Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

n-BuLi-Promoted Nucleophilic Addition of Unactivated C(sp^3)-H Bonds to Diazo Compounds as *N*-Terminal Electrophiles: Efficient Synthesis of Hydrazine Derivatives

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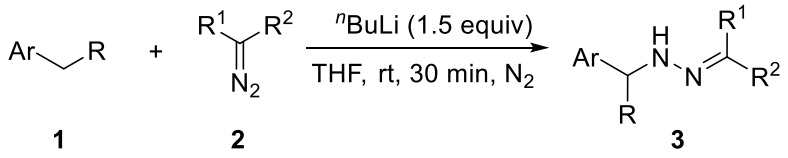
Table of contents

I. General Information:

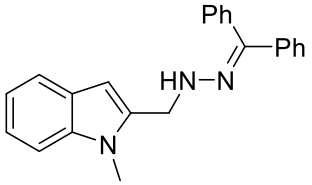
Unless noted otherwise, all the reactions were performed under a nitrogen atmosphere in a reaction vessel. Room temperature (r.t.) was approximately 25 °C. All solvents were freshly distilled and degassed according to the handbook Purification of Laboratory Chemicals (4th Edition, Butterworth Heinemann, W. L. F. Armarego and Douglas Dalzell Perrin). Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 400MHz, 500 MHz and 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz and 126 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 565 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). These compounds **3i**, **3s**, **5k** and **7** were glued on a glass fiber. X-ray single-crystal data of **3i**, **3s**, **5k** and **7** were collected by a Bruker D8 Venture diffractometer (Mo Kα radiation, λ = 0.71073 Å (Cu Kα radiation, λ = 1.54178 Å)) at 293(2) K, and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

II. General Procedure for the Preparation of 3 (3a as example):



To a stirred solution of **1a** (0.75 mmol, 108.9 mg) in dry THF (2.0 mL) in an oven-dried Schlenk flask under N_2 atmosphere at room temperature was slowly added 1.6 M n-BuLi in hexane (0.75 mmol, 0.47 mL) and the reaction mixture was stirred at room temperature for 28 min. Then, the mixture of **2a** (0.5 mmol, 97.1 mg) in dry THF (2.0 mL) was added under N_2 atmosphere at room temperature. The reaction mixture was stirred at room temperature for 2 min and subsequently 1.0 mL H_2O was added. The resulting solution was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by flash silica gel column chromatography (petroleum ether/aether = 10/1, v/v) to give **3a** (159.5 mg, 94%) as a white solid.

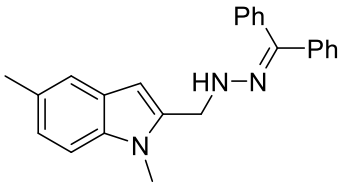
2-((2-(Diphenylmethylene)hydrazineyl)methyl)-1-methyl-1*H*-indole (3a):



White solid; mp: 127 – 128 °C; 159.5 mg, 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.41 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.23 – 7.15 (m, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 5.37 (t, *J* = 5.4 Hz, 1H), 4.63 (d, *J* = 5.5 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 146.06, 138.48, 137.77, 137.46, 133.32, 129.44, 128.89, 128.87, 128.13, 127.86, 127.35,

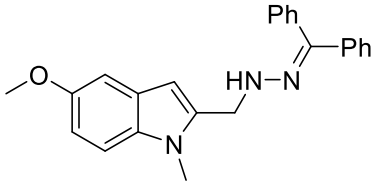
126.36, 121.43, 120.36, 119.41, 109.10, 101.21, 47.49, 30.05. HRMS (ESI-TOF): [M + Na]$^+$ calculated for $C_{23}H_{21}N_3Na^+$: 362.1628, found: 362.1630.

2-((2-(Diphenylmethylene)hydrazineyl)methyl)-1,5-dimethyl-1*H*-indole (3b):



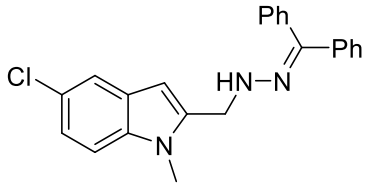
White solid; mp: 140 – 141 °C; 167.9 mg, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.30 (s, 1H), 7.27 – 7.20 (m, 3H), 7.19 (d, *J* = 7.1 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.22 (s, 1H), 5.35 (s, 1H), 4.58 (s, 2H), 3.69 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.07, 138.68, 137.64, 136.38, 133.52, 129.59, 129.04, 129.02, 128.69, 128.28, 127.99, 127.76, 126.51, 123.17, 120.20, 108.95, 100.82, 47.65, 30.18, 21.57. HRMS (ESI-TOF): [M + Na]$^+$ calculated for $C_{24}H_{23}N_3Na^+$: 376.1784, found: 376.1785.

2-((2-(Diphenylmethylene)hydrazineyl)methyl)-5-methoxy-1-methyl-1*H*-indole (3c):



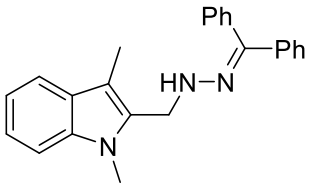
White solid; mp: 148 – 150 °C; 170.0 mg, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.24 (s, 1H), 5.37 (t, *J* = 4.9 Hz, 1H), 4.58 (d, *J* = 5.0 Hz, 2H), 3.79 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 154.15, 146.10, 138.60, 138.13, 133.45, 133.24, 129.54, 128.98, 128.91, 128.23, 127.95, 127.73, 126.45, 111.71, 109.90, 102.31, 100.89, 55.98, 47.60, 30.23. HRMS (ESI-TOF): [M + Na]$^+$ calculated for $C_{24}H_{23}N_3NaO^+$: 392.1733, found: 392.1735.

5-Chloro-2-((2-(diphenylmethylene)hydrazineyl)methyl)-1-methyl-1*H*-indole (3d):



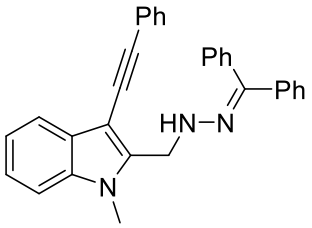
White solid; mp: 147 – 148 °C; 177.6 mg, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.50 – 7.41 (m, 5H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.21 – 7.17 (m, 2H), 7.11 – 7.06 (m, 2H), 6.22 (s, 1H), 5.38 (t, *J* = 5.0 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 2H), 3.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.44, 139.19, 138.52, 136.28, 133.39, 129.59, 129.07, 128.96, 128.46, 128.27, 128.06, 126.49, 125.14, 121.69, 119.78, 110.20, 100.88, 47.44, 30.29. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{20}ClN_3Na^+$: 396.1238, found: 396.1236.

2-((2-(Diphenylmethylene)hydrazineyl)methyl)-1,3-dimethyl-1*H*-indole (3e):



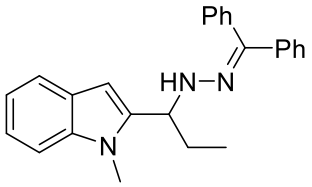
Yellow solid; mp: 121 – 122 °C; 148.5 mg, 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 5.24 (s, 1H), 4.61 (d, *J* = 3.5 Hz, 2H), 3.74 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.27, 138.41, 136.83, 133.24, 132.66, 129.37, 128.80, 128.76, 128.06, 127.80, 126.26, 121.60, 118.66, 109.02, 108.85, 44.61, 29.95, 8.68. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{24}H_{23}N_3Na^+$: 376.1784, found: 376.1793.

2-((2-(Diphenylmethylene)hydrazineyl)methyl)-1-methyl-3-(phenylethynyl)-1*H*-indole (3f):



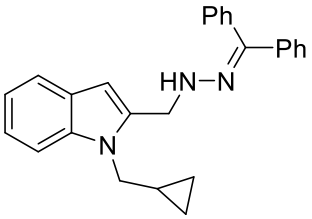
Yellow solid; mp: 51 – 53 °C; 211.0 mg, 96% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.38 – 7.35 (m, 2H), 7.32 – 7.22 (m, 9H), 7.19 – 7.16 (m, 1H), 7.16 – 7.13 (m, 2H), 5.60 (t, *J* = 5.5 Hz, 1H), 4.77 (d, *J* = 5.4 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 147.28, 141.37, 138.45, 136.77, 133.12, 131.28, 129.52, 128.92, 128.84, 128.32, 128.17, 128.02, 127.51, 126.62, 126.46, 124.34, 122.75, 120.55, 119.95, 109.69, 97.17, 93.54, 82.88, 45.70, 30.64. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{31}H_{26}N_3^+$: 440.2121, found: 440.2131.

2-(1-(2-(Diphenylmethylene)hydrazineyl)propyl)-1-methyl-1*H*-indole (3g):



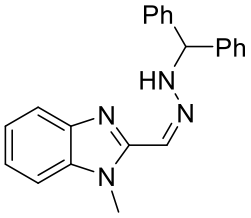
Yellow liquid, 158.0 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.41 (m, 4H), 7.40 – 7.36 (m, 1H), 7.30 – 7.22 (m, 4H), 7.20 – 7.15 (m, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.29 (s, 1H), 5.32 (d, *J* = 7.6 Hz, 1H), 4.68 (q, *J* = 7.4 Hz, 1H), 3.81 (s, 3H), 2.16 – 2.05 (m, 1H), 2.01 – 1.90 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 145.13, 140.94, 138.77, 137.55, 133.46, 129.44, 128.92, 128.79, 128.09, 127.87, 127.64, 126.27, 121.25, 120.33, 119.32, 109.10, 98.96, 58.36, 30.13, 27.33, 11.20. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{26}N_3^+$: 368.2121, found: 368.2128.

1-(Cyclopropylmethyl)-2-((2-(diphenylmethylene)hydrazineyl)methyl)-1*H*-indole (3h):



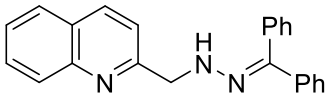
Yellow liquid, 170.8 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.19 (m, 5H), 7.18 – 7.12 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 5.38 (t, *J* = 5.5 Hz, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 4.11 (d, *J* = 6.4 Hz, 2H), 1.22 – 1.15 (m, 1H), 0.54 – 0.44 (m, 2H), 0.35 (q, *J* = 5.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 145.92, 138.39, 137.22, 136.99, 133.25, 129.32, 128.79, 128.04, 127.78, 127.44, 126.28, 121.28, 120.30, 119.28, 109.65, 101.41, 47.59, 47.33, 11.69, 4.09. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{26}H_{26}N_3^+$: 380.2121, found: 380.2131.

(*Z*)-2-((2-Benzhydrylhydrazineylidene)methyl)-1-methyl-1*H*-benzo[*d*]imidazole (3i):



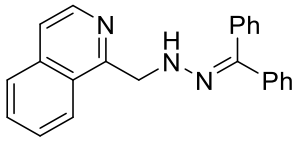
White solid; mp: 137 – 138 °C; 115.7 mg, 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 11.99 (d, *J* = 5.7 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.7 Hz, 4H), 7.31 (d, *J* = 4.0 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.16 (s, 1H), 5.95 (d, *J* = 5.9 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 147.23, 142.40, 142.04, 133.82, 128.54, 127.72, 127.19, 123.44, 122.37, 119.64, 114.98, 109.03, 68.50, 29.68. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{22}H_{20}N_4Na^+$: 363.1580, found: 363.1590.

2-((2-(Diphenylmethylene)hydrazineyl)methyl)quinolone (3j):



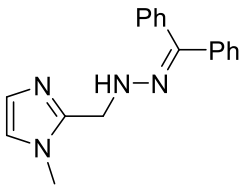
White solid; mp: 140 – 141 °C; 128.0 mg, 76% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.32 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 9.2 Hz, 2H), 7.76 – 7.72 (m, 1H), 7.62 (t, J = 7.6 Hz, 2H), 7.57 – 7.49 (m, 3H), 7.37 – 7.33 (m, 2H), 7.30 – 7.26 (m, 2H), 7.23 (t, J = 7.4 Hz, 2H), 7.21 – 7.17 (m, 1H), 6.74 (t, J = 4.8 Hz, 1H), 4.66 (d, J = 4.5 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ: 161.27, 147.40, 144.47, 138.96, 136.86, 134.04, 130.04, 129.95, 129.22, 129.20, 128.78, 128.55, 128.32, 127.81, 127.033, 126.49, 126.00, 120.63, 56.17. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{19}N_3Na^+$: 360.1471, found: 360.1481.

1-((2-(Diphenylmethylene)hydrazineyl)methyl)isoquinoline (3k):



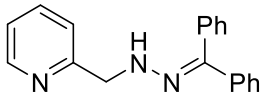
White solid; mp: 112 – 113 °C; 119.8 mg, 71% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.36 (d, J = 5.7 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.0 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.51 – 7.43 (m, 5H), 7.39 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.0 Hz, 2H), 7.26 – 7.16 (m, 3H), 6.39 (t, J = 5.3 Hz, 1H), 5.10 (d, J = 5.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 157.89, 146.38, 141.54, 138.66, 136.03, 133.72, 129.89, 129.18, 128.90, 128.59, 127.90, 127.55, 127.09, 127.07, 126.52, 126.26, 124.96, 120.00, 53.76. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{19}N_3Na^+$: 360.1471, found: 360.1480.

2-((2-(Diphenylmethylene)hydrazineyl)methyl)-1-methyl-1*H*-imidazole (3l):



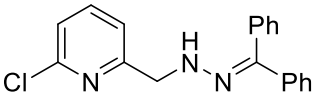
Yellow liquid, 106.0 mg, 73% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48 – 7.42 (m, 4H), 7.42 – 7.37 (m, 1H), 7.29 – 7.24 (m, 3H), 7.20 – 7.13 (m, 2H), 6.91 (d, *J* = 1.1 Hz, 1H), 6.80 (d, *J* = 0.9 Hz, 1H), 5.60 (t, *J* = 5.8 Hz, 1H), 4.52 (d, *J* = 5.8 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.83, 145.81, 138.33, 133.08, 129.38, 128.83, 128.70, 128.02, 127.84, 127.37, 126.25, 121.33, 47.02, 33.12. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{19}N_4^+$: 291.1604, found: 291.1611.

2-((2-(Diphenylmethylene)hydrazineyl)methyl)pyridine (3m):



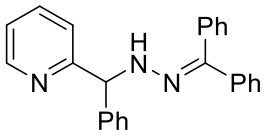
Yellow solid; mp: 76 – 78 °C; 117.8 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.50 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.46 – 7.40 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.20 (m, 5H), 7.15 – 7.10 (m, 1H), 5.97 (t, *J* = 5.5 Hz, 1H), 4.57 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 159.63, 149.17, 146.31, 138.53, 136.38, 133.53, 129.35, 128.85, 128.73, 127.97, 127.66, 126.25, 122.18, 121.89, 56.35. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{18}N_3^+$: 288.1495, found: 288.1493.

2-Chloro-6-((2-(diphenylmethylene)hydrazineyl)methyl)pyridine (3n):



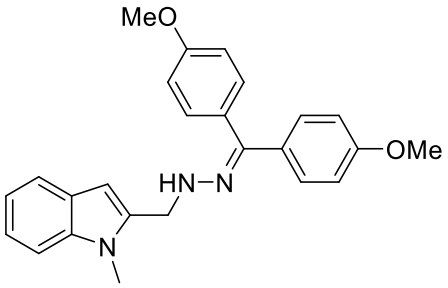
Yellow solid; mp: 128 – 130 °C; 133.6 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.57 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.30 – 7.21 (m, 6H), 7.16 (d, *J* = 7.9 Hz, 1H), 5.98 (t, *J* = 5.5 Hz, 1H), 4.51 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 160.93, 150.76, 147.07, 139.04, 138.34, 133.39, 129.40, 128.84, 128.79, 127.97, 127.79, 126.27, 122.37, 120.55, 55.49. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{19}H_{17}ClN_3^+$: 322.1106, found: 322.1115.

2-((2-(Diphenylmethylene)hydrazineyl)(phenyl)methyl)pyridine (3o):



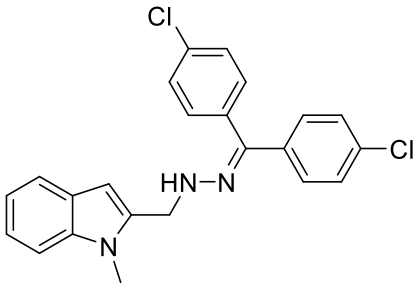
White solid; mp: 117 – 119 °C; 170.8 mg, 94% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.52 – 8.47 (m, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.33 – 7.28 (m, 5H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.16 (m, 4H), 7.07 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 6.48 (d, *J* = 7.0 Hz, 1H), 5.84 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 161.43, 149.25, 146.76, 141.45, 138.66, 136.32, 133.54, 129.24, 128.88, 128.70, 128.34, 127.86, 127.71, 127.64, 127.18, 126.39, 122.43, 121.88, 68.90. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{21}N_3Na^+$: 386.1628, found: 386.1636.

2-((2-(Bis(4-methoxyphenyl)methylene)hydrazineyl)methyl)-1-methyl-1*H*-indole (3p):



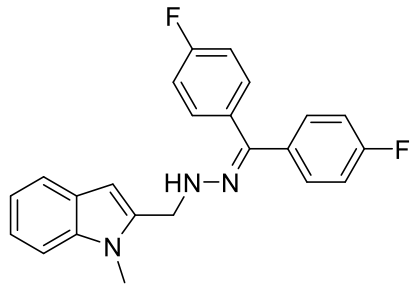
White solid; mp: 123 – 125 °C; 179.8 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.18 – 7.10 (m, 3H), 7.04 (t, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.31 (s, 1H), 5.29 (s, 1H), 4.57 (s, 2H), 3.76 (s, 3H), 3.74 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 159.86, 159.71, 146.47, 137.88, 137.82, 131.89, 130.40, 128.00, 127.53, 125.54, 121.48, 120.45, 119.49, 114.83, 113.64, 109.21, 101.27, 55.37, 55.35, 47.60, 30.12. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{26}N_3O_2^+$: 400.2020, found: 400.2015.

2-((2-(Bis(4-chlorophenyl)methylene)hydrazineyl)methyl)-1-methyl-1*H*-indole (3q):



White solid; mp: 149 – 151 °C; 173.5 mg, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.39 – 7.35 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.20 – 7.16 (m, 1H), 7.15 – 7.12 (m, 2H), 7.09 – 7.05 (m, 1H), 6.32 (s, 1H), 5.34 (t, *J* = 5.5 Hz, 1H), 4.62 (d, *J* = 5.5 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 143.41, 137.86, 137.11, 136.73, 135.24, 133.88, 131.17, 130.43, 130.01, 128.44, 127.48, 127.38, 121.67, 120.49, 119.60, 109.21, 101.45, 47.53, 30.09. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{23}H_{20}Cl_2N_3^+$: 408.1029, found: 408.1028.

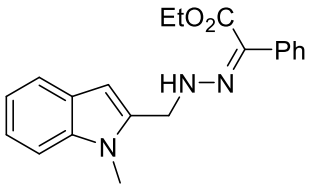
2-((2-(Bis(4-fluorophenyl)methylene)hydrazineyl)methyl)-1-methyl-1*H*-indole (3r):



White solid; mp: 113 – 114 °C; 150.2 mg, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.17 (m, 3H), 7.14 (t, *J* = 8.6 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.32 (s, 1H), 5.29 (t, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.54 (d, *J* = 11.4 Hz), 161.90 (d, *J* = 9.9 Hz), 144.03, 137.74, 137.19, 134.58 (d, *J* = 3.1 Hz), 130.85 (d, *J* = 8.2 Hz), 128.84 (d, *J* = 3.6 Hz), 127.94 (d, *J* = 8.0 Hz), 127.29, 121.50, 120.35, 119.46, 116.67 (d, *J* = 21.6 Hz), 115.05 (d, *J* = 21.6 Hz), 109.08, 101.24, 47.41, 29.95; ^{19}F NMR (565 MHz, $CDCl_3$) δ: -111.22 – -111.32 (m, 1F), -113.83 – -113.92 (m, 1F). HRMS (ESI-TOF): $[M + Na]^+$ calculated

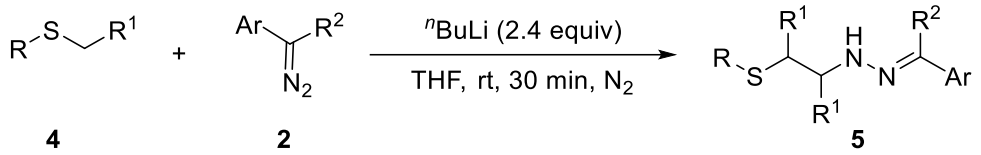
for $C_{23}H_{19}F_2N_3Na^+$: 398.1439, found: 398.1436.

Ethyl (*Z*)-2-(2-((1-methyl-1*H*-indol-2-yl)methyl)hydrazineylidene)-2-phenylacetate (3s):



Yellow solid; mp: 114 – 115 °C; 72.1 mg, 43% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.58 (t, *J* = 4.2 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.07 (m, 1H), 6.46 (s, 1H), 4.85 (d, *J* = 4.6 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.70, 138.05, 136.93, 135.95, 128.35, 127.88, 127.46, 127.18, 126.91, 121.82, 120.67, 119.65, 109.23, 101.95, 60.63, 48.60, 30.14, 14.26. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{20}H_{21}N_3NaO_2^+$: 358.1526, found: 358.1532.

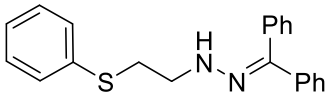
III. General Procedure for the Preparation of 5 (5a as example):



4 **2** **5**

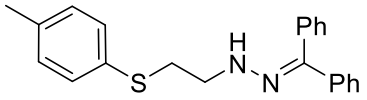
To a stirred solution of **4a** (1.2 mmol, 149.0 mg) in dry THF (2.0 mL) in an oven-dried schlenk flask under N_2 atmosphere at room temperature was slowly added 1.6 M n-BuLi in hexane (1.2 mmol, 0.75 mL) and the reaction mixture was stirred at room temperature for 28 min. Then, the mixture of **2a** (0.5 mmol, 97.1 mg) in dry THF (2.0 mL) was added under N_2 atmosphere. The reaction mixture was stirred at room temperature for 2 min and subsequently 1.0 mL H_2O was added. The resulting solution was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by flash silica gel column chromatography (petroleum ether/aether = 10/1, v/v) to give **5a** (154.6 mg, 93%) as a yellow liquid.

1-(Diphenylmethylene)-2-(2-(phenylthio)ethyl)hydrazine (5a):



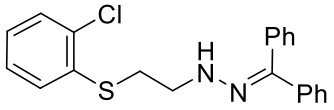
Yellow liquid, 154.6 mg, 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 – 7.45 (m, 4H), 7.42 (t, J = 7.5 Hz, 1H), 7.30 – 7.20 (m, 9H), 7.14 (t, J = 7.3 Hz, 1H), 5.60 (t, J = 5.3 Hz, 1H), 3.44 (q, J = 6.3 Hz, 2H), 3.15 (t, J = 6.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.59, 138.59, 135.70, 133.64, 129.46, 129.43, 129.01, 128.97, 128.87, 128.16, 127.86, 126.32, 126.16, 49.25, 33.92. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{21}H_{21}N_2S^+$: 333.1420, found: 333.1420.

1-(Diphenylmethylene)-2-(2-(p-tolylthio)ethyl)hydrazine (5b):



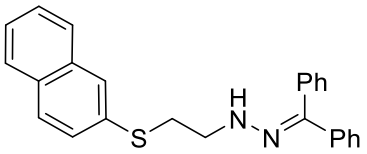
Yellow liquid, 157.7 mg, 91% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.51 (t, *J* = 7.5 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.30 – 7.22 (m, 5H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.61 (t, *J* = 5.5 Hz, 1H), 3.42 (q, *J* = 6.3 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.56, 138.58, 136.38, 133.63, 131.72, 130.34, 129.77, 129.42, 128.95, 128.83, 128.11, 127.80, 126.29, 49.18, 34.64, 21.05. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{22}H_{22}N_2NaS^+$: 369.1396, found: 369.1391.

1-(2-((2-Chlorophenyl)thio)ethyl)-2-(diphenylmethylene)hydrazine (5c):



Yellow liquid, 150.4 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.51 (t, *J* = 7.5 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.33 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.29 – 7.24 (m, 5H), 7.18 (td, *J* = 7.7, 1.2 Hz, 1H), 7.09 (td, *J* = 7.8, 1.4 Hz, 1H), 5.64 (t, *J* = 5.4 Hz, 1H), 3.47 (q, *J* = 6.3 Hz, 2H), 3.20 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.84, 138.50, 135.03, 134.00, 133.51, 129.79, 129.46, 128.96, 128.91, 128.86, 128.12, 127.87, 127.18, 126.75, 126.30, 48.78, 32.92. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{21}H_{19}ClN_2NaS^+$: 389.0850, found: 389.0855.

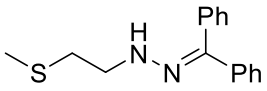
1-(Diphenylmethylene)-2-(2-(naphthalen-2-ylthio)ethyl)hydrazine (5d):



Yellow liquid, 183.6 mg, 96% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.29 – 7.21 (m, 5H),

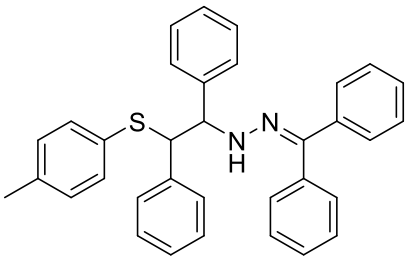
5.62 (t, J = 5.4 Hz, 1H), 3.48 (q, J = 6.4 Hz, 2H), 3.24 (t, J = 6.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 146.59, 138.64, 133.85, 133.64, 133.27, 131.87, 129.48, 129.00, 128.90, 128.56, 128.21, 127.92, 127.78, 127.49, 127.17, 127.15, 126.65, 126.40, 125.78, 49.38, 33.81. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{25}H_{23}N_2S^+$: 383.1576, found: 383.1579.

1-(Diphenylmethylene)-2-(2-(methylthio)ethyl)hydrazine (5e):



Yellow liquid, 104.1 mg, 77% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.51 (t, J = 7.5 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.30 – 7.23 (m, 5H), 5.62 (t, J = 5.1 Hz, 1H), 3.45 (q, J = 6.3 Hz, 2H), 2.71 (t, J = 6.5 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 145.34, 137.54, 132.62, 128.37, 127.85, 127.74, 127.03, 126.70, 125.20, 48.17, 33.41, 14.35. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{16}H_{18}N_2NaS^+$: 293.1083, found: 293.1089.

