

Synthesis of Cyclobutane-Fused Angular Tetracyclic Spiroindolines *via* Visible-Light-Promoted Intramolecular Dearomatization of Indole Derivatives

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Table of Contents

1. General methods	S2
2. Reaction details and characterization data	S3
3. Transformations of products	S20
4. Experimental details for mechanistic studies	S23
5. X-Ray crystal data	S42
6. References	S70
7. Copies of NMR spectra	S71

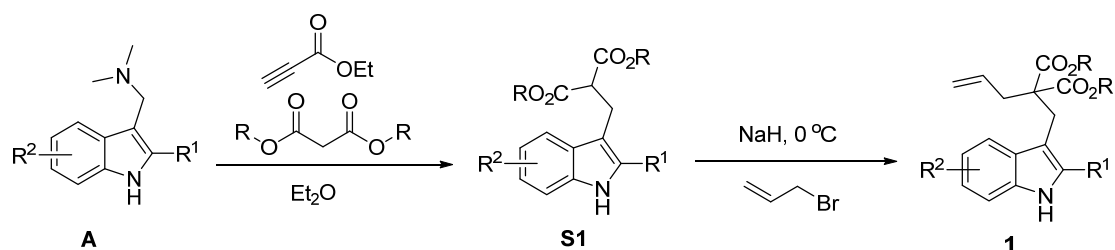
1. General methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^1H and ^{13}C NMR spectra were recorded on an Agilent instrument (400 MHz and 100 MHz, respectively) or an Agilent instrument (600 MHz and 150 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Agilent instrument (376 MHz) and referenced relative to CFCl_3 . Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm). UV/vis absorption spectra were recorded on a Thermo Nanodrop 2000c UV/Vis spectrometer.

Substrates **1** were synthesized according to the literature procedures.^[1] Solvents are commercially available from Alfa Aesar, and were used without further purification.

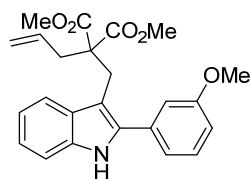
2. Reaction details and characterization data

General procedure for the synthesis of substrates^[1]:



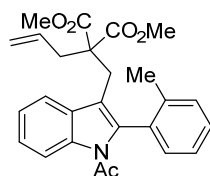
In a round bottom flask, **A** (21 mmol) was dissolved into reagent grade Et₂O. After the addition of dialkyl malonate (23 mmol), ethylpropiolate (2.3 mL, 23 mmol) was added at once. After the reaction was complete (monitored by TLC), it was quenched with water. The aqueous layer was extracted with EtOAc (30 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/Acetone = 12/1) to afford the desired product **S1**.

To a solution of the above **S1** (2 g, 5.7 mmol, 1.0 equiv) in THF was added NaH (272 mg, 6.8 mmol), followed by the dropwise addition of allyl bromide (0.6 mL, 6.8 mmol) under ice bath. Then the reaction was allowed to warm to room temperature. After the reaction was complete (monitored by TLC), it was quenched with water. The mixture was extracted with EtOAc (30 mL x 3). The organic layer was washed with brine, dried over Na₂SO₄ and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 12/1) to afford the desired product **1**.

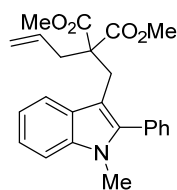


1h, white solid, 1.7 g, 85% yield, m.p. = 116.7-118.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (br, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.34-7.27 (m, 2H), 7.17-7.06 (m, 4H), 6.89

(dd, $J = 8.4, 2.8$ Hz, 1H), 5.41-5.31 (m, 1H), 4.84-4.75 (m, 2H), 3.82 (s, 3H), 3.70 (s, 2H), 3.42 (s, 6H), 2.35 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 159.9, 136.8, 135.5, 134.8, 132.8, 130.0, 129.5, 122.2, 121.3, 119.6, 119.4, 118.1, 114.3, 113.7, 110.8, 106.4, 59.5, 55.3, 52.0, 37.0, 27.2. IR (thin film): $\nu_{\text{max}}(\text{cm}^{-1}) = 3405, 2954, 1727, 1611, 1578, 1478, 1458, 1344, 1292, 1261, 1240, 1207, 1162, 1038, 916, 877, 843, 779, 747$. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_5$ $[\text{M}+\text{NH}_4]^+$: 425.2071. Found: 425.2075.

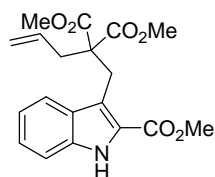


1m^[2], colorless oil, 0.3 g, 17% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.0$ Hz, 1H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.41-7.24 (m, 6H), 4.97-4.87 (m, 1H), 4.78-4.65 (m, 2H), 3.48-3.44 (m, 7H), 3.24 (d, $J = 14.8$ Hz, 1H), 2.34-2.24 (m, 2H), 2.21 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 170.8, 138.4, 136.6, 136.2, 132.3, 132.1, 131.6, 130.8, 129.5, 126.4, 125.1, 123.0, 119.1, 118.5, 116.1, 116.0, 58.6, 52.14, 52.07, 37.5, 26.9, 26.6, 19.7. IR (thin film): $\nu_{\text{max}}(\text{cm}^{-1}) = 3018, 2951, 1729, 1699, 1602, 1452, 1436, 1369, 1302, 1201, 1126, 1100, 1073, 1035, 1009, 965, 922, 746, 679, 665, 648, 622$. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{O}_5$ $[\text{M}+\text{NH}_4]^+$: 451.2227. Found: 451.2231.

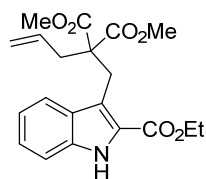


1r^[3], brown solid, 0.3 g, 54% yield, m.p. = 150.1-151.8 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 7.6$ Hz, 1H), 7.48-7.38 (m, 5H), 7.28 (d, $J = 8.4$ Hz, 1H), 7.21-7.17 (m, 1H), 7.10 (t, $J = 7.2$ Hz, 1H), 5.01-4.91 (m, 1H), 4.73-4.68 (m, 2H), 3.57 (s, 2H), 3.50 (s, 3H), 3.47 (s, 6H), 2.29 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 140.0, 136.7, 132.6, 132.0, 131.1, 128.7, 128.2, 128.0, 121.6, 119.2, 119.1, 117.8, 109.3, 106.4, 59.4, 52.0, 36.8, 30.7, 27.2. IR (thin film): $\nu_{\text{max}}(\text{cm}^{-1}) = 2948, 2927, 1747, 1721,$

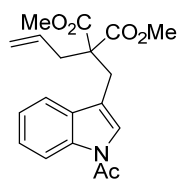
1469, 1431, 1403, 1367, 1332, 1316, 1292, 1260, 1243, 1215, 1066, 824, 805, 757, 704, 660. HRMS (ESI) calcd for C₂₄H₂₉N₂O₄ [M+NH₄]⁺: 409.2122. Found: 409.2124.



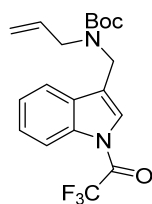
1w, white solid, 1.1 g, 50% yield, m.p. = 156.1-157.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.12 (br, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.34-7.24 (m, 2H), 7.15-7.08 (m, 1H), 5.99-5.88 (m, 1H), 5.10-5.06 (m, 2H), 3.90-3.88 (m, 5H), 3.59 (s, 6H), 2.64 (d, *J* = 6.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 162.4, 135.7, 133.6, 128.2, 125.5, 124.8, 121.4, 120.1, 118.2, 117.8, 111.7, 59.3, 52.1, 51.7, 38.1, 28.4. IR (thin film): ν_{max} (cm⁻¹) = 3335, 2953, 1731, 1677, 1639, 1621, 1531, 1457, 1425, 1374, 1336, 1292, 1254, 1220, 1207, 1150, 1129, 1096, 1057, 925, 746, 691, 555. HRMS (ESI) calcd for C₁₉H₂₅N₂O₆ [M+NH₄]⁺: 377.1707. Found: 377.1708.



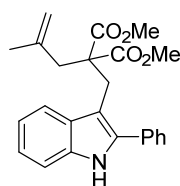
1x, white solid, 1.9 g, 49% yield, m.p. = 180.1-181.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.98 (br, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.36-7.27 (m, 2H), 7.11 (td, *J* = 8.0, 1.2 Hz, 1H), 5.98-5.87 (m, 1H), 5.09-5.04 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 2H), 3.60 (s, 6H), 2.63 (d, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.6, 162.0, 135.5, 133.7, 128.3, 125.5, 125.1, 121.5, 120.1, 118.2, 117.7, 111.7, 61.0, 59.4, 52.2, 38.3, 28.7, 14.3. IR (thin film): ν_{max} (cm⁻¹) = 3329, 2984, 2951, 2353, 1747, 1725, 1671, 1639, 1621, 1575, 1535, 1477, 1438, 1244, 1226, 1202, 773, 743, 672. HRMS (ESI) calcd for C₂₀H₂₇N₂O₆ [M+NH₄]⁺: 391.1864. Found: 391.1868.



1y^[2], yellow oil, 1.2 g, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.28-7.25 (m, 2H), 5.83-5.72 (m, 1H), 5.18-5.12 (m, 2H), 3.64 (s, 6H), 3.33 (s, 2H), 2.72 (d, *J* = 7.2 Hz, 2H), 2.60 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 168.3, 135.3, 132.3, 130.8, 125.2, 124.1, 123.3, 119.4, 118.7, 116.6, 116.4, 58.3, 52.4, 37.7, 27.9, 23.9. IR (thin film): ν_{max} (cm⁻¹) = 3012, 2952, 1730, 1704, 1451, 1384, 1370, 1352, 1326, 1288, 1244, 1211, 1146, 931, 746, 656, 627, 576, 561. HRMS (ESI) calcd for C₁₉H₂₅N₂O₅ [M+NH₄]⁺: 361.1758. Found: 361.1761.

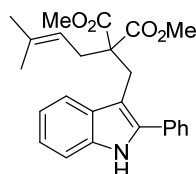


1z^[4], yellow solid, 2.2 g, 99% yield, m.p. = 49.1-50.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.72 (br, 1H), 7.45-7.36 (m, 3H), 5.76 (s, 1H), 5.16-5.10 (m, 2H), 4.58 (s, 2H), 3.90-3.79 (m, 2H), 1.52 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 155.4, 154.3, 153.9, 153.5, 153.1, 136.3, 133.5, 129.7, 126.5, 125.6, 123.1, 122.0, 120.2, 119.8, 116.93, 116.85, 114.1, 111.2, 80.2, 48.6, 40.3, 28.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -69.4 (s, 3F). IR (thin film): ν_{max} (cm⁻¹) = 2985, 2933, 1720, 1687, 1643, 1609, 1407, 1392, 1367, 1335, 1285, 1235, 1196, 1149, 1131, 797, 754, 728, 689. HRMS (EI) calcd for C₁₉H₂₁F₃N₂O₃ [M]⁺: 382.1504. Found: 382.1509.



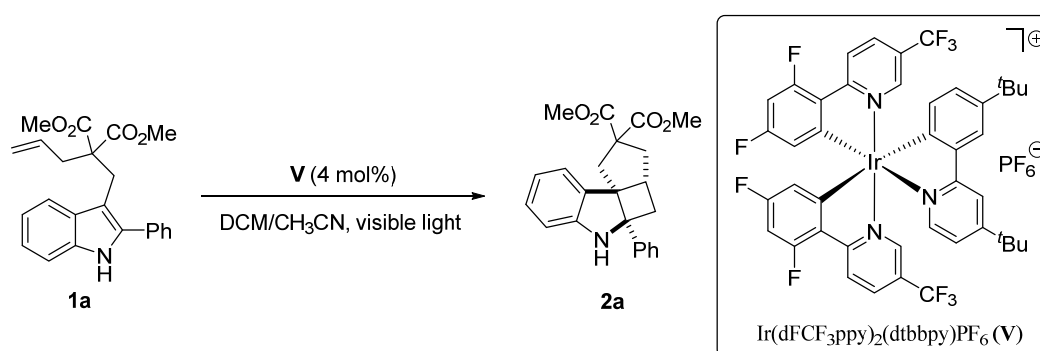
1aa, white solid, 0.6 g, 60% yield, m.p. = 139.9-141.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.38-7.36 (m, 2H), 7.24-7.05 (m, 6H), 4.71 (s, 1H), 4.63 (s, 1H), 3.85 (s, 2H), 3.26 (s, 6H), 2.42 (s, 2H), 1.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 141.9, 136.6, 135.5, 133.5, 129.8, 128.6, 128.6, 127.5, 121.8, 119.3, 111.6, 110.8, 106.1, 58.2, 51.88, 51.85, 39.7, 27.8, 24.2. IR (thin film): ν_{max} (cm⁻¹) = 3433, 3050, 1745, 1722, 1650, 1602, 1449, 1435, 1240, 1199, 1182, 1127, 887,

864, 770, 756, 736, 699, 673, 667, 612. HRMS (ESI) calcd for $C_{24}H_{29}N_2O_4$ $[M+NH_4]^+$: 409.2122. Found: 409.2125.



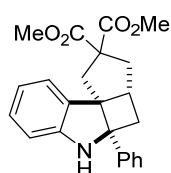
1a, white solid, 0.9 g, 70% yield, m.p. = 170.1-171.5 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 6.8 Hz, 2H), 7.28-7.23 (m, 3H), 7.16 (d, J = 7.2 Hz, 1H), 7.10-7.03 (m, 2H), 4.69 (t, J = 6.8 Hz, 1H), 3.70 (s, 2H), 3.33 (s, 6H), 2.30 (d, J = 6.8 Hz, 2H), 1.49 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 136.9, 135.5, 134.5, 133.4, 129.4, 128.7, 128.6, 127.5, 121.7, 119.2, 119.1, 117.9, 110.8, 105.9, 58.8, 51.8, 30.6, 26.9, 25.7, 17.5. IR (thin film): ν_{max} (cm^{-1}) = 3367, 2951, 1748, 1719, 1606, 1450, 1431, 1372, 1299, 1257, 1212, 1179, 1123, 1068, 846, 787, 770, 753, 702. HRMS (ESI) calcd for $C_{25}H_{31}N_2O_4$ $[M+NH_4]^+$: 423.2278. Found: 423.2281.

General procedure for visible-light promoted intramolecular dearomatization of indole derivatives (1a as an example).

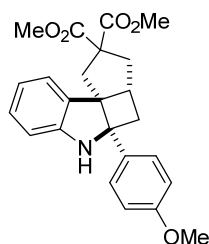


A flame-dried sealed tube were added indole derivative **1a** (75.5 mg, 0.2 mmol) and photosensitizer **V** (8.8 mg, 0.008 mmol) and DCM/ CH_3CN (15 mL/5 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from 24 W blue LEDs. The mixture was stirred at room temperature for the indicated time (monitored by TLC) under argon atmosphere. Afterwards, the reaction mixture was

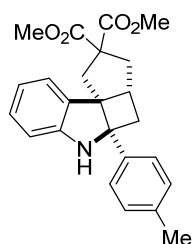
concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 20/1) to afford the desired product **2a**. The analytical data of the products are summarized below.



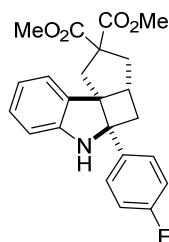
2a, brown oil, 72.0 mg, 95% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, $J = 7.2$ Hz, 2H), 7.24–7.16 (m, 3H), 7.04 (dd, $J = 16.0, 7.6$ Hz, 2H), 6.72 (t, $J = 7.2$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 4.23 (s, 1H), 3.71 (s, 3H), 3.34 (s, 3H), 2.99–2.93 (m, 1H), 2.83–2.79 (m, 2H), 2.61–2.53 (m, 2H), 2.47–2.36 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 171.8, 152.1, 142.0, 132.6, 128.3, 127.8, 127.3, 126.4, 122.4, 118.4, 108.2, 71.1, 65.1, 63.5, 52.8, 52.4, 45.4, 40.4, 39.1, 36.5. IR (thin film): ν_{max} (cm^{-1}) = 3378, 3026, 1726, 1603, 1482, 1461, 1446, 1253, 1201, 1139, 1100, 1081, 1023, 976, 745, 699, 665, 629, 578, 448. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 378.1700. Found: 378.1690.



2b, red oil, 16.0 mg, 20% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.04 (m, 4H), 6.85 (d, J = 8.8 Hz, 2H), 6.74 (t, J = 7.6 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 4.19 (s, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.42 (s, 3H), 2.99-2.93 (m, 1H), 2.82-2.75 (m, 2H), 2.60-2.53 (m, 2H), 2.44-2.42 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 172.0, 158.8, 152.1, 134.4, 132.8, 127.91, 127.87, 122.6, 118.5, 113.7, 108.3, 71.0, 65.0, 63.7, 55.3, 52.9, 52.5, 45.5, 40.7, 39.3, 36.9. IR (thin film): ν_{max} (cm^{-1}) = 3363, 2919, 1727, 1645, 1632, 1604, 1510, 1482, 1461, 1433, 1285, 1245, 1201, 1087, 744, 705. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 408.1805. Found: 408.1796.

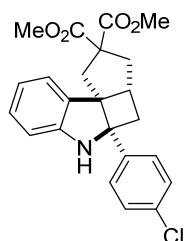


2c, brown oil, 58.0 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, J = 8.0 Hz, 2H), 7.07-7.03 (m, 4H), 6.74 (t, J = 7.6 Hz, 1H), 6.57 (d, J = 7.6 Hz, 1H), 4.18 (s, 1H), 3.73 (s, 3H), 3.38 (s, 3H), 3.00-2.93 (m, 1H), 2.81-2.76 (m, 2H), 2.61-2.53 (m, 2H), 2.43-2.42 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 172.0, 152.2, 139.1, 137.0, 132.8, 129.0, 127.9, 126.5, 122.5, 118.5, 108.3, 71.2, 65.1, 63.7, 52.9, 52.4, 45.5, 40.6, 39.3, 36.8, 21.0. IR (thin film): ν_{max} (cm^{-1}) = 3385, 3024, 1727, 1604, 1511, 1482, 1461, 1253, 1200, 1139, 1118, 817, 744, 665, 632, 577, 551. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 392.1856. Found: 392.1845.

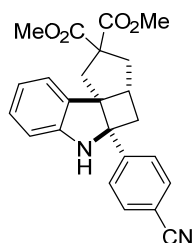


2d, green oil, 64.1 mg, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.15 (m, 2H), 7.08-6.98 (m, 4H), 6.75 (t, J = 7.6 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 4.20 (s, 1H), 3.74 (s, 3H), 3.42 (s, 3H), 3.00-2.94 (m, 1H), 2.83-2.75 (m, 2H), 2.60-2.52 (m, 2H), 2.44-2.42 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 172.0, 162.0 (d, J = 245.0 Hz), 151.9, 138.1 (d, J = 3.0 Hz), 132.4, 128.4 (d, J = 7.0 Hz), 128.0, 122.6, 118.62, 115.2

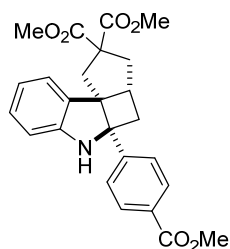
(d, $J = 21.0$ Hz), 108.3, 70.6, 65.1, 63.6, 52.9, 52.5, 45.5, 40.5, 39.1, 36.8. ^{19}F NMR (376 MHz, CDCl_3) δ -114.66 - -114.74 (m, 1F). IR (thin film): ν_{max} (cm^{-1}) = 3376, 2950, 1726, 1603, 1507, 1482, 1461, 1433, 1253, 1202, 1159, 1085, 836, 809, 744, 631. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{FNO}_4$ $[\text{M}+\text{H}]^+$: 396.1606. Found: 396.1597.



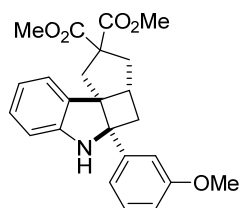
2e, brown oil, 75.0 mg, 92% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.05 (t, $J = 7.6$ Hz, 2H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 7.6$ Hz, 1H), 4.21 (s, 1H), 3.74 (s, 3H), 3.42 (s, 3H), 3.00-2.94 (m, 1H), 2.82-2.73 (m, 2H), 2.59-2.51 (m, 2H), 2.42 (d, $J = 6.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 171.9, 151.8, 140.6, 133.2, 132.3, 128.5, 128.09, 128.05, 122.5, 118.7, 108.3, 70.6, 65.2, 63.5, 52.9, 52.5, 45.5, 40.5, 39.1, 36.7. IR (thin film): ν_{max} (cm^{-1}) = 3411, 2942, 1744, 1721, 1646, 1484, 1461, 1431, 1397, 1284, 1254, 1167, 1142, 1089, 745, 735, 720. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{ClNO}_4$ $[\text{M}+\text{H}]^+$: 412.1310. Found: 412.1300.



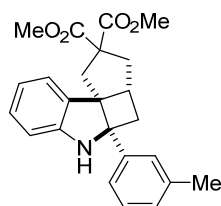
2f, pale solid, m.p. = 140.1-141.5 $^{\circ}\text{C}$, 75.1 mg, 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.07 (t, $J = 7.6$ Hz, 2H), 6.76 (t, $J = 7.6$ Hz, 1H), 6.59 (d, $J = 7.6$ Hz, 1H), 4.29 (s, 1H), 3.75 (s, 3H), 3.43 (s, 3H), 3.04-2.98 (m, 1H), 2.81-2.74 (m, 2H), 2.61 (dd, $J = 13.2, 8.8$ Hz, 1H), 2.51-2.38 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 171.8, 151.5, 147.3, 132.2, 131.9, 128.2, 127.4, 122.5, 118.9, 118.6, 111.2, 108.3, 70.5, 65.7, 63.5, 53.0, 52.6, 45.6, 40.5, 39.1, 36.3. IR (thin film): ν_{max} (cm^{-1}) = 3336, 2950, 2232, 1730, 1648, 1602, 1590, 1500, 1483, 1461, 1433, 1403, 1255, 1241, 1198, 1181, 752, 702, 586, 550. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 403.1652. Found: 403.1646.



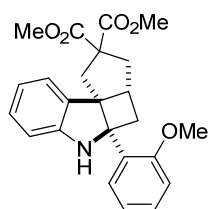
2g, red oil, 87.0 mg, 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 7.07 (t, J = 6.8 Hz, 2H), 6.76 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 7.6 Hz, 1H), 4.28 (s, 1H), 3.90 (s, 3H), 3.74 (s, 3H), 3.37 (s, 3H), 3.04-2.97 (m, 1H), 2.84-2.79 (m, 2H), 2.60 (dd, J = 13.2, 9.2 Hz, 1H), 2.52 (d, J = 15.6 Hz, 1H), 2.44 (d, J = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 171.9, 166.7, 151.9, 147.1, 132.3, 129.7, 129.1, 128.1, 126.6, 122.5, 118.7, 108.3, 70.8, 65.6, 63.5, 52.9, 52.5, 52.1, 45.6, 40.5, 39.1, 36.6. IR (thin film): ν_{max} (cm^{-1}) = 3358, 2996, 1751, 1727, 1602, 1483, 1467, 1434, 1187, 1106, 1088, 1059, 1016, 978, 958, 940, 911, 724, 706. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_6$ $[\text{M}+\text{H}]^+$: 436.1755. Found: 436.1744.



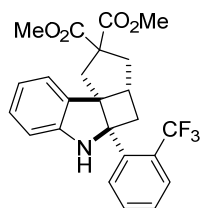
2h, red oil, 60.8 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.24 (t, J = 8.0 Hz, 1H), 7.05 (t, J = 8.0 Hz, 2H), 6.80-6.72 (m, 4H), 6.58 (d, J = 7.6 Hz, 1H), 4.22 (s, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.41 (s, 3H), 3.00-2.93 (m, 1H), 2.82-2.75 (m, 2H), 2.62-2.54 (m, 2H), 2.48-2.39 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 172.0, 159.6, 152.1, 143.8, 132.7, 129.5, 127.9, 122.5, 118.9, 118.5, 112.5, 112.4, 108.4, 71.2, 65.2, 63.7, 55.2, 52.9, 52.5, 45.5, 40.6, 39.2, 36.8. IR (thin film): ν_{max} (cm^{-1}) = 3374, 3002, 1727, 1602, 1482, 1461, 1432, 1321, 1288, 1255, 1202, 1170, 1085, 1044, 746, 700, 666, 617, 576. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 408.1805. Found: 408.1815.



2i, brown oil, 72.1 mg, 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.18 (m, 1H), 7.08-6.97 (m, 5H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 7.6$ Hz, 1H), 4.20 (s, 1H), 3.73 (s, 3H), 3.36 (s, 3H), 2.99-2.93 (m, 1H), 2.82-2.77 (m, 2H), 2.64-2.54 (m, 2H), 2.48-2.38 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 171.9, 152.1, 142.0, 138.0, 132.8, 128.3, 128.2, 127.9, 127.1, 123.6, 122.4, 118.4, 108.3, 71.2, 65.1, 63.6, 52.9, 52.4, 45.5, 40.6, 39.2, 36.9, 21.5. IR (thin film): ν_{max} (cm^{-1}) = 3380, 3025, 2949, 1727, 1604, 1482, 1461, 1432, 1396, 1254, 1200, 1138, 1104, 786, 744, 705. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 392.1856. Found: 392.1845.

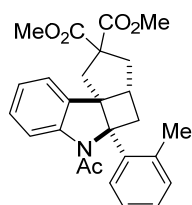


2j, brown oil, 21.9 mg, 27% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.17 (m, 2H), 7.02-6.99 (m, 2H), 6.93 (t, $J = 7.6$ Hz, 1H), 6.81 (d, $J = 8.4$ Hz, 1H), 6.72 (t, $J = 7.6$ Hz, 1H), 6.51 (d, $J = 7.6$ Hz, 1H), 3.74 (s, 3H), 3.39 (m, 3H), 3.29 (m, 3H), 2.95-2.84 (m, 2H), 2.77 (dd, $J = 12.8, 6.0$ Hz, 1H), 2.68-2.60 (m, 2H), 2.43-2.34 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 172.1, 158.1, 152.5, 134.9, 129.6, 128.8, 128.1, 127.1, 120.9, 120.1, 118.2, 110.9, 108.4, 70.9, 64.9, 63.6, 54.6, 52.9, 52.4, 44.8, 40.7, 39.7, 38.7. IR (thin film): ν_{max} (cm^{-1}) = 3335, 2998, 1727, 1645, 1604, 1581, 1484, 1460, 1431, 1389, 1201, 1176, 1143, 1101, 1087, 1052, 1025, 761, 738, 717, 678, 642. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 408.1805. Found: 408.1792.

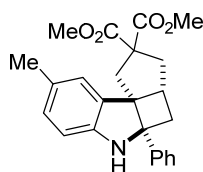


2k, white solid, m.p. = 156.7-157.1 $^{\circ}\text{C}$, 61.0 mg, 69% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 7.2$ Hz, 1H), 7.41-7.34 (m, 2H), 7.18 (d, $J = 7.2$ Hz, 1H), 6.99 (dd, $J = 16.4, 8.0$ Hz, 2H), 6.71 (t, $J = 7.6$ Hz, 1H), 6.49 (d, $J = 8.0$ Hz, 1H), 4.39 (s, 1H), 3.78 (s, 3H), 3.50 (s, 3H), 3.17 (d, $J = 15.2$ Hz, 1H), 3.03-2.89 (m, 3H), 2.71-2.66 (m, 1H), 2.48-2.40 (m, 1H), 2.23 (d, $J = 14.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 172.1, 151.6, 141.0, 132.6, 132.0, 127.90, 127.87, 127.6, 127.00, 126.94, 124.2 (q, $J =$

272.0 Hz), 121.0, 118.2, 108.6, 72.0, 65.2, 63.8, 53.0, 52.7, 44.5, 40.6 (q, $J = 6.0$ Hz), 39.9, 39.1. ^{19}F NMR (376 MHz, CDCl_3) δ -57.06 (s, 3F). IR (thin film): ν_{max} (cm^{-1}) = 3418, 2953, 1739, 1713, 1645, 1606, 1573, 1483, 1465, 1301, 1259, 1210, 1166, 1055, 1036, 973, 942, 915, 747, 740. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{F}_3\text{NO}_4$ $[\text{M}+\text{H}]^+$: 446.1574. Found: 446.1562.

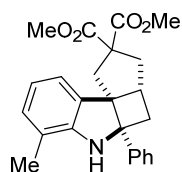


2m, white solid, m.p. = 150.1-151.8 °C, 84.1 mg, 96% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.32-7.22 (m, 4H), 7.17-7.10 (m, 2H), 3.77 (s, 3H), 3.44 (s, 3H), 3.36 (dd, $J = 13.6, 4.0$ Hz, 1H), 2.92-2.85 (m, 1H), 2.81 (d, $J = 15.2$ Hz, 1H), 2.71 (dd, $J = 13.6, 8.8$ Hz, 1H), 2.56 (dd, $J = 13.6, 8.4$ Hz, 1H), 2.39-2.28 (m, 2H), 1.77 (s, 3H), 1.67 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.2, 171.2, 169.7, 144.6, 137.9, 136.5, 135.8, 132.8, 129.1, 128.4, 128.1, 125.8, 124.4, 121.5, 117.4, 73.4, 63.8, 62.9, 52.9, 52.7, 44.6, 41.2, 40.5, 35.2, 25.5, 21.7. IR (thin film): ν_{max} (cm^{-1}) = 2987, 2956, 1733, 1649, 1593, 1476, 1455, 1430, 1377, 1348, 1200, 1174, 1139, 753, 728, 697, 681, 671, 499. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 434.1962. Found: 434.1956.

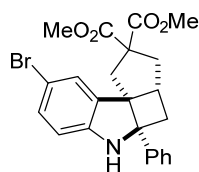


2n, brown oil, 68.1 mg, 87% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, $J = 7.2$ Hz, 2H), 7.23 (d, $J = 7.2$ Hz, 1H), 7.17 (d, $J = 7.6$ Hz, 2H), 6.87 (d, $J = 9.6$ Hz, 2H), 6.50 (d, $J = 7.6$ Hz, 1H), 4.10 (s, 1H), 3.74 (s, 3H), 3.35 (s, 3H), 3.00-2.93 (m, 1H), 2.83-2.78 (m, 2H), 2.62-2.53 (m, 2H), 2.49-2.36 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 172.0, 150.0, 142.3, 133.1, 128.4, 128.3, 127.9, 127.4, 126.5, 123.1, 108.4, 71.5, 65.3, 63.5, 52.9, 52.5, 45.5, 40.4, 39.0, 36.5, 20.8. IR (thin film): ν_{max} (cm^{-1}) = 3373, 3001, 1727, 1613, 1490, 1445, 1432, 1396, 1249, 1201, 1146, 1119, 845,

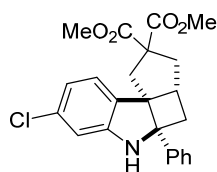
806, 751, 699, 666, 615. HRMS (ESI) calcd for C₂₄H₂₆NO₄ [M+H]⁺: 392.1856. Found: 392.1845.



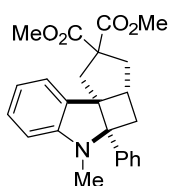
2o, green oil, 62.0 mg, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.27-7.24 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.93 (dd, *J* = 14.8, 7.6 Hz, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 4.02 (s, 1H), 3.73 (s, 3H), 3.35 (s, 3H), 3.00-2.93 (m, 1H), 2.87-2.79 (m, 2H), 2.63-2.57 (m, 1H), 2.48-2.37 (m, 1H), 2.10 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 171.9, 150.7, 142.4, 132.1, 128.8, 128.4, 127.4, 126.6, 119.9, 118.7, 117.7, 71.1, 65.6, 63.6, 52.9, 52.4, 45.6, 40.5, 39.4, 36.8, 16.8. IR (thin film): ν_{max} (cm⁻¹) = 3369, 3052, 1727, 1596, 1492, 1462, 1445, 1432, 1251, 1200, 1180, 1143, 1100, 1081, 745, 699. HRMS (ESI) calcd for C₂₄H₂₆NO₄ [M+H]⁺: 392.1856. Found: 392.1845.



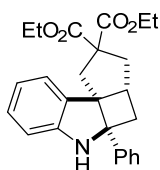
2p, dark oil, 84.2 mg, 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 6.4 Hz, 1H), 7.16-7.11 (m, 4H), 6.43 (d, *J* = 8.4 Hz, 1H), 4.24 (s, 1H), 3.74 (s, 3H), 3.36 (s, 3H), 3.02-2.96 (m, 1H), 2.80 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.74 (d, *J* = 15.6 Hz, 1H), 2.61-2.56 (m, 2H), 2.47-2.37 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 171.8, 151.1, 141.6, 135.0, 130.5, 128.5, 127.6, 126.4, 125.5, 109.7, 109.4, 71.8, 64.9, 63.5, 53.0, 52.5, 45.5, 40.4, 39.0, 36.8. IR (thin film): ν_{max} (cm⁻¹) = 3378, 3025, 1726, 1598, 1473, 1445, 1431, 1253, 1202, 1143, 1101, 1083, 1058, 805, 752, 699, 666, 590, 576. HRMS (ESI) calcd for C₂₃H₂₃BrNO₄ [M+H]⁺: 456.0805. Found: 456.0788.



2q, red oil, 83.2 mg, 98% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (t, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 2H), 6.96 (d, $J = 7.6$ Hz, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 6.51 (s, 1H), 4.32 (s, 1H), 3.72 (s, 3H), 3.35 (s, 3H), 2.98-2.91 (m, 1H), 2.83-2.73 (m, 2H), 2.60-2.53 (m, 2H), 2.48-2.35 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 171.8, 153.1, 141.5, 133.4, 131.2, 128.5, 127.6, 126.5, 123.2, 118.0, 108.04, 108.00, 71.7, 64.5, 63.5, 52.9, 52.5, 45.5, 40.4, 39.0, 36.6. IR (thin film): ν_{max} (cm^{-1}) = 3399, 2950, 1727, 1600, 1480, 1445, 1432, 1317, 1241, 1204, 1184, 1140, 1118, 975, 950, 935, 916, 723, 700. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{ClNO}_4$ $[\text{M}+\text{H}]^+$: 412.1310. Found: 412.1302.

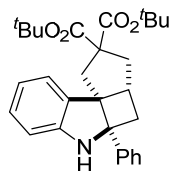


2r, green oil, 22.1 mg, 29% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.33 (t, $J = 7.6$ Hz, 2H), 7.26 (t, $J = 3.2$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.61 (t, $J = 7.6$ Hz, 1H), 6.29 (d, $J = 7.6$ Hz, 1H), 3.74 (s, 3H), 3.40 (s, 3H), 2.95-2.88 (m, 1H), 2.76 (d, $J = 15.2$ Hz, 1H), 2.65 (dd, $J = 13.2, 5.6$ Hz, 1H), 2.56 (dd, $J = 13.2, 8.8$ Hz, 1H), 2.49-2.43 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 171.9, 153.1, 139.2, 133.0, 128.2, 127.5, 127.4, 122.0, 116.2, 110.0, 104.0, 74.9, 63.6, 63.5, 52.9, 52.5, 45.2, 40.7, 39.3, 31.9, 28.5. IR (thin film): ν_{max} (cm^{-1}) = 2949, 1729, 1601, 1486, 1446, 1433, 1374, 1308, 1242, 1201, 1180, 1155, 1137, 1124, 745, 700. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 392.1856. Found: 392.1848.

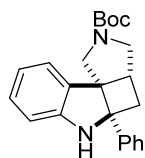


2s, brown oil, 78.0 mg, 94% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.29 (m, 2H), 7.25-7.18 (m, 3H), 7.10 (d, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.57 (d, $J = 7.6$ Hz, 1H), 4.25-4.13 (m, 3H), 4.01-3.93 (m, 1H), 3.71-3.63 (m, 1H), 3.00-2.94 (m, 1H), 2.86-2.80 (m, 2H), 2.59-2.53 (m, 2H), 2.47-2.36 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 3H), 0.99 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.2, 171.5, 152.1, 142.1, 132.9, 128.3, 127.8, 127.4, 126.6, 122.5, 118.5, 108.3, 71.3, 65.3, 63.8,

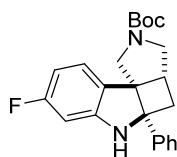
61.6, 61.2, 45.6, 40.4, 39.1, 36.5, 14.0, 13.6. IR (thin film): ν_{max} (cm⁻¹) = 3391, 2981, 1748, 1724, 1604, 1483, 1466, 1445, 1251, 1241, 1184, 1159, 1143, 1100, 1078, 1063, 764, 748, 719. HRMS (ESI) calcd for C₂₅H₂₈NO₄ [M+H]⁺: 406.2013. Found: 406.2001.



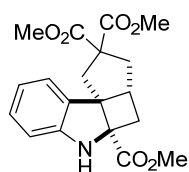
2t, green oil, 93.0 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, J = 7.6 Hz, 2H), 7.24-7.17 (m, 4H), 7.04 (t, J = 7.6 Hz, 1H), 6.73 (t, J = 7.6 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 4.21 (s, 1H), 2.98-2.91 (m, 1H), 2.78 (dd, J = 12.8, 6.0 Hz, 1H), 2.71 (d, J = 15.6 Hz, 1H), 2.57 (dd, J = 12.8, 8.4 Hz, 1H), 2.50-2.38 (m, 2H), 2.27 (dd, J = 14.0, 4.4 Hz, 1H), 1.47 (s, 9H), 1.26 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 171.6, 170.9, 152.0, 142.3, 133.7, 128.4, 127.7, 127.3, 126.6, 122.9, 118.5, 108.3, 81.3, 80.9, 71.8, 65.6, 65.4, 45.9, 40.8, 39.1, 36.5, 27.8, 27.6. IR (thin film): ν_{max} (cm⁻¹) = 3389, 2978, 1743, 1714, 1606, 1483, 1463, 1447, 1392, 1257, 1216, 1151, 1133, 1097, 843, 749, 698, 651, 627. HRMS (ESI) calcd for C₂₉H₃₆NO₄ [M+H]⁺: 462.2639. Found: 462.2629.



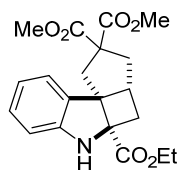
2u, pale oil, 47.0 mg, 66% yield. Two rotamers were observed by NMR. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.23 (m, 5H), 7.09 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 6.65 (d, J = 7.6 Hz, 1H), 4.37 (s, 1H), 3.74-3.27 (m, 4H), 3.02-2.99 (m, 1H), 2.80-2.63 (m, 2H), 1.45-1.26 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 154.3, 152.8, 141.0, 128.5, 127.4, 126.3, 126.0, 122.6, 118.3, 109.9, 108.2, 79.1, 70.7, 63.7, 49.3, 43.6, 37.4, 28.2. IR (thin film): ν_{max} (cm⁻¹) = 3350, 2983, 1677, 1606, 1484, 1464, 1414, 1364, 1345, 1323, 1273, 1156, 1115, 777, 759, 739, 709, 696, 630. HRMS (ESI) calcd for C₂₃H₂₇N₂O₂ [M+H]⁺: 363.2067. Found: 363.2059.



2v, pale oil, 74.1 mg, 98% yield. Two rotamers were observed by NMR. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.23 (m, 5H), 6.86 (t, $J = 6.8$ Hz, 1H), 6.39-6.31 (m, 2H), 4.51 (s, 1H), 3.72-3.20 (m, 4H), 2.96-2.94 (m, 1H), 2.78-2.62 (m, 2H), 1.44-1.25 (m, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.0, 162.6, 154.1, 154.0, 140.5, 128.5, 127.5, 126.3, 124.4, 123.0, 104.1, 103.9, 95.8, 95.6, 79.2, 71.5, 62.8, 51.5, 49.2, 43.5, 37.3, 28.4, 28.32, 28.29, 28.2. ^{19}F NMR (376 MHz, CDCl_3) δ -114.4 - -114.6 (m, 1F). IR (thin film): ν_{max} (cm^{-1}) = 3330, 2975, 1672, 1616, 1601, 1495, 1468, 1445, 1286, 1273, 1237, 1224, 1094, 1074, 953, 924, 875, 821, 792, 761. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{26}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 381.1973. Found: 381.1964.

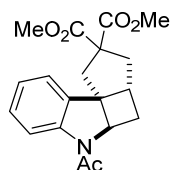


2w, brown oil, 70.1 mg, 97% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.08 (m, 2H), 6.83 (t, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 4.64 (s, 1H), 3.82-3.76 (m, 9H), 2.95-2.88 (m, 1H), 2.82 (d, $J = 15.6$ Hz, 1H), 2.69-2.60 (m, 4H), 2.33 (dd, $J = 13.2, 8.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 172.3, 171.7, 150.9, 133.7, 128.3, 123.0, 120.5, 111.6, 71.0, 66.4, 64.5, 52.8, 52.7, 52.5, 46.4, 42.7, 41.6, 37.3. IR (thin film): ν_{max} (cm^{-1}) = 3354, 3001, 1723, 1604, 1484, 1464, 1433, 1258, 1236, 1213, 1167, 1114, 1089, 1024, 978, 936, 916, 745, 665. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_6$ $[\text{M}+\text{H}]^+$: 360.1442. Found: 360.1435.

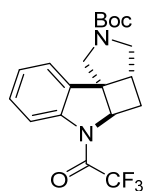


2x, red oil, 60.0 mg, 81% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.08 (m, 2H), 6.83 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 4.66 (s, 1H), 4.35-4.23 (m, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 2.95-2.87 (m, 2H), 2.75-2.59 (m, 4H), 2.33 (dd, $J = 13.2, 8.8$ Hz, 1H), 1.34 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 171.9, 171.5, 151.0, 134.1, 128.3, 123.2, 120.6, 111.9, 71.0, 66.3, 64.6, 61.9, 52.8, 52.7, 46.3, 42.9, 41.7, 37.5, 14.1. IR (thin film): ν_{max} (cm^{-1}) = 3359, 2951, 2849, 1725, 1604, 1483, 1464, 1433,

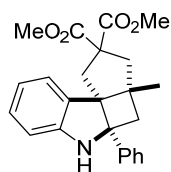
1367, 1290, 1257, 1233, 1210, 1165, 1089, 1015, 741, 634, 586. HRMS (ESI) calcd for $C_{20}H_{24}NO_6$ $[M+H]^+$: 374.1598. Found: 374.1594.



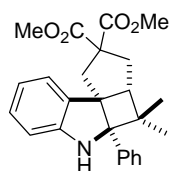
2y, yellow oil, 51.0 mg, 79% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 1H), 7.24 (td, J = 7.6, 1.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.06 (td, J = 7.6, 1.2 Hz, 1H), 4.45 (t, J = 6.0 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 2.92-2.87 (m, 1H), 2.84 (d, J = 14.4 Hz, 1H), 2.66-2.48 (m, 3H), 2.26 (dd, J = 6.8, 4.4 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.8, 168.3, 144.1, 134.5, 128.5, 124.0, 122.5, 117.2, 62.9, 62.2, 57.9, 53.1, 52.9, 45.4, 43.3, 40.5, 32.9, 23.8. IR (thin film): ν_{max} (cm^{-1}) = 2968, 2955, 1751, 1729, 1646, 1593, 1477, 1457, 1433, 1405, 1353, 1257, 1240, 1150, 1105, 771, 751. HRMS (ESI) calcd for $C_{19}H_{22}NO_5$ $[M+H]^+$: 344.1492. Found: 344.1489.



2z, white solid, m.p. = 161.1-161.8 °C, 75.1 mg, 98% yield. 1H NMR (600 MHz, $CDCl_3$, 60 °C) δ 8.31 (d, J = 8.4 Hz, 1H), 7.34 (dd, J = 7.8, 1.2 Hz, 1H), 7.27-7.25 (m, 1H), 7.22 (t, J = 7.8 Hz, 1H), 4.79 (t, J = 7.8 Hz, 1H), 3.95 (d, J = 12.6 Hz, 1H), 3.69 (d, J = 12.0 Hz, 1H), 3.59 (dd, J = 12.0, 8.4 Hz, 1H), 3.41 (d, J = 12.0 Hz, 1H), 2.94-2.90 (m, 1H), 2.48-2.37 (m, 2H), 1.52 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.0, 154.4 (q, J = 37.5 Hz), 143.6, 132.6, 129.3, 126.4, 123.3, 118.9, 116.0 (q, J = 286.5 Hz), 80.2, 62.1, 57.9, 54.5, 52.9, 44.5, 34.4, 28.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.31 (s, 3F). IR (thin film): ν_{max} (cm^{-1}) = 2977, 2928, 1683, 1599, 1481, 1461, 1433, 1296, 1270, 1248, 1235, 1224, 1178, 1151, 1123, 761, 740. HRMS (EI) calcd for $C_{19}H_{21}F_3N_2O_3$ $[M]^+$: 382.1504. Found: 382.1505.

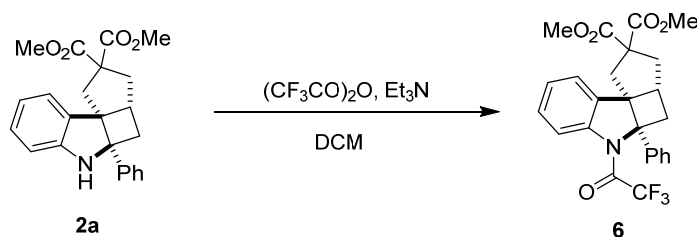


3, red oil, 38.0 mg, 50% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.21 (m, 3H), 7.15 (d, $J = 7.6$ Hz, 2H), 7.07 (t, $J = 8.8$ Hz, 2H), 6.77 (t, $J = 7.6$ Hz, 1H), 6.56 (d, $J = 8.0$ Hz, 1H), 4.15 (s, 1H), 3.70 (s, 3H), 3.21 (s, 3H), 3.10-2.97 (m, 2H), 2.79-2.68 (m, 2H), 2.16 (d, $J = 13.2$ Hz, 1H), 1.89 (d, $J = 14.0$ Hz, 1H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 171.8, 153.1, 142.4, 129.7, 128.4, 128.0, 127.4, 126.6, 123.9, 118.3, 108.2, 69.3, 67.2, 61.4, 52.9, 52.4, 48.4, 47.7, 42.4, 38.8, 24.2. IR (thin film): ν_{max} (cm^{-1}) = 3372, 3026, 2951, 1729, 1632, 1603, 1483, 1461, 1445, 1248, 1224, 1200, 1165, 1139, 745, 701, 684. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 392.1856. Found: 392.1845.

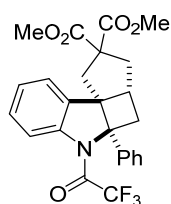


4, yellow oil, 46.0 mg, 58% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.22 (m, 5H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.73 (t, $J = 7.6$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 1H), 4.76 (s, 1H), 3.79 (s, 3H), 3.61 (s, 3H), 2.91 (d, $J = 14.8$ Hz, 1H), 2.70-2.62 (m, 2H), 2.52 (dd, $J = 12.4, 7.2$ Hz, 1H), 1.68 (t, $J = 13.2$ Hz, 1H), 1.37 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.2, 172.4, 149.3, 142.9, 136.0, 129.0, 127.9, 126.5, 126.0, 123.3, 119.0, 109.1, 66.2, 57.4, 56.4, 54.4, 52.9, 52.8, 52.5, 38.8, 37.3, 32.7, 29.1. IR (thin film): ν_{max} (cm^{-1}) = 3381, 2950, 2920, 1727, 1645, 1605, 1486, 1463, 1433, 1252, 1201, 1157, 1140, 1118, 817, 773, 743, 720. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 406.2013. Found: 406.2002.

