Supporting Information

Mild Arylboronic Acid Catalyzed Selective [4+3] Cycloadditions: Access to Cyclohepta[b]benzofurans and Cyclohepta[b]indoles

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General Information

All solvents and chemicals (AR grade) were obtained from commercial sources and were used without further purification. Petroleum ether (PE) refers to the fraction boiling in the 60–90℃ range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on Silicycle silica gel (300–400 mesh). ^{1}H and ^{13}C NMR spectra were obtained using Bruker DRX 300 (300 MHz) and Bruker DRX 400 (400 MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. Mass spectra were conducted at Agilent Technologies 5973N (EI). The known compounds were identified by comparison of their physical and spectral data with those reported in the literature. Diastereomeric ratios (dr) were determined by crude ^{1}H NMR. Chemical shifts were expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants were reported as Hertz (Hz), signal shapes and splitting patterns were indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dm = doublet of a multiplet, m = multiplet, br = broad.

Compound **1a**, **1b**, **1c** were prepared according to published literature procedures[1]; **1d**, **1h** were prepared according to published literature procedures[2]; **1e** was prepared according to published literature procedures[3]; **1i** was prepared according to published literature procedures[4]; **1f**, **1g, 1k** were prepared according to published literature procedures[5]; **1j** was prepared according to published literature procedures[6] (Figure 1). Dienes were all commercially available.

The alcohols (1a-1k) used in mild and selective [4+3] Cycloadditions

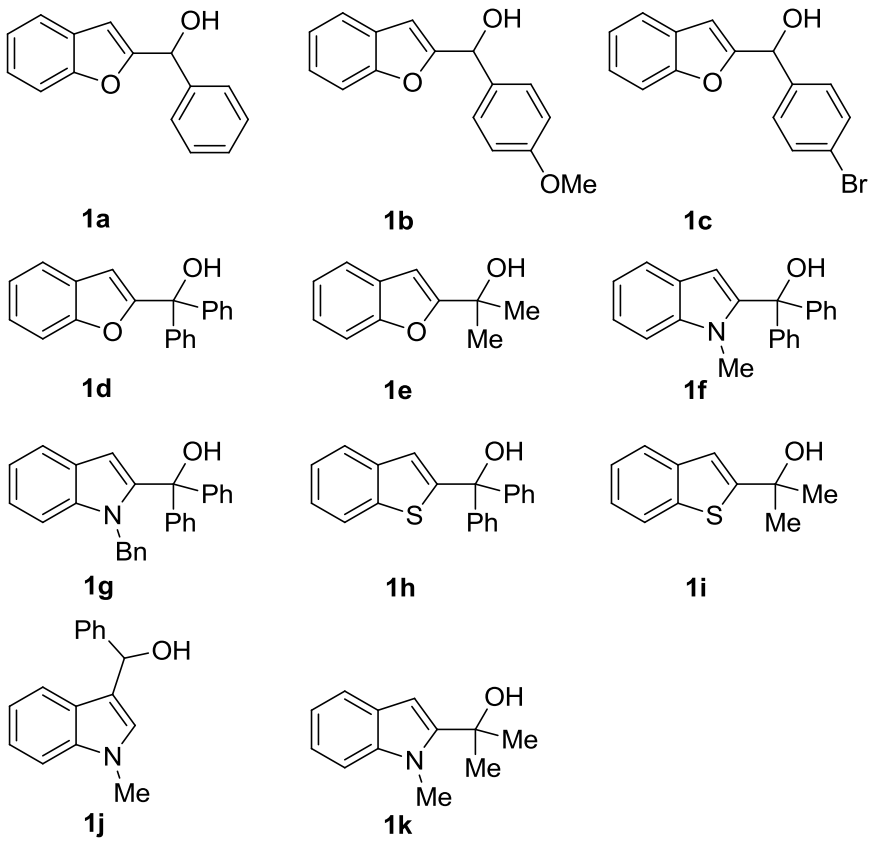
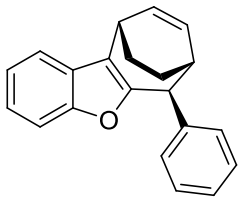


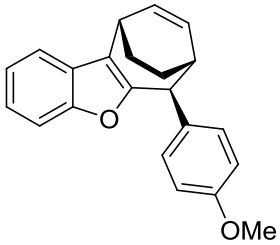
Figure 1. The alcohols (**1a**-**1k**) used in mild and selective [4+3] Cycloadditions.

General procedure for the mild and selective [4+ 3] Cycloadditions.

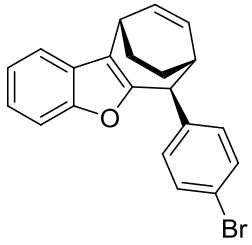
To a solution of alcohol **1** (0.1 mmol) and **2** (0.2 mmol) in DCM was added catalytic amount of 3,5-bis (trifluoromethyl) phenylboronic acid and the reaction was stirred for 24 h at the corresponding temperature. Progress of the reaction was monitored by TLC. The reaction mixture was then quenched with aq $NaHCO_3$ solution, extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography over silica gel column.



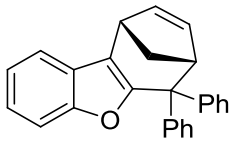
According to general procedure, **3a** was obtained as a white solid in 70% yield and 12:1 d.r. at rt; mp: 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 1H), 7.39-7.32 (m, 3H), 7.31-7.11 (m, 5H), 6.69 (dd, J_1 = 7.2 Hz, J_2 = 8.4 Hz, 1H), 6.34 (t, J = 7.6 Hz, 1H), 4.50 (d, J = 2.8 Hz,1H), 3.67-3.61 (m, 1H), 2.80-2.74 (m, 1H), 2.26-2.18 (m, 1H), 2.00-1.90 (m, 2H), 1.48-1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 152.4, 141.4, 138.7, 130.9, 128.9, 128.4, 127.8, 126.8, 123.2, 122.2, 122.1, 118.1, 111.1, 49.3, 39.2, 31.0, 28.1, 18.6. HRMS (EI) calcd. for $C_{21}H_{18}O$ (m/z M^+): 286.1358, found: 286.1361. Diagnostic correlations observed in 2D NOESY experiments: for the major isomer: δ 7.16 ppm with 1.94 ppm.



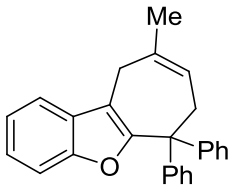
According to general procedure, **3b** was obtained as a white solid in 76% yield and >20:1 d.r. at rt; mp: 99-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 1H), 7.37-7.33 (m, 1H), 7.25-7.17 (m, 2H), 7.12-7.08 (m, 2H), 6.91-6.87 (m, 2H), 6.67 (dd, J_1 = 7.6 Hz, J_2 = 8.8 Hz, 1H), 6.32 (t, J = 8.0 Hz, 1H), 4.45 (d, J = 2.8 Hz, 1H), 3.82 (S, 3H), 3.65-3.61 (m, 1H), 2.75-2.70 (m, 1H), 2.25-2.15 (m, 1H), 2.02-1.92 (m, 2H), 1.48-1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5, 153.6, 152.7, 138.6, 133.4, 130.9, 129.8, 127.8, 123.2, 122.1, 122.0, 118.1, 113.9, 111.1, 55.3, 48.5, 39.3, 31.1, 28.1, 18.6. HRMS (EI) calcd. for $C_{22}H_{20}O_2$ (m/z M^+): 316.1463, found: 316.1466.



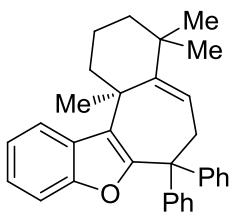
According to general procedure, **3c** was obtained as a white solid in 67% yield and >20:1 d.r. at rt; mp: 78-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 1H), 7.49-7.43 (m, 2H), 7.36-7.32 (m, 1H), 7.27-7.19 (m, 2H), 7.08-7.03 (m, 2H), 6.68 (dd, J_1 = 7.2 Hz, J_2 = 8.4 Hz, 1H), 6.31 (t, J = 7.6 Hz, 1H), 4.45 (d, J = 3.2 Hz, 1H), 3.66-3.61 (m, 1H), 2.76-2.70 (m, 1H), 2.24-2.15 (m, 1H), 2.03-1.85 (m, 2H), 1.48-1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 151.7, 140.5, 138.9, 131.5, 130.6, 127.6, 123.4, 122.4, 122.3, 120.6, 118.2, 111.1, 48.8, 39.1, 30.9, 28.0, 18.6. HRMS (EI) calcd. for $C_{21}H_{17}BrO$ (m/z M^+): 364.0463, found: 364.0464.



According to general procedure, **3d** was obtained as a white powder in 90% yield at 50 °C; mp: 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.40-7.35 (m, 3H), 7.31-7.27 (m, 1H), 7.25-7.12 (m, 4H), 7.04-6.99 (m, 2H), 6.96 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 5.70-5.65 (m, 1H), 5.42-5.37 (m, 1H), 4.31-4.24 (m, 1H), 3.87 (d, J = 4.8 Hz, 1H), 3.80-3.73 (m, 1H), 2.31-2.21 (m, 1H), 1.80-1.71 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.3, 154.9, 142.0, 140.9, 138.2, 132.5, 131.1, 131.0, 130.6, 130.2, 129.1, 128.2, 128.1, 126.6, 126.3, 125.8, 124.0, 122.3, 113.4, 110.0, 57.4, 56.1, 45.8, 34.8. HRMS (EI) calcd. for $C_{26}H_{20}O$ (m/z M^+): 348.1514, found: 348.1518.

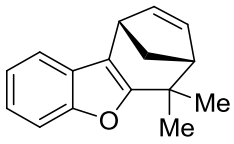


According to general procedure, **3e** was obtained as a white powder in 94% yield at 50 °C; mp: 176-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 1H), 7.34-7.30 (m, 1H), 7.29-7.16 (m, 12H), 5.33-5.27 (m, 1H), 3.47 (S, 2H), 3.19 (d, J = 7.2 Hz, 2H), 3.47 (S, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3, 153.0, 145.8, 139.7, 129.5, 128.7, 127.8, 126.3, 123.6, 122.6, 122.2, 118.6, 113.6, 111.2, 53.5, 39.2, 27.5, 25.1. HRMS (EI) calcd. for $C_{26}H_{22}O$ (m/z M^+): 350.1671, found: 350.1667.

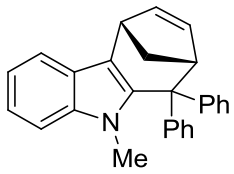


According to general procedure, **3f** was obtained as a colorless oil in 81% yield at 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2H), 7.39-7.29 (m, 8H), 7.24-7.18 (m, 2H), 6.99-6.93 (m, 2H), 5.57 (t, J = 3.6 Hz, 1H), 5.22 (t, J = 6.8 Hz, 1H), 4.47 (q, J = 4.0 Hz, 1H), 2.68-2.59 (m, 1H), 2.42-2.31 (m, 1H), 2.04-1.96 (br, 2H), 1.71 (d, J = 0.8 Hz, 3H), 1.34 (t, J = 6.0 Hz, 2H), 0.88 (d, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.8, 156.2, 145.1, 139.9, 139.3, 133.4, 130.5, 129.4, 129.0, 128.8, 128.3, 127.9, 127.2, 126.3, 125.7, 124.4, 121.9, 120.9, 116.4,

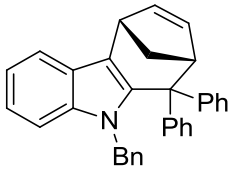
109.6, 44.7, 39.9, 34.5, 33.4, 28.0, 27.7, 22.9, 21.9. HRMS (EI) calcd. for $C_{32}H_{32}O$ (m/z M^+): 432.2453, found: 432.2451.



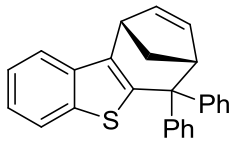
According to general procedure, **3g** was obtained as a white solid in 80% yield at rt; mp: 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.45 (m, 1H), 7.42-7.33 (m, 1H), 7.21-7.14 (m, 2H), 6.50 (q, J = 2.8 Hz, 1H), 5.86 (q, J = 2.8 Hz, 1H), 3.52 (t, J = 3.6 Hz, 1H), 2.71 (dd, J_1 = 3.2 Hz, J_2 = 4.8 Hz, 1H), 2.19-2.13 (m, 1H), 2.07 (d, J = 10.0 Hz, 1H), 1.47 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2, 153.3, 142.0, 131.0, 127.0, 122.4, 122.1, 118.2, 117.8, 111.1, 51.8, 41.7, 37.9, 36.1, 28.3, 22.4. HRMS (EI) calcd. for $C_{16}H_{16}O$ (m/z M^+): 224.1201, found: 224.1202.



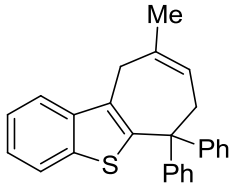
According to general procedure, **3h** was obtained as a yellow solid in 96% yield at rt; mp: 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.62 (m, 1H), 7.41-7.34 (m, 4H), 7.31-7.13 (m, 9H), 6.66 (q, J = 2.8 Hz, 1H), 5.54 (q, J = 2.8 Hz, 1H), 3.73 (t, J = 3.6 Hz, 1H), 3.59 (dd, J_1 = 3.2 Hz, J_2 = 5.2 Hz, 1H), 2.90 (s, 3H), 2.12-2.05 (m, 1H), 1.93 (d, J = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 143.1, 140.4, 135.9, 134.8, 129.7, 128.4, 127.8, 127.1, 126.8, 125.5, 125.3, 123.9, 119.7, 117.9, 116.8, 115.4, 108.0, 54.7, 53.7, 41.3, 35.4, 30.4. HRMS (EI) calcd. for $C_{27}H_{23}N$ (m/z M^+): 361.1830, found: 361.1828.



