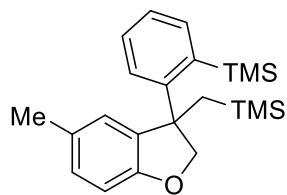
trimethyl((3-(3-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)-2,3-dihydrobenzofuran-3-yl)methyl) silane (3h)



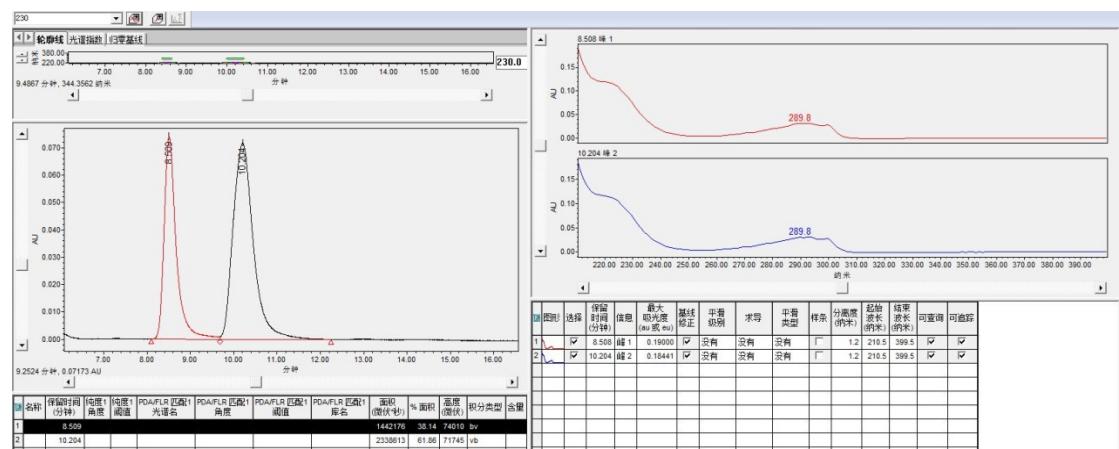
	Time/min	Area	Height	Area%
1	11.814	1470607	33844	50.76
2	15.731	1425275	20924	49.22



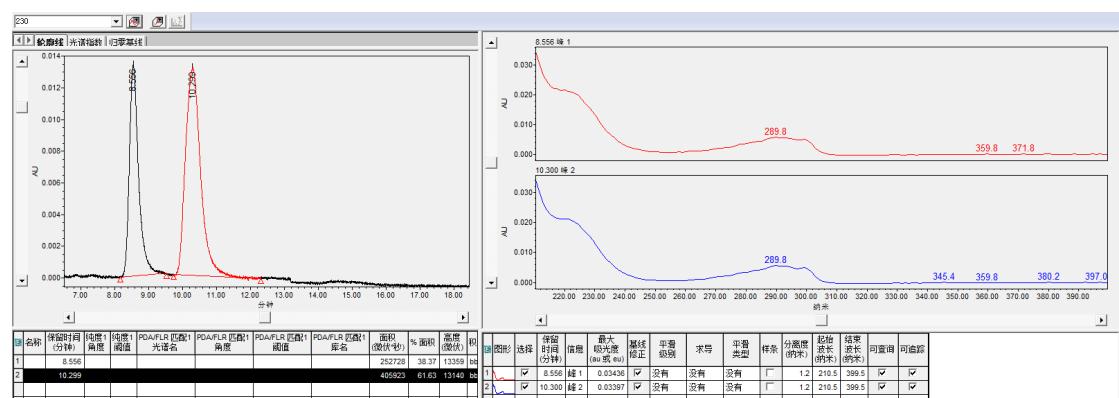
	Time/min	Area	Height	Area%
1	11.725	147224	4355	23.27
2	16.077	485471	7777	76.73



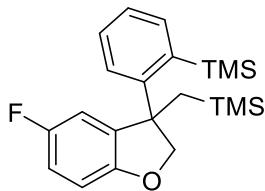
trimethyl(2-(5-methyl-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (3i)