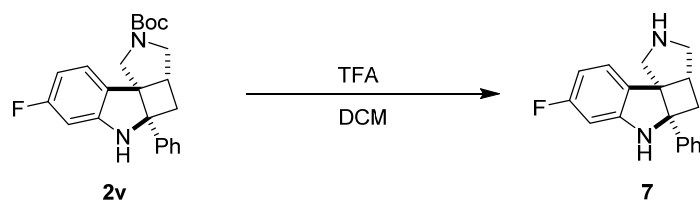
3. Transformations of products



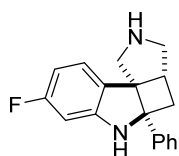
2a (153.0 mg, 0.41 mmol), $(\text{CF}_3\text{CO})_2\text{O}$ (0.3 mL, 2.1 mmol) and Et_3N (0.3 mL, 2.1 mmol) were added into a flask containing DCM (10 mL). The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), it was quenched with water. The mixture was extracted with EtOAc (10 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 15/1) to afford the desired product **6**.



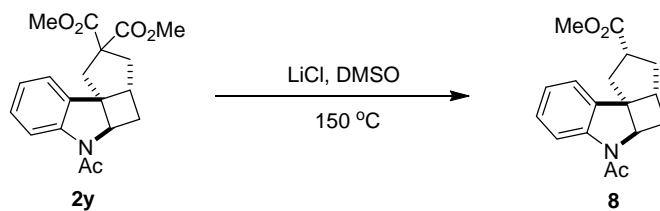
6, brown solid, m.p. = 154.5-155.1 °C, 163.0 mg, 88% yield. Two rotamers were observed by NMR. ^1H NMR (400 MHz, CDCl_3) δ 8.45 (br, 1H), 7.66-6.85 (m, 8H), 3.76 (s, 3H), 3.56 (s, 3H), 3.29-3.22 (m, 1H), 2.99-2.92 (m, 1H), 2.82-2.73 (m, 2H), 2.51 (br, 2H), 2.18 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 171.6, 144.3, 138.3, 135.7, 129.3, 128.5, 128.2, 126.6, 126.4, 123.1, 118.3, 74.9, 65.8, 63.5, 53.00, 52.97, 52.78, 52.75, 45.1, 40.7, 39.6, 34.7. ^{19}F NMR (376 MHz, CDCl_3) δ -69.04 (s, 3F), -72.53* (s, 3F). IR (thin film): ν_{max} (cm^{-1}) = 2954, 1753, 1728, 1666, 1571, 1478, 1457, 1446, 1296, 1276, 1255, 1224, 1201, 1148, 1090, 1073, 1056, 746, 727, 702. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_5$ $[\text{M}+\text{NH}_4]^+$: 491.1788. Found: 491.1782.



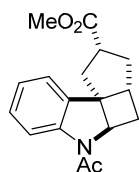
To a mixture of **2v** (40.0 mg, 0.11 mmol) and TFA (1 mL) was added DCM (1 mL) under argon at room temperature. The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), it was quenched with sodium carbonate aqueous solution. The mixture was extracted with EtOAc (10 mL x 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford the desired product **7**.



7, pale solid, m.p. = 160.2-161.5 °C, 25.0 mg, 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (t, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 3H), 6.85 (dd, *J* = 8.0, 6.0 Hz, 1H), 6.40-6.35 (m, 1H), 6.30 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.40 (s, 1H), 2.99-2.86 (m, 5H), 2.68-2.57 (m, 2H), 2.33 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 163.6 (d, *J* = 140.0 Hz), 154.5 (d, *J* = 12.0 Hz), 140.9, 128.7, 127.7, 126.2, 125.6 (d, *J* = 2.0 Hz), 122.6 (d, *J* = 10.0 Hz), 104.0 (d, *J* = 23.0 Hz), 95.5 (d, *J* = 26.0 Hz), 71.4, 63.9, 53.5, 50.7, 45.6, 36.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -115.27 - -115.33 (m, 1F). IR (thin film): ν_{max} (cm⁻¹) = 3202, 2976, 2959, 1611, 1493, 1462, 1443, 1427, 1410, 1330, 1269, 1249, 1192, 1141, 1079, 990, 917, 883, 696, 666. HRMS (ESI) calcd for C₁₈H₁₈FN₂ [M+H]⁺: 281.1449. Found: 281.1444.



2y (40.0 mg, 0.12 mmol), LiCl (25.2 mg, 0.60 mmol) and H₂O (0.1 mL) were added into a flask containing DMSO (10 mL). The reaction mixture was heated to 150 °C and gradually turned dark. After heating at 150 °C for 3 h, the solution was cooled to rt, diluted with ether and washed with brine (6 mL x 3). The organic extracts were dried with Na₂SO₄, filtered, and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 15/1) to afford the desired product **8**.



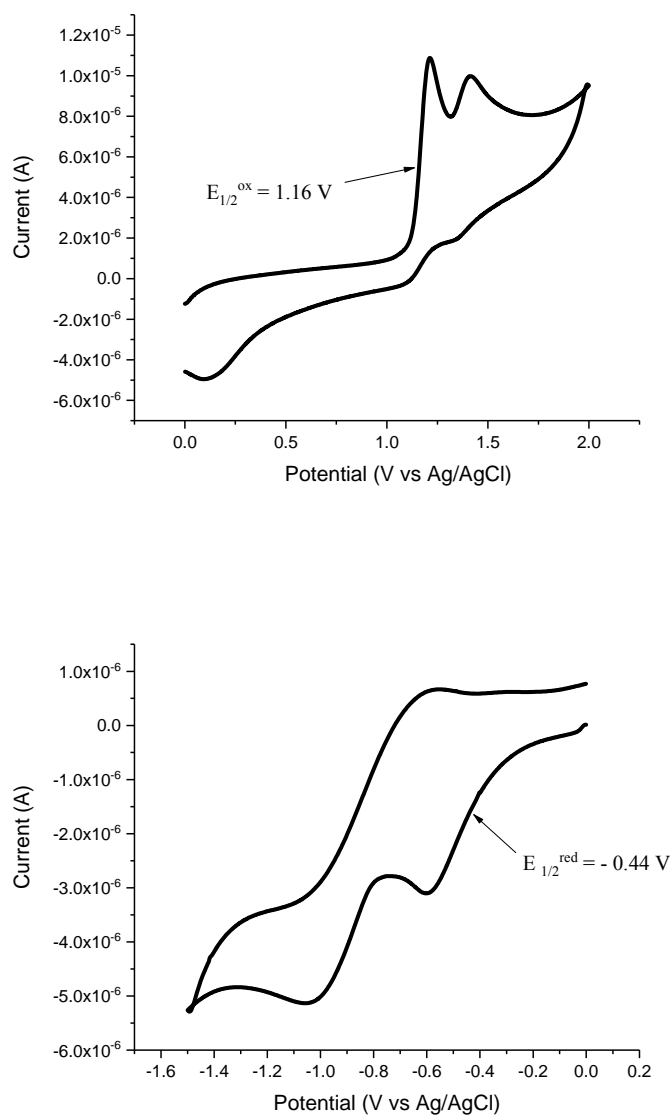
8, white solid, m.p. = 140.5-142.2 °C, 18.0 mg, 50% yield, >20/1 dr. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 1H), 7.09-7.03 (m, 2H), 4.51 (t, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.31-3.23 (m, 1H), 2.81-2.70 (m, 1H), 2.55 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.38-2.13 (m, 5H), 2.10 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.0, 168.5, 144.2, 135.8, 128.1, 123.9, 122.0, 117.2, 62.6, 57.7, 51.9, 46.6, 45.9, 39.2, 36.7, 33.2, 23.8. IR (thin film): ν_{max} (cm⁻¹) = 2932, 1726, 1658, 1596, 1477, 1458, 1433, 1390, 1354, 1318, 1287, 1192, 1104, 1069, 753, 667, 615, 599, 560. HRMS (ESI) calcd for C₁₇H₂₀NO₃ [M+H]⁺: 286.1438. Found: 286.1437.

4. Experimental details for mechanistic studies

4.1 Cyclic voltammetry

Cyclic voltammograms were recorded using a CHI660E potentiostat and a Pt working electrode (area = 0.03 cm²), a Ag/AgCl reference electrode and a Pt sheet auxiliary electrode. The voltammograms were recorded at room temperature in 0.1 M tetrabutylammonium hexafluorophosphate in MeCN containing **1a** (1 mM). The scan rate was 100 mV s⁻¹.

Cyclic voltammogram of substrate **1a**:

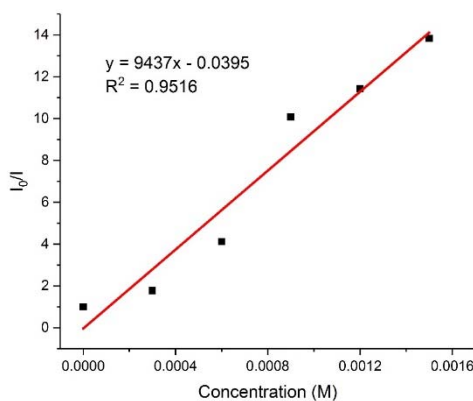


4.2 Stern-Volmer luminescence quenching studies

Stern-Volmer experiments^[5] were conducted on a Hitachi F4600 Fluorescence Spectrophotometer. Each component was prepared in DCE prior to each set of experiments. The solutions were irradiated at 350 nm and the luminescence measured at 480 nm. The value for I_0/I from each run was averaged to yield a value of I_0/I for the experiment. Linear regression of I_0/I against concentration was performed in Origin.

species	concentration (mM)
Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	0.2
1a	varied

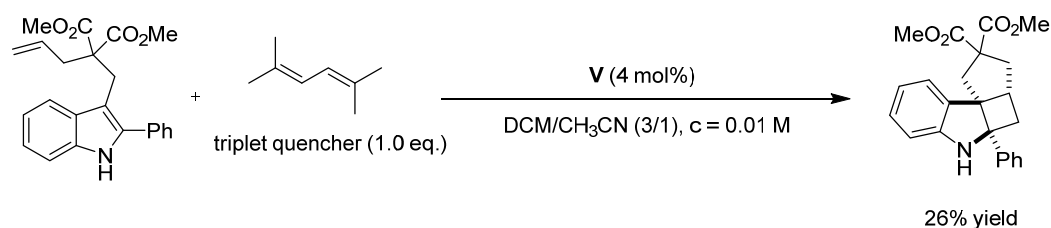
substrate (mM)	0	0.3	0.6	0.9	1.2	1.5
I_0/I_1	1	1.76	4.11	10.09	11.50	13.80
I_0/I_2	0.99	1.77	4.13	10.06	11.36	13.85
average	1	1.77	4.12	10.08	11.43	13.83



4.3 Control experiment with triplet quencher

2,5-Dimethylhexa-2,4-diene is known as a triplet quencher.^[6] The model reaction **1a** → **2a** is significantly inhibited in the presence of 1.0 equivalent of 2,5-dimethylhexa-

2,4-diene.



Conclusion of this experiment: This experiment supports the involvement of excited triplet state intermediates.

4.4 Computational studies

Cartesian coordinates and energies and of all optimized structures

1a

Opt @ B3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(RB3LYP) = -1246.01750594 a.u.
 Zero-point correction = 0.414726 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.660539 a.u.

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O,0,1.9693868005,4.8892386056,7.7871178285
O,0,2.5881426555,4.5020645285,5.6514048561
O,0,1.7684910435,7.3815312395,3.8939930835
O,0,0.1946023331,6.2321229375,5.030559613
N,0,5.7529675266,7.6617821015,9.0251445824
C,0,6.1408191983,6.4061537019,8.6260675527
C,0,7.0702473959,5.5251787956,9.1916345988
C,0,7.2863141822,4.3157041582,8.5406859987
C,0,6.5969455633,3.9959633285,7.351304439
C,0,5.6717896095,4.8730946943,6.796577057
C,0,5.4215752821,6.1034691289,7.4362595828
C,0,4.5831450312,7.2418330257,7.1349639057
C,0,4.8448665551,8.1892711237,8.1181519331
C,0,4.3706183249,9.5722462513,8.3169499606
C,0,4.3668447112,10.4983196889,7.2585365201
C,0,3.9509876275,11.8136531721,7.4669411731
C,0,3.5412372949,12.2310061766,8.7356861842
C,0,3.5532990875,11.3237809418,9.7976421281
C,0,3.9642498661,10.0068849929,9.592033358
C,0,3.6128872085,7.3307760822,5.9855993722
C,0,2.1688854015,6.7696855605,6.2348243313
C,0,1.3756516809,7.574040912,7.3086755648
C,0,0.9489986895,8.9466380558,6.8611270686
C,0,-0.3235513756,9.3267290592,6.7282477105
C,0,2.2222751879,5.2989391684,6.6743881849
C,0,2.6253559674,3.0866041326,5.9348152781
  
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C,0,1.3902022943,6.8361698536,4.9092204811
 C,0,-0.6555085578,6.271568793,3.8653993281
 H,0,6.1762612037,8.1917910761,9.7738767183
 H,0,7.6055394586,5.7830192613,10.100921278
 H,0,8.0024614573,3.609037231,8.9501863361
 H,0,6.7989833603,3.0487123568,6.8590884343
 H,0,5.1567578166,4.617043743,5.8766042159
 H,0,4.7162443711,10.1925792148,6.2776004254
 H,0,3.9594941469,12.5161809181,6.6384264682
 H,0,3.2367656634,11.6391555732,10.787780349
 H,0,3.9559096217,9.3033993838,10.4198939822
 H,0,4.0259457501,6.7962586362,5.1254705531
 H,0,3.4889978792,8.3652572317,5.661849798
 H,0,0.4954918782,6.9933241756,7.5931839596
 H,0,2.014462976,7.6453845069,8.1955892445
 H,0,1.7394075924,9.6626118986,6.6439992907
 H,0,-0.5869233834,10.3332455514,6.413257768
 H,0,-1.1486211762,8.6495078225,6.939938597
 H,0,2.9385270085,2.6111625916,5.0054982839
 H,0,1.6332618785,2.7333187321,6.2261489598
 H,0,3.3393347866,2.8724971635,6.732401075
 H,0,-0.1706561421,5.7783058086,3.0196784291
 H,0,-0.8906808661,7.3051626805,3.6009592993
 H,0,-1.5624763898,5.7367632559,4.146759486
 H,0,3.2200185232,13.2560089767,8.8962523731

1a-T₁

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(UB3LYP) = -1245.92230959 a.u.

Zero-point correction = 0.410594 Hartree/Particle

Sum of electronic and thermal Free Energies = -1245.571242 a.u.

O,0,2.0563781601,4.6850031861,7.5949667143
 O,0,2.702980491,4.5138561497,5.4388699922
 O,0,1.7127627306,7.4906860755,3.9358895602
 O,0,0.2140800214,6.1661927308,4.9809789602
 N,0,5.408425181,7.6154550346,9.2512436946
 C,0,5.8805436403,6.3875853152,8.7878561753
 C,0,6.7017862913,5.4742472651,9.411828863
 C,0,7.0211840455,4.2850860681,8.7046842952
 C,0,6.517640293,4.0456615932,7.4241607197
 C,0,5.6775239913,4.9733473241,6.7965740216
 C,0,5.3431744806,6.1704906925,7.4771277585
 C,0,4.5412488135,7.2815973309,7.1372283591
 C,0,4.7186873342,8.2932314931,8.2445723109
 C,0,4.4073533929,9.657249217,8.3454751587
 C,0,4.0686328434,10.4754148789,7.2073503618
 C,0,3.8166836346,11.8281219124,7.3460966839
 C,0,3.8724074773,12.4571207415,8.6039782488
 C,0,4.2031821086,11.6825088221,9.7341477967
 C,0,4.4688727589,10.3327827611,9.6215885141
 C,0,3.5935800596,7.3332315737,5.9782257335
 C,0,2.1715474002,6.699464993,6.21123779
 C,0,1.3588581334,7.3757663242,7.3571447438
 C,0,0.8550529245,8.7559546518,7.0293880854
 C,0,-0.4380468431,9.0742375729,6.9402165854

C,0,2.2950139715,5.1992514277,6.5236581967
 C,0,2.8050806218,3.0817753885,5.5968089394
 C,0,1.3735407798,6.8402482181,4.9016340917
 C,0,-0.6553411334,6.2628862374,3.8324269334
 H,0,5.8895188843,8.1127106943,9.9886228799
 H,0,7.0901873504,5.6510629502,10.4098089874
 H,0,7.6697151917,3.5519437527,9.1748036873
 H,0,6.7871762878,3.1311570476,6.9042405656
 H,0,5.3067458926,4.7925244276,5.7937502522
 H,0,4.0742941934,10.0433708271,6.2149455294
 H,0,3.5864016317,12.4148667864,6.4604016629
 H,0,4.2421408421,12.1503648618,10.7146756981
 H,0,4.6793240609,9.7609245064,10.5202882986
 H,0,4.0418912778,6.8058852854,5.1307177939
 H,0,3.4177237005,8.354792175,5.6436144062
 H,0,0.5136216831,6.727915872,7.5997332913
 H,0,2.0019043776,7.405952978,8.2435068731
 H,0,1.6027531288,9.5300086358,6.8677674802
 H,0,-0.759646199,10.0875541739,6.7135668508
 H,0,-1.2222389026,8.3371597621,7.1014056085
 H,0,3.1584786264,2.707092654,4.6365161835
 H,0,1.8262738163,2.6575458566,5.8332115972
 H,0,3.5134166818,2.8321493728,6.388964114
 H,0,-0.1589608384,5.8696169709,2.9422524965
 H,0,-0.9450418686,7.3023209381,3.6624478246
 H,0,-1.5298686216,5.6604686822,4.0769200287
 H,0,3.6675941991,13.5183358102,8.7017986022

TS1

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(UB3LYP) = -1245.90379693 a.u.
 Zero-point correction = 0.410292 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.551087 a.u.
 Imaginary Frequency = -444.926 cm⁻¹

O,0,4.0905708176,11.2476135935,11.0144913785
 O,0,3.942288844,13.0323675078,12.3839137415
 O,0,0.8156456251,14.3142983727,12.0506983917
 O,0,1.0095841456,12.1177669742,12.5268128309
 N,0,0.4511496991,12.5219296228,6.2054746843
 C,0,1.8104070084,12.337379314,5.9825878221
 C,0,2.5043957631,12.2302846925,4.786875288
 C,0,3.8926424253,11.9939012982,4.8589938025
 C,0,4.5396299,11.8586614477,6.0872015069
 C,0,3.8231523473,11.9738793403,7.2917725952
 C,0,2.4492604347,12.2267877637,7.2423610024
 C,0,1.4526487811,12.4451398966,8.283300358
 C,0,1.6479987547,11.8866578187,9.6715766854
 C,0,2.2892026179,12.8923851544,10.693084961
 C,0,2.7694268288,14.1819893216,9.9623252629
 C,0,1.8940504252,14.6043882531,8.8005139497
 C,0,0.6740425186,15.2308870414,8.9324578258
 C,0,0.1313924345,12.5216152889,7.5577094103
 C,0,-1.2176964489,12.4627828553,8.0004460466
 C,0,-1.6112937447,12.6887137483,9.35807473
 C,0,-2.9370782981,12.6211533425,9.7505738859

C,0,-3.9568230625,12.331585179,8.8265039419
 C,0,-3.6016615164,12.1090706055,7.4887965606
 C,0,-2.277802532,12.1672053762,7.0785203827
 C,0,3.525301286,12.26238748,11.3662429252
 C,0,5.1271950411,12.5856789125,13.0803702488
 C,0,1.295397222,13.2236544091,11.8170919462
 C,0,0.0857997203,12.2831438477,13.624561753
 H,0,1.9974010142,12.3094153876,3.8300726535
 H,0,4.4606064768,11.9049017702,3.9373399817
 H,0,5.6070763316,11.6610732934,6.1158702431
 H,0,4.3280119092,11.8560552949,8.2459176969
 H,0,2.3223076873,11.0280679424,9.6099354222
 H,0,0.706037383,11.5089250494,10.0690207723
 H,0,2.85754751,14.9857672871,10.6983922528
 H,0,3.7737249677,13.9919316386,9.5733272081
 H,0,2.4206074552,14.7603296841,7.863159445
 H,0,0.1843197579,15.6714886613,8.0696474722
 H,0,0.1487304744,15.2684527394,9.8800378407
 H,0,-0.8678212873,12.9752770849,10.0890679827
 H,0,-3.1890078501,12.8128638625,10.7906785039
 H,0,-4.9946203459,12.2857341155,9.1412522504
 H,0,-4.3704563287,11.8732684431,6.7569224855
 H,0,-2.0490847907,11.9384936373,6.0421838616
 H,0,5.9771440402,12.5400822772,12.3958398097
 H,0,4.959565816,11.6017626765,13.524185469
 H,0,5.3041955933,13.3282335736,13.8578121425
 H,0,-0.884791942,12.6271510039,13.2599909787
 H,0,0.4797983852,12.9992001511,14.3494270382
 H,0,-0.0079833668,11.2963454326,14.077077561
 H,0,-0.2131312285,12.696564935,5.4662720706

TS1'

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(UB3LYP) = -1245.89817958 a.u.
 Zero-point correction = 0.410583 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.544363 a.u.
 Imaginary Frequency = -452.7571 cm⁻¹

O,0,4.0959193427,11.2511850363,10.7440829837
 O,0,3.8490772151,13.023452737,12.1118515571
 O,0,0.514078055,13.7688915096,12.0805441299
 O,0,1.0592978081,11.601233221,12.3956066983
 N,0,0.6507764029,13.0031326103,6.1960913844
 C,0,2.0055438536,12.7567572548,6.0154652364
 C,0,2.8162491383,13.0477742928,4.9302254285
 C,0,4.1883066303,12.7285390783,5.0288135749
 C,0,4.7181758461,12.1486027613,6.1869947969
 C,0,3.899641305,11.8521907159,7.2830306277
 C,0,2.5187215928,12.1400357746,7.2025306764
 C,0,1.4425824266,11.9714417572,8.1070257968
 C,0,1.5339316674,11.5781820054,9.5454799241
 C,0,2.0930355442,12.675216939,10.553306437
 C,0,2.3322722928,14.0746510762,9.9226846831
 C,0,1.2844205773,14.6159273039,8.9948994276
 C,0,-0.0180958352,14.1845930182,8.845058448
 C,0,0.2011375225,12.4688809195,7.4273835104

C,0,-1.1442568194,11.8997944561,7.4757790557
 C,0,-2.2073864991,12.543623463,6.7926929889
 C,0,-3.5031667877,12.042259221,6.8409472259
 C,0,-3.7917976687,10.8838011165,7.5729048565
 C,0,-2.7552786046,10.2309657789,8.2460298533
 C,0,-1.4529069208,10.7245967863,8.2002342741
 C,0,3.4489434549,12.2052739037,11.1250214132
 C,0,5.1219469888,12.7143134417,12.7220511616
 C,0,1.1350266122,12.7807847112,11.7496663043
 C,0,0.1801656524,11.5591082629,13.5399522666
 H,0,2.4135199429,13.514072943,4.0360511832
 H,0,4.8421883699,12.9472542547,4.1893913818
 H,0,5.779661521,11.9224805144,6.2349500928
 H,0,4.3097414792,11.3965528213,8.178595203
 H,0,2.1893781466,10.7086342519,9.6449951191
 H,0,0.5515392559,11.273056472,9.9041574867
 H,0,2.5098290285,14.7798914892,10.7454720226
 H,0,3.2781505244,14.0327696868,9.3671252939
 H,0,1.6504992659,15.3761616234,8.3069860791
 H,0,-0.6925538686,14.7503448168,8.2088531003
 H,0,-0.4998336987,13.5846160691,9.6095153751
 H,0,-2.014935993,13.4568794356,6.2356240203
 H,0,-4.2962393504,12.5604572551,6.3085129653
 H,0,-4.8053510081,10.4962978891,7.6127295084
 H,0,-2.9577925972,9.3182372635,8.8002572601
 H,0,-0.6634034768,10.1690616019,8.6926145314
 H,0,5.9219890872,12.7610464153,11.9797976985
 H,0,5.0968311384,11.719654565,13.172789184
 H,0,5.269139046,13.4753978468,13.487763528
 H,0,-0.8464133663,11.7855107439,13.2427447024
 H,0,0.5069458813,12.2735823146,14.2990871515
 H,0,0.248204409,10.5411290225,13.9227983183
 H,0,0.0258170292,13.0920966519,5.4070546227

INT1

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(UB3LYP) = -1245.92803736 a.u.
 Zero-point correction = 0.412049 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.572751 a.u.

O,0,4.0370824318,11.2084643944,10.8399782873
 O,0,4.0028524637,12.9394952635,12.2862970132
 O,0,0.8110959641,14.2305516305,12.1693895881
 O,0,1.0713070535,12.0237331942,12.5572205373
 N,0,0.4897007414,12.3622774756,6.1952396021
 C,0,1.8556231895,12.209558886,6.0330576218
 C,0,2.5671580444,11.8879130517,4.8769829159
 C,0,3.9548217091,11.7500539783,4.988631342
 C,0,4.5989793205,11.9199033312,6.2177319723
 C,0,3.8629385963,12.2512710498,7.3674821444
 C,0,2.4854805466,12.40943511,7.2737349001
 C,0,1.4338130108,12.8210219883,8.310164376
 C,0,1.541323166,12.0001355456,9.634371805
 C,0,2.2517812774,12.887667557,10.7010100033
 C,0,2.6553185852,14.1987146167,9.9662386287
 C,0,1.7181702426,14.3467284188,8.7505822687

C,0,0.51763418,15.1840652067,9.0248050462
 C,0,0.1357739054,12.6106877915,7.51453173
 C,0,-1.2257926683,12.5375417249,7.9396931881
 C,0,-1.6524864176,12.9005585917,9.2529569026
 C,0,-2.9837519403,12.8128140559,9.6360017846
 C,0,-3.9676604861,12.3680023431,8.7422597834
 C,0,-3.5787683816,12.0069035952,7.4464930684
 C,0,-2.2499609967,12.0829837199,7.0507427675
 C,0,3.5117184596,12.2164584957,11.264914958
 C,0,5.2181756886,12.4463798428,12.891061989
 C,0,1.3066863518,13.1607986524,11.8791542289
 C,0,0.1787247567,12.1267469009,13.6874948201
 H,0,2.0594254536,11.7388512578,3.9287195599
 H,0,4.535121219,11.495290669,4.1061664662
 H,0,5.6748477134,11.791245601,6.2878354556
 H,0,4.3725697251,12.3561768274,8.3197784179
 H,0,2.1220045394,11.0906859374,9.4734845719
 H,0,0.5572304794,11.6894051324,9.9848990018
 H,0,2.6025178257,15.0577837791,10.6374275912
 H,0,3.6902100301,14.1126398775,9.6242899463
 H,0,2.261949855,14.8089987901,7.9161200703
 H,0,-0.1110314566,15.5195599217,8.206618007
 H,0,0.2444253403,15.4639567498,10.0353498601
 H,0,-0.933917993,13.2866465478,9.9639013687
 H,0,-3.2611324531,13.1051399467,10.6456435142
 H,0,-5.0077972546,12.3062466559,9.0470387636
 H,0,-4.3212556275,11.6522666581,6.7360124519
 H,0,-2.0002990152,11.7613559409,6.0446822533
 H,0,6.0285932066,12.4270190062,12.1586586799
 H,0,5.064678687,11.4426328777,13.2938816933
 H,0,5.4492038819,13.1464506131,13.6935262607
 H,0,-0.8115254046,12.4554986454,13.3636199181
 H,0,0.575066147,12.8287586997,14.4247317097
 H,0,0.1251603068,11.1231878275,14.1086868174
 H,0,-0.1696229999,12.2393676255,5.4417853479

INT1'

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(UB3LYP) = -1245.92888124 a.u.
 Zero-point correction = 0.412639 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.573365 a.u.

O,0,4.1143354345,11.3901015482,10.7741371059
 O,0,3.8635294645,13.1241718514,12.1898931075
 O,0,0.5252923487,13.9152273702,12.1689501703
 O,0,1.0951479185,11.7653413885,12.5543012481
 N,0,0.735808218,13.398907646,6.4564409806
 C,0,1.9193609379,12.7712796174,6.1237943757
 C,0,2.6512769965,12.8411247219,4.941782462
 C,0,3.8848091984,12.1732719703,4.8856963621
 C,0,4.3815970392,11.4614709561,5.9923955155
 C,0,3.6515747115,11.3791599327,7.1755402746
 C,0,2.3875283628,12.012397069,7.2500204197
 C,0,1.4053558274,12.0763362988,8.2557259556
 C,0,1.5076864217,11.6612078815,9.6836812472
 C,0,2.0838724693,12.7774313639,10.6558134397

C,0,2.3092341988,14.1589617851,9.97719666
 C,0,1.1644055067,14.7745562536,9.2275877054
 C,0,-0.0582051032,14.0559176619,8.7650967493
 C,0,0.2239228616,12.8874911435,7.7524649139
 C,0,-1.0628883316,12.0681404155,7.510311918
 C,0,-2.2576842573,12.7204755556,7.1612135931
 C,0,-3.4203562948,11.9961734533,6.8951553059
 C,0,-3.4152732723,10.6016956143,6.9777152573
 C,0,-2.2352989401,9.941551877,7.3216285587
 C,0,-1.0707040597,10.66825043,7.5826555414
 C,0,3.4573431859,12.3205226017,11.1928459521
 C,0,5.1539017254,12.8247781871,12.7663279429
 C,0,1.1514003554,12.9215325123,11.8652514766
 C,0,0.2341793815,11.7577651554,13.7126810336
 H,0,2.2841822905,13.4083072271,4.091176833
 H,0,4.4695182456,12.216718196,3.9711081648
 H,0,5.3472440231,10.9689192863,5.9207129859
 H,0,4.037112582,10.8354081251,8.0324178108
 H,0,2.1554382671,10.7871469144,9.7779454578
 H,0,0.5194947861,11.364962226,10.0473306737
 H,0,2.6510161107,14.858456328,10.7493676726
 H,0,3.1667963053,14.0426123222,9.2943143302
 H,0,1.3254715475,15.7964989747,8.8943618315
 H,0,-0.7539932712,14.7652318307,8.3083002895
 H,0,-0.5857568136,13.6053721905,9.6180575592
 H,0,-2.2853984311,13.8039076685,7.0884711712
 H,0,-4.3312896927,12.5234395855,6.6252786123
 H,0,-4.3209469929,10.0374564645,6.7743093335
 H,0,-2.2159145621,8.8570751945,7.3866446782
 H,0,-0.1585126921,10.1395349176,7.8397458505
 H,0,5.9376461573,12.9051053118,12.0096750445
 H,0,5.1569680486,11.8189665453,13.192461004
 H,0,5.3028339004,13.5693221234,13.5478711885
 H,0,-0.798969178,11.9644792833,13.4236765269
 H,0,0.5656552858,12.5021717854,14.4404289553
 H,0,0.3168881295,10.7550969738,14.1314491863
 H,0,0.0655474484,13.615185393,5.728872137

MECP1

Singlet Sp @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(UB3LYP) = -1245.92609039 a.u.

Triplet Sp @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(UB3LYP) = -1245.92611147 a.u.

8	4.02137	11.21778	10.86648
8	4.02882	12.99069	12.26068
8	0.71347	14.18898	12.15085
8	1.14062	12.02493	12.62792
7	0.49498	12.44318	6.20703
6	1.85643	12.22987	6.05421
6	2.56621	11.89575	4.90102
6	3.94696	11.69962	5.02552
6	4.5863	11.82601	6.26171
6	3.85157	12.16781	7.41015
6	2.48375	12.37827	7.30128
6	1.43935	12.81727	8.33478

6	1.5298	12.00267	9.66088
6	2.23613	12.8972	10.72492
6	2.61929	14.21803	9.99582
6	1.73497	14.32782	8.73179
6	0.50915	15.16682	8.90574
6	0.13212	12.65577	7.53157
6	-1.23804	12.57341	7.93967
6	-1.68698	12.81844	9.27354
6	-3.02086	12.70136	9.62942
6	-3.99726	12.3452	8.68631
6	-3.58995	12.0996	7.37161
6	-2.25393	12.19973	7.00284
6	3.50882	12.23926	11.27517
6	5.26729	12.51806	12.83383
6	1.28784	13.14791	11.90384
6	0.25364	12.10528	13.76457
1	2.06406	11.7808	3.94522
1	4.52462	11.43352	4.14475
1	5.65587	11.65615	6.33848
1	4.35051	12.24098	8.37171
1	2.10852	11.09009	9.51366
1	0.5431	11.69616	10.00583
1	2.50364	15.07848	10.65736
1	3.6711	14.16887	9.69976
1	2.32226	14.76814	7.9185
1	0.11765	15.744	8.07408
1	-0.00253	15.22665	9.85954
1	-0.98352	13.14879	10.02578
1	-3.31028	12.9072	10.65688
1	-5.04296	12.26969	8.96905
1	-4.32266	11.8188	6.6192
1	-1.99778	11.96688	5.97435
1	6.05031	12.48202	12.07282
1	5.13365	11.52486	13.26823
1	5.52435	13.24027	13.60831
1	-0.75055	12.39541	13.4482
1	0.63192	12.82743	14.49217
1	0.24193	11.10457	14.19544
1	-0.16094	12.33357	5.44859

----- **MECP2**

Singlet Sp @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(UB3LYP) = -1245.92855211 a.u.

Triplet Sp @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(UB3LYP) = -1245.92850852 a.u.

8	4.12414	11.40432	10.75594
8	3.85634	13.12521	12.1848
8	0.54851	13.92011	12.18082
8	1.08801	11.75765	12.53926
7	0.7367	13.37213	6.44454
6	1.93117	12.76253	6.12103
6	2.67172	12.84441	4.94465
6	3.90861	12.18346	4.89331
6	4.40156	11.46893	6.00032
6	3.66508	11.37803	7.17867

6	2.39676	12.00366	7.24835
6	1.40655	12.05856	8.24812
6	1.50656	11.65245	9.68013
6	2.08139	12.7748	10.64568
6	2.30106	14.15389	9.95655
6	1.1348	14.7882	9.25838
6	-0.05962	14.0558	8.76405
6	0.23288	12.87373	7.7441
6	-1.06297	12.06671	7.51379
6	-2.25443	12.72654	7.16734
6	-3.42367	12.00993	6.90908
6	-3.42913	10.61592	6.99723
6	-2.25236	9.94817	7.33712
6	-1.08108	10.66691	7.58953
6	3.45881	12.32594	11.18062
6	5.14703	12.83157	12.7634
6	1.15677	12.92046	11.86163
6	0.23515	11.75095	13.70358
1	2.30682	13.41293	4.09406
1	4.49903	12.23391	3.98285
1	5.36994	10.98129	5.93227
1	4.0502	10.83473	8.03595
1	2.15342	10.77862	9.78142
1	0.51777	11.35937	10.04415
1	2.69211	14.84961	10.70702
1	3.1209	14.01429	9.23242
1	1.2726	15.82606	8.96702
1	-0.76032	14.75612	8.30207
1	-0.59228	13.58603	9.60336
1	-2.27544	13.80986	7.09147
1	-4.33174	12.54326	6.64152
1	-4.34059	10.05802	6.80189
1	-2.24037	8.86378	7.40569
1	-0.17117	10.13265	7.84306
1	5.93185	12.91661	12.00855
1	5.15416	11.82537	13.18856
1	5.29074	13.57594	13.54624
1	-0.79867	11.96523	13.42251
1	0.57598	12.49032	14.43209
1	0.31389	10.74606	14.11791
1	0.067	13.58562	5.71618

----- **INT1-OSS**

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(UB3LYP) = -1245.93019906 a.u.

Zero-point correction = 0.411998 Hartree/Particle

Sum of electronic and thermal Free Energies = -1245.573911 a.u.

O,0,4.0544275595,11.2225946444,10.8219535694

O,0,4.0467882454,12.9885530997,12.2252976723

O,0,0.8418994745,14.1956351974,12.235904839

O,0,1.1279037025,11.9865355846,12.5911011372

N,0,0.5082638267,12.2655539604,6.2018726082

C,0,1.8783055209,12.1548147197,6.0610838764

C,0,2.6170419757,11.8531595977,4.9160811066

C,0,4.0046972628,11.7515075876,5.0500838371

C,0,4.6233047319,11.9373141092,6.290809574
 C,0,3.8613822105,12.2505014236,7.4275897219
 C,0,2.4805701458,12.3737551992,7.3134893979
 C,0,1.3980627228,12.7593441576,8.3262470593
 C,0,1.5203590066,11.9651220962,9.6658089374
 C,0,2.2412707738,12.8755979949,10.7058640956
 C,0,2.5859010503,14.1926121651,9.9518696948
 C,0,1.609444971,14.2982835015,8.76166784
 C,0,0.3883854204,15.06950724,9.0784499432
 C,0,0.1334721346,12.5113886086,7.5163804091
 C,0,-1.235912152,12.5029445282,7.9092926556
 C,0,-1.6631252667,12.8650227077,9.2226252999
 C,0,-3.0112572273,12.8893591002,9.5666412295
 C,0,-3.9998387411,12.5457442849,8.6397940338
 C,0,-3.6073020752,12.1686601703,7.3464930267
 C,0,-2.2690708942,12.1448989164,6.9859907349
 C,0,3.531352963,12.2353227939,11.238189272
 C,0,5.2868675885,12.5234894024,12.8015426732
 C,0,1.332325406,13.1321635777,11.9166378601
 C,0,0.2782508113,12.0738550764,13.755308417
 H,0,2.1282158404,11.6927371139,3.9597350891
 H,0,4.6062669399,11.5121769792,4.1776054239
 H,0,5.7005422282,11.8339114529,6.3794501761
 H,0,4.3561748191,12.3659504818,8.38590761
 H,0,2.0981132979,11.0521055935,9.5159568165
 H,0,0.5406420448,11.661724441,10.0341583716
 H,0,2.5214810254,15.0538486755,10.6184684405
 H,0,3.6133216846,14.1388441263,9.5830544403
 H,0,2.1027413334,14.7743980394,7.9048729297
 H,0,-0.2916732296,15.3711659131,8.2892949079
 H,0,0.159371688,15.3693454913,10.0940212504
 H,0,-0.9357233469,13.1371879379,9.9731955561
 H,0,-3.2911569857,13.1780086083,10.5765595427
 H,0,-5.0495721458,12.5613128524,8.9164588535
 H,0,-4.3580640459,11.8855970014,6.6132029958
 H,0,-2.0197375855,11.8265648595,5.9786403621
 H,0,6.0729131344,12.4938829976,12.0433612748
 H,0,5.1578360747,11.528747848,13.2341415518
 H,0,5.5362375844,13.2459668887,13.5781887014
 H,0,-0.7242496899,12.4038562254,13.4731116057
 H,0,0.7005189084,12.76834649,14.4852775321
 H,0,0.243026069,11.0653376541,14.1664278158
 H,0,-0.1368357914,12.1457728834,5.4359192303

INT1'-OSS

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(UB3LYP) = -1245.92883114 a.u.
 Zero-point correction = 0.412409 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.572638 a.u.

O,0,4.1154530261,11.3898693836,10.7771039068
 O,0,3.8634952853,13.1242297523,12.1923115187
 O,0,0.5234167347,13.9149792923,12.1661248144
 O,0,1.0957235993,11.7663202444,12.5546575707
 N,0,0.7355252332,13.4017352841,6.4577581231
 C,0,1.9174465408,12.7719301937,6.1232514738

C,0,2.6476906146,12.8404769538,4.9401488711
 C,0,3.8805780057,12.1714669702,4.8825761676
 C,0,4.3783721994,11.4596047298,5.9887513983
 C,0,3.6498513993,11.3782670709,7.1729094178
 C,0,2.3864727468,12.0126413098,7.2488808656
 C,0,1.4061574444,12.0780368313,8.256126599
 C,0,1.5098745788,11.66169147,9.6834270452
 C,0,2.0855041082,12.777691133,10.6563261818
 C,0,2.3115591001,14.1591309521,9.9783422193
 C,0,1.1682356092,14.7734304529,9.225352298
 C,0,-0.0575821519,14.0565387163,8.7653950117
 C,0,0.223192071,12.8887189206,7.7536735816
 C,0,-1.0621055269,12.0679925722,7.5105965703
 C,0,-2.2572915061,12.7196353726,7.1614131712
 C,0,-3.41939583,11.9947180877,6.8946450711
 C,0,-3.4133578377,10.6001919464,6.9765521721
 C,0,-2.2330588211,9.94069394,7.3205906941
 C,0,-1.0690427032,10.6680685905,7.5823905057
 C,0,3.4582127482,12.3204884907,11.1949836423
 C,0,5.1530818287,12.8245081895,12.7703484341
 C,0,1.1513106084,12.9218009531,11.8644139152
 C,0,0.2331105033,11.758784381,13.7118212451
 H,0,2.2800270543,13.4077821874,4.0898724567
 H,0,4.464040434,12.2141487116,3.9671535341
 H,0,5.3435010231,10.9662244956,5.9158772335
 H,0,4.0359933477,10.8342758353,8.0293721222
 H,0,2.1586863471,10.7882948762,9.7764687424
 H,0,0.5222100775,11.3641096243,10.0474831193
 H,0,2.6499398718,14.858867883,10.7518166952
 H,0,3.1715372196,14.04417798,9.2982616035
 H,0,1.3272158733,15.7970989981,8.8965389077
 H,0,-0.7522528301,14.7673137563,8.309126891
 H,0,-0.5851841472,13.6087838528,9.6199100055
 H,0,-2.2855563379,13.8031186753,7.0892832579
 H,0,-4.3306289991,12.5214682592,6.6247615192
 H,0,-4.3185707281,10.0354215959,6.7725626791
 H,0,-2.2129848547,8.8562002564,7.3851329663
 H,0,-0.1566553691,10.1397742185,7.8396730259
 H,0,5.9377387344,12.9041584069,12.0145721154
 H,0,5.1551951389,11.8188742546,13.1969087457
 H,0,5.3014542264,13.5693119542,13.551750443
 H,0,-0.7998265577,11.9642395004,13.4211865523
 H,0,0.5628206972,12.5040969494,14.4394465109
 H,0,0.3162536607,10.7565327793,14.1314967053
 H,0,0.0648003093,13.6186998945,5.7307542521

TS2

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(UB3LYP) = -1245.92209308 a.u.
 Zero-point correction = 0.411553 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.566225 a.u.
 Imaginary Frequency = -310.6912 cm⁻¹

O,0,4.0806162385,11.2869802658,11.0028706039
 O,0,3.8671000164,12.9927032389,12.4632679866
 O,0,0.6525175763,14.2423272454,12.0119517412

O,0,0.9824270625,12.0687158056,12.5210210407
 N,0,0.4585405785,12.7447809695,6.2215687015
 C,0,1.7771161539,12.391134581,5.9650597076
 C,0,2.3864334785,12.0949582469,4.747199973
 C,0,3.7381136903,11.7237907445,4.7718898947
 C,0,4.4462380312,11.6494635658,5.9736391938
 C,0,3.8137051369,11.961898548,7.19065759
 C,0,2.4787139252,12.3370139676,7.181106433
 C,0,1.5658337642,12.8318691583,8.3014163583
 C,0,1.6665566898,12.0017093793,9.6114775006
 C,0,2.2658760844,12.9159232218,10.7257556921
 C,0,2.7189898124,14.2261605939,10.0163299435
 C,0,1.9561261676,14.3177680284,8.6755589365
 C,0,0.7129559263,15.1652309619,8.6597492707
 C,0,0.1863142456,12.8801275817,7.5799387435
 C,0,-1.1512796711,12.6130481136,8.0638467976
 C,0,-1.558945404,12.861610021,9.4027628123
 C,0,-2.8564291974,12.6039642719,9.827086837
 C,0,-3.818027881,12.0991560154,8.9424698397
 C,0,-3.4443389674,11.8484398612,7.619213698
 C,0,-2.1439214056,12.090609575,7.1876846892
 C,0,3.4882213418,12.2713171901,11.394542656
 C,0,5.0404134171,12.5268272117,13.1645498096
 C,0,1.2208069759,13.1871796523,11.8142824527
 C,0,0.0064720698,12.1741086857,13.5797562537
 H,0,1.8315518941,12.1379259581,3.814722708
 H,0,4.2366804247,11.481815855,3.8373333097
 H,0,5.4897723416,11.3494505581,5.9703732622
 H,0,4.363613853,11.8974459898,8.1258438994
 H,0,2.3291322986,11.1464468019,9.4695230221
 H,0,0.6979657436,11.6007903573,9.9123130319
 H,0,2.5513179407,15.0955173335,10.6552146891
 H,0,3.7931281091,14.1668181222,9.8143959179
 H,0,2.6331443118,14.7035186983,7.9084858356
 H,0,0.5959436472,15.9393106416,7.9076685605
 H,0,0.0622240524,15.2112885664,9.5253447277
 H,0,-0.861310261,13.295765646,10.1062279088
 H,0,-3.1267064647,12.8144217936,10.8586121419
 H,0,-4.8329934845,11.9084351833,9.2776854026
 H,0,-4.1689226946,11.445939705,6.9159822368
 H,0,-1.8862678998,11.8379335811,6.1644664634
 H,0,5.9097248293,12.5356195912,12.5029633989
 H,0,4.8808999476,11.5156713383,13.5461013167
 H,0,5.1837080485,13.2254106655,13.9885137401
 H,0,-0.9749278394,12.4281021497,13.1727962112
 H,0,0.3100853578,12.9324890626,14.3049475115
 H,0,-0.0222305095,11.1905382687,14.0479473215
 H,0,-0.2385165031,12.8305584302,5.4969632256

TS2'

Opt @ UB3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(UB3LYP) = -1245.92825355 a.u.
 Zero-point correction = 0.411999 Hartree/Particle
 Sum of electronic and thermal Free Energies = -1245.571672 a.u.
 Imaginary Frequency = -58.4828 cm⁻¹

O,0,4.1803958545,11.4465225736,11.0403028223
 O,0,3.6590855939,13.1226380315,12.4522350346
 O,0,0.4337795032,13.9233335084,11.9691169822
 O,0,0.8815229214,11.7413519902,12.3267530968
 N,0,0.707419316,13.3941899674,6.3727450546
 C,0,1.8559977686,12.7504174186,5.9590768755
 C,0,2.4655294404,12.7526830316,4.7081690241
 C,0,3.6933732676,12.0854252542,4.5668279484
 C,0,4.3010272819,11.4354595513,5.6553022756
 C,0,3.6903346304,11.4173128288,6.9074322008
 C,0,2.4397133107,12.0580633997,7.0741515051
 C,0,1.5643135118,12.1794779872,8.1700708102
 C,0,1.7701191575,11.6964395458,9.5648152502
 C,0,2.1616894898,12.7992228935,10.6353528923
 C,0,2.477771437,14.1917600075,10.0215500818
 C,0,1.5077973295,14.7492708108,9.0225871504
 C,0,0.1640848218,14.175903012,8.6859263147
 C,0,0.3176375307,12.947175605,7.7383530509
 C,0,-0.9646627607,12.0948916572,7.6564481217
 C,0,-2.2306300311,12.7018317326,7.6748009766
 C,0,-3.3937696046,11.9406130014,7.5410403061
 C,0,-3.3147610836,10.5551199691,7.3883860188
 C,0,-2.0620764416,9.9389722314,7.3677863809
 C,0,-0.9001903137,10.7018816442,7.4993472481
 C,0,3.4404958407,12.3466969867,11.3774588241
 C,0,4.847584643,12.8291692514,13.2196352303
 C,0,1.0636536287,12.9205462192,11.7034080299
 C,0,-0.1247222485,11.7169769635,13.3612042879
 H,0,2.0104282508,13.2682564716,3.8672982342
 H,0,4.1843156206,12.079429386,3.5977275181
 H,0,5.2565753378,10.9379721601,5.515466611
 H,0,4.1594817197,10.9106590982,7.7457828644
 H,0,2.5680418555,10.9513558157,9.5741827642
 H,0,0.8657695266,11.1897695517,9.9173445824
 H,0,2.6069222745,14.8937615281,10.857897212
 H,0,3.4672004686,14.127482379,9.5448704314
 H,0,1.8583674008,15.6122129931,8.4624610802
 H,0,-0.4596574813,14.9350368904,8.2031067816
 H,0,-0.3635406001,13.8557994517,9.5916032135
 H,0,-2.3177787854,13.7772109169,7.793132114
 H,0,-4.3621862759,12.4330225676,7.5592019965
 H,0,-4.219490705,9.9622865931,7.2882778493
 H,0,-1.9860455388,8.8614151769,7.2503910928
 H,0,0.0670138593,10.2095595952,7.4793704084
 H,0,5.7405269846,12.9570192567,12.6035646566
 H,0,4.8102685279,11.8074806615,13.604253405
 H,0,4.847138988,13.5449751024,14.0411176836
 H,0,-1.1043706426,11.9682782812,12.94805606
 H,0,0.1281957517,12.4213424866,14.1571030916
 H,0,-0.1253555284,10.6965164554,13.7435716596
 H,0,-0.0321498041,13.5724291068,5.7042148949

2a

Opt @ B3LYP/6-31G(d,p) in dichloromethane (SMD model)
 SCF Done: E(RB3LYP) = -1246.00508765 a.u.
 Zero-point correction = 0.417140 Hartree/Particle

Sum of electronic and thermal Free Energies = -1245.642984 a.u.