According to general procedure, **3i** was obtained as a yellow solid in 68% yield at rt; mp: 203-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.6 Hz, 1H), 7.38-7.34 (m, 2H), 7.33-7.27 (m, 2H), 7.27-7.24 (m, 1H), 7.21-7.14 (m, 3H), 7.11-7.05 (m, 1H), 7.04-6.84 (m, 7H), 6.72 (q, J = 2.8 Hz, 1H), 6.51 (d, J = 7.2 Hz, 1H), 5.63 (q, J = 2.8 Hz, 1H), 4.83 (d, J = 17.2 Hz, 1H), 4.66 (d, J = 17.2 Hz, 1H), 3.79 (t, J =3.2 Hz, 1H), 3.54 (dd, J_1 = 3.2 Hz, J_2 = 5.2 Hz, 1H), 2.14-2.08 (m, 1H), 1.98 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.6, 143.9, 140.5, 137.3, 136.5, 136.1, 131.2, 129.7, 129.2, 128.0, 127.6, 126.6, 126.3, 126.2, 126.2, 125.4, 121.1, 119.3, 117.9, 116.8, 110.9, 56.2, 54.9, 48.7, 42.7, 36.5. HRMS (EI) calcd. for $C_{33}H_{27}N$ (m/z M^+): 437.2143, found: 437.2147.

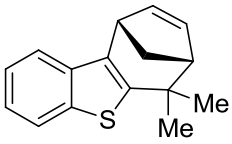


According to general procedure, **3j** was obtained as a white solid in 97% yield at 50 °C; mp: 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, J_1 = 3.6 Hz, J_2 = 8.0 Hz, 1H), 7.58-7.54 (m, 2H), 7.36-7.29 (m, 3H), 7.26-7.19 (m, 2H), 7.18-7.12 (m, 3H), 6.92-6.87 (m, 2H), 6.39 (q, J = 2.8 Hz, 1H), 5.12 (q, J = 2.8 Hz, 1H), 3.85 (t, J = 3.2 Hz, 1H), 3.65 (dd, J_1 = 3.6 Hz, J_2 = 4.4 Hz, 1H), 2.58-2.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3, 146.2, 141.4, 140.5, 139.1, 137.2, 137.2, 133.2, 129.2, 129.1, 127.9, 127.3, 126.4, 126.2, 124.0, 123.9, 122.4, 120.8, 54.5, 51.0, 42.6, 38.2. HRMS (EI) calcd. for $C_{26}H_{20}S$ (m/z M^+): 364.1286, found: 364.1281.

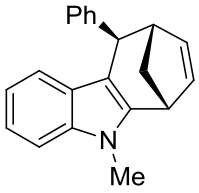


According to general procedure, **3k** was obtained as a white solid in 98% yield at 50 °C; mp: 167-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.38-7.32 (m, 1H), 7.30-7.17 (m, 11H), 5.28-5.22 (m, 1H), 3.57 (s, 2H), 3.40 (d, J = 6.4 Hz, 2H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ148.0, 147.9, 140.6, 138.4, 135.5, 128.8, 127.8,

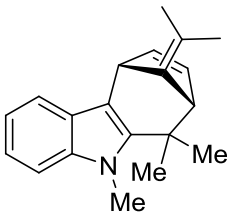
127.8, 126.5, 123.9, 123.8, 122.9, 122.0, 121.3, 54.4, 39.8, 32.7, 25.6. HRMS (EI) calcd. for $C_{26}H_{22}S$ (m/z M^+): 366.1442, found: 366.1439.



According to general procedure, **3l** was obtained as a colorless oil in 95% yield at 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.23-7.18 (m, 1H), 7.13-7.08 (m, 1H), 6.33 (q, J = 2.8 Hz, 1H), 5.76 (q, J = 3.2 Hz, 1H), 3.55 (t, J = 3.6 Hz, 1H), 2.57 (dd, J_1 = 3.2 Hz, J_2 = 4.8 Hz, 1H), 2.14-2.00 (m, 2H), 1.39 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.7, 141.3, 137.9, 137.6, 134.6, 131.5, 123.8, 123.2, 122.6, 120.5, 51.6, 40.6, 38.5, 38.2, 33.0, 27.4. HRMS (EI) calcd. for $C_{16}H_{16}S$ (m/z M^+): 240.0973, found: 240.0976.



According to general procedure, **3m** was obtained as a white solid in 52% yield, 3:1 d.r. (20% of catalyst) and 89% yield, 3:1 d.r. (1 equiv of catalyst) at 50℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.27 (m, 5H), 7.26-7.21 (m, 1H), 7.16-7.10 (m, 1H), 6.98-6.92 (m, 2H), 6.42 (q, J = 2.7 Hz, 1H), 6.07 (q, J = 2.7 Hz, 1H), 4.06 (s, 1H), 3.79 (s, 3H), 3.67 (dd, J_1 = 2.7 Hz, J_2 = 4.2 Hz, 1H), 2.97 (t, J = 3.3 Hz, 1H), 2.11 (d, J = 10.2 Hz, 1H), 2.11-2.05 (m, 1H); The NMR data obtained for **3m** corresponded to those reported in the literature.[6]



According to general procedure, **3o** was obtained as a yellow oil in 75% yield at rt; mp: 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 1H), 7.23-7.18 (m, 1H), 7.13-7.03 (m, 2H), 6.70-6.40 (m, 1H), 6.00-5.94 (m, 1H), 4.23-4.17 (m, 1H), 4.71-4.68 (m, 3H), 3.18-3.15 (br, 1H), 1.72-1.66 (m, 6H), 1.47-1.43 (m, 3H), 1.40-1.36 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.0, 141.9, 139.9, 136.4, 131.4, 124.5, 120.4, 119.0, 117.6, 115.5, 112.6, 108.9, 55.9, 40.8, 39.0, 31.6, 28.2, 23.7, 20.2, 20.0. HRMS (EI) calcd. for $C_{20}H_{23}N$ (m/z M^+): 277.1830, found: 277.1825.

References:

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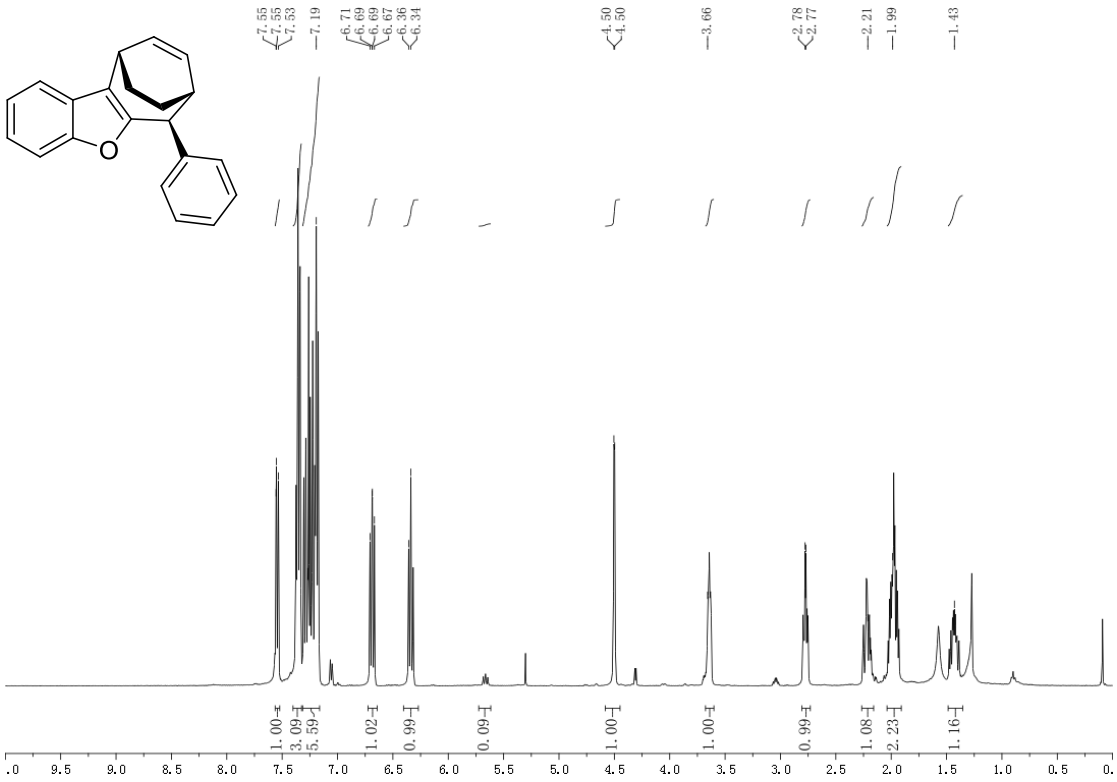
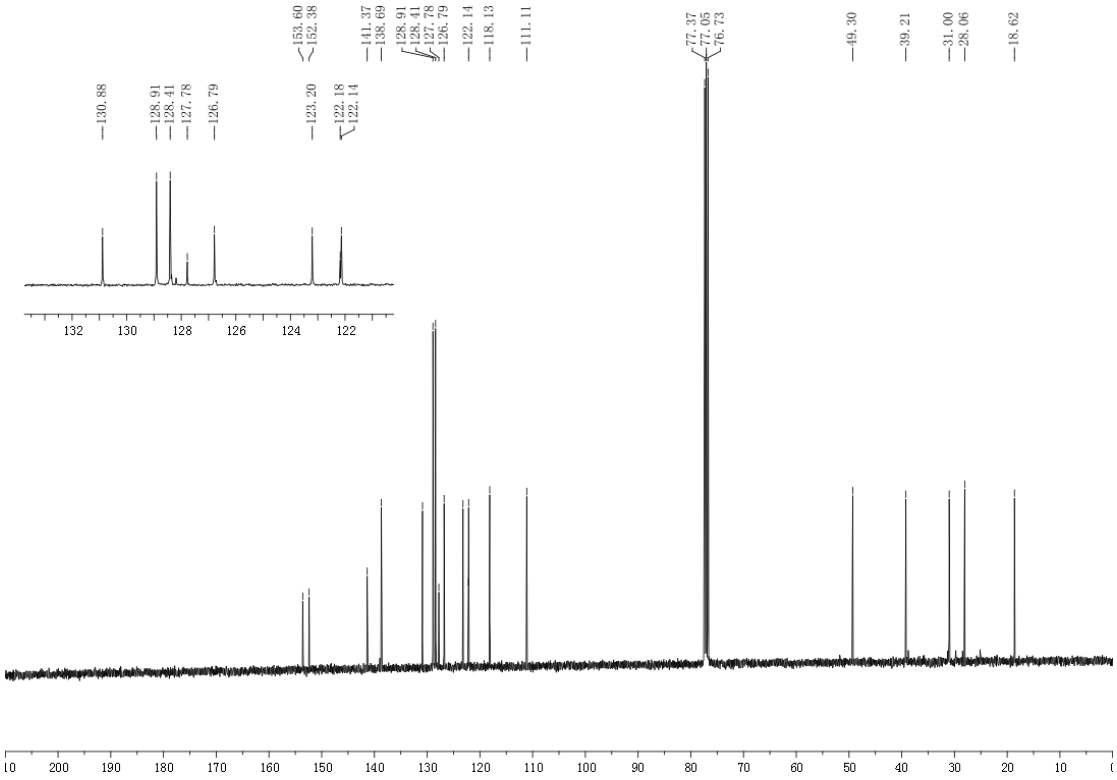
[5] F. Faigl, G. Tarkanyi, K. Fogassy, D. Tepfenhardt, A. Thurner, *Tetrahedron* **2008**, *64*, 1371-1377.

[6] X. Han, H. Li, R. P. Hughes, J. Wu, *Angew. Chem. Int. Ed.* **2012**, *51*, 10390-10393.

