Supporting Information

Rhodium(II)-catalyzed intermolecular [3+2] annulation of N-vinyl indoles with N-tosyl-1,2,3-triazoles via aza-vinyl Rh carbene

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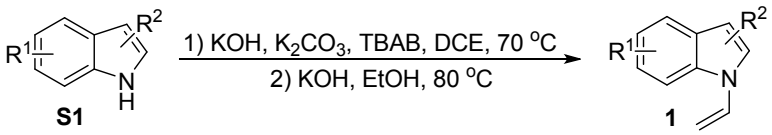
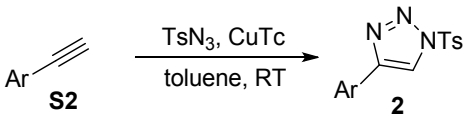
1. General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 400-MR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard; Chemical shifts (δ) are expressed in ppm and *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Infrared 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. The structures of **3da**, **3la** were assigned by X-ray analysis.

2. General procedure for the preparation of indole derivatives 1



In a round-bottom flask, substrate **S1** (4.0 mmol, 1.0 equiv.), tetrabutylammonium bromide (TBAB) (0.1 equiv.), KOH (10.0 equiv.), K_2CO_3 (4.0 equiv.) and the solvent DCE (15.0 mL) were added. Then, the mixture was stirred at 70 °C for 12 h. After the reaction completion monitored by TLC analysis, the solvent was evaporated under reduced pressure. The mixture of the residue, KOH (4.0 equiv.) and EtOH (20.0 mL) was stirred in a preheated oil at 80 °C for 3 h. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered and evaporated under vacuum. The residue was purified by a silica-gel column chromatography using ethyl acetate/hexane (1:50) as an eluent to obtain the product **1** in good to excellent yield.

3. General procedure for the synthesis of 1,2,3-triazoles 2

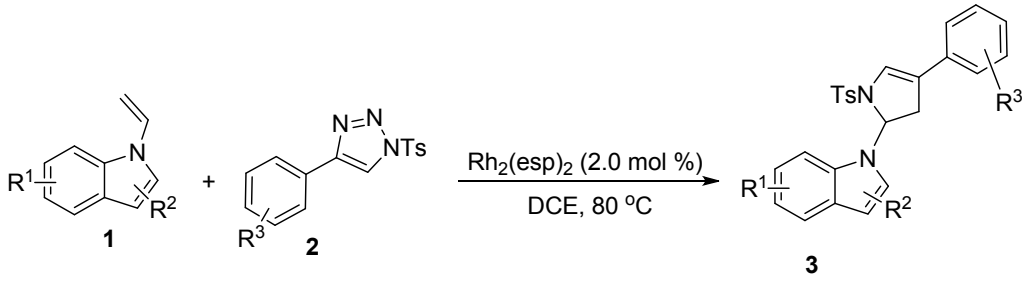


To a stirred solution of alkyne **S2** (5.0 mmol 1.0 equiv.) in 20.0 mL toluene was added copper(I) thoiphene-carboxylate (CuTc, 0.1 equiv.). The reaction mixture was cooled to 0 °C and treated dropwise with a solution of 4-methylbenzenesulfonyl azide (1.2 equiv.) in ethyl acetate. The reaction mixture was stirred for further 6 h at room temperature, filtered through a celite, and then purified by a silica-gel column chromatography using ethyl acetate/hexane (1:8) as an eluent to obtain the white solid **2**.[1]

Reference:

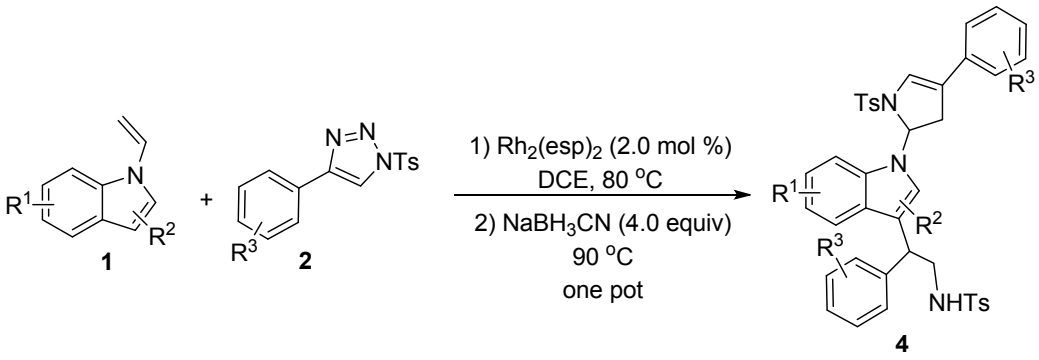
[1] J. E. Spangler, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 6802.

4. General procedure for the synthesis of products 3



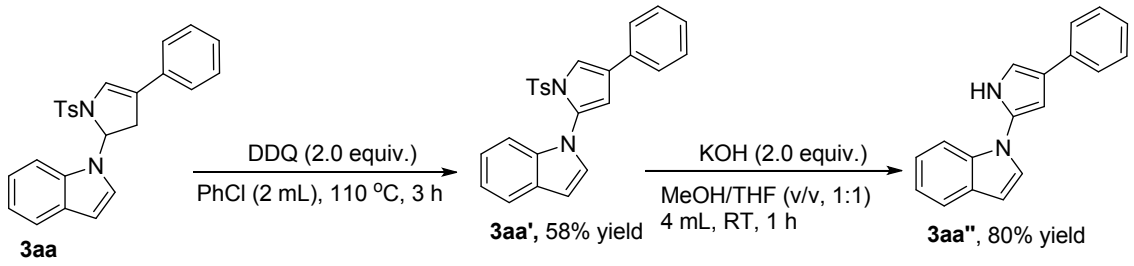
To an oven dried 20 mL schlenk tube equipped with a stir bar, 1,2,3-triazole **1** (0.2 mmol, 1.0 equiv.) and $Rh_2(esp)_2$ (0.004 mmol, 2.0 mol%) were added under argon atmosphere. Subsequently, a solution of indole derivative **1** (0.4 mmol, 2.0 equiv.) in DCE (2.0 mL) was introduced via a syringe. 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 (1:10) as an eluent to give the desired product **3**.

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



To an oven dried schlenk tube equipped with a magnetic stir bar, 1,2,3-triazole **2** (1.25 mmol, 2.5 equiv.) and $Rh_2(esp)_2$ (0.01 mmol, 2.0 mol%) were added under nitrogen atmosphere. Subsequently, a solution of indole derivative **1** (0.5 mmol, 1.0 equiv.) in DCE (5.0 mL) was introduced via a syringe. The reaction tube was sealed and the mixture was stirred in a preheated oil bath at 80 °C for further 4 h. After the reaction completion monitored by TLC analysis, followed by the addition of $NaBH_3CN$ (2.0 mmol, 4.0 equiv.) and the mixture was stirred in a preheated oil at 90 °C for further 6 h. The reaction mixture was filtered through a celite, and then purified by a silica-gel column chromatography using ethyl acetate/hexanes (1:6) as an eluent to give the desired product **4**.

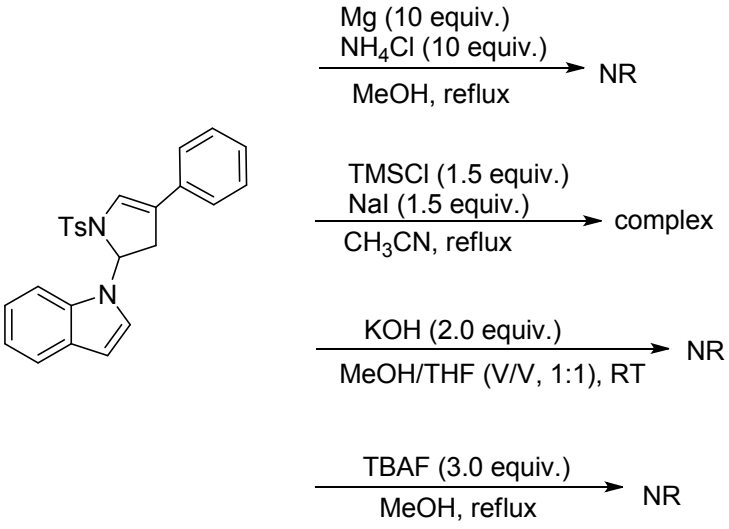
6. General procedure for the transformation of 3aa



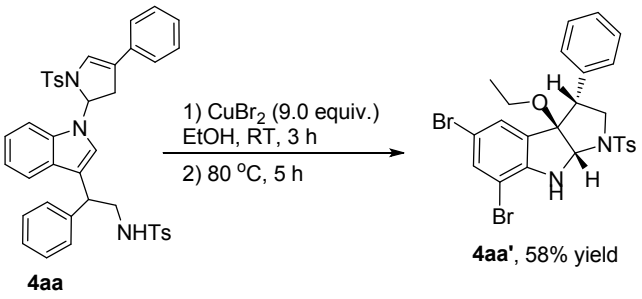
To an oven dried schlenk tube equipped with a magnetic stir bar, **3aa** (0.5 mmol, 1.0 equiv.) was added, and then PhCl (5.0 mL) was introduced via a syringe. The reaction mixture was stirred in a preheated oil bath at 110 °C. Then, DDQ was added in portion for 1.5 h. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered through a celite, and then purified by a silica-gel column chromatography using ethyl acetate/hexanes (1:15) as an eluent to give the desired product **3aa'**.

To an oven dried schlenk tube equipped with a magnetic stir bar, **3aa'** (0.1 mmol, 1.0 equiv.) and KOH (2.0 equiv.) were added, and then MeOH/THF (v/v, 1:1) (4.0 mL) was introduced via a syringe. The reaction mixture was stirred at room temperature. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered through a celite, and then purified by a silica-gel column chromatography using ethyl acetate/hexanes (1:10) as an eluent to give the desired product **3aa''**.

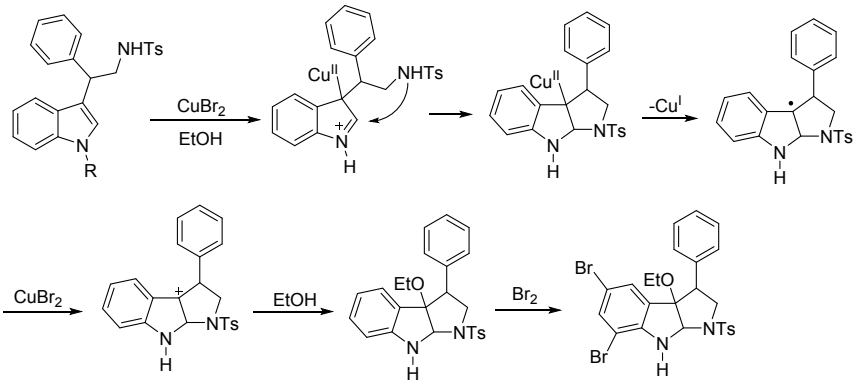
7. Deprotection of product 3aa



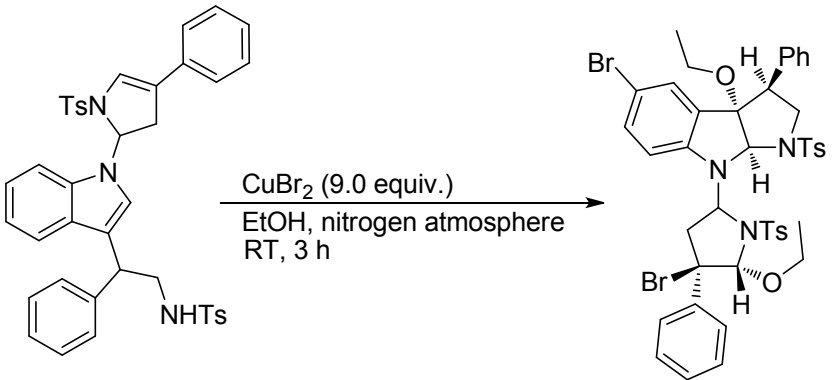
8. General procedure for the transformation of 4aa



4aa **4aa'**, 58% yield



To an oven dried schlenk tube equipped with a magnetic stir bar, **4aa** (0.2 mmol, 1.0 equiv.) and copper dibromide (1.8 mmol, 9.0 equiv.) was added, and then EtOH (4.0 mL) was introduced via a syringe. The reaction mixture was stirred at RT for 3 h. Then, the reaction mixture was stirred at 80 °C. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered through a celite, and concentrated under reduced pressure and then the residue was purified by a silica-gel column chromatography using ethyl acetate/hexanes (1:25) as an eluent to give the desired product **4aa'**.

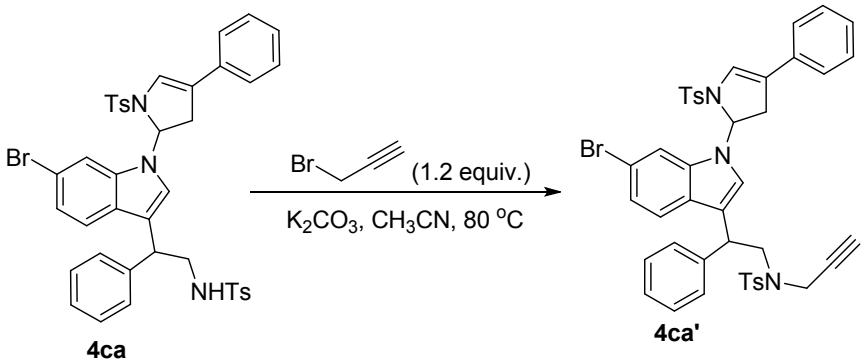


4aa **4aa''**, 25% yield

To an oven dried schlenk tube equipped with a magnetic stir bar, **4aa** (0.5 mmol, 1.0 equiv.) and copper dibromide (4.5 mmol, 9.0 equiv.) was added under nitrogen atmosphere, and then EtOH (8.0 mL) was introduced via a syringe. The reaction mixture was stirred at RT for 3 h. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered through a celite,

and concentrated under reduced pressure and then the residue was purified by a silica-gel column chromatography using ethyl acetate/hexanes (1:25) as an eluent to give the desired product **4aa''**.

9. General procedure for the transformation of 4ca

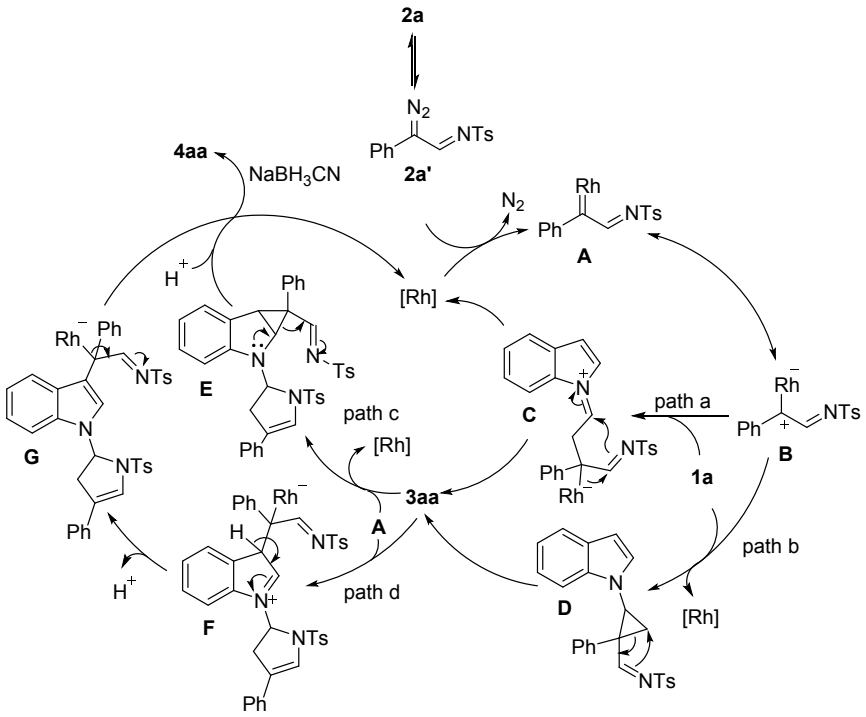


To an oven dried schlenk tube equipped with a magnetic stir bar, **4ca** (0.5 mmol, 1.0 equiv.) and K_2CO_3 (1.2 equiv.) were added. Then, 3-bromoprop-1-yne (1.2 equiv.) and CH_3CN (5.0 mL) was introduced via a syringe. The reaction mixture was stirred at 80 ^oC. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered through a celite, and then purified by a silica-gel column chromatography using ethyl acetate/hexanes (1:5) as an eluent to give the desired product **4ca'**.

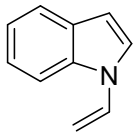
10. A proposed reaction mechanism

On the basis of the above results and the previously reported literature, the following plausible mechanism of this reaction is outlined. The 4-phenyl-1-tosyl-1,2,3-triazole **2a** exists in an equilibrium with its diazoimine tautomer **2a'**, which can be efficiently transformed into the highly reactive azavinyl rhodium(II) carbene **A** and its diazoimine tautomer **B** upon release of N_2. Intermediate A undergoes a nucleophilic attack by N-vinyl indole 1a to give the zwitterionic intermediate C in path a. The cyclization of intermediate **C** furnishes the desired product 3aa along with the regeneration of rhodium catalyst. Alternatively, N-vinyl indole 1a can react with the rhodium(II) carbenoid intermediate **A** to give intermediate **D** through a cyclopropanation process, followed by ring-opening process to furnish **3aa** (path b). When 1.0 equiv of N-vinyl indole **1a** is used to react with 2.5 equiv of 4-phenyl-N-sulfonyl-1,2,3-triazole **2a**, the rhodium(II) carbenoid intermediate **A** can further react with the indole's double bond of 3aa to afford the strained cyclopropanation intermediate **E**, which undergoes the ring-opening process and reduction with $NaBH_3CN$ to give the desired product 4aa as syn and anti-isomeric mixture (path c). Similarly, as an alternative plausible mechanism, the reaction of **3aa** with intermediate **A** produces the zwitterionic intermediate **F**, which undergoes the aromatization to give intermediate **G**. The

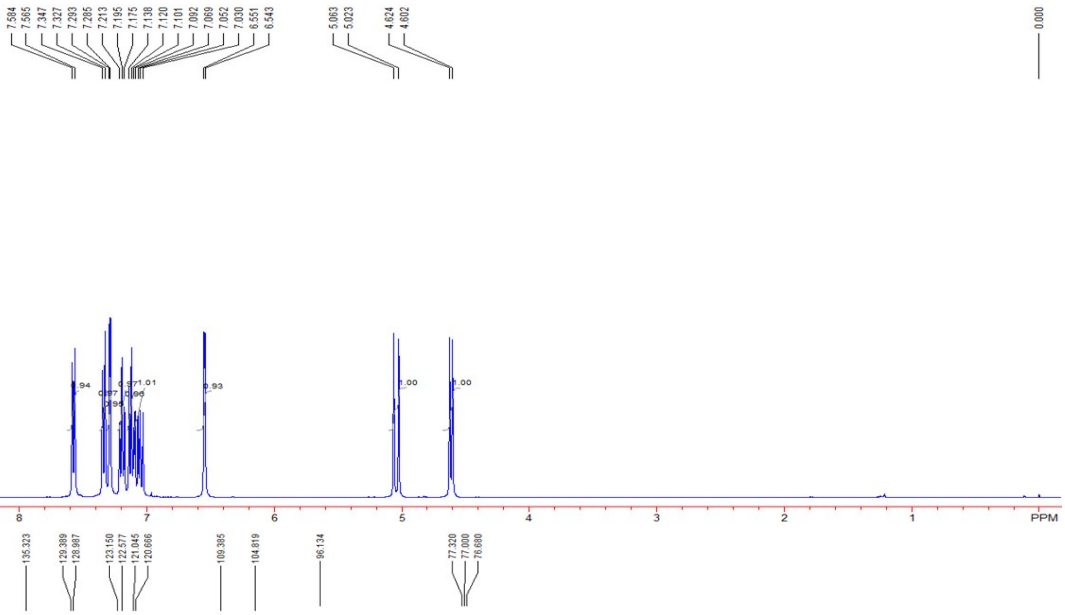
elimination of Rh catalyst and reduction with $NaBH_3CN$ can also furnish the desired product **4aa** (path d).

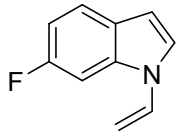


11. Spectroscopic data of the substrates 1

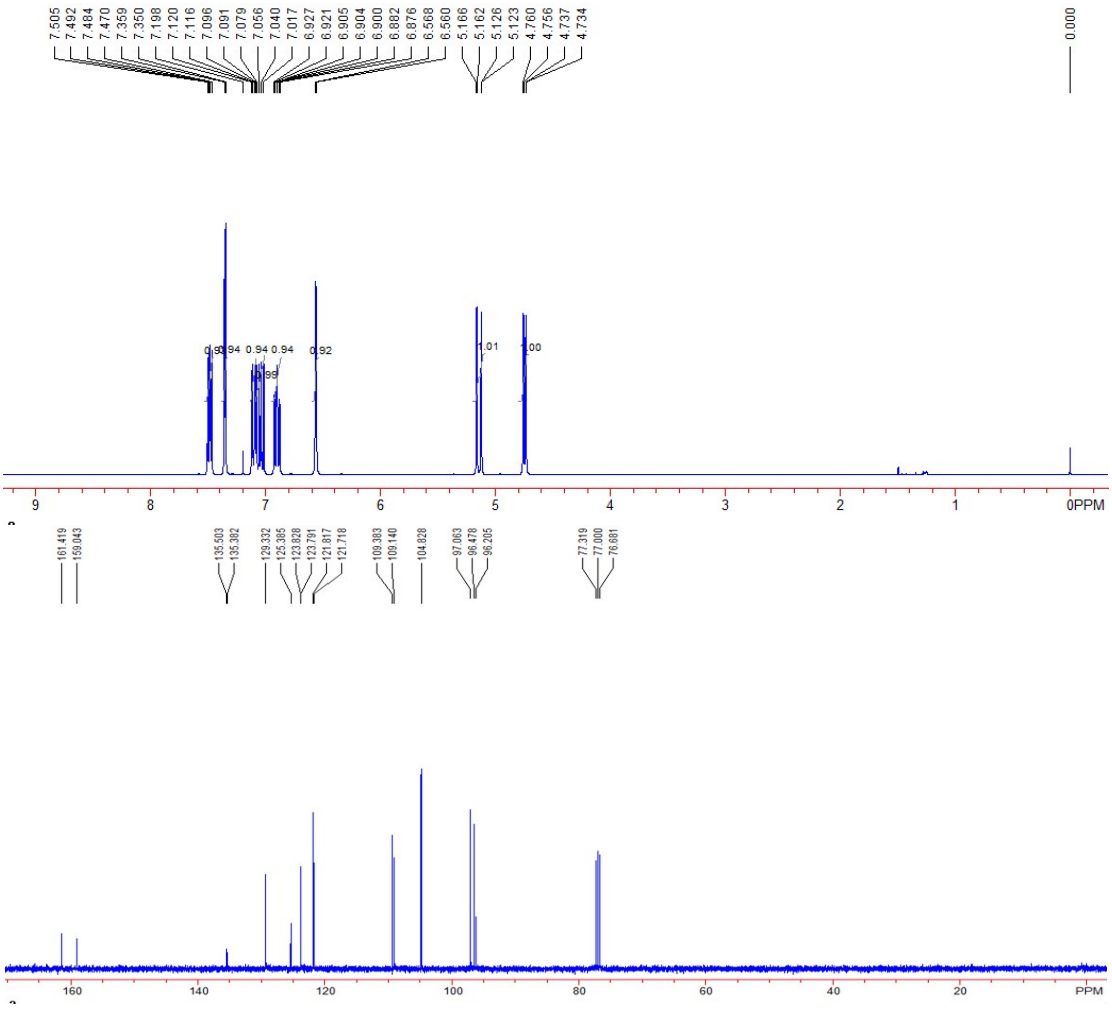


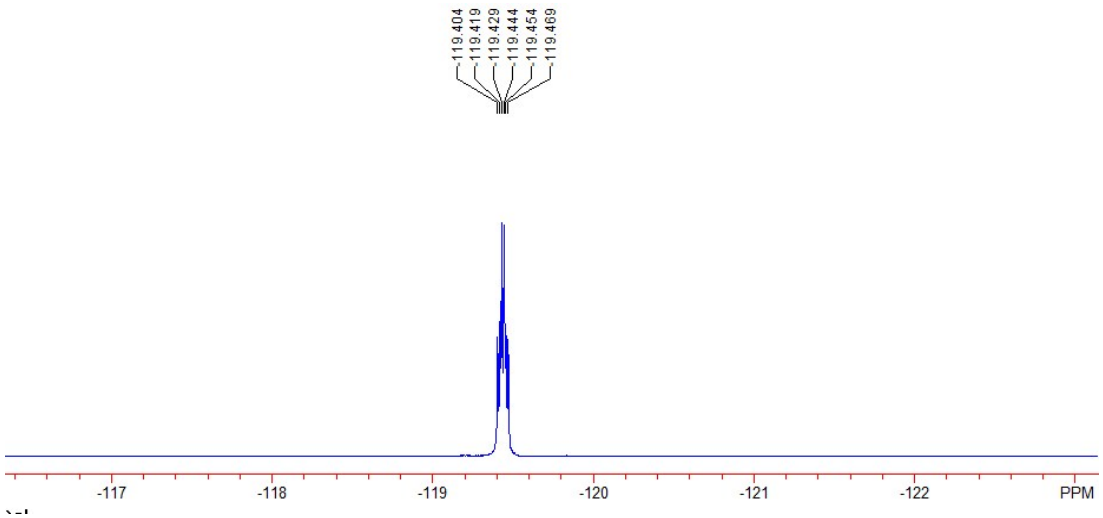
Compound 1a: Yield: 300 mg, 70%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.61 (d, 1H, J = 8.8 Hz), 5.04 (d, 1H, J = 16.0 Hz), 6.55 (d, 1H, J = 3.2 Hz), 7.06 (dd, 1H, J_1 = 16.0 Hz, J_2 = 8.8 Hz), 7.19 (dd, 1H, J_1 = J_2 = 8.0 Hz), 7.12 (dd, 1H, J_1 = J_2 = 7.2 Hz), 7.29 (d, 1H, J = 3.2 Hz), 7.33 (d, 1H, J = 8.0 Hz), 7.57 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 96.1, 104.8, 109.3, 120.6, 121.0, 122.5, 123.1, 128.9, 129.3, 135.3; IR (neat): ν 3106, 3050, 1638, 1521, 1459, 1396, 1325, 1305, 1229, 1188, 1010, 955, 848, 763, 736, 717, 699 cm^{-1}; MS (EI) m/z (%) 143 (M^+, 100), 115 (48.83), 89 (43.31), 71 (4.27), 63 (22.25), 51 (8.58). HRMS (EI) Calcd. for $C_{10}H_9N$ [M^+]: 143.0735, found: 143.0732.

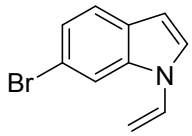




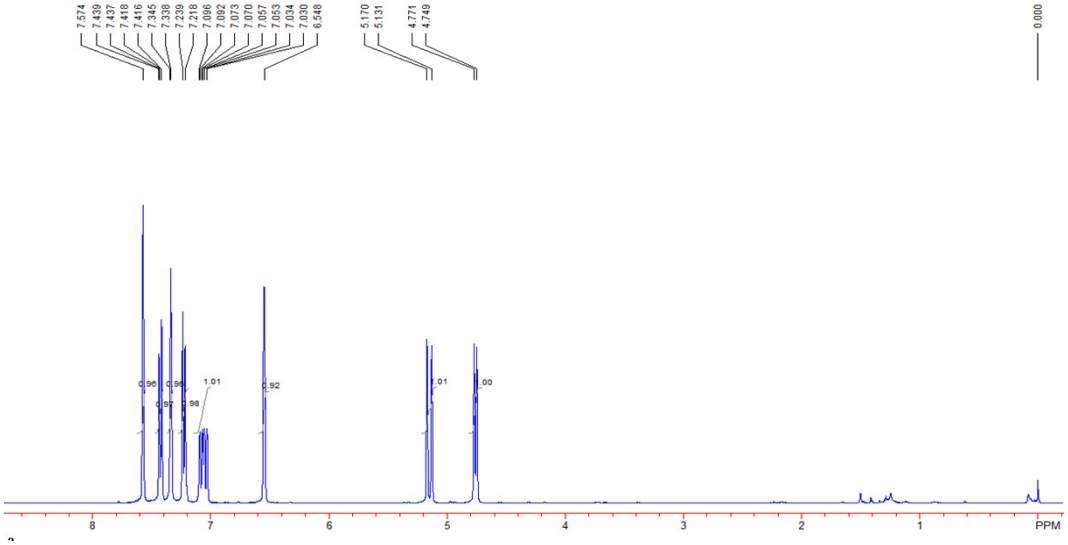
Compound 1b: Yield: 310 mg, 74%; A white solid; Mp: 60-62 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.74 (dd, 1H, J_1 = 9.2 Hz, J_2 = 1.2 Hz), 5.14 (dd, 1H, J_1 = 16.0 Hz, J_2 = 1.2 Hz), 6.56 (d, 1H, J = 3.2 Hz), 6.87-6.93 (m, 1H), 7.01-7.12 (m, 2H), 7.35 (d, 1H, J = 1.8 Hz), 7.48 (dd, 1H, J_1 = 8.8 Hz, J_2 = 5.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 96.3 (d, J = 26.5 Hz), 96.8, 104.8, 109.2 (d, J = 23.5 Hz), 121.7 (d, J = 10.6 Hz), 123.7 (d, J = 3.8 Hz), 125.3, 129.2, 135.3 (d, J = 12.1 Hz), 160.2 (d, J = 237.5 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -119.47 ~ -119.40 (m); IR (neat): ν 2956, 2923, 2845, 1642, 1613, 1520, 1482, 1456, 1332, 1323, 1287, 1225, 1201, 1188, 1169, 1084, 961, 943, 857, 835, 825, 805, 719, 696, 670 cm^{-1}; MS (EI) m/z (%) 161 (M^+, 100), 160 (27.46), 133 (32.98), 108 (30.33), 107 (26.99), 81 (6.37). HRMS (EI) Calcd. for $C_{10}H_8NF$ [M^+]: 161.0641, found: 161.0645.

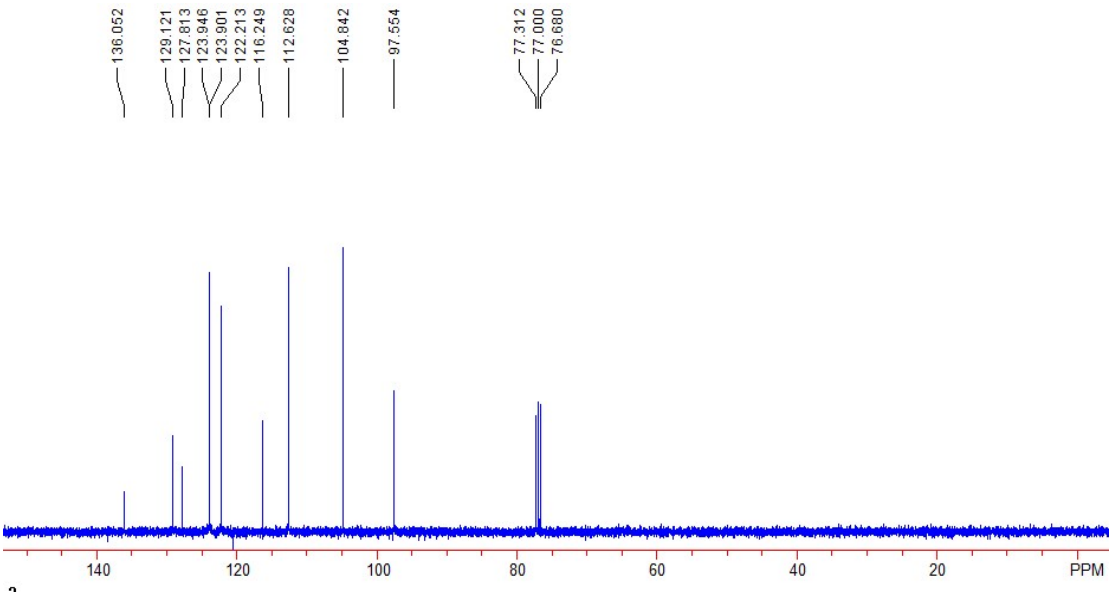


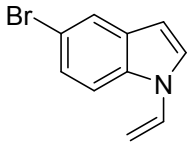




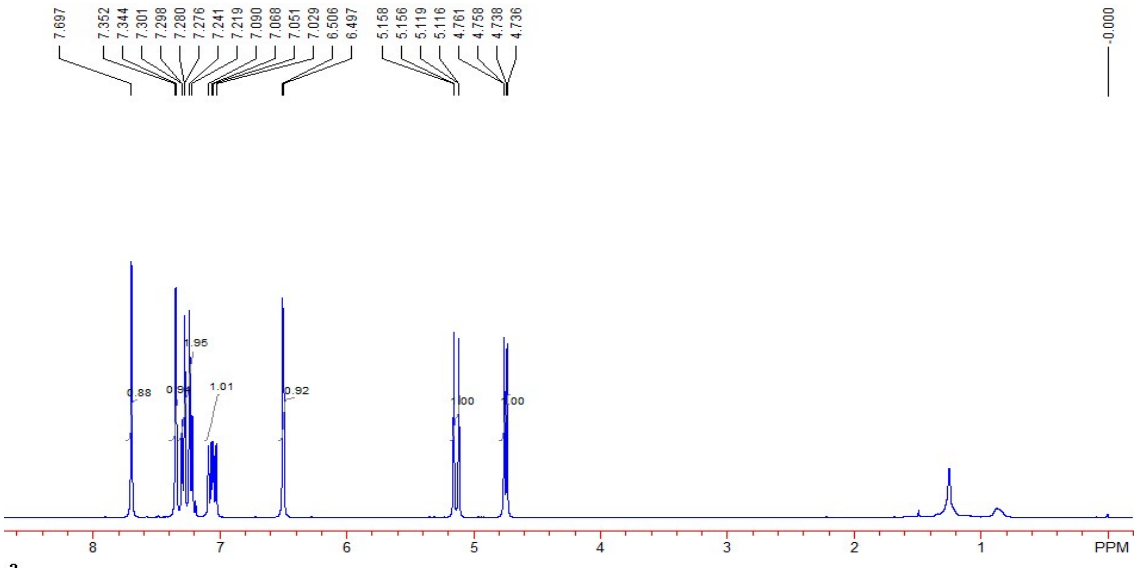
Compound 1c: Yield: 554 mg, 84%; A white solid; Mp: 44-46 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.76 (d, 1H, *J* = 8.8 Hz), 5.15 (d, 1H, *J* = 15.6 Hz), 6.54 (s, 1H), 7.03-7.09 (m, 1H), 7.23 (d, 1H, *J* = 8.4 Hz), 7.34 (d, 1H, *J* = 2.8 Hz), 7.41-7.44 (m, 1H), 7.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 97.5, 104.8, 112.6, 116.2, 122.2, 123.90, 123.94, 127.8, 129.1, 136.0; IR (neat): ν 3106, 3036, 1631, 1601, 1508, 1459, 1444, 1325, 1306, 1284, 1222, 1096, 1055, 960, 885, 845, 811, 802, 791, 745, 717 cm^{-1}; MS (EI) m/z (%) 221 (M^+, 99.66), 142 (47.85), 115 (100), 89 (36.71), 71 (16.70), 63 (19.41), 50 (7.83). HRMS (EI) Calcd. for $C_{10}H_8NBr$ [M^+]: 220.9840, found: 220.9839.

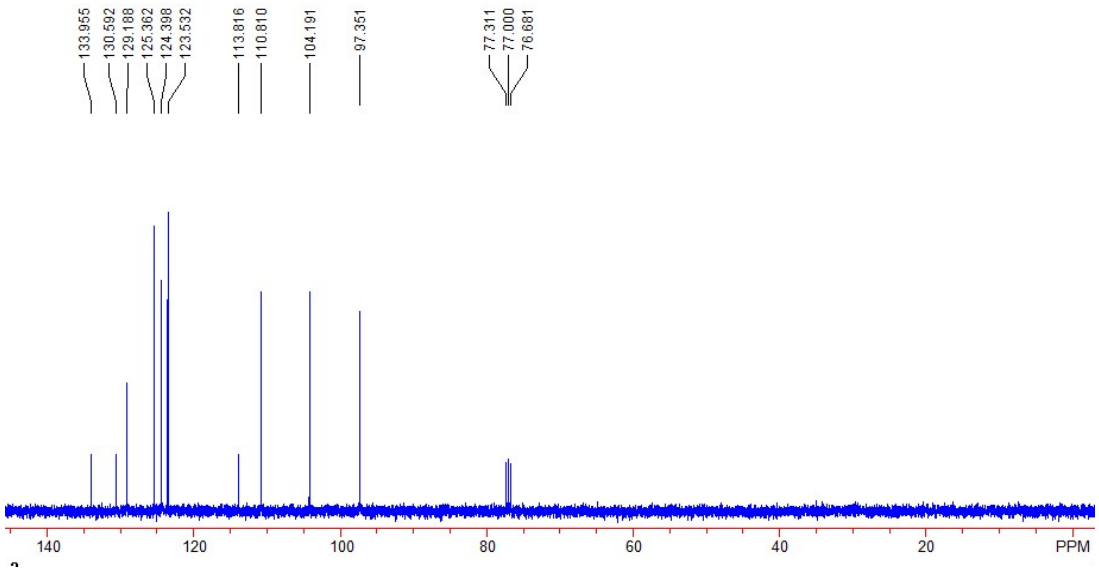


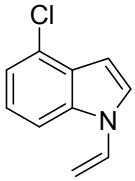




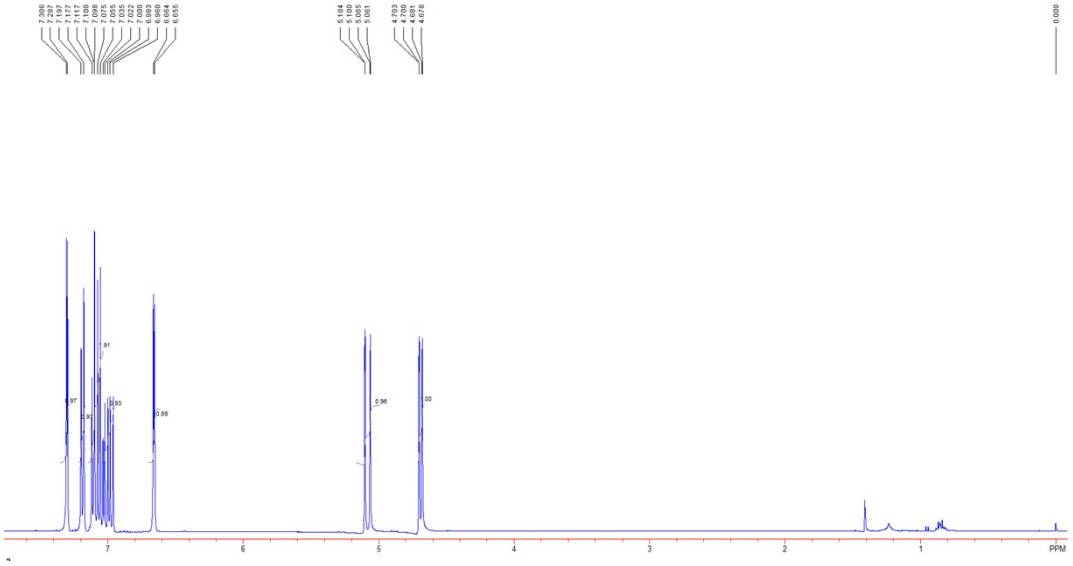
Compound 1d: Yield: 488 mg, 74%; A white solid; Mp: 73-75 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.74 (dd, 1H, J_1 = 8.8 Hz, J_2 = 0.8 Hz), 5.13 (dd, 1H, J_1 = 16.0 Hz, J_2 = 1.2 Hz), 6.50 (d, 1H, J = 3.6 Hz), 7.06 (dd, 1H, J_1 = 16.0 Hz, J_2 = 8.8 Hz), 7.21-7.30 (m, 2H), 7.34 (d, 1H, J = 3.2 Hz), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 97.3, 104.1, 110.8, 113.8, 123.5, 124.3, 125.3, 129.1, 130.5, 133.9; IR (neat): ν 3109, 3075, 1635, 1513, 1458, 1388, 1311, 1275, 1227, 1193, 1094, 1056, 1029, 956, 884, 856, 797, 757, 723, 690 cm^{-1}; MS (EI) m/z (%) 221 (M^+, 95.99), 142 (45.75), 141(33.69), 116 (30.7), 115 (100), 89 (32.32), 71 (22.13), 63 (19.14). HRMS (EI) Calcd. for $C_{10}H_8NBr$ [M^+]: 220.9840, found: 220.9833.

