

Regioselectivities in Alkyne Activation: Synthesis of 2-(bicyclo[3.1.0]hexan-1-yl)furan Derivatives by Au-Catalyzed Cyclization and Cyclopropanation

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Table of Contents

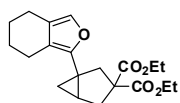
1. Experimentals	2
2. Spectroscopic data of compounds 2a-2t , 3m , and 4m	2
3. ¹ H and ¹³ C NMR Spectra of Compounds 2a-2t , 3m , and 4m	7

1. Experimentals

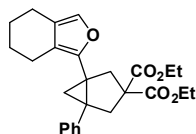
A General Information. All solvents were reagent grade. All chemicals were purchased from Aldrich Chemical Co. Reactions were normally carried out under argon atmosphere in flame-dried glassware. Merck silica gel 60 (partial size 0.04-0.063 mm) was employed for flash chromatography. The sample was analyzed and/or separated on a μ -Porasil column (25 cm x 2.5 cm) by elution with gradient of ethyl acetate and hexane. The flow rate of the indicated elution solvent was maintained at 3-5 mL/min. ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 at 400 MHz Varian NMR spectrometer.

Typical Procedure. To a 5 mL new test tube containing AuBr_3 (5 mol%) in dry toluene (0.5 mL) was added a toluene solution (0.5 mL) of 2-alkynyl-1-cyclohexenecarbaldehyde **1m** (0.14 mmol) at 0°C under argon atmosphere. The reaction mixture was stirred for 0.1h at 0°C by monitoring the reaction progress by TLC periodically. Upon completion, the reaction was quenched with a drop of triethylamine and the solvent was removed under vacuum. The crude product was subjected for flash column chromatography (SiO_2 , n-hexane/ EtOAc = 20:1) to afford the pure products **2m** in 80% yield. The spectral data of all products are the followings.

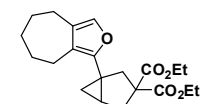
2. Spectroscopic data of compounds 2a-2t, 3m, and 4m



Spectroscopic data of compound 2a: (colorless oil, R_f = 0.24, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2981, 2933, 2857, 1732, 1444, 1368, 1244, 1181, 1154, 1095; ^1H -NMR (400MHz, CDCl_3) δ 6.96 (s, 1H), 4.22~4.12 (m, 4H), 2.86 (d, J = 13.6 Hz, 1H), 2.71 (d, J = 13.6Hz, 1H), 2.65~2.60 (m, 2H), 2.55~2.52 (m, 2H), 2.50~2.47 (m, 2H), 1.73~1.60 (m, 5H), 1.27~1.20 (m, 6H), 0.98~0.94 (m, 1H), 0.60~0.57 (m, 1H); ^{13}C -NMR (100 MHz, CDCl_3) δ 172.71, 171.61, 149.03, 134.59, 122.39, 116.42, 94.36, 61.74, 61.61, 59.63, 39.10, 35.78, 26.22, 24.45, 23.44, 23.12, 20.99, 20.33, 15.67, 13.97; HRMS (EI) calculated for $\text{C}_{20}\text{H}_{26}\text{O}_5$ 346.1780; found, 346.1782.

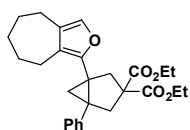


Spectroscopic data of compound 2b: (colorless oil, R_f = 0.22, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2930, 2855, 1730, 1445, 1246, 1182, 1094; ^1H -NMR (400MHz, CDCl_3) δ 7.18~7.08 (m, 5H), 6.90 (s, 1H), 4.27~4.16 (m, 4H), 3.09~2.89 (m, 1H), 2.39~2.34 (m, 2H), 2.27~2.24 (m, 2H), 1.64~1.57 (m, 2H), 1.46 (d, J = 5.2Hz, 2H), 1.30~1.22 (m, 7H), 1.13 (d, J = 5.6Hz, 1H); ^{13}C -NMR (100MHz, CDCl_3) δ 172.72, 171.63, 145.81, 140.72, 135.29, 128.03, 127.81, 125.98, 122.15, 118.59, 61.87, 61.74, 57.89, 42.44, 40.05, 38.54, 33.36, 29.68, 23.32, 22.97, 21.22, 20.23, 19.73, 13.99; HRMS (EI) calculated for $\text{C}_{26}\text{H}_{30}\text{O}_5$ 422.2093; found, 422.2090.



Spectroscopic data of compound 2c: (colorless oil, R_f = 0.35, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2980, 2921, 2846, 1732, 1446, 1366, 1245; ^1H -NMR (400MHz, CDCl_3) δ 6.94 (s, 1H), 4.23~4.12 (m, 4H), 2.85 (d, J = 13.6Hz, 1H), 2.66~2.42 (m, 7H), 1.76 (bs, 2H), 1.68~1.63 (m, 5H), 1.28~1.20 (m, 6H), 0.90~0.86 (m, 1H), 0.63~0.60 (m, 1H); ^{13}C -NMR (100MHz, CDCl_3) δ 172.73, 171.56, 150.43, 135.28, 128.32, 123.26, 61.72, 61.63, 59.77, 40.63, 35.79, 32.78, 29.69, 29.42,

25.95, 25.61, 25.27, 24.19, 15.13, 13.98; HRMS (EI) calculated for $C_{21}H_{28}O_5$ 360.1937; found, 360.1934.



Spectroscopic data of compound 2d: (colorless oil, $R_f = 0.29$, hexane/EtOAc=10/1);

FT-IR (neat, cm^{-1}) 2981, 2930, 2855, 1833, 1733, 1447, 1250, 1094; 1H -NMR (400MHz,

$CDCl_3$) δ 7.14~7.06 (m, 3H), 7.00 (d, $J = 7.2$ Hz, 2H), 6.92 (s, 1H), 4.28~4.17 (m, 4H),

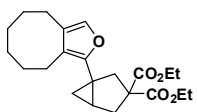
3.02~2.96 (m, 2H), 2.98 (ABq, $\Delta\delta = 124.0$ Hz, $J = 14.0$ Hz, 2H), 2.43~2.37 (m, 1H),

2.31~2.25 (m, 3H), 1.73~1.65 (m, 1H), 1.60~1.49 (m, 3H), 1.44~1.33 (m, 2H), 1.30~1.22 (m, 6H), 1.19 (d, $J =$

6.0Hz, 1H), 0.98~0.88 (m, 1H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 172.63, 171.66, 147.12, 140.39, 135.88, 128.31,

127.68, 126.99, 125.74, 125.00, 61.88, 61.76, 57.78, 41.89, 40.00, 37.38, 33.56, 32.61, 29.66, 28.78, 25.91, 25.72,

20.93, 13.98; HRMS (EI) calculated for $C_{27}H_{32}O_5$ 436.2250; found, 436.2242.



Spectroscopic data of compound 2e: (colorless oil, $R_f = 0.48$, hexane/EtOAc=10/1);

FT-IR (neat, cm^{-1}) 2979, 2930, 2856, 1731, 1445, 1366, 1249, 1180, 1094, 1068, 1012;

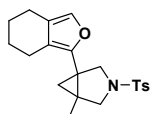
1H -NMR (400MHz, $CDCl_3$) δ 6.96 (s, 1H), 4.23~4.12 (m, 4H), 2.86 (d, $J = 13.6$ Hz, 1H),

2.66~2.42 (m, 7H), 1.76 (bs, 2H), 1.68~1.63 (m, 5H), 1.26 (t, $J = 7.6$ Hz, 6H), 0.90~0.86

(m, 1H), 0.63~0.60 (m, 1H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 172.72, 171.61, 150.61, 135.60, 126.83, 120.81, 61.74,

61.61, 59.74, 40.38, 35.81, 31.69, 30.39, 25.64, 25.59, 24.23, 22.28, 21.30, 15.67, 13.97; HRMS (EI) calculated

for $C_{22}H_{30}O_5$ 374.2093; found, 374.2098.



Spectroscopic data of compound 2f: (colorless oil, $R_f = 0.37$, hexane/EtOAc=10/1); FT-

IR (neat, cm^{-1}) 2930, 2858, 1757, 1597, 1447, 1346, 1167; 1H -NMR (400MHz, $CDCl_3$) δ

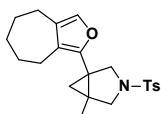
7.68 (d, $J = 8$ Hz, 2H), 7.33 (d, $J = 7.6$ Hz, 2H), 6.96 (s, 1H), 3.61 (d, $J = 9.2$ Hz, 2H), 3.27

(d, $J = 8.8$ Hz, 1H), 2.97 (d, $J = 9.2$ Hz, 1H), 2.44 (s, 3H), 2.40 (bs, 2H), 2.38~2.25 (m, 2H),

1.68~1.65 (m, 2H), 1.61~1.58 (m, 2H), 1.03 (ABq, $\Delta\delta = 68.0$ Hz, $J = 4.8$ Hz, 2H), 0.98 (s, 3H); ^{13}C -NMR (100MHz,

$CDCl_3$) δ 144.45, 143.45, 136.03, 133.57, 129.62, 127.54, 122.22, 119.88, 54.67, 52.44, 28.91, 28.71, 23.28, 23.00,

21.50, 20.96, 20.15, 18.61, 15.75; HRMS (EI) calculated for $C_{21}H_{25}NO_3S$ 371.1555; found, 371.1551.



Spectroscopic data of compound 2g: (colorless oil, $R_f = 0.37$, hexane/EtOAc=10/1); FT-

IR (neat, cm^{-1}) 2928, 2857, 1758, 1597, 1446, 1345, 1164; 1H -NMR (400MHz, $CDCl_3$) δ

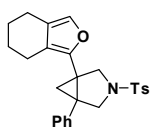
7.67 (d, $J = 8$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 6.94 (s, 1H), 3.62 (d, $J = 9.2$ Hz, 2H), 3.06

(ABq, $\Delta\delta = 44.0$ Hz, $J = 9.2$ Hz, 2H), 2.44 (s, 3H), 2.42~2.39 (m, 2H), 2.35~2.31 (m, 2H),

1.78~1.69 (m, 2H), 1.57~1.45 (m, 2H), 0.99 (ABq, $\Delta\delta = 112.0$ Hz, $J = 4.4$ Hz), 0.98 (s, 3H); ^{13}C -NMR (100MHz,

$CDCl_3$) δ 145.90, 143.45, 136.62, 133.53, 129.60, 128.21, 127.53, 126.15, 54.72, 53.85, 32.68, 29.59, 28.48, 28.45,

27.95, 25.85, 25.70, 21.52, 19.35, 16.05; HRMS (EI) calculated for $C_{22}H_{27}NO_3S$ 385.1712; found, 385.1717.



Spectroscopic data of compound 2h: (colorless oil, $R_f = 0.37$, hexane/EtOAc=10/1); FT-IR

(neat, cm^{-1}) 2930, 2856, 1598, 1446, 1348, 1164, 1104, 1015; 1H -NMR (400MHz, $CDCl_3$) δ

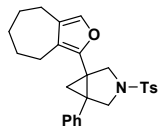
7.72 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.18~7.12 (m, 3H), 6.98~6.96 (m, 2H), 6.89

(s, 1H), 3.82 (ABq, $\Delta\delta = 52.0$ Hz, $J = 9.2$ Hz, 2H), 3.47 (ABq, $\Delta\delta = 40.0$ Hz, $J = 9.2$ Hz, 2H),

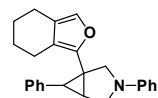
2.46 (s, 3H), 2.38~2.28 (m, 4H), 2.18~2.14 (m, 1H), 1.66 (d, $J = 5.2$ Hz, 1H), 1.61~1.55 (m, 2H), 1.47 (bs, 2H);

^{13}C -NMR (100MHz, $CDCl_3$) δ 143.65, 142.76, 137.26, 136.12, 133.41, 129.73, 128.08, 127.60, 126.72, 122.24,

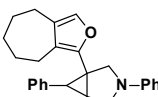
120.04, 54.75, 52.58, 36.85, 31.64, 23.13, 22.83, 21.57, 20.98, 20.08, 18.39; HRMS (EI) calculated for $C_{26}H_{27}NO_3S$ 433.1711; found, 433.1709.



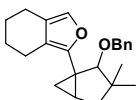
Spectroscopic data of compound 2i: (colorless oil, $R_f = 0.37$, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2922, 2848, 1763, 1598, 1447, 1348, 1166, 1104, 1028; 1H -NMR (400MHz, $CDCl_3$) δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.16~7.11 (m, 3H), 6.91~6.89 (m, 3H), 3.83 (ABq, $\Delta\delta = 56.0$ Hz, $J = 9.2$ Hz, 2H), 3.57 (d, $J = 9.2$ Hz, 1H), 3.33 (d, $J = 9.6$ Hz, 1H), 2.45 (s, 3H), 2.36 (d, $J = 6.4$ Hz, 1H), 2.30 (d, $J = 9.6$ Hz, 1H), 2.23~2.21 (m, 2H), 1.63 (dd, $J = 5.6$ Hz, 4H), 1.41~1.38 (m, 3H), 1.10 (d, $J = 6$ Hz, 1H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 143.89, 143.67, 137.13, 136.69, 133.32, 129.69, 128.29, 127.97, 127.58, 127.12, 126.49, 53.90, 53.79, 35.86, 32.50, 31.65, 29.50, 28.84, 25.74, 25.61, 21.51, 19.73; HRMS (EI) calculated for $C_{27}H_{29}NO_3S$ 447.1868; found, 447.1870.



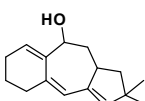
Spectroscopic data of compound 2j: (colorless oil, $R_f = 0.40$, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2929, 2850, 1598, 1504, 1476, 1364, 1199, 1119; 1H -NMR (400MHz, $CDCl_3$) δ 7.22 (d, $J = 8.7$ Hz, 2H), 7.14~7.08 (m, 2H), 6.94 (s, 1H), 6.84 (d, $J = 6.8$ Hz, 2H), 6.72 (t, $J = 7.2$ Hz, 1H), 6.62 (d, $J = 8.0$ Hz, 2H), 3.92 (ABq, $\Delta\delta = 68.0$ Hz, $J = 9.2$ Hz, 1H), 3.56 (dd, $J = 4.0, 4.4$ Hz, 1H), 3.36 (d, $J = 9.2$ Hz, 1H), 2.54 (t, $J = 4.0$ Hz, 1H), 2.41 (d, $J = 4.8$ Hz, 3H), 2.36~2.29 (m, 1H), 2.33 (ddd, $J = 14.0, 3.6, 6.4$ Hz, 1H), 1.57 (m, 2H), 1.43~1.39 (m, 1H), 1.25 (bs, 1H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 147.98, 144.26, 138.29, 135.71, 129.23, 127.66, 127.03, 125.64, 122.11, 120.38, 116.68, 112.31, 55.01, 50.58, 33.64, 33.46, 29.39, 23.13, 23.10, 20.47, 20.14; HRMS (EI) calculated for $C_{25}H_{25}NO$ 355.1936; found, 355.1930.



Spectroscopic data of compound 2k: (colorless oil, $R_f = 0.41$, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2921, 2843, 1674, 1599, 1505, 1365, 1199, 1031; 1H -NMR (400MHz, $CDCl_3$) δ 7.25~7.21 (m, 2H), 7.13~7.06 (m, 2H), 6.95 (s, 1H), 6.76~6.70 (m, 3H), 6.61 (d, $J = 8.0$ Hz, 2H), 3.88 (ABq, $\Delta\delta = 40.0$ Hz, $J = 9.2$ Hz, 1H), 3.58 (dd, $J = 4.0, 4.0$ Hz, 1H), 3.36 (d, $J = 9.2$ Hz, 1H), 2.51 (t, $J = 4.4$ Hz, 1H), 2.38 (d, $J = 4.4$ Hz, 2H), 2.31~2.19 (m, 3H), 1.67~1.57 (m, 2H), 1.47~1.42 (m, 42H), 1.36~1.19 (m, 2H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 147.95, 145.02, 138.45, 136.14, 129.20, 128.30, 127.61, 126.76, 126.39, 125.58, 116.67, 112.30, 55.66, 50.62, 33.60, 33.50, 32.54, 29.89, 29.71, 28.56, 25.94, 25.64 ; HRMS (EI) calculated for $C_{25}H_{25}NO$ 369.2093; found, 369.2098.



