Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iron-catalyzed or iodine-induced intramolecular halocyclization of *N*-vinyl-tethered methylenecyclopropanes: Facile access to halogenated 1,2-dihydroquinolines

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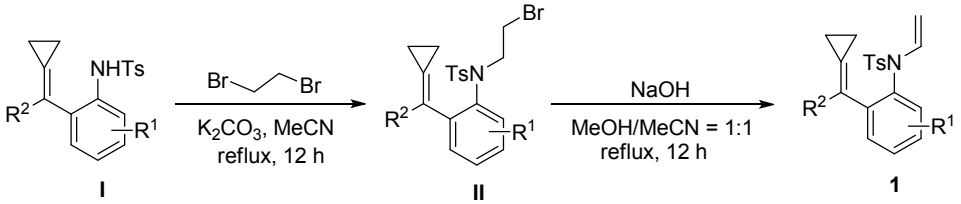
Content

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. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN and 1,2-dichloroethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. 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

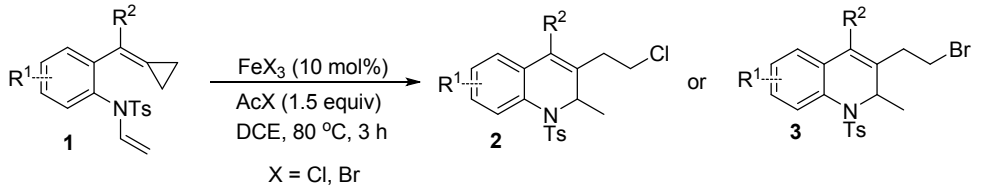
Substrates were synthesized from MCPs[1] by the procedure shown below:



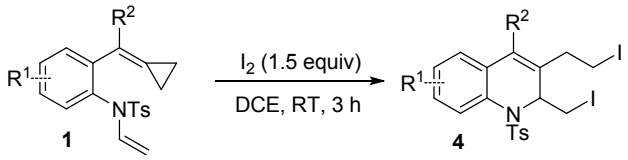
To a solution of MCPs **I** (1.0 equiv, 2 mmol) in MeCN (15 mL) was added K_2CO_3 (5.0 equiv, 10 mmol) and 1,2-dibromoethane (5.0 equiv, 10 mmol). The mixture was heated and stirred for 12 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue, which is purified by chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product **II**.

Elimination step: NaOH (5.0 equiv, 5.0 mmol) was added to solution of substrate **II** (1.0 equiv, 1.0 mmol) in MeOH/MeCN (1/1, 20 mL). The mixture was heated and stirred for 12 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue, which is purified by a chromatography on silica gel (PE/EA = 10/1) to afford the corresponding ***N***-vinylbenzenesulfonamide product **1**.

3. General procedure for the preparation of 2,3 and 4



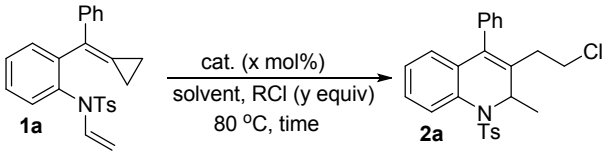
In a Schlenk tube, *N*-vinylbenzenesulfonamide substrate **1** (1.0 equiv, 0.2 mmol), FeX_3 (0.1 equiv, 0.02 mmol) was added under Ar. Then, the solvent DCE (2.0 mL) and AcX (1.5 equiv, 0.3 mmol) were added. The mixture was stirred at 80 °C for 3 h. Upon completion, the solvent was evaporated under vacuum, and the residue was purified by a column chromatography on silica gel (300-400) using PE/EA (20/1, v/v) as an eluent to give pure product **2** or **3**.



In a Schlenk tube, *N*-vinylbenzenesulfonamide substrate **1** (1.0 equiv, 0.2 mmol), I_2 (0.1 equiv, 0.02 mmol) was added under Ar. Then, the solvent DCE (2.0 mL) was added. The mixture was stirred at room temperature for 3 h. Upon completion, the solvent was evaporated under vacuum, and the residue was purified by a column chromatography on silica gel (300-400) using PE/EA (20/1, v/v) as an eluent to give pure product **4**.

4. Details for Condition Optimization

Table S1. Optimization of the reaction conditions

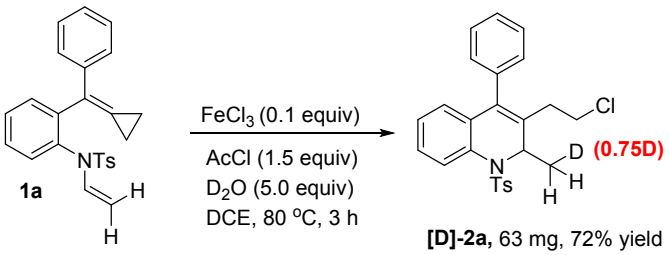


entry[a]	cat.	x	Solvent	RCl (y equiv)	t [h]	Yield [%][b]
1	$NiCl_2(dppe)$	10	DCE	-	5	NR
2	CuOTf	10	DCE	-	5	NR
3	$Fe(acac)_3$	10	DCE	-	5	NR
4	$Fe(OTf)_2$	10	DCE	-	5	complex
5	$FeCl_3$	10	DCE	-	5	**23**
6	$FeCl_3$	50	DCE	-	5	87
7	$FeCl_3$	10	DCE	TMSCl (1.5)	5	23
8	$FeCl_3$	10	DCE	NaCl (1.5)	5	23
9	$FeCl_3$	10	DCE	AcCl (1.5)	5	80
10	$FeCl_3$	10	DCE	AcCl (1.5)	3	87
11	-	-	DCE	AcCl (1.5)	3	53
12	$FeCl_3$	10	THF	AcCl (1.5)	3	< 5
13	$FeCl_3$	10	MeCN	AcCl (1.5)	3	< 5
14	$FeCl_3$	10	$MeCO_2Et$	AcCl (1.5)	3	46
15	$FeCl_3$	10	Toluene	AcCl (1.5)	3	84
16	-	-	DCE	NaI (1.5)	3	NR
17	-	-	DCE	KI (1.5)	3	NR

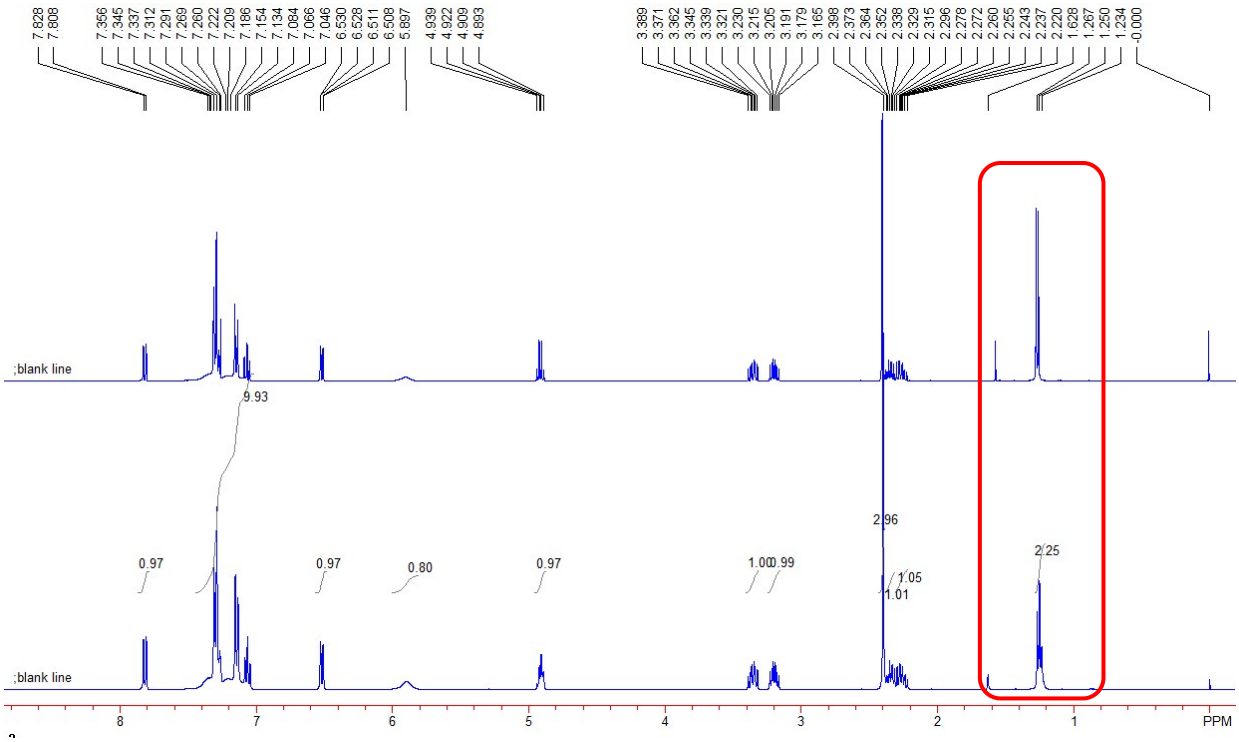
[a] Substrate **2a** (0.2 mmol), cat. (x mol%), RCl (y equiv) and the corresponding solvent (2 mL).
[b] Isolated yields.

5. Mechanistic studies

5.1 Deuterium isotope labeling studies



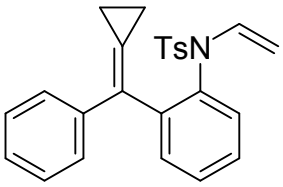
In a Schlenk tube, substrate **1a** (1.0 equiv, 0.2 mmol), $FeCl_3$ (0.1 equiv, 0.02 mmol) was added under Ar. Then, the solvent DCE (2.0 mL), D_2O (5.0 equiv, 1.0 mmol) and AcCl (1.5 equiv, 0.3 mmol) were added. The mixture was stirred at 80 °C for 3 h. Upon completion, the solvent was evaporated under vacuum, and the residue was purified by column chromatography on silica gel (300-400) using PE/EA (20/1, v/v) as an eluent to afford [**D]-2a** as a white solid in 72% yield (63 mg) along with 75% D content.



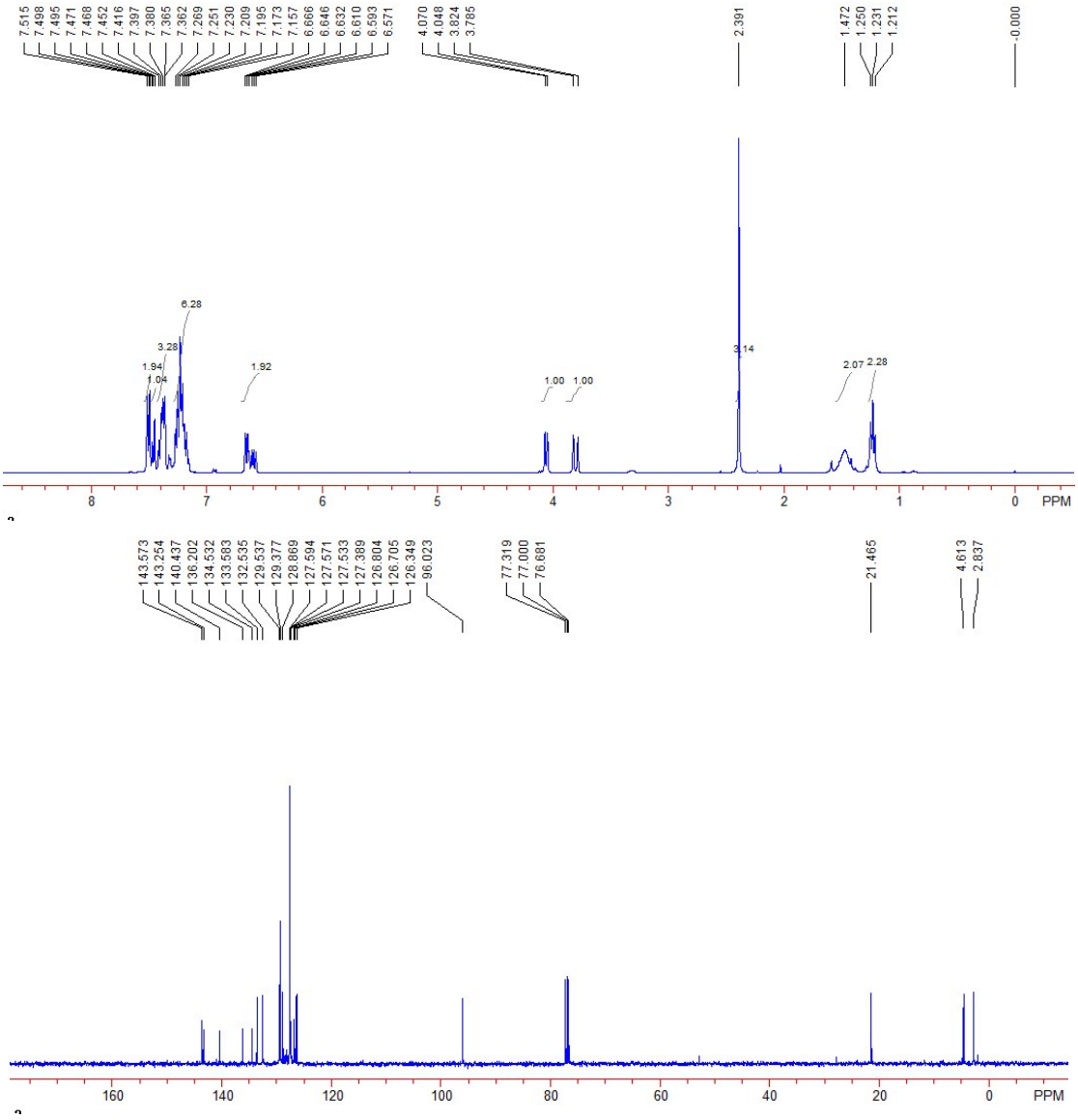
References:

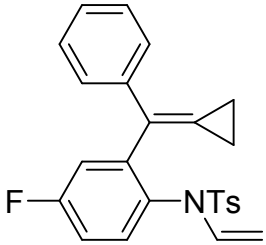
[1] K. Chen, R. Sun, Q. Xu, Y. Wei, M. Shi, *Org. Biomol. Chem.* **2013**, *11*, 3949-3953.

Spectroscopic data

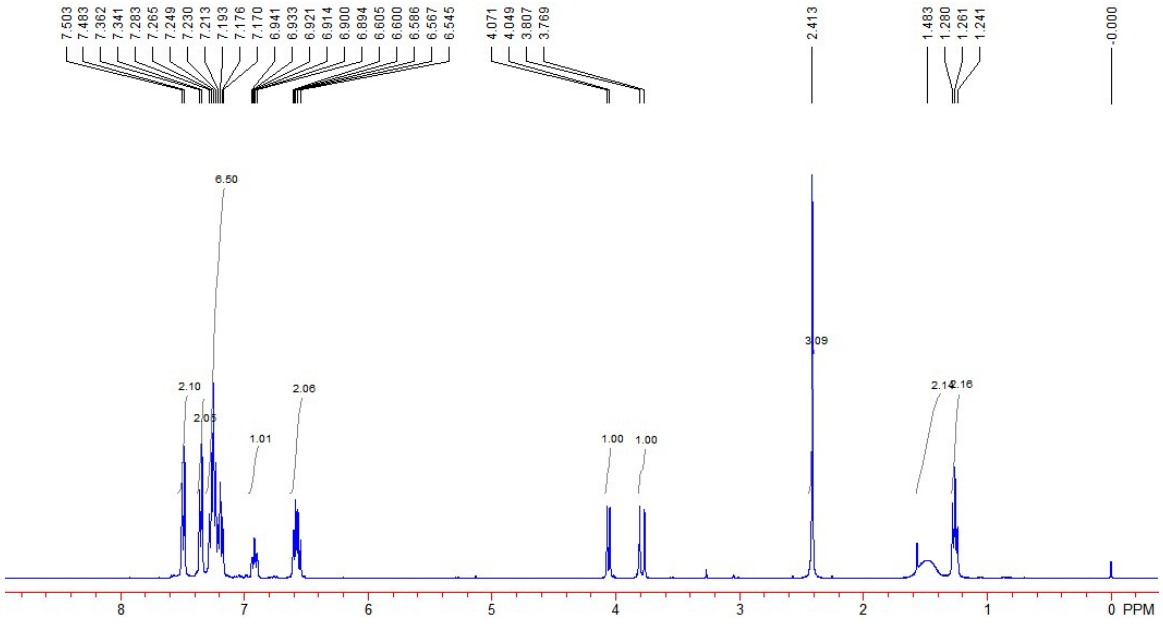


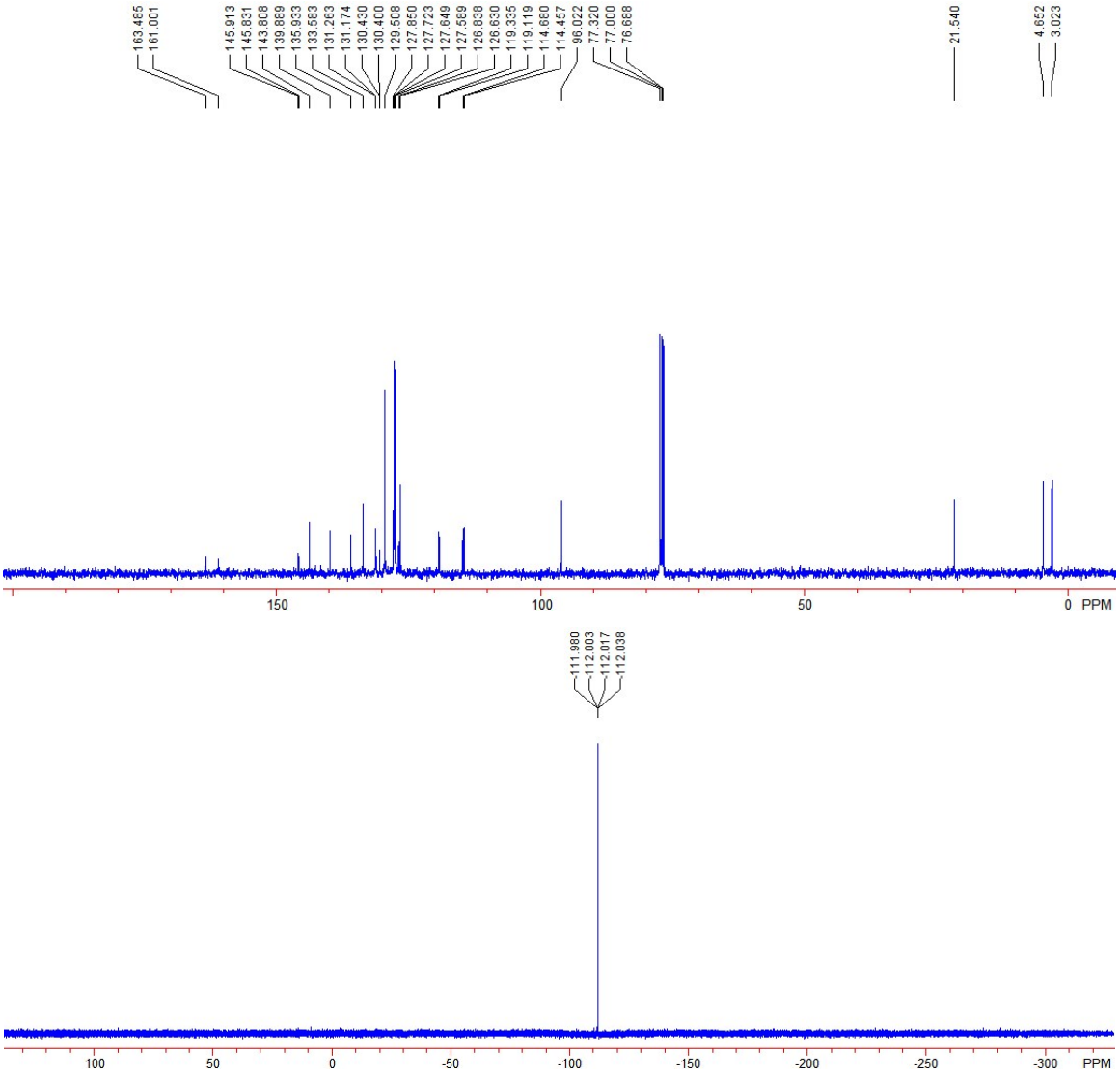
Compound 1a: Yield: 340 mg, 85%. A light yellow solid. Mp: 150-152 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, 3H, *J* = 7.6 Hz), 1.47 (br, 2H), 2.39 (s, 3H), 3.80 (d, 1H, *J* = 15.6 Hz), 4.06 (d, 1H, *J* = 8.8 Hz), 6.57-6.66 (m, 2H), 7.15-7.26 (m, 6H), 7.36-7.41 (m, 3H), 7.45-7.47 (m, 1H), 7.49-7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.8, 4.6, 21.4, 96.0, 126.3, 126.7, 126.8, 127.3, 127.57, 127.59, 128.8, 129.3, 129.5, 132.5, 133.5, 134.5, 136.2, 140.4, 143.2, 143.5; IR (neat): ν 2927, 1622, 1492, 1362, 1164, 771 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{24}NO_2S$ $[M+H]^+$: 402.1522, found: 402.1519.

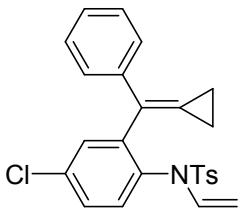




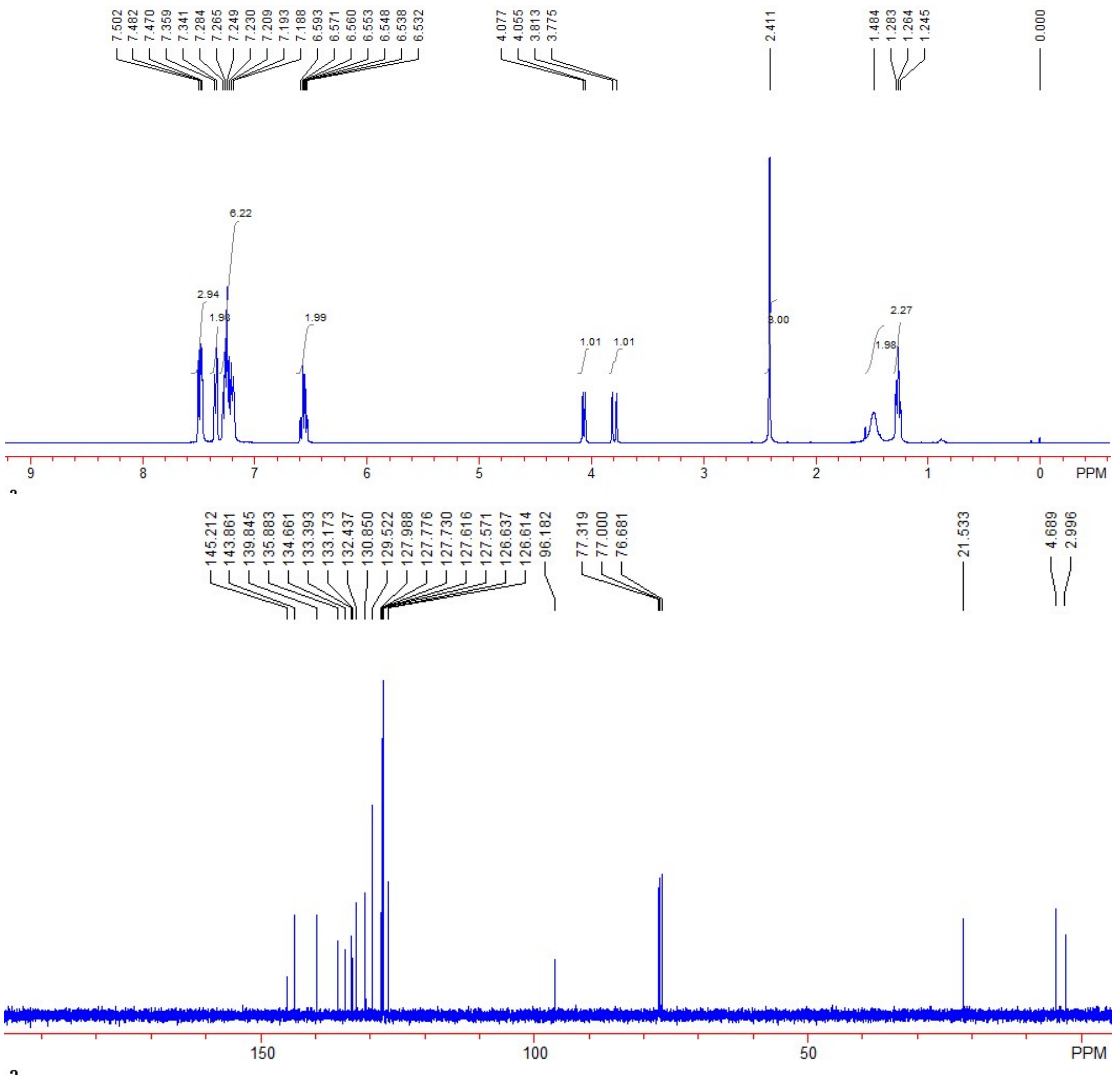
Compound 1b: Yield: 360 mg, 86%. A light yellow solid. Mp: 166-168 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (t, 2H, *J* = 8.0 Hz), 1.48 (br, 2H), 2.41 (s, 3H), 3.78 (d, 1H, *J* = 15.2 Hz), 4.06 (d, 1H, *J* = 8.8 Hz), 6.54-6.66 (m, 2H), 6.89-6.94 (m, 1H), 7.17-7.28 (m, 6H), 7.35 (d, 2H, *J* = 8.4 Hz), 7.49 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.0, 4.6, 21.5, 96.0, 114.5 (d, *J* = 22.3 Hz), 119.2 (d, *J* = 21.6 Hz), 126.6, 126.8, 127.5, 127.6, 127.7, 127.8, 129.5, 130.4 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 8.9 Hz), 133.5, 135.9, 139.8, 143.8, 145.8 (d, *J* = 7.2 Hz), 162.2 (d, *J* = 248.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -112.0~-111.9 (m); IR (neat): ν 2924, 1626, 1356, 1173, 1088, 811 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}FN_2O_2S$ $[M+NH_4]^+$: 437.1694, found: 437.1691.

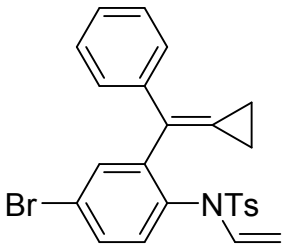




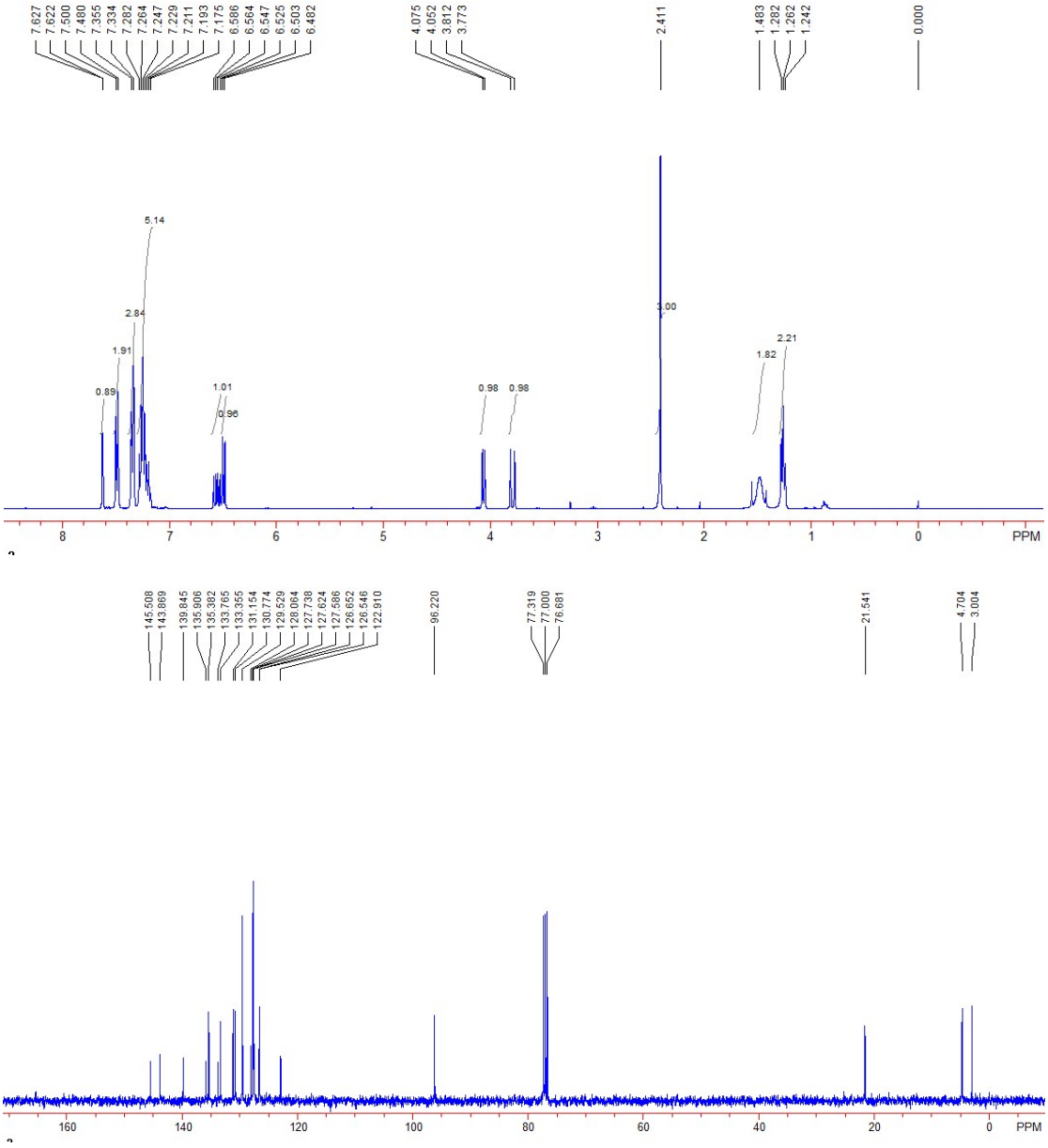


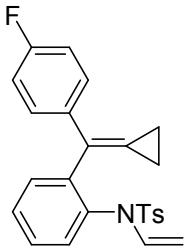
Compound 1c: Yield: 318 mg, 73%. A light yellow solid. Mp: 193-194 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (t, 2H, *J* = 7.6 Hz), 1.48 (br, 2H), 2.41 (s, 3H), 3.79 (d, 1H, *J* = 15.2 Hz), 4.06 (d, 1H, *J* = 8.8 Hz), 6.53-6.59 (m, 2H), 7.18-7.28 (m, 6H), 7.35 (d, 2H, *J* = 7.2 Hz), 7.47-7.50 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.9, 4.6, 21.5, 96.1, 126.61, 126.63, 127.5, 127.6, 127.73, 127.77, 127.9, 129.5, 130.8, 132.4, 133.1, 133.3, 134.6, 135.8, 139.8, 143.8, 145.2; IR (neat): ν 2968, 1624, 1362, 1165, 1086, 818 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}ClN_2O_2S$ $[M+NH_4]^+$: 453.1398, found: 453.1394.





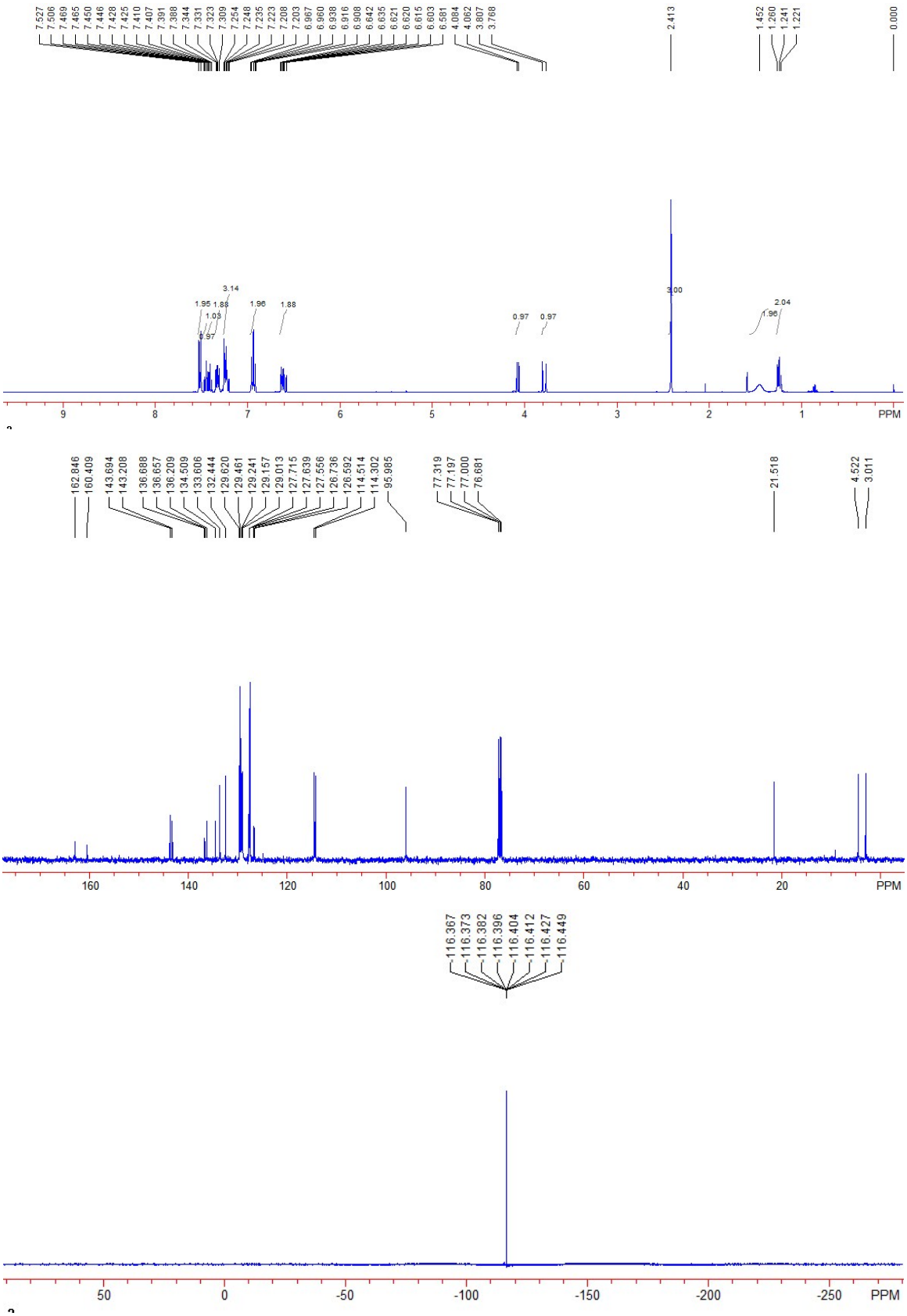
Compound 1d: Yield: 386 mg, 81%. A light yellow solid. Mp: 196-198 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (t, 2H, J = 8.0 Hz), 1.48 (br, 2H), 2.41 (s, 3H), 3.79 (d, 1H, J = 15.6 Hz), 4.06 (d, 1H, J = 9.2 Hz), 6.49 (d, 1H, J = 8.4 Hz), 6.55 (dd, 1H, J_1 = 15.6 Hz, J_2 = 9.2 Hz), 7.17-7.28 (m, 5H), 7.34 (d, 3H, J = 8.4 Hz), 7.49 (d, 2H, J = 8.0 Hz), 7.62 (d, 1H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.0, 4.7, 21.5, 96.2, 122.9, 126.5, 126.6, 127.5, 127.6, 127.7, 128.0, 129.5, 130.7, 131.1, 133.3, 133.7, 135.3, 135.9, 139.8, 143.8, 145.5; IR (neat): ν 2968, 1624, 1361, 1164, 1075, 770 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}BrN_2O_2S$ $[M+NH_4]^+$: 497.0893, found: 497.0889.

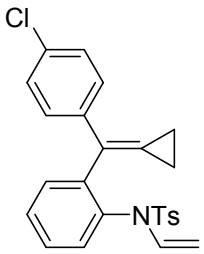




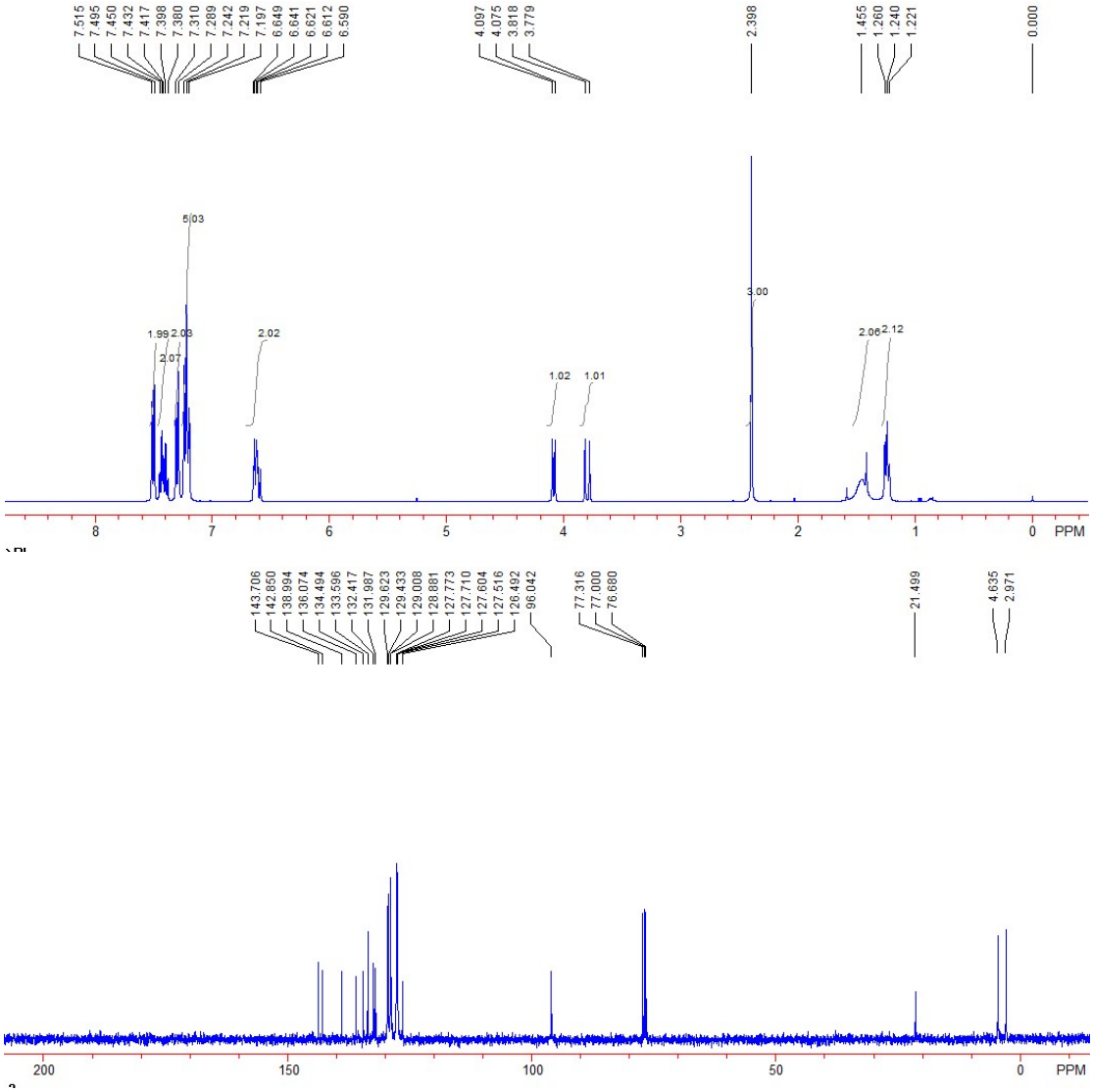
Compound 1e: Yield: 348 mg, 83%. A light yellow solid. Mp: 170-172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, 2H, *J* = 8.0 Hz), 1.45 (br, 2H), 2.41 (s, 3H), 3.78 (d, 1H, *J* = 15.6 Hz), 4.07 (d, 1H, *J* = 8.8 Hz), 6.58-6.64 (m, 2H), 6.90-6.96 (m, 2H), 7.20-7.25 (m, 3H), 7.30-7.34 (m, 2H), 7.38-7.46 (m, 2H), 7.51 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.0, 4.5, 21.5, 95.9, 114.4 (d, *J* = 21.2 Hz), 126.6 (d, *J* = 4.4 Hz), 127.5, 127.6, 127.7, 129.0, 129.1, 129.2, 129.4,

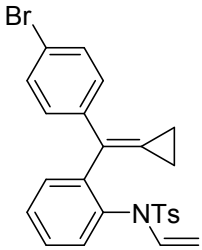
129.6, 132.4, 133.6, 134.5, 136.2, 136.6 (d, J = 3.1 Hz), 161.6 (d, J = 243.7 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -116.4~-116.3 (m); IR (neat): ν 3067, 2973, 1621, 1488, 1357, 1169 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{23}FNO_2S$ $[M+H]^+$: 420.1428, found: 420.1425.