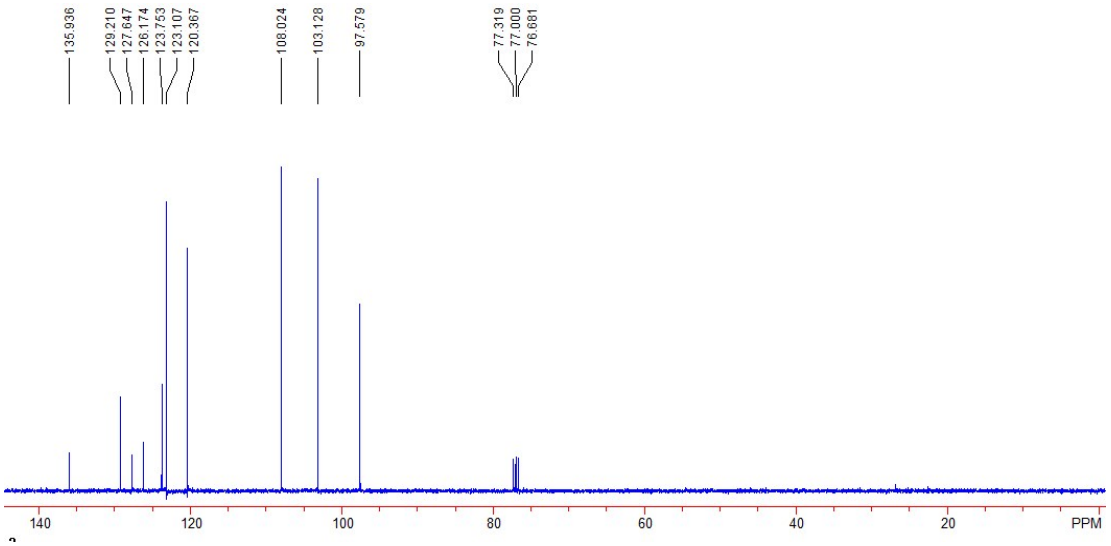


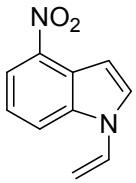




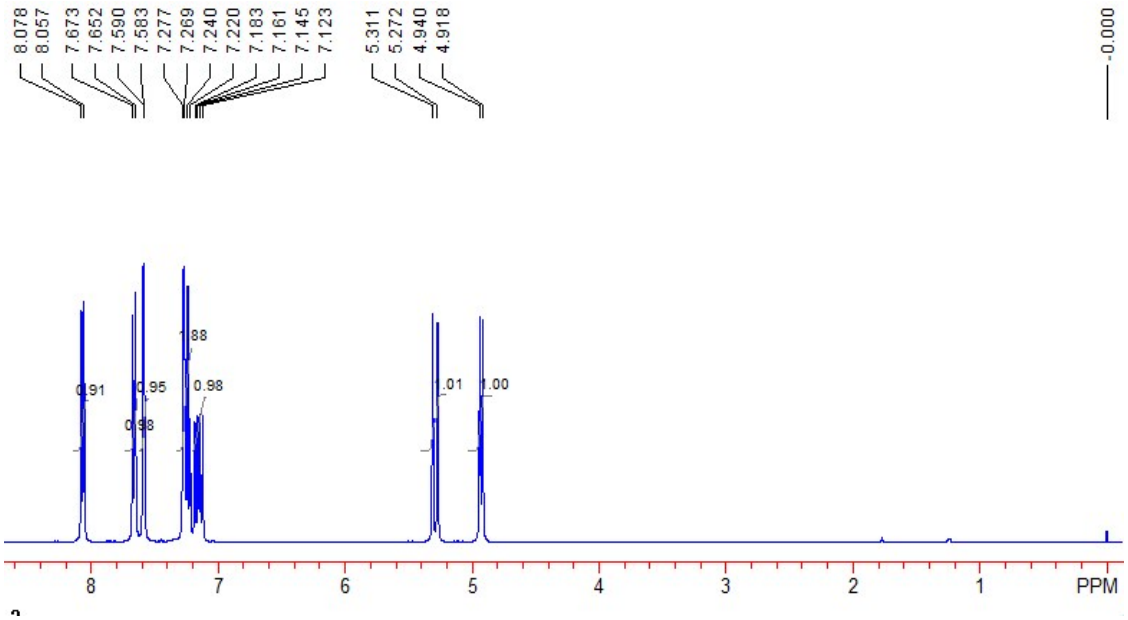
Compound 1e: Yield: 467 mg, 88%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.69 (dd, 1H, J_1 = 9.2 Hz, J_2 = 1.6 Hz), 5.08 (dd, 1H, J_1 = 15.6 Hz, J_2 = 1.6 Hz), 6.05 (d, 1H, J = 3.2 Hz), 6.99 (dd, 1H, J_1 = 15.6 Hz, J_2 = 9.2 Hz), 7.03-7.11 (m, 2H), 7.18 (d, 1H, J = 8.0 Hz), 7.26 (d, 1H, J = 3.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 97.5, 103.1, 108.0, 120.3, 123.1, 123.7, 126.1, 127.6, 129.2, 135.9; IR (neat): ν 3136, 3111, 3006, 1640, 1565, 1514, 1474, 1438, 1321, 1276, 1180, 952, 898, 855, 842, 737, 714, 699 cm^{-1}; MS (EI) m/z (%) 177 (M^+, 100), 142 (44.12), 141(16.24), 115 (41.62), 114 (13.28), 89 (27.8), 63 (10.53). HRMS (EI) Calcd. for $C_{10}H_8NCl$ [M^+]: 177.0345, found: 177.0341.

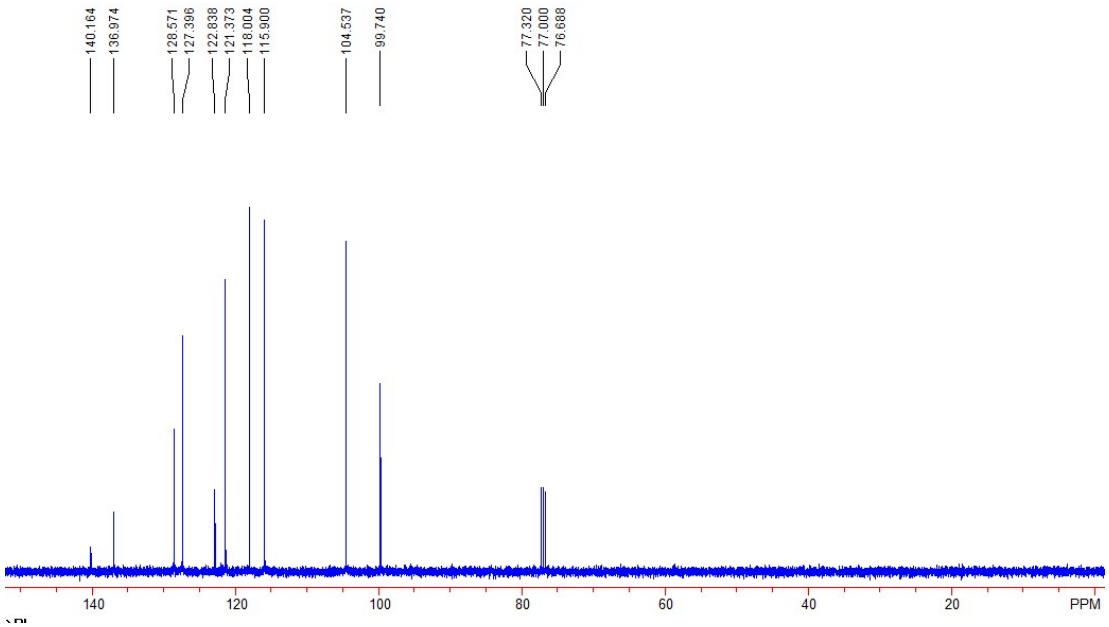


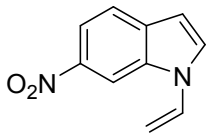




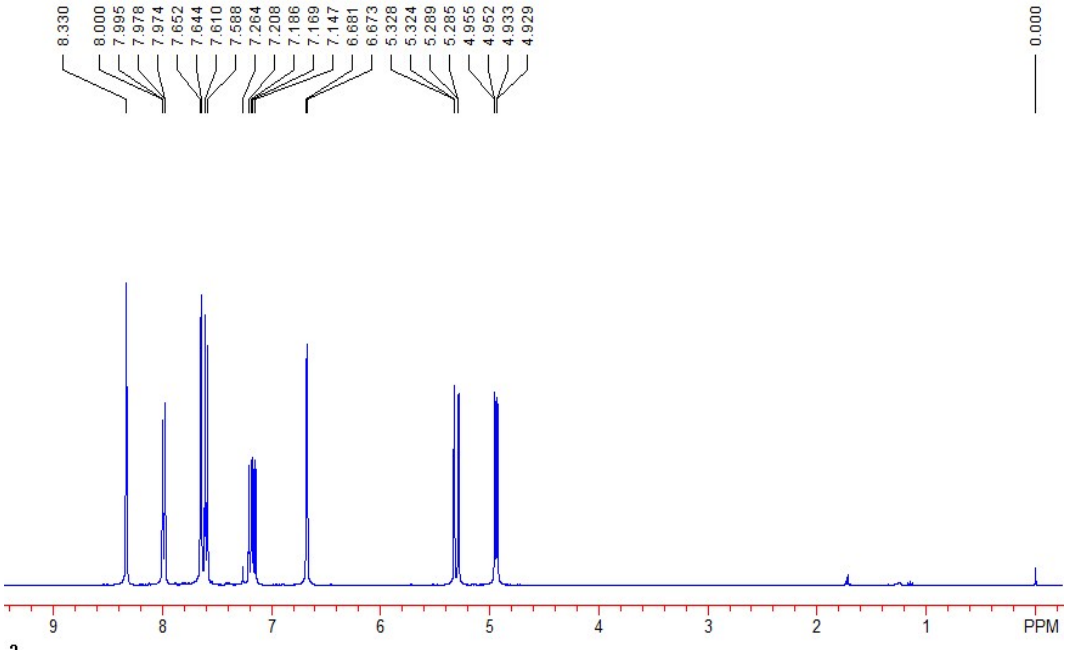
Compound 1f: Yield: 524 mg, 93%; A yellow solid; Mp: 90-92 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.93 (d, 1H, J = 8.8 Hz), 5.29 (d, 1H, J = 15.6 Hz), 7.15 (dd, 1H, J_1 = 15.6 Hz, J_2 = 8.8 Hz), 7.22-7.27 (m. 2H), 7.58 (d, 1H, J = 2.8 Hz), 7.66 (d, 1H, J = 8.4 Hz), 8.06 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 99.7, 104.5, 115.9, 118.0, 121.3, 122.8, 127.3, 128.5, 136.9, 140.1; IR (neat): ν 3128, 3095, 3009, 1639, 1612. 1516, 1499, 1448, 1405, 1361, 1314, 1278, 1190, 1117, 1068, 954, 940, 857, 791, 755, 734, 704, 684 cm^{-1}; HRMS (ESI) Calcd. for $C_{10}H_9N_2O_2$ $[M+H]^+$: 189.0659, found: 189.0657.

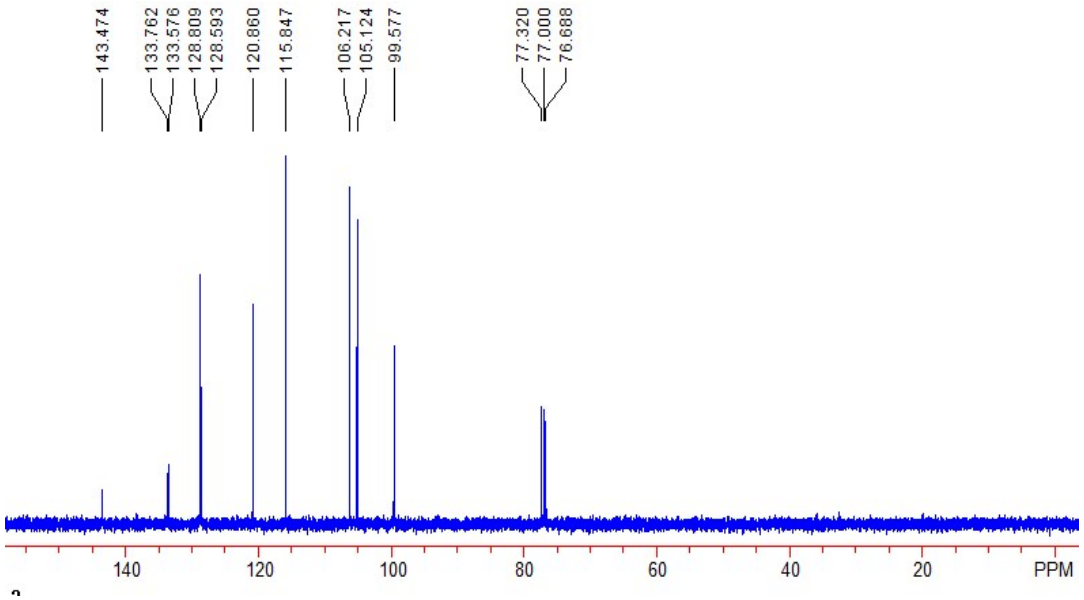


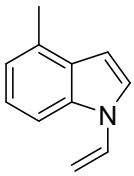




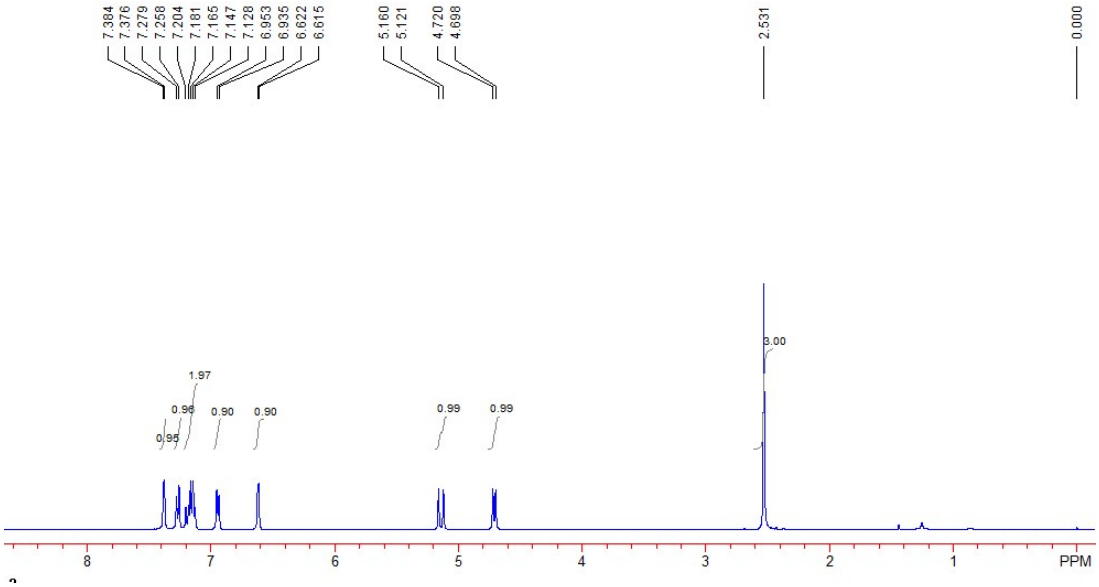
Compound 1g: Yield: 524 mg, 93%; A yellow solid; Mp: 100-102 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.94 (dd, 1H, J_1 = 9.2 Hz, J_2 = 1.6 Hz), 5.30 (dd, 1H, J_1 = 15.6 Hz, J_2 = 1.6 Hz), 6.67 (d, 1H, J = 3.2 Hz), 7.17 (dd, 1H, J_1 = 15.6 Hz, J_2 = 9.2 Hz), 7.60 (d, 1H, J = 8.8 Hz), 7.64 (d, 1H, J = 3.2 Hz), 7.98 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 8.33 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 99.5, 105.1, 106.2, 115.8, 120.8, 128.5, 128.8, 133.5, 133.7, 143.4; IR (neat): ν 3100, 2923, 1636, 1508, 1497, 1468, 1335, 1325, 1310, 1283, 1226, 1204, 1109, 1072, 965, 872. 838, 816, 793, 765, 736, 725, 716 cm^{-1}; HRMS (ESI) Calcd. for $C_{10}H_9N_2O_2$ $[M+H]^+$: 189.0659, found: 189.0656.

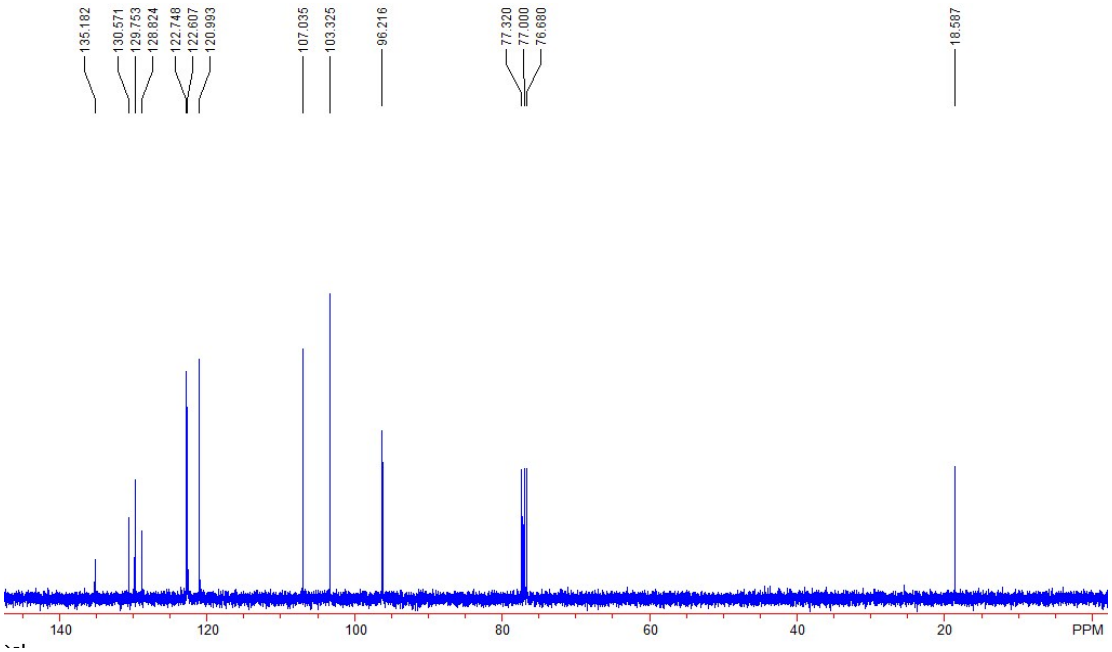


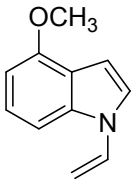




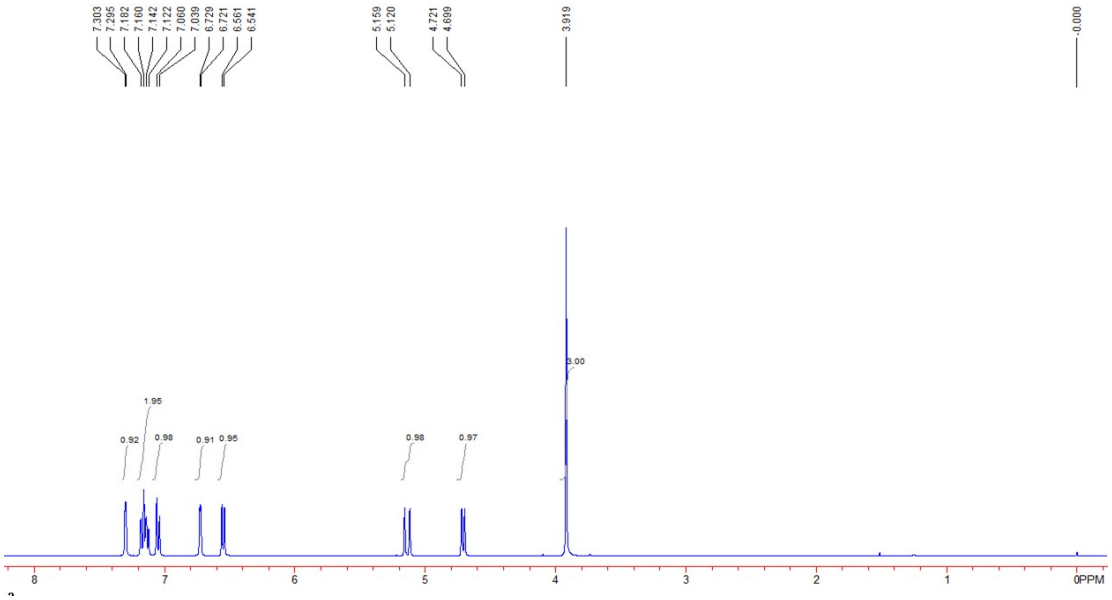
Compound 1h: Yield: 217 mg, 74%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.53 (s, 3H), 4.71 (d, 1H, *J* = 8.8 Hz), 5.14 (d, 1H, *J* = 15.6 Hz), 6.61 (d, 1H, *J* = 2.8 Hz), 6.94 (d, 1H, *J* = 7.2 Hz), 7.12-7.20 (m, 2H), 7.27 (d, 1H, *J* = 8.4 Hz), 7.37 (d, 1H, *J* = 3.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.5, 96.2, 103.3, 107.0, 120.9, 122.6, 122.7, 128.8, 129.7, 130.5, 135.1; IR (neat): ν 3109, 3050, 2917, 2853, 1637, 1587, 1517, 1487, 1455, 1434, 1315, 1286, 1243, 1160, 955, 934, 848, 743, 709, 674 cm^{-1}; HRMS (ESI) Calcd. for $C_{11}H_{12}N$ $[M+H]^+$: 158.0964, found: 158.0961.

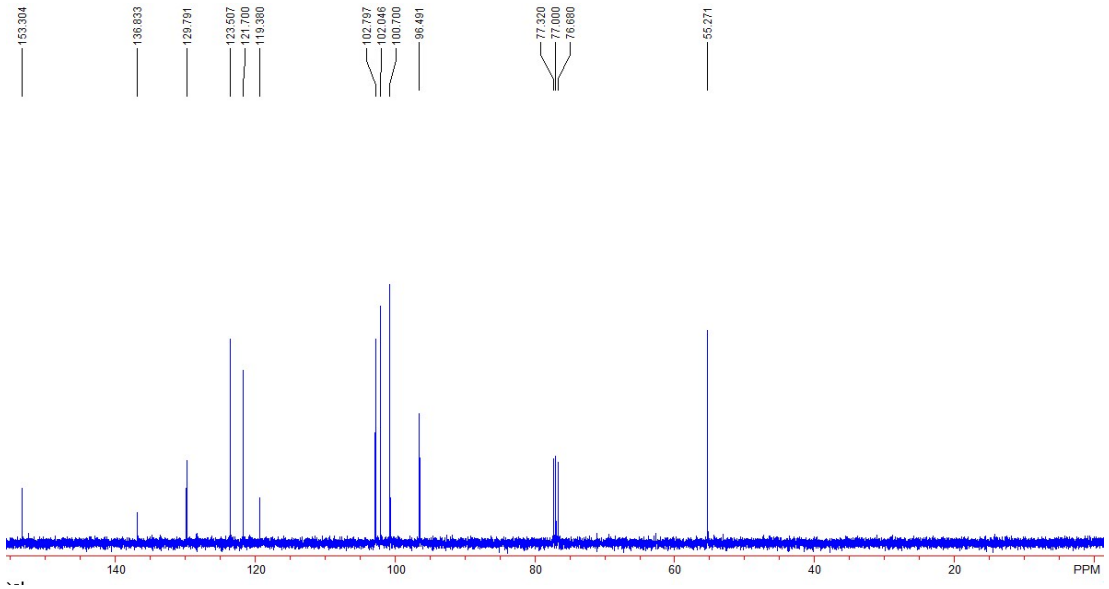


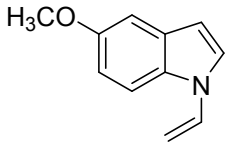




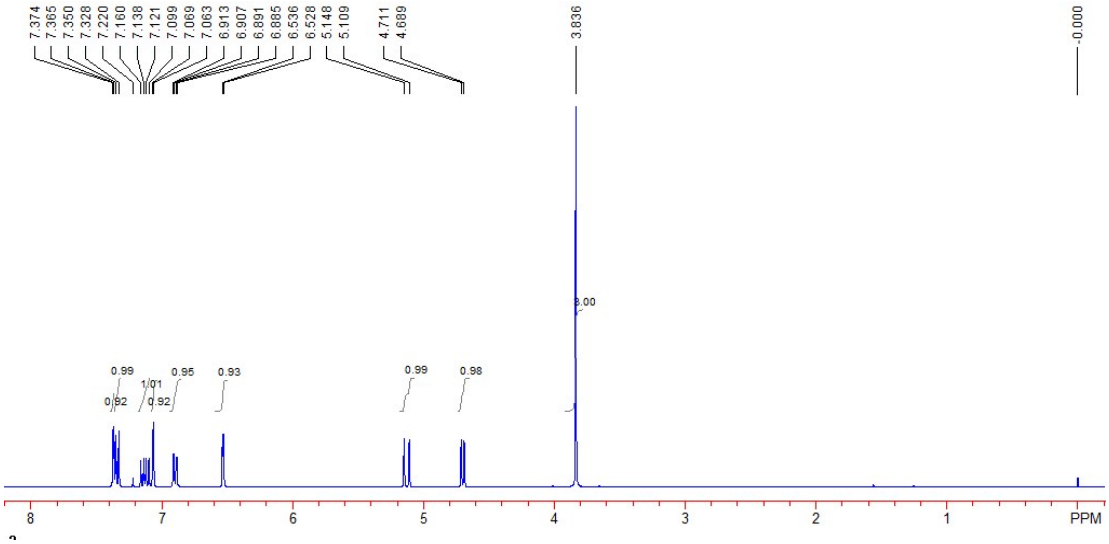
Compound 1i: Yield: 332 mg, 74%; A white solid; Mp: 84-86 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.91 (s, 3H), 4.71 (d, 1H, *J* = 8.8 Hz), 5.14 (d, 1H, *J* = 15.6 Hz), 6.55 (d, 1H, *J* = 8.0 Hz), 6.72 (d, 1H, *J* = 3.2 Hz), 7.05 (d, 1H, *J* = 8.4 Hz), 7.12-7.18 (m, 2H), 7.29 (d, 1H, *J* = 3.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.2, 96.4, 100.7, 102.0, 102.7, 119.3, 121.7, 123.5, 129.7, 136.8, 153.3; IR (neat): ν 3136, 3109, 2964, 2945, 2911, 2837, 1638, 1578, 1489, 1446, 1331, 1254, 1149, 1069, 1023, 957, 851, 842, 736, 703, 690 cm^{-1}; HRMS (ESI) Calcd. for $C_{11}H_{12}NO$ $[M+H]^+$: 174.0913, found: 174.0910.

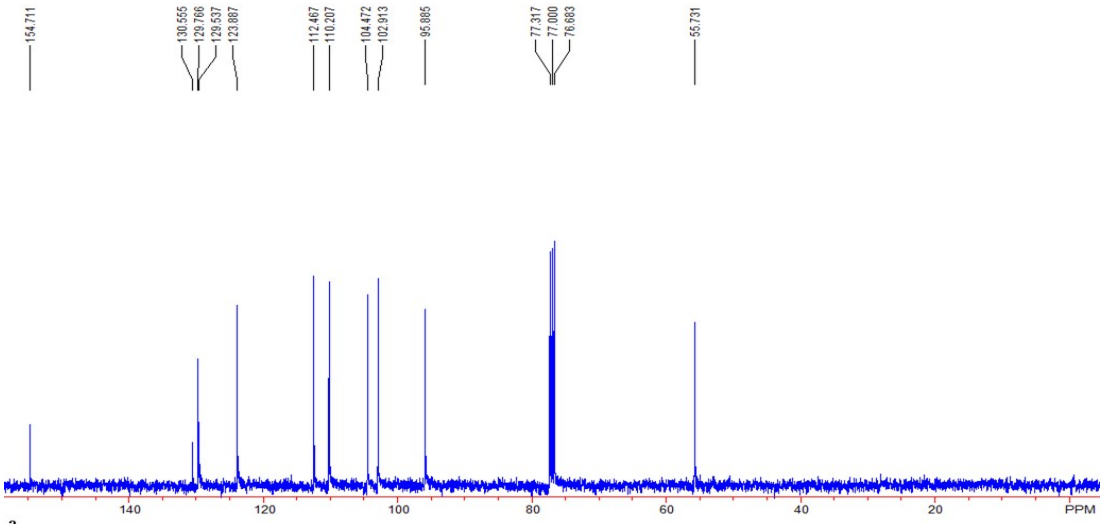


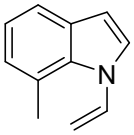




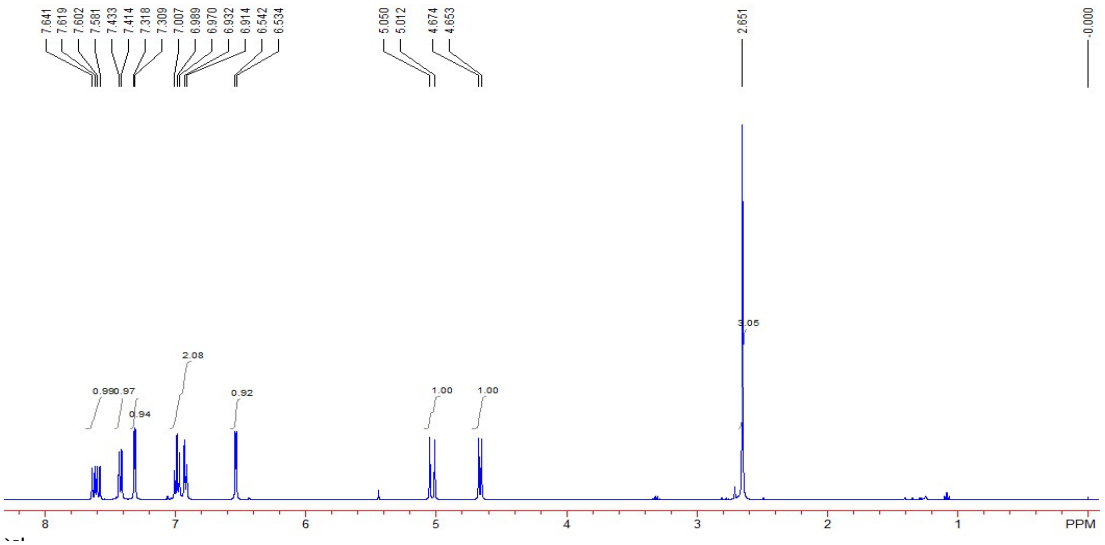
Compound 1j: Yield: 264 mg, 51%; A white solid; Mp: 97-99 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.83 (s, 3H), 4.70 (d, 1H, J = 8.8 Hz), 5.13 (d, 1H, J = 15.6 Hz), 6.53 (d, 1H, J = 8.0 Hz), 6.89 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.06 (d, 1H, J = 2.4 Hz), 7.13 (dd, 1H, J_1 = 15.6 Hz, J_2 = 8.8 Hz), 7.34 (d, 1H, J = 8.8 Hz), 7.37 (d, 1H, J = 3.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.7, 95.8, 102.9, 104.4, 110.2, 112.4, 123.8, 129.5, 129.7, 130.5, 154.7; IR (neat): ν 3136, 3114, 2989, 2959, 2828, 1636, 1612, 1475, 1447, 1435, 1390, 1318, 1287, 1246, 1223, 1150, 1135, 1021, 957, 935, 842, 799, 759, 727 cm^{-1}; HRMS (ESI) Calcd. for $C_{11}H_{12}NO$ $[M+H]^+$: 174.0913, found: 174.0921.

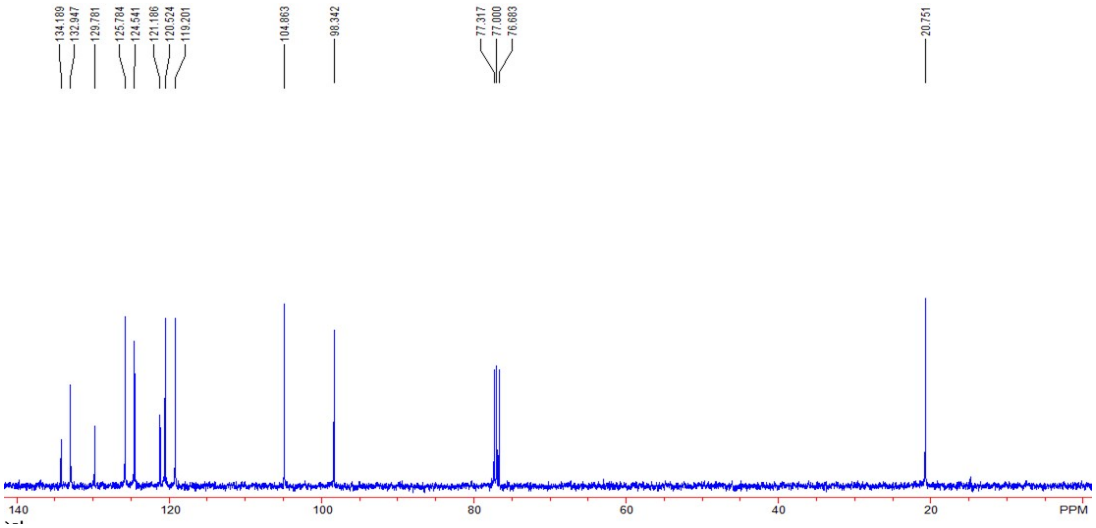


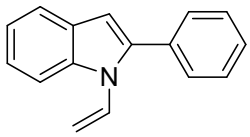




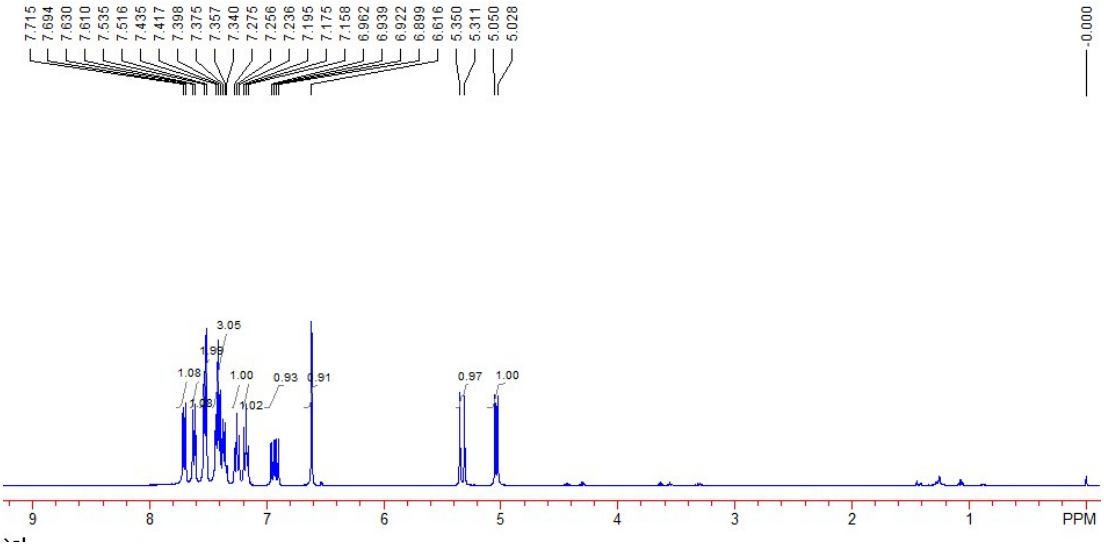
Compound 1k: Yield: 188 mg, 40%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.65 (s, 3H), 4.66 (d, 1H, J = 8.4 Hz), 5.03 (d, 1H, J = 15.2 Hz), 6.54 (d, 1H, J = 3.2 Hz), 6.92 (d, 1H, J = 7.2 Hz), 6.98 (dd, 1H, $J_1 = J_2$ = 7.2 Hz), 7.31 (d, 1H, J = 3.6 Hz), 7.42 (d, 1H, J = 7.6 Hz), 7.61 (dd, 1H, J_1 = 15.2 Hz, J_2 = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.7, 98.3, 104.8, 119.2, 120.5, 121.1, 124.5, 125.7, 129.7, 132.9, 134.1; IR (neat): ν 2972, 2928, 2864, 1632, 1463, 1424, 1379, 1324, 1304, 1279, 1242, 1216, 1081, 1045, 955, 879, 841, 782, 745, 717, 704 cm^{-1}; MS (EI) m/z (%) 157 (M^+, 32.64), 156 (35.72), 154 (16.90), 144 (100), 142 (20.24), 129 (20.56), 77 (20.33). HRMS (EI) Calcd. for $C_{11}H_{11}N$ [M^+]: 157.0891, found: 157.0887.

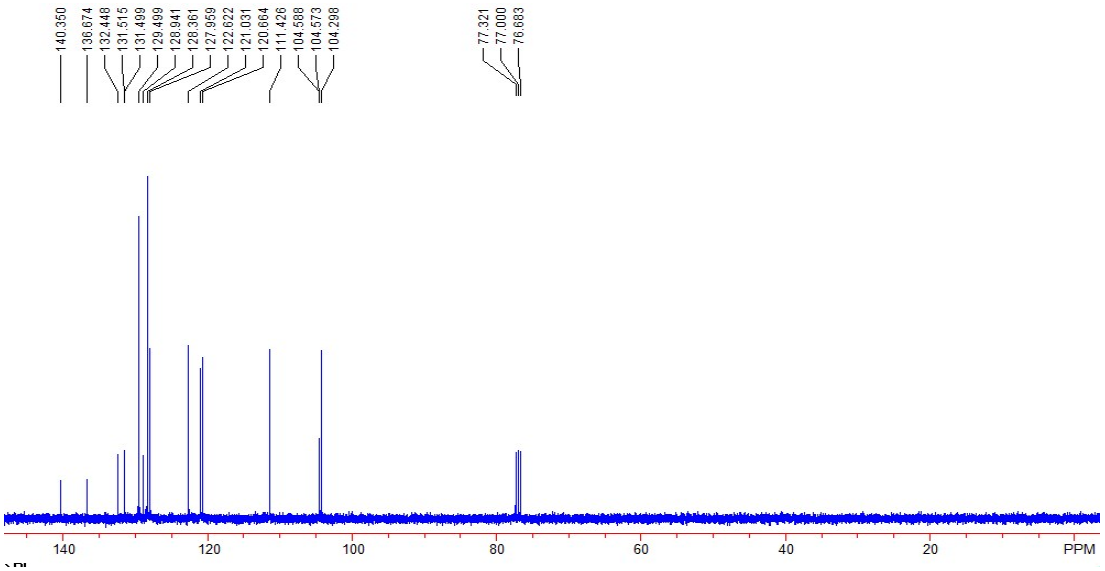


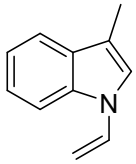




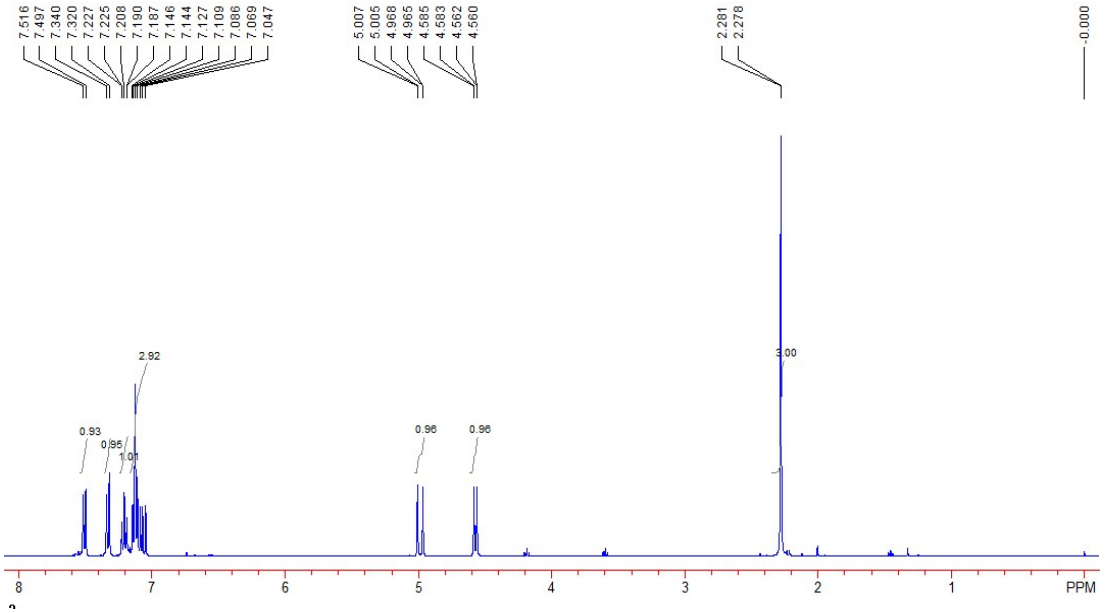
Compound 1l: Yield: 295 mg, 45%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 5.04 (d, 1H, J = 8.8 Hz), 5.34 (d, 1H, J = 15.6 Hz), 6.61 (s, 1H), 6.93 (dd, 1H, J_1 = 15.6 Hz, J_2 = 8.8 Hz), 7.15-7.19 (m, 1H), 7.23-7.27 (m, 1H), 7.34-7.43 (m, 3H), 7.52 (d, 2H, J = 7.6 Hz), 7.62 (d, 1H, J = 8.0 Hz), 7.70 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 104.3, 104.57, 104.58, 111.4, 120.6, 121.0, 122.6, 127.9, 128.3, 128.9, 129.4, 131.4, 131.5, 132.4, 136.6, 140.3; IR (neat): ν 3059, 3022, 1639, 1604, 1456, 1442, 1364, 1335, 1299, 1165, 963, 877, 795, 762, 747, 735, 696 cm^{-1}; MS (EI) m/z (%) 219 (M^+, 88.04), 218 (100), 217 (46.87), 216 (11.09), 165 (10.08), 109 (26.84), 102 (10.19), 77 (5.28). HRMS (EI) Calcd. for $C_{16}H_{13}N$ [M^+]: 219.1048, found: 219.1041.

