Supporting Information

Light-promoted Ni-Catalyzed Aryl C-N Coupling of Benzophenone Hydrazone for the Synthesis of Nitrogen-Containing Heterocycles

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1. General information

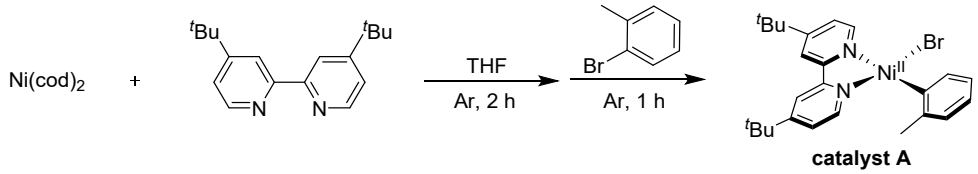
Commercially available reagents were used without further purification unless otherwise stated. All reactions were performed under argon atmosphere with glass storage tubes, and all solvents were purified by VG-P7 solvent drying system from Vigor, or commercial super dry solvents. Analytical thin-layer chromatography (TLC) was conducted with TLC plates (silica gel 60 F254, Qingdao Haiyang) and visualization on TLC was achieved by UV light (254 nm) or iodine. Flash column chromatography was performed on silica gel 200-300 mesh saturated with triethylamine in volume ratio of 1% with freshly distilled solvents. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 600, 400 MHz in $CDCl_3$ solvent. All chemical shifts in ^1H NMR spectra were given in parts per million (ppm) relative to the residual or $CDCl_3$ (7.26 ppm) as internal standards and coupling constants (J) were given in Hertz (Hz). ^{13}C NMR chemical shifts were reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) as internal standards. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, brs = broad), coupling constant (Hz), and integration. HRMS (ESI, APCI) were performed on fourier transform ion cyclotron resonance mass spectrometer.

The general reactions were carried with the assembled photoreactor (Figure S1). Each of lamp include: 9 W purple LED (390-395 nm, 3 LED lamp beads in series), aluminium radiator with fan, electric driver (XC-8W600-OS). The optical power up to 200 ± 10mw at 1 cm axis distance detected by Thorlabs' Optical Power Meter (PM100D, S120VC). The LED beads were purchased from Zhuhai UV Optoelectronics Co., Ltd. (TH-UV395T3WL-3535 60). The photoreactor used for light source screening was purchased from Xi'an Huatai Kesi Chemical Technology Co., Ltd.

Figure S1. Pictures of assembled photoreactor.

(Notes: the thermal radiation of LEDs increased the temperature of reaction mixture as an average level at 70 °C approximately, and there are no external heating units were equipped.)

2. Synthesis of Ni complexes A-C



In a nitrogen-filled glove box, $Ni(cod)_2$ (1.0 equiv, 2.0 mmol, 550 mg), 4,4′-di-*tert*-butyl-2,2′-pyridine (1.0 equiv, 2.0 mmol, 537 mg) and THF (6 mL) were placed into an oven-dried 15 mL storage tube with a magnetic stir bar. The resulting deep purple solution was stirred at room temperature for 2 h. Then 2-bromotoluene (5.0 equiv, 10.0 mmol, 1.71 g, 1.2 mL) was added and stirred for additional 1 h. To the resulting red solution was added pentane and red precipitate was observed. The insoluble solids were collected by filtration, washed with pentane. After drying under vacuum, the desired product Ni complex **A** was obtained as a red powder (700 mg, 1.4 mmol, 70% yield).

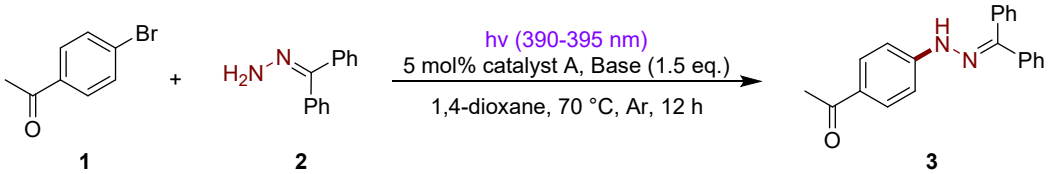
Ni(dtbbpy)(*o*-tolyl)Br (catalyst A): ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.35 (d, *J* = 5.8 Hz, 1H), 7.78 (s, 1H), 7.75 (s, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 5.0 Hz, 1H), 7.12-7.08 (m, 2H), 6.82 (m, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 3.08 (s, 3H), 1.41 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ

163.2, 162.3, 155.8, 152.7, 150.9, 150.7, 148.7, 142.3, 136.0, 127.5, 123.63, 123.6, 123.3, 122.5, 117.2, 116.5, 35.5, 35.4, 30.4, 30.2, 25.7. The spectral data match those previously reported.[1]

The synthesis of compounds Ni complexes **B** and **C** were accomplished according to the reported procedure.[1] The spectral data is consistent with the literature data.

3. Optimization of reaction conditions

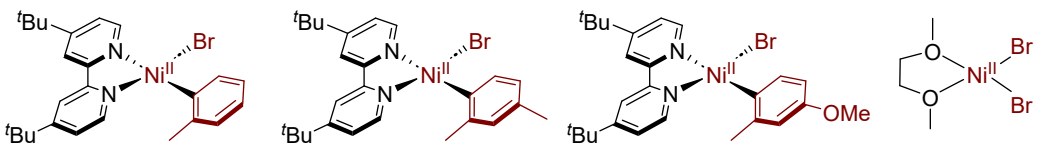
Table S1. Optimization of C–N coupling conditions.



1 **2** **3**

Entry	Variation from the standard conditions	Yield (%)[a][b]
1	**standard conditions**	**95, 90[b]**
2	white LEDs	71%
3	blue LEDs (460-465nm)	73%
4	green LEDs (530-535 nm)	70%
5	UV (365-370 nm)	80%
6	catalyst B instead of catalyst A	86%
7	catalyst C instead of catalyst A	85%
8	NiBr•glyme instead of catalyst A	57%
9	no catalyst A	NR
10	no base	NR
11	no light, r.t.	NR
12	no light, 70 °C	70%
13	air instead of Ar	54%

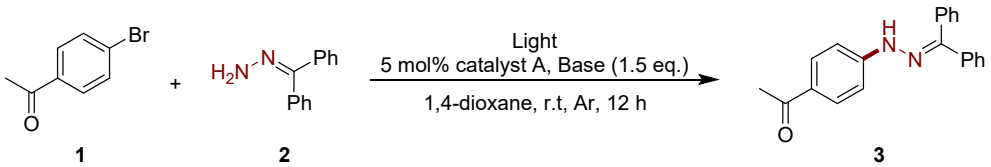
Catalysts



A **B** **C** **D**

[a]Reaction conditions: **1** (0.5 mmol), **2** (1.25 mmol, 2.5 equiv), nickel catalyst (5 mol%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.75 mmol), 1,4-dioxane (2 mL), purple LEDs (390–395 nm), 70 °C, Ar, 12 h. ^{1}H NMR spectroscopy with 1,3-benzodioxole as the internal standard. [b]Isolated yield.

Table S2. The screening of light sources

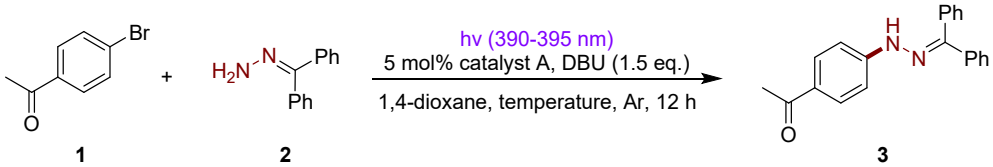


1 **2** **3**

Entry	Light sources	Yield (%)[a]
1	white LEDs	trace
2	blue LEDs(460-465nm)	trace
3	green LEDs (530-535 nm)	trace
4	UV (365-370 nm)	trace
5	**Purple LEDs (390-395 nm)**	20%

Reaction conditions: **1** (1.0 equiv, 0.5 mmol), **2** (2.5 equiv, 2.5 mmol), catalyst A (5.0 mol%), DBU (1.5 equiv, 0.75 mmol), 1,4-dioxane (2.0 mL), purple LEDs (390-395 nm), r.t, Ar, 12 h. Yields determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard.

Table S3. The screening of temperature

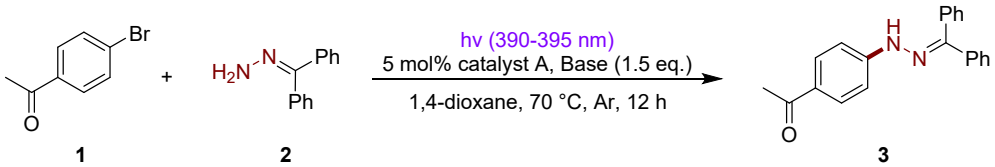


1 **2** **3**

Entry	Temperature (°C)	Yield (%)[a]
1	r.t.	20%
2	40	32%
3	**70**	**95%**

Reaction conditions: **1** (1.0 equiv, 0.5 mmol), **2** (2.5 equiv, 2.5 mmol), catalyst A (5.0 mol%), DBU (1.5 equiv, 0.75 mmol), 1,4-dioxane (2.0 mL), purple LEDs (390-395 nm), temperature, Ar, 12 h. Yields determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard.

Table S4. The screening of base

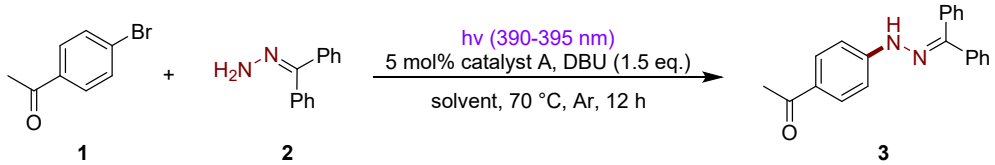


1 **2** **3**

Entry	Base	Yield (%)[a]
1	NEt_3	15%
2	TMG	60%
3	DMAP	NR
4	**DBU**	**95%**
5	quinuclidine	58%
6	DABCO	35%
7	DIPEA	trace
8	Cy_2NH	16%
9	Cy_2NMe	NR
10	Na_3PO_4	30%
11	K_3PO_4	trace
12	K_2CO_3	trace
13	Cs_2CO_3	trace

Reaction conditions: **1** (1.0 equiv, 0.5 mmol), **2** (2.5 equiv, 2.5 mmol), catalyst A (5.0 mol%), base (1.5 equiv, 0.75 mmol), 1,4-dioxane (2.0 mL), purple LEDs (390-395 nm), 70 °C, Ar, 12 h. Yields determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard.

Table S5. The screening of solvent



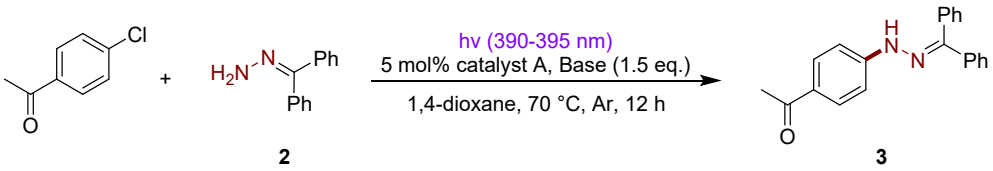
1 **2** **3**

Entry	Solvent	Yield (%)[a]
1	CH_3CN	trace
2	THF	84%
3	PhMe	76%
4	**1,4-dioxane**	**95%**
5	DMF	60%
6	DMAc	75%

Reaction conditions: **1** (1.0 equiv, 0.5 mmol), **2** (2.5 equiv, 2.5 mmol), catalyst A (5.0 mol%), DBU (1.5 equiv, 0.75 mmol), solvent (2.0 mL), purple LEDs (390-395 nm), 70 °C, Ar, 12 h. Yields

determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard.

Table S6. The screening of reaction concentration



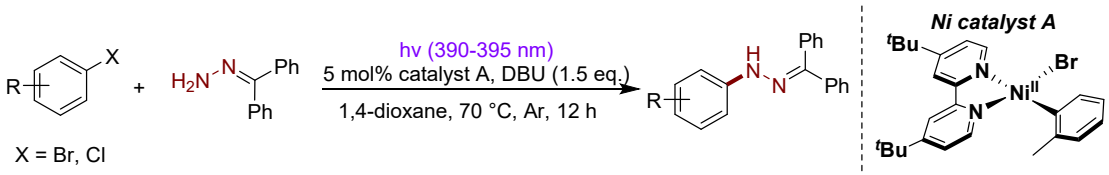
2 **3**

Entry	Concentration [1,4-dioxane (mL)]	Yield (%)[a][b]
1	1.0 M (0.5 mL)	77%
2	**0.5 M (1.0 mL)**	**88%, 85%[b]**
3	0.33 M (1.5 mL)	77%
4	0.25 M (2.0 mL)	70%

Reaction conditions: *p*-acetylchlorobenzene (1.0 equiv, 0.5 mmol), **2** (2.0 equiv, 2.0 mmol), catalyst A (5.0 mol%), DBU (1.5 equiv, 0.75 mmol), 1,4-dioxane (x mL), purple LEDs, 70 °C, Ar, 12 h. Yields determined by ^{1}H NMR analysis using 1,3-benzodioxole as internal standard.

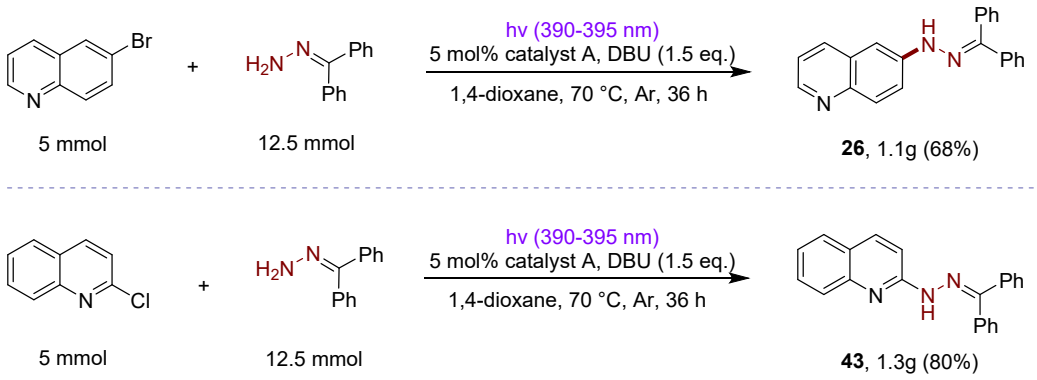
4. General procedure

4.1 Procedures for the C-N cross-coupling of aryl halide and benzophenone hydrazone



To an oven-dried 10 mL storage tube with a magnetic stir bar, Ni catalyst A (5 mol%, 0.025 mmol), aryl halide (0.5 mmol, 1.0 equiv) and benzophenone hydrazone (1.25 mmol, 2.5 equiv) were added. The tube was evacuated/backfilled with argon for three times. Under a positive pressure of argon, DBU (0.75 mmol, 1.5 equiv) and 1,4-dioxane (2.0 mL, X = Cl, 1.0 mL) were added *via* syringe. The tube was sealed with the Teflon screw valve. The reaction mixture was then irradiated with two purple LED lamps (1.0 cm from the tube, optical power: 200 ± 10mw/cm^2) for 12 h at 70 °C. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography saturated with triethylamine in a volume ratio of 1% to obtain the desired product.

4.2 Procedure for the synthesis of *N*-aryl benzophenone hydrazone at gram-scale



To an oven-dried 100 mL storage tube with a magnetic stir bar, Ni catalyst A (5 mol%, 0. 25 mmol), aryl halide (5 mmol, 1.0 equiv) and benzophenone hydrazone (12.5 mmol, 2.5 equiv) were added. The tube was evacuated/backfilled with argon for three times. Under a positive pressure of argon, DBU (7.5 mmol, 1.5 equiv) and 1,4-dioxane (20 mL, X = Cl, 1.0 mL) were added *via* syringe. The tube was sealed with the Teflon screw valve. The reaction mixture was then irradiated with eight 9W 390-395 nm purple LED lamps for 36 h at 70 °C. After cooling to room temperature, The resulting mixture was diluted with 200mL EtOAc, and washed with saturated NaCl (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography saturated with triethylamine in a volume ratio of 1% to obtain the desired product.

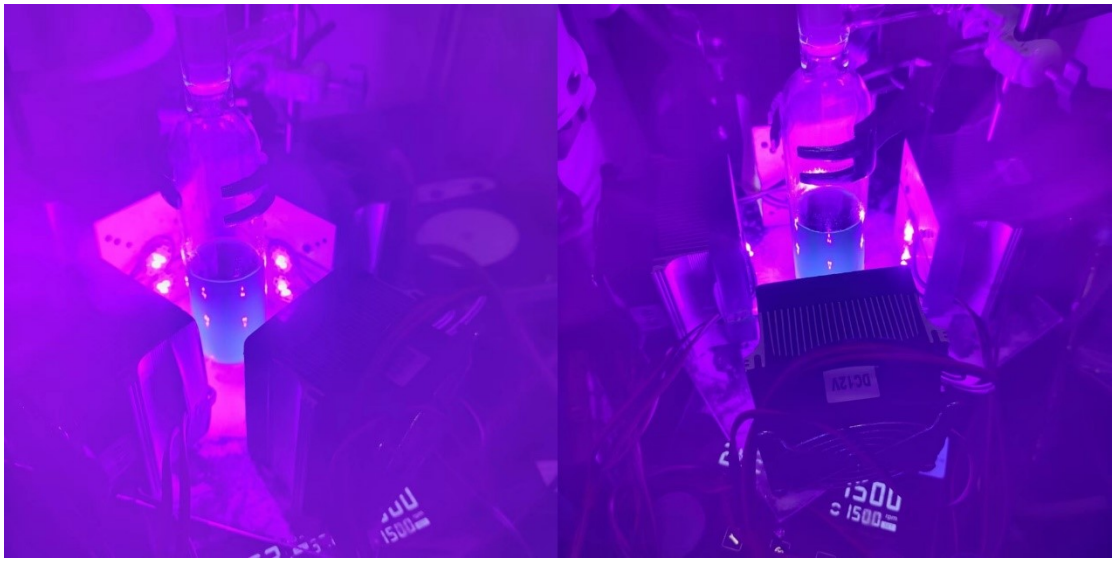
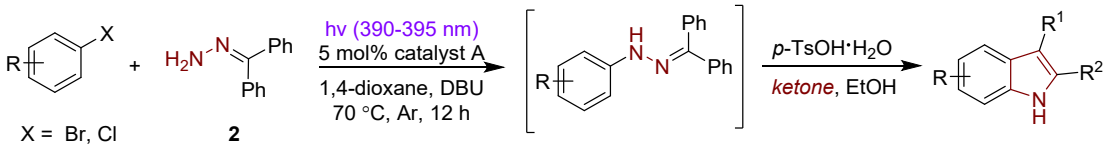


Figure S2. Pictures of gram-scale reaction setup.

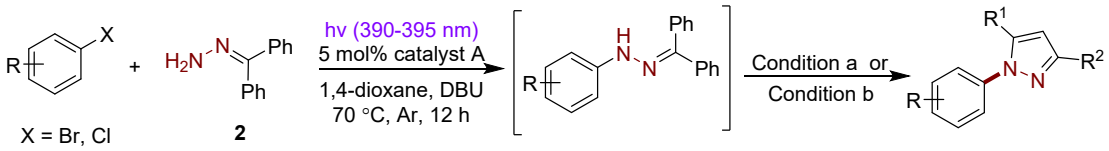
4.3 Procedures for the synthesis of indoles



To an oven-dried 10 mL storage tube with a magnetic stir bar, Ni catalyst A (5 mol%, 0.025 mmol), aryl halide (0.5 mmol, 1.0 equiv) and benzophenone hydrazone (1.25 mmol, 2.5 equiv) were added. The tube was evacuated/backfilled with argon for three times. Under a positive pressure of argon, DBU (0.75 mmol, 1.5 equiv) and 1,4-dioxane (2.0 mL) were added *via* syringe. The tube was sealed with the Teflon screw valve. The reaction mixture was then irradiated with two purple LED lamps (1.0 cm from the tube, optical power: 200 ± 10mw/cm^2) for 12 h at 70 °C. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was used in the subsequent step without further purification.

The obtained crude product was dissolved in 3.0 mL EtOH, then 3.0-6.0 equiv of *p*-TsOH·H_2O and 2.0-3.0 equiv of ketone were added, the reaction was heated to reflux temperature for 12-24 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel to give the desired product.

4.4 Procedures for the synthesis of *N*-arylpyrazoles



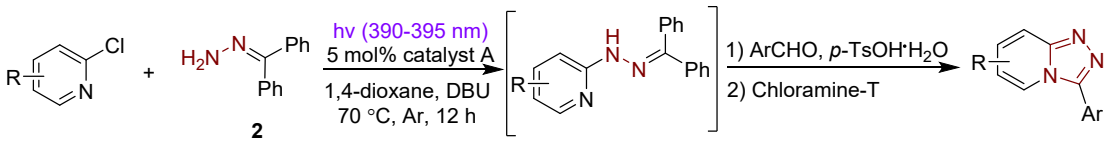
To an oven-dried 10 mL storage tube with a magnetic stir bar, Ni catalyst **A** (5 mol%, 0.025 mmol), aryl halide (0.5 mmol, 1.0 equiv) and benzophenone hydrazone (1.25 mmol, 2.5 equiv) were added. The tube was evacuated/backfilled with argon for three times. Under a positive pressure of argon, DBU (0.75 mmol, 1.5 equiv) and 1,4-dioxane (2.0 mL) were added *via* syringe. The tube was sealed with the Teflon screw valve. The reaction mixture was then

irradiated with two purple LED lamps (1.0 cm from the tube, optical power: 200 ± 10mw/cm^2) for 12 h at 70 °C. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated NaCl (2 × 10 mL), dried ove Na_2SO_4, and concentrated *in vacuo*. The crude residue was used in the subsequent step without further purification.

Condition a: The obtained crude product was dissolved in 3.0 mL EtOH, then *p*-TsOH·H_2O (1.5 mmol, 3.0 equiv) and PhCHO (1.0 mmol, 2.0 equiv) were added, the reaction was heated to reflux temperature for 12-24 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was transferred to an oven-dried 10 mL storage tube vial equipped with 3.0 mL THF, then tetrafluoroboric acid (48 wt.% in H_2O, 5 mmol, 10 equiv) and *β*-diketone (1.0 mmol, 2.0 equiv) were added. The reaction was heated to 70 °C for 12 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated $NaHCO_3$ (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel to give the desired product.

Condition b: The residue was transferred to an oven-dried 10 mL storage tube vial equipped with 3.0 mL THF, then tetrafluoroboric acid (48 wt.% in H_2O, 5 mmol, 10 equiv) and *β*-diketone (1.0 mmol, 2.0 equiv) were added. The reaction was heated to 70 °C for 12 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated $NaHCO_3$ (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel to give the desired product.

4.5 Procedures for the synthesis of triazolopyridines and triazoloquinolines

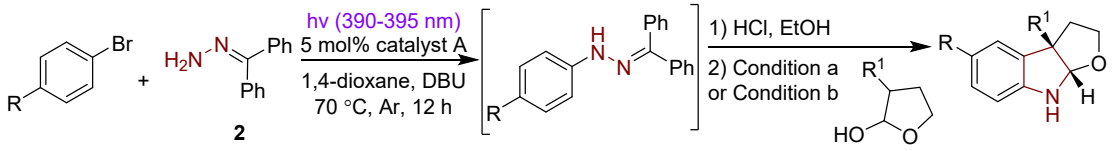


To an oven-dried 10 mL storage tube with a magnetic stir bar, Ni catalyst A (5 mol%, 0.025 mmol), aryl chlorides (0.5 mmol, 1.0 equiv) and benzophenone hydrazone (1.25 mmol, 2.5

equiv) were added. The tube was evacuated/backfilled with argon for three times. Under a positive pressure of argon, DBU (0.75 mmol, 1.5 equiv) and 1,4-dioxane (2.0 mL) were added *via* syringe. The tube was sealed with the Teflon screw valve. The reaction mixture was then irradiated with two purple LED lamps (1.0 cm from the tube, optical power: 200 ± 10mw/cm^2) for 12 h at 70 °C. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and were washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was used in the subsequent step without further purification.

The obtained crude product was dissolved in 3.0 mL EtOH, then *p*-TsOH·H_2O (1.5 mmol, 3.0 equiv) and ArCHO (1.0 mmol, 2.0 equiv) were added, the reaction was heated to reflux temperature for 12-24 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was transferred to an oven-dried 10 mL storage tube vial equipped with 3.0 mL 2-Me-THF, then chloramine-T (1.2 equiv, 0.6 mmol) was added. The reaction was heated to 60 °C for 12 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and washed with saturated $NaHCO_3$ (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel to give the desired product.

4.6 Procedures for the synthesis of furoindolines.



To an oven-dried 10 mL storage tube with a magnetic stir bar, Ni catalyst A (5 mol%, 0.025 mmol), aryl bromides (0.5 mmol, 1.0 equiv) and benzophenone hydrazone (1.25 mmol, 2.5 equiv) were added. The tube was evacuated/backfilled with argon for three times. Under a positive pressure of argon, DBU (0.75 mmol, 1.5 equiv) and 1,4-dioxane (2.0 mL) were added via syringe. The tube was sealed with the Teflon screw valve. The reaction mixture was then irradiated with two purple LED lamps (1.0 cm from the tube, optical power: 200 ± 10mw/cm^2)

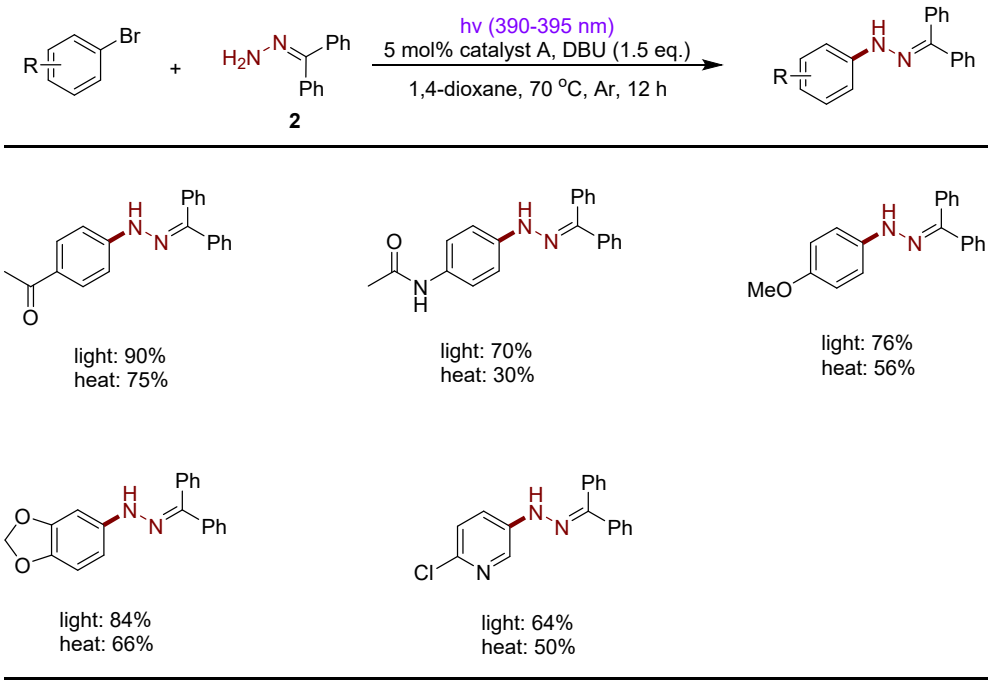
for 12 h at 70 °C. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and were washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was used in the subsequent step without further purification.

The obtained crude product was dissolved in 3.0 mL EtOH, then 12 M HCl (1.0 mL) were added. The reaction was heated to reflux temperature for 12 h. After the reaction is completed, the reaction mixture was diluted with EtOAc, and filtered to obtain a residue.

Condition a: The residue was transferred to an oven-dried 10 mL storage tube vial equipped, then 2.0 mL (AcOH:H_2O = 1:1) and latent aldehydes (1.0 equiv) were added. The reaction was heated to 60 °C for 2 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and were washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel to give the desired product.

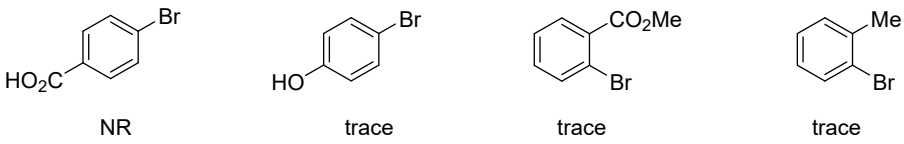
Condition b: The residue was transferred to an oven-dried 10 mL storage tube vial equipped, then 2.0 mL (1,4-dioxane:H_2O = 3:1), *p*-TsOH·H_2O (2.0 equiv) and latent aldehydes (1.0 equiv) were added. The reaction was heated to 60 °C for 4 h. After cooling to room temperature, The resulting mixture was diluted with 20 mL EtOAc, and were washed with saturated NaCl (2 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel to give the desired product.

4.7 Comparison of standard conditions and thermal reaction conditions.

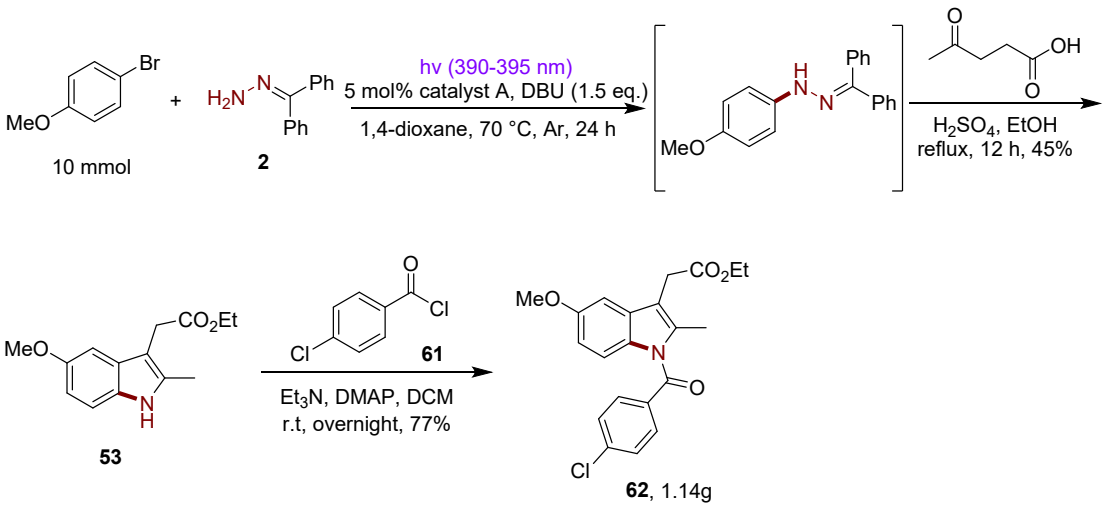


We have selected some different substrates and performed the reaction under standard and 70 °C conditions respectively. We found that the yields under standard conditions were higher than under 70 °C conditions.

4.8 Unsuccessful substrates



5. Gram scale preparation of indomethacin methyl ester



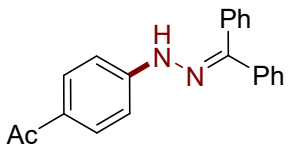
To an oven-dried 100 mL storage tube with a magnetic stir bar, Ni catalyst A (5 mol%, 0. 25

mmol), 4-bromoanisole (10 mmol, 1.0 equiv) and benzophenone hydrazone (25 mmol, 2.5 equiv) were added. The tube was evacuated/backfilled with argon for three times. Under a positive pressure of argon, DBU (15 mmol, 1.5 equiv) and 1,4-dioxane (40 mL) were added *via* syringe. The tube was sealed with the Teflon screw valve. The reaction mixture was then irradiated with eight 9W 390-395 nm purple LED lamps for 24 h at 70 °C. After cooling to room temperature, The resulting mixture was diluted with 200mL EtOAc, and washed with saturated NaCl (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was used in the subsequent step without further purification.

The obtained crude product was dissolved in 60 mL EtOH, then 3.0 equiv of *p*-TsOH·H_2O and 2.0 equiv of Levulinic acid were added, the reaction was heated to reflux temperature for 12 h. After cooling to room temperature, The resulting mixture was diluted with 200 mL EtOAc, and washed with saturated NaCl (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography to give compound **53** as a yellow oil (1.11 g, 45%).

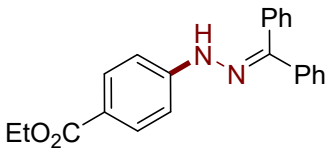
To a 100 mL reaction vial equipped with a magnetic stir bar were added compound **53** (950 mg, 3.8 mmol, 1.0 equiv.), Et_3N (7.6 mmol, 2.0 equiv.), DMAP (1.9 mmol, 0.5 equiv.) and dry DCM (20 mL), the reaction was stirred overnight at room temperature. TLC analysis indicated the complete conversion, the reaction was diluted with 1.0 M HCl solution and extracted with DCM (30 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to give compound **62** as a white soild (1.14 g, 77% yield).

6. Characterization data

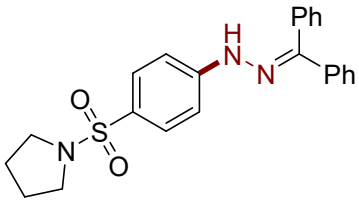


1-{4-[2-(Diphenylmethylene) hydrazinyl] phenyl} ethan-1-one (3): yellow foam; 90%; (X = Cl, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.76 (s, 1H), 7.62-7.55 (m, 5H), 7.35-7.33 (m, 5H), 7.10 (d, *J* = 8.7 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 148.4, 147.0, 137.9, 132.3, 130.6, 129.9, 129.7, 129.5, 129.1, 128.8, 128.4, 126.9, 112.3, 26.3;

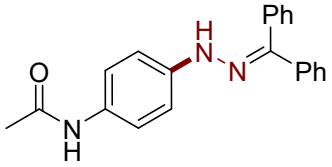
HRMS (ESI) m/z calcd. for $C_{21}H_{18}N_2NaO$ $[M+Na]^+$: 337.1311, found: 337.1319.



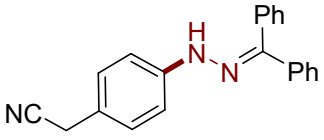
Ethyl 4-[2-(diphenylmethylene) hydrazinyl] benzoate (4): yellow solid; 78%; (X = Cl, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.71 (s, 1H), 7.62-7.55 (m, 5H), 7.35-7.33 (m, 5H), 7.09 (d, *J* = 8.8 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 148.2, 146.5, 138.0, 132.4, 131.5, 129.9, 129.7, 129.2, 128.7, 128.4, 126.9, 121.8, 112.2, 60.6, 14.6; HRMS (ESI) m/z calcd. for $C_{22}H_{20}N_2NaO_2$ $[M+Na]^+$: 367.1417, found: 367.1430.



1-((4-(2-(Diphenylmethylene)hydrazinyl)phenyl)sulfonyl)pyrrolidine (5): white solid; 82% ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 3H), 7.63-7.55 (m, 5H), 7.36-7.32 (m, 5H), 7.15 (d, *J* = 8.8 Hz, 2H), 3.23-3.19 (m, 4H), 1.75-1.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 147.2, 137.7, 132.2, 129.9, 129.8, 129.5, 129.0, 128.9, 128.4, 126.9, 126.8, 112.6, 48.0, 25.2; HRMS (ESI) m/z calcd. for $C_{23}H_{23}N_3NaO_2S$ $[M+Na]^+$: 428.1403, found: 428.1407.

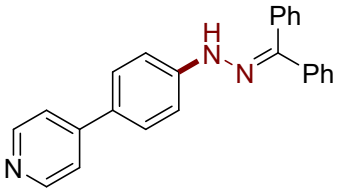


***N*-(4-(2-(diphenylmethylene)hydrazinyl)phenyl)acetamide (6):** yellow solid; 70%; ^{1}H NMR (400 MHz, DMSO) δ 9.68 (s, 1H), 8.72 (s, 1H), 7.62-7.54 (m, 3H), 7.45-7.40 (m, 4H), 7.35-7.27 (m, 5H), 7.16 (d, *J* = 8.9 Hz, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 167.5, 142.3, 141.2, 138.8, 133.1, 131.7, 129.5, 129.1, 128.9, 128.2, 127.5, 125.9, 120.2, 113.0, 23.8; HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_3NaO$ $[M+Na]^+$: 352.1420, found: 352.1414.

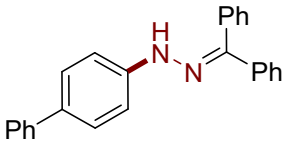


2-(4-(2-(Diphenylmethylene)hydrazinyl)phenyl)acetonitrile (7): yellow oil; 82%; ^{1}H NMR (400

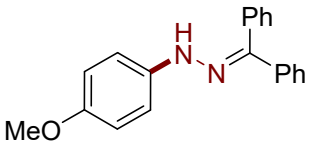
MHz, $CDCl_3$) δ 7.61-7.53 (m, 5H), 7.52 (s, 1H), 7.33 (m, 5H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 3.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.6, 138.3, 132.7, 129.9, 129.5, 129.2, 129.0, 128.4, 126.7, 120.9, 118.5, 113.5, 23.1; HRMS (ESI) m/z calcd. for $C_{21}H_{17}N_3Na$ $[M+Na]^+$: 334.1315, found: 334.1319.



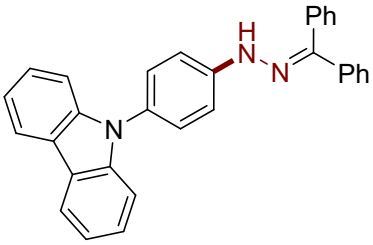
4-(4-(2-(Diphenylmethylene)hydrazinyl)phenyl)pyridine (8): yellow solid; 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 6.1 Hz, 2H), 7.64-7.55 (m, 8H), 7.48 (d, *J* = 6.1 Hz, 2H), 7.36-7.31 (m, 5H), 7.18 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 148.0, 145.6, 145.5, 138.2, 132.6, 129.8, 129.5, 129.2, 129.1, 128.4, 128.3, 127.9, 126.7, 120.7, 113.5; HRMS (ESI) m/z calcd. for $C_{24}H_{20}N_3$ $[M+H]^+$: 350.1652, found: 350.1646.



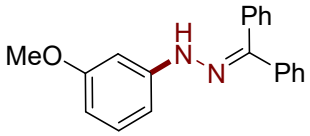
1-(Diphenylmethylene)-2-(4-biphenyl) hydrazine (9): yellow solid; 78%; (X = Cl, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.50 (m, 10H), 7.43-7.28 (m, 8H), 7.17 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 144.1, 141.1, 138.4, 133.0, 132.8, 129.9, 129.4, 129.3, 128.8, 128.3, 128.2, 128.0, 126.7, 126.6, 126.5, 113.4; HRMS (ESI) m/z calcd. for $C_{25}H_{20}N_2Na$ $[M+Na]^+$: 371.1519, found: 371.1532.



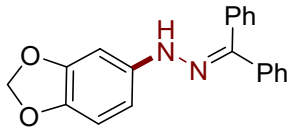
1-(Diphenylmethylene)-2-(4-methoxyphenyl) hydrazine (10)[2]: yellow oil; 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.49 (m, 5H), 7.37 (s, 1H), 7.35-7.28 (m, 5H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 143.5, 139.0, 138.6, 133.0, 129.8, 129.3, 129.2, 128.3, 127.9, 126.4, 114.9, 114.1, 55.6; HRMS (ESI) m/z calcd. for $C_{20}H_{18}N_2NaO$ $[M+Na]^+$: 325.1317, found: 325.1324.



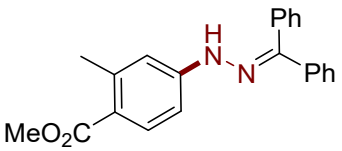
9-{4-[2-(Diphenylmethylene) hydrazinyl] phenyl}-9*H*-carbazole (11): yellow foam; 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.66-7.62 (m, 5H), 7.58-7.55 (m, 1H), 7.42-7.37 (m, 6H), 7.35-7.32 (m, 4H), 7.30-7.25 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 144.1, 141.6, 138.3, 132.7, 129.9, 129.6, 129.5, 129.2, 128.5, 128.4, 128.4, 126.7, 125.9, 123.2, 120.3, 119.6, 114.0, 109.9; HRMS (ESI) m/z calcd. for $C_{31}H_{23}N_3Na$ $[M+Na]^+$: 460.1784, found: 460.1778.



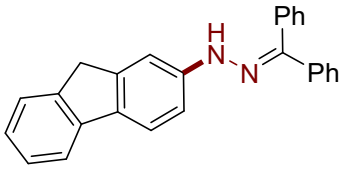
1-(Diphenylmethylene)-2-(3-methoxyphenyl) hydrazine (12)[2]: yellow oil; 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.51 (s, 1H), 7.36-7.30 (m, 5H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.81 (t, *J* = 2.0 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.43 (dd, *J* = 8.1, 2.2 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 146.1, 144.4, 138.4, 132.9, 130.1, 129.8, 129.4, 129.3, 128.3, 128.2, 126.6, 105.8, 105.7, 98.9, 55.4; HRMS (ESI) m/z calcd. for $C_{20}H_{18}N_2NaO$ $[M+Na]^+$: 325.1311, found:325.1312.



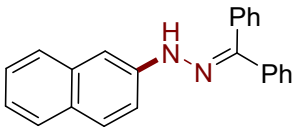
1-(Benzo[d][1,3]dioxol-5-yl)-2-(diphenylmethylene) hydrazine (13): yellow oil; 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.49 (m, 5H), 7.37 (s, 1H), 7.34-7.27 (m, 5H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.37 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 143.8, 141.5, 140.5, 138.5, 133.0, 130.2, 129.8, 129.4, 129.3, 128.4, 128.3, 128.0, 126.5, 108.6, 104.9, 101.0, 96.0; HRMS (ESI) m/z calcd. for $C_{20}H_{16}N_2NaO_2$ $[M+Na]^+$: 339.1104, found: 339.1111.



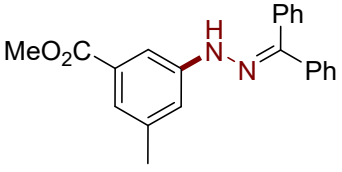
Methyl 2-methyl-4-[2-(diphenylmethylene) hydrazinyl] benzoate (14): yellow solid; 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.64 (s, 1H), 7.62-7.54 (m, 5H), 7.37-7.32 (m, 5H), 6.92 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.89 (s, 1H), 3.85 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 147.3, 146.3, 143.1, 138.1, 133.1, 132.5, 129.9, 129.7, 129.2, 128.7, 128.4, 126.9, 120.5, 115.3, 109.9, 51.5, 22.6; HRMS (ESI) m/z calcd. for $C_{22}H_{20}N_2NaO_2$ $[M+Na]^+$: 367.1417, found: 367.1416.



1-(Diphenylmethylene)-2-(9*H*-fluoren-2-yl) hydrazine (15): yellow solid; 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.54 (m, 8H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.37-7.28 (m, 7H), 7.21 (td, *J* = 7.4, 0.9 Hz, 1H), 7.02 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 144.3, 144.1, 142.7, 142.2, 138.5, 134.5, 132.9, 129.9, 129.4, 129.3, 128.4, 128.1, 126.8, 126.6, 125.4, 124.9, 120.6, 118.9, 112.1, 109.6, 37.1; HRMS (ESI) m/z calcd. for $C_{26}H_{20}N_2Na$ $[M+Na]^+$: 383.1519, found: 383.1526.

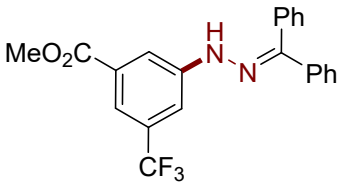


1-(2-Naphthyl)-2-(diphenylmethylene) hydrazine (16)[2]**:** yellow solid; 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.56 (m, 9H), 7.46 (s, 1H), 7.43-7.26 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 142.4, 138.5, 134.9, 132.9, 129.9, 129.5, 129.3, 129.2, 129.1, 128.4, 128.3, 127.9, 126.7, 126.6, 126.5, 123.0, 115.7, 107.2; HRMS (ESI) m/z calcd. for $C_{23}H_{18}N_2Na$ $[M+Na]^+$: 345.1362, found: 345.1364.

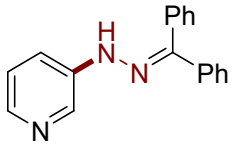


Methyl 3-[2-(diphenylmethylene) hydrazinyl]-5-methylbenzoate (17): yellow solid; 79%; ^{1}H

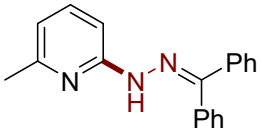
NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 3H), 7.58 (s, 1H), 7.56-7.54 (m, 2H), 7.39 (s, 1H), 7.37-7.30 (m, 6H), 7.25 (s, 1H), 3.89 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 147.3, 146.3, 143.1, 138.0, 133.0, 132.4, 129.9, 129.7, 129.1, 128.7, 128.4, 126.9, 120.5, 115.3, 109.9, 51.5, 22.6; HRMS (ESI) m/z calcd. for $C_{22}H_{20}N_2NaO_2$ $[M+Na]^+$: 367.1417, found: 367.1418.



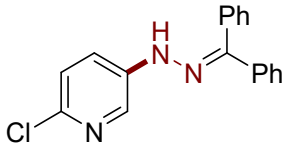
Methyl 3-[2-(diphenylmethylene) hydrazinyl]-5-trifluoromethylbenzoate (18): yellow solid; 75%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.74 (m, 2H), 7.68 (s, 1H), 7.64-7.56 (m, 6H), 7.36-7.33 (m, 5H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 147.0, 145.4, 137.7, 132.4, 132.1 (q, *J* = 32.5 Hz), 131.9, 130.0, 129.8, 129.0, 128.9, 128.4, 127.0, 123.9 (q, *J* = 271.0 Hz), 117.4 (q, *J* = 3.9 Hz), 117.0, 113.5 (d, *J* = 3.8 Hz), 52.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.92 (s); HRMS (ESI) m/z calcd. for $C_{22}H_{17}F_3N_2NaO_2$ $[M+Na]^+$: 421.1134, found: 421.1136.



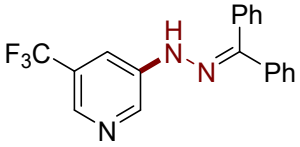
3-(2-(Diphenylmethylene)hydrazinyl)pyridine (19)[3]: yellow solid; 70%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.6 Hz, 1H), 8.10 (dd, *J* = 4.7, 1.2 Hz, 1H), 7.63-7.51 (m, 6H), 7.47 (s, 1H), 7.36-7.30 (m, 5H), 7.18 (dd, *J* = 8.3, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 141.5, 141.1, 138.0, 135.8, 132.4, 129.9, 129.6, 129.1, 128.6, 128.4, 126.8, 123.9, 119.7; HRMS (ESI) m/z calcd. for $C_{18}H_{16}N_3$ $[M+H]^+$: 274.1339, found: 274.1335.



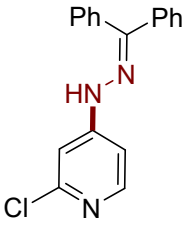
2-(2-(Diphenylmethylene)hydrazinyl)-6-methylpyridine (20): yellow solid; 77%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.60-7.48 (m, 6H), 7.35-7.30 (m, 6H), 6.62 (d, *J* = 7.3 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 156.4, 145.9, 138.5, 138.3, 132.8, 129.9, 129.5, 129.1, 128.5, 128.3, 126.8, 115.4, 104.7, 24.1; HRMS (ESI) m/z calcd. for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495, found: 288.1497.



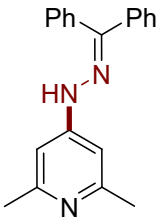
2-Chloro-5-(2-(diphenylmethylene)hydrazinyl)pyridine (21): yellow solid; 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.9 Hz, 1H), 7.63-7.52 (m, 6H), 7.47 (s, 1H), 7.35-7.32 (m, 5H), 7.20 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 141.5, 140.3, 137.8, 134.7, 132.2, 129.9, 129.8, 129.0, 128.8, 128.4, 126.8, 124.4, 123.1; HRMS (ESI) m/z calcd. for $C_{18}H_{14}ClN_3Na$ $[M+Na]^+$: 330.0768, found: 330.0767.



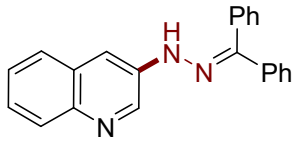
3-(2-(Diphenylmethylene)hydrazinyl)-5-(trifluoromethyl)pyridine (22): yellow solid; 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.5 Hz, 1H), 8.34 (d, *J* = 0.9 Hz, 1H), 7.71 (t, *J* = 2.0 Hz, 1H), 7.66-7.54 (m, 6H), 7.40-7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 140.9, 138.81 (d, *J* = 1.2 Hz), 137.6, 137.5 (q, *J* = 4.2 Hz), 132.1, 130.0, 129.9, 129.1, 129.0, 128.6, 127.1 (q, *J* = 32.4 Hz), 127.0, 123.8 (q, *J* = 271.1 Hz), 116.2 (q, *J* = 3.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.53 (s); HRMS (ESI) m/z calcd. for $C_{19}H_{15}F_3N_3$ $[M+H]^+$: 342.1213, found: 342.1209.



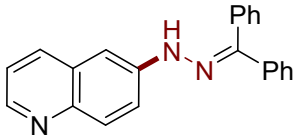
2-Chloro-4-(2-(diphenylmethylene)hydrazinyl)pyridine (23): yellow solid; 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.7 Hz, 1H), 7.68 (s, 1H), 7.63-7.56 (m, 5H), 7.38-7.30 (m, 5H), 7.04 (s, 1H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 152.2, 149.7, 149.1, 137.3, 131.9, 130.0, 129.4, 128.9, 128.5, 127.2, 107.3, 107.2; HRMS (ESI) m/z calcd. for $C_{18}H_{15}ClN_3$ $[M+H]^+$: 308.0949, found: 308.0943.



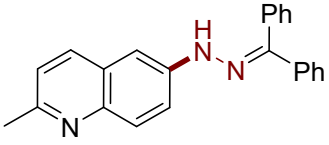
4-(2-(Diphenylmethylene)hydrazinyl)-2,6-dimethylpyridine (24): yellow oil; 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.50 (m, 6H), 7.39-7.28 (m, 5H), 6.65 (s, 2H), 2.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 151.0, 147.1, 137.8, 132.3, 129.9, 129.7, 129.0, 128.8, 128.3, 126.9, 104.5, 24.6; HRMS (ESI) m/z calcd. for $C_{20}H_{20}N_3$ $[M+H]^+$: 302.1652, found: 302.1653.



3-[2-(Diphenylmethylene) hydrazinyl] quinolone (25): yellow solid; 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.6 Hz, 1H), 8.00-7.98 (m, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.75-7.72 (m, 1H), 7.71 (s, 1H), 7.66-7.57 (m, 5H), 7.50-7.46 (m, 2H), 7.40-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 143.9, 141.1, 138.2, 138.0, 132.4, 123.0, 129.8, 129.3, 129.2, 129.1, 128.8, 128.5, 127.2, 126.9, 126.7, 126.1, 114.0; HRMS (ESI) m/z calcd. for $C_{22}H_{17}N_3Na$ $[M+Na]^+$: 346.1315, found: 346.1321.

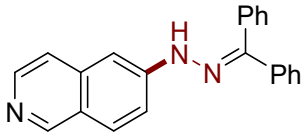


6-[2-(Diphenylmethylene) hydrazinyl] quinolone (26): yellow solid; 76%; (X = Cl, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 9.8 Hz, 1H), 7.74 (s, 1H), 7.66-7.55 (m, 5H), 7.44-7.42 (m, 2H), 7.39-7.32 (m, 5H), 7.30 (dd, *J* = 8.3, 4.2 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 145.9, 144.5, 142.6, 138.2, 134.6, 132.6, 130.6, 129.9, 129.8, 129.6, 129.2, 128.5, 128.4, 126.8, 121.7, 119.1, 106.2; HRMS (ESI) m/z calcd. for $C_{22}H_{17}N_3Na$ $[M+Na]^+$: 346.1315, found: 346.1323.

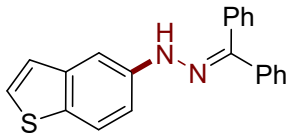


2-Methyl-6-[2-(diphenylmethylene) hydrazinyl] quinolone (27): yellow solid; 75%; (X = Cl, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.87 (m, 2H), 7.69 (s, 1H), 7.66-7.52 (m, 5H), 7.43-

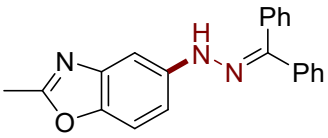
7.40 (m, 2H), 7.38-7.31 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 145.5, 144.0, 142.0, 138.3, 134.9, 132.7, 129.9, 129.7, 129.5, 129.2, 128.4, 128.3, 127.9, 126.7, 122.5, 118.9, 106.4, 25.1; HRMS (ESI) m/z calcd. for $C_{23}H_{19}N_3Na$ $[M+Na]^+$: 360.1471, found: 360.1475.



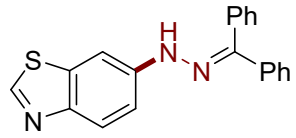
6-[2-(Diphenylmethylene) hydrazinyl] isoquinolone (28): yellow solid; 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.36 (d, *J* = 5.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.66-7.56 (m, 5H), 7.48 (d, *J* = 5.8 Hz, 1H), 7.39-7.34 (m, 6H), 7.31 (dd, *J* = 8.8, 1.9 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 146.8, 145.7, 143.7, 140.0, 137.8, 132.5, 129.9, 129.7, 129.3, 129.1, 128.8, 128.4, 127.0, 124.6, 119.5, 116.9, 104.8; HRMS (ESI) m/z calcd. for $C_{22}H_{17}N_3Na$ $[M+Na]^+$: 346.1315, found: 346.1323.



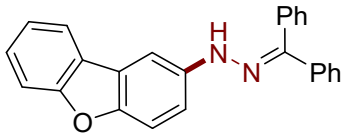
1-(Benzo[b]thiophen-6-yl)-2-(diphenylmethylene) hydrazine (29): yellow solid; 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.7 Hz, 1H), 7.64-7.52 (m, 7H), 7.41-7.28 (m, 6H), 7.24 (d, *J* = 5.4 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.4, 141.0, 139.0, 133.0, 131.8, 129.9, 129.4, 129.3, 128.4, 128.1, 127.4, 126.6, 123.7, 123.0, 112.5, 107.2; HRMS (ESI) m/z calcd. for $C_{21}H_{16}N_2NaS$ $[M+Na]^+$: 351.0926, found: 351.0933.



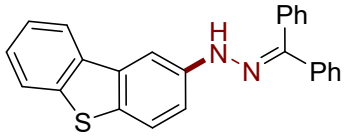
5-(2-(Diphenylmethylene)hydrazinyl)-2-methylbenzo[*d*]oxazole (30): yellow oil; 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.55-7.51 (m, 2H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.37-7.27 (m, 6H), 6.99 (dd, *J* = 8.7, 2.2 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 145.9, 144.3, 142.7, 142.3, 138.4, 132.9, 129.8, 129.4, 129.2, 128.3, 128.1, 126.6, 110.7, 110.3, 103.0, 14.7; HRMS (ESI) m/z calcd. for $C_{21}H_{18}N_3O$ $[M+H]^+$: 328.1444, found: 328.1447.



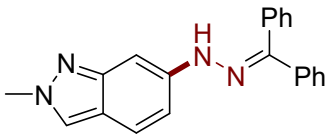
6-(2-(Diphenylmethylene)hydrazinyl)benzo[d]thiazole (31): yellow oil; 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 2.1 Hz, 1H), 7.65-7.54 (m, 6H), 7.37-7.31 (m, 5H), 7.09 (dd, *J* = 8.8, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 147.8, 145.4, 143.0, 138.2, 135.8, 132.6, 129.8, 129.5, 129.2, 128.4, 128.3, 126.7, 123.8, 113.6, 104.1; HRMS (ESI) m/z calcd. for $C_{20}H_{16}N_3S$ $[M+H]^+$: 330.1059, found: 330.1061.



1-(Benzo[b,d]furan-5-yl)-2-(diphenylmethylene) hydrazine (32): yellow oil; 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.66-7.60 (m, 5H), 7.57-7.52 (m, 2H), 7.45-7.29 (m, 8H), 7.14 (dd, *J* = 8.8, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 151.3, 144.3, 141.0, 138.6, 133.1, 129.9, 129.4, 129.3, 128.4, 128.1, 127.1, 126.6, 125.1, 124.7, 122.5, 120.9, 113.6, 112.0, 111.8, 104.0; HRMS (ESI) m/z calcd. for $C_{25}H_{18}N_2NaO$ $[M+Na]^+$: 385.1311, found: 385.1313.

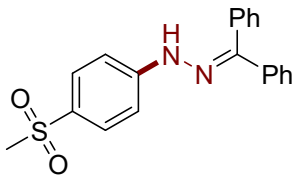


1-(Dibenzo[b,d]thiophen-3-yl)-2-(diphenylmethylene)hydrazine (33): yellow solid; 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.68-7.55 (m, 7H), 7.40-7.33 (m, 7H), 7.07 (dd, *J* = 8.6, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 145.2, 144.0, 141.5, 138.6, 138.3, 136.0, 132.8, 130.2, 129.9, 129.5, 129.3, 128.8, 128.4, 126.7, 125.3, 124.4, 122.7, 122.2, 120.5, 111.4, 105.7; HRMS (ESI) m/z calcd. for $C_{25}H_{18}N_2NaS$ $[M+Na]^+$: 401.1083, found: 401.1093.

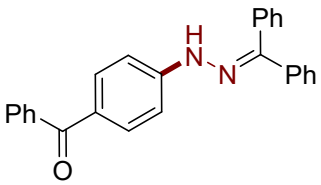


6-(2-(Diphenylmethylene)hydrazinyl)-2-methyl-2*H*-indazole (34): yellow soild; 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.64-7.48 (m, 7H), 7.38-7.28 (m, 6H), 6.86 (dd, *J* = 8.9, 1.2 Hz,

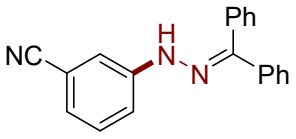
1H), 4.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 144.3, 143.0, 138.5, 132.9, 129.8, 129.4, 129.3, 128.3, 128.1, 126.6, 123.7, 120.8, 118.2, 113.5, 95.9, 40.1; HRMS (ESI) m/z calcd. for $C_{21}H_{18}N_4Na$ $[M+Na]^+$: 327.1604, found: 327.1596.



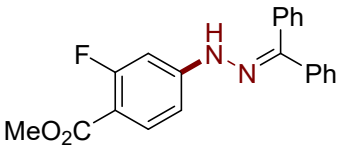
1-(Diphenylmethylene)-2-(4-(methylsulfonyl)phenyl)hydrazine (35): white solid; 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.77-7.76 (m, 2H), 7.63-7.56 (m, 5H), 7.37-7.32 (m, 5H), 7.17 (d, *J* = 8.8 Hz, 2H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 147.8, 137.7, 132.2, 130.6, 130.0, 129.9, 129.3, 129.1, 129.0, 128.5, 127.0, 112.8, 45.1; HRMS (ESI) m/z calcd. for $C_{20}H_{18}N_2NaO_2S$ $[M+Na]^+$: 373.0981, found: 373.0984.



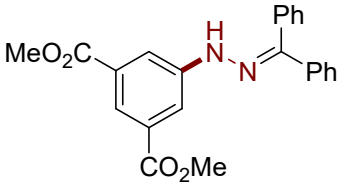
2-[2-(Diphenylmethylene) hydrazinyl] quinolone (36): yellow solid; 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.73 (m, 5H), 7.64-7.60 (m, 4H), 7.58-7.53 (m, 2H), 7.48-7.45 (m, 2H), 7.36-7.33 (m, 5H), 7.13 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 148.2, 147.0, 138.9, 137.9, 132.8, 132.3, 131.6, 129.9, 129.7, 129.7, 129.1, 129.0, 128.8, 128.4, 128.2, 127.0, 112.2; HRMS (ESI) m/z calcd. for $C_{26}H_{20}N_2NaO$ $[M+Na]^+$: 399.1468, found: 399.1476.



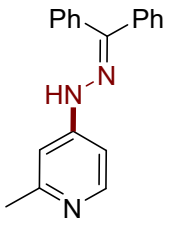
3-(2-(Diphenylmethylene)hydrazinyl)benzonitrile (37): white solid; 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.53 (m, 6H), 7.42 (t, *J* = 1.6 Hz, 1H), 7.35-7.32 (m, 5H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.21-7.19 (m, 1H), 7.10 (dt, *J* = 7.5, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 145.2, 137.8, 132.4, 130.0, 129.9, 129.7, 129.0, 128.8, 128.4, 126.9, 123.4, 119.3, 117.2, 116.4, 113.1; HRMS (ESI) m/z calcd. for $C_{20}H_{15}N_3Na$ $[M+Na]^+$: 320.1158, found: 320.1158.



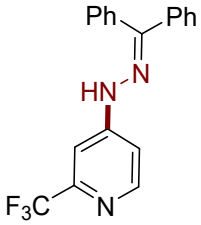
Methyl 4-(2-(diphenylmethylene)hydrazinyl)-2-fluorobenzoate (38): white solid; 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 8.4 Hz, 1H), 7.71 (s, 1H), 7.63-7.55 (m, 5H), 7.36-7.31 (m, 5H), 6.96 (dd, *J* = 13.2, 2.0 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.1 (d, *J* = 4.2 Hz), 164.0 (d, *J* = 256.7 Hz), 149.9 (d, *J* = 12.0 Hz), 147.7, 137.6, 133.6 (d, *J* = 2.7 Hz), 132.1, 129.9, 129.8, 129.0, 128.4, 127.0, 109.2 (d, *J* = 10.0 Hz), 108.3 (d, *J* = 2.3 Hz), 100.6, 100.3, 51.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.95 (dd, *J* = 12.7, 8.3 Hz); HRMS (ESI) m/z calcd. for $C_{21}H_{17}FN_2NaO_2$ $[M+Na]^+$: 371.1166, found: 371.1161.



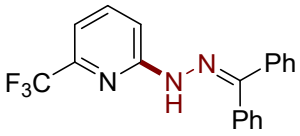
Dimethyl 5-(2-(diphenylmethylene)hydrazinyl)isophthalate (39): yellow oil; 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, *J* = 1.4 Hz, 1H), 7.89 (d, *J* = 1.4 Hz, 2H), 7.64-7.55 (m, 6H), 7.35-7.32 (m, 5H), 3.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 146.4, 145.2, 137.9, 132.5, 131.6, 130.0, 129.7, 129.1, 128.7, 128.4, 126.9, 122.0, 118.0, 52.5; HRMS (ESI) m/z calcd. for $C_{23}H_{20}N_2NaO_4$ $[M+Na]^+$: 411.1315, found: 411.1322.



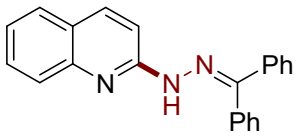
4-(2-(Diphenylmethylene)hydrazinyl)-2-methylpyridine (40): yellow solid; 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.7 Hz, 1H), 7.62-7.53 (m, 6H), 7.37-7.31 (m, 5H), 6.83 (s, 1H), 6.76 (d, *J* = 5.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 150.6, 149.8, 147.5, 137.8, 132.3, 129.9, 129.8, 129.0, 128.9, 128.4, 127.0, 106.9, 105.6, 24.7; HRMS (ESI) m/z calcd. for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1495, found: 288.1495.



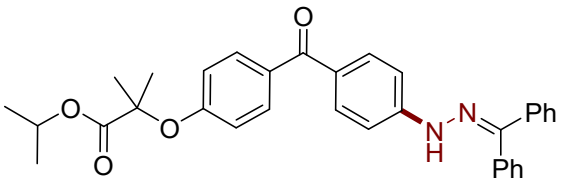
4-(2-(Diphenylmethylene)hydrazinyl)-2-(trifluoromethyl)pyridine (41): yellow stick; 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 5.6 Hz, 1H), 7.82 (s, 1H), 7.64-7.58 (m, 5H), 7.37-7.32 (m, 6H), 7.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 150.6, 149.6, 149.3 (q, *J* = 33.7.0 Hz), 137.3, 131.9, 130.1, 130.0, 129.5, 128.9, 128.5, 127.3, 121.8 (q, *J* = 272.6 Hz), 109.8, 104.9 (q, *J* = 2.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.37 (s); HRMS (ESI) m/z calcd. for $C_{19}H_{15}F_3N_3$ $[M+H]^+$: 342.1213, found: 342.1208.



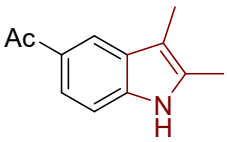
2-(2-(Diphenylmethylene)hydrazinyl)-6-(trifluoromethyl)pyridine (42): yellow solid; 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.80-7.68 (m, 2H), 7.63-7.50 (m, 5H), 7.35-7.32 (m, 5H), 7.12 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 147.9, 146.4 (q, *J* = 34.0 Hz), 139.1, 137.9, 132.4, 130.0, 129.9, 129.03, 129.0, 128.4, 127.1, 121.6 (q, *J* = 272.2 Hz), 112.1 (q, *J* = 3.2 Hz), 111.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.44 (s); HRMS (ESI) m/z calcd. for $C_{19}H_{14}F_3N_3Na$ $[M+Na]^+$: 364.1032, found: 364.1031.



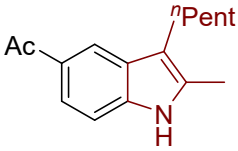
2-[2-(Diphenylmethylene) hydrazinyl] quinolone (43)[4]**:** yellow solid; 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.65-7.52 (m, 7H), 7.38-7.34 (m, 5H), 7.32-7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 147.4, 146.9, 138.4, 138.1, 132.6, 130.0, 129.9, 129.7, 129.1, 128.8, 128.4, 127.9, 127.0, 126.3, 125.2, 123.3, 110.2; HRMS (ESI) m/z calcd. for $C_{22}H_{17}N_3Na$ $[M+Na]^+$: 346.1315, found: 346.1322.



2-[2-(Diphenylmethylene) hydrazinyl] quinolone (44): yellow solid; 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 3H), 7.71 (d, *J* = 8.7, Hz, 2H), 7.63-7.55 (m, 5H), 7.36-7.33 (m, 5H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.12-5.06 (m, 1H), 1.66 (s, 6H), 1.21 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 173.4, 158.9, 147.9, 146.8, 137.9, 132.5, 132.3, 131.9, 131.7, 129.9, 129.7, 129.5, 129.1, 128.7, 128.4, 126.9, 117.3, 112.1, 79.4, 69.4, 25.5, 21.6; HRMS (ESI) m/z calcd. for $C_{33}H_{32}N_2NaO_4$ $[M+Na]^+$: 543.2254, found: 543.2255.

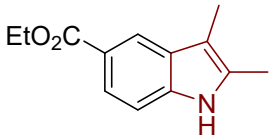


1-(2,3-Dimethyl-1*H*-indol-5-yl)ethan-1-one (45)[5]**:** yellow solid; 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.96 (m, 1H), 7.79 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.26 (m, 1H), 2.67 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 138.2, 132.5, 129.3, 129.2, 121.8, 120.1, 109.9, 108.9, 26.8, 11.7, 8.5; HRMS (ESI) m/z calcd. for $C_{12}H_{13}NNaO$ $[M+Na]^+$: 210.0889, found: 210.0887.

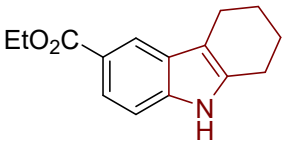


1-(2-Methyl-3-pentyl-1*H*-indol-5-yl)ethan-1-one (46): yellow solid; 43%; ^{1}H NMR (400 MHz,

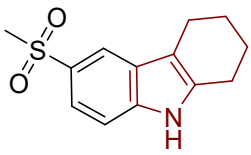
$CDCl_3$) δ 8.18 (s, 1H), 8.11 (s, 1H), 7.78 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.67 (s, 3H), 2.38 (s, 3H), 1.67-1.58 (m, 2H), 1.35-1.32 (m, 4H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 138.2, 132.4, 129.3, 128.6, 121.7, 120.2, 114.3, 109.9, 31.9, 30.7, 26.8, 24.0, 22.7, 14.2, 11.8; HRMS (ESI) m/z calcd. for $C_{16}H_{21}NNaO$ $[M+Na]^+$: 266.1515, found: 266.1514.



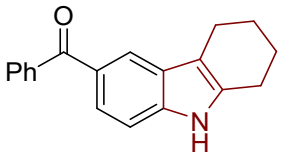
Ethyl 2,3-dimethyl-1*H*-indole-5-carboxylate (47)[5]: yellow solid; 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.88 (s, 1H), 7.84 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.26 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.0, 132.2, 129.2, 122.6, 121.4, 120.9, 109.7, 108.6, 60.6, 14.6, 11.6, 8.5; HRMS (ESI) m/z calcd. for $C_{13}H_{15}NNaO_2$ $[M+Na]^+$: 240.0995, found: 240.0994.



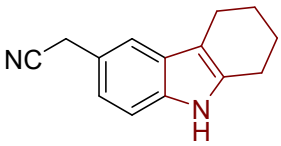
Ethyl 2,3,4,9-tetrahydro-1*H*-carbazole-6-carboxylate (48)[5]: yellow solid; 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.87 (s, 1H), 7.84 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 5.1 Hz, 4H), 1.99-1.83 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 138.5, 135.7, 127.6, 122.7, 121.4, 120.7, 111.7, 110.0, 60.6, 23.3, 23.2, 23.1, 20.9, 14.6; HRMS (ESI) m/z calcd. for $C_{15}H_{17}NNaO_2$ $[M+Na]^+$: 266.1151, found: 266.1154.



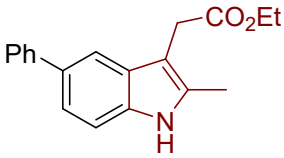
6-(Methylsulfonyl)-2,3,4,9-tetrahydro-1*H*-carbazole (49)[6]: yellow solid; 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.09 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 3.07 (s, 3H), 2.76-2.72 (m, 4H), 1.94-1.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.3, 130.7, 127.7, 119.5, 118.5, 111.8, 111.0, 45.5, 23.3, 23.1, 23.0, 20.8; HRMS (ESI) m/z calcd. for $C_{13}H_{15}NNaO_2S$ $[M+Na]^+$: 272.0716, found: 272.0717.



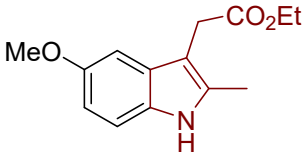
Phenyl(2,3,4,9-tetrahydro-1*H*-carbazol-6-yl)methanone (50): yellow solid; 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.82-7.80 (m, 2H), 7.68 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.59-7.54 (m, 1H), 7.40-7.46 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 5.9 Hz, 2H), 1.95-1.86 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 139.49, 138.59, 136.2, 131.6, 130.0, 128.8, 128.1, 127.4, 123.8, 122.0, 111.7, 110.2, 23.3, 23.2, 23.1, 20.9; HRMS (ESI) m/z calcd. for $C_{19}H_{17}NNaO$ $[M+Na]^+$: 298.1202, found: 298.1203.



2-(2,3,4,9-Tetrahydro-1*H*-carbazol-6-yl)acetonitrile (51): yellow oil; 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.42 (s, 1H), 7.28 (s, 1H), 7.04 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.85 (s, 2H), 2.77-2.70 (m, 4H), 1.96-1.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 135.2, 128.4, 120.8, 120.4, 119.2, 117.3, 111.0, 110.2, 23.8, 23.3, 23.3, 23.2, 20.9; HRMS (ESI) m/z calcd. for $C_{14}H_{14}N_2Na$ $[M+Na]^+$: 233.1049, found: 233.1057.

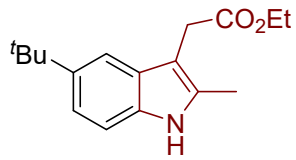


Ethyl 2-(2-methyl-5-phenyl-1*H*-indol-3-yl)acetate (52): yellow solid; 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.74 (s, 1H), 7.65 (s, 1H), 7.64 (s, 1H), 7.44-7.36 (m, 3H), 7.32-7.26 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 2H), 2.44 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 142.9, 134.8, 133.6, 133.2, 129.1, 128.7, 127.5, 126.3, 121.1, 116.8, 110.6, 105.1, 60.9, 30.6, 14.4, 11.9; HRMS (ESI) m/z calcd. for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$: 316.1308, found: 316.1310.

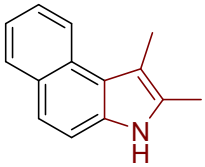


Ethyl 2-(5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (53)[5]**:** yellow oil; 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.77 (dd, *J* = 8.7, 2.4 Hz,

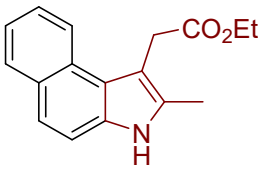
1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 3.64 (s, 2H), 2.39 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 154.2, 133.7, 130.3, 129.1, 111.1, 111.0, 104.6, 100.6, 60.8, 56.0, 30.7, 14.4, 11.9; HRMS (ESI) m/z calcd. for $C_{14}H_{17}NNaO_3$ $[M+Na]^+$: 270.1101, found: 270.1102.



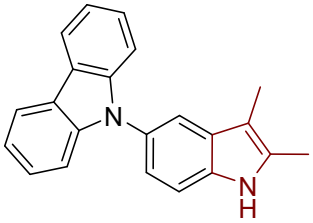
Ethyl 2-(5-(tert-butyl)-2-methyl-1*H*-indol-3-yl)acetate (54)[7]**:** yellow oil; 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.53 (s, 1H), 7.20 (d, *J* = 1.2 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 2H), 2.40 (s, 3H), 1.38 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 142.5, 133.4, 132.8, 128.4, 119.5, 114.2, 109.8, 104.8, 60.7, 34.7, 32.1, 30.7, 14.4, 11.9; HRMS (ESI) m/z calcd. for $C_{17}H_{23}NNaO_2$ $[M+Na]^+$: 296.1621, found: 296.1621.



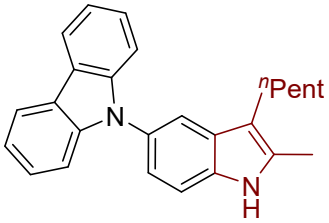
1,2-Dimethyl-3*H*-benzo[e]indole (55)[8]**:** yellow solid; 46%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.2 Hz, 1H), 8.05 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.52 (m, 2H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.40-7.36 (m, 1H), 2.63 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 129.8, 129.3, 129.1, 128.8, 125.4, 123.3, 122.7, 122.0, 121.9, 112.4, 109.9, 12.5, 11.6; HRMS (ESI) m/z calcd. for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found: 196.1122.



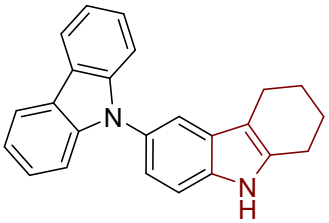
Ethyl 2-(2-methyl-3*H*-benzo[e]indol-1-yl)acetate (56): yellow solid; 46%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.43-7.36 (m, 2H), 4.17 (qd, *J* = 7.1, 1.3 Hz, 2H), 4.05 (s, 2H), 2.48 (d, *J* = 11.5 Hz, 3H), 1.23 (td, *J* = 7.1, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 131.7, 131.4, 130.0, 129.0, 128.5, 125.5, 123.1, 122.9, 122.4, 121.3, 112.5, 107.1, 61.0, 32.7, 14.4, 11.7; HRMS (ESI) m/z calcd. for $C_{17}H_{17}NNaO_2$ $[M+Na]^+$: 290.1151, found: 290.1152.