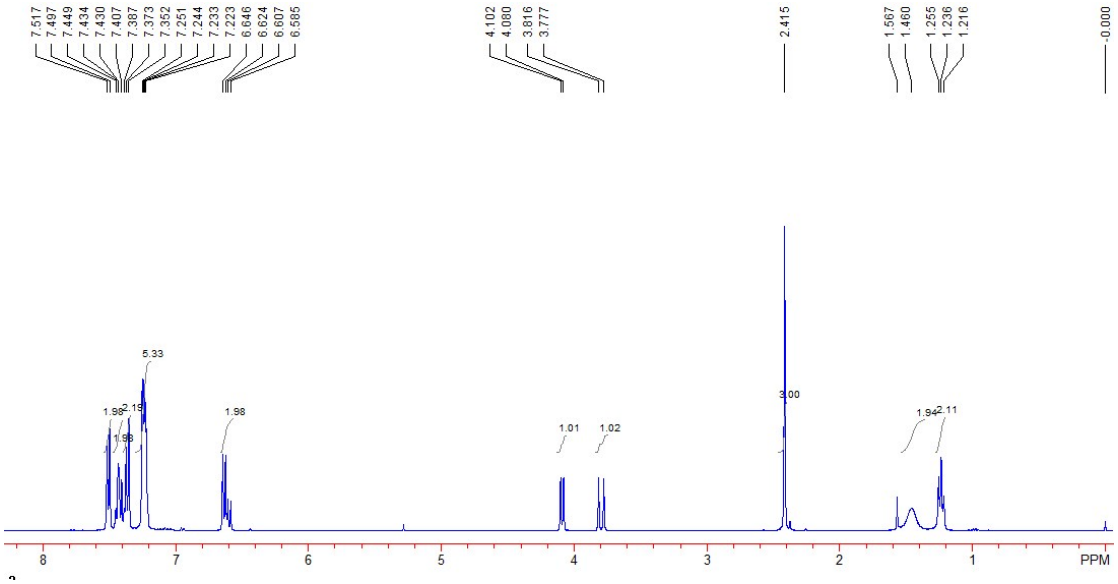


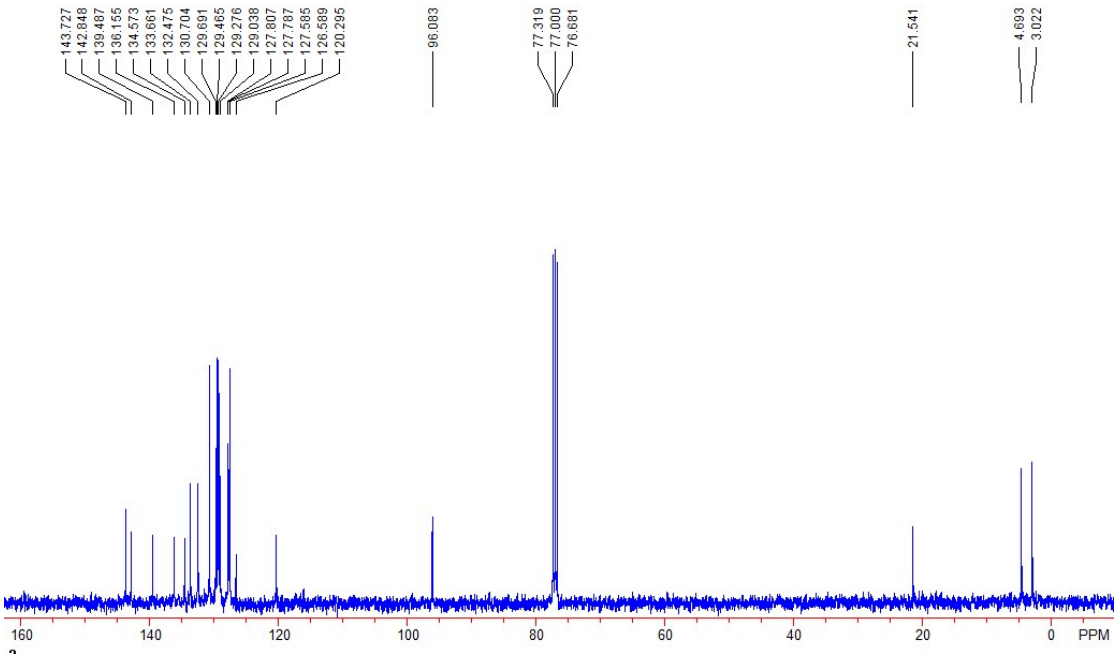
Compound 1f: Yield: 285 mg, 65%. A light yellow solid. Mp: 148-150 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, 2H, *J* = 8.0 Hz), 1.45 (br, 2H), 2.39 (s, 3H), 3.79 (d, 1H, *J* = 15.6 Hz), 4.08 (d, 1H, *J* = 8.8 Hz), 6.59-6.64 (m, 2H), 7.19-7.24 (m, 5H), 7.29 (d, 2H, *J* = 8.4 Hz), 7.38-7.45 (m, 2H), 7.50 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.9, 4.6, 21.4, 96.0, 126.4, 127.5, 127.6, 127.71, 127.77, 128.8, 129.0, 129.4, 129.6, 131.9, 132.4, 133.5, 134.4, 136.0, 138.9, 142.8, 143.7; IR (neat): ν 3061, 2976, 1359, 1171, 1088, 1043, 891 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{23}ClNO_2S$ $[M+H]^+$: 436.1133, found: 436.1130.

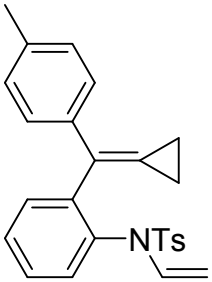




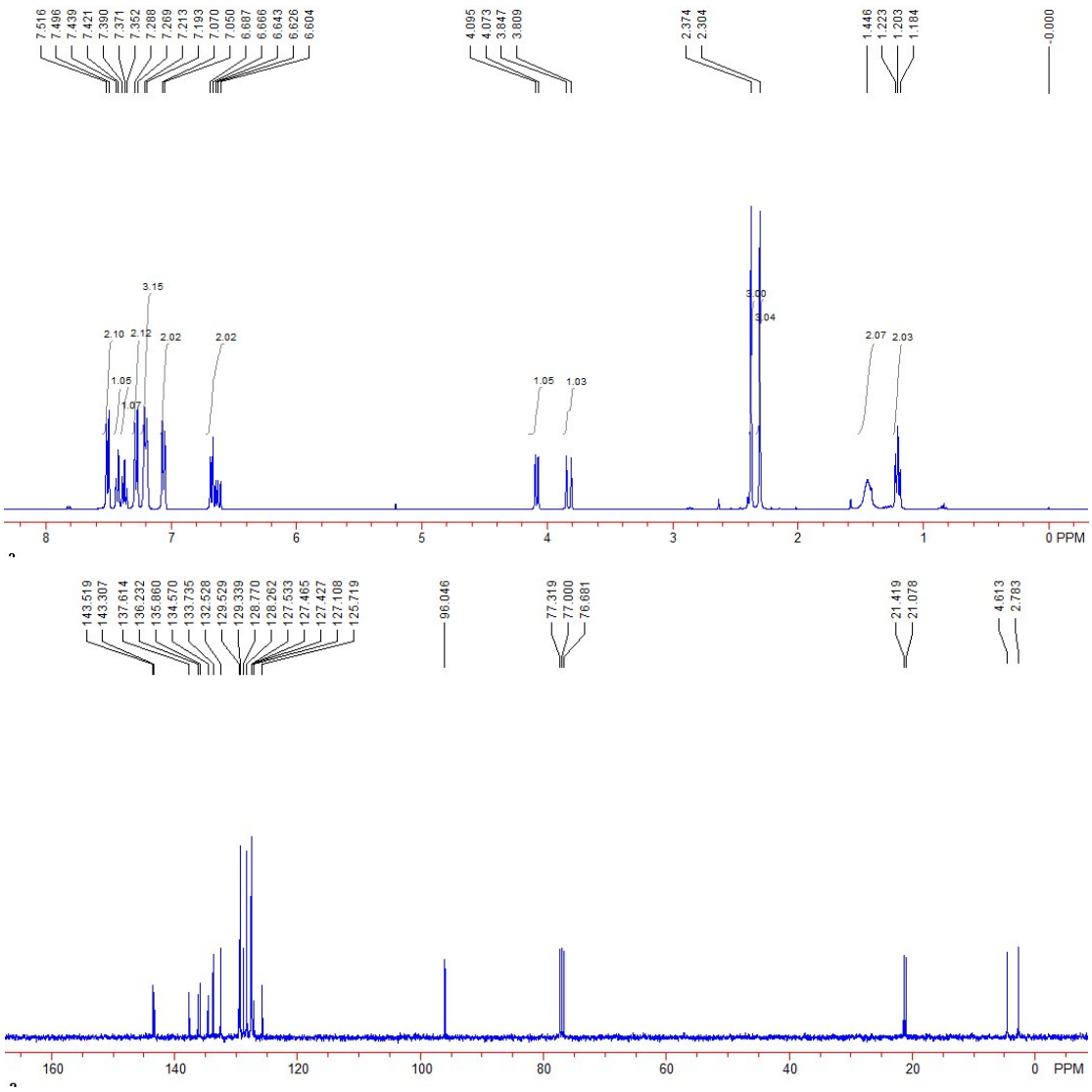
Compound 1g: Yield: 335 mg, 81%. A light yellow solid. Mp: 120-122 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, 2H, *J* = 8.0 Hz), 1.46 (br, 2H), 2.41 (s, 3H), 3.79 (d, 1H, *J* = 15.6 Hz), 4.09 (d, 1H, *J* = 8.8 Hz), 6.58-6.64 (m, 2H), 7.22-7.25 (m, 5H), 7.35-7.44 (m, 4H), 7.50 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.0, 4.6, 21.5, 96.0, 120.2, 126.5, 127.5, 127.7, 127.8, 129.0, 129.2, 129.4, 129.6, 130.7, 132.4, 133.6, 134.5, 136.1, 139.4, 142.8, 143.7; IR (neat): ν 3051, 2973, 1618, 1359, 1170, 1042 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{23}BrNO_2S$ $[M+H]^+$: 480.0627, found: 480.0625.

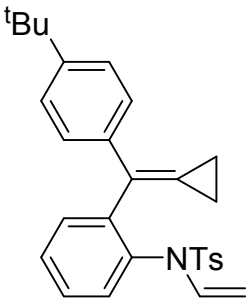






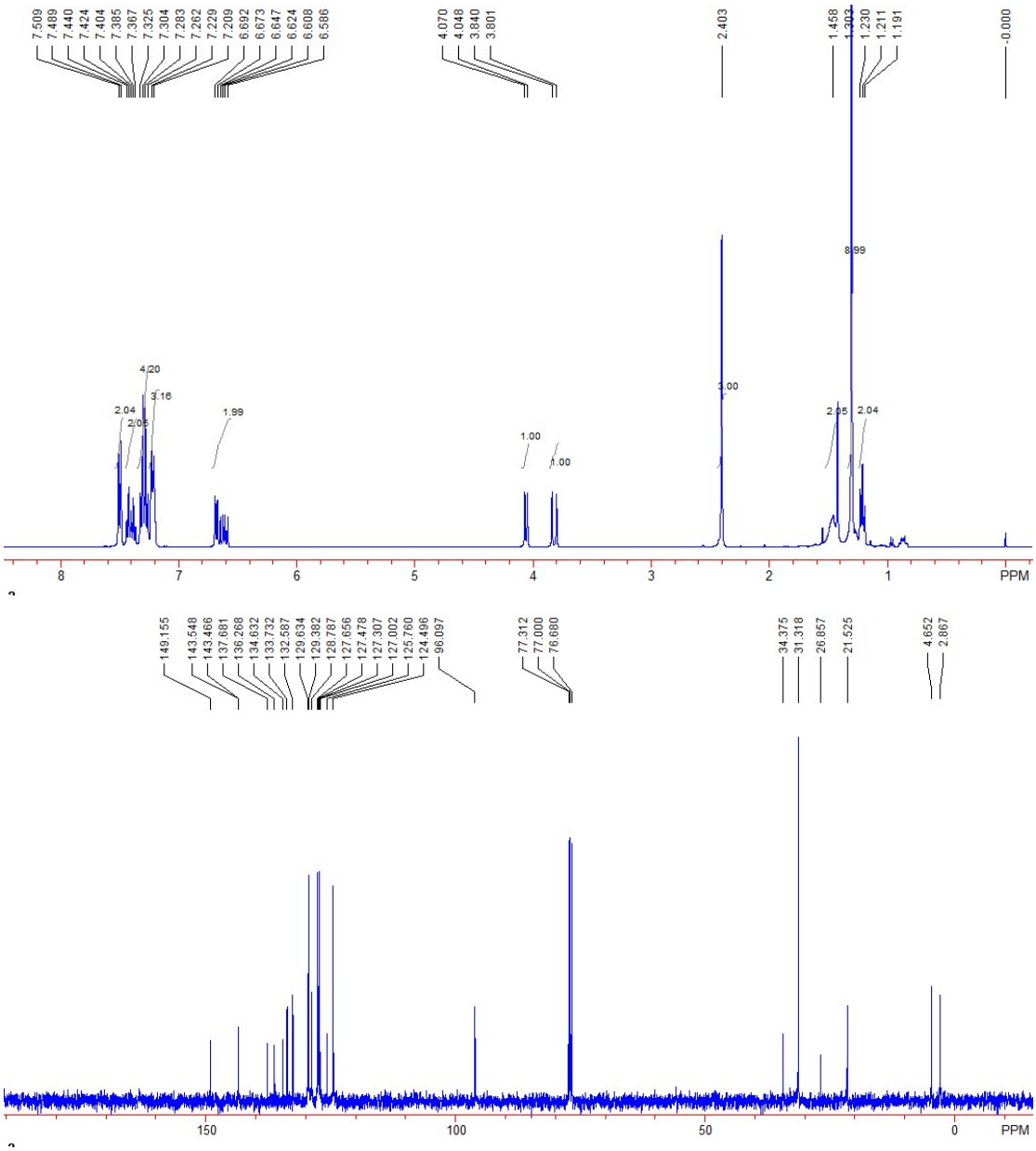
Compound 1h: Yield: 323 mg, 78%. A light yellow solid. Mp: 146-148 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.20 (t, 2H, J = 8.0 Hz), 1.44 (br, 2H), 2.30 (s, 3H), 2.37 (s, 3H), 3.82 (d, 1H, J = 15.2 Hz), 4.08 (d, 1H, J = 8.8 Hz), 6.60-6.68 (m, 2H), 7.06 (d, 3H, J = 8.0 Hz), 7.20 (d, 3H, J = 8.0 Hz), 7.27 (d, 2H, J = 7.6 Hz), 7.37 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.43 (d, 1H, J = 7.2 Hz), 7.50 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.7, 4.6, 21.0, 21.4, 96.0, 125.7, 127.1, 127.42, 127.46, 127.5, 128.2, 128.7, 129.3, 129.5, 132.5, 133.7, 134.5, 135.8, 136.2, 137.6, 143.3, 143.5; IR (neat): ν 2958, 1624, 1357, 1173, 1088, 1045, 869 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}NO_2S$ $[M+H]^+$: 416.1679, found: 416.1675.

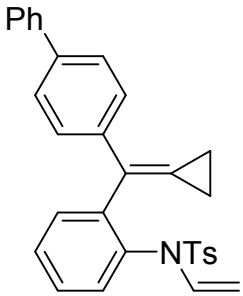




Compound 1i: Yield: 528 mg, 76%. A light yellow solid. Mp: 46-48 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21 (t, 2H, *J* = 8.0 Hz), 1.30 (s, 9H), 1.45 (br, 2H), 2.40 (s, 3H), 3.82 (d, 1H, *J* = 15.6 Hz), 4.05 (d, 1H, *J* = 8.8 Hz), 6.58-6.69 (m, 2H), 7.20-7.32 (m, 7H), 7.36-7.44 (m, 2H), 7.49 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.8, 4.6, 21.5, 26.8, 31.3, 34.3, 96.0, 124.4, 125.7, 127.0, 127.3, 127.4, 127.6, 128.7, 129.3, 129.6, 132.5, 133.7, 134.6, 136.2, 137.6, 143.4, 143.5, 149.1; IR (neat): ν 2966, 1624, 1361, 1165, 1087, 1042, 813 cm^{-1}; HRMS (ESI)

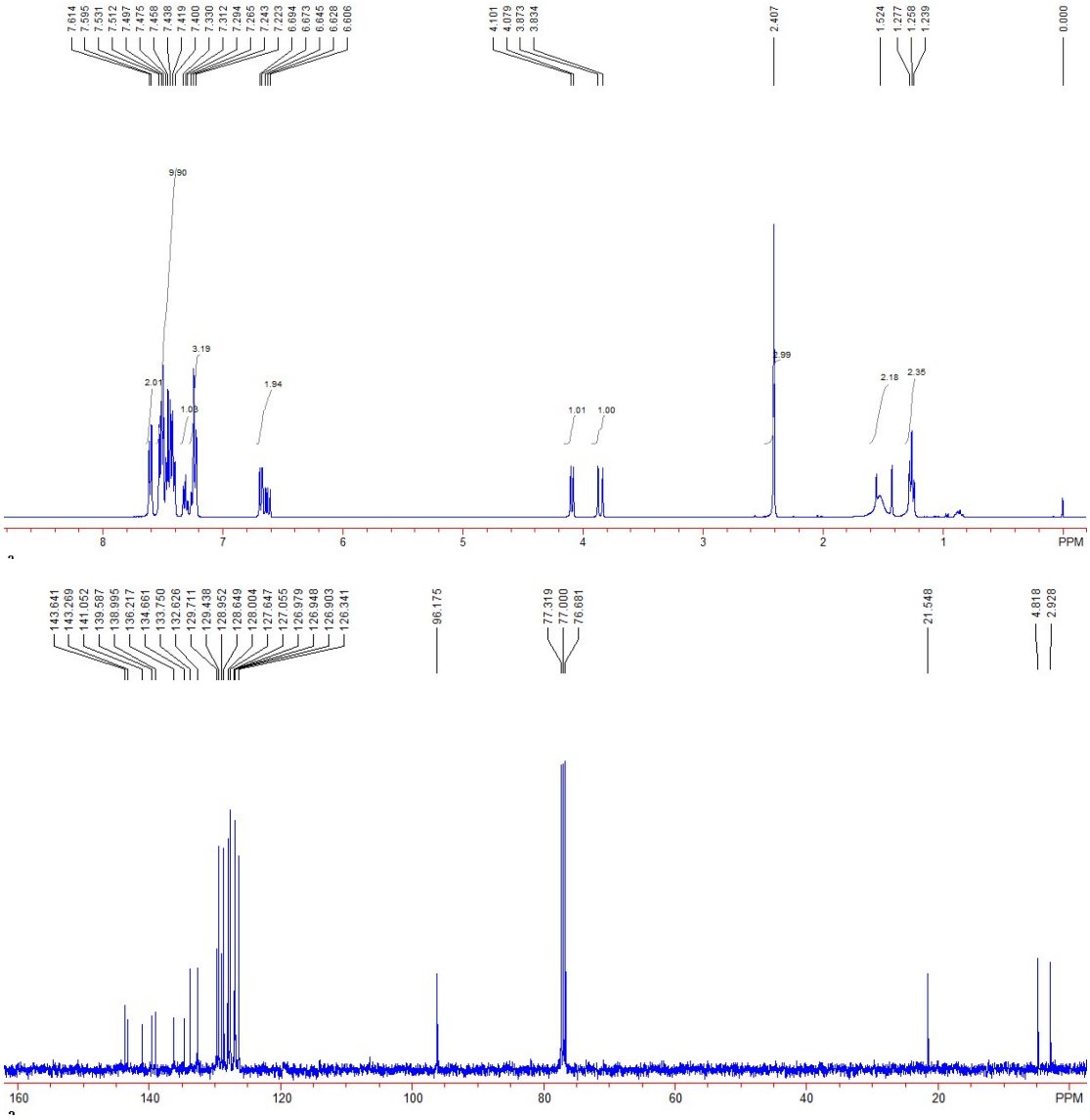
Calcd. for $C_{27}H_{33}N_2O_2S$ $[M+H]^+$: 449.2257, found: 449.2252.

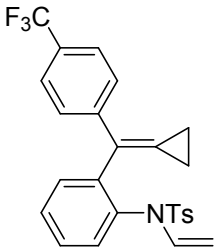




Compound 1j: Yield: 239 mg, 50%. A light yellow solid. Mp: 178-180 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (t, 2H, *J* = 7.6 Hz), 1.52 (br, 2H), 2.40 (s, 3H), 3.85 (d, 1H, *J* = 15.6 Hz), 4.09 (d, 1H, *J* = 8.8 Hz), 6.60-6.69 (m, 2H), 7.22-7.33 (m, 4H), 7.40-7.53 (m, 10H), 7.60 (d, 2H, *J* = 7.6

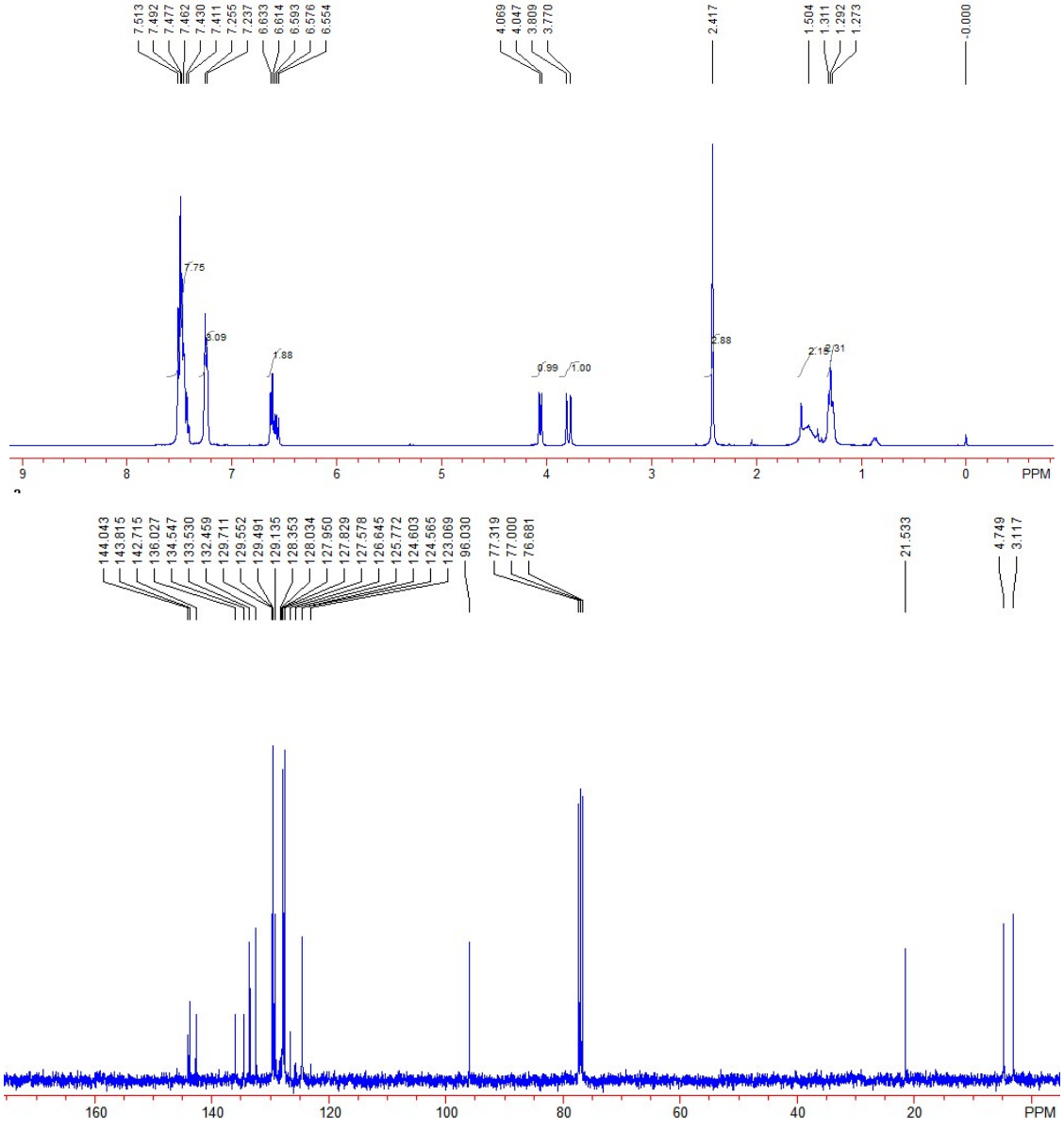
Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.9, 4.8, 21.5, 96.1, 126.3, 126.90, 126.94, 126.97, 127.0, 127.6, 128.0, 128.6, 128.9, 129.4, 129.7, 132.6, 133.7, 134.6, 136.2, 138.9, 139.5, 141.0, 143.2, 143.6; IR (neat): ν 3031, 2978, 1625, 1485, 1361, 1164, 1087, 765 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{28}NO_2S$ $[M+H]^+$: 478.1835, found: 478.1833.

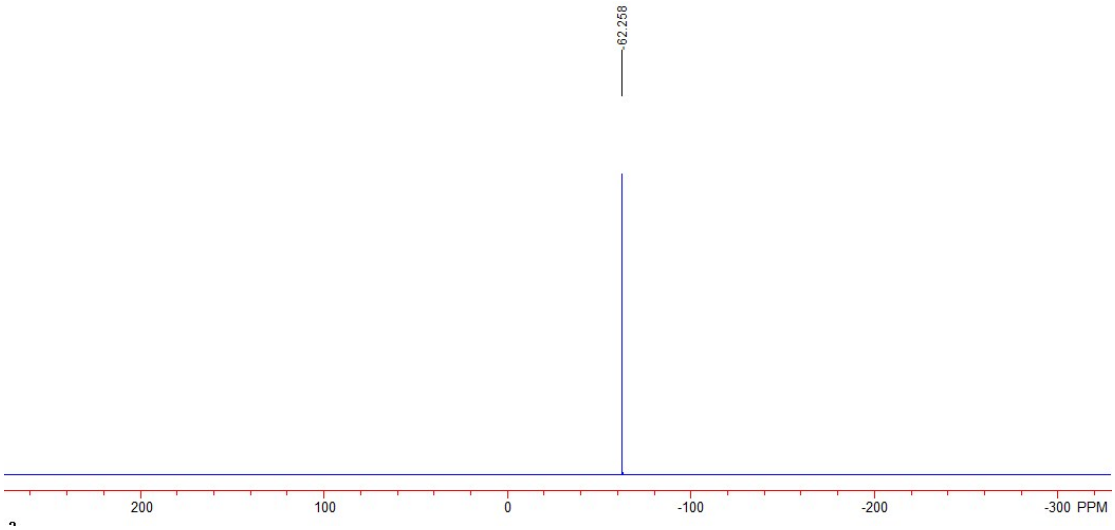


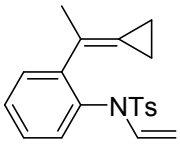


Compound 1k: Yield: 358 mg, 76%. A light yellow solid. Mp: 109-111 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.29 (t, 2H, *J* = 7.6 Hz), 1.50 (br, 2H), 2.41 (s, 3H), 3.78 (d, 1H, *J* = 15.6 Hz), 4.05

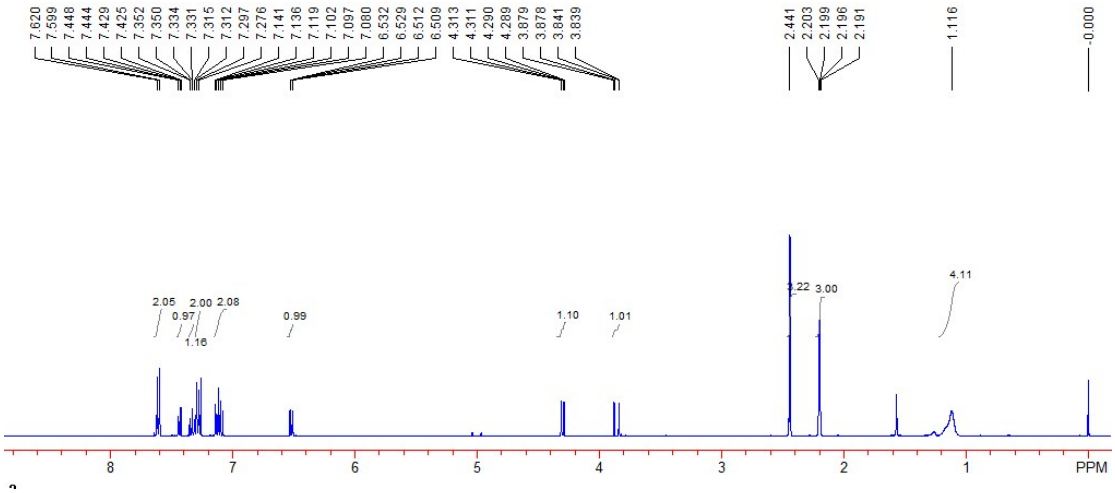
(d, 1H, J = 8.8 Hz), 6.55-6.63 (m, 2H), 7.23-7.25 (m, 3H), 7.41-7.51 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.1, 4.7, 21.5, 96.0, 124.4 (q, J = 270.3 Hz), 124.5 (q, J = 3.8 Hz), 126.6, 127.5, 127.8, 127.9, 128.1 (q, J = 31.9 Hz), 129.1, 129.4, 129.5, 129.7, 132.4, 133.5, 134.5, 136.0, 142.7, 143.8, 144.0; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -62.2 (s); IR (neat): ν 2966, 1621, 1323, 1161, 1128, 837 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}F_3NO_2S$ $[M+H]^+$: 470.1396, found: 470.1393.

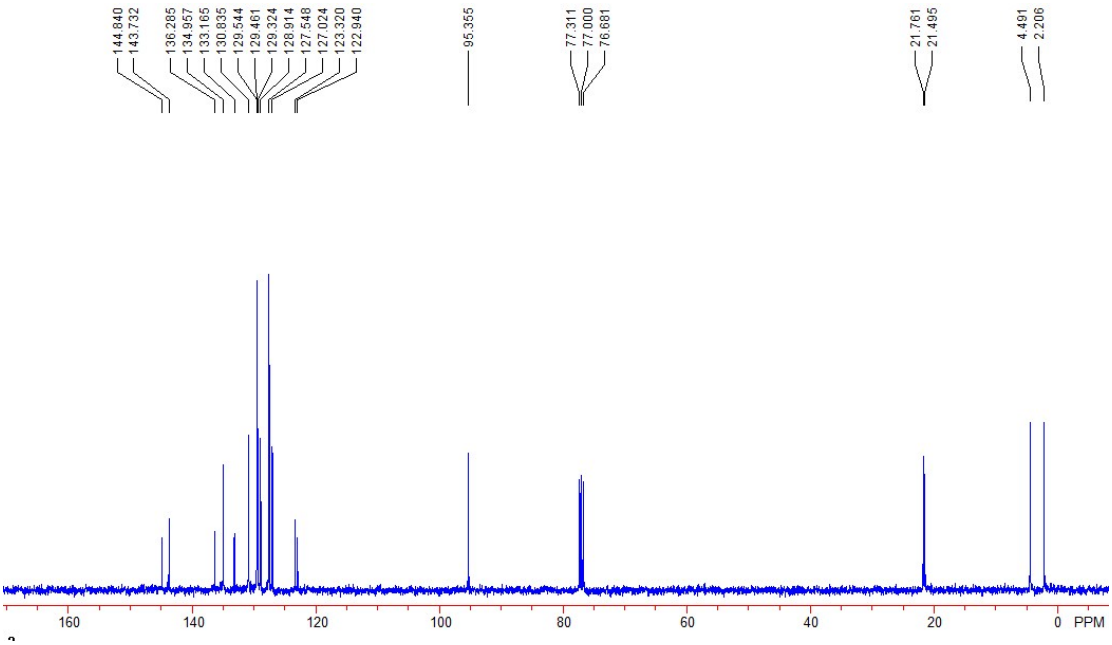


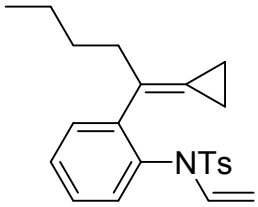




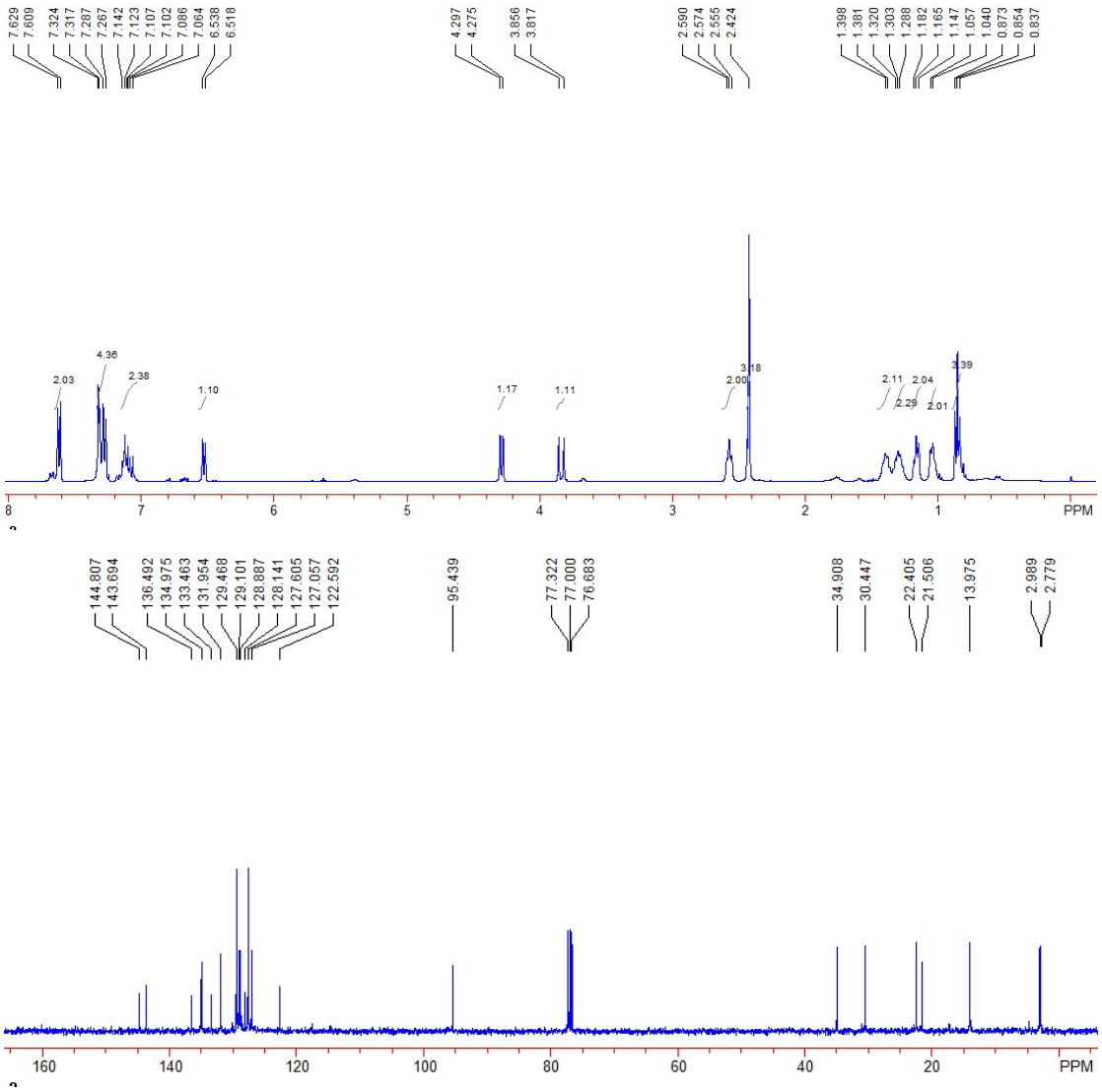
Compound 1l: Yield: 243 mg, 71%. A light yellow solid. Mp: 95-97 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (br, 4H), 2.19-2.20 (m, 3H), 2.44 (s, 3H), 3.85 (dd, 1H, J_1 = 15.6 Hz, J_2 = 0.8 Hz), 4.30 (dd, 1H, J_1 = 8.8 Hz, J_2 = 0.8 Hz), 6.52 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.08-7.14 (m, 2H), 7.27-7.35 (m, 3H), 7.43 (d, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.60 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.2, 4.4, 21.4, 21.7, 95.3, 122.9, 123.3, 127.0, 127.5, 128.9, 129.3, 129.4, 129.5, 130.8, 133.1, 134.9, 136.2, 143.7, 144.8; IR (neat): ν 2919, 2849, 1620, 1360, 1167, 1045, 911 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{22}NO_2S$ $[M+H]^+$: 340.1366, found: 340.1364.