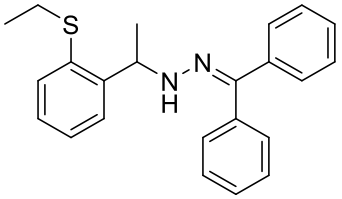
1-(1,2-Diphenyl-2-(p-tolylthio)ethyl)-2-(diphenylmethylene)hydrazine (5f):



Colorless liquid, 162.1 mg, 65% yield, dr = 10:7. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 6H × 1 + 6H × 0.7), 7.31 – 7.29 (m, 1H × 1 + 1H × 0.7), 7.25 – 7.20 (m, 4H × 1 + 4H × 0.7), 7.13 – 7.08 (m, 5H × 1 + 5H × 0.7), 7.06 – 7.01 (m, 4H × 1 + 4H × 0.7), 7.0 – 6.98 (m, 1H × 1 + 1H × 0.7), 6.96 – 6.94 (m, 2H × 1 + 2H × 0.7), 6.93 – 6.89 (m, 1H × 1 + 1H × 0.7), 6.11 (s, 1H × 1), 5.94 (d, J = 5.1 Hz, 1H × 0.7), 4.89 – 4.86 (m, 1H × 0.7), 4.84 (d, J = 7.2 Hz, 1H × 1), 4.72 (d, J = 7.5 Hz, 1H × 1), 4.64 (d, J = 6.5 Hz, 1H × 0.7), 2.24 (s, 3H × 1), 2.21 (s, 3H × 0.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.16, 146.09, 139.95, 139.66, 139.28, 139.11, 138.79, 138.66, 137.08, 137.03, 133.63, 133.58, 132.51, 132.35, 131.52, 131.41, 129.55, 129.48, 129.31,

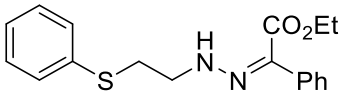
129.26, 129.15, 129.14, 128.94, 128.85, 128.81, 128.65, 128.32, 128.16, 128.09, 128.05, 128.00, 127.95, 127.72, 127.66, 127.43, 127.21, 127.17, 126.95, 126.48, 126.39, 67.69, 67.61, 59.85, 58.84, 21.09, 21.07. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{34}H_{30}N_2NaS^+$: 521.2022, found: 521.2023.

1-(Diphenylmethylene)-2-(1-(2-(ethylthio)phenyl)ethyl)hydrazine (5g):



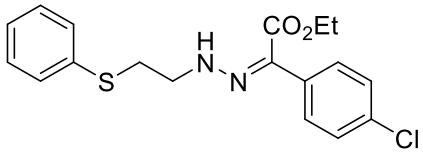
Colorless liquid, 104.6 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.41 (m, 3H), 7.24 – 7.17 (m, 8H), 7.07 (d, *J* = 7.4 Hz, 1H), 5.46 (s, 1H), 4.55 (q, *J* = 6.7 Hz, 1H), 2.91 (q, *J* = 7.2 Hz, 2H), 1.50 (d, *J* = 6.8 Hz, 3H), 1.27 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.60, 138.75, 133.59, 129.41, 129.23, 128.97, 128.86, 128.76, 128.00, 127.64, 127.54, 127.23, 127.18, 126.31, 124.13, 59.16, 27.63, 21.48, 14.37. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{23}H_{25}N_2S^+$: 361.1733, found: 361.1730.

Ethyl (*Z*)-2-phenyl-2-(2-(2-(phenylthio)ethyl)hydrazineylidene)acetate (5h):



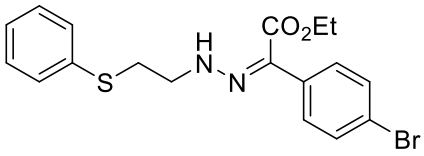
Yellow liquid, 106.7 mg, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.66 (s, 1H), 7.53 – 7.49 (m, 2H), 7.38 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.21 – 7.16 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.70 (td, *J* = 6.8, 4.6 Hz, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.42, 136.93, 135.24, 129.81, 128.94, 128.21, 127.69, 126.94, 126.77, 126.32, 60.39, 50.43, 34.04, 14.17. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{21}N_2O_2S^+$: 329.1318, found: 329.1316.

Ethyl (*Z*)-2-(4-chlorophenyl)-2-(2-(2-(phenylthio)ethyl)hydrazineylidene)acetate (5i):



Yellow liquid, 110.7 mg, 61% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.72 (t, *J* = 4.2 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.29 – 7.25 (m, 4H), 7.21 – 7.17 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.71 (td, *J* = 6.7, 4.6 Hz, 2H), 3.17 (t, *J* = 6.7 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.17, 135.40, 135.14, 132.69, 129.89, 129.44, 128.96, 127.81, 126.40, 125.40, 60.51, 50.50, 34.08, 14.16. HRMS (ESI-TOF): $[M + H]^+$ calculated for $C_{18}H_{20}ClN_2O_2S^+$: 363.0929, found: 363.0937.

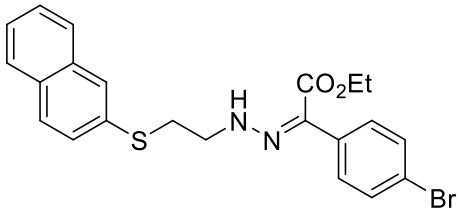
Ethyl (*Z*)-2-(4-bromophenyl)-2-(2-(2-(phenylthio)ethyl)hydrazineylidene)acetate (5j):



Yellow liquid, 116.1 mg, 57% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.73 (t, *J* = 4.1 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.41 – 7.36 (m, 4H), 7.29 – 7.25 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.71 (td, *J* = 6.7, 4.6 Hz, 2H), 3.18 (t, *J* = 6.7 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.16, 135.89, 135.14, 130.79, 129.94, 129.79, 128.99, 126.44, 125.43, 120.93, 60.55, 50.54, 34.11, 14.19. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{18}H_{19}BrN_2NaO_2S^+$: 429.0243, found: 429.0250.

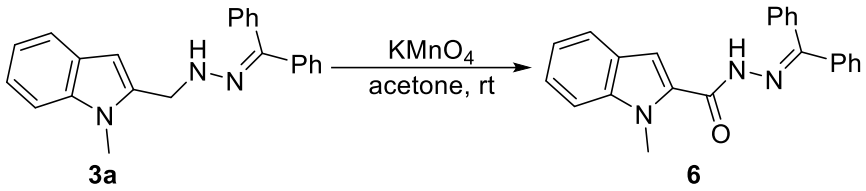
Ethyl (*Z*)-2-(4-bromophenyl)-2-(2-(2-(naphthalen-2-ylthio)ethyl) hydrazineylide

ne)acetate (5k):



White solid; mp: 102 – 104 °C; 132.6 mg, 58% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.74 (s, 1H), 7.80 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.39 (m, 5H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.75 (q, *J* = 6.5 Hz, 2H), 3.26 (t, *J* = 6.6 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.05, 135.85, 133.64, 132.60, 131.84, 130.73, 129.77, 128.49, 127.80, 127.64, 127.62, 127.08, 126.52, 125.79, 125.40, 120.88, 60.46, 50.73, 33.97, 14.09. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{22}H_{21}BrN_2NaO_2S^+$: 479.0399, found: 479.0392.

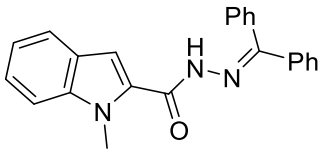
IV. General Procedure for the Preparation of 6:



3a **6**

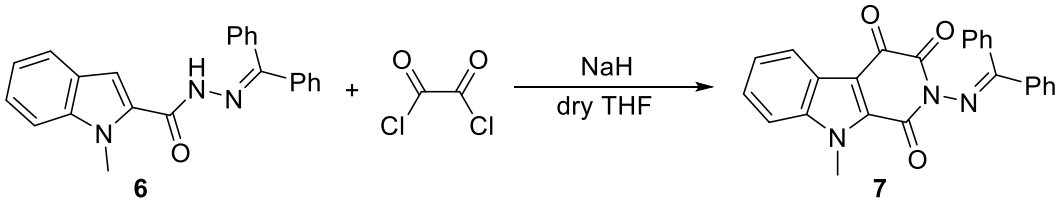
A sealed tube equipped with a magnetic stir bar was charged with **3a** (0.3 mmol, 101.8 mg) in acetone (3.0 mL), then $KMnO_4$ (0.9 mmol, 142.2 mg) was added. The reaction mixture was then stirred at room temperature for 0.5 h. After the reaction was complete, the reaction mixture was poured into saturated aqueous NaCl (30 mL) and extracted with DCM (10 mL×3), the combined organic extracts were washed with H_2O, dried (Na_2SO_4) and concentrated under vacuum. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:10, V/V) to afford product **6** (79.5 mg, 75%) as a yellow solid.

N'-(diphenylmethylene)-1-methyl-1*H*-indole-2-carbohydrazide (6):



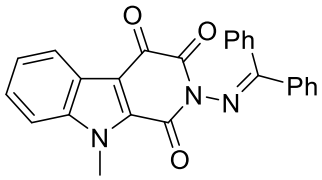
Yellow solid, 79.5 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.63 (s, 1H), 7.70 – 7.67 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.30 (m, 7H), 7.29 – 7.26 (m, 2H), 7.21 – 7.19 (m, 1H), 7.02 (ddd, *J* = 7.9, 5.7, 2.1 Hz, 1H), 6.82 (s, 1H), 3.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 167.23, 153.09, 140.45, 137.88, 136.44, 133.73, 130.42, 129.67, 129.03, 128.61, 128.30, 127.71, 127.23, 124.41, 121.68, 120.08, 111.41, 109.68, 32.00. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{23}H_{19}N_3NaO^+$: 376.1420, found: 376.1416.

V. General Procedure for the Preparation of 7:



Oxalyl chloride (1.2 mmol, 152.3 mg) was added dropwise into the solution of **6** (0.2 mmol, 70.7 mg) and 60% NaH (0.6 mmol, 24.0 mg) in dry THF (2 mL). The reaction mixture was then stirred at 60°C for 12 h. After the reaction was complete, the reaction mixture was poured into saturated aqueous NaCl (30 mL) and extracted with DCM (10 mL×3), the combined organic extracts were washed with H_2O, dried (Na_2SO_4) and concentrated under vacuum. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 4:10, V/V) to afford product **7** (44.8 mg, 55%) as a yellow solid.

2-((Diphenylmethylene)amino)-9-methyl-1*H*-pyrido[3,4-*b*]indole-1,3,4(2*H*,9*H*)-trione (7):



Yellow solid, 44.8 mg, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.21 (d, J = 8.0 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.42 (t, J = 7.9 Hz, 3H), 7.35 – 7.31 (m, 3H), 7.28 – 7.26 (m, 2H), 4.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 181.12, 168.72, 154.92, 154.62, 140.09, 135.59, 134.15, 132.41, 132.14, 129.98, 129.92, 128.44, 128.32, 127.66, 127.18, 125.57, 123.27, 123.16, 116.03, 111.25, 32.26. HRMS (ESI-TOF): $[M + Na]^+$ calculated for $C_{25}H_{17}N_3NaO_3^+$: 430.1162, found: 430.1152.

VI. ORTEP Drawing of Compounds 3i, 3s, 5k and 7:

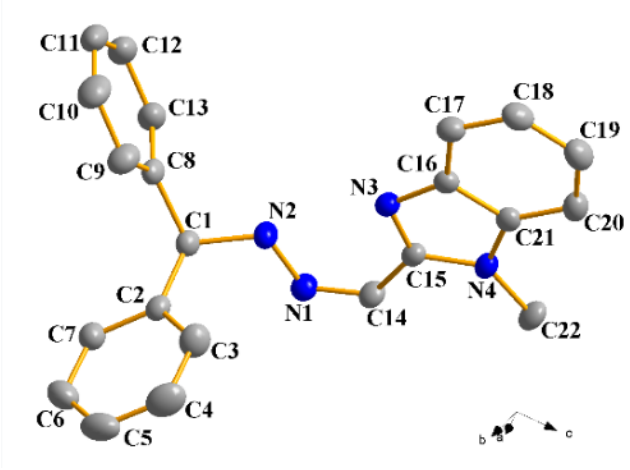


Figure 1. The ORTEP drawing of crystal 3i (The ellipsoid contour percent probability level is 50%).

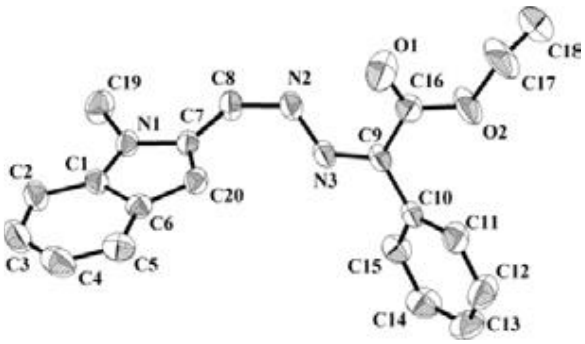


Figure 2. The ORTEP drawing of crystal 3s (The ellipsoid contour percent probability level is 50%).

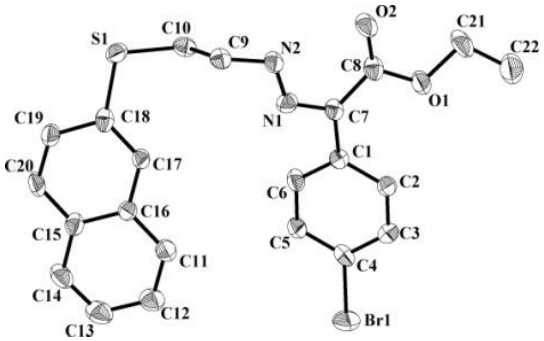


Figure 3. The ORTEP drawing of crystal 5k (The ellipsoid contour percent probability level is 50%).

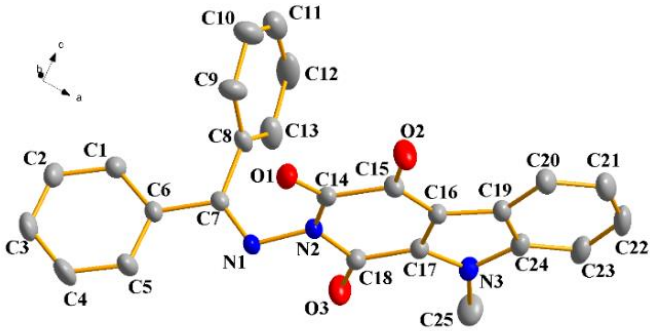


Figure 4. The ORTEP drawing of crystal 7 (The ellipsoid contour percent probability level is 50%).

Method of Crystallization: The **3i**, **3s**, **5k** and **7** were recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

VII. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of Compounds 3 and 5-7:

