Supporting Information

For

Photoredox-Neutral Alkene Aminoarylation for the Synthesis of 1,4,5,6-Tetrahydropyridazines

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Table of Contents

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). High-resolution mass (HRMS) spectroscopy data of the products were collected using 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 15 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 35 °C. Optimum yields were then observed.

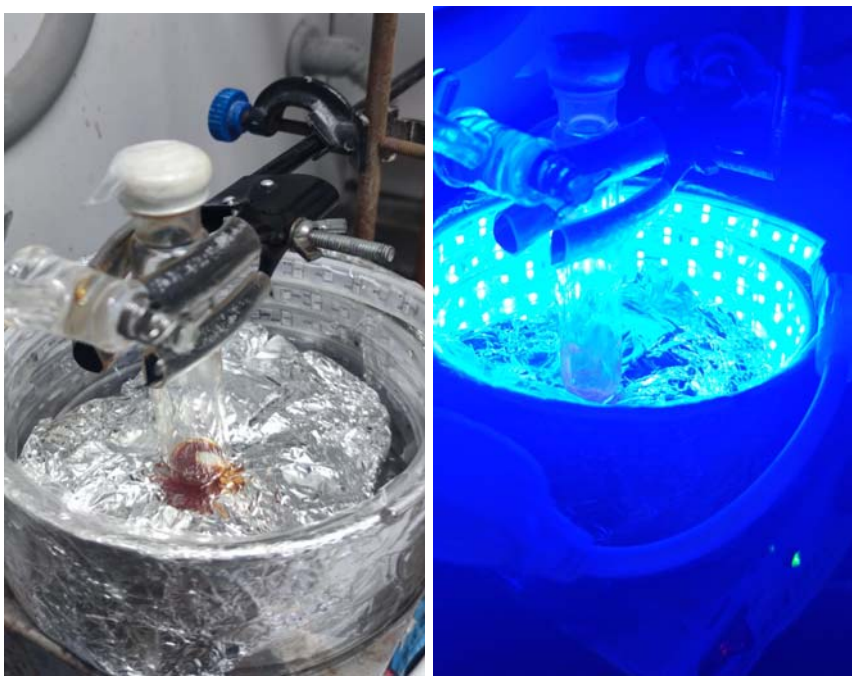


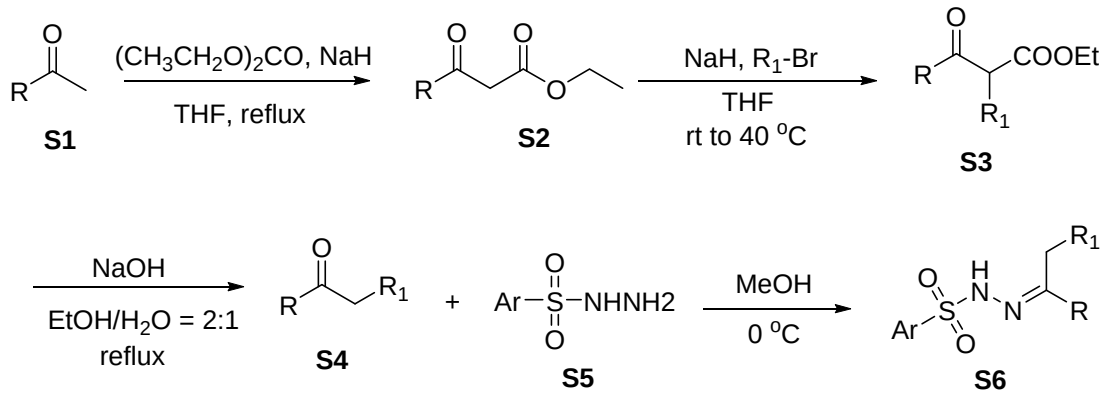
Figure S1. Reaction setup

3. General procedures for synthesis of substrates

3.1 Procedures for the preparation of Aryl sulfonyl hydrazide (S5).

The hydrazine hydrate (40%) (2.3 equiv.) was added into the solution of aryl sulfonyl chloride (1.0 equiv.) in THF (50 mL) at 0 ºC. Subsequently, the mixture was stirred at room temperature for 30 minutes. The solvent was removed by evaporation, and the residue was extracted with dichloromethane. The organic layer was washed with water, and brine, and dried over Na_2SO_4. The organic solvent was evaporated under reduced pressure and the residue was purified on silica gel flash chromatography to give the products. [1]

3.2 Preparation of Sulfonyl hydrazones.

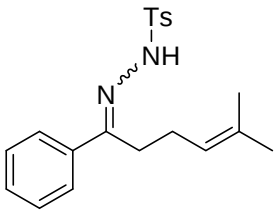


1) To a stirred solution of ketones **S1** (20 mmol) in toluene (100 mL), diethyl carbonate (60 mmol) and NaH (100 mmol, 60 %) were added. The reaction mixture was refluxed overnight. After cooling to room temperature, the reaction mixture was quenched by ice water, then extracted with EtOAc (100 mL × 3). The combined organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **S2**.[2]

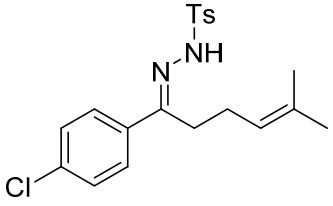
2) A solution of **S2** (1.0 equiv.) in THF (0.2 M) was treated with NaH (1.0 equiv., 60 % in mineral oil), stirred for 1h and treated with the bromide substrates (1.1 quiv.). The mixture was warmed to 40 ºC and stirred overnight. The mixture was cooled to room temperature. The crude product was absorbed on silica and purified by column chromatography on silica gel eluting with petrol–ethyl acetate (50:1) to give **S3**. [3]

3) A solution of **S3** (1.0 equiv.) in EtOH/H_2O (0.01M, 2:1) was treated with NaOH (4.0 equiv.) and refluxed for 2 h. The mixture was cooled to room temperature and MeOH was removed in vacuo. EtOAc was added and the layers were separated. The aqueous layer was then washed with EtOAc (100 ml × 3) and the combined organic fractions were dried ($MgSO_4$), filtered and evaporated. Purification is done by running column chromatography on silica gel, eluting with petrol/ethyl acetate (100:1) to obtain **S4**. [3]

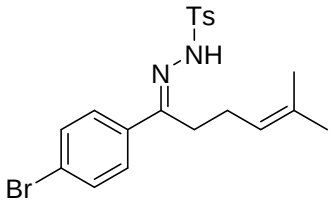
4) To a stirred solution of **S4** (1.0 equiv.) in MeOH (10 mL), **S5** (1.5 equiv.) was added at 0 ºC. The mixture was stirred at the same temperature until the reaction was completed, monitored by TLC. Then, the solvent was removed and the residue was purified by flash column chromatography to give compound **S6** as a white solid. [4]



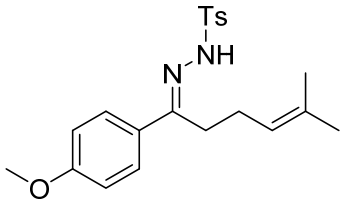
4-Methyl-*N'*-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (1aa): Prepared via general procedure as a white solid (*E*/*Z* = 8:1); m.p. 131-132 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (s, 0.88H)/7.48 (s, 0.11H), 7.93 (d, *J* = 8.3 Hz, 1.78H)/7.80 (d, *J* = 8.3 Hz, 0.22H), 7.69 – 7.59 (m, 1.78H), 7.38 – 7.29 (m, 5H), 7.10 – 7.02 (m, 0.22H), 5.10 – 5.01 (m, 0.88H)/5.01 – 4.92 (m, 0.11H), 2.66 (t, *J* = 7.4 Hz, 1.78H)/2.53 – 2.46 (m, 0.22H), 2.43 (s, 0.33H)/2.40 (s, 2.67H), 2.17 (q, *J* = 7.4 Hz, 1.78H)/ 2.10 (q, *J* = 7.4 Hz, 0.22H), 1.59 (s, 3H), 1.48 (s, 0.33H)/1.45 (s, 2.67H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.2, 144.1, 136.3, 135.5, 135.3, 129.60, 129.56, 128.4, 128.2, 126.4, 122.1, 27.0, 25.6, 24.51, 21.6, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3192, 2925, 1599, 1380, 1328, 1168, 815, 668; **HRMS** (ESI) Calculated for $C_{20}H_{25}N_2O_2S$ $[M + H]^+$: 357.1631, found 357.1635.



(*E*)-*N'*-(1-(4-Chlorophenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1ba): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 135-136 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.36 – 7.28 (m, 4H), 5.08 – 5.01 (m, 1H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 2.16 (q, *J* = 7.3 Hz, 2H), 1.60 (s, 3H), 1.45 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.9, 144.2, 135.6, 135.4, 134.8, 129.6, 128.6, 128.1, 127.7, 121.9, 26.9, 25.6, 24.4, 21.6, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3215, 2918, 1599, 1484，1386, 1347, 1174, 816, 674; **HRMS** (ESI) Calculated for $C_{20}H_{23}{}^{35}ClN_2O_2NaS$ [M + Na]$^+$: 413.1061, found 413.1053.

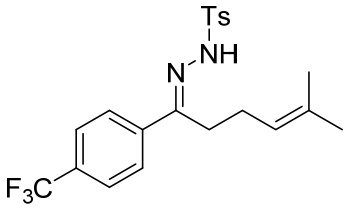


(*E*)-*N'*-(1-(4-Bromophenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1ca): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 139-140 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.44 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.09 – 5.00 (m, 1H), 2.62 (t, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 2.16 (q, *J* = 7.3 Hz, 2H), 1.60 (s, 3H), 1.45 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0, 144.2, 135.5, 135.4, 135.3, 131.6, 129.6, 128.1, 128.0, 124.0, 121.8, 26.9, 25.6, 24.4, 21.6, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3215, 2964, 1605, 1514, 1380, 1249, 1164, 926, 671; **HRMS** (ESI) Calculated for $C_{20}H_{24}{}^{79}BrN_2O_2S$ [M + H]$^+$: 435.0736, found 435.0739.

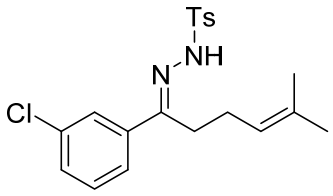


(*E*)-*N'*-(1-(4-Methoxyphenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1da): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 120-121 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.83 (s, 1H), 7.65 – 7.58 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.89 – 6.83 (m, 2H), 5.07 (t, *J* = 7.5, 4.4, 1.3 Hz, 1H), 3.81 (s, 3H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.61 (s, 3H), 1.46 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**

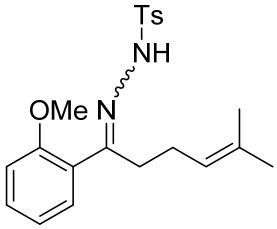
δ 160.8, 156.2, 144.0, 135.6, 135.3, 129.5, 128.8, 128.2, 127.9, 122.1, 113.7, 55.3, 26.9, 25.6, 24.6, 21.6, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3222, 2964, 1605, 1514, 1383, 1243, 1168, 926, 668; **HRMS** (ESI) Calculated for $C_{21}H_{26}N_2O_3NaS$ $[M + Na]^+$ 409.1556, found 409.1547.



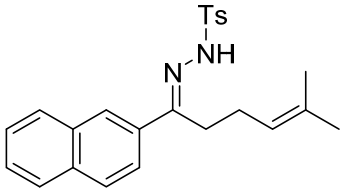
(*E*)-4-Methyl-*N'*-(5-methyl-1-(4-(trifluoromethyl)phenyl)hex-4-en-1-ylidene)benzenesulfonohydrazide (1ea): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 124-125 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (s, 1H), 7.95 – 7.87 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.11 – 5.02 (m, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.62 (s, 3H), 1.46 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 144.4, 139.7, 135.8, 135.3, 131.3 (q, *J* = 35.1 Hz), 129.6, 128.2 126.7, 125.4 (q, *J* = 3.8 Hz), 121.7, 121.3 (q, *J* = 272.3 Hz), 27.0, 25.6, 24.3, 21.6, 17.7; **FT-IR (thin film, KBr): ν (cm^{-1}):** 3219, 2925, 1605 1390, 1324, 1171, 1109, 1066, 926, 681; **HRMS** (ESI) Calculated for $C_{21}H_{23}F_3N_2O_2NaS$ $[M + Na]^+$ 447.1325, found 447.1318.



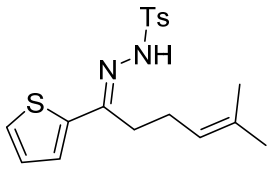
(*E*)-*N'*-(1-(3-Chlorophenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (1fa): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 126-127 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (s, 1H), 7.91 – 7.86 (m, 2H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.47 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.23 (t, *J* = 3.9 Hz, 1H), 5.09 – 4.96 (m, 1H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 2.14 (q, *J* = 7.3 Hz, 2H), 1.58 (s, 3H), 1.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 144.3, 138.2, 135.5, 135.3, 134.5, 129.6, 129.5, 128.2, 126.7, 124.5, 121.8, 27.0, 25.6, 24.4, 21.6, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3199, 2967, 1602, 1390, 1344, 1161, 929, 668; **HRMS** (ESI) Calculated for $C_{20}H_{23}{}^{35}ClN_2O_2NaS$ $[M + Na]^+$ 413.1061, found 413.1055.



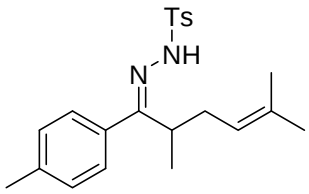
***N'*-(1-(2-Methoxyphenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfono hydrazide (1ga):** Prepared via general procedure as a white solid (*E*/*Z* = 1.2:1); m.p. 111-112 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 – 7.78 (m, 2H), 7.41 – 7.28 (m, 3H), 7.08 (d, *J* = 6.3 Hz, 0.5H)/6.99 (td, *J* = 7.5, 0.8 Hz, 0.5H), 6.95 – 6.83 (m, 2H), 5.04 – 4.90 (m, 1H), 3.76 (s, 1.6H)/3.63 (s, 1.4H), 2.67 – 2.57 (m, 1H), 2.53 – 2.40 (m, 4H), 2.15 – 2.01 (m, 2H), 1.60 (d, *J* = 0.7 Hz, 1.6H)/1.59 (d, *J* = 1.0 Hz, 1.4H), 1.48 (s, 1.4H)/1.46 (s, 1.6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.3, 156.3, 155.1, 143.7, 135.8, 134.3, 132.0, 131.2, 130.5, 129.4, 129.3, 128.3, 128.0, 123.2, 122.7, 121.9, 121.5, 120.6, 111.5, 110.9, 55.5/55.4, 38.0, 25.6/24.6, 23.9, 21.6, 17.7/17.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3219, 2925, 1602, 1383, 1350, 1321, 1168, 1115, 1063, 929, 678; **HRMS** (ESI) Calculated for $C_{21}H_{27}N_2O_3S$ $[M + H]^+$ 387.1737, found 387.1742.



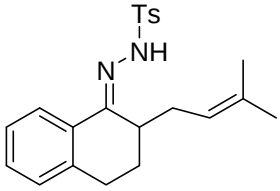
(*E*)-4-Methyl-*N'*-(5-methyl-1-(naphthalen-2-yl)hex-4-en-1-ylidene)benzenesulfonohydrazide (1ha): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 146-147 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 – 7.92 (m, 5H), 7.86 – 7.78 (m, 3H), 7.53 – 7.46 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.17 – 5.08 (m, 1H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 2.26 (q, *J* = 7.4 Hz, 2H), 1.64 (s, 3H), 1.49 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.9, 144.2, 135.6, 135.5, 133.9, 133.7, 132.9, 129.6, 128.6, 128.2, 128.1, 127.6, 126.9, 126.4, 126.3, 123.8, 122.1, 26.9, 25.7, 24.7, 21.6, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3199, 2957, 2921, 1592, 1393, 1337, 1161, 926, 674; **HRMS** (ESI) Calculated for $C_{24}H_{26}N_2O_2NaS$ $[M + Na]^+$ 429.1607, found 429.1604.



(*E*)-4-Methyl-*N'*-(5-methyl-1-(thiophen-2-yl)hex-4-en-1-ylidene)benzenesulfono hydrazide (1ia): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 123-124 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.95 – 7.87 (m, 2H), 7.62 (s, 1H), 7.35 – 7.29 (m, 3H), 7.19 (dd, *J* = 3.7, 1.1 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.12 – 5.04 (m, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.23 (q, *J* = 7.4 Hz, 2H), 1.61 (s, 3H), 1.46 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 152.8, 144.1, 142.1, 135.9, 135.3, 129.4, 128.4, 128.3, 127.1, 126.6, 121.9, 28.1, 25.6, 24.9, 21.6, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3202, 2967, 1599, 1439, 1393, 1337, 1163, 926, 619; **HRMS** (ESI) Calculated for $C_{18}H_{22}N_2NaO_2S_2$ $[M + H]^+$ 385.1015, found 385.1005.

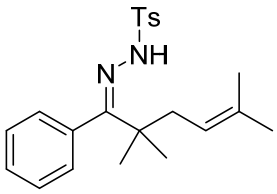


(*E*)-*N'*-(2,5-Dimethyl-1-(p-tolyl)hex-4-en-1-ylidene)-4-methylbenzenesulfono hydrazide (1ja): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 112-113 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 – 7.72 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.19 (m, 3H), 6.84 (d, *J* = 8.1 Hz, 2H), 4.94 – 4.84 (m, 1H), 2.58 (h, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 2.09 (dt, *J* = 13.4, 6.5 Hz, 1H), 1.94 (dt, *J* = 14.8, 7.4 Hz, 1H), 1.59 (d, *J* = 0.9 Hz, 3H), 1.48 (s, 3H), 0.99 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 162.2, 143.8, 139.7, 135.5, 132.9, 130.1, 129.5, 129.2, 128.0, 127.0, 122.0, 42.2, 32.3, 25.7, 21.6, 21.3, 17.9, 17.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3196, 2967, 2921, 1599, 1453, 1394, 1329, 1159, 823, 672; **HRMS** (ESI) Calculated for $C_{22}H_{29}N_2O_2S$ $[M + H]^+$ 385.1944, found 385.1950.

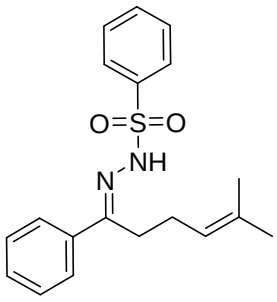


(*E*)-4-Methyl-*N'*-(2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-ylidene)benzenesulfonohydrazide (1ka): Prepared via general procedure as a white

solid (*E*/*Z* > 20:1); m.p. 132-133 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.85 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 5.12 – 5.05 (m, 1H), 3.01 (ddd, *J* = 10.9, 7.4, 3.5 Hz, 1H), 2.98 – 2.86 (m, 1H), 2.68 (dt, *J* = 7.3, 4.0 Hz, 1H), 2.43 (s, 3H), 2.12 (t, *J* = 7.6 Hz, 2H), 1.98 – 1.89 (m, 2H), 1.66 (s, 3H), 1.46 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.1, 144.0, 138.2, 136.6, 135.6, 130.7, 129.7, 129.5, 128.8, 128.2, 126.3, 125.8, 121.4, 34.1, 28.1, 26.8, 25.8, 24.3, 21.6, 17.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3199, 2925, 1579, 1393, 1347, 1161, 923, 671; **HRMS** (ESI) Calculated for $C_{22}H_{26}N_2O_2NaS$ $[M + Na]^+$ 405.1607, found 405.1603.

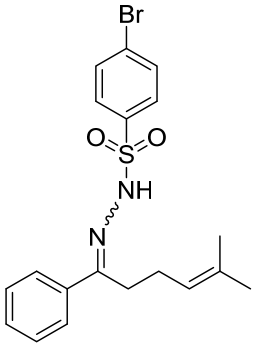


(*E*)-4-Methyl-*N'*-(2,2,5-trimethyl-1-phenylhex-4-en-1-ylidene)benzenesulfono hydrazide (1la): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 125-126 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 – 7.73 (m, 2H), 7.43 – 7.38 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 1H), 6.84 – 6.78 (m, 2H), 4.88 – 4.80 (m, 1H), 2.44 (s, 3H), 2.02 (d, *J* = 6.9 Hz, 2H), 1.60 (s, 3H), 1.49 (s, 3H), 1.02 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.4, 143.9, 135.5, 133.5, 131.7, 129.5 129.4, 129.3, 128.0, 127.5, 120.2, 42.1, 38.2, 25.84, 25.78, 21.6, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3225, 2970, 1599, 1384, 1332, 1152, 891, 666; **HRMS** (ESI) Calculated for $C_{22}H_{29}N_2O_2S$ $[M + H]^+$ 385.1944, found 385.1947.

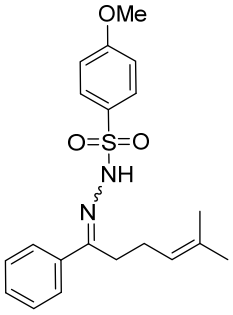


(*E*)-*N'*-(5-Methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (1ab): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 120-121 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (s, 1H), 8.07 – 8.03 (m, 2H), 7.67 – 7.62 (m, 2H),

7.59 (dt, *J* = 2.7, 2.0 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.39 – 7.31 (m, 3H), 5.14 – 5.00 (m, 1H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.18 (q, *J* = 7.4 Hz, 2H), 1.60 (s, 3H), 1.44 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.5, 138.5, 136.3, 135.2, 133.2, 129.6, 128.9, 128.4, 128.1, 126.5, 122.1, 27.1, 25.6, 24.5, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3222, 2970, 2915, 1445, 1383, 1382, 1174, 919, 691; **HRMS** (ESI) Calculated for $C_{19}H_{22}N_2NaO_2S$ $[M + Na]^+$ 365.1294, found 365.1295.

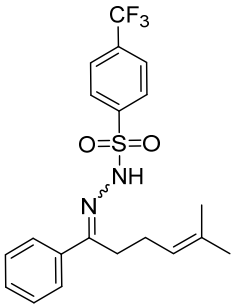


4-Bromo-*N'*-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (1bb): Prepared via general procedure as a white solid (*E*/*Z* = 5:1); m.p. 133-134 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 – 7.86 (m, 1.67H)/7.81 – 7.75 (m, 0.33H), 7.82 (s, 1H), 7.71 – 7.05 (m, 7H), 5.14 – 5.05 (m, 0.85H)/5.03 – 4.93 (m, 0.16H), 2.67 (t, *J* = 7.3 Hz, 1.72H)/2.56 – 2.46 (m, 0.36H), 2.20 (q, *J* = 7.3 Hz, 1.77H)/2.11 (dd, *J* = 14.8, 7.3 Hz, 0.36H), 1.63 (s, 3H), 1.49 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.0, 137.4, 136.0, 135.9, 132.2, 129.9, 129.7, 128.5, 126.7, 126.4, 122.0, 27.2, 25.7, 24.6, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3205, 2964, 2918, 1573, 1466, 1393, 1321, 1168, 913, 632; **HRMS** (ESI) Calculated for $C_{19}H_{21}{}^{79}BrN_2O_2NaS$ $[M + Na]^+$ 443.0399, found 443.0390.

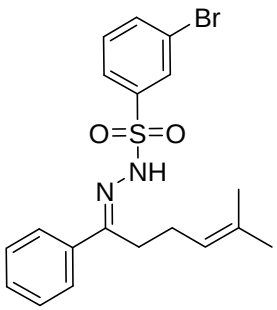


4-Methoxy-*N'*-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (1cb): Prepared via general procedure as a white solid (*E*/*Z* = 5:1); m.p. 128-129 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 – 7.92 (m, 1.72H)/7.89 – 7.82 (m, 0.37H), 7.78 (s, 1H), 7.70 – 7.61 (m, 1.76H)/7.11 – 7.04 (m, 0.34H), 7.46 – 7.30 (m, 3H), 7.03 –

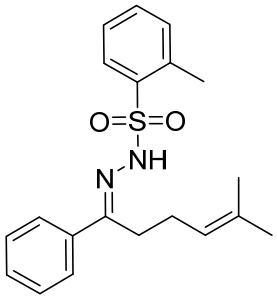
6.96 (m, 2H), 5.13 – 5.03 (m, 1H)/5.00 – 4.93 (m, 0.16H), 3.88 (s, 0.53H)/3.86 (s, 2.54H), 2.66 (t, *J* = 7.3 Hz, 1.71H)/ 2.57 – 2.40 (m, 0.35H), 2.19 (q, *J* = 7.4 Hz, 1.75H)/ 2.14 – 2.06 (m, 0.36H), 1.63 (s, 3H), 1.48 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.4/156.1, 136.3/135.5, 130.5/130.4, 130.1/130.0, 129.8/129.6, 129.6/128.6, 128.4/128.1, 126.8, 126.4, 122.1, 114.5/114.1, 55.6/38.2, 27.1/26.6, 25.7, 24.7/24.5, 17.8/17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3205, 2918, 1599, 1442, 1396, 1334, 1161, 812, 666; **HRMS** (ESI) Calculated for $C_{20}H_{24}N_2O_3NaS$ $[M + Na]^+$ 395.1400, found 395.1408.



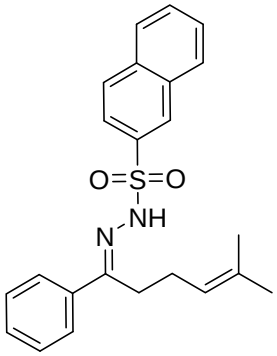
***N'*-(5-Methyl-1-phenylhex-4-en-1-ylidene)-4-(trifluoromethyl)benzenesulfono hydrazide (1db):** Prepared via general procedure as a white solid (*E*/*Z* = 6:1); m.p. 120-121 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.2 Hz, 1.77H)/8.06 (d, *J* = 8.2 Hz, 0.36H), 7.98 (s, 0.83H)/7.51 (s, 0.16H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.61 (m, 1.82H)/7.14 – 7.06 (m, 0.31H), 7.47 – 7.33 (m, 3H), 5.13 – 5.04 (m, 0.90H)/5.00 – 4.92 (m, 0.16H), 2.68 (t, *J* = 7.3 Hz, 1.83H)/2.57 – 2.47 (m, 0.37H), 2.21 (q, *J* = 7.3 Hz, 1.85H)/2.12 (q, *J* = 7.2 Hz, 0.39H), 1.61 (d, *J* = 3.7 Hz, 3H), 1.48 (d, *J* = 5.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.3, 142.0, 136.0, 135.8, 130.0, 128.54, 126.69, 126.43, 126.06 (q, *J* = 3.7 Hz), 125.88 (dd, *J* = 463.1, 253.5 Hz), 121.99, 27.22, 25.63, 24.56, 17.74; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3215, 2970, 2918, 1612, 1451, 1403, 1328, 1164, 1060, 932, 717; **HRMS** (ESI) Calculated for $C_{20}H_{22}F_3N_2O_2S$ $[M + H]^+$ 411.1349, found 411.1342.



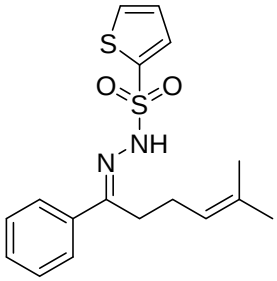
(*E*)-3-Bromo-*N'*-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (1eb): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 127-128 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.23 (t, *J* = 1.6 Hz, 1H), 8.20 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.39 – 7.33 (m, 3H), 5.08 (t, *J* = 7.5 Hz, 1H), 2.70 (t, *J* = 7.3 Hz, 2H), 2.20 (q, *J* = 7.3 Hz, 2H), 1.61 (s, 3H), 1.45 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 157.4, 140.2, 136.2, 136.1, 135.4, 131.2, 130.5, 129.9, 128.5, 126.7, 126.6, 122.9, 122.1, 27.2, 25.7, 24.6, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3192, 2925, 1687, 1592, 1494, 1311, 1272, 1151, 1021, 910, 678; **HRMS** (ESI) Calculated for $C_{19}H_{21}{}^{79}BrN_2O_2NaS$ $[M + Na]^+$ 443.0399, found 443.0402.



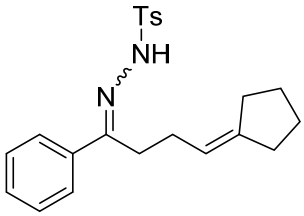
(*E*)-2-Methyl-*N'*-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (1fb): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 113-114 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.15 – 8.08 (m, 1H), 8.00 (s, 1H), 7.61 – 7.54 (m, 2H), 7.47 (td, *J* = 7.5, 1.1 Hz, 1H), 7.37 – 7.28 (m, 5H), 5.18 – 5.11 (m, 1H), 2.75 (s, 3H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.23 (q, *J* = 7.4 Hz, 2H), 1.66 (s, 3H), 1.52 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.3, 138.2, 136.7, 136.3, 135.2, 133.3, 132.5, 130.6, 129.5, 128.4, 126.4, 126.3, 122.0, 26.9, 25.7, 24.6, 21.0, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3232, 2918, 1592, 1448, 1386, 1311, 1161, 1021, 936, 694; **HRMS** (ESI) Calculated for $C_{20}H_{24}N_2O_2NaS$ $[M + Na]^+$ 379.1451, found 379.1446.



(*E*)-*N'*-(5-Methyl-1-phenylhex-4-en-1-ylidene)naphthalene-2-sulfonohydrazide (1gb): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 137-138 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (s, 1H), 8.38 (s, 1H), 8.09 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.04 – 7.95 (m, 2H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.70 – 7.57 (m, 4H), 7.37 – 7.29 (m, 3H), 5.06 (t, *J* = 7.5 Hz, 1H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.56 (s, 3H), 1.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.6, 136.4, 135.4, 135.1, 135.0, 132.2, 129.8, 129.6, 129.4, 129.2, 129.0, 128.4, 128.0, 127.6, 126.5, 123.2, 122.1, 27.2, 25.6, 24.5, 17.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3232, 2918, 1592, 1448, 1386, 1311, 1161, 1021, 936, 694; **HRMS** (ESI) Calculated for $C_{23}H_{25}N_2O_2S$ $[M + H]^+$ 393.1631, found 393.1636.

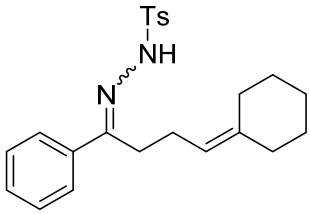


(*E*)-*N'*-(5-Methyl-1-phenylhex-4-en-1-ylidene)thiophene-2-sulfonohydrazide (1hb): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 127-128 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (s, 1H), 7.78 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.64 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.10 (dd, *J* = 5.0, 3.8 Hz, 1H), 5.15 – 5.06 (m, 1H), 2.70 (t, *J* = 7.3 Hz, 2H), 2.22 (q, *J* = 7.3 Hz, 2H), 1.60 (s, 3H), 1.46 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.2, 138.4, 136.0, 133.4, 133.2, 129.9, 128.5, 127.1, 126.6, 122.1, 27.3, 25.6, 24.6, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3212, 2974, 1680, 1448, 1383, 1344, 1168, 1071, 913, 671; **HRMS** (ESI) Calculated for $C_{17}H_{20}N_2O_2NaS_2$ $[M + Na]^+$ 371.0858, found 371.0849.

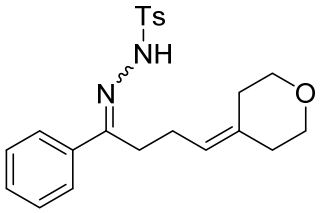


***N'*-(4-Cyclopentylidene-1-phenylbutylidene)-4-methylbenzenesulfonohydrazide (1ib):** Prepared via general procedure A as a white solid (*E*/*Z* = 7:1); m.p. 120-121 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (s, 0.88H)/7.46 (s, 0.12H), 7.97 – 7.89 (d,

1.77H)/7.80 (d, J = 8.3 Hz, 0.23H), 7.70 – 7.61 (m, 1.77H)/7.08 – 7.03 (m, 0.23H), 7.44 – 7.29 (m, 5H), 5.19 – 5.11 (m, 0.88H)/5.07 (m, J = 9.2, 4.7, 2.3 Hz, 0.12H), 2.68 (t, J = 7.3 Hz, 1.77H)/2.56 – 2.49 (m, 0.23H), 2.44 (s, 0.38H)/2.41 (s, 2.62H), 2.24 – 2.06 (m, 4H), 2.05 – 1.96 (m, 2H), 1.65 – 1.47 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.3, 147.0, 144.1, 136.4, 135.6, 129.8/129.6, 128.4, 128.1/128.0, 126.8/126.5, 118.2/117.5, 38.0/33.6, 28.7/28.6, 26.9/26.4, 26.3/26.2, 26.1, 21.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3215, 2957, 1603, 1391, 1348, 1169, 927, 676; **HRMS** (ESI) Calculated for $C_{22}H_{26}N_2O_2NaS$ $[M + Na]^+$ 405.1607, found 405.1600.

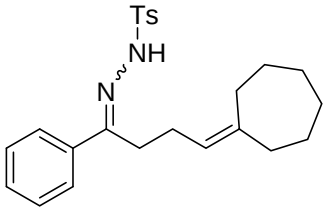


***N'*-(4-Cyclohexylidene-1-phenylbutylidene)-4-methylbenzenesulfonohydrazide (1jb)**: Prepared via general procedure as a white solid (E/Z = 13:1); m.p. 135-136 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (s, 1H), 7.93 (d, J = 8.3 Hz, 1.86H)/7.80 (d, J = 8.3 Hz, 0.14H), 7.70 – 7.62 (m, 1.86H)/7.09 – 7.03 (m, 0.14H), 7.46 – 7.29 (m, 5H), 5.00 (t, J = 7.6 Hz, 0.93H)/4.91 (t, J = 7.1 Hz, 0.07H), 2.66 (t, J = 7.3 Hz, 1.86H)/2.52 – 2.46 (m, 0.14H), 2.44 (s, 0.26H)/ 2.42 (s, 2.73H), 2.19 (q, J = 7.3 Hz, 1.84H)/2.11 (q, 7.4 Hz, 0.24H), 2.01 – 1.90 (m, 4H), 1.55 – 1.42 (m, 4H), 1.42 – 1.33 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.3, 144.1, 143.3, 136.3, 135.6, 129.6, 129.5, 128.4, 128.2, 126.5, 118.7, 36.9, 28.6, 28.3, 27.6, 27.4, 26.7, 23.6, 21.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3205, 2928, 1599, 1448, 1399, 1331, 1161, 929, 674; **HRMS** (ESI) Calculated for $C_{23}H_{28}N_2O_2NaS$ $[M + Na]^+$ 419.1764, found 419.1755.

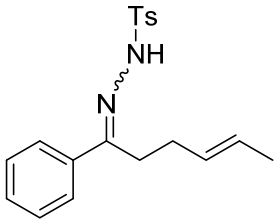


4-Methyl-*N'*-(1-phenyl-4-(tetrahydro-4H-pyran-4-ylidene)butylidene)benzenesulfonohydrazide (1kb): Prepared via general procedure as a white solid (E/Z = 13:1); m.p. 141-142 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 (s, 0.92H)/7.54 (s, 0.07H), 7.94 (d, J = 8.3 Hz, 1.88H)/7.81 (d, J = 8.3 Hz, 0.12H), 7.68 – 7.59 (m, 1.89H)/7.11 – 7.05 (m, 0.11H), 7.45 – 7.28 (m, 5H)/, 5.11 (t, J = 7.5 Hz,

0.93H)/5.05 (t, *J* = 7.2 Hz, 0.07H), 3.62 (t, *J* = 5.4 Hz, 0.12H)/3.50 (t, *J* = 5.5 Hz, 1.88H), 3.60 – 3.56 (m, 0.12H)/3.43 (t, *J* = 5.5 Hz, 1.88H), 2.68 (t, *J* = 7.4 Hz, 1.88H)/2.57 – 2.47 (m, 0.12H), 2.43 (s, 0.23H)/2.41 (s, 2.77H), 2.23 (q, *J* = 7.4 Hz, 1.88H)/2.18 – 2.13 (m, 0.12H), 2.14 – 1.96 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.7, 144.2, 137.0, 136.4, 135.5, 129.64, 129.62, 128.4, 128.1, 126.5, 120.6, 69.2, 68.4, 36.7, 29.5, 26.8, 23.3, 21.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3238, 2974, 1593, 1446, 1377, 1332, 1169, 898, 669; **HRMS** (ESI) Calculated for $C_{22}H_{26}N_2O_3NaS$ $[M + Na]^+$ 421.1556, found 421.1546.

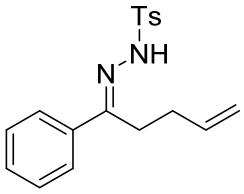


***N'*-(4-Cycloheptylidene-1-phenylbutylidene)-4-methylbenzenesulfonohydrazide (1lb)**: Prepared via general procedure as a white solid (*E*/*Z* = 3:1); m.p. 147-148 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (s, 0.75H)/7.46 (s, 0.25H), 7.96 – 7.88 (m, 1.5H)/7.80 (d, *J* = 8.3 Hz, 0.5H), 7.68 – 7.60 (m, 1.5H)/7.10 – 7.03 (m, 0.5H), 7.44 – 7.29 (m, 5H), 5.04 (t, *J* = 7.4 Hz, 0.75H)/4.97 (t, *J* = 6.9 Hz, 0.25H), 2.66 (t, *J* = 7.5 Hz, 1.5H)/2.50 (dd, *J* = 8.5, 6.7 Hz, 0.5H), 2.44 (s, 0.75H)/2.41 (s, 2.25H), 2.21 – 2.08 (m, 6H), 1.54 – 1.38 (m, 8H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.2/156.2, 144.6/144.0, 144.1/142.3, 136.4/135.4, 135.5/132.9, 129.8/129.6, 128.4, 128.2/128.0, 126.8/126.5, 123.0/122.2, 38.2/37.7, 30.0/29.9, 30.0/29.8, 29.3/29.1, 29.1/28.9, 27.03/26.96, 26.9, 24.2/24.1, 21.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2909, 2928, 1593, 1708, 1440, 1394, 1342, 1156, 934, 669; **HRMS** (ESI) Calculated for $C_{24}H_{31}N_2O_2S$ $[M + H]^+$ 411.2101, found 411.2097.

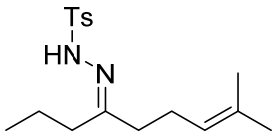


4-Methyl-N'-((E)-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (1mb): Prepared via general procedure as a white solid (*E*/*Z* = 7:1); m.p. 117-118 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (s, 0.87H)/7.49 (s, 0.13H), 7.97 – 7.89 (m,

1.75H)/7.80 (d, *J* = 8.3 Hz, 0.25H), 7.68 – 7.58 (m, 1.75H)/7.09 – 7.02 (m, 0.25H), 7.44 – 7.29 (m, 5H), 5.51 – 5.25 (m, 2H), 2.69 – 2.62 (m, 1.75H)/2.54 – 2.49 (m, 0.25H), 2.43 (s, 0.37H)/2.41 (s, 2.63H), 2.22 – 2.06 (m, 2H), 1.55 (dd, *J* = 6.2, 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.8/155.7, 144.1, 136.4, 135.5, 129.8/129.6, 129.6, 128.7, 128.4, 128.1/128.0, 127.8/126.8, 126.5/125.9, 38.05/28.74, 29.0/27.2, 21.6, 17.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3166, 2977, 2912, 1606, 1443, 1329, 1156, 917, 666; **HRMS** (ESI) Calculated for $C_{19}H_{22}N_2O_2NaS$ $[M + Na]^+$ 365.1294, found 365.1289.

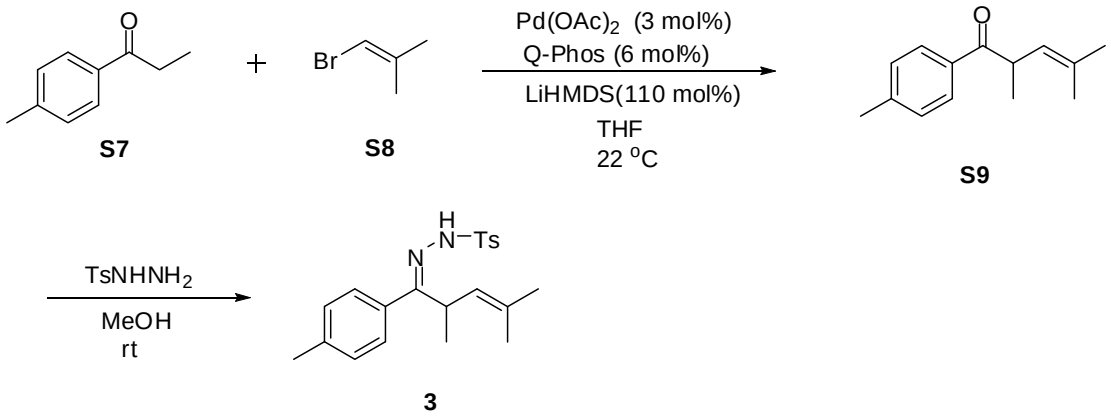


(*E*)-4-Methyl-*N'*-(1-phenylpent-4-en-1-ylidene)benzenesulfonohydrazide (1nb): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); m.p. 110-111 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.68 – 7.58 (m, 2H), 7.41 – 7.29 (m, 5H), 5.70 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H), 5.08 – 4.88 (m, 2H), 2.75 – 2.66 (m, 2H), 2.42 (s, 3H), 2.21 (dt, *J* = 16.8, 8.4 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.3, 144.2, 136.3, 136.1, 135.4, 129.6, 128.4, 128.1, 126.5, 116.7, 29.8, 26.4, 21.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2902, 2921, 1595, 1452, 1386, 1341, 1168, 916, 661; **HRMS** (ESI) Calculated for $C_{18}H_{20}N_2O_2NaS$ $[M + Na]^+$ 351.1138, found 351.1136.



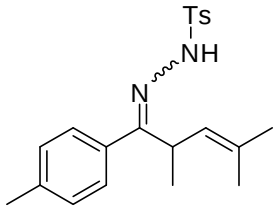
(*E*)-4-methyl-*N'*-(8-methylnon-7-en-4-ylidene)benzenesulfonohydrazide(1ob): Prepared via general procedure as a white solid (*E*/*Z* > 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.99 (t, *J* = 6.5 Hz, 1H), 2.40 (s, 3H), 2.22 – 2.06 (m, 6H), 1.60 (s, 3H), 1.50 (s, 3H), 1.49 – 1.40 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.4, 143.7, 135.6, 133.7, 129.3, 128.0, 122.5, 38.7, 29.6, 25.5, 23.7, 21.5, 19.2, 17.6, 13.5; **FT-IR (thin film, KBr): ν (cm^{-1}):**3219, 2960, 1459, 1384, 1341, 1167, 932, 652; **HRMS** (CI) $[M + H]^+$ Calculated for $C_{17}H_{27}N_2O_2S$ 323.1788, found 323.1786.

3.3 Preparation of compound 3



1) To a stirred solution of 4-methylpropiophenone **S7** (1.48 g, 10 mmol) in THF (20 mL), LiHMDS (8.5 ml, 1.3 M in THF) was added to prepare ketone enolate. In another dry two-necked bottle containing **S8** (1.5 mL, 15 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol) and Q-Phos (426 mg, 0.6 mmol), ketone enolate was added in 22 ºC. The reaction mixture stirred 45 min. The reaction mixture was quenched by Saturated ammonium chloride, then extracted with EtOAc (100 mL × 3). The combined organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **S9**. [5]

2) To a stirred solution of **S9** (1.0 equiv.) in MeOH (10 mL), $TsNHNH_2$ (1.5 equiv.) was added at 0 ºC. The mixture was stirred at the same temperature until the reaction was completed, monitored by TLC. Then, the solvent was removed and the residue was purified by flash column chromatography to give compound **3** as a colorless liquid (*E*/*Z* = 3.5:1). [4]



***N'*-(2,4-Dimethyl-1-(p-tolyl)pent-3-en-1-ylidene)-4-methylbenzenesulfono hydrazide (3)**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (s, 0.22H)/7.19 (s, 0.78H), 7.80 (d, *J* = 8.3 Hz, 0.44H)/7.75 (d, *J* = 8.3 Hz, 1.56H), 7.48 (d, *J* = 8.2 Hz, 0.44H)/6.80 (d, *J* = 8.0 Hz, 1.56H), 7.34 – 7.27 (m, 2H), 7.17 (d, *J* = 4.5 Hz, 1.56H)/7.13 (d, *J* = 8.1 Hz, 0.44H), 5.25 (d, *J* = 4.9 Hz, 0.22H)/4.89 – 4.81 (m, 0.78H), 3.88 – 3.76 (m,

0.22H)/3.44 (tt, *J* = 13.8, 6.9 Hz, 0.78H), 2.43 (s, 2.34H)/2.39 (s, 0.66H), 2.35 (s, 2.34H)/ 2.33 (s, 0.66H), 1.66 (s, 0.66H)/1.59 (s, 2.34H), 1.34 (s, 2.34H)/1.04 (s, 0.66H), 1.28 (d, *J* = 7.5 Hz, 0.66H)/1.07 (d, *J* = 6.9 Hz, 2.34H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.7/157.0, 143.9/143.8, 139.5/139.3, 139.0/135.5, 134.5/133.5, 129.9/129.2, 129.4/129.3, 129.0, 128.0/127.9, 127.1/126.7, 125.5/123.0, 41.0/34.5, 25.6/25.5, 21.6/21.6, 21.3/21.2, 19.0/18.6, 17.8/17.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 3208, 2918, 1677, 1595,1396, 1341, 1161, 818, 671; **HRMS** (ESI) Calculated for $C_{21}H_{26}N_2O_2NaS$ $[M + Na]^+$ 393.1607, found 393.1605.

Reference

(1) X. Yu, X. Li, B. Wan, *Org. Biomol. Chem.* **2012**, *10*, 7479.

(2) Q. Wang, W. Huang, H. Yuan, Q. Cai, L. Chen, H. Lv, X. Zhang, *J. Am. Chem. Soc*. **2014**, *136*, 16120.

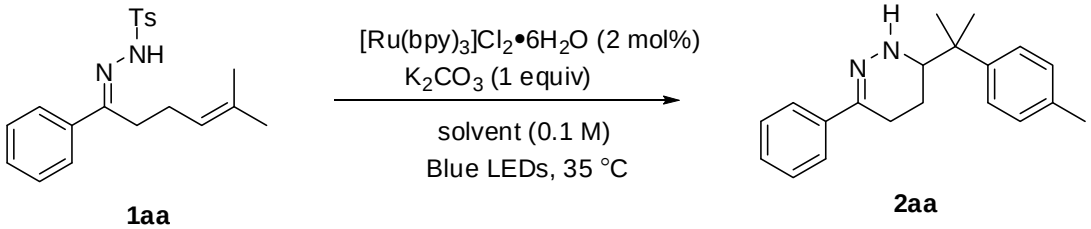
(3) J. Davies, N. S. Sheikh, D. Leonori, *Angew. Chem., Int. Ed*. **2017**, *56*, 13361.

(4) X-Q. Hu, J-R. Chen, Q. Wei, F-L. Liu, Q-H. Deng, A. M. Beauchemin, W-J. Xiao. *Angew. Chem., Int. Ed*. **2014**, *53*, 12163.

(5) M. Grigalunas, T. Ankner, P. O. Norrby, O. Wiest, P. Helquist, *Org. Lett.* **2014**, *16*, 3970.

4. Optimization of the reaction conditions

Table S1. Screening of solvents.