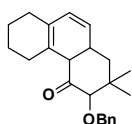
Spectroscopic data of compound 2m: (colorless oil, $R_f = 0.48$, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2931, 2860, 1558, 1453, 1100, 1073, 1027; 1H -NMR (400MHz, $CDCl_3$) δ 7.31~7.42 (m, 5H), 7.02(s, 1H), 4.52 (ABq, $\Delta\delta = 142.0$ Hz, $J = 12$ Hz, 2H), 3.79 (s, 1H), 2.51 (bs, 4H), 1.84~1.75 (m, 1H), 1.66 (bs, 4H), 1.47 (d, $J = 10.4$ Hz, 2H), 1.21~1.19 (m, 2H), 1.16 (s, 3H), 1.00 (s, 3H); ^{13}C -NMR (100MHz, $CDCl_3$) δ 151.04, 140.09, 135.65, 128.80, 127.92, 127.72, 122.79, 116.38, 90.85, 70.69, 49.843, 43.87, 33.824, 30.43, 27.29, 24.25, 24.12, 23.79, 22.32, 21.39, 21.10; HRMS (EI) calculated for $C_{17}H_{20}O$ 336.2089; found, 336.2087.



Spectroscopic data of compound 3m: (colorless oil, $R_f = 0.12$, hexane/EtOAc=10/1); FT-IR (neat, cm^{-1}) 2929, 2860, 1452, 1063; 1H -NMR (400MHz, $CDCl_3$) δ 6.02 (bs, 1H), 5.98 (s, 1H), 5.43 (s, 1H), 4.27 (m, 1H), 2.97~2.95 (m, 1H), 2.33~2.22 (m, 4H), 2.11 (dt, $J = 3.6$ Hz, 1H),

1.97~1.92 (m, 1H), 1.79~1.71 (m, 3H), 1.67 (dd, $J = 2.8\text{Hz}$, 2H), 1.43~1.37 (m, 1H), 1.09 (s, 3H), 1.02 (s, 3H);

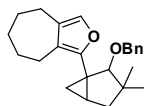
^{13}C -NMR (100MHz, CDCl_3) δ 142.22, 141.30, 140.21, 133.61, 126.21, 121.78, 74.51, 48.40, 43.46, 43.00, 42.81, 35.78, 29.36, 26.87, 26.05, 23.85; HRMS (EI) calculated for $\text{C}_{17}\text{H}_{20}\text{O}$ 230.1671; found, 230.1673.



Spectroscopic data of compound 4m: (colorless oil, $R_f = 0.33$, hexane/EtOAc=10/1); FT-IR

(neat, cm^{-1}) 2978, 2860, 1728, 1591, 1450, 1427; ^1H -NMR (400MHz, CDCl_3) δ 7.34~7.29 (m, 5H), 5.84 (s, 1H), 5.37 (bs, 1H), 4.48 (ABq, $\Delta\delta = 48\text{Hz}$, $J = 12.0\text{Hz}$, 2H), 3.64 (bd, $J = 96.0\text{Hz}$, 1H), 3.33 (s, 1H), 2.28 (bs, 2H), 2.13~2.01 (m, 2H), 1.86~1.81 (m, 2H), 1.1.74~1.1.68 (m, 1H),

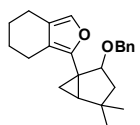
1.62~1.58 (m, 1H), 1.35~1.26 (m, 2H), 1.08 (s, 3H), .87(s, 3H); ^{13}C -NMR (100MHz, CDCl_3) δ 213.69, 138.36, 135.15, 129.08, 128.80, 128.42, 128.36, 127.35, 120.87, 91.67, 72.60, 49.76, 42.20, 40.13, 37.83, 33.52, 32.22, 27.47, 26.85, 24.53, 23.405; HRMS (EI) calculated for $\text{C}_{17}\text{H}_{20}\text{O}$ 336.2089; found, 336.2087



Spectroscopic data of compound 2n: (colorless oil, $R_f = 0.51$, hexane/EtOAc=10/1); FT-IR

(neat, cm^{-1}) 2921, 2850, 1762, 1604, 1448, 1363, 1127, 1074, 1028; ^1H -NMR (400MHz, CDCl_3) δ 7.20~7.23 (m, 5H), 7.00 (s, 1H), 4.52 (ABq, $\Delta\delta = 147.2\text{Hz}$, $J = 12.4\text{Hz}$, 2H), 3.72 (s,

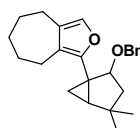
1H), 6.2.60~2.45 (m, 4H), 1.89~1.84 (m, 1H), 1.78~1.74 (m, 2H), 1.68~1.51 (m, 6H), 1.30 (t, $J = 4.4\text{Hz}$, 1H), 1.18 (s, 3H), 1.12~1.09 (m, 1H), 1.00 (s, 3H); ^{13}C -NMR (100MHz, CDCl_3) δ 151.72, 139.41, 135.47, 128.11, 127.15, 127.02, 122.65, 91.35, 70.36, 47.78, 43.15, 32.83, 30.27, 29.73, 29.23, 25.97, 25.90, 25.73, 24.01, 19.92; HRMS (EI) calculated for $\text{C}_{24}\text{H}_{30}\text{O}_2$ 350.2246; found, 350.2250.



Spectroscopic data of compound 2o: (colorless oil, $R_f = 0.48$, hexane/EtOAc=10/1); FT-IR

(neat, cm^{-1}) 2932, 2862, 1758, 1684, 1453, 1364, 1095; ^1H -NMR (400MHz, CDCl_3) δ 7.27~7.18 (m, 5H), 7.03 (s, 1H), 4.47 (t, $J = 8.4\text{Hz}$, 1H), 4.40 (ABq, $\Delta\delta = 48.4\text{Hz}$, $J = 12.0\text{Hz}$, 2H),

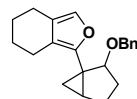
2.57~2.41 (m, 4H), 1.30 (m, 1H), 1.18 (m, 1H), 1.14 (s, 3H), 1.00 (s, 3H); ^{13}C -NMR (100MHz, CDCl_3) δ 149.37, 139.02, 134.86, 128.15, 127.55, 127.22, 122.28, 116.97, 81.91, 71.27, 41.47, 37.04, 36.72, 29.93, 29.30, 26.34, 23.45, 23.19, 21.09, 20.40, 10.11; HRMS (EI) calculated for $\text{C}_{24}\text{H}_{30}\text{O}_2$ 336.2089; found, 336.2083.



Spectroscopic data of compound 2p: (colorless oil, $R_f = 0.50$, hexane/EtOAc=10/1); FT-IR

(neat, cm^{-1}) 2921, 2831, 1563, 1449, 1364, 1342, 1098; ^1H -NMR (400MHz, CDCl_3) δ 7.29~7.17 (m, 5H), 7.01 (s, 1H), 4.40 (ABq, $\Delta\delta = 51.2\text{Hz}$, $J = 12.0\text{Hz}$, 2H), 4.36 (t, $J = 8.4\text{Hz}$, 1H), 2.59

(td, $J = 8\text{Hz}$, 2H), 2.47 (m, 2H), 1.74 (m, 4H), 1.60 (m, 4H), 1.29~1.26 (m, 1H), 1.21 (t, $J = 5.2\text{Hz}$, 1H), 1.17 (s, 3H), 1.15~1.12 (m, 1H), 1.00 (s, 3H), 0.89 (m, 1H); ^{13}C -NMR (100MHz, CDCl_3) δ 150.77, 139.02, 135.46, 128.23, 128.15, 127.40, 127.17, 123.66, 82.85, 71.31, 41.64, 36.97, 36.07, 32.84, 29.87, 29.83, 28.76, 26.46, 26.04, 25.64, 10.84; HRMS (EI) calculated for $\text{C}_{24}\text{H}_{30}\text{O}_2$ 350.2246; found, 350.2249.

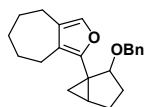


Spectroscopic data of compound 2q: (colorless oil, $R_f = 0.34$, hexane/EtOAc=10/1); FT-IR

(neat, cm^{-1}) 2930, 2862, 1452, 1340, 1102, 1072, 1028; ^1H -NMR (400MHz, CDCl_3) δ

7.29~7.19 (m, 5H), 7.02 (s, 1H), 4.43 (ABq, $\Delta\delta = 51.0\text{Hz}$, $J = 12.0\text{Hz}$, 2H), 4.45 (t, $J = 7.6\text{Hz}$, 1H), 2.55~2.41 (m, 4H), 1.93 (m, 2H), 1.79 (m, 1H), 1.65 (q, 2H), 1.50 (m, 1H), 1.32 (m, 2H), 1.20 (t, $J = 4.8\text{Hz}$, 1H), 1.05 (m, 1H); ^{13}C -NMR (100MHz, CDCl_3) δ 149.36, 138.97, 134.80, 128.15, 127.62, 127.25, 122.29, 117.27, 82.97, 71.36, 28.90, 27.26, 24.82, 24.66, 23.43, 23.22, 20.97, 20.36, 10.42; HRMS (EI) calculated for $\text{C}_{22}\text{H}_{26}\text{O}_2$

308.1776; found, 308. 1772.



Spectroscopic data of compound 2r: (colorless oil, R_f = 0.28, hexane/EtOAc=10/1); FT-IR

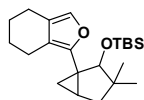
(neat, cm^{-1}) 2929, 2866, 1452, 1389, 1072; $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 7.29~7.17 (m, 5H),

7.01 (s, 1H), 4.41 (ABq, $\Delta\delta$ = 58.8Hz, J = 12.4Hz, 2H), 4.30 (t, J = 8Hz, 1H), 2.55~2.46 (m,

4H), 1.96 (m, 2H), 1.82~1.73 (m, 4H), 1.60 (m, 2H), 1.46 (q, J = 6Hz, 1H), 1.32 (m, 3H), 0.95 (m, 1H); $^{13}\text{C-NMR}$

(100MHz, CDCl_3) δ 150.99, 138.93, 135.43, 128.26, 128.13, 127.53, 127.20, 123.83, 83.98, 71.33, 32.82, 29.81,

29.28, 28.11, 27.39, 26.05, 25.69, 24.62, 10.71; HRMS (EI) calculated for $\text{C}_{22}\text{H}_{26}\text{O}_2$ 322.1933; found, 322.1938.



Spectroscopic data of compound 2s: (colorless oil, R_f = 0.24, hexane/EtOAc=40/1); FT-IR

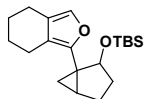
(neat, cm^{-1}) 2933, 2857, 1688, 1559, 1470, 1361, 1249, 1082, 1010; $^1\text{H-NMR}$ (400MHz,

CDCl_3) δ 7.06 (s, 1H), 4.23 (s, 1H), 2.63~2.44 (m, 4H), 1.89 (m, 1H), 1.73 (m, 2H), 1.65~1.52

(m, 4H), 1.32 (t, J = 4.4Hz, 1H), 1.13 (m, 1H), 0.93 (s, 9H), 0.00 (s, 3H), -0.09 (s, 3H); $^{13}\text{C-NMR}$ (100MHz,

CDCl_3) δ 150.21, 135.04, 122.25, 116.51, 84.49, 46.39, 43.05, 35.42, 30.65, 26.13, 25.32, 24.93, 23.81, 23.44,

21.81, 20.62, 18.39, 17.85, -4.70, -4.83; HRMS (CI) calculated for $\text{C}_{22}\text{H}_{37}\text{O}_2\text{Si}$ 361.2563; found, 361.2563.



Spectroscopic data of compound 2t: (colorless oil, R_f = 0.35, hexane/EtOAc=40/1); FT-IR

(neat, cm^{-1}) 2929, 2856, 1755, 1250, 1094, 1077, 1015; $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 7.00 (s,

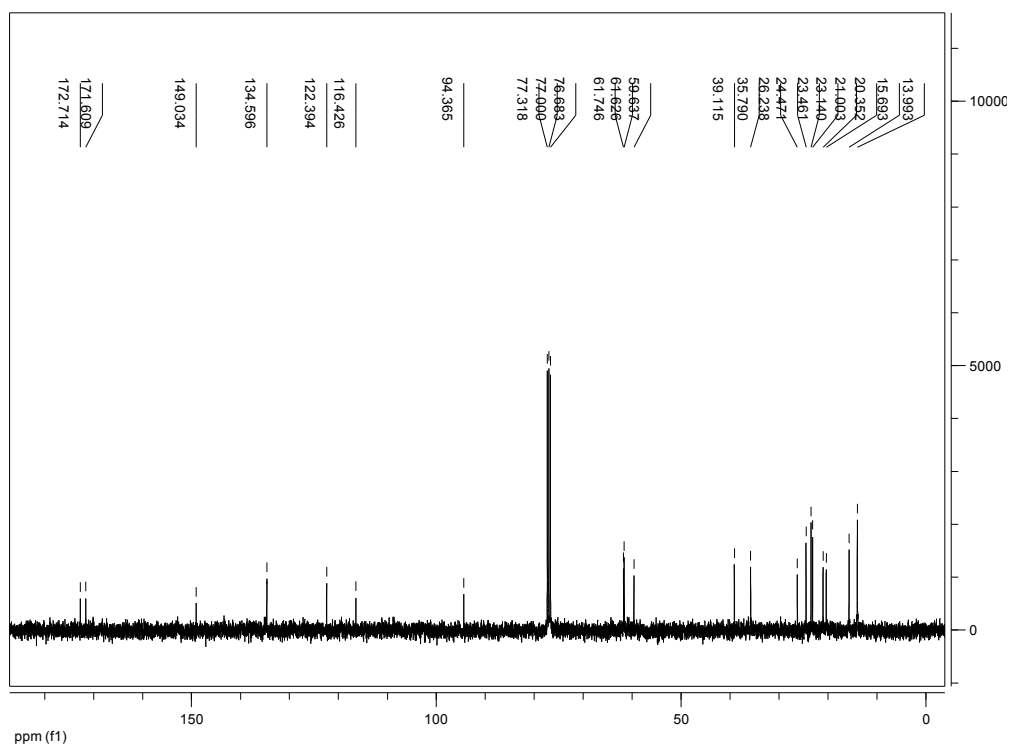
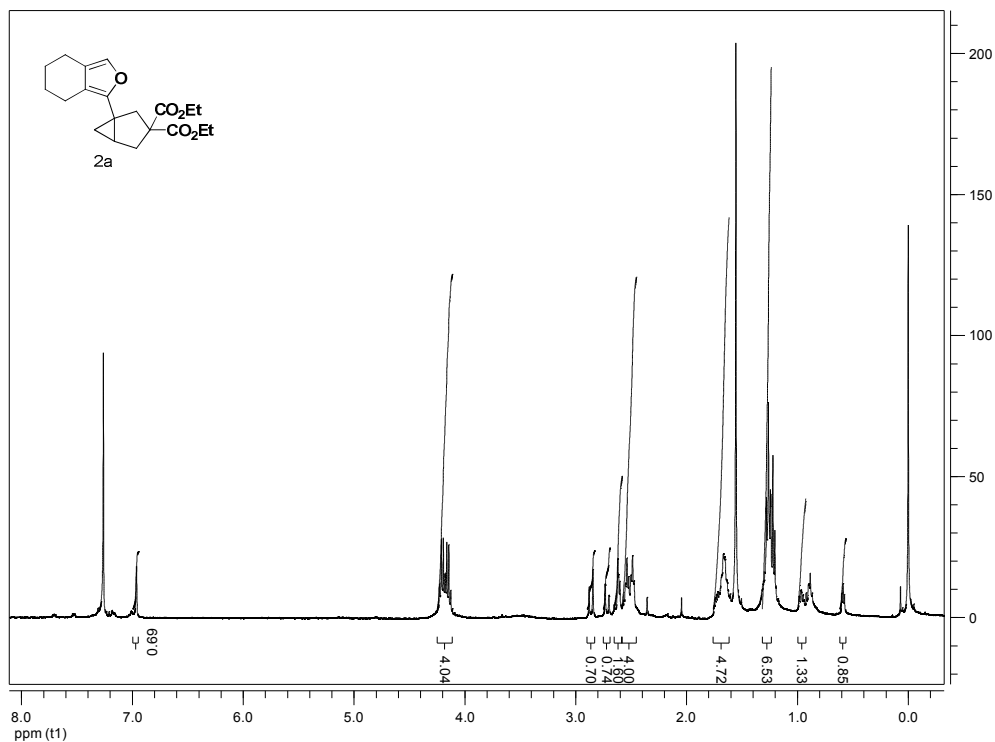
1H), 4.61 (t, J = 8Hz, 1H), 2.49 (m, 4H), 2.17 (m, 1H), 1.91 (m, 1H), 1.83~1.51 (m, 5H), 1.41

