Supporting Information

Rh(I)-catalyzed Pauson-Khand-type cycloaddition reaction of ene-vinylidenecyclopropanes and CO

Wei Yuan,[†] Xiang Dong,[†] Min Shi,*[,†] Patrick Mcdowell[§] and Guigen Li*[,‡,§]

[†]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China;* and [‡]Institute of Chemistry & Biomedical Sciences, Nanjing University, Nanjing 210093, P. R. China; and [§]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA

mshi@mail.sioc.ac.cn; guigen.li@ttu.edu

Fax 86-21-64166128; 001-806-742-1289

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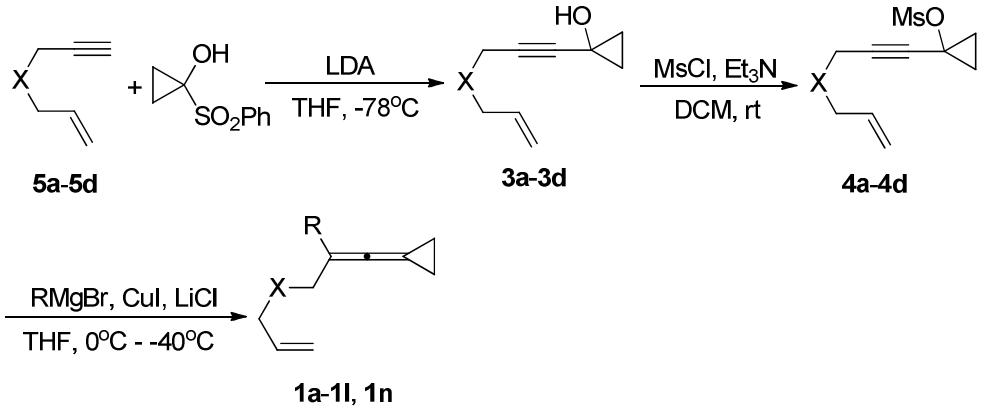
General Remarks. ^{1}H and ^{13}C NMR spectra were recorded at 400 (or 300) and 100 (or 75) MHz, respectively. Mass and HRMS spectra were recorded by ESI or EI method. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

General procedure for the preparation of compounds 1a-1l, and 1n



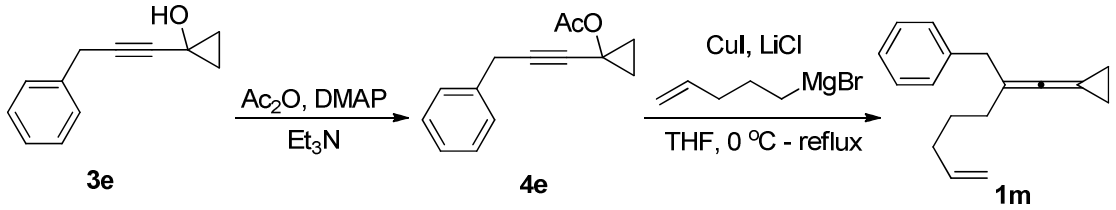
Under argon atmosphere, compound **5** (10 mmmol) was dissolved in THF (10 mL) in a three-necked bottle at -78 ^{o}C. Then, LDA (2.0 mol/L in THF, 12 mmol, 6.0 mL) was added dropwise. After stirring for 2 h, 1-(phenylsulfonyl)cyclopropanol (5.0 mmol) dissolved in THF (10 mL) was added. The reaction mixture was warmed to room temperature slowly, and stirred overnight. The reaction was quenched with saturated NH_4Cl solution, extracted with EA (20 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **3**.

Under argon atmosphere, compound **3** (2.0 mmol) was dissolved in DCM (5.0 mL) at 0 ^{o}C, Et_3N (4.0 mmol) and MsCl (3.0 mmol) was added. After stirring for 1 h, the reaction was quenched with H_2O (5.0 mL), extracted with DCM (5 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **4**.

Under argon atmosphere, CuI (4.0 mmol) and LiCl (4.0 mmol) in a three-necked bottle was dried upon heating. Then THF (10 mL) was added. At 0 ^{o}C, RMgBr (2.0 mol/L in THF, 4.0 mmol, 2.0 mL) was added to the reaction. 10 min later, **4** (2.0 mmol) dissolved in THF (10 mL) was added at -40 ^{o}C. After stirring for 8 h, the reaction was quenched with saturated NH_4Cl solution, extracted with EA (20 mL x 3), and dried over anhydrous Na_2SO_4. The

solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **1**.

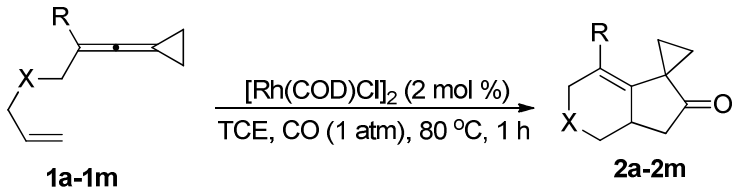
Procedure for the preparation of compound 1m



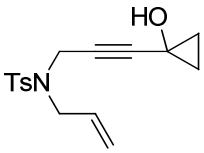
Compound **3e** (2.0 mmol) was dissolved in Et_3N (5.0 mL), DMAP (0.1 mmol) and Ac_2O (3.0 mmol) was added. After stirring for overnight, the reaction was quenched with saturated $NaHCO_3$ solution (5.0 mL), extracted with EA (5 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **4e**.

Under argon atmosphere, CuI (4.0 mmol) and LiCl (4.0 mmol) in a three-necked bottle was dried by heating. Then THF (10 mL) was added. At 0 ^oC, pent-4-en-1-ylmagnesium bromide (2.0 mol/L in THF, 4.0 mmol, 2.0 mL) was added to the reaction. 10 min later, compound **4e** (2.0 mmol) dissolved in THF (10 mL) was added. After refluxing for 8 h, the reaction was quenched with saturated NH_4Cl solution, extracted with EA (20 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **1m**.

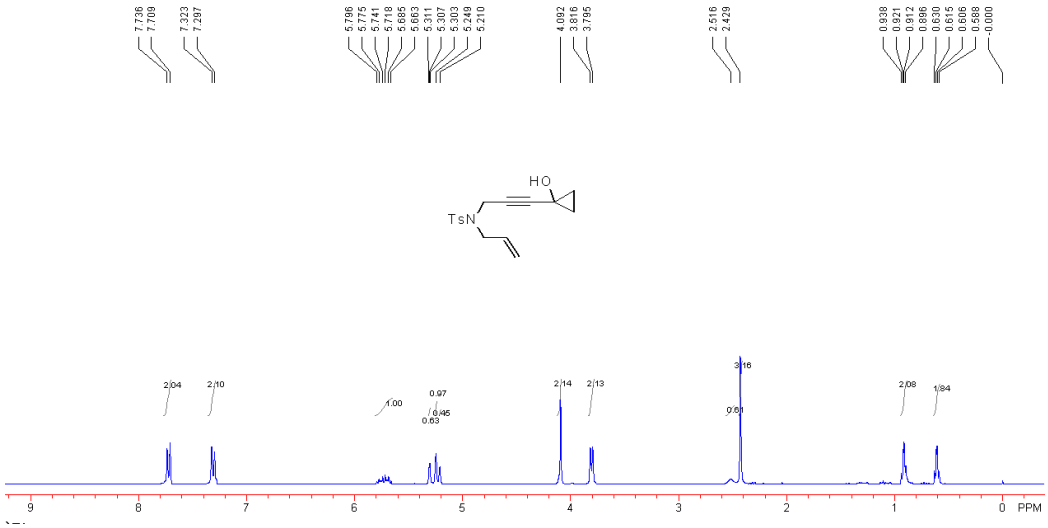
General procedure for the preparation of compounds 2a-2m

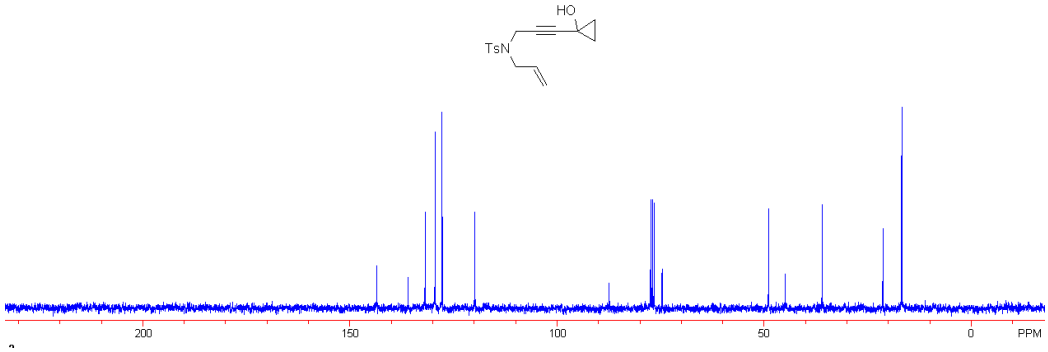


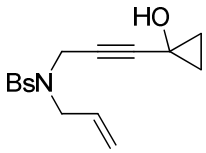
Under CO atmosphere, compound **1** (0.2 mmol) and $[Rh(COD)Cl]_2$ (0.004 mmol) was added, in an Schlenk tube and then TCE (2.0 mL) was added. After stirring for 1 h at 80 ^{o}C, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **2**.



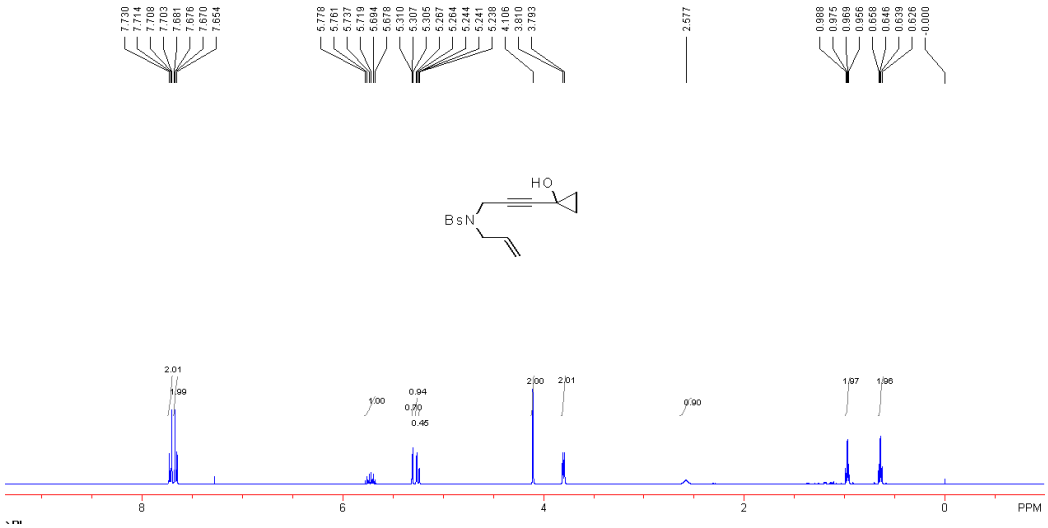
Compound 3a: A yellow oil. 2.004 g, 47%. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.61 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 2H), 0.92 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 2H), 2.43 (s, 3H), 2.52 (s, 0.6H), 3.81 (d, *J* = 6.3 Hz, 2H), 4.09 (s, 2H), 5.23 (d, *J* = 11.7 Hz, 2H), 5.28 (d, *J* = 17.4 Hz, 2H), 5.66-5.80 (m, 1H), 7.31 (d, *J* = 7.8, 2H), 7.72 (d, *J* = 7.8, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 16.9, 21.4, 36.1, 45.0, 49.0, 74.7, 87.4, 119.8, 127.7, 129.4, 129.6, 131.8, 136.0, 143.5. IR(neat) ν 3486, 3010, 2237, 1597, 1417, 1344, 1235, 1155, 1119, 1090, 896, 755. 664 cm^{-1}. HRMS (ESI) Calcd: $C_{16}H_{19}NO_3S$, 305.1086, Found: 305.1080.

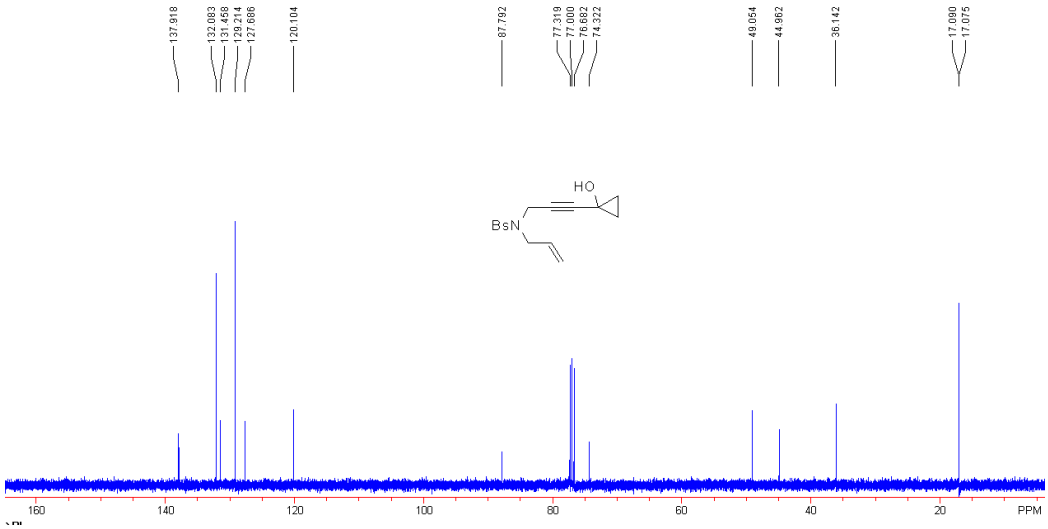


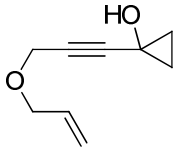




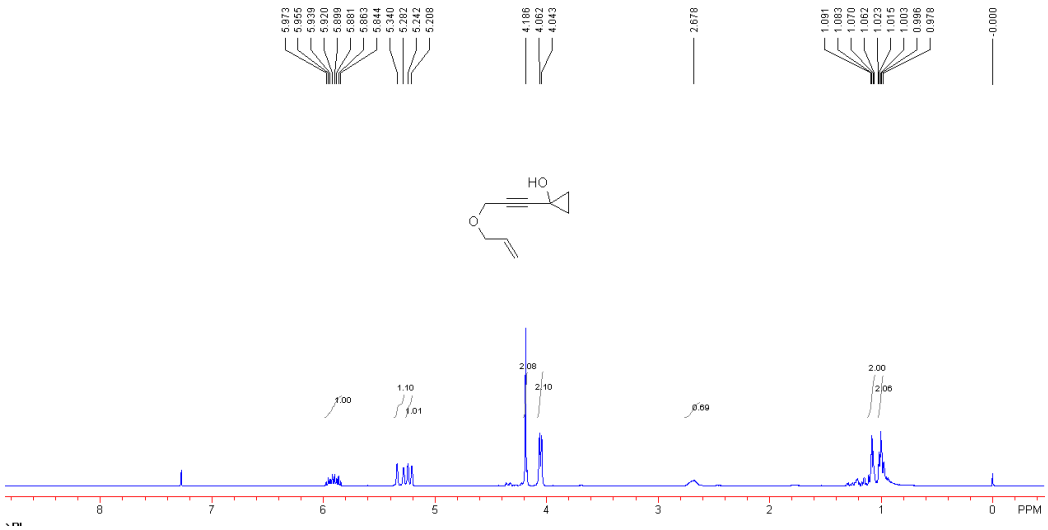
Compound 3b: A yellow oil. 773 mg, 41%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.64 (dd, *J* = 5.2 Hz, *J* = 8.0 Hz, 2H), 0.97 (dd, *J* = 5.2 Hz, *J* = 8.0 Hz, 2H), 2.58 (s, 1H), 3.80 (d, *J* = 6.8 Hz, 2H), 4.11 (s, 2H), 5.25 (dd, *J* = 1.2 Hz, *J* = 10.4 Hz, 1H), 5.29 (dd, *J* = 1.2 Hz, *J* = 17.2 Hz, 1H), 5.68-5.78 (m, 1H), 7.67 (dt, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H), 7.72 (dt, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.08, 17.09, 36.1, 45.0, 49.1, 74.3, 87.8, 120.1, 127.7, 129.2, 131.5, 132.1, 137.9. IR (neat) ν 3485, 3087, 2236, 1574, 1346, 1234, 1160, 1089, 1067, 895, 764, 730, 658 cm^{-1}. HRMS (ESI) Calcd: $C_{15}H_{16}BrNO_3S$, 369.0034, Found: 369.0026.

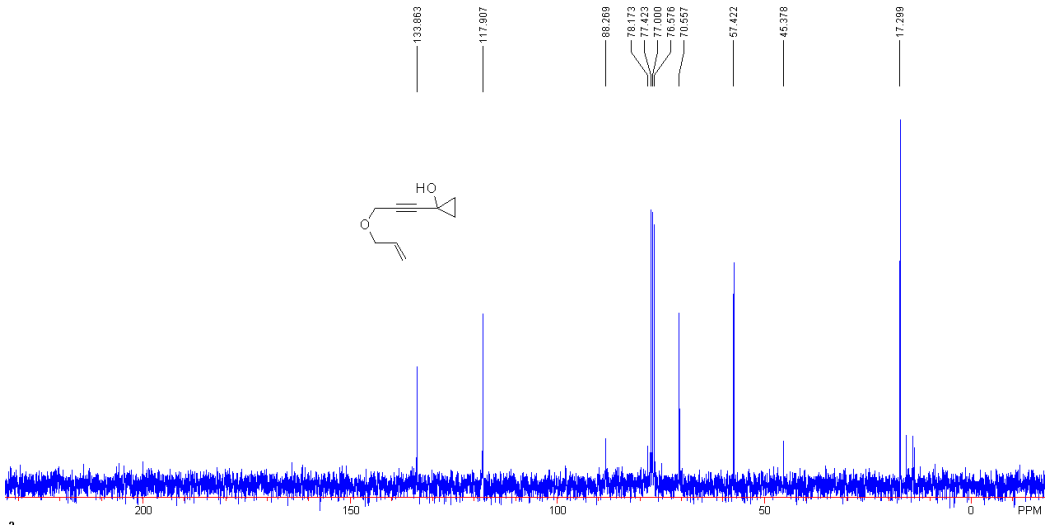


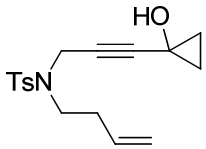




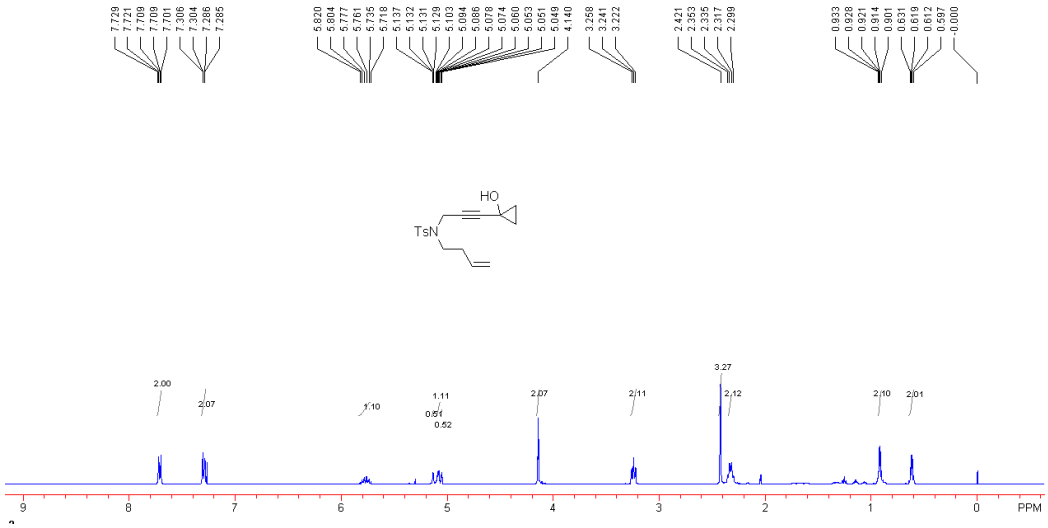
Compound 3c: A yellow oil. 425 mg, 44%. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.98-1.02 (m, 2H), 1.06-1.09 (m, 2H), 2.68 (s, 1H), 4.05 (d, J = 5.7 Hz, 2H), 4.19 (s, 2H), 5.23 (d, J = 10.2 Hz, 1H), 5.31 (d, J = 17.4 Hz, 1H), 5.84-5.97 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.3, 45.4, 57.4, 70.6, 78.2, 88.3, 117.9, 133.9. IR (neat) ν 3344, 2857, 2235, 1719, 1356, 1236, 1075, 1018, 970, 928, 879, 851 cm^{-1}. HRMS (ESI) Calcd: $C_9H_{12}O_2$, 152.0837, Found: 152.0844.