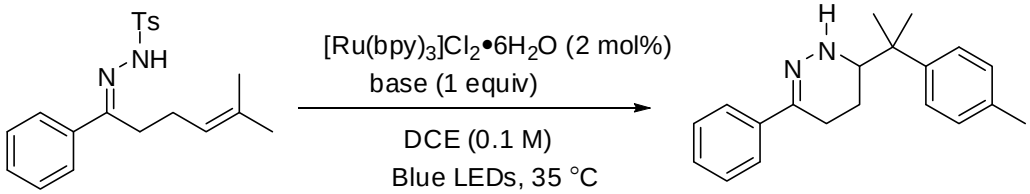
1aa **2aa**

entry	solvent	base (1.0 equiv.)	yield (%)[a]
1	DCM	K_2CO_3	65

2	HFIP	K_2CO_3	< 5
3	Toluene	K_2CO_3	10
4	$CHCl_3$	K_2CO_3	45
5	DMSO	K_2CO_3	43
6	1,4-Dioxane	K_2CO_3	52
7	**DCE**	**K_2CO_3**	**72**
8	THF	K_2CO_3	46
9	DMF	K_2CO_3	37
10	CH_3CN	K_2CO_3	22
11	CH_3CH_2OH	K_2CO_3	42

[a]Isolated yield.

Table S2. Screening of bases.

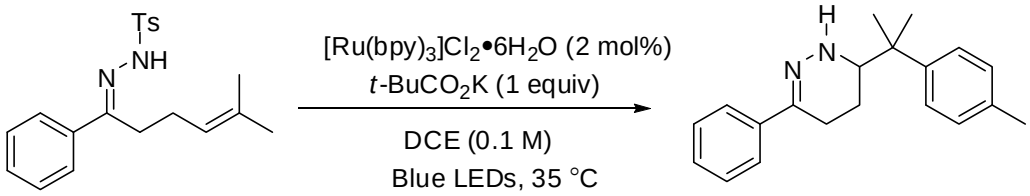


1aa **2aa**

entry	solvent	base (1.0 equiv.)	yield (%)[a]
1	DCE	Na_2CO_3	68
2	DCE	Li_2CO_3	38
3	DCE	Cs_2CO_3	41
4	DCE	K_3PO_4	53
5	DCE	KOH	< 5
6	DCE	*t*-BuOK	34
7	**DCE**	***t*-$BuCO_2K$**	**85**
8	DCE	CH_3CO_2K	65
9	DCE	$PhCO_2K$	78
10	DCE	KF	42

[a]Isolated yield.

Table S3. Control experiments

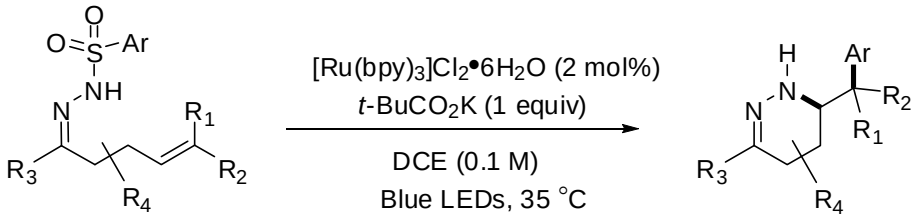


1aa **2aa**

entry	base	photocatalyst	yield (%)[a]
1	–	$[Ru(bpy)_3]Cl_2•6H_2O$	< 5
2	*t*-$BuCO_2K$	–	0
3[b]	*t*-$BuCO_2K$	$[Ru(bpy)_3]Cl_2•6H_2O$	82
4[c]	*t*-$BuCO_2K$	$[Ru(bpy)_3]Cl_2•6H_2O$	75
5[d]	*t*-$BuCO_2K$	$[Ru(bpy)_3]Cl_2•6H_2O$	< 5

[a]Isolated yield. [b]25 °C. [c]55 °C. [d]In the dark.

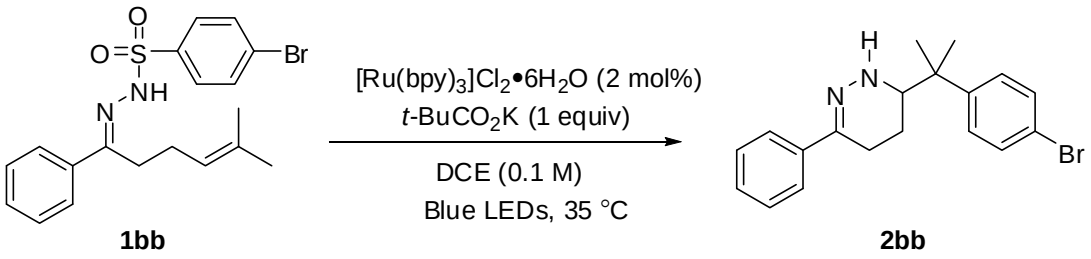
5. General procedures for synthesis of 1,4,5,6-tetrahydropyridazines



1 **2**

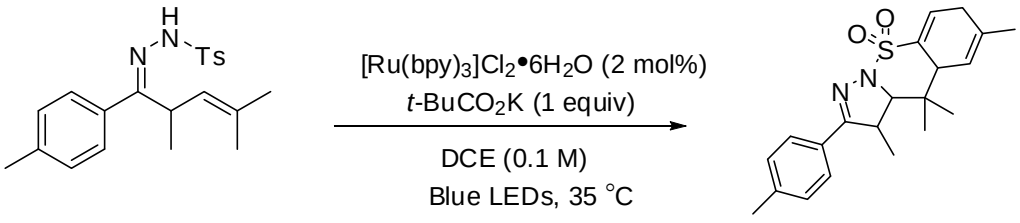
General procedure: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar, the hydrazone compound (0.2 mmol, 1.0 equiv.), $[Ru(bpy)_3]Cl_2•6H_2O$ (3.0 mg, 0.004 mmol, 2 mol%), and potassium pivalate (28 mg, 0.2 mmol, 1.0 equiv.) was added. The resulting mixture was sealed and DCE (2 mL) 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 35 °C 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.



1bb **2bb**

Gram-scale synthesis of compound 2bb: To a 100 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, **1bb** (0.84 g, 2 mmol), $[Ru(bpy)_3]Cl_2•6H_2O$ (30 mg, 0.04 mmol), and potassium pivalate (280 mg, 2 mmol) was added. The resulting mixture was sealed and DCE (20 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 35 ℃ 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 =10:1 to give **2bb** in 74% yield (0.53 g).



3 **4**

Radical cascade reaction of compound 3: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stir bar, compound **3** (74 mg, 0.2 mmol, 1.0 equiv.), $[Ru(bpy)_3]Cl_2•6H_2O$ (3.0 mg, 0.004 mmol, 2 mol%), and potassium pivalate (28 mg, 0.2 mmol, 1.0 equiv.) was added. The resulting mixture was sealed and DCE (2 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 35 ℃ 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 =10:1 to give **4** in 56% yield (41 mg).

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 $[Ru(bpy)_3]Cl_2 \bullet 6H_2O$ solutions were excited at 450 nm and the emission intensity was collected at 540-660 nm. In a typical experiment, the CH_3CN solution of $[Ru(bpy)_3]Cl_2 \bullet 6H_2O$ (0.04 μM) was added the appropriate amount of potassium pivalate and γ,δ-unsaturated hydrazone **1aa** in a screw-top 1.0 cm quartz cuvette. After degassing with argon for 10 min, the emission spectra of the samples were collected.

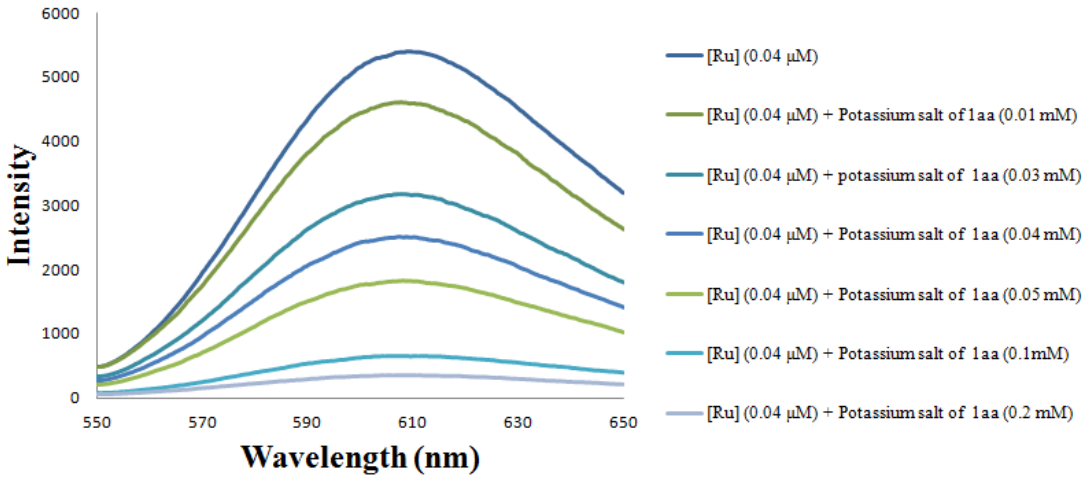


Figure S2. Fluorescence quenching by potassium salt of **1aa**.

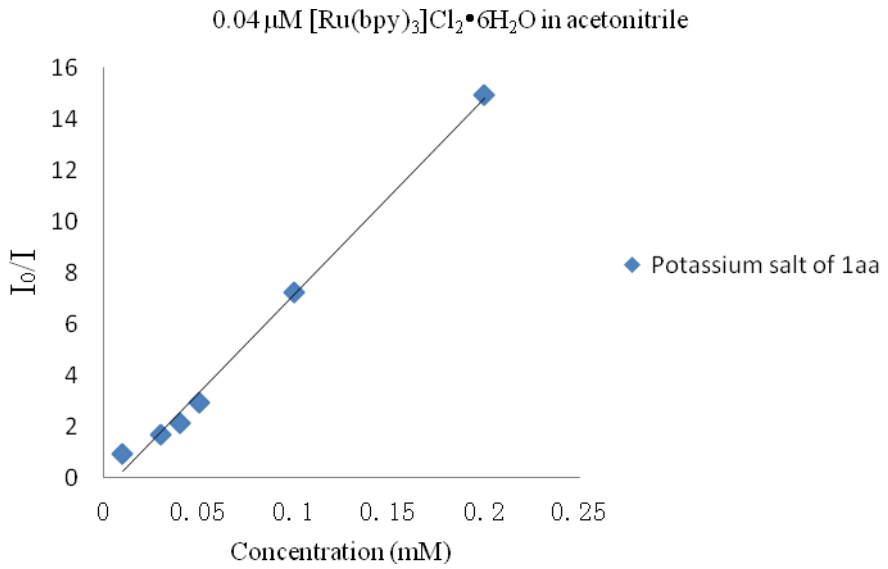
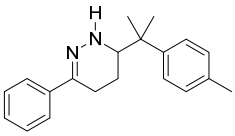
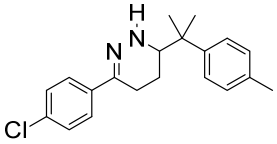


Figure S3. Stern−Volmer fluorescence quenching

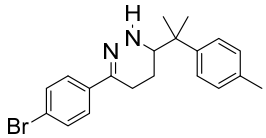
7. Characterization of the products



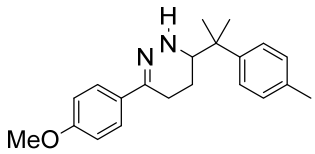
3-Phenyl-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2aa): Followed the general procedure with 4-methyl-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (58 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 50 mg of the title compound (colorless oil; 85% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.33 – 7.26 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.39 (s, 1H), 3.20 (d, *J* = 11.0 Hz, 1H), 2.71 (dd, *J* = 8.6, 4.3 Hz, 2H), 2.39 (s, 3H), 2.19 – 2.04 (m, 1H), 1.96 – 1.77 (m, 1H), 1.45 (s, 3H), 1.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.9, 143.0, 138.5, 135.9, 129.2, 128.2, 127.6, 126.1, 124.3, 60.5, 39.3, 26.0, 24.2, 21.8, 20.9, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2974, 1684, 1448, 1161, 910, 724; **HRMS** (ESI) Calculated for $C_{20}H_{25}N_2$ $[M + H]^+$ 293.2012, found 293.2005.



3-(4-Chlorophenyl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2ba): Followed the general procedure with (*E*)-*N*′-(1-(4-chlorophenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (65 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 47 mg of the title compound (yellow oil; 71% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 – 7.44 (m, 2H), 7.32 – 7.22 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.35 (s, 1H), 3.14 (dd, *J* = 11.2, 2.1 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.33 (s, 3H), 2.11 – 2.00 (m, 1H), 1.88 – 1.72 (m, 1H), 1.38 (s, 3H), 1.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 141.5, 137.0, 136.0, 133.3, 129.3, 128.3, 126.1, 125.4, 60.4, 39.2, 26.0, 24.0, 21.7, 20.8, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 1684, 1589, 1089, 821; **HRMS** (ESI) Calculated for $C_{20}H_{23}{}^{35}ClN_2Na$ $[M + Na]^+$ 349.1442, found 349.1445.

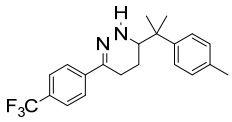


3-(4-Bromophenyl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2ca): Followed the general procedure with (*E*)-*N*′-(1-(4-bromophenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (87 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 51 mg of the title compound (yellow oil; 72% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.37 (m, 4H), 7.31 – 7.27 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.35 (s, 1H), 3.14 (dd, *J* = 11.2, 2.3 Hz, 1H), 2.60 (dd, *J* = 9.2, 4.8 Hz, 2H), 2.33 (s, 3H), 2.11 – 2.00 (m, 1H), 1.88 – 1.74 (m, 1H), 1.38 (s, 3H), 1.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 141.5, 137.4, 136.0, 131.2, 129.3, 126.1, 125.8, 121.5, 60.4, 39.2, 26.1, 24.0, 21.7, 20.9, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2974, 1681, 1511, 1122, 822, 728; **HRMS** (ESI) Calculated for $C_{20}H_{23}{}^{79}BrN_2Na$ $[M + Na]^+$ 393.0937, found 343.0941.

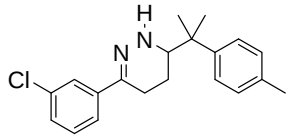


3-(4-Methoxyphenyl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2da): Followed the general procedure with (*E*)-*N*′-(1-(4-methoxyphenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (77 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 50 mg of

the title compound (yellow oil; 78% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.46 (m, 2H), 7.33 – 7.26 (m, 2H), 7.17 – 7.11 (m, 2H), 6.89 – 6.77 (m, 2H), 5.23 (s, 1H), 3.78 (s, 3H), 3.11 (dd, *J* = 11.2, 2.3 Hz, 1H), 2.61 (dt, *J* = 18.1, 9.1 Hz, 2H), 2.10 – 1.95 (m, 1H), 1.90 – 1.69 (m, 1H), 1.38 (s, 3H), 1.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.3, 144.0, 143.2, 135.9, 131.4, 129.2, 126.1, 125.6, 113.5, 60.6, 55.3, 39.3, 26.0, 24.3, 21.8, 21.1, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 1661, 1515, 1436, 1247, 816, 708; **HRMS** (ESI) Calculated for $C_{21}H_{27}N_2O$ $[M + H]^+$ 323.2118, found 323.2114.

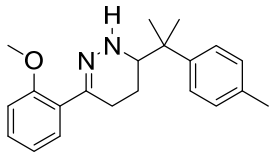


6-(2-(*p*-Tolyl)propan-2-yl)-3-(4-(trifluoromethyl)phenyl)-1,4,5,6-tetrahydropyridazine (2ea): Followed the general procedure with (*E*)-4-methyl-*N*′-(5-methyl-1-(4-(trifluoromethyl)phenyl)hex-4-en-1-ylidene)benzenesulfonohydrazide (84 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 51 mg of the title compound (yellow oil; 71% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.46 (s, 1H), 3.18 (dd, *J* = 11.2, 2.0 Hz, 1H), 2.64 (dd, *J* = 10.0, 5.7 Hz, 2H), 2.34 (s, 3H), 2.14 – 2.02 (m, 1H), 1.89 – 1.75 (m, 1H), 1.40 (s, 3H), 1.37 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.7, 141.8, 140.7, 136.1, 129.3, 129.1 (q, *J* = 32.2 Hz), 126.1, 125.1 (q, *J* = 3.9 Hz), 124.2, 124.3 (q, *J* = 271.6 Hz), 60.4, 39.2, 26.1, 24.0, 21.6, 20.9, 20.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 1678, 1599, 1449, 1123, 816, 734; **HRMS** (ESI) Calculated for $C_{21}H_{24}F_3N_2$ $[M + H]^+$ 361.1886, found 361.1888.

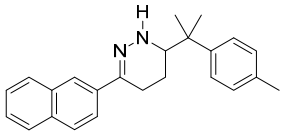


3-(3-Chlorophenyl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2fa): Followed the general procedure with (*E*)-*N*′-(1-(3-chlorophenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (65 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 48 mg of the title compound (yellow oil; 73% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (s, 1H), 7.43 (s, 1H), 7.28 (d, *J* = 6.6 Hz, 2H), 7.22 – 7.12 (m, 4H), 5.38 (s, 1H), 3.14 (d, *J* = 10.6 Hz, 1H), 2.65 – 2.52 (m, 2H), 2.33 (s, 3H), 2.12 – 1.96 (m, 1H), 1.88 – 1.73 (m, 1H),

1.38 (s, 3H), 1.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 141.1, 140.4, 136.04134.3, 129.4, 129.3, 127.4, 126.1, 124.4, 122.2, 60.5, 39.2, 26.1, 24.0, 21.7, 20.9, 20.8; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.8, 141.1, 140.4, 136.0, 134.3, 129.4, 129.3, 127.4, 126.1, 124.4, 122.2, 60.5, 39.2, 26.1, 24.0, 21.7, 20.9, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2974, 1684, 1599, 1446, 1280, 761, 702; **HRMS** (ESI) Calculated for $C_{20}H_{23}{}^{35}ClN_2Na$ $[M + Na]^+$ 349.1442, found 349.1444.

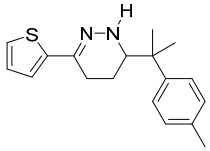


3-(2-Methoxyphenyl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2ga): Followed the general procedure with *N*′-(1-(2-methoxyphenyl)-5-methylhex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (77 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 26 mg of the title compound (yellow oil; 40% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.26 (m, 3H), 7.26 – 7.19 (m, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.98 – 6.81 (m, 2H), 5.32 (s, 1H), 3.79 (s, 3H), 3.16 (d, *J* = 10.7 Hz, 1H), 2.81 (ddd, *J* = 18.8, 10.9, 8.3 Hz, 1H), 2.49 (dd, *J* = 18.4, 5.8 Hz, 1H), 2.31 (s, 3H), 2.00 – 1.84 (m, 1H), 1.82 – 1.69 (m, 1H), 1.36 (s, 3H), 1.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.2, 146.7, 144.1, 135.8, 129.2, 129.1, 128.9, 126.2, 120.7, 111.0, 60.7, 55.4, 39.4, 27.4, 25.8, 22.1, 21.3, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2974, 1678, 1599, 1453, 1244, 911, 695; **HRMS** (ESI) Calculated for $C_{21}H_{27}N_2O$ $[M + H]^+$ 323.2118, found 323.2122.

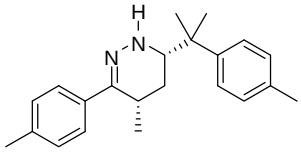


3-(Naphthalen-2-yl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2ha): Followed the general procedure with (*E*)-4-methyl-*N*′-(5-methyl-1-(naphthalen-2-yl)hex-4-en-1-ylidene)benzenesulfonohydrazide (81 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 52 mg of the title compound (yellow oil; 76% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.86 (s, 1H), 7.83 – 7.77 (m, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.11 (m, 1H), 5.43 (s, 1H), 3.21 (dd, *J* = 11.1, 1.5 Hz, 1H), 2.89 – 2.71 (m, 2H), 2.35 (s, 3H), 2.17 – 2.07 (m, 1H), 1.94 – 1.80 (m, 1H), 1.41 (d, *J* = 12.5 Hz, 6H); **^{13}C**

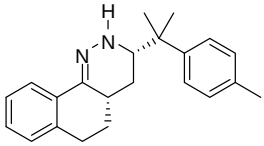
NMR (100 MHz, $CDCl_3$) δ 143.9, 142.6, 136.0, 136.0, 133.4, 133.0, 129.2, 128.2, 127.7, 127.6, 126.1, 126.0, 125.7, 123.0, 122.7, 60.6, 39.3, 26.1, 24.1, 21.8, 20.9, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 1681, 1603, 1508, 1123, 904, 816, 728; **HRMS** (ESI) Calculated for $C_{24}H_{27}N_2$ $[M + H]^+$ 343.2169, found 343.2164.



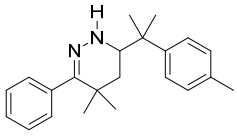
3-(Thiophen-2-yl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2ia): Followed the general procedure with (*E*)-4-methyl-*N*′-(5-methyl-1-(thiophen-2-yl)hex-4-en-1-ylidene)benzenesulfonohydrazide (72 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 55 mg of the title compound (yellow oil; 92% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.18 – 7.11 (m, 3H), 7.00 – 6.91 (m, 2H), 5.23 (s, 1H), 3.13 (dd, *J* = 11.2, 1.9 Hz, 1H), 2.78 – 2.53 (m, 2H), 2.33 (s, 3H), 2.07 – 1.98 (m, 1H), 1.87 – 1.74 (m, 1H), 1.38 (s, 3H), 1.36 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.4, 143.7, 140.2, 136.0, 129.2, 126.9, 126.0, 124.8, 122.5, 60.7, 39.2, 25.9, 24.5, 21.7, 20.8, 20.6; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2977, 1666, 1511, 1440, 1413, 819, 708; **HRMS** (ESI) Calculated for $C_{18}H_{23}N_2S$ $[M + H]^+$ 299.1576, found 299.1573.



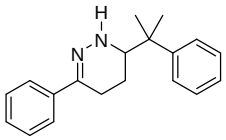
4-Methyl-3-(p-tolyl)-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2ja): Followed the general procedure with (*E*)-*N*′-(2,5-dimethyl-1-(p-tolyl)hex-4-en-1-ylidene)-4-methylbenzenesulfonohydrazide (77 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 38 mg of the title compound (yellow oil; the major isomer; 59% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.33 (s, 1H), 3.22 (dd, *J* = 11.6, 2.5 Hz, 1H), 3.12 – 2.98 (m, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.83 (td, *J* = 12.1, 5.9 Hz, 1H), 1.76 – 1.66 (m, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.18 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.2, 144.0, 137.0, 135.9, 135.2, 129.2, 128.9, 126.1, 124.9, 55.8, 39.0, 27.7, 26.9, 25.9, 22.1, 21.9, 21.1, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 1688, 1590, 1440, 1449, 911, 699; **HRMS** (ESI) Calculated for $C_{22}H_{29}N_2$ $[M + H]^+$ 321.2325, found 321.2329.



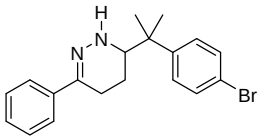
3-(2-(*p*-Tolyl)propan-2-yl)-2,3,4,4a,5,6-hexahydrobenzo[*h*]cinnoline (2ka): Followed the general procedure with (*E*)-4-methyl-*N*′-(2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-ylidene)benzenesulfonohydrazide (76 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 49 mg of the title compound (yellow oil; the major isomer; 76% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 – 7.78 (m, 1H), 7.33 – 7.27 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.11 – 7.05 (m, 1H), 5.22 (s, 1H), 3.36 (dd, *J* = 11.3, 1.9 Hz, 1H), 2.94 – 2.78 (m, 2H), 2.57 – 2.43 (m, 1H), 2.35 (s, 3H), 2.12 – 1.99 (m, 2H), 1.64 – 1.45 (m, 2H), 1.39 (s, 3H), 1.39 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.9, 142.4, 137.0, 135.9, 133.2, 129.2, 128.8, 127.2, 126.1, 126.1, 123.3, 61.1, 39.3, 35.3, 29.8, 29.6, 28.4, 25.8, 21.9, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 1687, 1590, 1484, 1393, 1011, 737; **HRMS** (ESI) Calculated for $C_{22}H_{27}N_2$ $[M + H]^+$ 319.2169, found 319.2166.



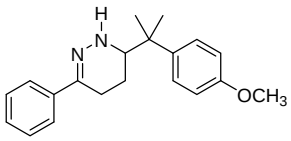
4,4-Dimethyl-3-phenyl-6-(2-(p-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2la): Followed the general procedure with (*E*)-4-methyl-*N*′-(2,2,5-trimethyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (77 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 35 mg of the title compound (yellow oil; 55% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.23 (m, 7H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.32 (s, 1H), 3.27 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 3H), 1.73 – 1.58 (m, 2H), 1.38 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.05 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.7, 143.9, 139.1, 135.9, 129.2, 128.4, 127.7, 127.2, 126.1, 58.4, 39.0, 38.2 34.4, 30.4, 28.4, 25.6, 22.1, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2931, 1684, 1590, 1448, 913, 733; **HRMS** (ESI) Calculated for $C_{22}H_{29}N_2$ $[M + H]^+$ 321.2325, found 321.2330.



3-Phenyl-6-(2-phenylpropan-2-yl)-1,4,5,6-tetrahydropyridazine (2ab): Followed the general procedure with (*E*)-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (68 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 46 mg of the title compound (yellow oil; 82% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.54 (m, 2H), 7.45 – 7.38 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 5.32 (s, 1H), 3.18 (dd, *J* = 11.2, 2.3 Hz, 1H), 2.66 (dd, *J* = 9.3, 4.9 Hz, 2H), 2.11 – 2.00 (m, 1H), 1.91 – 1.75 (m, 1H), 1.41 (s, 3H), 1.38 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.0, 143.1, 138.5, 128.6, 128.2, 127.6, 126.5, 126.2, 124.2, 60.5, 39.6, 26.0, 24.2, 21.7, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2980, 1684, 1599, 1449, 1280, 761, 695; **HRMS** (ESI) Calculated for $C_{19}H_{23}N_2$ $[M + H]^+$ 279.1856, found 279.1850.

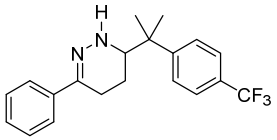


6-(2-(4-Bromophenyl)propan-2-yl)-3-phenyl-1,4,5,6-tetrahydropyridazine (2bb): Followed the general procedure with 4-bromo-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (84 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 67 mg of the title compound (yellow oil; 70% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.53 (m, 2H), 7.52 – 7.41 (m, 2H), 7.33 – 7.20 (m, 5H), 5.29 (s, *J* = 4.9 Hz, 1H), 3.13 (dd, *J* = 11.2, 2.3 Hz, 1H), 2.71 – 2.57 (m, 2H), 2.09 – 1.96 (m, 1H), 1.90 – 1.70 (m, 1H), 1.39 (s, 3H), 1.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.0, 143.3, 138.3, 131.6, 128.2, 128.1, 127.8, 124.3, 120.4, 60.3, 39.6, 25.7, 24.1, 22.0, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2974, 1687, 1592, 1488, 1089, 812; **HRMS** (ESI) Calculated for $C_{19}H_{22}{}^{79}BrN_2$ $[M + H]^+$ 357.0961, found 357.0955.

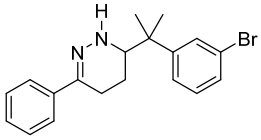


6-(2-(4-Methoxyphenyl)propan-2-yl)-3-phenyl-1,4,5,6-tetrahydropyridazine (2cb): Followed the general procedure with 4-methoxy-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (74 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 51 mg of the title compound

(yellow oil; 82% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 7.55 (m, 2H), 7.35 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 6.91 – 6.84 (m, 2H), 5.35 (s, 1H), 3.80 (s, 3H), 3.12 (dd, *J* = 11.2, 2.2 Hz, 1H), 2.65 (dd, *J* = 9.1, 4.7 Hz, 2H), 2.10 – 2.01 (m, 1H), 1.86 – 1.73 (m, 1H), 1.39 (s, 3H), 1.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.0, 143.1, 139.0, 138.5, 128.2, 127.6, 127.3, 124.2, 113.9, 60.6, 55.3, 39.0, 26.1, 24.2, 21.9, 21.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2970, 1690, 1615, 1511, 1243, 1030, 822, 727; **HRMS** (ESI) Calculated for $C_{20}H_{25}N_2O$ $[M + H]^+$ 309.1961, found 309.1952.

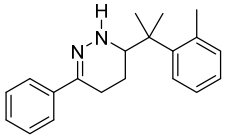


3-Phenyl-6-(2-(4-(trifluoromethyl)phenyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2db): Followed the general procedure with *N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)-4-(trifluoromethyl)benzenesulfonohydrazide (82 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 52 mg of the title compound (yellow oil; 75% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.48 (m, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.20 – 7.15 (m, 1H), 5.18 (s, 1H), 3.12 (dd, *J* = 11.2, 2.2 Hz, 1H), 2.64 – 2.53 (m, 2H), 2.02 – 1.90 (m, 1H), 1.79 – 1.67 (m, 1H), 1.37 (s, 3H), 1.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.2, 143.5, 138.3, 128.8 (q, *J* = 32.6 Hz), 128.2, 127.8, 126.7, 125.4 (q, *J* = 3.8 Hz), 124.3, 124.2 (q, *J* = 271.8 Hz), 60.3, 40.1, 25.7, 24.1, 22.0, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2980, 1684, 1622, 1409, 1331, 1112, 838, 694; **HRMS** (ESI) Calculated for $C_{20}H_{22}F_3N_2$ $[M + H]^+$ 347.1730, found 347.1726.

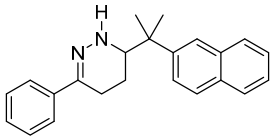


6-(2-(3-Bromophenyl)propan-2-yl)-3-phenyl-1,4,5,6-tetrahydropyridazine (2eb): Followed the general procedure with (*E*)-3-bromo-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (84 mg, 0.24 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 47 mg of the title compound (yellow oil; 66% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.56 (m, 2H), 7.54 (t, *J* = 1.9 Hz, 1H), 7.38 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.27 – 7.19 (m, 2H), 5.30 (s, 1H), 3.15 (dd, *J* = 11.2, 2.4 Hz, 1H), 2.66 (dd, *J* = 9.1, 4.7 Hz, 2H),

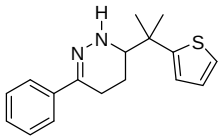
2.07 – 1.99 (m, 1H), 1.86 – 1.74 (m, 1H), 1.39 (s, 3H), 1.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.6, 143.3, 138.3, 130.1, 129.63, 129.58, 128.2, 127.8, 125.0, 124.3, 123.0, 60.3, 39.9, 25.8, 24.1, 21.8, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2977, 1691, 1590, 1449, 1159, 699; **HRMS** (ESI) Calculated for $C_{19}H_{22}{}^{79}BrN_2$ $[M + H]^+$ 357.0961, found 357.0967.



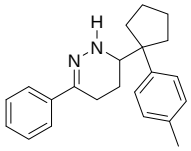
3-Phenyl-6-(2-(o-tolyl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2fb): Followed the general procedure with (*E*)-2-methyl-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (72 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 32 mg of the title compound (yellow oil; 55% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 – 7.57 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.12 (m, 4H), 5.23 (s, 1H), 3.57 (dd, *J* = 11.1, 2.1 Hz, 1H), 2.73 – 2.65 (m, 2H), 2.54 (s, 3H), 2.11 – 2.00 (m, 1H), 1.96 – 1.83 (m, 1H), 1.52 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.0, 142.8, 138.5, 136.3, 133.5, 128.2, 128.1, 127.6, 126.8, 126.1, 124.2, 57.2, 41.3, 25.5, 24.5, 24.4, 23.9, 21.1; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 1687, 1595, 1455, 1014, 910, 759; **HRMS** (ESI) Calculated for $C_{20}H_{25}N_2$ $[M + H]^+$ 293.2012, found 293.2005.



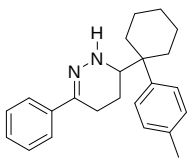
6-(2-(Naphthalen-2-yl)propan-2-yl)-3-phenyl-1,4,5,6-tetrahydropyridazine (2gb): Followed the general procedure with (*E*)-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)naphthalene-2-sulfonohydrazide (78 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 15 mg of the title compound (yellow oil; 23% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.77 (m, 4H), 7.60 – 7.53 (m, 3H), 7.52 – 7.43 (m, 2H), 7.33 – 7.19 (m, 3H), 5.35 (s, 1H), 3.30 (dd, *J* = 11.2, 2.2 Hz, 1H), 2.67 (dd, *J* = 9.1, 4.7 Hz, 2H), 2.13 – 2.04 (m, 1H), 1.92 – 1.79 (m, 1H), 1.53 (s, 3H), 1.47 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.3, 143.0, 138.4, 133.3, 132.1, 128.3, 128.2, 128.1, 127.6, 127.4, 126.2, 125.8, 125.0, 124.4, 124.2, 60.1, 39.8, 25.9, 24.2, 21.9, 21.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2964, 1684, 1599, 1452, 1158, 818, 697; **HRMS (ESI)** Calculated for $C_{23}H_{25}N_2$ $[M + H]^+$ 329.2012, found 329.2017.



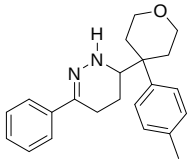
3-Phenyl-6-(2-(thiophen-2-yl)propan-2-yl)-1,4,5,6-tetrahydropyridazine (2hb): Followed the general procedure with (*E*)-*N*′-(5-methyl-1-phenylhex-4-en-1-ylidene)thiophene-2-sulfonohydrazide (70 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 42 mg of the title compound (yellow oil; 74% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.57 (m, 2H), 7.34 – 7.18 (m, 4H), 6.99 – 6.92 (m, 2H), 5.53 (s, 1H), 3.12 (dd, *J* = 11.2, 2.4 Hz, 1H), 2.71 – 2.59 (m, 2H), 2.07 (tdd, *J* = 5.8, 4.2, 2.6 Hz, 1H), 1.89 – 1.73 (m, 1H), 1.46 (s, 3H), 1.44 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.8, 143.1, 138.4, 128.2, 127.7, 126.6, 124.3, 123.8, 123.6, 61.1, 39.6, 27.6, 24.0, 23.2, 21.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 1677, 1592, 1452, 825, 697; **HRMS** (ESI) Calculated for $C_{17}H_{21}N_2S$ $[M + H]^+$ 285.1420, found 285.1414.



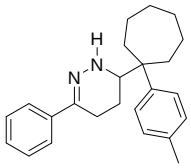
3-Phenyl-6-(1-(p-tolyl)cyclopentyl)-1,4,5,6-tetrahydropyridazine (2ib): Followed the general procedure with *N*′-(4-cyclopentylidene-1-phenylbutylidene)-4-methylbenzenesulfonohydrazide (76 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 39 mg of the title compound (yellow oil; 61% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.18 (m, 5H), 7.12 (d, *J* = 7.6 Hz, 2H), 5.57 (s, 1H), 3.15 (d, *J* = 11.0 Hz, 1H), 2.63 – 2.48 (m, 2H), 2.30 (s, 3H), 2.22 – 1.84 (m, 6H), 1.64 – 1.49 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.1, 141.9, 138.5, 135.8, 128.9, 128.2, 127.6, 127.4, 124.2, 59.7, 53.0, 35.1, 33.1, 24.1, 24.0, 23.8, 22.0, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2954, 1687, 1517, 1452, 910, 733; **HRMS** (ESI) Calculated for $C_{22}H_{26}N_2Na$ $[M + Na]^+$ 341.1988, found 341.1986.



3-Phenyl-6-(1-(p-tolyl)cyclohexyl)-1,4,5,6-tetrahydropyridazine (2jb): Followed the general procedure with *N′*-(4-cyclohexylidene-1-phenylbutylidene)-4-methylbenzenesulfonohydrazide (79 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 42 mg of the title compound (yellow oil; 63% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.52 (m, 2H), 7.32 – 7.26 (m, 4H), 7.23 (dt, *J* = 4.9, 2.0 Hz, 1H), 7.19 (t, *J* = 6.5 Hz, 2H), 5.47 (s, 1H), 2.89 (dd, *J* = 11.2, 2.0 Hz, 1H), 2.60 (dd, *J* = 9.1, 4.8 Hz, 2H), 2.47 – 2.37 (m, 1H), 2.35 (s, 3H), 2.28 – 2.18 (m, 1H), 2.14 – 2.01 (m, 1H), 1.83 – 1.68 (m, 2H), 1.68 – 1.53 (m, 4H), 1.50 – 1.39 (m, 1H), 1.35 – 1.21 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.1, 139.2, 138.5, 135.6, 129.3, 128.1, 127.9, 127.5, 124.2, 61.6, 43.9, 32.4, 29.8, 26.9, 24.3, 22.1, 22.0, 20.9, 20.8; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2931, 1684, 1448, 910, 730; **HRMS** (ESI) $[M + H]^+$ Calculated for $C_{23}H_{29}N_2$ 333.2325, found 333.2324.

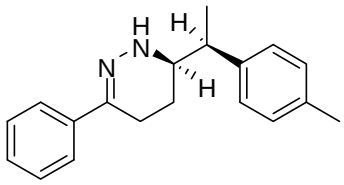


3-Phenyl-6-(4-(p-tolyl)tetrahydro-2H-pyran-4-yl)-1,4,5,6-tetrahydropyridazine (2kb): Followed the general procedure with 4-methyl-*N′*-(1-phenyl-4-(tetrahydro-4H-pyran-4-ylidene)butylidene)benzenesulfonohydrazide (80 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 43 mg of the title compound (yellow oil; 64% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.16 (m, 7H), 5.41 (s, 1H), 3.92 – 3.76 (m, 2H), 3.57 (t, *J* = 11.6 Hz, 1H), 3.45 – 3.26 (m, 1H), 2.97 (d, *J* = 10.9 Hz, 1H), 2.62 (dd, *J* = 8.5, 4.4 Hz, 2H), 2.35 (s, 3H), 2.33 (d, *J* =10.9 Hz, 1H), 2.20 – 2.03 (m, 3H), 1.97 (td, *J* = 14.0, 4.1 Hz, 1H), 1.83 – 1.69 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.4, 138.3, 137.5, 136.4, 129.7, 128.2, 127.9, 127.7, 124.3, 64.4, 64.1, 61.0, 42.2, 32.7, 29.9, 24.1, 20.9, 20.7; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2954, 2863, 1684, 1599, 1453, 1022, 734; **HRMS** (ESI) Calculated for $C_{22}H_{26}N_2ONa$ $[M + H]^+$ 335.2118, found 335.2111.

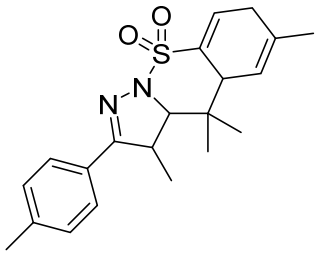


3-Phenyl-6-(1-(p-tolyl)cycloheptyl)-1,4,5,6-tetrahydropyridazine (2lb): Followed the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid

(34 mg, 0.2 mmol) and 4-vinylbenzyl 2-(1,3-dioxoisoindolin-2-yl)acetate (82 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 26 mg of the title compound (yellow oil; 38% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.28 (m, 5H), 7.23 (d, *J* = 7.6 Hz, 2H), 5.43 (s, 1H), 3.10 – 3.00 (m, 1H), 2.75 – 2.63 (m, 2H), 2.46 (d, *J* = 9.4 Hz, 1H), 2.41 (s, 3H), 2.23 – 2.16 (m, 1H), 2.16 – 2.06 (m, 2H), 1.97 – 1.47 (m, 10H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.1, 142.6, 138.5, 135.6, 129.1, 128.1, 127.6, 127.4, 124.2, 63.5, 46.6, 35.2, 32.2, 29.6, 29.3, 24.4, 24.1, 23.7, 21.0, 20.9; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2974, 1680, 1517, 1452, 815, 701; **HRMS (ESI)** Calculated for $C_{24}H_{31}N_2$ $[M + H]^+$ 347.2482, found 347.2478.



3-Phenyl-6-(1-(p-tolyl)ethyl)-1,4,5,6-tetrahydropyridazine (2mb): Followed the general procedure with 4-methyl-N'-((E)-1-phenylhex-4-en-1-ylidene)benzenesulfonohydrazide (68 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) to give 24 mg of the title compound (yellow oil; 43% yield); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 5.7 Hz, 1H), 7.16 – 7.10 (m, 4H), 5.34 (s, 1H), 3.04 (t, *J* = 9.6 Hz, 1H), 2.69 – 2.60 (m, 3H), 2.32 (s, 3H), 2.30 – 2.25 (m, 1H), 1.86 – 1.73 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.3, 140.5, 138.6, 136.5, 129.5, 128.2, 127.7, 127.5, 124.3, 56.5, 43.0, 24.0, 23.0, 21.0, 18.0; **FT-IR** (thin film, KBr): ν (cm^{-1}) 2967, 1684, 1599, 1445, 1357, 1145, 759; **HRMS (ESI)** Calculated for $C_{19}H_{23}N_2$ $[M + H]^+$ 279.1856, found 279.1855.

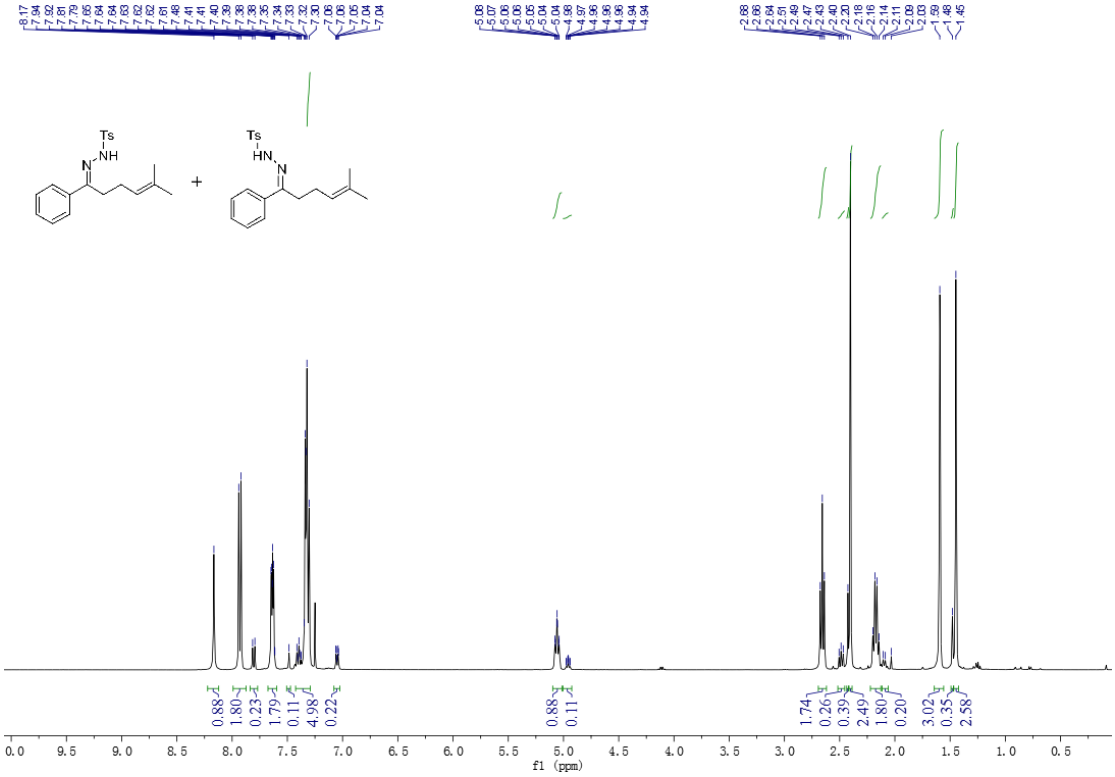


3,4,4,6-Tetramethyl-2-(*p*-tolyl)-3a,4,4a,7-tetrahydro-*3H*-benzo[e]pyrazolo[*1,5-b*][*1,2*]thiazine 9,9-dioxide (4): white solid; m.p. 113-114 ℃; 56% yield (41 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 3.2 Hz, 1H), 5.44 (d, *J* = 1.4 Hz, 1H), 3.96 (d, *J* = 3.2 Hz, 1H), 3.57 – 3.37 (m,

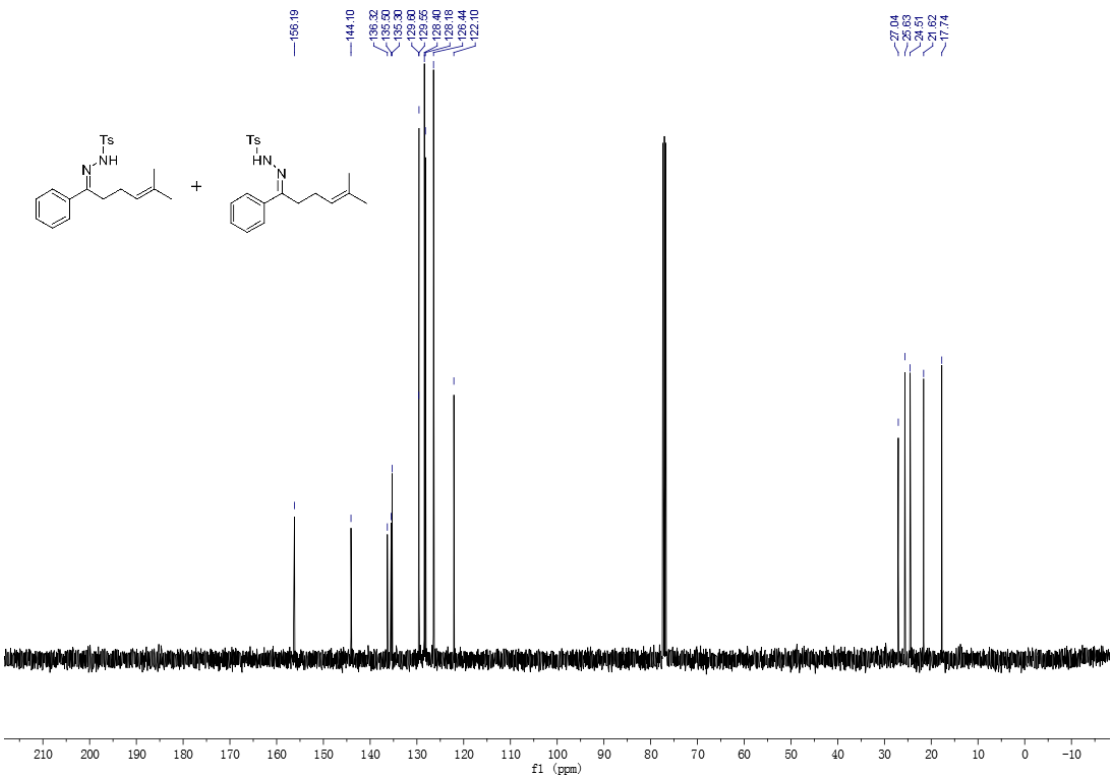
2H), 2.37 (s, 3H), 1.75 (s, 3H), 1.31 (d, J = 7.1 Hz, 3H), 1.06 (s, 3H), 0.65 (s, 3H)；**^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.5, 140.4, 134.9, 133.5, 130.7, 129.4, 127.1, 126.9, 117.3, 46.1, 43.1 41.6, 30.9, 23.1, 22.0, 21.5, 17.3, 15.9; **FT-IR** (thin. film, KBr): ν (cm^{-1}) 2980, 1679, 1452, 1360, 812, 704; **HRMS** (ESI) Calculated for $C_{21}H_{26}N_2O_2NaS$ $[M + Na]^+$ 393.1607, found 393.1603.