9-(2,3-Dimethyl-1*H*-indol-5-yl)-9*H*-carbazole (57): white foam; 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.89 (s, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.31-7.34 (m, 4H), 7.27 (dd, *J* = 14.4, 1.4 Hz, 1H), 7.27 (m, 1H), 7.22 (dd, *J* = 8.4, 2.0 Hz, 1H), 2.44 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 134.5, 132.5, 130.4, 129.3, 125.8, 123.0, 120.7, 120.3, 119.4, 117.3, 111.1, 110.1, 107.9, 11.8, 8.6; HRMS (ESI) m/z calcd. for $C_{22}H_{18}N_2$ $[M+H]^+$: 311.1543, found: 311.1554.

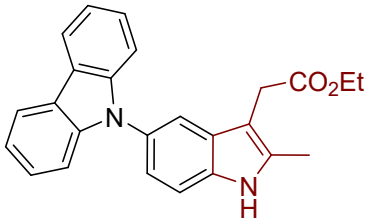


9-(2-Methyl-3-pentyl-1*H*-indol-5-yl)-9*H*-carbazole (58): white foam; 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.89 (s, 1H), 7.64 (d, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.40-7.37 (m, 4H), 7.30-7.26 (m, 2H), 7.22 (dd, *J* = 8.4, 2.0 Hz, 1H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.62-1.59 (m, 2H), 1.34-1.31 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 134.5, 132.4, 129.9, 129.2, 125.8, 123.1, 120.5, 120.3, 119.4, 117.4, 113.2, 111.2, 110.1, 32.0, 30.7, 24.2, 22.8, 14.2, 11.9; HRMS (ESI) m/z calcd. for $C_{26}H_{26}N_2Na$ $[M+Na]^+$: 389.1988, found: 389.1996.

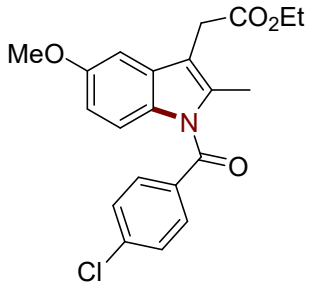


6,7,8,9-Tetrahydro-5*H*-3,9'-bicarbazole (59): yellow foam; 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.88 (s, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.41-7.34 (m, 4H), 7.28 (dd, *J* = 14.4, 1.4 Hz, 1H), 7.27 (m, 1H), 7.23 (dd, *J* = 8.4, 2.0 Hz, 1H), 2.80 (t, *J* = 6.0 Hz, 2H), 2.71 (t, *J* = 6.0 Hz, 2H), 2.00-1.94 (m, 2H), 1.93-1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 136.0, 134.9, 129.3, 128.8, 125.8, 123.0, 120.8, 120.2, 119.4, 117.1, 111.4,

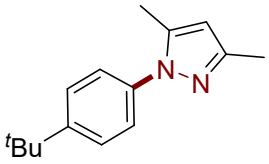
110.8, 110.1, 23.4, 23.3, 23.2, 21.0; HRMS (ESI) m/z calcd. for $C_{24}H_{20}N_2Na$ $[M+Na]^+$: 359.1519, found: 359.1525.



Ethyl 2-(5-(9*H*-carbazol-9-yl)-2-methyl-1*H*-indol-3-yl)acetate (60): yellow oil; 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.7 Hz, 2H), 8.07 (s, 1H), 7.68 (d, *J* = 1.7 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.42-7.35 (m, 4H), 7.29-7.26 (m, 2H), 7.23 (dd, *J* = 8.2, 1.9 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 2H), 2.48 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 142.0, 134.6, 134.4, 129.7, 129.5, 125.8, 123.1, 120.9, 120.3, 119.5, 117.3, 111.5, 110.1, 105.2, 60.1, 30.5, 14.3, 11.9; HRMS (ESI) m/z calcd. for $C_{25}H_{22}N_2NaO_2$ $[M+Na]^+$: 405.1573, found: 405.1573.

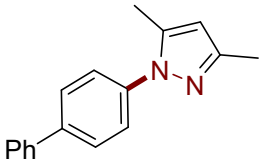


Ethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (62)[9]: yellow soild; 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.63 (m, 2H), 7.49-7.44 (m, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.65 (s, 2H), 2.38 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 168.42, 156.2, 139.4, 136.0, 134.1, 131.3, 130.9, 130.8, 129.2, 115.1, 112.8, 111.8, 101.5, 61.1, 55.8, 30.6, 14.4, 13.5; HRMS (ESI) m/z calcd. for $C_{21}H_{20}ClNNaO_4$ $[M+Na]^+$: 408.0973, found: 408.0971.

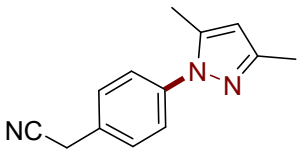


1-(4-(Tert-butyl)phenyl)-3,5-dimethyl-1*H*-pyrazole (63)[10]: yellow oil; 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.35-7.31 (m, 2H), 5.97 (s, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.8, 139.4, 137.5, 126.0, 124.5, 106.7, 34.7, 31.5,

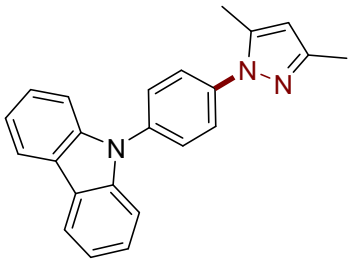
13.6, 12.4; HRMS (ESI) m/z calcd. for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1699, found: 229.1700.



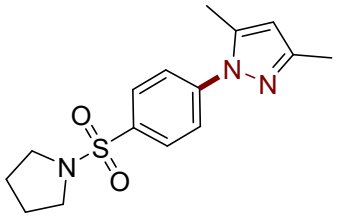
1-([1,1'-Biphenyl]-4-yl)-3,5-dimethyl-1*H*-pyrazole (64)[11]: yellow solid; 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.63-7.61 (m, 2H), 7.52-7.44 (m, 4H), 7.39-7.35 (m, 1H), 6.02 (s, 1H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 140.4 140.2, 139.5, 139.3, 129.0, 127.8, 127.7, 127.2, 125.0, 107.2, 13.7, 12.6; HRMS (ESI) m/z calcd. for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386, found: 249.1389.



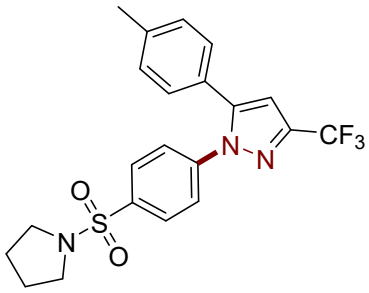
2-(4-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenyl)acetonitrile (65): yellow oil; 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.42-7.40 (m, 2H), 6.01 (s, 1H), 3.80 (s, 2H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 139.9, 139.6, 128.9, 128.7, 125.2, 117.7, 107.5, 23.3, 13.5, 12.5; HRMS (ESI) m/z calcd. for $C_{13}H_{14}N_3$ $[M+H]^+$: 212.1182, found: 212.1183.



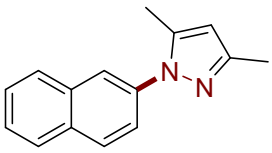
9-(4-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenyl)-9*H*-carbazole (66): yellow solid; 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.72-7.65 (m, 4H), 7.44-7.41 (m, 4H), 7.33-7.29 (m, 2H), 6.07 (s, 1H), 2.44 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 140.9, 139.6, 139.0, 136.6, 127.8, 126.2, 126.0, 123.6, 120.5, 120.3, 109.8, 107.6, 13.7, 12.7; HRMS (ESI) m/z calcd. for $C_{23}H_{20}N_3$ $[M+H]^+$: 338.1652, found: 338.1654.



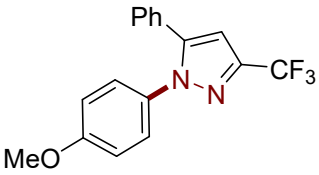
3,5-Dimethyl-1-(4-(pyrrolidin-1-ylsulfonyl)phenyl)-1*H*-pyrazole (67): yellow solid; 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.87 (m, 2H), 7.63-7.60 (m, 2H), 6.03 (s, 1H), 3.25-3.21 (m, 4H), 2.37 (s, 3H), 2.27 (s, 3H), 1.77-1.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 143.4, 139.8, 134.9, 128.6, 124.2, 108.6, 48.1, 25.3, 13.6, 12.9; HRMS (ESI) m/z calcd. For $C_{15}H_{20}N_3O_2S$ $[M+H]^+$: 306.1271, found: 306.1273.



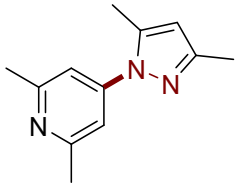
1-(4-(Pyrrolidin-1-ylsulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (68)[12]: yellow solid; 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.49-7.47 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.74 (s, 1H), 3.24-3.20 (m, 4H), 2.37 (s, 3H), 1.78-1.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 144.2 (q, *J* = 38.3 Hz), 142.6, 139.9, 136.7, 132.7, 129.8, 129.1, 128.8, 128.5, 127.6, 125.7, 121.2 (q, *J* = 267.6 Hz), 106.3, 48.1, 25.4, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.44 (s); HRMS (ESI) m/z calcd. For $C_{21}H_{20}F_3N_3NaO_2S$ $[M+Na]^+$: 458.1121, found: 458.1117.



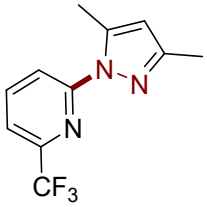
3,5-Dimethyl-1-(naphthalen-2-yl)-1*H*-pyrazole (69)[10]: yellow solid; 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.7 Hz, 1H), 7.89-7.86 (m, 3H), 7.61 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.55-7.49 (m, 2H), 6.04 (s, 1H), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 139.8, 137.6, 133.4, 132.3, 129.1, 128.2, 127.9, 126.9, 126.4, 123.5, 122.7, 107.2, 13.7, 12.7; HRMS (ESI) m/z calcd. for$C_{15}H_{15}N_2$ $[M+H]^+$: 223.1230, found: 223.1229.



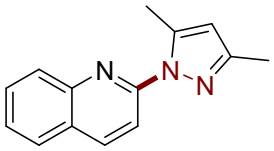
1-(4-Methoxyphenyl)-5-phenyl-3-(trifluoromethyl)-1*H*-pyrazole (70)[13]**:** yellow solid; 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 3H), 7.23-7.21 (m, 4H), 6.89-6.84 (m, 2H), 6.73 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 144.7, 143.2 (q, *J* = 38.0 Hz), 132.6, 129.4, 129.0, 128.9, 128.8, 127.0, 122.8 (q, *J* = 267.1 Hz), 114.4, 105.30 (q, *J* = 1.9 Hz), 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.14 (s); HRMS (ESI) m/z calcd. for $C_{17}H_{13}F_3N_2NaO$ $[M+Na]^+$: 341.0872, found: 341.0881.



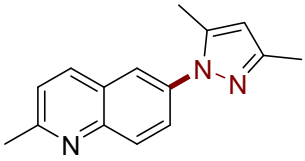
4-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2,6-dimethylpyridine (71): yellow oil; 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 6.02 (s, 1H), 2.56 (s, 6H), 2.41 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 150.3, 147.4, 139.8, 114.0, 109.0, 24.6, 13.6, 13.2; HRMS (ESI) m/z calcd. for $C_{12}H_{16}N_3$ $[M+H]^+$: 202.1339, found: 202.1342.



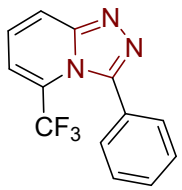
2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-6-(trifluoromethyl)pyridine (72): yellow solid; 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 6.01 (s, 1H), 2.69 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 150.9, 146.1 (q, *J* = 35.1 Hz), 142.7, 139.6, 122.8 (q, *J* = 272.3 Hz), 117.8, 116.6 (q, *J* = 2.8 Hz), 110.1, 15.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.33 (s); HRMS (ESI) m/z calcd. for $C_{11}H_{10}F_3N_3Na$ $[M+Na]^+$: 264.0179, found: 264.0720.



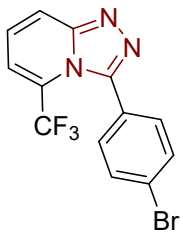
2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)quinolone (73): yellow solid; 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 6.05 (s, 1H), 2.82 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 150.2, 146.5, 142.4, 138.4, 129.9, 128.7, 127.6, 126.4, 125.9, 115.2, 109.7, 15.2, 13.8; HRMS (ESI) m/z calcd. for $C_{14}H_{13}N_3Na$ $[M+Na]^+$: 246.1002, found: 246.1003.



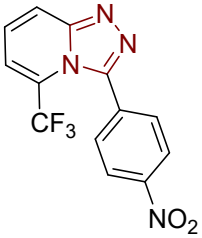
6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-methylquinoline (74): yellow oil; 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 7.83 (d, *J* = 2.2 Hz, 1H), 7.79 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 1H), 2.77 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 149.6, 146.7, 139.8, 137.3, 136.3, 129.7, 126.7, 126.5, 122.9, 122.2, 107.5, 25.5, 13.7, 12.7; HRMS (ESI) m/z calcd. for $C_{15}H_{15}N_3Na$ $[M+Na]^+$: 260.1158, found: 260.1159.



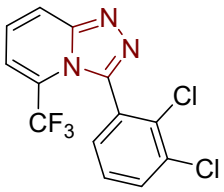
3-Phenyl-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine (75): white solid; 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.03 (m, 1H), 7.57-7.52 (m, 1H), 7.49-7.46 (m, 4H), 7.37-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 147.5, 131.0 (q, *J* = 1.9 Hz), 130.5, 128.1, 127.6 (q, *J* = 1.7 Hz), 125.3 (q, *J* = 36.8 Hz), 125.2, 121.5, 119.6 (q, *J* = 271.0 Hz), 116.20 (q, *J* = 5.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.12 (s); HRMS (ESI) m/z calcd. for $C_{13}H_8F_3N_3Na$ $[M+Na]^+$: 286.0563, found: 286.0565.



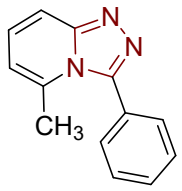
3-(4-Bromophenyl)-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine (76): white solid; 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.37-7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 146.4, 132.6 (q, *J* = 1.9 Hz), 131.4, 126.6 (q, *J* = 1.5 Hz), 152.3, 125.2, 125.1 (q, *J* = 36.9 Hz), 121.5, 119.6 (q, *J* = 271.2 Hz), 116.3 (q, *J* = 5.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.03 (s); HRMS (ESI) m/z calcd. for $C_{13}H_7BrF_3N_3Na$ $[M+Na]^+$: 363.9668, found: 363.9665.



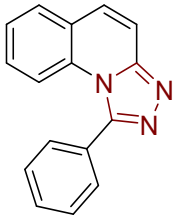
3-(4-Nitrophenyl)-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine (77): yellow solid; 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.6 Hz, 2H), 8.12-8.09 (m, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.44-7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 149.2, 145.3, 134.3 (q, *J* = 1.6 Hz), 132.3 (q, *J* = 2.0 Hz), 125.8, 125.0 (q, *J* = 37.0 Hz), 123.3, 121.7, 119.6 (q, *J* = 271.0 Hz), 116.7 (q, *J* = 5.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.16 (s); HRMS (ESI) m/z calcd. for $C_{13}H_7F_3N_4NaO_2$ $[M+Na]^+$: 331.0413, found: 331.0411.



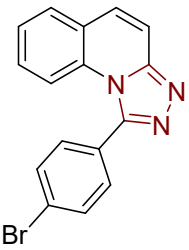
3-(2,3-Dichlorophenyl)-5-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine (78): yellow solid; 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 1H), 7.67 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.45-7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 144.2, 135.1, 133.4, 132.9, 131.5 (q, *J* = 2.0 Hz), 129.3 (q, *J* = 1.2 Hz), 127.1, 125.6, 125.0 (q, *J* = 37.2 Hz), 121.6, 119.5 (q, *J* = 271.1 Hz), 116.42 (q, *J* = 5.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28 (s). HRMS (ESI) m/z calcd. for $C_{13}H_6Cl_2F_3N_3Na$ $[M+Na]^+$: 353.9783, found: 353.9780.



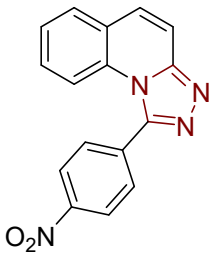
5-Methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (79)[14]**:** yellow solid; 44%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 9.2 Hz, 1H), 7.58-7.53 (m, 3H), 7.50-7.46 (m, 2H), 7.18 (dd, *J* = 9.2, 6.6 Hz, 1H), 6.53 (d, *J* = 6.6 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 147.3, 135.0, 131.2, 130.1, 129.6, 128.0, 127.5, 114.7, 114.4, 21.0; HRMS (ESI) m/z calcd. for $C_{13}H_{11}N_3Na$ $[M+Na]^+$: 232.0845, found: 232.0846.



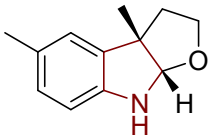
1-Phenyl-[1,2,4]triazolo[4,3-a]quinolone (80)[15]**:** yellow solid; 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.71-7.68 (m, 3H), 7.64-7.54 (m, 5H), 7.47-7.43 (m, 1H), 7.36-7.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.1, 131.9, 130.6, 130.0, 129.8, 129.6, 129.4, 129.2, 129.0, 126.2, 124.7, 116.8, 115.1; HRMS (ESI) m/z calcd. for $C_{16}H_{11}N_3Na$ $[M+Na]^+$: 268.0845, found: 268.0842.



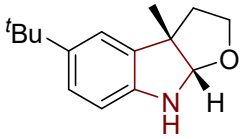
1-(4-Bromophenyl)-[1,2,4]triazolo[4,3-a]quinolone (81)[16]**:** yellow solid; 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.76-7.74 (m, 2H), 7.71 (d, *J* = 9.5 Hz, 1H), 7.61-7.56 (m, 4H), 7.51-7.47 (m, 1H), 7.43-7.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 148.1, 132.5, 131.8, 131.6, 130.0, 129.6, 129.2, 128.5, 126.4, 125.2, 124.7, 116.7, 115.1; HRMS (ESI) m/z calcd. for $C_{16}H_{10}BrN_3Na$ $[M+Na]^+$: 345.9950, found: 345.9949.



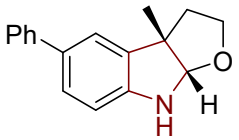
1-(4-Nitrophenyl)-[1,2,4]triazolo[4,3-a]quinolone (82): yellow solid; 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50-8.46 (m, 2H), 7.98-7.94 (m, 2H), 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.76 (d, *J* = 9.5 Hz, 1H), 7.67 (d, *J* = 9.5 Hz, 1H), 7.55-7.51 (m, 2H), 7.45-7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.1, 147.2, 135.9, 131.5, 131.1, 130.5, 129.9, 129.4, 126.8, 124.9, 124.3, 116.6, 115.1; HRMS (ESI) m/z calcd. for $C_{16}H_{10}N_4NaO_2$ $[M+Na]^+$: 313.0696, found: 313.0694.



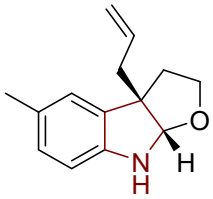
(3aS,8aS)-3a,5-Dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-b]indole (83)[17]**:** yellow oil; 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 5.26 (s, 1H), 4.45 (bs, 1H), 3.96-3.92 (m, 1H), 3.60-3.52 (m, 1H), 2.27 (s, 3H), 2.20-2.13 (m, 1H), 2.12-2.02 (m, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 134.5, 128.5, 128.4, 123.8, 108.5, 100.2, 67.5, 54.0, 41.6, 24.9, 20.1; HRMS (ESI) m/z calcd. for $C_{12}H_{15}NNaO$ $[M+Na]^+$: 212.1046, found: 212.1046.



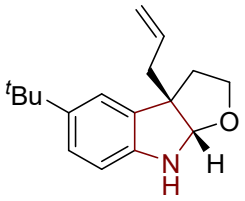
(3aS,8aS)-5-(Tert-butyl)-3a-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-b]indole (84): yellow oil; 35%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.07 (m, 2H), 6.53 (d, *J* = 8.0 Hz, 1H), 5.29 (s, 1H), 4.48 (bs, 1H), 3.97-3.93 (m, 1H), 3.63-3.55 (m, 1H), 2.21-2.15 (m, 1H), 2.13-2.03 (m, 1H), 1.48, (s, 3 H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 142.4, 134.1, 124.8, 120.0, 108.0, 100.4, 67.5, 54.2, 41.8, 34.4, 31.9, 25.1; HRMS (ESI) m/z calcd. for $C_{15}H_{21}NNaO$ $[M+Na]^+$: 254.1515, found: 254.1514.



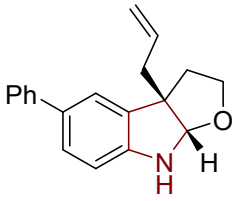
(3aS,8aS)-3a-Methyl-5-phenyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-b]indole (85): yellow oil; 42%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.32-7.30 (m, 2H), 7.29-7.26 (m, 1H), 6.66 (d, *J* = 8.6 Hz, 1H), 5.33 (s, 1H), 4.64 (bs, 1H), 3.98 (t, *J* = 7.5 Hz, 1H), 3.66-3.58 (m, 1H), 2.27-2.20 (m, 1H), 2.17-2.07 (m, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 141.2, 134.9, 132.5, 128.8, 127.2, 126.6, 126.3, 122.0, 108.5, 100.1, 67.6, 54.1, 41.7, 25.0; HRMS (ESI) m/z calcd. for $C_{17}H_{17}NNaO$ $[M+Na]^+$: 274.1202, found: 274.1205.



(3aS,8aS)-3a-Allyl-5-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-b]indole (86): yellow oil; 47%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.75-5.65 (m, 1H), 5.35 (s, 1H), 5.11-5.04 (m, 2H), 4.43 (bs, 1H), 3.96-3.92 (m, 1H), 3.60-3.52 (m, 1H), 2.64-2.57 (m, 1H), 2.52-2.44 (m, 1H), 2.27 (s, 3H), 2.18-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 134.4, 132.6, 128.6, 128.3, 124.3, 118.0, 108.4, 97.9, 67.2, 57.7, 42.5 39.7, 21.0; HRMS (ESI) m/z calcd. for $C_{14}H_{17}NNaO$ $[M+Na]^+$: 238.1202, found: 238.1202.



(3aS,8aS)-3a-allyl-5-(Tert-butyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (87): yellow oil; 33%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 11.3 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.78-5.67 (m, 1H), 5.37 (s, 1H), 5.10-5.06 (m, 2H), 4.45 (bs, 1H), 3.95 (t, *J* = 7.1 Hz, 1H), 3.63-3.54 (m, 1H), 2.64-2.56 (m, 1H), 2.52-2.44 (m, 1H), 2.19-2.09 (m, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 142.2, 134.5, 132.3, 124.9, 120.7, 118.1, 107.9, 98.2, 67.2, 57.9, 42.7, 39.6, 34.4, 31.9; HRMS (ESI) m/z calcd. for $C_{17}H_{23}NNaO$ $[M+Na]^+$: 280.1672, found: 280.1669.



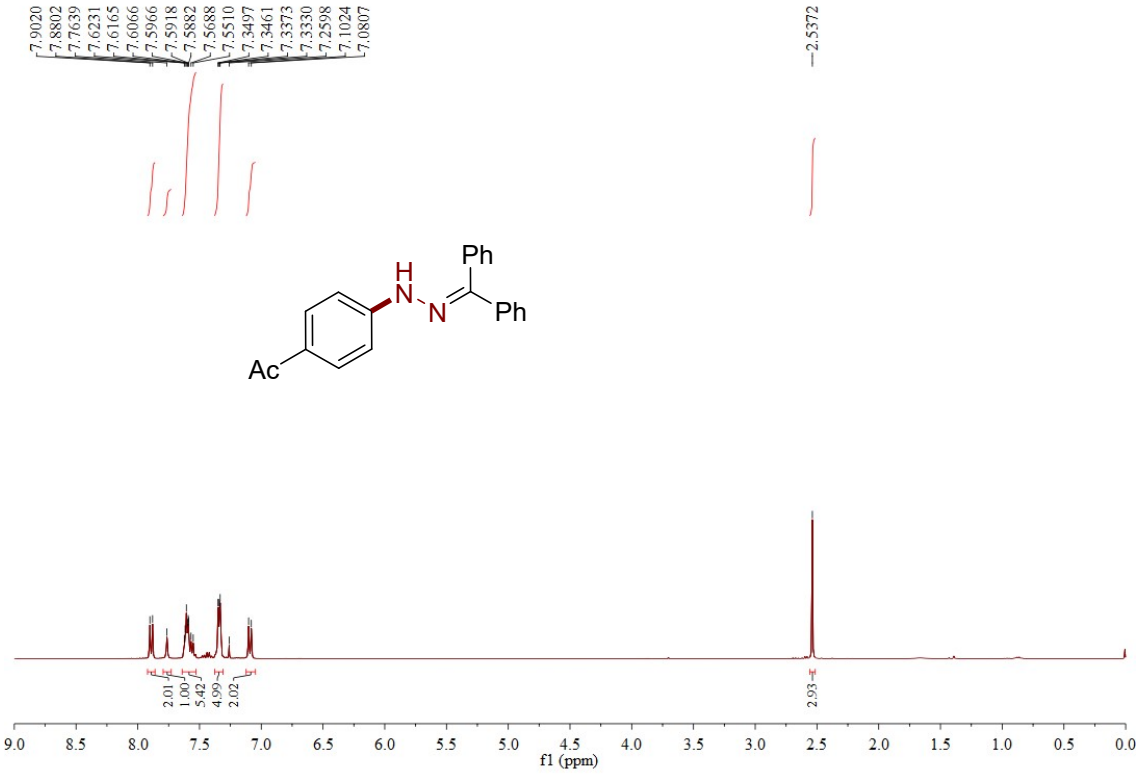
(3aS,8aS)-3a-Allyl-5-phenyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-b]indole (88): yellow oil; 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33-7.31 (m, 2H), 7.29-7.25 (m, 1H), 6.65 (d, *J* = 5.7 Hz, 1H), 5.81-5.71 (m, 1H), 5.42 (s, 1H), 5.16-5.06 (m, 2H), 4.64 (bs, 1H), 4.01-3.97 (m, 1H), 3.65-3.58 (m, 1H), 2.71-2.63 (m, 1H), 2.57-2.50 (m, 1H), 2.21-2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 141.8, 134.3, 133.0, 132.3, 128.8, 127.4, 126.6, 126.3, 122.6, 118.4, 108.5, 97.9, 67.3, 57.8, 42.6, 39.8; HRMS (ESI) m/z calcd. for $C_{19}H_{19}NNaO$ $[M+Na]^+$: 300.1359, found: 300.1358.

7. References

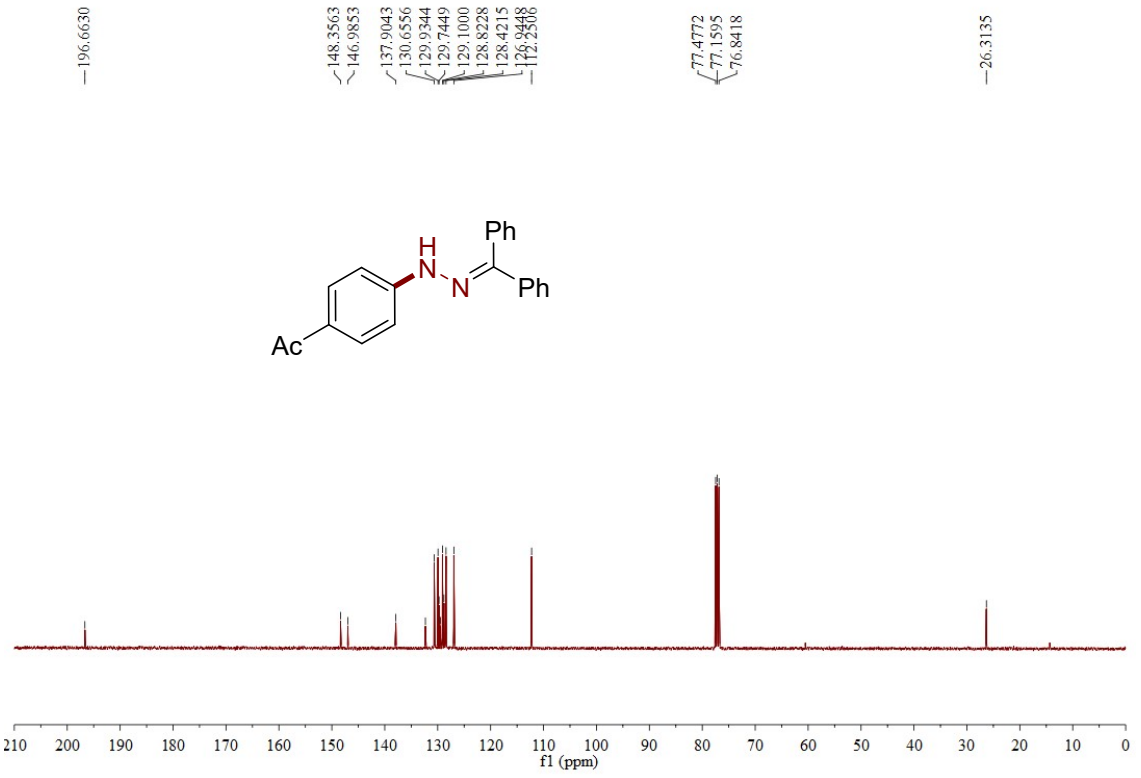
1. 1 a) B. J. Shields, B. Kudisch, G. D. Scholes and A. G. Doyle, Long-Lived Charge-Transfer States of Nickel(II) Aryl Halide Complexes Facilitate Bimolecular Photoinduced Electron Transfer, *J. Am. Chem. Soc.*, 2018, **140**, 3035; b) L. Yang, H.-H. Lu, C.-H. Lai, G. Li, W. Zhang, R. Cao, F. Liu, C. Wang, J. Xiao and D. Xue, Light-Promoted Nickel Catalysis: Etherification of Aryl Electrophiles with Alcohols Catalyzed by a Ni^{II}-Aryl Complex, *Angew. Chem. Int. Ed.*, 2020, **59**, 12714; c) G. Li, L. Yang, J.-J. Liu, W. Zhang, R. Cao, C. Wang, Z. Zhang, J. Xiao and D. Xue. Light-Promoted C–N Coupling of Aryl Halides with Nitroarenes, *Angew. Chem. Int. Ed.*, 2021, **60**, 5230.
2. W. Wu, X. H. Fan, L. P. Zhang and L. M. Yang, Nickel-catalyzed N-arylation of benzophenone hydrazone with bromoarenes, *RSC Adv.*, 2014, **4**, 3364.
3. Q. Shen, S. Shekhar, J. P. Stambuli and J. F. Hartwig, Highly Reactive, General, and Long-Lived Catalysts for Coupling Heteroaryl and Aryl Chlorides with Primary Nitrogen Nucleophiles, *Angew. Chem. Int. Ed.*, 2005, **44**, 1371.
4. S. Tassini, D. Castagnolo, N. Scalacci, M. Kissova, J. I. Armijos-Rivera, F. Giagnorio, G. Maga, G. Costantino, E. Crespan and M. Radi, A multicomponent pharmacophore fragment-decoration approach to identify selective LRRK2-targeting probes, *Med. Chem. Commun.*, 2016, **7**, 484.
5. B. A. Haag, Z.-G. Zhang, J.-S. Li and P. Knochel, Fischer Indole Synthesis with Organozinc Reagents, *Angew. Chem. Int. Ed.,* 2010, **49**, 9513.
6. S. E. Kassab, M. A. Khedr, H. I. Ali and M. M. Abdalla, Discovery of new indomethacin-based analogs with potentially selective cyclooxygenase-2 inhibition and observed diminishing to PGE2 activities, *Eur. J. Med. Chem.*, 2017, **141**, 306.
7. Y.-K. Lim and C.-G. Cho, Expedient synthesis of indoles from *N*-Boc arylhydrazines, *Tetrahedron Lett.*, 2004, **45**, 1857.
8. M. Tursky, L. L. R. Lorentz-Petersen, L. B. Olsen and R. Madsen, Iridium- and ruthenium-catalysed synthesis of 2,3-disubstituted indoles from anilines and vicinal diols, *Org. Biomol. Chem.*, 2010, **8**, 5576.

9. D. A. Vargas, A. Tinoco, V. Tyagi and R. Fasan, Myoglobin-Catalyzed C−H Functionalization of Unprotected Indoles, *Angew. Chem. Int. Ed.*, 2018, **57**, 9911.
10. J. Y. Wang, K. Choi, S. J. Zuend, K. Borate, H. Shinde, R. Goetz and J. F. Hartwig, Cross-Coupling between Hydrazine and Aryl Halides with Hydroxide Base at Low Loadings of Palladium by Rate-Determining Deprotonation of Bound Hydrazine, *Angew. Chem. Int. Ed.*, 2021, **133**, 403.
11. E. B. Landstrom, N. Akporji, N. R. Lee, C. M. Gabriel, F. C. Braga and B. H. Lipshutz, One-Pot Synthesis of Indoles and Pyrazoles via Pd-Catalyzed Couplings/Cyclizations Enabled by Aqueous Micellar Catalysis, *Org. Lett.*, 2020, **22**, 6543.
12. L. F. T. Novaes, J. S. K. Ho, K. Mao, K. Liu, M. Tanwar, M. Neurock, E. Villemure, J. A. Terrett and S. Lin, Exploring Electrochemical C(sp^3)–H Oxidation for the Late-Stage Methylation of Complex Molecules, *J. Am. Chem. Soc.*, 2022, **144**, 1187.
13. M.-T. Hsieh, S.-C. Kuo and H.-C. Lin, Solvent- and Transition Metal Catalyst-Dependent Regioselectivity in the [3+2] Cyclocondensation of Trifluoromethyl-α,β-ynones with Hydrazines: Switchable Access to 3- and 5-Trifluoromethylpyrazoles, *Adv. Synth. Catal.*, 2015, **357**, 683.
14. M. A. Schmidt and X. Qian, A mild synthesis of [1,2,4]triazolo[4,3-*a*]pyridines, *Tetrahedron Lett.*, 2013, **54**, 5721.
15. O. R. Thiel, M. M. Achmatowicz, A. Reichelt and R. D. Larsen, Palladium-Catalyzed Coupling of Aldehyde-Derived Hydrazones: Practical Synthesis of Triazolopyridines and Related Heterocycles, *Angew. Chem. Int. Ed.* 2010, **49**, 8395.
16. P. R. Thorve, K. Maji and B. Maji, Construction of 1,2,4-triazole-fused heterocycles *via* an amine oxidase-inspired catalyst, *Org. Chem. Front.*, 2023, **10**, 480.
17. B. W. Boal, A. W. Schammel and N. K. Garg, An Interrupted Fischer Indolization Approach toward Fused Indoline-Containing Natural Products, *Org. Lett.*, 2009, **11**, 3458.

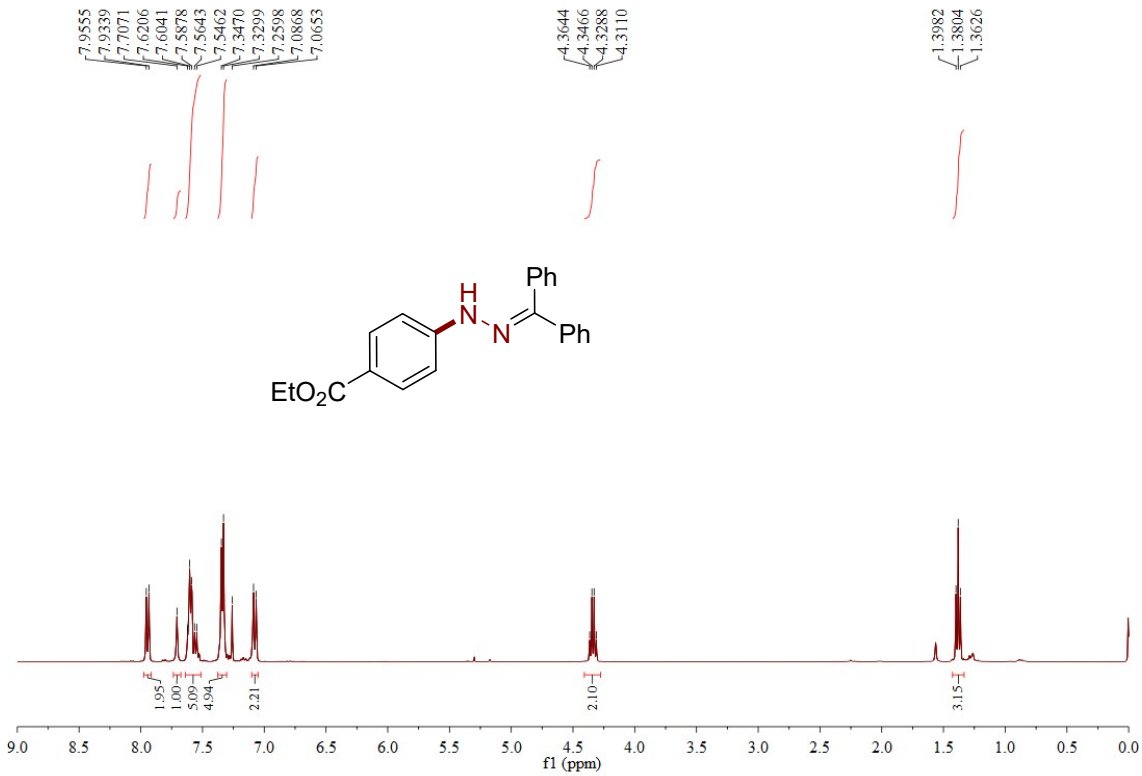
8. Copies of NMR spectra for products



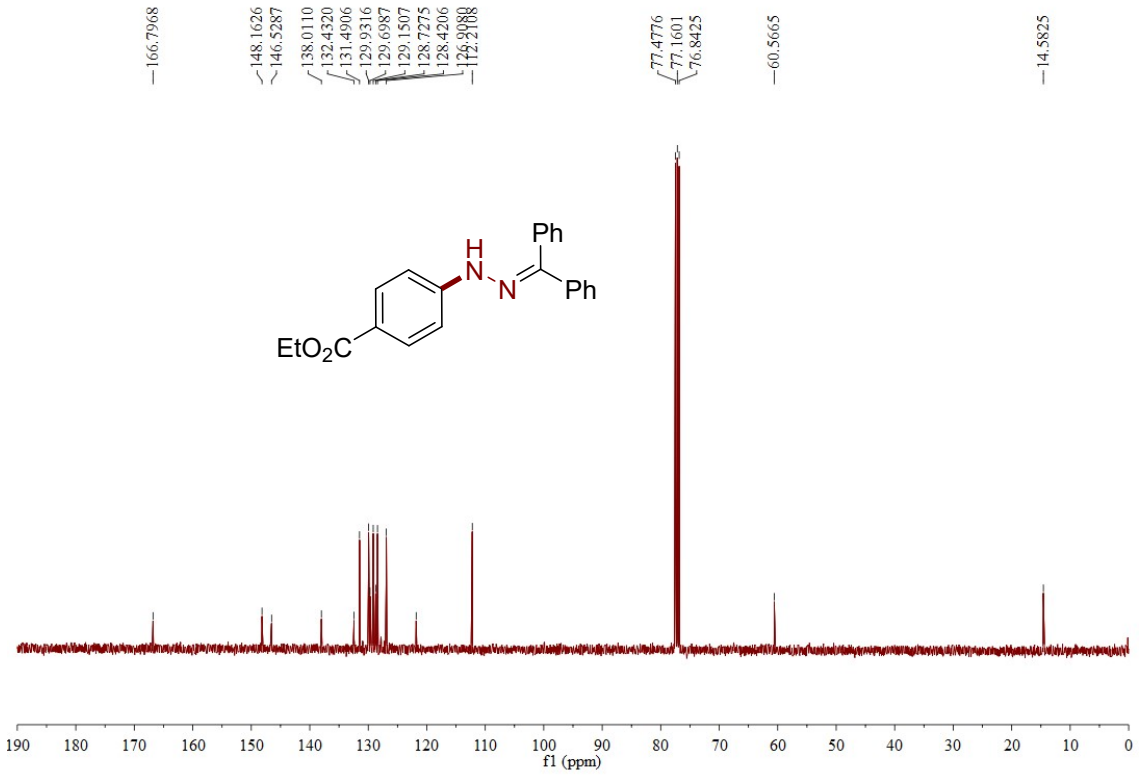
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**



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



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



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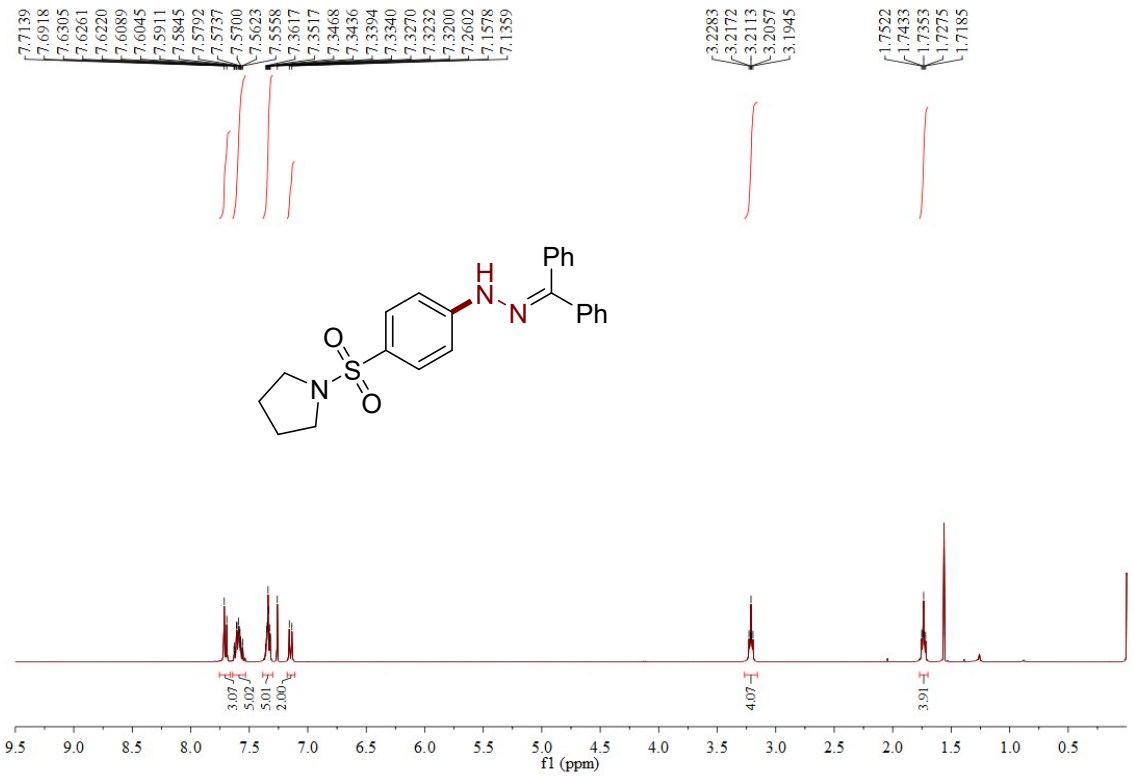
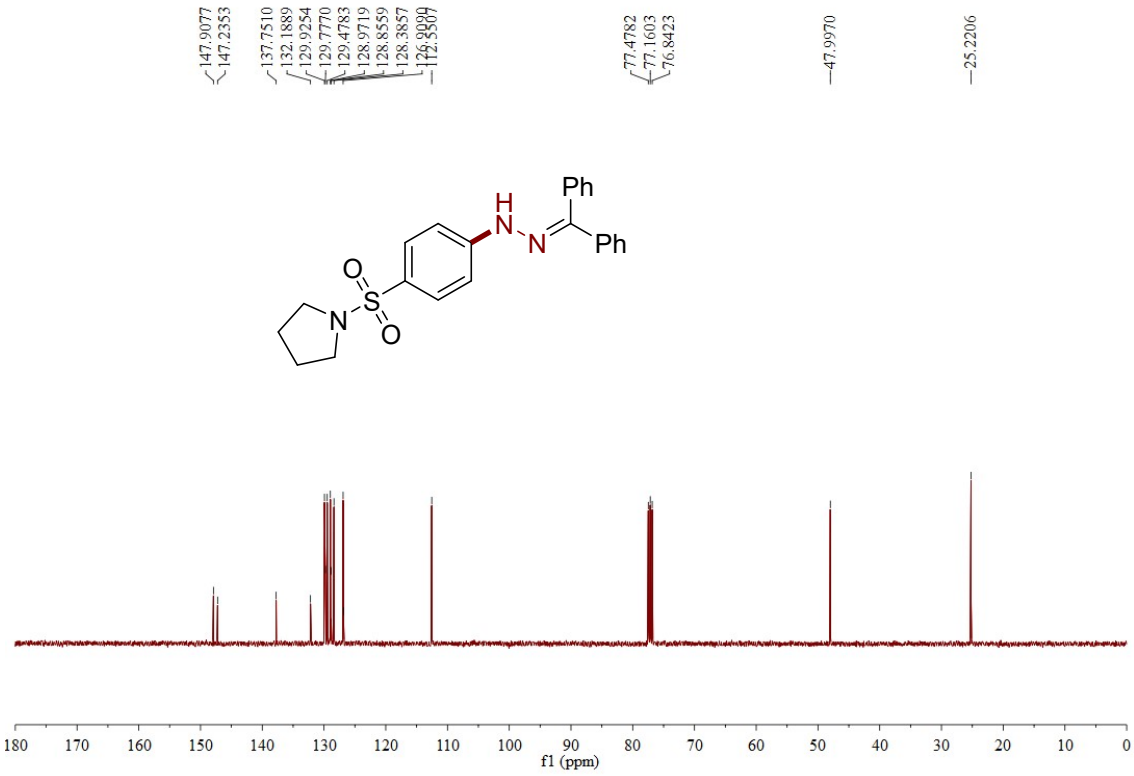
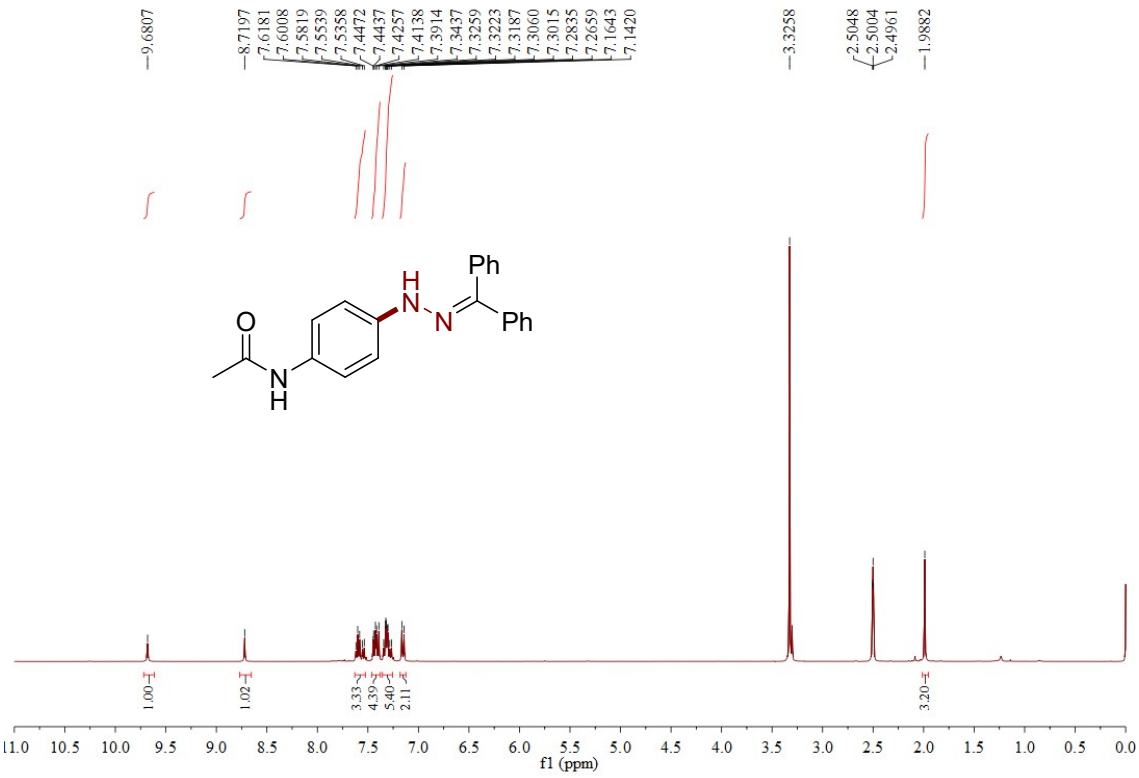


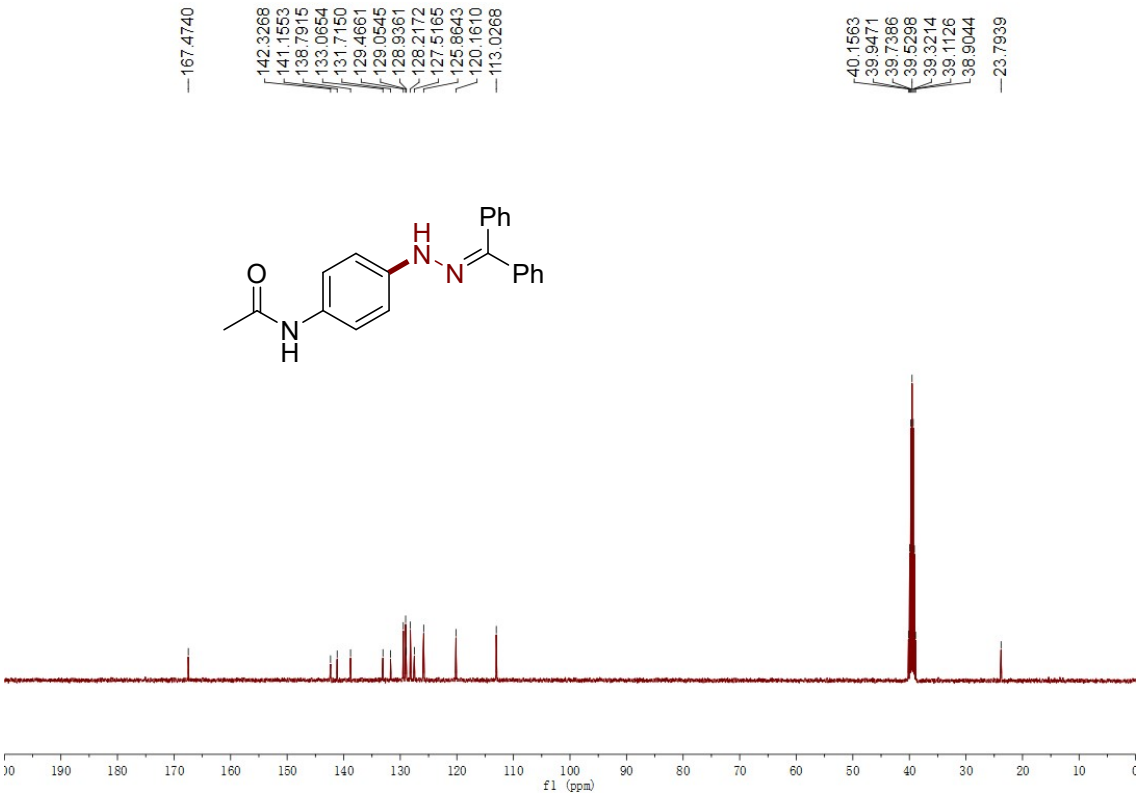
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**



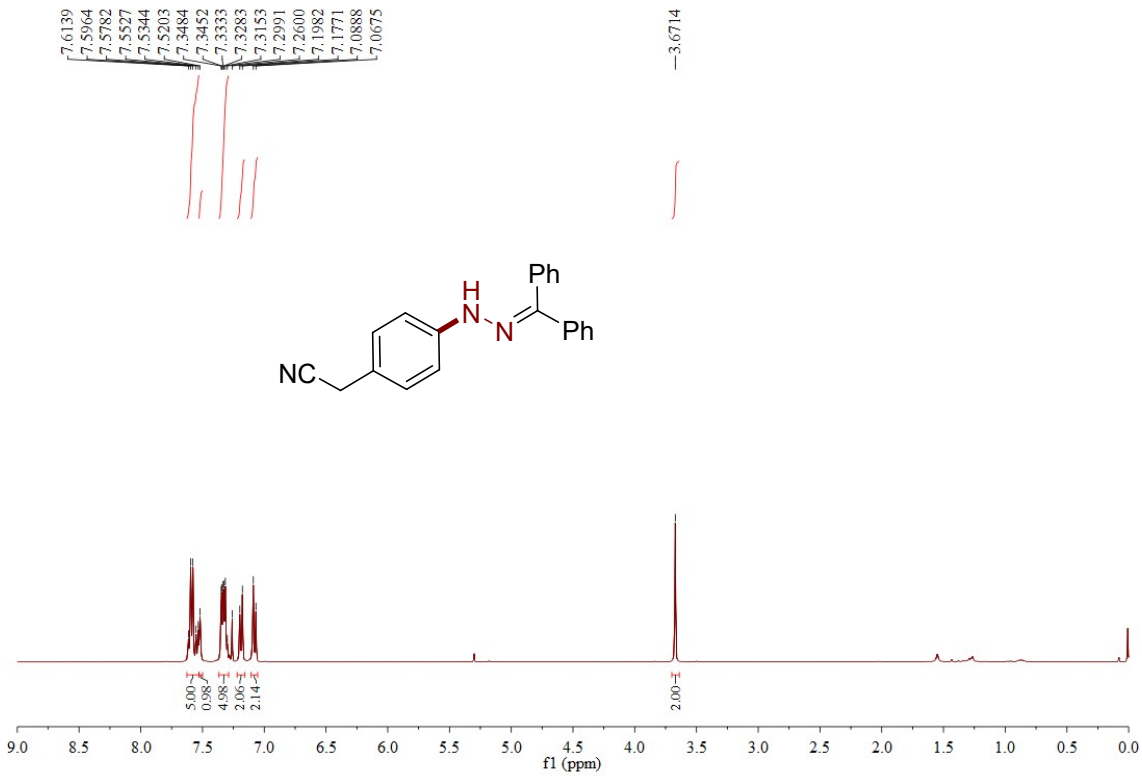
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5**



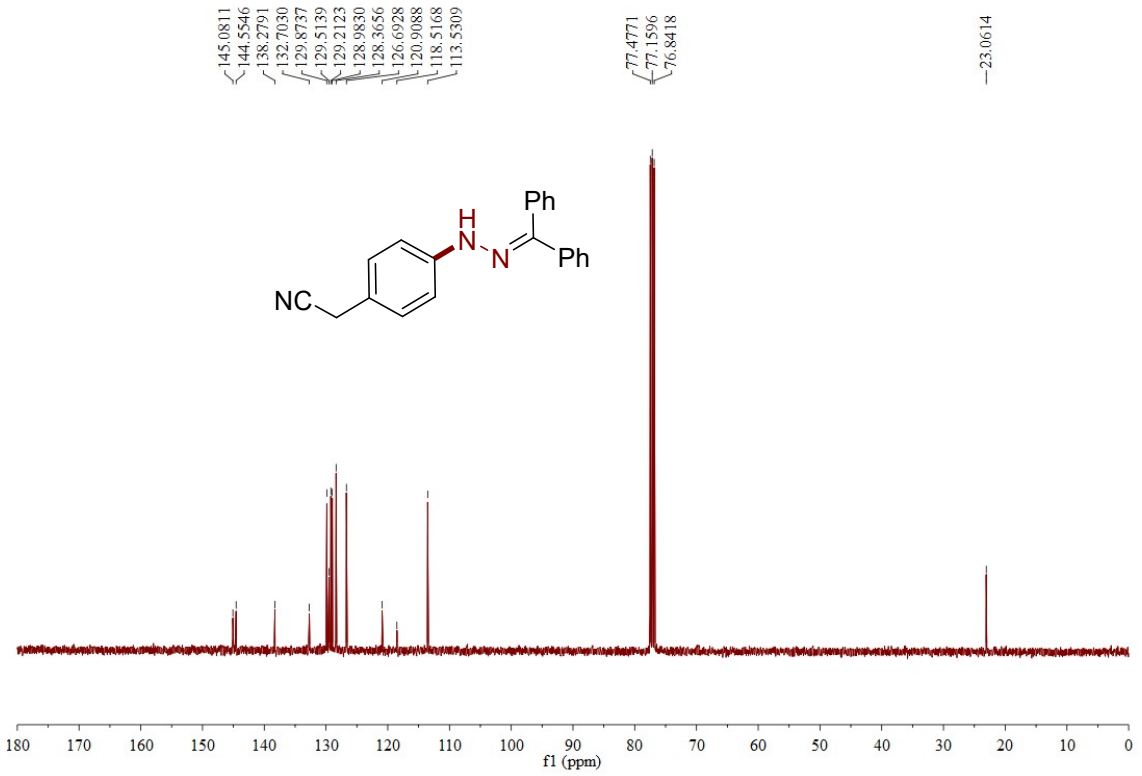
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **6**



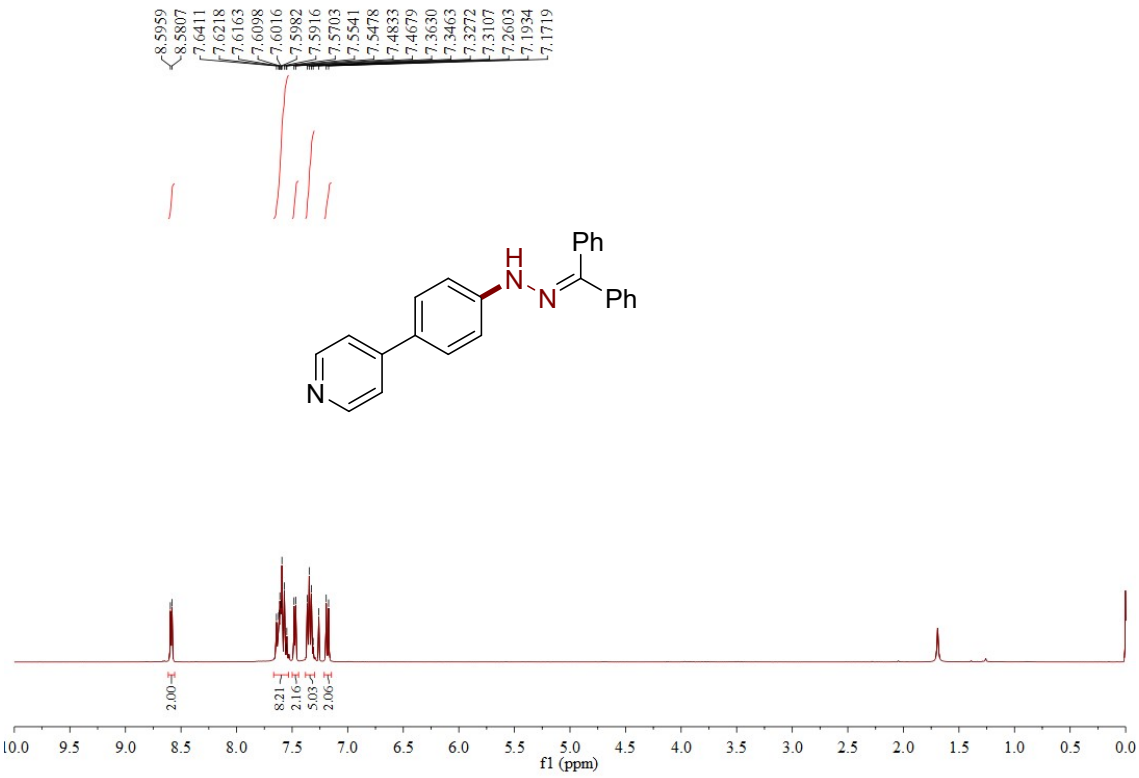
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **6**



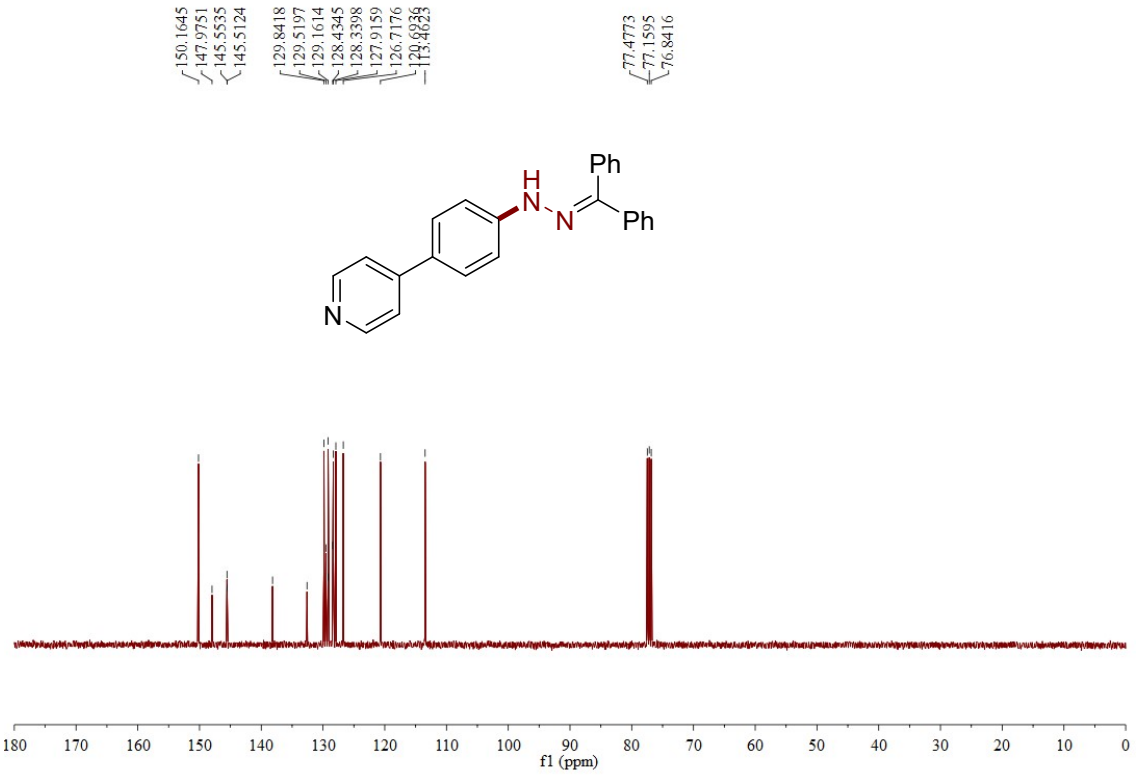
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**



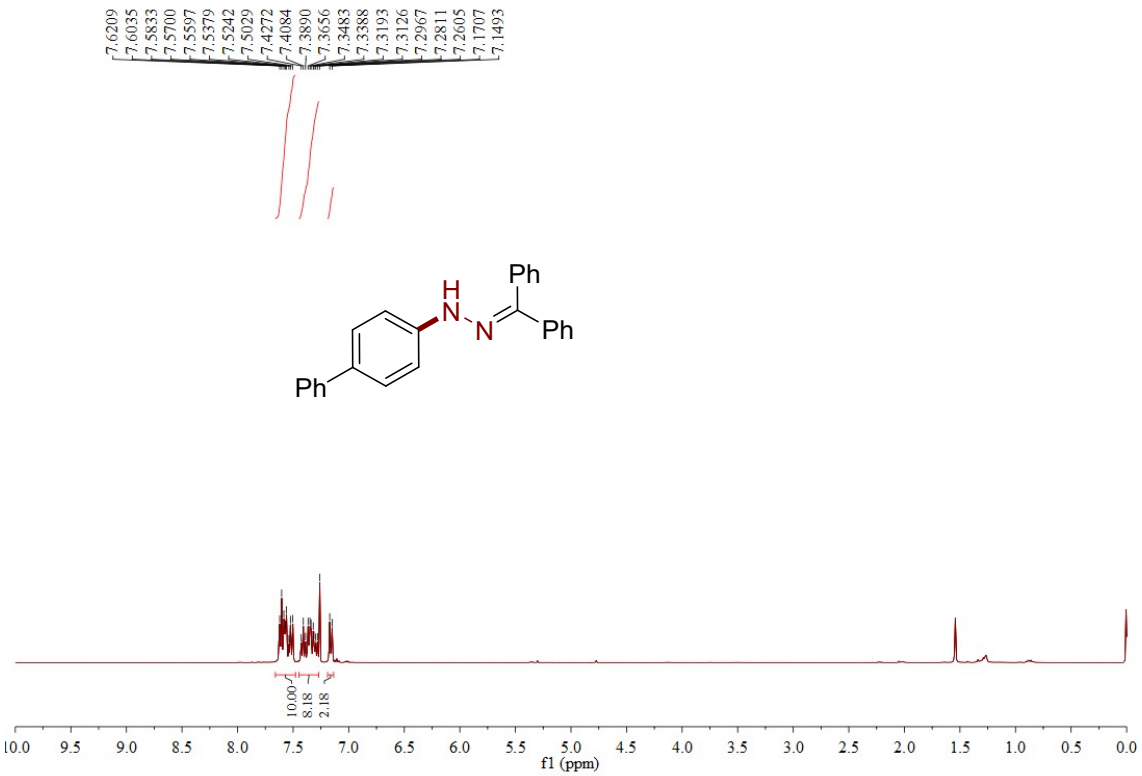
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7**



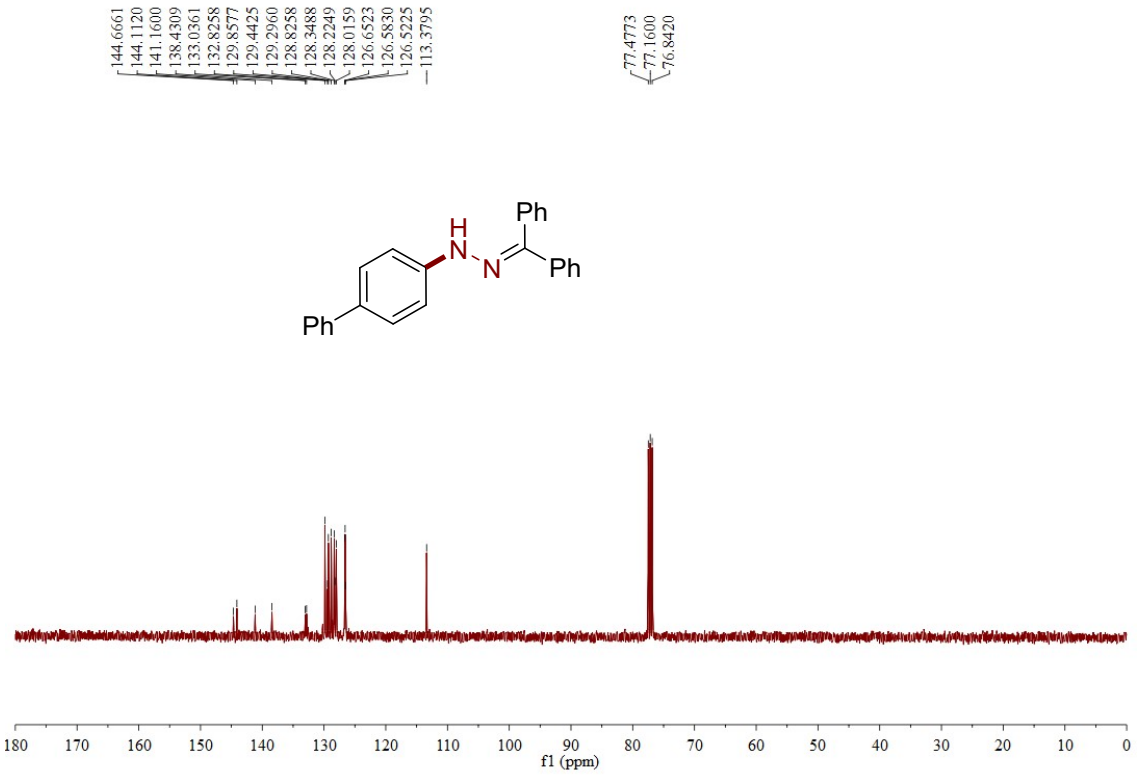
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



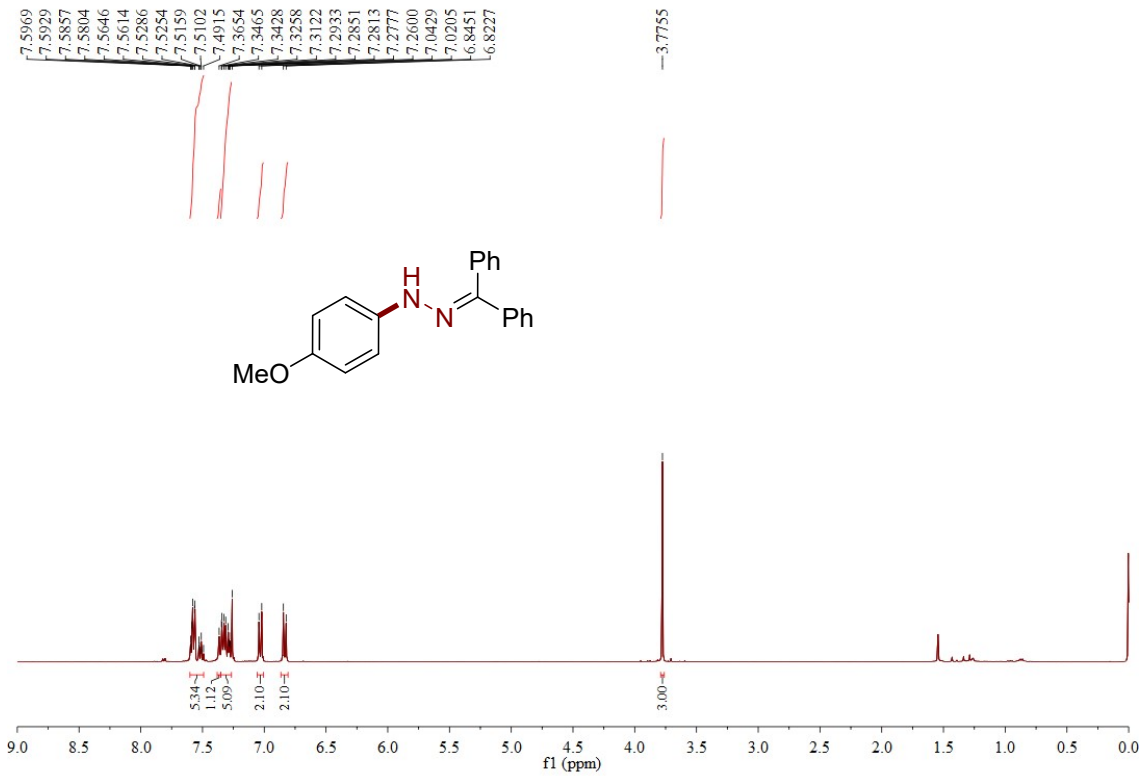
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8**



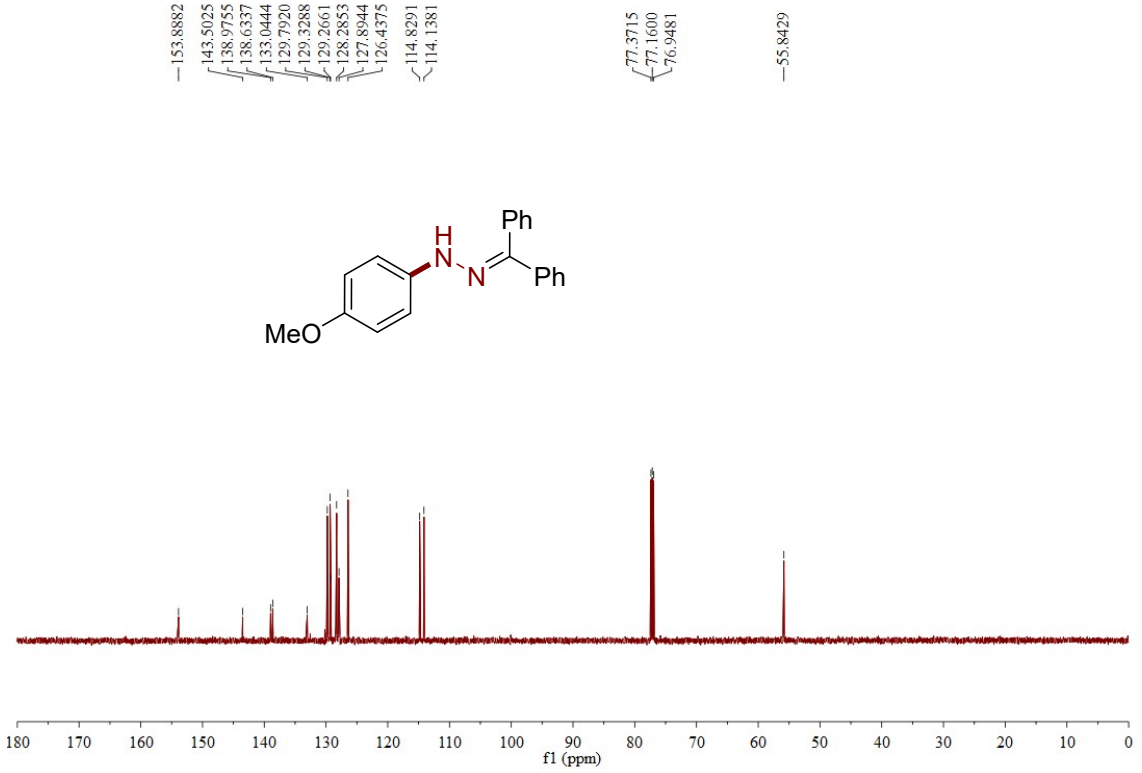
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**



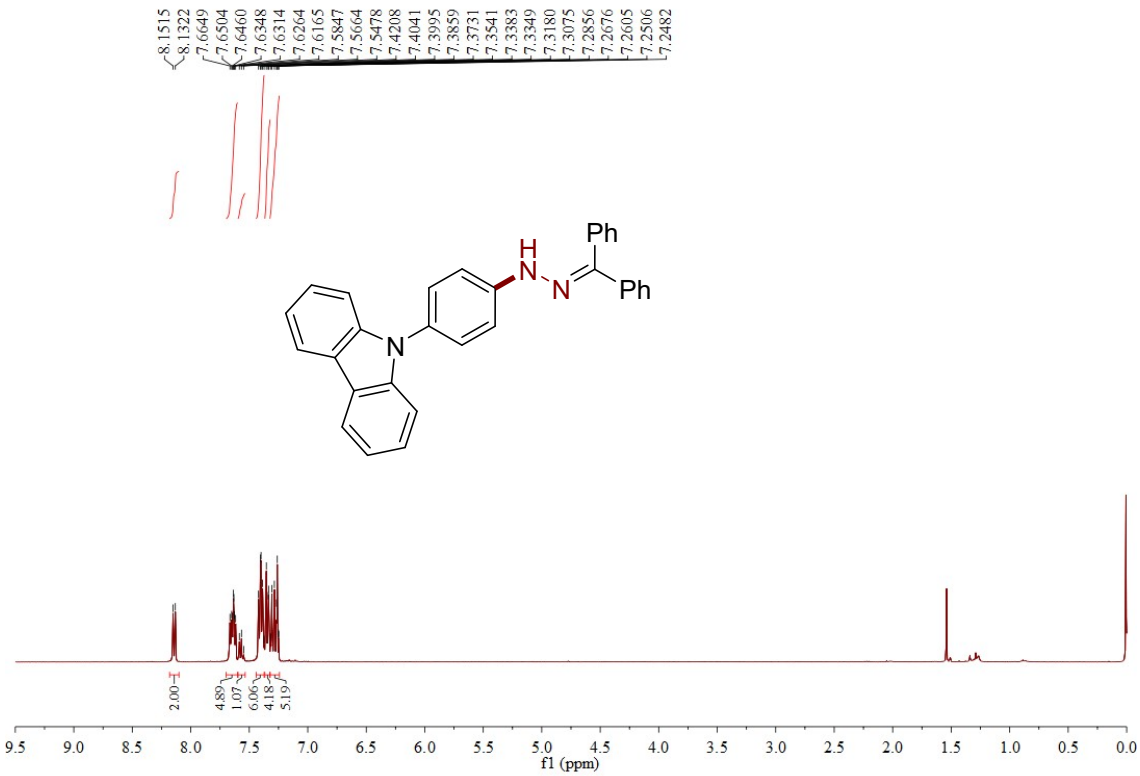
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **9**