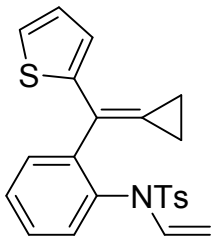




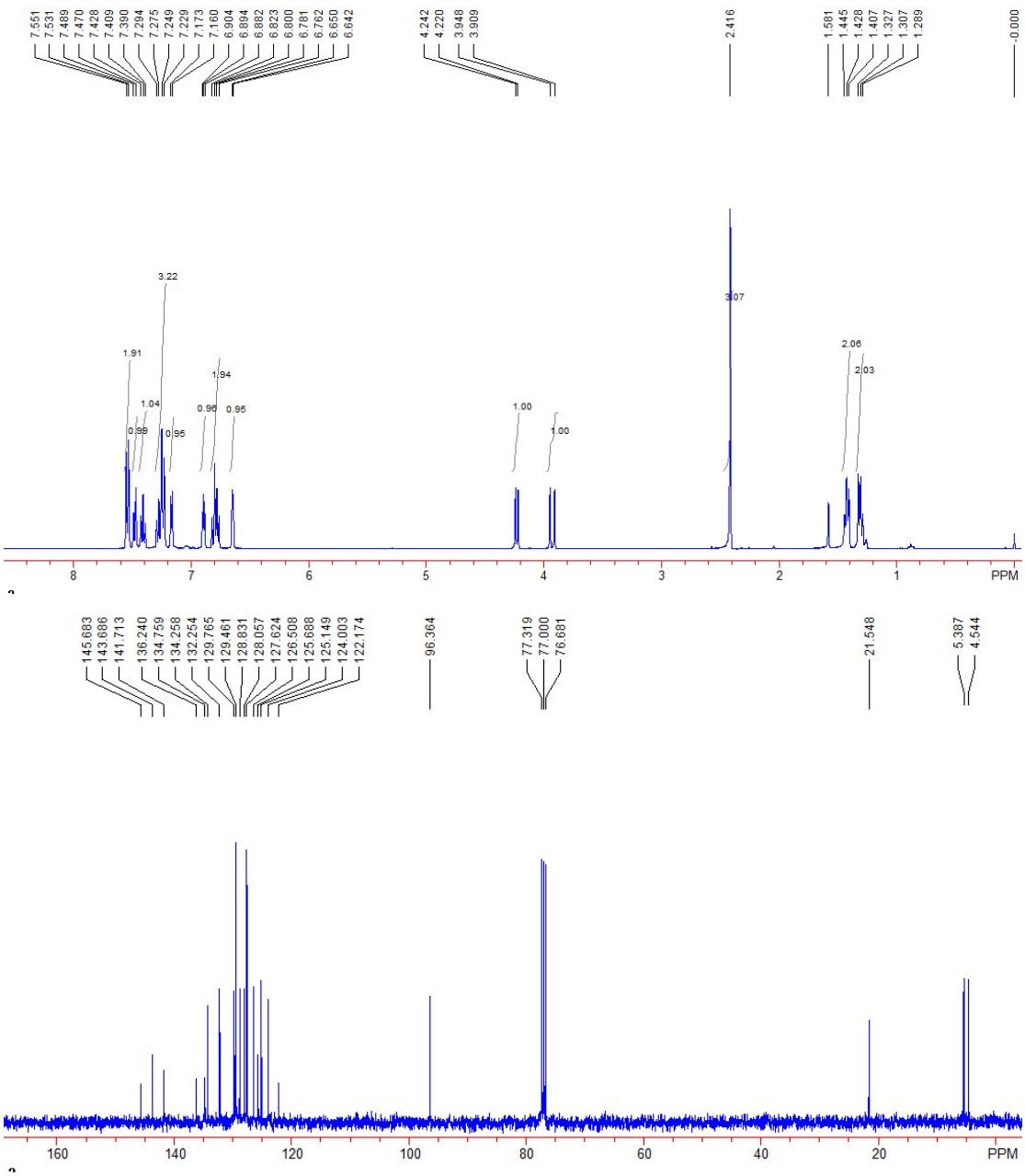


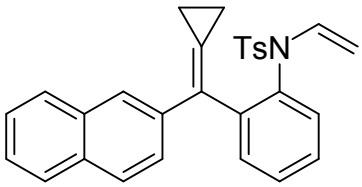
Compound 1m: Yield: 265 mg, 70%. A light yellow solid. Mp: 66-68 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.85 (t, 3H, *J* = 7.6 Hz), 1.04-1.05 (m, 2H), 1.14-1.18 (m, 2H), 1.28-1.32 (m, 2H), 1.38-1.39 (m, 2H), 2.42 (s, 3H), 2.57 (t, 2H, *J* = 7.6 Hz), 3.83 (d, 1H, *J* = 15.6 Hz), 4.28 (d, 1H, *J* = 8.8 Hz), 6.52 (d, 1H, *J* = 8.0 Hz), 7.06-7.14 (m, 2H), 7.26-7.32 (m, 4H), 7.61 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.7, 2.9, 13.9, 21.5, 22.4, 30.4, 34.9, 95.4, 122.5, 127.0, 127.6, 128.1, 128.8, 129.1, 129.4, 131.9, 133.4, 134.9, 136.4, 143.6, 144.8; IR (neat): ν 2960, 2922, 1623, 1359, 1166, 1037, 913 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{28}NO_2S$ $[M+H]^+$: 382.1835, found: 382.1833.





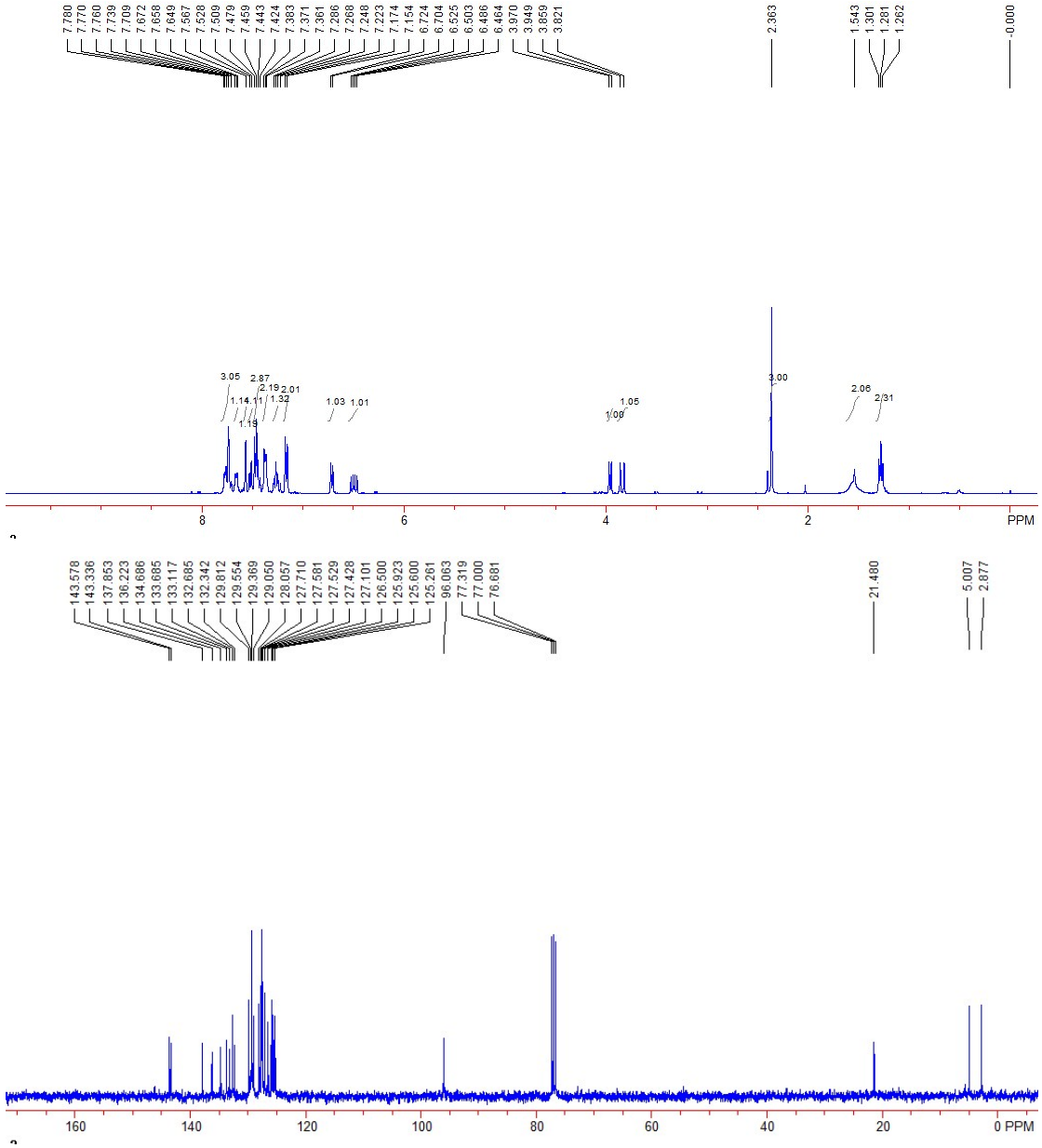
Compound 1n: Yield: 309 mg, 76%. A light yellow solid. Mp: 168-170 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28-1.32 (m, 2H), 1.40-1.44 (m, 2H), 2.41 (s, 3H), 3.92 (d, 1H, J = 15.6 Hz), 4.23 (d, 1H, J = 8.8 Hz), 6.64 (d, 1H, J = 3.2 Hz), 3.76-6.82 (m, 2H), 6.89 (dd, 1H, $J_1 = J_2$ = 4.8 Hz), 7.16 (d, 1H, J = 2.8 Hz), 7.22-7.29 (m, 3H), 7.40 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.47 (d, 1H, J = 7.6 Hz), 7.54 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 4.5, 5.3, 21.5, 96.3, 122.1, 124.0, 125.1, 125.6, 126.5, 127.6, 128.0, 128.8, 129.4, 129.7, 132.2, 134.2, 134.7, 136.2, 141.7, 143.6, 145.6; IR (neat): ν 2968, 1624, 1506, 1358, 1166, 1086, 804 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{22}NO_2S_2$ $[M+H]^+$: 408.1086, found: 408.1086.

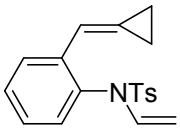




Compound 1o: Yield: 356 mg, 79%. A light yellow solid. Mp: 164-165 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28 (t, 2H, J = 8.0 Hz), 1.54 (br, 2H), 2.36 (s, 3H), 3.84 (d, 1H, J = 15.6 Hz), 3.96 (d, 1H, J = 8.4 Hz), 6.49 (dd, 1H, J_1 = 15.6 Hz, J_2 = 8.4 Hz), 6.71 (d, 1H, J = 8.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 7.24-7.28 (m, 1H), 7.36-7.56 (m, 7H), 7.64-7.78 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.8, 5.0, 21.4, 96.0, 125.2, 125.6, 125.9, 126.5, 127.1, 127.4, 127.52, 127.58, 127.7, 128.0, 129.0, 129.3, 129.5, 129.8, 132.3, 132.6, 133.1, 133.6, 134.6, 136.2, 137.8, 143.3, 143.5; IR

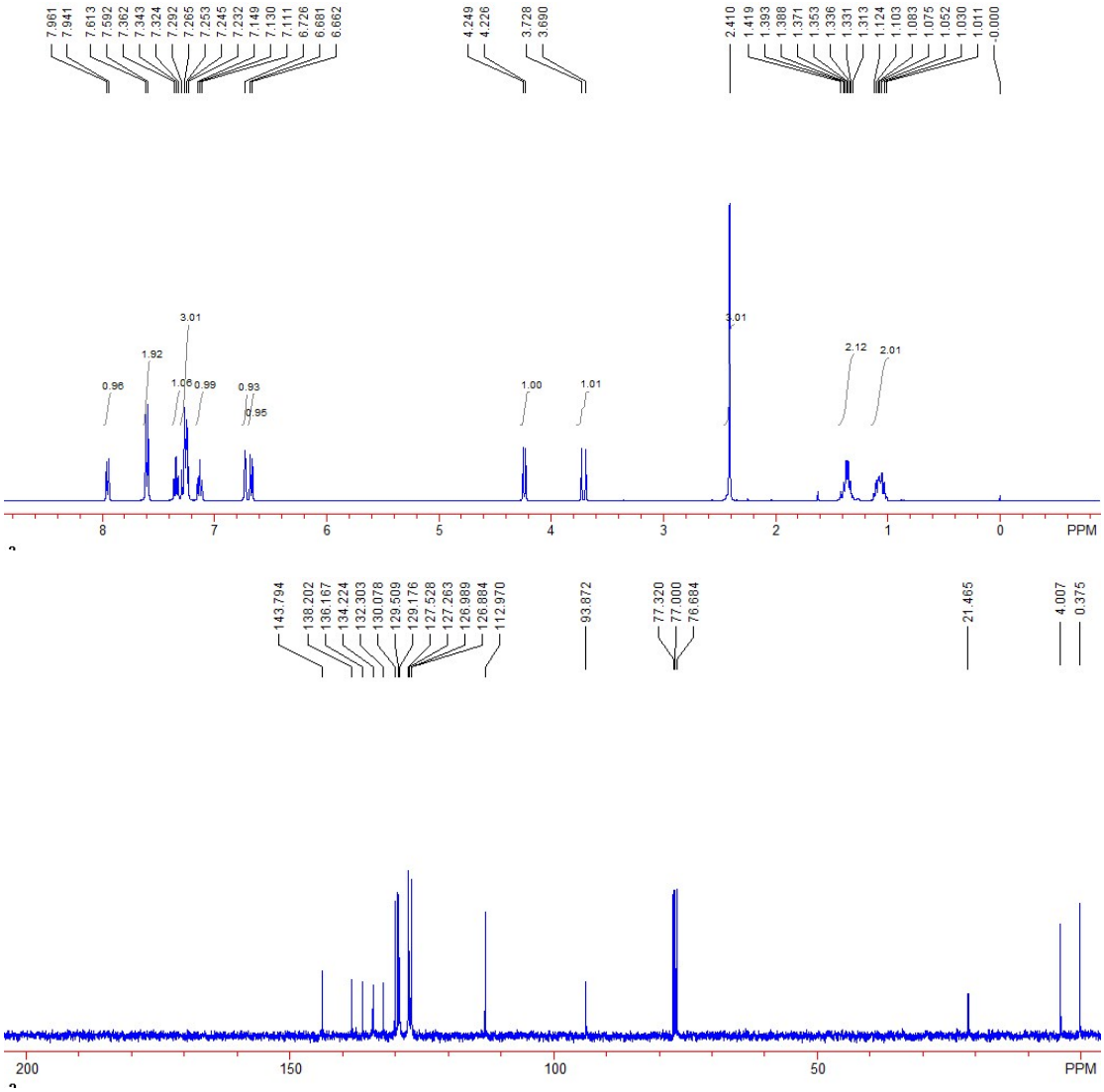
(neat): ν 3059, 1621, 1363, 1166, 1038, 845 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{29}N_2O_2S$ $[M+NH_4]^+$: 469.1944, found: 469.1941.

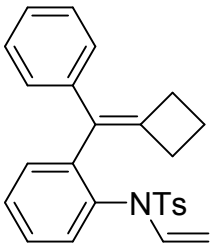




Compound 1p Yield: 214 mg, 33%. A light yellow solid. Mp: 105-107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.01-1.12 (m, 2H), 1.31-1.41 (m, 2H), 2.41 (s, 3H), 3.70 (d, 1H, J = 15.2 Hz), 4.23 (d, 1H, J = 9.6 Hz), 6.66-6.72 (m, 2H), 7.13 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.23-7.29 (m, 3H), 7.34 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.95 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.3, 4.0, 21.4, 93.8, 112.9, 126.8, 126.9, 127.2, 127.5, 129.1, 129.5, 130.0, 132.3,

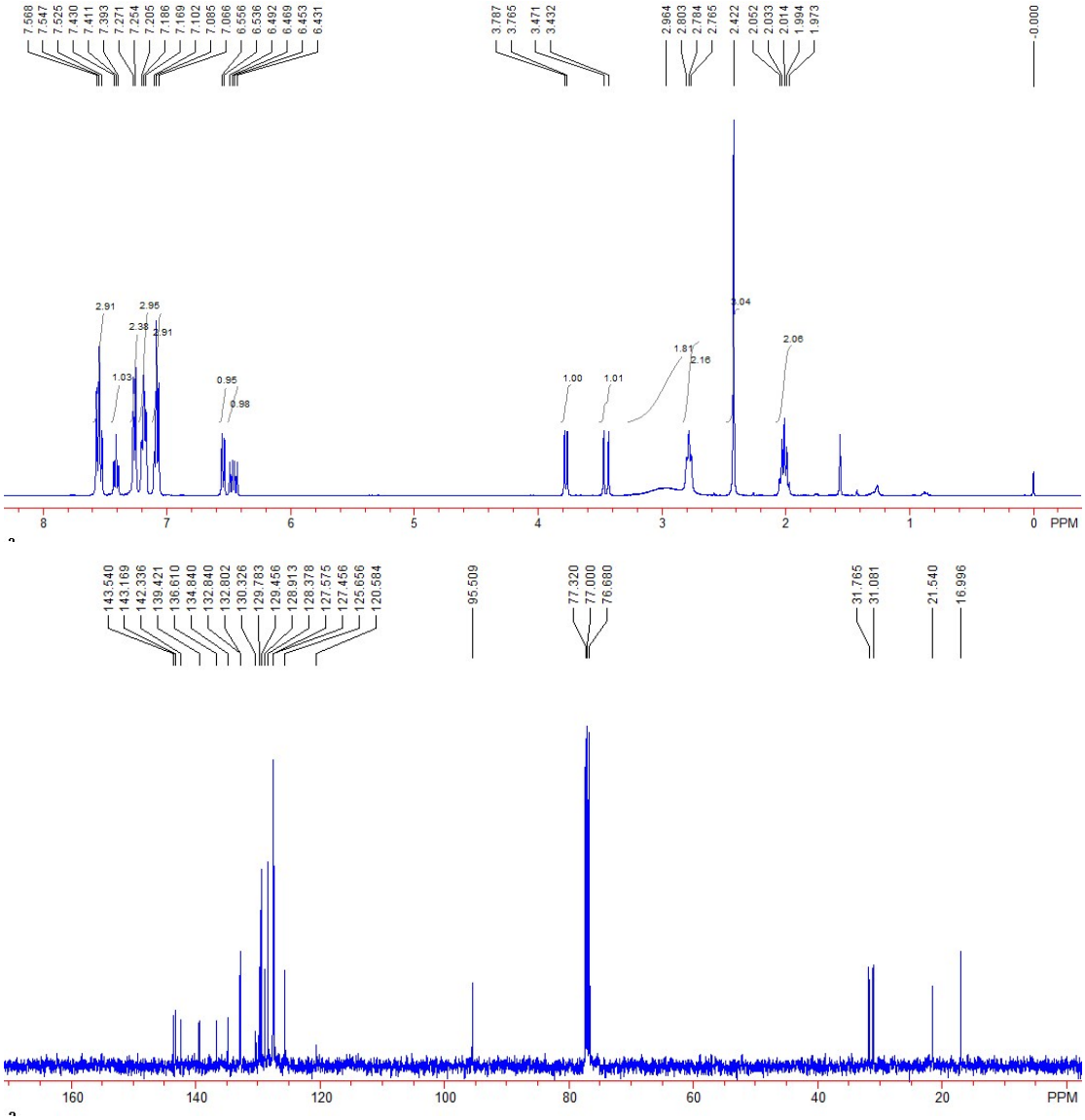
134.2, 136.1, 138.2, 143.7; IR (neat): ν 1620, 1356, 1172, 1087, 916, 800 cm^{-1}; HRMS (ESI) Calcd. for $C_{19}H_{20}NO_2S$ $[M+H]^+$: 326.1209, found: 326.1208.

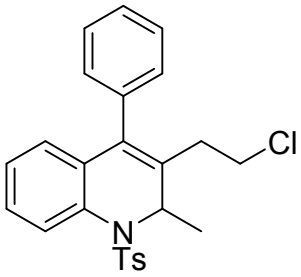




Compound 5: Yield: 657 mg, 72%. A light yellow solid. Mp: 185-187 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.97-2.05 (m, 2H), 2.42 (s, 3H), 2.78 (t, 2H, J = 7.6 Hz), 2.96 (br, 2H), 3.45 (d, 1H, J = 15.6 Hz), 3.77 (d, 1H, J = 8.8 Hz), 6.46 (dd, 1H, J_1 = 15.6 Hz, J_2 = 8.8 Hz), 6.54 (d, 1H, J = 8.0 Hz), 7.06-7.10 (m, 3H), 7.16-7.20 (m, 3H), 7.26 (d, 2H, J = 6.8 Hz), 7.41 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.52-7.56 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 16.9, 21.5, 31.0, 31.7, 95.5, 120.5, 125.6, 127.4, 127.5, 128.3, 128.9, 129.4, 129.7, 130.3, 132.80, 132.84, 134.8, 136.6, 139.4, 142.3,

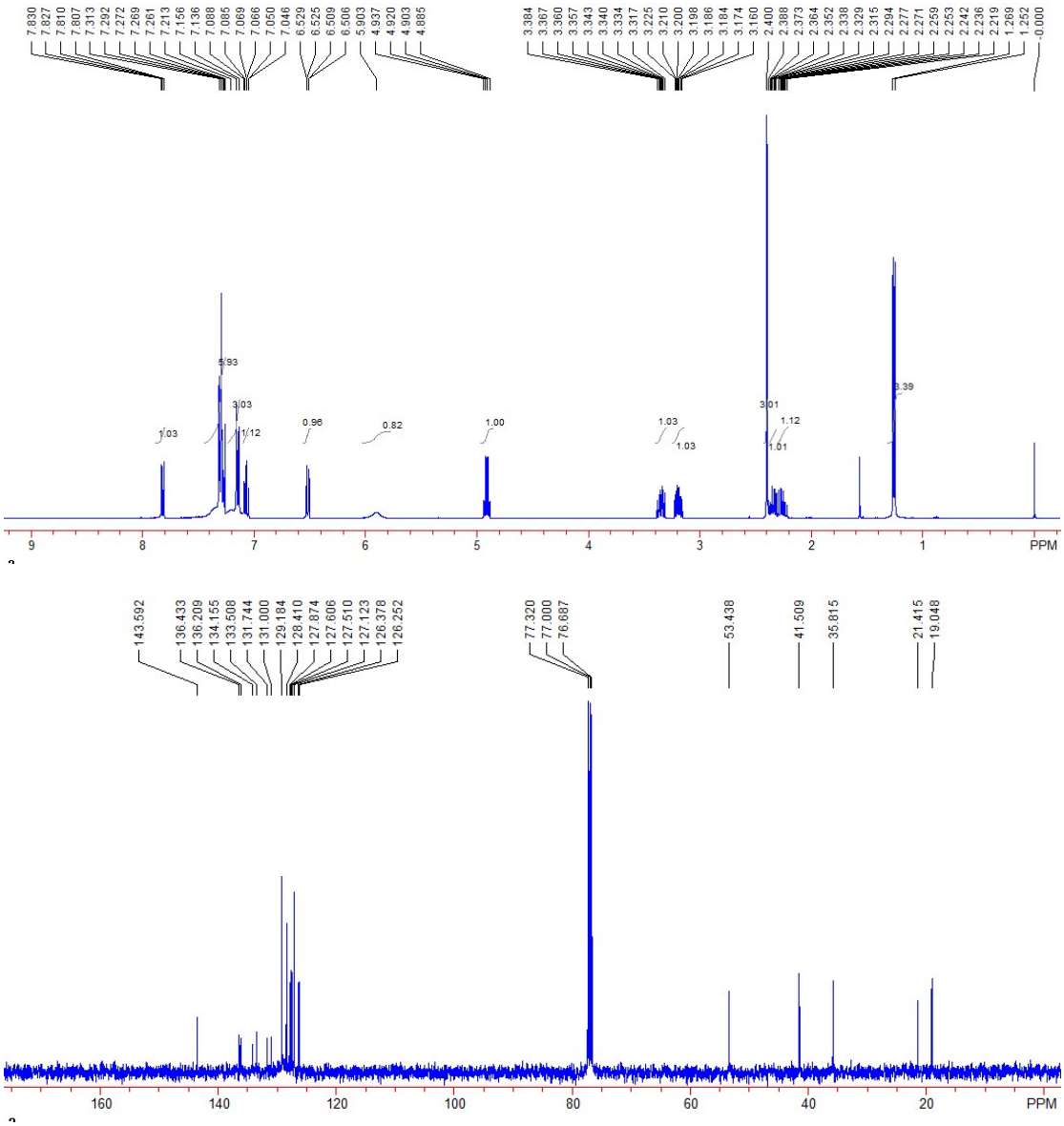
143.1, 143.5; IR (neat): ν 2919, 1624, 1356, 1164, 1084, 1042, 767 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{26}NO_2S$ $[M+H]^+$: 416.1679, found: 416.1675.

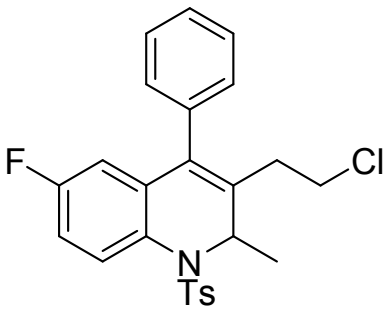




Compound 2a: Yield: 76 mg, 87%. A light yellow solid. Mp: 112-115 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (d, 3H, J = 6.8 Hz), 2.21-2.29 (m, 1H), 2.31-2.38 (m, 1H), 2.40 (s, 3H), 3.16-3.22 (m, 1H), 3.31-3.38 (m, 1H), 4.91 (q, 1H, J = 6.8 Hz), 5.90 (br, 1H), 6.51 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.04-7.15 (m, 4H), 7.21-7.31 (m, 6H), 7.81 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz); ^{13}C

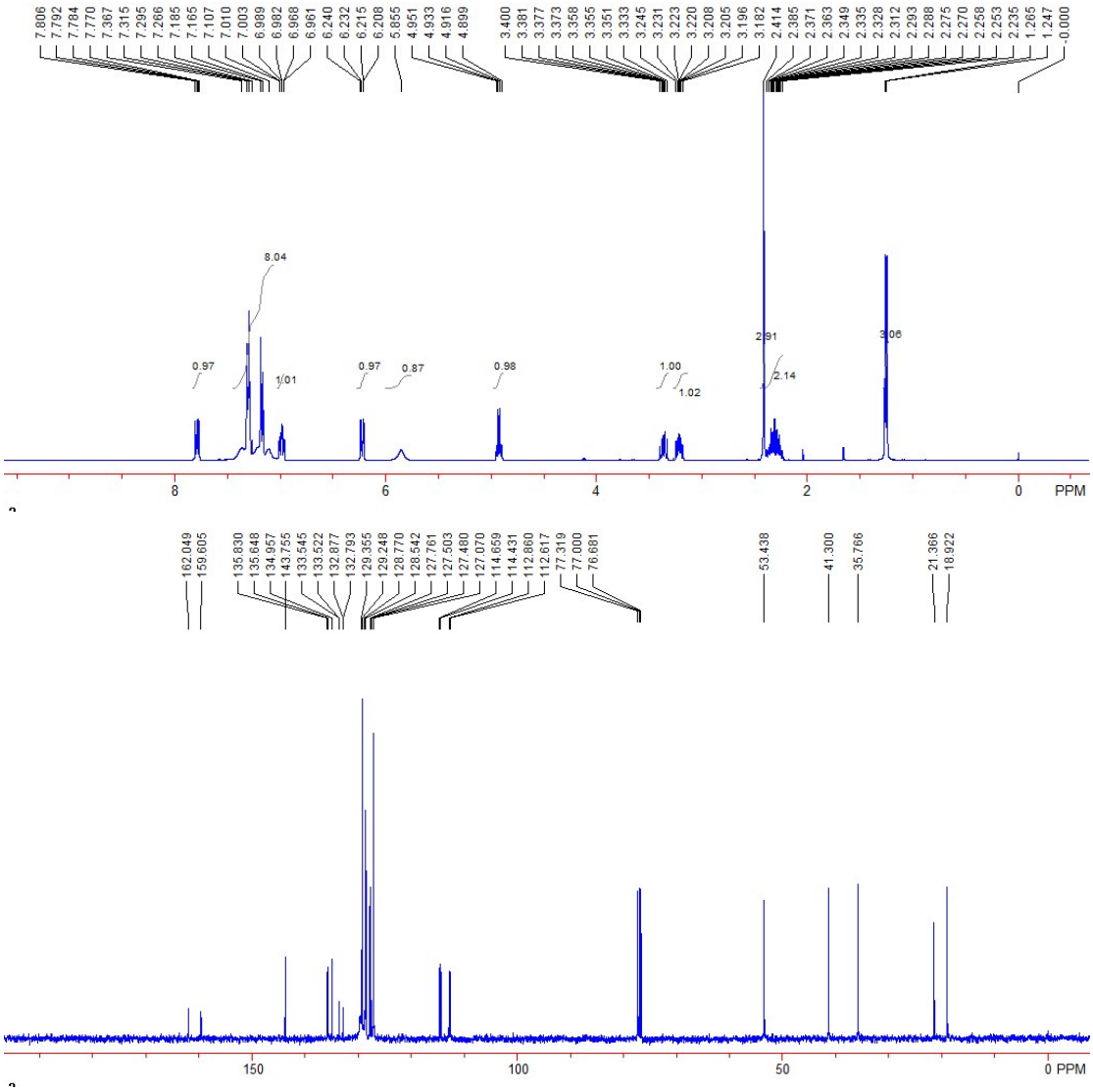
NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 35.8, 41.5, 53.4, 126.2, 126.3, 127.1, 127.5, 127.6, 127.8, 128.4, 129.1, 131.0, 131.7, 133.5, 134.1, 136.2, 136.4, 143.5; IR (neat): ν 2968, 2919, 1595, 1345, 1161, 1091, 819 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{28}ClN_2O_2S$ $[M+NH_4]^+$: 455.1555, found: 455.1556.

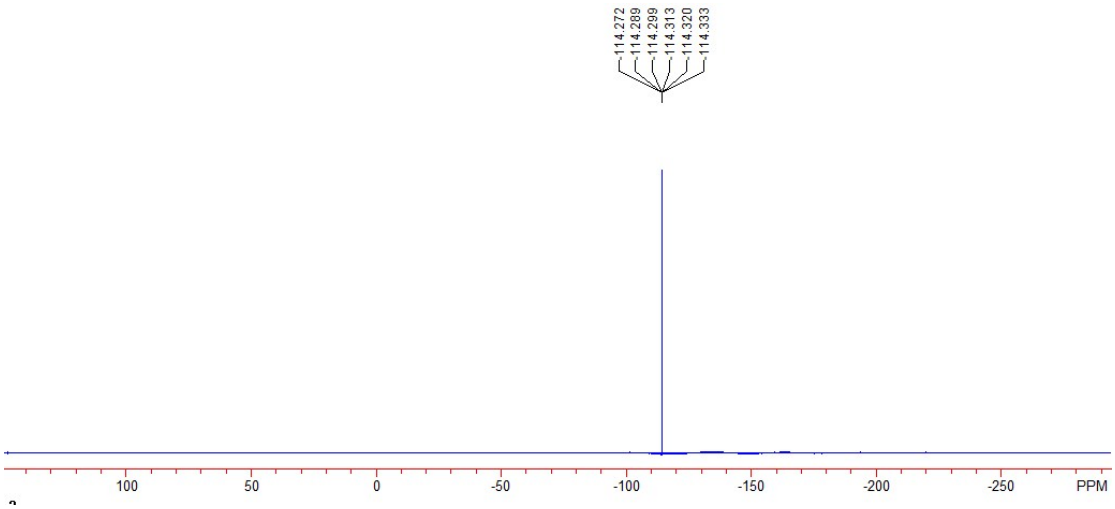


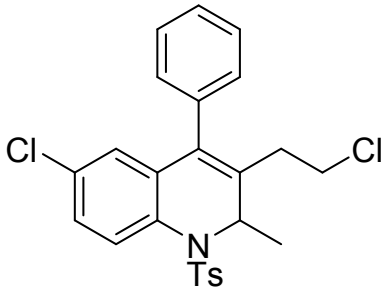


Compound 2b: Yield: 76 mg, 84%. A light yellow solid. Mp: 148-150 ^oC. ^1H NMR ($CDCl_3$, 400

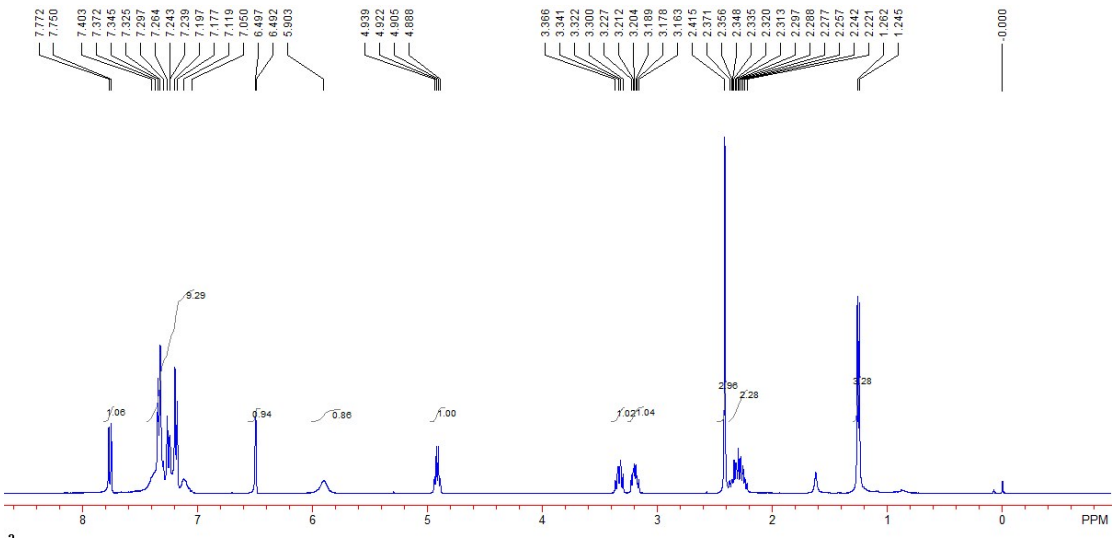
MHz, TMS) δ 1.25 (d, 3H, J = 7.2 Hz), 2.23-2.38 (m, 2H), 2.41 (s, 3H), 3.18-3.24 (m, 1H), 3.33-3.40 (m, 1H), 4.92 (q, 1H, J = 7.2 Hz), 5.85 (br, 1H), 6.22 (dd, 1H, J_1 = 9.6 Hz, J_2 = 2.8 Hz), 6.96-7.01 (m, 1H), 7.10-7.36 (m, 8H), 7.77-7.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.3, 35.7, 41.3, 53.4, 112.7 (d, J = 24.3 Hz), 114.5 (d, J = 22.8 Hz), 127.0, 127.4 (d, J = 2.3 Hz), 127.7, 128.5, 128.7, 129.2, 129.3, 129.6, 132.8 (d, J = 8.4 Hz), 133.5 (d, J = 2.3 Hz), 134.9, 135.6, 135.8, 143.7, 160.8 (d, J = 244.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -114.3~-114.2 (m); IR (neat): ν 2924, 1598, 1482, 1348, 1164, 1082, 819 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}ClFN_2O_2S$ $[M+NH_4]^+$: 473.1460, found: 473.1460.

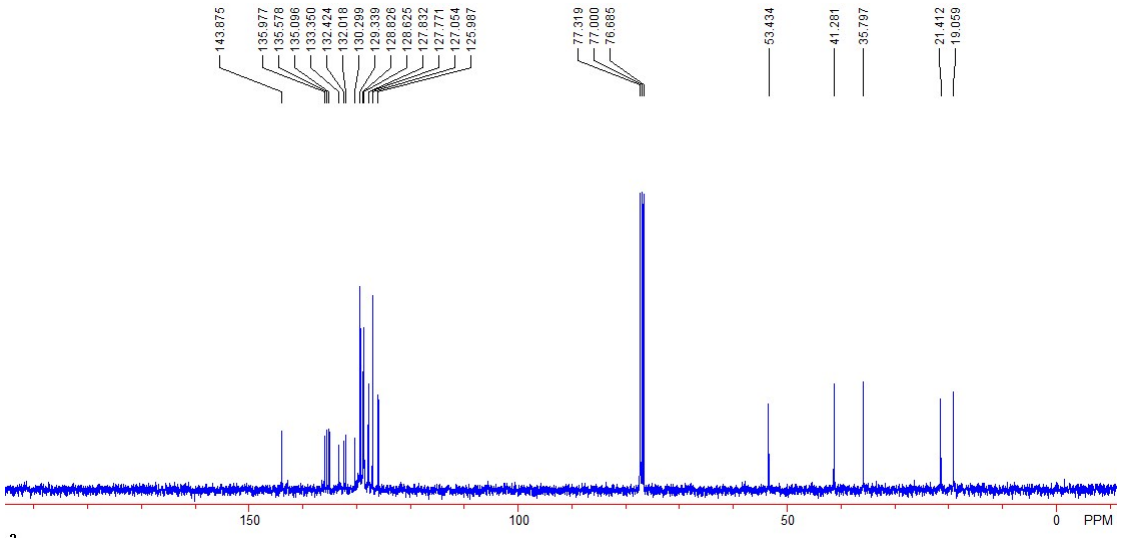


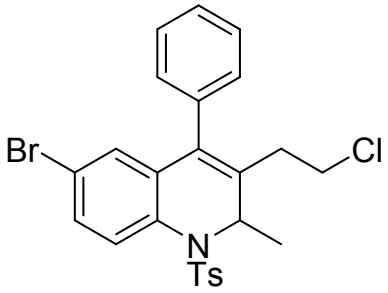




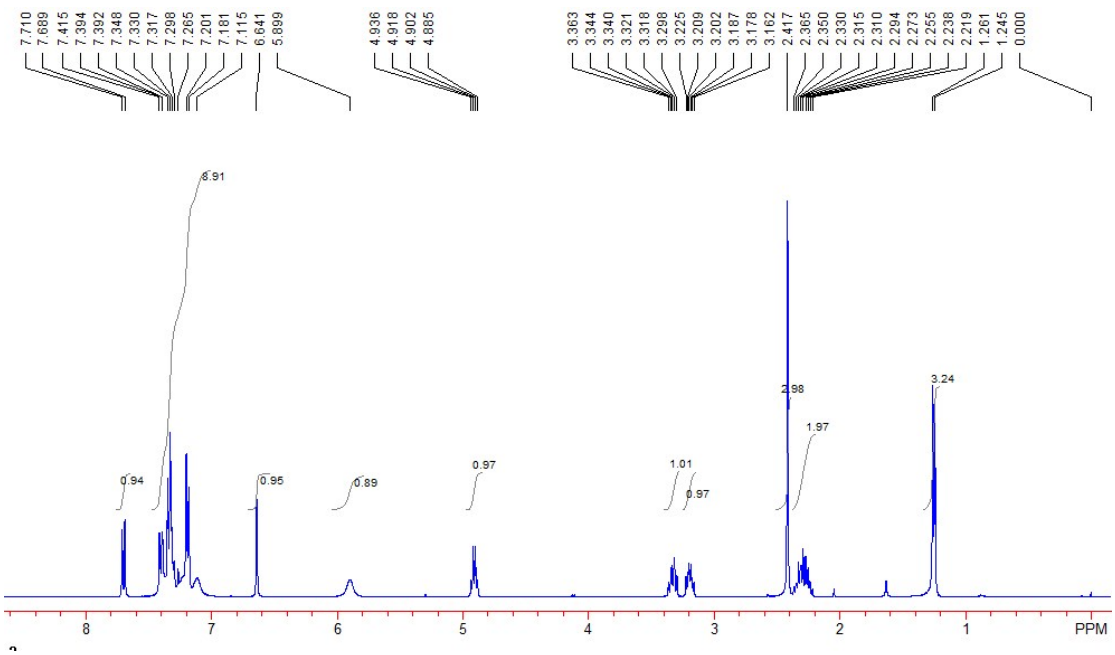
Compound 2c: Yield: 81 mg, 86%. A light yellow solid. Mp: 146-149 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, *J* = 6.8 Hz), 2.22-2.37 (m, 2H), 2.41 (s, 3H), 3.16-3.22 (m, 1H), 3.30-3.36 (m, 1H), 4.91 (q, 1H, *J* = 6.8 Hz), 5.90 (br, 1H), 6.49 (d, 1H, *J* = 2.0 Hz), 7.05-7.40 (m, 9H), 7.76 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 35.7, 41.2, 53.4, 125.9, 127.0, 127.7, 127.8, 128.6, 128.8, 129.3, 130.2, 132.0, 132.4, 133.3, 135.0, 135.5, 135.9, 143.8; IR (neat): ν 2919, 1592, 1471, 1348, 1163, 1081, 877 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}Cl_2N_2O_2S$ $[M+NH_4]^+$: 489.1165, found: 489.1166.

