Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Radical-mediated alkene carboamination/dearomatization of arylsulfonyl-*o*-allylanilines via photoredox catalysis

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1. General remarks

^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR) agilent NMR spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) and 77.16 ppm (for ^{13}C NMR). HRMS was recorded on an Agilent 6540 Q-TOF (ESI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified.

2. Photochemical reaction setup

Household blue LED strips (22 W) were coiled around the inside of a glassware with 12 cm diameter (Figure S1). The LED strips were wrapped in aluminum foil to maintain a specific reaction temperature. In this case, the reaction temperature is approximately 45 °C. Optimum yields were then observed.

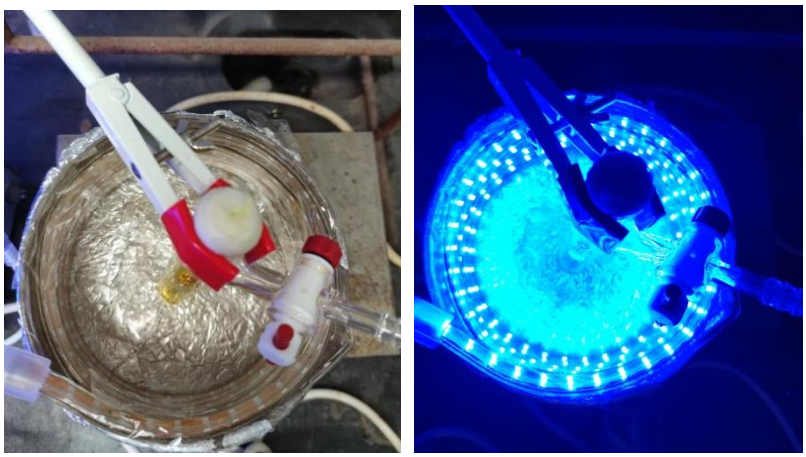
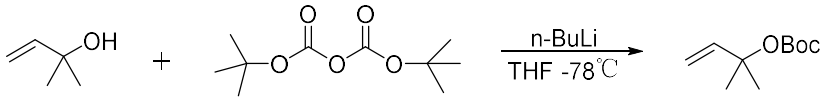


Figure S1. Reaction setup

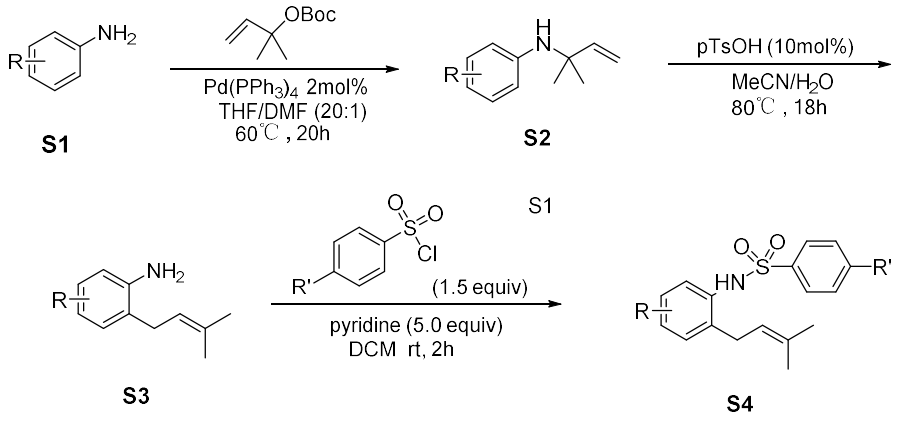
3. General procedures for synthesis of substrates

3.1 Procedures for the preparation of *t*-butyl (2-methylbut-3-en-2-yl) carbonate



To a solution of 2-methylbut-3-en-2-ol (5.2 mL, 50 mmol, 1.0 equiv.) in THF (90 mL) was added *n*-BuLi in hexanes (2.5 M, 20 mL, 50 mmol, 1.0 equiv.) at 0 °C over the course of 10 min. The clear solution was stirred at 0 °C for 20 min and then di-*tert*-butyl dicarbonate (14.72 g, 67.5 mmol, 1.35 equiv.) was added as a solid in one portion. The clear solution was stirred at room temperature for 4 h. Before sat. aq. $NaHCO_3$ (200 mL) was added to the by then thick suspension. The mixture was extracted with ethyl acetate. The organic layer washed with sat. aq. NaCl (150 mL), dried over $NaSO_4$, and concentrated under reduced pressure to give the title carbonate as clear, pale, light-yellow liquid (9.2 g, 49 mmol, 98%), which was used without further purification.

3.2 Preparation of Sulfanilamide olefins

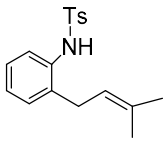


1) A solution of aniline **S1** (1.82 mL, 20 mmol) and *tert*-butyl-(2-methylbut-3-en-2-yl) carbonate (5.02 g, 27mmol) in THF (40 mL) and DMF (2 mL) was treated with $Pd(PPh_3)_4$ (462.4 mg, 2 mol%) under inert atmosphere was heated at 60 °C for 24 h. The resulting mixture was cooled and washed with saturated NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc (50 mL × 2), and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by flash chromatography (petroleum ether/EtOAc,

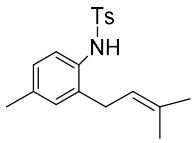
60:1) to give aniline **S2** as a yellowish oil (2.45 g, 75%). All spectra and characterization data matches that previously reported in the literature.

2) To a solution of aniline **S2** (2.45 g, 15.2 mmol) in MeCN/H_2O (40 mL/4 mL) under inert atmosphere was added *p*-TsOH·H_2O (289.7 mg, 1.52 mmol, 0.1 equiv.), and it was heated at 80 ℃ overnight. After cooling back to room temperature, it was washed with water (40 mL). The aqueous layer was extracted with EtOAc (20 mL × 2) The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was directly used in next step without further purification.

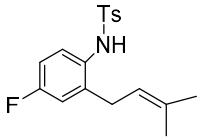
3) To a solution of the above crude material in pyridine (5 equiv.) at room temperature under inert atmosphere was added paratoluensulfonyl chloride (1.5 equiv.). After 6 h, DCM (50 mL) was added, and it was washed with 10% aq. HCl (100 mL). The aqueous layer was extracted with EtOAc (30 mL × 2). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated. Flash column chromatography (petroleum ether/EtOAc, 15: 1) afforded 1.8 g (33% over two steps) of compound **S4** as a white solid.



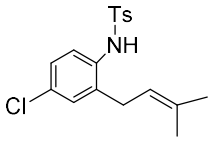
4-Methyl-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (1aa): White solid; m.p. 89-92 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.10 – 7.04 (m, 2H), 6.62 (s, 1H), 5.03 – 4.93 (m, 1H), 2.97 (d, *J* = 7.0 Hz, 2 H), 2.38 (s, 3H), 1.73 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 136.8, 135.0 134.7, 133.6, 129.9, 129.6, 127.3, 127.1, 125.9, 123.7, 121.3, 31.0, 25.7, 21.5, 17.8; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3279, 1490, 1404, 1328, 1159, 1086, 904, 811, 744, 664; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{21}NO_2SNa$ 338.1185, found 338.1189.



4-Methyl-*N*-(4-methyl-2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (1ba): White solid; m.p. 94-97 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.86 (s, 1H), 6.51 (s, 1H), 4.95 (t, *J* = 7.0 Hz, 1H), 2.92 (d, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 2.26 (s, 3H), 1.72 (s, 3H), 1.68 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.6, 136.9, 136.0, 134.4, 134.2, 132.2, 130.6, 129.5, 127.8, 127.1, 124.5, 121.5, 30.9, 25.7, 21.5, 20.9, 17.8; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3260, 2965, 2930, 1496, 1393, 1330, 1159, 1091, 883, 817, 672, 665; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{19}H_{23}NO_2SNa$ 352.1342, found 352.1349.

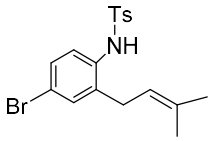


***N*-(4-Fluoro-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1ca):** White solid; m.p. 113-117 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.31 (dd, *J* = 8.8, 5.3 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.84 (td, *J* = 8.4, 3.0 Hz, 1H), 6.78 (dd, *J* = 9.3, 2.9 Hz, 1H), 6.54 (s, 1H), 4.97 – 4.88 (m, 1H), 2.91 (d, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.72 (s, 3H), 1.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.9 (d, *J* = 245.9 Hz), 143.9, 138.1 (d, *J* = 7.6 Hz), 136.5, 135.1, 130.3 (d, *J* = 2.3 Hz), 129.6, 127.3 (d, *J* = 8.6 Hz), 127.1, 120.4, 116.2 (d, *J* = 22.8 Hz), 113.6 (d, *J* = 22.4 Hz), 30.3, 25.6, 21.5, 17.7; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3276, 2976, 2925, 1494, 1397, 1327,1158, 1088, 893, 810, 664; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{20}FNO_2SNa$ 356.1091, found 356.1094.

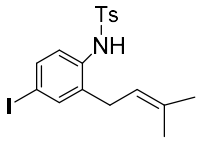


***N*-(4-Chloro-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1da):** White solid; m.p. 93-96 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.64 (s, 1H), 4.95 – 4.89 (m, 1H), 2.93 (d, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.0, 136.5,

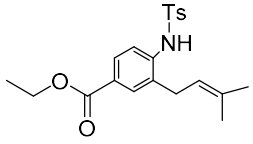
136.0, 135.5, 133.5, 131.4, 129.7, 127.2, 127.1, 125.4, 120.3, 30.6, 25.7, 21.6, 17.8; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3262, 2980, 2920, 1478, 1412, 1386, 1340, 1164, 1091, 873, 810, 672; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{20}{}^{35}ClNO_2SNa$ 372.0795, found 372.0795.



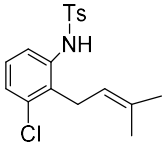
***N*-(4-Bromo-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1ea):** White solid; m.p. 88-90 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 1.7 Hz, 1H), 6.64 (s, 1H), 4.97 – 4.89 (m, 1H), 2.93 (d, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.73 (d, *J* = 1.0 Hz, 3.2H), 1.66 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 144.1, 136.5, 135.9, 135.6, 134.1, 132.6, 130.2, 129.7, 127.1, 125.4, 120.3, 119.3, 30.7, 25.7, 21.6, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3260, 2961, 2919, 1595, 1473, 1381, 1332, 1161, 1090, 910, 812, 726, 671; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{18}H_{21}{}^{79}BrNO_2S$ 394.0471, found 394.0470.



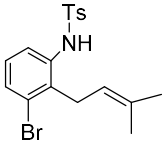
***N*-(4-Iodo-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1fa):** White solid; m.p. 101-105 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.36 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.48 (s, 1H), 4.82 – 4.79 (m, 1H), 2.79 (d, *J* = 7.0 Hz, 2H), 2.28 (s, 3H), 1.62 (s, 3H), 1.57 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 144.0, 138.6, 136.4, 136.3, 135.6, 135.5, 134.9, 129.7, 127.0, 125.2, 120.3, 90.3, 30.6, 25.7, 21.5, 17.8; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3262, 2964, 2922, 1594, 1470, 1380, 1331, 1159, 1088, 908, 812, 665; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{20}INO_2SNa$ 464.0152, found 464.0150.



Ethyl 3-(3-methylbut-2-en-1-yl)-4-((4-methylphenyl)sulfonamido)benzoate (1ga): White solid; m.p. 67-71 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.93 (s, 1H), 5.01 – 4.92 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.09 (d, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 1.75 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.1, 144.2, 139.6, 136.4, 135.7, 131.5, 131.2, 129.7, 128.9, 127.1, 126.8, 120.6, 61.0, 31.3, 25.7, 21.5, 17.9, 14.3; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3281, 2982, 2902, 1710, 1608, 1495, 1396, 1336, 1264, 1160, 1084, 908, 815, 766, 665; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{21}H_{25}NO_4SNa$ 410.1397, found 410.1397.

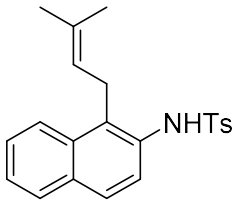


***N*-(3-Chloro-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1ha):** White solid; m.p. 94-96 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.03 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.63 (s, 1H), 4.92 (t, *J* = 6.7 Hz, 1H), 2.94 (d, *J* = 6.9 Hz, 2H), 2.39 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.1, 136.4, 136.2, 135.5, 132.7, 131.3, 130.9, 129.7, 127.1, 125.6, 122.9, 120.6, 30.7, 25.7, 21.6, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3188, 2968, 2912, 1448, 1406, 1323, 1149, 1092, 956, 813, 735, 666; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{20}{}^{35}ClNO_2SNa$ 372.0795, found 372.0793.

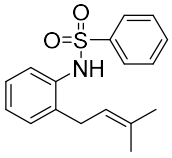


***N*-(3-Bromo-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1ia):** White solid; m.p. 89-94 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.57 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.58 (s, 1H), 4.96 – 4.88 (m, 1H), 2.92 (d, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.74 (s, 3H), 1.69 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.1, 136.3, 135.5, 131.8, 131.2, 129.7, 128.6, 127.1, 125.8, 120.5, 120.4, 30.7, 25.7, 21.5, 17.8; **FT-IR (thin film, KBr): ν (cm^{-1}):**

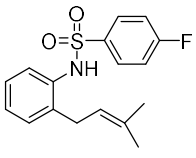
3295, 2961, 2920, 1567, 1447, 1385, 1327, 1159, 1093, 909, 815, 730, 663; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{20}{}^{79}BrNO_2SNa$ 416.0290, found 416.0286.



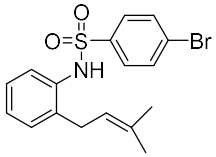
4-Methyl-*N*-(1-(3-methylbut-2-en-1-yl)naphthalen-2-yl)benzenesulfonamide (1ja): White solid; m.p. 83-86 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.50 – 7.39 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 4.86 – 4.77 (m, 1H), 3.36 (d, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 1.83 (s, 3H), 1.67 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 136.7, 133.9, 132.2, 132.1, 129.6, 129.4, 128.7, 127.7, 127.1, 126.5, 125.4, 124.1, 123.4, 121.3, 25.7, 25.6, 21.5, 18.1; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3319, 2913, 1596, 1441, 1404, 1369, 1320, 1225, 1152, 1093, 898, 808, 761, 739, 675, 664; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{22}H_{23}NO_2SNa$ 388.1342, found 388.1340.



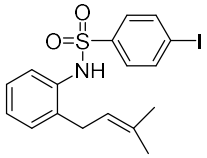
***N*-(2-(3-Methylbut-2-en-1-yl)phenyl)benzenesulfonamide (1ab):** White solid; m.p. 68-70 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 – 7.66 (m, 2H), 7.61 – 7.48 (m, 1H), 7.46 – 7.36 (m, 3H), 7.22 – 7.12 (m, 1H), 7.12 – 7.01 (m, 2 H), 6.66 (s, 1H), 5.08 – 4.84 (m, 1H), 2.95 (d, *J* = 7.0 Hz, 2H), 1.73 (s, 3H), 1.69 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 139.6, 134.82, 134.76, 133.7, 132.9, 129.9, 128.9, 127.3, 127.0, 126.1, 123.9, 121.2, 31.0, 25.7, 17.8; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3257, 2970, 2921, 1490, 1446, 1395, 1331, 1159, 1090, 907, 754, 724, 686, 655; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{17}H_{19}NO_2SNa$ 324.1029, found 324.1026.



4-Fluoro-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (1bb): White solid; m.p. 95-99 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.77 – 7.63 (m, 2H), 7.44 – 7.38 (m, 1H), 7.22 – 7.14 (m, 1H), 7.13 – 7.01 (m, 4H), 6.70 (s, 1H), 5.01 – 4.94 (m, 1H), 2.99 (d, *J* = 7.0 Hz, 2H), 1.73 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.2 (d, *J* = 255.3 Hz), 135.7 (d, *J* = 3.1 Hz), 134.8, 134.6, 134.0, 130.1, 129.8 (d, *J* = 9.4 Hz), 127.4, 126.3, 124.0, 121.2, 116.2 (d, *J* = 22.6 Hz), 31.0, 25.7, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3259,1591, 1492, 1404, 1338, 1155, 1086, 916, 812, 752, 675; **HRMS** (ESI) [M + Na]$^+$ Calculated for $C_{17}H_{18}FNO_2SNa$ 342.0934, found 342.0936.

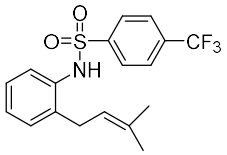


4-Bromo-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (1cb): White solid; m.p.100-104 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.51 (m, 4.19H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.01 (m, 3H), 6.78 (s, 1H), 4.97 (t, *J* = 6.9 Hz, 1H), 3.00 (d, *J* = 7.0 Hz, 2H), 1.73 (s, 3H), 1.69 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 138.7, 134.9, 134.5, 134.0, 132.3, 130.1, 128.6, 128.0, 127.4, 126.4, 124.0, 121.2, 31.0, 25.7, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3298, 2963, 2908, 1577, 1493, 1397, 1338, 1272, 1166, 1089, 910, 820, 737, 610; **HRMS** (ESI) [M + Na]$^+$ Calculated for $C_{17}H_{18}{}^{79}BrNO_2SNa$ 402.0134, found 402.0131.

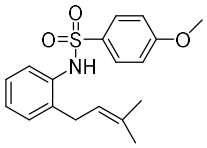


4-Iodo-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (1db): White solid; m.p. 133-135 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.83 – 7.73 (m, 2H), 7.43 – 7.36 (m, 3H), 7.22 – 7.15 (m, 1H), 7.13 – 7.03 (m, 2H), 6.65 (s, 1H), 5.06 – 4.83 (m, 1H), 2.98 (d, *J* = 7.0 Hz, 2H), 1.74 (d, *J* = 1.2 Hz, 3H), 1.69 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 139.4, 138.2, 134.9, 134.5, 133.8, 130.1, 128.4, 127.4, 126.4, 123.9, 121.1, 100.5, 31.1, 25.7, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3245, 1494, 1396,

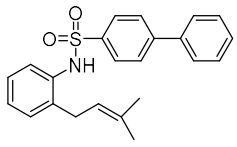
1329, 1165, 1089, 904, 812, 723, 659; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{17}H_{18}INO_2SNa$ 449.9995, found 449.9997.



***N*-(2-(3-Methylbut-2-en-1-yl)phenyl)-4-(trifluoromethyl)benzenesulfonamide (1eb):** White solid; m.p. 101-105 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 6.9 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.04 (m, 3H), 6.75 (s, 1H), 5.00 – 4.89 (m, 1H), 2.97 (d, *J* = 6.0 Hz, 2H), 1.73 (s, 3H), 1.68 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.2, 134.9, 134.5 (q, *J* = 33.1 Hz), 134.2, 134.1, 130.1, 127.6, 127.4, 126.6, 126.1 (q, *J* = 3.6 Hz), 124.1, 123.1 (q, *J* = 273.0 Hz), 121.0, 30.8, 25.6, 17.8; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3277, 2977, 2922, 1607, 1486, 1404, 1318, 1168, 1134, 1062, 1017, 907, 830, 765, 712, 659, 600; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{18}F_3NO_2SNa$ 392.0903, found 392.0900.

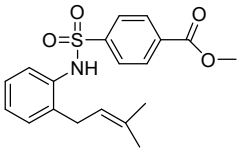


4-Methoxy-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (1fb): White solid; m.p. 75-79 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 – 7.55 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.12 (m, 1H), 7.10 – 7.04 (m, 2H), 6.90 – 6.83 (m, 2H), 6.63 (s, 1H), 5.05 – 4.94 (t, 1H), 3.81 (s, 3H), 2.99 (d, *J* = 7.0 Hz, 2H), 1.73 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.1, 135.1, 134.7, 133.6, 131.3, 130.0, 129.2, 127.3, 125.9, 123.7, 121.3, 114.1, 55.6, 31.1, 25.7, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3259, 2971, 2911, 1595, 1494, 1395, 1330, 1262, 1159, 1094, 907, 831, 751, 675; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{21}NO_3SNa$ 354.1134, found 354.1137.

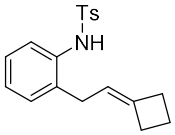


***N*-(2-(3-Methylbut-2-en-1-yl)phenyl)-[1,1'-biphenyl]-4-sulfonamide (1gb):** White solid; m.p. 104-108 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 – 7.75 (m, 2H), 7.67 –

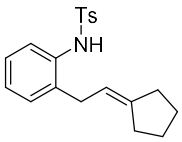
7.62 (m, 2H), 7.61 – 7.54 (m, 2H), 7.53 – 7.38 (m, 4H), 7.24 – 7.17 (m, 1H), 7.15 – 7.04 (m, 2H), 6.73 (s, 1H), 5.24 – 4.76 (m, 1H), 3.02 (d, *J* = 7.0 Hz, 2H), 1.74 (s, 3H), 1.71 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 145.8, 139.1, 138.3, 134.9, 134.8, 133.8, 130.0, 129.1, 128.6, 127.6, 127.5, 127.4, 127.3, 126.1, 123.9, 121.3, 31.0, 25.7, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3264, 2973, 2913, 1482, 1395, 1334, 1162, 1082, 908, 45, 764, 675; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{23}H_{23}NO_2SNa$ 400.1342, found 400.1344.



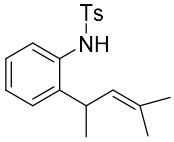
methyl 4-(N-(2-(3-methylbut-2-en-1-yl)phenyl)sulfamoyl)benzoate (1hb): White solid; m.p. 74-78 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.13 – 8.00 (m, 2H), 7.91 – 7.67 (m, 2H), 7.42 (d, *J* = 8.0, 0.7 Hz, 1H), 7.18 (td, *J* = 7.7, 1.8 Hz, 1H), 7.13 – 7.02 (m, 2H), 6.68 (s, 1H), 5.01 – 4.85 (m, 1H), 3.93 (s, 3H), 2.94 (d, *J* = 7.0 Hz, 2H), 1.72 (s, 3H), 1.69 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.6, 143.5, 135.0, 134.5, 134.0, 133.9, 130.2, 127.5, 127.1, 126.5, 124.0, 121.1, 52.7, 31.1, 25.7, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3273, 1725, 1491, 1454, 1432, 1399, 1158, 1087, 908, 766, 735, 690; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{19}H_{22}NO_4S$ 360.1264, found 360.1269.



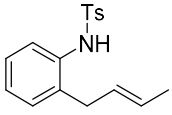
***N*-(2-(2-Cyclobutylideneethyl)phenyl)-4-methylbenzenesulfonamide (1ib):** White solid; m.p. 89-94 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.63 – 7.55 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.10 (m, 3H), 7.05 (d, *J* = 4.2 Hz, 2H), 6.73 (s, 1H), 4.98 – 4.78 (m, 1H), 2.85 (d, *J* = 7.0 Hz, 2H), 2.73 – 2.62 (m, 4H), 2.37 (s, 3H), 2.09 – 1.89 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 143.7, 143.4, 136.8, 135.3, 132.7, 130.1, 129.5, 127.4, 127.1, 125.7, 123.2, 117.1, 31.3, 31.1, 29.4, 21.5, 17.0; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3275, 2985, 2954, 1490, 1402, 1328, 1160, 1087, 903, 812, 750, 663; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{19}H_{22}NO_2S$ 328.1366, found 328.1366.



***N*-(2-(2-Cyclopentylideneethyl)phenyl)-4-methylbenzenesulfonamide (1jb):** White solid; m.p. 94-97 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.12 (m, 3H), 7.05 (d, *J* = 4.1 Hz, 2H), 6.69 (s, 1H), 5.14 – 5.02 (m, 1H), 2.97 (d, *J* = 7.0 Hz, 2H), 2.37 (s, 3H), 2.30 – 2.14 (m, 4H), 1.81 – 1.70 (m, 2H), 1.68 – 1.59 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.8, 143.8, 136.8, 135.2, 133.2, 129.9, 129.6, 127.3, 127.1, 125.7, 123.2, 116.7, 33.7, 32.7, 29.0, 26.3, 26.3, 21.5; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3219, 2948, 2868, 1600, 1495, 1402, 1319, 1146, 1091, 914, 816, 761, 685; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{20}H_{23}NO_2SNa$ 364.1342, found 364.1344.

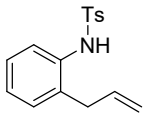


4-Methyl-*N*-(2-(4-methylpent-3-en-2-yl)phenyl)benzenesulfonamide (1kb): White solid; m.p. 78-82 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.28 – 7.09 (m, 5H), 6.62 (s, 1H), 4.92 (d, *J* = 9.5 Hz, 1H), 3.43 – 3.05 (m, 1H), 2.38 (s, 3H), 1.74 (s, 3H), 1.71 (s, 3H), 1.10 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.7, 138.1, 136.8, 134.7, 133.1, 129.5, 128.4, 127.1, 126.9, 126.1, 126.0, 123.7, 33.1, 25.6, 21.5, 19.5, 17.7; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3239, 2952, 2922, 2857, 1596, 1493, 1409, 1320, 1304, 1153, 1089, 909, 822, 756, 678; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{19}H_{23}NO_2SNa$ 352.1342, found 352.1339.



(*E*)-*N*-(2-(But-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1lb): White solid (*E*:*Z* > 10:1); m.p. 87-91 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.13 – 7.02 (m, 2H), 6.68 (s, 1H), 5.56 – 5.05 (m, 2H), 2.95 – 2.91 (m, 2H), 2.38 (s, 3H), 1.68 – 1.64 (m, 3H); **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 143.8, 136.8, 135.1, 132.5, 130.4, 129.6, 128.3, 127.8, 127.5, 127.1, 126.0, 124.0, 35.1, 21.5, 17.9; **FT-IR (thin film, KBr): ν (cm^{-1}):**3284, 1490, 1396, 1328, 1157, 1089, 918, 813, 766, 664; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{17}H_{19}NO_2SNa$ 324.1029, found 324.1030.



***N*-(2-Allylphenyl)-4-methylbenzenesulfonamide (1mb):** White solid; m.p. 80-85 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.13 – 7.02 (m, 2H), 6.77 (br, 1H), 5.90 – 5.67 (m, 1H), 5.08 (dd, *J* = 10.1, 1.2 Hz, 1H), 4.93 (dd, *J* = 17.2, 1.5 Hz, 1H), 3.06 (d, *J* = 5.9 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.8, 136.7, 135.6, 134.9, 132.2, 130.4, 129.6, 127.6, 127.1, 126.3, 124.5, 117.0, 36.0, 21.5; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3277, 2967, 2924, 1492, 1399, 1330, 1157, 1091, 914, 813, 755, 662; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{16}H_{17}NO_2SNa$ 310.0872, found 310.0872.

Reference

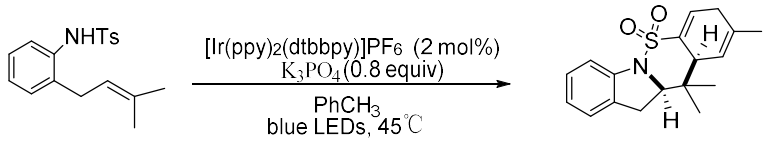
1) Q.-Q. Zhao and W.-J. Xiao, A visible-light photocatalytic N-radical cascade of hydrazones for the synthesis of dihydropyrazole-fused benzosultams. *Chem. Commun.* **2016**, *52*, 12749-12752.

2) R. C. McAtee and C. R. J. Stephenson, Arene dearomatization through a catalytic N-centered radical cascade reaction. *Nat. Commun.* **2020**, *15*, 2502-2505.

3) H. Xu and Y. Li, Domino Aryne Annulation via a Nucleophilic–Ene Process. *J. Am. Chem. Soc.* **2018**, *140*, 3555–3559.

4. Optimization of the reaction conditions

Table S1. Screening of photocatalyst.



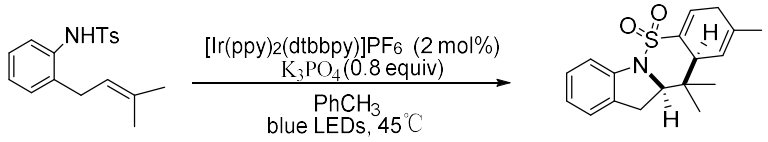
1aa **2aa**

entry	photocatalyst	base	solvent	yield(%)[a]
1	fac-Ir(ppy)$_3$	K_3PO_4	$PhCF_3$	34
2	Ru(bpy)$_3$Cl$_2$·6H$_2$O	K_3PO_4	$PhCF_3$	40
3	**[Ir(ppy)$_2$(dtbbpy)]PF$_6$**	**K_3PO_4**	**$PhCF_3$**	**48**
4	[Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4	$PhCF_3$	30
5	[Ir(dFCF$_3$ppy)$_2$(dCF$_3$bpy)]PF$_6$	K_3PO_4	$PhCF_3$	21

[a]Isolated yield.

Table S2. Screening of bases.

Optimization of the catalyst loading

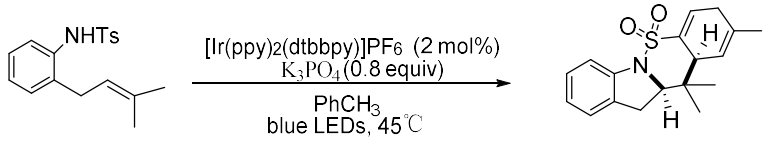


1aa **2aa**

entry	photocatalyst	Base (equiv)	solvent	Yield (%)[a]
1	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4 (0.2equiv)	$PhCF_3$	38
2	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4 (0.4equiv)	$PhCF_3$	42
3	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4 (0.6equiv)	$PhCF_3$	50
4	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4 (0.7equiv)	$PhCF_3$	61
5	**[Ir(ppy)$_2$(dtbbpy)]PF$_6$**	**K_3PO_4 (0.8equiv)**	**$PhCF_3$**	**70**
6	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4 (0.9equiv)	$PhCF_3$	58
7	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4 (1.0equiv)	$PhCF_3$	45
8	[Ir(ppy)$_2$(dtbbpy)]PF$_6$	K_3PO_4 (1.2equiv)	$PhCF_3$	32

[a]Isolated yield.

Table S3. Screening of solvent.



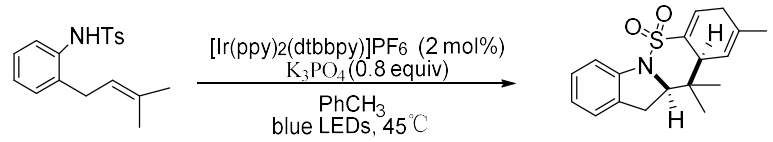
1aa **2aa**

entry	photocatalyst	base	solvent	yield(%)[a]

1	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	$PhCF_3$	70
2	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	MeCN	38
3	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	DCM	30
4	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	DCE	25
5	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	1,4-dioxane	31
6	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	Acetone	11
7	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	PhCF3/TBA (1:1)	43
8	**$[Ir(ppy)_2(dtbbpy)]PF_6$**	**K_3PO_4**	**PhMe**	**80**
9	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	PhF	55
10	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	PhCl	56

[a]Isolated yield.

Table S4. Control experiments

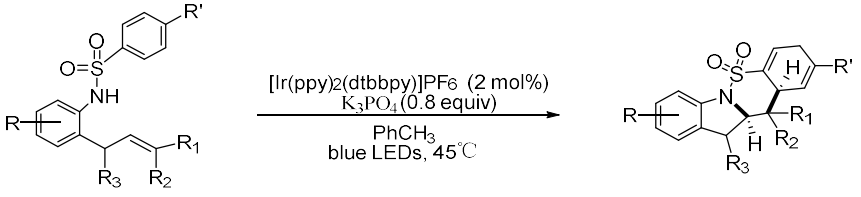


1aa **2aa**

entry	photocatalyst	base	yield(%)[a]
1	$[Ir(ppy)_2(dtbbpy)]PF_6$	-	0
2	-	K_3PO_4	0
3[b]	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	51
4[c]	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	75
5[d]	$[Ir(ppy)_2(dtbbpy)]PF_6$	K_3PO_4	0

[a]Isolated yield. [b]35℃. [c]55℃. [d]in the dark.

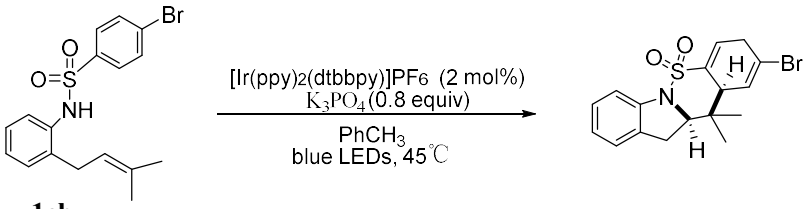
5. General procedures for synthesis of products



1 **2**

General procedure: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar, the compound 1 (0.2 mmol, 1.0 equiv.), $[Ir(ppy)_2(dtbbpy)]PF_6$ (3.83 mg, 0.004 mmol, 2 mol%), and tripotassium phosphate (34.7 mg, 0.16 mmol, 0.8 equiv.) was added. The resulting mixture was sealed and PhMe (2.5 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 12 hours. The temperature was maintained at 45℃ when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was

removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



1cb **2cb**

Gram-scale synthesis of compound 2cb: To a 100 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, **1cb** (1.14 g, 3 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (57 mg, 0.06 mmol), and tripotassium phosphate (520 mg, 2.4 mmol) was added. The resulting mixture was sealed and PhMe (37.5 mL) were then added under argon atmosphere. After that, the reaction was placed under a 22W blue LED and irradiated for 24 hours. The temperature was maintained at 45 ℃ when the LED light was on. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel with petrol: ethyl acetate =30: 1 to give **2cb** in 64% yield (0.72 g).

6. Stern-Volmer fluorescence quenching experiments

Emission intensities were recorded using F-320 Luminescence Spectrometer for all experiments. Acetonitrile was degassed with argon for at least 30 minutes by ultrasonic treatment. All $[Ir(ppy)_2(dtbbpy)]PF_6$ solutions were excited at 392 nm and the emission intensity was collected at 540-680 nm. In a typical experiment, the CH_3CN solution of $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.05 mM) was added the appropriate amount of potassium pivalate and substrate **1aa** in a screw-top 1.0 cm quartz cuvette. After degassing with argon for 10 min, the emission spectra of the samples xwere collected.

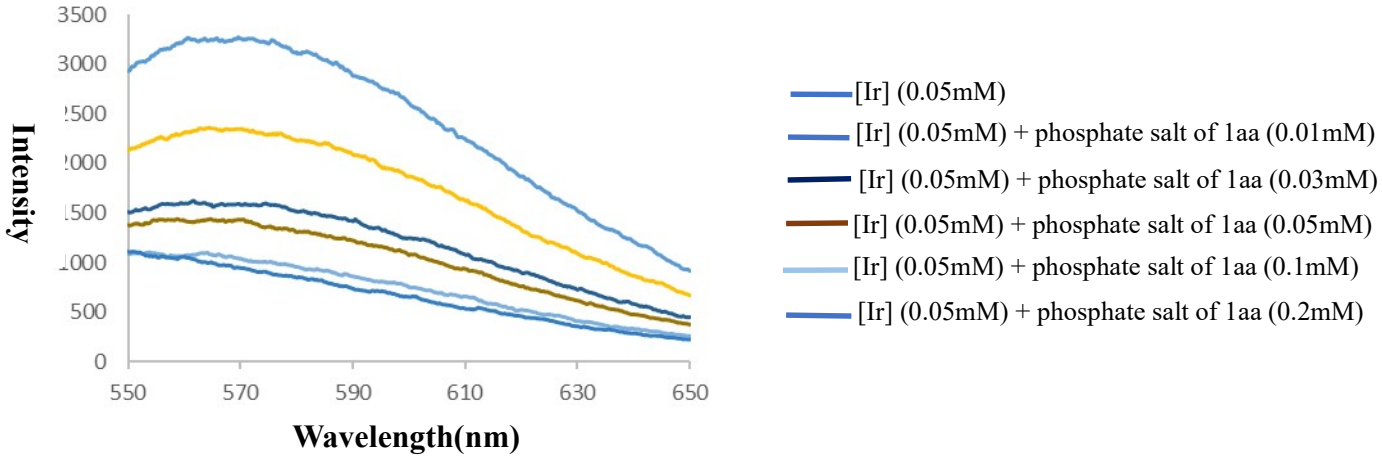


Figure S2. Fluorescence quenching by phosphate salt of 1aa.

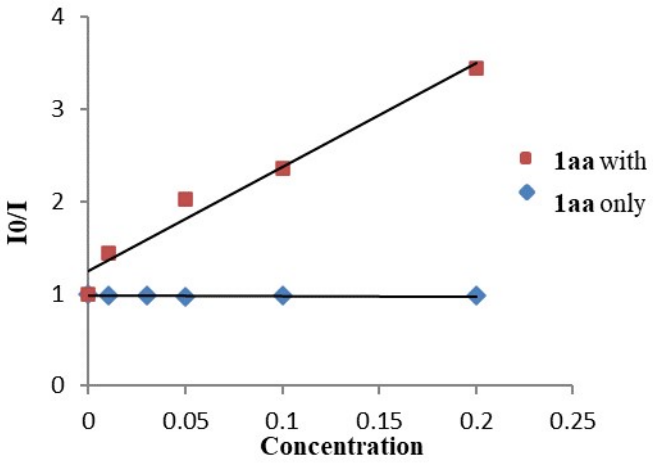
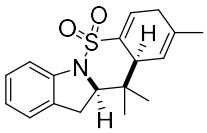


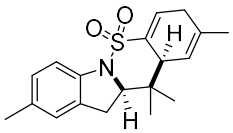
Figure S3. Stern−Volmer fluorescence quenching

7. Characterization of the products

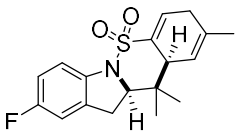


2,12,12-Trimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2aa): Followed the general procedure with 4-methyl-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (**1aa**, 63 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 53 mg of the title compound (white solid; m.p. 134-138 ℃; 84% yield) ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.18 – 7.11 (m, 2H), 6.94 (t, *J* =

7.4 Hz, 1H), 6.89 (t, *J* = 3.3 Hz, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 4.26 (t, *J* = 9.6 Hz, 1H), 3.37 – 3.29 (m, 1H), 3.12 (dd, *J* = 15.5, 9.0 Hz, 1H), 2.94 (dd, *J* = 15.5, 10.2 Hz, 1H) , 2.90 – 2.70 (m, 2H), 1.78 (s, 3H), 1.10 (s, 3H), 0.78 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 142.8, 135.7, 132.8, 130.8, 128.5, 127.8, 124.8, 122.8, 117.4, 113.4, 71.9, 46.4, 40.6, 30.9, 30.7, 23.0, 22.8, 14.3; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2971, 2912, 1601, 1477, 1315, 1236, 1147, 969, 919, 761, 678, 622; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{21}NO_2SNa$ 338.1185, found 338.1189.

