Supporting Information

Reductive alkylation of azoarenes to *N*-alkylated hydrazines enabled by hexafluoroisopropanol

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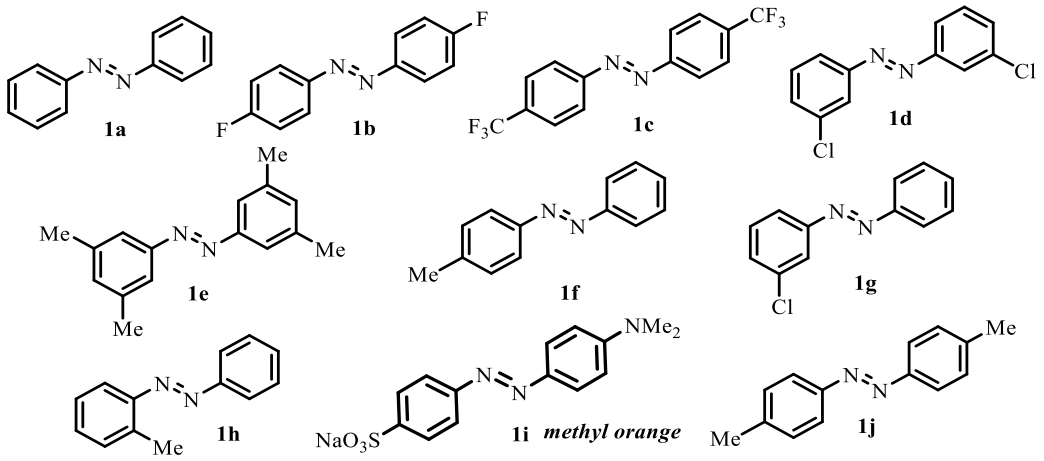
1. General Information

All the reagents and chemicals were purchased from common commercial suppliers like Sigma-Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd., Finar Chemicals, and BLD Pharma directly used as received without any further purification unless otherwise mentioned. Hantzsch ester was synthesized according to the reported literature.[1] ^{1}H, ^{13}C, and ^{19}F NMR spectra of the compounds were measured in $CDCl_3$, as a solvent by using TMS as an internal standard. Chemical shifts, δ (in ppm), are reported relative to TMS δ (^{1}H) 0.0 ppm, δ (^{13}C) 0.0 ppm, which was used as the internal reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^{1}H) 7.26 ppm, δ (^{13}C) 77.16 ppm), were also used for calibration. Bruker Avance III 600, 500 and 400 spectrometers were used to record the NMR spectra. Chemical shifts (δ) values were reported in ppm and spin-spin coupling constant (J) were expressed in Hz, and other data were reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, pent = pentate, sext = sextet, hept = heptane, br = broad, and brs = broad singlet. IR spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass (UHPLC - Q-TOF - HRMS). Merck silica gel 60 - 120 was used for column chromatography. otherwise stated. All the final reactions were carried out under air and in preheated oil baths unless otherwise mentioned. Completion of reactions was examined by thin layer chromatography carried out on pre-coated Merck silica gel-60 F_{254} aluminium plates with ultraviolet light (UV) or iodine as visualizing agents.

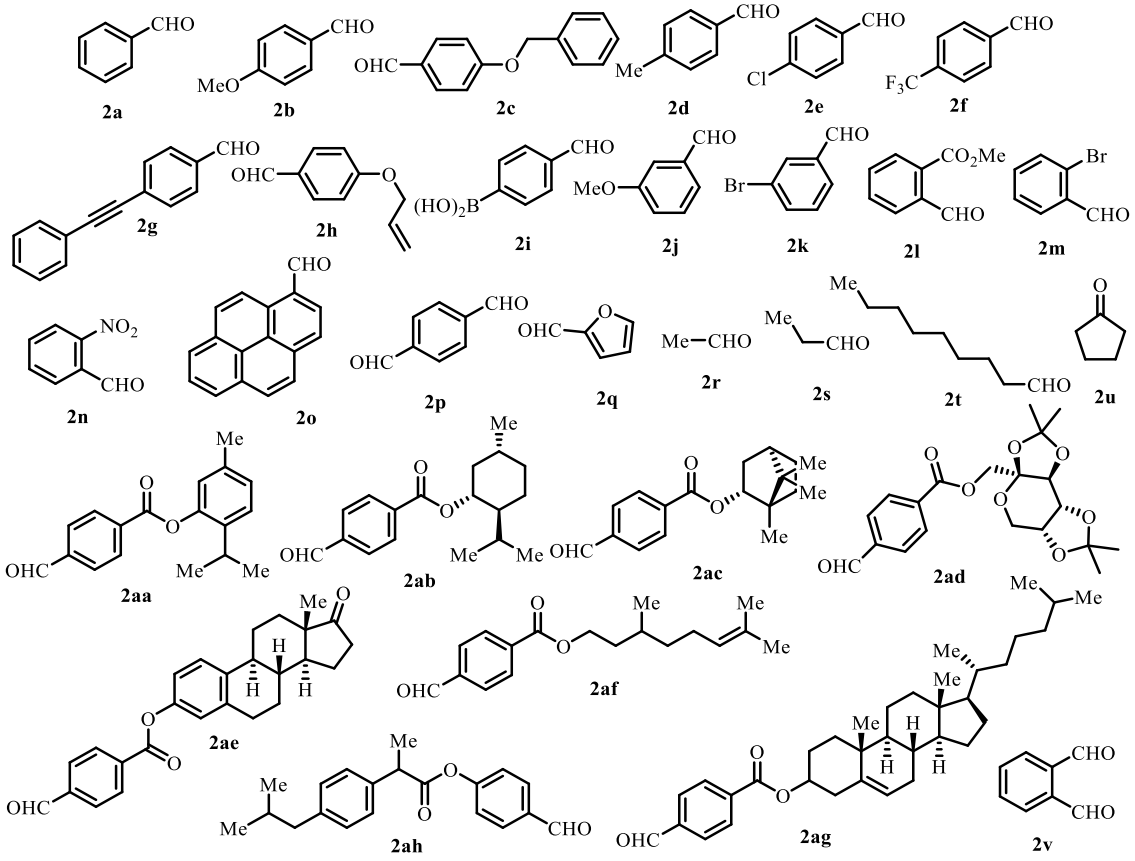
2. Synthesis of starting material

2.1 Azoarenes employed in the reaction:



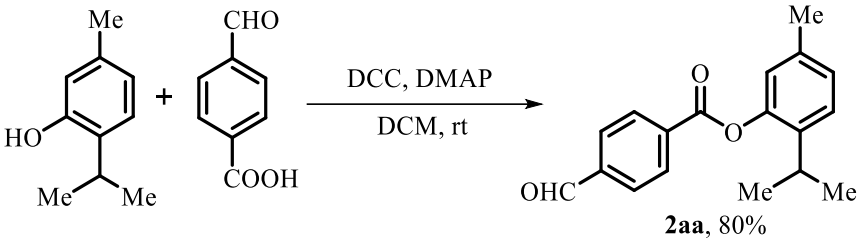
Compounds **1b-1h, 1j** are synthesized by known procedures.[2-5]

2.2 Aldehydes and ketone employed in the reaction:



Compounds **2c**,[6] **2g**,[7] **2h**,[8] are synthesized by known procedure. The biologically relevant motifs containing aldehyde derivatives **2ab**,[9] **2ac,**[10] **2ad,**[11] **2ae**,[12] **2af**,[13] **2ag**,[9] **2ah**,[14] were synthesized by the known procedure.

Synthesis of 2-isopropyl-5-methylphenyl 4-formylbenzoate (2aa)



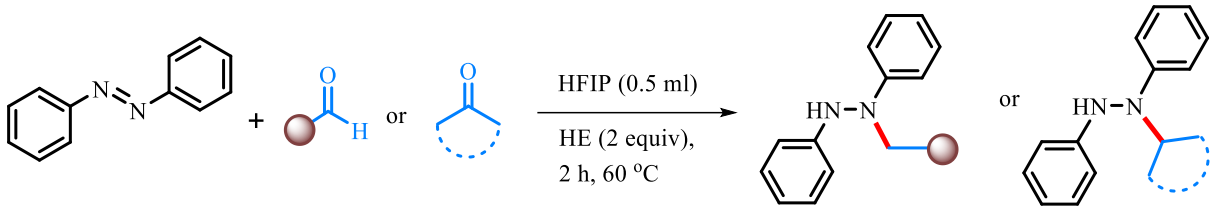
Scheme S1: Synthesis of 2-isopropyl-5-methylphenyl 4-formylbenzoate

Reaction conditions: To a 100 mL round-bottom flask were added 4-formylbenzoic acid (0.225 g, 1.5 mmol, 0.5 equiv), 2-isopropyl-5-methylphenol (0.225 g, 1.5 mmol, 0.5 equiv), *N*, *N*'-dicyclohexylcarbodiimide (0.340 g, 1.65 mmol, 0.55 equiv) and DMAP (0.018 g, 0.15 mmol, 0.05 equiv). DCM (15 mL) was then added at room temperature. The mixture was stirred at room temperature until the acid was consumed as monitored by TLC. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 10:1, v/v) to yield the desired compound **2aa** as yellow oil (0.339 g, 80%). Compound **2aa** was prepared for the first time following a known procedure.[9]

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.28 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.9 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.86 (s, 1H), 2.98 – 2.91 (m, 1H), 2.25 (s, 3H), 1.13 (d, J = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 191.6, 164.5, 148.0, 139.7, 137.1, 136.9, 134.6, 130.8, 129.8, 127.6, 126.7, 122.7, 27.4, 23.1, 20.9. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{18}H_{18}NaO_3$: 305.1149; found: 305.1163.

3. General procedure for synthesis of *N*-alkyl trisubstituted hydrazines

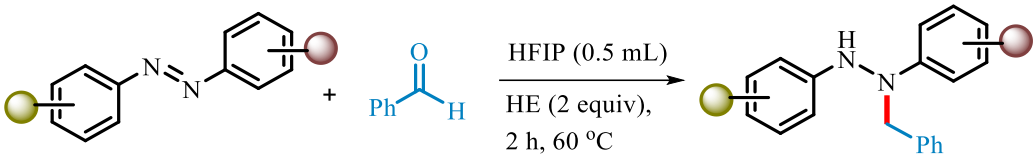
3.1. General procedure for synthesis of *N*-substituted hydrazines with different carbonyls (GP-1)



Scheme S2. Synthesis of *N*-substituted hydrazines

Reaction condition: A mixture of azobenzene **1a** (0.5 mmol), aldehyde or cyclic ketone (0.5 mmol), HE (1 mmol) and HFIP (0.5 ml) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 2 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

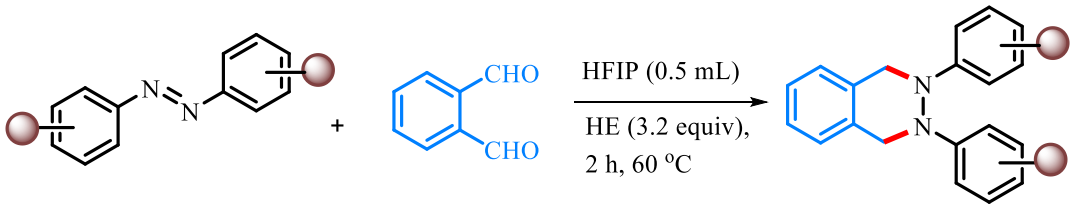
3.2. General procedure for synthesis of *N*-substituted hydrazines with substituted azobenzene (GP-2)



Scheme S3. Synthesis of *N*-substituted hydrazines

Reaction condition: A mixture of symmetrical or unsymmetrical azobenzene (0.5 mmol), benzaldehyde (0.5 mmol), HE (2 equiv) and HFIP (0.5 ml) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 2 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

4. General procedure for synthesis of tetrahydrophthalazine derivative (GP-3)

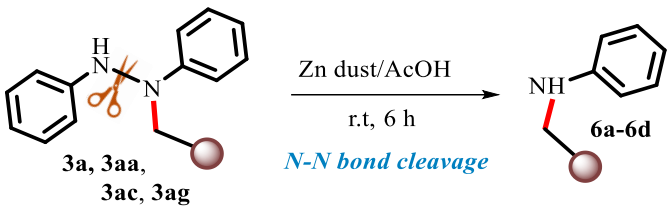


Scheme S4. Synthesis of tetrahydrophthalazine derivatives

Reaction condition: A mixture of substituted azobenzene (0.5 mmol), phthalaldehyde **2v** (0.5 mmol), HE (3.2 equiv.) and HFIP (0.5 ml) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 °C with continuous stirring for 2 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

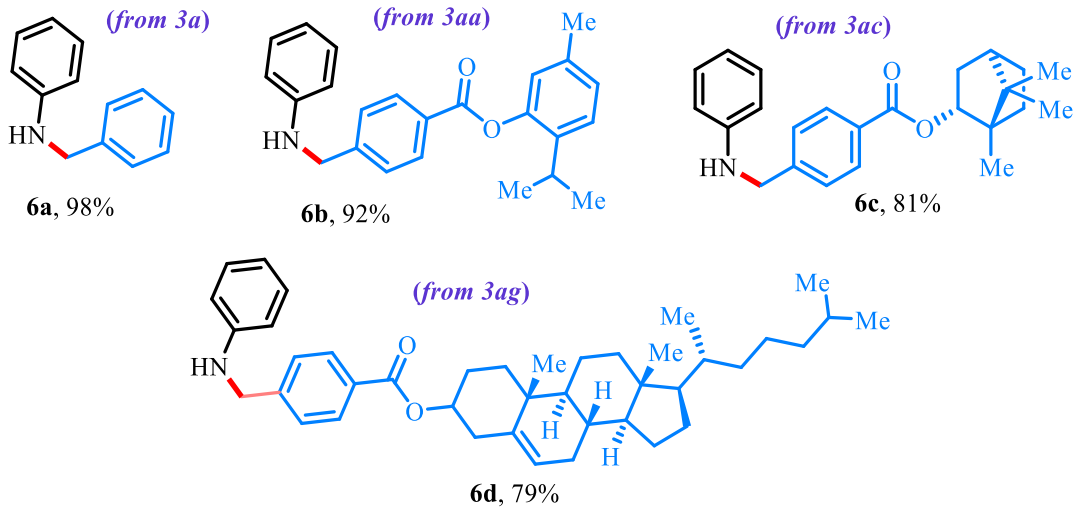
5. Reductive N-N bond cleavage of hydrazine derivatives and post-synthetic modification

5.1 Reductive N-N bond cleavage of various hydrazine derivatives



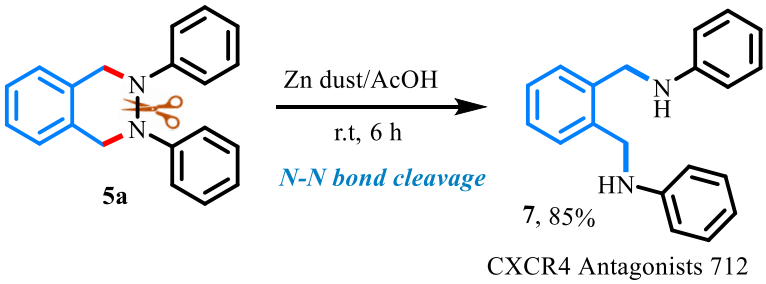
Scheme S5. Reductive N-N bond cleavage of various hydrazine derivatives

Reaction condition:[15] A mixture of hydrazine derivatives (0.216 mmol), Zn dust (100 equiv), AcOH (1.5 mL) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at r.t with continuous stirring for 6 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography. Compound **6a**, **6b**, **6c** and **6d** were prepared using the following procedure.



5.2 Post Synthetic Modification

Synthesis of *N, N'*-(1,2-phenylenebis(methylene)) dianiline (7)



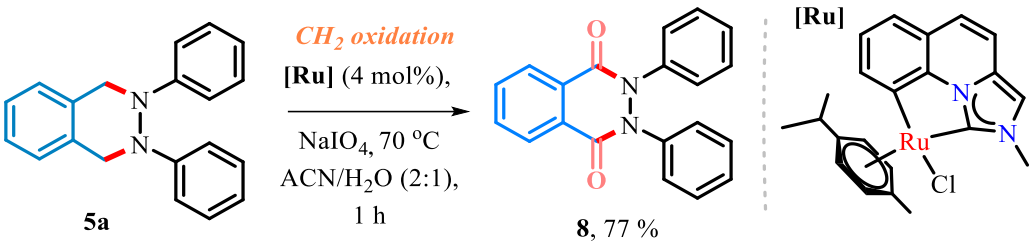
Scheme S6. Synthesis of *N, N'*-(1,2-phenylenebis(methylene)) dianiline

Experimental procedure: A mixture of **5a** (0.216 mmol), Zn dust (100.0 equiv), AcOH (1.5 mL) were added into a round bottom flask (50 mL) equipped with stirring bar. The reaction

tube was properly closed and placed in a preheated oil bath at rt with continuous stirring for 6 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography to yield the desired compound **7** as white solid (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.41 (m, 2H), 7.32 – 7.28 (m, 2H), 7.20 – 7.16 (m, 4H), 6.75 – 6.71 (m, 2H), 6.65 – 6.63 (m, 4H), 4.39 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.2, 137.4, 129.4, 128.1, 118.0, 113.2, 46.4. Spectroscopic characterization data are in accordance with reported literature.[16]

Synthesis of 2, 3-diphenyl-2, 3-dihydrophthalazine-1, 4-dione (8)

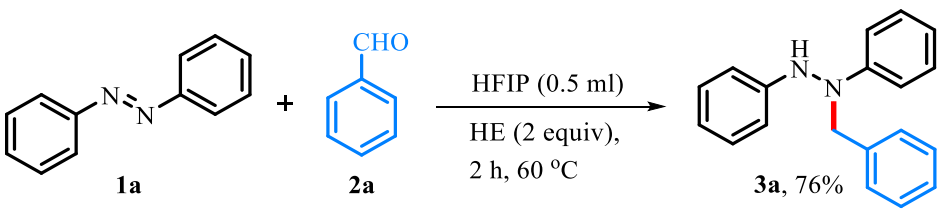


Scheme S7. Synthesis of 2, 3-diphenyl-2, 3-dihydrophthalazine-1, 4-dione

Experimental procedure: $NaIO_4$ (0.209 g) was taken in a screw- capped reaction tube and dissolved it in water (1 mL). Then compound **5a** (0.056 g), **Ru cat.**[17] (4 mol%) acetonitrile (2 mL) were added to the reaction tube and stirred the reaction mixture in a preheated oil bath at 70 °C for 1 h. After the completion of the reaction as confirmed by TLC, the reaction mixture was worked up with CH_2Cl_2 and water. The organic layer was separated and the aqueous layer was again extracted with CH_2Cl_2 (two times, 5 mL). The combined organic layer was washed with brine solution. The organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated under a vacuum. The crude product was purified through silica-gel column chromatography to get the pure product **8** as white solid (77%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.43 – 8.42 (m, 2H), 7.90 – 7.88 (m, 2H), 7.31 – 7.28 (m 5H), 7.27 – 7.25 (m, 3H), 7.18 (t, J = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.6, 137.8, 134.1, 129.7, 128.9, 128.8, 128.5, 128.4. Spectroscopic characterization data are in accordance with reported literature.[18]

6. Scale-up reaction

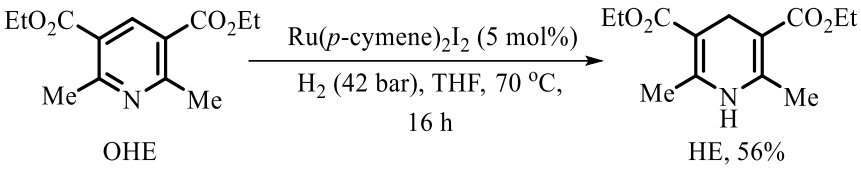


Scheme S8: Scale-up reaction

Experimental procedure: A mixture of **1a** (0.364 g, 2 mmol), **2a** (1.0 equiv), HE (2 equiv) and HFIP (2 mL) were added into a round bottom flak (50 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 60 ºC with continuous stirring for 2 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography to get pure compound as yellow oil of (0.417 g, 76%).

7. Recovery of Hantzsch-1,4-dihydropyridine (HE)

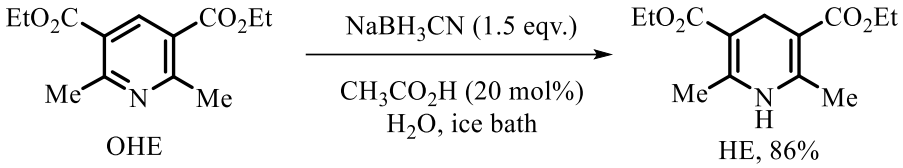
Route-A:



Scheme S9: Hydrogenation of oxidised Hantzsch ester

Experimental procedure:[19] A mixture of [Ru(*p*-cymene)I_2]$_2$ (10 mg, 0.01 mmol) and OHE (50.0 mg, 0.2 mmol) in THF (10 mL) was stirred at room temperature for 10 min in glove box, then the mixture was loaded to an autoclave. The hydrogenation was performed at 70 ºC under H_2 (42 bar) for 16 h. After carefully release of the hydrogen, the autoclave was opened. Isolated yield (yellow solid, 27 mg, 56%).

Route-B



Scheme S10: Reduction of oxidised Hantzsch ester to Hantzsch-1,4-dihydropyridine ester

Experimental procedure:[20] In a 50 mL round bottom flask, OHE (1.0 gm, 3.9 mmol), water (10 mL) and acetic acid (45 µL, 20 mol%) were charged and placed in an ice bath. In the reaction mixture $NaBH_3CN$ (0.294 gm, 1.2 equiv.) was slowly added and stirred for overnight. The reaction was monitored by thin layered chromatography (TLC) in hexane and ethyl acetate solvent system. Once the reaction was completed, solid precipitate was filtered, washed thoroughly by water and ice-cold acetone and dried on vacuum desiccator. Isolated yield: (0.830 g, 86%).

8. Mechanistic and Kinetic studies

8.1 Interaction of HFIP with azobenzene

To probe the nature of binding interaction with HFIP and azobenzene, the combination of azobenzene and HFIP (molar ratio 1:1, 1:2) in $CDCl_3$ at rt has been examined. The hydroxyl peak of HFIP was shifted to downfield from δ = 3.21 ppm to 3.61 ppm, supporting the weak hydrogen bonding interaction between quinoline '*N*'-atom and the hydrogen atom of – OH in the HFIP. -CH proton of HFIP was shifted to upfield from 4.39 ppm to 4.31 ppm. The signals corresponding to *ortho*-aromatic protons in azobenzene was slightly shifted in the upfield ($\Delta\delta$ 0.2 ppm) (Figure S1).