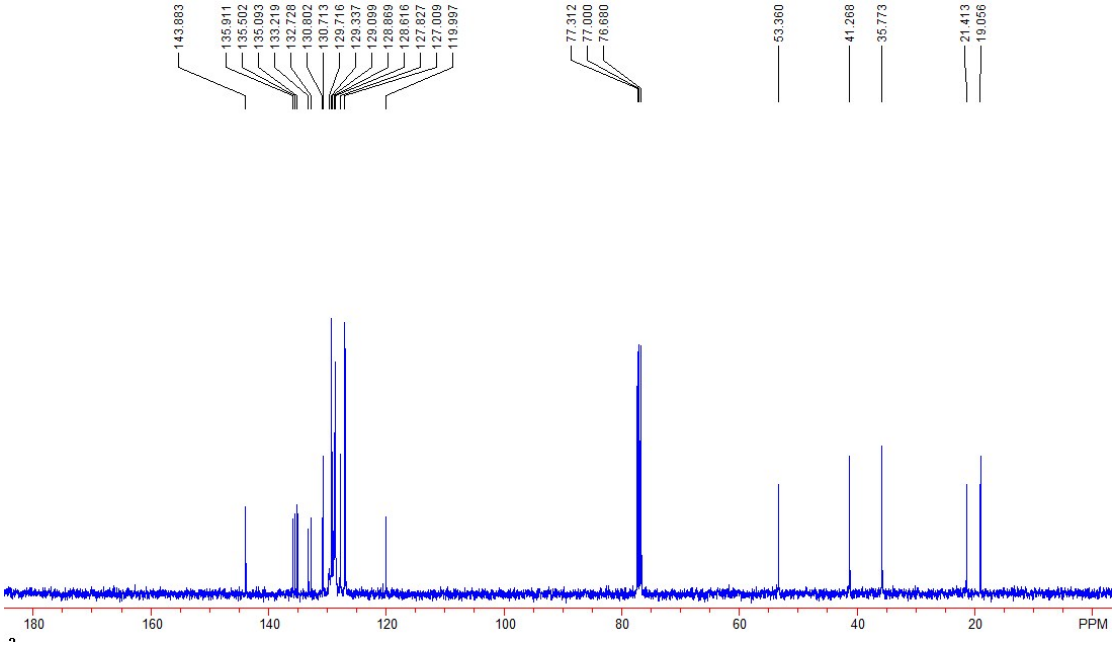


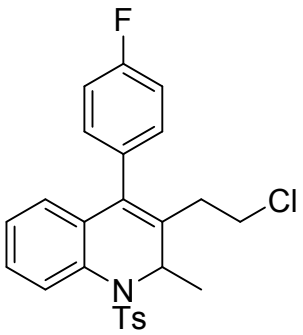




Compound 2d: Yield: 88 mg, 85%. A light yellow solid. Mp: 166-168 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, *J* = 6.4 Hz), 2.21-2.36 (m, 2H), 2.41 (s, 3H), 3.16-3.22 (m, 1H), 3.29-3.36 (m, 1H), 4.91 (q, 1H, *J* = 6.4 Hz), 5.89 (br, 1H), 6.64 (s, 1H), 7.11-7.41 (m, 9H), 7.70 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 35.7, 41.2, 53.3, 119.9, 127.0, 127.8, 128.6, 128.8, 129.0, 129.3, 129.7, 130.7, 130.8, 132.7, 133.2, 135.0, 135.5, 135.9, 143.8; IR (neat): ν 2924, 1598, 1474, 1347, 1162, 1081, 877 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}BrClN_2O_2S$ $[M+NH_4]^+$: 533.0660, found: 533.0660.

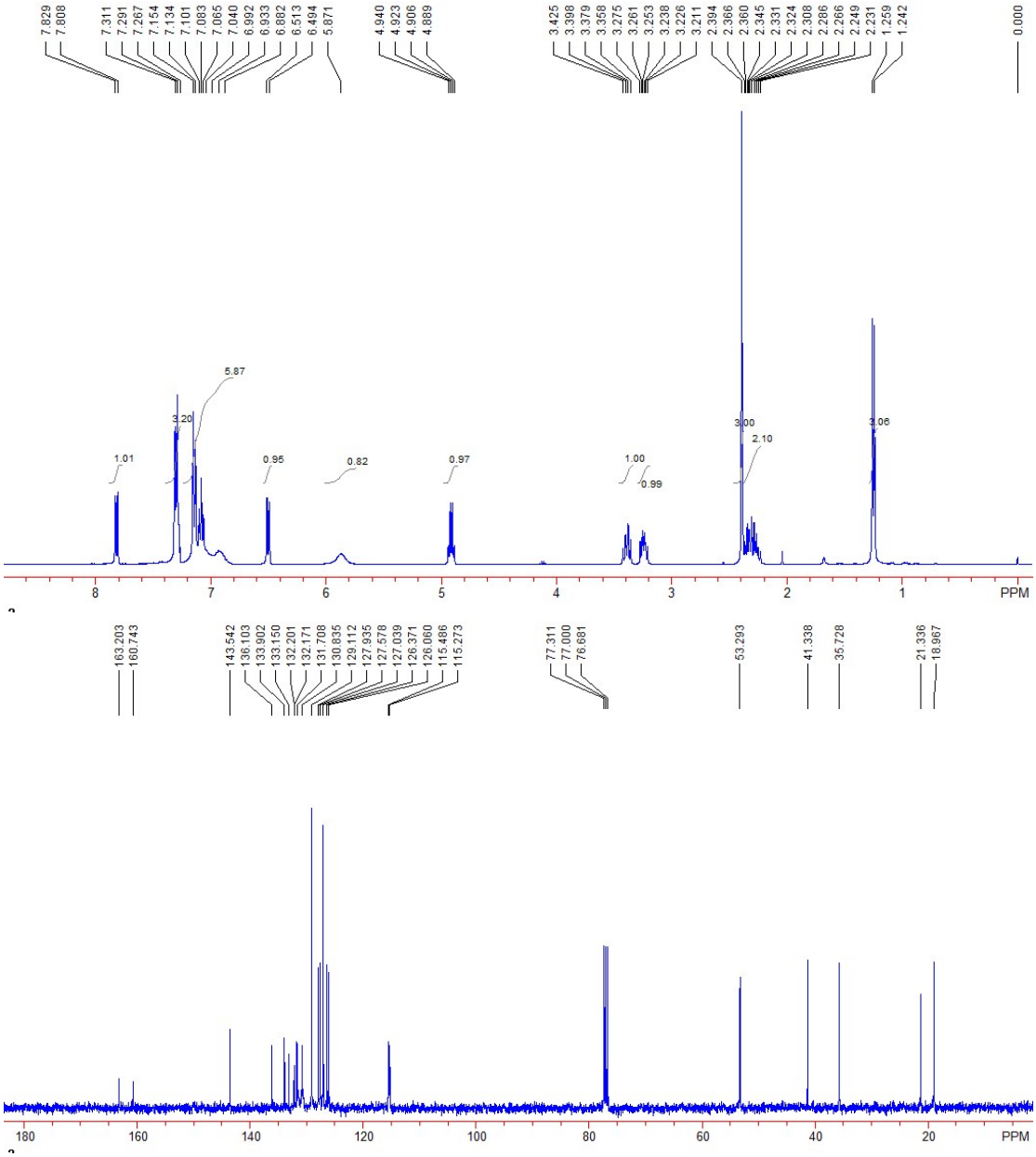


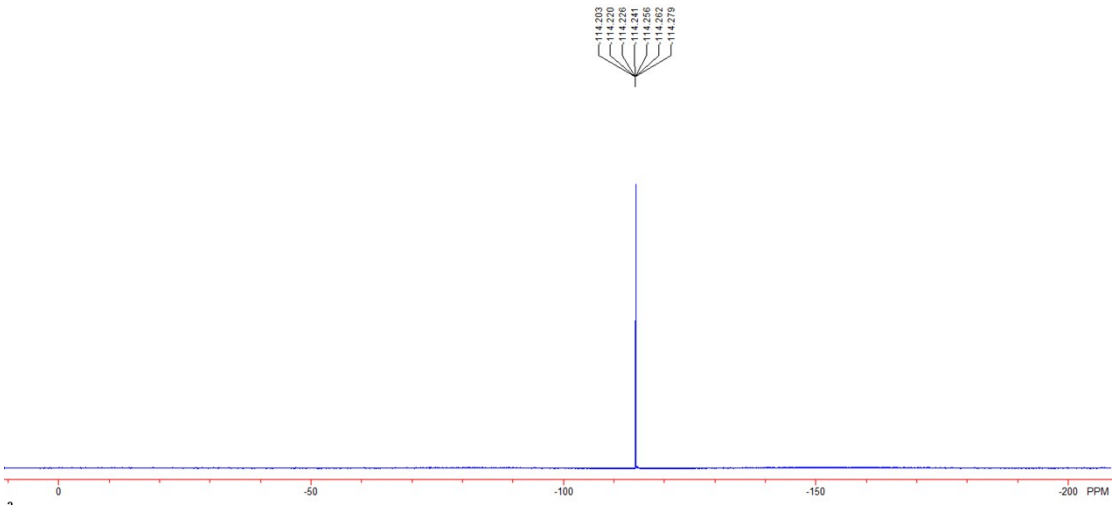


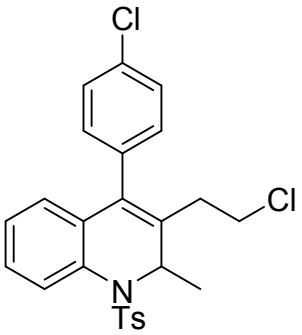


Compound 2e: Yield: 78 mg, 86%. A light yellow solid. Mp: 158-161 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, J = 6.8 Hz), 2.23-2.36 (m, 2H), 2.39 (s, 3H), 3.21-3.27 (m, 1H), 3.35-

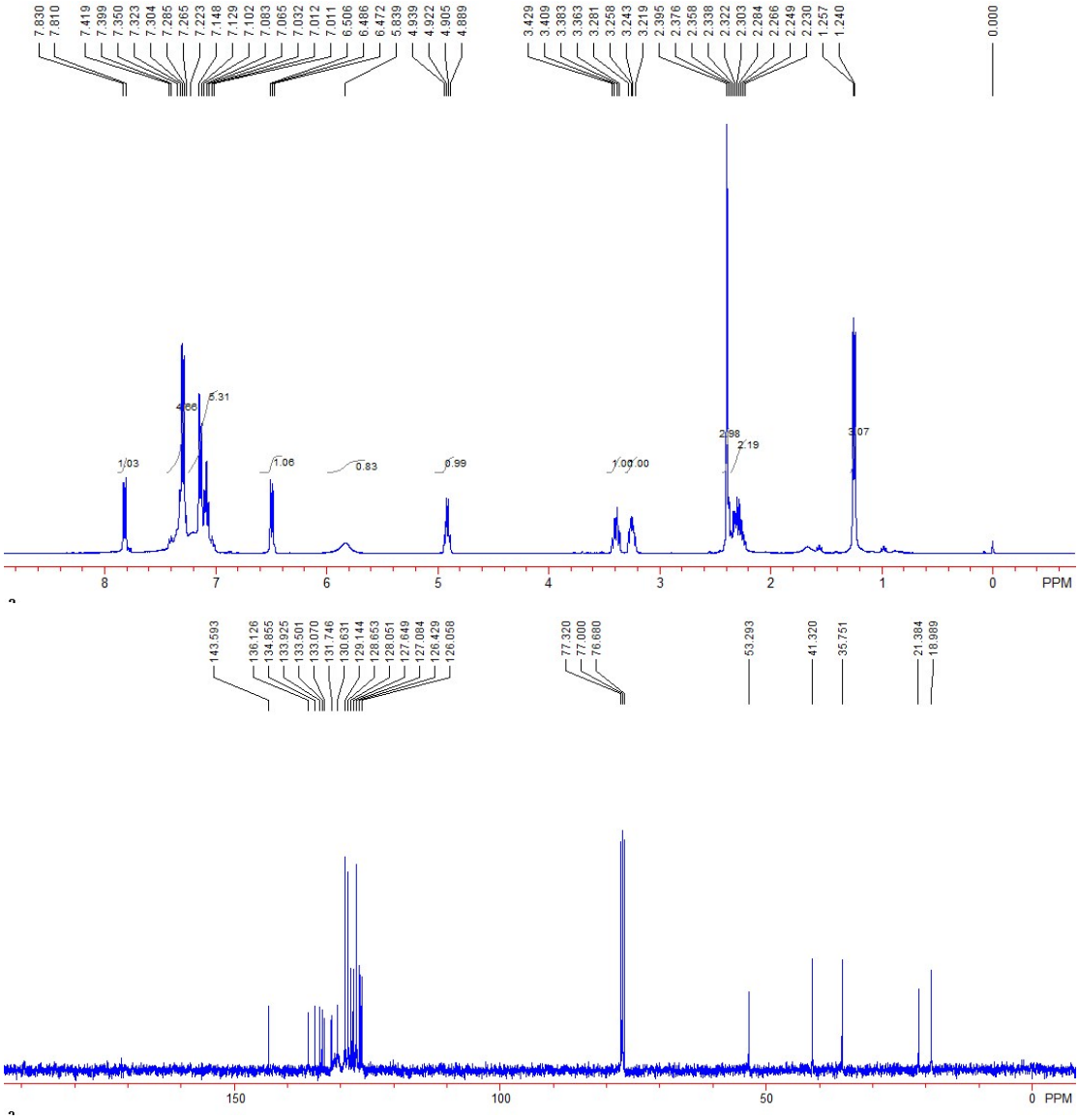
3.42 (m, 1H), 4.91 (q, 1H, J = 6.8 Hz), 5.87 (br, 1H), 6.50 (d, 1H, J = 7.6 Hz), 6.88-7.15 (m, 6H), 7.26-7.31 (m, 3H), 7.81 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.3, 35.7, 41.3, 53.2, 115.3 (d, J = 21.3 Hz), 126.0, 126.3, 127.5, 127.9, 129.1, 130.8, 131.7, 132.1 (d, J = 3.0 Hz), 133.1, 133.9, 136.1, 143.5, 161.9 (d, J = 246.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -114.27~-114.20 (m); IR (neat): ν 2919, 1595, 1507, 1344, 1220, 1158, 1084, 890 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}ClFN_2O_2S$ $[M+NH_4]^+$: 473.1460, found: 473.1463.

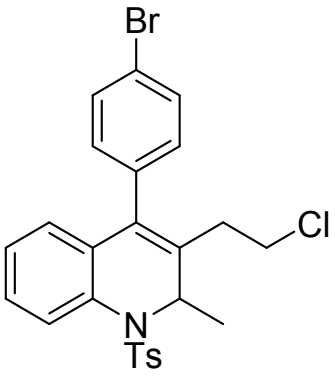






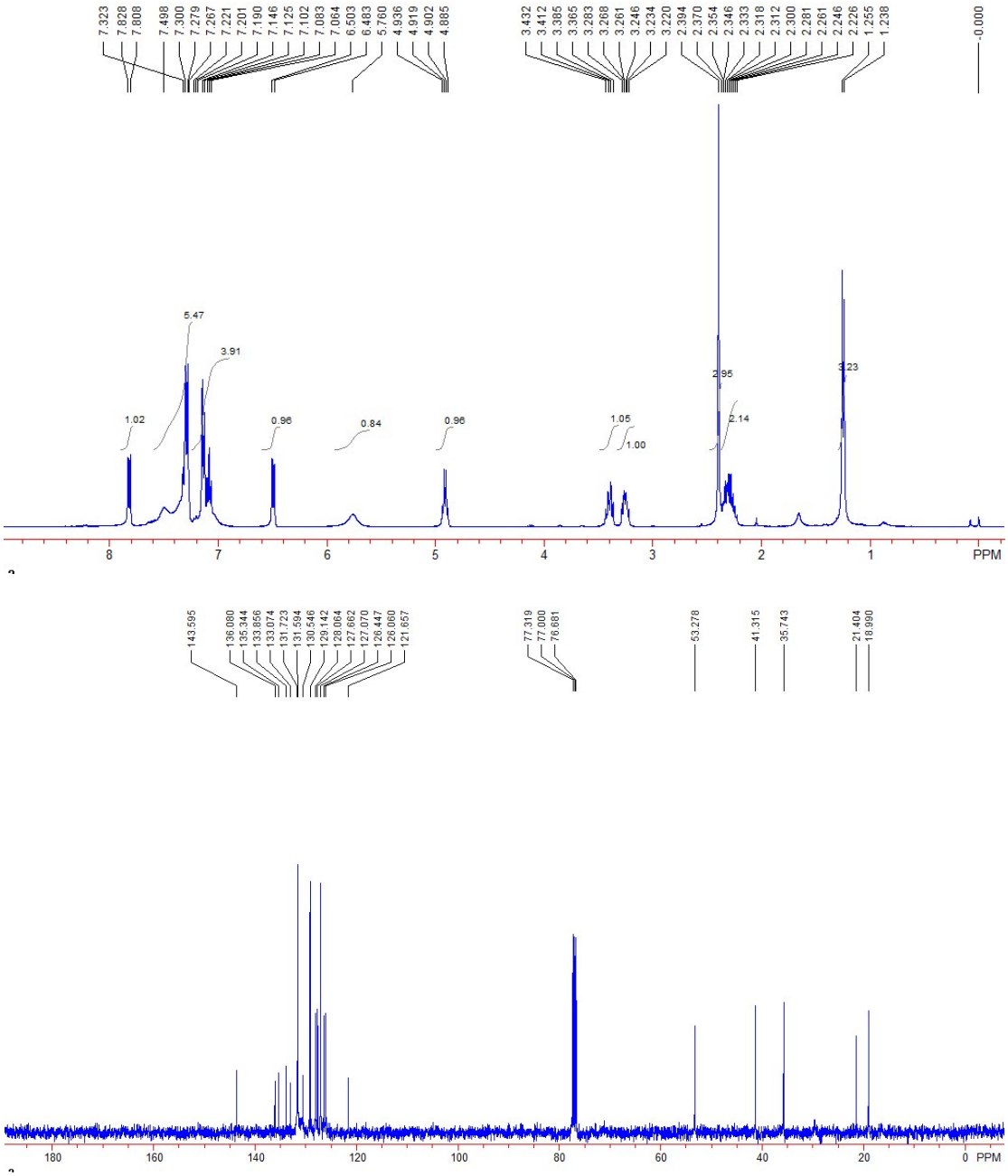
Compound 2f: Yield: 85 mg, 90%. A light yellow solid. Mp: 164-167 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (d, 3H, *J* = 6.8 Hz), 2.23-2.39 (m, 5H), 3.21-3.28 (m, 1H), 3.36-3.42 (m, 1H), 4.91 (q, 1H, *J* = 6.8 Hz), 5.83 (br, 1H), 6.47-6.50 (m, 1H), 7.01-7.22 (m, 5H), 7.26-7.41 (m, 4H), 7.82 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.3, 35.7, 41.3, 53.2, 126.0, 126.4, 127.0, 127.6, 128.0, 128.6, 129.1, 130.6, 131.7, 133.0, 133.5, 133.9, 134.8, 136.1, 143.5; IR (neat): ν 2973, 2919, 1592, 1481, 1343, 1159, 1082, 813, 779 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}Cl_2N_2O_2S$ $[M+NH_4]^+$: 489.1165, found: 489.1166.

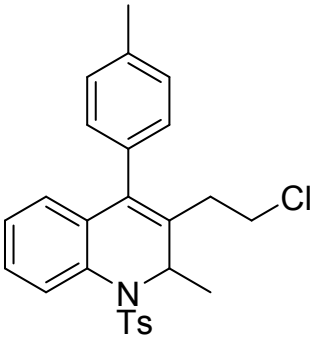




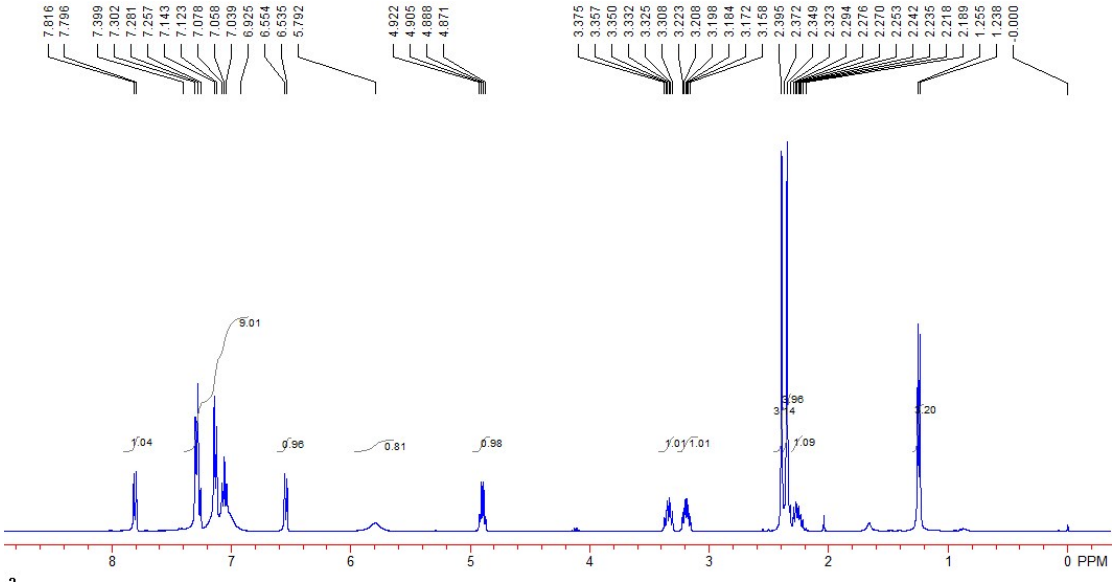
Compound 2g: Yield: 91 mg, 88%. A light yellow solid. Mp: 192-195 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (d, 3H, *J* = 6.8 Hz), 2.22-2.37 (m, 2H), 2.39 (s, 3H), 3.22-3.28 (m, 1H), 3.36-3.43 (m, 1H), 4.91 (q, 1H, *J* = 6.8 Hz), 5.76 (br, 1H), 6.49 (d, 1H, *J* = 8.0 Hz), 7.06-7.22 (m, 4H), 7.26-7.32 (m, 5H), 7.81 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.4, 35.7,

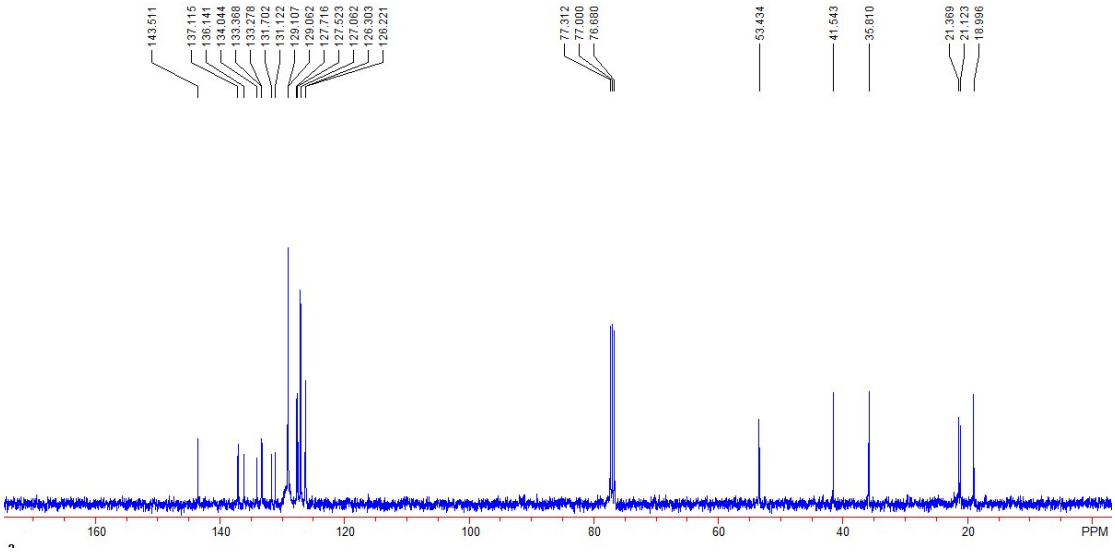
41.3, 53.2, 121.6, 126.0, 126.4, 127.0, 127.6, 128.0, 129.1, 130.5, 131.5, 131.7, 133.0, 133.8, 135.3, 136.0, 143.5; IR (neat): ν 2924, 1592, 1478, 1346, 1164, 1069, 820, 759 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}BrClN_2O_2S$ $[M+NH_4]^+$: 533.0660, found: 533.0659.

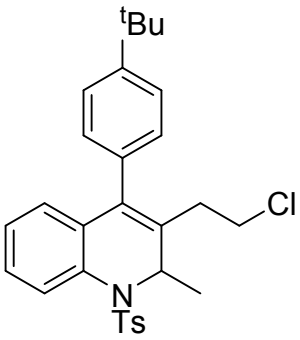




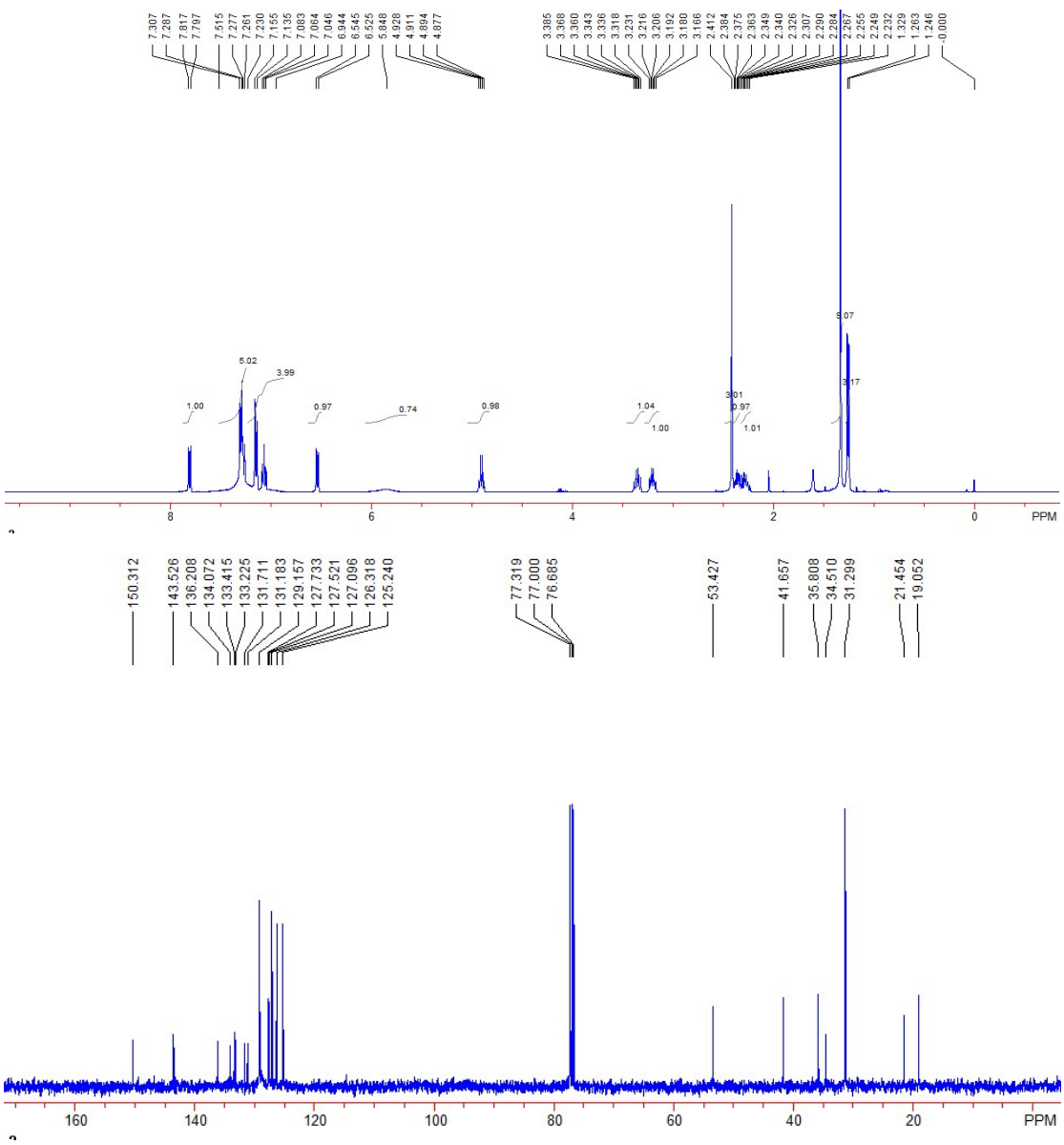
Compound 2h: Yield: 73 mg, 81%. A light yellow solid. Mp: 177-179 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (d, 3H, *J* = 6.8 Hz), 2.18-2.29 (m, 1H), 2.32-2.37 (m, 4H), 2.39 (s, 3H), 3.15-3.22 (m, 1H), 3.30-3.37 (m, 1H), 4.89 (q, 1H, *J* = 6.8 Hz), 5.79 (br, 1H), 6.54 (d, 1H, *J* = 7.6 Hz), 6.92-7.39 (m, 9H), 7.80 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.1, 21.3, 35.8, 41.5, 53.4, 126.2, 126.3, 127.0, 127.5, 127.7, 129.0, 129.1, 131.1, 131.7, 133.2, 133.3, 134.0, 136.1, 137.1, 143.5; IR (neat): ν 2979, 2932, 1598, 1440, 1342, 1164, 1093, 905 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{30}ClN_2O_2S$ $[M+NH_4]^+$: 469.1711, found: 469.1712.

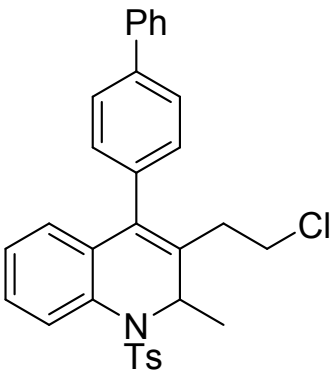






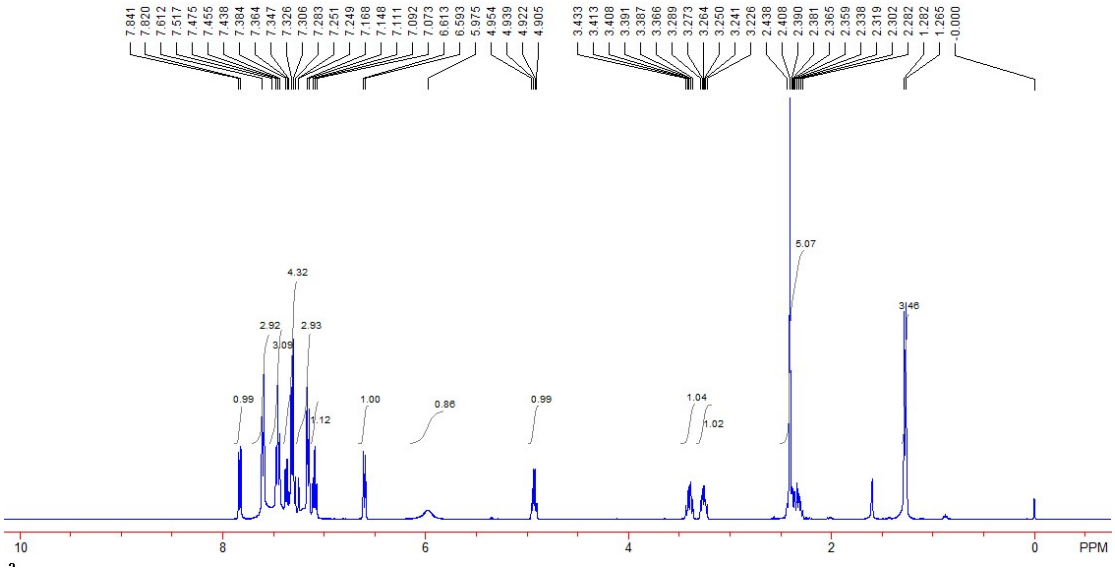
Compound 2i: Yield: 78 mg, 79%. A light yellow solid. Mp: 64-66 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, *J* = 6.8 Hz), 1.32 (s, 9H), 2.23-2.38 (m, 2H), 2.41 (s, 3H), 3.16-3.23 (m, 1H), 3.31-3.38 (m, 1H), 4.90 (q, 1H, *J* = 6.8 Hz), 5.84 (br, 1H), 6.53 (d, 1H, *J* = 8.0 Hz), 6.94-7.15 (m, 4H), 7.23-7.30 (m, 5H), 7.80 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 31.2, 34.5, 35.8, 41.6, 53.4, 125.2, 126.3, 127.0, 127.5, 127.7, 129.1, 131.1, 131.7, 133.2, 133.4, 134.0, 136.2, 143.5, 150.3; IR (neat): ν 2960, 1598, 1450, 1348, 1165, 1083, 813, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{33}ClNO_2S$ $[M+H]^+$: 494.1915, found: 494.1915.

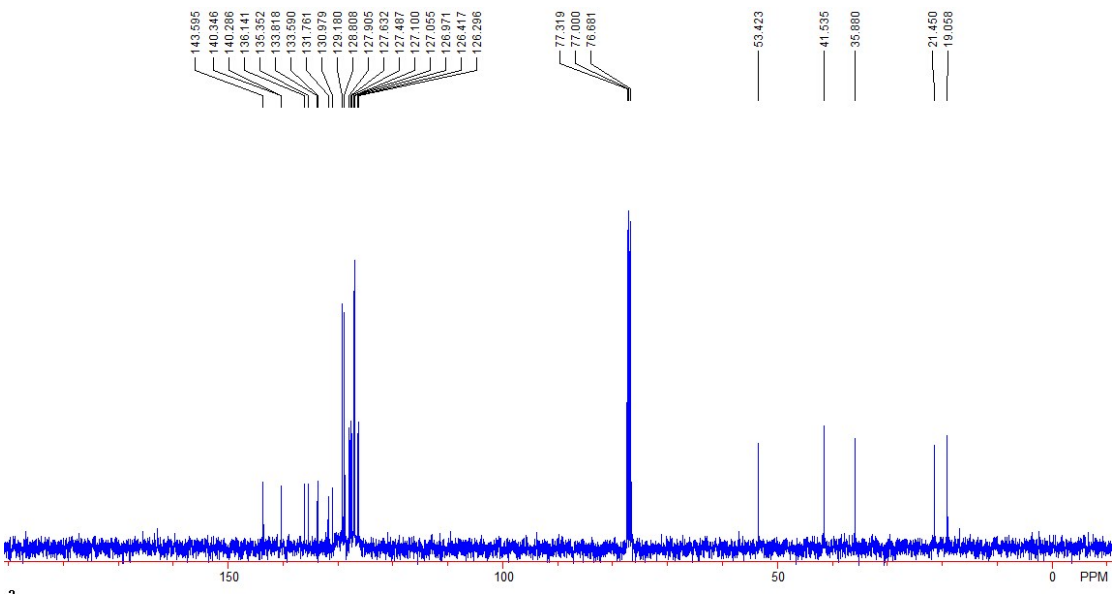


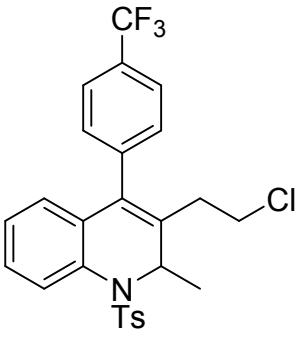


Compound 2j: Yield: 83 mg, 81%. A light yellow solid. Mp: 71-73 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.27 (d, 3H, J = 6.8 Hz), 2.28-2.43 (m, 5H), 3.22-3.28 (m, 1H), 3.36-3.43 (m, 1H), 4.93 (q, 1H, J = 6.8 Hz), 5.97 (br, 1H), 6.60 (d, 1H, J = 8.0 Hz), 7.09 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.14-7.16 (m, 3H), 7.24-7.38 (m, 4H), 7.43-7.47 (m, 3H), 7.60 (d, 3H, J = 8.0 Hz), 7.83 (d, 1H, J =

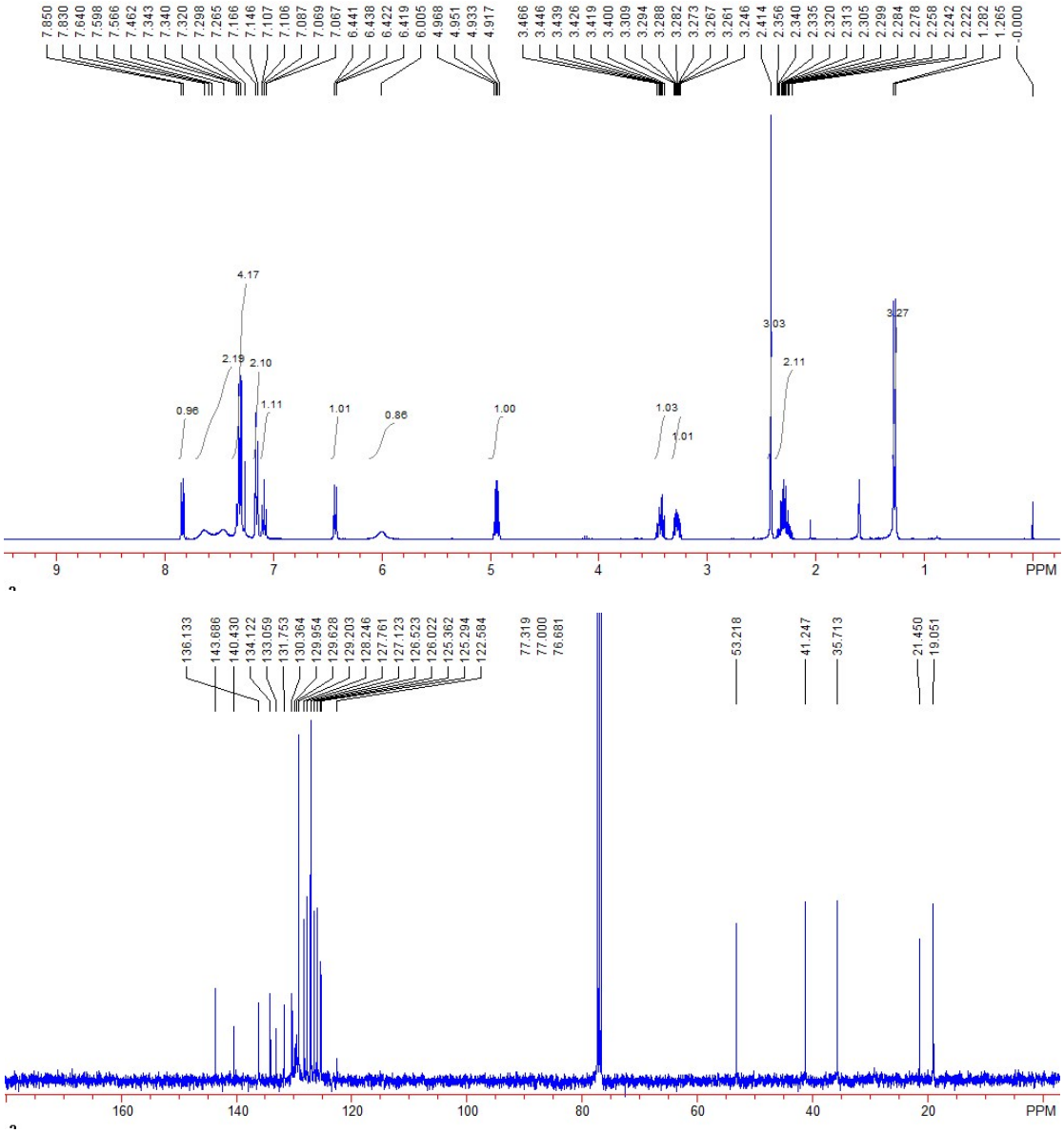
8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 35.8, 41.5, 53.4, 126.2, 126.4, 126.9, 127.0, 127.1, 127.4, 127.6, 127.9, 128.8, 129.1, 130.9, 131.7, 133.5, 133.8, 135.3, 136.1, 140.2, 140.3, 143.5; IR (neat): ν 2927, 1600, 1484, 1348, 1164, 1083, 814, 763 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{32}ClN_2O_2S$ $[M+NH_4]^+$: 531.1868, found: 531.1867.