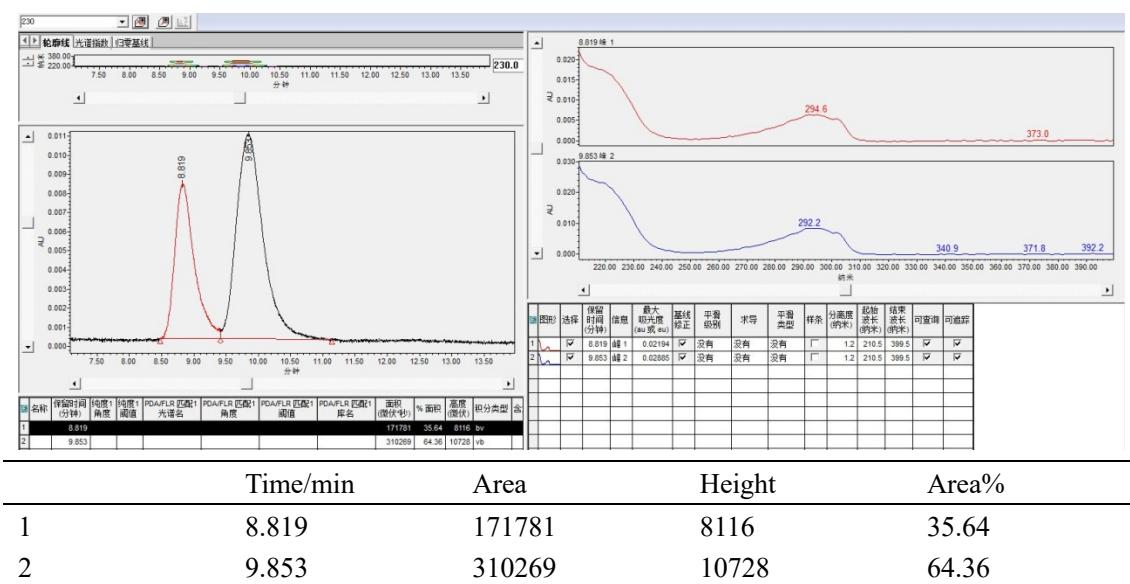
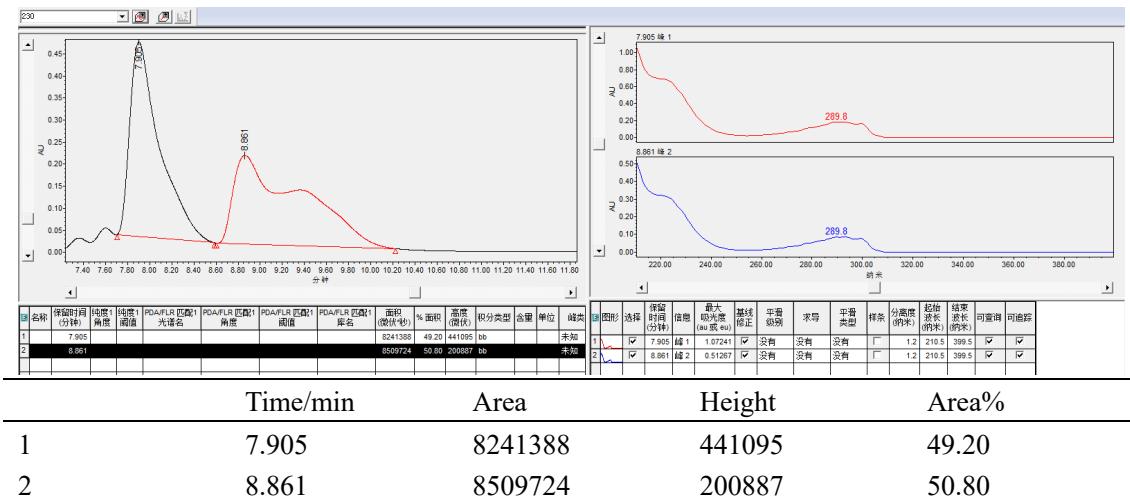
	Time/min	Area	Height	Area%
1	8.509	1442176	74010	38.14
2	10.204	2338613	71745	61.86