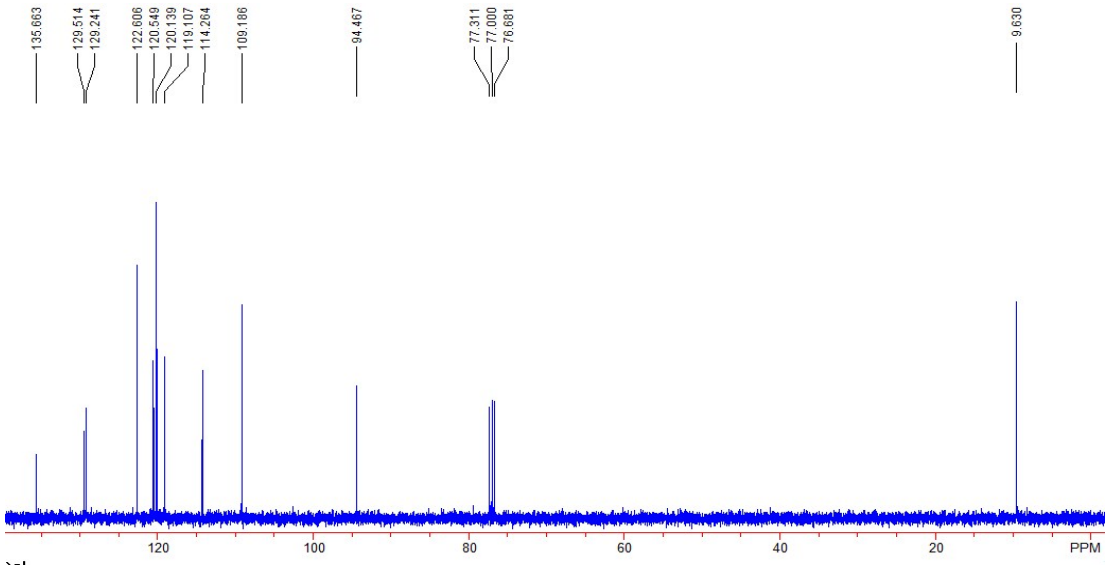


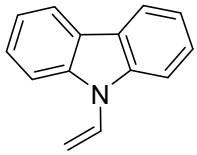




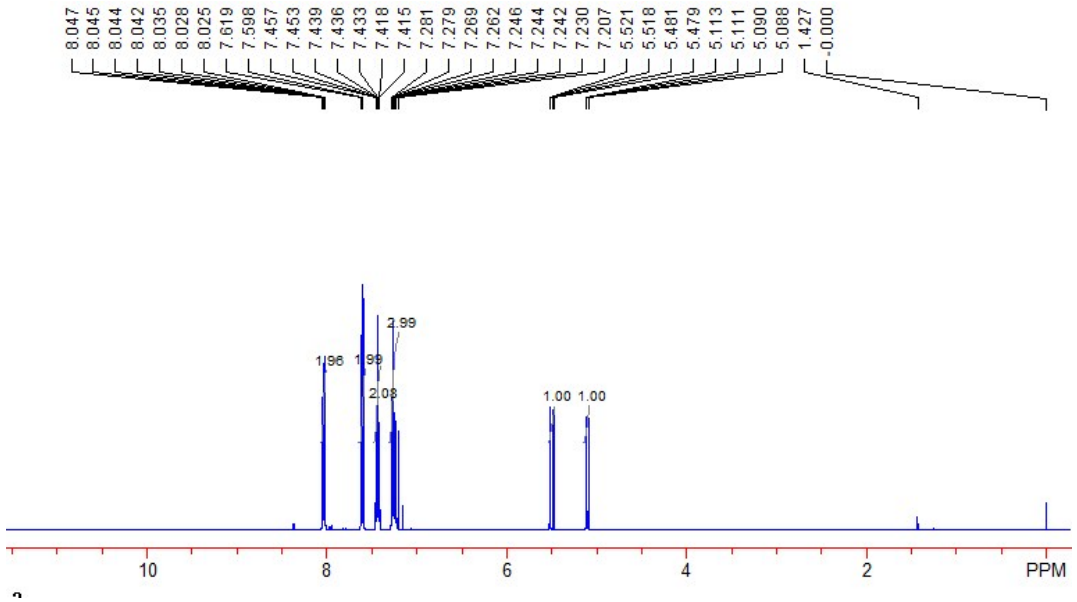
Compound 1m: Yield: 188 mg, 40%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.28 (d, 3H, J = 1.2 Hz), 4.57 (dd, 1H, J_1 = 9.2 Hz, J_2 = 0.8 Hz), 4.98 (dd, 1H, J_1 = 16.0 Hz, J_2 = 0.8 Hz), 7.04-7.14 (m, 3H), 7.18-7.22 (m, 1H), 7.33 (d, 1H, J = 8.0 Hz), 7.50 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 9.6, 94.4, 109.1, 114.2, 119.1, 120.1, 120.5, 122.6, 129.2, 129.5, 135.6; IR (neat): ν 3047, 2917,2859, 1637, 1461, 1388, 1347, 1320, 1231, 1202, 1099, 1016, 953, 840 cm^{-1}; MS (EI) m/z (%) 157 (M^+, 79.68), 156 (87.07), 144 (100), 130 (21.25), 128 (22.24), 115 (13.63), 103 (13.95), 77 (13.03). HRMS (EI) Calcd. for $C_{11}H_{11}N$ [M^+]: 157.0891, found: 157.0892.

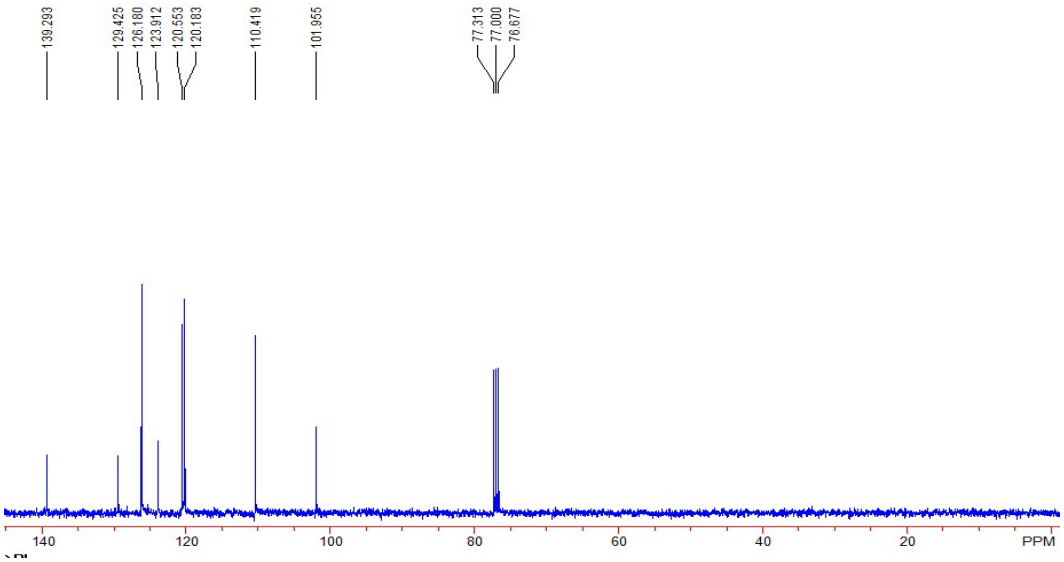


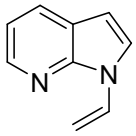




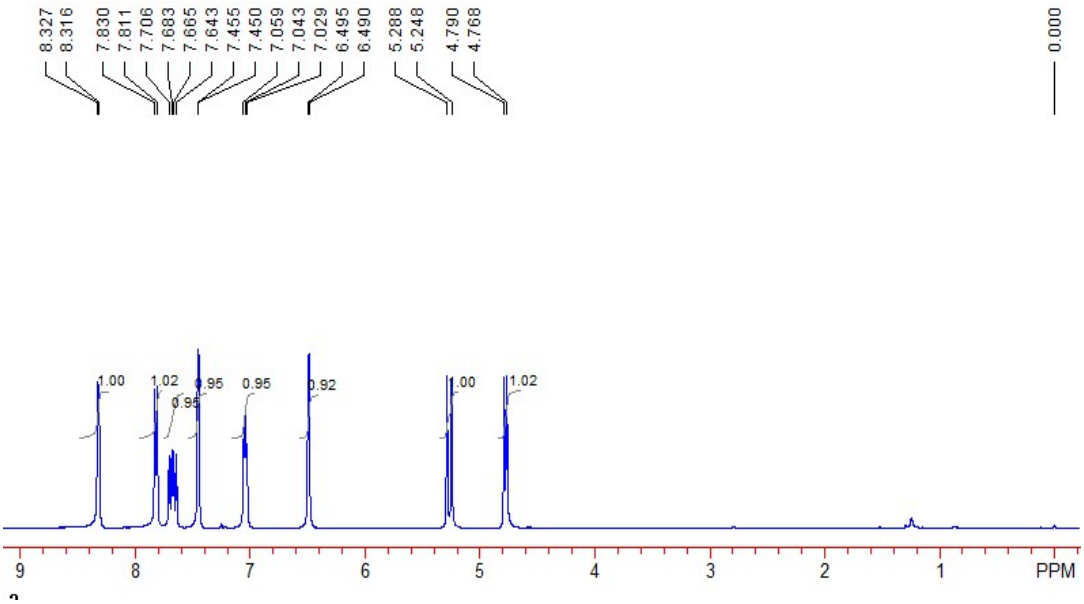
Compound 1n: Yield: 365 mg, 63%; A white solid; Mp: 65-67 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 5.10 (dd, 1H, J_1 = 9.6 Hz, J_2 = 0.8 Hz), 5.50 (dd, 1H, J_1 = 15.6 Hz, J_2 = 0.8 Hz), 7.20-7.28 (m, 3H), 7.41-7.45 (m, 2H), 7.61 (d, 2H, J = 8.4 Hz), 8.02-8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 101.9, 110.4, 120.1, 120.5, 123.9, 126.1, 129.4, 139.2; IR (neat): ν 3061, 3039, 2920, 1636, 1618, 1590, 1478, 1450, 1368, 1336, 1301, 1223, 1160, 1118, 961, 854, 747, 720 cm^{-1}; HRMS (ESI) Calcd. for $C_{14}H_{12}N$ $[M+H]^+$: 194.0964, found: 194.0962.

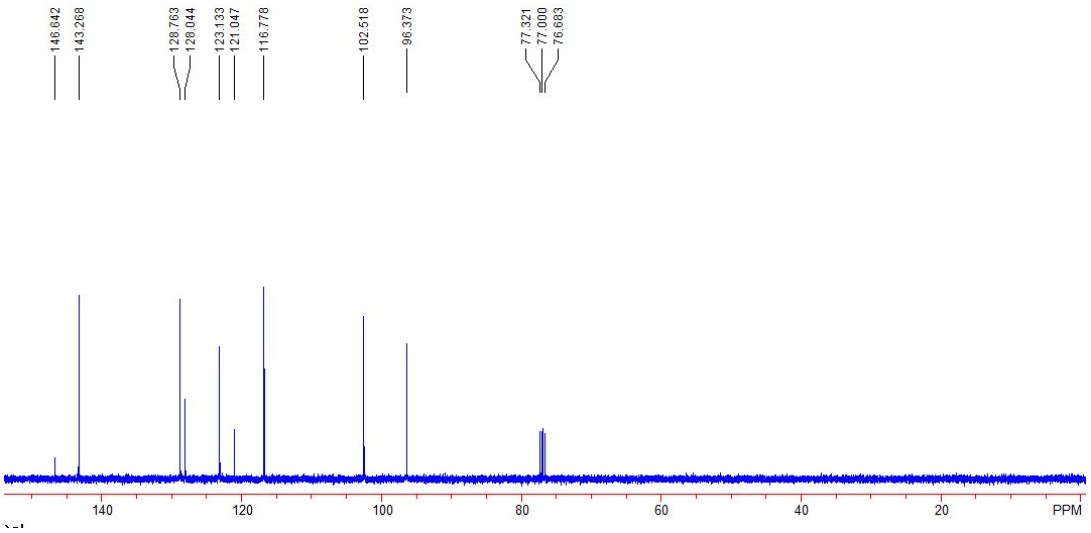


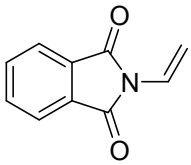




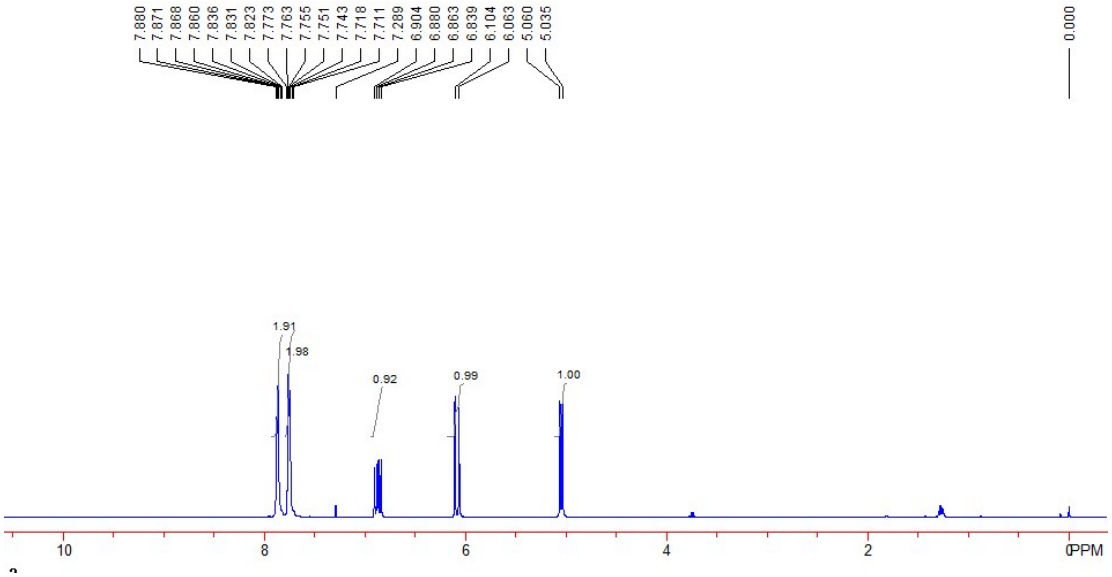
Compound 1o: Yield: 168 mg, 39%; A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 4.78 (d, 1H, J = 8.8 Hz), 5.27 (d, 1H, J = 16.0 Hz), 6.49 (d, 1H, J = 2.0 Hz), 7.04 (dd, 1H, $J_1 = J_2$ = 6.4 Hz), 7.45 (d, 1H, J = 2.0 Hz), 7.67 (dd, 1H, J_1 = 16.0 Hz, J_2 = 8.8 Hz), 7.82 (d, 1H, J = 7.6 Hz), 8.32 (d, 1H, J = 4.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 96.3, 102.5, 116.7, 121.0, 123.1, 128.0, 128.7, 143.2, 146.6; IR (neat): ν 3100, 3050, 3014, 1638, 1592, 1574, 1512, 1477, 1432, 1379, 1320, 1298, 1275, 1233, 1197, 1116, 1030, 968, 892, 853, 796, 772, 716, 706 cm^{-1}; HRMS (ESI) Calcd. for $C_9H_9N_2$ $[M+H]^+$: 145.0760, found: 145.0758.

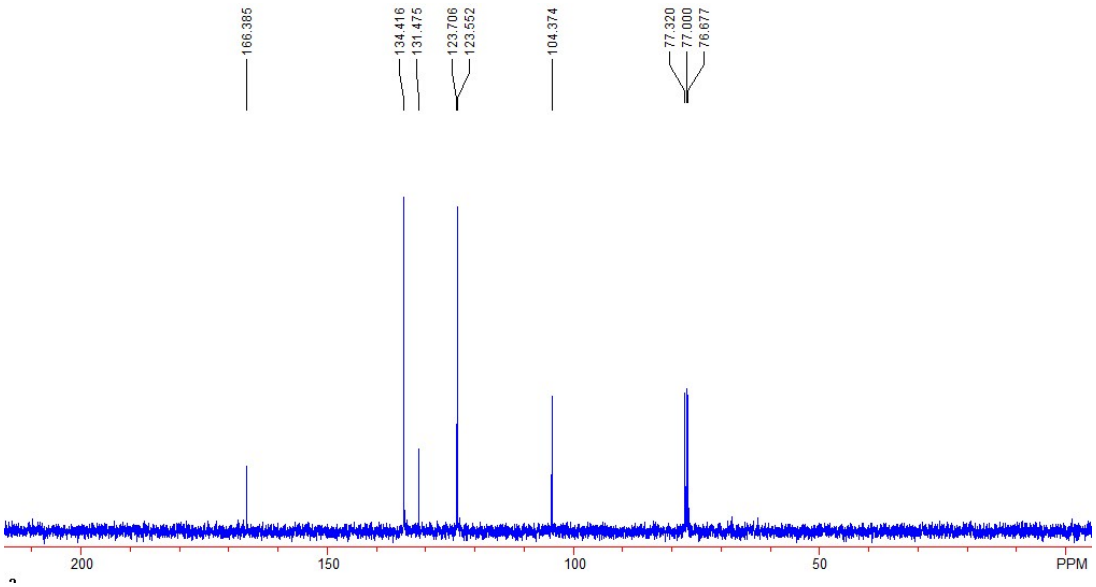




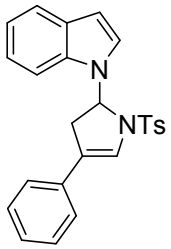


Compound 1o: Yield: 140 mg, 27%; A white solid; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 5.05 (d, 1H, J = 10.0 Hz), 6.08 (d, 1H, J = 16.4 Hz), 6.87 (dd, 1H, J_1 = 16.4 Hz, J_2 = 10.8 Hz), 7.71-7.77 (m, 2H), 7.83-7.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 104.3, 123.5, 123.7, 131.4, 134.4, 166.3;

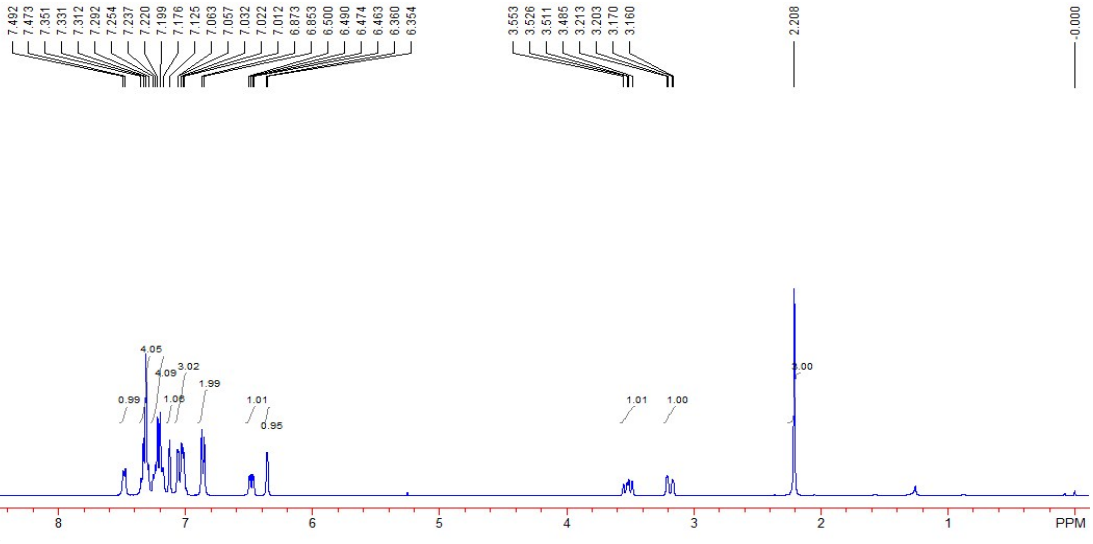


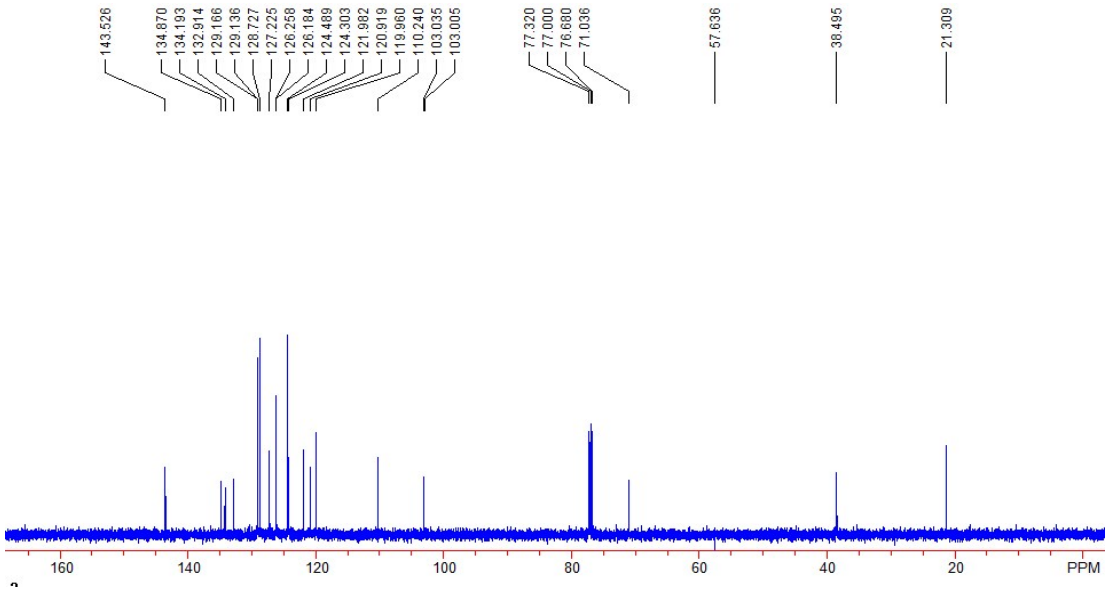

166.385
134.416
131.475
123.706
123.552
104.374
77.320
77.000
76.677
200
150
100
50
PPM

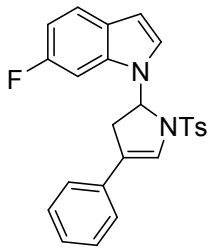
12. Spectroscopic data of the products 3



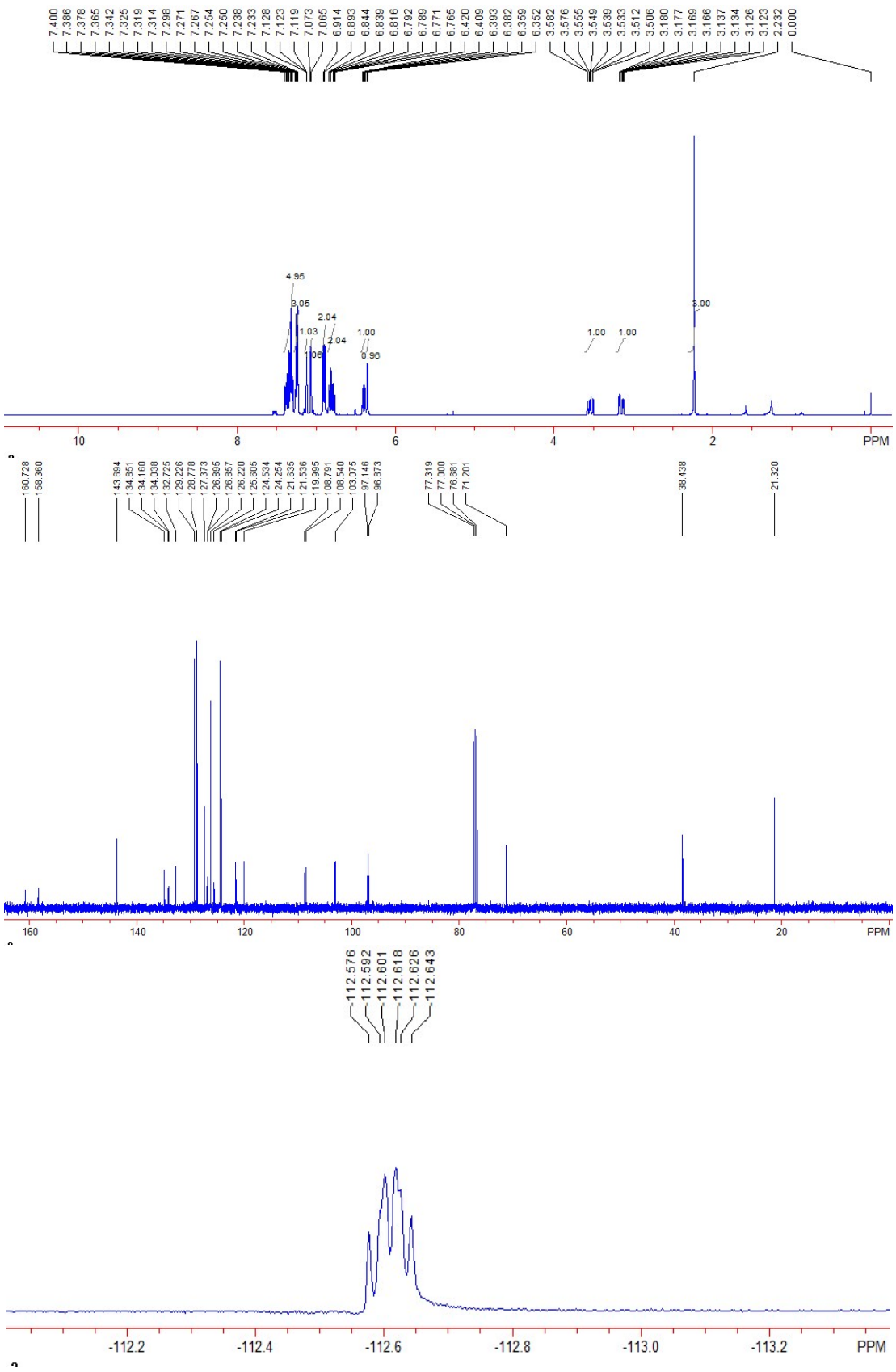
Compound 3aa: Yield: 77 mg, 93%; A white solid; Mp: 170-172 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.20 (s, 3H), 3.19 (dd, 1H, J_1 = 17.2 Hz, J_2 = 4.0 Hz), 3.52 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.4 Hz), 6.36 (d, 1H, J = 2.4 Hz), 6.48 (dd, 1H, J_1 = 10.4 Hz, J_2 = 4.0 Hz), 6.86 (d, 1H, J = 8.0 Hz), 7.01-7.06 (m, 3H), 7.12 (s, 1H), 7.17-7.25 (m, 4H), 7.29-7.35 (m, 4H), 7.48 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.5, 71.0, 103.0, 103.0, 110.2, 119.9, 120.9, 121.9, 124.3, 124.4, 126.1, 126.2, 127.2, 128.7, 129.1, 129.2, 132.9, 134.1, 134.8, 143.5; IR (neat): ν 3097, 2923, 2848, 1632, 1593, 1458, 1352, 1324, 1158, 1146, 1128, 1086, 1055, 978, 766, 753, 741, 704. 689. 672, 662 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{26}N_3O_2S$ $[M+NH_4]^+$: 432.1740, found: 432.1739.

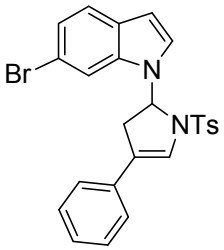




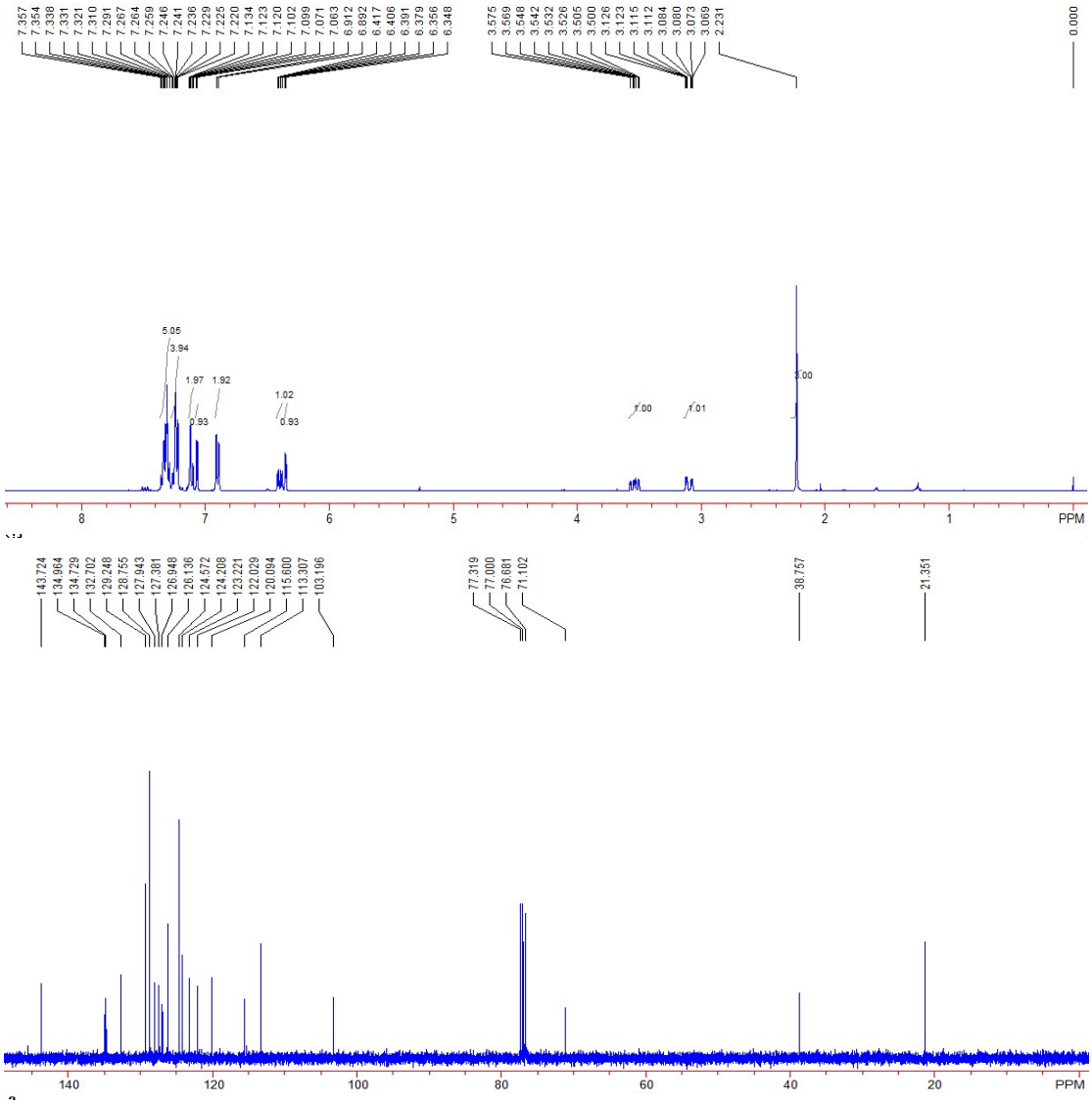


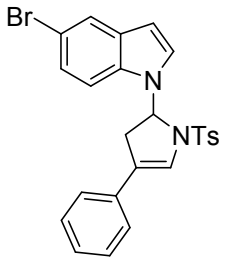
Compound 3ba: Yield: 61 mg, 71%; A white solid; Mp: 192-194 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.23 (s, 3H), 3.12-3.18 (m, 1H), 3.50-3.58 (m, 1H), 6.35 (d, 1H, J = 2.8 Hz), 6.40 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.76-6.84 (m, 2H), 6.90 (d, 2H, J = 8.4 Hz), 7.07 (d, 1H, J = 3.2 Hz), 7.12 (dd, 1H, J_1 = J_2 = 1.6 Hz), 7.23-7.27 (m, 3H), 7.29-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.3, 72.2, 97.0 (d, J = 27.3 Hz), 103.1, 108.7 (d, J = 25.1 Hz), 119.9, 121.6 (d, J = 9.9 Hz), 124.2, 124.5, 125.6, 126.2, 126.8 (d, J = 3.8 Hz), 127.4, 128.7, 129.2, 132.7, 134.1 (d, J = 12.2 Hz), 134.8, 143.7, 159.5 (d, J = 226.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -112.64 ~ -112.57 (m); IR (neat): ν 3386, 3100, 2953, 2917, 2845, 1615, 1579, 1489, 1460, 1405, 1351, 1334, 1203, 1158, 1118, 1086, 1065, 979, 941, 833, 817, 753, 715, 689, 661 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{25}FN_3O_2S$ $[M+NH_4]^+$: 450.1646, found: 450.1642.


7.400
7.386
7.378
7.365
7.342
7.325
7.319
7.314
7.298
7.271
7.267
7.254
7.250
7.238
7.233
7.128
7.123
7.119
7.073
7.065
6.914
6.893
6.844
6.839
6.816
6.792
6.789
6.771
6.765
6.420
6.409
6.393
6.382
6.359
6.352
3.582
3.576
3.555
3.549
3.539
3.533
3.512
3.506
3.180
3.177
3.169
3.166
3.137
3.134
3.126
3.123
2.232
0.000
4.95
3.05
2.04
1.03
2.04
1.06
1.00
0.96
1.00
1.00
3.00
10
8
6
4
2
PPM
160.728
158.360
143.694
134.851
134.160
134.038
132.725
129.226
128.778
127.373
126.895
126.857
126.220
125.605
124.534
124.254
121.635
121.536
119.995
108.791
108.540
103.075
97.146
96.873
77.319
77.000
76.681
71.201
38.438
21.320
160
140
120
100
80
60
40
20
PPM
112.576
112.592
112.601
112.618
112.626
112.643
-112.2
-112.4
-112.6
-112.8
-113.0
-113.2
PPM

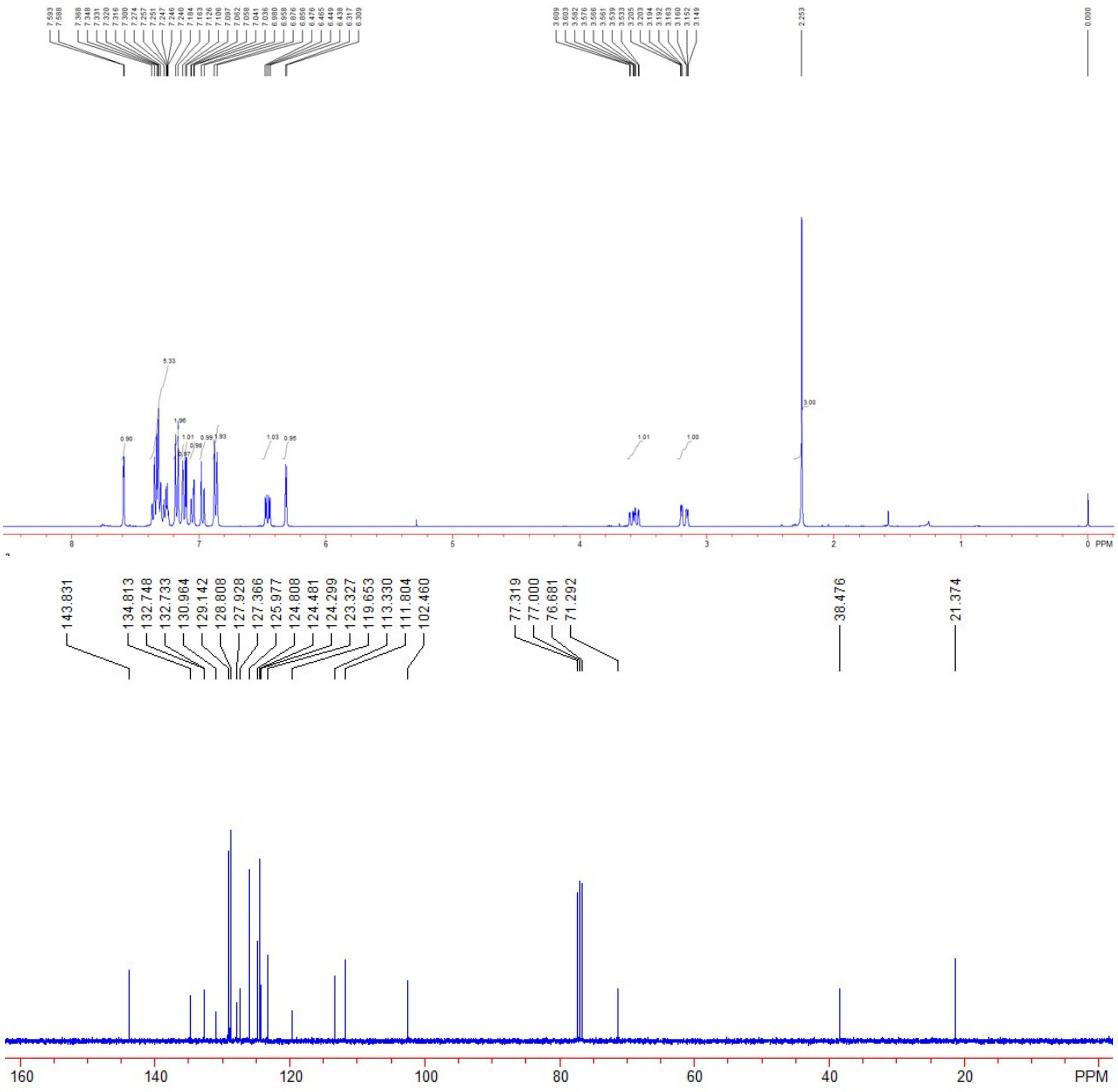


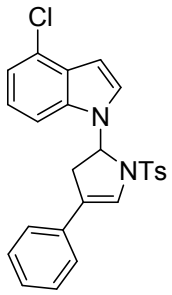
Compound 3ca: Yield: 84 mg, 86%; A white solid; Mp: 192-194 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.23 (s, 3H), 3.06-3.12 (m, 1H), 3.50-3.57 (m, 1H), 6.35 (d, 1H, J = 3.2 Hz), 6.40 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.8 Hz), 6.90 (d, 2H, J = 8.0 Hz), 7.06 (d, 1H, J = 3.2 Hz), 7.09-7.12 (m, 2H), 7.22-7.26 (m, 4H), 7.29-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.7, 71.1, 103.2, 113.3, 115.6, 120.0, 122.0, 123.2, 124.2, 124.5, 126.1, 126.9, 127.3, 127.9, 128.7, 129.2, 132.7, 134.7, 134.9, 143.7; IR (neat): ν 3103, 3031, 2920, 2850, 1632, 1590, 1459, 1402, 1351, 1323, 1159, 1130, 1086, 1053, 978, 891, 807, 753, 720, 705, 689, 674, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{25}BrN_3O_2S$ $[M+NH_4]^+$: 510.0845, found: 510.0838.