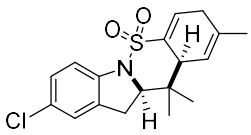


2,9,12,12-Tetramethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2ba): Followed the general procedure with 4-methyl-*N*-(4-methyl-2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (**1ba**, 66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 58 mg of the title compound (white solid; m.p. 132-135 ℃; 88% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.0 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.88 (t, *J* = 3.0 Hz, 1H), 5.49 (d, *J* = 1.4 Hz, 1H), 4.22 (dd, *J* = 10.0, 9.2 Hz, 1H), 3.36 – 3.27 (m, 1H), 3.06 (dd, *J* = 15.5, 8.9 Hz, 1H), 2.95 – 2.70 (m, 3H), 2.27 (s, 3H), 1.77 (s, 3H), 1.09 (s, 3H), 0.78 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 140.4, 135.7, 132.8, 132.4, 130.6, 128.7, 128.2, 125.5, 117.5, 113.2, 72.1, 46.5, 40.5, 30.9, 30.7, 23.0, 22.8, 20.9, 14.3; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2972, 2910, 2869, 1484, 1320, 1221, 1147, 964, 820, 698, 679, 627; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{19}H_{23}NO_2SNa$ 352.1342, found 352.1349.

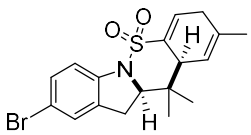


9-Fluoro-2,12,12-trimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2ca): Followed the general procedure with N-(4-fluoro-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (**1ca**, 67 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc =

30:1) to give 51mg of the title compound (white solid; m.p. 127-133 ℃; 76% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (dd, *J* = 8.6, 4.5 Hz, 1H), 6.90 – 6.79 (m, 3H), 5.49 (s, 1H), 4.25 (t, *J* = 9.6 Hz, 1H), 3.35 – 3.27 (m, 1H), 3.08 (dd, *J* = 15.8, 8.9 Hz, 1H), 2.98 – 2.64 (m, 3H), 1.77 (s, 3H), 1.08 (s, 3H), 0.77 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 159.0 (d, *J* = 240.8 Hz), 138.8, 135.5, 132.9, 131.1, 130.6 (d, *J* = 8.3 Hz), 117.3, 114.1 (d, *J* = 14.0 Hz), 114.0, 112.3 (d, *J* = 24.2 Hz), 72.4, 46.4, 40.5, 31.0, 30.7, 22.9, 22.7, 14.3; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2954, 2923, 2854, 1475, 1443, 1306, 1217,1171, 1148, 964, 913, 872, 676, 629; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{18}H_{21}FNO_2S$ 334.1272, found 334.1276.

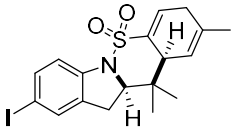


9-Chloro-2,12,12-trimethyl-11,11a,12,12a-tetrahydro-3H-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2da): Followed the general procedure with *N*-(4-chloro-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (**1da**, 70 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30: 1) to give 52 mg of the title compound (white solid; m.p. 125-129 ℃; 74% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 8.3 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.87 (dd, *J* = 4.8, 2.0 Hz, 1H), 5.48 (d, *J* = 1.0 Hz, 1H), 4.25 (t, *J* = 9.5 Hz, 1H), 3.34 – 3.27 (m, 1H), 3.08 (dd, *J* = 15.8, 9.1 Hz, 1H), 2.91 (dd, *J* = 15.8, 10.0 Hz, 1H), 2.88 – 2.72 (m, 2H), 1.77 (s, 3H), 1.07 (s, 3H), 0.75 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.5, 135.4, 132.9, 131.1, 130.6, 127.8, 127.7, 125.1, 117.3, 114.1, 72.1, 46.4, 40.7, 31.0, 30.5, 23.0, 22.6, 14.2; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2970,2916, 2873, 1467, 1319, 1230, 1176, 1148, 995, 961, 828, 718, 679, 624; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{18}H_{21}{}^{35}ClNO_2S$ 350.0976, found 350.0979.

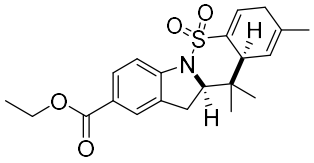


9-Bromo-2,12,12-trimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2ea): Followed the general procedure with

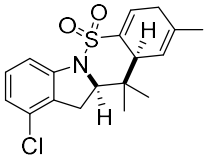
N-(4-bromo-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (**1ea**, 79 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 64 mg of the title compound (white solid; m.p. 135-138 ℃; 81% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 – 7.30 (m, 1H), 7.26 – 7.22 (m, 2H), 6.91 – 6.83 (m, 1H), 5.48 (d, *J* = 1.5 Hz, 1H), 4.26 (t, *J* = 9.5 Hz, 1H), 3.38 – 3.27 (m, 1H), 3.10 (dd, *J* = 15.8, 9.1 Hz, 1H), 2.98 – 2.58 (m, 3H), 1.77 (s, 3H), 1.08 (s, 3H), 0.75 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 142.0, 135.4, 132.9, 131.1, 130.9, 130.6, 127.9, 117.3, 115.2, 114.7, 72.0, 46.4, 40.7, 31.0, 30.4, 23.0, 22.6, 14.2; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2970, 2908, 2873, 1595, 1466, 1318, 1229, 1176, 1147, 960, 825, 733, 714, 679, 621; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{18}H_{21}{}^{79}BrNO_2S$ 394.0471, found 394.0471.



9-Iodo-2,12,12-trimethyl-11,11a,12,12a-tetrahydro-3H-benzo[5,6][1,2]thiazino[2, 3-a]indole 5,5-dioxide (2fa): Followed the general procedure with N-(4-iodo-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (**1fa**, 88 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 64 mg of the title compound (white solid; m.p. 130-136 ℃; 72% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.40 (m, 2H), 7.31 (d, *J* = 9.0 Hz, 1H), 6.88 (t, *J* = 3.0 Hz, 1H), 5.51 – 5.46 (m, 1H), 4.26 (t, *J* = 9.5 Hz, 1H), 3.36 – 3.28 (m, 1H), 3.10 (dd, *J* = 15.8, 9.1 Hz, 1H), 2.92 (dd, *J* = 15.8, 9.8 Hz, 1H), 2.85 – 2.68 (m, 2H), 1.77 (s, 3H), 1.08 (s, 3H), 0.75 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.8, 136.7, 135.5, 133.7, 133.0, 131.3, 131.1, 117.3, 115.3, 85.3, 71.9, 46.4, 40.7, 31.0, 30.3, 23.0, 22.7, 14.2; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2970, 2902, 1465, 1318, 1230, 1148, 960, 824, 712, 679, 620; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{18}H_{21}INO_2S$ 442.0332, found 442.0332.

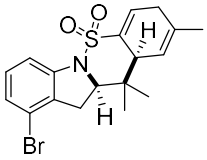


Ethyl 2,12,12-trimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole-9-carboxylate 5,5-dioxide (2ga): Followed the general procedure with ethyl 3-(3-methylbut-2-en-1-yl)-4-((4-methylphenyl)sulfonamido)benzoate (**1ga**, 77 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 46 mg of the title compound (white solid; m.p. 139-143 ℃; 60% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.81 (d, *J* = 1.1 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 6.97 – 6.82 (m, 1H), 5.51 – 5.46 (m, 1H), 4.40 – 4.29 (m, 3H), 3.35 (d, *J* = 3.7 Hz, 1H), 3.18 (dd, *J* = 15.9, 9.3 Hz, 1H), 2.97 (dd, *J* = 15.9, 9.1 Hz, 1H), 2.91 – 2.70 (m, 2H), 1.77 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.09 (s, 3H), 0.74 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 166.3, 146.9, 135.4, 133.0, 131.2, 130.4, 128.7, 126.2, 124.8, 117.3, 112.3, 72.0, 60.7, 46.3, 41.0, 31.0, 30.2, 23.0, 22.5, 14.3, 14.1; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2971, 2871, 1703, 1607, 1464, 1314, 1266, 1175, 967, 769, 680, 622; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{21}H_{26}NO_4S$ 388.1577, found 388.1582.

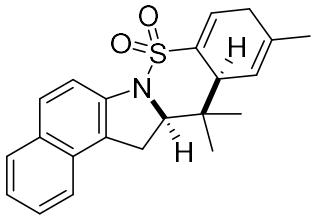


10-Chloro-2,12,12-trimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2ha): Followed the general procedure with N-(3-chloro-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (**1ha**, 70 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 46 mg of the title compound (white solid; m.p. 126-129 ℃; 72% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.1 Hz, 1H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.89 – 6.85 (m, 1H), 5.48 (d, *J* = 1.4 Hz, 1H), 4.29 (t, *J* = 9.5 Hz, 1H), 3.34 – 3.29 (m, 1H), 3.18 (dd, *J* = 16.1, 9.3 Hz, 1.3H), 2.91 (dd, *J* = 16.1, 9.8 Hz, 1H), 2.88 – 2.71 (m, 2H), 1.77 (s, 3H), 1.10 (s, 3H), 0.77 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.0, 135.4, 132.9, 131.1, 130.7, 129.3, 127.1, 122.8, 117.3, 111.5, 71.5, 46.3, 40.7, 31.0, 30.1, 23.0, 22.6, 14.5; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2916,

2855, 1595, 1448, 1328, 1244, 1152, 1052, 994, 785, 686, 622; **HRMS** (ESI) [M + Na]$^+$ Calculated for $C_{18}H_{20}{}^{35}ClNO_2SNa$ 372.0795, found 372.0793.

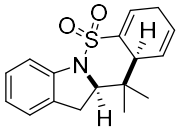


10-Bromo-2,12,12-trimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2ia): Followed the general procedure with N-(3-bromo-2-(3-methylbut-2-en-1-yl)phenyl)-4-methylbenzenesulfonamide (**1ia**, 79 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 57 mg of the title compound (white solid; m.p. 140-144 ℃; 72% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H) , 7.01 (t, *J* = 8.0 Hz, 1H) , 6.91 – 6.85 (m, 1H), 5.49 (s, 1H), 4.29 (t, *J* = 9.5 Hz, 1H), 3.39 – 3.26 (m, 1H), 3.15 (dd, *J* = 16.2, 9.3 Hz, 1H), 2.96 – 2.64 (m, 3H), 1.78 (s, 3H), 1.11 (s, 3H), 0.78 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.7, 135.4, 132.9, 131.5, 129.5, 129.2, 125.6, 119.6, 117.3, 112.0, 71.1, 46.3, 40.7, 32.2, 31.0, 23.0, 22.6, 14.2; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2972, 2919, 2849, 1593, 1445, 1323, 1244, 1151, 1047, 980, 767, 684, 638; **HRMS** (ESI) [M + H]$^+$ Calculated for $C_{18}H_{21}{}^{79}BrNO_2S$ 394.0471, found 394.0473.

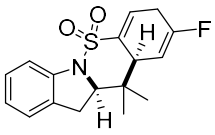


11,13,13-Trimethyl-12a,13,13a,14-tetrahydro-*10H*-benzo[e]benzo[5,6][1,2]thiazino[2,3-a]indole 8,8-dioxide (2ja): Followed the general procedure with 4-methyl-*N*-(1-(3-methylbut-2-en-1-yl)naphthalen-2-yl)benzenesulfonamide (**1ja**, 73 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 40 mg of the title compound (white solid; m.p. 135-138 ℃; 55% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 3.2 Hz, 1H), 5.52 (s, 1H), 4.44 (t, *J* = 9.9 Hz, 1H), 3.47 (dd, *J*

= 15.5, 9.5 Hz, 1H), 3.35 (d, *J* = 17.3 Hz, 1H), 3.16 (dd, *J* = 15.5, 10.3 Hz, 1H), 2.91 – 2.70 (m, 2H), 1.78 (s, 3H), 1.18 (s, 3H), 0.81 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.6, 135.9, 132.9, 130.7, 130.3, 130.2, 128.8, 128.7, 126.8, 124.0, 122.8, 121.7, 117.5, 114.4, 72.4, 46.6, 40.8, 31.0, 29.4, 23.0, 22.8, 14.4; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2965, 2924, 1601, 1460, 1316, 1232, 1157, 1135, 973, 764, 673; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{22}H_{23}NO_2SNa$ 388.1342, found 388.1340.

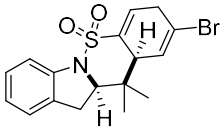


12,12-Dimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2ab): Followed the general procedure with *N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (**1ab**, 60 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 48 mg of the title compound (white solid; m.p. 136-140 ℃; 80% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.3 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.98 – 6.87 (m, 2H), 5.94 – 5.85 (m, 1H), 5.83 – 5.75 (m, 1H), 4.28 (t, *J* = 9.6 Hz, 1H), 3.41 – 3.31 (m, 1H), 3.13 (dd, *J* = 15.5, 9.0 Hz, 1H), 3.00 – 2.88 (m, 3H), 1.10 (s, 3H), 0.83 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 142.8, 135.7, 130.7, 128.5, 127.8, 125.3, 124.8, 123.1, 122.8, 113.4, 71.9, 45.4, 40.3, 30.7, 26.3, 22.7, 14.4; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2961, 2920, 2851, 1634, 1600, 1478, 1314, 1234, 1153, 1106, 967, 750, 711, 638; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{17}H_{19}NO_2SNa$ 324.1029, found 324.1032.

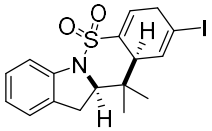


2-Fluoro-12,12-dimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2bb): Followed the general procedure with 4-fluoro-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (**1bb**, 64 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 52 mg of the title compound (white solid; m.p. 144-147 ℃; 82% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.99 – 6.92

(m, 1H), 6.88 – 6.75 (m, 1H), 5.43 – 5.28 (m, 1H), 4.28 (t, *J* = 9.5 Hz, 1H), 3.66 – 3.49 (m, 1H), 3.24 – 2.89 (m, 4H), 1.06 (s, 3H), 0.82 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.6 (d, *J* = 256.0 Hz), 142.5, 136.1 (d, *J* = 2.8 Hz), 128.48 (d, *J* = 11.4 Hz), 128.47, 128.0, 125.0, 123.1, 113.4, 99.5 (d, *J* = 17.9 Hz), 71.7, 47.0 (d, *J* = 7.4 Hz), 40.8, 30.8, 26.9 (d, *J* = 29.6 Hz), 22.8, 14.3; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2968, 2921, 1720, 1601, 1461, 1316, 1232, 1177, 1137, 962, 761, 625; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{17}H_{19}FNO_2S$ 320.1115, found 320.1116.

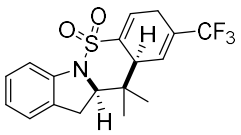


2-Bromo-12,12-dimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2cb): Followed the general procedure with 4-bromo-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (**1cb**, 76 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 65 mg of the title compound (white solid; m.p. 135-139 ℃; 85% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.96 (td, *J* = 7.5, 0.8 Hz, 1H), 6.84 – 6.65 (m, 1H), 6.22 – 6.12 (m, 1H), 4.27 (t, *J* = 9.5 Hz, 1H), 3.54 – 3.40 (m, 1H), 3.37 – 3.12 (m, 3H), 2.96 (dd, *J* = 15.6, 9.8 Hz, 1H), 1.12 (s, 3H), 0.84 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.5, 135.2, 129.6, 128.4, 128.0, 125.0, 124.9, 123.1, 120.1, 113.4, 71.5, 48.8, 40.9, 35.4, 30.7, 22.8, 14.6; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2964, 2919, 1675,1600, 1460, 1318, 1231, 1163, 964, 762, 619; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{17}H_{18}{}^{79}BrNO_2SNa$ 402.0134, found 402.0137.

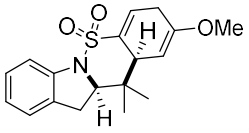


2-Iodo-12,12-dimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2db): Followed the general procedure with 4-iodo-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (**1db**, 85 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to

give 66 mg of the title compound (white solid; m.p. 130-135 °C; 77% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.12 (m, 2H), 6.95 (td, *J* = 7.5, 0.8 Hz, 1H), 6.66 – 6.62 (m, 1H), 6.48 – 6.44 (m, 1H), 4.26 (t, *J* = 9.5 Hz, 1H), 3.43 – 3.31 (m, 3H), 3.14 (dd, *J* = 15.6, 9.1 Hz, 1H), 2.96 (dd, *J* = 15.6, 9.8 Hz, 1H), 1.12 (s, 3H), 0.85 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.5, 134.9, 133.2, 130.1, 128.4, 128.0, 124.9, 123.1, 113.4, 93.3, 71.3, 49.4, 40.8, 39.3, 30.7, 22.7, 14.7; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2968, 2919, 1667,1600, 1460, 1317, 1231, 1163, 964, 761, 713, 619; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{17}H_{18}INO_2SNa$ 449.9995, found 449.9998.

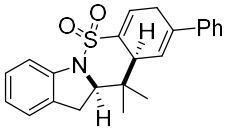


12,12-Dimethyl-2-(trifluoromethyl)-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2eb): Followed the general procedure with *N*-(2-(3-methylbut-2-en-1-yl)phenyl)-4-(trifluoromethyl)benzenesulfonamide (**1eb**, 74 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 53 mg of the title compound (white solid; m.p. 137-139 °C; 71% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.03 – 6.87 (m, 2H), 6.41 (s, 1H), 4.33 (t, *J* = 9.3 Hz, 1H), 3.52 (s, 1H), 3.29 – 2.90 (m, 4H), 1.17 (s, 3H), 0.81 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 142.4, 135.0, 128.4, 128.2, 128.0, 127.4 (q, *J* = 31.1 Hz), 126.2 (q, *J* = 5.5 Hz), 124.9, 123.2, 122.9 (q, *J* = 272.2 Hz), 113.4, 71.5, 45.7, 40.7, 30.6, 23.7, 22.7, 14.7; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2972, 2917, 1656, 1600, 1478, 1460, 1395, 1319, 1299, 1232, 1165, 1106, 969, 760, 710, 622; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{18}H_{19}F_3NO_2S$ 370.1073, found 370.1073.

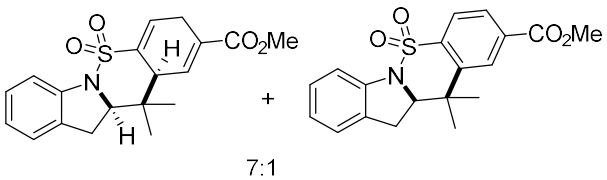


2-Methoxy-12,12-dimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2fb): Followed the general procedure with

4-methoxy-*N*-(2-(3-methylbut-2-en-1-yl)phenyl)benzenesulfonamide (**1fb**, 66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 50 mg of the title compound (white solid; m.p. 141-146 ℃; 76% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.12 (m, 2H), 6.94 (td, *J* = 7.5, 0.9 Hz, 1H), 6.86 – 6.82 (m, 1H), 4.73 – 4.65 (m, 1H), 4.31 – 4.24 (m, 1H), 3.61 (s, 3H), 3.52 – 3.46 (m, 1H), 3.14 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.05 – 2.86 (m, 3H), 1.09 (s, 3H), 0.79 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.8, 142.8, 136.0, 129.8, 128.6, 127.9, 124.9, 122.9, 113.4, 89.8, 71.9, 54.4, 46.8, 41.1, 30.9, 28.8, 23.0, 14.0; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2970, 2902, 1719, 1682, 1477, 1318, 1219, 1152, 965, 754, 625; **HRMS** (ESI) $[M + Na]^+$ Calculated for $C_{18}H_{21}NO_2SNa$ 354.1134, found 354.1127.

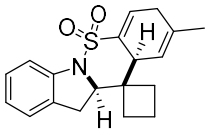


12,12-Dimethyl-2-phenyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2, 3-a]indole 5,5-dioxide (2gb): Followed the general procedure with *N*-(2-(3-methylbut-2-en-1-yl)phenyl)-[1,1'-biphenyl]-4-sulfonamide (**1gb**, 76 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 49 mg of the title compound (white solid; m.p. 132-135 ℃; 65% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.56 (m, 1H), 7.44 – 7.32 (m, 5H), 7.19 – 7.13 (m, 2H), 7.05 – 7.02 (m, 1H), 6.96 (td, *J* = 7.5, 0.9 Hz, 1H), 6.20 – 6.12 (m, 1H), 4.40 – 4.29 (m, 1H), 3.60 – 3.52 (m, 1H), 3.43 – 3.22 (m, 2H), 3.16 (dd, *J* = 15.6, 9.0 Hz, 1H), 2.98 (dd, *J* = 15.5, 10.1 Hz, 1H), 1.20 (s, 3H), 0.86 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.8, 140.0, 135.6, 135.3, 130.7, 128.6, 128.5, 128.0, 127.9, 125.3, 124.9, 123.0, 120.1, 113.5, 71.9, 46.9, 41.1, 30.7, 28.7, 22.9, 14.6; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2957, 2918, 2872, 1467, 1318, 1230, 1176, 1148, 961, 828, 718, 679, 624; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{23}H_{24}NO_2S$ 378.1522, found 378.1523.



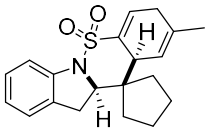
7:1

Methyl 12,12-dimethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole-2-carboxylate 5,5-dioxide (2hb): Followed the general procedure with methyl 4-(N-(2-(3-methylbut-2-en-1-yl)phenyl)sulfamoyl)benzoate (72 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 50 mg of the title mixture (white solid; m.p. 135-139 ℃; 70% yield); **diene: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.50 (m, 1H), 7.18 – 7.12 (m, 2H), 7.02 – 6.98 (m, 1H), 6.98 – 6.92 (m, 2H), 4.33 (t, *J* = 9.5 Hz, 1H), 3.80 (s, 3H), 3.58 – 3.50 (m, 1H), 3.20 – 3.11 (m, 3H), 2.96 (dd, *J* = 15.6, 9.9 Hz, 1H), 1.20 (s, 3H), 0.81 (s, 3H); **arene: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 7.6 Hz, 1H), 8.08 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.09 – 7.05 (m, 1H), 4.70 (t, *J* = 9.8 Hz, 1H), 3.97 (s, 3H), 3.39 (dd, *J* = 15.8, 9.8 Hz, 1), 3.27 – 3.20 (m, 1H), 1.52 (s, 3H), 1.32 (s, 3H); **mixture of diene and arene: ^{13}C NMR (150 MHz, $CDCl_3$)** δ 166.1, 165.6, 145.1, 142.5, 141.4, 140.4, 134.4, 134.2, 133.8, 130.3, 128.80, 128.77, 128.4, 128.3, 128.2, 128.0, 125.2, 124.9, 124.3, 124.0, 123.1, 114.5, 113.4, 71.7, 68.2, 52.7, 52.1, 46.8, 40.8, 39.8, 30.9, 30.6, 25.9, 24.7, 24.2, 22.8, 14.9; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2919, 2850, 1717, 1460, 1317, 1263, 1164, 966, 754, 655; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{19}H_{22}NO_4S$ 360.1264, found 360.1269.

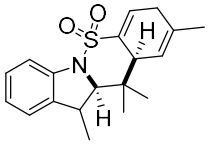


Methyl-3,11,11a,12a-tetrahydrospiro[benzo[5,6][1,2]thiazino[2,3-a]indole-12,1'-cyclobutane] 5,5-dioxide (2ib): Followed the general procedure with *N*-(2-(2-cyclobutylideneethyl)phenyl)-4-methylbenzenesulfonamide (**1ib**, 65 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 37 mg of the title compound (white solid; m.p. 133-138 ℃; 56% yield); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.95 (td, *J* = 7.5, 0.9 Hz, 1H), 6.90 – 6.86 (m, 1H), 5.80 (d, *J* = 1.5 Hz, 1H), 4.33 (t, *J* = 9.5 Hz, 1H), 3.47 – 3.38 (m, 1H), 3.32 (d, *J* = 9.5 Hz, 2H), 3.00 – 2.75 (m, 2H), 2.22 – 2.08 (m, 1H), 1.98 – 1.88 (m, 2H), 1.85 (s, 3H), 1.84 – 1.66 (m,

3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 142.8, 135.2, 133.3, 131.0, 128.6, 127.9, 124.8, 122.9, 117.8, 113.5, 69.8, 46.6, 43.8, 31.6, 31.1, 24.4, 23.1, 20.0, 14.3; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2960, 2852, 1635, 1474, 1311, 1228, 1151, 993, 750, 669; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{19}H_{22}NO_2S$ 328.1366, found 328.1366.

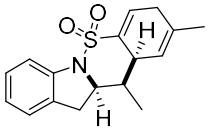


2-Methyl-3,11,11a,12a-tetrahydrospiro[benzo[5,6][1,2]thiazino[2,3-a]indole-12,1'-cyclopentane] 5,5-dioxide (2jb): Followed the general procedure with *N*-(2-(2-cyclopentylideneethyl)phenyl)-4-methylbenzenesulfonamide (**1jb**, 68 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 41 mg of the title compound (white solid; m.p. 130-134 ℃; 60% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.10 (m, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.88 (s, 1H), 5.49 (s, 1H), 4.48 (t, *J* = 9.8 Hz, 1H), 3.58 – 3.49 (m, 1H), 3.17 (dd, *J* = 15.3, 8.6 Hz, 1H), 3.04 – 2.67 (m, 3H), 1.97 – 1.83 (m, 1H), 1.81 (s, 3H), 1.75 – 1.39 (m, 7H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.0, 136.3, 132.8, 130.8, 128.5, 127.9, 124.8, 122.9, 118.5, 113.6, 71.9, 52.2, 46.2, 34.5, 31.9, 31.1, 28.1, 27.5, 26.6, 23.1; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2956, 2863,1601, 1478, 1317, 1235, 1153, 1001, 963, 752, 677, 639; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{20}H_{24}NO_2S$ 342.1522, found 342.1517.

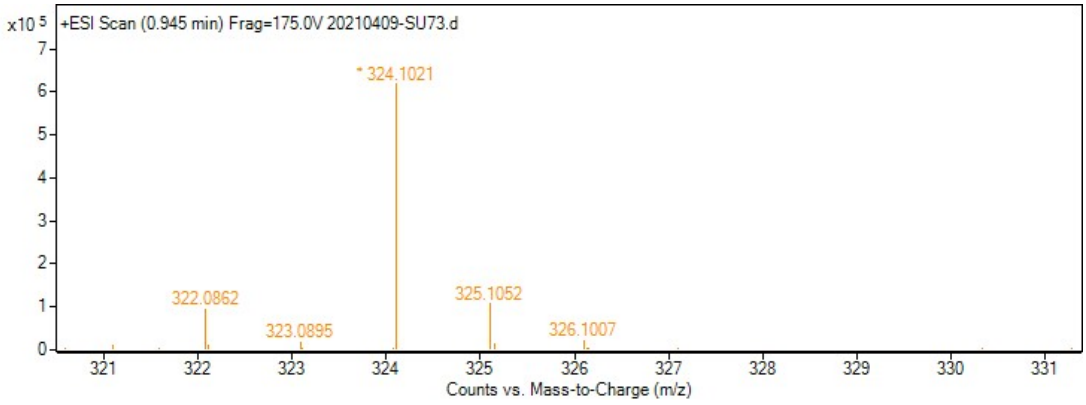


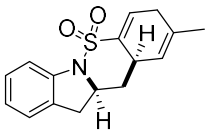
2,11,12,12-Tetramethyl-11,11a,12,12a-tetrahydro-*3H*-benzo[5,6][1,2]thiazino[2,3-a]indole 5,5-dioxide (2kb): Followed the general procedure with 4-methyl-*N*-(2-(4-methylpent-3-en-2-yl)phenyl)benzenesulfonamide (**1kb**, 66 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 30:1) to give 34 mg of the title compound (the major isomer, white solid; m.p. 121-125 ℃; 52% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.18 – 7.06 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.86 – 6.79 (m, 1H), 5.49 (d, *J* = 1.5 Hz, 1H), 3.90 (d, *J*

= 6.2 Hz, 1H), 3.41 – 3.33 (m, 1H), 3.24 (p, *J* = 6.7 Hz, 1H), 2.90 – 2.67 (m, 2H), 1.76 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.12 (s, 3H), 0.67 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 141.9 135.7, 133.9, 133.0, 129.5, 127.9, 123.8, 122.4, 117.4, 112.4, 78.1, 46.4, 41.9, 37.6, 30.8, 23.0, 22.2, 21.9, 14.6; **FT-IR (thin film, KBr): ν (cm^{-1}):** 2968, 2921, 1598, 1477, 1460, 1319, 1232, 1150, 997, 750, 688, 612; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{19}H_{24}NO_2S$ 330.1522, found 330.1525.

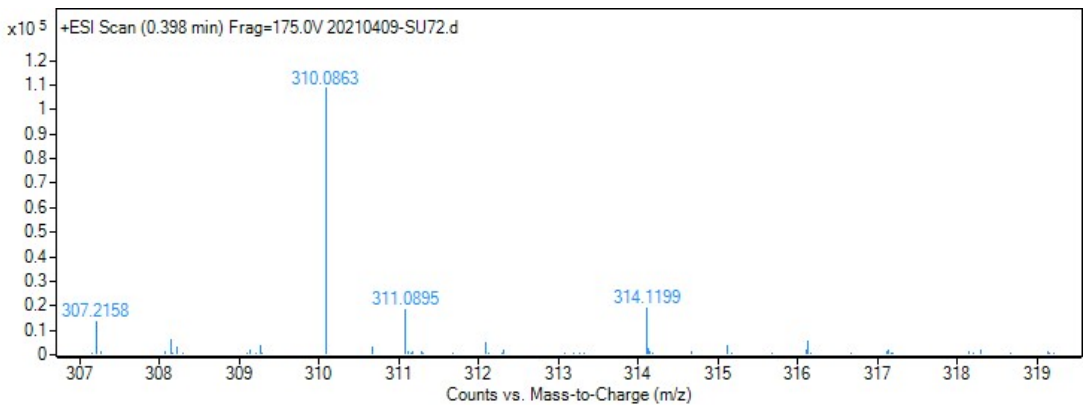


2lb: HRMS (ESI) $[M + Na]^+$ Calculated for $C_{17}H_{19}NO_2SNa$ 324.1029, found 324.1021.



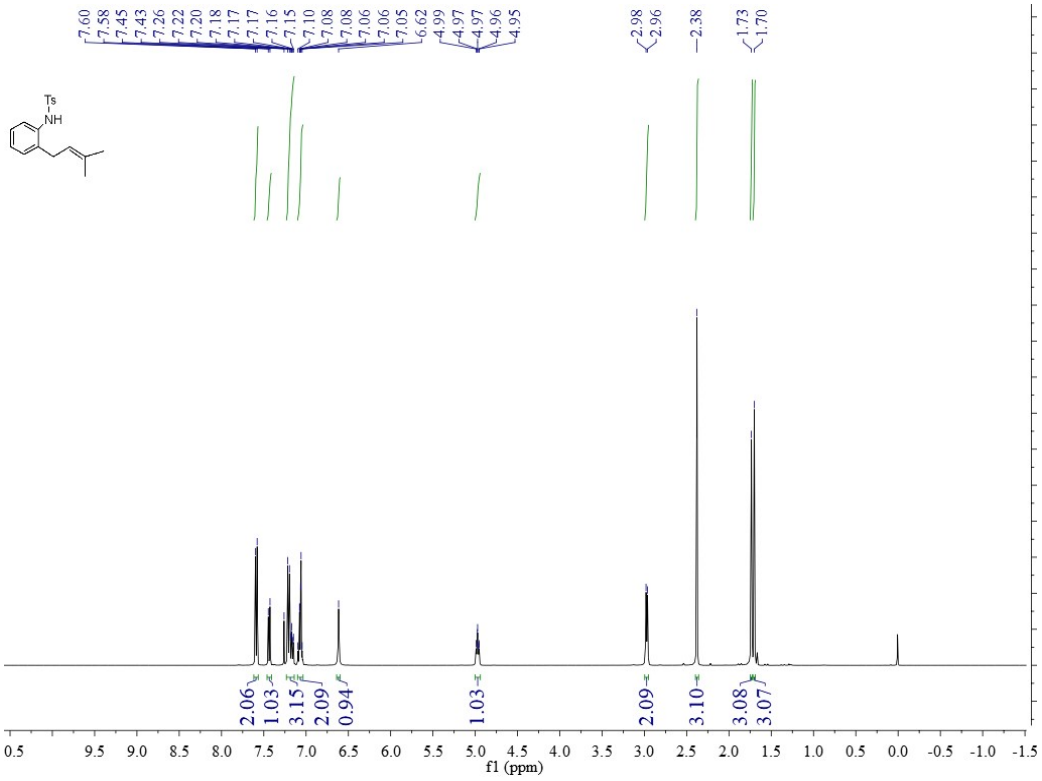


2mb: HRMS (ESI) $[M + Na]^+$ Calculated for $C_{16}H_{17}NO_2SNa$ 310.0872, found 310.0863.