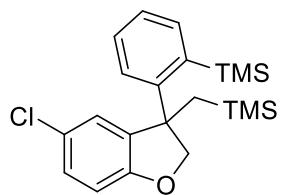


	Time/min	Area	Height	Area%
1	8.556	252728	13359	38.37
2	10.299	405923	13140	61.63

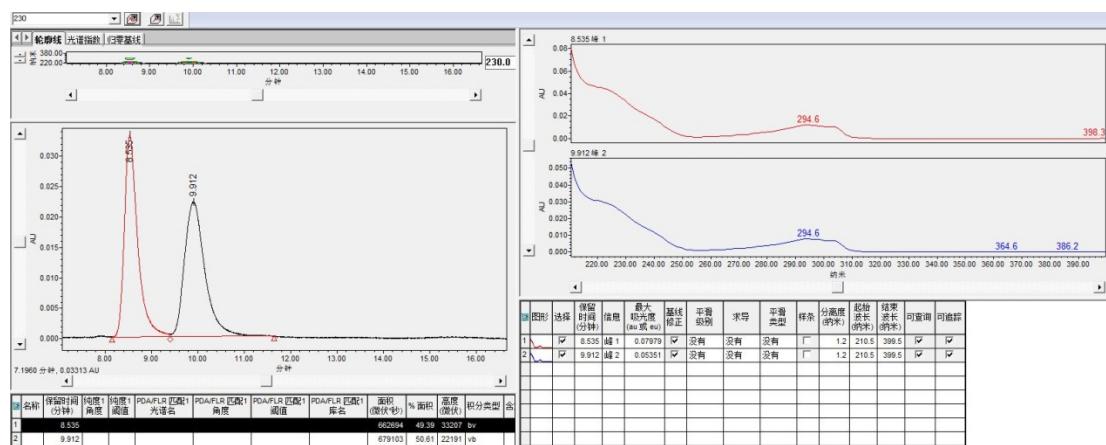


(2-(5-fluoro-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3j)

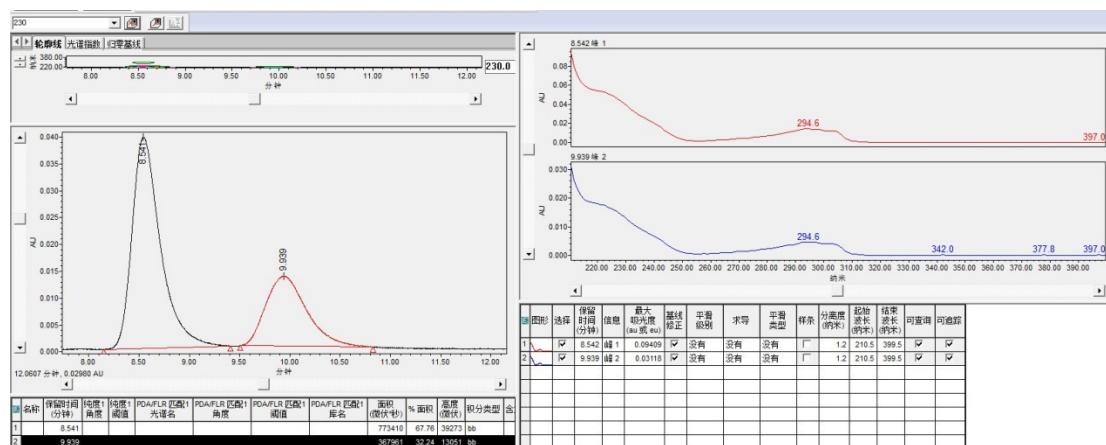




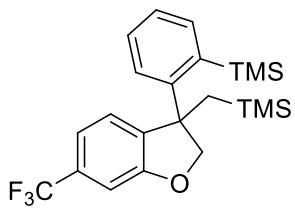
(2-(5-chloro-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)trimethylsilane (3k)