O,0,4.1109703825,11.4880307266,11.3414298533
O,0,3.1485967047,12.9875623744,12.7242879494
O,0,0.1492908801,13.7880019294,11.5317032665
O,0,0.5443567831,11.5820477663,11.7811949701
N,0,0.5827683009,13.2395672759,6.1396550953
C,0,1.7718965678,12.6496721359,5.7190230833
C,0,2.1790192827,12.3842035431,4.4083147863
C,0,3.4425341206,11.8146543256,4.2080354446
C,0,4.2828094909,11.5183938555,5.2846369104
C,0,3.8607612617,11.786267778,6.5967746427
C,0,2.6084030596,12.3481247127,6.812508173
C,0,1.9071409868,12.7546492131,8.0830688058
C,0,2.129471465,11.8672992532,9.3178672662
C,0,2.179598089,12.788514882,10.5711241522
C,0,2.5688320493,14.1960476106,10.0225506175
C,0,2.078024456,14.2447652065,8.5714927316
C,0,0.5668939705,14.5080395517,8.317918643
C,0,0.4247920538,13.1297331265,7.6127879878
C,0,-0.7506229931,12.2322570288,7.9558725436
C,0,-1.8949090484,12.7192085813,8.6017068996
C,0,-2.9847379941,11.8814830859,8.8605429199
C,0,-2.9440800618,10.5385124718,8.4853033702
C,0,-1.8087809423,10.0391031313,7.839835004
C,0,-0.7283638441,10.8786671604,7.5727112926
C,0,3.2520401095,12.3151193189,11.564812223
C,0,4.1283213988,12.6670774844,13.7357567226
C,0,0.8452843547,12.8133811869,11.3325957328
C,0,-0.674810883,11.4616448892,12.5444514236
H,0,1.5295801683,12.6106202954,3.5673177231
H,0,3.769754529,11.5984944536,3.1943383162
H,0,5.2595175364,11.077695877,5.1085196703
H,0,4.5109141434,11.5485927641,7.4351865091
H,0,3.1003319858,11.3721112625,9.2388289227
H,0,1.3791600209,11.0804282065,9.4188993702
H,0,2.1536672182,14.989788765,10.6479895081
H,0,3.6600737559,14.2904107784,10.0405760713
H,0,2.7328868225,14.8512838945,7.9421713417
H,0,0.3342169404,15.3627787379,7.6779321852
H,0,0.0019611631,14.5912071761,9.2472866034
H,0,-1.9473314445,13.7614309754,8.8986559403
H,0,-3.8652462627,12.2838071672,9.3539391647
H,0,-3.788050114,9.8862318113,8.6909399974
H,0,-1.7661286044,8.9952007976,7.5416667033
H,0,0.1436040315,10.4808036351,7.0615165909
H,0,5.1354553378,12.8907611992,13.3764886044
H,0,4.0633806785,11.6114942465,14.0096407276
H,0,3.8817700191,13.2968325593,14.5901679661
H,0,-1.5372519721,11.7273377786,11.9293628496
H,0,-0.6392824753,12.106054901,13.4259515941
H,0,-0.7303801977,10.414572948,12.8413376385
H,0,-0.2466210616,13.0652807233,5.584487621

iso-2a

Opt @ B3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(RB3LYP) = -1245.94101073 a.u.
Zero-point correction = 0.417769 Hartree/Particle
Sum of electronic and thermal Free Energies = -1245.577227 a.u.

C,0,0.4815054024,-0.370734875,-0.9306948808
C,0,-0.6259946733,-0.2770569697,-0.0330178699
C,0,-1.0810683387,0.9649635351,0.3990025823
C,0,-0.4292688479,2.1169080179,-0.0670404617
C,0,0.6573535696,2.0321976451,-0.9386079656
C,0,1.1279295903,0.7773194982,-1.3621614526
C,0,0.7352256008,-1.8662766428,-0.9989439409
C,0,-0.6911883168,-2.3904574933,-0.81172355
H,0,-1.9293440282,1.0430386186,1.0736197567
H,0,-0.7859170169,3.0915945087,0.2548599804
H,0,1.1452297075,2.9376989587,-1.2873707043
H,0,1.9832225683,0.7099752165,-2.0295968376
H,0,-2.1372585428,-1.5586507059,0.5225562067
N,0,-1.138170959,-1.5619374834,0.3351975482
C,0,1.6391073704,-2.130281172,0.2636497423
C,0,0.5637801483,-4.4458338023,0.2426663886
C,0,-0.0692415802,-3.8302237279,-1.0003110693
H,0,0.8981886516,-5.4640282218,0.0322353394
H,0,1.269554331,-1.5553298424,1.1109648475
H,0,2.6267618507,-1.7286682219,0.0175174195
H,0,-0.734963614,-4.5491534935,-1.4821594457
H,0,-0.1940320585,-4.507165372,1.0312954969
C,0,0.9681700504,-3.0885272893,-1.9488950159
H,0,1.978377506,-3.4953017514,-2.0028234844
H,0,0.5746718385,-2.9686147954,-2.9575029799
C,0,-1.7119063996,-2.1942551687,-1.9537545712
C,0,-2.9421943311,-2.8575103928,-1.7964445145
C,0,-1.541114806,-1.391023885,-3.089921264
C,0,-3.9686250846,-2.7163116926,-2.7295323959
H,0,-3.0974613453,-3.4953495528,-0.9287125749
C,0,-2.5676133941,-1.2506089017,-4.0299893365
H,0,-0.6062233684,-0.8680592423,-3.253028297
C,0,-3.7847109278,-1.9081399364,-3.8546313448
H,0,-4.908514133,-3.2407690301,-2.5804580285
H,0,-2.4082879282,-0.622745871,-4.9024689285
H,0,-4.5796023206,-1.7971536649,-4.5866538719
O,0,3.2086343966,-5.1620135749,-0.523503082
O,0,4.1449082181,-3.568717209,0.7674992933
O,0,1.5922140717,-2.7585011873,3.0372938503
O,0,2.1245762615,-4.9194088055,2.6724116503
C,0,1.7748627944,-3.6068030185,0.7346557806
C,0,3.0958881793,-4.2241036181,0.2386653729
C,0,5.4524871907,-4.0464618738,0.3862414375
C,0,1.8231984881,-3.6703373709,2.2727646665
C,0,2.1753207507,-5.136838093,4.0988354139
H,0,5.5910034726,-3.961230472,-0.6940607645
H,0,5.5828918426,-5.0876161273,0.6903410548
H,0,6.1613876984,-3.4061548495,0.9105685516
H,0,1.2040699668,-4.9273661106,4.5530807684
H,0,2.9372873956,-4.5009276091,4.5555538196
H,0,2.4333862818,-6.1880833909,4.2245487448

TS3

Opt @ B3LYP/6-31G(d,p) in dichloromethane (SMD model)

SCF Done: E(RB3LYP) = -1245.88747301 a.u.

Zero-point correction = 0.411298 Hartree/Particle

Sum of electronic and thermal Free Energies = -1245.531976 a.u.

Imaginary Frequency = -1588.1070 cm⁻¹

O,0,4.2923530361,11.5314399459,11.2408858227
O,0,3.145378828,12.8710656509,12.6454931604
O,0,0.1938225314,13.5301676394,11.4973364291
O,0,0.6233517825,11.3233892438,11.6757981201
N,0,0.5547171995,12.5888775456,6.1350114363
C,0,1.8839340441,12.5195687238,5.6673080944
C,0,2.3650093431,12.6595993095,4.3796272297
C,0,3.7520549187,12.4971039037,4.1896717766
C,0,4.5821886194,12.2161213515,5.2756336343
C,0,4.0722436158,12.0907920065,6.58001359
C,0,2.6968357636,12.2325833988,6.7874643597
C,0,1.8586855042,12.2840713776,7.9865741459
C,0,2.2429296233,11.594120676,9.271287713
C,0,2.2201322009,12.5920216848,10.4726740905
C,0,2.5109853193,13.9840550956,9.8647015675
C,0,1.8186192196,14.1638847372,8.5071279149
C,0,0.4705624748,14.651403077,8.395633842
C,0,0.4594941652,12.4640847828,7.4698835776
C,0,-0.8487899659,12.0258037145,8.0266218066
C,0,-2.0136944214,12.792004803,7.8522788009
C,0,-3.2497431975,12.3037742965,8.2634536025
C,0,-3.3461393851,11.0407120236,8.8605151869
C,0,-2.1995104478,10.2652725468,9.0207668494
C,0,-0.9561656903,10.7473906232,8.5977201426
C,0,3.3351434499,12.2405662695,11.4741178366
C,0,4.1559761063,12.6579620687,13.6551480191
C,0,0.8967800871,12.5726347564,11.2518101092
C,0,-0.5654603291,11.175064645,12.4789058112
H,0,1.7008243473,12.8759995431,3.5481595763
H,0,4.1707303174,12.592566734,3.1927031471
H,0,5.6495349353,12.0922873736,5.1127704211
H,0,4.7408616856,11.876398327,7.4089248789
H,0,3.2746775343,11.2479184682,9.1739872915
H,0,1.6467432582,10.7126545764,9.5157681398
H,0,2.1961442965,14.7754105423,10.5496047087
H,0,3.5935316955,14.06470165,9.7202944169
H,0,2.5012259203,14.5419861678,7.7447958936
H,0,0.2529503024,15.3687541412,7.6081637553
H,0,-0.1419827262,14.7107399289,9.2878629074
H,0,-1.9269803956,13.7845660859,7.4241281233
H,0,-4.1394283271,12.9117455332,8.1278293091
H,0,-4.3100207452,10.6667593618,9.1933429128
H,0,-2.2649344467,9.2768603585,9.4662391268
H,0,-0.0832335079,10.1120083031,8.6802750233
H,0,5.1272178244,13.0139143943,13.3039419518
H,0,4.2246908715,11.5976822064,13.9091773561
H,0,3.8302092646,13.2356210753,14.5197805215
H,0,-1.4479184791,11.5015780894,11.9253443074
H,0,-0.4767260303,11.7560560945,13.4003399156
H,0,-0.6329114977,10.1116180009,12.7081368645

H,0,-0.2481270931,12.745884497,5.5370524816

5. X-Ray crystal data

Figure S1: X-Ray crystal structure of **6** (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC 1879512):

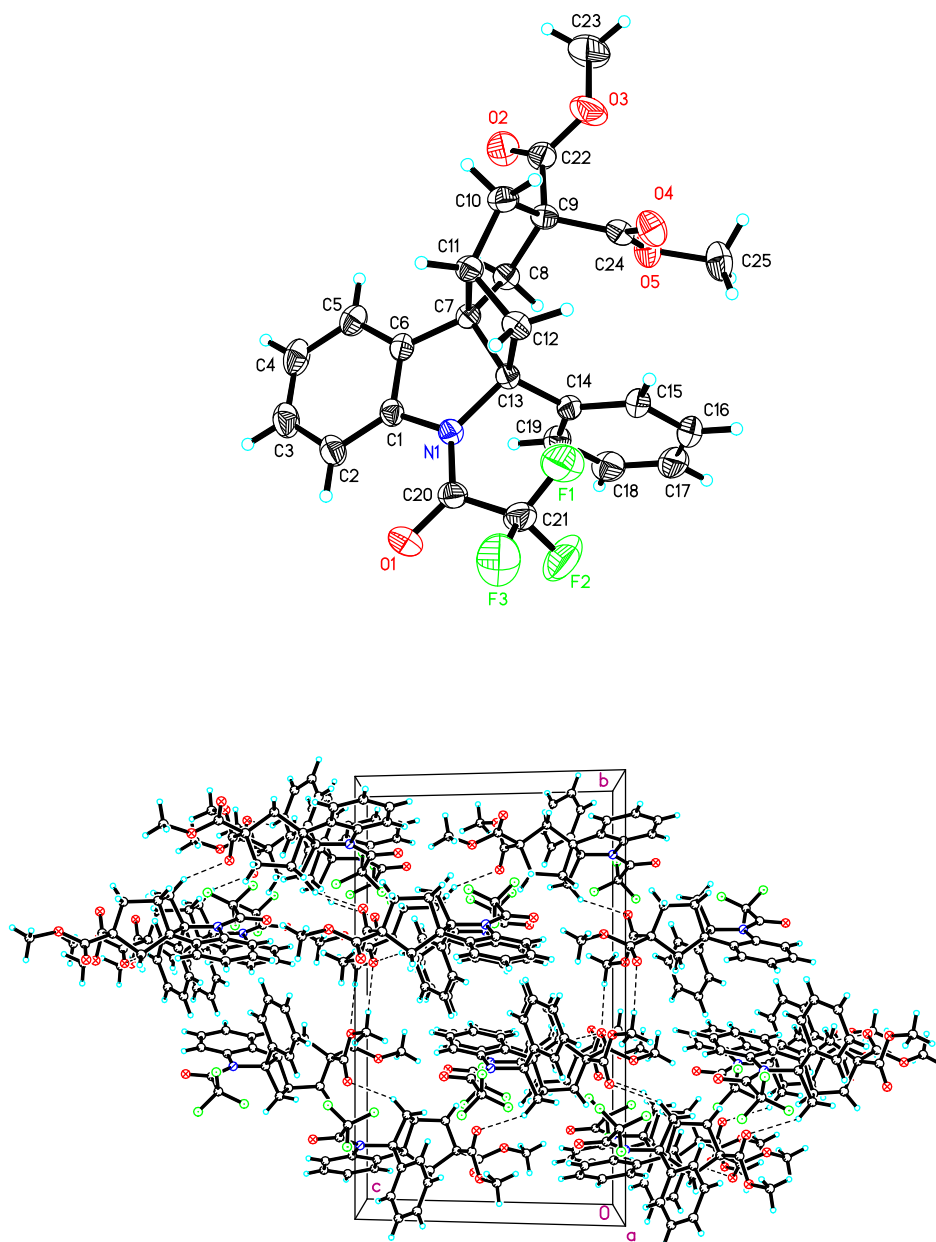


Table 1. Crystal data and structure refinement for mo_d8v18678_0m.

Identification code	mo_d8v18678_0m
Empirical formula	C ₂₅ H ₂₂ F ₃ N O ₅

Formula weight	473.43	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.5048(3) Å	$\alpha = 90^\circ$.
	b = 19.9335(6) Å	$\beta = 103.2580(10)^\circ$.
	c = 12.2973(4) Å	$\gamma = 90^\circ$.
Volume	2267.80(12) Å ³	
Z	4	
Density (calculated)	1.387 Mg/m ³	
Absorption coefficient	0.113 mm ⁻¹	
F(000)	984	
Crystal size	0.200 x 0.170 x 0.120 mm ³	
Theta range for data collection	3.004 to 25.998°.	
Index ranges	-10 ≤ h ≤ 11, -24 ≤ k ≤ 24, -15 ≤ l ≤ 13	
Reflections collected	12493	
Independent reflections	4408 [R(int) = 0.0279]	
Completeness to theta = 25.242°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6560	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4408 / 0 / 310	
Goodness-of-fit on F ²	1.060	
Final R indices [I > 2sigma(I)]	R1 = 0.0547, wR2 = 0.1332	
R indices (all data)	R1 = 0.0734, wR2 = 0.1489	
Extinction coefficient	0.015(4)	
Largest diff. peak and hole	0.518 and -0.315 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v18678_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	-120(2)	7423(1)	5731(2)	96(1)
F(2)	-1382(2)	6680(1)	4773(2)	121(1)
F(3)	-1002(2)	7592(1)	4026(2)	126(1)
O(1)	660(2)	6766(1)	3343(1)	73(1)
O(2)	7100(2)	5824(1)	9434(2)	83(1)
O(3)	6235(2)	6455(1)	10623(2)	90(1)
O(4)	2996(2)	6949(1)	9551(1)	65(1)
O(5)	3295(2)	5838(1)	9676(2)	64(1)
N(1)	2056(2)	6599(1)	5089(1)	41(1)
C(1)	3257(2)	6319(1)	4728(2)	43(1)
C(2)	3381(3)	6176(1)	3650(2)	56(1)
C(3)	4675(3)	5909(1)	3513(2)	68(1)
C(4)	5797(3)	5790(1)	4407(3)	70(1)
C(5)	5670(3)	5933(1)	5490(2)	60(1)
C(6)	4386(2)	6195(1)	5647(2)	45(1)
C(7)	3993(2)	6405(1)	6707(2)	40(1)
C(8)	4519(2)	5960(1)	7731(2)	46(1)
C(9)	4846(2)	6418(1)	8774(2)	47(1)
C(10)	5194(2)	7110(1)	8322(2)	53(1)
C(11)	4345(2)	7144(1)	7112(2)	46(1)
C(12)	2720(2)	7298(1)	6881(2)	45(1)
C(13)	2339(2)	6598(1)	6348(2)	38(1)
C(14)	1277(2)	6138(1)	6717(2)	42(1)
C(15)	448(2)	6333(1)	7451(2)	58(1)
C(16)	-502(3)	5886(2)	7768(2)	78(1)
C(17)	-626(3)	5248(2)	7367(3)	82(1)
C(18)	192(3)	5040(1)	6642(2)	71(1)
C(19)	1133(3)	5485(1)	6313(2)	54(1)
C(20)	861(2)	6816(1)	4352(2)	49(1)
C(21)	-394(3)	7138(1)	4752(2)	60(1)
C(22)	6184(3)	6182(1)	9628(2)	59(1)
C(23)	7493(4)	6297(3)	11506(3)	122(2)

C(24)	3604(2)	6451(1)	9365(2)	49(1)
C(25)	2201(4)	5794(2)	10320(2)	80(1)

Table 3. Bond lengths [Å] and angles [°] for mo_d8v18678_0m.

F(1)-C(21)	1.301(3)
F(2)-C(21)	1.314(3)
F(3)-C(21)	1.308(3)
O(1)-C(20)	1.216(3)
O(2)-C(22)	1.191(3)
O(3)-C(22)	1.330(3)
O(3)-C(23)	1.453(3)
O(4)-C(24)	1.196(3)
O(5)-C(24)	1.332(3)
O(5)-C(25)	1.447(3)
N(1)-C(20)	1.351(3)
N(1)-C(1)	1.430(3)
N(1)-C(13)	1.511(2)
C(1)-C(2)	1.386(3)
C(1)-C(6)	1.390(3)
C(2)-C(3)	1.385(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.366(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.394(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.381(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.495(3)
C(7)-C(8)	1.528(3)
C(7)-C(11)	1.566(3)
C(7)-C(13)	1.580(3)
C(8)-C(9)	1.548(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(24)	1.523(3)
C(9)-C(22)	1.527(3)
C(9)-C(10)	1.550(3)
C(10)-C(11)	1.523(3)
C(10)-H(10A)	0.9700

C(10)-H(10B)	0.9700
C(11)-C(12)	1.536(3)
C(11)-H(11)	0.9800
C(12)-C(13)	1.548(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.508(3)
C(14)-C(15)	1.383(3)
C(14)-C(19)	1.389(3)
C(15)-C(16)	1.386(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.360(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.374(4)
C(17)-H(17)	0.9300
C(18)-C(19)	1.384(3)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-C(21)	1.532(3)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(22)-O(3)-C(23)	116.7(3)
C(24)-O(5)-C(25)	116.5(2)
C(20)-N(1)-C(1)	121.75(17)
C(20)-N(1)-C(13)	127.74(17)
C(1)-N(1)-C(13)	110.51(15)
C(2)-C(1)-C(6)	121.5(2)
C(2)-C(1)-N(1)	128.7(2)
C(6)-C(1)-N(1)	109.83(17)
C(3)-C(2)-C(1)	117.8(2)
C(3)-C(2)-H(2)	121.1
C(1)-C(2)-H(2)	121.1

C(4)-C(3)-C(2)	121.3(2)
C(4)-C(3)-H(3)	119.3
C(2)-C(3)-H(3)	119.3
C(3)-C(4)-C(5)	120.7(2)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(6)-C(5)-C(4)	118.9(2)
C(6)-C(5)-H(5)	120.5
C(4)-C(5)-H(5)	120.5
C(5)-C(6)-C(1)	119.7(2)
C(5)-C(6)-C(7)	129.3(2)
C(1)-C(6)-C(7)	111.01(17)
C(6)-C(7)-C(8)	117.07(17)
C(6)-C(7)-C(11)	117.59(17)
C(8)-C(7)-C(11)	106.16(16)
C(6)-C(7)-C(13)	104.87(16)
C(8)-C(7)-C(13)	119.19(16)
C(11)-C(7)-C(13)	89.25(15)
C(7)-C(8)-C(9)	107.84(17)
C(7)-C(8)-H(8A)	110.1
C(9)-C(8)-H(8A)	110.1
C(7)-C(8)-H(8B)	110.1
C(9)-C(8)-H(8B)	110.1
H(8A)-C(8)-H(8B)	108.5
C(24)-C(9)-C(22)	107.44(18)
C(24)-C(9)-C(8)	113.03(17)
C(22)-C(9)-C(8)	111.41(19)
C(24)-C(9)-C(10)	112.70(18)
C(22)-C(9)-C(10)	107.99(18)
C(8)-C(9)-C(10)	104.22(17)
C(11)-C(10)-C(9)	106.38(17)
C(11)-C(10)-H(10A)	110.5
C(9)-C(10)-H(10A)	110.5
C(11)-C(10)-H(10B)	110.5
C(9)-C(10)-H(10B)	110.5
H(10A)-C(10)-H(10B)	108.6
C(10)-C(11)-C(12)	118.30(19)

C(10)-C(11)-C(7)	107.16(16)
C(12)-C(11)-C(7)	89.76(15)
C(10)-C(11)-H(11)	113.1
C(12)-C(11)-H(11)	113.1
C(7)-C(11)-H(11)	113.1
C(11)-C(12)-C(13)	91.52(15)
C(11)-C(12)-H(12A)	113.4
C(13)-C(12)-H(12A)	113.4
C(11)-C(12)-H(12B)	113.4
C(13)-C(12)-H(12B)	113.4
H(12A)-C(12)-H(12B)	110.7
C(14)-C(13)-N(1)	109.60(15)
C(14)-C(13)-C(12)	121.90(17)
N(1)-C(13)-C(12)	113.67(16)
C(14)-C(13)-C(7)	117.42(16)
N(1)-C(13)-C(7)	102.59(14)
C(12)-C(13)-C(7)	88.83(14)
C(15)-C(14)-C(19)	118.2(2)
C(15)-C(14)-C(13)	123.11(19)
C(19)-C(14)-C(13)	118.68(18)
C(14)-C(15)-C(16)	120.6(3)
C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7
C(17)-C(16)-C(15)	120.5(3)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(16)-C(17)-C(18)	120.1(2)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	119.8(3)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(18)-C(19)-C(14)	120.9(2)
C(18)-C(19)-H(19)	119.6
C(14)-C(19)-H(19)	119.6
O(1)-C(20)-N(1)	124.7(2)
O(1)-C(20)-C(21)	114.2(2)

N(1)-C(20)-C(21)	121.09(19)
F(1)-C(21)-F(3)	107.1(2)
F(1)-C(21)-F(2)	106.1(2)
F(3)-C(21)-F(2)	106.7(2)
F(1)-C(21)-C(20)	118.28(19)
F(3)-C(21)-C(20)	108.9(2)
F(2)-C(21)-C(20)	109.1(2)
O(2)-C(22)-O(3)	123.8(2)
O(2)-C(22)-C(9)	125.3(2)
O(3)-C(22)-C(9)	110.8(2)
O(3)-C(23)-H(23A)	109.5
O(3)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
O(3)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
O(4)-C(24)-O(5)	123.9(2)
O(4)-C(24)-C(9)	126.0(2)
O(5)-C(24)-C(9)	110.10(19)
O(5)-C(25)-H(25A)	109.5
O(5)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(5)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v18678_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	73(1)	121(2)	87(1)	-21(1)	4(1)	43(1)
F(2)	71(1)	140(2)	164(2)	-21(2)	52(1)	-37(1)
F(3)	102(1)	160(2)	122(2)	74(2)	35(1)	71(1)
O(1)	71(1)	100(1)	43(1)	7(1)	0(1)	-2(1)
O(2)	61(1)	113(2)	72(1)	18(1)	10(1)	28(1)
O(3)	76(1)	132(2)	50(1)	-8(1)	-13(1)	19(1)
O(4)	84(1)	57(1)	58(1)	-4(1)	25(1)	12(1)
O(5)	79(1)	55(1)	67(1)	7(1)	34(1)	4(1)
N(1)	42(1)	43(1)	37(1)	1(1)	9(1)	-2(1)
C(1)	49(1)	40(1)	44(1)	-1(1)	17(1)	-6(1)
C(2)	70(2)	56(1)	47(1)	-5(1)	21(1)	-8(1)
C(3)	83(2)	70(2)	62(2)	-14(1)	38(2)	-7(1)
C(4)	68(2)	67(2)	90(2)	-13(1)	47(2)	2(1)
C(5)	48(1)	62(1)	73(2)	-2(1)	22(1)	5(1)
C(6)	45(1)	43(1)	49(1)	-2(1)	18(1)	-2(1)
C(7)	38(1)	41(1)	42(1)	0(1)	9(1)	1(1)
C(8)	46(1)	44(1)	46(1)	2(1)	9(1)	5(1)
C(9)	45(1)	49(1)	43(1)	2(1)	4(1)	2(1)
C(10)	51(1)	52(1)	52(1)	-1(1)	3(1)	-8(1)
C(11)	50(1)	42(1)	44(1)	2(1)	8(1)	-7(1)
C(12)	53(1)	39(1)	43(1)	-1(1)	9(1)	3(1)
C(13)	40(1)	39(1)	36(1)	1(1)	10(1)	3(1)
C(14)	37(1)	49(1)	40(1)	3(1)	8(1)	1(1)
C(15)	48(1)	78(2)	53(1)	-9(1)	20(1)	-7(1)
C(16)	57(2)	122(3)	61(2)	-6(2)	26(1)	-24(2)
C(17)	68(2)	108(2)	70(2)	14(2)	18(1)	-38(2)
C(18)	78(2)	62(2)	71(2)	7(1)	10(2)	-23(1)
C(19)	57(1)	49(1)	58(1)	2(1)	16(1)	-4(1)
C(20)	48(1)	50(1)	45(1)	7(1)	4(1)	-8(1)
C(21)	46(1)	72(2)	57(1)	14(1)	3(1)	1(1)
C(22)	50(1)	73(2)	51(1)	11(1)	6(1)	2(1)
C(23)	87(2)	199(5)	60(2)	13(2)	-24(2)	12(3)

C(24)	55(1)	51(1)	37(1)	-1(1)	4(1)	2(1)
C(25)	99(2)	80(2)	73(2)	6(2)	47(2)	-3(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for mo_d8v18678_0m.

	x	y	z	U(eq)
H(2)	2620	6257	3039	68
H(3)	4782	5810	2798	82
H(4)	6655	5611	4293	85
H(5)	6437	5853	6098	71
H(8A)	5385	5720	7668	55
H(8B)	3782	5634	7789	55
H(10A)	4904	7469	8755	63
H(10B)	6222	7150	8364	63
H(11)	4845	7398	6631	55
H(12A)	2427	7665	6361	54
H(12B)	2371	7367	7555	54
H(15)	528	6767	7734	70
H(16)	-1058	6024	8258	94
H(17)	-1265	4951	7584	98
H(18)	114	4602	6374	86
H(19)	1676	5345	5814	65
H(23A)	8352	6440	11287	184
H(23B)	7534	5822	11636	184
H(23C)	7423	6526	12179	184
H(25A)	1347	6027	9936	120
H(25B)	2558	5994	11041	120
H(25C)	1971	5331	10410	120

Table 6. Torsion angles [°] for mo_d8v18678_0m.

C(20)-N(1)-C(1)-C(2)	-5.2(3)
C(13)-N(1)-C(1)-C(2)	173.9(2)
C(20)-N(1)-C(1)-C(6)	174.56(18)
C(13)-N(1)-C(1)-C(6)	-6.3(2)
C(6)-C(1)-C(2)-C(3)	-0.5(3)
N(1)-C(1)-C(2)-C(3)	179.3(2)
C(1)-C(2)-C(3)-C(4)	-0.1(4)
C(2)-C(3)-C(4)-C(5)	0.1(4)
C(3)-C(4)-C(5)-C(6)	0.3(4)
C(4)-C(5)-C(6)-C(1)	-0.8(3)
C(4)-C(5)-C(6)-C(7)	-178.2(2)
C(2)-C(1)-C(6)-C(5)	0.9(3)
N(1)-C(1)-C(6)-C(5)	-178.91(19)
C(2)-C(1)-C(6)-C(7)	178.75(19)
N(1)-C(1)-C(6)-C(7)	-1.0(2)
C(5)-C(6)-C(7)-C(8)	-40.3(3)
C(1)-C(6)-C(7)-C(8)	142.07(18)
C(5)-C(6)-C(7)-C(11)	88.0(3)
C(1)-C(6)-C(7)-C(11)	-89.6(2)
C(5)-C(6)-C(7)-C(13)	-174.9(2)
C(1)-C(6)-C(7)-C(13)	7.5(2)
C(6)-C(7)-C(8)-C(9)	146.44(18)
C(11)-C(7)-C(8)-C(9)	12.8(2)
C(13)-C(7)-C(8)-C(9)	-85.6(2)
C(7)-C(8)-C(9)-C(24)	96.9(2)
C(7)-C(8)-C(9)-C(22)	-142.00(19)
C(7)-C(8)-C(9)-C(10)	-25.8(2)
C(24)-C(9)-C(10)-C(11)	-93.9(2)
C(22)-C(9)-C(10)-C(11)	147.54(19)
C(8)-C(9)-C(10)-C(11)	29.0(2)
C(9)-C(10)-C(11)-C(12)	77.8(2)
C(9)-C(10)-C(11)-C(7)	-21.5(2)
C(6)-C(7)-C(11)-C(10)	-127.90(19)
C(8)-C(7)-C(11)-C(10)	5.4(2)
C(13)-C(7)-C(11)-C(10)	125.68(17)

C(6)-C(7)-C(11)-C(12)	112.44(19)
C(8)-C(7)-C(11)-C(12)	-114.24(17)
C(13)-C(7)-C(11)-C(12)	6.02(15)
C(10)-C(11)-C(12)-C(13)	-115.59(19)
C(7)-C(11)-C(12)-C(13)	-6.15(15)
C(20)-N(1)-C(13)-C(14)	63.9(2)
C(1)-N(1)-C(13)-C(14)	-115.11(17)
C(20)-N(1)-C(13)-C(12)	-76.3(2)
C(1)-N(1)-C(13)-C(12)	104.67(18)
C(20)-N(1)-C(13)-C(7)	-170.60(18)
C(1)-N(1)-C(13)-C(7)	10.37(19)
C(11)-C(12)-C(13)-C(14)	128.09(18)
C(11)-C(12)-C(13)-N(1)	-97.14(17)
C(11)-C(12)-C(13)-C(7)	6.09(15)
C(6)-C(7)-C(13)-C(14)	109.82(18)
C(8)-C(7)-C(13)-C(14)	-23.6(3)
C(11)-C(7)-C(13)-C(14)	-131.77(17)
C(6)-C(7)-C(13)-N(1)	-10.38(19)
C(8)-C(7)-C(13)-N(1)	-143.82(17)
C(11)-C(7)-C(13)-N(1)	108.03(15)
C(6)-C(7)-C(13)-C(12)	-124.38(16)
C(8)-C(7)-C(13)-C(12)	102.17(19)
C(11)-C(7)-C(13)-C(12)	-5.98(15)
N(1)-C(13)-C(14)-C(15)	-128.5(2)
C(12)-C(13)-C(14)-C(15)	7.8(3)
C(7)-C(13)-C(14)-C(15)	115.0(2)
N(1)-C(13)-C(14)-C(19)	52.2(2)
C(12)-C(13)-C(14)-C(19)	-171.41(19)
C(7)-C(13)-C(14)-C(19)	-64.2(2)
C(19)-C(14)-C(15)-C(16)	-0.2(3)
C(13)-C(14)-C(15)-C(16)	-179.4(2)
C(14)-C(15)-C(16)-C(17)	0.4(4)
C(15)-C(16)-C(17)-C(18)	0.0(5)
C(16)-C(17)-C(18)-C(19)	-0.6(4)
C(17)-C(18)-C(19)-C(14)	0.9(4)
C(15)-C(14)-C(19)-C(18)	-0.4(3)
C(13)-C(14)-C(19)-C(18)	178.8(2)

C(1)-N(1)-C(20)-O(1)	3.8(3)
C(13)-N(1)-C(20)-O(1)	-175.2(2)
C(1)-N(1)-C(20)-C(21)	-177.84(18)
C(13)-N(1)-C(20)-C(21)	3.2(3)
O(1)-C(20)-C(21)-F(1)	-156.6(2)
N(1)-C(20)-C(21)-F(1)	24.9(3)
O(1)-C(20)-C(21)-F(3)	-34.0(3)
N(1)-C(20)-C(21)-F(3)	147.4(2)
O(1)-C(20)-C(21)-F(2)	82.1(3)
N(1)-C(20)-C(21)-F(2)	-96.4(3)
C(23)-O(3)-C(22)-O(2)	-0.2(4)
C(23)-O(3)-C(22)-C(9)	-177.2(3)
C(24)-C(9)-C(22)-O(2)	144.1(3)
C(8)-C(9)-C(22)-O(2)	19.8(3)
C(10)-C(9)-C(22)-O(2)	-94.1(3)
C(24)-C(9)-C(22)-O(3)	-38.9(3)
C(8)-C(9)-C(22)-O(3)	-163.2(2)
C(10)-C(9)-C(22)-O(3)	82.9(3)
C(25)-O(5)-C(24)-O(4)	-2.9(3)
C(25)-O(5)-C(24)-C(9)	175.8(2)
C(22)-C(9)-C(24)-O(4)	113.8(2)
C(8)-C(9)-C(24)-O(4)	-122.9(2)
C(10)-C(9)-C(24)-O(4)	-5.0(3)
C(22)-C(9)-C(24)-O(5)	-64.9(2)
C(8)-C(9)-C(24)-O(5)	58.4(2)
C(10)-C(9)-C(24)-O(5)	176.27(17)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_d8v18678_0m [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
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Figure S2: X-Ray crystal structure of **8** (The crystal was obtained by slow evaporation of the solution of DCM and PE) (CCDC 1888962):

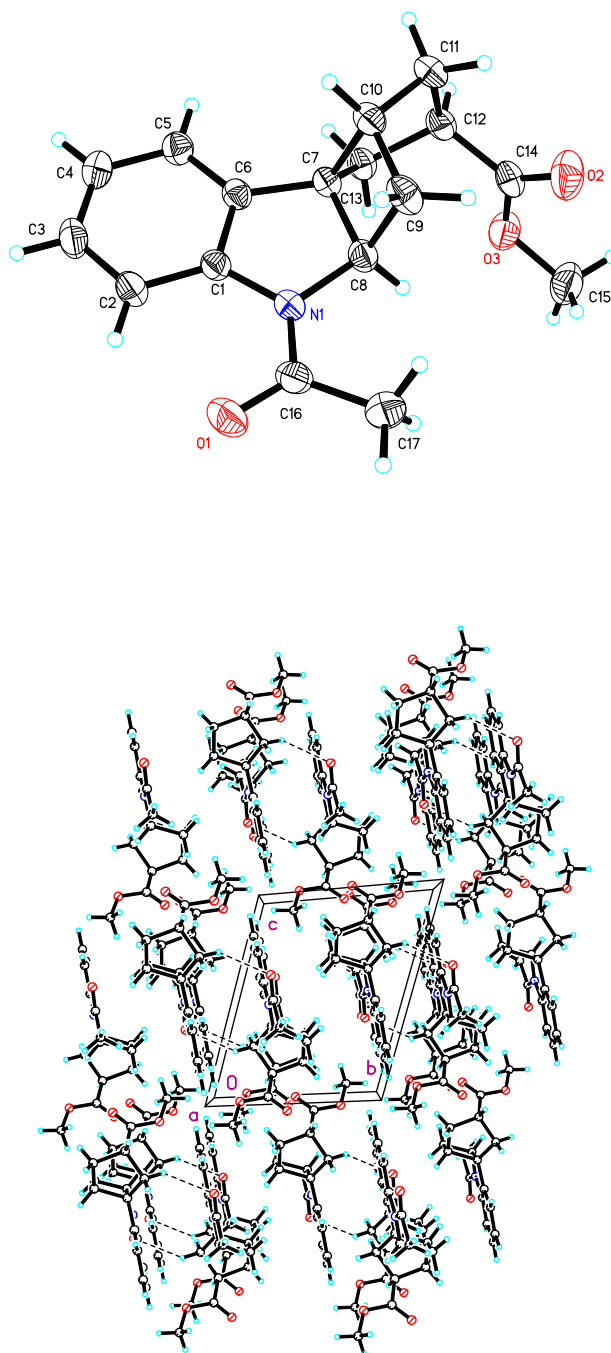


Table 1. Crystal data and structure refinement for mo_d8v19014_0m.

Identification code	mo_d8v19014_0m
Empirical formula	C ₁₇ H ₁₉ N O ₃

Formula weight	285.33	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.9322(4) Å	$\alpha = 65.743(2)^\circ$.
	b = 9.3914(5) Å	$\beta = 71.707(2)^\circ$.
	c = 10.8992(6) Å	$\gamma = 63.078(2)^\circ$.
Volume	733.98(7) Å ³	
Z	2	
Density (calculated)	1.291 Mg/m ³	
Absorption coefficient	0.088 mm ⁻¹	
F(000)	304	
Crystal size	0.160 x 0.130 x 0.070 mm ³	
Theta range for data collection	2.565 to 25.999°.	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13	
Reflections collected	7535	
Independent reflections	2860 [R(int) = 0.0262]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6612	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2860 / 0 / 193	
Goodness-of-fit on F ²	1.047	
Final R indices [I > 2sigma(I)]	R1 = 0.0475, wR2 = 0.1123	
R indices (all data)	R1 = 0.0630, wR2 = 0.1253	
Extinction coefficient	0.082(15)	
Largest diff. peak and hole	0.179 and -0.159 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v19014_0m. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	5697(2)	2038(2)	6138(1)	75(1)
O(2)	2893(2)	4867(2)	-199(2)	88(1)
O(3)	3754(2)	2102(2)	341(1)	70(1)
N(1)	3994(2)	2324(2)	4817(1)	46(1)
C(1)	2843(2)	1653(2)	5852(2)	44(1)
C(2)	2877(2)	911(2)	7243(2)	56(1)
C(3)	1568(3)	377(2)	8055(2)	63(1)
C(4)	264(3)	568(2)	7515(2)	60(1)
C(5)	235(2)	1304(2)	6124(2)	51(1)
C(6)	1525(2)	1847(2)	5292(2)	43(1)
C(7)	1751(2)	2722(2)	3787(2)	42(1)
C(8)	3421(2)	3011(2)	3490(2)	46(1)
C(9)	2446(2)	4929(2)	2998(2)	58(1)
C(10)	776(2)	4684(2)	3240(2)	49(1)
C(11)	92(2)	5029(2)	1985(2)	54(1)
C(12)	1122(2)	3455(2)	1530(2)	50(1)
C(13)	1516(2)	2000(2)	2870(2)	47(1)
C(14)	2665(2)	3591(2)	481(2)	55(1)
C(15)	5260(3)	2095(3)	-664(2)	86(1)
C(16)	5330(2)	2506(2)	5006(2)	53(1)
C(17)	6344(3)	3297(3)	3756(2)	72(1)

Table 3. Bond lengths [Å] and angles [°] for mo_d8v19014_0m.

O(1)-C(16)	1.225(2)
O(2)-C(14)	1.193(2)
O(3)-C(14)	1.332(2)
O(3)-C(15)	1.444(2)
N(1)-C(16)	1.364(2)
N(1)-C(1)	1.415(2)
N(1)-C(8)	1.4732(19)
C(1)-C(2)	1.388(2)
C(1)-C(6)	1.399(2)
C(2)-C(3)	1.385(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.375(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.387(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.381(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.497(2)
C(7)-C(13)	1.523(2)
C(7)-C(8)	1.548(2)
C(7)-C(10)	1.574(2)
C(8)-C(9)	1.540(2)
C(8)-H(8)	0.9800
C(9)-C(10)	1.537(2)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.527(2)
C(10)-H(10)	0.9800
C(11)-C(12)	1.537(2)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(14)	1.508(3)
C(12)-C(13)	1.540(2)
C(12)-H(12)	0.9800
C(13)-H(13A)	0.9700

C(13)-H(13B)	0.9700
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(17)	1.494(3)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600

C(14)-O(3)-C(15)	116.58(16)
C(16)-N(1)-C(1)	126.27(14)
C(16)-N(1)-C(8)	123.55(14)
C(1)-N(1)-C(8)	109.78(13)
C(2)-C(1)-C(6)	120.72(16)
C(2)-C(1)-N(1)	129.10(15)
C(6)-C(1)-N(1)	110.18(13)
C(3)-C(2)-C(1)	118.07(17)
C(3)-C(2)-H(2)	121.0
C(1)-C(2)-H(2)	121.0
C(4)-C(3)-C(2)	121.61(17)
C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(3)-C(4)-C(5)	120.26(18)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	119.27(17)
C(6)-C(5)-H(5)	120.4
C(4)-C(5)-H(5)	120.4
C(5)-C(6)-C(1)	120.07(15)
C(5)-C(6)-C(7)	129.50(15)
C(1)-C(6)-C(7)	110.40(14)
C(6)-C(7)-C(13)	117.80(13)
C(6)-C(7)-C(8)	103.82(12)
C(13)-C(7)-C(8)	118.53(13)
C(6)-C(7)-C(10)	118.57(13)
C(13)-C(7)-C(10)	105.94(12)
C(8)-C(7)-C(10)	89.29(12)

N(1)-C(8)-C(9)	115.59(14)
N(1)-C(8)-C(7)	105.81(12)
C(9)-C(8)-C(7)	90.26(12)
N(1)-C(8)-H(8)	114.2
C(9)-C(8)-H(8)	114.2
C(7)-C(8)-H(8)	114.2
C(10)-C(9)-C(8)	91.00(12)
C(10)-C(9)-H(9A)	113.5
C(8)-C(9)-H(9A)	113.5
C(10)-C(9)-H(9B)	113.5
C(8)-C(9)-H(9B)	113.5
H(9A)-C(9)-H(9B)	110.8
C(11)-C(10)-C(9)	117.28(15)
C(11)-C(10)-C(7)	106.40(13)
C(9)-C(10)-C(7)	89.40(12)
C(11)-C(10)-H(10)	113.7
C(9)-C(10)-H(10)	113.7
C(7)-C(10)-H(10)	113.7
C(10)-C(11)-C(12)	105.98(13)
C(10)-C(11)-H(11A)	110.5
C(12)-C(11)-H(11A)	110.5
C(10)-C(11)-H(11B)	110.5
C(12)-C(11)-H(11B)	110.5
H(11A)-C(11)-H(11B)	108.7
C(14)-C(12)-C(11)	112.88(15)
C(14)-C(12)-C(13)	114.63(14)
C(11)-C(12)-C(13)	104.05(13)
C(14)-C(12)-H(12)	108.3
C(11)-C(12)-H(12)	108.3
C(13)-C(12)-H(12)	108.3
C(7)-C(13)-C(12)	105.72(13)
C(7)-C(13)-H(13A)	110.6
C(12)-C(13)-H(13A)	110.6
C(7)-C(13)-H(13B)	110.6
C(12)-C(13)-H(13B)	110.6
H(13A)-C(13)-H(13B)	108.7
O(2)-C(14)-O(3)	122.38(18)

O(2)-C(14)-C(12)	125.54(18)
O(3)-C(14)-C(12)	112.02(15)
O(3)-C(15)-H(15A)	109.5
O(3)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
O(3)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(1)-C(16)-N(1)	122.18(17)
O(1)-C(16)-C(17)	121.11(17)
N(1)-C(16)-C(17)	116.71(16)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v19014_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	74(1)	95(1)	62(1)	-9(1)	-32(1)	-37(1)
O(2)	113(1)	63(1)	70(1)	-10(1)	8(1)	-43(1)
O(3)	75(1)	60(1)	62(1)	-17(1)	6(1)	-27(1)
N(1)	44(1)	49(1)	40(1)	-8(1)	-13(1)	-16(1)
C(1)	44(1)	41(1)	41(1)	-11(1)	-9(1)	-11(1)
C(2)	60(1)	58(1)	44(1)	-10(1)	-17(1)	-18(1)
C(3)	76(1)	67(1)	37(1)	-7(1)	-9(1)	-29(1)
C(4)	65(1)	64(1)	47(1)	-14(1)	1(1)	-31(1)
C(5)	55(1)	51(1)	48(1)	-12(1)	-9(1)	-22(1)
C(6)	48(1)	38(1)	41(1)	-11(1)	-10(1)	-13(1)
C(7)	46(1)	39(1)	38(1)	-8(1)	-11(1)	-15(1)
C(8)	50(1)	49(1)	38(1)	-10(1)	-10(1)	-18(1)
C(9)	75(1)	46(1)	57(1)	-2(1)	-27(1)	-28(1)
C(10)	54(1)	42(1)	45(1)	-11(1)	-15(1)	-11(1)
C(11)	57(1)	50(1)	50(1)	-8(1)	-22(1)	-13(1)
C(12)	59(1)	54(1)	43(1)	-11(1)	-19(1)	-22(1)
C(13)	56(1)	47(1)	43(1)	-12(1)	-11(1)	-22(1)
C(14)	72(1)	54(1)	39(1)	-8(1)	-18(1)	-25(1)
C(15)	87(2)	84(2)	66(1)	-21(1)	13(1)	-33(1)
C(16)	48(1)	53(1)	56(1)	-13(1)	-17(1)	-14(1)
C(17)	58(1)	88(2)	71(1)	-12(1)	-14(1)	-37(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for mo_d8v19014_0m.

	x	y	z	U(eq)
H(2)	3754	775	7618	67
H(3)	1571	-122	8990	75
H(4)	-601	203	8084	72
H(5)	-644	1431	5757	62
H(8)	4281	2563	2785	55
H(9A)	2431	5499	3572	70
H(9B)	2817	5465	2050	70
H(10)	-97	5153	3930	58
H(11A)	242	6016	1267	65
H(11B)	-1108	5216	2210	65
H(12)	384	3301	1133	61
H(13A)	584	1604	3287	57
H(13B)	2543	1066	2703	57
H(15A)	4945	2691	-1557	129
H(15B)	6007	954	-609	129
H(15C)	5831	2635	-495	129
H(17A)	6842	2616	3167	108
H(17B)	7228	3384	4011	108
H(17C)	5615	4401	3288	108

Table 6. Torsion angles [°] for mo_d8v19014_0m.