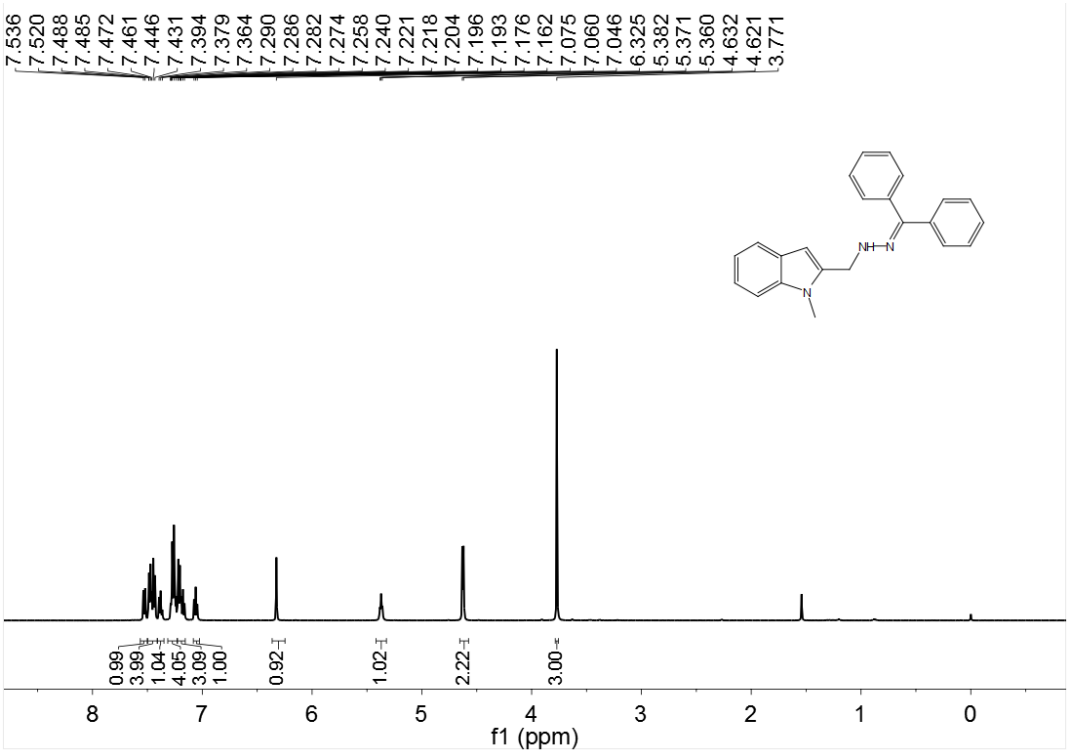


Figure 5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3a**

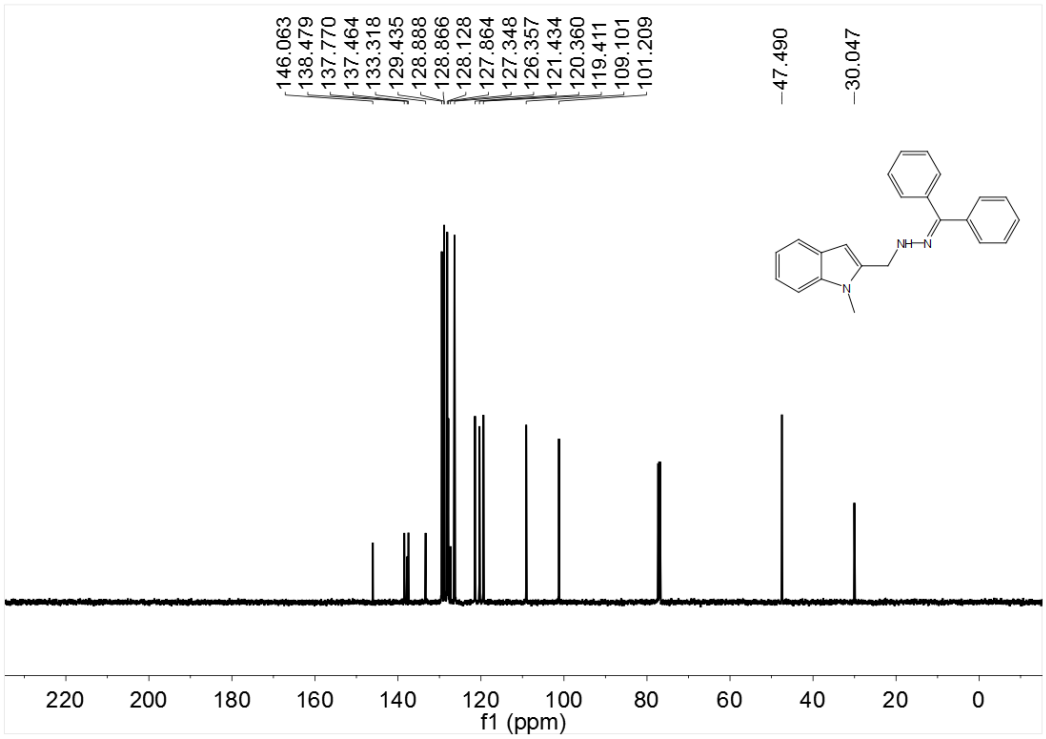


Figure 6. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3a**

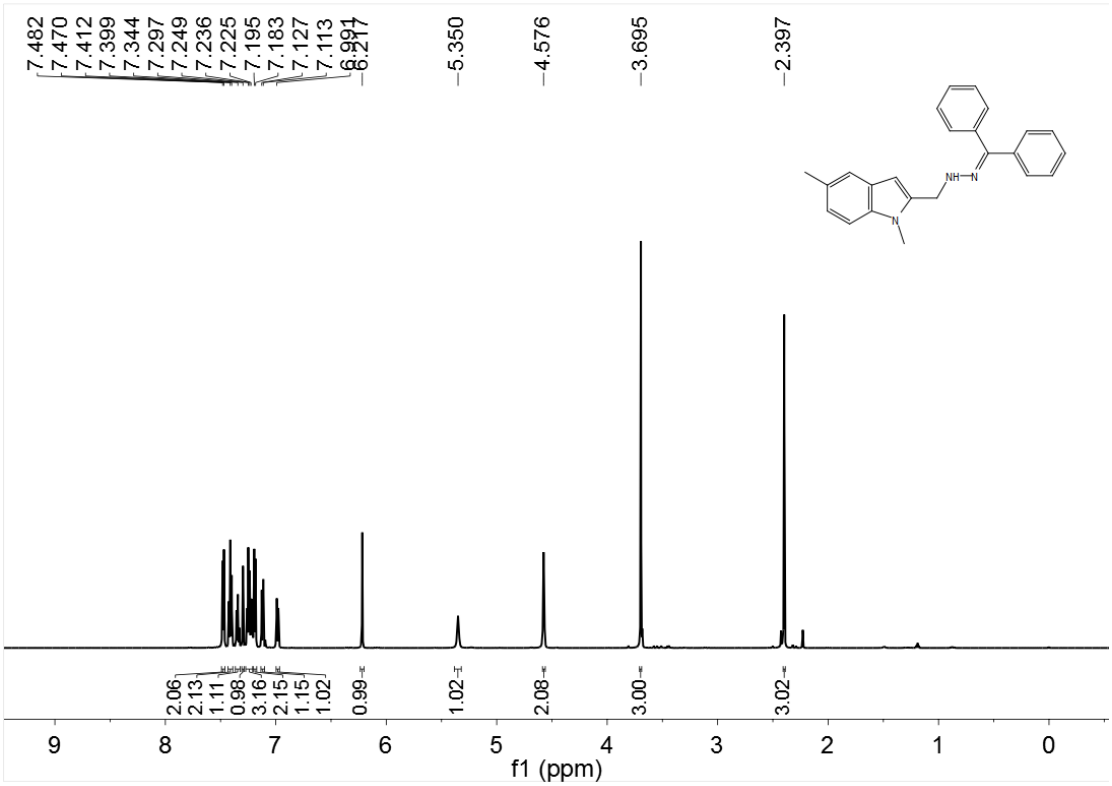


Figure 7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3b**

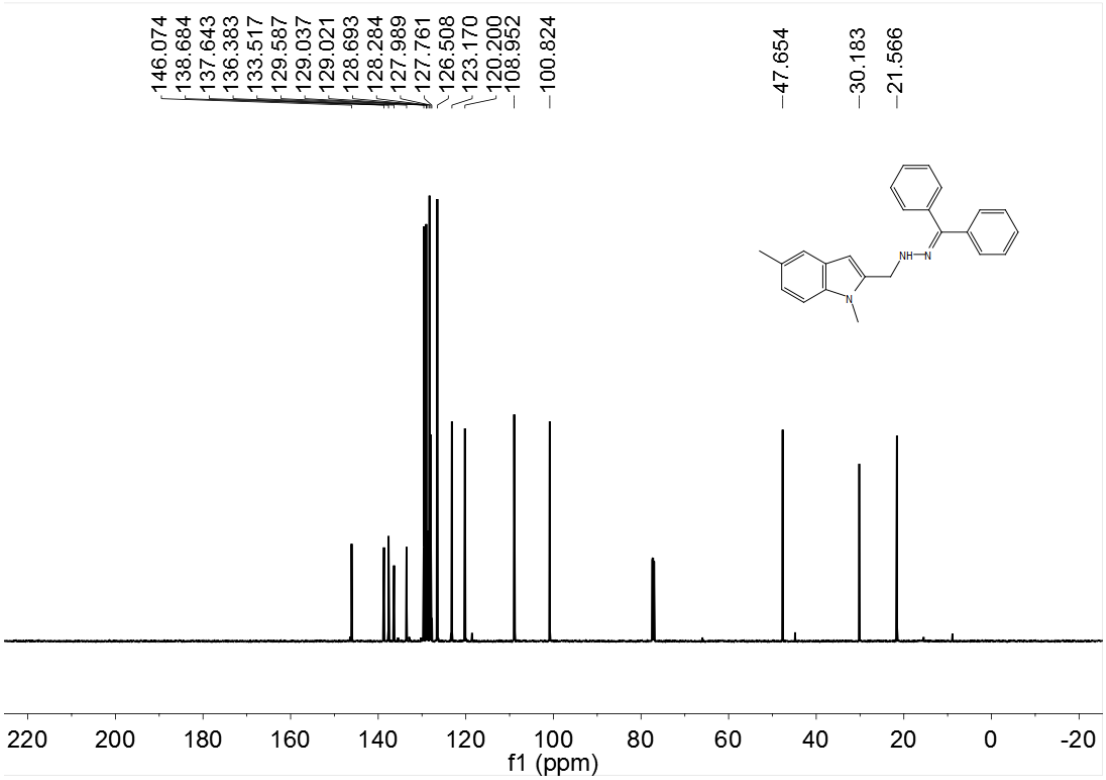


Figure 8. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3b**

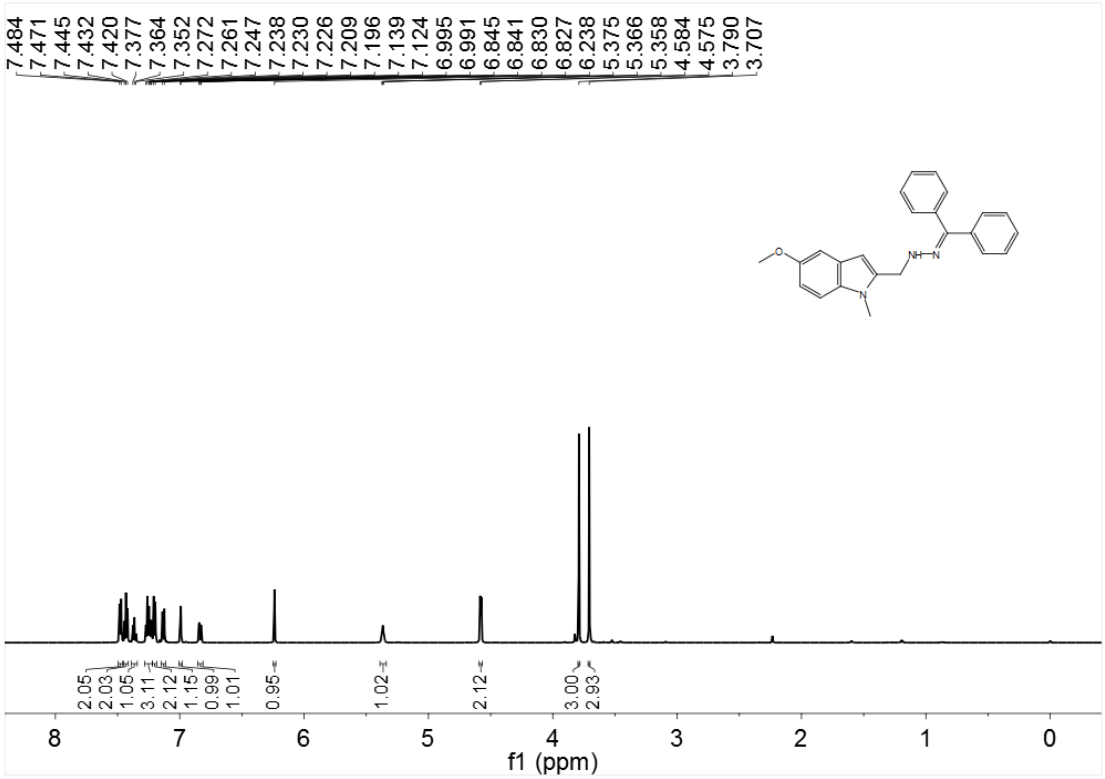


Figure 9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3c**

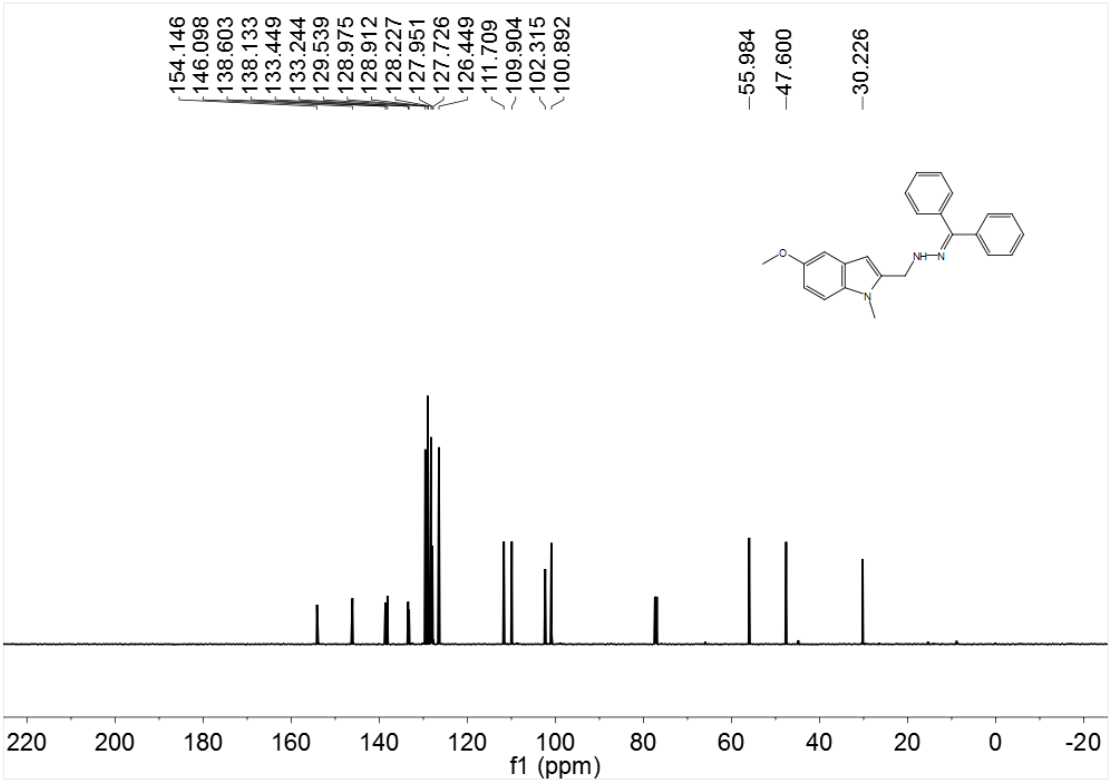


Figure 10. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3c**

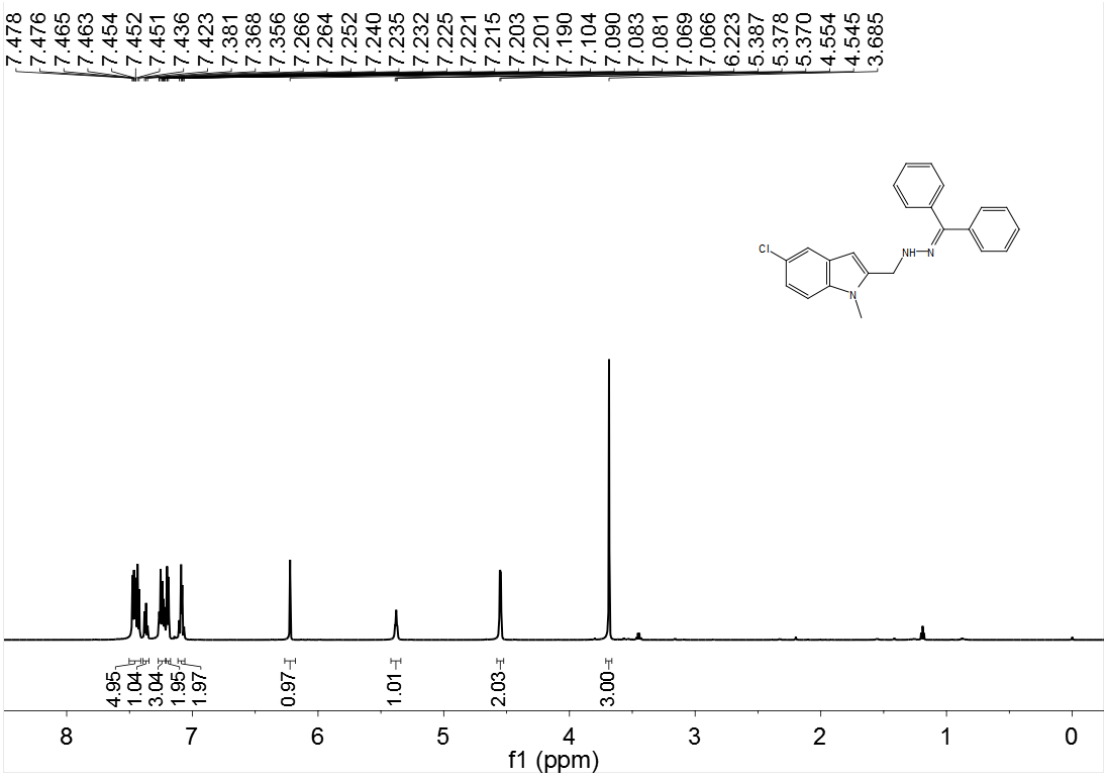


Figure 11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3d**

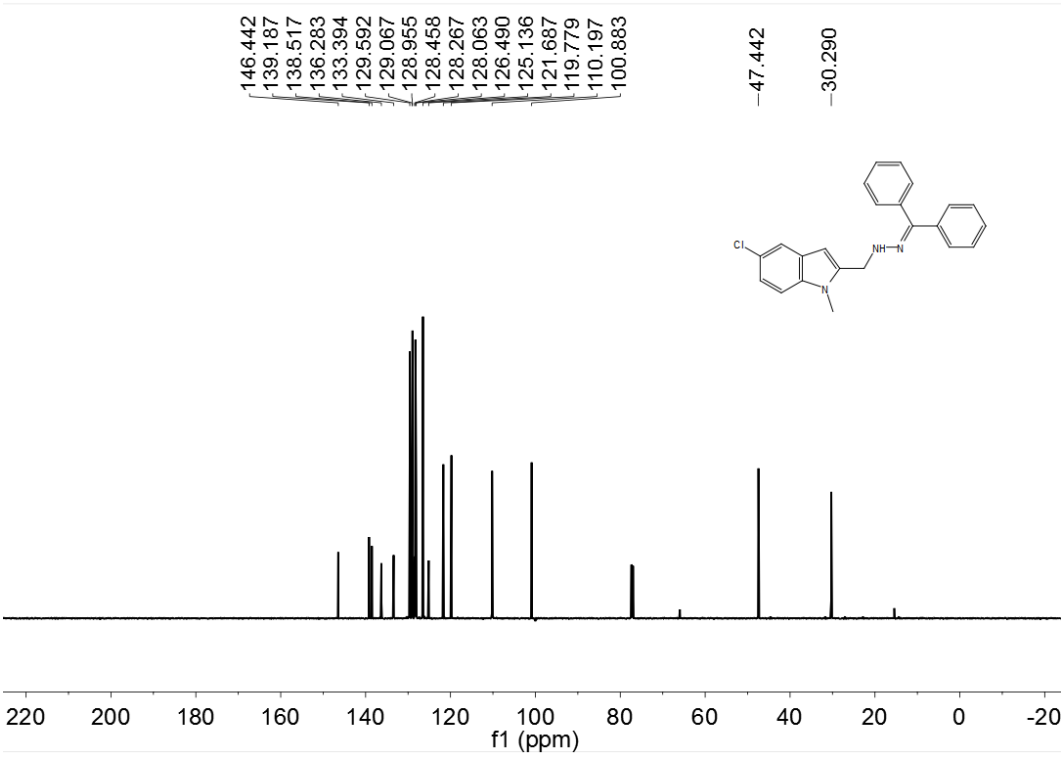


Figure 12. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3d**

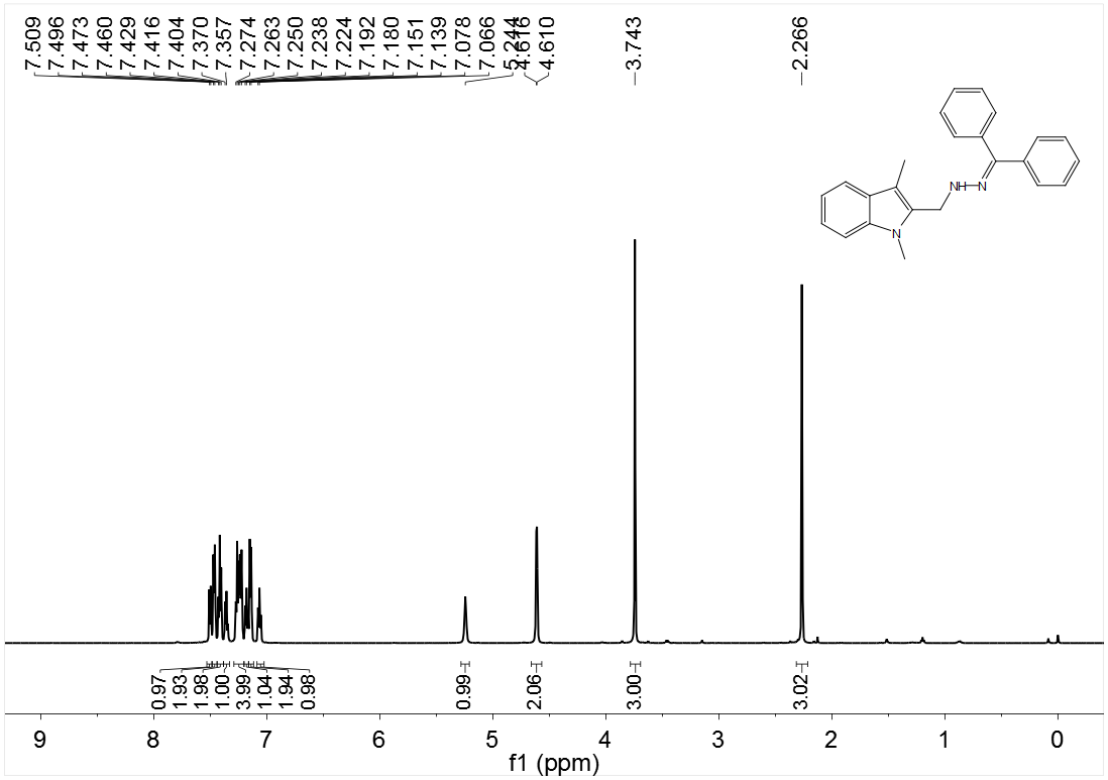


Figure 13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3e**

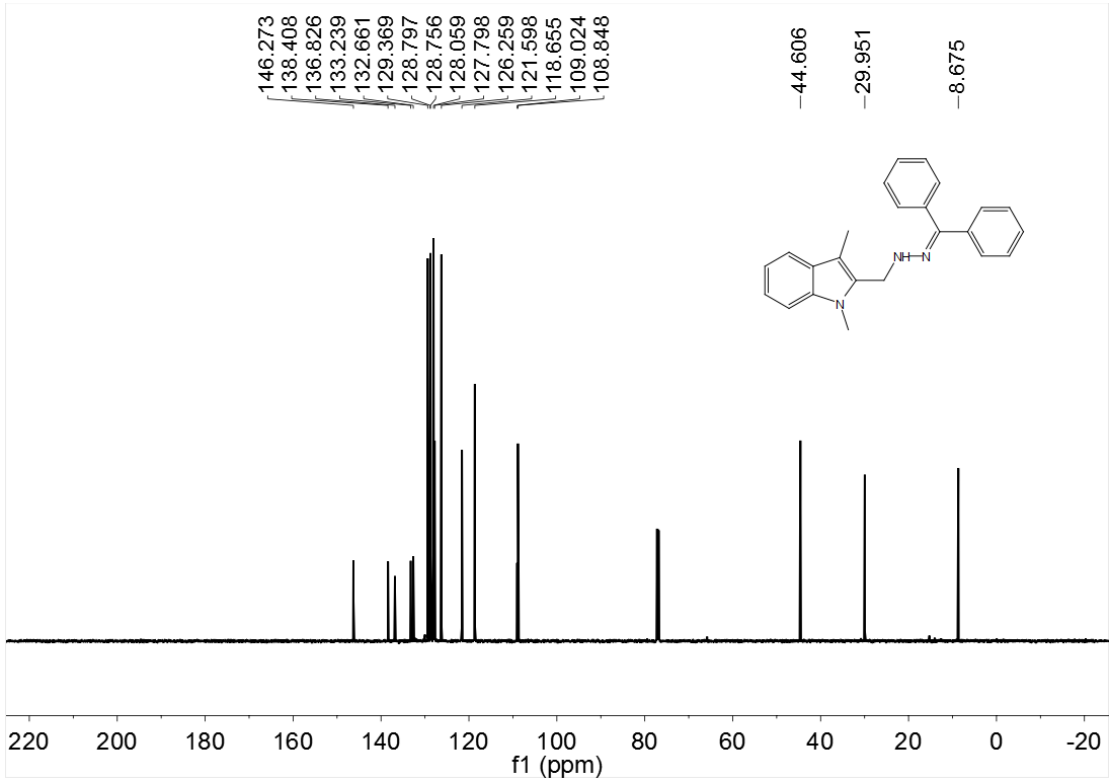


Figure 14. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3e**

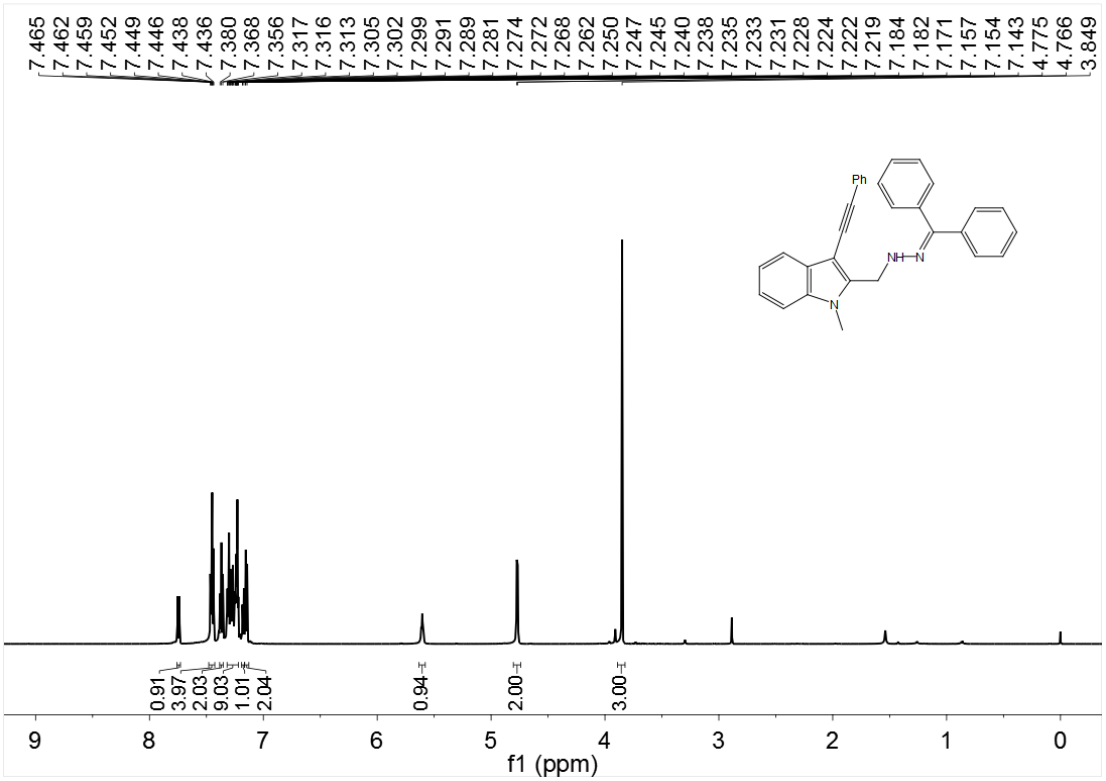


Figure 15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3f**