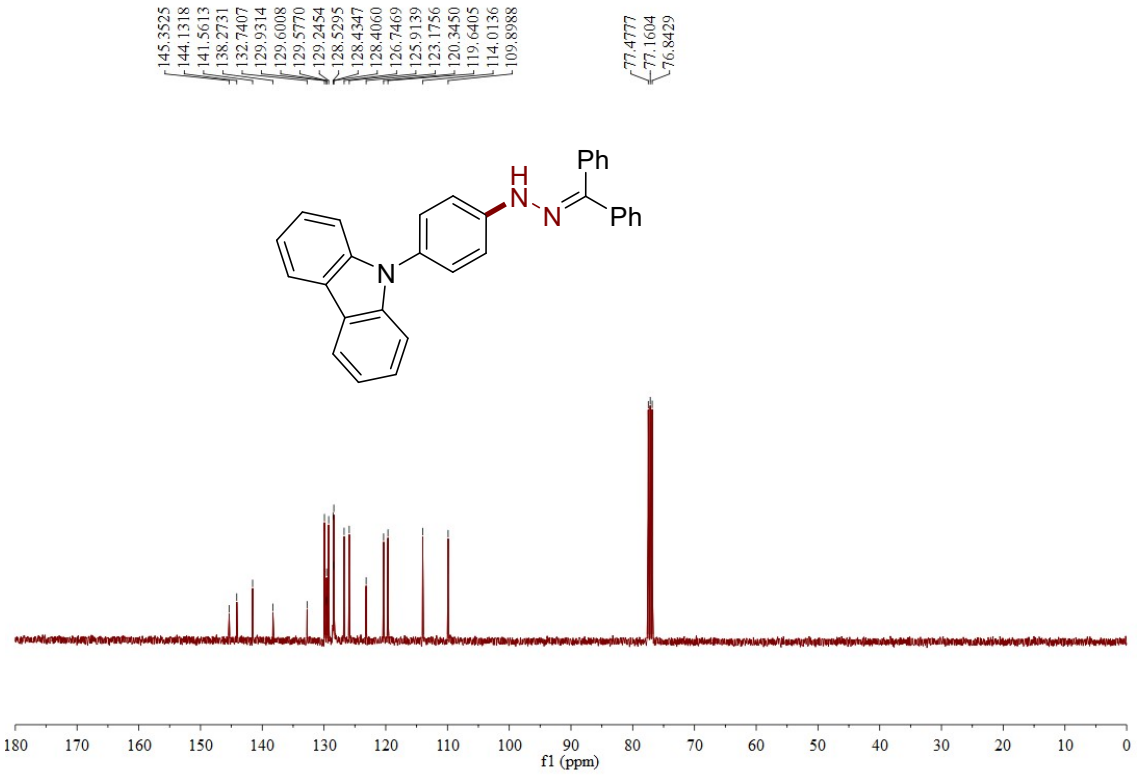
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**



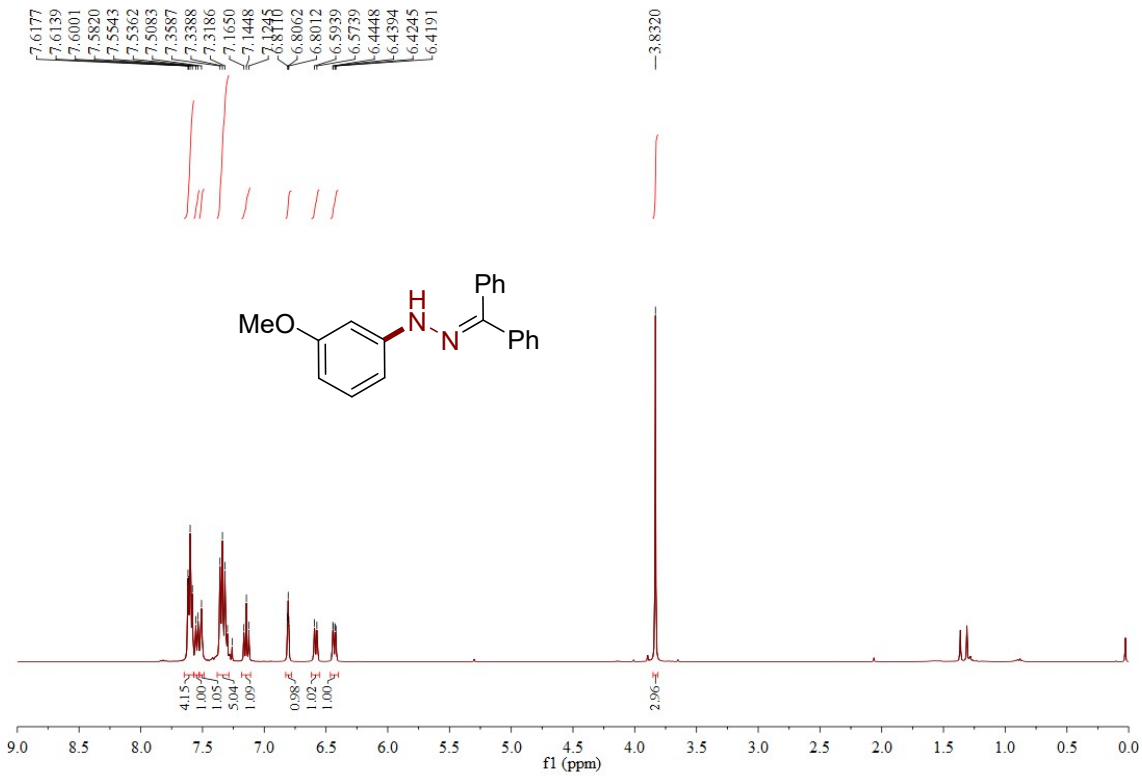
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **10**



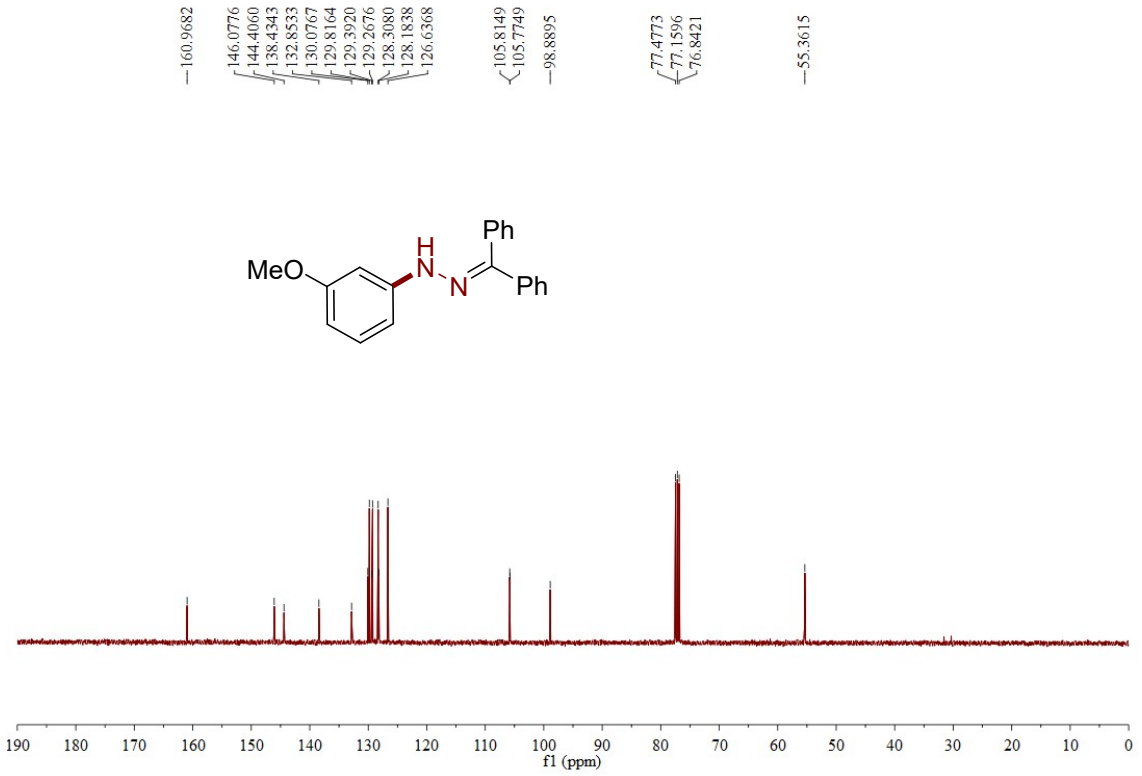
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**



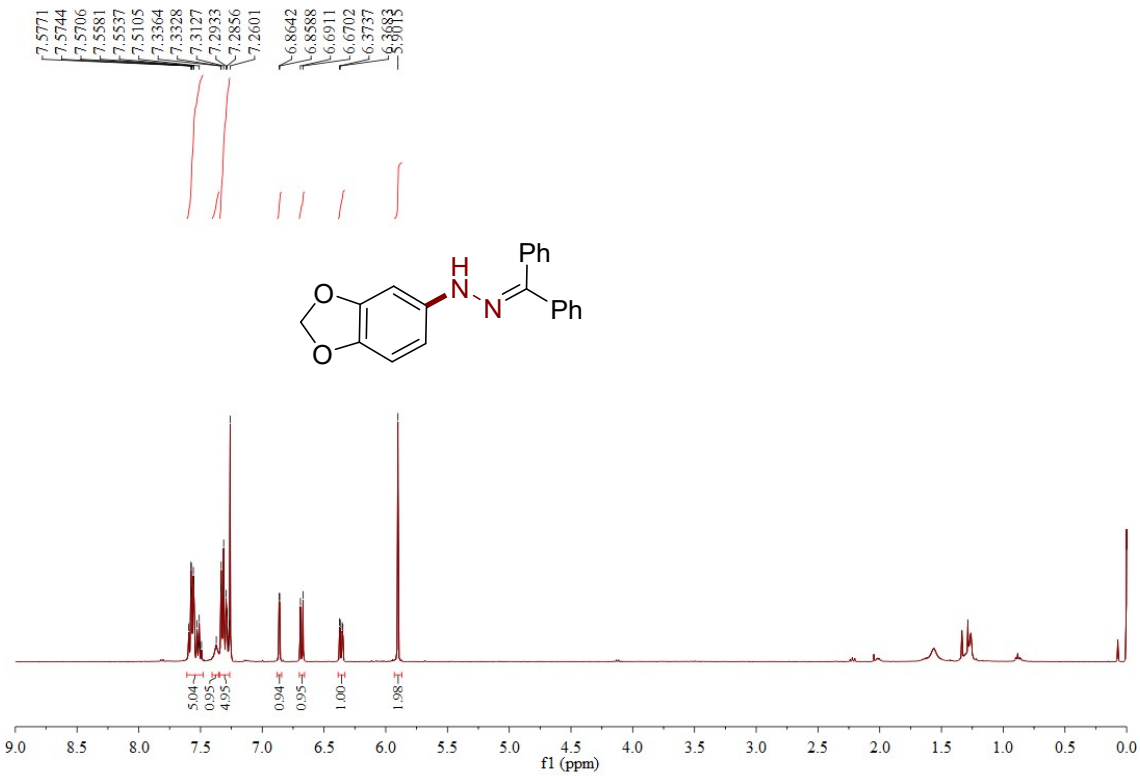
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11**



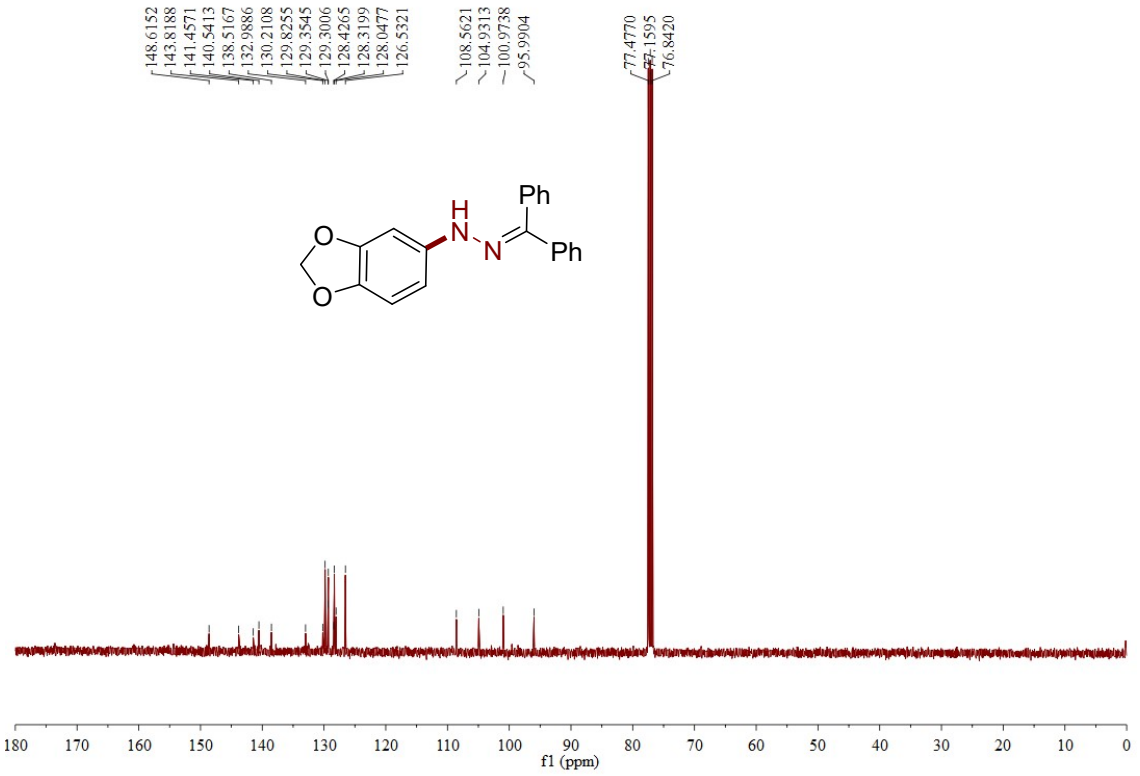
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **12**



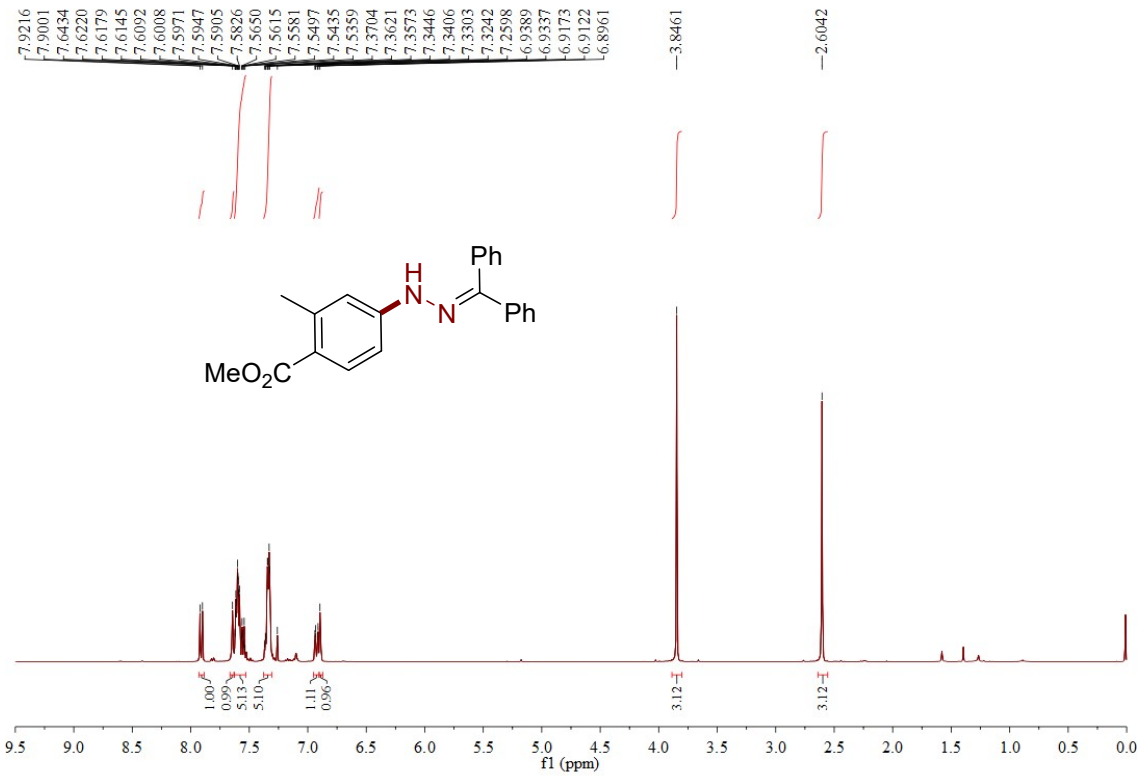
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **12**



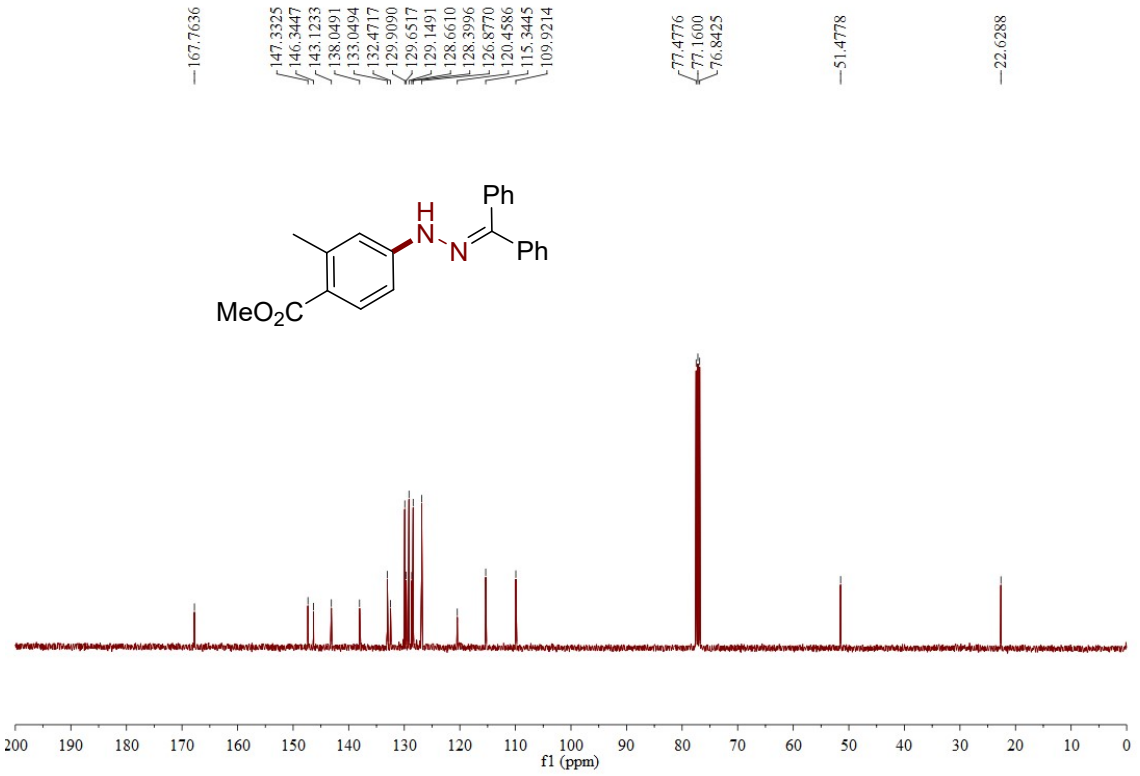
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13**



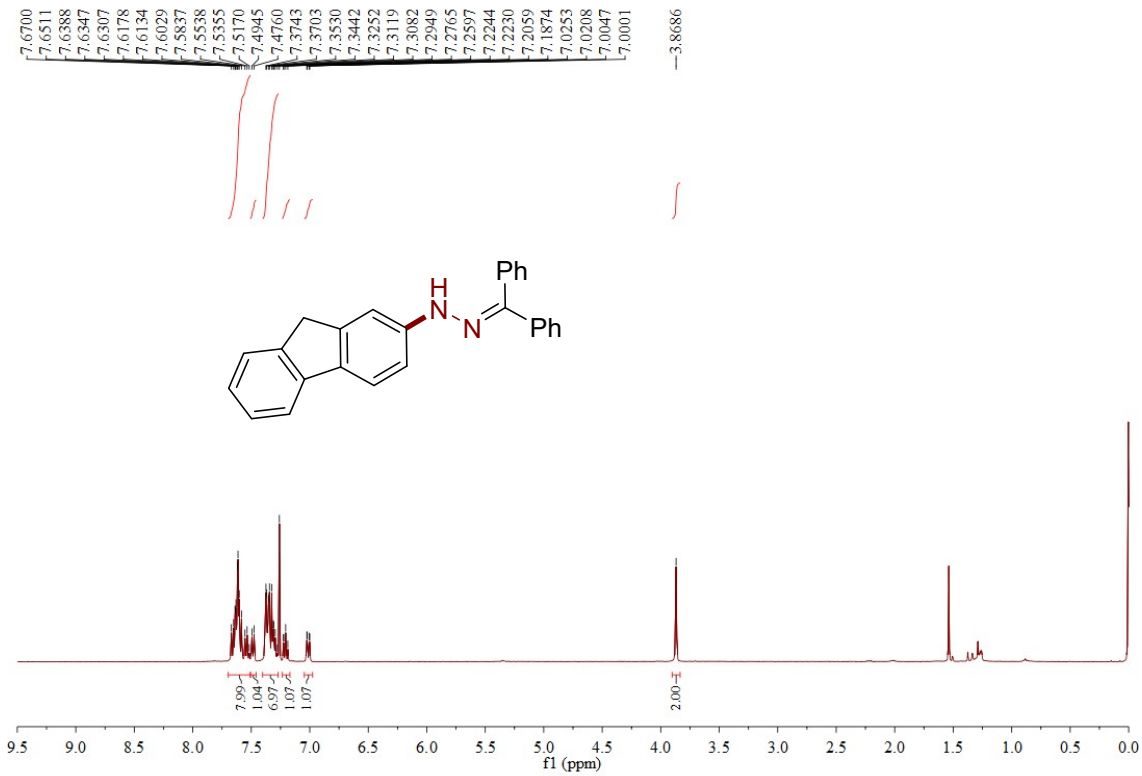
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13**



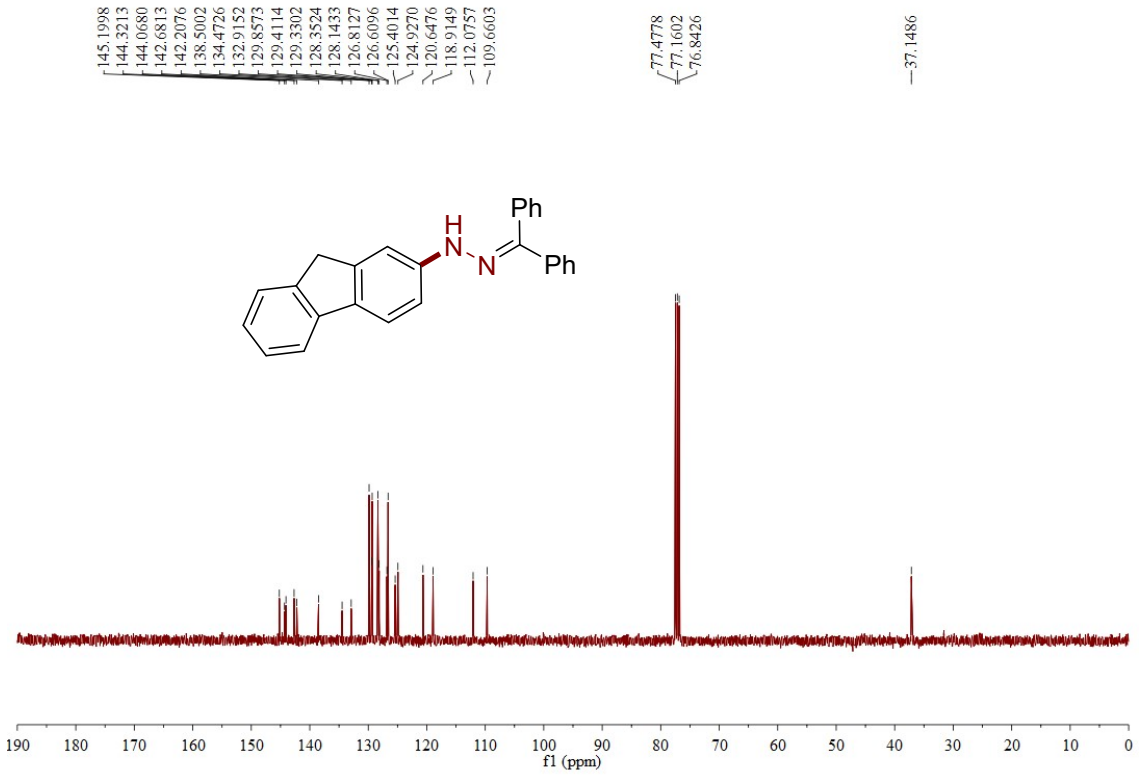
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **14**



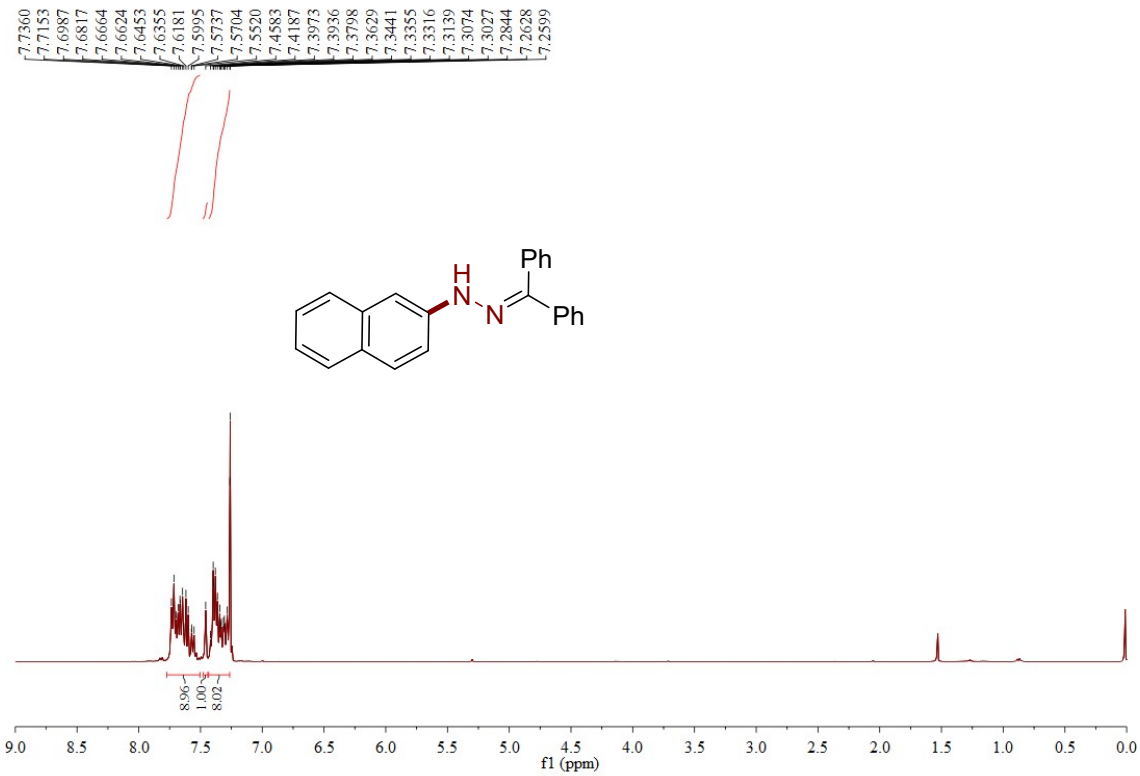
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **14**



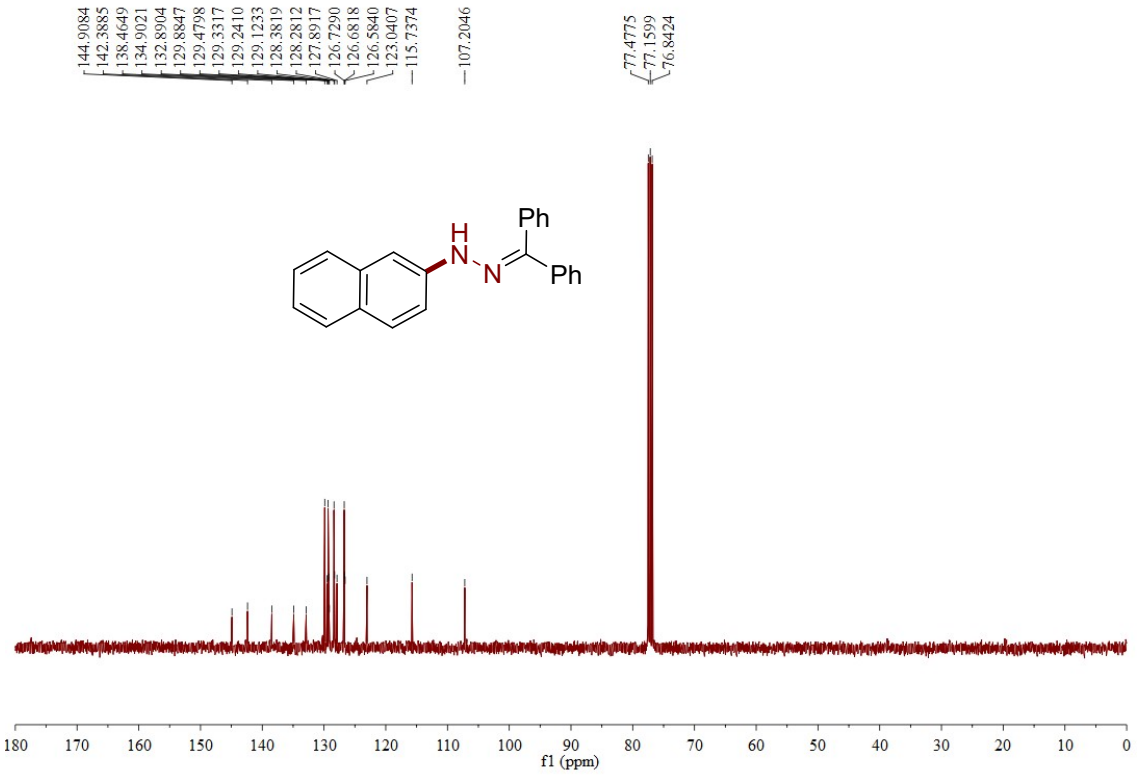
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **15**



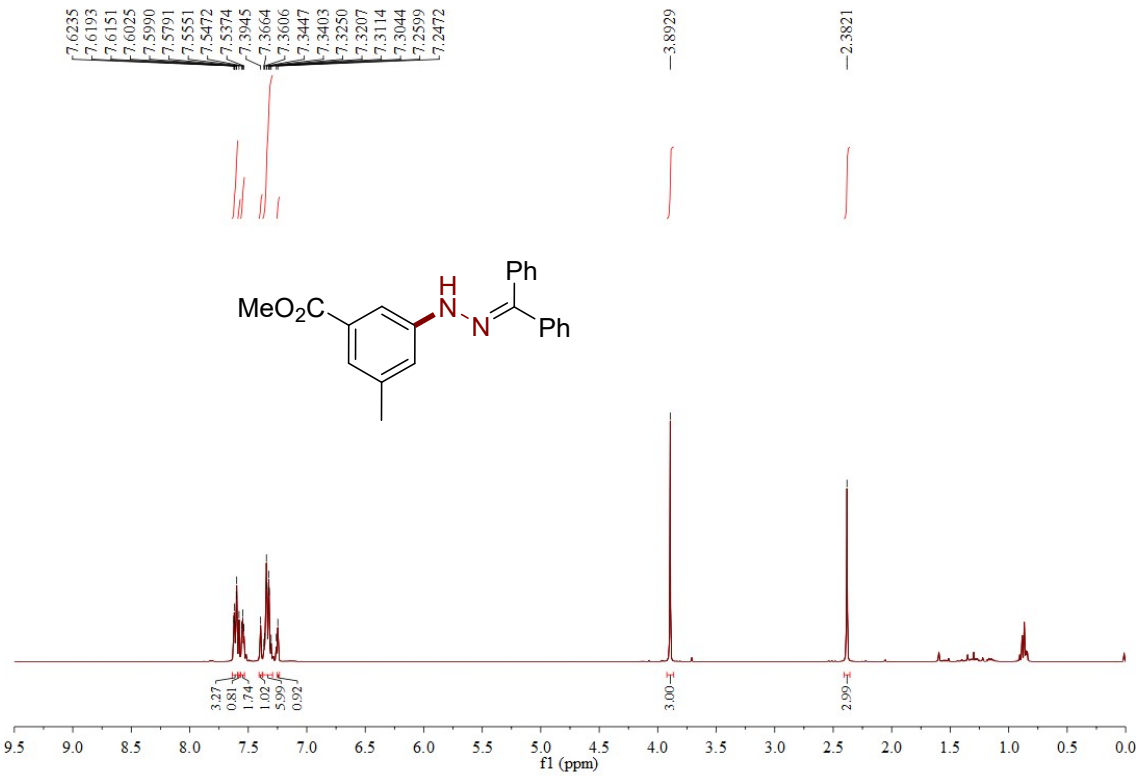
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **15**



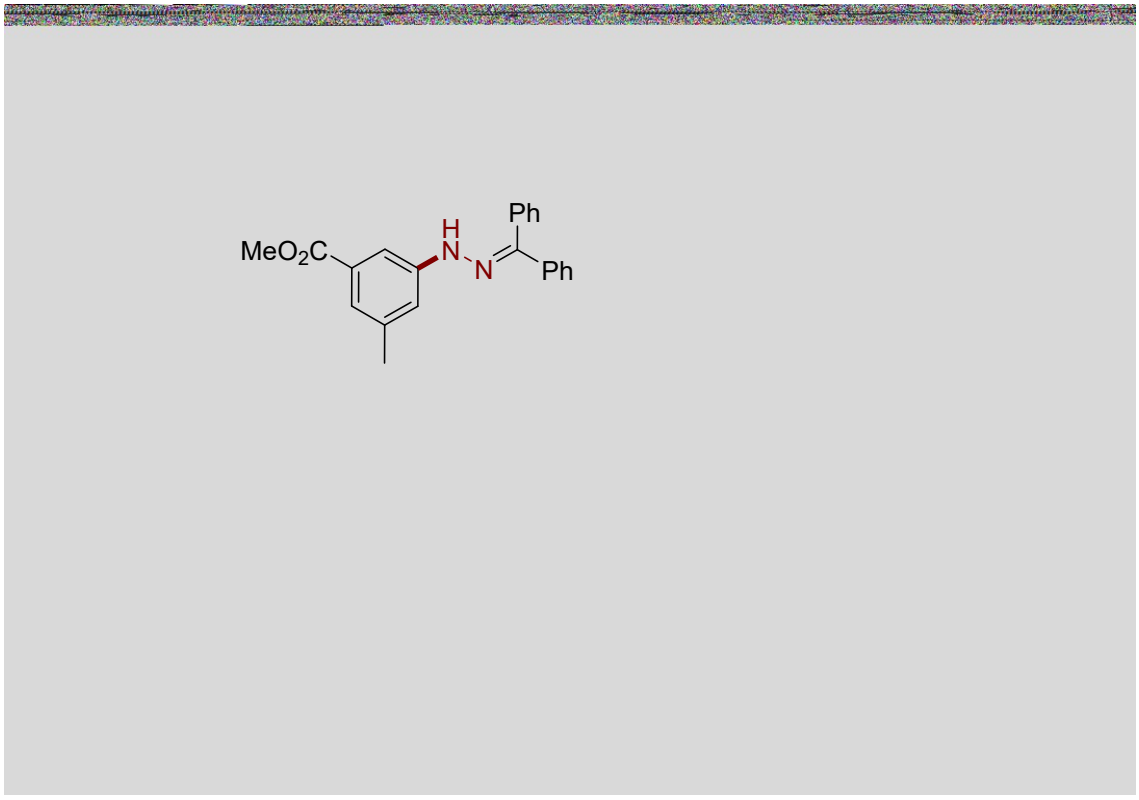
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **16**



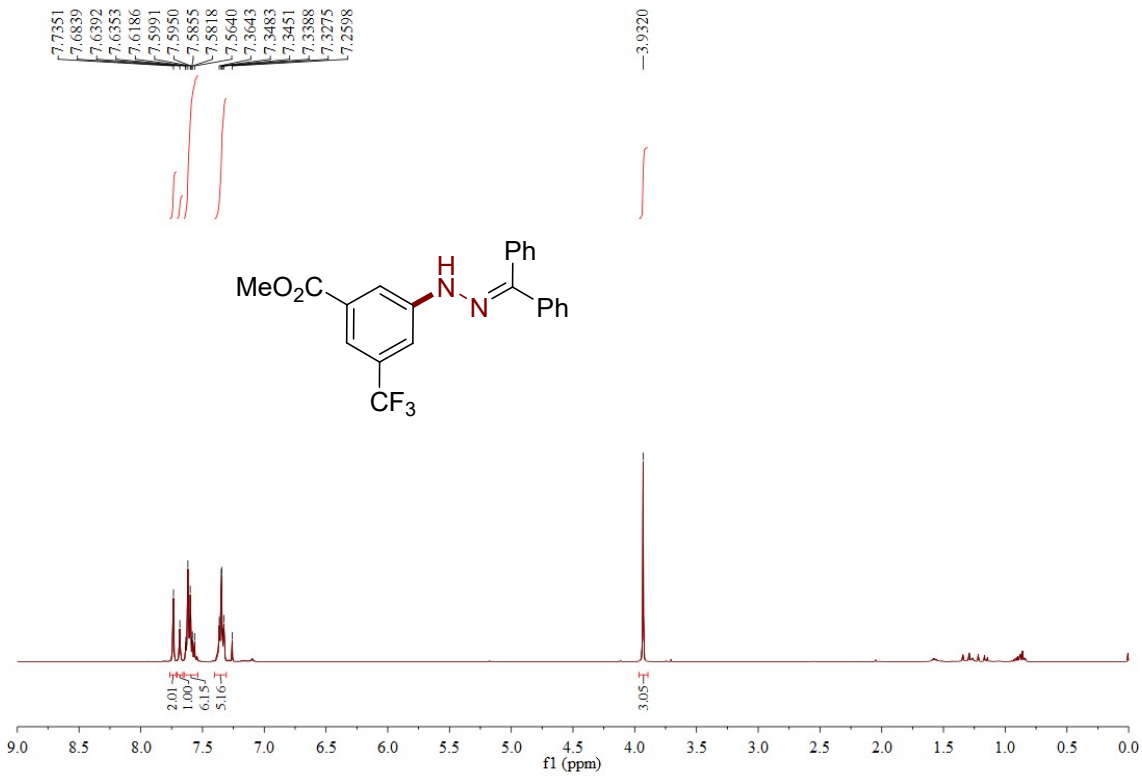
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **16**



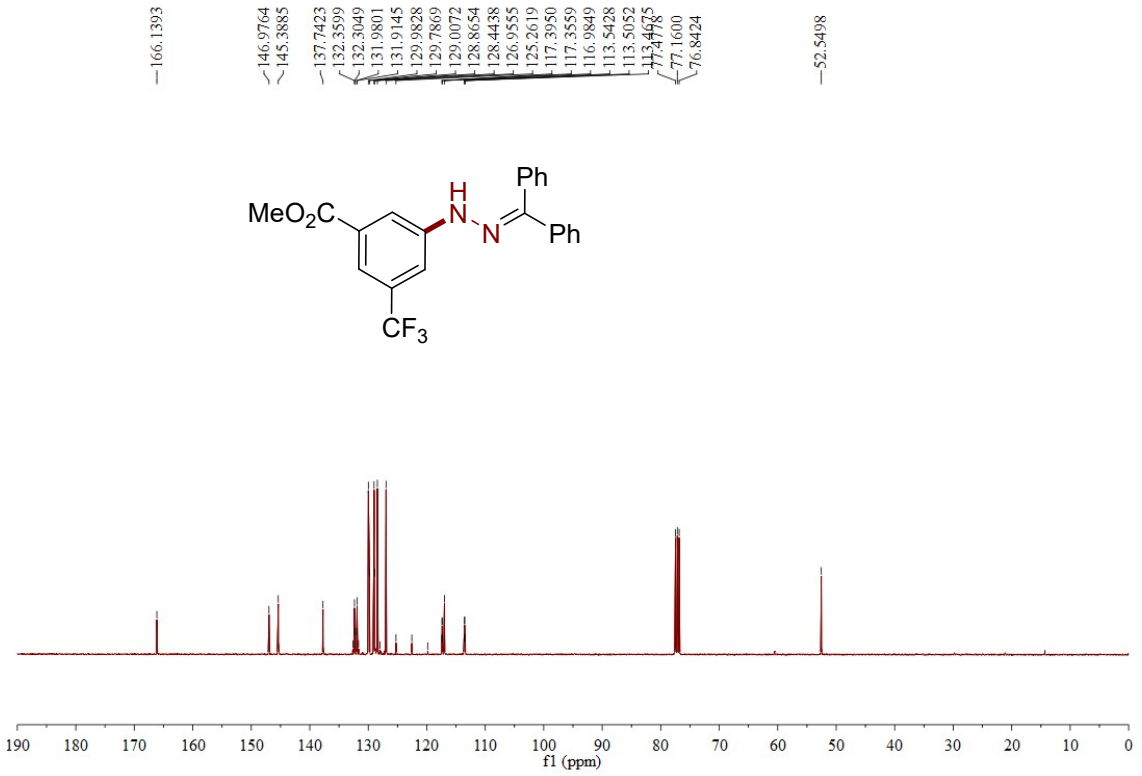
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **17**



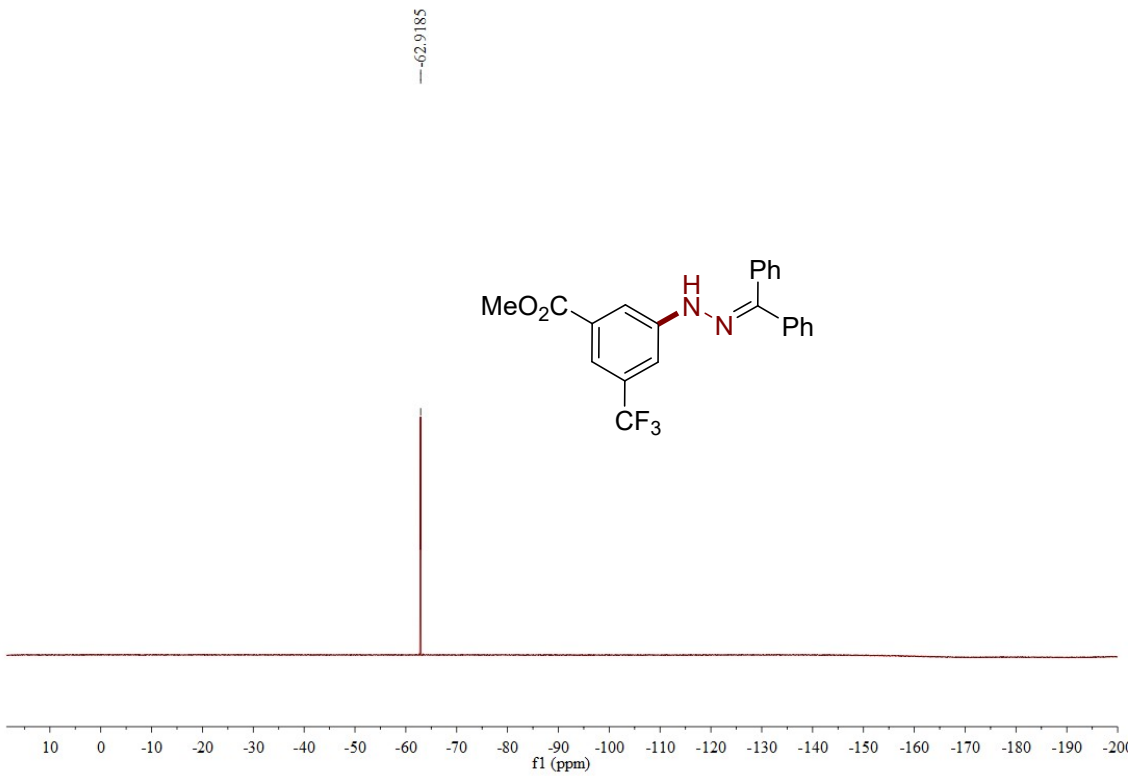
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **17**



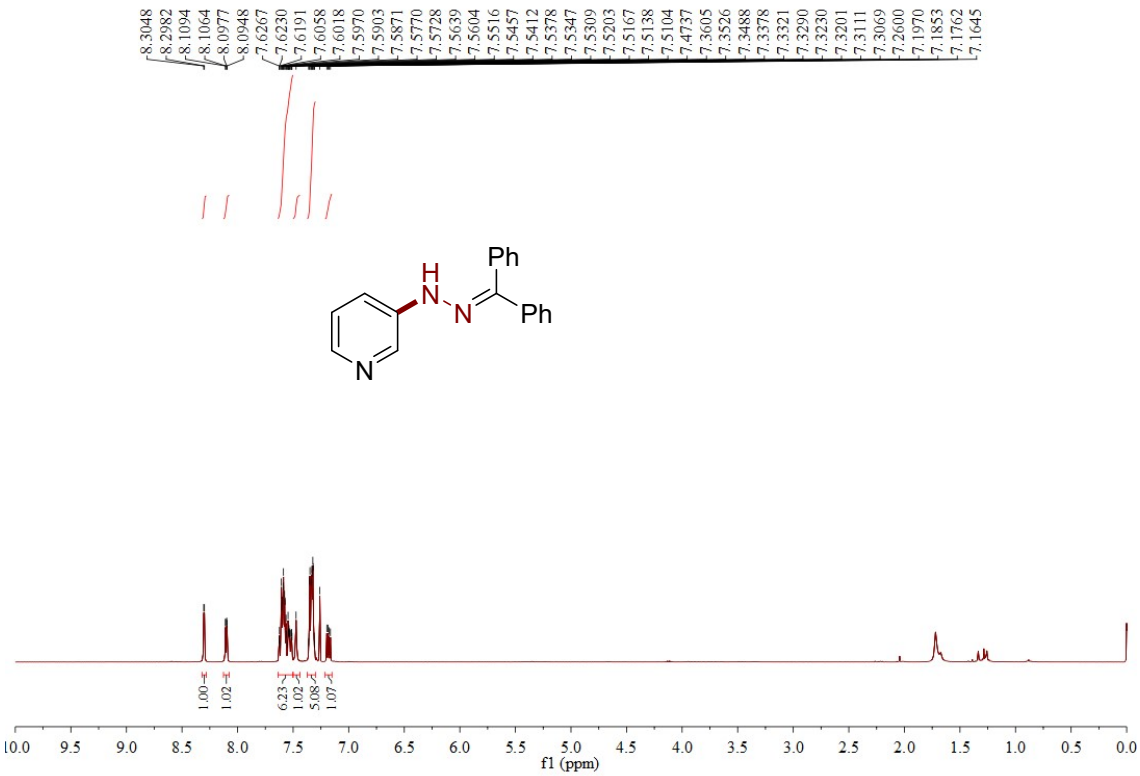
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **18**



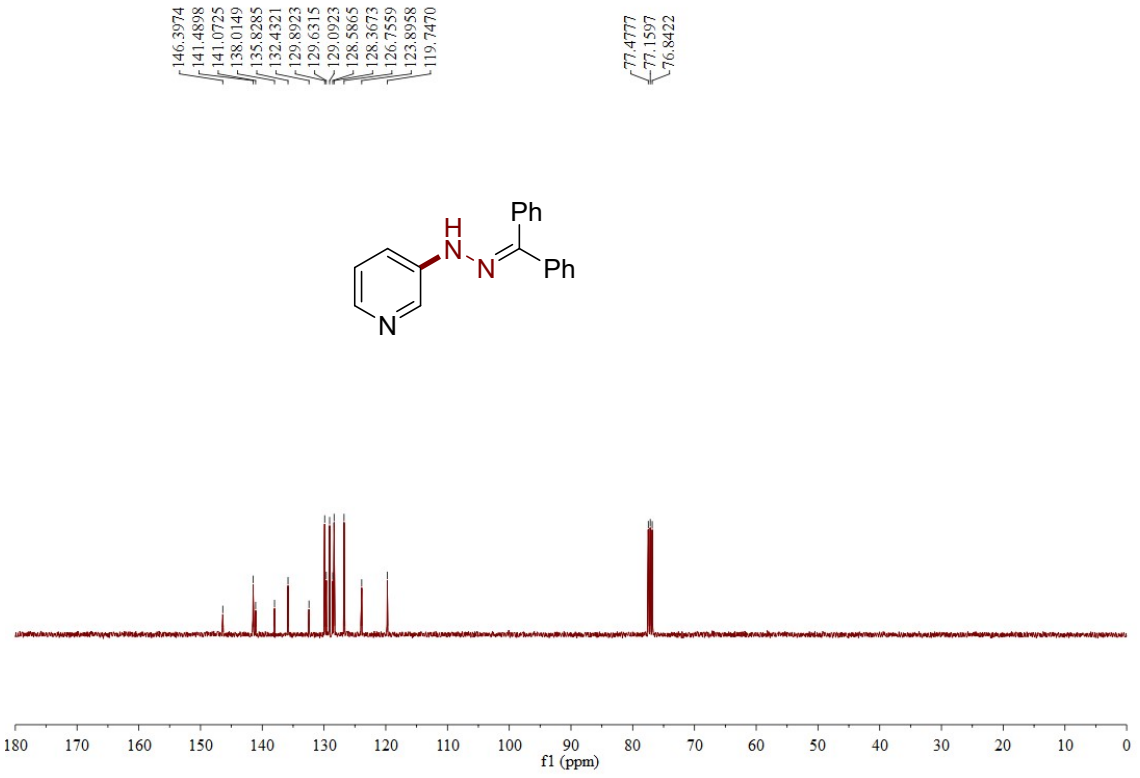
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **18**



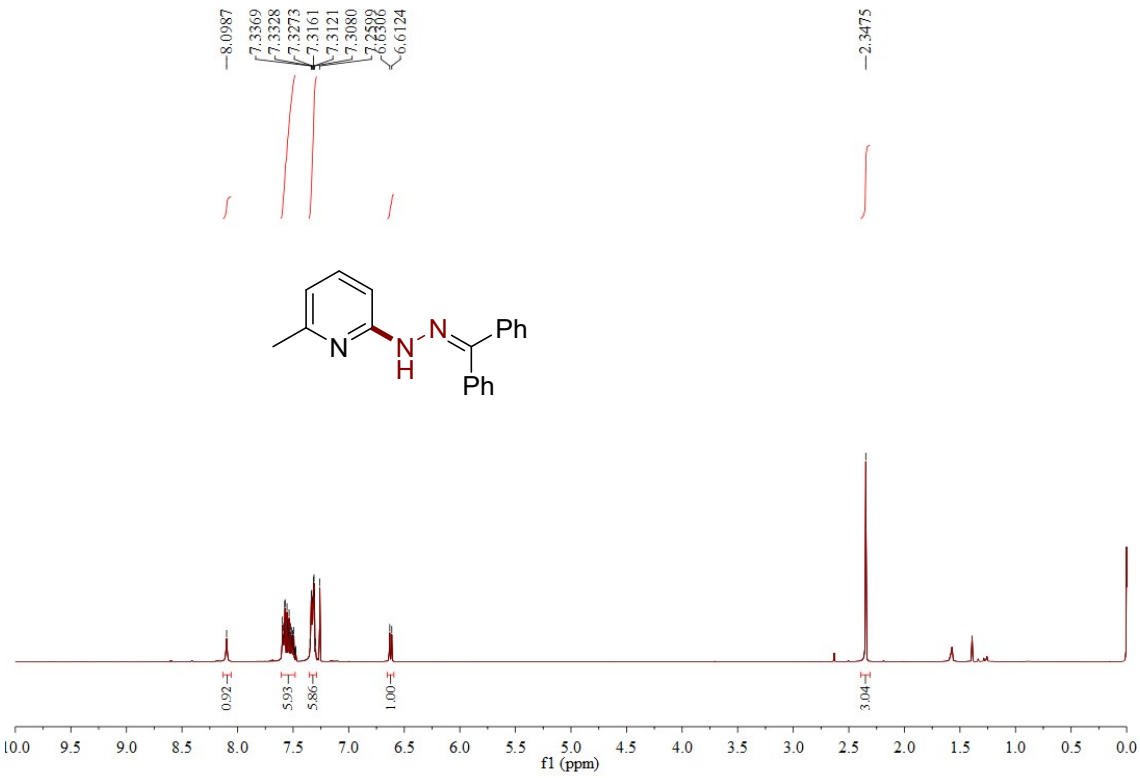
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **18**



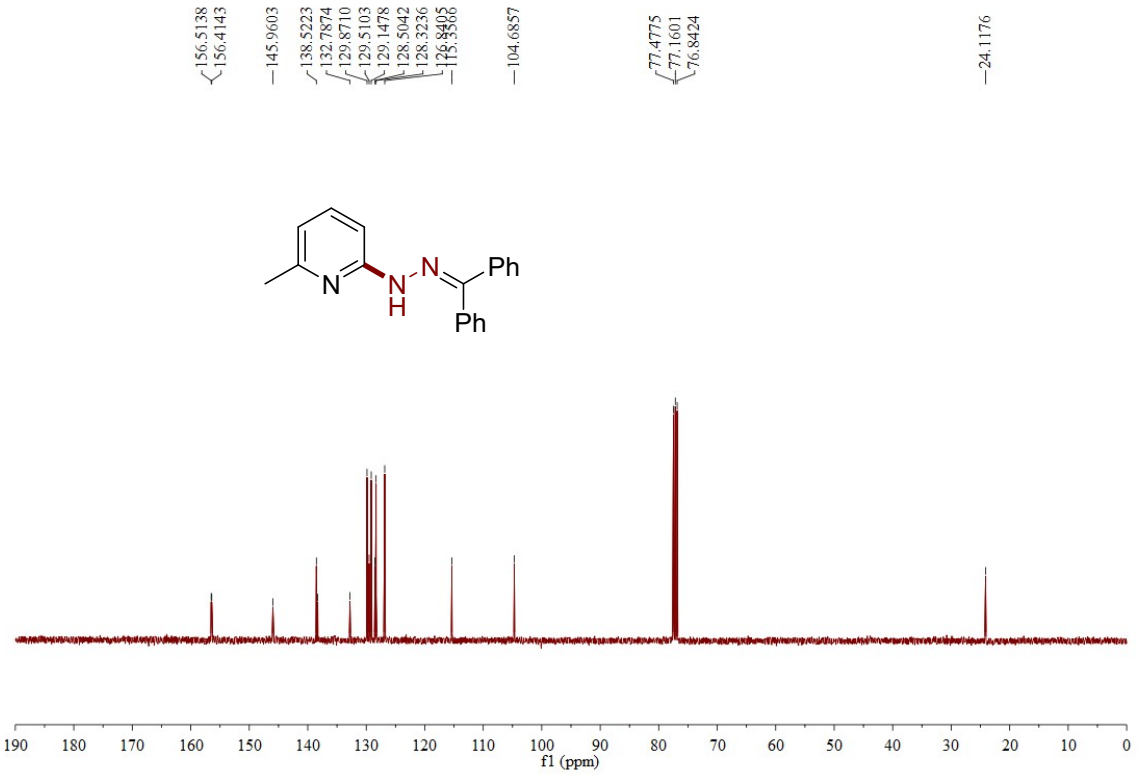
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **19**



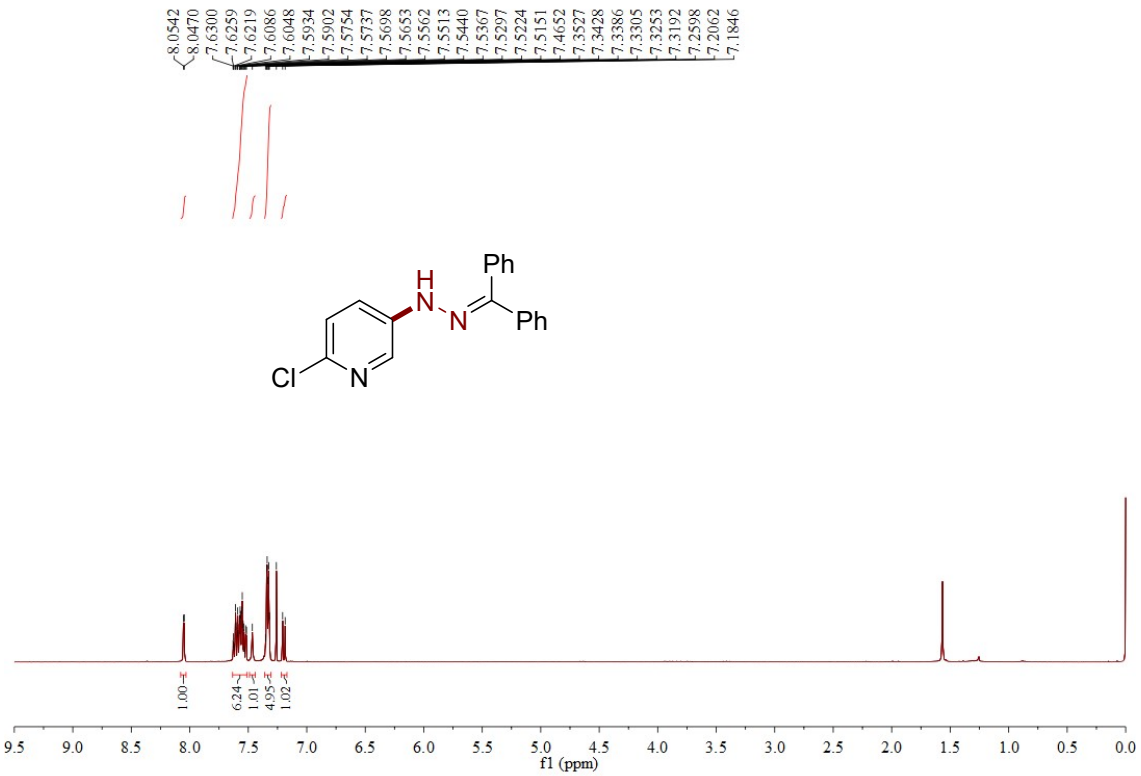
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **19**



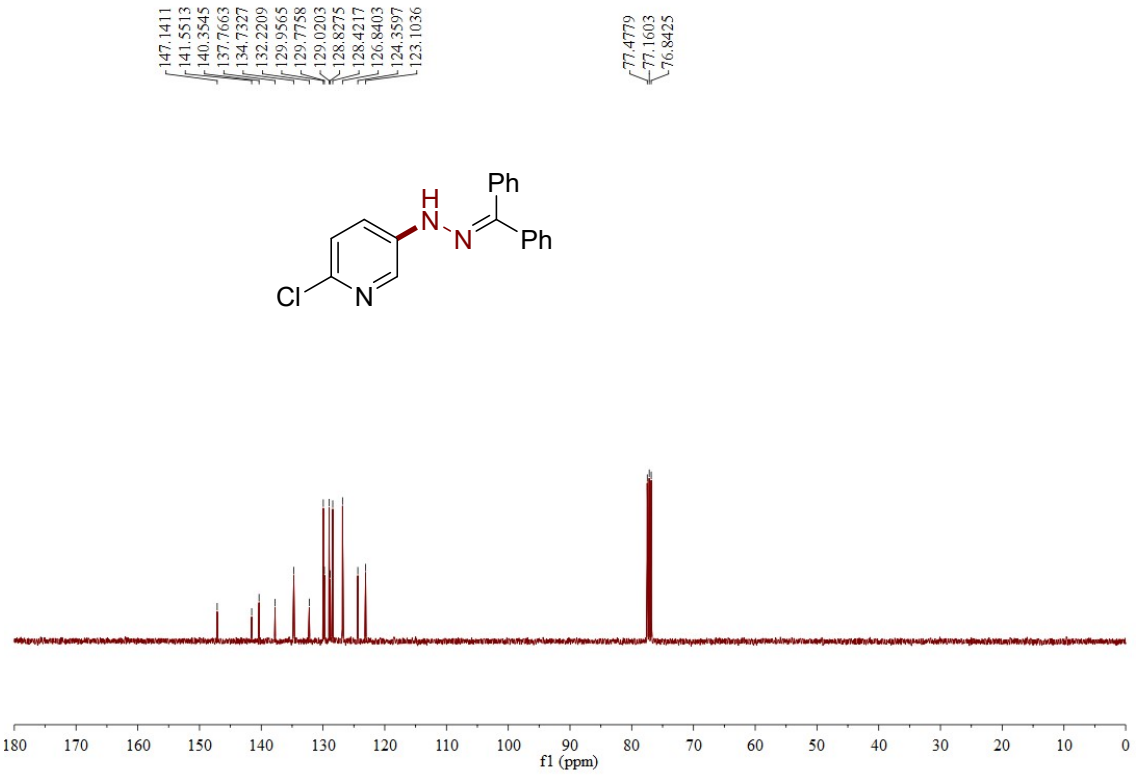
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **20**



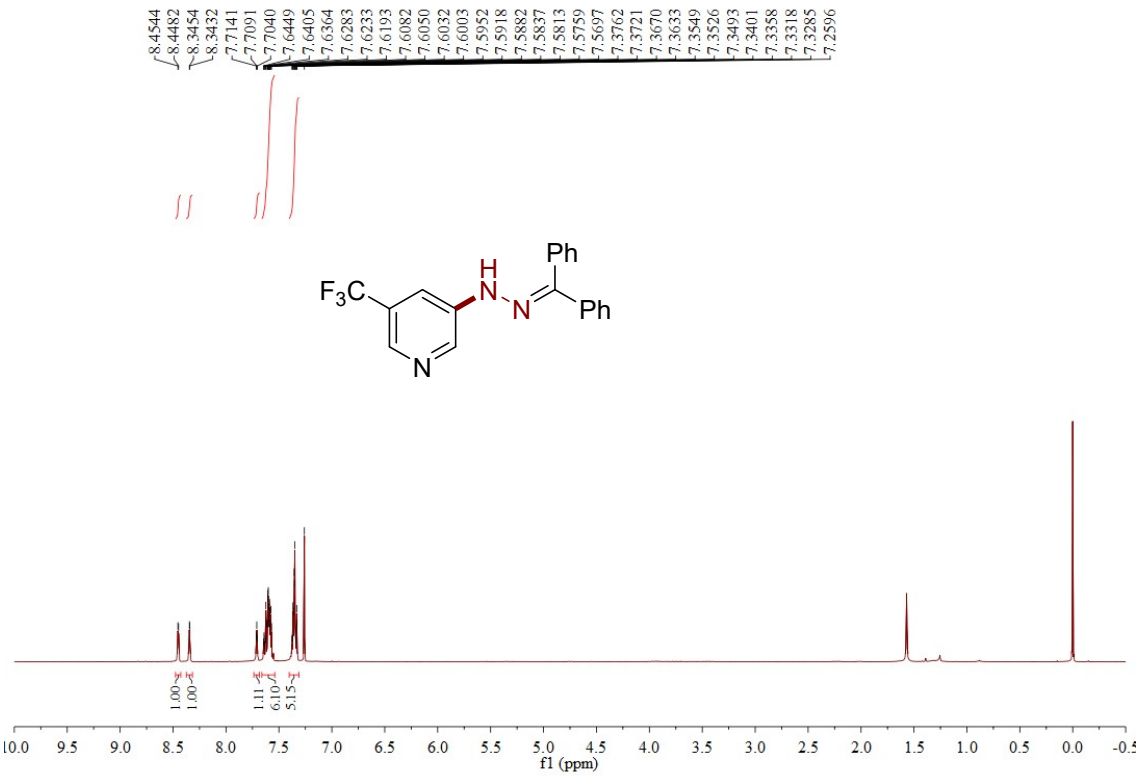
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **20**



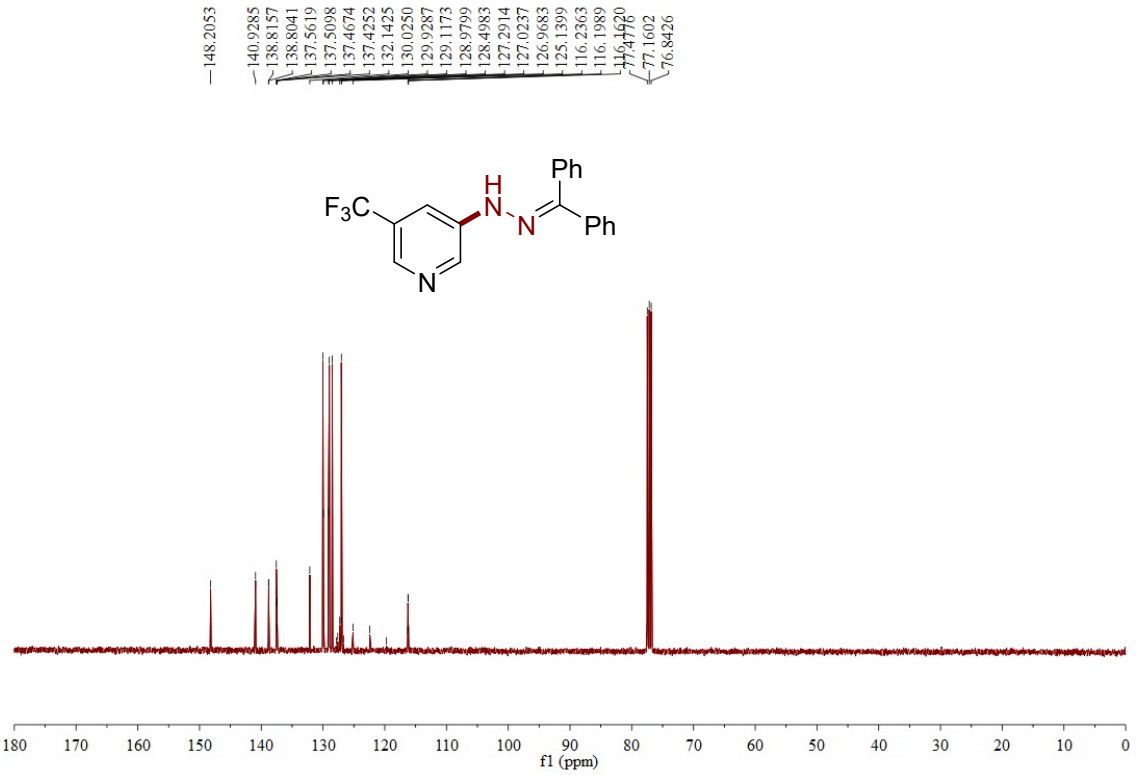
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **21**



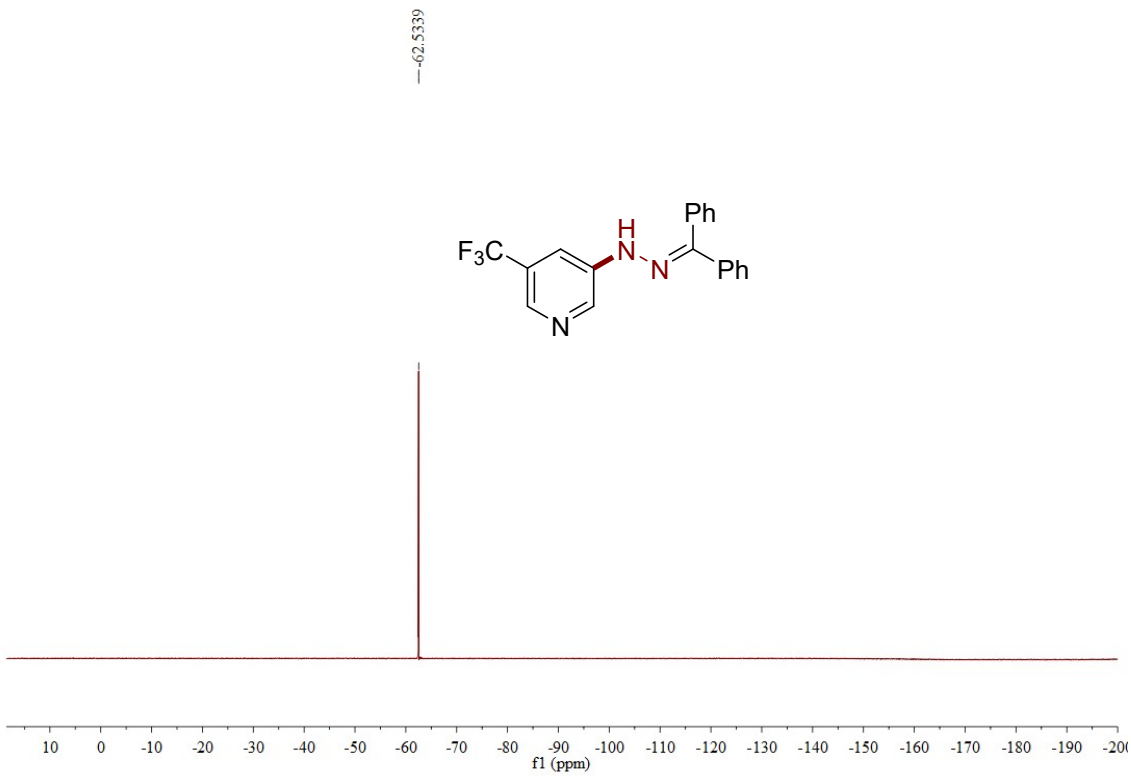
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **21**



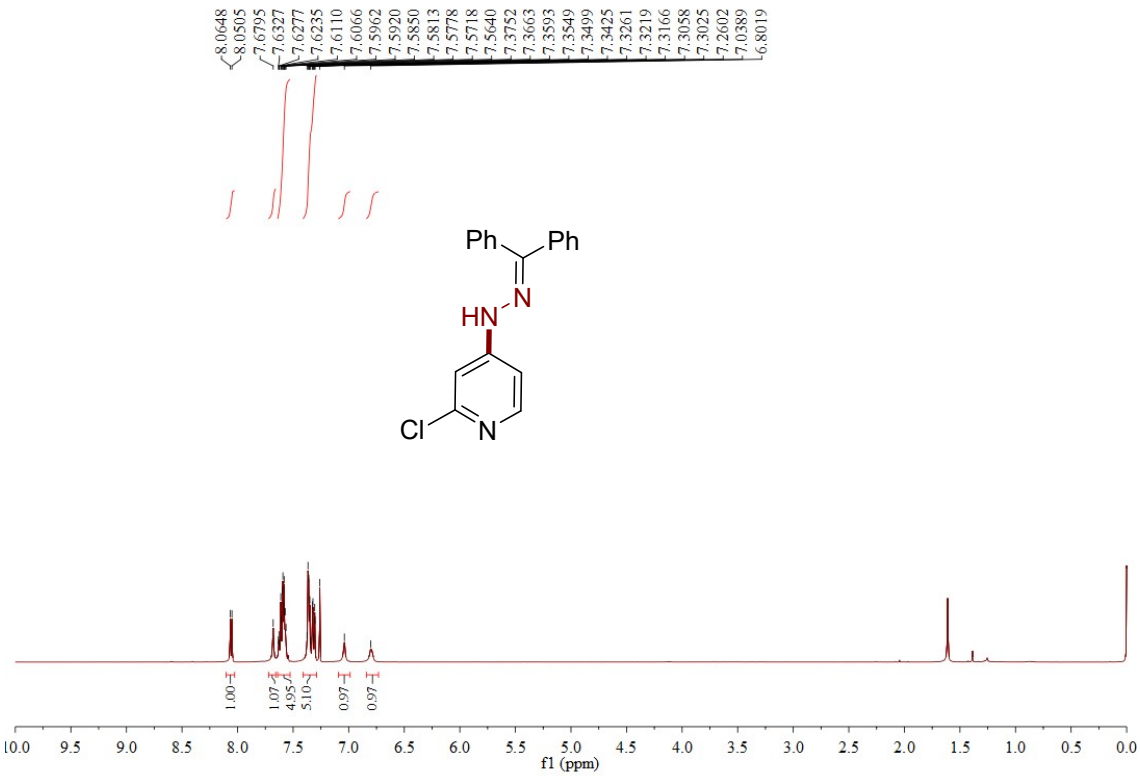
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **22**



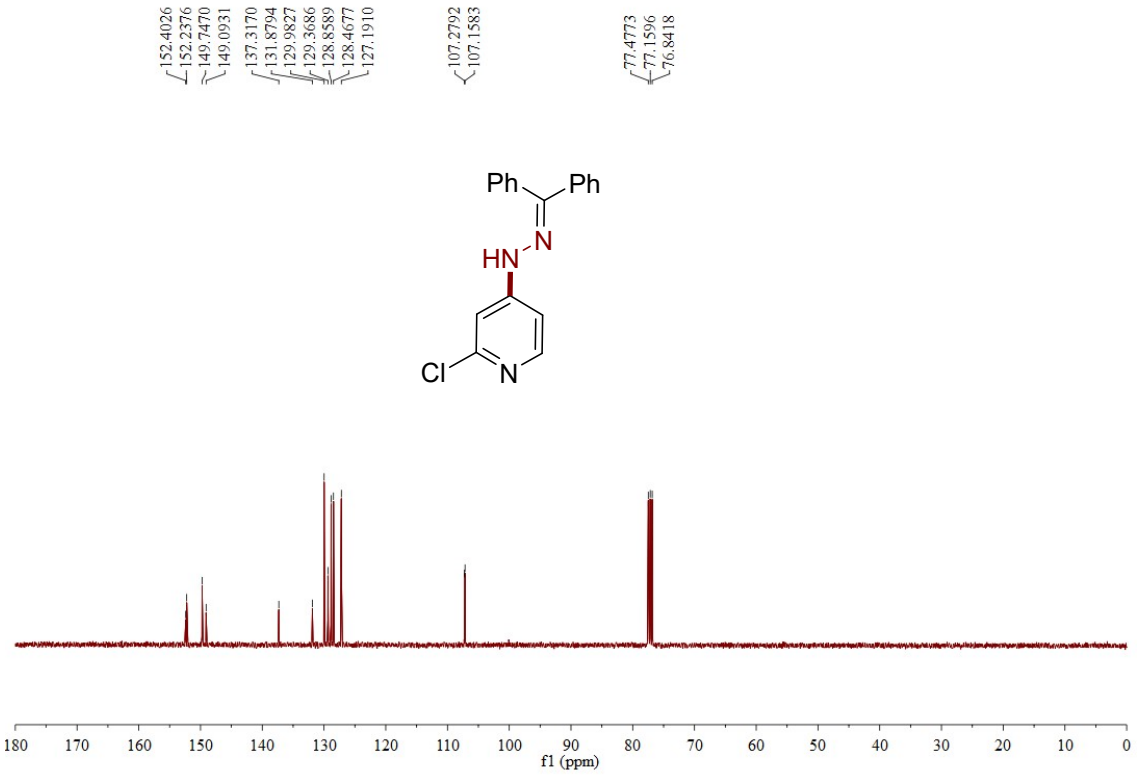
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **22**



