Supporting Information

Gold- and silver-catalyzed intramolecular annulation and rearrangement of aniline-linked 1,6-enyens containing methylenecyclopropane

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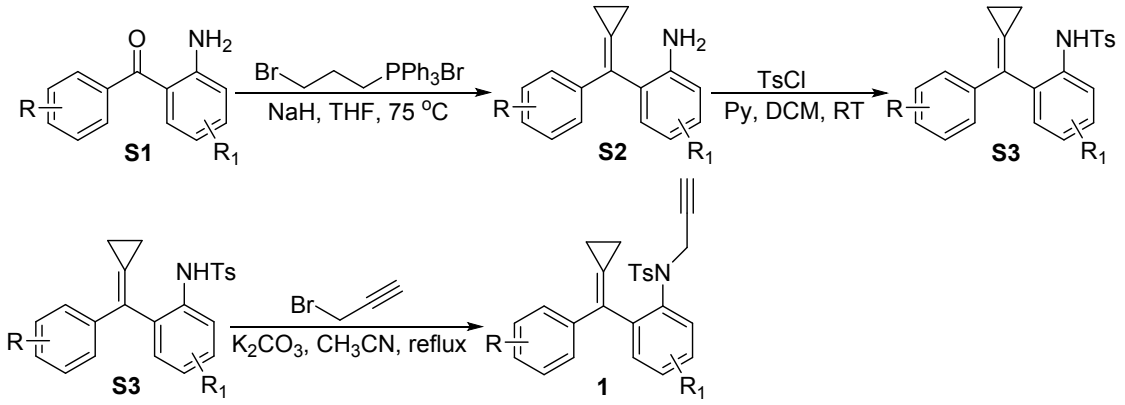
1. General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 400-MR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard; Chemical shifts (δ) are expressed in ppm and *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Dichloroethane were distilled from CaH_2 under argon (Ar) atmosphere. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

2. General procedure for the preparation of substrates 1

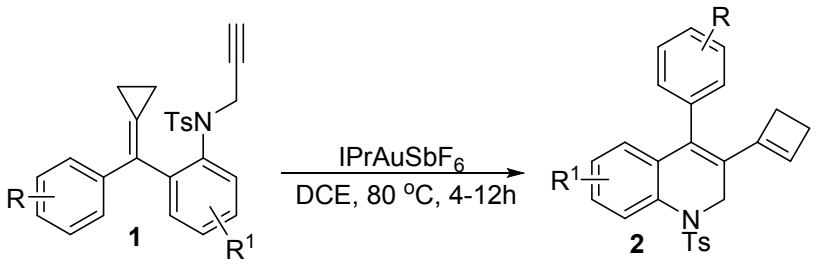


S1, **S2** and **S3** were prepared according to the previous literaure.[1]

In a round-bottom flask, **S3** (3.0 mmol, 1.0 equiv.), 3-bromoprop-1-yne (1.2 equiv.), K_2CO_3 (3.0 equiv.), and the solvent CH_3CN (15.0 mL) were added. Then, the mixture was stirred at 75 °C. After the reaction completion monitored by TLC analysis, the solid was filtered from the solution via a celite, and the filtrate was evaporated under reduced pressure. The residue was purified by a silica-gel column chromatography using ethyl acetate/hexane (1:20) as an eluent to obtain the product **1** in good to excellent yield.

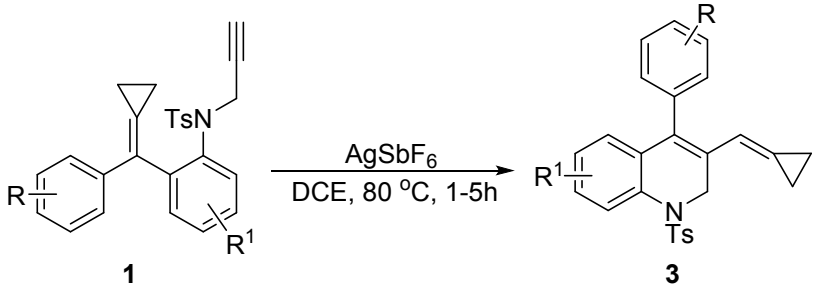
[1] X. Fan, L. -Z. Yu, Y. Wei, M. Shi, *Org. Lett.*, **2017**, *19*, 4476–4479.

3. General procedure for the synthesis of products 2



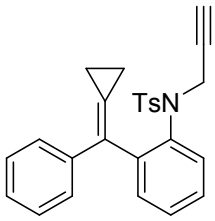
To an oven dried 20 mL schlenk tube equipped with a magnetic stir bar, substrates **1** (0.2 mmol, 1.0 equiv.) and $IPrAuSbF_6$ (0.02 mmol, 10.0 mol%) were added under argon atmosphere. Subsequently, DCE (1.0 mL) was introduced via a syringe. The reaction tube was sealed and the mixture was stirred in a preheated oil bath at 80 °C. After the reaction completion monitored by TLC analysis, the reaction mixture was cooled to room temperature and purified by a silica-gel column chromatography using ethyl acetate/hexane (1:20) as an eluent to give the desired product **2**.

4. General one-pot procedure for the synthesis of products 3

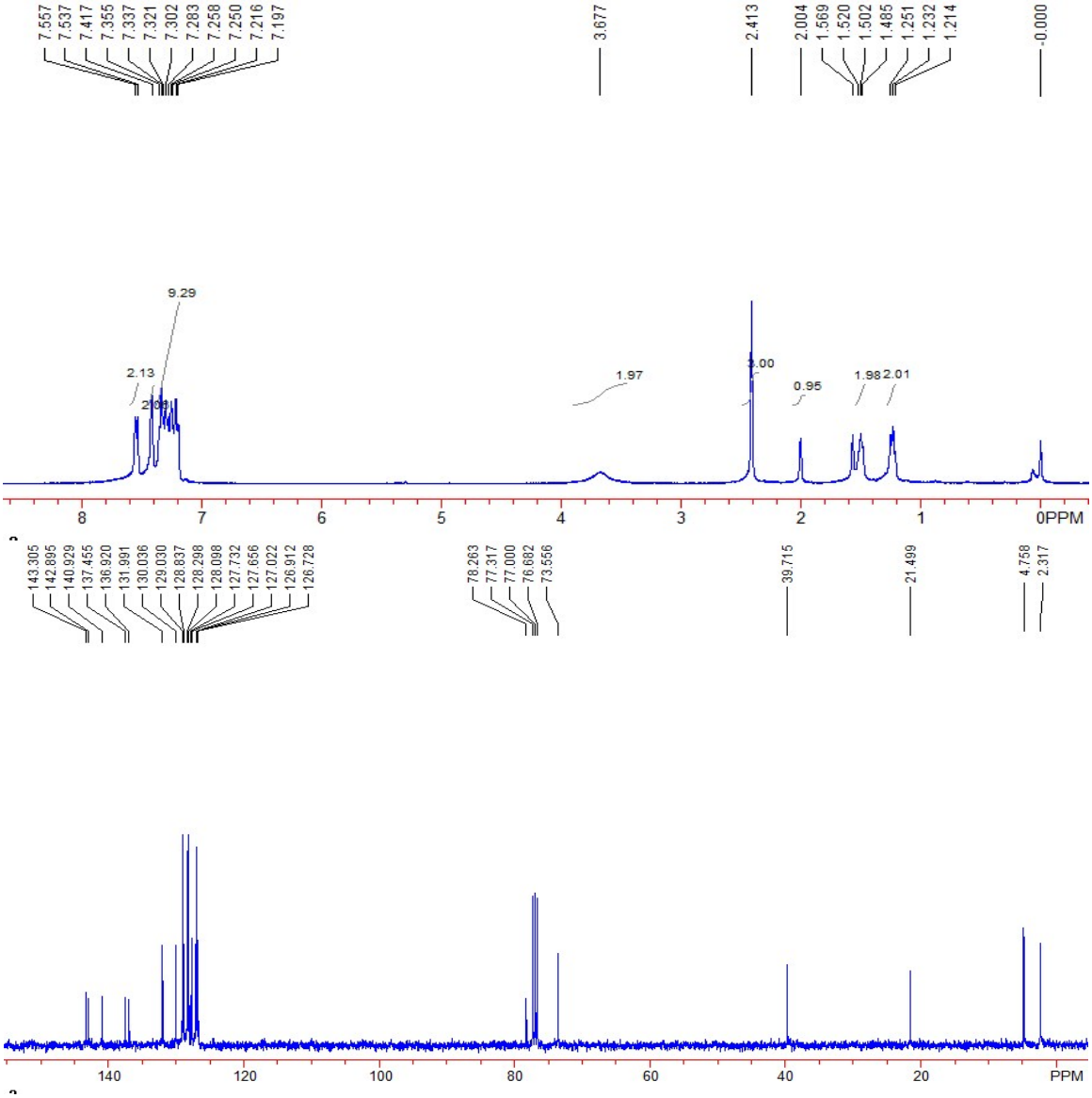


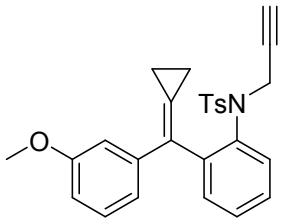
To an oven dried 20 mL schlenk tube equipped with a magnetic stir bar, substrates **1** (0.2 mmol, 1.0 equiv.) and $AgSbF_6$ (0.02 mmol, 10.0 mol%) were added under argon atmosphere. Subsequently, DCE (1.0 mL) was introduced via a syringe. The reaction tube was sealed and the mixture was stirred in a preheated oil bath at 80 °C. After the reaction completion monitored by TLC analysis, the reaction mixture was cooled to room temperature and purified by a silica-gel column chromatography using ethyl acetate/hexane (1:20) as an eluent to give the desired product **3**.

5. Spectroscopic data of the substrates 1

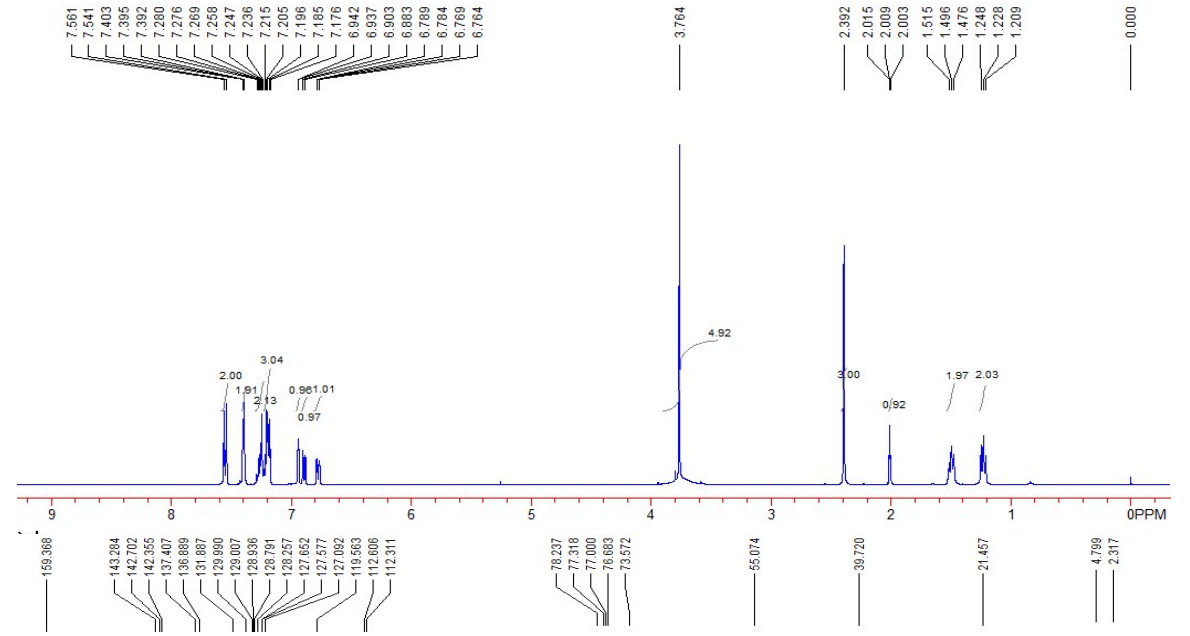


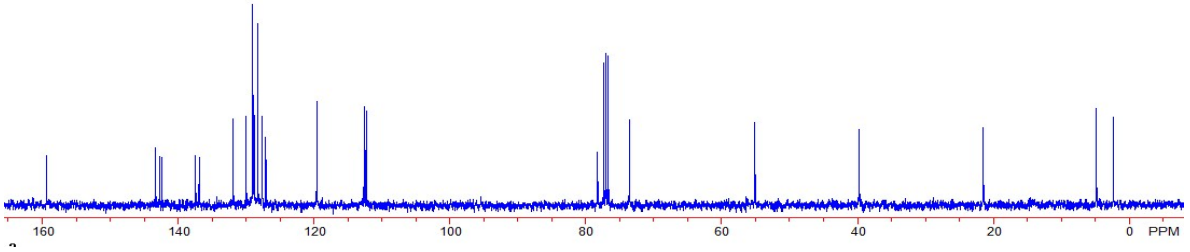
Compound 1a: Yield: 1.2 g, 89%; A white solid, m.p. 191-193 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, 2H, *J* = 7.2 Hz), 1.50 (t, 2H, *J* = 7.2 Hz), 2.00 (s, 1H), 2.41 (s, 3H), 3.68 (s, 2H), 7.19-7.35 (m, 9H), 7.42 (s, 2H), 7.54 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.3, 4.7, 21.5, 39.7, 73.5, 78.2, 126.7, 126.9, 127.0, 127.6, 127.7, 128.1, 128.3, 128.8, 129.0, 130.0, 132.0, 136.9, 137.4, 140.9, 142.9, 143.3; IR (neat): ν 3259, 3052, 2974, 2935, 1597, 1482, 1437, 1348, 1162, 1091, 1082, 853, 814, 772, 723, 661 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{27}N_2O_2S$ $[M+NH_4]^+$: 431.1788, found: 431.1781.

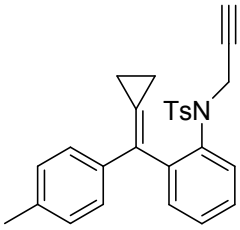




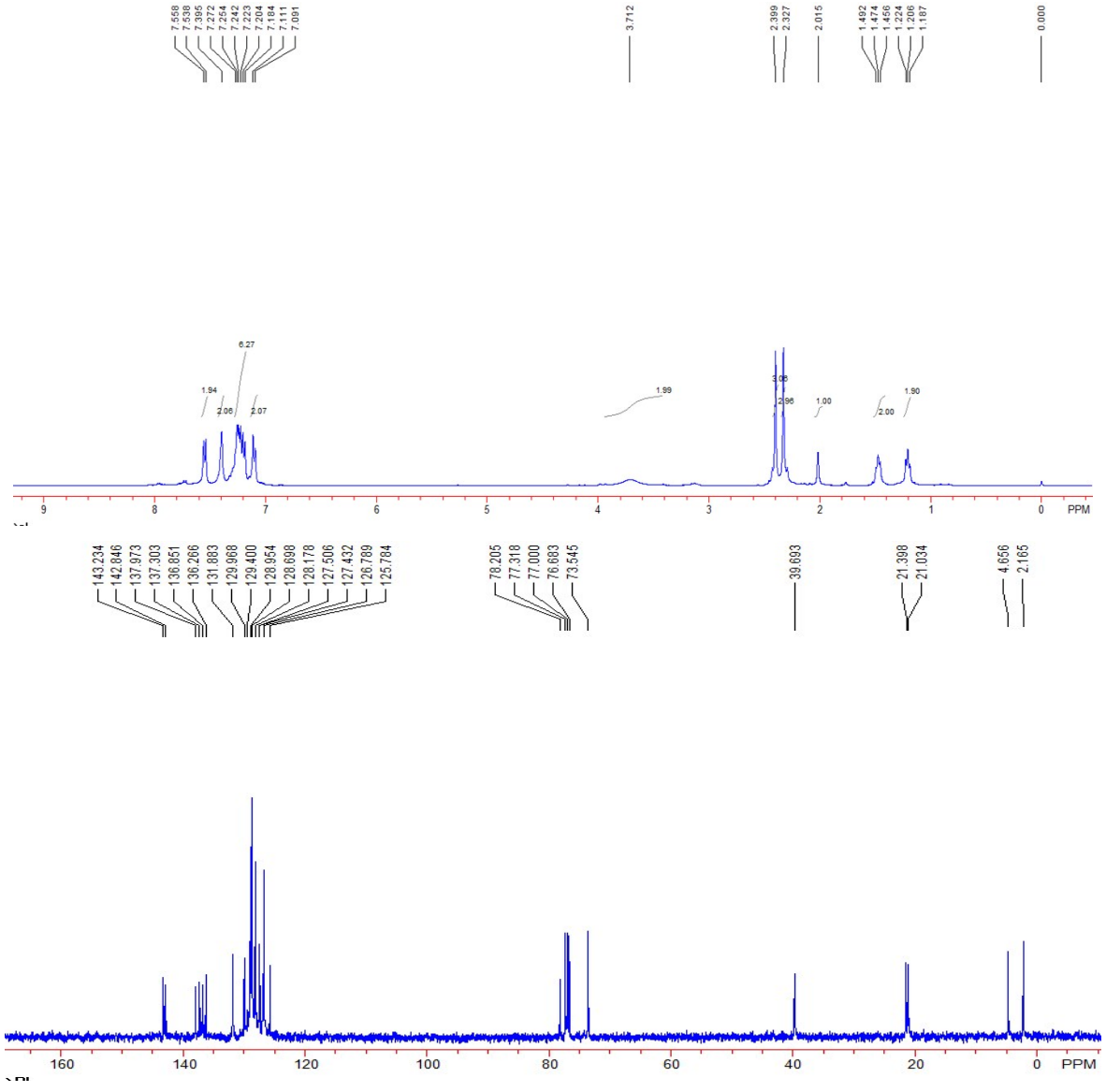
Compound 1b: Yield: 1.6 g, 98%; A white solid, m.p. 150-152 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.22 (t, 2H, J = 8.0 Hz), 1.50 (t, 2H, J = 8.0 Hz), 2.00 (t, 1H, J = 2.4 Hz), 2.39 (s, 3H), 3.76 (s, 5H), 6.77 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 6.89 (d, 1H, J = 8.0 Hz), 6.94 (d, 1H, J = 2.0 Hz), 7.17-7.21 (m, 3H), 7.23-7.28 (m, 2H), 7.39-7.40 (m, 2H), 7.55 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.3, 4.8, 21.4, 39.7, 55.1, 73.6, 78.2, 112.3, 112.6, 119.6, 127.1, 127.6, 127.7, 128.2, 128.8, 128.9, 129.0, 130.0, 131.9, 136.9, 137.4, 142.3, 142.7, 143.3, 159.4; IR (neat): ν 3269, 3042, 2912, 2825, 1596, 1486, 1351, 1336, 1322, 1091, 1038, 882, 865, 795, 730, 698, 659 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{29}NO_3S$ $[M+NH_4]^+$: 461.1893, found: 461.1887.

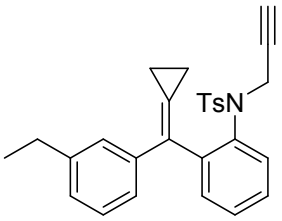




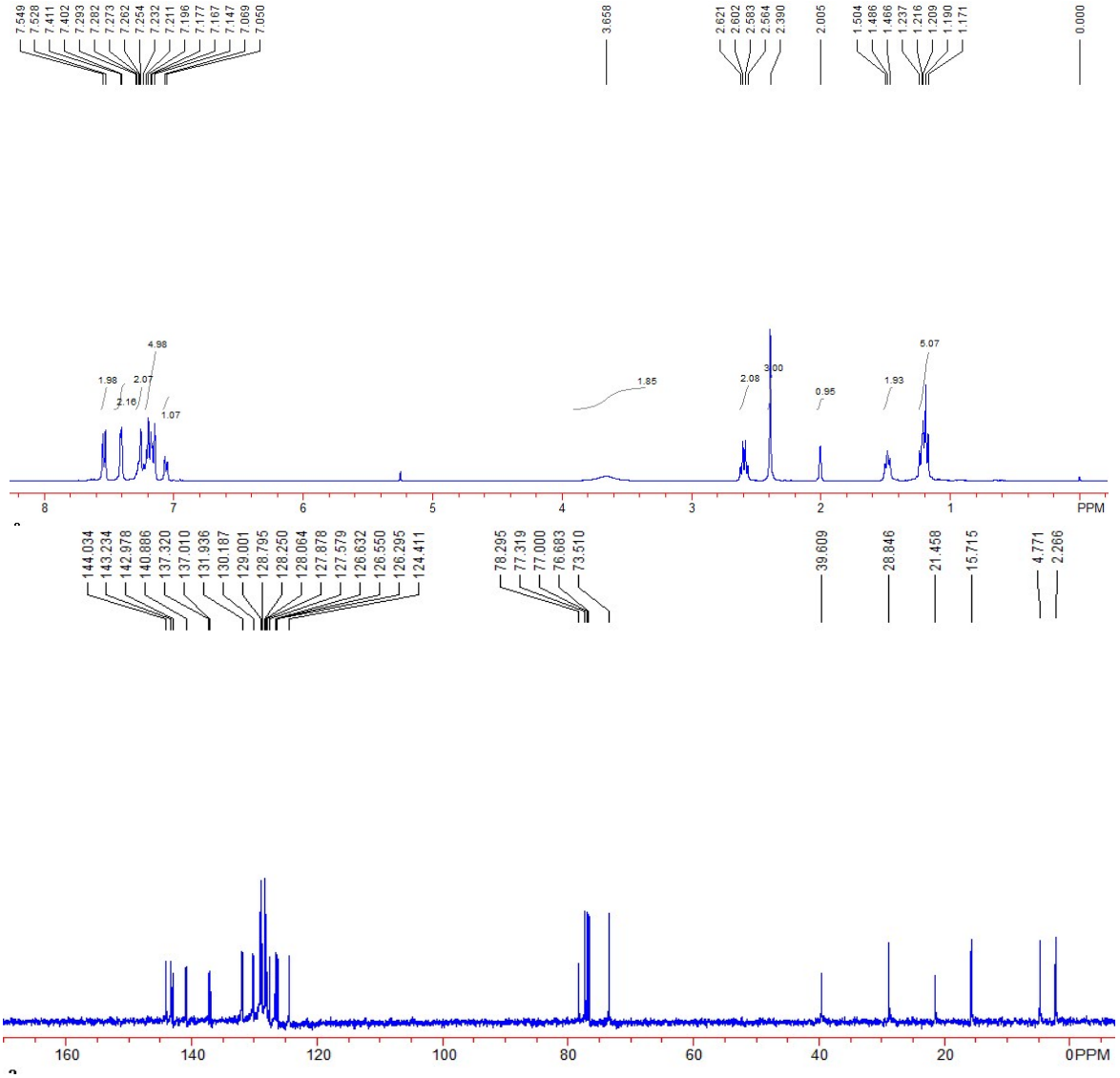


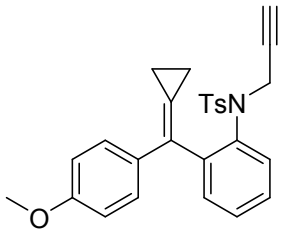
Compound 1c: Yield: 1.7 g, 91%; A white solid, m.p. 181-183 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21 (t, 2H, *J* = 7.2 Hz), 1.47 (t, 2H, *J* = 7.2 Hz), 2.01 (s, 1H), 2.33 (s, 3H), 2.40 (s, 3H), 3.71 (s, 2H), 7.10 (d, 2H, *J* = 8.0 Hz), 7.18-7.27 (m, 6H), 7.39 (s, 2H), 7.54 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.1, 4.6, 21.0, 21.4, 39.7, 73.5, 78.2, 125.8, 126.8, 127.4, 127.5, 128.2, 128.7, 128.9, 129.4, 129.9, 131.9, 136.2, 136.8, 137.3, 137.9, 142.8, 143.2; IR (neat): ν 3303, 3026, 2972, 2917, 1597, 1513, 1351, 1160, 1091, 1077, 907, 834, 812, 660 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{27}N_2O_2S$ $[M+H]^+$: 428.1679, found: 428.1673.



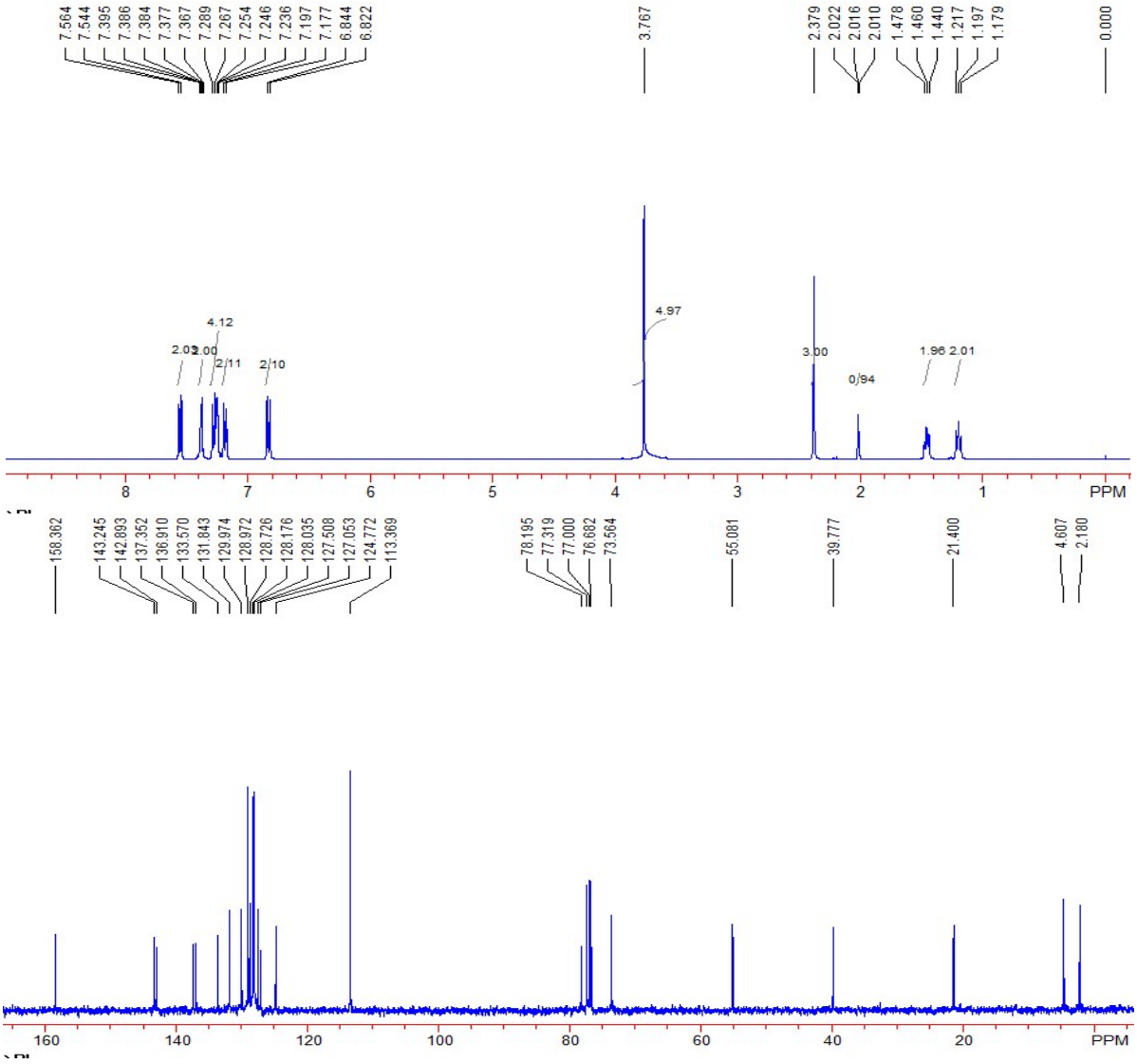


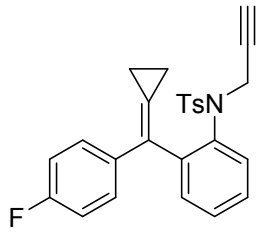
Compound 1d: Yield: 700 mg, 80%; A white solid, m.p. 148-150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.17-1.23 (m, 5H), 1.48 (t, 2H, *J* = 8.0 Hz), 2.00 (s, 1H), 2.39 (s, 3H), 2.56-2.62 (m, 2H), 3.66 (s, 2H), 7.06 (d, 1H, *J* = 7.6 Hz), 7.14-7.21 (m, 5H), 7.25-7.29 (m, 2H), 7.41 (d, 2H, *J* = 3.6 Hz), 7.53 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.3, 4.8, 15.7, 21.4, 28.8, 39.6, 73.5, 78.3, 124.4, 126.3, 126.5, 126.6, 127.6, 127.9, 128.0, 128.2, 128.8, 129.0, 130.2, 131.9, 137.0, 137.3, 140.9, 143.0, 143.2, 144.0; IR (neat): ν 3261, 3055, 2977, 2917, 1594, 1482, 1346, 1159, 1091, 844, 815, 751, 706, 657 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{31}N_2O_2S$ $[M+NH_4]^+$: 459.2101, found: 459.2095.