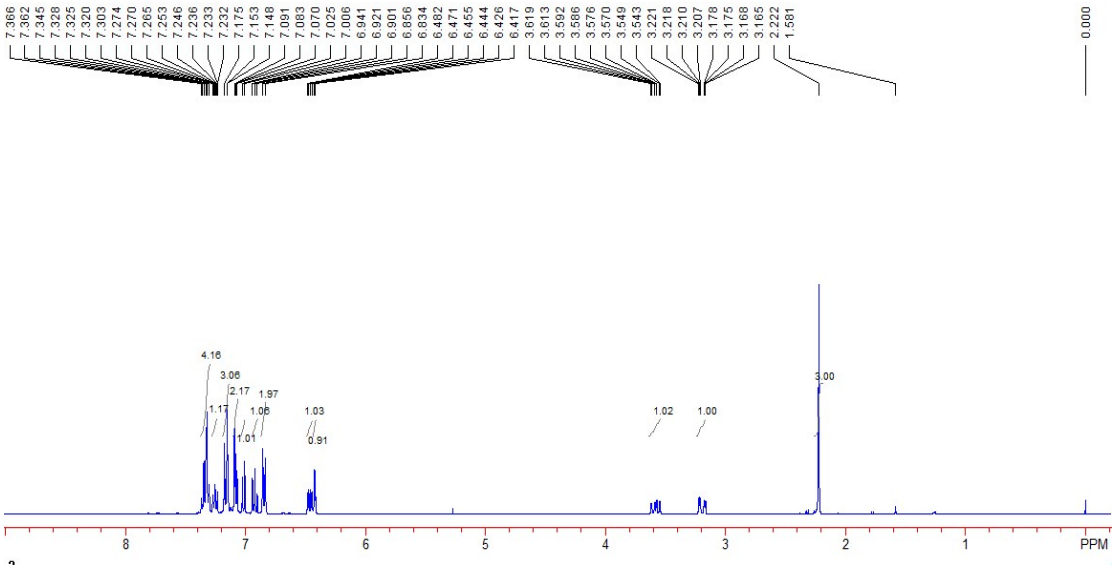


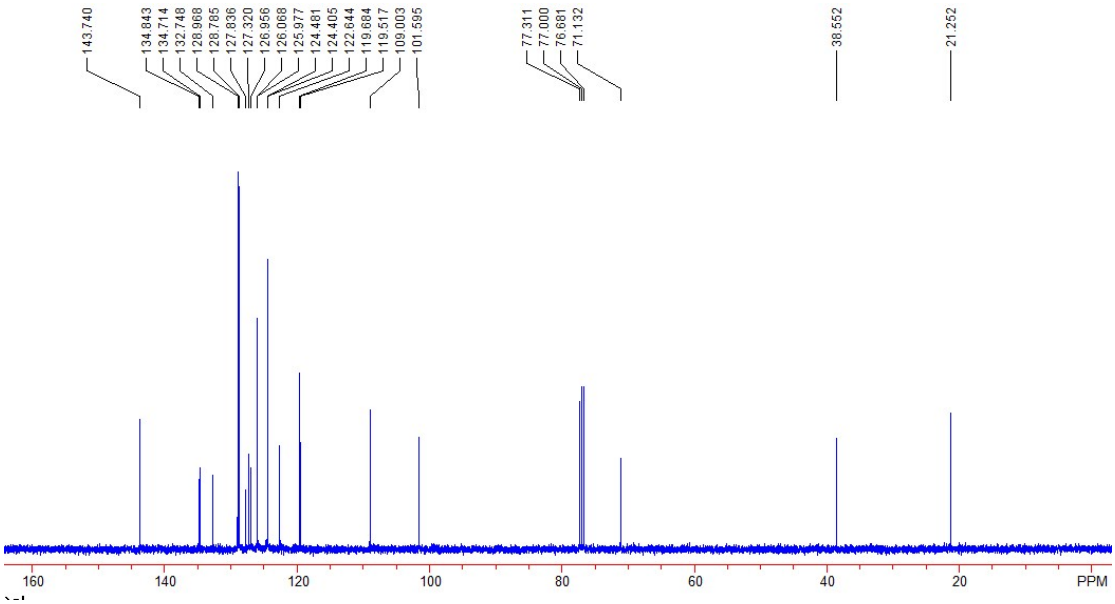
Compound 3da: Yield: 86 mg, 88%; A white solid; Mp: 166-168 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.25 (s, 3H), 3.12-3.20 (m, 1H), 3.53-3.61 (m, 1H), 6.31 (d, 1H, J = 3.2 Hz), 6.45 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.86 (d, 2H, J = 8.0 Hz), 6.97 (d, 1H, J = 8.8 Hz), 7.03-7.06 (m, 1H), 7.09 (d, 1H, J = 3.6 Hz), 7.12 (s, 1H), 7.17 (d, 2H, J = 8.4 Hz), 7.24-7.37 (m, 5H), 7.58 (d, 1H, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.4, 71.2, 102.4, 111.8, 113.3, 119.6, 123.3, 124.3, 124.4, 124.8, 125.9, 127.3, 127.9, 128.8, 129.1, 130.9, 132.73, 132.75, 134.8, 143.8; IR (neat): ν 3100, 3020, 2920, 1626, 1593, 1455, 1354, 1324, 1161, 1089, 1054, 998, 779, 754, 720, 703, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{21}N_2BrNaO_2S$ $[M+Na]^+$: 515.0399, found: 515.0404.

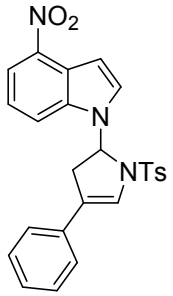




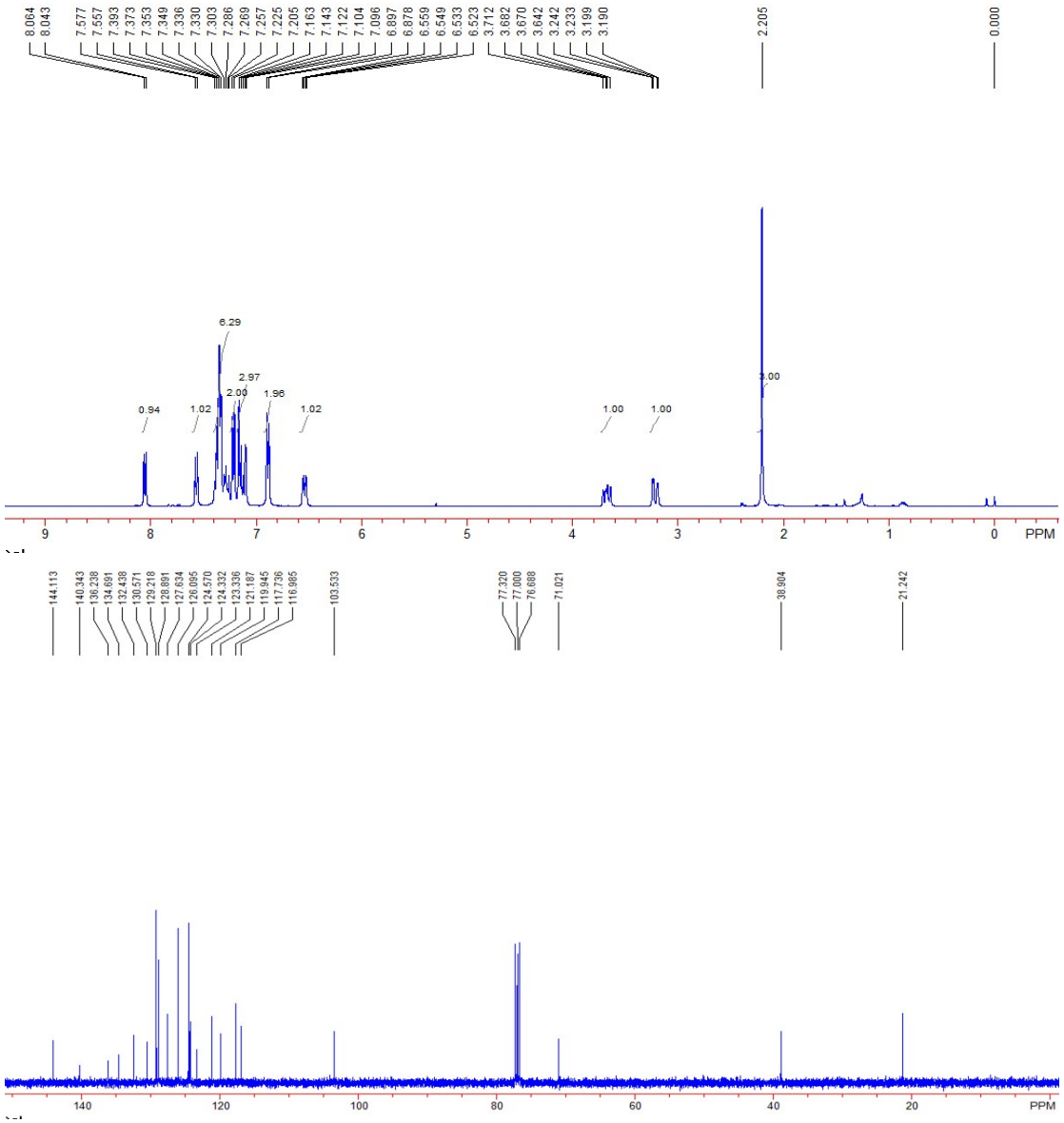
Compound 3ea: Yield: 80 mg, 89%; A white solid; Mp: 166-168 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 3.16-3.22 (m, 1H), 3.54-3.63 (m, 1H), 6.42 (d, 1H, J = 4.4 Hz), 6.46 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.86 (d, 2H, J = 8.8 Hz), 6.90-6.94 (m, 1H), 7.01 (d, 1H, J = 8.8 Hz), 7.07-7.09 (m, 2H), 7.15-7.17 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 38.5, 71.1, 101.5, 109.0, 119.5, 119.6, 122.6, 124.4, 124.5, 125.9, 126.0, 126.9, 127.3, 127.8, 128.7, 128.9, 132.7, 134.7, 134.8, 143.7; IR (neat): ν 3100, 2917, 2845, 1624, 1432, 1353, 1328, 1266, 1165, 1142, 1089, 986, 896, 782, 762, 701, 692, 675, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{25}ClN_3O_2S$ $[M+NH_4]^+$: 466.1351, found: 466.1347.

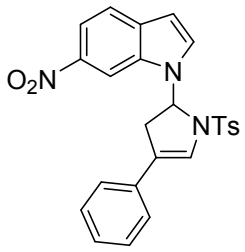






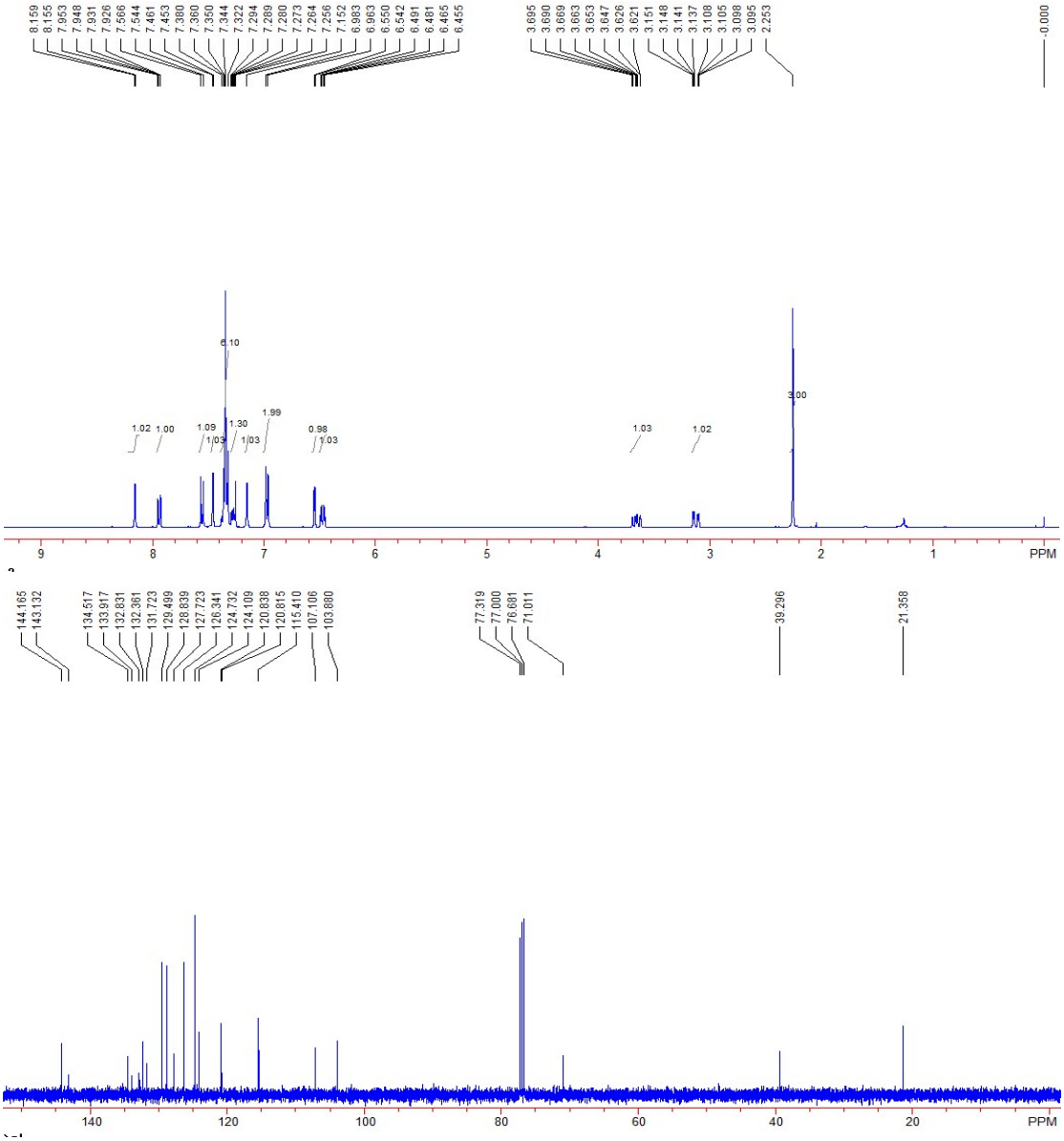
Compound 3fa: Yield: 88 mg, 96%; A yellow solid; Mp: 200-202 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.20 (s, 3H), 3.21 (dd, 1H, J_1 = 17.2 Hz, J_2 = 4.0 Hz), 3.67 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.4 Hz), 6.54 (dd, 1H, J_1 = 10.4 Hz, J_2 = 4.0 Hz), 6.88 (d, 2H, J = 7.6 Hz), 7.09-7.16 (m, 3H), 7.21 (d, 2H, J = 8.0 Hz), 7.25-7.39 (m, 6H), 7.56 (d, 1H, J = 8.0 Hz), 8.05 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 38.9, 71.0, 103.5, 116.9, 117.7, 119.9, 121.1, 123.3, 124.3, 124.5, 126.0, 127.6, 128.9, 129.2, 130.5, 132.4, 134.7, 136.2, 140.3, 144.1; IR (neat): ν 3097, 2928, 2845, 1629, 1515, 1503, 1350, 1320, 1166, 1121, 1090, 1069, 788, 761, 733, 1090, 689, 673, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{21}N_3O_4NaS$ $[M+Na]^+$: 482.1145, found: 482.1143.

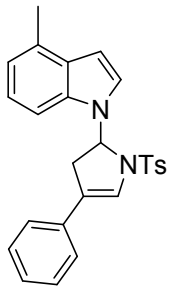




Compound 3ga: Yield: 89 mg, 97%; A yellow solid; Mp: 229-231 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.25 (s, 3H), 3.09-3.15 (m, 1H), 3.62-3.69 (m, 1H), 6.47 (dd, 1H, J_1 = 10.4 Hz, J_2 = 4.0 Hz), 6.54 (d, 1H, J = 3.2 Hz), 6.97 (d, 2H, J = 8.0 Hz), 7.15 (s, 1H), 7.25-7.29 (m, 1H), 7.32-7.38 (m, 6H), 7.45 (d, 1H, J = 3.2 Hz), 7.55 (d, 1H, J = 8.8 Hz), 7.94 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.0 Hz), 8.15 (d, 1H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 39.2, 71.0, 103.8, 107.1, 115.4, 120.81, 121.84, 124.1, 124.7, 126.3, 127.7, 128.8, 129.4, 131.7, 132.3, 132.8, 133.9, 134.5, 143.1 144.1; IR (neat): ν 3100, 3028, 2914, 2842, 1593, 1518, 1503. 1457, 1333, 1158, 1125, 1074, 1063,

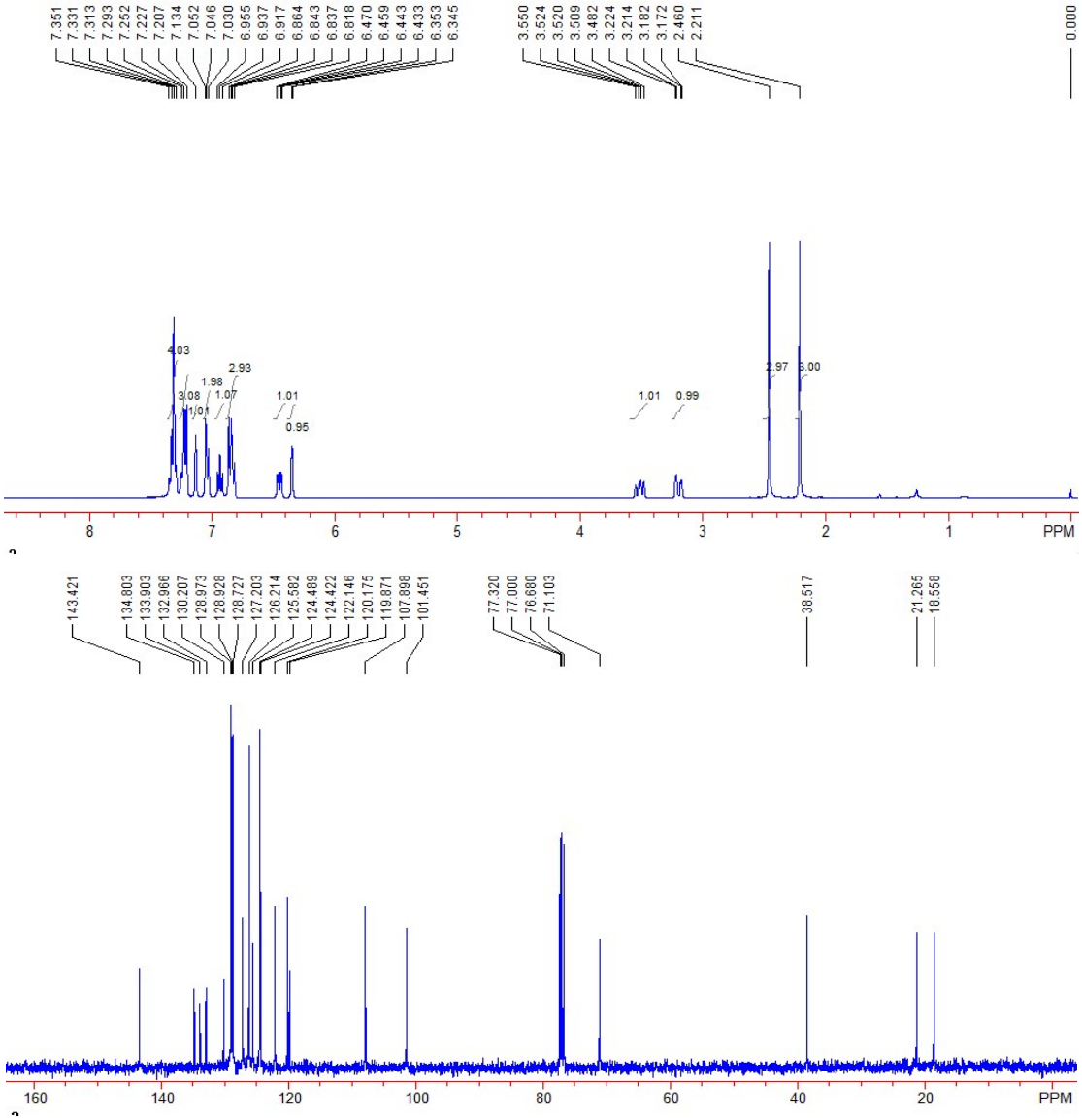
1049, 978. 836, 824, 763 705, 691, 661 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{21}N_3NaO_4S$ $[M+Na]^+$: 482.1145, found: 482.1155.

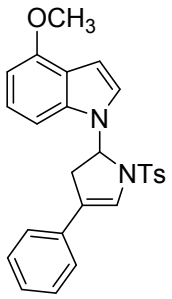




Compound 3ha: Yield: 82 mg, 96%; A white solid; Mp: 159-161 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.21 (s, 3H), 2.46 (s, 3H), 3.19 (dd, 1H, J_1 = 17.6 Hz, J_2 = 4.0 Hz), 3.48-3.55 (m, 1H), 6.34 (d, 1H, J = 3.2 Hz), 6.45 (dd, 1H, J_1 = 10.4 Hz, J_2 = 4.0 Hz), 6.81-6.86 (m, 3H), 6.93 (dd, 1H, J_1 = J_2 = 8.0 Hz), 7.03-7.05 (m, 2H), 7.13 (s, 1H), 7.20-7.25 (m, 3H), 7.29-7.35 (m, 4H); ^{13}C NMR

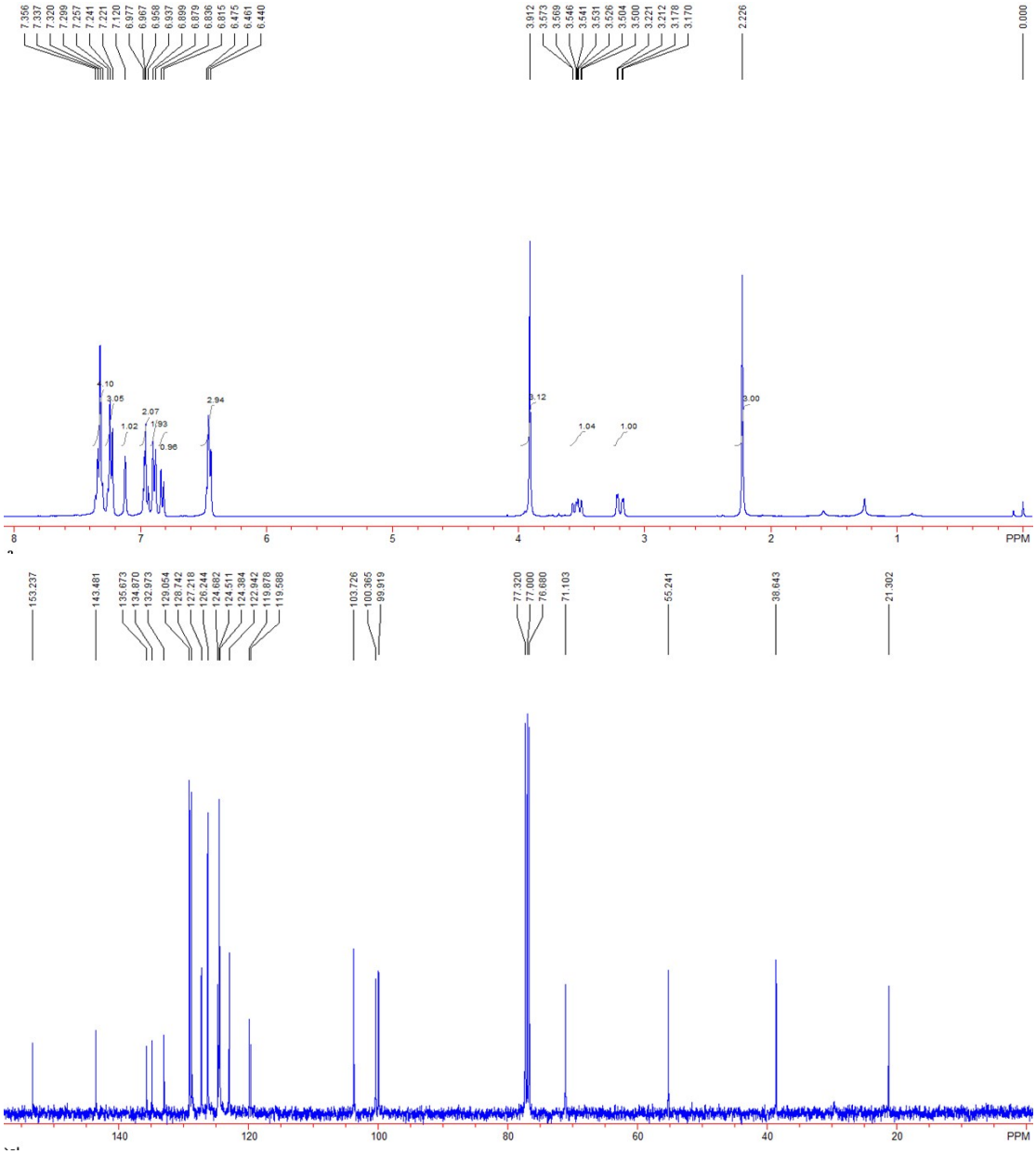
($CDCl_3$, 100 MHz, TMS) δ 18.5, 21.2, 38.5, 71.1, 101.4, 107.9, 119.8, 120.1, 122.1, 124.42, 124.48, 125.5, 126.2, 127.2, 128.7, 128.92, 128.97, 130.2, 132.9, 133.9, 134.8, 143.4; IR (neat): ν 3095, 3050, 2920, 2850, 1627, 1596, 1457, 1353, 1160, 1089, 1017, 982, 814, 752, 712, 704, 689, 667 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{25}N_2O_2S$ $[M+H]^+$: 429.1631, found: 429.1628.

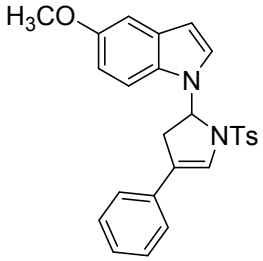




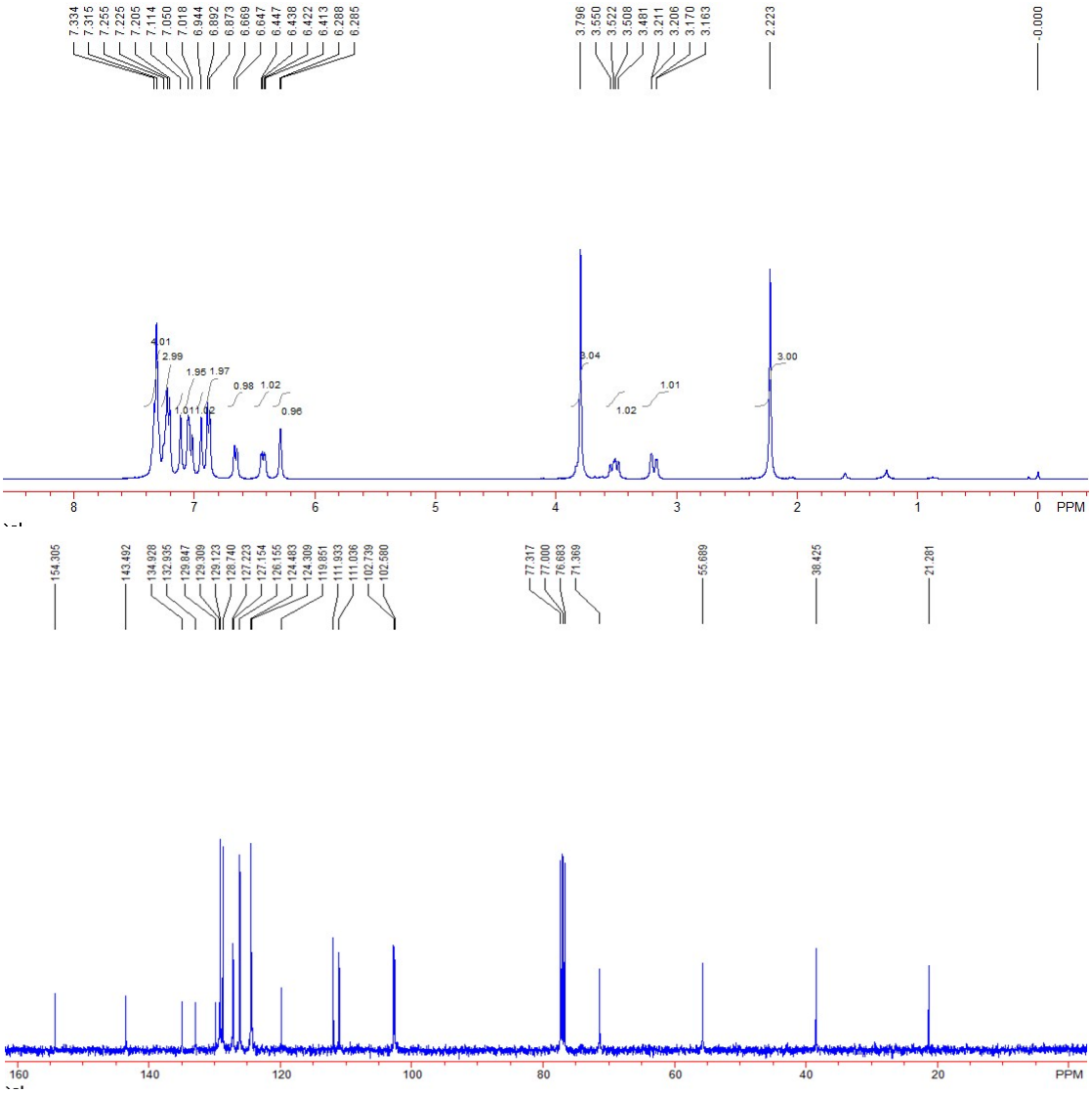
Compound 3ia: Yield: 50 mg, 56%; A white solid; Mp: 161-163 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 3.19 (dd, 1H, J_1 = 16.8 Hz, J_2 = 3.2 Hz), 3.50-3.57 (m, 1H), 3.91 (s, 3H), 6.44-6.47 (m, 3H), 6.82 (d, 1H, J = 8.4 Hz), 6.88

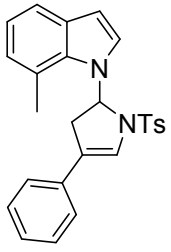
(d, 2H, J = 8.0 Hz), 6.93-6.97 (m, 2H), 7.12 (s, 1H), 7.22-7.26 (m, 3H), 7.29-7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.6, 55.2, 71.1, 99.9, 100.3, 103.7, 119.5, 119.8, 122.9, 124.3 124.5, 124.6, 126.2, 127.2, 128.7, 129.0, 132.9, 134.8, 135.6, 143.4, 153.2; IR (neat): ν 3100, 2920, 2837, 1629, 1495, 1353, 1443, 1353, 1325, 1263, 1245, 1159, 1090, 1067, 996, 983, 733, 720, 702, 685, 670, 662 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{24}N_2NaO_3S$ $[M+Na]^+$: 467.1400, found: 467.1397.



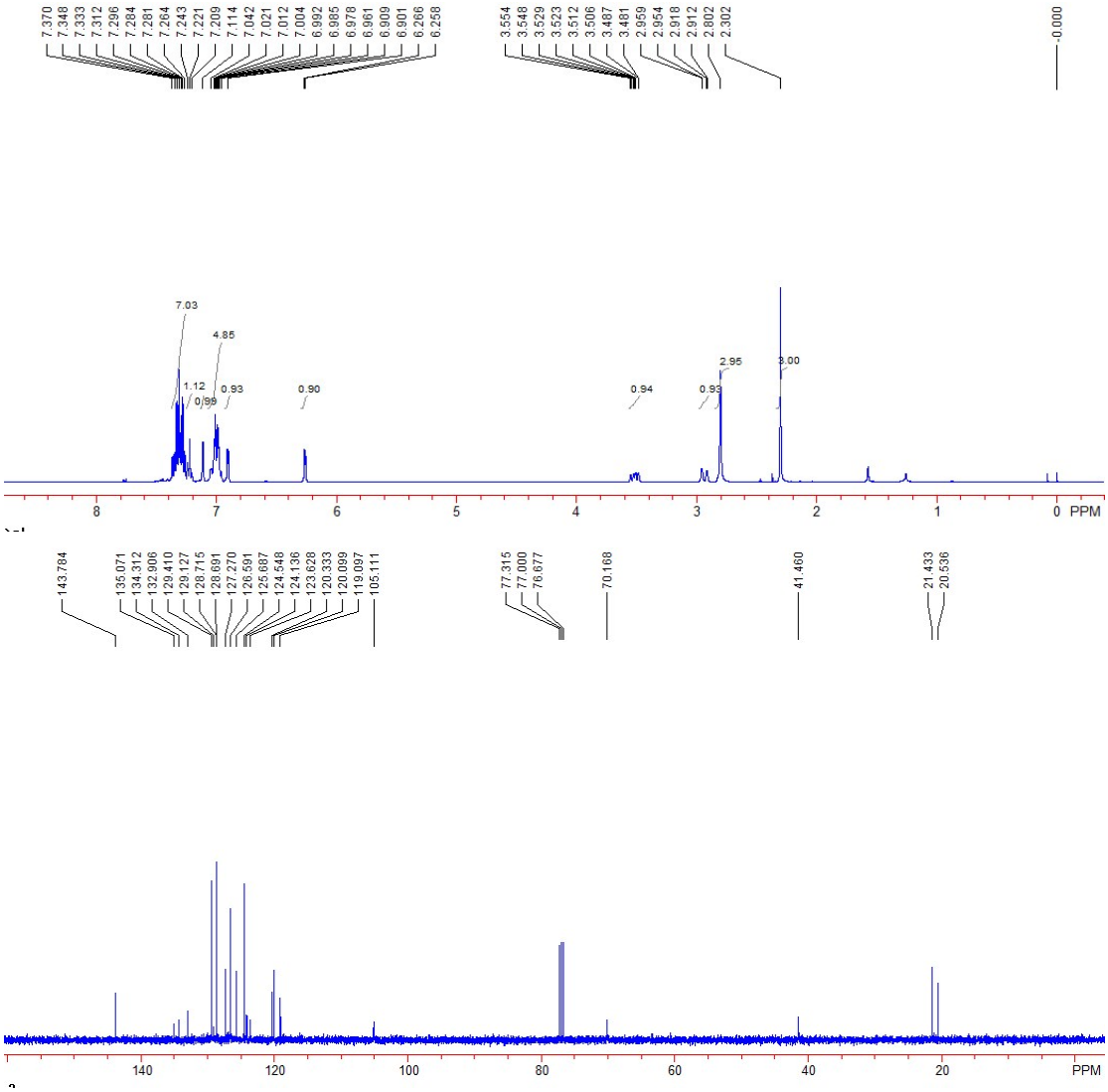


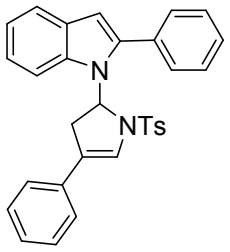
Compound 3ja: Yield: 58 mg, 65%; A white solid; Mp: 128-130 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 3.18 (dd, 1H, J_1 = 16.8 Hz, J_2 = 2.8 Hz), 3.51 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.0 Hz), 3.79 (s, 3H), 6.28 (d, 1H, J = 1.2 Hz), 6.43 (dd, 1H, J_1 = 10.0 Hz, J_2 = 2.8 Hz), 6.66 (d, 1H, J = 8.8 Hz), 6.88 (d, 2H, J = 7.6 Hz), 6.94 (s, 1H), 7.01-7.05 (m, 2H), 7.11 (s, 1H), 7.20-7.25 (m, 3H), 7.31-7.33 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.4, 55.6, 71.3, 102.5, 102.7, 111.0, 111.9, 119.8, 124.3 124.4, 126.1, 127.1, 127.2, 128.7, 129.1, 129.3, 129.8, 132.9, 134.9, 143.4, 154.3; IR (neat): ν 3097, 2925, 2828, 1621, 1479, 1447, 1351, 1241, 1162, 1089. 800, 754, 718, 703, 692, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{24}N_2NaO_3S$ $[M+Na]^+$: 467.1400, found: 467.1399.



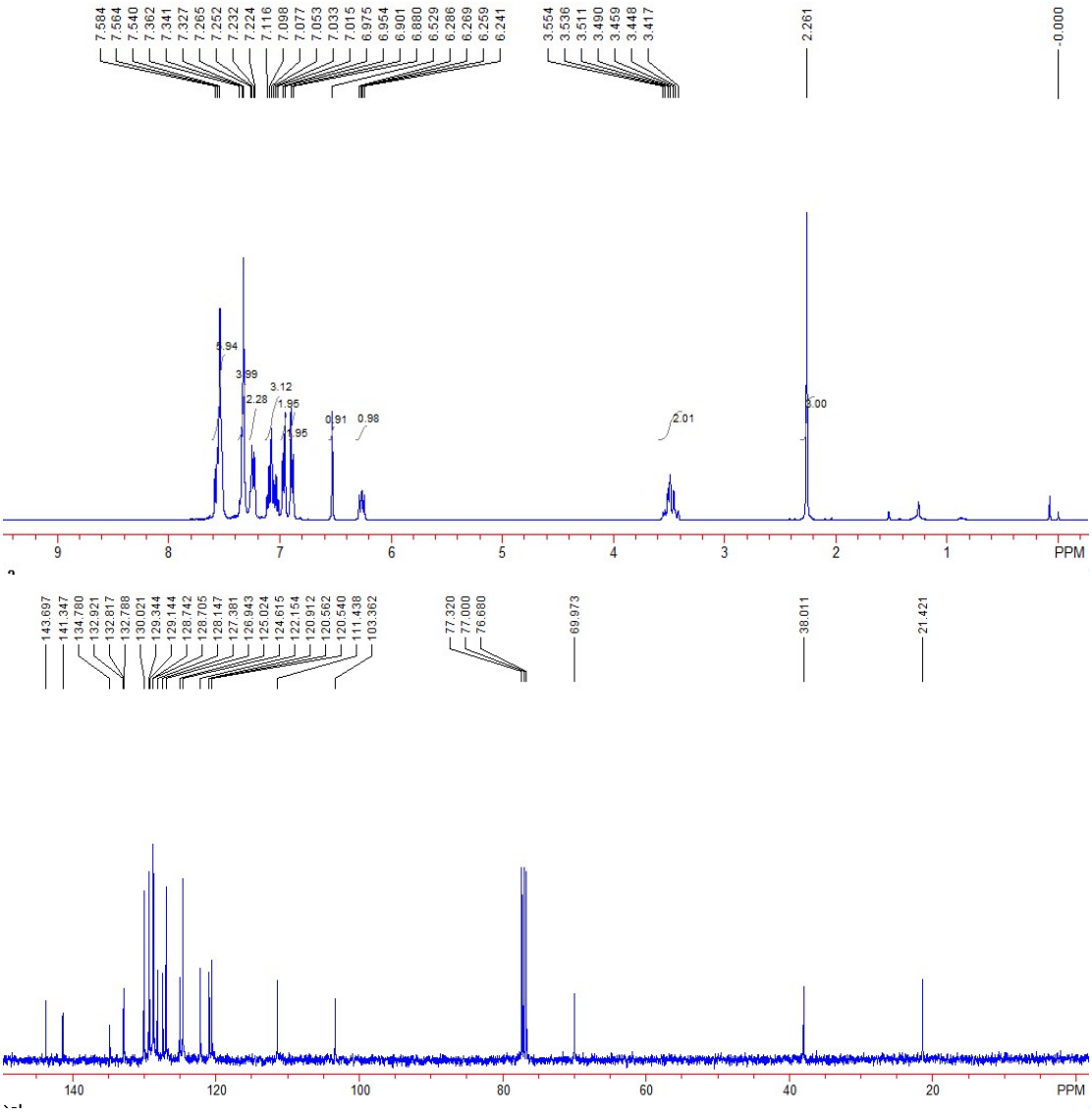


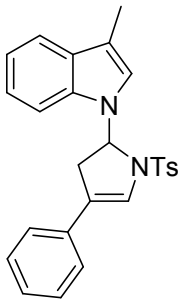
Compound 3ka: Yield: 45 mg, 53%; A white solid; Mp: 156-158 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.30 (s, 3H), 2.80 (s, 3H), 2.94 (dd, 1H, J_1 = 16.8 Hz, J_2 = 2.4 Hz), 3.48-3.55 (m, 1H), 6.26 (d, 1H, J = 3.2 Hz), 6.90 (d, 1H, J = 3.2 Hz), 6.96-7.04 (m, 5H), 7.11 (s, 1H), 7.20-7.24 (m, 1H), 7.24-7.37 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.5, 21.4, 41.4, 70.1, 105.1, 119.0, 120.1, 120.3, 123.6, 124.1, 124.5, 125.6, 126.6, 127.2, 128.6, 128.7, 129.1, 129.4, 132.9, 134.3, 135.0, 143.7; IR (neat): ν 2956, 2923, 2745, 2920, 1621, 1446, 1345, 1326, 1149, 1161, 1092, 1077, 1044, 782, 715, 755, 702, 726, 755; HRMS (ESI) Calcd. for $C_{26}H_{25}N_2O_2S$ $[M+H]^+$: 429.1631, found: 429.1626.