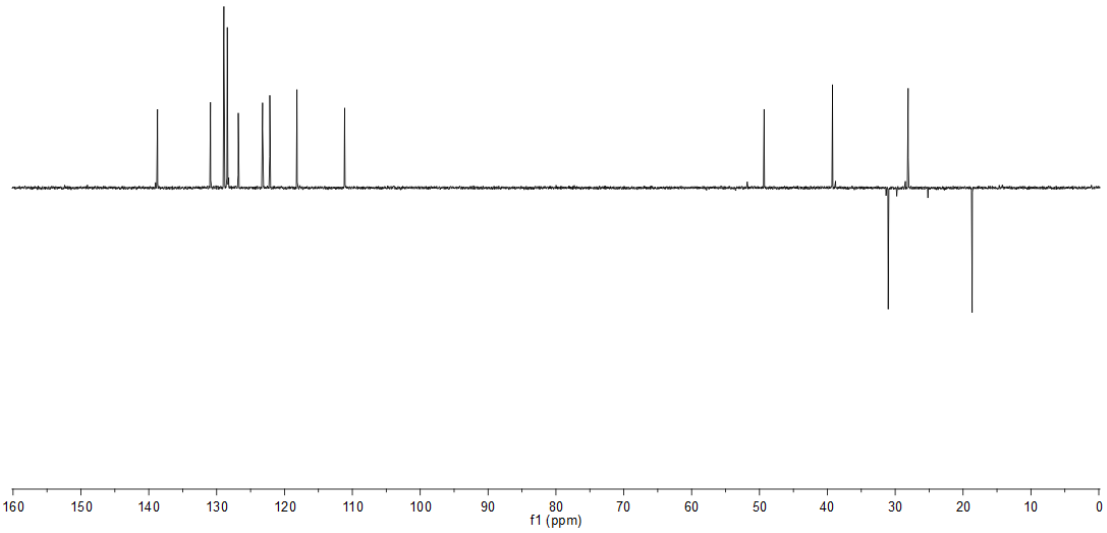
3a ^{1}H NMR, 400MHz, $CDCl_3$



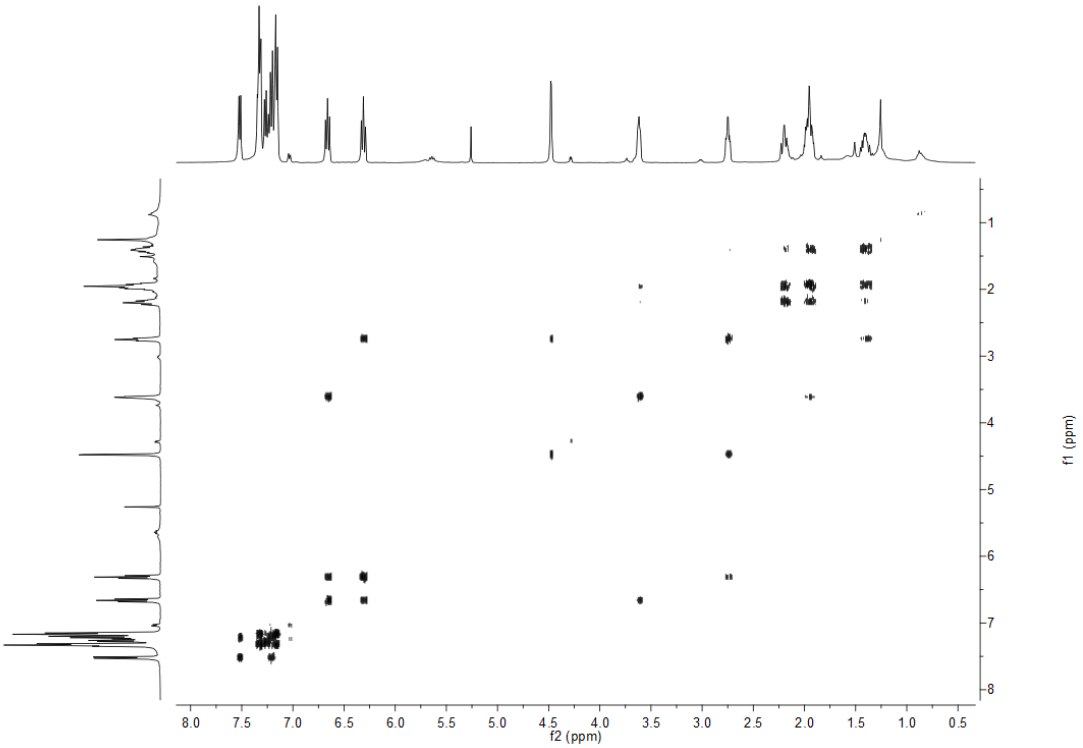
3a ^{13}C NMR, 400MHz, $CDCl_3$



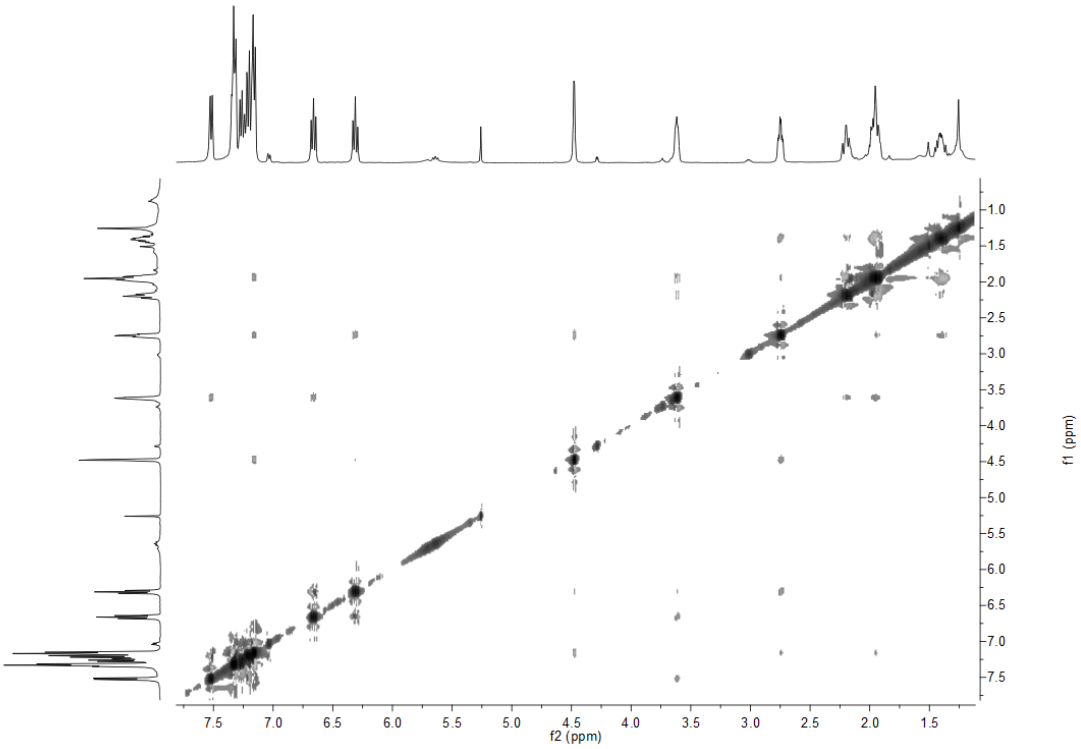
3a DEPT 135, 400MHz, $CDCl_3$



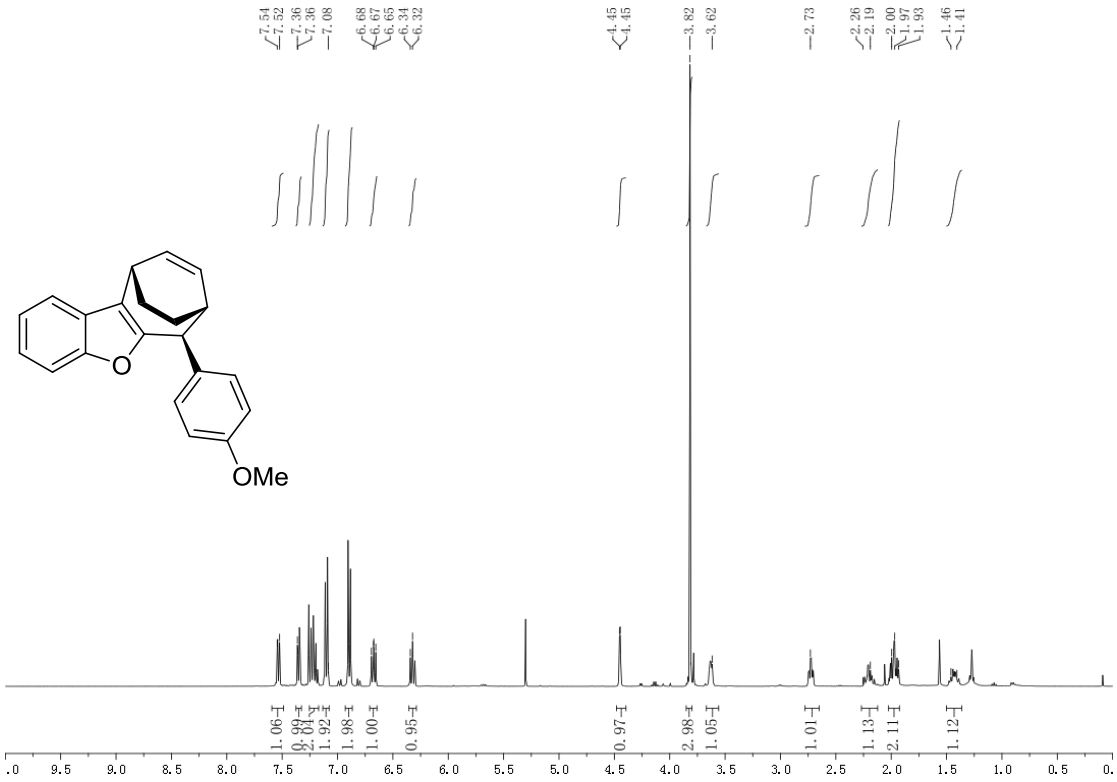
3a H-H COSY, 400MHz, $CDCl_3$



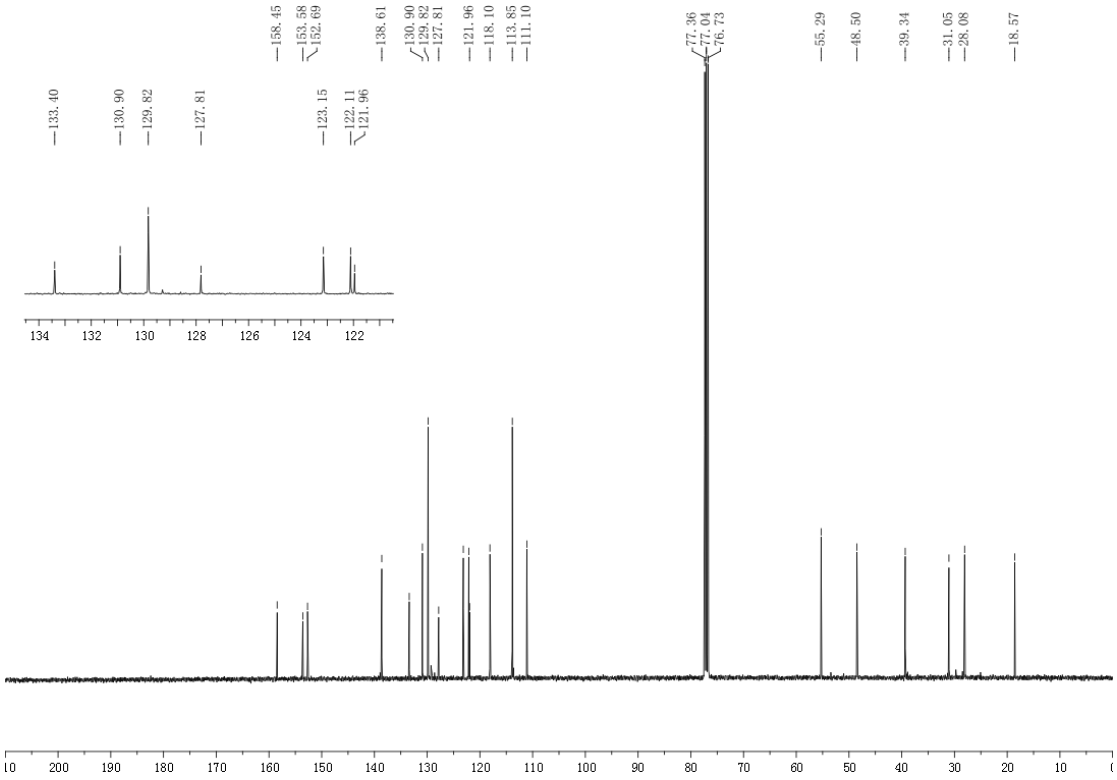
3a NOE, 400MHz, $CDCl_3$



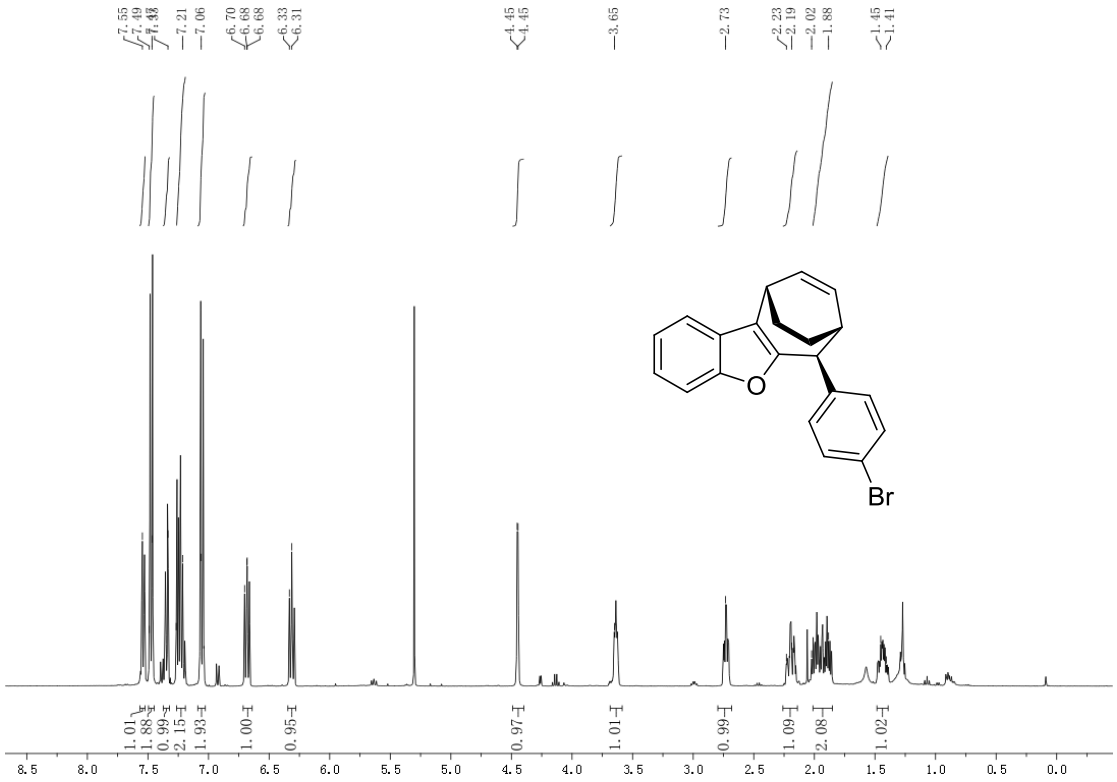