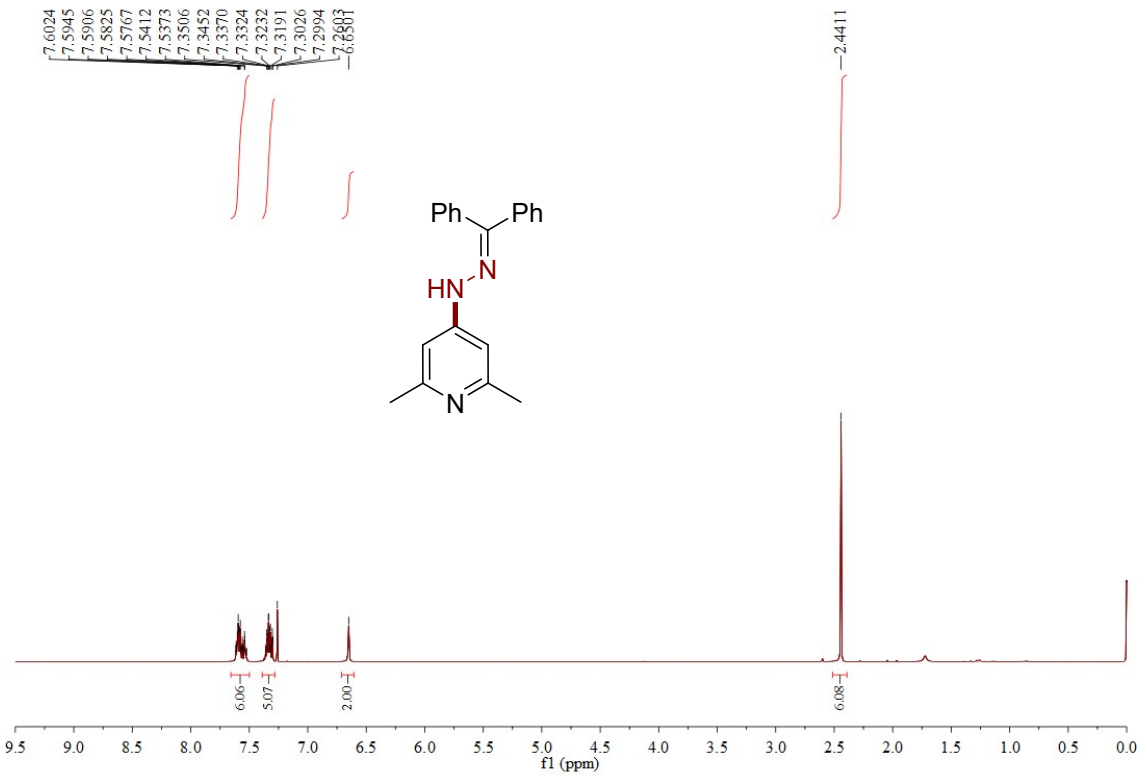
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **22**



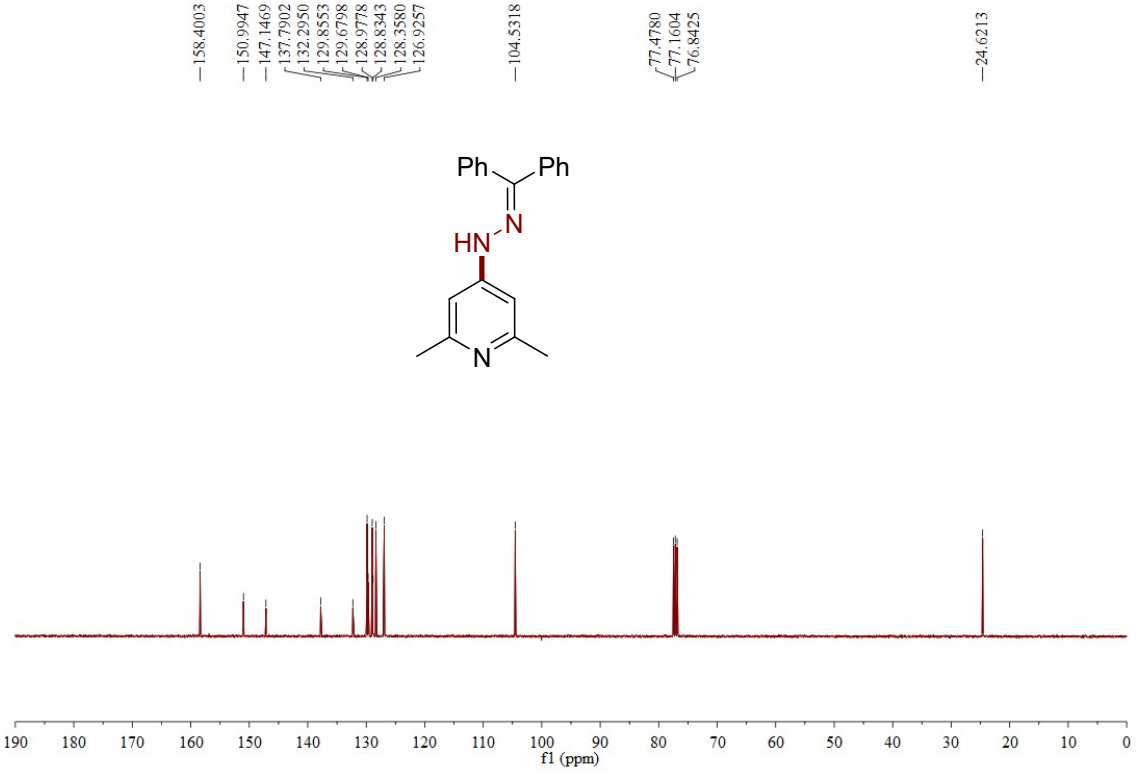
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **23**



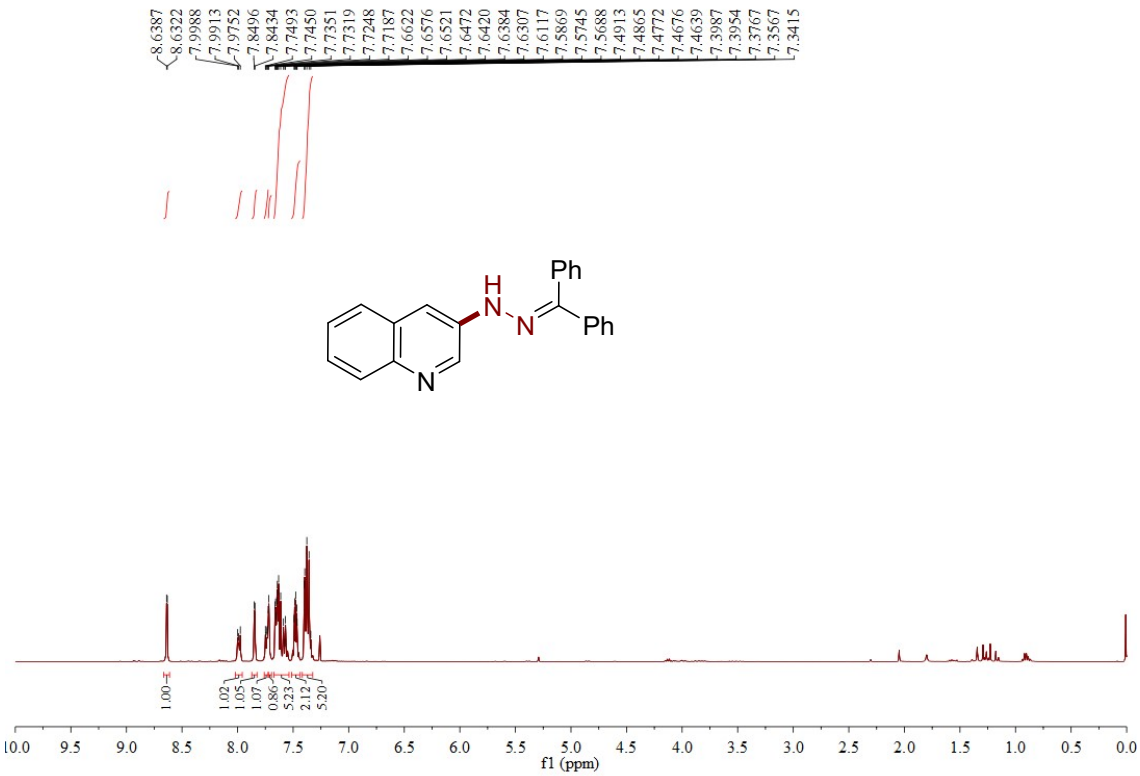
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **23**



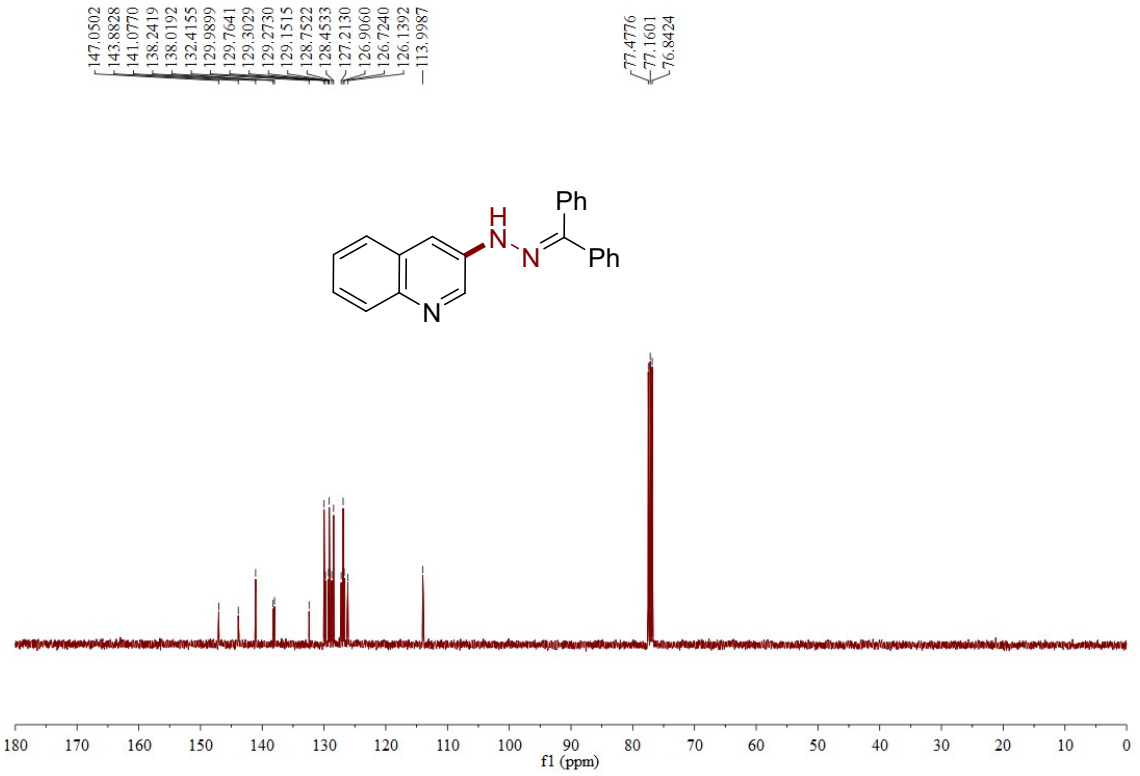
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **24**



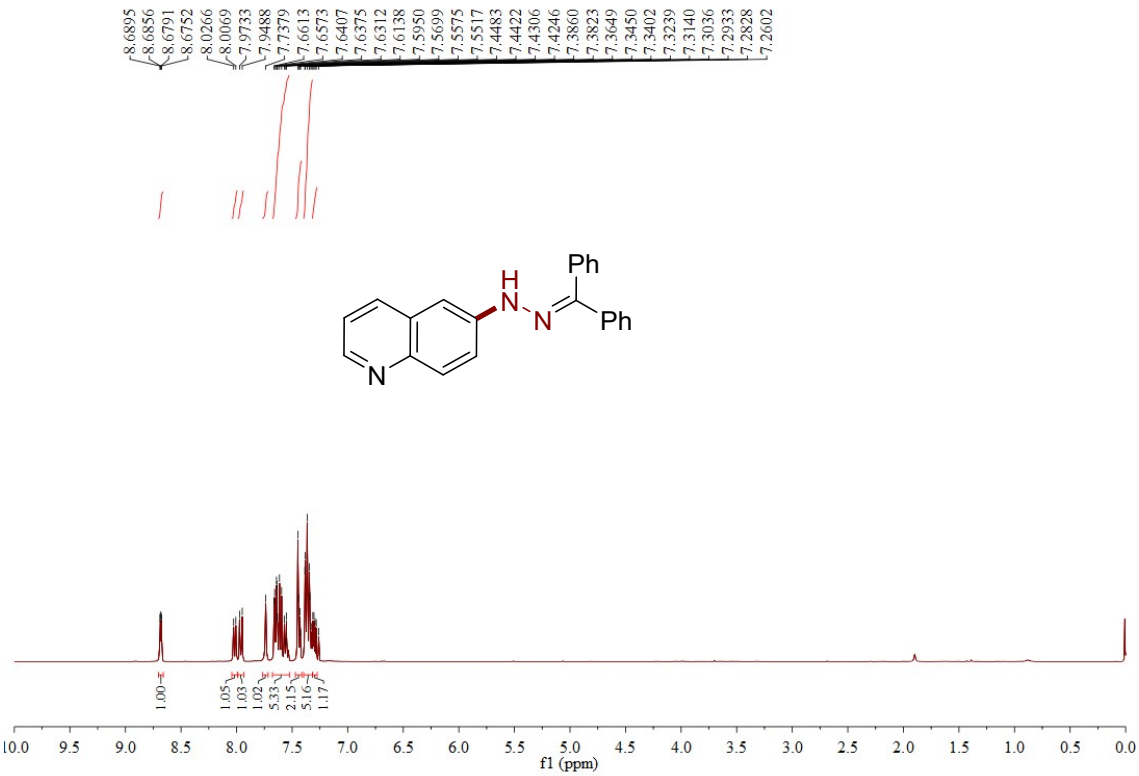
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **24**



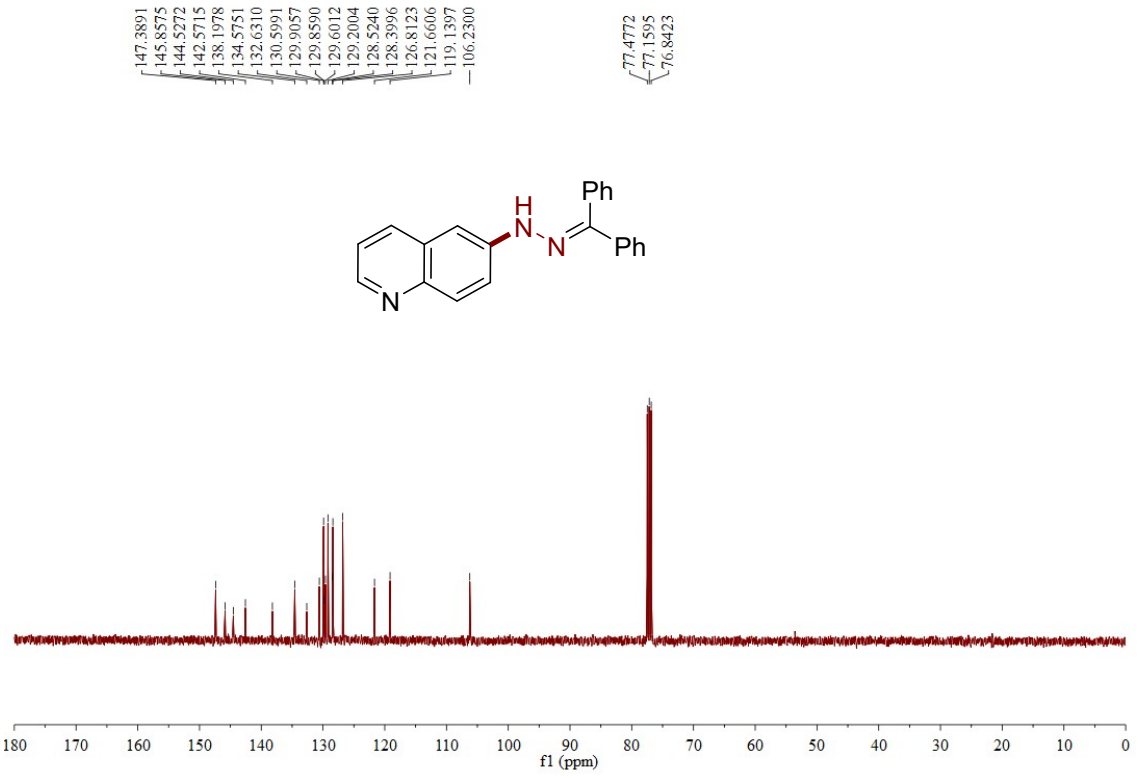
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **25**



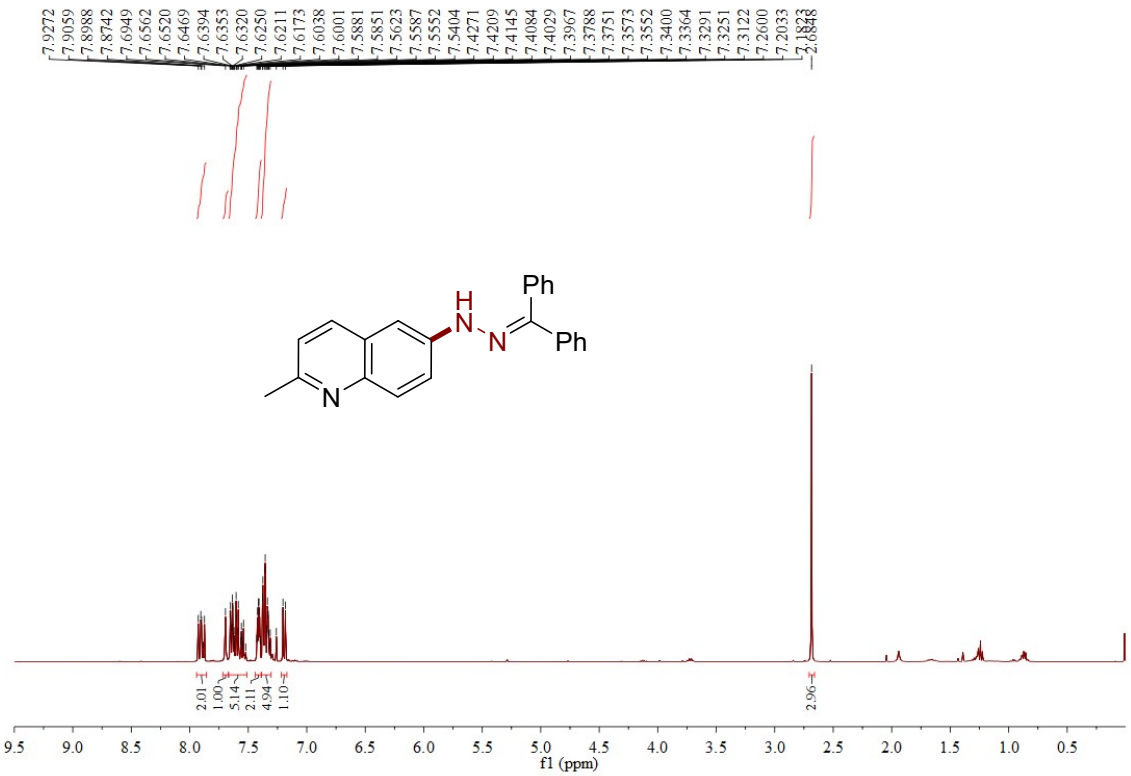
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **25**



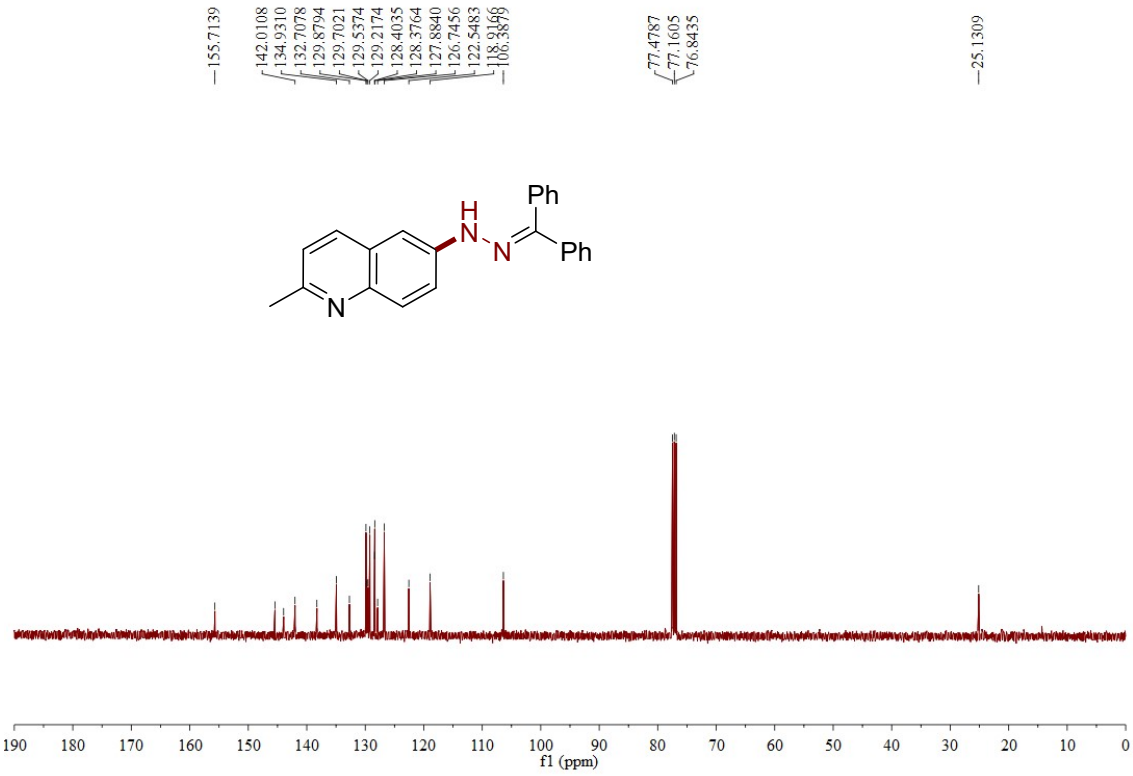
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **26**



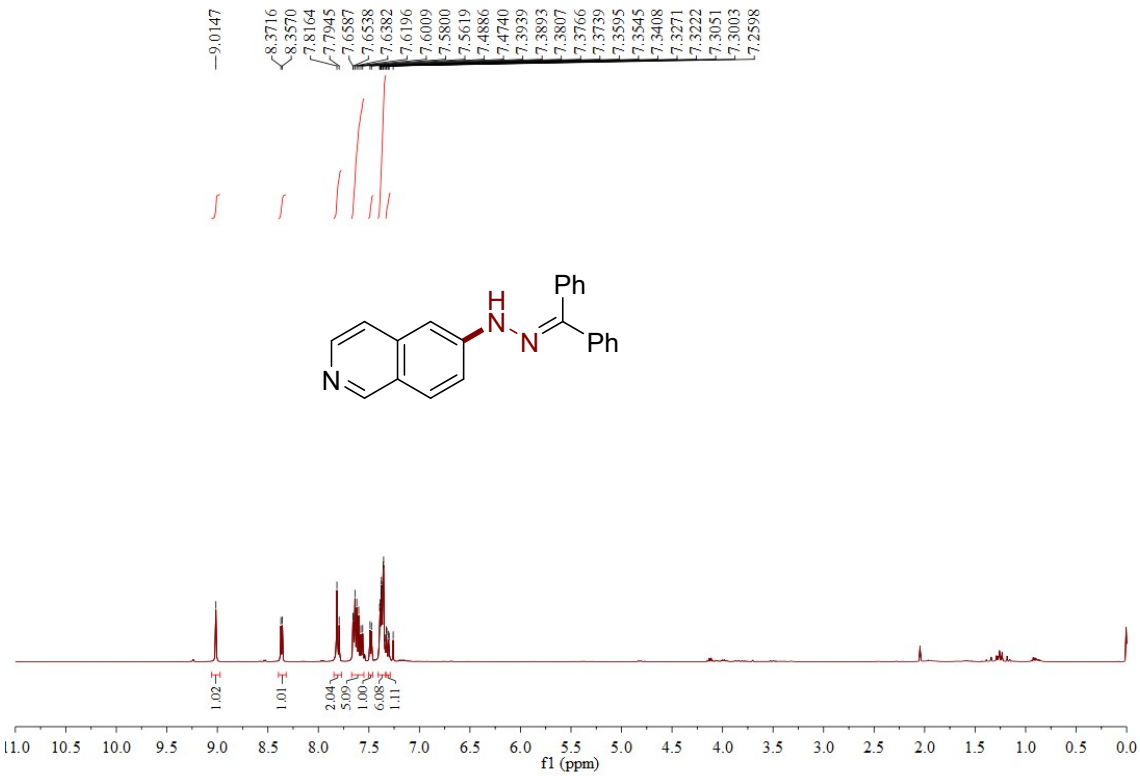
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **26**



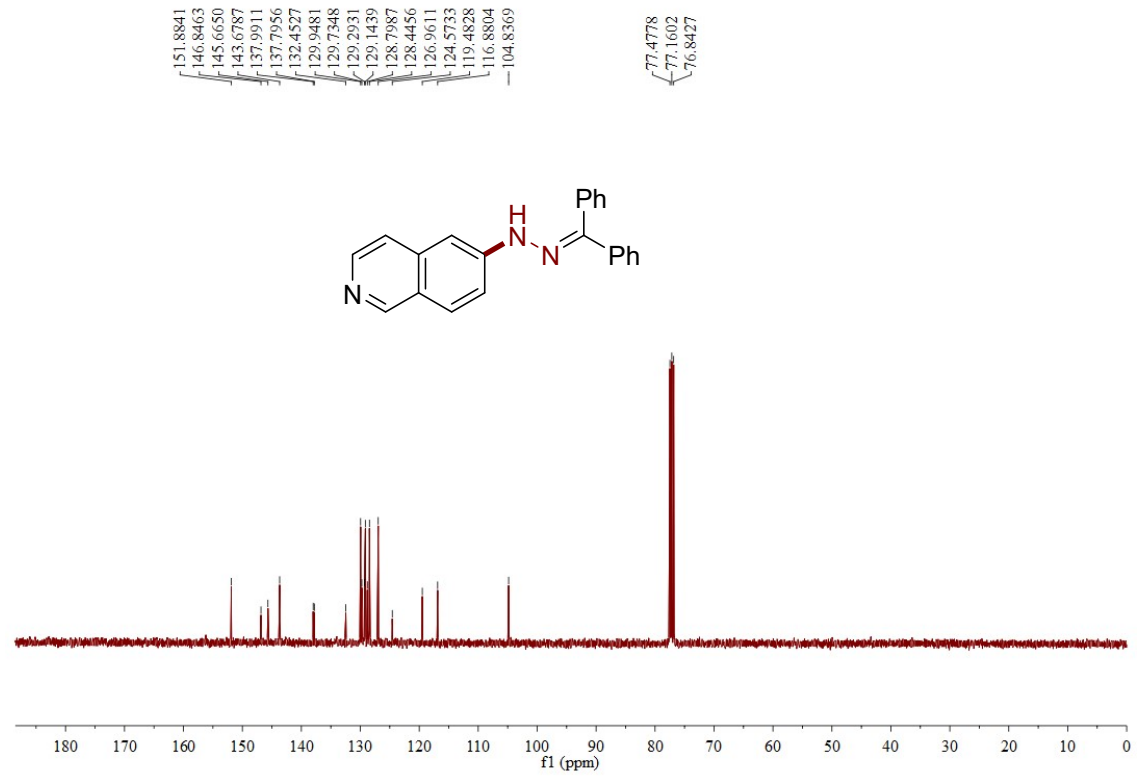
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **27**



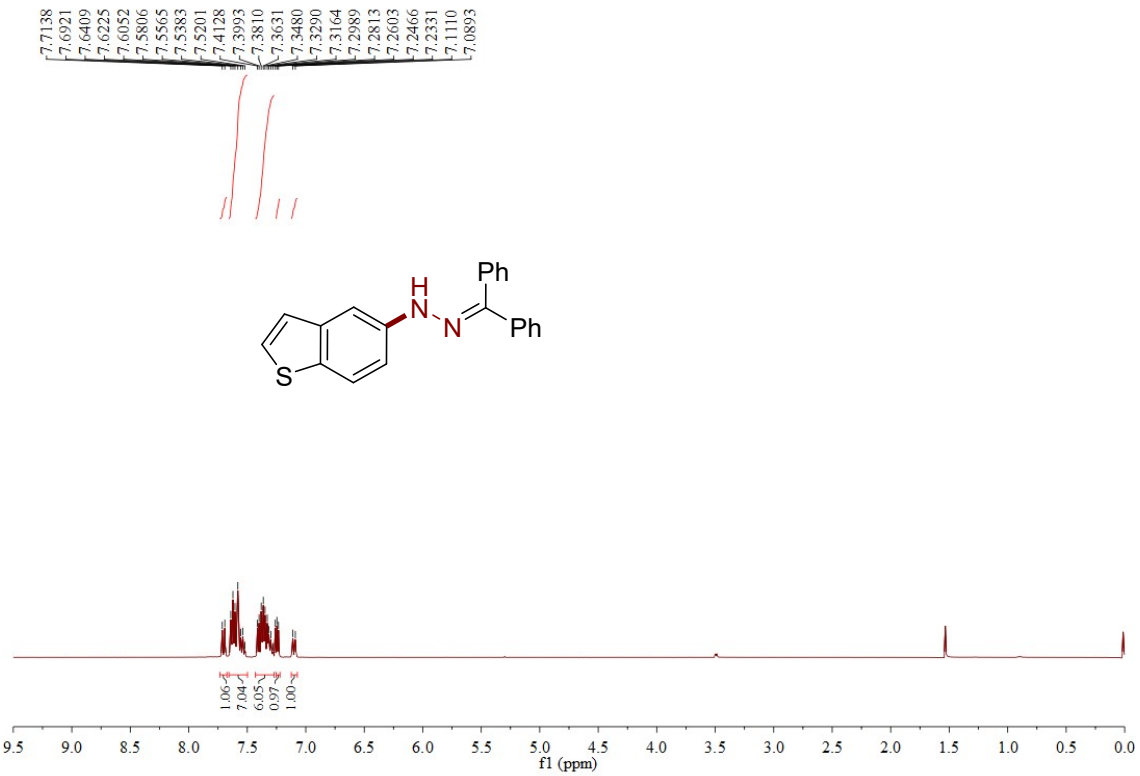
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **27**



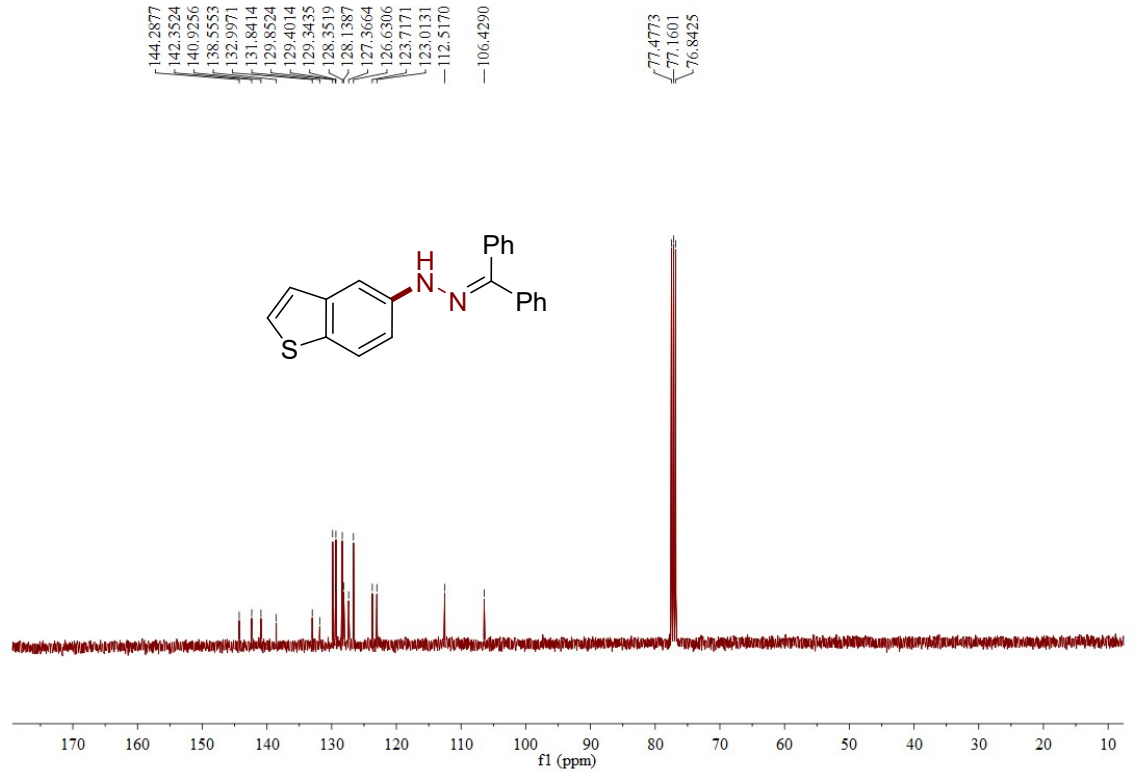
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **28**



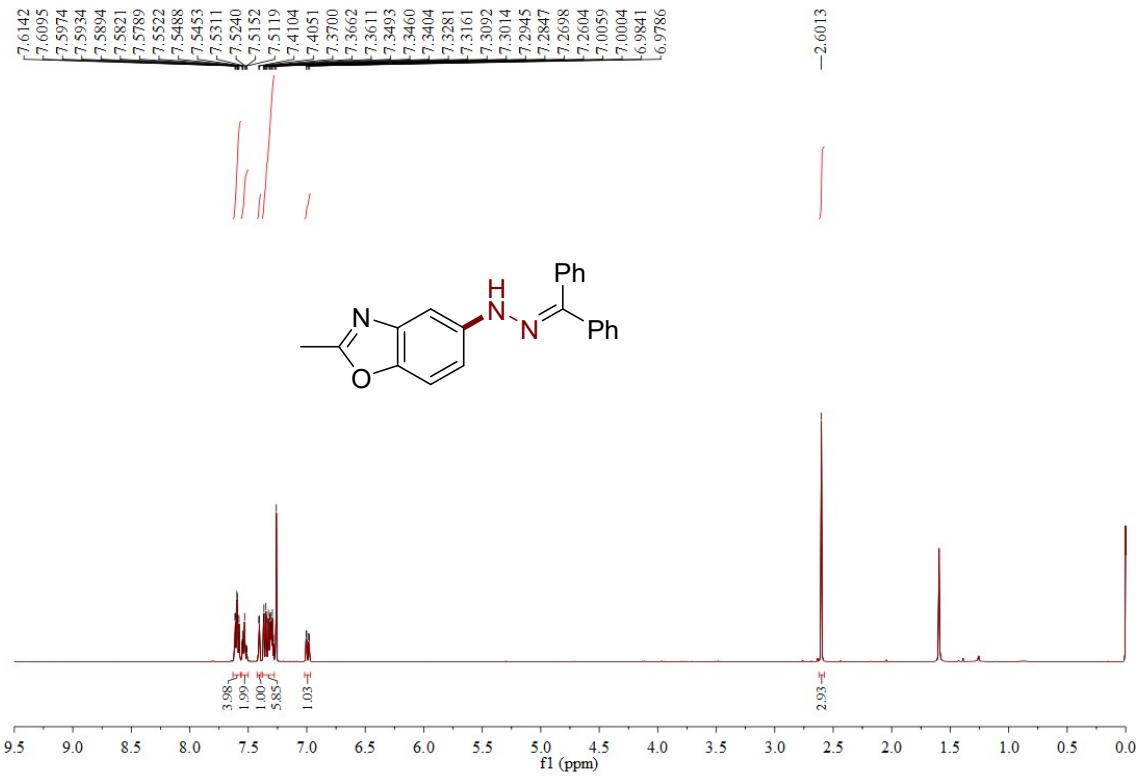
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **28**



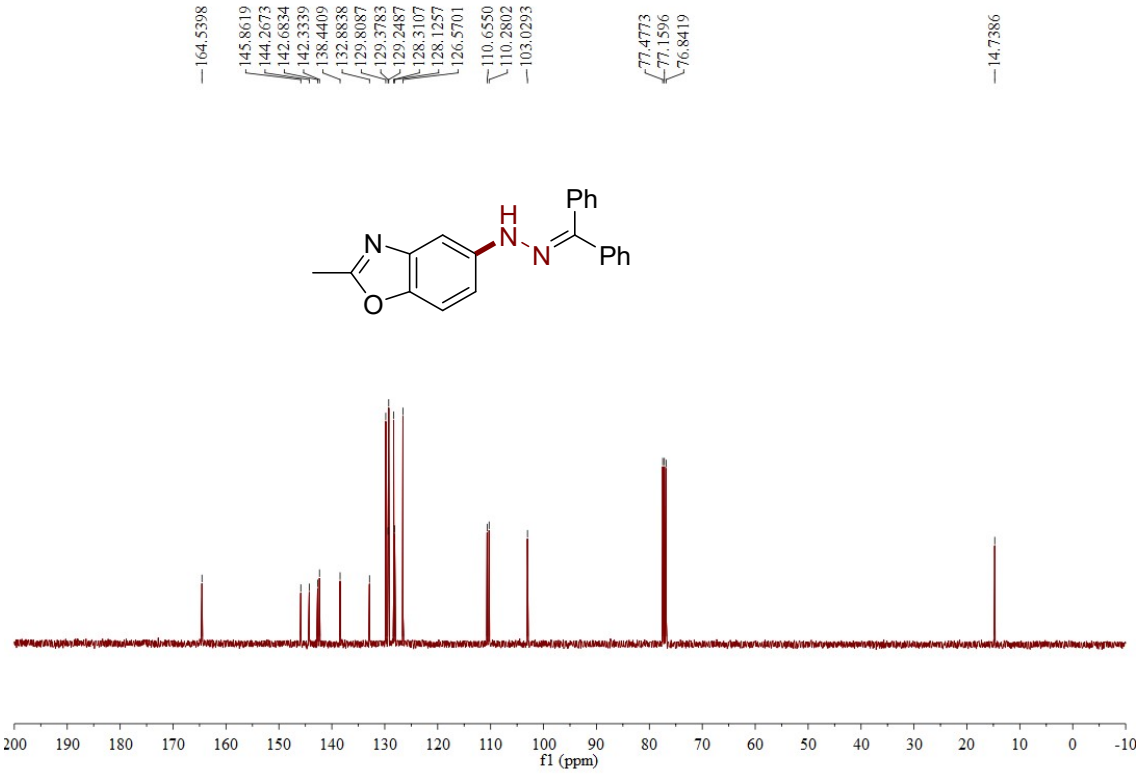
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **29**



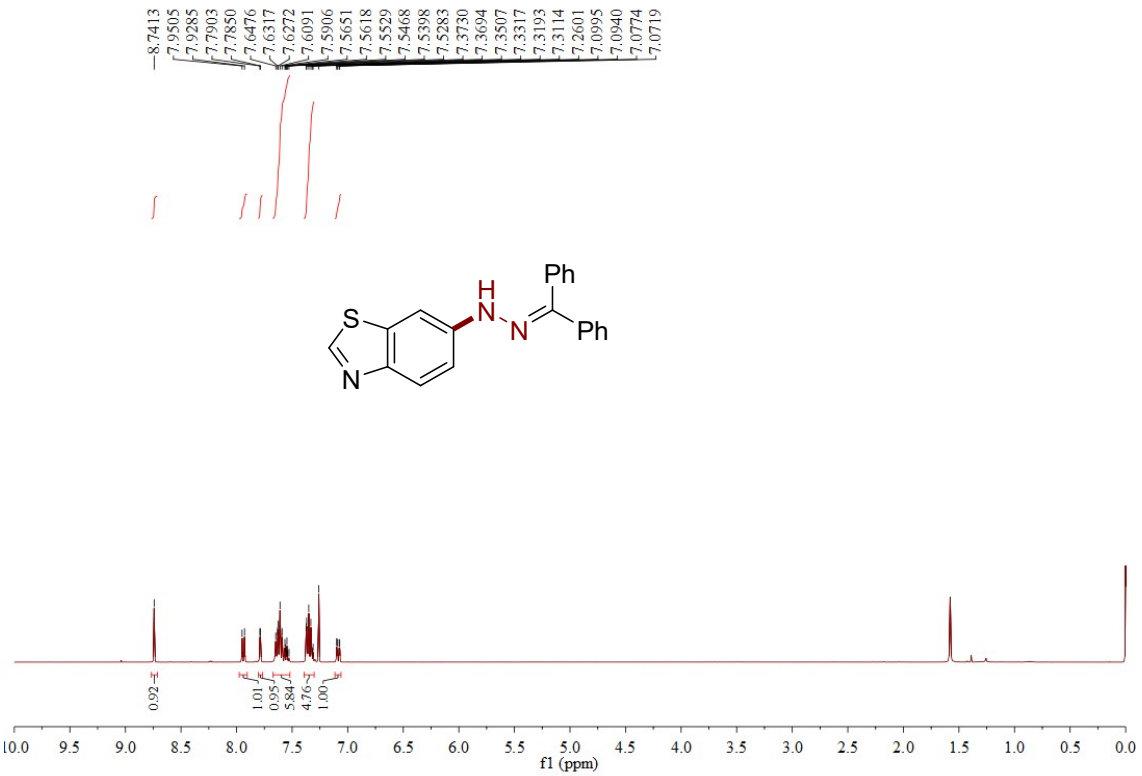
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **29**



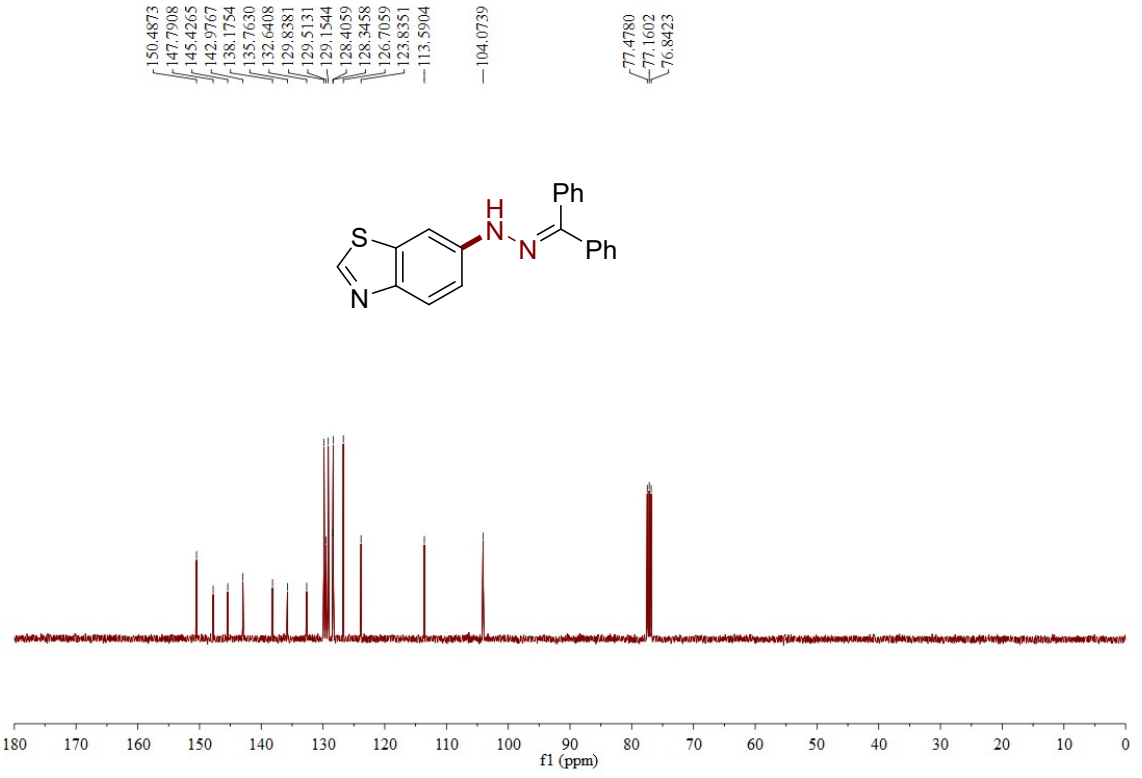
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **30**



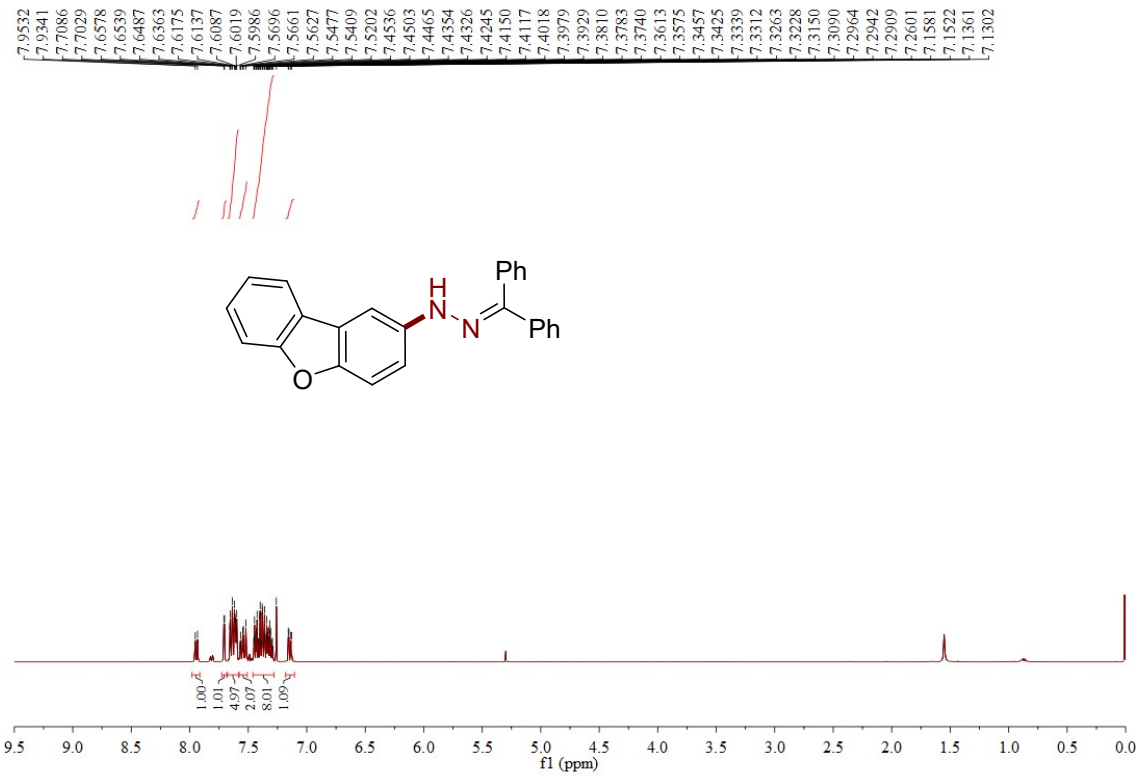
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **30**



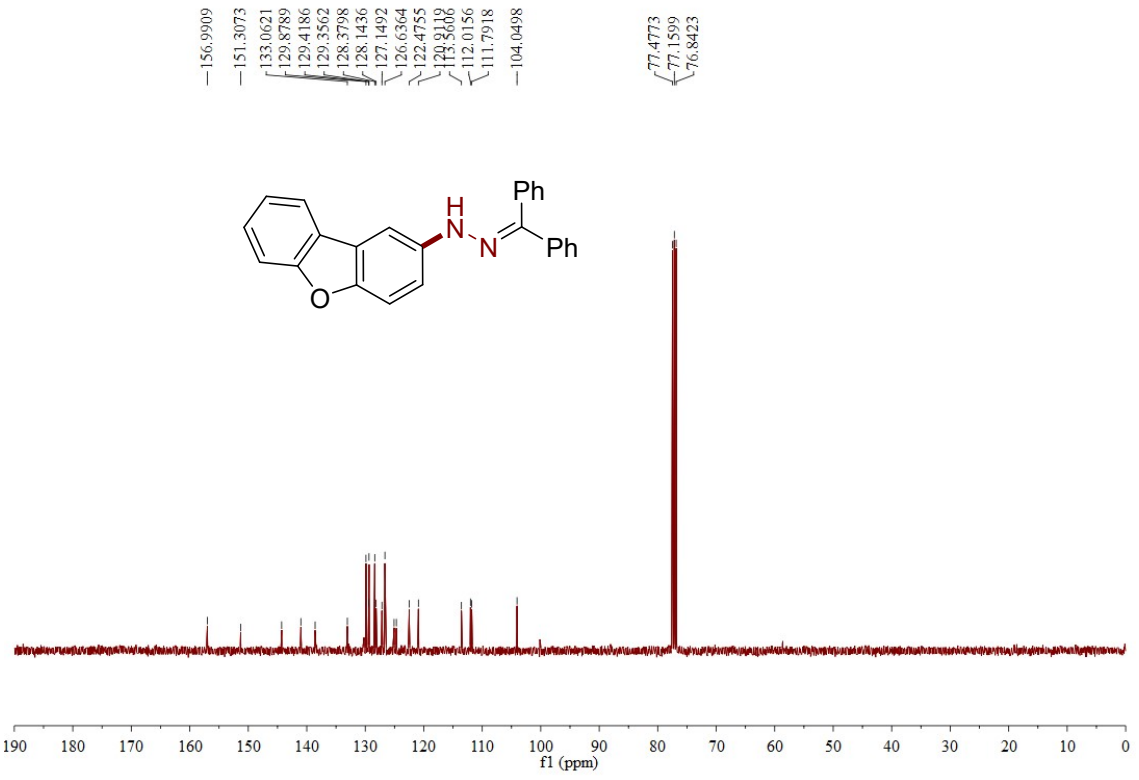
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **31**



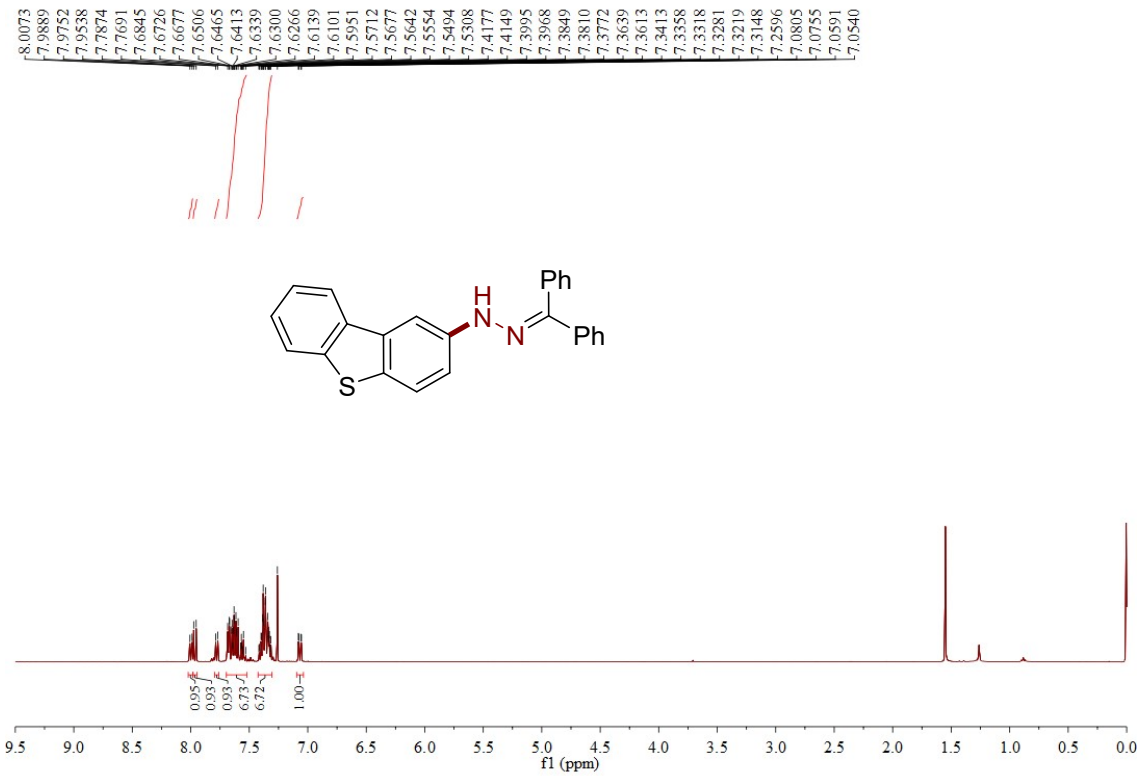
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **31**



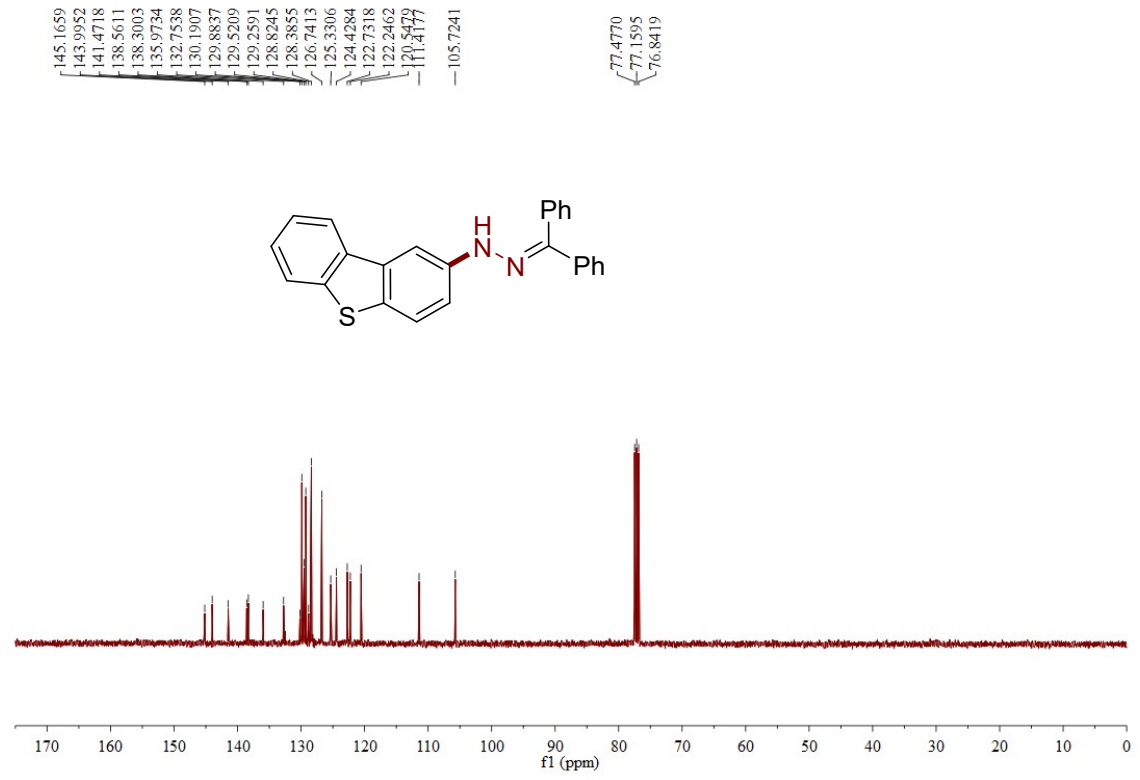
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **32**



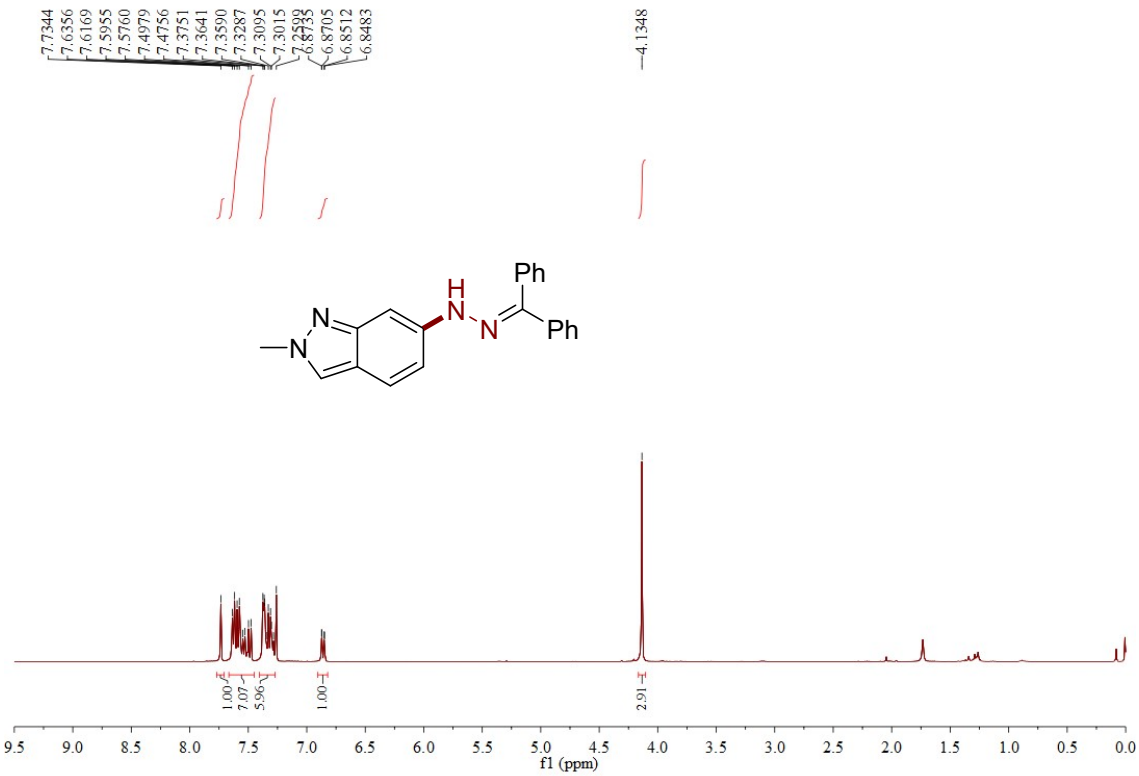
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **32**



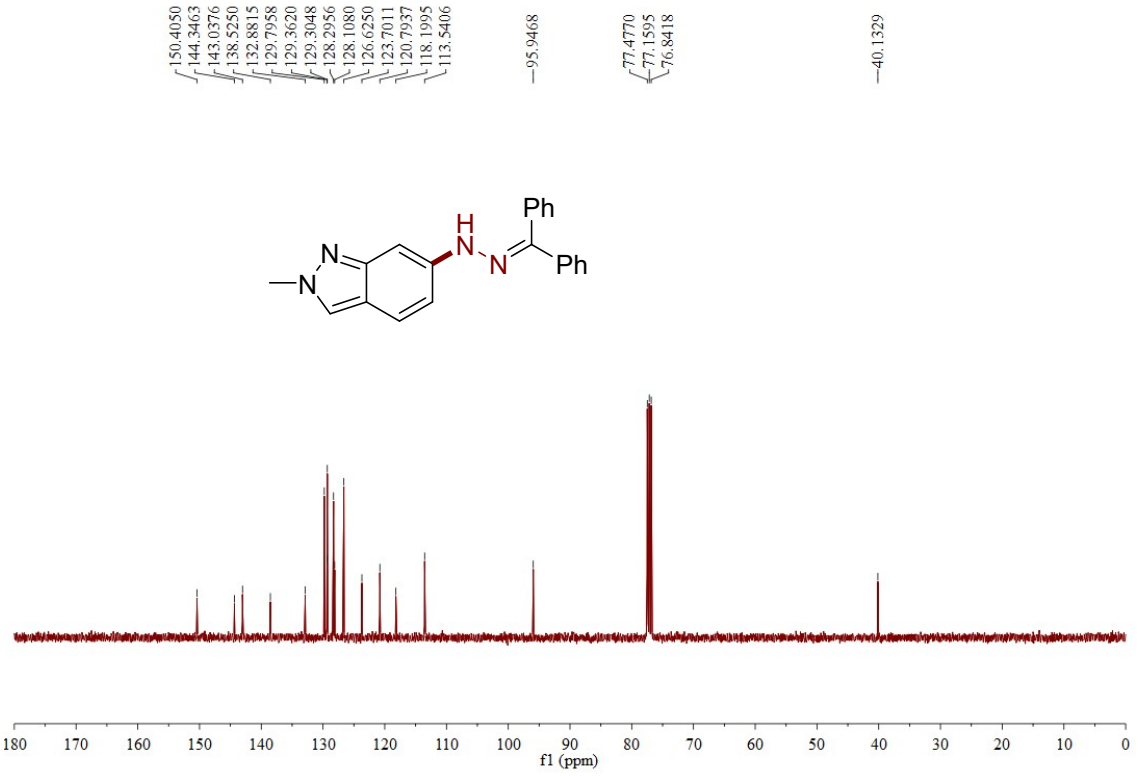
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **33**



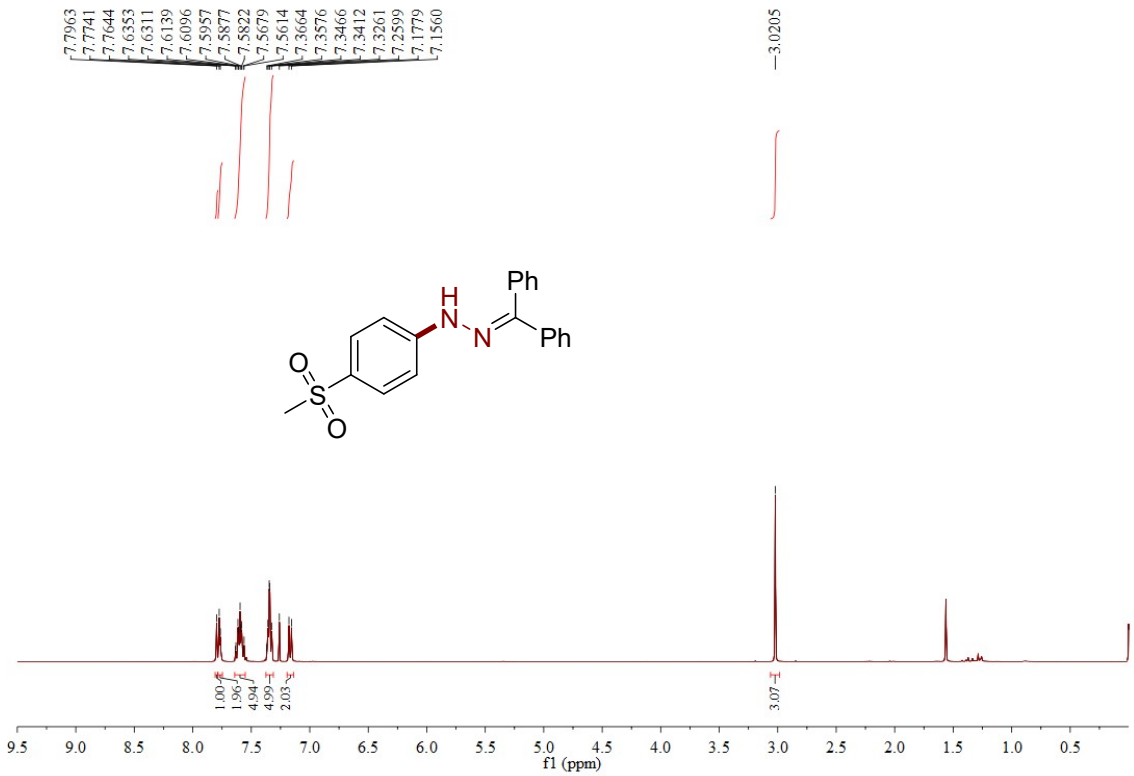
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **33**



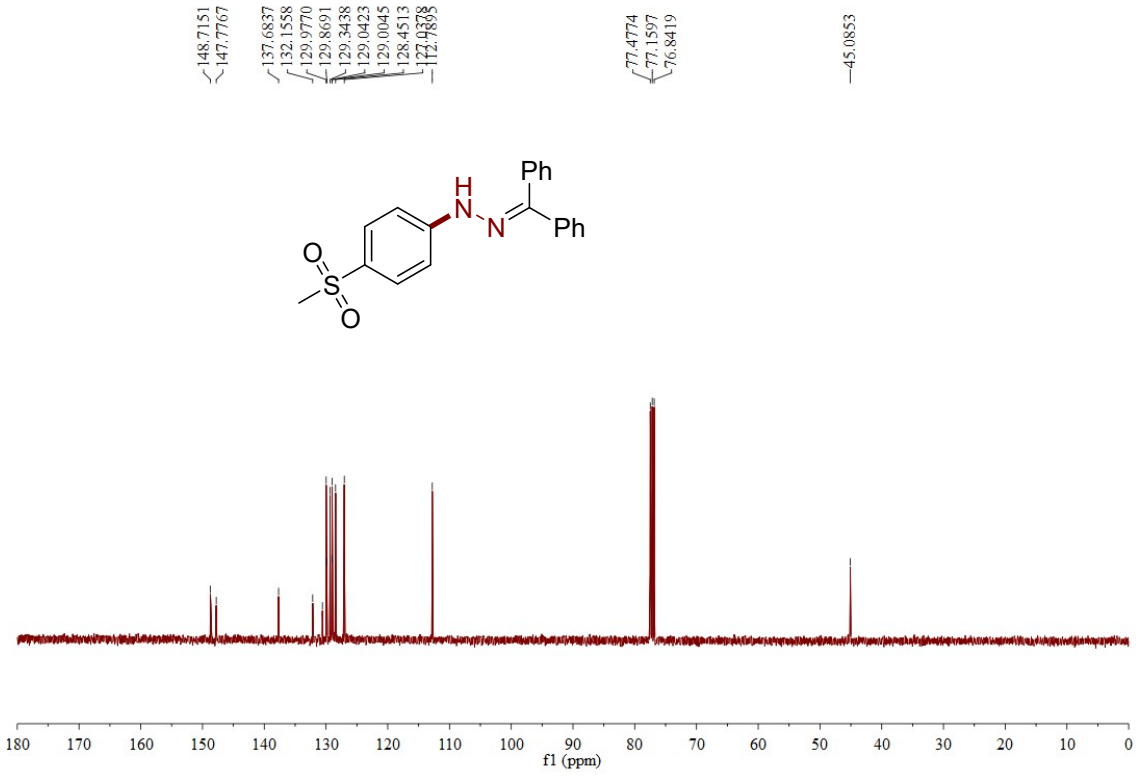
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **34**



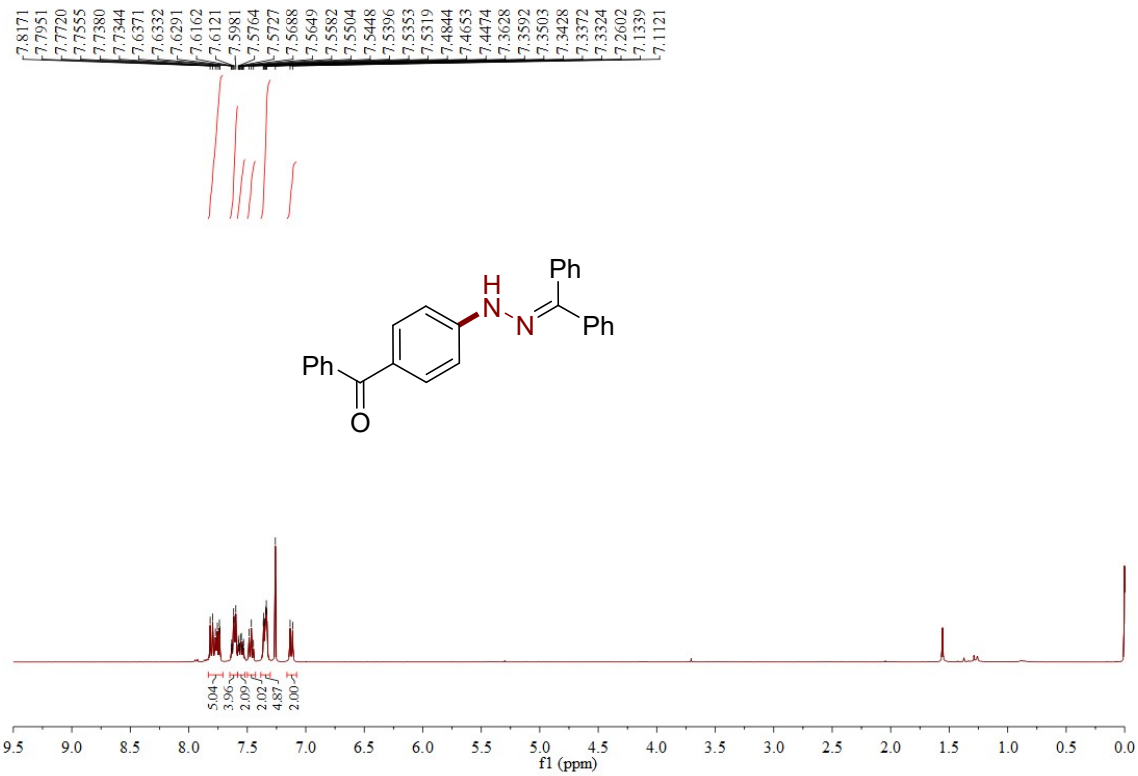
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **34**



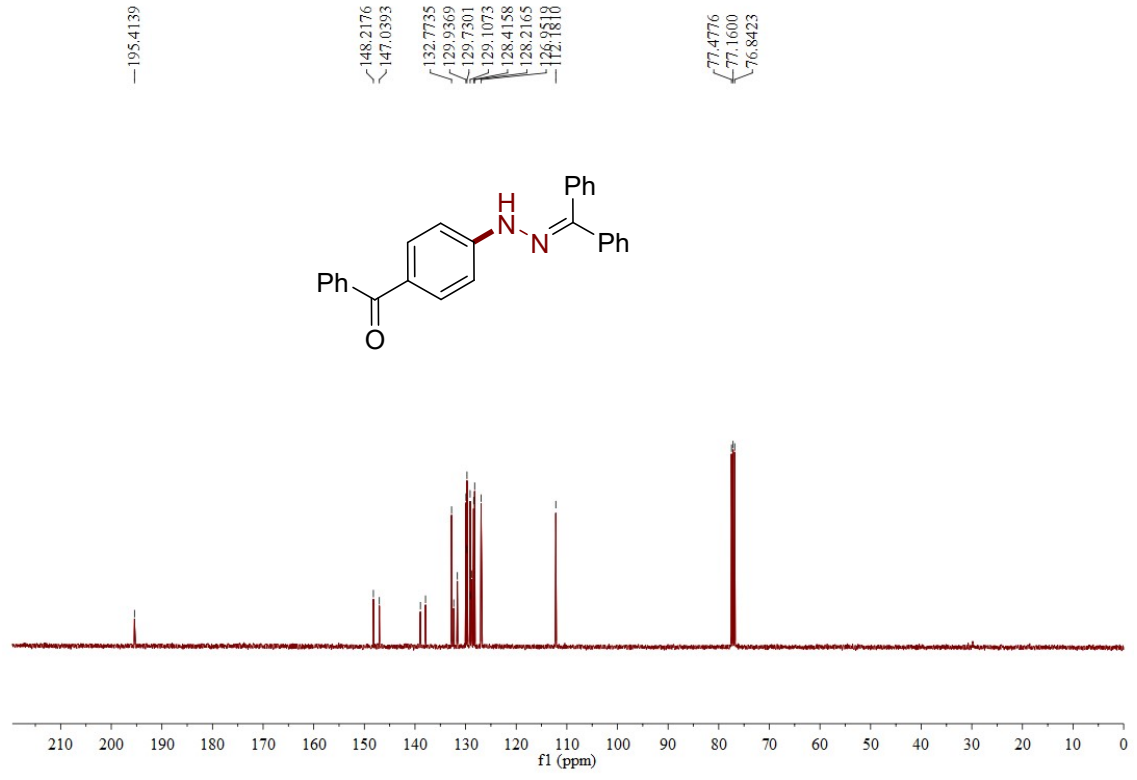
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **35**



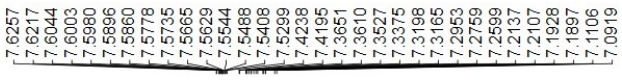
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **35**

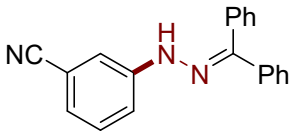


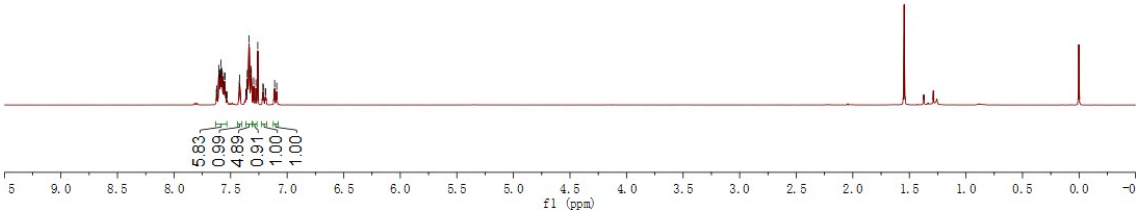
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **36**



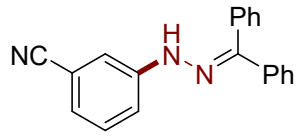
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **36**