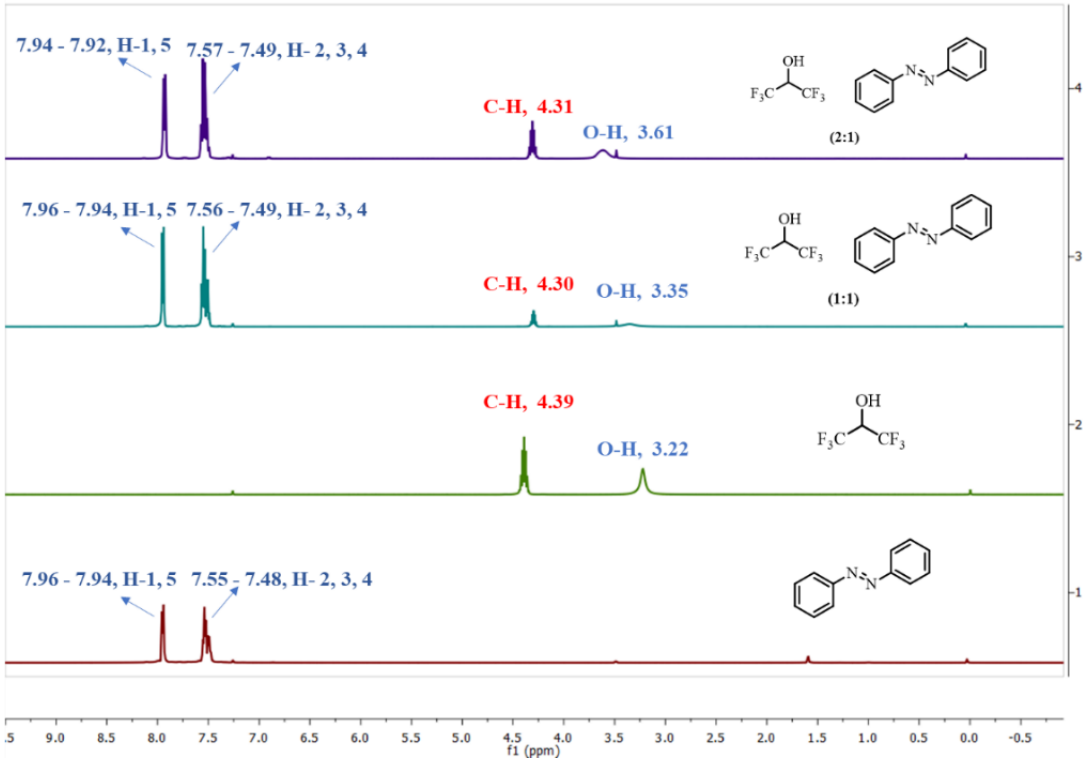


Figure S1: ^{1}H NMR spectra of azobenzene (14 mg, 0.079 mmol), HFIP (13.2 mg, 0.079 mmol), and the mixture of azobenzene and HFIP (molar ratio 1:1, 1:2) in $CDCl_3$ at 298 K.

8.2 Interaction of HFIP with aldehyde

In order to illustrate the interaction of HFIP and aldehyde, we performed the ^{1}H, ^{13}C NMR, and IR spectroscopic experiments by using HFIP and 4-trifluoromethyl benzaldehyde, respectively. While two equivalents of HFIP was added to 4-trifluoromethyl benzaldehyde in $CDCl_3$, a downfield shift of nearly 0.52 ppm for hydroxyl peak of HFIP in ^{1}H NMR and 2.76 ppm for carbonyl signal of aldehyde in ^{13}C NMR were observed (Figure S2, S3).

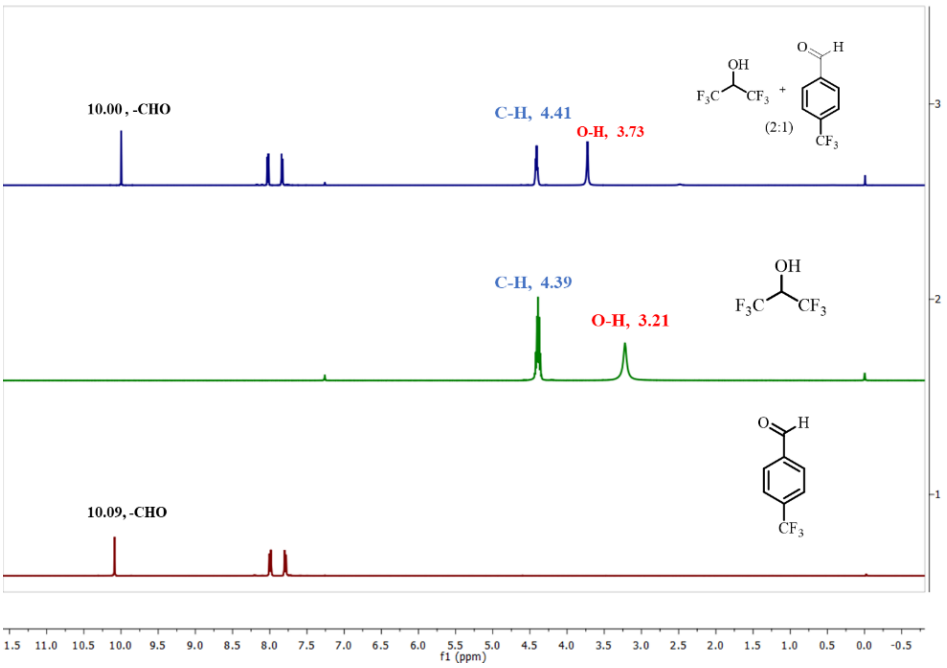


Figure S2: ^{1}H NMR spectra of 4-trifluoromethylbenzaldehyde (14 mg, 0.079 mmol), HFIP (26.4 mg, 0.158 mmol), and the mixture of 4-trifluoromethylbenzaldehyde and HFIP (molar ratio 1:2) in $CDCl_3$ at 298 K.

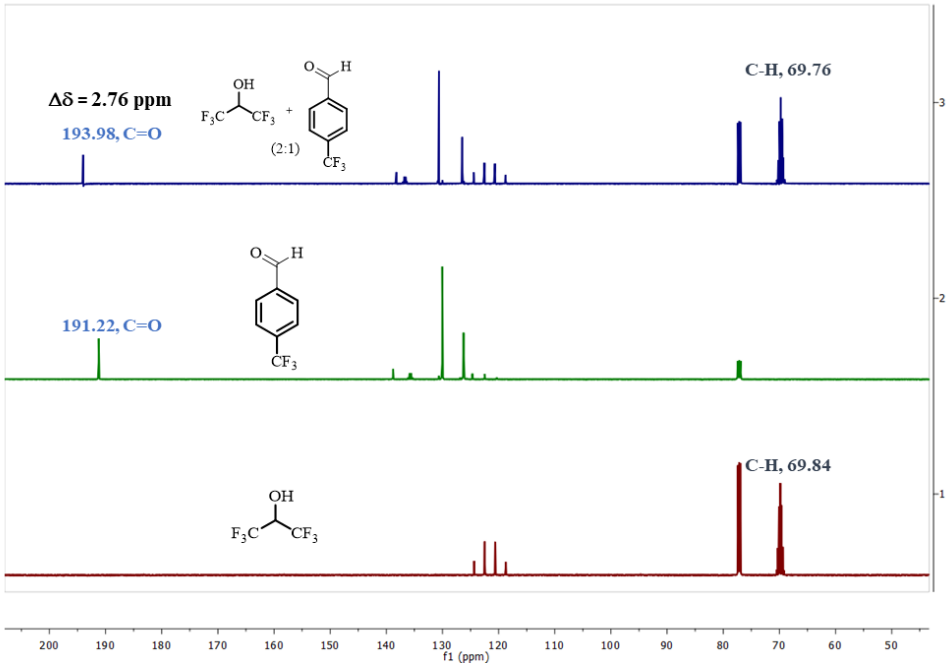


Figure S3: ^{13}C NMR spectra of 4-trifluoromethylbenzaldehyde (14 mg, 0.079 mmol), HFIP (26.4 mg, 0.158mmol), and the mixture of 4-trifluoromethylbenzaldehyde and HFIP (molar ratio 1:2) in $CDCl_3$ at 298 K.

In IR, the carbonyl value shifted to a lower wave number from 1708.03 cm^{-1} to 1694.12 cm^{-1} after mixing with HFIP at room temperature (Figure S5). Approximately 14 cm^{-1} lower wave number has been observed for the carbonyl group in a mixture compared to free aldehyde, which supports hydrogen bonding interaction between aldehyde and HFIP (Figure S4). A downfield shift for hydroxyl peak of HFIP in ^{1}H NMR and ensuing downfield shift for carbonyl in aldehyde in ^{13}C NMR supports weak hydrogen bonding interaction with aldehyde and HFIP. It has been further reinforced by using IR spectroscopic experiments in the solid-state.

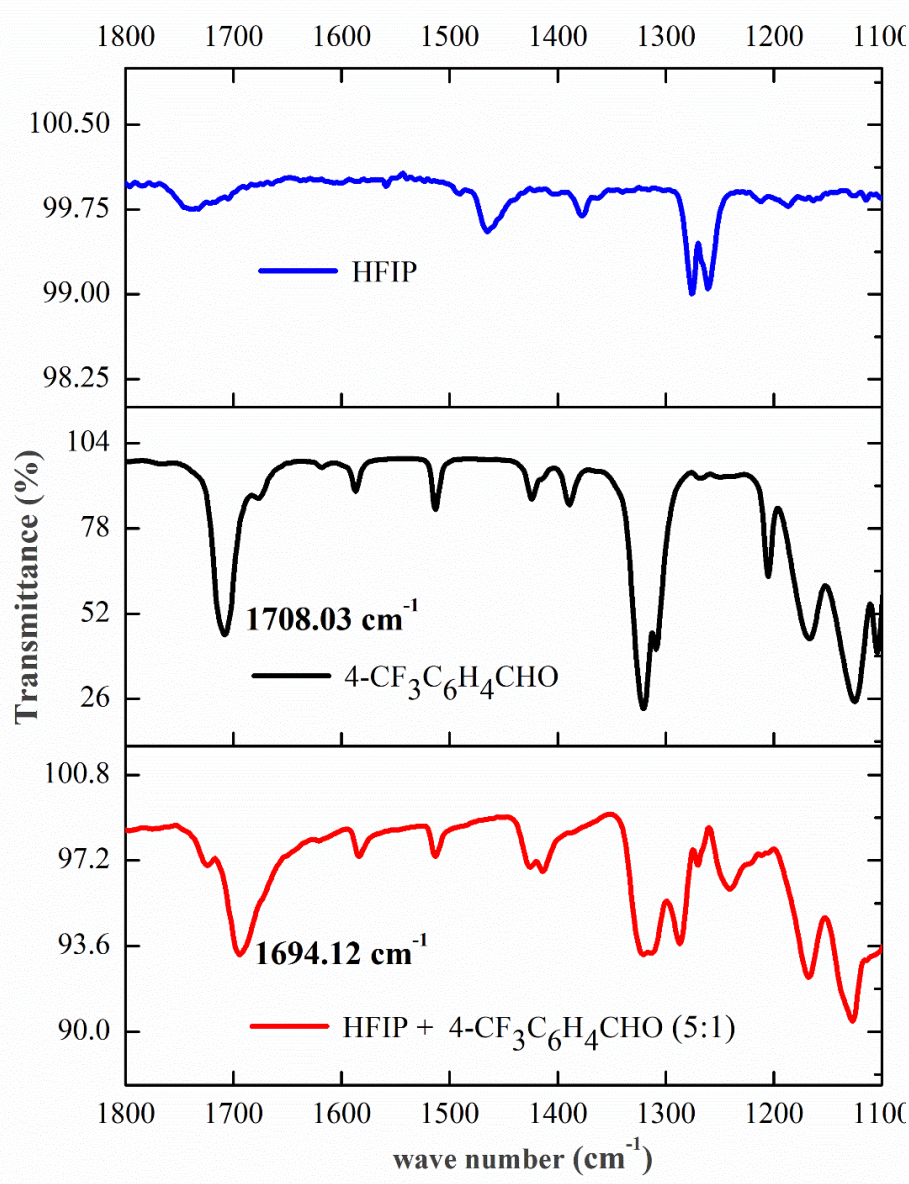


Figure S4: IR spectroscopy to support the interaction of 4-trifluoromethyl benzaldehyde and HFIP.

8.3 Interaction of HFIP with Hantzsch ester

To examine the interaction of HFIP and Hantzsch ester, we have checked the 1H NMR with the combination of Hantzsch ester and HFIP (molar ratio 1:2) in $CDCl_3$ at rt. whereas no characteristic –OH proton signal was shifted while mixing with HFIP (Figure S5).

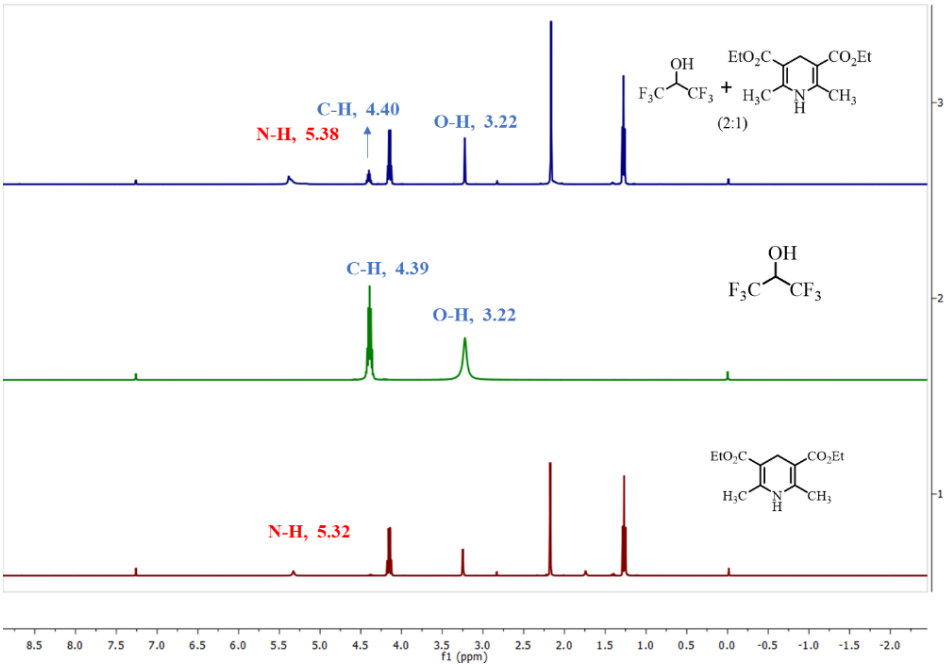


Figure S5: ^{1}H NMR spectra of HFIP (26.4 mg, 0.158 mmol), Hantzsch ester (20 mg, 0.079 mmol), and the mixture of HFIP and Hantzsch ester (molar ratio 2:1) in $CDCl_3$ at 298 K.

However, in ^{13}C NMR, the carbonyl value in Hantzsch ester was shifted downfield from 168.22 to 168.91 ppm ($\Delta\delta$ = 0.7 ppm). A weak hydrogen bonding interaction may exist between Hantzsch ester and –OH of HFIP. (Figure S6).

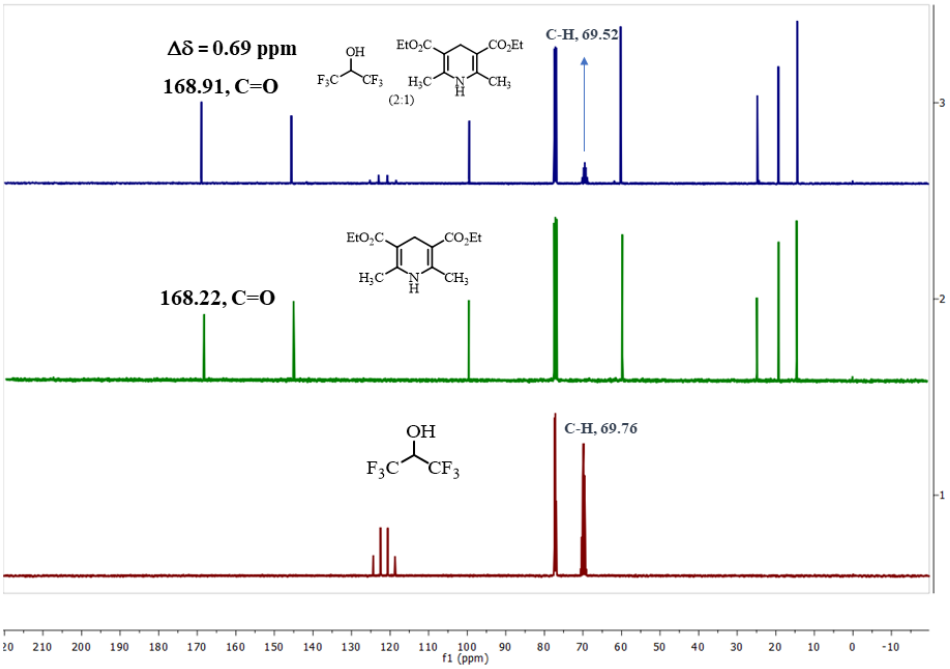
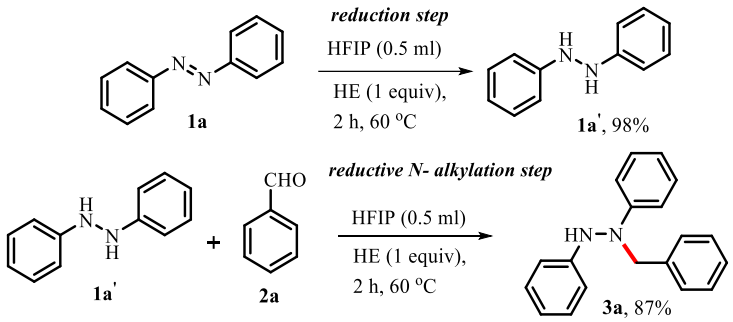


Figure S6. ^{13}C spectra of HFIP (26.4 mg, 0.158 mmol), Hantzsch ester (20 mg, 0.079 mmol), and the mixture of HFIP and Hantzsch ester (molar ratio 2:1) in $CDCl_3$ at 298 K.

8.4 Proof of 1, 2-diphenyl hydrazine as the intermediate

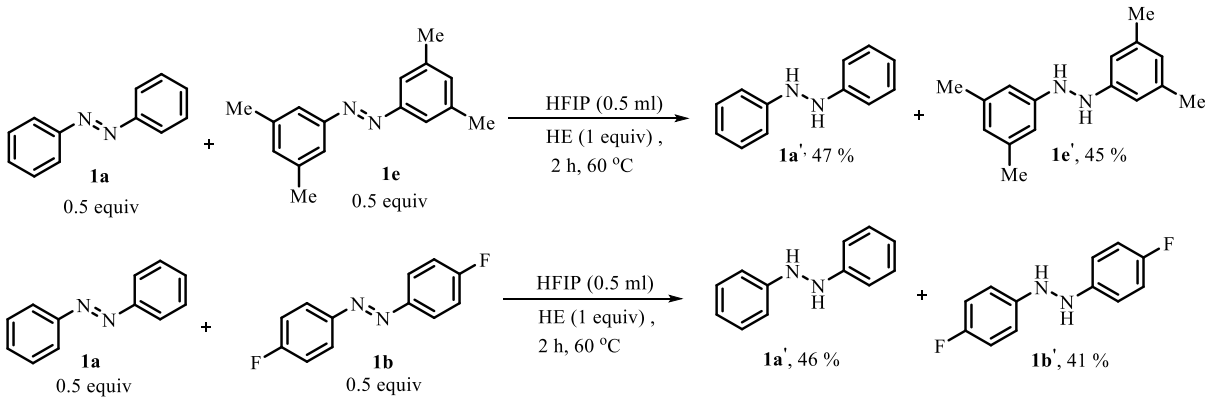
To gain more insight into the reaction pathway, we performed the reaction with azobenzene (0.5 mmol), HE (1 equiv), and HFIP (0.5 mL) at 60 °C for 2 h. As expected 1, 2-diphenyl hydrazine **1a**' obtained in 98% yield. For the subsequent step the reaction was conducted with the formed **1a**', and aldehyde **2a** (1 equiv), HE (1 equiv), and HFIP (0.5 mL) at 60 °C for 2 h under standard conditions the desired product **3a** was obtained in 87%, yield, from we can conclude reaction possibly occurs in two steps i) reduction of azobenzene and ii) reductive *N*-alkylation of hydrazobenzene (Scheme S11).



Scheme S11: Proof of 1, 2-diphenylhydrazine as the intermediate

8.5 Electronic effect for the 1st step

To know the electronic effect in the 1st step, we performed **1a** (0.25 mmol), **1e** (0.25 mmol), and HE (0.5 mmol), and HFIP (0.5 mL) at 60 °C for 2 h. As expected we obtained its corresponding hydrogenated product **1a**' (47%) and **1e**' (45%). Then we performed **1a** (0.25 mmol), **1b** (0.25 mmol), and HE (0.5 mmol) in HFIP (0.5 mL) at 60 °C for 2 h, providing the hydrogenated product **1a**' (46%) and **1b**' (41%). Since a comparable yield was obtained in both the case, one can infer that there is no considerable effect on the electronics in the azobenzene reduction step (Scheme S12).

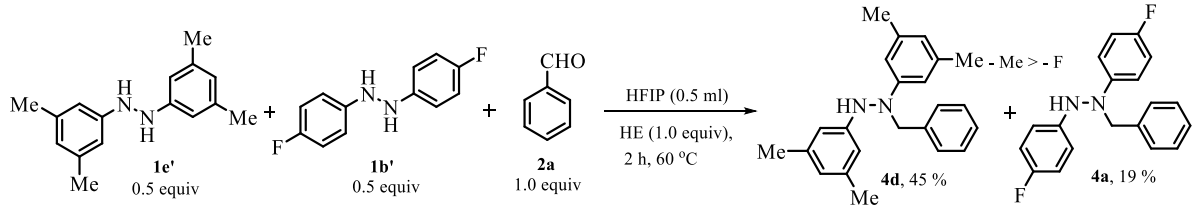


Scheme S12: Electronic effect of the azobenzene hydrogenation step

8.6 Electronic effect for the 2nd step

To know the electronic effect in the 2nd step, at first the reaction was examined with substituted azobenzenes. A competitive reaction suggested that the electron-donating group (-Me) on the hydrazobenzene enhanced the rate of the reaction with respect to an electron-withdrawing group (*p*-F) (Scheme S13).

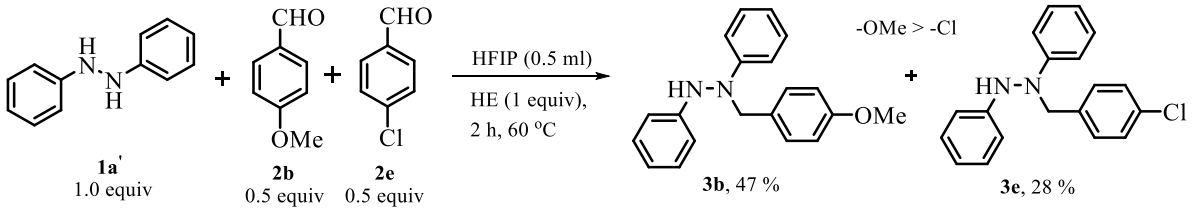
Reaction conditions: substituted azobenzene **1e'** (0.5 equiv), **1b'** (0.5 equiv), aldehyde **2a** (0.5 mmol), HE (1 equiv), and HFIP (0.5 mL) at 60 °C for 2 h, the product **4d** and **4a** was obtained in 45% yield and 19% yield respectively.



Scheme S13: Competitive reaction with substituted azobenzene.

Likewise, competitive reaction with aldehyde suggested that electron-donating group (*p*-OMe) on the benzaldehyde enhanced the rate of the reaction with respect to an electron-withdrawing group (*p*-Cl) (Scheme S14).

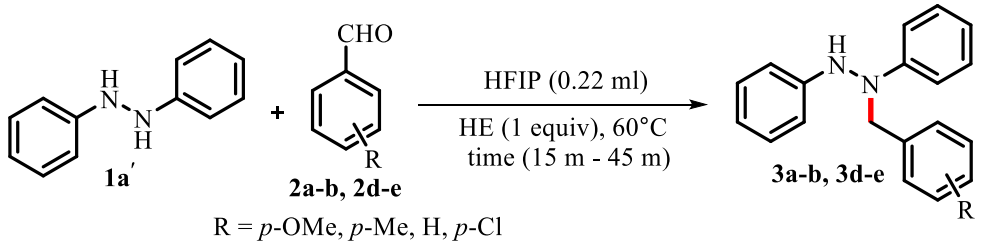
Reaction conditions: hydrazobenzene **1a'** (0.5 mmol), substituted aldehyde **2b** (0.5 equiv), **2e** (0.5 equiv), HE (1 equiv), and HFIP (0.5 mL) at 60 °C for 2 h, the product **3b** and **3e** was obtained in 47% yield and 28% yield respectively.



Scheme S14. Competitive reaction with aldehyde

8.7 Hammett Studies

An oven dried reaction tube, a mixture of **1a'** (0.217 mmol, 1 equiv), substituted aldehyde derivative (0.217 mmol, 1 equiv), HE (0.217 mmol, 1 equiv), and HFIP (0.22 mL) at 60 °C for different time intervals were taken. The reaction tube was properly closed and placed in a pre-heated oil bath at 60 °C for the specified times. The progress of the reaction was analyzed by NMR using 1,3,5 trimethoxy benzene as an internal standard. The measure yield of product was plotted against to obtain the slope which gave the rate constant for each substrate.