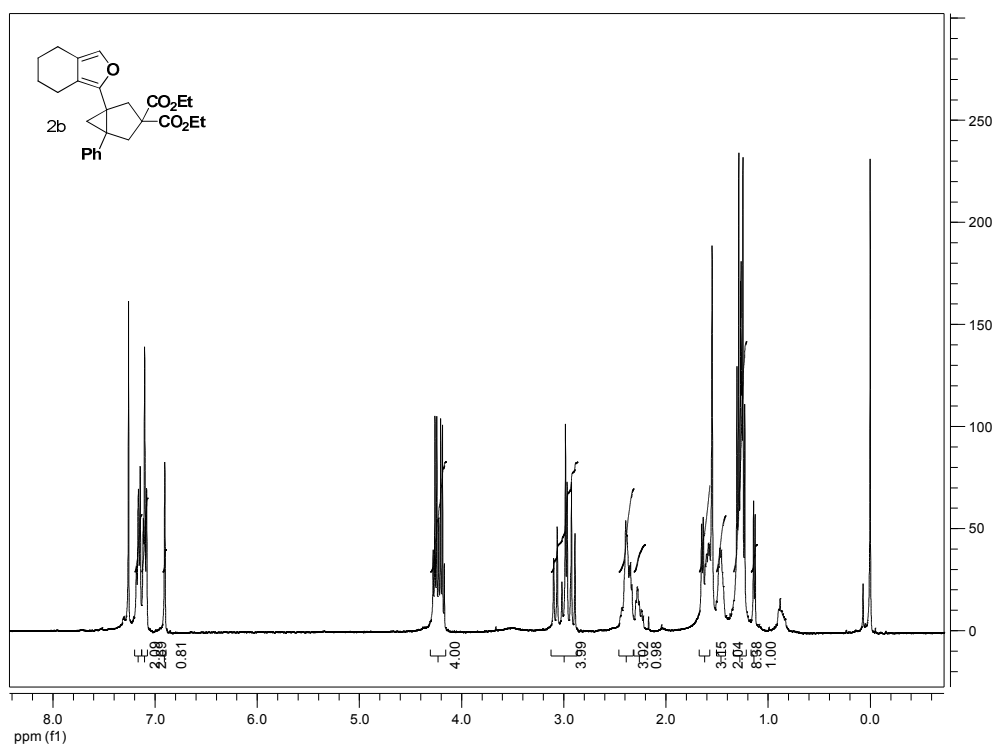
(q, J = 4.4Hz, 4H), 1.26 (m, 2H), 1.41 (t, J = 4.4Hz, 1H), 0.80 (s, 9H), -0.16 (d, J = 2.8Hz, 6H); $^{13}\text{C-NMR}$

(100MHz, CDCl_3) δ 149.02, 134.86, 122.09, 118.38, 77.53, 30.11, 29.32, 25.74, 24.66, 23.45, 23.33, 22.90, 20.89,

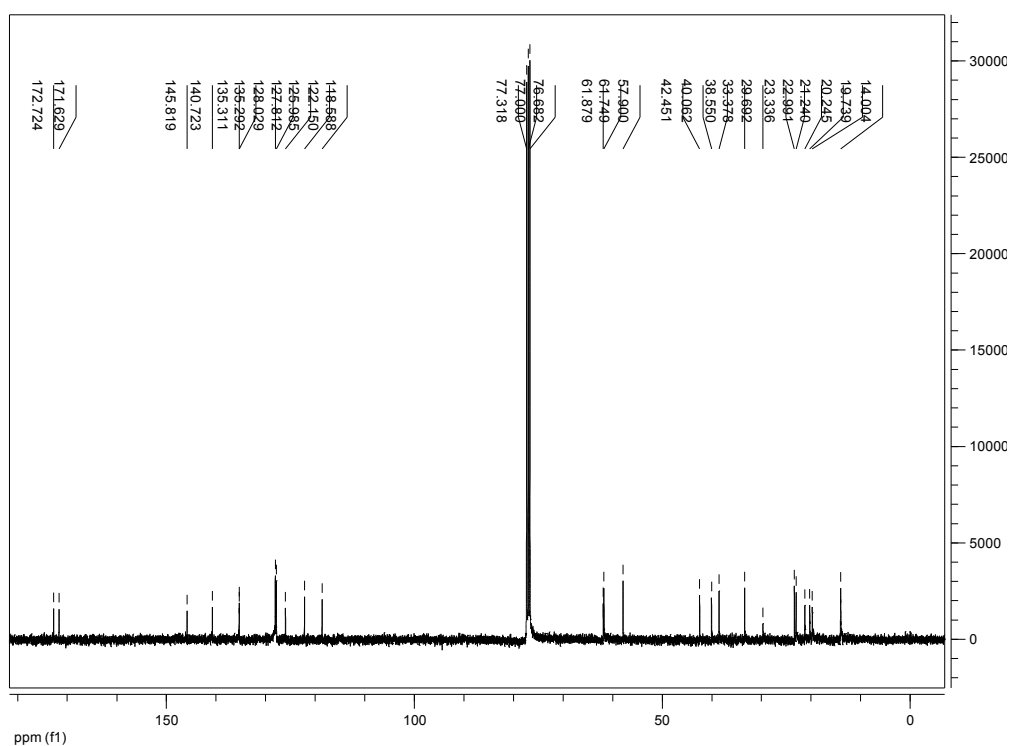
20.34, 18.13, 9.38, -5.17, -5.47; HRMS (CI) calculated for $\text{C}_{20}\text{H}_{33}\text{O}_2\text{Si}$ 333.2250; found, 323.2242.

3. ^1H and ^{13}C NMR Spectra of Compounds 2a-2t, 3m, and 4m

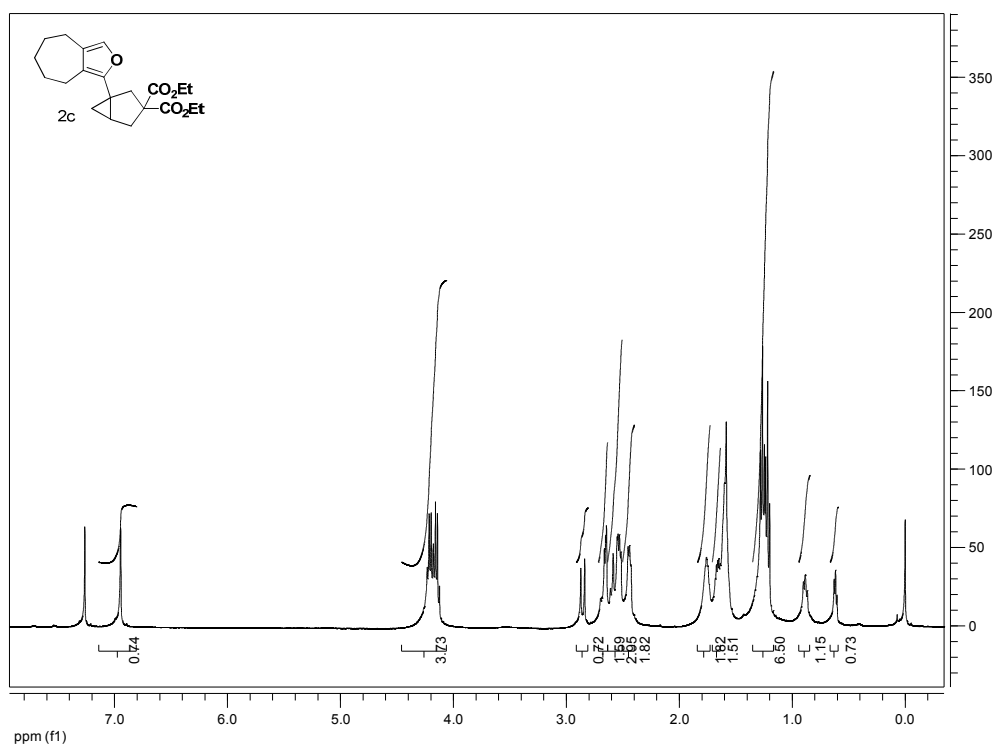




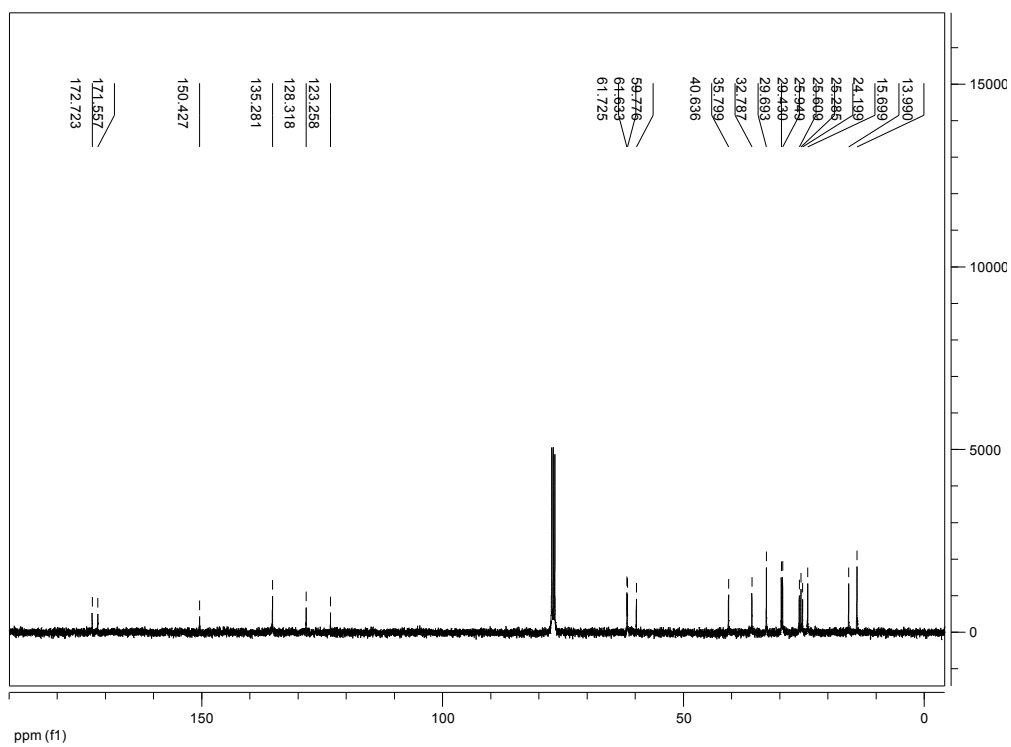
¹H-NMR Spectrum of Compound **2b**



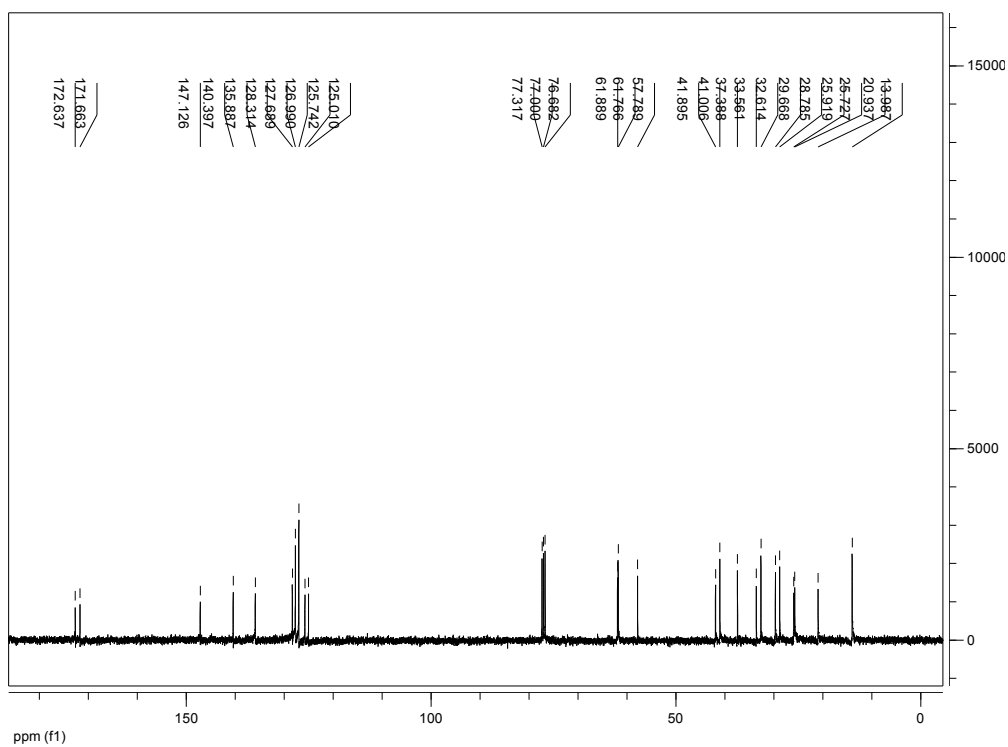
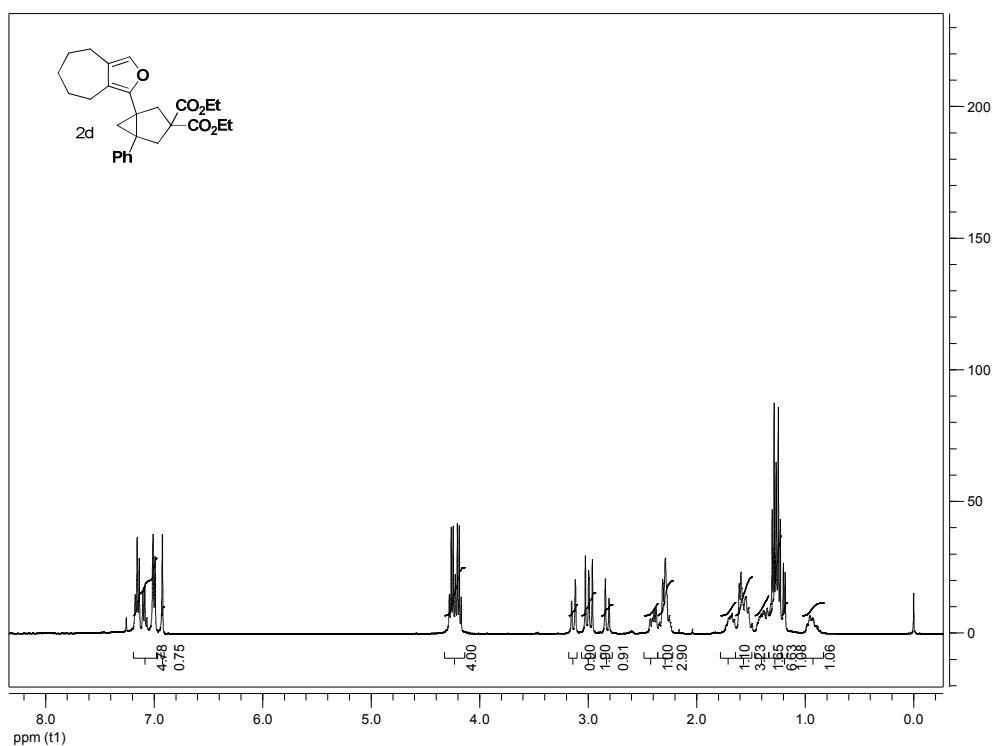
¹³C-NMR Spectrum of Compound **2b**