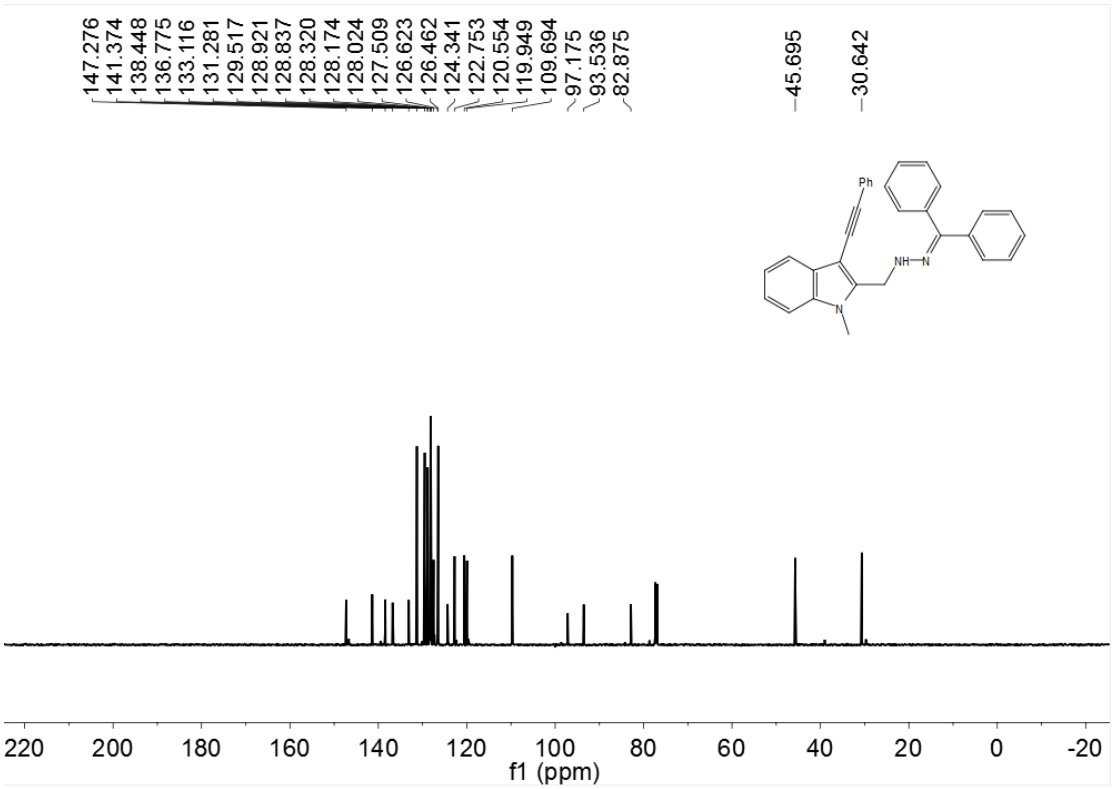


Figure 16. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3f**

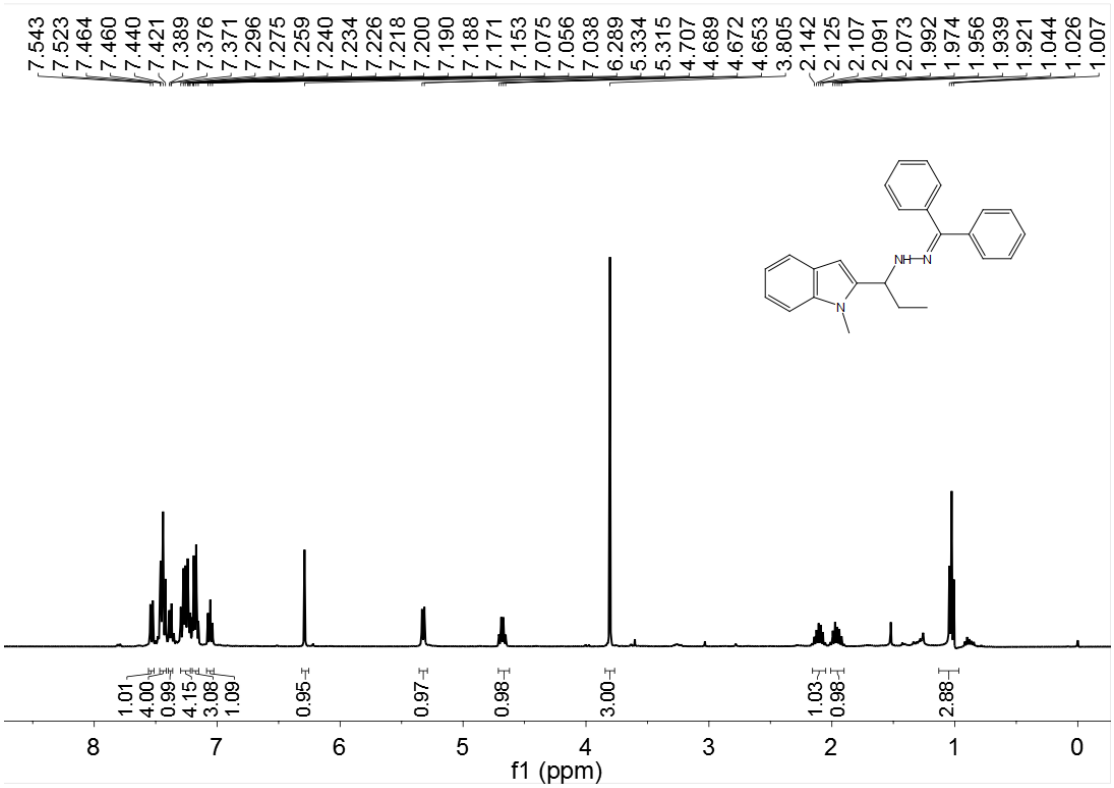


Figure 17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g**

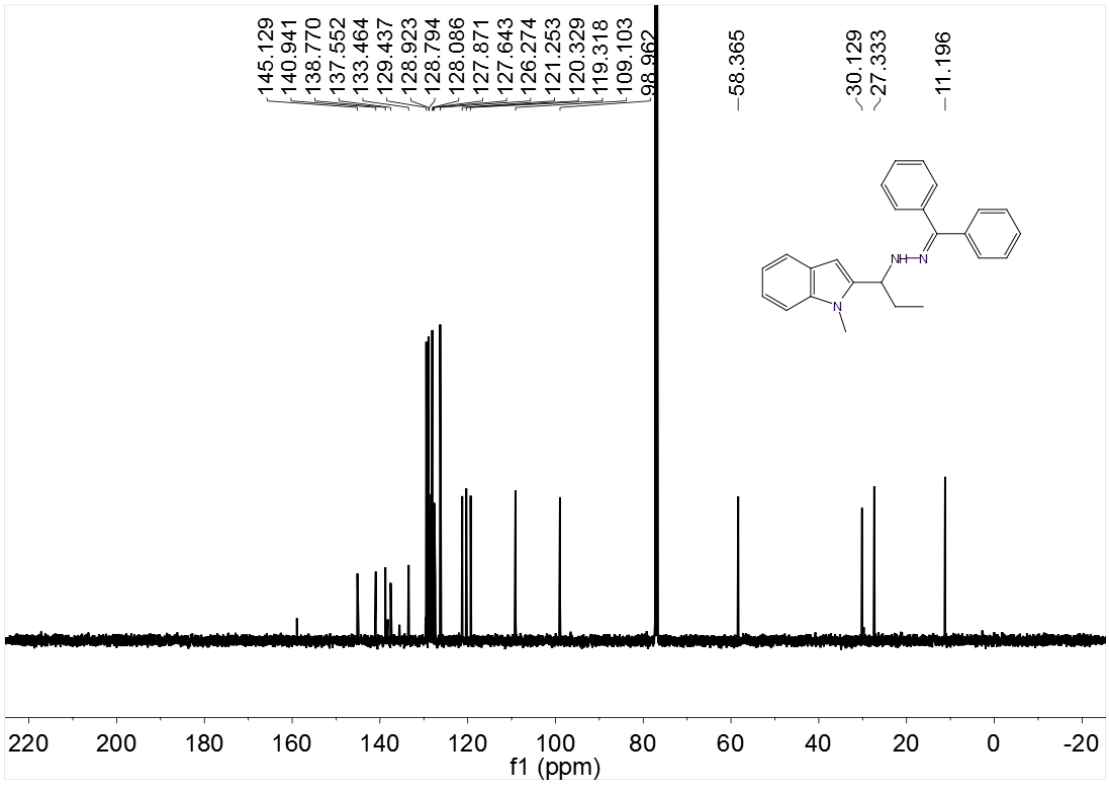


Figure 18. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3g**

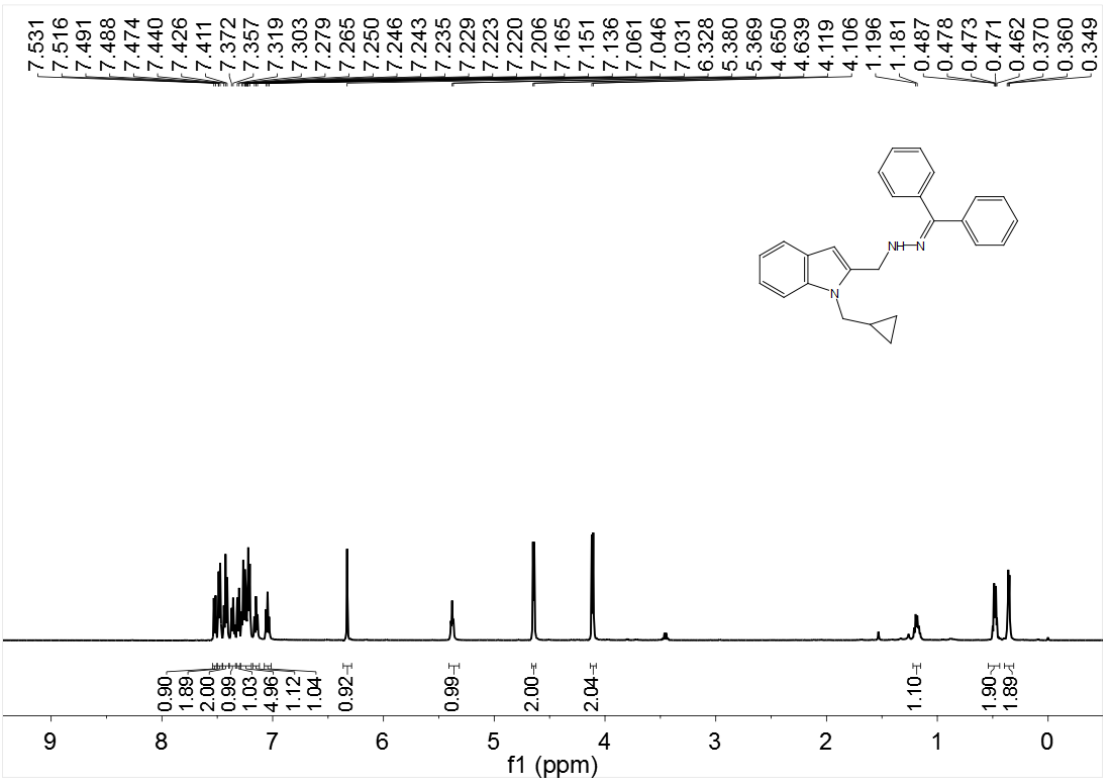


Figure 19. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3h**

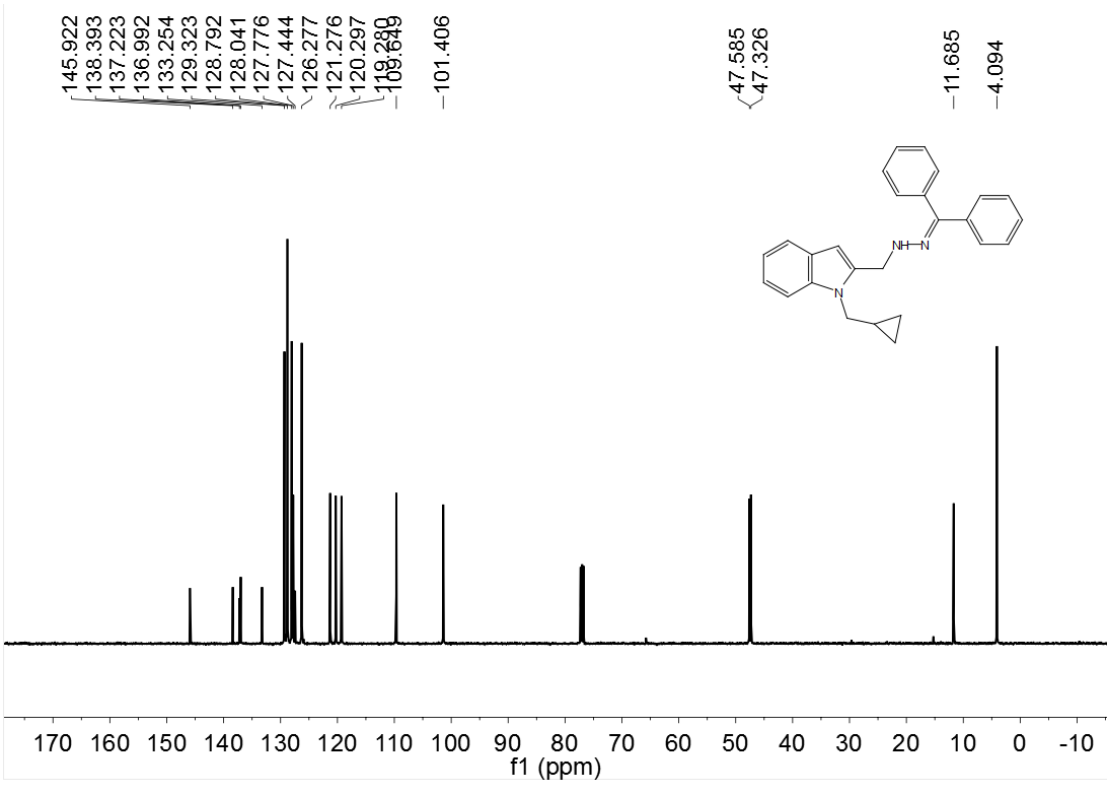


Figure 20. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3h**

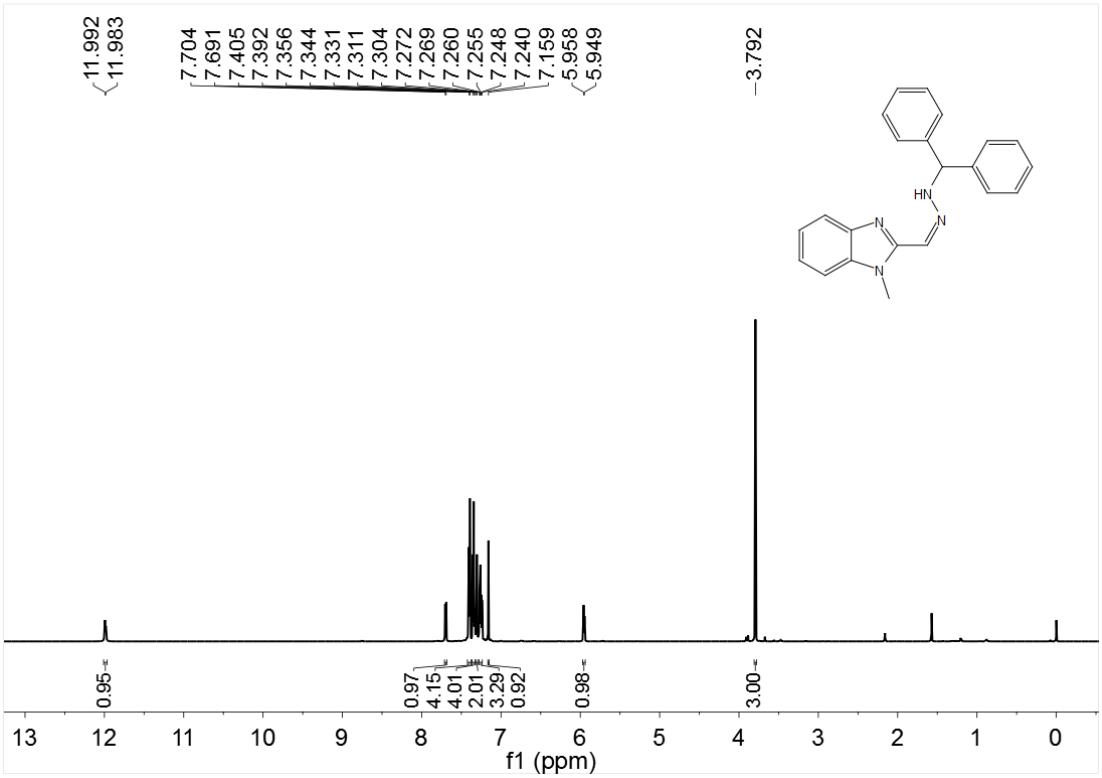


Figure 21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3i**

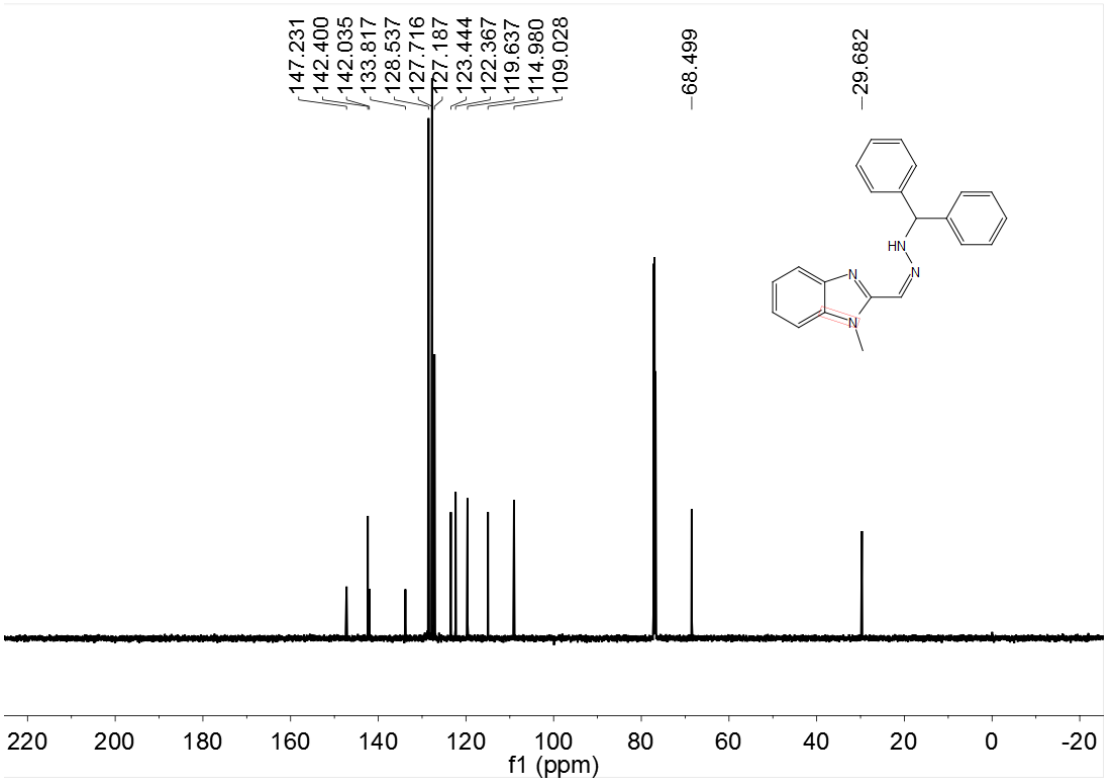


Figure 22. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3i**

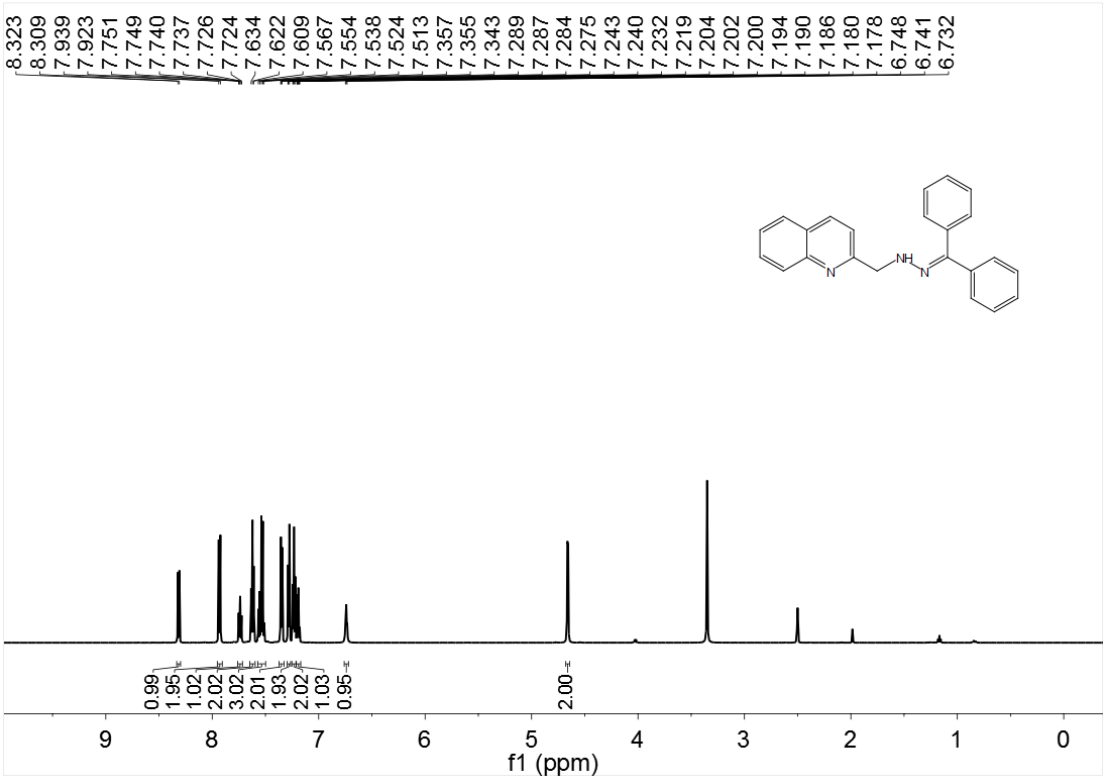


Figure 23. ^{1}H NMR spectrum (600 MHz, DMSO) of **3j**

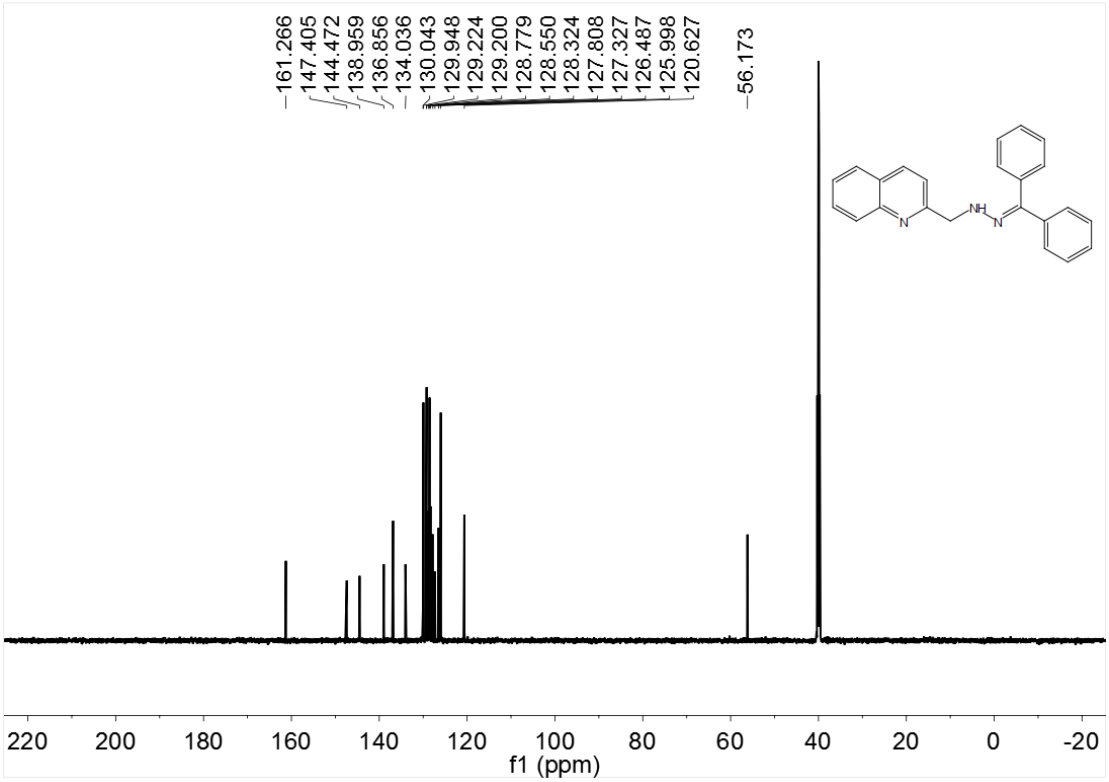


Figure 24. ^{13}C NMR spectrum (151 MHz, DMSO) of **3j**

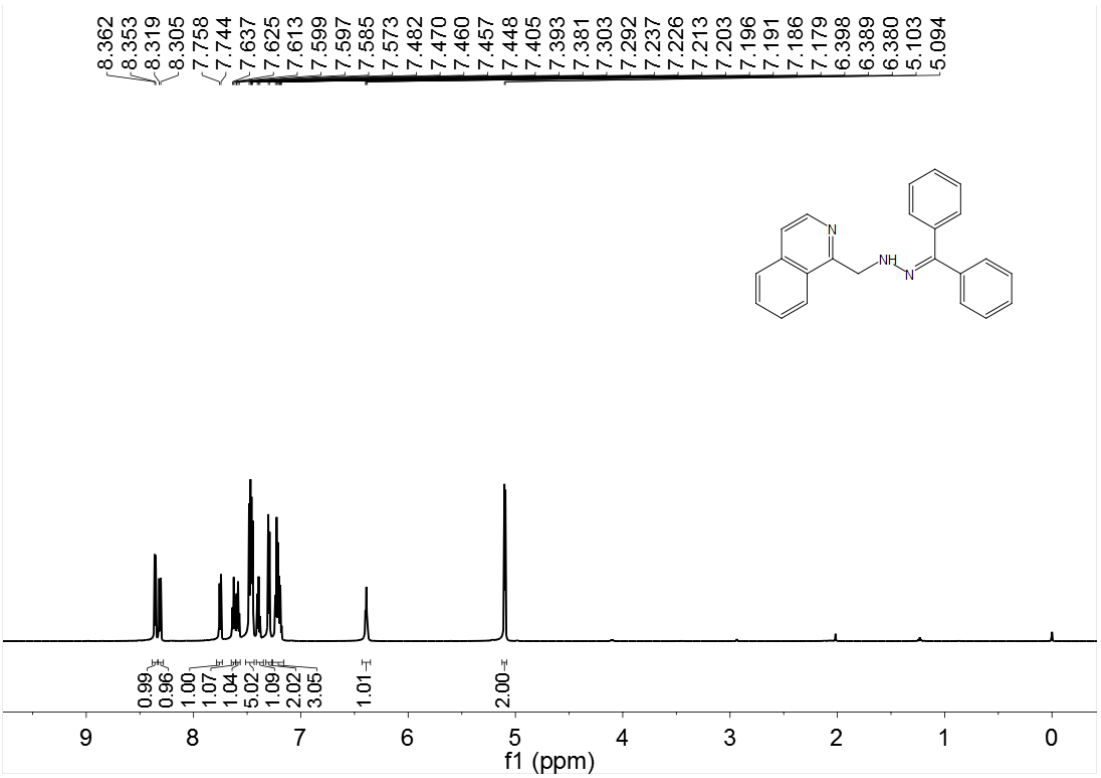


Figure 25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3k**

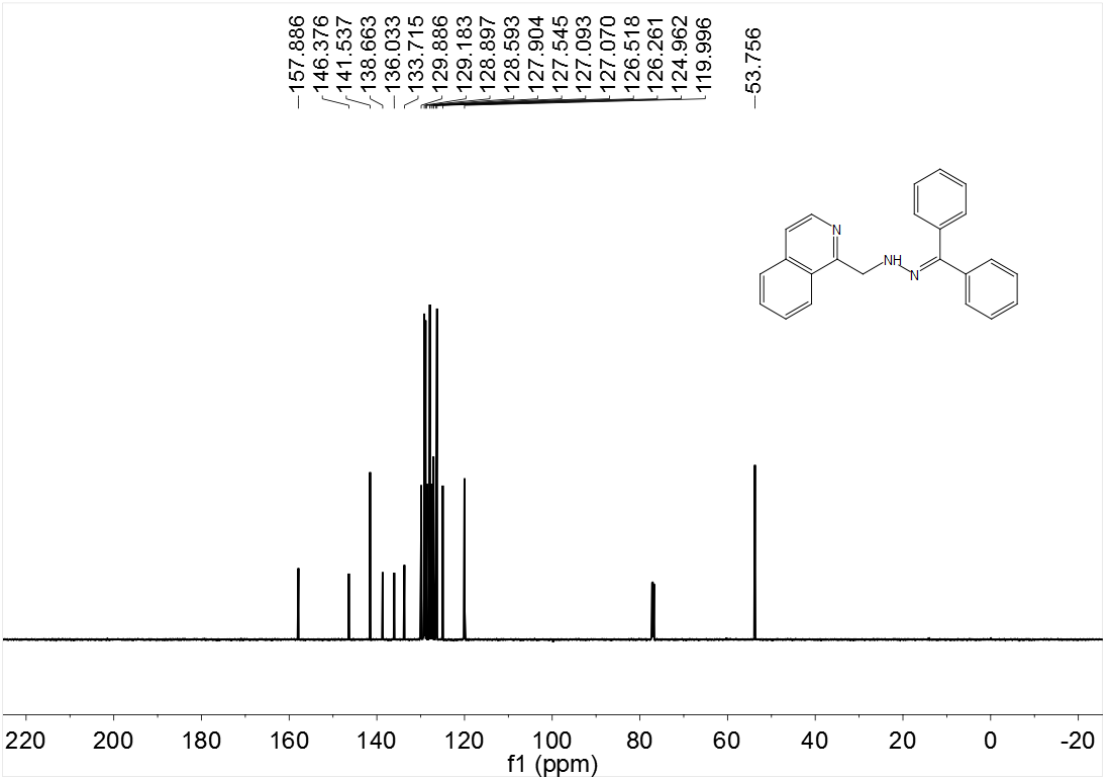


Figure 26. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3k**