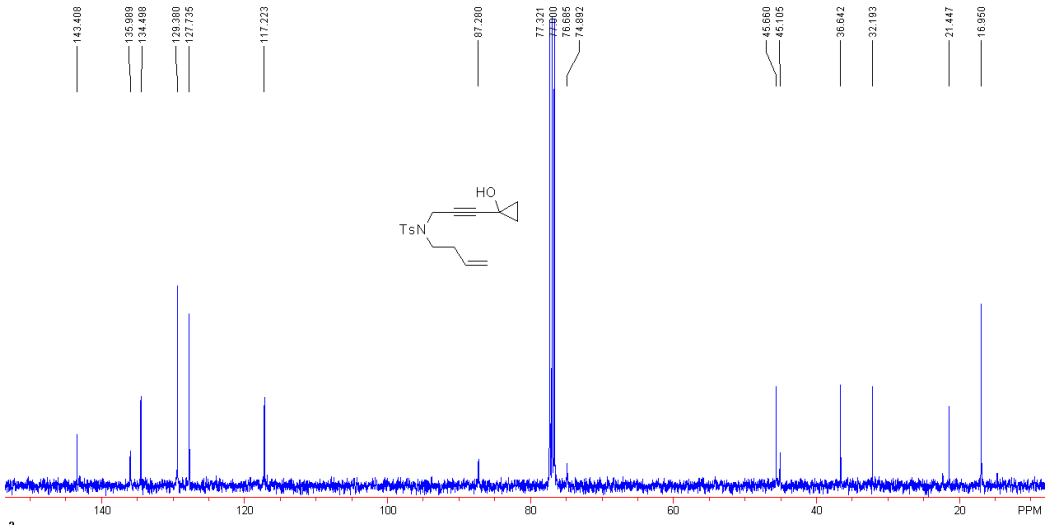


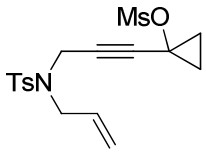




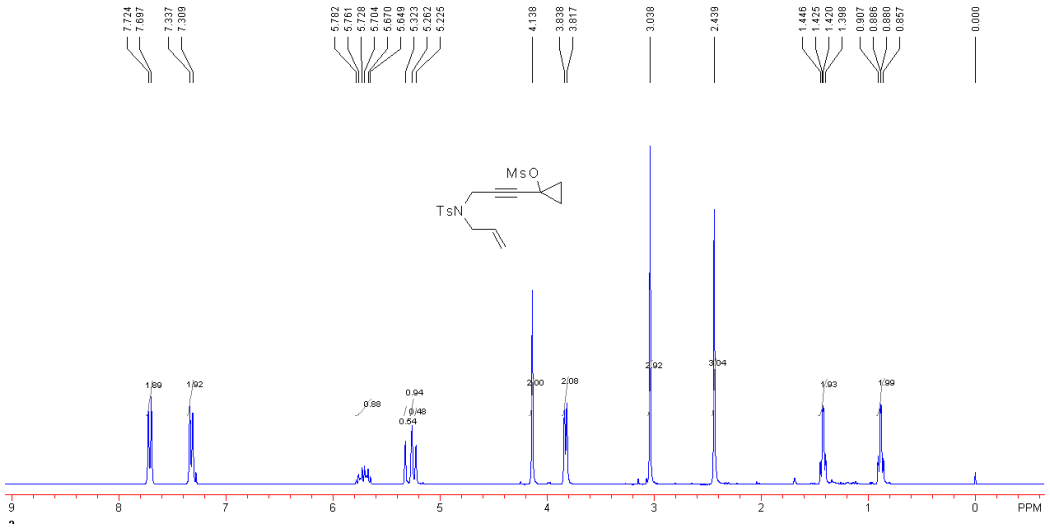
Compound 3d: A yellow oil. 605 mg, 39%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.60-0.63 (m, 2H), 0.90-0.93 (m, 2H), 2.33 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 3.24 (t, *J* = 7.2 Hz, 2H), 4.14 (s, 2H), 5.06 (d, *J* = 10.0 Hz, 1H), 5.11 (d, *J* = 16.8 Hz, 1H), 5.72-5.82 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.0, 21.4, 32.2, 36.6, 45.1, 45.7, 74.9, 87.3, 117.2, 127.7, 129.4, 134.5, 136.0, 143.4. IR (neat) ν 3475, 2925, 2237, 1641, 1620, 1598, 1447, 1343, 1234, 1155, 1089, 912, 814, 728, 664 cm^{-1}. HRMS (ESI) Calcd: $C_{17}H_{21}NO_3S$, 319.1242, Found: 319.1238.

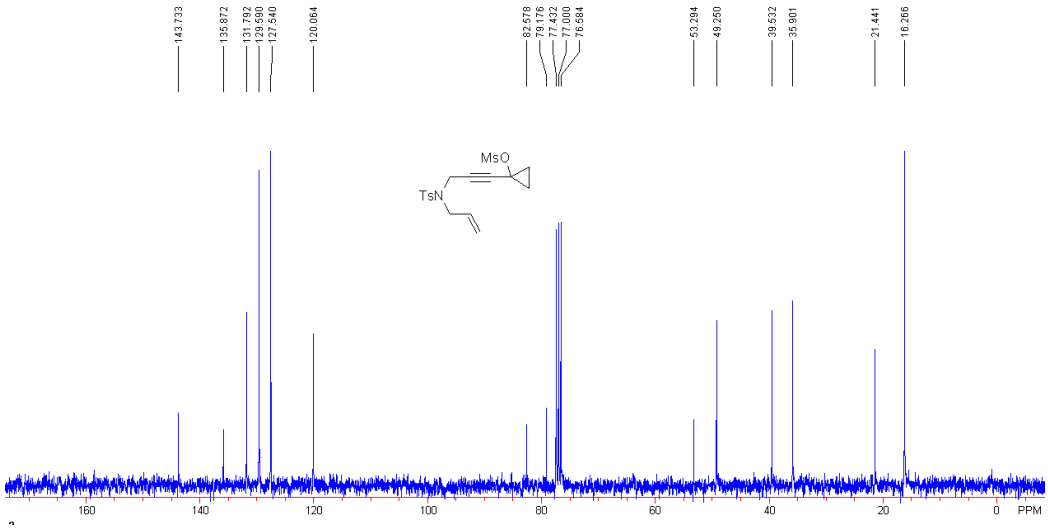


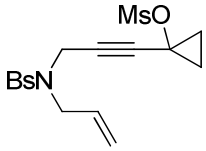




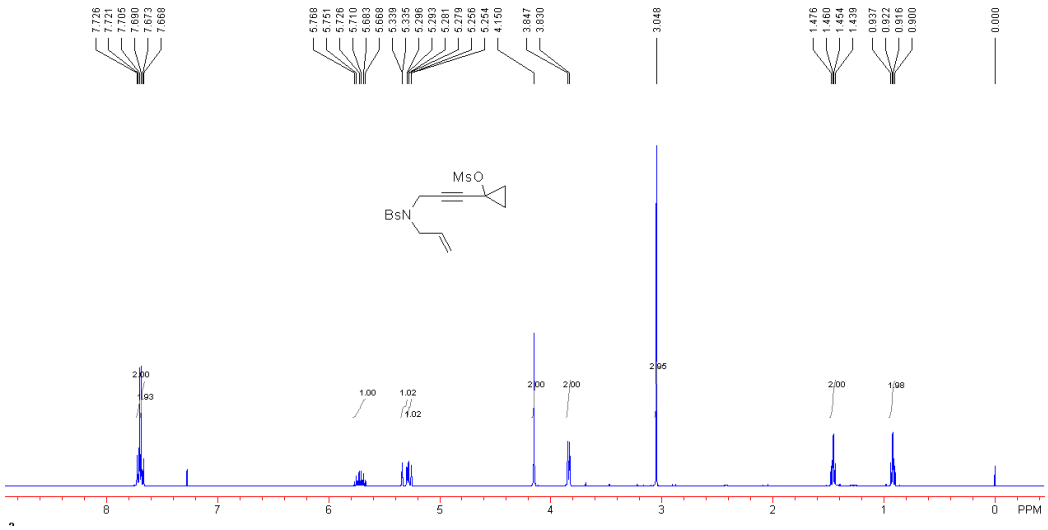
Compound 4a: A yellow solid. 1.963 g, 83%. Mp: 61-63 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.88 (dd, *J* = 6.6 Hz, *J* = 8.1 Hz, 2H), 1.42 (dd, *J* = 6.6 Hz, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 3.04 (s, 3H), 3.83 (d, *J* = 6.3 Hz, 2H), 4.14 (s, 2H), 5.24 (d, *J* = 11.1 Hz, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.65-5.78 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 16.3, 21.4, 35.9, 49.3, 53.3, 79.2, 82.6, 120.1, 127.5, 129.6, 131.8, 135.9, 143.7. IR (neat) ν 3029, 2935, 2861, 1645, 1596, 1412, 1361, 1163, 1092, 943, 870, 824, 757, 667 cm^{-1}. HRMS (ESI) Calcd: $C_{17}H_{21}BrNO_5S_2$, 383.0861, Found: 383.0855.

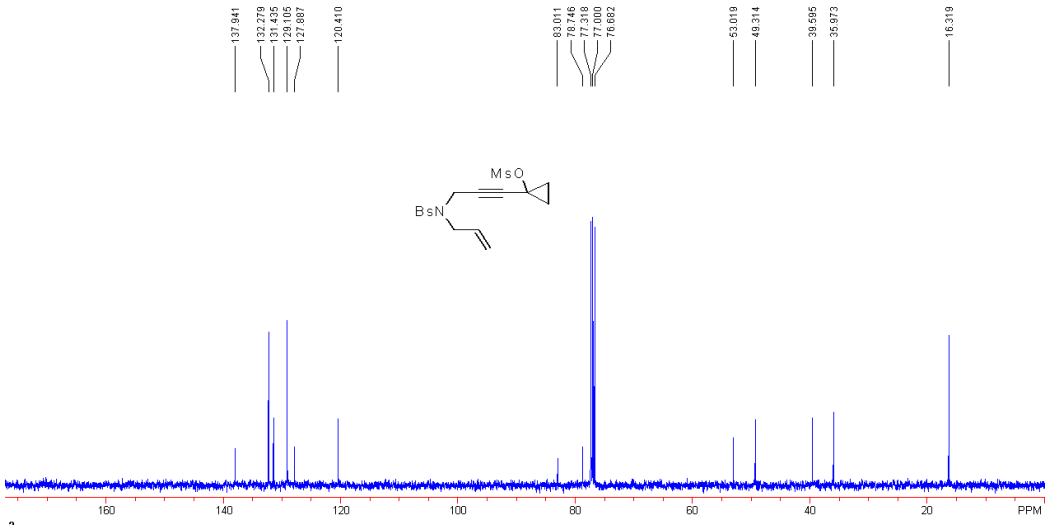


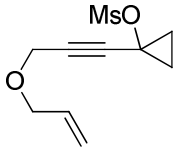




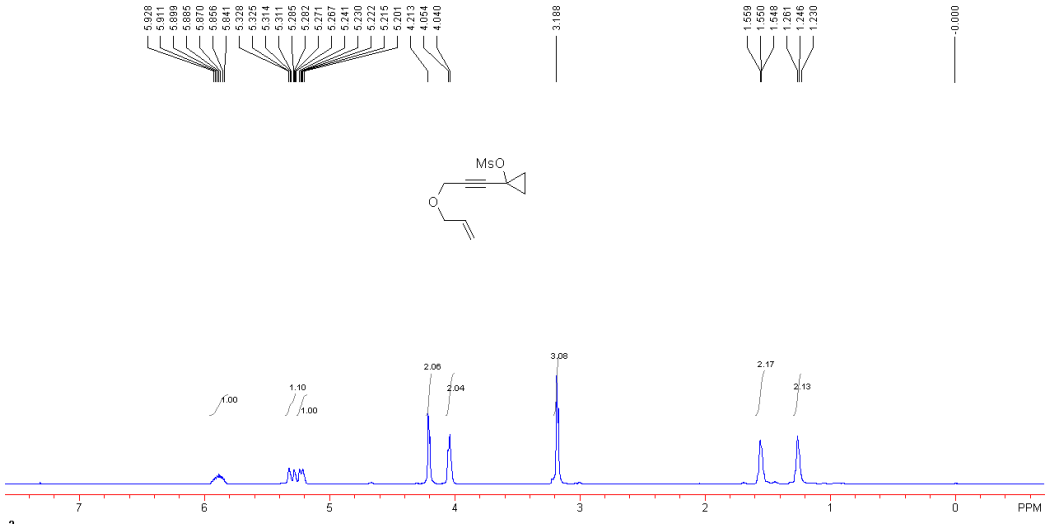
Compound 4b: A yellow solid. 817 mg, 94%. Mp: 56-58 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.92 (dd, J = 6.4 Hz, J = 8.8 Hz, 2H), 1.46 (dd, J = 6.4 Hz, J = 8.8 Hz, 2H), 3.05 (s, 3H), 3.84 (d, J = 6.8 Hz, 2H), 4.15 (s, 2H), 5.27 (dd, J = 0.8 Hz, J = 10.0 Hz, 1H), 5.32 (dd, J = 1.2 Hz, J = 16.8 Hz, 1H), 5.67-5.77 (m, 1H), 7.68 (dt, J = 8.8 Hz, J = 2.0 Hz, 2H), 7.72 (dt, J = 8.8 Hz, J = 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.3, 36.0, 39.6, 49.3, 53.0, 78.7, 83.0, 120.4, 127.9, 129.1, 131.4, 132.3, 137.9. IR (neat) ν 3082, 2996, 2933, 1730, 1645, 1575, 1349, 1163, 1068, 934, 869, 805, 761, 729, 662 cm^{-1}. HRMS (ESI) Calcd: $C_{16}H_{18}BrNO_5S_2$, 446.9810, Found: 446.9821.

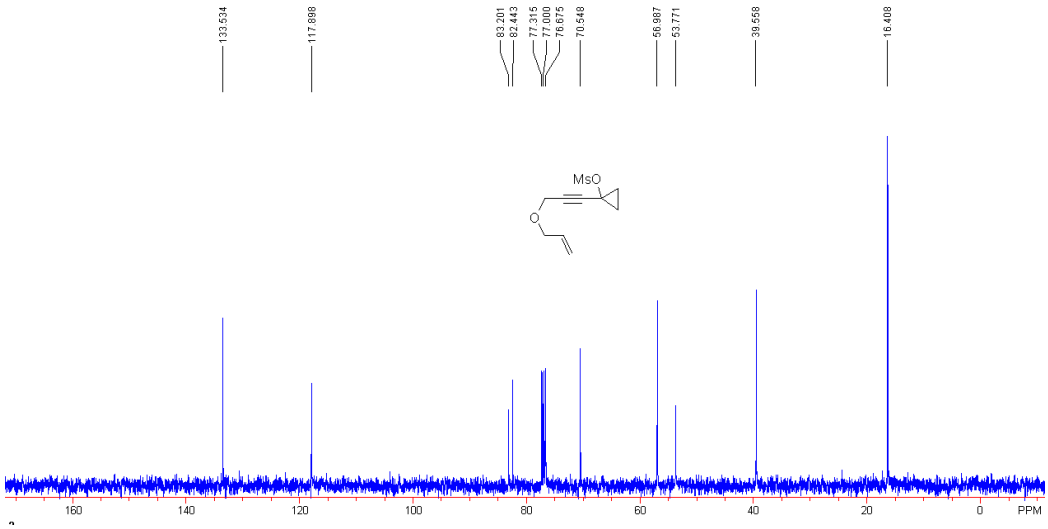


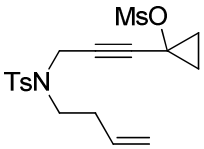




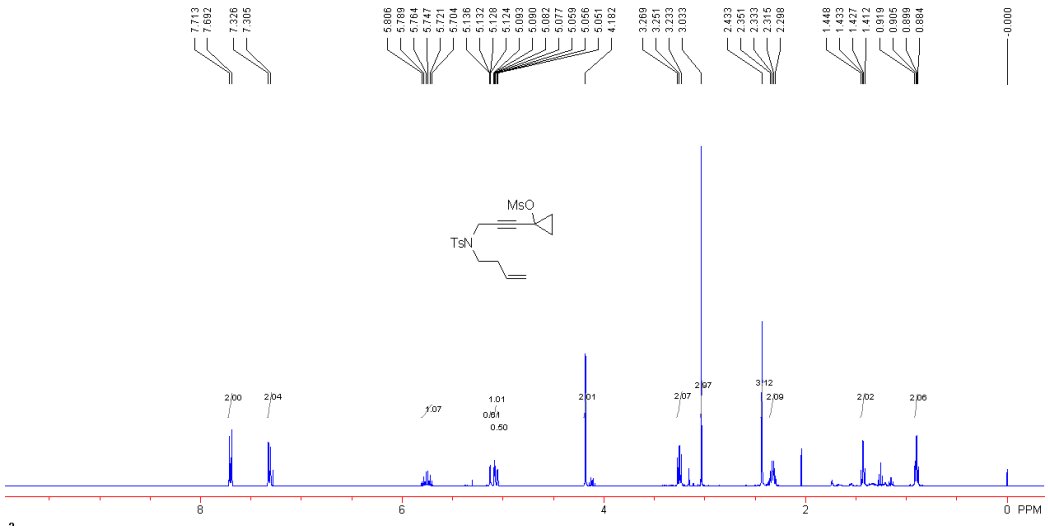
Compound 4c: A colorless oil. 370 mg, 83%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23-1.26 (m, 2H), 1.55-1.56 (m, 2H), 3.19 (s, 3H), 4.05 (d, J = 5.6 Hz, 2H), 4.21 (s, 2H), 5.23 (d, J = 10.4 Hz, 1H), 5.31 (d, J = 12.0 Hz, 1H), 5.84-5.93 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.4, 39.6, 53.8, 57.0, 70.5, 82.4, 83.2, 117.9, 133.5. IR (neat) ν 3022, 2939, 2855, 1739, 1417, 1359, 1214, 1168, 1086, 939, 873, 802, 766, 730, 665 cm^{-1}. HRMS (ESI) Calcd: $C_{10}H_{14}NO_4S$, 230.0613, Found: 230.0620.

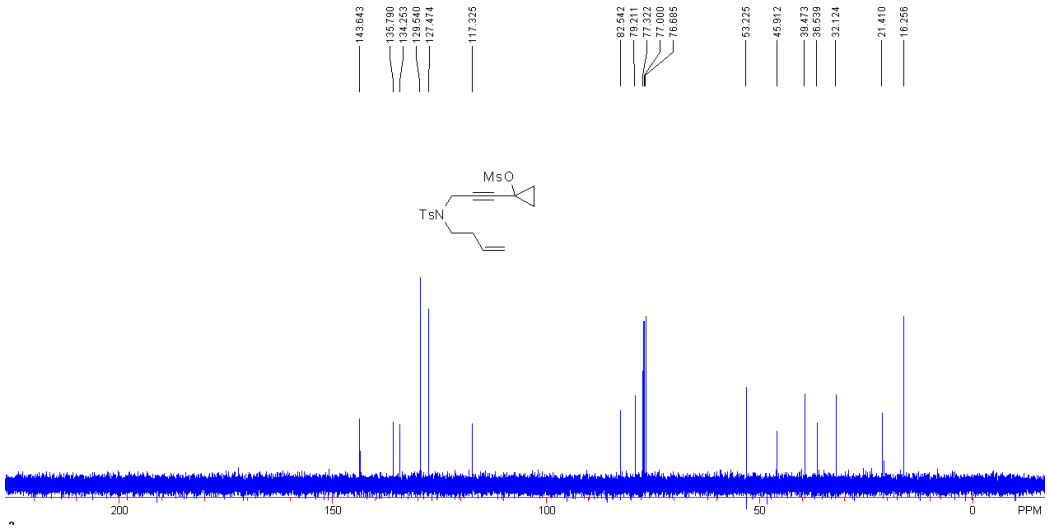


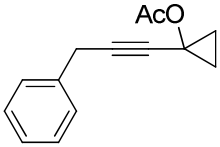




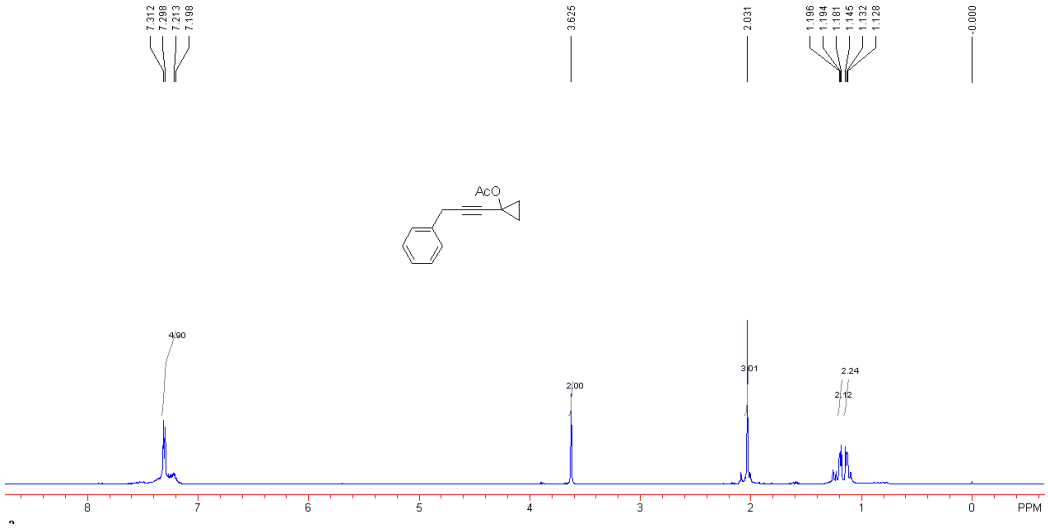
Compound 4d: A yellow oil. 670 mg, 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.90 (dd, *J* = 6.0 Hz, *J* = 8.4 Hz, 2H), 1.43 (dd, *J* = 6.0 Hz, *J* = 8.4 Hz, 2H), 2.32 (q, *J* = 5.4 Hz, 2H), 2.43 (s, 3H), 3.03 (s, 3H), 3.25 (t, *J* = 5.4 Hz, 2H), 4.18 (s, 2H), 5.07 (dd, *J* = 2.0 Hz, *J* = 10.4 Hz, 1H), 5.11 (dd, *J* = 2.0 Hz, *J* = 16.8 Hz, 1H), 5.70-5.81 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.3, 21.4, 32.1, 36.5, 39.5, 45.9, 53.2, 79.2, 82.5, 117.3, 127.5, 129.5, 134.3, 135.8, 143.6. IR (neat) ν 3022, 2978, 2937, 2869, 1641, 1597, 1417, 1347, 1214, 1157, 1090, 972, 941, 911, 873, 802, 726, 665 cm^{-1}. HRMS (ESI) Calcd: $C_{18}H_{23}NO_5S_2$, 397.1018, Found: 397.1011.

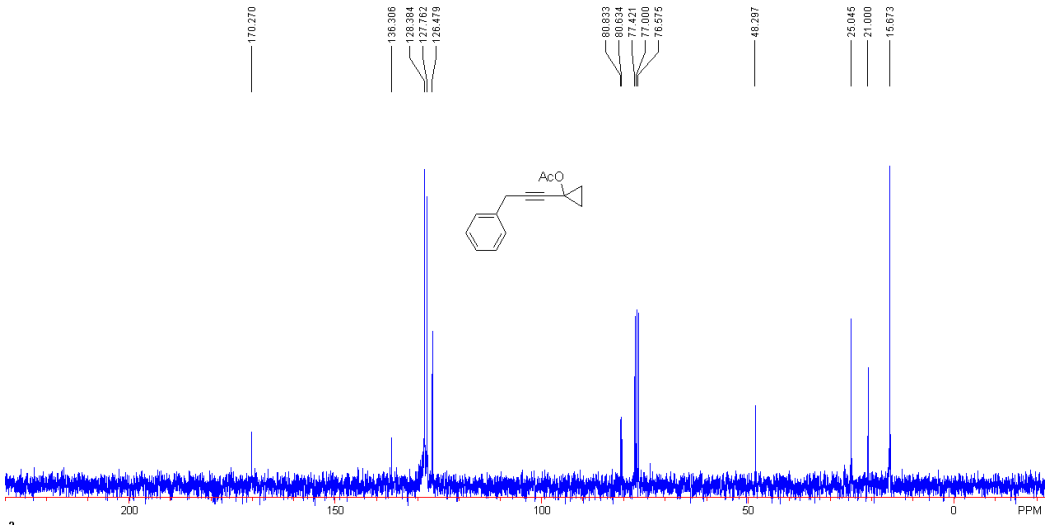


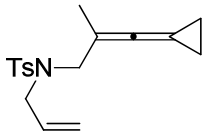




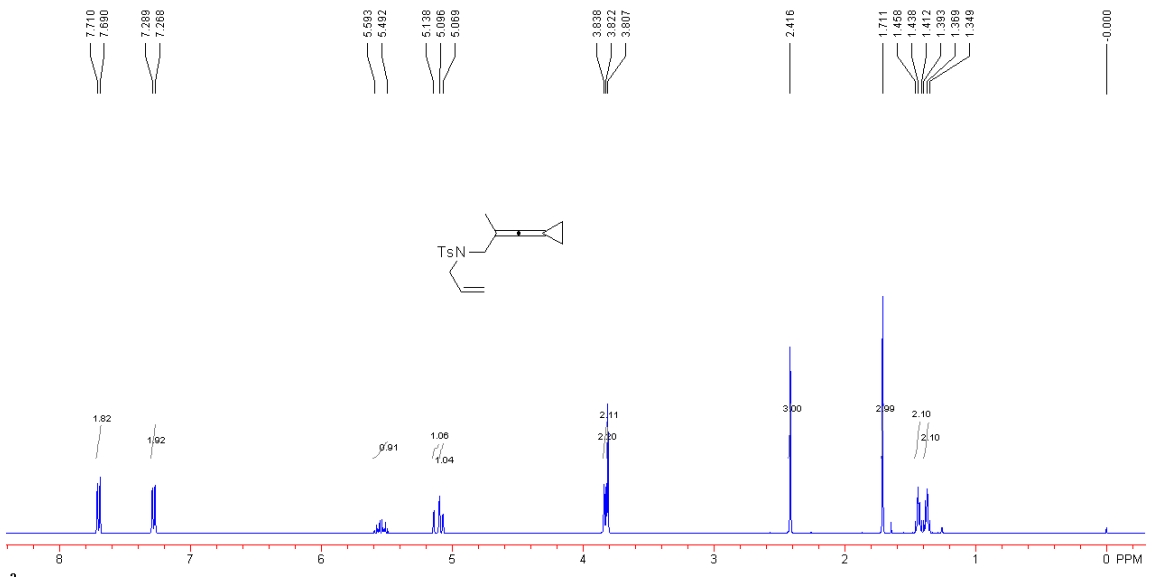
Compound 4e: A yellow oil. 321 mg, 82%. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.13-1.15 (m, 2H), 1.18-1.20 (m, 2H), 2.03 (s, 3H), 3.63 (s, 2H), 7.20-7.31 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.7, 21.0, 25.0, 48.3, 80.6, 80.8, 126.5, 127.8, 128.4, 136.3, 170.3. IR (neat) ν 3028, 2917, 1751, 1602, 1495, 1454, 1368, 1200, 1027, 981, 731, 699 cm^{-1}. HRMS (ESI) Calcd: $C_{14}H_{14}O_2$, 214.0994, Found: 214.0983.