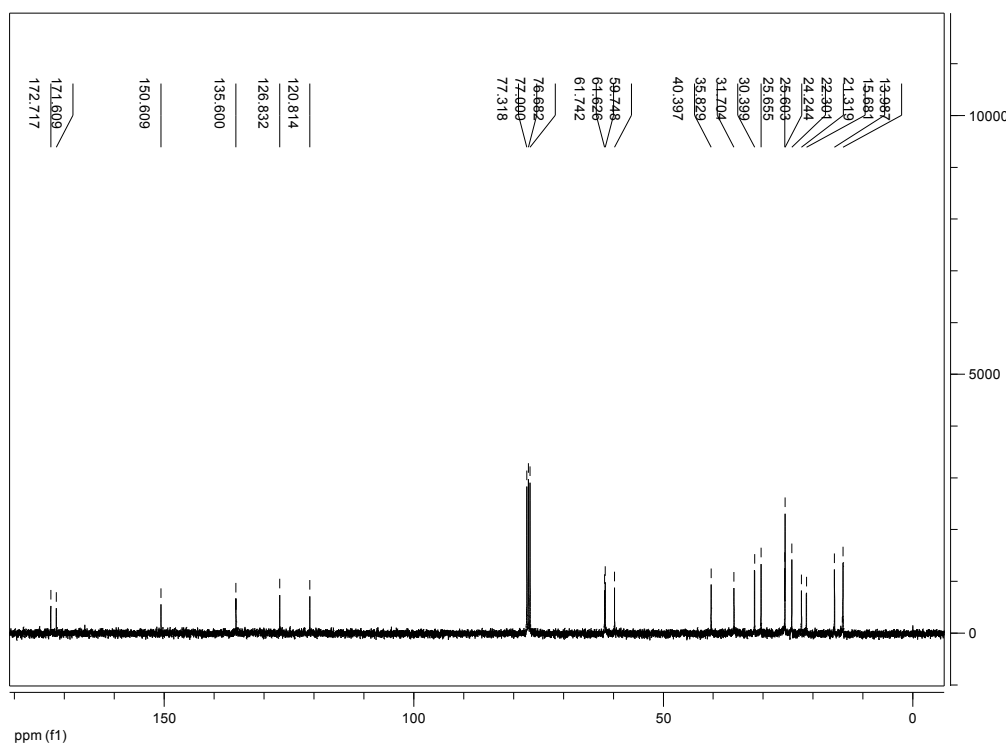
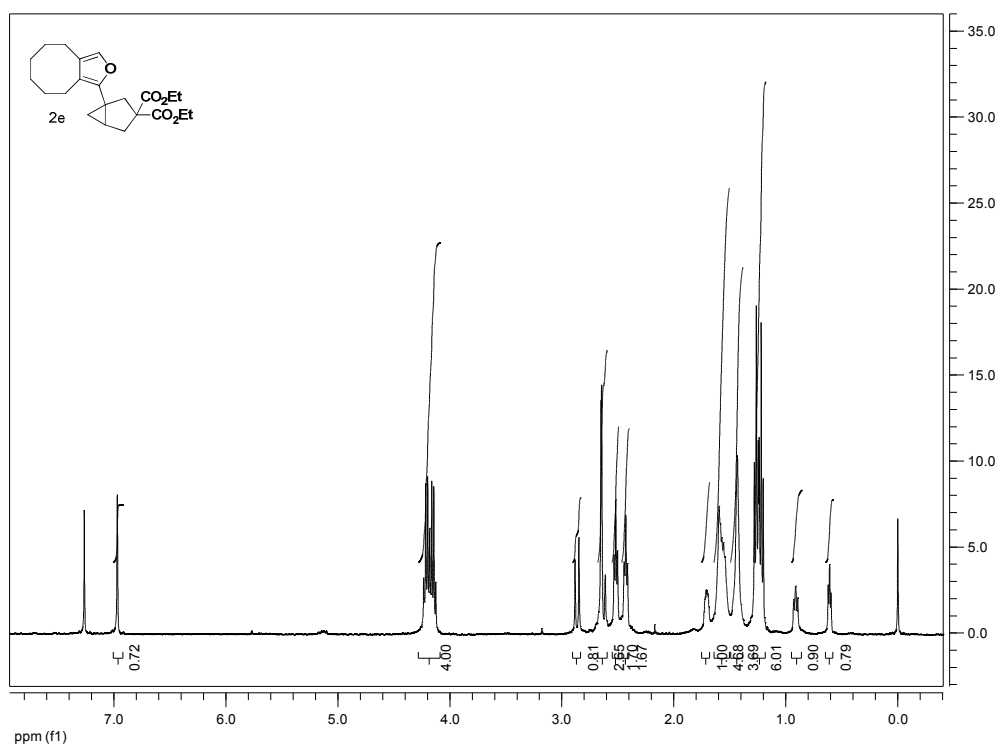