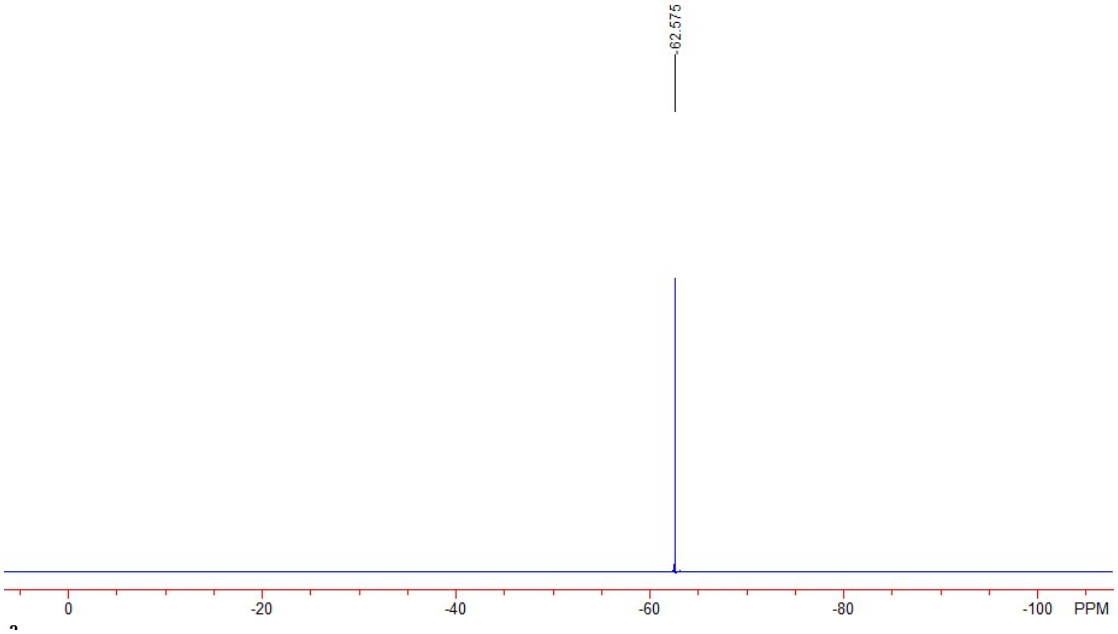


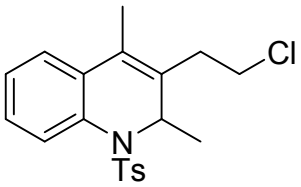




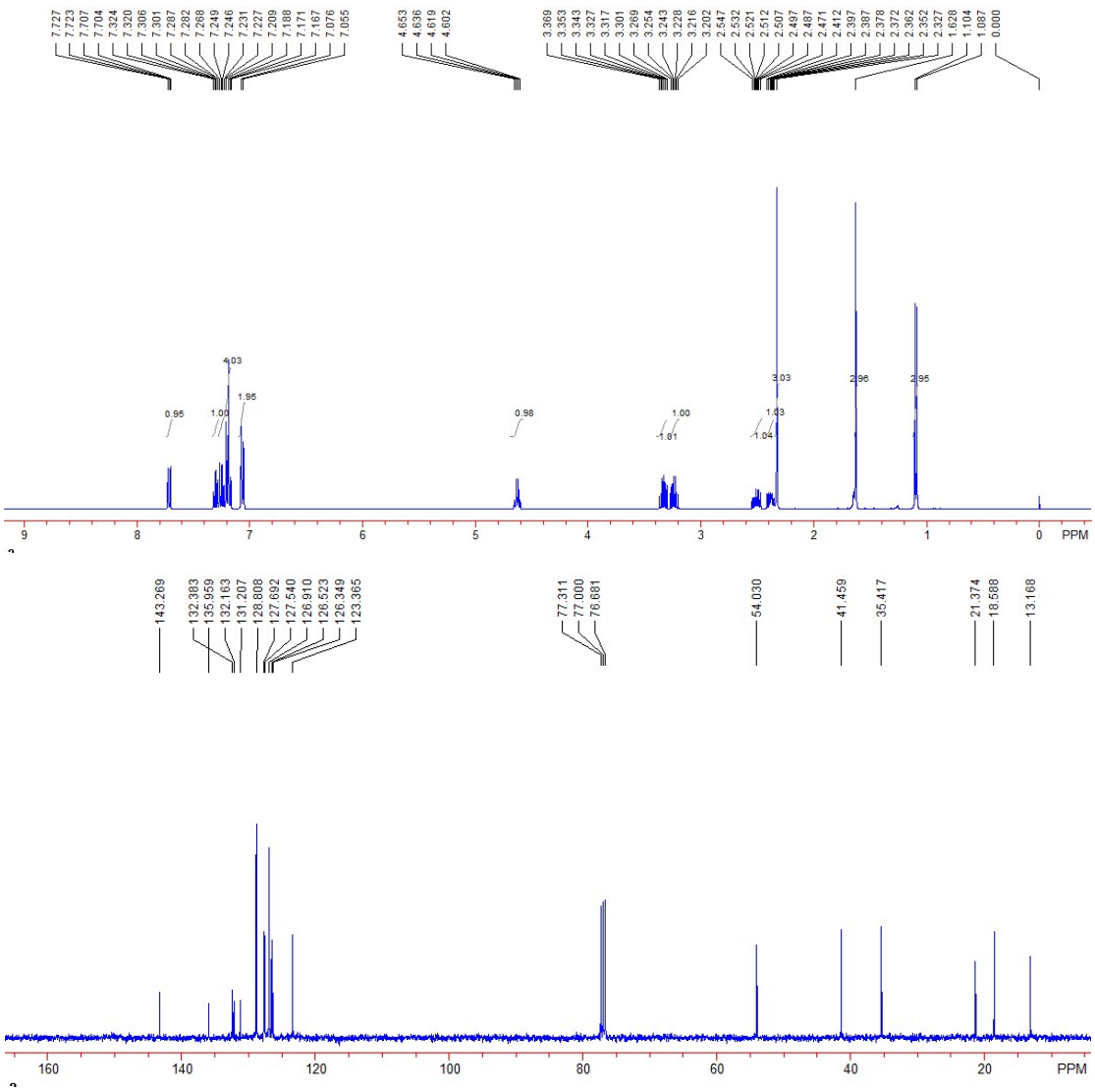
Compound 2k: Yield: 78 mg, 77%. A light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.27 (d, 3H, J = 6.8 Hz), 2.22-2.35 (m, 2H), 2.41 (s, 3H), 3.24-3.30 (m, 1H), 3.40-3.46 (m, 1H), 4.94 (q, 1H, J = 6.8 Hz), 6.00 (br, 1H), 6.43 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.06-7.16 (m, 3H), 7.26-7.46 (m, 4H), 7.56-7.64 (m, 2H), 7.84 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 35.7, 41.2, 53.2, 123.9 (q, J = 271.0 Hz), 125.3, 126.0, 126.5, 127.1, 127.7, 128.2, 129.2, 129.7 (q, J = 32.6 Hz), 130.3, 131.7, 133.0, 134.1, 136.1, 140.4, 143.6; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -62.5 (s); IR (neat): ν 2933, 1615, 1455, 1321, 1162, 1065, 760 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{27}ClF_3N_2O_2S$ $[M+NH_4]^+$: 523.1428, found: 523.1428.

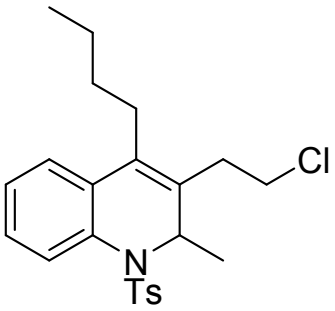






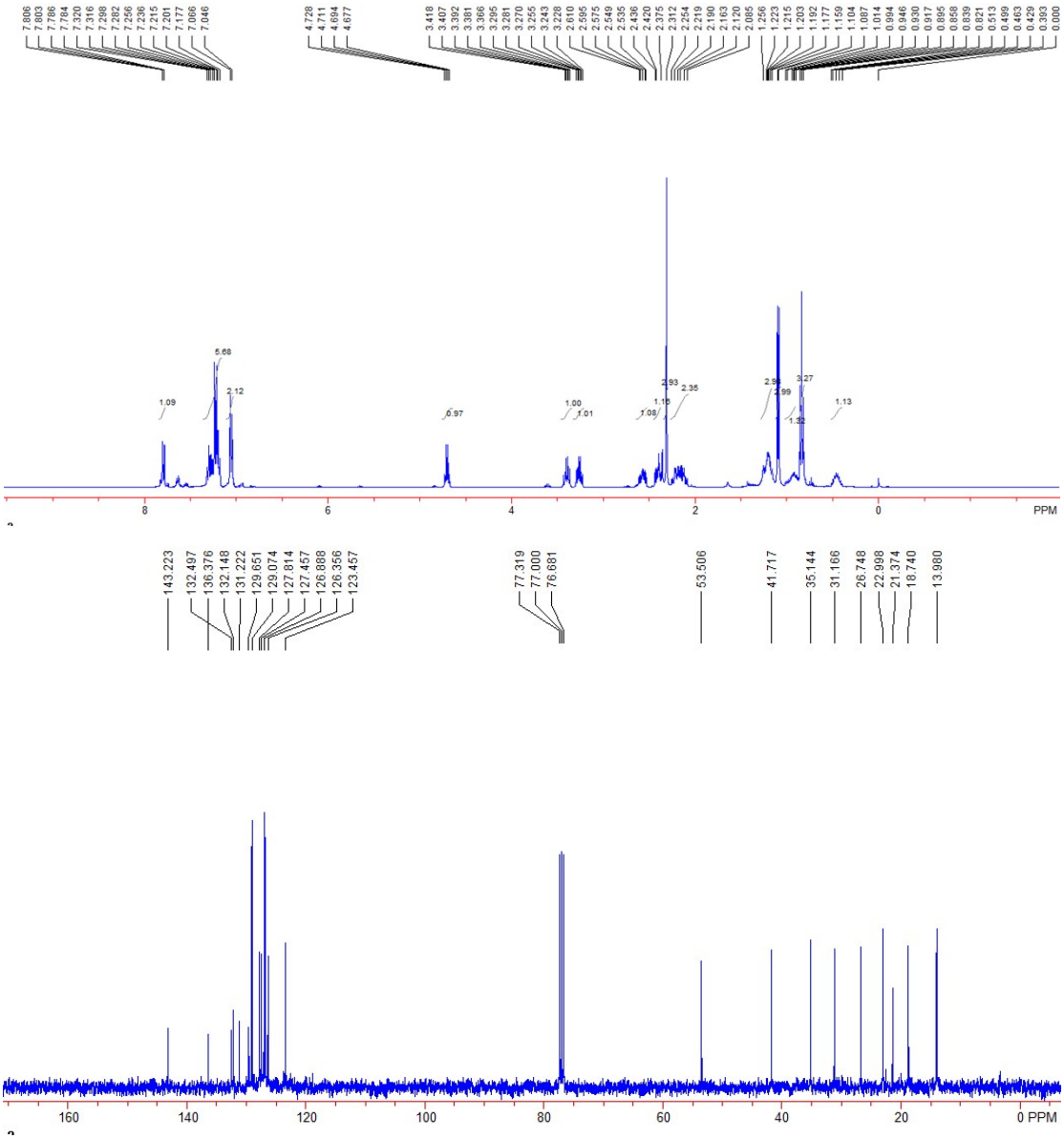
Compound 2l: Yield: 53 mg, 70%. A light yellow solid. Mp: 85-88 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (d, 3H, J = 6.8 Hz), 1.62 (s, 3H), 2.32 (s, 3H), 2.35-2.41 (m, 1H), 2.47-2.54 (m, 1H), 3.20-3.26 (m, 1H), 3.30-3.36 (m, 1H), 4.62 (q, 1H, J = 6.8 Hz), 7.06 (d, 2H, J = 8.4 Hz), 7.16-7.32 (m, 5H), 7.71 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.1, 18.5, 21.3, 35.4, 41.4, 54.0, 123.3, 126.3, 126.5, 126.9, 127.5, 127.6, 128.8, 131.2, 132.1, 132.3, 135.9, 143.2; IR (neat): ν 2968, 1592, 1450, 1339, 1162, 1091, 814, 764 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{26}ClN_2O_2S$ $[M+NH_4]^+$: 393.1398, found: 393.1399.

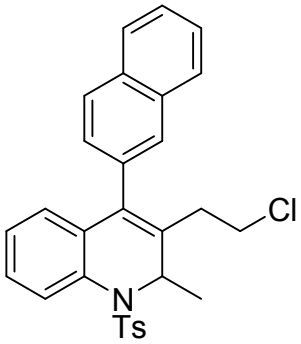




Compound 2m: Yield: 59 mg, 71%. A light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.41-0.51 (m, 1H), 0.83 (t, 3H, *J* = 7.6 Hz), 0.89-1.01 (m, 1H), 1.09 (d, 3H, *J* = 6.8 Hz), 1.15-1.25 (m, 2H), 2.08-2.25 (m, 2H), 2.31 (s, 3H), 2.37-2.43 (m, 1H), 2.53-2.61 (m, 1H), 3.22-3.29 (m, 1H), 3.36-3.41 (m, 1H), 4.70 (q, 1H, *J* = 6.8 Hz), 7.05 (d , 2H, *J* = 8.0 Hz), 7.17-7.32 (m, 5H), 7.78-7.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 18.7, 21.3, 22.9, 26.7, 31.1, 35.1, 41.7, 53.5, 123.4, 126.3, 126.8, 127.4, 127.8, 129.0, 129.6, 131.2, 132.1, 132.4, 136.3, 143.2; IR (neat):

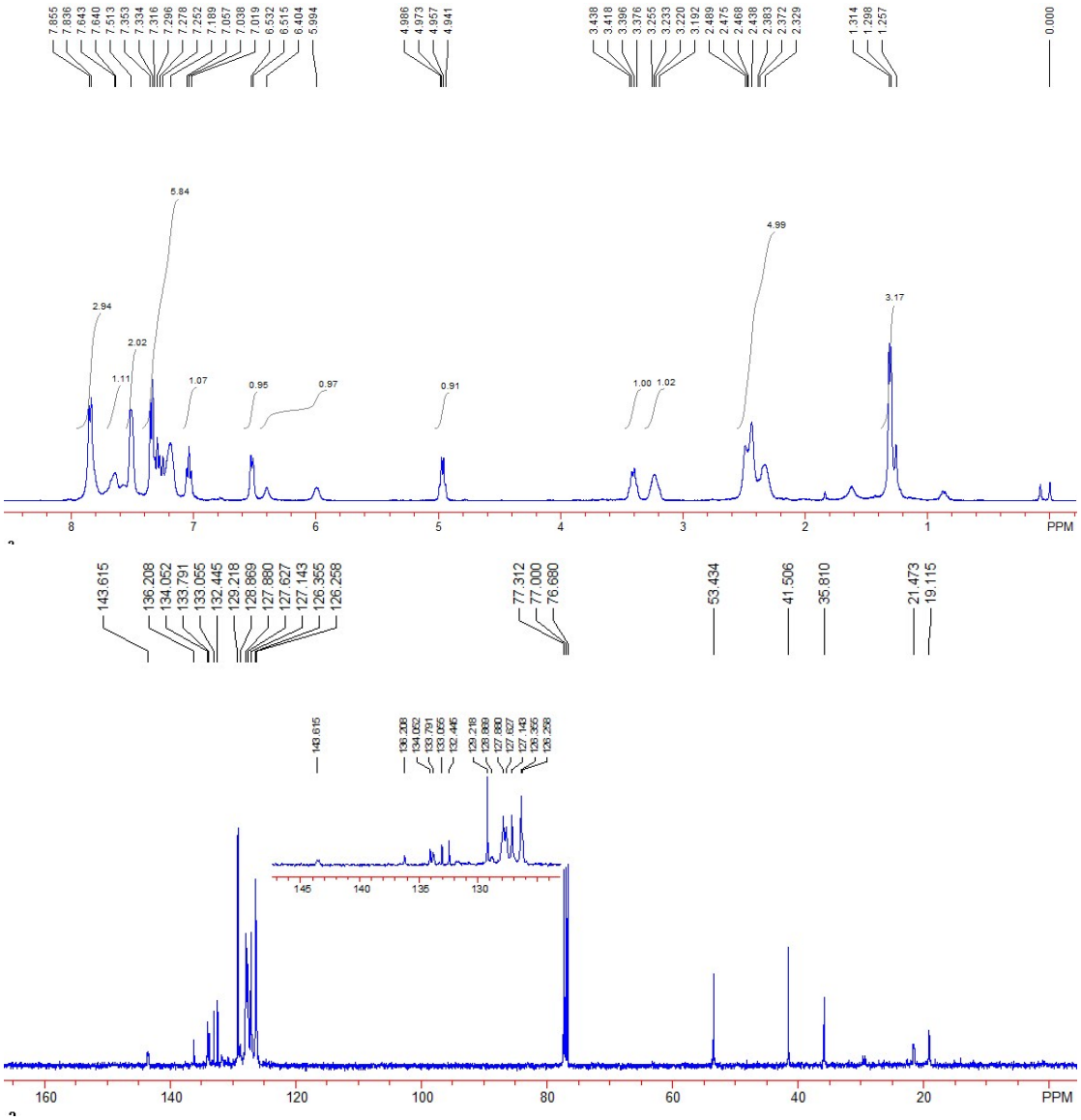
ν 2958, 1595, 1447, 1345, 1161, 1090, 812, 759 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{32}ClN_2O_2S$ $[M+NH_4]^+$: 435.1868, found: 435.1868.

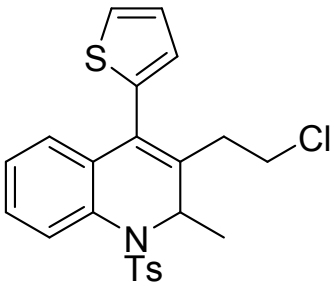




Compound 2o: Yield: 83 mg, 85%. A light yellow solid. Mp: 168-170 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.30 (d, 3H, J = 6.4 Hz), 2.32-2.48 (m, 5H), 3.19-3.25 (m, 1H), 3.37-3.43 (m, 1H), 4.96 (q, 1H, J = 6.4 Hz), 6.19 (d, 1H, J = 164.0 Hz), 6.52 (d, 1H, J = 6.8 Hz), 7.03 (dd, 1H, $J_1 = J_2$

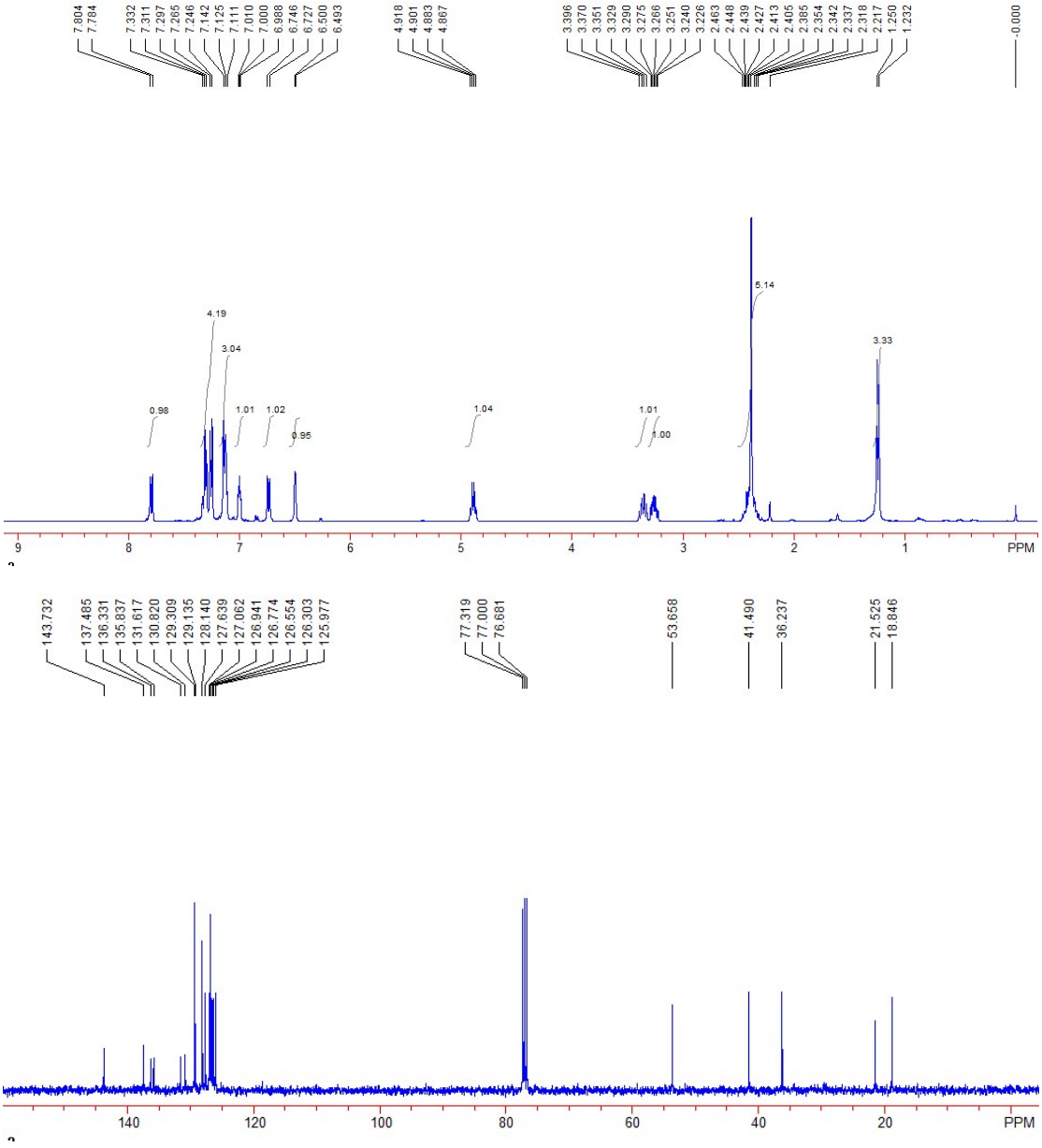
= 7.6 Hz), 7.18-7.35 (m, 6H), 7.51 (s, 2H), 7.64 (s, 1H), 7.83-7.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 35.8, 41.5, 53.4, 126.2, 126.3, 127.1, 127.6, 127.8, 128.8, 129.2, 132.4, 133.0, 133.7, 134.0, 136.2, 143.6; IR (neat): ν 2920, 1592, 1344, 1163, 1083, 812, 755 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{30}ClN_2O_2S$ $[M+NH_4]^+$: 505.1711, found: 505.1711.

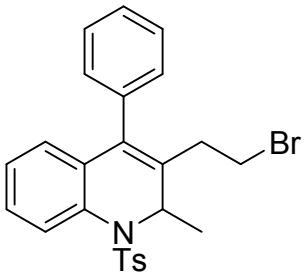




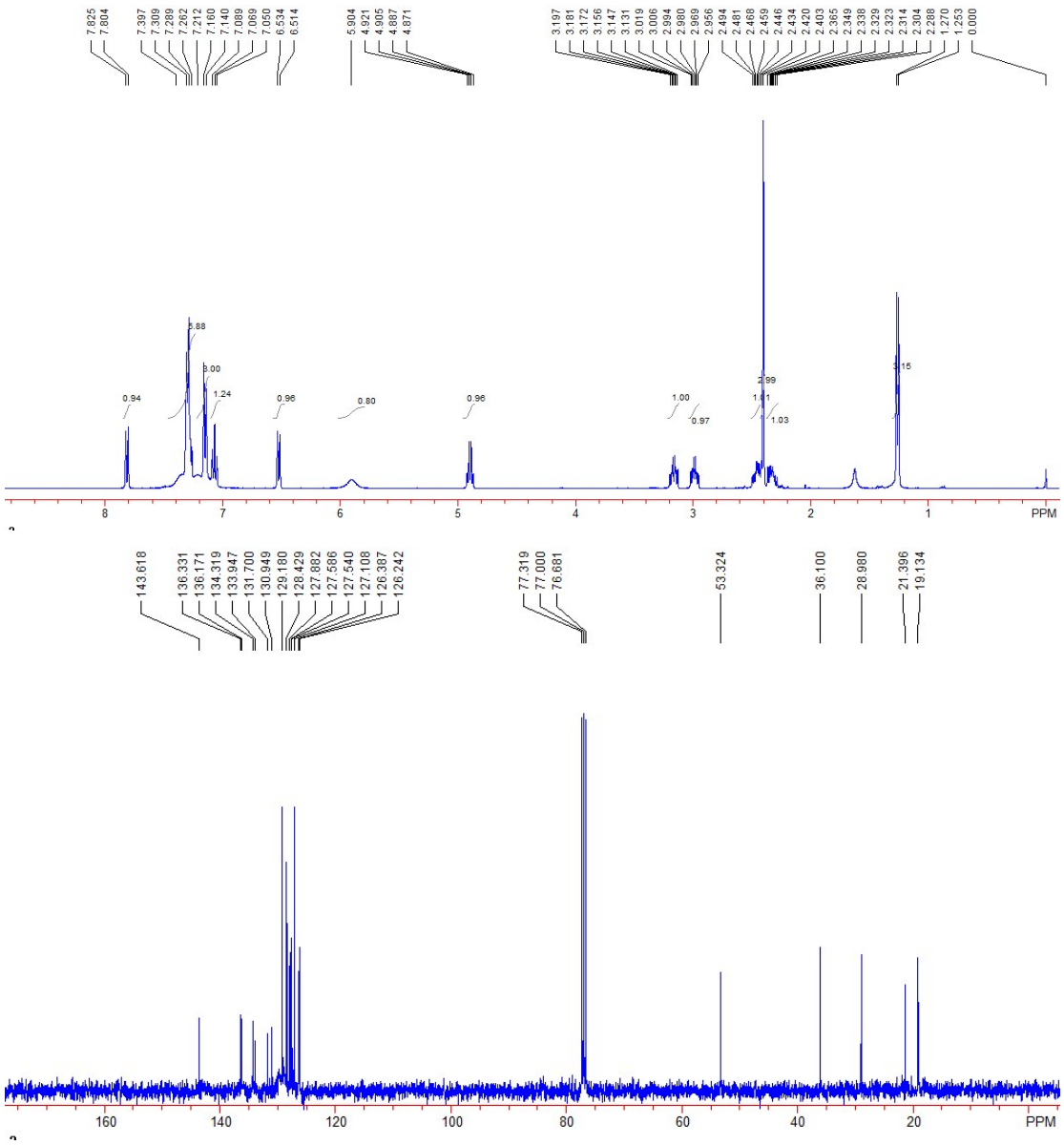
Compound 2n: Yield: 71 mg, 80%. A light yellow solid. Mp: 128-130 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (d, 3H, *J* = 7.2 Hz), 2.21-2.46 (m, 5H), 3.22-3.28 (m, 1H), 3.32-3.39 (m, 1H),

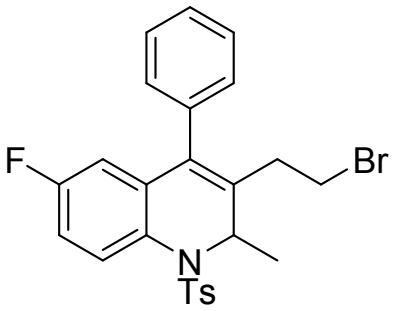
4.89 (q, 1H, J = 7.2 Hz), 6.49 (d, 1H, J = 2.8 Hz), 6.73 (d, 1H, J = 7.6 Hz), 6.98-7.01 (m, 1H), 7.11-7.14 (m, 3H), 7.24-7.33 (m, 4H), 7.79 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.8, 21.5, 36.2, 41.4, 53.6, 125.9, 126.3, 126.5, 126.7, 126.9, 127.0, 127.6, 128.1, 129.3, 130.8, 131.6, 135.8, 136.3, 137.5, 143.7; IR (neat): ν 2932, 1598, 1450, 1347, 1164, 1082, 814, 767 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{26}ClN_2O_2S_2$ $[M+NH_4]^+$: 461.1119, found: 461.1118.



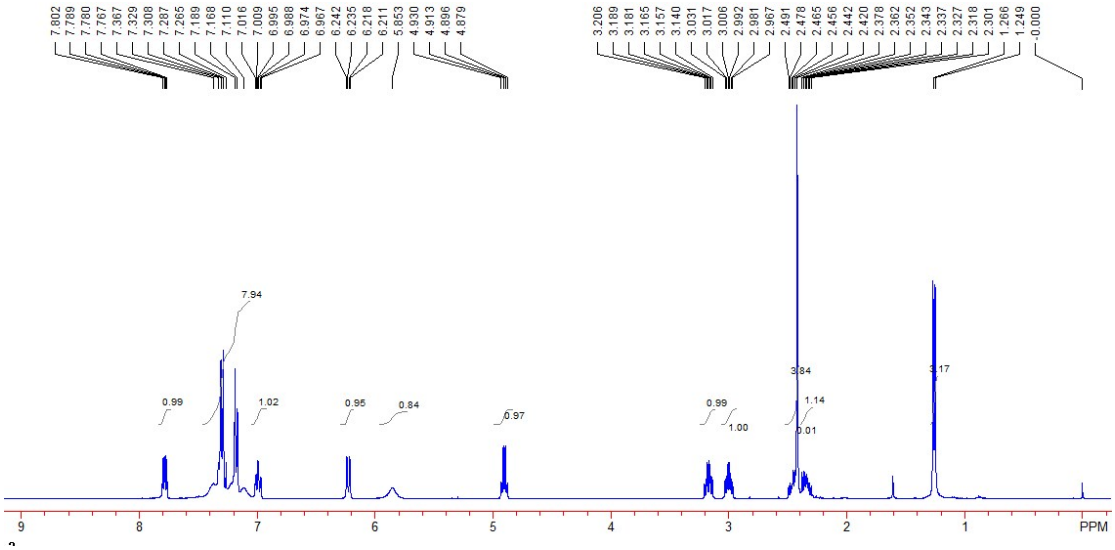


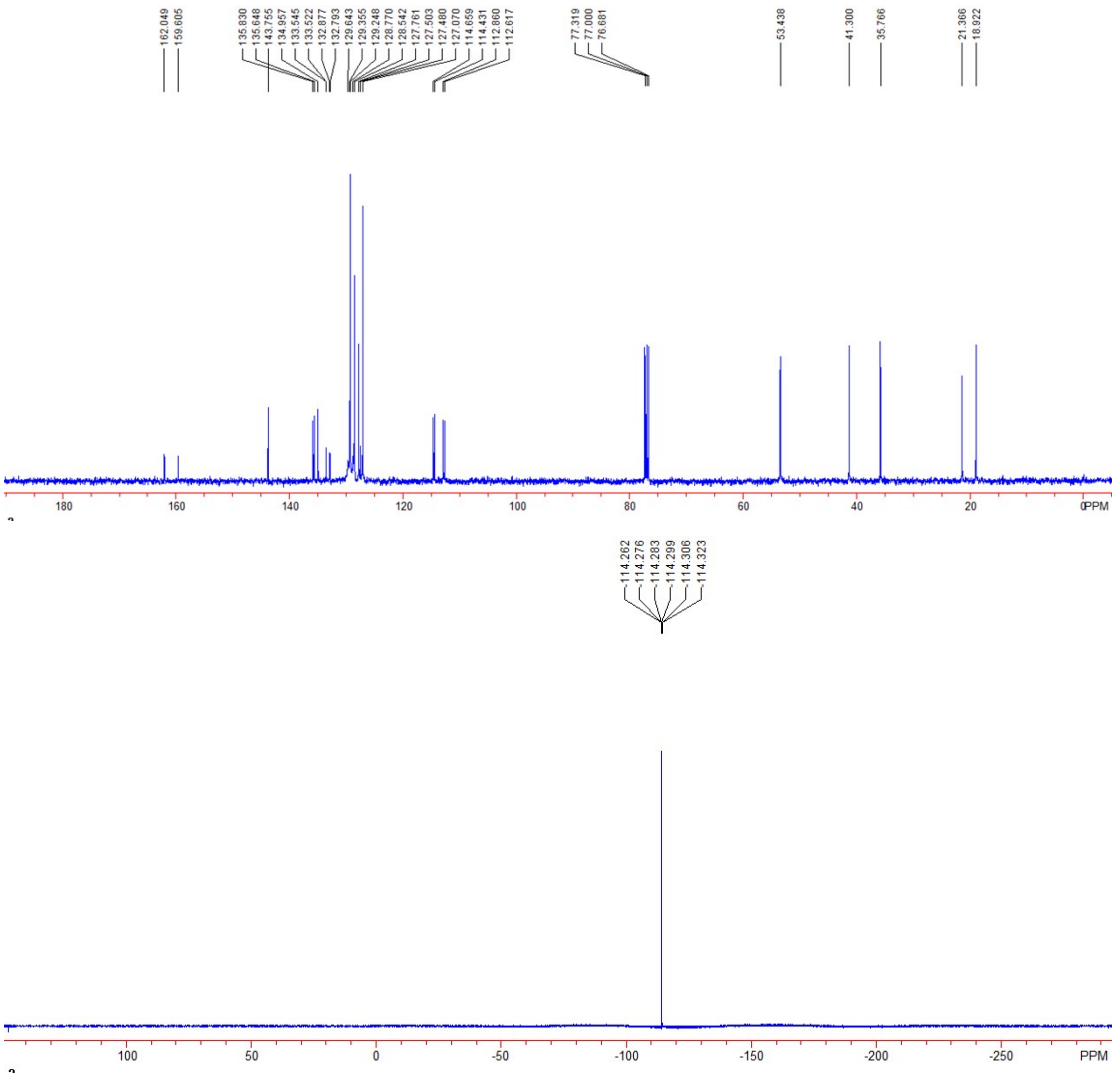
Compound 3a: Yield: 78 mg, 81%. A light yellow solid. Mp: 128-130 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.26 (d, 3H, J = 6.8 Hz), 2.28-2.36 (m, 1H), 2.40 (s, 3H), 2.42-2.49 (m, 1H), 2.95-3.01 (m, 1H), 3.13-3.19 (m, 1H), 4.89 (q, 1H, J = 6.4 Hz), 5.90 (br, 1H), 6.52 (d, 1H, J = 8.0 Hz), 7.06 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.14-7.16 (m, 3H), 7.21-7.39 (m, 6H), 7.81 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.3, 28.9, 36.1, 53.3, 126.2, 126.3, 127.1, 127.54, 127.58, 127.8, 128.4, 129.1, 130.9, 131.7, 133.9, 134.3, 136.1, 136.3, 143.6; IR (neat): ν 2964, 2922, 1592, 1342, 1161, 1090, 812, 762 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{28}BrN_2O_2S$ $[M+NH_4]^+$: 499.1049, found: 499.1050.

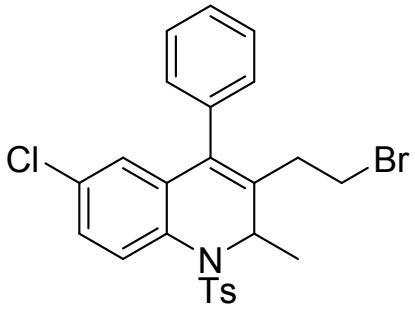




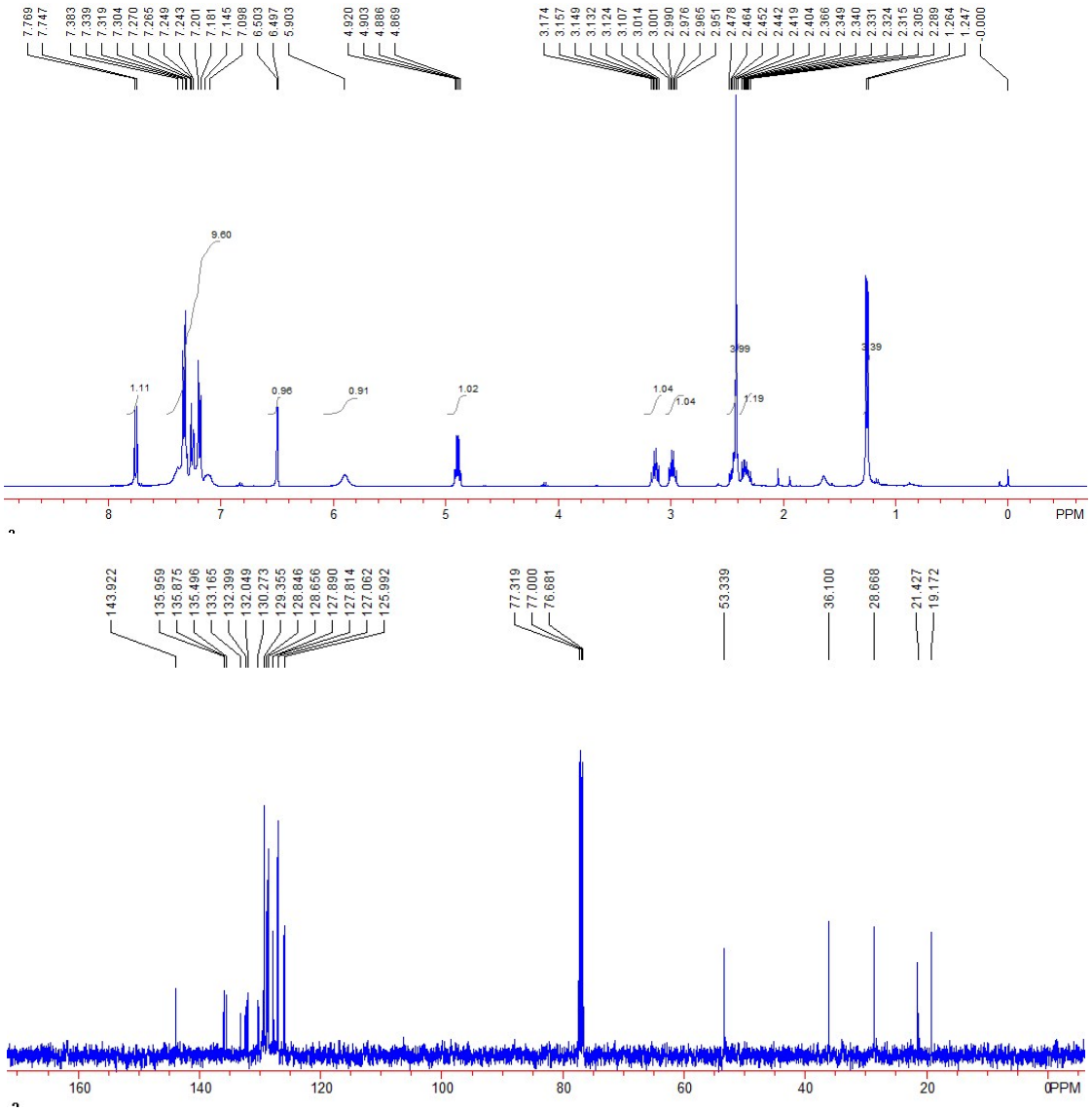
Compound 3b: Yield: 78 mg, 78%. A light yellow solid. Mp: 179-182 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, J = 6.8 Hz), 2.30-2.37 (m, 1H), 2.42-2.49 (m, 4H), 2.96-3.03 (m, 1H), 3.14-3.20 (m, 1H), 4.90 (q, 1H, J = 6.8 Hz), 5.85 (br, 1H), 6.22 (dd, 1H, J_1 = 9.6 Hz, J_2 = 2.8 Hz), 6.96-7.01 (m, 1H), 7.11-7.36 (m, 8H), 7.78 (dd, 1H, J_1 = 8.8 Hz, J_2 = 5.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 28.7, 36.1, 53.3, 112.7 (d, J = 24.3 Hz), 114.6 (d, J = 22.7 Hz), 127.1, 127.5 (d, J = 2.3 Hz), 127.8, 128.6, 129.2, 129.3, 132.8 (d, J = 6.6 Hz), 133.3, 135.6, 135.7, 135.8, 143.8, 160.8 (d, J = 243.6 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -114.3~-114.2 (m); IR (neat): ν 2920, 1480, 1347, 1163, 1090, 818 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{24}BrFNO_2S$ $[M+H]^+$: 500.0690, found: 500.0690.