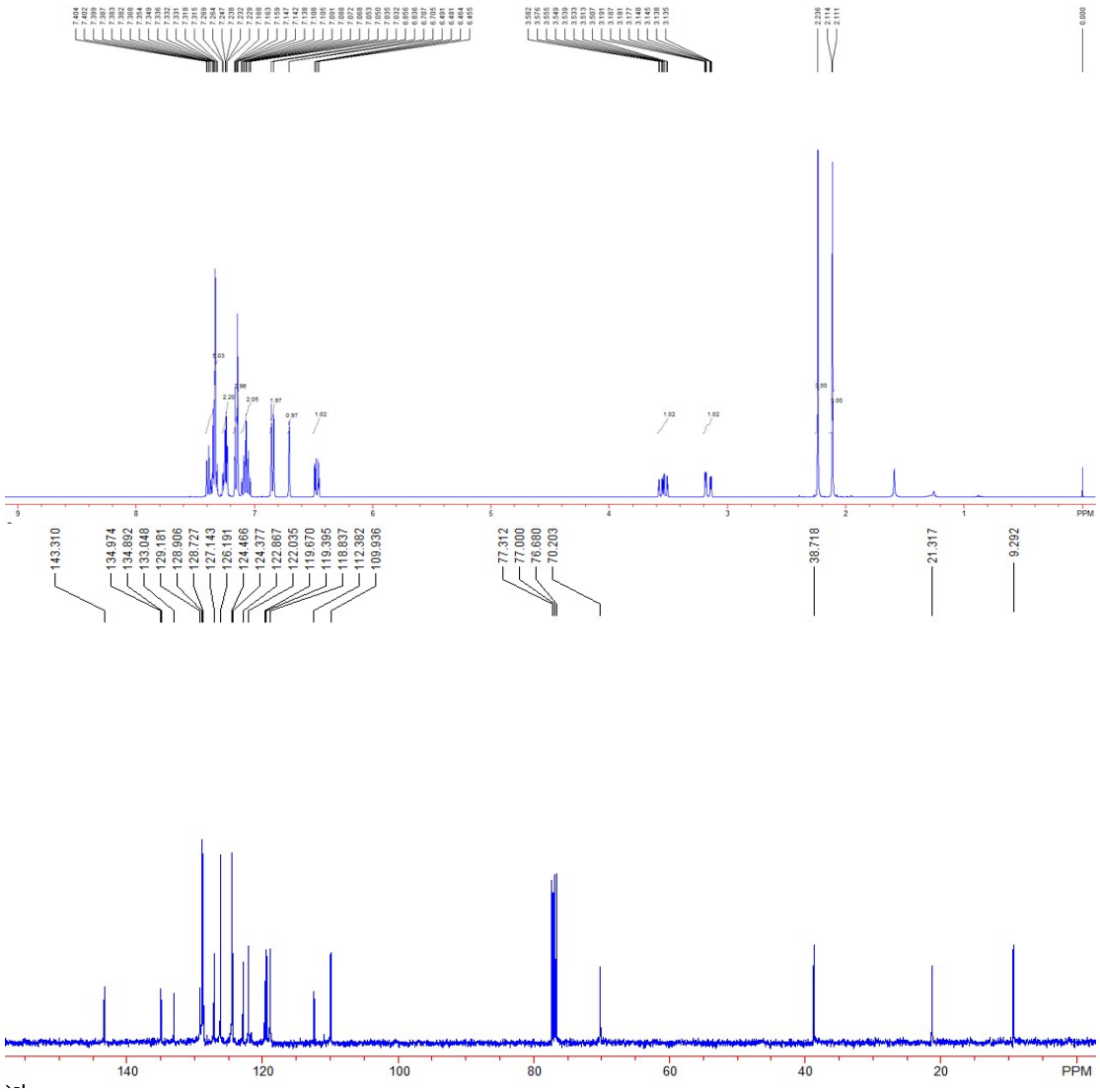


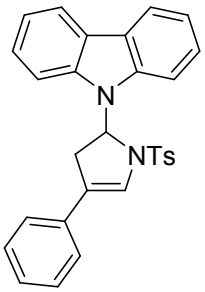
Compound 3la: Yield: 88 mg, 90%; A white solid; Mp: 221-223 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.26 (s, 3H), 3.41-3.55 (m, 2H), 6.26 (dd, 1H, J_1 = 11.2 Hz, J_2 = 7.2 Hz), 6.53 (s, 1H), 6.89 (d, 2H, J = 8.4 Hz), 6.96 (d, 2H, J = 8.4 Hz), 7.01-7.11 (m, 3H), 7.22-7.26 (m, 2H), 7.32-7.36 (m, 4H), 7.54-7.58 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 38.0, 69.9, 103.3, 111.4, 120.54, 120.56, 120.9, 122.1, 124.6, 125.0, 126.9, 127.3, 128.1, 128.70, 128.74, 129.1, 129.3, 130.0, 132.7, 132.8, 132.9, 134.7, 141.3, 143.6; IR (neat): ν 3103, 3056, 2923, 2848, 1635, 1455, 1402, 1353, 1332, 1306, 1195, 1168, 1089, 1078, 1013, 996, 988, 819, 761, 748, 701, 691, 661 cm^{-1}; LRMS (ESI) Calcd. for $C_{31}H_{26}N_2O_2S$ $[M]^+$: 489.16, found: 489.16.



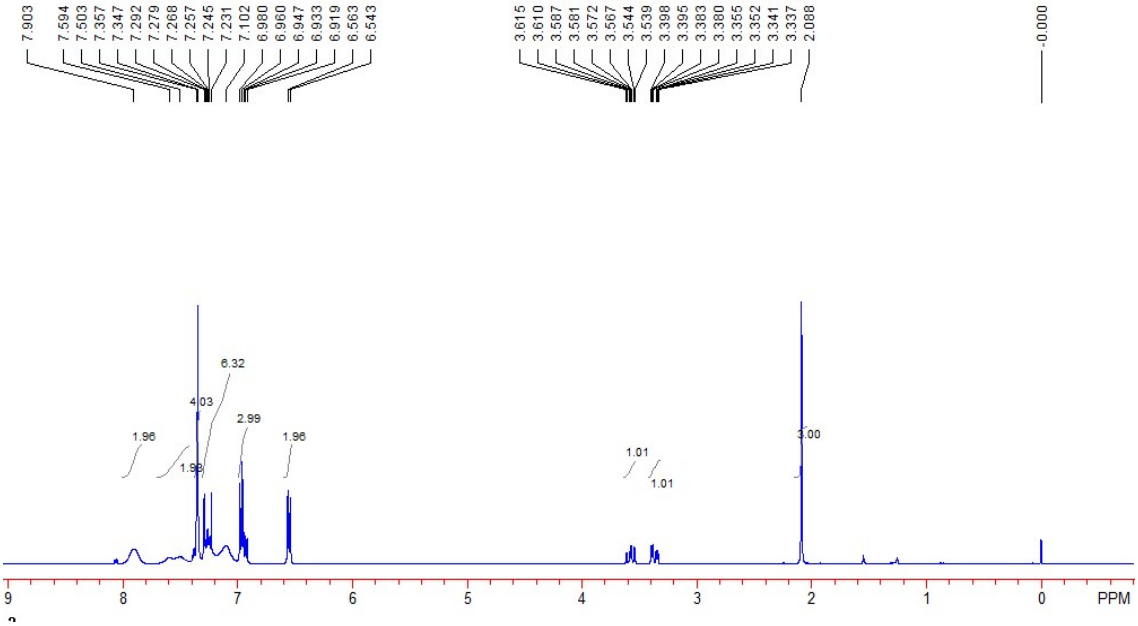


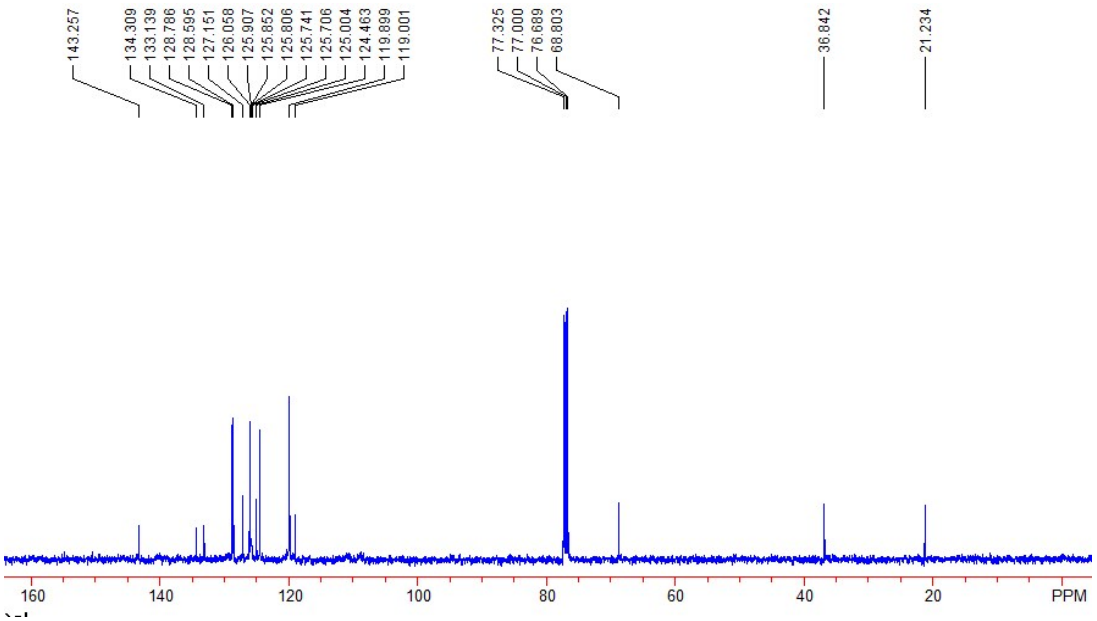
Compound 3ma: Yield: 69 mg, 81%; A white solid; Mp: 90-92 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.11 (d, 3H, J = 1.2 Hz), 2.23 (s, 3H), 3.13-3.19 (m, 1H), 3.50-3.58 (m, 1H), 6.47 (dd, 1H, J_1 = 10.4 Hz, J_2 = 3.6 Hz), 6.70 (d, 1H, J = 0.8 Hz), 6.84 (d, 2H, J = 8.0 Hz), 7.03-7.10 (m, 2H), 7.12-7.17 (m, 3H), 7.22-7.27 (m, 2H), 7.31-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 9.3, 21.3, 38.7, 70.2, 109.9, 112.3, 118.8, 119.3, 119.6, 122.0, 122.8, 124.3, 124.4, 126.2, 127.1, 128.7, 128.9, 129.1, 133.0, 134.8, 134.9, 143.3; IR (neat): ν 3056, 2920, 2856, 1624, 1596, 1458, 1348, 1160, 1090, 1071, 997, 808, 753, 739, 692, 681, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{28}N_3O_2S$ $[M+NH_4]^+$: 446.1897, found: 446.1897.

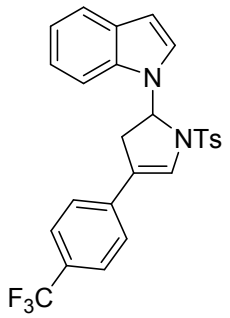




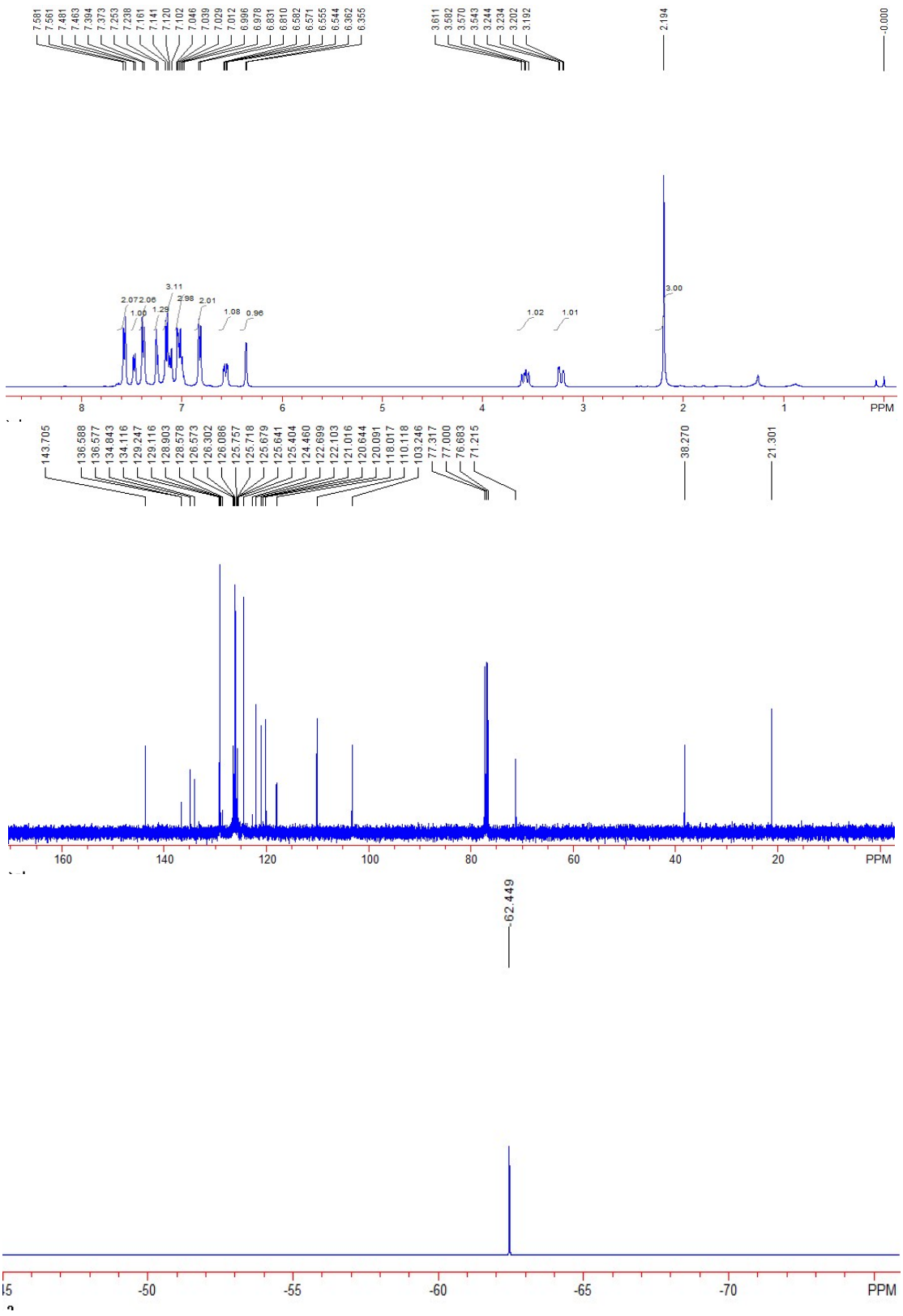
Compound 3na: Yield: 86 mg, 93%; A white solid; Mp: 90-92 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.08 (s, 3H), 3.33-3.39 (m, 1H), 3.53-3.61 (m, 1H), 6.55 (d, 2H, *J* = 8.0 Hz), 6.92-6.9 (m, 3H), 7.10-7.29 (m, 6H), 7.35 (d, 4H, *J* = 4.0 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.90 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 36.8, 68.8, 119.0, 119.8, 124.4, 125.0, 125.70, 125.74, 125.80, 125.85, 125.9, 126.0, 127.1, 128.5, 128.7, 133.1, 134.3, 143.2; IR (neat): ν 3095, 3053, 2917, 2848, 1626, 1590, 1488, 1452, 1353, 1327, 1227, 1162, 1152, 1087, 1067, 1001, 838, 810, 766, 751, 703, 694, 672, 662cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{28}N_3O_2S$ $[M+NH_4]^+$: 482.1897, found: 482.1893.







Compound 3ab: Yield: 61 mg, 83%; A white solid; Mp: 175-177 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.19 (s, 3H), 3.22 (dd, 1H, J_1 = 16.8 Hz, J_2 = 4.0 Hz), 3.58 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.8 Hz), 6.35 (d, 1H, J = 2.8 Hz), 6.56 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.82 (d, 2H, J = 8.4 Hz), 6.98-7.04 (m, 3H), 7.10-7.16 (m, 3H), 7.25 (s, 1H), 7.38 (d, 2H, J = 8.4 Hz), 7.47 (d, 1H, J = 7.2 Hz), 7.57 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.3, 71.2, 103.2, 110.1, 108.0, 120.1, 121.0, 121.7 (dd, J = 270.5 Hz), 122.1, 124.4, 125.7 (q, J = 3.8 Hz), 126.1, 126.3, 126.6, 128.7 (dd, J = 32.5 Hz), 129.1, 129.2, 134.1, 134.8，136.6 (q, J = 1.1 Hz), 143.7; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -62.45 (m); IR (neat): ν 3097, 2923, 2850, 1607, 1454, 1322, 1162, 1090, 990, 829, 743, 669 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{25}F_3N_3O_2S$ $[M+NH_4]^+$: 500.1614, found: 500.1613.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6.996
6.978
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6.571
6.555
6.544
6.362
6.355
3.611
3.582
3.570
3.543
3.244
3.234
3.202
3.192
2.194
0.000
2.07
2.06
1.00
1.29
3.11
2.98
2.01
1.08
0.96
1.02
1.01
3.00
8
7
6
5
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3
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1
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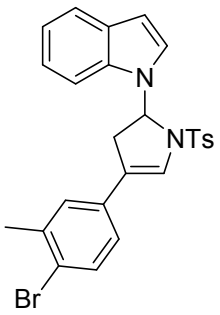
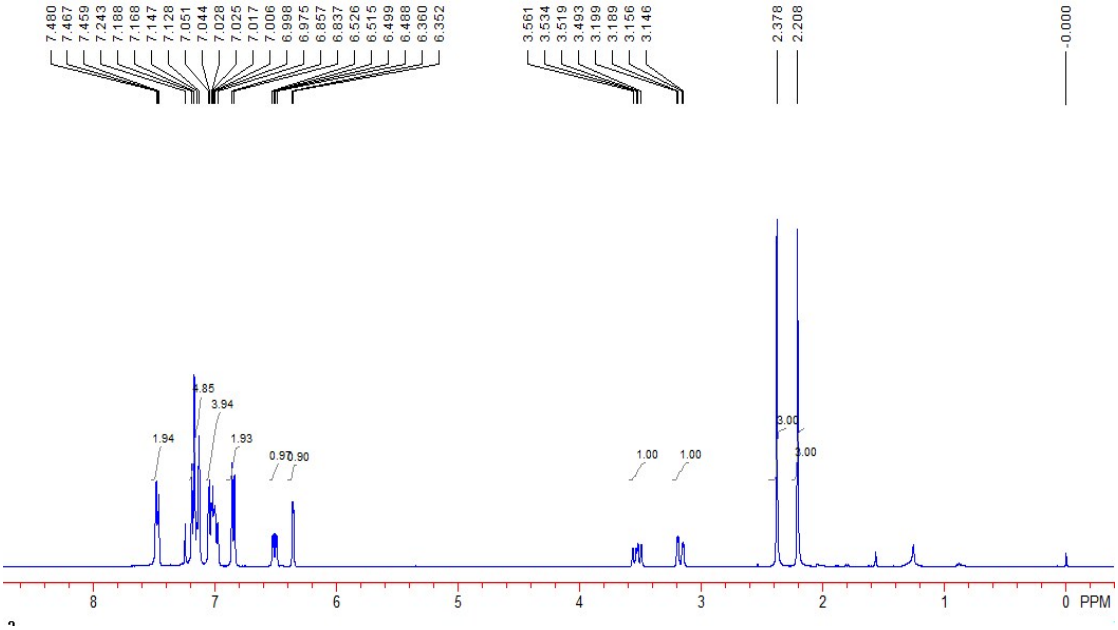
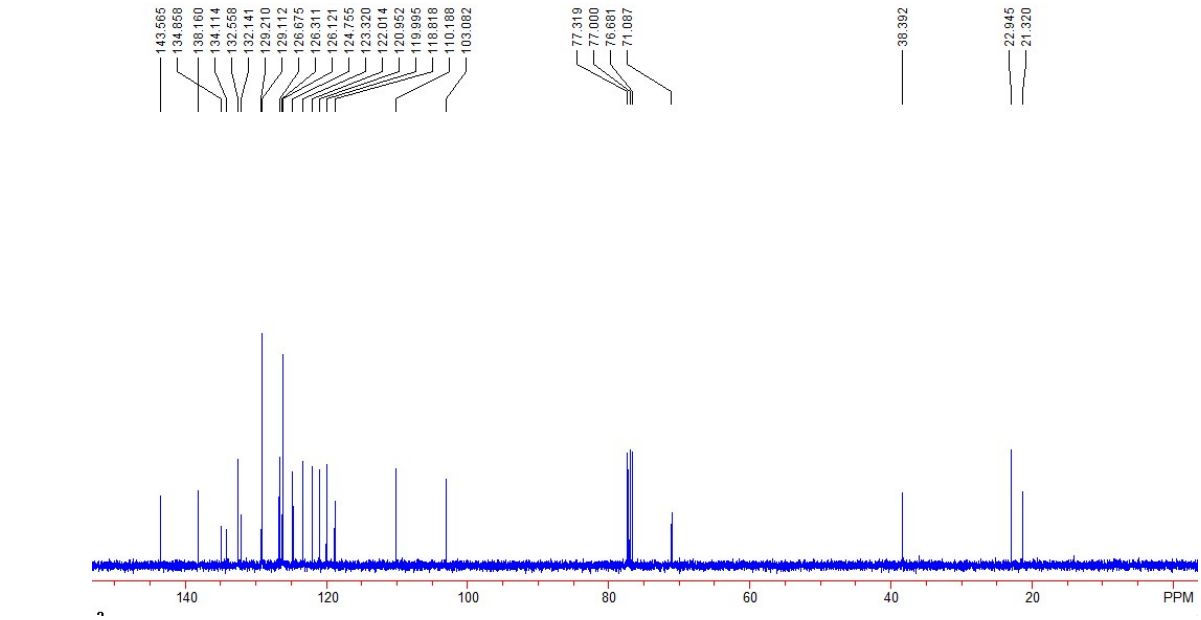
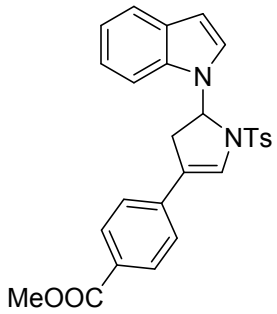
-70
PPM



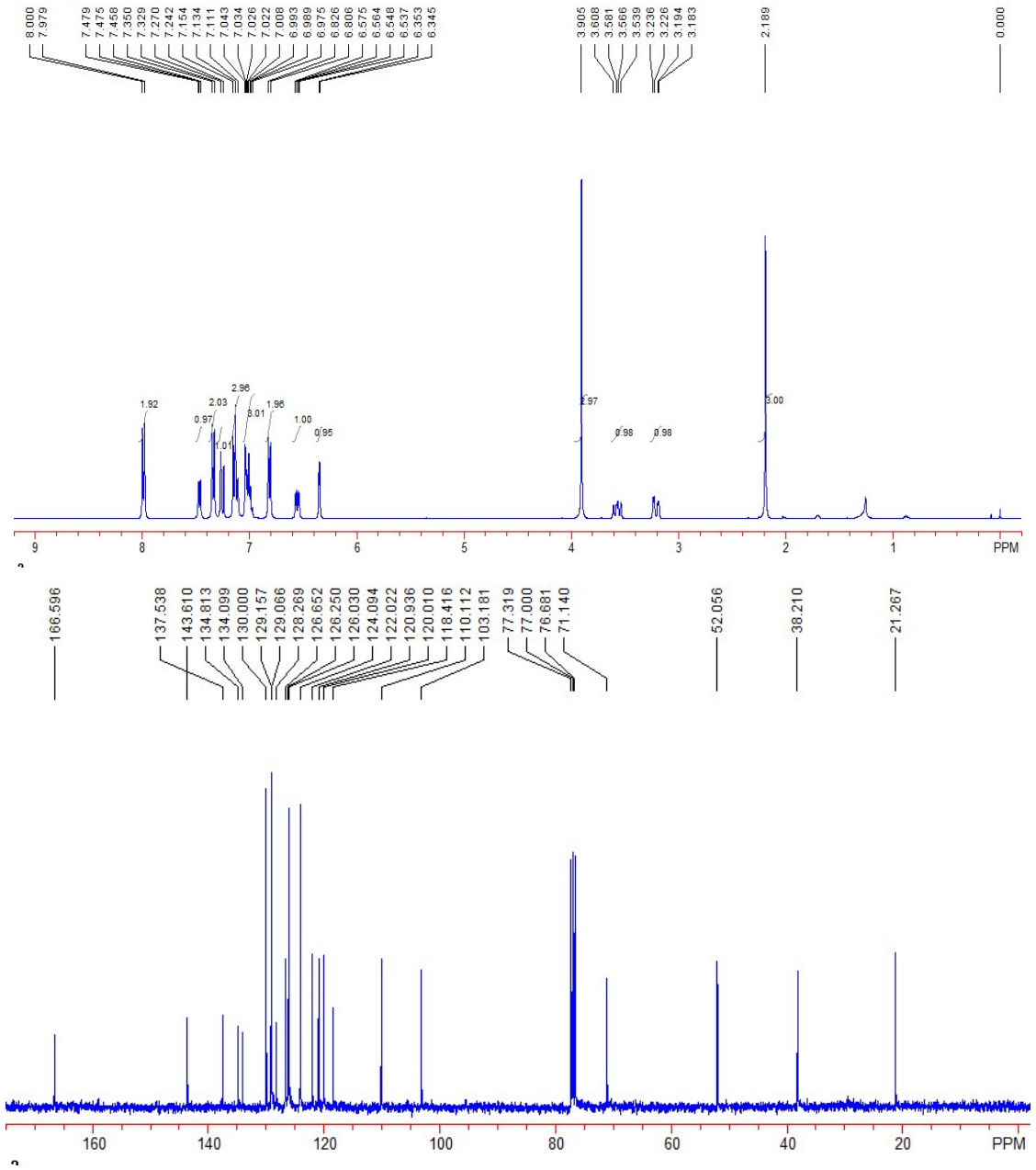
Compound 3ac: Yield: 76 mg, 75%; A white solid; Mp: 190-192 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.20 (s, 3H), 2.37 (s, 3H), 3.17 (dd, 1H, J_1 = 17.2 Hz, J_2 = 4.4 Hz), 3.52 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.8 Hz), 6.35 (d, 1H, J = 3.2 Hz), 6.50 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.84 (d, 2H, J = 8.0 Hz), 6.97-7.05 (m, 4H), 7.12-7.19 (m, 5H), 7.45-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 22.9, 38.4, 71.1, 103.1, 110.2, 118.8, 120.0, 120.9, 122.0, 123.33, 123.36, 124.7, 126.1, 126.3, 126.7, 129.1, 129.2, 132.1, 132.5, 134.1, 134.9, 138.2, 143.5; IR (neat): ν 3100, 2920, 2848, 1626, 1458, 1348, 1319, 1159, 1127, 1088, 1002, 807, 740, 703, 668 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{23}BrN_2NaO_2S$ $[M+Na]^+$: 529.0556, found: 529.0554.

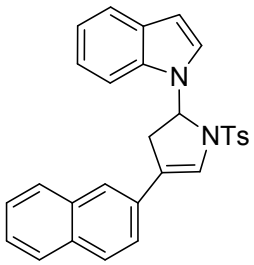






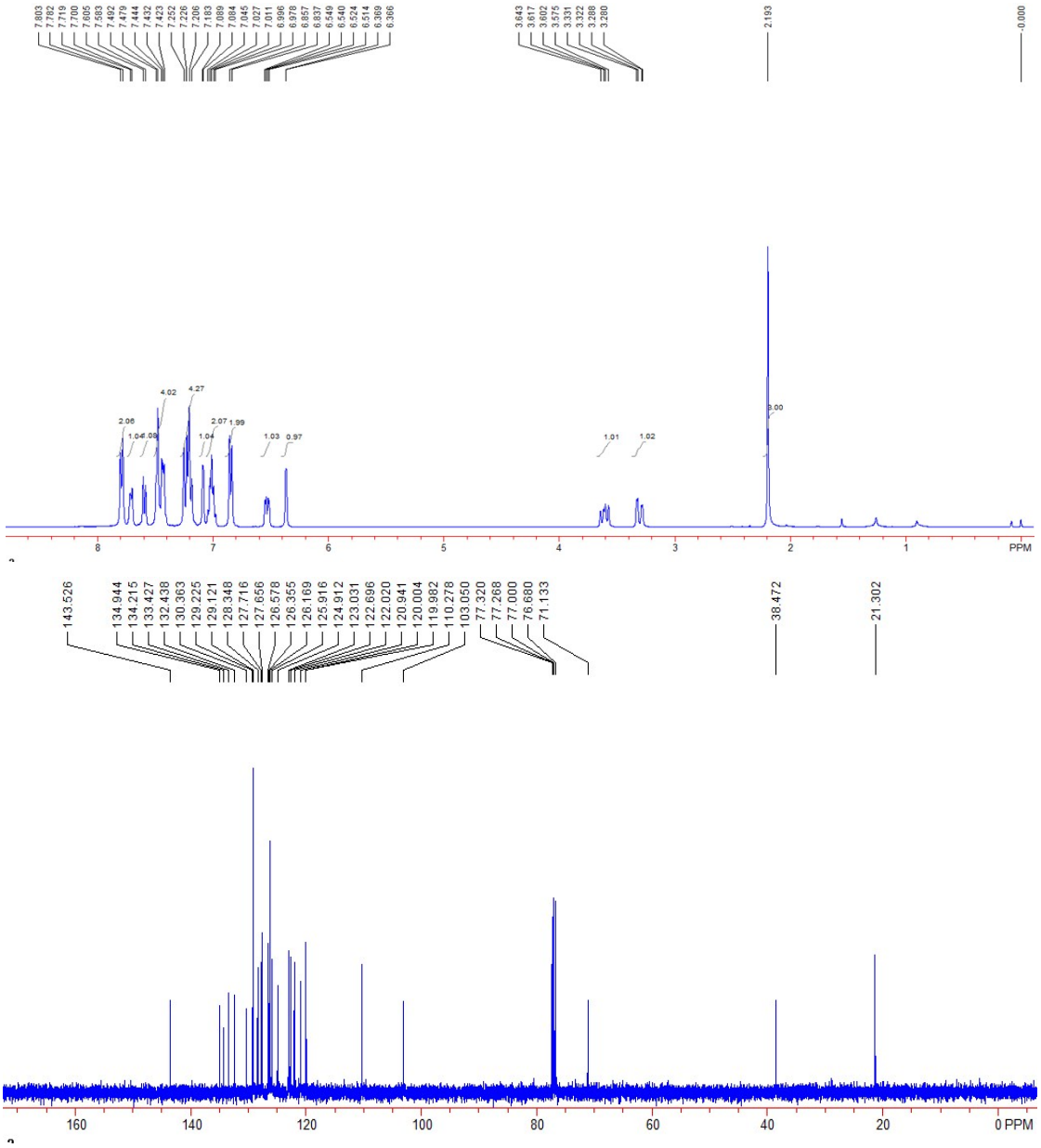
Compound 3ad: Yield: 90 mg, 96%; A white solid; Mp: 172-174 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.19 (s, 3H), 3.21 (dd, 1H, J_1 = 17.2 Hz, J_2 = 4.4 Hz), 3.58 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.8 Hz), 3.90 (s, 3H), 6.35 (d, 1H, J = 3.2 Hz), 6.55 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.81 (d, 2H, J = 8.0 Hz), 6.97-7.04 (m, 3H), 7.11-7.15 (m, 3H), 7.27 (s, 1H), 7.34 (d, 2H, J = 8.4 Hz), 7.45-7.48 (m, 1H), 7.98 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 38.2, 52.0, 71.1, 103.1, 110.1, 118.4, 120.0, 120.9, 122.0, 124.0, 126.0, 126.2, 126.6, 128.2, 129.0, 129.1, 130.0, 134.1, 134.8, 137.5, 143.6, 166.6; IR (neat): ν 3095, 2950, 2848, 1713, 1603, 1454, 1160, 1109, 716, 666 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{24}N_2NaO_4S$ $[M+Na]^+$: 495.1349, found: 495.1350.

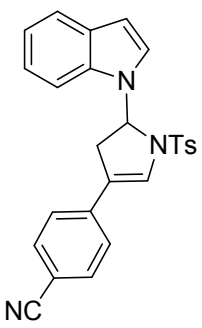




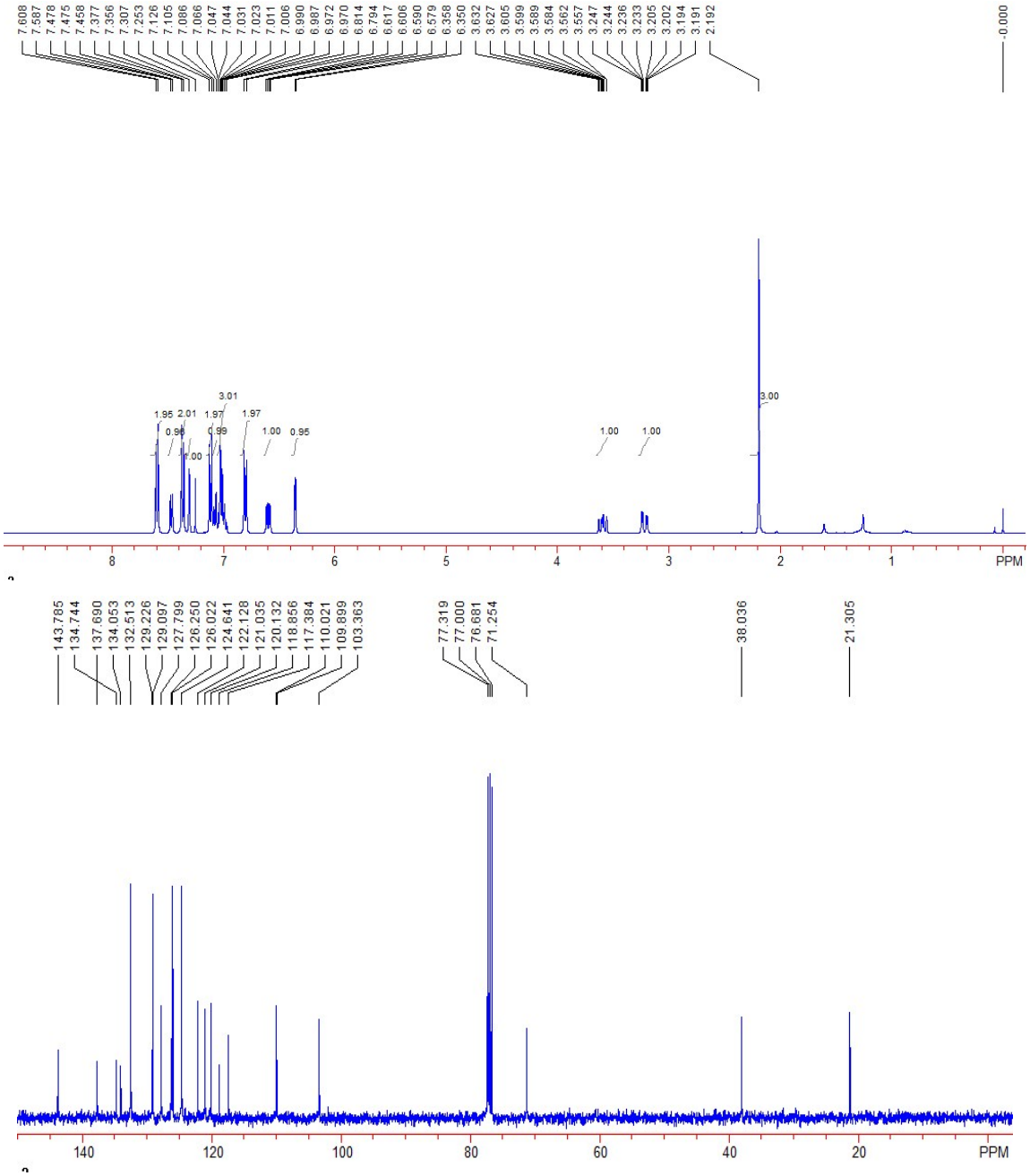
Compound 3ae: Yield: 77 mg, 83%; A white solid; Mp: 158-160 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.19 (s, 3H), 3.30 (dd, 1H, J_1 = 16.4 Hz, J_2 = 3.6 Hz), 3.61 (dd, 1H, J_1 = 16.4 Hz, J_2 = 10.8 Hz), 6.35 (d, 1H, J = 1.2 Hz), 6.53 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 6.84 (d, 2H, J = 8.0 Hz), 6.97-7.04 (m, 2H), 7.08 (d, 1H, J = 2.0 Hz), 7.18-7.25 (m, 4H), 7.42-7.49 (m, 4H), 7.59 (d, 1H, J = 8.8 Hz), 7.70-7.72 (m, 1H), 6.79 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.4, 71.1, 103.0, 110.2, 119.9, 120.0, 120.9,

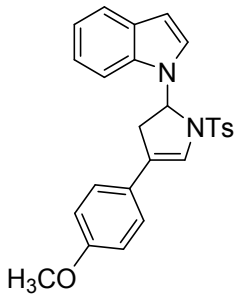
122.0, 122.6, 123.0, 124.9, 125.9, 126.1, 126.3, 126.5, 127.6, 127.7, 128.3, 129.1, 129.2, 130.3, 132.4, 133.4, 134.2, 134.9, 143.5; IR (neat): ν 3100, 3053. 2917, 1624, 1457, 1350, 1326. 1159, 1089, 1067, 988, 764, 740, 714, 703, 667 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{25}N_2O_2S$ $[M+H]^+$: 465.1631, found: 465.1627.



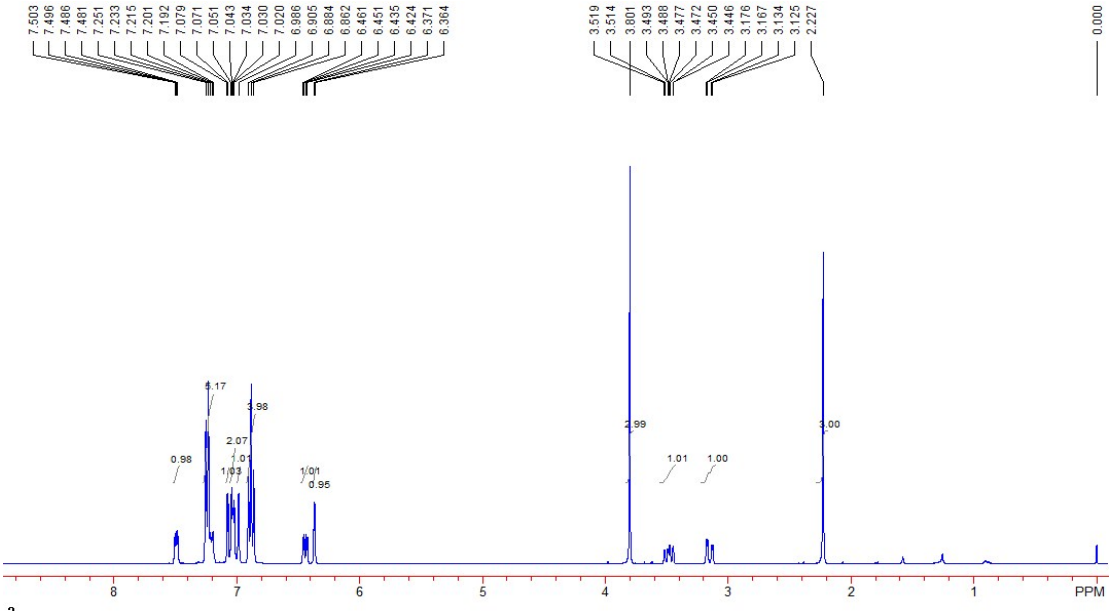


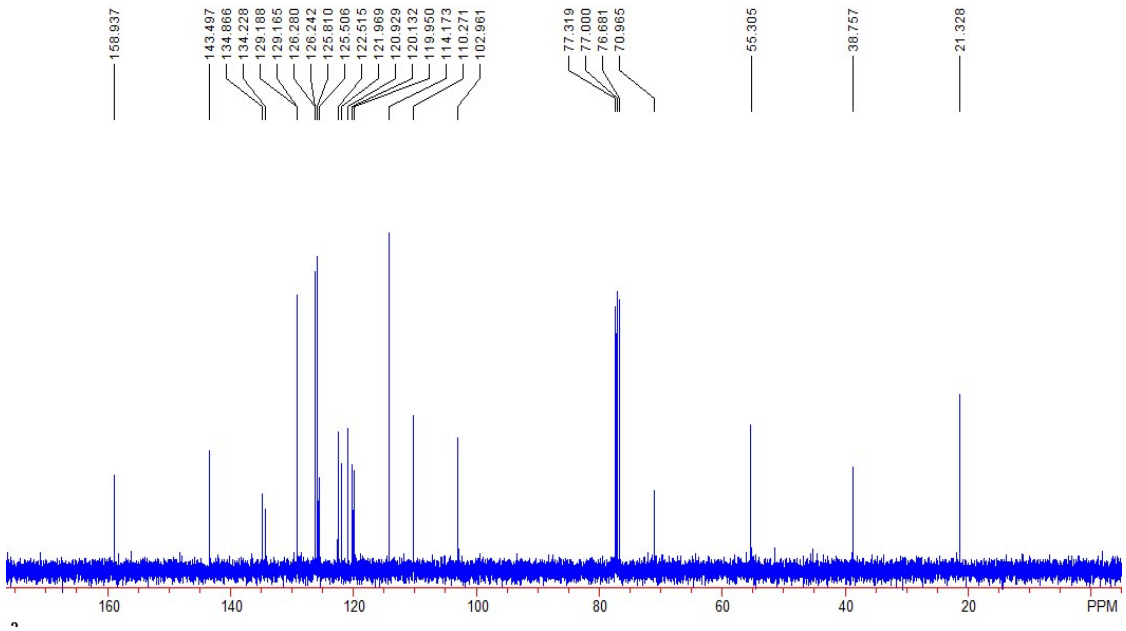
Compound 3af: Yield: 60 mg, 68%; A white solid; Mp: 168-170 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.19 (s, 3H), 3.19-3.24 (m, 1H), 3.55-3.63 (m, 1H), 6.35 (d, 1H, J = 3.2 Hz), 6.60 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.80 (d, 2H, J = 8.0 Hz), 6.97-7.04 (m, 3H), 7.07 (d, 1H, J = 8.0 Hz), 7.11 (d, 2H, J = 8.4 Hz), 7.30 (s, 1H), 7.36 (d, 2H, J = 8.4 Hz), 7.46 (d, 1H, J = 6.8 Hz), 7.59 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.0, 71.2, 103.3, 109.9, 110.0, 117.3, 118.8, 120.1, 121.0, 122.1, 124.6, 126.0, 126.2, 127.8, 129.0, 129.2, 132.5, 134.0, 134.7, 137.7, 143.7; IR (neat): ν 3092, 2925, 2845, 2218, 1621, 1161, 1601, 1457, 1354, 1161, 1089. 10598, 1068, 986, 828, 764, 741, 703, 666 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{21}N_3NaO_2S$ $[M+Na]^+$: 462.1247, found: 462.1247.