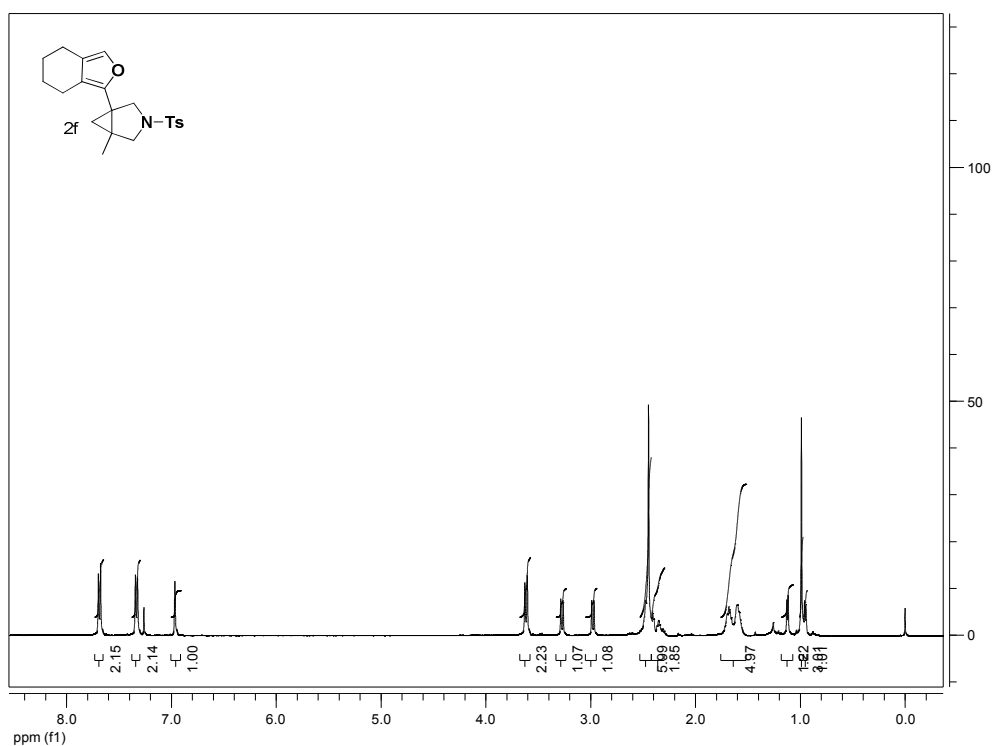
¹H-NMR Spectrum of Compound 2c



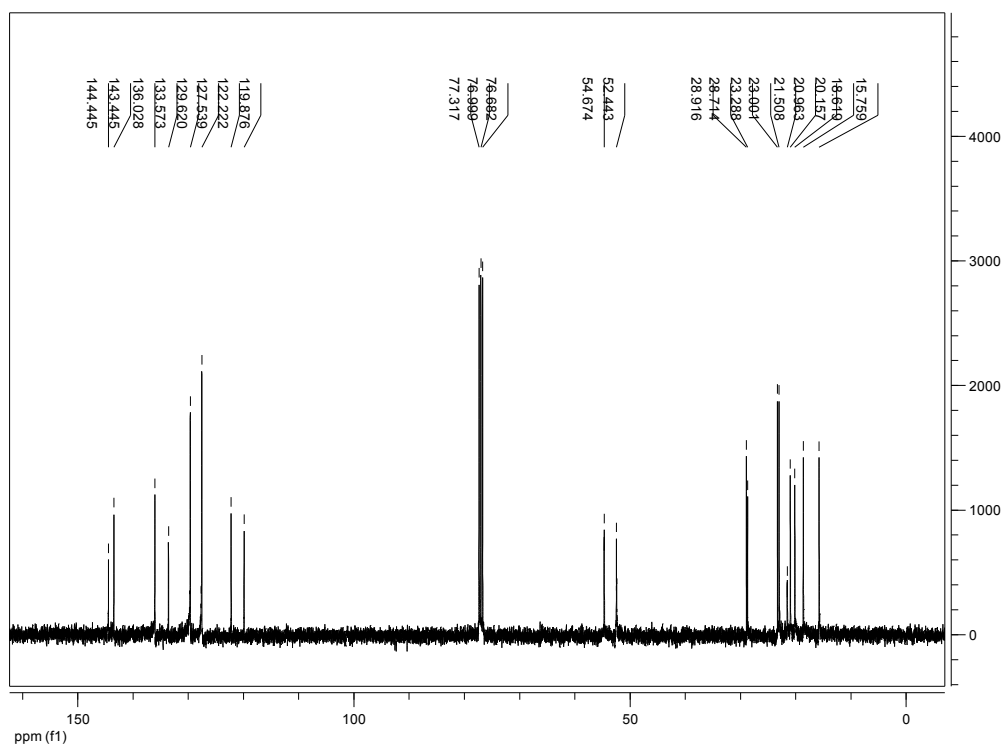
¹³C-NMR Spectrum of Compound 2c



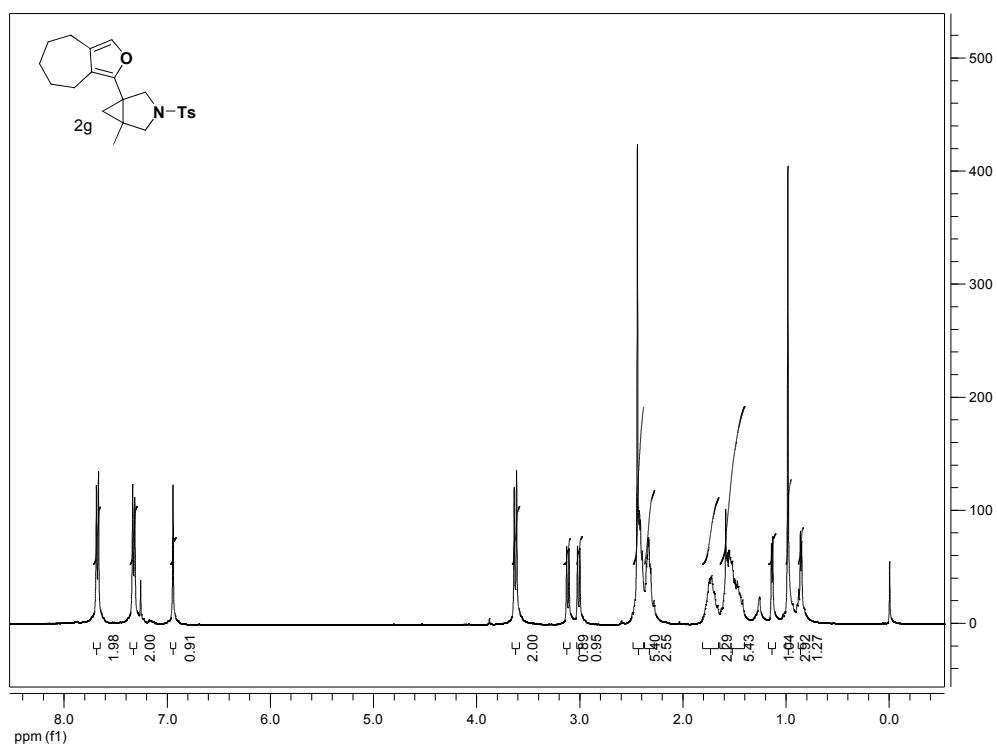




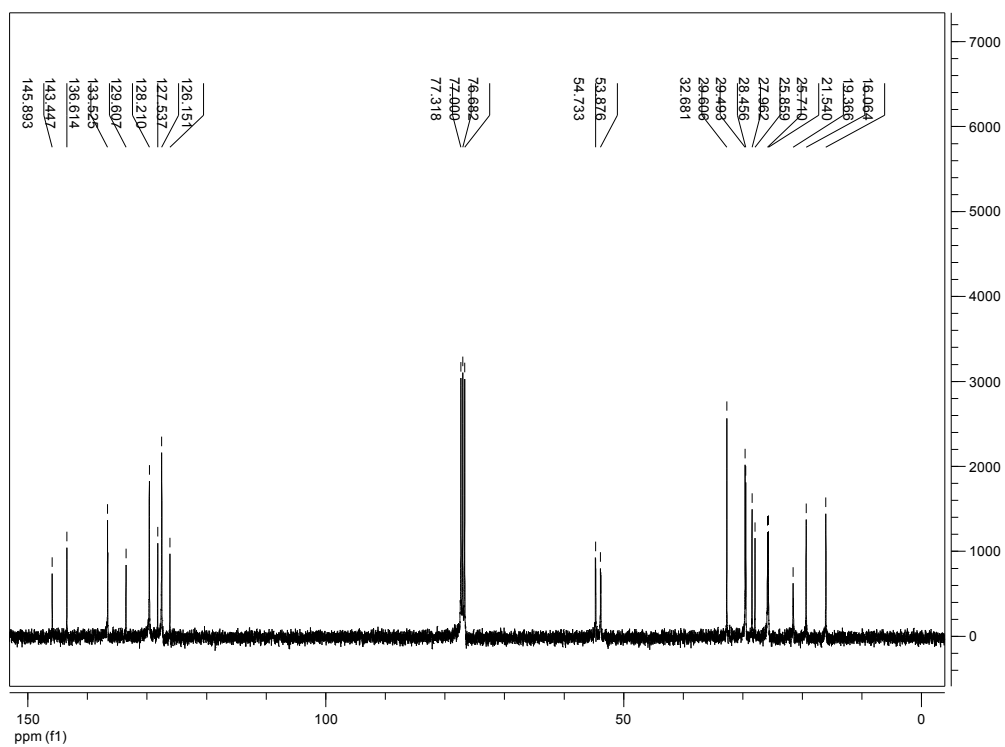
¹H-NMR Spectrum of Compound **2f**



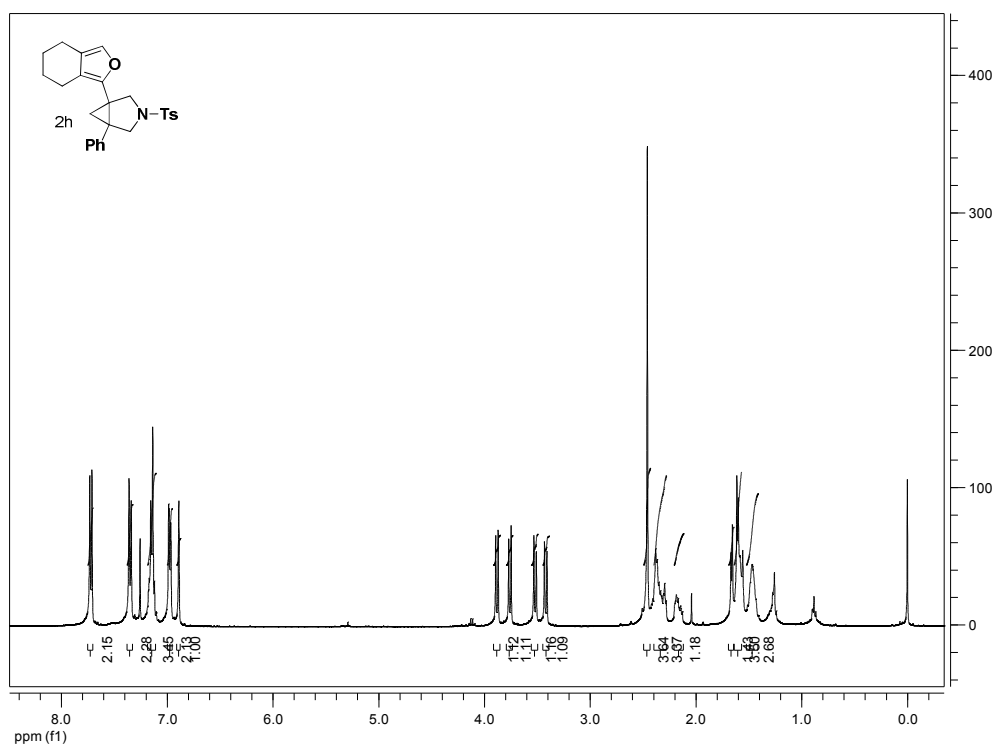
¹³C-NMR Spectrum of Compound **2f**



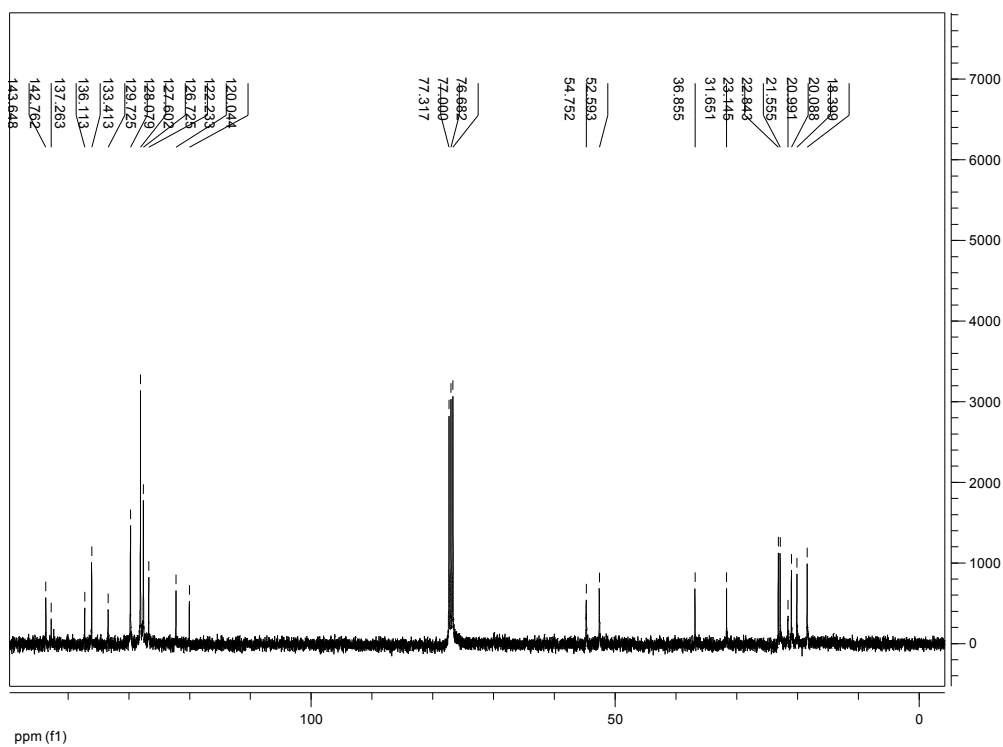
¹H-NMR Spectrum of Compound **2g**



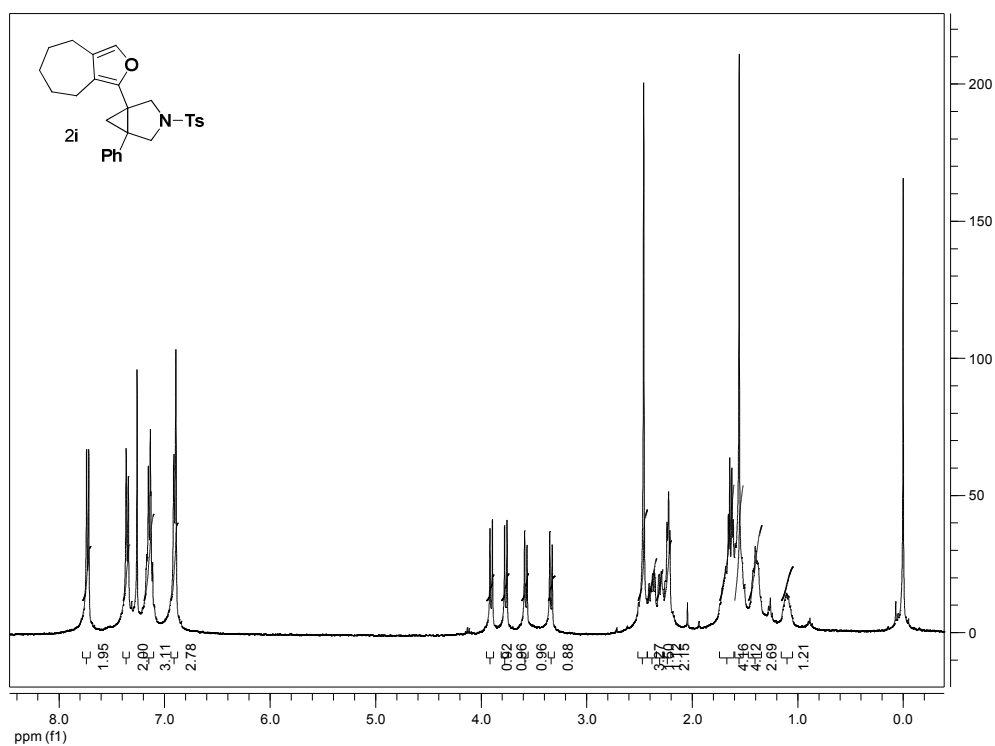
¹³C-NMR Spectrum of Compound **2g**



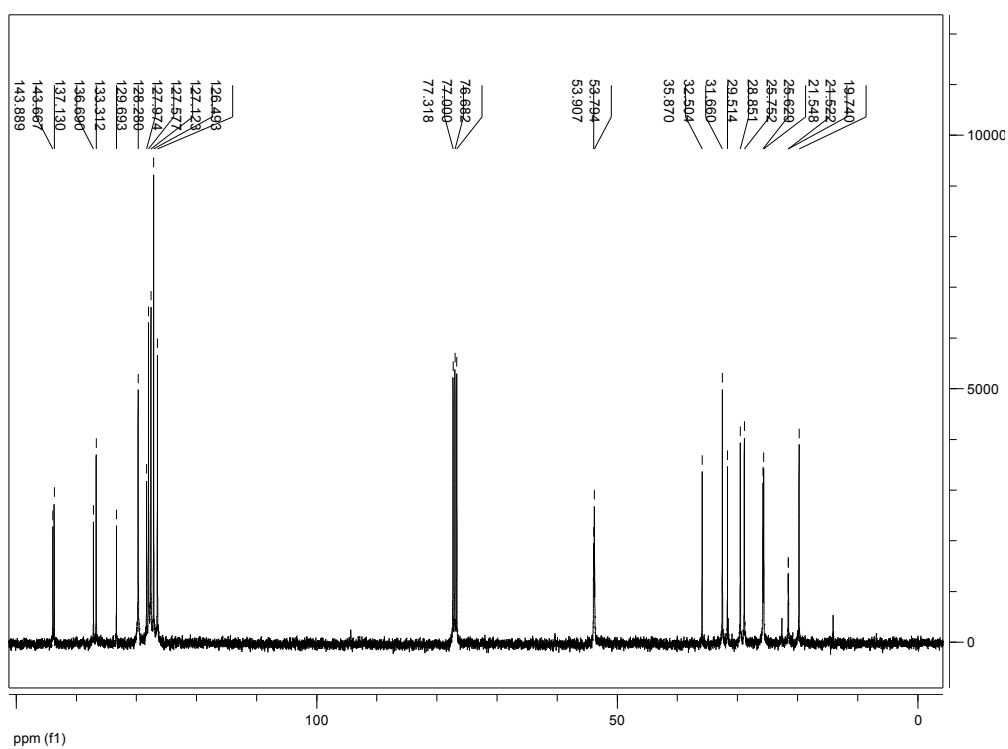
¹H-NMR Spectrum of Compound 3h



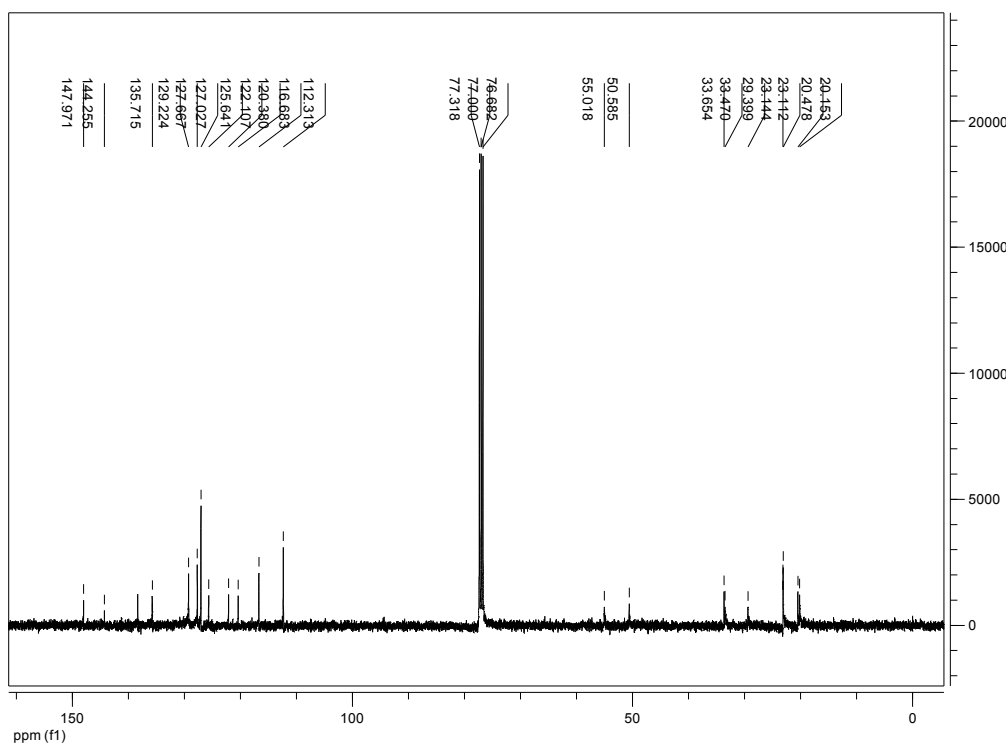
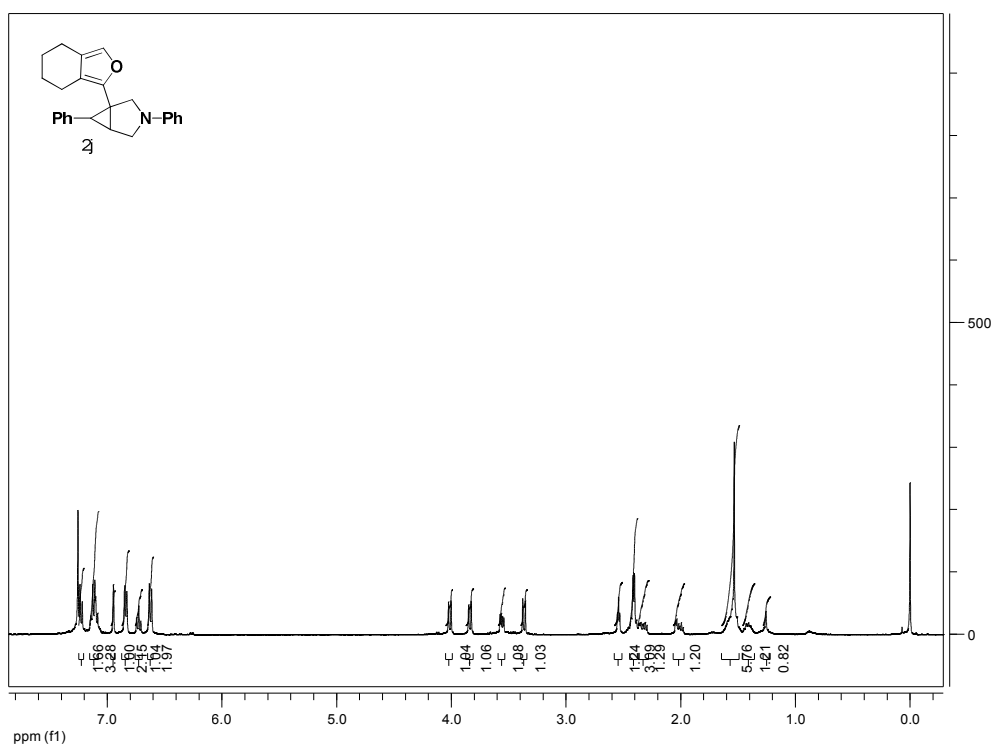
¹³C-NMR Spectrum of Compound 3h