8. NMR spectra the substrates and products

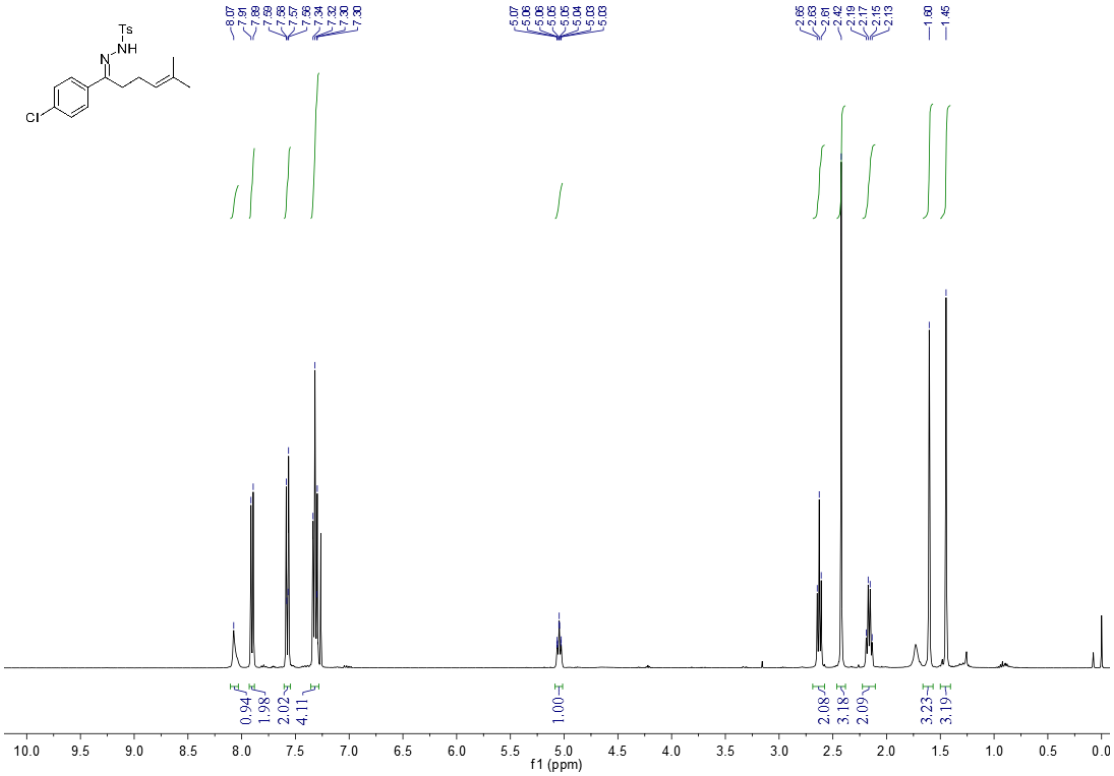
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1aa**



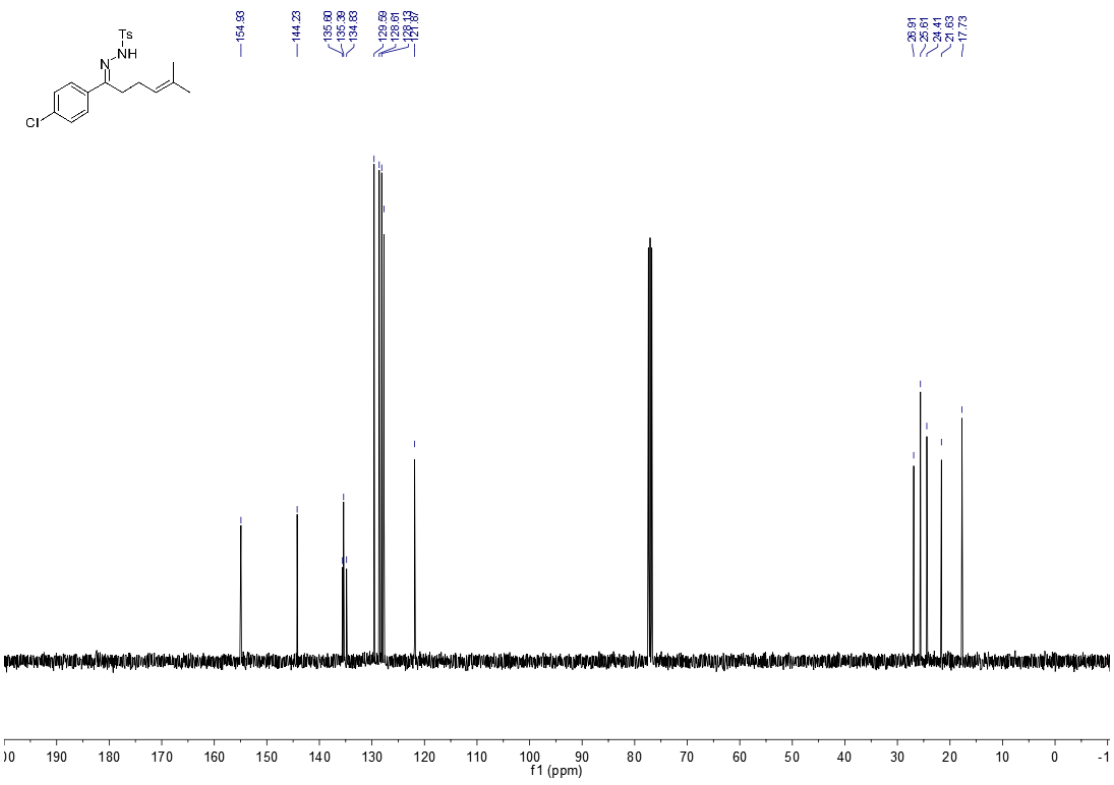
^{13}C NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1aa**



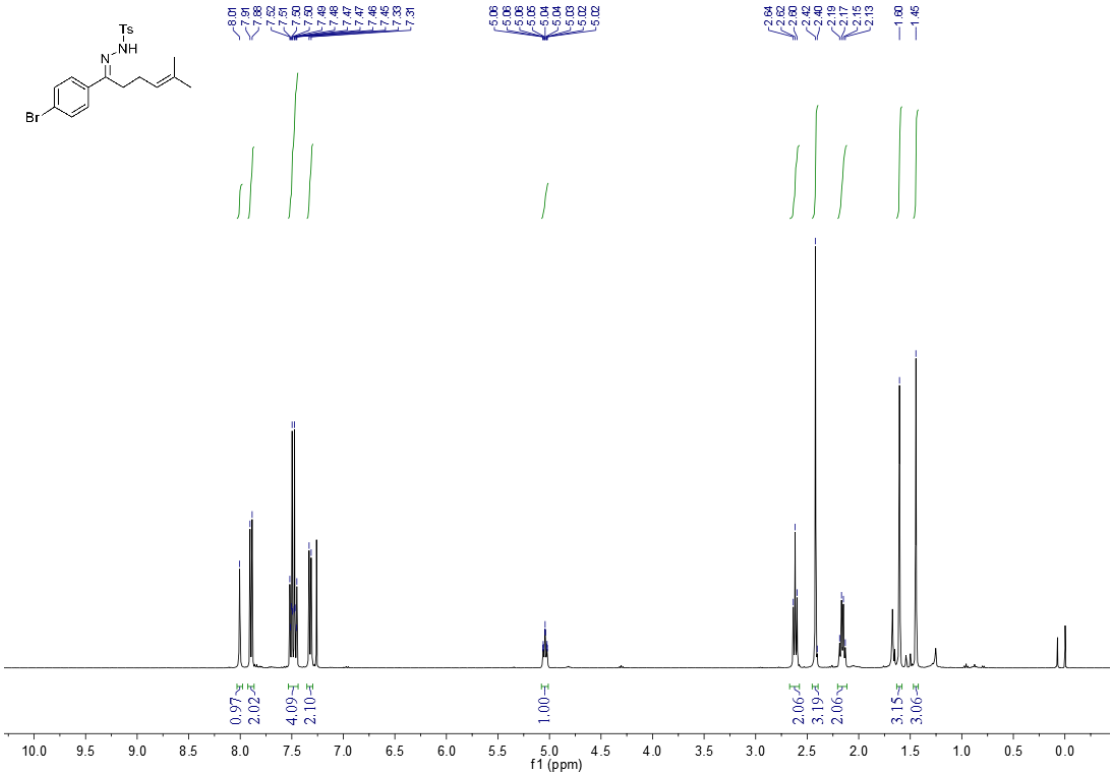
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ba**



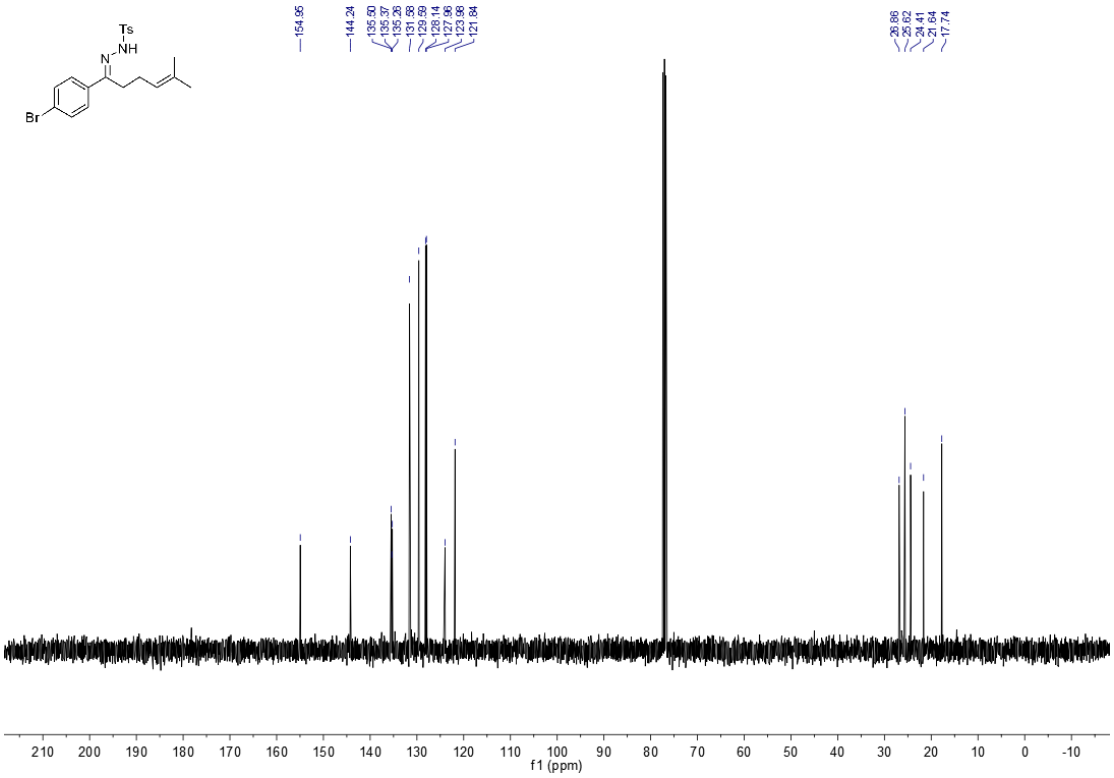
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ba**



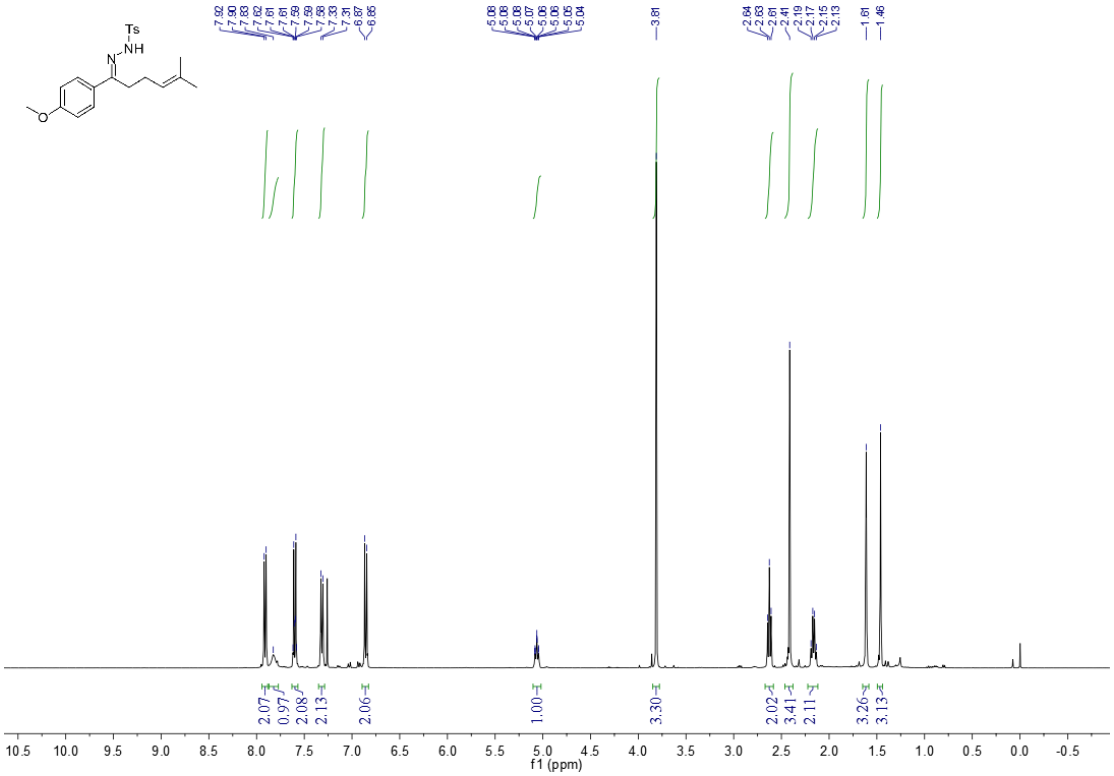
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ca**



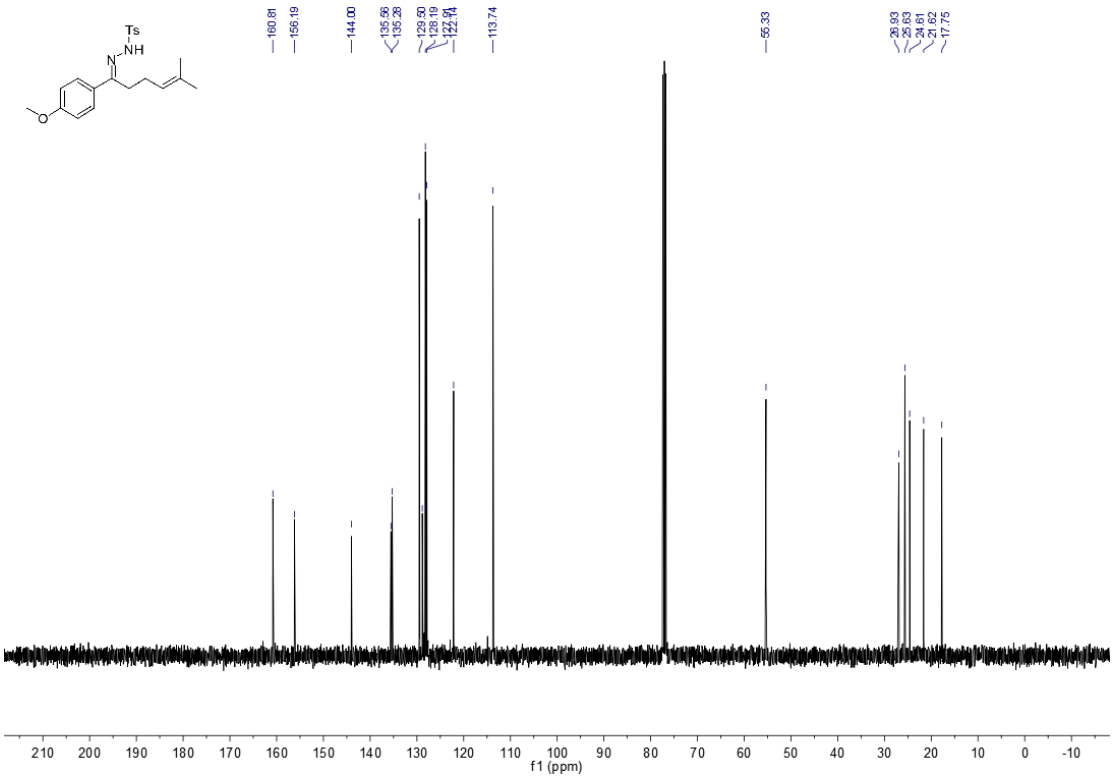
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **1ca**



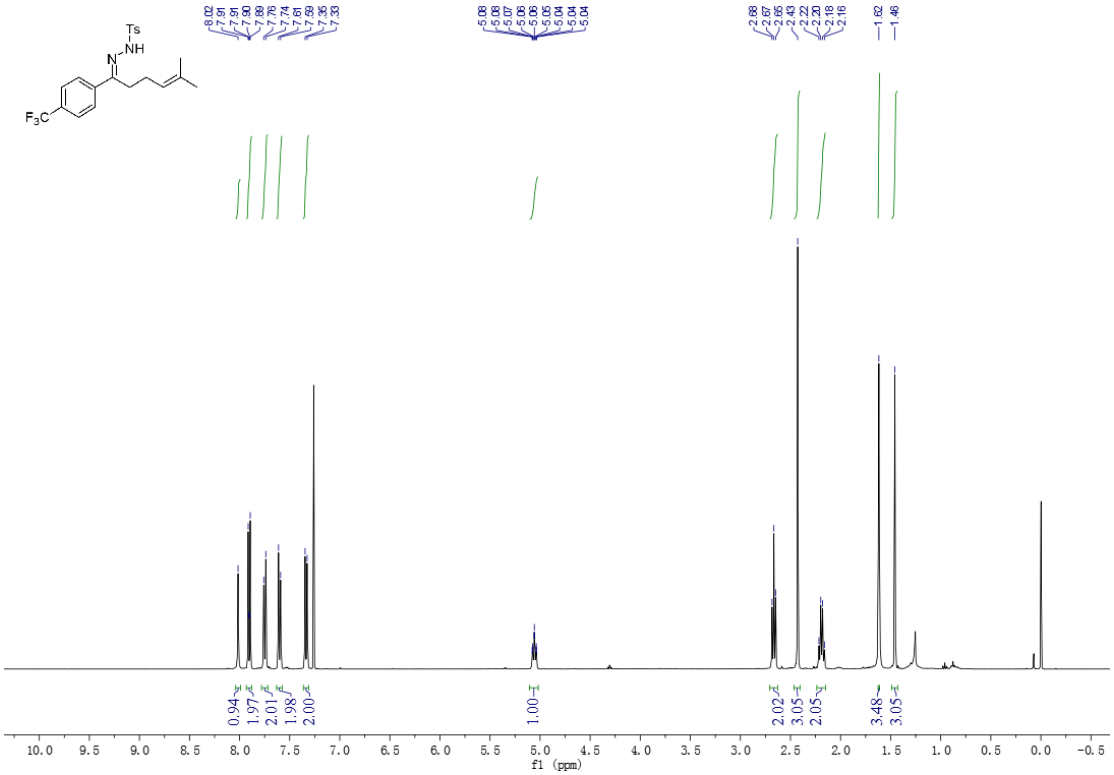
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1da**



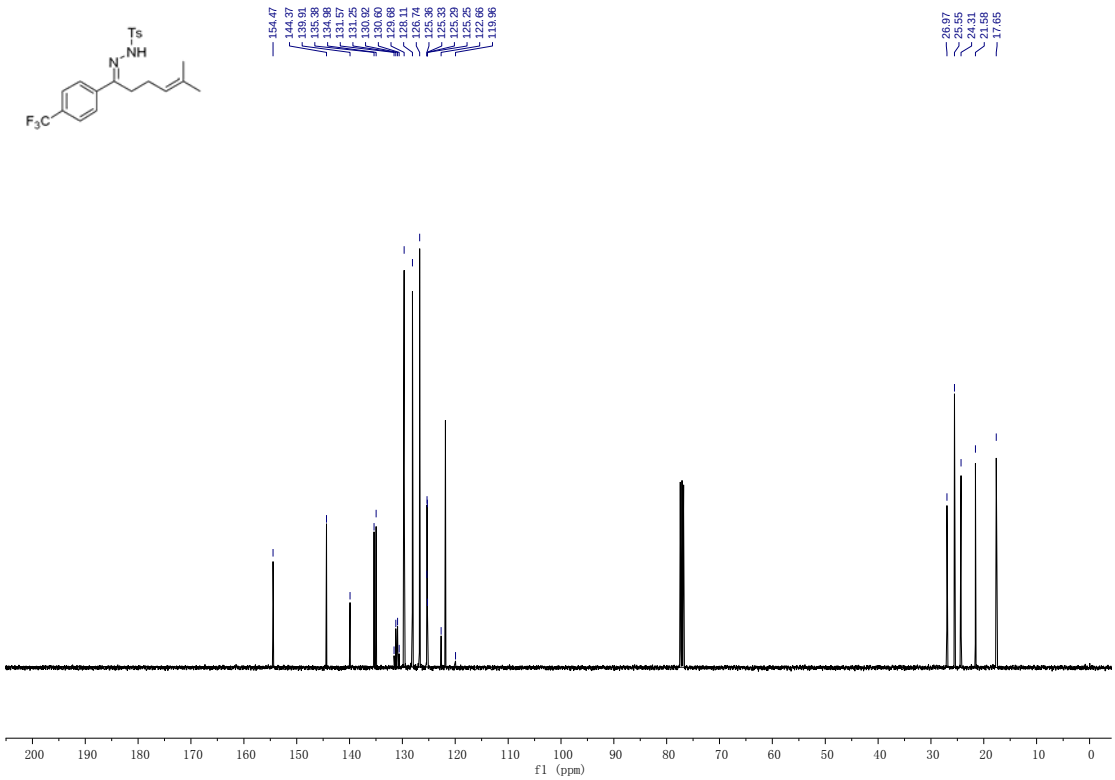
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1da**



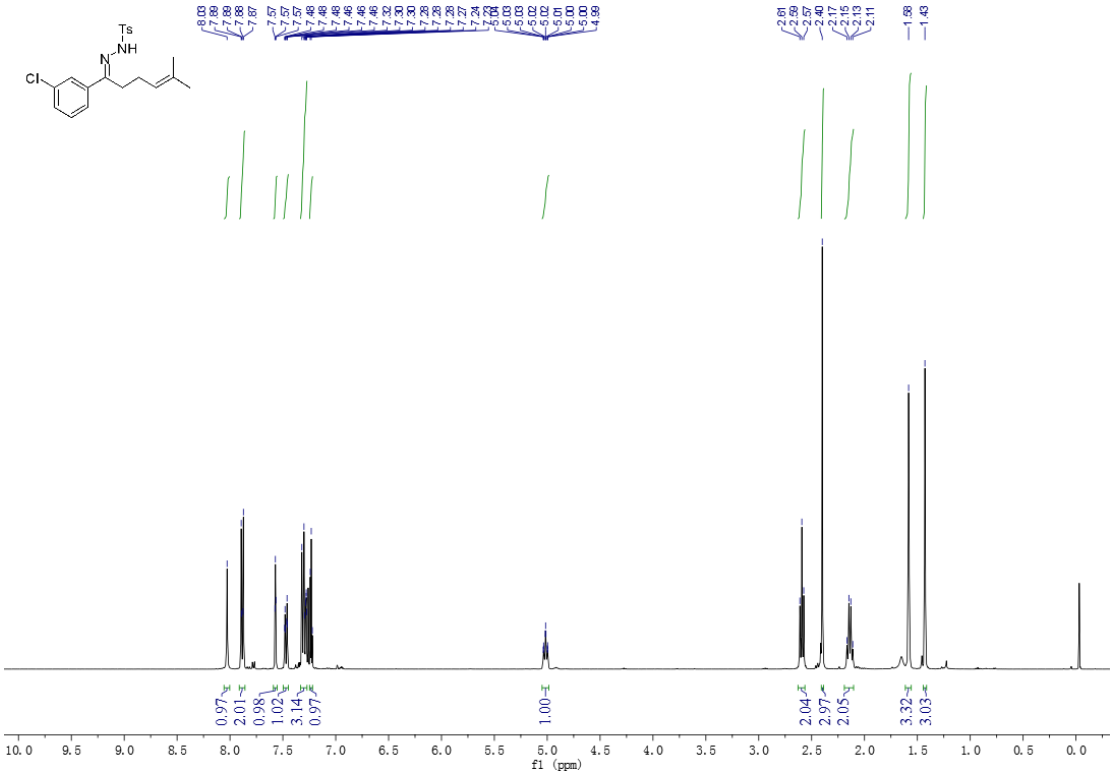
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ea**



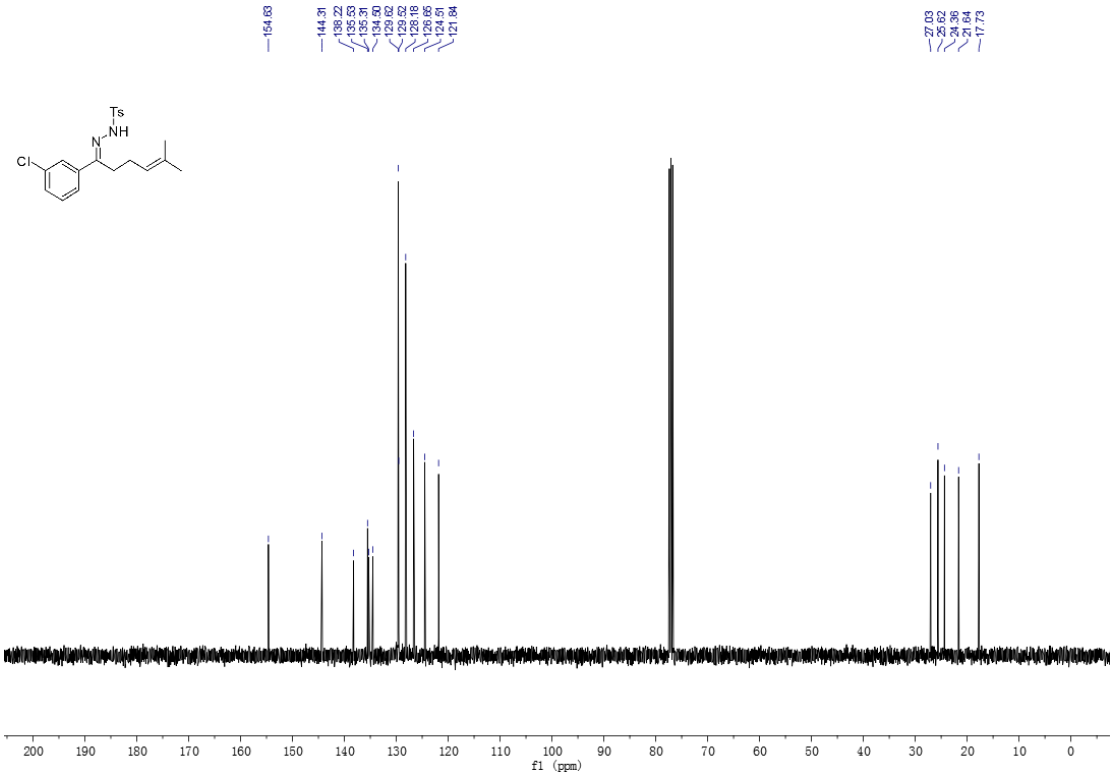
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ea**



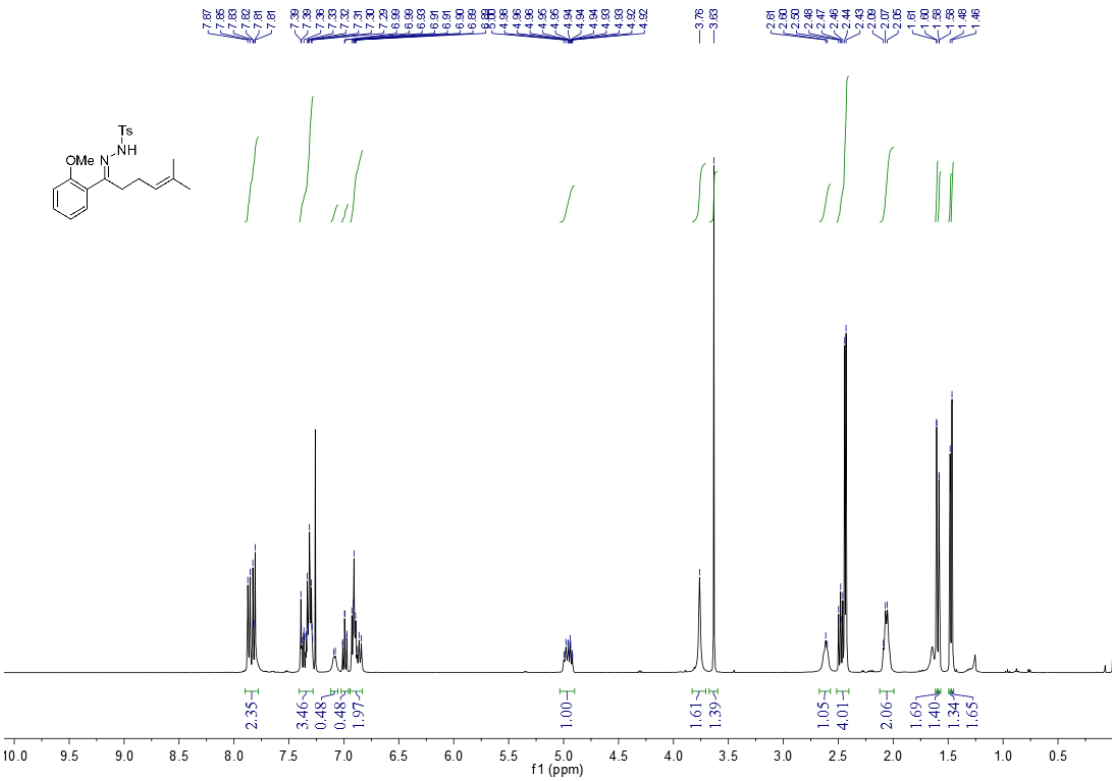
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1fa**



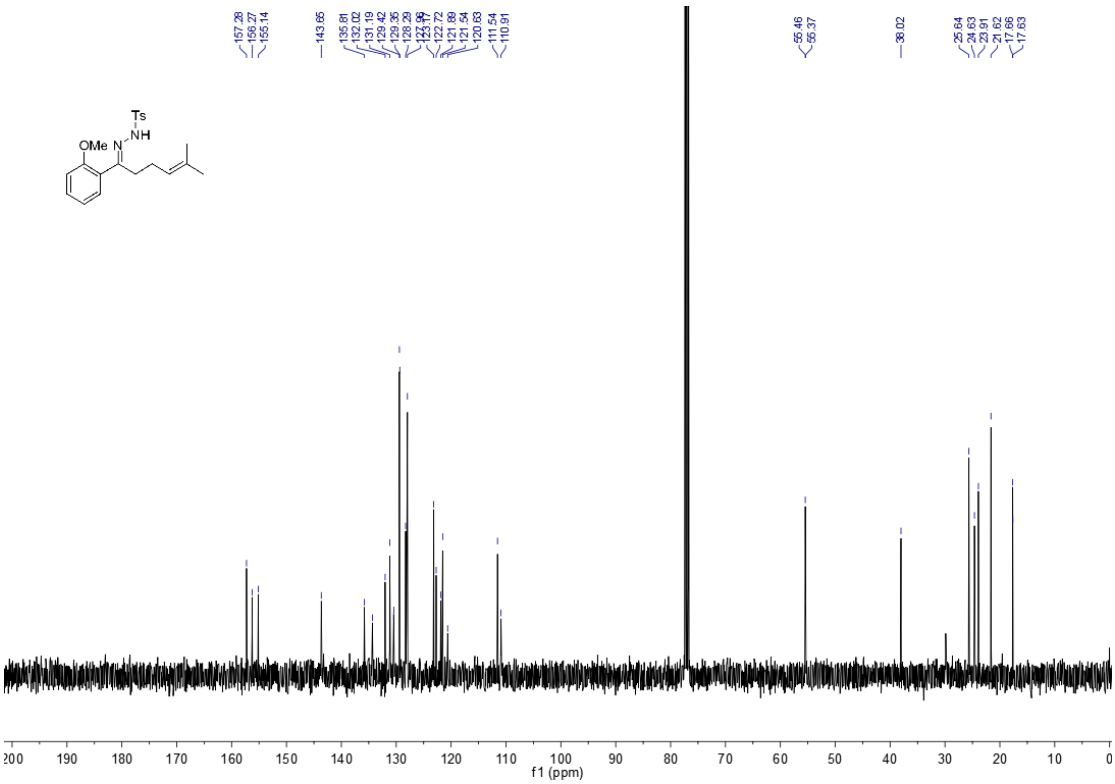
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1fa**



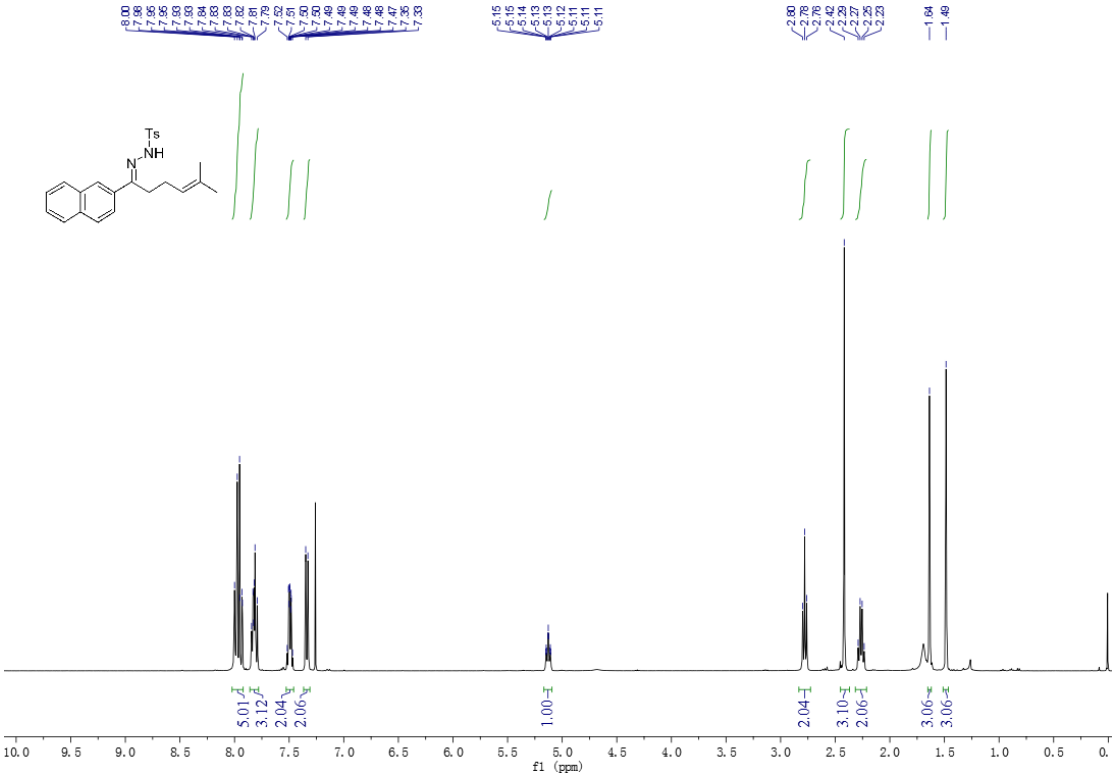
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ga**



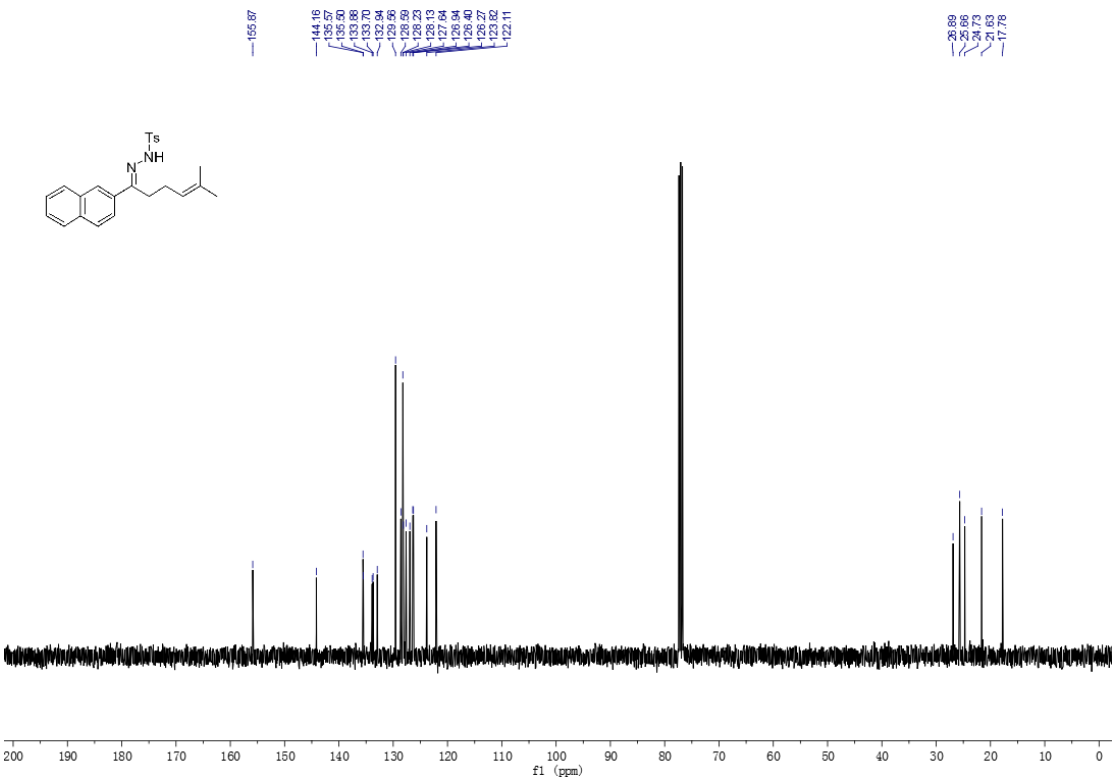
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ga**



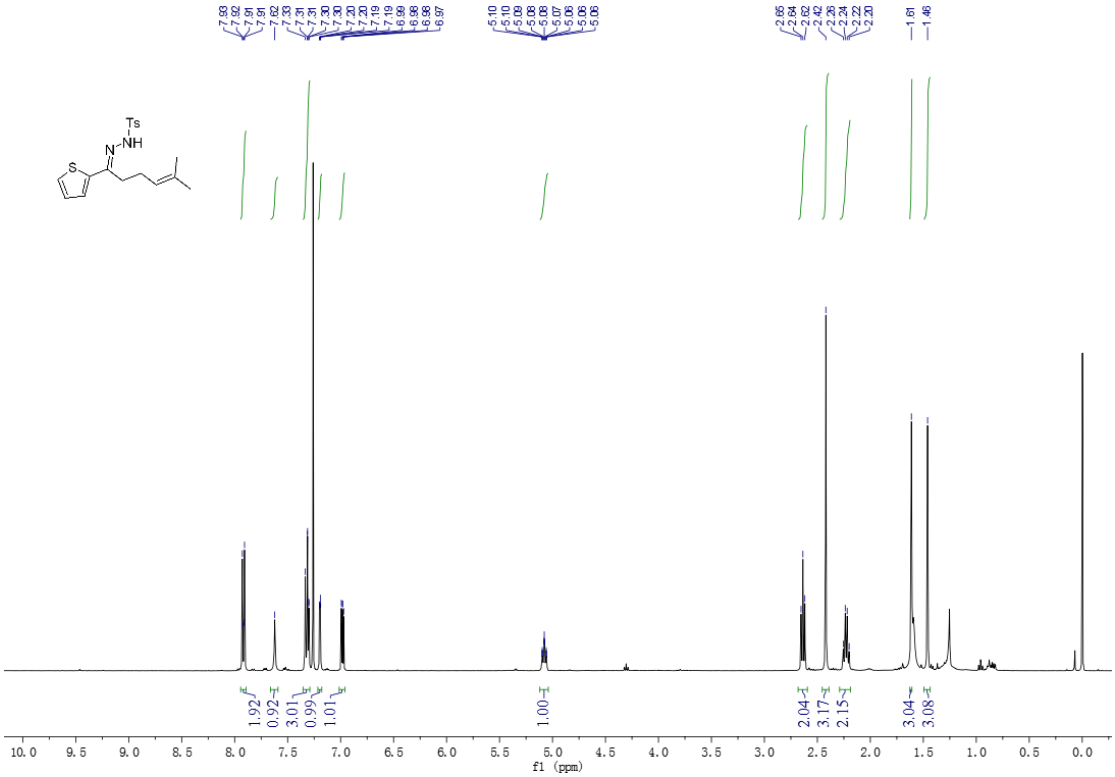
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ha**



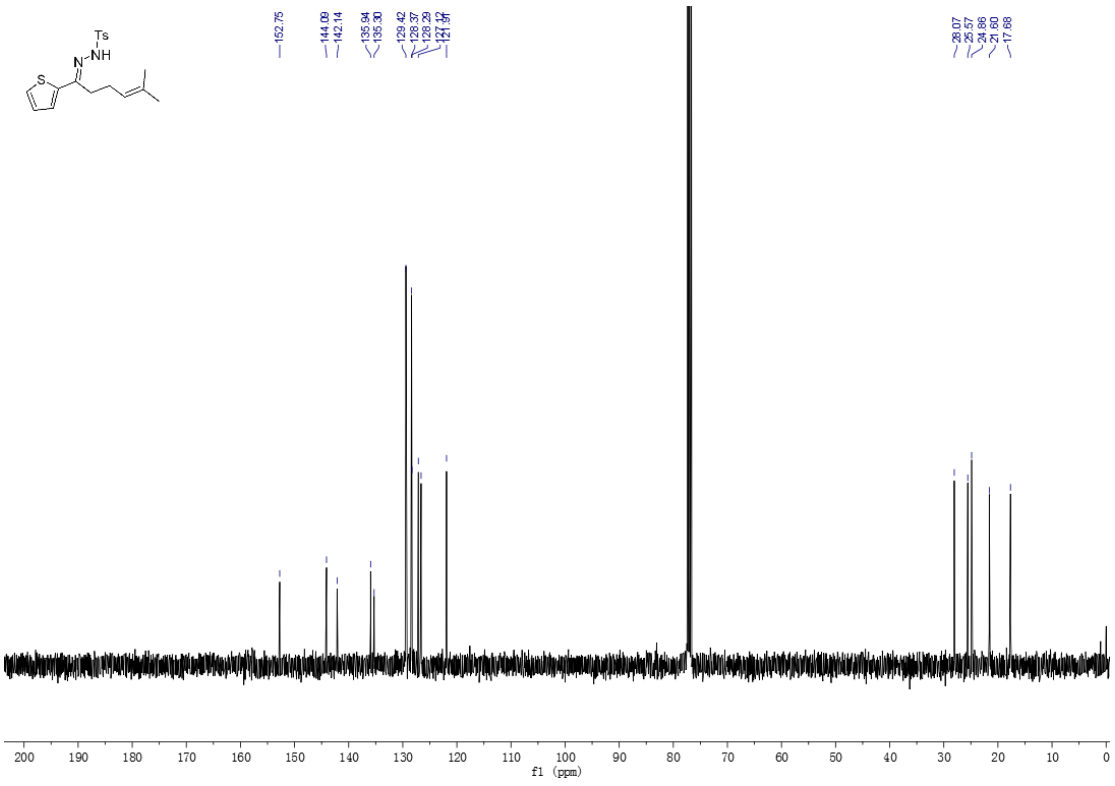
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ha**



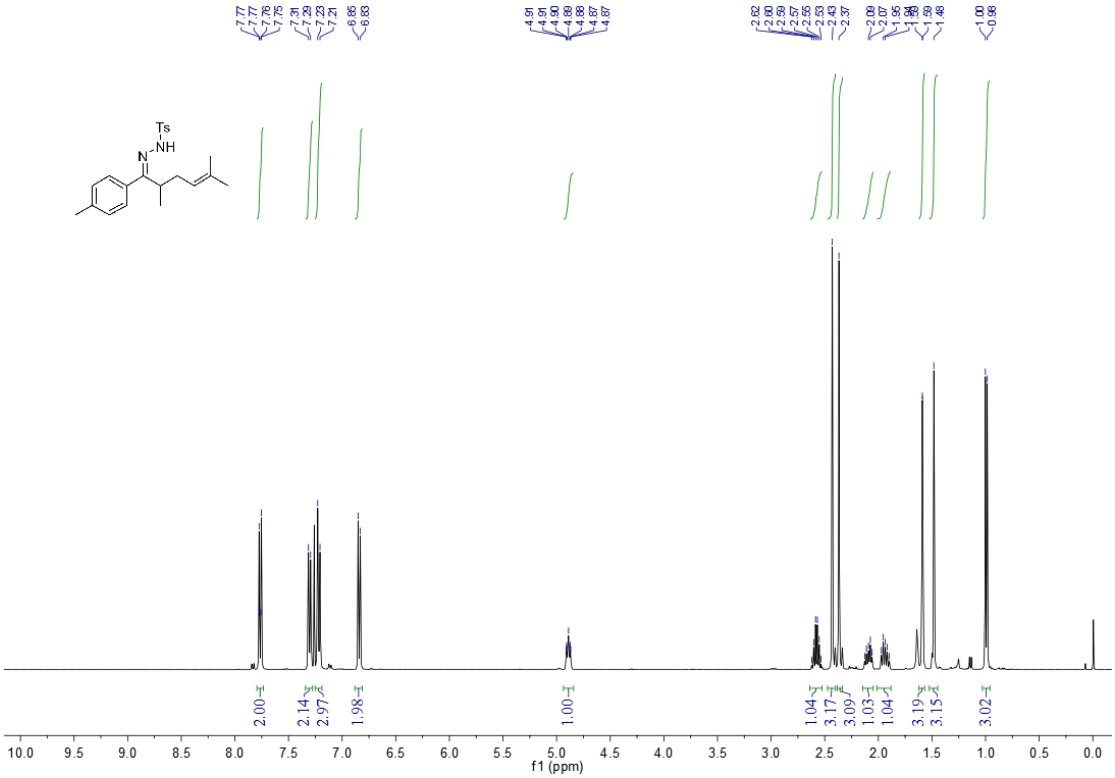
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ia**



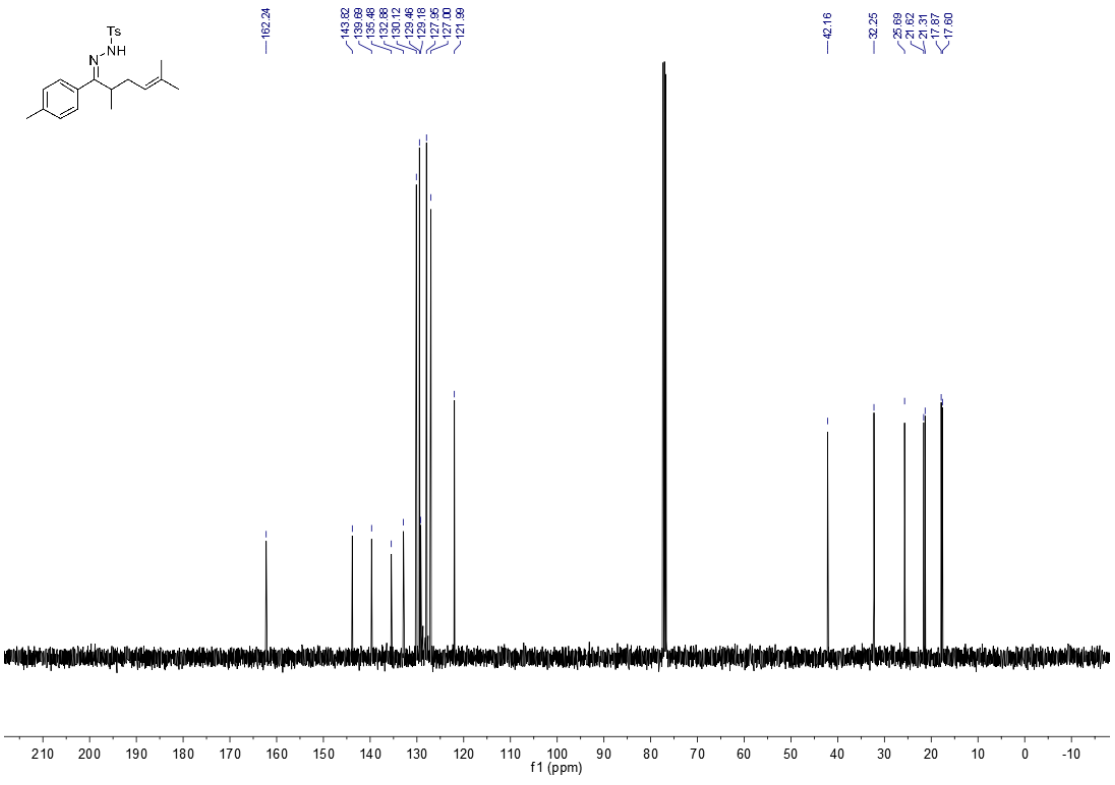
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ia**