3b ^{1}H NMR, 400MHz, $CDCl_3$



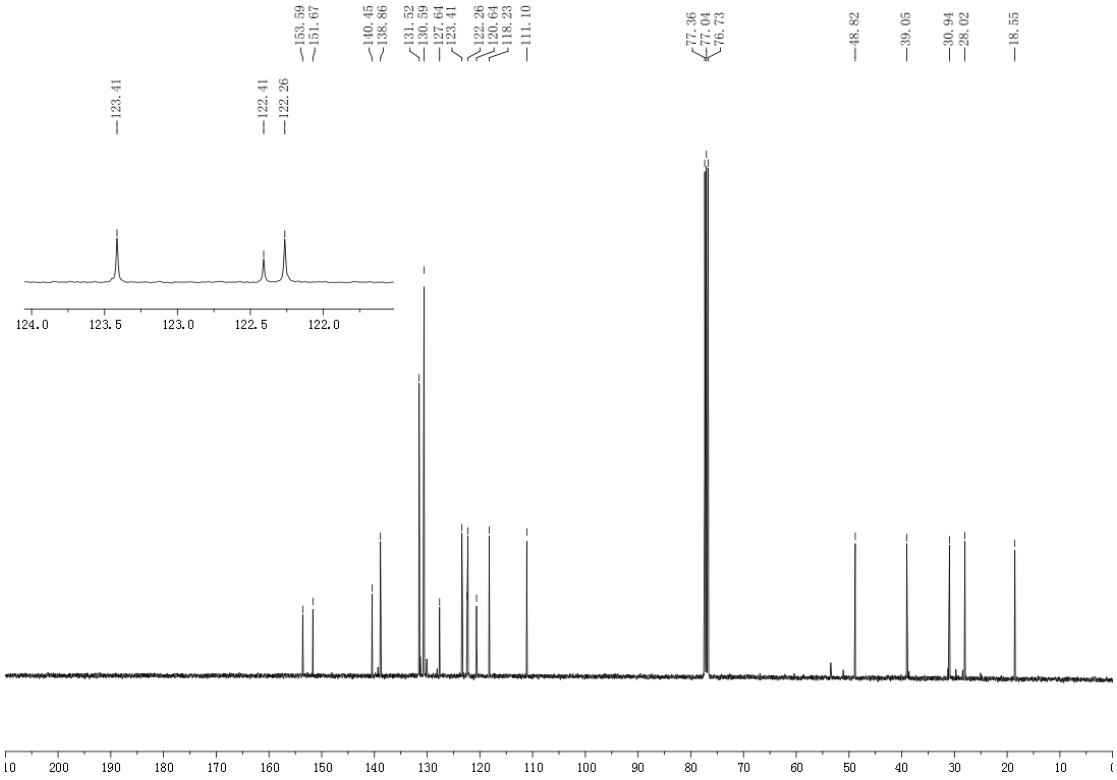
3b ^{13}C NMR, 400MHz, $CDCl_3$



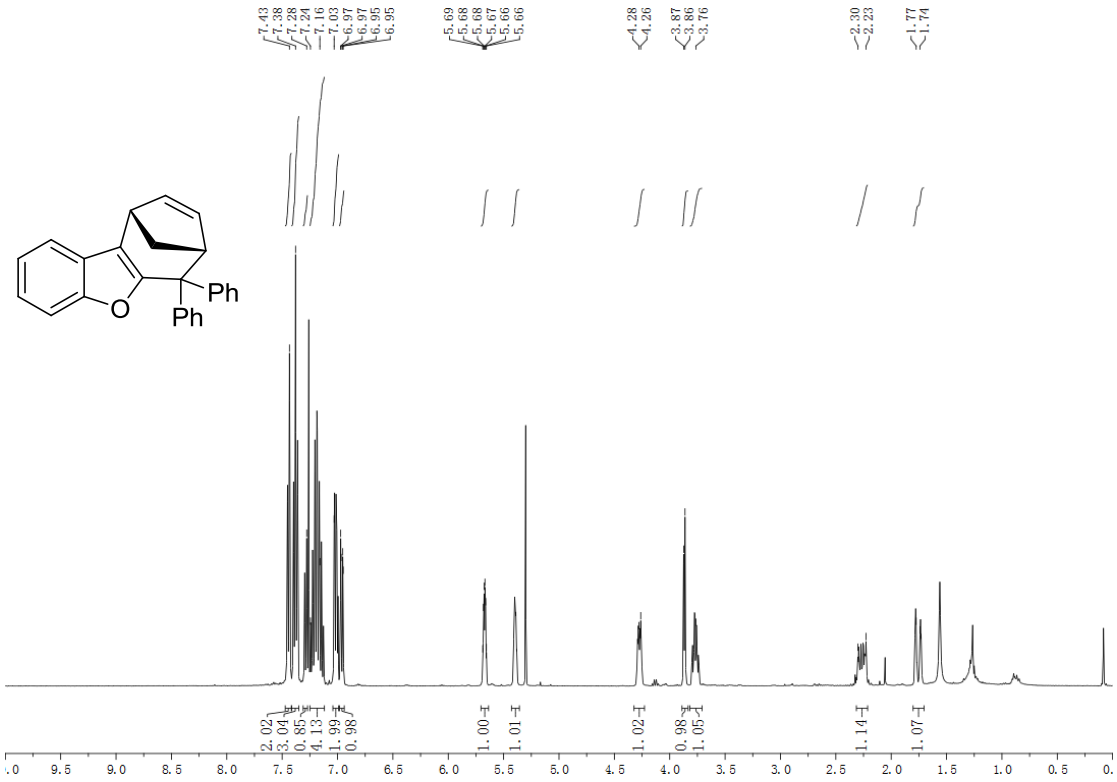
3c ^{1}H NMR, 400MHz, $CDCl_3$



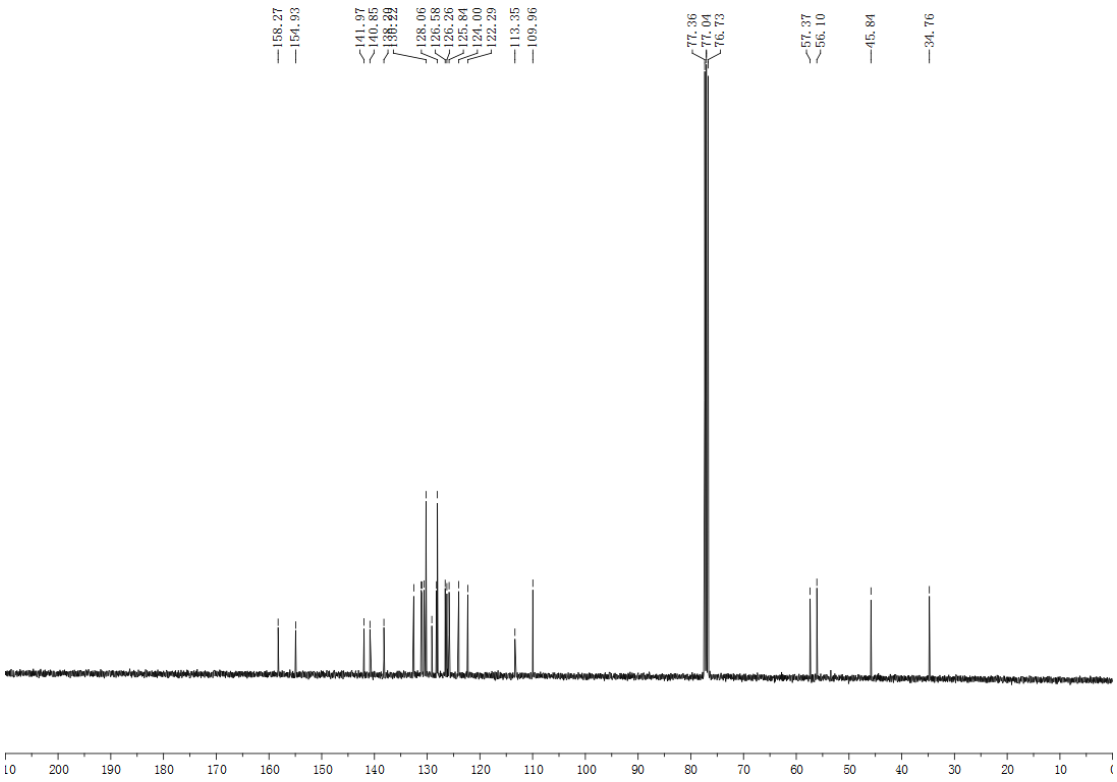
3c ^{13}C NMR, 400MHz, $CDCl_3$



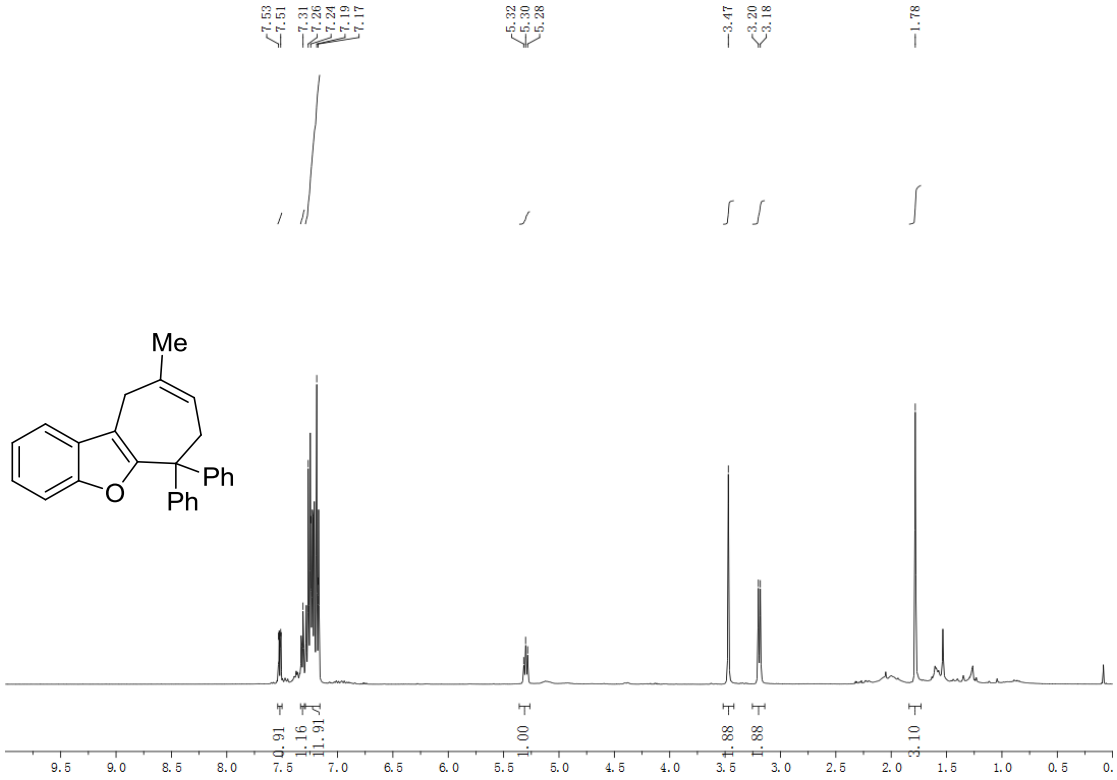
3d ^{1}H NMR, 400MHz, $CDCl_3$



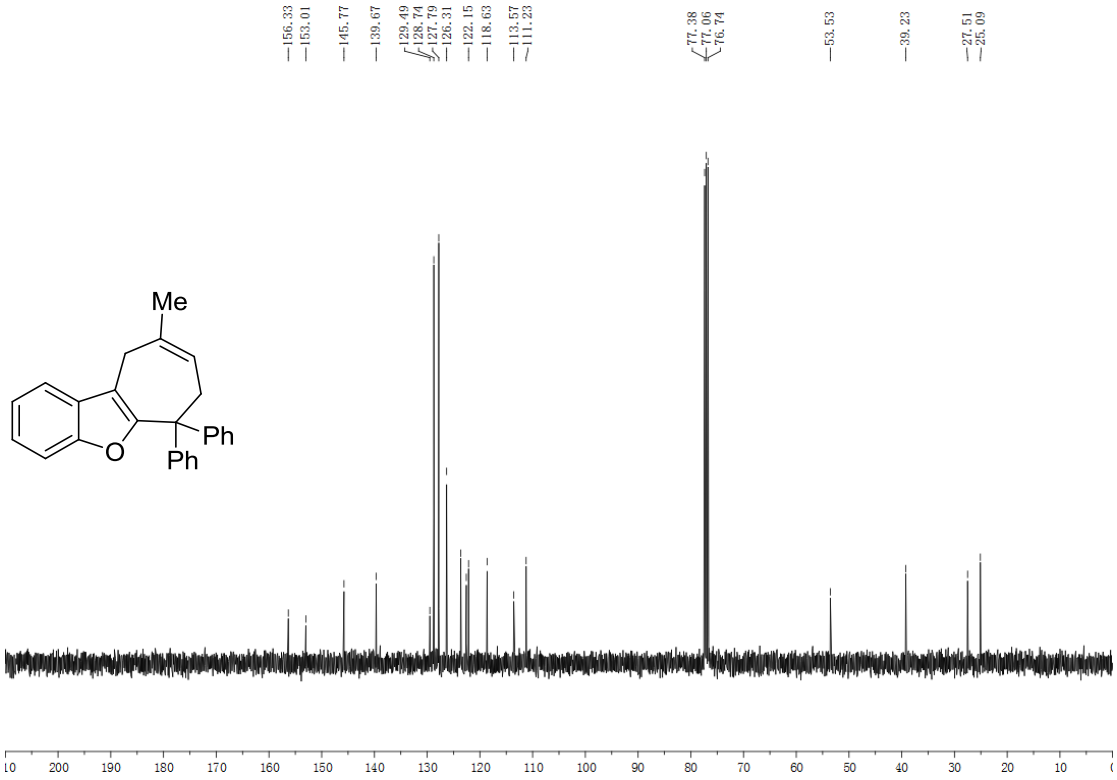