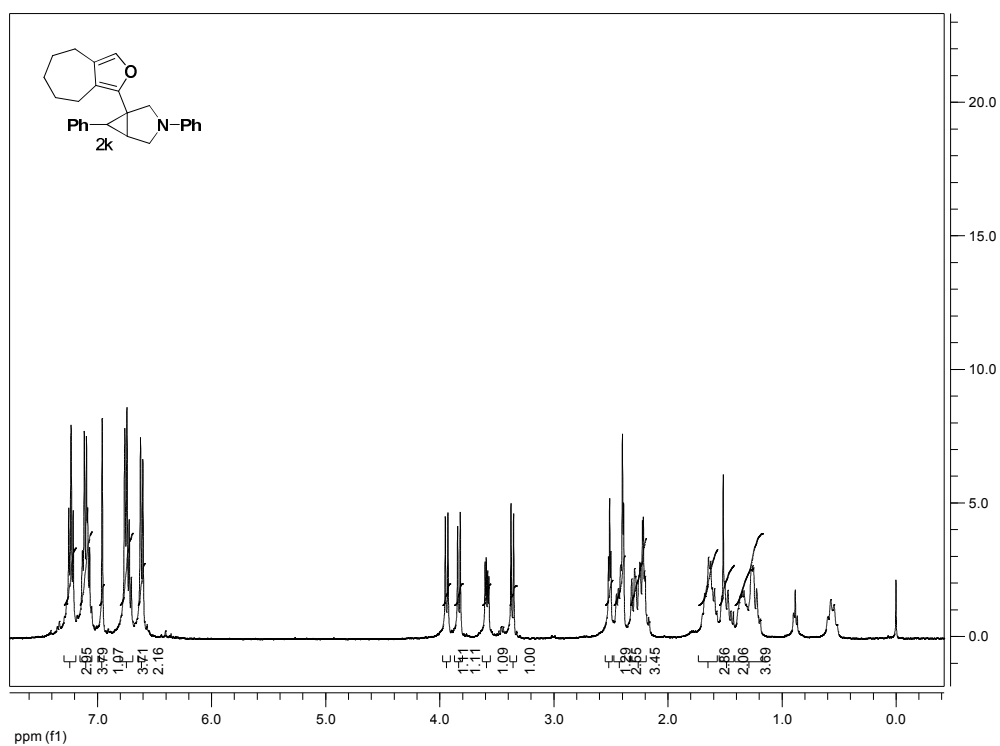


¹H-NMR Spectrum of Compound 2i

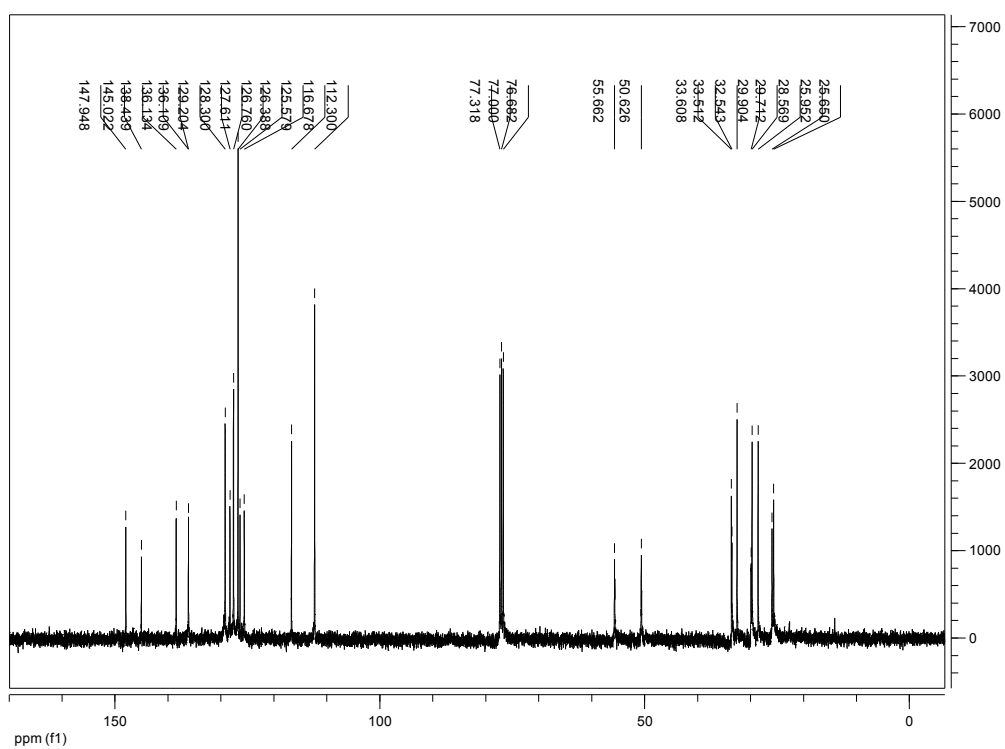


¹³C-NMR Spectrum of Compound 2i

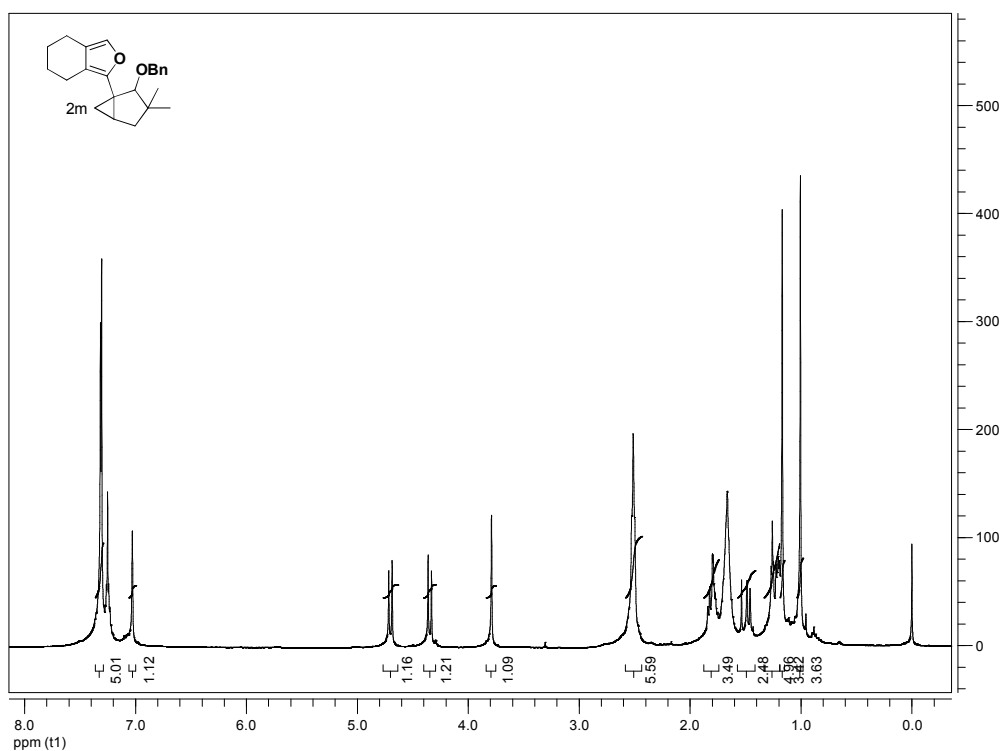




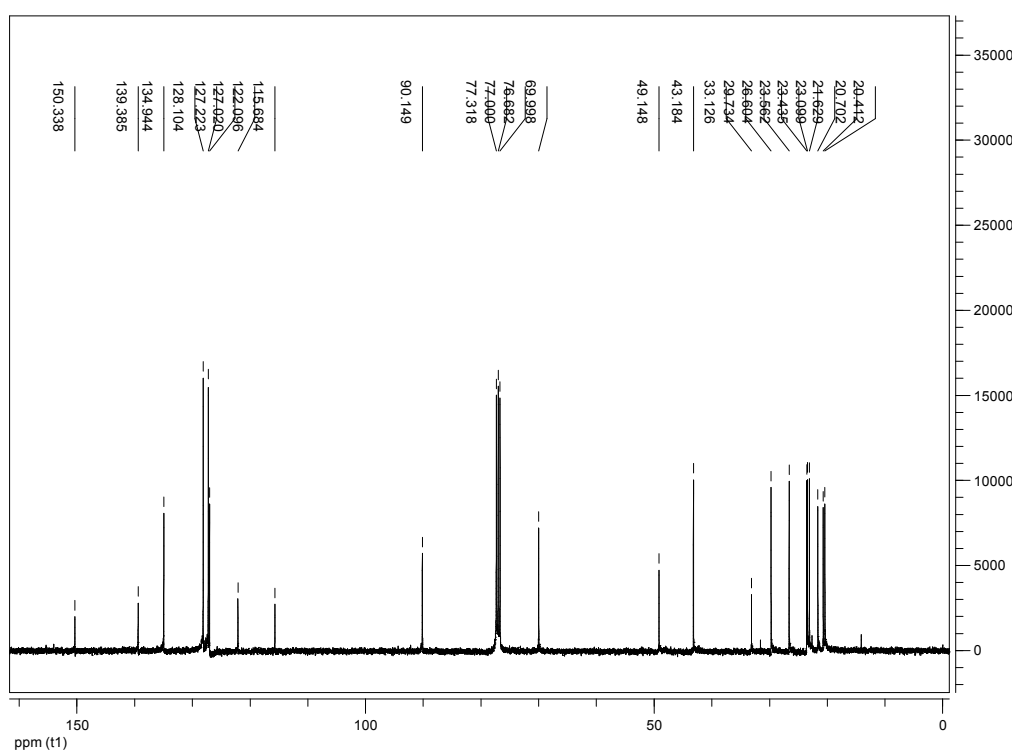
¹H-NMR Spectrum of Compound **2k**



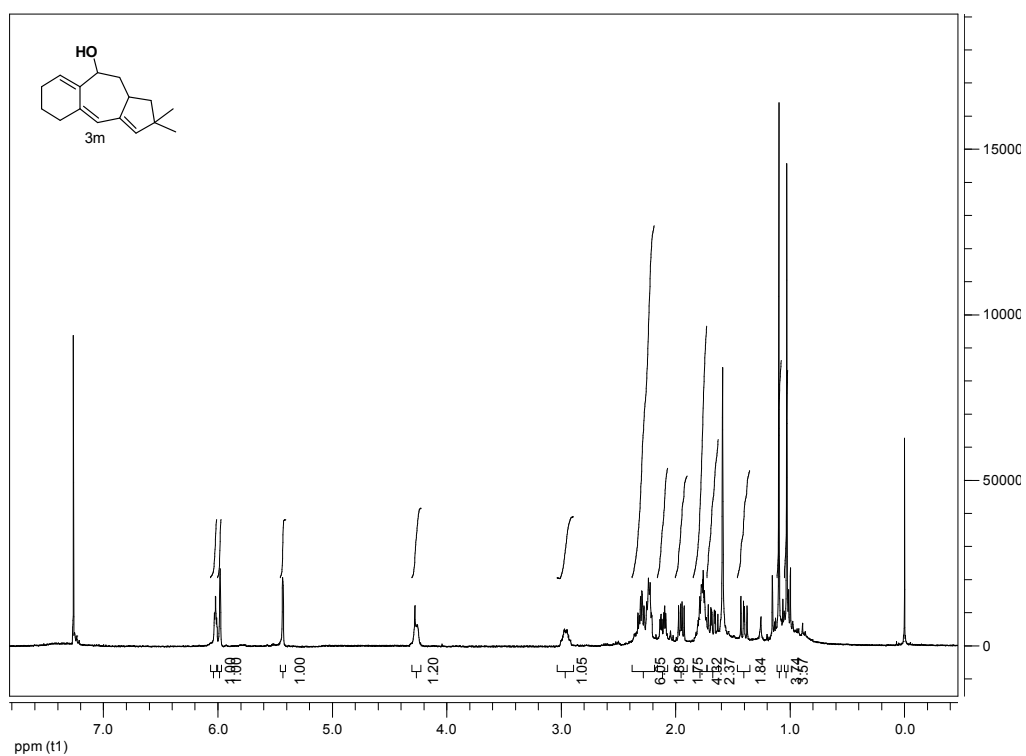
¹³C-NMR Spectrum of Compound **2k**



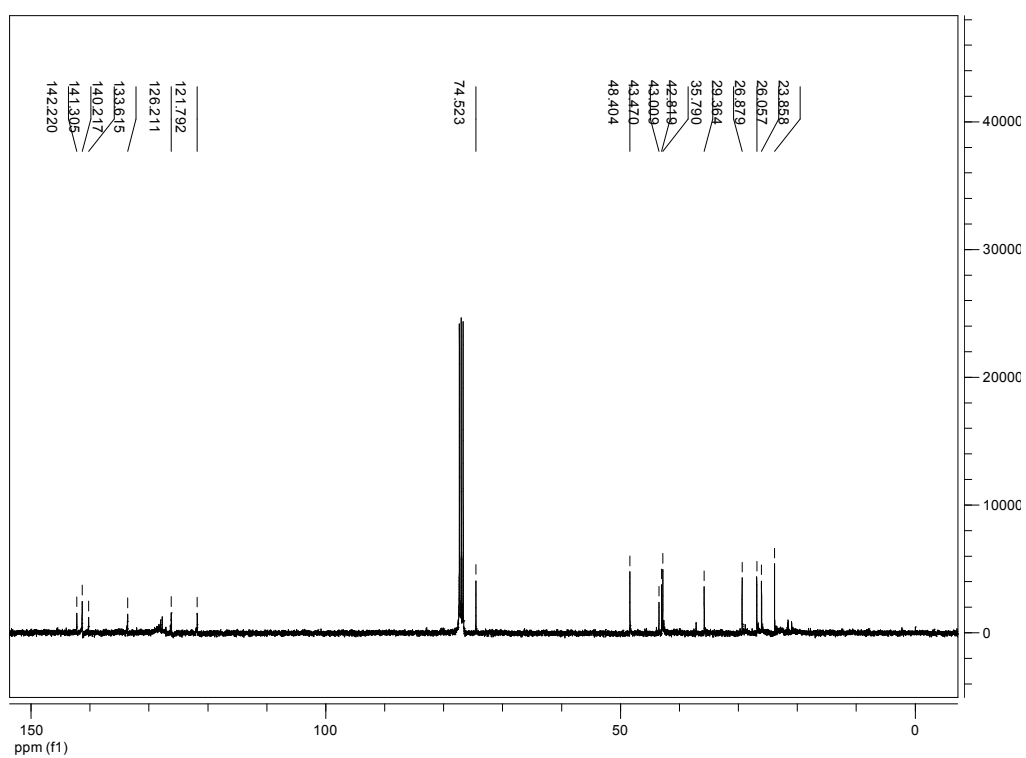
¹H-NMR Spectrum of Compound **2m**



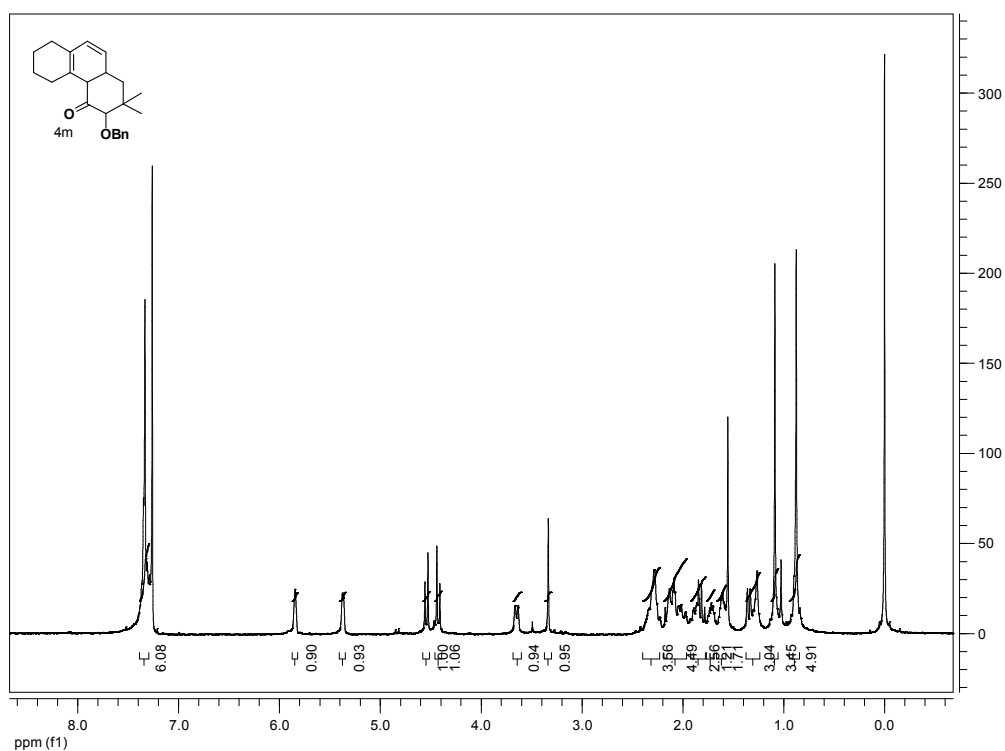
¹³C-NMR Spectrum of Compound **2m**



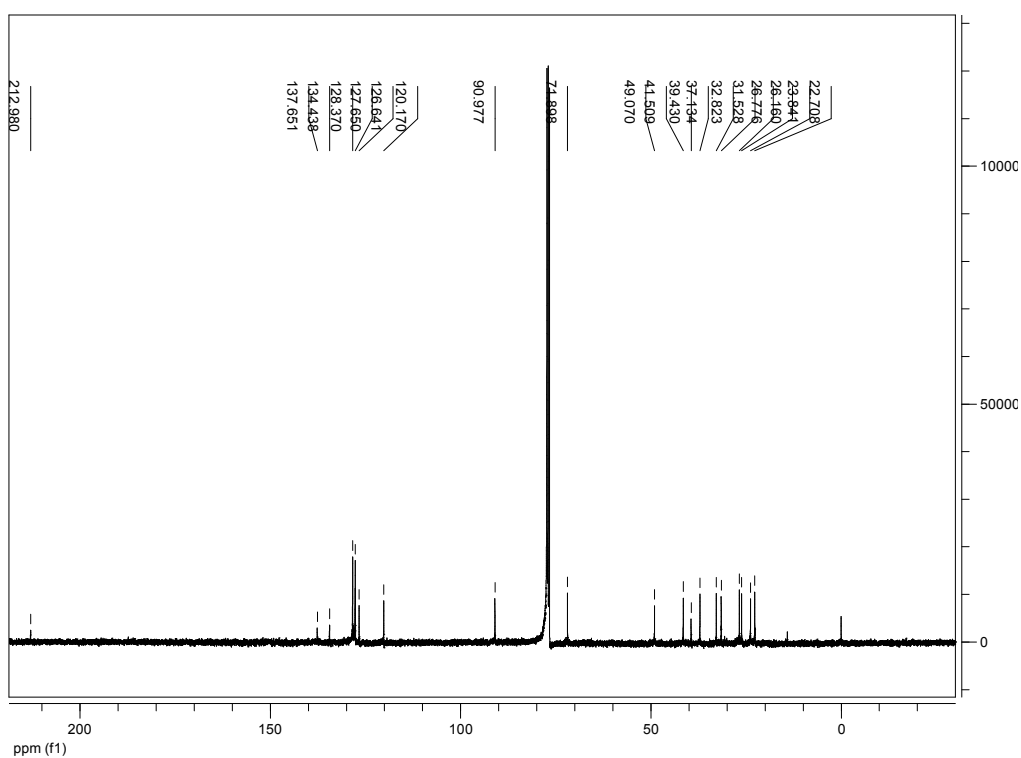
¹H-NMR Spectrum of Compound **3m**