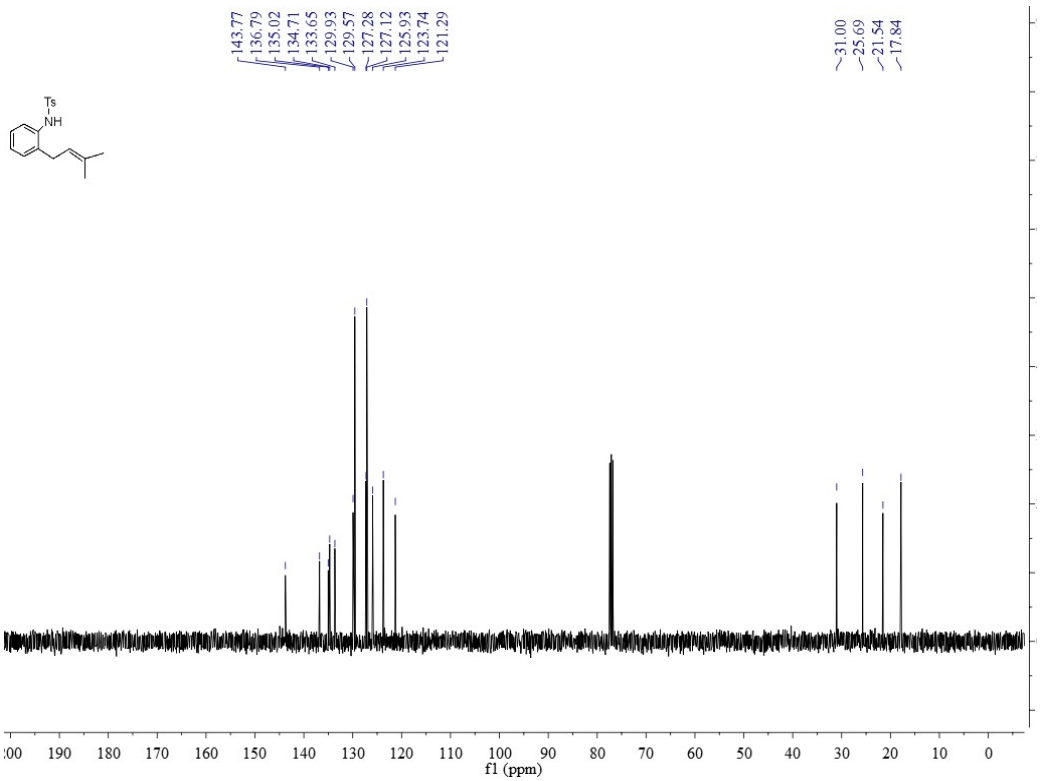


8. NMR spectra for the substrates and products

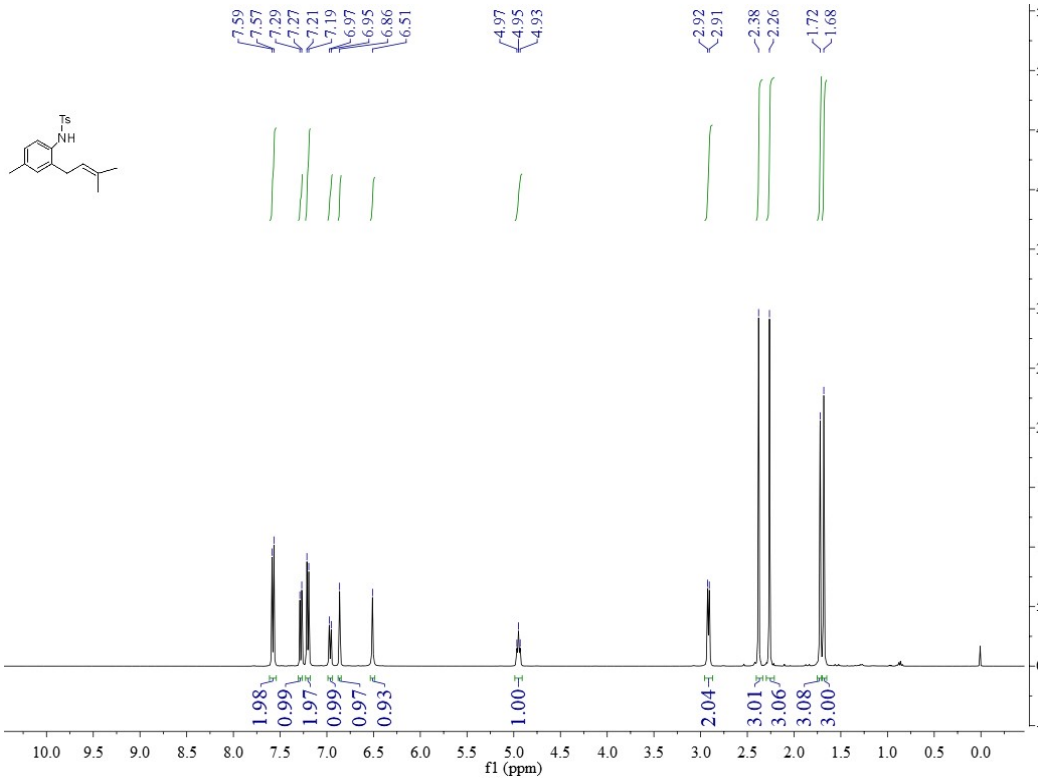
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1aa**



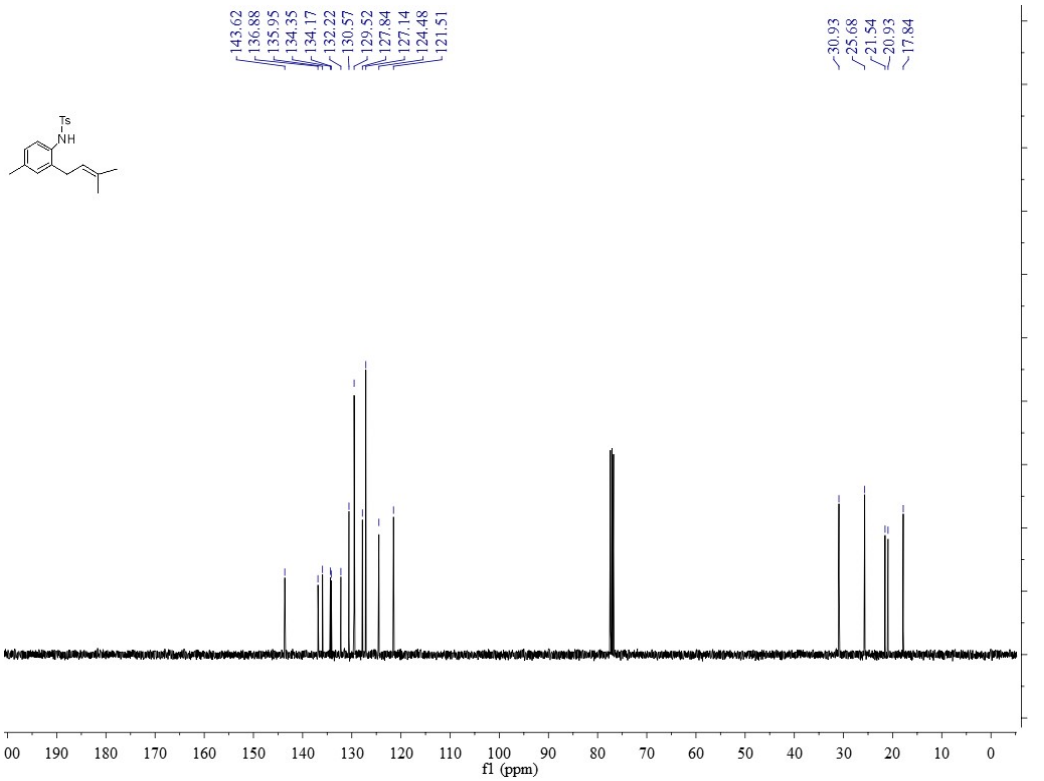
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1aa**



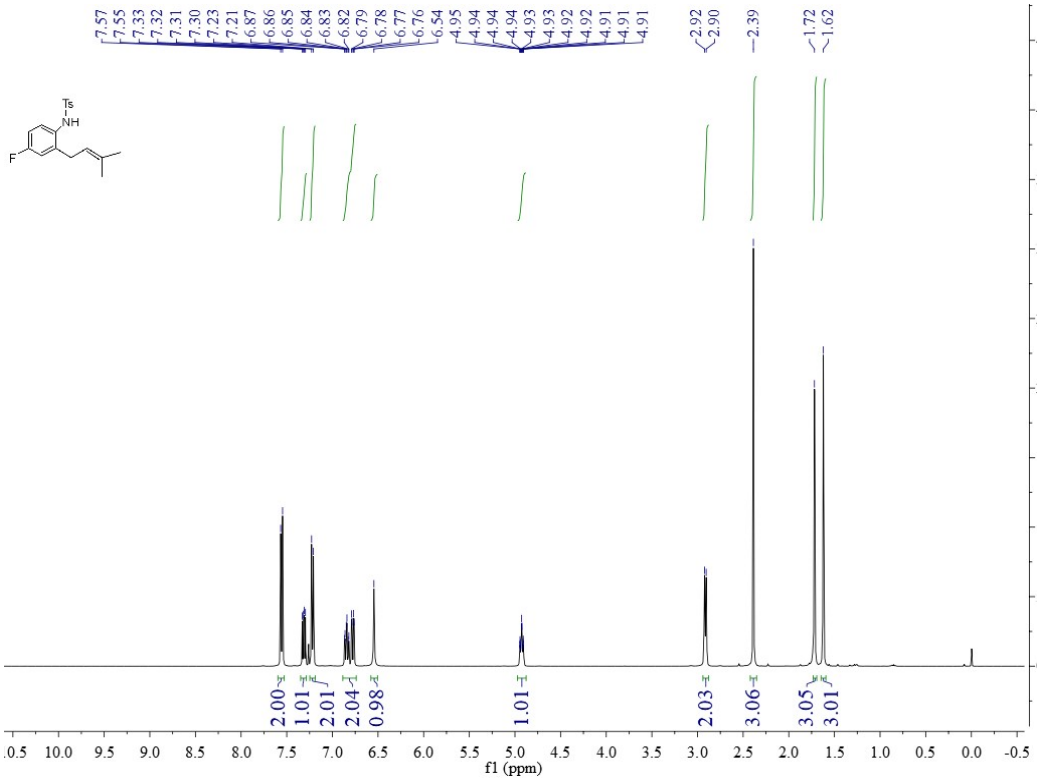
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ba**



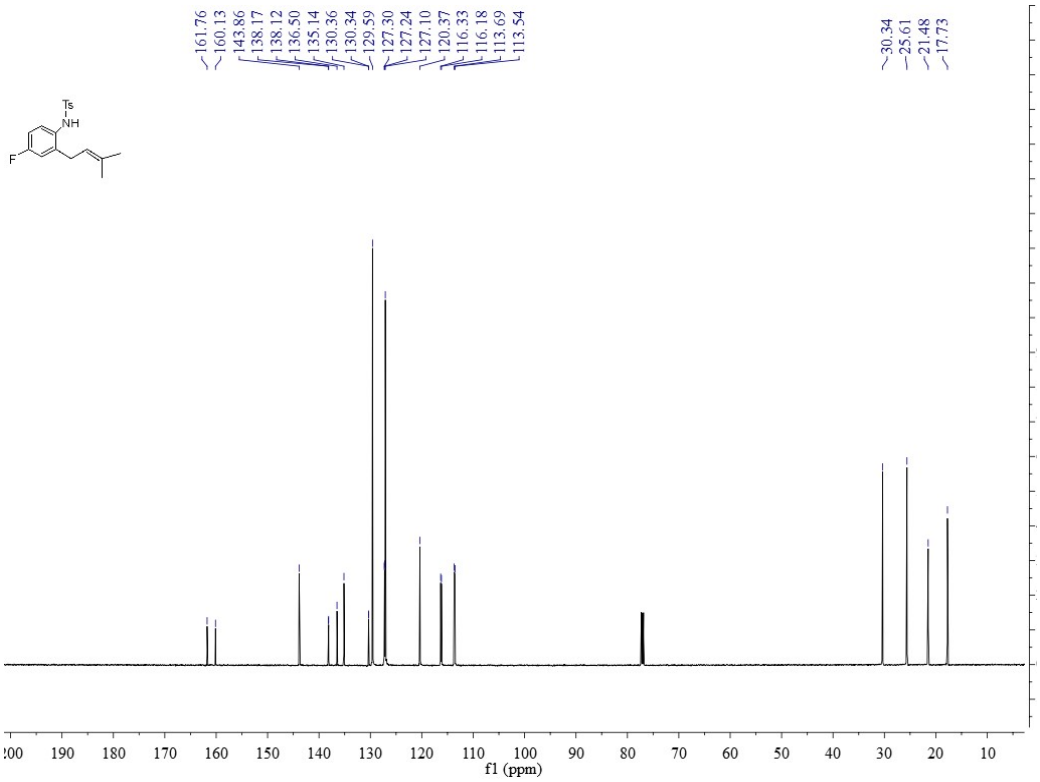
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ba**



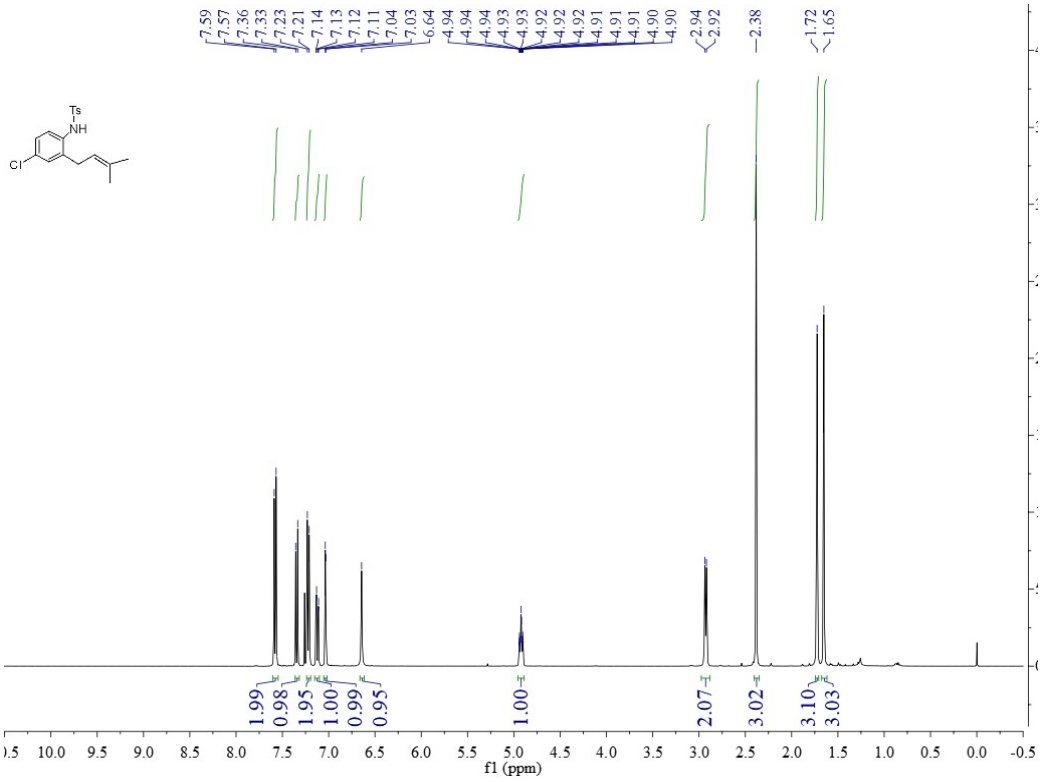
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ca**



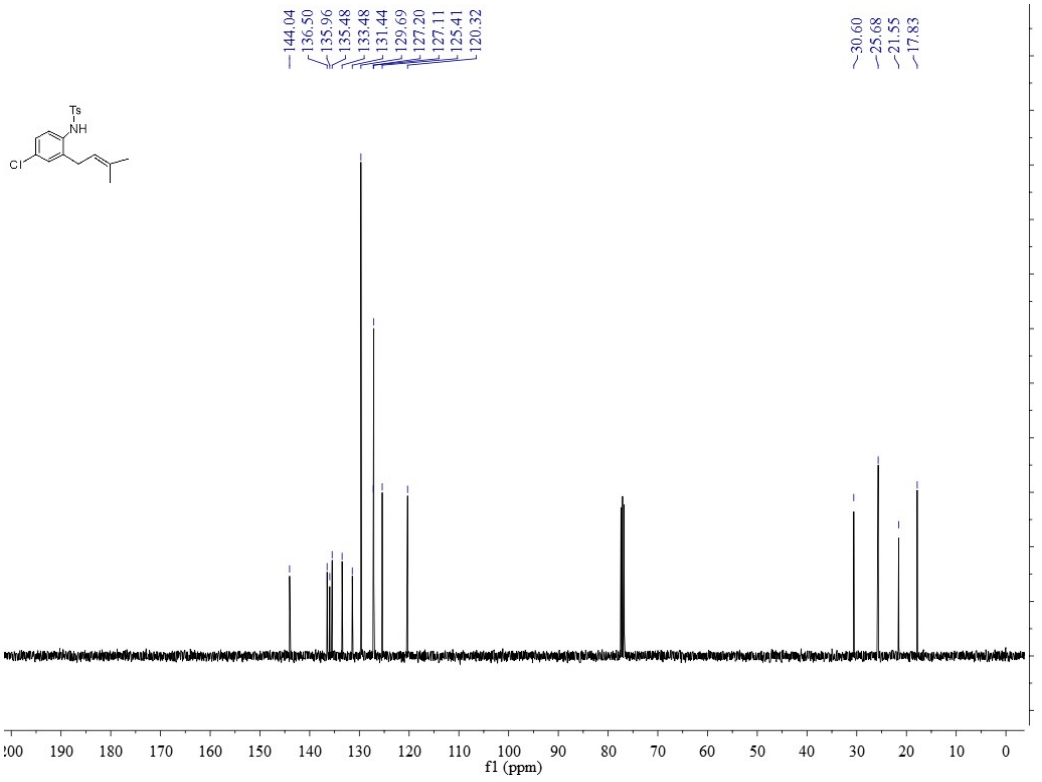
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ca**



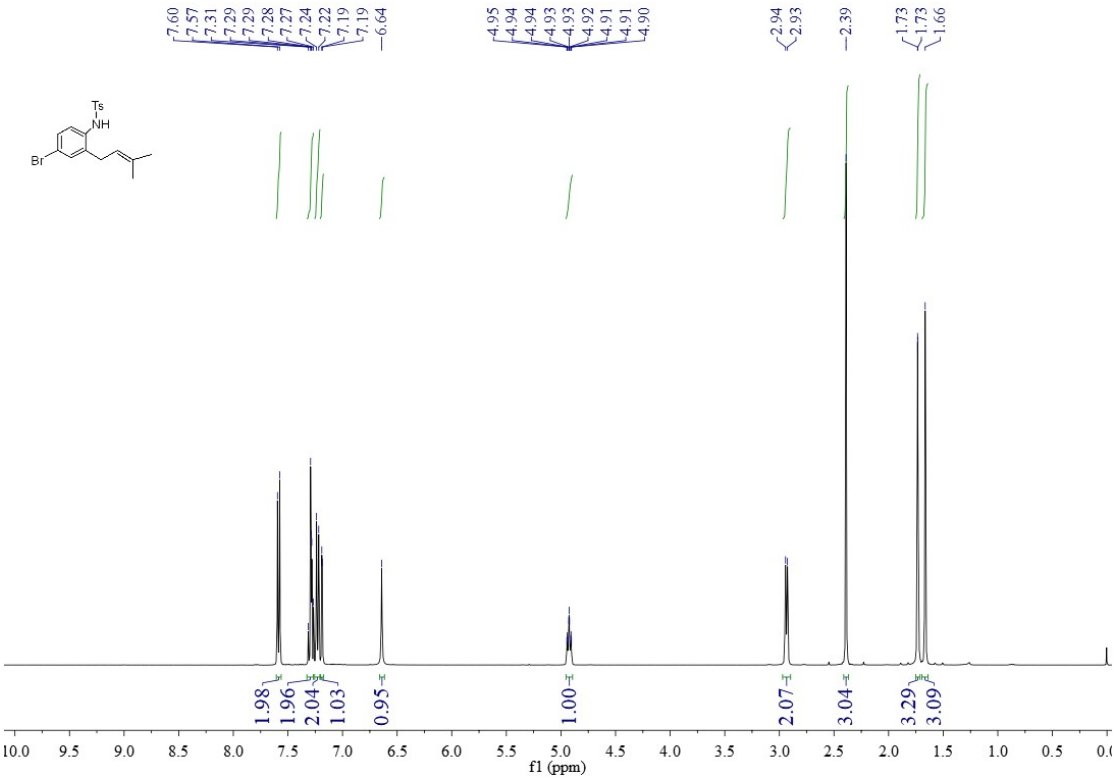
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1da**



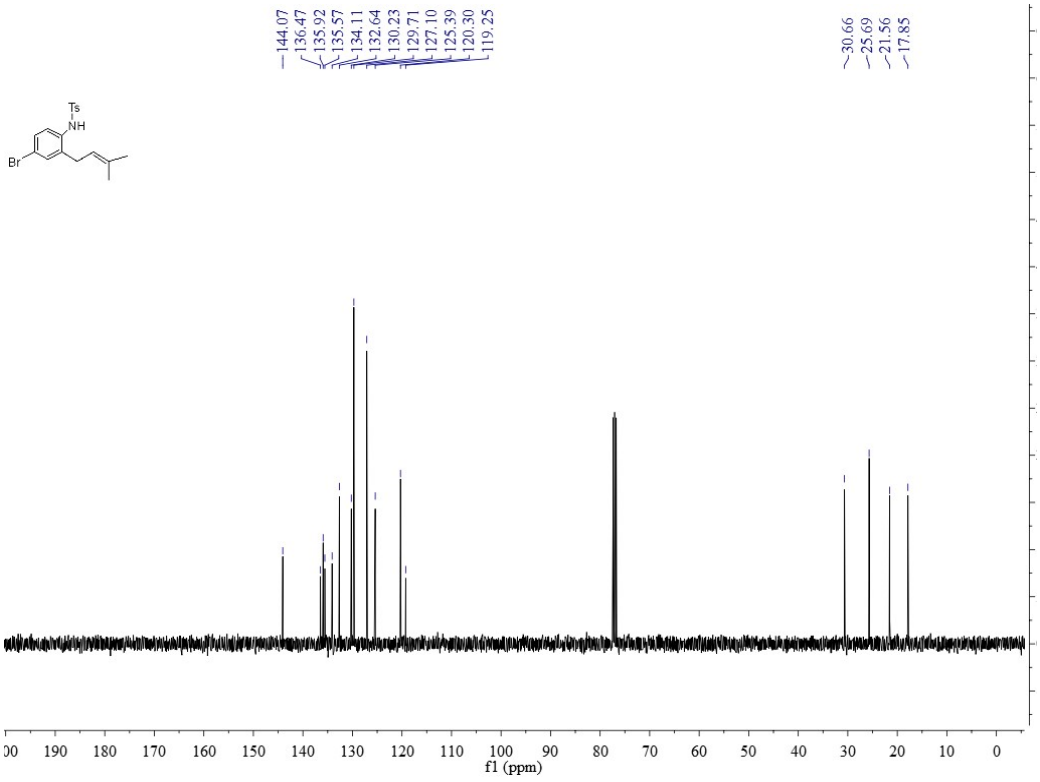
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1da**



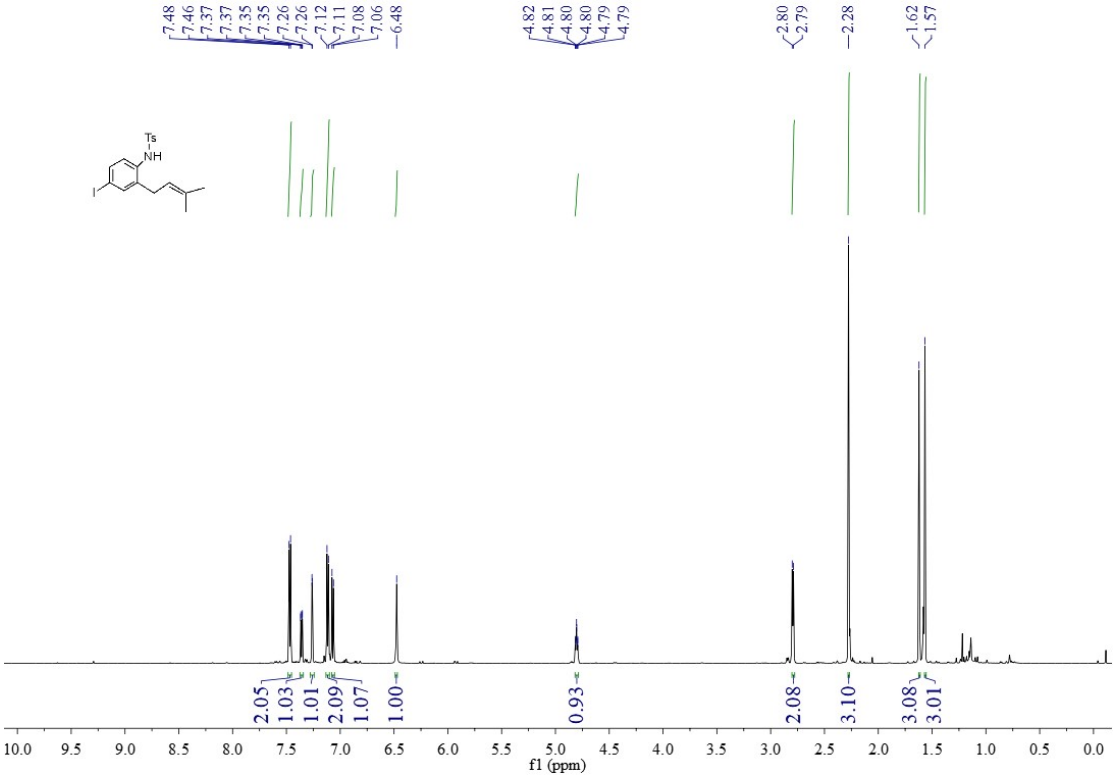
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ea**



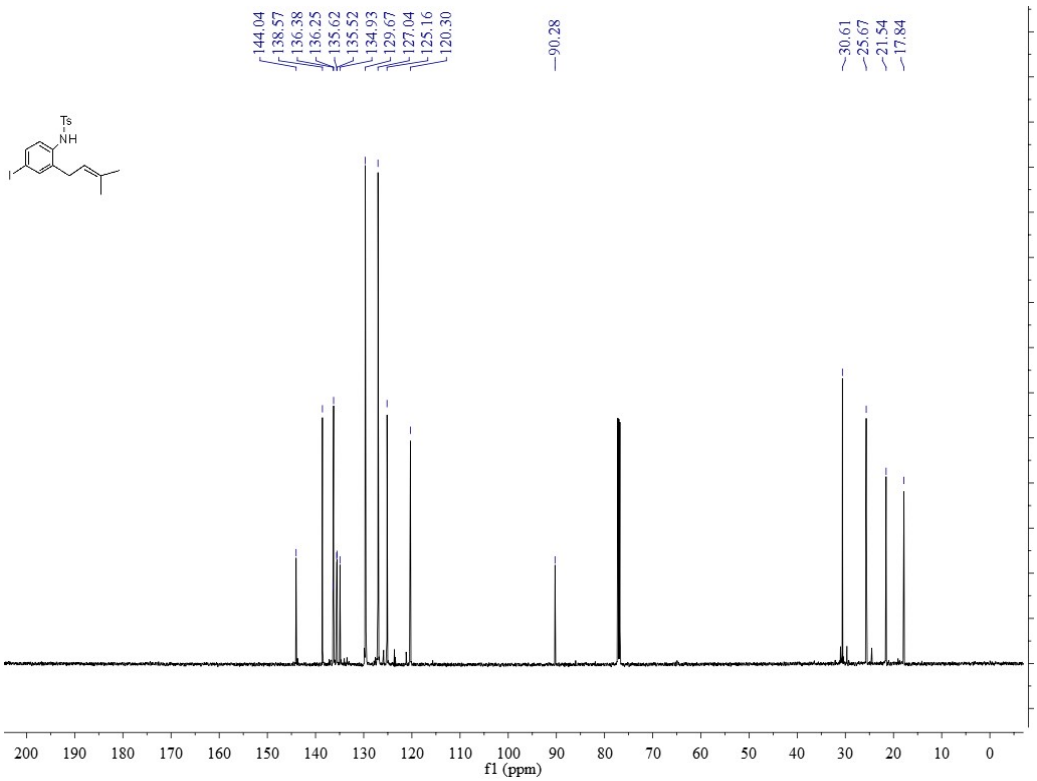
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ea**



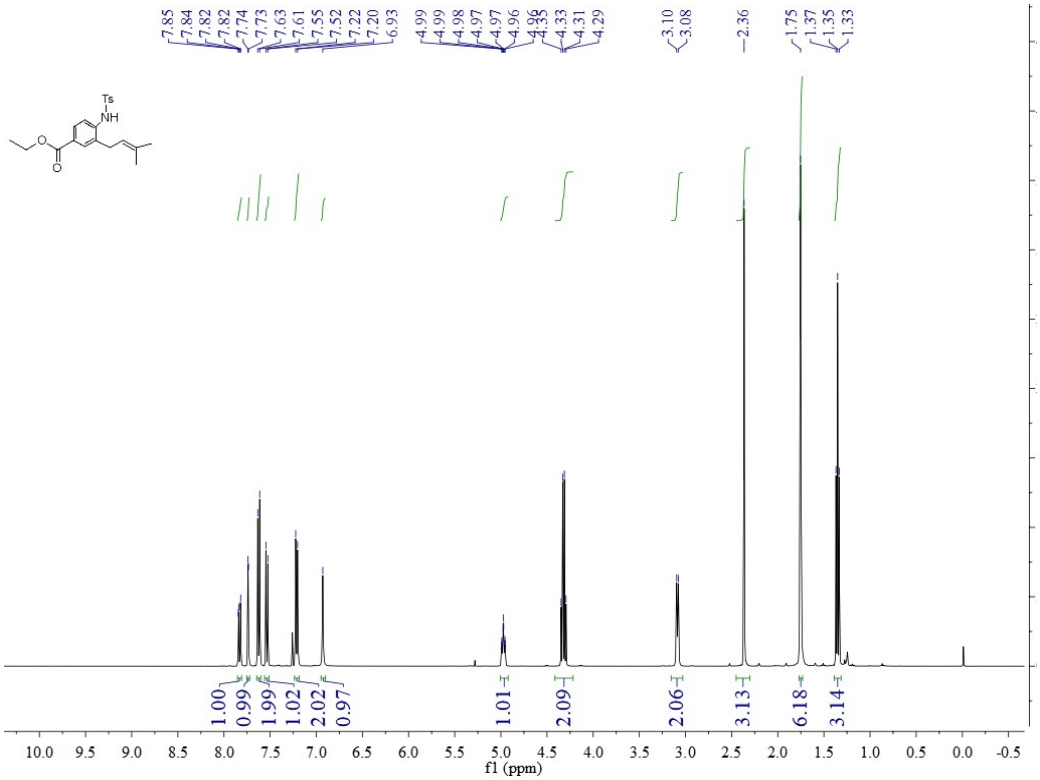
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1fa**



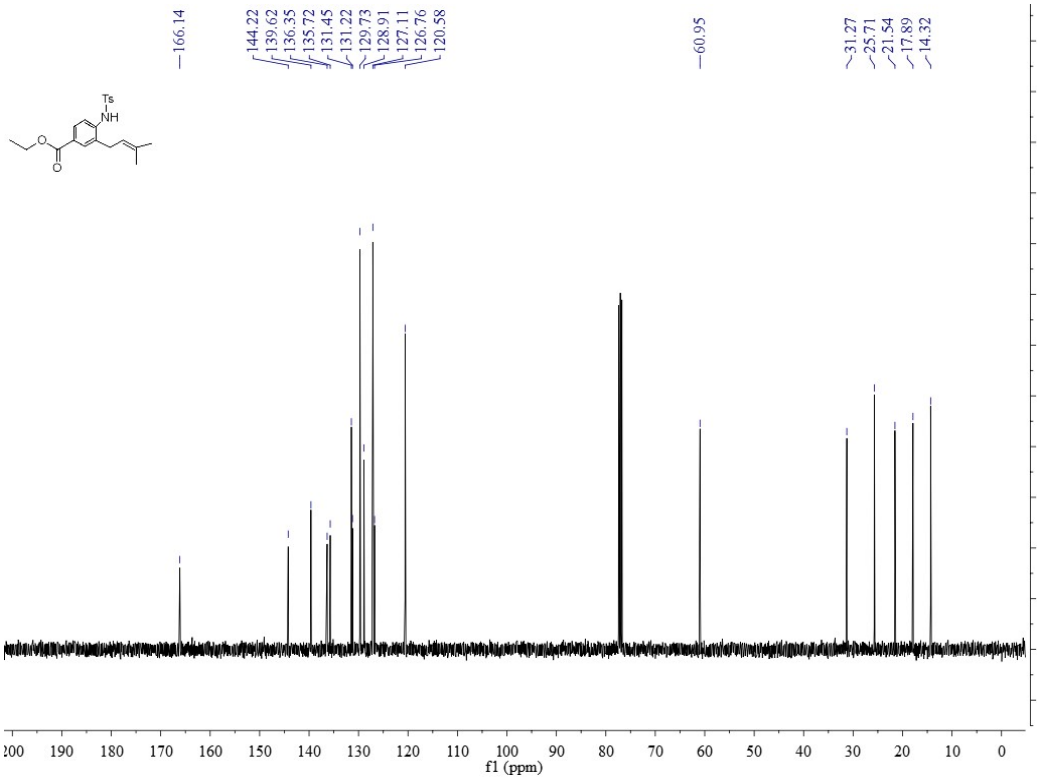
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1fa**



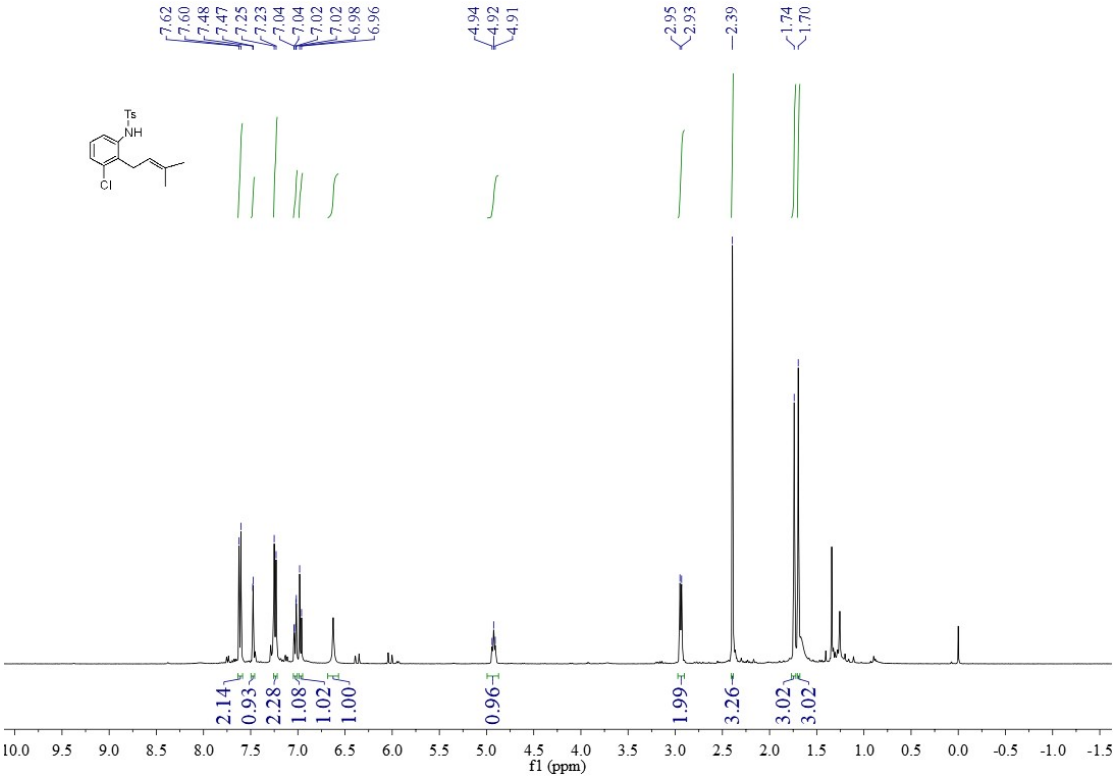
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ga**



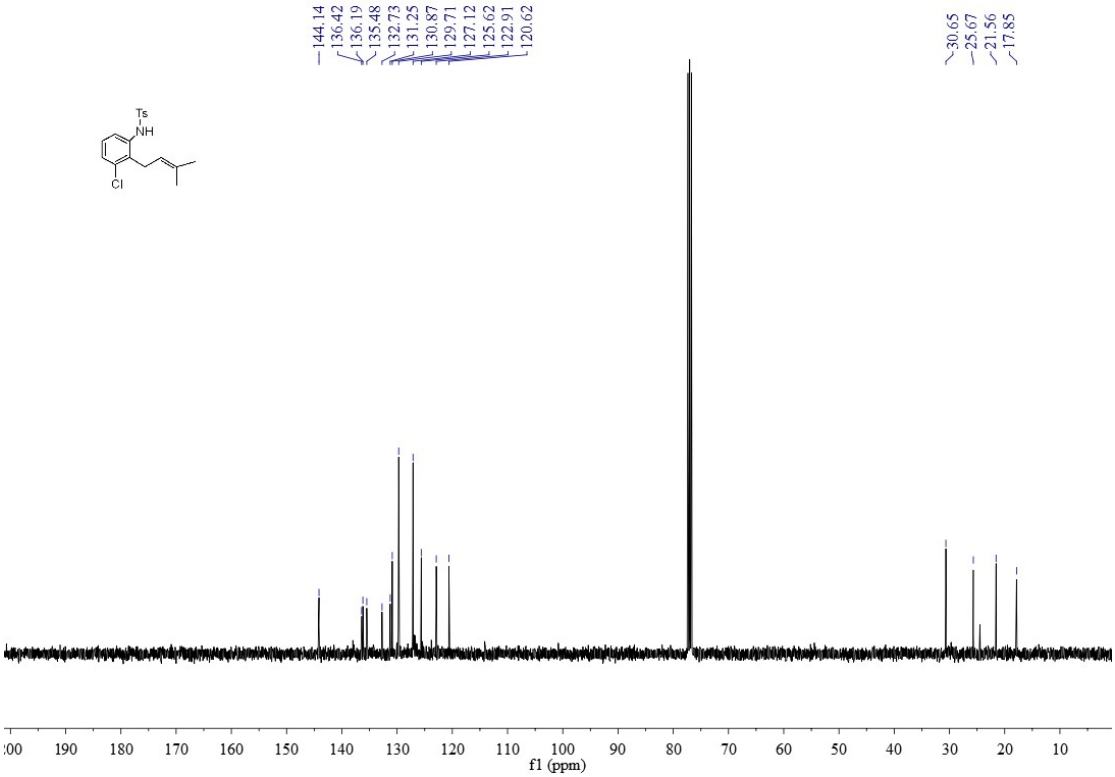
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ga**



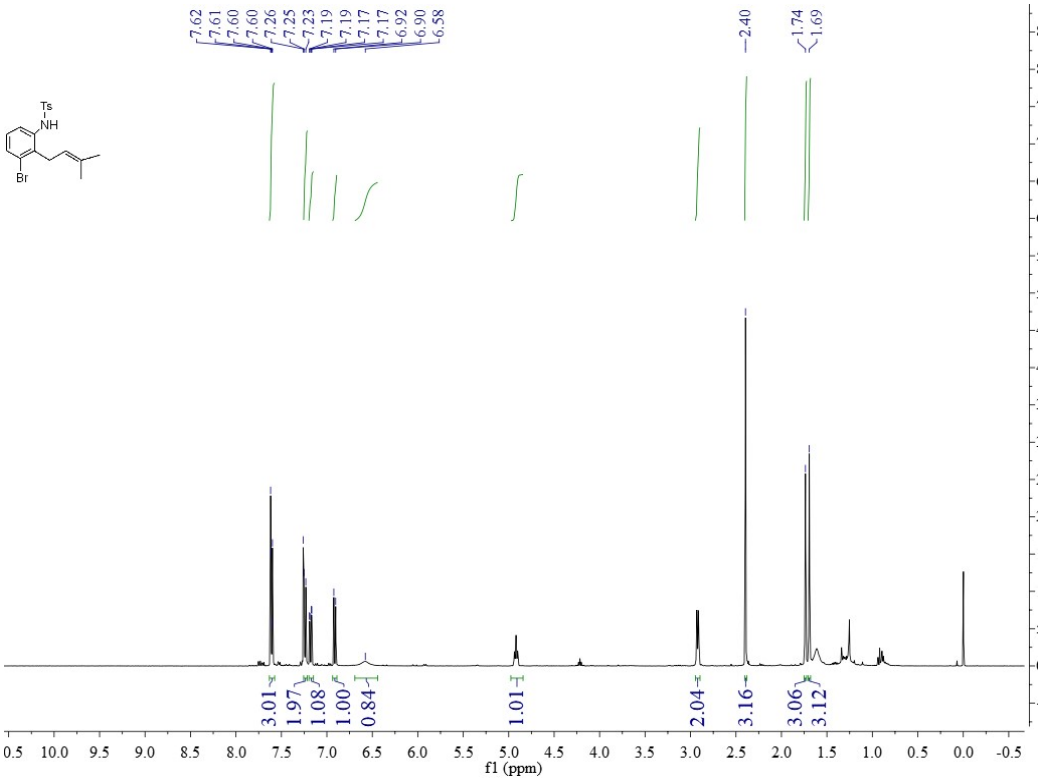
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ha**