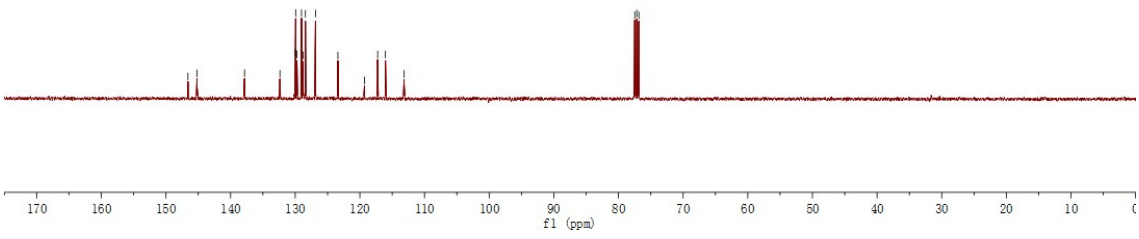




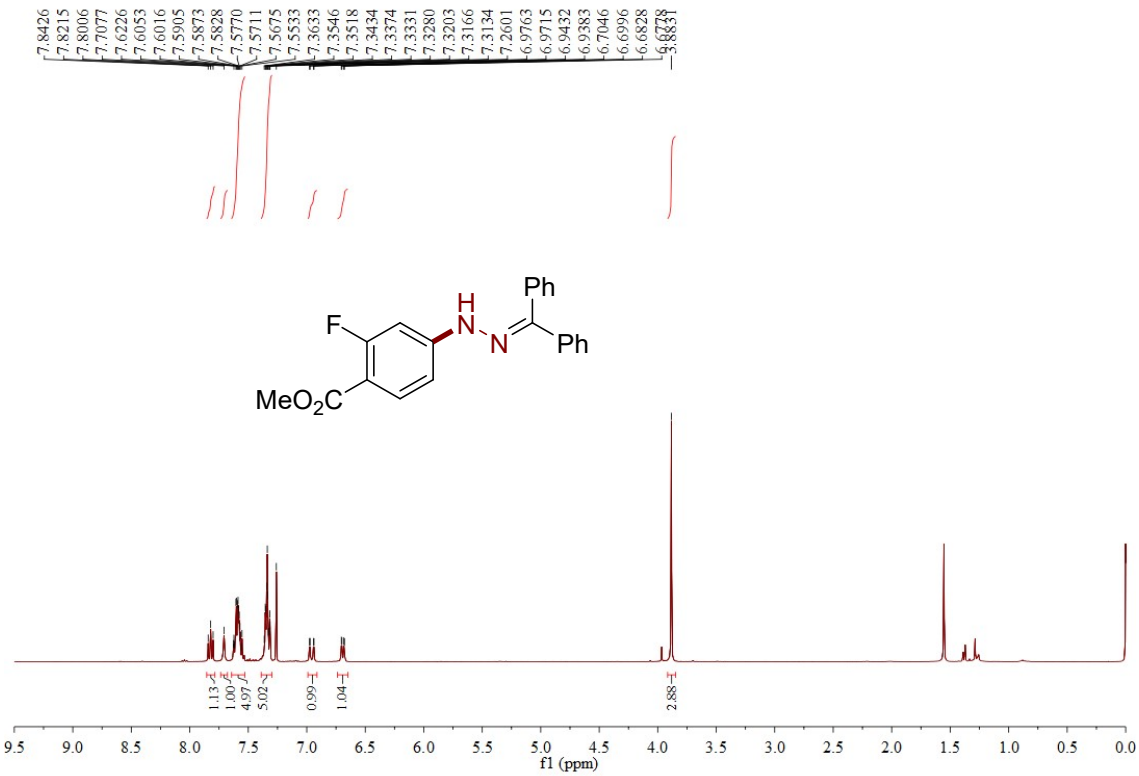


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **37**

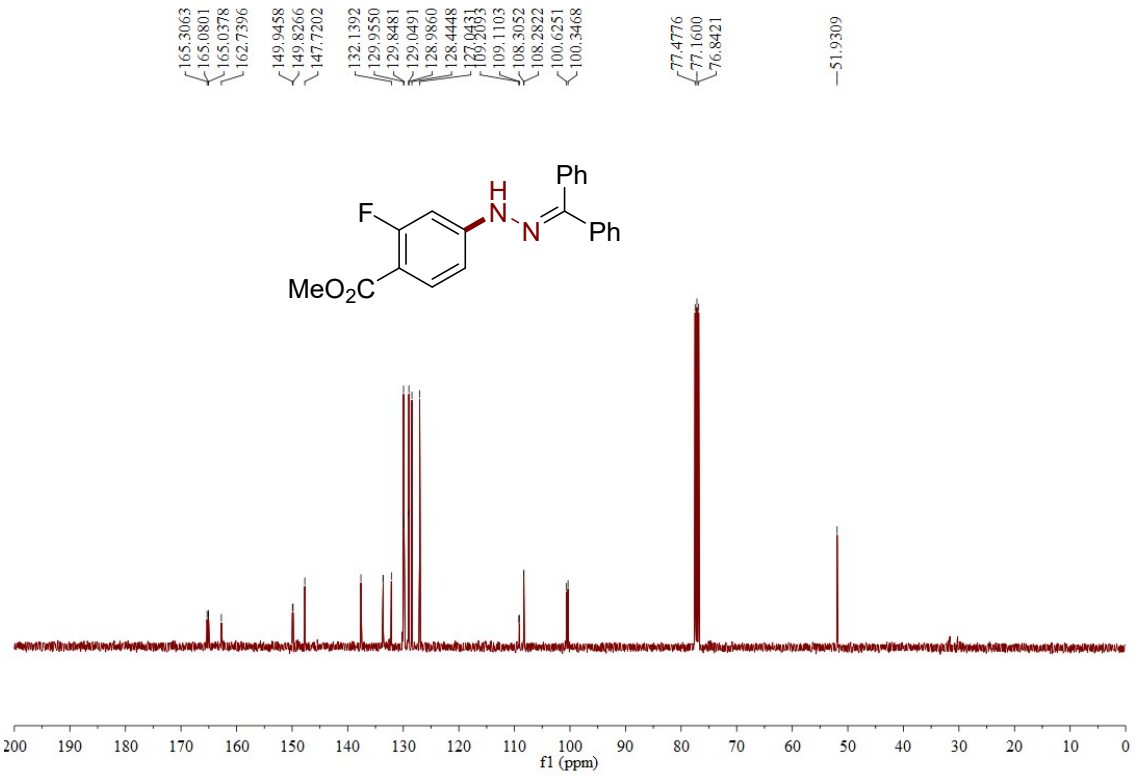




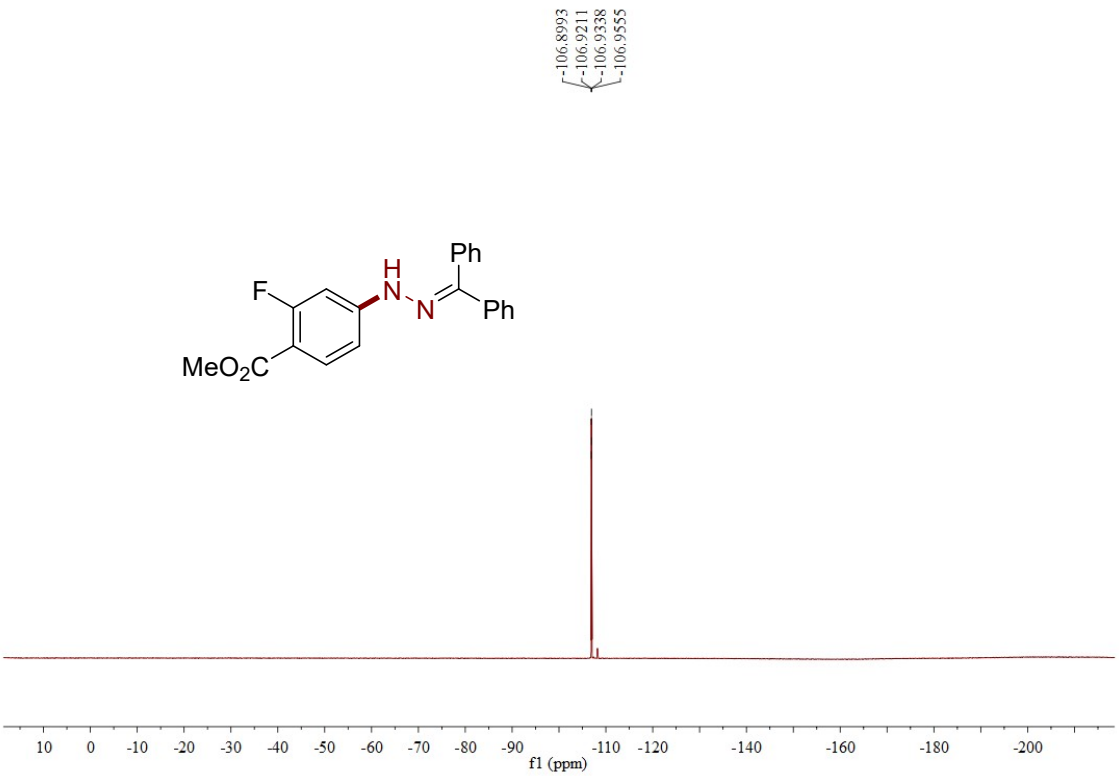
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **37**



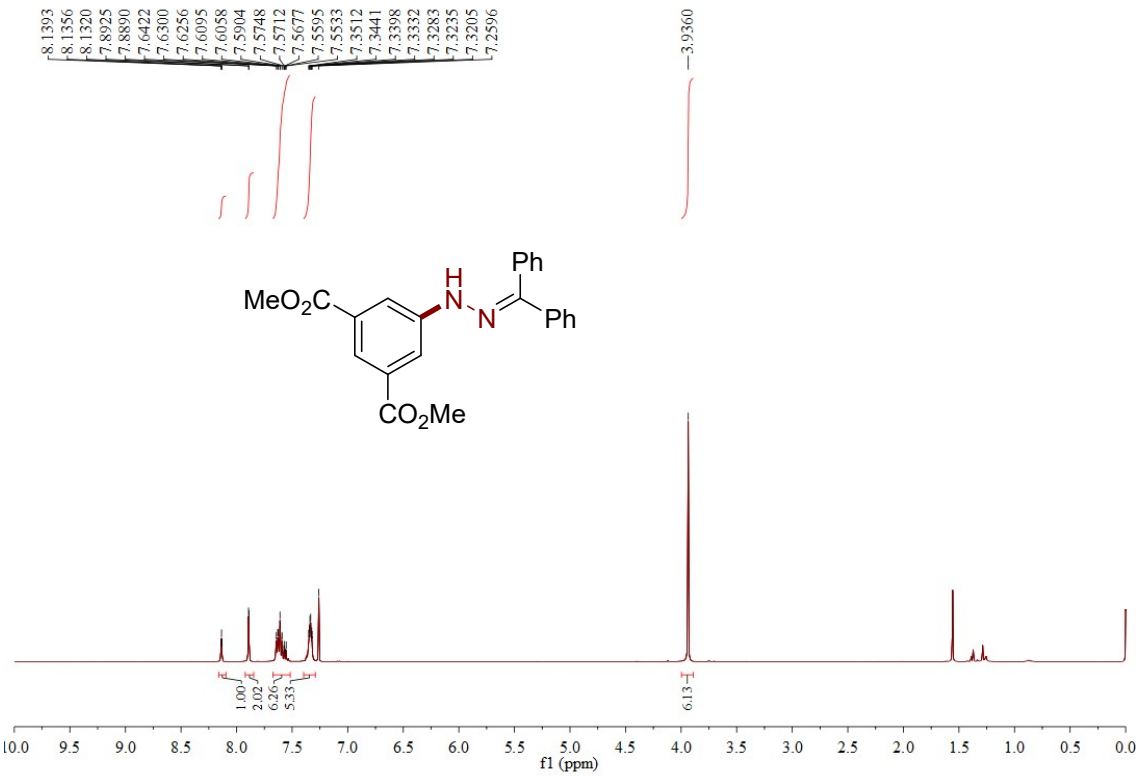
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **38**



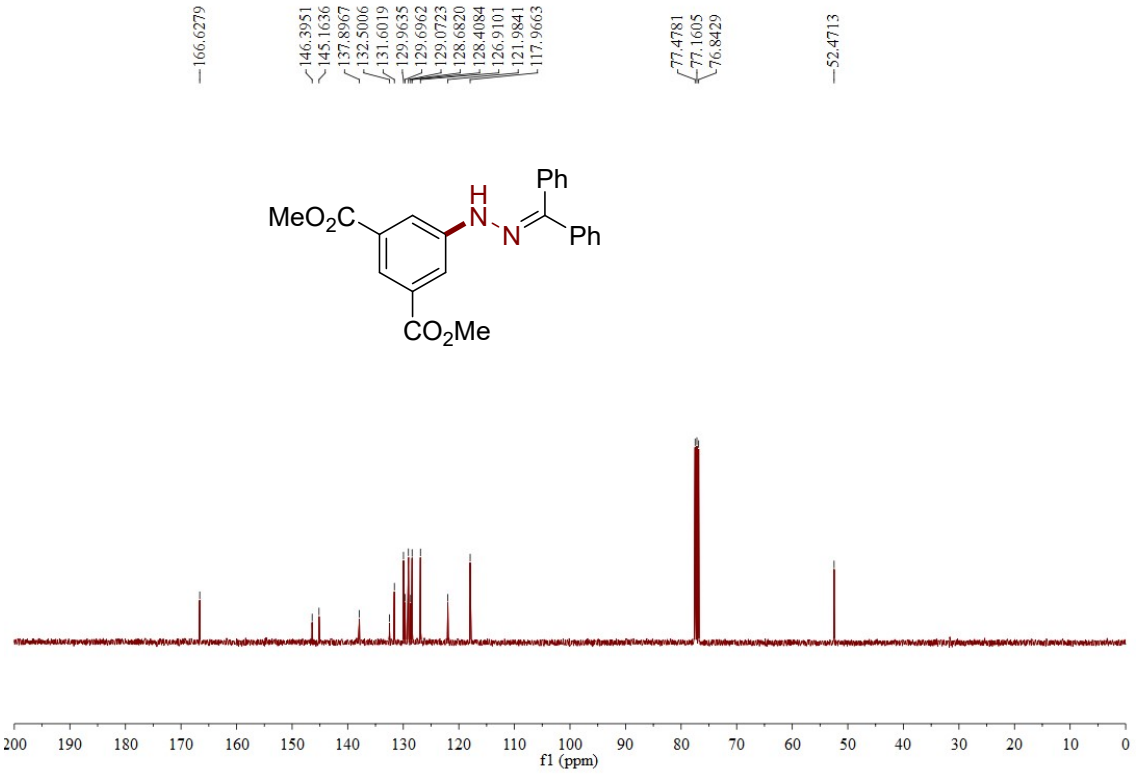
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **38**



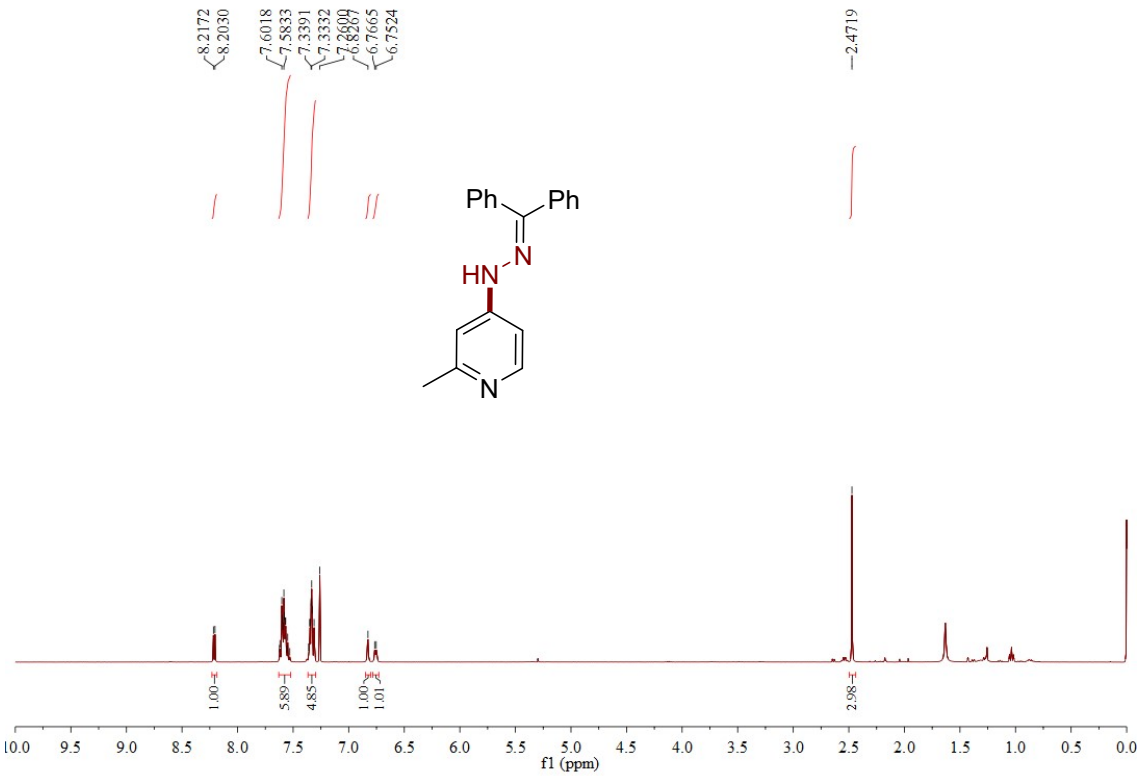
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **38**



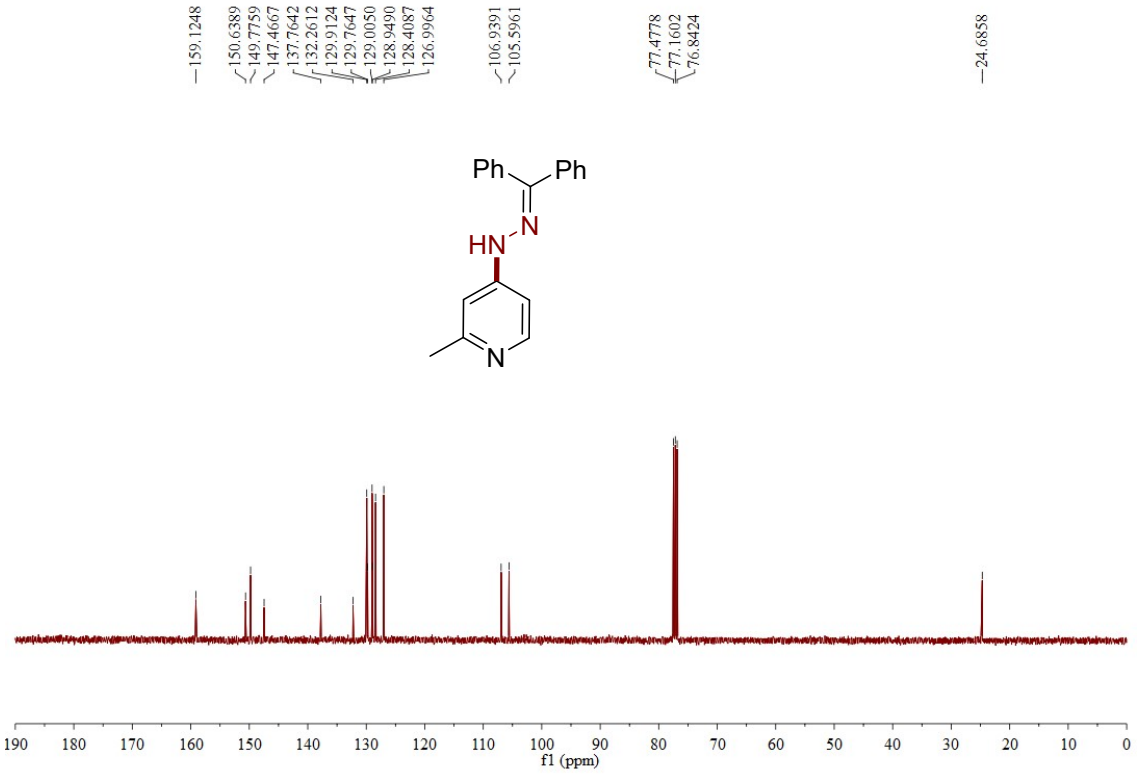
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **39**



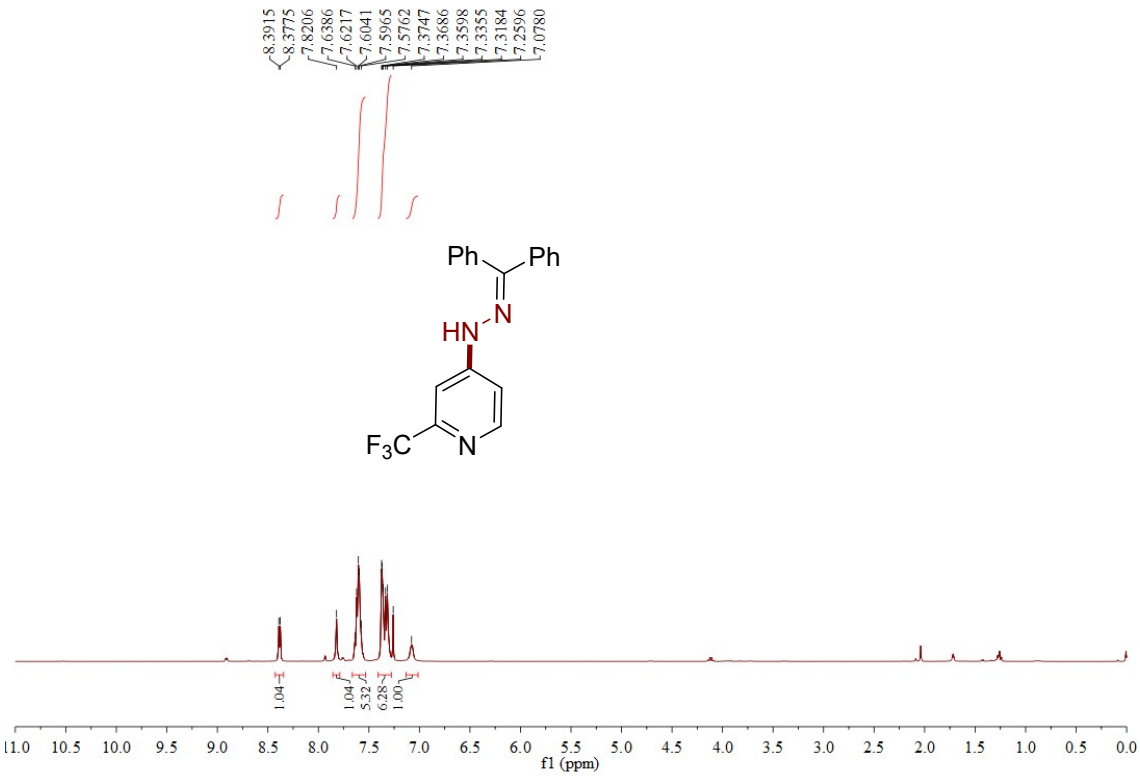
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **39**



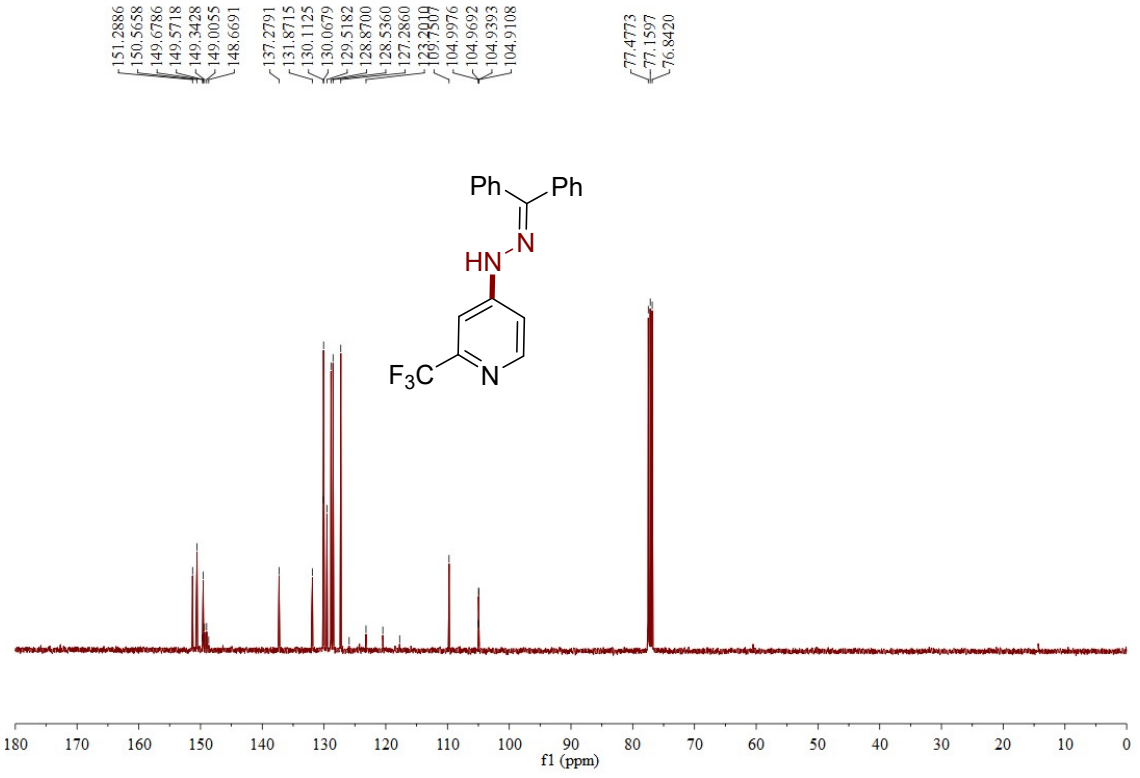
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **40**



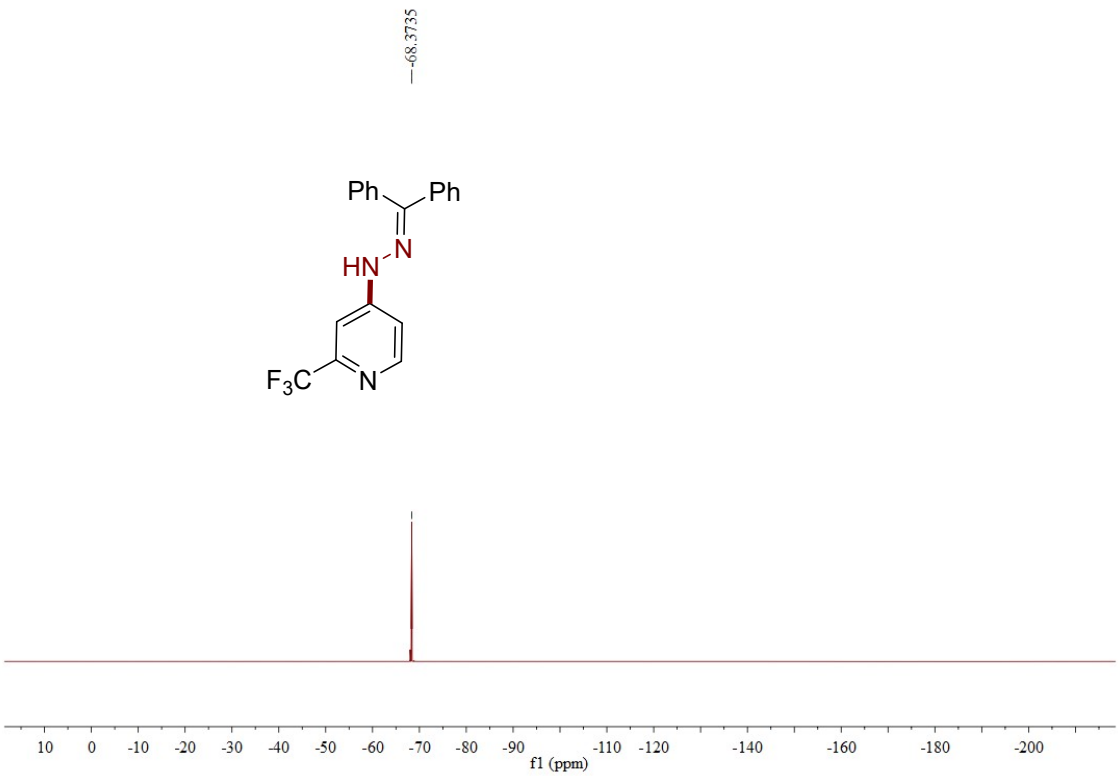
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **40**



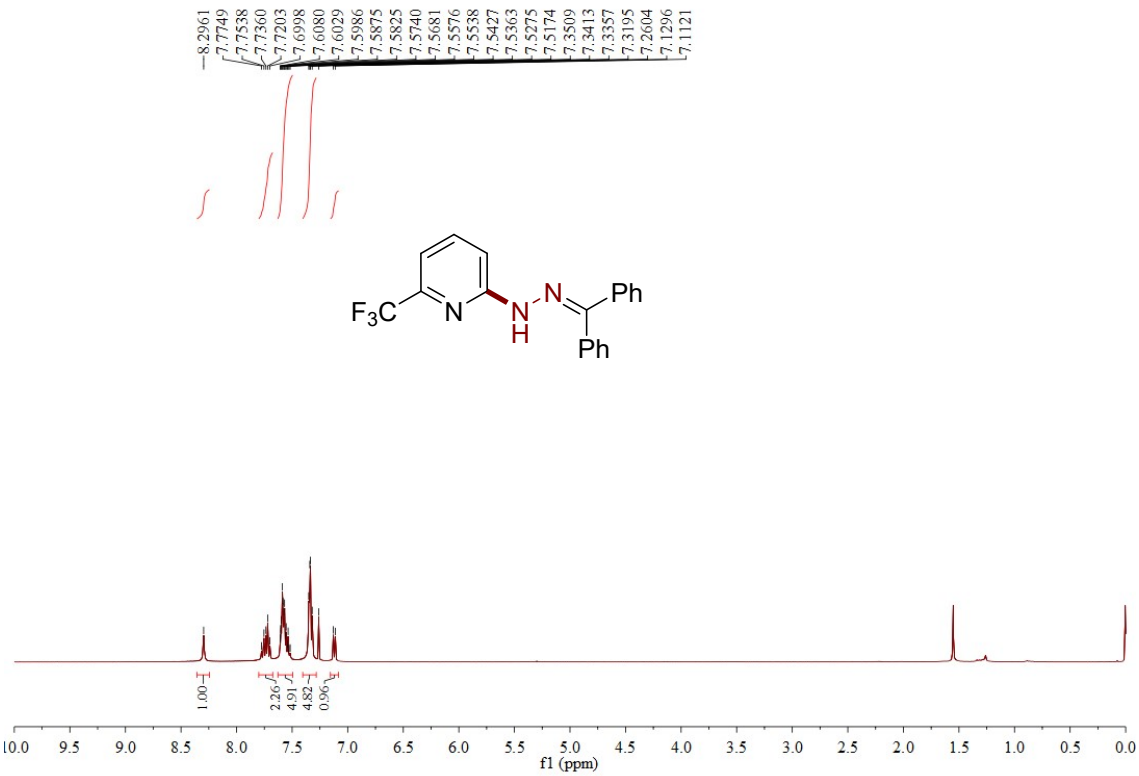
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **41**



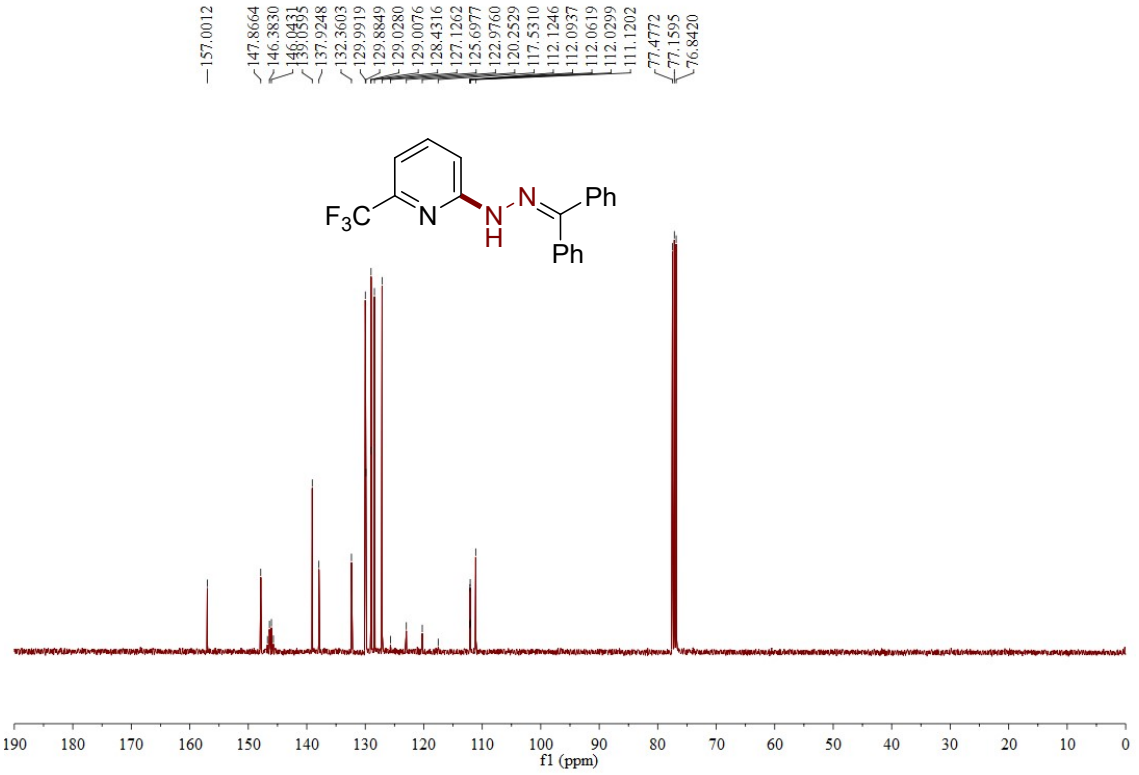
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **41**



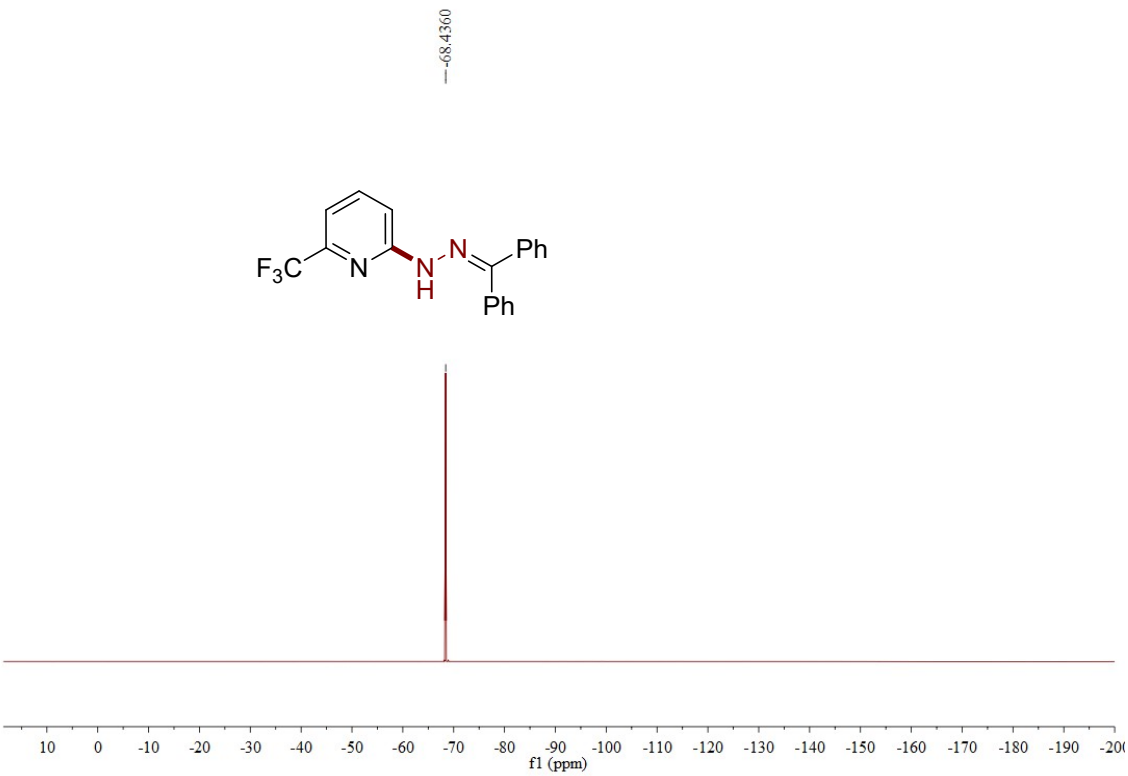
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **41**



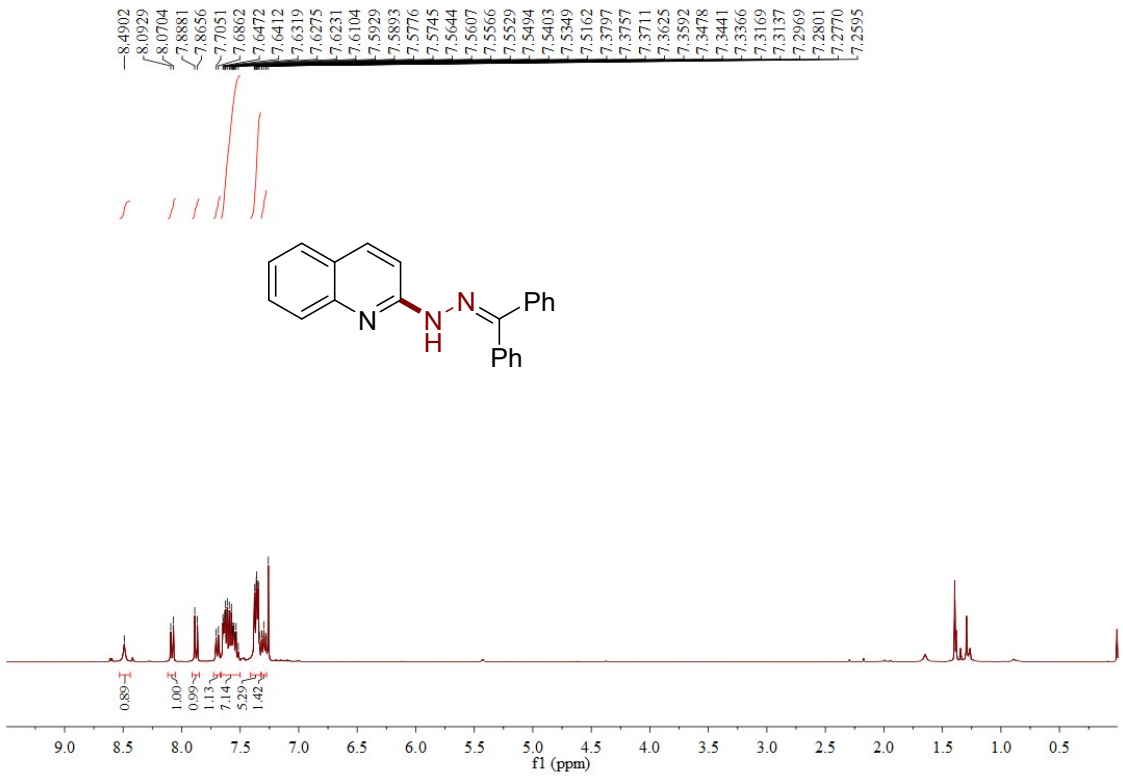
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **42**



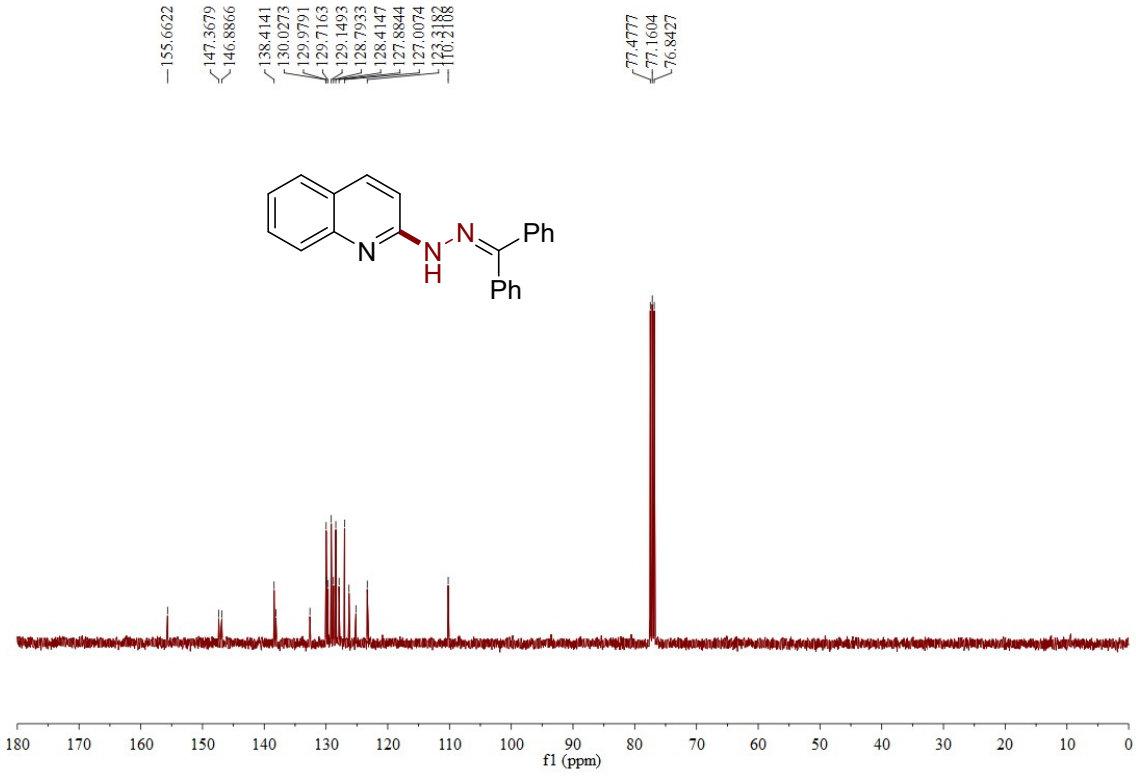
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **42**



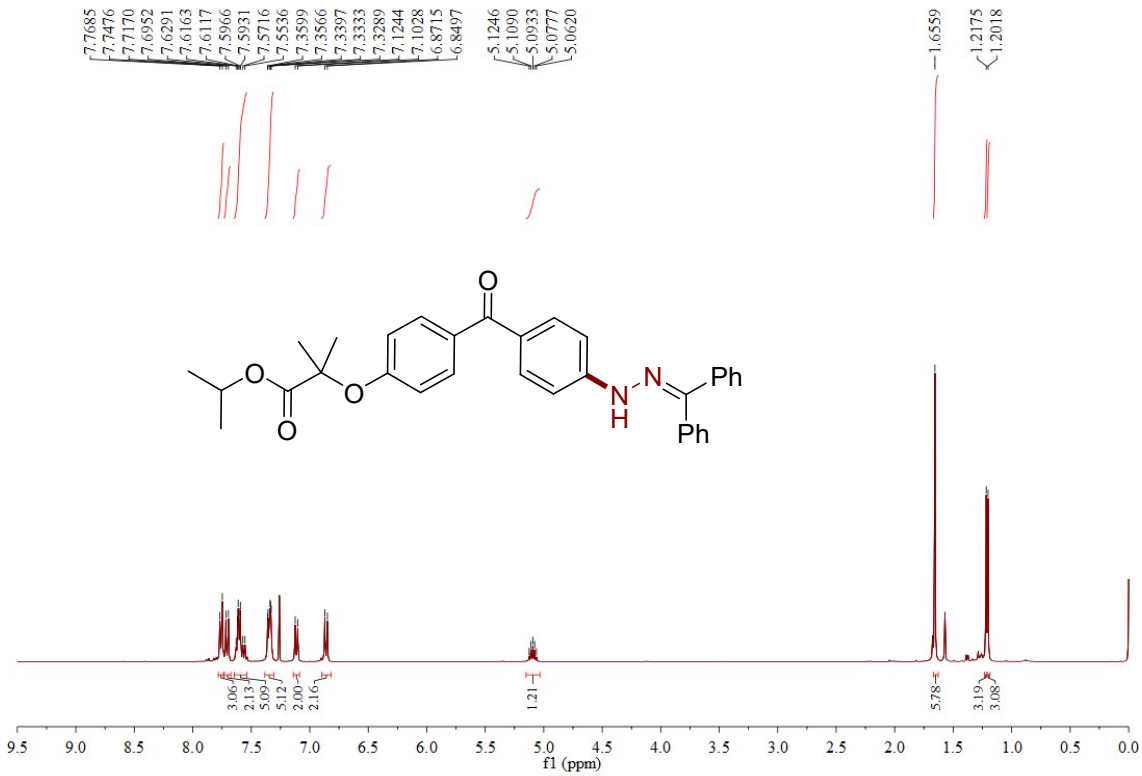
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **42**



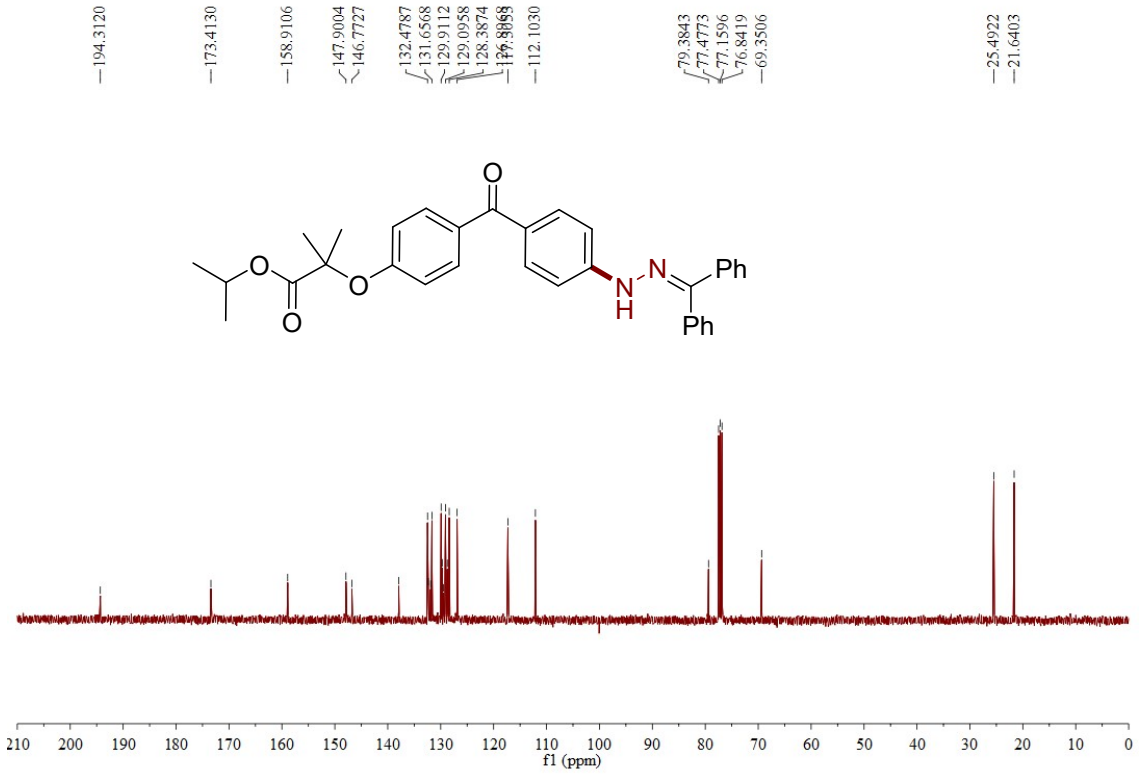
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **43**



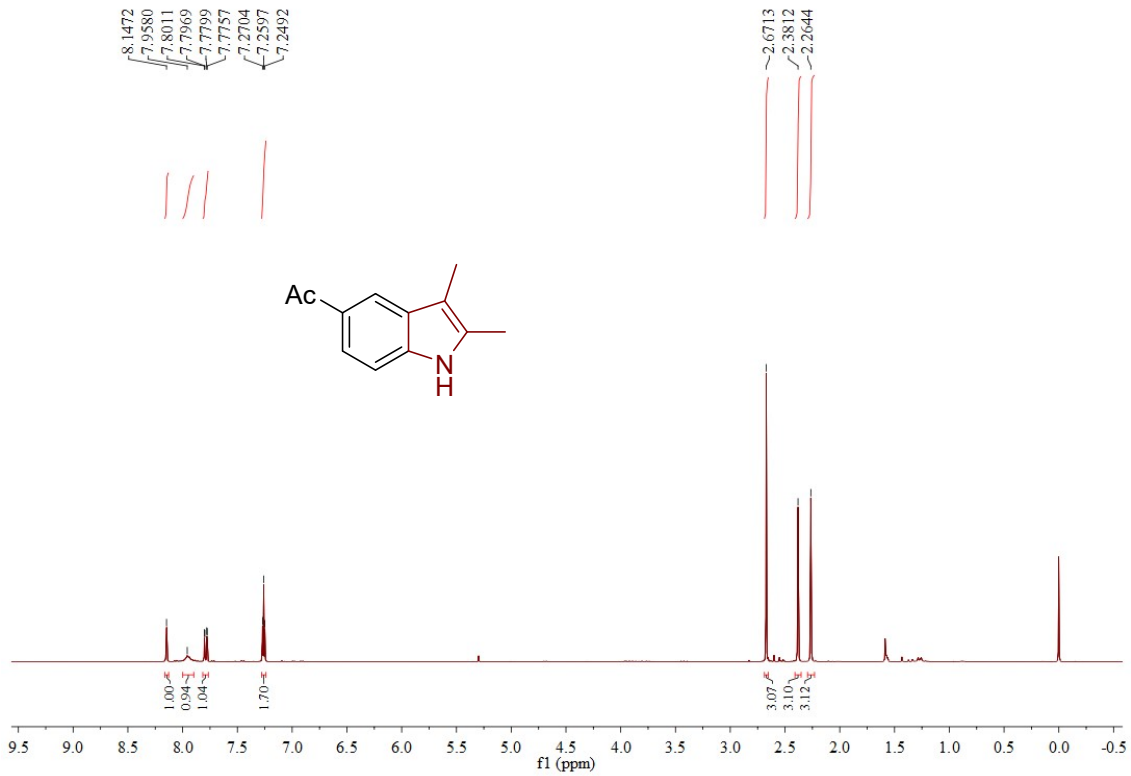
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **43**



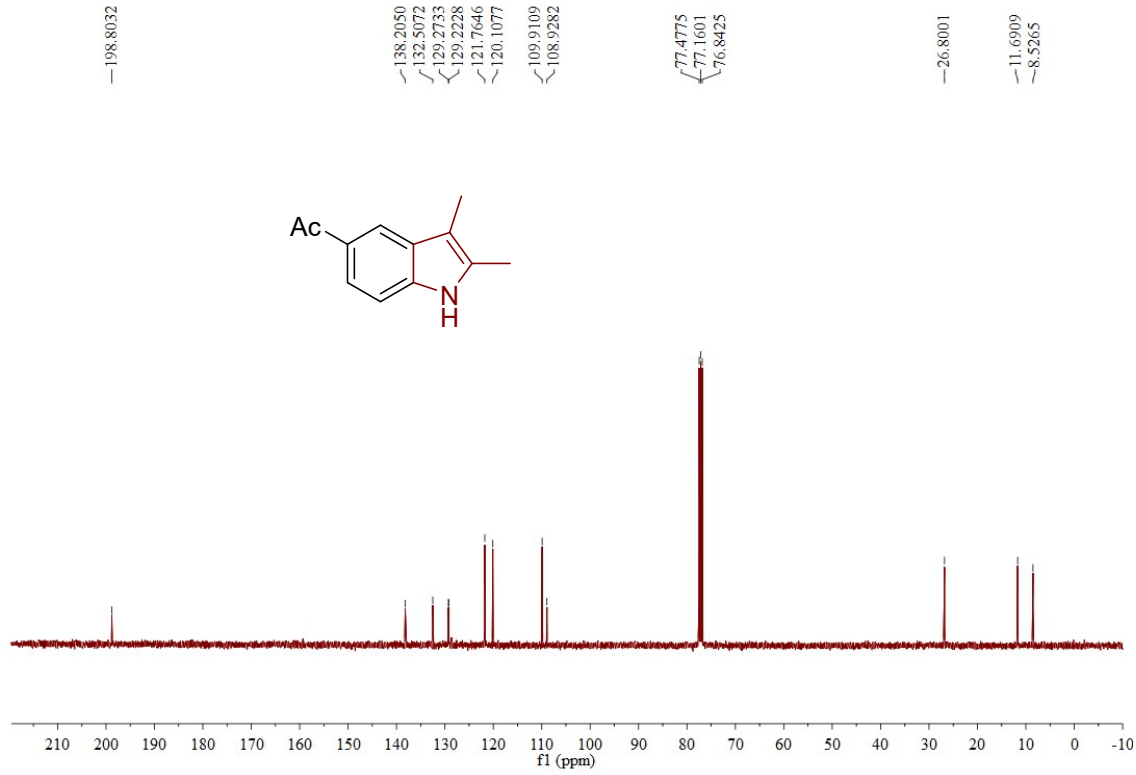
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **44**



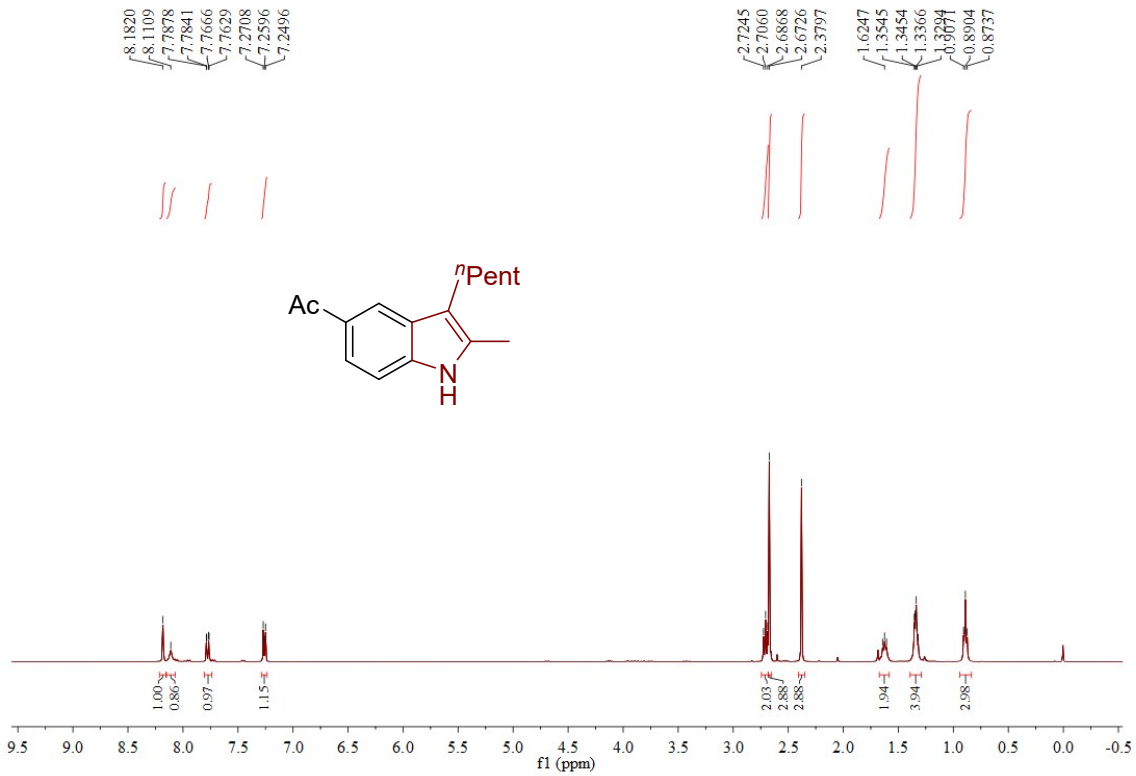
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **44**



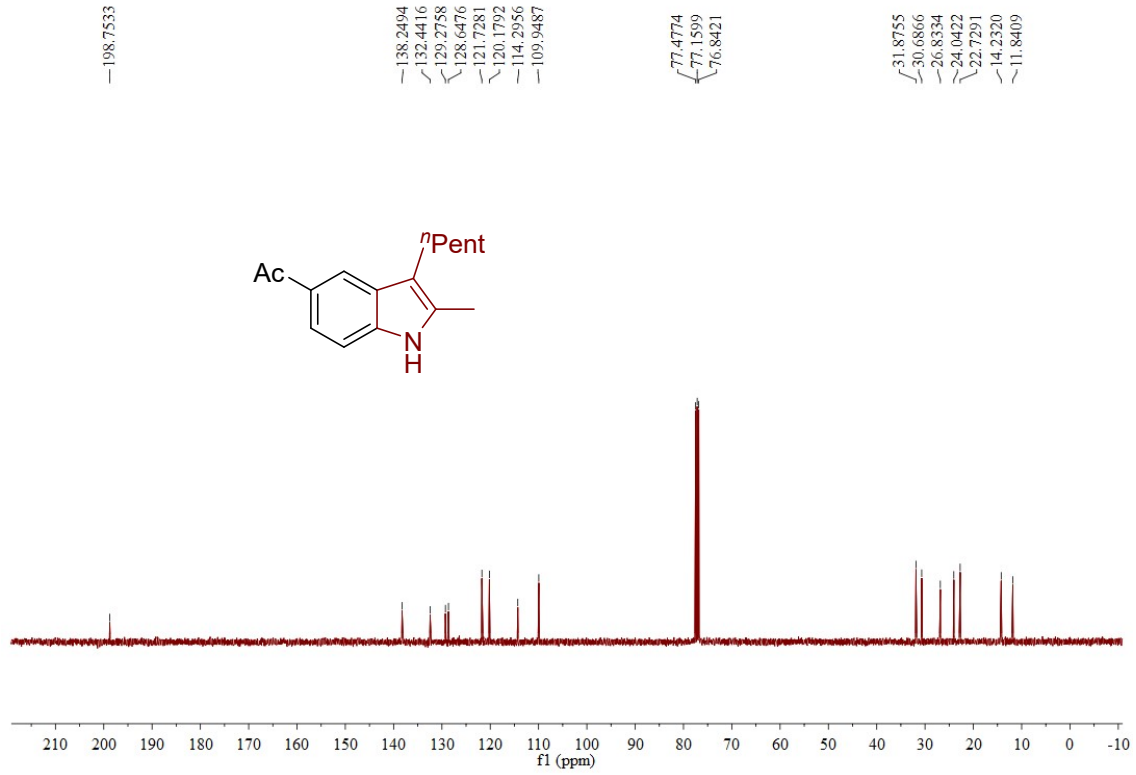
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **45**



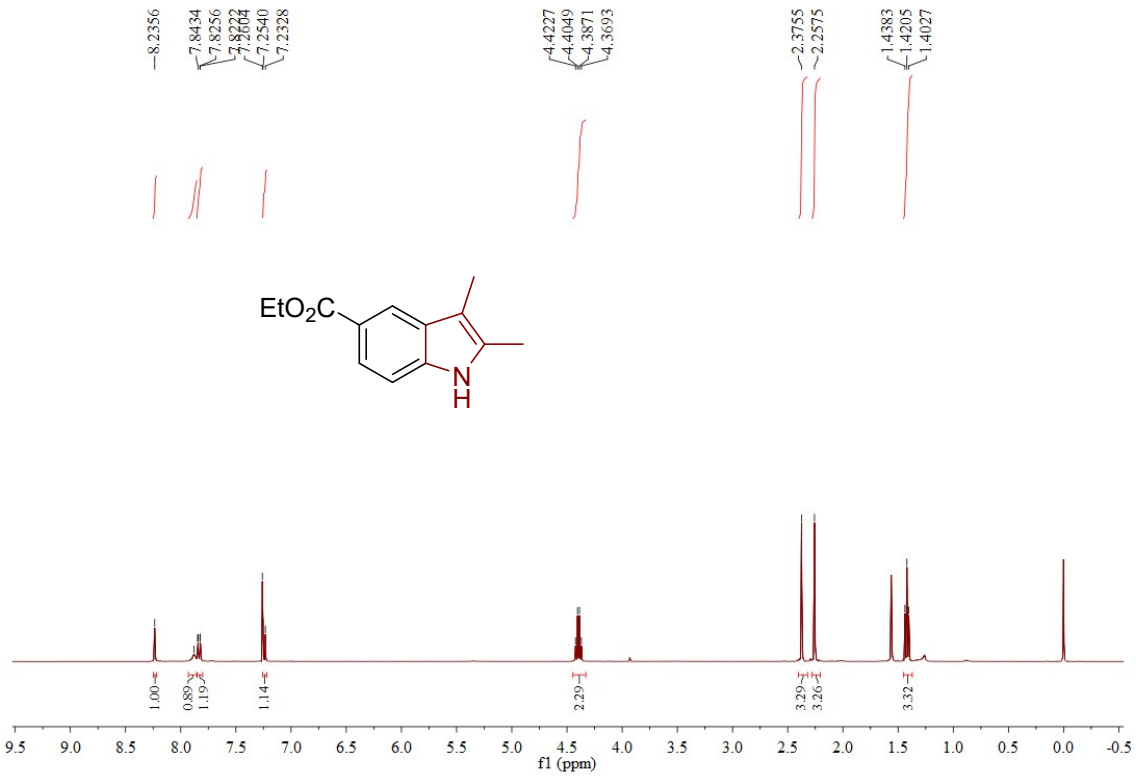
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **45**



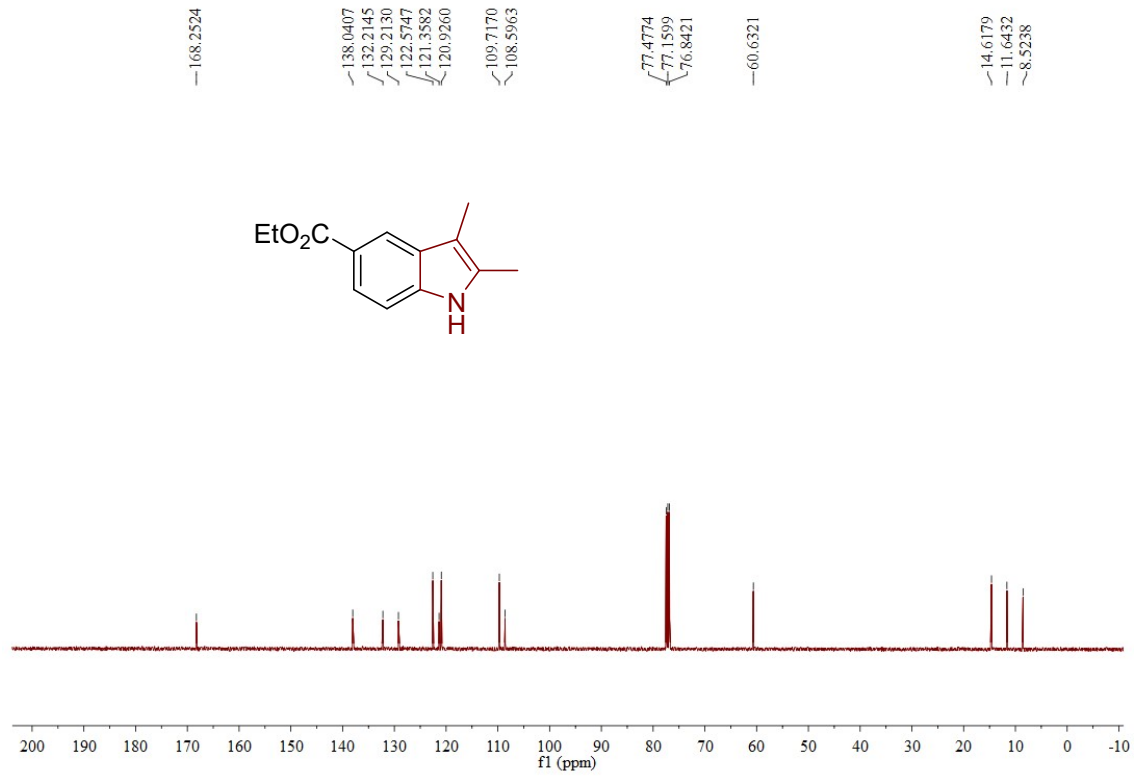
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **46**



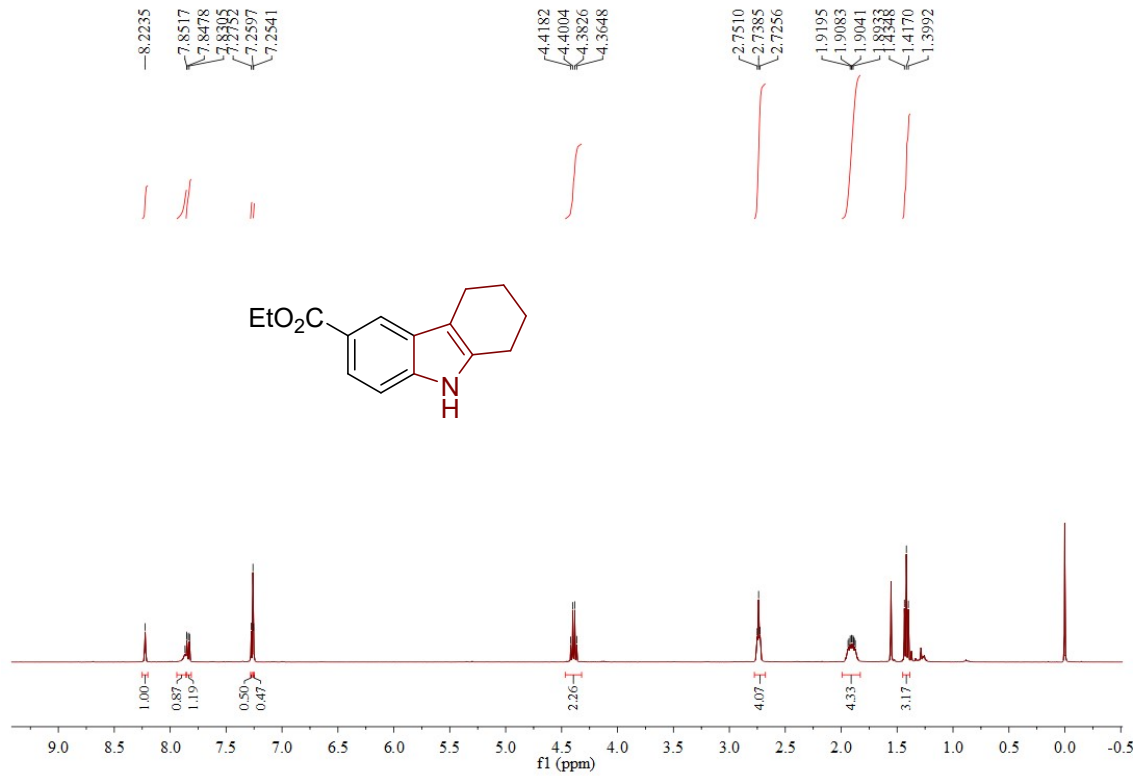
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **46**



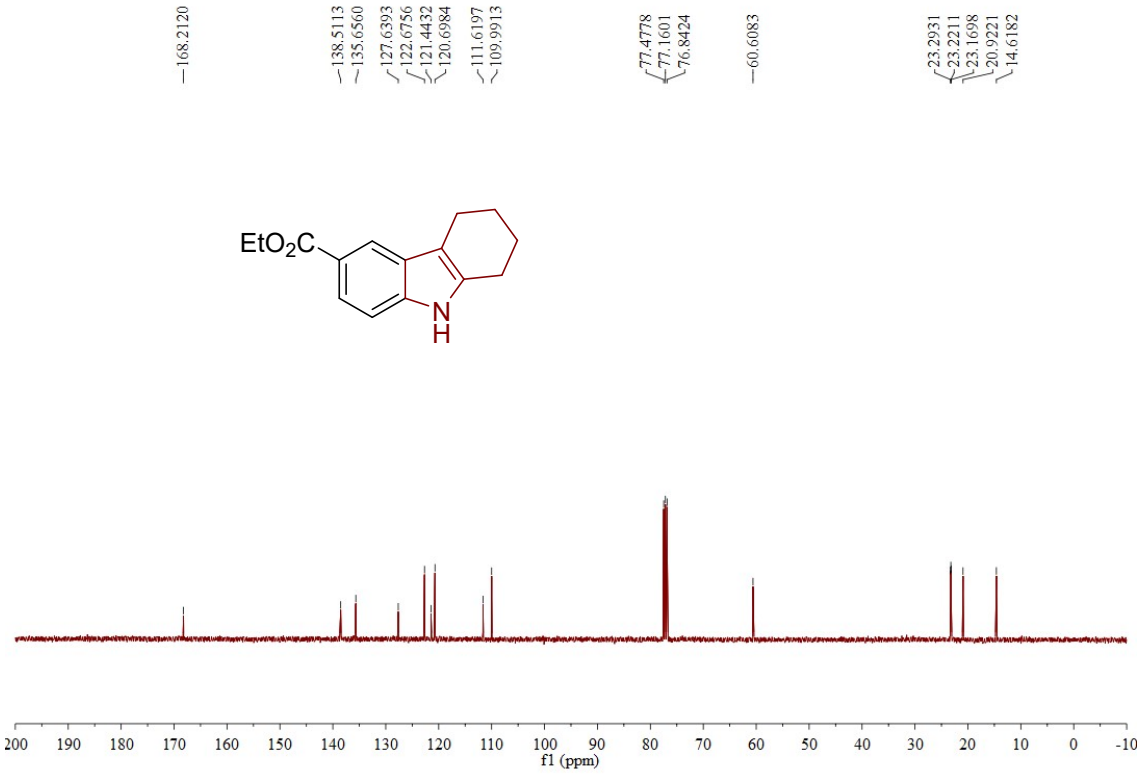
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **47**



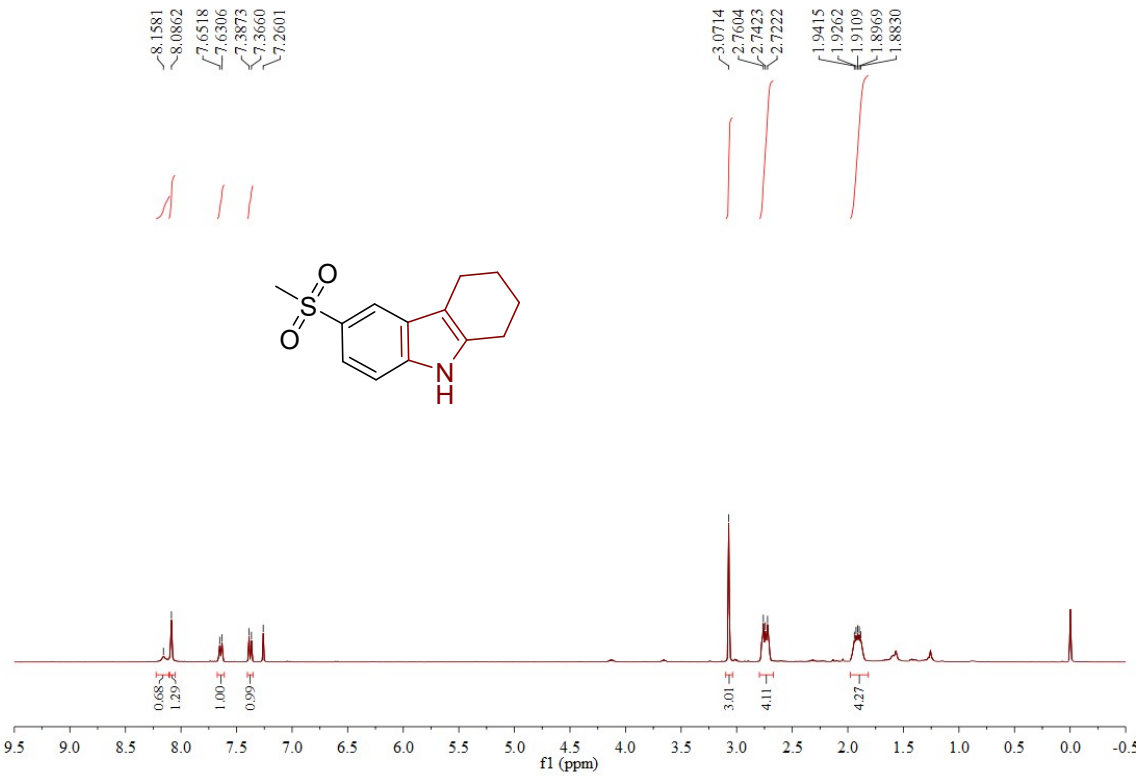
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **47**



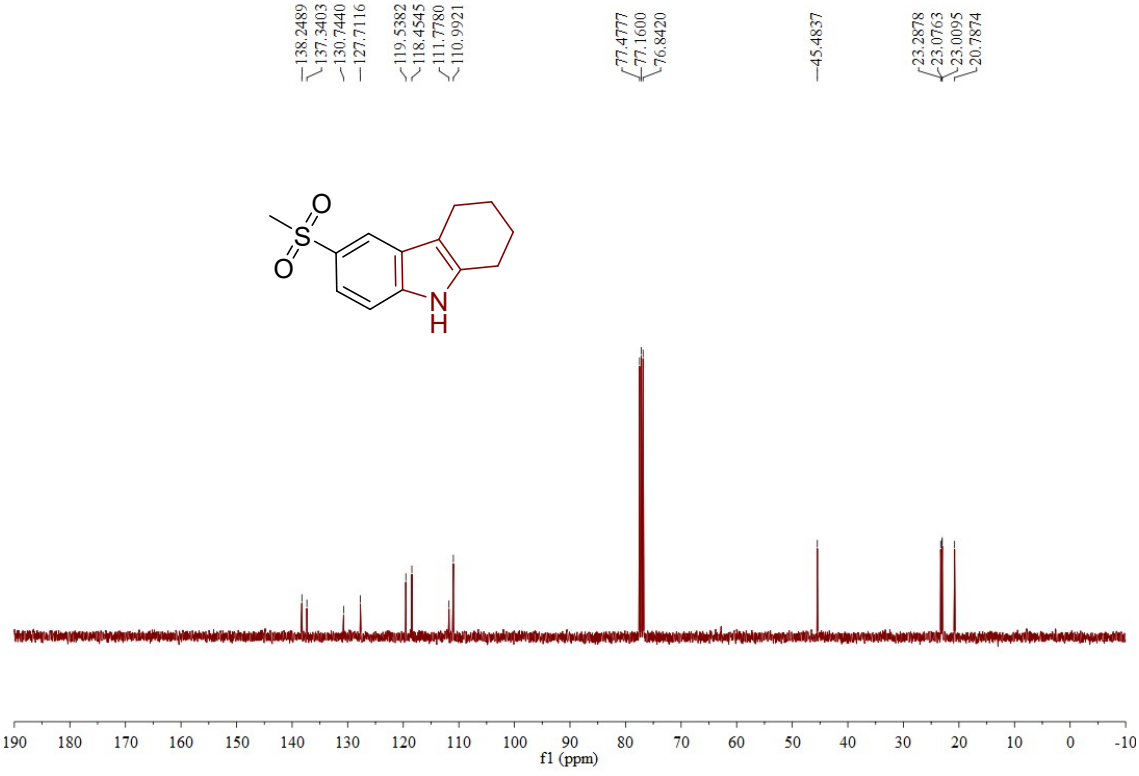
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **48**



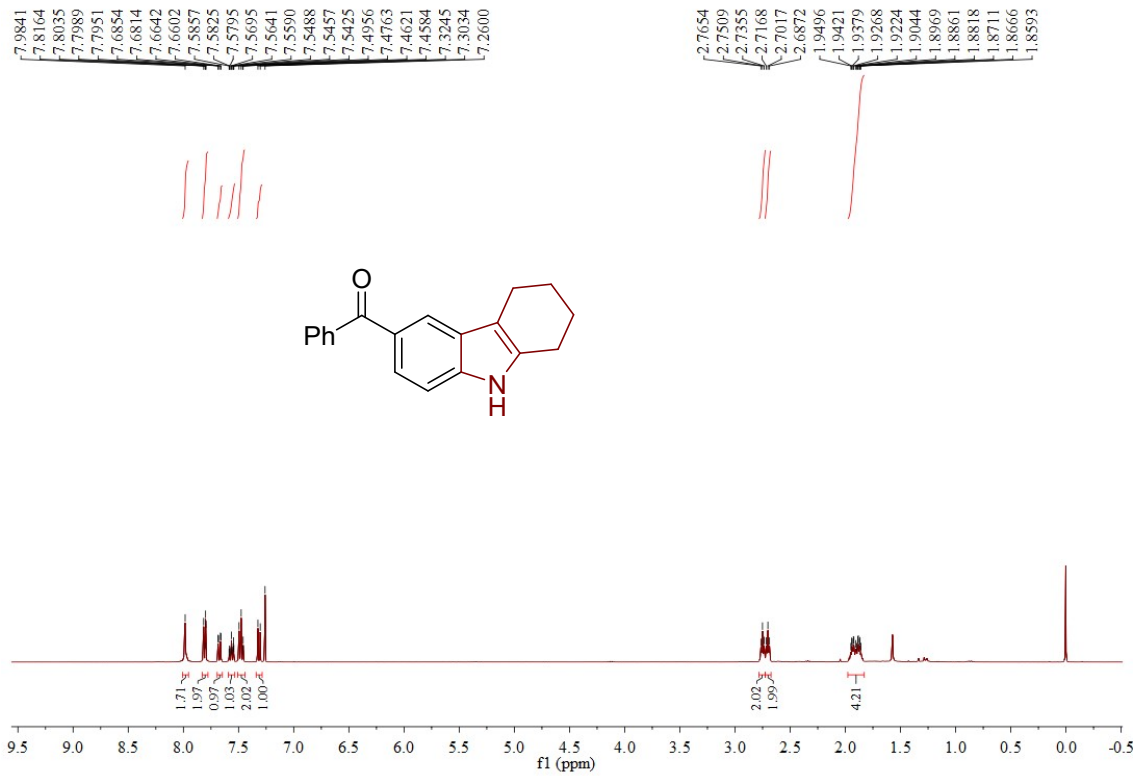
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **48**