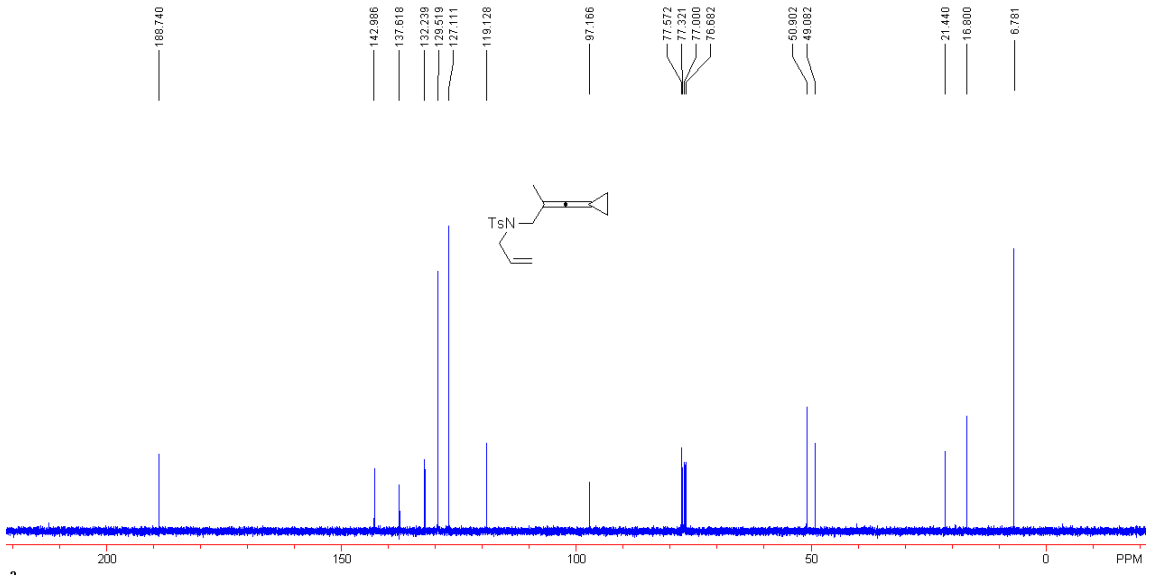


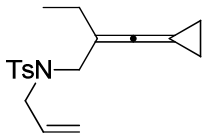




Compound 1a: A white solid. 1.002 g, 67%. Mp: 72-74 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.35-1.40 (m, 2H), 1.41-1.46 (m, 2H), 1.71 (s, 3H), 2.42(s, 3H), 3.81 (s, 2H), 3.83 (d, J = 6.8 Hz, 2H), 5.08 (dd, J = 1.6 Hz, J = 10.0 Hz, 1H), 5.12 (dd, J = 1.6 Hz, J = 17.2 Hz, 1H). 5.49-5.59 (m, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.8, 16.8, 21.4, 49.1, 50.9, 77.6, 97.2, 119.1, 127.1, 129.5, 132.2, 137.6, 143.0, 188.7. IR (neat) ν 2981, 2918, 2849, 2024, 1595, 1495, 1438, 1344, 1330, 1162, 1087, 1016, 940, 898, 878, 812, 799, 763, 660 cm^{-1}. HRMS (ESI) Calcd: $C_{17}H_{21}NO_2S$, 303.1293, Found: 303.1300.

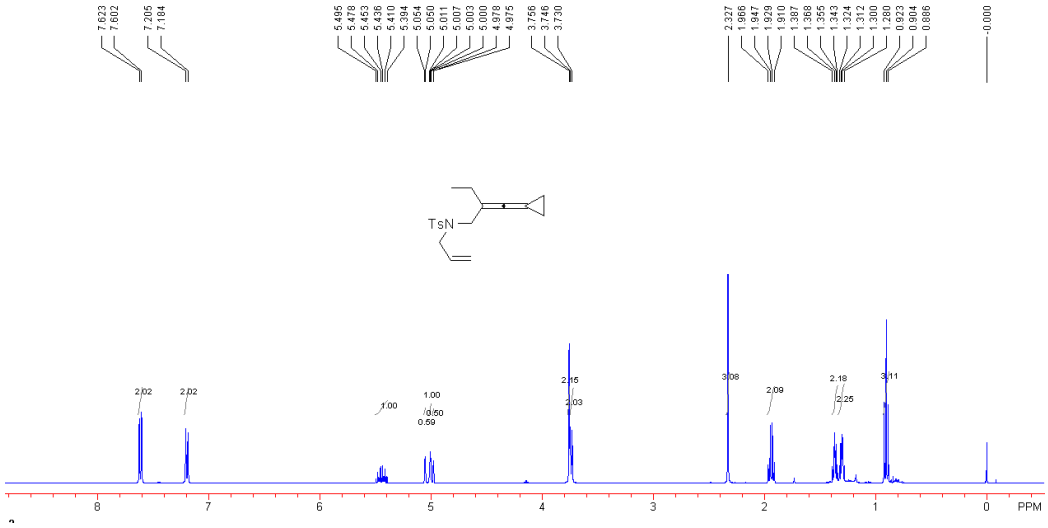


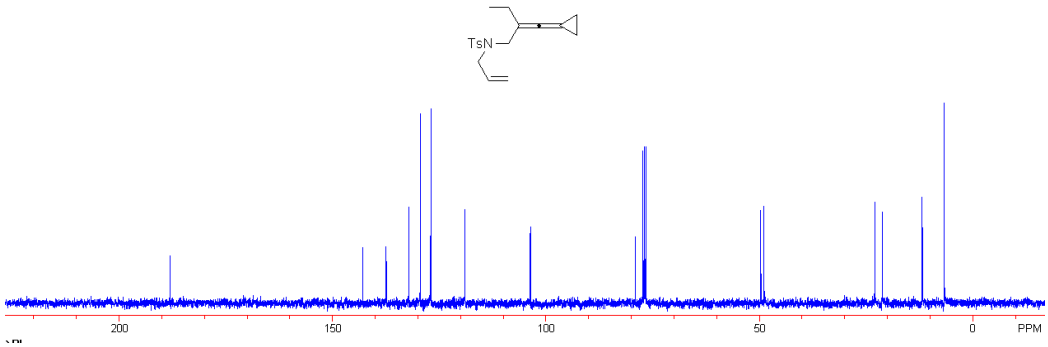


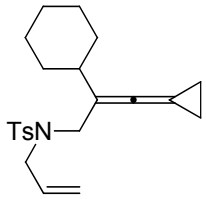


Compound 1b: A white solid. 118 mg, 42%. Mp: 78-80 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.90 (t, *J* = 7.6 Hz, 3H), 1.28-1.32 (m, 2H), 1.34-1.39 (m, 2H), 1.94 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 3.74 (d, *J* = 6.4 Hz, 2H), 3.76 (s, 2H), 4.99 (dd, *J* = 10.0 Hz, *J* = 1.6 Hz, 2H), 5.03 (dq, *J* = 17.2 Hz, *J* = 1.6 Hz, 2H), 5.39-5.50 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.8, 11.9, 21.3, 23.1, 49.0, 49.7, 79.1, 103.7, 119.0, 127.0, 129.4, 132.2, 137.4, 143.0, 188.0. IR (neat) ν 3064, 2859, 2027,

1646, 1595 1440, 1338, 1150, 1088, 993, 903, 754, 658 cm^{-1}. HRMS (ESI) Calcd: $C_{18}H_{23}NO_2S$, 317.1449, Found: 317.1442.

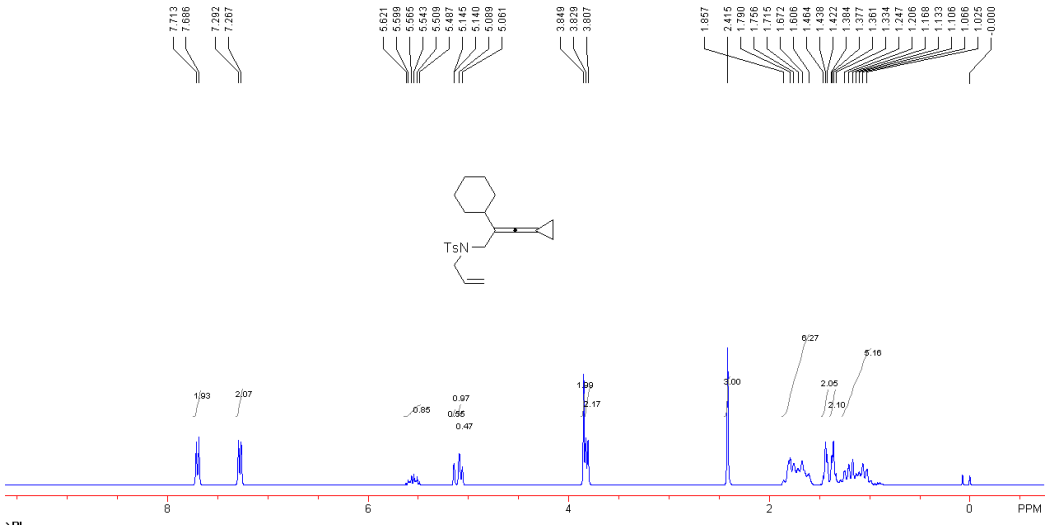


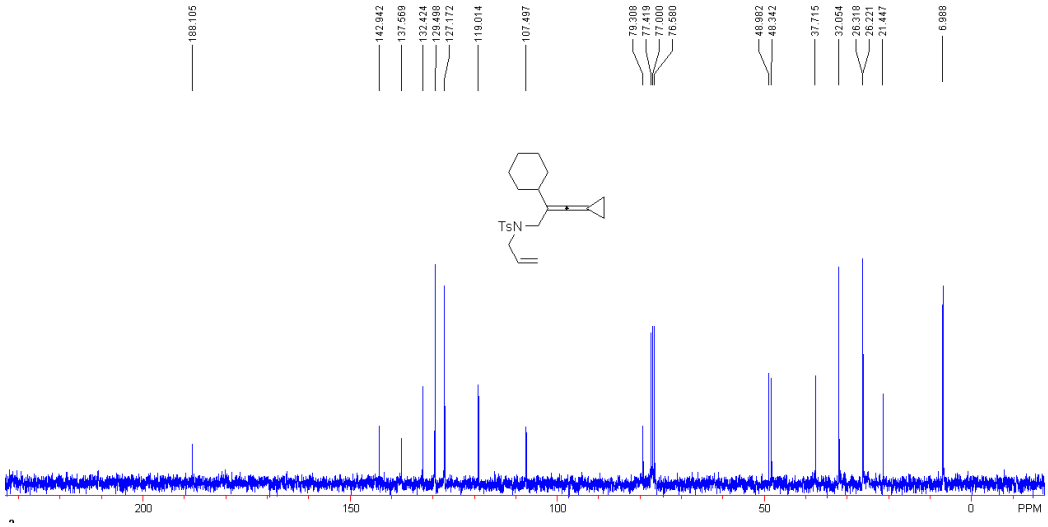


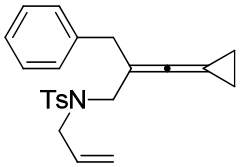


Compound 1c: A white solid. 343 mg, 92%. Mp: 87-89 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.03-1.25 (m, 5H), 1.33-1.38 (m, 2H), 1.42-1.46 (m, 2H), 1.61-1.86 (m, 6H), 2.42 (s, 3H), 3.82 (d, J = 6.6 Hz, 2H), 3.85 (s, 2H), 5.08 (d, J = 8.4 Hz, 1H), 5.11 (d, J = 15.3 Hz, 1H), 5.49-5.62 (m, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75

MHz, TMS) δ 7.0, 21.4, 26.2, 26.3, 32.1, 37.7, 48.3, 49.0, 79.3, 107.5, 119.0, 127.2, 129.5, 132.4, 137.6, 142.9, 188.1. IR (neat) ν 2913, 2844, 2016, 1597, 1444, 1347, 1328, 1158, 1090, 904, 755, 658 cm^{-1}. HRMS (ESI) Calcd: $C_{22}H_{29}NO_2S$, 371.1919, Found: 371.1910.

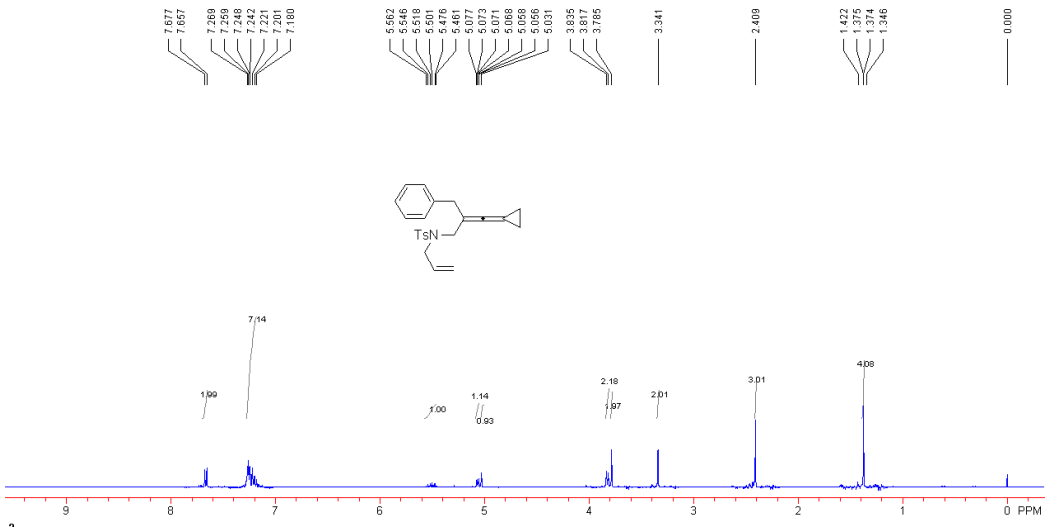


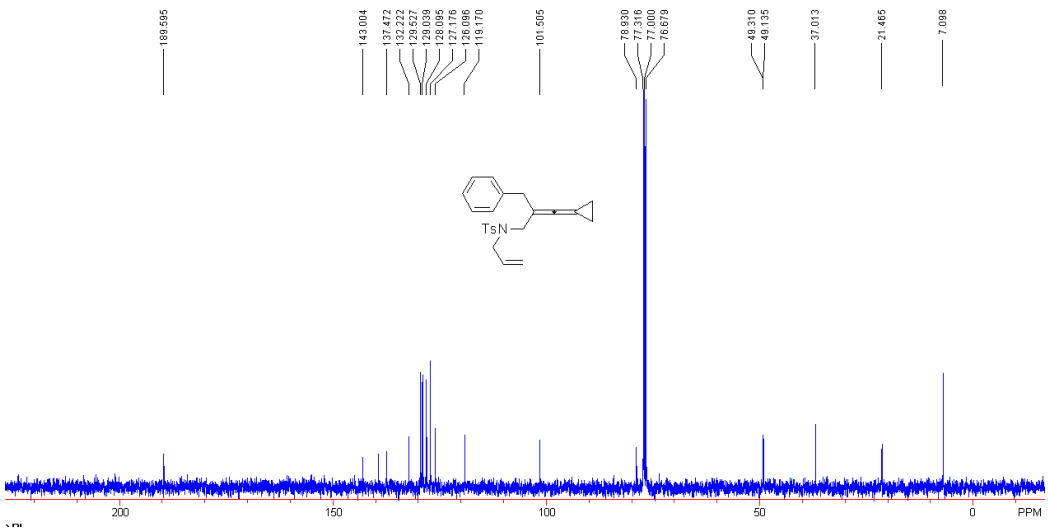


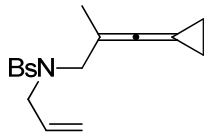


Compound 1d: A colorless oil. 261 mg, 68%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.35-1.42 (m, 4H), 2.41 (s, 3H), 3.34 (s, 2H), 3.79 (s, 2H), 3.83 (d, J = 7.2 Hz, 2H), 5.03 (s, 1H), 5.07 (d, J = 8.0 Hz, 1H), 5.46-5.56 (m, 1H), 7.18-7.27 (m, 7H), 7.67 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 7.1, 21.5, 37.0, 49.1, 49.3, 78.9, 101.5, 119.2, 126.1, 127.2, 128.1,

129.0, 129.5, 132.2, 137.5, 143.0, 189.6. IR (neat) ν 3027, 2919, 2021, 1728, 1598, 1494, 1343, 1155, 1090, 900, 745, 699, 661 cm^{-1}. HRMS (ESI) Calcd: $C_{23}H_{25}NO_2S$, 379.1606, Found: 379.1598.

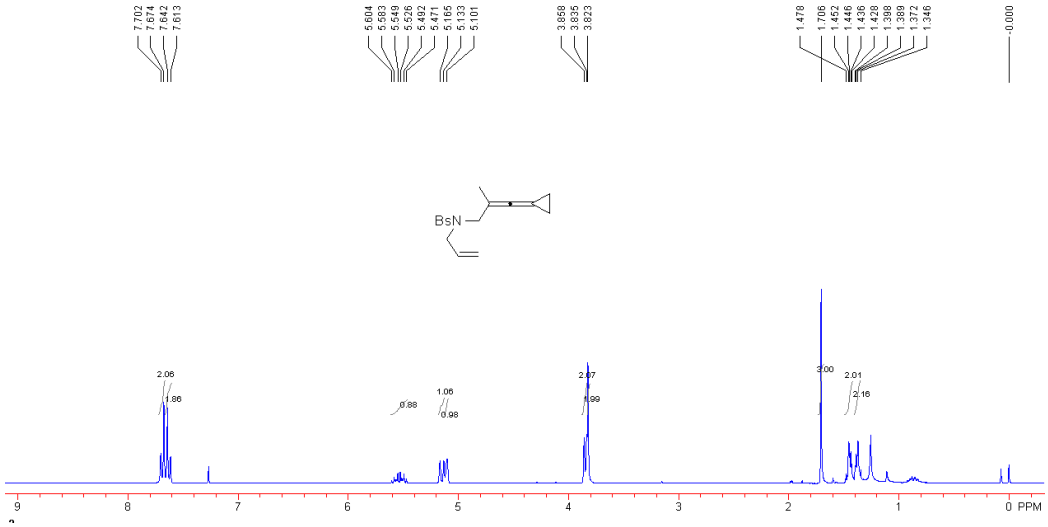


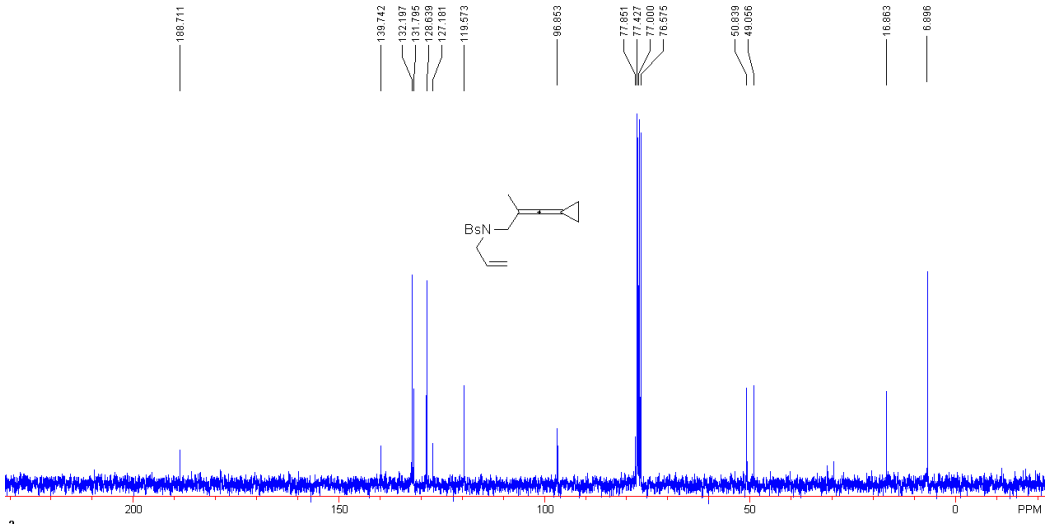


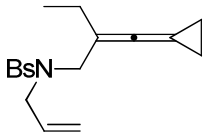


Compound 1e: A white solid. 372 mg, 98%. Mp: 74-76 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.35-1.40 (m, 2H), 1.43-1.48 (m, 2H), 1.71 (s, 3H), 3.82 (s, 2H), 3.85 (d, J = 6.9 Hz, 2H), 5.12 (d, J = 9.6 Hz, 1H), 5.13 (d, J = 19.2 Hz, 1H), 5.47-5.60 (m, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 6.9, 16.9, 49.1, 50.8, 77.9, 96.9, 119.6, 127.2, 128.6, 131.8, 132.2, 139.7, 188.7. IR (neat) ν 3094, 2919, 2853, 2022,

1573, 1469, 1442, 1344, 1318, 1162, 1086, 898, 768, 733, 661 cm^{-1}. HRMS (ESI) Calcd: $C_{16}H_{18}NO_2SBr$, 367.0242, Found: 367.0242.