C(16)-N(1)-C(1)-C(2)	-6.1(3)
C(8)-N(1)-C(1)-C(2)	-178.93(16)
C(16)-N(1)-C(1)-C(6)	173.02(15)
C(8)-N(1)-C(1)-C(6)	0.14(18)
C(6)-C(1)-C(2)-C(3)	-0.3(3)
N(1)-C(1)-C(2)-C(3)	178.69(16)
C(1)-C(2)-C(3)-C(4)	0.1(3)
C(2)-C(3)-C(4)-C(5)	0.2(3)
C(3)-C(4)-C(5)-C(6)	-0.2(3)
C(4)-C(5)-C(6)-C(1)	0.0(2)
C(4)-C(5)-C(6)-C(7)	-177.67(16)
C(2)-C(1)-C(6)-C(5)	0.3(2)
N(1)-C(1)-C(6)-C(5)	-178.87(14)
C(2)-C(1)-C(6)-C(7)	178.35(14)
N(1)-C(1)-C(6)-C(7)	-0.81(18)
C(5)-C(6)-C(7)-C(13)	-47.8(2)
C(1)-C(6)-C(7)-C(13)	134.39(15)
C(5)-C(6)-C(7)-C(8)	178.92(16)
C(1)-C(6)-C(7)-C(8)	1.10(16)
C(5)-C(6)-C(7)-C(10)	82.1(2)
C(1)-C(6)-C(7)-C(10)	-95.77(16)
C(16)-N(1)-C(8)-C(9)	-74.5(2)
C(1)-N(1)-C(8)-C(9)	98.64(16)
C(16)-N(1)-C(8)-C(7)	-172.57(14)
C(1)-N(1)-C(8)-C(7)	0.55(16)
C(6)-C(7)-C(8)-N(1)	-0.97(15)
C(13)-C(7)-C(8)-N(1)	-133.84(14)
C(10)-C(7)-C(8)-N(1)	118.34(13)
C(6)-C(7)-C(8)-C(9)	-117.72(13)
C(13)-C(7)-C(8)-C(9)	109.40(15)
C(10)-C(7)-C(8)-C(9)	1.58(12)
N(1)-C(8)-C(9)-C(10)	-109.33(15)
C(7)-C(8)-C(9)-C(10)	-1.62(13)
C(8)-C(9)-C(10)-C(11)	-106.60(15)
C(8)-C(9)-C(10)-C(7)	1.60(12)

C(6)-C(7)-C(10)-C(11)	-137.86(15)
C(13)-C(7)-C(10)-C(11)	-2.79(17)
C(8)-C(7)-C(10)-C(11)	116.76(14)
C(6)-C(7)-C(10)-C(9)	103.80(16)
C(13)-C(7)-C(10)-C(9)	-121.14(14)
C(8)-C(7)-C(10)-C(9)	-1.59(12)
C(9)-C(10)-C(11)-C(12)	79.63(18)
C(7)-C(10)-C(11)-C(12)	-18.38(18)
C(10)-C(11)-C(12)-C(14)	-92.46(17)
C(10)-C(11)-C(12)-C(13)	32.43(18)
C(6)-C(7)-C(13)-C(12)	158.33(14)
C(8)-C(7)-C(13)-C(12)	-75.23(17)
C(10)-C(7)-C(13)-C(12)	22.86(17)
C(14)-C(12)-C(13)-C(7)	89.49(17)
C(11)-C(12)-C(13)-C(7)	-34.27(17)
C(15)-O(3)-C(14)-O(2)	1.2(3)
C(15)-O(3)-C(14)-C(12)	178.57(17)
C(11)-C(12)-C(14)-O(2)	-18.0(3)
C(13)-C(12)-C(14)-O(2)	-136.9(2)
C(11)-C(12)-C(14)-O(3)	164.79(14)
C(13)-C(12)-C(14)-O(3)	45.9(2)
C(1)-N(1)-C(16)-O(1)	2.2(3)
C(8)-N(1)-C(16)-O(1)	174.15(16)
C(1)-N(1)-C(16)-C(17)	-178.23(16)
C(8)-N(1)-C(16)-C(17)	-6.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_d8v19014_0m [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(15)-H(15A)...O(1)#1	0.96	2.64	3.404(3)	136.7
C(2)-H(2)...O(1)	0.93	2.36	2.894(2)	116.5

Symmetry transformations used to generate equivalent atoms:

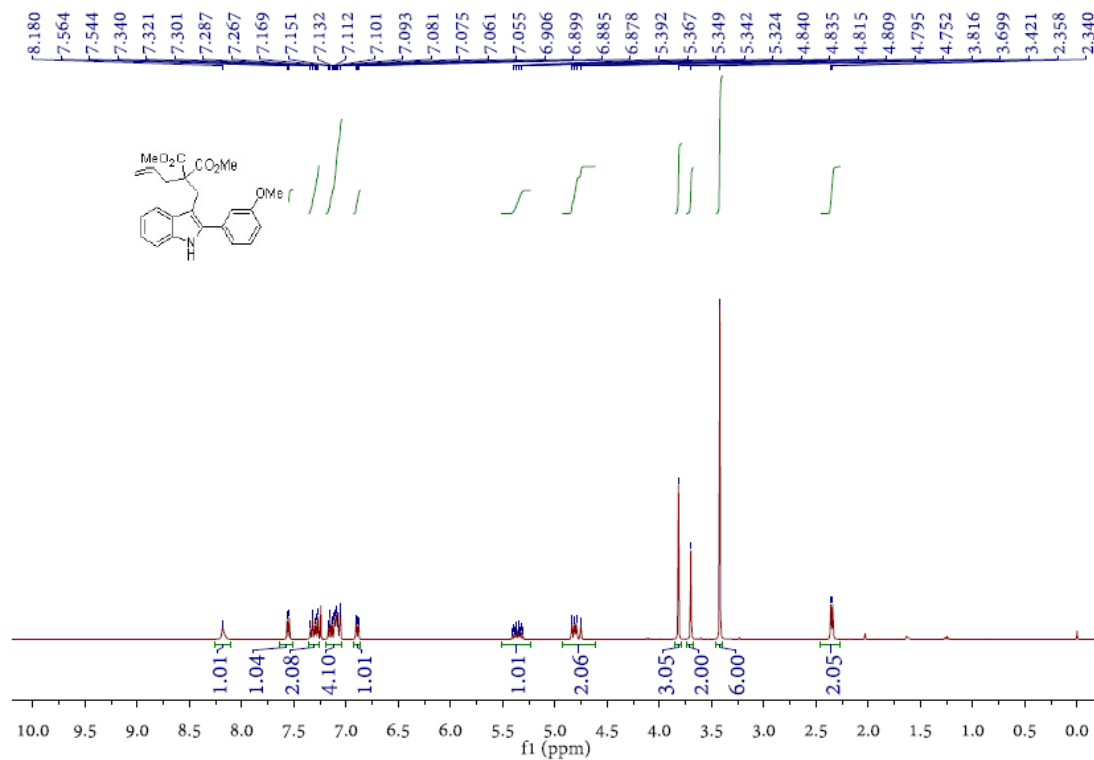
#1 x,y,z-1

6. References

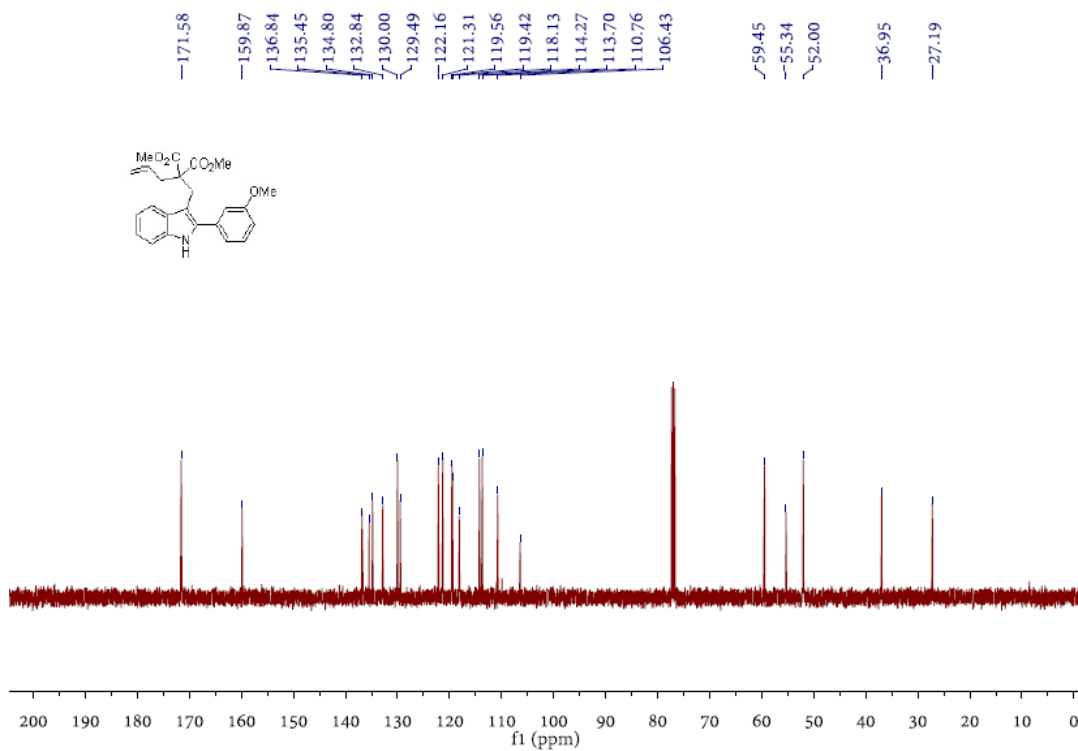
- [1] Zhu, M.; Zhou, K.; Zhang, X.; You, S.-L. *Org. Lett.* **2018**, *20*, 4379-4383.
- [2] Morimoto, N.; Nishina, Y. *Org. Lett.* **2016**, *18*, 2020-2023.
- [3] Kong A.-D.; Han X.-L.; Lu X.-Y. *Org. Lett.* **2006**, *8*, 1339-1342.
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- [5] Zhao, J.-N.; Kwon, O. *J. Am. Chem. Soc.* **2017**, *139*, 9807-9810.
- [6] *Handbook of Photochemistry*, 3rd ed, Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T., Ed.; CRC, Taylor & Francis Group, Boca Raton, FL, 2006.