3d ^{13}C NMR, 400MHz, $CDCl_3$



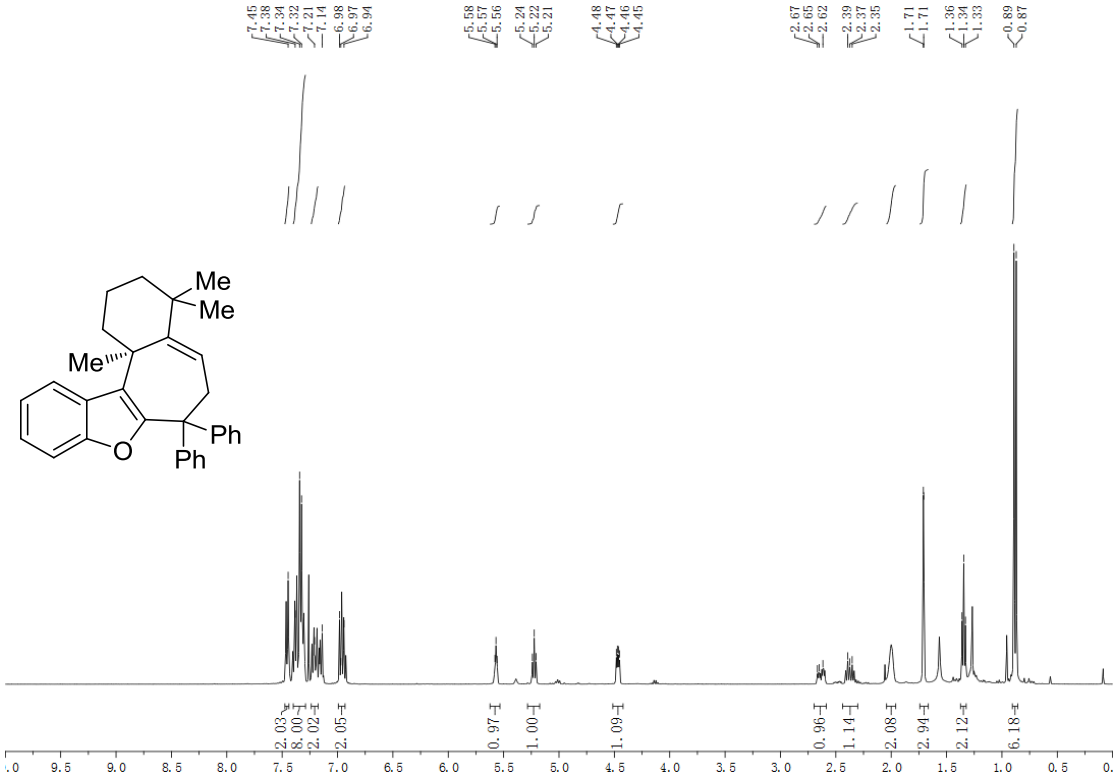
3e ^{1}H NMR, 400MHz, $CDCl_3$



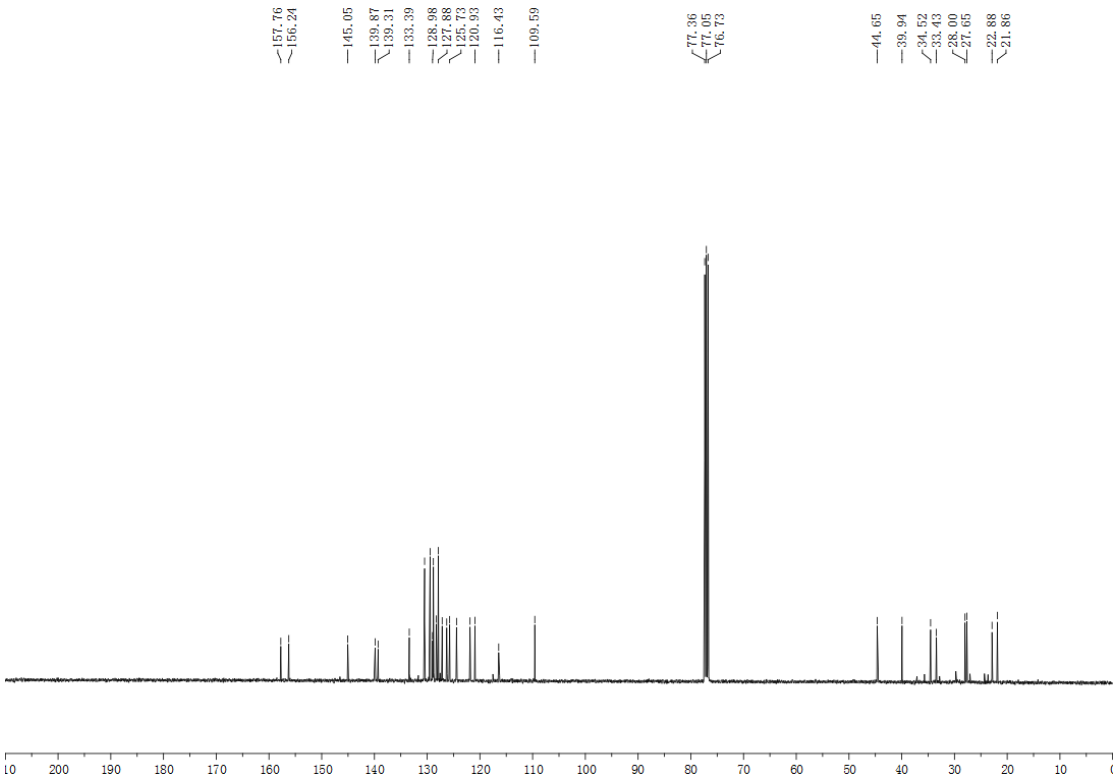
3e ^{13}C NMR, 400MHz, $CDCl_3$



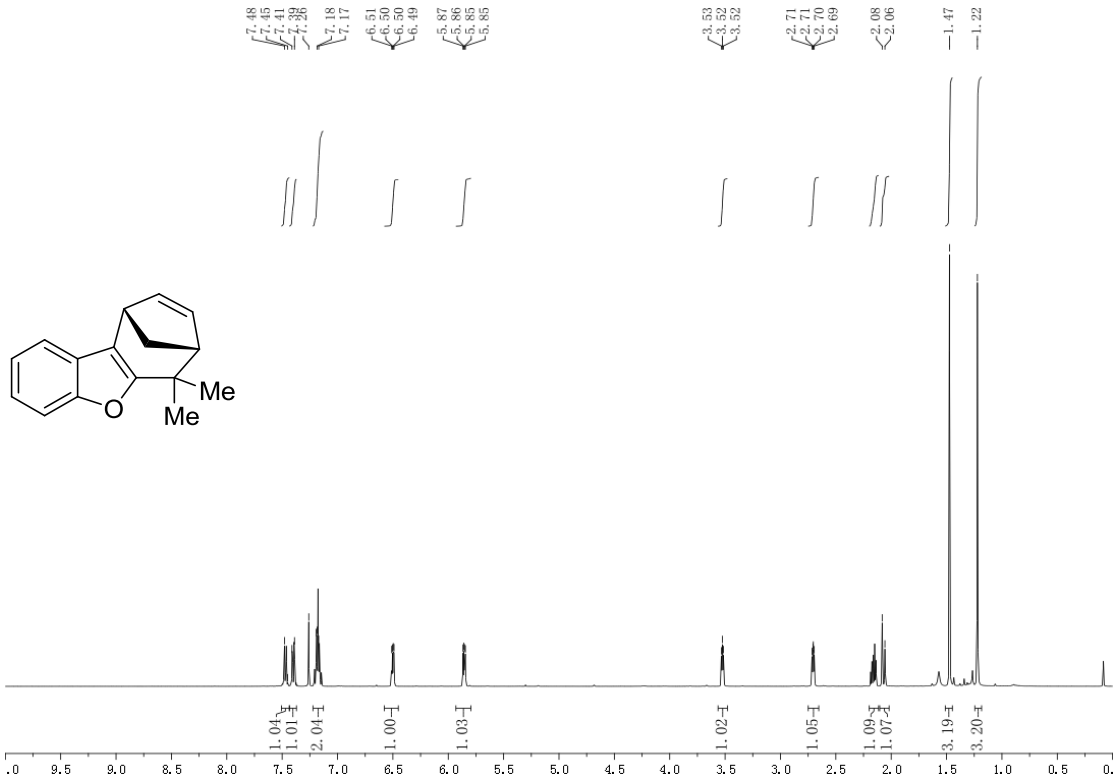
3f ^{1}H NMR, 400MHz, $CDCl_3$



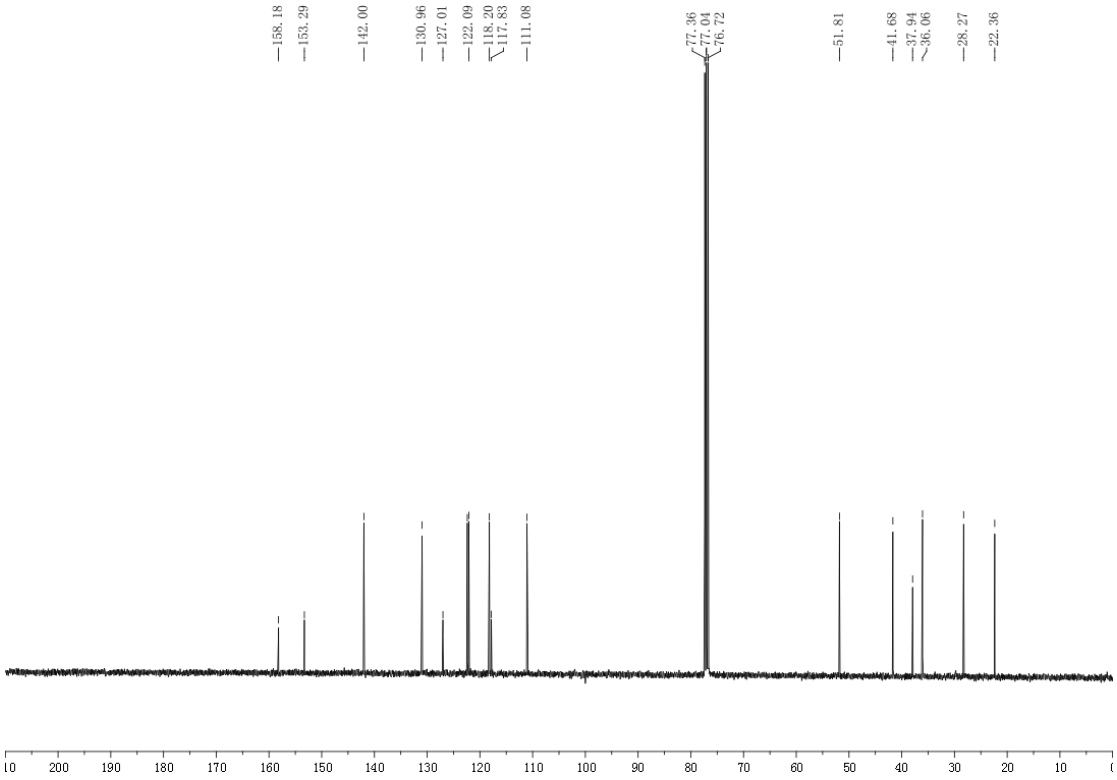
3f ^{13}C NMR, 400MHz, $CDCl_3$



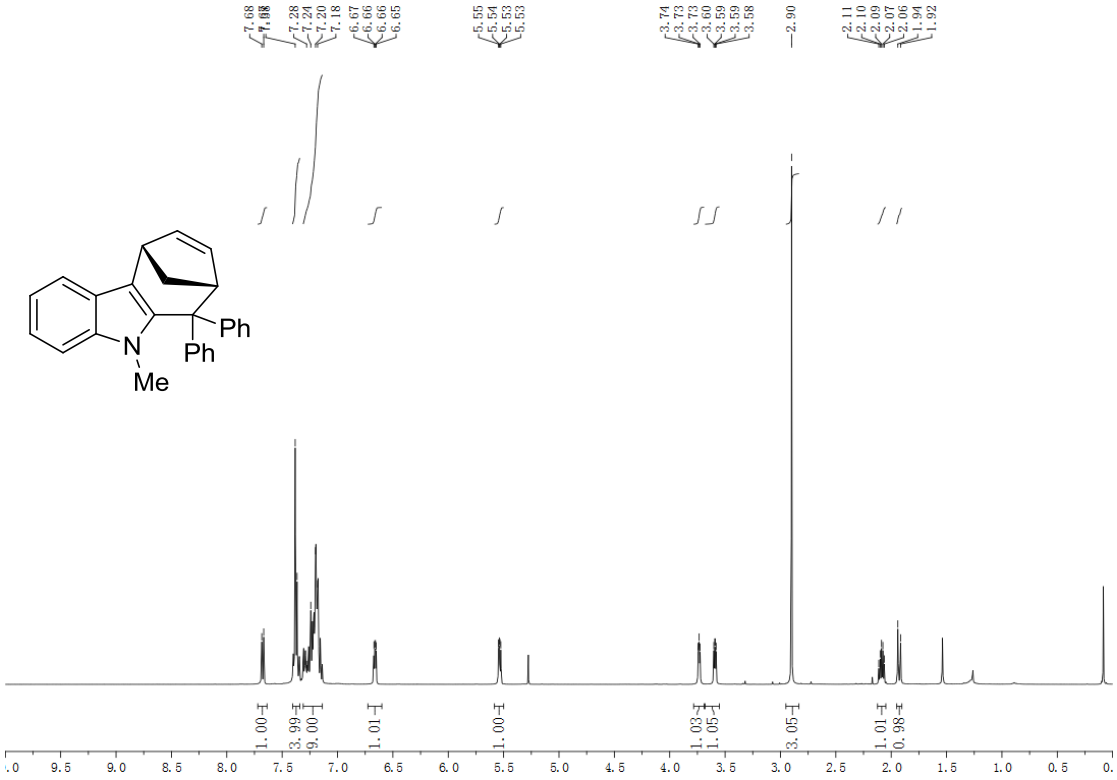
3g ^{1}H NMR, 400MHz, $CDCl_3$