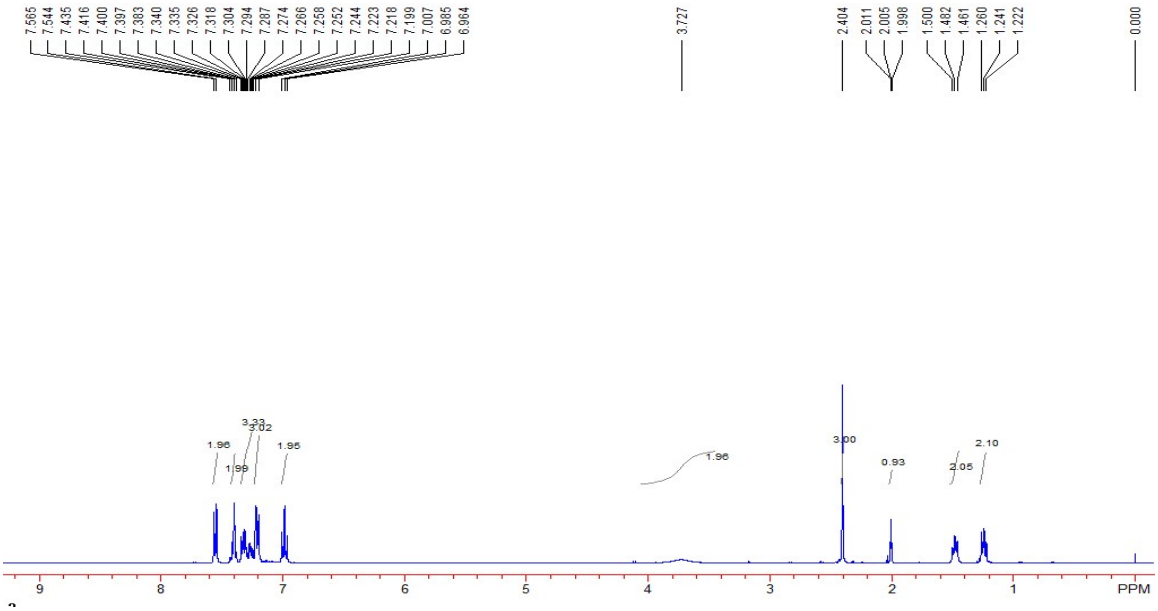


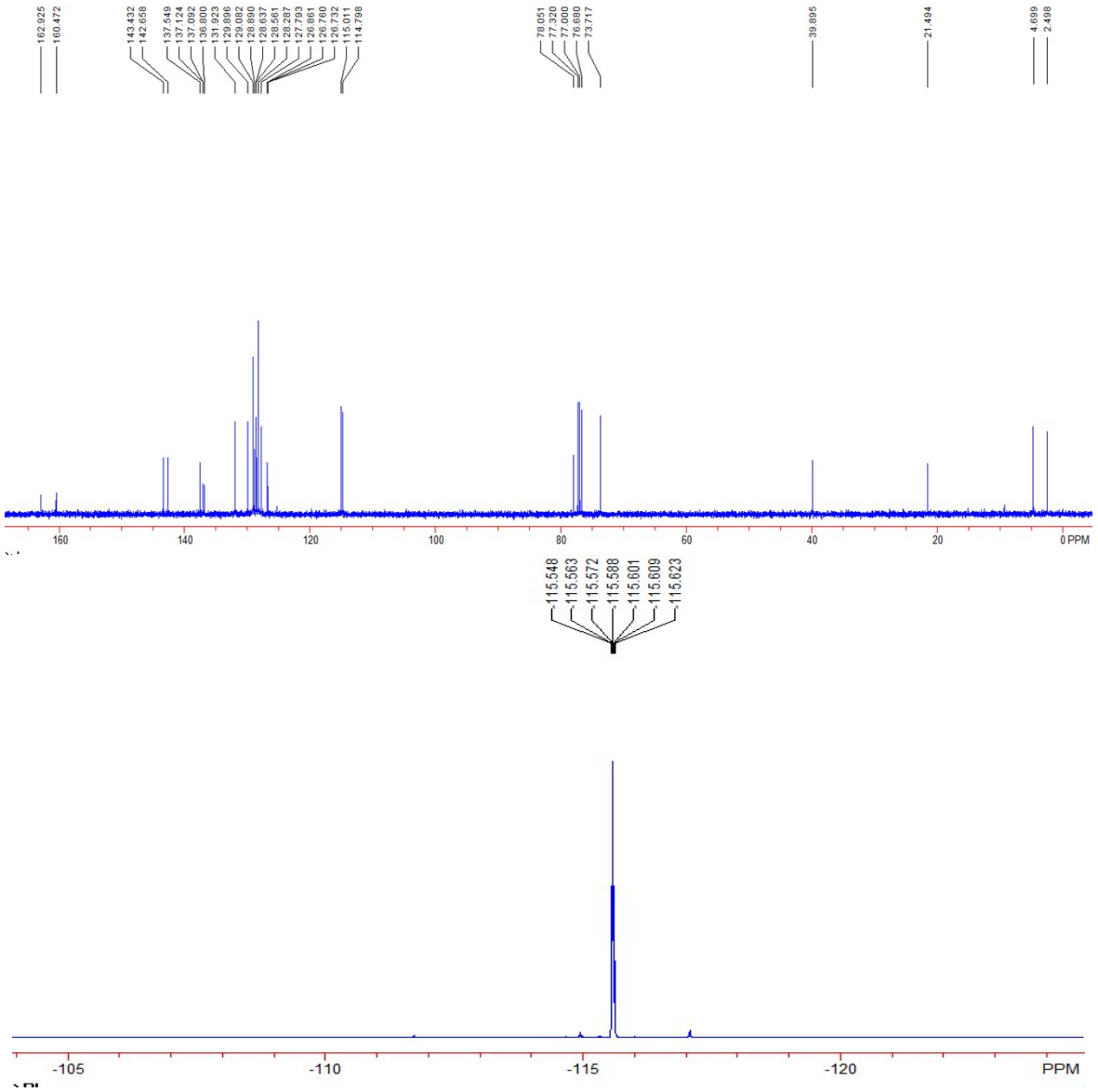
Compound 1e: Yield: 1.1 g, 88%; A white solid, m.p. 145-147 ^{o}C;; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20 (t, 2H, *J* = 8.0 Hz), 1.46 (t, 2H, *J* = 8.0 Hz), 2.02 (t, 1H, *J* = 2.4 Hz), 2.38 (s, 3H), 3.77 (s, 5H), 6.83 (d, 2H, *J* = 8.8 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 7.23-7.29 (m, 4H), 7.36-7.40 (m, 2H), 7.55 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.2, 4.6, 21.4, 39.8, 55.0, 73.5, 78.2, 113.4, 124.8, 127.0, 127.5, 128.0, 128.1, 128.7, 128.9, 129.9, 131.8, 133.5, 136.9, 137.3, 142.9, 143.2, 158.3; IR (neat): ν 3272, 3026, 2925, 2841, 1610, 1443, 1336, 1253, 1178, 1158, 1092, 1059, 859, 809, 728, 709, 658 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_3S$ $[M+H]^+$: 444.1628, found: 444.1621.

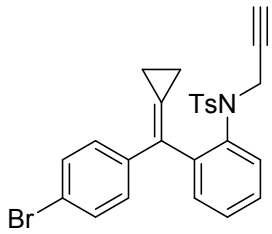




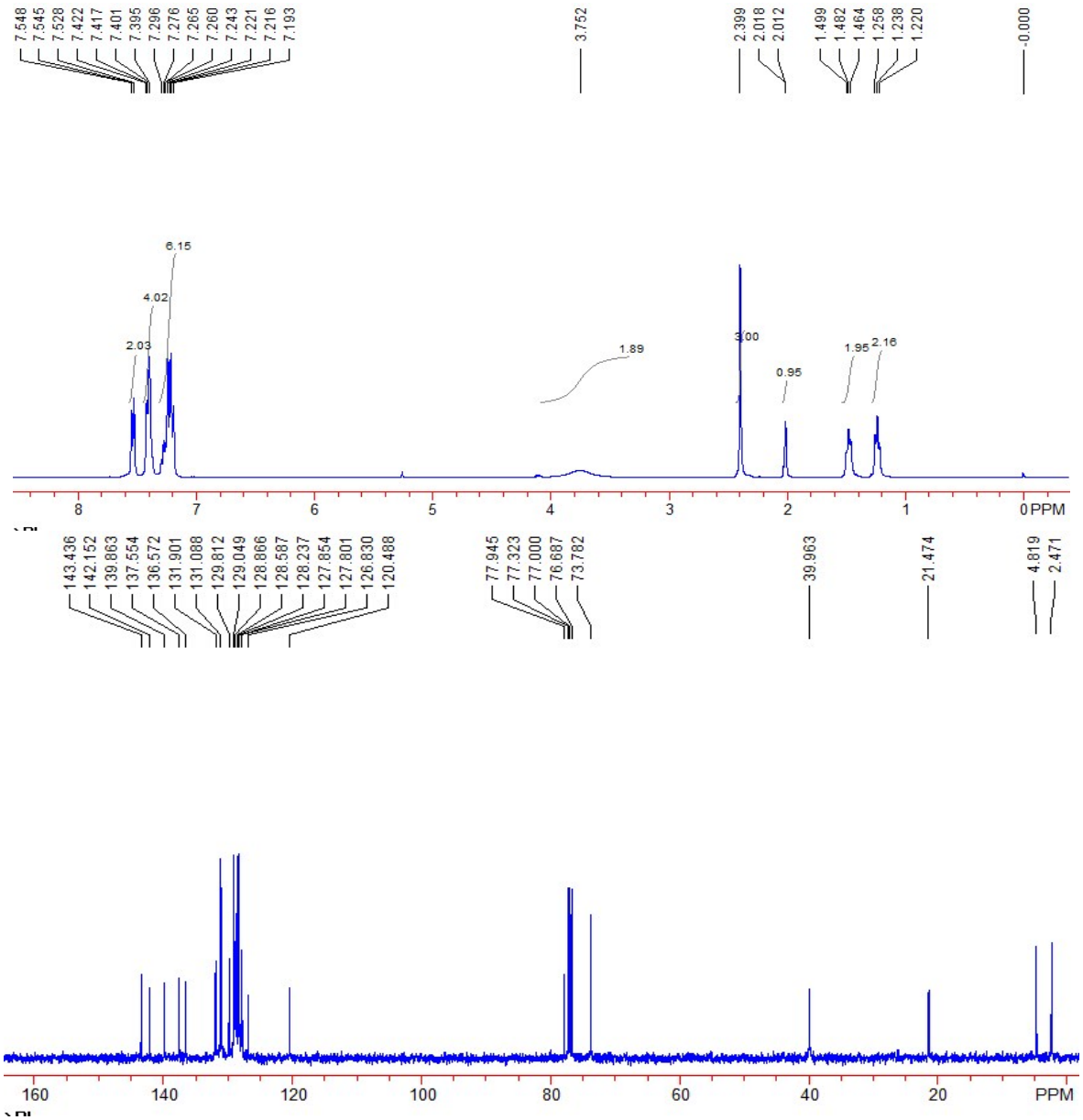
Compound 1f: Yield: 646 mg, 75%; A white solid, m.p. 150-152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, 2H, *J* = 7.6 Hz), 1.48 (t, 2H, *J* = 7.2 Hz), 2.00 (t, 1H, *J* = 2.4 Hz), 2.40 (s, 3H), 3.73 (s, 2H), 6.98 (dd, 2H, $J_1 = J_2$ = 8.4 Hz), 7.19-7.22 (m, 3H), 7.24-7.34 (m, 2H), 7.55 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.5, 4.7, 21.5, 39.9, 73.7, 78.1, 114.9 (d, *J* = 21.4 Hz), 126.7, 126.9, 127.8, 128.3, 128.6 (d, *J* = 7.6 Hz), 128.9, 129.0, 129.9, 131.9, 136.8, 137.1 (d, *J* = 3.2 Hz), 137.5, 142.6, 143.4, 161.7 (d, *J* = 245.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -115.62 ~ -115.54 (m); IR (neat): ν 3259, 3026, 2964, 2925, 1602, 1505, 1445, 1351, 1335, 1225, 1155, 1092, 1080, 882, 861, 832, 811, 728, 712 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{26}FN_2O_2S$ $[M+NH_4]^+$: 449.1694, found: 449.1689.

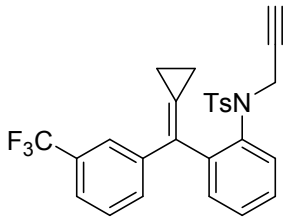






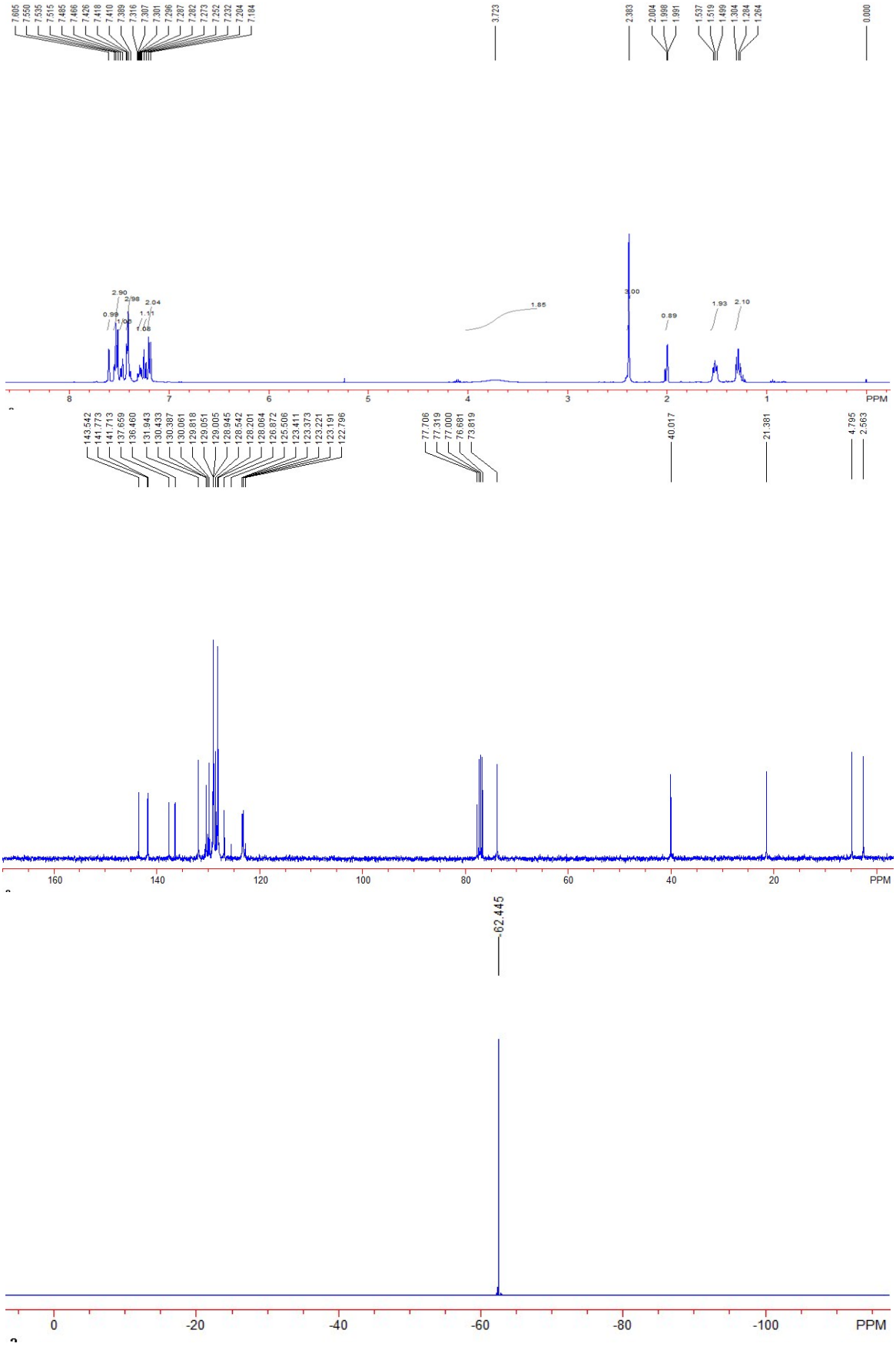
Compound 1g: Yield: 1.7 g, 91%; A white solid, m.p. 148-150 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, 2H, J = 8.0 Hz), 1.48 (t, 2H, J = 7.2 Hz), 2.01 (d, 1H, J = 2.4 Hz), 2.40 (s, 3H), 3.75 (s, 2H), 7.19-7.30 (m, 6H), 7.39-7.42 (m, 4H), 7.52-7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.5, 4.8, 21.5, 40.0, 73.8, 78.0, 120.5, 126.8, 127.80, 127.85, 128.2, 128.6, 128.9, 129.0, 129.8, 131.1, 131.9, 136.6, 137.5, 139.9, 142.1, 143.4; IR (neat): ν 3300, 3058, 2974, 2912, 1484, 1443, 1348, 1336, 1162, 1090, 1071, 1002, 851, 835, 822, 814, 752, 724, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{26}BrN_2O_2S$ $[M+NH_4]^+$: 509.0893, found: 509.0888.

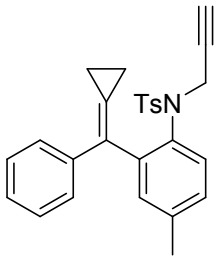




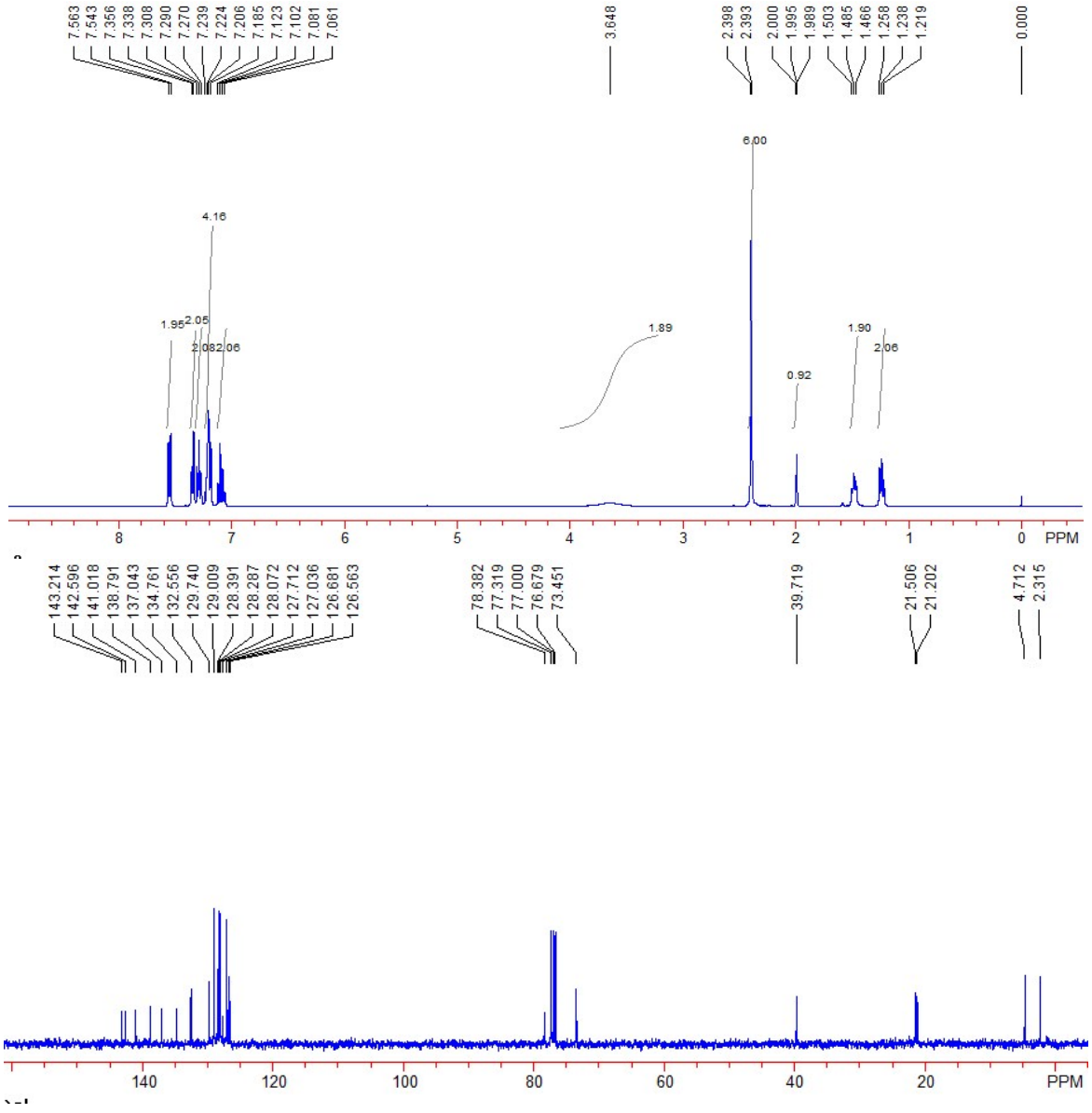
Compound 1h: Yield: 900 mg, 99%; A white solid, m.p. 142-144 ^{o}C;; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28 (t, 2H, *J* = 8.0 Hz), 1.52 (t, 2H, *J* = 8.0 Hz), 2.00 (t, 1H, *J* = 2.8 Hz), 2.38 (s, 3H), 3.72 (s, 2H), 7.19 (d, 2H, *J* = 8.0 Hz), 7.24 (d, 1H, *J* = 8.0 Hz), 7.27-7.32 (m, 1H), 7.39-7.43 (m, 3H), 7.47 (d, 1H, *J* = 7.6 Hz), 7.51-7.55 (m, 3H), 7.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.5, 4.8 21.3, 40.0, 73.8, 77.7, 123.2 (q, *J* = 3.0 Hz), 123.4 (q, *J* = 3.8 Hz), 125.5 (q, *J* = 271.0 Hz), 126.6, 128.0, 128.2, 128.7 (q, *J* = 40.3 Hz), 129.00, 129.05, 129.8, 130.2 (q, *J* = 32.6 Hz), 130.4, 131.9, 136.4, 137.6, 141.71, 141.77, 143.5; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -62.44; IR (neat):

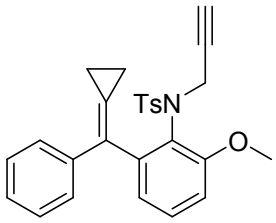
ν 3264, 3068, 2985, 2927, 1597, 1492, 1427, 1349, 1154, 1092, 1065, 887, 865, 809, 726, 679, 658 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}F_3N_2O_2S$ $[M+NH_4]^+$: 499.1662, found: 499.1653.



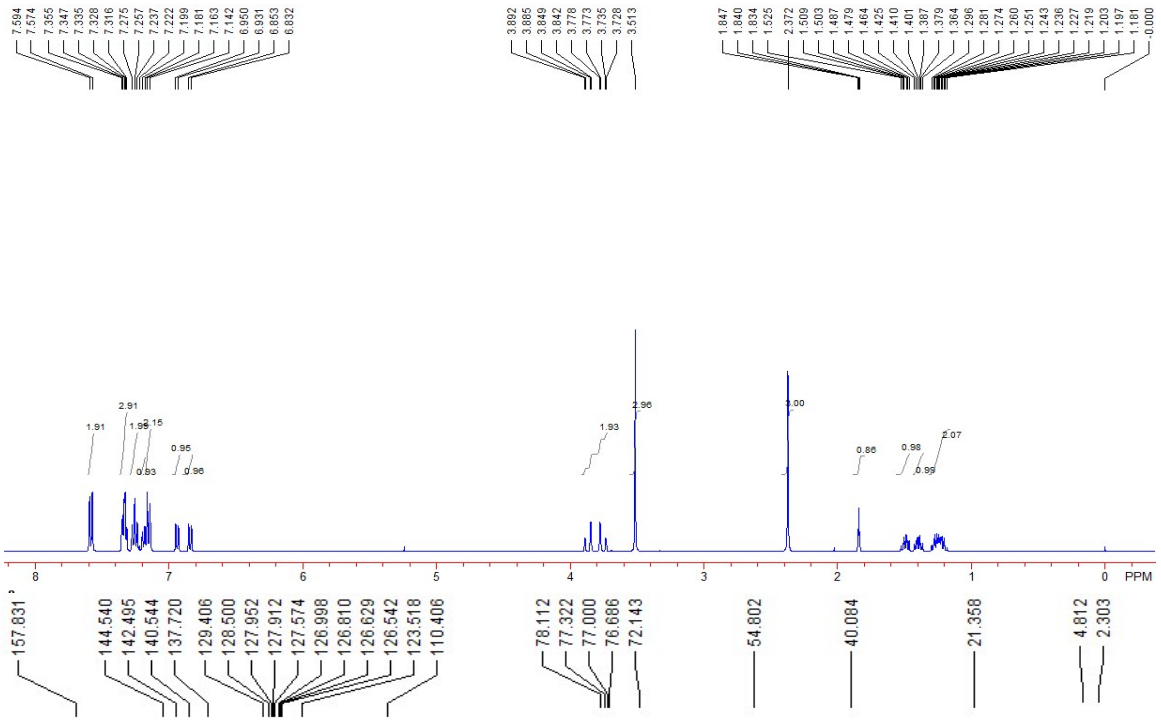


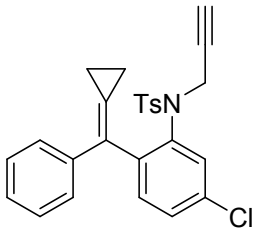
Compound 1i: Yield: 1.4 g, 90%; A white solid, m.p. 175-177 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, 2H, *J* = 8.0 Hz), 1.48 (t, 2H, *J* = 7.6 Hz), 1.99 (t, 1H, *J* = 2.0 Hz), 2.393 (s, 3H), 2.398 (s, 3H), 3.65 (s, 2H), 7.06-7.12 (m, 2H), 7.18-7.24 (m, 4H), 7.29 (t, 2H, *J* = 8.0 Hz), 7.34 (d, 2H, *J* = 7.2 Hz), 7.55 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.3, 4.7, 21.2, 21.5, 39.7, 73.4, 78.4, 126.6, 126.7, 127.0, 127.7, 128.0, 128.3, 128.4, 129.0, 129.7, 132.5, 134.8, 137.0, 138.8, 141.0, 142.6, 143.2; IR (neat): ν 3253, 3045, 2966, 2922, 1597, 1490, 1350, 1338, 1161, 1070, 859, 768, 710, 677, 657 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_2S$ $[M+H]^+$: 428.1679, found: 428.1674.



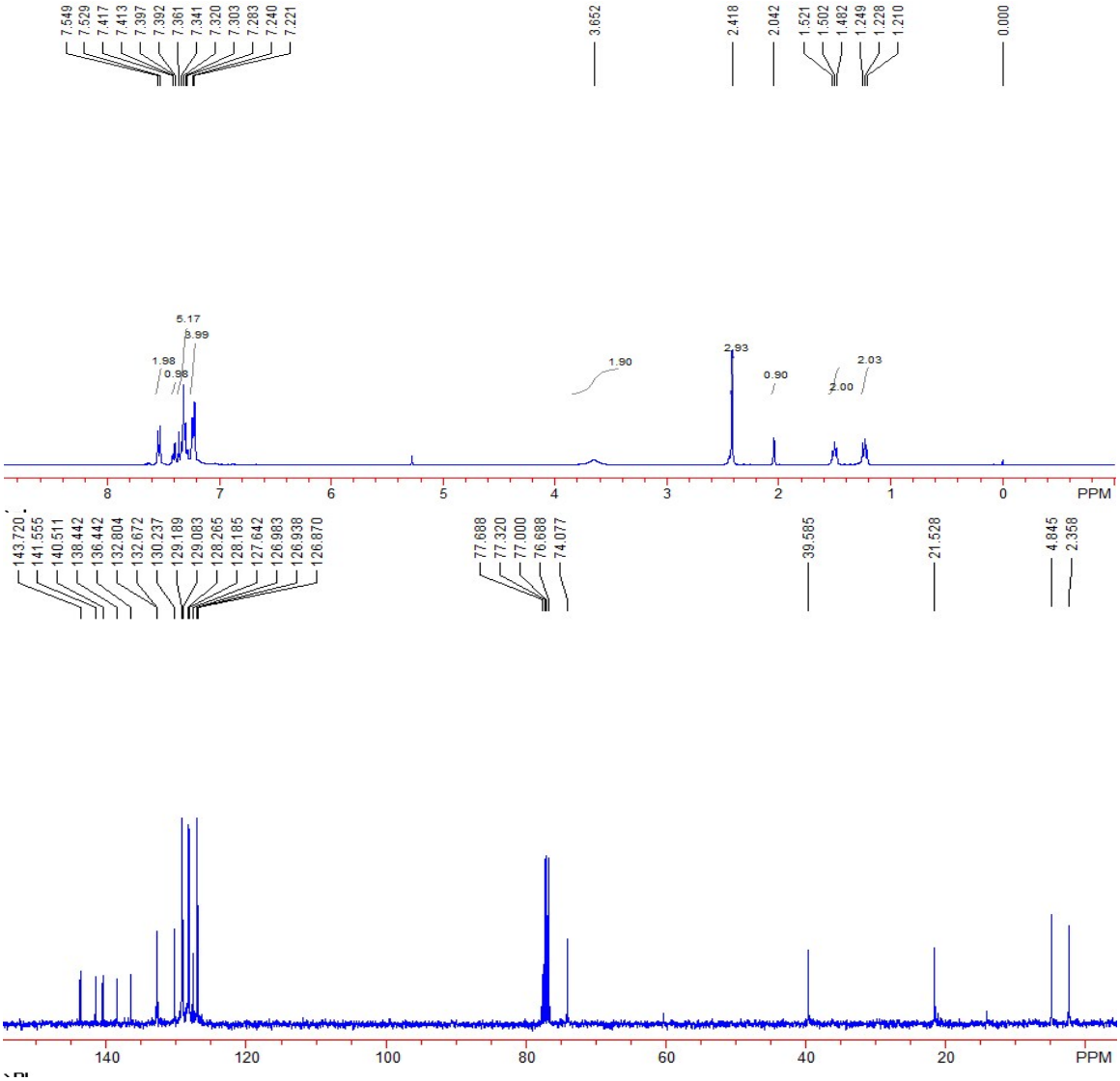


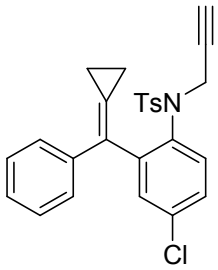
Compound 1j: Yield: 1.5 g, 85%; A white solid, m.p. 152-154 ^{o}C;; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.18-1.30 (m, 2H), 1.36-1.42 (m, 1H), 1.46-1.53 (m, 1H), 2.37 (s, 3H), 3.51 (s, 3H), 3.72-3.89 (m, 2H), 6.84 (d, 1H, J = 8.4 Hz), 6.94 (d, 1H, J = 7.6 Hz), 7.15 (d, 2H, J = 8.4 Hz), 7.19 (d, 1H, J = 6.8 Hz), 7.25 (dd, 2H, J_1 = J_2 = 8.0 Hz), 7.31-7.35 (m, 3H), 7.58 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.3, 4.8, 21.3, 40.0, 54.8, 72.1, 78.1, 110.4, 123.5, 126.5, 126.6, 126.8, 127.0, 127.5, 127.91, 127.95, 128.5, 129.4, 137.7, 140.5, 142.5, 144.5, 157.8; IR (neat): ν 3290, 3039, 2966, 2831, 1594, 1578, 1341, 1268, 1159, 1087, 816, 795, 761, 716, 666 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_3S$ $[M+H]^+$: 444.1628, found: 444.1622.