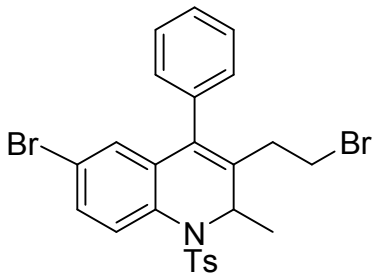






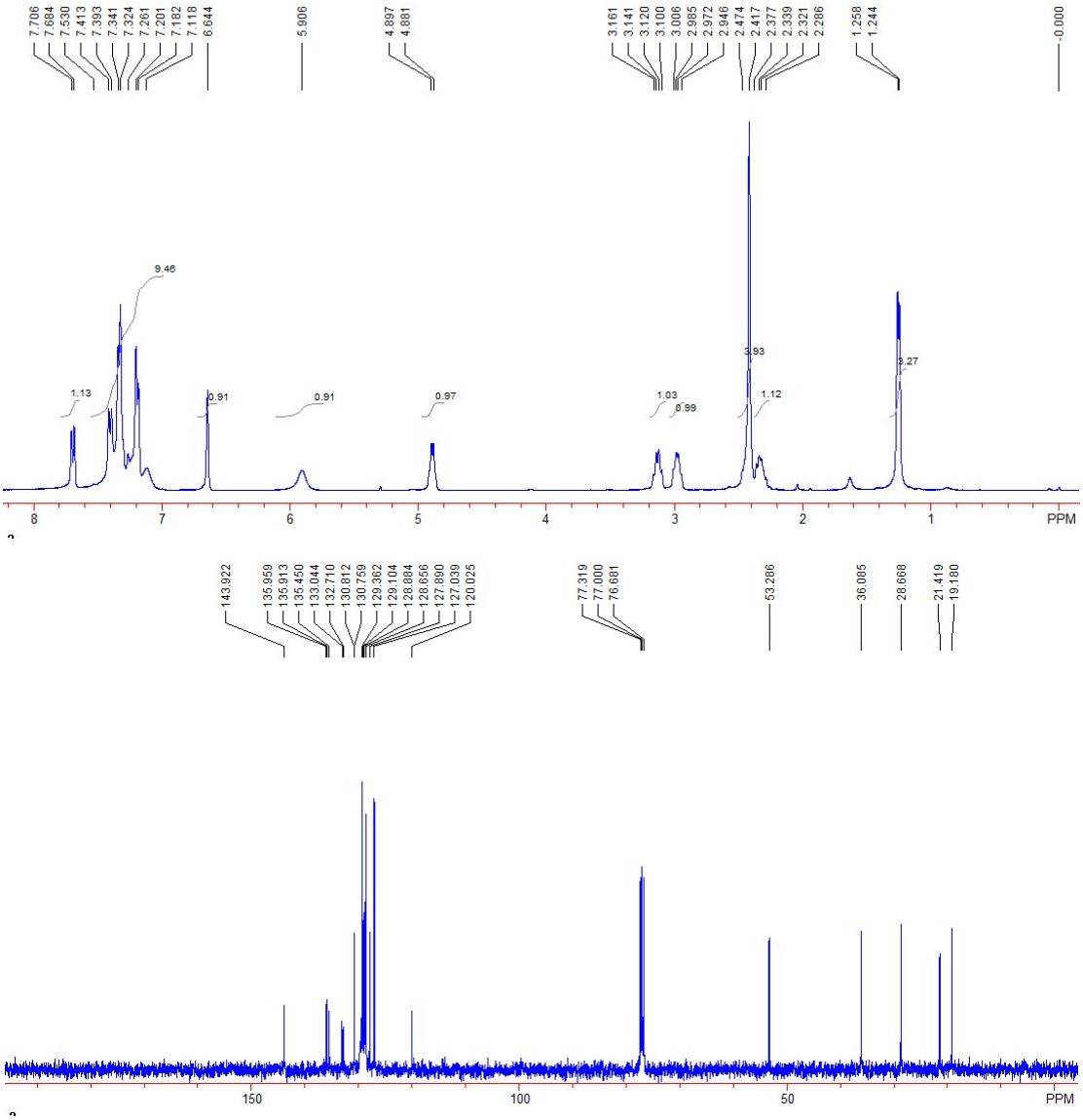
Compound 3c: Yield: 77 mg, 74%. A light yellow solid. Mp: 191-193 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, J = 6.8 Hz), 2.28-2.36 (m, 1H), 2.40-2.47 (m, 4H), 2.95-3.01 (m, 1H), 3.10-3.17 (m, 1H), 4.89 (q, 1H, J = 6.8 Hz), 5.90 (br, 1H), 6.49 (d, 1H, J = 2.4 Hz), 7.09-7.38 (m, 9H), 7.75 (d, 1H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 28.6, 36.1, 53.3, 125.9, 127.0, 127.81, 127.89, 128.6, 128.8, 129.3, 130.2, 132.0, 132.3, 133.1, 135.4, 135.8, 135.9, 143.9; IR (neat): ν 2920, 1473, 1347, 1164, 1091, 878, 819 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}BrClN_2O_2S$ $[M+NH_4]^+$: 533.0660, found: 533.0659.

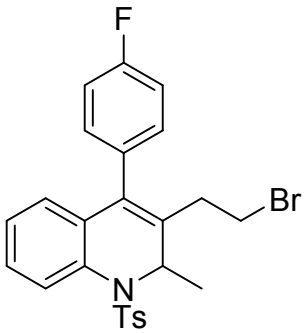




Compound 3d: Yield: 89 mg, 79%. A light yellow solid. Mp: 168-170 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, *J* = 5.6 Hz), 2.28-2.41 (m, 1H), 2.47 (s, 4H), 2.94-3.00 (m, 1H), 3.10-3.16 (m, 1H), 4.88 (q, 1H, *J* = 6.4 Hz), 5.90 (br, 1H), 6.64 (s, 1H), 7.11-7.53 (m, 9H), 7.69 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 28.6, 36.0, 53.2, 120.0, 127.0, 127.8, 128.6, 128.8, 129.1, 129.3, 130.7, 130.8, 132.7, 133.0, 135.4, 135.91, 135.95, 143.9; IR (neat): ν 2927, 1595, 1473, 1347, 1161, 1091, 876, 771 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}Br_2N_2O_2S$

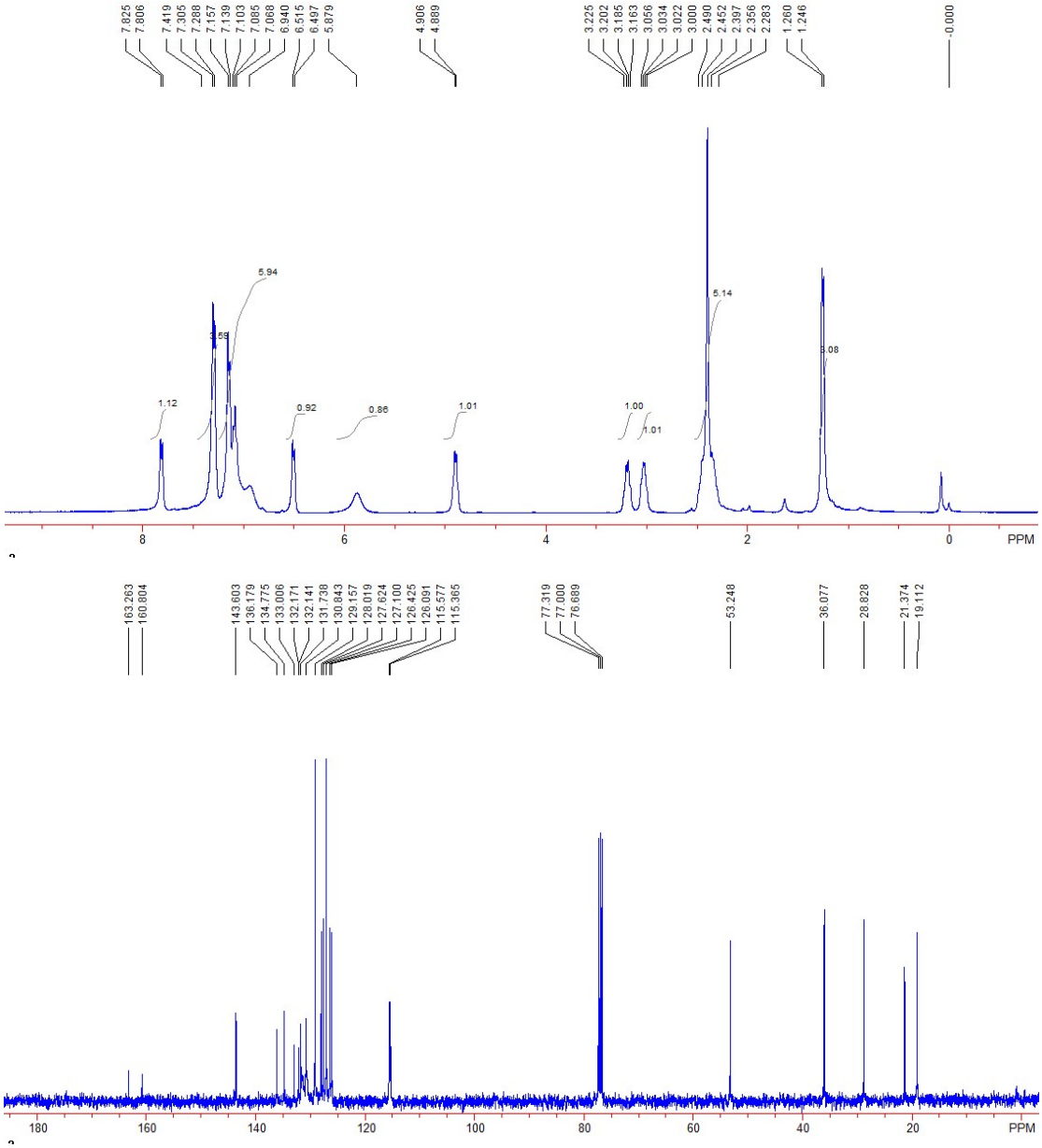
$[M+NH_4]^+$: 577.0155, found: 577.0147.

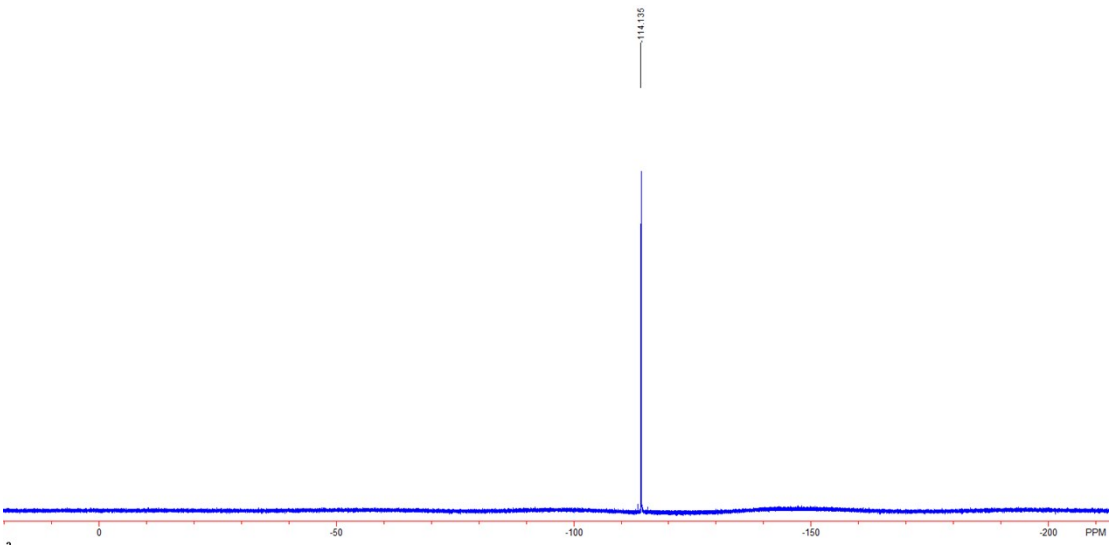


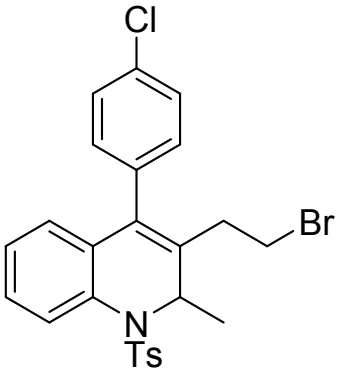


Compound 3e: Yield: 85 mg, 85%. A light yellow solid. Mp: 178-180 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, *J* = 5.6 Hz), 2.28-2.49 (m, 5H), 3.00-3.05 (m, 1H), 3.16-3.22 (m, 1H), 4.89 (q, 1H, *J* = 6.8 Hz), 5.87 (br, 1H), 6.50 (d, 1H, *J* = 7.2 Hz), 6.94-7.15 (m, 6H), 7.28-7.41 (m, 3H), 7.81 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.3, 28.8, 36.0, 53.2,

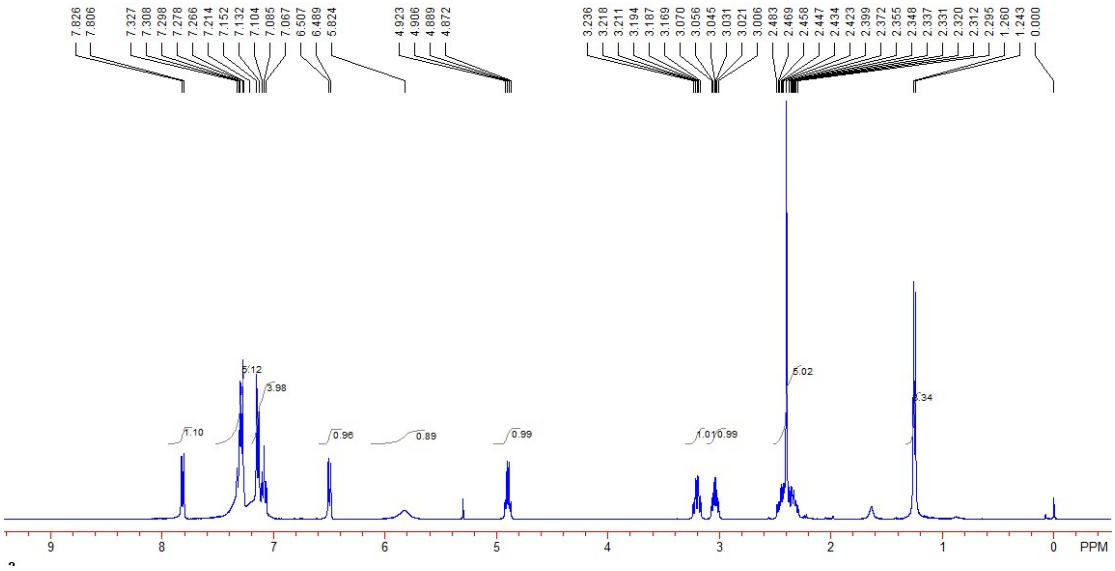
115.4 (d, J = 21.2 Hz), 126.0, 126.4, 127.1, 127.6, 128.0, 129.1, 130.8, 131.7, 132.1 (d, J = 3.0 Hz), 133.0, 134.7, 136.1, 143.6, 162.0 (d, J = 245.9 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -114.1 (s); IR (neat): ν 2920, 1597, 1507, 1343, 1221, 1158, 1090, 890, 805 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}BrFN_2O_2S$ $[M+NH_4]^+$: 517.0955, found: 517.0956.

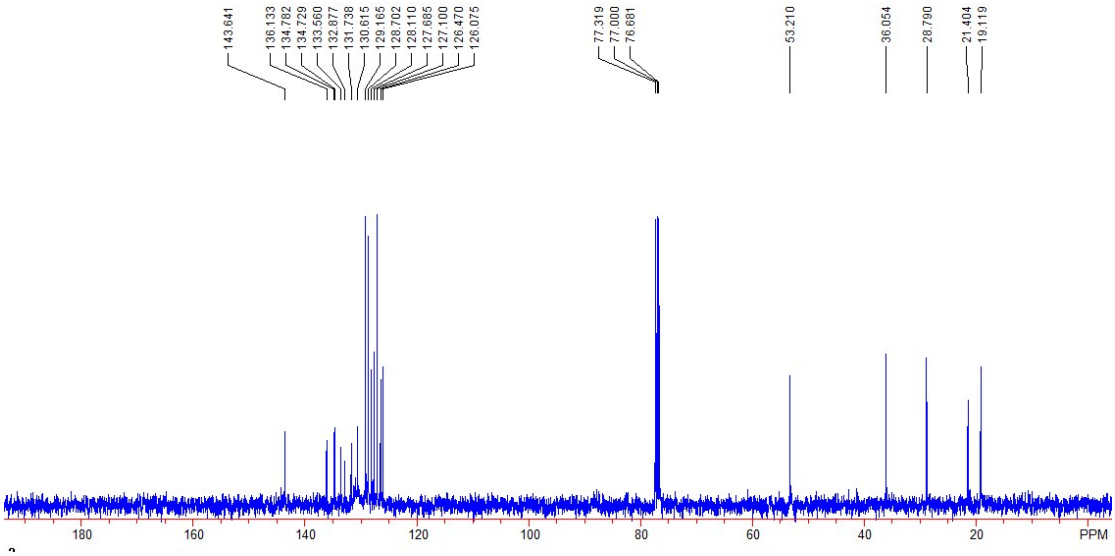


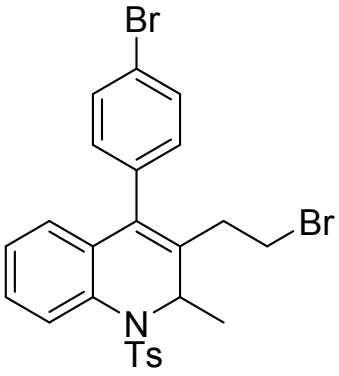




Compound 3f: Yield: 82 mg, 79%. A light yellow solid. Mp: 186-189 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (d, 3H, *J* = 6.8 Hz), 2.29-2.48 (m, 5H), 3.00-3.07 (m, 1H), 3.16-3.23 (m, 1H), 4.89 (q, 1H, *J* = 6.8 Hz), 5.82 (br, 1H), 6.49 (d, 1H, *J* = 7.2 Hz), 7.06-7.21 (m, 4H), 7.26-7.32 (m, 5H), 7.81 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 28.7, 36.0, 53.2, 126.0, 126.4, 127.1, 127.6, 128.1, 128.7, 129.1, 130.6, 131.7, 132.8, 133.5, 134.72, 134.78, 136.1, 143.6; IR (neat): ν 2977, 2920, 1483, 1343, 1157, 1087, 778 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}BrClN_2O_2S$ $[M+NH_4]^+$: 533.0660, found: 533.0658.

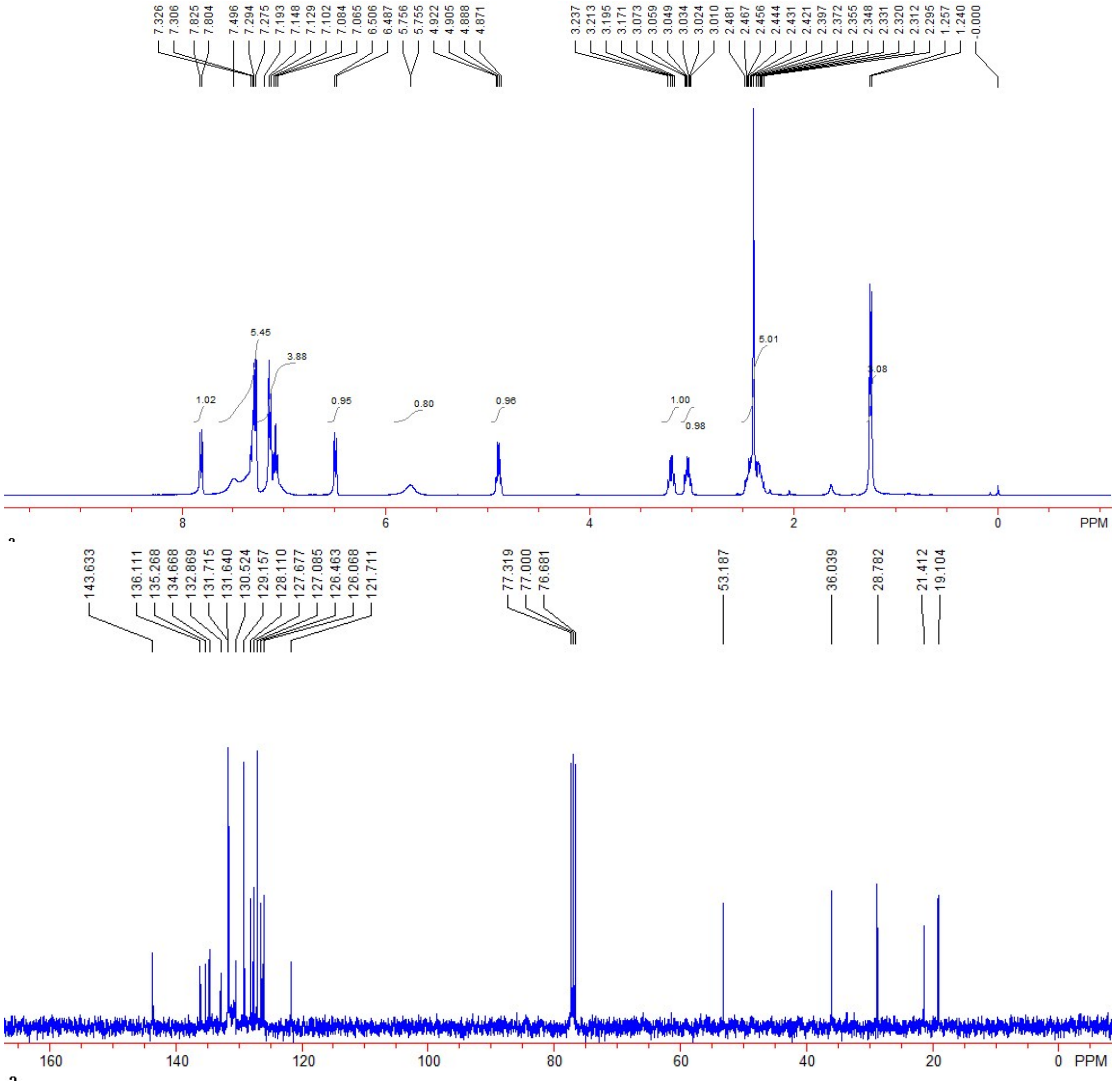


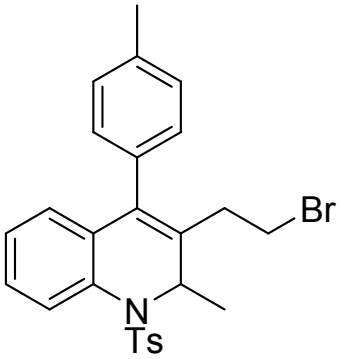




Compound 3g: Yield: 89 mg, 79%. A light yellow solid. Mp: 168-170 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (d, 3H, *J* = 6.8 Hz), 2.29-2.48 (m, 5H), 3.01-3.07 (m, 1H), 3.17-3.23 (m, 1H), 4.89 (q, 1H, *J* = 6.8 Hz), 5.75 (br, 1H), 6.49 (d, 1H, *J* = 7.6 Hz), 7.06-7.19 (m, 4H), 7.27-7.32 (m, 5H), 7.81 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 28.7, 36.0, 53.1,

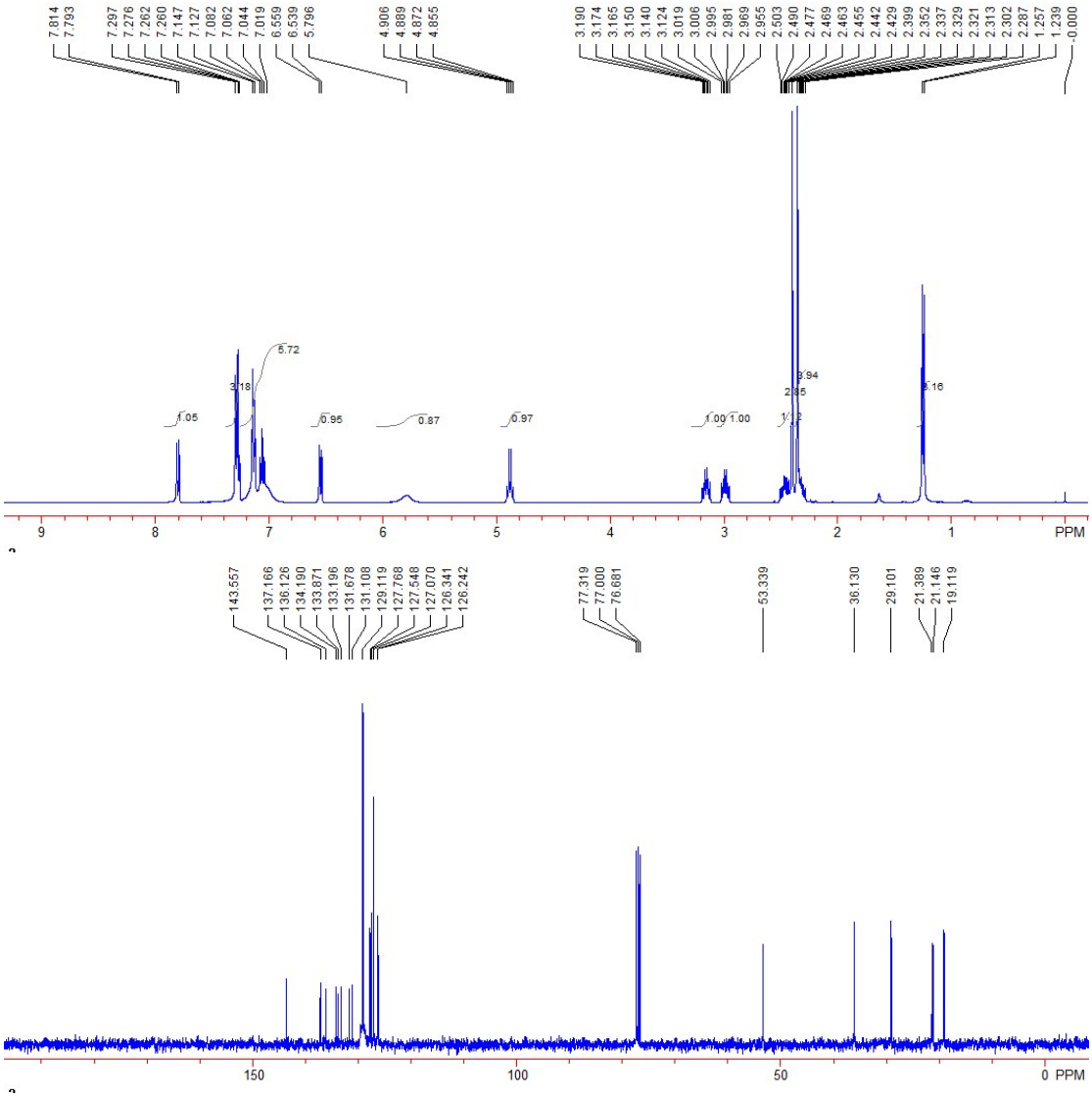
121.7, 126.0, 126.4, 127.0, 127.6, 128.1, 129.1, 130.5, 131.6, 131.7, 132.8, 134.6, 135.2, 136.1, 143.6; IR (neat): ν 2929, 1595, 1481, 1345, 1164, 1088, 820, 759 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{27}Br_2N_2O_2S$ $[M+NH_4]^+$: 577.0155, found: 577.0147.

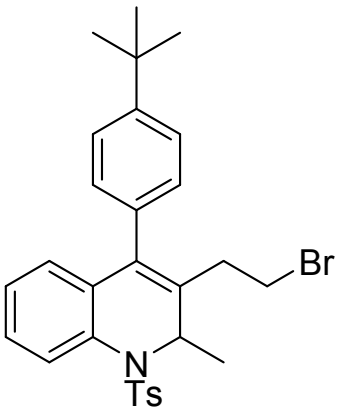




Compound 3h: Yield: 77 mg, 78%. A light yellow solid. Mp: 170-172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (d, 3H, *J* = 7.2 Hz), 2.28-2.35 (m, 4H), 2.39 (s, 3H), 2.42-2.50 (m, 1H), 2.95-3.01 (m, 1H), 3.12-3.19 (m, 1H), 4.88 (q, 1H, *J* = 7.2 Hz), 5.79 (br, 1H), 6.54 (d, 1H, *J* = 8.0 Hz),

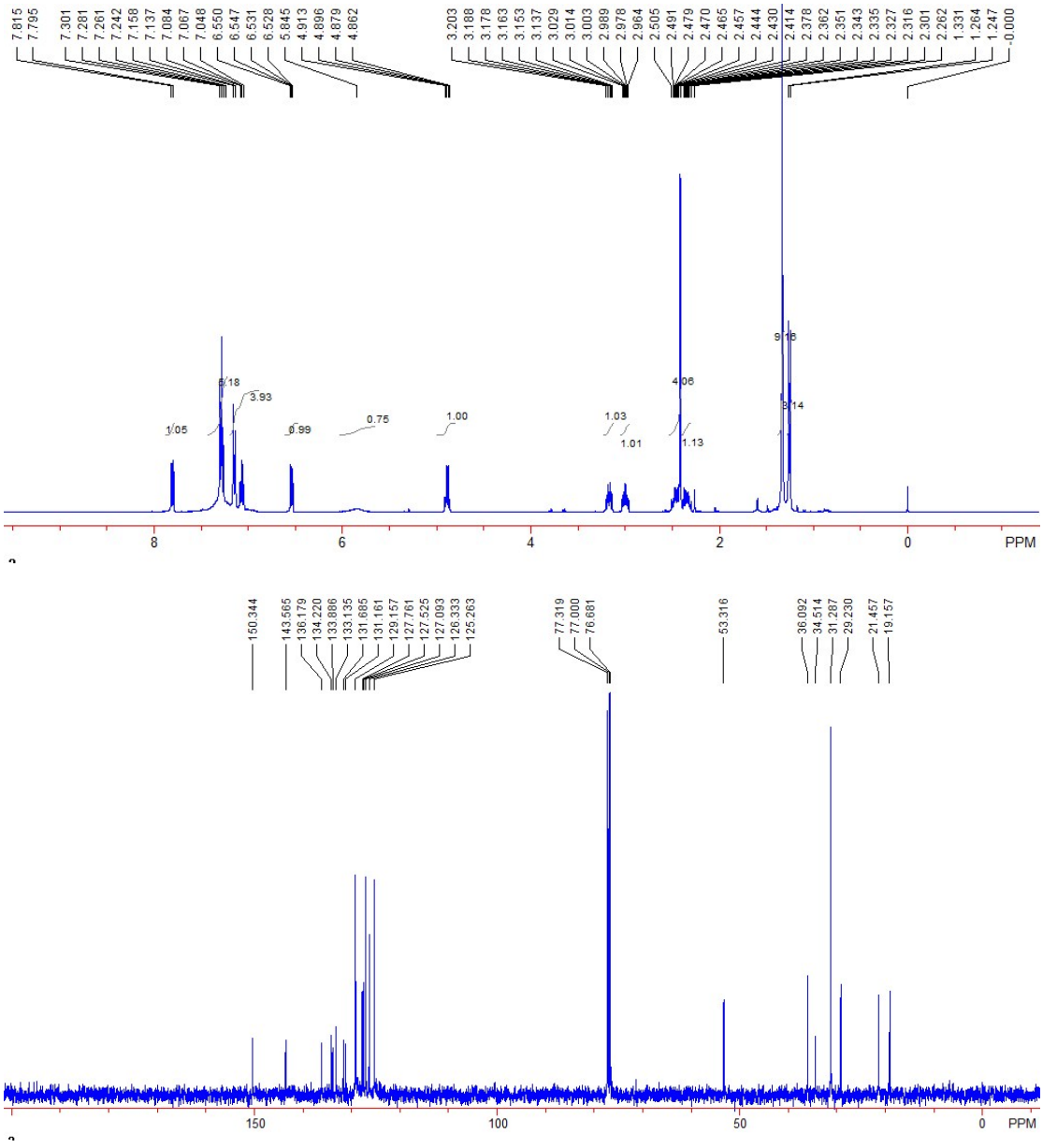
7.01-7.14 (m, 6H), 7.26-7.29 (m, 3H), 7.80 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.1, 21.3, 29.1, 36.1, 53.3, 126.2, 126.3, 127.0, 127.5, 127.7, 129.1, 131.1, 131.6, 133.1, 133.8, 134.1, 136.1, 137.1, 143.5; IR (neat): ν 2925, 1595, 1344, 1164, 1090, 816, 762 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{30}BrN_2O_2S$ $[M+NH_4]^+$: 513.1206, found: 513.1206.

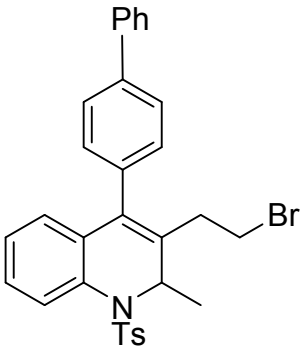




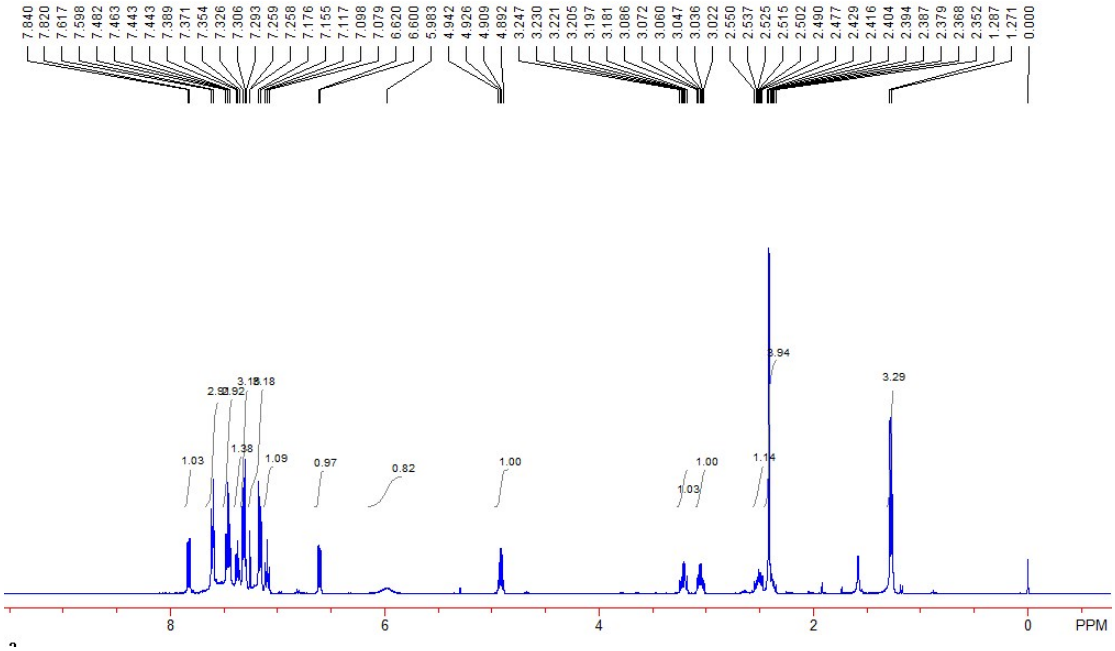
Compound 3i: Yield: 74 mg, 69%. A light yellow solid. Mp: 68-70 °C. ^{1}H NMR ($CDCl_3$, 400

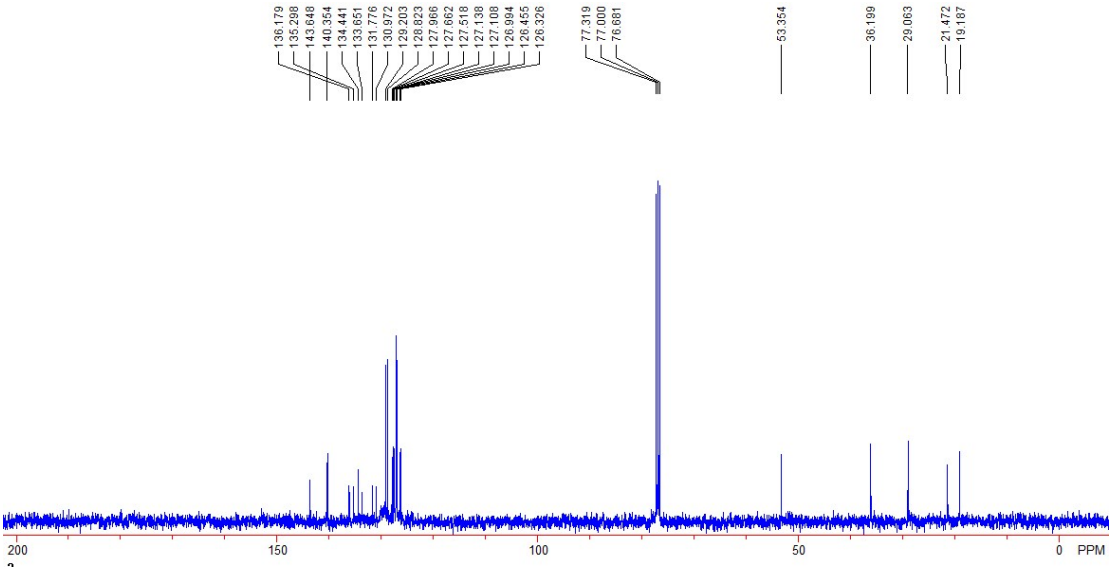
MHz, TMS) δ 1.25 (d, 3H, J = 6.8 Hz), 1.33 (s, 9H), 2.26-2.37 (m, 1H), 2.41-2.50 (m, 4H), 2.96-3.02 (m, 1H), 3.13-3.20 (m, 1H), 4.88 (q, 1H, J = 6.8 Hz), 5.84 (br, 1H), 6.53 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.04-7.15 (m, 4H), 7.24-7.30 (m, 5H), 7.80 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 29.2, 31.2, 34.5, 36.0, 53.3, 125.2, 126.3, 127.0, 127.5, 127.7, 129.1, 131.1, 131.6, 133.1, 133.8, 134.2, 136.1, 143.5, 150.3; IR (neat): ν 2961, 1597, 1445, 1348, 1165, 1090, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{33}BrNO_2S$ $[M+H]^+$: 538.1410, found: 538.1411.