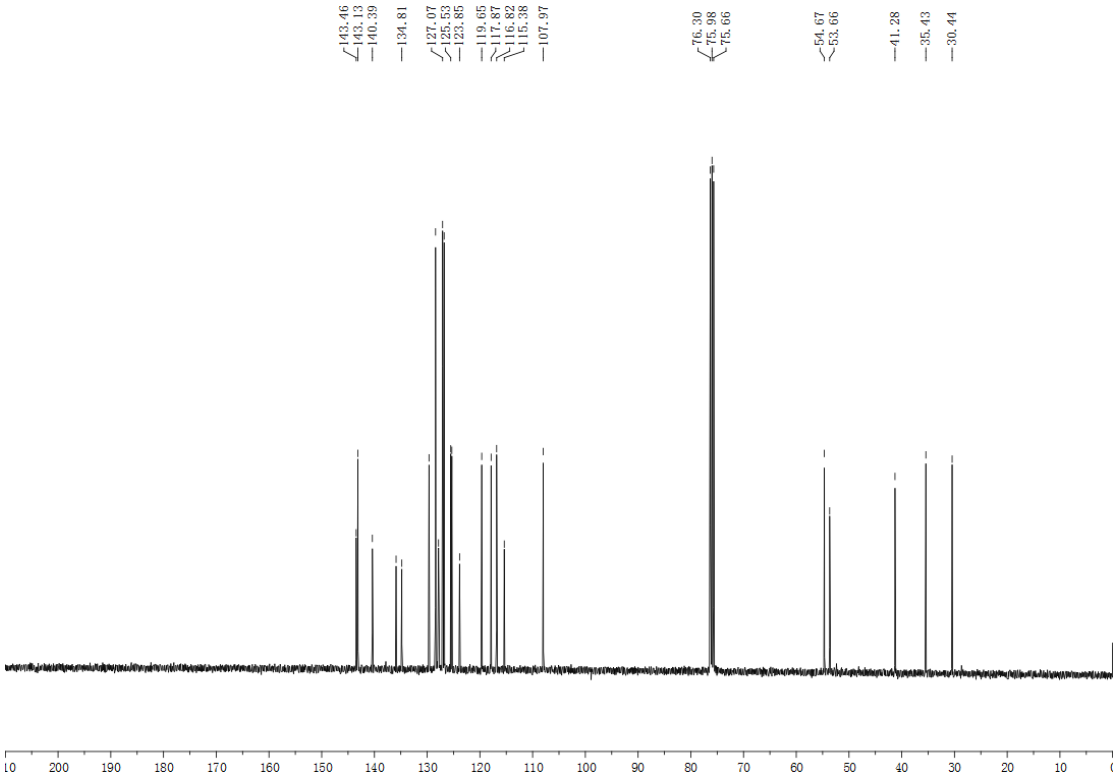
3g ^{13}C NMR, 400MHz, $CDCl_3$



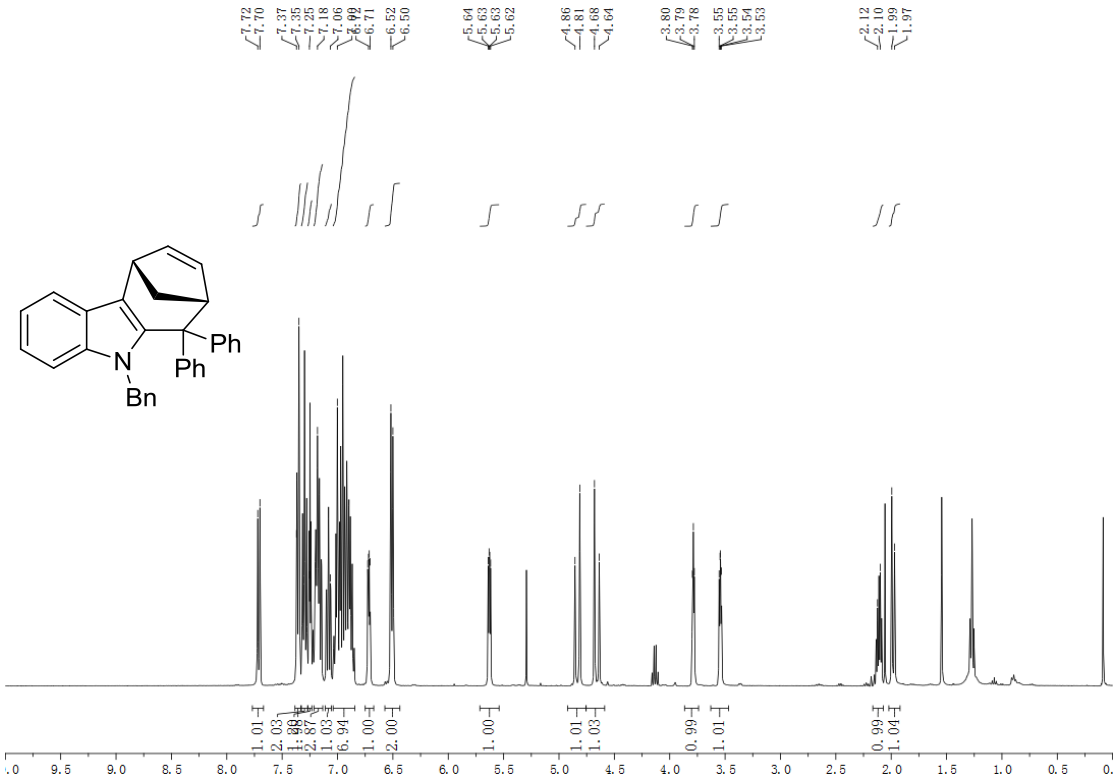
3h ^{1}H NMR, 400MHz, $CDCl_3$



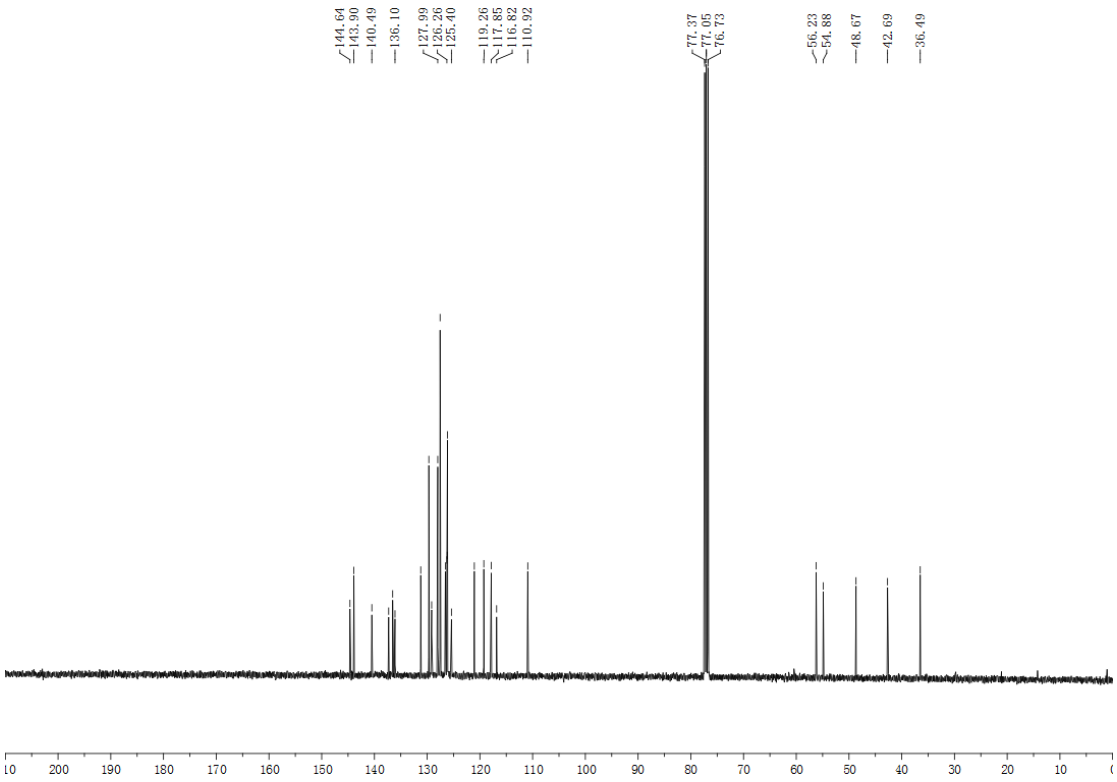
3h ^{13}C NMR, 400MHz, $CDCl_3$



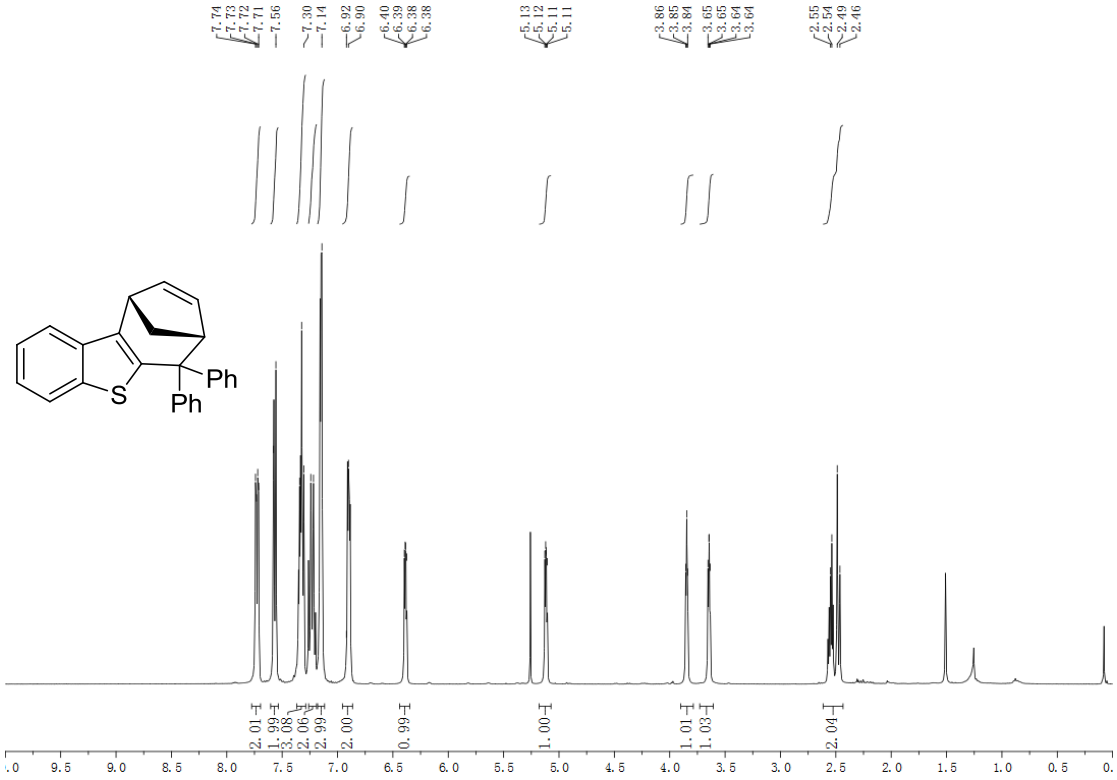
3i ^{1}H NMR, 400MHz, $CDCl_3$



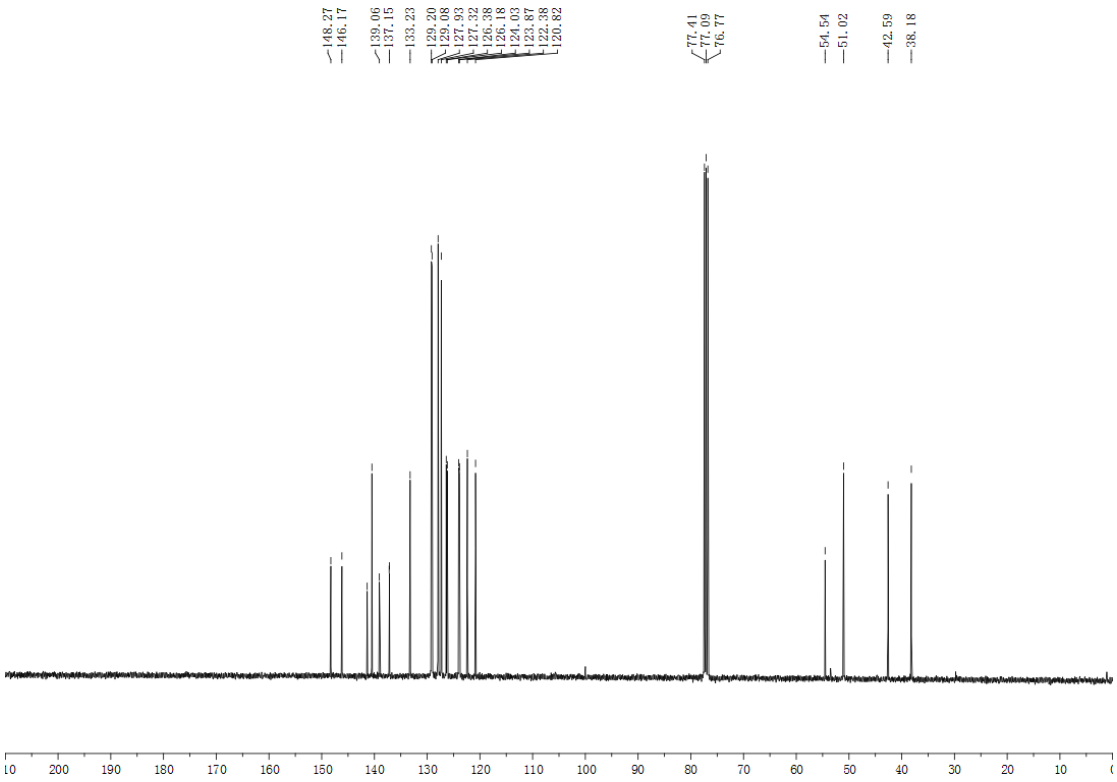
3i ^{13}C NMR, 400MHz, $CDCl_3$



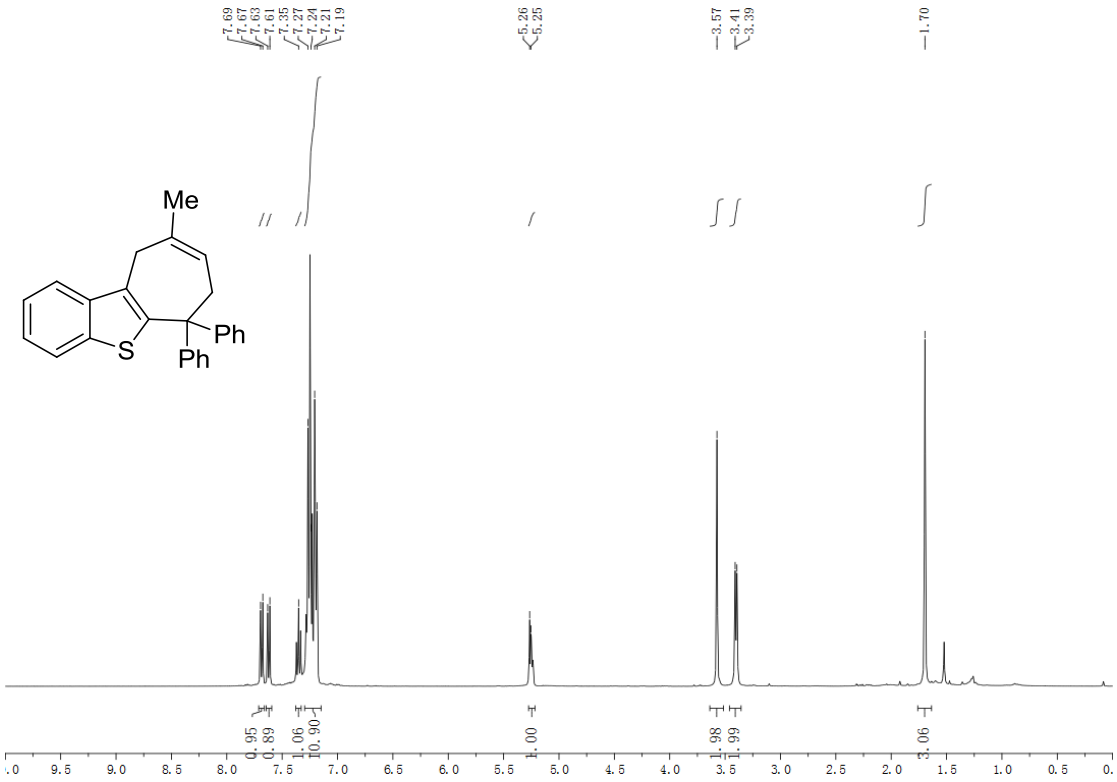