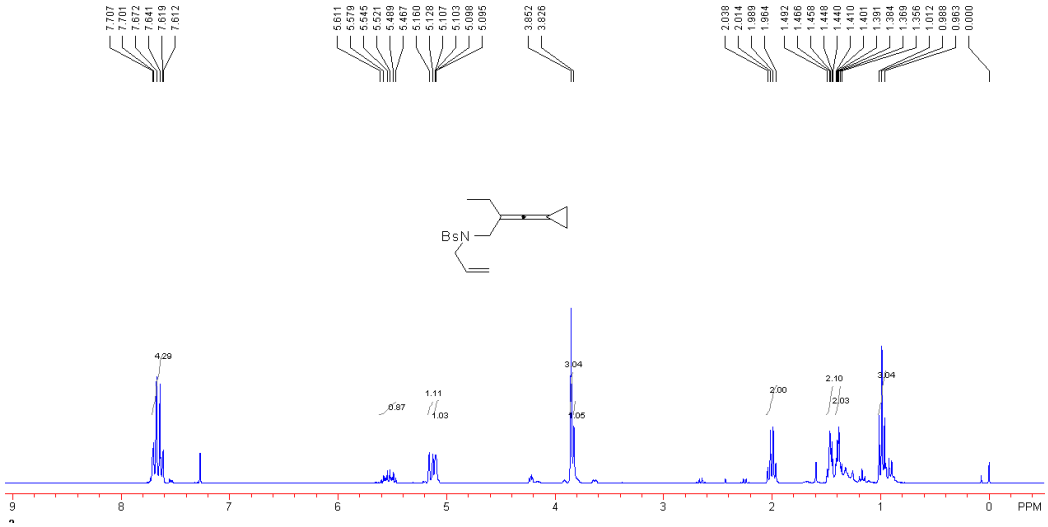


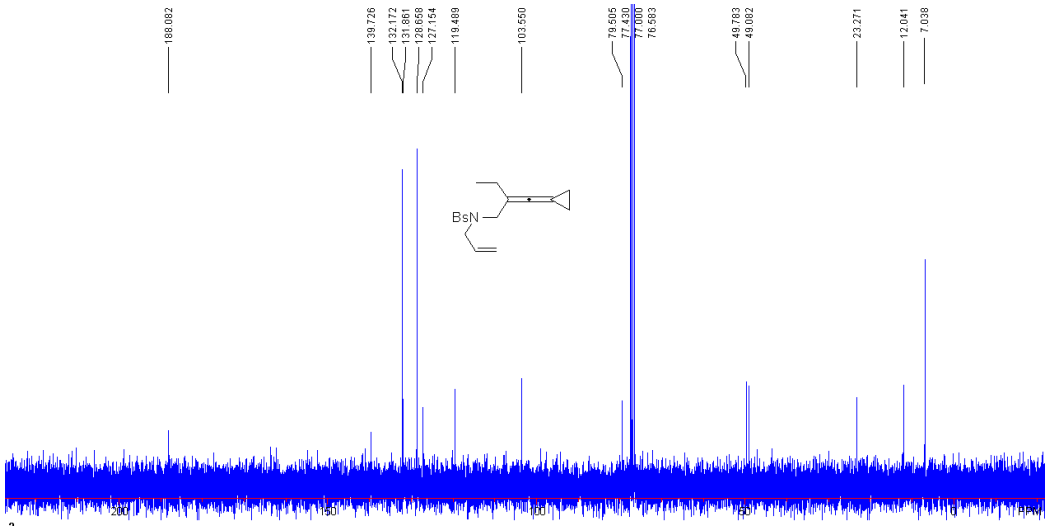


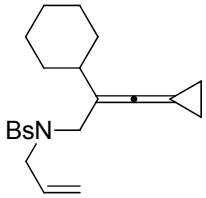


Compound 1f: A white solid. 284 mg, 68%. Mp: 82-84 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.99 (t, *J* = 7.5 Hz, 3H), 1.36-1.41 (m, 2H), 1.44-1.49 (m, 2H), 2.00 (q, *J* = 7.5 Hz, 2H), 3.84 (d, *J* = 6.0 Hz, 2H), 3.85 (s, 2H), 5.12 (d, *J* = 8.4 Hz, 1H), 5.14 (d, *J* = 18.0 Hz, 1H), 5.47-5.61 (m, 1H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 7.0, 12.0, 23.3, 49.1, 49.8, 79.5, 103.6, 119.5, 127.2, 128.7, 131.9, 132.2, 139.7,

188.1. IR (neat) ν 2923, 2851, 2023, 1725, 1574, 1348, 1161, 1088, 902, 768, 732 cm^{-1}. HRMS (ESI) Calcd: $C_{17}H_{20}BrNO_2S$, 381.0398, Found: 381.0395.

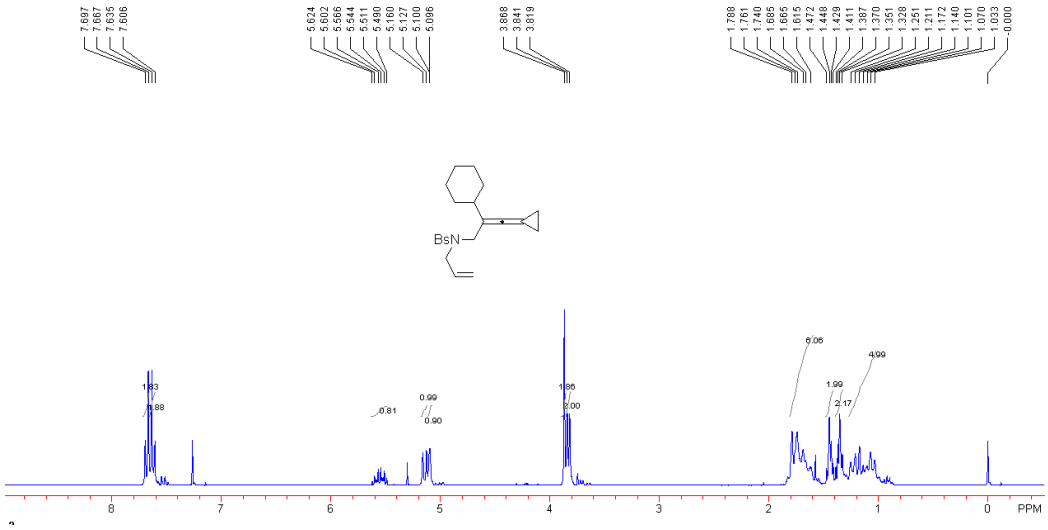


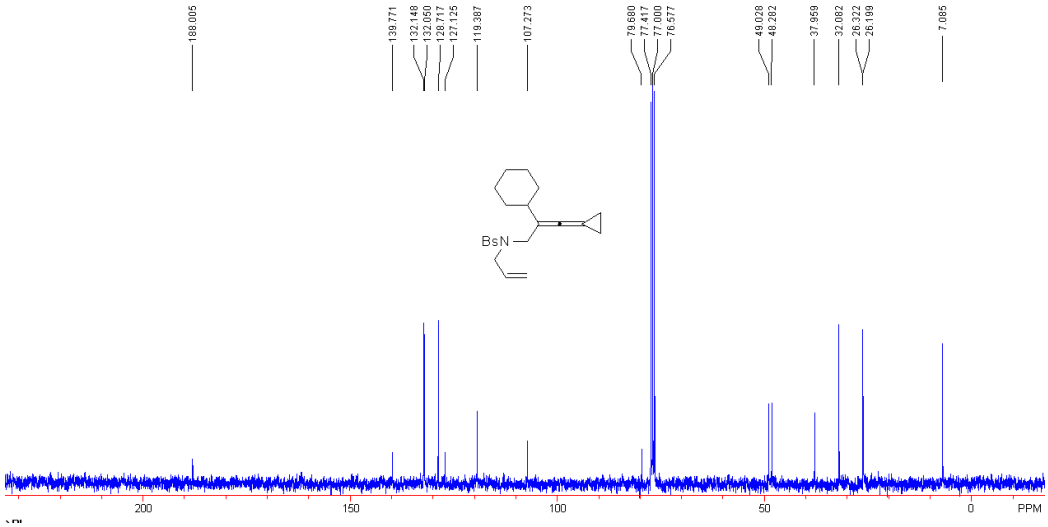


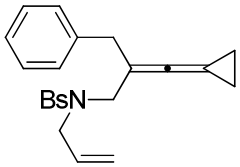


Compound 1g: A colorless oil. 205 mg, 84%. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.03-1.25 (m, 5H), 1.33-1.39 (m, 2H), 1.41-1.47 (m, 2H), 1.62-1.79 (m, 6H), 3.83 (d, *J* = 6.6 Hz, 2H), 3.87 (s, 2H), 5.11 (d, *J* = 8.7 Hz, 1H), 5.13 (d, *J* = 18.6 Hz, 1H), 5.49-5.62 (m, 1H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 7.1, 26.2, 26.3

32.1, 38.0, 48.3, 49.0, 79.7, 107.3, 119.4, 127.1, 128.7, 132.05, 132.15, 139.8, 188.0. IR (neat) ν 3084, 2922, 2849, 2018, 1724, 1642, 1574, 1447, 1346, 1158, 1039, 903, 766, 731 cm^{-1}. HRMS (ESI) Calcd: $C_{21}H_{26}BrNO_2S$, 435.0868, Found: 435.0865.

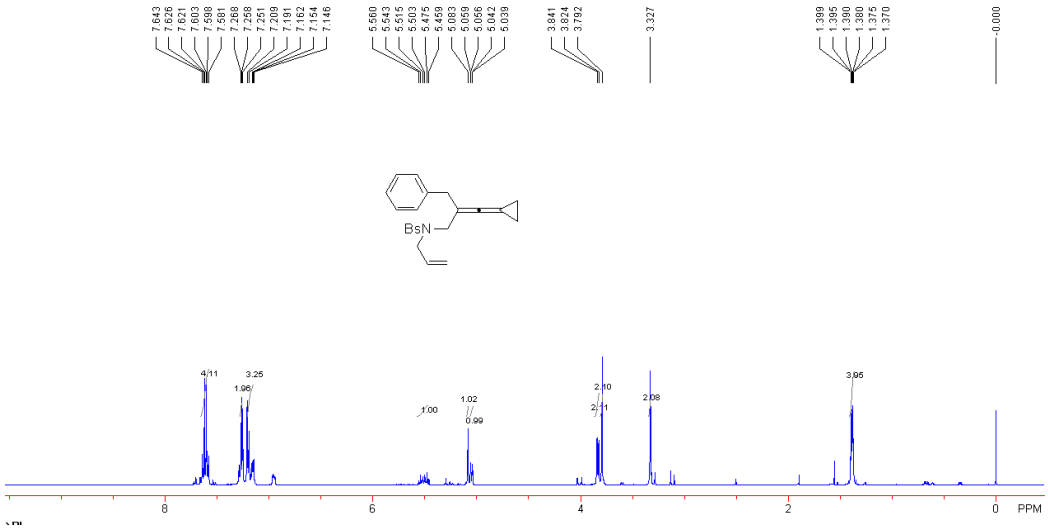


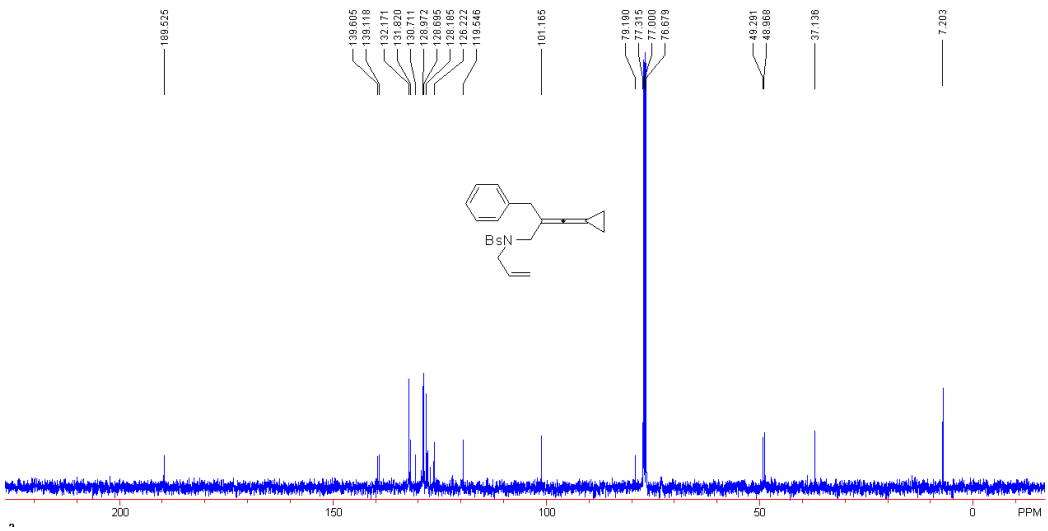


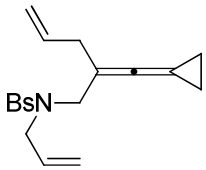


Compound 1h: A yellow oil. 342 mg, 75%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.37-1.40 (m, 4H), 3.33 (s, 2H), 3.79 (s, 2H), 3.83 (d, J = 6.8 Hz, 2H), 5.06 (d, J = 17.2 Hz, 1H), 5.07 (d, J = 10.0 Hz, 1H), 5.46-5.56 (m, 1H), 7.15-7.20 (m, 3H), 7.25-7.27 (m, 2H), 7.58-7.64 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 7.2, 37.1, 49.0, 49.3, 79.2, 101.2, 119.5, 126.2, 128.2,

128.7, 129.0, 130.7, 131.8, 132.2, 139.1, 139.6, 189.5. IR (neat) ν 3061, 2917, 2021, 1574, 1347, 1160, 1088, 901, 768, 730, 698 cm^{-1}. HRMS (ESI) Calcd: $C_{23}H_{22}BrNO_2S$, 443.0555, Found: 443.0555.

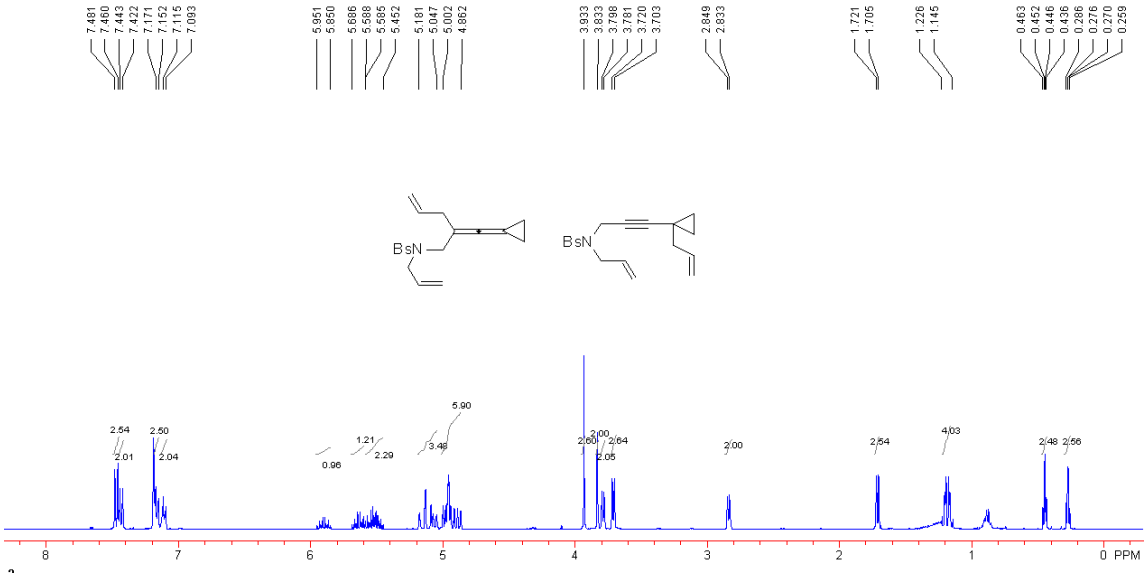


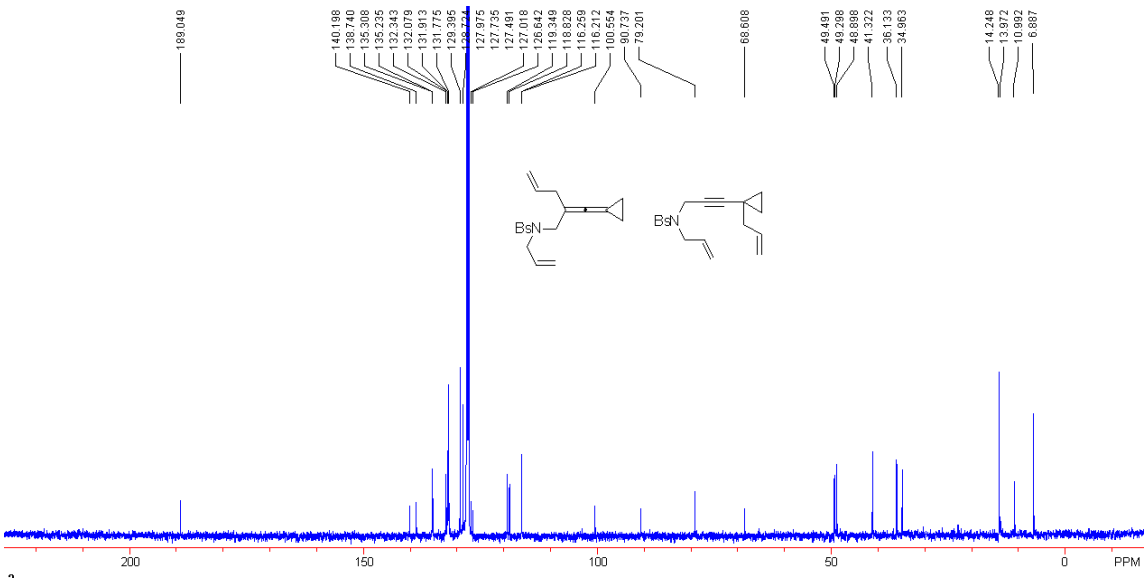


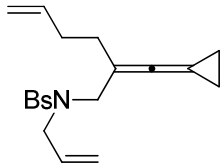


Compound 1i: A colorless oil containing some amount of byproduct shown in the charts. 247 mg, 43%. ^{1}H NMR (C_6D_6, 400 MHz, TMS) δ 1.15-1.23 (m, 4H), 2.84 (d, J = 6.4 Hz, 2H), 3.79 (d, J = 6.8 Hz, 2H), 3.83 (s, 2H), 4.94-5.12 (m, 4H), 5.45-5.59 (m, 1H), 5.85-5.95 (m, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H). ^{13}C NMR (C_6D_6, 100 MHz, TMS) δ

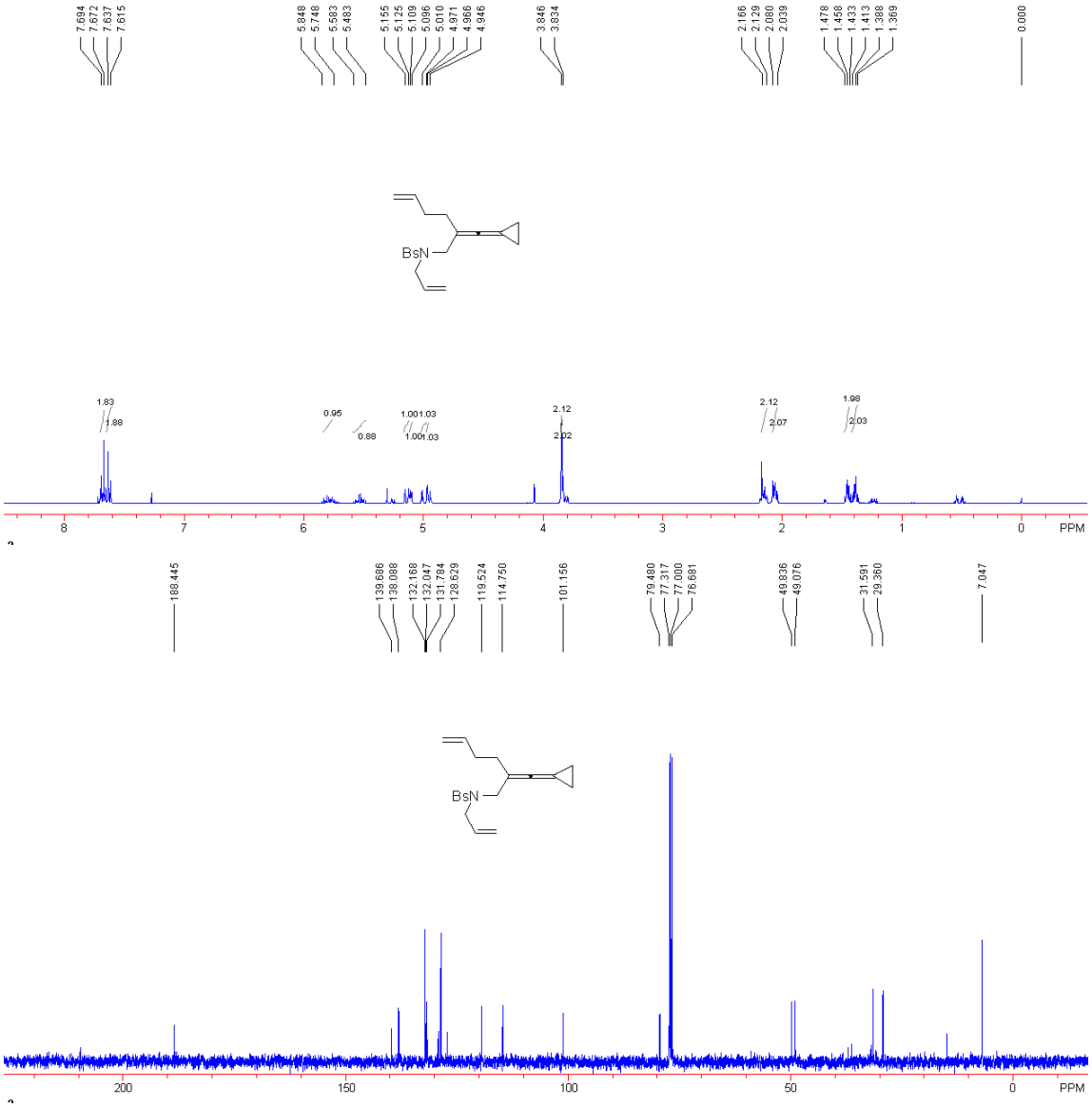
6.9, 35.0, 49.3, 49.5, 79.2, 100.6, 116.2, 118.8, 127.0, 128.7, 129.4, 131.8, 132.1, 140.2, 189.0. IR (neat) ν 3084, 2981, 2924, 2240, 2022, 1642, 1575, 1471, 1434, 1389, 1350, 1260, 1164, 1089, 1068, 1009, 907, 823, 768, 732, 702 cm^{-1}. HRMS (ESI) Calcd: $C_{18}H_{20}BrNO_2S$, 393.0398, Found: 393.0396.