7. Copies of NMR spectra

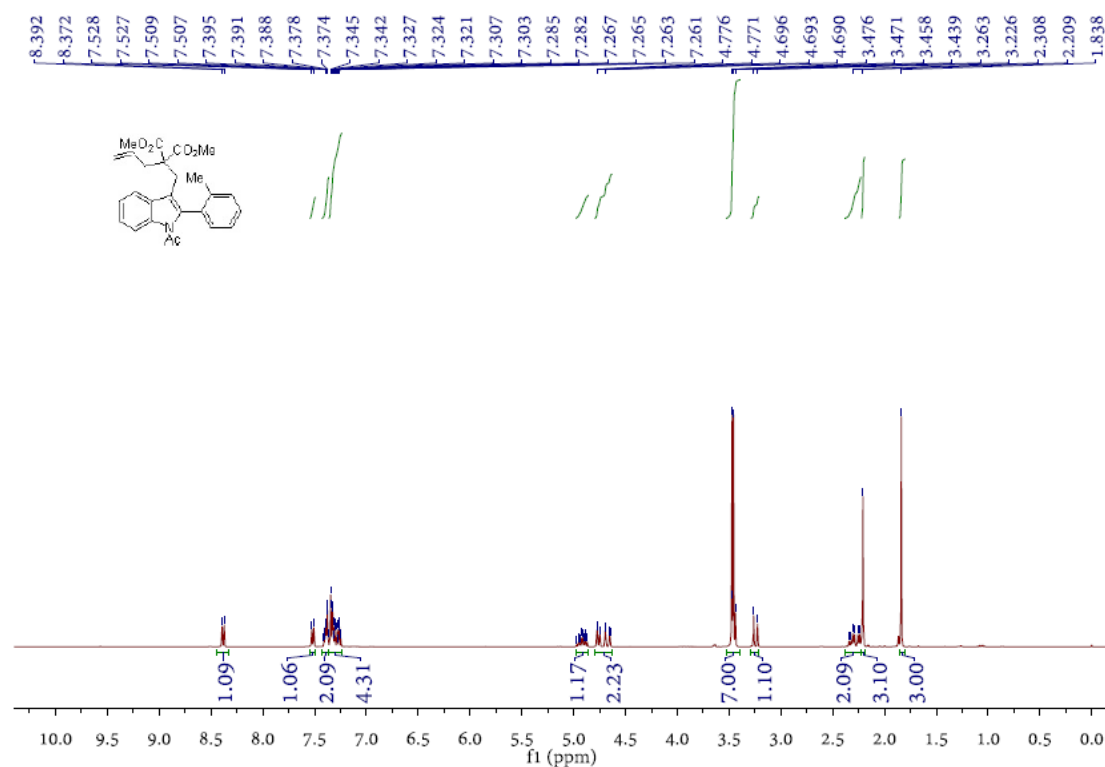
^1H NMR Spectrum of **1h**



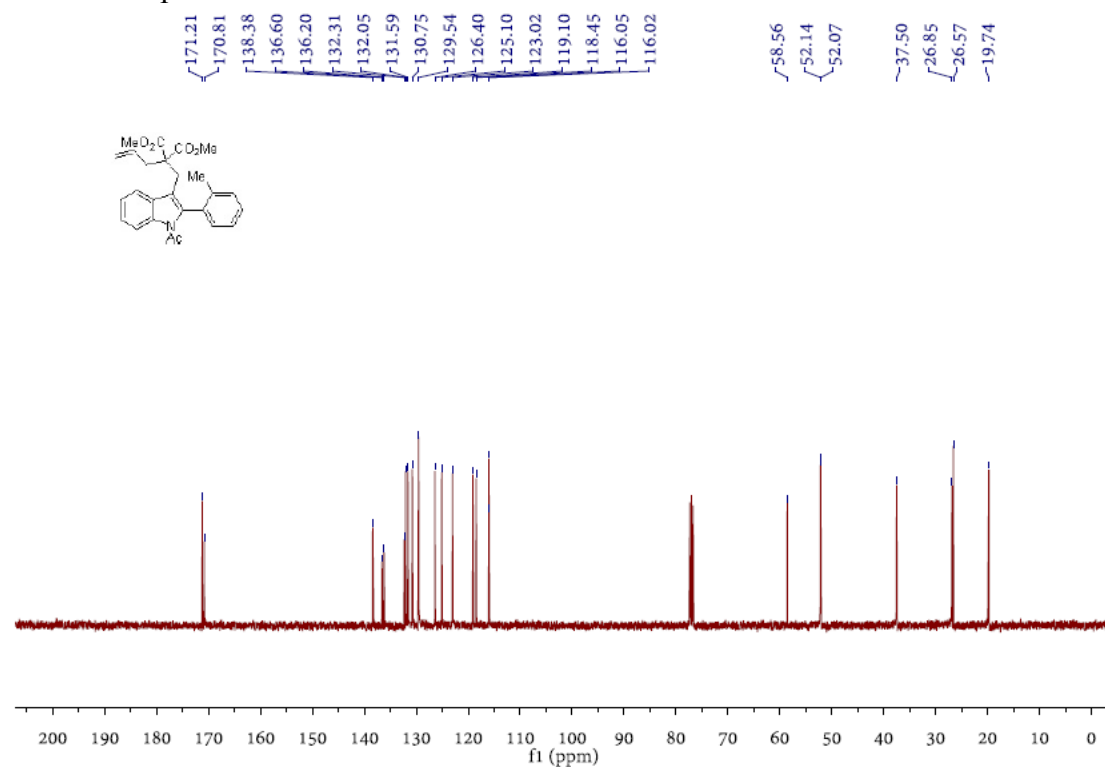
^{13}C NMR Spectrum of **1h**



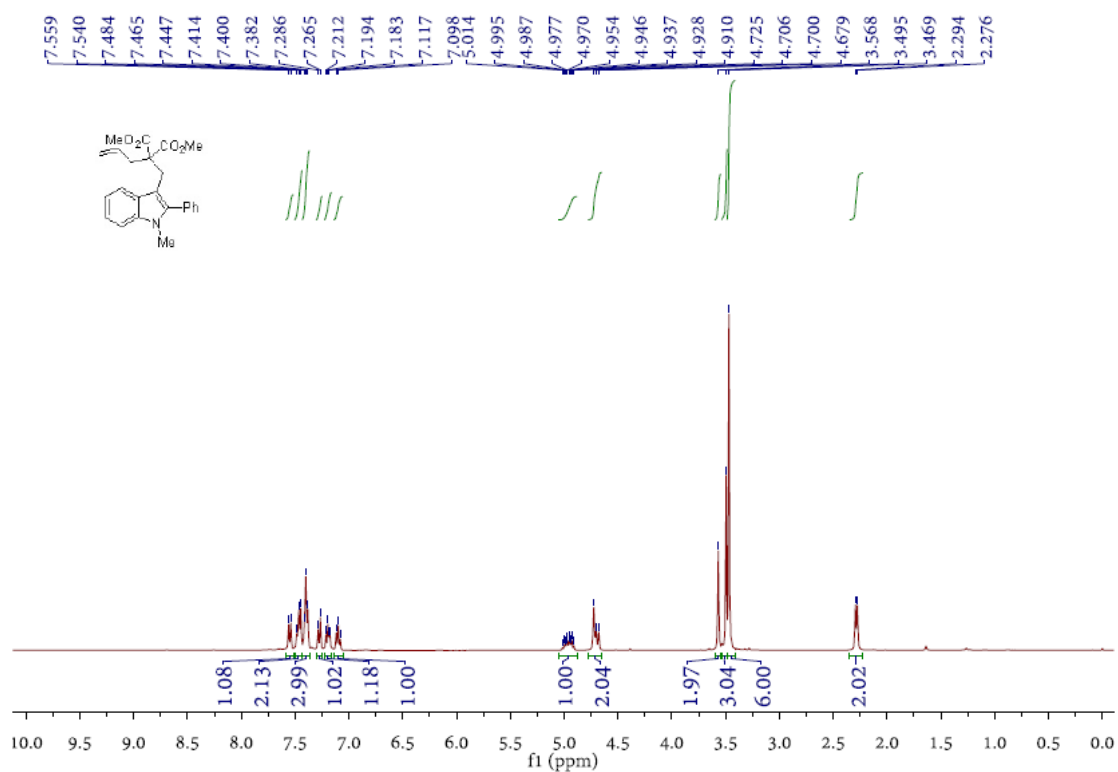
¹H NMR Spectrum of **1m**



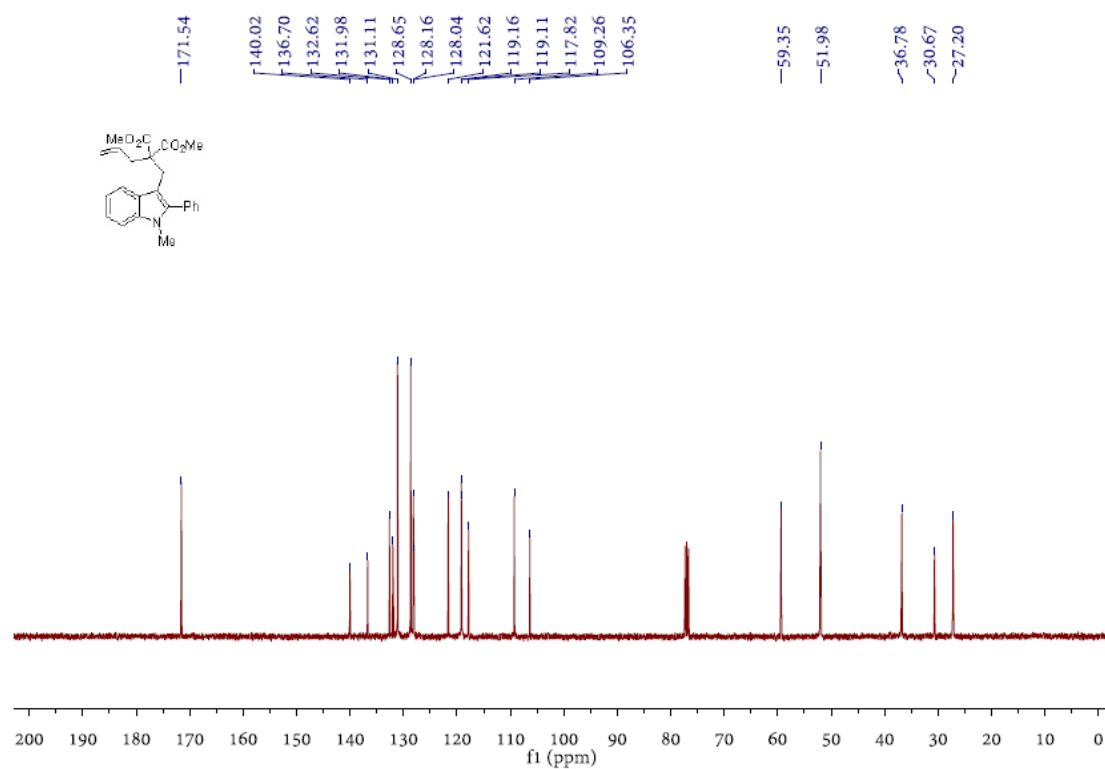
¹³C NMR Spectrum of **1m**



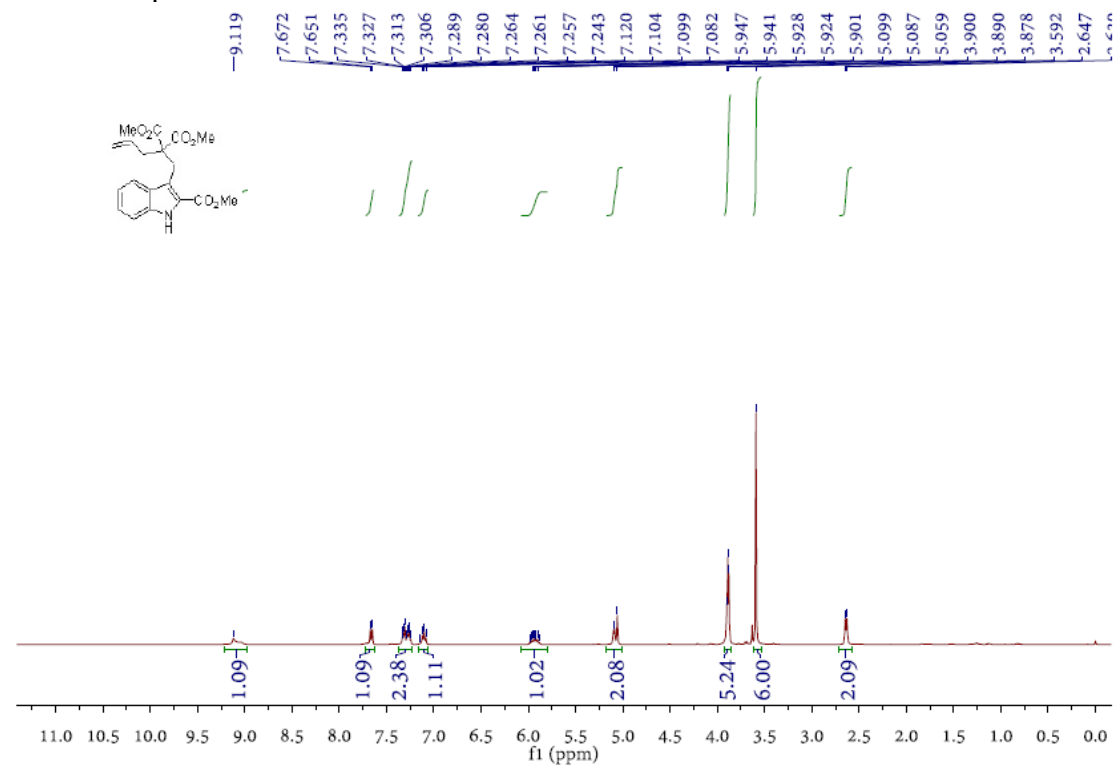
¹H NMR Spectrum of **1r**



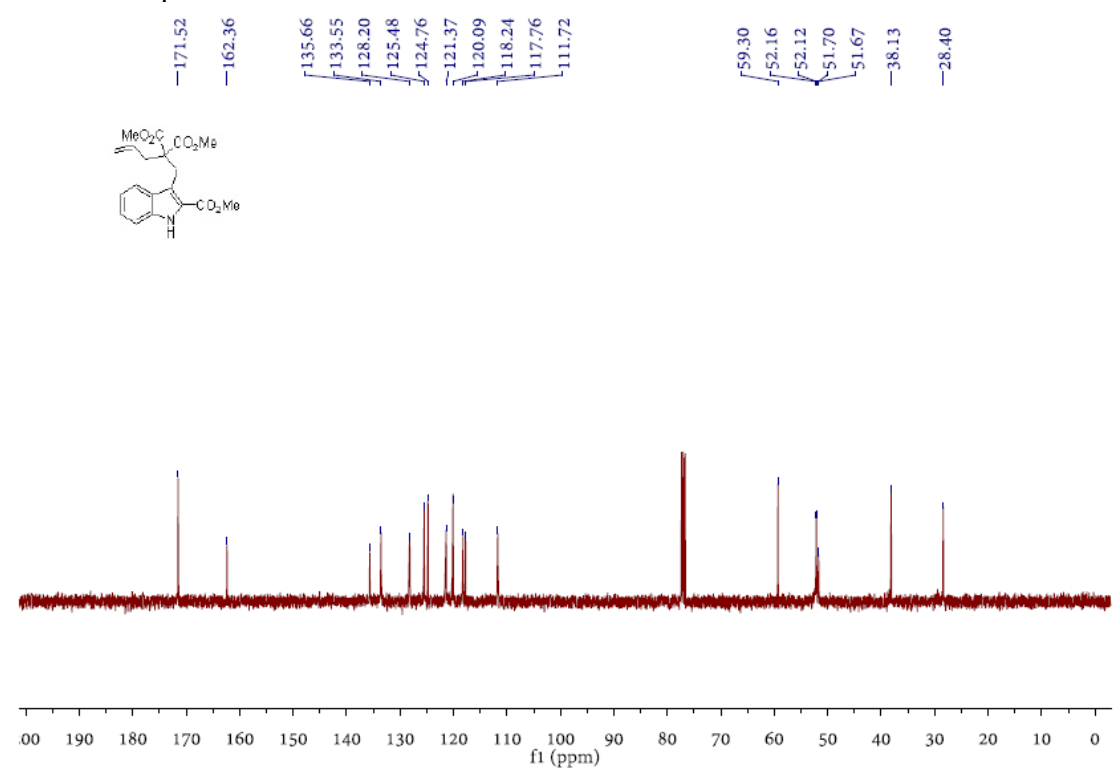
¹³C NMR Spectrum of **1r**



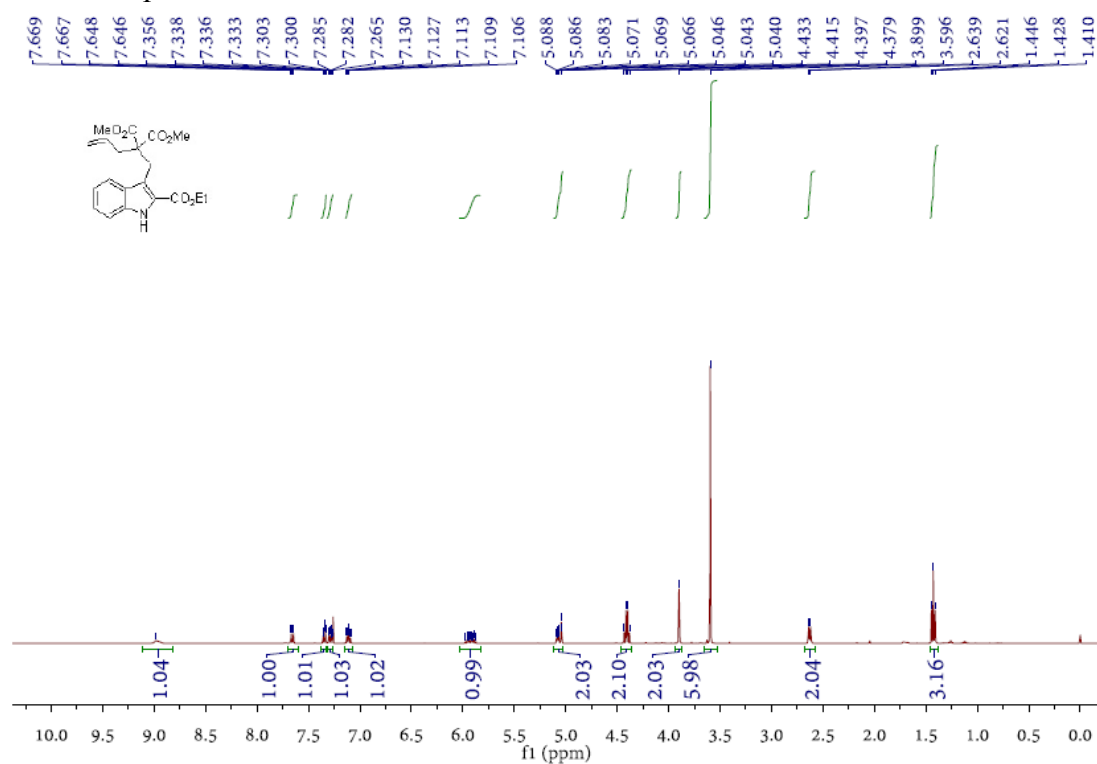
¹H NMR Spectrum of **1w**



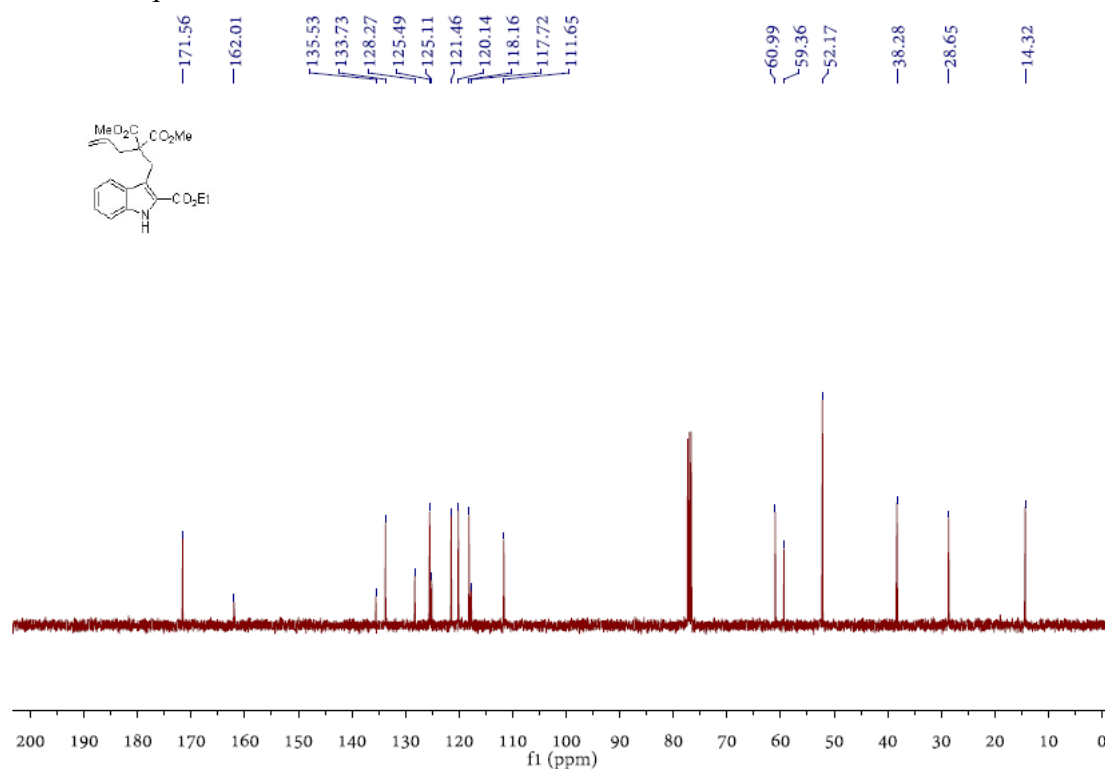
¹³C NMR Spectrum of **1w**



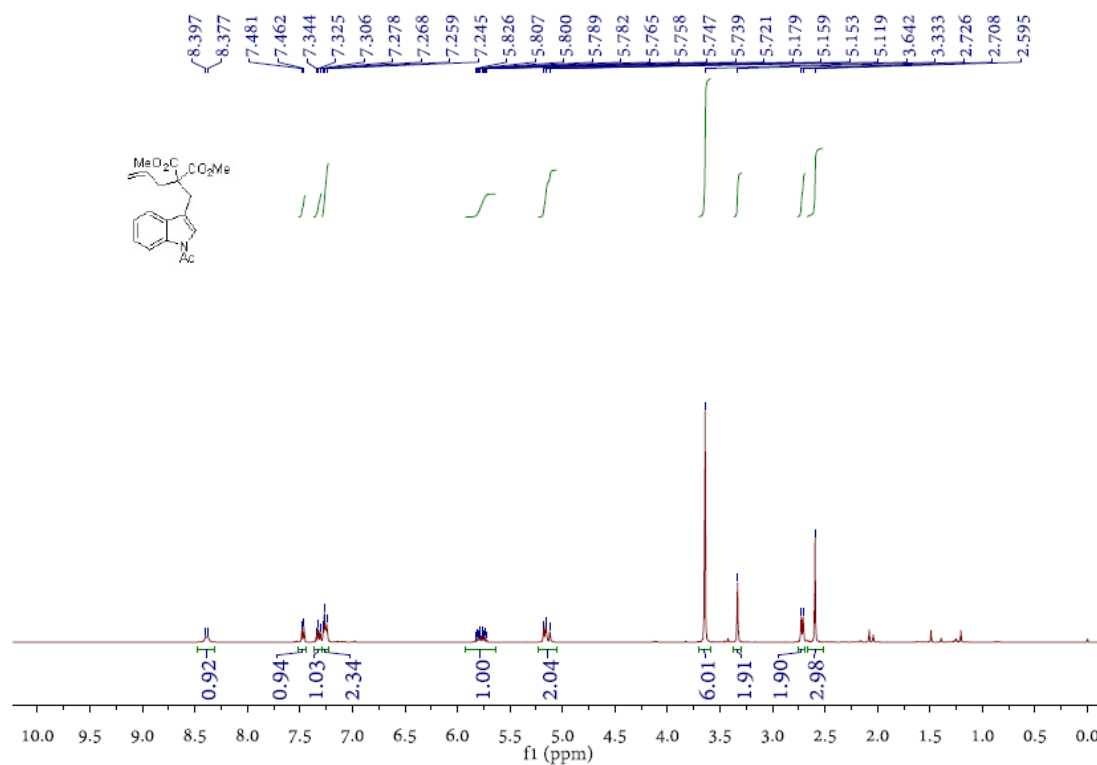
¹H NMR Spectrum of **1x**



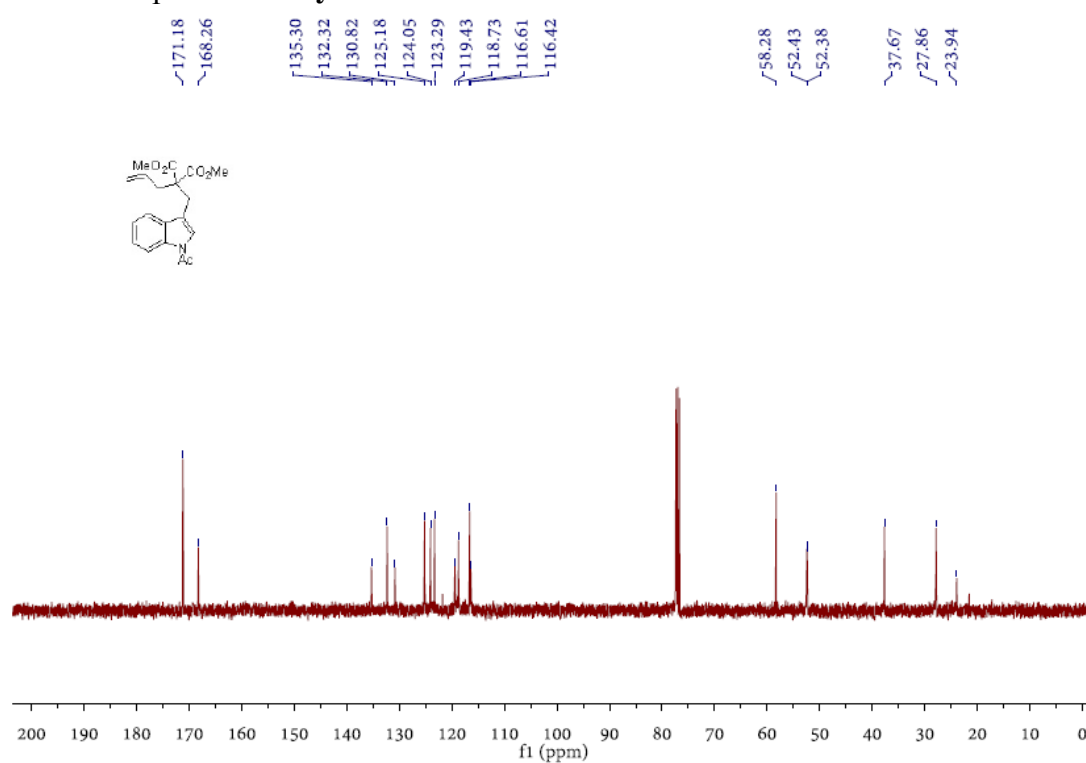
¹³C NMR Spectrum of **1x**



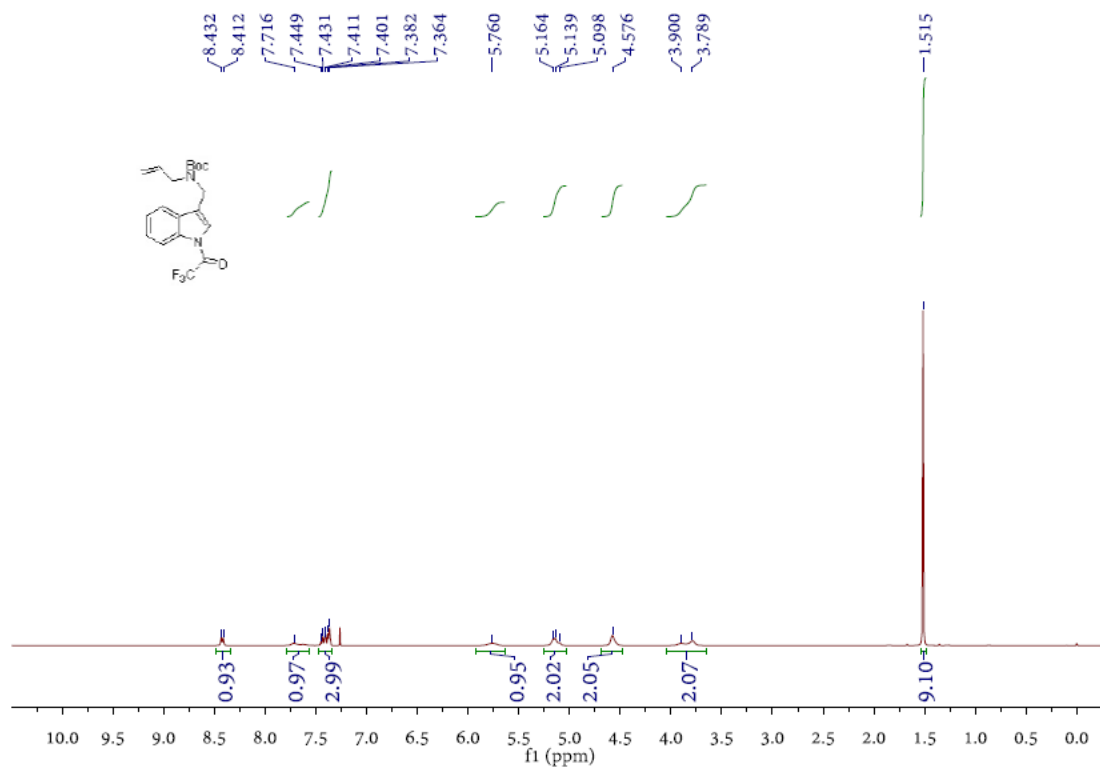
¹H NMR Spectrum of **1y**



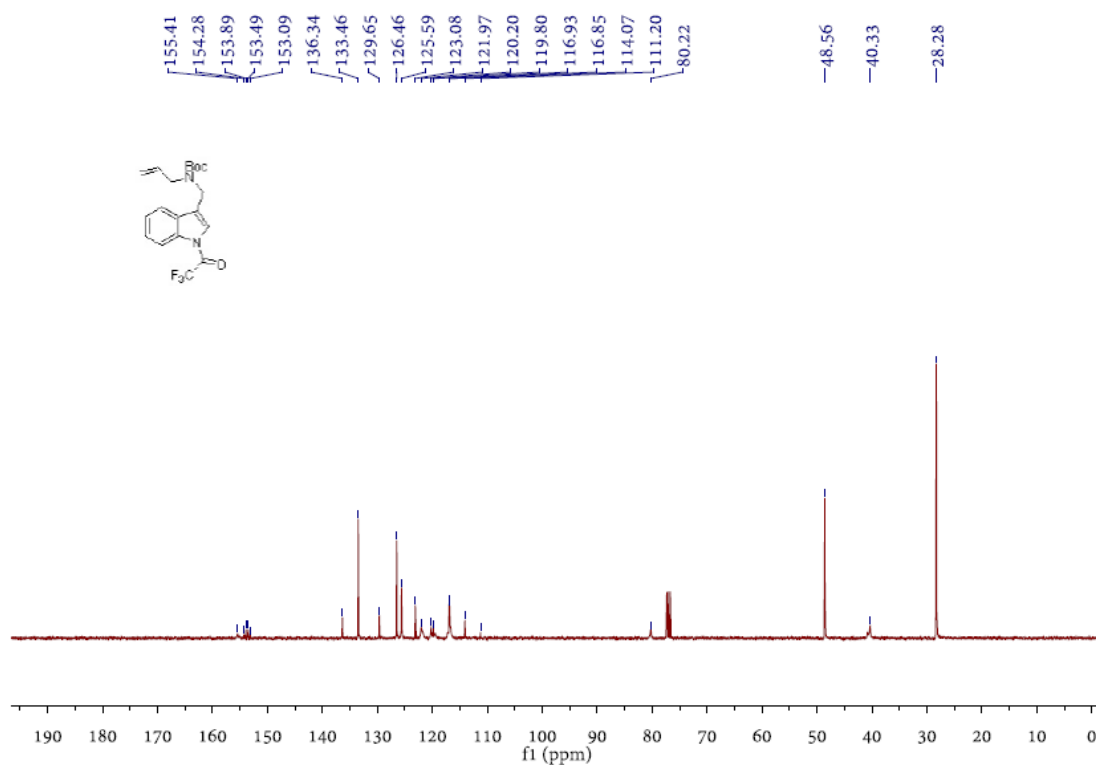
¹³C NMR Spectrum of **1y**



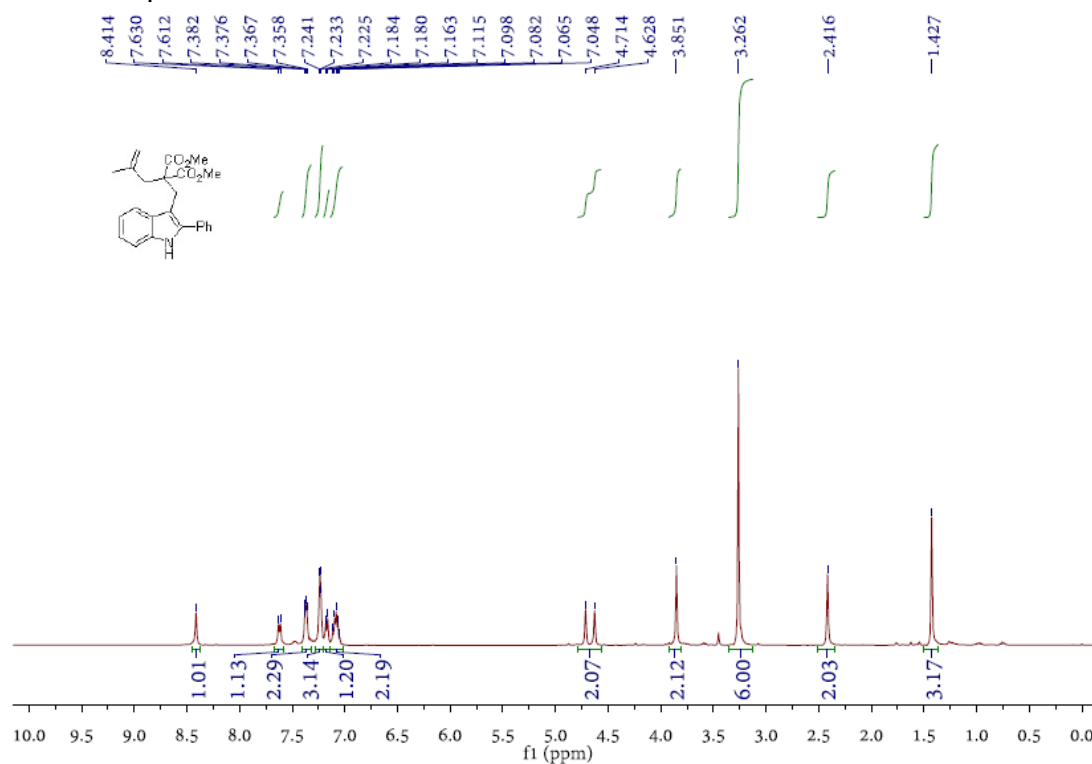
¹H NMR Spectrum of **1z**



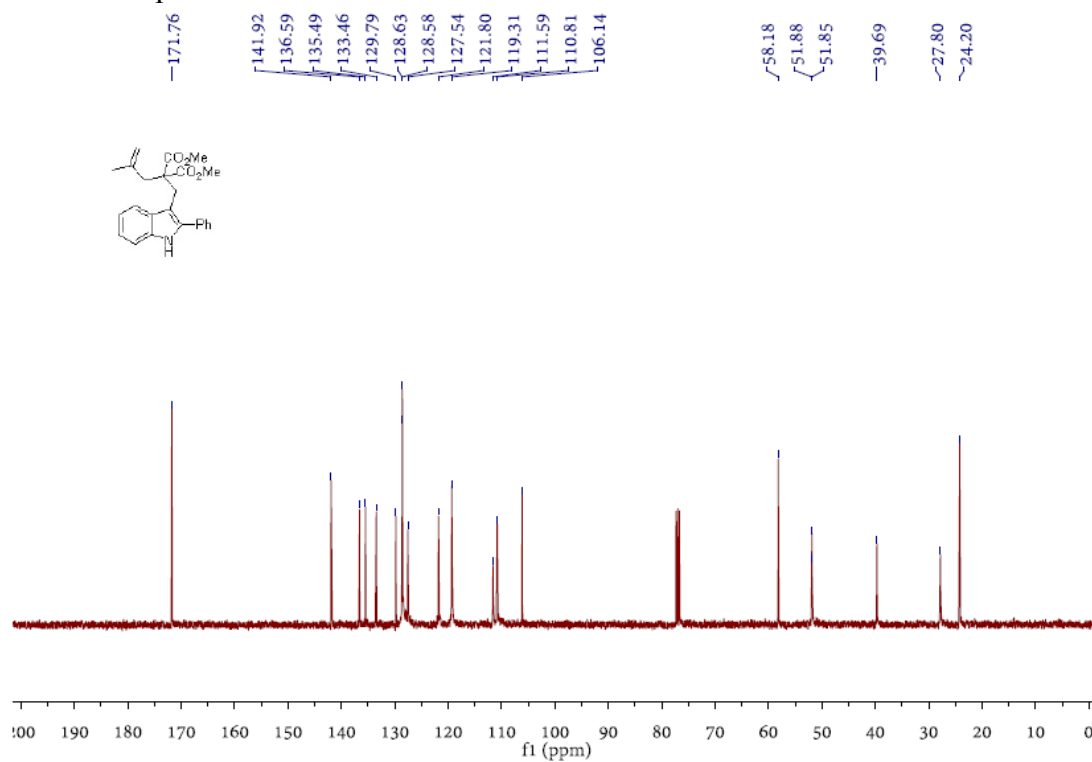
¹³C NMR Spectrum of **1z**



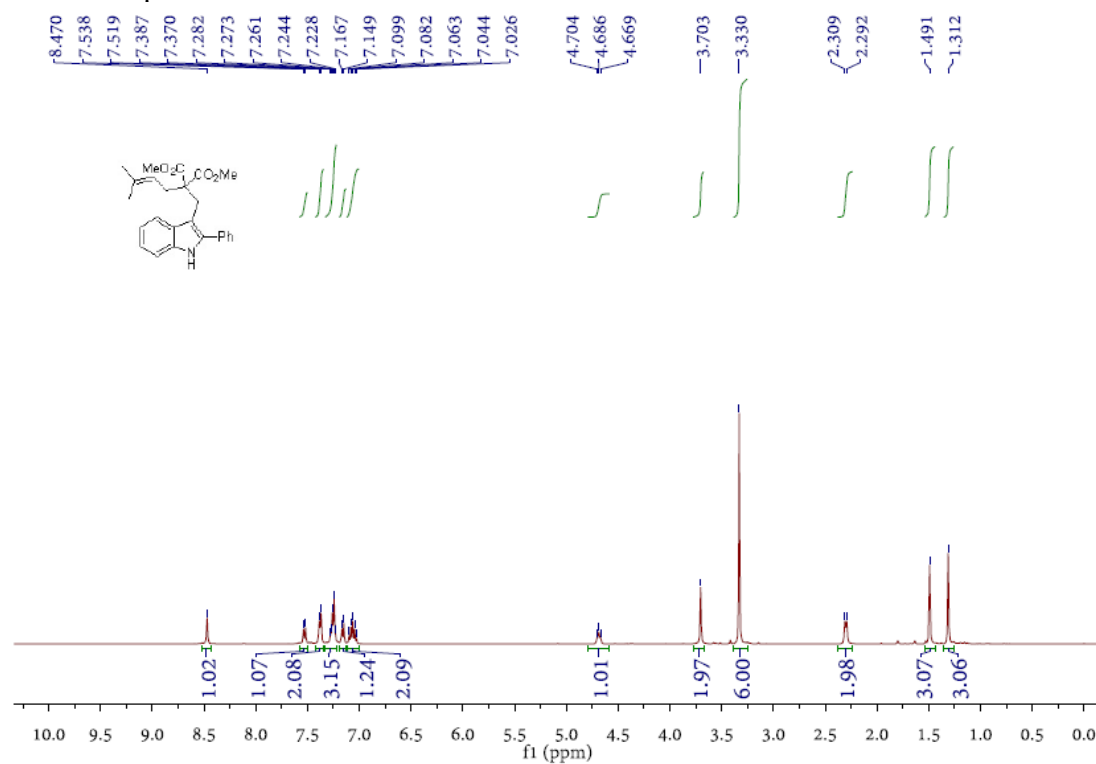
¹H NMR Spectrum of **1aa**



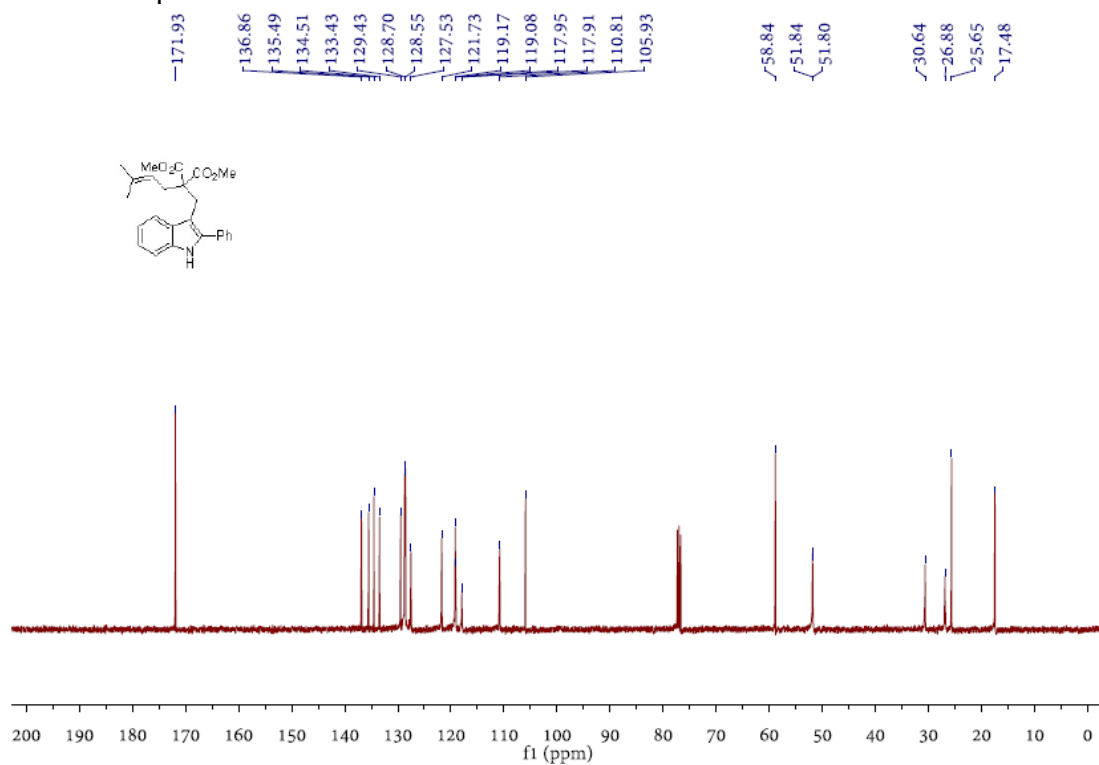
¹³C NMR Spectrum of **1aa**



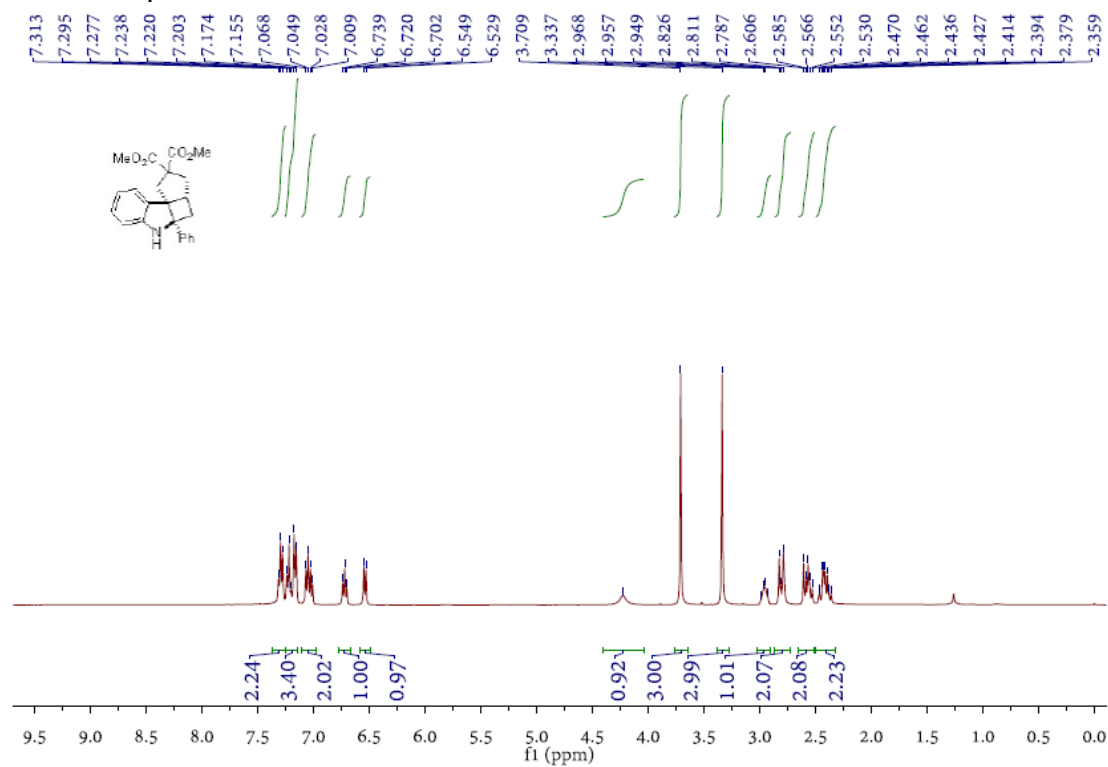
¹H NMR Spectrum of **1ab**



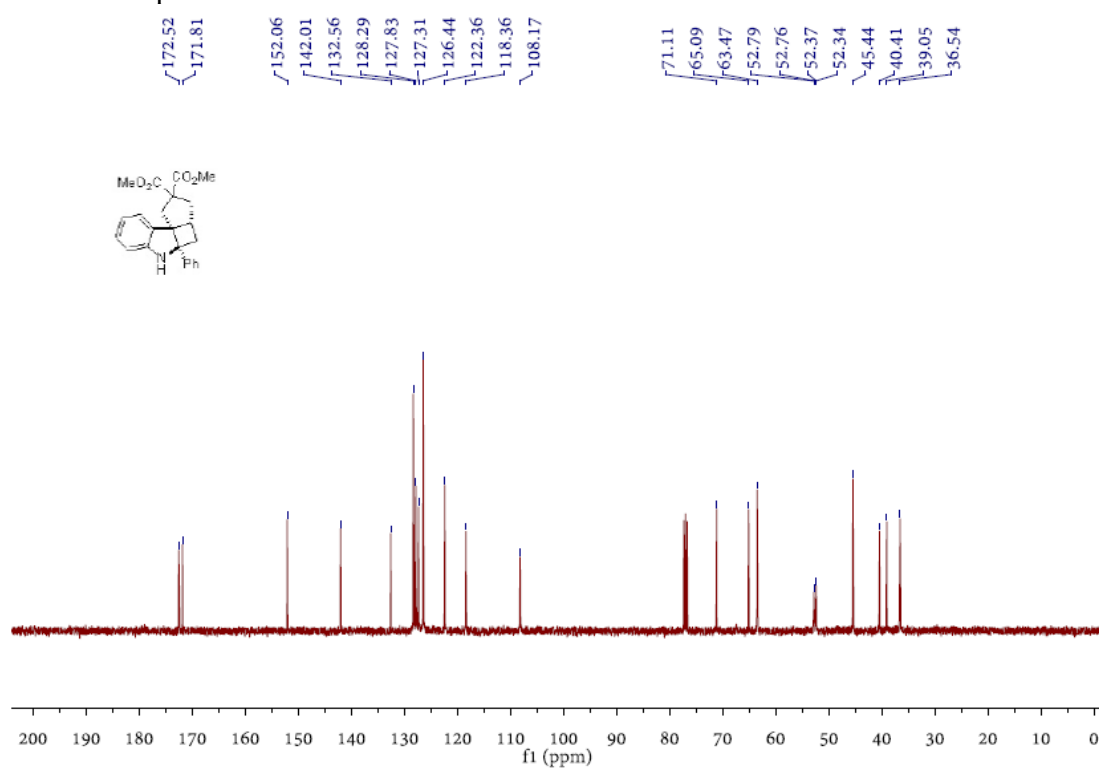
¹³C NMR Spectrum of **1ab**



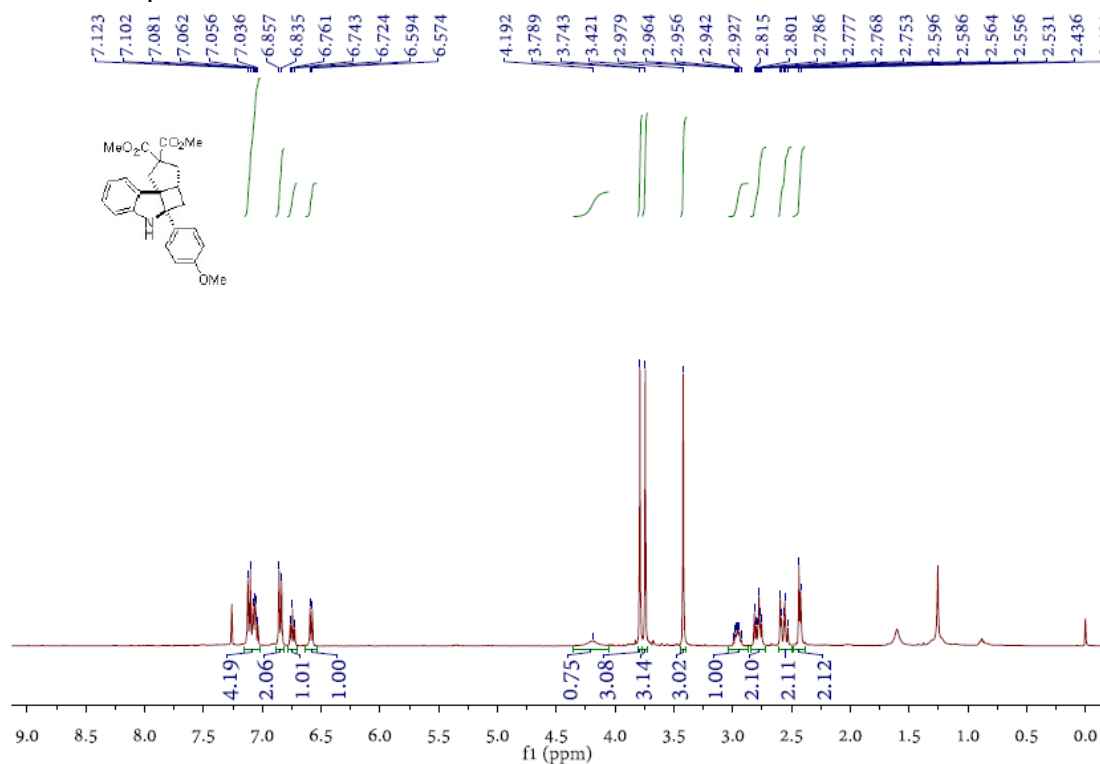
¹H NMR Spectrum of **2a**



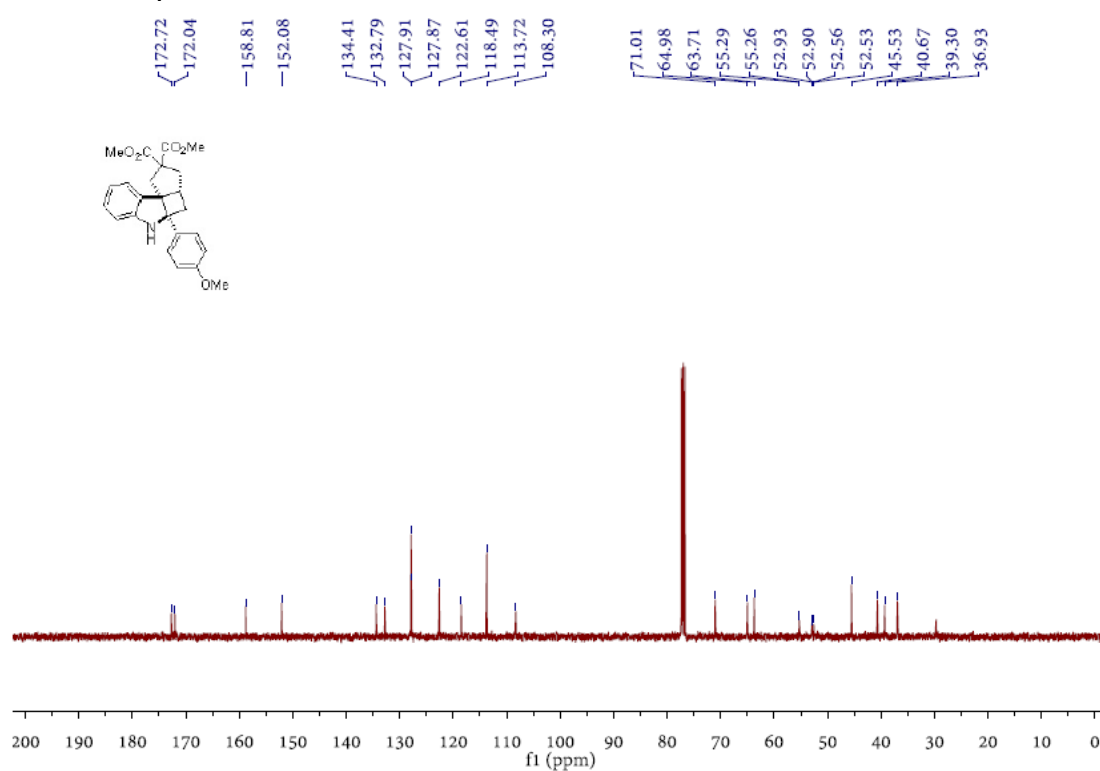
¹³C NMR Spectrum of **2a**