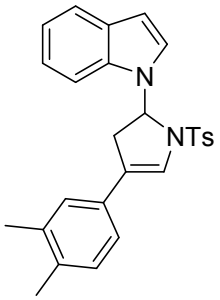




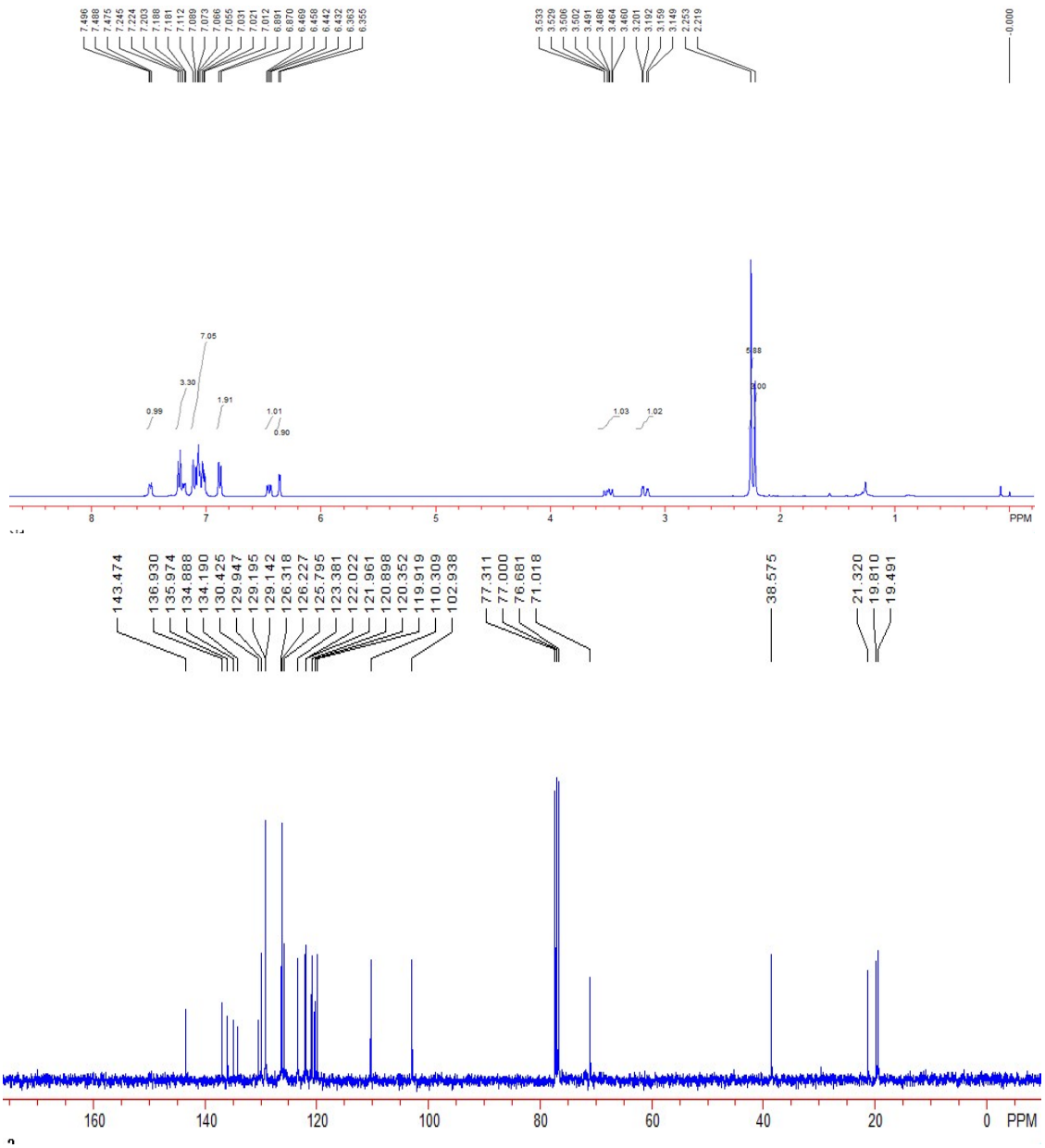
Compound 3ag: Yield: 67 mg, 75%; A white solid; Mp: 170-172 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 3.15 (dd, 1H, J_1 = 16.8 Hz, J_2 = 3.6 Hz), 3.44-3.52 (m, 1H), 3.80 (s, 3H), 6.36 (d, 1H, J = 2.8 Hz), 6.44 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 6.88 (dd, 4H, J_1 = J_2 = 8.8 Hz), 6.98 (s, 1H), 7.02-7.05 (m, 2H), 7.07 (d, 1H, J = 3.2 Hz), 7.19-7.25 (m, 5H), 7.49 (dd, 1H, J_1 = 6.0 Hz, J_2 = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.7, 55.3, 70.9, 102.9, 110.2, 114.1, 119.9, 120.1, 120.9, 121.9, 122.5, 125.5, 125.8, 126.2, 126.3, 129.1, 129.2, 134.2, 134.8, 143.4. 158.9; IR (neat): ν 3100, 2925, 2834, 1610, 1513, 1463, 1410, 1352, 1255, 1180, 1159, 1086, 1055, 1026, 982, 818, 743, 728, 705, 669 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{25}N_3O_2S$ $[M+H]^+$: 445.1580, found: 445.1576.

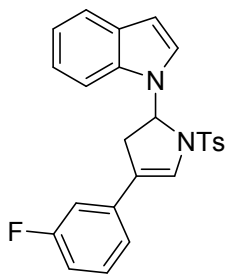






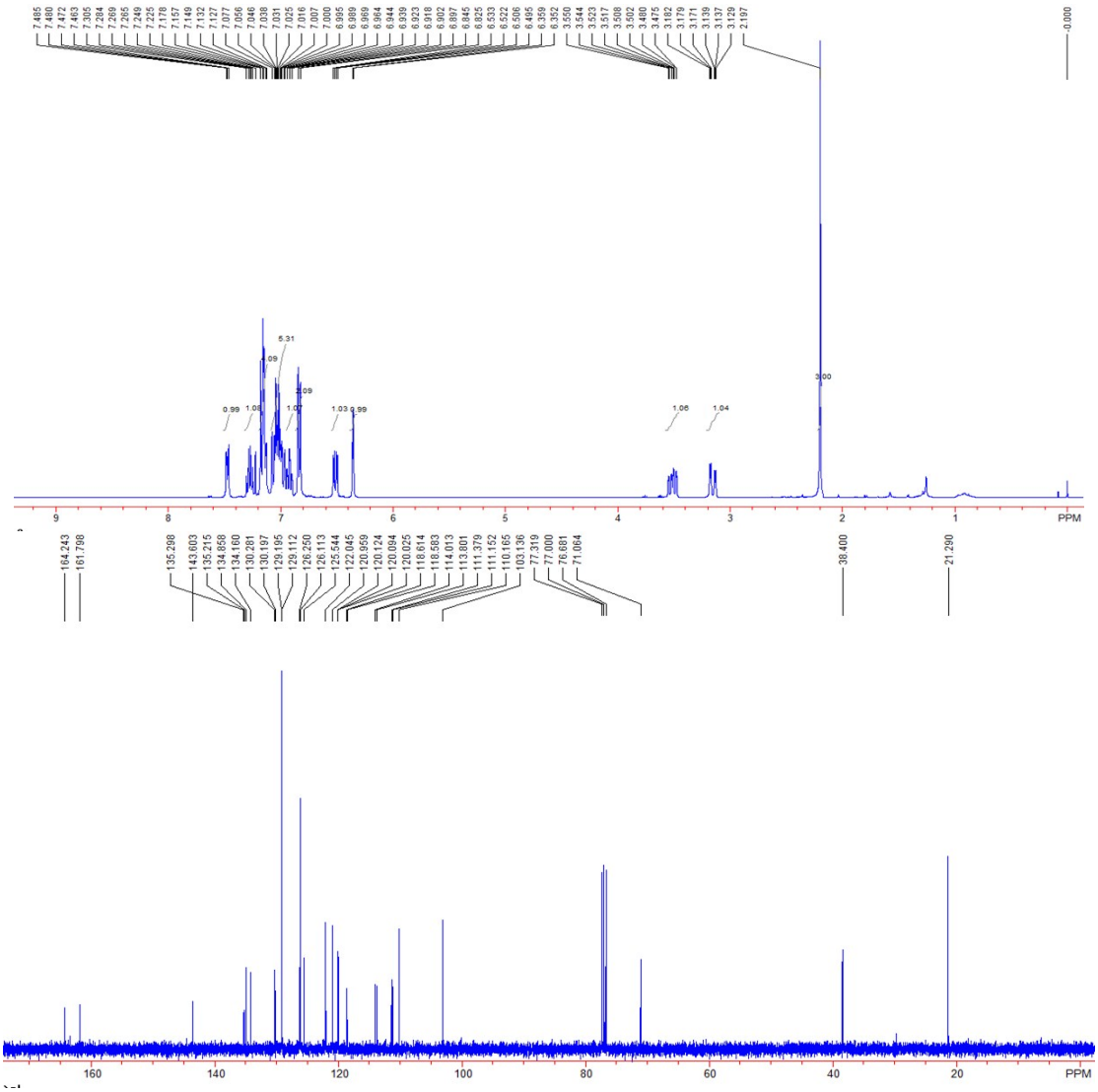
Compound 3ah: Yield: 83 mg, 94%; A white solid; Mp: 128-130 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 2.25 (s, 6H), 3.17 (dd, 1H, J_1 = 17.2 Hz, J_2 = 4.0 Hz), 3.46-3.53 (m, 1H), 6.36 (d, 1H, J = 3.2 Hz), 6.45 (dd, 1H, J_1 = 10.4 Hz, J_2 = 4.0 Hz), 6.88 (d, 2H, J = 8.4 Hz), 7.01-7.11 (m, 7H), 7.18-7.24 (m, 3H), 7.47-7.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.5, 19.8, 21.3, 38.5, 71.0, 102.9, 110.3, 119.9, 120.3, 120.9, 121.9, 122.0, 123.3, 125.8, 126.2, 126.3, 129.14, 129.19, 129.9, 130.4, 134.2, 134.9, 135.9, 136.9, 143.4; IR (neat): ν 3053, 2920, 2850, 1629, 1457, 1347, 1316, 1158, 1090, 1004, 807. 741, 703, 669 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{27}N_2O_2S$ $[M+H]^+$: 443.1788, found: 443.1787.

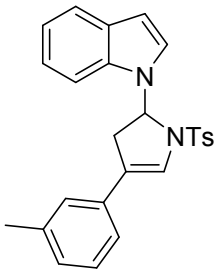




Compound 3ai: Yield: 81 mg, 94%; A white solid; Mp: 89-91 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.19 (s, 3H), 3.12-3.18 (m, 1H), 3.47-3.55 (m, 1H), 6.35 (d, 1H, J = 2.8 Hz), 6.61 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.83 (d, 2H, J = 8.0 Hz), 6.89-6.97 (m, 1H), 6.98-7.07 (m, 5H), 7.12-7.18 (m, 4H), 7.24-7.30 (m, 1H), 7.46-7.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 38.4, 71.0, 103.1, 110.2, 111.2 (d, J = 22.7 Hz), 113.9 (d, J = 21.2 Hz), 118.6 (d, J = 3.1 Hz), 120.02, 120.09, 120.1, 120.9, 122.0, 125.5, 126.1, 126.2, 129.1, 129.2, 130.2 (d, J = 8.4 Hz), 134.1,

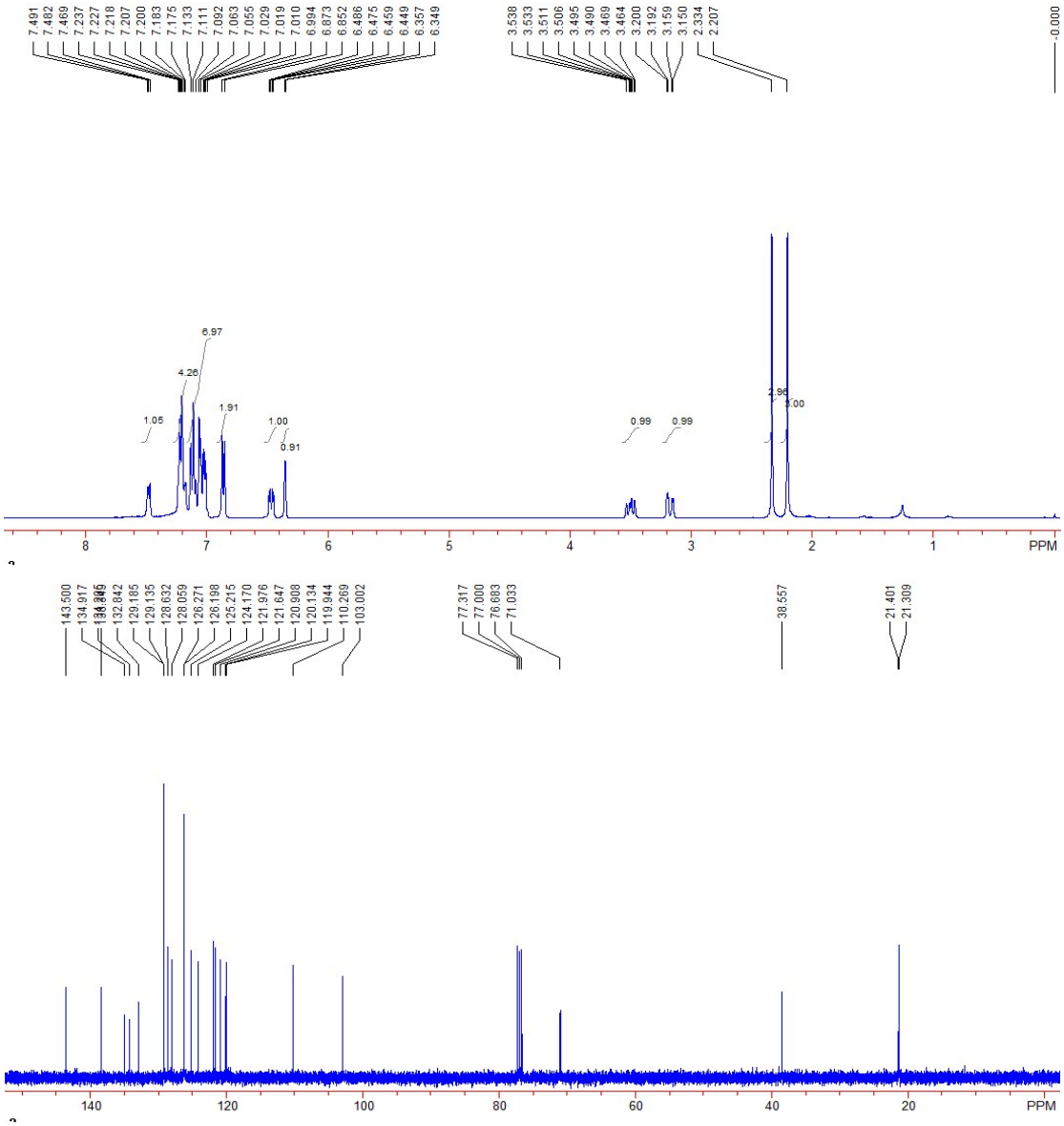
134.8, 135.2 (d, J = 8.3 Hz), 143.6, 163.0 (d, J = 244.5 Hz); IR (neat): ν 3100, 3056, 2925, 2848, 1629, 1610, 1579, 1457, 1185, 1158, 1089, 990, 807, 780, 764, 668 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{25}FN_2O_2S$ $[M+H]^+$: 450.1646, found: 450.1643.

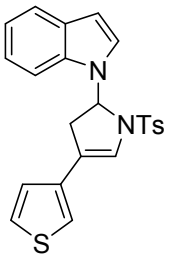




Compound 3aj: Yield: 63 mg, 74%; A white solid; Mp: 160-162 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.20 (s, 3H), 2.33 (s, 3H), 3.17 (dd, 1H, J_1 = 16.8 Hz, J_2 = 3.6 Hz), 3.46-3.53 (m, 1H), 6.35 (d, 1H, J = 3.2 Hz), 6.46 (dd, 1H, J_1 = 10.4 Hz, J_2 = 3.6 Hz), 6.86 (d, 2H, J = 8.4 Hz), 7.01-7.13 (m, 7H), 7.17-7.23 (m, 4H), 7.46-7.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 21.4, 38.5, 71.0, 103.0, 110.2, 119.9, 120.1, 120.9, 121.6, 121.9, 124.1, 125.2, 126.1, 126.2, 128.0, 128.6,

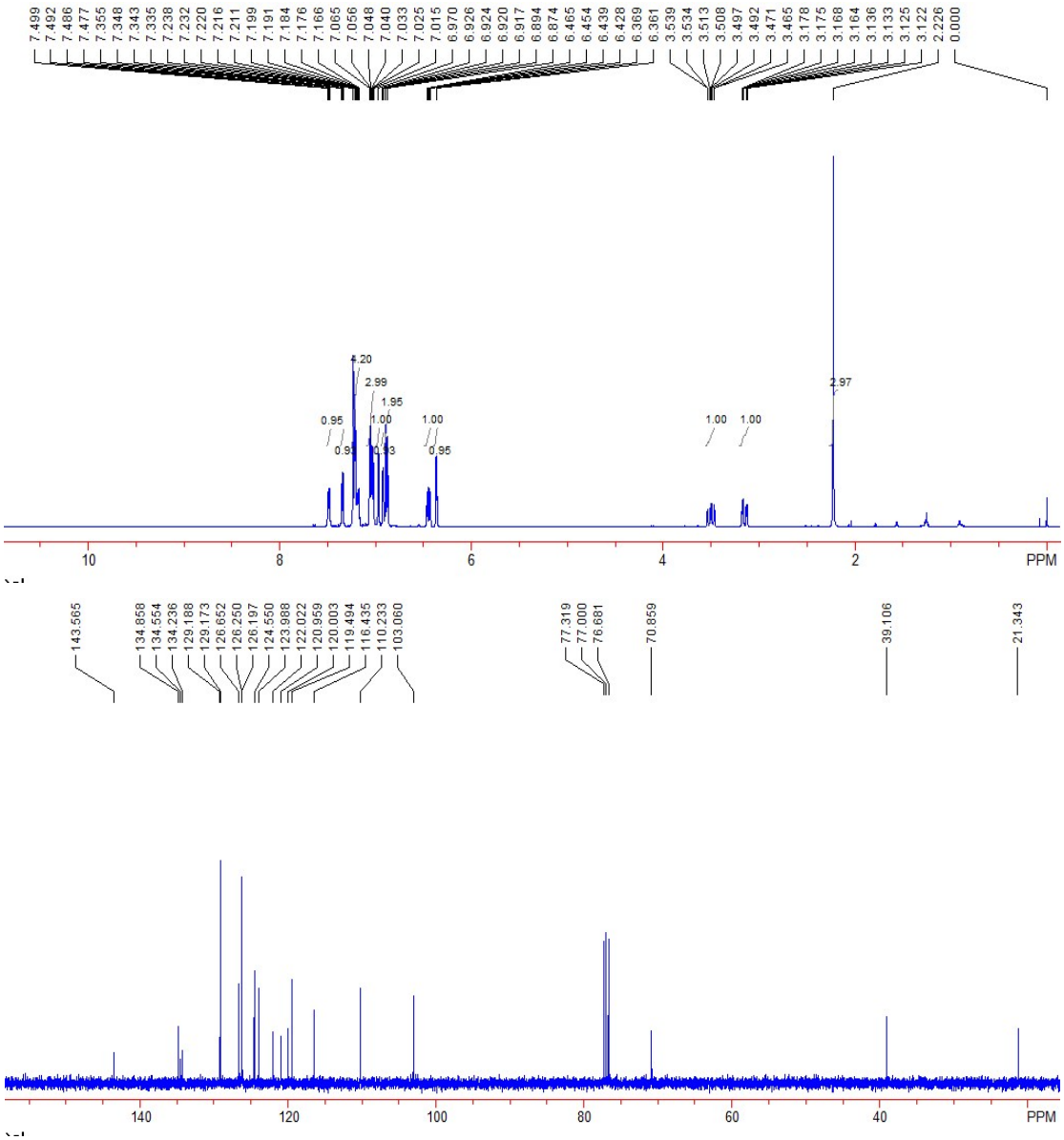
129.13, 129.18, 132.8, 134.2, 134.9, 138.3, 143.5; IR (neat): ν 3097, 3009, 2923, 1635, 1627, 1457, 1351, 1161, 1091, 1024, 999, 785, 770, 763, 741, 703, 664 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{25}N_2O_2S$ $[M+H]^+$: 429.1631, found: 429.1630.

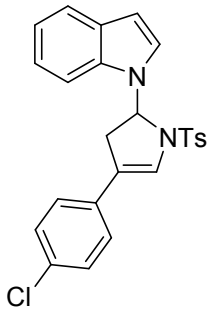




Compound 3ak: Yield: 80 mg, 95%; A white solid; Mp: 153-155 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 3.12-3.17 (m, 1H), 3.46-3.53 (m, 1H), 6.36 (d, 1H, J = 3.2 Hz), 6.44 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.88 (d, 2H, J = 8.0 Hz), 6.92 (dd, 1H, J_1 = 2.8 Hz, J_2 = 1.2 Hz), 6.97 (s, 1H), 7.01-7.06 (m, 3H), 7.16-7.23 (m, 4H), 7.34 (dd, 1H, J_1 = 5.2 Hz, J_2 = 3.2 Hz), 7.47-7.49 (m,

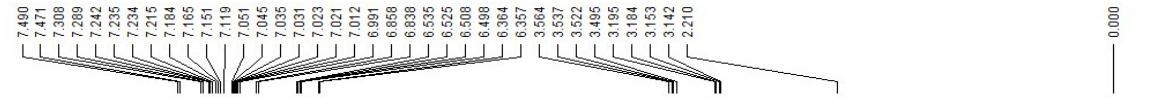
1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 39.1, 70.8, 103.0, 110.2, 116.4, 119.4, 120.0, 120.9, 122.0, 123.9, 124.5, 126.1, 126.2, 126.6, 129.1, 129.2, 134.2, 134.5, 134.8 143.5; IR (neat): ν 3100, 2920, 2848, 1637, 1457, 1351, 1306, 1224, 1161, 1089, 988, 772, 741, 704, 666 cm^{-1}; HRMS (ESI) Calcd. for $C_{23}H_{24}N_3O_2S_2$ $[M+NH_4]^+$: 438.1304, found: 438.1302.

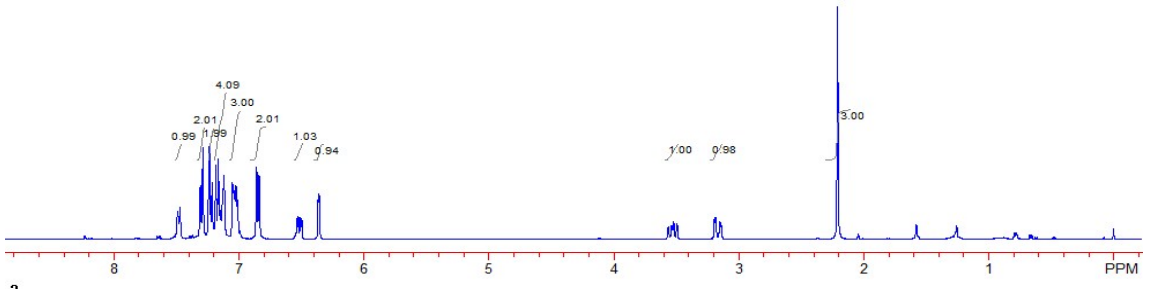


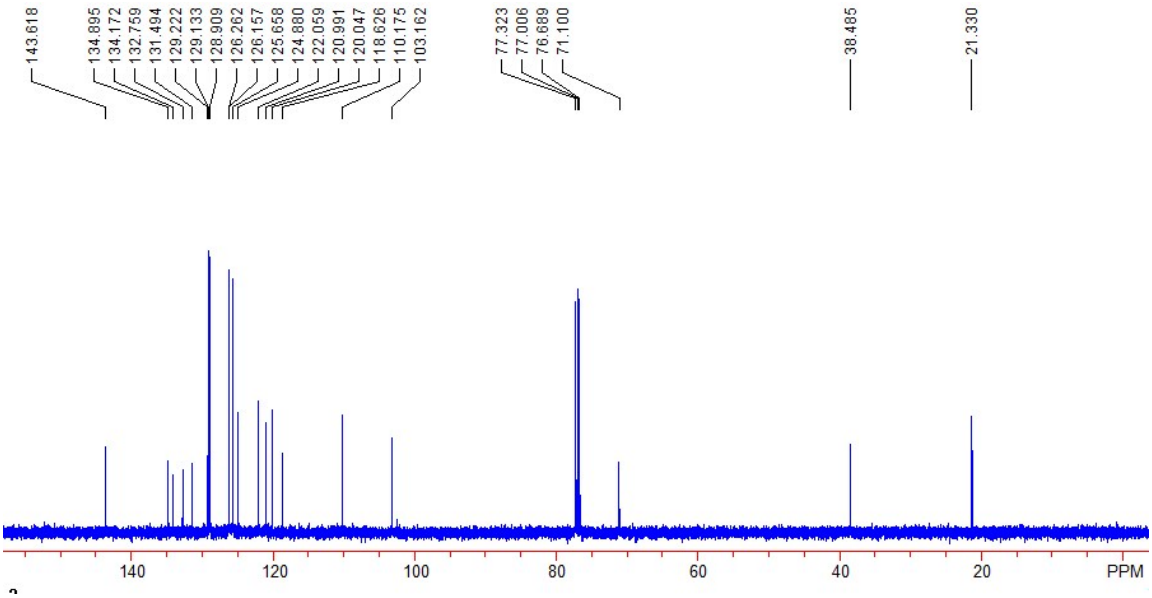


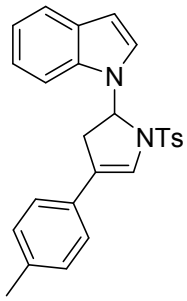
Compound 3al: Yield: 68 mg, 76%; A white solid; Mp: 158-160 ^oC; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.21 (s, 3H), 3.17 (dd, 1H, J_1 = 16.8 Hz, J_2 = 4.0 Hz), 3.53 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.8

Hz), 6.36 (d, 1H, J = 2.8 Hz), 6.51 (dd, 1H, J_1 = 10.8 Hz, J_2 = 4.0 Hz), 6.84 (d, 2H, J = 8.0 Hz), 6.99-7.05 (m, 3H), 7.12-7.18 (m, 4H), 7.21-7.23 (m, 2H), 7.29-7.30 (m, 2H), 7.48 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 38.4, 71.0, 103.1, 110.1, 118.6, 120.0, 120.9, 122.0, 124.8, 125.6, 126.1, 126.2, 128.9, 129.1, 129.2, 131.4, 132.8, 134.1, 134.8, 143.6; IR (neat): ν 3089, 2917, 2845, 1715, 1627, 1490, 1349, 1336, 1332, 1184, 1160, 1092, 1078, 1000, 815, 764, 751, 718, 703, 668 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{21}ClN_2NaO_2S$ $[M+Na]^+$: 471.0904, found: 471.0897.

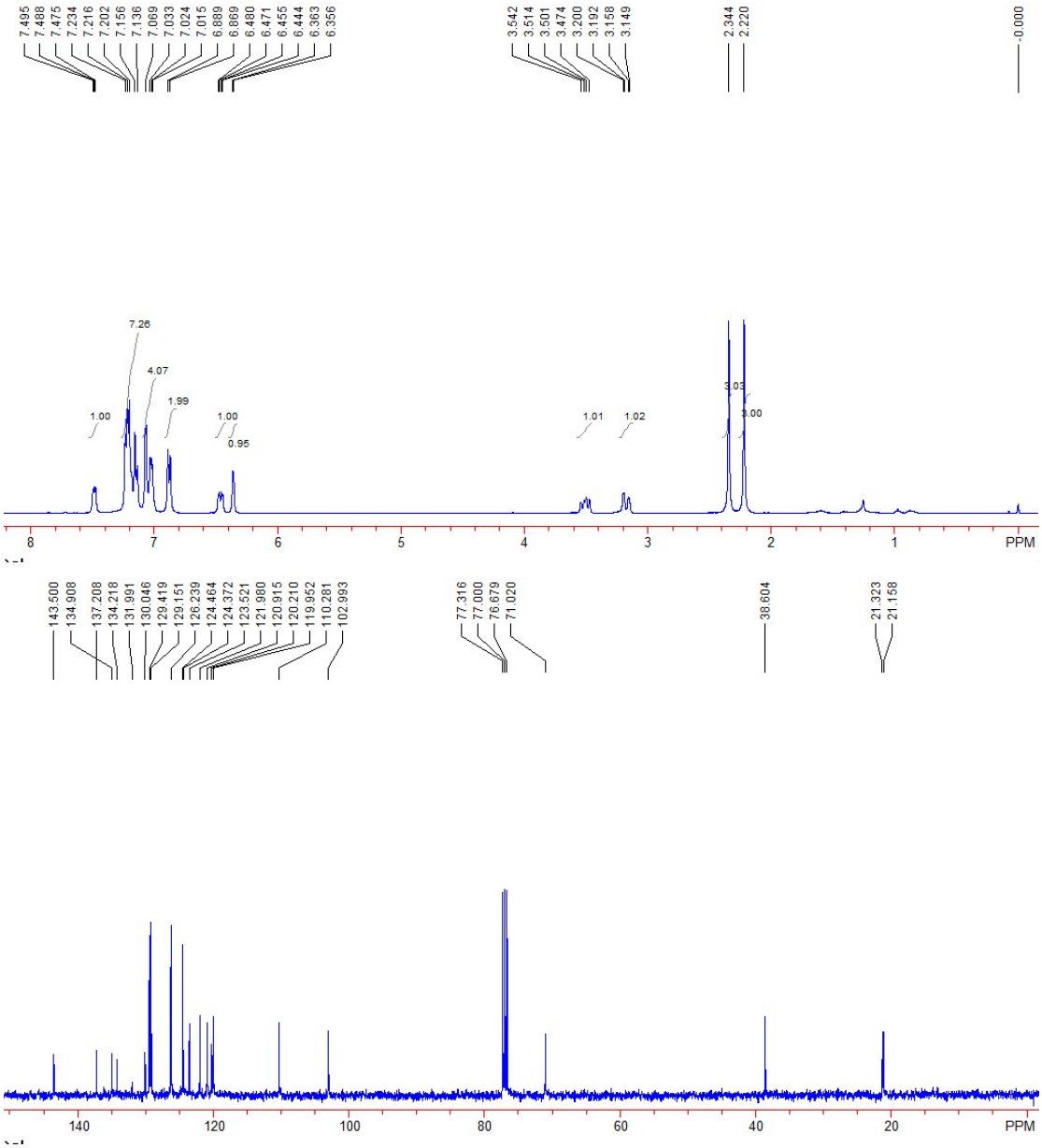




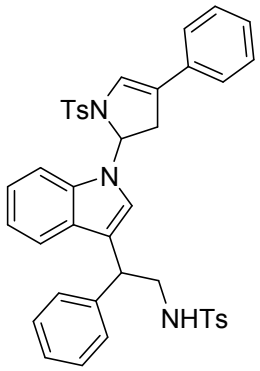




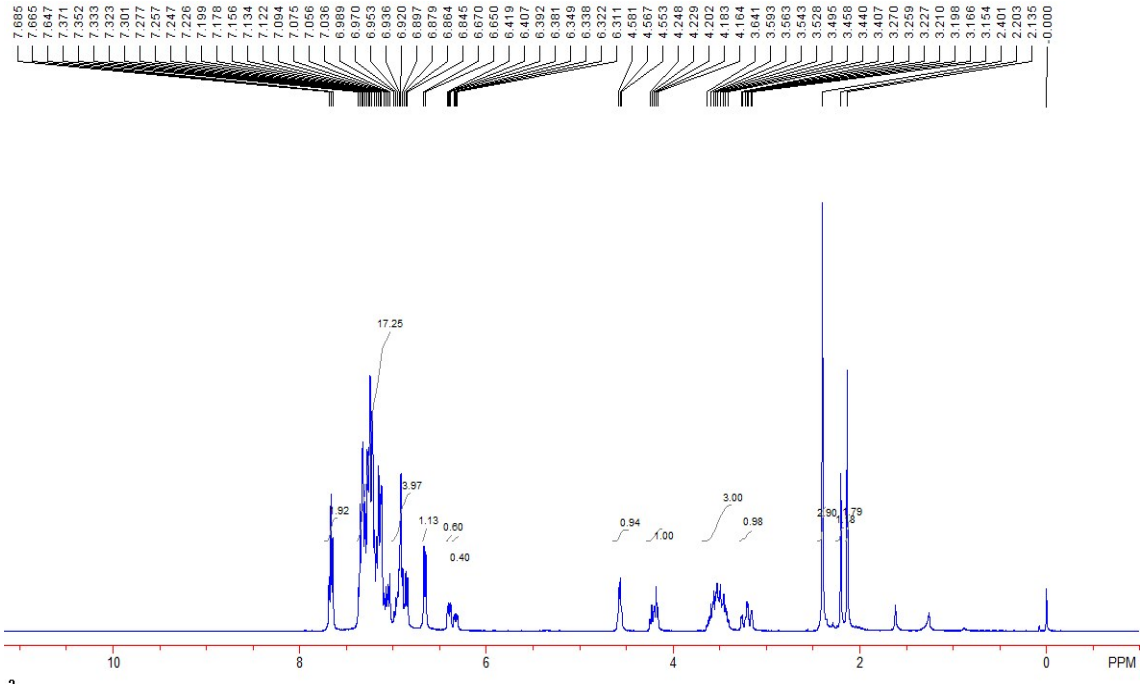
Compound 3am: Yield: 62 mg, 73%; A white solid; Mp: 161-163 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 2.34 (s, 3H), 3.17 (dd, 1H, J_1 = 16.8 Hz, J_2 = 3.6 Hz), 3.50 (dd, 1H, J_1 = 16.8 Hz, J_2 = 10.8 Hz), 6.36 (d, 1H, J = 2.8 Hz), 6.46 (dd, 1H, J_1 = 10.8 Hz, J_2 = 3.6 Hz), 6.80 (d, 2H, J = 8.0 Hz), 7.01-7.07 (m, 4H), 7.13-7.23 (m, 7H), 7.47-7.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 21.3, 38.6, 71.0, 103.0, 110.2, 119.9, 120.2, 120.9, 121.9, 123.5, 124.3, 124.4, 126.2, 129.1, 129.4, 130.0, 131.9, 134.2, 134.9, 137.2, 143.5; IR (neat): ν 3092, 2914, 2853, 1629, 1513, 1345, 1456, 1345, 1327, 1182, 1158, 1126, 1001, 812, 763, 750, 715, 704, 669 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{25}N_2O_2S$ $[M+H]^+$: 429.1631, found: 429.1630.

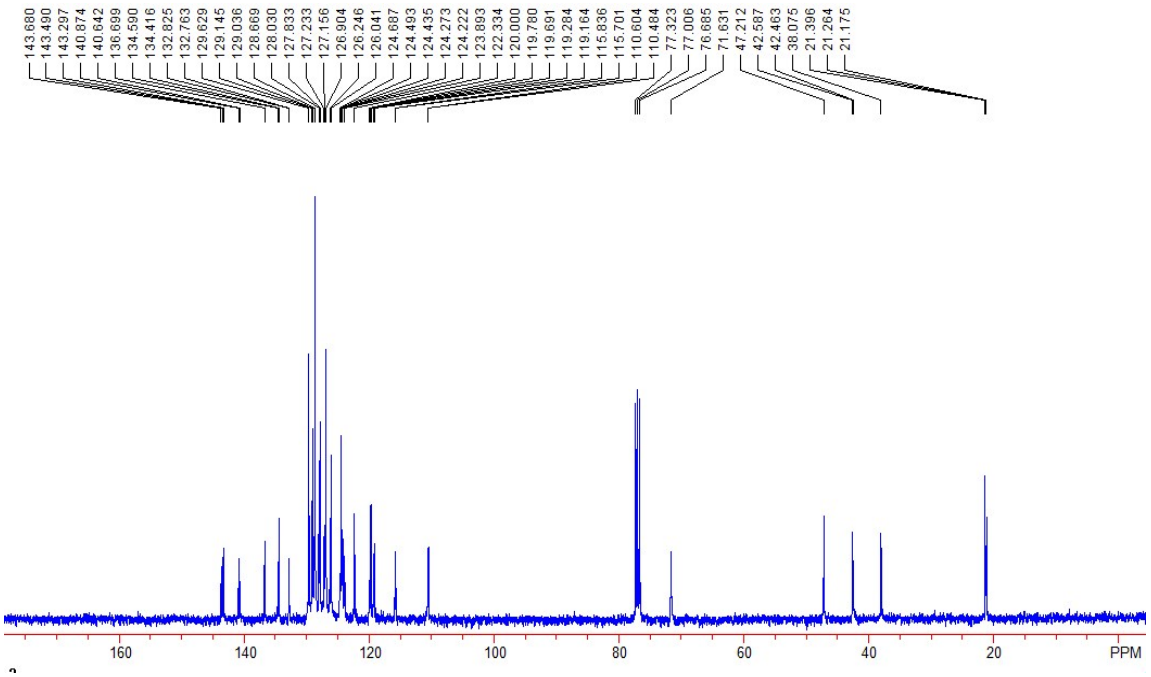


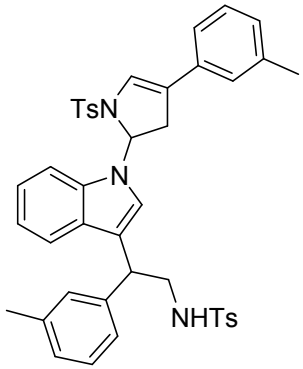
13. Spectroscopic data of the products 4



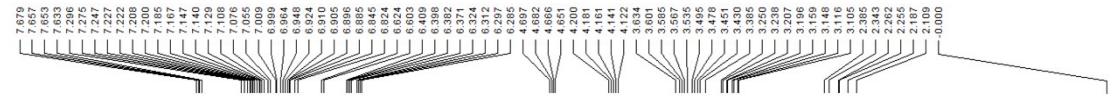
Compound 4aa: Yield: 200 mg, 58% (dr = 1.6:1); A white solid; Mp: 136-138 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.13 (s, 1.80H), 2.20 (s, 1.20H), 2.40 (s, 3H), 3.18 (dd, 0.60H, J_1 = 17.6 Hz, J_2 = 4.8 Hz), 3.25 (dd, 0.40H, J_1 = 17.2 Hz, J_2 = 4.4 Hz), 3.40-3.64 (m, 3H), 4.16-4.24 (m, 1H), 4.55-4.58 (m, 1H), 6.33 (dd, 0.40H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.40 (dd, 0.60H, J_1 = 10.4 Hz, J_2 = 4.4 Hz), 6.66 (d, 1H, J = 8.0 Hz), 6.84-6.99 (m, 4H), 7.03-7.37 (m, 17H) , 7.64-7.68 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 21.2, 21.3, 38.0, 42.4, 42.5, 47.2, 71.6, 110.4, 110.6, 115.7, 115.8, 119.1, 119.2, 119.6, 119.7, 120.0, 121.5, 122.3, 123.8, 124.22, 124.27, 124.43, 124.49, 124.6, 126.0, 126.2, 126.9, 127.1, 127.2, 127.8, 128.0, 128.6, 129.0, 129.1, 129.6, 132.7, 132.8, 134.4, 134.5, 134.7, 140.6, 140.8, 143.2, 143.4, 143.6; IR (neat): ν 3275, 2917, 2848, 2626, 1457, 1327, 1158, 1091, 812, 755, 740, 702, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{40}H_{41}N_4O_4S_2$ $[M+NH_4]^+$: 705.2564, found: 705.2562.