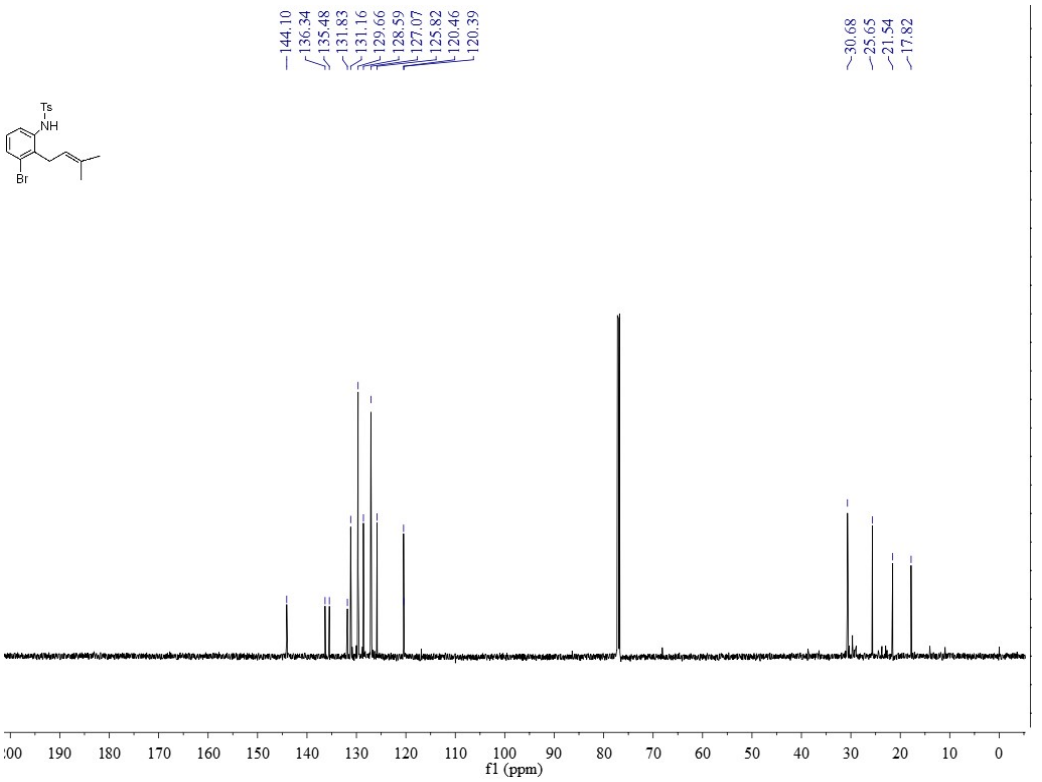
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ha**



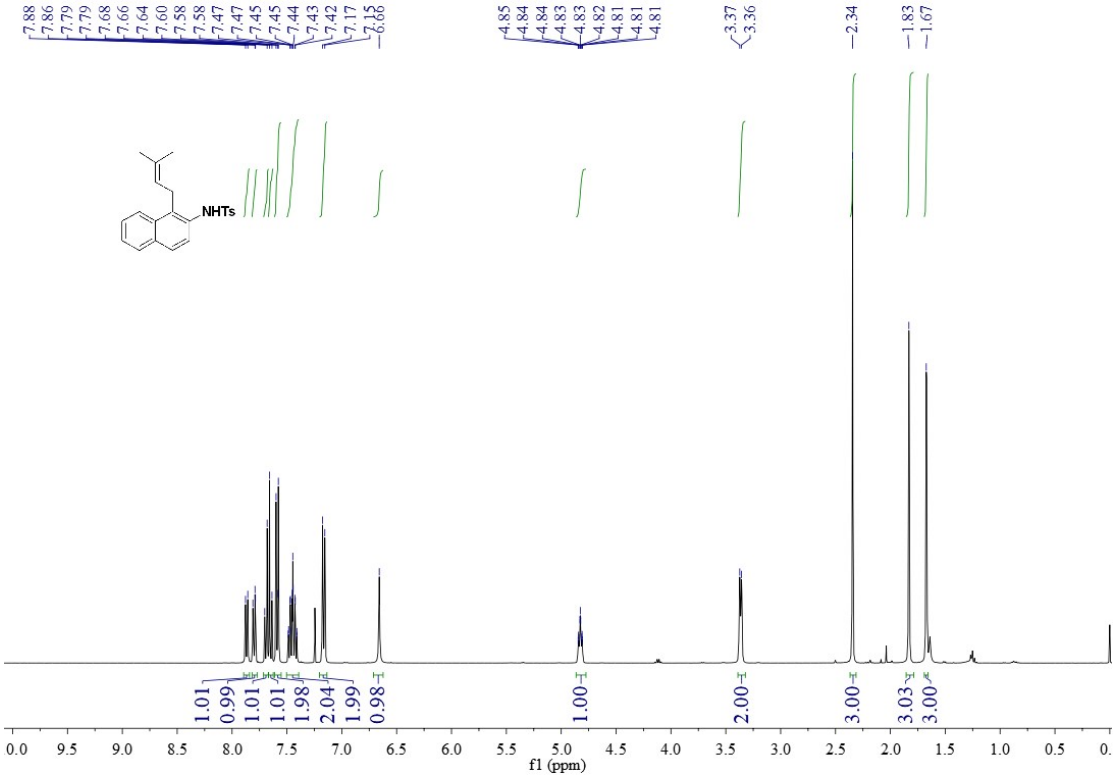
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ia**



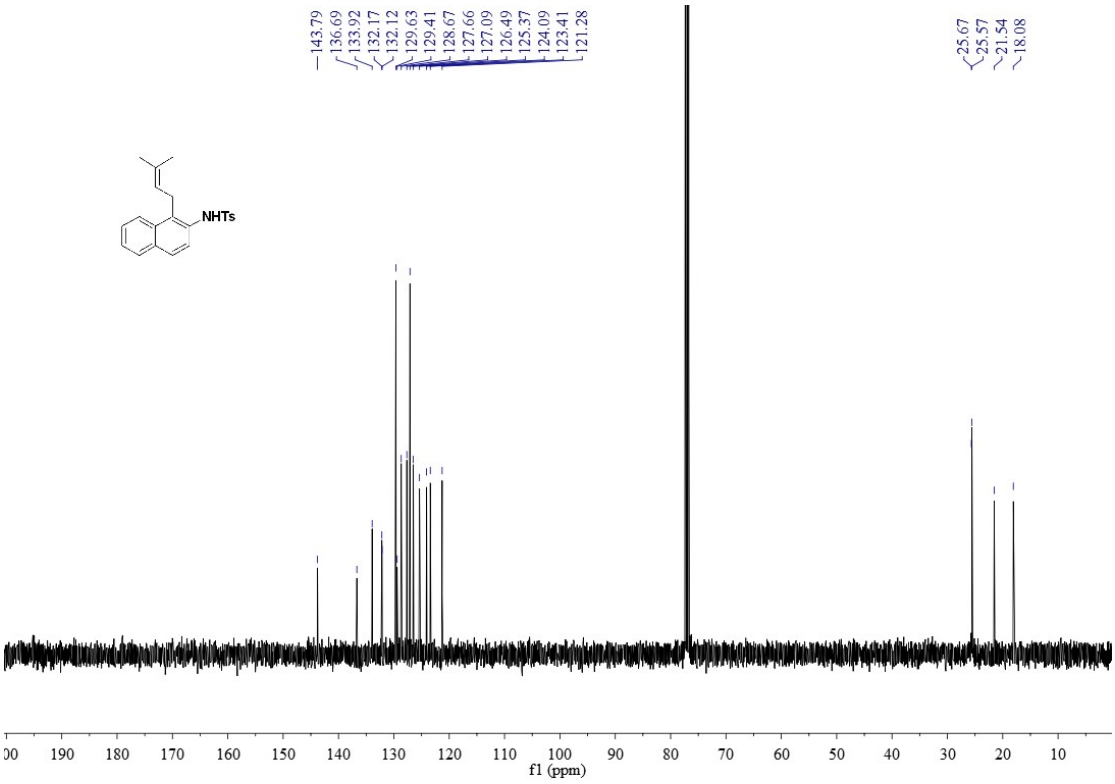
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ia**



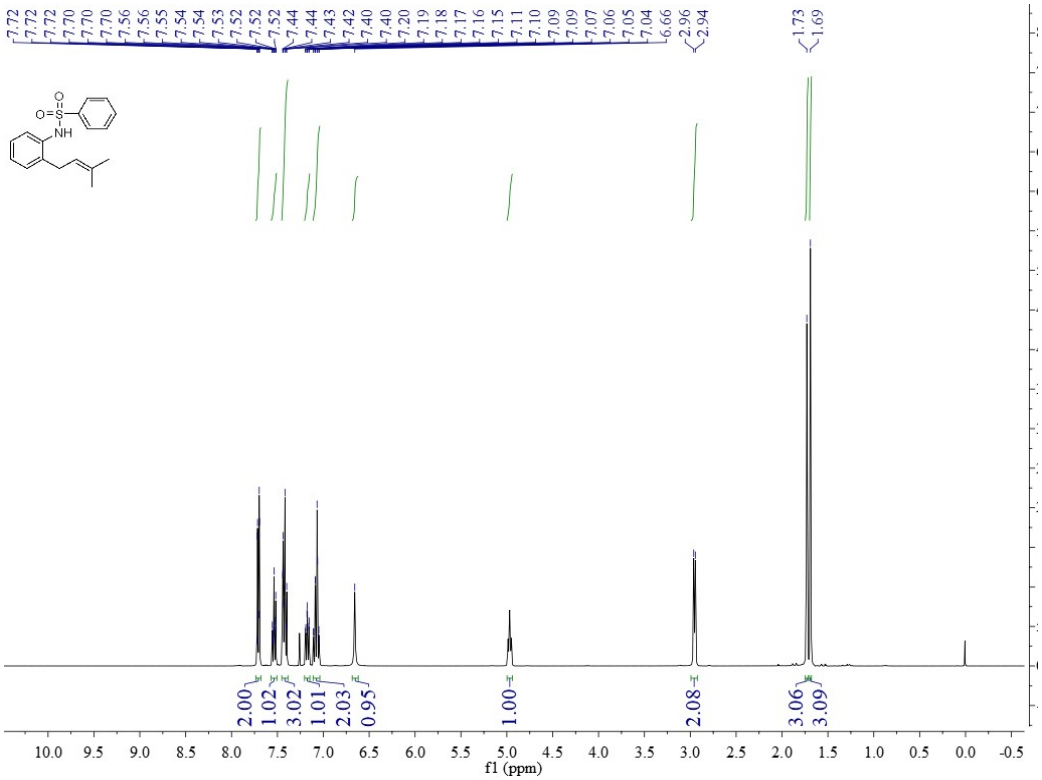
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ja**



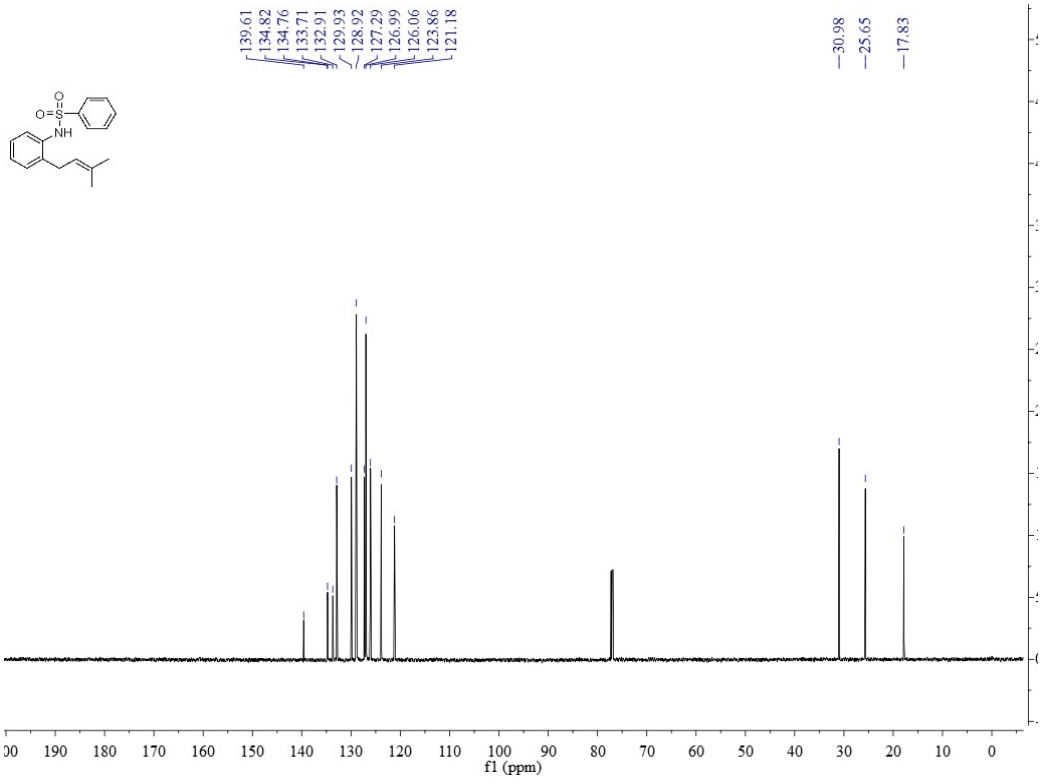
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ja**



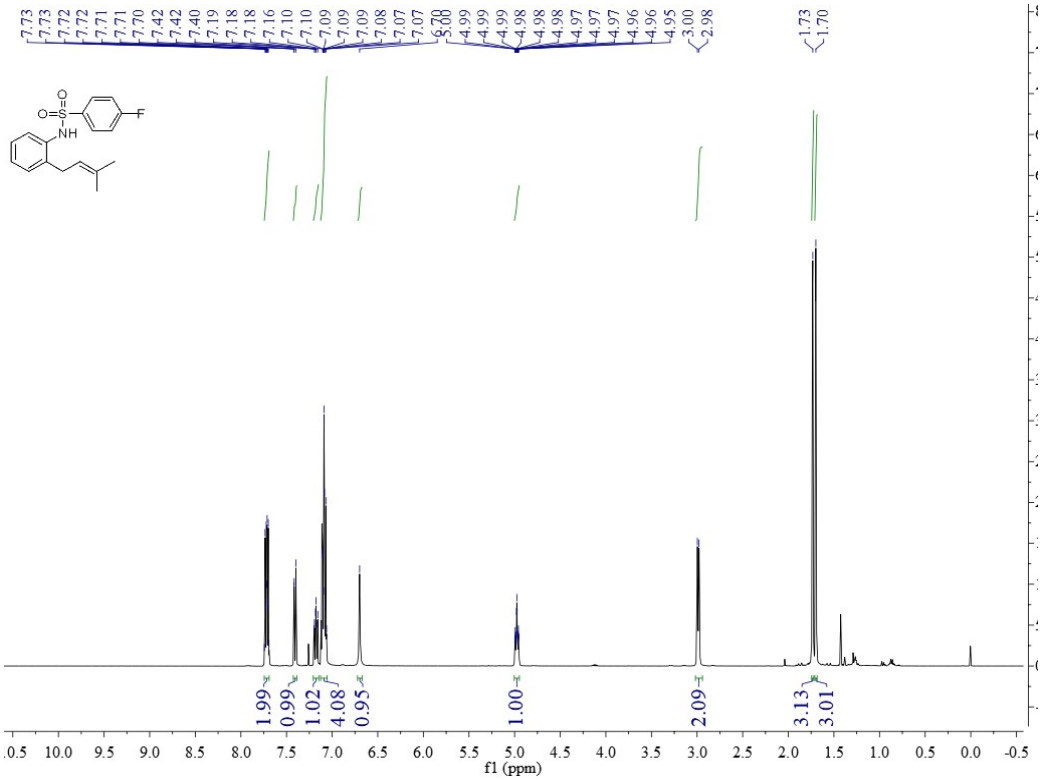
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ab**



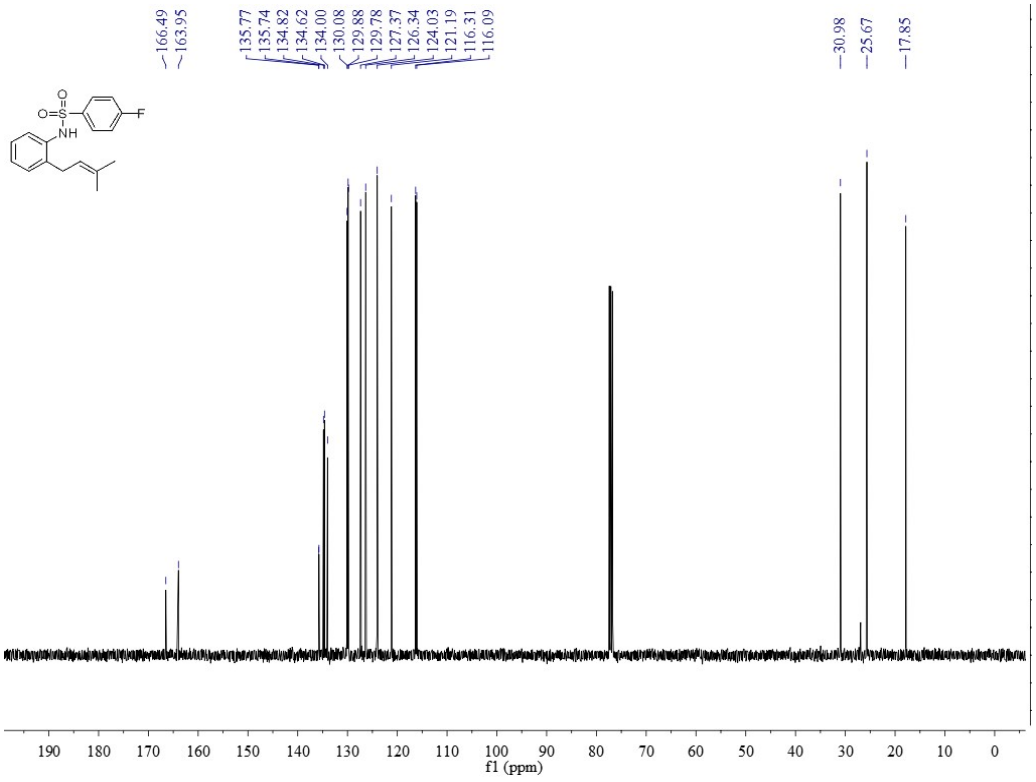
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ab**



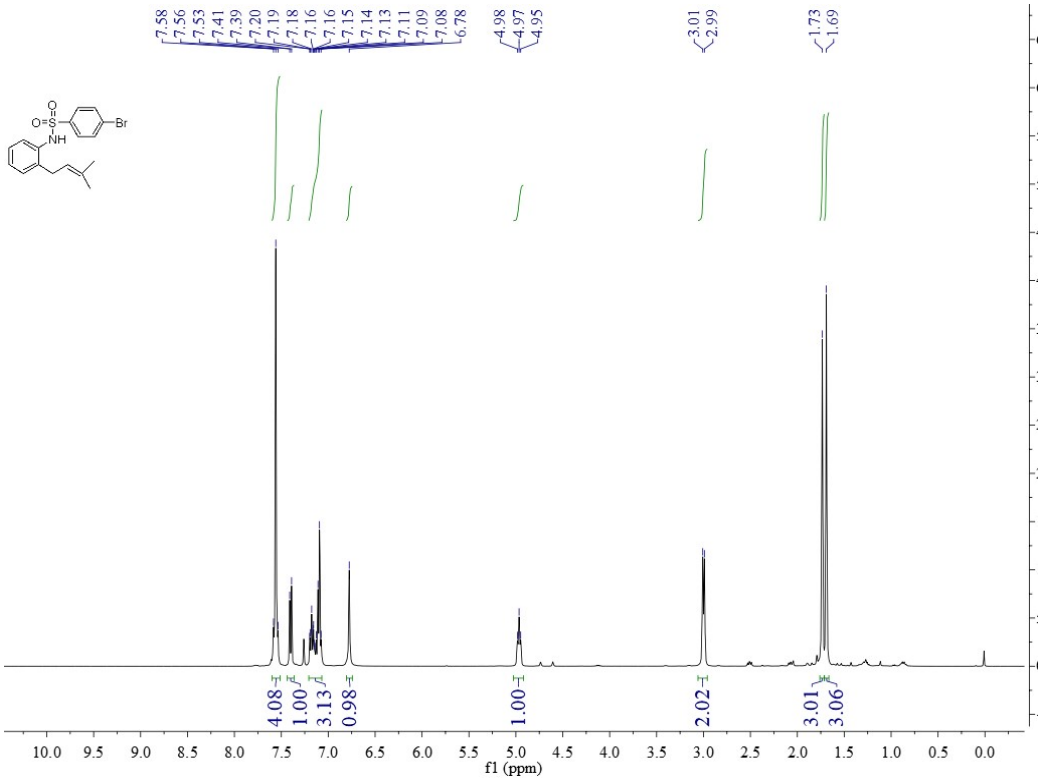
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1bb**



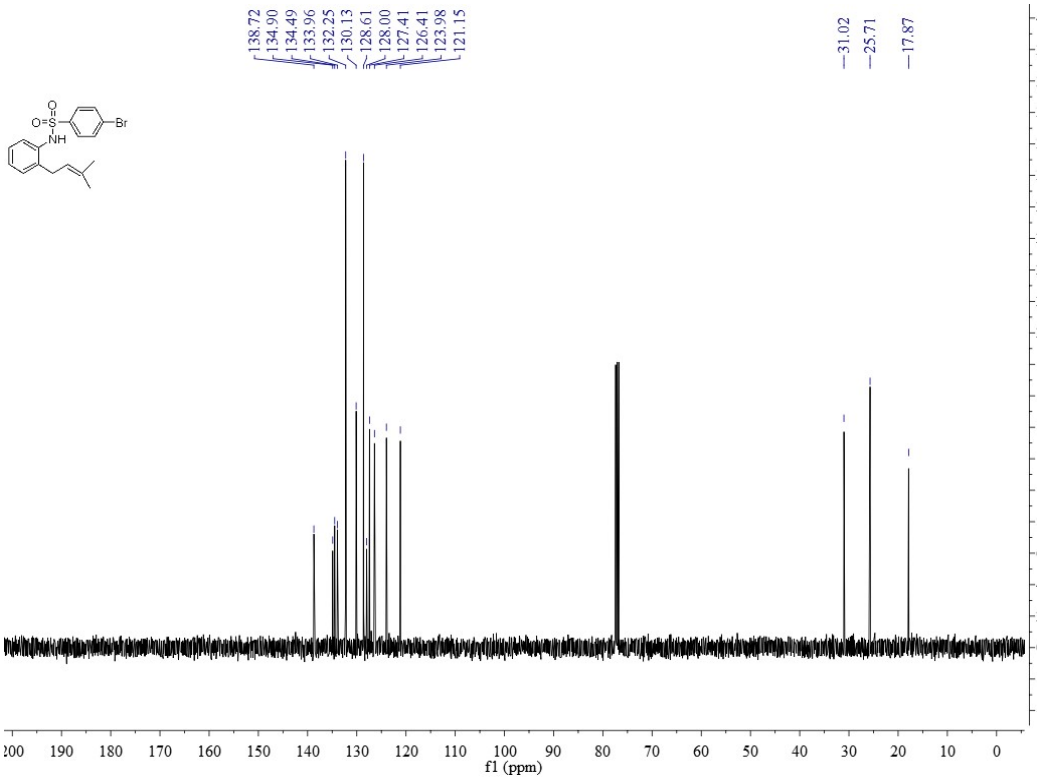
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1bb**



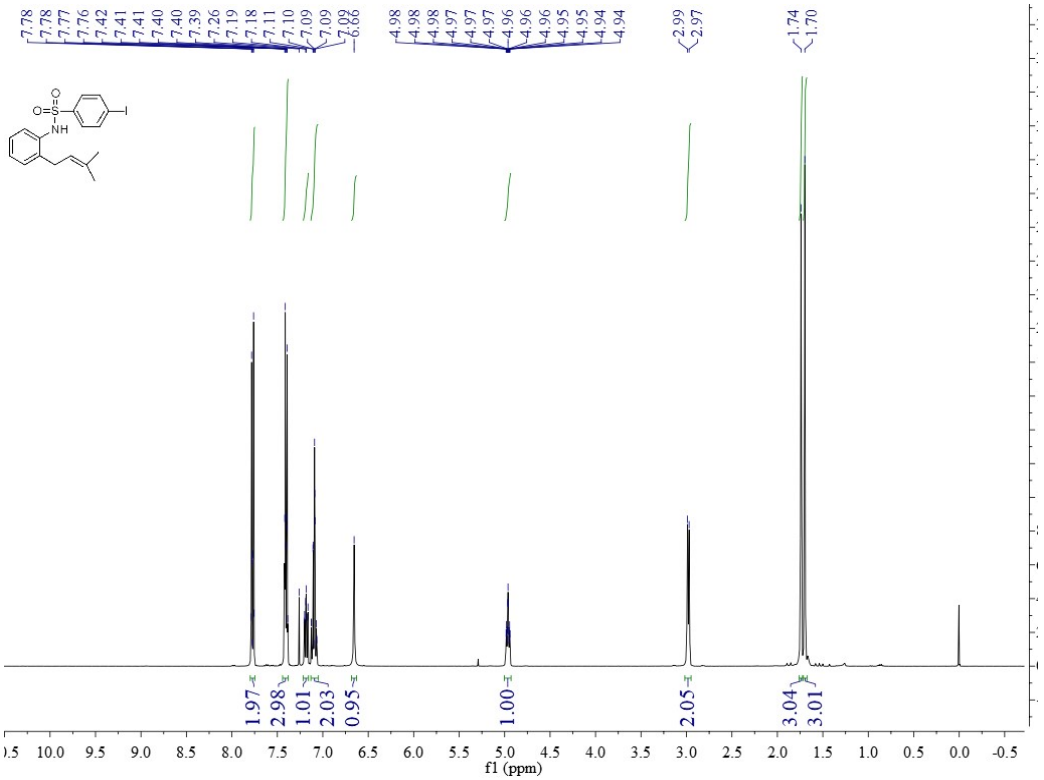
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1cb**



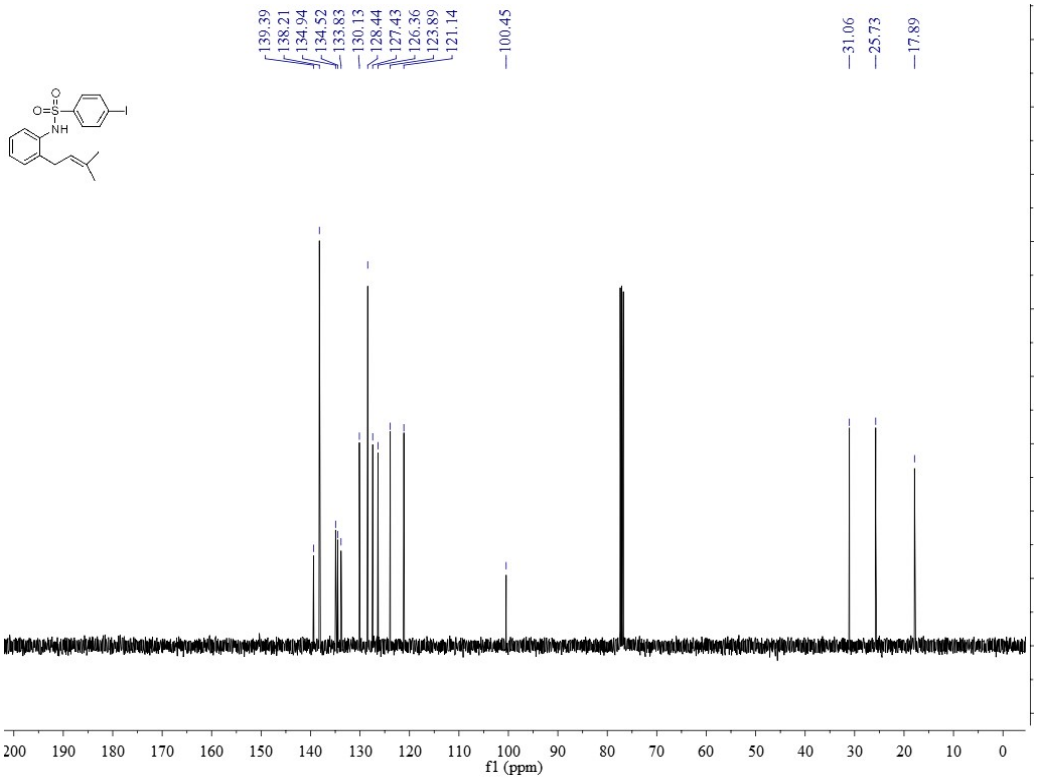
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1cb**



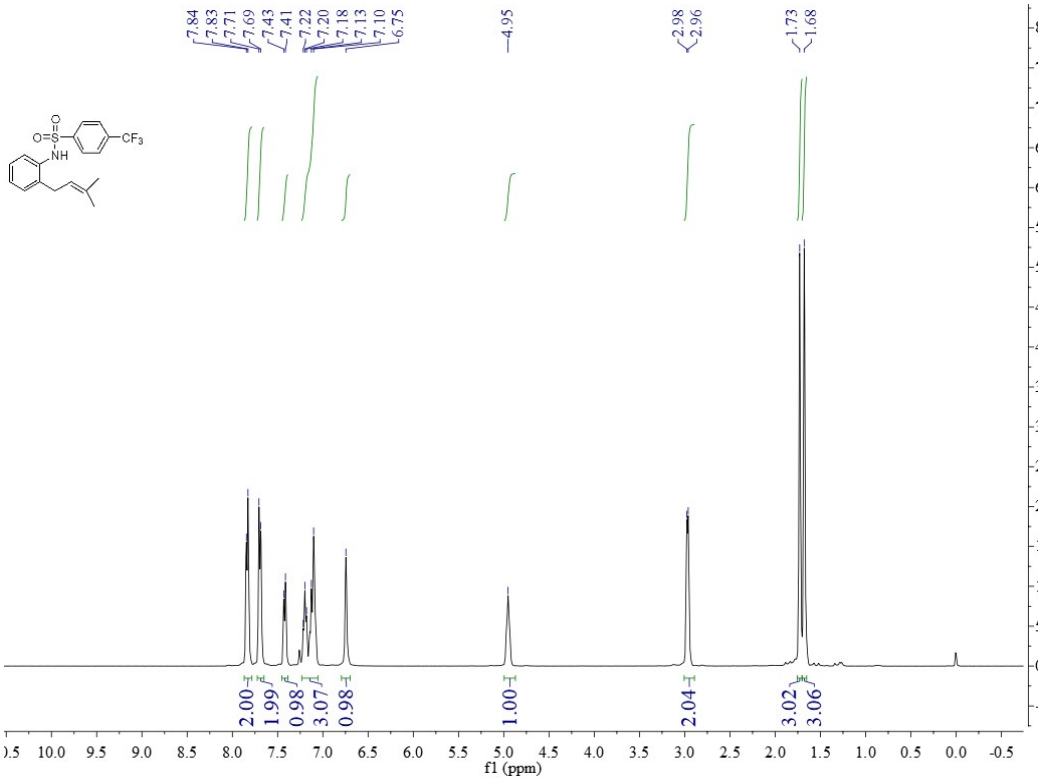
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1db**



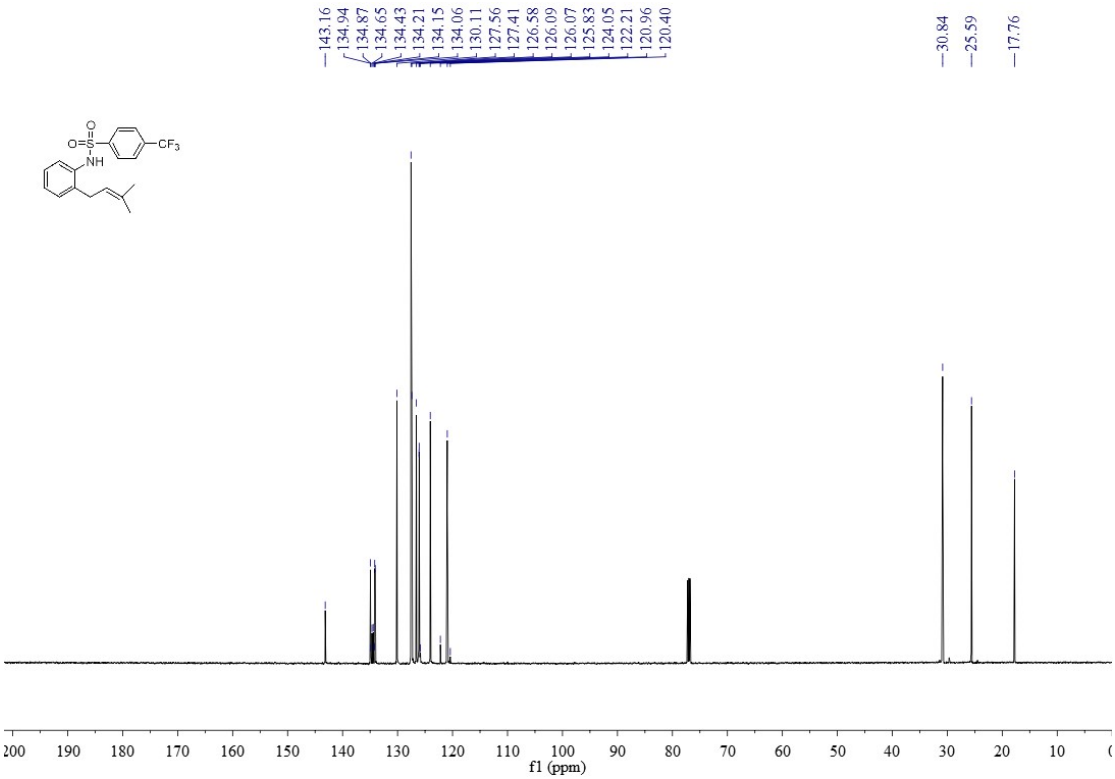
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1db**



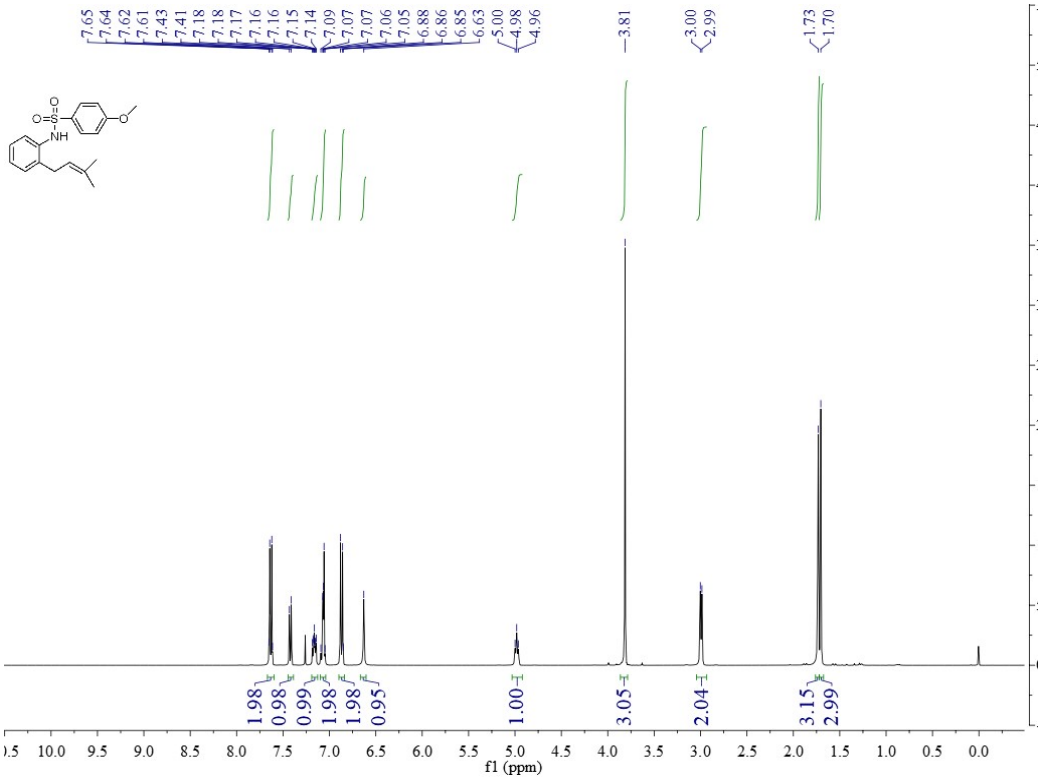
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1eb**