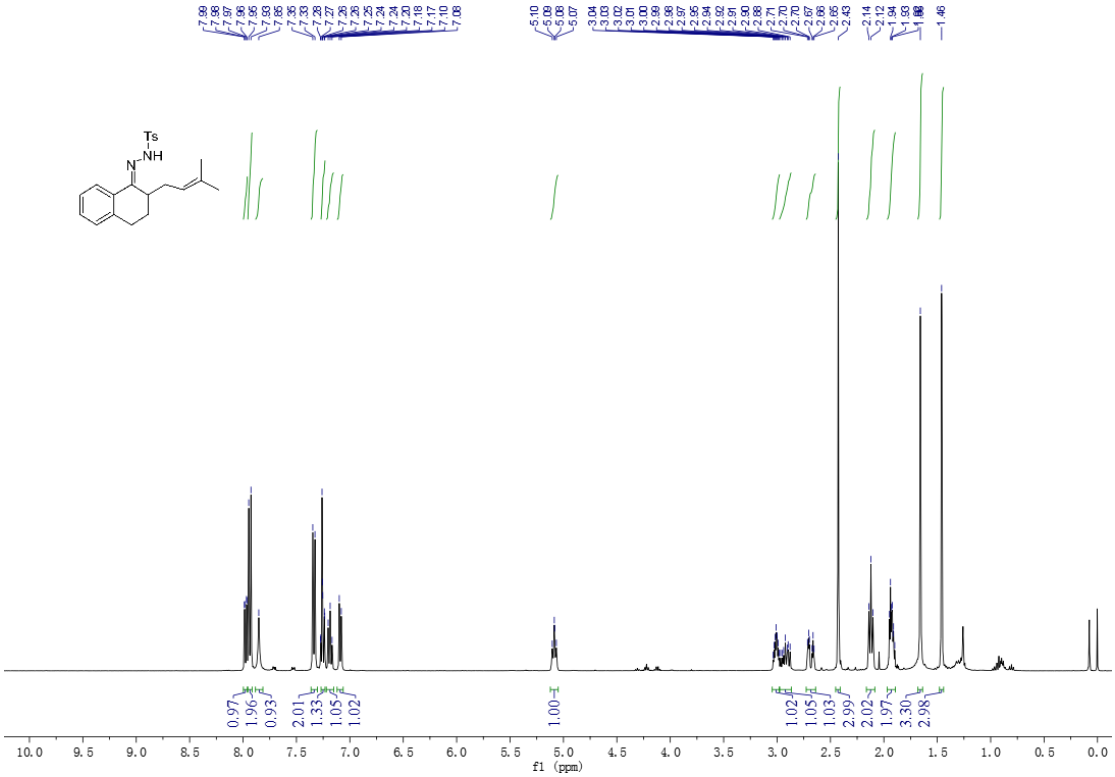
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ja**



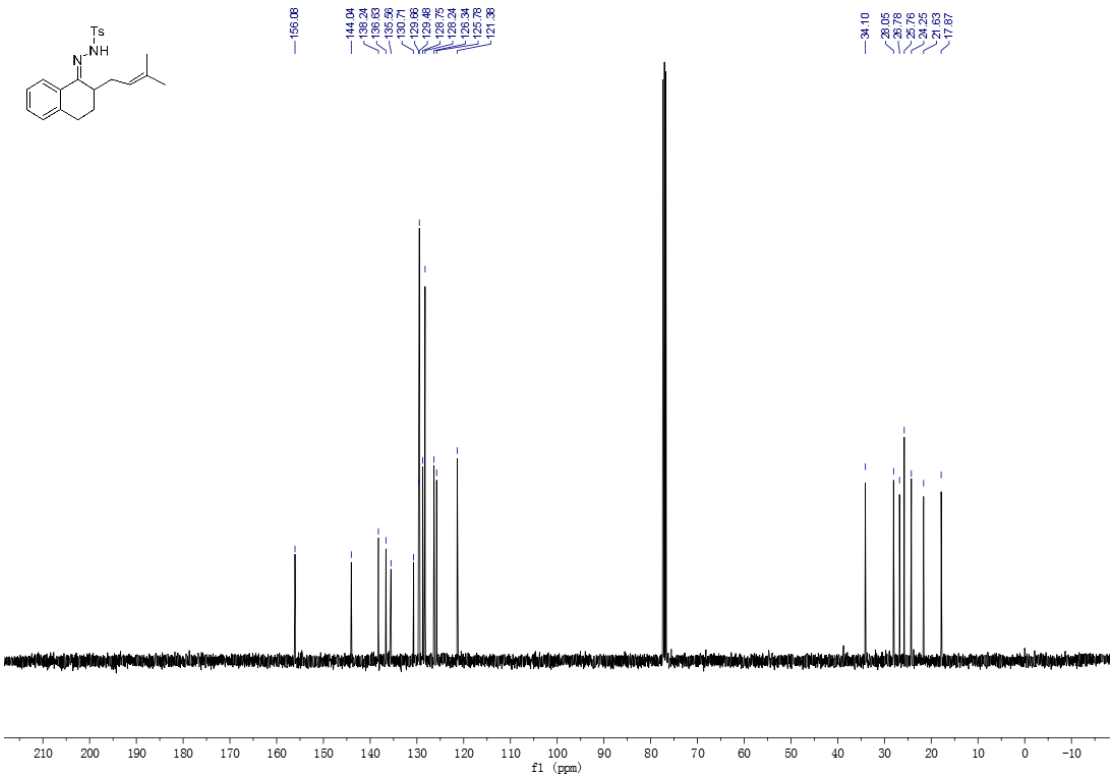
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ja**



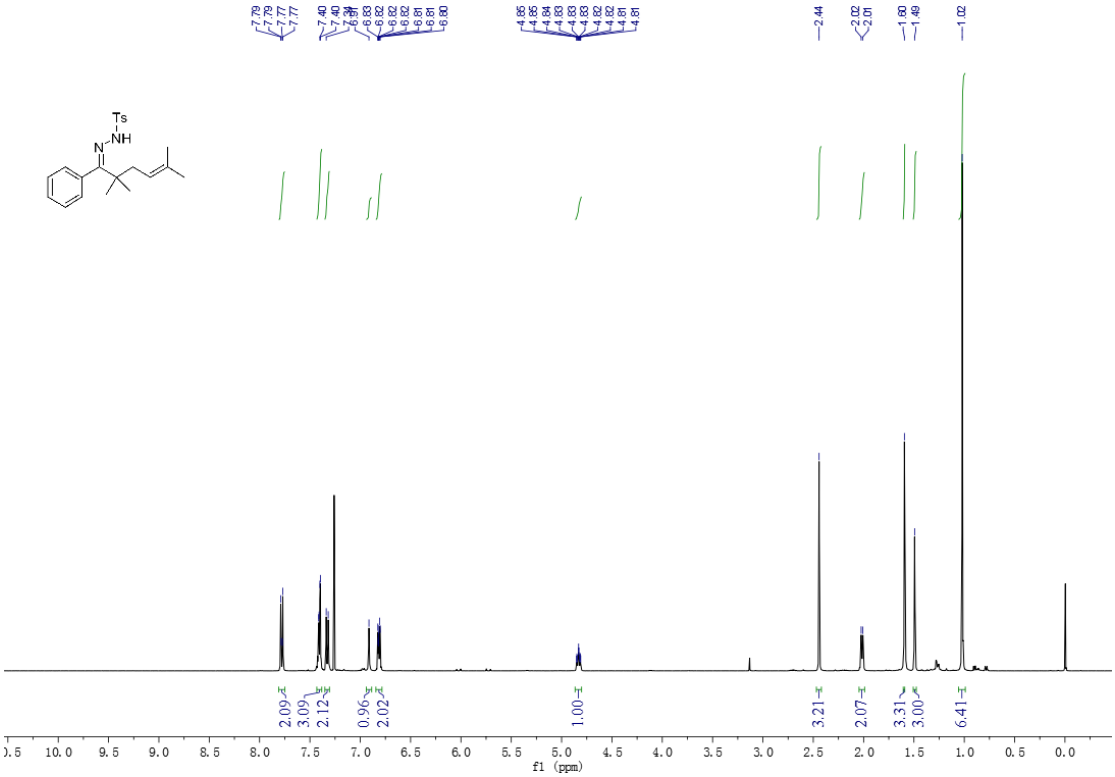
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ka**



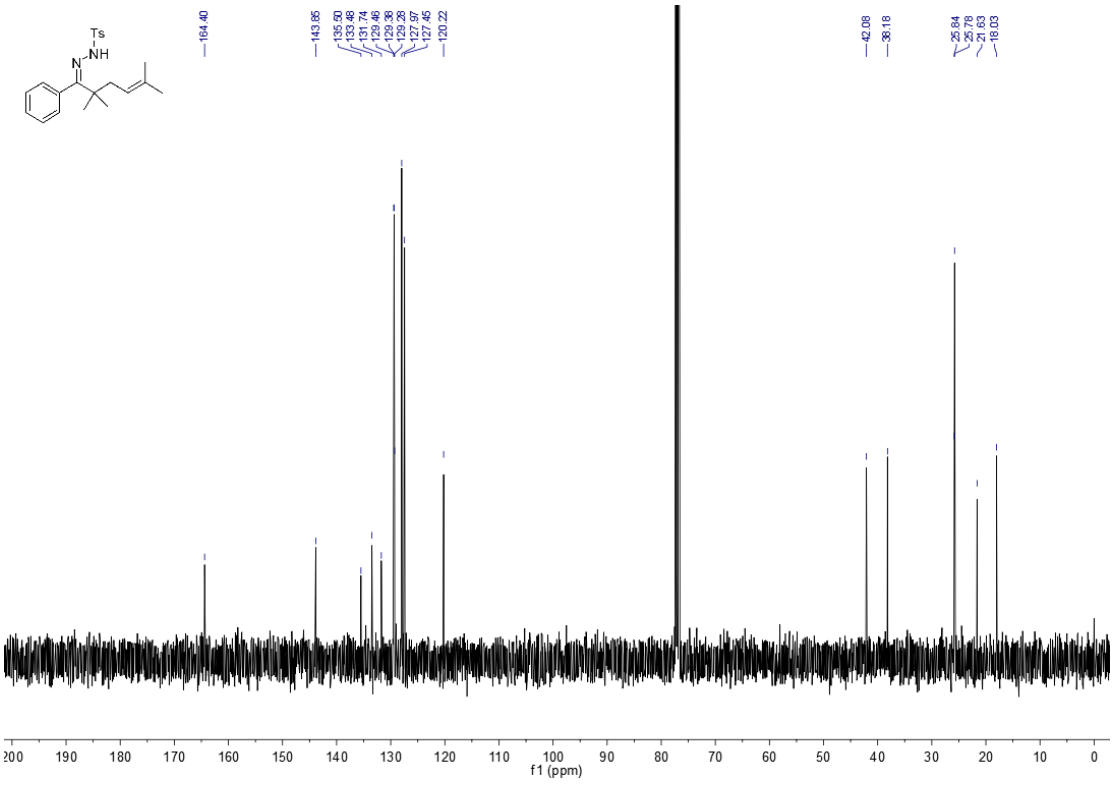
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ka**



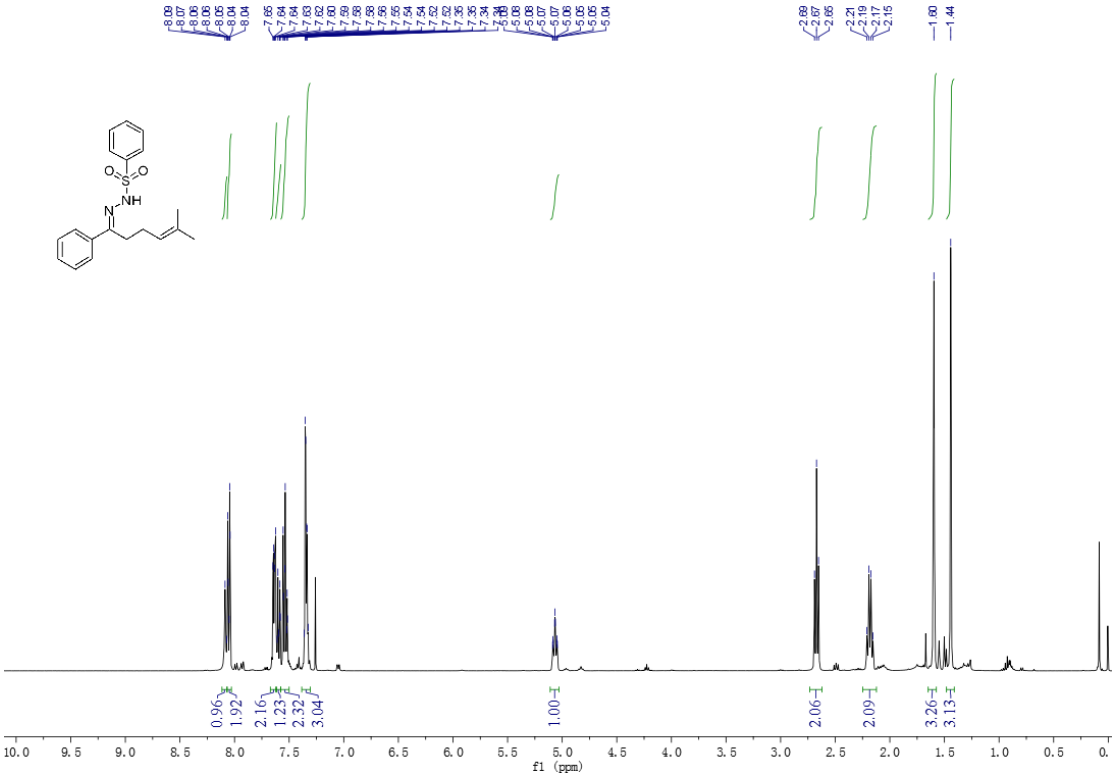
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1la**



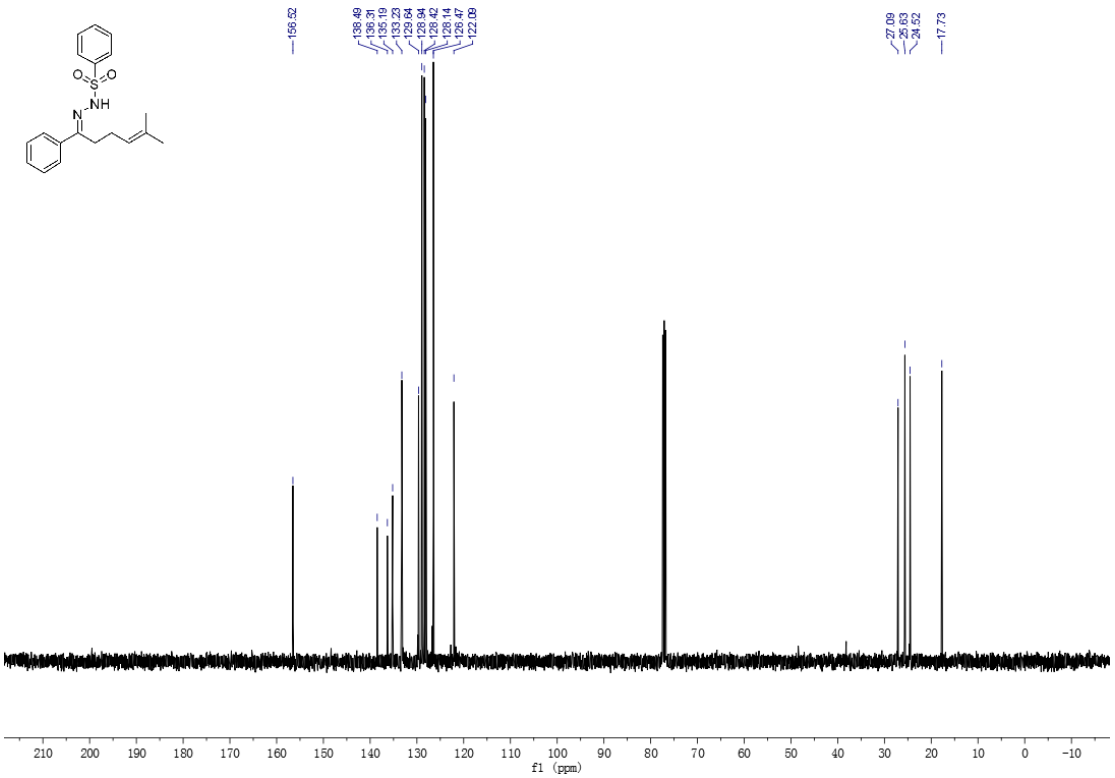
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1la**



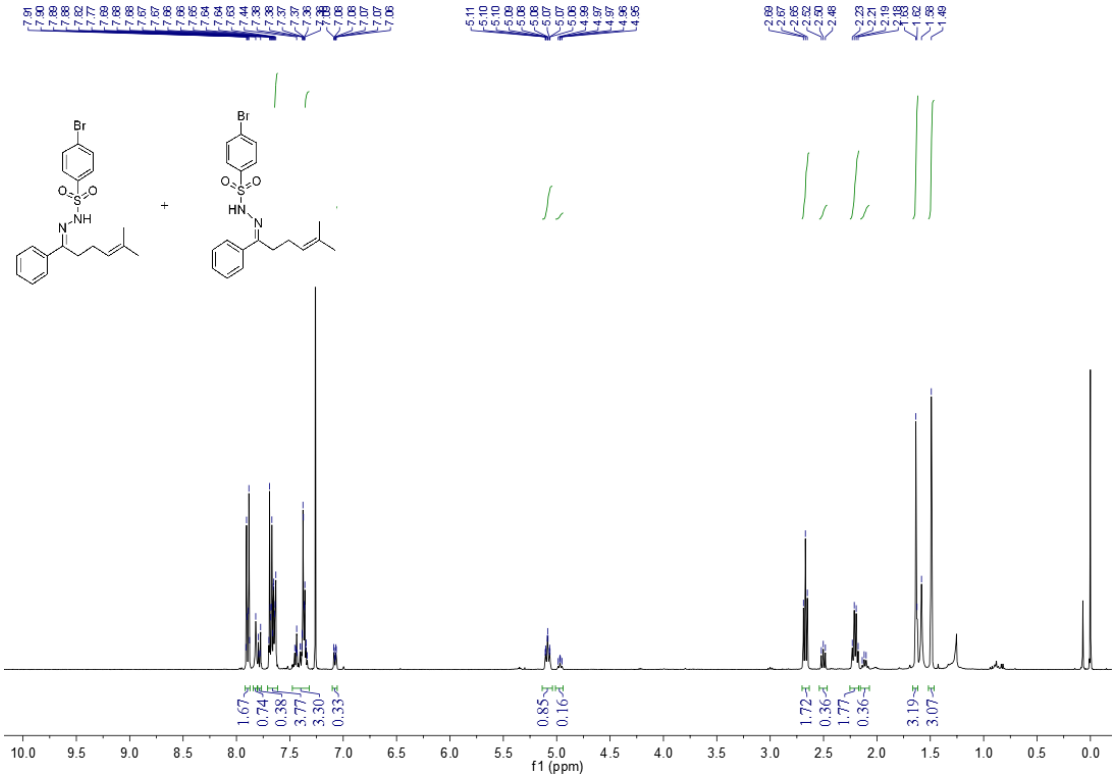
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ab**



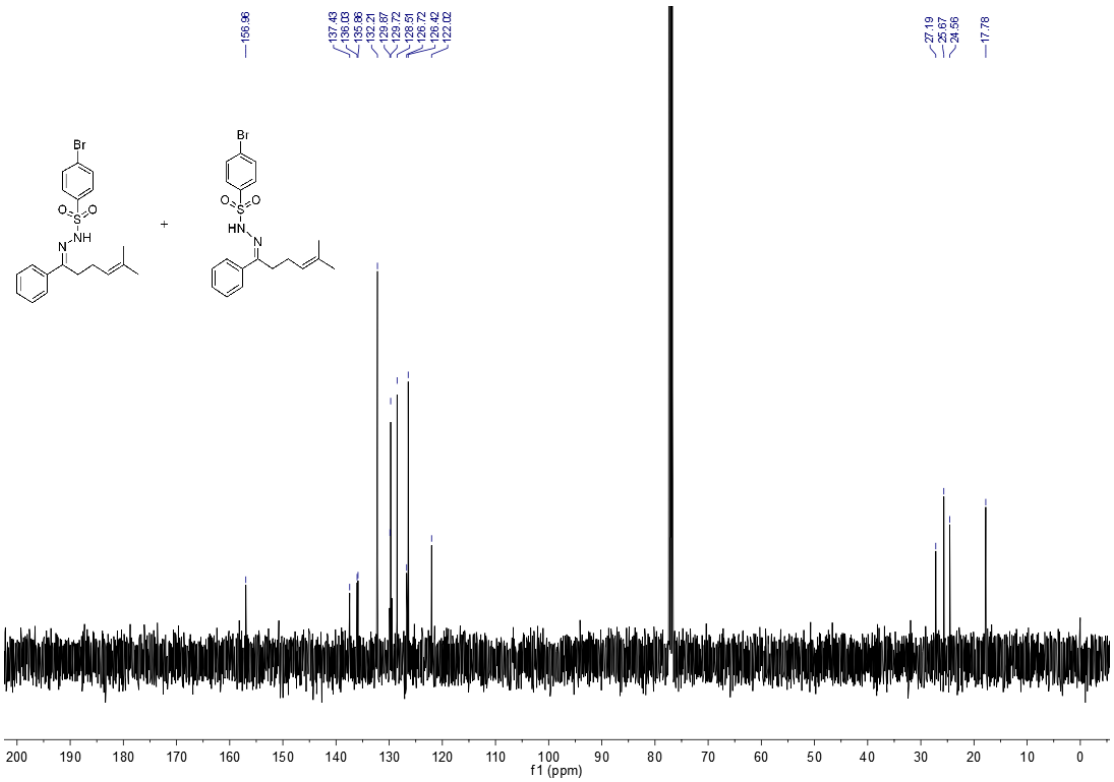
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ab**



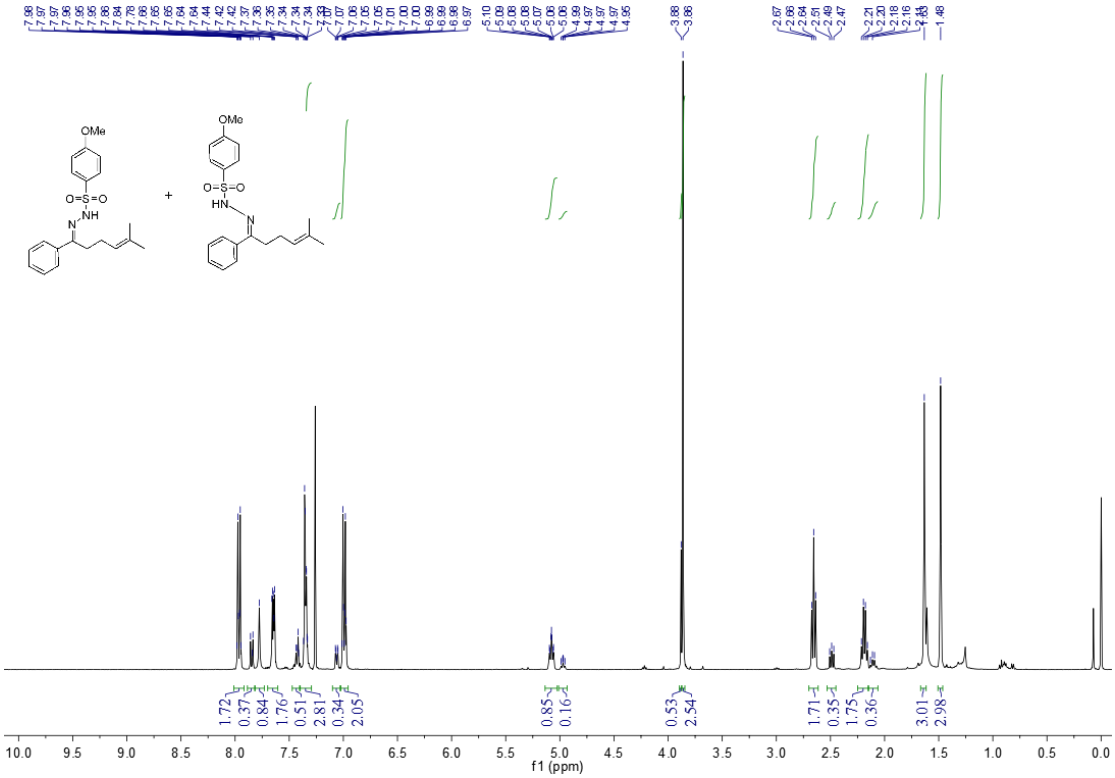
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1bb**



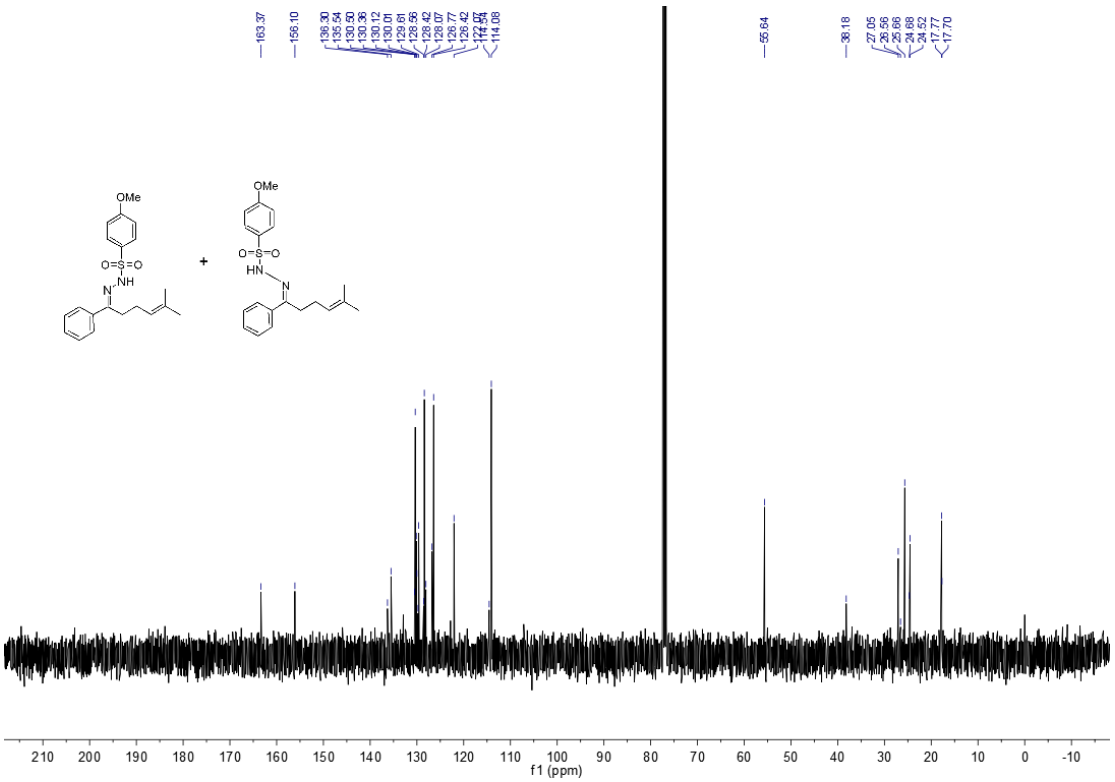
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1bb**



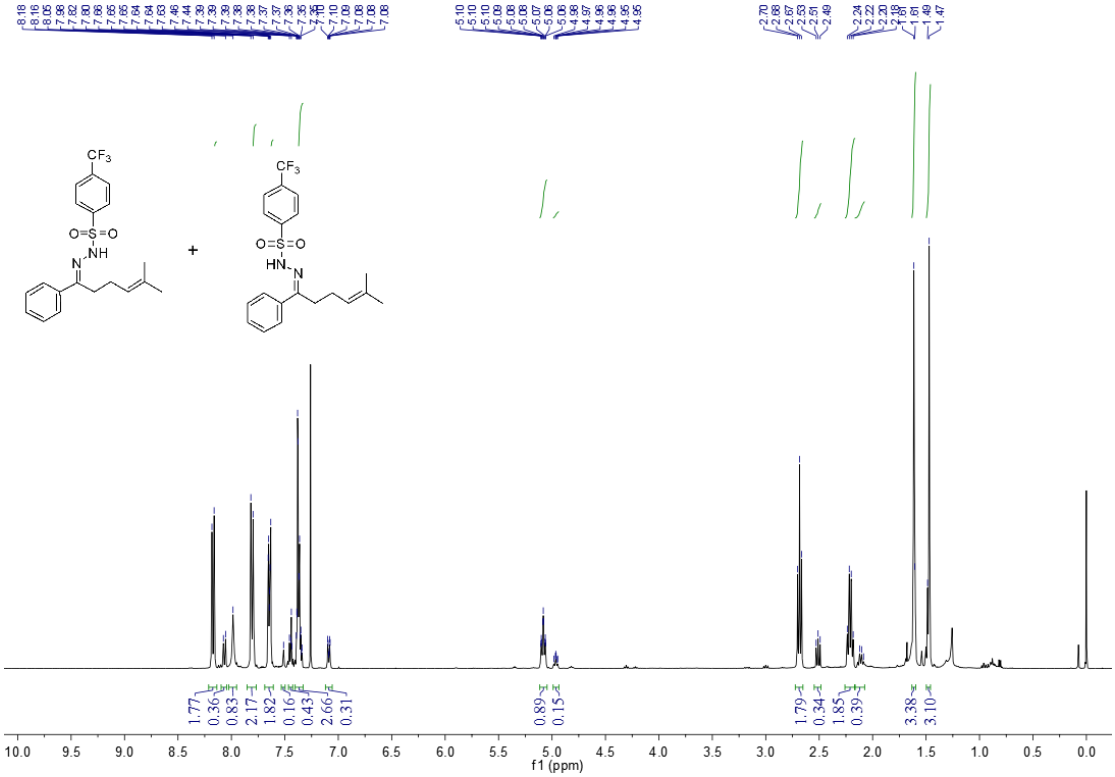
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1cb**



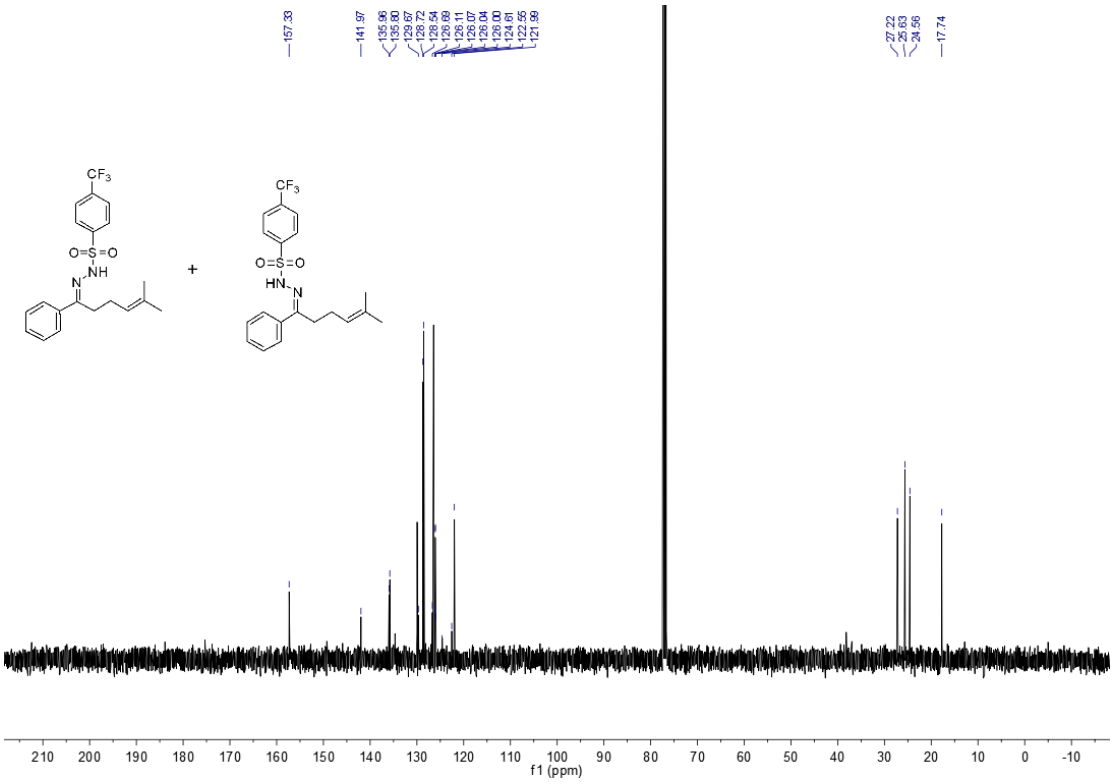
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1cb**



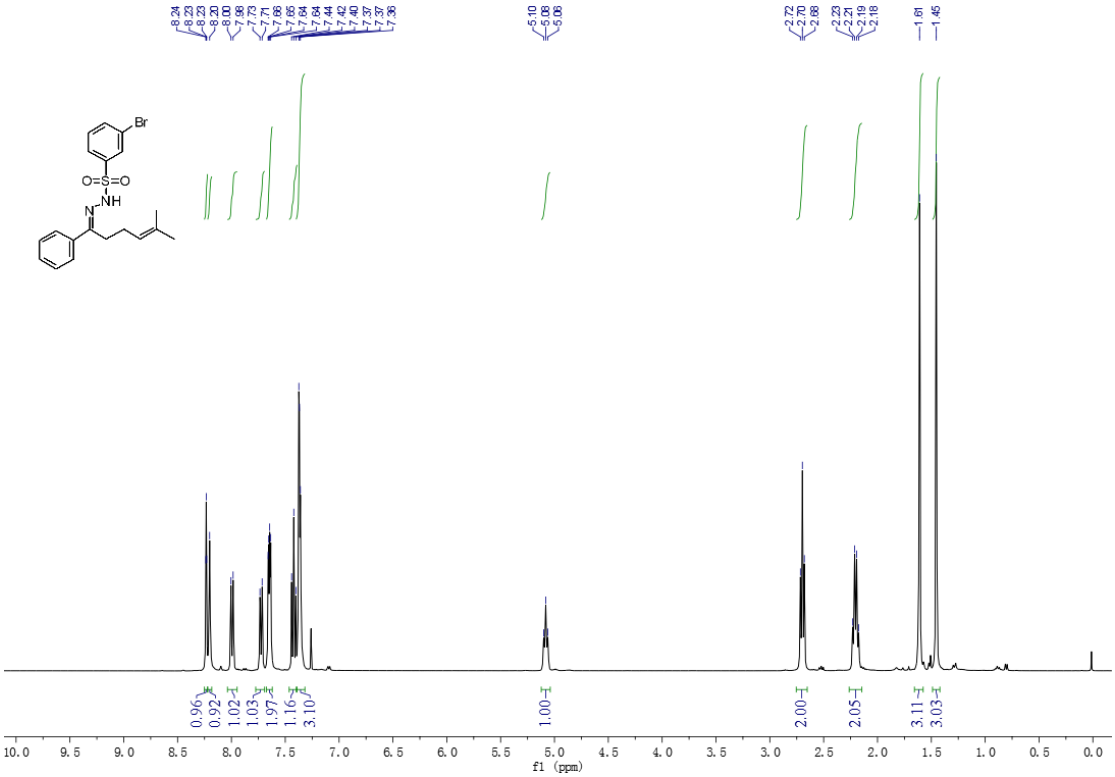
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1db**



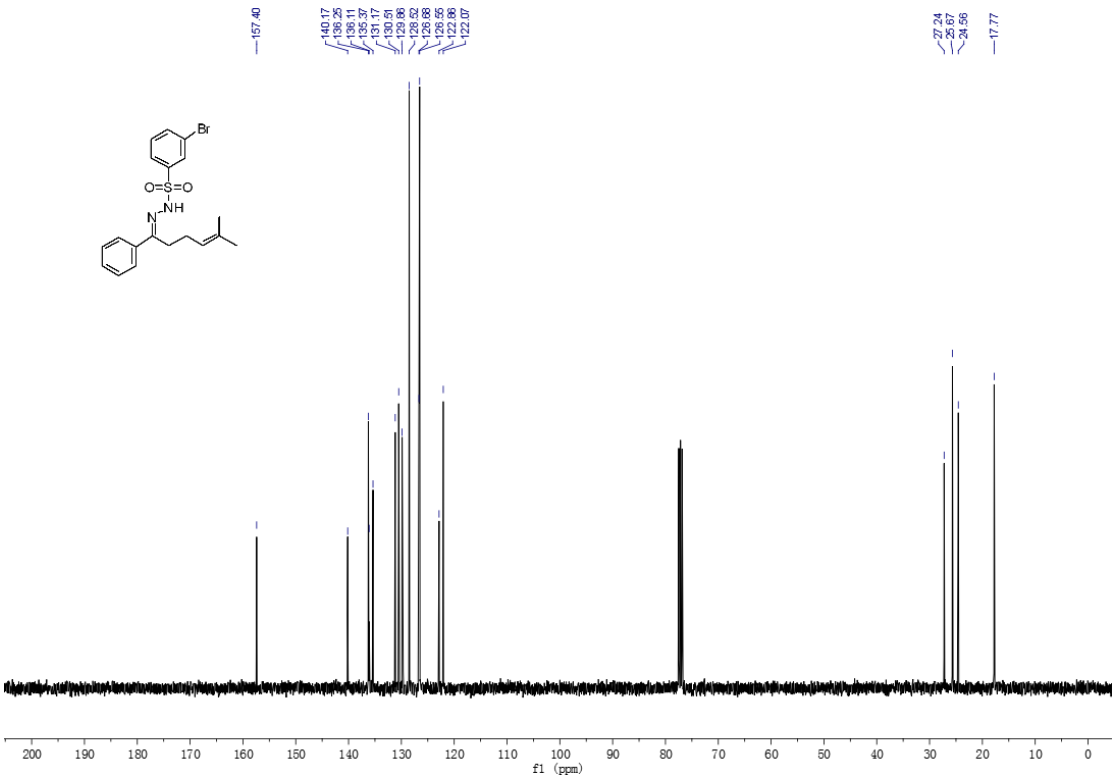
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1db**



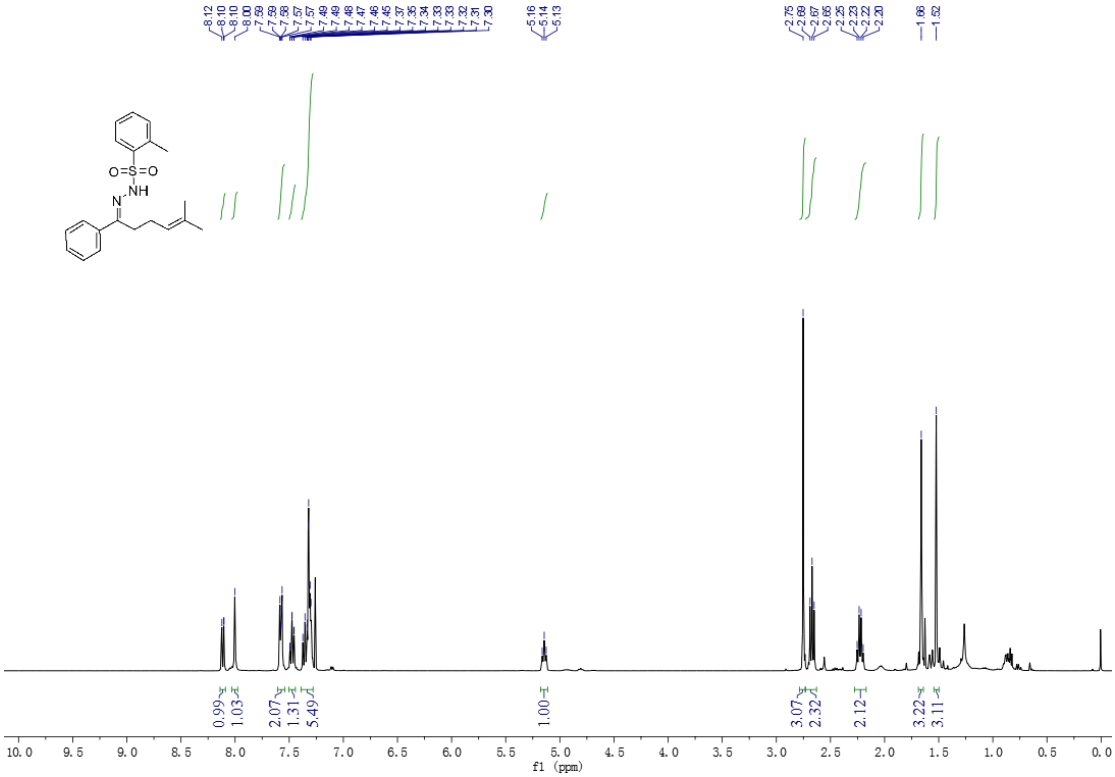
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1eb**



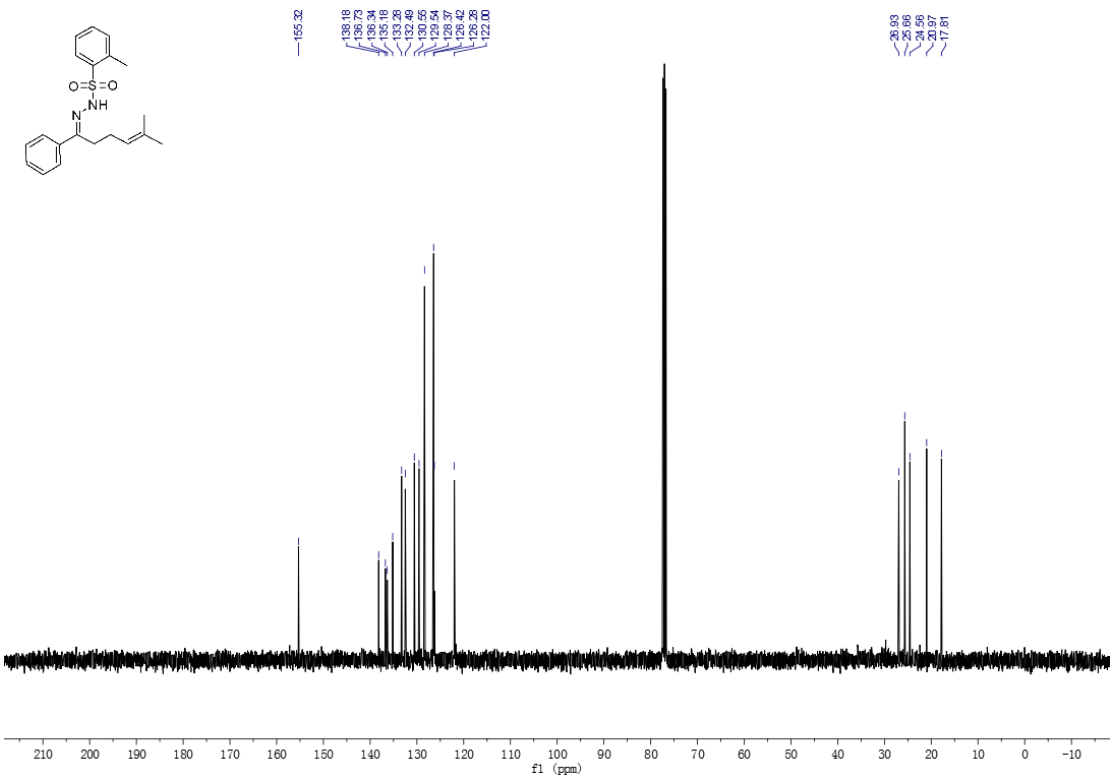
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1eb**



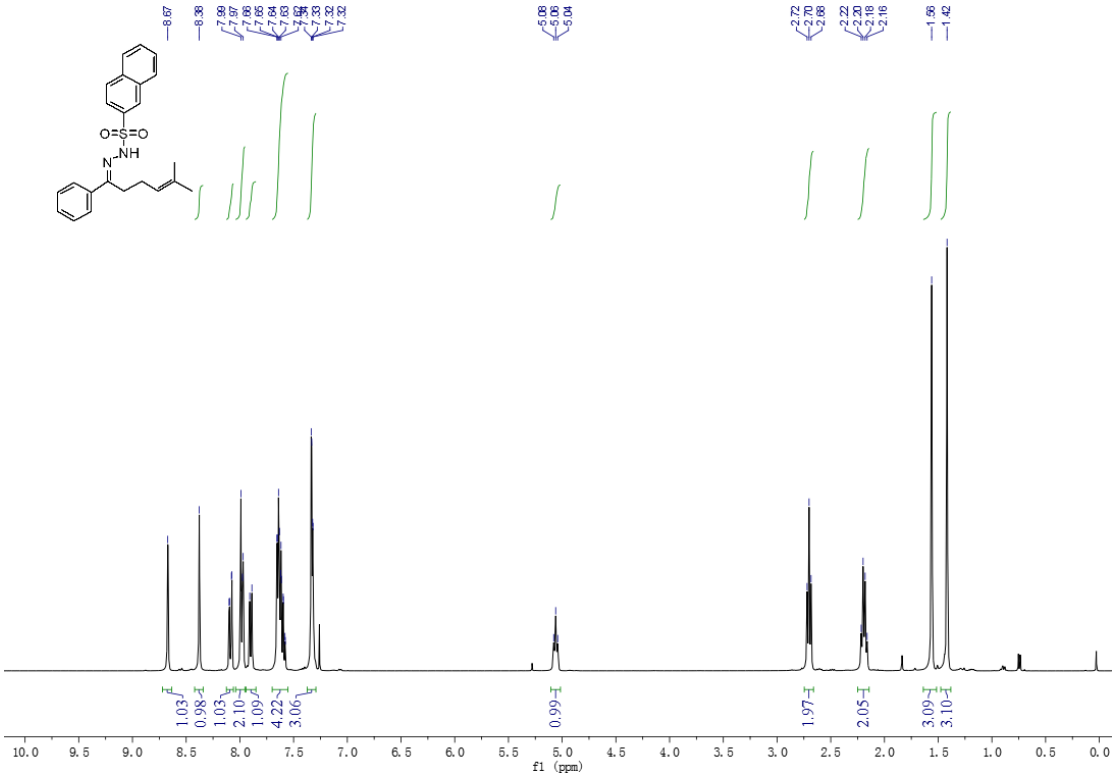
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1fb**