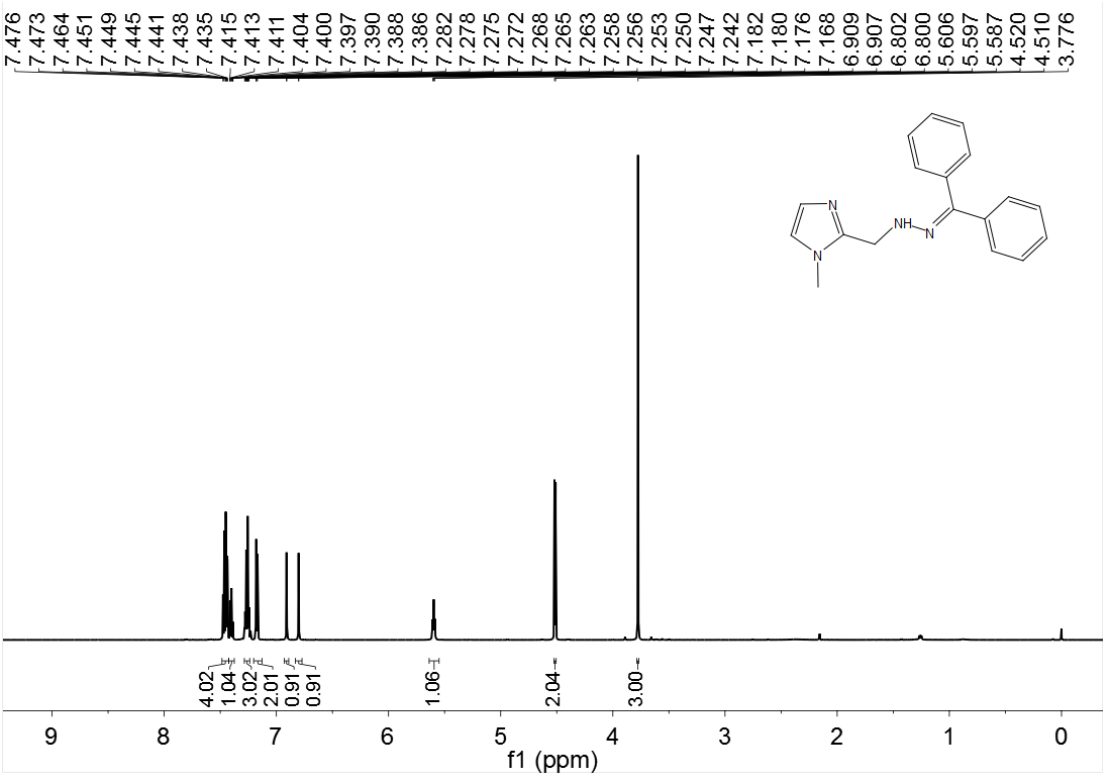


Figure 27. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3l**

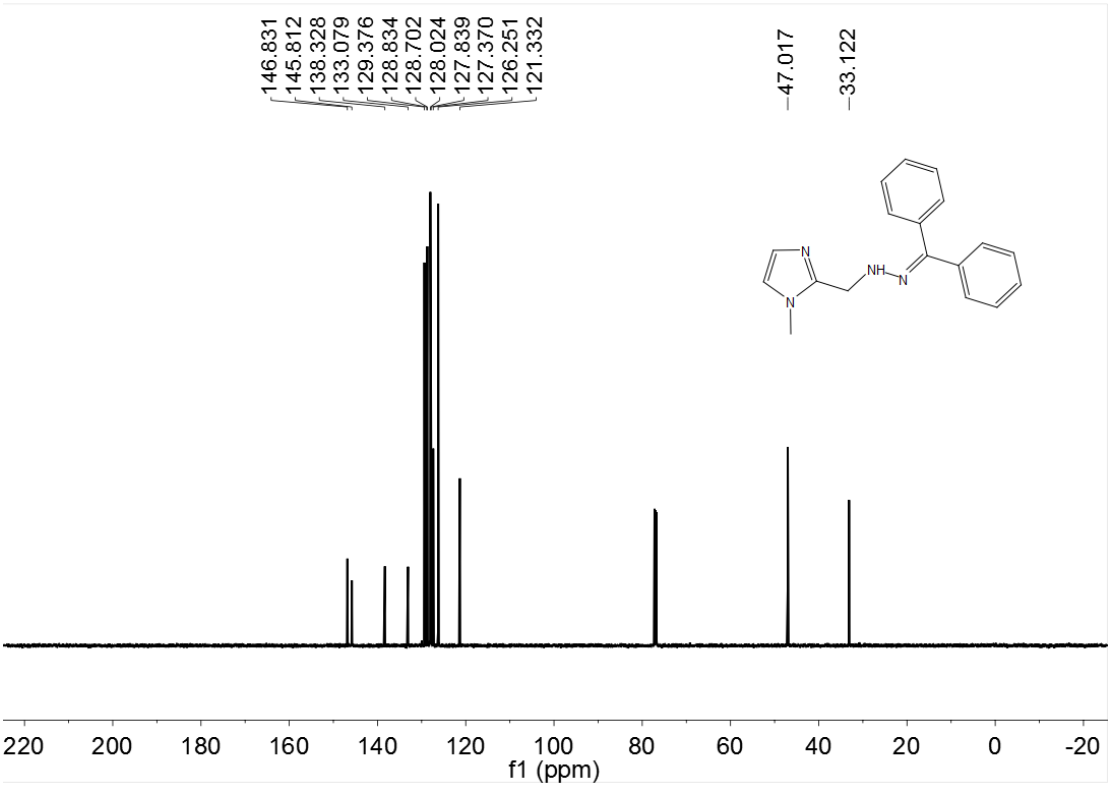


Figure 28. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3l**

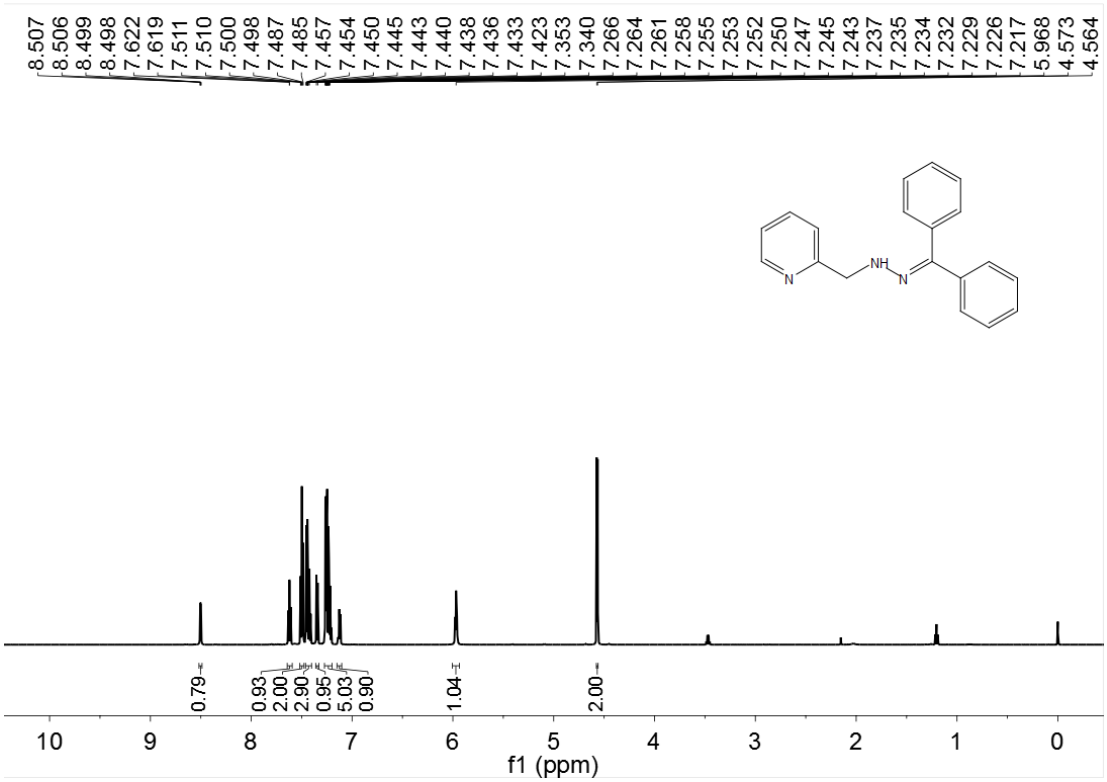


Figure 29. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3m**

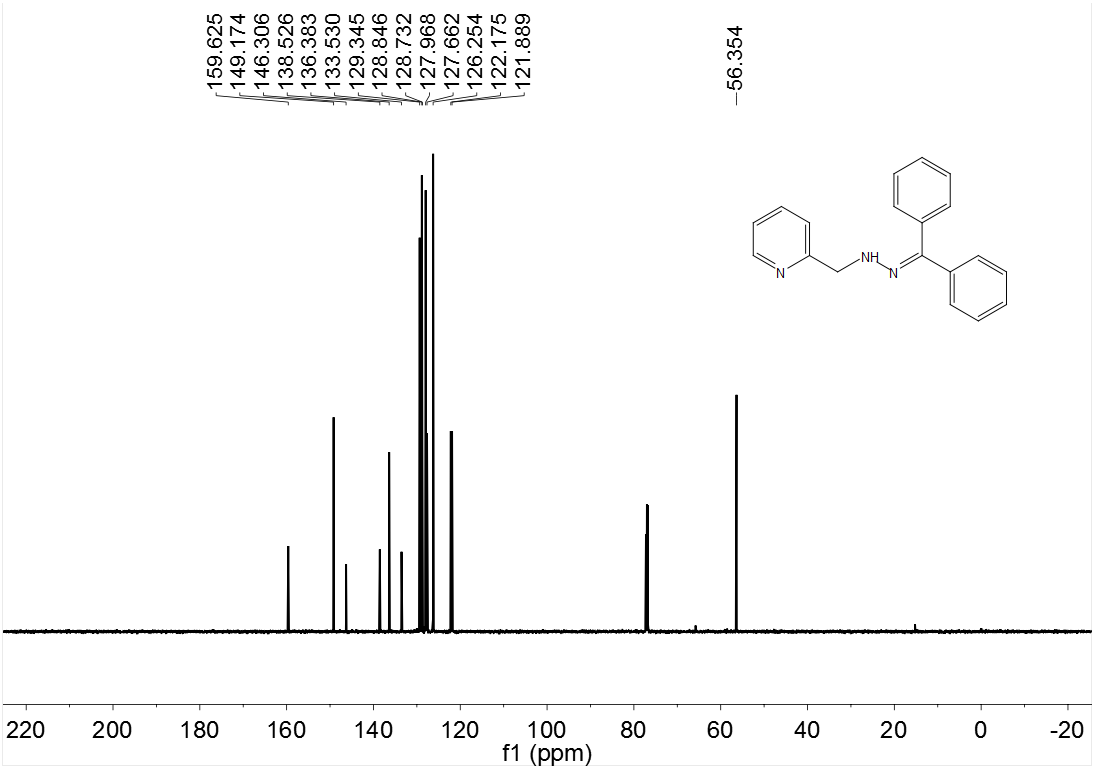


Figure 30. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3m**

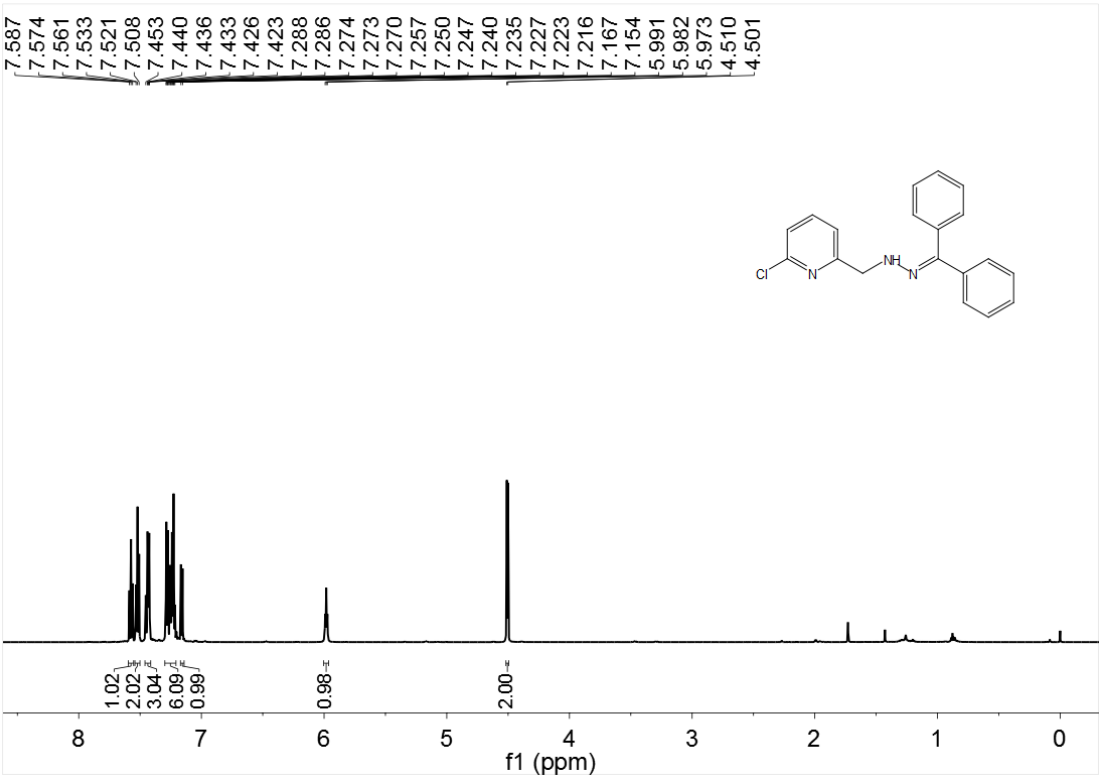


Figure 31. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3n**

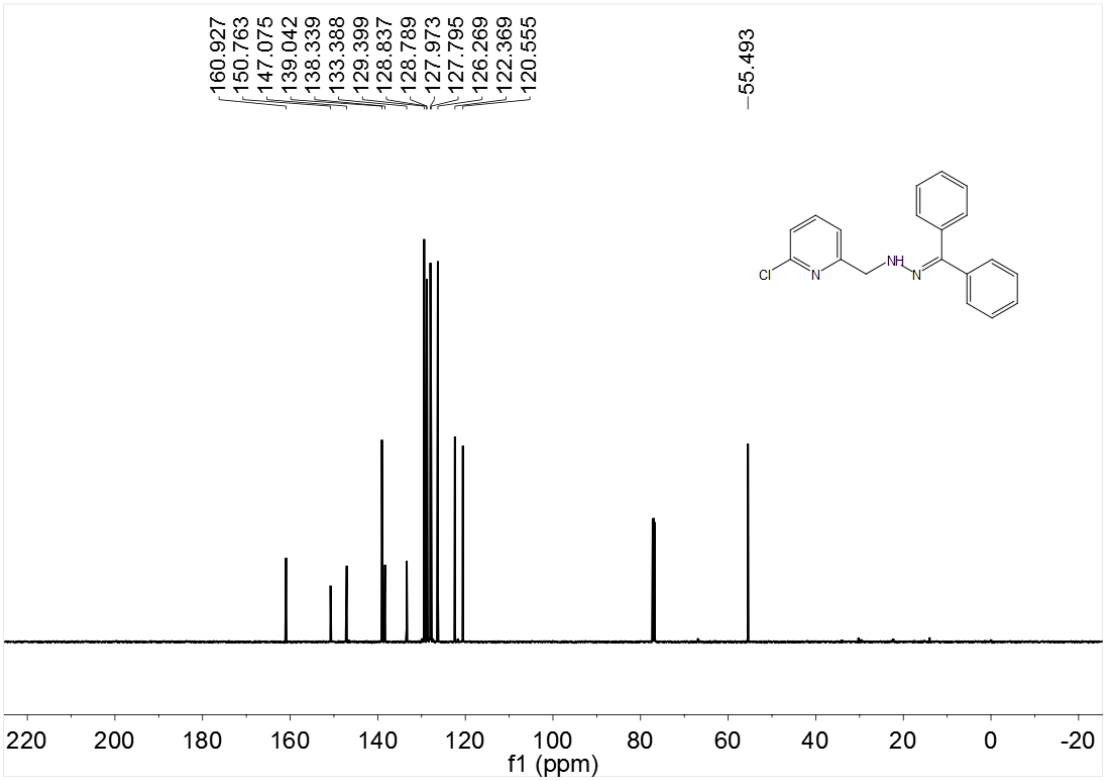


Figure 32. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3n**

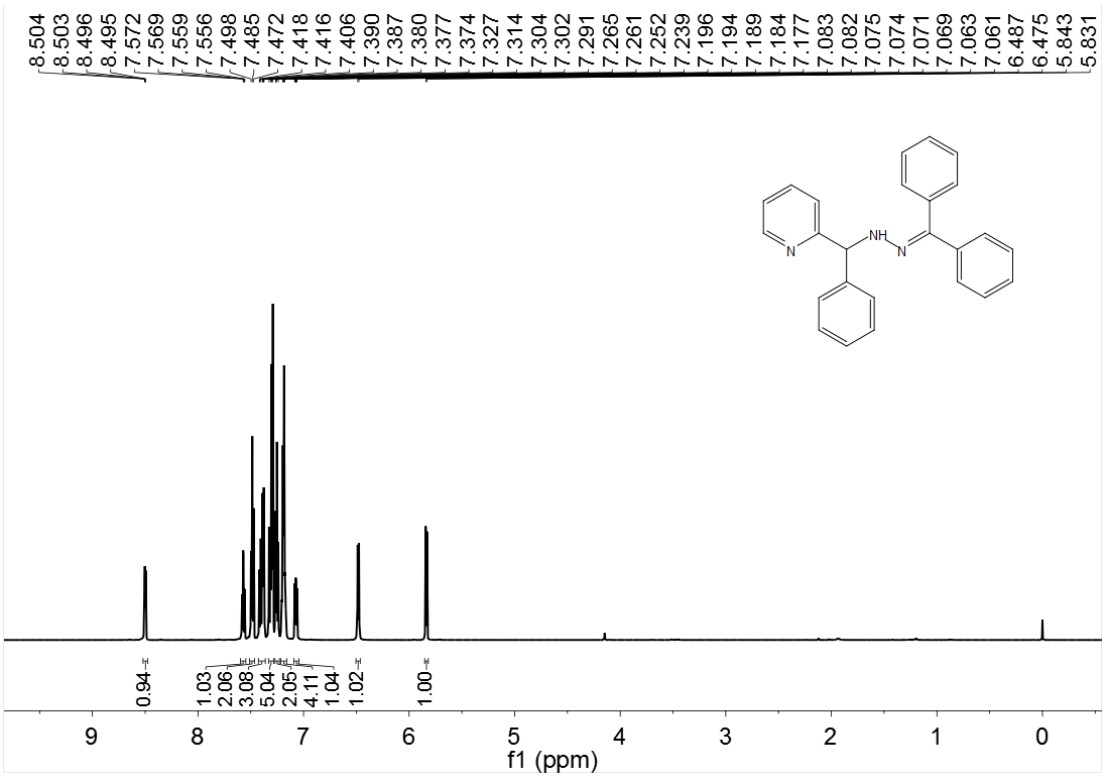


Figure 33. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3o**

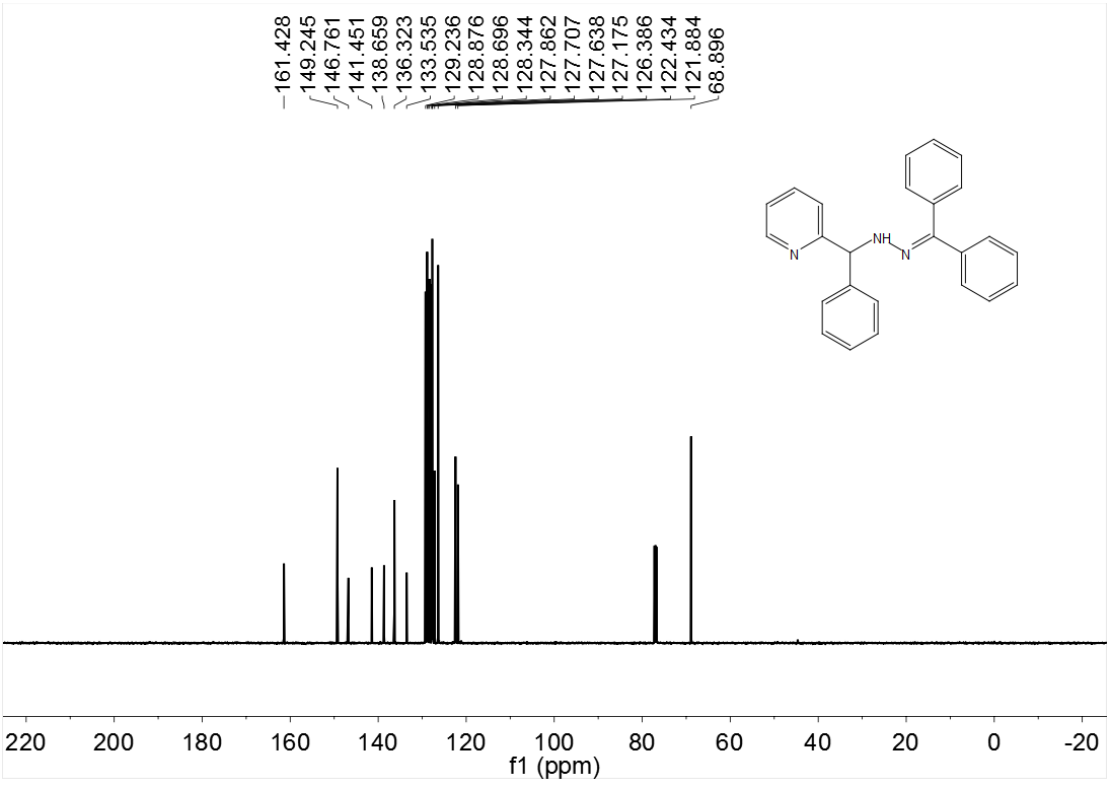


Figure 34. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3o**

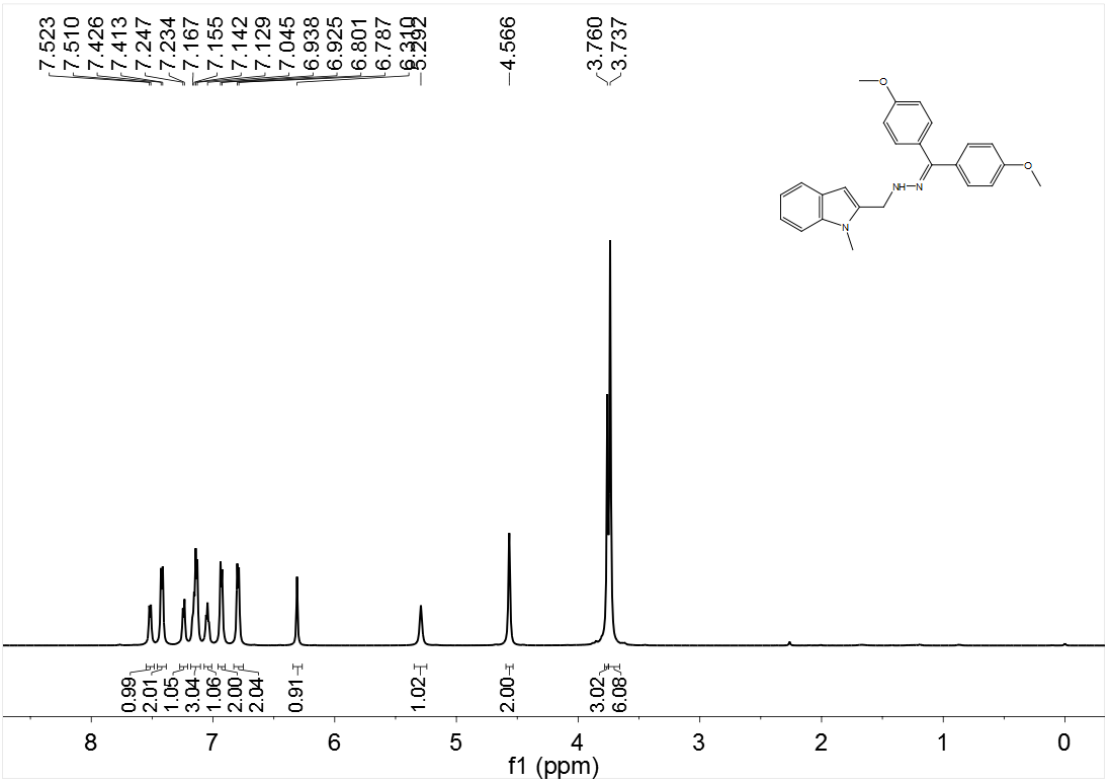


Figure 35. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3p**

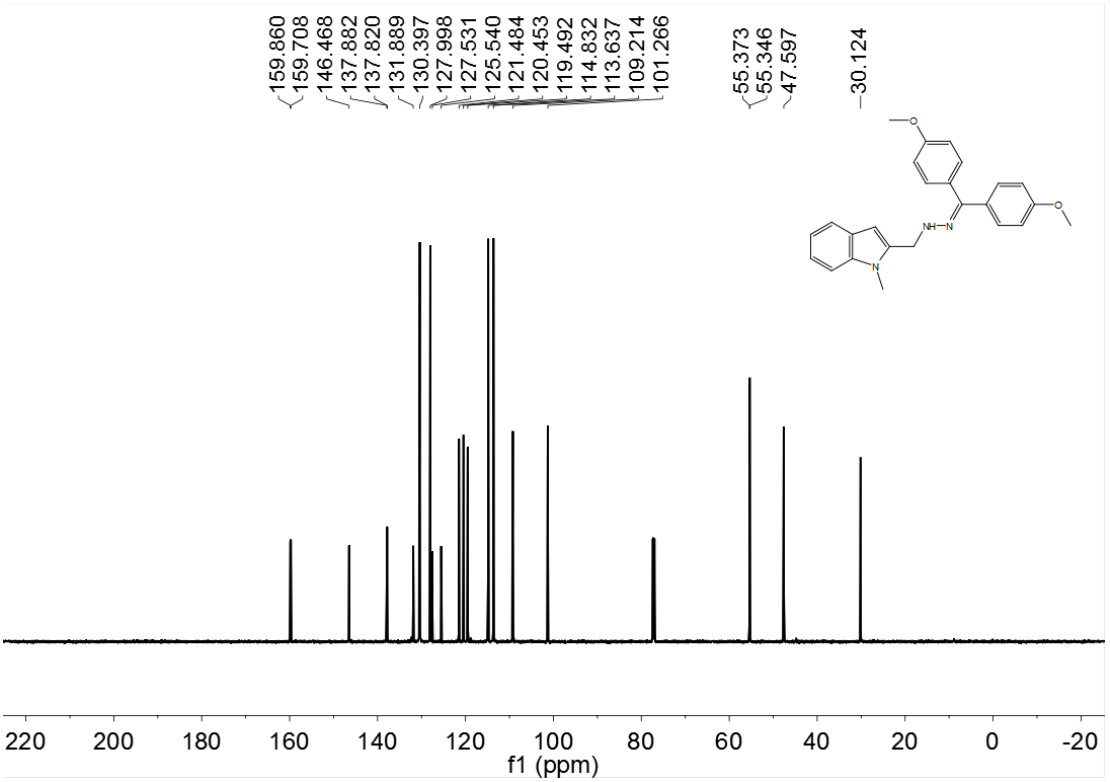


Figure 36. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3p**

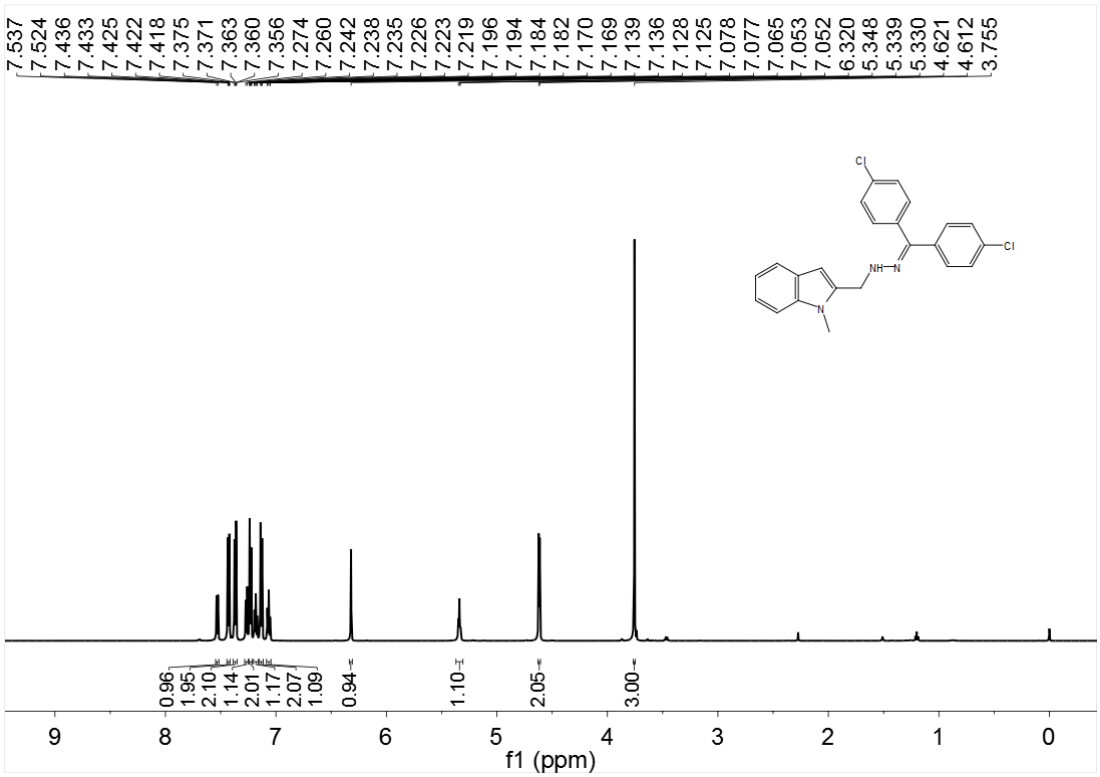