R = *p*-OMe, *p*-Me, H, *p*-Cl

substrate	k (min^{-1})	k_X/k_H	log (k_X/k_H)	σ_p	ρ
p-OMe	0.590 ×10^{-3}	2.27	+0.356	-0.27	**-1.298**
p-Me	0.444 × 10^{-3}	1.71	+0.234	-0.17	
H	0.259 × 10^{-3}	1	0	0	
p-Cl	0.133 × 10^{-3}	0.513	-0.289	+0.23	

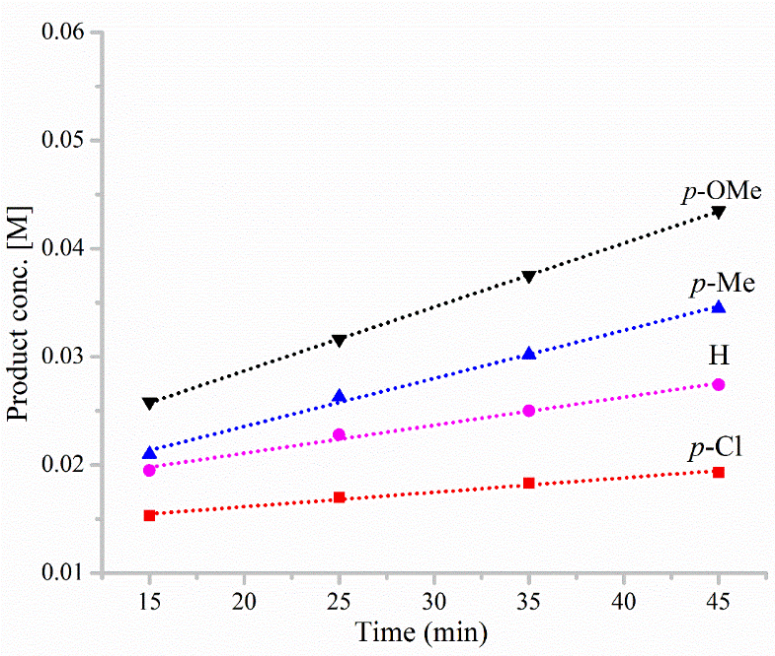


Figure S7: Concentration [Product] *vs* time plot for different substrates.

The individual rate constants (log k_X/k_H) were then plotted against the substituent constants (σ) and a Hammett correlation with a negative slope was obtained (ρ = -1.3, R^2 = 0.9994).

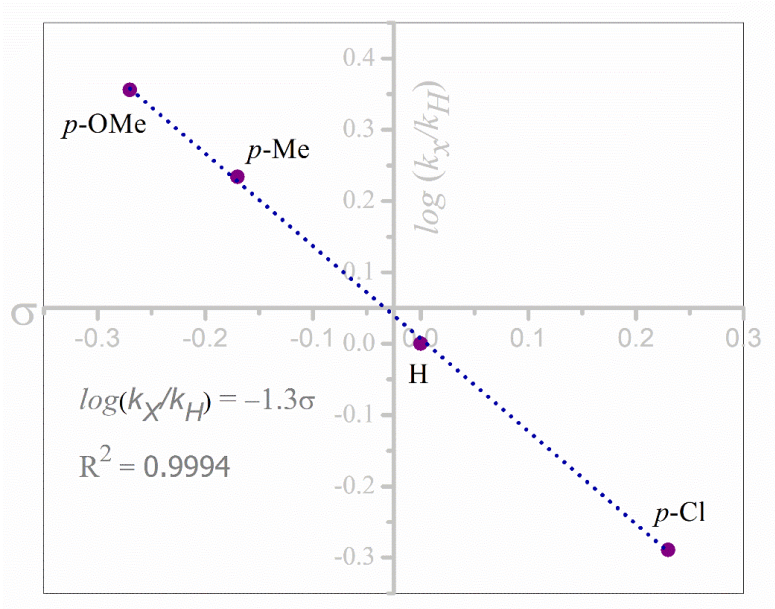
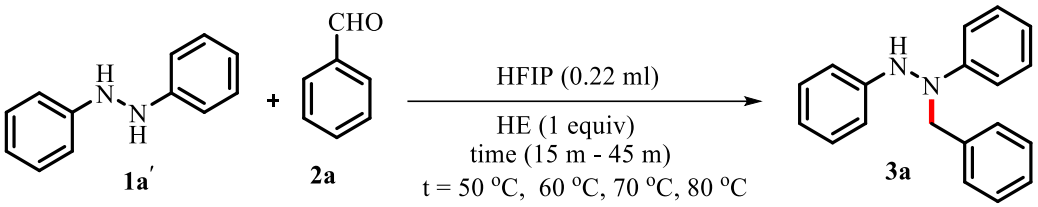


Figure S8: Hammett plot

8.8 Eyring Studies

An oven dried reaction tube, **1a**' (0.217 mmol, 1 equiv), benzaldehyde (0.217 mmol, 1 equiv), HE (0.217 mmol, 1 equiv), and HFIP (0.22 mL) were taken. The reaction tube was properly closed and placed in a pre-heated oil bath at respective temperature for the specified times. The progress of the reaction was analyzed by NMR using 1, 3, 5 trimethoxy benzene as an internal standard. The measure yield of product was plotted against to obtain the slope which gave the rate constant for each substrate.



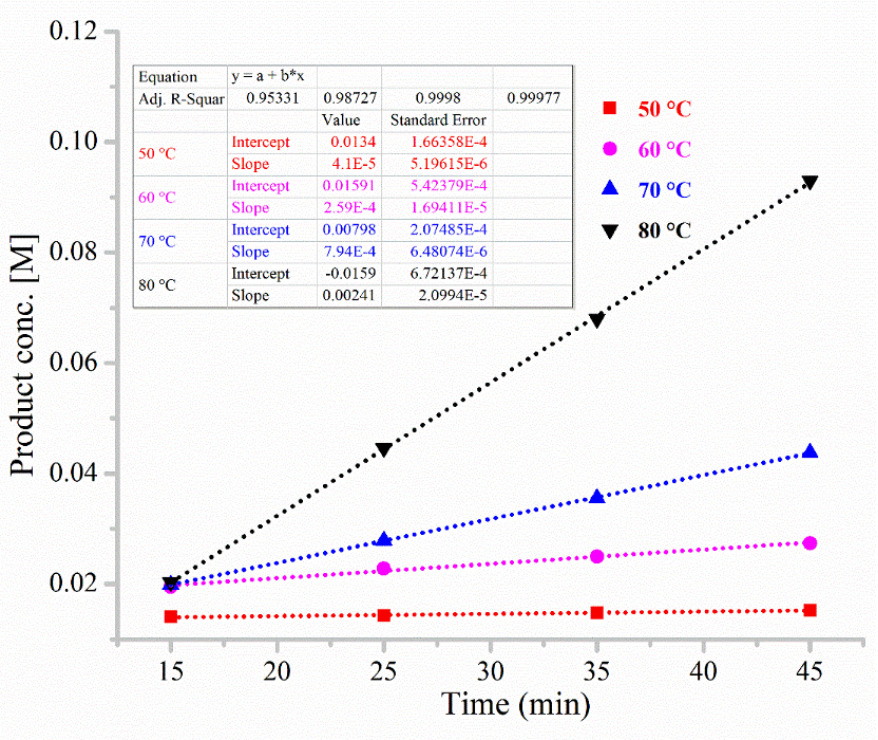


Figure S9: Concentration [Product] *vs* time plot at different temperatures.

Temp	1/T	k	ln(k/T)
323 K (50 °C)	0.003095	0.041×10^{-3}	-15.87
333 K (60 °C)	0.003003	0.259×10^{-3}	-14.06
343 K (70 °C)	0.002915	0.794×10^{-3}	-12.97
353 K (80 °C)	0.002832	2.41×10^{-3}	-11.89

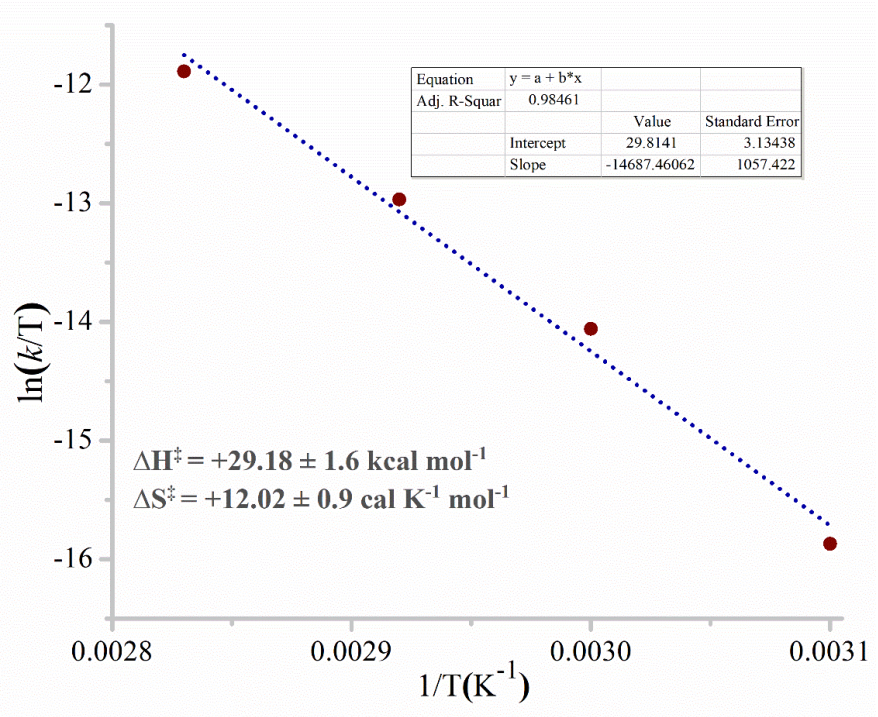


Figure S10: Arrhenius-Eyring plot

Activation enthalpy ($\Delta H^{\#}$) and activation entropy ($\Delta S^{\#}$) values were obtained from the slope and intercept of plots of ln(*k*/*T*) vs 1/*T* (Figure S10) using the following equation:

$$\mathbf{\ln(k/T) = -\Delta H^{\#}/R.(1/T) + \ln k_B/h + \Delta S^{\#}/R}$$

where k_B = Boltzmann constant, R = universal gas constant, and h = Planck's constant.

From the plot of ln(*k*/*T*) vs 1/*T*,

$$\text{Slope} = -14687.2$$

$$\textit{Or}, -\Delta H^{\ddagger}/R = -14687.2$$

$$\textit{Or}, \Delta H^{\ddagger} = -(-14687.2) \times (1.987 \text{ cal } K^{-1}mol^{-1})$$

$$= 29183.4 \text{ cal } mol^{-1}$$

$$= 29.18 \text{ kcal } mol^{-1}$$

And,

$$\text{Intercept} = 29.81$$

$$\textit{Or}, \ln (k_B/h) + \Delta S^{\#}/R = 29.81$$

$$\textit{Or}, \ln (1.38 \times 10^{-23} \text{ J } K^{-1}/6.626 \times 10^{-34} \text{ J s}) + \Delta S^{\#}/1.987 \text{ cal } K^{-1} mol^{-1} = 29.81$$

$$\textit{Or}, \ln (2.083 \times 10^{10} \text{ } K^{-1} s^{-1}) + \Delta S^{\#}/1.987 \text{ cal } K^{-1} mol^{-1} = 29.81$$

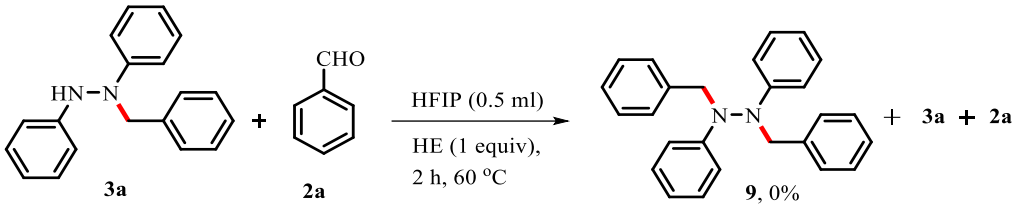
$$\textit{Or}, 23.76 + \Delta S^{\#}/1.987 \text{ cal } K^{-1} mol^{-1} = 29.81$$

$$\textit{Or}, \Delta S^{\#}/1.987 \text{ cal } K^{-1} mol^{-1} = 6.05$$

$$\textit{Or}, \Delta S^{\#} = 12.02 \text{ cal } K^{-1} mol^{-1}$$

8.9 Effort to synthesize tetrasubstituted hydrazine derivatives

The reaction between **3a** (0.5 mmol), **2a** (0.5 mmol) under standard conditions in the presence of HE (1 equiv), and HFIP (0.5 ml) at 60 °C for 2 h. We failed to obtain the tetrasubstituted hydrazine **9**, respective precursor was recovered (Scheme S11).



Scheme S11: Reaction between **2a** with **3a**

9. Crystallographic data

Crystallographic data of 3ac

Single crystals of compound **3ac** suitable for X-ray diffraction were obtained by slow evaporation of the saturated solution of the compound in petroleum ether at room temperature. X-ray crystallographic data were collected using Bruker D8 QUEST diffractometer. Data refinement and cell reduction were carried out by APEX4. Structures were solved by direct methods using Olex2 v1.5 and refined by a full-matrix least-squares method using Olex2 v1.5. All of the non-H atoms were refined anisotropically. The ORTEP diagram was obtained with ORTEP3 software with 40% thermal ellipsoid (see below, Figure S11). The crystallographic parameters and refinement data were listed in Table S1.

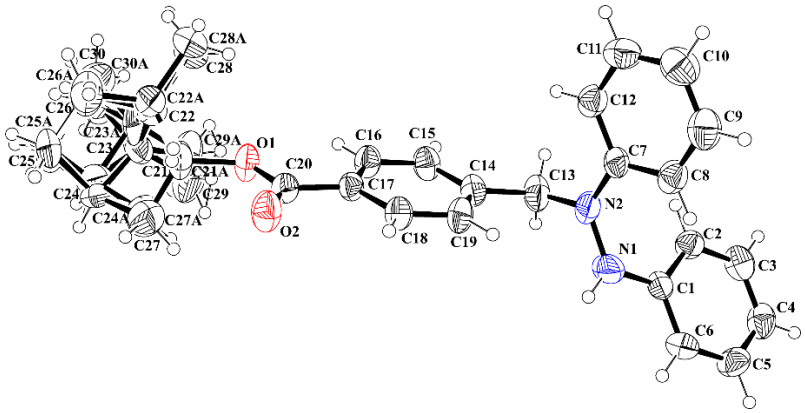


Figure S11: Molecular structure of compound **3ac** (thermal ellipsoid 40% probability level).

Please note that the terminal ligand bonded to O1 is unequally disordered over two sites. The disorder atoms C21 to C30, C21A to C30A and H21 to H30, H21A to H30A are splitted over two positions with occupancy 0.6, and 0.4 respectively.

Table S1: Crystal data and structure refinement for **3ac**

Identification code	SK_716_0m_a
CCDC	2359136
Empirical formula	$C_{30}H_{34}N_2O_2$
Formula weight	454.59

Temperature/K	295.00	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.5525(8)Å	α = 90°
	b = 7.9187(6) Å	β =96.854(2) °
	c = 28.056(2) Å	γ = 90°
Volume/$Å^3$	2548.2(3)	
Z	4	
$\rho_{calc}g/cm^3$	1.185	
μ/mm^{-1}	0.074	
F (000)	976.0	
Crystal size/mm^3	0.39 × 0.37 × 0.18	
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection/°	3.676 to 49.996	
Index ranges	-13 ≤ h ≤ 13, -9 ≤ k ≤ 9, -33 ≤ l ≤ 33	
Reflections collected	53951	
Independent reflections	4482 [R_{int} = 0.0632, R_{sigma} = 0.0324]	
Data/restraints/parameters	4482/213/375	
Goodness-of-fit on F^2	1.142	
Final R indexes [I>=2σ (I)]	R_1 = 0.0994, wR_2 = 0.2239	
Final R indexes [all data]	R_1 = 0.1246, wR_2 = 0.2439	
Largest diff. peak/hole / e $Å^{-3}$	0.94/-0.31	

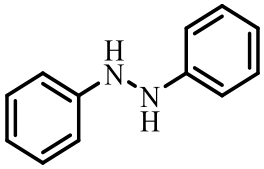
Table S2: Atomic Occupancy for **3ac**

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C21	0.60(2)	H21	0.60(2)	C22	0.60(2)
C23	0.60(2)	C24	0.60(2)	H24	0.60(2)
C25	0.60(2)	H25A	0.60(2)	H25B	0.60(2)
C26	0.60(2)	H26A	0.60(2)	H26B	0.60(2)
C27	0.60(2)	H27A	0.60(2)	H27B	0.60(2)
C28	0.60(2)	H28A	0.60(2)	H28B	0.60(2)
H28C	0.60(2)	C29	0.60(2)	H29A	0.60(2)
H29B	0.60(2)	H29C	0.60(2)	C30	0.60(2)
H30A	0.60(2)	H30B	0.60(2)	H30C	0.60(2)
C21A	0.40(2)	H21A	0.40(2)	C27A	0.40(2)
H27C	0.40(2)	H27D	0.40(2)	C24A	0.40(2)

H24A	0.40(2)	C25A	0.40(2)	H25C	0.40(2)
H25D	0.40(2)	C26A	0.40(2)	H26C	0.40(2)
H26D	0.40(2)	C22A	0.40(2)	C23A	0.40(2)
C29A	0.40(2)	H29D	0.40(2)	H29E	0.40(2)
H29F	0.40(2)	C30A	0.40(2)	H30D	0.40(2)
H30E	0.40(2)	H30F	0.40(2)	C28A	0.40(2)
H28D	0.40(2)	H28E	0.40(2)	H28F	0.40(2)

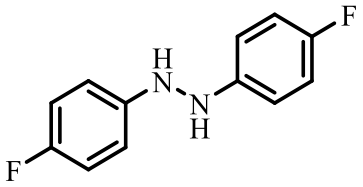
10. Analytical data of the products

1, 2-diphenylhydrazine (1a')



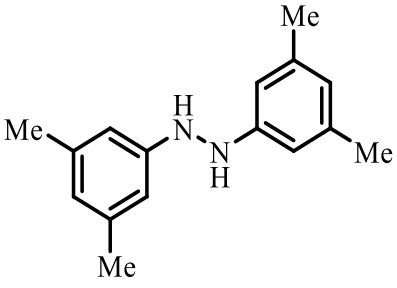
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.20 (m, 4H), 6.87 – 6.83, 6H), 5.62 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.0, 129.5, 120.1, 112.5. Spectroscopic characterization data are in accordance with reported literature.[3]

1, 2-bis(4-fluorophenyl) hydrazine (1b')



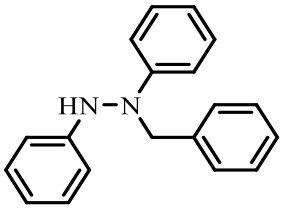
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 – 6.90 (m, 4H), 6.81 – 6.77 (m, 4H), 5.55 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.3 (d, $J_{C\text{-}F}$ = 237.7 Hz), 145.0 (d, $J_{C\text{-}F}$ = 2.2 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.8 Hz), 113.5 (d, $J_{C\text{-}F}$ = 7.7 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ -124.96. Spectroscopic characterization data are in accordance with reported literature.[21]

1,2-bis(3,5-dimethylphenyl) hydrazine (1e')



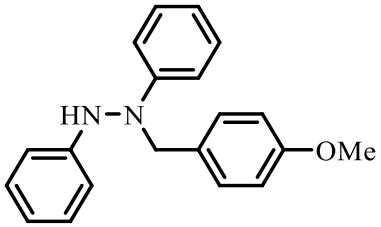
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (s, 6H), 5.46 (s, 2H), 2.25 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.4, 139.3, 121.9, 110.2, 21.6. Spectroscopic characterization data are in accordance with reported literature.[22]

1-benzyl-1, 2-diphenylhydrazine (3a)



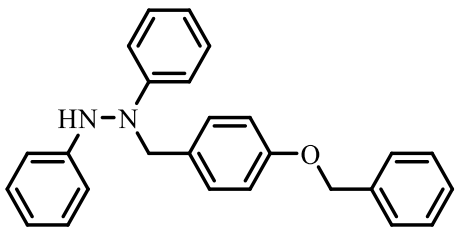
By following the **GP-1**, the title compound **3a** was isolated as light-yellow oil (0.126 g, 92%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.20 (m, 9H), 7.01 (d, J = 7.9 Hz, 2H), 6.86 – 6.76 (m, 4H), 5.66 (s, 1H), 4.76 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.0, 147.0, 136.9, 129.5, 129.4, 128.9, 127.9, 127.6, 120.1, 118.8, 113.04, 112.96, 54.4. Spectral data is in accordance to the reported literature.[23]

1-(4-methoxybenzyl)-1, 2-diphenylhydrazine (3b)



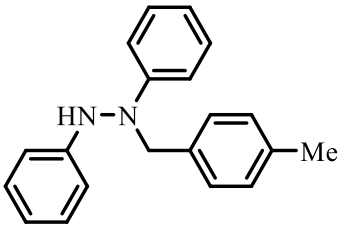
By following the **GP-1**, the title compound **3b** was isolated as light-yellow oil (0.145 g, 95%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.19 (m, 4H), 7.15 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.85 – 6.79 (m, 4H), 6.77 (d, J = 7.9 Hz, 2H), 5.59 (s, 1H), 4.68 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 150.1, 147.1, 129.5, 129.41, 129.39, 128.6, 120.0, 118.8, 114.2, 113.2, 113.1, 55.4, 53.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{21}N_2O$: 305.1649; found: 305.1648.

1-(4-(benzyloxy) benzyl)-1, 2-diphenylhydrazine (3c)



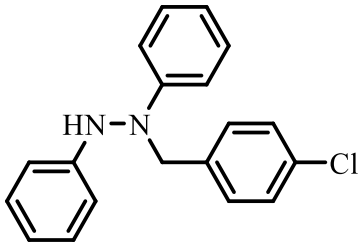
By following the **GP-1**, the title compound **3c** was isolated as light-yellow oil (0.173 g, 91%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 4H), 7.34 – 7.29 (m, 1H), 7.25 – 7.19 (m, 4H), 7.14 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.85 – 6.78 (m, 2H), 6.78 – 6.75 (m, 2H), 5.60 (s, 1H), 5.03 (s, 2H), 4.67 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.4, 150.1, 147.1, 137.1, 129.5, 129.42, 129.38, 128.9, 128.7, 128.1, 127.6, 123.0, 120.0, 118.8, 115.2, 113.10, 113.08, 70.2, 53.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{26}H_{25}N_2O$: 381.1962; found: 381.1961.

1-(4-methylbenzyl)-1, 2-diphenylhydrazine (3d)



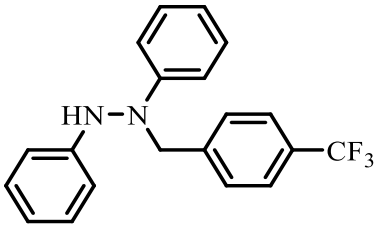
By following the **GP-1**, the title compound **3d** was isolated as light-yellow oil (0.127 g, 88%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1 R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.19 (m, 4H), 7.14 – 7.10 (m, 4H), 7.02 (d, J = 8.1 Hz, 2H), 6.85 – 6.76 (m, 4H), 5.64 (s, 1H), 4.71 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.1, 147.1, 137.2, 136.8, 136.4, 133.7, 129.54, 129.52, 129.4, 129.0, 128.8, 127.9, 120.0, 118.7, 113.1, 113.0, 54.0, 21.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{21}N_2$: 289.1700; found: 289.1701.