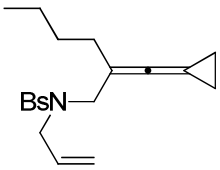




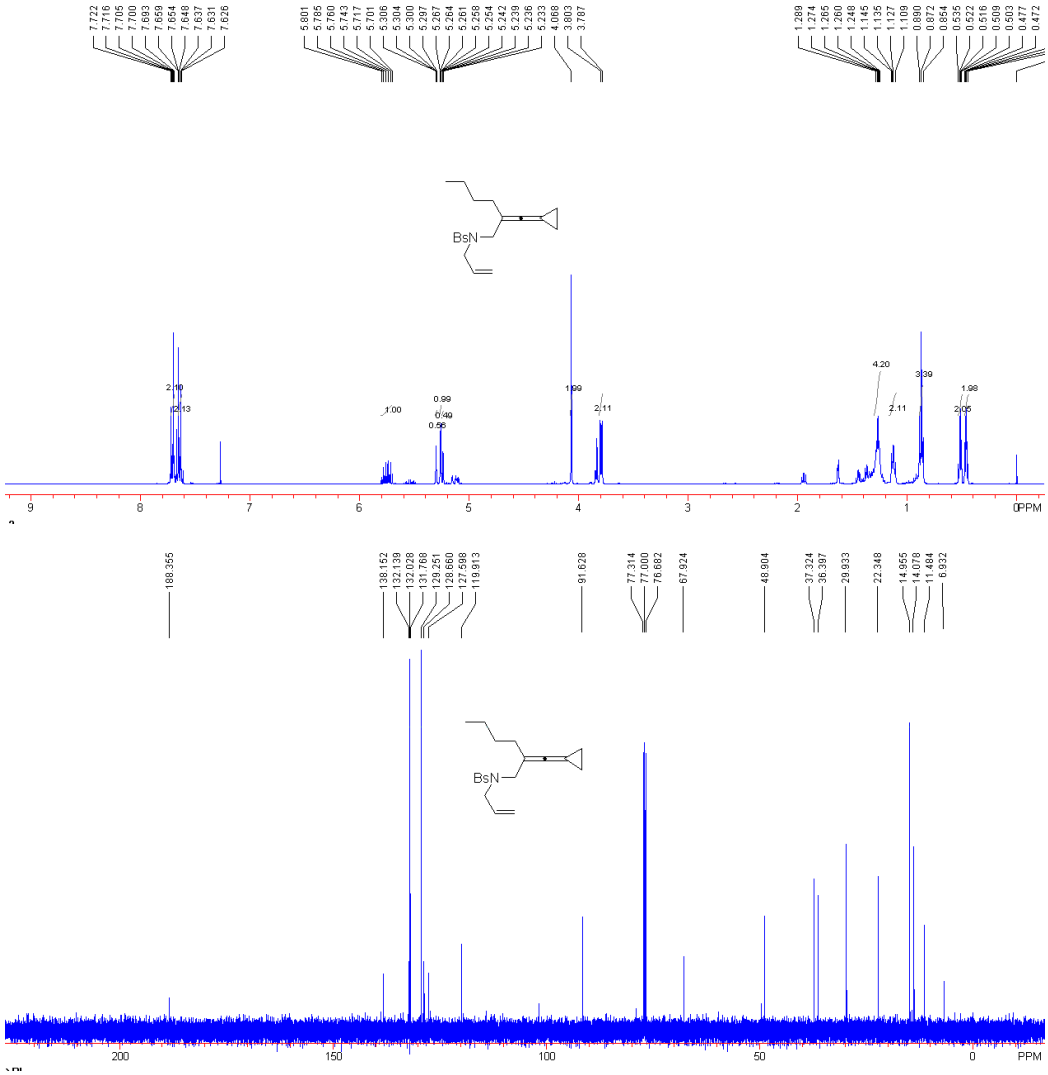


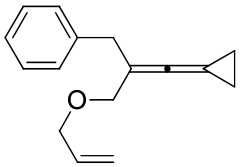
Compound 1j: A colorless oil. 298 mg, 50%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.37-1.41 (m, 2H), 1.43-1.48 (m, 2H), 2.04-2.08 (m, 2H), 2.13-2.17 (m, 2H), 3.84 (d, *J* = 4.8 Hz, 2H), 3.85 (s, 2H), 4.96 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 15.6 Hz, 1H), 5.10 (d, *J* = 5.2 Hz, 1H), 5.40 (d, *J* = 12.0 Hz, 1H), 5.48-5.58 (m, 1H), 5.75-5.85 (m, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 7.0, 29.4, 31.6, 49.1, 49.8, 79.5, 101.2, 114.8, 119.5, 127.2, 128.6, 129.2, 131.8, 132.0, 138.1, 139.7, 188.4. IR (neat) ν 3078, 2981, 2920, 2850, 2021, 1722, 1640, 1574, 1471, 1440, 1389, 1347, 1274, 1159, 1088, 1067, 1008, 904, 822, 765, 730, 702 cm^{-1}. HRMS (ESI) Calcd: $C_{19}H_{22}BrNO_2S$, 407.0555, Found: 407.0549.



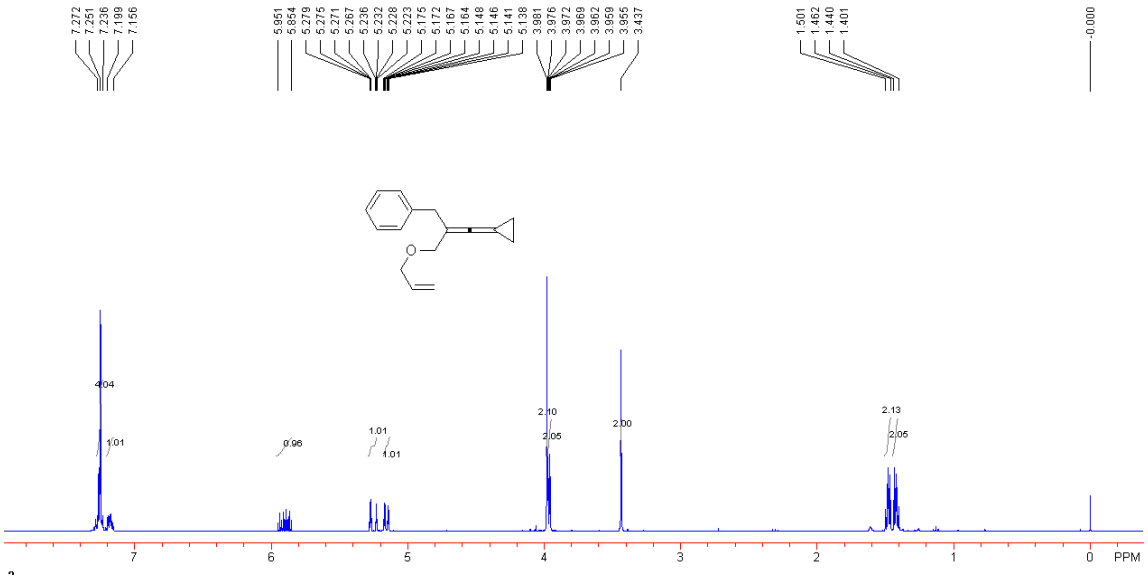


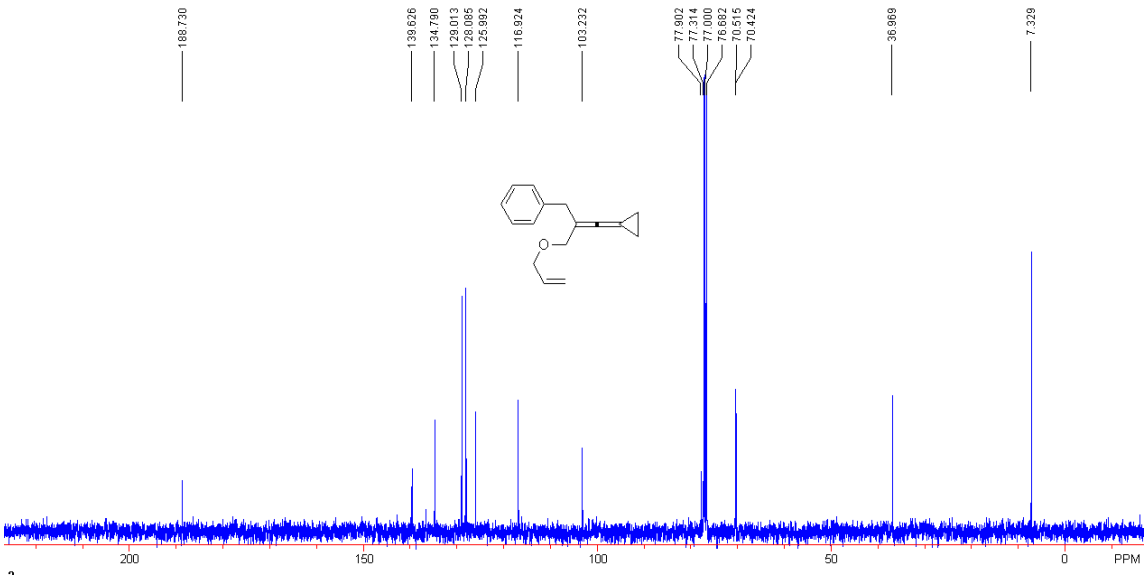
Compound 1k: A colorless oil. 170 mg, 42%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.45-0.48 (m, 2H), 0.50-0.54 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H), 1.11-1.15 (m, 2H), 1.25-1.29 (m, 4H), 3.80 (d, *J* = 6.4 Hz, 2H), 4.07 (s, 2H), 5.25 (dq, *J* = 8.4 Hz, *J* = 1.2 Hz, 2H), 5.29 (dq, *J* = 15.6 Hz, *J* = 1.2 Hz, 2H), 5.70-5.80 (m, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.9, 11.5, 14.1, 15.0, 22.3, 29.9, 36.4, 37.3, 48.9, 67.9, 91.6, 119.9, 127.6, 128.7, 129.3, 131.8, 132.0, 132.1, 138.2, 188.4. IR (neat) ν 2927, 2857. 2236. 1575. 1469, 1350, 1163, 1067, 1009, 897, 765, 731 cm^{-1}. HRMS (ESI) Calcd: $C_{19}H_{24}BrNO_2S$, 409.0711, Found: 409.0697.

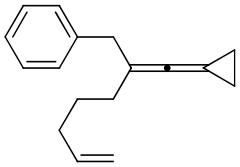




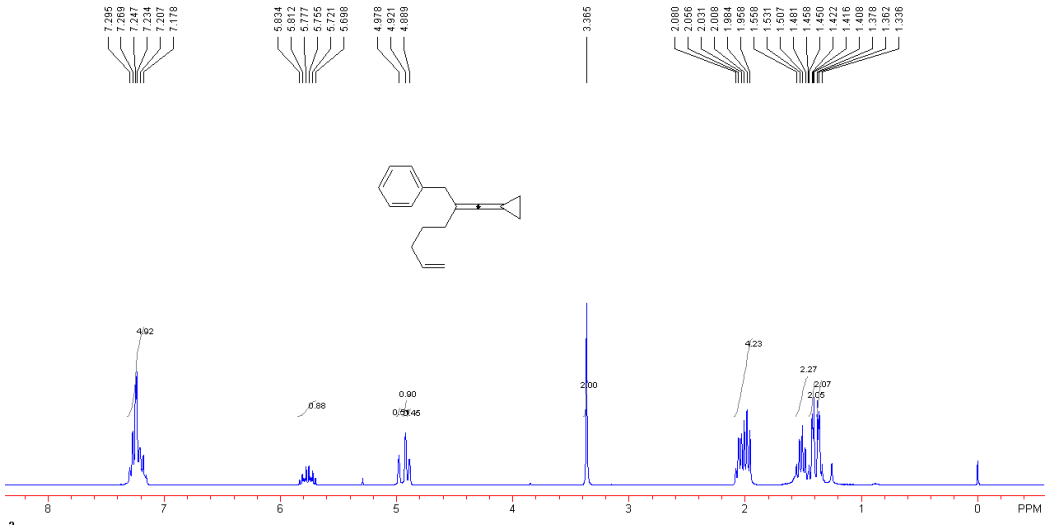
Compound 1l: A yellow oil. 342 mg, 75%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.40-1.44 (m, 2H), 1.46-1.50 (m, 2H), 3.44 (s, 2H), 3.97 (dt, *J* = 5.2 Hz, *J* = 1.6 Hz, 2H), 3.98 (s, 2H), 5.16 (dq, *J* = 10.4 Hz, *J* = 1.6 Hz, 1H), 5.25 (dq, *J* = 17.2 Hz, *J* = 1.6 Hz, 1H), 5.85-5.95 (m, 1H), 7.16-7.20 (m, 1H), 7.24-7.27 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 7.3, 37.0, 70.4, 70.5, 77.9, 103.2, 116.9, 126.0, 128.1, 129.0, 134.8, 139.6, 188.7. IR (neat) ν 3027, 2922, 2854, 2022, 1732, 1602, 1494, 1453, 1347, 1073, 924, 746 cm^{-1}. HRMS (ESI) Calcd: $C_{16}H_{18}O$, 226.1358, Found: 226.1366.

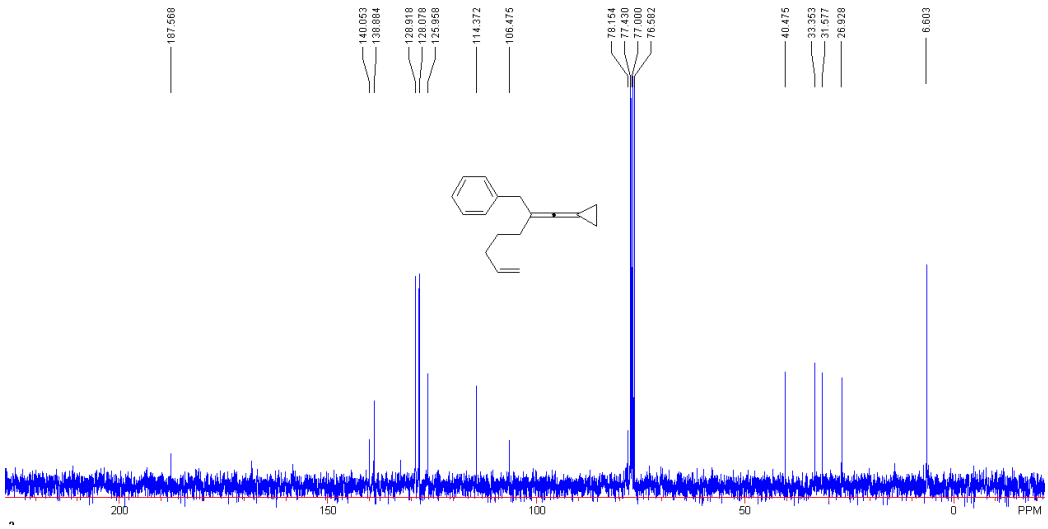


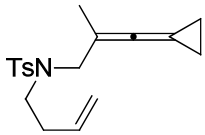




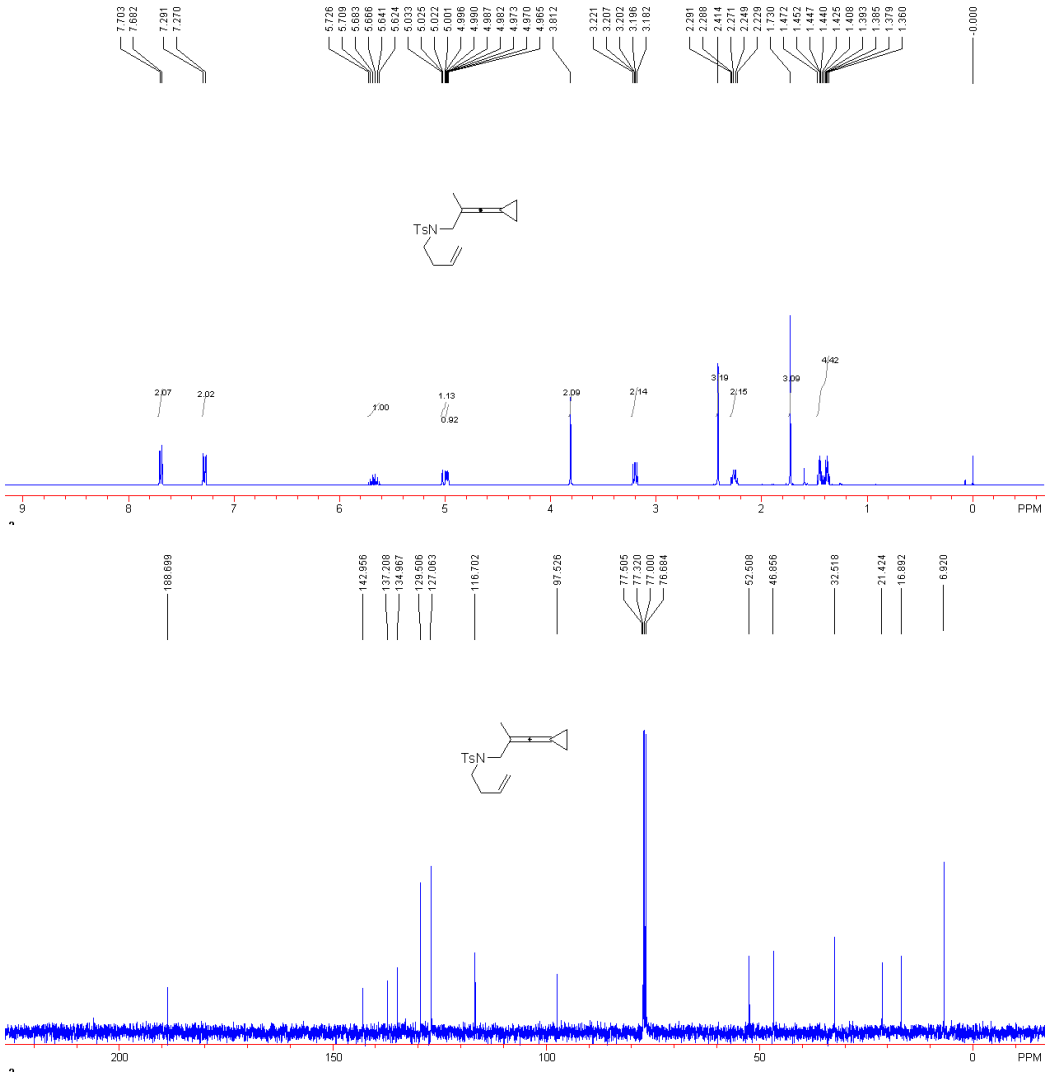
Compound 1m: A colorless oil. 180 mg, 83%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.34-1.38 (m, 2H), 1.41-1.45 (m, 2H), 1.46-1.56 (m, 2H), 1.96-2.08 (m, 4H), 2.37 (s, 2H), 4.91 (d, *J* = 9.6 Hz, 1H), 4.95 (d, *J* = 17.1 Hz, 1H), 5.70-5.83 (m, 1H), 7.18-7.30 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.6, 26.9, 31.6, 33.4, 40.5, 78.2, 106.5, 114.4, 126.0, 128.1, 128.9, 138.9, 140.1, 187.6. IR (neat) ν 2927, 2857, 2236, 1575, 1469, 1350, 1163, 1067, 1009, 897, 765, 731 cm^{-1}. MS (EI): 224, 195, 189, 182, 178, 168, 167, 163, 152, 139. HRMS (EI) Calcd: $C_{17}H_{20}$, 224.1565, Found: 224.1566.

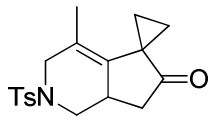






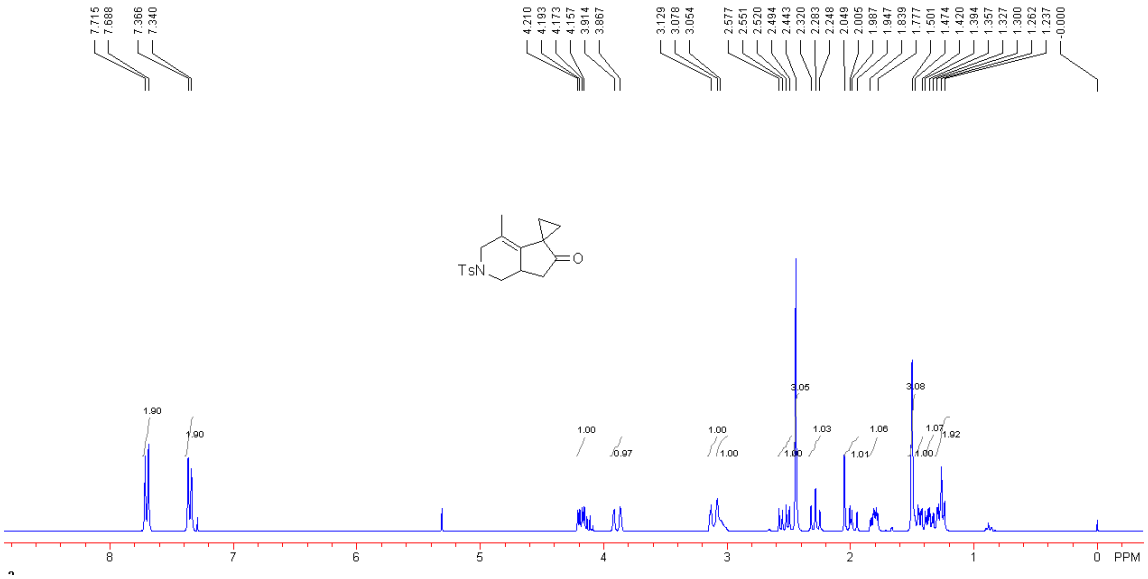
Compound 1n: A colorless oil. 270 mg, 85%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.36-1.41 (m, 2H), 1.43-1.47 (m, 2H), 1.73 (s, 3H), 2.26 (q, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 3.18-3.22 (m, 2H), 3.81 (m, 2H), 4.97-4.99 (m, 1H), 4.99-5.03 (m, 1H), 5.62-5.73 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 6.9, 16.9, 21.4, 32.5, 46.9, 52.5, 77.5, 97.5, 116.7, 127.1, 129.5, 135.0, 137.2, 143.0, 188.7. IR (neat) ν 2981, 2917, 2022, 1641, 1598, 1441, 1336, 1155, 1088, 993, 909, 813, 745, 658 cm^{-1}. HRMS (ESI) Calcd: $C_{18}H_{23}NO_2S$, 317.1449, Found: 317.1445.