Figure 37. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3q**

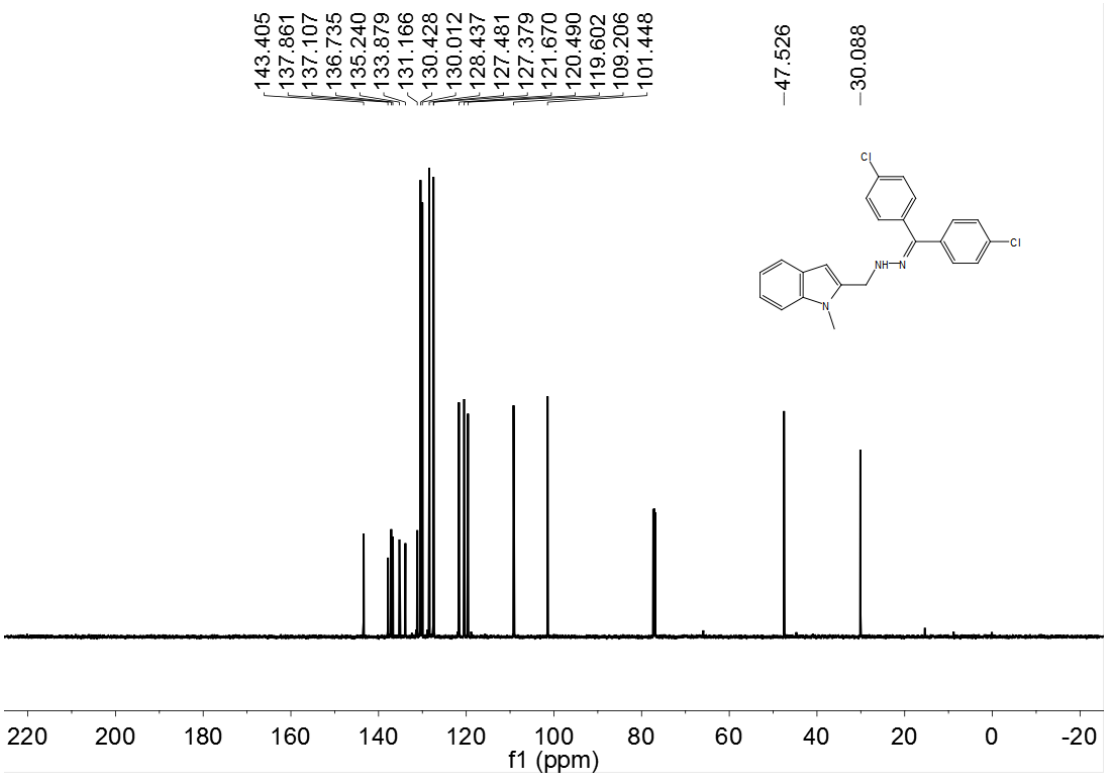


Figure 38. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3q**

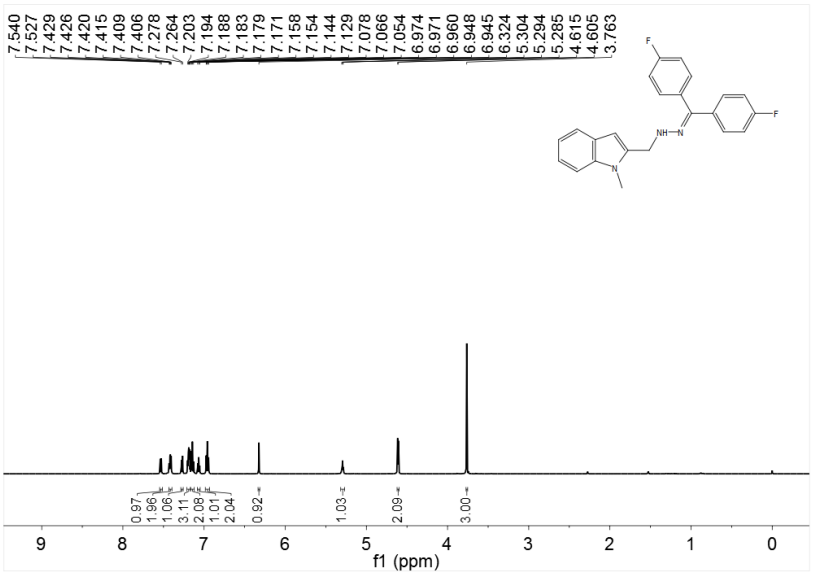


Figure 39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3r**

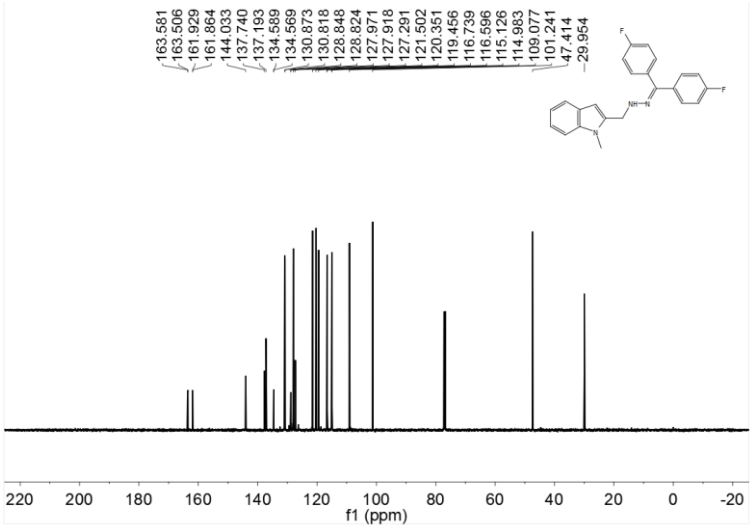


Figure 40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3r**

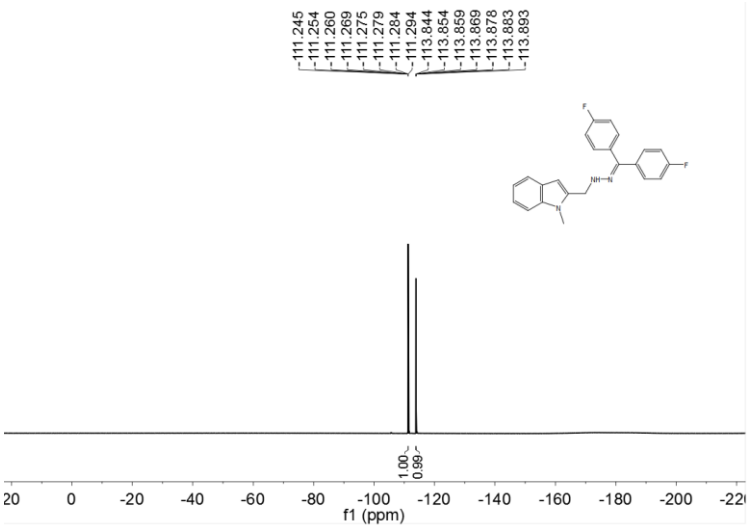


Figure 41. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3r**

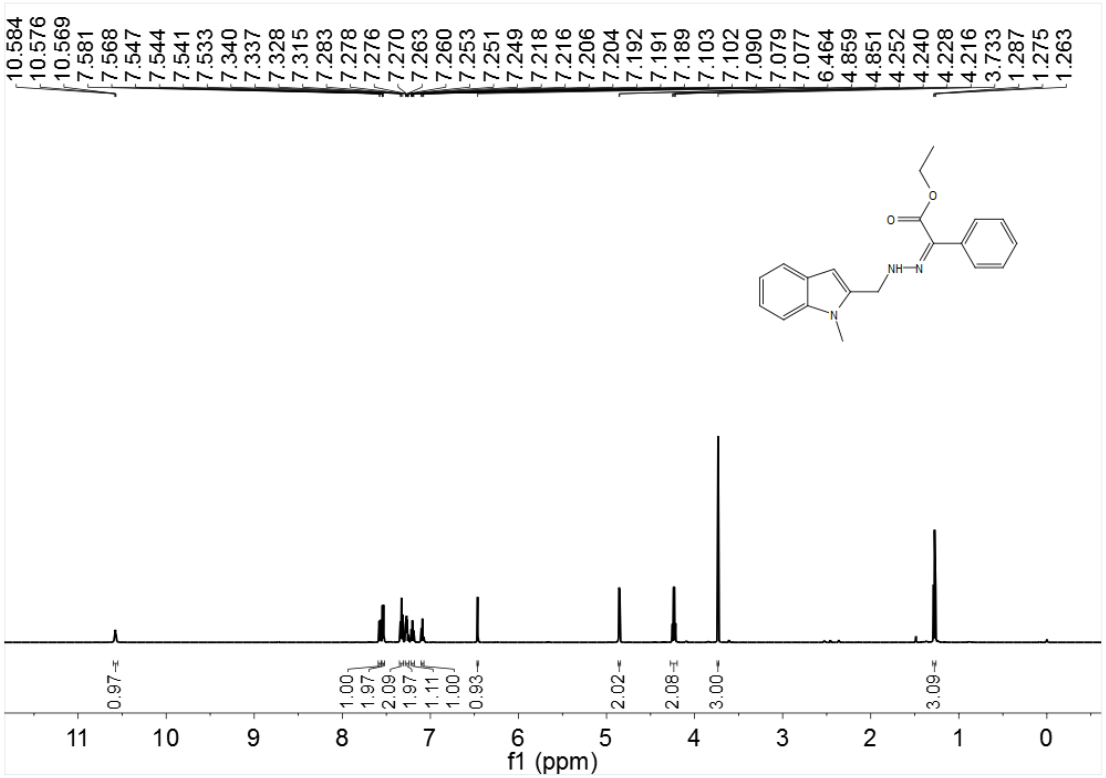


Figure 42. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3s**

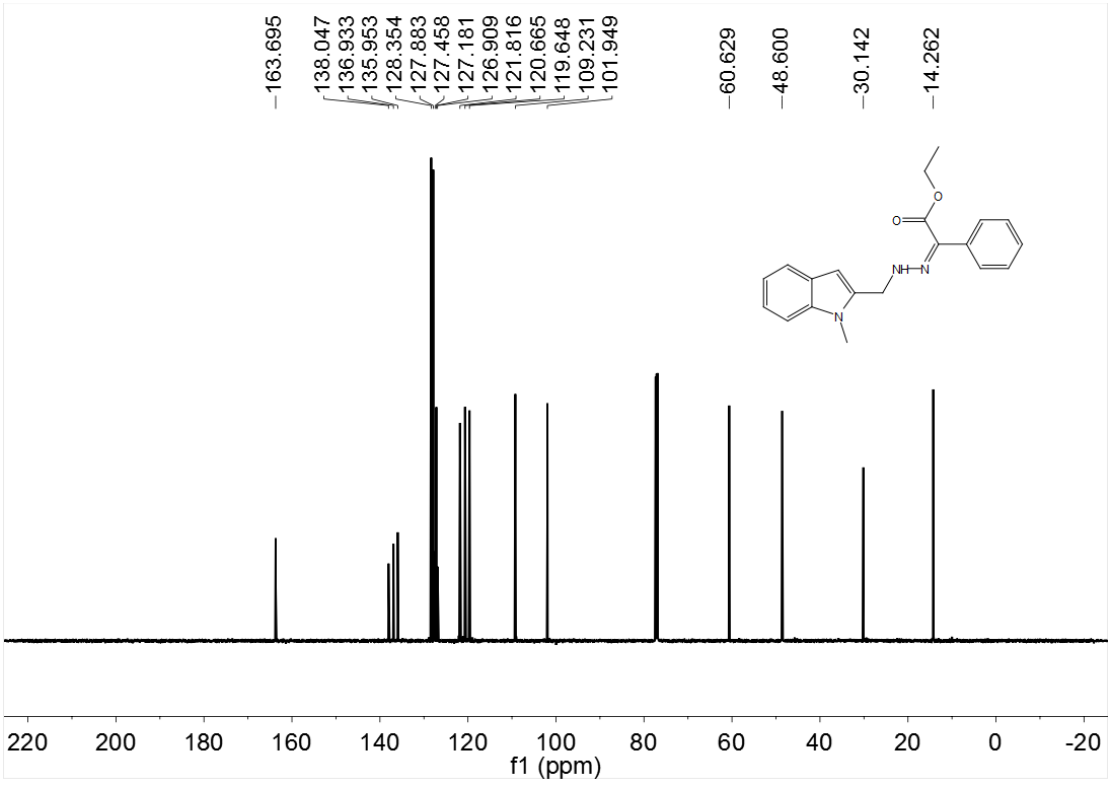


Figure 43. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3s**

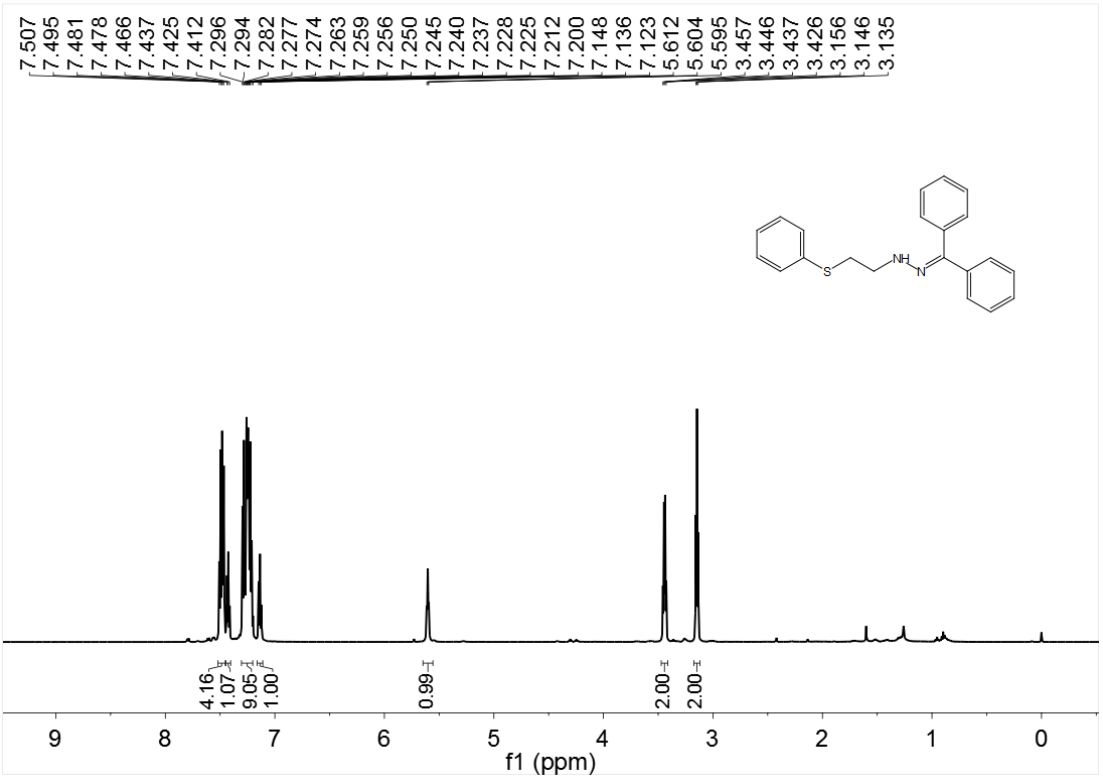


Figure 44. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5a**

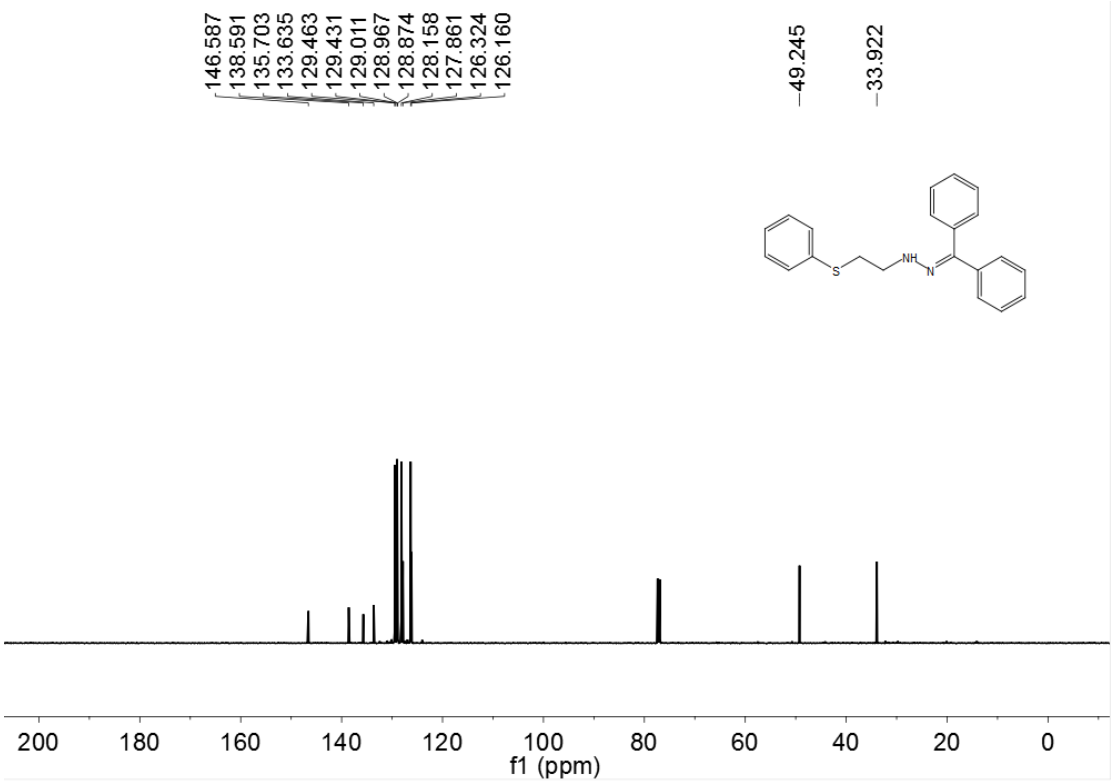


Figure 45. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5a**

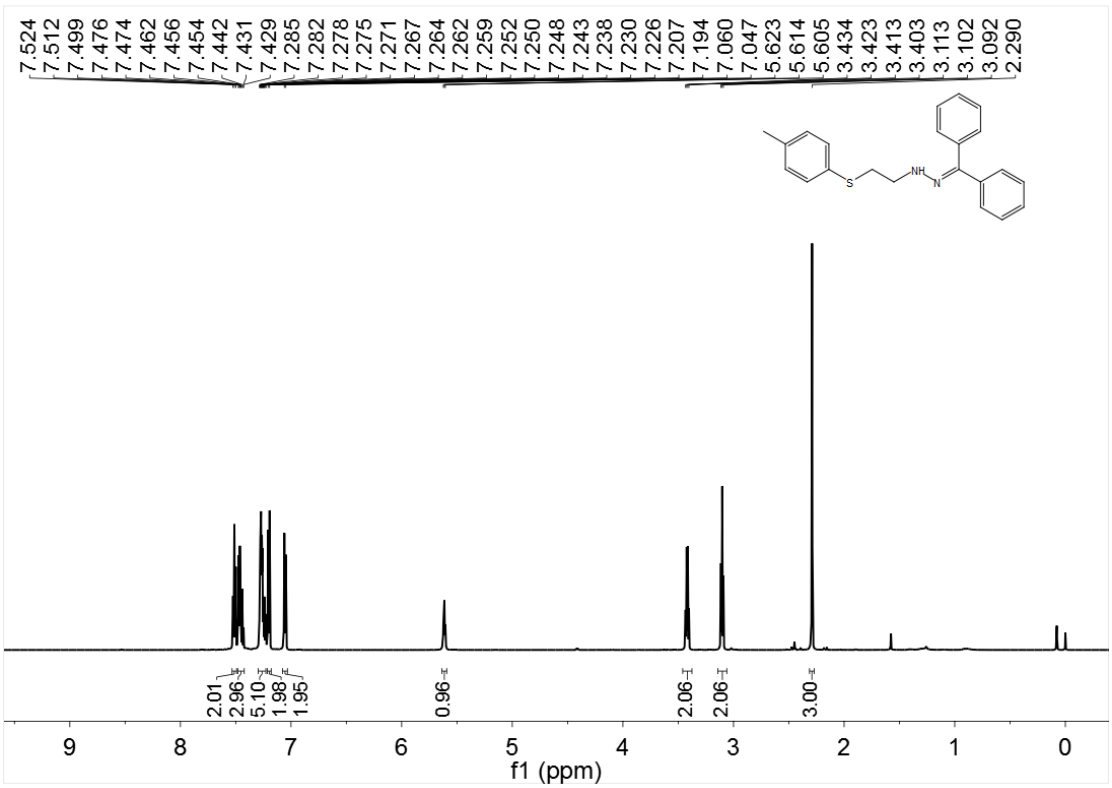


Figure 46. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5b**

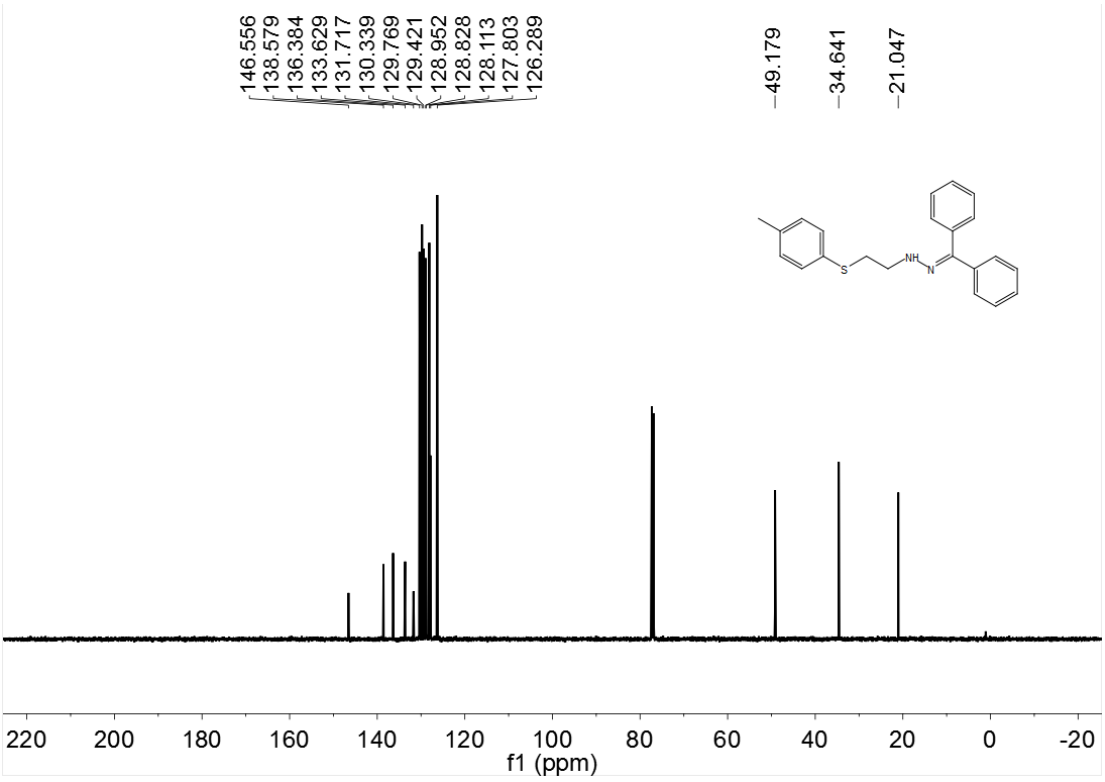


Figure 47. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5b**

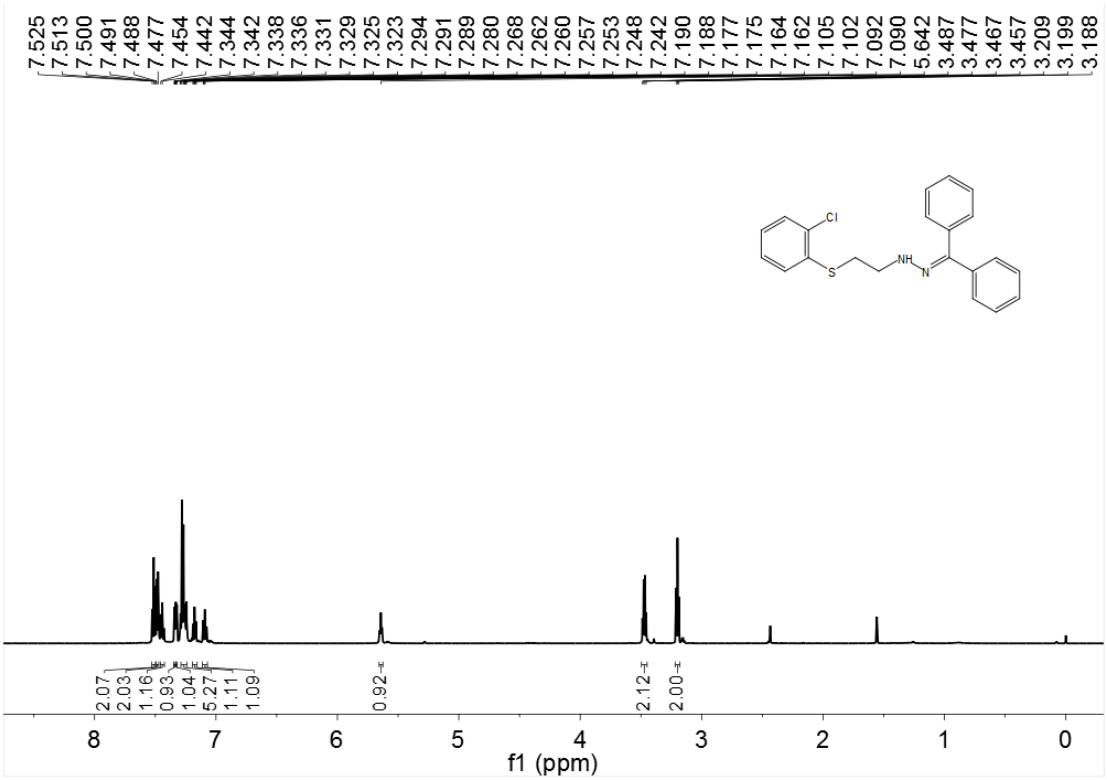