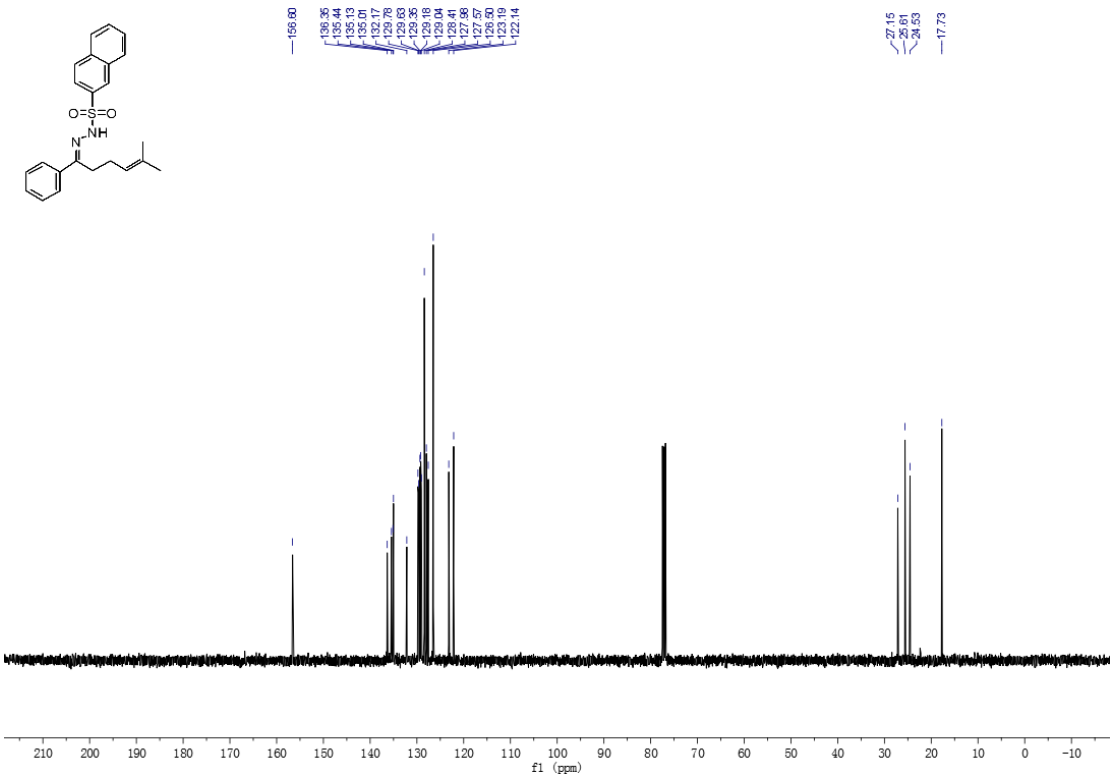
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1fb**



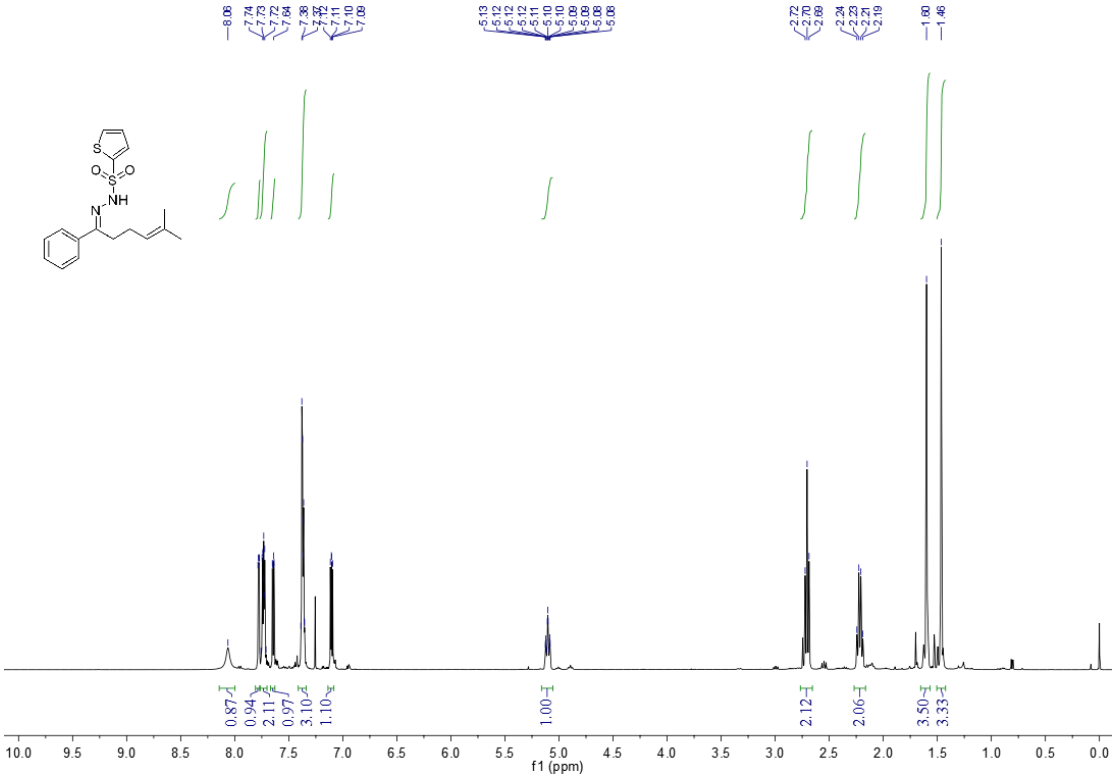
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1gb**



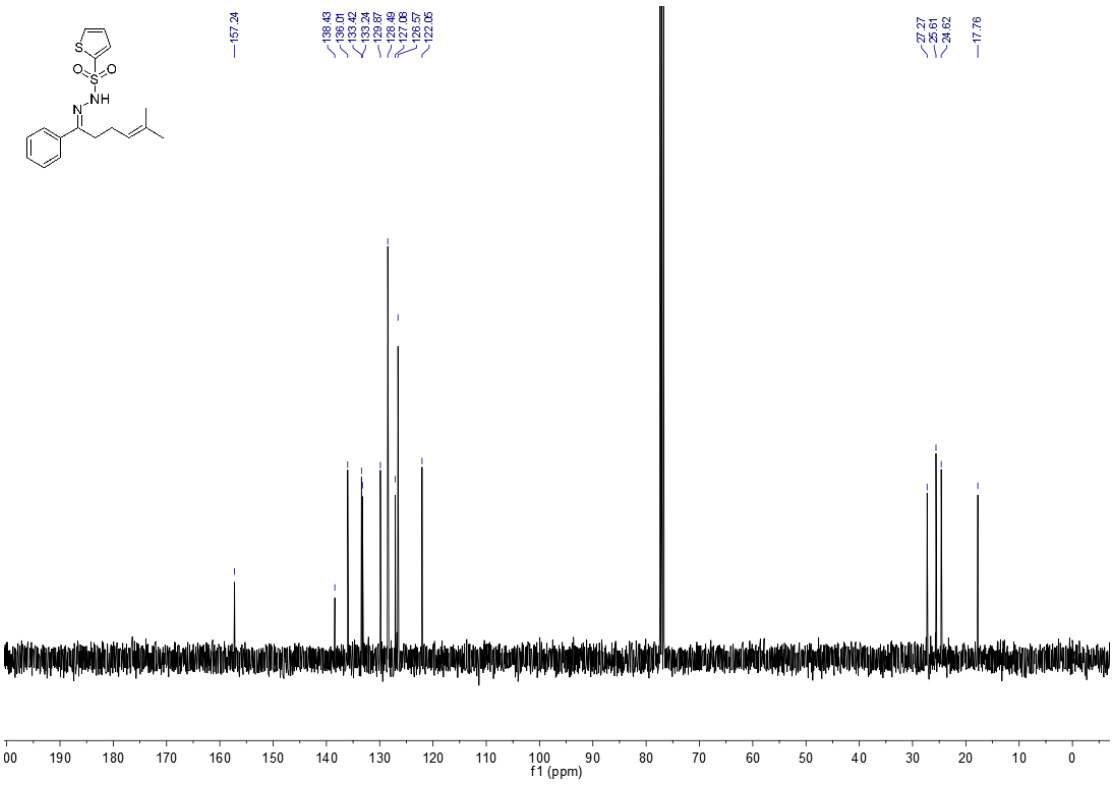
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1gb**



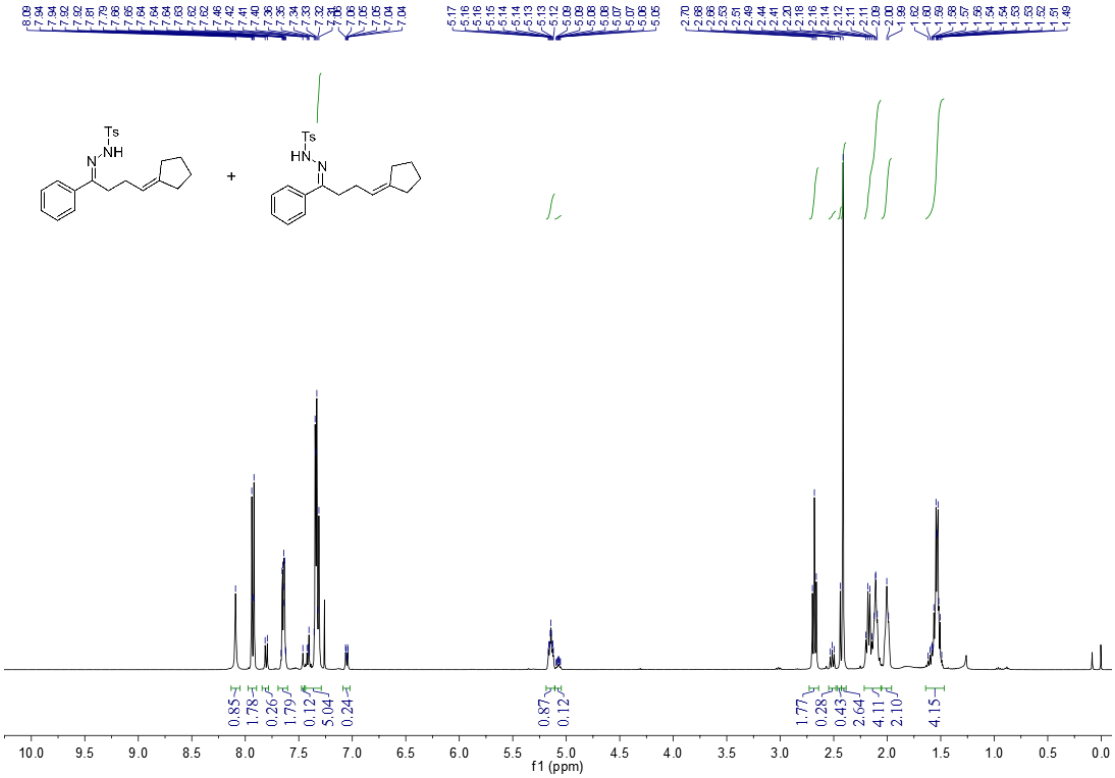
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **1hb**



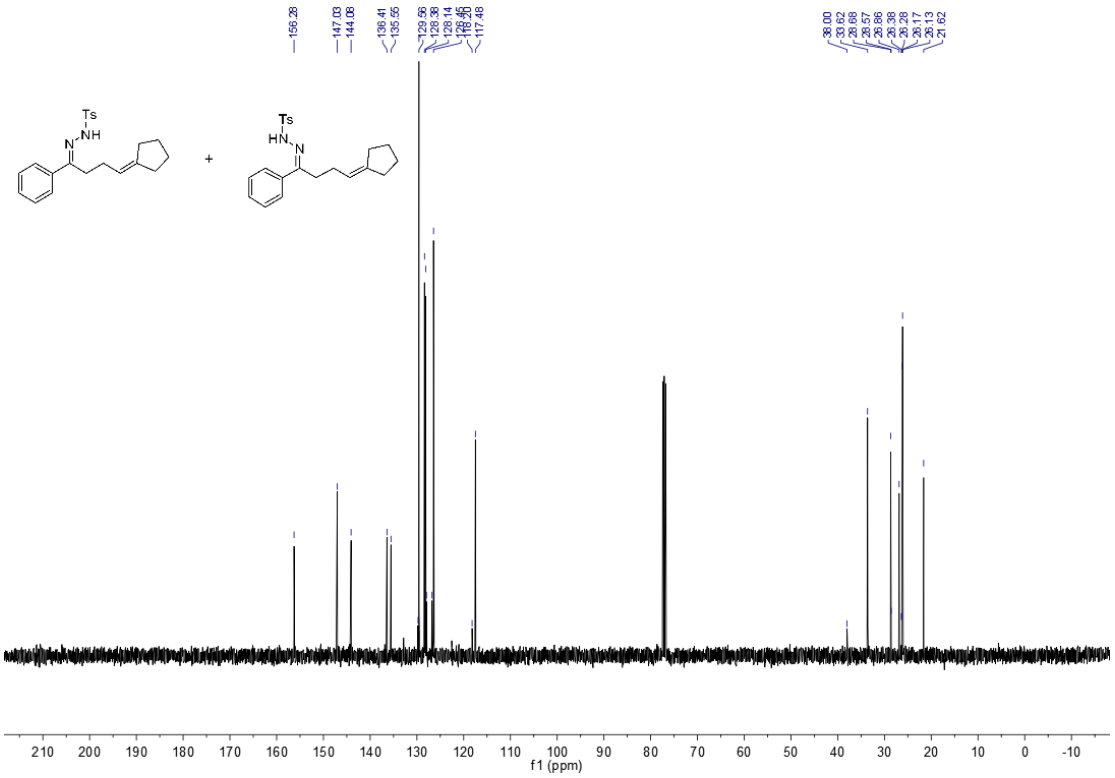
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1hb**



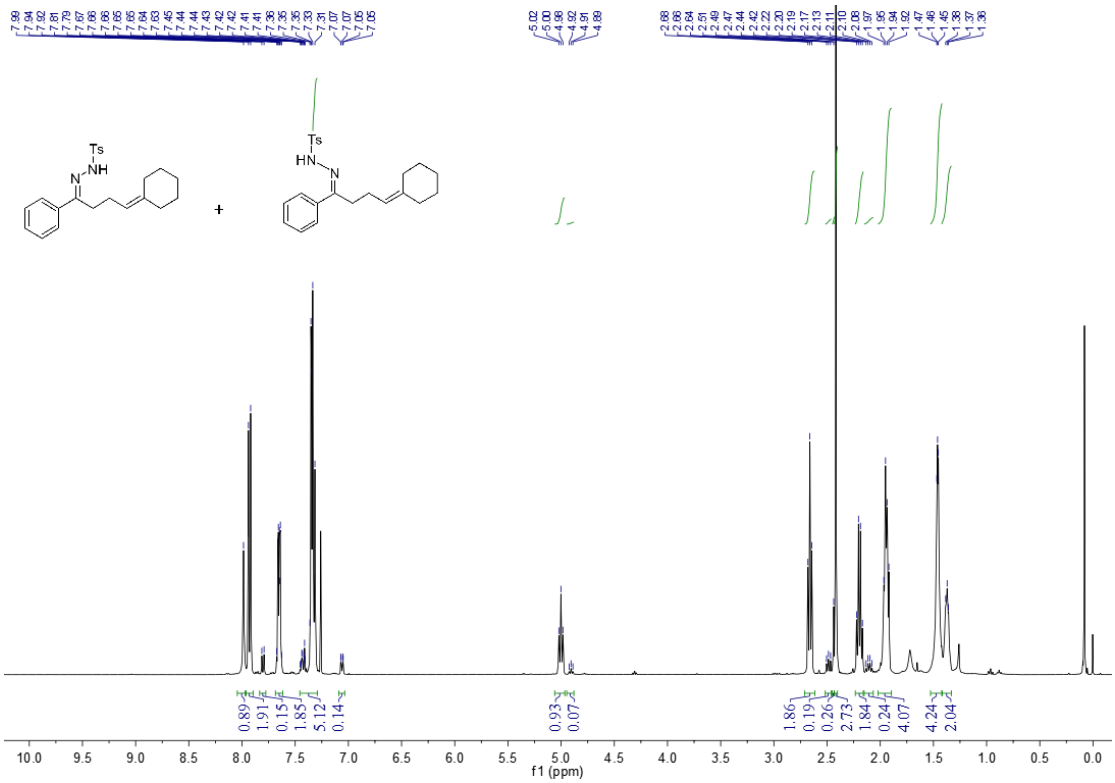
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ib**



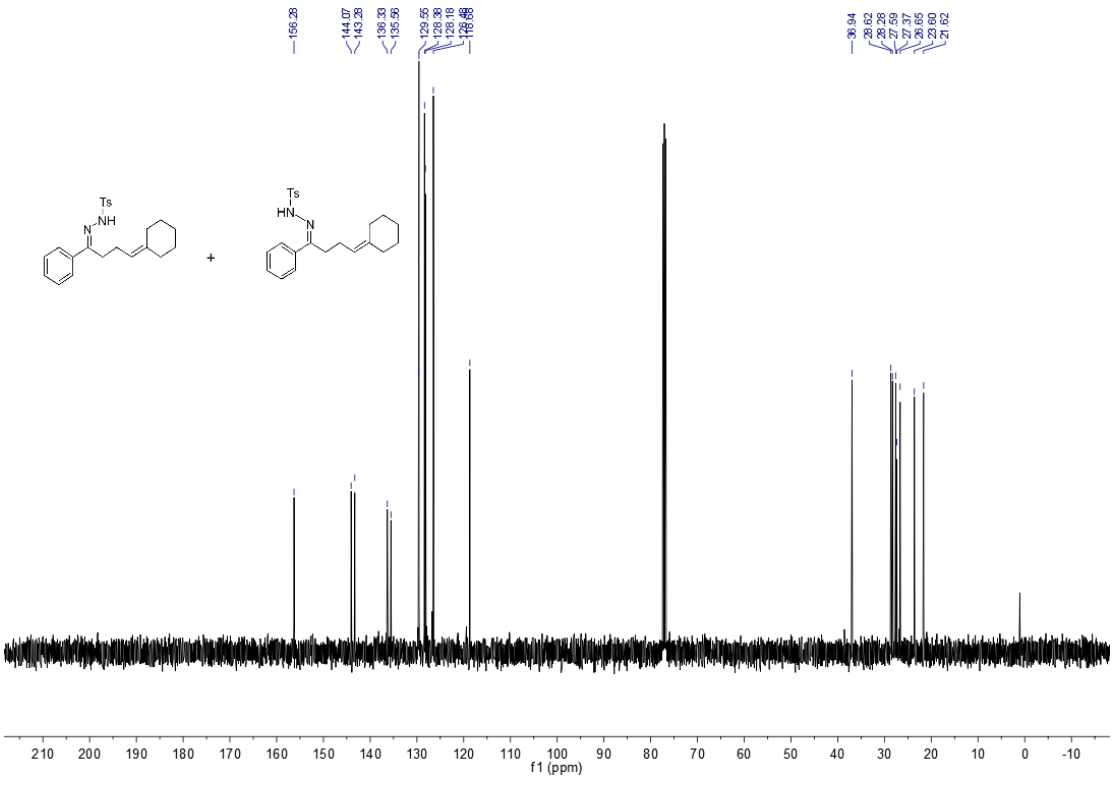
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ib**



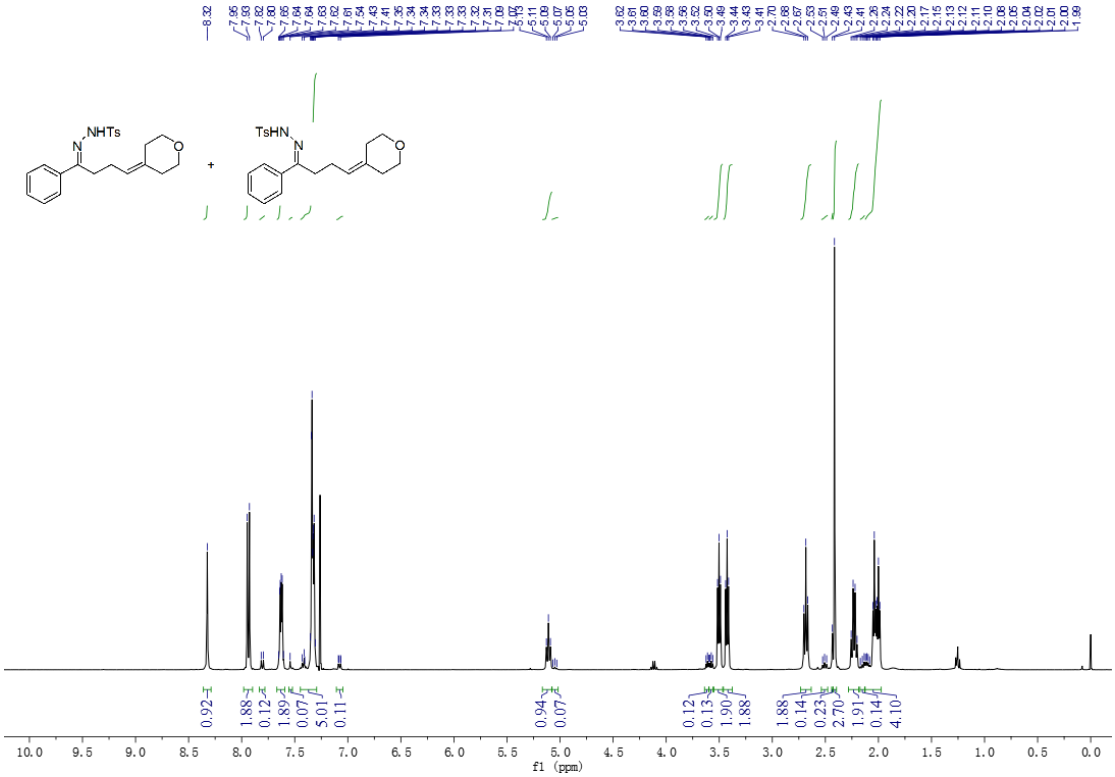
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1jb**



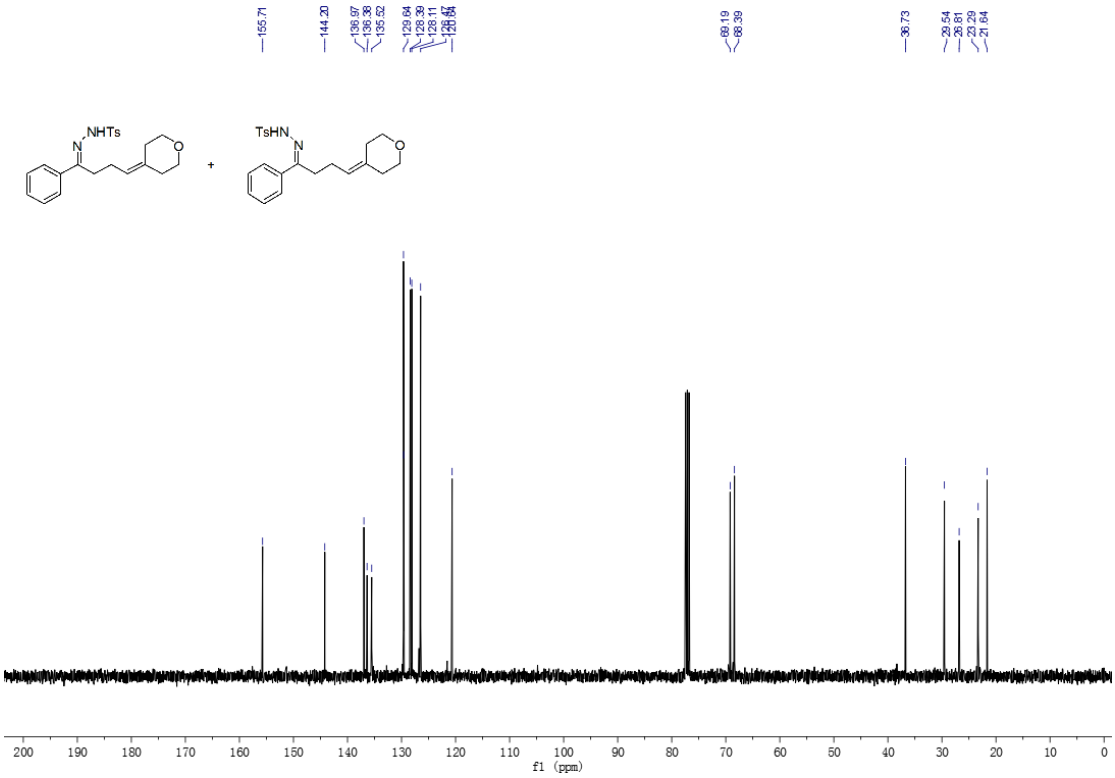
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1jb**



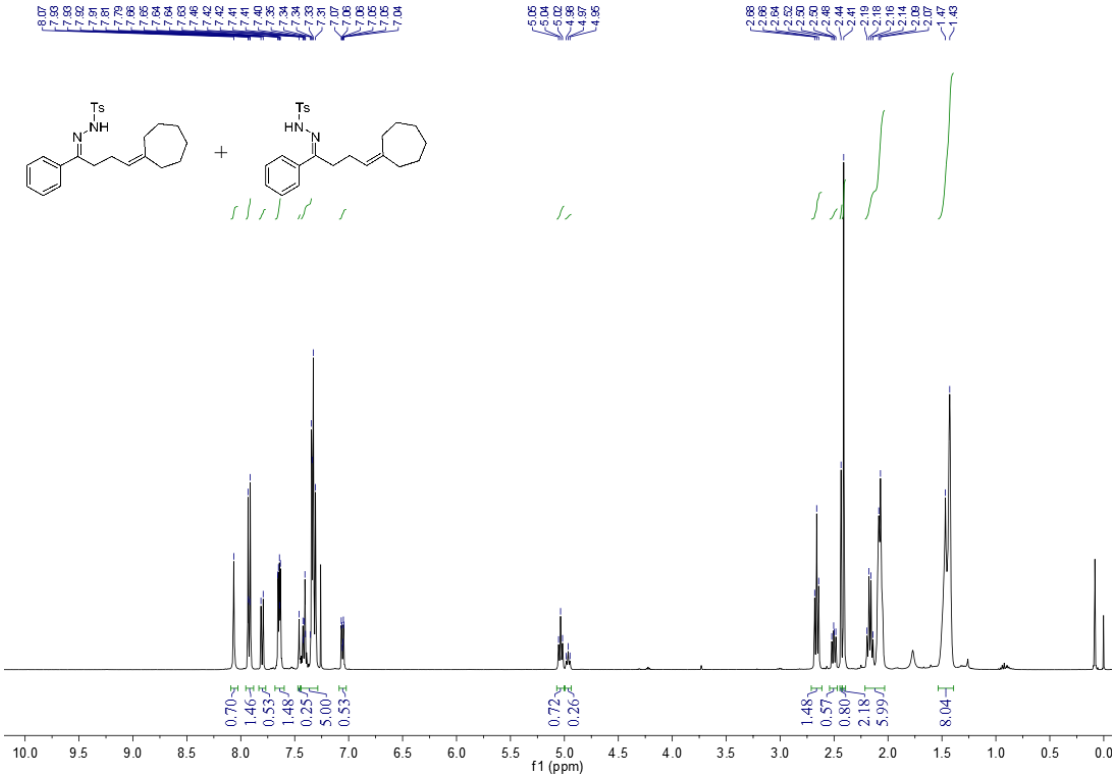
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1kb**



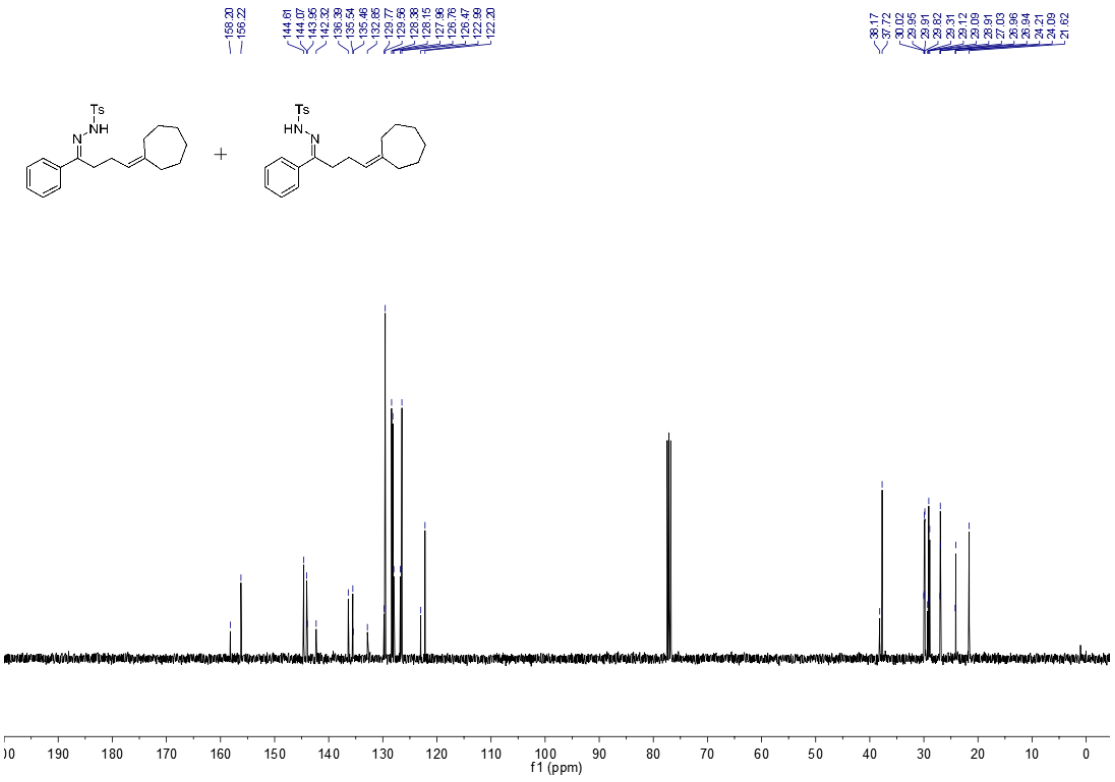
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1kb**



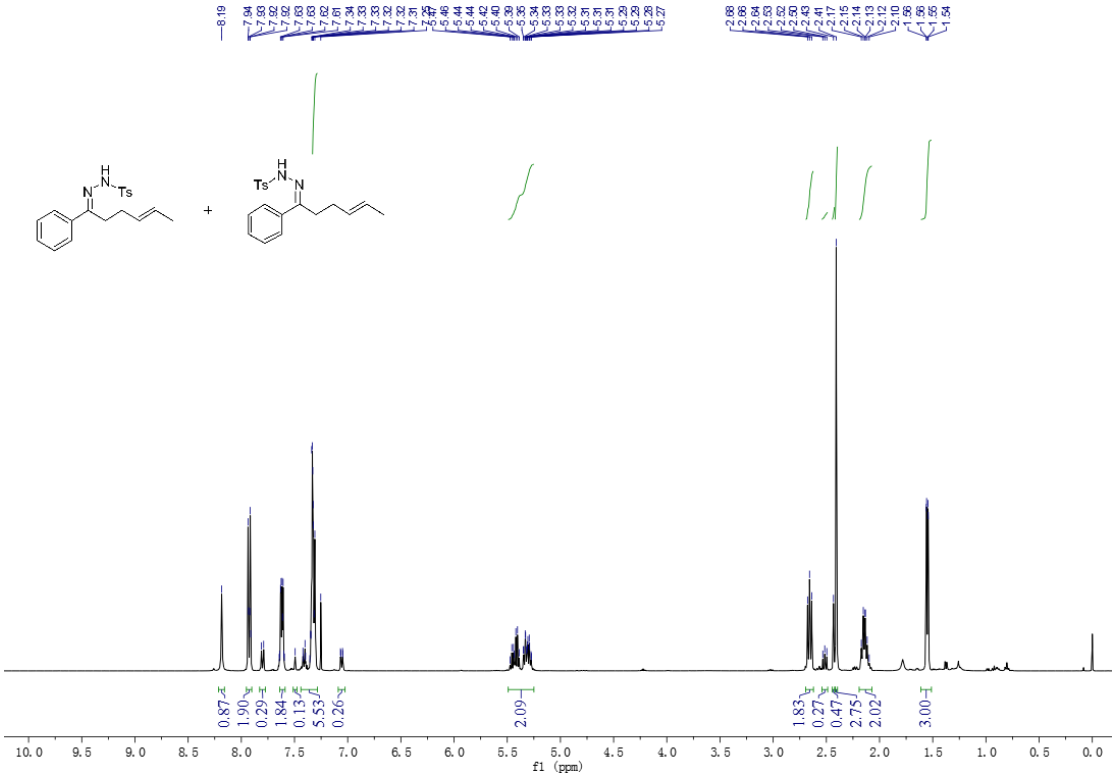
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1lb**



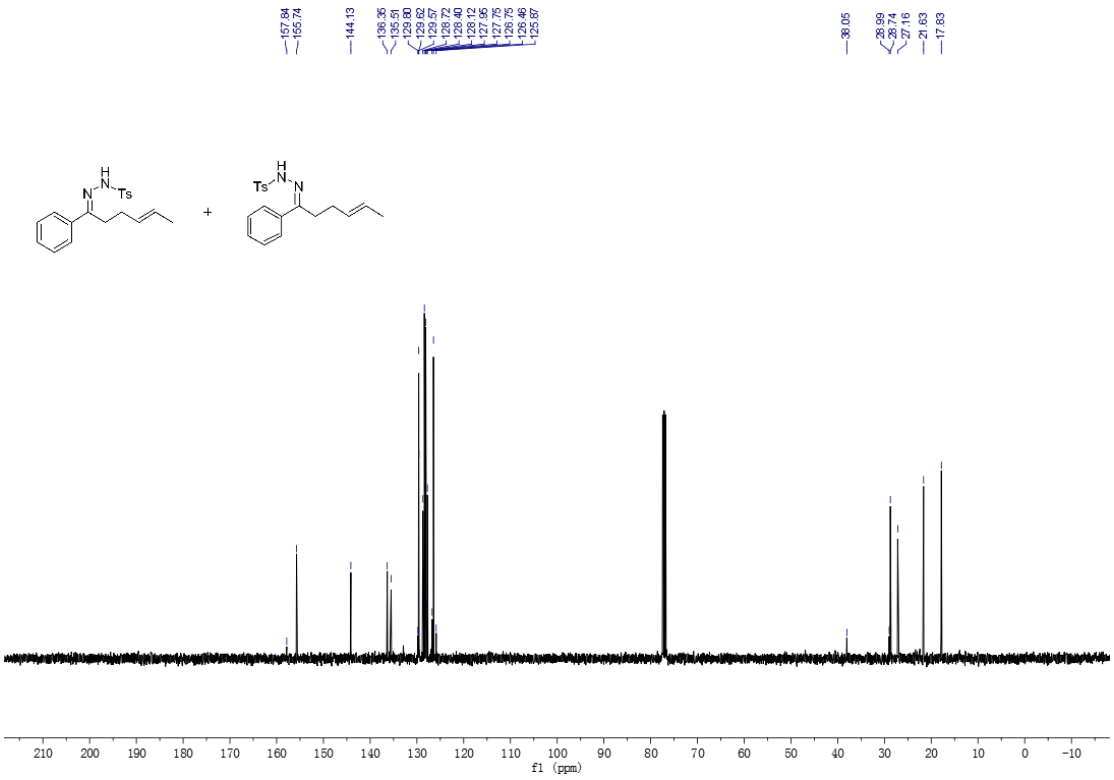
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1lb**



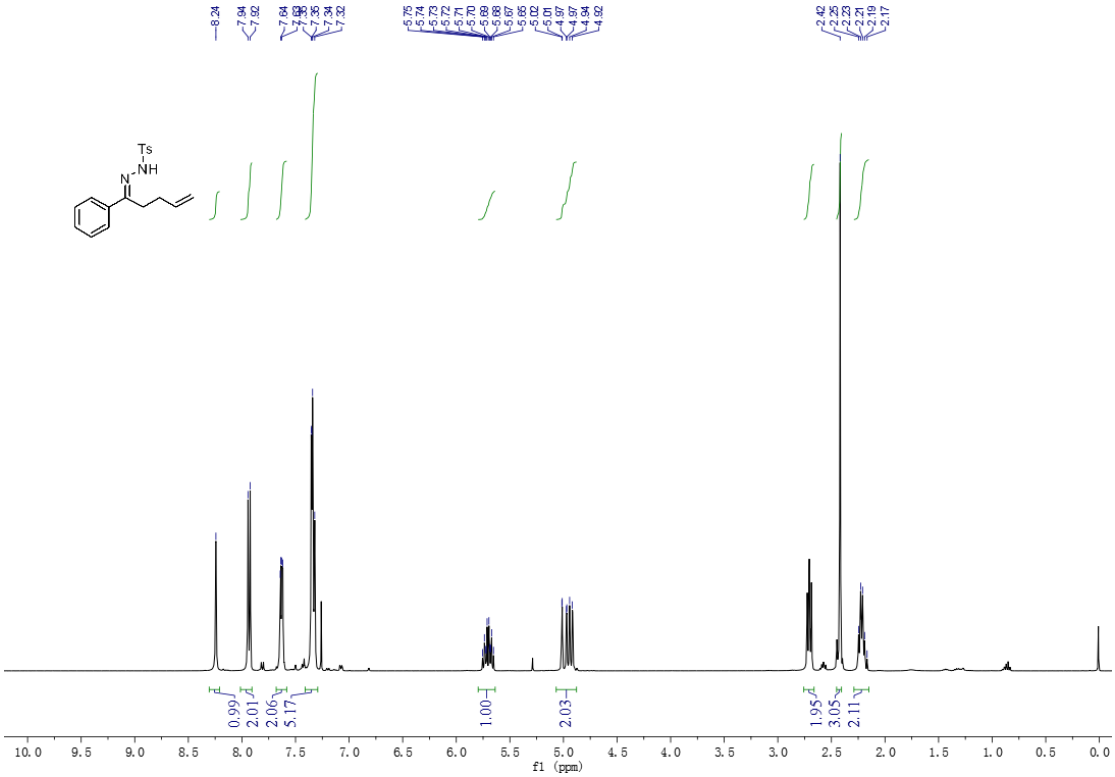
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **lmb**



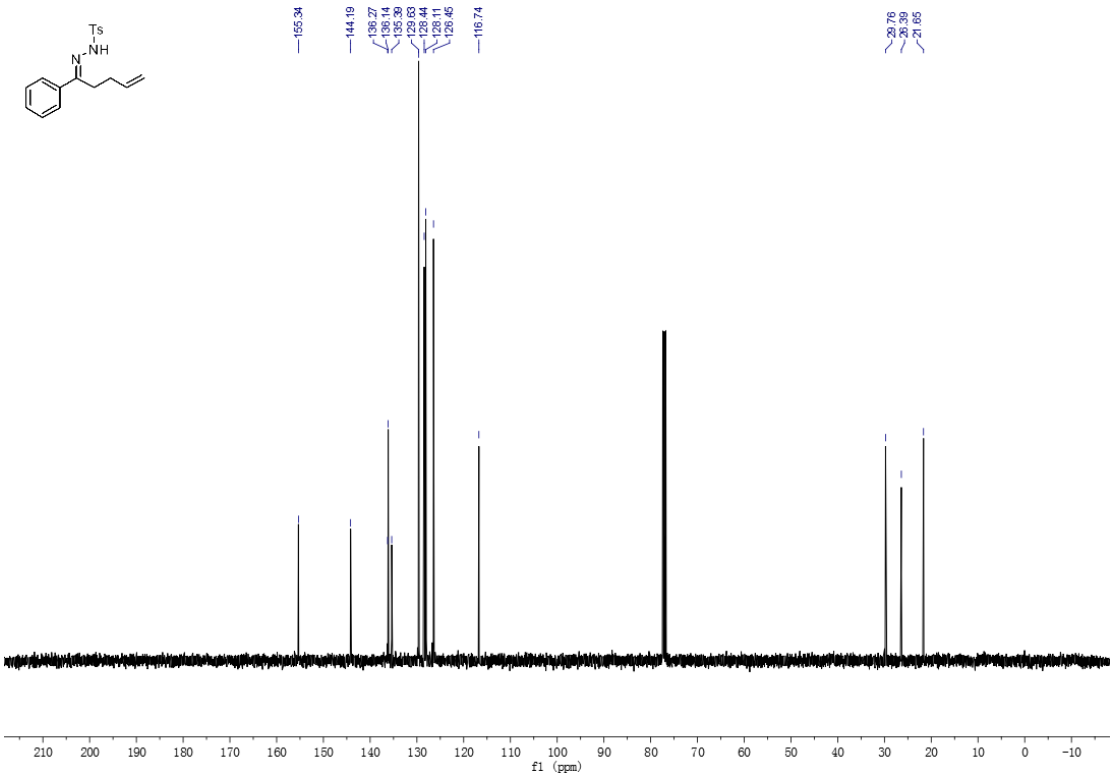
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **lmb**



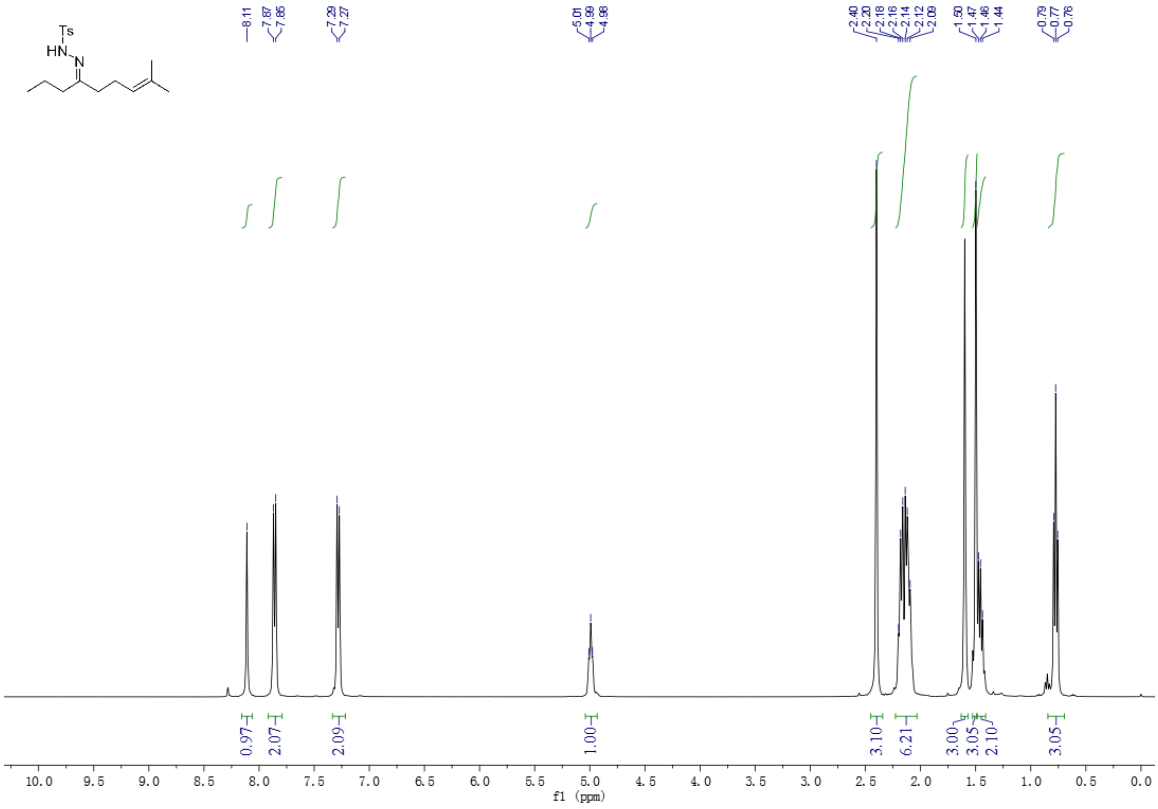
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1nb**



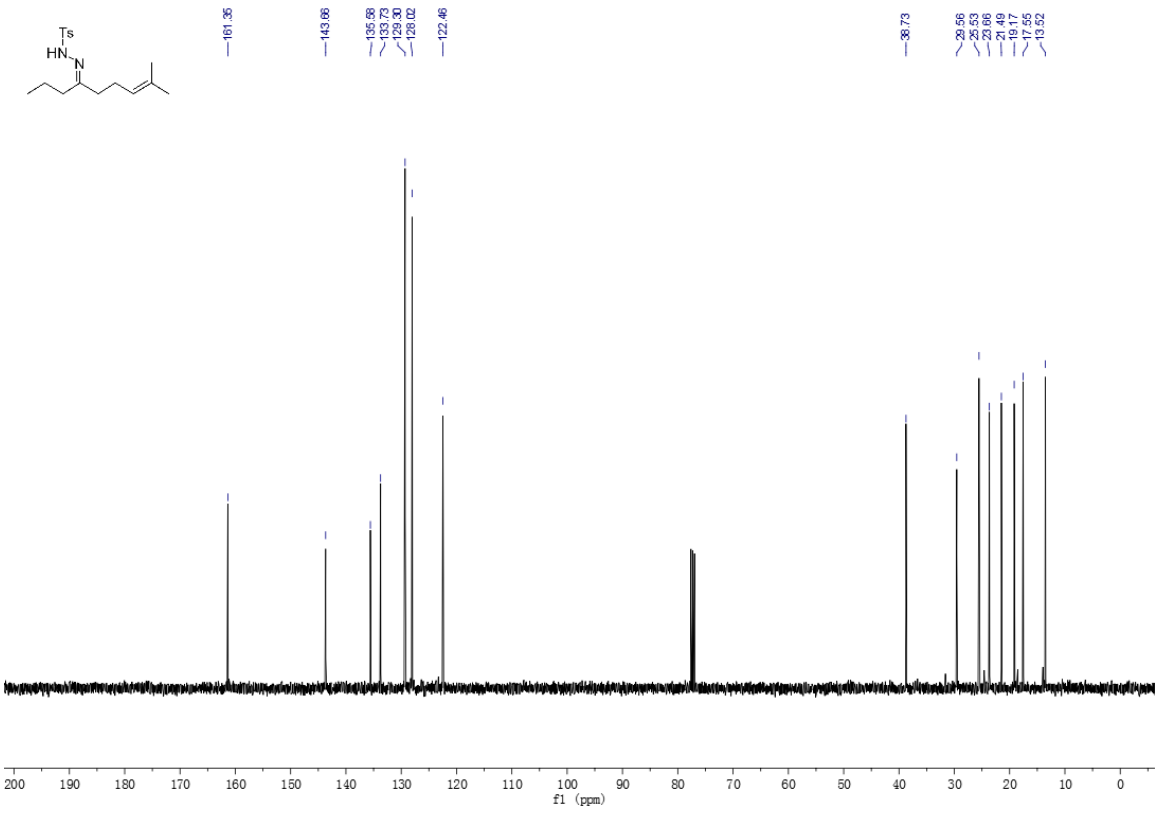
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1nb**