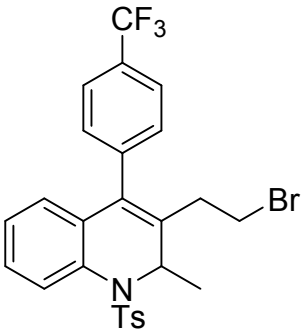




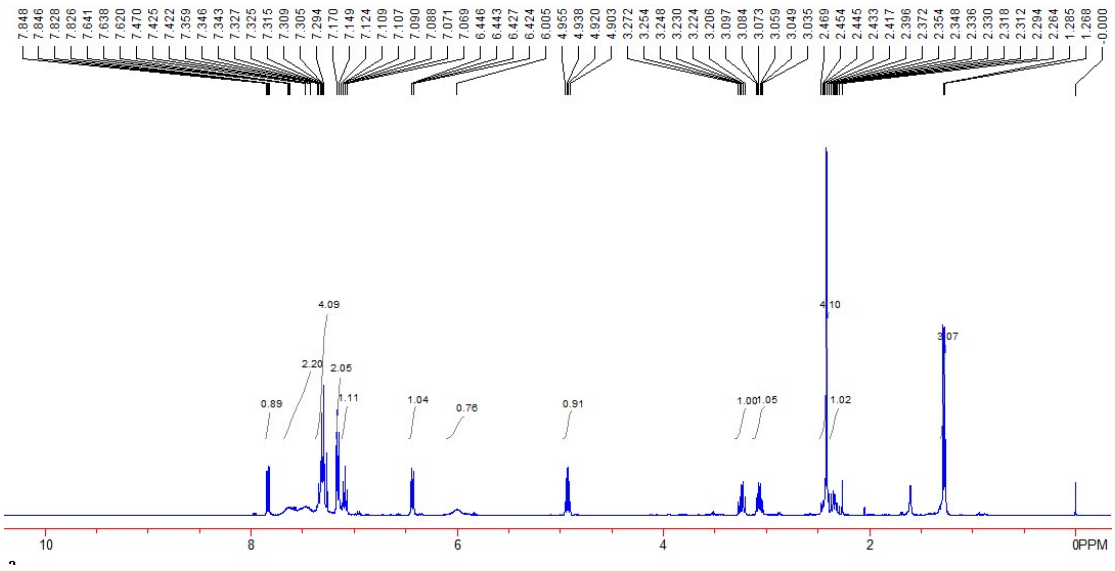
Compound 3j: Yield: 81 mg, 73%. A light yellow solid. Mp: 72-75 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28 (d, 3H, *J* = 6.4 Hz), 2.35-2.42 (m, 4H), 2.47-2.55 (m, 1H), 3.02-3.08 (m, 1H), 3.18-3.24 (m, 1H), 4.91 (q, 1H, *J* = 6.4 Hz), 5.98 (br, 1H), 6.61 (d, 1H, *J* = 8.0 Hz), 7.09-7.17 (m, 4H), 7.25-7.48 (m, 6H), 7.59-7.61 (m, 3H), 7.83 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 29.0, 36.1, 53.3, 126.3, 126.4, 126.9, 127.1, 127.5, 127.6, 127.9, 128.8, 129.2, 130.9, 131.7, 133.6, 134.4, 135.2, 136.1, 140.3, 143.6; IR (neat): ν 2925, 1595, 1482, 1347, 1163, 1090, 813, 762 cm^{-1}; HRMS (MALDI)) Calcd. for $C_{31}H_{29}BrNO_2S$ $[M+H]^+$: 558.1097, found: 558.1093.







Compound 3k: Yield: 89 mg, 81%. A light yellow solid. Mp: 53-56 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.27 (d, 3H, J = 6.8 Hz), 2.26-2.46 (m, 6H), 3.03-3.09 (m, 1H), 3.20-3.27 (m, 1H), 4.92 (q, 1H, J = 6.8 Hz), 6.00 (br, 1H), 6.43 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.06-7.17 (m, 3H), 7.29-7.47 (m, 4H), 7.62-7.64 (m, 2H), 7.83 (dd, 1H, J_1 = 8.0 Hz, J_2 = 0.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 21.4, 28.6, 35.9, 53.1, 123.9 (q, J = 271.0 Hz), 125.4 (q, J = 3.0 Hz), 126.0, 126.5, 127.1, 127.7, 128.2, 129.2, 129.8 (q, J = 32.6 Hz), 130.3, 131.7, 132.8, 134.9, 136.1, 140.3, 143.7; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -62.5 (s); IR (neat): ν 2964, 2925, 1610, 1321, 1162, 1124, 1065, 760 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{27}BrF_3N_2O_2S$ $[M+NH_4]^+$: 567.0923, found: 567.0919.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2.294
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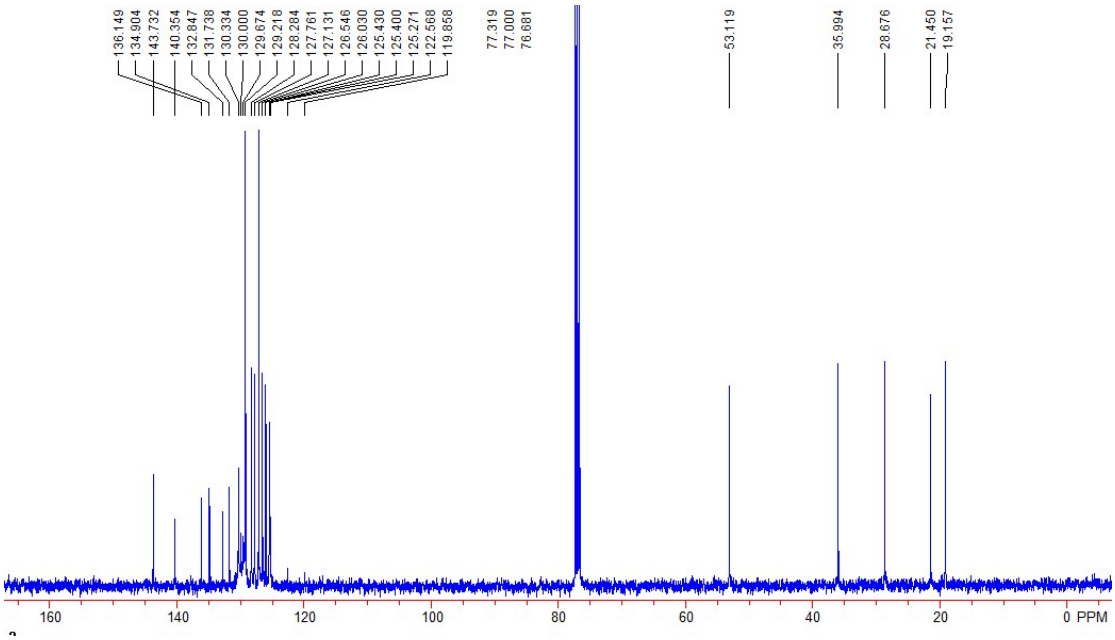
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126.030
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125.400
125.271
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119.858
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140
120
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80
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40
20
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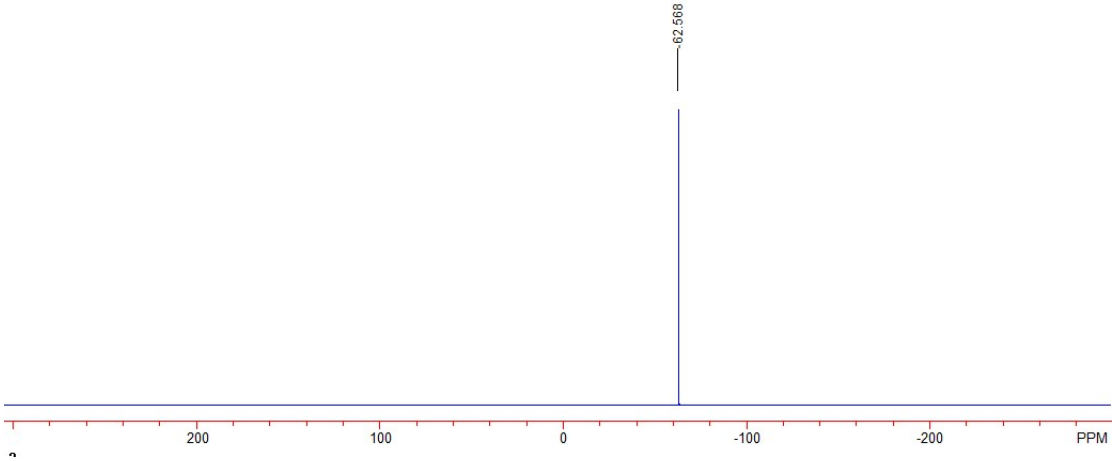
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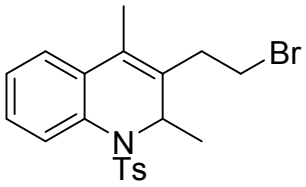
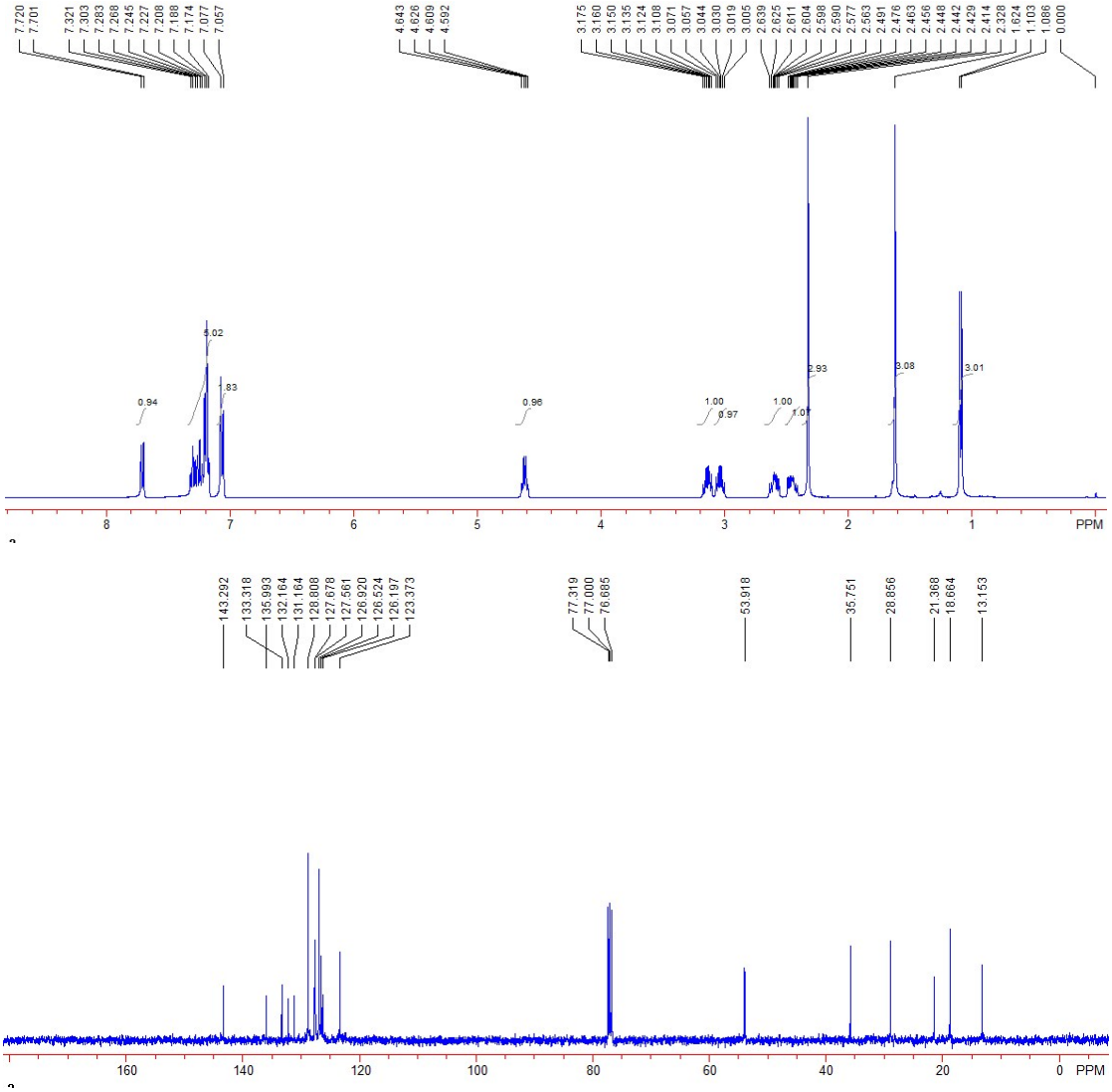
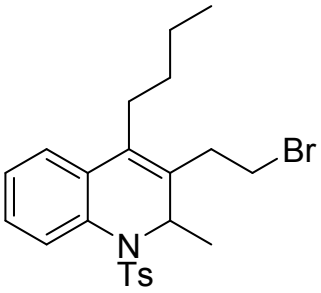
-200
PPM

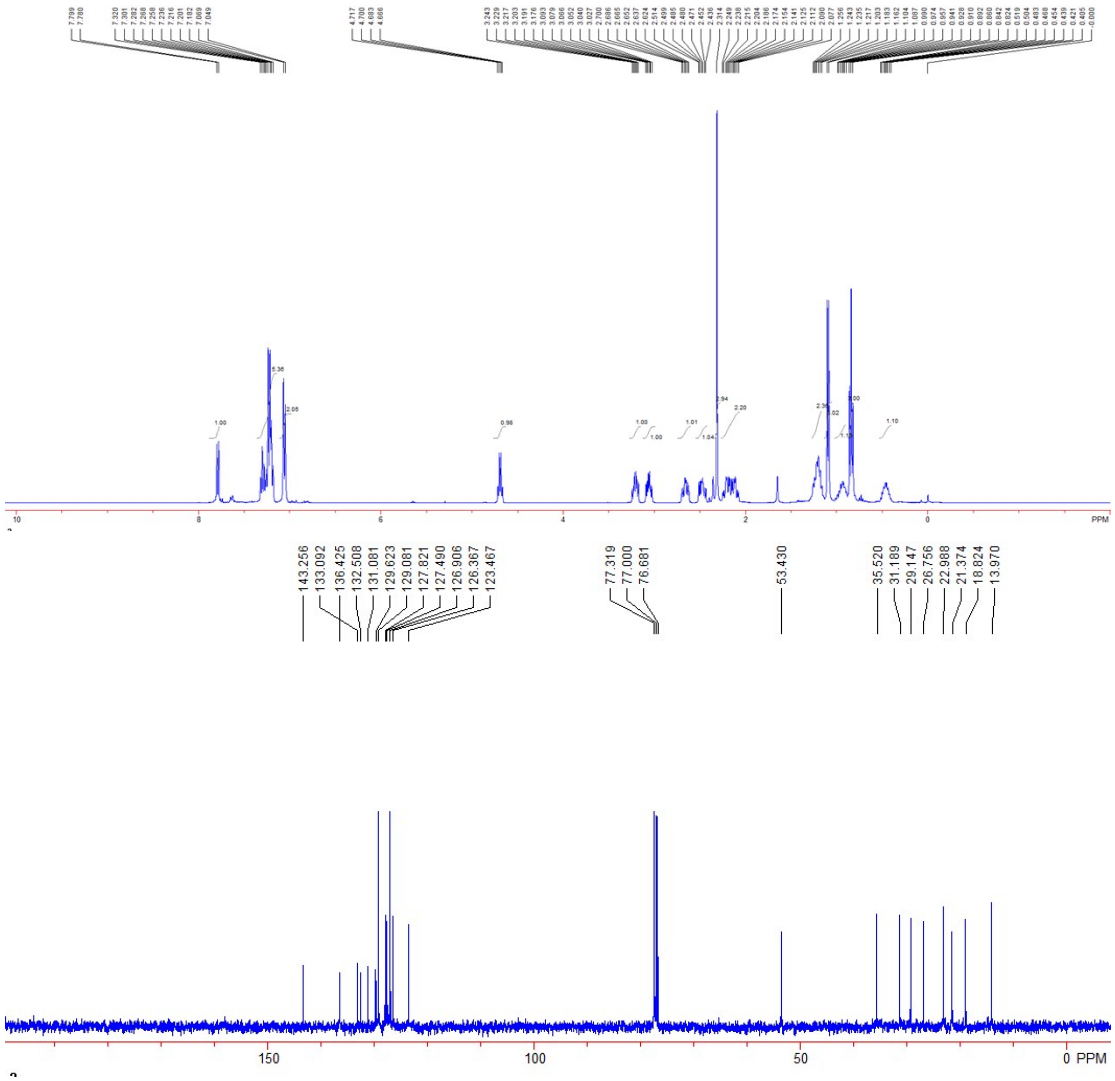


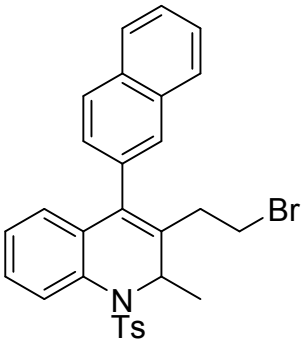
Compound 3l: Yield: 71 mg, 85%. A light yellow solid. Mp: 92-95 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (d, 3H, J = 6.8 Hz), 1.62 (s, 3H), 2.32 (s, 3H), 2.41-2.49 (m, 1H), 2.56-2.63 (m, 1H), 3.00-3.07 (m, 1H), 3.10-3.17 (m, 1H), 4.61 (q, 1H, J = 6.8 Hz), 7.06 (d, 2H, J = 8.0 Hz), 7.17-7.32 (m, 5H), 7.71 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.1, 18.6, 21.3, 28.8, 35.7, 53.9, 123.3, 126.1, 126.5, 126.9, 127.5, 127.6, 128.8, 131.1, 132.1, 133.3, 135.9, 143.2; IR (neat): ν 2969, 2920, 1597, 1450, 1339, 1161, 1092, 814, 759 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{26}BrN_2O_2S$ $[M+NH_4]^+$: 437.0893, found: 437.0893.



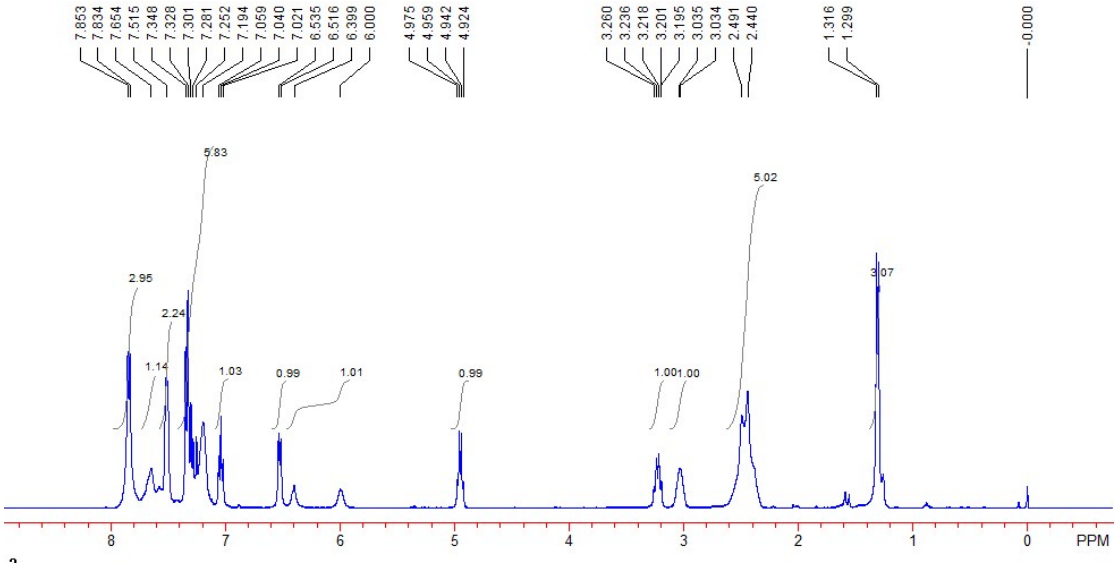


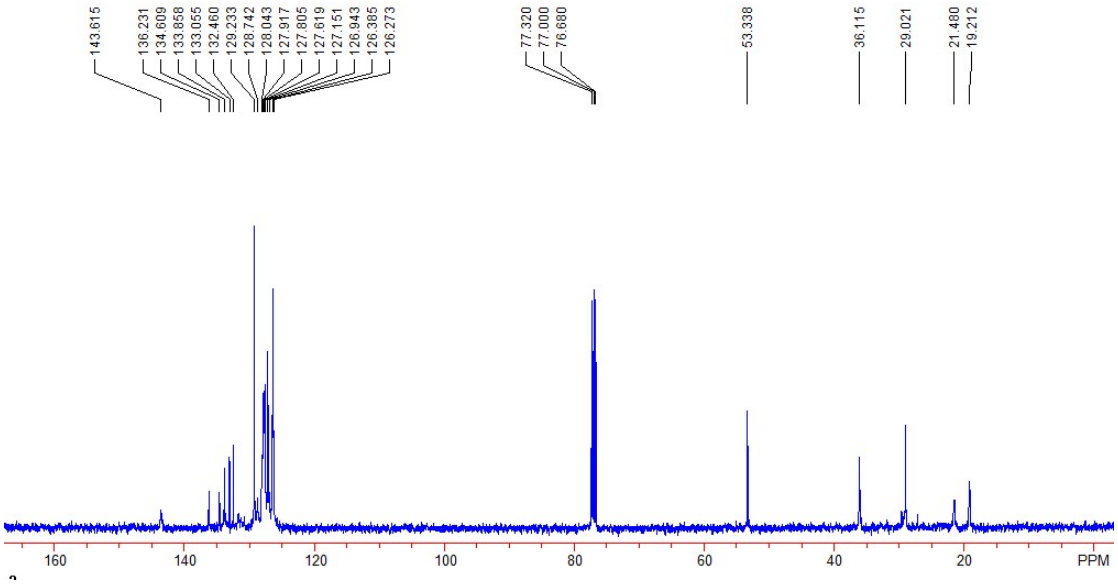
Compound 3m: Yield: 73 mg, 79%. A light yellow solid. Mp: 75-77 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.40-0.51 (m, 1H), 0.84 (t, 3H, *J* = 7.2 Hz), 0.89-0.99 (m, 1H), 1.09 (d, 3H, *J* = 6.8 Hz), 1.16-1.25 (m, 2H), 2.07-2.24 (m, 2H), 2.31 (s, 3H), 2.43-2.51 (m, 1H), 2.62-2.70 (m, 1H), 3.02-3.09 (m, 1H), 3.17-3.24 (m, 1H), 4.69 (q, 1H, *J* = 6.8 Hz), 7.05 (d , 2H, *J* = 8.0 Hz), 7.18-7.32 (m, 5H), 7.78 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 18.8, 21.3, 22.9, 26.7, 29.1, 31.1, 35.5, 53.4, 123.4, 126.3, 126.9, 127.4, 127.8, 129.0, 129.6, 131.0, 132.5, 133.0, 136.4, 143.2; IR (neat): ν 2956, 2925, 1597, 1450, 1343, 1161, 1091, 814, 765 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{32}BrN_2O_2S$ $[M+NH_4]^+$: 479.1362, found: 479.1363.

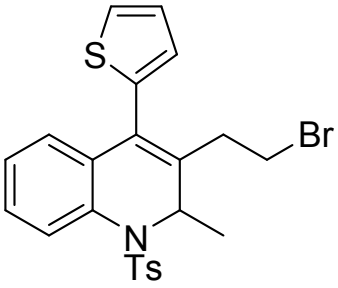




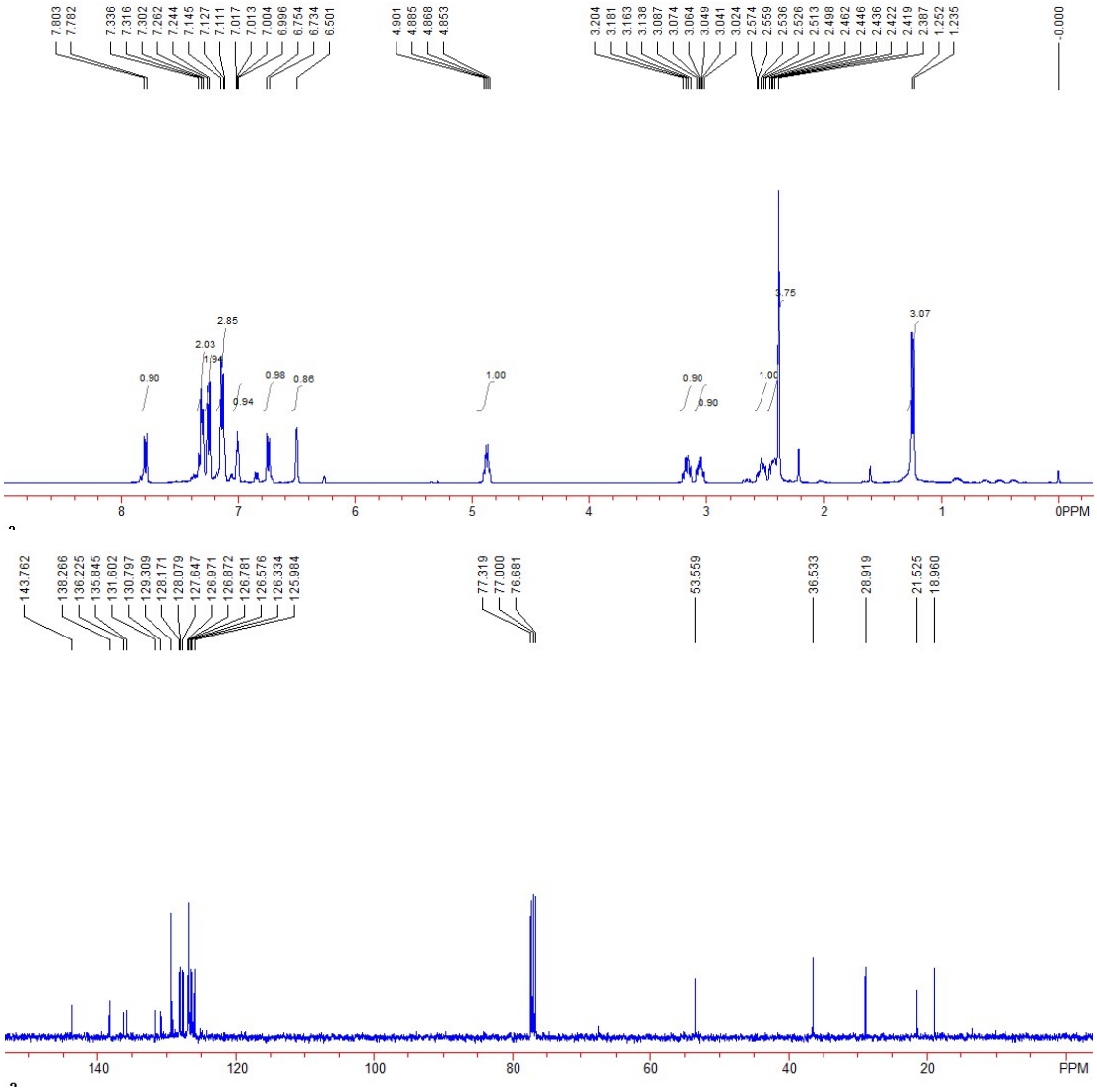
Compound 3o: Yield: 74 mg, 69%. A light yellow solid. Mp: 194-196 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.30 (d, 3H, *J* =6.8 Hz), 2.38-2.49 (m, 5H), 3.03 (s, 1H), 3.19-3.26 (m, 1H), 4.95 (q, 1H, *J* = 6.8 Hz), 6.20 (d, 1H, *J* = 159.6 Hz), 6.52 (d, 1H, *J* = 7.6 Hz), 7.04 (dd, 1H, $J_1 = J_2$ = 7.6 Hz), 7.19-7.34 (m, 6H), 7.51-7.65 (m, 3H), 7.84 (d, 3H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.2, 21.4, 29.0, 36.1, 53.3, 126.2, 126.3, 126.9, 127.1, 127.6, 127.8, 127.9, 128.0, 128.7, 129.2, 132.4, 133.0, 133.8, 134.6, 136.2, 143.6; IR (neat): ν 2927, 2925, 1597, 1345, 1163, 1090, 810, 749 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{27}BrNO_2S$ $[M+H]^+$: 532.0940, found: 532.0928.

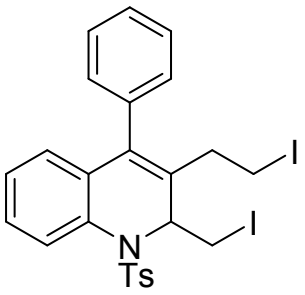






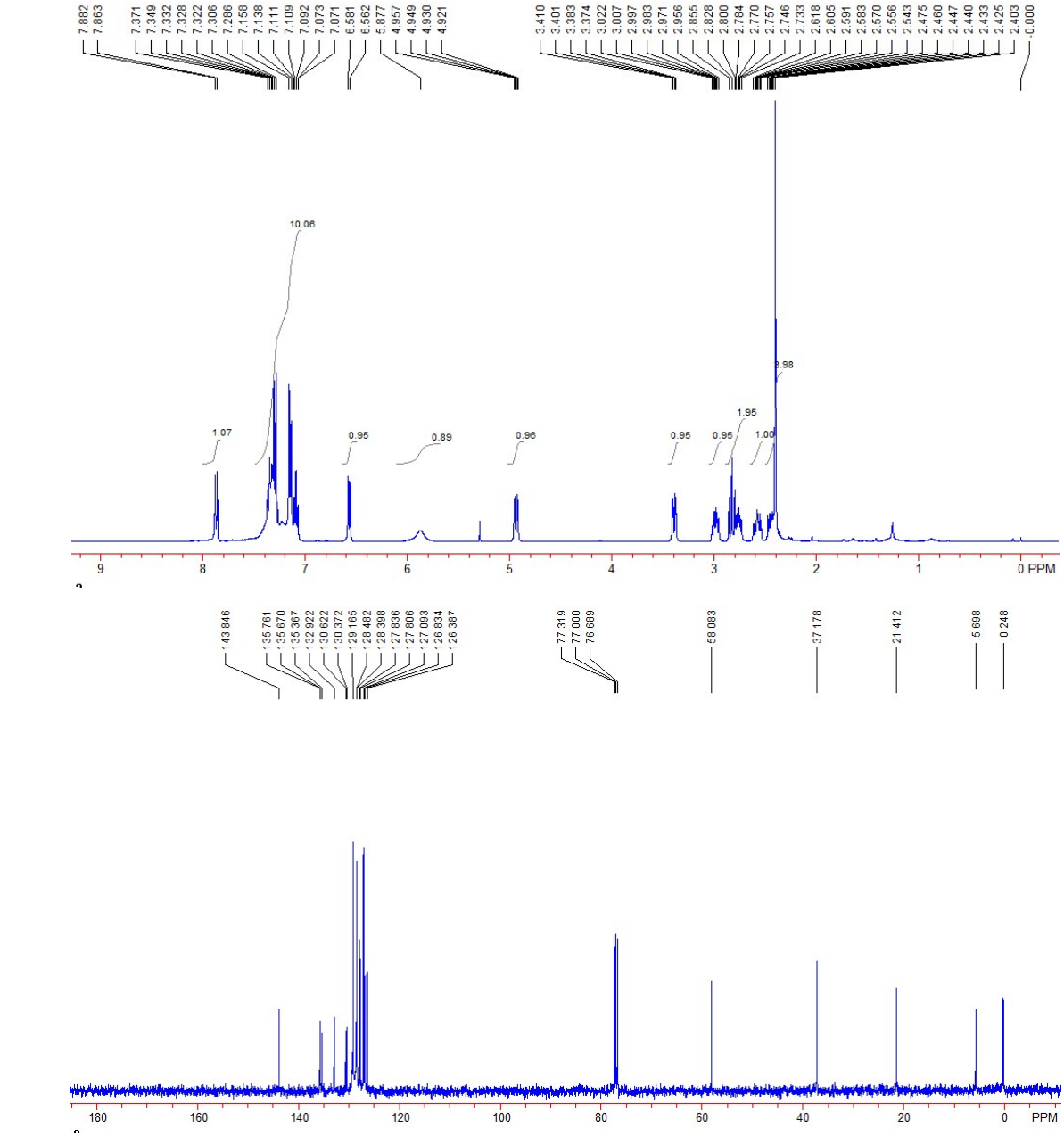
Compound 3n: Yield: 73 mg, 75%. A light yellow solid. Mp: 128-130 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (d, 3H, *J* = 6.8 Hz), 2.38-2.46 (m, 4H), 2.49-2.57 (m, 1H), 3.02-3.08 (m, 1H), 3.13-3.20 (m, 1H), 4.87 (q, 1H, *J* = 6.8 Hz), 6.50 (s, 1H), 6.74 (d, 1H, *J* = 8.0 Hz), 6.99-7.01 (m, 1H), 7.11-7.14 (m, 3H), 7.25 (d, 2H, *J* = 7.2 Hz), 7.30-7.33 (m, 2H), 7.79 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.5, 28.9, 36.5, 53.5, 125.9, 126.3, 126.5, 126.7, 126.9, 127.6, 128.0, 128.1, 129.3, 130.7, 131.6, 135.8, 136.2, 138.2, 143.7; IR (neat): ν 2920, 1595, 1338, 1170, 1089, 818, 763 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{26}BrN_2O_2S_2$ $[M+NH_4]^+$: 505.0614, found: 505.0614.

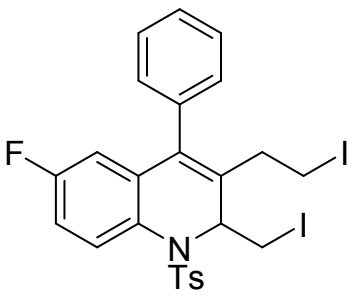




Compound 4a: Yield: 105 mg, 80%. A light yellow solid. Mp: 185-188 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40-2.47 (m, 4H), 2.54-2.61 (m, 1H), 2.73-2.85 (m, 2H), 2.95-3.02 (m, 1H), 3.39 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 4.93 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 5.87 (br, 1H), 6.57 (d, 1H, J = 7.6 Hz), 7.07-7.37 (m, 10H), 7.87 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.2, 5.6, 21.4, 37.1, 58.0, 126.3, 126.8, 127.0, 127.80, 127.83, 128.3, 128.4, 129.1, 130.3, 130.6, 132.9, 135.3, 135.6, 135.7, 143.8; IR (neat): ν 2927, 1592, 1479, 1343, 1161, 1081, 906 cm^{-1};

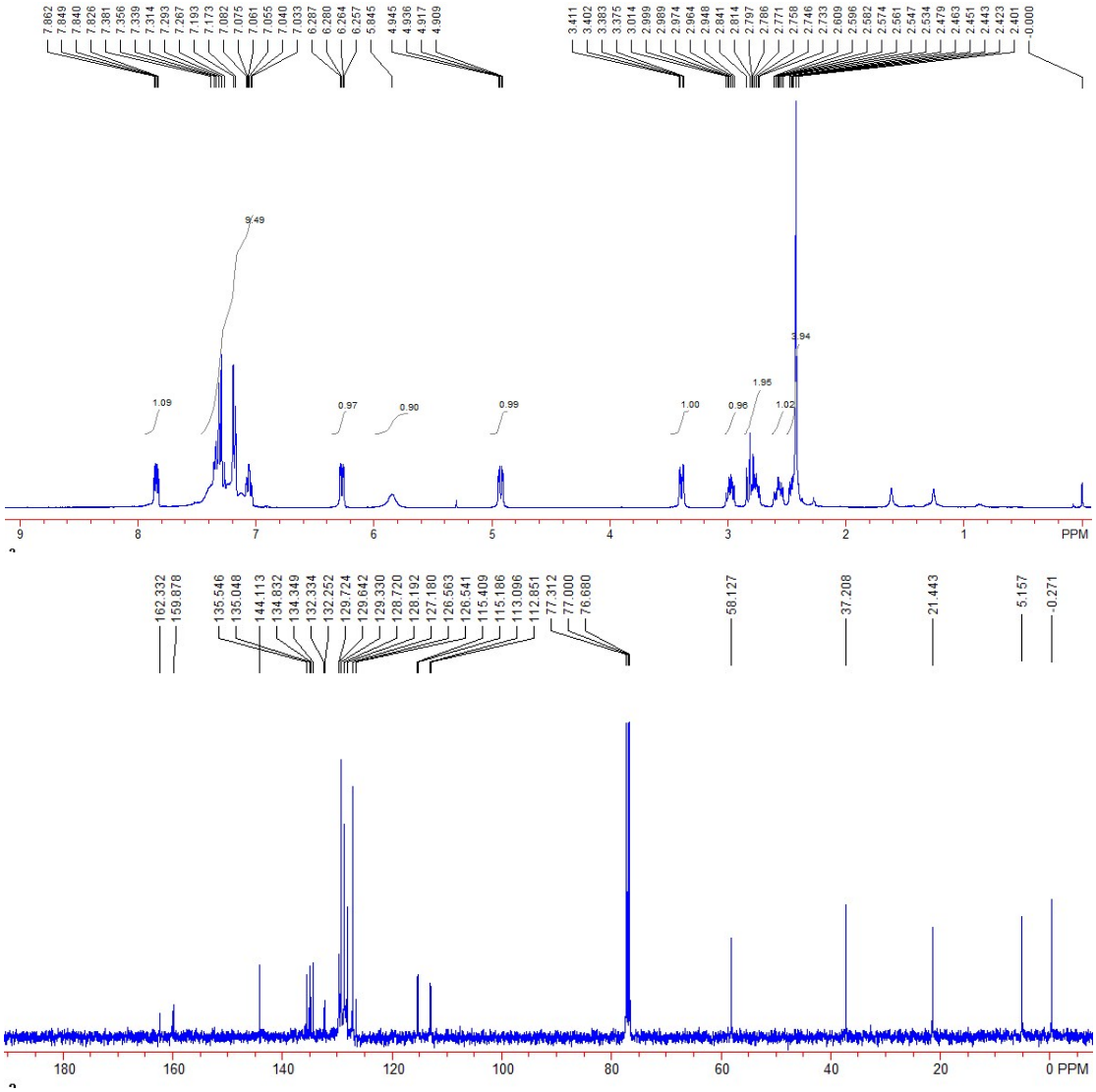
HRMS (ESI) Calcd. for $C_{25}H_{27}I_2N_2O_2S$ $[M+NH_4]^+$: 672.9877, found: 672.9869.