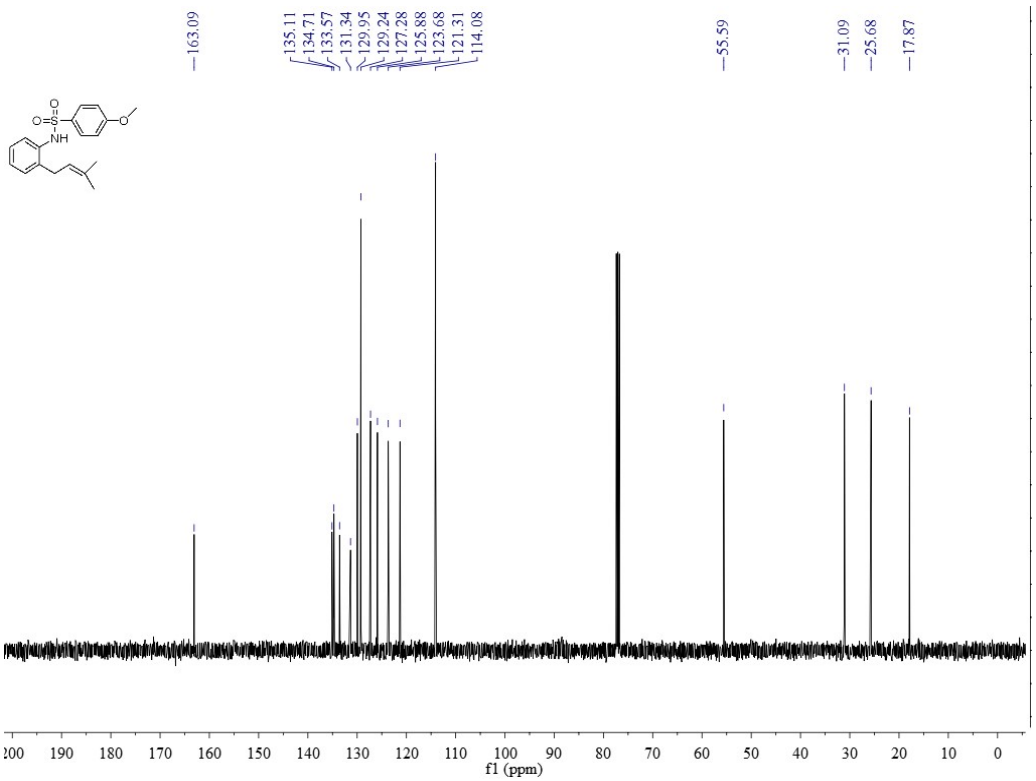
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1eb**



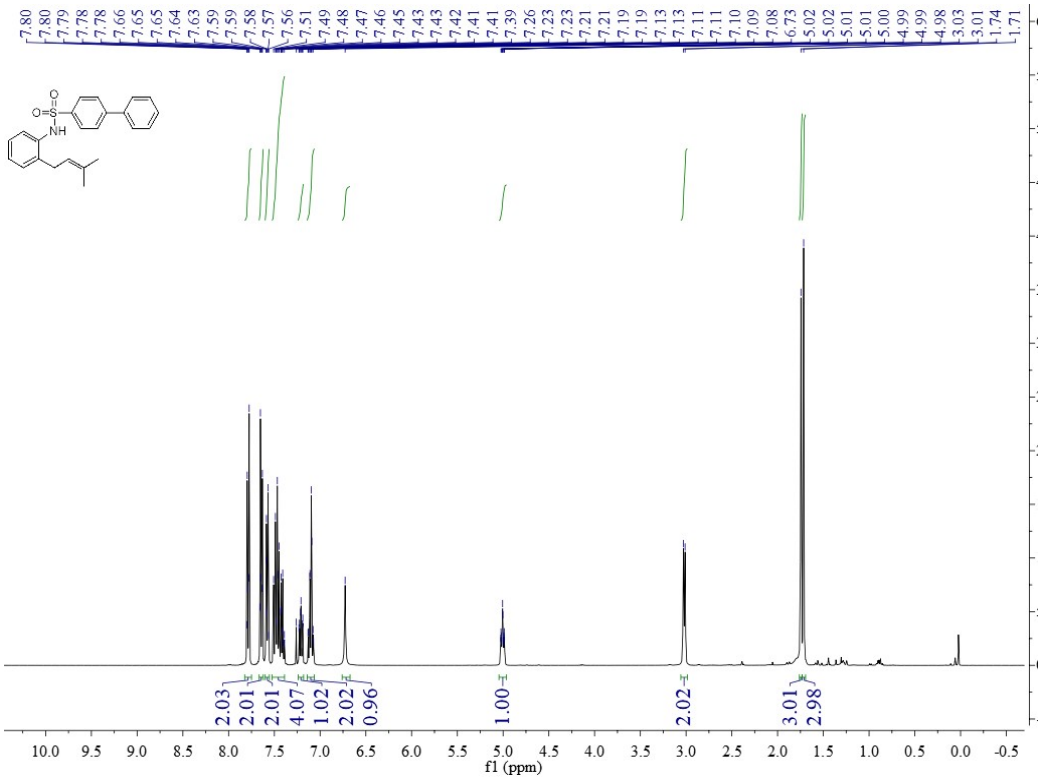
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1fb**



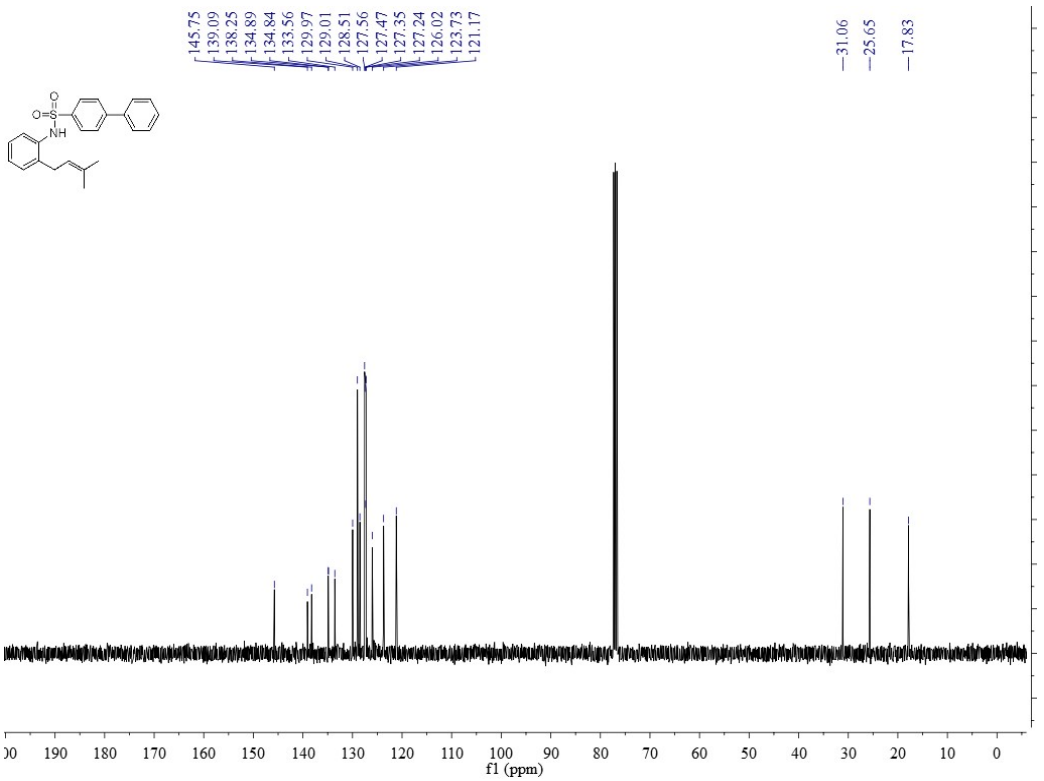
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1fb**



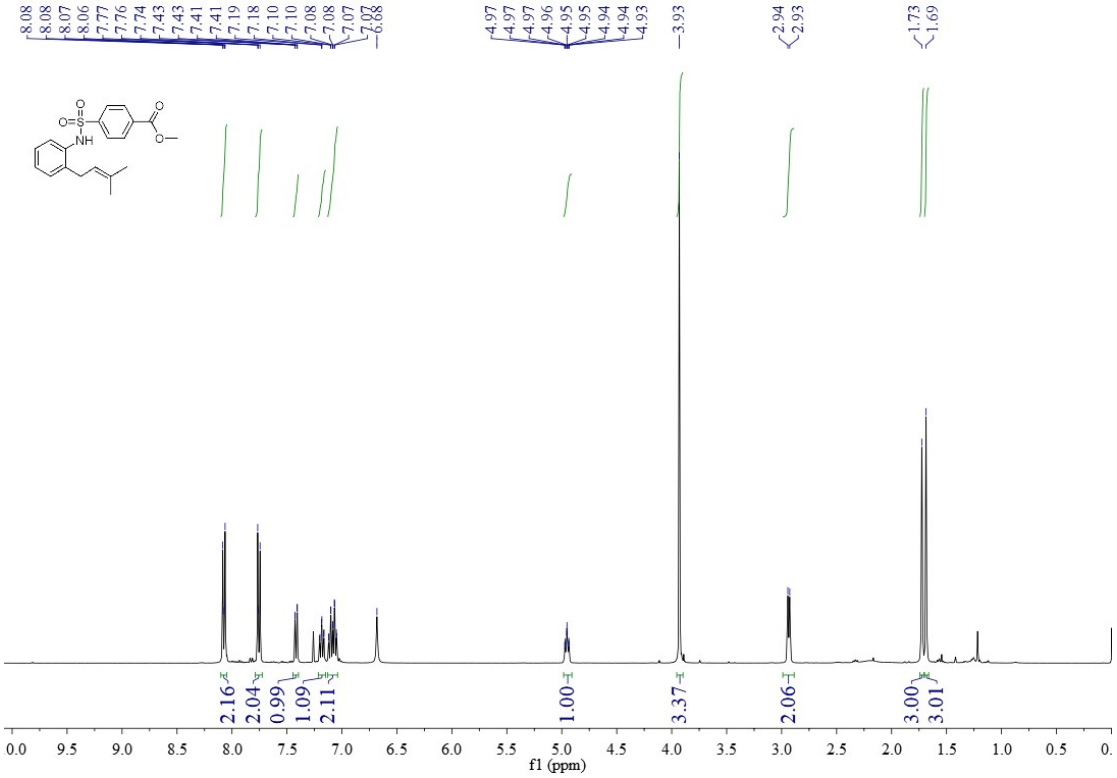
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1gb**



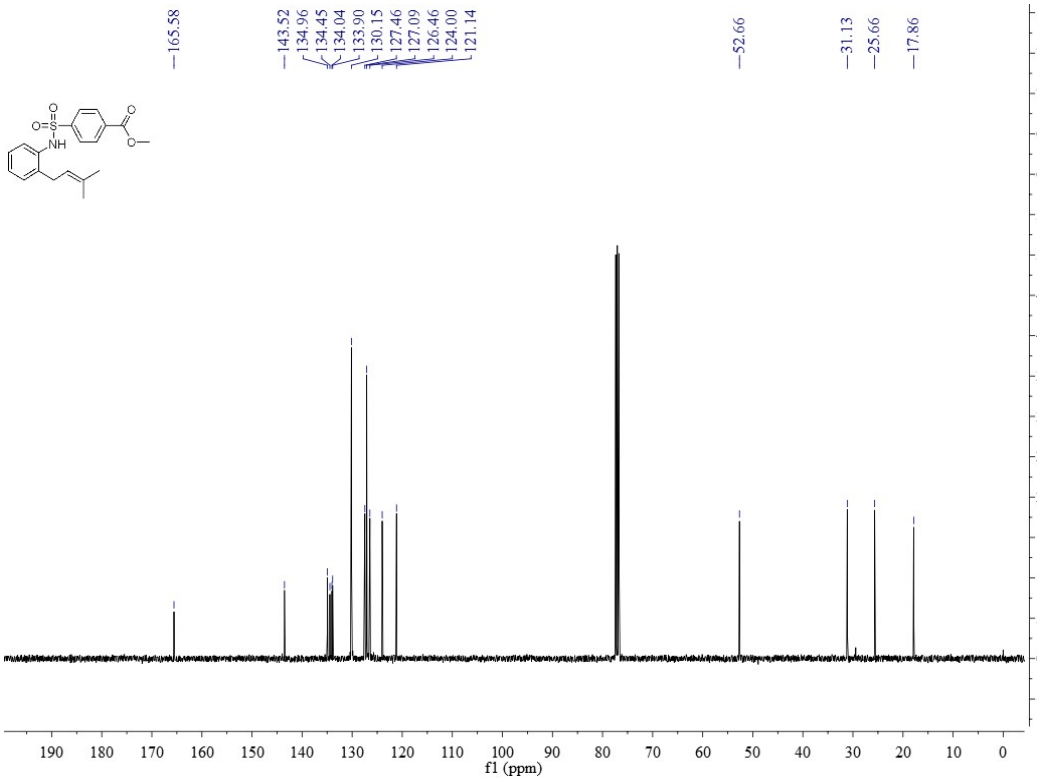
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1gb**



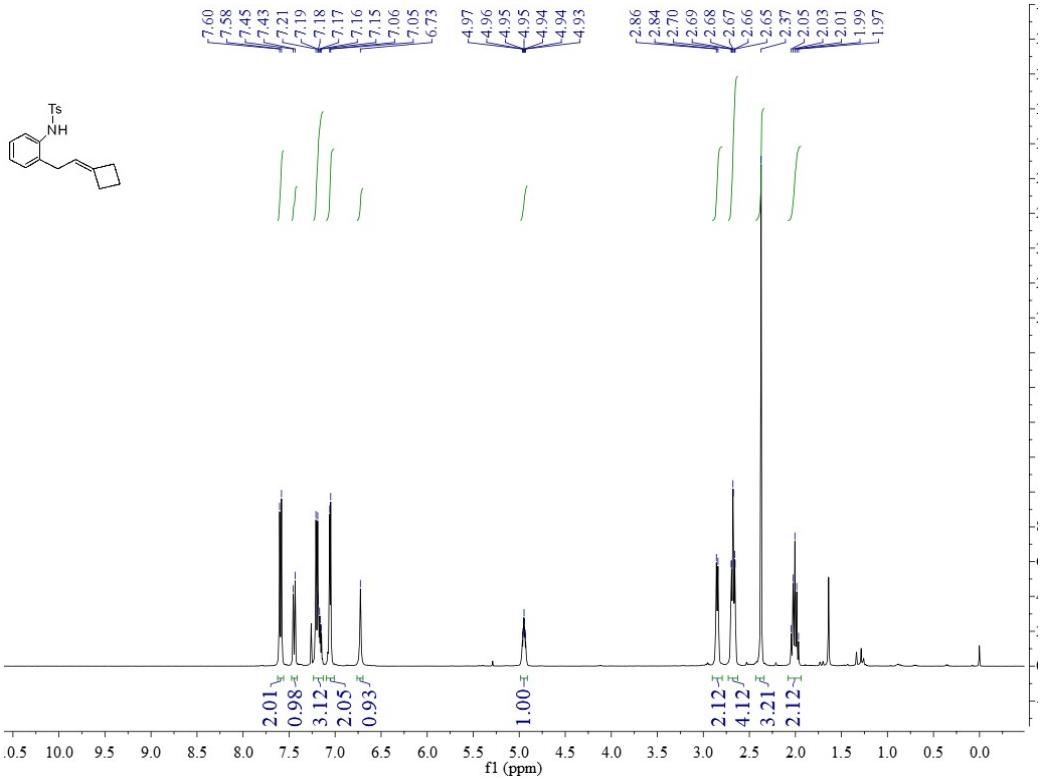
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1hb**



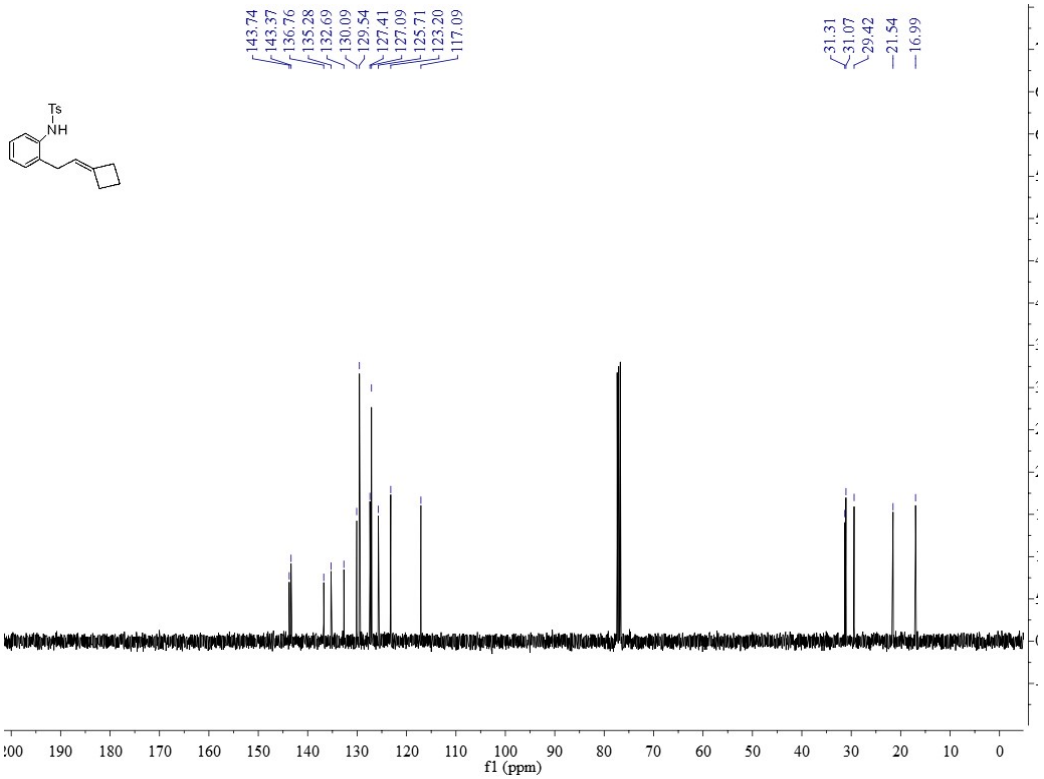
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1hb**



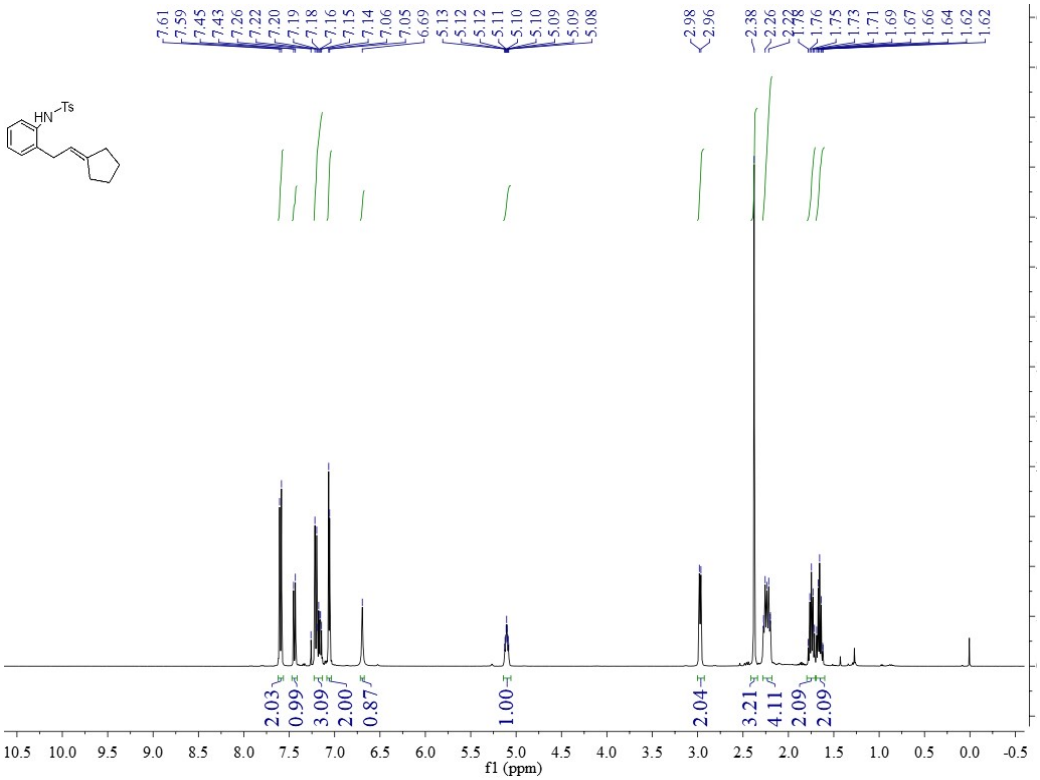
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ib**



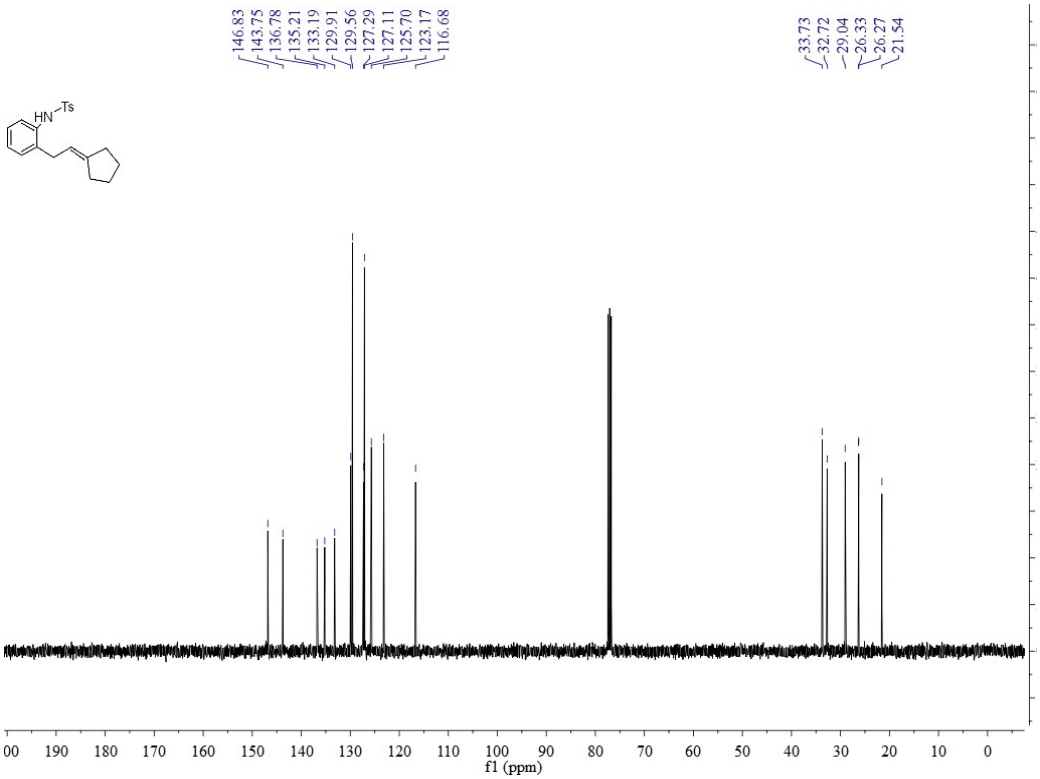
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ib**



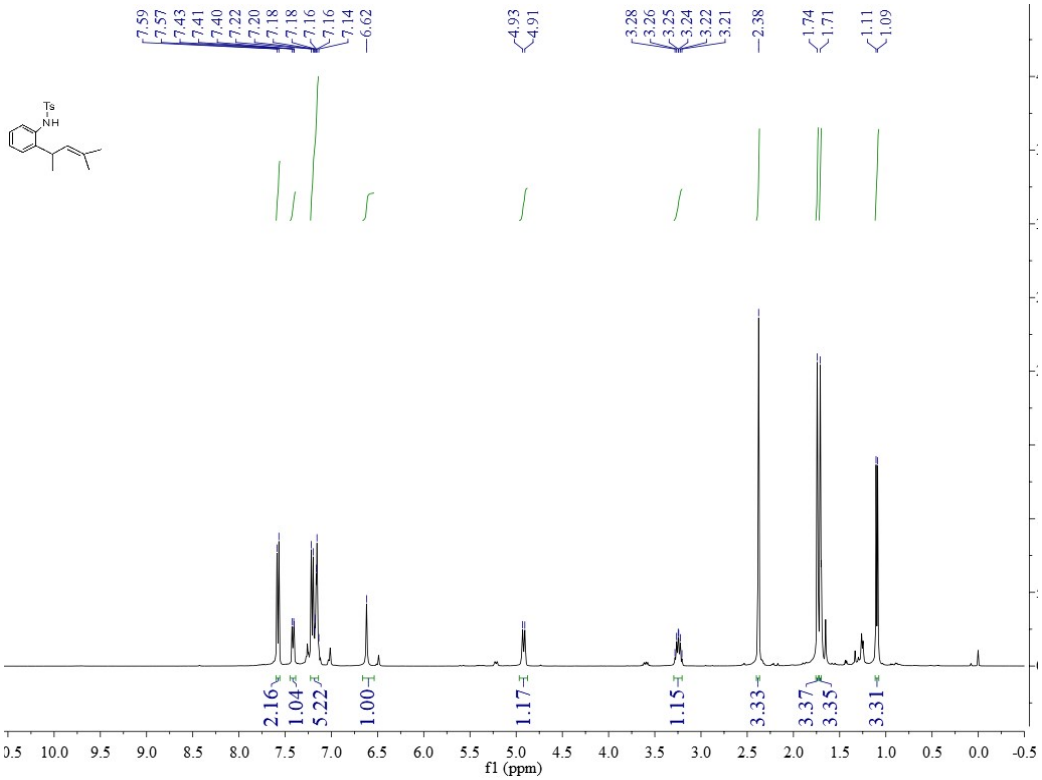
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1jb**



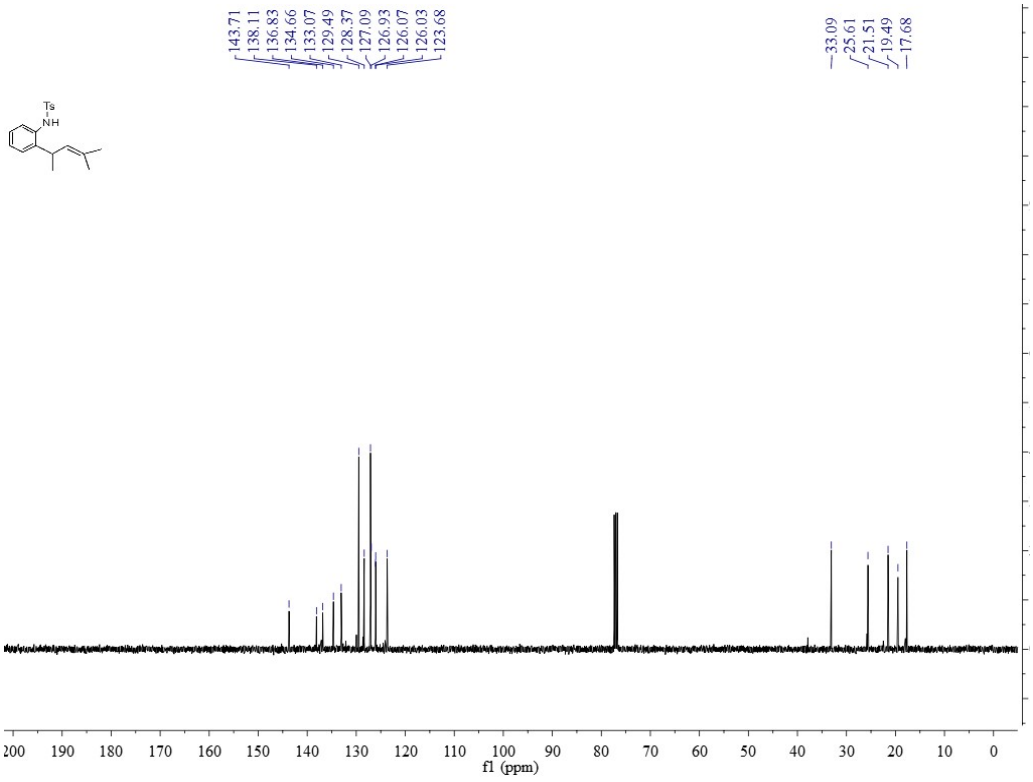
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1jb**



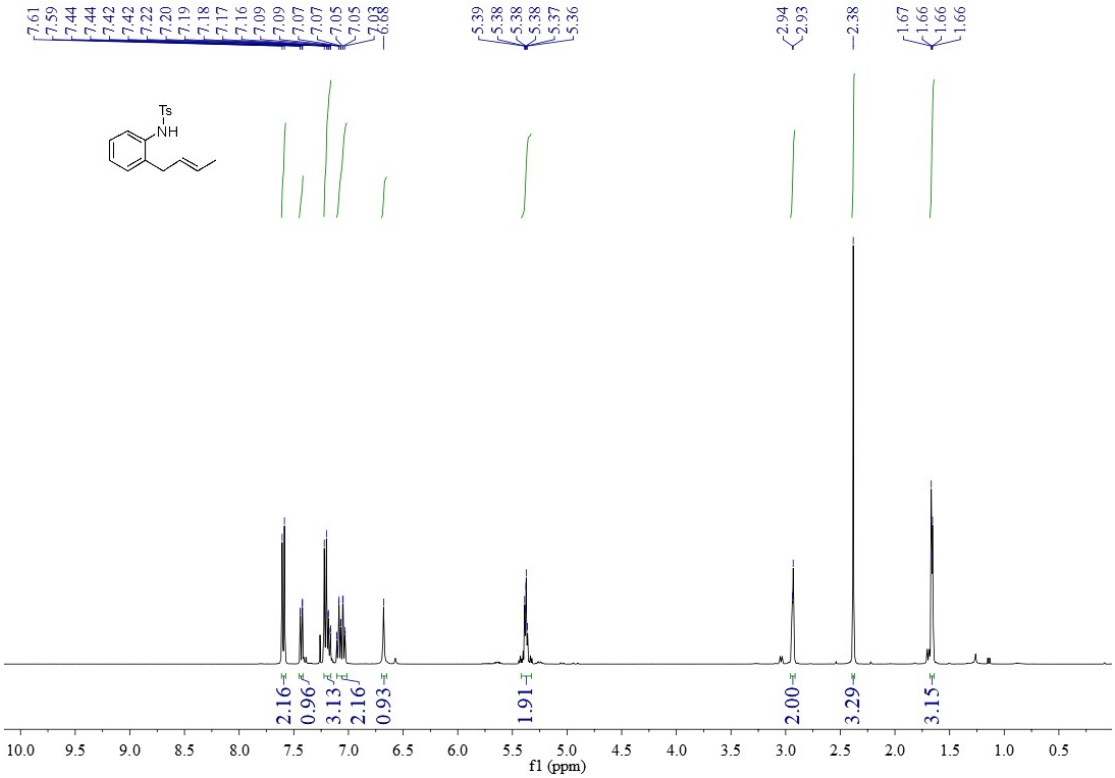
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1kb**



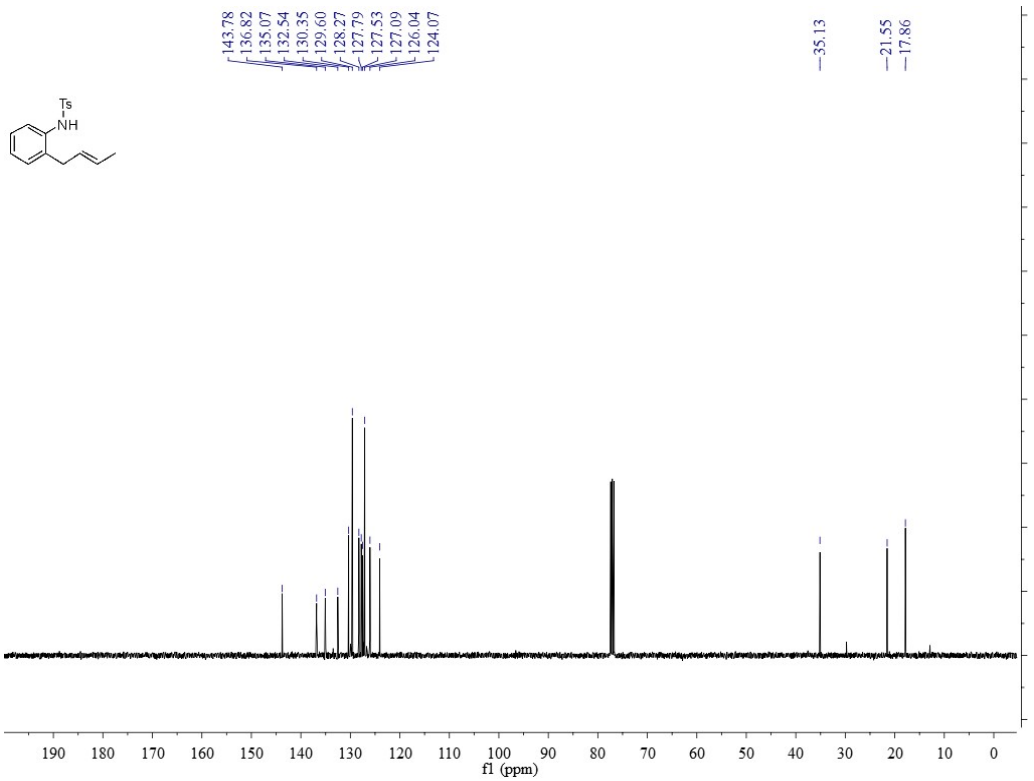
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1kb**



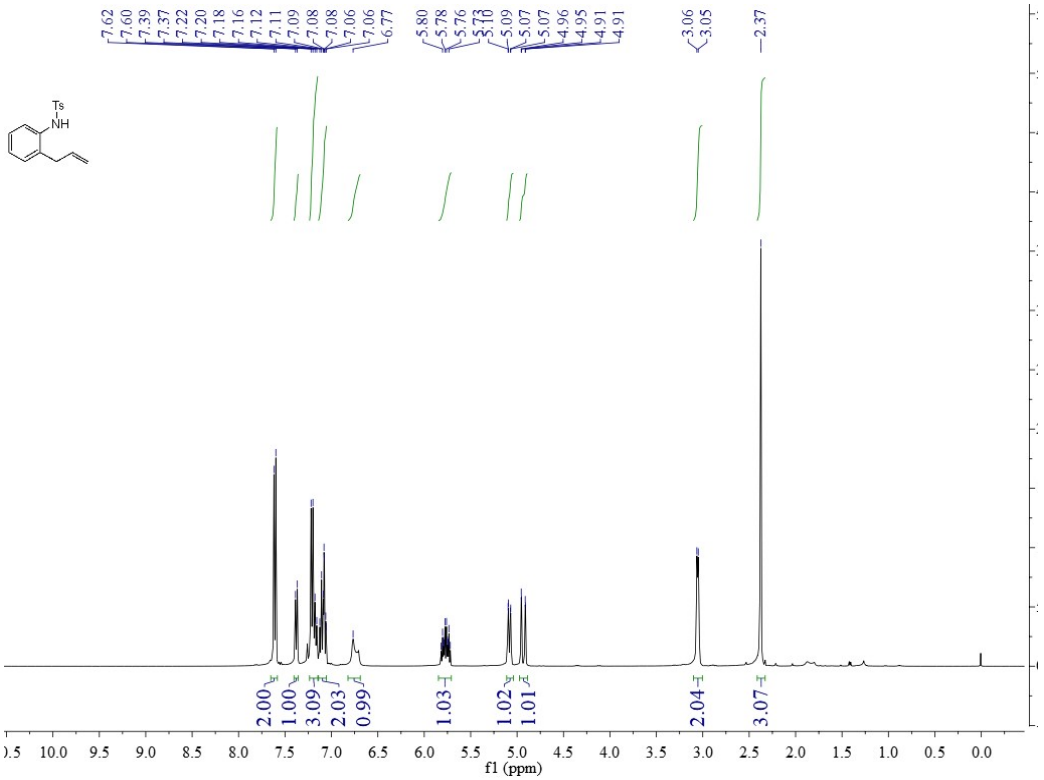
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1lb**



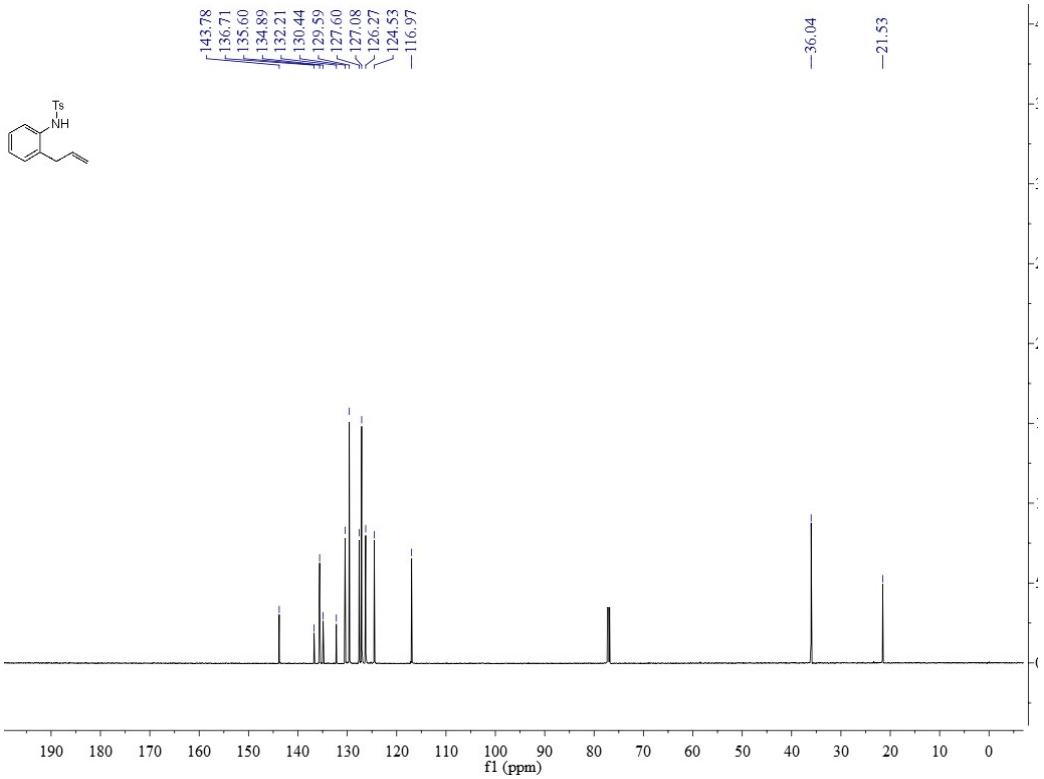
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1lb**