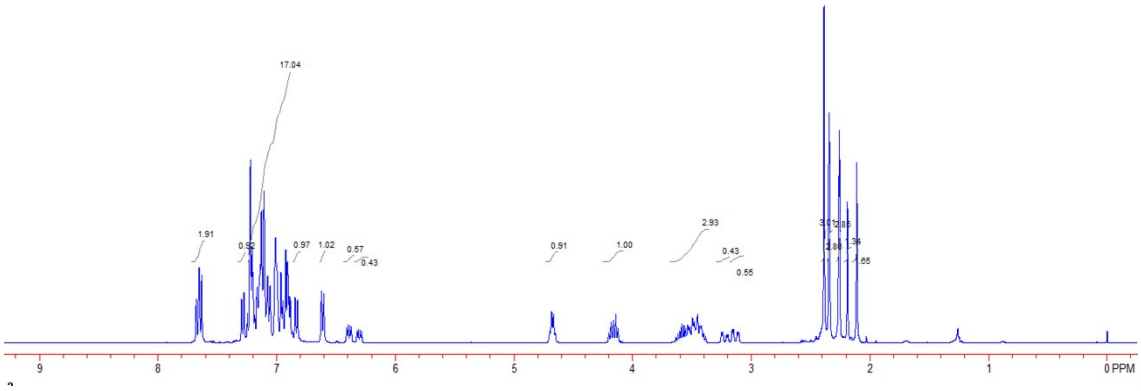


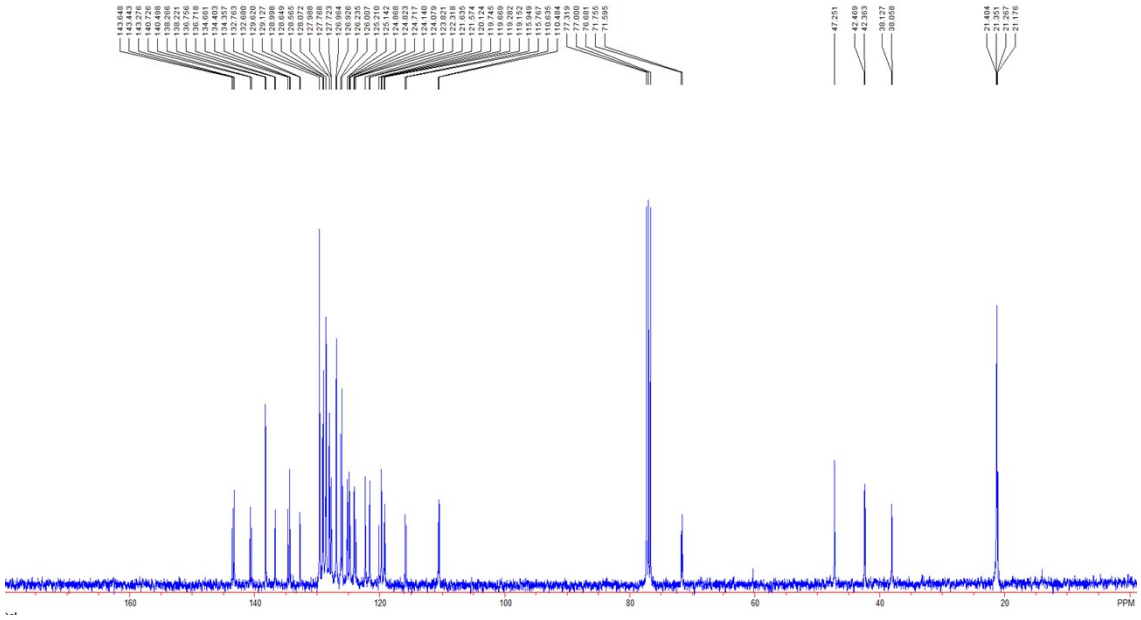


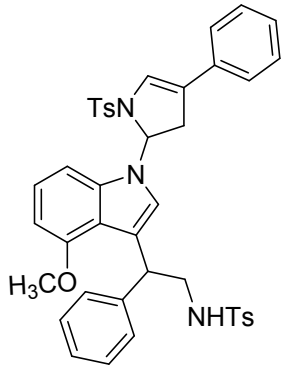


Compound 4ai: Yield: 229 mg, 64% (dr = 1.3:1); A white solid; Mp: 130-132 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.11 (s, 1.71H), 2.19 (s, 1.29H), 2.25 (s, 1.71H), 2.26 (s, 1.29H), 2.34 (s, 3H), 2.38 (s, 3H), 3.13 (dd, 0.57H, J_1 = 17.2 Hz, J_2 = 4.0 Hz), 3.22 (dd, 0.43H, J_1 = 16.8 Hz, J_2 = 4.4 Hz), 3.38-3.63 (m, 3H), 4.12-4.20 (m, 1H), 4.65-4.70 (m, 1H), 6.30 (dd, 0.43H, J_1 = 10.8 Hz, J_2 = 4.8 Hz), 6.39 (dd, 0.57H, J_1 = 10.8 Hz, J_2 = 4.4 Hz), 6.61 (d, 1H, J = 8.4 Hz), 6.83 (d, 1H, J = 8.4 Hz), 6.88-7.22 (m, 17H), 7.28 (d, 1H, J = 8.4 Hz), 7.63-7.68 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 21.2, 21.3, 21.4, 38.0, 38.1, 42.3, 42.4, 47.2, 71.6, 71.7, 110.4, 110.6, 115.7, 115.9, 119.1, 119.2, 119.6, 119.7, 120.1, 121.5, 121.6, 122.3, 123.8, 124.0, 124.1, 124.7, 124.82, 124.86, 125.1, 125.2, 126.0, 126.2, 126.92, 126.96, 127.72, 127.76, 127.9, 128.0, 128.5, 128.6, 129.0, 129.1, 129.6, 132.6, 132.7, 134.3, 134.4, 134.6, 136.71, 136.75, 138.22, 138.26, 140.5, 140.7, 143.2, 143.4, 143.6; IR (neat): ν 3028, 2917, 1457, 1324, 1158, 1088, 808, 702, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{42}H_{45}N_4O_4S_2$ $[M+NH_4]^+$: 733.2877, found: 733.2873.



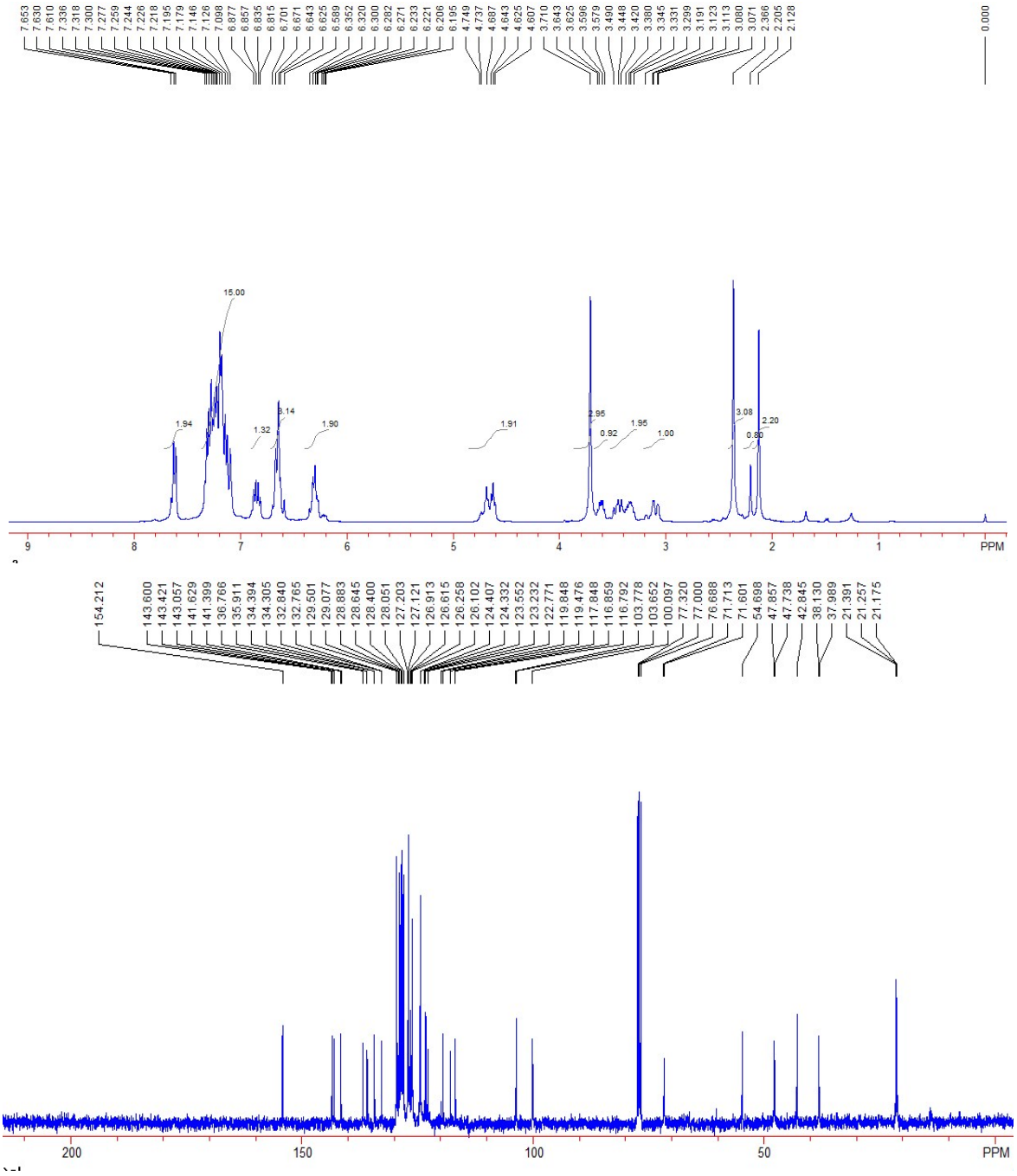


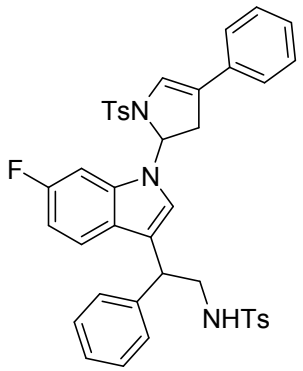




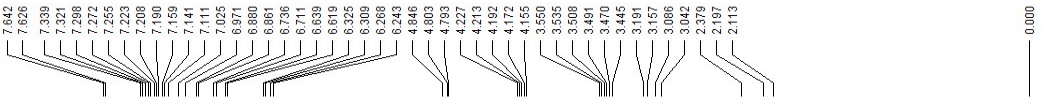
Compound 4ia: Yield: 229 mg, 64% (dr = 2.8:1); A white solid; Mp: 133-135 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.12 (s, 2.21H), 2.20 (s, 0.79H), 2.36 (s, 3H), 3.07-3.19 (m, 1H), 3.30-3.49 (m, 2H), 3.58-3.64 (m, 1H), 3.71 (s, 3H), 4.60-4.75 (m, 2H), 6.19-6.35 (m, 2H), 6.58-6.70 (m, 3H), 6.81-6.87 (m, 1H), 7.09-7.33 (m, 15H), 7.61-

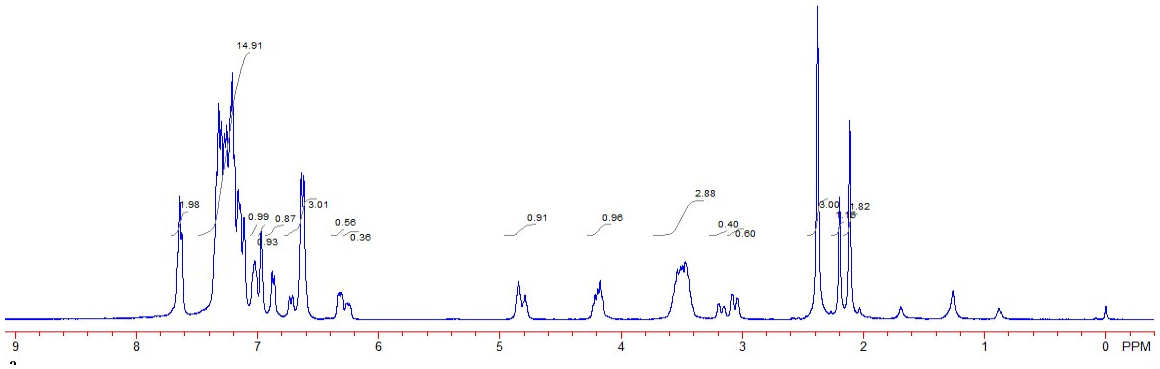
7.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 21.2, 21.3, 38.0, 38.1, 42.8, 47.7, 47.8, 54.7, 71.6, 71.7, 100.1, 103.6, 103.7, 116.7, 116.8, 117.8, 119.4, 119.8, 122.7, 123.2, 123.5, 124.3, 124.4, 126.1, 126.2, 126.6, 126.9, 127.1, 127.2, 128.0, 128.4, 128.6, 128.8, 129.0, 129.5, 132.7, 132.8, 134.3, 134.4, 135.9, 136.7, 141.4, 141.6, 143.0, 143.4, 143.6, 154.2; IR (neat): ν 3297, 3025, 2923, 2596, 1490, 1438, 1326, 1260, 1157, 1091, 1070, 813, 757, 733, 701, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{41}H_{43}N_4O_5S_2$ $[M+NH_4]^+$: 735.2669, found: 735.2667.

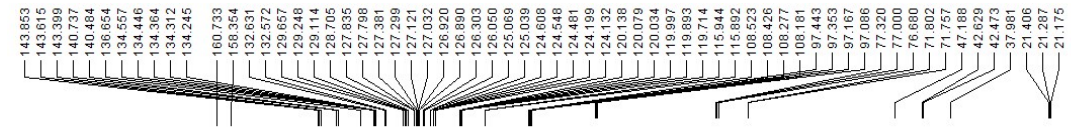


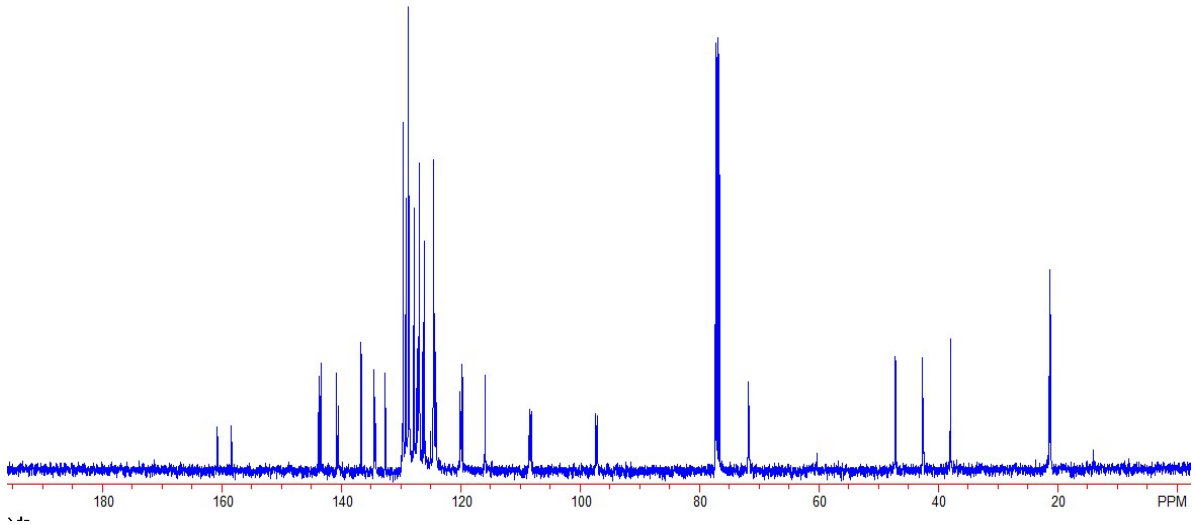


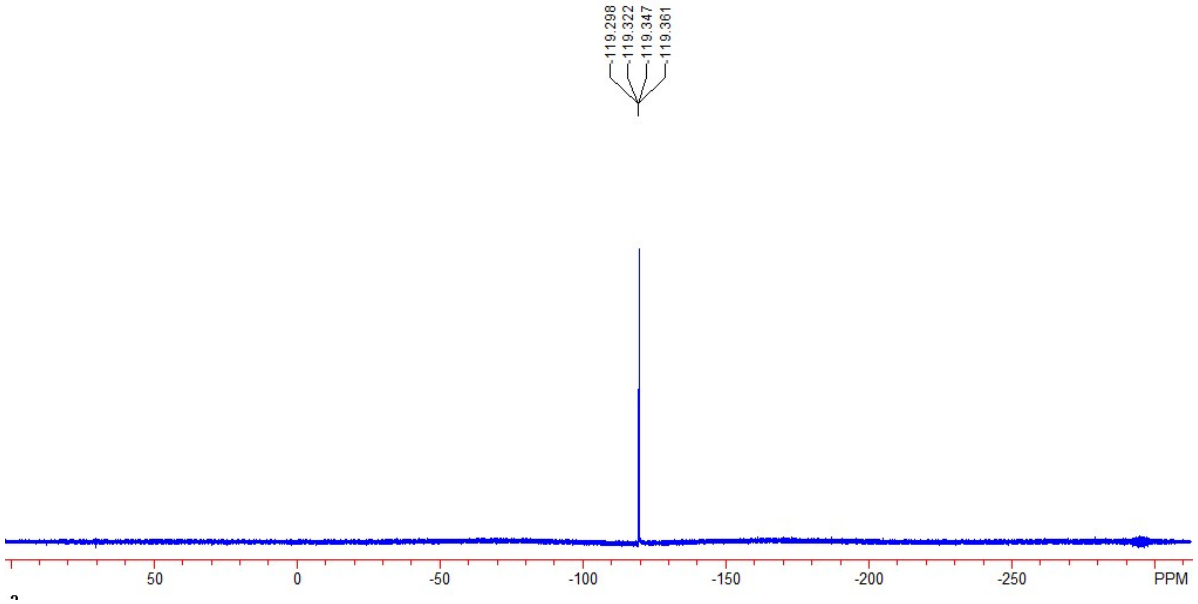
Compound 4ba: Yield: 260 mg, 74% (dr = 1.6:1); A white solid; Mp: 129-131 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.11 (s, 1.80H), 2.19 (s, 1.20H), 2.38 (s, 3H), 3.06 (d, 0.60H, *J* = 17.6 Hz), 3.17 (d, 0.40H, *J* = 13.6 Hz), 3.44-3.55 (m, 3H), 4.15-4.22 (m, 1H), 4.79-4.84 (m, 1H), 6.25 (d, 0.40H, *J* = 10.0 Hz), 6.32 (d, 0.60H, *J* = 6.4 Hz), 6.62-6.73 (m, 3H), 6.87 (d, 1H, *J* = 7.6 Hz), 6.97 (s, 1H), 7.02 (s, 1H), 7.11-7.34 (m, 15H), 7.62-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 21.2, 21.4, 37.9, 42.4, 42.6, 47.1, 71.7, 71.8, 97.2 (d, *J* = 26.7 Hz), 97.4 (d, *J* = 27.6 Hz), 108.3 (d, *J* = 24.5 Hz), 108.4 (d, *J* = 24.5 Hz), 115.8, 115.9, 119.7, 119.8, 119.9 (d, *J* = 10.4 Hz), 120.0 (d, *J* = 10.4 Hz), 124.13, 124.19, 124.4, 124.5, 124.6, 125.0 (d, *J* = 3.0 Hz), 126.0, 126.3, 126.8, 126.9, 127.0, 127.1, 127.2, 127.3, 127.7, 127.8, 128.7, 129.1, 129.2, 129.6, 132.5, 132.6, 134.2 (d, *J* = 6.7 Hz), 134.4 (d, *J* = 8.2 Hz), 134.5, 136.6, 140.4, 140.7, 143.4, 143.6, 143.8, 159.5 (d, *J* = 237.9 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -119.36 ~ -119.29 (m); IR (neat): ν 3289, 3025, 2920, 1618, 1599, 1449, 1326, 1156, 1091, 811, 755, 696, 664 cm^{-1}; HRMS (ESI) Calcd. for $C_{40}H_{40}FN_4O_4S_2$ $[M+NH_4]^+$: 723.2470, found: 723.2467.

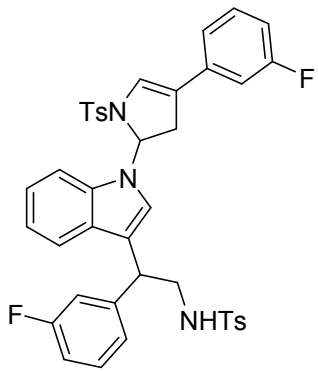






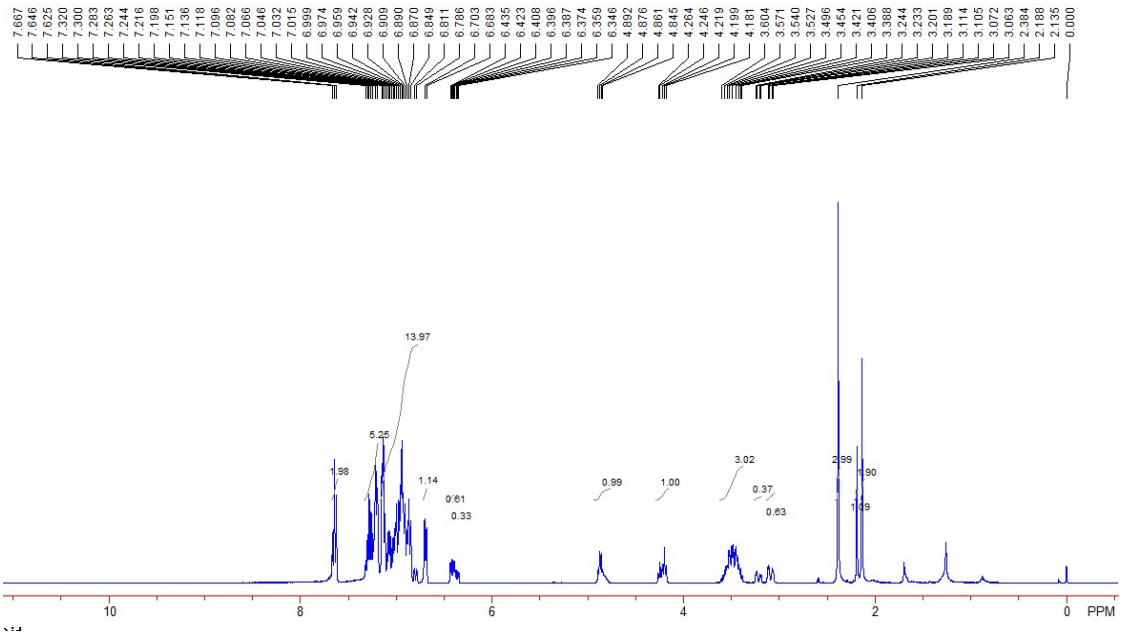


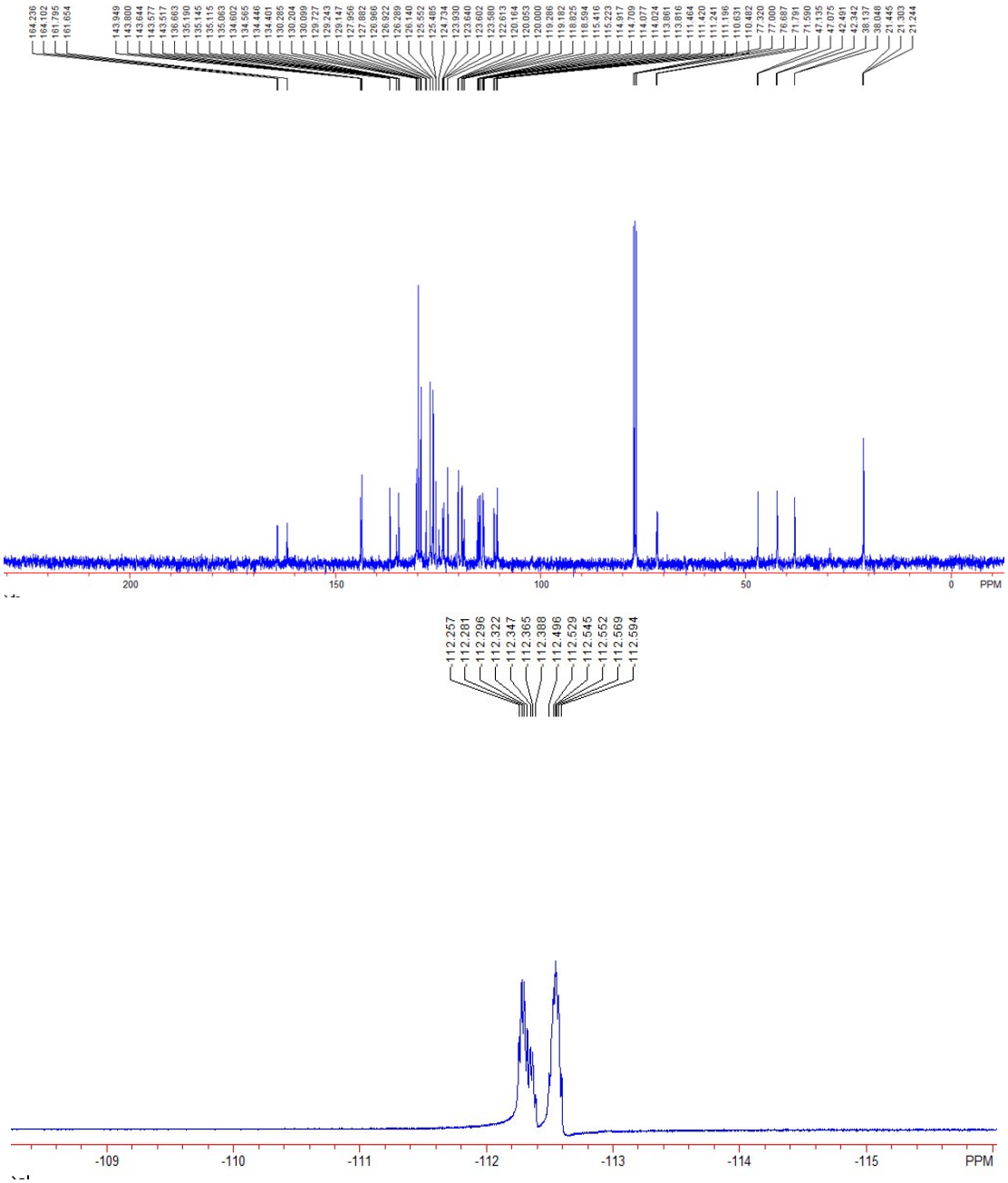


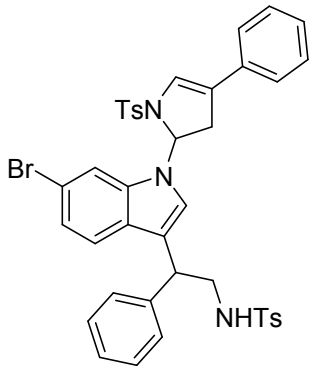


Compound 4ah: Yield: 209 mg, 58% (dr = 1.7:1); A white solid; Mp: 120-122 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.13 (s, 1.89H), 2.18

(s, 1.11H), 2.38 (s, 3H), 3.09 (dd, 0.63H, J_1 = 16.8 Hz, J_2 = 3.6 Hz), 3.21 (dd, 0.37H, J_1 = 17.6 Hz, J_2 = 4.8 Hz), 3.38-3.60 (m, 3H), 4.18-4.26 (m, 1H), 4.84-4.89 (m, 1H), 6.37 (dd, 0.37H, J_1 = 12.4 Hz, J_2 = 5.2 Hz), 6.41 (dd, 0.63H, J_1 = 10.8 Hz, J_2 = 4.8 Hz), 6.69 (d, 1H, J = 8.0 Hz), 6.78-7.15 (m, 14H), 7.19-7.32 (m, 5H), 7.62-7.66 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 21.3, 21.4, 38.0, 38.1, 42.3, 42.4, 47.0, 47.1, 71.5, 71.7, 110.4, 110.6, 111.31 (d, J = 22.4 Hz), 111.35 (d, J = 22.3 Hz), 113.92 (d, J = 21.6 Hz), 113.97 (d, J = 20.8 Hz), 114.0, 114.7, 114.9, 115.2, 115.4, 118.5, 118.8, 119.2 (d, J = 10.4 Hz), 120.1 (d, J = 11.1 Hz), 122.6, 123.5 (d, J = 2.2 Hz), 123.6, 123.9, 124.7, 125.4, 125.5, 126.1, 126.2, 126.92, 126.96, 127.8, 127.9, 129.1, 129.2, 129.7, 130.1, 130.20, 130.28, 134.40, 134.44, 134.5, 134.6, 135.0 (d, J = 5.2 Hz), 135.2 (d, J = 5.5 Hz), 136.6, 143.51, 143.57, 143.6, 143.8, 143.9, 162.8 (d, J = 244.8 Hz), 163.0 (d, J = 244.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -112.59 ~ -112.49 (m), -112.38 ~ -112.25 (m); IR (neat): ν 3286, 3056, 2923, 1612, 1579, 1488, 1460, 1327, 1185, 1156, 1090, 994, 811, 780, 740, 703, 662 cm^{-1}; HRMS (ESI) Calcd. for $C_{40}H_{39}F_2N_4O_4S_2$ $[M+NH_4]^+$: 741.2375, found: 741.2372.

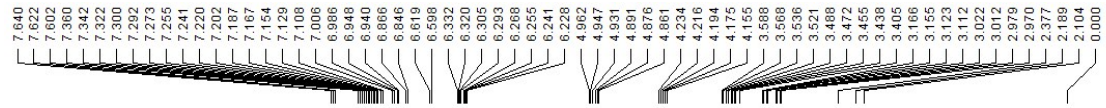


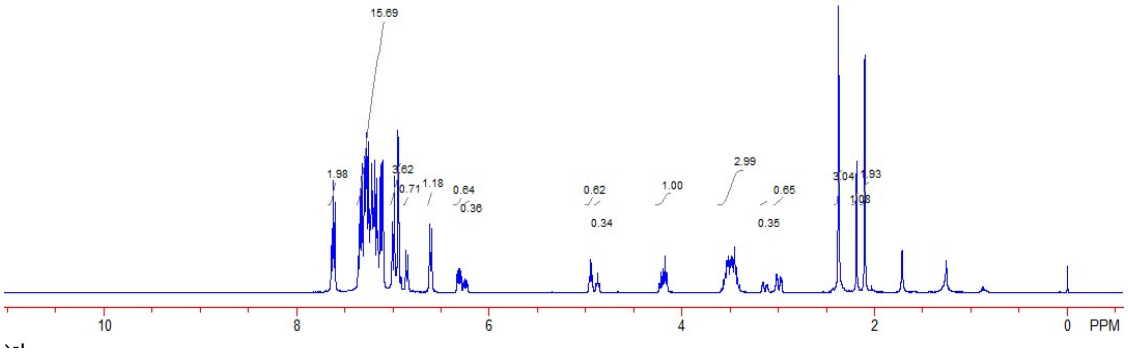


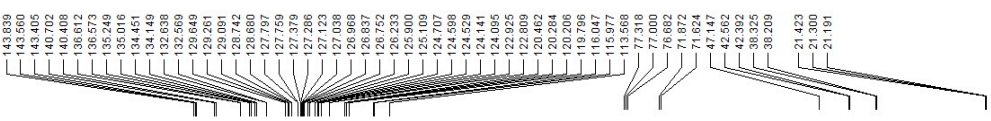


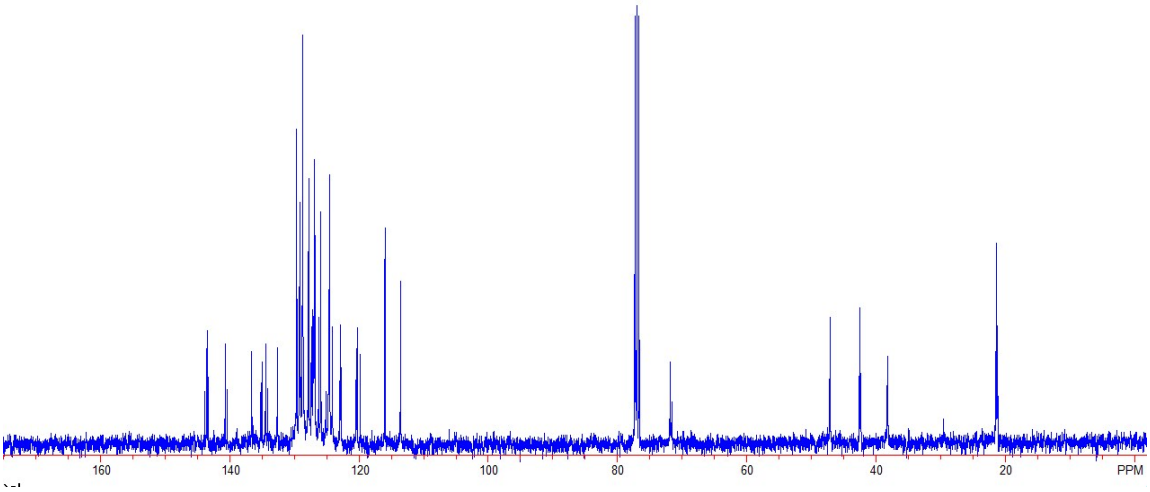
Compound 4ca: Yield: 210 mg, 55% (dr = 1.9:1); A white solid; Mp: 128-130 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.10 (s, 1.95H), 2.19 (s, 1.05H), 2.37 (s, 3H), 2.99 (dd, 0.65H, J_1 = 16.8 Hz, J_2 = 3.6 Hz), 3.14 (dd, 0.35H, J_1 = 17.2 Hz, J_2 = 4.4 Hz), 3.40-3.58 (m, 3H), 4.15-4.23 (m, 1H),

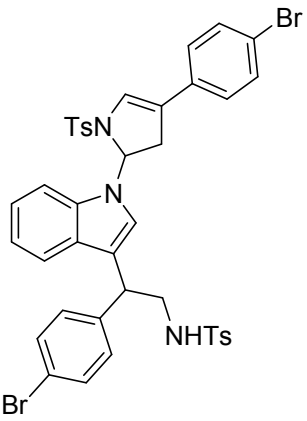
4.87 (dd, 0.35H, $J_1 = J_2 = 10.0$ Hz), 4.94 (dd, 0.65H, $J_1 = J_2 = 10.0$ Hz), 6.25 (dd, 0.35H, $J_1 = 10.8$ Hz, $J_2 = 5.2$ Hz), 6.31 (dd, 0.65H, $J_1 = 10.8$ Hz, $J_2 = 4.8$ Hz), 6.61 (d, 1H, $J = 8.4$ Hz), 6.85 (d, 0.65H, $J = 8.0$ Hz), 6.94-7.00 (m, 3.65H), 7.10-7.36 (m, 15.65H), 7.60-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 21.3, 21.4, 38.2, 38.3, 42.4, 42.5, 47.1, 71.6, 71.8, 113.5, 115.9, 116.0, 119.7, 120.2, 120.4, 122.8, 122.9, 124.0, 124.1, 124.52, 124.59, 124.7, 125.1, 125.9, 126.2, 126.7, 126.8, 126.9, 127.0, 127.1, 127.2, 127.3, 127.75, 127.79, 128.6, 128.7, 129.0, 129.2, 129.6, 132.5, 132.6, 134.1, 134.4, 135.0, 135.2, 136.5, 136.6, 140.4, 140.7, 143.4, 143.5, 143.8; IR (neat): ν 3278, 3031, 2920, 1593, 1449, 1324, 1158, 1091, 810, 754, 701, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{40}H_{40}BrN_4O_4S_2$ $[M+NH_4]^+$: 783.1669, found: 783.1663.



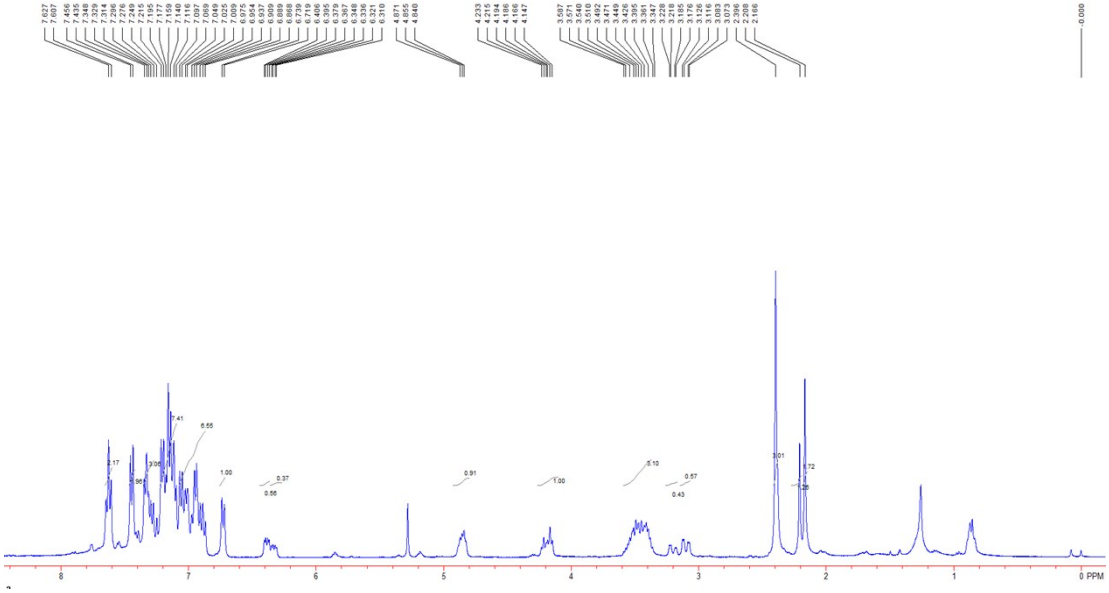


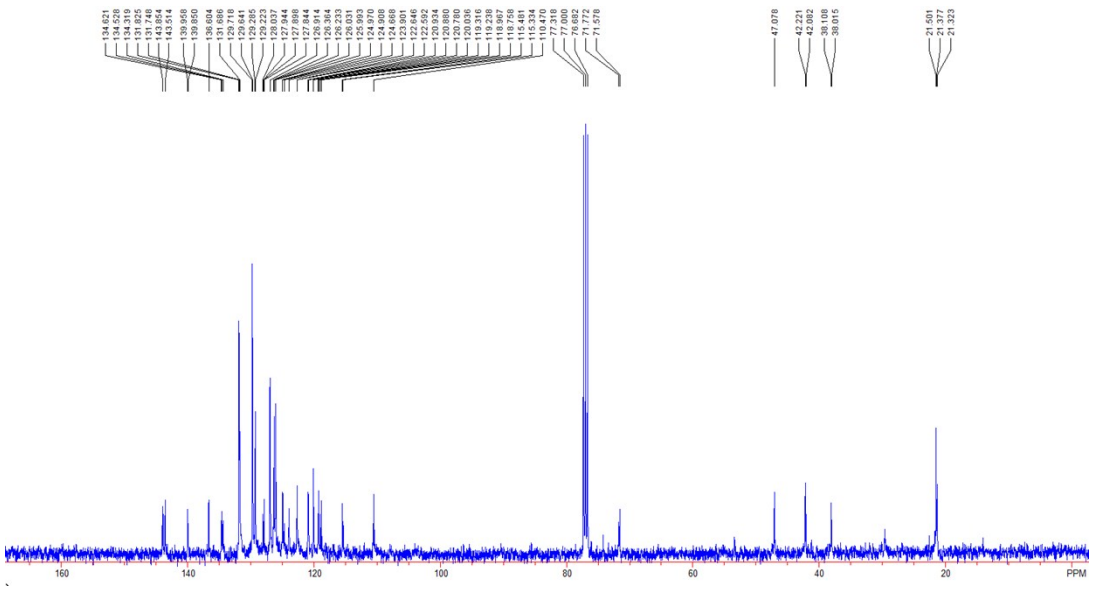






Compound 4as: Yield: 190 mg, 45% (dr = 1.3:1); A white solid; Mp: 150-152 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.16 (s, 1.71H), 2.20 (s, 1.29H), 2.40 (s, 3H), 3.10 (dd, 0.57H, J_1 = 17.2 Hz, J_2 = 4.0 Hz), 3.20 (dd, 0.43H, J_1 = 17.2 Hz, J_2 = 4.0 Hz), 3.33-3.58 (m, 3H), 4.14-4.23 (m, 1H), 4.80-4.87 (m, 1H), 6.33 (dd, 0.43H, J_1 = 10.8 Hz, J_2 = 4.8 Hz), 6.38 (dd, 0.57H, J_1 = 11.2 Hz, J_2 = 4.8 Hz), 6.73 (d, 1H, J = 8.0 Hz), 6.86-7.06 (m, 6.57H), 7.09-7.21 (m, 7.43H), 7.24-7.34 (m, 3H), 7.43-7.45 (m, 2H), 7.60-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.32, 21.37, 21.5, 38.0, 38.1, 42.0, 42.2, 47.0, 71.5, 71.7, 110.4, 115.3, 115.4, 118.7, 118.9, 119.2, 119.3, 120.0, 120.7, 120.8, 120.9, 122.5, 122.6, 123.9, 124.6, 124.90, 124.97, 125.9, 126.0, 126.2, 126.3, 126.9, 127.84, 127.89, 127.9, 128.0, 129.2, 129.6, 129.7, 131.6, 131.7, 131.8, 134.3, 134.5, 134.6, 136.6, 139.8, 139.9, 143.5, 143.6; IR (neat): ν 3294, 3053, 2923, 1624, 1593, 1488, 1460, 1329, 1156, 1090, 1074, 1007, 81, 738, 703, 665 cm^{-1}; HRMS (ESI) Calcd. for $C_{40}H_{39}Br_2N_4O_4S_2$ $[M+NH_4]^+$: 861.0774, found: 861.0761.