1-(4-chlorobenzyl)-1, 2-diphenylhydrazine (3e)



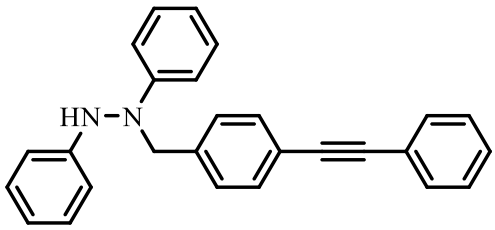
By following the **GP-1**, the title compound **3e** was isolated as light-yellow oil (0.133 g, 86%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.21 (m, 5H), 7.19 – 7.17 (m, 3H), 6.98 (d, J = 8.1 Hz, 2H), 6.86 – 6.81 (m, 2H), 6.76 (d, J = 7.9 Hz, 2H), 5.62 (s, 1H), 4.71 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.7, 146.8, 135.5, 133.4, 129.6, 129.5, 129.3, 129.0, 123.0, 120.2, 119.2, 113.1, 113.0, 54.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{18}ClN_2$: 309.1154; found: 309.1152.

1, 2-diphenyl-1-(4-(trifluoromethyl) benzyl) hydrazine (3f)



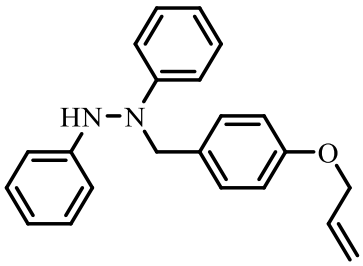
By following the **GP-1**, the title compound **3f** was isolated as light-yellow oil (0.142 g, 83%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H), 7.26 – 7.21 (m, 4H), 6.97 (d, J = 8.0 Hz, 2H), 6.87 – 6.83 (m, 2H), 6.78 (d, J = 7.7 Hz, 2H), 5.68 (s, 1H), 4.81 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.6, 146.7, 141.4, 129.64, 129.57, 128.0, 125.8 (CF_3, q, $J_{C\text{-}F}$ = 3.7 Hz), 120.3, 119.3, 113.0, 112.9, 54.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.48. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{18}F_3N_2$: 343.1417; found: 343.1416.

1, 2-diphenyl-1-(4- (phenyl ethynyl) benzyl) hydrazine (3g)



By following the **GP-1**, the title compound **3g** was isolated as light-yellow oil (0.148 g, 79%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.51 (m, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.26 – 7.20 (m, 6H), 7.00 (d, J = 7.9 Hz, 2H), 6.87 – 6.81 (m, 2H), 6.77 (d, J = 7.6 Hz, 2H), 5.67 (s, 1H), 4.76 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$): δ 149.9, 146.9, 137.3, 132.1, 131.7, 129.6, 129.5, 128.5, 128.4, 127.9, 123.3, 123.0, 122.6, 120.2, 119.1, 113.04, 113.01, 89.8, 89.2, 54.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{27}H_{23}N_2$: 375.1856; found: 375.1858.

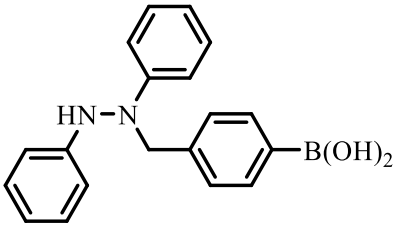
1-(4-(allyloxy) benzyl)-1, 2-diphenylhydrazine (3h)



By following the **GP-1**, the title compound **3h** was isolated as light-yellow oil (0.124 g, 75%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 – 7.19 (m, 4H), 7.13 (d, J = 7.9 Hz, 2H), 7.02 (d, J

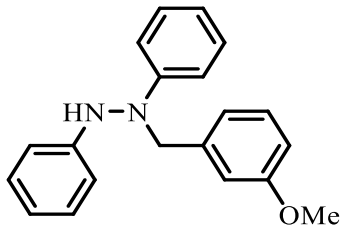
= 8.1 Hz, 2H), 6.85 – 6.79 (m, 4H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.06 – 6.00 (m, 1H), 5.60 (s, 1H), 5.39 (d, 17.3 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.67 (s, 2H), 4.50 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 158.1, 150.0, 147.0, 133.3, 129.5, 129.4, 129.3, 128.8, 120.0, 118.7, 117.9, 115.0, 113.07, 113.05, 68.9, 53.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{22}H_{23}N_2O$: 331.1805; found: 331.1803.

(4-((1,2-diphenylhydrazineyl) methyl) phenyl) boronic acid (3i)



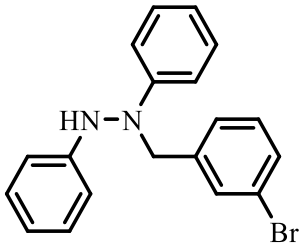
By following the **GP-1**, the title compound **3i** was isolated as white powder (0.129 g, 81%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 2:8, R_f = 0.25). m.p. 127 – 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.15 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.03 – 6.99 (m, 2H), 6.88 – 6.81 (m, 3H), 6.79 – 6.76 (m, 1H), 5.72 (s, 1H), 4.84 – 8.79 (m, 3H), 4.64 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 149.9, 147.0, 142.0, 136.2, 134.1, 129.6, 129.5, 127.5, 120.2, 119.1, 113.0, 55.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{20}BN_2O_2$: 319.1613; found: 319.1614.

1-(3-methoxybenzyl)-1, 2-diphenylhydrazine (3j)



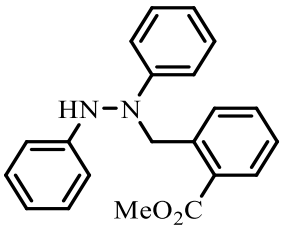
By following the **GP-1**, the title compound **3j** was isolated as light-yellow oil (0.128 g, 84%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.25 – 7.19 (m, 5H), 7.02 – 7.00 (m, 2H), 6.86 – 6.76 (m, 4H), 6.78 – 6.77 (m, 3H), 5.68 (s, 1H), 4.72 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 160.0, 150.0, 147.0, 138.6, 129.9, 129.5, 129.4, 120.1, 118.8, 113.4, 113.0, 112.93, 112.90, 55.3, 54.4. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{21}N_2O$: 305.1649; found: 305.1638.

1-(3-bromobenzyl)-1, 2-diphenylhydrazine (3k)



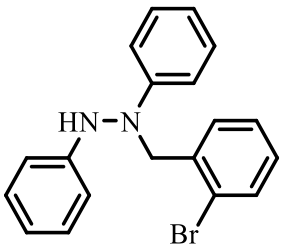
By following the **GP-1**, the title compound **3k** was isolated as light-yellow oil (0.132 g, 75%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 – 7.57 (m, 1H), 7.25 – 7.20 (m, 6H), 7.15 – 7.12 (m, 1H), 6.93 – 6.91 (m, 2H), 6.85 – 6.81 (m, 2H), 6.78 – 6.76 (m, 2H), 5.83 (s, 1H), 4.80 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.6, 147.0, 136.1, 133.3, 129.6, 129.5, 128.9, 128.8, 127.7, 123.5, 123.0, 120.2, 119.0, 112.8, 112.7, 56.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{17}BrN_2$: 353.0648; found: 353.0649.

Methyl 2-((1, 2-diphenylhydrazineyl) methyl) benzoate (3l)



By following the **GP-1**, the title compound **3l** was isolated as white powder (0.123 g, 74%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). m.p. 124 – 126 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 7.7 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.37 (d, J = 7.7 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.24 – 7.19 (m, 4H), 6.93 (d, J = 8.3 Hz, 2H), 6.84 – 6.80 (m, 2H), 6.75 (d, J = 8.0 Hz, 2H), 5.87 (s, 1H), 5.17 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 167.8, 149.9, 147.0, 139.3, 132.6, 131.4, 129.5, 129.42, 129.37, 128.0, 127.2, 120.0, 118.7, 112.8, 112.5, 54.1, 52.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{21}H_{21}N_2O_2$: 333.1598; found: 333.1591. Characteristic IR band: $\nu_{(C=0)}$: 1713 cm^{-1}.

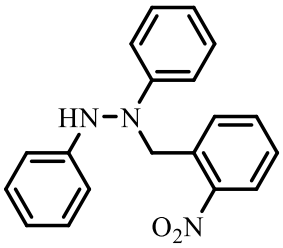
1-(2-bromobenzyl)-1, 2-diphenylhydrazine (3m)



By following the **GP-1**, the title compound **3m** was isolated as light-yellow oil (0.123 g, 70%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.38 (m, 2H), 7.24 – 7.19 (m, 4H), 7.17 – 7.14 (m,

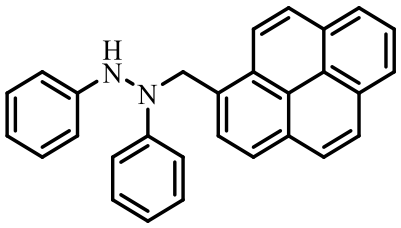
2H), 6.97 (d, J = 8.1 Hz, 2H), 6.86 – 6.80 (m, 2H), 6.75 (d, J = 7.9 Hz, 2H), 5.68 (s, 1H), 4.71 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.6, 146.7, 139.6, 130.8, 130.7, 130.4, 129.6, 129.5, 126.4, 123.0, 120.2, 119.2, 113.0, 112.9, 54.4. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{18}BrN_2$: 353.0648; found: 353.0645.

1-(2-nitrobenzyl)-1, 2-diphenylhydrazine (3n)



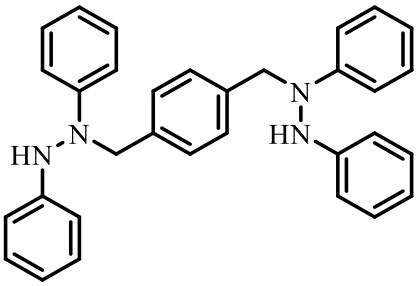
By following the **GP-1**, the title compound **3n** was isolated as light-yellow oil (0.117 g, 73%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 8.1 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.52 – 7.50 (m, 1H), 7.45 – 7.42 (m, 1H), 7.25 – 7.19 (m, 5H), 6.89 (d, J = 8.1 Hz, 2H), 6.84 (t, J = 7.3 Hz, 2H), 6.75 (d, J = 7.9 Hz, 2H), 5.80 (s, 1H), 5.15 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.4, 148.7, 146.6, 133.9, 133.7, 129.64, 129.59, 129.3, 128.3, 125.7, 120.4, 119.5, 112.8, 112.7, 54.1. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{18}N_3O_2$: 320.1394; found: 320.1395.

1, 2-diphenyl-1-(pyren-1-ylmethyl) hydrazine (3o)



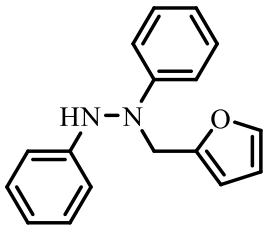
By following the **GP-1**, the title compound **3o** was isolated as light-yellow oil (0.165 g, 83%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 – 8.17 (m, 3H), 8.09 – 8.04 (m, 3H), 8.03 – 7.99 (m, 2H), 7.84 (d, J = 7.7 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.18 (t, J = 7.3 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.87 – 6.81 (m, 2H), 6.71 (d, J = 8.1 Hz, 2H), 5.74 (s, 1H), 5.48 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.1, 147.0, 131.4, 131.0, 130.9, 129.7, 129.6, 129.5, 129.2, 128.0, 127.6, 127.5, 126.2, 126.1, 125.5, 125.4, 125.2, 124.89, 124.86, 122.7, 120.1, 118.9, 113.1, 112.9, 52.4. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{29}H_{23}N_2$: 399.1856; found: 399.1835.

1, 4-bis ((1, 2-diphenylhydrazineyl) methyl) benzene (3p)



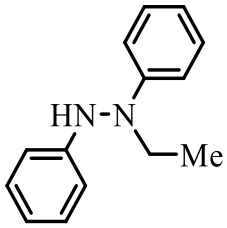
By following the **GP-1**, the title compound **3p** was isolated as light-yellow oil (0.186 g, 79%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (600 MHz, $CDCl_3$): 7.24 – 7.18 (m, 12H), 7.00 (d, J = 7.9 Hz, 4H), 6.85 – 6.80 (m, 4H), 6.76 (d, J = 7.7 Hz, 4H), 5.63 (s, 2H), 4.72 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.0, 147.0, 136.2, 129.54, 129.45, 128.4, 120.1 118.9, 113.02, 113.00, 54.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{32}H_{31}N_4$: 471.2544; found: 471.2535.

1-(furan-2-ylmethyl)-1, 2-diphenylhydrazine (3q)



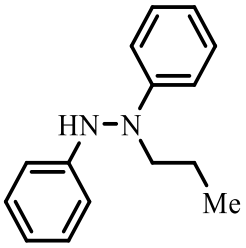
By following the **GP-1**, the title compound **3q** was isolated as light-yellow oil (0.102 g, 77%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 1H), 7.25 – 7.21 (m, 4H), 7.06 (d, J = 7.8 Hz, 2H), 6.87 – 6.80 (m, 4H), 6.29 – 6.28 (m, 1H), 6.20 (d, J = 2.7 Hz, 1H), 5.78 (s, 1H), 4.66 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.8, 149.5, 147.3, 142.6, 129.5, 129.3, 120.1, 119.3, 113.5, 112.9, 110.4, 108.9, 47.3. Spectral data is in accordance to the reported literature.[24]

1-ethyl-1, 2-diphenylhydrazine (3r)



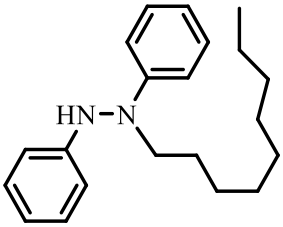
By following the **GP-1**, the title compound **3r** was isolated as light-yellow oil (0.040 g, 75%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.18 (m, 4H), 6.90 (d, J = 7.9 Hz, 2H), 6.82 – 6.77 (m, 4H), 5.55 (s, 1H), 3.56 (q, J = 7.0 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.7, 148.1, 129.5, 129.4, 119.6, 118.7, 113.2, 112.3, 46.0, 10.9. Spectral data is in accordance to the reported literature.[25]

1, 2-diphenyl-1-propylhydrazine (3s)



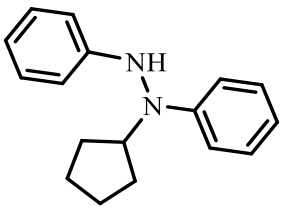
By following the **GP-1**, the title compound **3s** was isolated as light-yellow oil (0.040 g, 71%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.20 (m, 4H), 6.89 (d, J = 7.8 Hz, 2H), 6.83 – 6.78 (m, 4H), 5.59 (s, 1H), 3.47 – 3.44 (m, 2H), 1.73 – 1.68 (m, 2H), 0.97 (t, J = 8.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.0, 147.8, 129.5, 129.4, 119.6, 118.6, 112.9, 112.3, 54.0, 19.6, 11.7. Spectral data is in accordance to the reported literature.[24]

1-nonyl-1, 2-diphenylhydrazine (3t)



By following the **GP-1**, the title compound **3t** was isolated as light-yellow oil (0.054 g, 69%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 – 7.20 (m, 4H), 6.89 (d, J = 8.0 Hz, 2H), 6.83 – 6.77 (m, 4H), 5.60 (s, 1H), 3.50 – 3.47 (m, 2H), 1.66 (p, J = 7.3 Hz, 2H), 1.34 – 1.25 (m, 12H), 0.89 – 0.86 (m, 3H).^{13}C NMR (151 MHz, $CDCl_3$): δ 149.9, 147.8, 129.5, 129.4, 119.6, 118.5, 112.9, 112.3, 52.1, 32.0, 29.7, 29.6, 29.4, 27.3, 26.1, 22.8, 14.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{21}H_{31}N_2$: 311.2482; found: 311.2483.

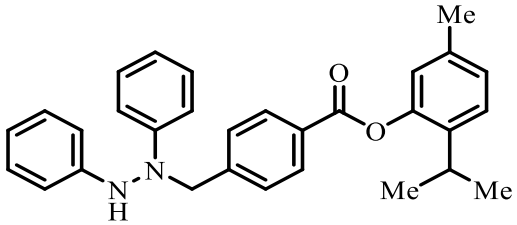
1-cyclopentyl-1, 2-diphenylhydrazine (3u)



By following the **GP-1**, the title compound **3u** was isolated as light-yellow oil (0.031 g, 49%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 – 7.92 (m, 2H), 7.54 – 7.42 (m, 3H), 7.31 – 7.29 (m,

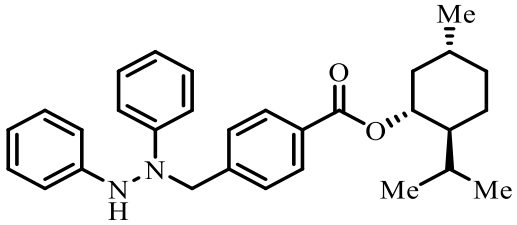
1H), 7.22 – 7.19 (m, 1H), 7.10 – 7.06 (m, 1H), 6.91 – 6.72 (m, 2H), 3.76 – 3.74 (m, 2H), 2.88 – 2.86 (m, 1H), 2.84 – 2.82 (m, 1H), 2.56 – 2.52 (m, 1H), 1.87 – 1.84 (m, 2H), 1.28 – 1.25 (brs, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 131.1, 129.4, 129.2, 128.8, 123.0, 120.6, 119.6, 118.6, 114.3, 111.8, 111.4, 68.1, 28.8, 26.0, 25.8, 24.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{21}N_2$: 253.1700; found: 253.1701.

2-isopropyl-5-methylphenyl 4-((1, 2-diphenylhydrazineyl) methyl) benzoate (3aa)



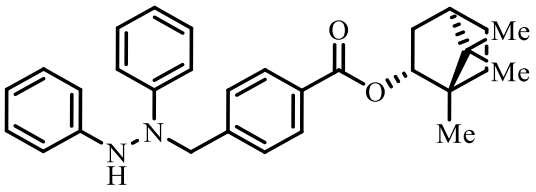
By following the **GP-1**, the title compound **3aa** was isolated as light-yellow oil (0.185 g, 82%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.27 – 7.21 (m, 5H), 7.07 – 7.05 (m, 1H), 7.00 – 6.98 (m, 2H), 6.92 (s, 1H), 6.88 – 6.82 (m, 2H), 6.80 – 6.78 (m, 2H), 5.74 (s, 1H), 4.85 (s, 2H), 3.08 – 2.98 (m, 1H), 2.33 (s, 3H), 1.20 (d, J = 6.9 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$): δ 165.3, 149.6, 148.2, 146.8, 143.4, 137.3, 136.8, 130.7, 129.6, 129.5, 128.9, 127.9, 127.3, 126.6, 122.9, 120.3, 119.3, 113.0, 112.9, 55.1, 27.4, 23.2, 21.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{30}H_{31}N_2O_2$: 451.2381; found: 451.2382.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((1,2-diphenylhydrazineyl) methyl) benzoate (3ab)



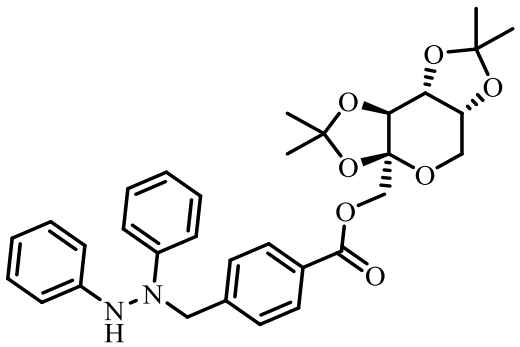
By following the **GP-1**, the title compound **3ab** was isolated as light-yellow oil (0.192 g, 84%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.25 – 7.21 (m, 4H), 6.98 (d, J = 8.3 Hz, 2H), 6.87 – 6.81 (m, 2H), 6.78 (d, J = 8.1 Hz, 2H), 5.70 (s, 1H), 4.94 – 4.89 (m, 1H), 4.81 (s, 2H), 2.12 – 2.10 (m, 1H), 1.96 – 1.92 (m, 1H), 1.73 – 1.71 (m, 2H), 1.57 – 1.51 (m, 3H), 1.15 – 1.05 (m, 2H), 0.93 – 0.90 (m, 6H), 0.78 (d, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.0, 149.7, 146.8, 142.2, 130.2, 129.6, 129.5, 127.6, 120.2, 119.2, 113.0, 112.9, 75.0, 54.8, 47.4, 41.1, 34.4, 31.6, 26.6, 23.7, 22.2, 20.9, 16.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{30}H_{37}N_2O_2$: 457.2850; found: 457.2848.

(1S,2R,4R)-1,7,7-trimethylbicyclo [2.2.1] heptan-2-yl 4-((1,2-diphenylhydrazineyl) methyl) benzoate (3ac)



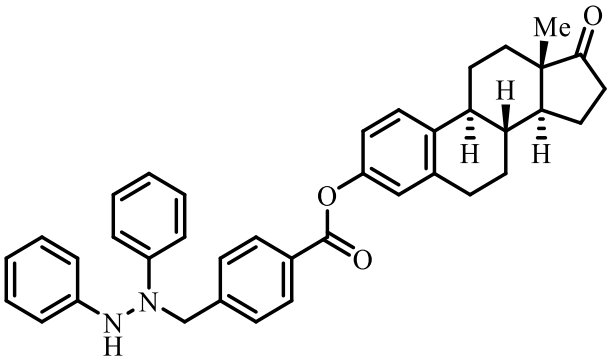
By following the **GP-1**, the title compound **3ac** was isolated as light-yellow solid (0.195 g, 86%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). m.p. 136 – 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.26 – 7.20 (m, 4H), 6.99 – 6.97 (m, 2H), 6.87 – 6.81 (m, 2H), 6.79 – 6.77 (m, 2H), 5.69 (s, 1H), 4.92 – 4.89 (m, 1H), 4.81 (s, 2H), 1.94 – 1.87 (m, 2H), 1.80 – 1.78 (m, 1H), 1.75 – 1.70 (m, 1H), 1.64 – 1.60 (m, 1H), 1.26 – 1.20 (m, 1H), 1.17 – 1.13 (m, 1H), 1.10 (s, 3H), 0.91 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.9, 149.7, 146.8, 142.3, 130.2, 130.1, 129.6, 129.5, 127.7, 120.3, 119.2, 112.98, 112.95, 81.8, 54.8, 49.2, 47.2, 45.3, 39.1, 33.9, 27.2, 20.3 20.2, 11.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{30}H_{35}N_2O_2$: 455.2694; found: 455.2693.