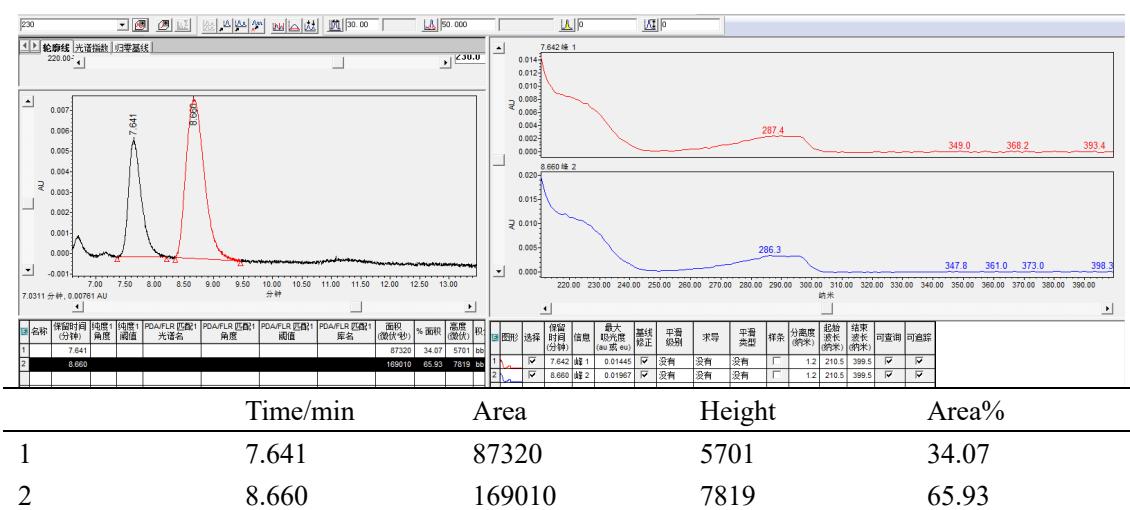
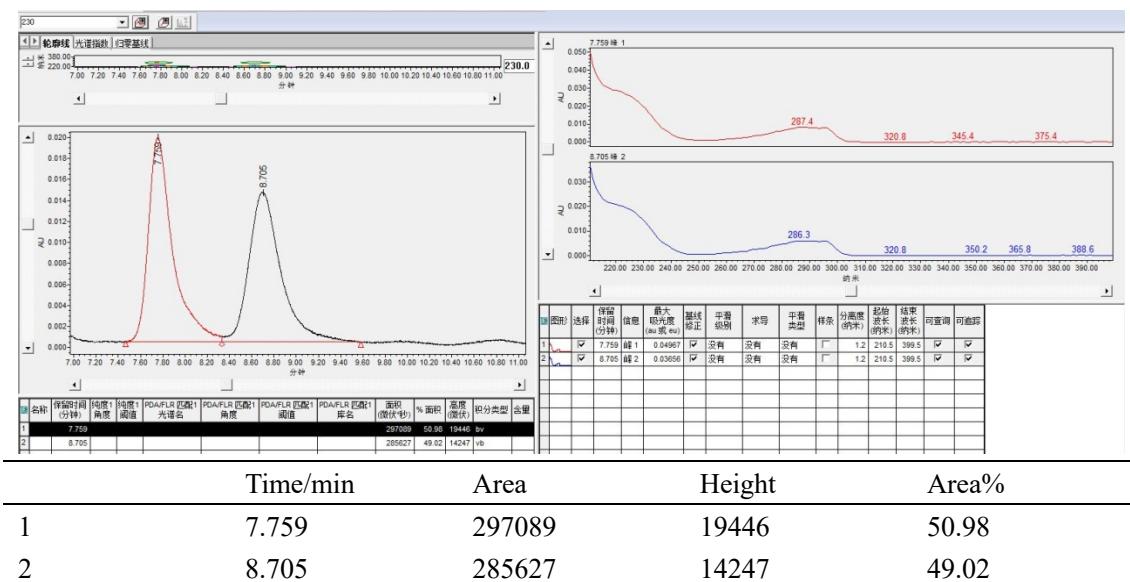
	Time/min	Area	Height	Area%
1	8.535	662694	33207	49.39
2	9.912	679103	22191	50.61