134.621
134.458
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131.825
131.748
131.464
143.514
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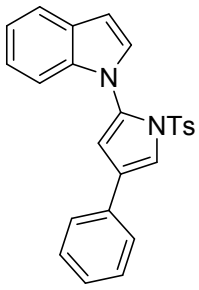
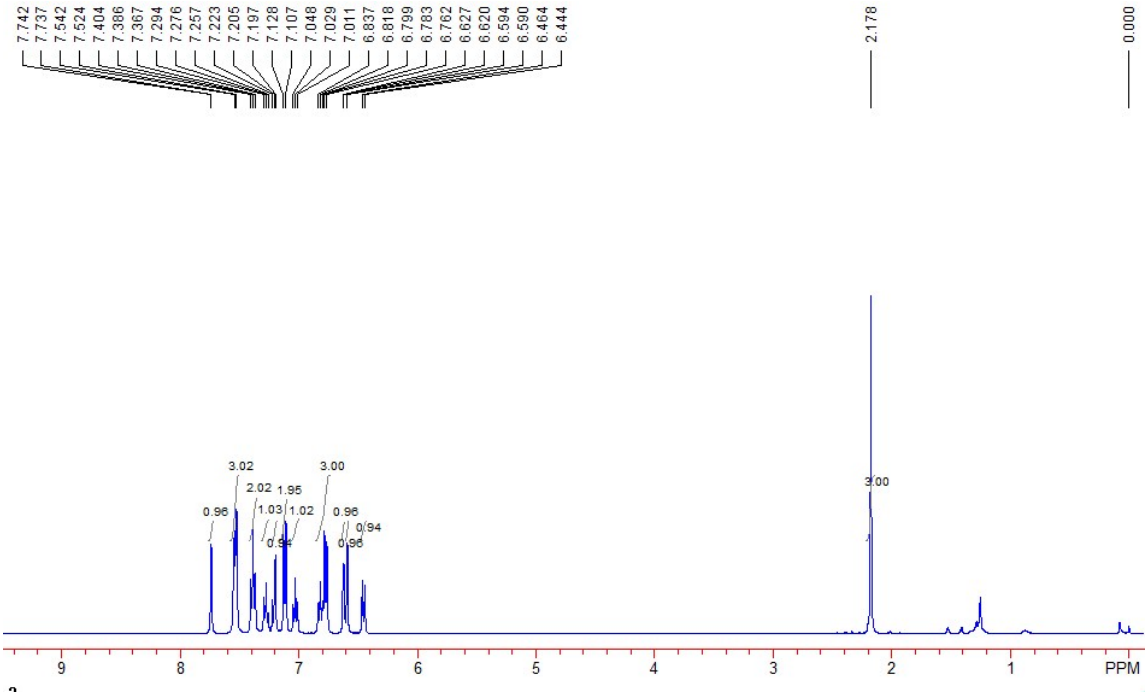
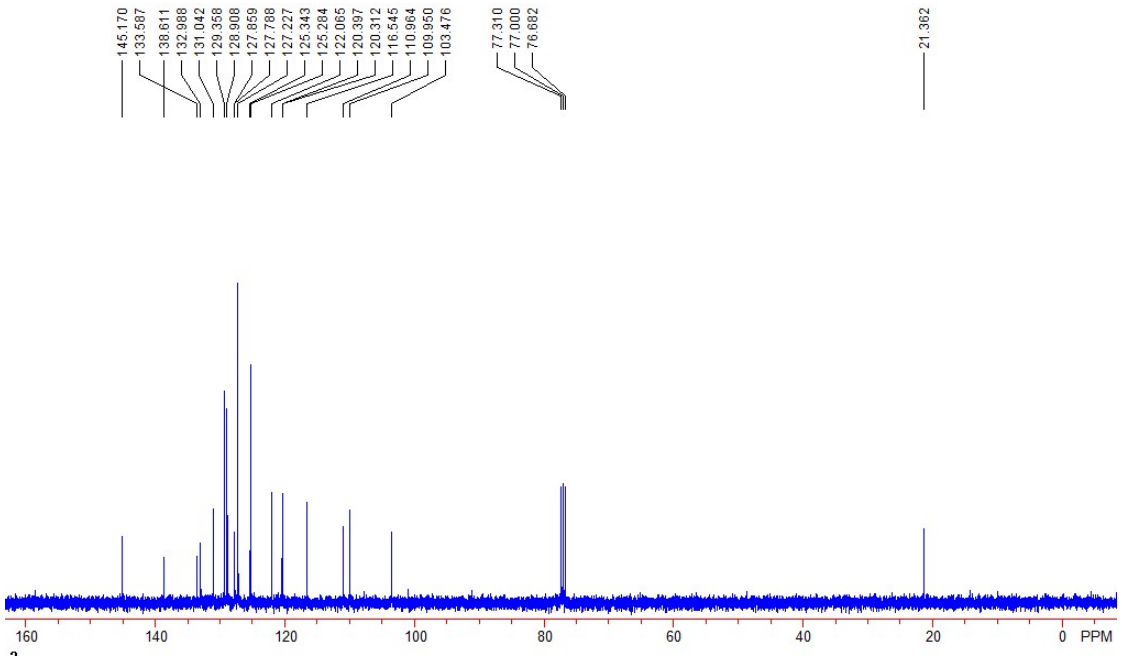
71.772
71.578
47.976
42.221
42.082
38.108
38.015
21.591
21.377
21.323
160
140
120
100
80
60
40
20
PPM

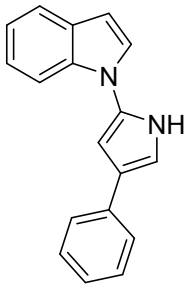
14. Spectroscopic data of the products 3aa', 3aa'', 4ca', 4aa'



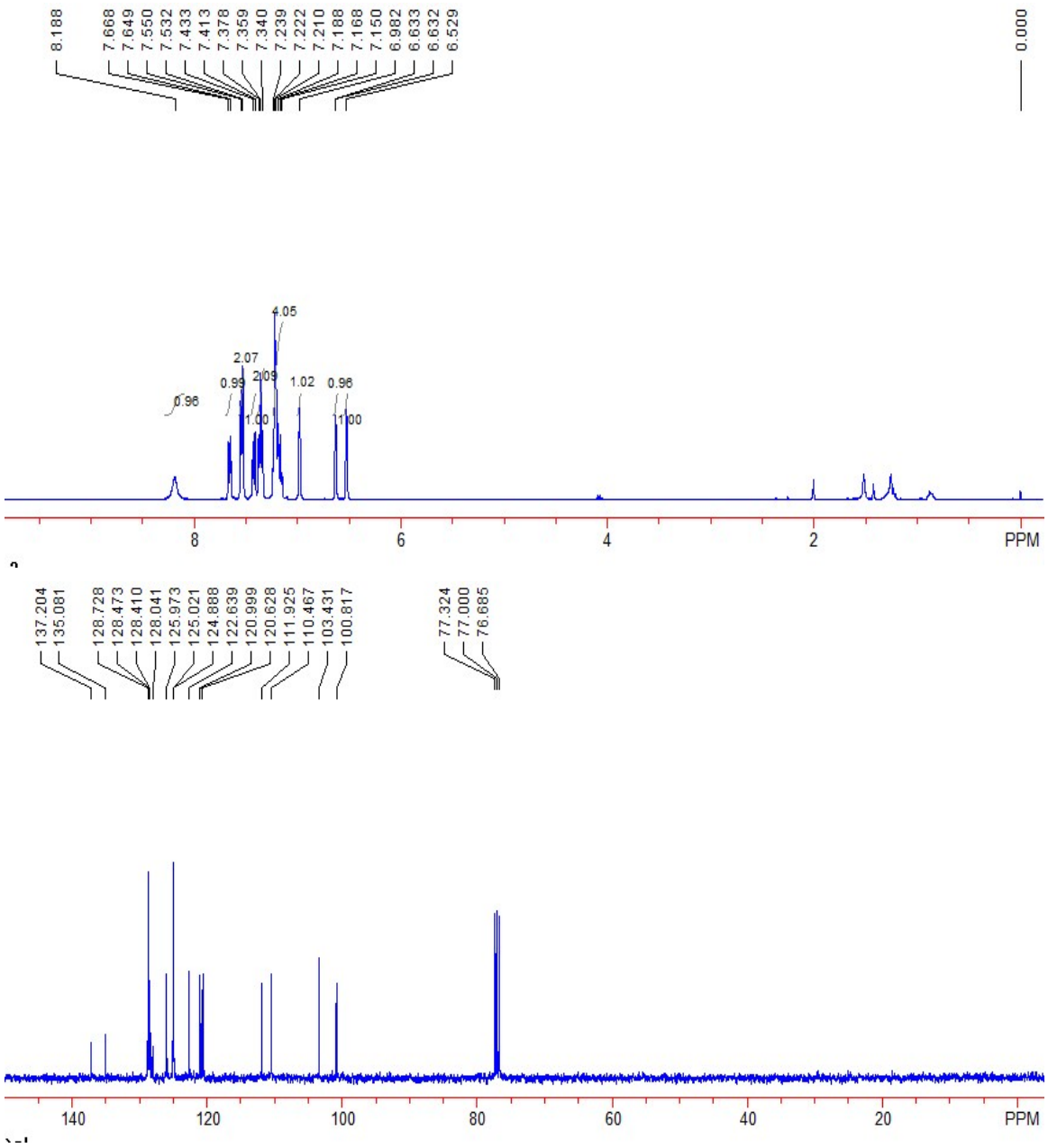
Compound 3aa': Yield: 120 mg, 58% A white solid; Mp: 119-121 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.17 (s, 3H), 6.45 (d, 1H, J = 8.0 Hz), 6.59 (d, 1H, J = 1.6 Hz), 6.62 (d, 1H, J = 2.8 Hz), 6.76-6.83 (m, 3H), 7.03 (dd, 1H, $J_1 = J_2$ = 7.2 Hz), 7.11 (d, 2H, J = 8.4 Hz), 7.20 (d, 1H, J = 3.2 Hz), 7.27 (dd, 1H, $J_1 = J_2$ = 7.2 Hz), 7.38 (dd, 2H, $J_1 = J_2$ = 7.2 Hz), 7.53 (d, 3H, J = 7.2 Hz), 7.74 (d, 1H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 103.4, 109.9, 110.9, 116.5, 120.31, 120.39, 122.0, 125.2, 125.3, 127.2, 127.7, 127.8, 128.9, 129.3, 131.0, 132.9, 133.5, 138.6, 145.1; IR (neat): ν 3136, 3106, 3025, 1598, 1534, 1452, 1364, 1302, 1287, 1205, 1187, 1167, 1132, 1108, 1090, 1042, 767, 757, 743, 716, 699, 693, 666, 659 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{21}N_2O_2S$ $[M+H]^+$: 413.1318, found: 413.1316.

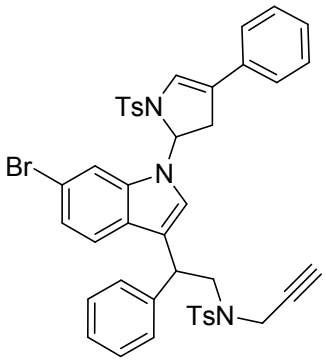






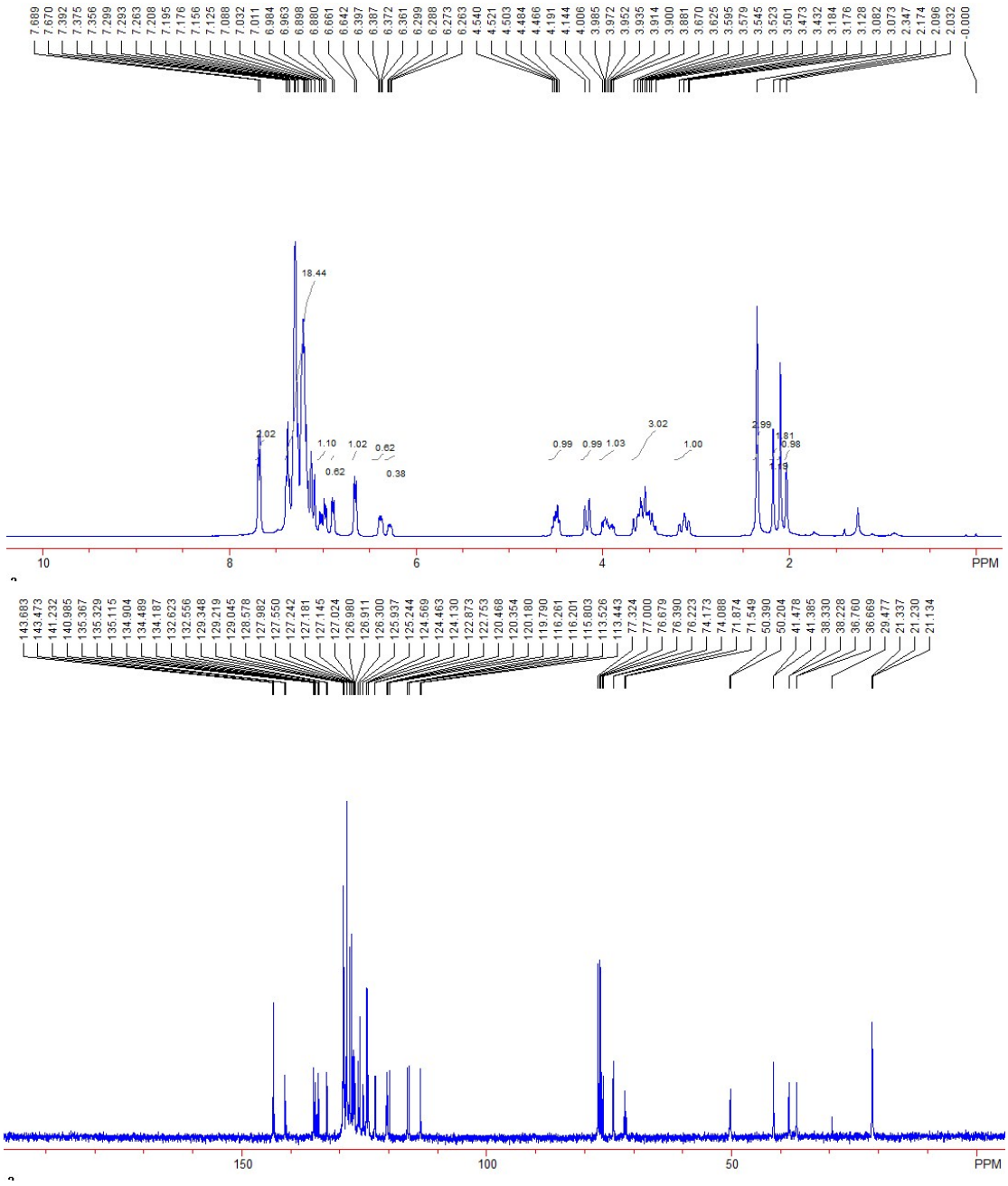
Compound 3aa'': Yield: 80 mg, 80%; A red solid; Mp: 126-128 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 6.52 (s, 1H), 6.63 (d, 1H, J = 0.4 Hz), 7.15-7.22 (m, 4H), 7.36 (dd, 2H, $J_1 = J_2$ = 7.6 Hz), 7.42 (d, 1H, J = 8.0 Hz), 7.54 (d, 2H, J = 7.2 Hz), 7.66 (d, 1H, J = 7.6 Hz), 8.18 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 100.8, 103.4, 110.4, 111.9, 120.6, 120.9, 122.6, 124.8, 125.0, 125.9, 128.0, 128.41, 128.47, 128.7, 135.0, 137.2; IR (neat): ν 3377, 2923, 2845, 1590, 1530, 1456, 1428, 1211, 1137, 1124, 1112, 923, 807, 746, 728, 694, 672 cm^{-1}; HRMS (ESI) Calcd. for $C_{18}H_{15}N_2$ $[M+NH_4]^+$: 259.1232, found: 259.1230.

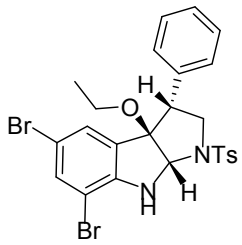




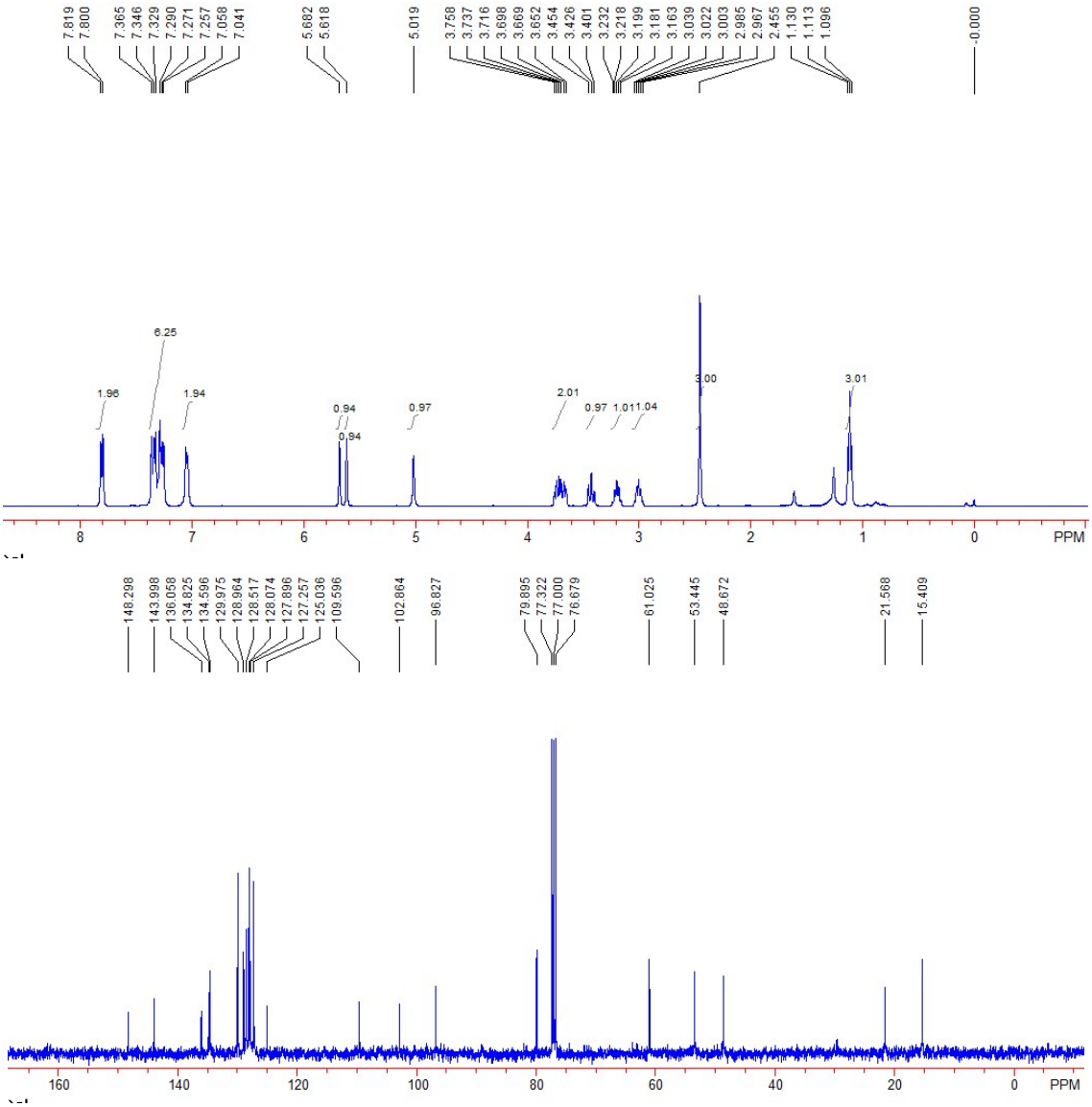
Compound 4ca': Yield: 310 mg, 77% A yellow solid; Mp: 160-162 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.03 (s, 1H), 2.09 (s, 1.86H), 2.17 (s, 1.14H), 2.34 (s, 3H), 3.07-3.18 (m, 1H), 3.43-3.67 (m, 3H), 3.88-4.00 (m, 1H), 4.17 (d, 1H, J = 18.8 Hz), 4.46-4.54 (m, 1H), 6.28 (dd, 0.38H, J_1 = 10.0 Hz, J_2 = 4.0 Hz), 6.38 (dd, 0.62H, J_1 = 10.0 Hz, J_2 = 4.0 Hz), 6.65 (d, 1H, J = 7.6 Hz), 6.89 (d,

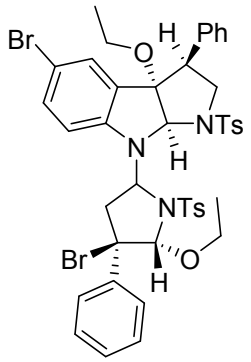
0.62H, J = 7.2 Hz), 6.96-7.03 (m, 1H), 7.08-7.39 (m, 18.38H), 7.68 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 21.2, 21.3, 29.4, 36.6, 36.7, 38.2, 38.3, 41.3, 41.4, 50.2, 50.3, 71.5, 71.8, 74.0, 74.1, 76.2, 76.3, 113.4, 113.5, 115.8, 116.20, 116.26, 119.7, 120.1, 120.3, 120.4, 122.7, 122.8, 124.1, 124.4, 124.5, 125.2, 125.9, 126.3, 126.91, 126.98, 127.0, 127.14, 127.18, 127.2, 127.5, 127.9, 128.5, 129.0, 129.2, 129.3, 132.5, 132.6, 134.1, 134.4, 134.9, 135.1, 135.32, 135.36, 140.9, 141.2, 143.4, 143.6; IR (neat): ν 3264, 3025, 2928, 2853, 1629, 1596, 1463, 1342, 1326, 1158, 1091, 996, 902, 806, 756, 702, 663 cm^{-1}; HRMS (ESI) Calcd. for $C_{43}H_{42}BrN_4O_4S_2$ $[M+NH_4]^+$: 821.1825, found: 821.1821.



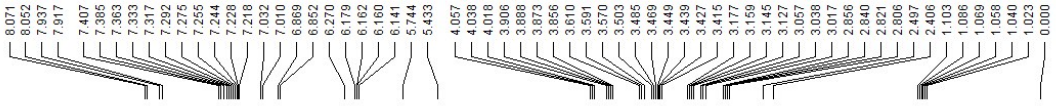


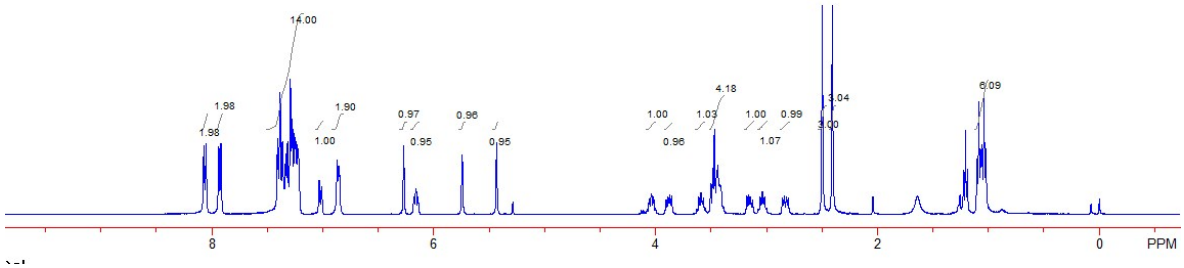
Compound 4aa': Yield: 68 mg, 58%; A white solid; Mp: 201-203 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, 3H, *J* = 6.8 Hz), 2.45 (s, 3H), 2.96-3.03 (m, 1H), 3.16-3.23 (m, 1H), 3.42 (t, 1H, *J* = 10.0 Hz), 3.65-3.75 (m, 2H), 5.01 (s, 1H), 5.61 (s, 1H), 5.68 (s, 1H), 7.05 (d, 2H, *J* = 6.8 Hz), 7.25-7.36 (m, 6H), 7.81 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.4, 21.5, 48.6, 53.4, 61.0, 79.8, 96.8, 102.8, 109.5, 125.0, 127.2, 127.8, 128.0, 128.5, 128.9, 129.9, 134.5, 134.8, 136.0, 143.9, 148.2; IR (neat): ν 3067, 2982, 2917, 1597, 1465, 1328, 1159, 1145, 1089, 1064, 1045, 1013, 965, 896, 810, 706, 660 cm^{-1}; HRMS (ESI) Calcd. for $C_{25}H_{25}Br_2N_2O_3S$ $[M+H]^+$: 590.9947, found: 590.9944.

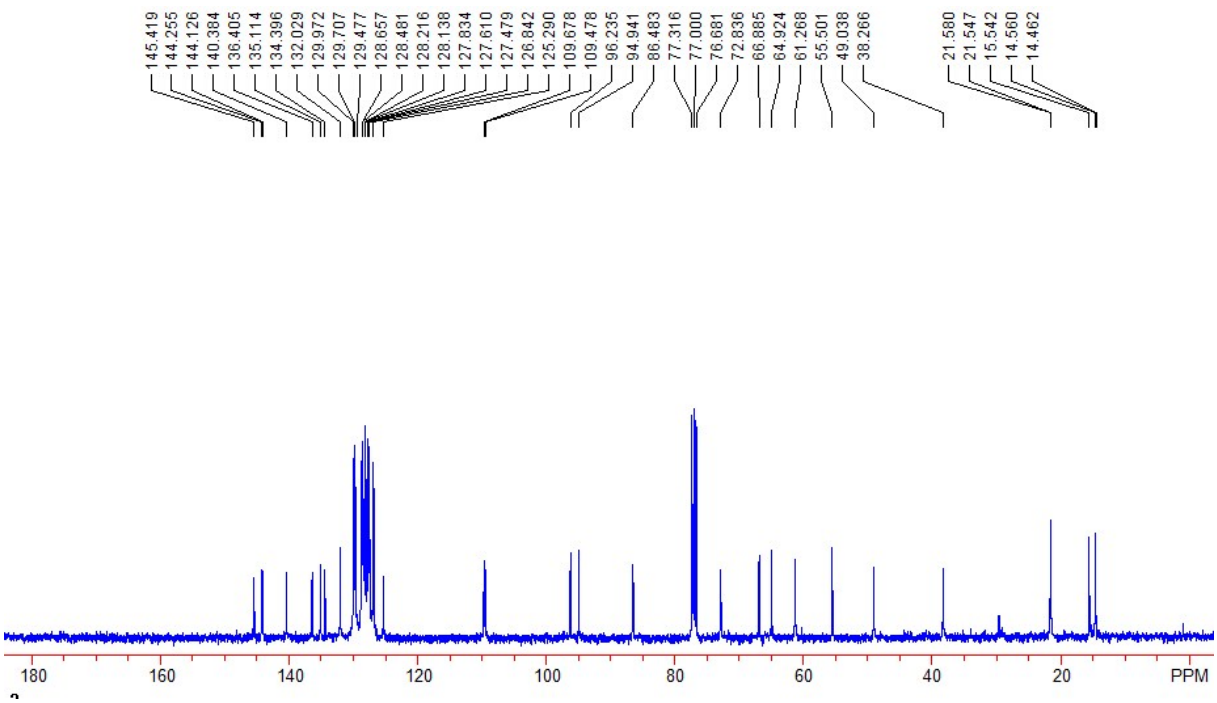




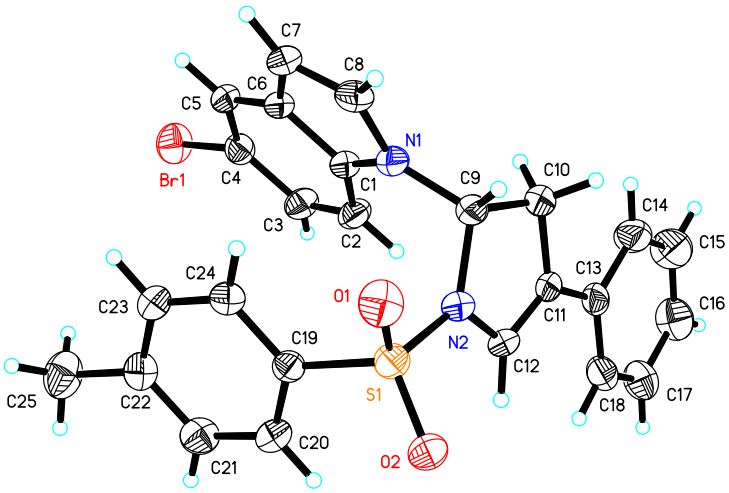
Compound 4aa'': Yield: 120 mg, 25%; A white solid; Mp: 155-157 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.02-1.10 (m, 6H), 2.40 (s, 3H), 2.49 (s, 3H), 2.83 (dd, 1H, J_1 = 14.0 Hz, J_2 = 6.0 Hz), 3.00-3.07 (m, 1H), 3.15 (dd, 1H, J_1 = 12.8 Hz, J_2 = 7.2 Hz), 3.41-3.50 (m, 4H), 3.5-3.6 (m, 1H), 3.88 (dd, 1H, J_1 = 12.8 Hz, J_2 = 7.2 Hz), 4.0-4.0 (m, 1H), 5.43 (s, 1H), 5.74 (s, 1H), 6.16 (d, 1H, J = 7.6 Hz), 6.27 (s, 1H), 6.86 (d, 2H, J = 6.8 Hz), 7.02 (d, 1H, J = 8.8 Hz), 7.21-7.40 (m, 14H), 7.92 (d, 2H, J = 8.0 Hz), 8.06 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.5, 15.5, 21.54, 21.58, 38.2, 49.0, 55.5, 61.2, 64.9, 66.8, 72.8, 86.4, 94.9, 96.2, 109.4, 109.6, 125.2, 126.8, 127.4, 127.6, 127.8, 128.1, 128.2, 128.4, 128.6, 129.7, 129.9, 132.0, 134.3, 135.1, 136.4, 140.3, 144.1, 144.2, 145.4; IR (neat): ν 2977, 2920, 1595, 1484, 1349, 1334, 1173, 1163, 2982, 2917, 1597, 1465, 1328, 1159, 1145, 1089, 1064, 1045, 1013, 1095, 1078, 1066, 1038, 1010, 1002, 948, 832, 817, 704, 698, 666 cm^{-1}; HRMS (DART) Calcd. for $C_{44}H_{46}Br_2N_3O_6S_2$ $[M+H]^+$: 934.1189, found: 934.1189.





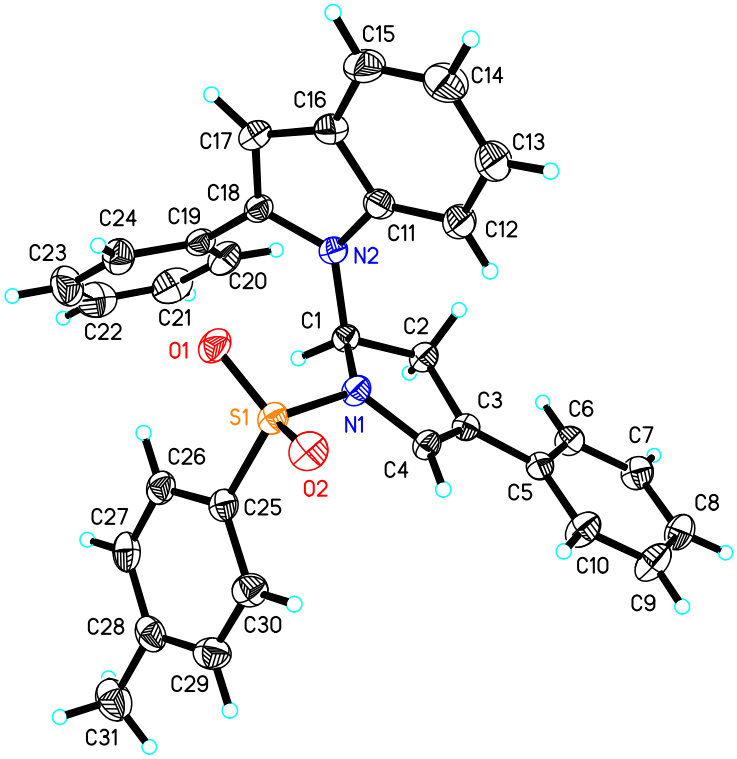

145.419
144.255
144.126
140.384
136.405
135.114
134.396
132.029
129.972
129.707
129.477
128.657
128.481
128.216
128.138
127.834
127.610
127.479
126.842
125.290
109.678
109.478
96.235
94.941
86.483
77.316
77.000
76.681
72.836
66.885
64.924
61.268
55.501
49.038
38.266
21.580
21.547
15.542
14.560
14.462
180
160
140
120
100
80
60
40
20
PPM

X-ray Crystal Data of 3da



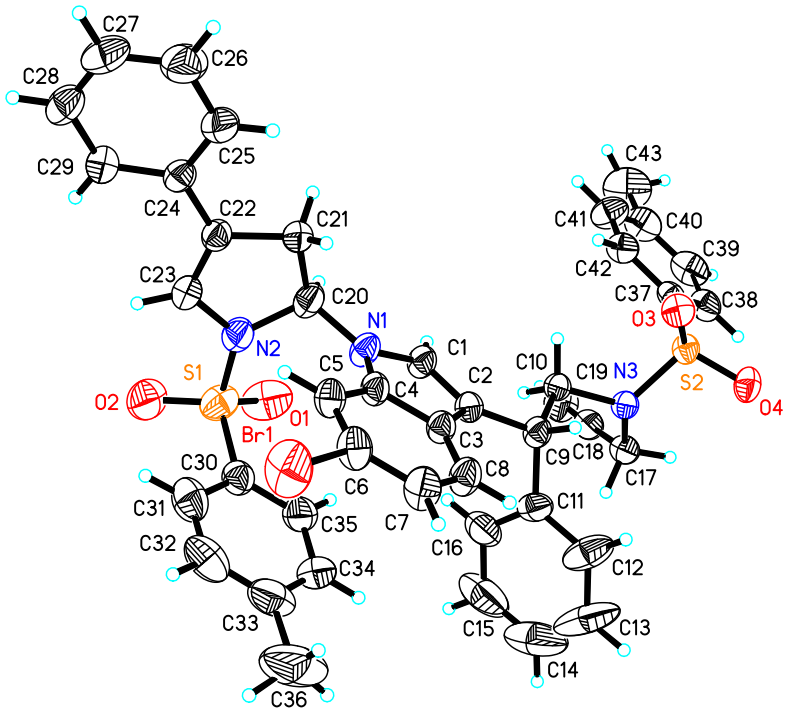
The crystal data of **3da** have been deposited in CCDC with number 1538040. Empirical formula: $C_{25}H_{21}BrN_2O_2S$, Formula weight: 493.41, Crystal system: Monoclinic, Space group: C 2/c, Unit cell dimensions: a = 24.816(3) Å, α = 90°; b = 10.4010(11) Å, β = 96.192(2)°; c = 16.9512(18) Å, γ = 90°. Volume: 4349.7(8) $Å^3$, Z = 8, Density (calculated): 1.507 Mg/m^3, $F_{(000)}$ = 2016, Crystal size: 0.200 x 0.180 x 0.120 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0429, wR2 = 0.0996.

X-ray Crystal Data of 3la



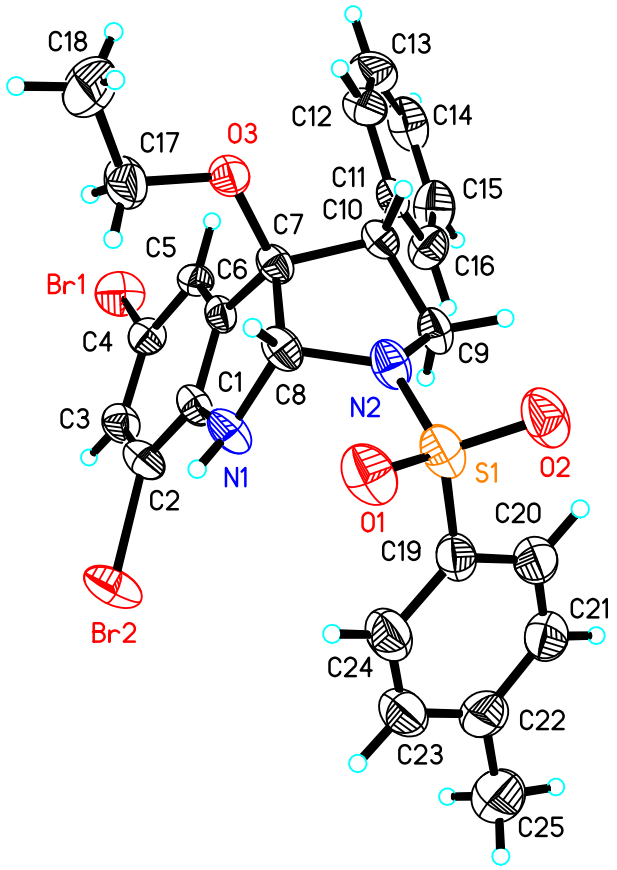
The crystal data of **3la** have been deposited in CCDC with number 1552681. Empirical formula: $C_{31}H_{26}N_2O_2S$, Formula weight: 490.60, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 10.688(2) Å, α = 103.535(4)°; b = 10.745(2) Å, β = 94.412(4)°; c = 11.245(2) Å, γ = 96.045(4)°. Volume: 1241.7(4) $Å^3$, Z = 2, Density (calculated): 1.312 Mg/m^3, $F_{(000)}$ = 516, Crystal size: 0.200 x 0.170 x 0.140 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0571, wR2 = 0.1430.

X-ray Crystal Data of 4ca'



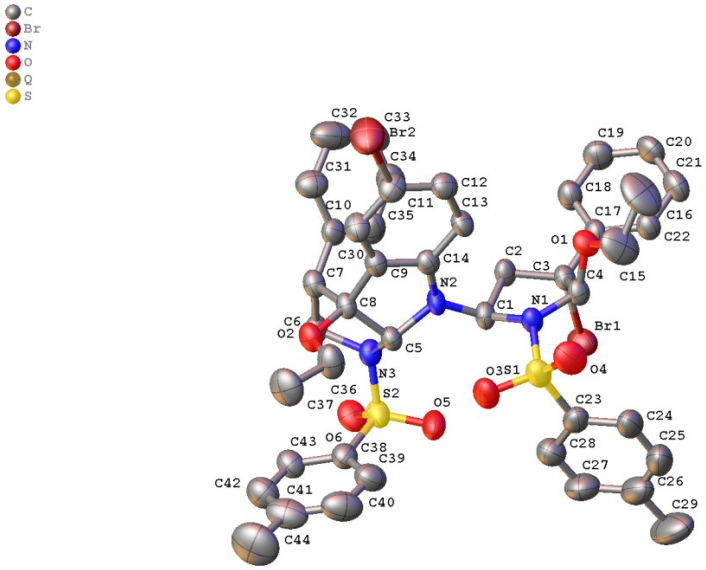
The crystal data of **4ca'** have been deposited in CCDC with number 1560323. Empirical formula: $C_{43}H_{38}BrN_3O_4S_2$, Formula weight: 804.79, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 11.9360(15) Å, α = 89.702(4)°; b = 13.1209(17) Å, β = 84.883(3)°; c = 13.8558(16) Å, γ = 66.690(3)°. Volume: 1983.8(4) $Å^3$, Z = 2, Density (calculated): 1.347 Mg/m^3, $F_{(000)}$ = 832, Crystal size: 0.200 x 0.160 x 0.120 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0590, wR2 = 0.1505.

X-ray Crystal Data of 4aa'



The crystal data of **4aa'** have been deposited in CCDC with number 1561913. Empirical formula: $C_{25}H_{24}Br_2N_2O_3S$, Formula weight: 592.34, Crystal system: Triclinic, Space group: P -1, Unit cell dimensions: a = 8.4549(14) Å, α = 117.552(3)°; b = 13.872(2) Å, β = 101.368(4)°; c = 14.009(2) Å, γ = 92.964(4)°. Volume: 1408.7(4) Å3, Z = 2, Density (calculated): 1.396 Mg/m3, F(000) = 596, Crystal size: 0.220 x 0.200 x 0.160 mm3, Final R indices [I>2sigma(I)]: R1 = 0.0508, wR2 = 0.1210.

X-ray Crystal Data of 4aa''



The crystal data of **4aa''** have been deposited in CCDC with number 1570336. Empirical formula: $C_{44}H_{45}Br_2N_3O_6S_2$, Formula weight: 935.77, Crystal system: Monoclinic, Space group: P 1 21/c 1, Unit cell dimensions: a = 13.823(2) Å, α = 90°; b = 11.5473(19) Å, β = 98.559(6)°; c = 30.267(5) Å, γ = 90°. Volume: 4777.3(14) Å3, Z = 4, Density (calculated): 1.301 Mg/m3, F(000) = 1920, Crystal size: 0.22 x 0.2 x 0.15 mm3, Final R indices [I>2sigma(I)]: R1 = 0.0663, wR2 = 0.1613.