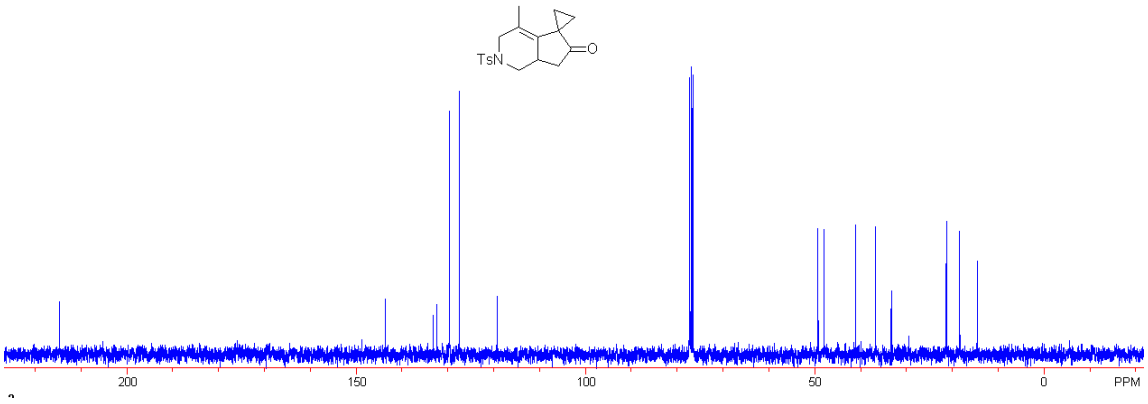


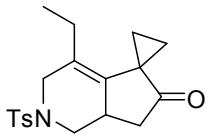


Compound 2a: A white solid. 60 mg, 99%, Mp: 120-122 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.24-1.30 (m, 2H), 1.33-1.1.39 (m, 1H), 1.42-1.47 (m, 1H), 1.50 (s, 3H), 1.78-1.84 (m, 1H), 2.00 (dd, J = 12.0 Hz, J = 17.1 Hz, 1H), 2.28 (t, J = 10.8 Hz, 1H), 2.44 (s, 3H), 2.54 (dd, J = 7.8 Hz, J = 17.1 Hz, 1H), 3.05 (br, 1H), 3.17 (d, J = 15.3 Hz, 1H), 3.89 (d, J = 15.3 Hz, 1H), 4.18 (dd, J = 5.1 Hz, J = 10.8 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.8, 18.5, 21.3, 21.5, 33.4, 36.8, 41.2, 48.1, 49.4, 119.2, 127.6, 129.7, 132.5, 133.2, 143.7, 214.6. IR (neat) ν 2921, 2862, 2828, 1733, 1703, 1596,

1459, 1342, 1319, 1160, 1088, 946, 814, 736, 663 cm^{-1}. HRMS (ESI) Calcd: $C_{18}H_{21}NO_3S$, 331.1242, Found: 331.1240.

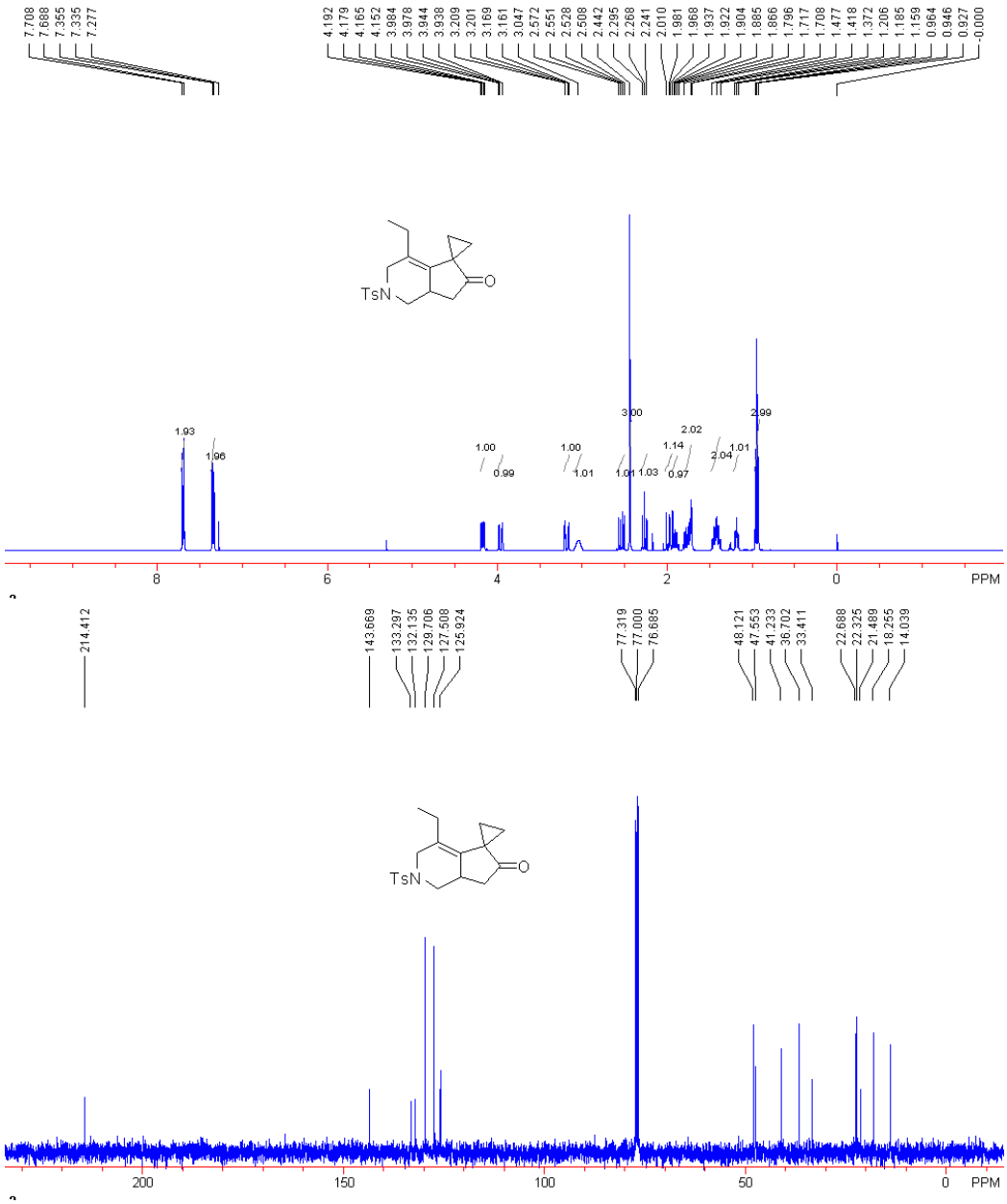


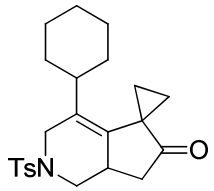




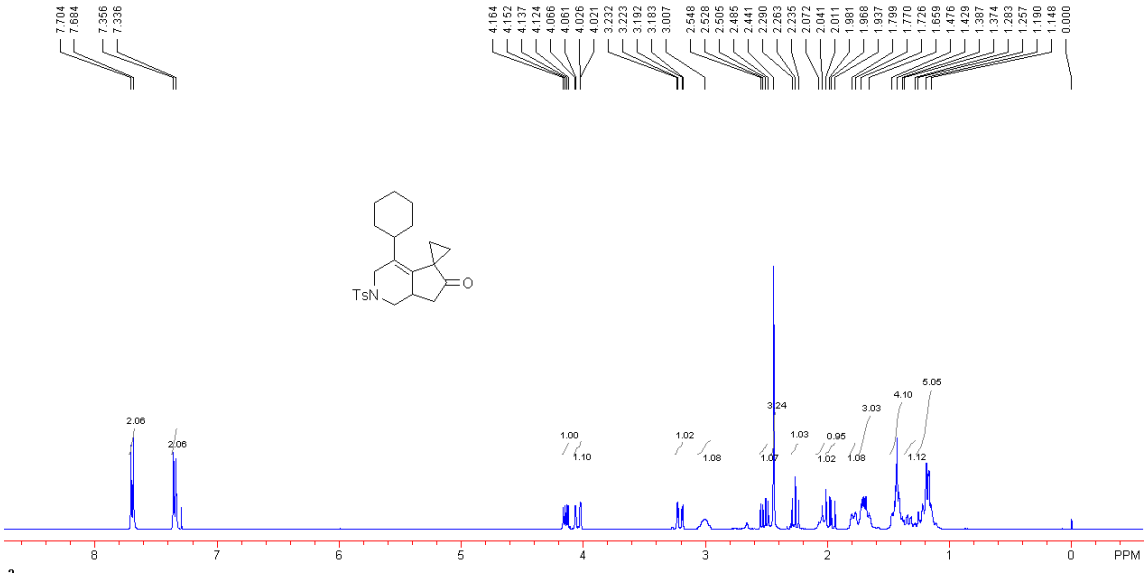
Compound 2b: A white solid. 44 mg, 95%, Mp: 126-128 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.95 (t, *J* = 7.6 Hz, 3H), 1.16-1.21 (m, 1H), 1.37-1.1.48 (m, 2H), 1.71-1.80 (m, 2H), 1.87-1.92 (m, 1H), 1.97 (dd, *J* = 12.0 Hz, *J* = 17.2 Hz, 1H), 2.27 (t, *J* = 10.8 Hz, 1H), 2.44 (s, 3H), 2.54 (dd, *J* = 8.0 Hz, *J* = 17.2 Hz, 1H), 3.16 (br, 1H), 3.19 (dd, *J* = 2.4 Hz, *J* = 15.6 Hz,

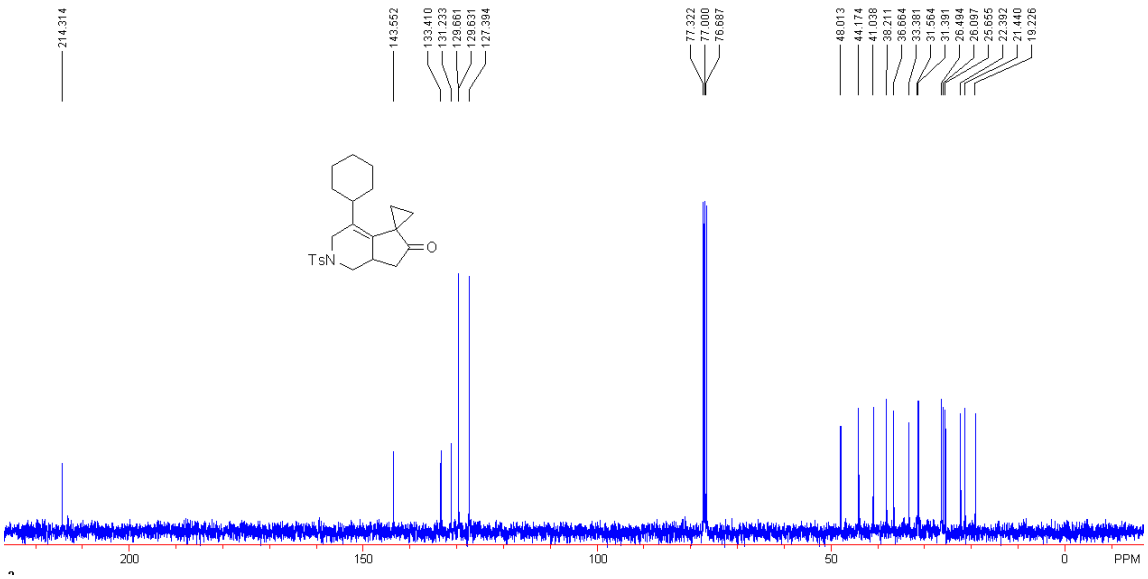
1H), 3.96 (dd, J = 2.4 Hz, J = 15.6 Hz, 1H), 4.17 (dd, J = 5.2 Hz, J = 10.8 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 18.3, 21.5, 22.3, 22.7, 33.4, 36.7, 41.2, 47.6, 48.1, 125.9, 127.5, 129.7, 132.1, 133.3, 143.7, 214.4. IR (neat) ν 3428, 2970, 2934, 2876, 1732, 1705, 1579, 1457, 1401, 1321, 1160, 1090, 1048, 958, 813, 734, 662 cm^{-1}. HRMS (ESI) Calcd: $C_{19}H_{23}NO_3S$, 345.1399, Found: 345.1391.

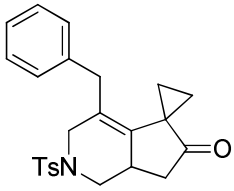




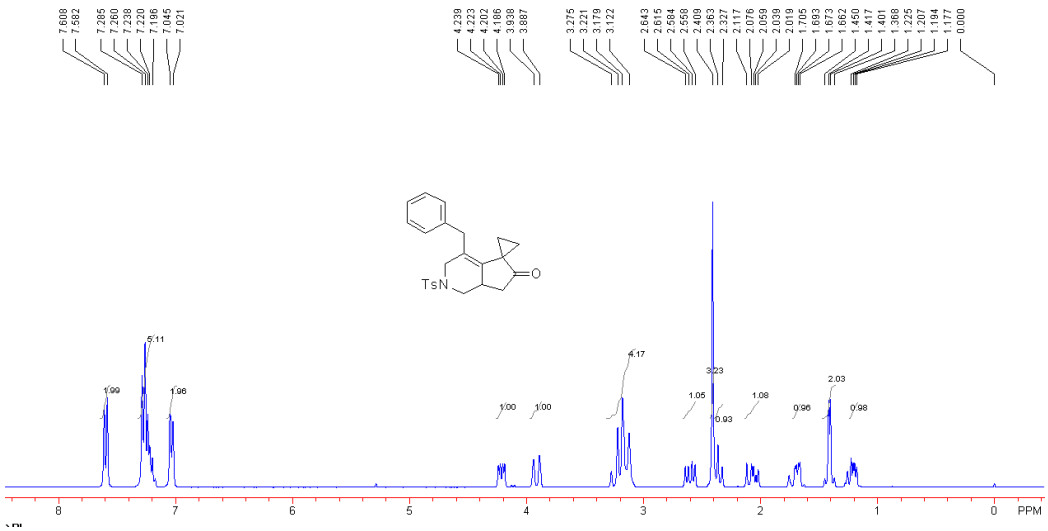
Compound 2c: A white solid. 75 mg, 94%, Mp: 163-165 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.15-1.26 (m, 5H), 1.28-1.38 (m, 1H), 1.39-1.48 (m, 4H), 1.66-1.73 (m, 3H), 1.78 (d, *J* = 11.6 Hz, 1H), 1.97 (dd, *J* = 12.0 Hz, *J* = 17.2 Hz, 1H), 2.04-2.07 (m, 1H), 2.26 (t, *J* = 10.8 Hz, 1H), 2.44 (s, 3H), 2.52 (dd, *J* = 8.0 Hz, *J* = 17.2 Hz, 1H), 3.01 (br, 1H), 3.21 (dd, *J* = 3.6 Hz, *J* = 16.0 Hz, 1H), 4.04 (dd, *J* = 2.0 Hz, *J* = 16.0 Hz, 1H), 4.14 (dd, *J* = 5.2 Hz, *J* = 10.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.2, 21.4, 22.4, 25.7, 26.1, 26.5, 31.4, 31.7, 33.4, 36.7, 38.2, 41.0, 44.2, 48.0, 127.4, 129.6, 129.7, 131.2, 133.4, 143.6, 214.3. IR (neat) ν 2926, 2851, 1730, 1598, 1576, 1463, 1447, 1347, 1335, 1322, 1158, 1094, 966, 894, 829, 812, 785, 739, 707, 684, 659 cm^{-1}. HRMS (ESI) Calcd: $C_{23}H_{29}NO_3S$, 399.1868, Found: 399.1860.

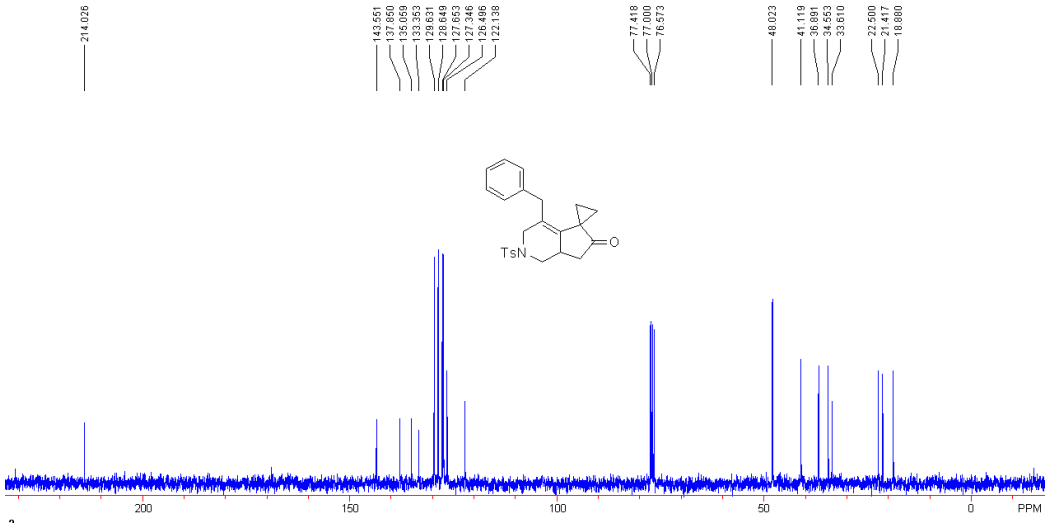


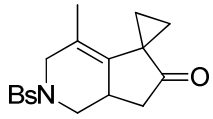




Compound 2d: A white solid. 75 mg, 92%. Mp: 121-123 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.20 (dd, *J* = 5.1 Hz, *J* = 9.0 Hz, 1H), 1.37-1.45 (m, 2H), 1.68 (dd, *J* = 3.3 Hz, *J* = 9.3 Hz, 1H), 2.02-2.12 (m, 1H), 2.36 (t, *J* = 10.8 Hz, 1H), 2.41 (s, 3H), 2.60 (dd, *J* = 8.1 Hz, *J* = 17.4 Hz, 1H), 3.12-3.28 (m, 4H), 3.91 (d, *J* = 15.3 Hz, 1H), 4.21 (dd, *J* = 4.8 Hz, *J* = 11.1 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 7.20-7.29 (m, 5H), 7.60 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.9, 21.4, 22.5, 33.6, 34.6, 36.9, 41.1, 48.0, 122.1, 126.5, 127.3, 127.7, 128.6, 129.6, 133.4, 135.1, 137.9, 143.6, 214.0. IR (neat) ν 3062, 2880, 1727, 1343, 1160, 1096, 946, 812, 725, 658 cm^{-1}. HRMS (ESI) Calcd: $C_{24}H_{25}NO_3S$, 407.1555, Found: 407.1550.

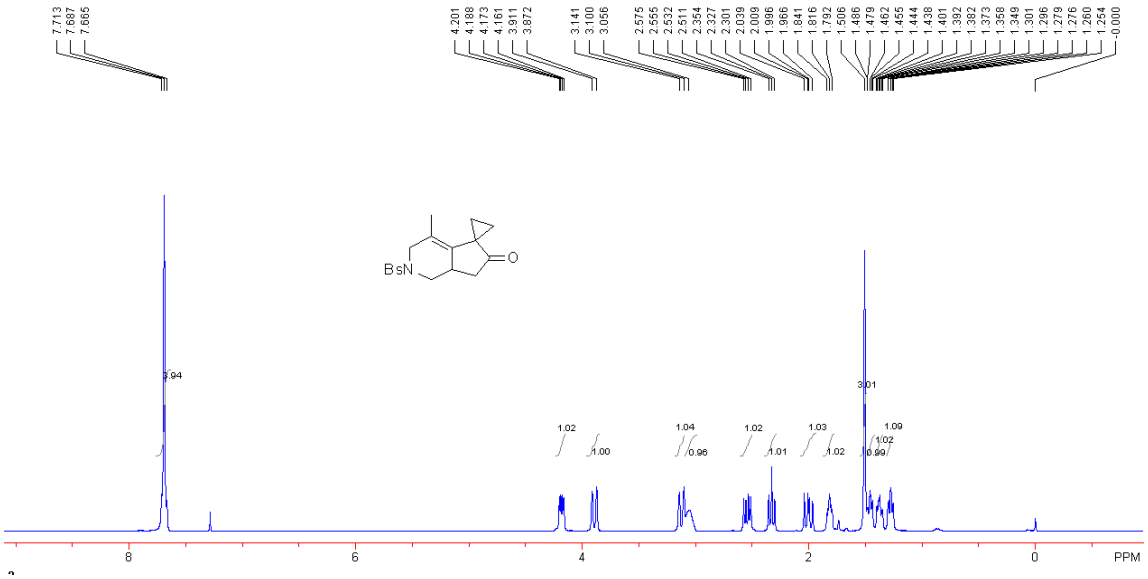


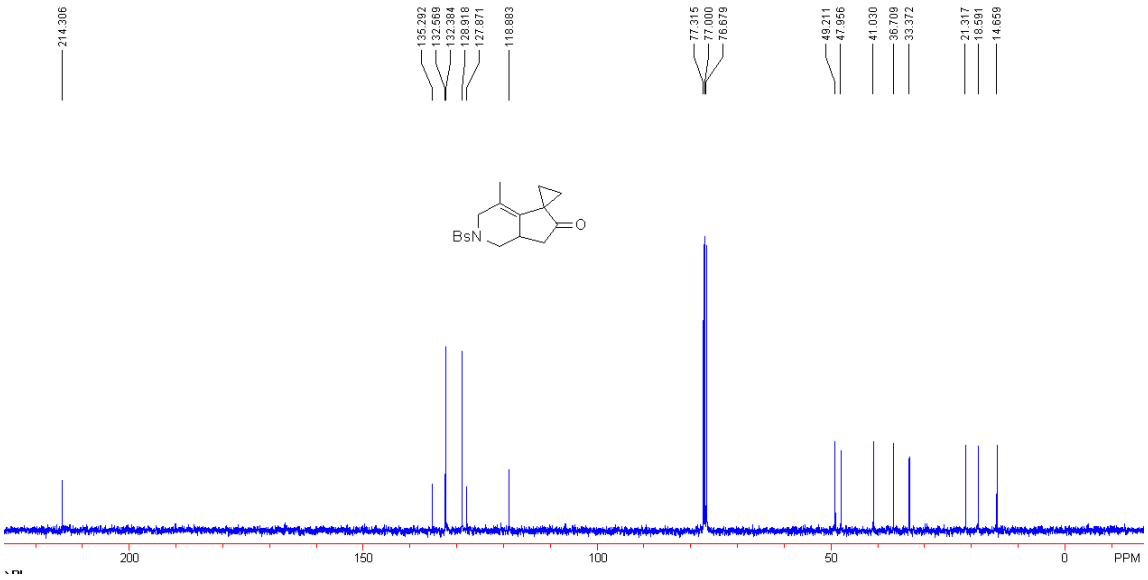


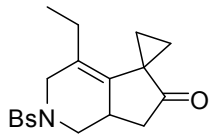


Compound 2e: A white solid. 66 mg, 95%, Mp: 136-138 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28 (dt, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 1.38 (dt, *J* = 3.6 Hz, *J* = 8.4 Hz, 1H), 1.46 (dt, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 1.51 (s, 3H), 1.79-1.84 (m, 1H), 2.00 (dd, *J* = 12.0 Hz, *J* = 17.2 Hz, 1H), 2.33 (t, *J* = 10.8 Hz, 1H), 2.54 (dd, *J* = 8.4 Hz, *J* = 17.2 Hz, 1H), 3.06 (br, 1H), 3.12 (d, *J* = 15.6 Hz, 1H), 3.89 (d, *J* = 15.6 Hz, 1H), 4.18 (dd, *J* = 4.8 Hz, *J* = 10.8 Hz, 1H), 7.67-7.71 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.7, 18.6, 21.3, 33.4, 36.7, 41.0, 48.0, 49.2, 118.9, 127.9, 128.9, 132.4, 132.7, 135.3, 214.3. IR (neat) ν 2878, 2843, 1731, 1700, 1464,

1385, 1345, 1319, 1275, 1221, 1158, 1135, 1036, 948, 815, 735, 700, 685 cm^{-1}. HRMS (ESI) Calcd: $C_{17}H_{18}NO_3SBr$, 395.0191, Found: 395.0183.