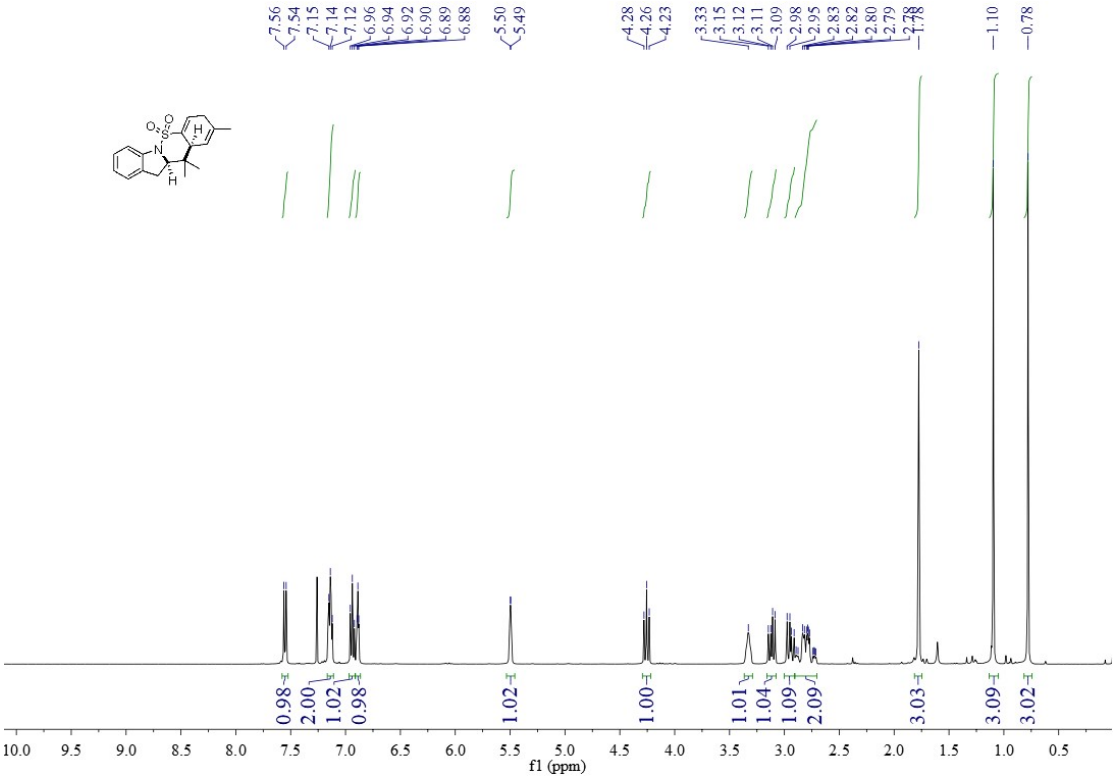
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1mb**



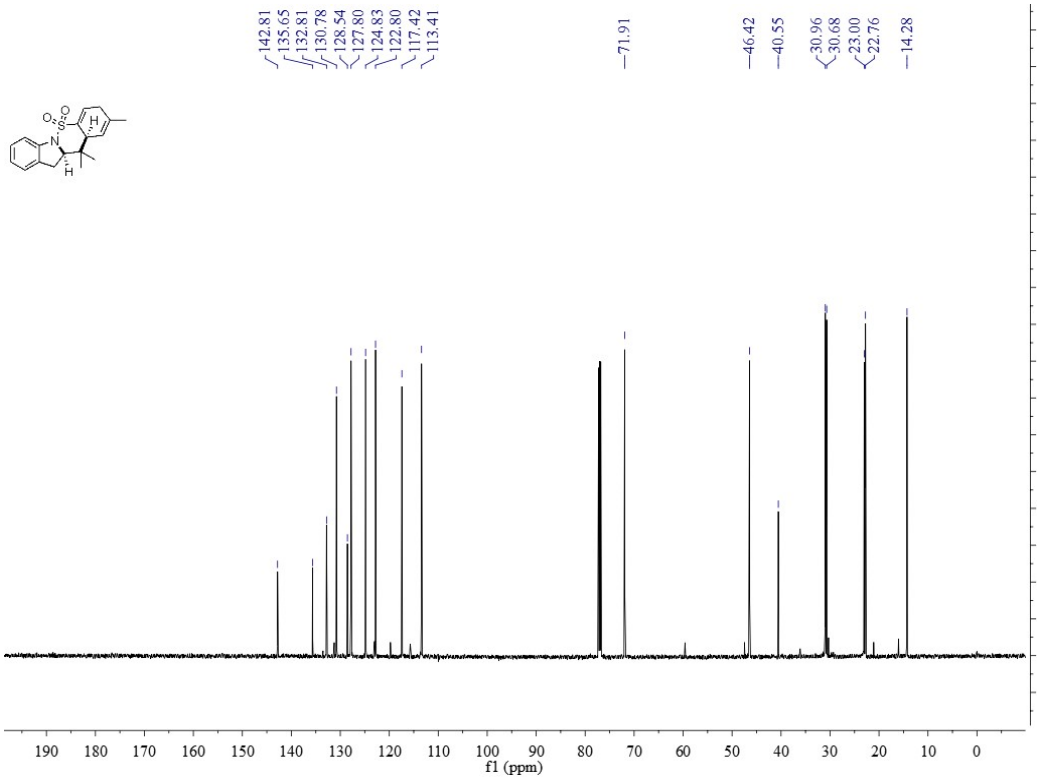
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1mb**



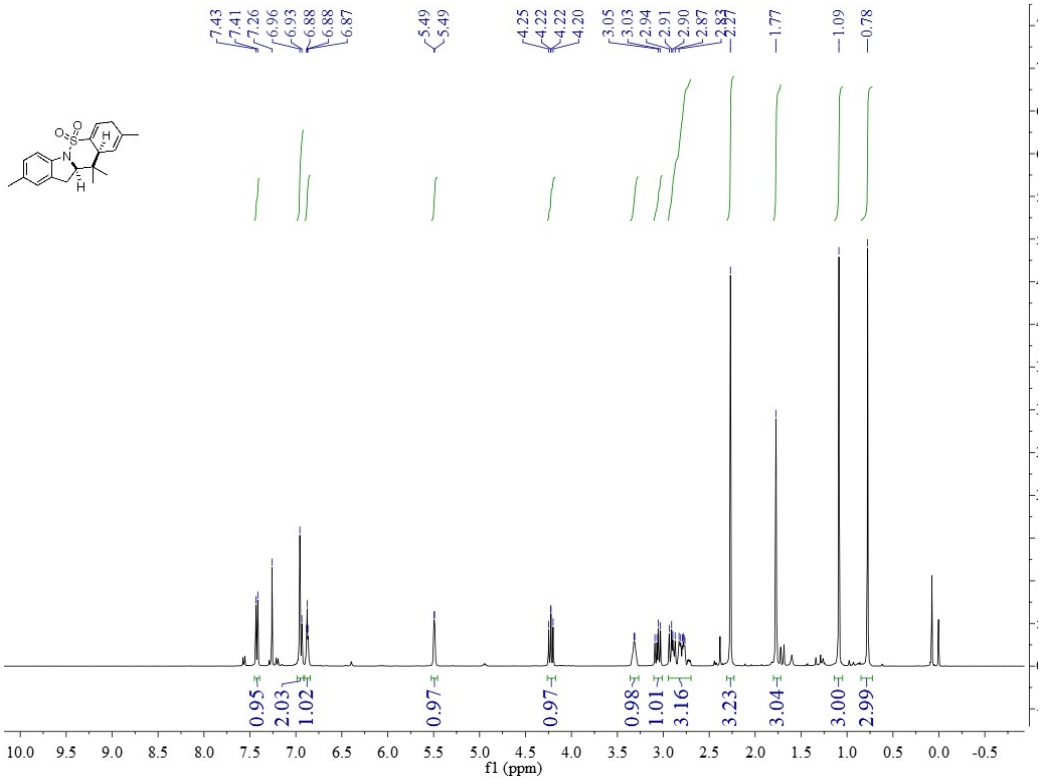
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2aa**



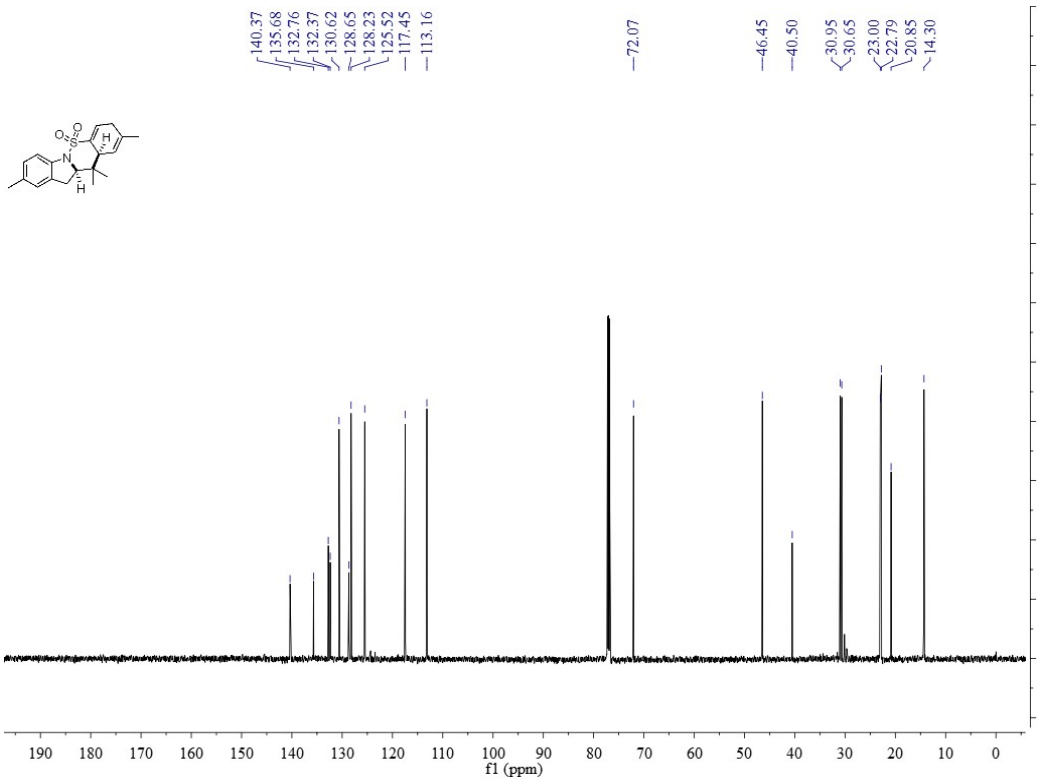
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2aa**



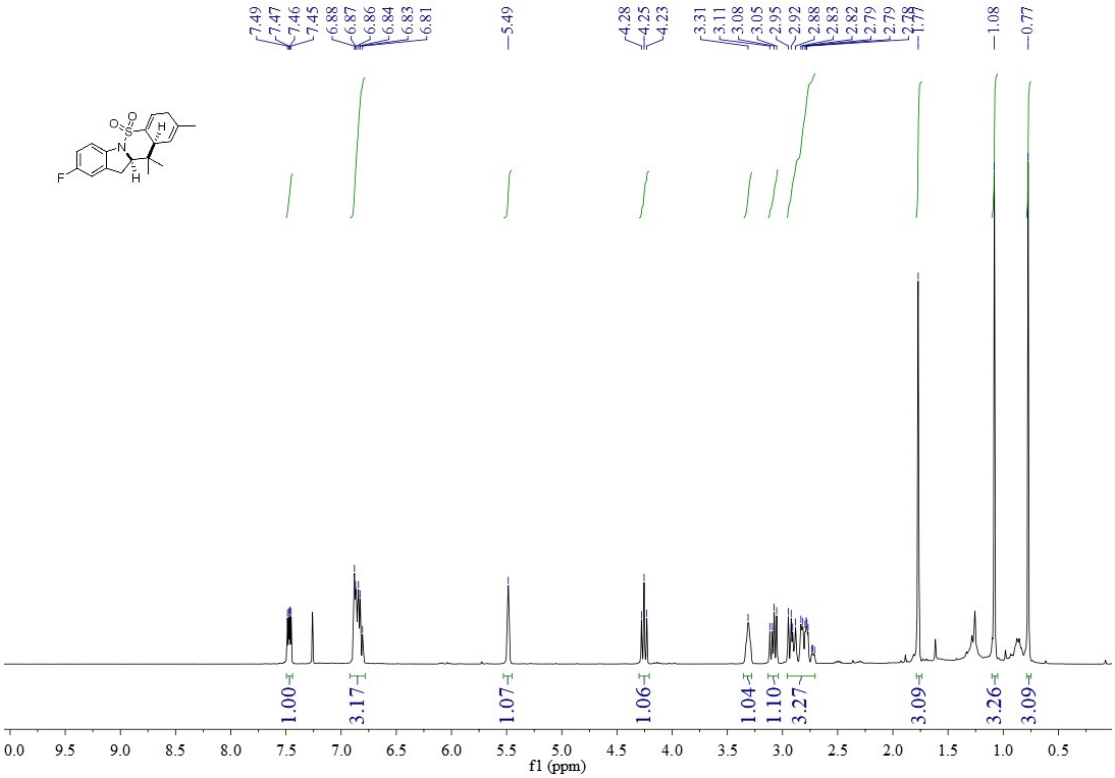
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ba**



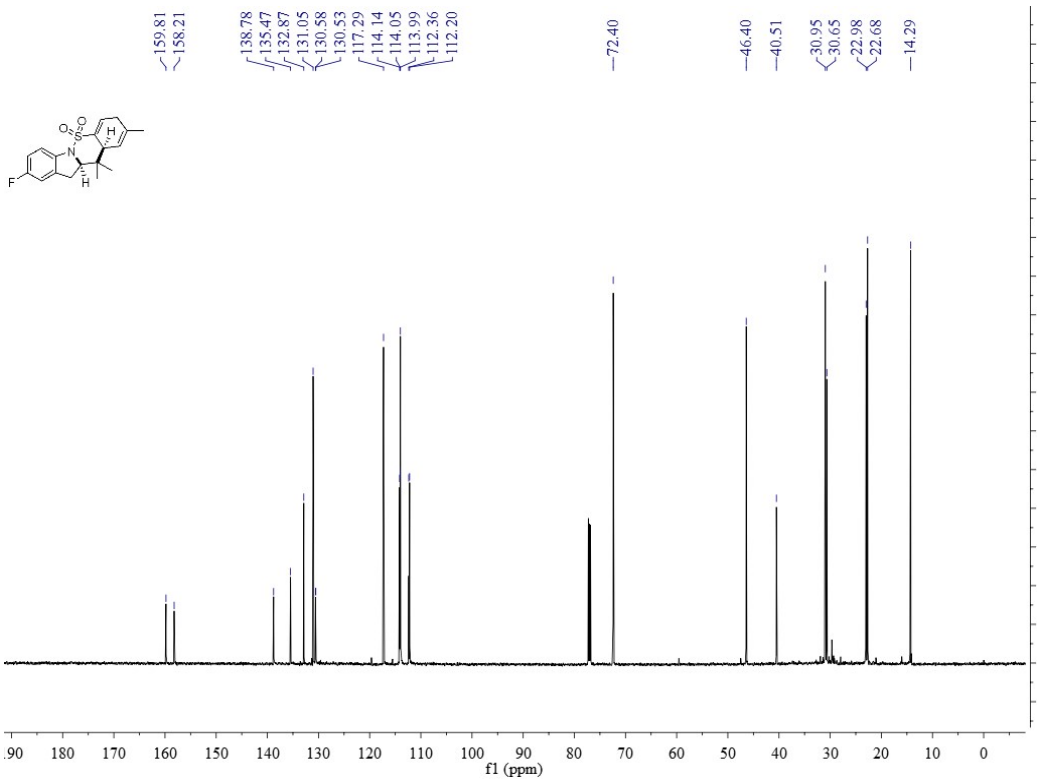
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ba**



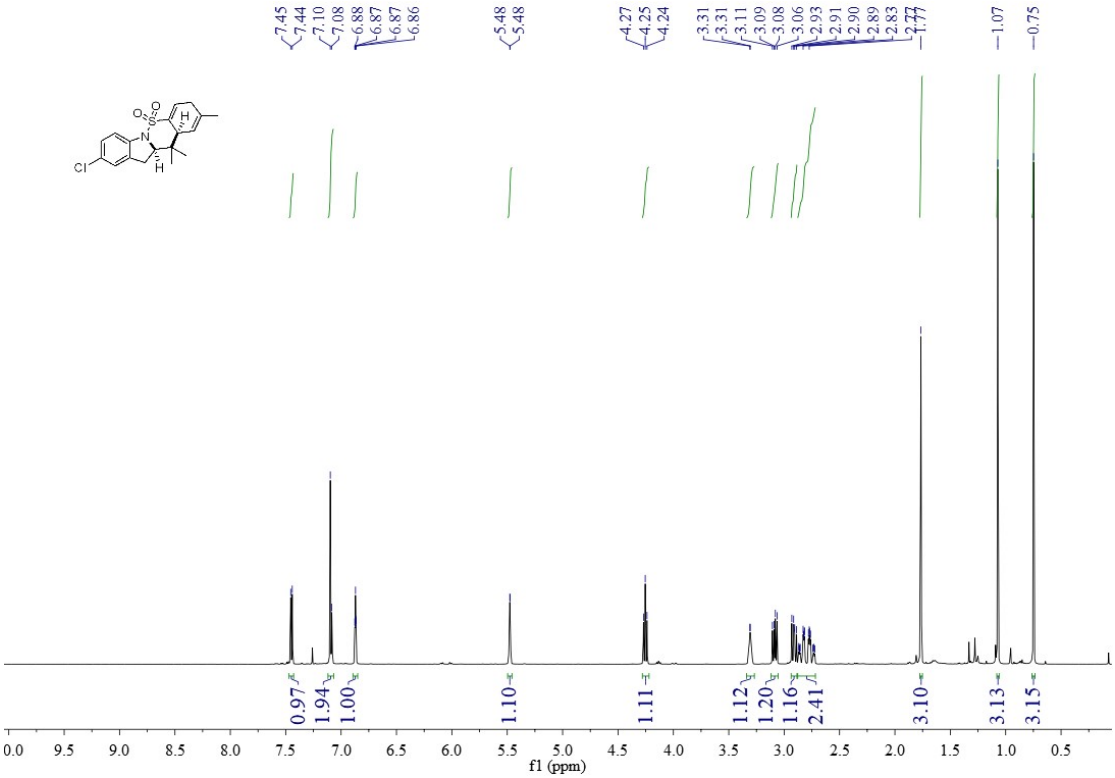
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ca**



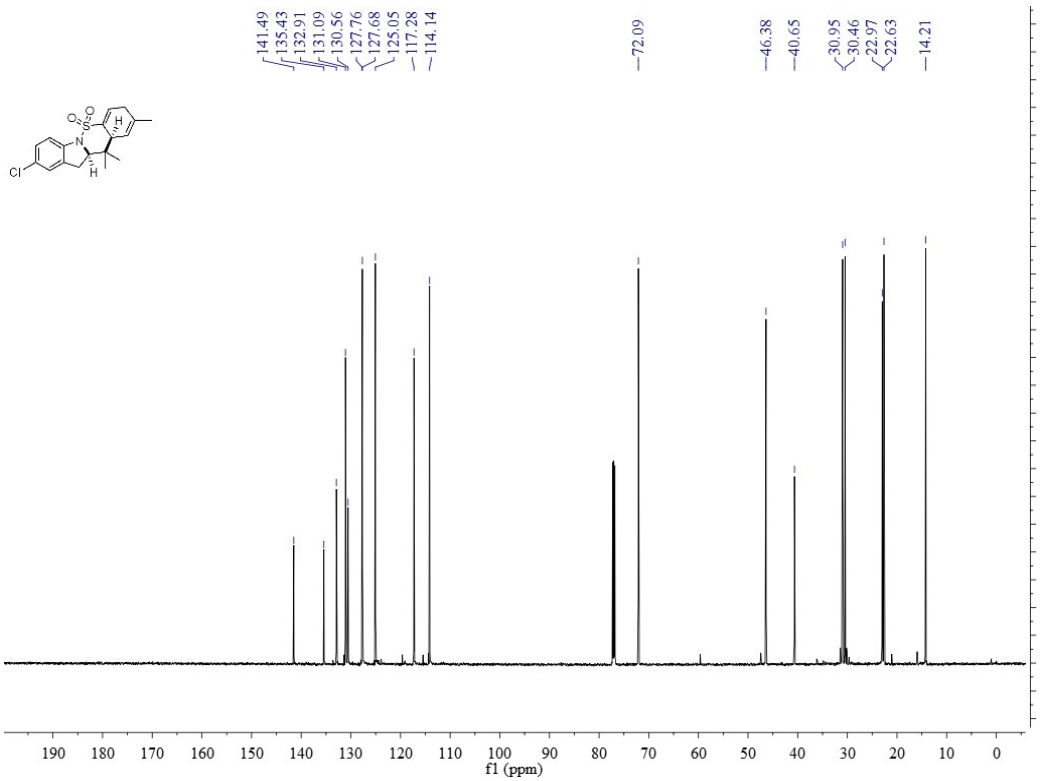
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ca**



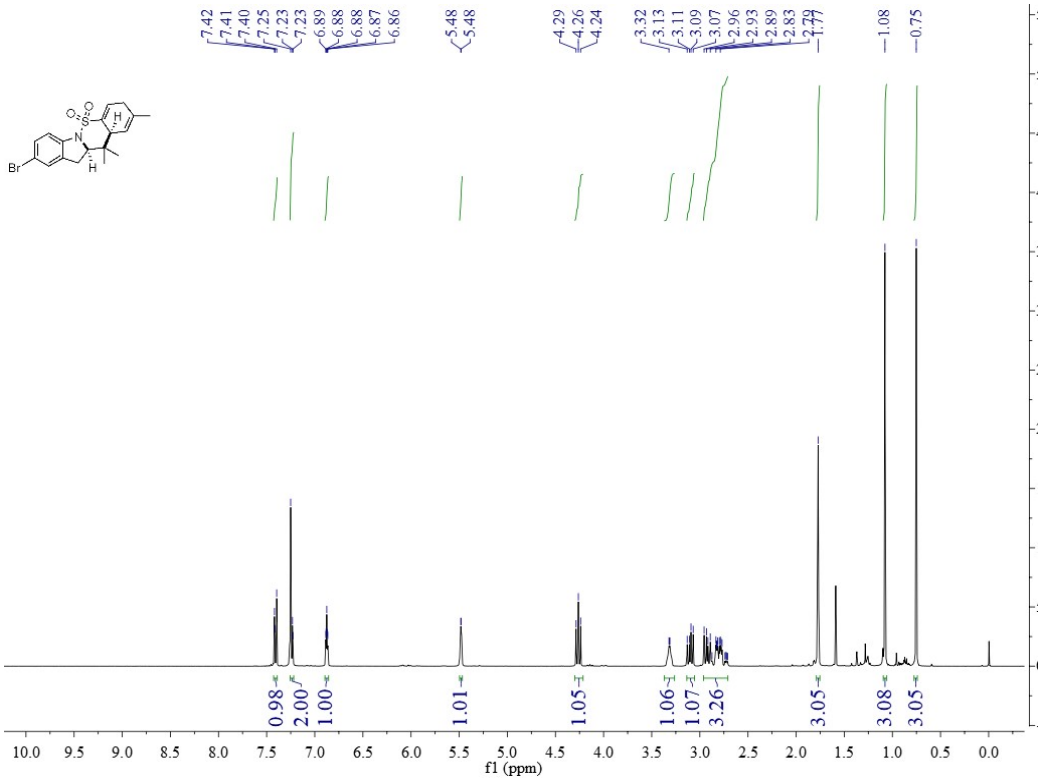
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2da**



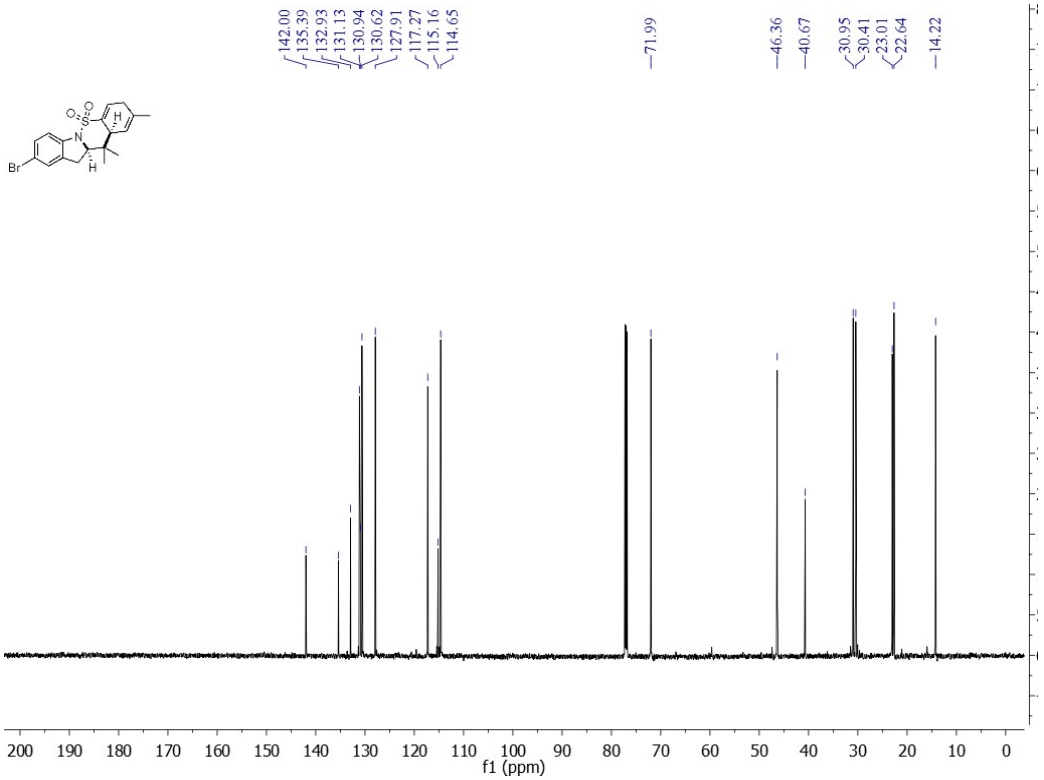
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2da**



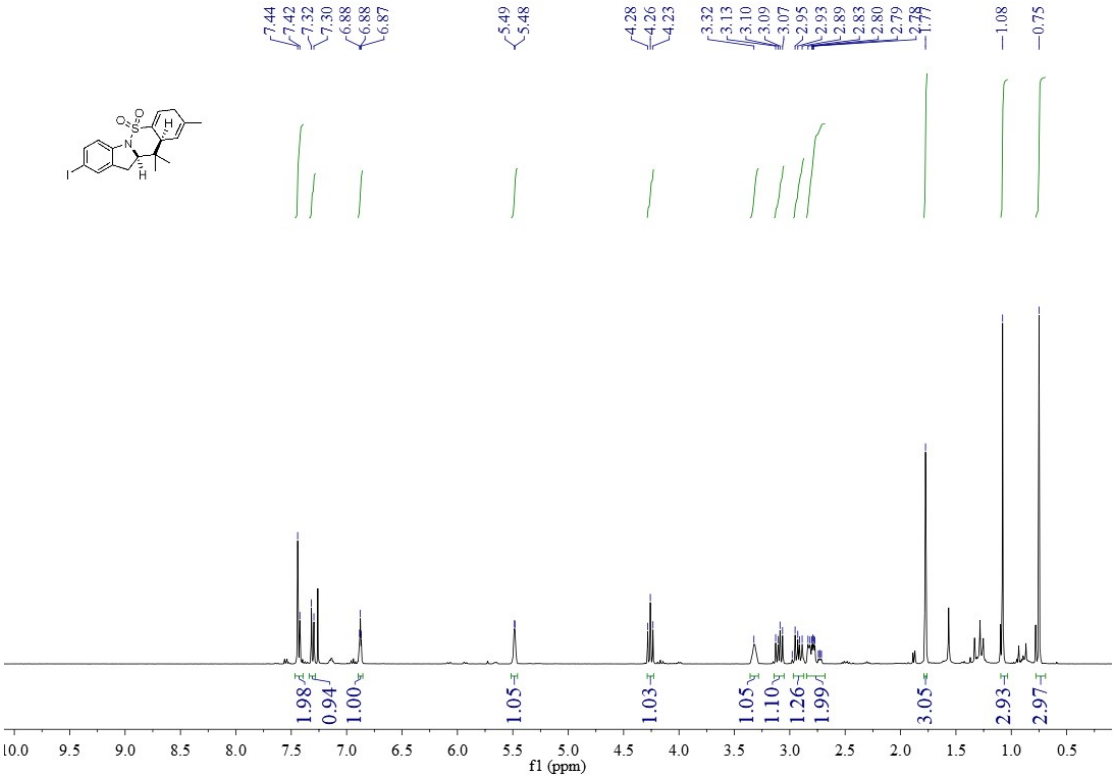
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ea**



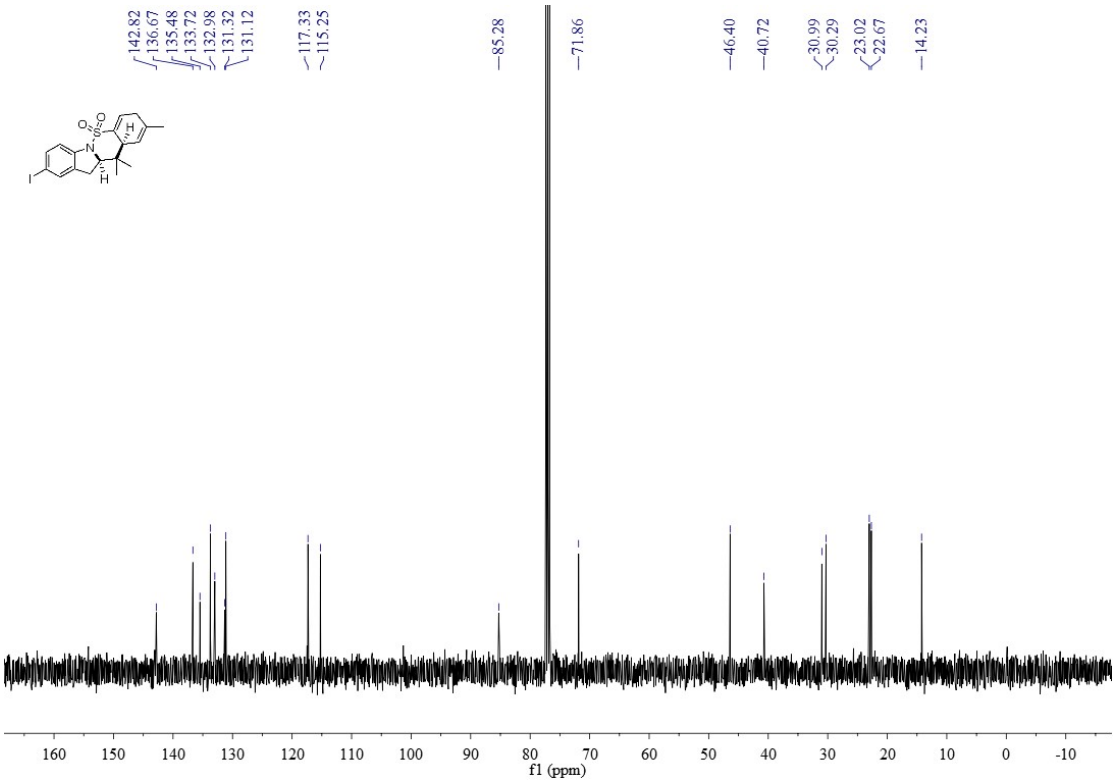
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ea**



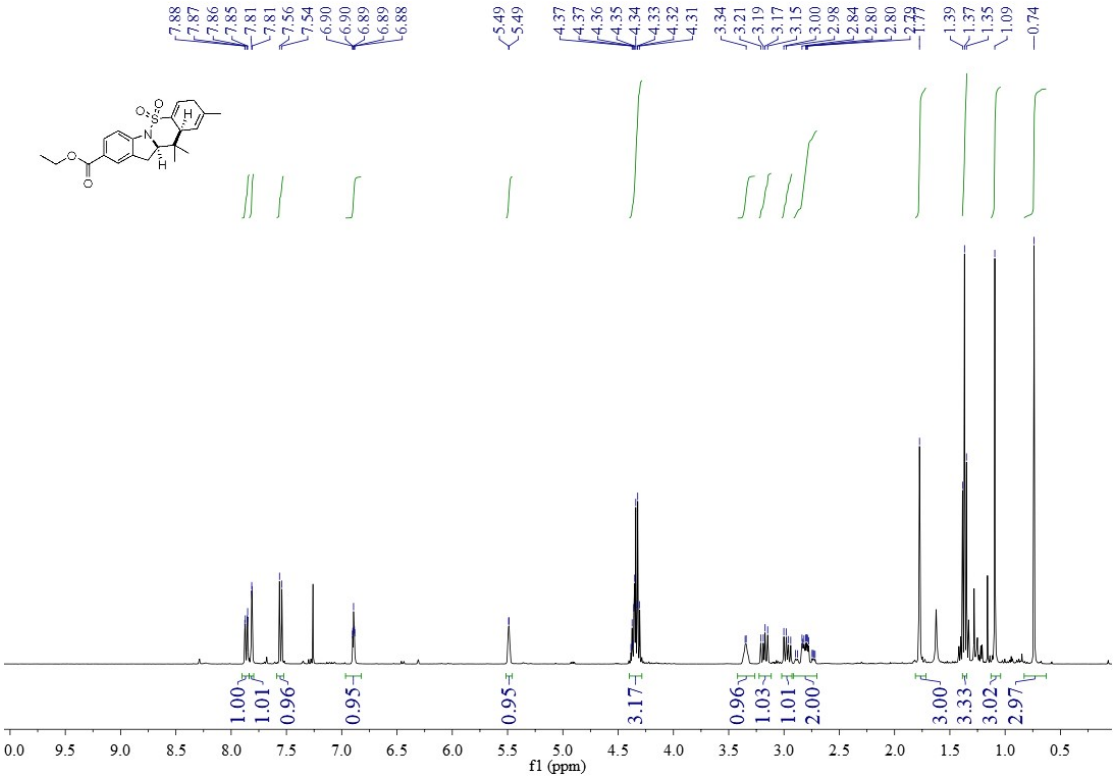
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2fa**



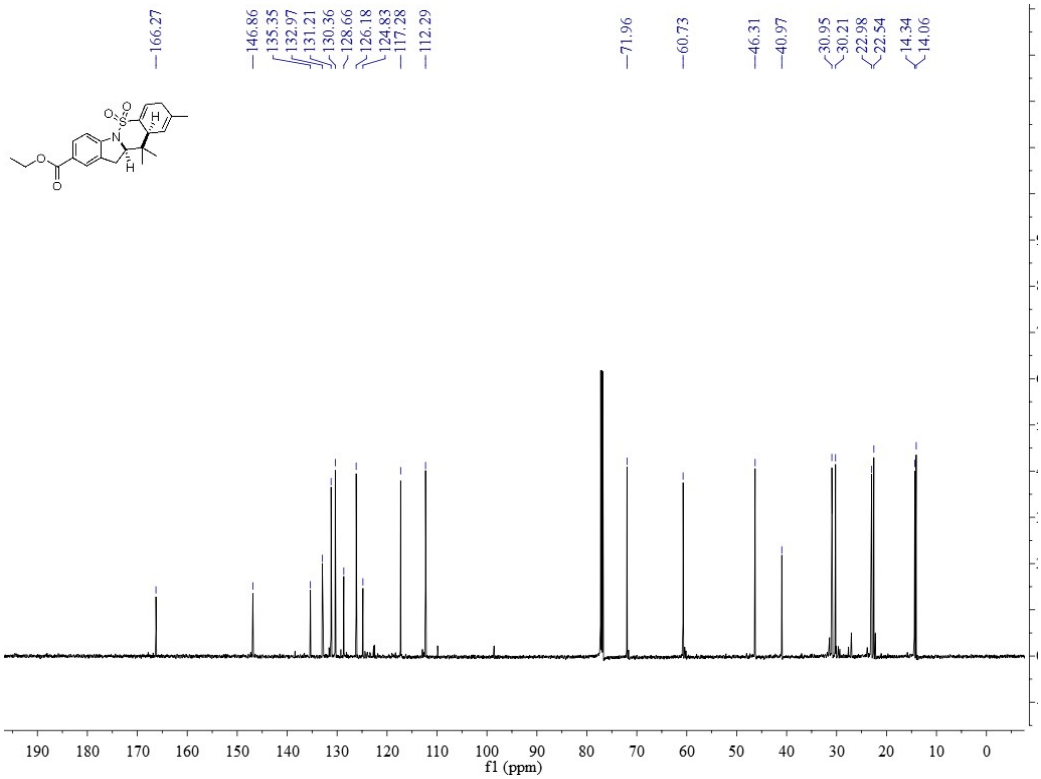
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2fa**