3j ^{1}H NMR, 400MHz, $CDCl_3$



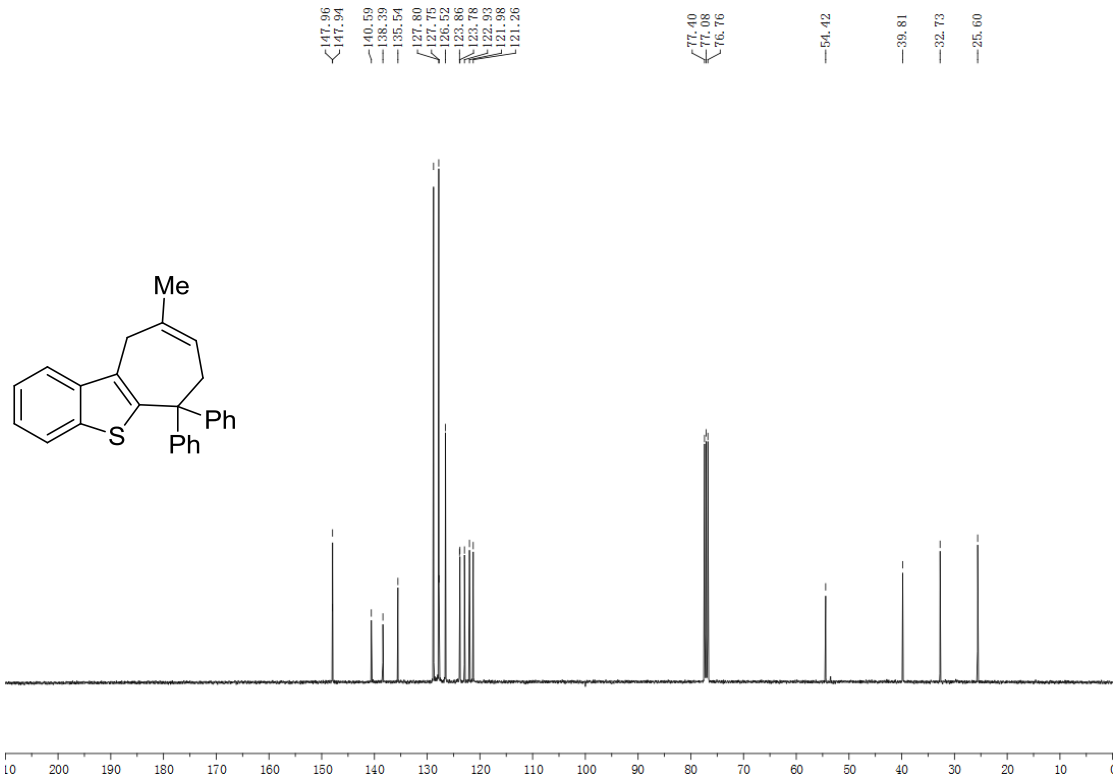
3j ^{13}C NMR, 400MHz, $CDCl_3$



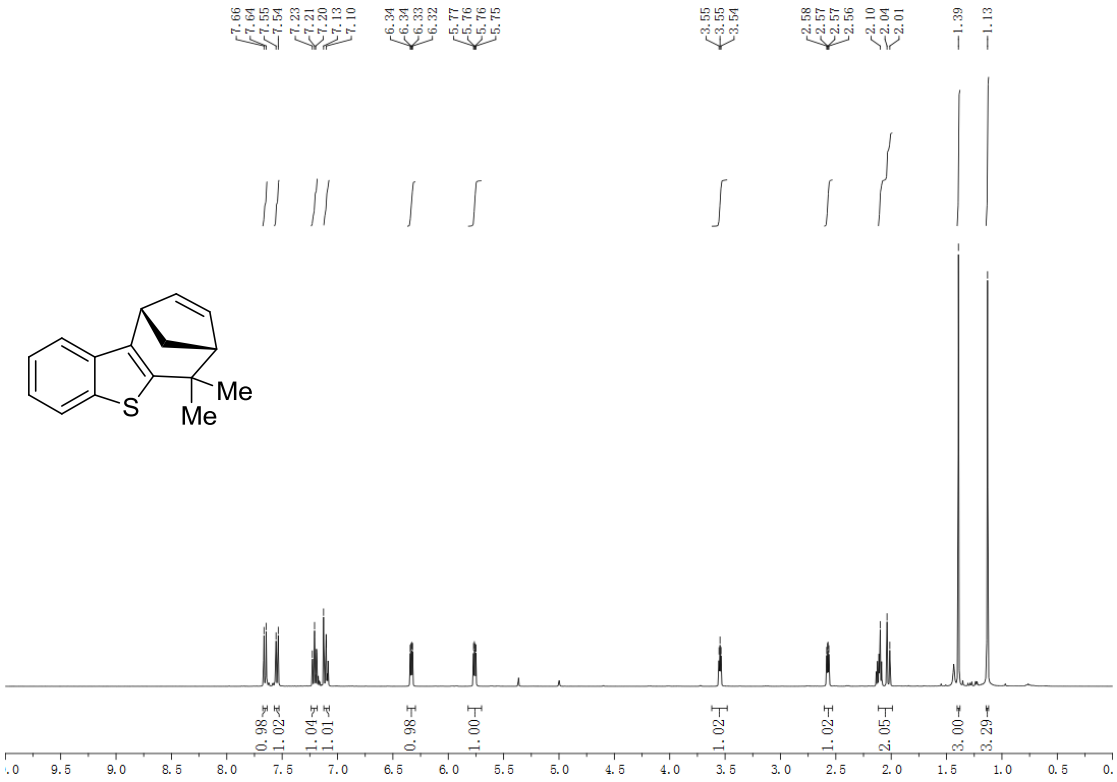
3k ^{1}H NMR, 400MHz, $CDCl_3$



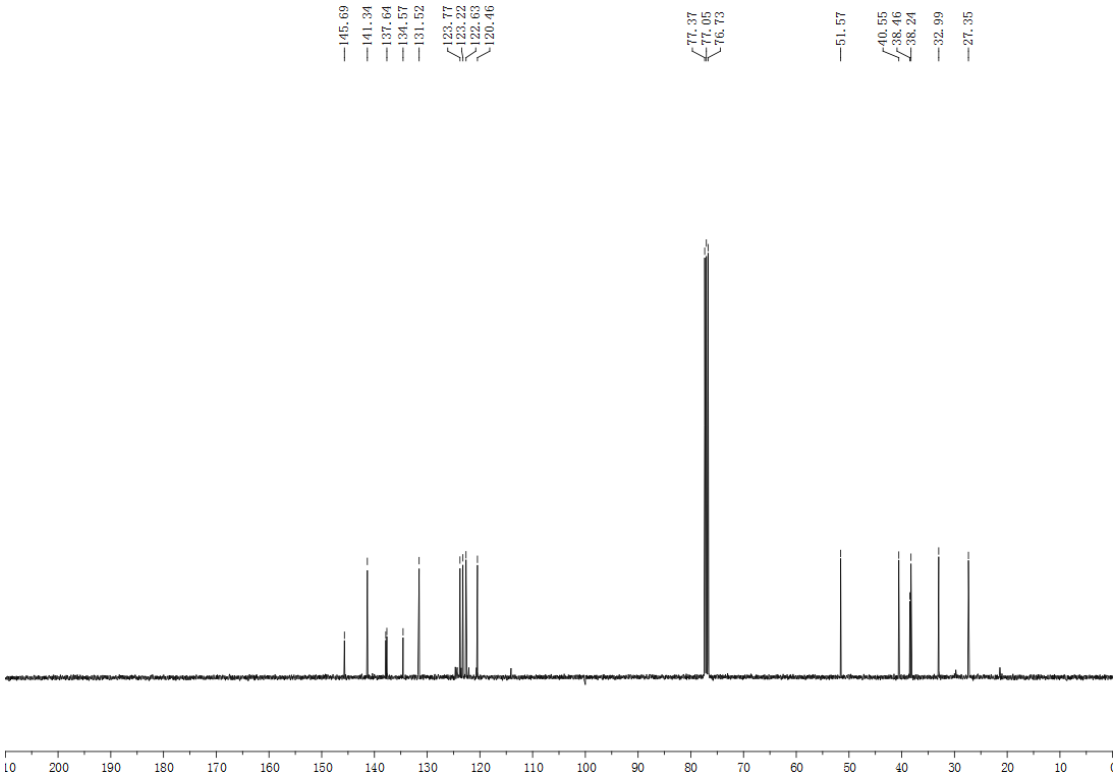
3k ^{13}C NMR, 400MHz, $CDCl_3$



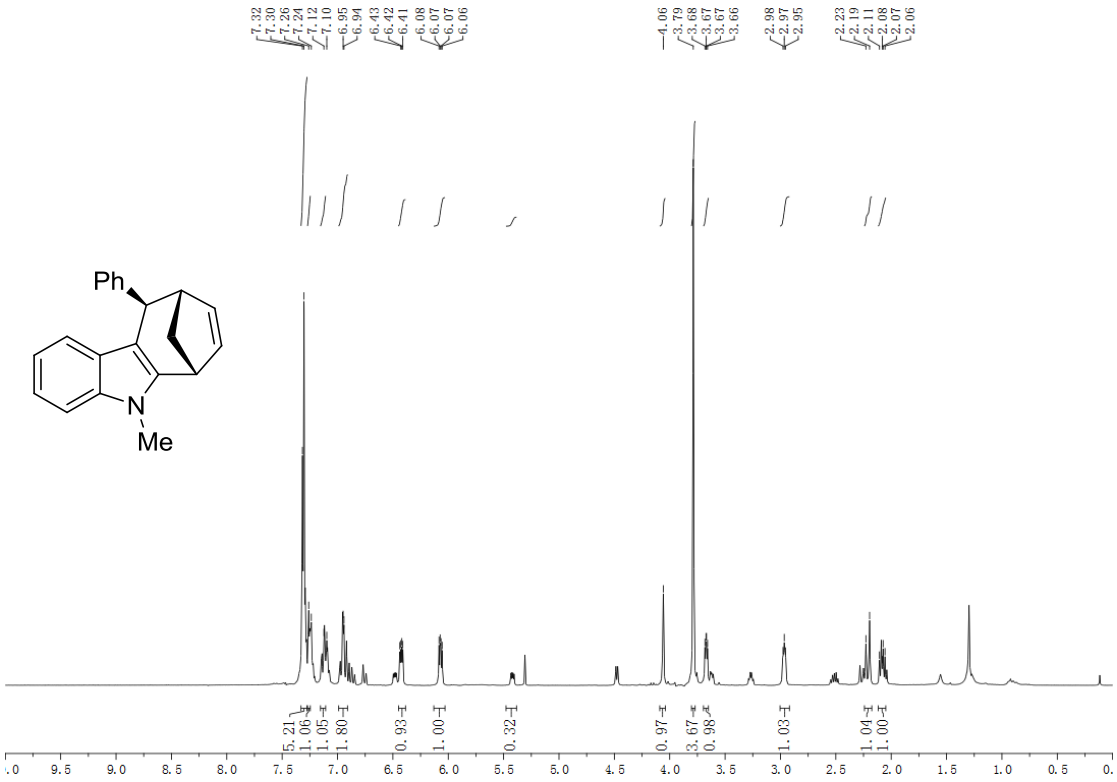
3l ^{1}H NMR, 400MHz, $CDCl_3$



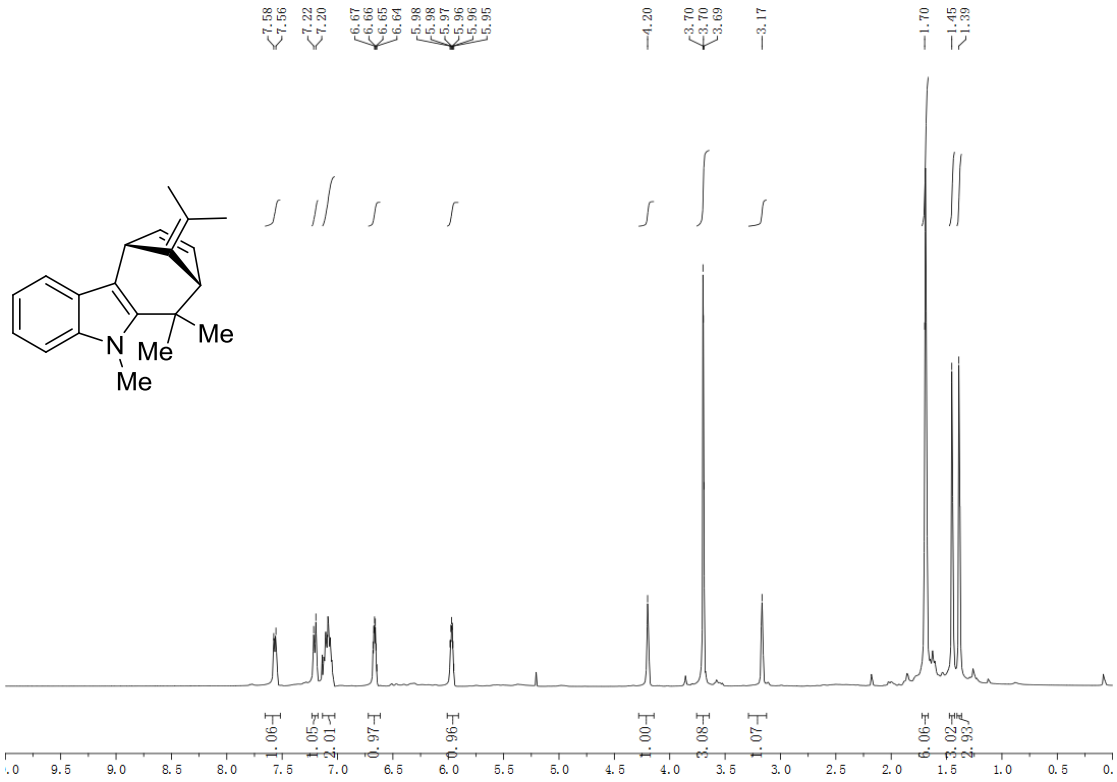