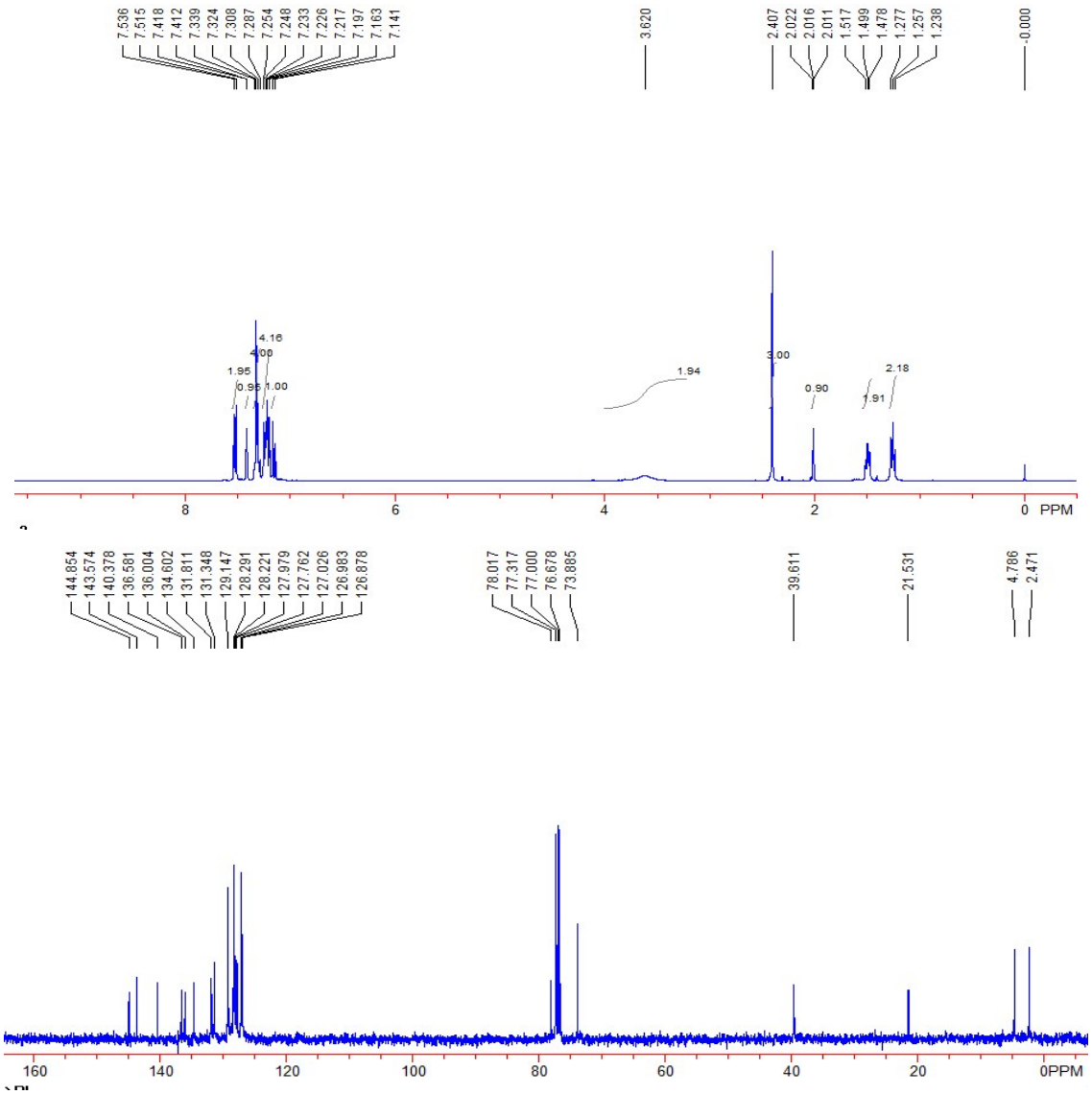


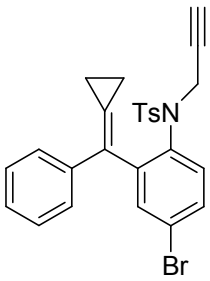
Compound 1k: Yield: 1.0 g, 75%; A white solid, m.p. 173-177 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.22 (t, 2H, *J* = 8.4 Hz), 1.50 (t, 2H, *J* = 8.0 Hz), 2.04 (s, 1H), 2.42 (s, 3H), 3.65 (s, 2H), 7.23 (d, 4H, *J* = 7.6 Hz), 7.28-7.36 (m, 5H), 7.39-7.41 (m, 1H), 7.53 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.3, 4.8, 21.5, 39.6, 74.0, 77.7, 126.8, 126.93, 126.98, 127.6, 128.1, 128.2, 129.0, 129.2, 130.2, 132.6, 132.8, 136.4, 138.4, 140.5, 141.5, 143.7; IR (neat): ν 3264, 3045, 2972, 2922, 1586, 1492, 1353, 1162, 1091, 1074, 886, 813, 779, 768, 697 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{26}ClN_2O_2S$ $[M+NH_4]^+$: 465.1398, found: 465.1395.



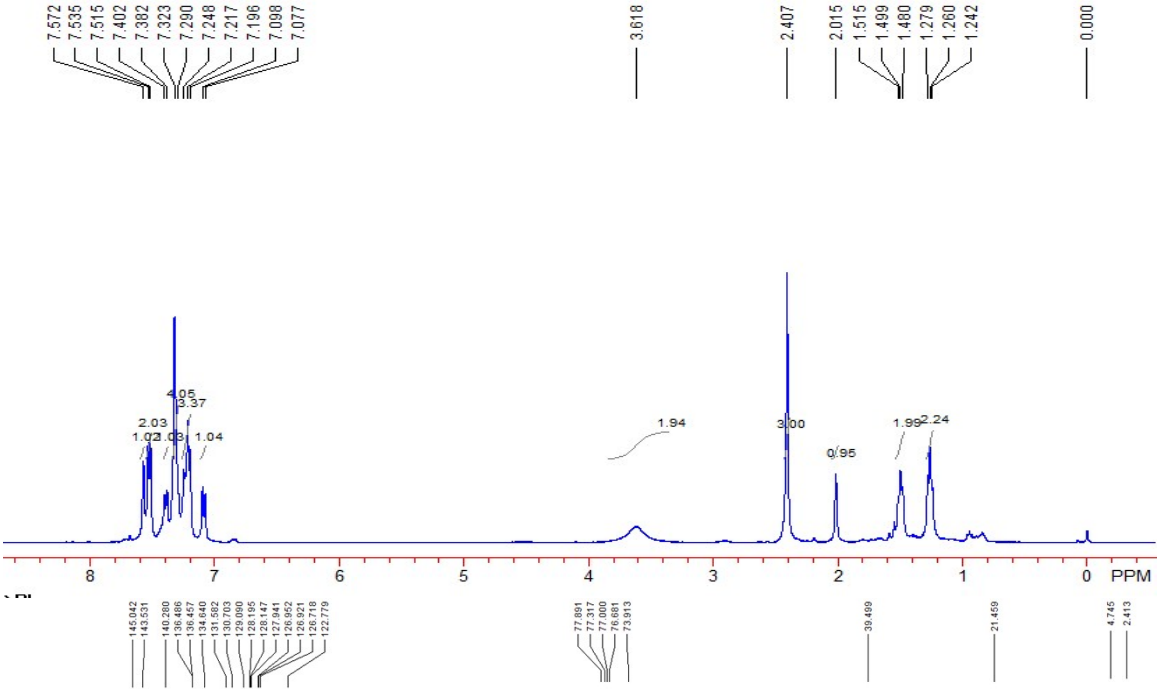


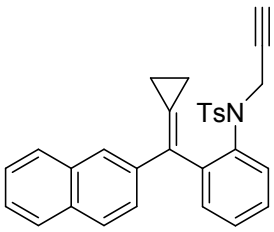
Compound 1l: Yield: 1.2 g, 88%; A white solid, m.p. 181-182 ^{o}C;; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (t, 2H, *J* = 8.0 Hz), 1.49 (t, 2H, *J* = 8.4 Hz), 2.02 (t, 1H, *J* = 2.0 Hz), 2.41 (s, 3H), 3.62 (s, 2H), 7.15 (d, 1H, *J* = 8.4 Hz), 7.19-7.25 (m, 4H), 7.28-7.34 (m, 4H), 7.41 (d, 1H, *J* = 2.4 Hz), 7.52 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.5, 4.8, 21.5, 39.6, 73.9, 78.0, 126.8, 126.9, 127.0, 127.7, 127.9, 128.2, 128.3, 129.1, 131.3, 131.8, 134.6, 136.0, 136.5, 140.4, 143.5, 144.8; IR (neat): ν 3253, 3034, 2974, 2925, 1591, 1474, 1349, 1161, 1090, 859, 815, 777, 707, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{26}ClN_2O_2S$ $[M+NH_4]^+$: 465.1398, found: 465.1393.



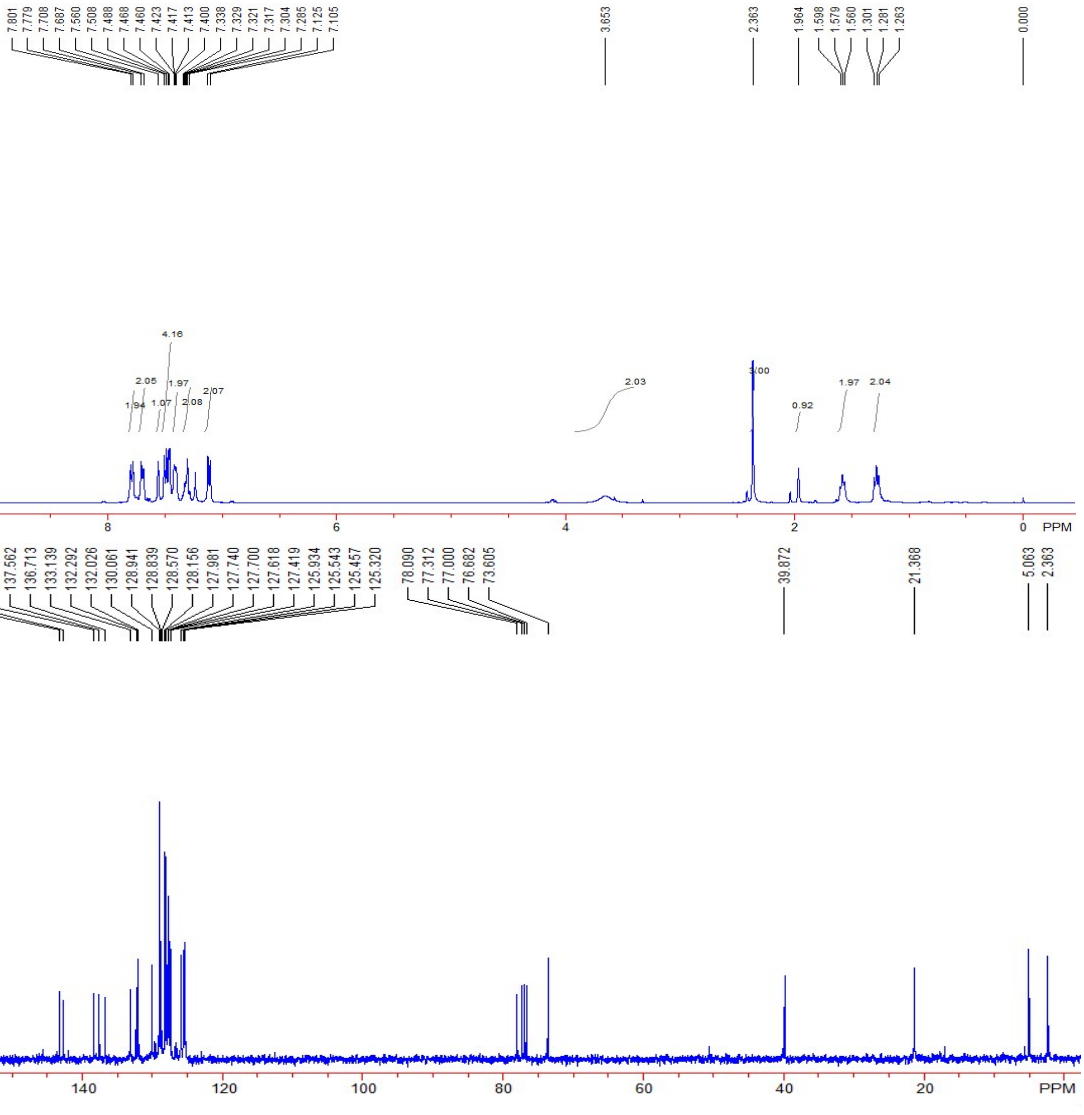


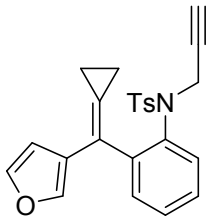
Compound 1m: Yield: 1.1 g, 86%; A white solid, m.p. 188-190 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (t, 2H, *J* = 7.6 Hz), 1.50 (t, 2H, *J* = 7.6 Hz), 2.01 (s, 1H), 2.41 (s, 3H), 3.62 (s, 2H), 7.08 (d, 1H, *J* = 8.4 Hz), 7.19-7.25 (m, 3H), 7.29-7.32 (m, 4H), 7.39 (d, 1H, *J* = 8.0 Hz), 7.52 (d, 2H, *J* = 8.0 Hz), 7.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.4, 4.7, 21.4, 39.5, 73.9, 77.9, 122.8, 126.7, 126.92, 126.95, 127.9, 128.14, 128.19, 129.1, 130.7, 131.6, 134.6, 136.45, 136.48, 140.3, 143.5, 145.0; IR (neat): ν 3266, 3052, 2979, 2932, 1597, 1160, 1091, 1082, 858, 772, 732, 706, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{26}BrN_2O_2S$ $[M+NH_4]^+$: 509.0893, found: 509.0897.



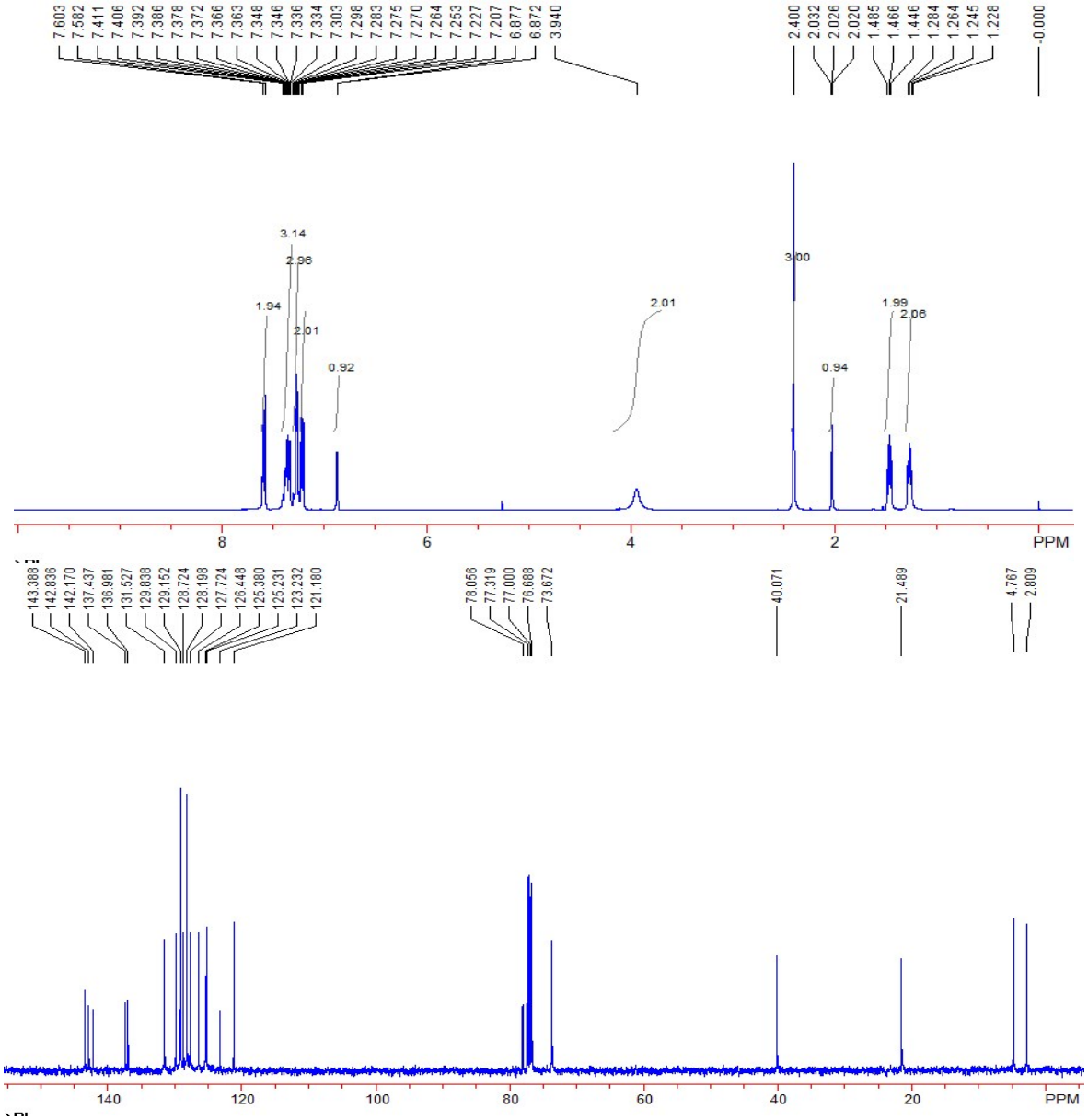


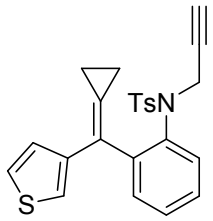
Compound 1n: Yield: 1.3 g, 85%; A white solid, m.p. 174-176 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28 (t, 2H, *J* = 8.0 Hz), 1.58 (t, 2H, *J* = 7.6 Hz), 1.96 (s, 1H), 2.36 (s, 3H), 3.65 (s, 2H), 7.11 (d, 2H, *J* = 8.0 Hz), 7.28-7.34 (m, 2H), 7.40-7.42 (m, 2H), 7.46-7.50 (m, 4H), 7.56 (s, 1H), 7.69 (d, 2H, *J* = 8.4 Hz), 7.79 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.3, 5.1, 21.4, 39.9, 73.6, 78.1, 125.3, 125.4, 125.5, 125.9, 127.4, 127.6, 127.70, 127.74, 127.9, 128.1, 128.6, 128.8, 128.9, 130.1, 132.0, 132.3, 133.1, 136.7, 137.6, 138.3, 142.6, 143.2; IR (neat): ν 3303, 3052, 2977, 2922, 1594, 1353, 1166, 1092, 1080, 849, 825, 751, 726 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{29}N_2O_2S$ $[M+NH_4]^+$: 481.1942, found: 481.1944.



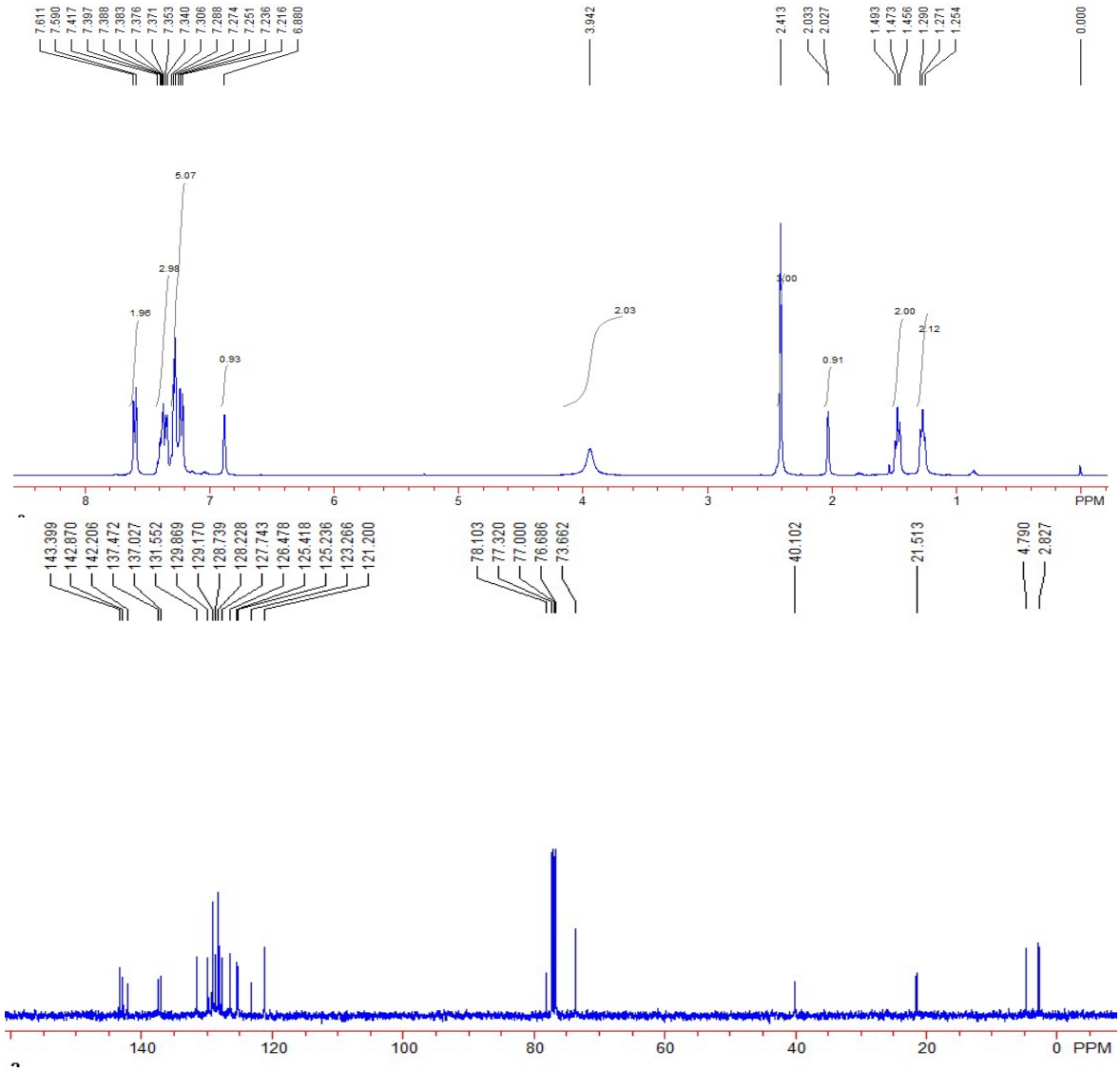


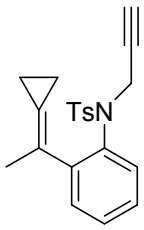
Compound 1o: Yield: 1.9 g, 82%; A white solid, m.p. 152-154 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (t, 2H, *J* = 8.0 Hz), 1.46 (t, 2H, *J* = 8.0 Hz), 2.02 (t, 1H, *J* = 3.6 Hz), 2.40 (s, 3H), 3.94 (s, 2H), 6.87 (d, 1H, *J* = 2.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 7.25-7.30 (m, 3H), 7.33-7.41 (m, 3H), 7.59 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.8, 4.8, 21.2, 40.0, 73.7, 78.0, 121.2, 123.2, 125.2, 125.4, 126.4, 127.7, 128.2, 128.7, 129.1, 129.8, 131.5, 137.0, 137.4, 142.1, 142.8, 143.4; IR (neat): ν 3259, 3045, 2972, 2927, 1487, 1437, 1341, 1302, 1161, 1091, 859, 813, 785, 725, 661 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{22}NO_3S$ $[M+H]^+$: 404.1315, found: 404.1310.



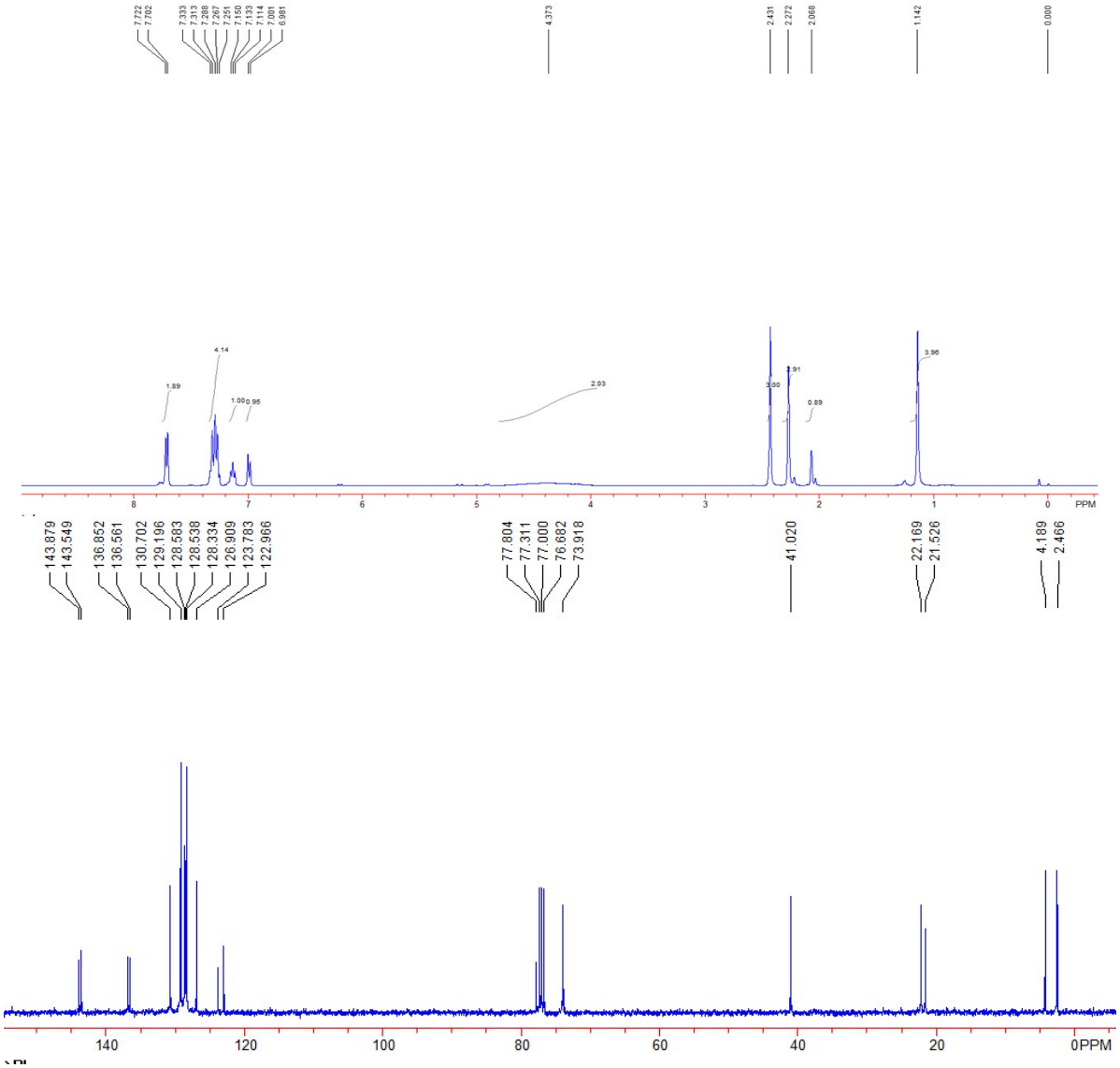


Compound 1p: Yield: 1.1 g, 90%; A white solid, m.p. 163-165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.27 (t, 2H, *J* = 6.8 Hz), 1.47 (t, 2H, *J* = 6.8 Hz), 2.03 (d, 1H, *J* = 2.4 Hz), 2.41 (s, 3H), 3.94 (s, 2H), 6.88 (s, 1H), 7.21-7.31 (m, 5H), 7.34-7.42 (m, 3H), 7.60 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.8, 4.8, 21.5, 40.1, 73.7, 78.1, 121.2, 123.3, 125.2, 125.4, 126.5, 127.7, 128.2, 128.7, 129.1, 129.9, 131.5, 137.0, 137.4, 142.2, 142.9, 143.4; IR (neat): ν 3251, 3039, 2972, 2925, 1597, 1492, 1440, 1340, 1161, 1091, 858, 843, 813, 785, 766, 744, 725, 701, 660 cm^{-1}; HRMS (ESI) Calcd. for $C_{24}H_{22}NO_2S_2$ $[M+H]^+$: 420.1086, found: 420.1080.