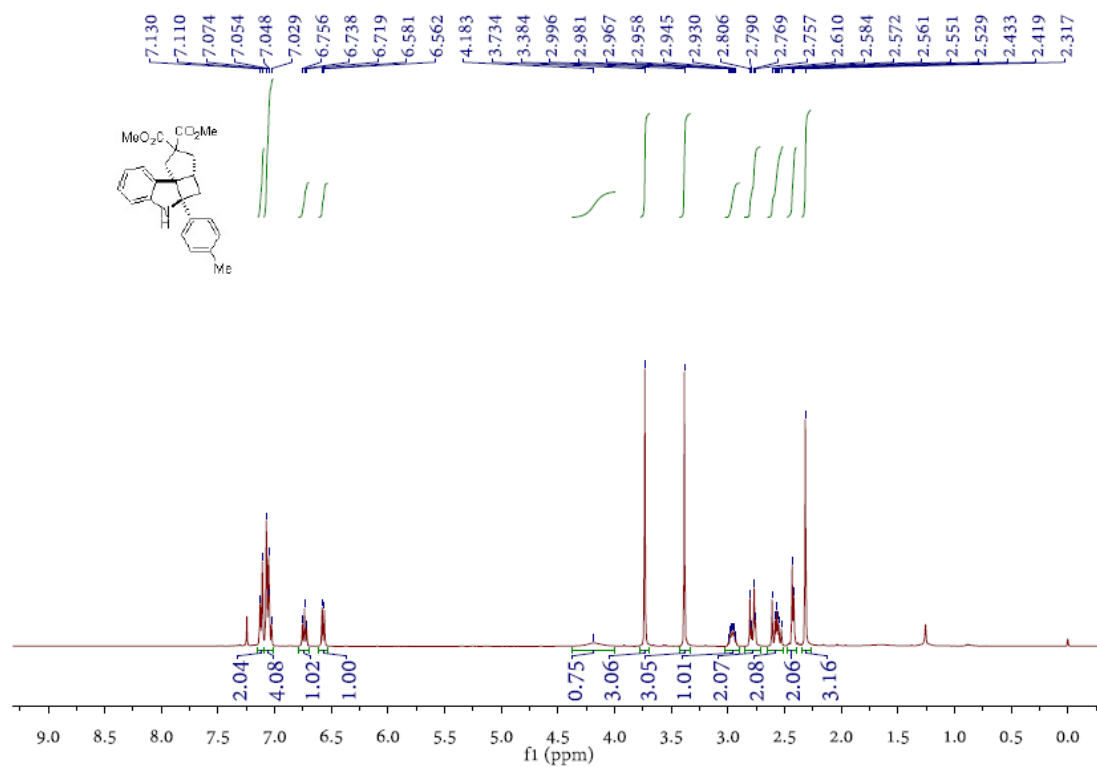
¹H NMR Spectrum of **2b**



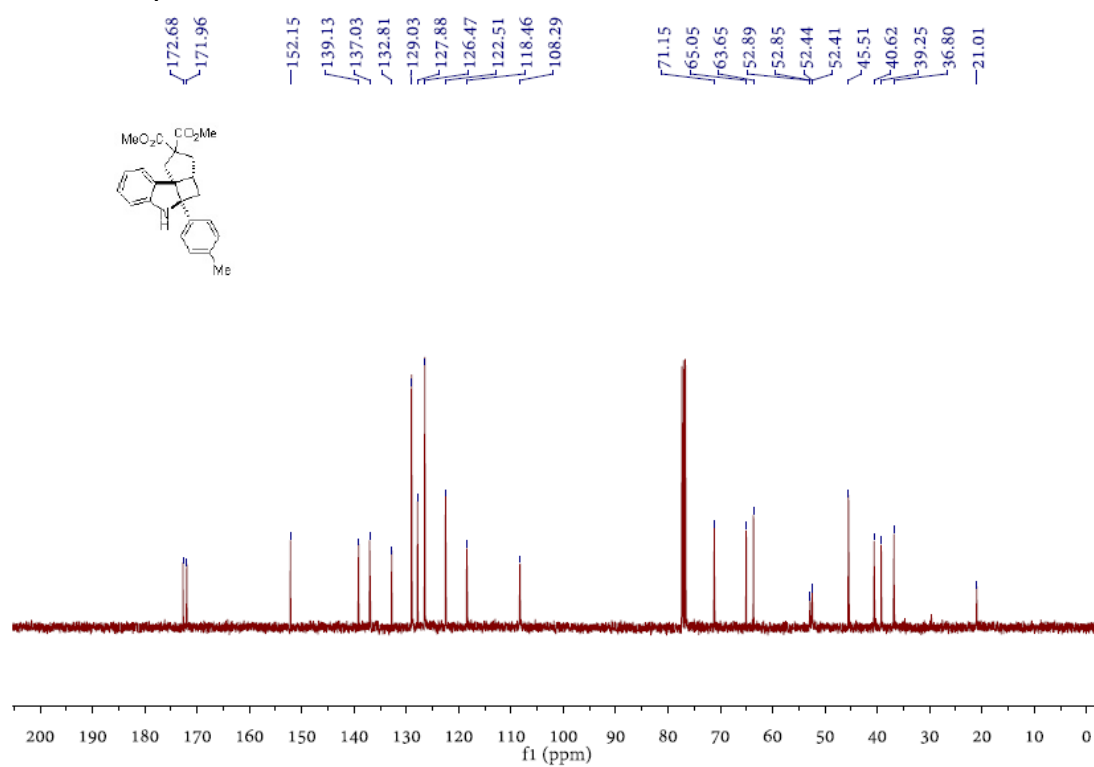
¹³C NMR Spectrum of **2b**



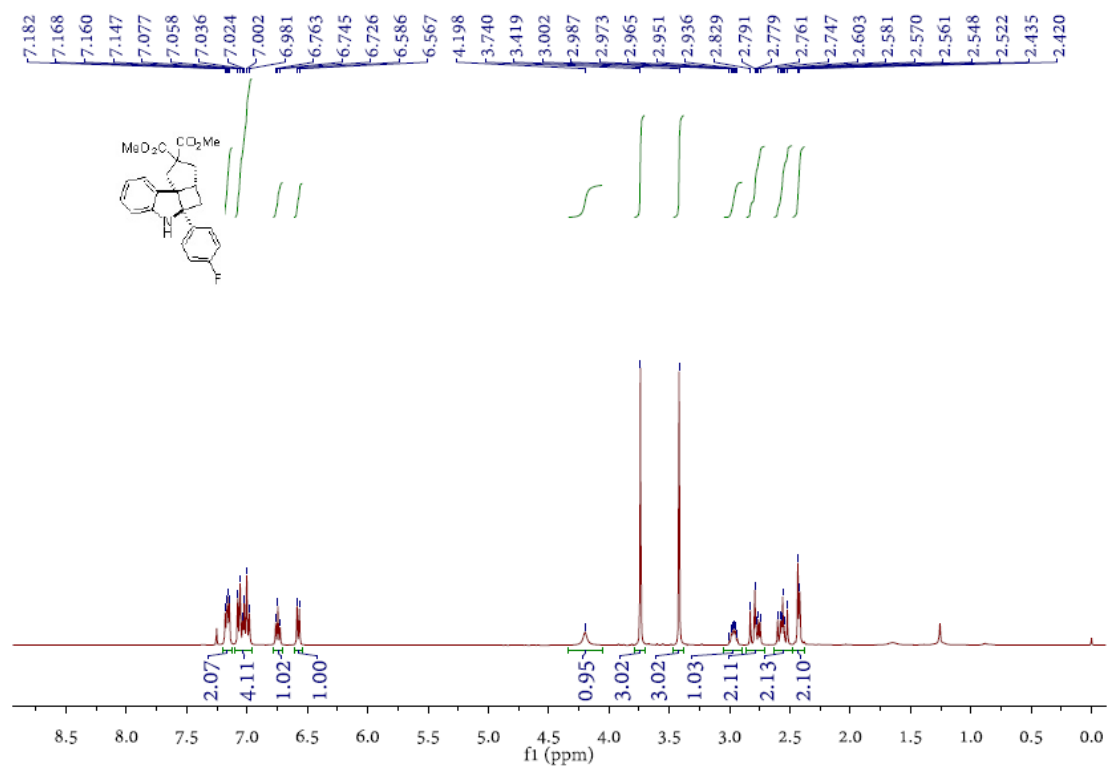
¹H NMR Spectrum of **2c**



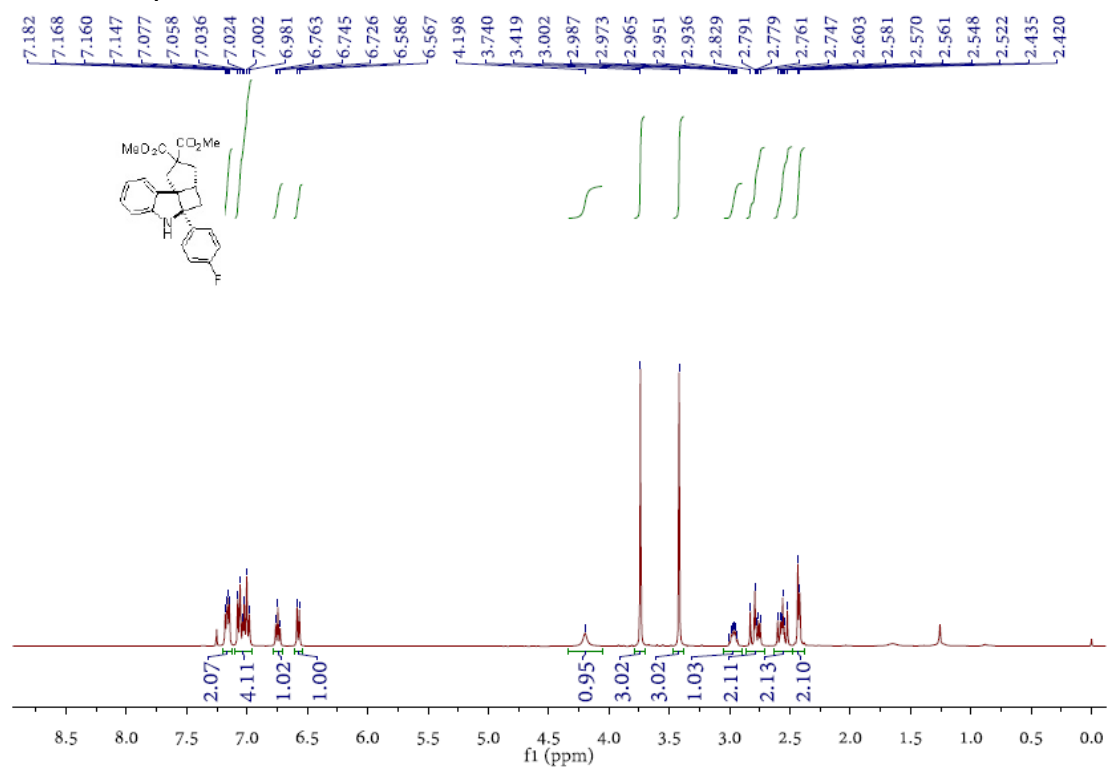
¹³C NMR Spectrum of **2c**



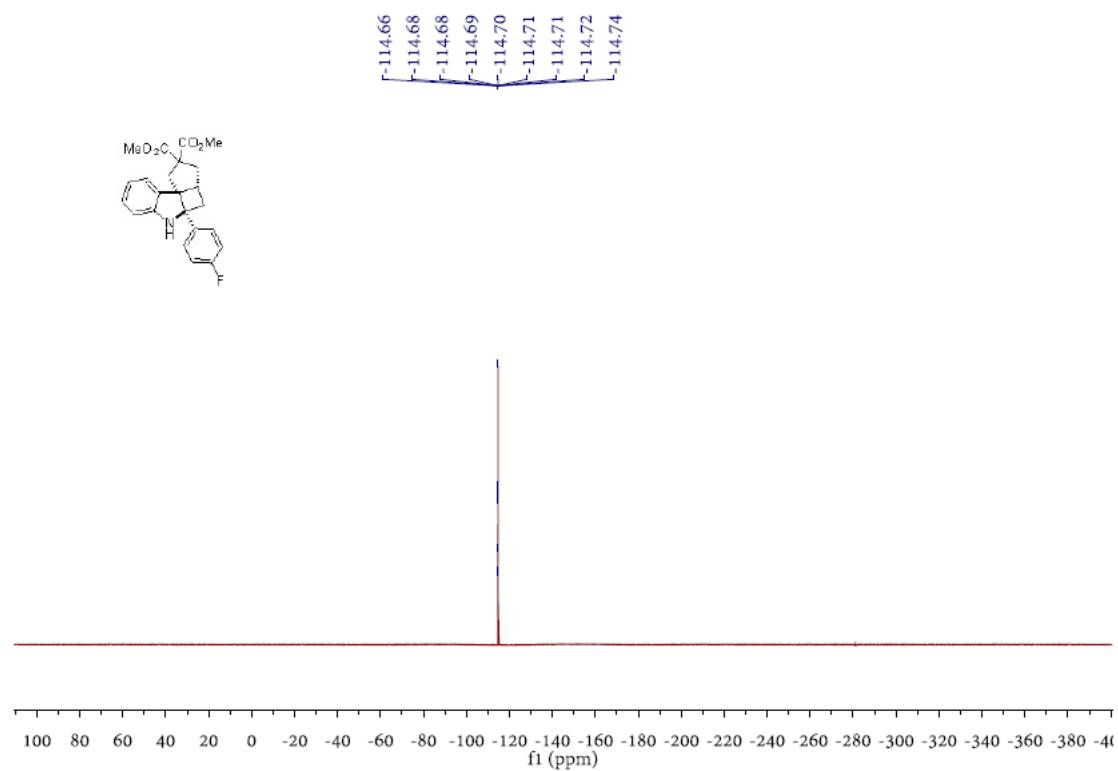
¹H NMR Spectrum of **2d**



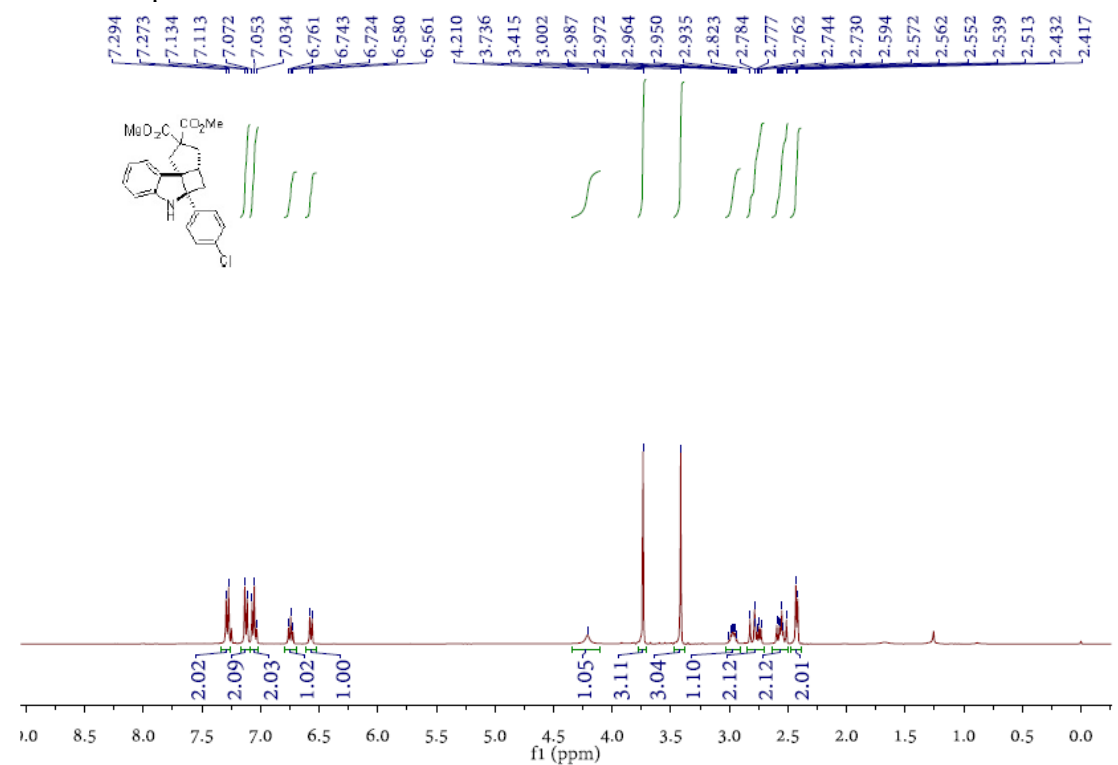
¹³C NMR Spectrum of **2d**



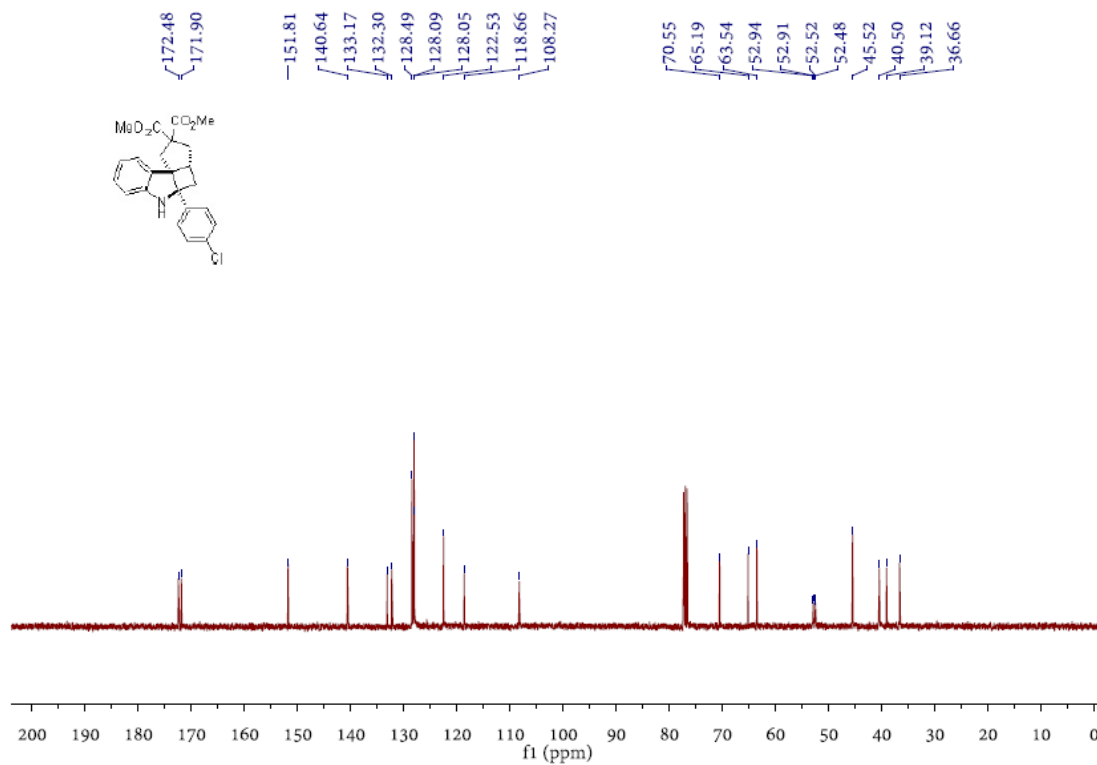
¹⁹F NMR Spectrum of **2d**



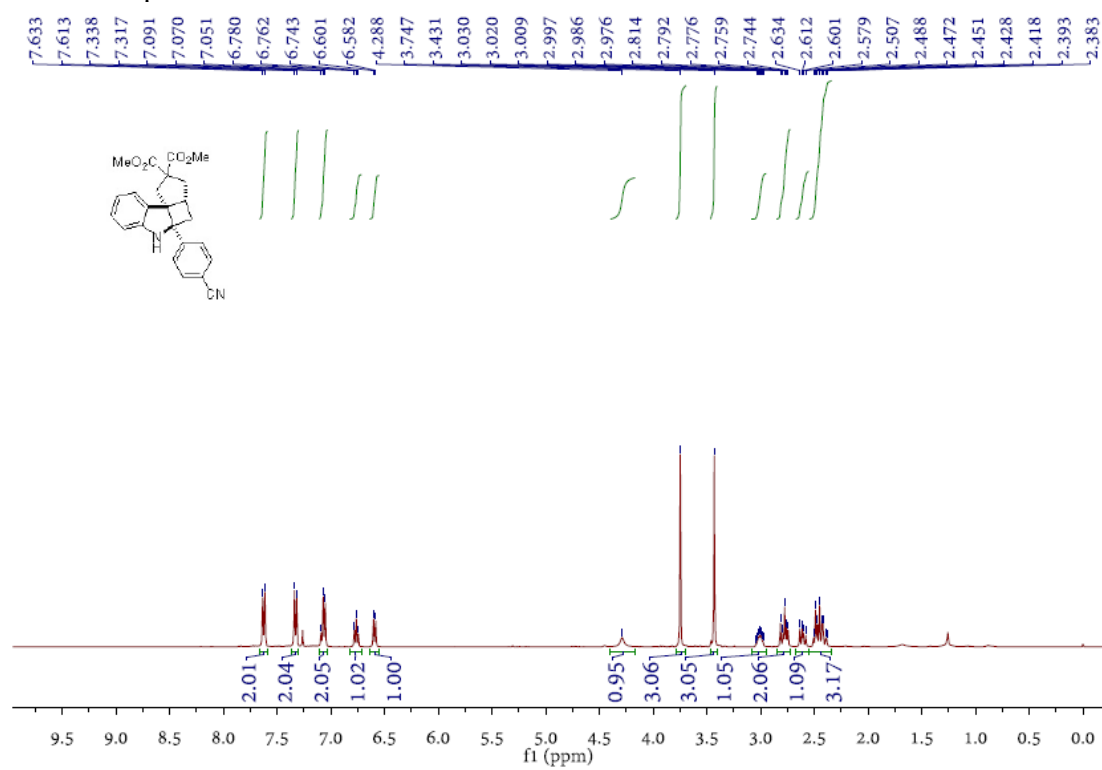
¹H NMR Spectrum of **2e**



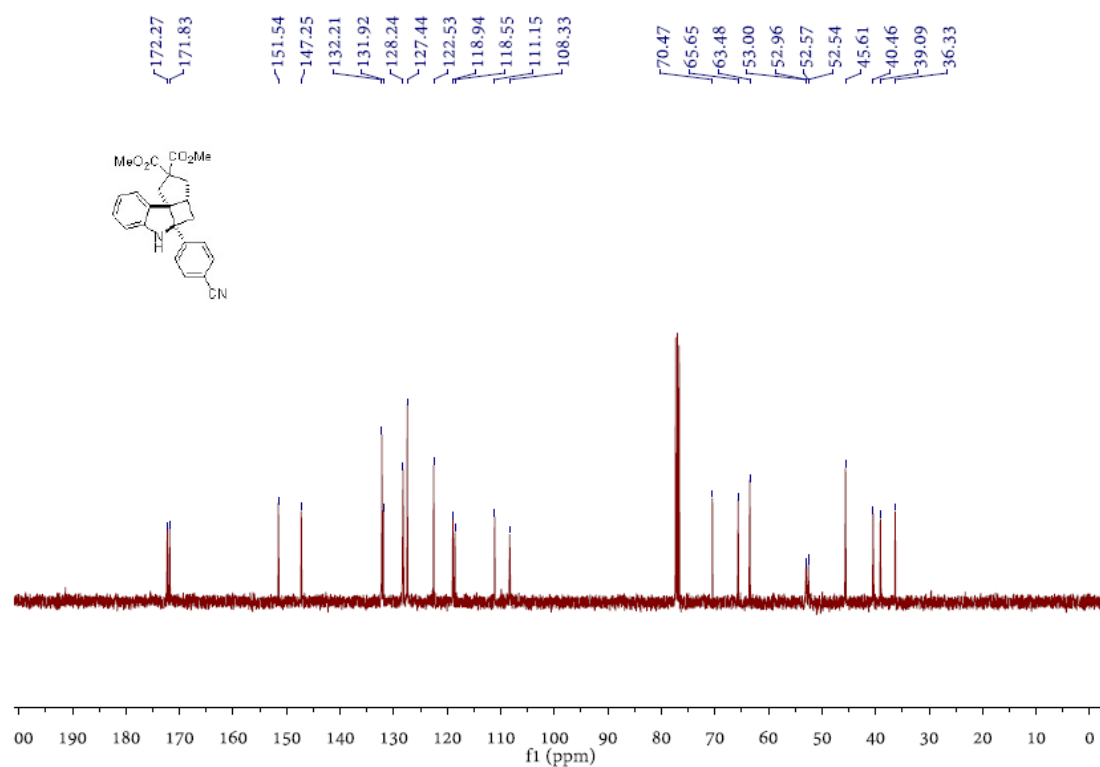
¹³C NMR Spectrum of **2e**



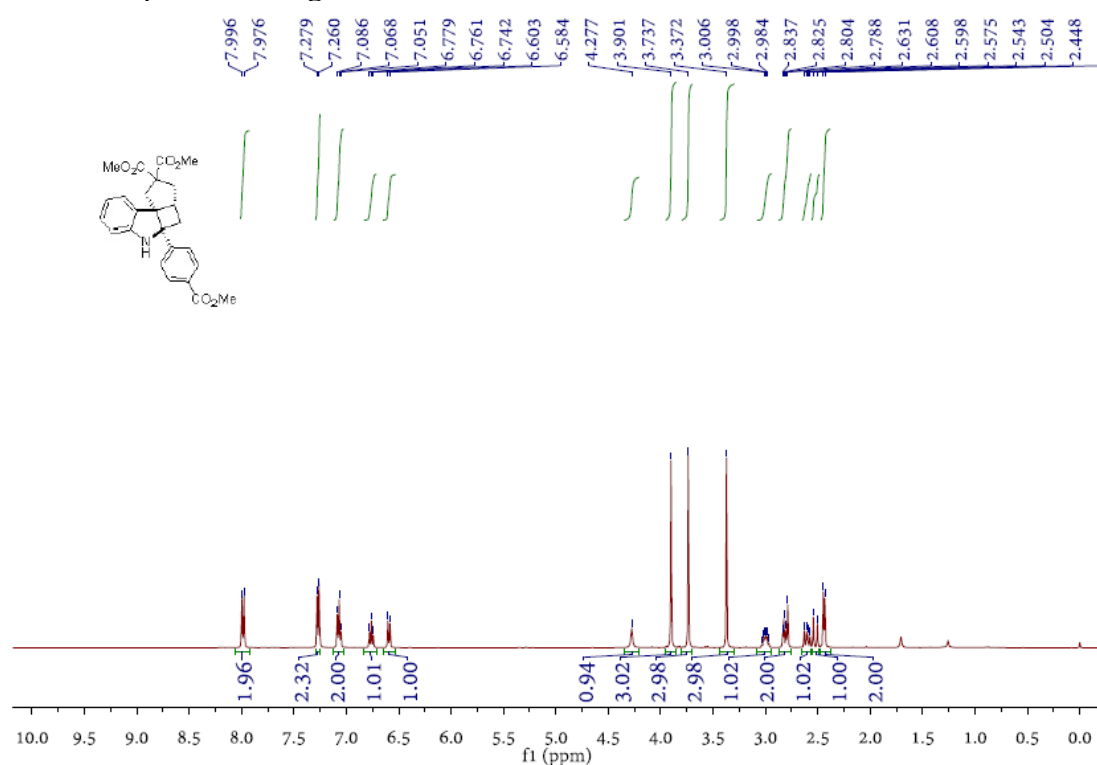
¹H NMR Spectrum of **2f**



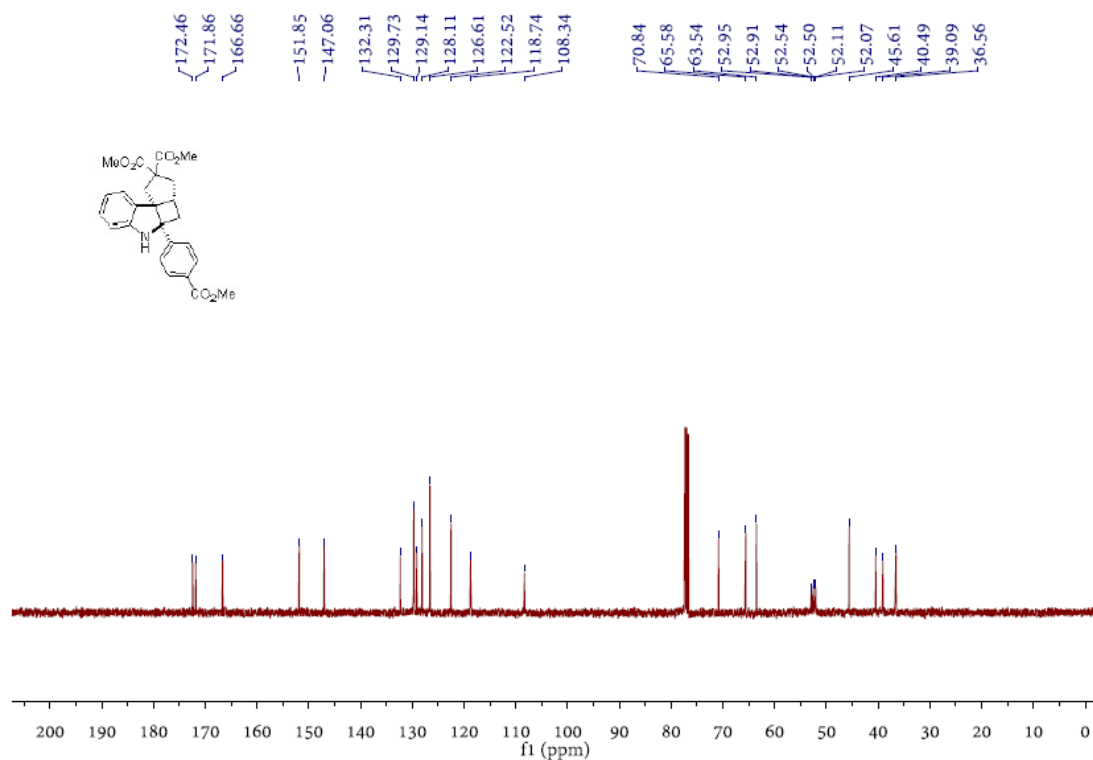
¹³C NMR Spectrum of **2f**



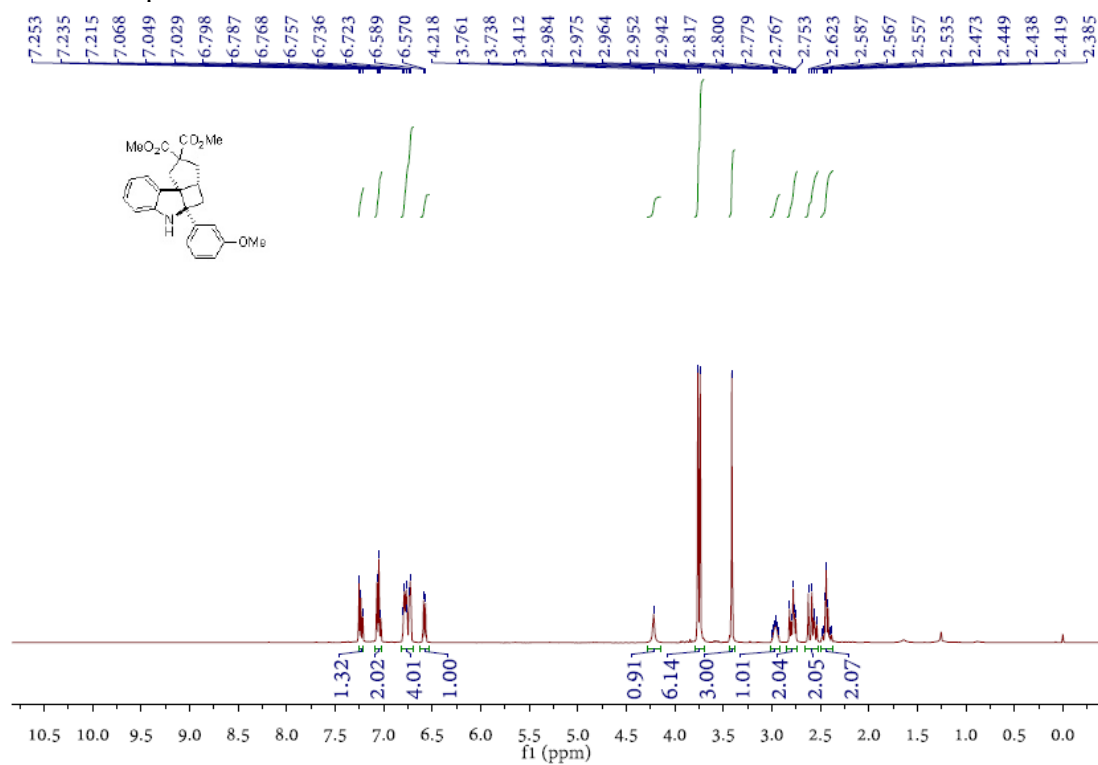
¹H NMR Spectrum of **2g**



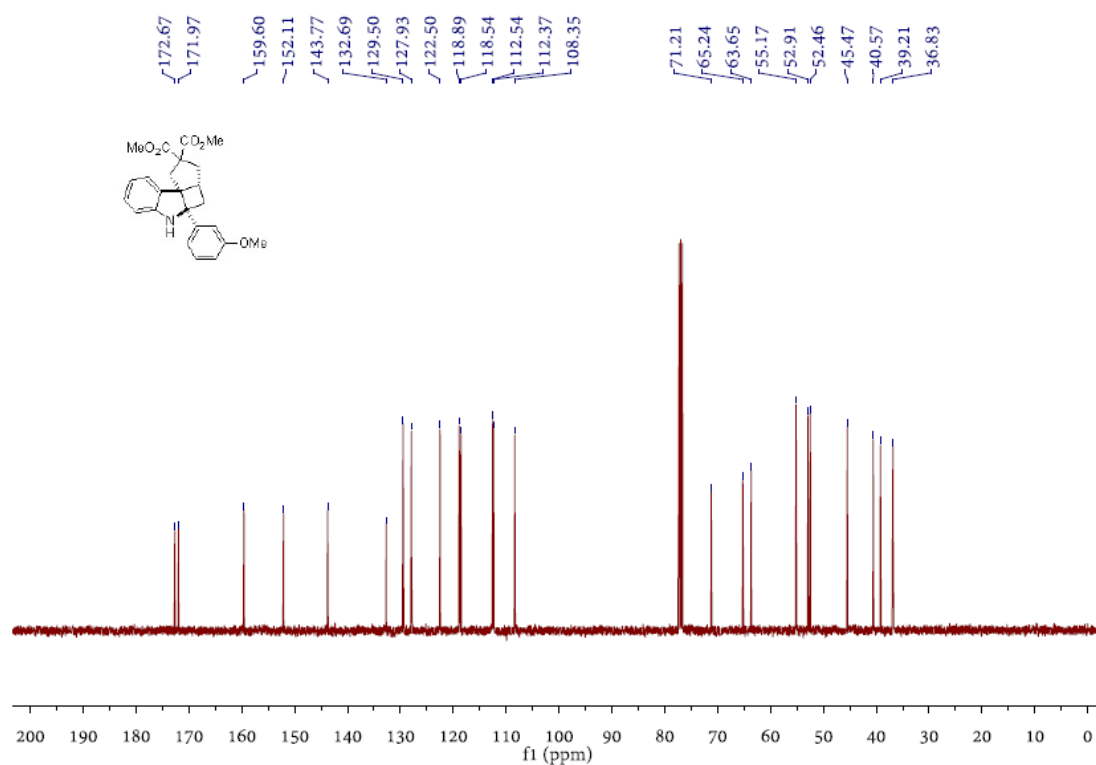
¹³C NMR Spectrum of **2g**



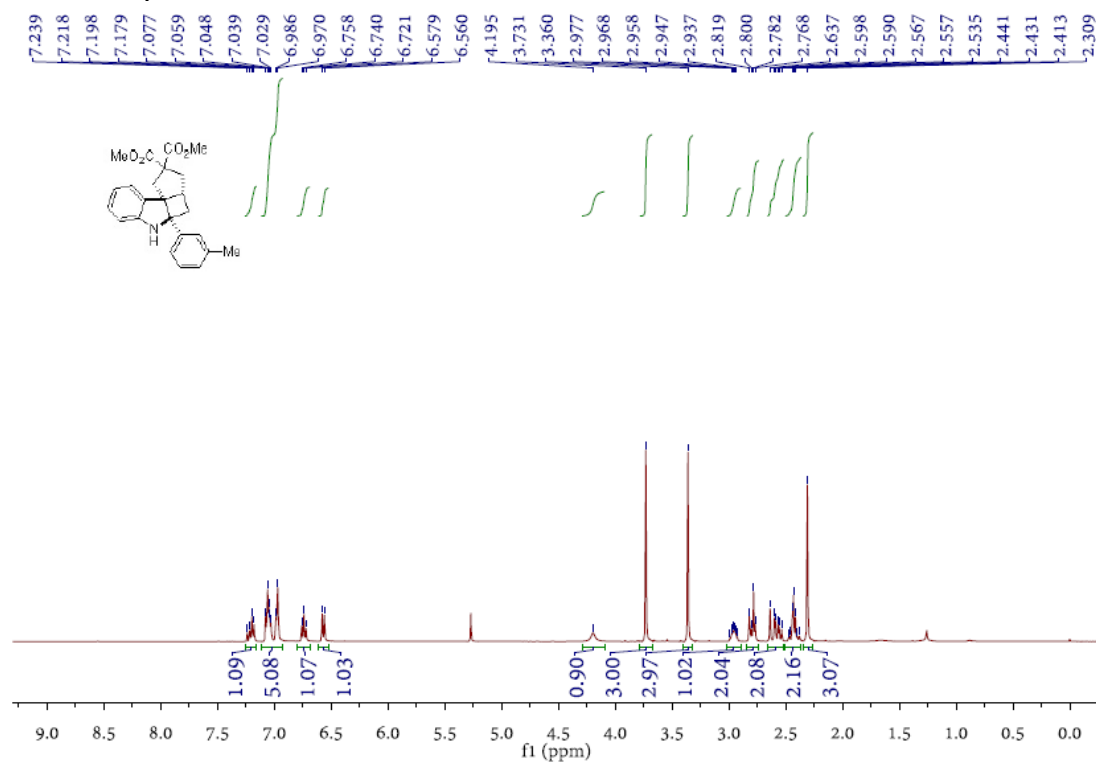
¹H NMR Spectrum of **2h**



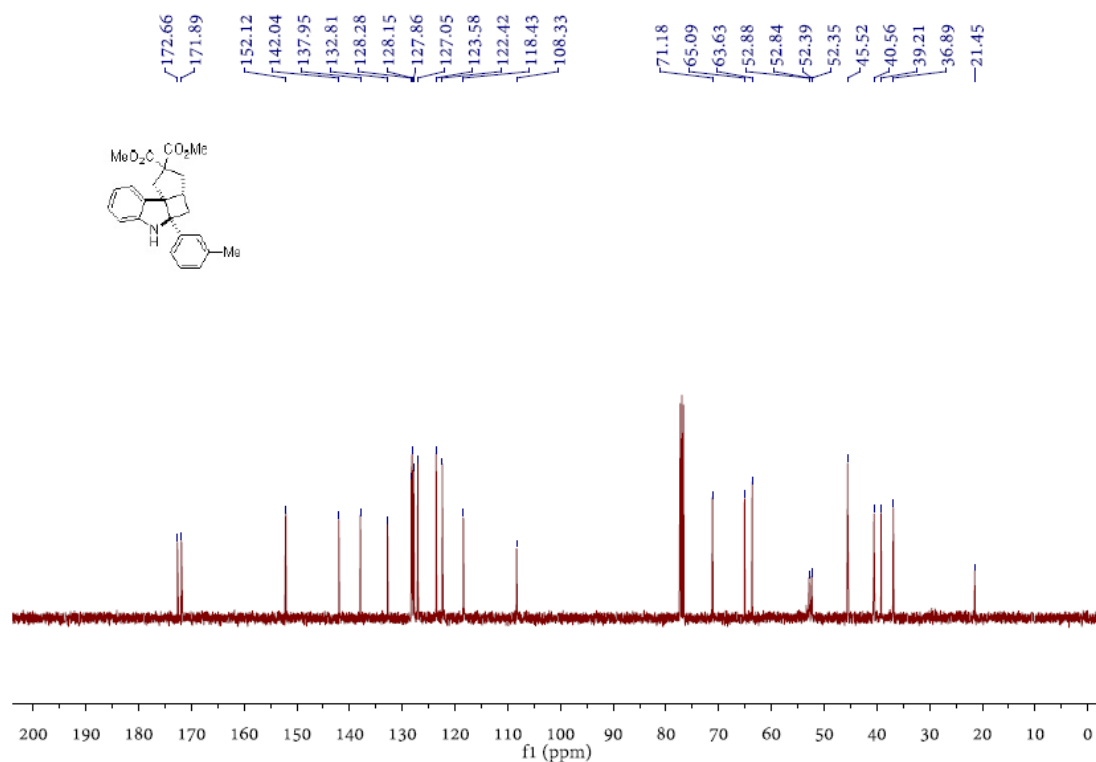
¹³C NMR Spectrum of **2h**



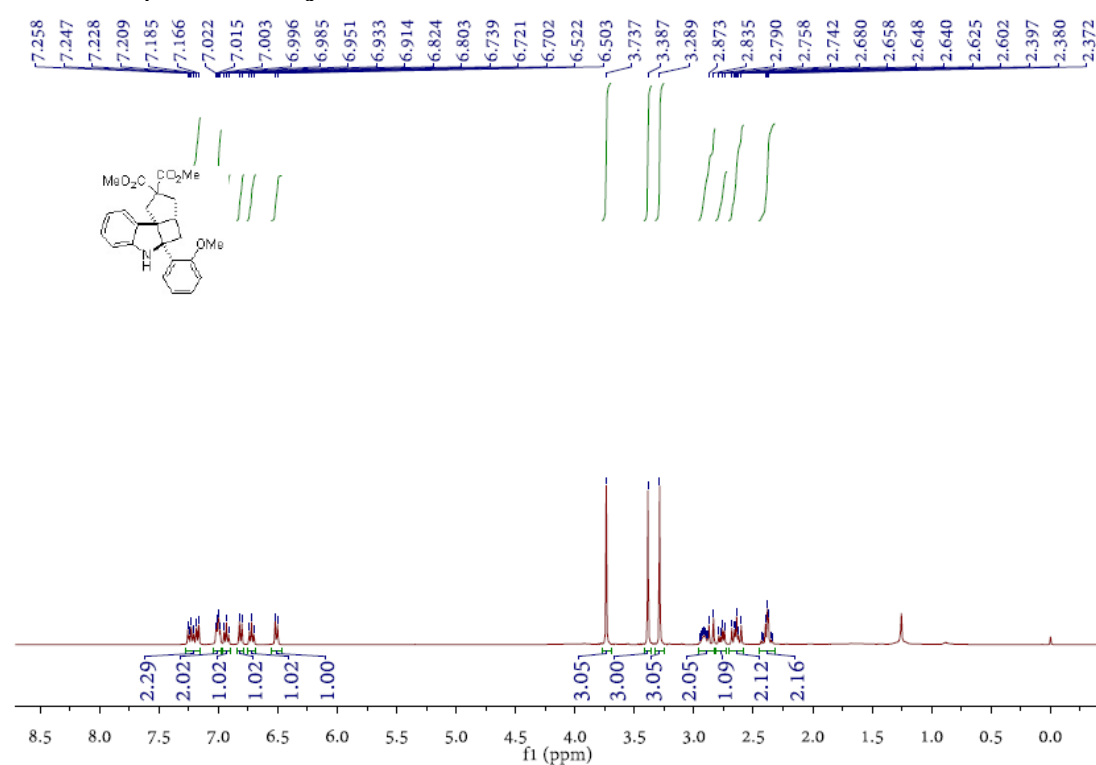
¹H NMR Spectrum of **2i**



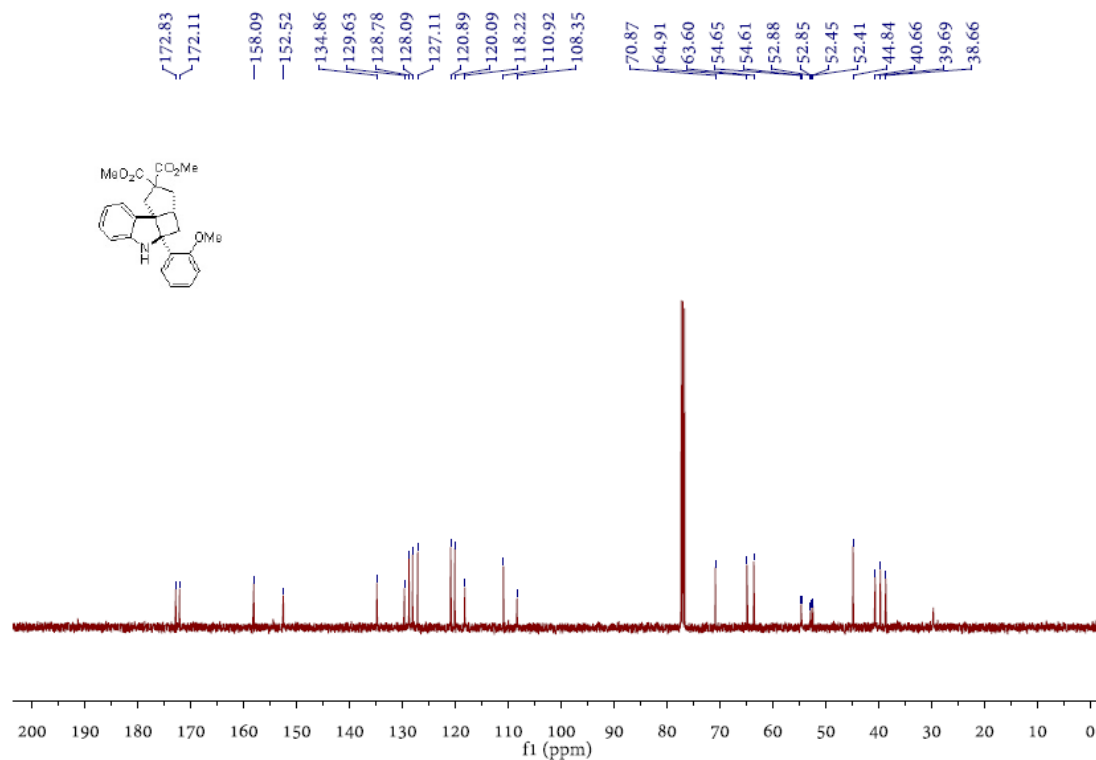
¹³C NMR Spectrum of **2i**



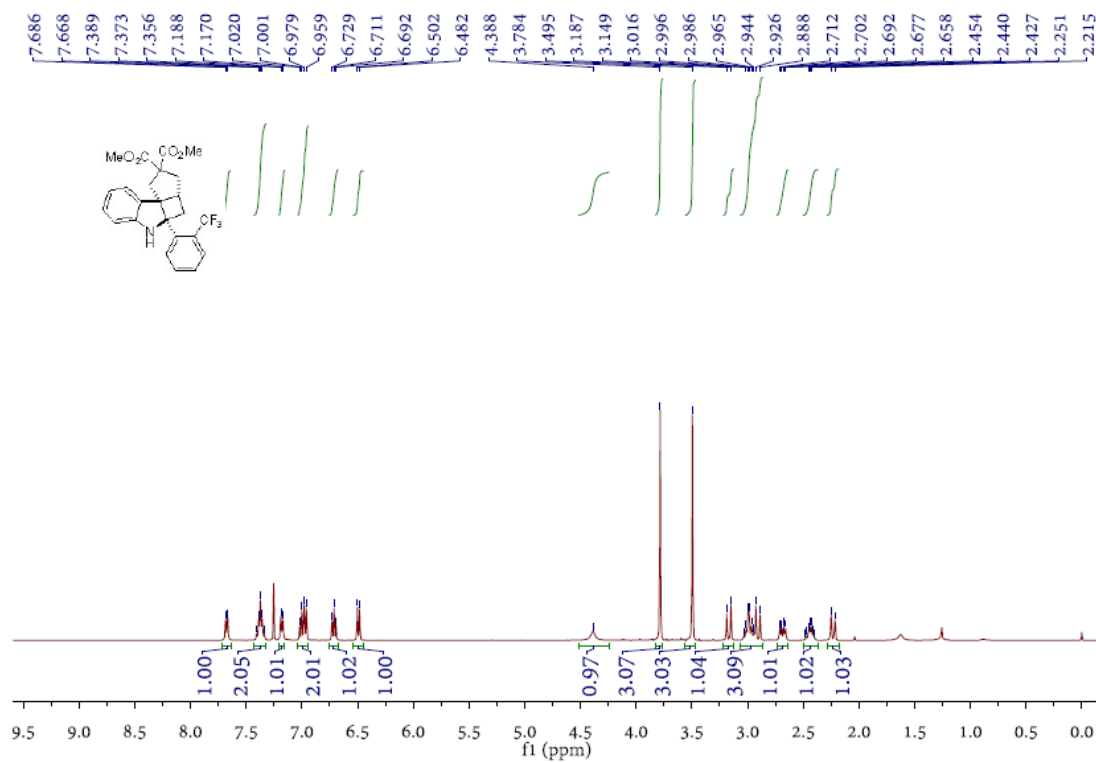
¹H NMR Spectrum of **2j**



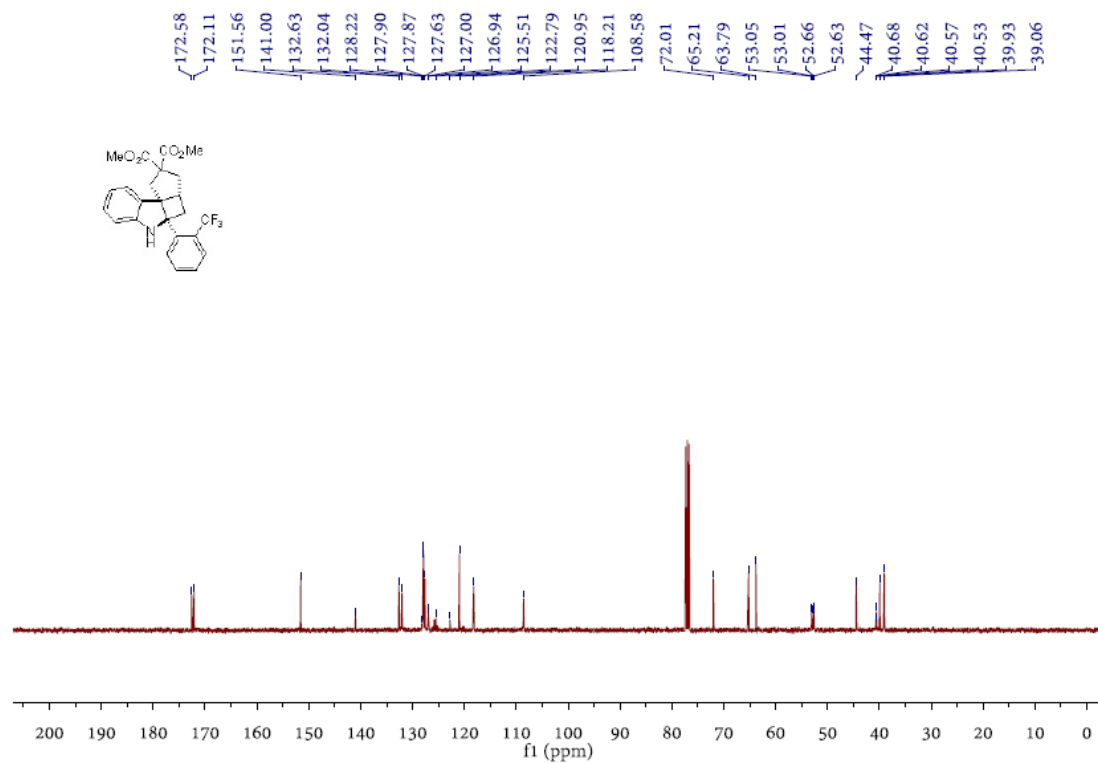
¹³C NMR Spectrum of **2j**



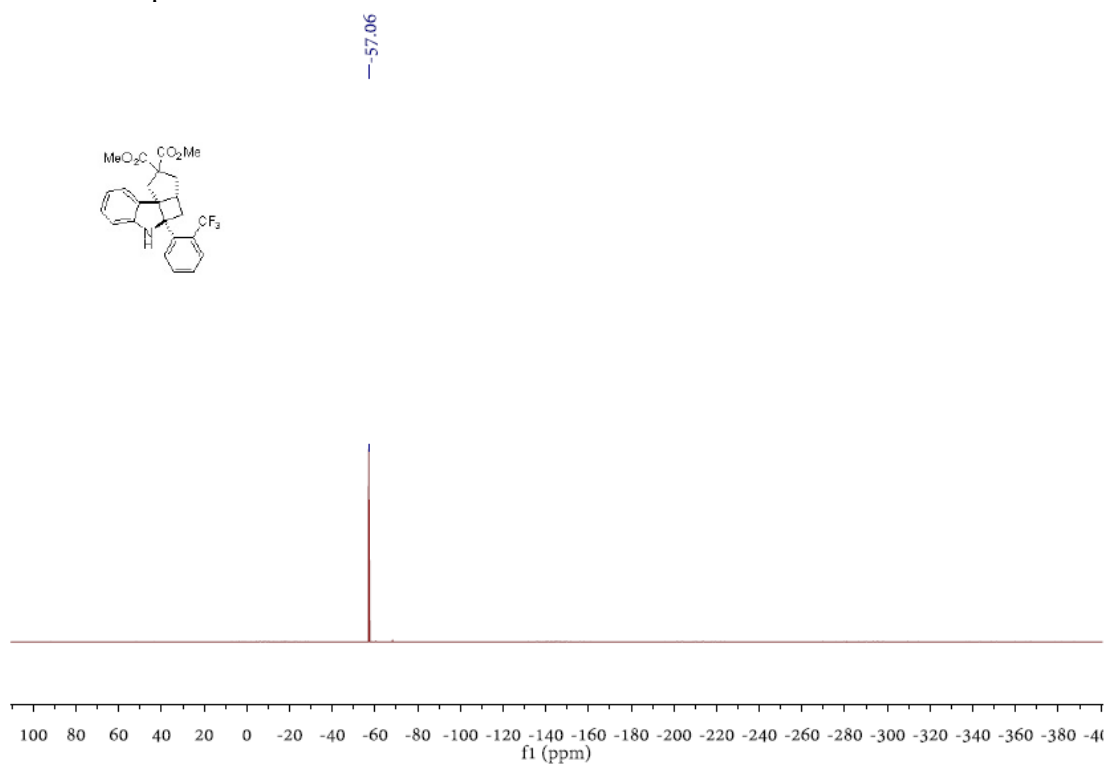
¹H NMR Spectrum of **2k**



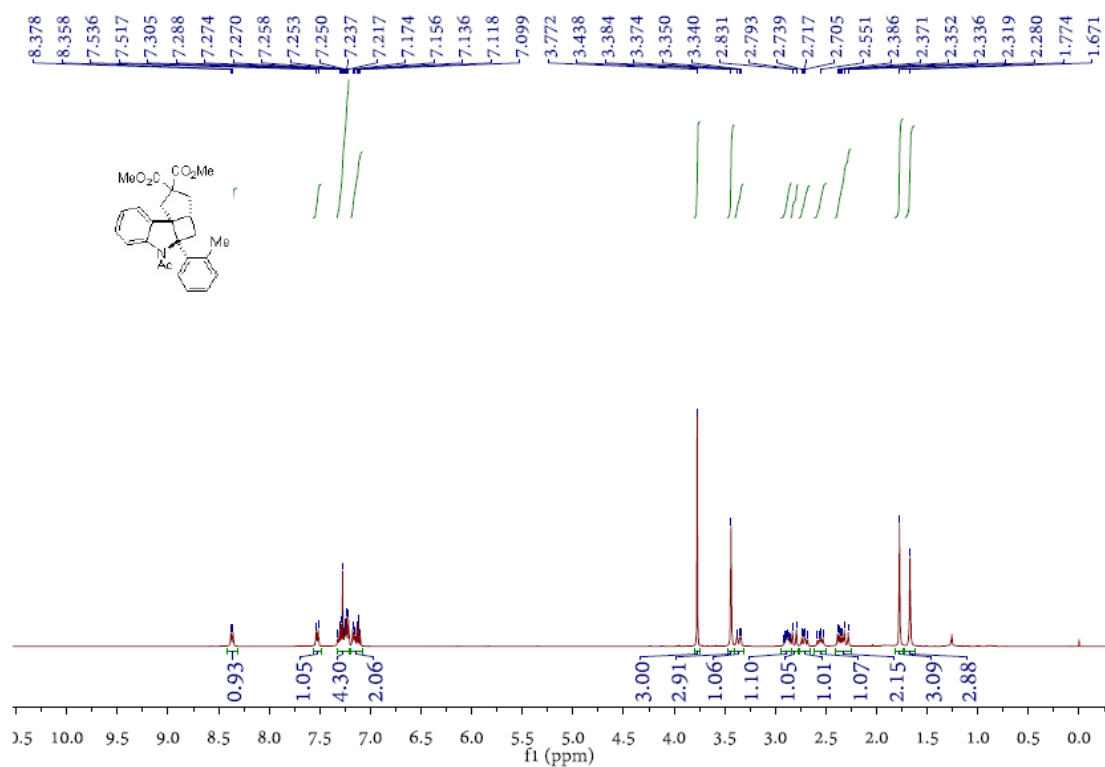
¹³C NMR Spectrum of **2k**