3l ^{13}C NMR, 400MHz, $CDCl_3$



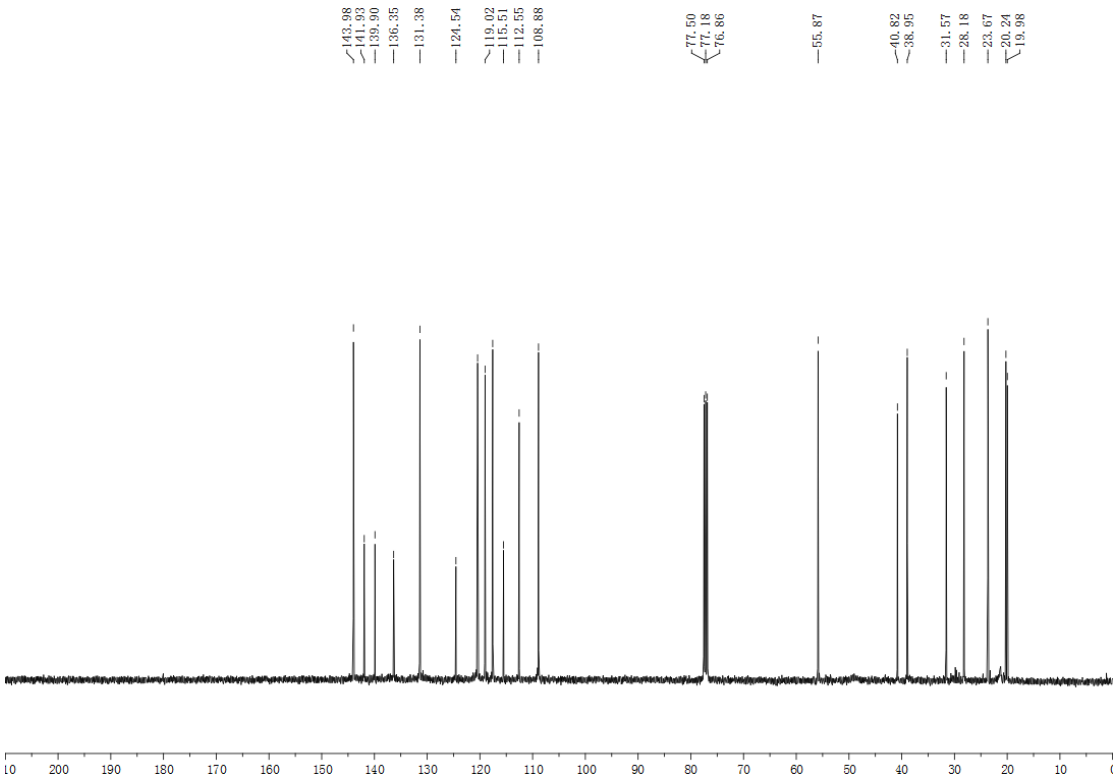
3m ^{1}H NMR, 400MHz, $CDCl_3$ (3:1 d.r.)



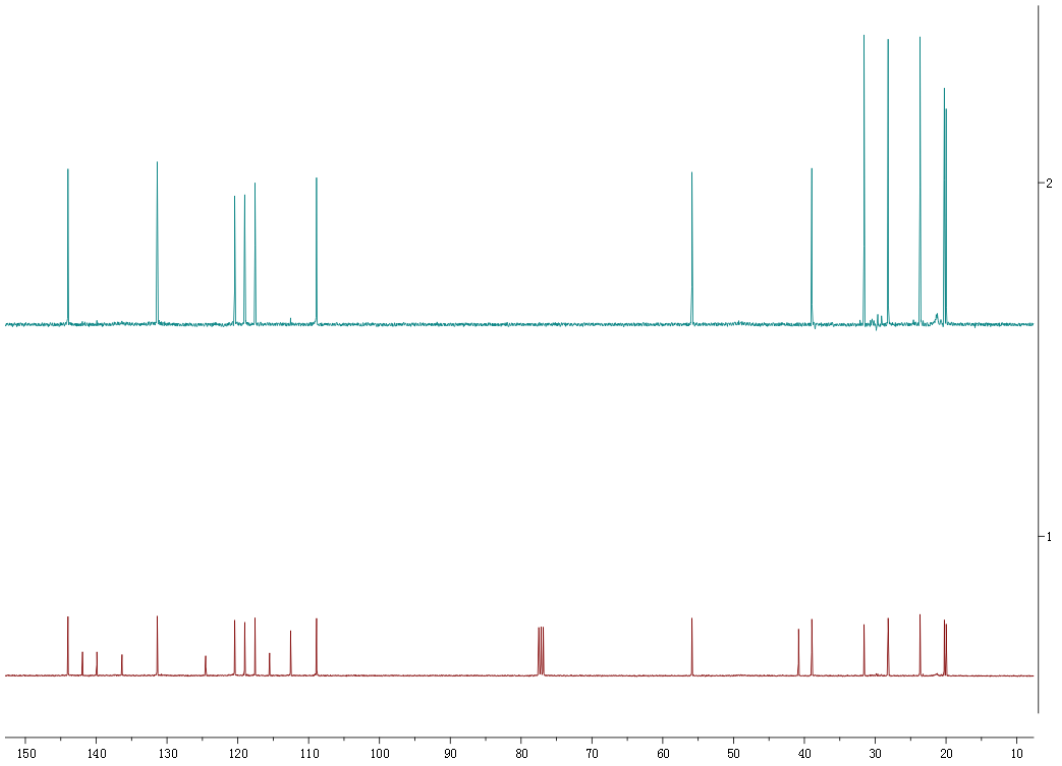
3o ^{1}H NMR, 400MHz, $CDCl_3$



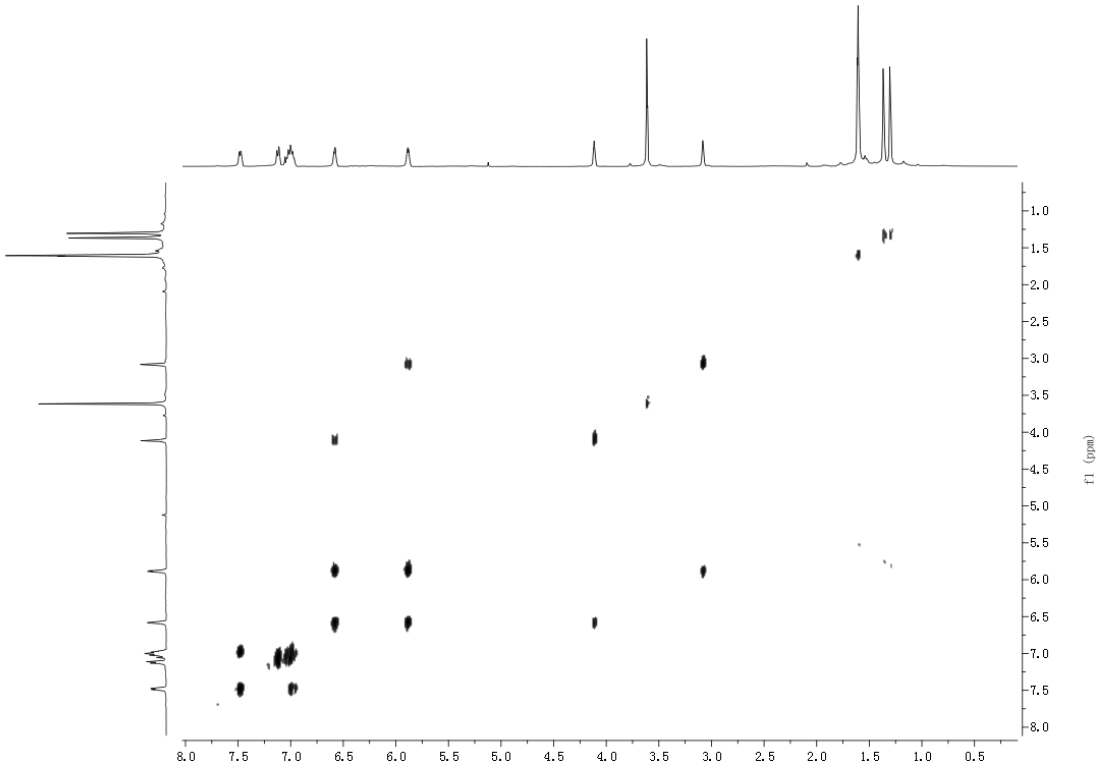
3o ^{13}C NMR, 400MHz, $CDCl_3$



3o DEPT 135, 400MHz, $CDCl_3$ and **2o** ^{13}C NMR, 400MHz, $CDCl_3$



3o H-H COSY, 400MHz, $CDCl_3$



3o C-H HSQC, 400MHz, $CDCl_3$