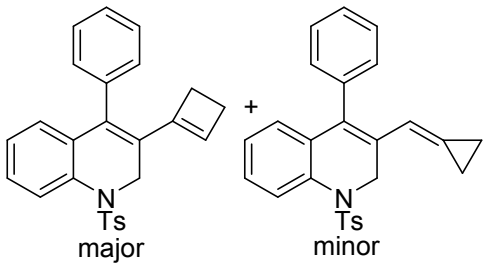




Compound 1q: Yield: 1.2 g, 82%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.14 (s, 4H), 2.07 (s, 1H), 2.27 (s, 3H), 2.43 (s, 3H), 4.37 (s, 2H), 6.99 (d, 1H, J = 8.0 Hz), 7.13 (t, 1H, J = 7.6 Hz), 7.25-7.33 (m, 4H), 7.71 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.5, 4.2, 21.5, 22.2, 41.0, 73.9, 77.8, 122.9, 123.8, 126.9, 128.3, 128.53, 128.58, 129.2, 130.7, 136.6, 136.8, 143.5, 143.8; IR (neat): ν 3277, 2974, 2919, 2854, 1597, 1347, 1158, 1091, 861, 813, 756, 721, 659 cm^{-1}; HRMS (ESI) Calcd. for $C_{21}H_{21}NO_2S$ $[M+H]^+$: 352.1366, found: 352.1361.

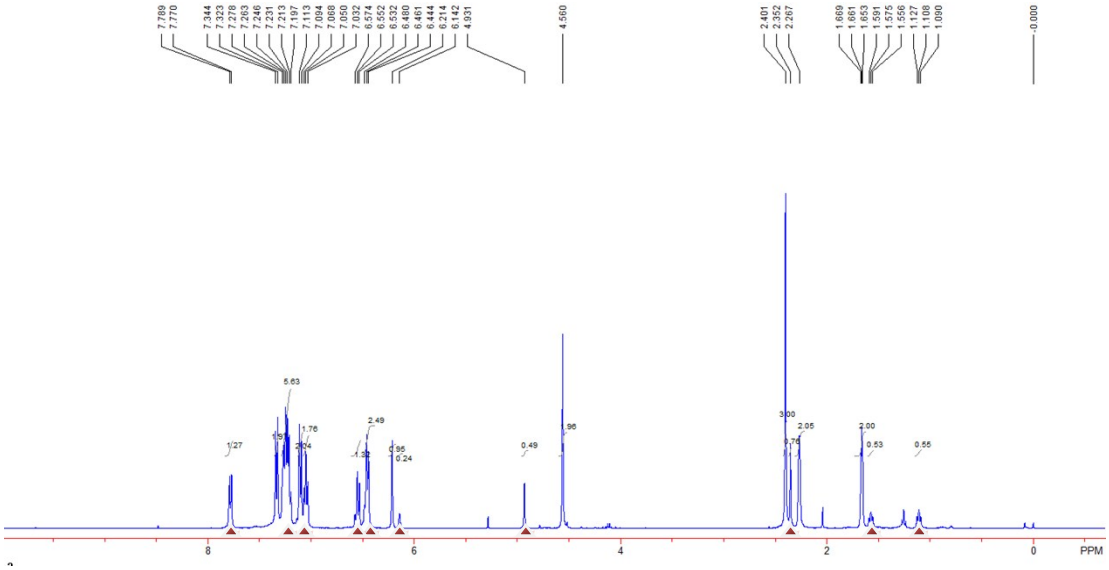


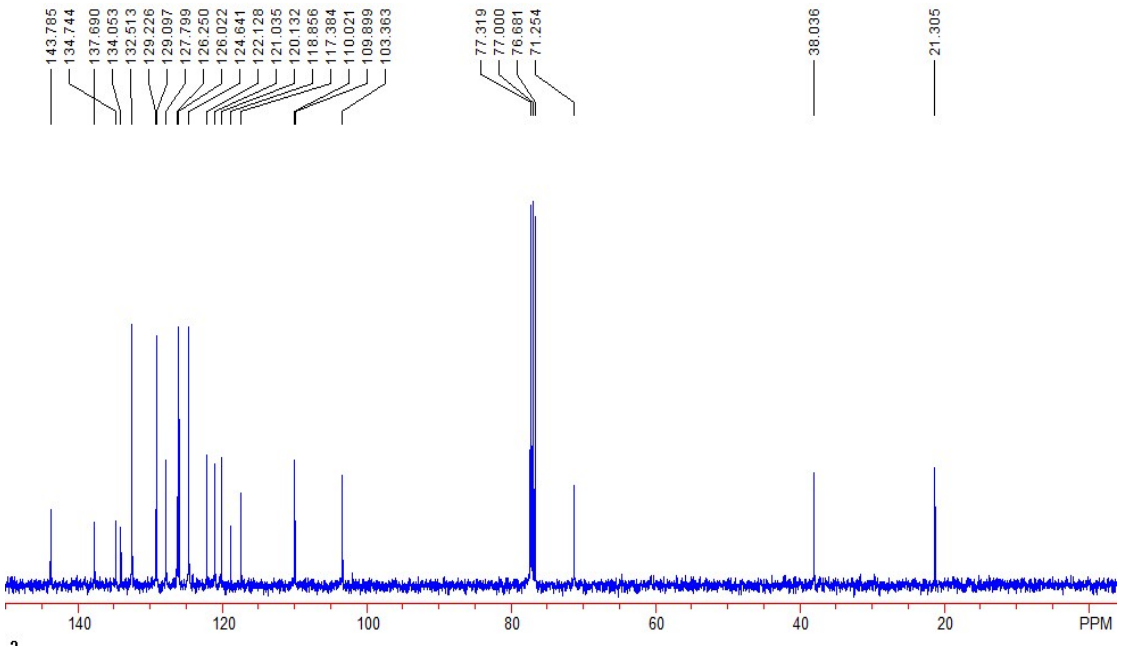
6. Spectroscopic data of the products 2

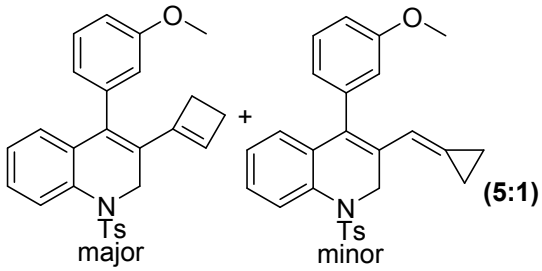


(4:1)

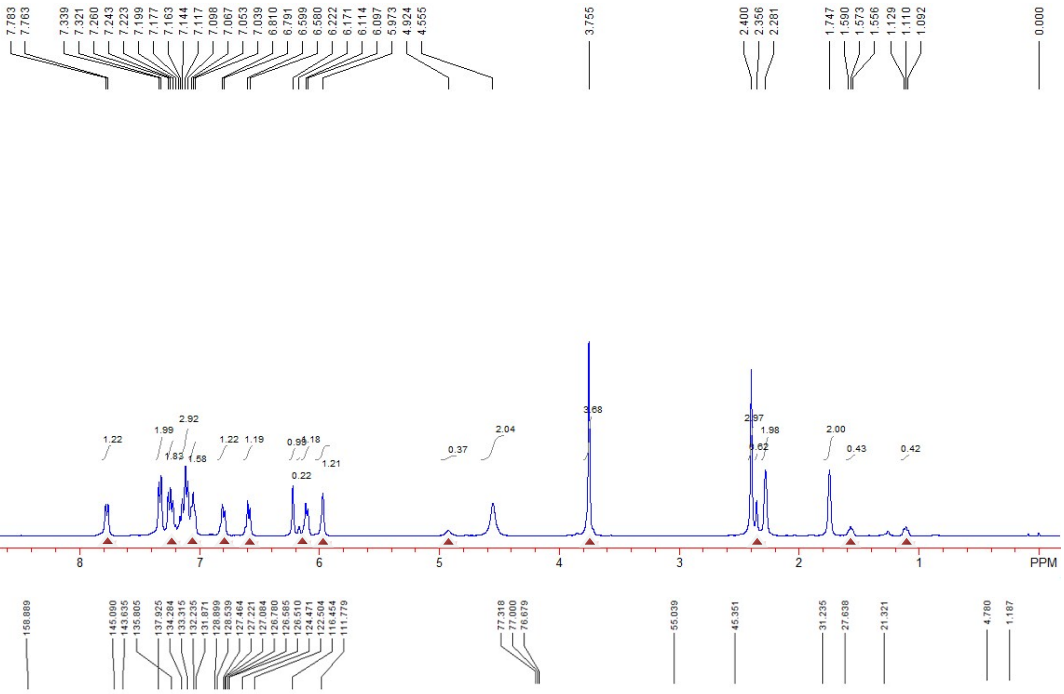
Compound 2a: Yield: 65 mg, 79%; A white solid; Mp: 173-175 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.66 (t, 2H, J = 7.2 Hz), 2.27 (s, 2H), 2.40 (s, 3H), 4.56 (s, 2H), 6.21 (s, 1H), 6.45 (d, 2H, J = 6.8 Hz), 6.54 (d, 1H, J = 8.0 Hz), 7.05 (dd, 1H, J_1 = J_2 = 7.6 Hz), 7.10 (d, 2H, J = 8.0 Hz), 7.19-7.28 (m, 4H), 7.33 (d, 2H, J = 8.4 Hz), 7.78 (d, 1H, J = 7.6 Hz); (minor) δ 1.11 (t, 0.5H, J = 7.6 Hz), 1.57 (t, 0.5H, J = 8.0 Hz), 2.35 (s, 0.75H), 4.93 (s, 0.5H), 6.14 (s, 0.25H), 6.45 (d, 0.5H, J = 6.8 Hz), 6.54 (d, 0.25H, J = 8.0 Hz), 7.05 (dd, 0.75H, J_1 = J_2 = 7.6 Hz), 7.19-7.28 (m, 1.5H), 7.78 (d, 0.25H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.3, 27.6, 31.2, 45.4, 124.6, 126.6, 126.8, 127.1, 127.4, 127.52, 127.55, 128.0, 129.3, 130.0, 132.1, 132.4, 133.3, 134.4, 135.8, 136.6, 143.5, 145.1; IR (neat): ν 2972, 2883, 1450, 1375, 1087, 879, 674 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{24}NO_2S$ $[M+H]^+$: 414.1522, found: 414.1522.

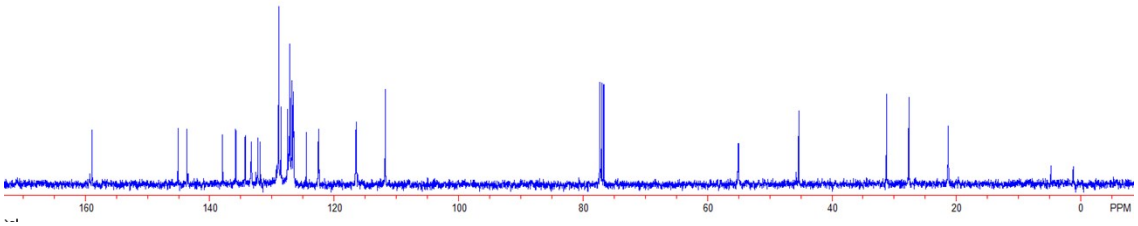


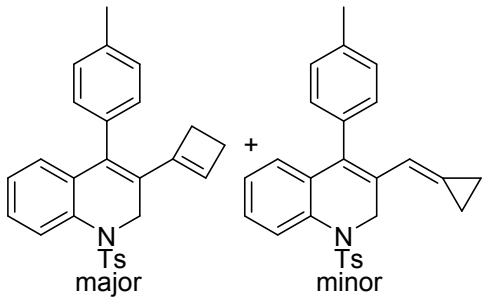




Compound 2b: Yield: 54 mg, 61%; A white solid; Mp: 125-127 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.75 (s, 2H), 2.28 (s, 2H), 2.40 (s, 3H), 3.75 (s, 3H), 4.55 (s, 2H), 5.97 (s, 1H), 6.10 (d, 1H, J = 7.2 Hz), 6.22 (s, 1H), 6.59 (d, 1H, J = 7.6 Hz), 6.80 (d, 1H, J = 7.6 Hz), 7.05 (dd, 1H, J_1 = J_2 = 6.4 Hz), 7.09-7.17 (m, 3H), 7.22-7.26 (m, 1H), 7.33 (d, 2H, J = 7.2 Hz), 7.77 (d, 1H, J = 8.0 Hz); (minor) δ 1.11 (t, 0.4H, J = 7.6 Hz), 1.57 (t, 0.2H, J = 6.8 Hz), 2.35 (s, 0.6H), 3.75 (s, 0.6H), 4.92 (s, 0.4H), 5.97 (s, 0.2H), 6.10 (d, 0.2H, J = 7.2 Hz), 6.17 (s, 0.2H), 6.59 (d, 0.2H, J = 7.6 Hz), 6.80 (d, 0.2H, J = 7.6 Hz), 7.05 (dd, 0.6H, J_1 = J_2 = 6.4 Hz), 7.22-7.26 (m, 0.8H), 7.77 (d, 0.2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.3, 27.6, 31.2, 45.3, 55.0, 116.4, 124.5, 126.51, 126.58, 126.7, 127.1, 127.2, 127.4, 128.5, 131.8, 132.2, 133.3, 134.3, 135.8, 137.9, 143.6, 145.1, 158.9; IR (neat): ν 3032, 2919, 2828, 1597, 1482, 1349, 1163, 1088, 810, 715, 704, 659 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_3S$ $[M+H]^+$: 444.1628, found: 444.1629.



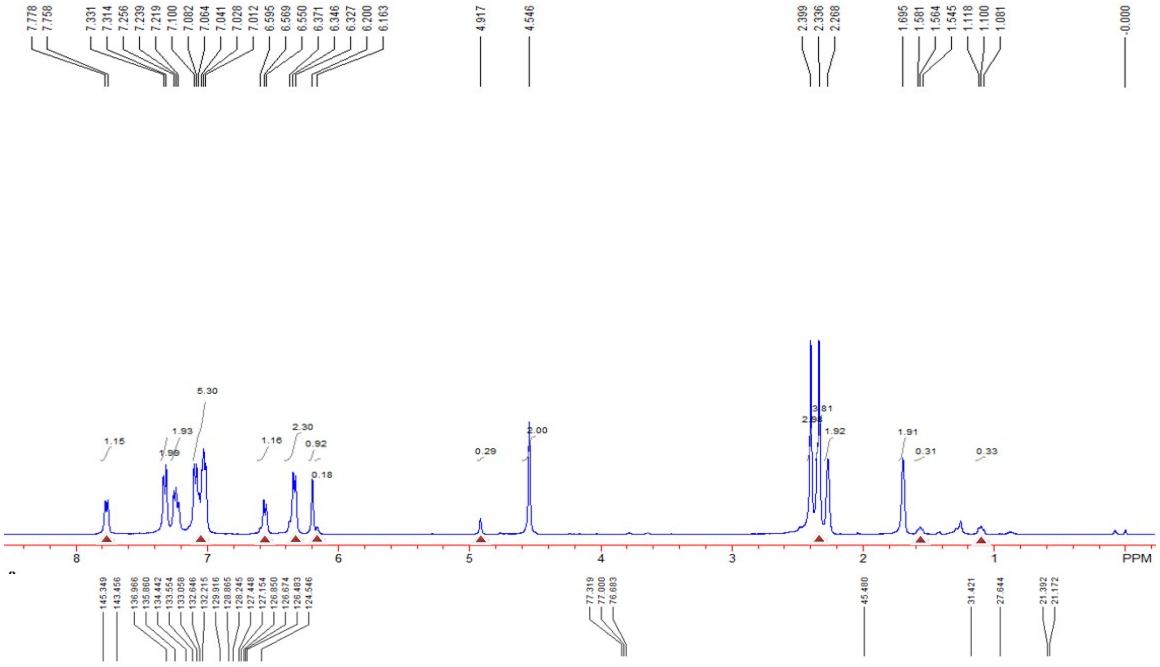


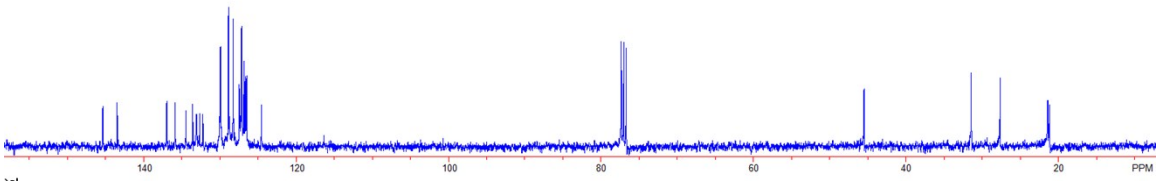


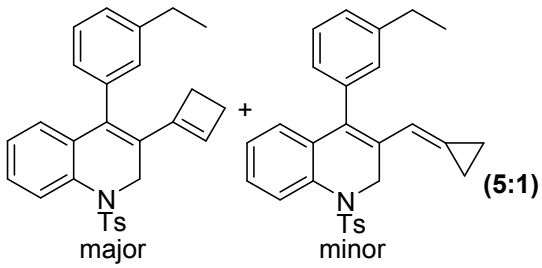
(6.7:1)

Compound 2c: Yield: 37 mg, 43%; A white solid; Mp: 175-177 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.69 (s, 2H), 2.27 (s, 2H), 2.33 (s, 3H), 2.40 (s, 3H), 4.55 (s, 2H), 6.20 (s, 1H), 6.33 (d, 2H, J = 7.6 Hz), 6.56 (d, 1H, J = 7.6 Hz), 7.01-7.10 (m, 4H), 7.22-7.26 (m, 2H), 7.32 (d, 2H, J = 6.8 Hz), 7.76 (d, 1H, J = 8.0 Hz); (minor) δ 1.10 (t, 0.3H, J = 7.6 Hz), 1.56 (t, 0.3H, J = 7.6 Hz), 2.33 (s, 0.9H), 4.92 (s, 0.3H), 6.16 (s, 0.15H), 6.37 (d, 0.3H, J = 6.8 Hz), 6.59 (d, 0.15H, J = 7.6 Hz), 7.01-7.10 (m, 1.25H), 7.78 (d, 0.15H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major)

δ 21.2, 21.4, 27.6, 31.4, 45.5, 124.5, 126.5, 126.7, 126.8, 127.1, 127.4, 128.2, 128.9, 129.9, 132.2, 132.6, 133.0, 133.5, 134.4, 135.9, 136.9, 143.4, 145.3; IR (neat): ν 3019, 2925, 2839, 1591, 1477, 1350, 1164, 1088, 853, 813, 765, 674, 659 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_2S$ $[M+H]^+$: 428.1679, found: 428.1678.

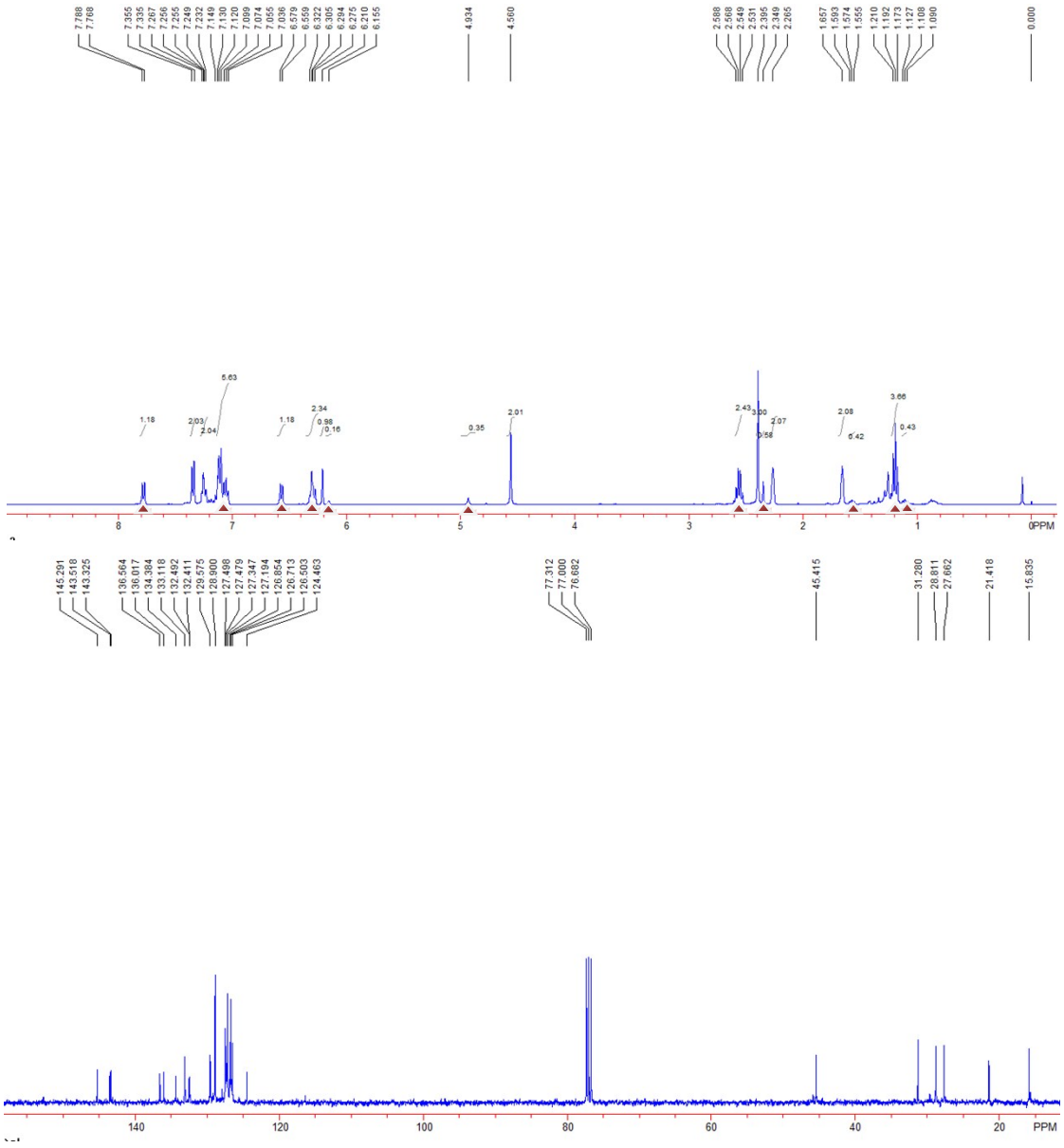


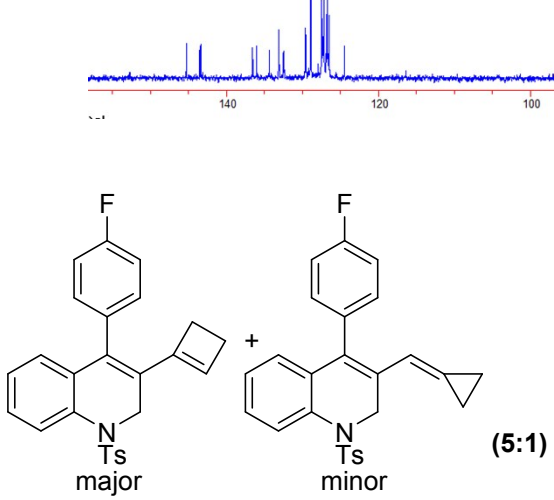




Compound 2d: Yield: 67 mg, 61%; A white solid; Mp: 115-117 °C; ^1H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.19 (t, 3H, *J* = 7.6 Hz), 1.65 (s, 2H), 2.26 (s, 2H), 2.39 (s, 3H), 4.56 (s, 2H), 6.21 (s, 1H), 6.27-6.32 (m, 2H), 6.56 (d, 1H, *J* = 8.0 Hz), 7.03-7.15 (m, 4H), 7.23-7.26 (m, 2H), 7.34 (d, 2H, *J* = 8.0 Hz), 7.77 (d, 1H, *J* = 8.0 Hz); (minor)

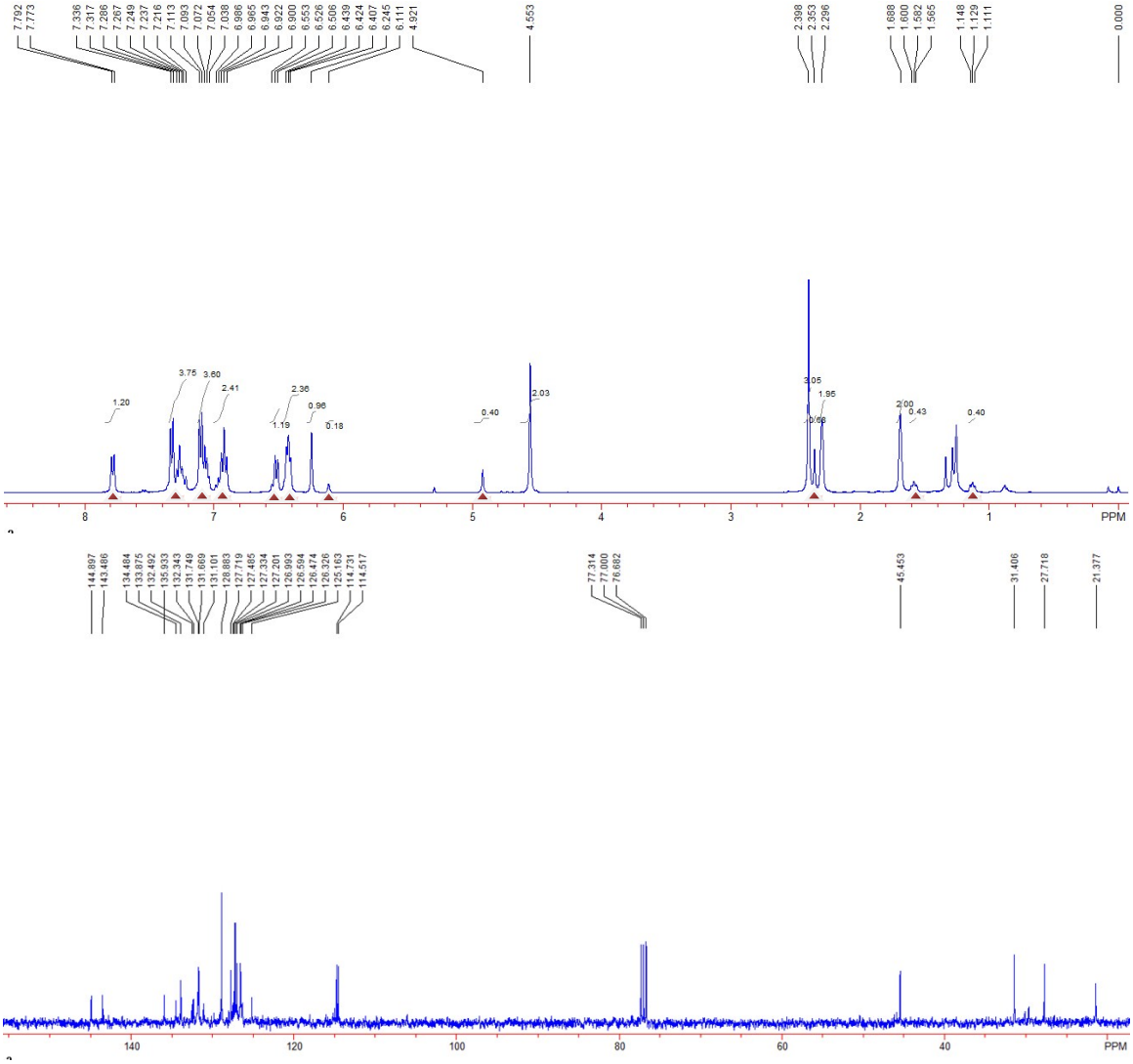
δ 1.11 (t, 0.4H, J = 7.6 Hz), 1.57 (t, 0.4H, J = 7.6 Hz), 2.35 (s, 0.6H), 4.93 (s, 0.4H), 6.15 (s, 0.2H), 6.27-6.32 (m, 0.4H), 6.56 (d, 0.2H, J = 8.0 Hz), 7.03-7.15 (m, 1.6H), 7.77 (d, 0.2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 15.8, 21.4, 27.6, 28.8, 31.3, 45.4, 124.4, 126.5, 126.7, 127.2, 127.3, 127.47, 127.49, 128.9, 129.5, 132.41, 132.49, 133.1, 134.4, 136.0, 136.5, 143.5, 143.3, 145.3; IR (neat): ν 2961, 2927, 2849, 1597, 1479, 1347, 1162, 1083, 859, 812, 742, 680, 658 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{28}NO_2S$ $[M+H]^+$: 442.1835, found: 442.1835.