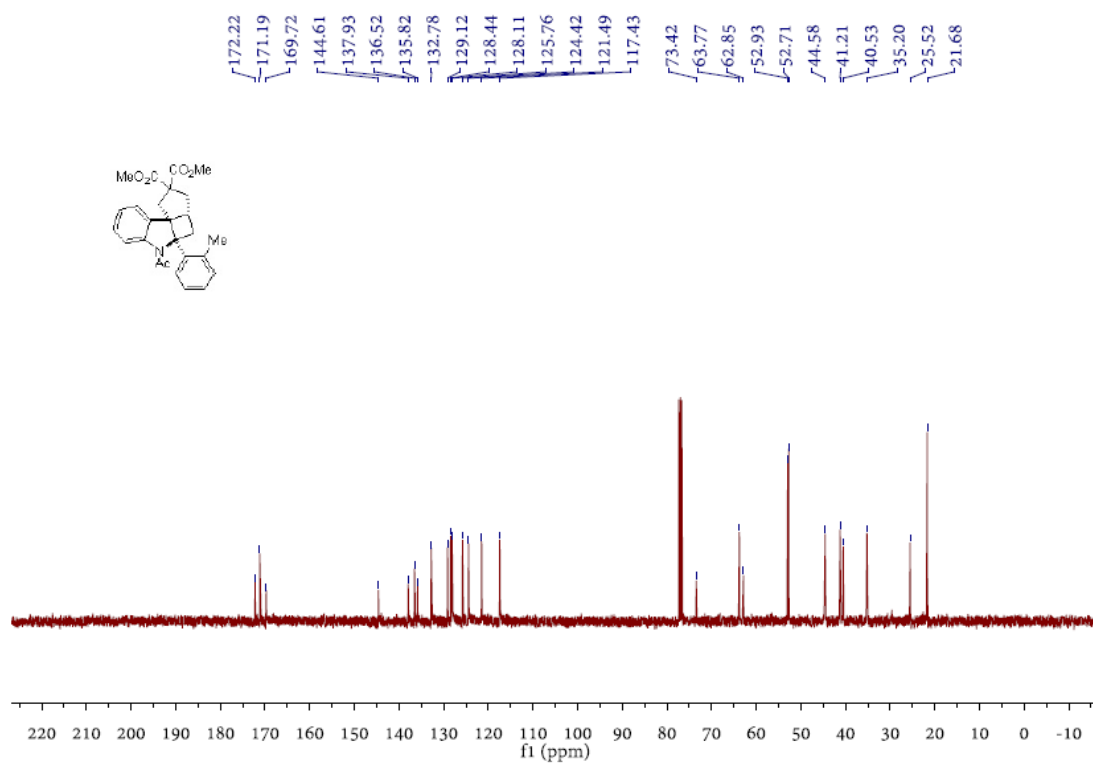
¹⁹F NMR Spectrum of **2k**



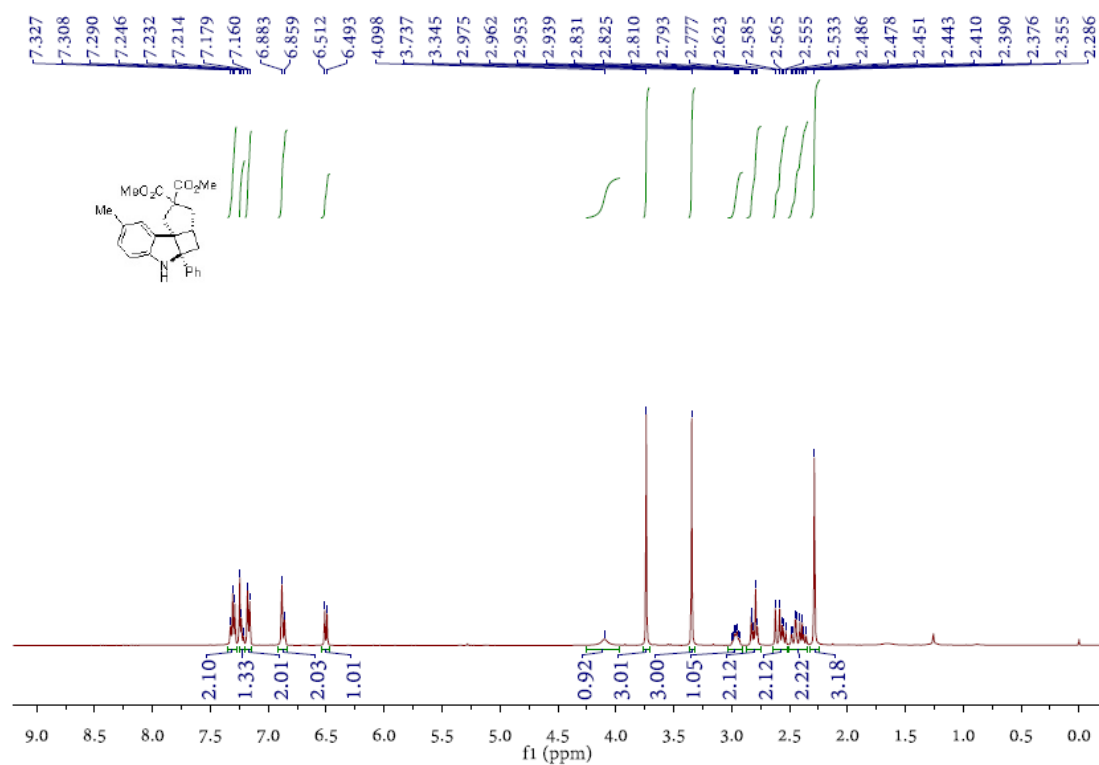
¹H NMR Spectrum of **2m**



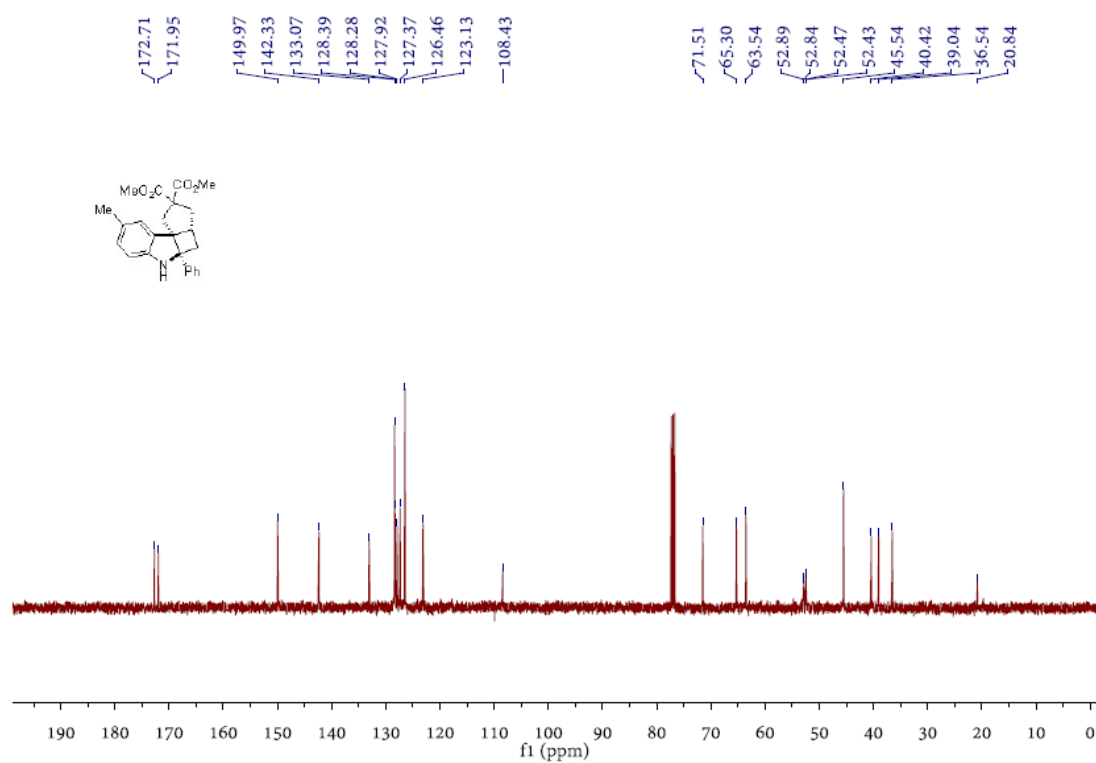
¹³C NMR Spectrum of **2m**



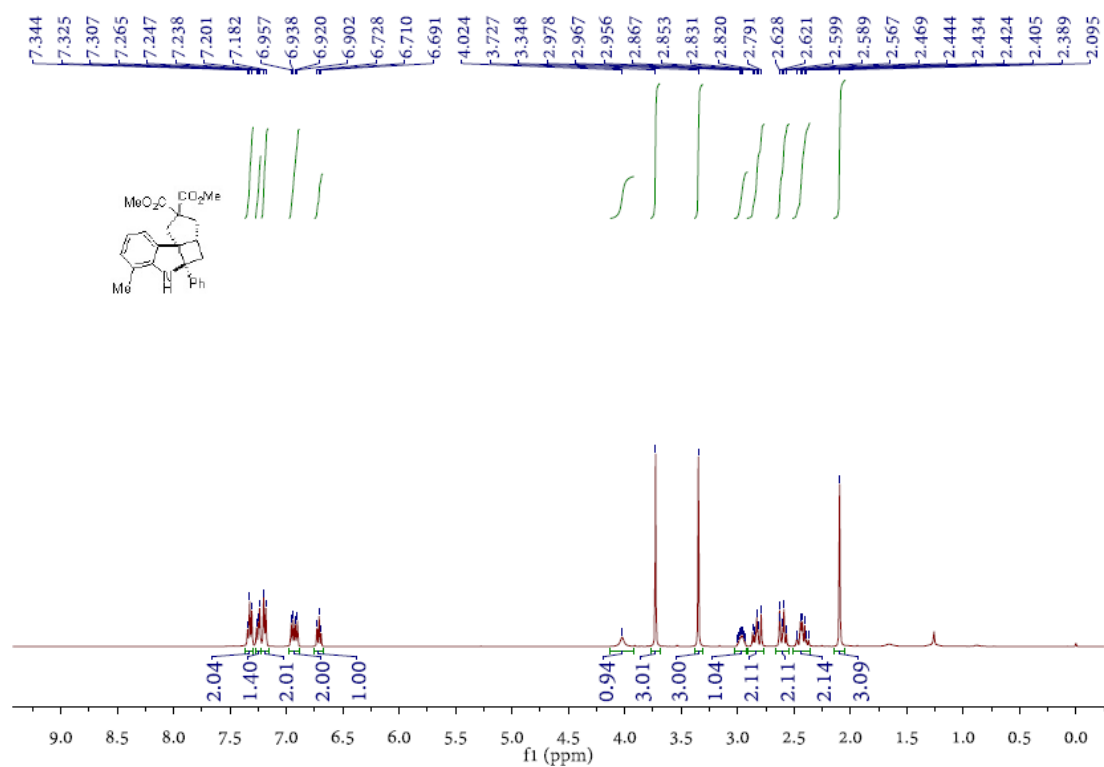
¹H NMR Spectrum of **2n**



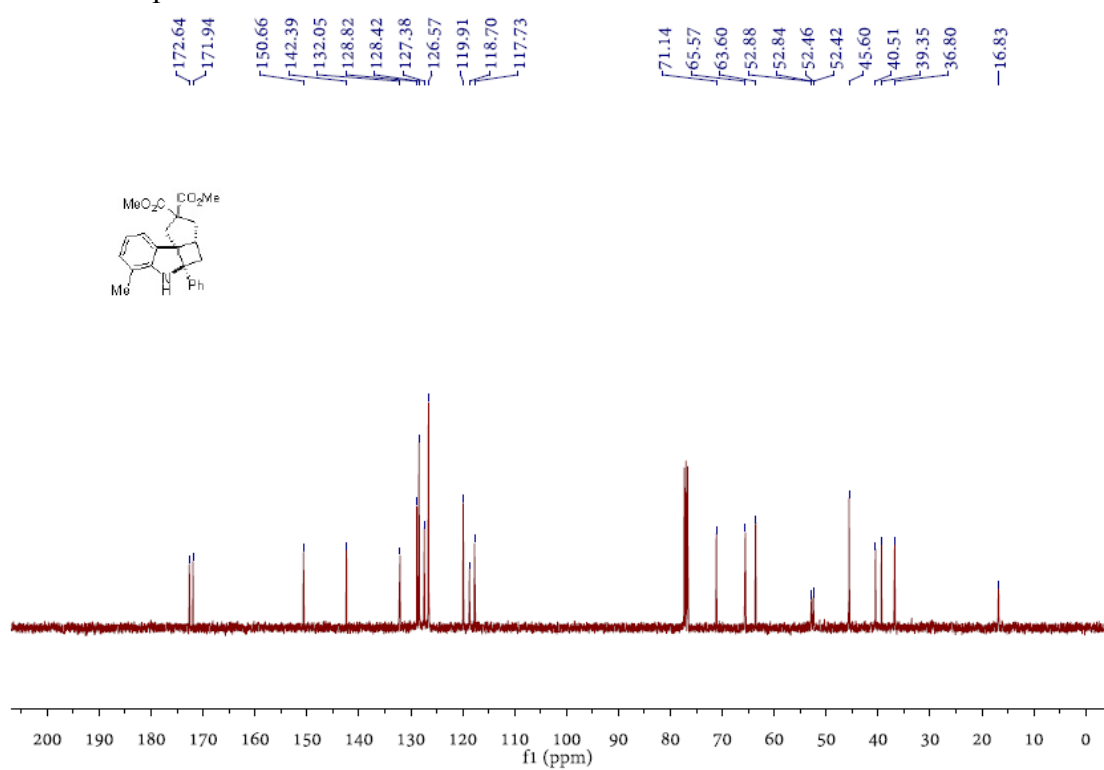
¹³C NMR Spectrum of **2n**



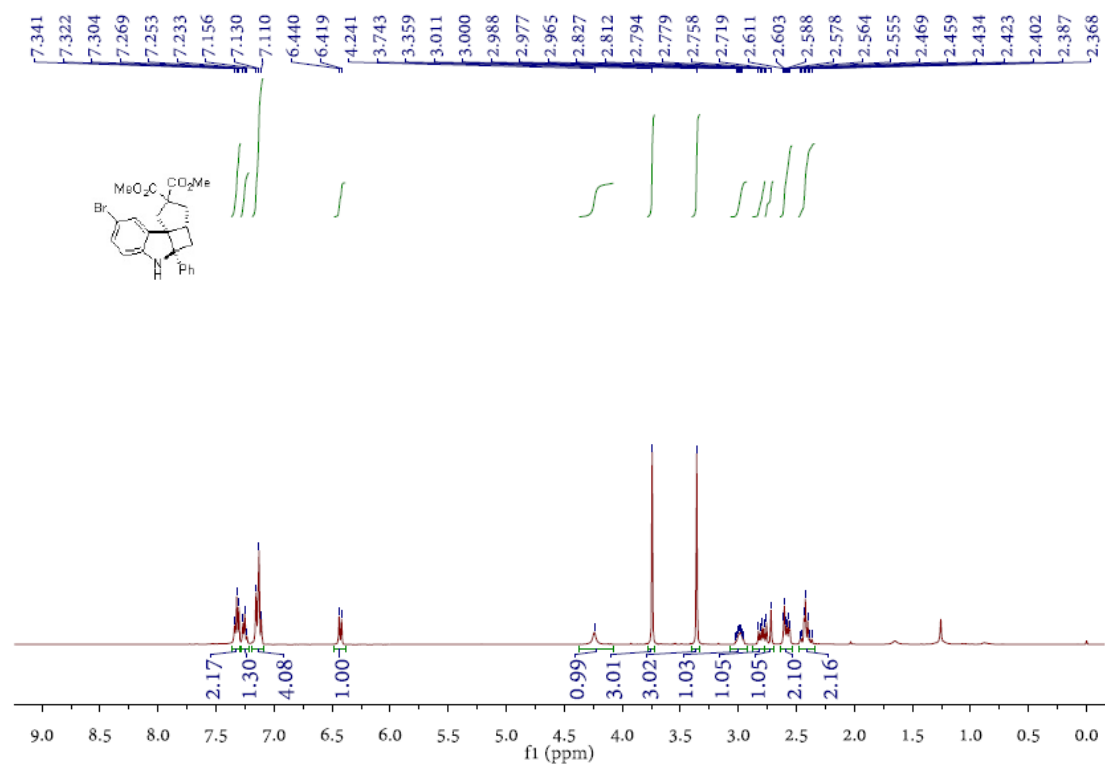
¹H NMR Spectrum of **2o**



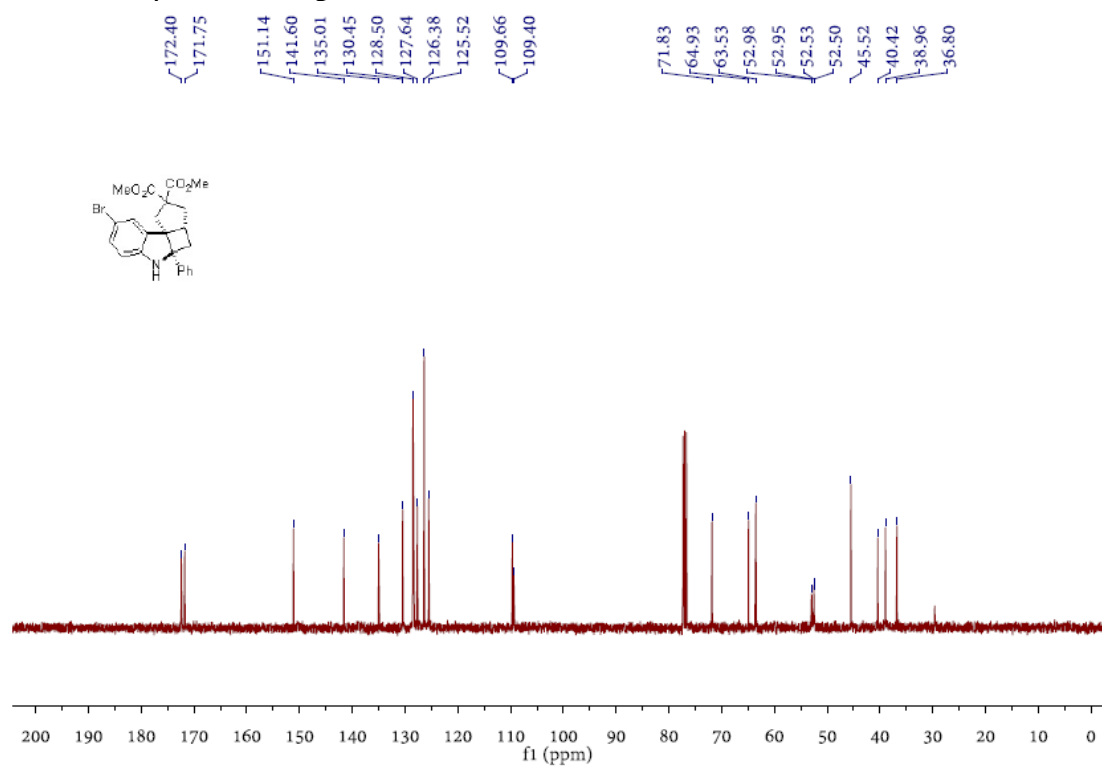
¹³C NMR Spectrum of **2o**



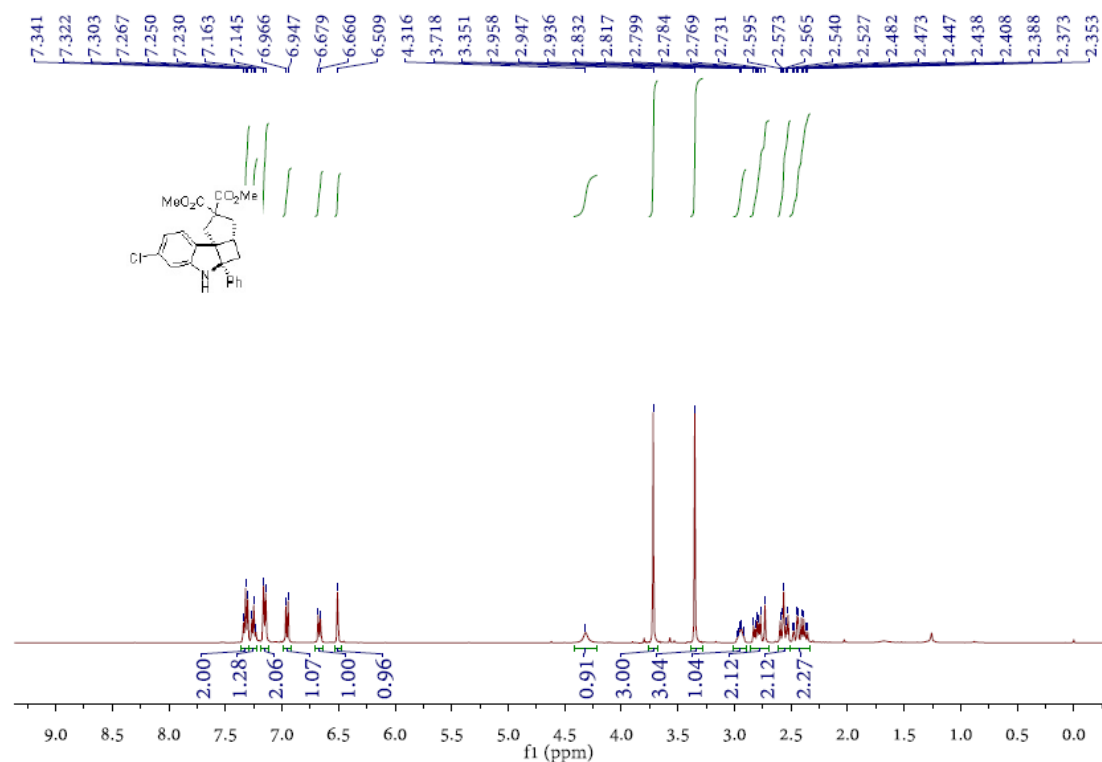
¹H NMR Spectrum of **2p**



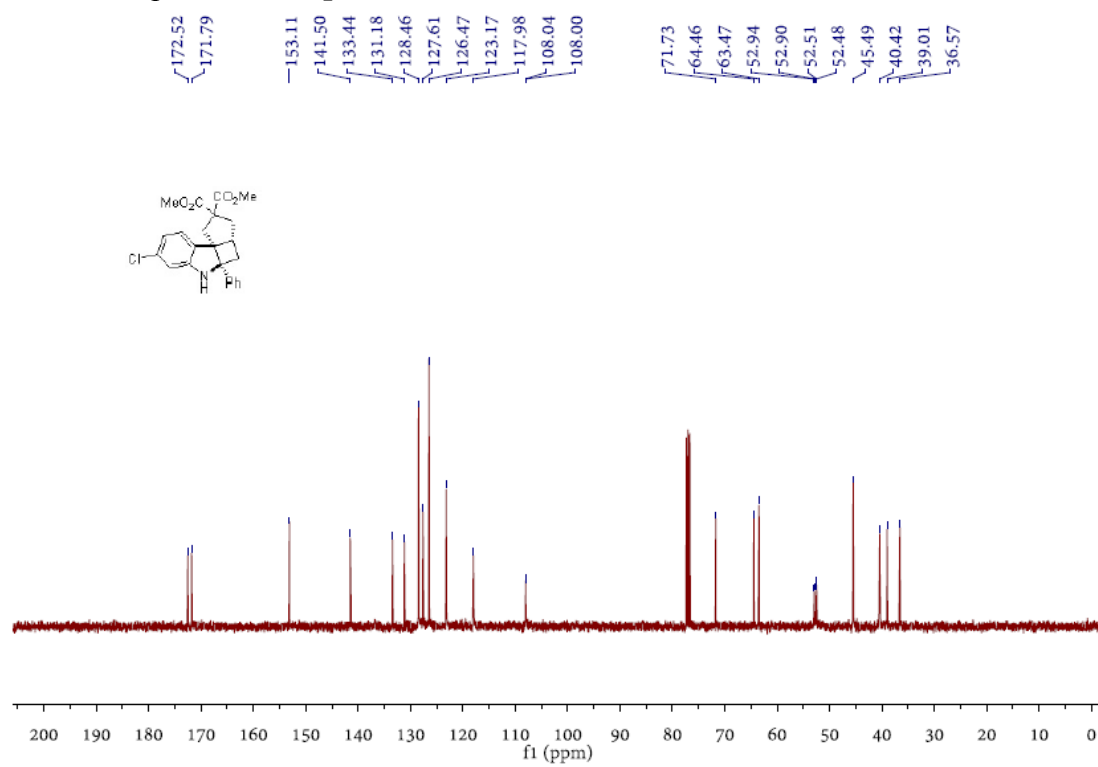
¹³C NMR Spectrum of **2p**



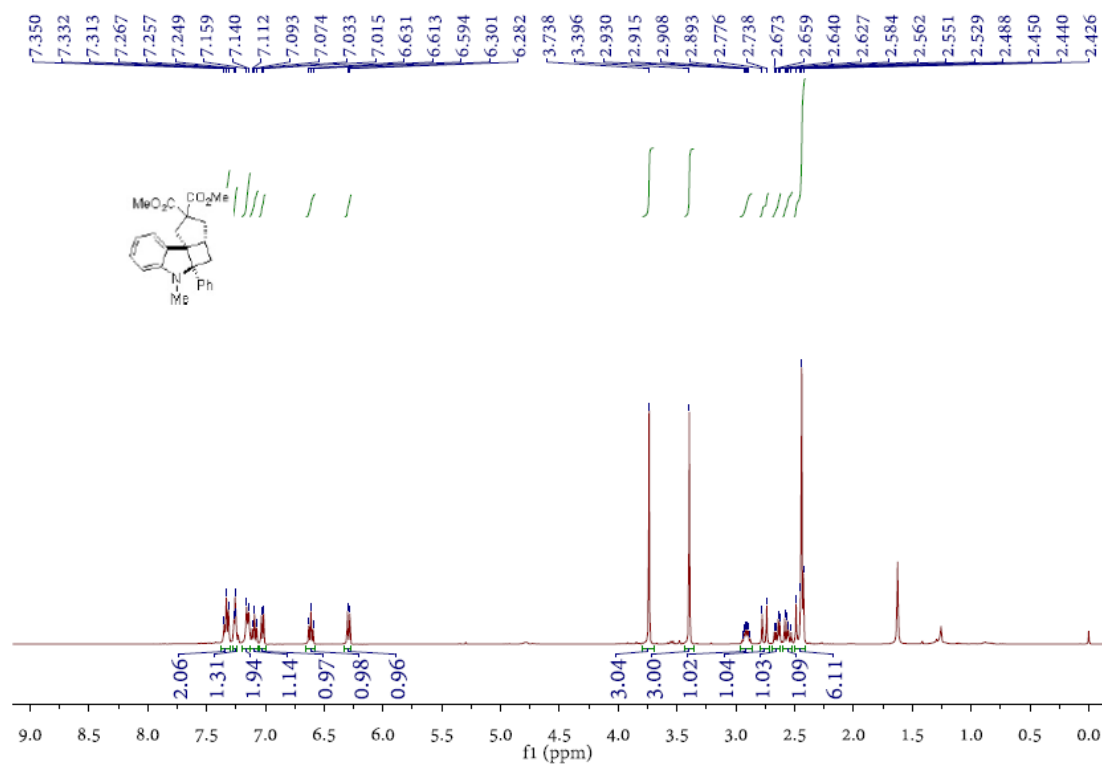
¹H NMR Spectrum of **2q**



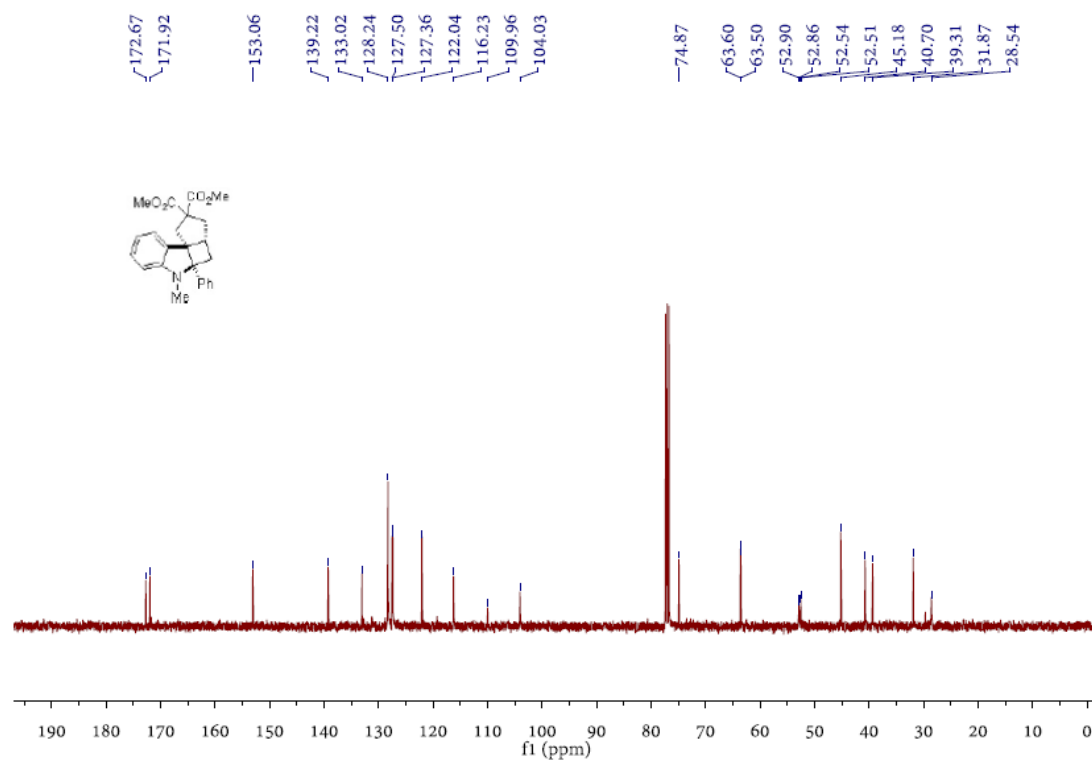
¹³C NMR Spectrum of **2q**



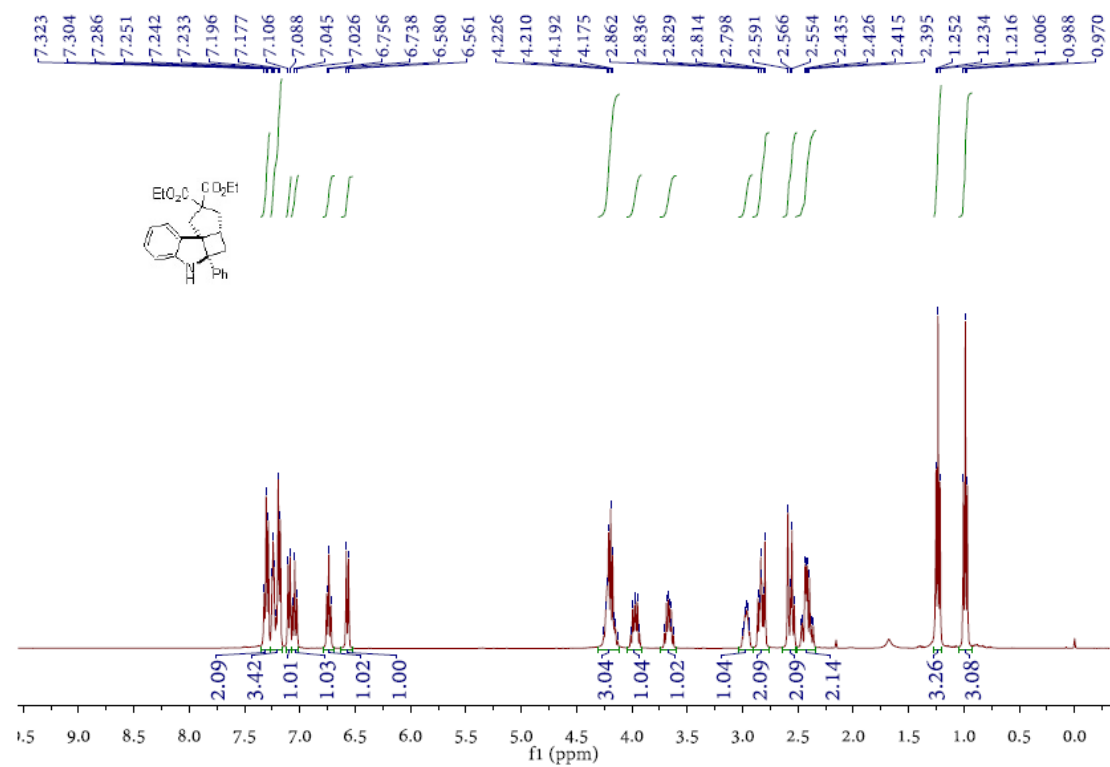
¹H NMR Spectrum of **2r**



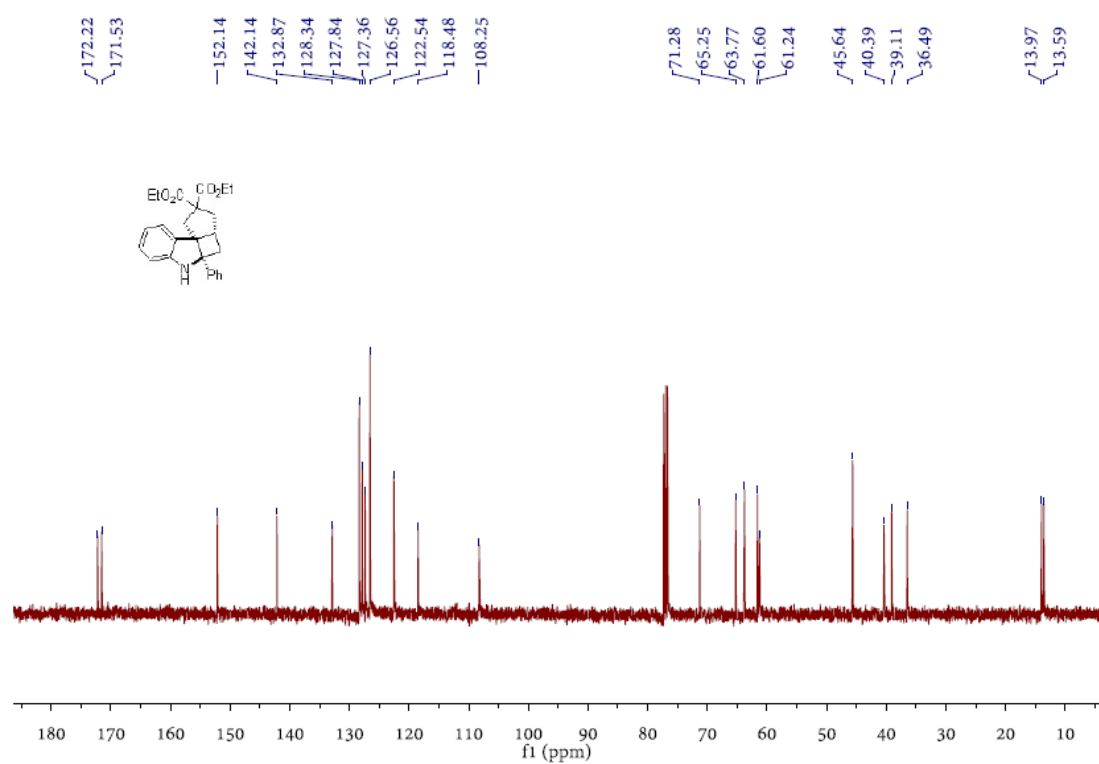
¹³C NMR Spectrum of **2r**



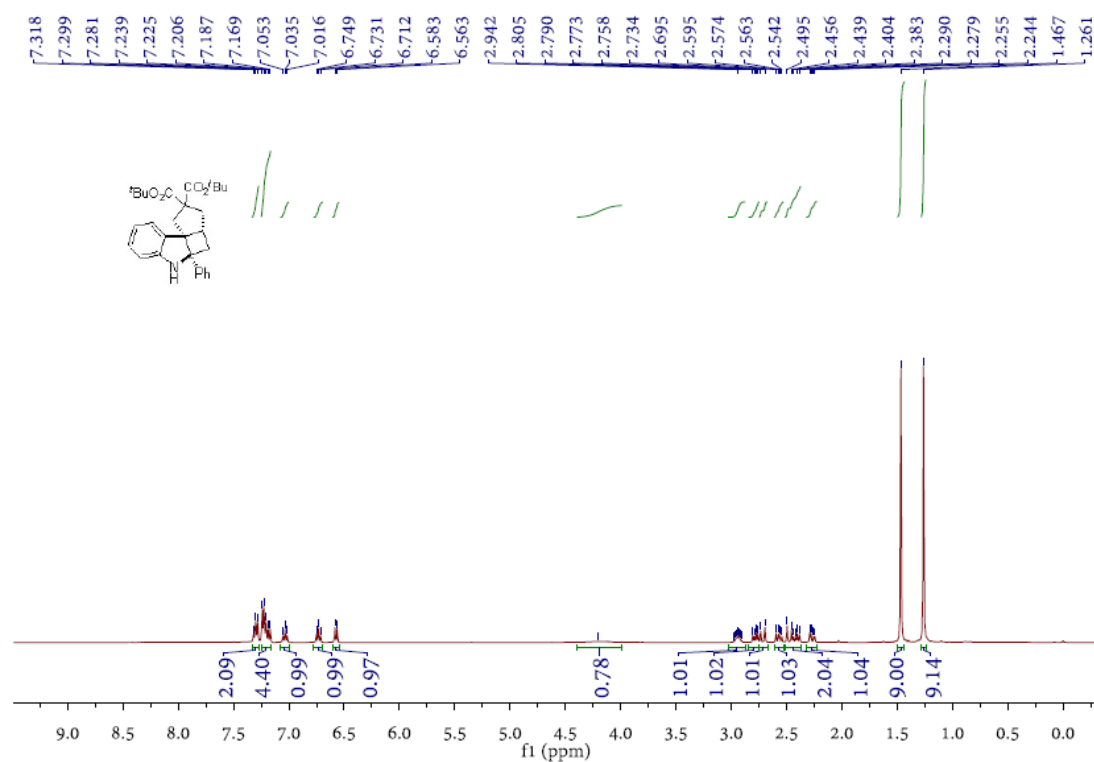
¹H NMR Spectrum of **2s**



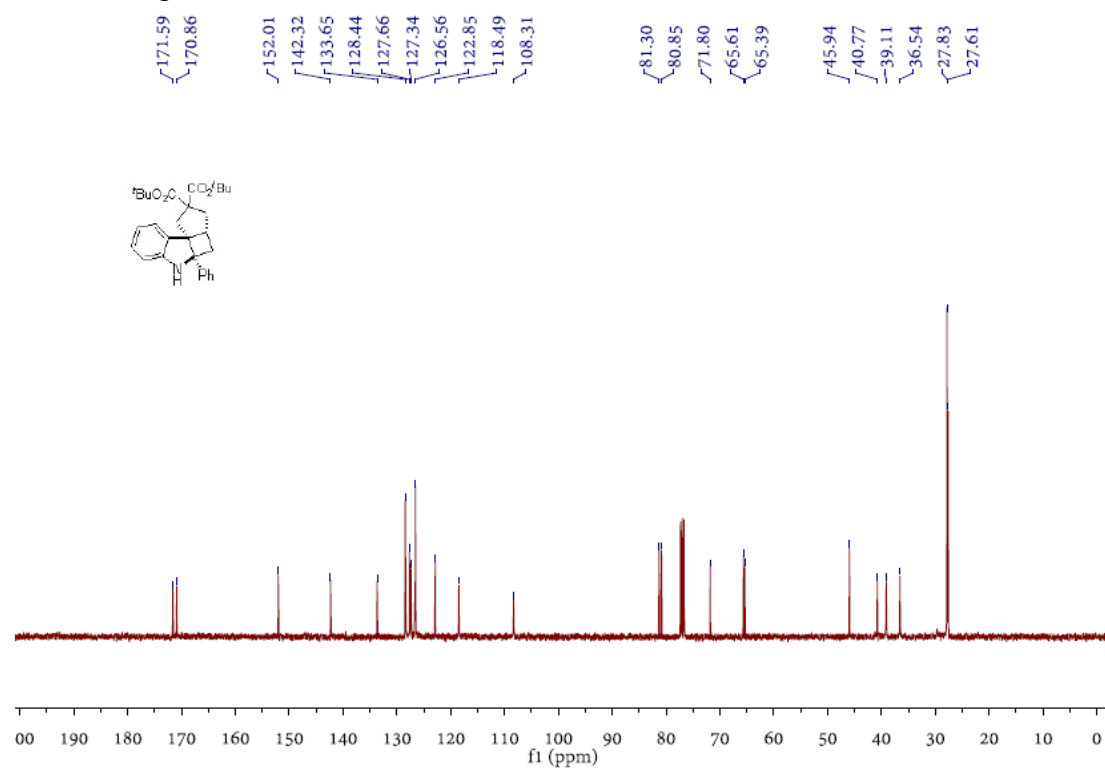
¹³C NMR Spectrum of **2s**



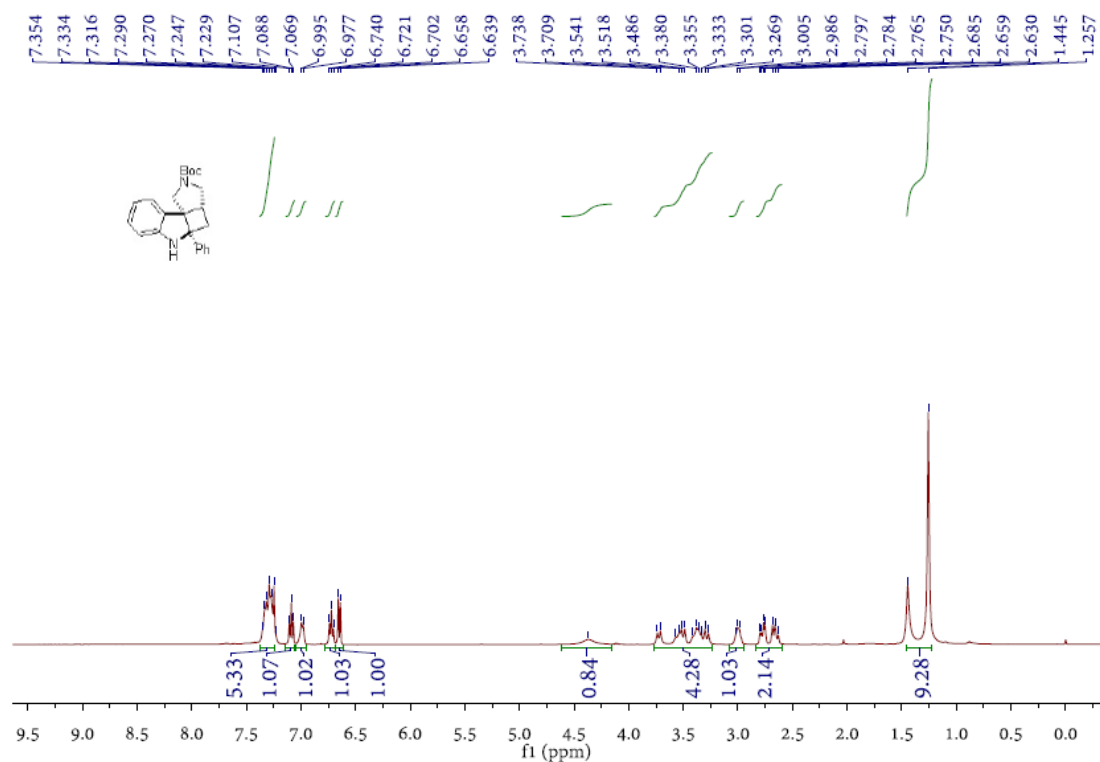
¹H NMR Spectrum of **2t**



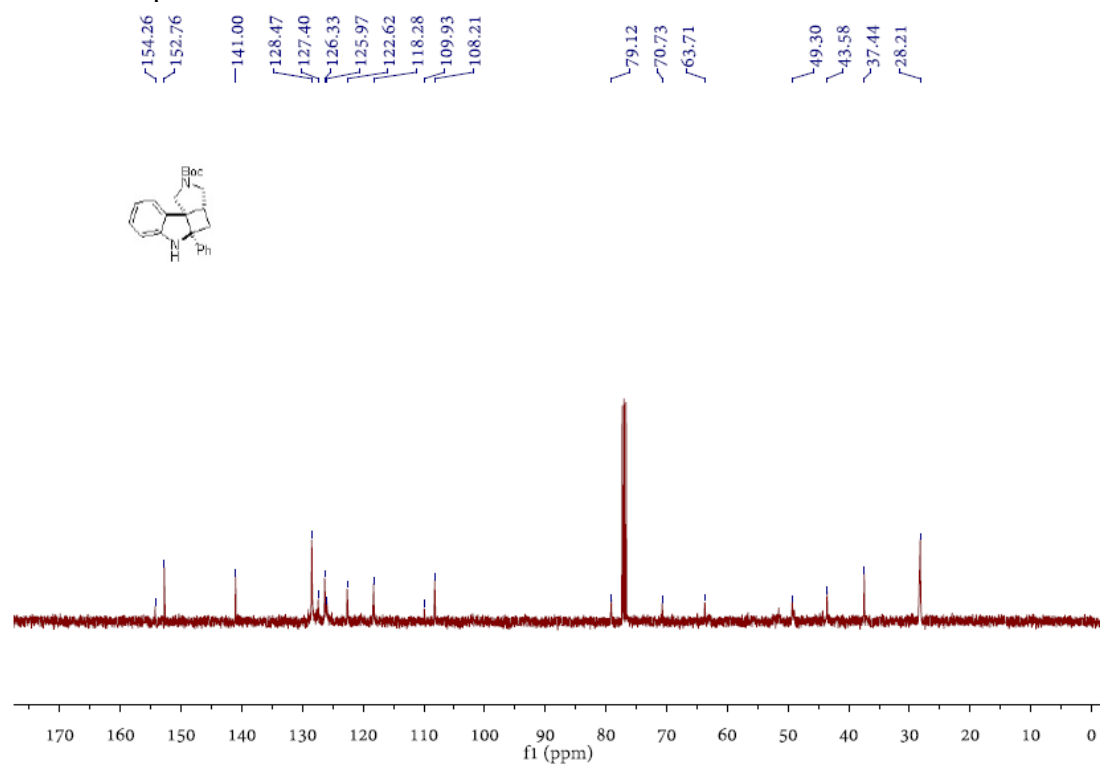
¹³C NMR Spectrum of **2t**



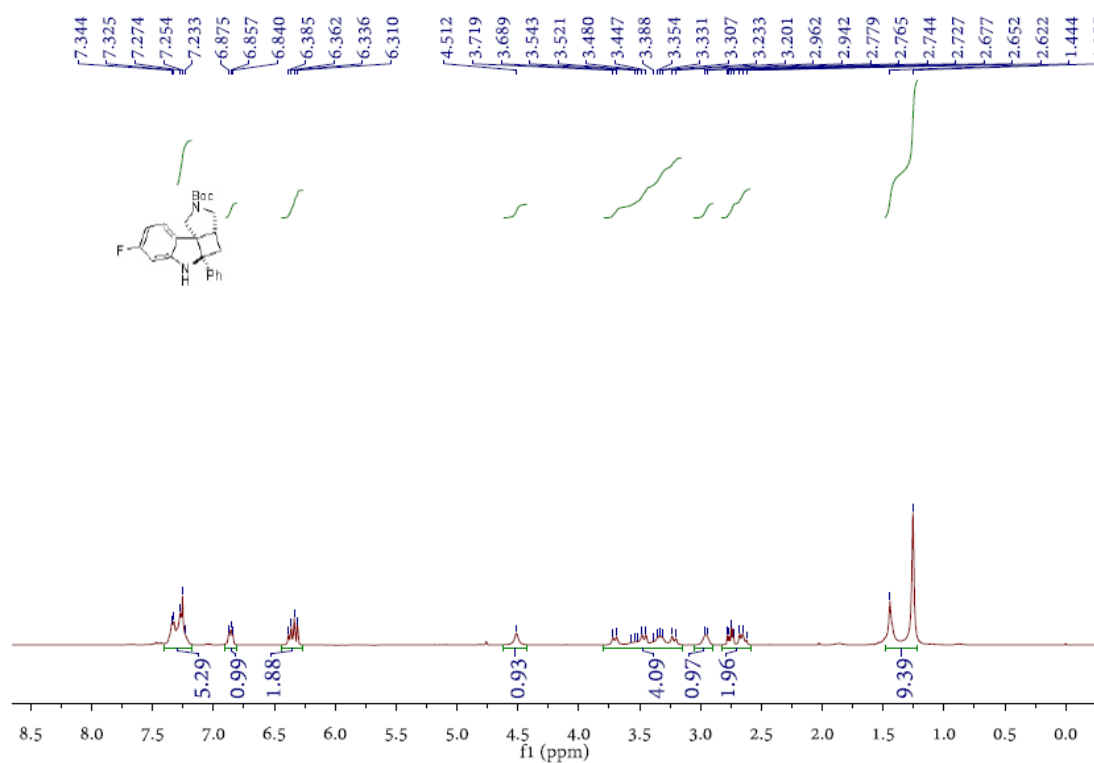
¹H NMR Spectrum of **2u**



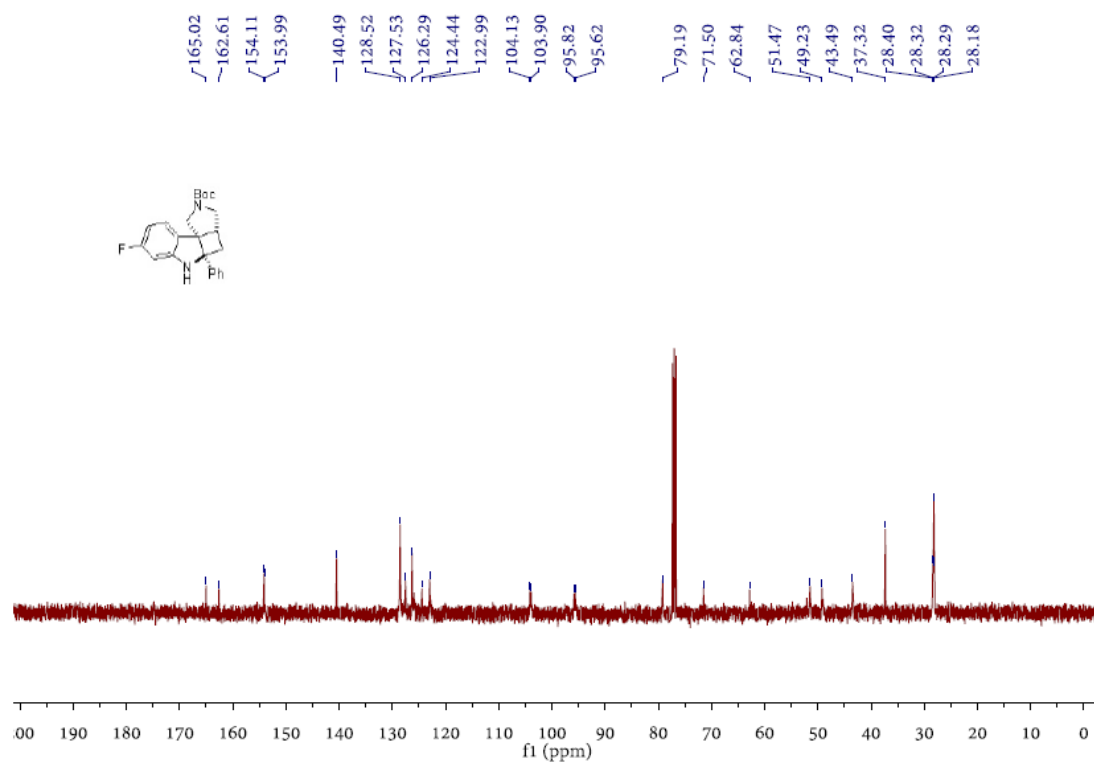
¹³C NMR Spectrum of **2u**



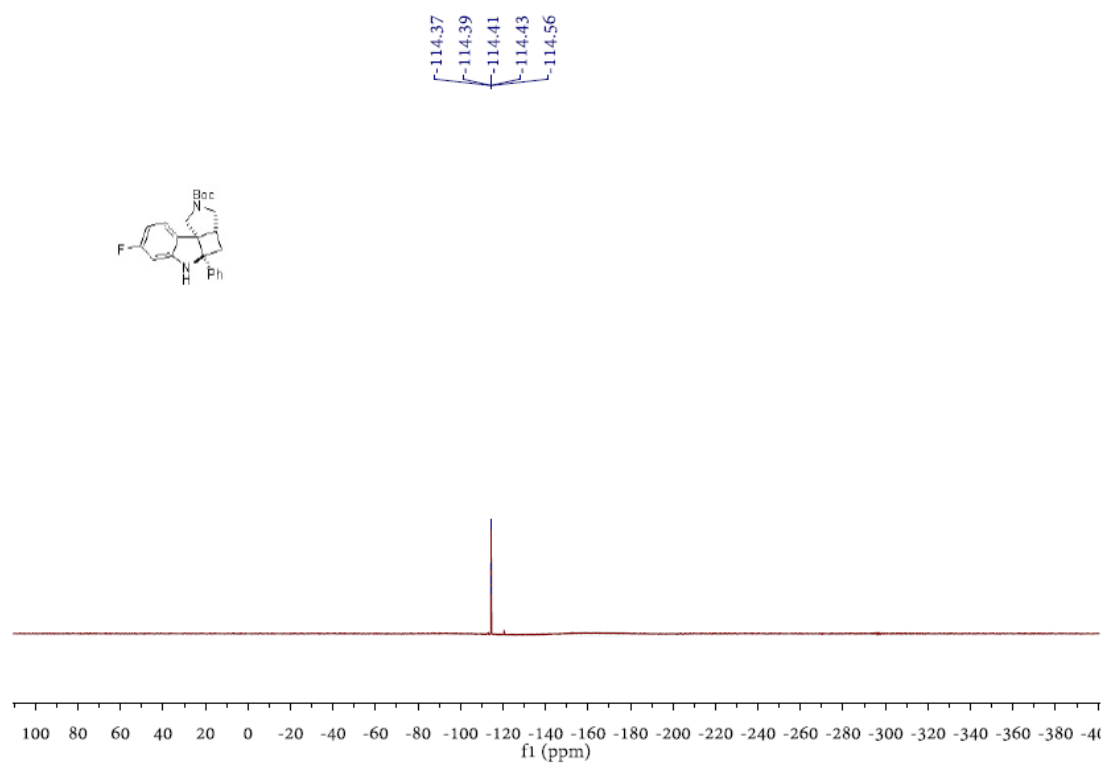
¹H NMR Spectrum of **2v**



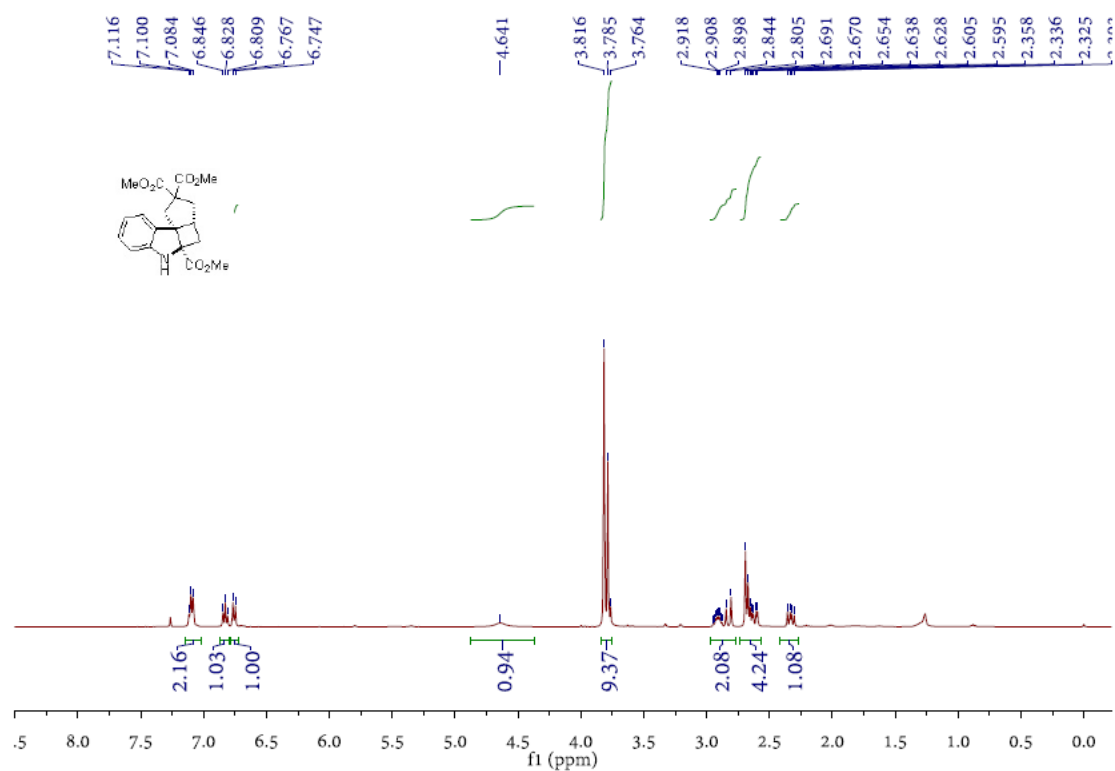