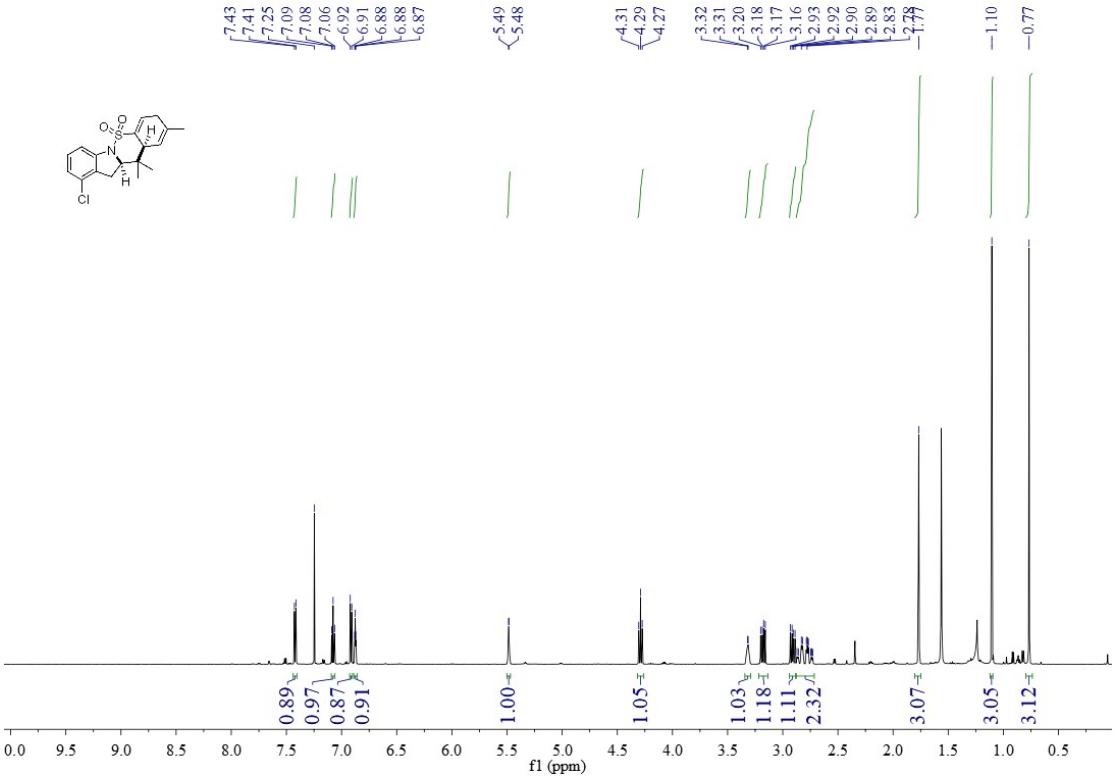
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ga**



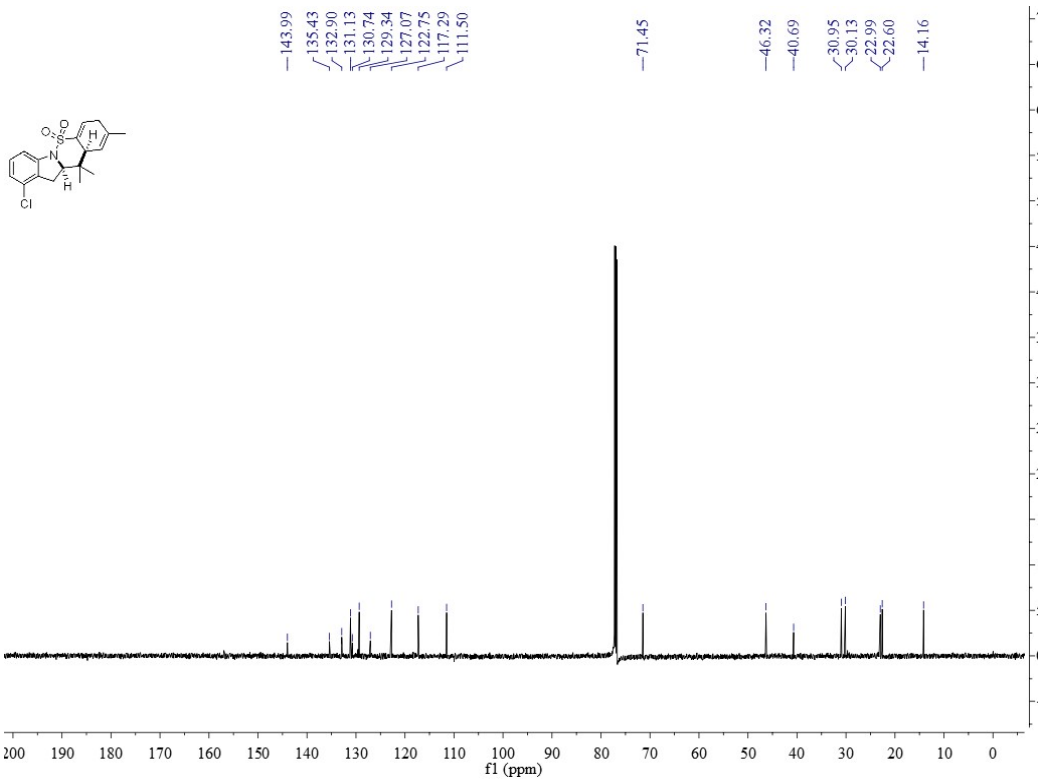
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ga**



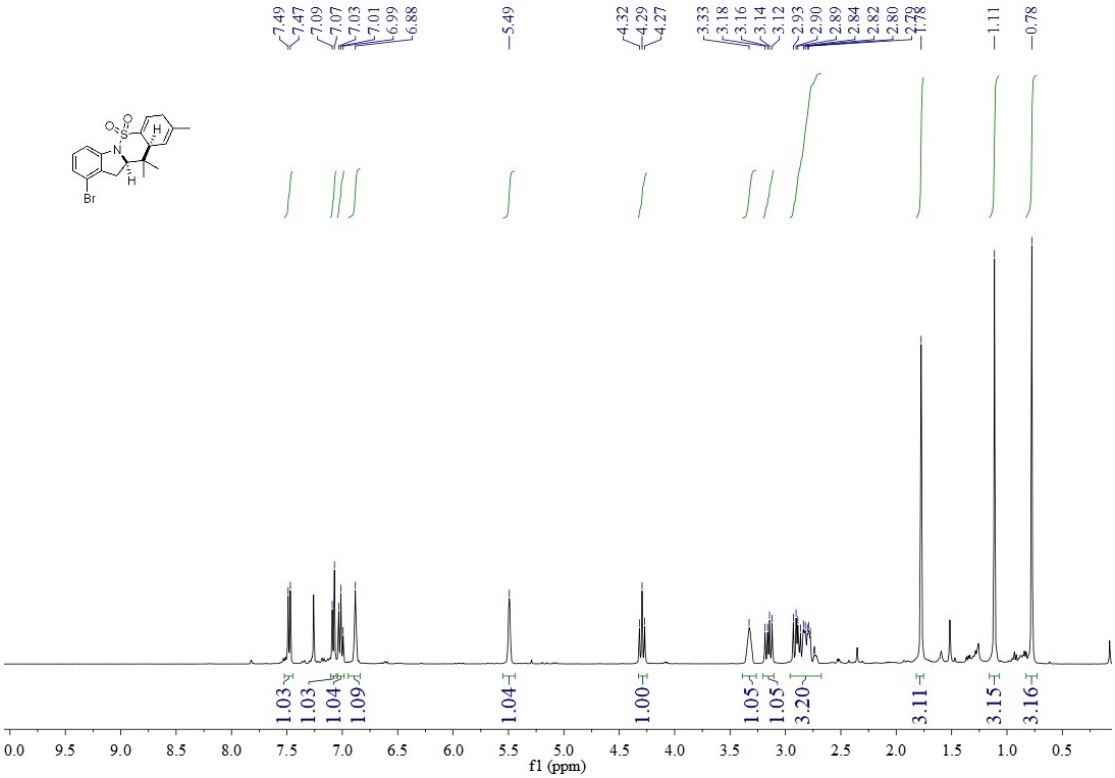
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ha**



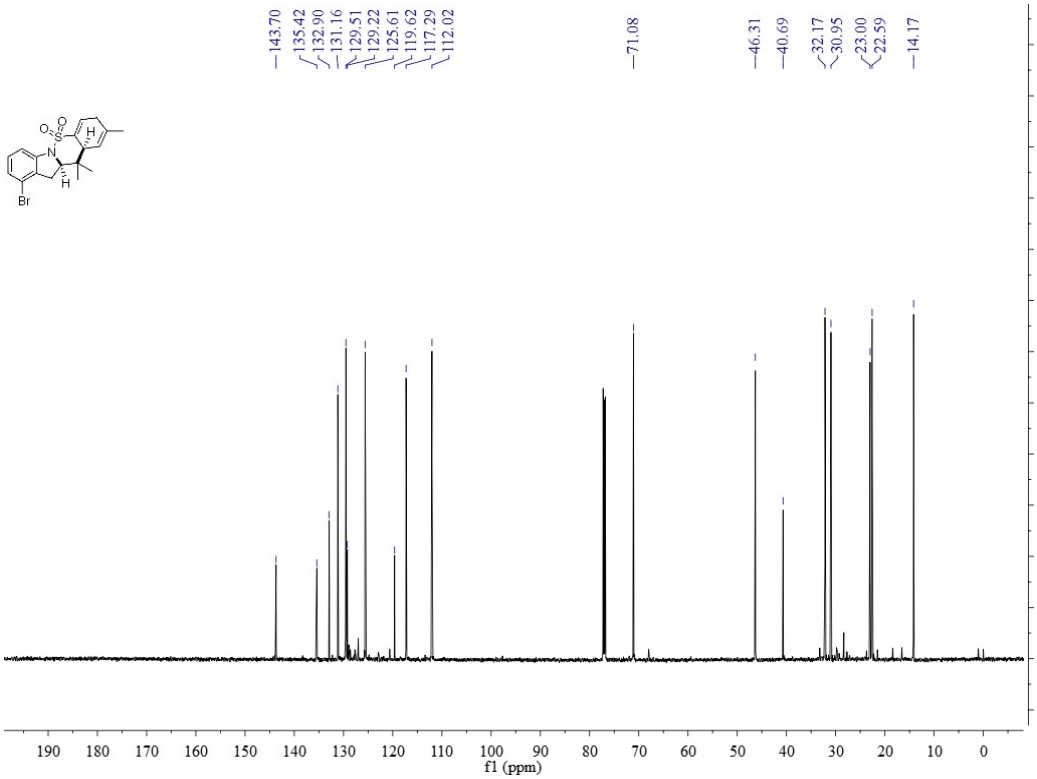
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ha**



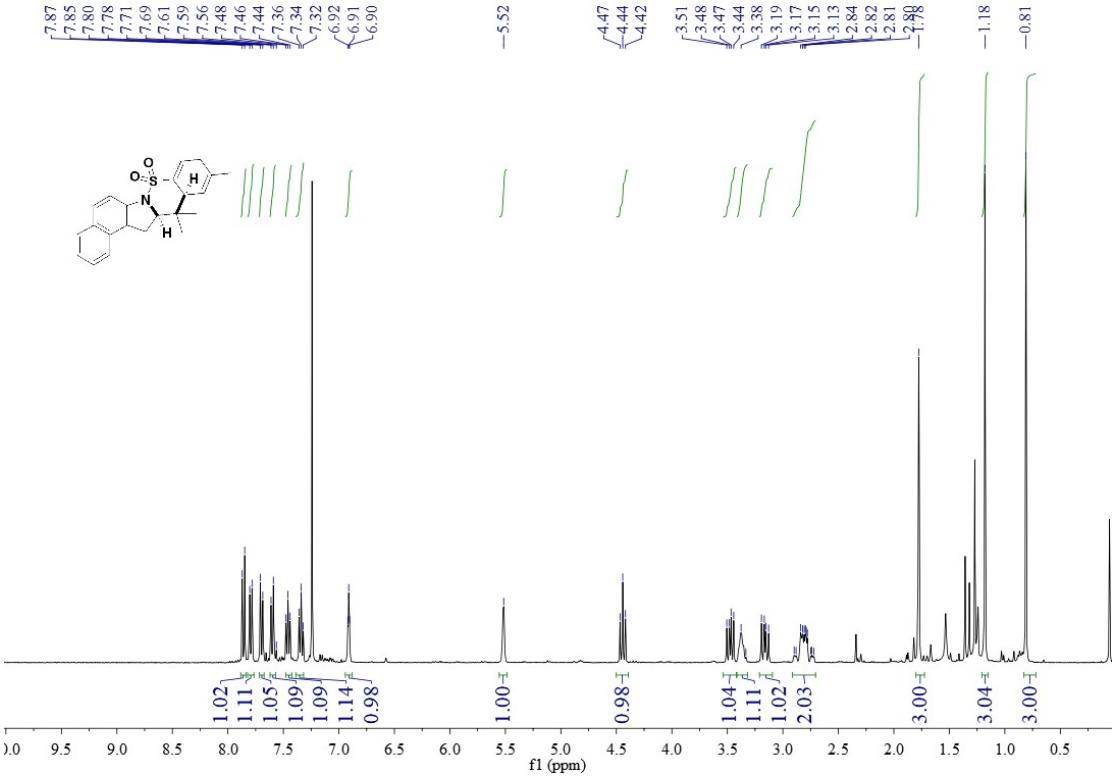
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ia**



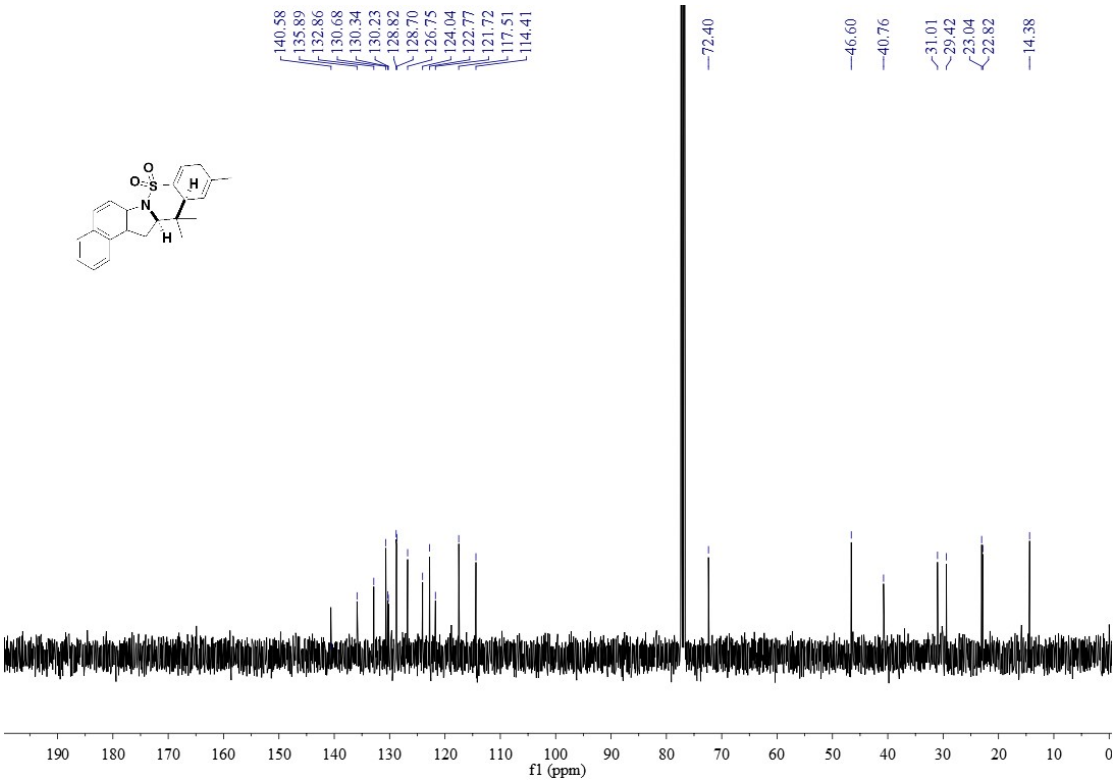
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ia**



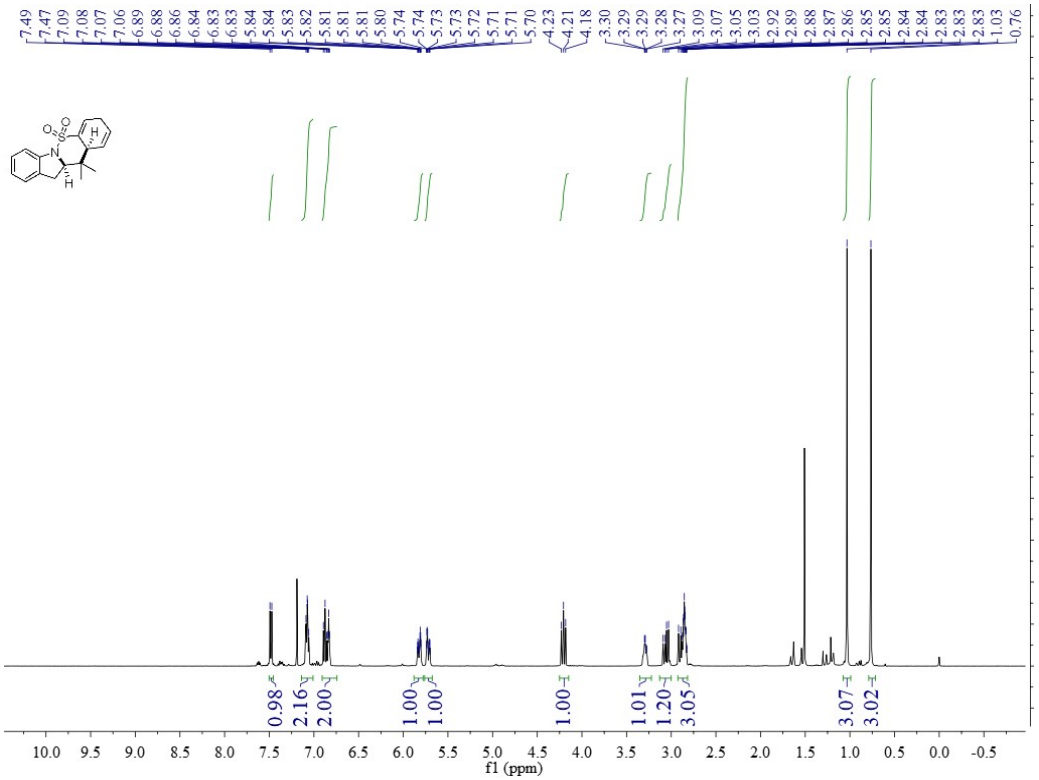
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ja**



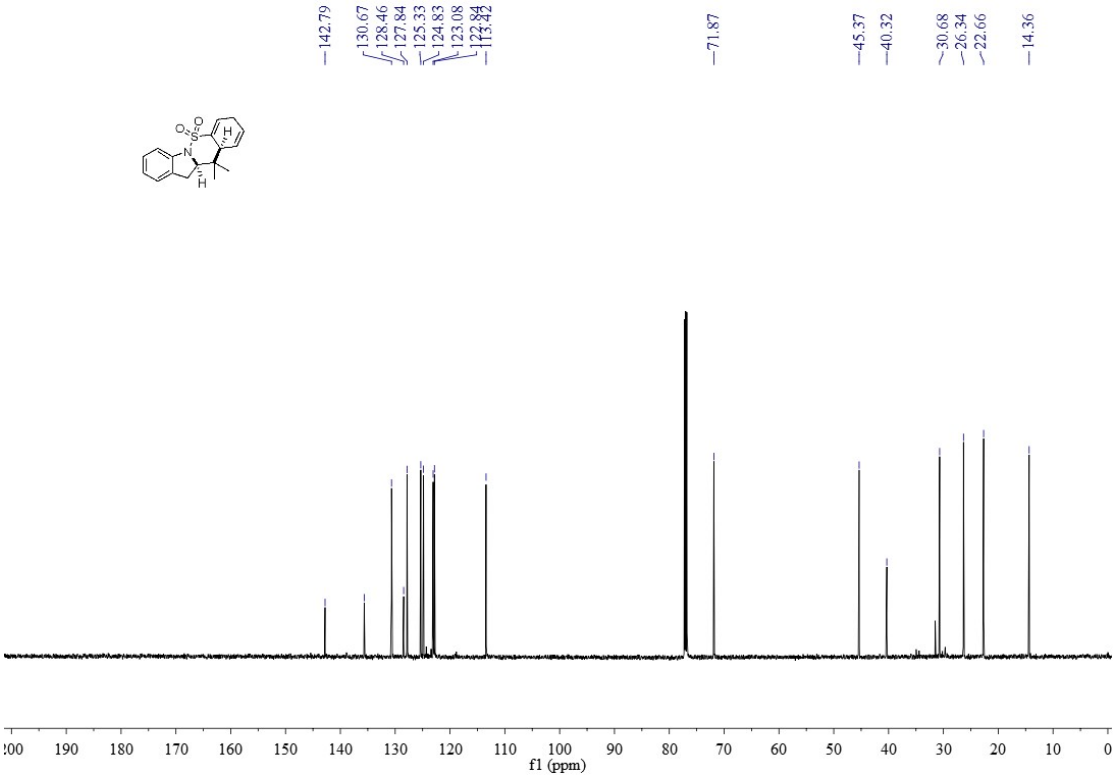
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ja**



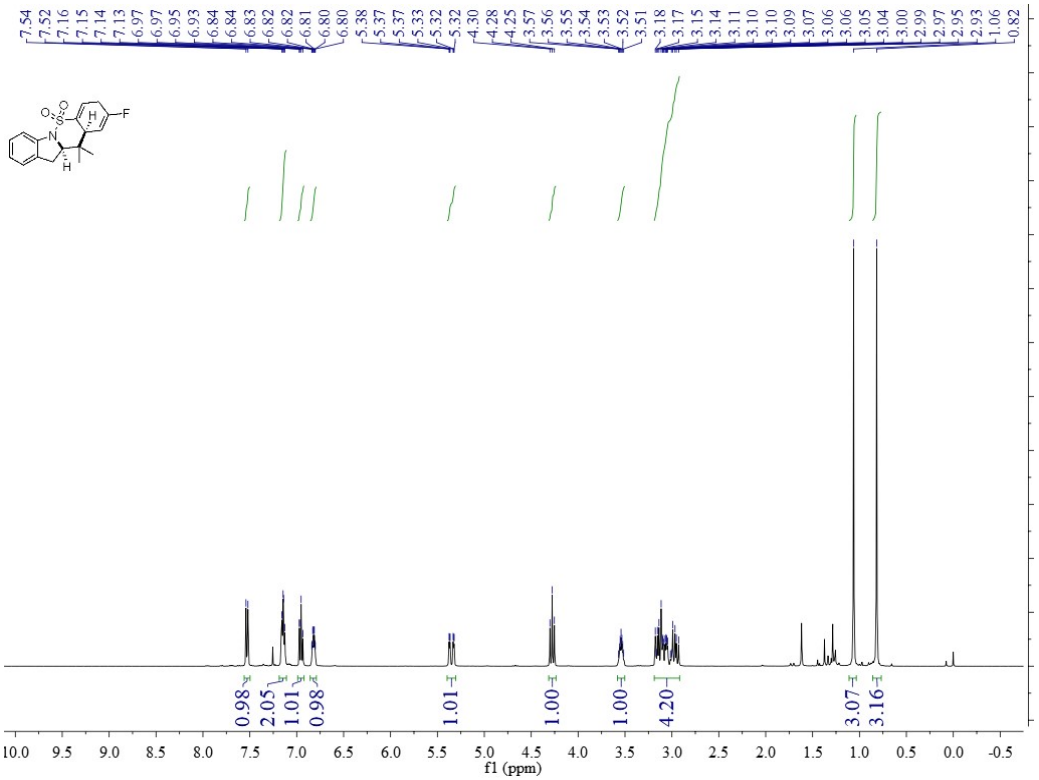
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ab**



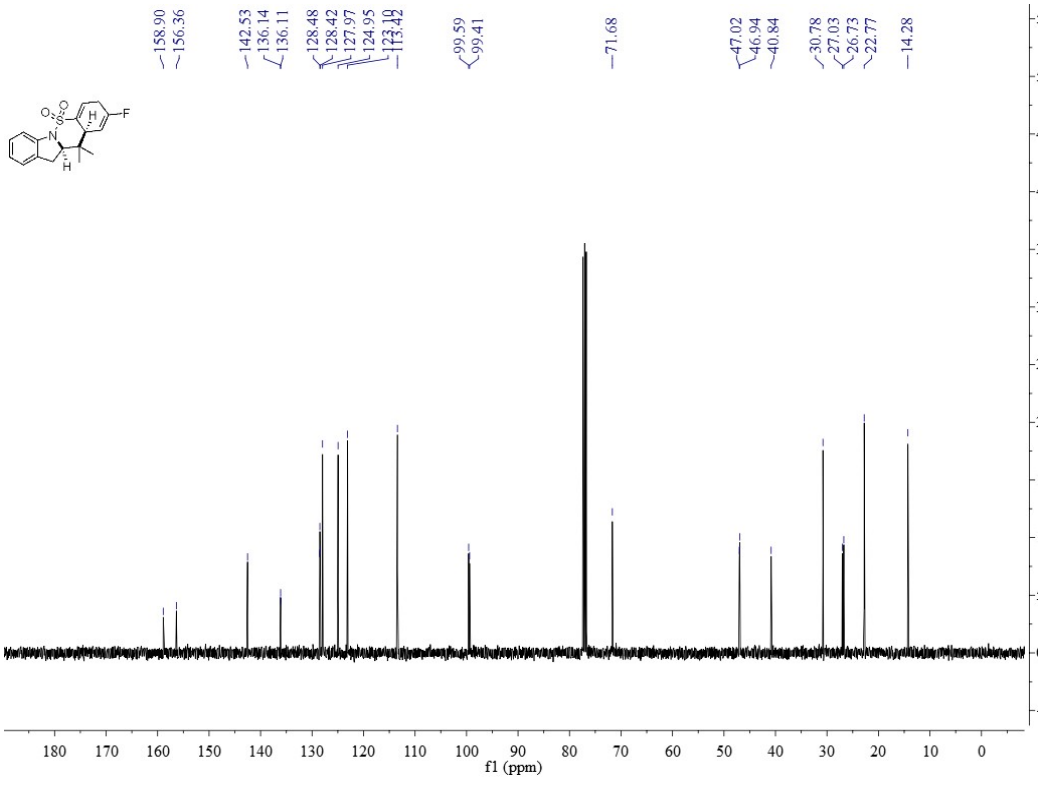
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ab**



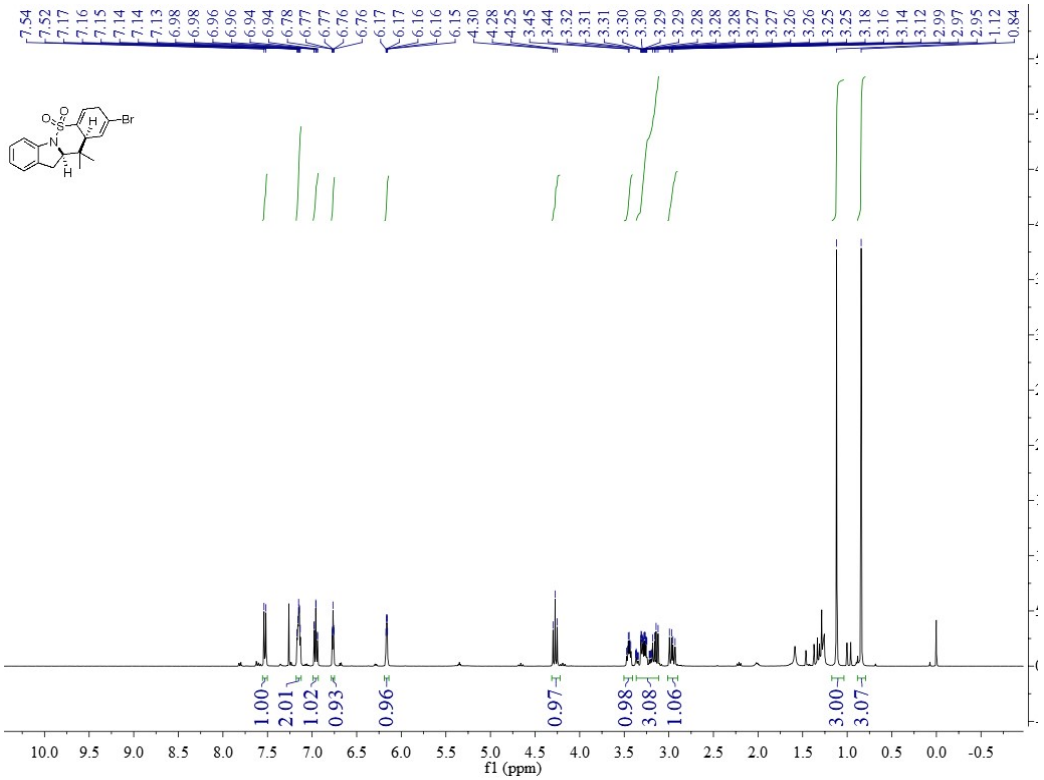
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2bb**



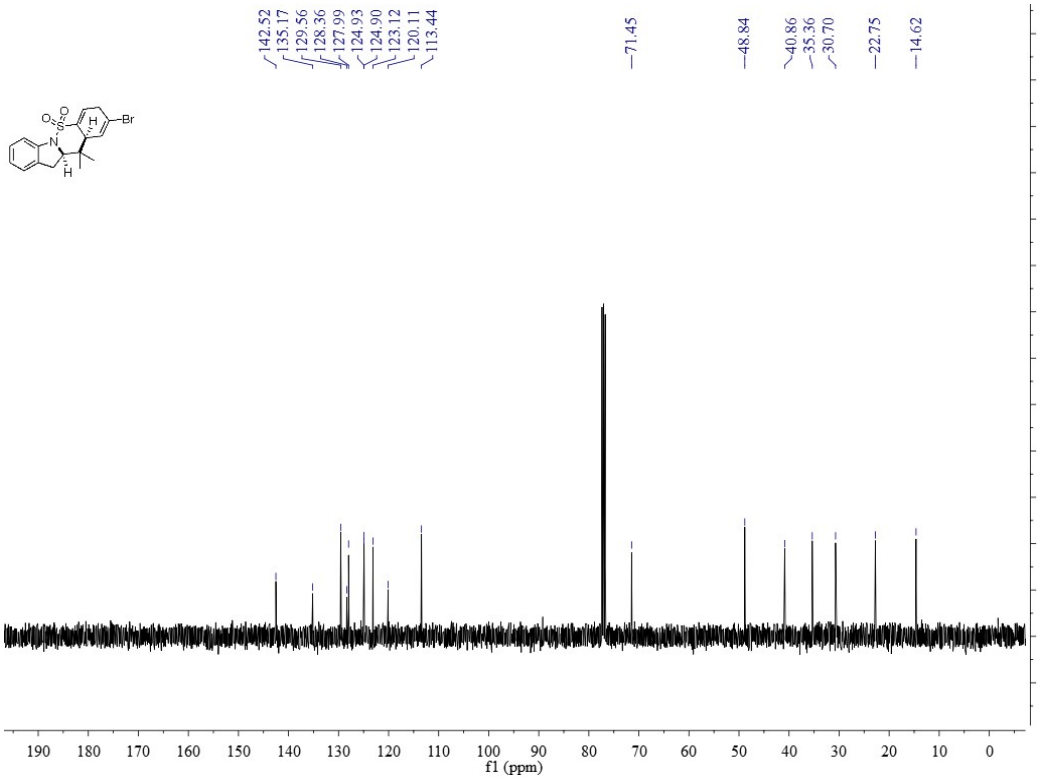
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2bb**



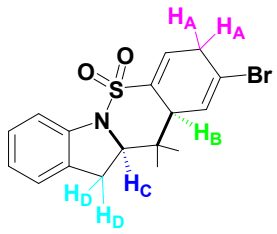
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2cb**