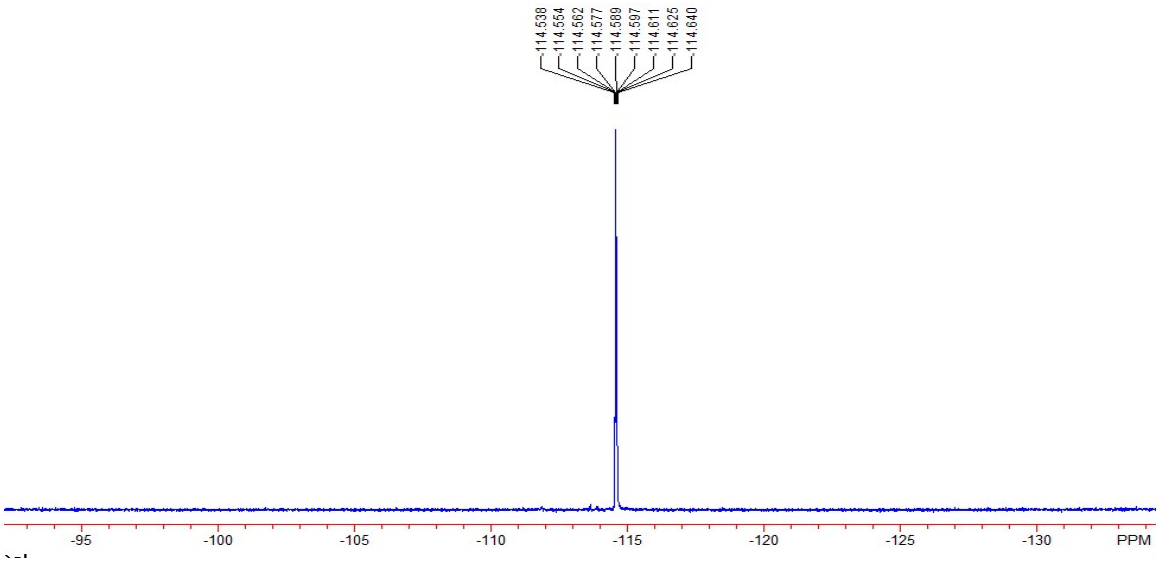


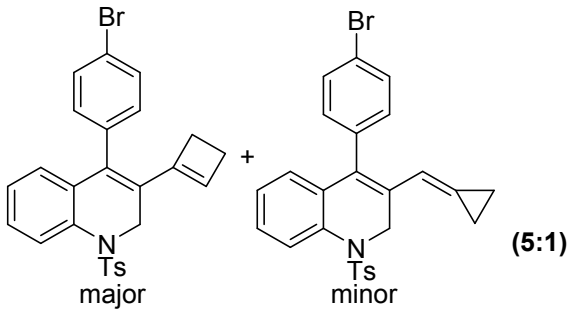


(5:1)

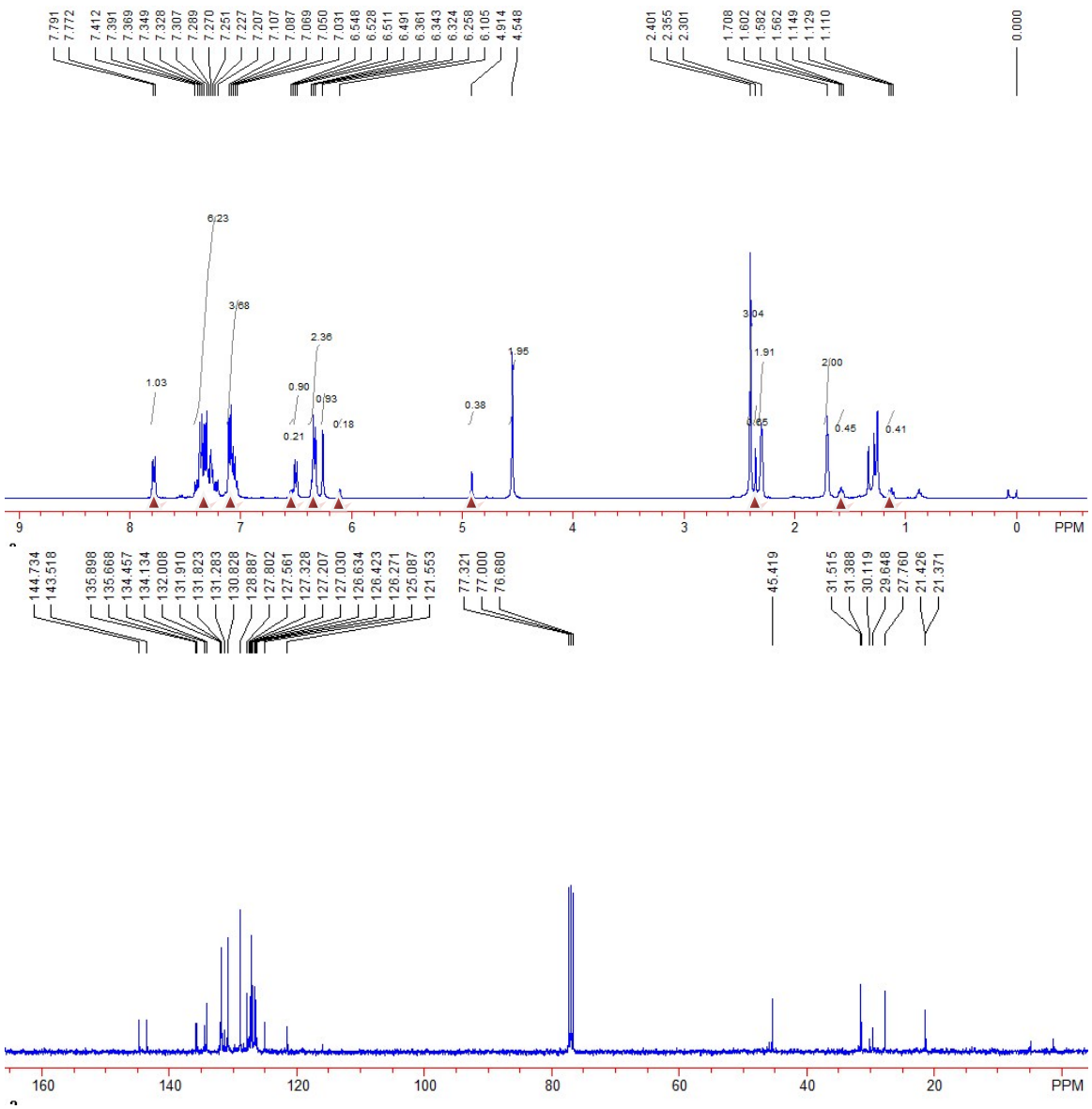
Compound 2f: Yield: 45 mg, 52%; A white solid; Mp: 180-182 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.69 (s, 2H), 2.30 (s, 2H), 2.40 (s, 3H), 4.55 (s, 2H), 6.24 (s, 1H), 6.40-6.44 (m, 2H), 6.50-6.55 (m, 1H), 6.90-6.95 (m, 2H), 7.03-7.11 (m, 3H), 7.21-7.34 (m, 3H), 7.78 (d, 1H, *J* = 7.6 Hz); (minor) δ 1.13 (t, 0.4H, *J* = 7.6 Hz), 1.58 (t, 0.4H, *J* = 7.6 Hz), 2.35 (s, 0.6H), 4.92 (s, 0.4H), 6.11 (s, 0.2H), 6.40-6.44 (m, 0.4H), 6.50-6.55 (m, 0.2H), 6.90-6.95 (m, 0.4H), 7.03-7.11 (m, 0.6H), 7.21-7.34 (m, 0.6H), 7.78 (d, 0.2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.4, 27.7, 31.4, 45.4, 114.6 (d, *J* = 21.4 Hz), 125.2, 126.5 (d, *J* = 12.0 Hz), 127.0, 127.2, 127.3, 127.5, 127.7, 128.9, 131.1, 131.6, 131.7, 132.3, 132.5 (d, *J* = 3.1 Hz), 133.8, 134.5, 135.9, 144.2 (d, *J* = 141.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -114.64 ~ -114.54 (m); IR (neat): ν 3047, 2917, 2849, 1594, 1505, 1348, 1163, 1083, 857, 807, 761, 672, 658 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}FNO_2S$ $[M+H]^+$: 432.1428, found: 432.1428.

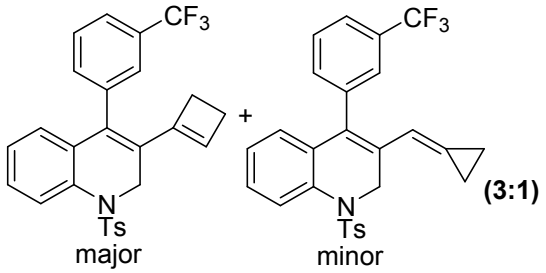






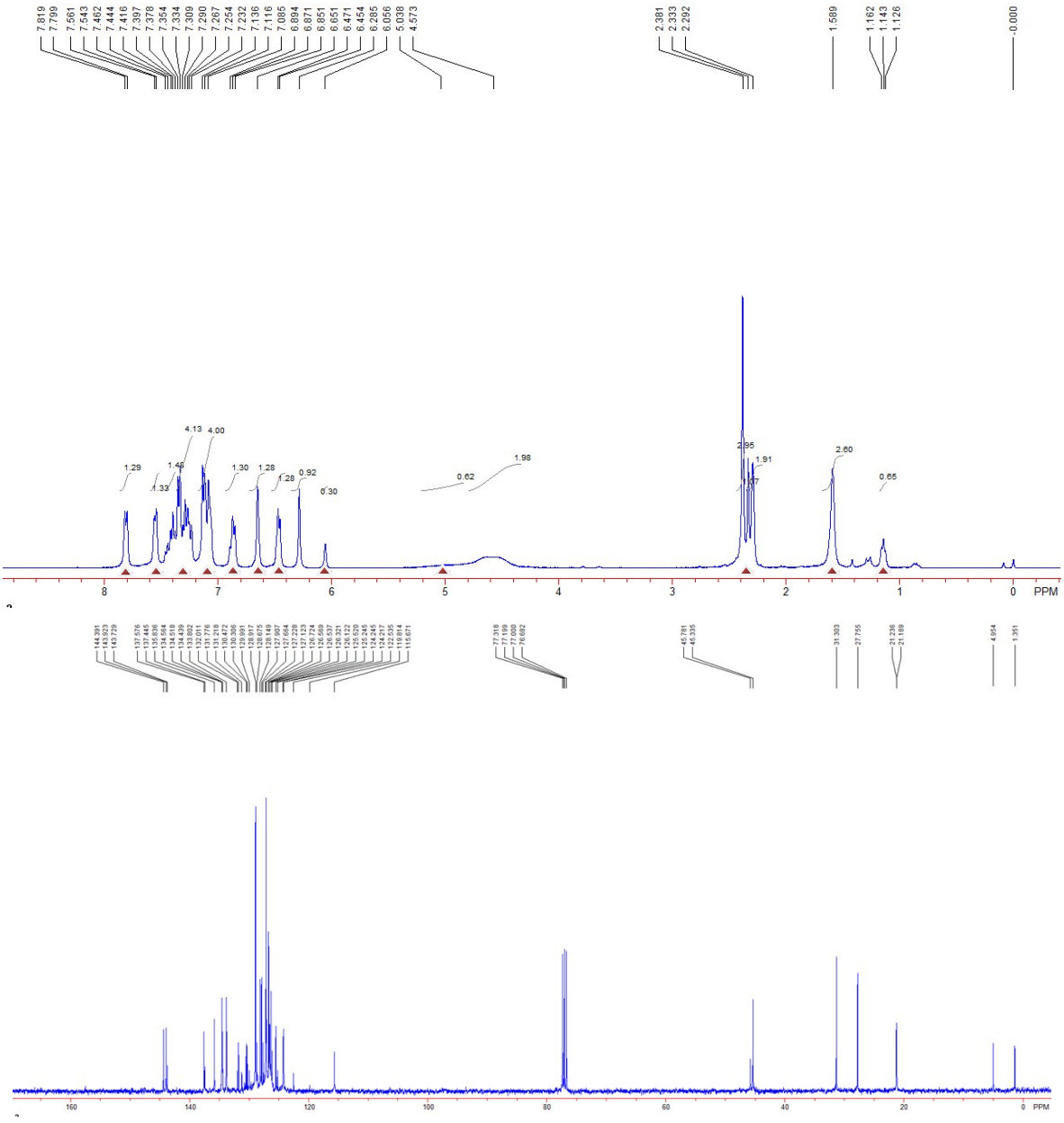
Compound 2g: Yield: 50 mg, 51%; A white solid; Mp: 206-208 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.71 (s, 2H), 2.30 (s, 2H), 2.40 (s, 3H), 4.55 (s, 2H), 6.26 (s, 1H), 6.33 (d, 2H, *J* = 7.6 Hz), 6.50 (d, 1H, *J* = 8.0 Hz), 7.03-7.10 (m, 3H), 7.21-7.41 (m, 6H), 7.78 (d, 1H, *J* = 7.6 Hz); (minor) δ 1.13 (t, 0.4H, *J* = 8.0 Hz), 1.58 (t, 0.4H, *J* = 8.0 Hz), 2.35 (s, 0.6H), 4.91 (s, 0.4H), 6.10 (s, 0.2H), 6.35 (d, 0.4H, *J* = 8.0 Hz), 6.53 (d, 0.2H, *J* = 7.2 Hz), 7.03-7.10 (m, 0.6H), 7.21-7.41 (m, 1H), 7.79 (d, 0.2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 27.8, 30.1, 31.4, 31.5, 121.5, 125.1, 126.3, 126.4, 126.6, 127.2, 127.3, 127.8, 128.9, 130.8, 131.8, 131.9, 132.0, 134.1, 134.4, 135.7, 135.9, 144.7; IR (neat): ν 3052, 2927, 2849, 1591, 1478, 1349, 1163, 1080, 852, 818, 759, 707, 655 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}BrNO_2S$ $[M+H]^+$: 492.0627, found: 492.0623.

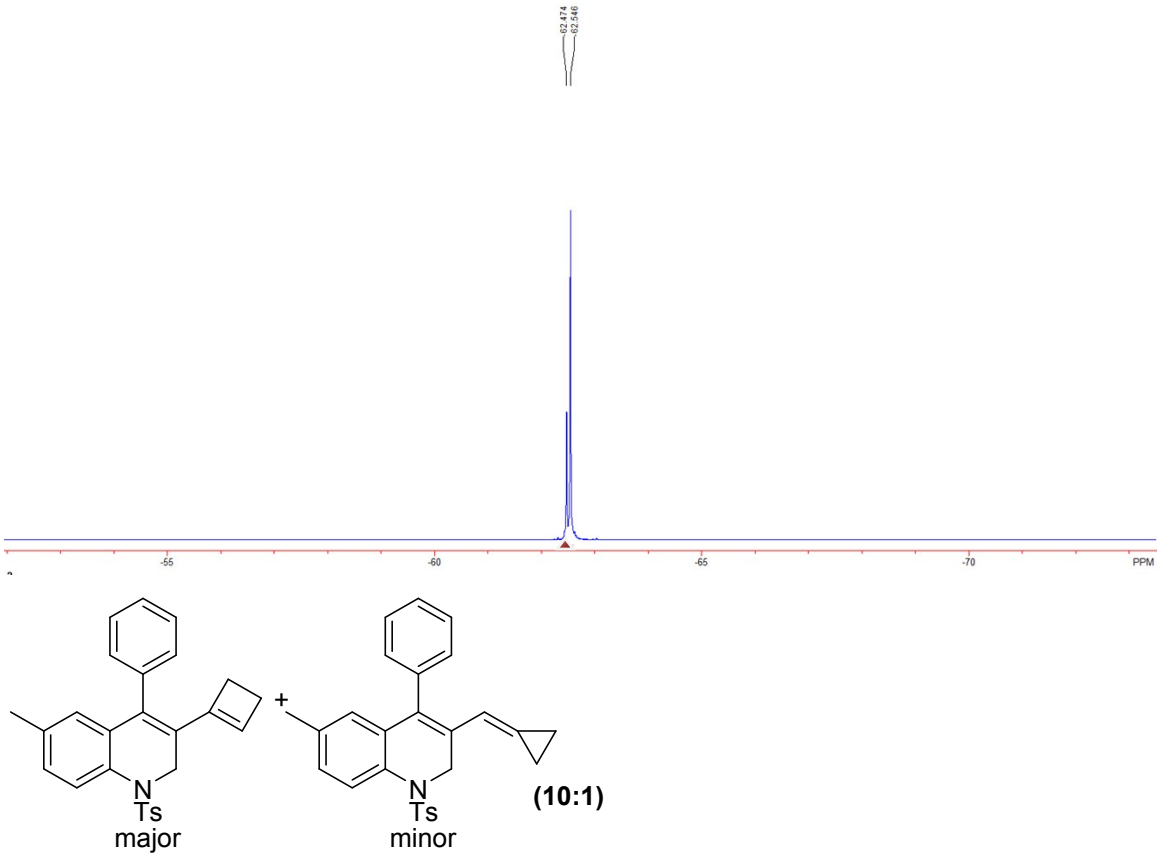




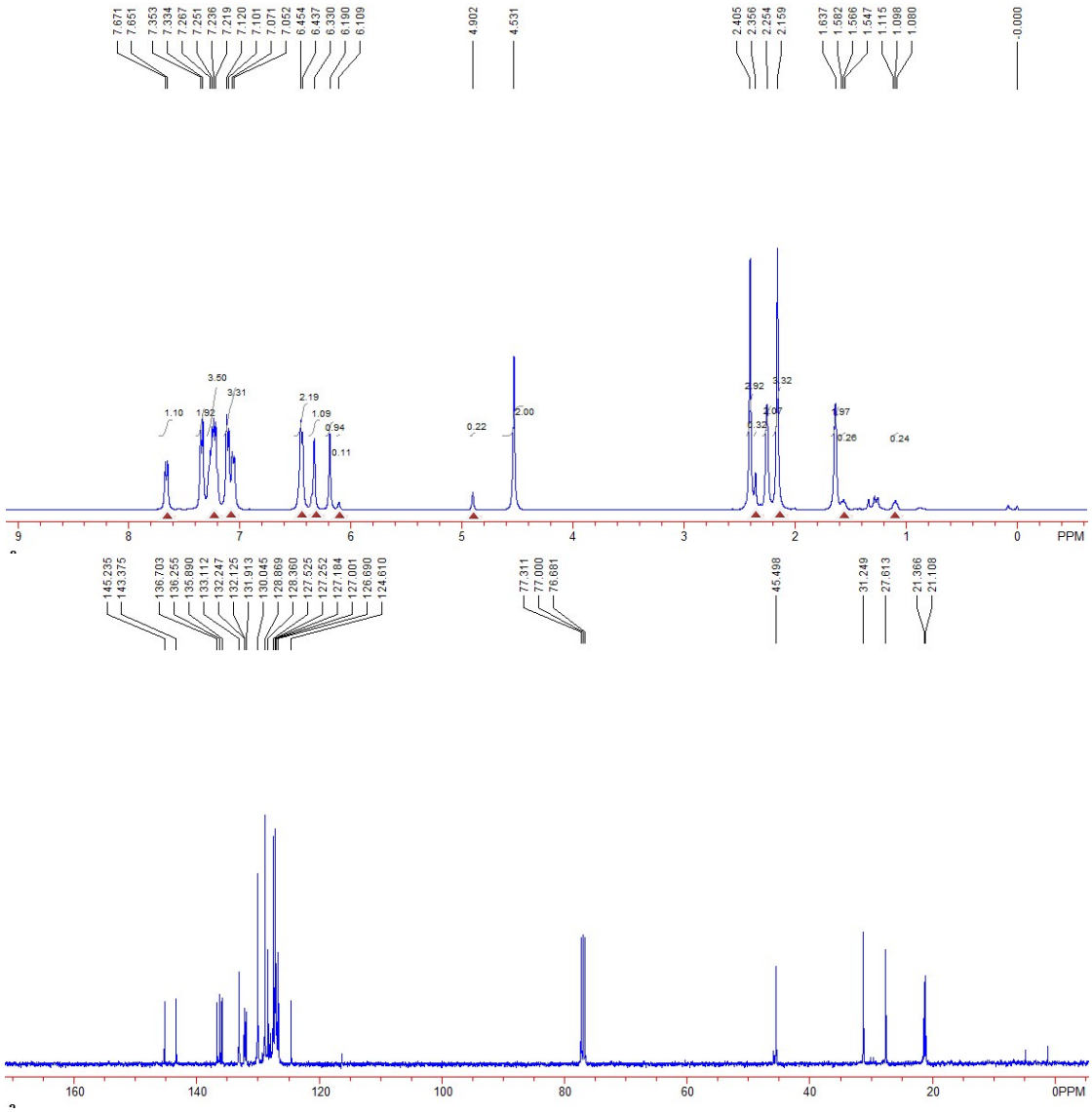
Compound 2h: Yield: 61 mg, 63%; A white solid; Mp: 96-98 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.59 (s, 2H), 2.29 (s, 2H), 2.38 (s, 3H), 4.57 (s, 2H), 6.28 (s, 1H), 6.46 (d, 1H, *J* = 6.8 Hz), 6.65 (s, 1H), 6.86 (d, 1H, *J* = 8.0 Hz), 7.08-7.13 (m, 3H), 7.23-7.35 (m, 3H), 7.38-7.46 (m, 1H), 7.55 (d, 1H, *J* = 7.2 Hz), 7.80 (d, 1H, *J* = 8.0 Hz); (minor) δ 1.44 (t, 0.67H, *J* = 7.6 Hz), 1.59 (s, 0.67H), 2.33 (s, 1H), 5.04 (s, 0.67H), 6.05 (s, 0.33H), 6.46 (d, 0.33H, *J* = 6.8 Hz), 6.65 (s, 0.33H), 6.88 (d, 0.33H, *J* = 8.0 Hz), 7.08-7.13 (m, 1H), 7.23-7.35 (m, 1H), 7.38-7.46 (m, 0.33H), 7.55 (d, 0.33H, *J* = 7.2 Hz), 7.80 (d, 0.33H, *J* = 8.0 Hz);

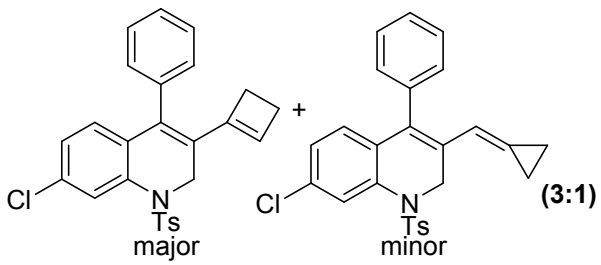
^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.2, 27.7, 31.3, 45.3, 124.2 (q, J = 2.8 Hz), 125.2 (q, J = 271.0 Hz), 125.5, 126.3, 126.5 (q, J = 3.2 Hz), 126.7, 127.1, 128.0 (q, J = 24.2 Hz), 128.9, 130.4, 131.8, 133.8, 134.4, 134.5, 135.8, 137.6, 143.9, 144.4; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) (major) δ -62.54 (s); IR (neat): ν 3047, 2919, 2823, 1591, 1479, 1351, 1162, 1090, 812, 763, 666 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{23}F_3NO_2S$ $[M+H]^+$: 482.1396, found: 482.1398.





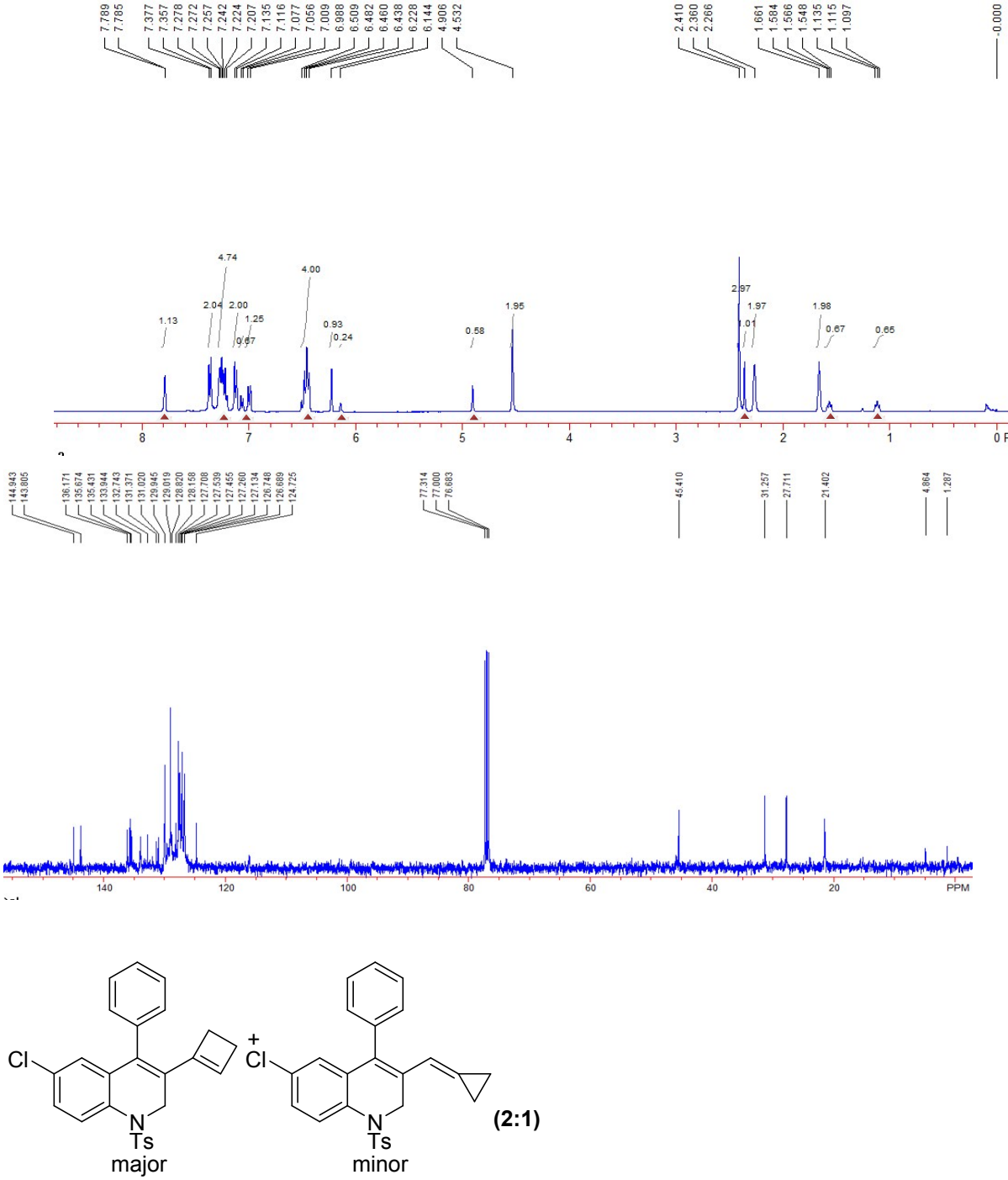
Compound 2i: Yield: 55 mg, 66%; A white solid; Mp: 116-118 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.64 (s, 2H), 2.16 (s, 3H), 2.25 (s, 2H), 2.40 (s, 3H), 4.53 (s, 2H), 6.19 (s, 1H), 6.33 (s, 1H), 6.44 (d, 2H, *J* = 6.8 Hz), 7.05-7.12 (m, 3H), 7.21-7.26 (m, 3H), 7.34 (d, 2H, *J* = 7.6 Hz), 7.66 (d, 1H, *J* = 7.6 Hz); (minor) δ 1.10 (t, 0.2H, *J* = 7.2 Hz), 1.56 (t, 0.2H, *J* = 7.6 Hz), 2.16 (s, 0.3H), 2.35 (s, 0.3H), 4.90 (s, 0.2H), 6.11 (s, 0.1H), 6.33 (s, 0.1H), 6.44 (d, 0.2H, *J* = 6.8 Hz), 7.05-7.12 (m, 0.3H), 7.21-7.26 (m, 0.5H), 7.66 (d, 0.1H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.1, 21.3, 27.6, 31.2, 45.5, 124.6, 126.7, 127.0, 127.1, 127.2, 127.5, 128.3, 128.8, 130.0, 131.9, 132.1, 132.2, 133.1, 135.8, 136.2, 136.7, 143.3, 145.2; IR (neat): ν 3024, 2925, 2854, 1594, 1484, 1349, 1163, 1088, 813, 703, 679 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_2S$ $[M+H]^+$: 428.1679, found: 428.1681.