((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-3a-yl) methyl 4-((1,2-diphenylhydrazineyl) methyl) benzoate (3ad)



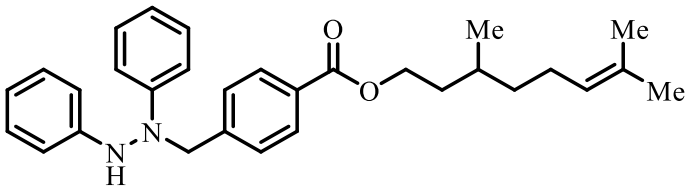
By following the **GP-1**, the title compound **3ad** was isolated as light-yellow oil (0.233 g, 83%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.42). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.25 – 7.19 (m, 4H), 6.97 (d, J = 8.1 Hz, 2H), 6.86 – 6.81 (m, 2H), 6.76 (d, J = 7.8 Hz, 2H), 5.69 (s, 1H), 4.80 (s, 2H), 4.66 – 4.62 (m, 2H), 4.44 (d, J = 2.5 Hz, 1H), 4.32 (d, J = 11.8 Hz, 1H), 4.25 (d, J = 8.0 Hz, 1H), 3.95 (d, J = 12.8 Hz, 1H), 3.80 (d, J = 13.0 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.8, 149.7, 146.8, 142.8, 130.3, 129.6, 129.5, 129.2, 127.7, 120.2, 119.2, 113.0, 112.9, 109.3, 109.0, 101.8, 70.9, 70.7, 70.2, 65.5, 61.5, 55.0, 26.7, 26.0, 25.7, 24.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{32}H_{37}N_2O_7$: 561.2596; found: 561.2597.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-((1, 2-diphenylhydrazineyl) methyl) benzoate (3ae)



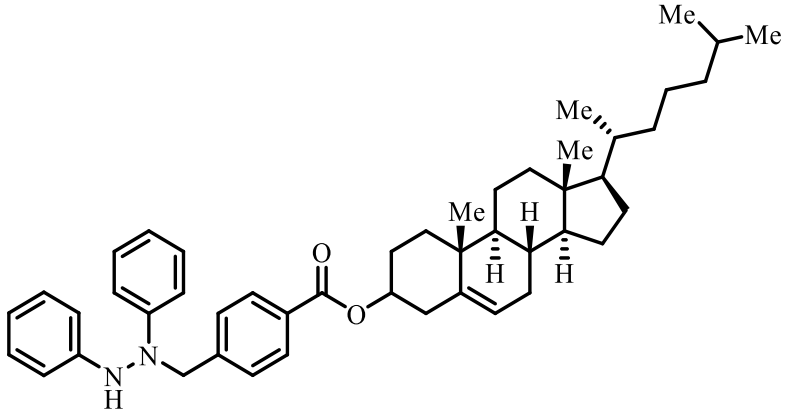
By following the **GP-1**, the title compound **3ae** was isolated as light-yellow oil (0.217 g, 76%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.42). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.5 Hz, 1H), 7.26 – 7.21 (m, 4H), 6.99 – 6.96 (m, 3H), 6.93 (s, 1H), 6.88 – 6.83 (m, 2H), 6.79 (d, J = 7.8 Hz, 2H), 5.72 (s, 1H), 4.84 (s, 2H), 2.94 – 2.92 (m, 2H), 2.54 – 2.49 (m, 1H), 2.44 – 2.41 (m, 1H), 2.35– 2.29 (m, 1H), 2.19 – 2.12 (m, 1H), 2.09 – 1.97 (m, 4H), 1.66 – 1.61 (m, 2H),1.56 – 1.43 (m, 5H), 0.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 220.9, 165.3, 149.7, 148.9, 146.8, 143.3, 138.2, 137.6, 130.8, 129.64, 129.55, 129.0, 127.9, 126.6, 121.8, 120.3, 119.3, 119.0, 113.1, 113.0, 55.2, 50.6, 48.1, 44.3, 38.2, 36.0, 31.7, 29.6, 26.5, 25.9, 21.7, 14.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{38}H_{39}N_2O_3$: 571.2956; found: 571.2957.

3,7-dimethyloct-6-en-1-yl 4-((1, 2-diphenylhydrazineyl) methyl) benzoate (3af)



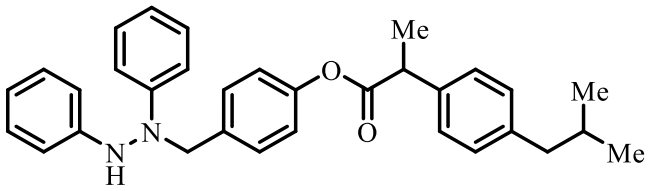
By following the **GP-1**, the title compound **3af** was isolated as light-yellow oil (0.178 g, 78%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.26 – 7.20 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 6.87 – 6.81 (m, 2H), 6.77 (d, J = 7.8 Hz, 2H), 5.68 (s, 1H), 5.09 (t, J = 7.1 Hz, 1H), 4.81 (s, 2H), 4.37 – 4.30 (m, 2H), 2.07 – 1.93 (m, 2H), 1.84 – 1.76 (m, 2H), 1.66 (s, 3H), 1.60 (s, 3H), 1.43 – 1.36 (m, 1H), 1.25 – 1.19 (m, 2H), 0.96 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.5, 149.7, 146.8, 142.4, 131.5, 130.1, 129.9, 129.6, 129.5, 129.2, 127.7, 124.7, 123.0, 120.3, 119.2, 113.03, 112.95, 63.7, 54.9, 37.1, 35.6, 29.7, 25.9, 25.5, 19.6, 17.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{30}H_{37}N_2O_2$: 457.2850; found: 457.2846.

(8S, 9S, 10R, 13R, 14S, 17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((1, 2-diphenyl-2l2-diazaneyl) methyl) benzoate (3ag)



By following the **GP-1**, the title compound **3ag** was isolated as light-yellow solid (0.285 g, 83%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). m.p. 130 – 133 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.25 – 7.20 (m, 4H), 6.97 (d, J = 8.2 Hz, 2H), 6.86 – 6.81 (m, 2H), 6.77 (d, J = 7.9 Hz, 2H), 5.69 (s, 1H), 5.41 (m, 1H), 4.87 – 4.80 (m, 3H), 2.44 (d, J = 7.8 Hz, 2H), 2.04 – 1.97 (m, 3H), 1.92 – 1.90 (m, 1H), 1.86 – 1.82 (m, 1H), 1.74 – 1.68 (m, 1H), 1.57 – 1.42 (m, 6H), 1.38 – 1.33 (m, 3H), 1.20 – 1.08 (m, 7H), 1.06 (s, 3H), 1.03 – 0.96 (m, 4H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 – 0.86 (m, 6H), 0.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.8, 149.7, 146.8, 142.2, 139.7, 130.3, 130.1, 129.6, 129.5, 127.6, 123.0, 120.2, 119.2, 113.0, 112.9, 74.8, 56.8, 56.2, 54.9, 50.2, 42.4, 39.9, 39.6, 38.3, 37.1, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{47}H_{63}N_2O_7$: 687.4885; found: 687.4884.

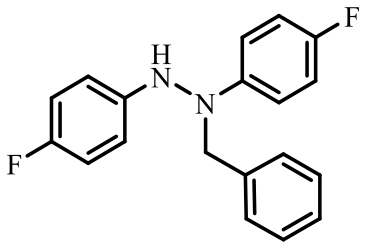
4-((1, 2-diphenylhydrazineyl) methyl) phenyl 2-(4-isobutylphenyl) propanoate (3ah)



By following the **GP-1**, the title compound **3ah** was isolated as light-yellow oil (0.203 g, 85%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 3H), 7.23 – 7.19 (m, 5H), 7.15 – 7.13 (m, 2H), 7.00 – 6.98 (m, 2H), 6.95 – 6.93 (m, 2H), 6.87 – 6.83 (m, 1H), 6.83 – 6.79 (m, 1H), 6.77 – 6.75 (m, 2H), 5.64 (s, 1H), 4.72 (s, 2H), 3.92 (q, J = 7.2 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.92 – 1.81 (m, 1H), 1.60 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.4, 150.3, 149.8, 149.0, 146.9, 141.0, 137.3, 134.3, 131.1, 129.7, 129.6, 129.50, 129.47, 129.2, 128.9, 127.3, 123.0, 121.8, 120.12, 120.05, 118.9, 113.02, 113.01, 112.5, 53.9,

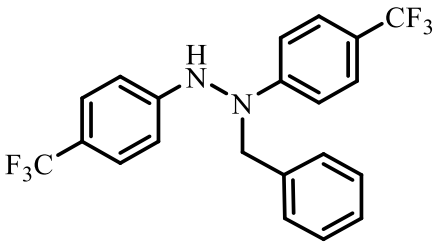
45.4, 45.2, 30.3, 22.5, 18.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{32}H_{35}N_2O_2$: 479.2694; found: 479.2693.

1-benzyl-1, 2-bis(4-fluorophenyl) hydrazine (4a)



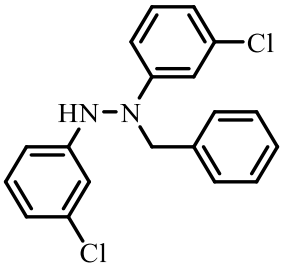
By following the **GP-2**, the title compound **4a** was isolated as light-yellow oil (0.090 g, 58%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 3H), 7.19 (d, J = 6.9 Hz, 2H), 6.95 – 6.90 (m, 6H), 6.73 – 6.70 (m, 2H), 5.52 (s, 1H), 4.67 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.4 (*d*, $J_{C\text{-}F}$ = 237.8 Hz), 156.8 (*d*, $J_{C\text{-}F}$ = 237.8 Hz) 146.5 (*d*, $J_{C\text{-}F}$ = 1.8 Hz), 143.1 (*d*, $J_{C\text{-}F}$ = 1.8 Hz), 136.2, 128.9, 128.1, 127.8, 116 (*d*, $J_{C\text{-}F}$ = 22.6 Hz), 115.8 (*d*, $J_{C\text{-}F}$ = 22.6 Hz), 114.6 (*d*, $J_{C\text{-}F}$ = 7.6 Hz), 114.2 (*d*, $J_{C\text{-}F}$ = 7.6 Hz), 55.3. ^{19}F NMR (471 MHz, $CDCl_3$): δ -124.82, -126.39. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{17}F_2N_2$: 311.1355; found: 311.1356.

1-benzyl-1,2-bis(4-(trifluoromethyl) phenyl) hydrazine (4b)



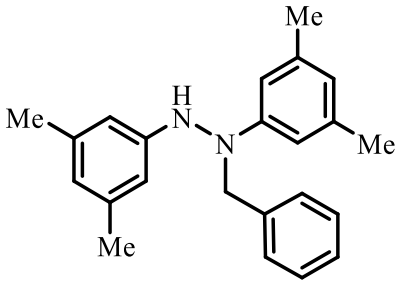
By following the **GP-2**, the title compound **4b** was isolated as light-yellow oil (0.111 g, 54%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:4, R_f = 0.52). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (t, J = 7.0 Hz, 4H), 7.36 – 7.30 (m, 3H), 7.21 (d, J = 7.0 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 5.97 (s, 1H), 4.53 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.9, 149.1, 135.5, 129.2, 128.2, 127.8, 127.1 (CF_3, q, $J_{C\text{-}F}$ = 3.6 Hz), 127.0 (CF_3, q, $J_{C\text{-}F}$ = 3.6 Hz), 112.4, 112.2, 54.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.29, -61.44. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{21}H_{17}F_6N_2$: 411.1291; found: 411.1292.

1-benzyl-1, 2-bis(3-chlorophenyl) hydrazine (4c)



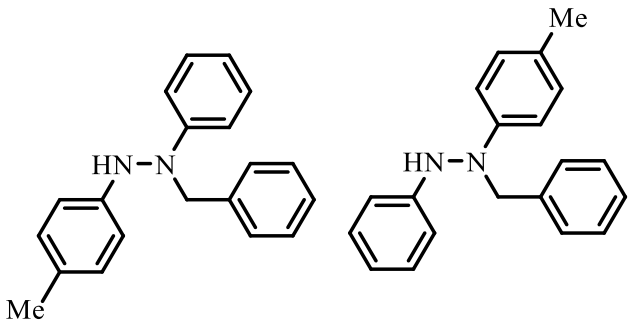
By following the **GP-2**, the title compound **4c** was isolated as light-yellow oil (0.110 g, 64%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 3H), 7.20 – 7.12 (m, 4H), 7.05 (s, 1H), 6.89 – 6.80 (m, 3H), 6.76 (s, 1H), 6.61 (d, J = 7.9 Hz, 1H), 5.67 (s, 1H), 4.73 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.9, 147.9, 135.7, 135.54, 134.52, 130.7, 130.5, 129.1, 128.0, 127.9, 120.5, 119.1, 113.1, 112.9, 111.2, 111.0, 54.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{17}Cl_2N_2$: 343.0764; found: 343.0765.

1-benzyl-1, 2-bis(3,5-dimethylphenyl) hydrazine (4d)



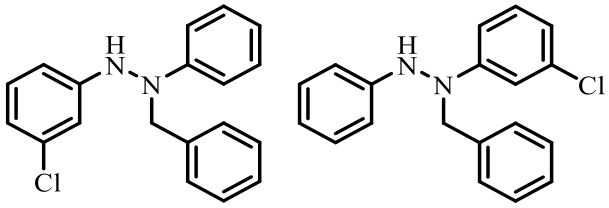
By following the **GP-2**, the title compound **4d** was isolated as light-yellow oil (0.145 g, 88%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.33 – 7.31 (m, 1H), 7.30 – 7.28 (m, 1H), 7.23 – 7.22 (m, 2H), 6.69 (s, 2H), 6.50 – 6.48 (m, 2H), 6.42 (s, 2H), 5.53 (s, 1H), 4.74 (s, 2H), 2.26 (s, 6H), 2.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.1, 150.4, 147.2, 139.3, 139.1, 138.9, 137.0, 132.7, 128.9, 127.9, 127.4, 122.0, 120.7, 120.6, 110.8, 110.6, 53.5, 21.9, 21.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{23}H_{27}N_2$: 331.2169; found: 331.2168.

1-benzyl-1-phenyl-2-(*p*-tolyl) hydrazine and 1-benzyl-2-phenyl-1-(*p*-tolyl) hydrazine (4e-1 + 4e-2)



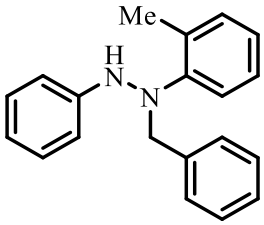
By following the **GP-2**, an inseparable mixture of the title compound **4e-1 + 4e-2** was isolated as light-yellow oil (0.057 g, 79%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR analysis of the reaction mixture showed 2:1, as determined by comparison of the following signals: δ 5.62 (s, N*H*)-major, 5.59 (s, N*H*)-minor.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.19 (m, 7H, **4e-1**, major, 67% + m, 7H, **4e-2**, minor, 33%), 7.04 – 7.01 (m, 4H, **4e-1**, major, 67%), 6.92 – 6.91 (m, 4H, **4e-2**, minor, 33%), 6.84 – 6.81 (m, 2H, **4e-2**, minor, 33%), 6.79 – 6.77 (m, 2H, **4e-1**, major, 67%), 6.69 – 6.67 (m, 1H, **4e-1**, major, 67%), 6.65 – 6.63 (m, 1H, **4e-2**, minor, 33%), 5.62 (s, 1H, **4e-1**, major, 67%), 5.59 (s, 1H, **4e-2**, minor, 33%), 4.74 – 4.72 (brs, 2H, **4e-1**, major, 67% + 2H, **4e-2**, minor, 33%), 2.26 (s, 3H, **4e-1**, major, 67% + 3H, **4e-2**, minor, 33%). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.2, 147.8, 147.3, 144.6, 137.0, 130.0, 129.9, 129.5, 129.4, 129.0, 128.9, 128.8, 128.8, 128.1, 128.0, 127.9, 127.7, 127.5, 127.5, 127.4, 125.7, 122.5, 119.9, 118.6, 117.7, 113.2, 113.0, 112.9, 54.9, 54.2, 20.7, 20.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{17}Cl_2N_2$: 289.1700; found: 289.1691.

1-benzyl-1-(3-chlorophenyl)-2-phenylhydrazine and 1-benzyl-2-(3-chlorophenyl)-1-phenylhydrazine (4f-1 + 4f-2)



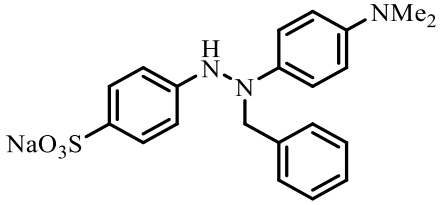
By following the **GP-2**, an inseparable mixture of the title compound **4f-1 + 4f-2** was isolated as light-yellow oil (0.100 g, 65%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR analysis of the reaction mixture showed 75:25, as determined by comparison of the following signals: δ 5.67 (s, N*H*)-major, 5.65 (s, N*H*)-minor. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 4H, **4f-1**, major, 75%), 7.25 – 7.19 (m, 11H, **4f-2**, minor, 25%), 7.15 – 7.06 (m, 2H, **4f-1**, major, 75% + m, 1H, **4f-2**, minor, 25%), 7.01 – 6.99 (m, 2H, **4f-1**, major, 75% + m, 1H, **4f-2**, minor, 25%), 6.89 – 6.82 (m, 2H, **4f-1**, major, 75%), 6.80 – 6.73 (m, 3H, **4f-1**, major, 75% + m, 1H, **4f-2**, minor, 25%), 6.63 (d, *J* = 6.8 Hz, 1H, **4f-1**, major, 75%), 5.67 (s, 1H, **4f-1,** major, 75%), 5.65 (s, 1H, **4f-2**, minor, 25%), 4.73 (brs, 2H, **4f-1**, major, 75% + brs, 2H, **4f-2**, minor, 25%). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.3, 149.6, 148.5, 146.4, 136.4, 136.2, 135.5, 135.4, 130.6, 130.4, 129.6, 129.5, 129.0, 128.9, 128.0, 127.8, 127.7, 120.5, 120.0, 119.3, 118.6, 113.21, 113.18, 112.9, 112.8, 111.1, 110.8, 54.7, 53.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{18}ClN_2$: 309.1154; found: 309.1153.

1-benzyl- 2-phenyl-1-(o-tolyl) hydrazine (4g)



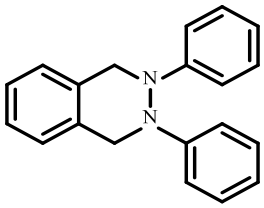
By following the **GP-2**, the title compound **4g** was isolated as light-yellow oil (0.086 g, 60%) along with 25% of corresponding azobenzene **1h** is recovered using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.22 (m, 7H), 7.12 – 7.06 (m, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.82 – 6.76 (m, 2H), 5.56 (s, 1H), 4.74 (s, 2H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.0, 144.3, 136.9, 130.7, 129.4, 128.9, 128.1, 127.6, 127.4, 121.6, 119.5, 118.8, 112.9, 112.1, 54.3, 17.1. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{17}Cl_2N_2$: 289.1700; found: 289.1696.

Sodium 4-(2-benzyl-2-(4-(dimethylamino) phenyl) hydrazineyl) benzenesulfonate (4h)



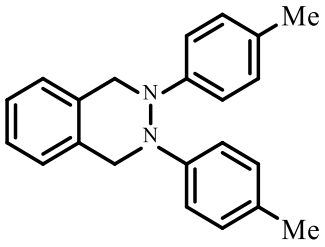
By following the **GP-2**, the title compound **4h** was isolated as light-yellow oil (0.103 g, 49%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 5:1, R_f = 0.30). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.31 (m, 5H), 7.28 – 7.24 (m, 4H), 6.74 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.28 (s, 2H), 2.99 (brs, 1H), 2.82 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.1, 128.8, 128.7, 128.5, 127.7, 127.2, 122.4, 116.1, 114.5, 113.1, 49.6, 42.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{21}H_{23}N_3NaO_3S$: 420.1353; found: 420.1360.

2, 3-diphenyl-1, 2, 3, 4-tetrahydrophthalazine (5a)



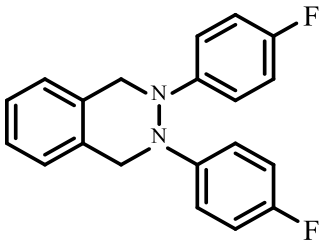
By following the **GP-3**, the title compound **5a** was isolated as light-yellow oil (0.129 g, 90%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.20 (m, 4H), 7.18 – 7.12 (m, 4H), 6.99 – 6.97 (m, 4H), 6.82 – 6.77 (m, 2H), 4.65 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.4, 132.7, 129.6, 126.8, 126.7, 119.3, 113.5, 45.3. Spectral data is in accordance to the reported literature.[26]

2, 3-di-*p*-tolyl-1, 2, 3, 4-tetrahydrophthalazine (5b)



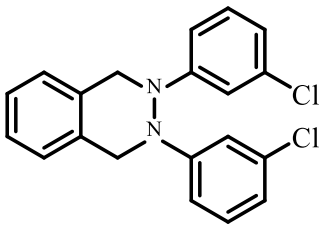
By following the **GP-3**, the title compound **5b** was isolated as light-yellow oil (0.137 g, 87%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 – 7.11 (m, 4H), 7.03 (d, J = 8.3 Hz, 4H), 6.90 – 6.88 (m, 4H), 4.61 (s, 4H), 2.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.2, 132.9, 130.0, 128.4, 126.7, 126.6, 113.7, 45.3, 20.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{22}H_{23}N_2$: 315.1856; found: 315.1856.

2, 3-bis(4-fluorophenyl)-1, 2, 3, 4-tetrahydrophthalazine (5c)



By following the **GP-3**, the title compound **5c** was isolated as light-yellow oil (0.110 g, 68%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 – 7.19 (m, 2H), 7.15 – 7.13 (m, 2H), 6.92 – 6.90 (m, 8H), 4.57 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 132.3, 127.0, 126.7, 116.1, 115.9, 115.03, 114.99, 45.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -125.77. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{17}F_2N_2$: 323.1355; found: 323.1345.

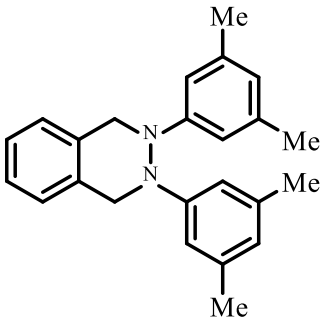
2, 3-bis(3-chlorophenyl)-1, 2, 3, 4-tetrahydrophthalazine (5d)



By following the **GP-3**, the title compound **5d** was isolated as light-yellow oil (0.128 g, 72%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 – 7.20 (m, 2H), 7.16 – 7.13 (m, 4H), 6.97 (s, 2H), 6.82 – 6.79 (m, 4H), 4.64 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.3, 135.6, 131.9, 130.7,

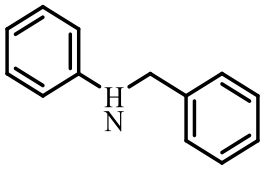
127.1, 126.8, 119.6, 113.6, 111.6, 45.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{17}Cl_2N_2$: 355.0764; found: 355.0763.

2,3-bis(3,5-dimethylphenyl)-1,2,3,4-tetrahydrophthalazine (5e)



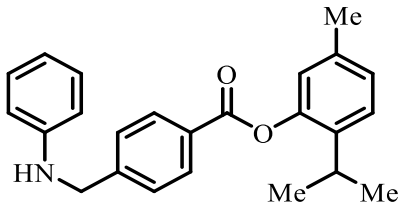
By following the **GP-3**, the title compound **5e** was isolated as light-yellow oil (0.139 g, 81%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.13 (m, 4H), 6.65 (s, 4H), 6.48 (s, 2H), 4.64 (s, 4H), 2.26 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.5, 139.2, 132.8, 126.6, 126.6, 121.1, 111.2, 44.8, 21.9. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{24}H_{27}N_2$: 343.2169; found: 343.2168.