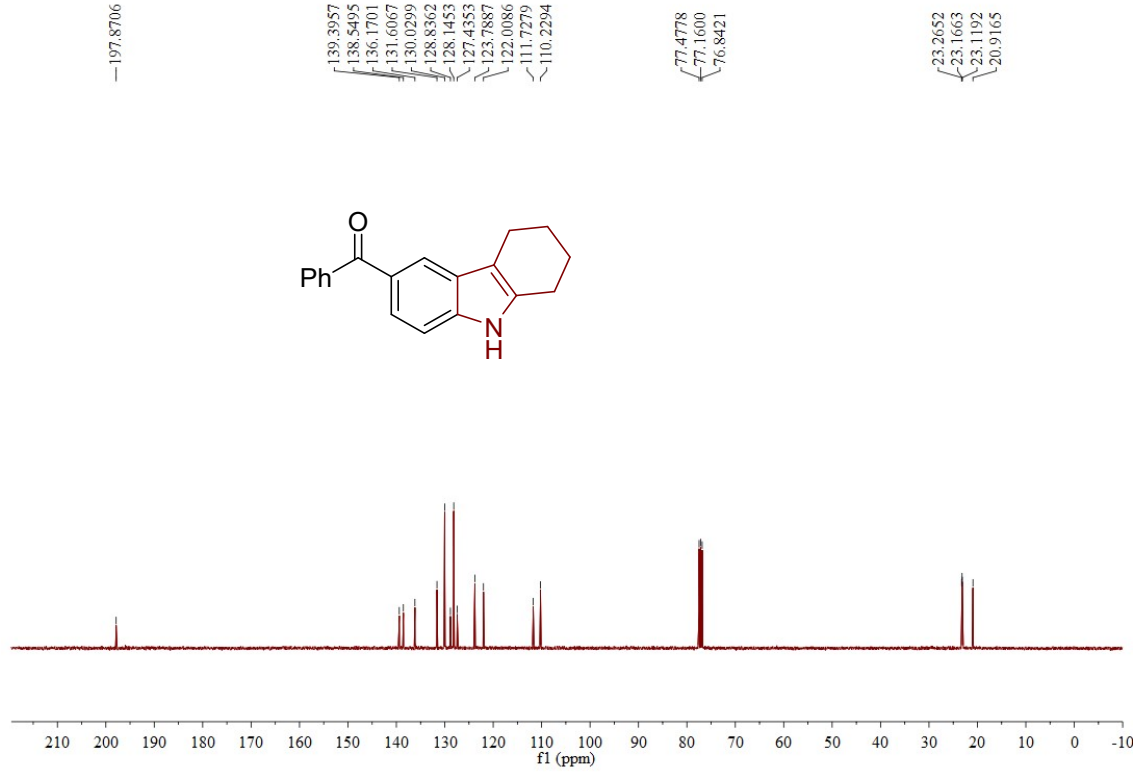
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **49**



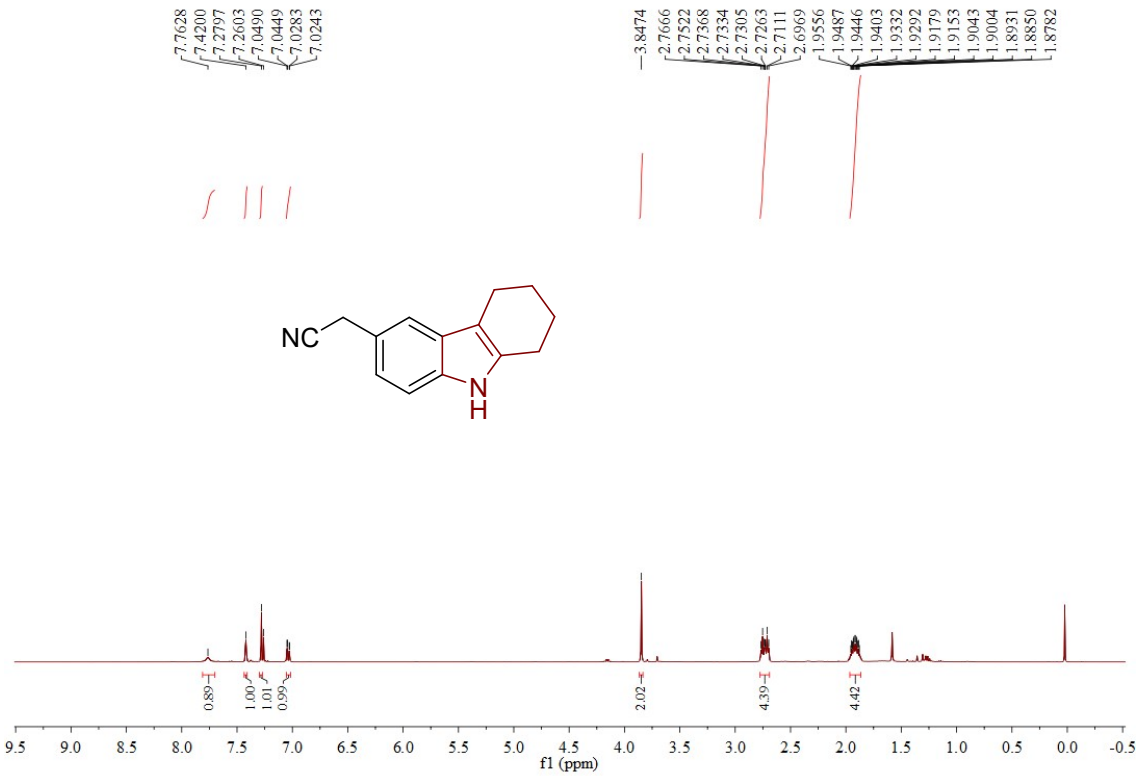
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **49**



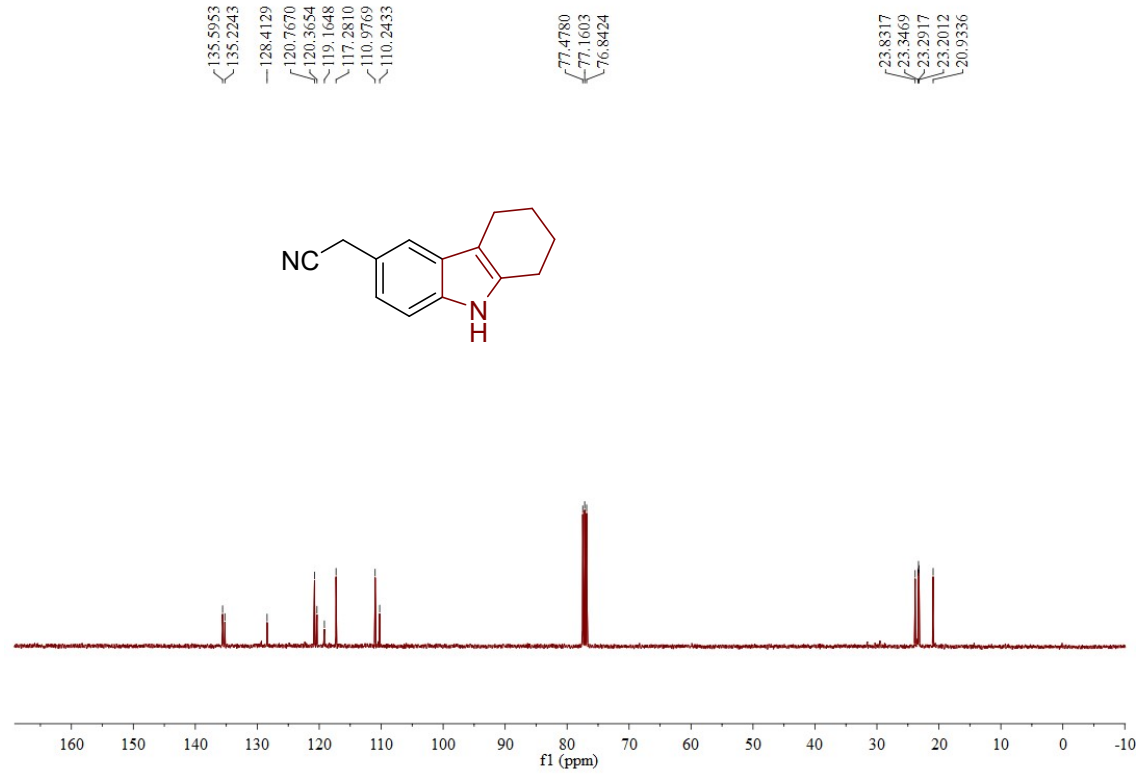
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **50**



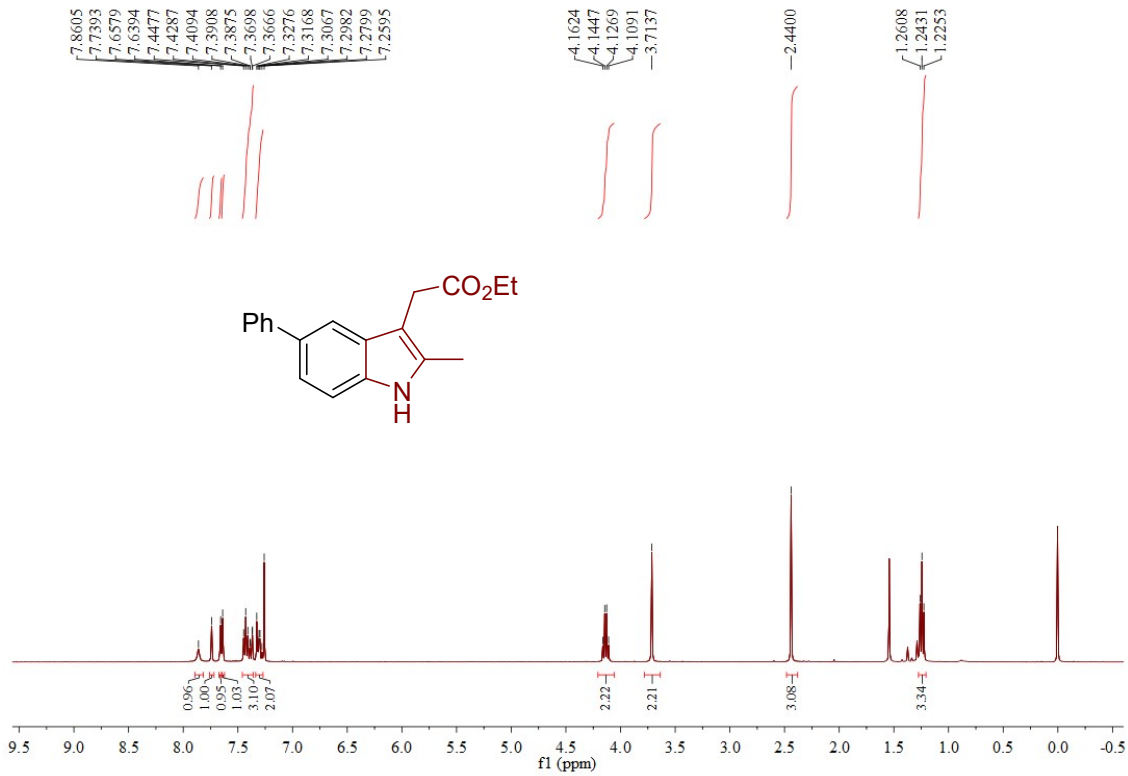
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **50**



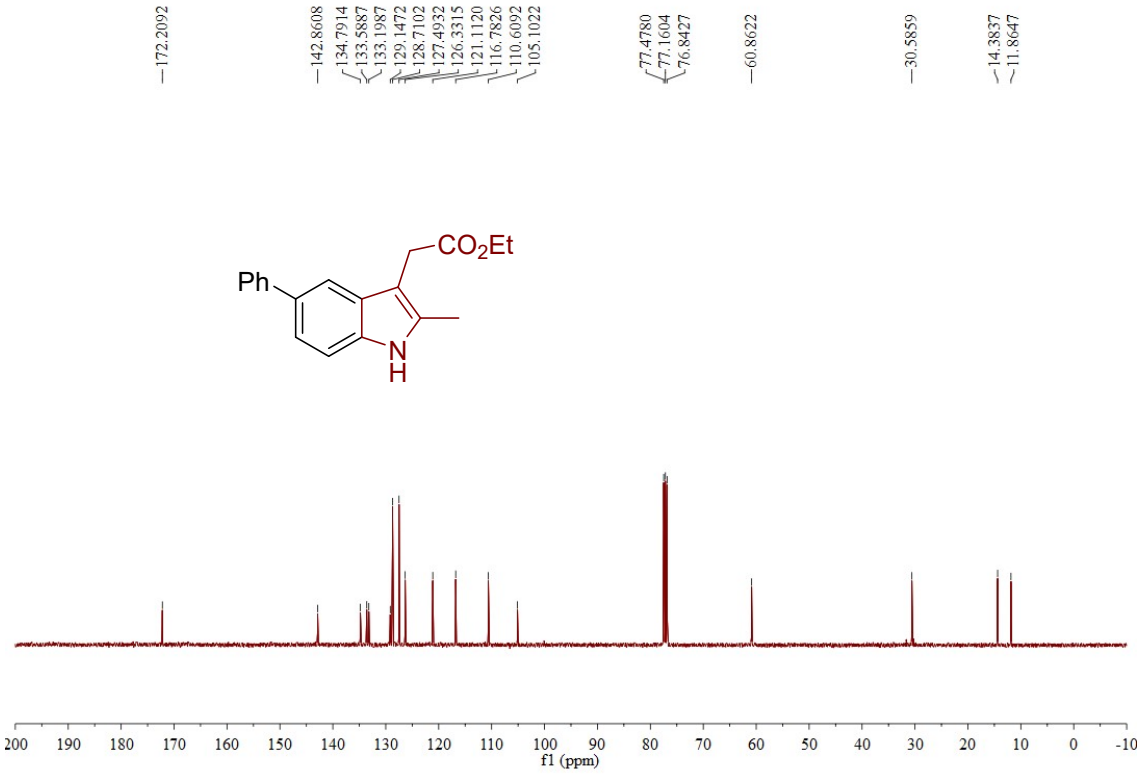
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **51**



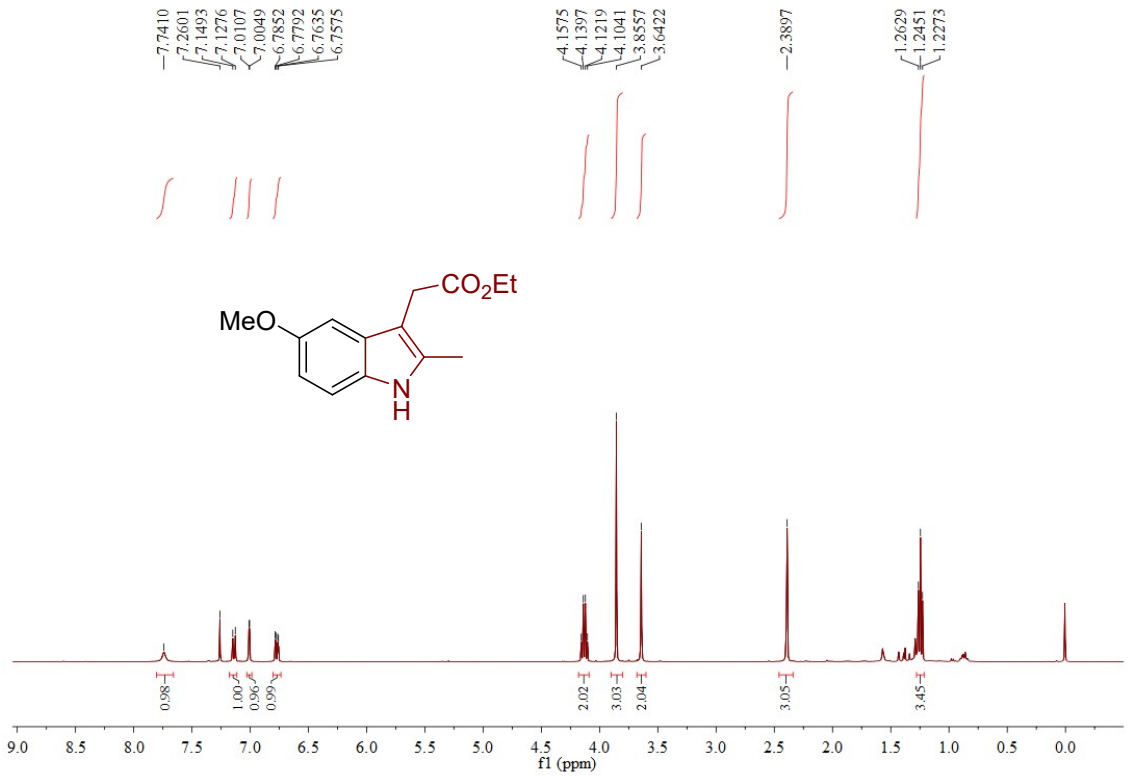
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **51**



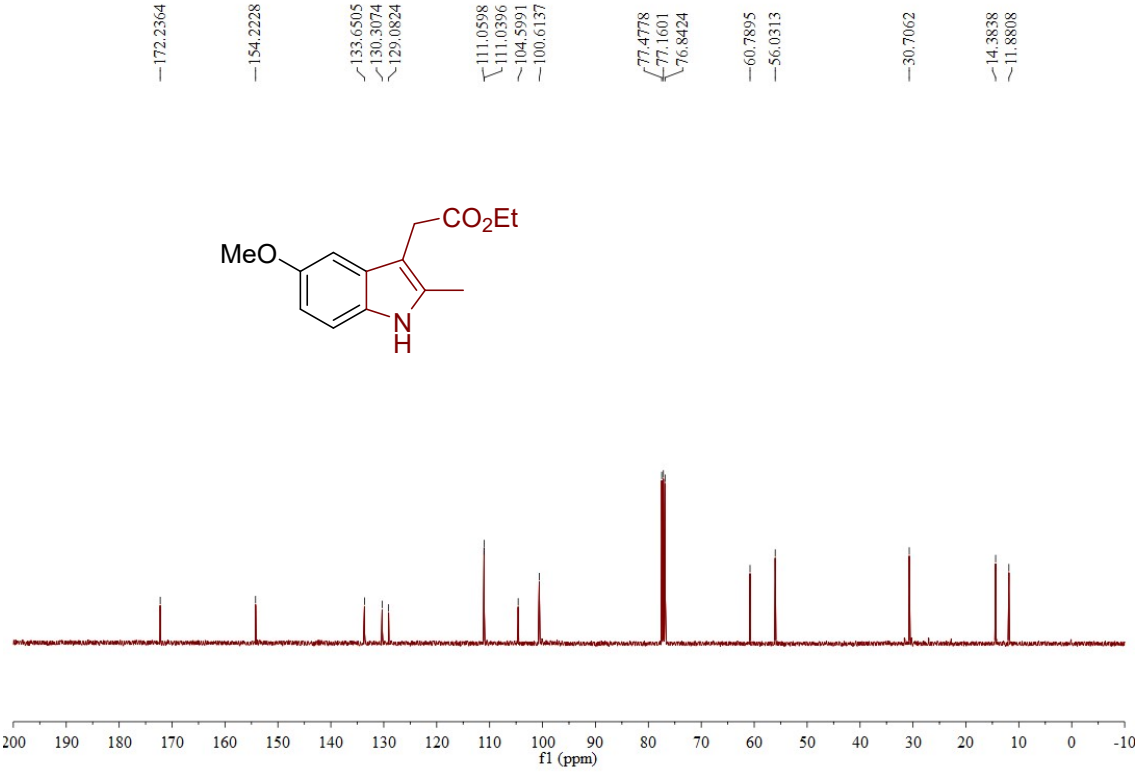
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **52**



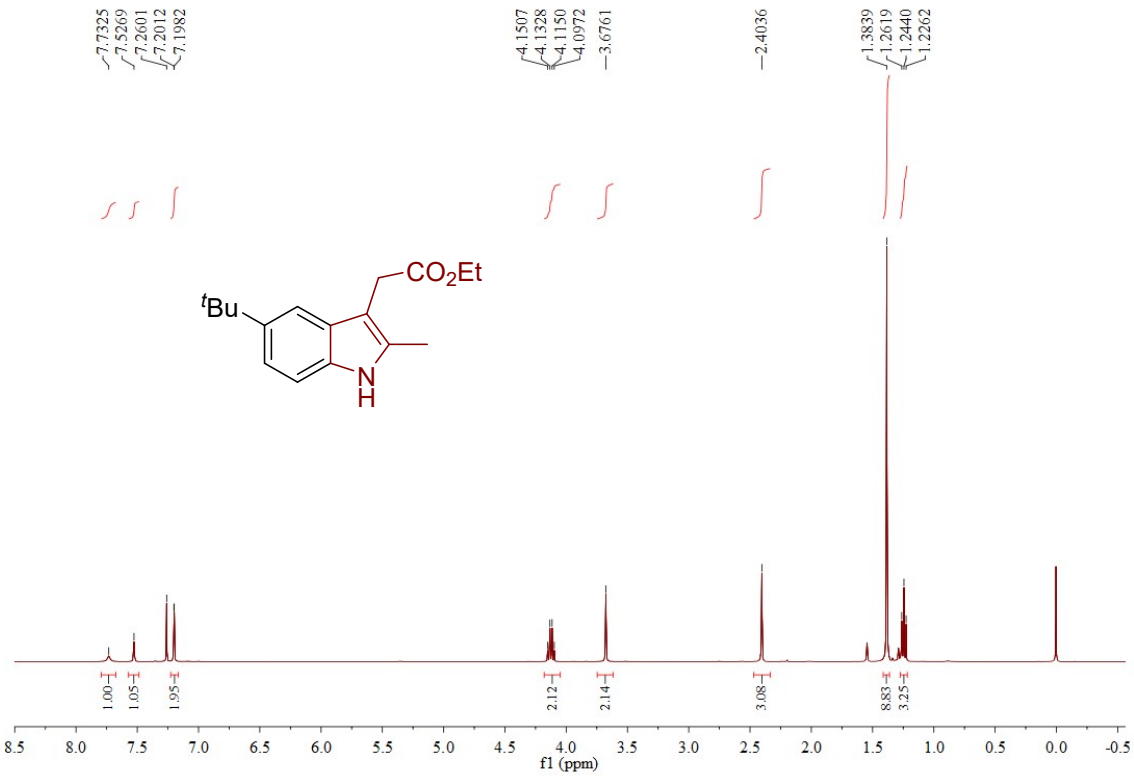
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **52**



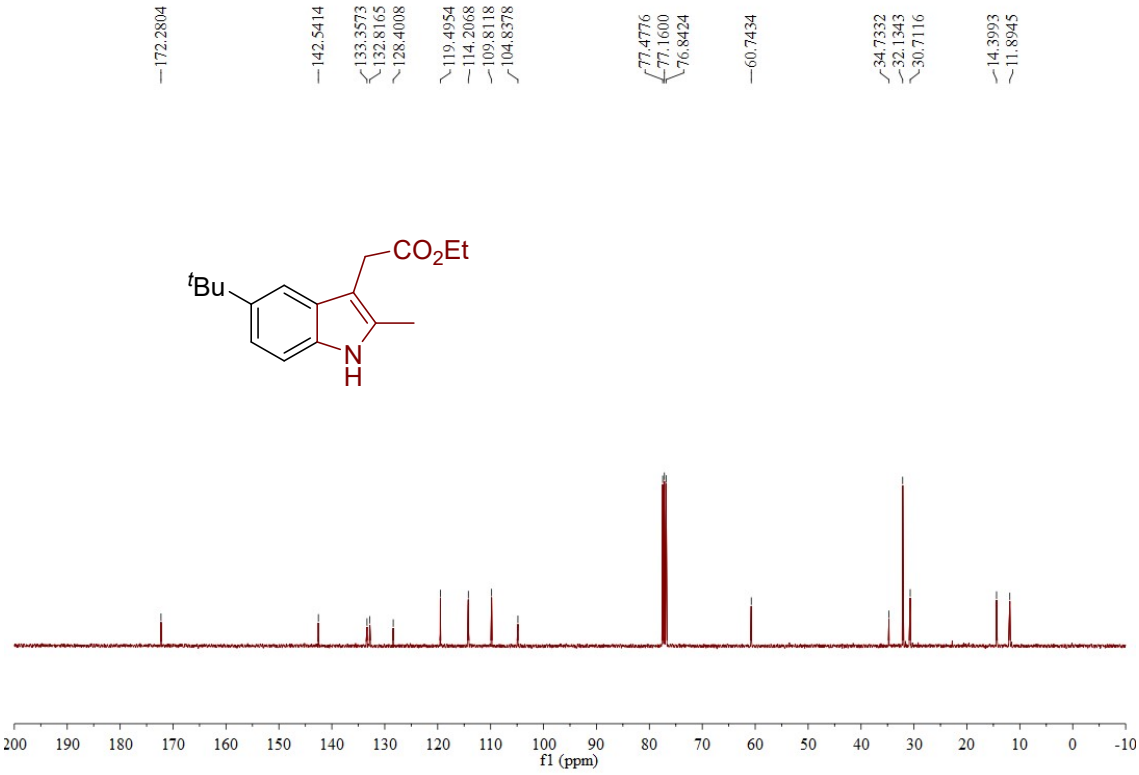
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **53**



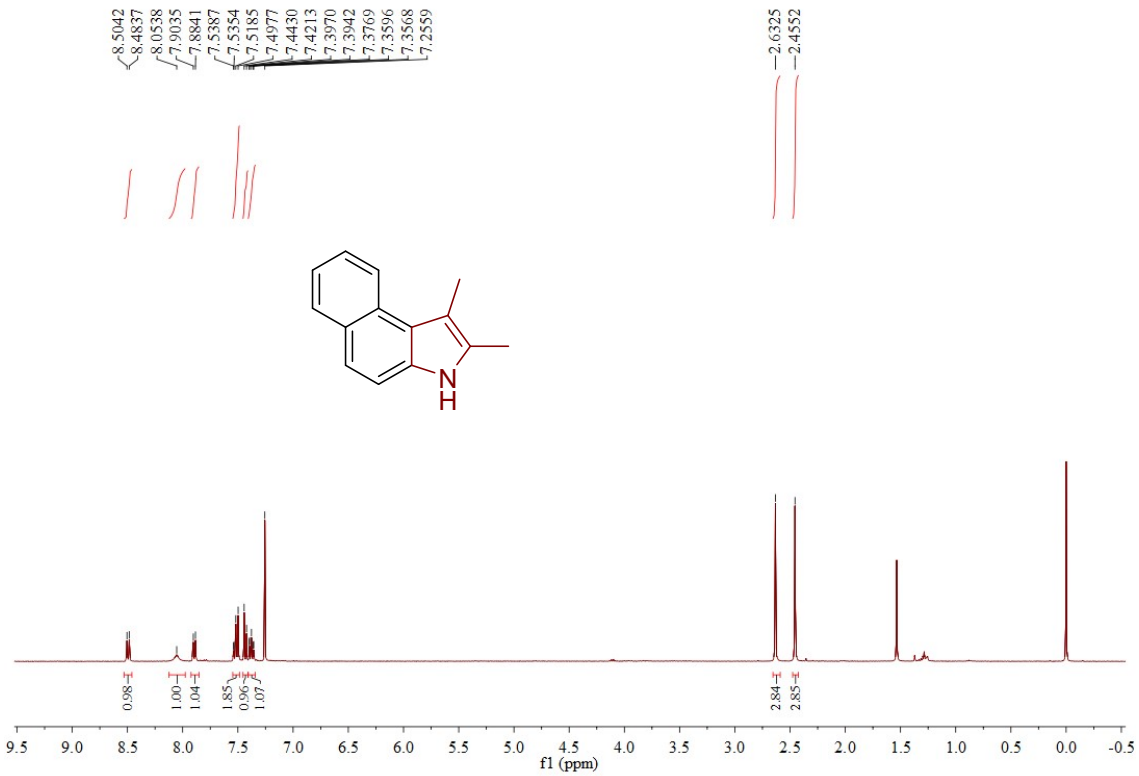
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **53**



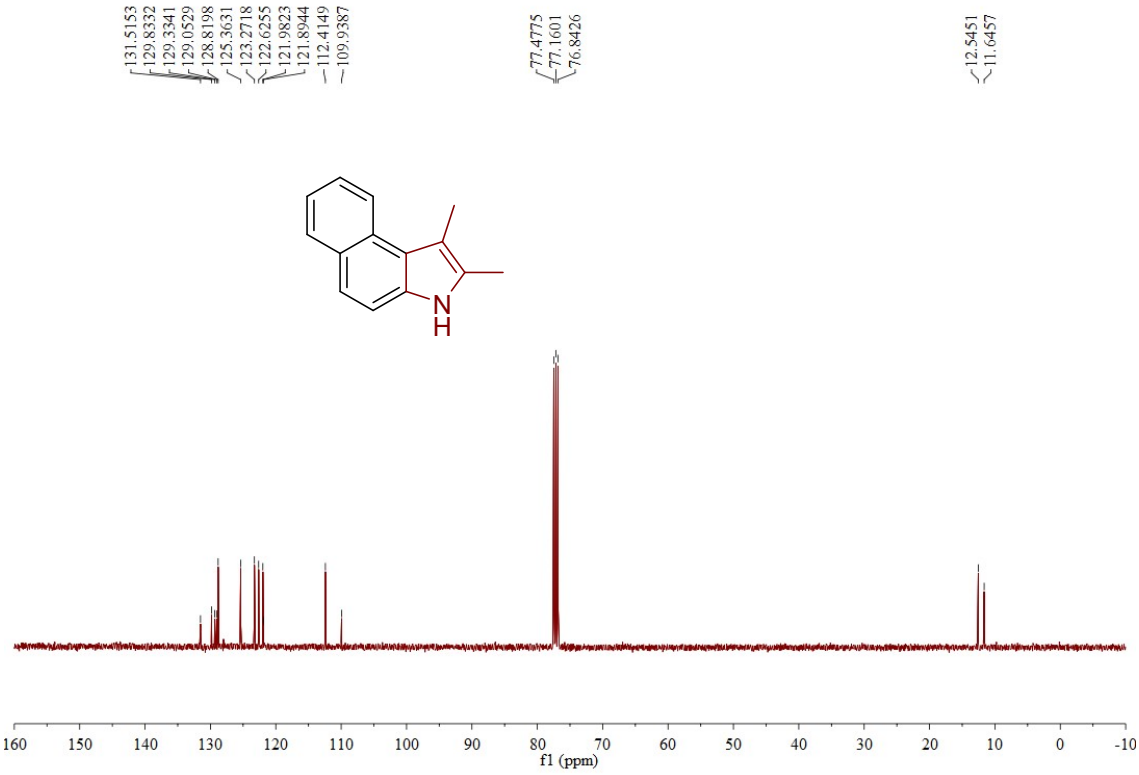
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **54**



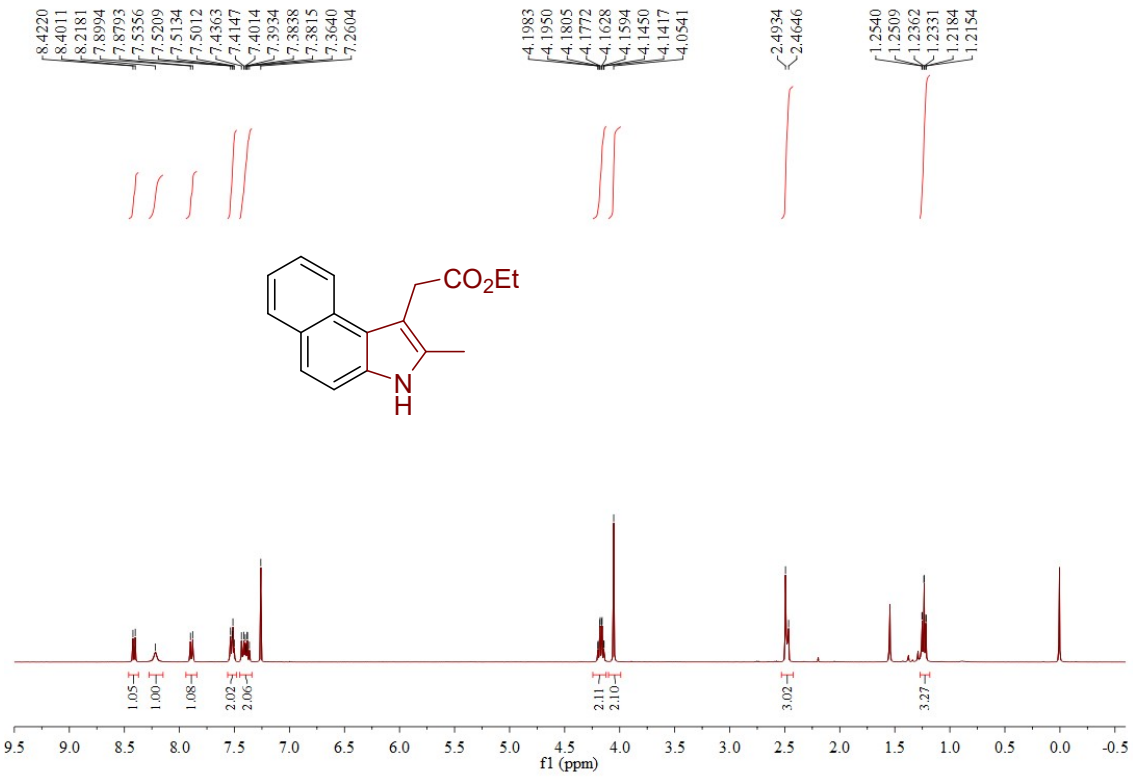
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **54**



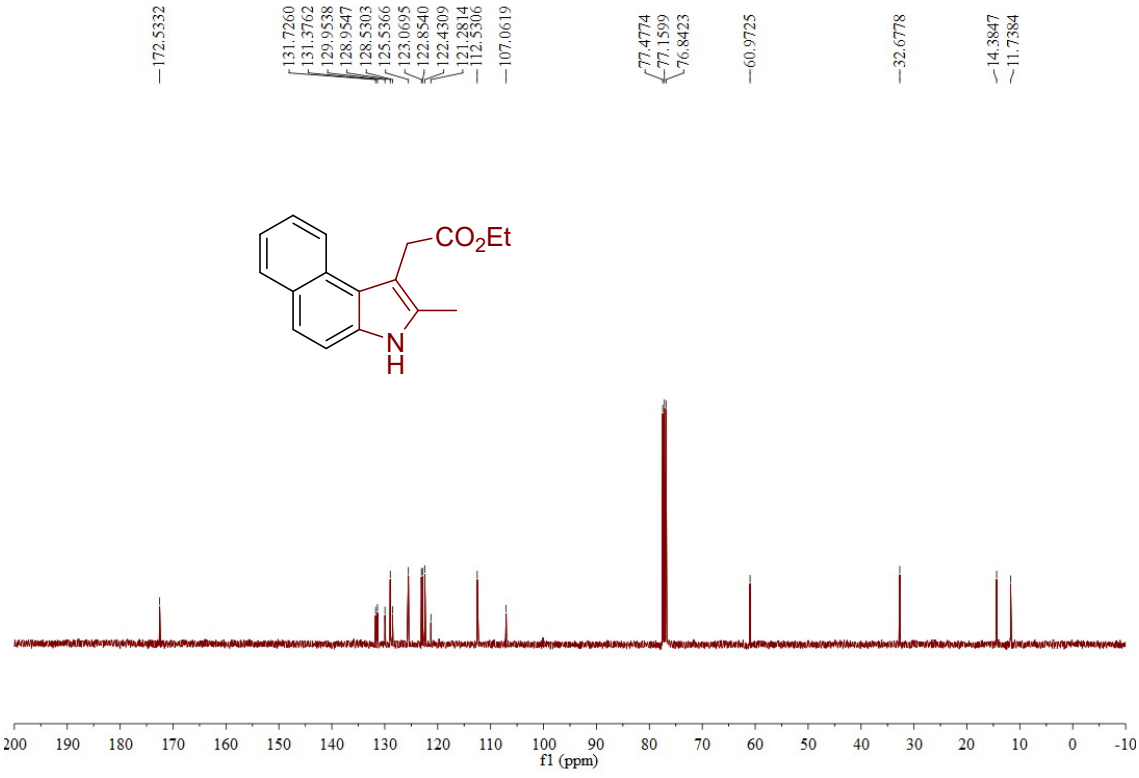
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **55**



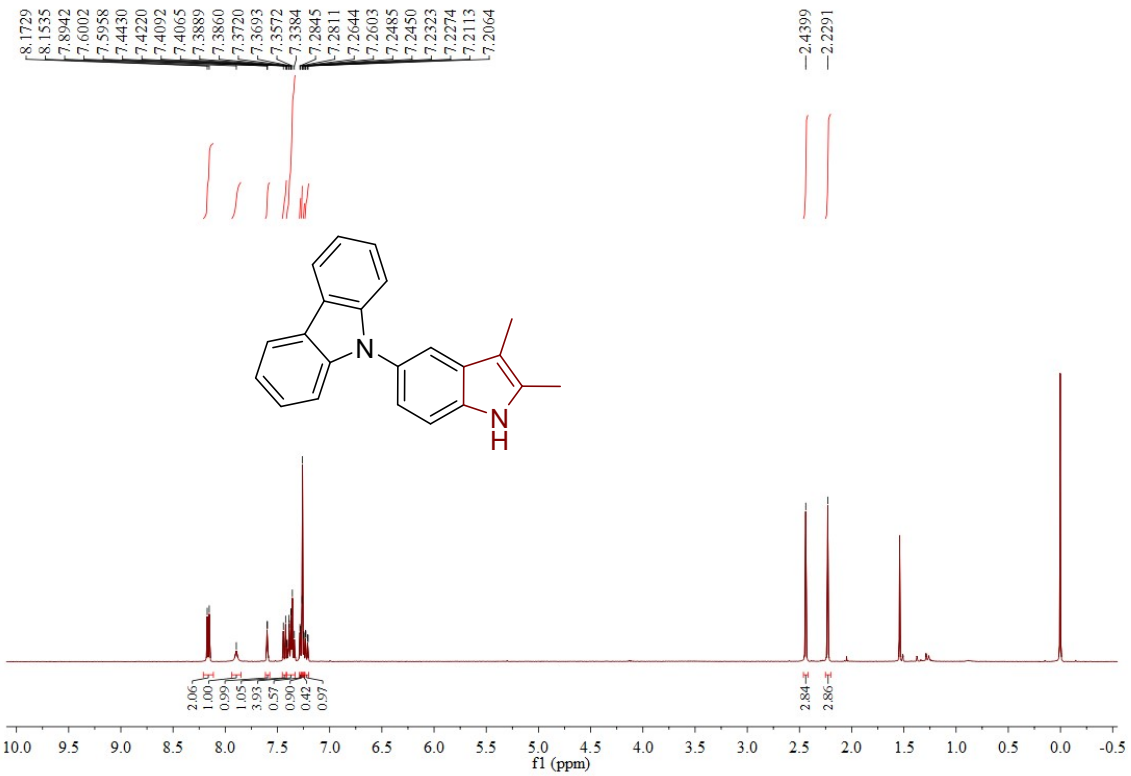
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **55**



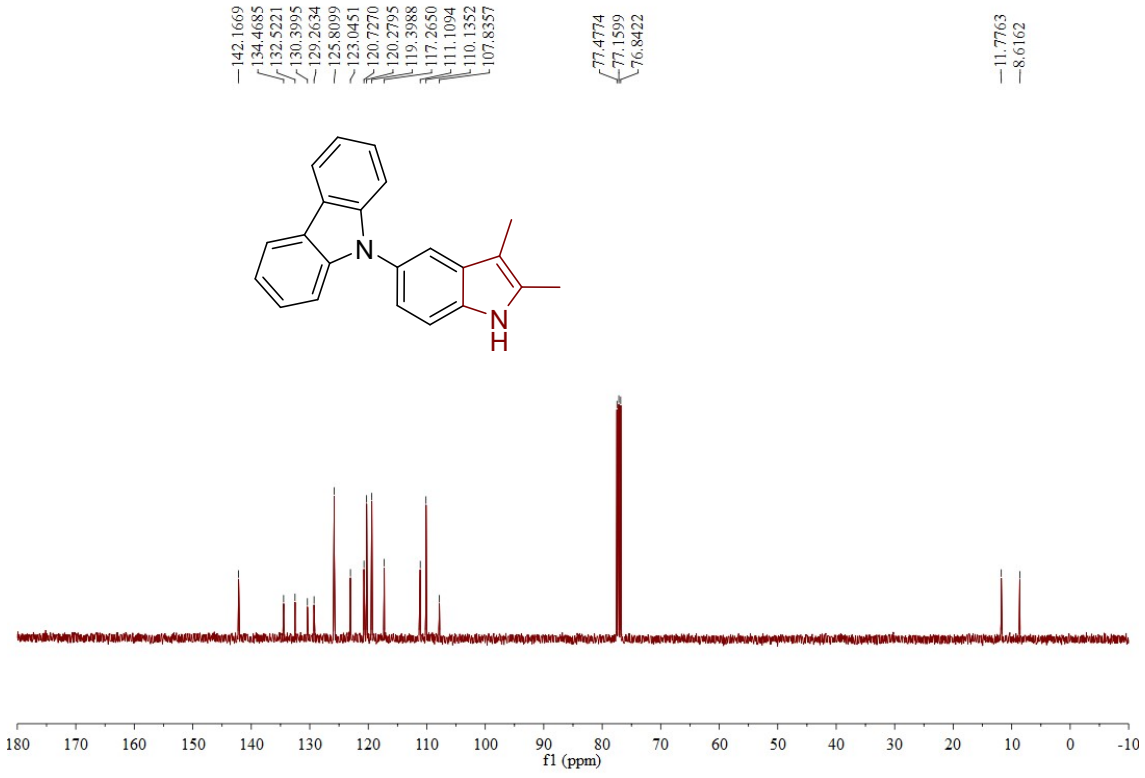
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **56**



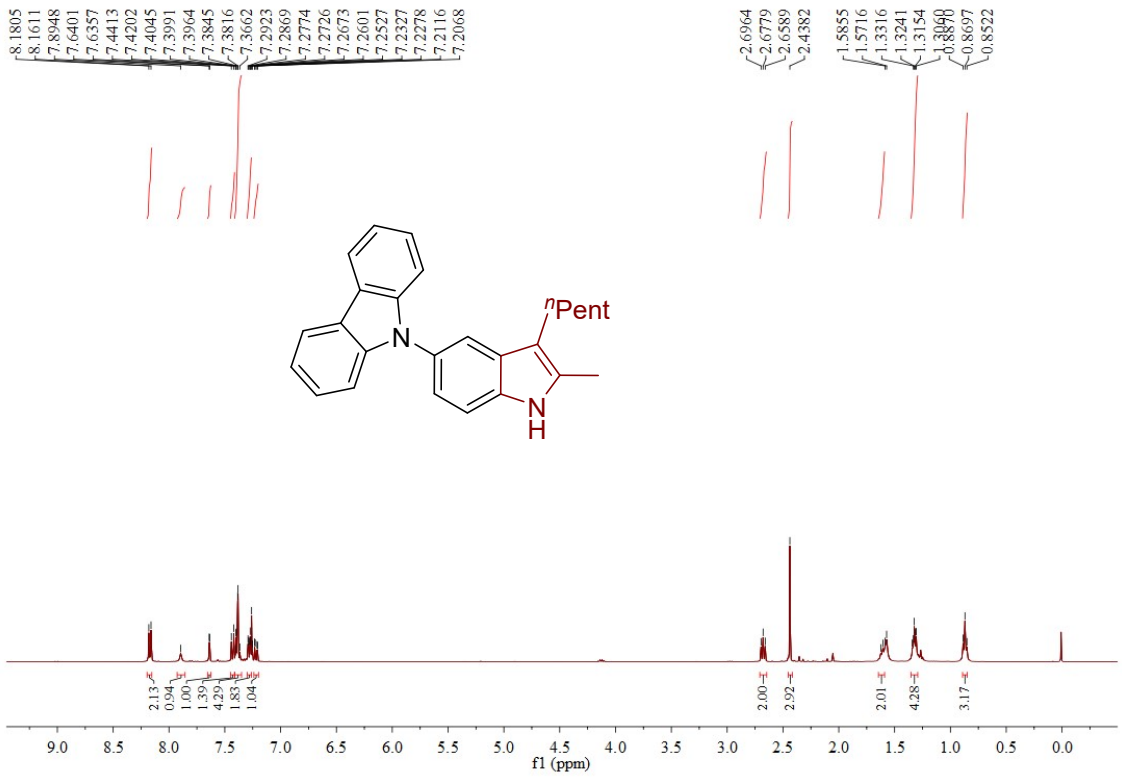
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **56**



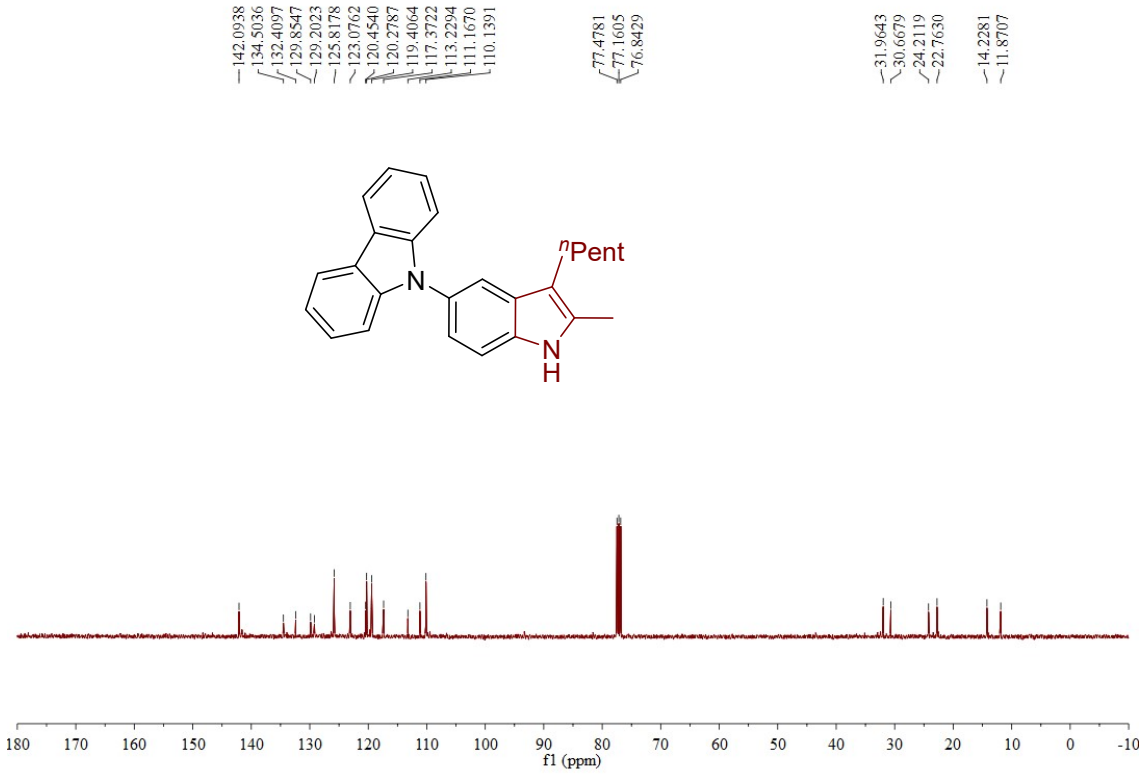
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **57**



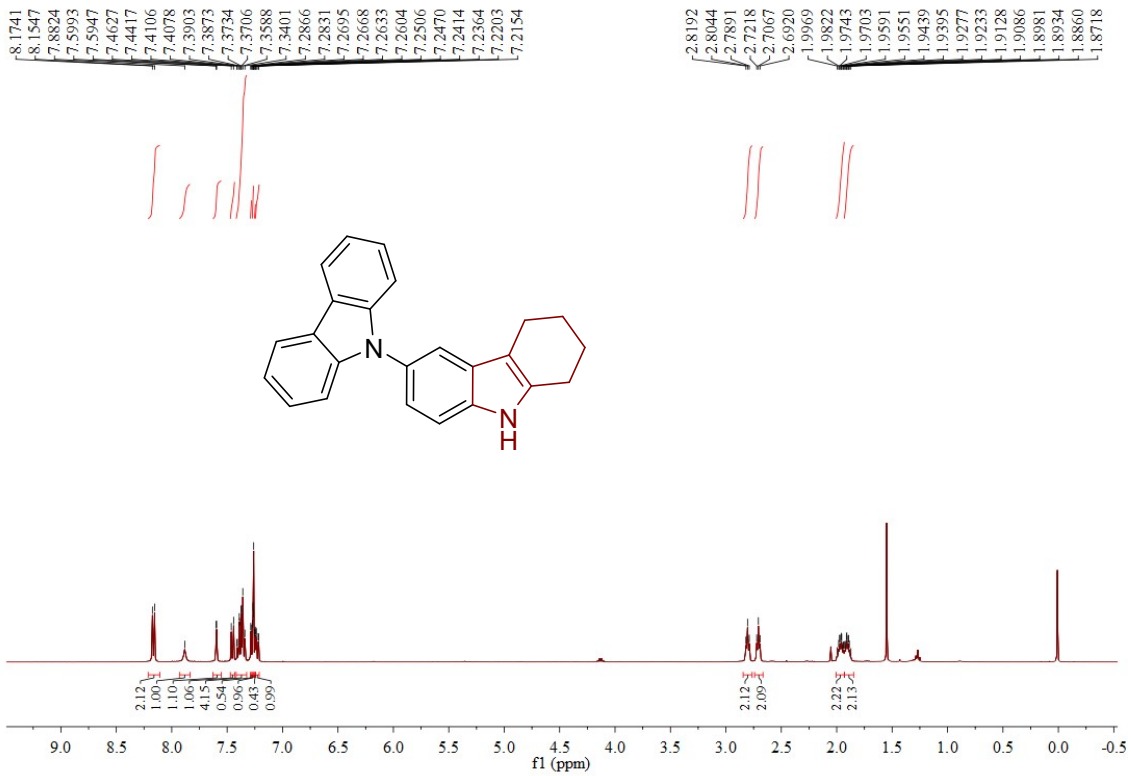
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **57**



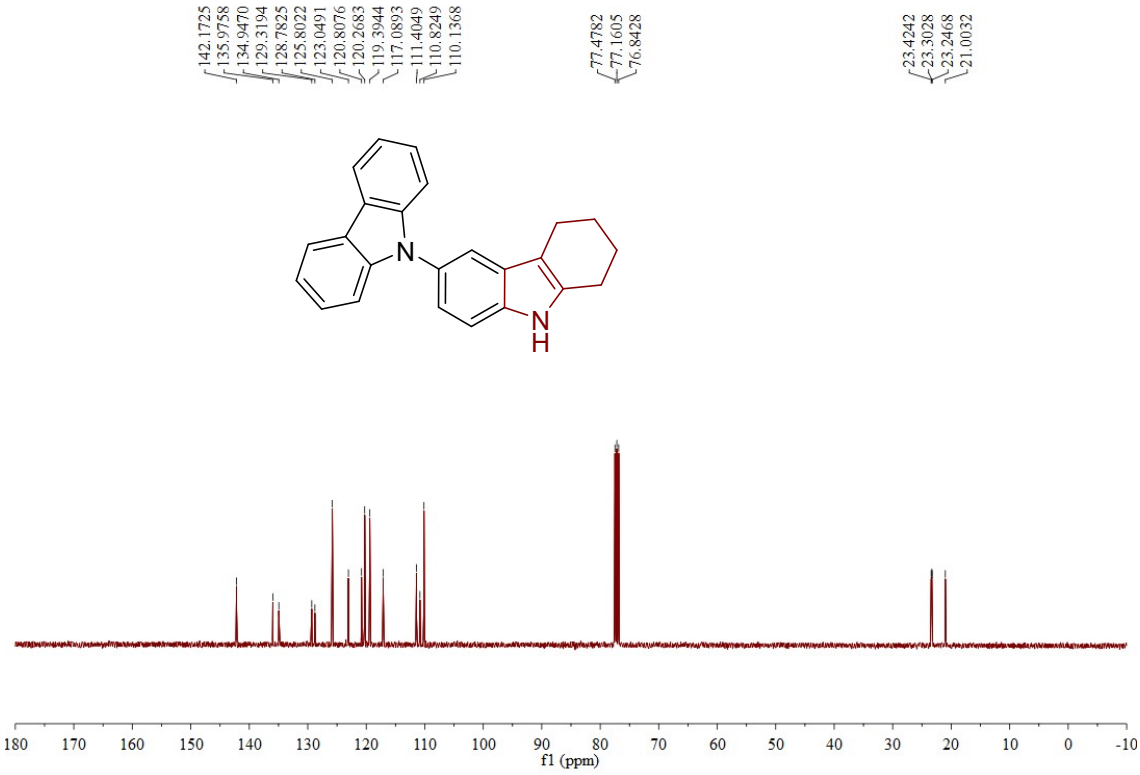
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **58**



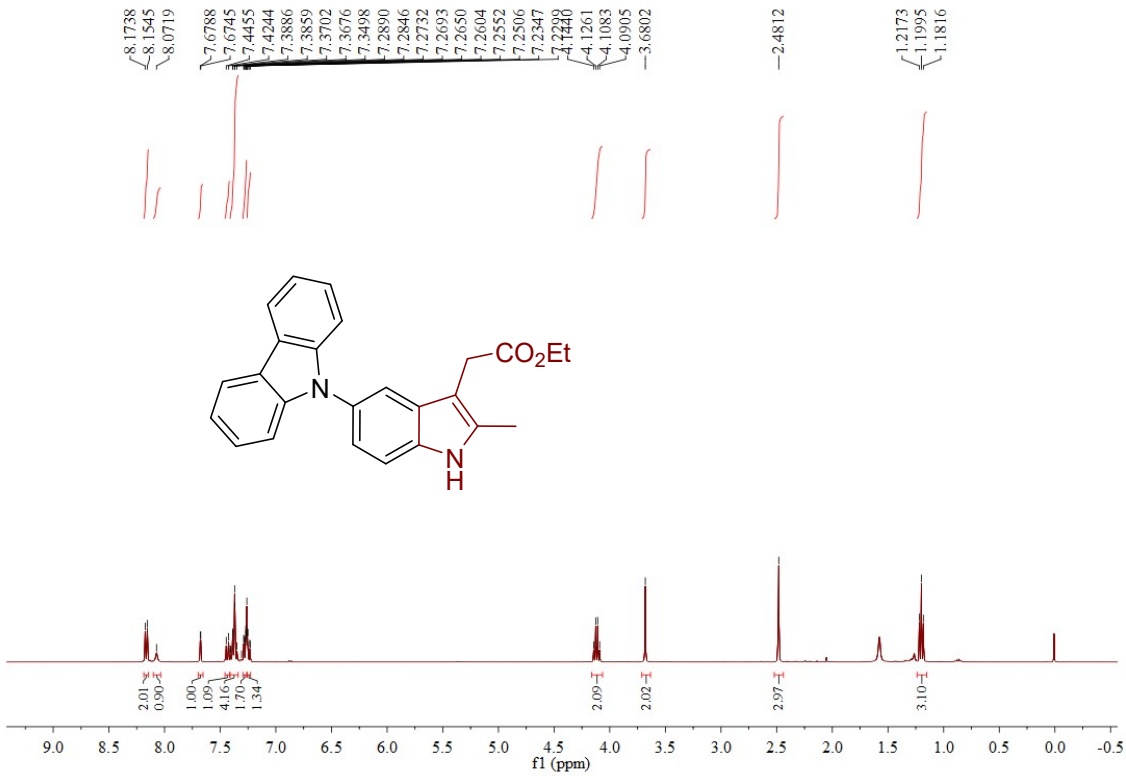
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **58**



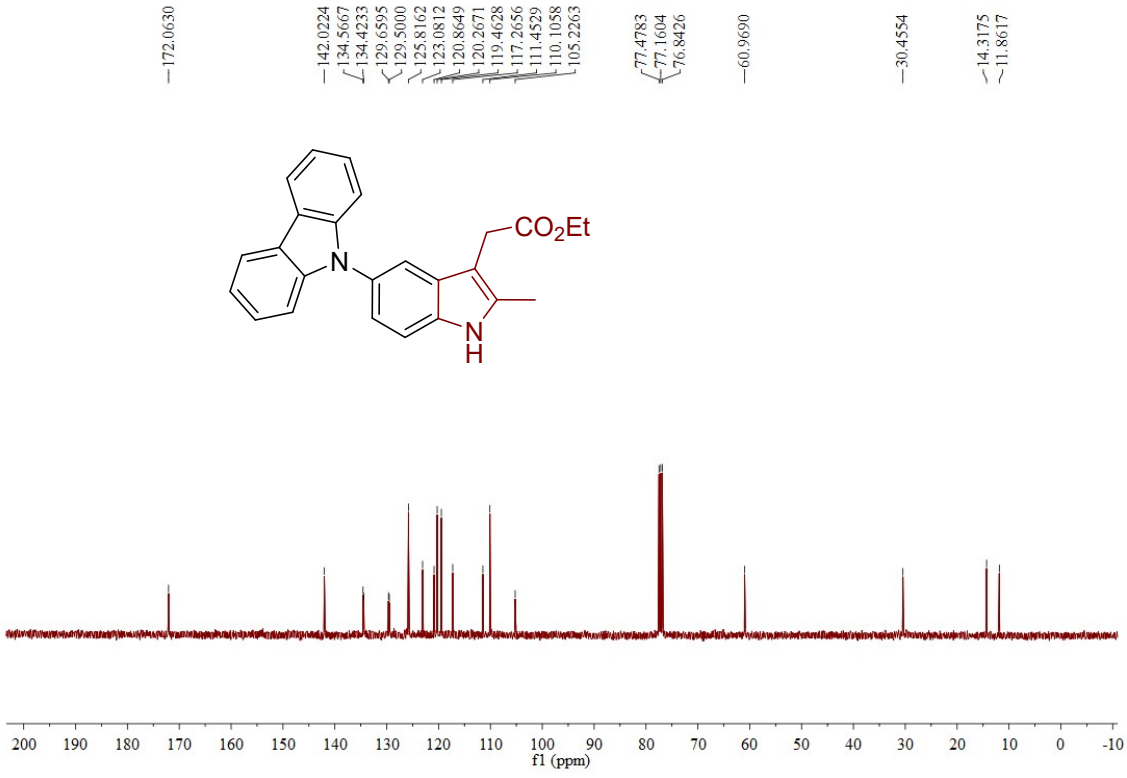
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **59**



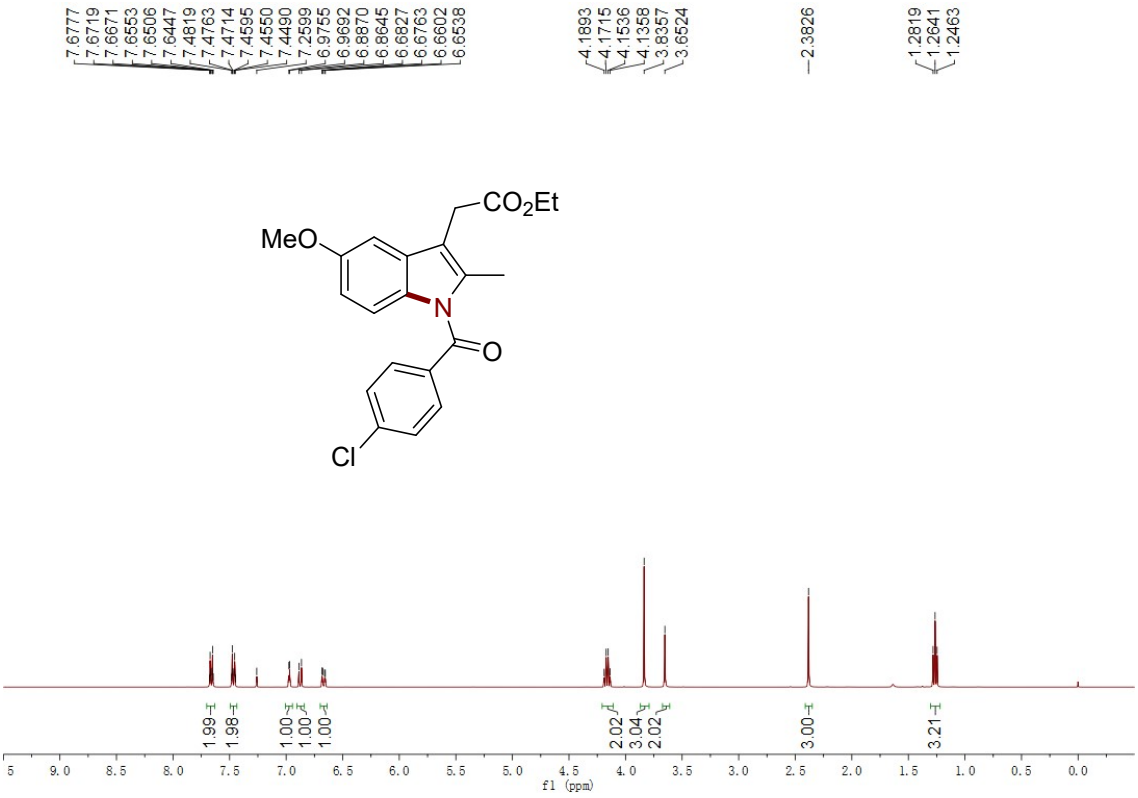
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **59**



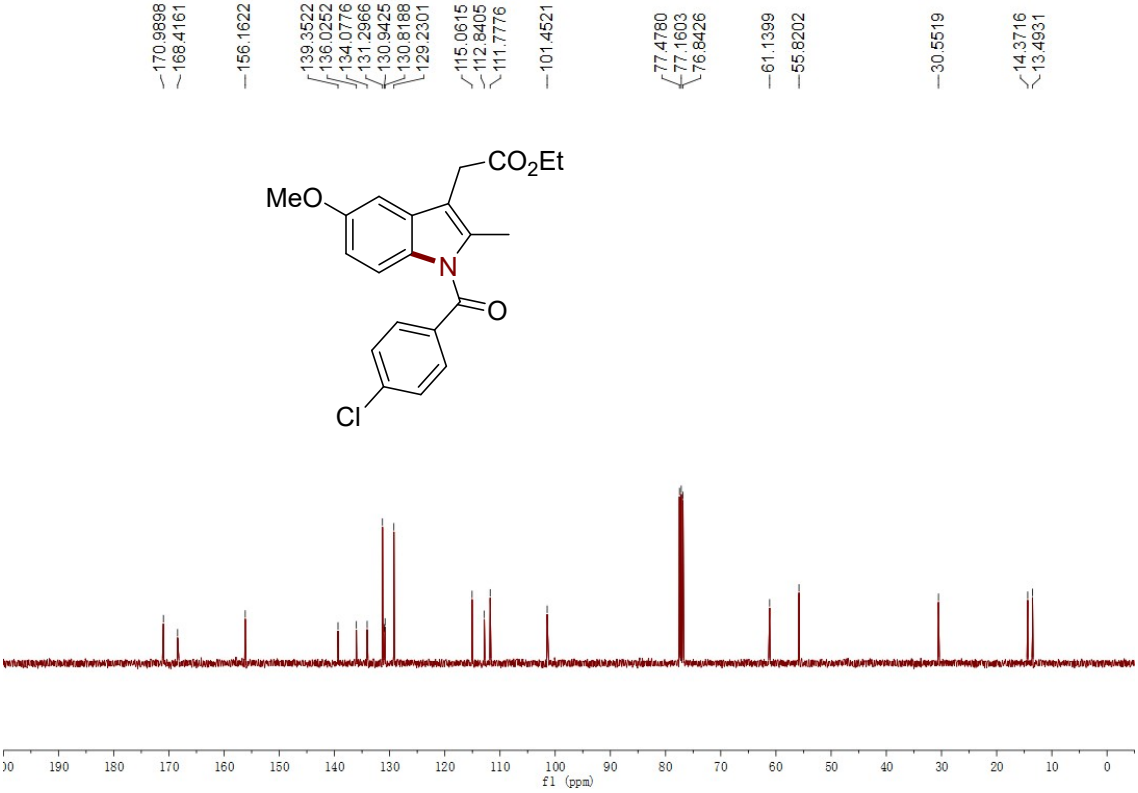
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **60**



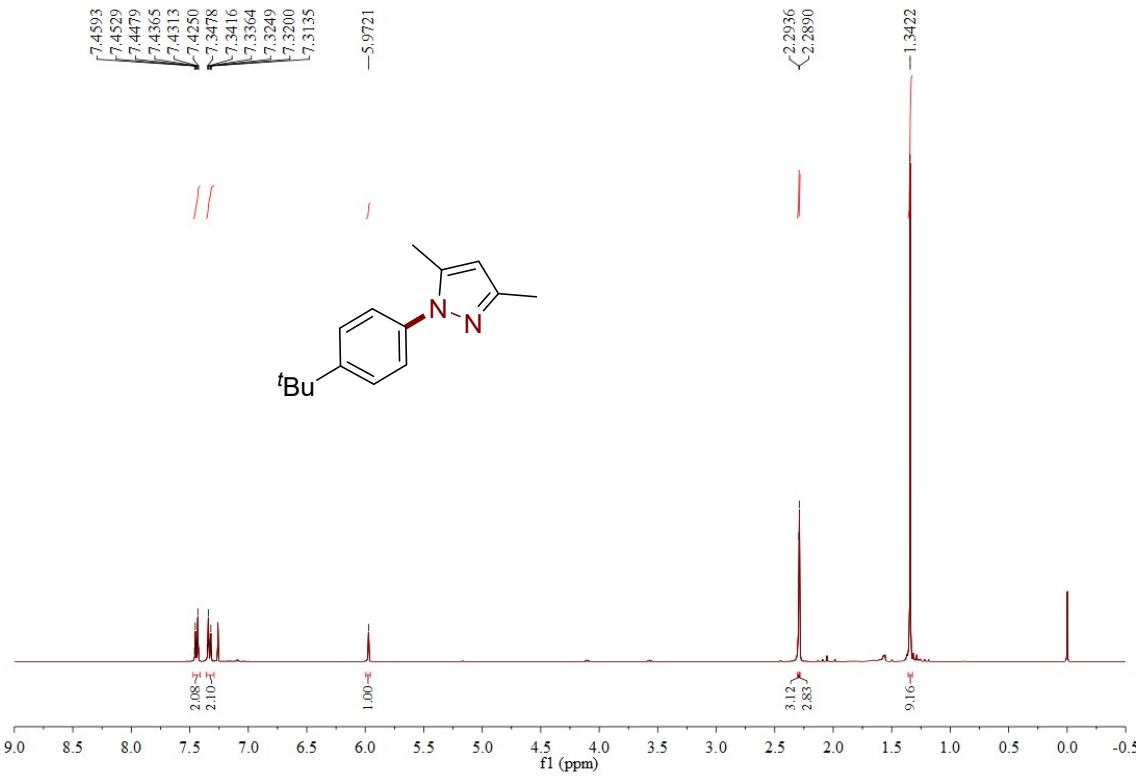
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **60**



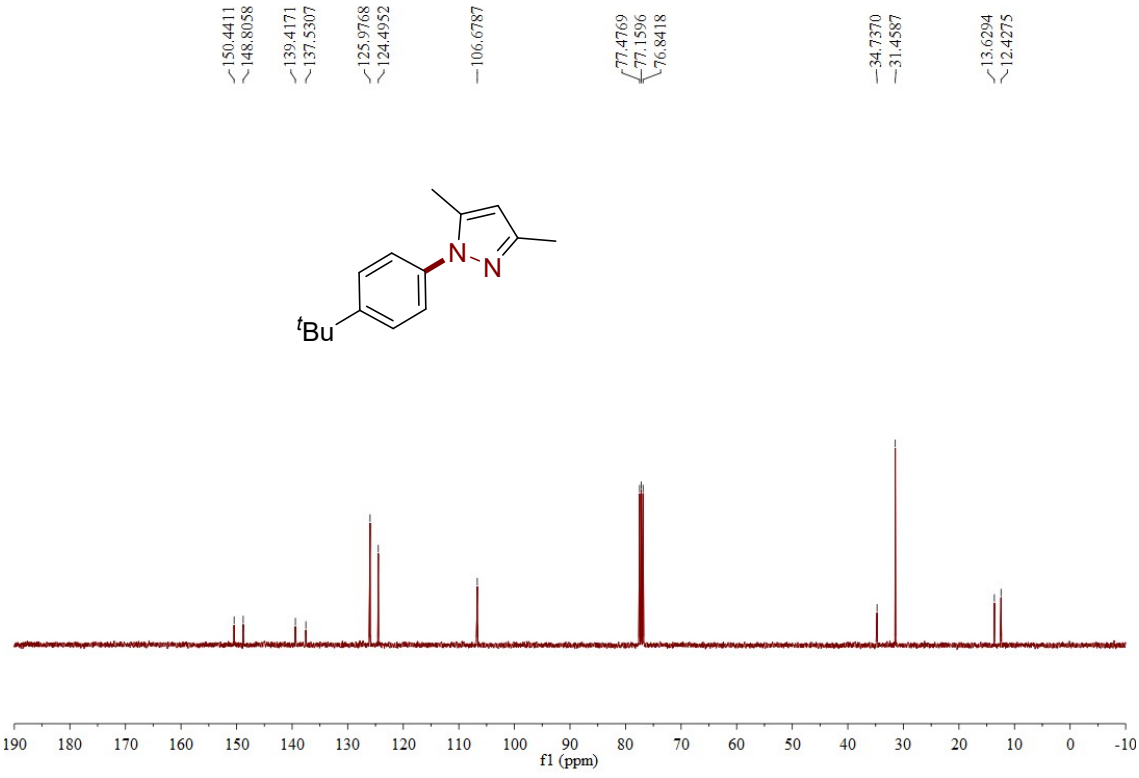
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **62**



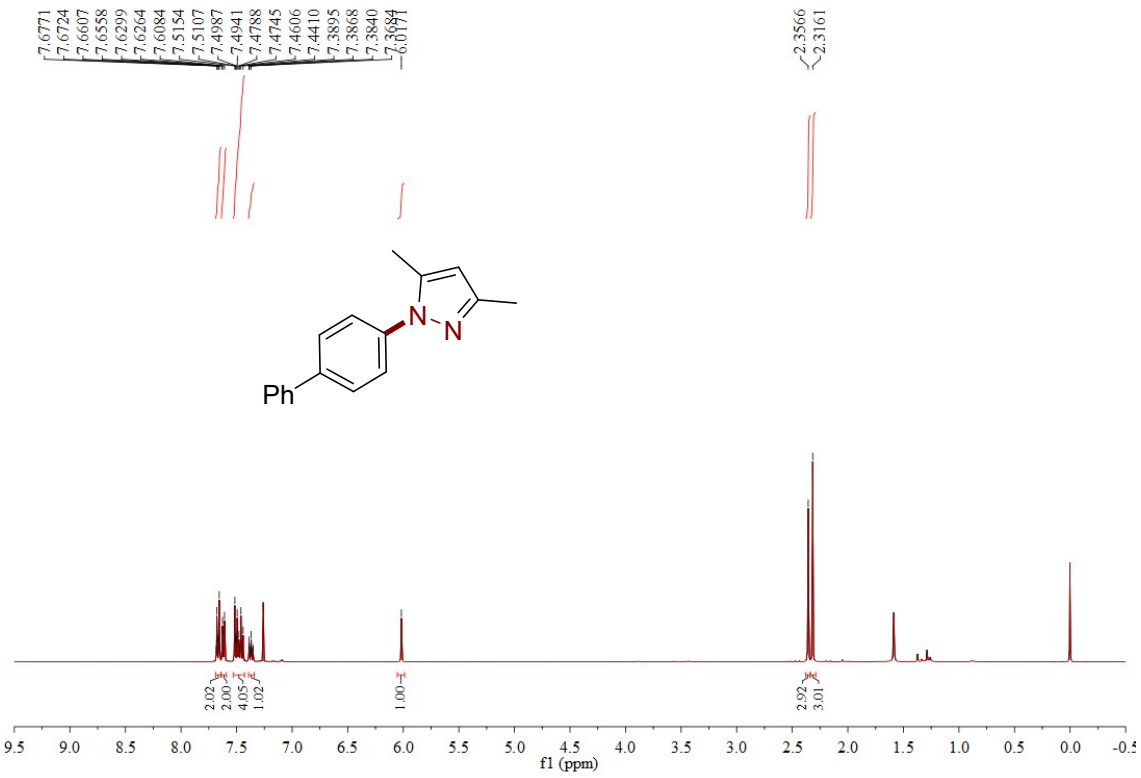
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **62**



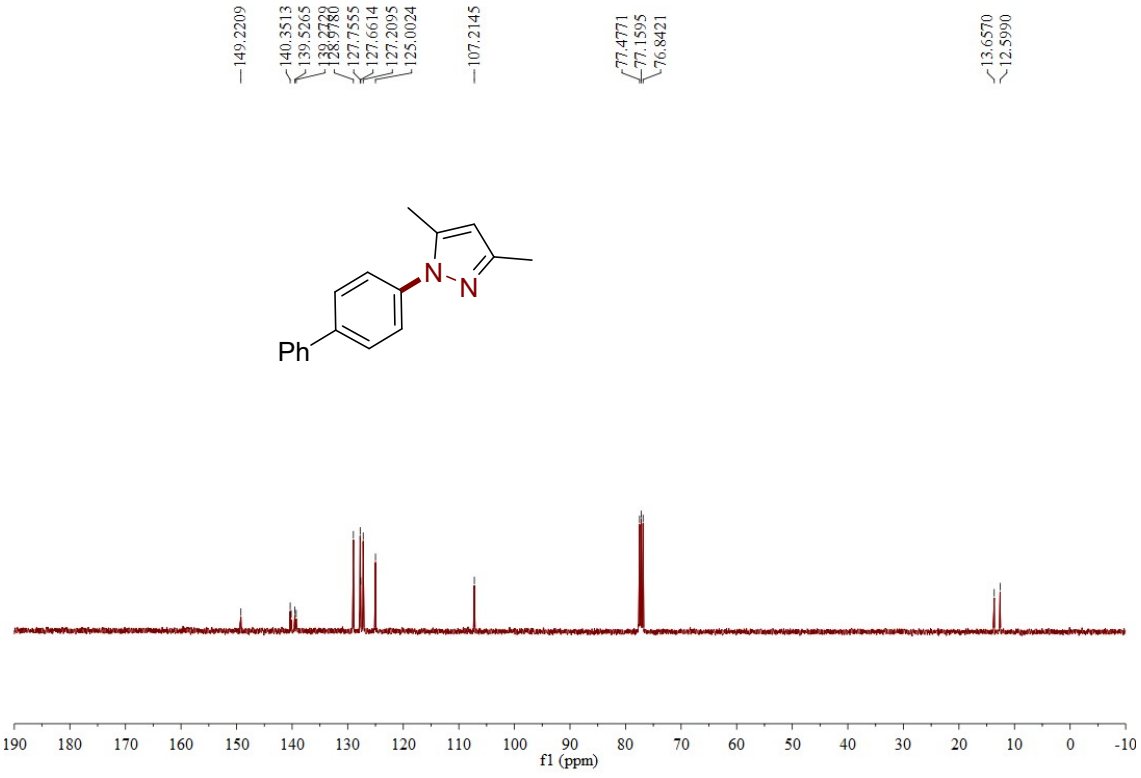
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **63**