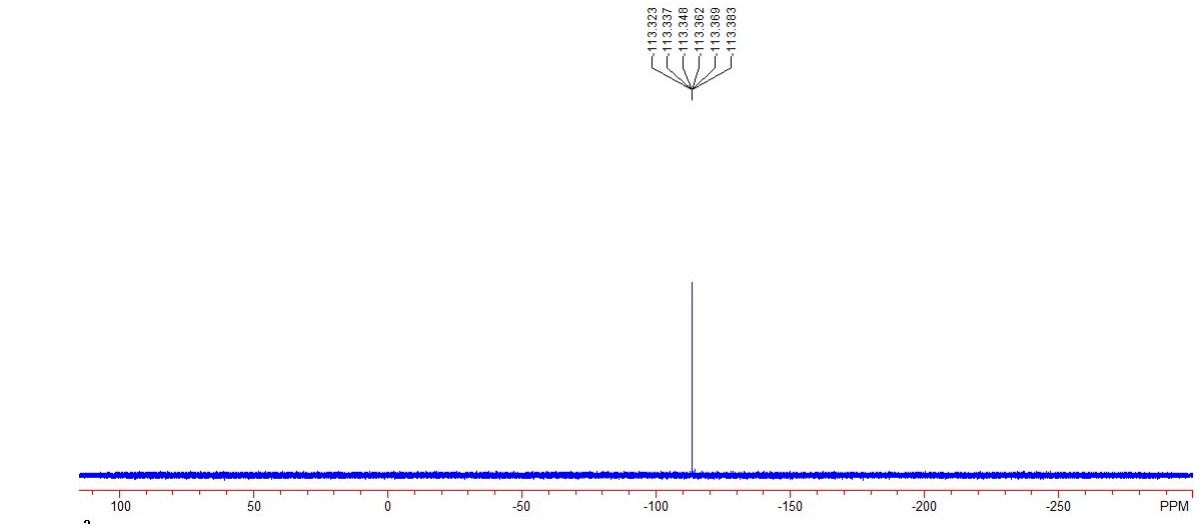


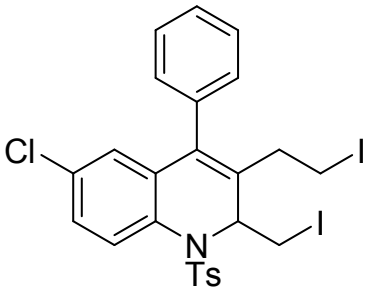


Compound 4b: Yield: 47 mg, 35%. A light yellow solid. Mp: 192-195 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40-2.47 (m, 4H), 2.53-2.60 (m, 1H), 2.73-2.84 (m, 2H), 2.94-3.04 (m, 1H), 3.39 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 4.92 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 5.84 (br, 1H), 6.27

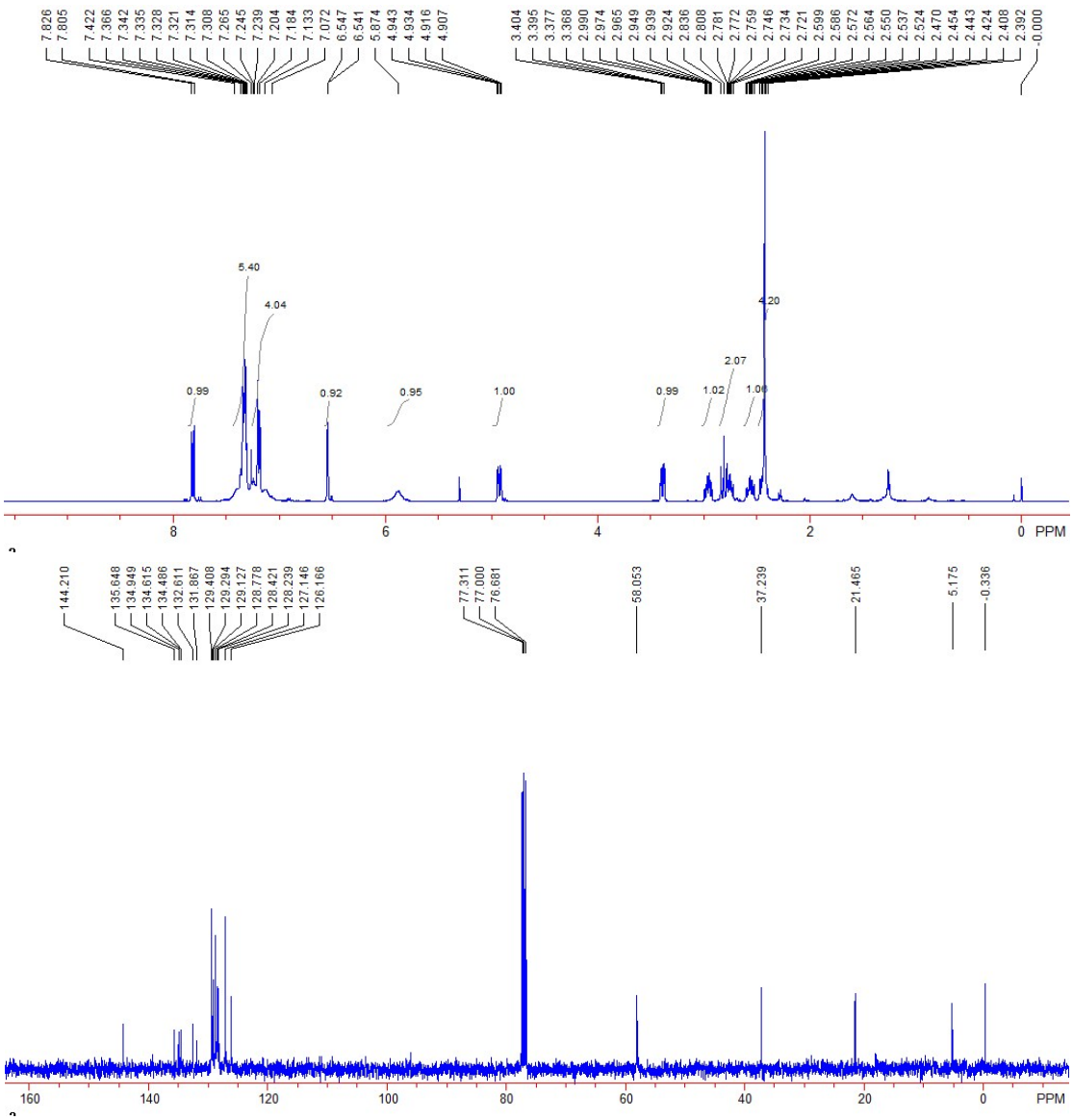
(dd, 1H, J_1 = 9.2 Hz, J_2 = 2.8 Hz), 7.03-7.38 (m, 9H), 7.84 (dd, 1H, J_1 = 9.2 Hz, J_2 = 5.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ -0.2, 5.1, 21.4, 37.2, 58.1, 112.9 (d, J = 24.5 Hz), 115.2 (d, J = 22.3 Hz), 126.5 (d, J = 2.2 Hz), 127.1, 128.1, 128.7, 129.3, 129.6 (d, J = 8.2 Hz), 132.2 (d, J = 8.2 Hz), 134.3, 134.8, 135.0, 135.5, 144.1, 161.1 (d, J = 245.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -113.82~-113.32 (m); IR (neat): ν 2920, 1597, 1480, 1344, 1163, 1090, 816 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}FI_2N_2O_2S$ $[M+NH_4]^+$: 690.9783, found: 690.9777.

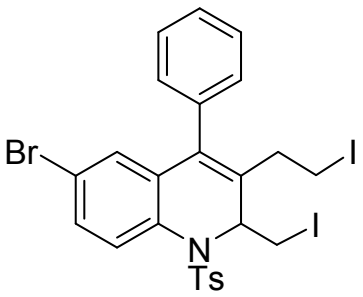






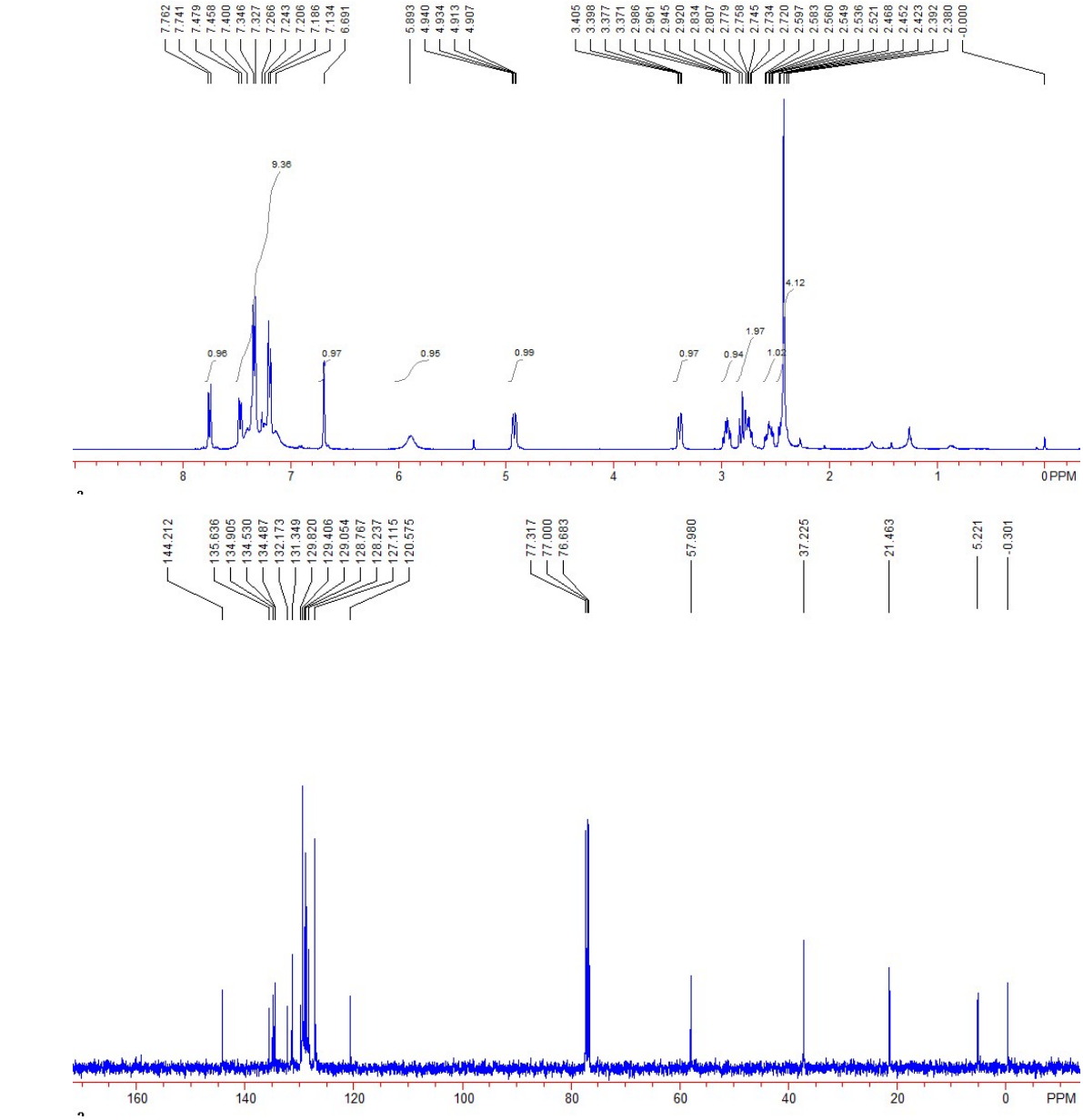
Compound 4c: Yield: 55 mg, 40%. A light yellow solid. Mp: 199-201 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.39-2.47 (m, 4H), 2.52-2.59 (m, 1H), 2.72-2.83 (m, 2H), 2.92-2.99 (m, 1H), 3.38 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 4.92 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 5.87 (br, 1H), 6.54 (d, 1H, J = 2.4 Hz), 7.07-7.26 (m, 4H), 7.30-7.42 (m, 5H), 7.81 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ -0.3, 5.1, 21.4, 37.2, 58.0, 126.1, 127.1, 128.2, 128.4, 128.7, 129.1, 129.2, 129.4, 131.8, 132.6, 134.4, 134.6, 134.9, 135.6, 144.2; IR (neat): ν 2920, 1597, 1473, 1344, 1166, 904, 815 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}ClI_2N_2O_2S$ $[M+NH_4]^+$: 706.9487, found: 706.9476.

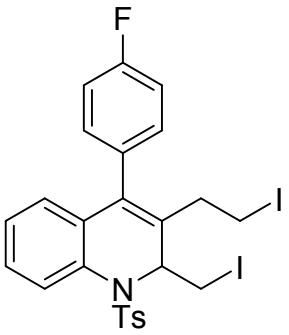




Compound 4d: Yield: 102 mg, 69%. A light yellow solid. Mp: 208-210 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.38-2.46 (m, 4H), 2.52-2.59 (m, 1H), 2.72-2.83 (m, 2H), 2.92-2.98 (m, 1H), 3.38 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.4 Hz), 4.92 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.4 Hz), 5.89 (br, 1H), 6.69 (s, 1H), 7.13-7.47 (m, 9H), 7.75 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ -0.3, 5.2, 21.4, 37.2, 57.9, 120.5, 127.1, 128.2, 128.7, 129.0, 129.4, 129.8, 131.3, 132.1, 134.4, 134.5, 134.9, 135.6, 144.2; IR (neat): ν 2964, 1592, 1471, 1353, 1163, 1078, 904, 815 cm^{-1}; HRMS (ESI) Calcd.

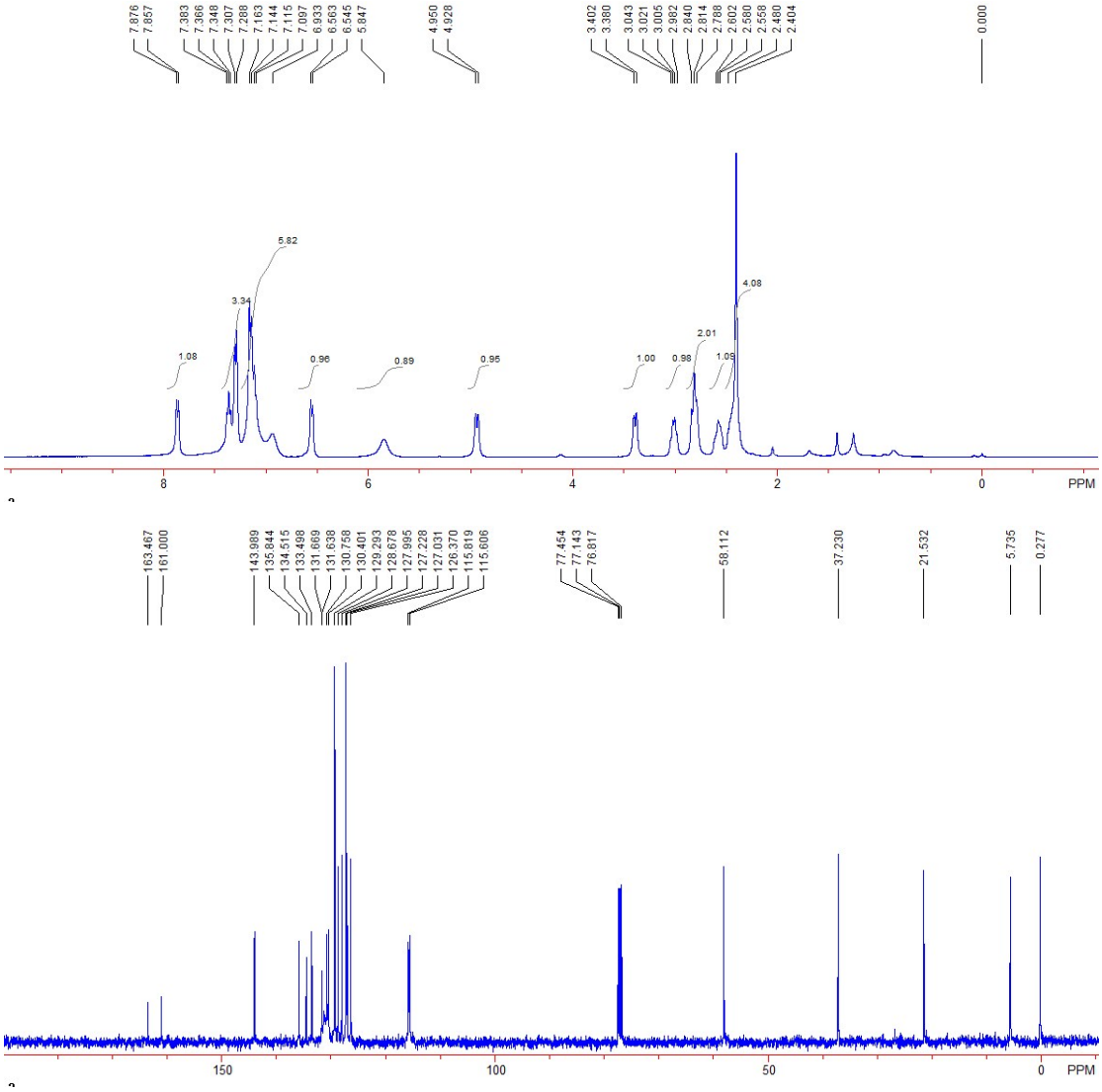
for $C_{25}H_{26}BrI_2N_2O_2S$ $[M+NH_4]^+$: 750.8982, found: 750.8980.

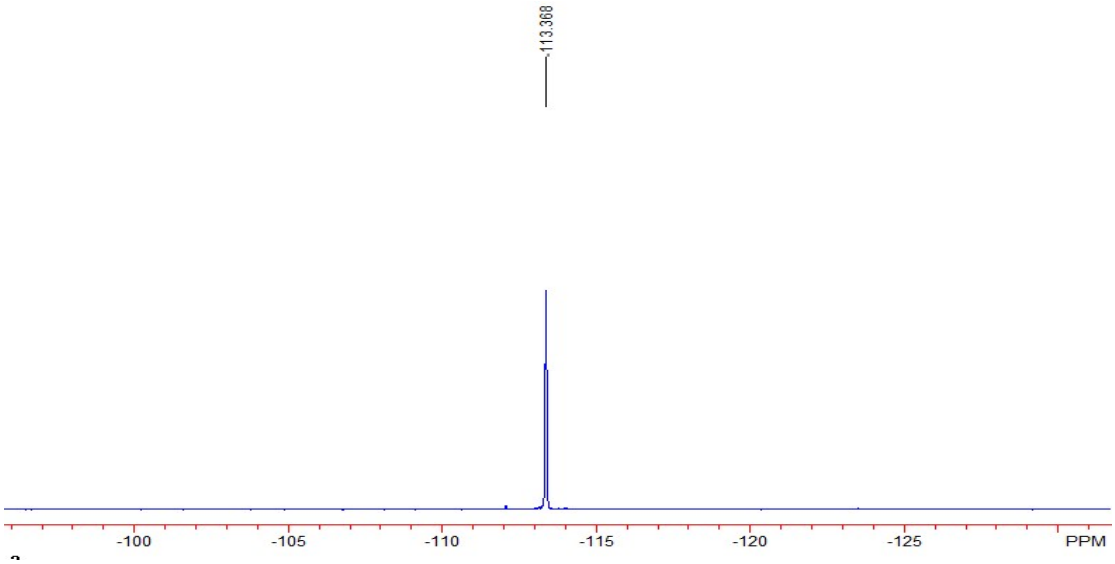


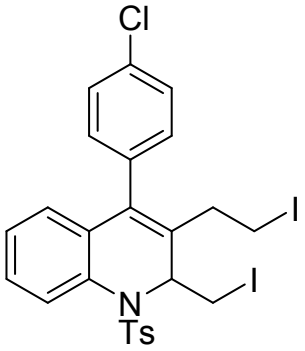


Compound 4e: Yield: 109 mg, 81%. A light yellow solid. Mp: 152-155 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40-2.48 (m, 4H), 2.55-2.60 (m, 1H), 2.78-2.84 (m, 2H), 2.98-3.04 (m, 1H), 3.39 (d, 1H, *J* = 8.8 Hz), 4.93 (d, 1H, *J* = 8.8 Hz), 5.84 (br, 1H), 6.55 (d, 1H, *J* = 7.2 Hz), 6.93-7.16 (m,

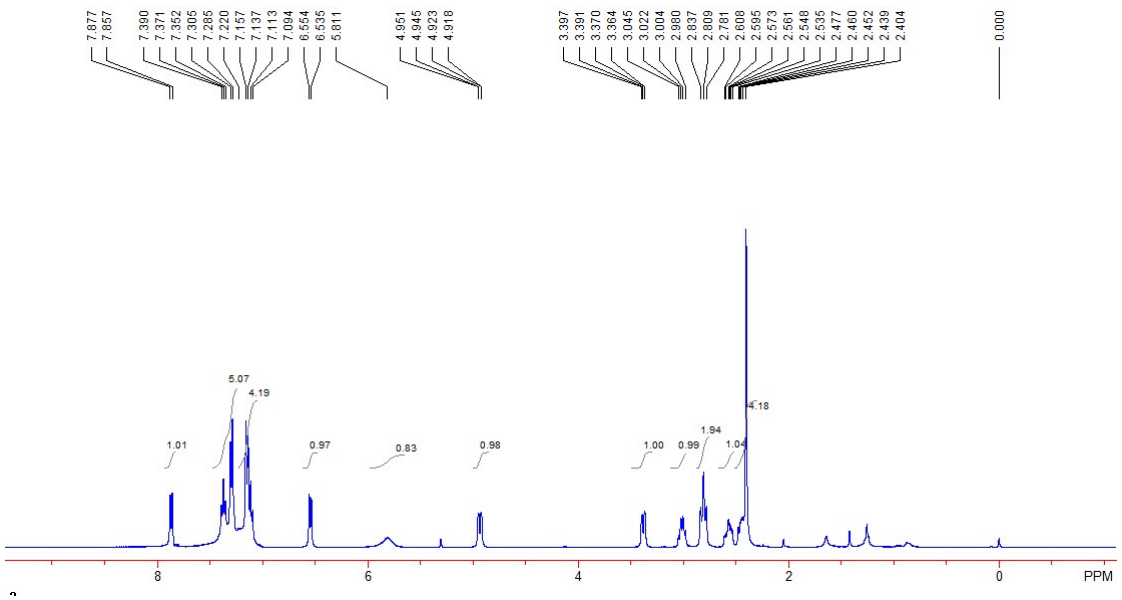
6H), 7.28-7.38 (m, 3H), 7.86 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.2, 5.7, 21.5, 37.2, 58.1, 115.7 (d, J = 21.3 Hz), 126.3, 127.0, 127.2, 127.9, 128.6, 129.2, 130.4, 130.7, 131.6 (d, J = 3.1 Hz), 133.4, 134.5, 135.8, 143.9, 162.2 (d, J = 246.7 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -113.3 (s); IR (neat): ν 2920, 1597, 1352, 1162, 1089, 765 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}FI_2N_2O_2S$ $[M+NH_4]^+$: 690.9783, found: 690.9778.

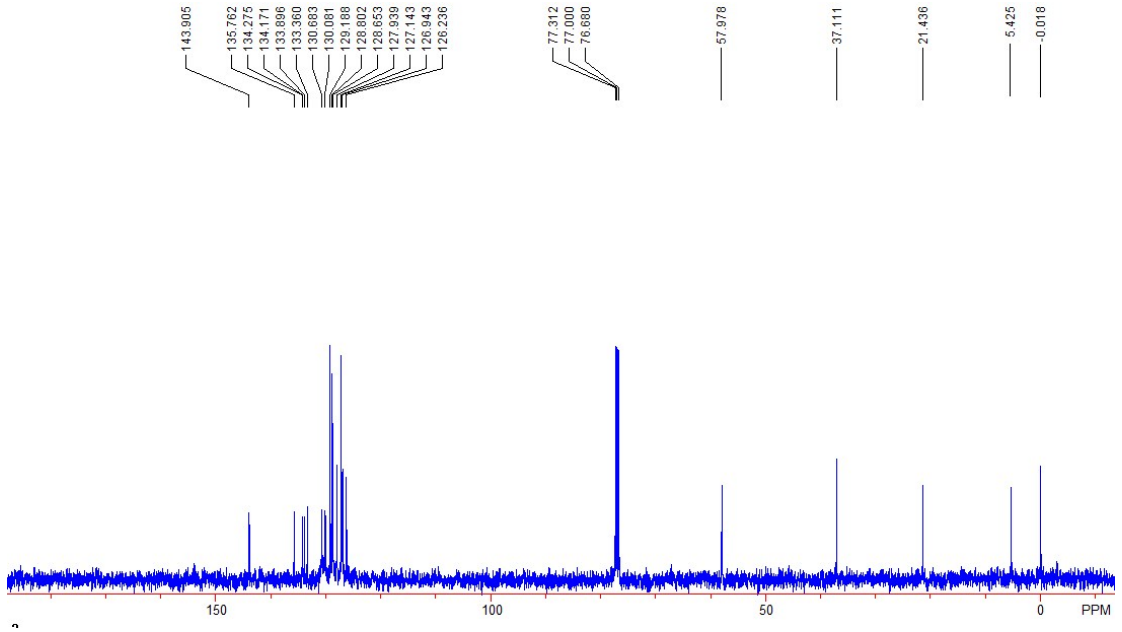


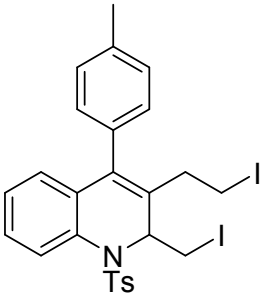




Compound 4f: Yield: 82 mg, 60%. A light yellow solid. Mp: 85-87 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40-2.47 (m, 4H), 2.53-2.60 (m, 1H), 2.78-2.83 (m, 2H), 2.98-3.04 (m, 1H), 3.38 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.4 Hz), 4.93 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.4 Hz), 5.81 (br, 1H), 6.54 (d, 1H, J = 7.6 Hz), 7.09-7.22 (m, 4H), 7.28-7.39 (m, 5H), 7.86 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ -0.01, 5.4, 21.4, 37.1, 57.9, 126.2, 126.9, 127.1, 127.9, 128.6, 128.8, 129.1, 130.0, 130.6, 133.3, 133.8, 134.1, 134.2, 135.7, 143.9; IR (neat): ν 2922, 1595, 1479, 1348, 1163, 1088, 903 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}ClI_2N_2O_2S$ $[M+NH_4]^+$: 706.9487, found: 706.9474.

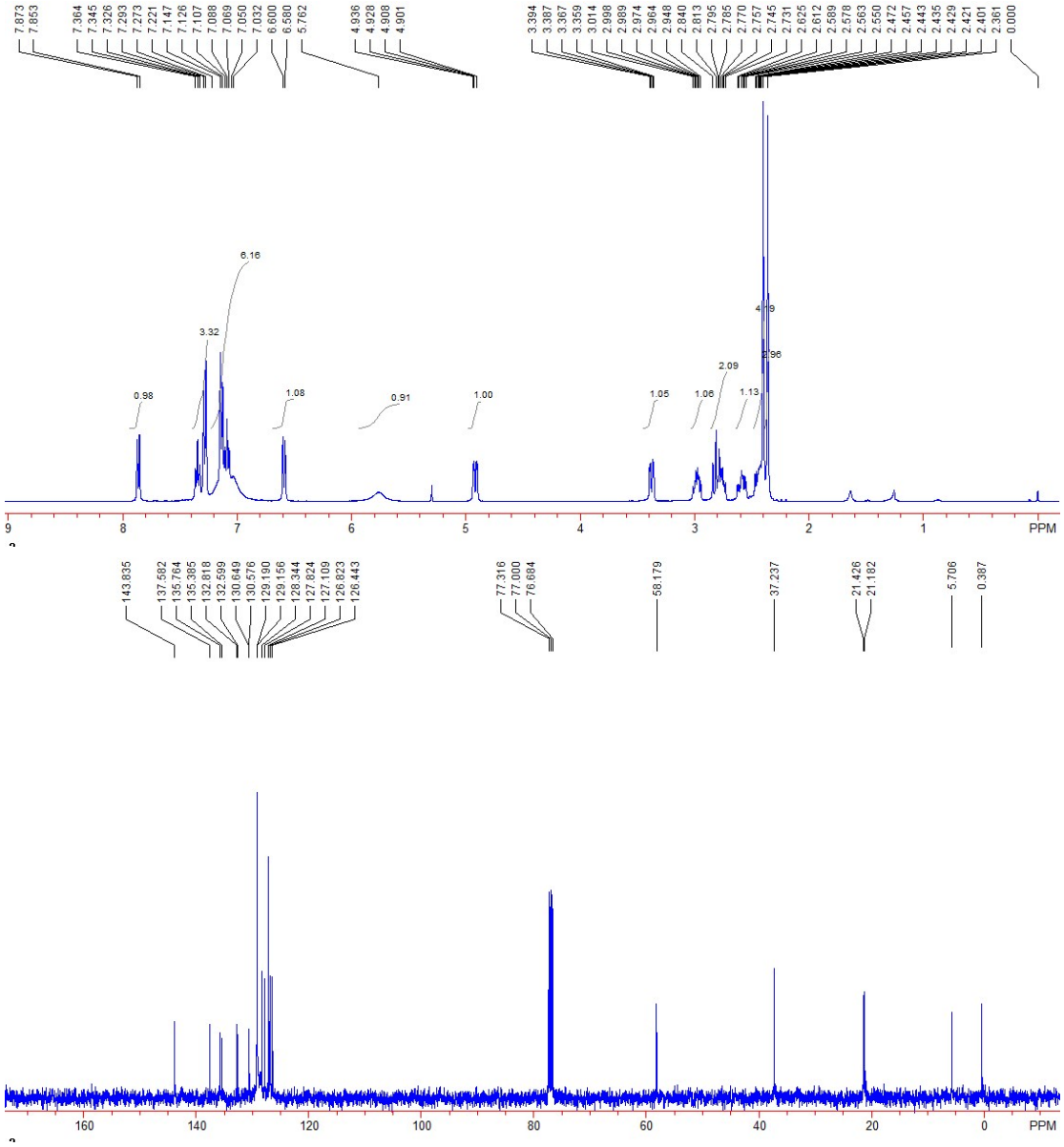


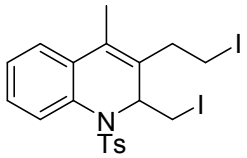




Compound 4h: Yield: 77 mg, 58%. A light yellow solid. Mp: 193-195 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.36 (s, 3H), 2.40-2.47 (m, 4H), 2.55-2.62 (m, 1H), 2.73-2.84 (m, 2H), 2.94-3.01 (m, 1H), 3.37 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.2 Hz), 4.91 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.2 Hz), 5.76 (br, 1H), 6.59 (d, 1H, J = 8.0 Hz), 7.03-7.14 (m, 6H), 7.22-7.36 (m, 3H), 7.86 (d, 1H, J = 8.0 Hz); ^{13}C

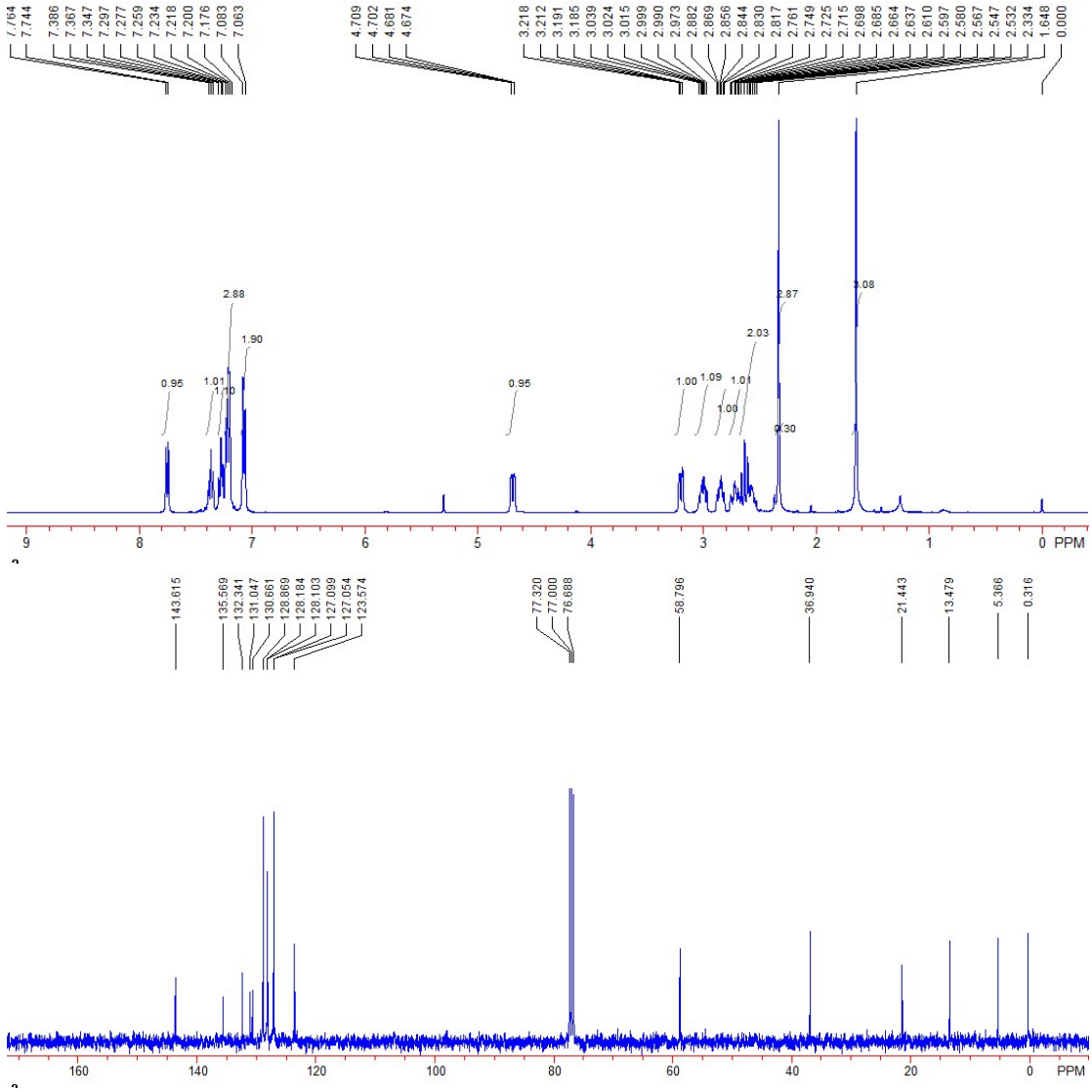
NMR ($CDCl_3$, 100 MHz, TMS) δ 0.3, 5.7, 21.1, 21.4, 37.2, 58.1, 126.4, 126.8, 127.1, 127.8, 128.3, 129.15, 129.19, 130.5, 130.6, 132.5, 132.8, 135.3, 135.7, 143.8; IR (neat): ν 2917, 1597, 1345, 1163, 1079, 814 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{29}I_2N_2O_2S$ $[M+NH_4]^+$: 687.0034, found: 687.0027.



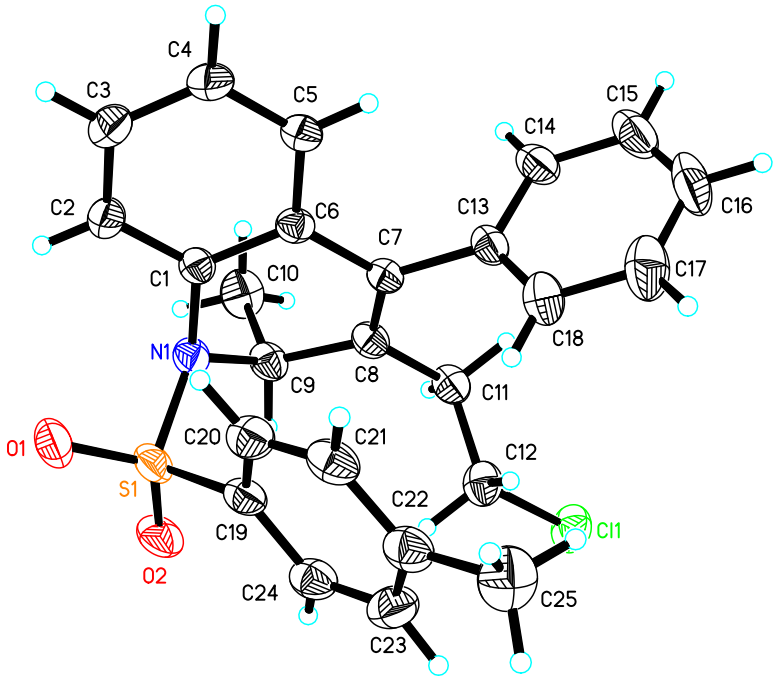


Compound 4l: Yield: 72 mg, 61%. A light yellow solid. Mp: 168-171 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.64 (s, 3H), 2.33 (s, 3H), 2.53-2.66 (m, 2H), 2.68-2.76 (m, 1H), 2.81-2.88 (m, 1H), 2.97-3.03 (m, 1H), 3.20 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.4 Hz), 4.79 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.4 Hz), 7.07 (d, 2H, J = 8.0 Hz), 7.17-7.23 (m, 3H), 7.25-7.29 (m, 1H), 7.34-7.38 (m, 1H), 7.75 (d,

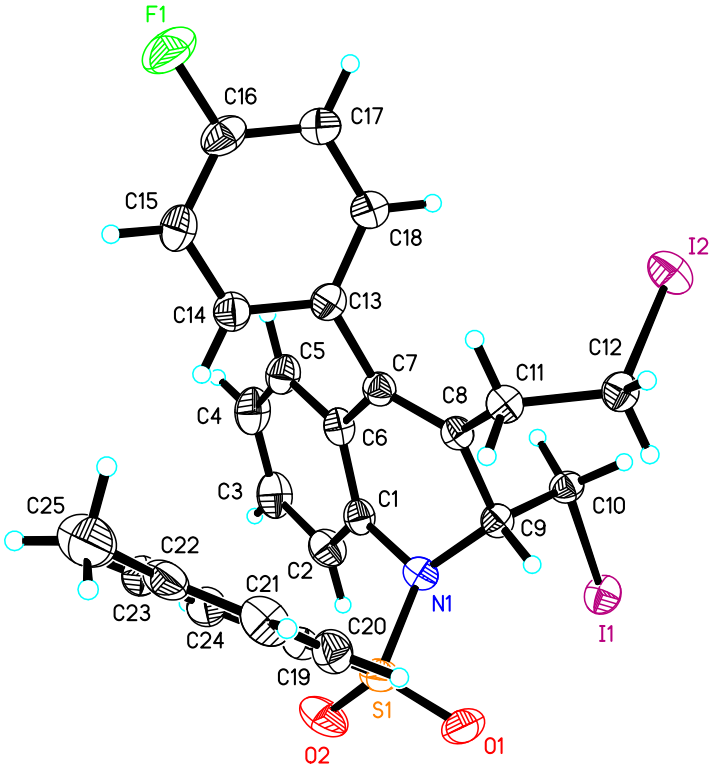
1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.3, 5.3, 13.4, 21.4, 36.9, 58.7, 123.5, 127.05, 127.09, 128.10, 128.18, 128.8, 130.6, 131.0, 132.3, 135.5, 143.6; IR (neat): ν 2917, 1592, 1479, 1133, 1163, 1083, 766 cm^{-1}; HRMS (ESI) Calcd. for $C_{20}H_{25}I_2N_2O_2S$ $[M+NH_4]^+$: 610.9721, found: 610.9719.



X-ray Crystal Data of 2a and 4e



The crystal data of **2a** have been deposited in CCDC with number 1503535. Empirical Formula: $C_{25}H_{24}ClNO_2S$; Formula Weight: 437.96; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 13.2671(17)Å, b = 18.296(3)Å, c = 19.283(3)Å, α = 90°, β = 108.684(3)°, γ = 90°, V = 4434.0(10)$Å^3$; Space group: P 21/c; Z = 8; D_{calc} = 1.312 g/cm^3; F_{000} = 1840; Final R indices [I>2sigma(I)] R1 = 0.0688, wR2 = 0.1689.



The crystal data of **4e** have been deposited in CCDC with number 1534541. Empirical Formula: $C_{25}H_{22}FI_2NO_2S$; Formula Weight: 673.29; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 8.7048(10)Å, b = 10.5461(13)Å, c = 13.9946(17)Å, α = 82.330(2)°, β = 79.359(2)°, γ = 79.100(2)°, V = 1233.4(3)$Å^3$; Space group: P -1; Z = 2; D_{calc} = 1.813 g/cm^3; F_{000} = 652; Final R indices [I>2sigma(I)] R1 = 0.0293, wR2 = 0.0767.