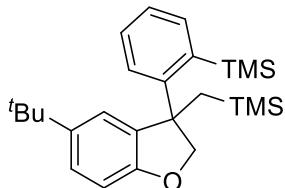


	Time/min	Area	Height	Area%
1	8.541	67.76	39273	67.76
2	9.939	32.24	13051	32.24

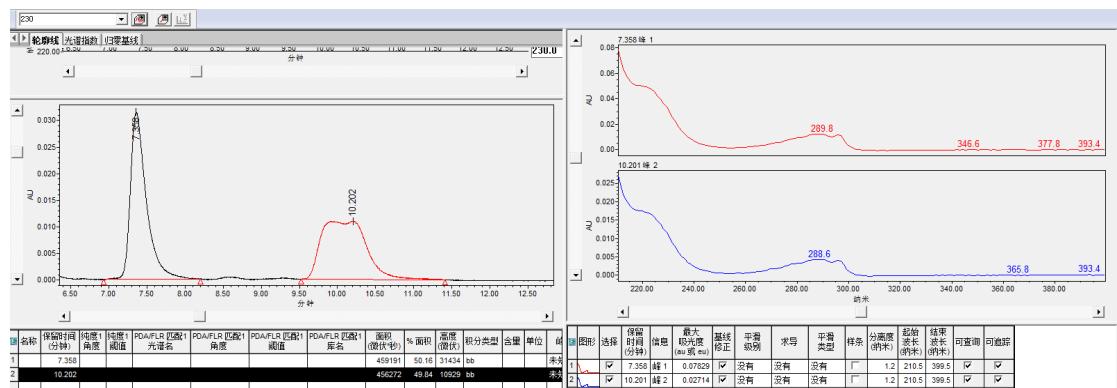


trimethyl(2-(6-(trifluoromethyl)-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)silane (3l)

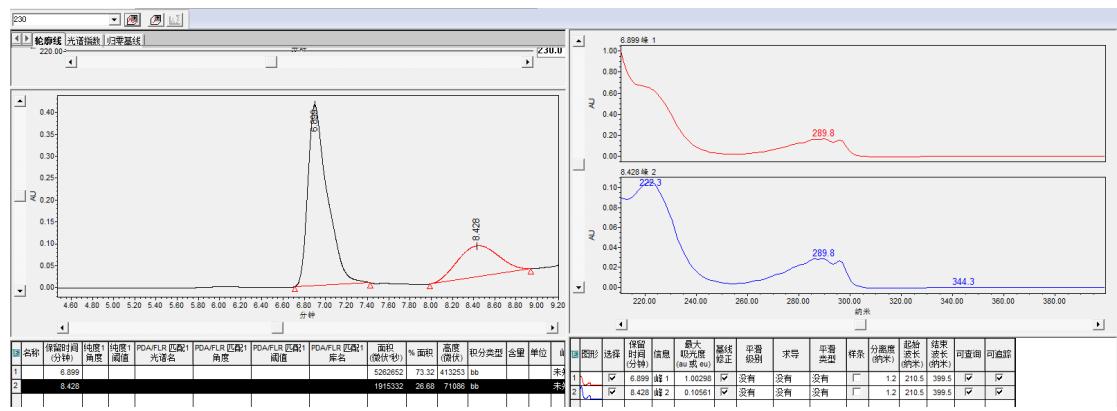




(2-(5-(tert-butyl)-3-((trimethylsilyl)methyl)-2,3-dihydrobenzofuran-3-yl)phenyl)rimethylsilane (3m)



	Time/min	Area	Height	Area%
1	7.358	459191	31434	50.16
2	10.202	456272	10929	49.84



	Time/min	Area	Height	Area%
1	6.899	5262652	413253	73.32
2	8.428	1915332	71086	26.68