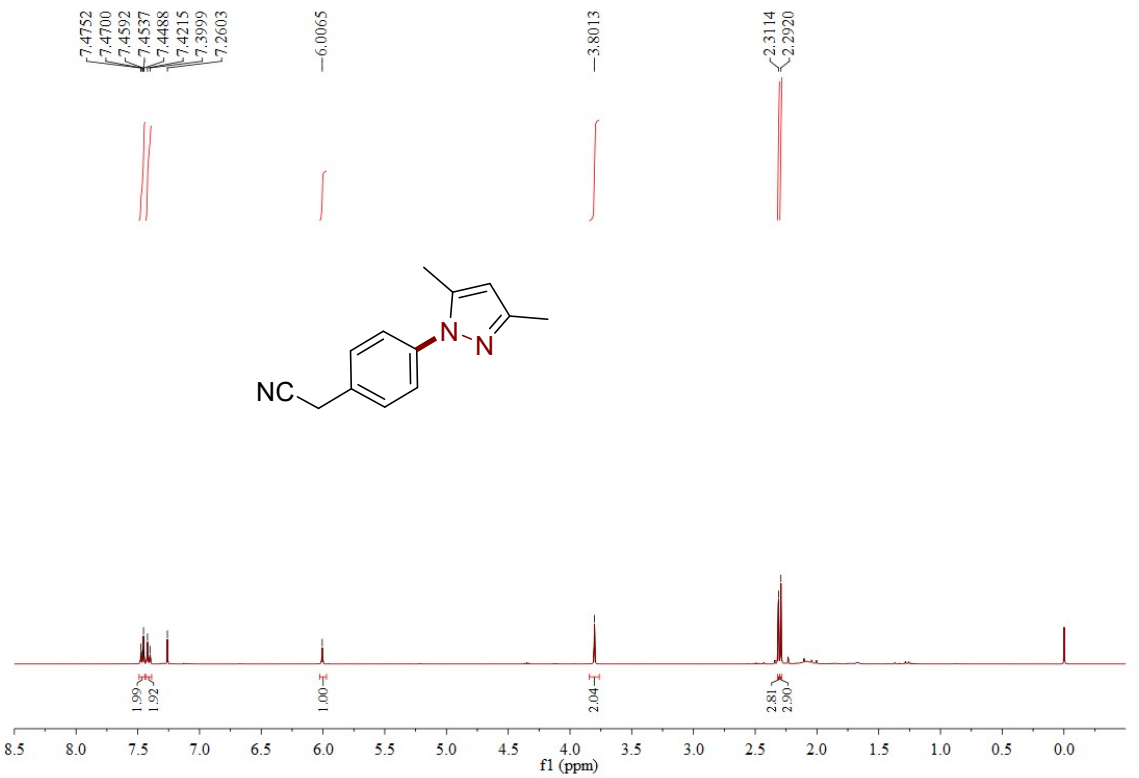
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **63**



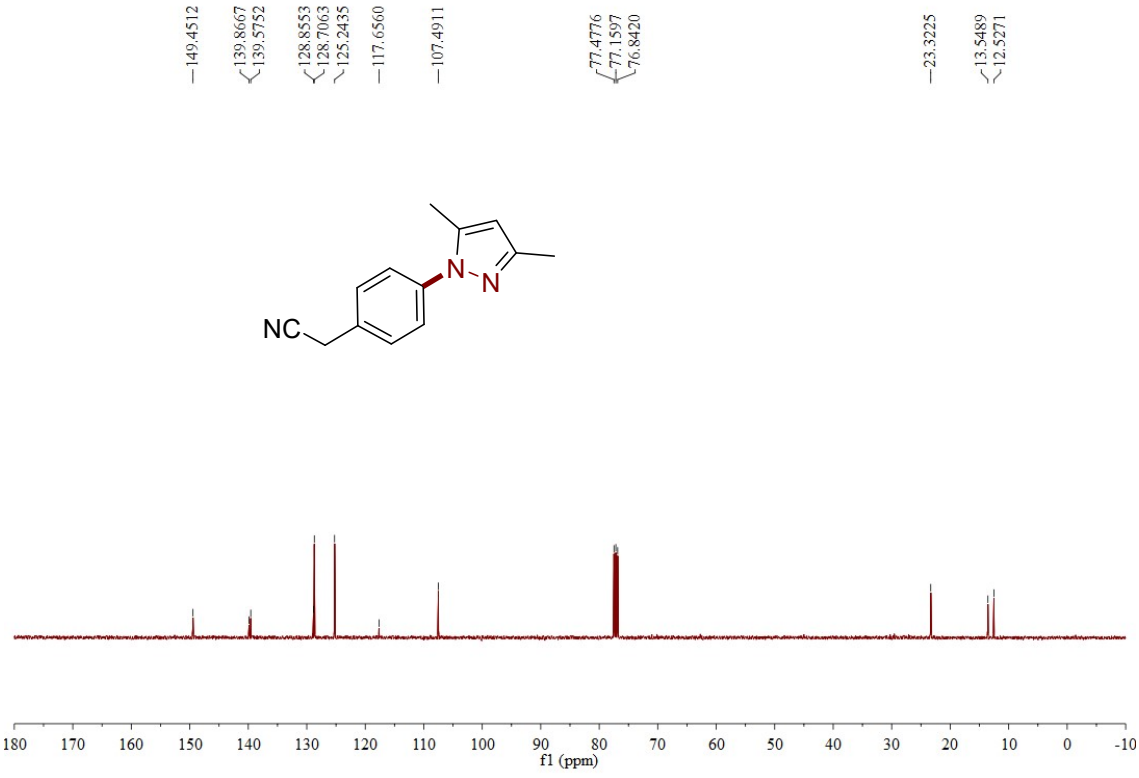
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **64**



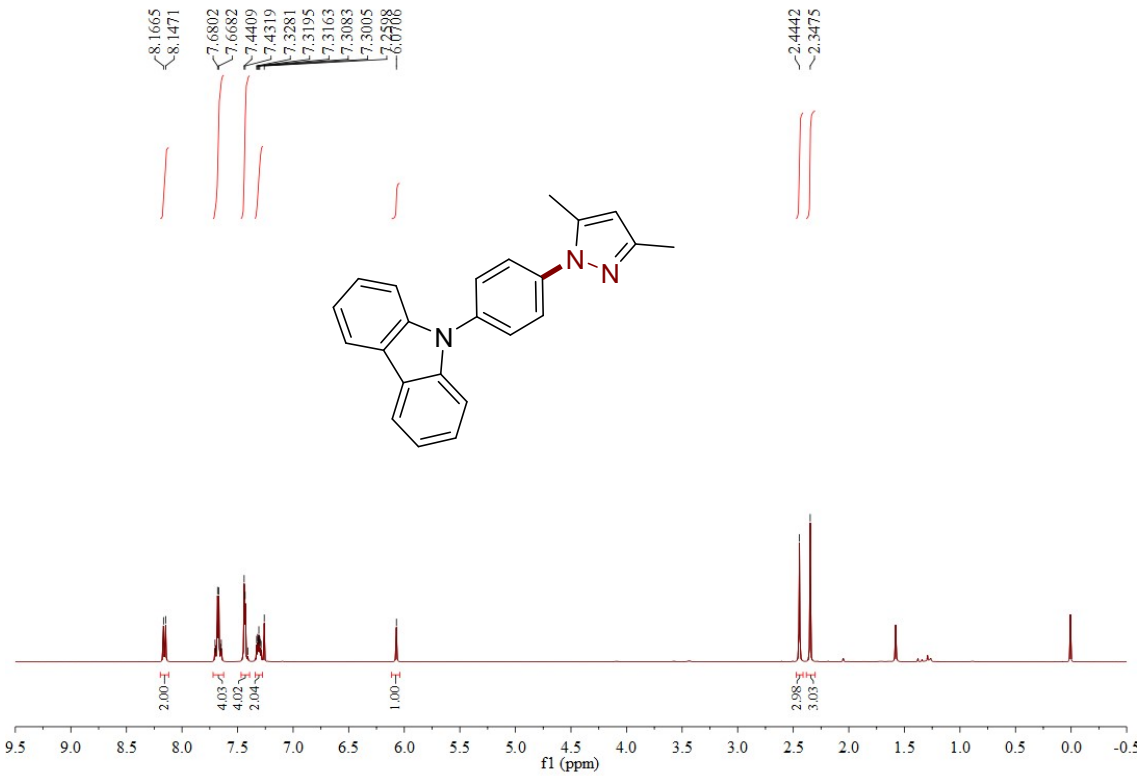
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **64**



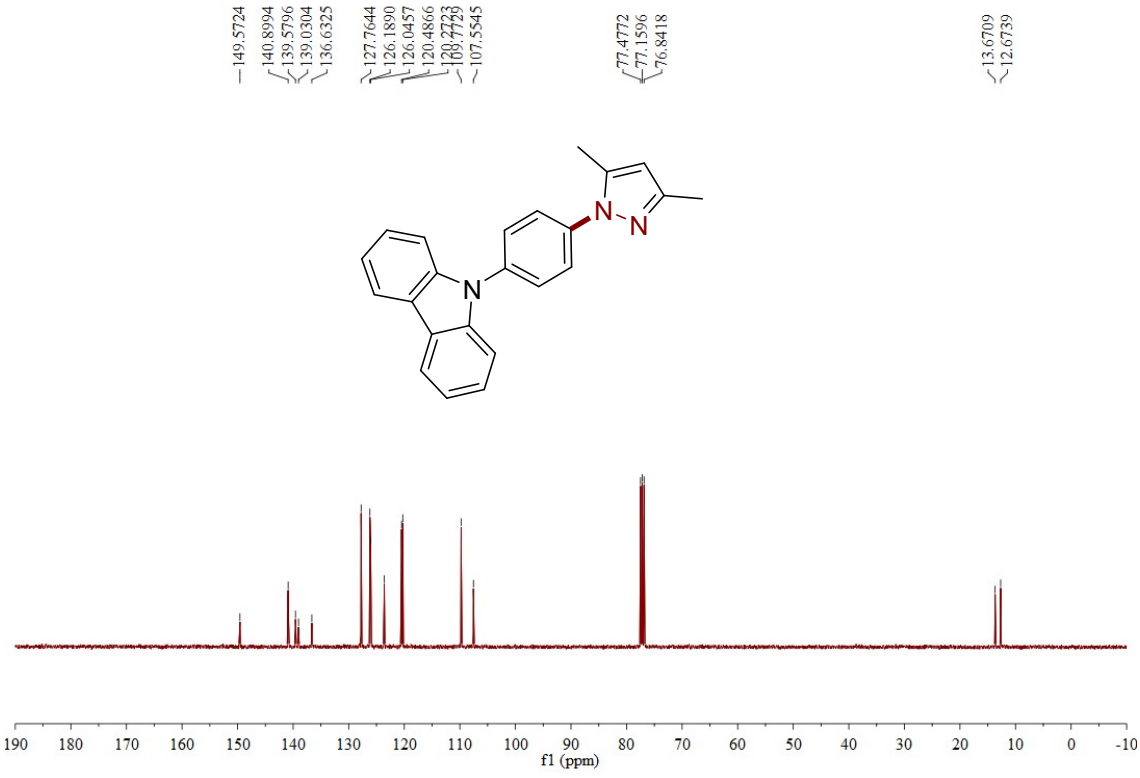
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **65**



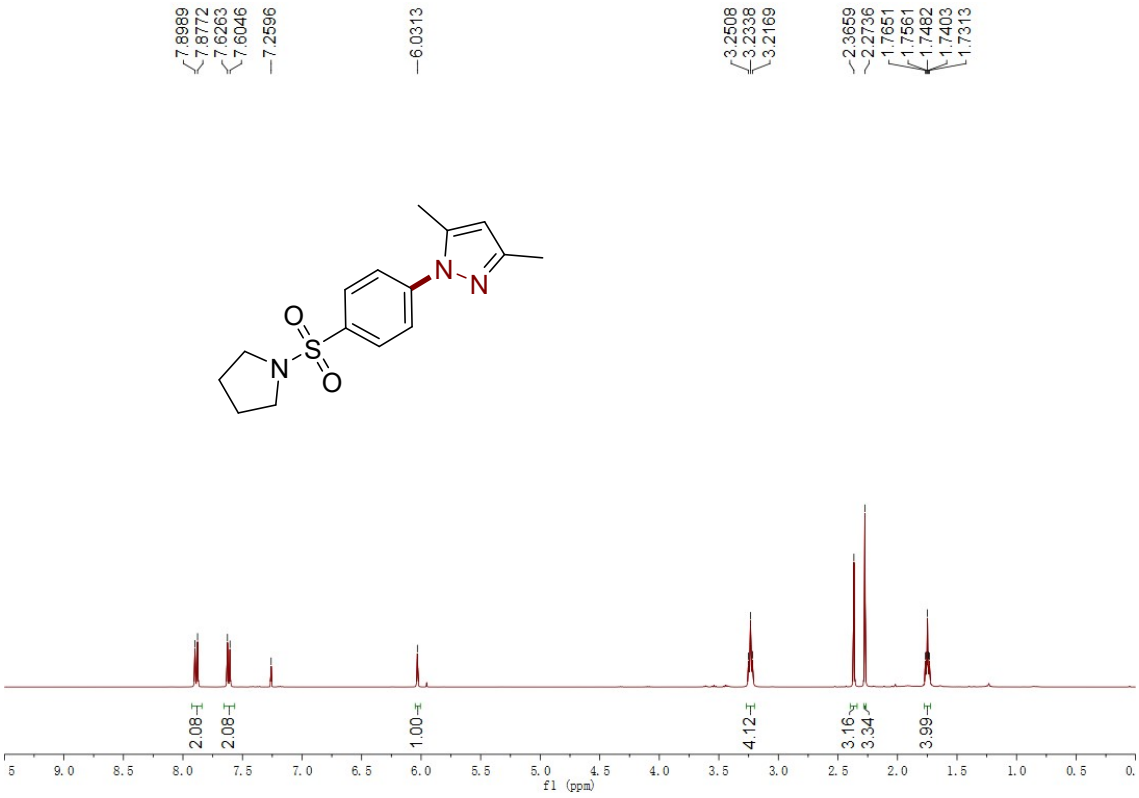
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **65**



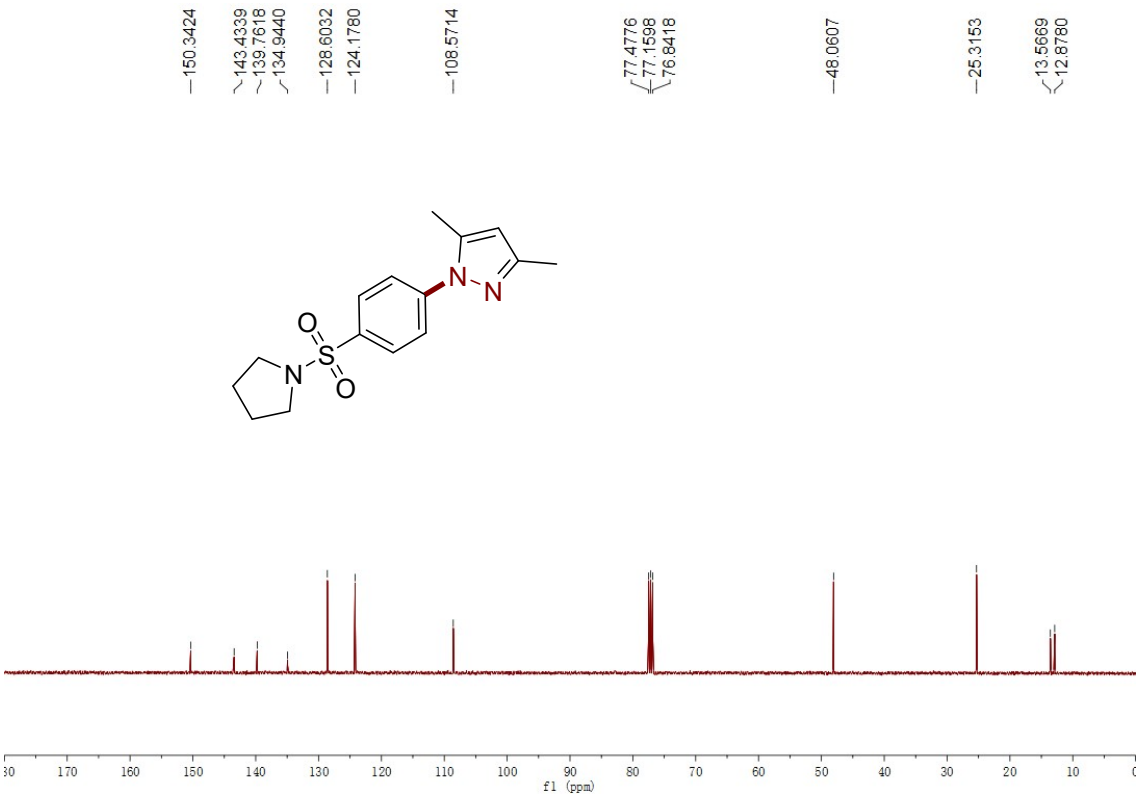
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **66**



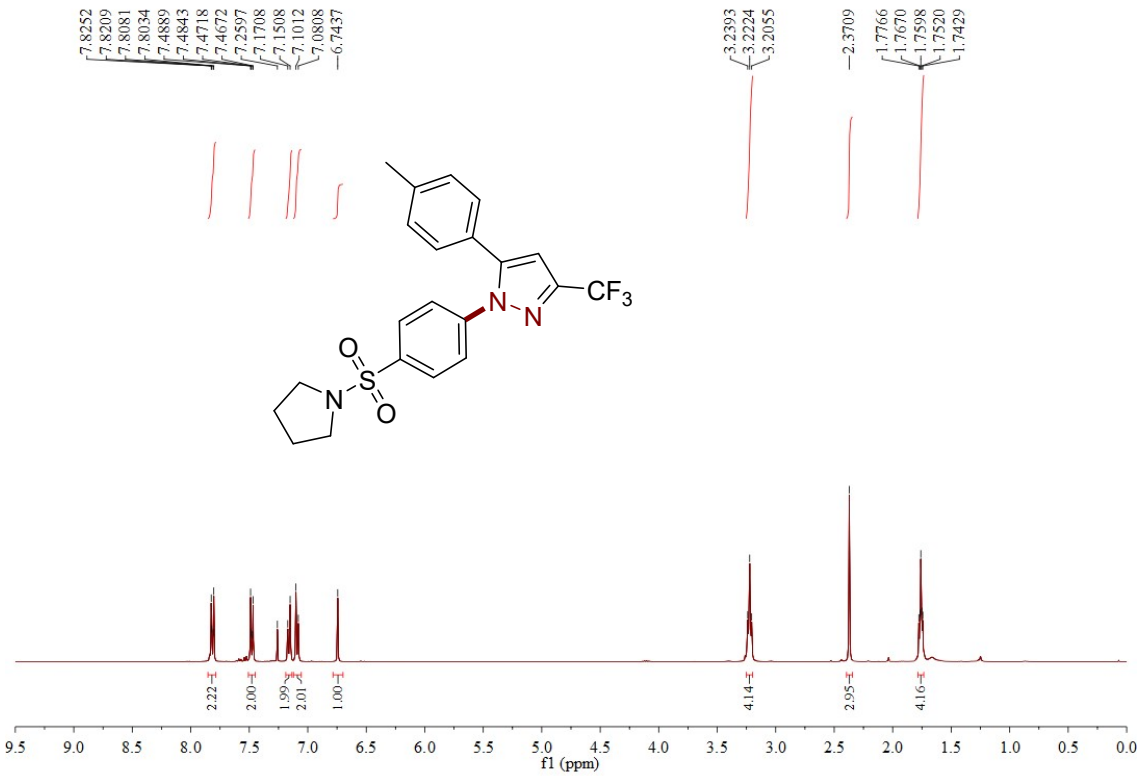
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **66**



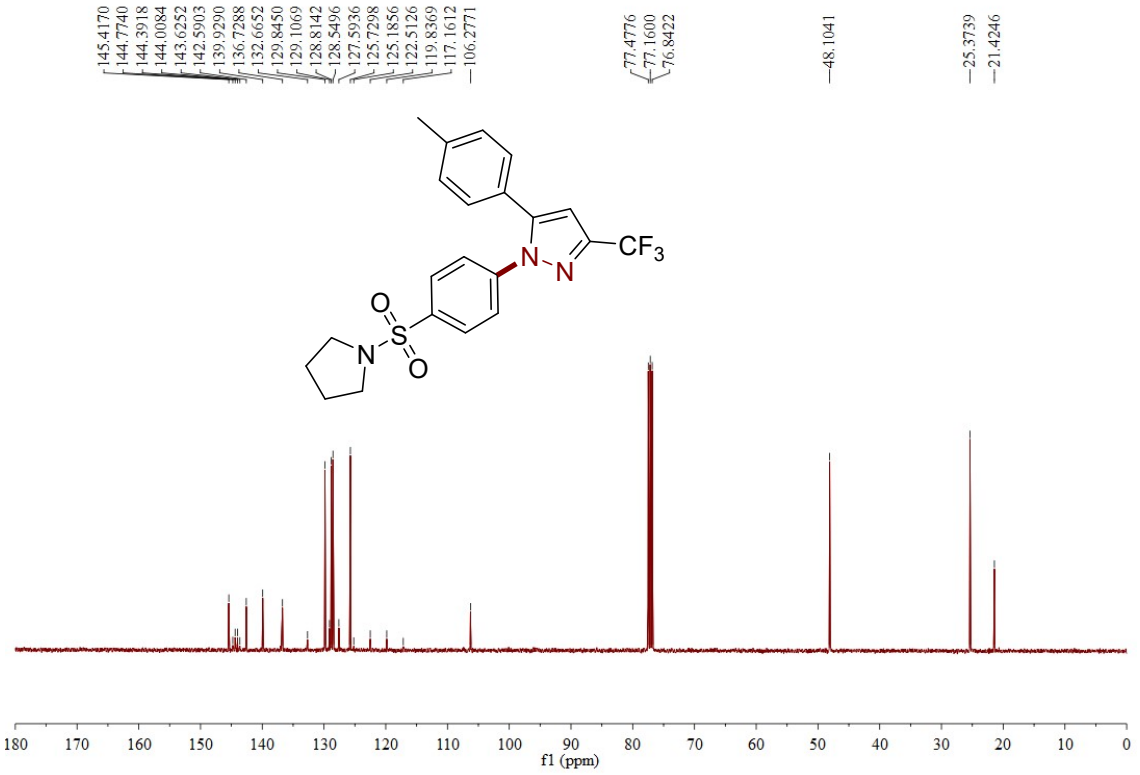
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **67**



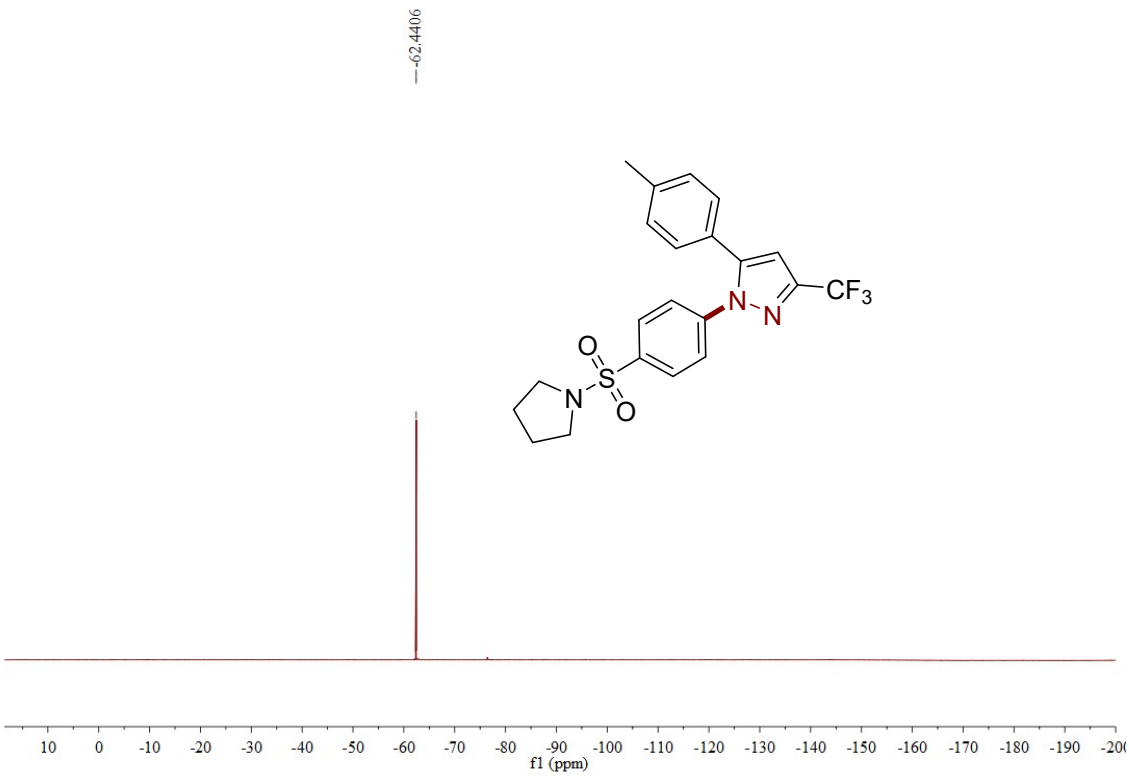
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **67**



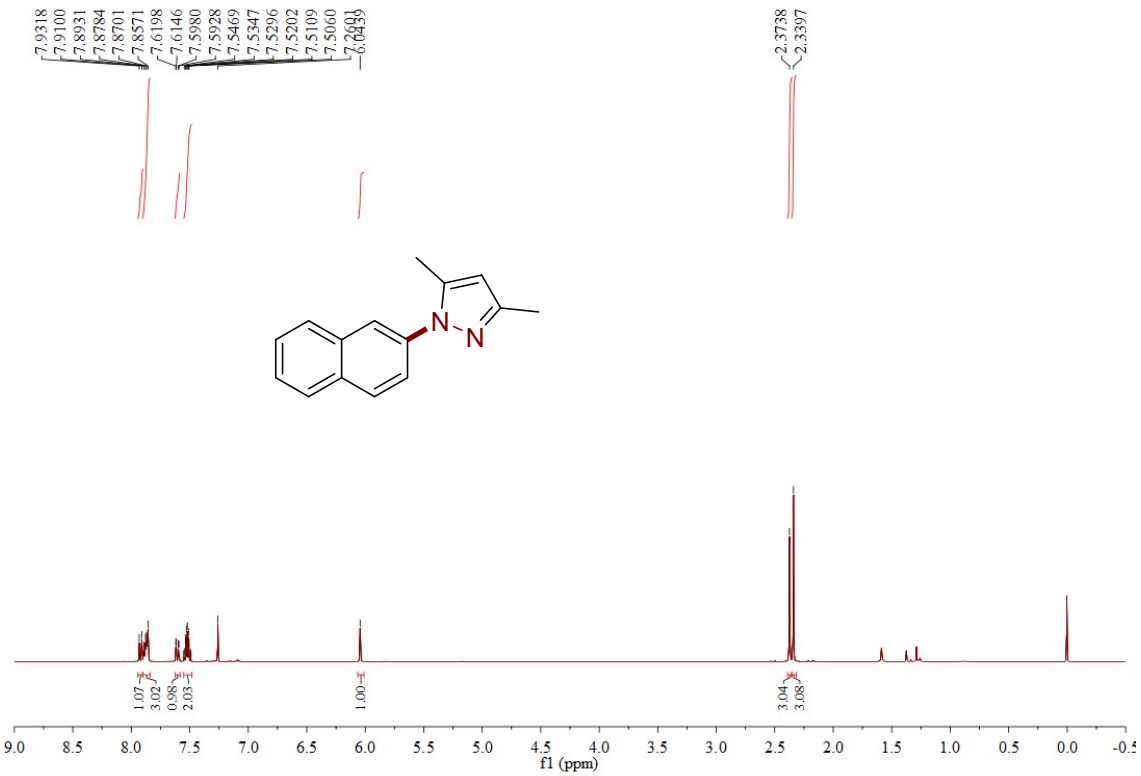
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **68**



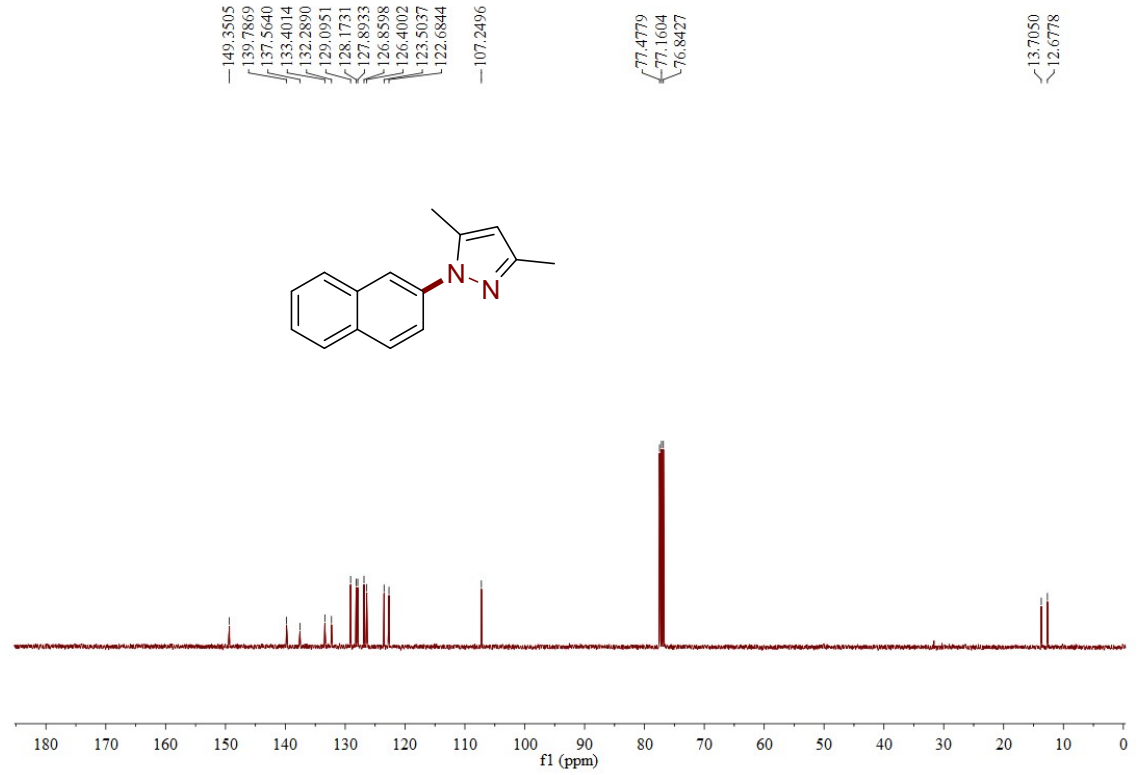
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **68**



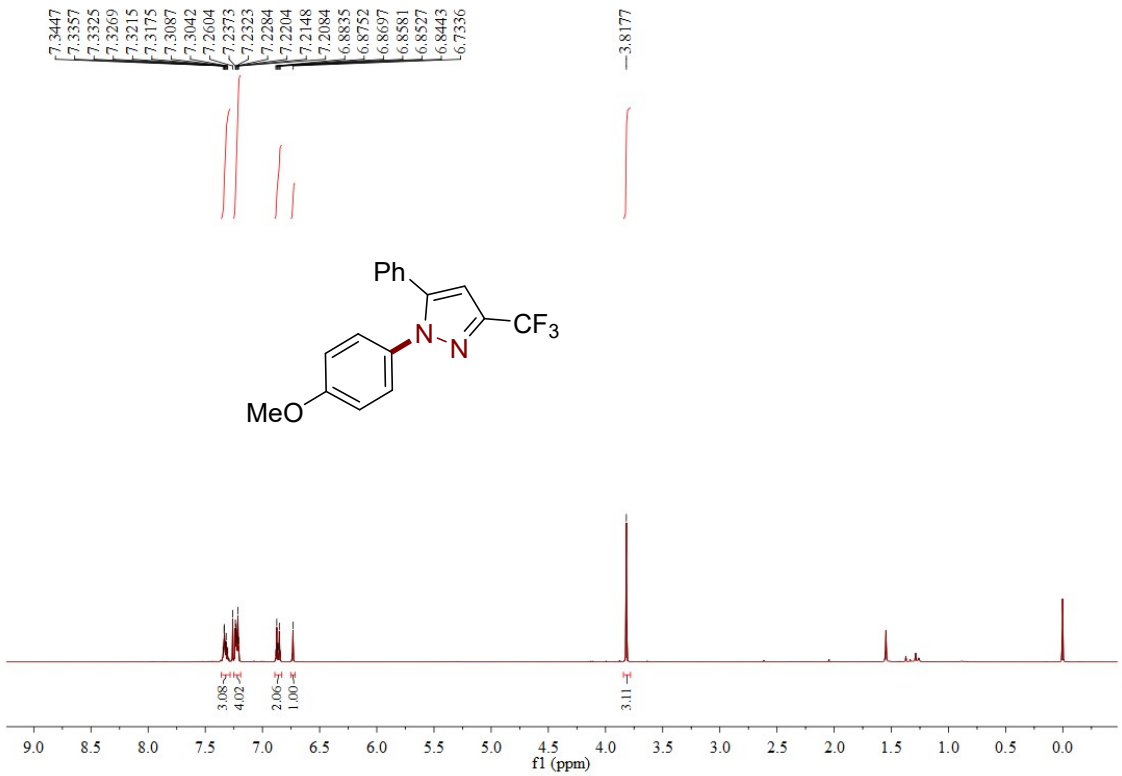
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **68**



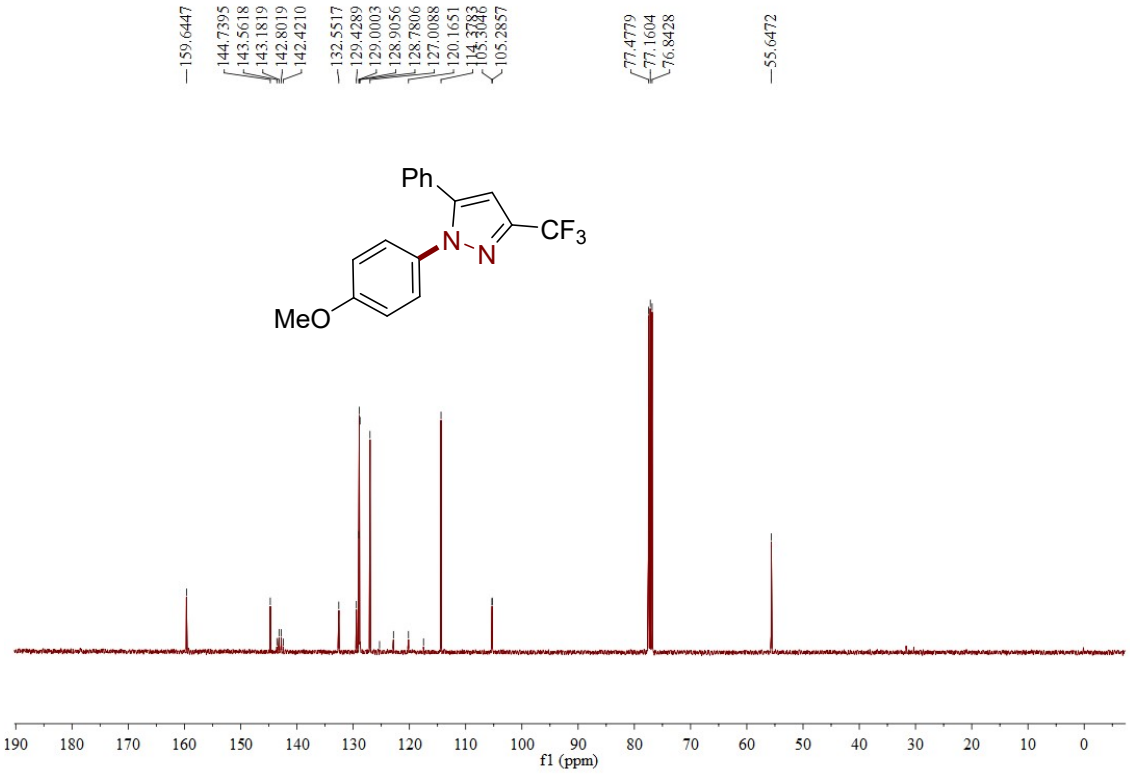
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **69**



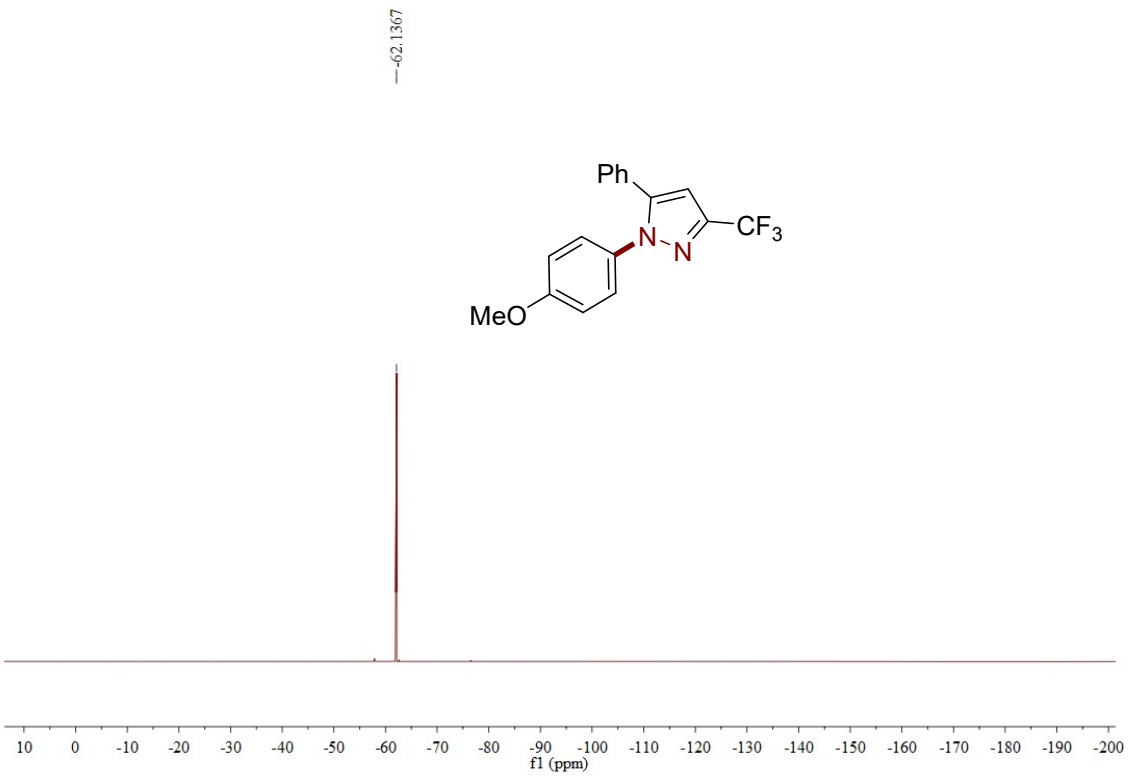
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **69**



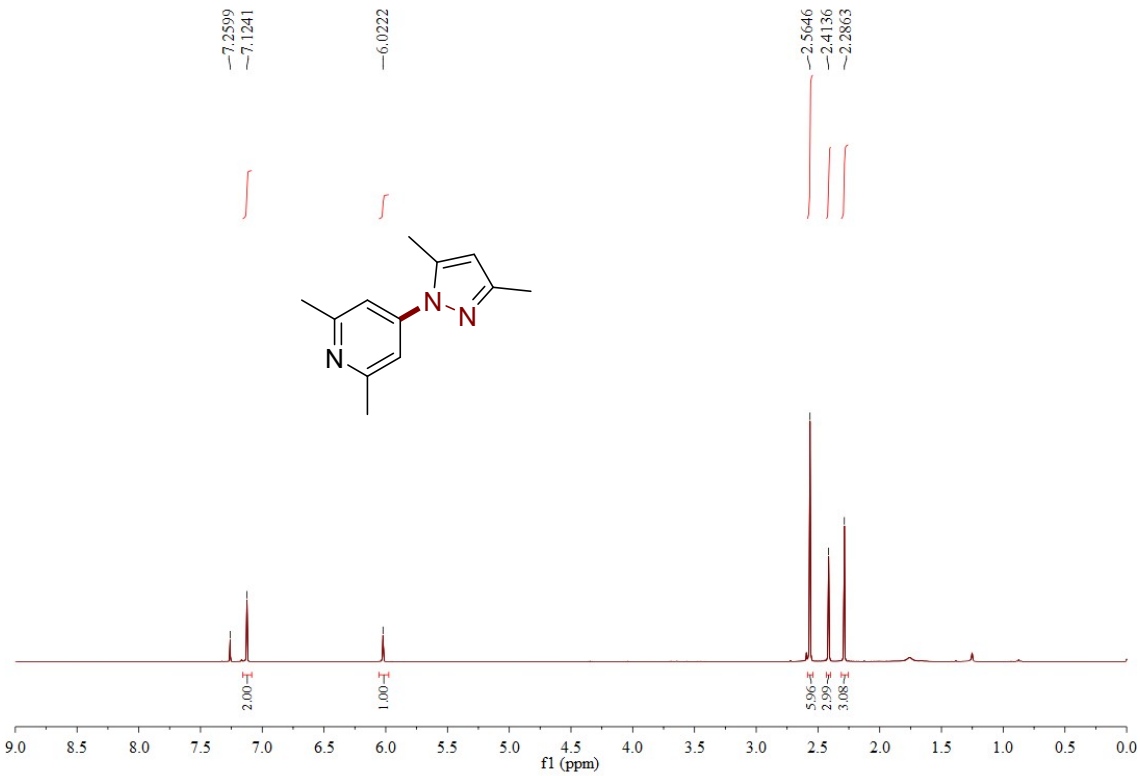
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **70**



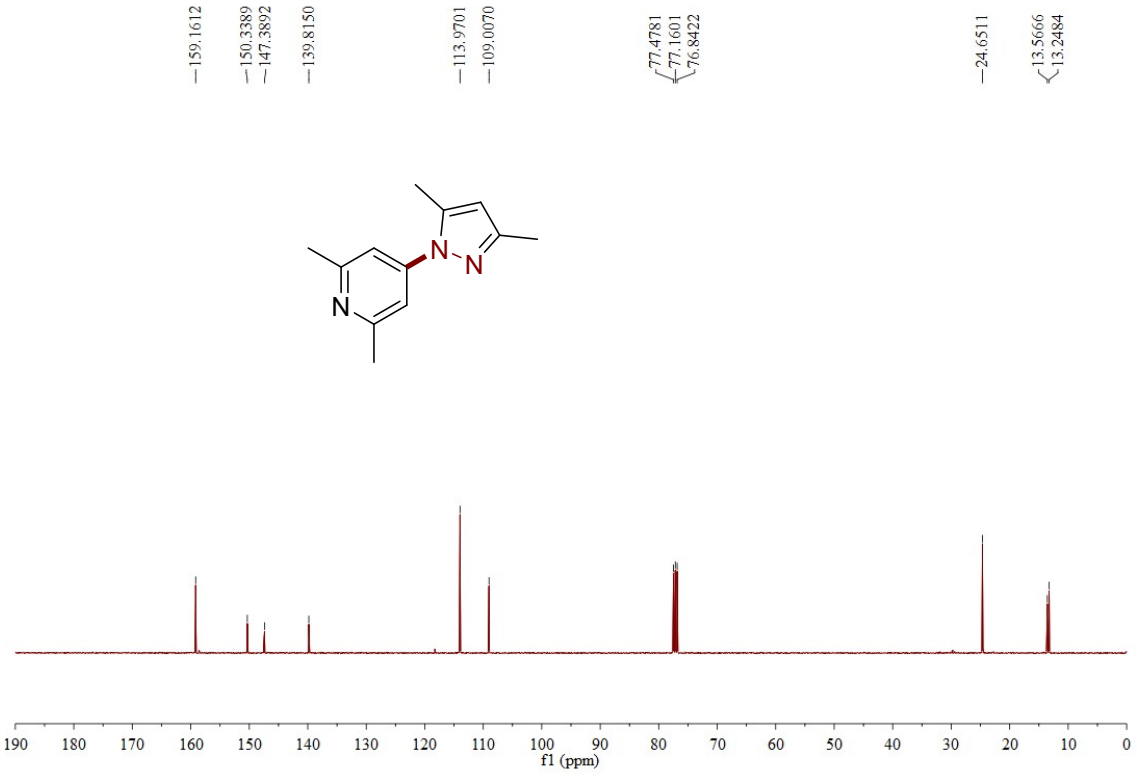
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **70**



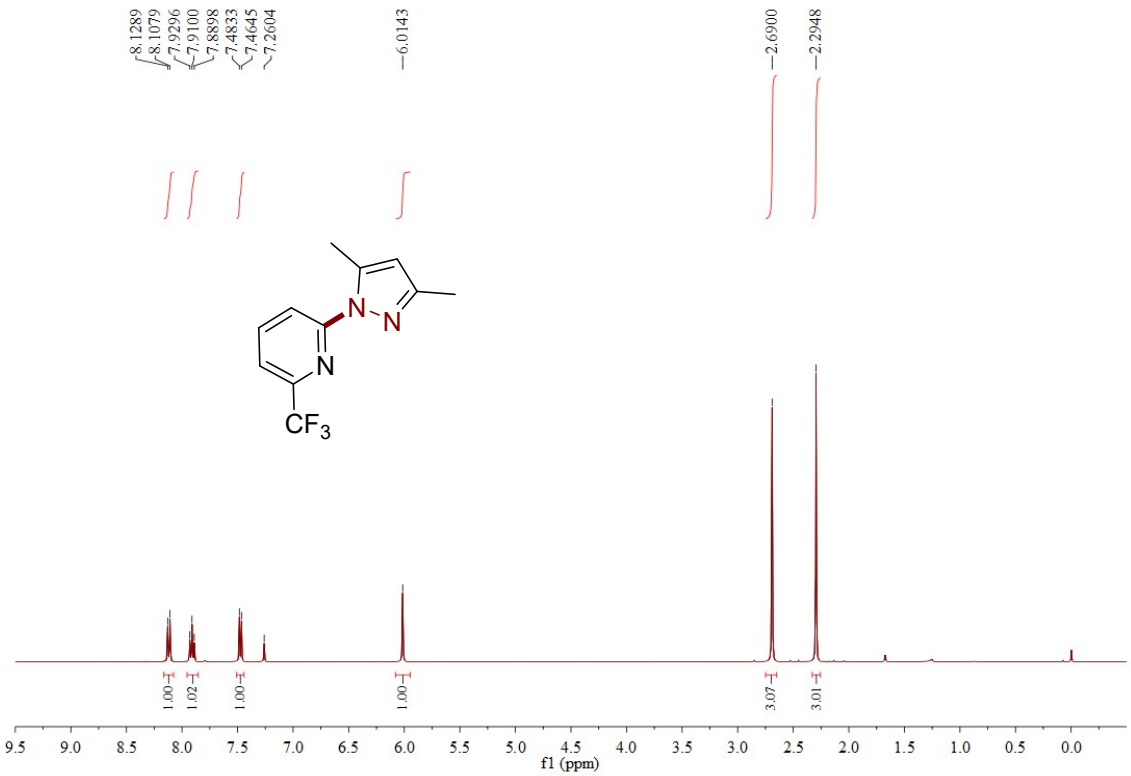
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **70**



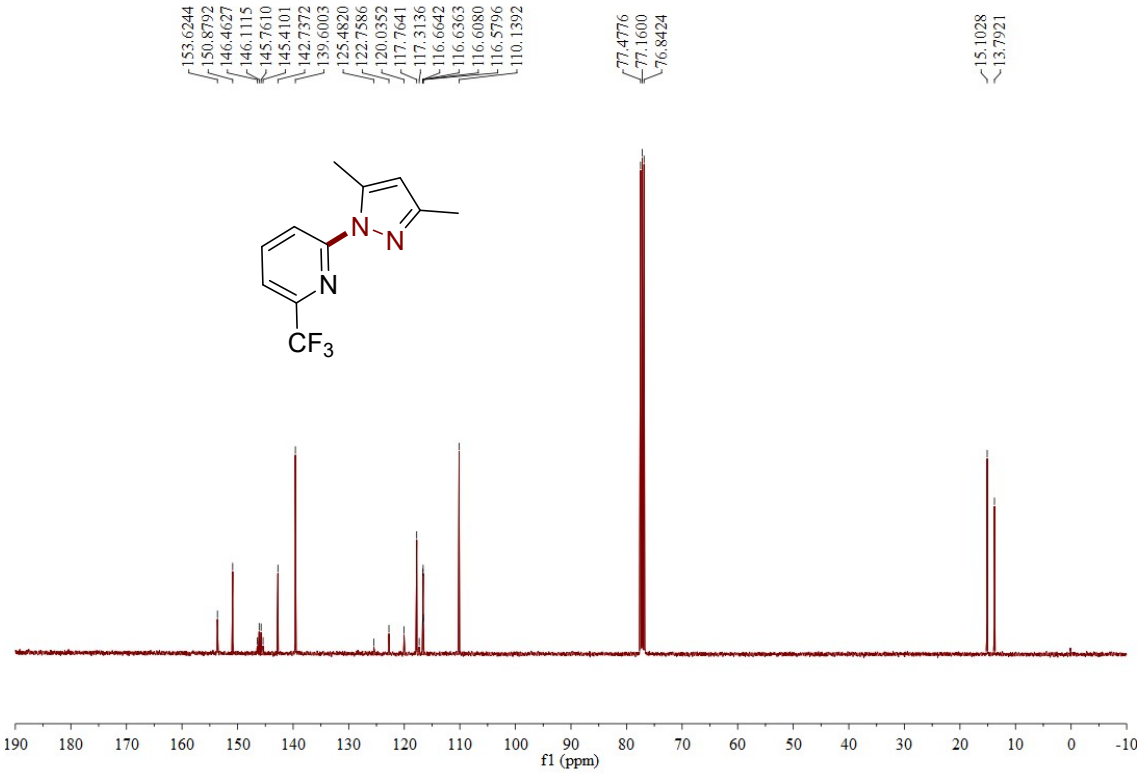
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **71**



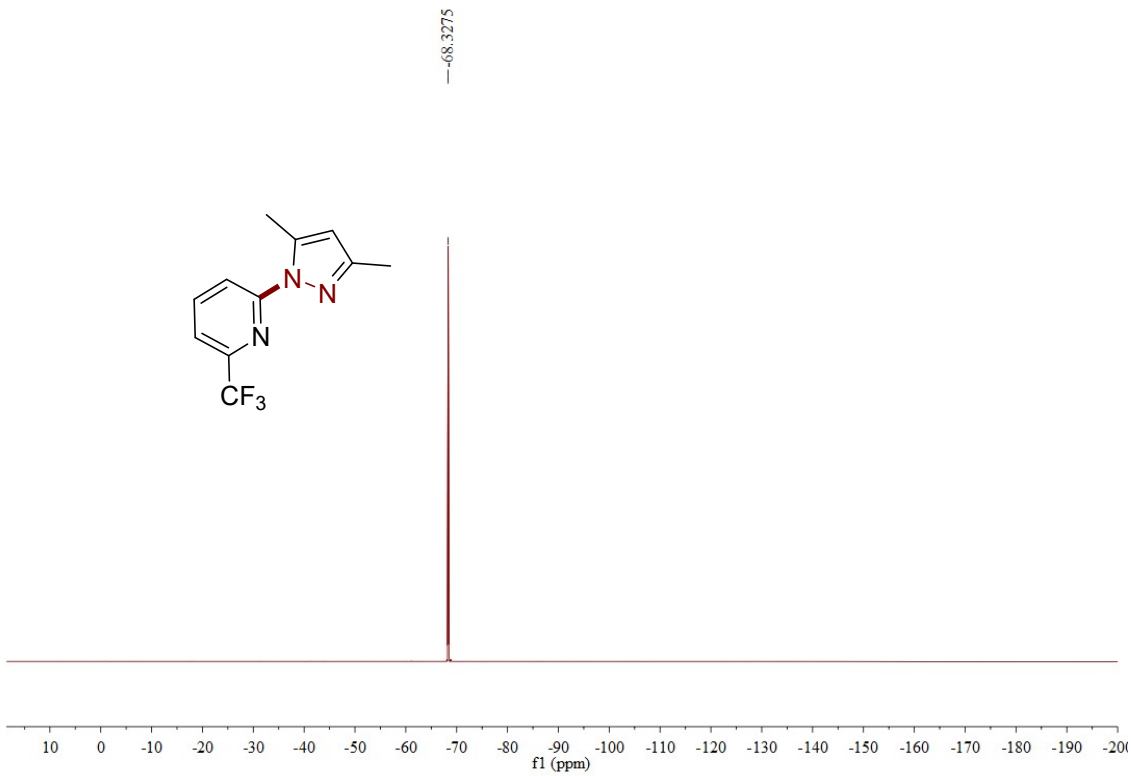
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **71**



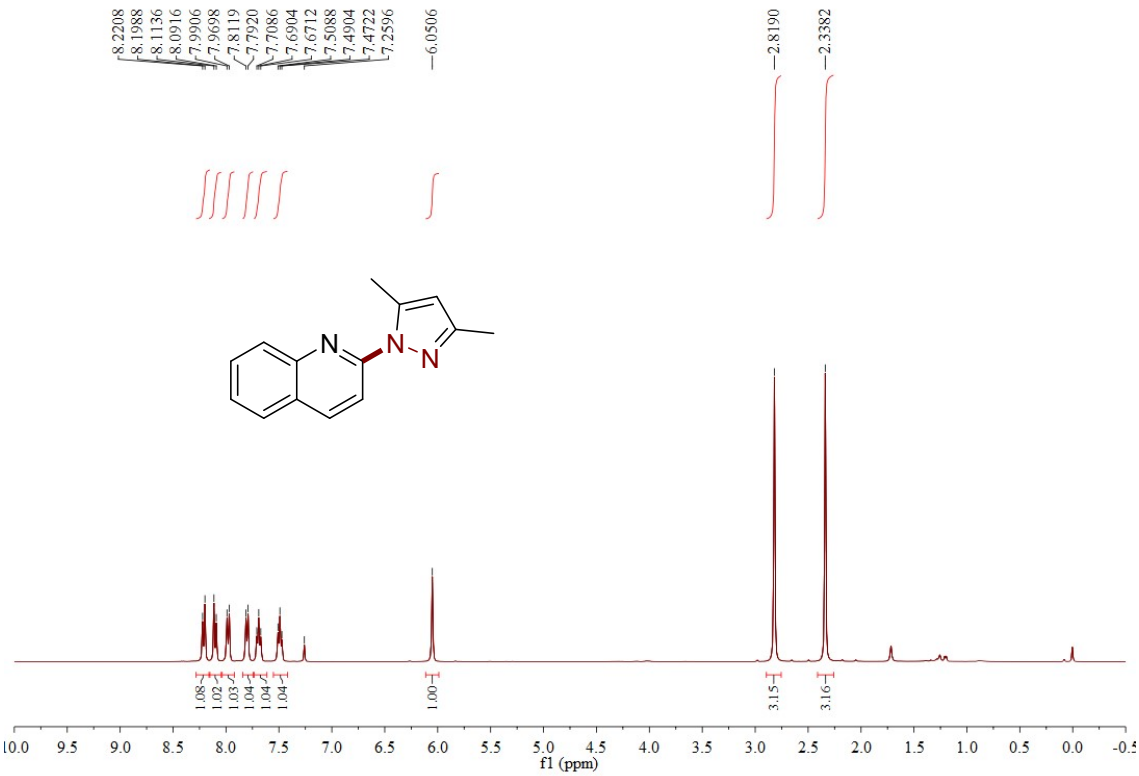
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **72**



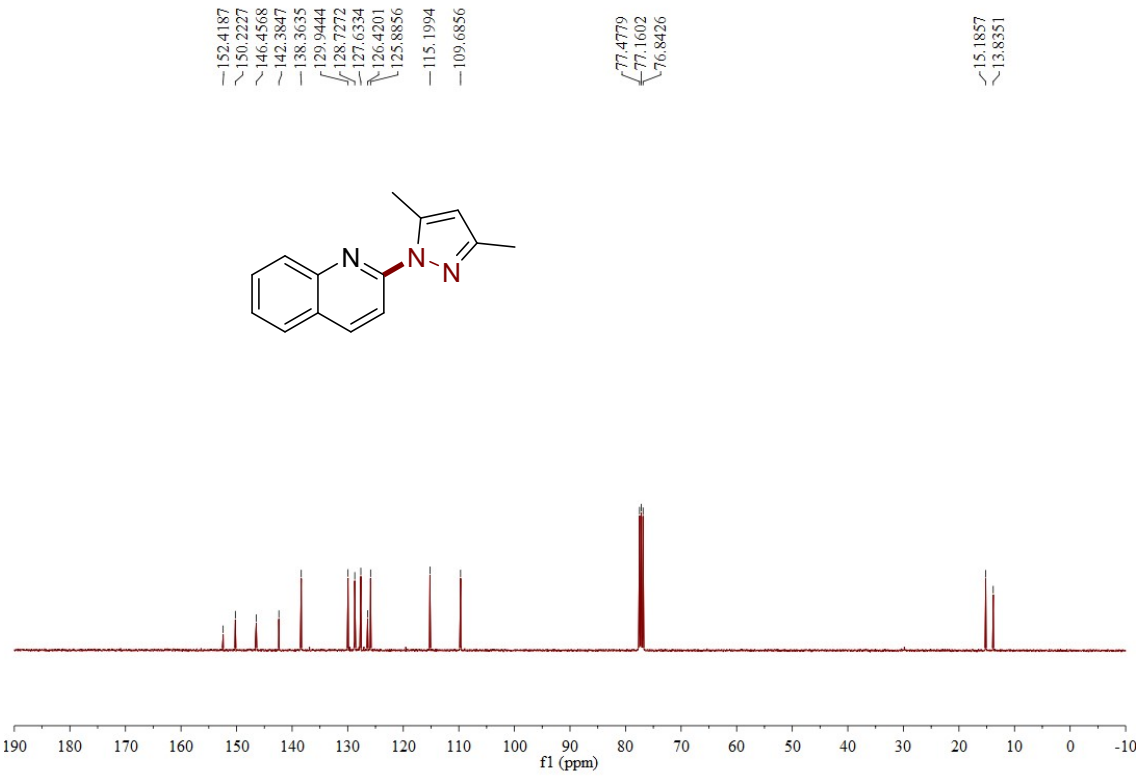
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **72**



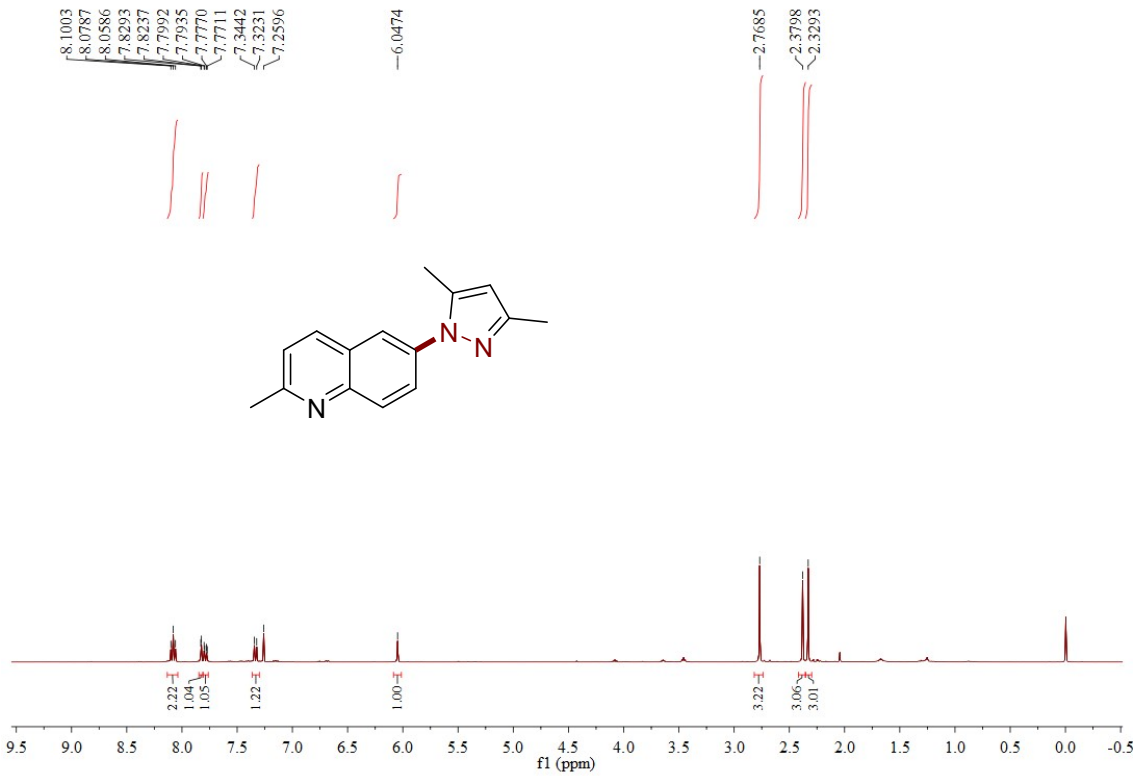
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **72**



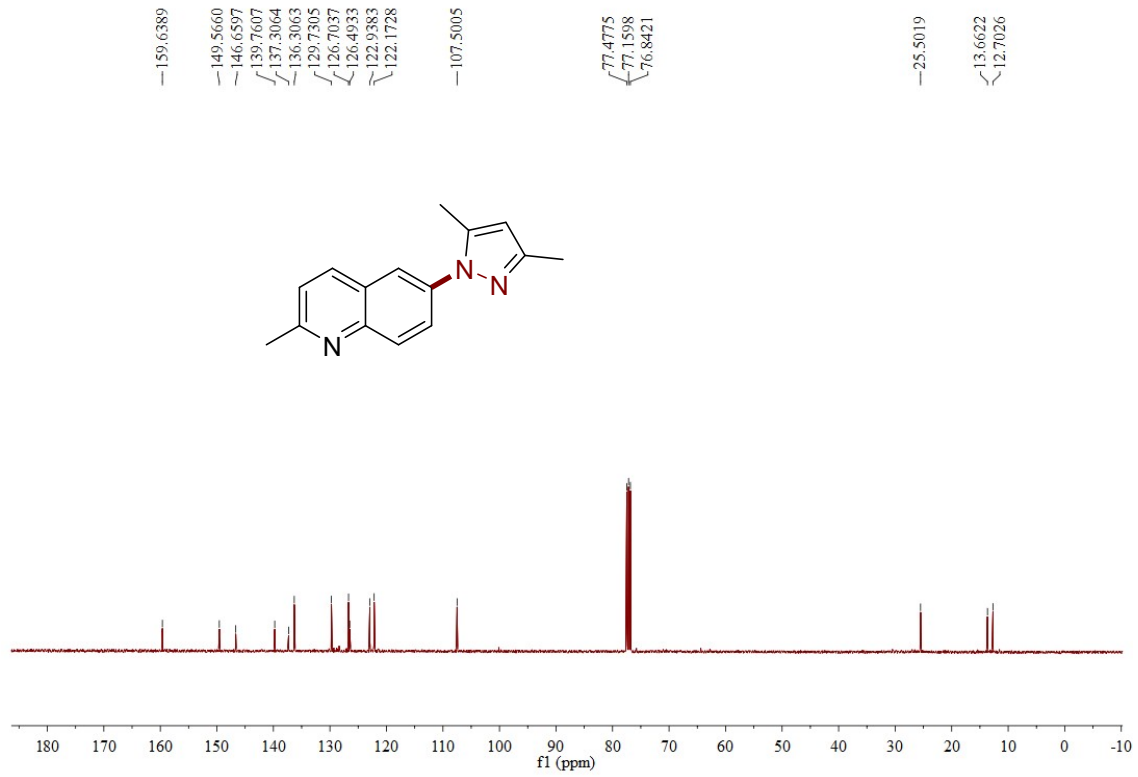
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **73**



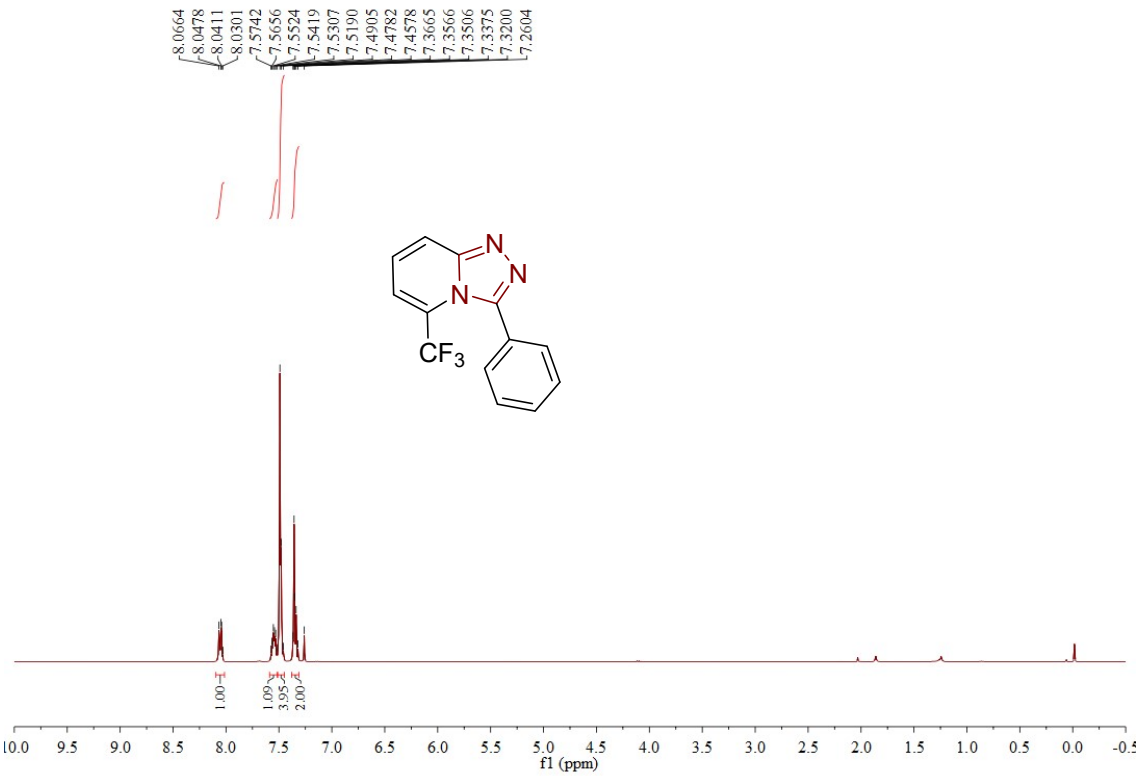
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **73**



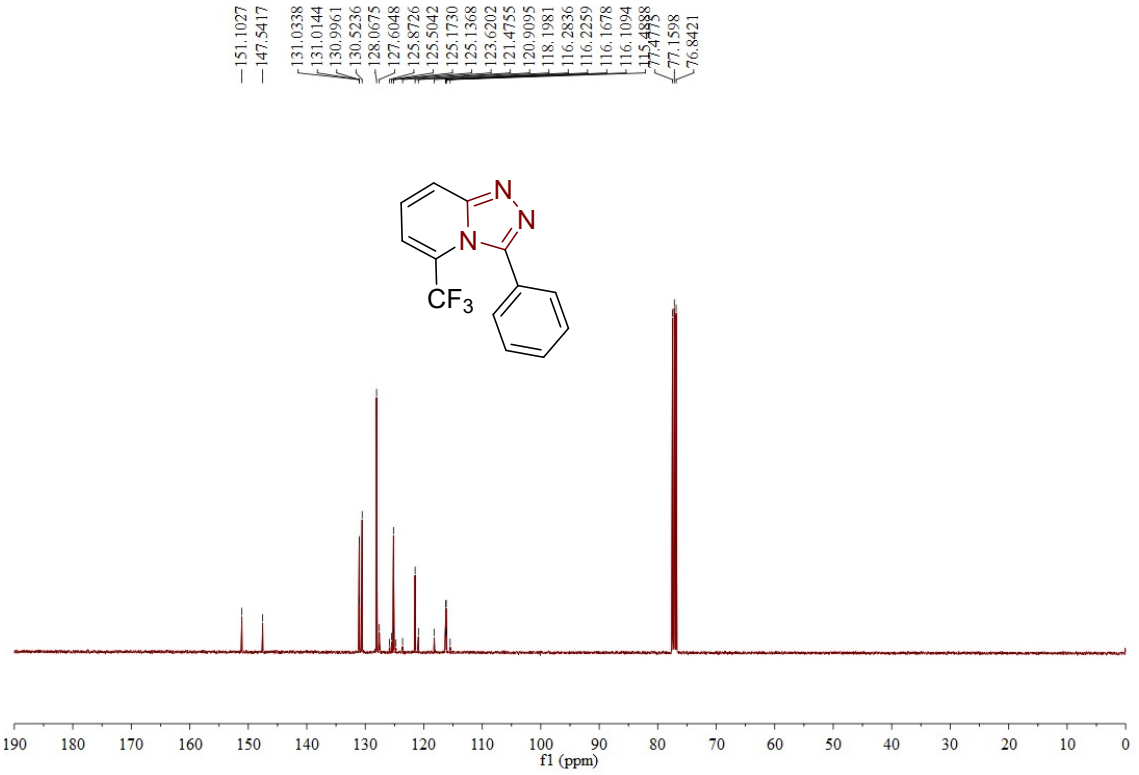
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **74**



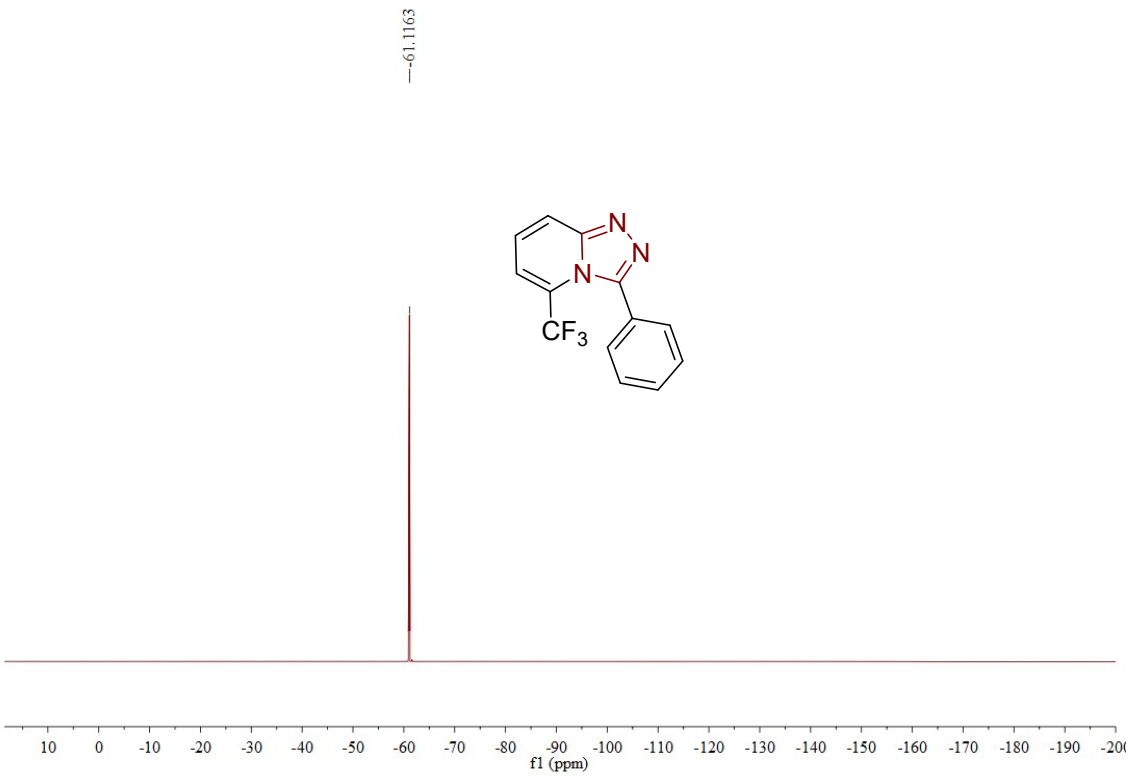
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **74**



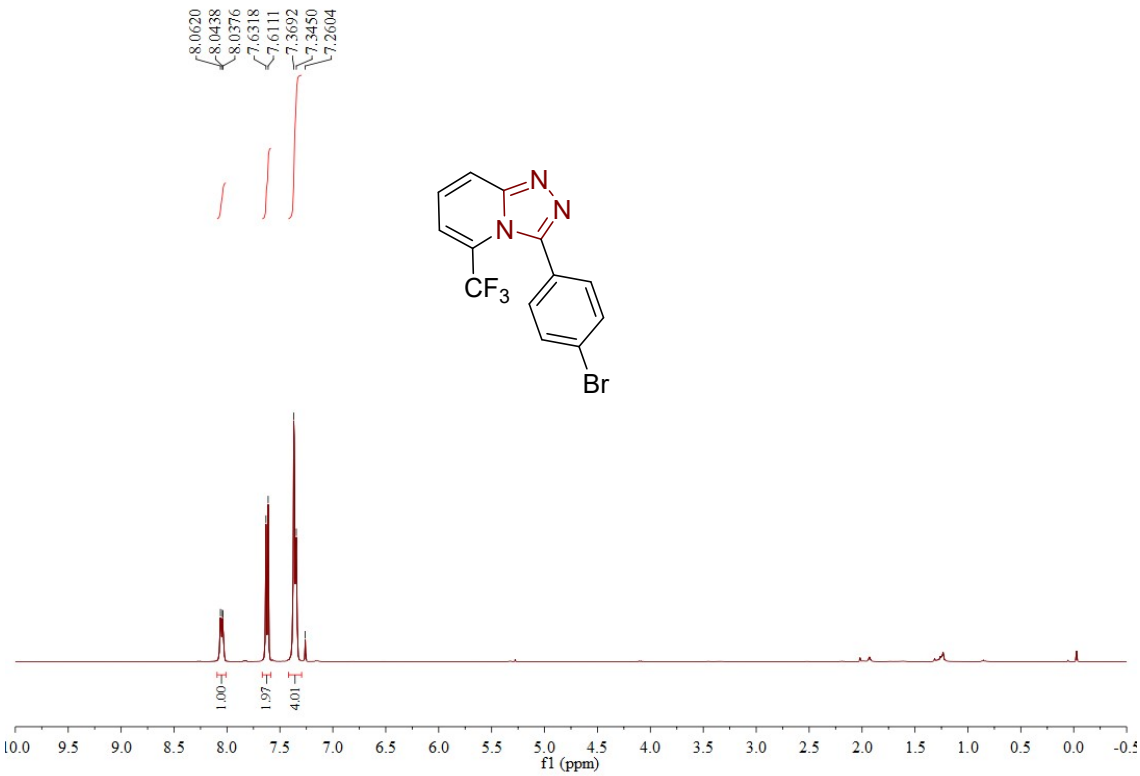
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **75**



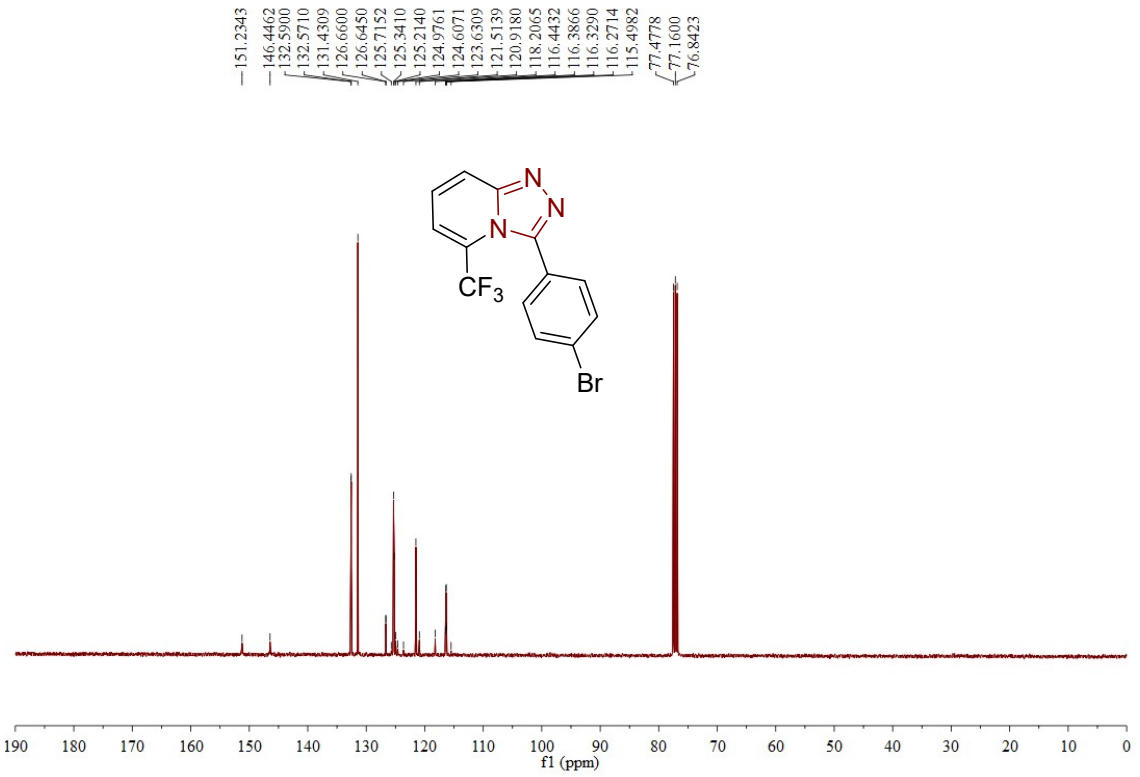
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **75**