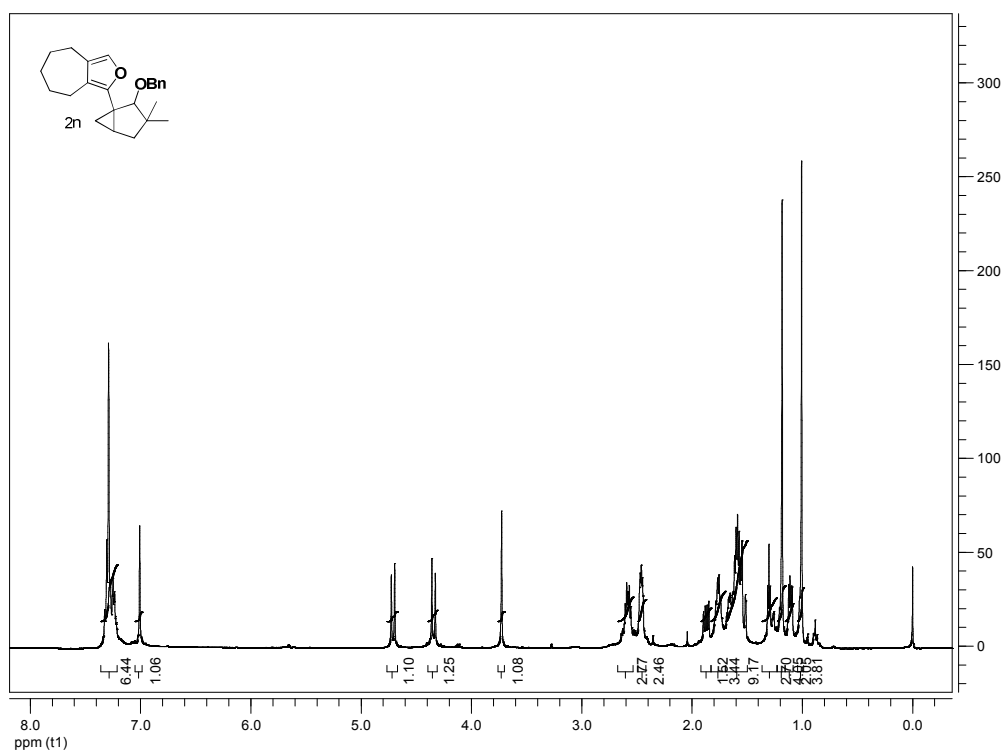
¹³C-NMR Spectrum of Compound **3m**



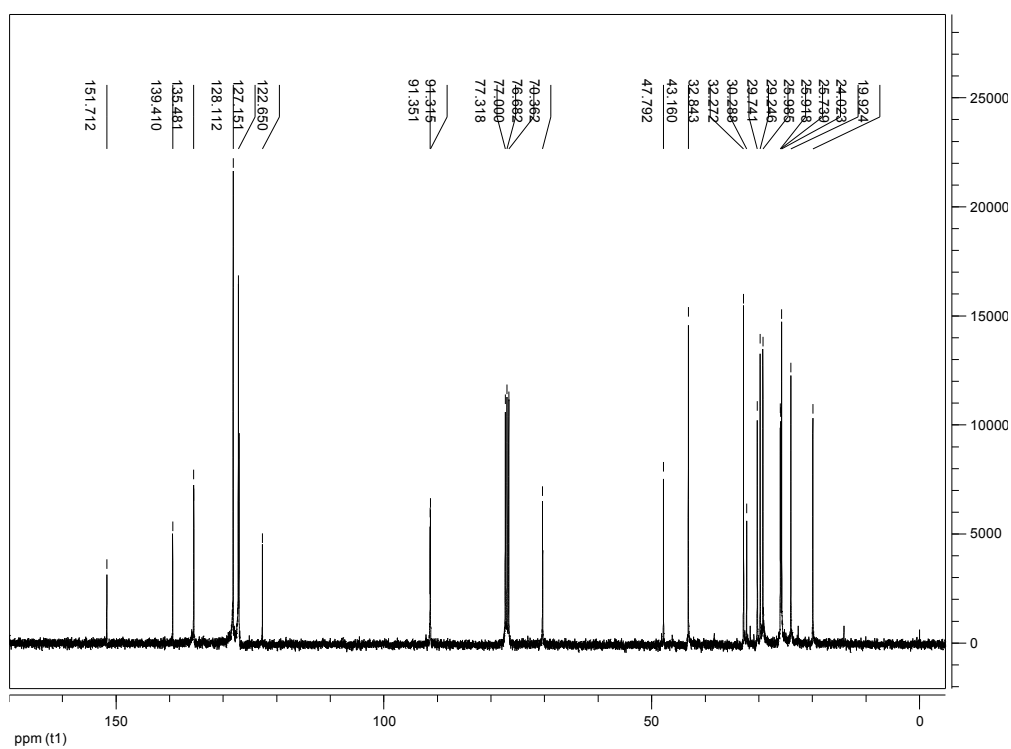
¹H-NMR Spectrum of Compound **4m**



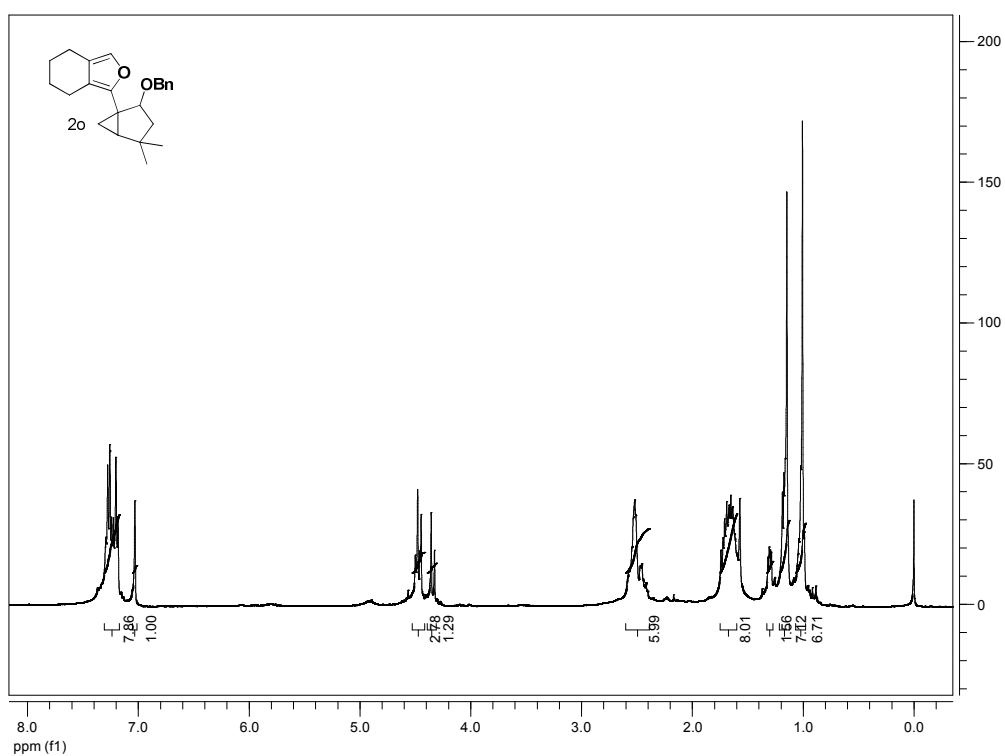
¹³C-NMR Spectrum of Compound **4m**



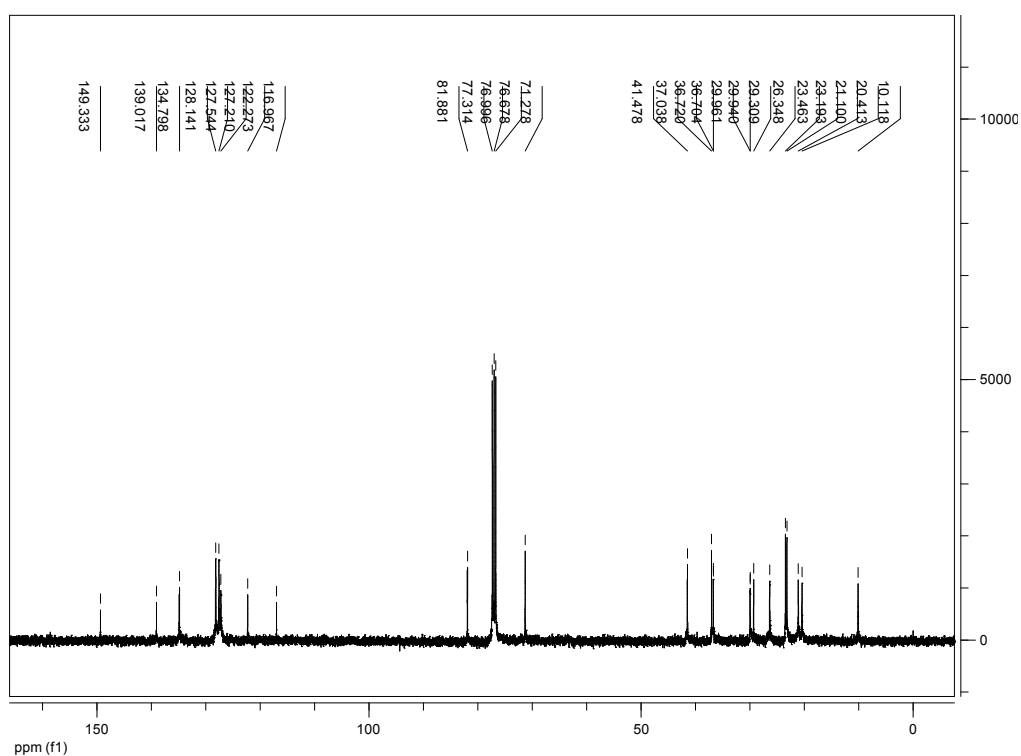
¹H-NMR Spectrum of Compound **2n**



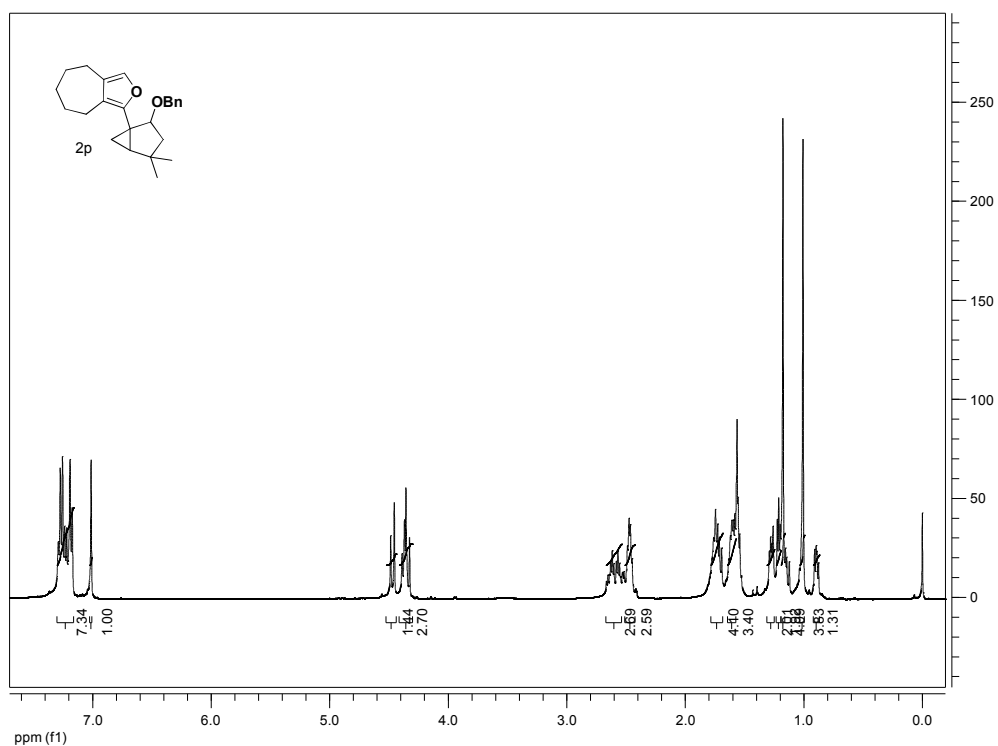
¹³C-NMR Spectrum of Compound **2n**



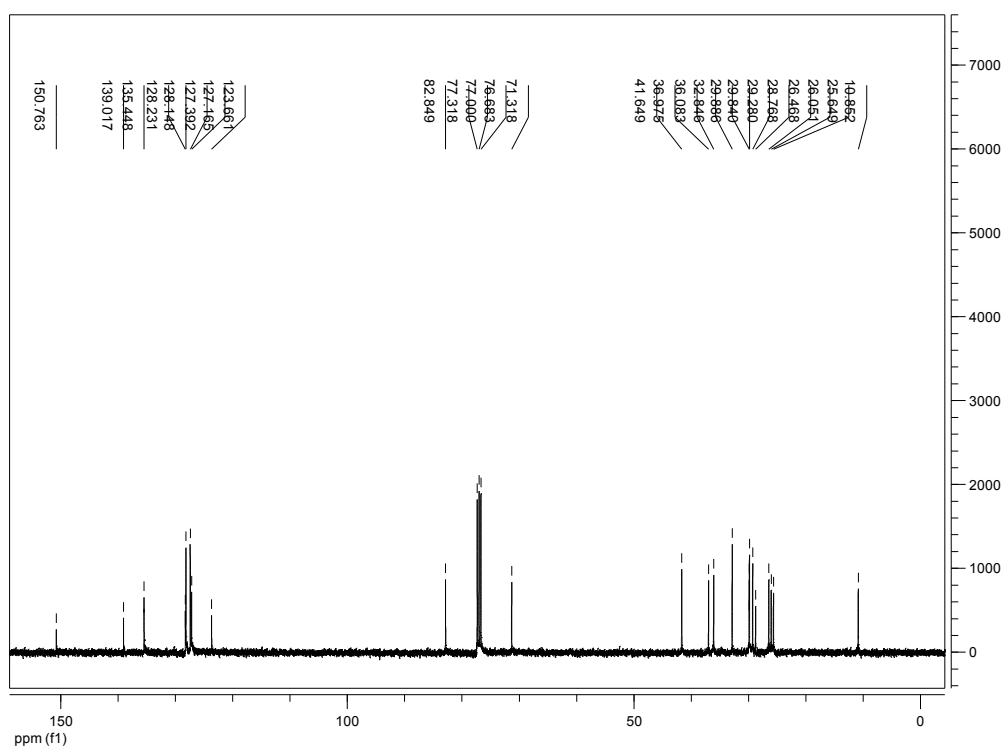
¹H-NMR Spectrum of Compound **2o**



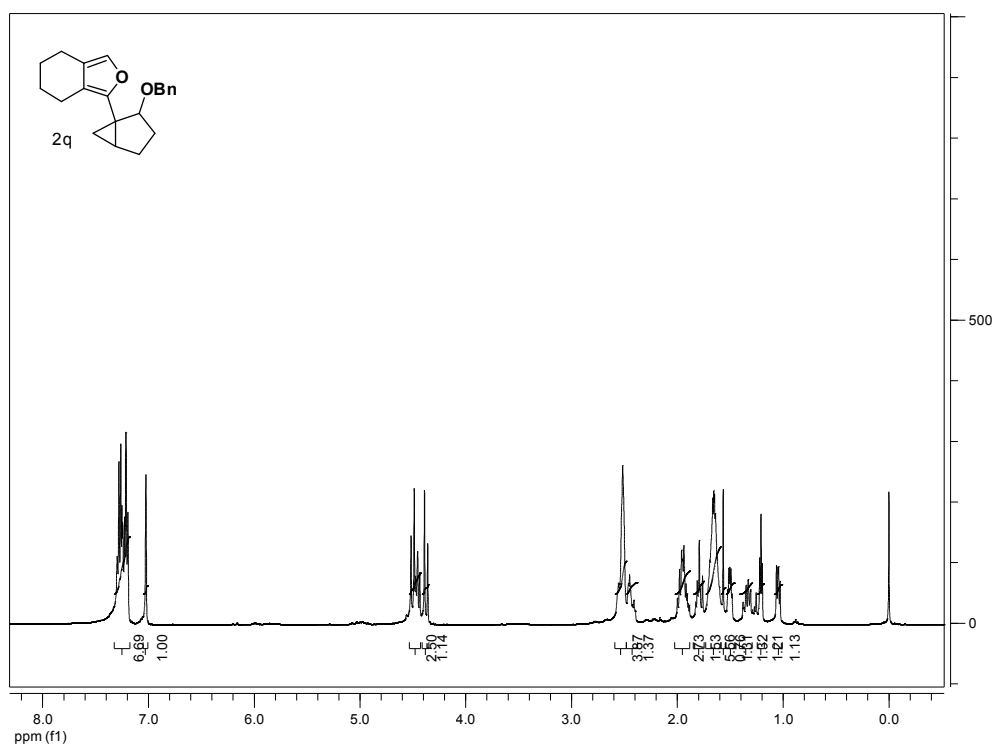
¹³C-NMR Spectrum of Compound **2o**



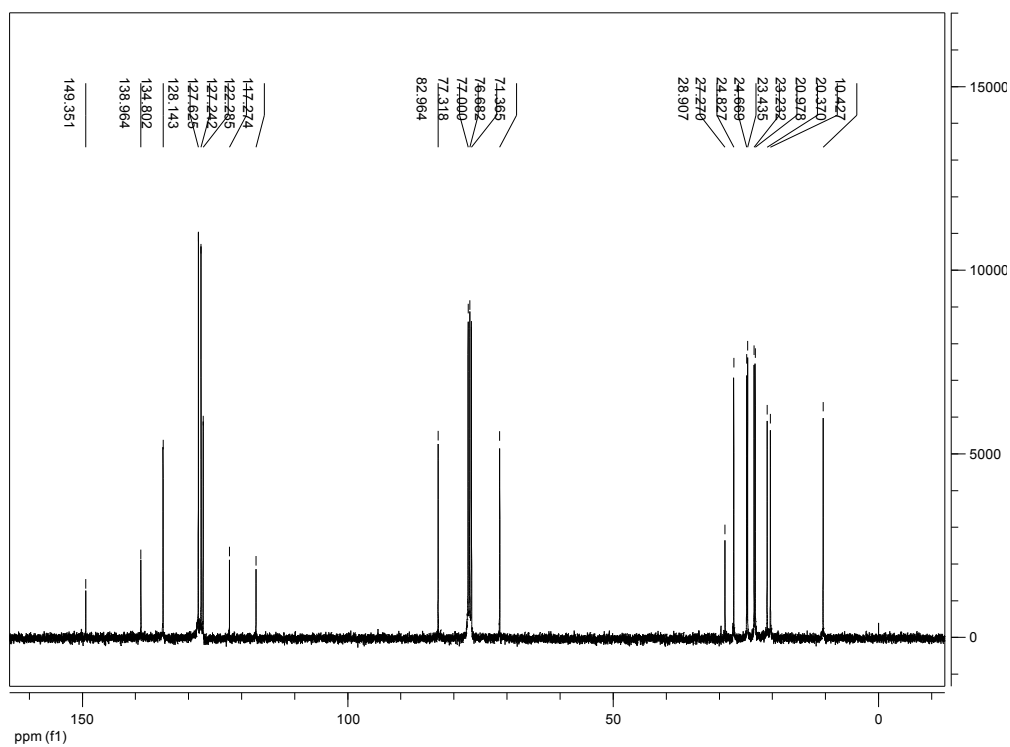
¹H-NMR Spectrum of Compound 2p