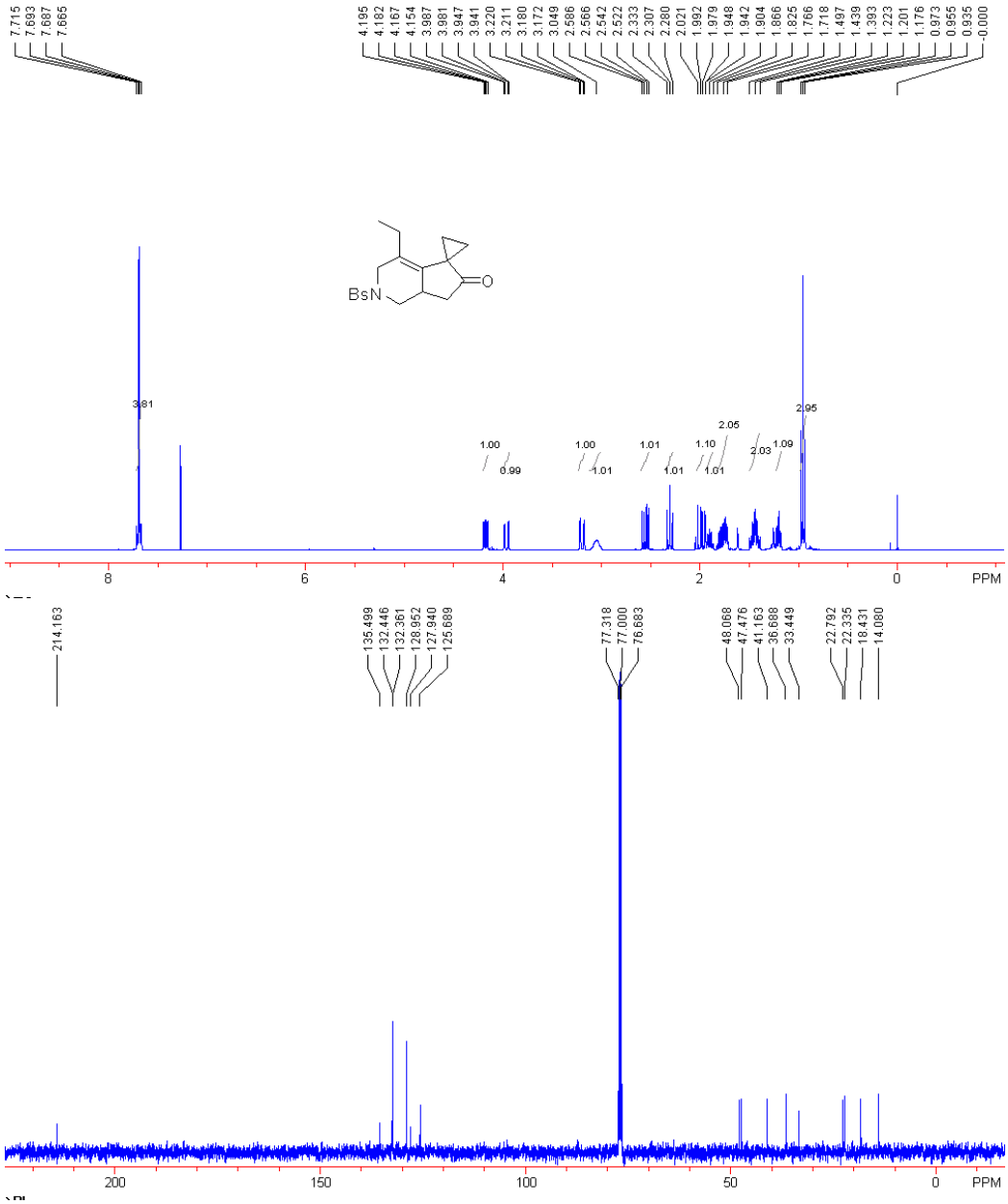


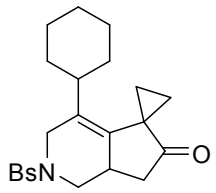




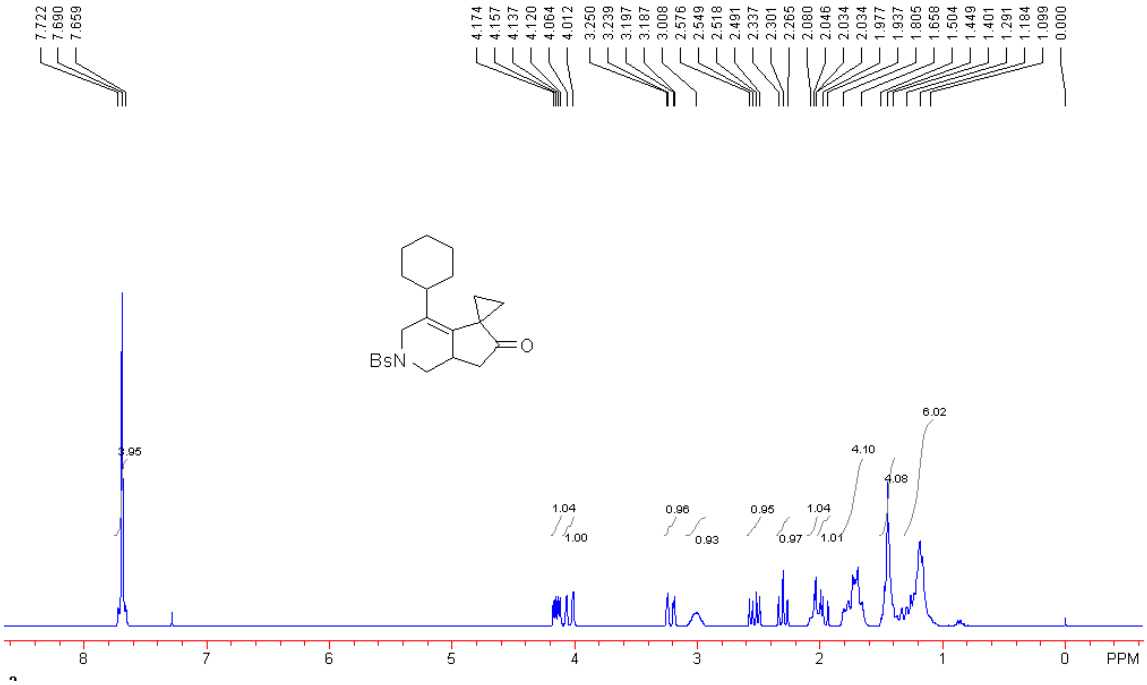
Compound 2f: A white solid. 29 mg, 94%, Mp: 155-157 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.96 (t, *J* = 7.6 Hz, 3H), 1.18-1.22 (m, 1H), 1.39-1.50 (m, 2H), 1.72-1.77 (m, 2H), 1.83-1.90 (m, 1H), 1.99 (dd, *J* = 12.0 Hz, *J* = 17.6 Hz, 1H), 2.31 (t, *J* = 10.8 Hz, 1H), 2.55 (dd, *J* = 8.0 Hz, *J* = 17.6 Hz, 1H), 3.05 (br, 1H), 3.20 (dd, *J* = 3.2 Hz, *J* = 16.0 Hz, 1H), 3.96 (dd, *J*

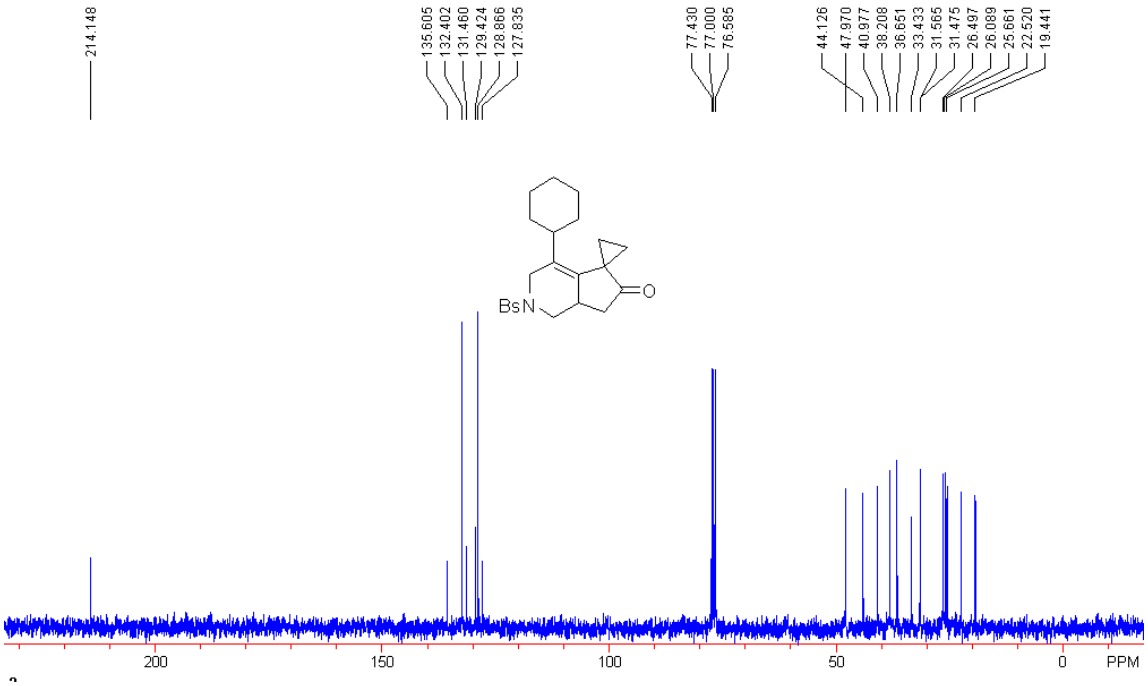
= 2.4 Hz, J = 16.0 Hz, 1H), 4.17 (dd, J = 5.2 Hz, J = 10.8 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 18.4, 22.3, 22.8, 33.4, 36.7, 41.2, 47.5, 48.1, 125.7, 127.9, 129.0, 132.36, 132.44, 135.5, 214.2. IR (neat) ν 3086, 2965, 2870, 1732, 1696, 1573, 1466, 1387, 1274, 1244, 1163, 1134, 1097, 1086, 1065, 1005, 941, 915, 894, 819, 737, 702 cm^{-1}. HRMS (ESI) Calcd: $C_{18}H_{20}NO_3SBr$, 409.0347, Found: 409.0342.

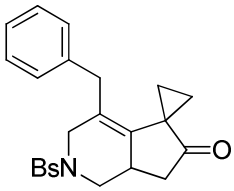




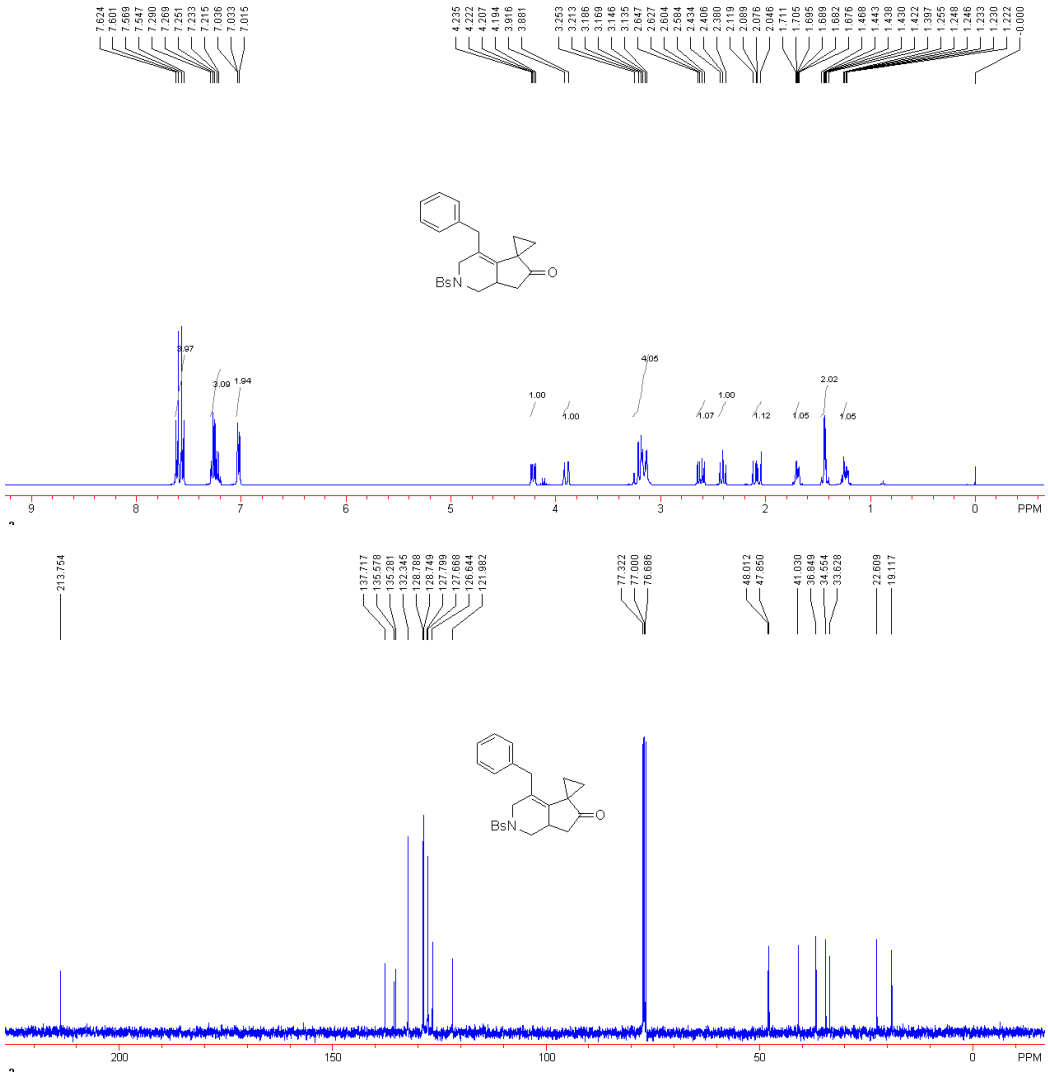
Compound 2g: A white solid. 72 mg, 92%, Mp: 160-162 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.10-1.29 (m, 6H), 1.40-1.50 (m, 4H), 1.66-1.81 (m, 4H), 1.99 (dd, *J* = 12.0 Hz, *J* = 17.1 Hz, 1H), 2.01-2.08 (m, 1H), 2.30 (t, *J* = 10.8 Hz, 1H), 2.53 (dd, *J* = 8.1 Hz, *J* = 17.1 Hz, 1H), 3.01 (br, 1H), 3.22 (dd, *J* = 3.0 Hz, *J* = 15.6 Hz, 1H), 4.04 (d, *J* = 15.6 Hz, 1H), 4.15 (dd, *J* = 5.1 Hz, *J* = 10.8 Hz, 1H), 7.66-7.72 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.4, 22.5, 25.7, 26.1, 26.5, 31.5, 31.6, 33.4, 36.7, 38.2, 41.0, 44.1, 48.0, 127.8, 128.9, 129.4, 131.5, 132.4, 135.6, 214.1. IR (neat) ν 2927, 2853, 1726, 1574, 1466, 1447, 1388, 1348, 1319, 1259, 1165, 1096, 1067, 1050, 1032, 1008, 978, 962, 943, 915, 893, 849, 818, 788, 737, 703, 689, 680 cm^{-1}. HRMS (ESI) Calcd: $C_{22}H_{26}NO_3SBr$, 463.0817, Found: 463.0817.

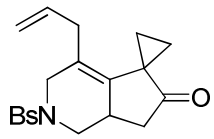






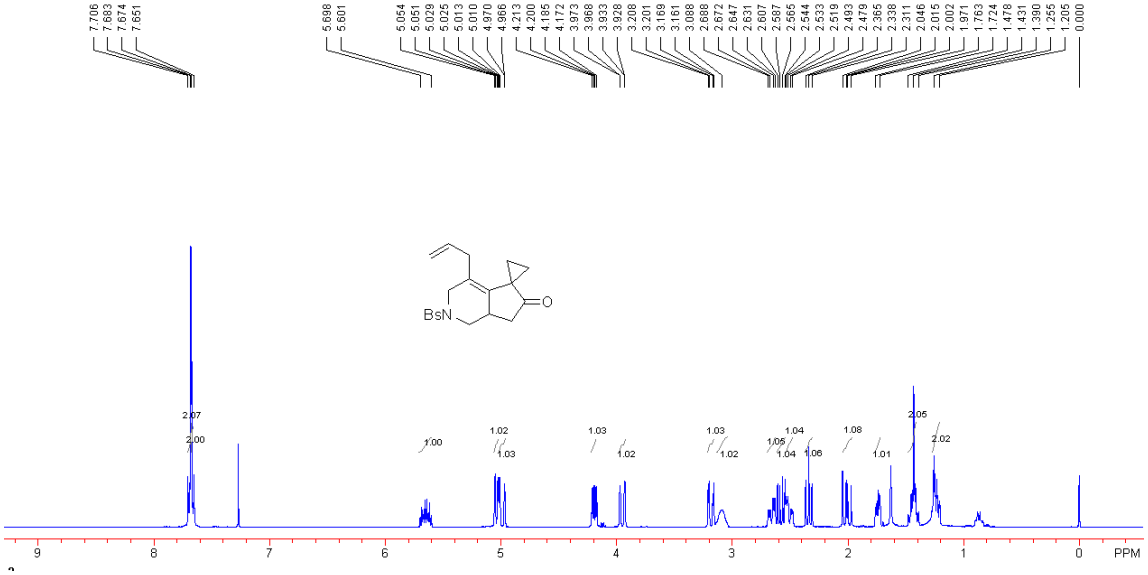
Compound 2h: A white solid. 90 mg, 96%. Mp: 146-148 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.22-1.26 (m, 1H), 1.40-1.47 (m, 2H), 1.68-1.71 (m, 1H), 2.08 (dd, J = 12.0 Hz, J = 17.2 Hz, 1H), 2.41 (t, J = 10.8 Hz, 1H), 2.62 (dd, J = 8.0 Hz, J = 17.2 Hz, 1H), 3.14-3.25 (m, 4H), 3.90 (d, J = 14.0 Hz, 1H), 4.21 (dd, J = 5.2 Hz, J = 11.2 Hz, 1H), 7.02 (d, J = 7.2 Hz, 2H), 7.22-7.29 (m, 3H), 7.55-7.62 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 22.6, 33.6, 34.6, 36.8, 41.0, 47.9, 48.0, 122.0, 126.6, 127.7, 127.8, 128.7, 128.8, 132.3, 135.3, 135.6, 137.7, 213.8. IR (neat) ν 3095, 2843, 1729, 1341, 1154, 1096, 837, 740, 726, 696 cm^{-1}. HRMS (ESI) Calcd: $C_{23}H_{22}BrNO_3S$, 471.0504, Found: 471.0498.

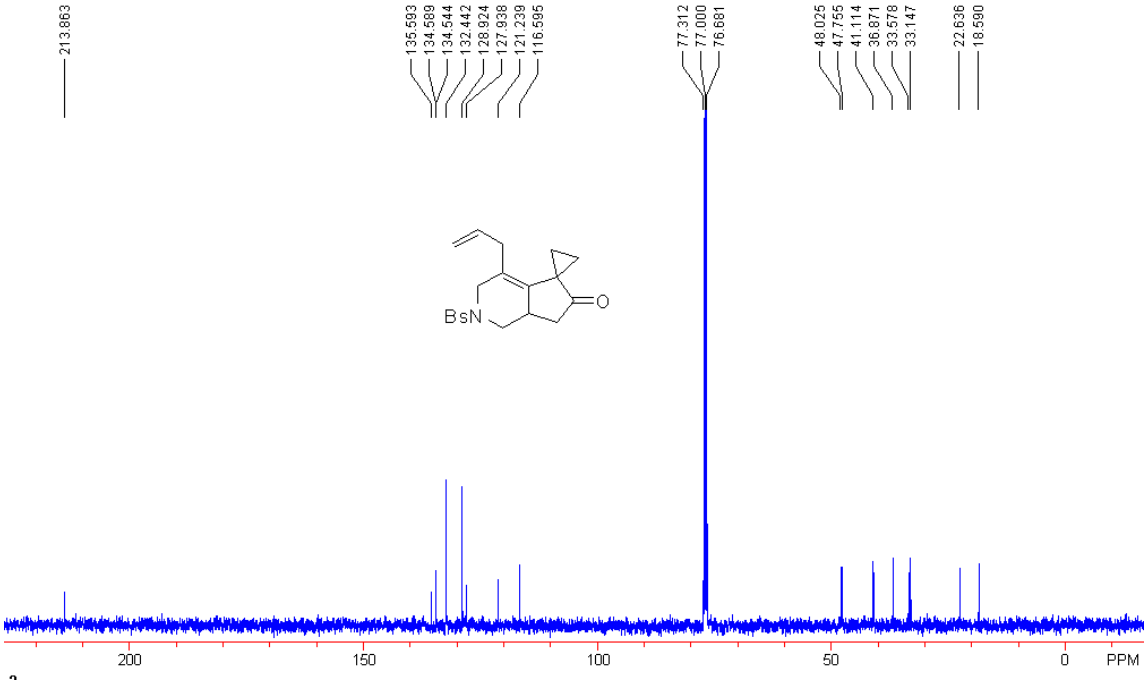


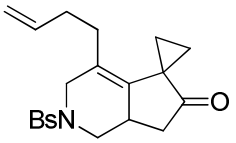


Compound 2i: A white solid. 40 mg, 97%, Mp: 121-123 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21-1.26 (m, 2H), 1.39-1.48 (m, 2H), 1.72-1.76 (m, 1H), 2.01 (dd, *J* = 12.4 Hz, *J* = 17.6 Hz, 1H), 2.34 (t, *J* = 10.8 Hz, 1H), 2.51 (dd, *J* = 5.2 Hz, *J* = 16.0 Hz, 1H), 2.58 (dd, *J* = 8.0 Hz, *J* = 17.2 Hz, 1H), 2.66 (dd, *J* = 6.0 Hz, *J* = 16.0 Hz, 1H), 3.09 (br, 1H), 3.19 (dd, *J* = 3.2 Hz, *J* = 16.0 Hz, 1H), 3.95 (dd, *J* = 2.0 Hz, *J* = 16.0 Hz, 1H), 4.19 (dd, *J* = 5.2 Hz, *J* = 10.8 Hz, 1H), 4.99 (dd, *J* = 1.6 Hz, *J* = 17.6 Hz, 1H), 5.04 (dd, *J* = 1.6 Hz, *J* = 10.4 Hz, 1H), 5.60-5.70 (m, 1H), 7.66 (d, *J* = 9.2 Hz, 2H), 7.69 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.6, 22.6, 33.1, 33.6, 36.9, 41.1, 47.8, 48.0, 116.6, 121.2, 127.9, 128.9, 132.4,

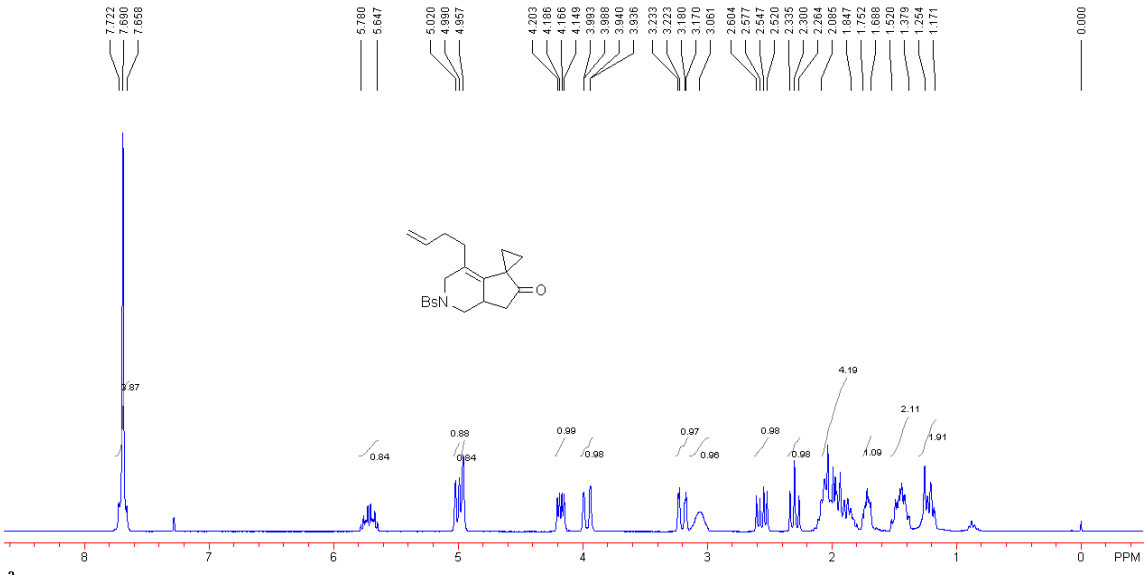
134.5, 134.6, 135.6, 213.9. IR (neat) ν 3084, 2974, 2888, 2855, 1735, 1633, 1574, 1468, 1415, 1387, 1347, 1316, 1278, 1228, 1162, 1095, 1086, 1007, 975, 918, 894, 810, 738, 700 cm^{-1}. HRMS (ESI) Calcd: $C_{19}H_{20}NO_3SBr$, 421.0347, Found: 421.0343.