Figure 48. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5c**

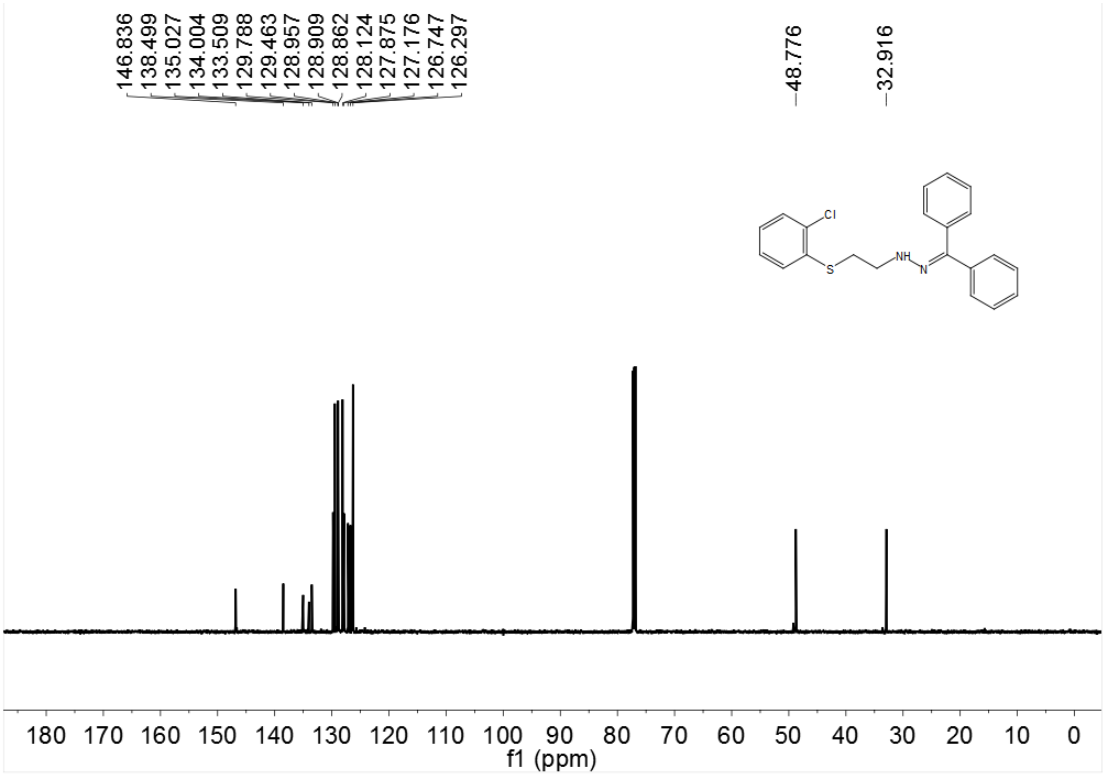


Figure 49. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5c**

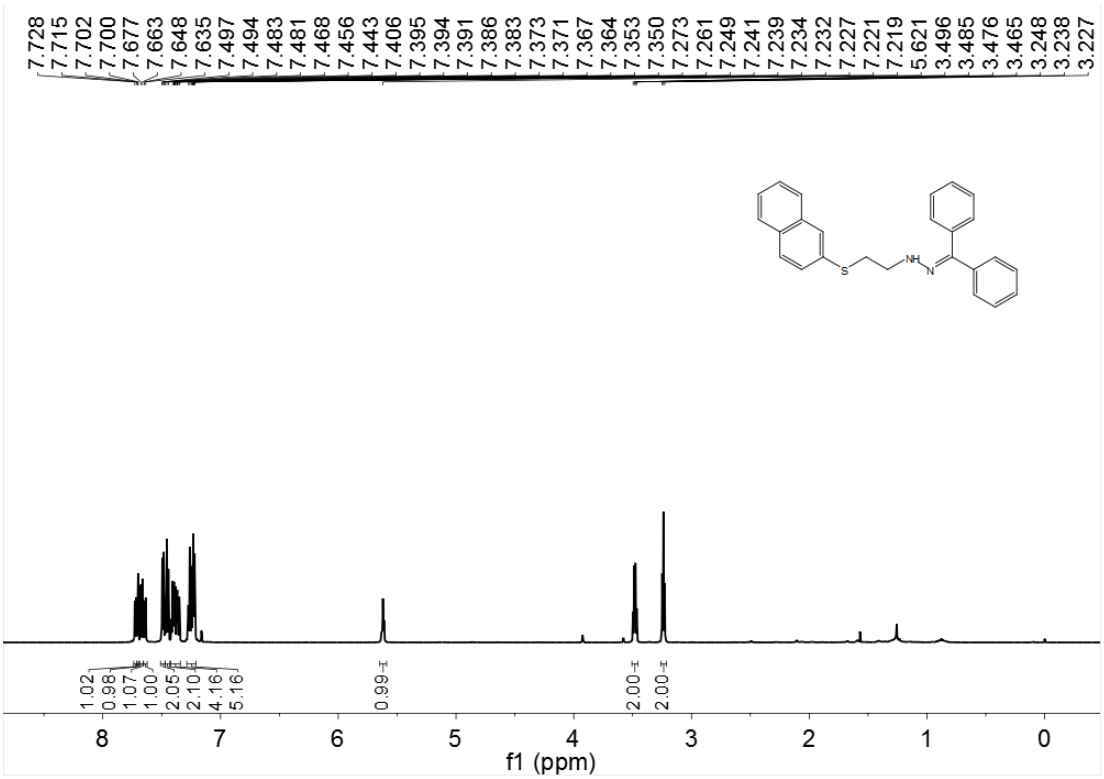


Figure 50. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5d**

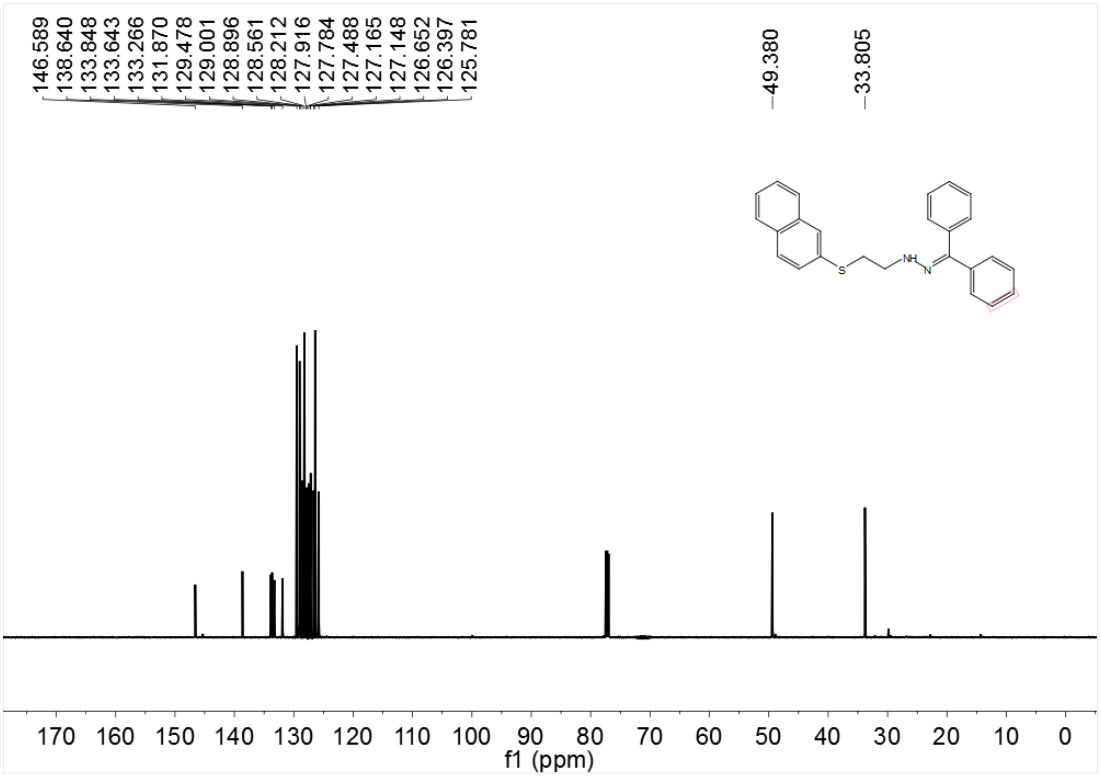


Figure 51. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5d**

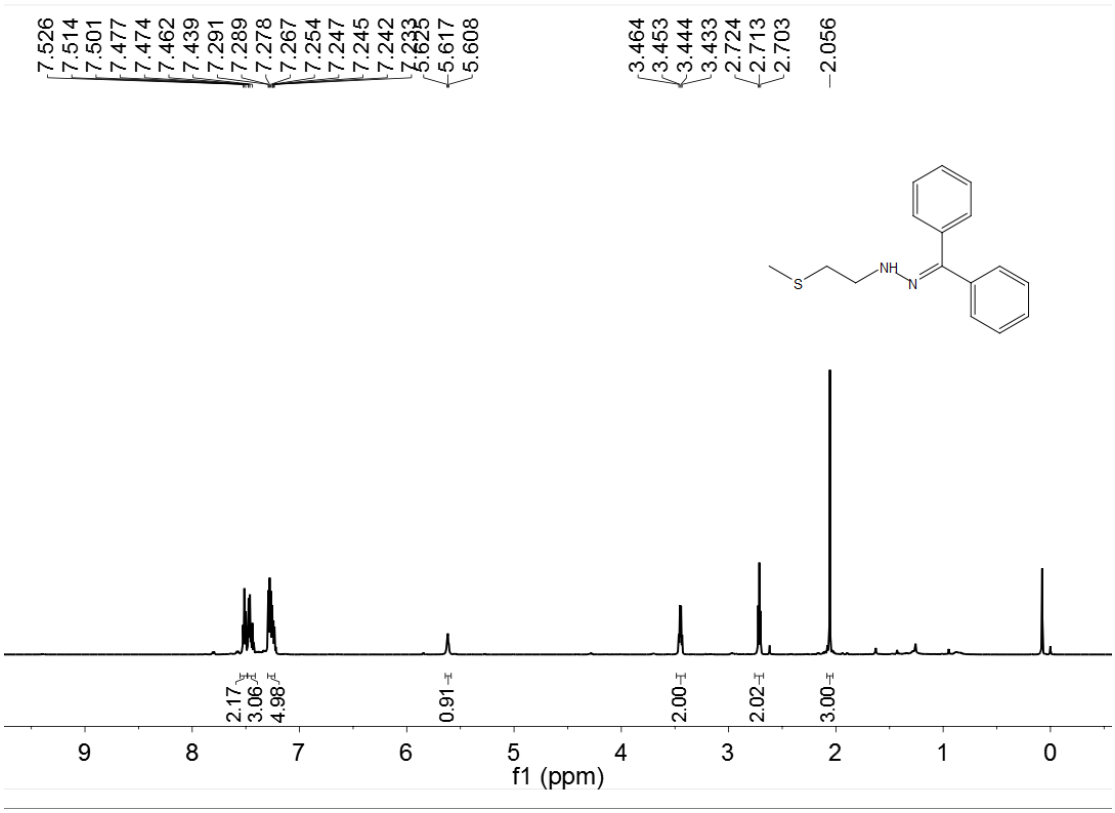


Figure 52. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5e**

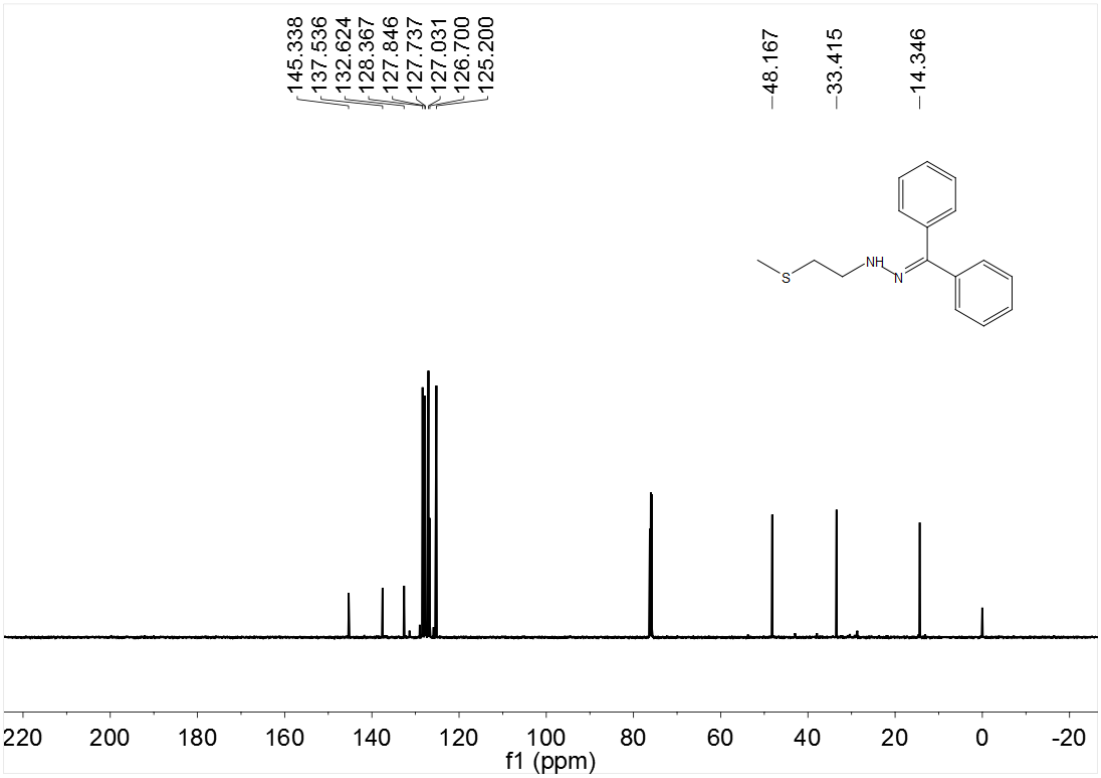


Figure 53. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5e**

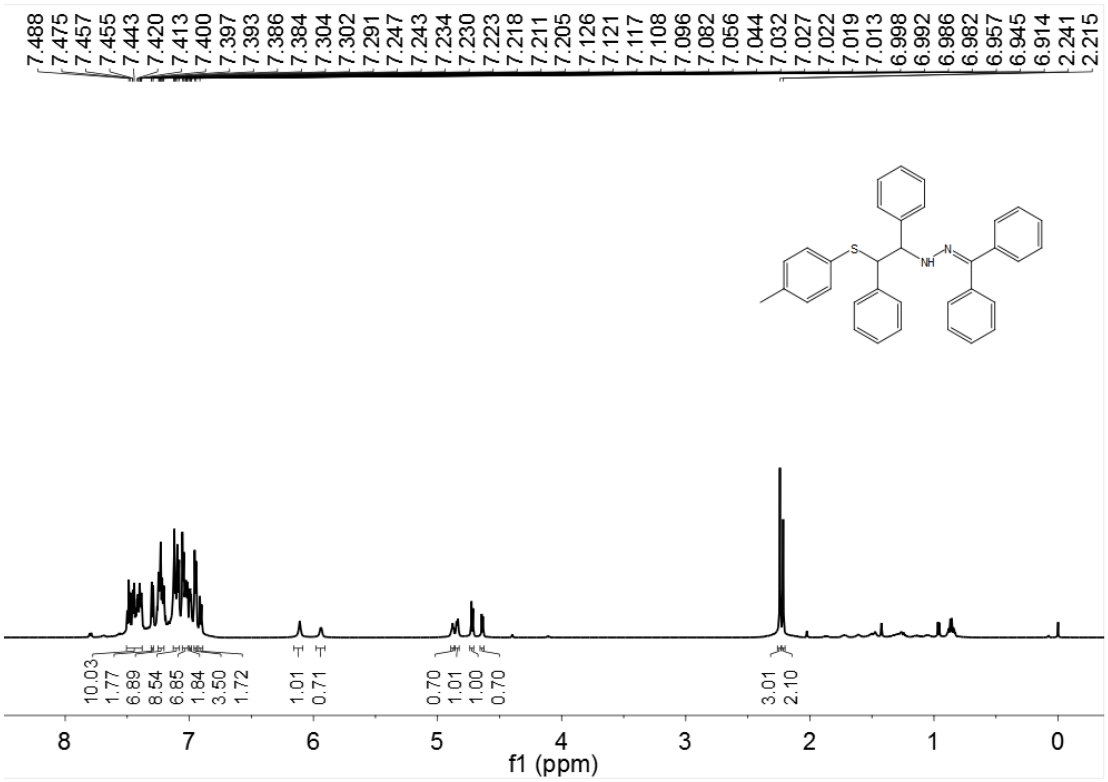


Figure 54. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5f**

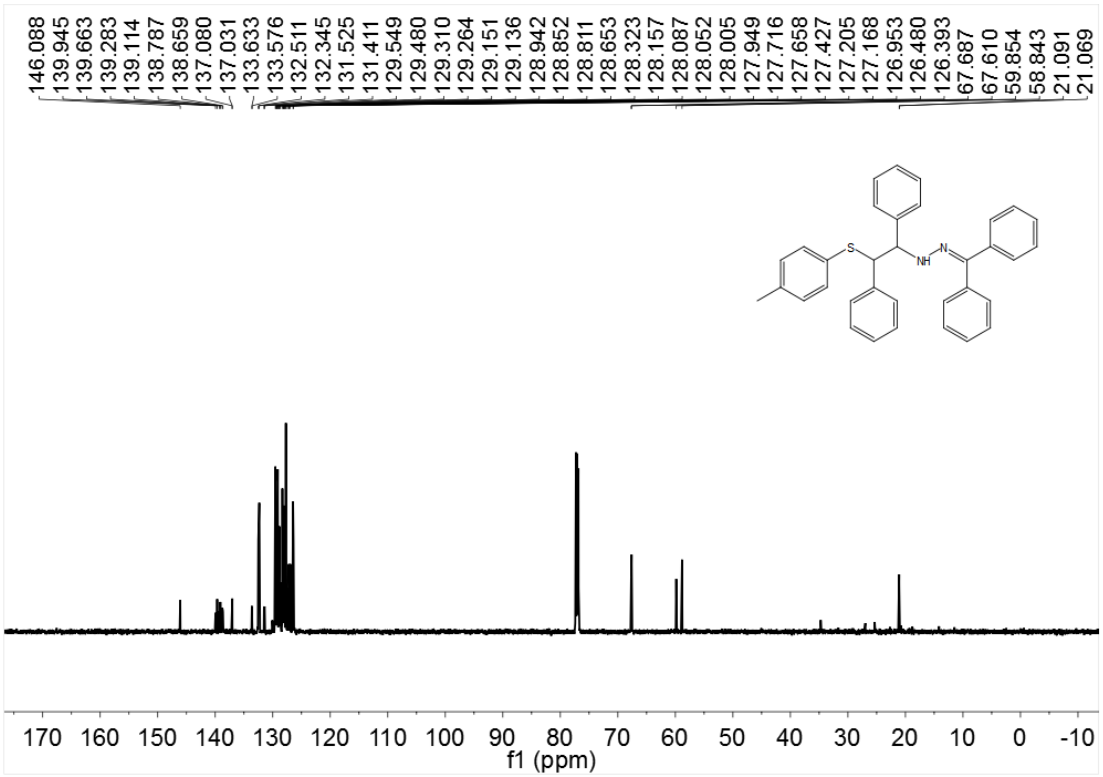


Figure 55. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5f**

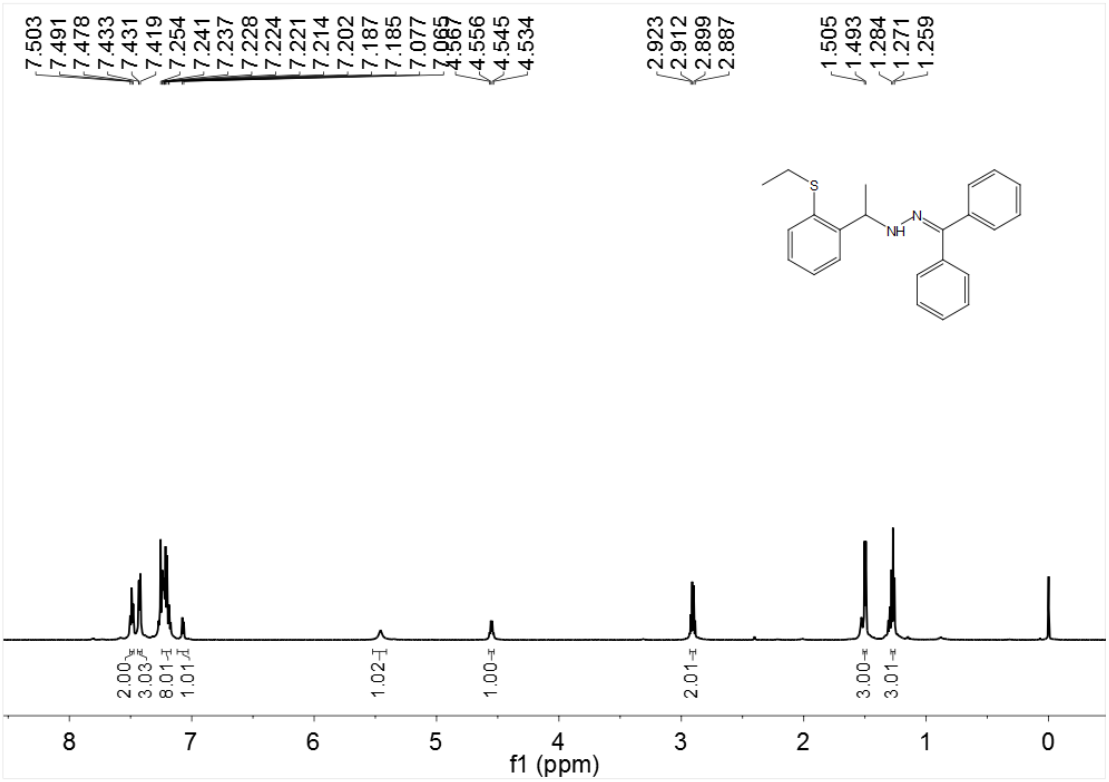


Figure 56. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5g**

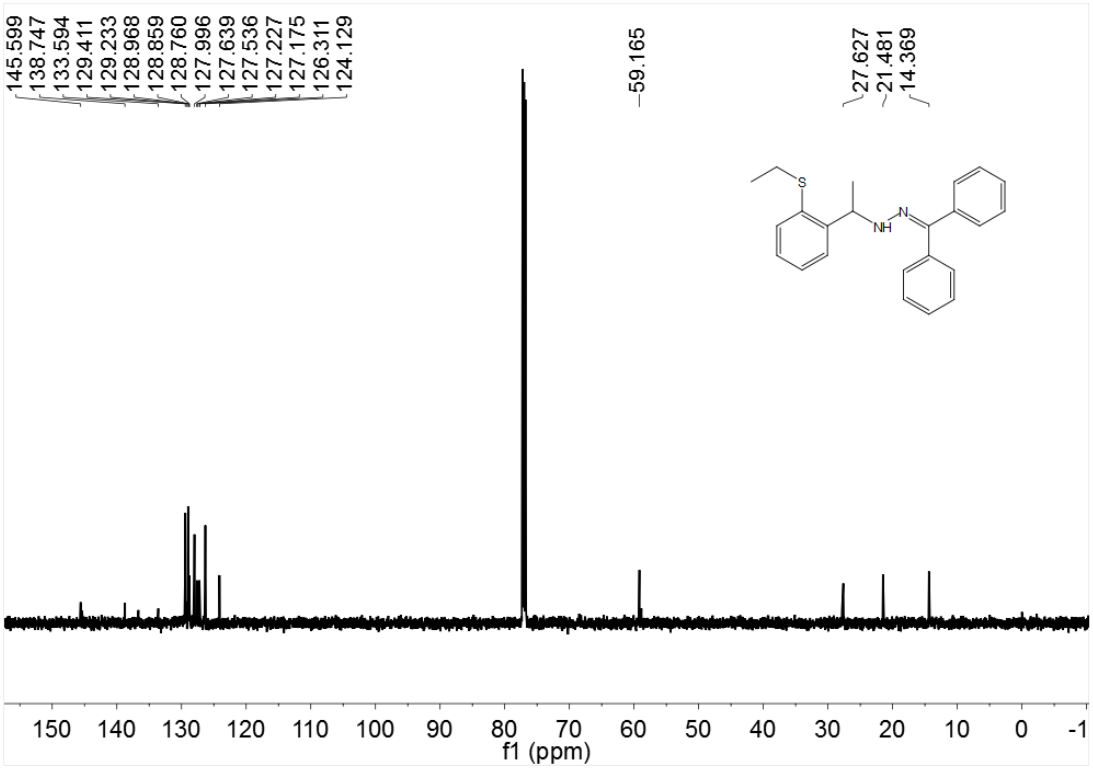


Figure 57. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5g**

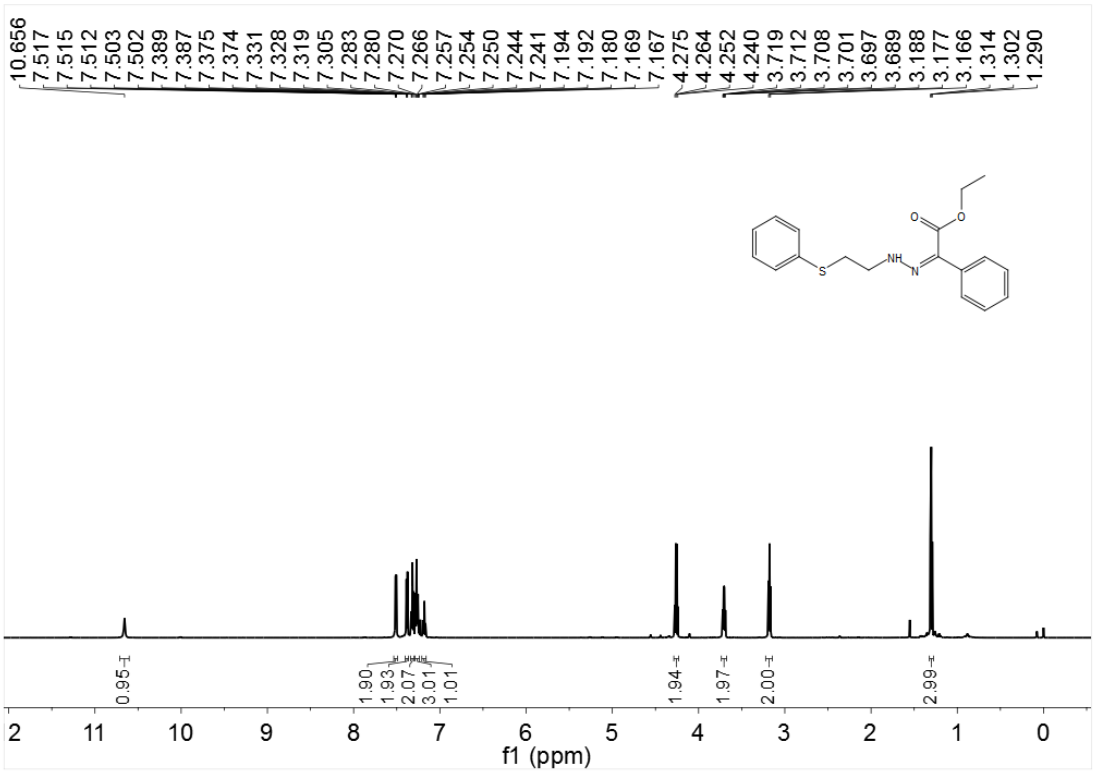


Figure 58. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5h**

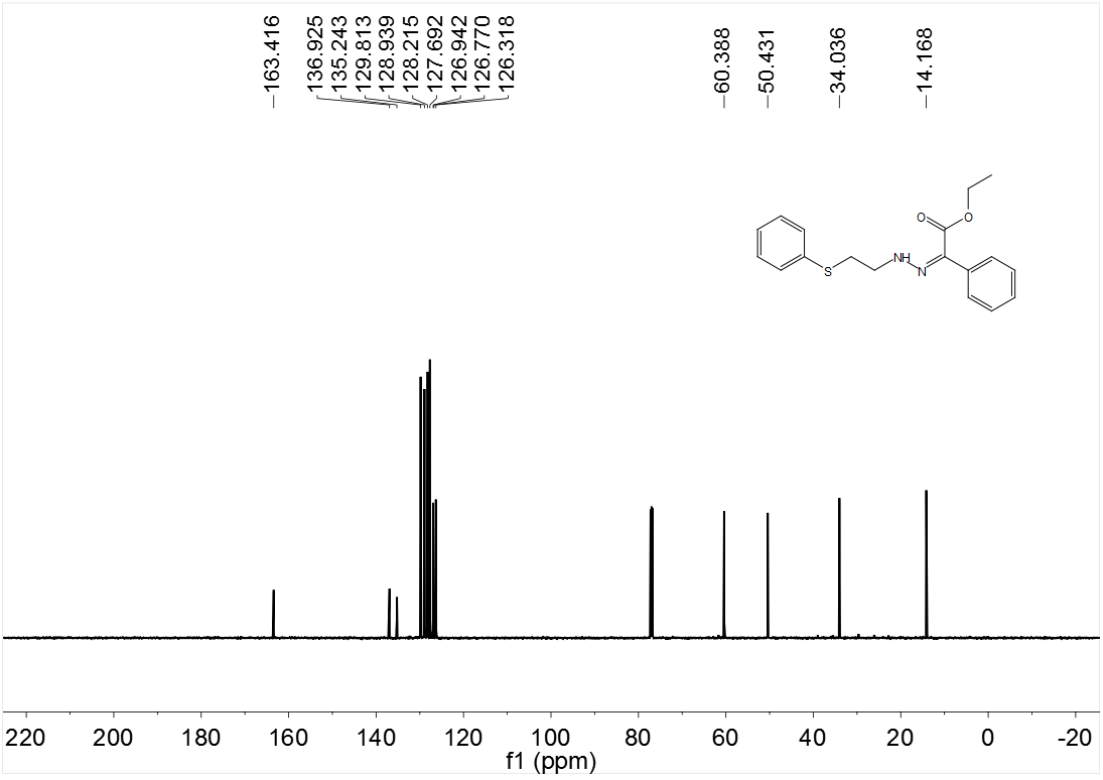