***N*-benzyl aniline (6a)**



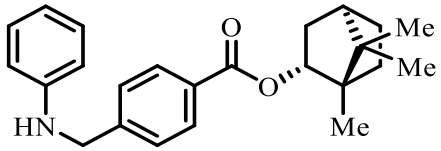
Using the reaction condition given in Scheme S5, the title compound **6a** was isolated as light-yellow oil (98%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.36 (m, 3H), 7.35 – 7.33 (m, 1H), 7.29 – 7.28 (m, 1H), 7.20 – 7.17 (m, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.65 (d, J = 8.1 Hz, 2H), 4.34 (s, 2H), 4.01 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.3, 139.6, 129.4, 128.8, 127.7, 127.4, 117.7, 113.04, 113.01, 48.5. Spectral data is in accordance to the reported literature.[27]

2-isopropyl-5-methylphenyl 4-((phenylamino)methyl) benzoate (6b)



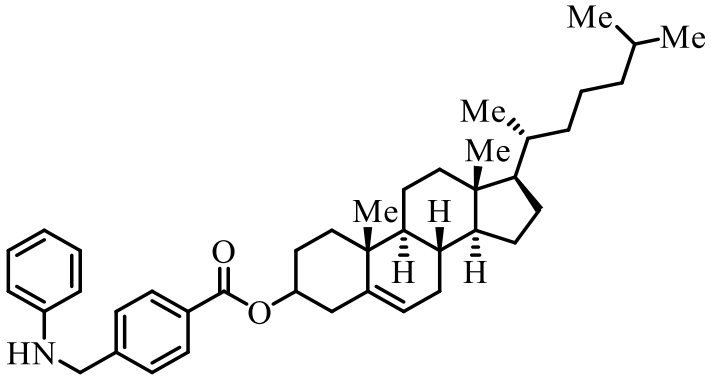
Using the reaction condition given in Scheme S5, the title compound **6b** was isolated as light-yellow oil (92%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz,$CDCl_3$): δ 8.18 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.18 (t, J = 7.8 Hz, 2H), 7.06 (d, J = 7.9 Hz, 1H), 6.93 (s, 1H), 6.74 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 8.0 Hz, 2H), 4.46 (s, 2H), 3.04 (hept, J = 6.8 Hz, 1H), 2.34 (s, 3H), 1.20 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.3, 148.3, 147.8, 145.9, 137.3, 136.8, 130.7, 129.5, 128.7, 127.5, 127.3, 126.6, 123.0, 118.1, 113.1, 48.1, 27.4, 23.2, 21.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{24}H_{26}NO_2$: 360.1959; found: 360.1960

(1S,2R,4R)-1,7,7-trimethylbicyclo [2.2.1] heptan-2-yl 4-((phenylamino)methyl) benzoate (6c)



Using the reaction condition given in Scheme S5, the title compound **6c** was isolated as light-yellow oil (81%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.18 – 7.15 (m, 2H), 6.74 – 6.71 (m, 1H), 6.61 – 6.60 (m, 2H), 4.92 – 4.89 (m, 1H), 4.41 (s, 2H), 1.94 – 1.88 (m, 2H), 1.80 (t, J = 3.9 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.63 – 1.57 (m, 1H), 1.26 – 1.21 (m, 2H), 1.17 – 1.12 (m, 1H), 1.11 (s, 3H), 0.92 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.0, 147.9, 144.9, 130.0, 129.5, 127.3, 118.0, 113.0, 81.7, 49.2, 48.1, 47.2, 45.2, 39.1, 33.9, 27.2, 20.3, 20.2, 11.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{24}H_{30}NO_2$: 364.2272; found: 364.2275.

(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((phenylamino)methyl) benzoate (6d)



Using the reaction condition given in Scheme S5, the title compound **6d** was isolated as light-yellow oil (79%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:2, R_f = 0.66). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 8.1 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 8.0 Hz, 2H), 5.42 – 5.41 (m, 1H), 4.88 – 4.82 (m, 1H), 4.40 (s, 2H), 4.13 (s, 1H), 2.45 (d, J = 7.9 Hz, 2H), 2.03 – 1.97

(m, 3H), 1.92 – 1.90 (m, 1H), 1.86 – 1.80 (m, 1H), 1.77 – 1.68 (m, 1H), 1.57 – 1.43 (m, 6H), 1.38 – 1.33 (m, 3H), 1.21 – 1.09 (m, 7H), 1.06 (s, 3H), 1.04 – 0.96 (m, 4H), 0.92 (d, J = 6.5 Hz, 3H), 0.88 – 0.86 (m, 6H), 0.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.0, 147.9, 144.9, 139.8, 130.1, 129.9, 129.4, 127.2, 122.9, 118.0, 113.1, 74.7, 56.9, 56.3, 50.2, 48.2, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{41}H_{58}NO_2$: 596.4463; found: 596.4464.

11. ^{1}H, ^{13}C, and ^{19}F NMR spectra of the starting materials and products

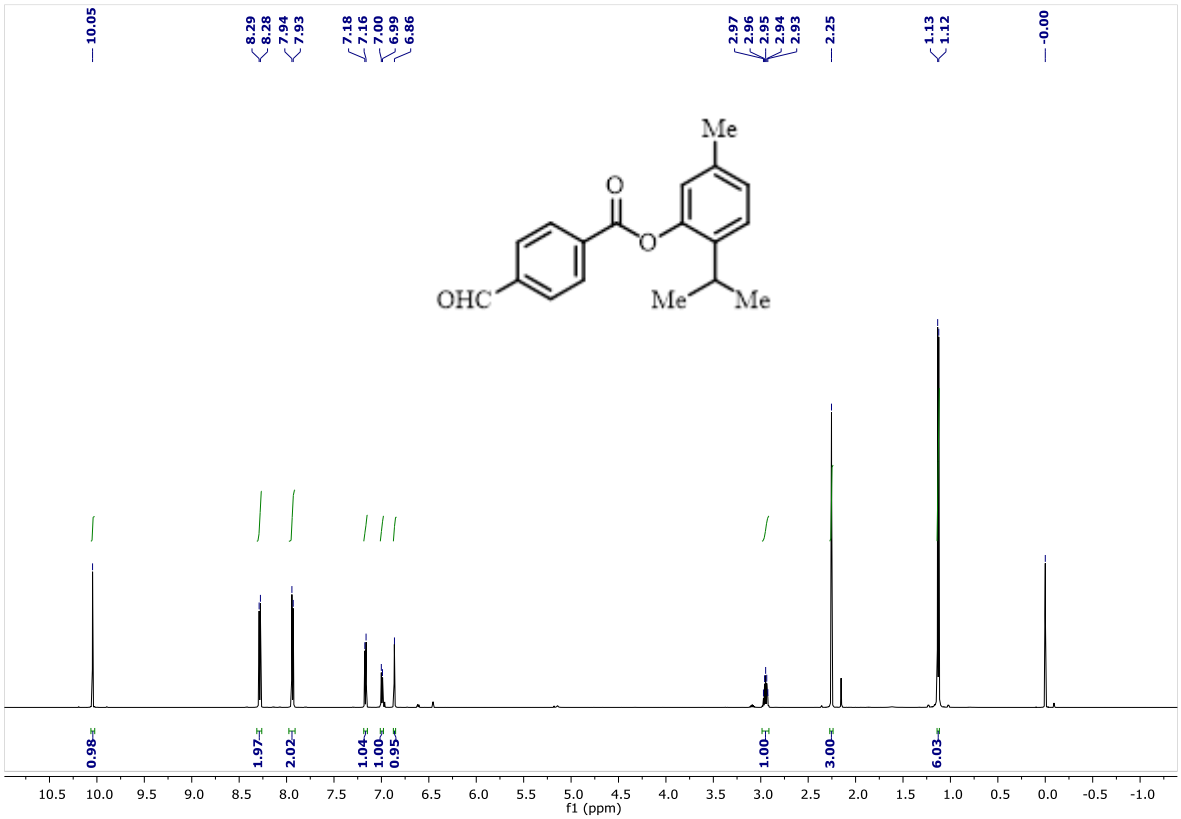


Figure S13: ^{1}H NMR Spectrum of **2aa** ($CDCl_3$, 600 MHz, 298 K)

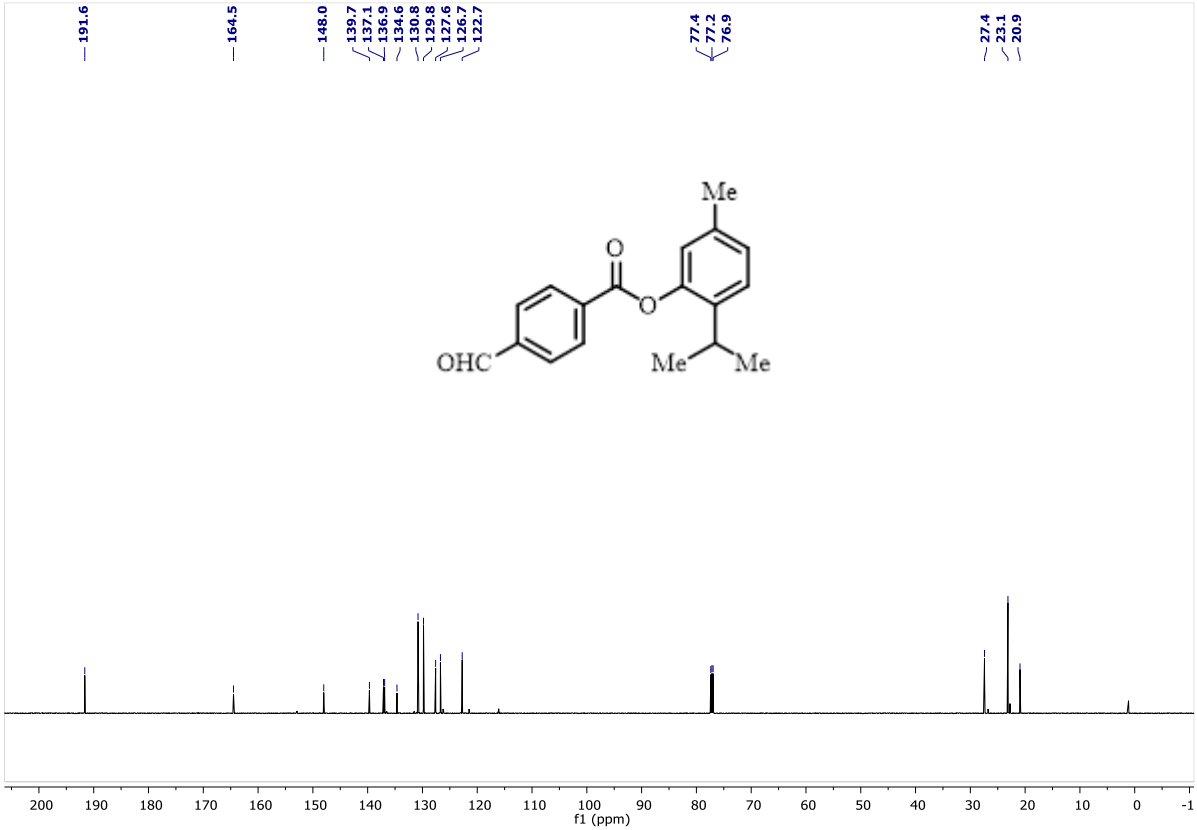


Figure S14: $^{13}C\{^{1}H\}$ NMR Spectrum of **2aa** ($CDCl_3$, 151 MHz, 298 K)

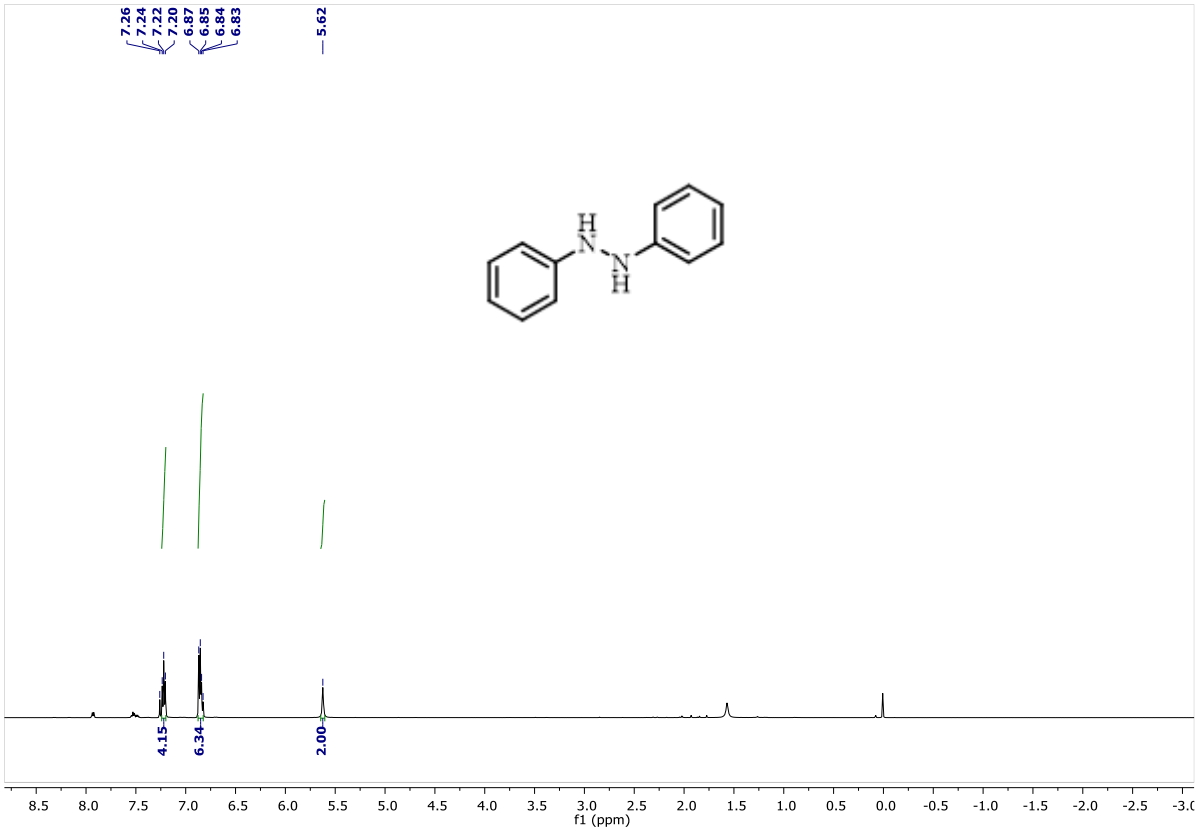


Figure S15: ^{1}H NMR Spectrum of **1a'** ($CDCl_3$, 500 MHz, 298 K)

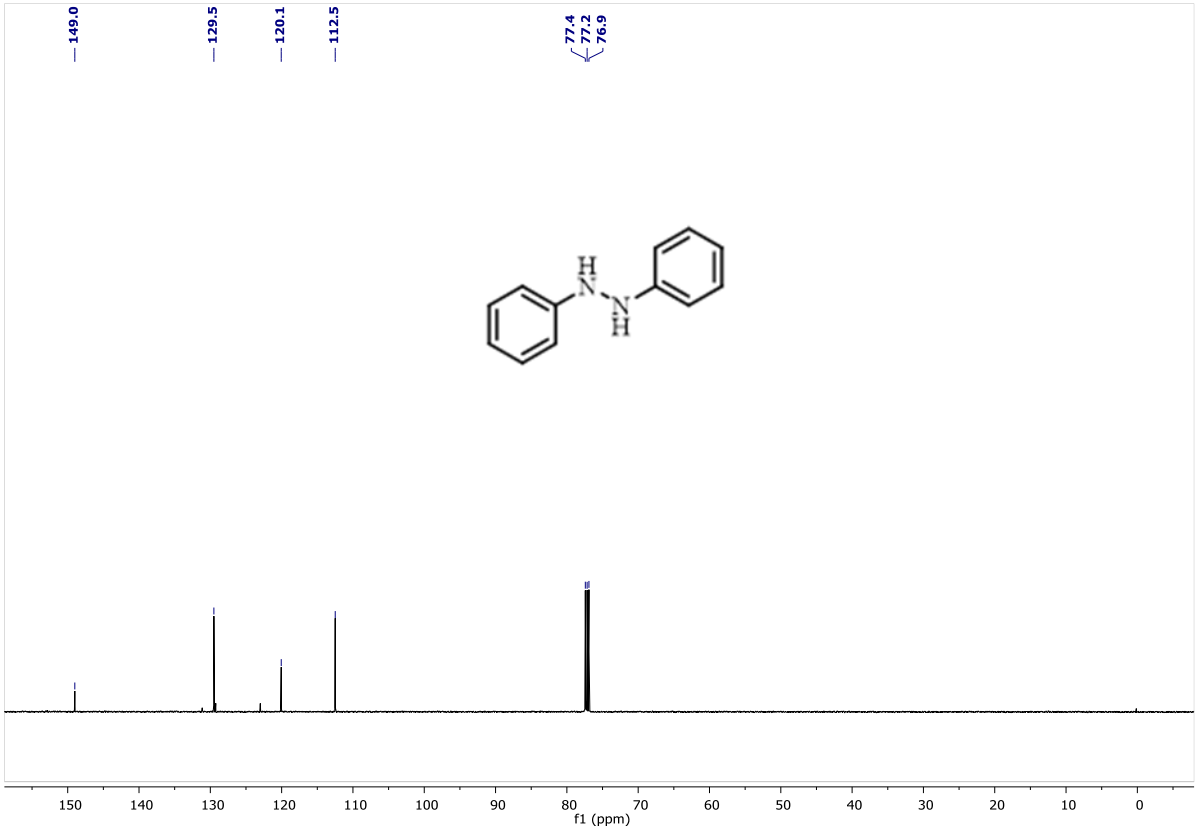


Figure S16: $^{13}C\{^{1}H\}$ NMR Spectrum of **1a'** ($CDCl_3$, 126 MHz, 298 K)

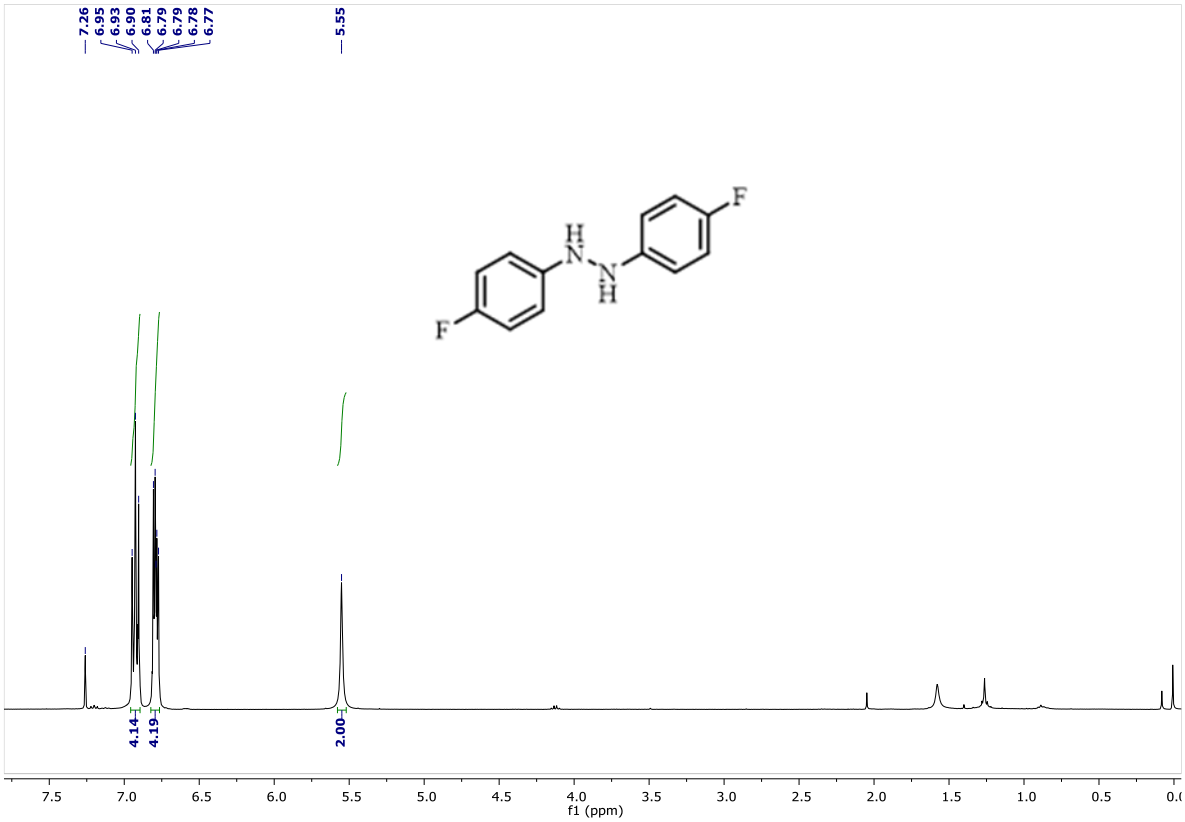


Figure S17: ^{1}H NMR Spectrum of **1b'** ($CDCl_3$, 400 MHz, 298 K)

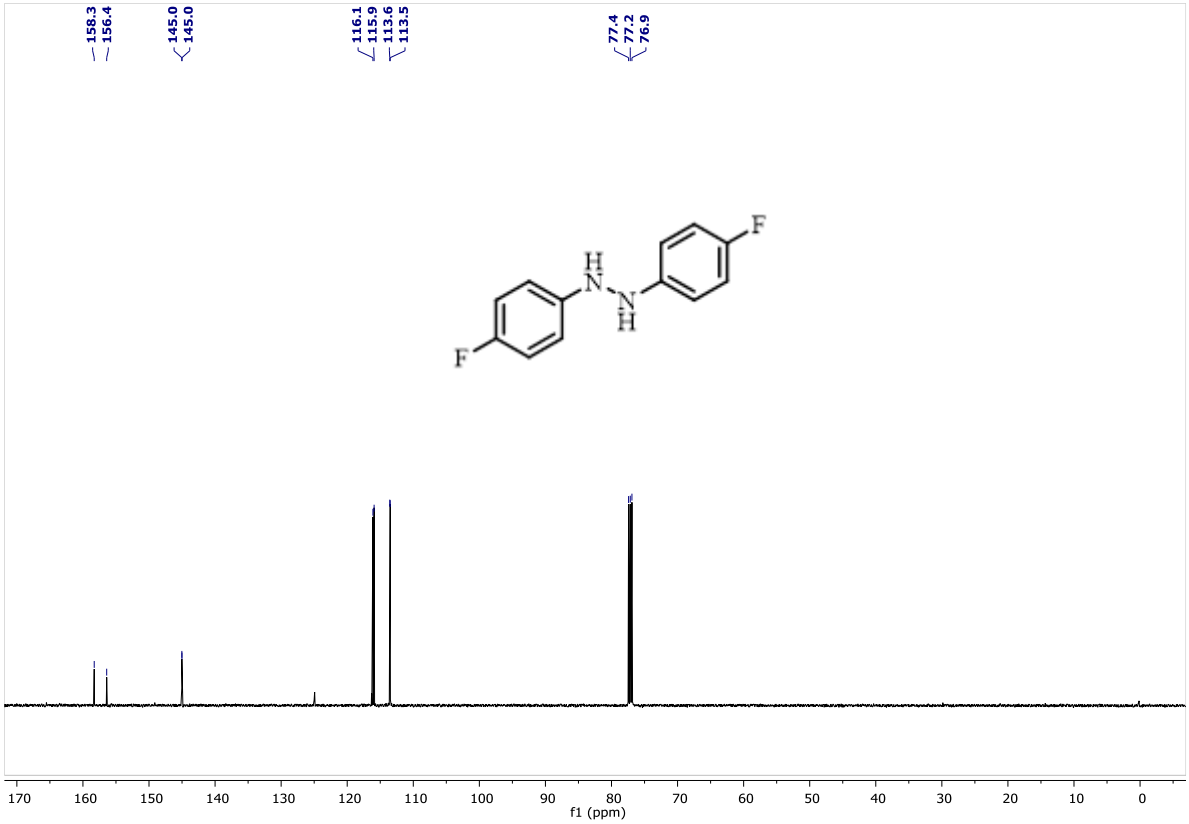


Figure S18: $^{13}C\{^{1}H\}$ NMR Spectrum of **1b'** ($CDCl_3$, 126 MHz, 298 K)