¹³C NMR Spectrum of **2v**



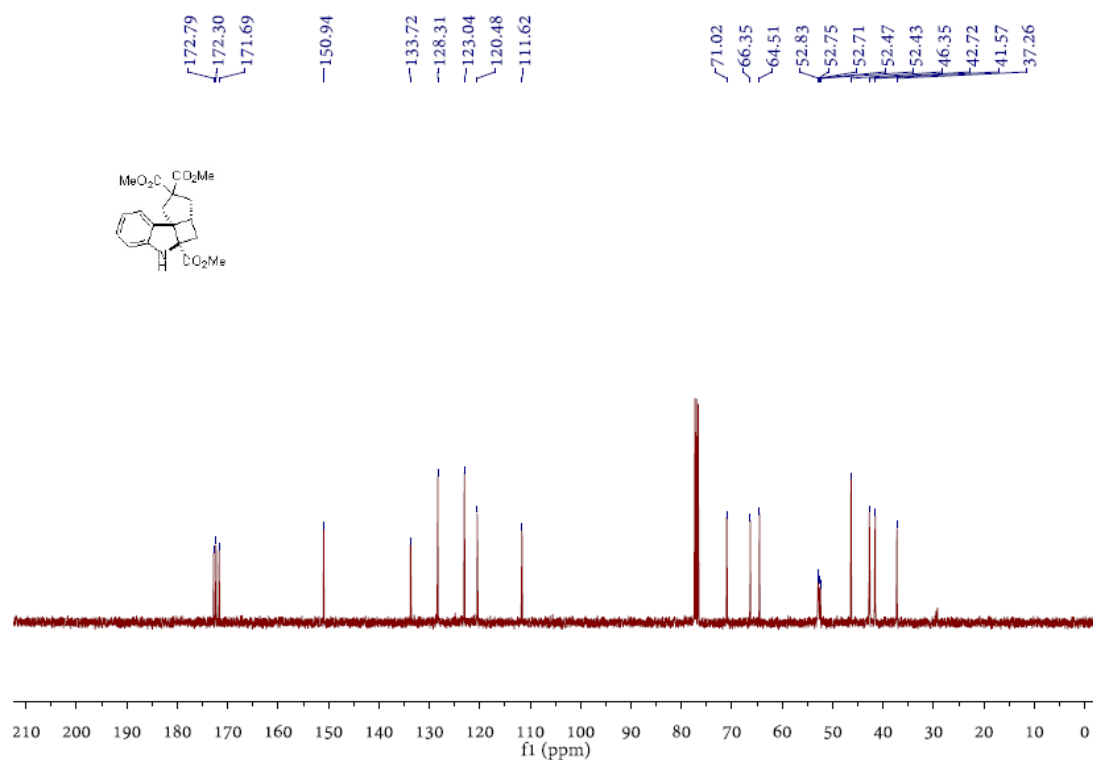
¹⁹F NMR Spectrum of **2v**



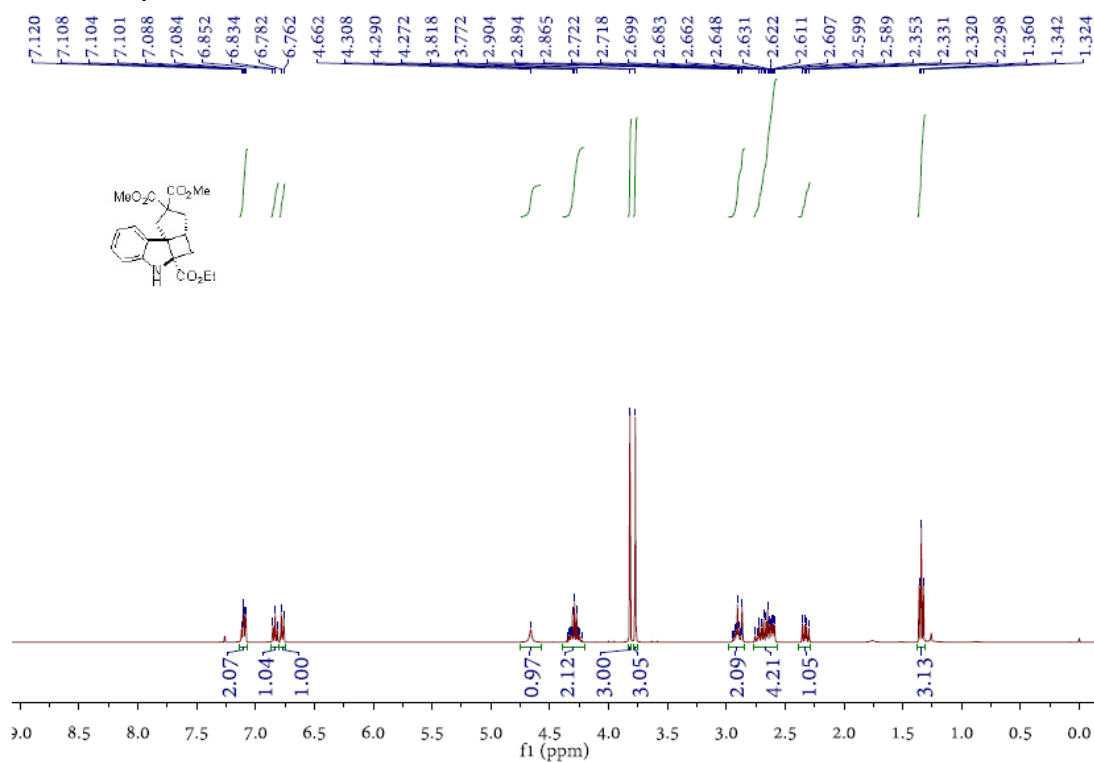
¹H NMR Spectrum of **2w**



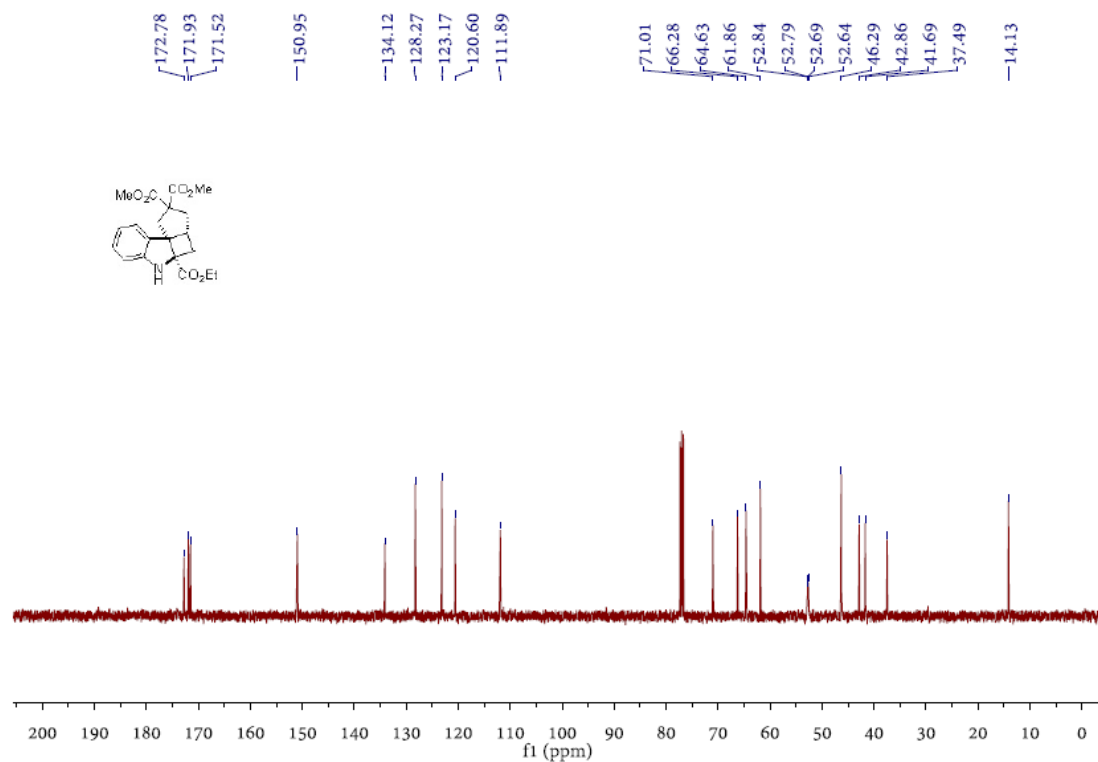
¹³C NMR Spectrum of **2w**



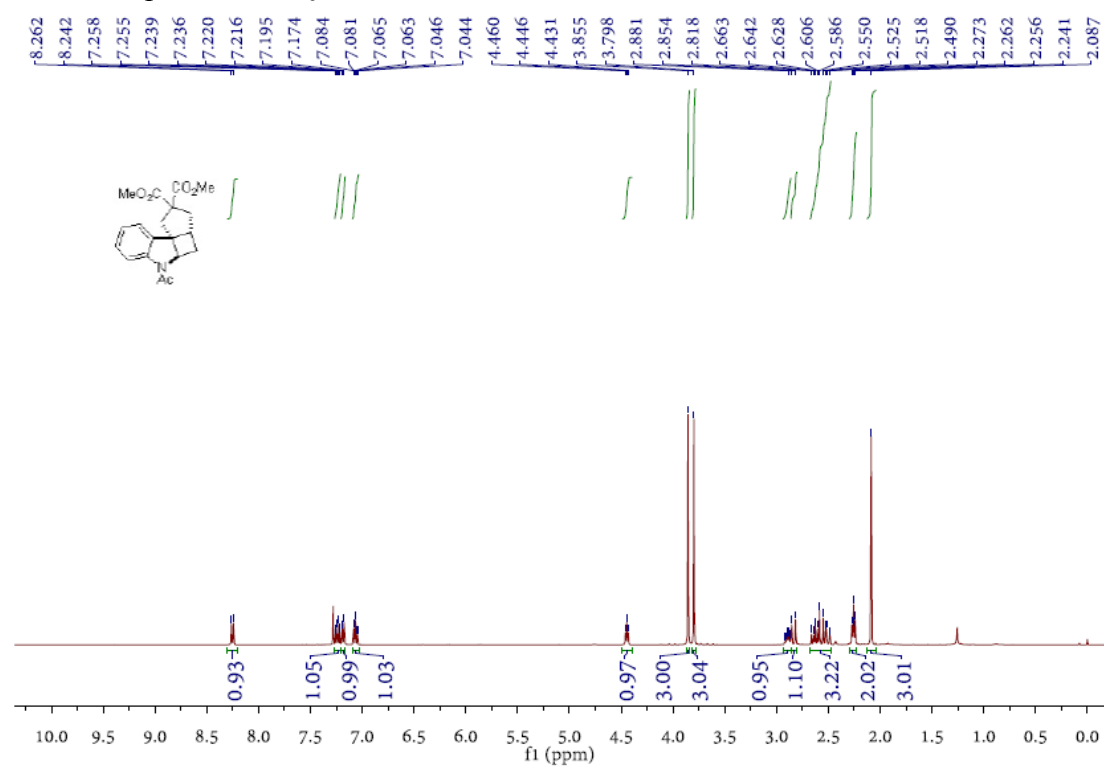
¹H NMR Spectrum of **2x**



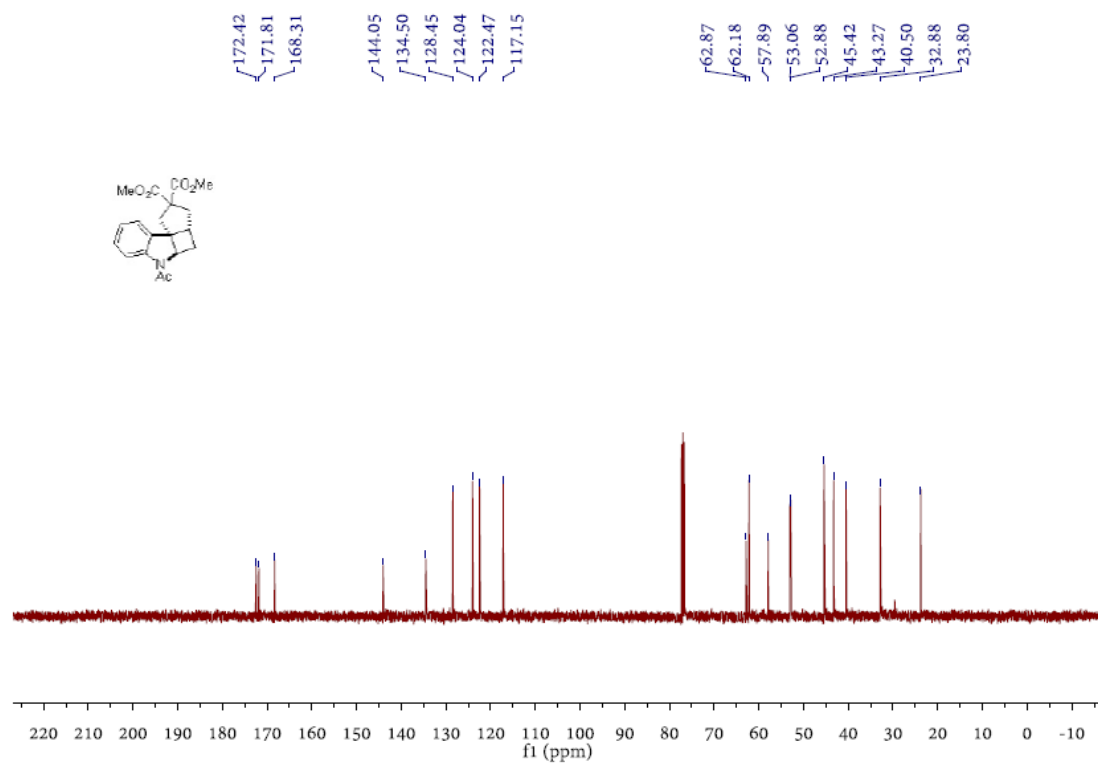
¹³C NMR Spectrum of **2x**



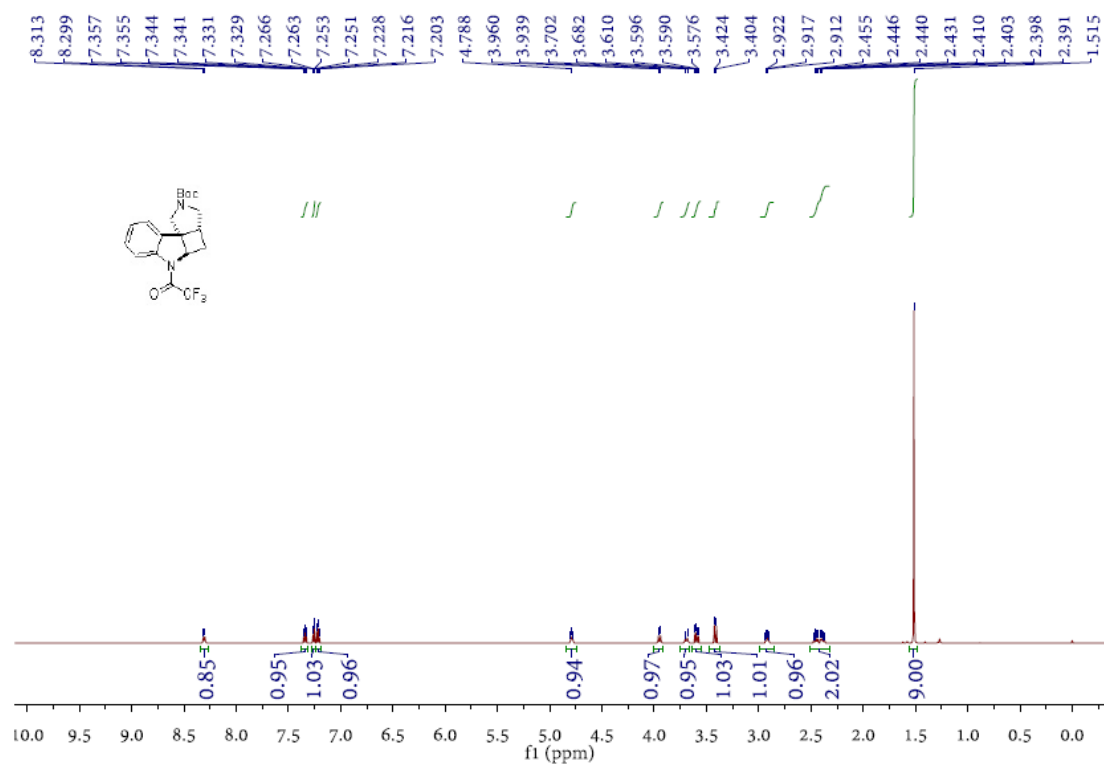
¹H NMR Spectrum of **2y**



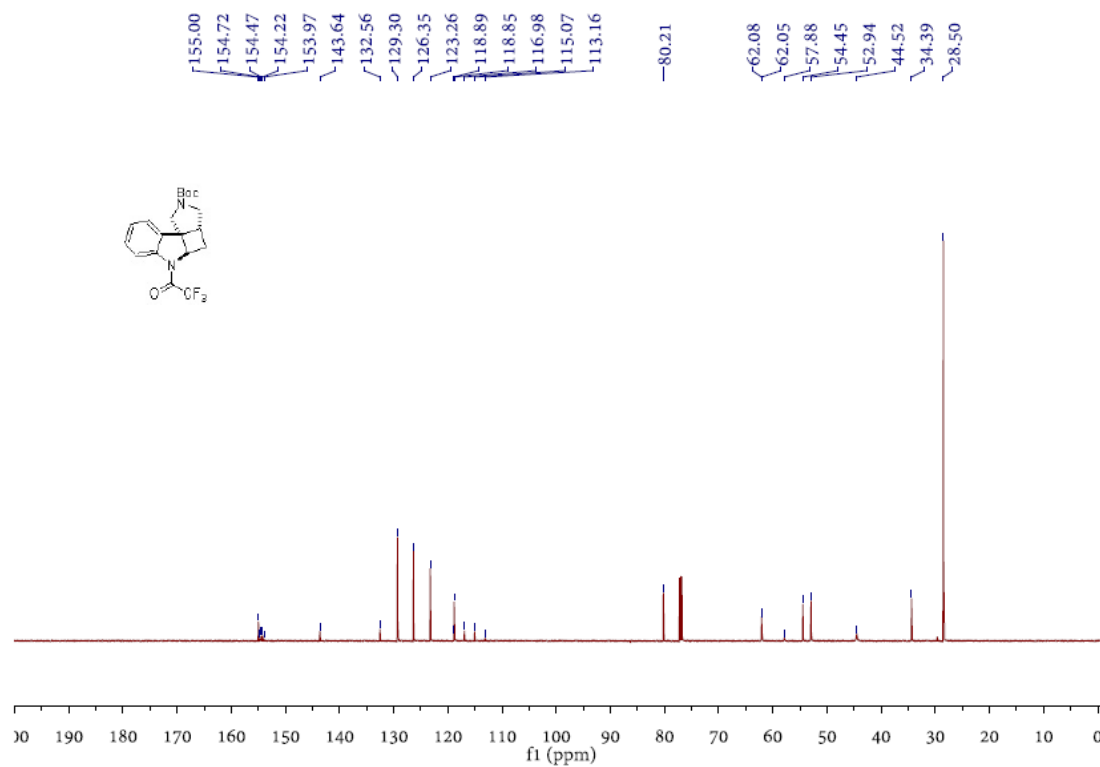
¹³C NMR Spectrum of **2y**



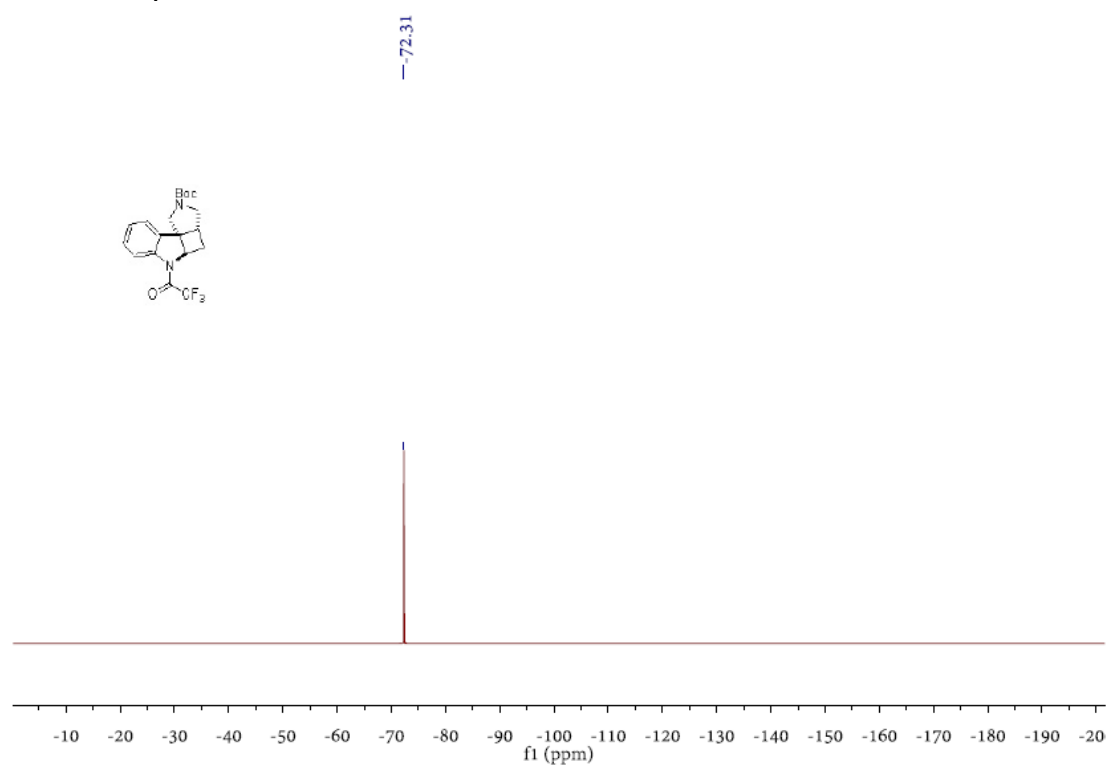
¹H NMR Spectrum of **2z**



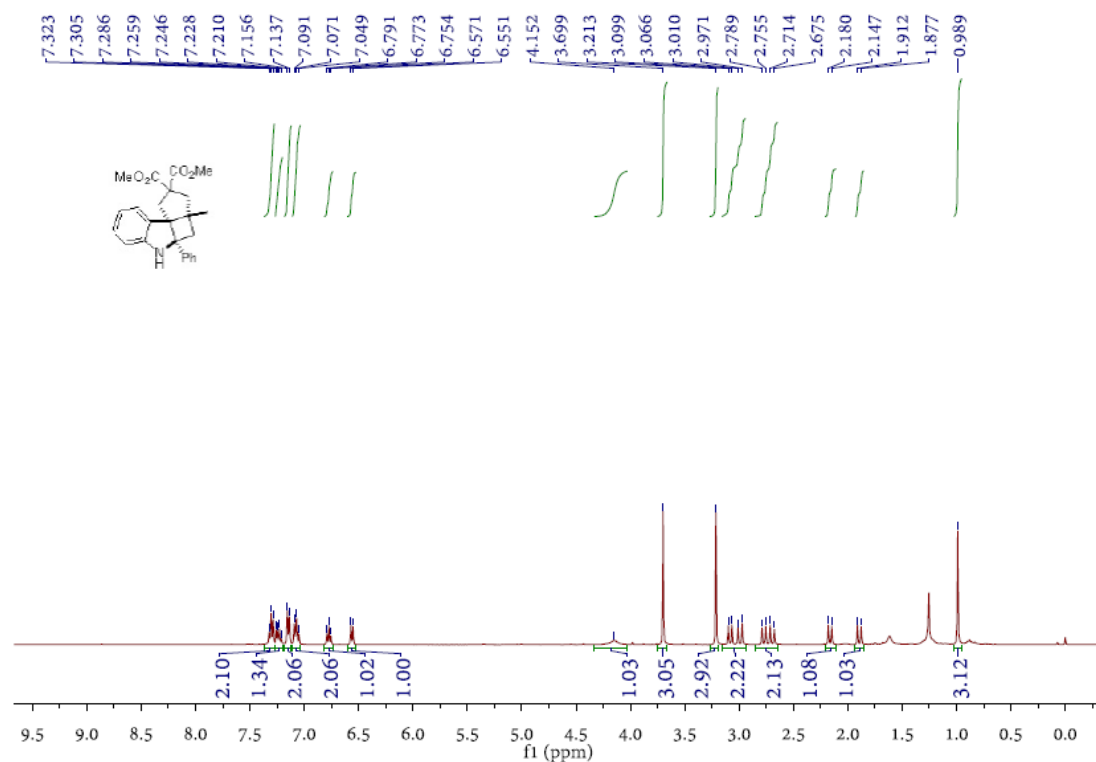
¹³C NMR Spectrum of **2z**



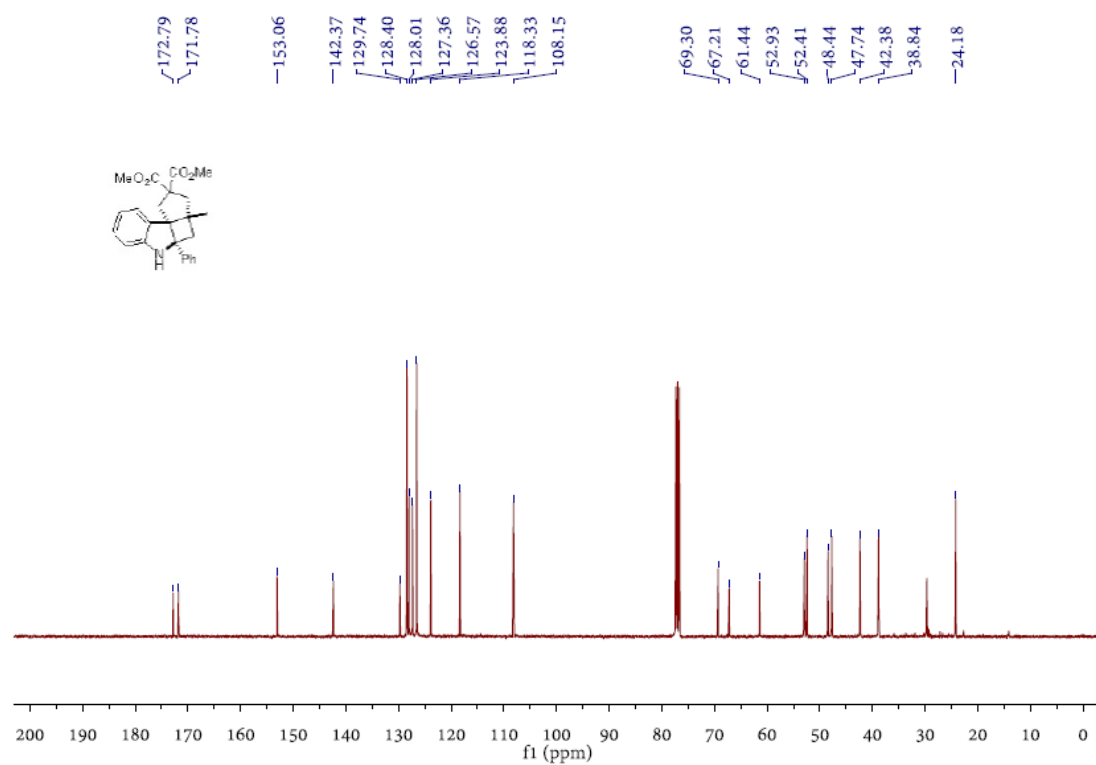
¹⁹F NMR Spectrum of **2z**



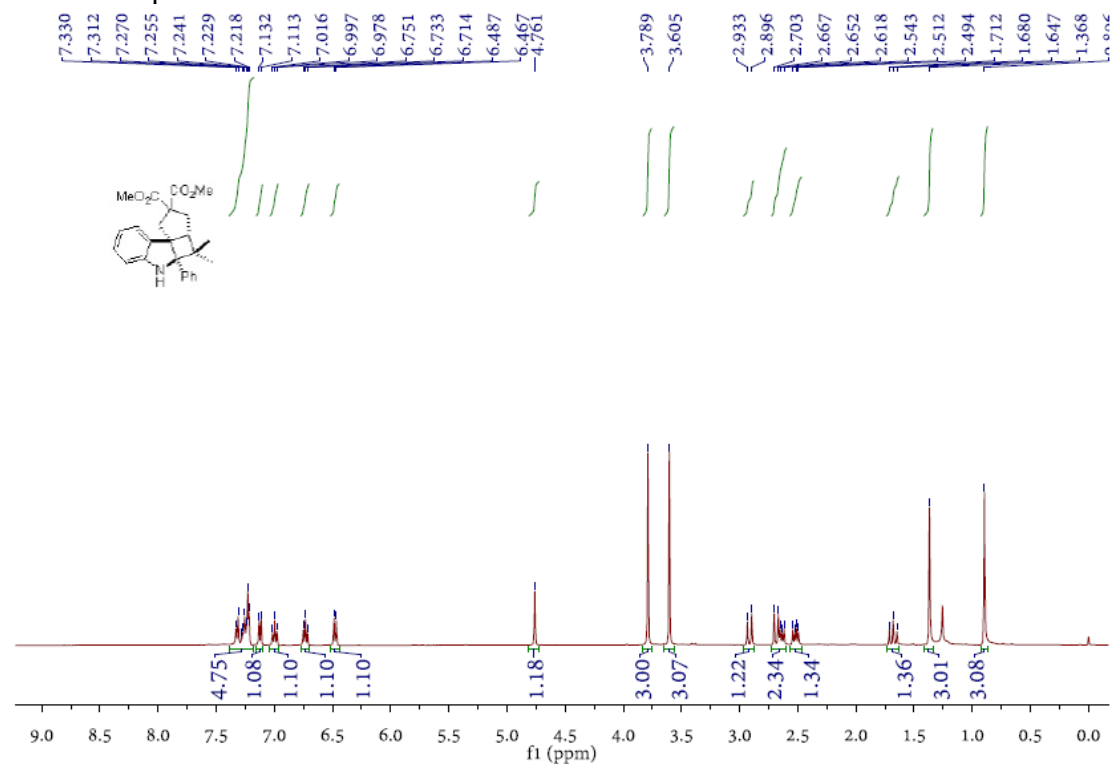
¹H NMR Spectrum of **3**



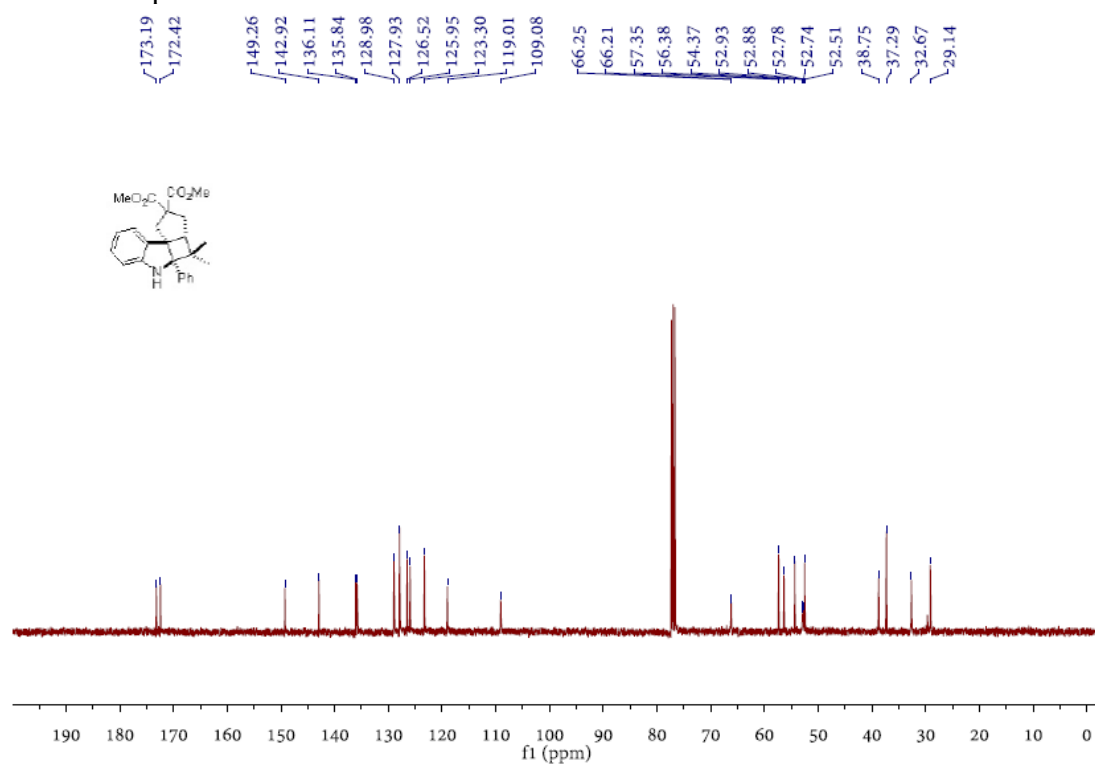
¹³C NMR Spectrum of **3**



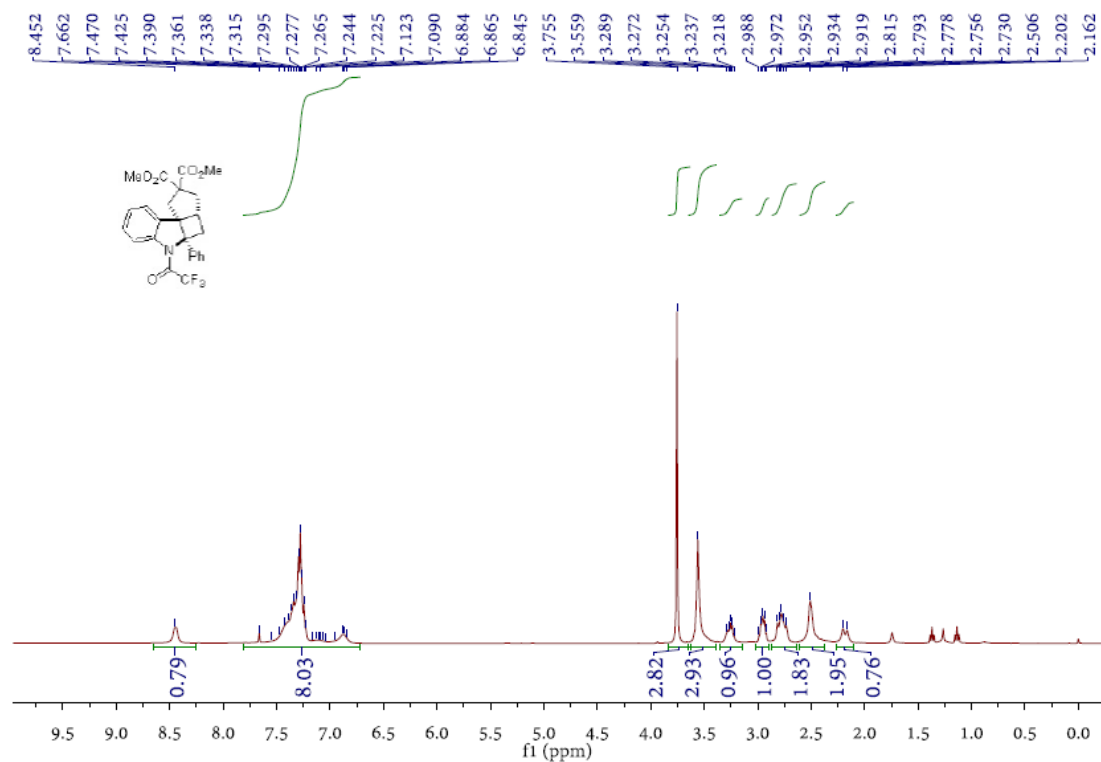
¹H NMR Spectrum of **4**



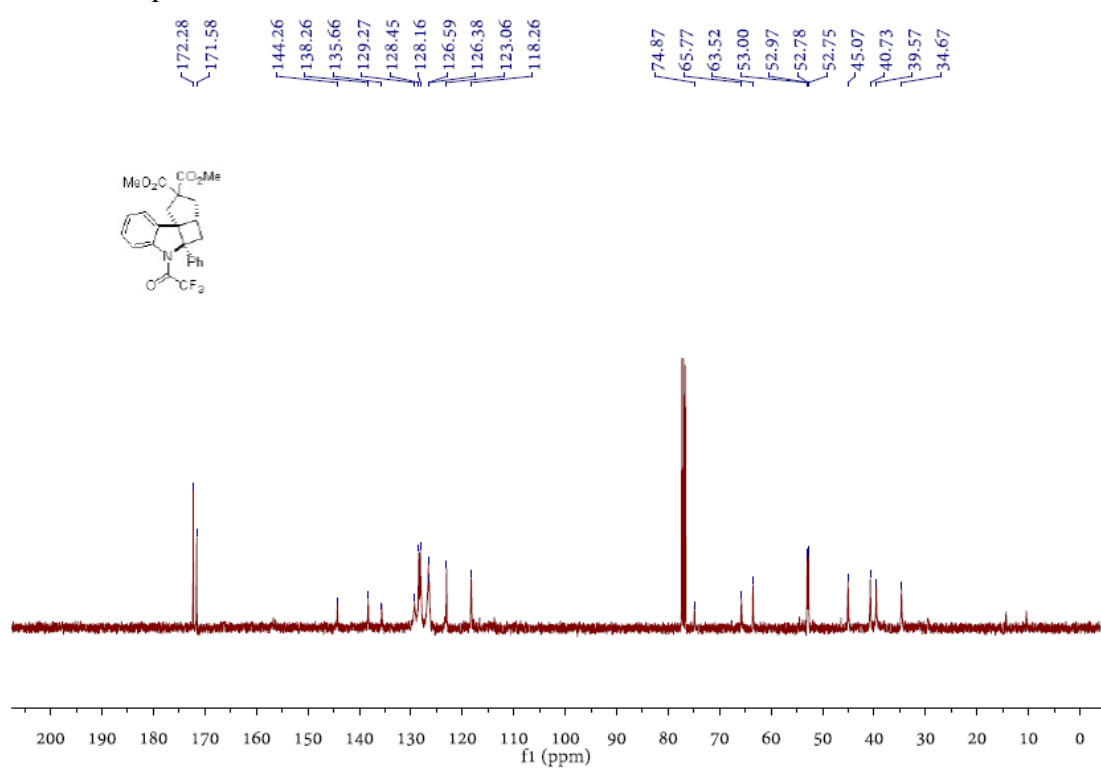
¹³C NMR Spectrum of **4**



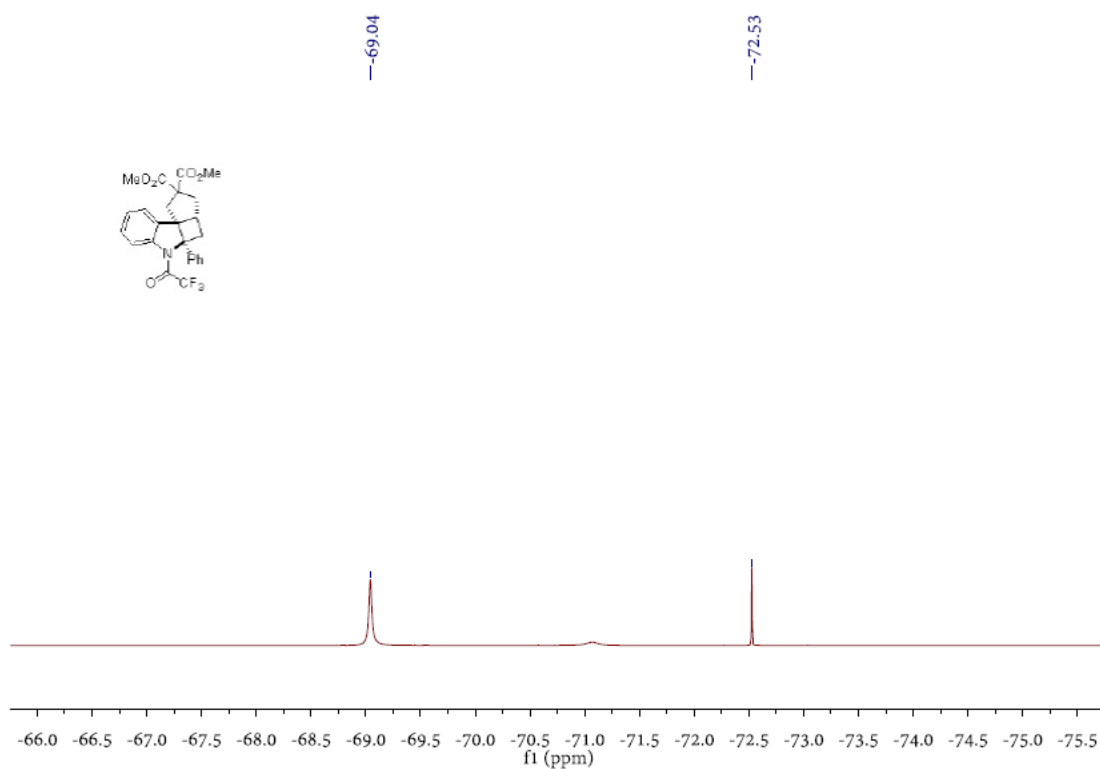
¹H NMR Spectrum of **6**



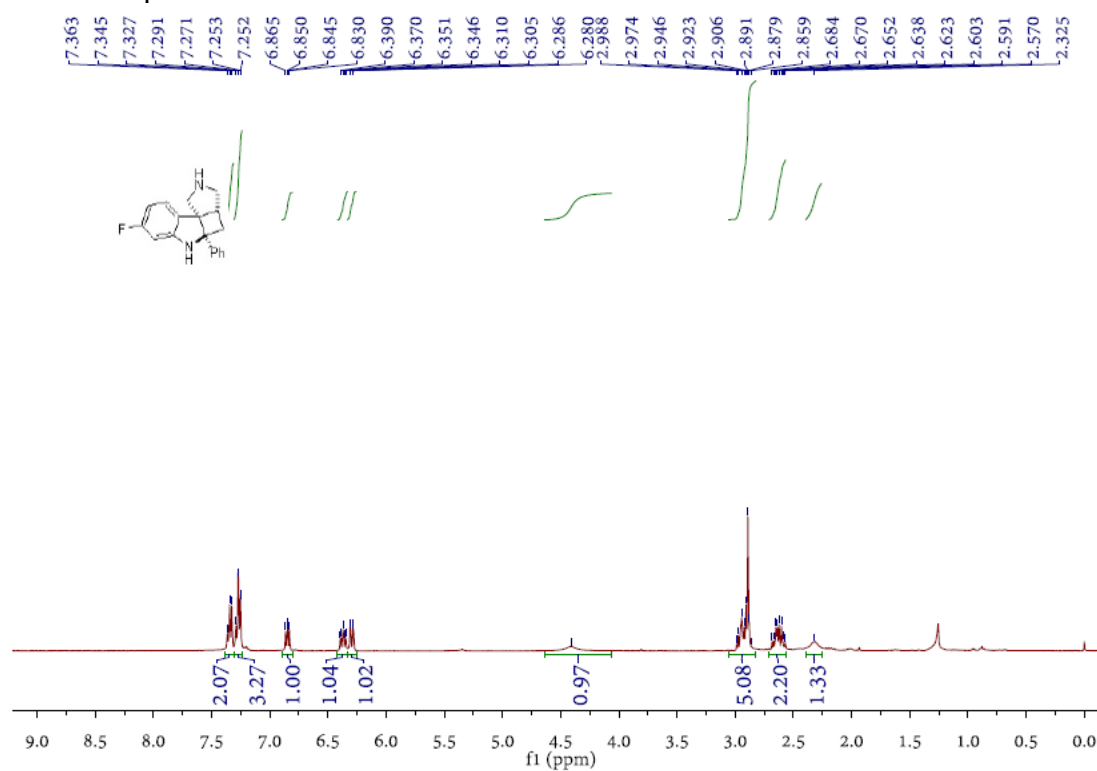
¹³C NMR Spectrum of **6**



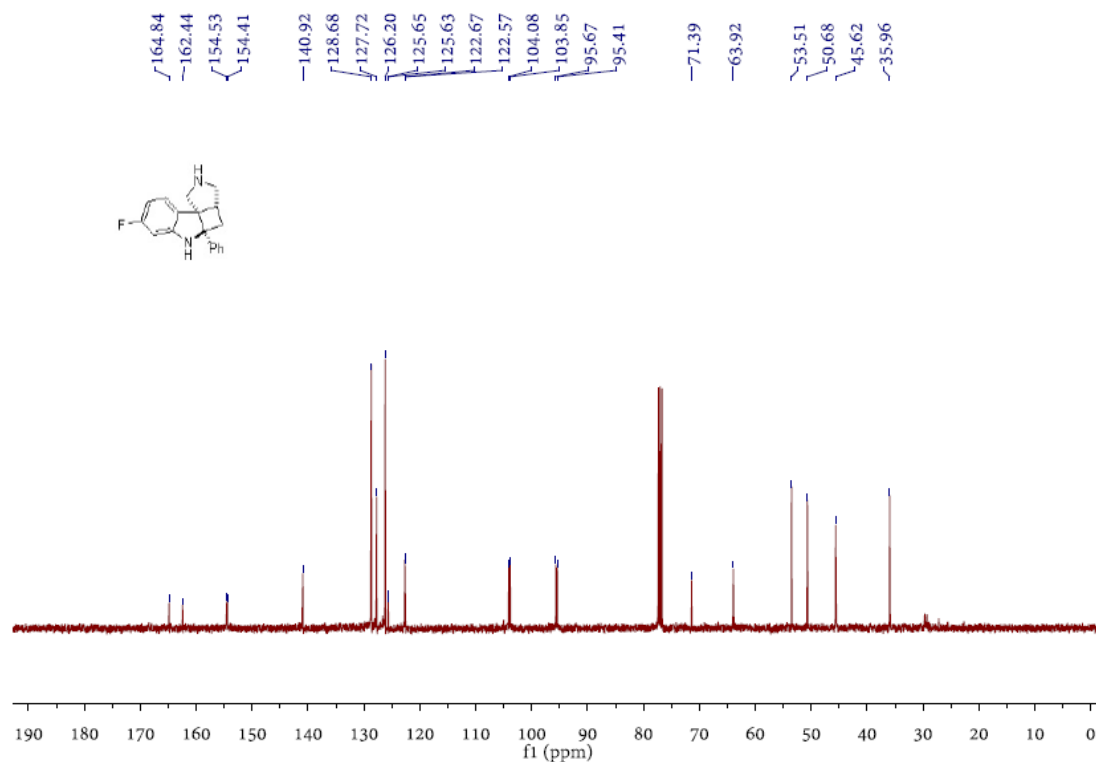
¹⁹F NMR Spectrum of **6**



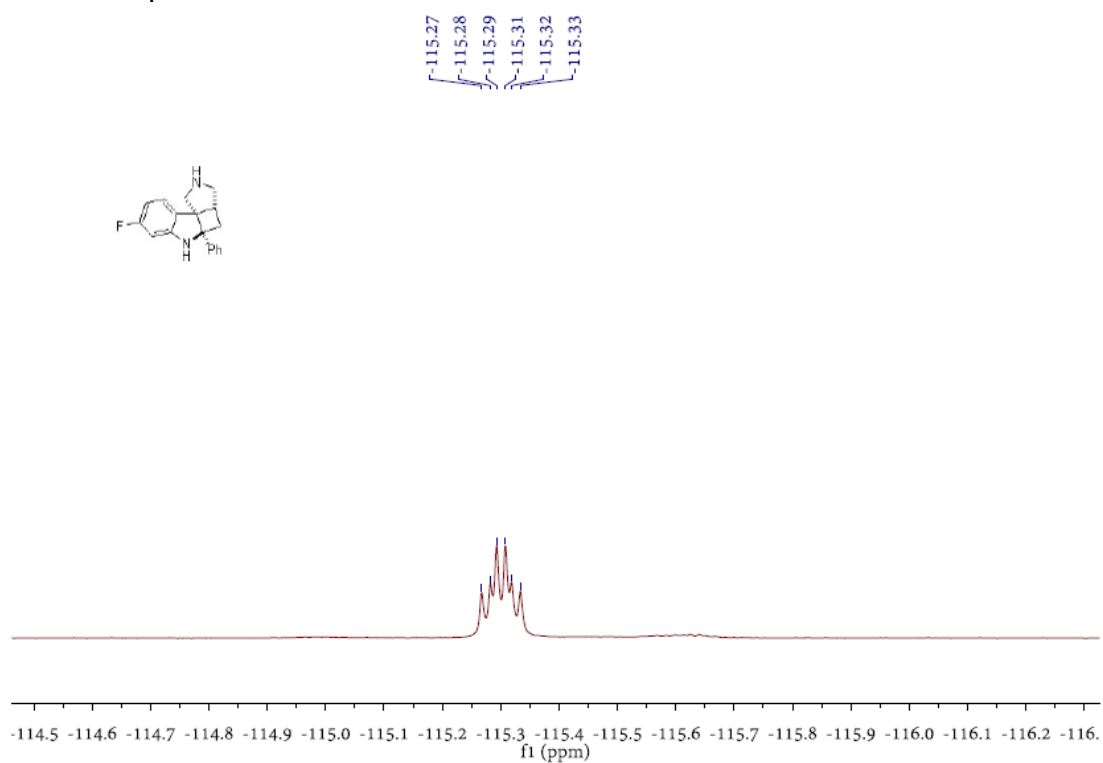
¹H NMR Spectrum of **7**



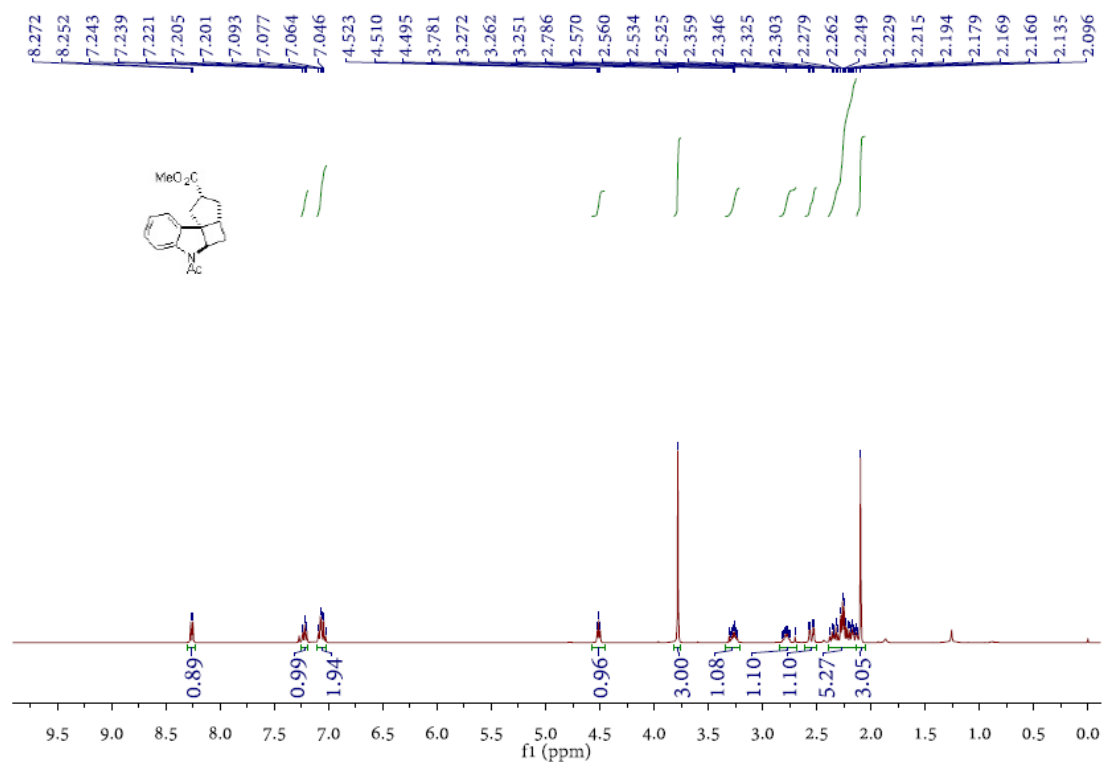
¹³C NMR Spectrum of **7**



¹⁹F NMR Spectrum of **7**



¹H NMR Spectrum of **8**



¹³C NMR Spectrum of **8**