Figure 59. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5h**

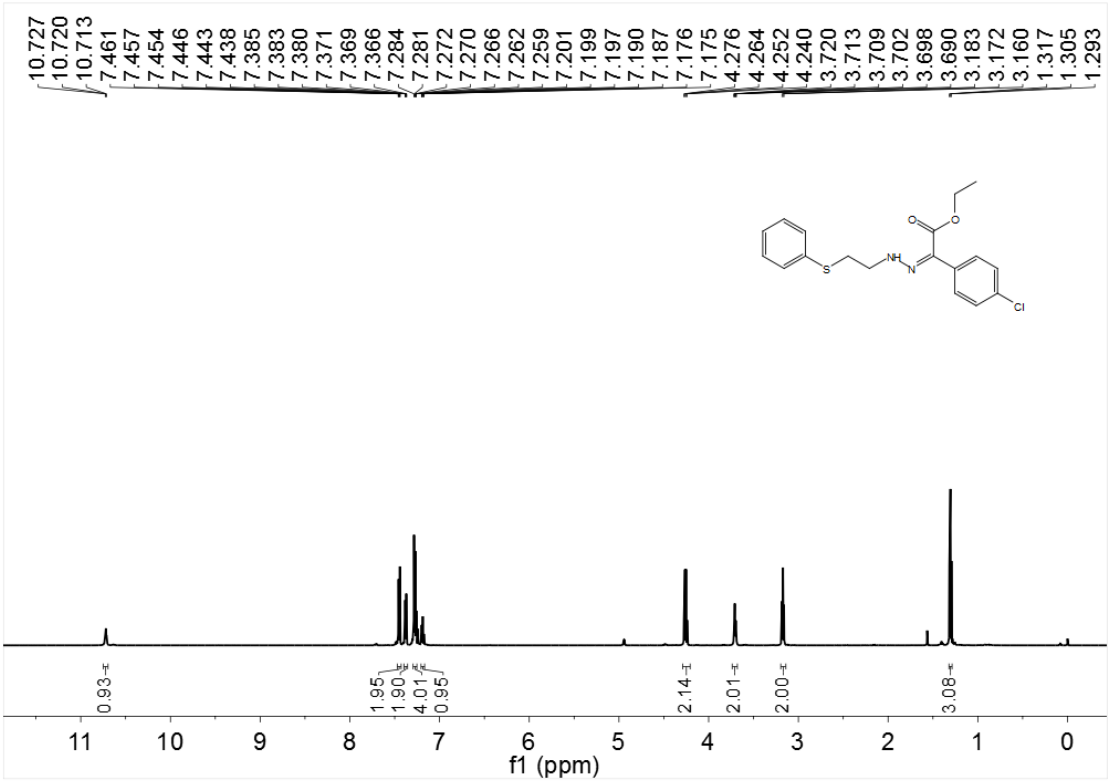


Figure 60. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5i**

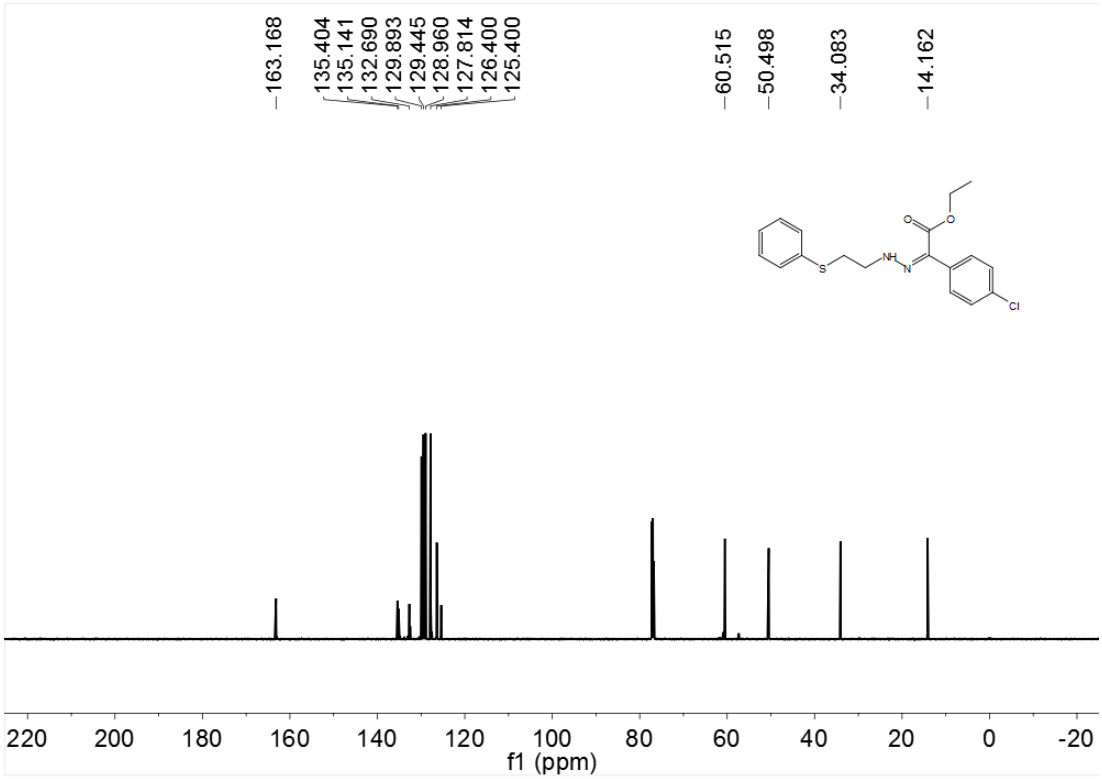


Figure 61. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5i**

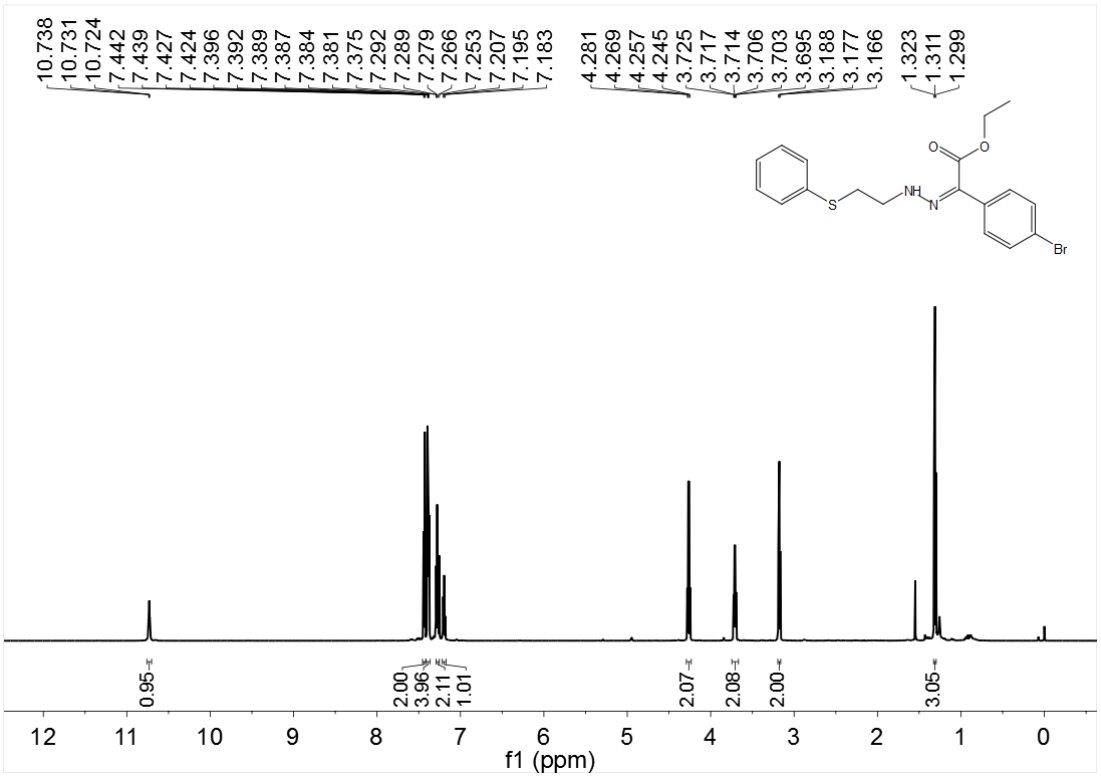


Figure 62. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5j**

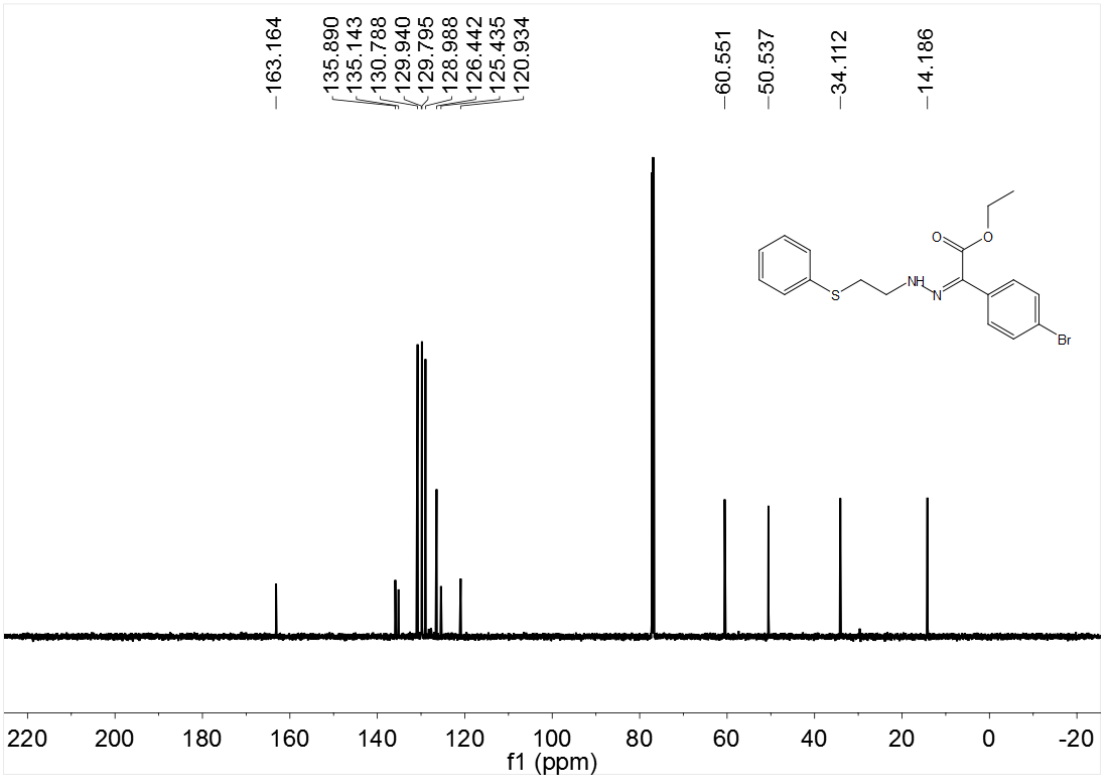


Figure 63. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5j**

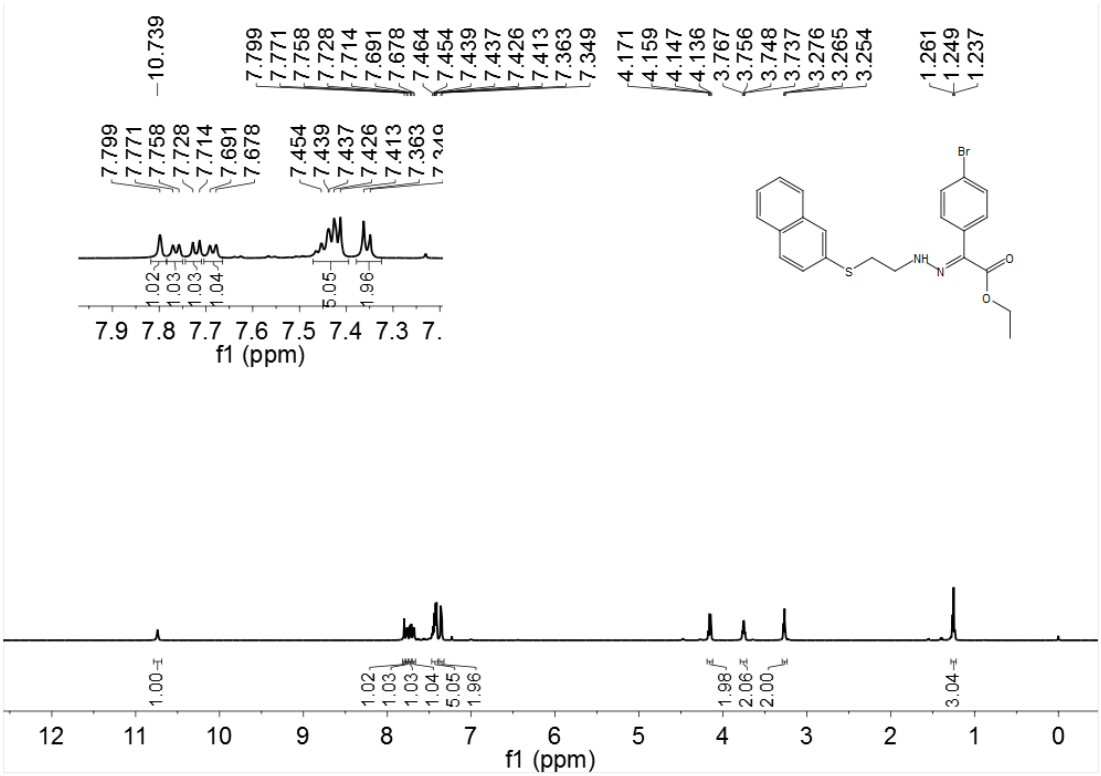


Figure 64. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5k**

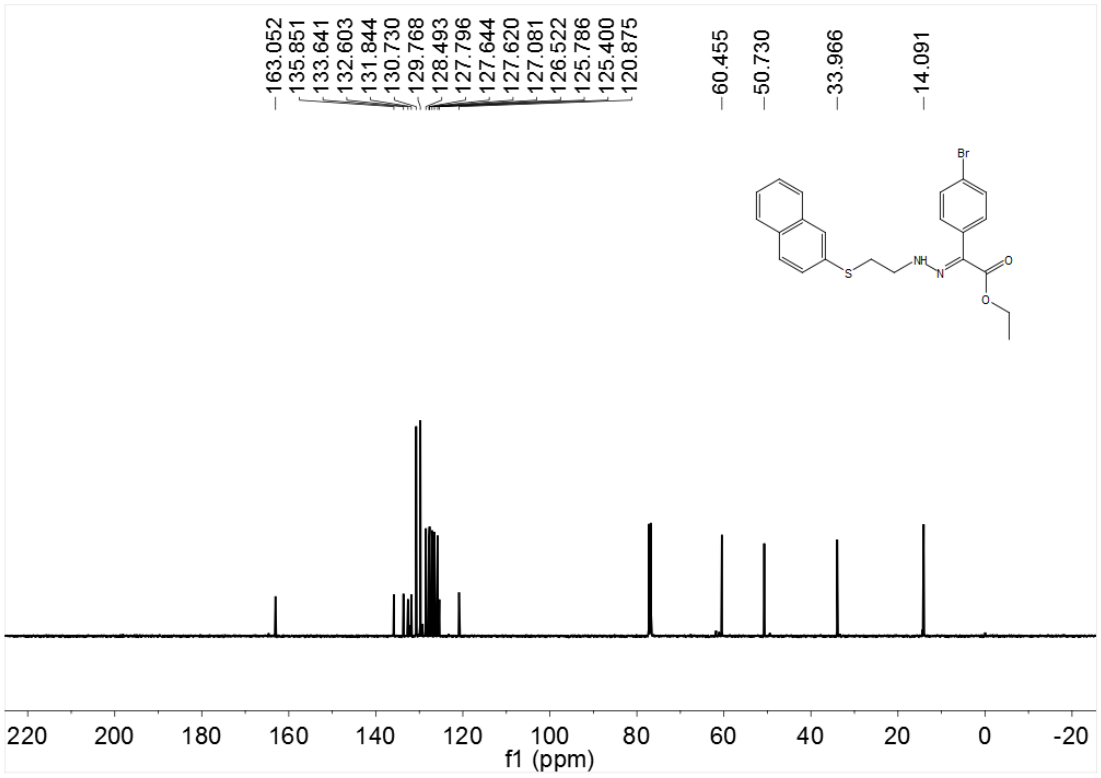


Figure 65. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5k**

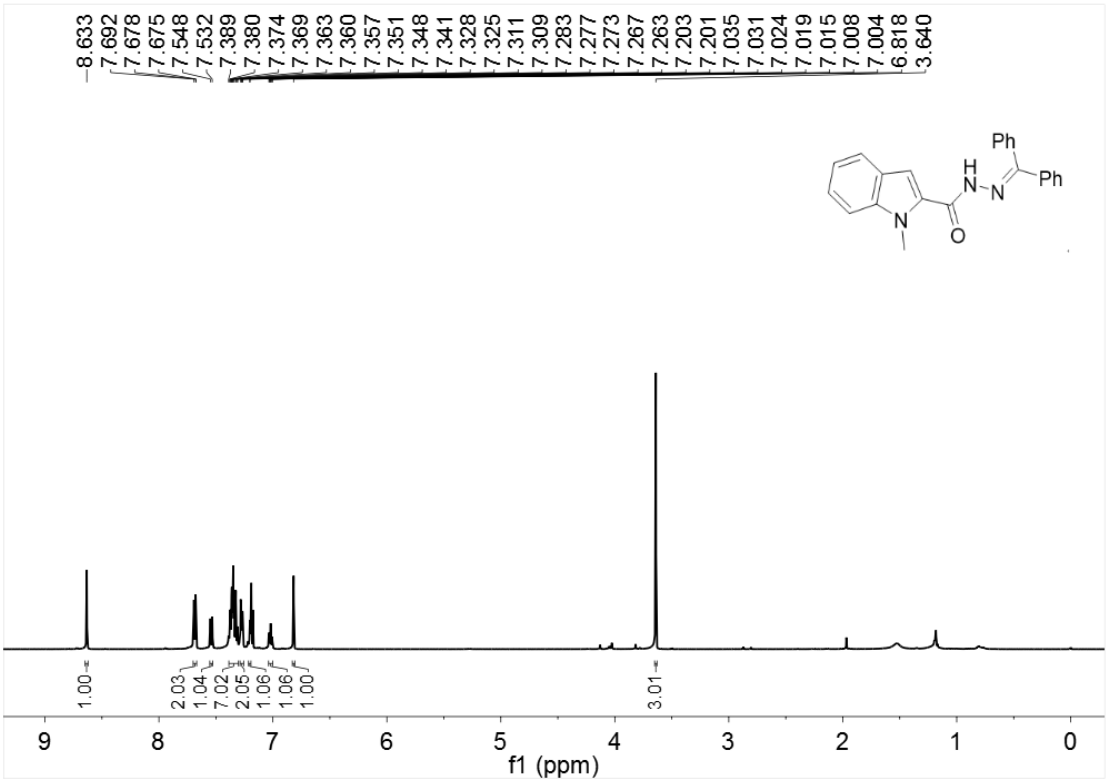


Figure 66. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **6**

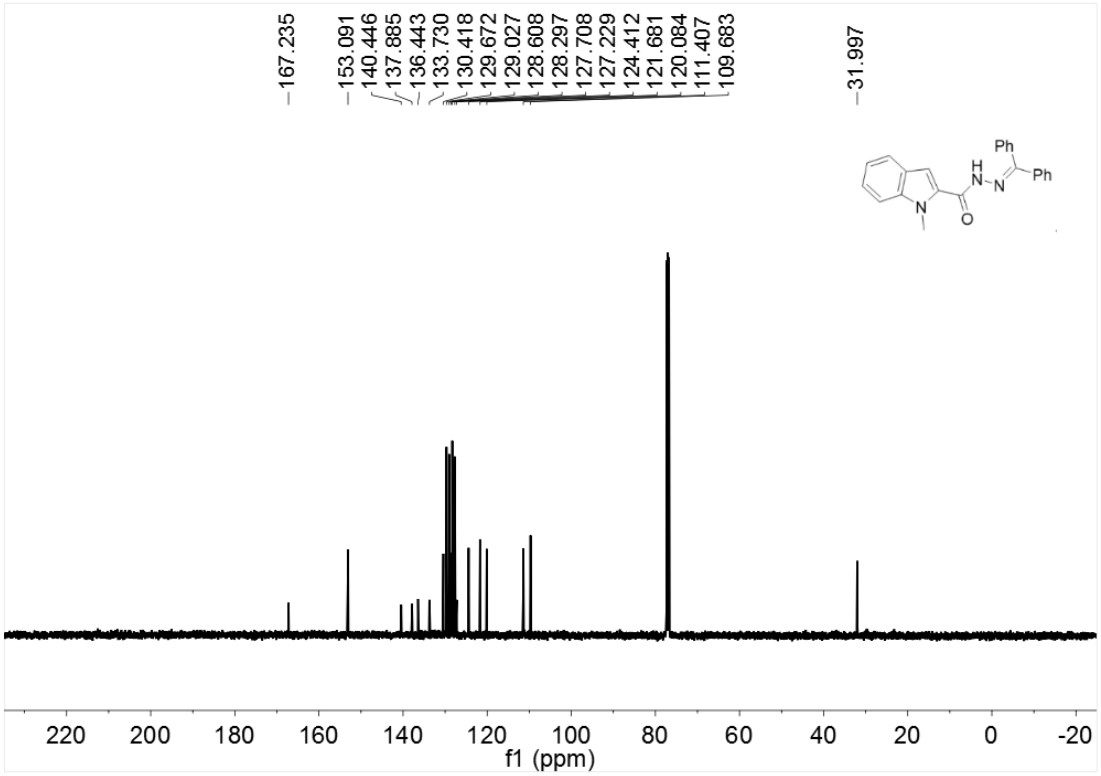


Figure 67. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **6**

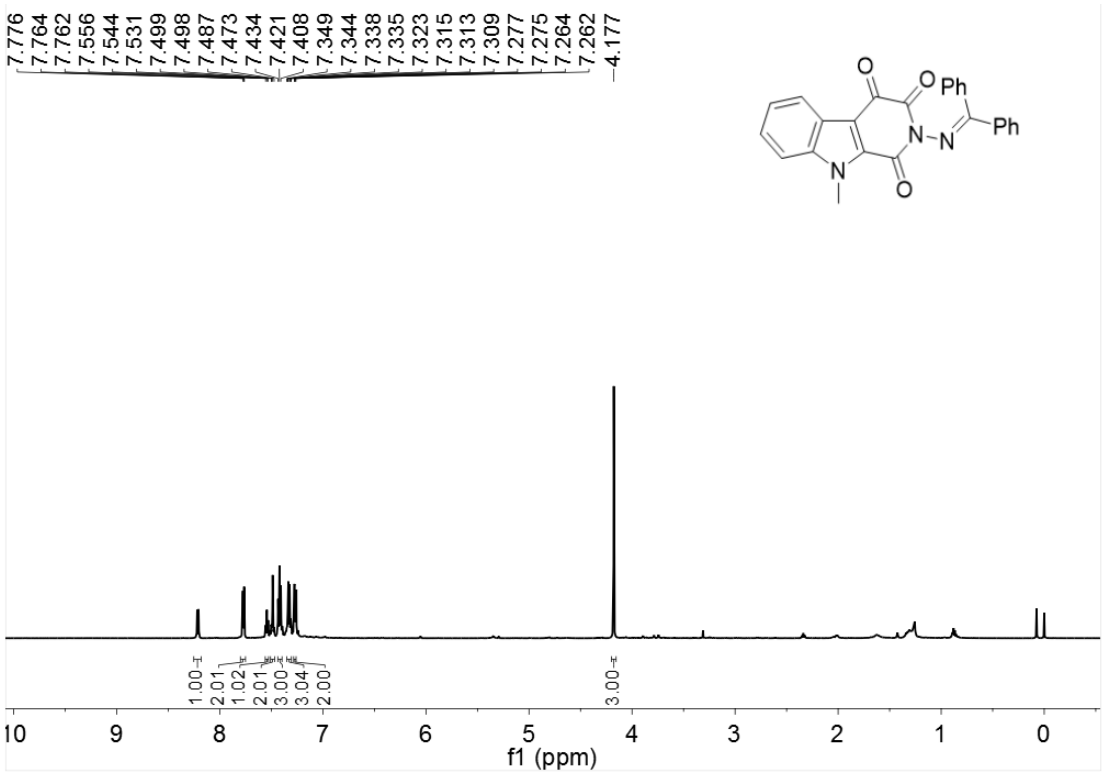


Figure 68. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **7**

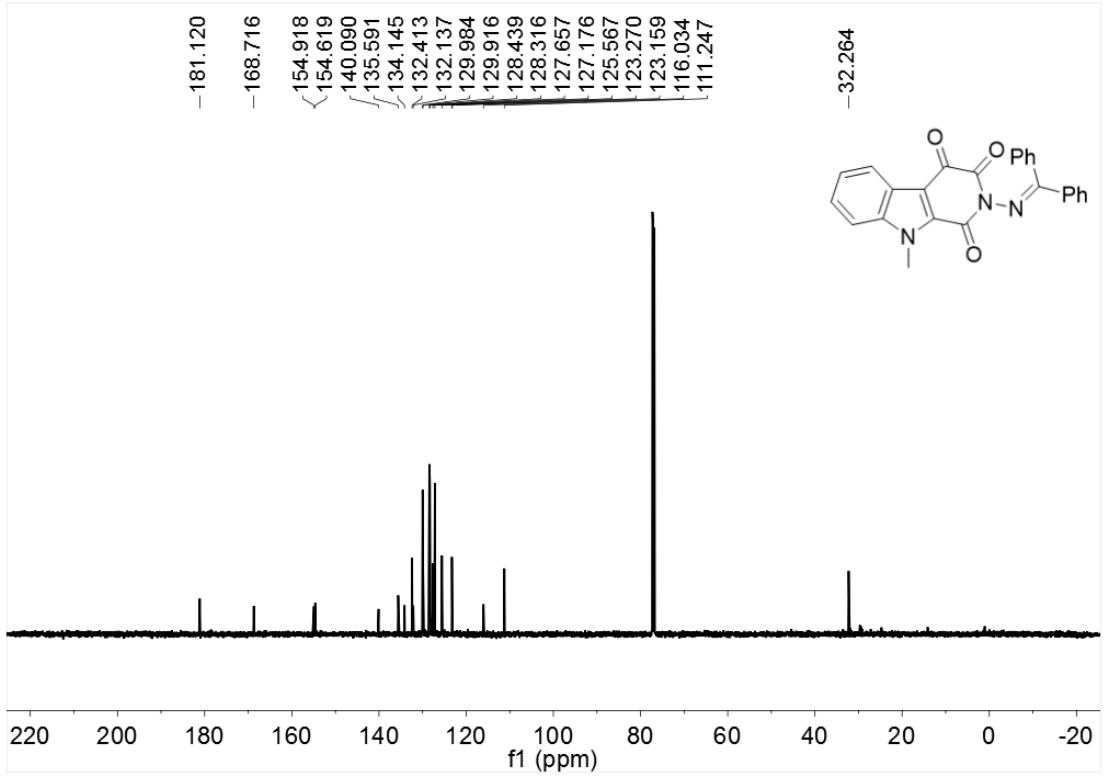


Figure 69. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7**