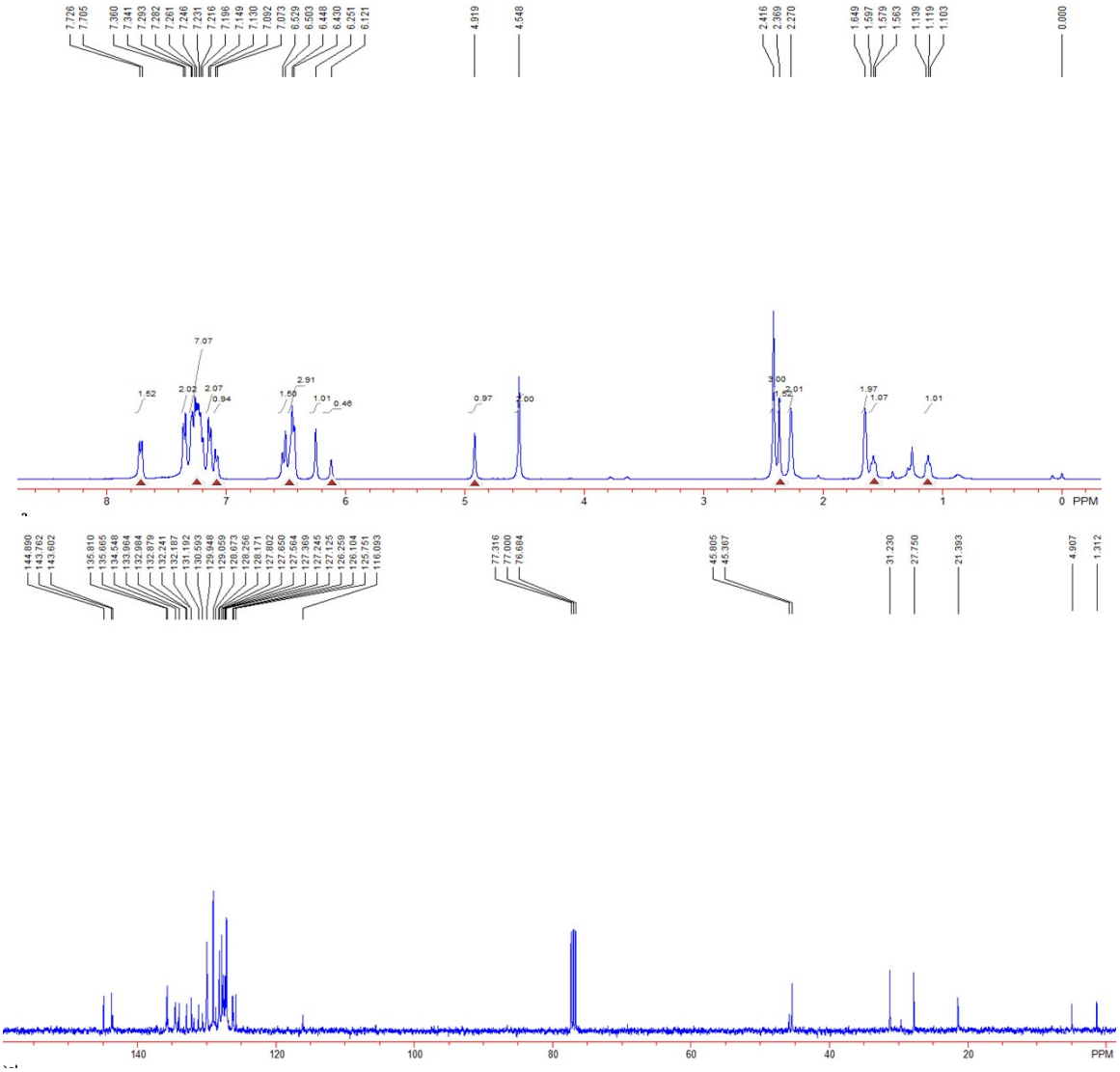
Compound 2k: Yield: 46 mg, 52%; A white solid; Mp: 88-90 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.66 (s, 2H), 2.26 (s, 2H), 2.41 (s, 3H), 4.53 (s, 2H), 6.22 (s, 1H), 6.43-6.51 (m, 3H), 6.99 (d, 1H, J = 8.4 Hz), 7.12 (d, 2H, J = 7.6 Hz), 7.20-7.28 (m, 3H), 7.36 (d, 2H, J = 8.0 Hz), 7.78 (s, 1H); (minor) δ 1.11 (t, 0.67H, J = 8.0 Hz), 1.56 (t, 0.67H, J = 7.2 Hz), 2.36 (s, 1H), 4.91 (s, 0.67H), 6.14 (s, 0.33H), 6.43-6.51 (m, 1H), 6.99 (d, 0.33H, J = 8.4 Hz), 7.06 (d, 0.67H, J = 8.4 Hz), 7.20-7.28 (m, 1.67H), 7.78 (s, 0.33H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.4, 27.7, 31.2, 45.4, 124.7, 126.7, 127.1, 127.2, 127.4, 127.5, 127.7, 128.8, 129.0, 129.9, 131.3, 132.7, 133.94, 133.98, 135.4, 136.1, 143.8, 144.9; IR

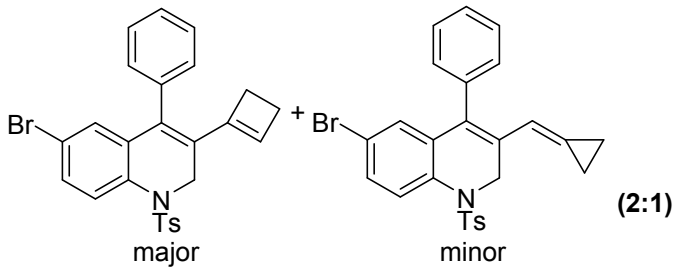
(neat): ν 3060, 2927, 2828, 1594, 1475, 1352, 1165, 1091, 888, 810, 769, 671, 652 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}ClNO_2S$ $[M+H]^+$: 448.1133, found: 448.1130.



Compound 2l: Yield: 54 mg, 60%; A white solid; Mp: 193-195 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.65 (s, 2H), 2.27 (s, 2H), 2.42 (s, 3H), 4.55 (s, 2H), 6.25 (s, 1H), 6.44 (d, 3H, *J* = 6.8 Hz), 7.14 (d, 2H, *J* = 7.6 Hz), 7.19-7.29 (m, 4H), 7.35 (d, 2H, *J* = 7.6 Hz), 7.71 (d, 1H, *J* = 8.4 Hz); (minor) δ 1.12 (t, 1H, *J* = 7.6 Hz), 1.58 (t, 1H, *J* = 7.2 Hz), 2.37 (s, 1.5H), 4.92 (s, 1H), 6.12 (s, 0.5H), 6.51 (d, 1.5H, *J* = 6.8 Hz), 7.08 (d, 1H, *J* = 7.6 Hz), 7.19-7.29 (m, 3H), 7.71 (d, 0.5H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.4, 27.7, 31.2, 45.4, 125.7, 126.2, 127.3, 127.5, 127.6, 127.8, 129.9, 130.6, 131.2, 132.1, 132.2, 132.8, 133.9, 134.5, 135.6, 135.8, 143.7, 144.9; IR

(neat): ν 3050, 2914, 2846, 1591, 1473, 1349, 1164, 1085, 859, 815, 747, 680, 669 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}ClNO_2S$ $[M+H]^+$: 448.1133, found: 448.1137.

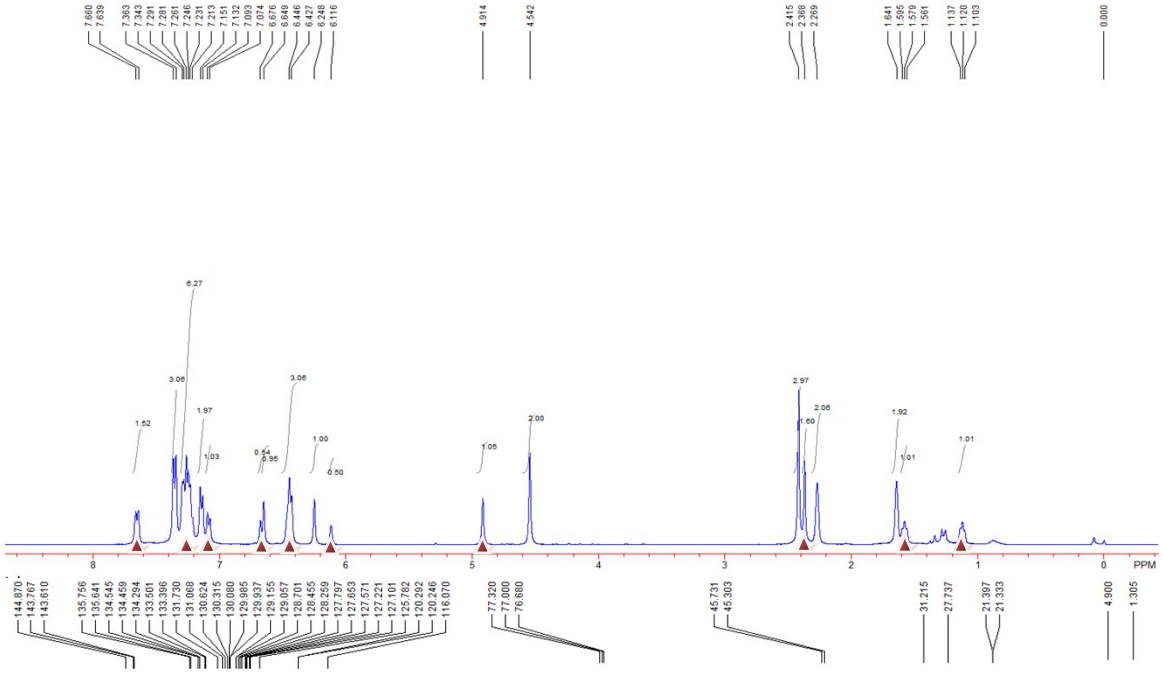


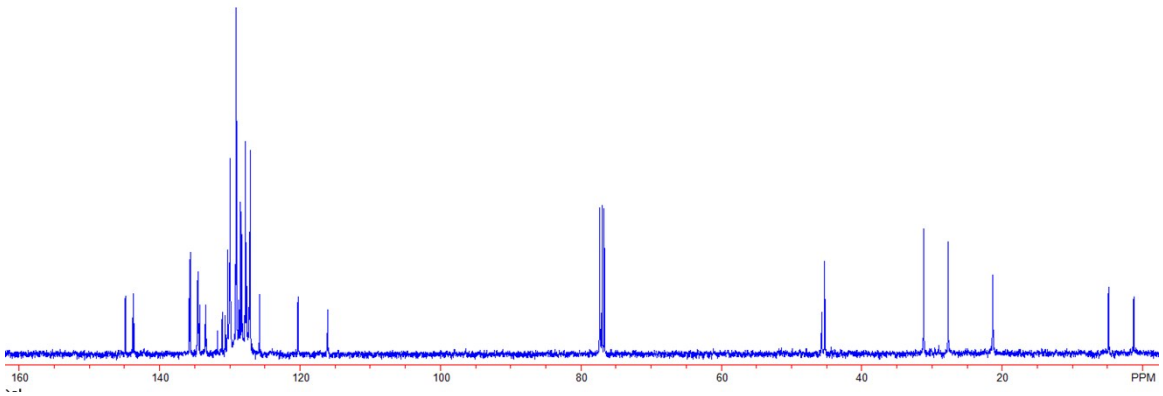


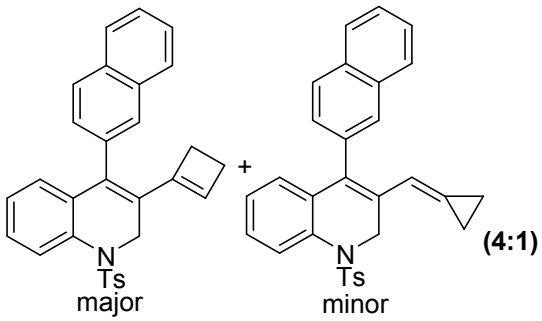
(2:1)

Compound 2m: Yield: 57 mg, 58%; A white solid; Mp: 176-178 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.64 (s, 2H), 2.27 (s, 2H), 2.41 (s, 3H), 4.54 (s, 2H), 6.25 (s, 1H), 6.45 (s, 2H), 6.65 (s, 1H), 7.14 (d, 2H, *J* = 7.6 Hz), 7.21-7.29 (m, 4H), 7.35 (d, 2H, *J* = 8.0 Hz), 7.65 (d, 1H, *J* = 8.4 Hz); (minor) δ 1.12 (t, 1H, *J* = 6.8 Hz), 1.58 (t, 1H, *J* = 6.8 Hz), 2.37 (s, 1.5H), 4.91 (s, 1H), 6.12 (s, 0.5H), 6.43 (s, 1H), 6.68 (d, 0.5H), 7.08 (d, 1H, *J* = 7.6 Hz), 7.21-7.29 (m, 2H), 7.35 (d, 1H, *J* = 8.0 Hz), 7.65 (d, 0.5H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.3, 27.7, 31.2, 45.3,

120.24, 120.29, 125.8, 127.1, 127.6, 127.8, 128.4, 129.1, 129.93, 129.98, 130.3, 131.1, 133.4, 134.2, 134.5, 135.7, 143.8, 144.9; IR (neat): ν 3052, 2927, 2833, 1602, 1470, 1351, 1164, 1086, 856, 812, 748, 701, 662 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}BrNO_2S$ $[M+H]^+$: 492.0627, found: 492.0623.

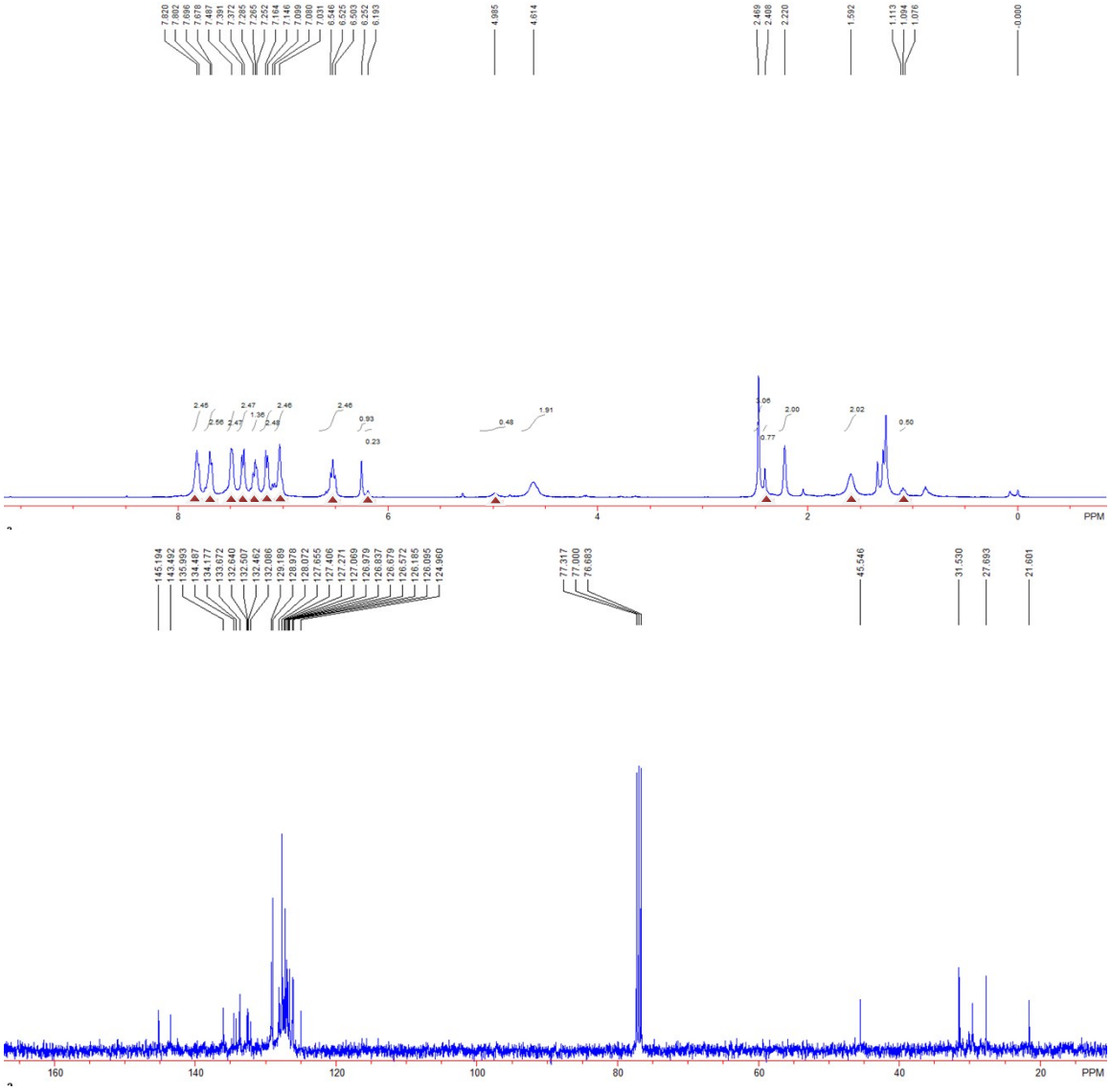




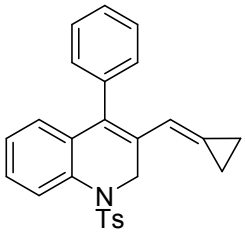


Compound 2n: Yield: 38 mg, 41%; A white solid; Mp: 212-214 °C; ^1H NMR ($CDCl_3$, 400 MHz, TMS) (major) δ 1.59 (s, 2H), 2.22 (s, 2H), 2.47 (s, 3H), 4.61 (s, 2H), 6.25 (s, 1H), 6.50-6.54 (m, 2H), 7.03 (s, 2H), 7.15 (d, 2H, *J* = 8.0 Hz), 7.25-7.28 (m, 1H), 7.38 (d, 2H, *J* = 7.6 Hz), 7.48 (s, 2H),

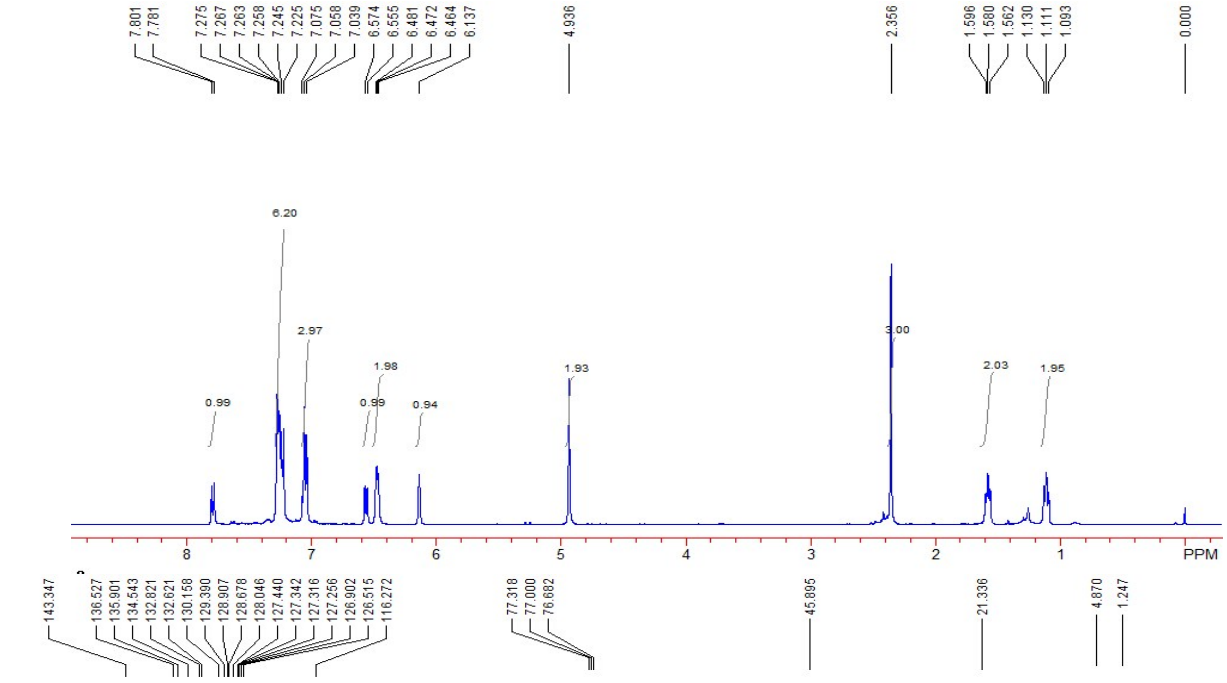
7.67-7.69 (m, 2H), 7.80-7.82 (m, 2H); (minor) δ 1.09 (t, 0.5H, *J* = 7.6 Hz), 1.59 (s, 0.5H), 2.41 (s, 0.75H), 4.97 (s, 0.5H), 6.19 (s, 0.25H), 6.50-6.54 (m, 0.5H), 7.03 (s, 0.5H), 7.15 (d, 0.5H, *J* = 8.0 Hz), 7.25-7.28 (m, 0.25H), 7.38 (d, 0.5H, *J* = 7.6 Hz), 7.48 (s, 0.5H), 7.67-7.69 (m, 0.5H), 7.80-7.82 (m, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (major) δ 21.6, 27.7, 31.5, 45.5, 124.9, 126.1, 126.2, 126.5, 126.6, 126.8, 126.9, 127.0, 127.2, 127.4, 127.6, 128.0, 128.9, 129.2, 132.1, 132.4, 132.5, 132.6, 133.6, 134.2, 134.5, 136.0, 143.5, 145.2; IR (neat): ν 3052, 2925, 2849, 1594, 1456, 1350, 1163, 1087, 862, 812, 747, 712, 666 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{26}NO_2S$ $[M+H]^+$: 464.1679, found: 464.1678.

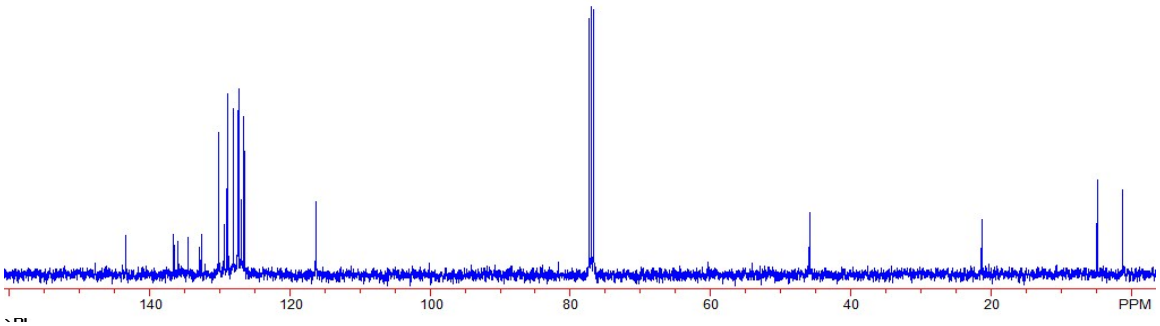


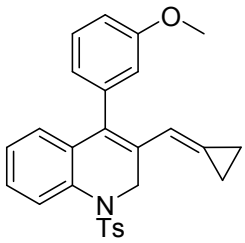
7. Spectroscopic data of the products 3



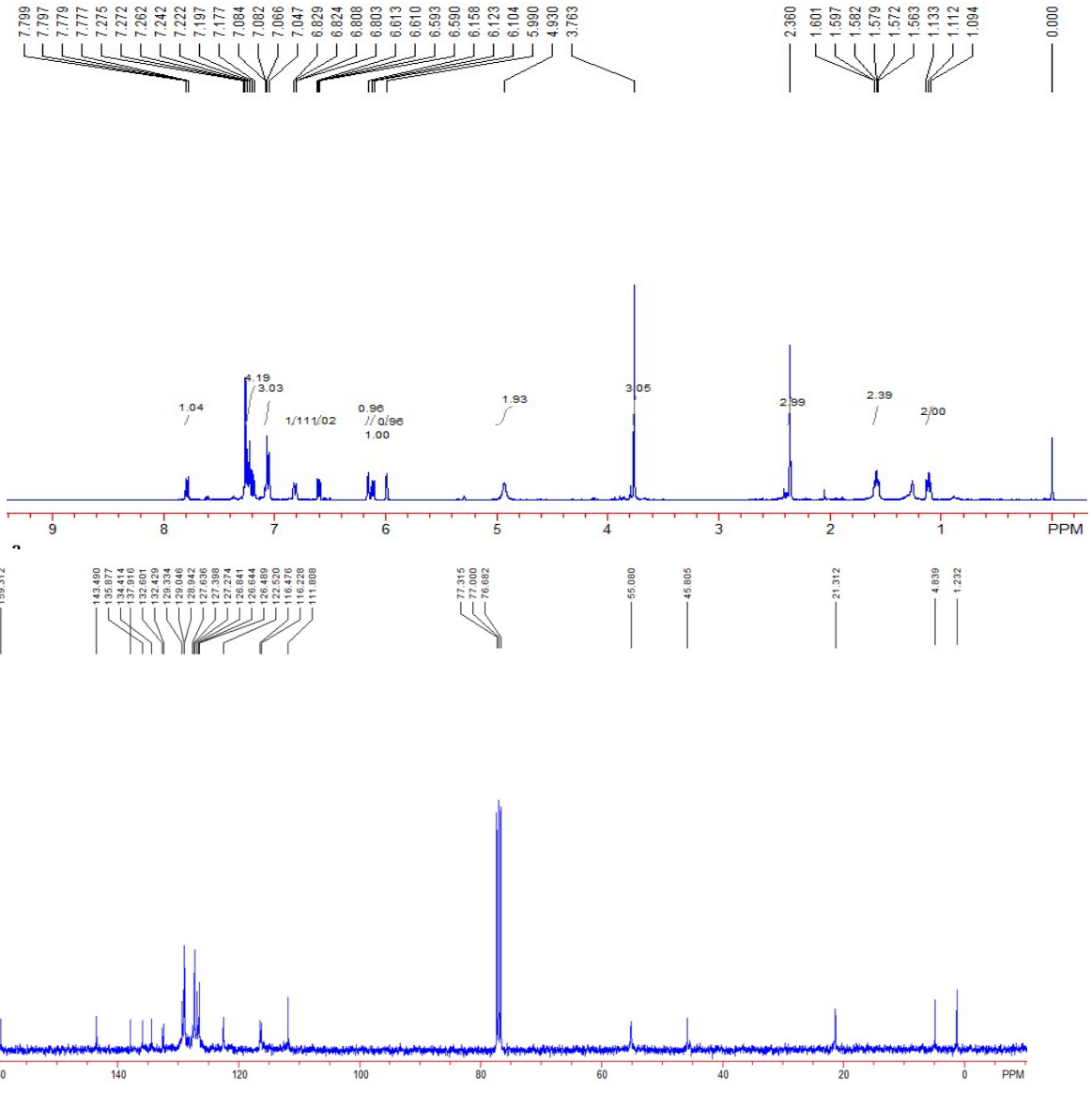
Compound 3a: Yield: 50 mg, 60%; A white solid; Mp: 171-173 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, 2H, *J* = 7.6 Hz), 1.59 (t, 2H, *J* = 7.2 Hz), 2.36 (s, 3H), 4.94 (s, 2H), 6.14 (s, 1H), 6.46-6.48 (m, 2H), 6.56 (d, 1H, *J* = 7.6 Hz), 7.03-7.07 (m, 3H), 7.22-7.27 (m, 6H), 7.79 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.2, 4.9, 21.3, 45.9, 116.2, 126.5, 126.9, 127.2, 127.31, 127.34, 127.4, 128.0, 128.6, 128.9, 129.4, 130.1, 132.6, 132.8, 134.5, 135.9, 136.5, 143.3; IR (neat): ν 2922, 2852, 1591, 1477, 1448, 1347, 1164, 1079, 853, 815, 765, 699 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{24}NO_2S$ $[M+H]^+$: 414.1522, found: 414.1524.