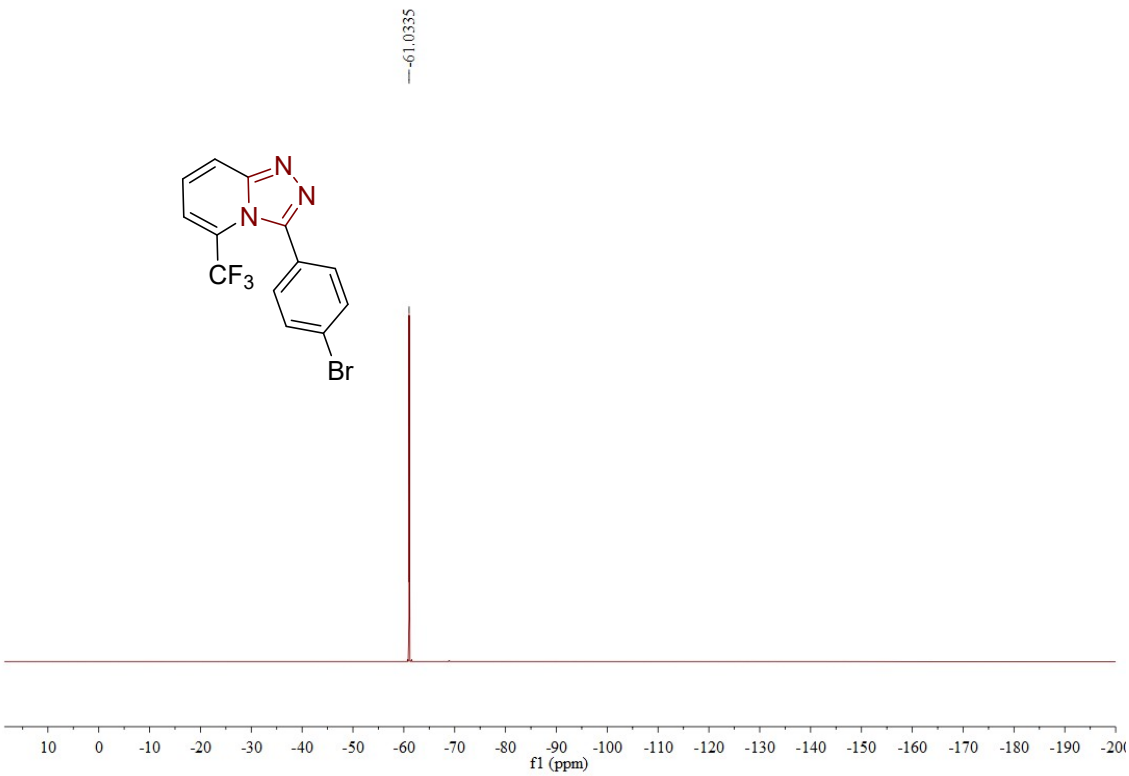
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **75**



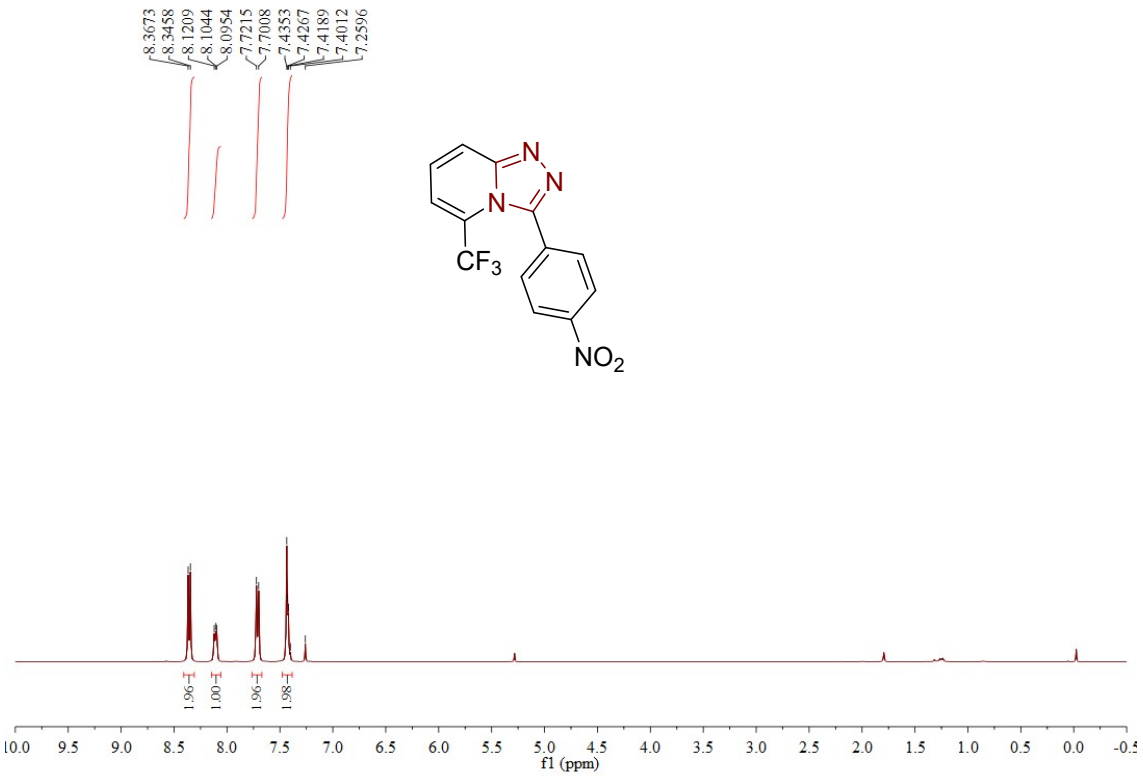
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **76**



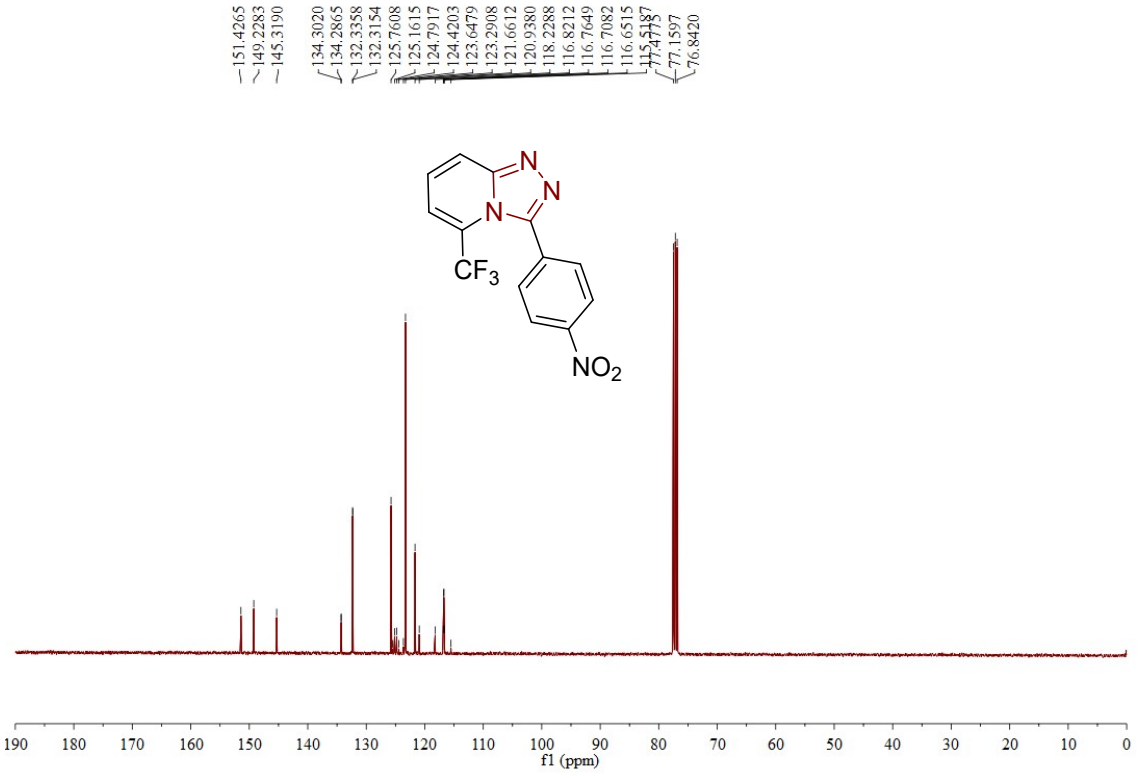
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **76**



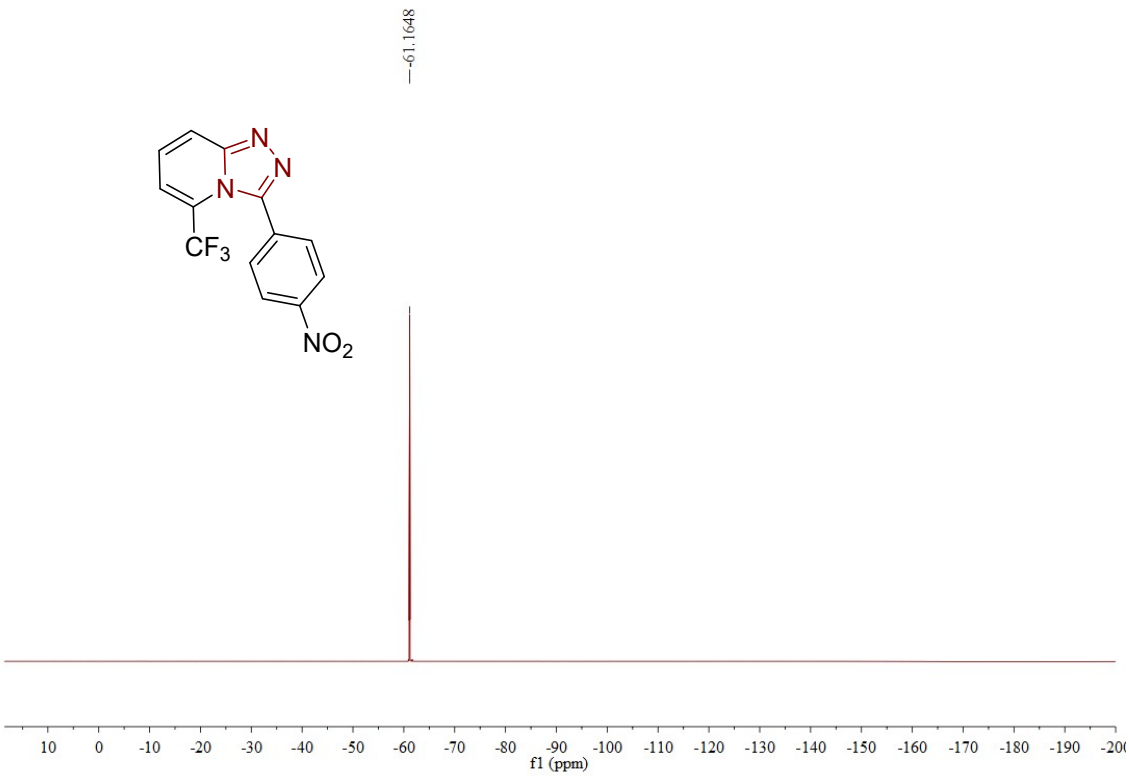
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **76**



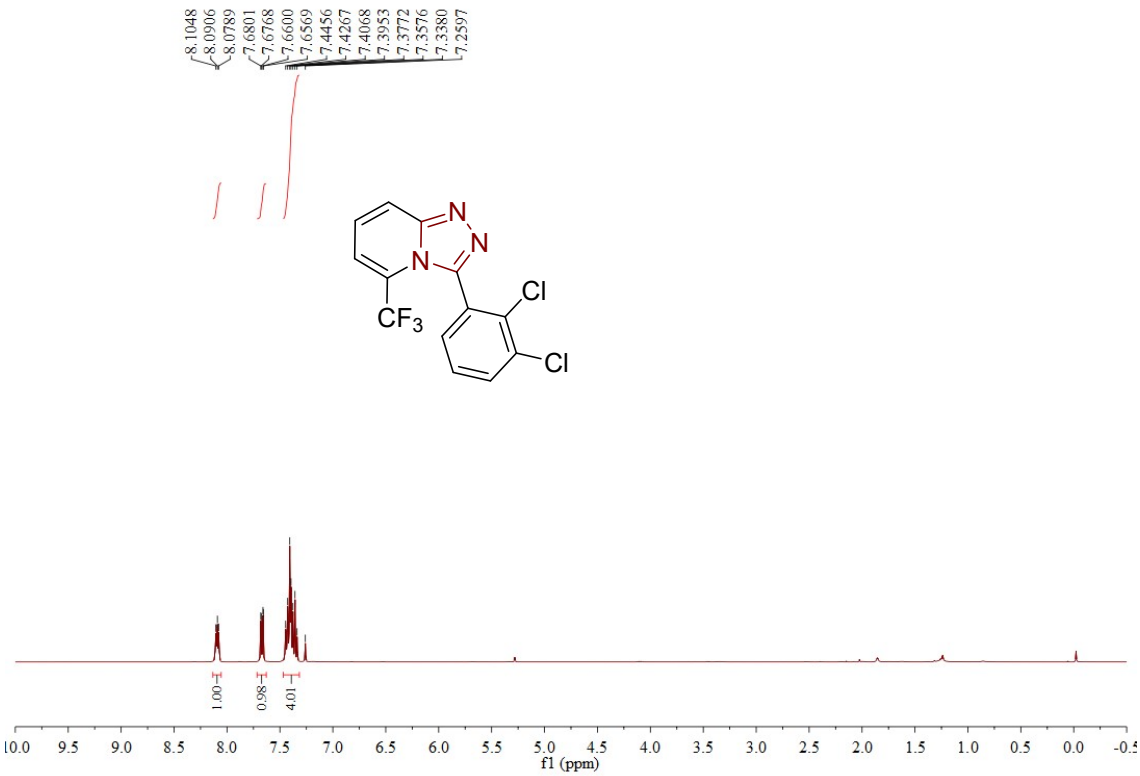
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **77**



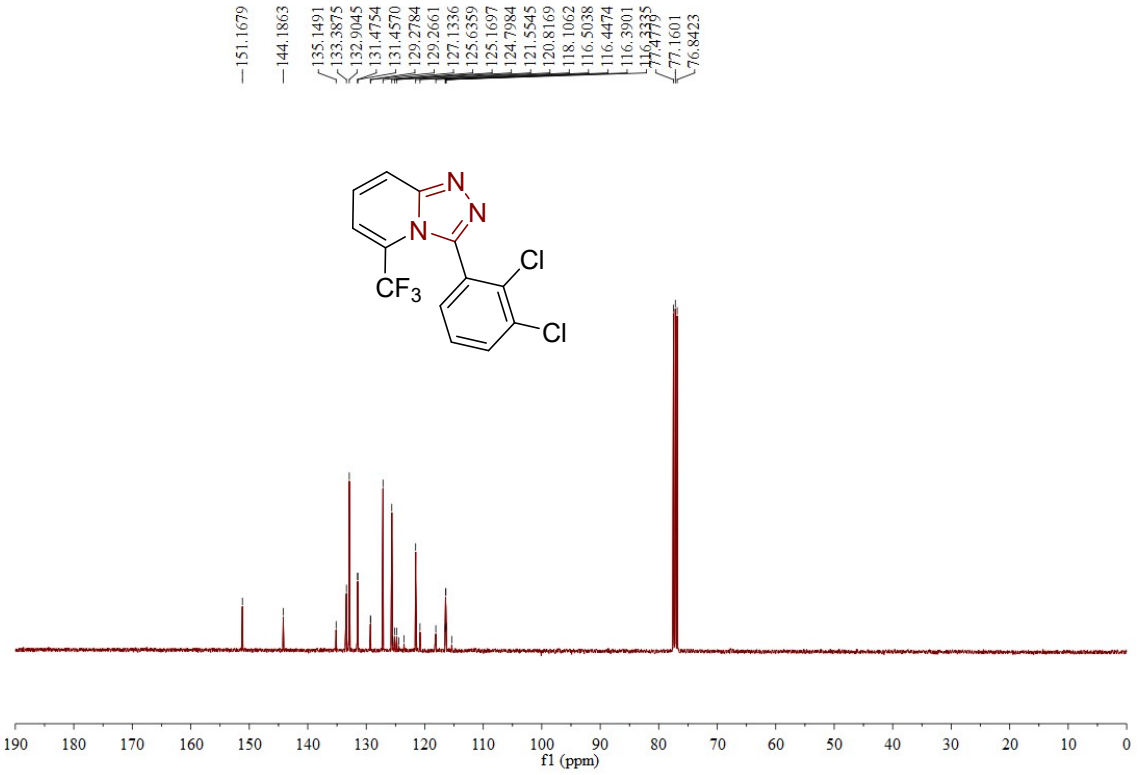
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **77**



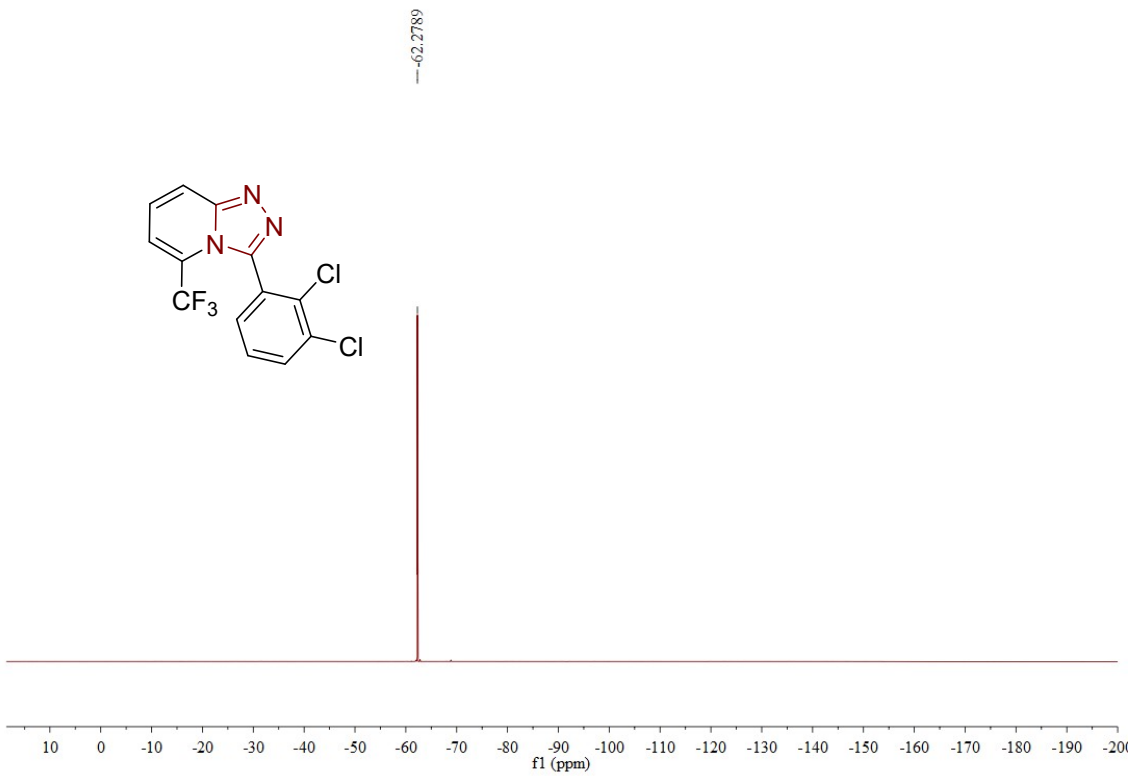
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **77**



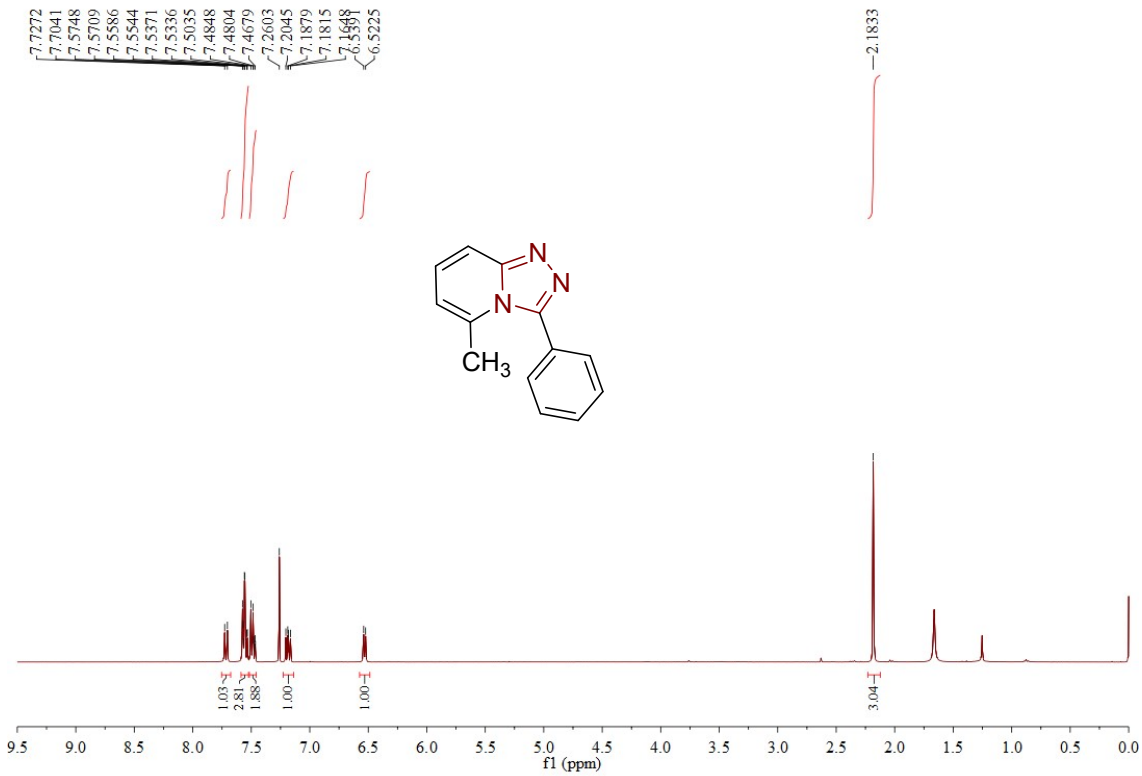
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **78**



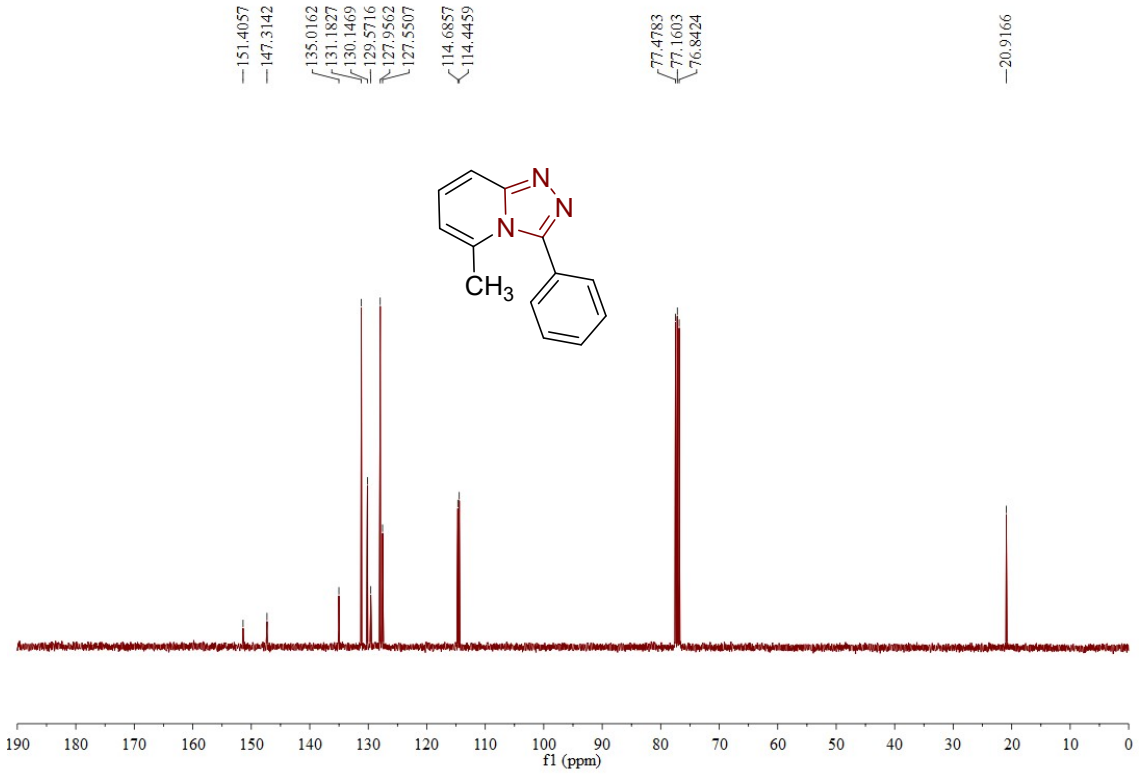
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **78**



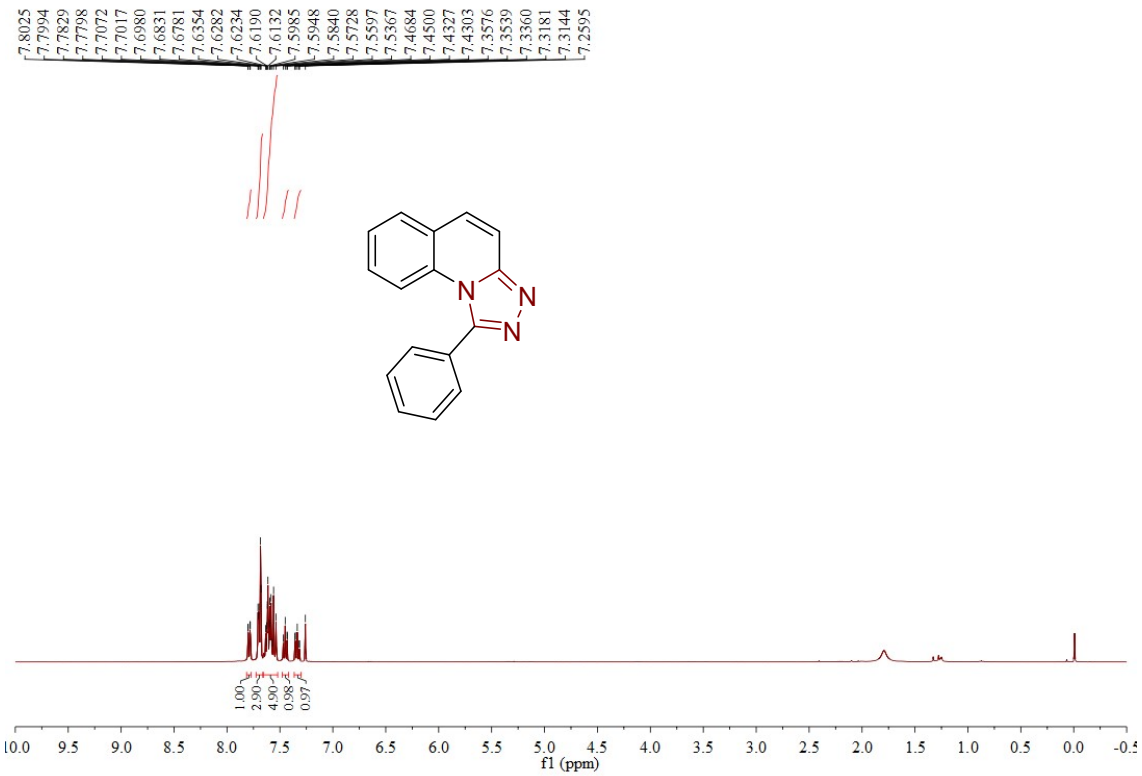
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **78**



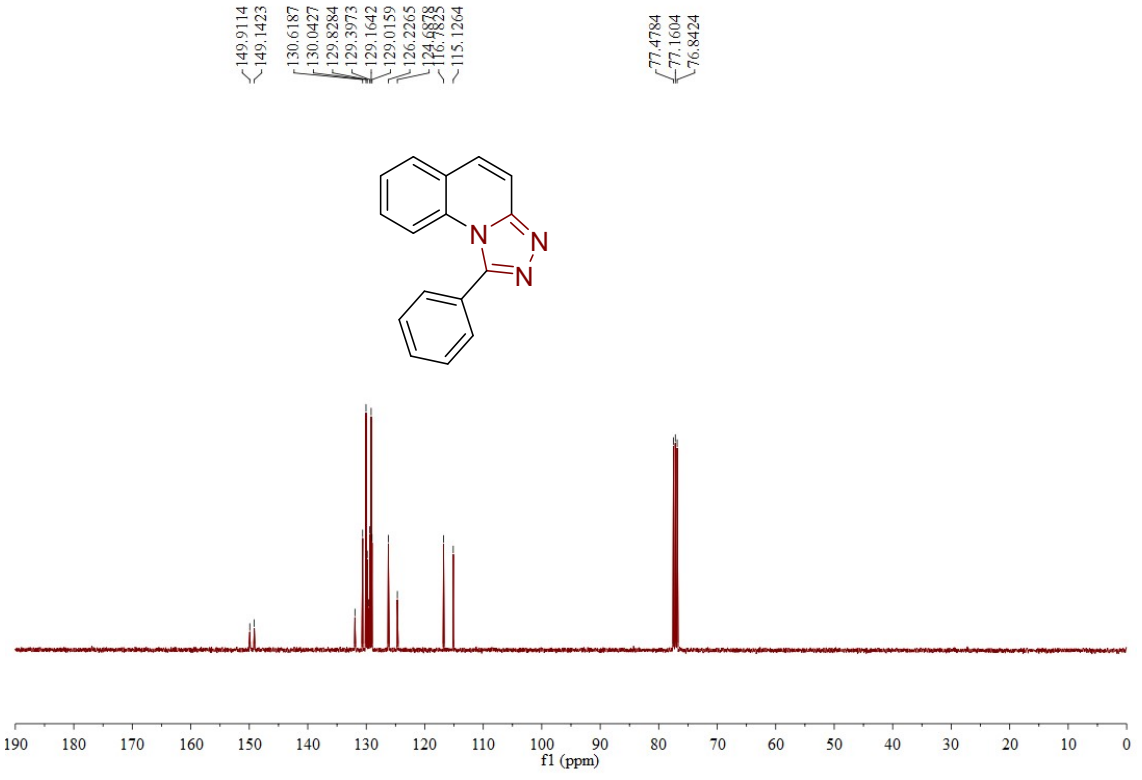
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **79**



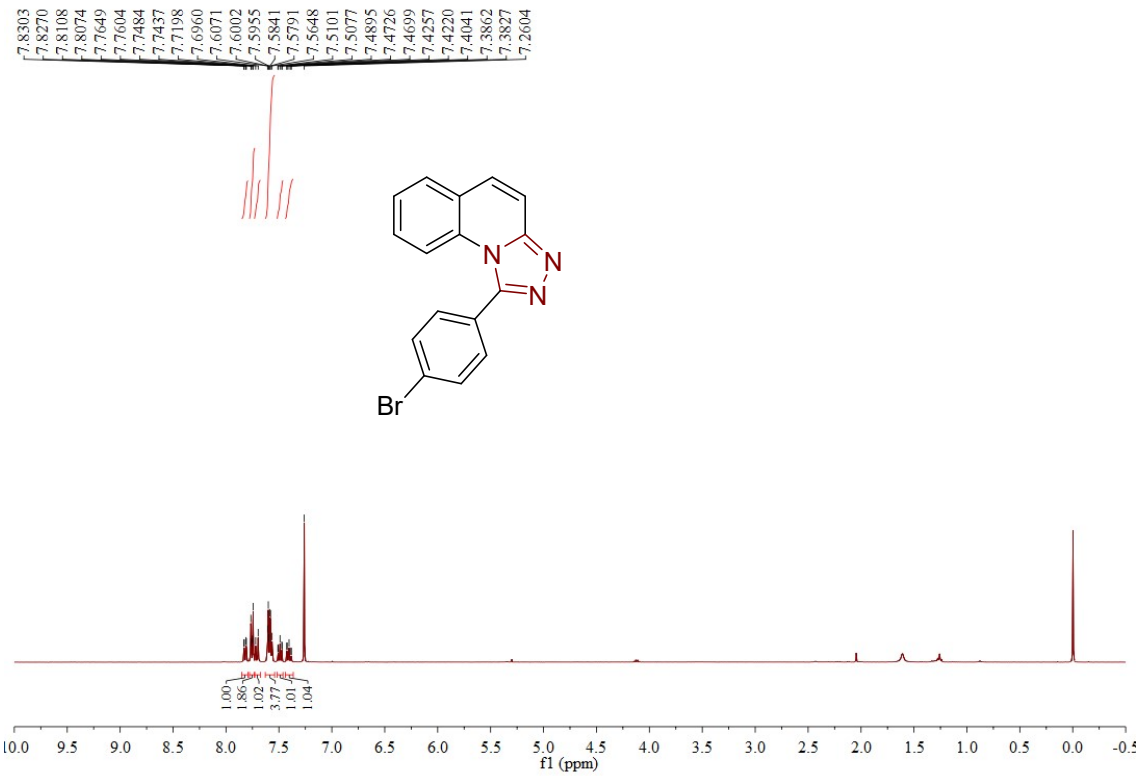
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **79**



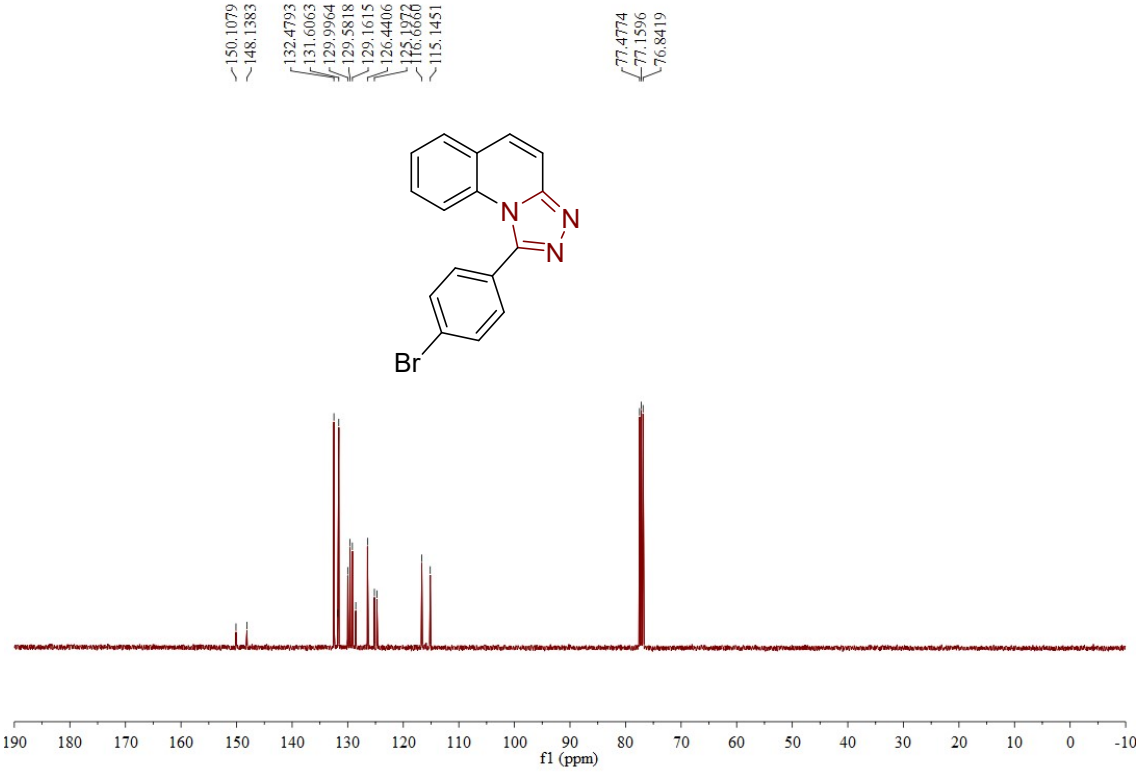
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **80**



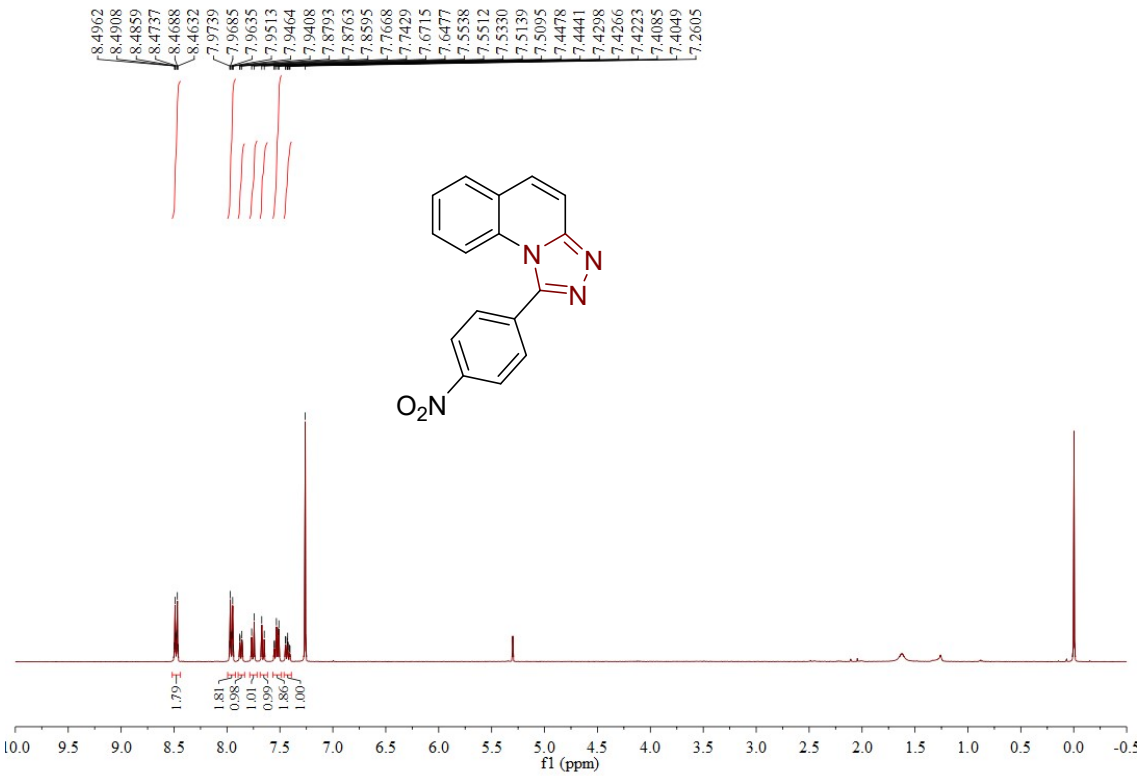
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **80**



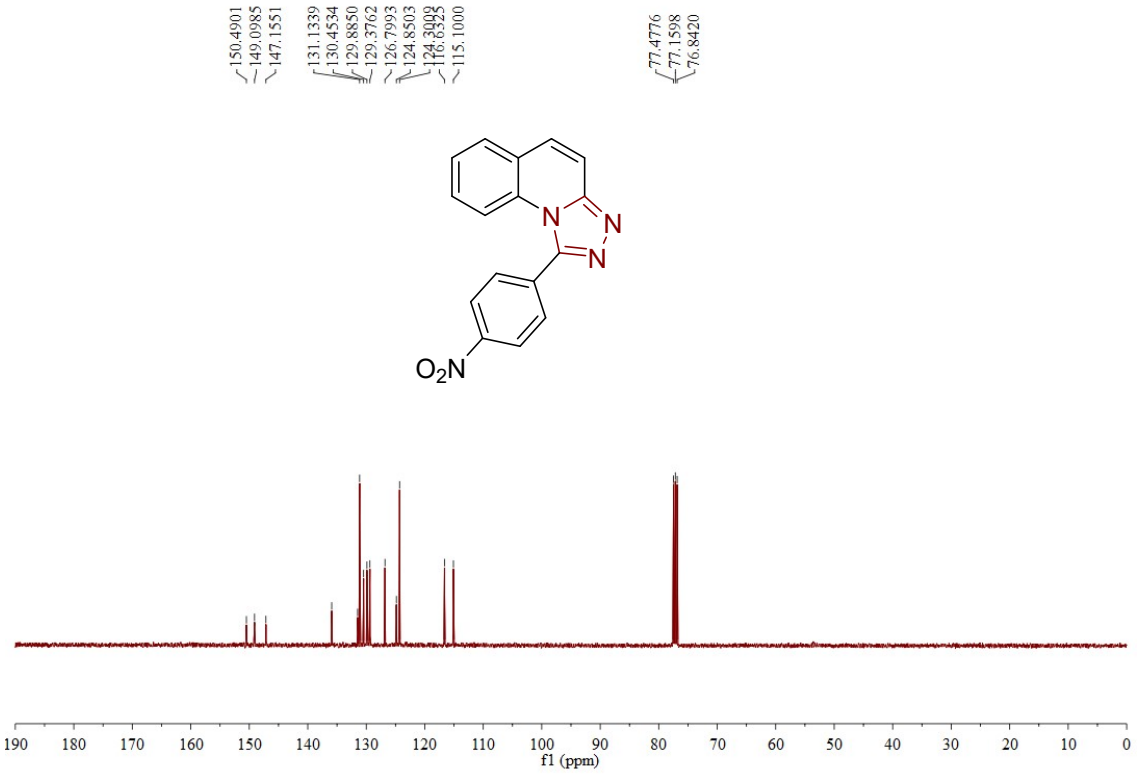
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **81**



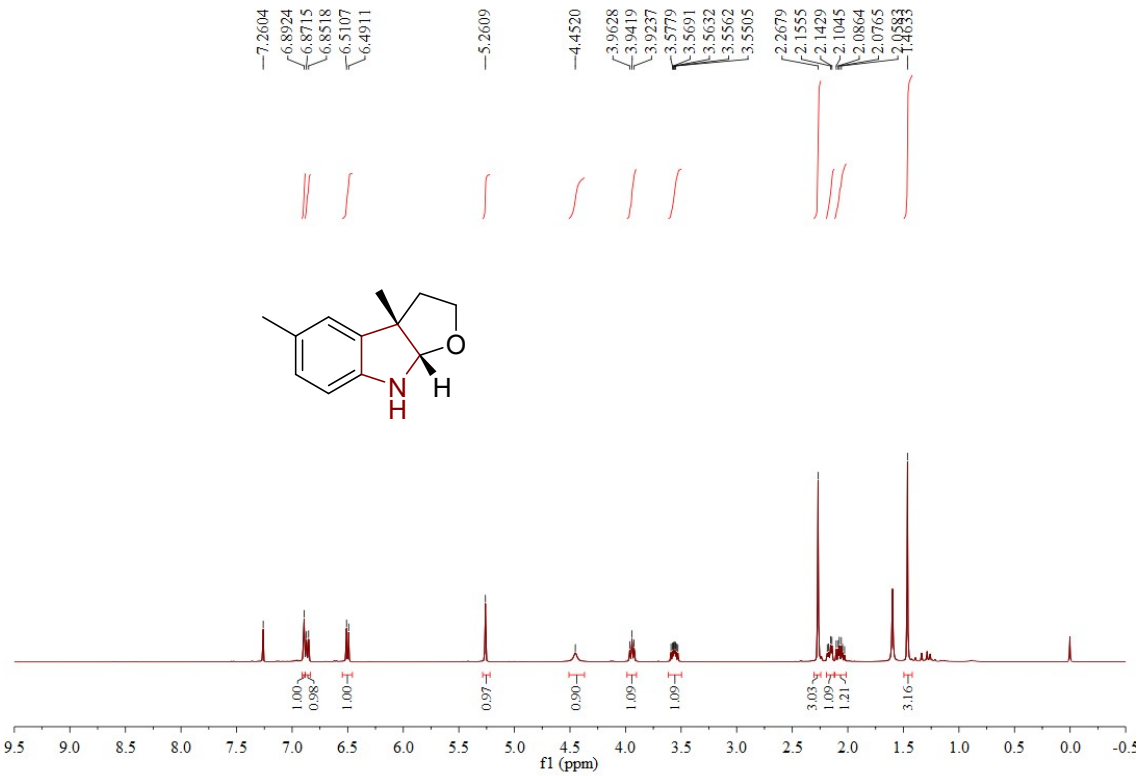
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **81**



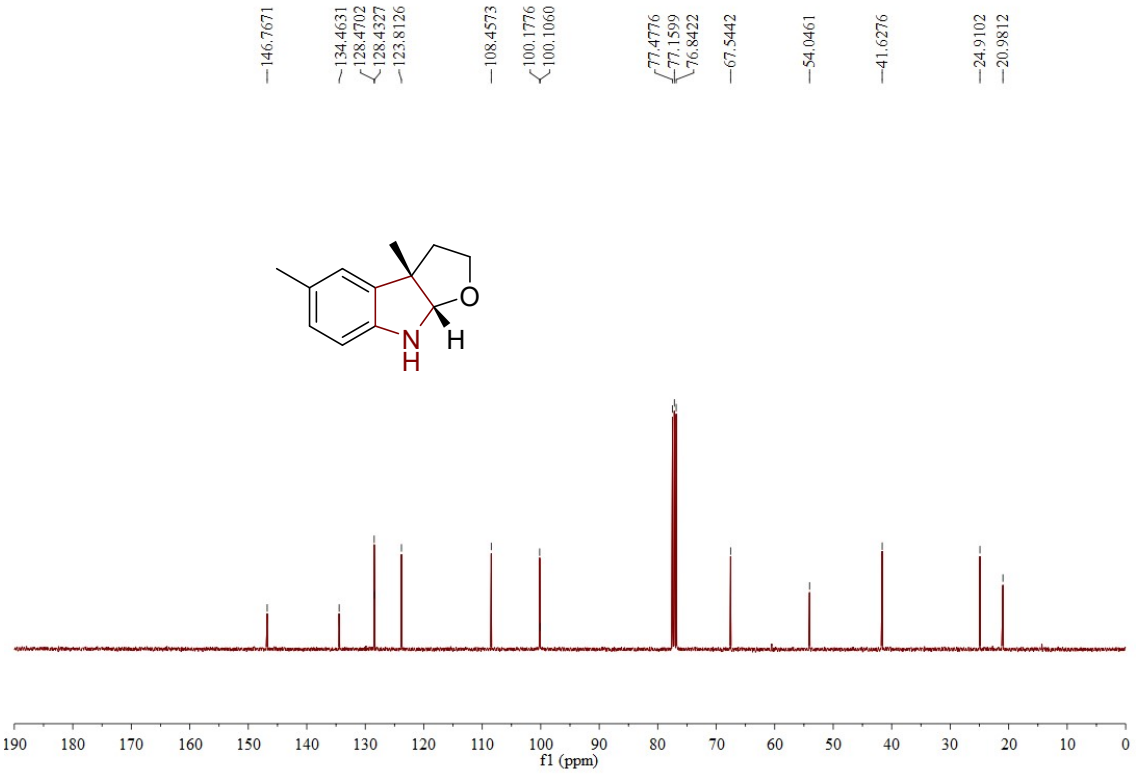
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **82**



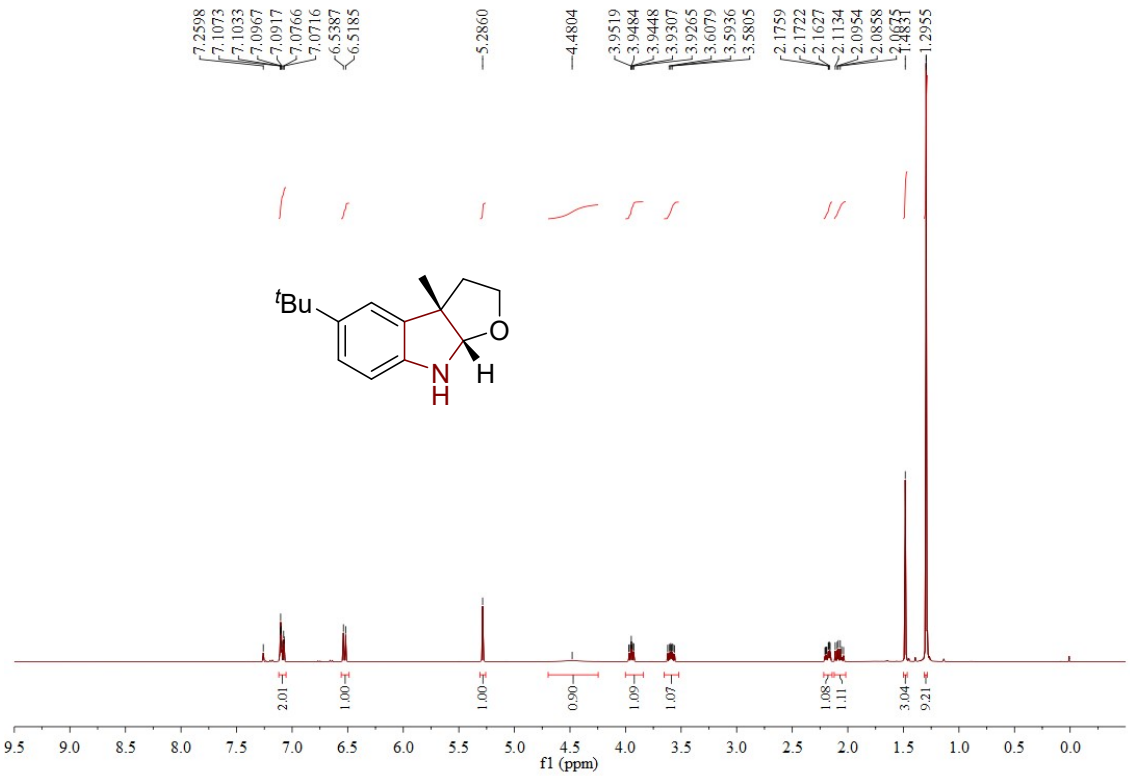
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **82**



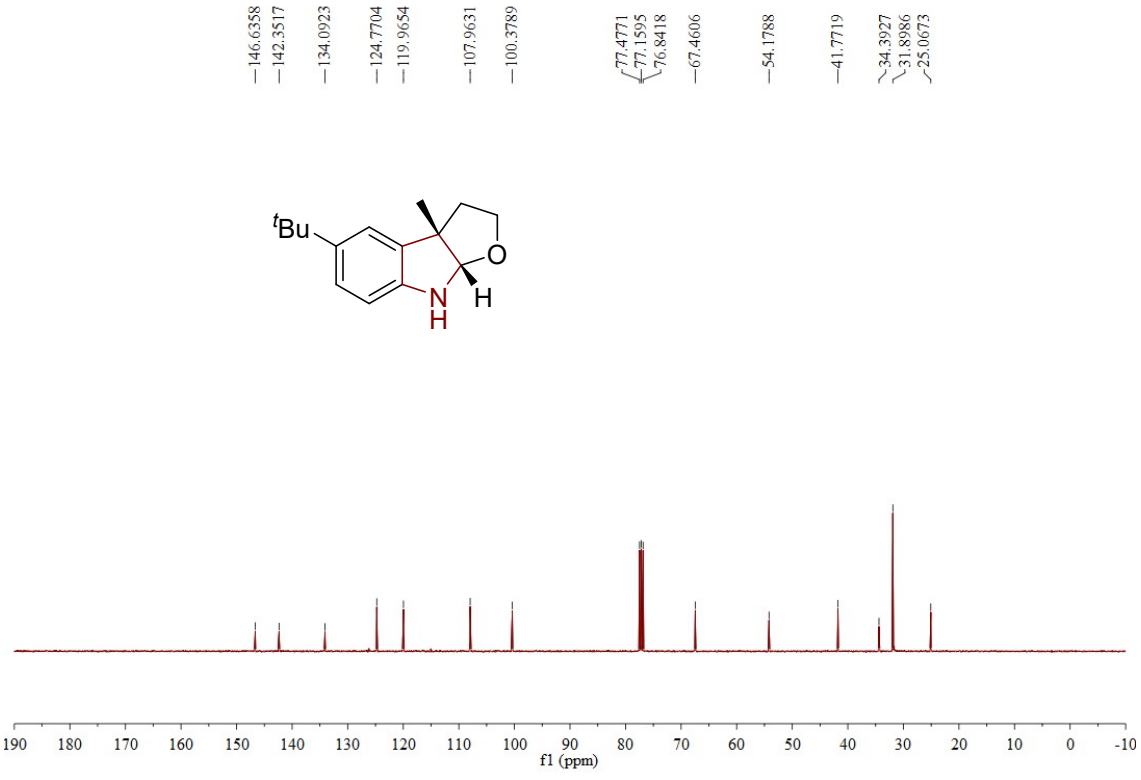
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **83**



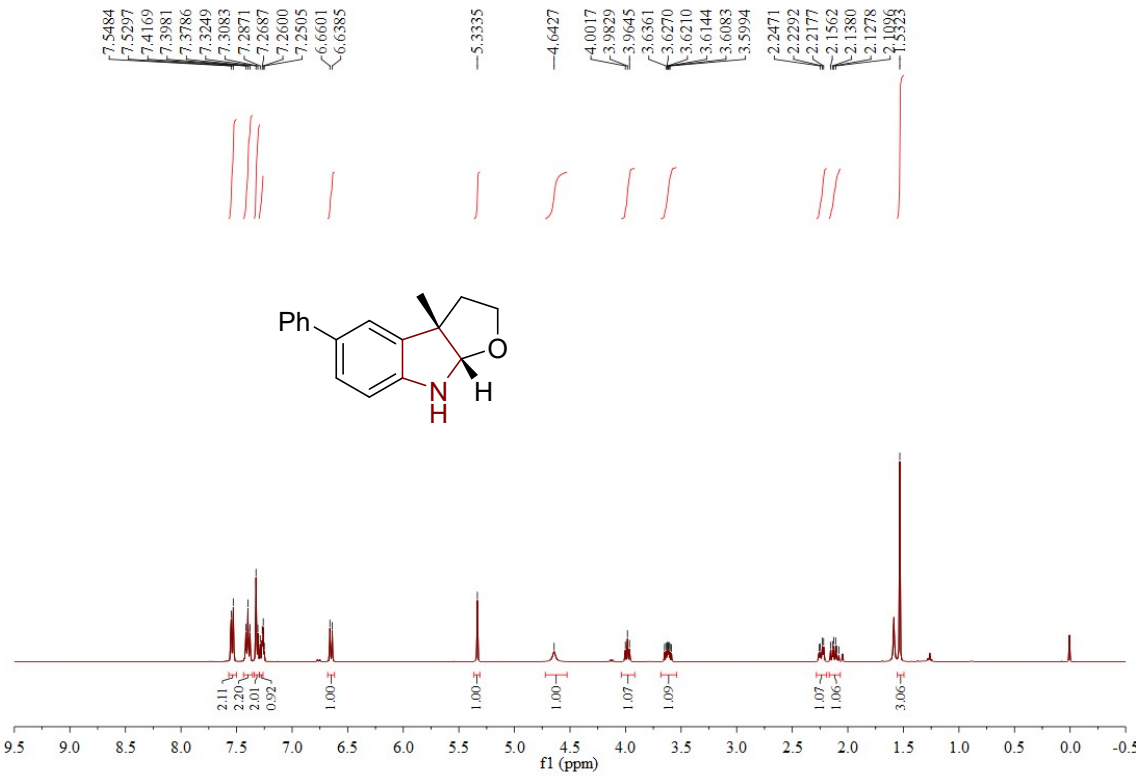
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **83**



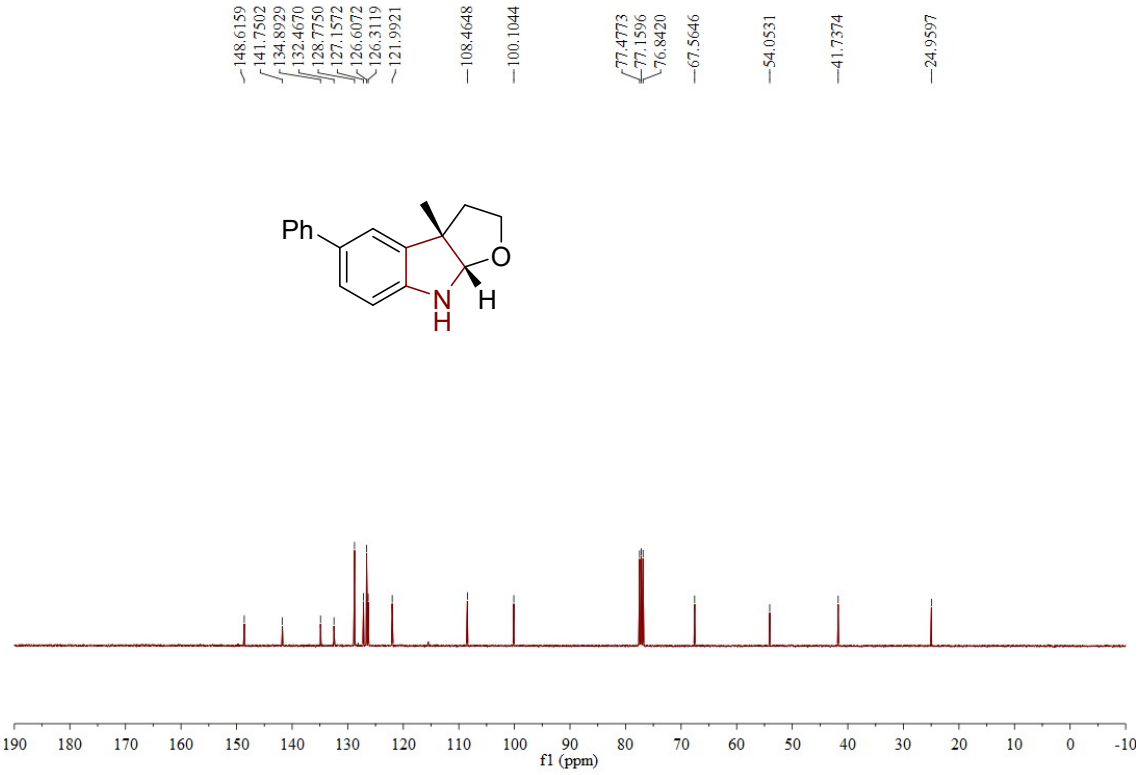
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **84**



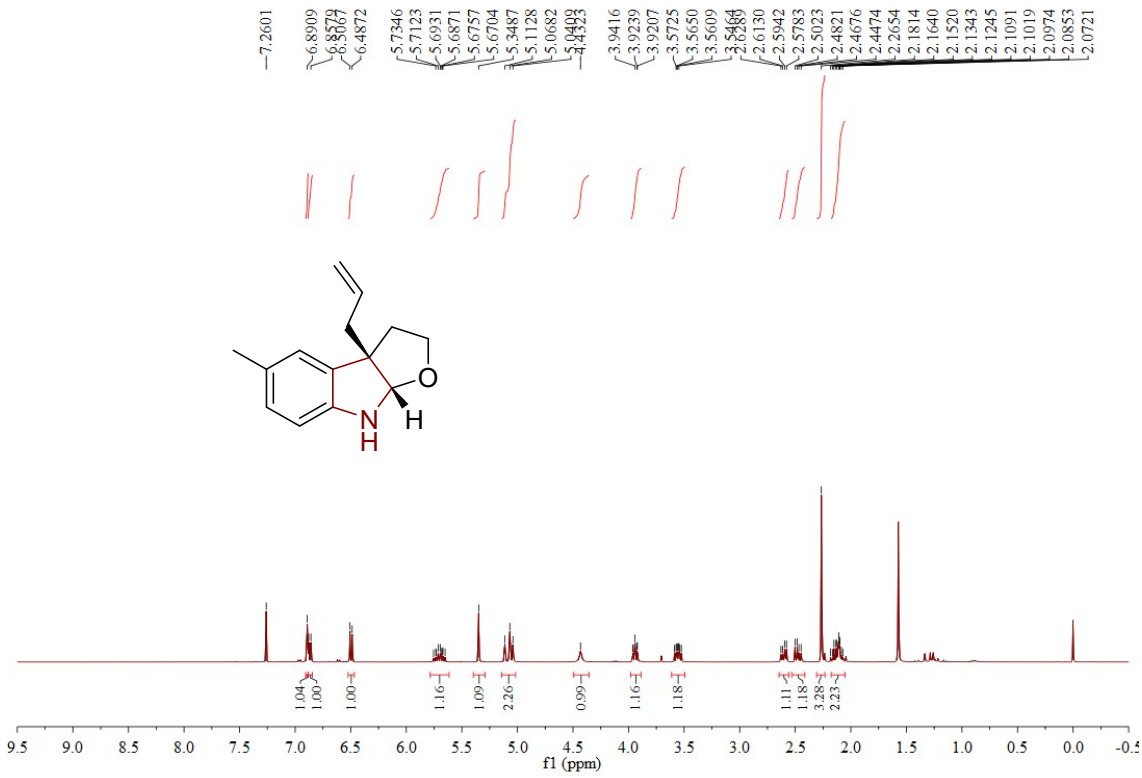
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **84**



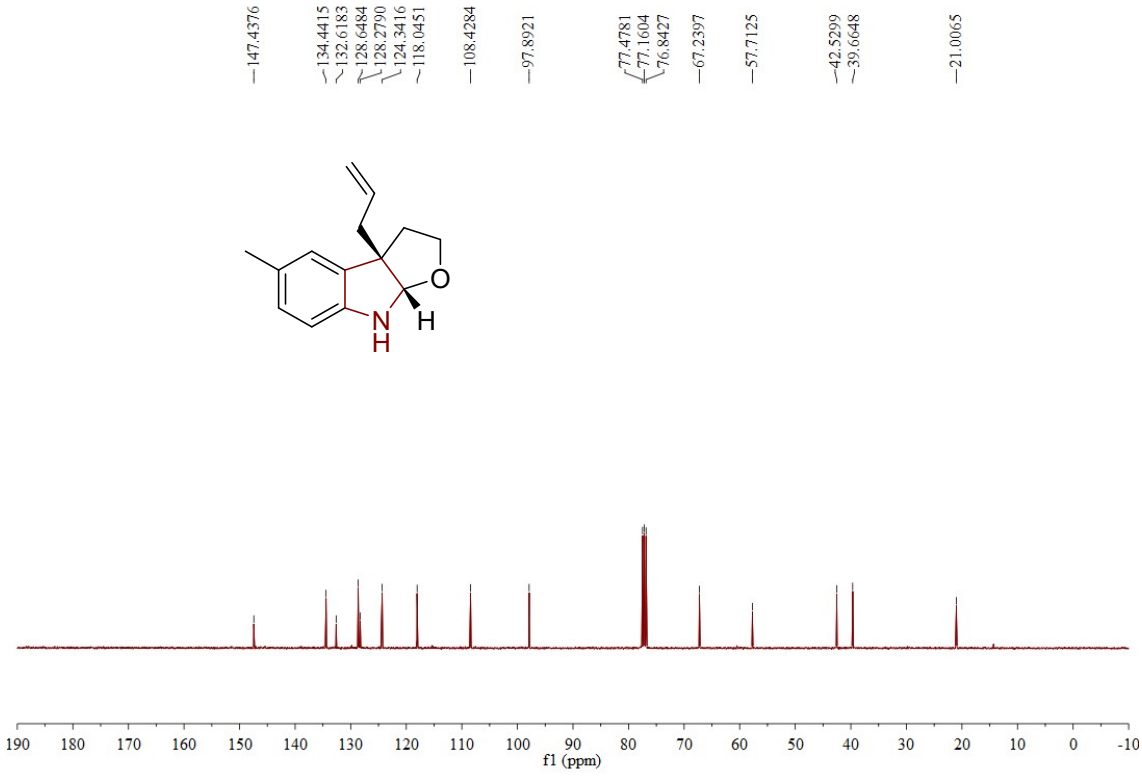
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **85**



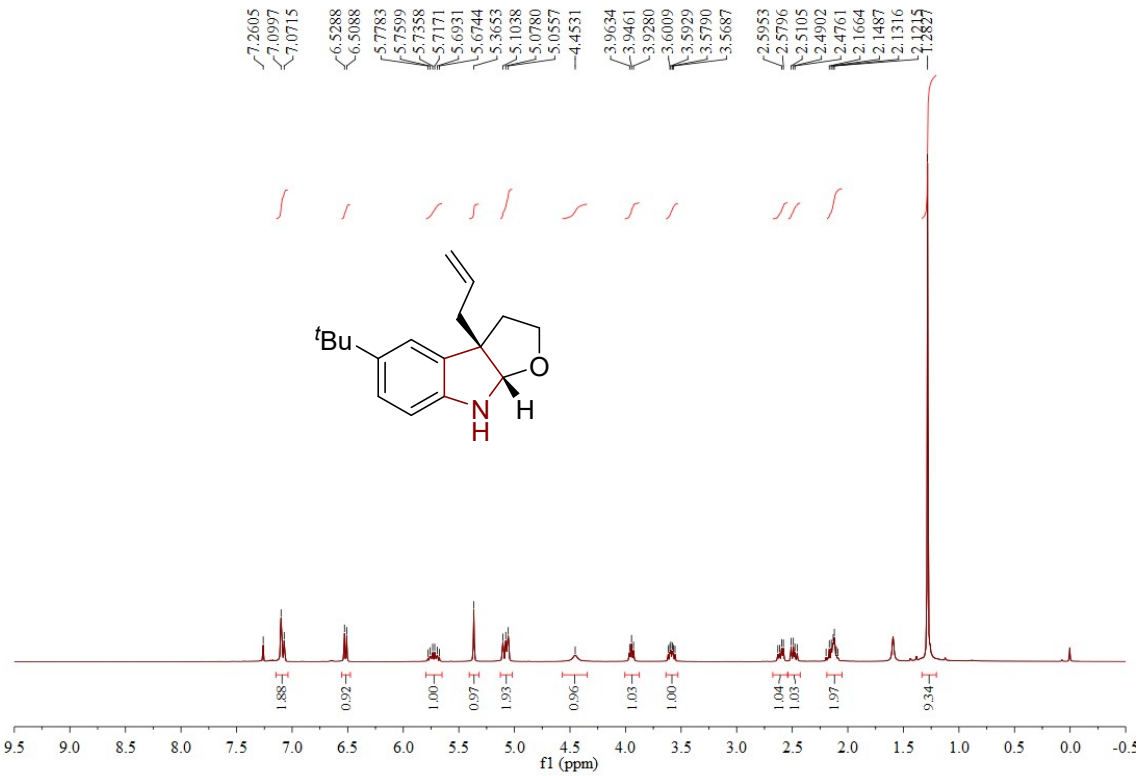
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **85**



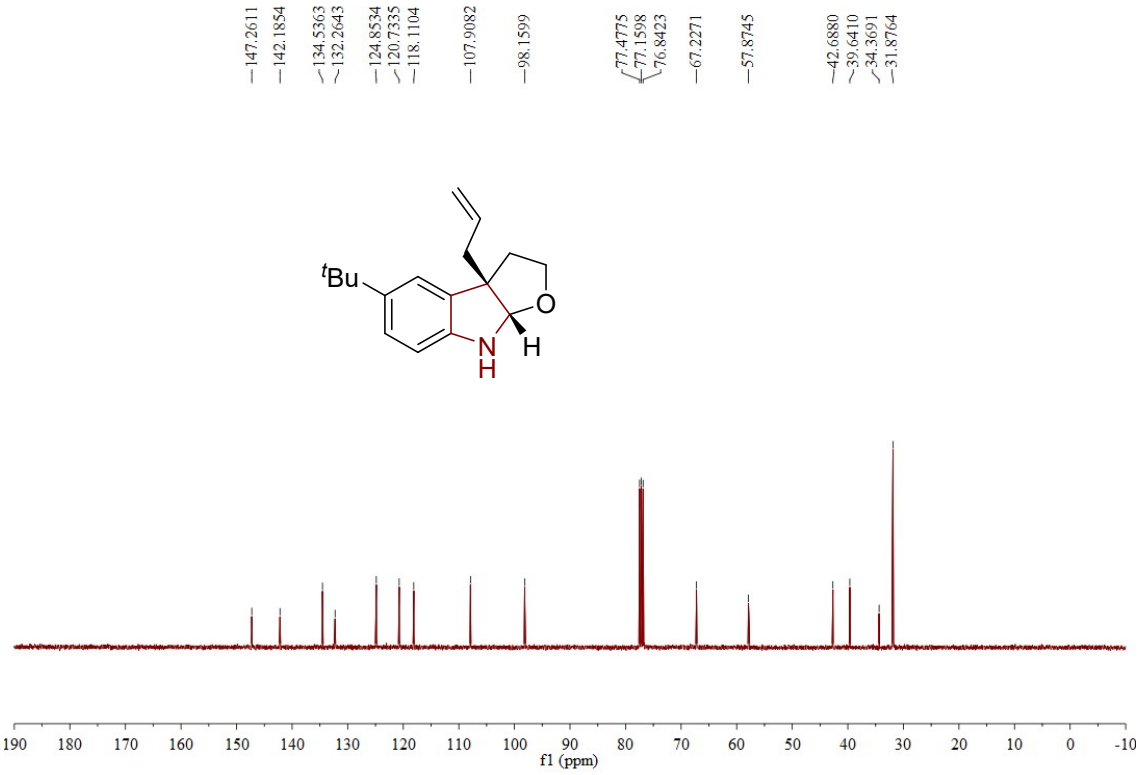
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **86**



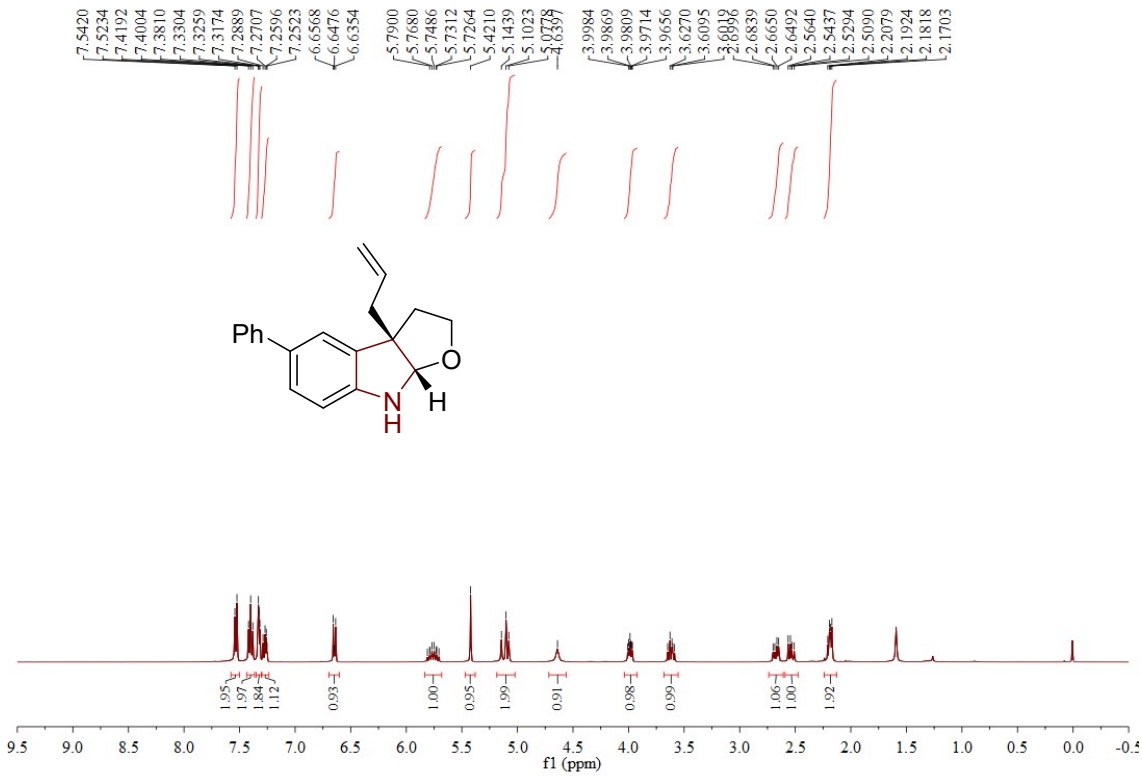
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **86**



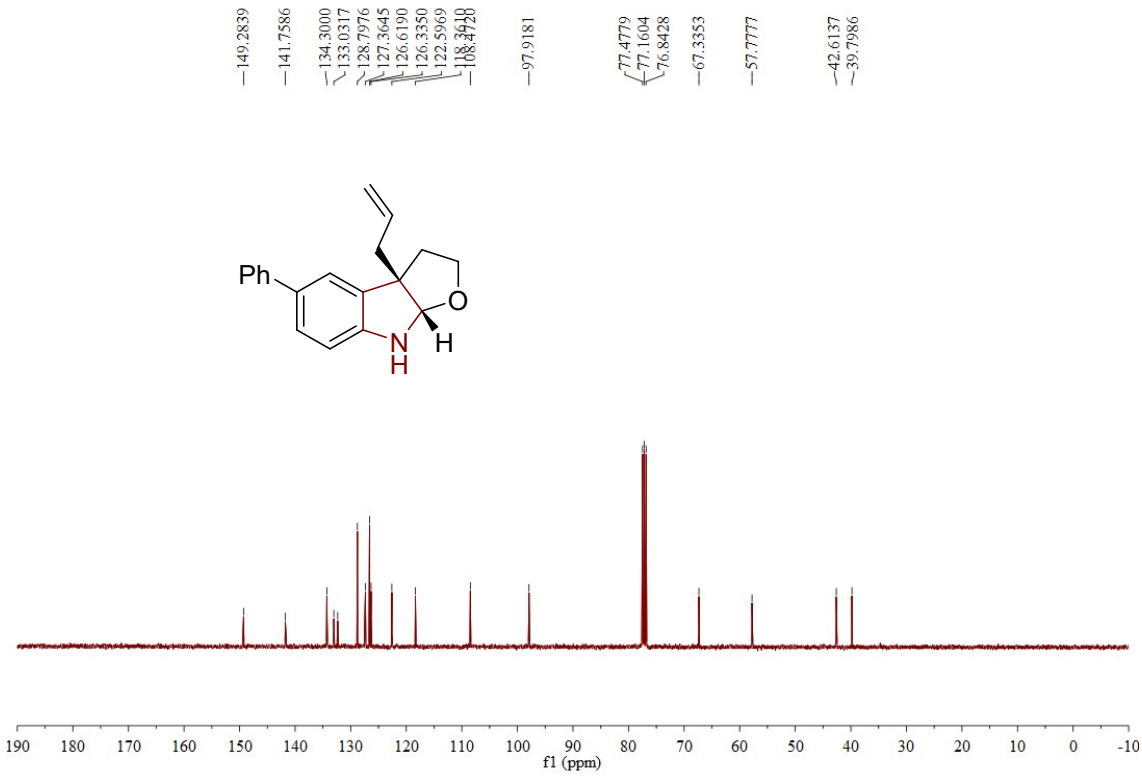
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **87**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **87**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **88**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **88**