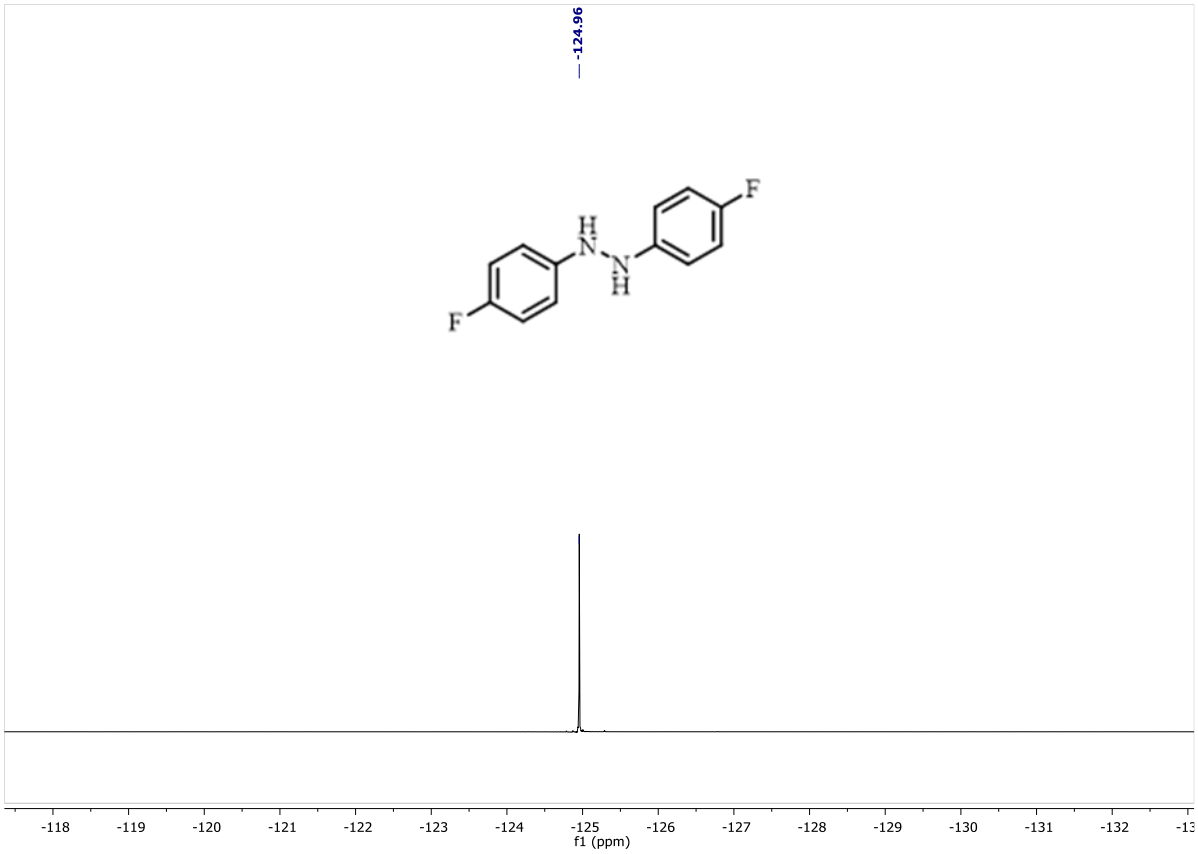


Figure S19: $^{19}F\{^{1}H\}$ NMR Spectrum of **1b′** ($CDCl_3$, 471 MHz, 298 K)

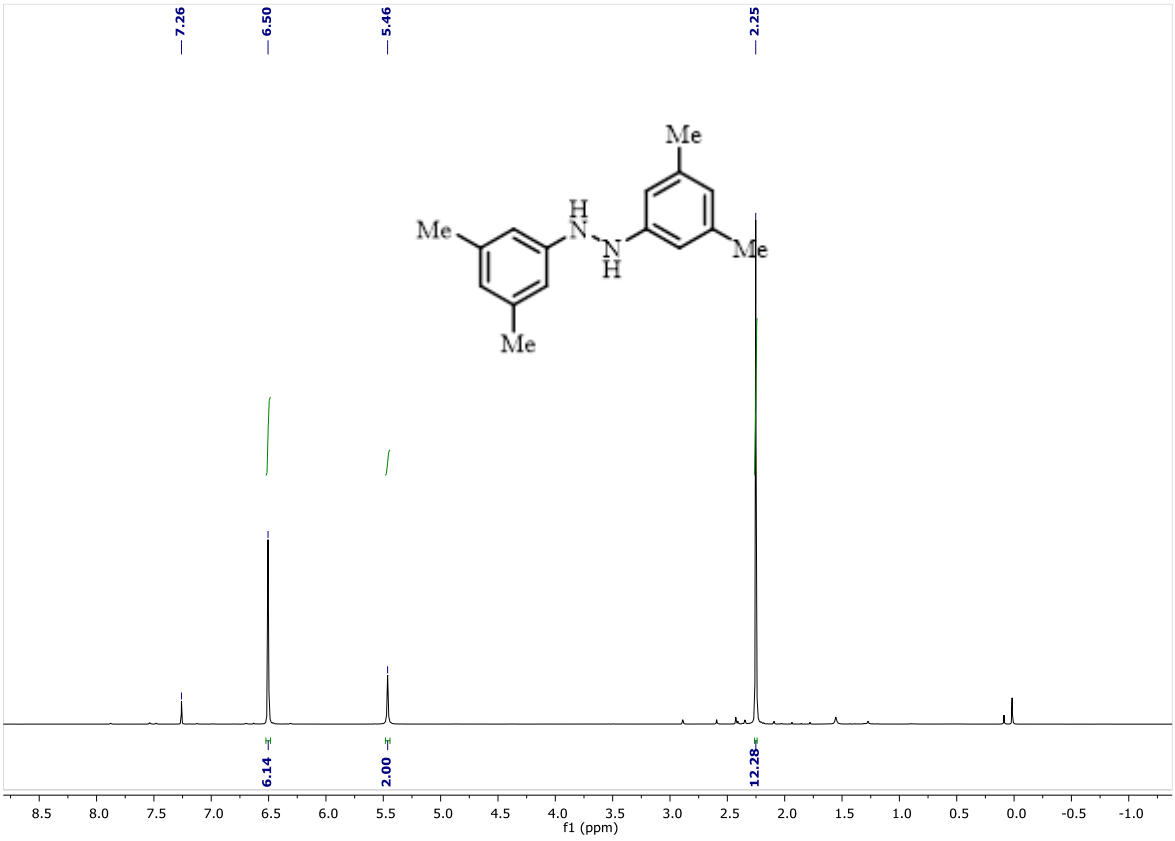


Figure S20: ^{1}H NMR Spectrum of **1d'** ($CDCl_3$, 400 MHz, 298 K)

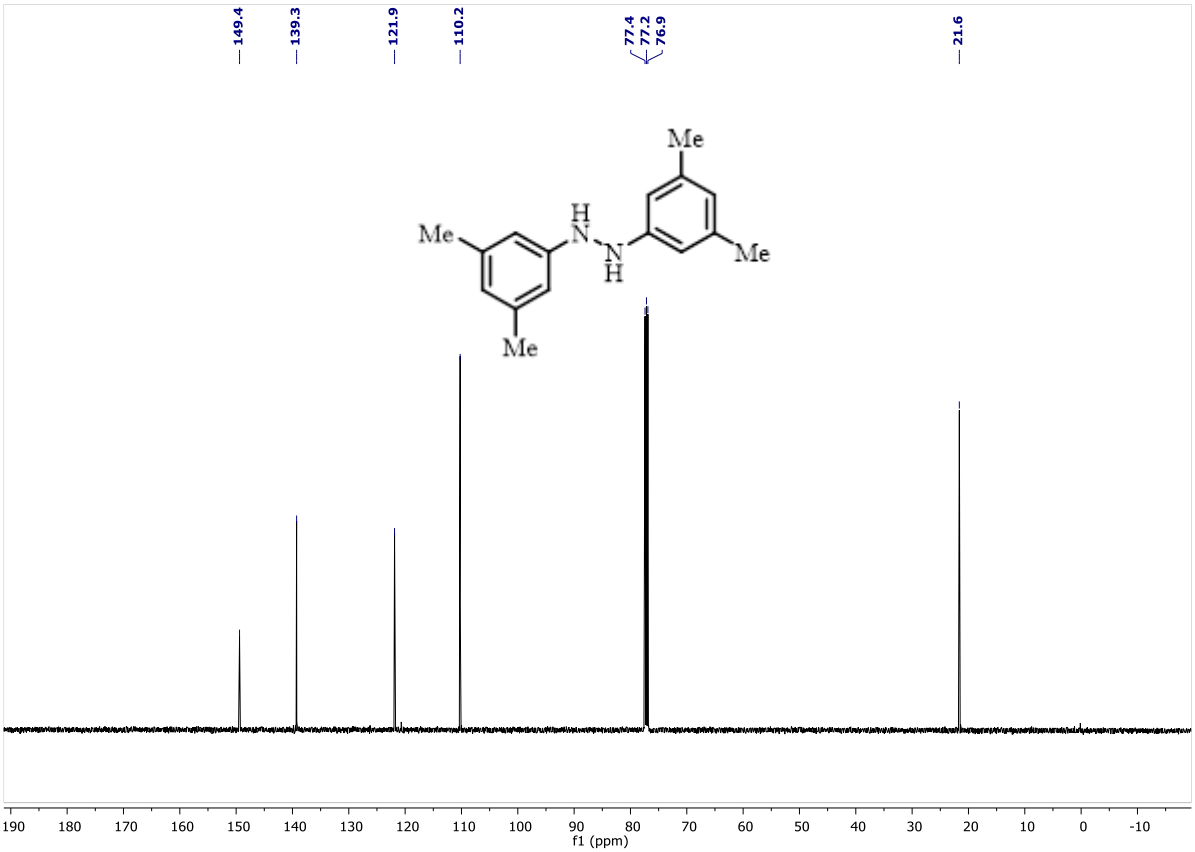


Figure S21: $^{13}C\{^{1}H\}$ NMR Spectrum of **1d'** ($CDCl_3$, 126 MHz, 298 K)

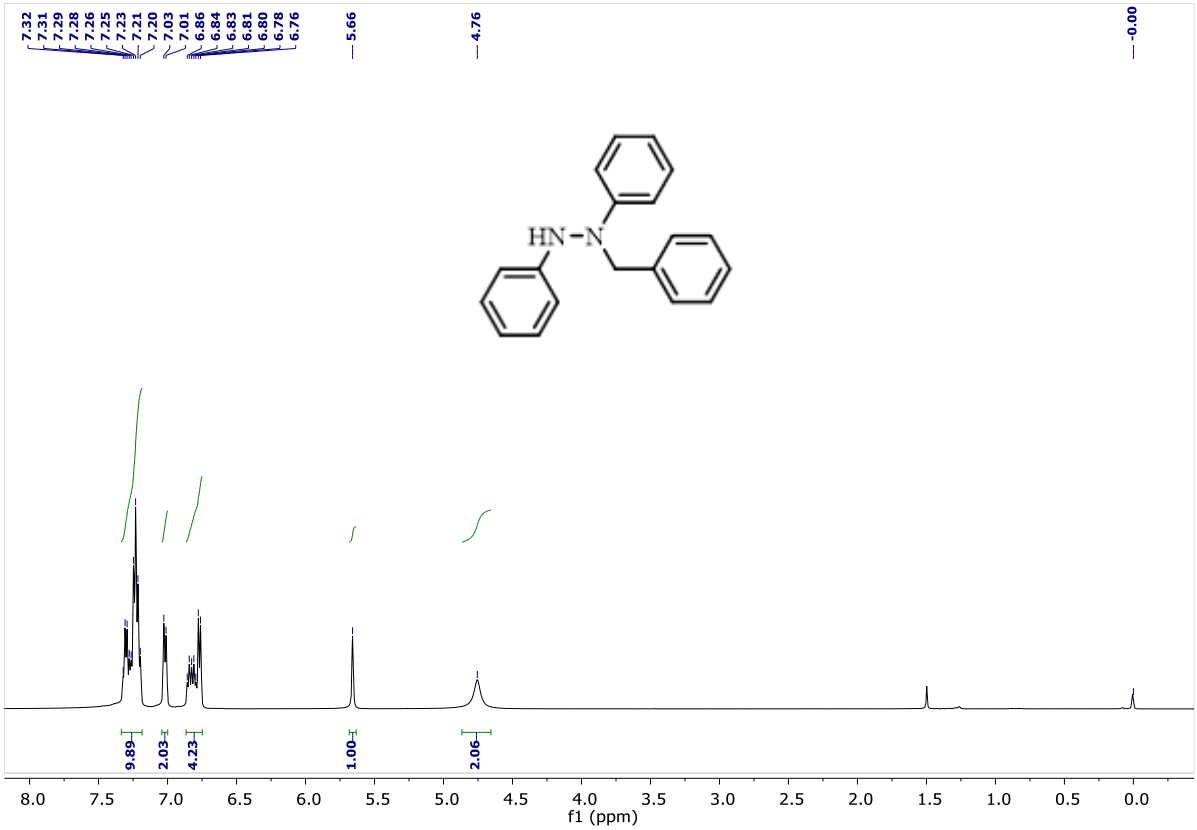


Figure S22: ^{1}H NMR Spectrum of **3a** ($CDCl_3$, 500 MHz, 298 K)

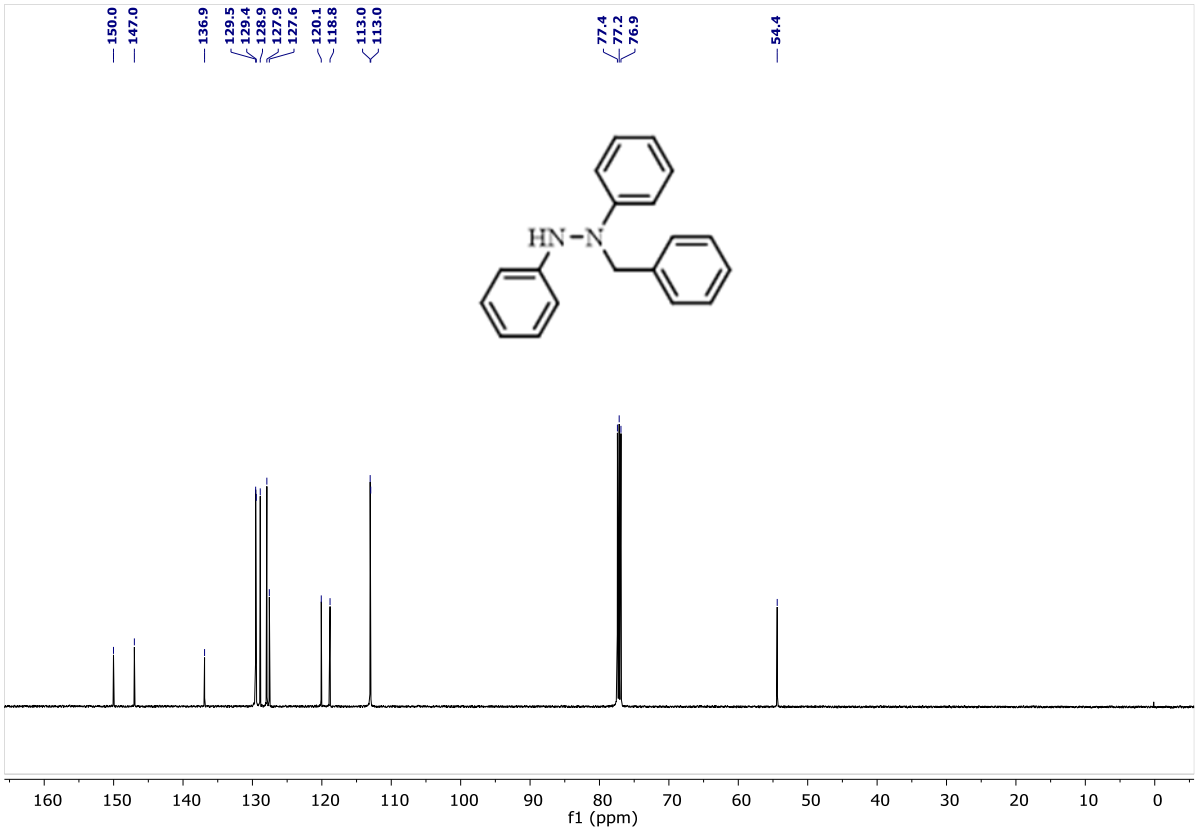


Figure S23: $^{13}C\{^{1}H\}$ NMR Spectrum of **3a** ($CDCl_3$, 126 MHz, 298 K)

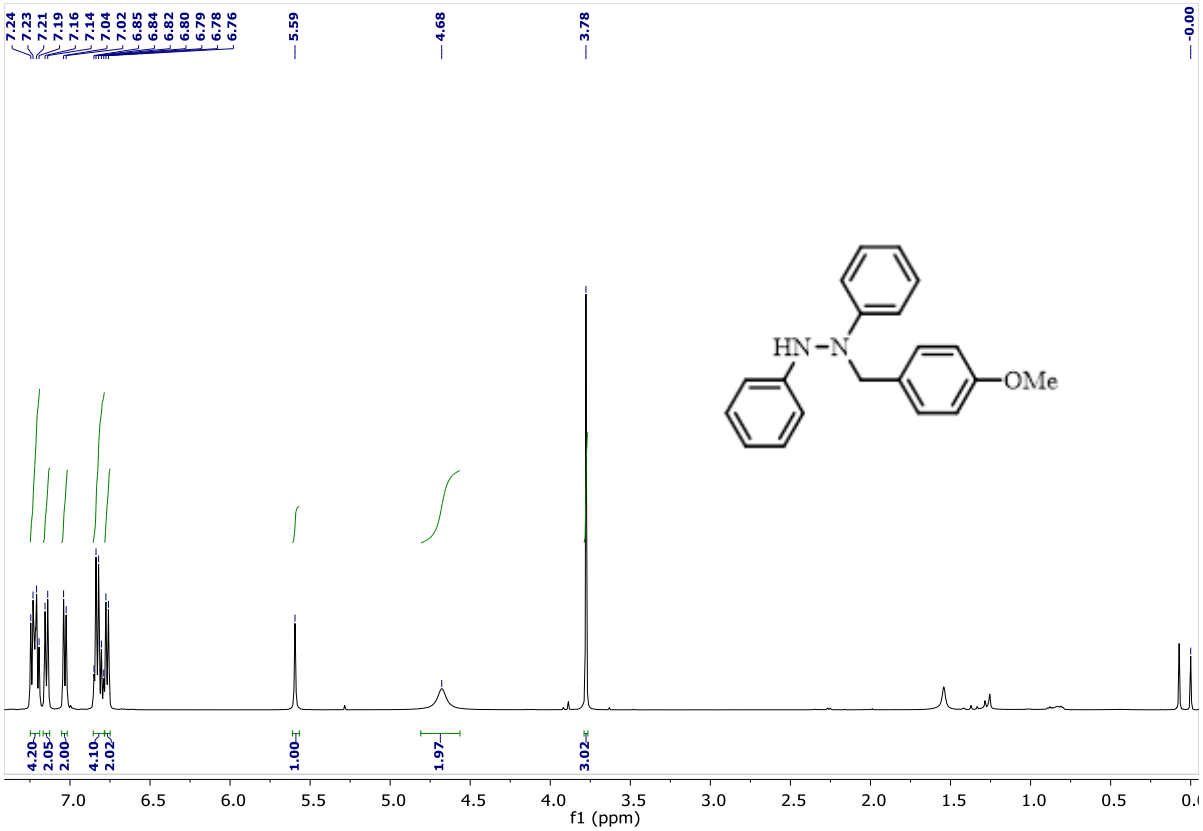


Figure S24: ^{1}H NMR Spectrum of **3b** ($CDCl_3$, 500 MHz, 298 K)

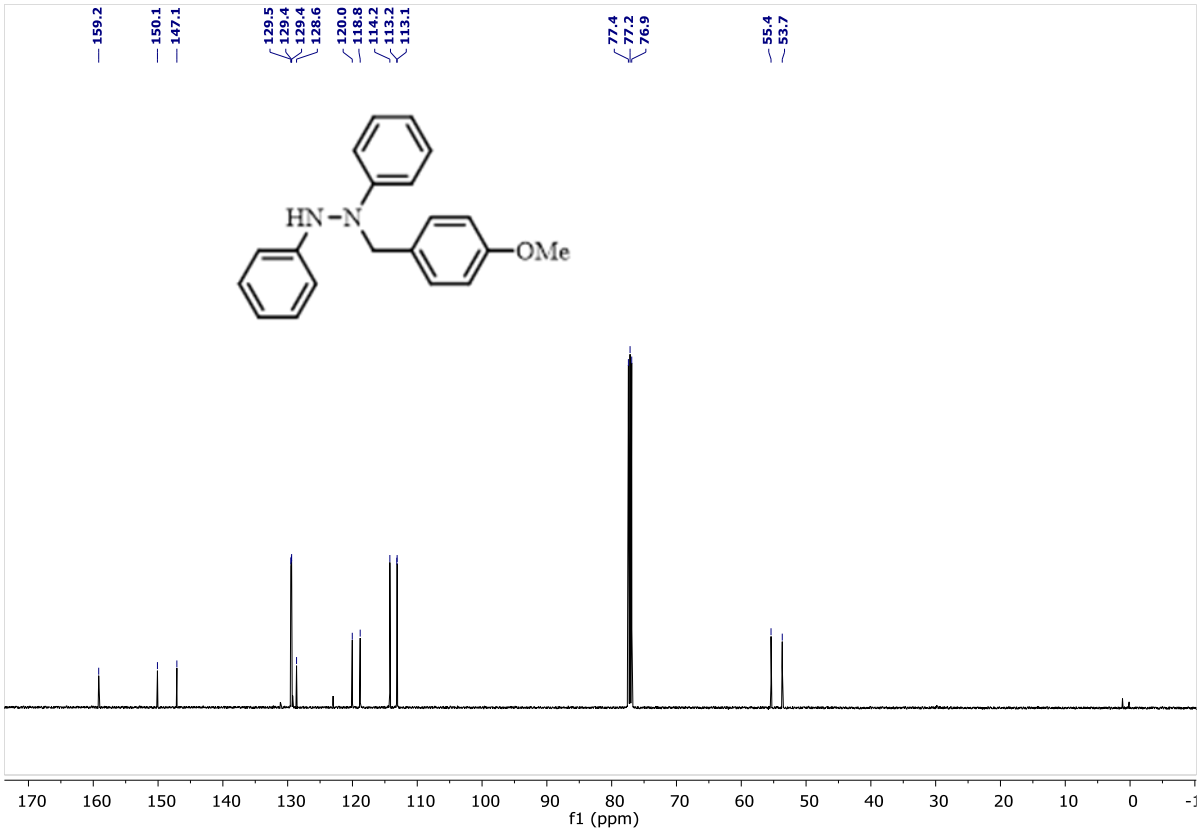


Figure S25: $^{13}C\{^{1}H\}$ NMR Spectrum of **3b** ($CDCl_3$, 126 MHz, 298 K)

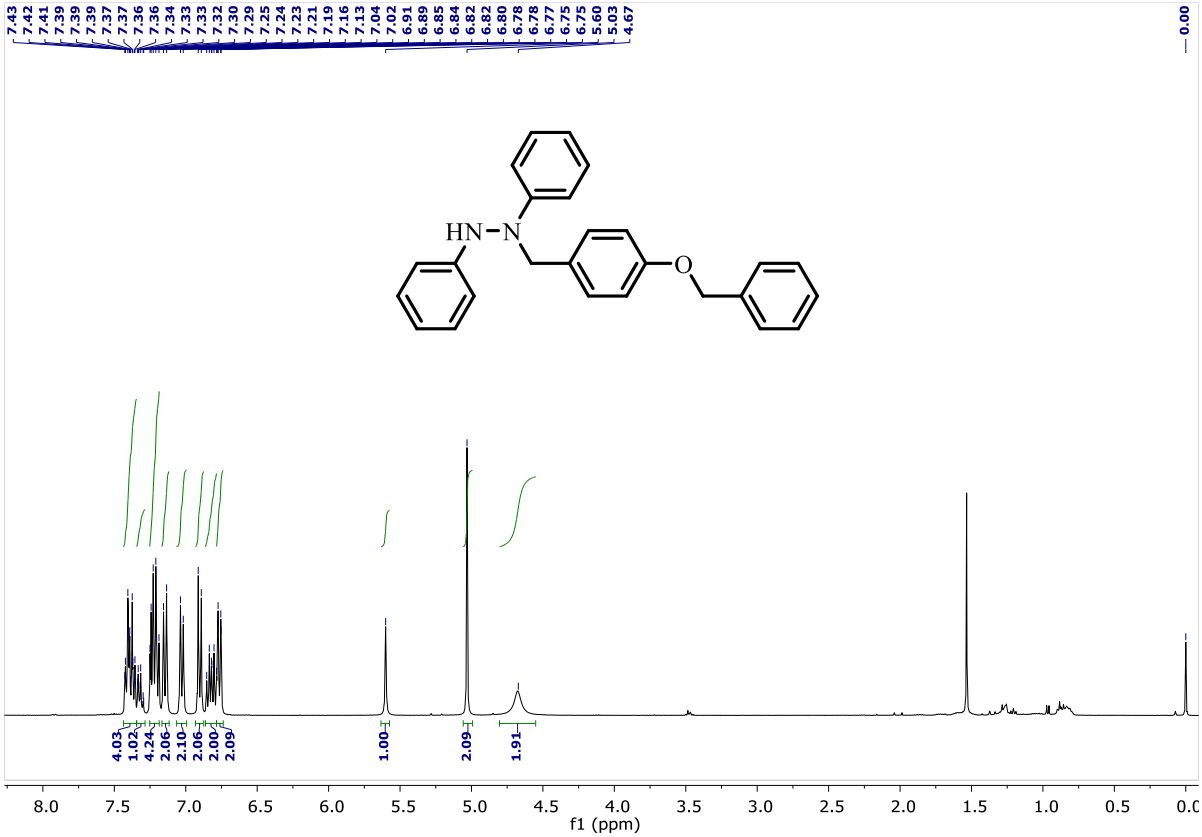


Figure S26: ^{1}H NMR Spectrum of **3c** ($CDCl_3$, 400 MHz, 298 K)