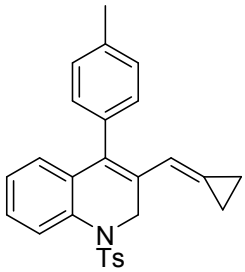




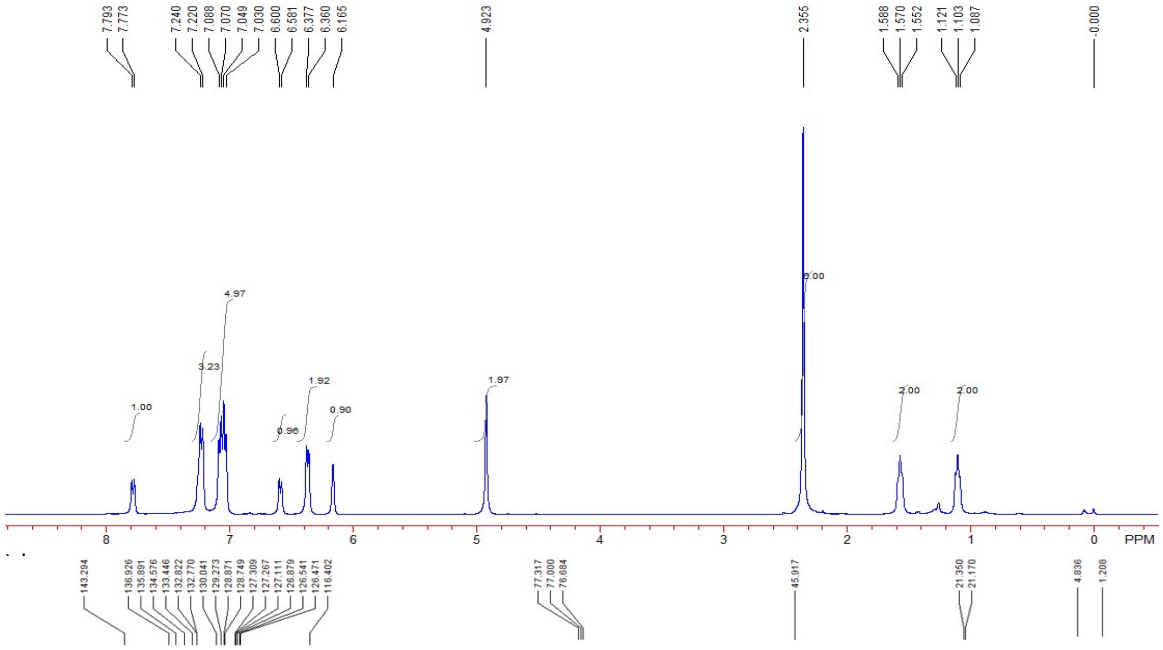


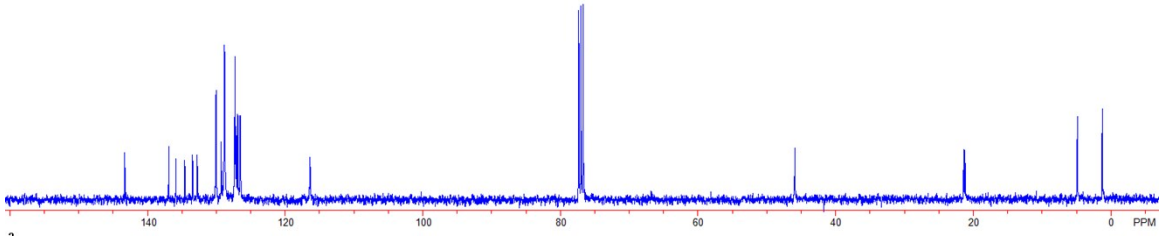
Compound 3b: Yield: 56 mg, 63%; A colorless oil; Mp: 118-120 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) 1.11 (t, 2H, J = 8.4 Hz), 1.56-1.60 (m, 2H), 2.36 (s, 3H), 3.76 (s, 3H), 4.93 (s, 2H), 5.99 (s, 1H), 6.11 (d, 1H, J = 7.6 Hz), 6.16 (s, 1H), 6.60 (dd, 1H, J_1 =8.0 Hz, J_2 = 1.2 Hz), 6.81 (dd, 1H, J_1 =8.4 Hz, J_2 = 2.0 Hz), 7.04-7.08 (m, 3H), 7.17-7.27 (m, 4H), 7.78 (dd, 1H, J_1 = 8.0 Hz, J_2 = 0.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.2, 4.9, 21.3, 45.8, 55.0, 111.8, 116.2, 116.4, 122.5, 126.4, 126.6, 127.2, 127.3, 127.6, 128.7, 128.9, 129.0, 129.3, 132.4, 132.6, 134.4, 135.8, 137.9, 143.4, 159.3; IR (neat): ν 2990, 2896, 1672, 1403, 1390, 1166, 1072, 1033, 866, 806, 772, 709, 678 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_3S$ $[M+H]^+$: 444.1628, found: 444.1629.

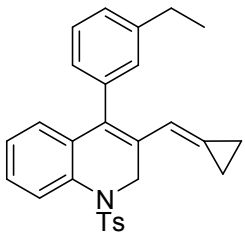




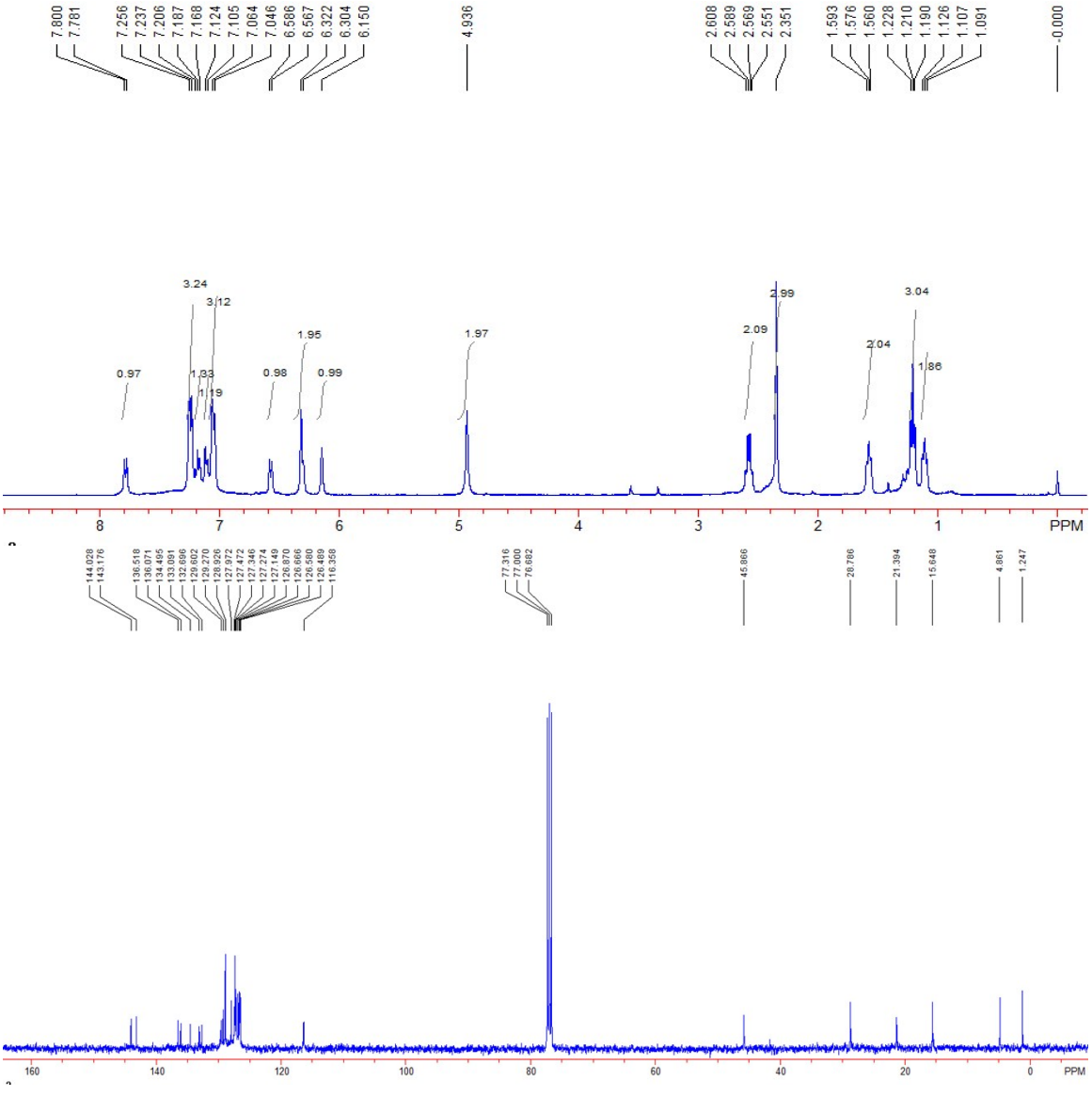
Compound 3c: Yield: 50 mg, 58%; A white solid; Mp: 175-177 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (t, 2H, *J* = 6.8 Hz), 1.57 (t, 2H, *J* = 7.2 Hz), 2.35 (s, 6H), 4.92 (s, 2H), 6.16 (s, 1H), 6.37 (d, 2H, *J* = 6.8 Hz), 6.59 (d, 1H, *J* = 7.6 Hz), 7.03-7.09 (m, 5H), 7.23 (d, 3H, *J* = 8.0 Hz), 7.78 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.2, 4.8, 21.2, 21.3, 45.9, 116.4, 126.4, 126.5, 126.8, 127.1, 127.2, 127.3, 128.7, 128.9, 129.2, 130.0, 132.7, 132.8, 133.4, 134.6, 135.9, 136.9, 143.3; IR (neat): ν 2974, 2914, 2852, 1482, 1344, 1163, 1088, 1078, 854, 813, 775, 682, 670, 654 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_2S$ $[M+H]^+$: 428.1679, found: 428.1677.

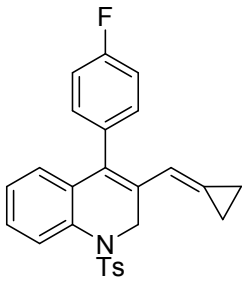




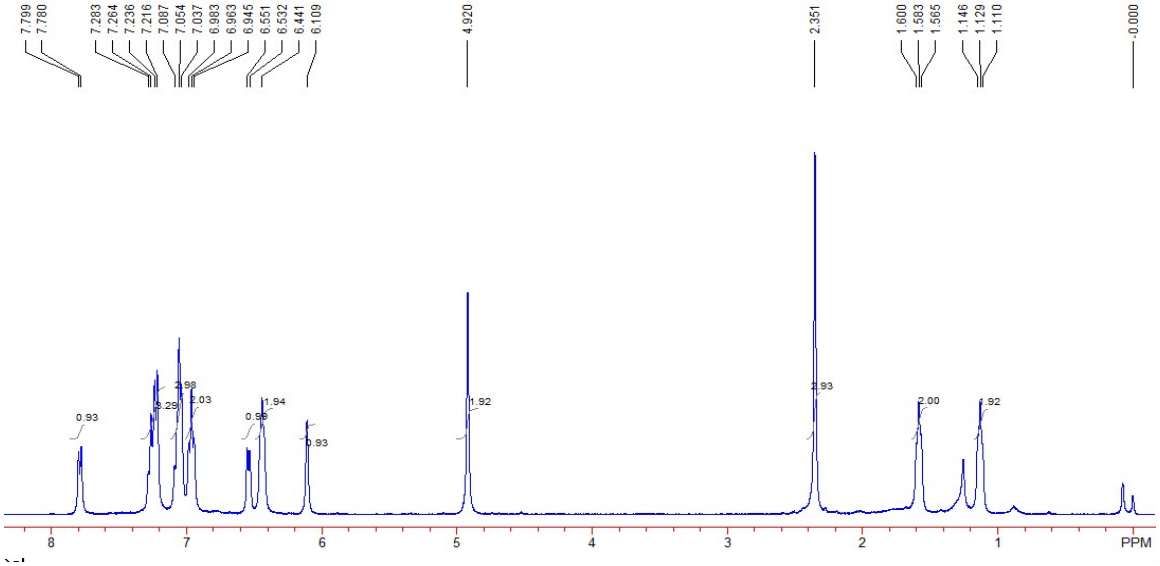


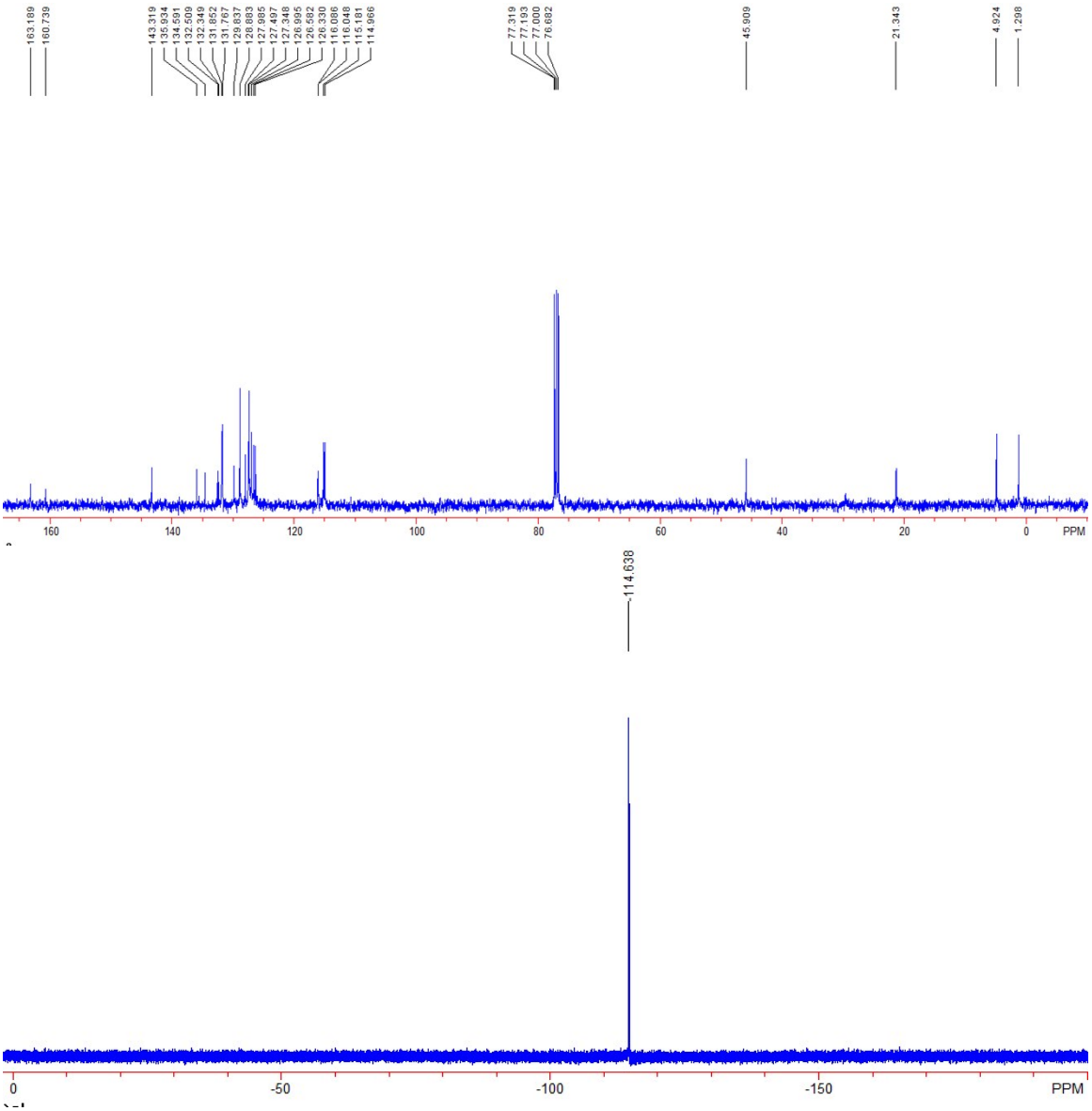
Compound 3d: Yield: 40 mg, 45%; A white solid; Mp: 112-114 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, 2H, J = 7.2 Hz), 1.21 (t, 3H, J = 8.0 Hz), 1.57 (t, 2H, J = 7.6 Hz), 2.35 (s, 3H), 2.58 (q, 2H, J = 7.6 Hz), 4.94 (s, 2H), 6.15 (s, 1H), 6.30-6.32 (m, 2H), 6.57 (d, 1H, J = 7.2 Hz), 7.05 (d, 3H, J = 7.6 Hz), 7.11 (d, 1H, J = 7.6 Hz), 7.19 (dd, 1H, J_1 = J_2 = 7.6 Hz), 7.24 (d, 3H, J = 7.6 Hz), 7.79 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.2, 4.9, 15.6, 21.4, 28.8, 45.9, 116.3, 126.5, 126.6, 126.7, 126.9, 127.1, 127.2, 127.3, 127.4, 127.9, 128.9, 129.2, 129.6, 132.7, 133.1, 134.5, 136.1, 136.5, 143.2, 144.0; IR (neat): ν 3042, 2966, 2854, 1597, 1479, 1349, 1162, 1089, 863, 804, 765, 710, 677, 656 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{28}NO_2S$ $[M+H]^+$: 442.1835, found: 442.1837.

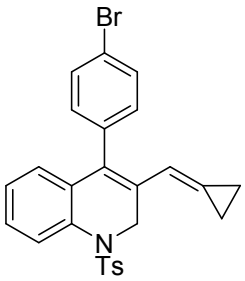




Compound 3f: Yield: 47 mg, 55%; A white solid; Mp: 180-182 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (t, 2H, *J* = 7.6 Hz), 1.58 (t, 2H, *J* = 7.2 Hz), 2.35 (s, 3H), 4.92 (s, 2H), 6.11 (s, 1H), 6.44 (s, 2H), 6.54 (d, 1H, *J* = 7.6 Hz), 6.96 (dd, 2H, $J_1 = J_2$ = 8.0 Hz), 7.03-7.09 (m, 3H), 7.21-7.28 (m, 3H), 7.79 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.3, 4.9, 21.3, 45.9, 115.0 (d, *J* = 21.5 Hz), 116.0, 126.3, 126.6, 127.0, 127.3, 127.5, 128.0, 128.9, 129.8, 131.7, 131.8, 132.3 (d, *J* = 3.4 Hz), 132.5, 134.6, 135.9, 143.3, 162.0 (d, *J* = 225.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -114.64 (s); IR (neat): ν 3066, 2923, 2850, 1600, 1504, 1471, 1341, 1155, 1087, 1013, 858, 833, 808, 763, 682, 671, 657 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}FNO_2S$ $[M+H]^+$: 432.1428, found: 432.1430.

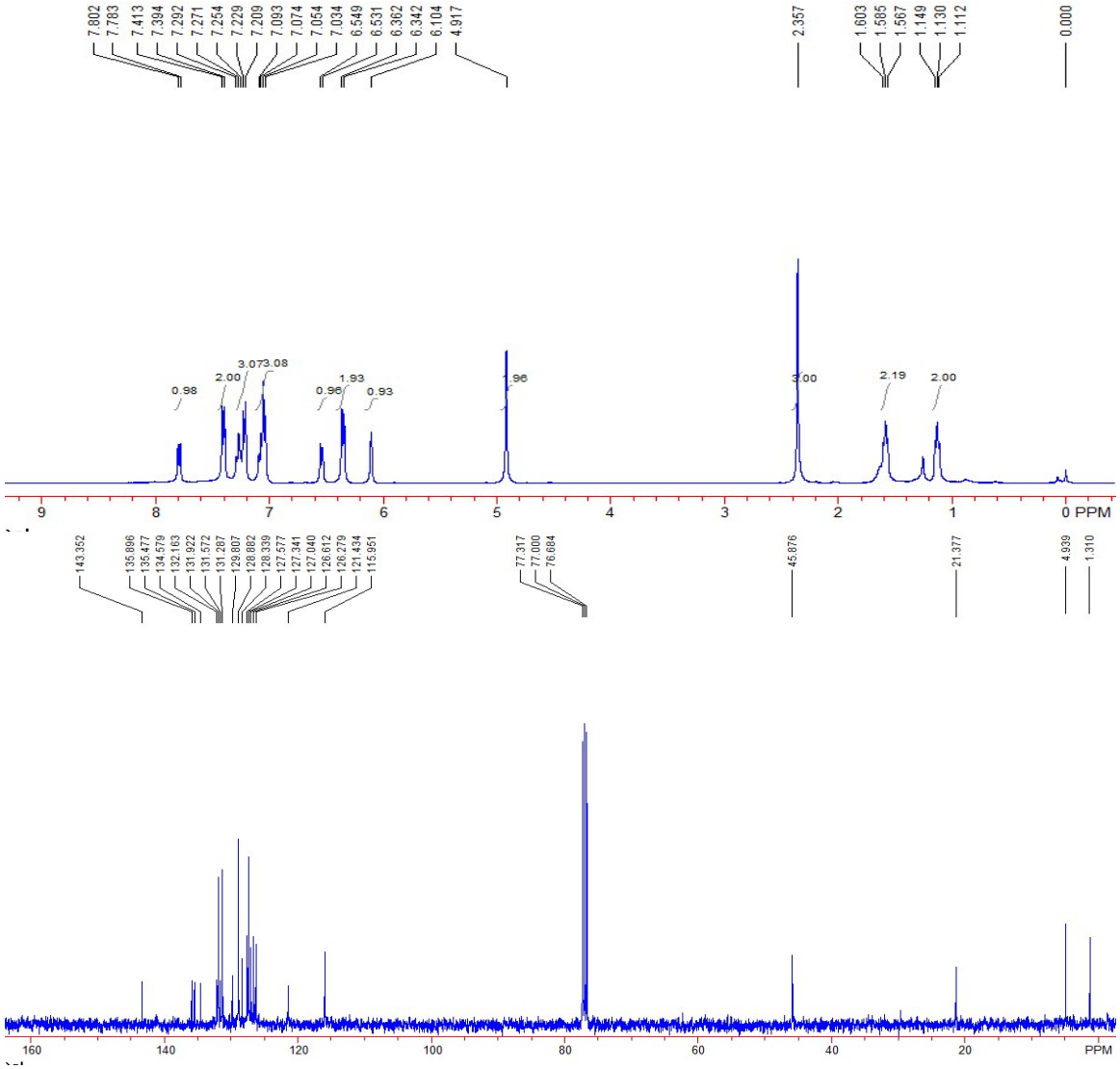


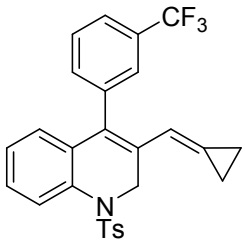




Compound 3g: Yield: 69 mg, 70%; A white solid; Mp: 196-198 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (t, 2H, *J* = 7.6 Hz), 1.58 (t, 2H, *J* = 7.2 Hz), 2.35 (s, 3H), 4.92 (s, 2H), 6.10 (s, 1H), 6.35 (d, 2H, *J* = 8.0 Hz), 6.54 (d, 1H, *J* = 7.2 Hz), 7.03-7.09 (m, 3H), 7.20-7.29 (m, 3H), 7.40 (d, 2H, *J* = 7.6 Hz), 7.79 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.3, 4.9, 21.4, 45.9, 115.9, 121.4, 126.3, 126.6, 127.0, 127.3, 127.6, 128.3, 128.9, 129.8, 131.3, 131.6, 131.9, 132.2, 134.6, 135.5, 135.9, 143.3; IR (neat): ν 2979, 2919, 2849, 1597, 1345, 1163, 1088, 1078, 854, 823,

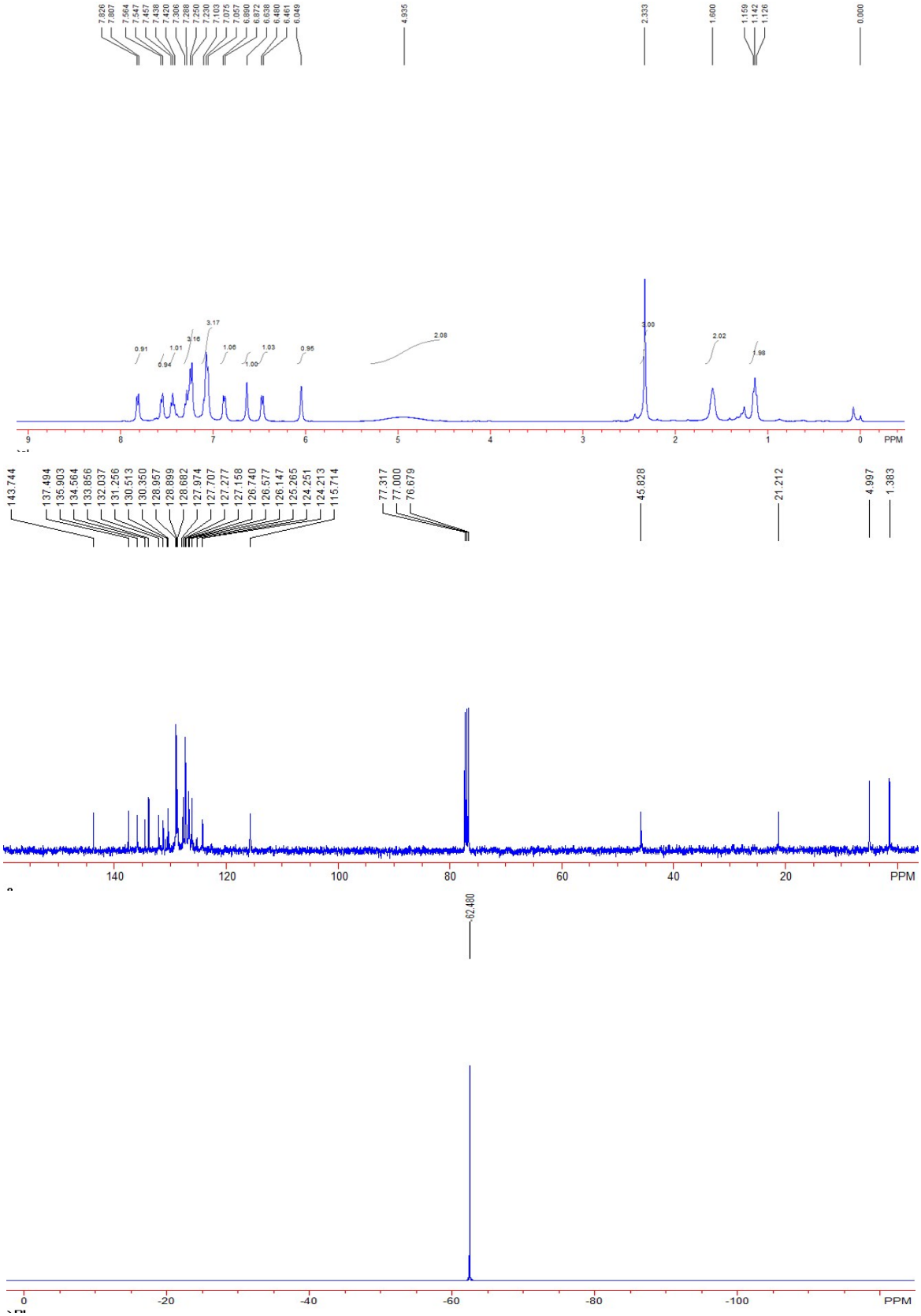
799, 774, 741, 704, 678 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}BrNO_2S$ $[M+H]^+$: 492.0627, found: 492.0620.

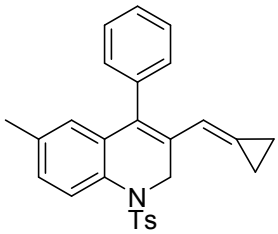




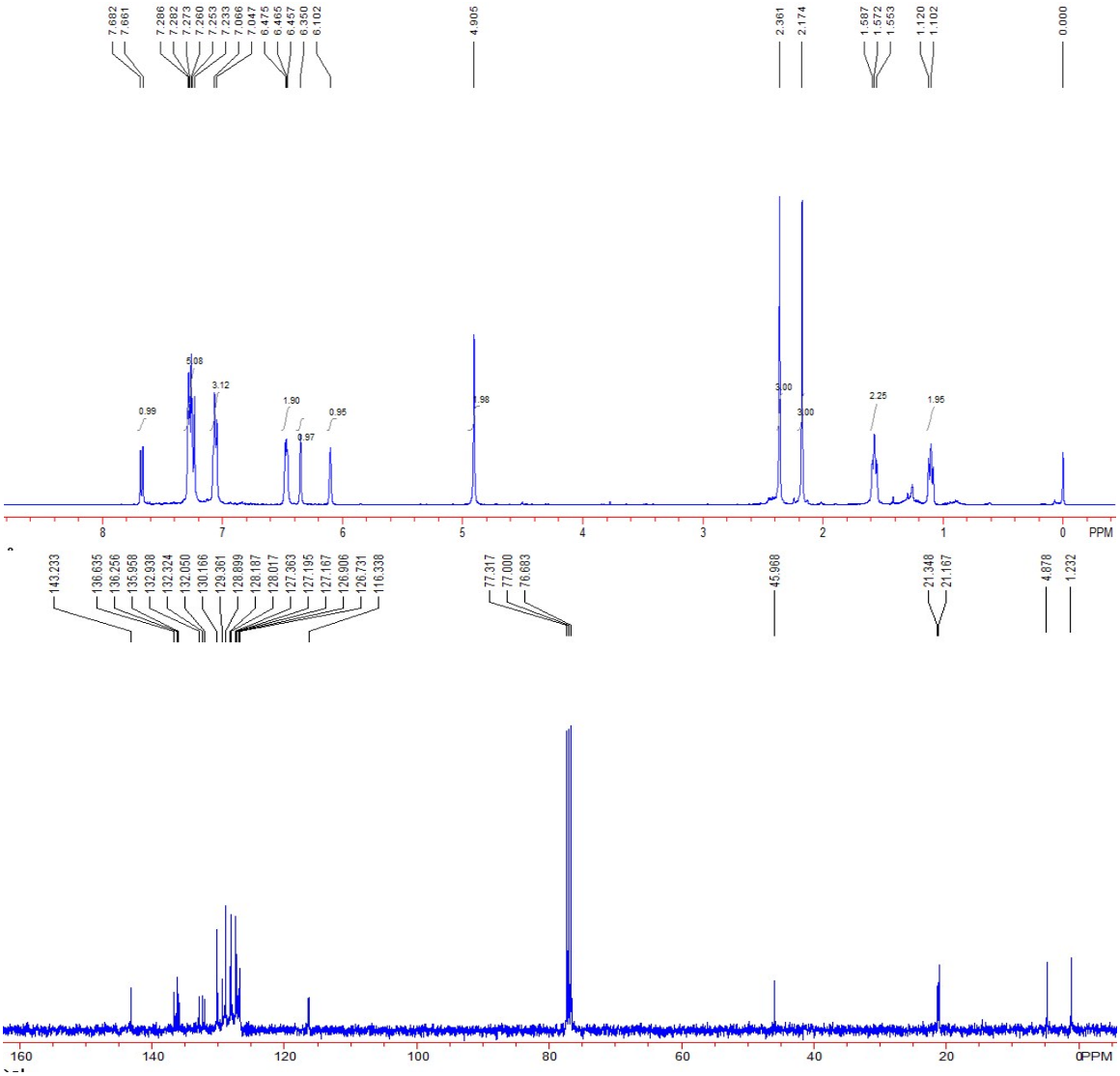
Compound 3h: Yield: 68 mg, 71%; A white solid; Mp: 167-169 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.14 (t, 2H, J = 6.8 Hz), 1.60 (s, 2H), 2.33 (s, 3H), 4.94 (s, 2H), 6.05 (s, 1H), 6.47 (d, 1H, J = 7.6 Hz), 6.64 (s, 1H), 6.88 (d, 1H, J = 7.2 Hz), 7.05-7.10 (m, 3H), 7.23-7.30 (m, 3H), 7.43 (dd, 1H, J_1 = J_2 = 7.2 Hz), 7.55 (d, 1H, J = 6.8 Hz), 7.81 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.4, 5.0, 21.2, 45.8, 115.7, 124.2 (q, J = 3.8 Hz), 126.1, 126.5, 126.6 (q, J = 270.9 Hz), 126.7, 127.1, 127.2, 127.7, 128.7 (q, J = 27.5 Hz), 128.9, 130.3, 130.5, 131.2, 132.0, 133.6, 134.5, 135.9, 137.5, 143.7; ^{19}F NMR ($CDCl_3$,

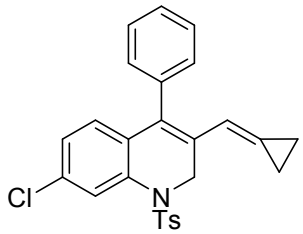
376 MHz, $CFCl_3$) δ -62.48 (s); IR (neat): ν 3060, 2925, 2852, 1479, 1350, 1337, 1328, 1304, 1182, 1161, 1119, 1090, 1072, 813, 800, 790, 766, 703, 683,668, 660, 654 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{23}F_3NO_2S$ $[M+H]^+$: 482.1396, found: 482.1399.