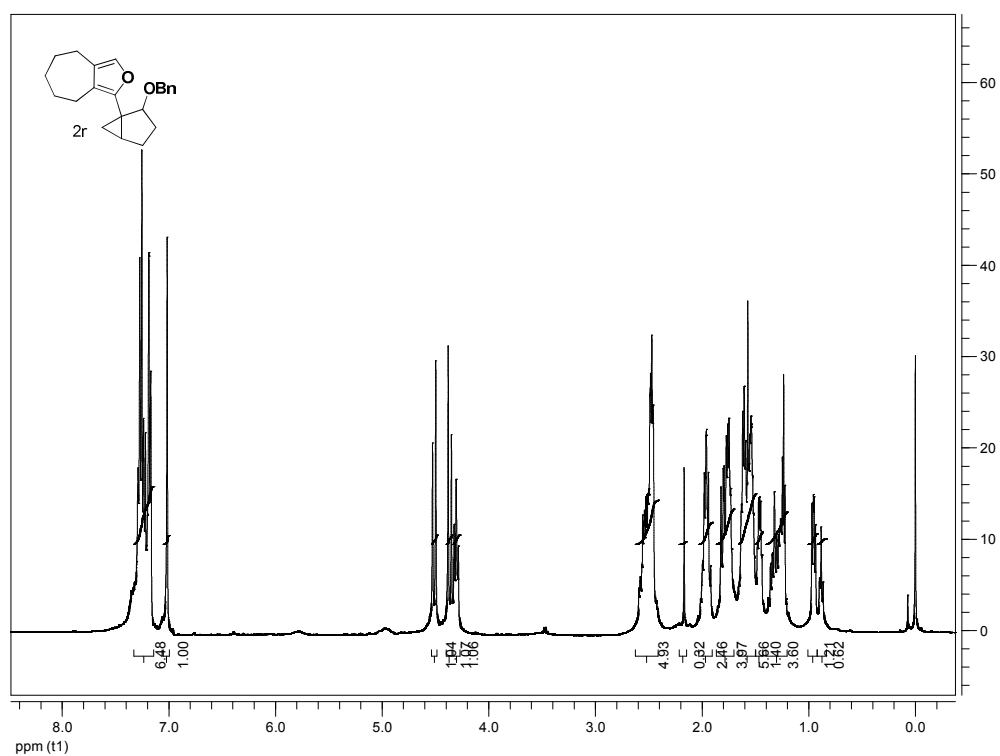
¹³C-NMR Spectrum of Compound 2p



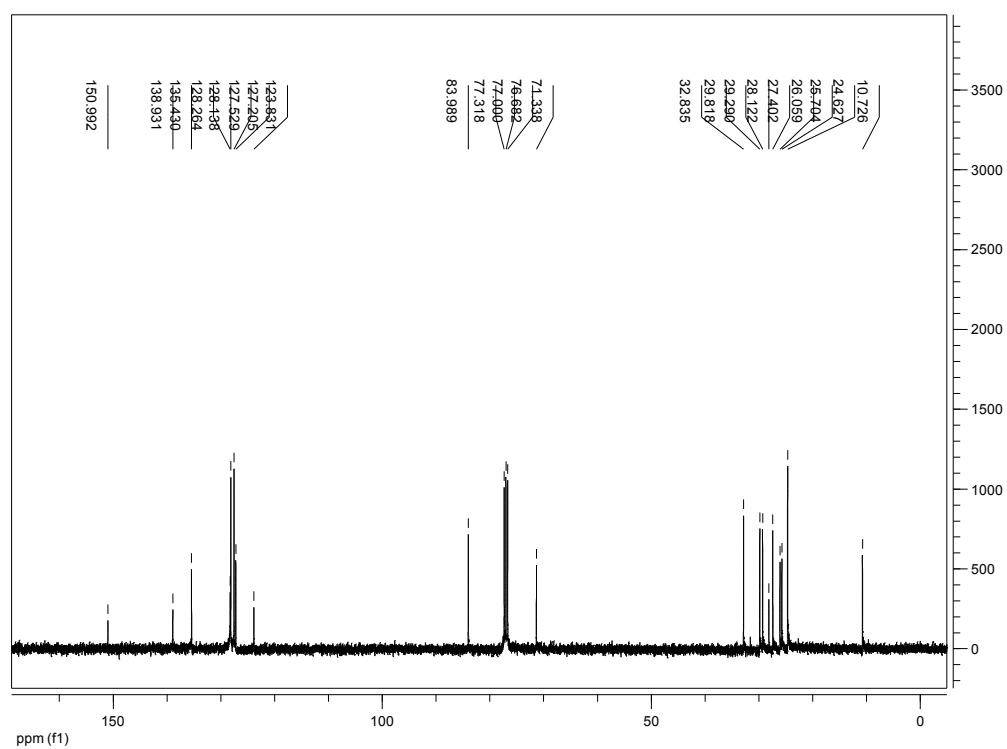
¹H-NMR Spectrum of Compound **2q**



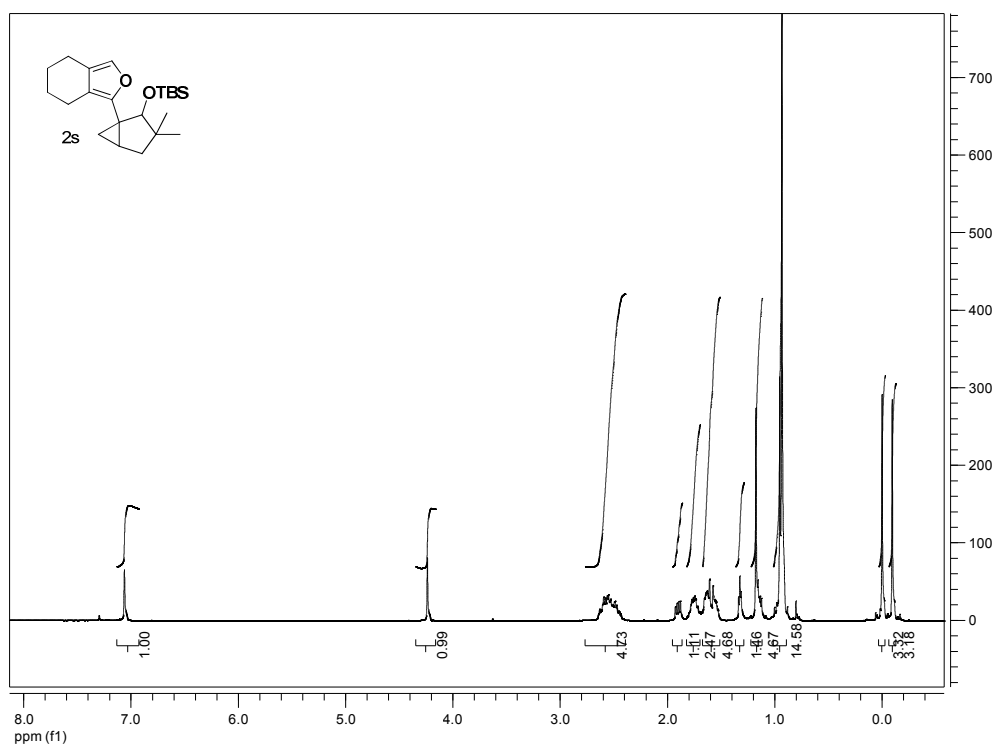
¹³C-NMR Spectrum of Compound **2q**



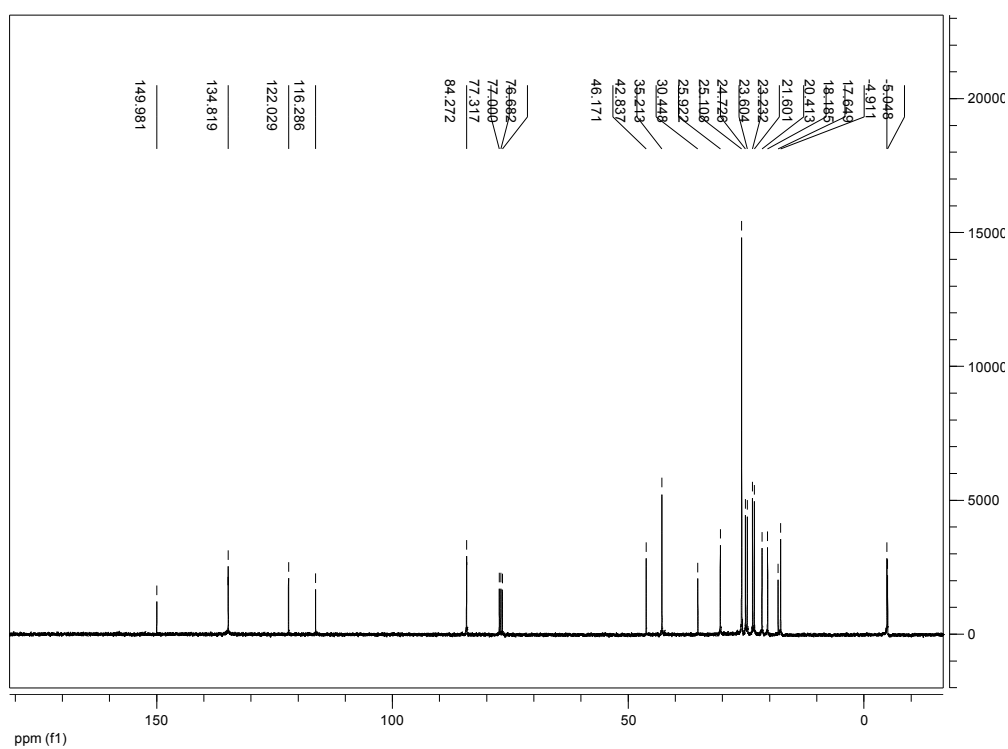
¹H-NMR Spectrum of Compound **2r**



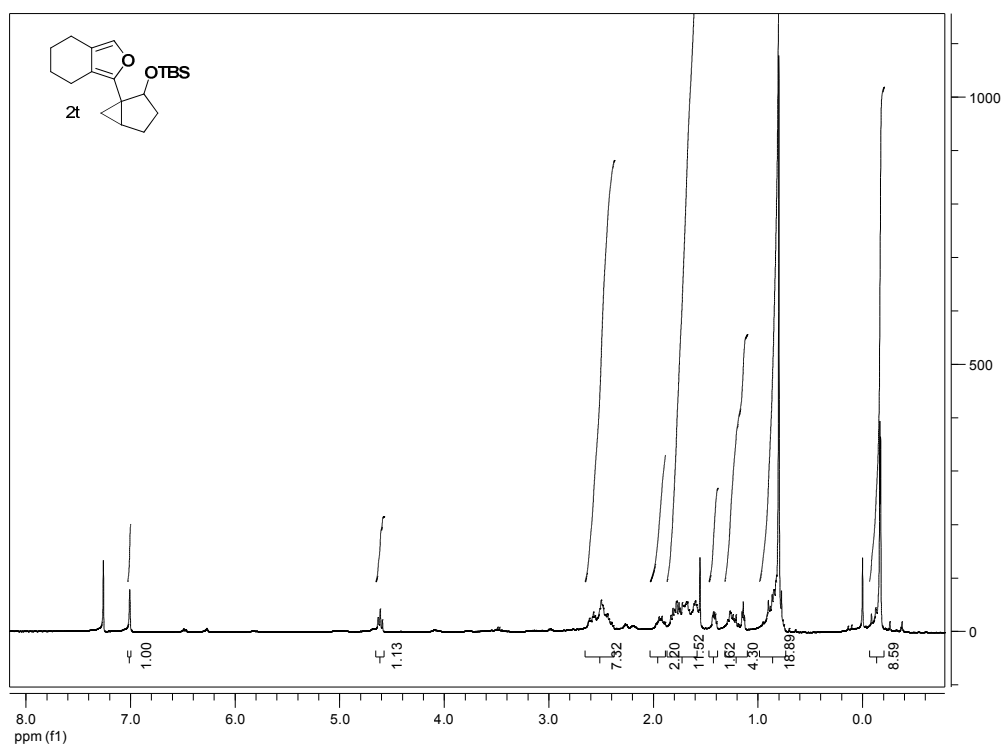
¹³C-NMR Spectrum of Compound **2r**



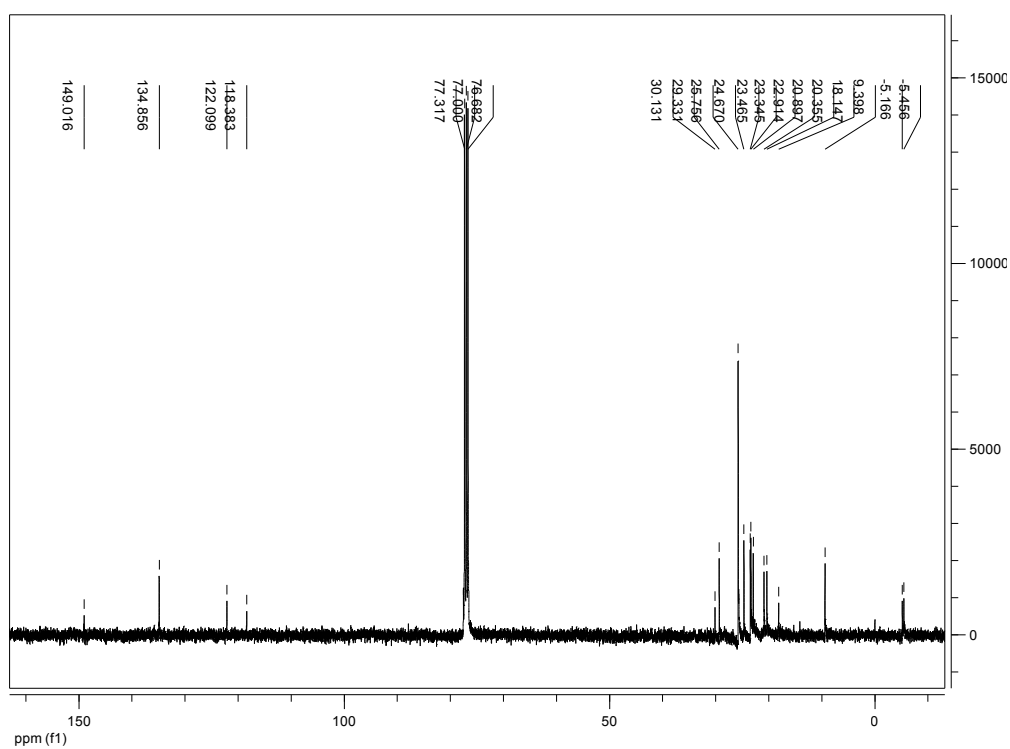
^1H -NMR Spectrum of Compound **2s**



^{13}C -NMR Spectrum of Compound **2s**



¹H-NMR Spectrum of Compound **2t**



¹³C-NMR Spectrum of Compound **2t**