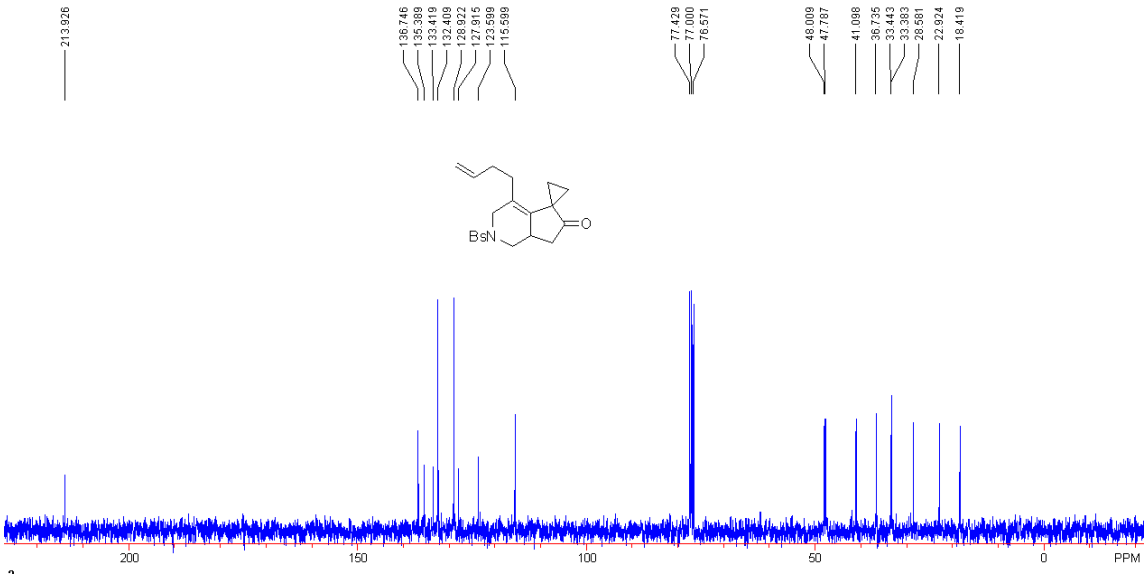


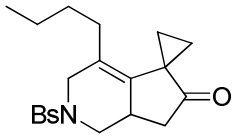




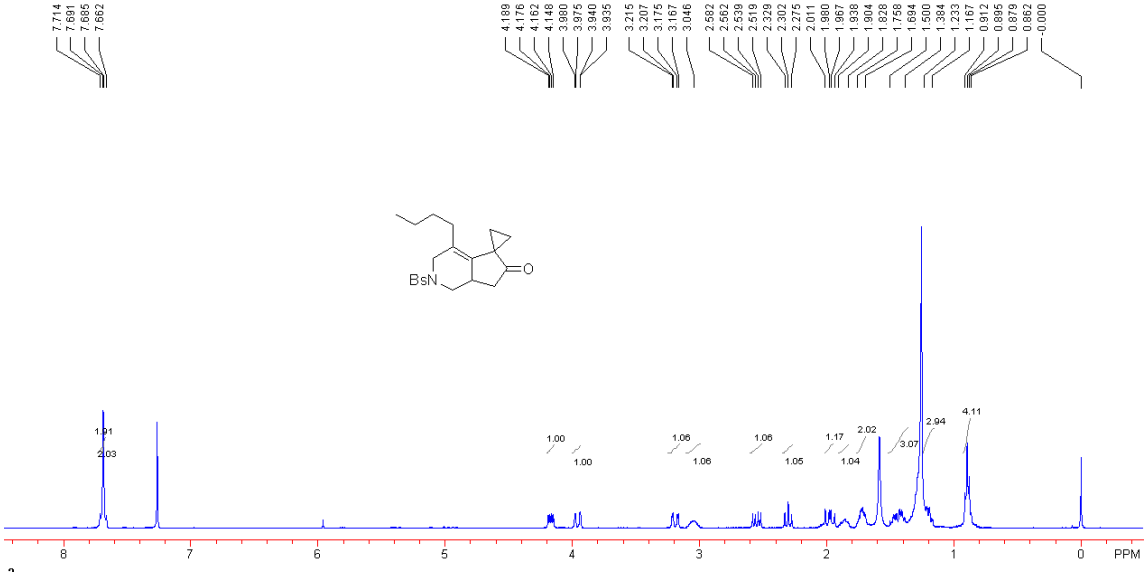
Compound 2j: A white solid. 40 mg, 97%, Mp: 121-123 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.17-1.25 (m, 2H), 1.38-1.52 (m, 2H), 1.69-1.75 (m, 1H), 1.85-2.09 (m, 4H), 2.30 (t, *J* = 10.8 Hz, 1H), 2.56 (dd, *J* = 8.1 Hz, *J* = 17.1 Hz, 1H), 3.06 (br, 1H), 3.20 (dd, *J* = 3.0 Hz, *J* = 15.9 Hz, 1H), 3.96 (dd, *J* = 1.5 Hz, *J* = 15.9 Hz, 1H), 4.18 (dd, *J* = 5.1 Hz, *J* = 11.1 Hz, 1H), 4.96 (d, *J* = 9.9 Hz, 1H), 4.99 (d, *J* = 18.9 Hz, 1H), 5.65-5.78 (m, 1H), 7.66-7.72 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.4, 22.9, 28.6, 33.38, 33.44, 36.7, 41.1, 47.8, 48.0, 115.6, 123.6, 127.9, 128.9, 132.4, 133.4, 135.4, 136.7, 213.9. IR (neat) ν 2950, 2919, 2868, 1725, 1575, 1466, 1376, 1345, 1317, 1280, 1262, 1222, 1165, 1088, 1068, 1050, 1008, 989, 916, 888, 825, 740, 705, 686, 666 cm^{-1}. HRMS (ESI) Calcd: $C_{20}H_{22}NO_3SBr$, 435.0504, Found: 435.0507.

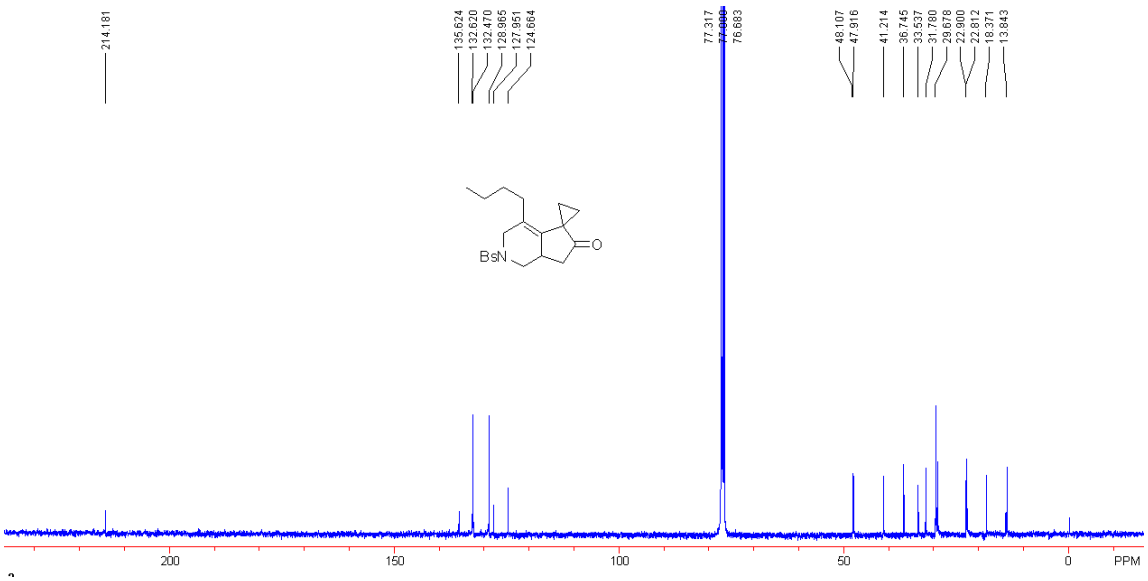


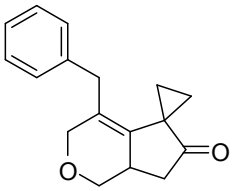




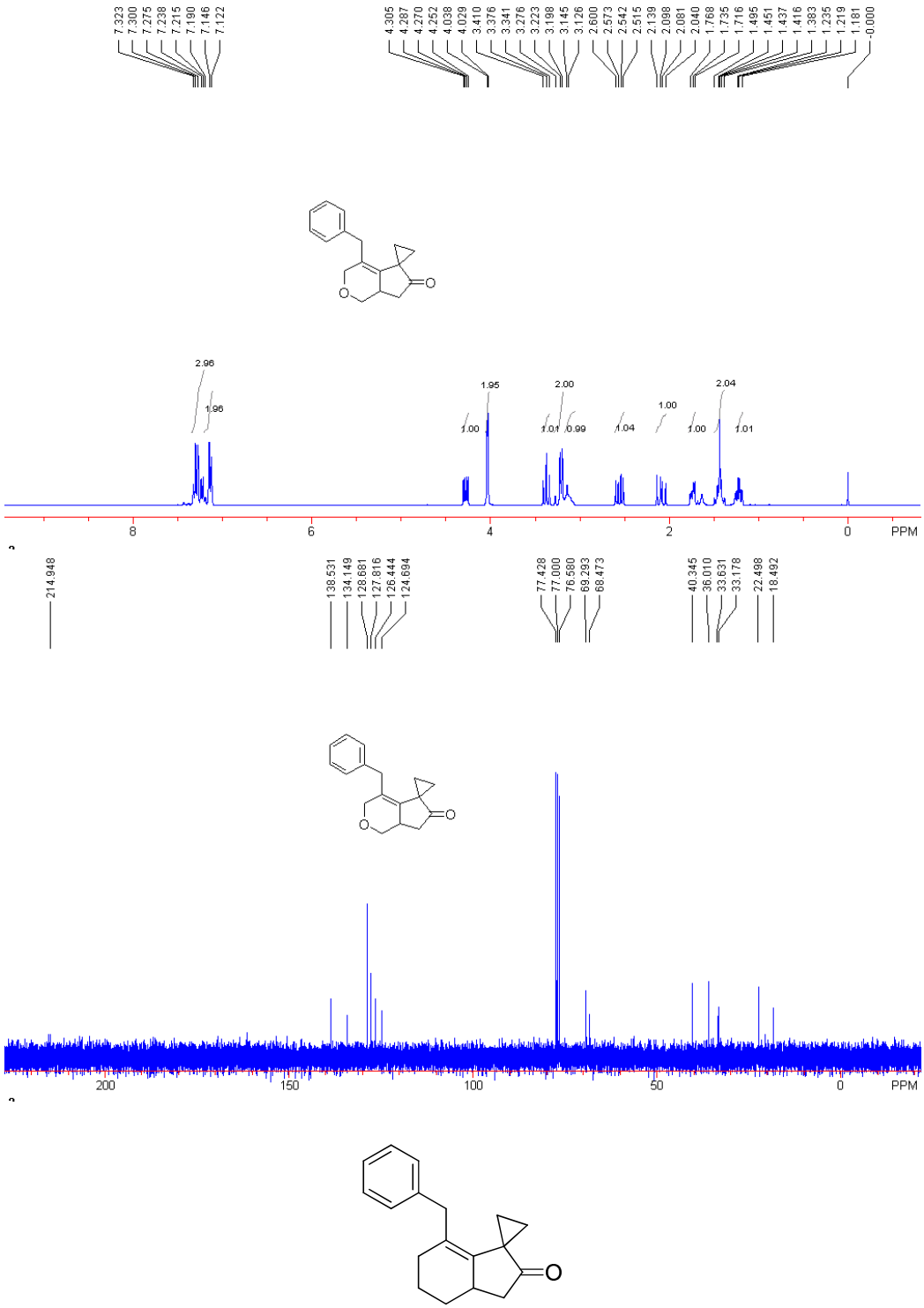
Compound 2k: A white solid. 80 mg, 97%, Mp: 174-176 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.86-0.91 (m, 4H), 1.17-1.23 (m, 3H), 1.38-1.50 (m, 3H), 1.69-1.76 (m, 2H), 1.83-1.90 (m, 1H), 1.94-2.01 (m, 1H), 2.30 (t, *J* = 10.8 Hz, 1H), 2.55 (dd, *J* = 8.0 Hz, *J* = 17.2 Hz, 1H), 3.05 (br, 1H), 3.19 (dd, *J* = 3.2 Hz, *J* = 16.0 Hz, 1H), 3.96 (dd, *J* = 2.4 Hz, *J* = 16.0 Hz, 1H), 4.17 (dd, *J* = 5.2 Hz, *J* = 10.8 Hz, 1H), 7.67 (d, *J* = 9.2 Hz, 2H), 7.70 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 18.4, 22.8, 22.9, 29.7, 31.8, 33.5, 36.7, 41.2, 47.9, 48.1, 124.7, 128.0, 129.0, 132.5, 132.6, 135.6, 214.2. IR (neat) ν 3401, 2957, 2927, 2858, 1733, 1575, 1470, 1389, 1350, 1319, 1265, 1222, 1168, 1090, 1068, 1010, 965, 889, 817, 736, 704 cm^{-1}. HRMS (ESI) Calcd: $C_{20}H_{24}NO_3SBr$, 437.0660, Found: 437.0645.





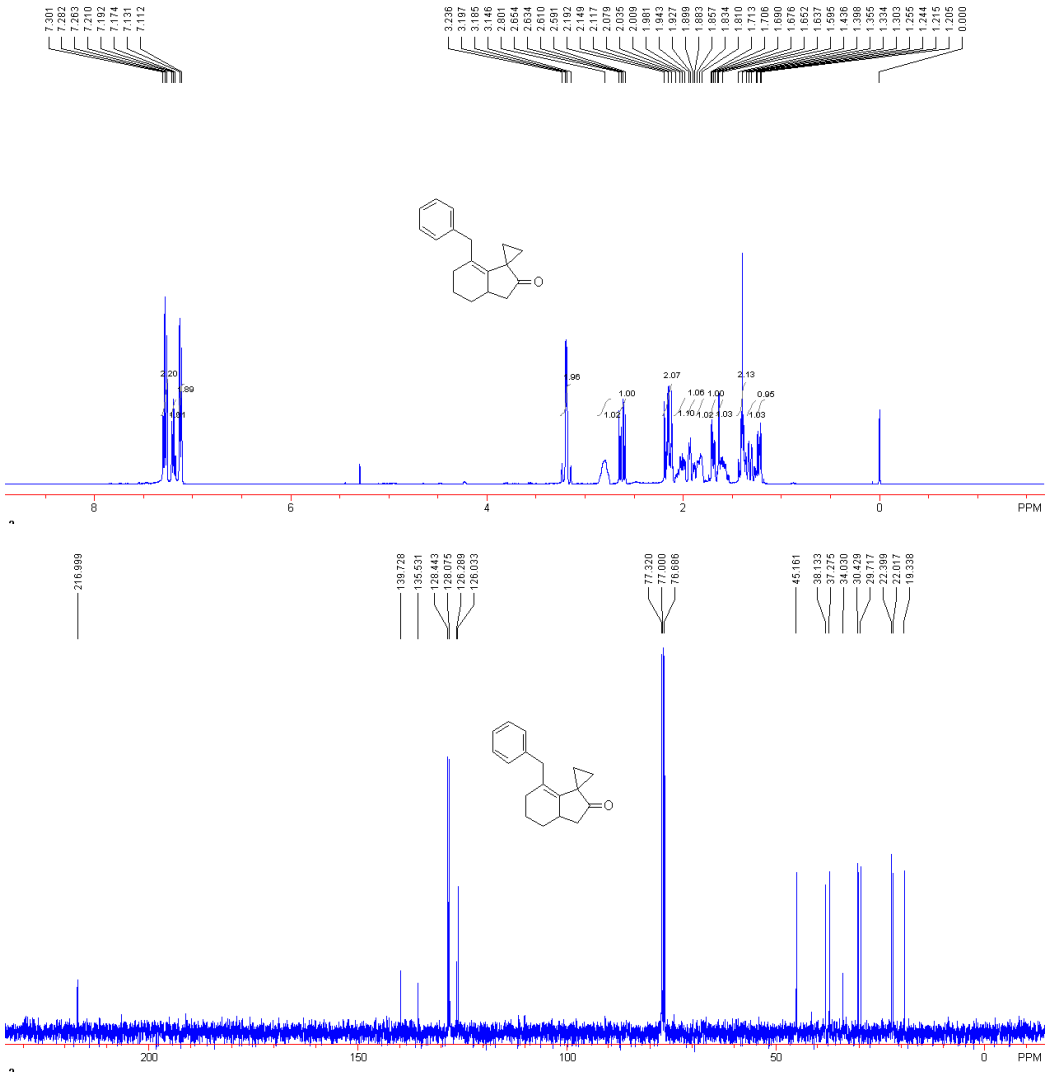


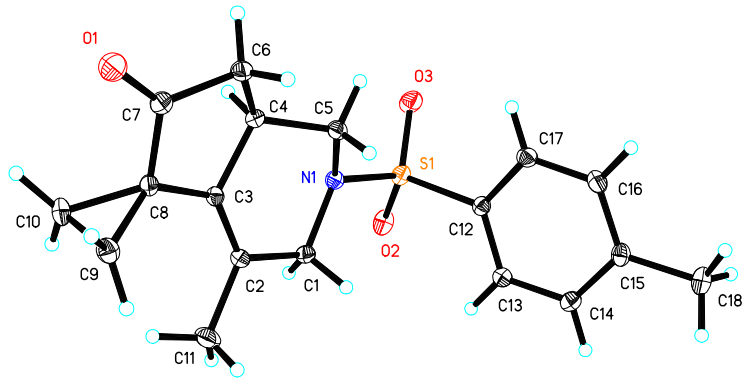
Compound 2l: A white solid. 44 mg, 91%. Mp: 96-98 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.18-1.24 (m, 1H), 1.38-1.50 (m, 2H), 1.72-1.77 (m, 1H), 2.09 (dd, *J* = 6.4 Hz, *J* = 17.4 Hz, 1H), 2.58 (dd, *J* = 6.4 Hz, *J* = 17.4 Hz, 1H), 3.13 (br, 1H), 3.21 (dd, *J* = 15.9 Hz, *J* = 17.4 Hz, 2H), 3.38 (t, *J* = 10.5 Hz, 1H), 4.03 (d, *J* = 2.7 Hz, 2H), 4.28 (dd, *J* = 5.4 Hz, *J* = 10.5 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.19-7.32 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.5, 22.5, 33.2, 33.6, 36.0, 40.3, 68.5, 69.3, 124.7, 126.4, 127.8, 128.7, 134.1, 138.5, 214.9. IR (neat) ν 3427, 2956, 2925, 2854, 1602, 1495, 1453, 1320, 1269, 1216, 1174, 1095, 1029, 940, 734, 701 cm^{-1}. HRMS (ESI) Calcd: $C_{17}H_{16}O_2$, 252.1150, Found: 252.1141.



Compound 2m: A colorless oil. 45 mg, 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21-1.24 (m, 1H), 1.26-1.33 (m, 1H), 1.36-1.44 (m, 2H), 1.60-1.65 (m, 1H), 1.68-1.71 (m, 1H), 1.81-1.86 (m, 1H), 1.88-1.94 (m, 1H), 1.98-2.08 (m, 1H), 2.12-2.19 (m, 2H), 2.62 (dd, J = 8.0 Hz, J = 17.2 Hz, 1H), 2.80 (br, 1H), 3.15-3.24 (m, 2H), 7.12 (d, J = 7.6 Hz, 2H), 7.17-7.21 (m,

1H), 7.26-7.30 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.3, 22.0, 22.4, 29.7, 30.4, 34.0, 37.3, 38.1, 45.2, 126.0, 126.3, 128.1, 128.4, 135.5, 139.7, 217.0. IR (neat) ν 3092, 2841, 1733, 1329, 1150, 1092, 842, 738, 723, 684 cm^{-1}. HRMS (ESI) Calcd: $C_{18}H_{20}O$, 252.1514, Found: 252.1512.





The crystal data of **2a** have been deposited in CCDC with number 830675. Empirical Formula: $C_{18}H_{21}NO_3S$; Formula Weight: 331.42; Crystal Color, Habit: colorless; Crystal System: Orthorhombic; Lattice Type: Primitive; Crystal size: 0.35 x 0.20 x 0.10; Lattice Parameters: a = 20.4027(19)Å, b = 7.1468(7)Å, c = 22.129(2)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 3226.7(5)$Å^3$; Space group: Pbca; Z = 8; D_{calc} = 1.364 g/cm^3; F_{000} = 1408; Final R indices [I>2sigma(I)]: R1 = 0.0403; wR2 = 0.1066.