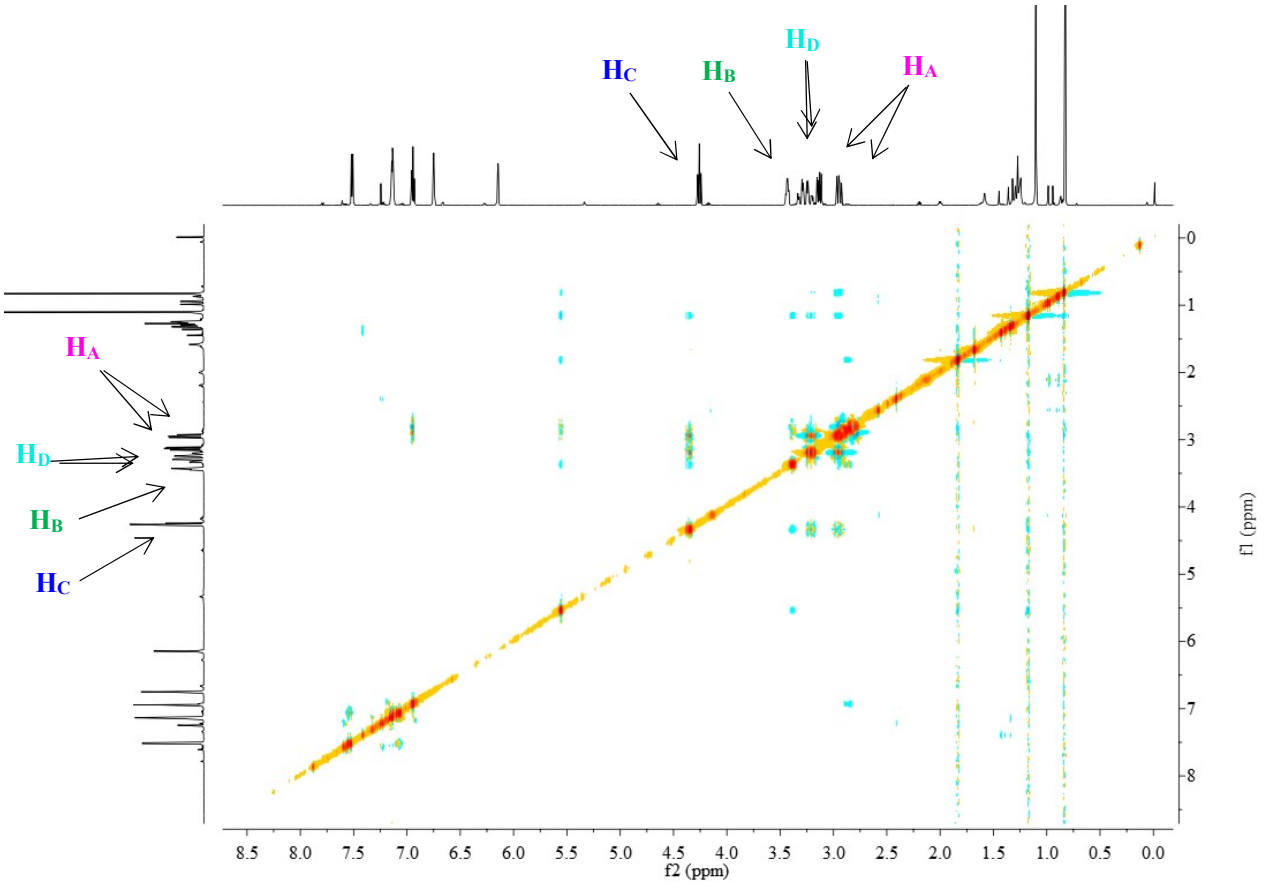


^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2cb**

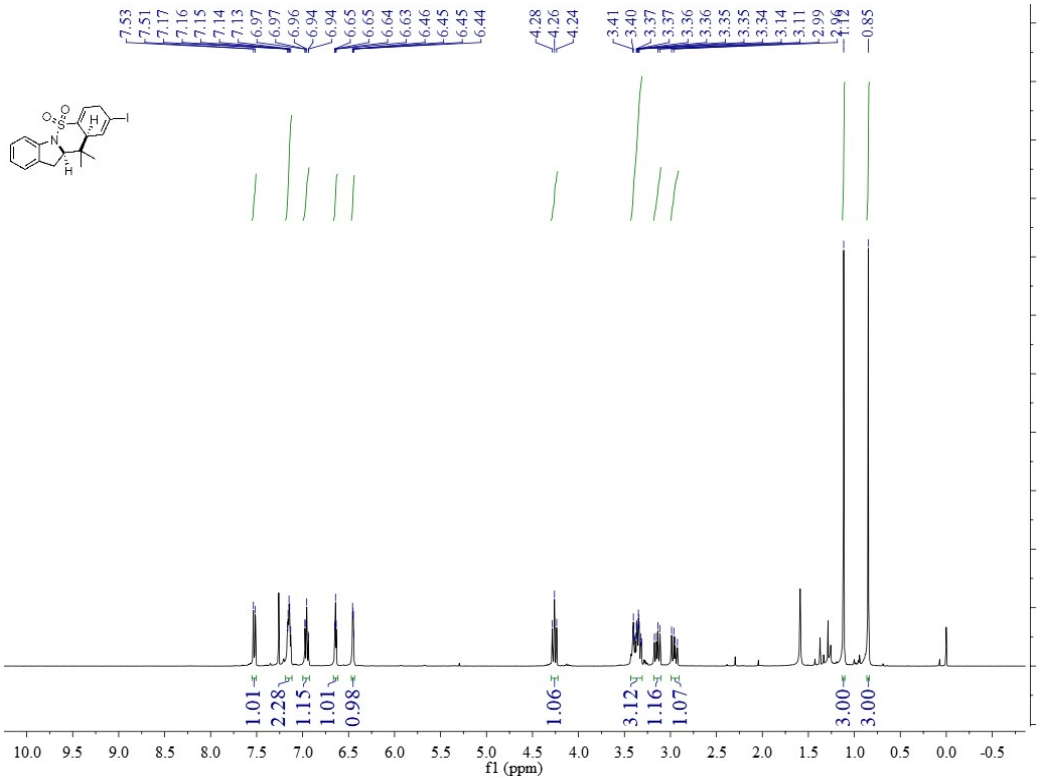


NOESY of **2cb**

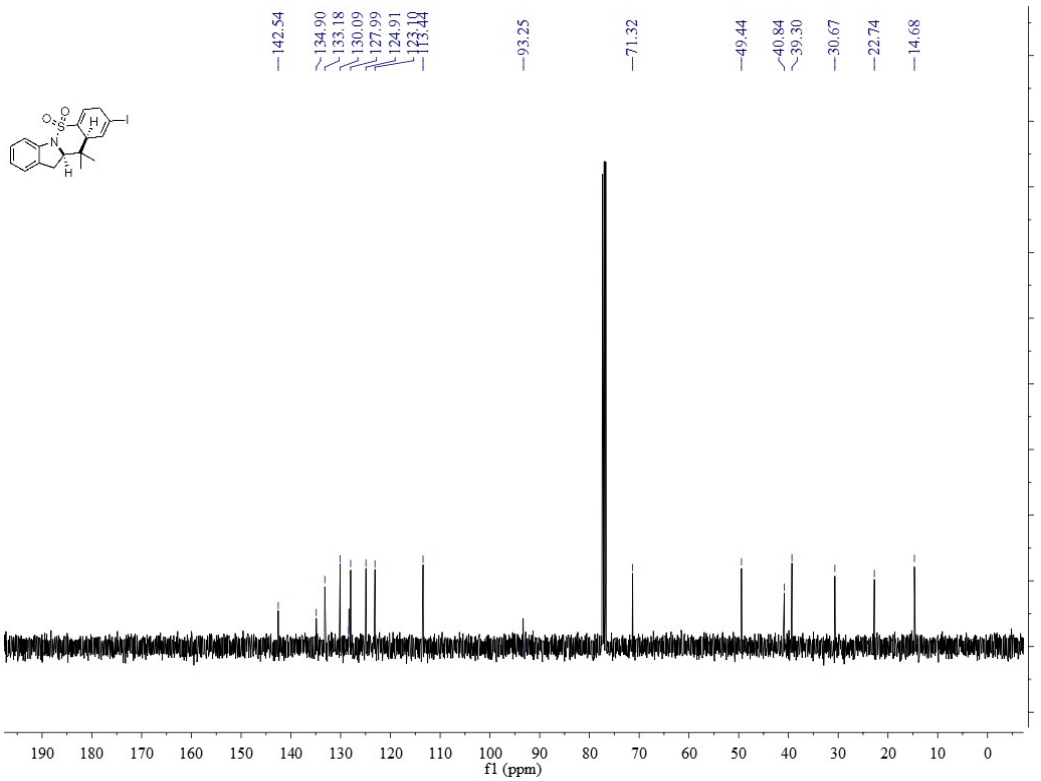

HA
HA
O
O
S
Br
N
HB
HC
HD
HD


HC
HB
HD
HA
HA
HD
HB
HC
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

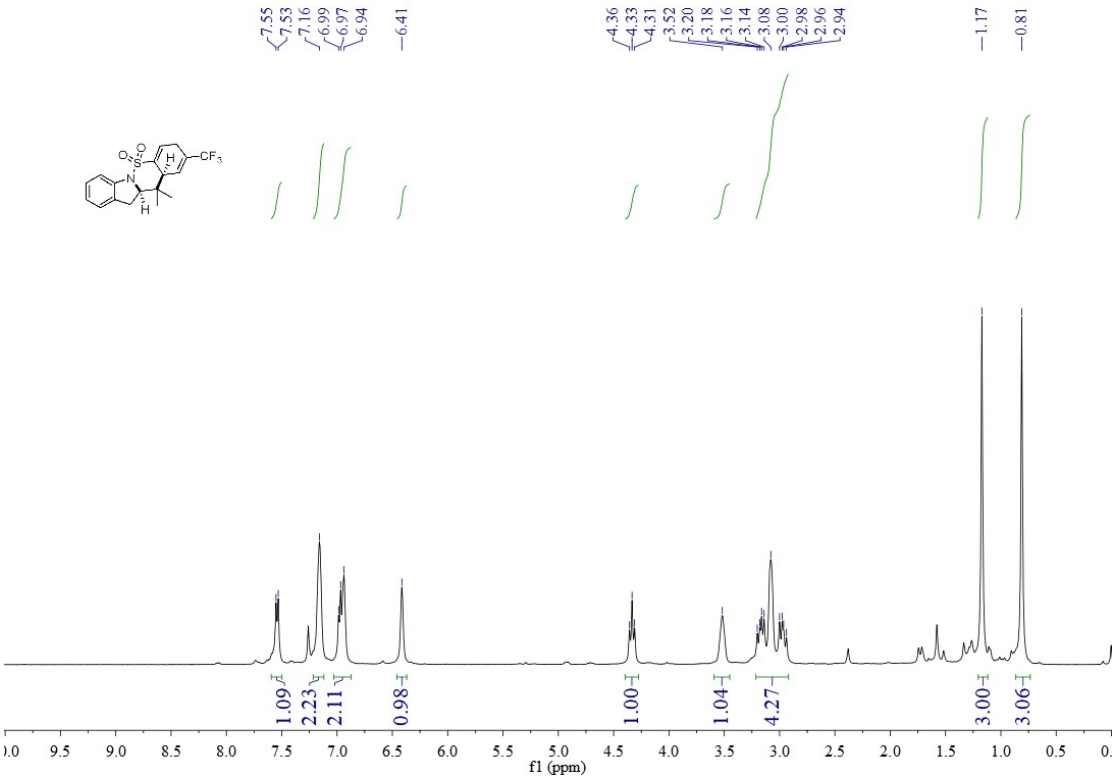
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2db**



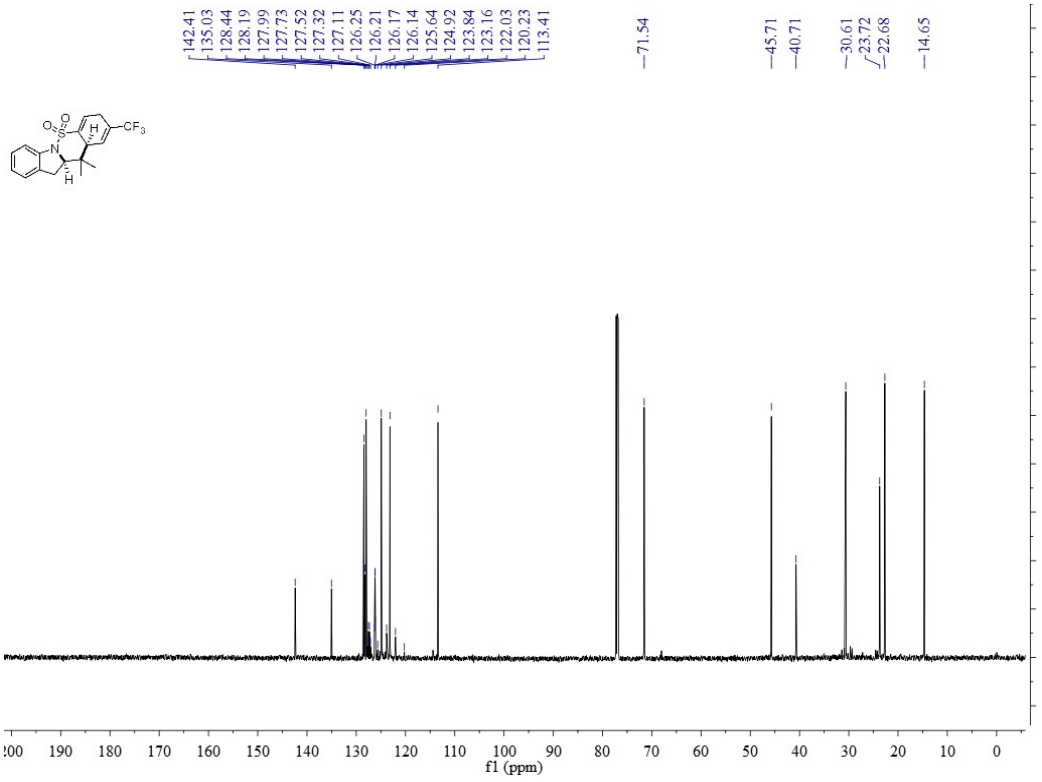
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2db**



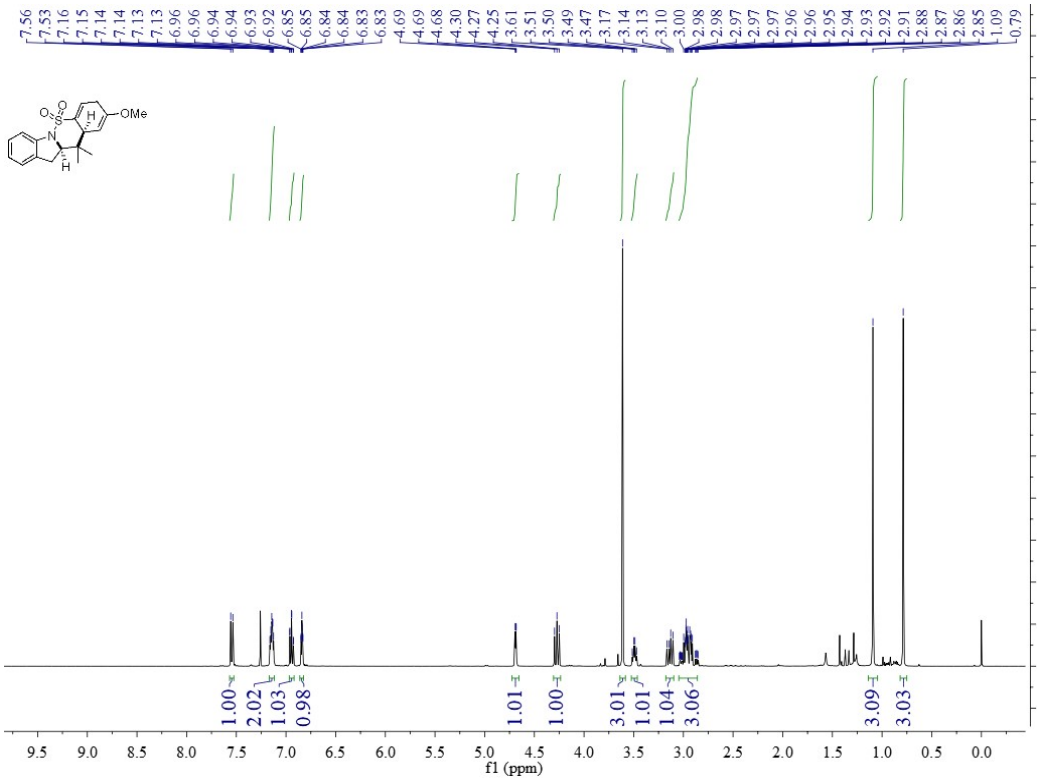
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2eb**



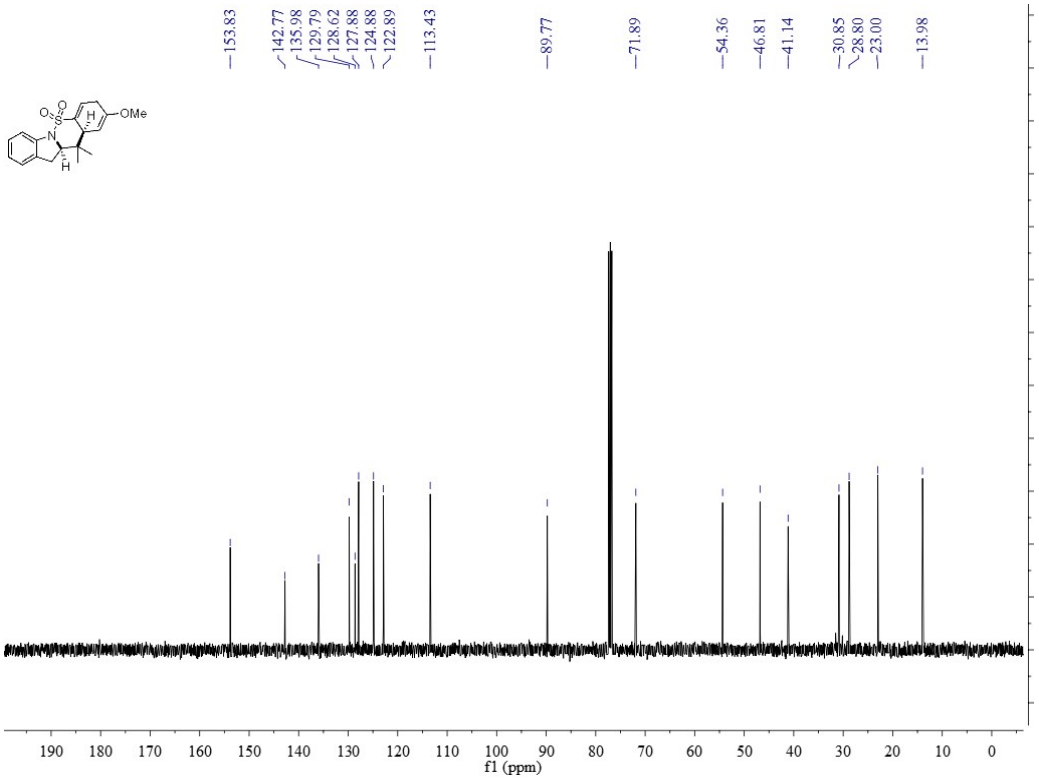
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2eb**



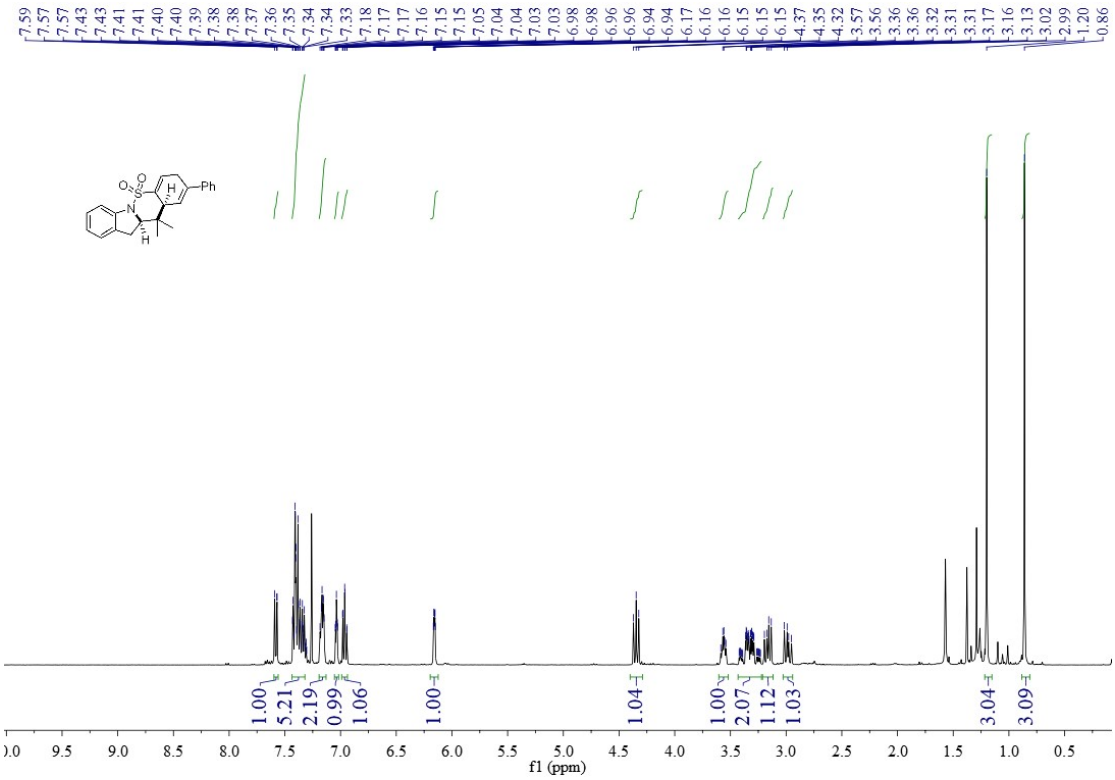
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2fb**



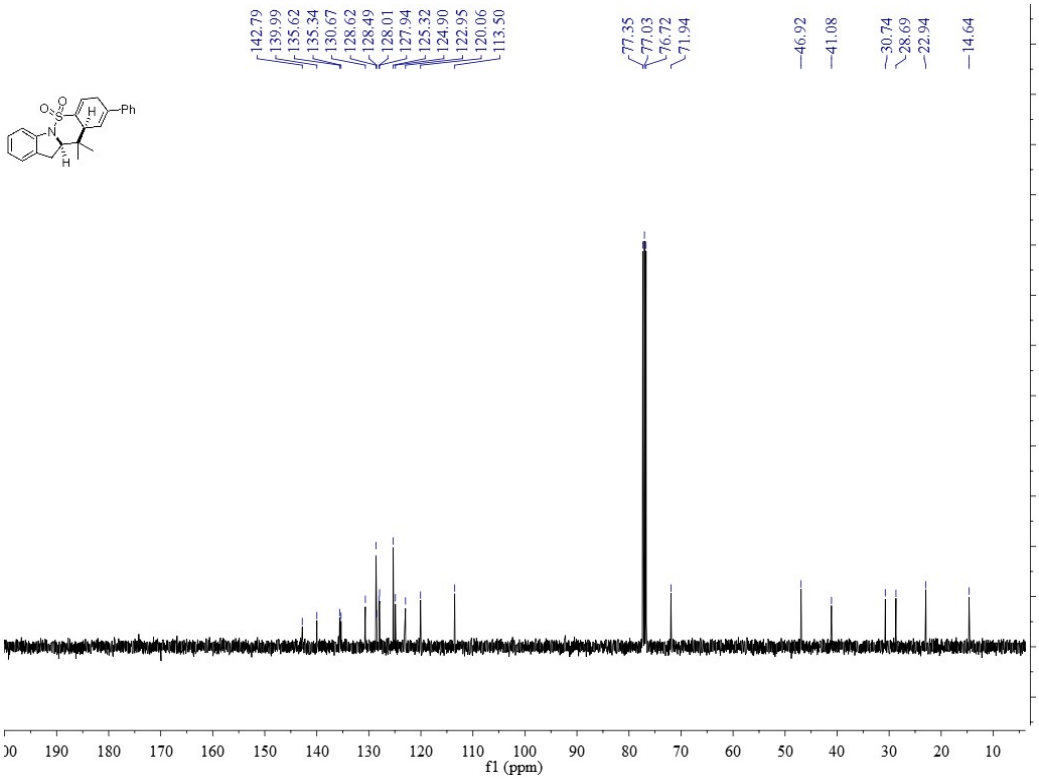
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2fb**



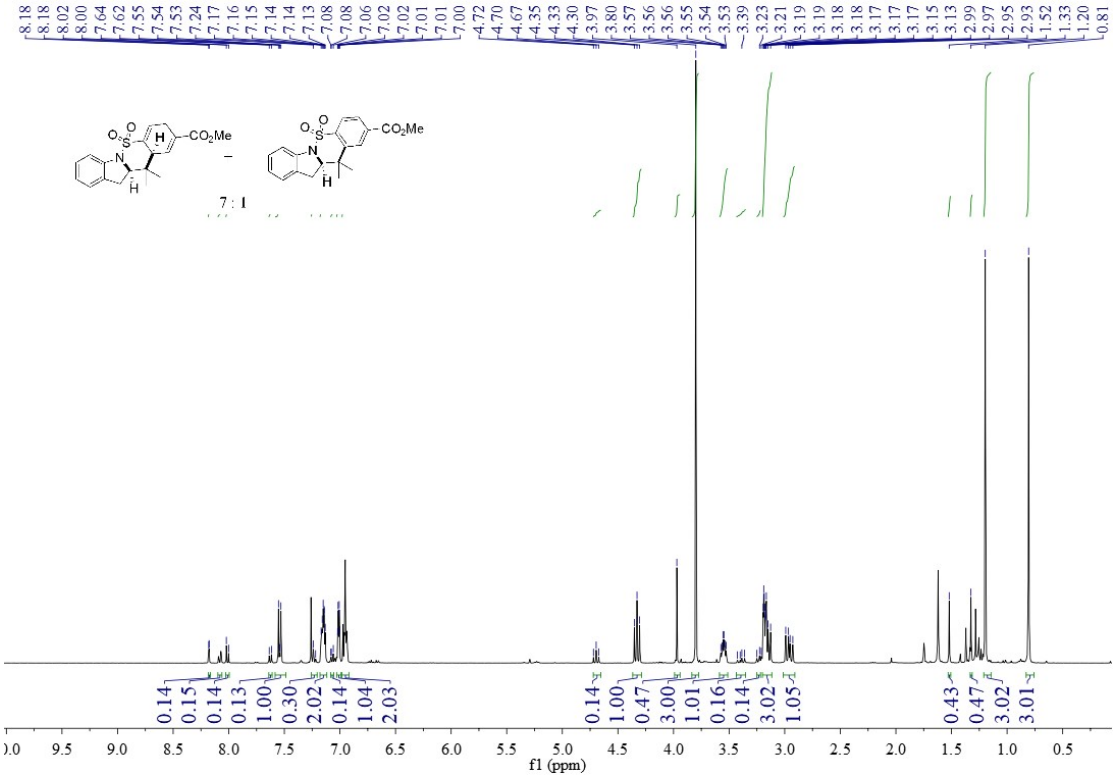
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2gb**



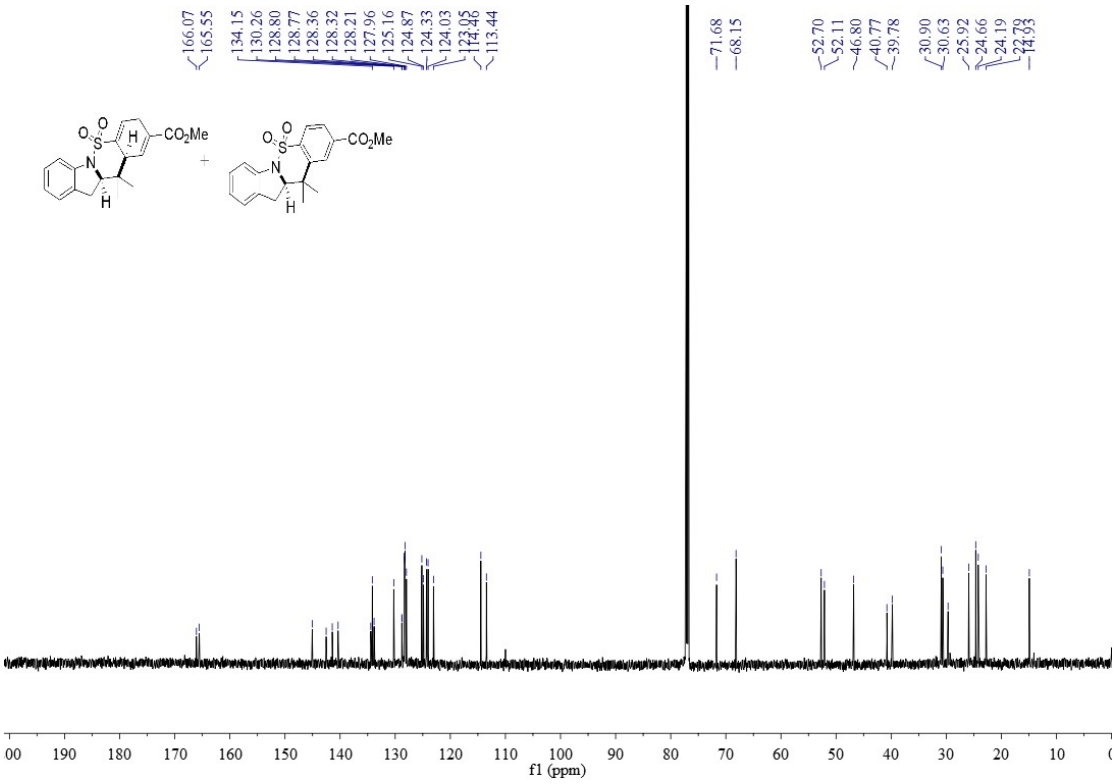
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2gb**



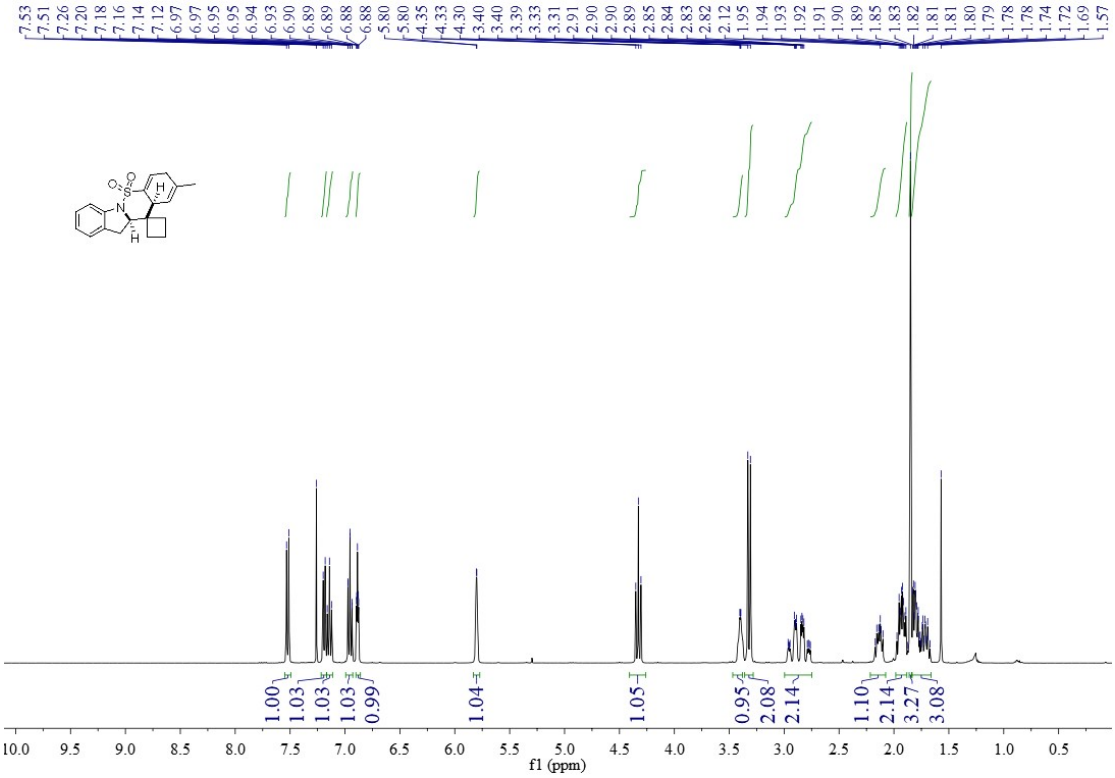
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2hb**



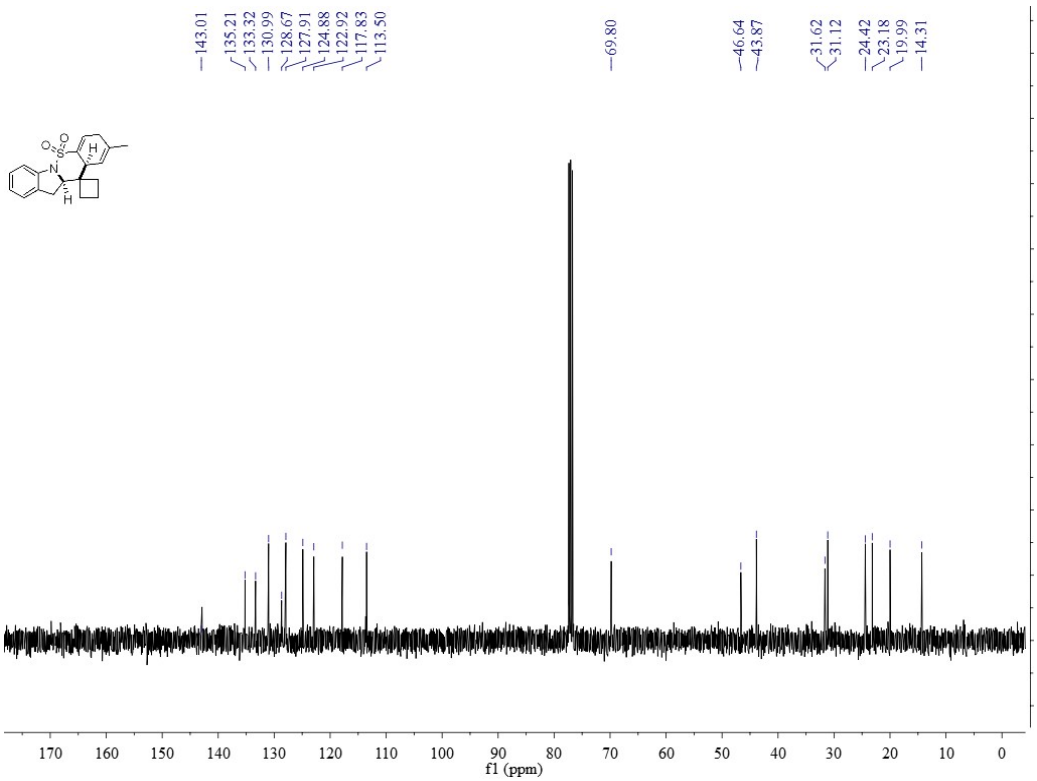
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2hb**



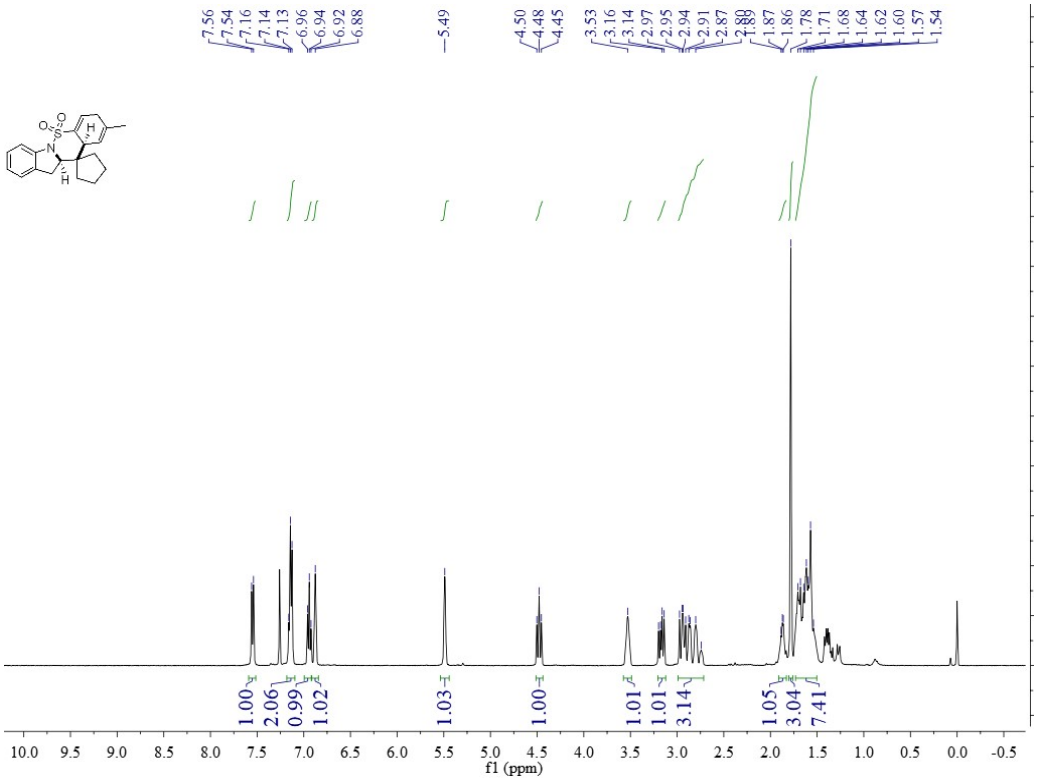
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ib**



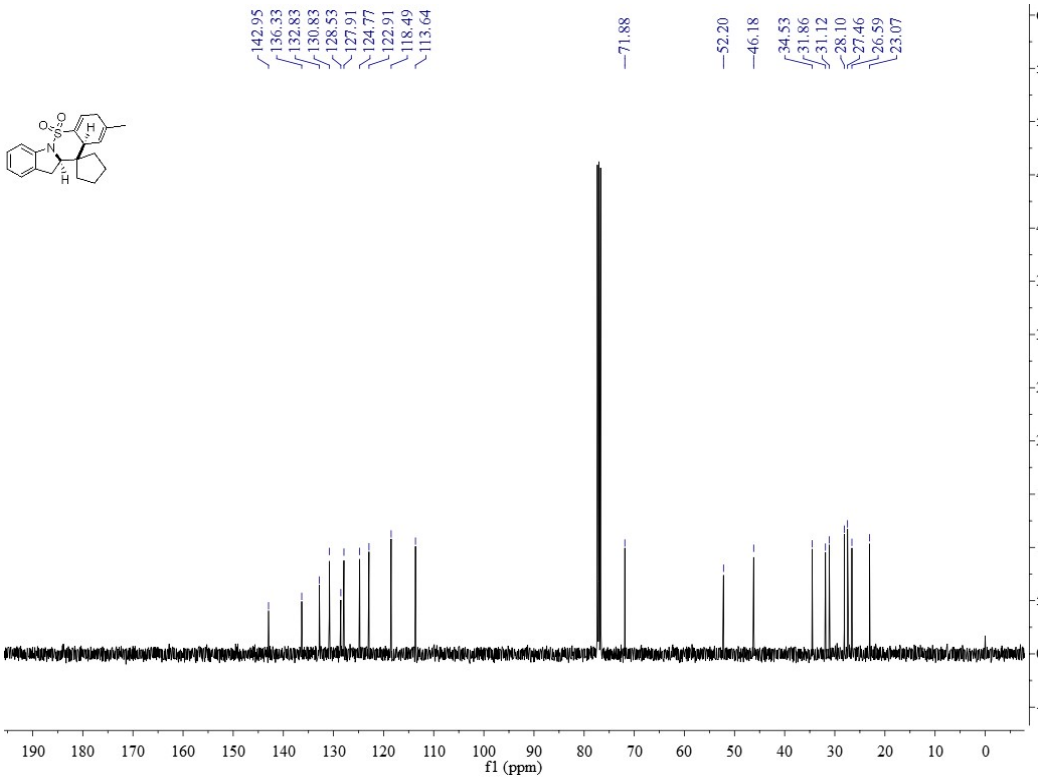
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ib**



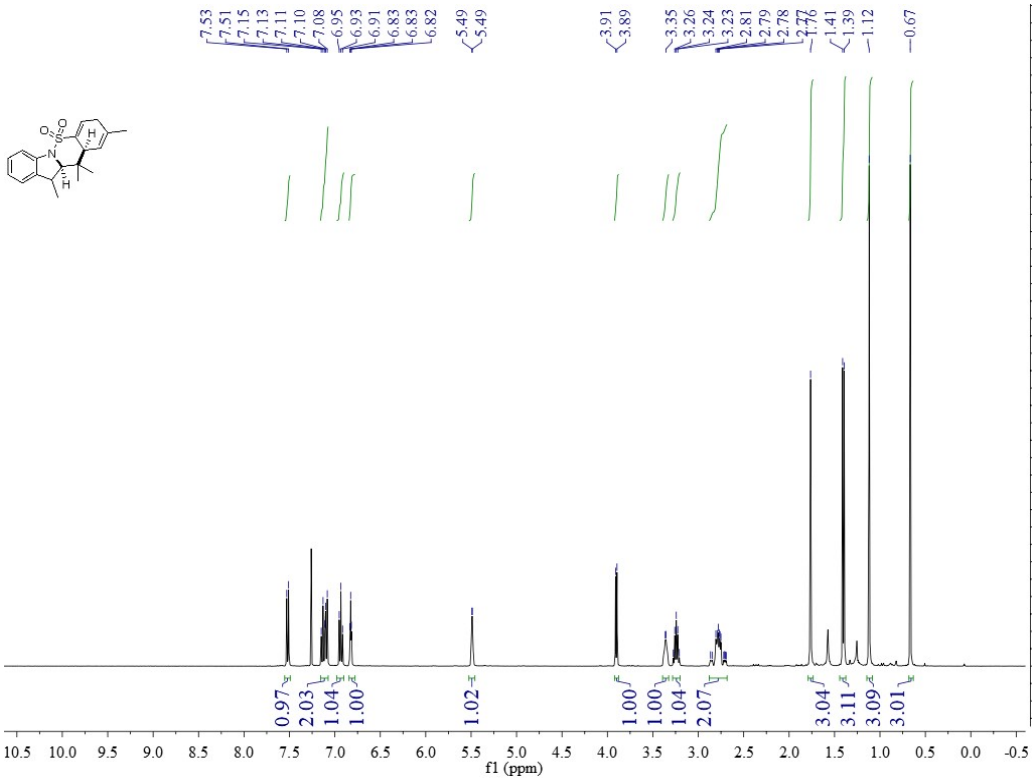
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2jb**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2jb**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2kb**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2kb**