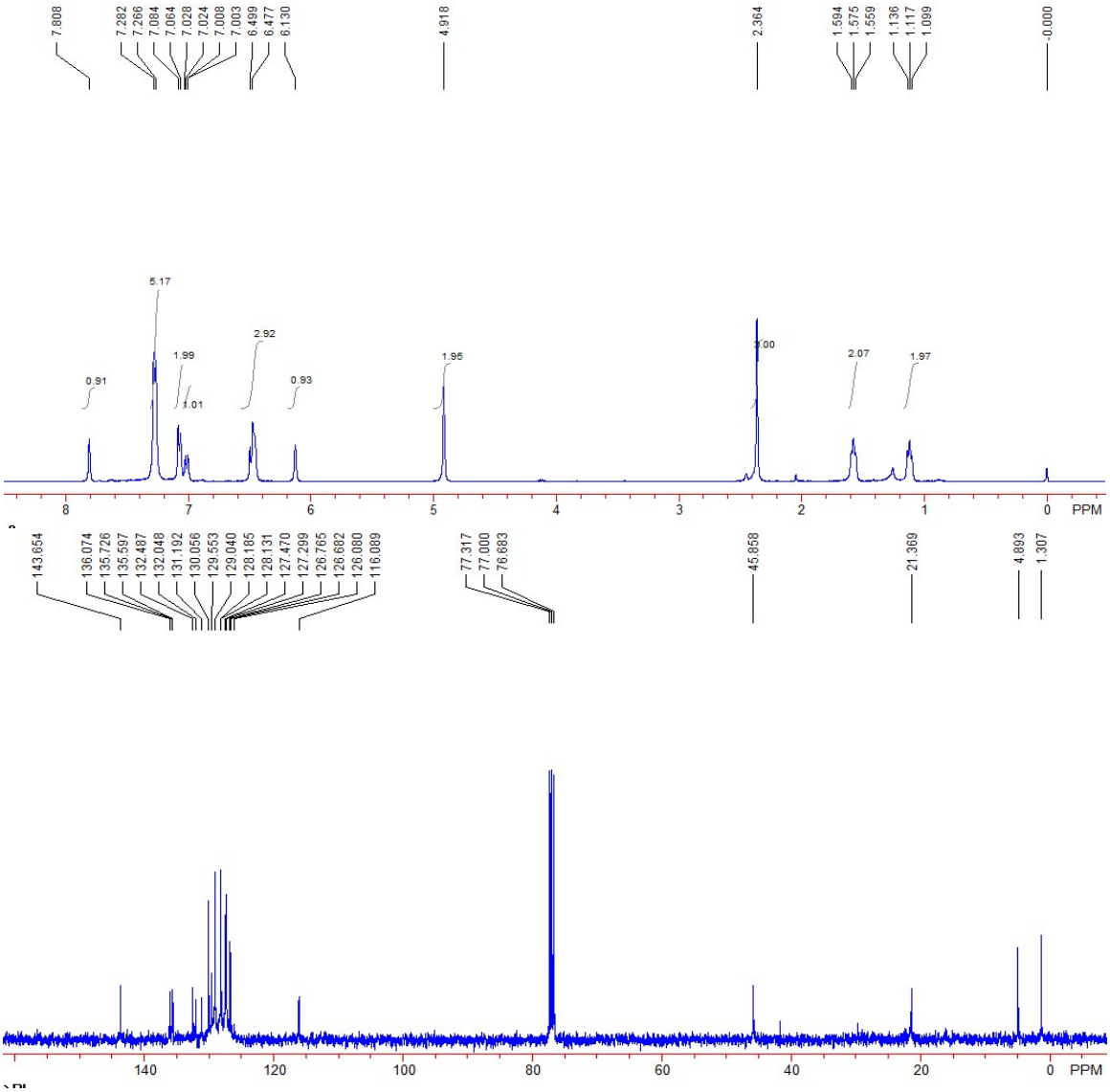


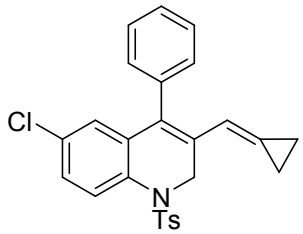
Compound 3i: Yield: 44 mg, 52%; A white solid; Mp: 175-177 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) 1.10 (t, 2H, J = 8.0 Hz), 1.57 (t, 2H, J = 7.6 Hz), 2.17 (s, 3H), 2.36 (s, 3H), 4.91 (s, 2H), 6.10 (s, 1H), 6.35 (s, 1H), 6.45-6.47 (m, 2H), 7.05 (d, 3H, J = 7.6 Hz), 7.23-7.28 (m, 5H), 7.67 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.2, 4.9, 21.2, 21.3, 45.9, 116.3, 126.7, 126.9, 127.16, 127.19, 127.3, 128.0, 128.2, 128.9, 129.3, 130.1, 132.0, 132.3, 132.9, 135.9, 136.2, 136.6, 143.2; IR (neat): ν 2919, 2849, 1599, 1484, 1340, 1160, 1086, 866, 828, 812, 763, 704, 678, 659 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_2S$ $[M+H]^+$: 428.1679, found: 428.1676.



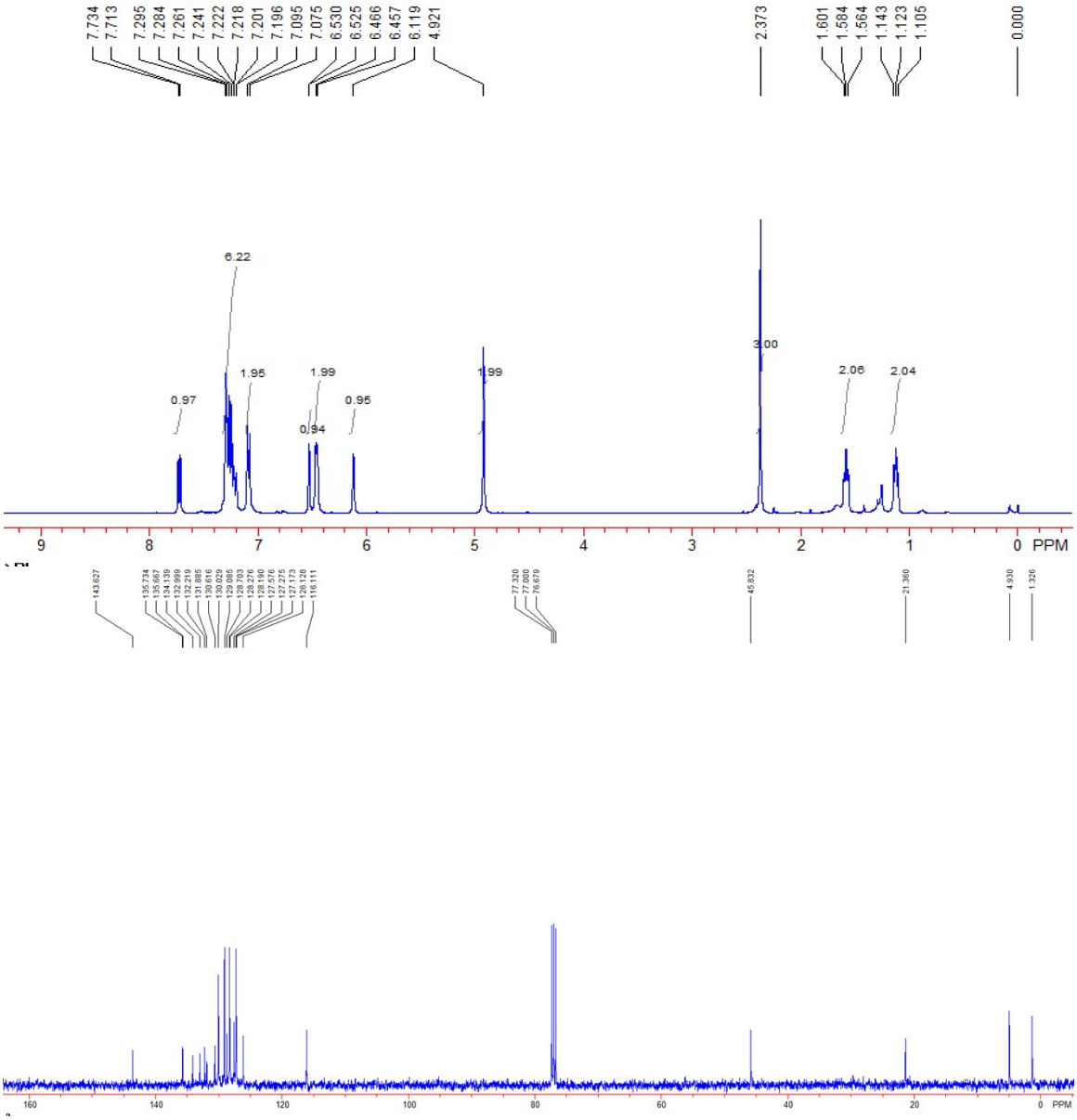


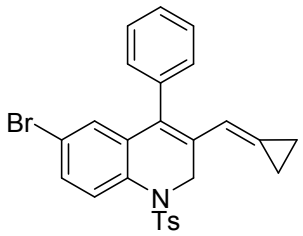
Compound 3k: Yield: 46 mg, 51%; A white solid; Mp: 184-186 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, 2H, *J* = 7.6 Hz), 1.57 (t, 2H, *J* = 7.6 Hz), 2.36 (s, 3H), 4.92 (s, 2H), 6.13 (s, 1H), 6.46-6.50 (m, 3H), 7.00-7.02 (m, 1H), 7.07 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 5H, *J* = 6.4 Hz), 7.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.3, 4.9, 21.3, 45.8, 116.1, 126.1, 126.6, 126.7, 127.3, 127.4, 128.1, 128.2, 129.0, 129.5, 130.0, 131.2, 132.0, 132.5, 135.6, 135.7, 136.1, 143.6; IR (neat): ν 3060, 2972, 2852, 1484, 1352, 1166, 1091, 886, 810, 777, 701, 651 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}ClNO_2S$ $[M+H]^+$: 448.1133, found: 448.1132.



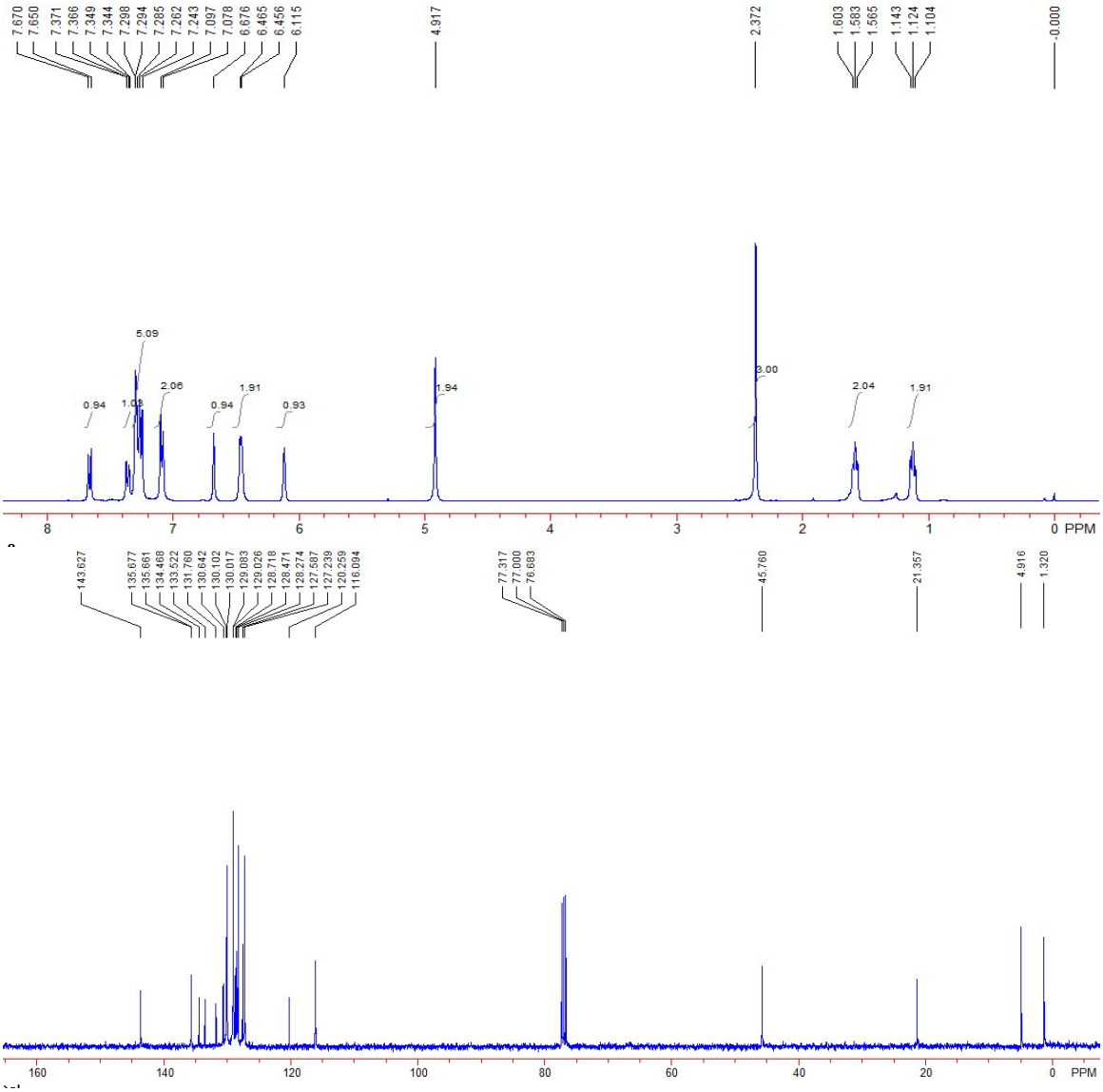


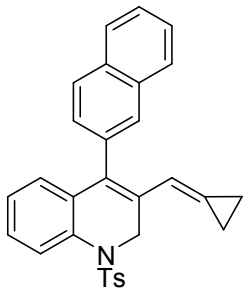
Compound 3l: Yield: 54 mg, 60%; A white solid; Mp: 187-189 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) 1.11 (t, 2H, J = 7.2 Hz), 1.58 (t, 2H, J = 8.0 Hz), 2.37 (s, 3H), 4.92 (s, 2H), 6.12 (s, 1H), 6.46 (d, 2H, J = 3.6 Hz), 6.53 (d, 1H, J = 2.0 Hz), 7.08 (d, 2H, J = 8.0 Hz), 7.19-7.29 (m, 6H), 7.72 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.3, 4.9, 21.3, 45.8, 116.1, 126.1, 127.1, 127.2, 127.5, 128.2, 128.3, 128.7, 129.1, 130.0, 130.6, 131.9, 132.2, 133.0, 134.1, 135.6, 135.7, 143.6; IR (neat): ν 3060, 2925, 2852, 1599, 1471, 1348, 1347, 1165, 1085, 856, 816, 779, 699, 667 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{26}ClN_2O_2S$ $[M+NH_4]^+$: 465.1398, found: 465.1394.



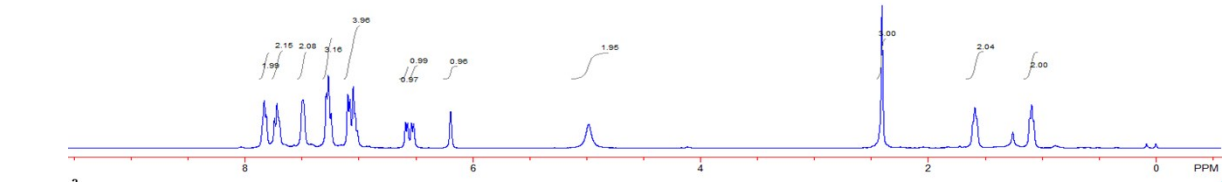


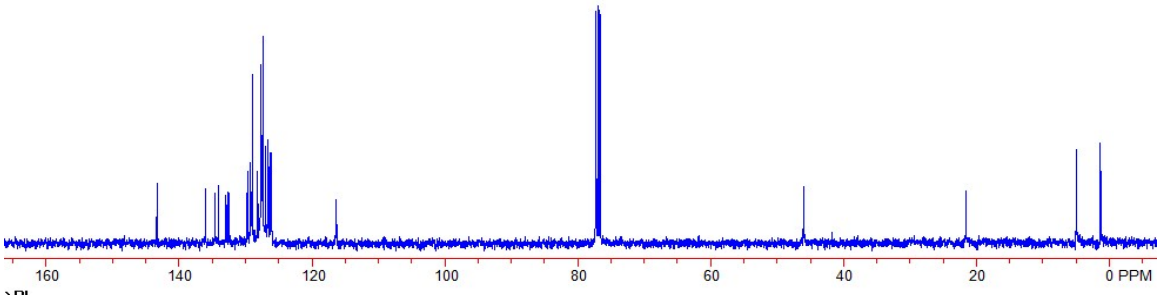
Compound 3m: Yield: 61 mg, 62%; A white solid; Mp: 195-197 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, 2H, *J* = 8.0 Hz), 1.58 (t, 2H, *J* = 7.6 Hz), 2.37 (s, 3H), 4.92 (s, 2H), 6.11 (s, 1H), 6.45 (d, 2H, *J* = 7.6 Hz), 6.68 (s, 1H), 7.08 (d, 2H, *J* = 8.0 Hz), 7.24-7.30 (m, 5H), 7.35 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 7.66 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.3, 4.9, 21.3, 45.7, 116.1, 120.2, 127.2, 127.6, 128.3, 128.5, 128.7, 129.02, 129.08, 130.0, 130.1, 130.6, 131.7, 133.5, 134.5, 135.66, 135.67, 143.6; IR (neat): ν 2974, 2912, 2854, 1599, 1342, 1160, 1086, 864, 814, 762, 704, 681, 660 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}BrNO_2S$ $[M+H]^+$: 492.0627, found: 492.0620.



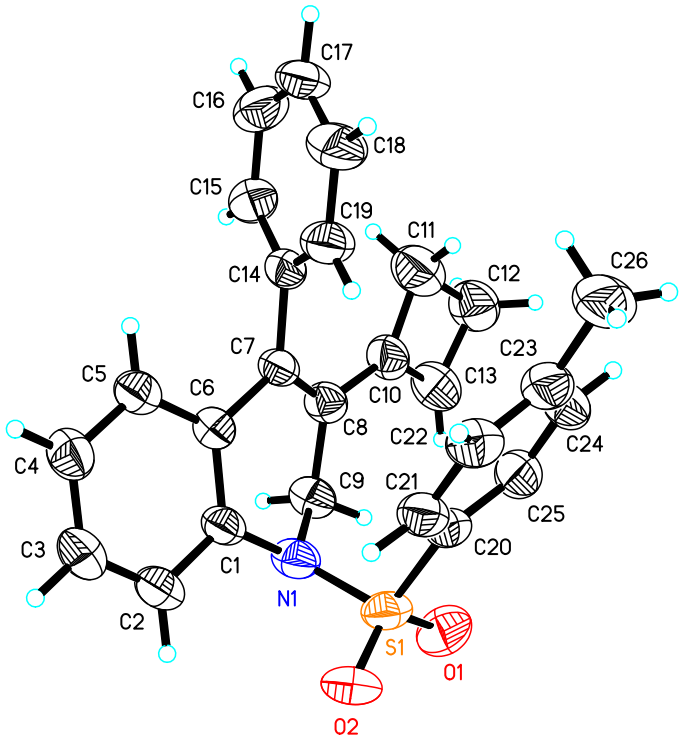


Compound 3n: Yield: 48 mg, 52%; A white solid; Mp: 212-214 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (t, 2H, *J* = 7.6 Hz), 1.59 (s, 2H), 2.41 (s, 3H), 4.98 (s, 2H), 6.19 (s, 1H), 6.53 (d, 1H, *J* = 8.0 Hz), 6.58 (d, 1H, *J* = 7.6 Hz), 7.01-7.10 (m, 4H), 7.24-7.29 (m, 3H), 7.49 (s, 2H), 7.72-7.74 (m, 2H), 7.81-7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.2, 4.9, 21.5, 46.0, 116.3, 126.1, 126.2, 126.5, 126.6, 126.9, 127.4, 127.5, 127.6, 127.7, 128.1, 128.9, 129.2, 129.7, 132.4, 132.6, 132.7, 133.0, 134.0, 134.6, 136.0, 143.3; IR (neat): ν 3063, 2922, 2844, 1599, 1477, 1348, 1164, 1082, 823, 807, 770, 682, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{26}NO_2S$ $[M+H]^+$: 464.1679, found: 464.1678.



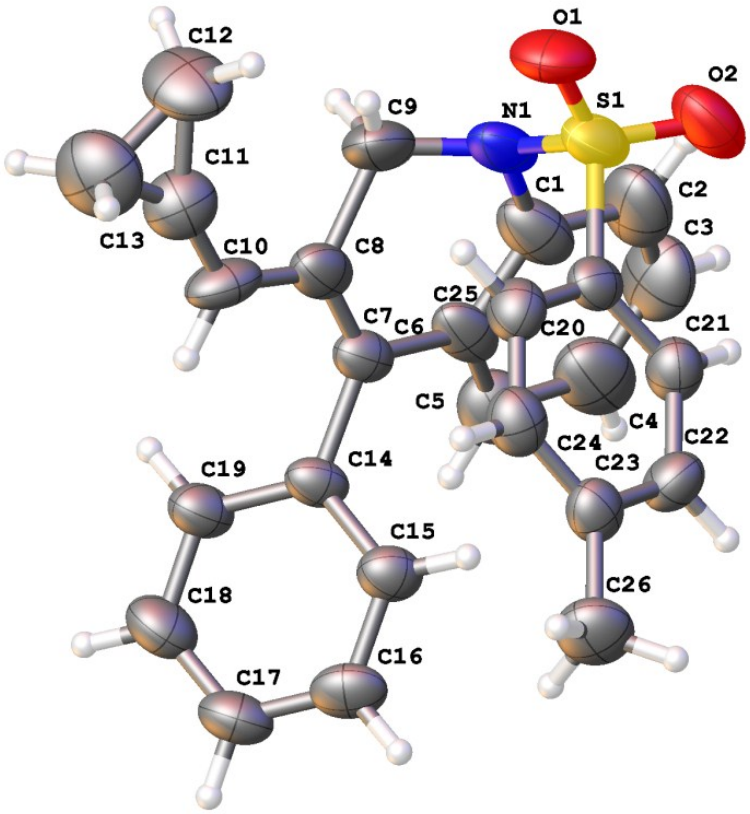


X-ray Crystal Data of 2a



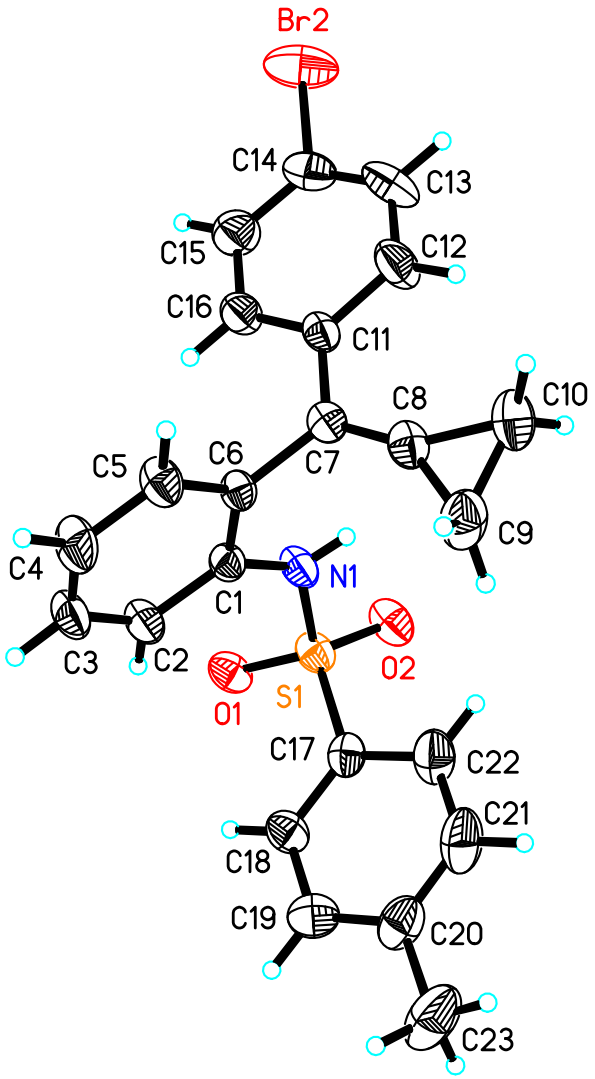
The crystal data of **2a** have been deposited in CCDC with number 1575471. Empirical formula: $C_{26}H_{23}NO_2S$, Formula weight: 413.51, Crystal system: Monoclinic, Space group: P 21/n, Unit cell dimensions: a = 11.7526(16) Å, α = 90°; b = 13.4984(19) Å, β = 92.440(4)°; c = 13.5265(19) Å, γ = 90°. Volume: 2143.9(5) Å3, Z = 4, Density (calculated): 1.281 Mg/m3, F(000) = 872, Crystal size: 0.100 x 0.070 x 0.040 mm3, Final R indices [I>2sigma(I)]: R1 = 0.0757, wR2 = 0.1824.

X-ray Crystal Data of 3a



The crystal data of **3a** have been deposited in CCDC with number 1580620. Empirical formula: $C_{26}H_{23}NO_2S$, Formula weight: 413.51, Crystal system: Triclinic, Space group: P-1, Unit cell dimensions: a = 9.447(4) Å, α = 76.431(8)°; b = 10.559(5) Å, β = 77.755(9)°; c = 12.512(6) Å, γ = 64.585(7)°. Volume: 1087.1(9) Å3, Z = 2, Density (calculated): 1.263 Mg/m3, F(000) = 436, Crystal size: 0.15 x 0.12 x 0.05 mm3, Final R indices [I>2sigma(I)]: R1 = 0.0964, wR2 = 0.2442.

X-ray Crystal Data of starting material S3



The crystal data of **starting material S3** have been deposited in CCDC with number 1535807. Empirical Formula: $C_{23}H_{20}BrNO_2S$; Formula Weight: 454.37; Crystal Color, Habit: colorless, Crystal Dimensions: 0.150 x 0.130 x 0.090 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 10.0726(19)Å, b = 10.735(2)Å, c = 19.604(4)Å, α = 82.045(4)°, β = 86.428(5)°, γ = 81.212(5)°, V = 2073.0(7)$Å^3$; Space group: P -1; Z = 4; D_{calc}= 1.456 g/cm^3; F_{000} = 928; Final R indices [I>2sigma(I)] R1 = 0.0618, wR2 = 0.1248.