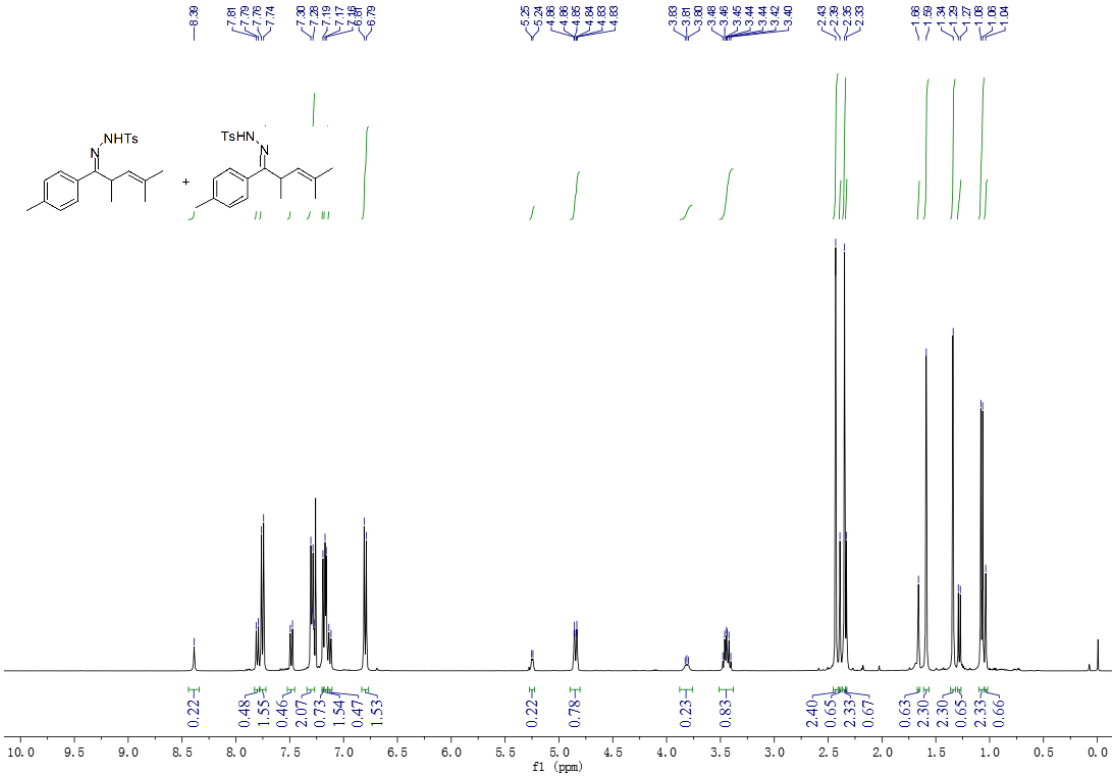
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **1ob**



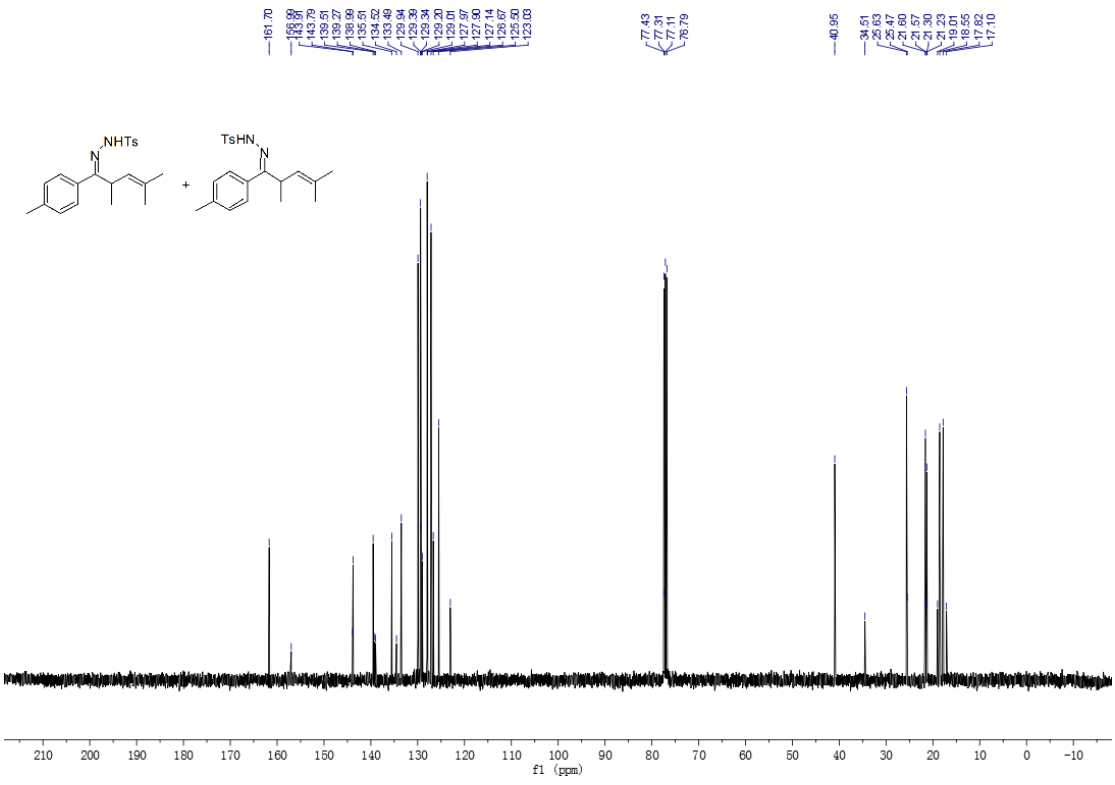
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **1ob**



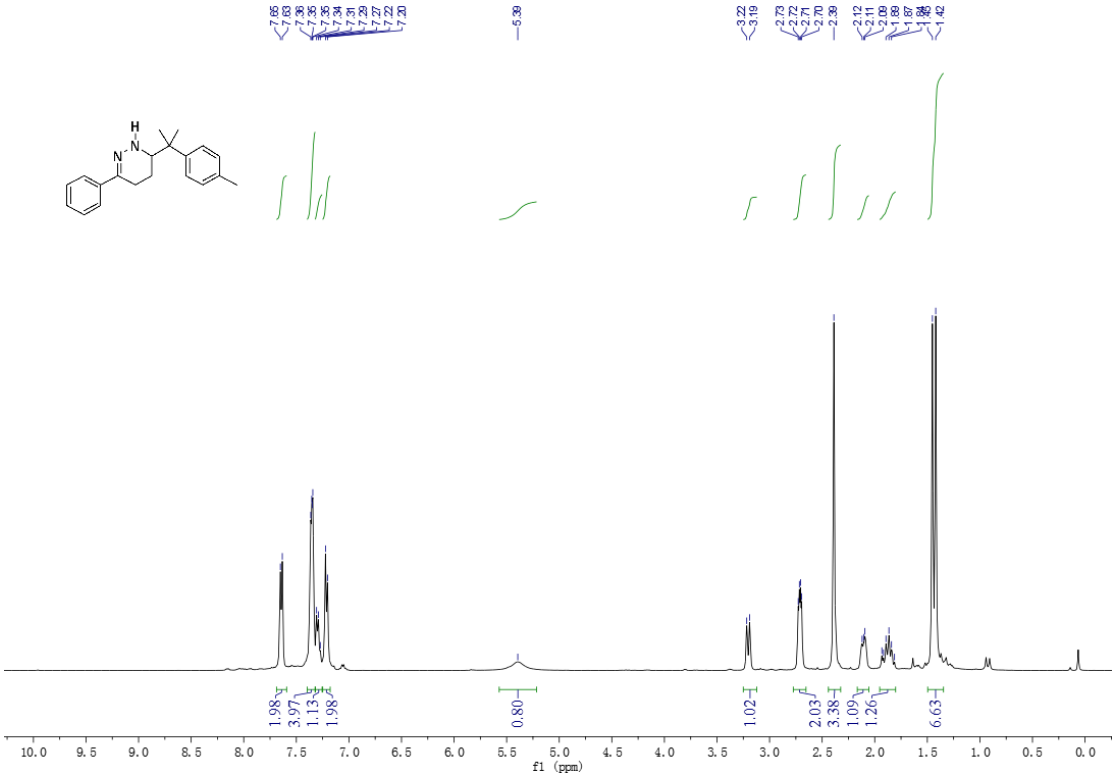
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **3**



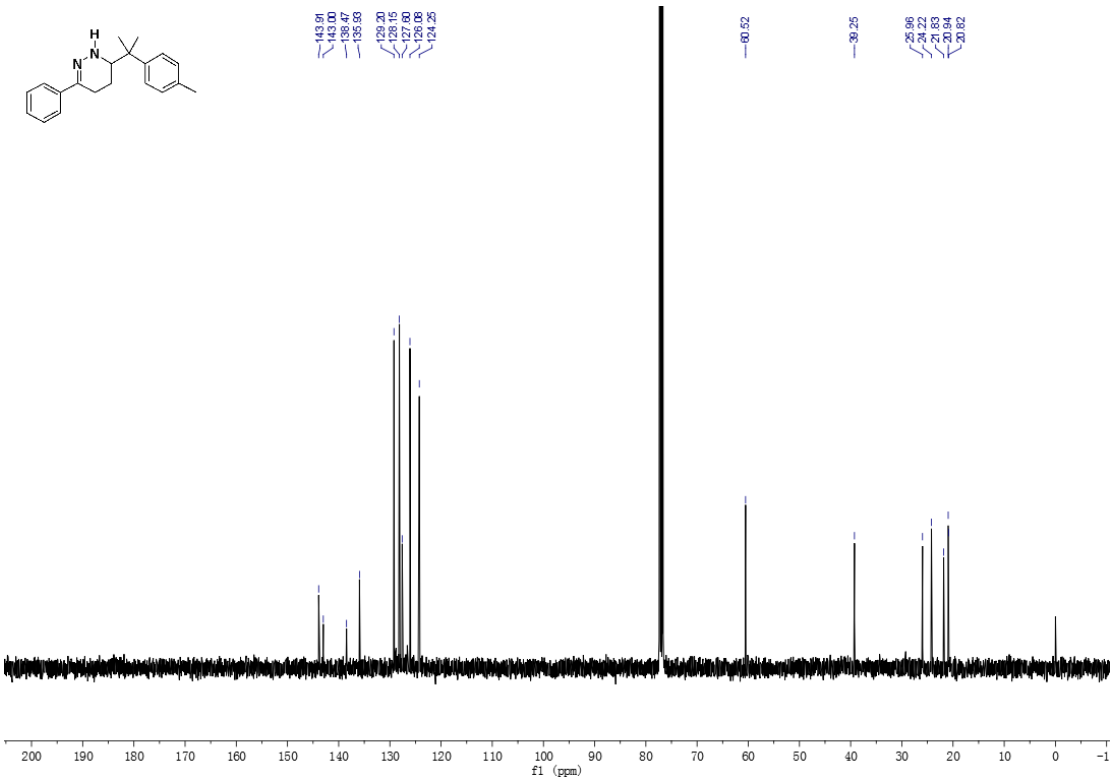
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **3**



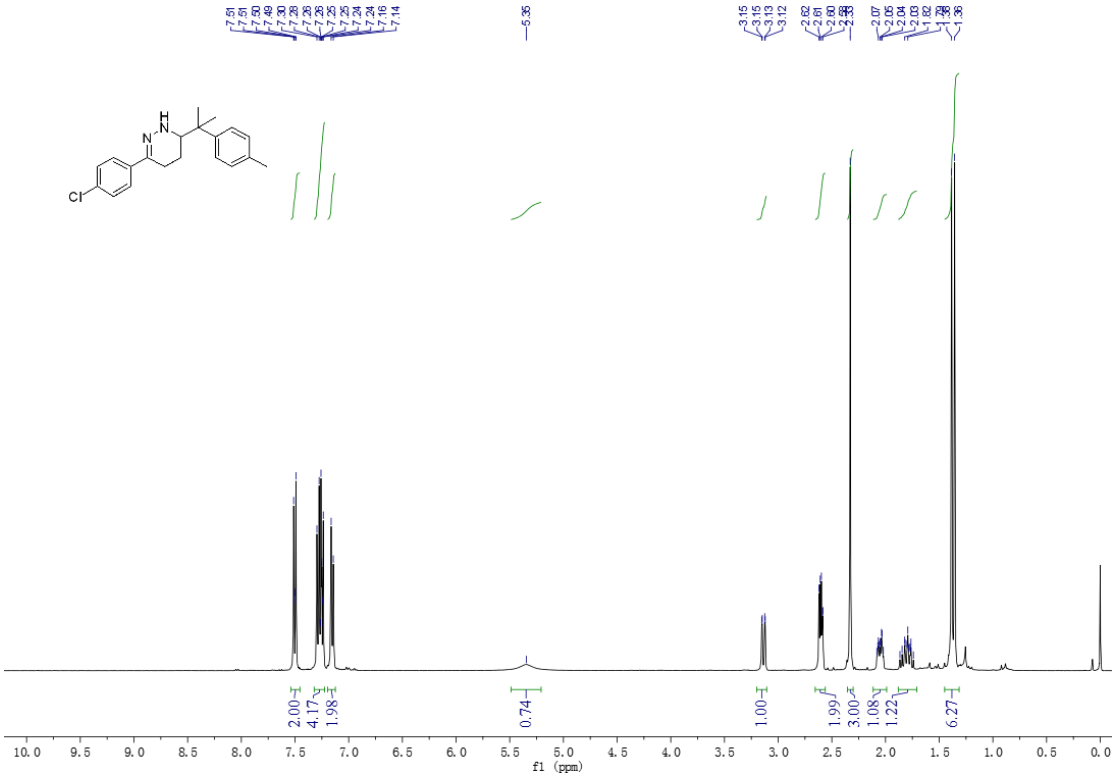
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2aa**



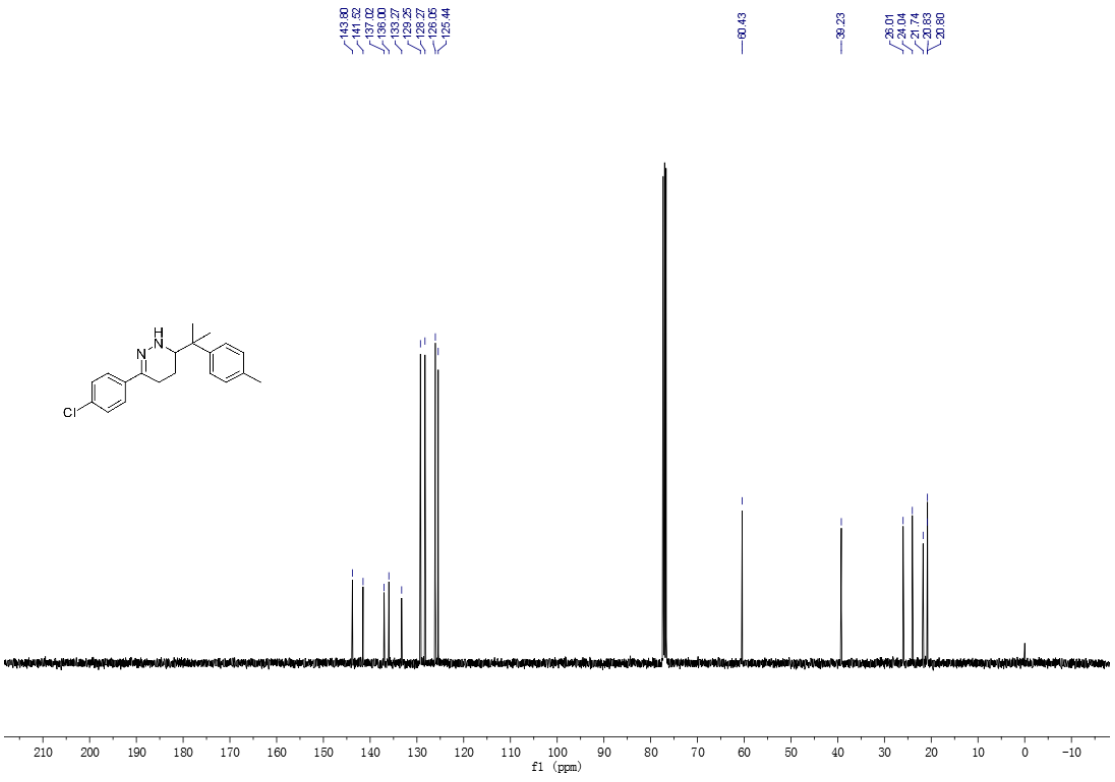
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2aa**



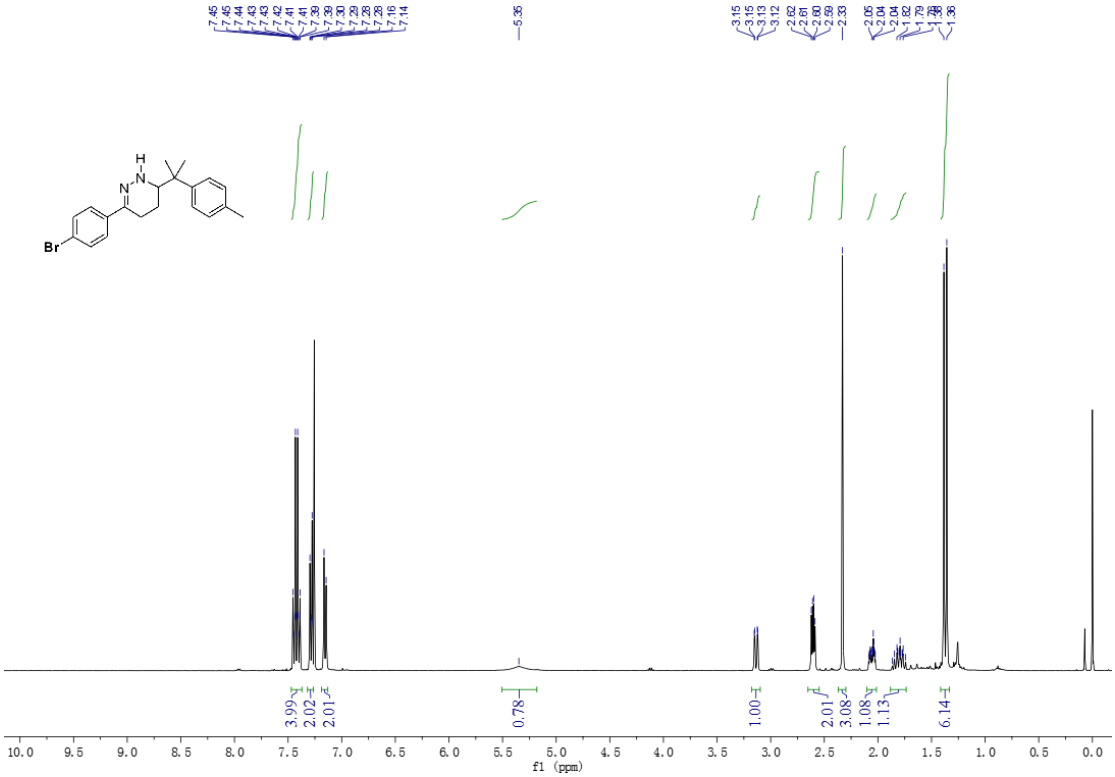
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ba**



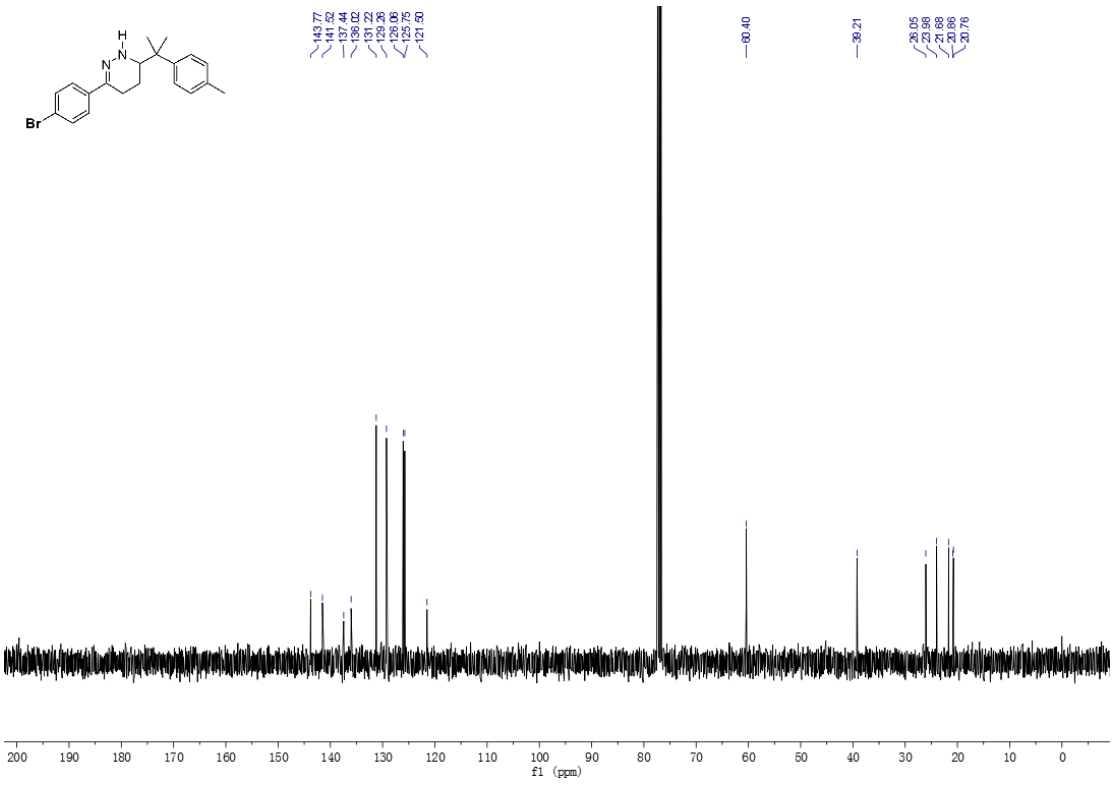
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2ba**



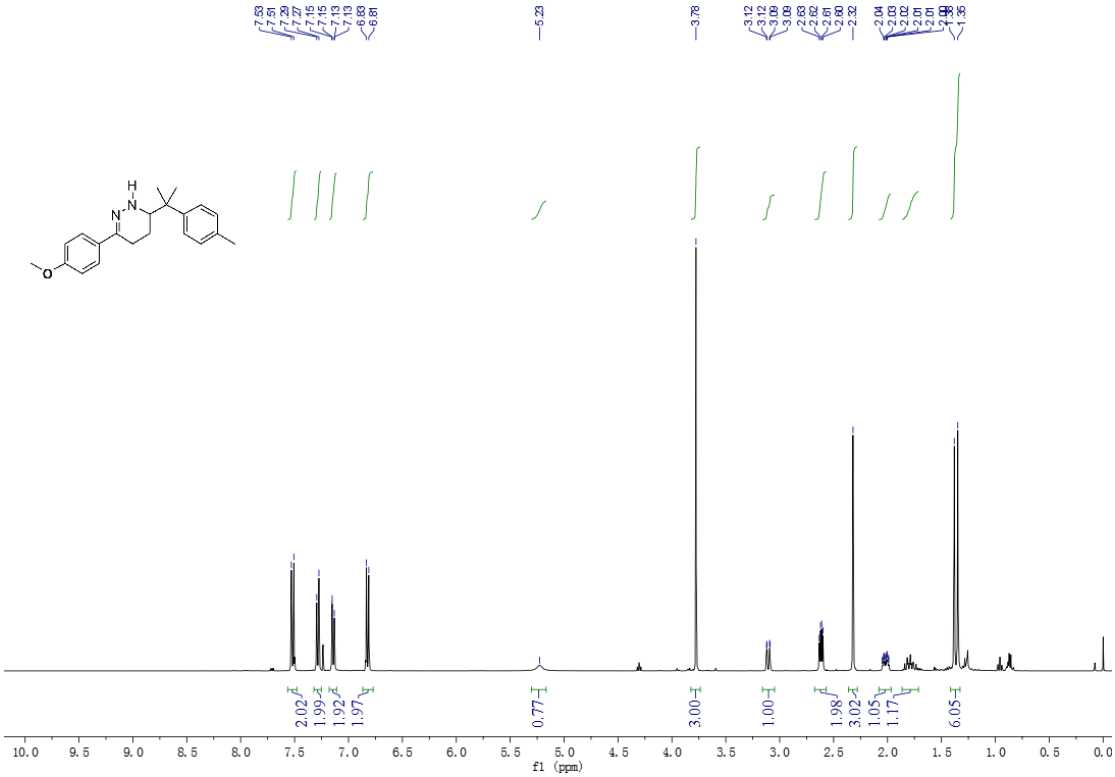
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ca**



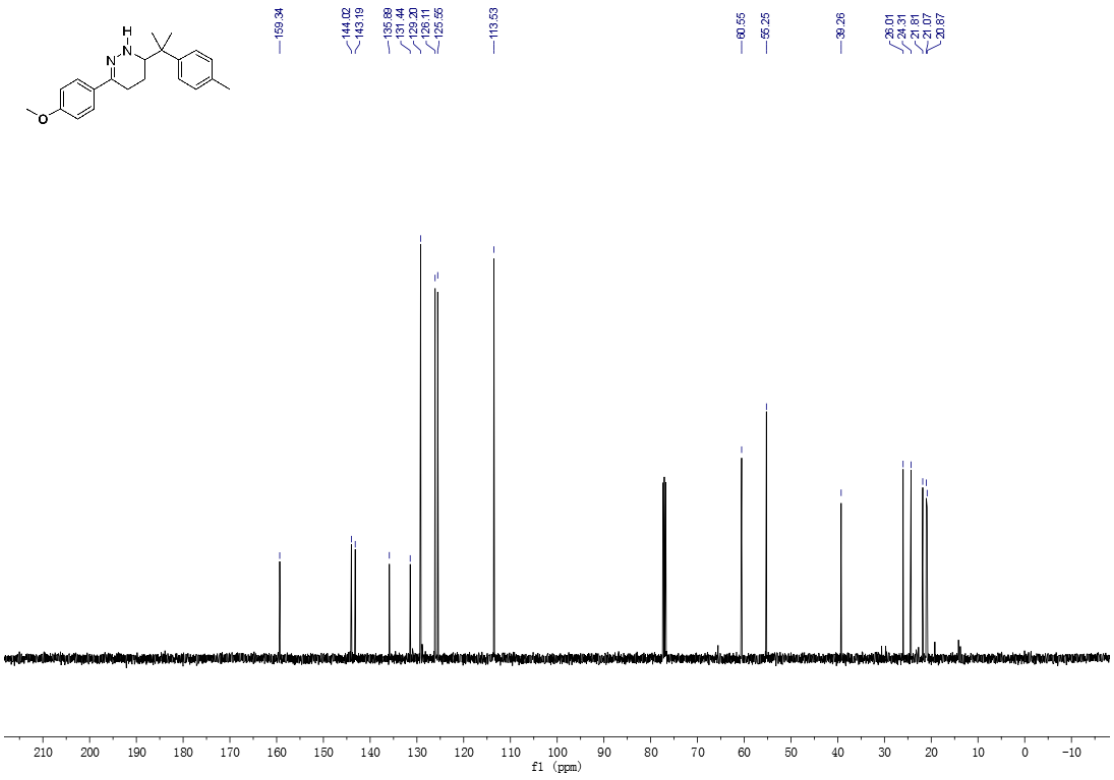
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ca**



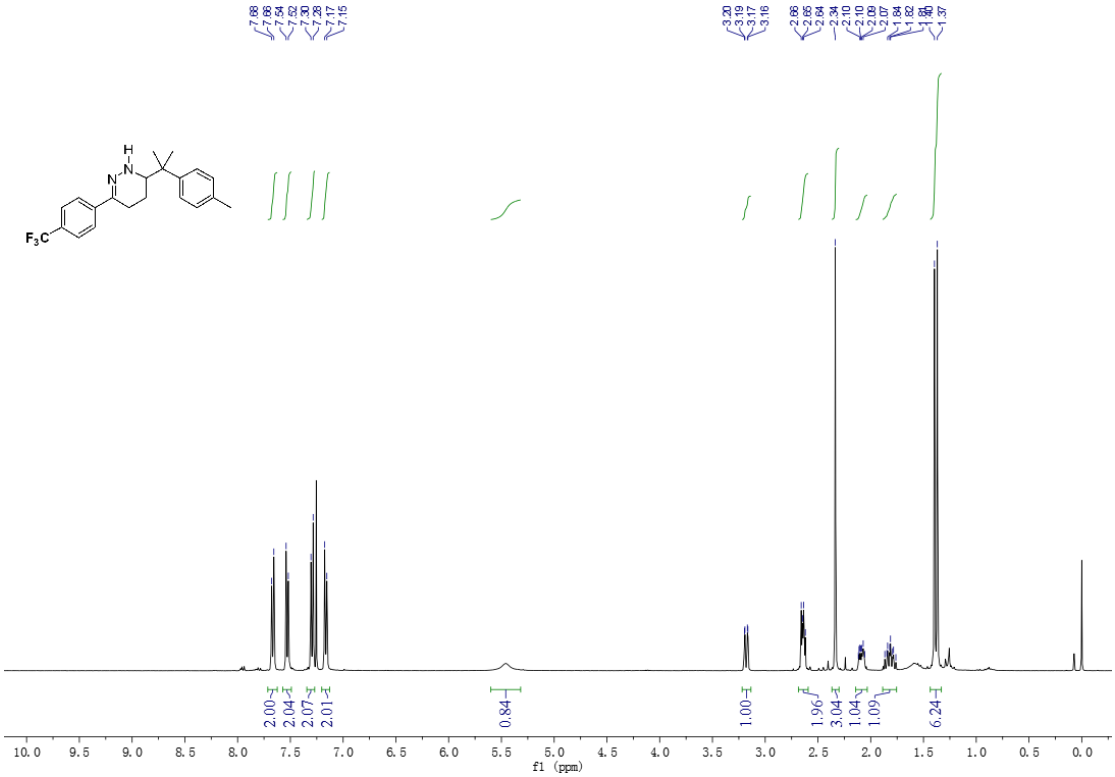
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2da**



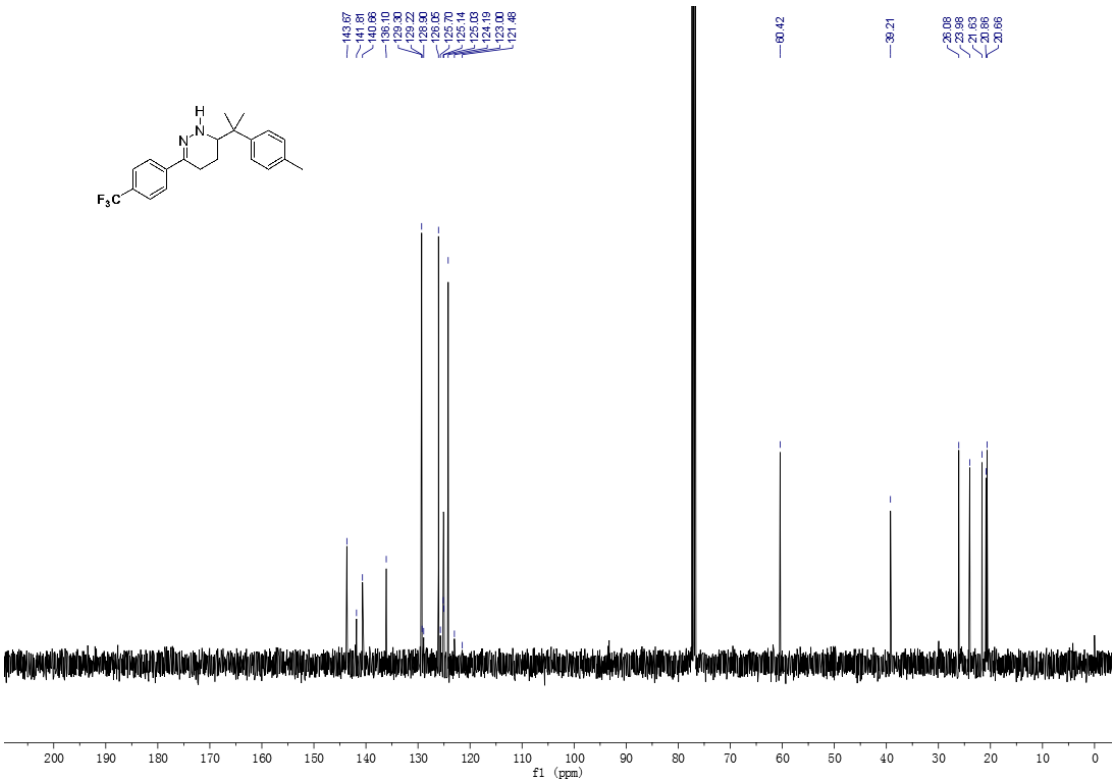
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2da**



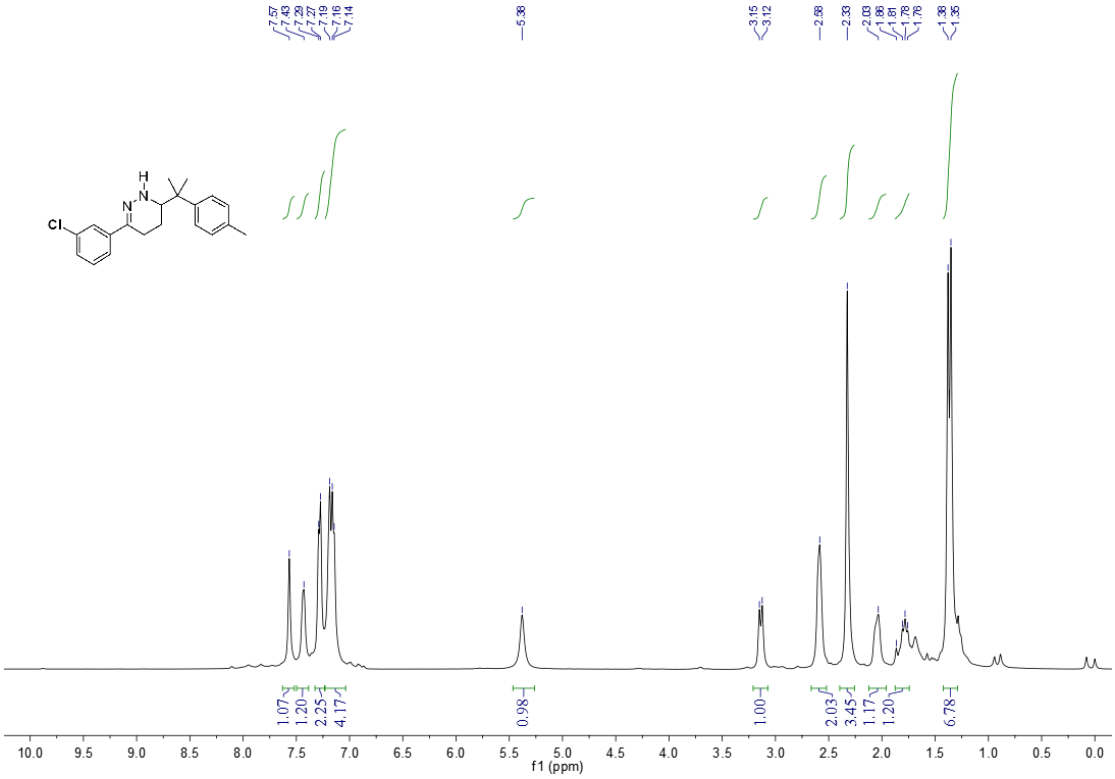
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ea**



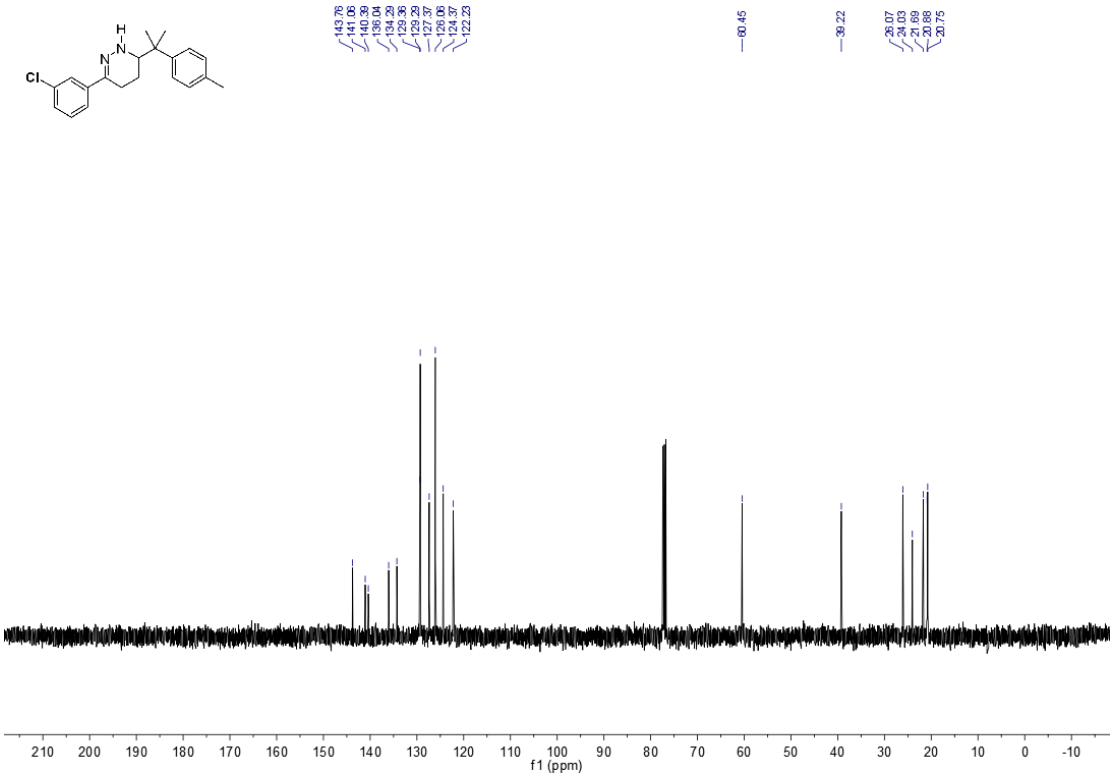
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ea**



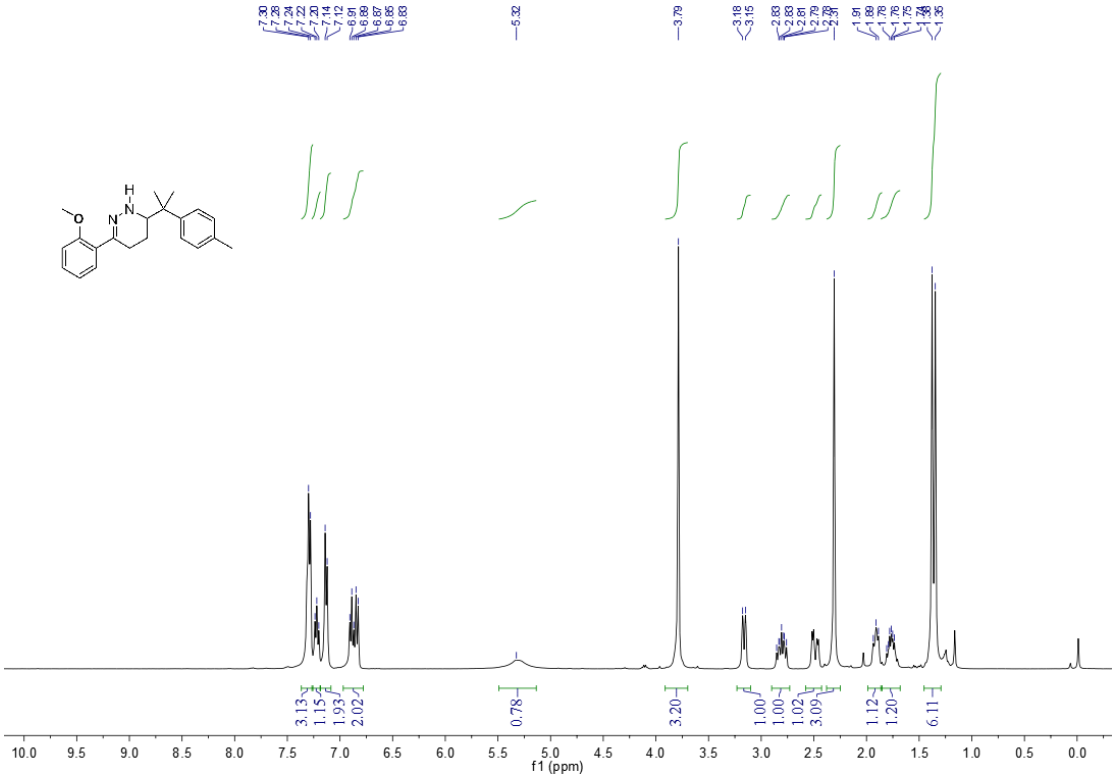
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2fa**



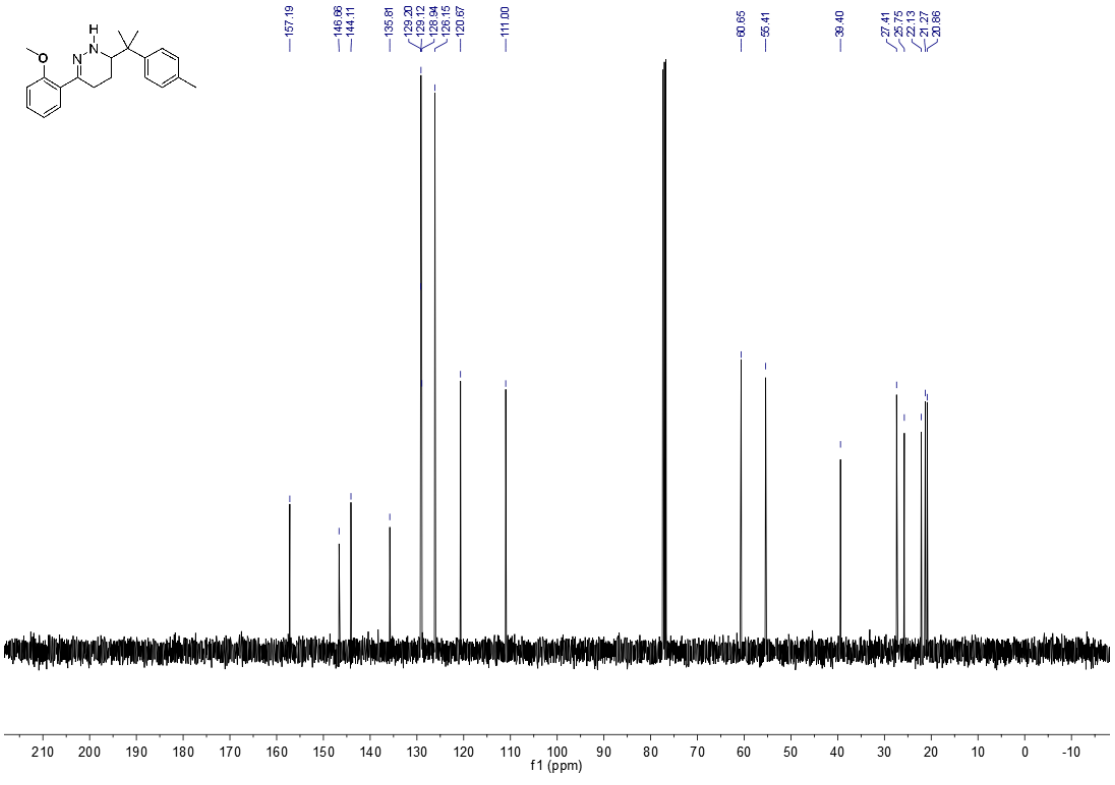
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2fa**



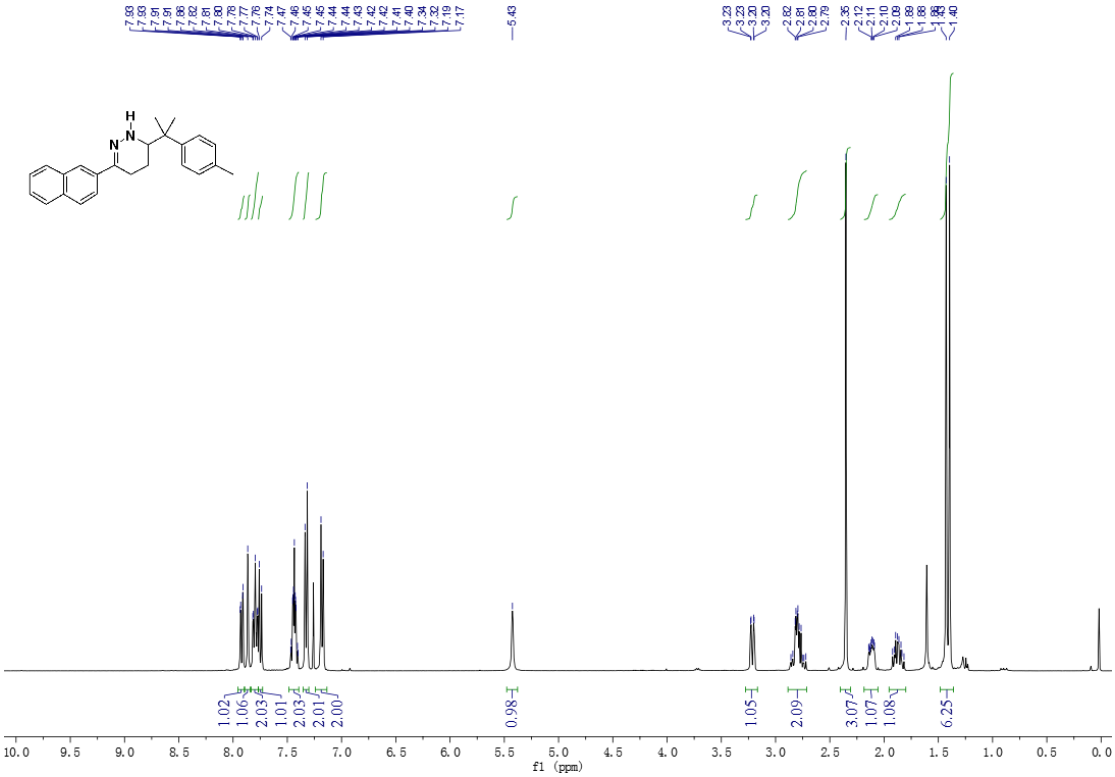
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ga**



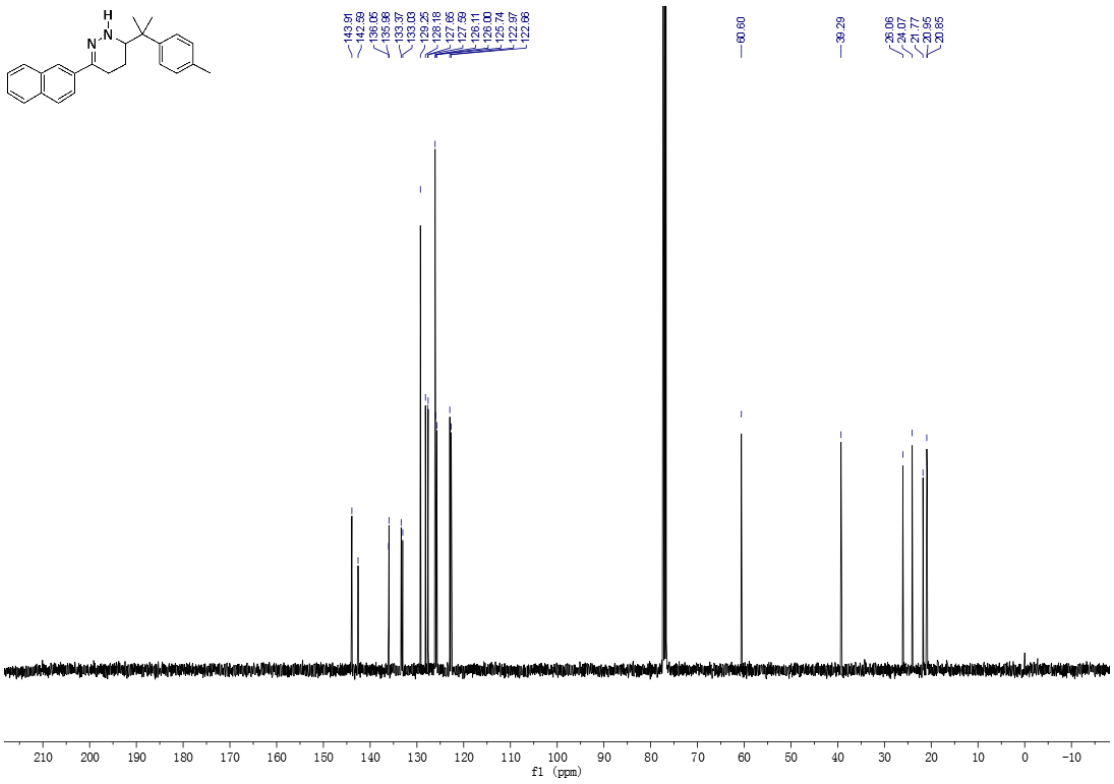
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ga**



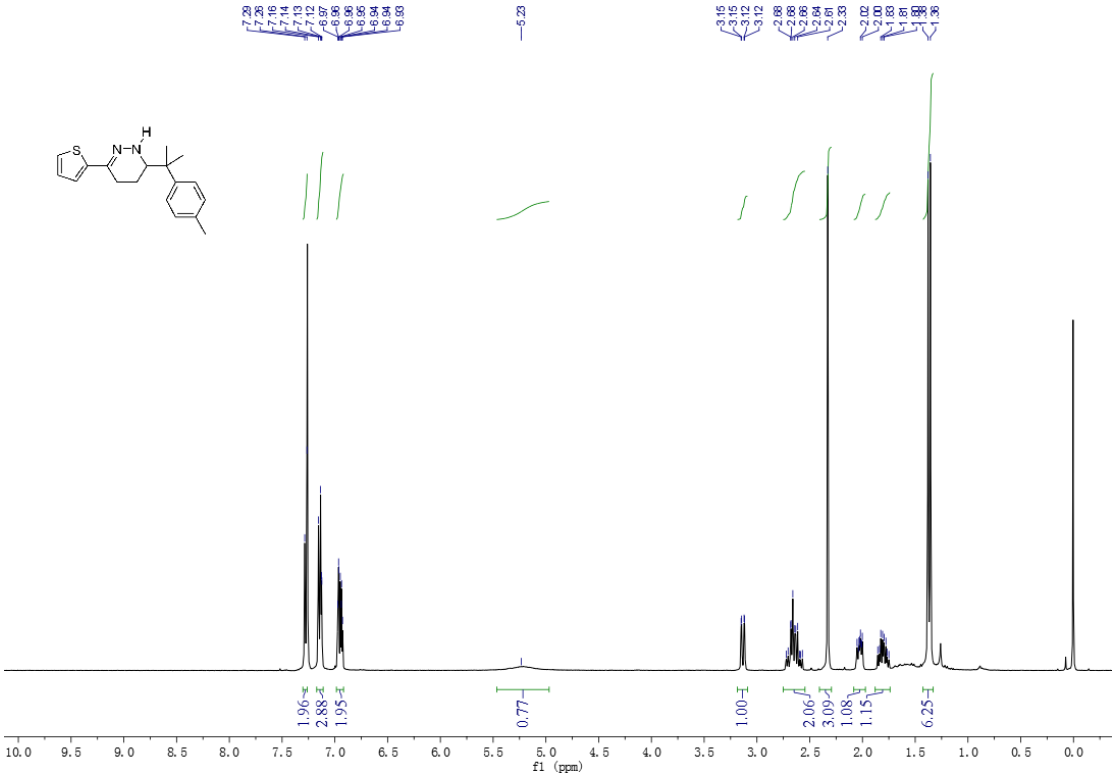
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ha**



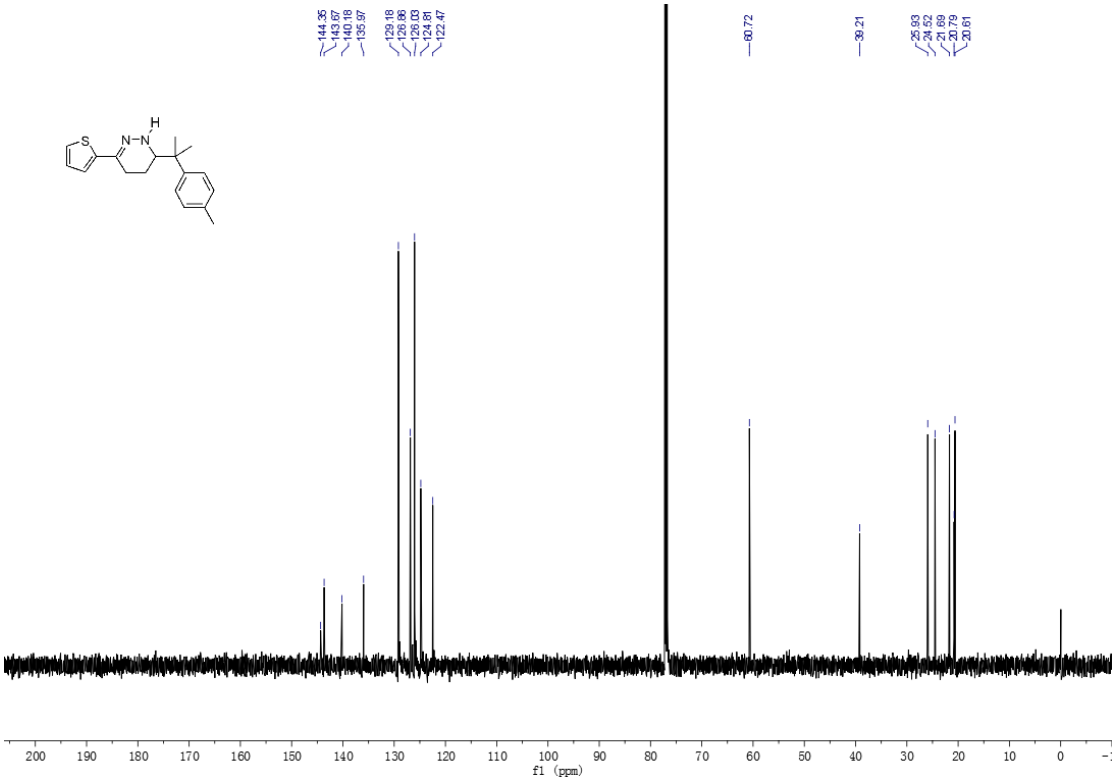
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ha**



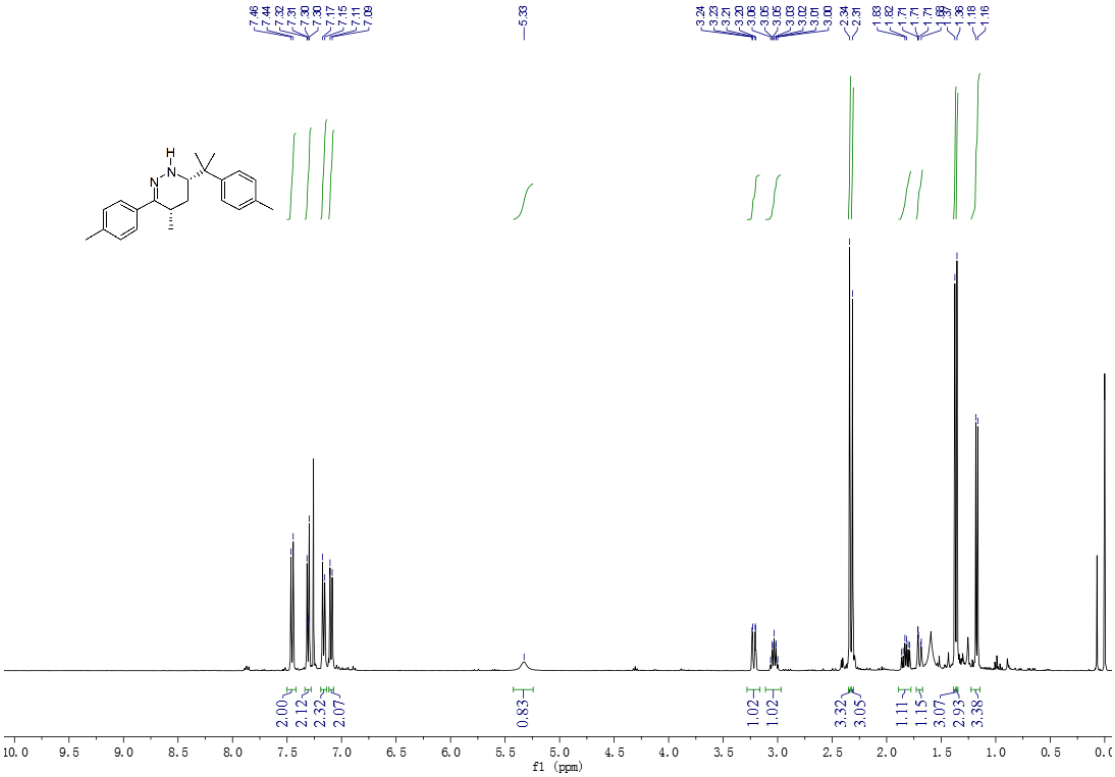
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ia**



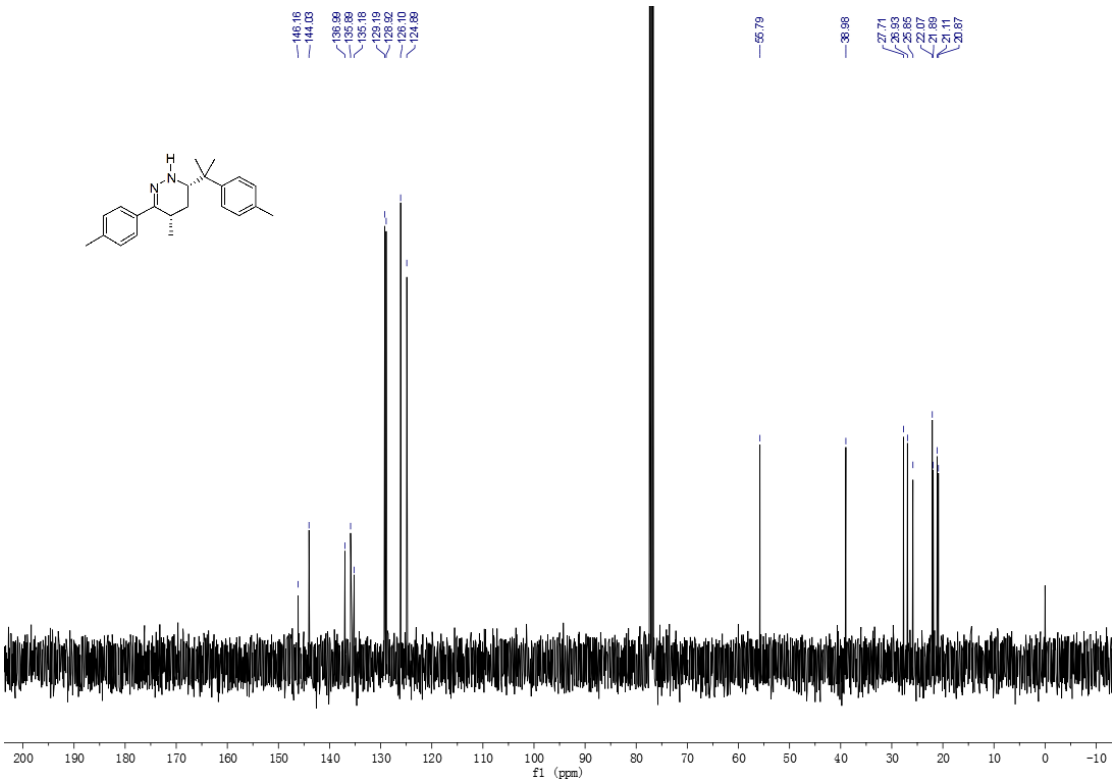
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 23 ºC) of **2ia**



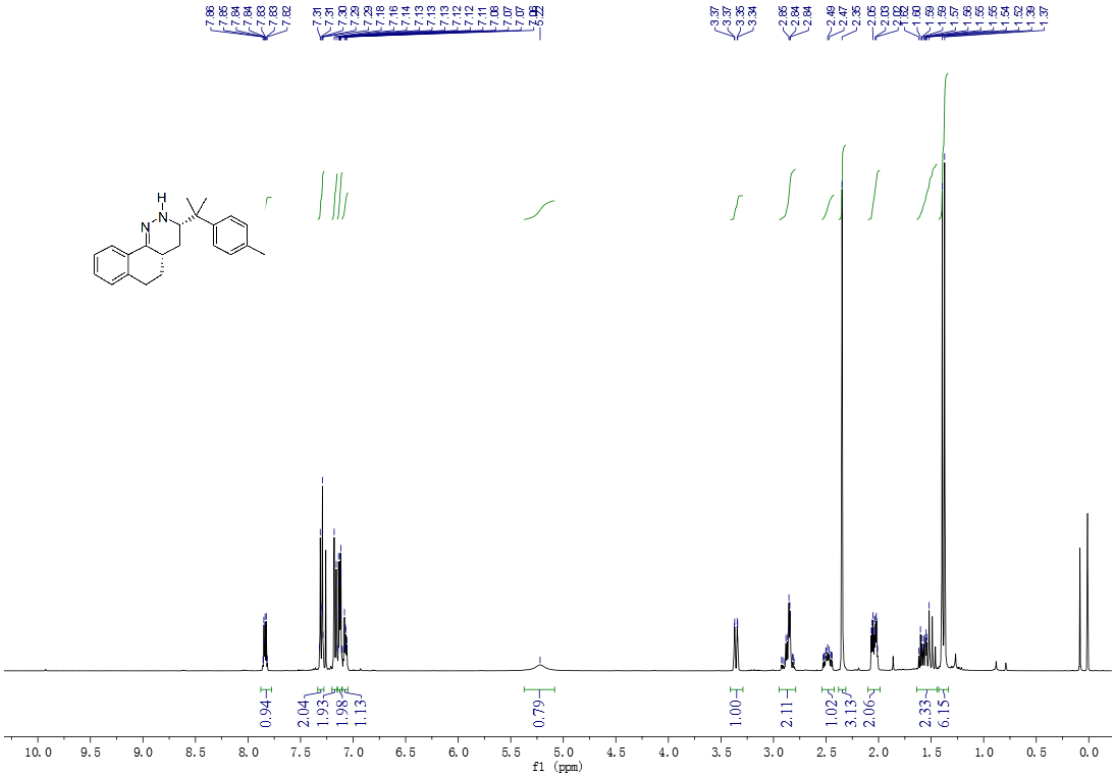
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ja**



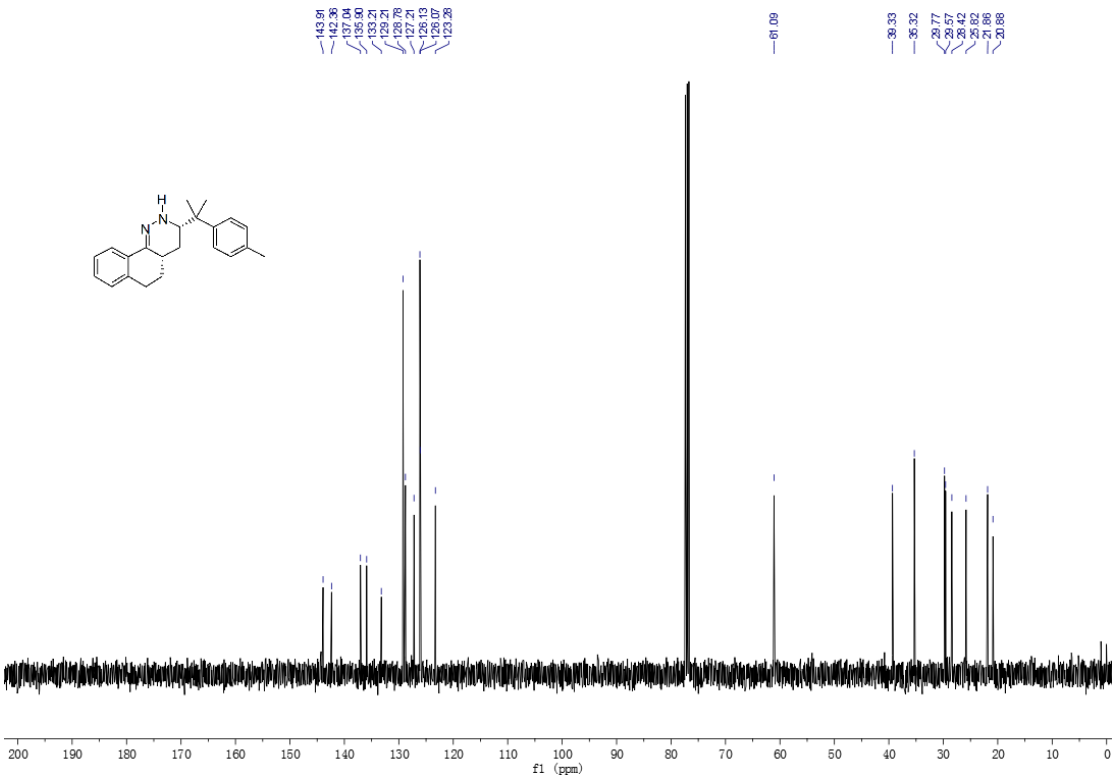
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ja**



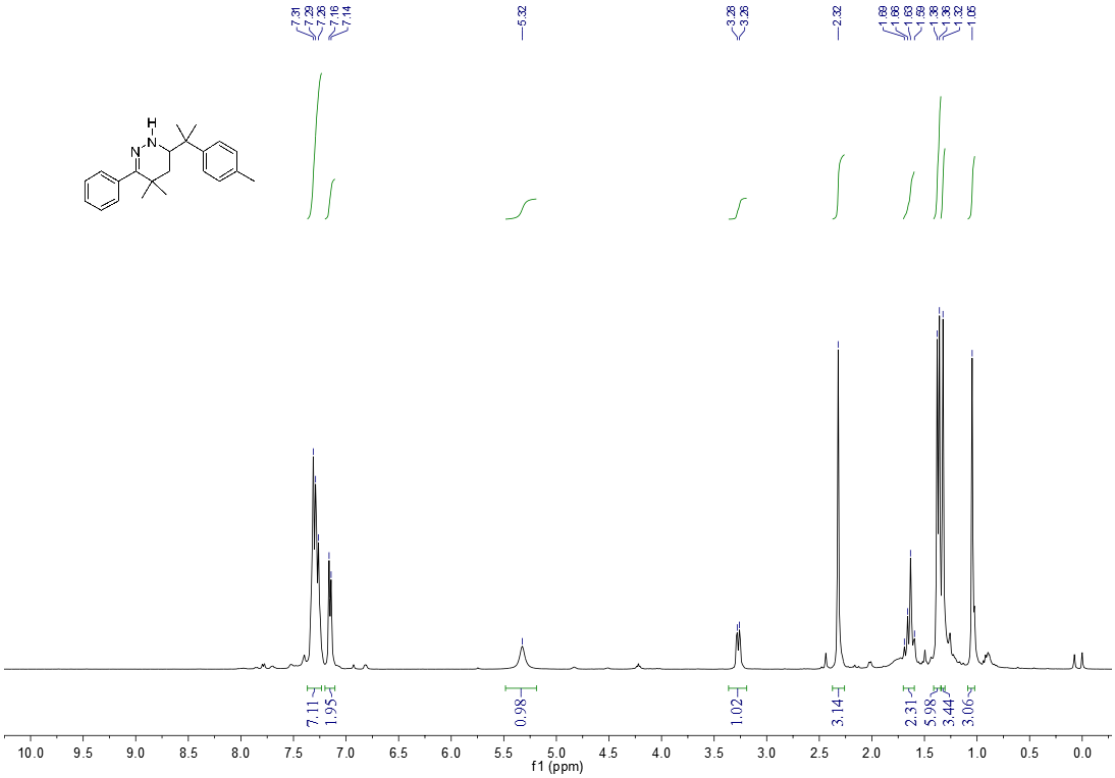
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ka**



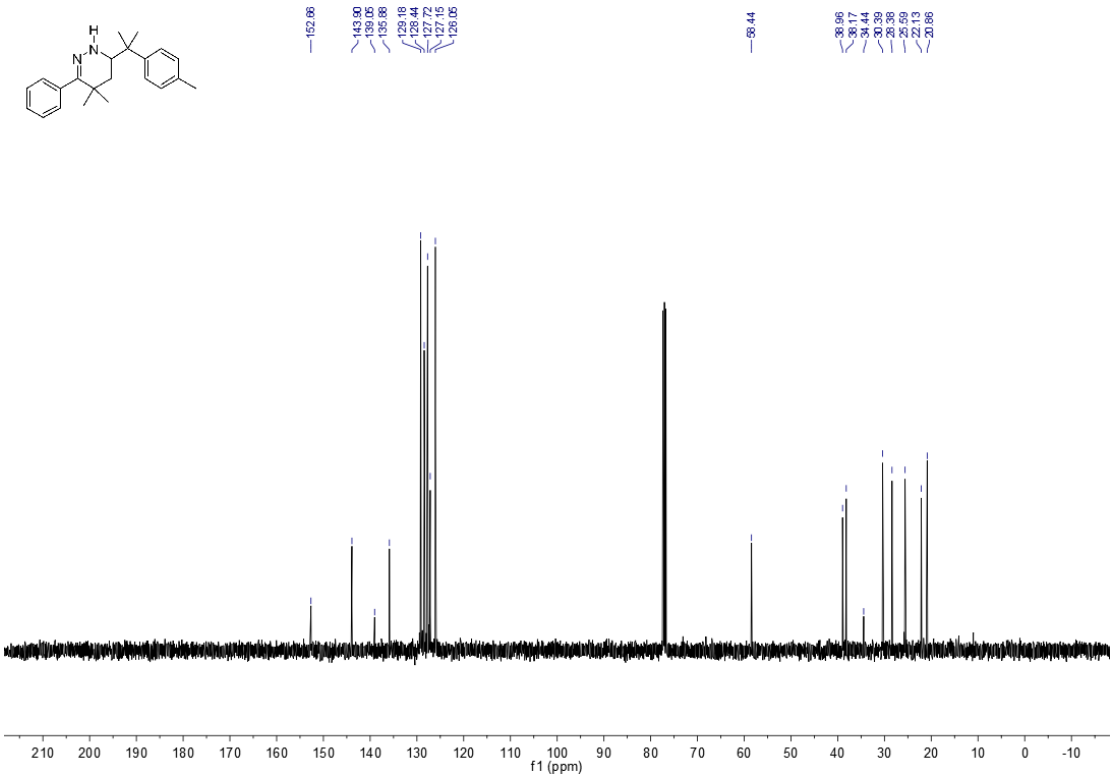
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ka**



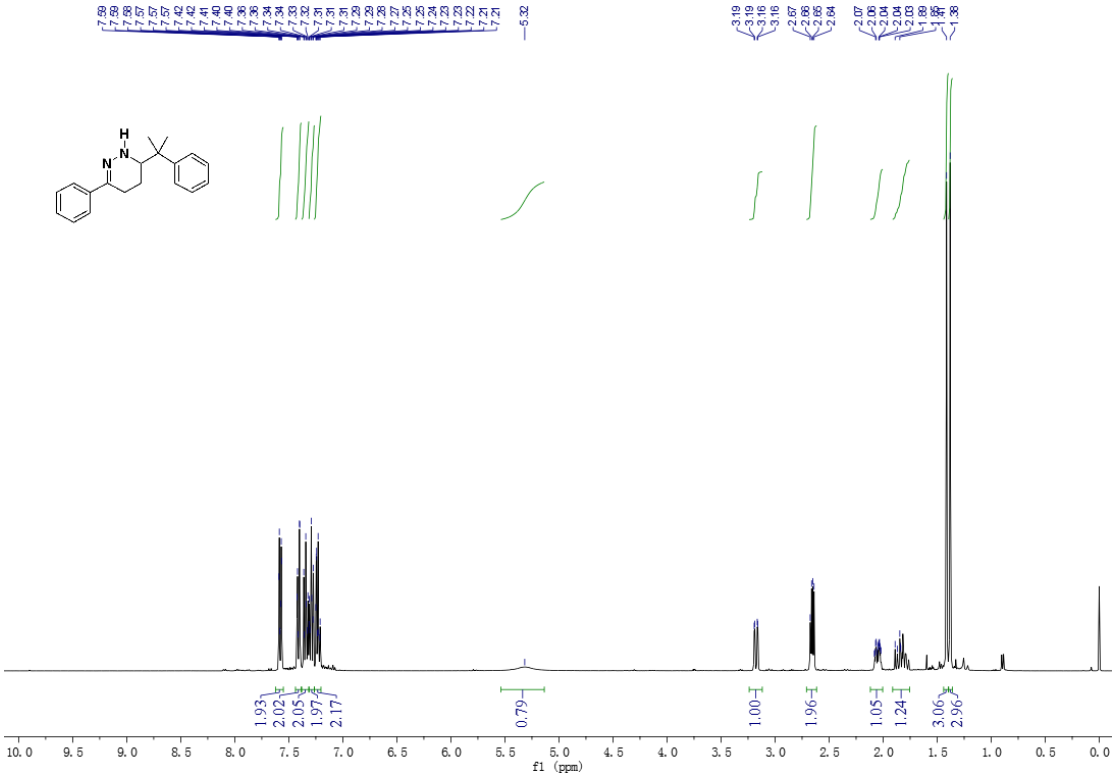
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2la**



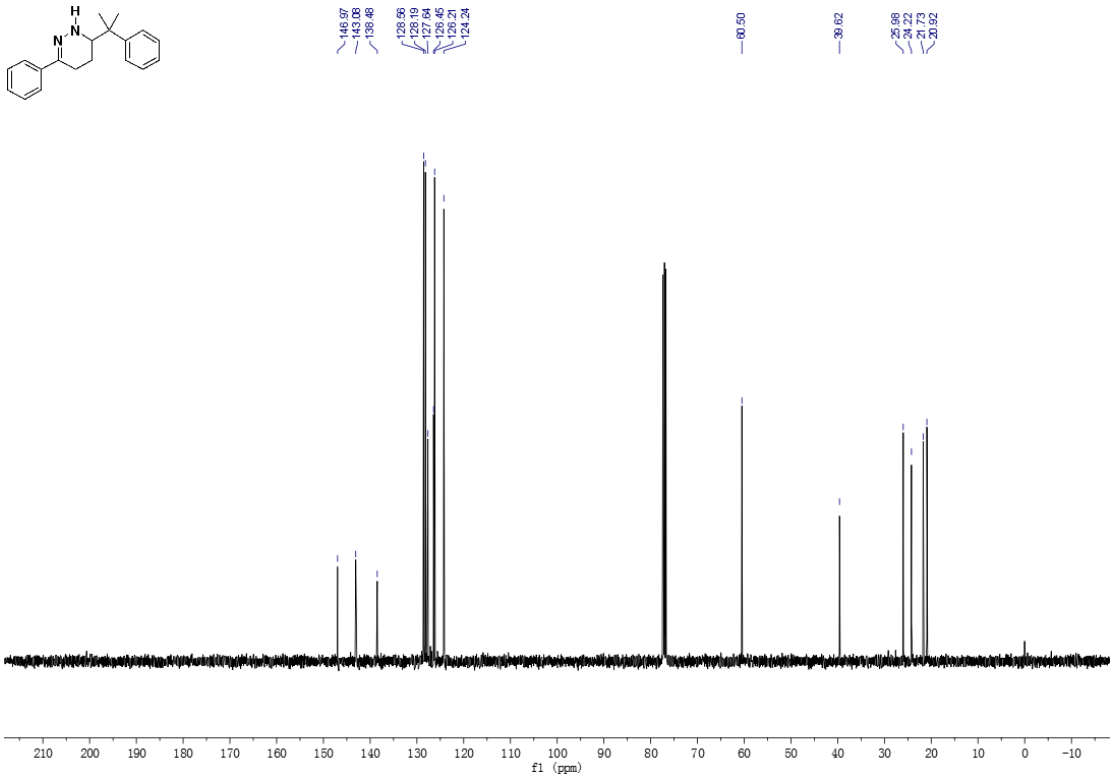
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2la**



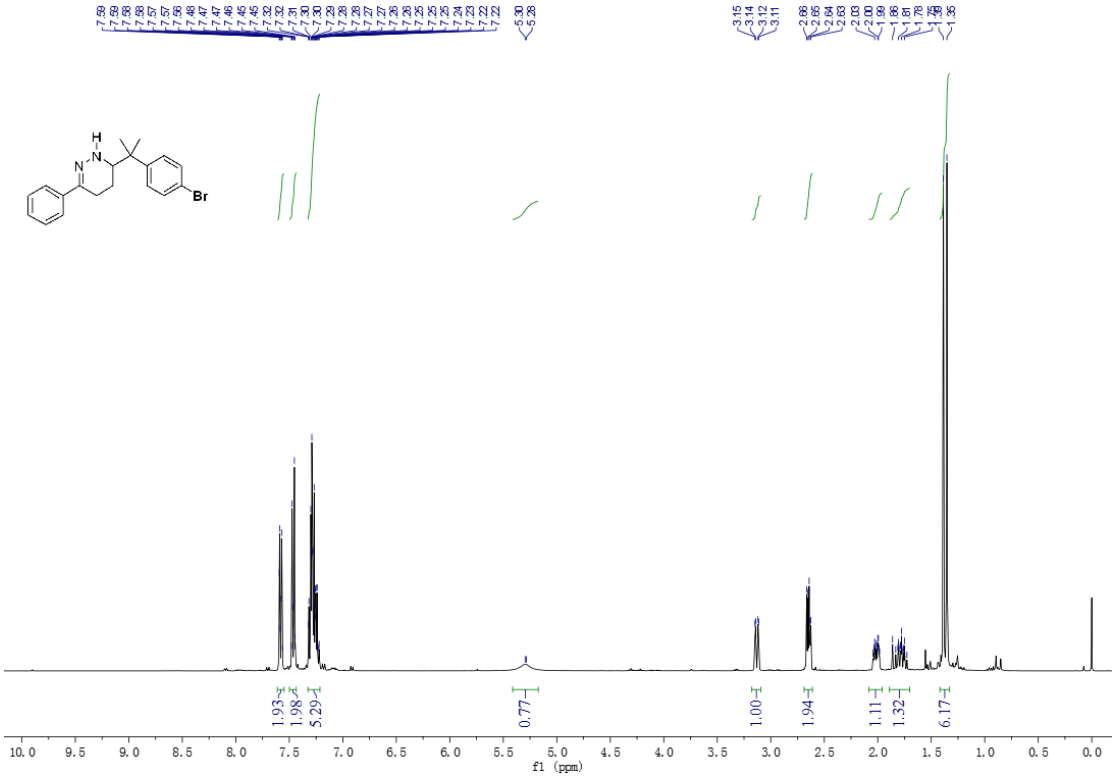
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ab**



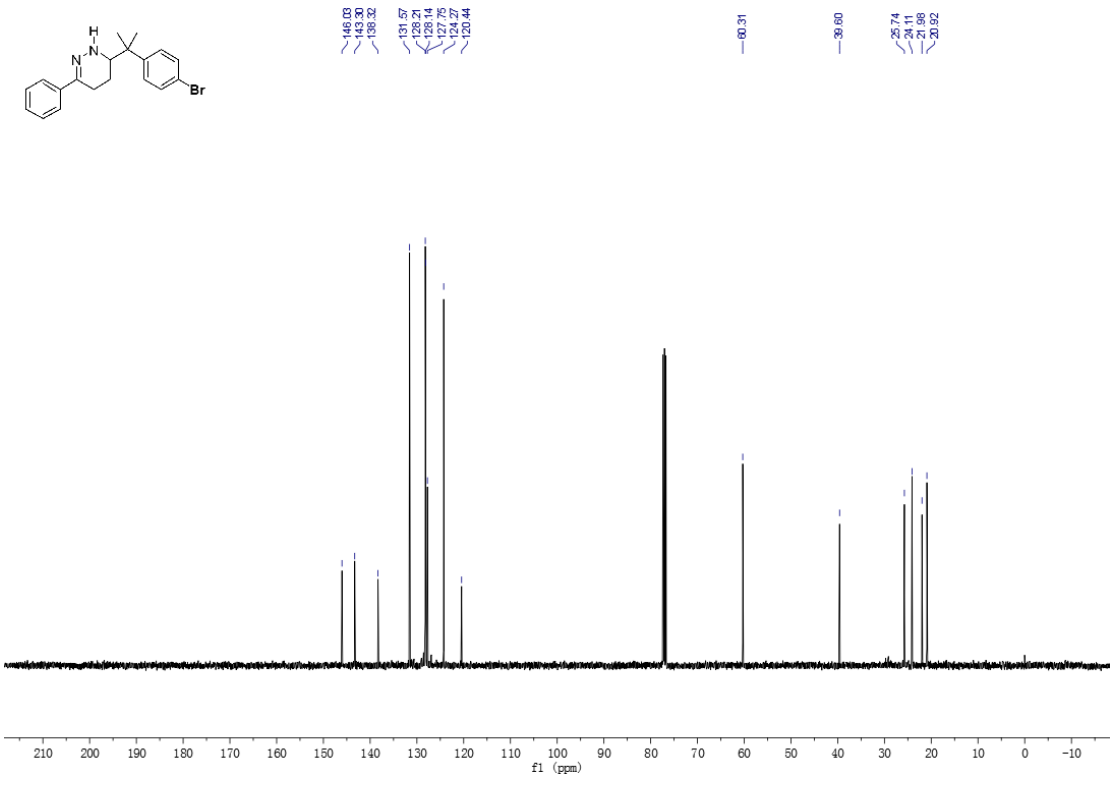
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ab**



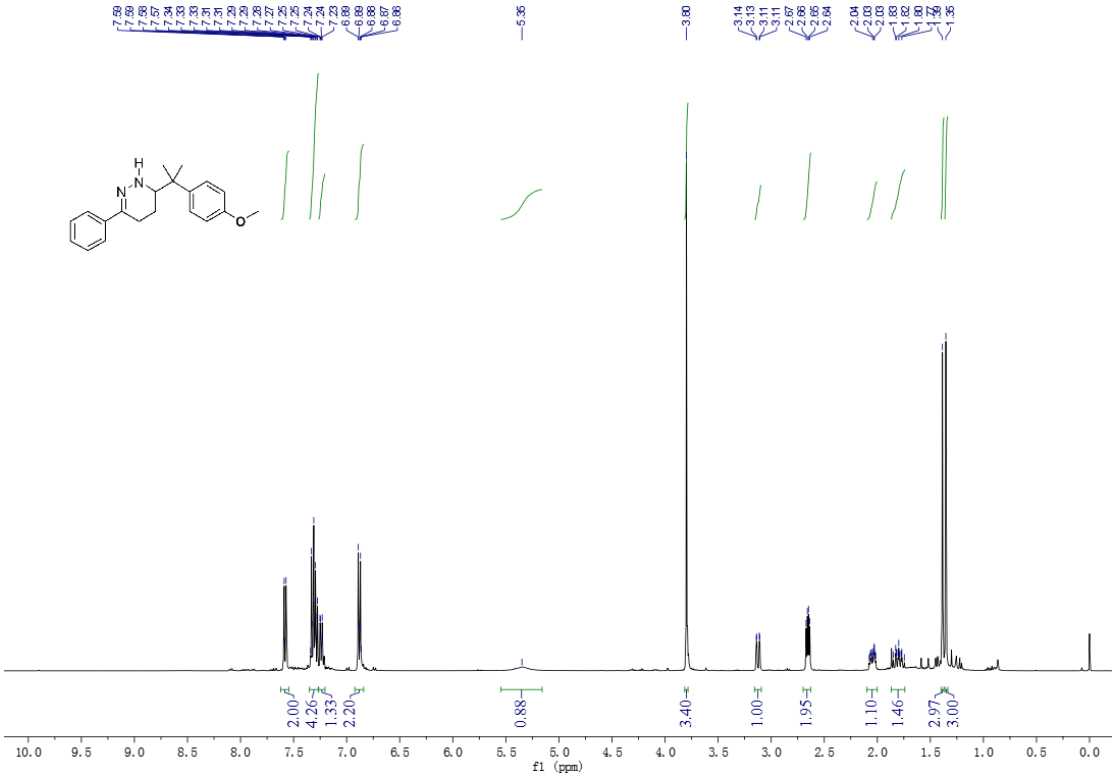
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2bb**



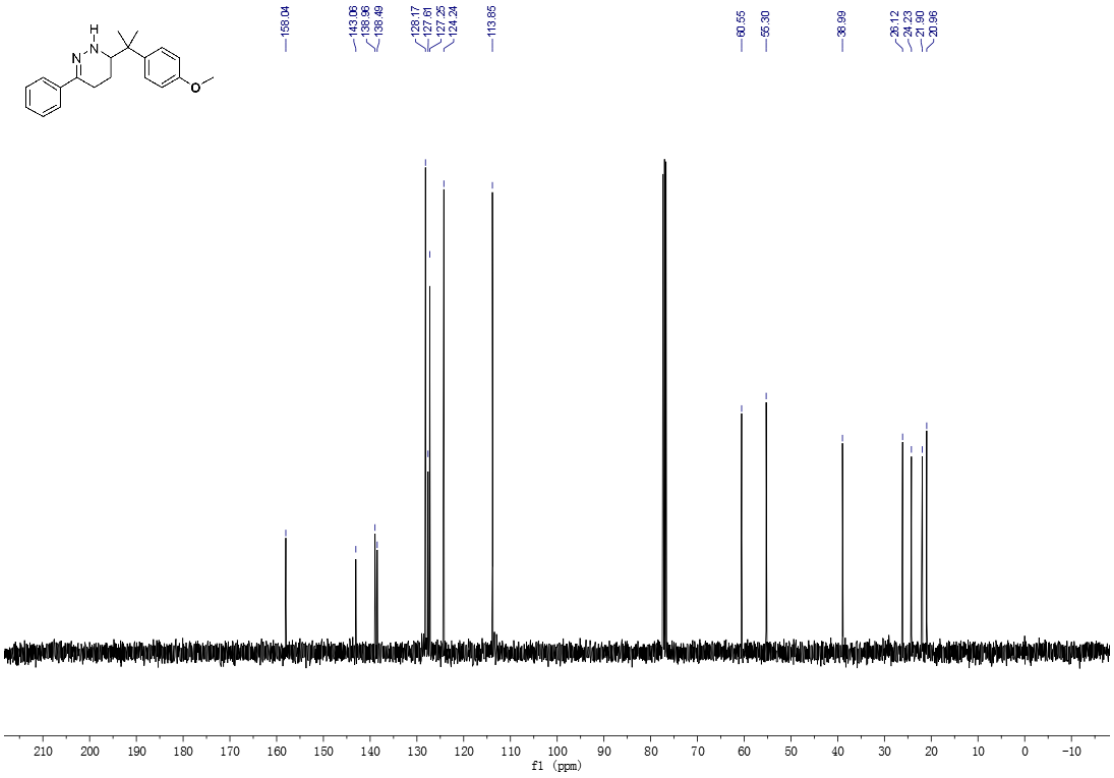
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2bb**



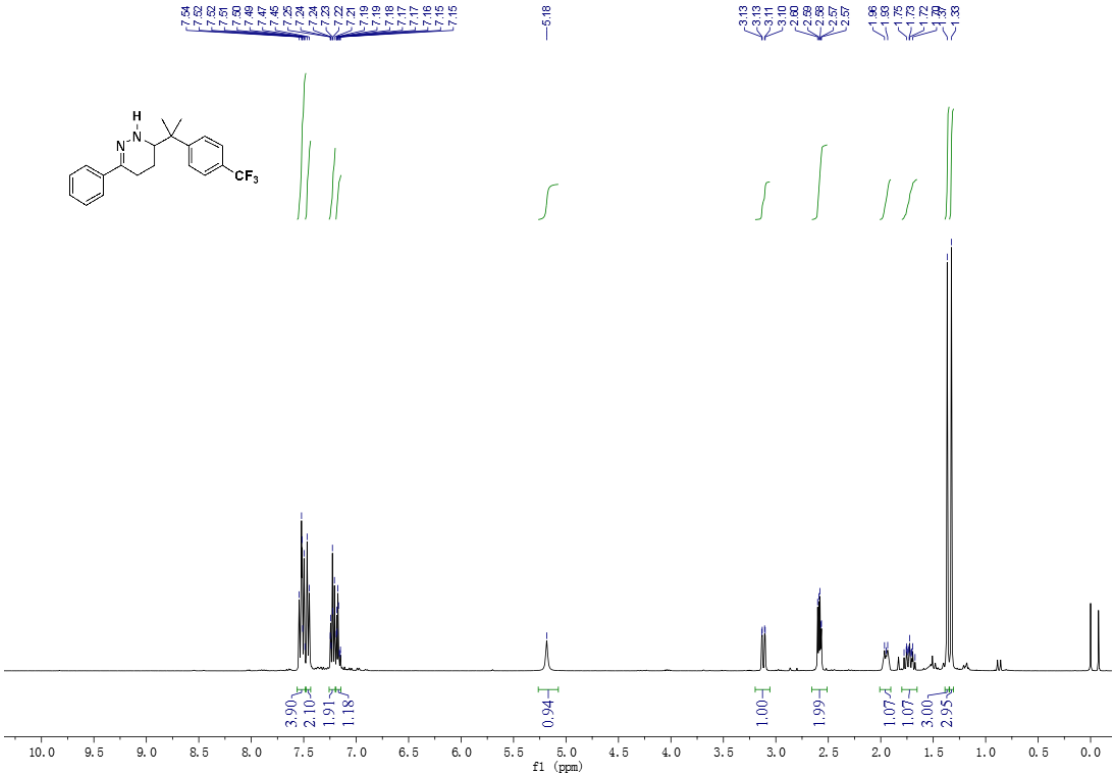
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2cb**



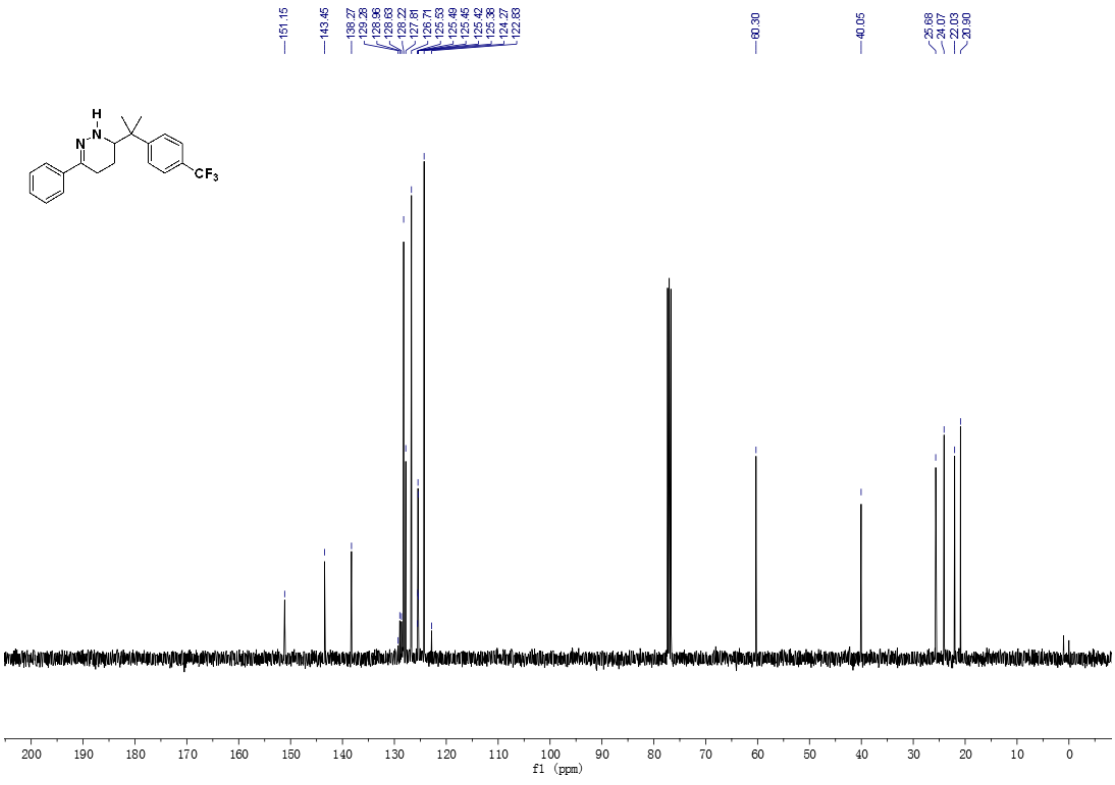
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2cb**



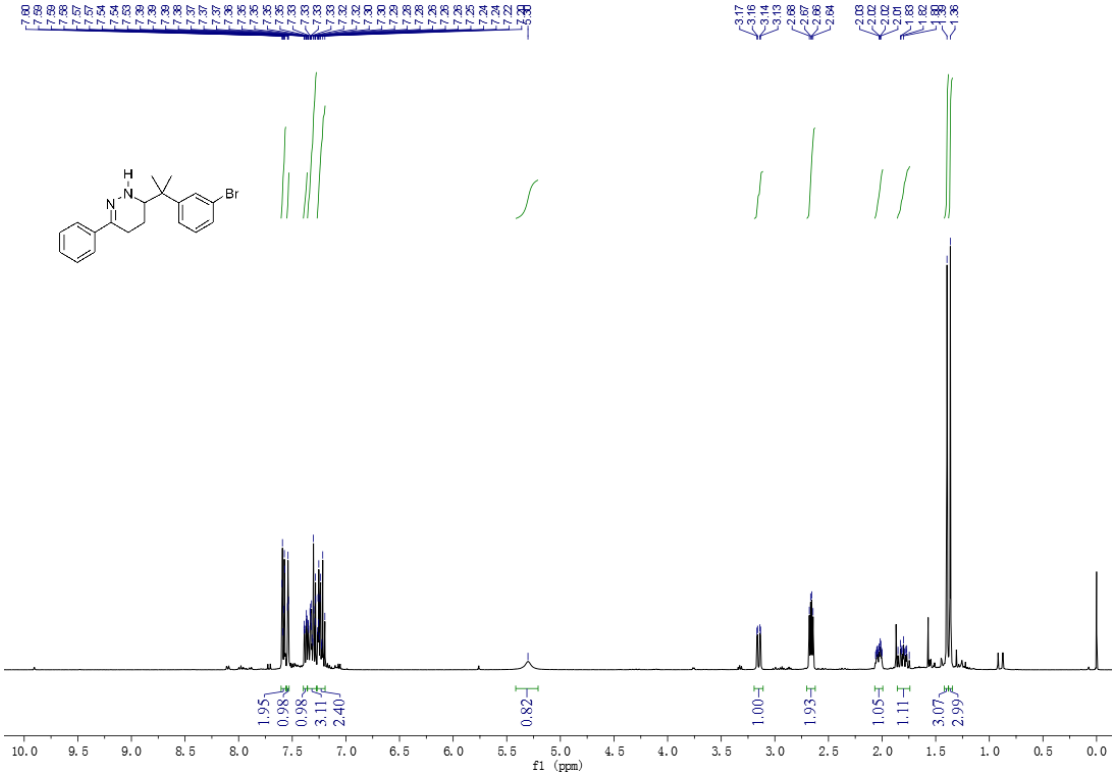
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2db**



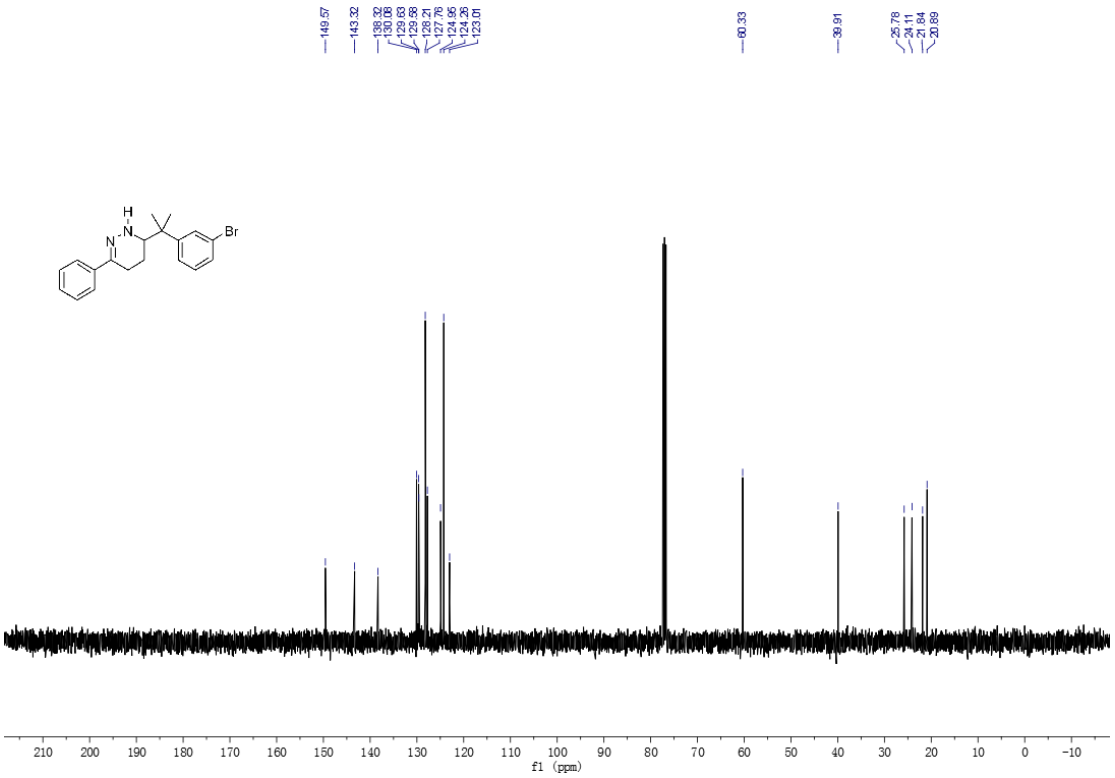
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2db**



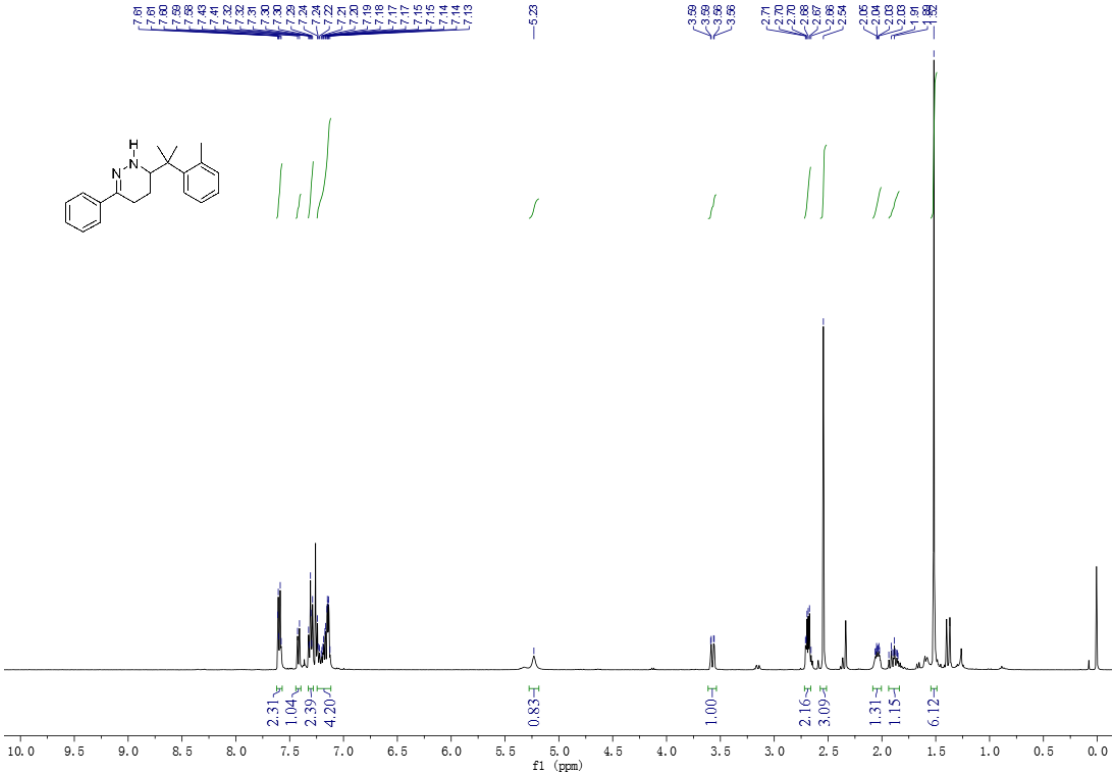
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2eb**



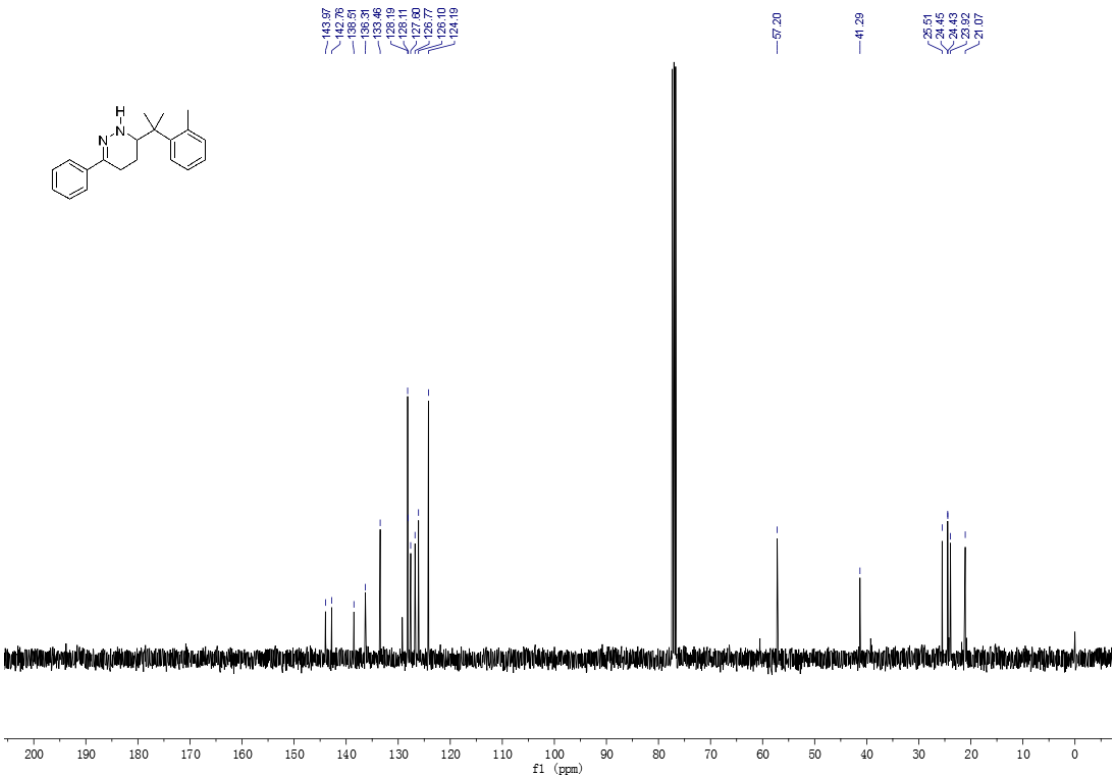
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2eb**



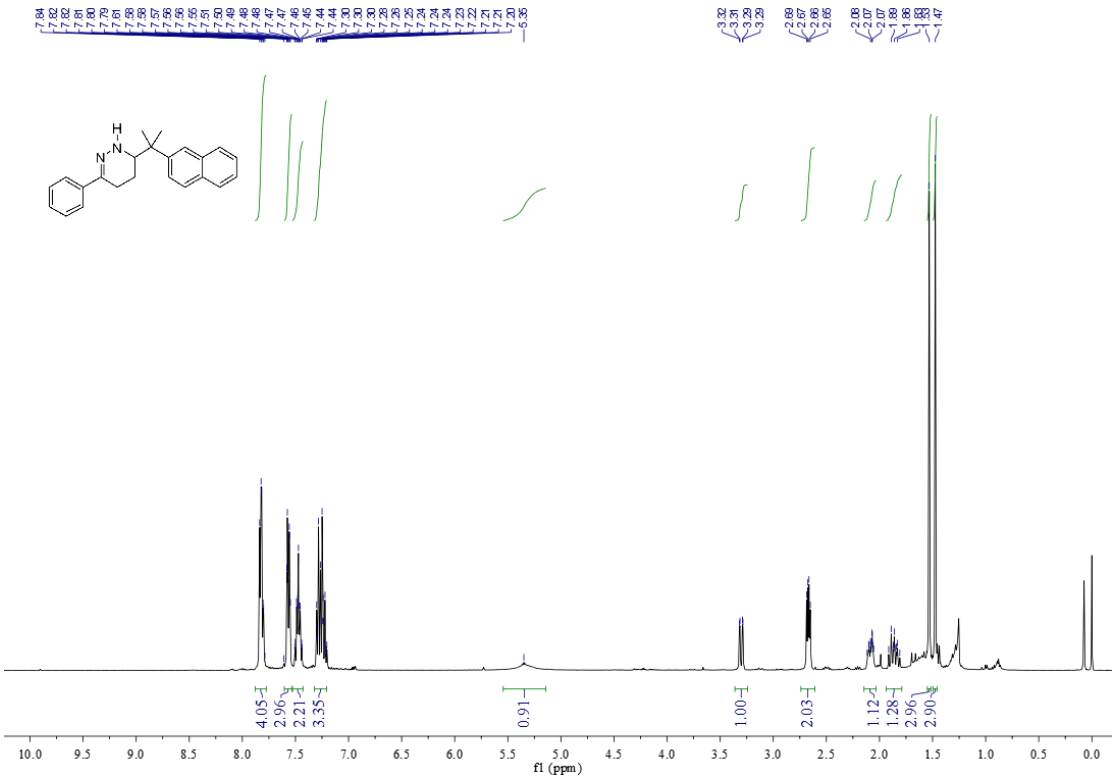
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2fb**



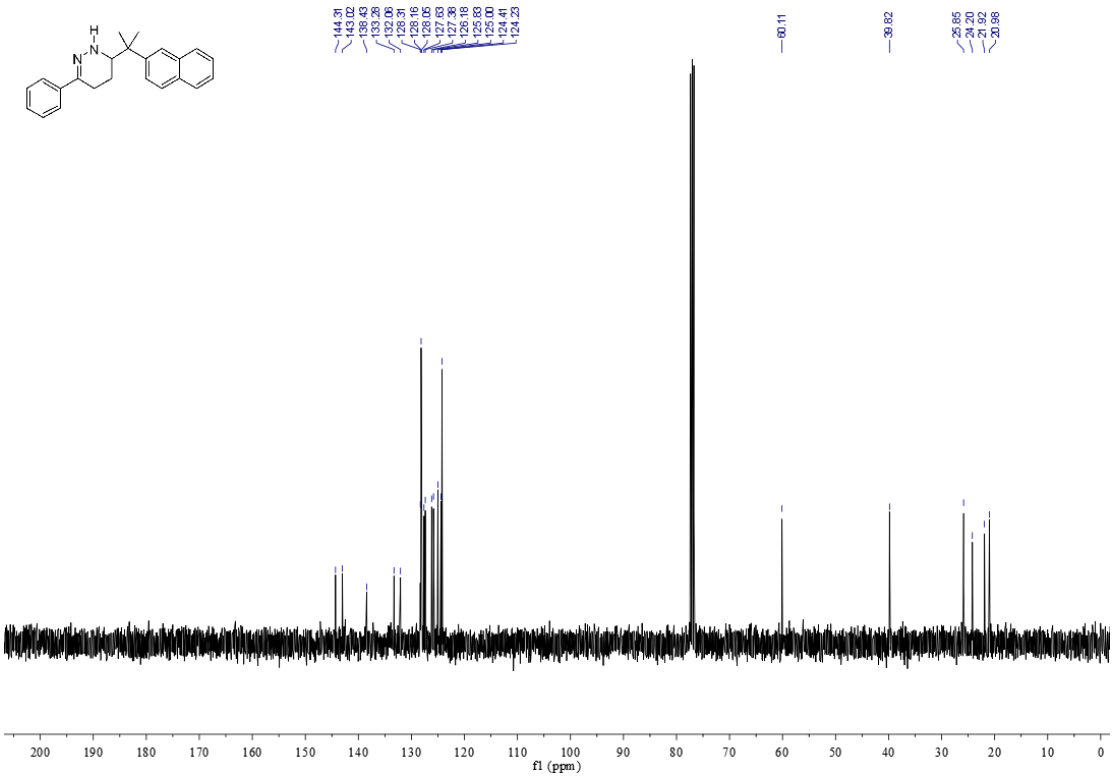
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2fb**



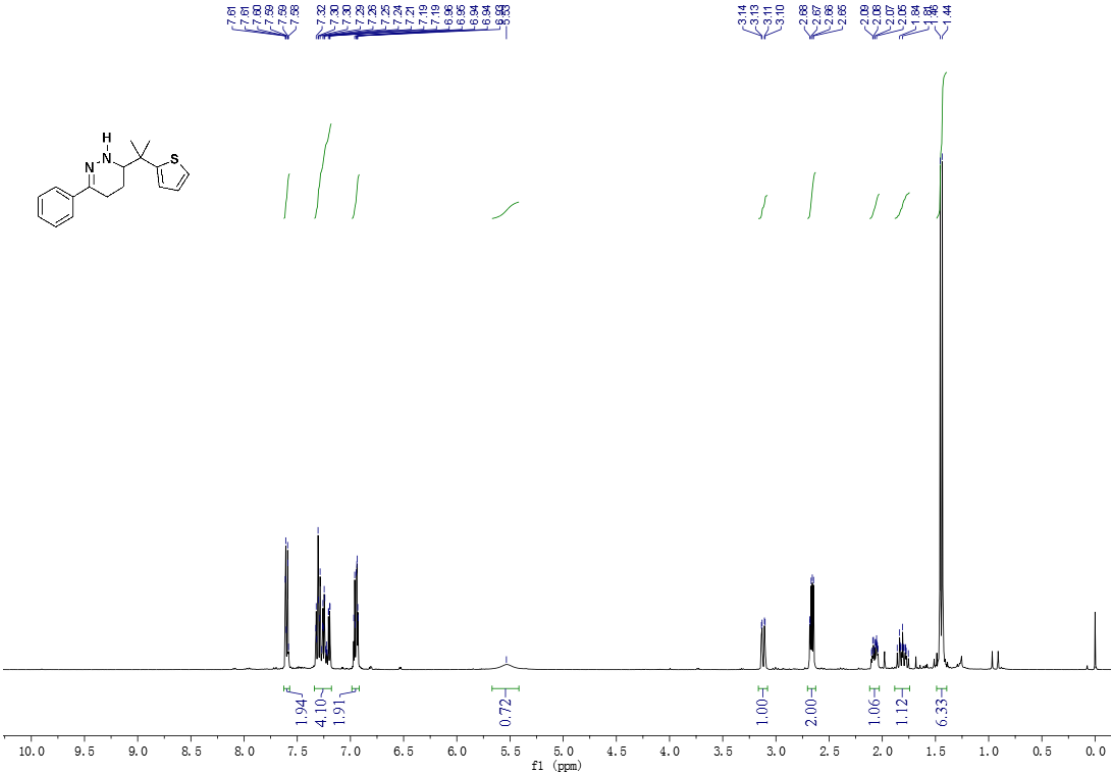
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2gb**



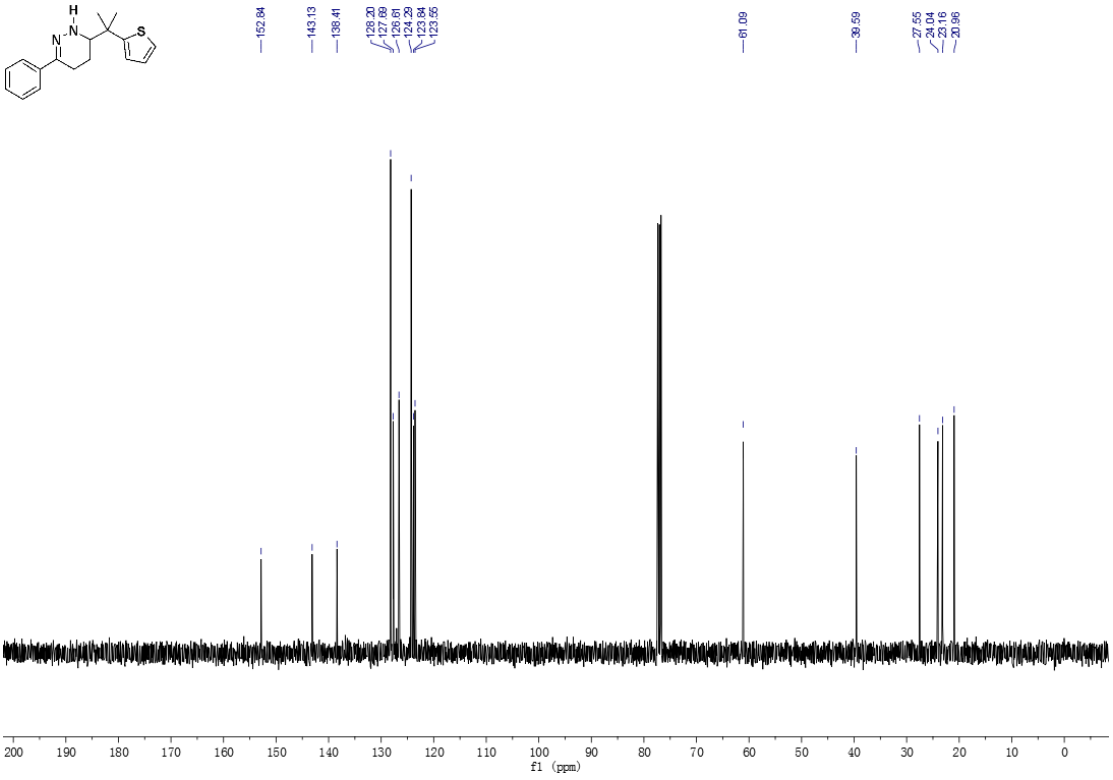
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2gb**



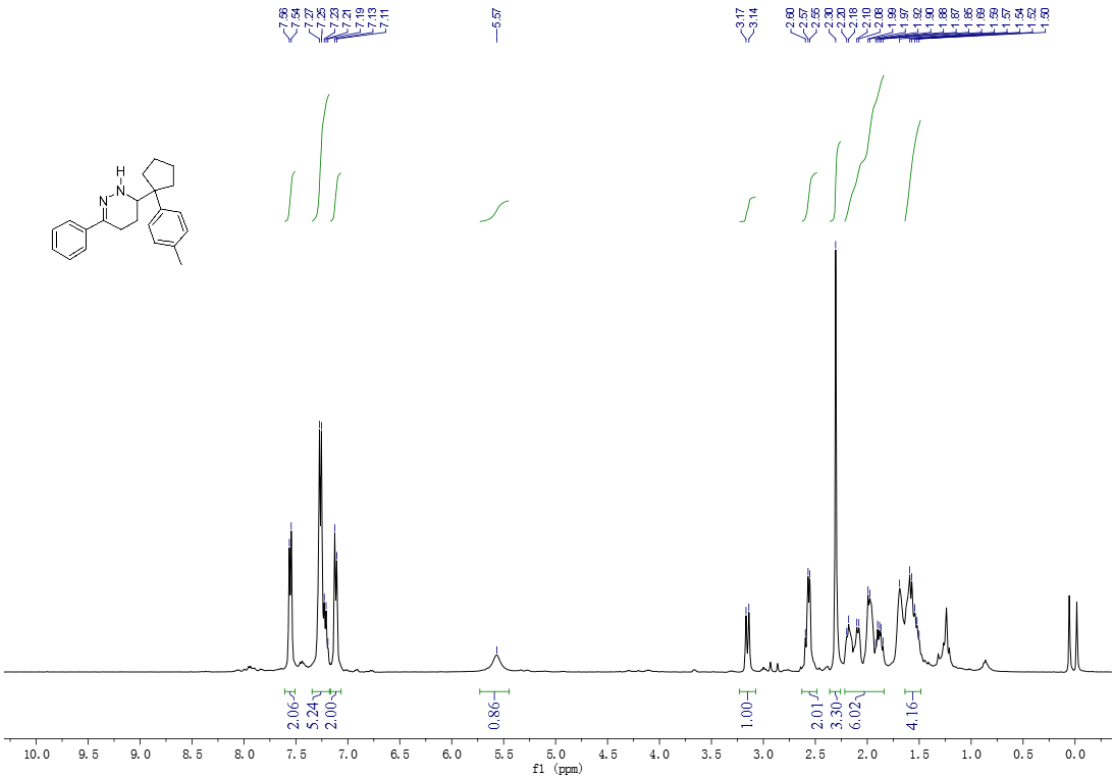
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2hb**



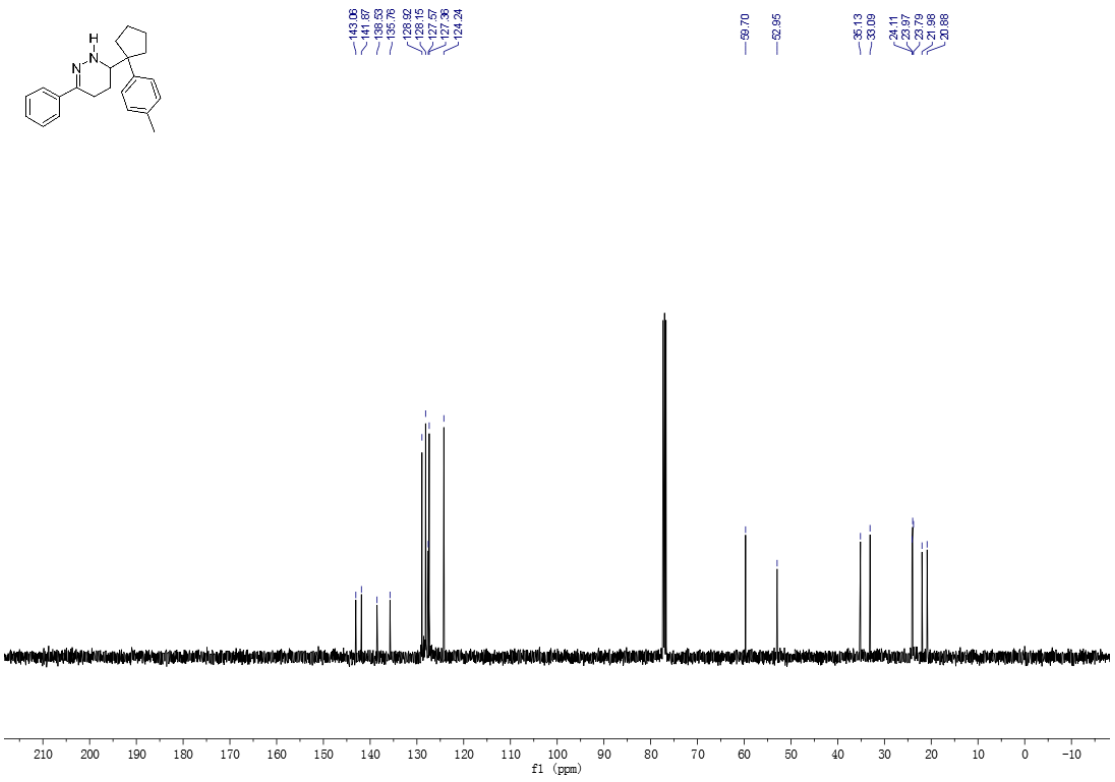
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2hb**



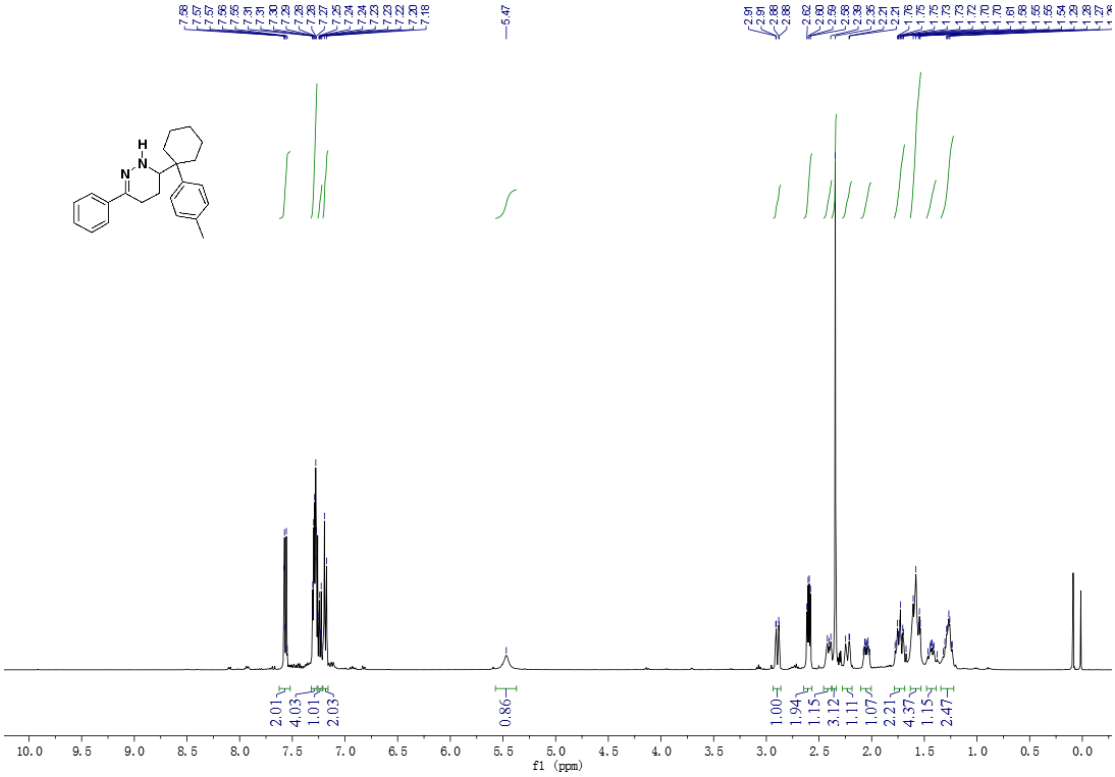
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2ib**



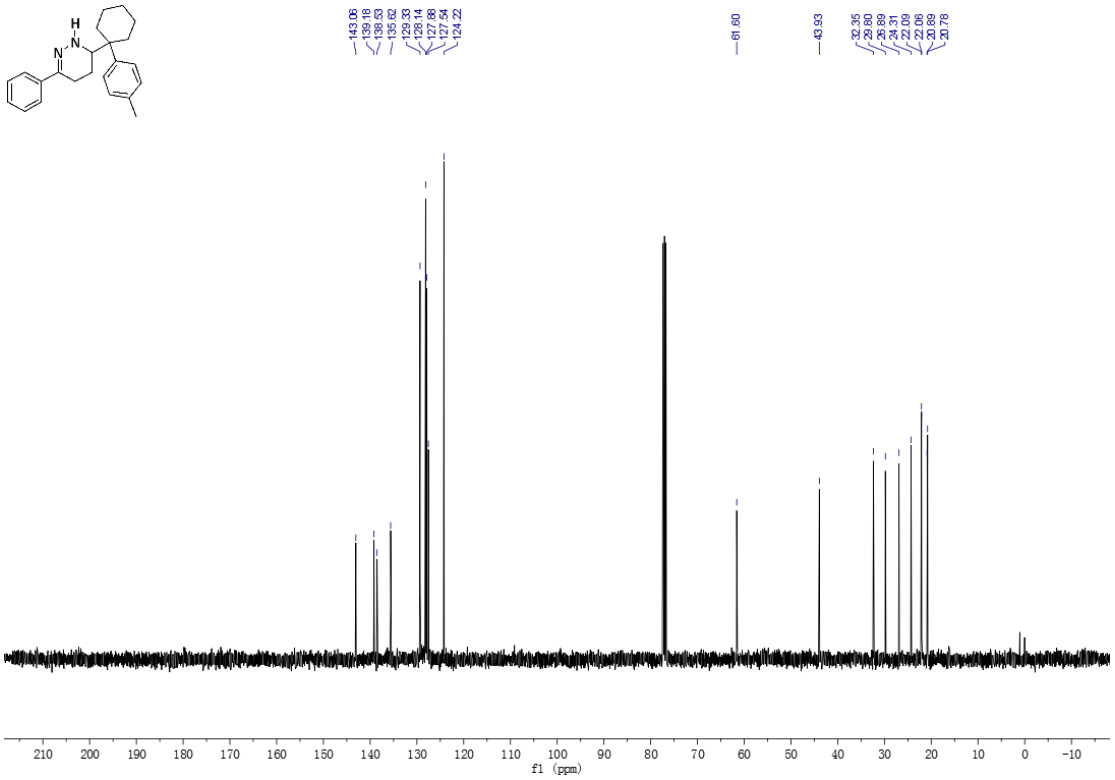
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2ib**



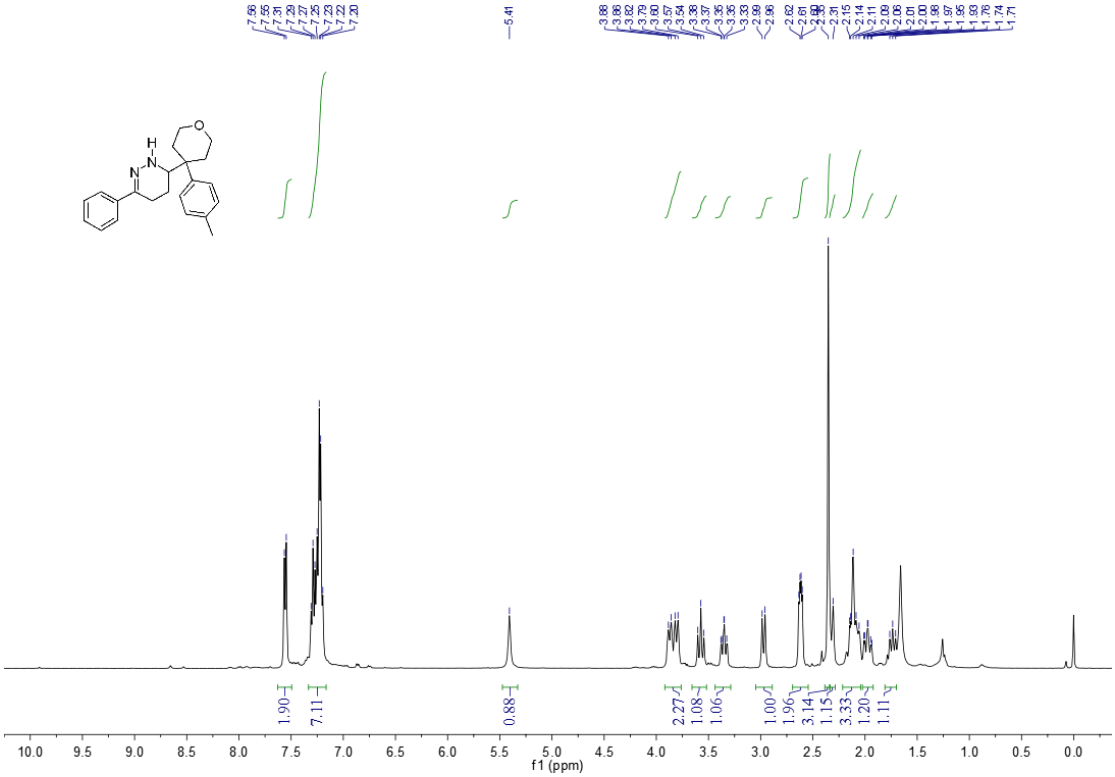
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2jb**



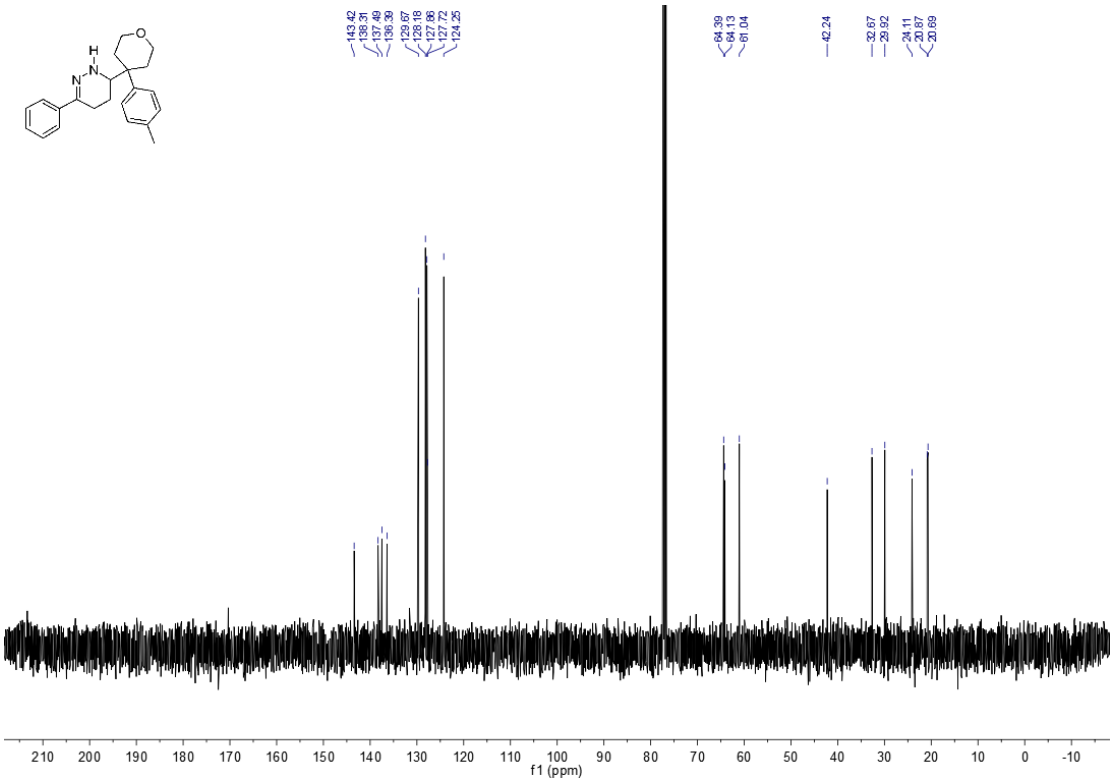
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2jb**



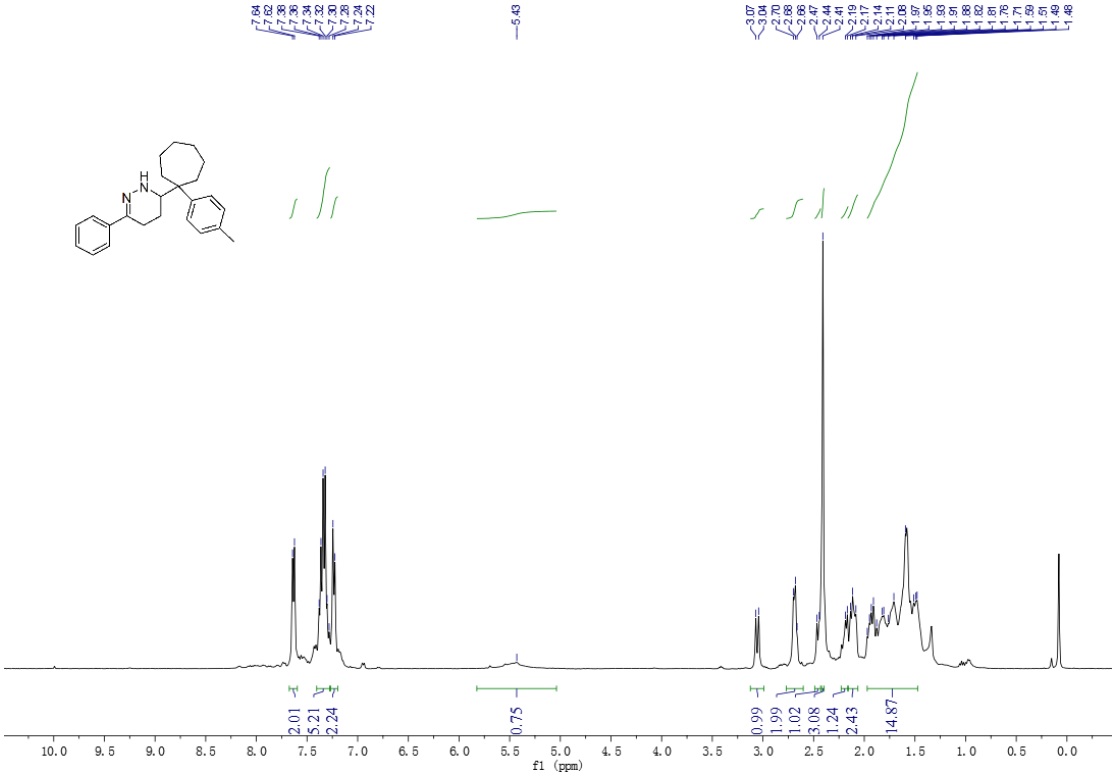
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2kb**



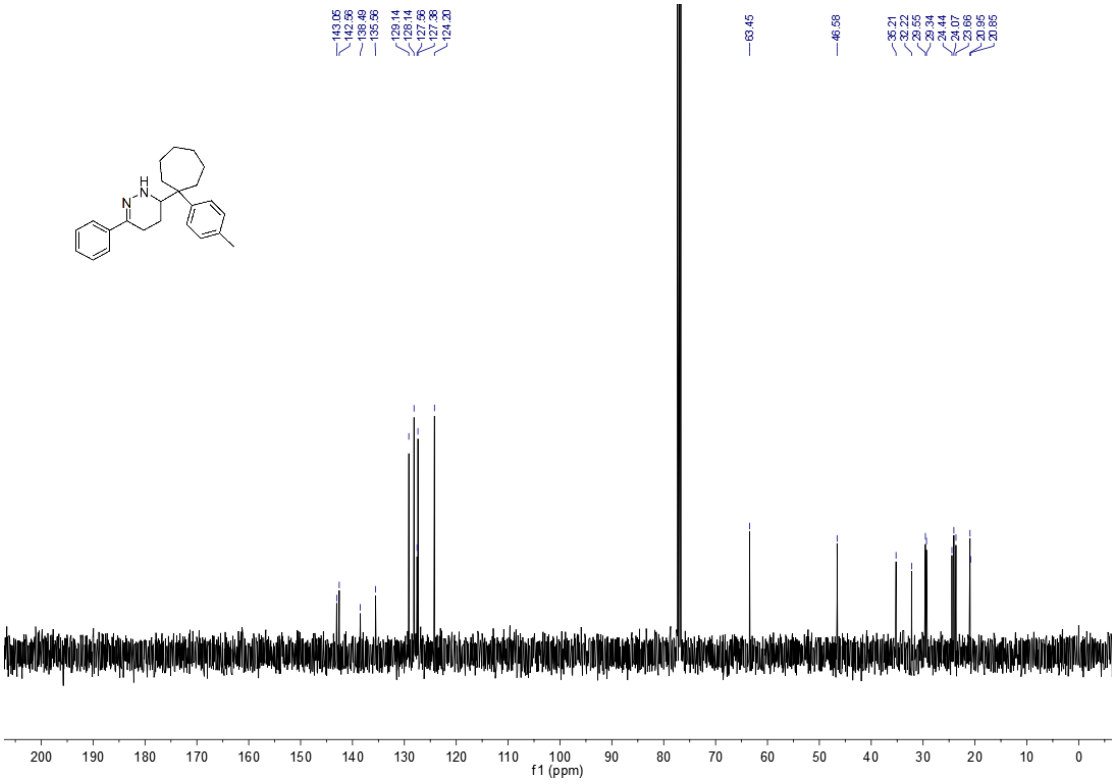
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2kb**



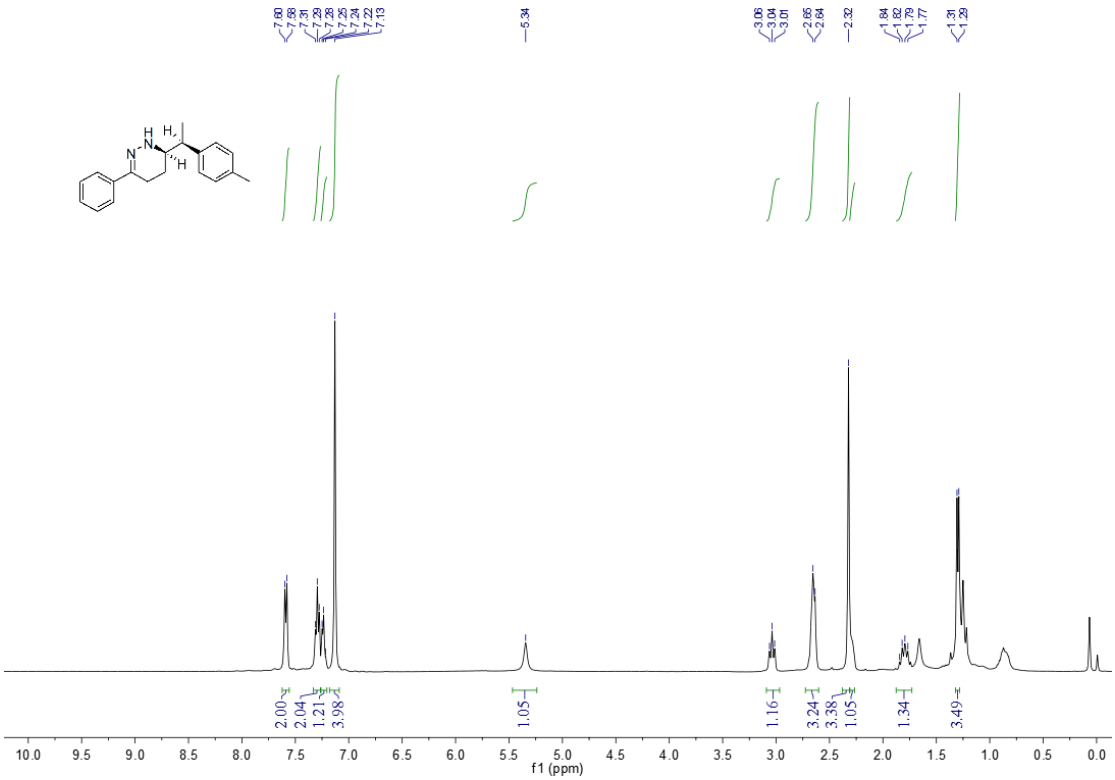
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2lb**



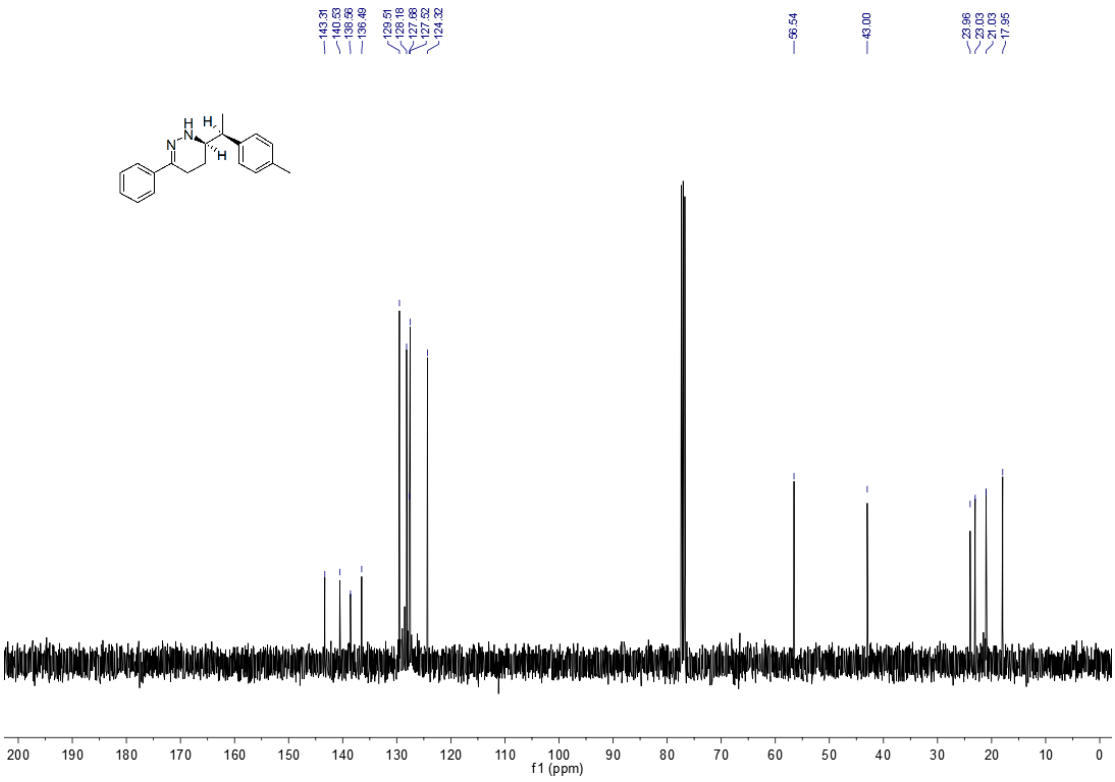
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **2lb**



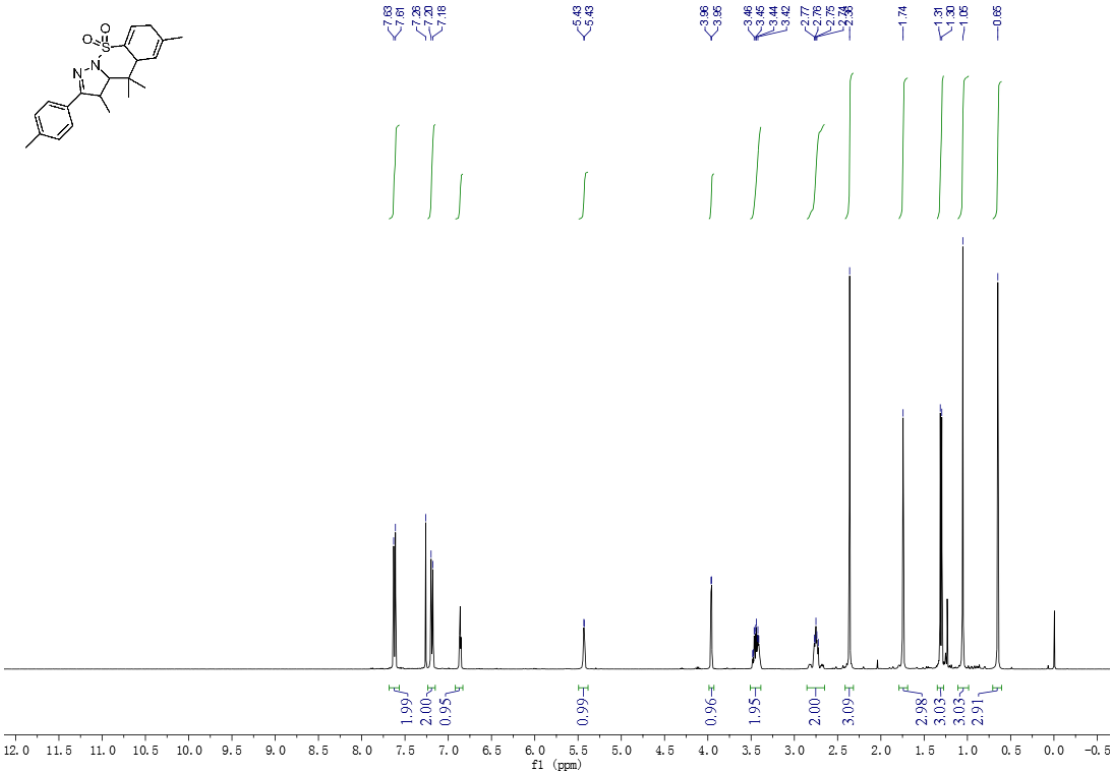
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **2mb**



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



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of **4**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ºC) of **4**