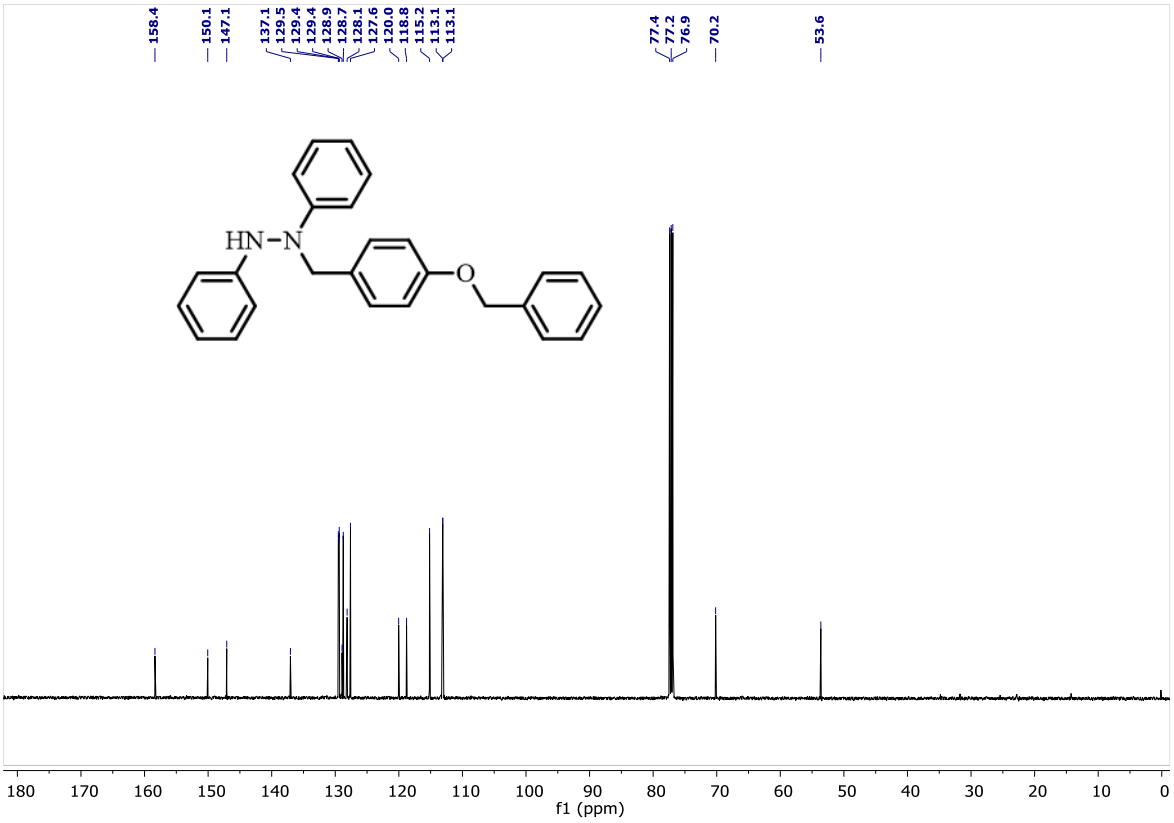


Figure S27: $^{13}C\{^{1}H\}$ NMR Spectrum of **3c** ($CDCl_3$, 126 MHz, 298 K)

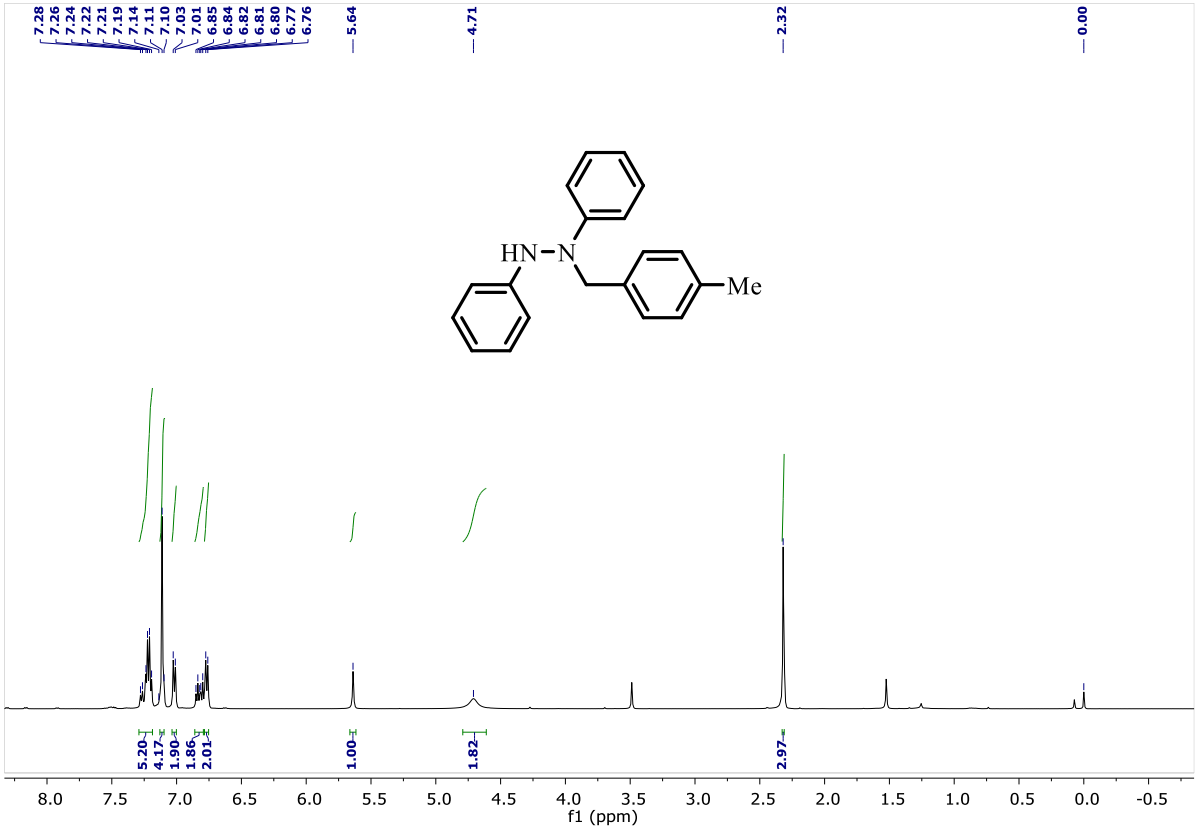


Figure S28: ^{1}H NMR Spectrum of **3d** ($CDCl_3$, 500 MHz, 298 K)

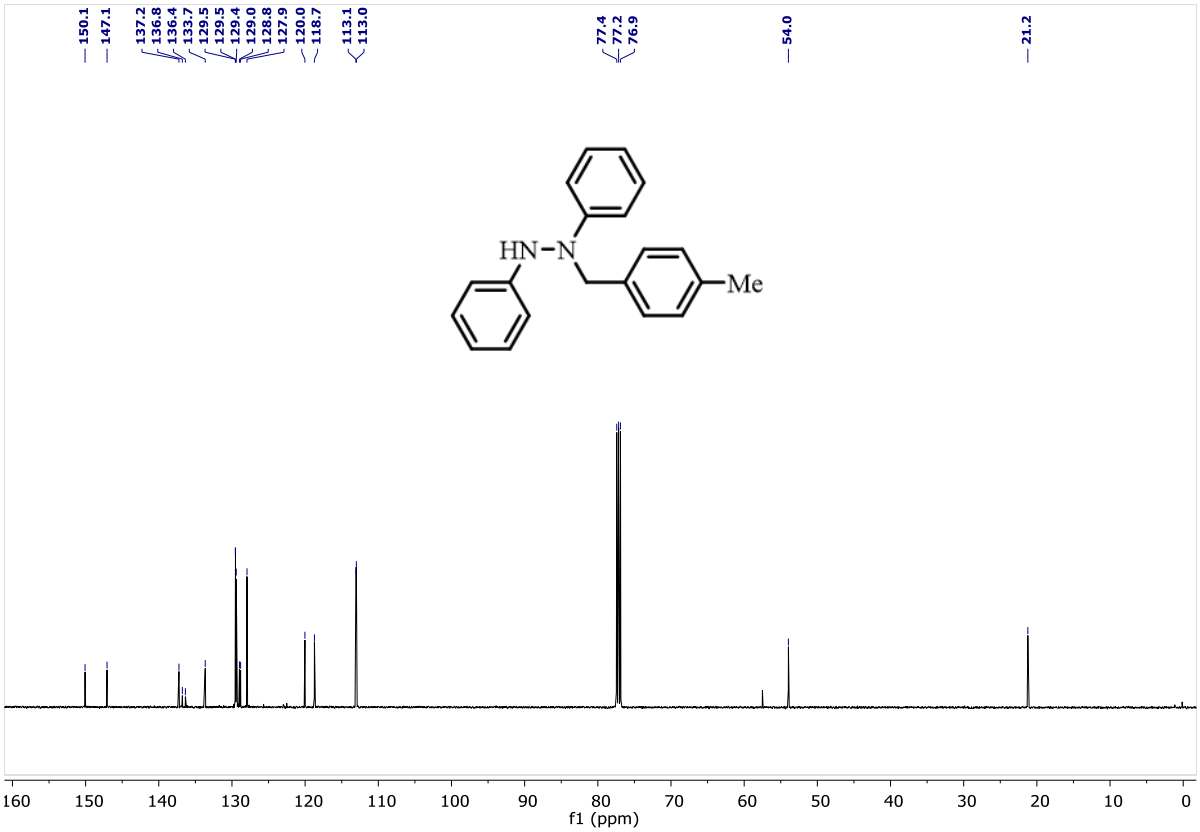


Figure S29: $^{13}C\{^{1}H\}$ NMR Spectrum of **3d** ($CDCl_3$, 126 MHz, 298 K)

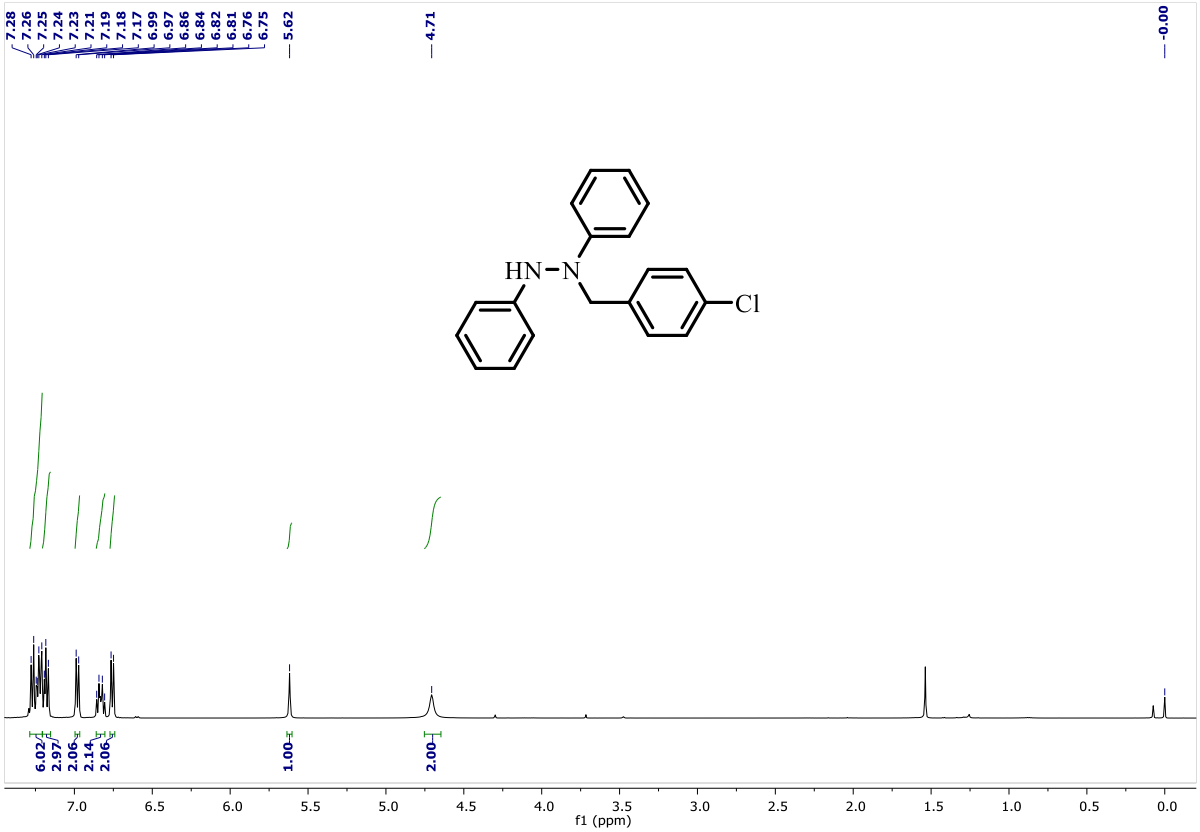


Figure S30: ^{1}H NMR Spectrum of **3e** ($CDCl_3$, 500 MHz, 298 K)

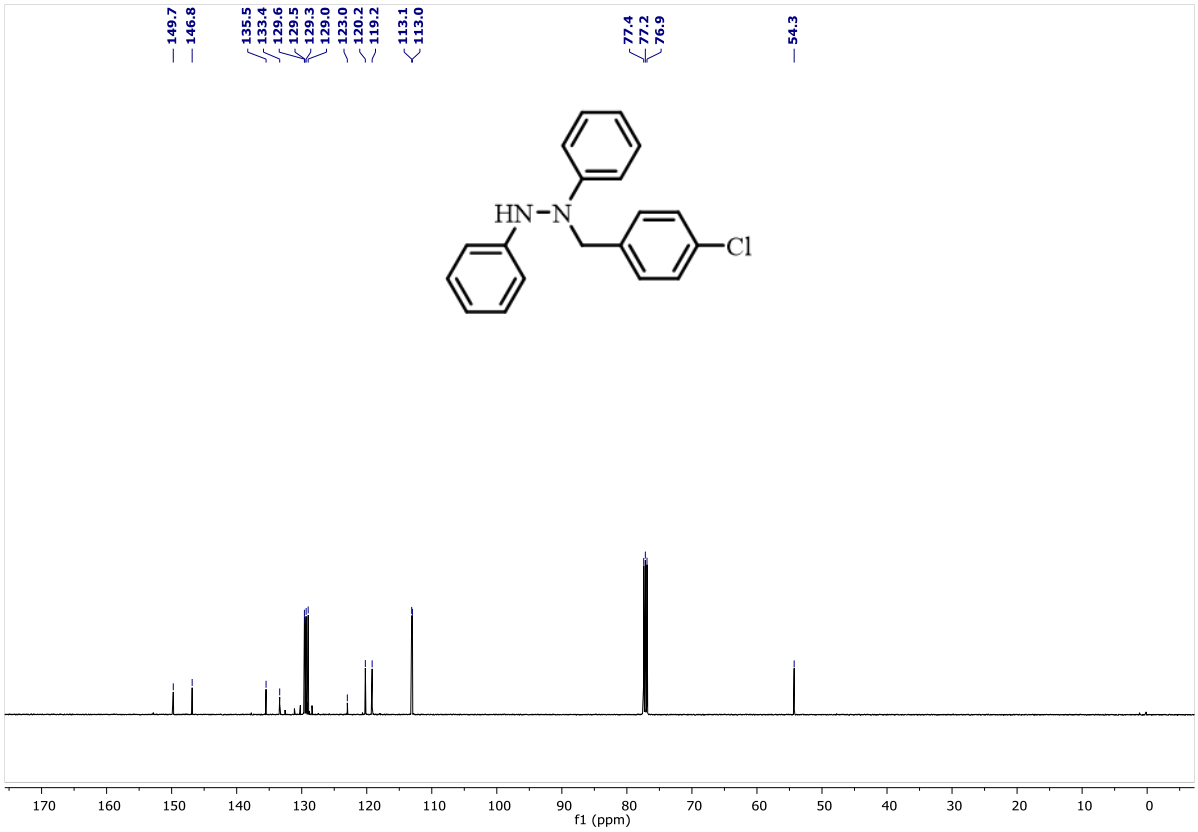


Figure S31: $^{13}C\{^{1}H\}$ NMR Spectrum of **3e** ($CDCl_3$, 126 MHz, 298 K)

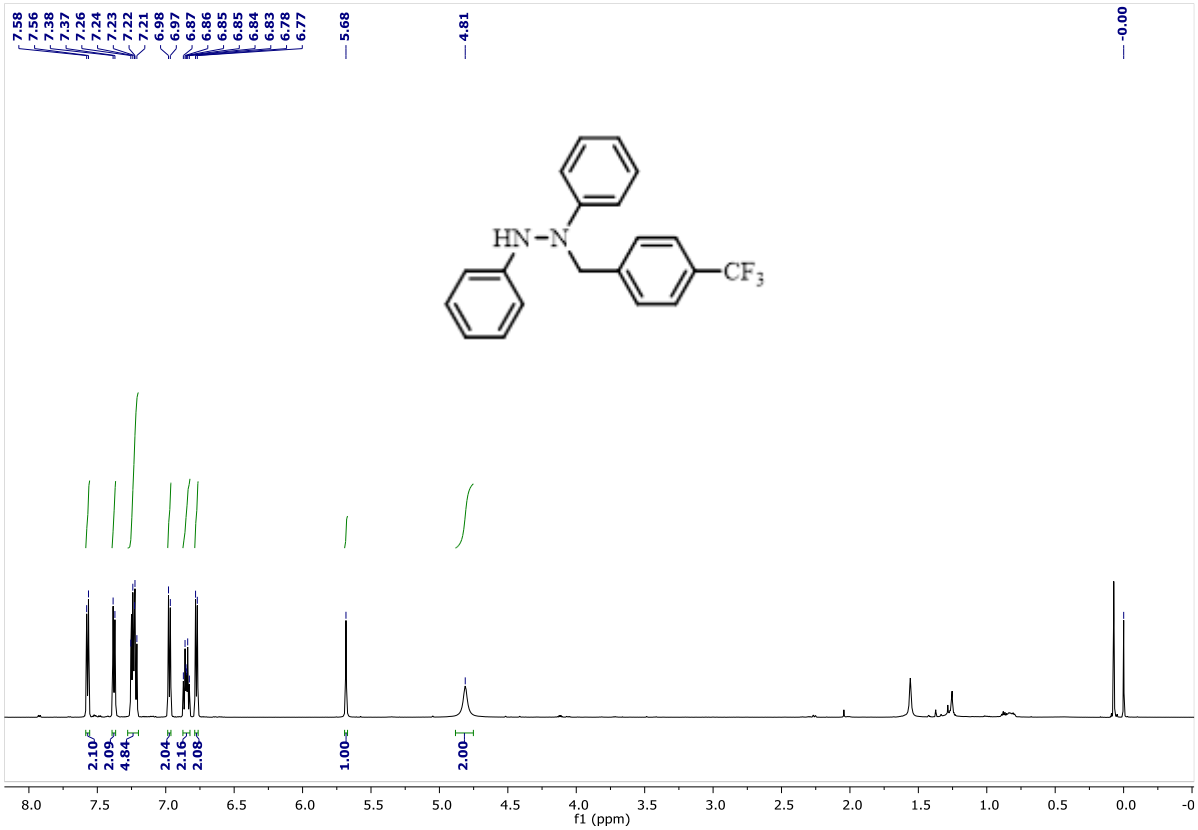


Figure S32: ^{1}H NMR Spectrum of **3f** ($CDCl_3$, 600 MHz, 298 K)

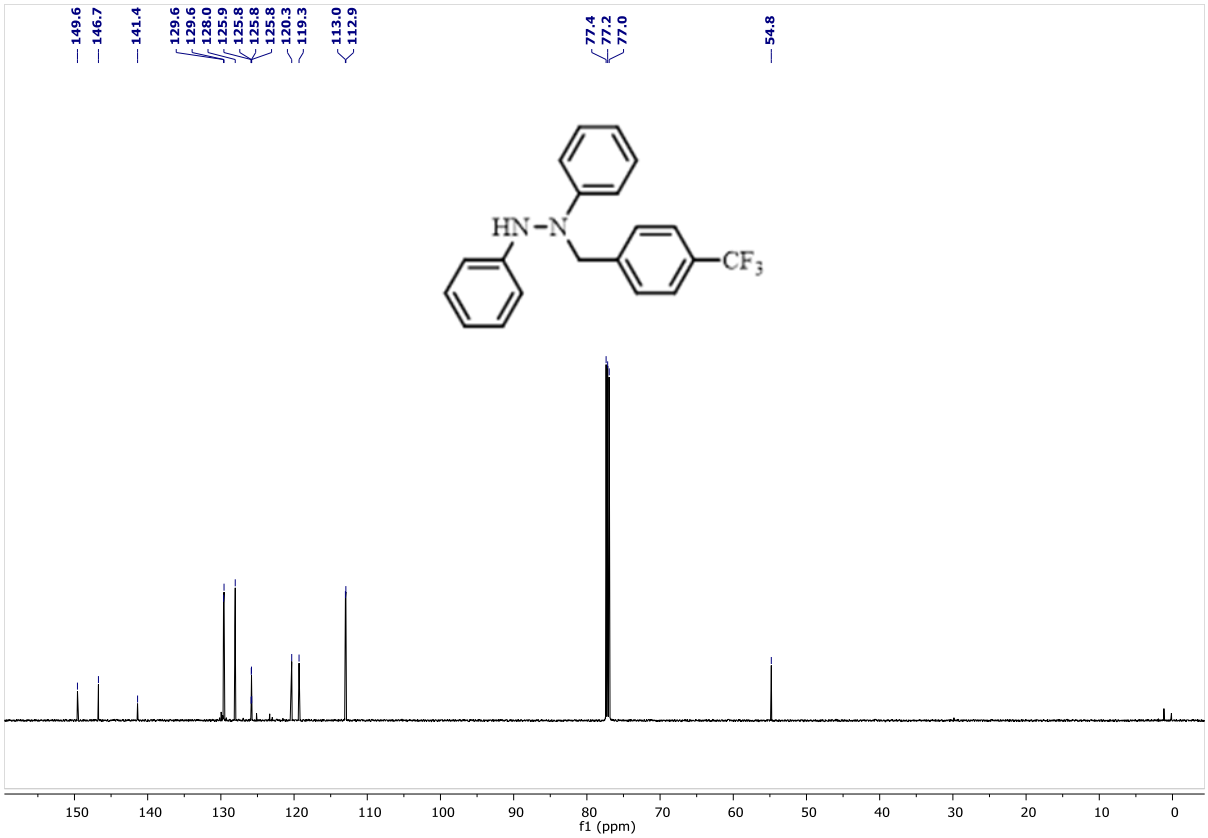


Figure S33: $^{13}C\{^{1}H\}$ NMR Spectrum of **3f** ($CDCl_3$, 151 MHz, 298 K)

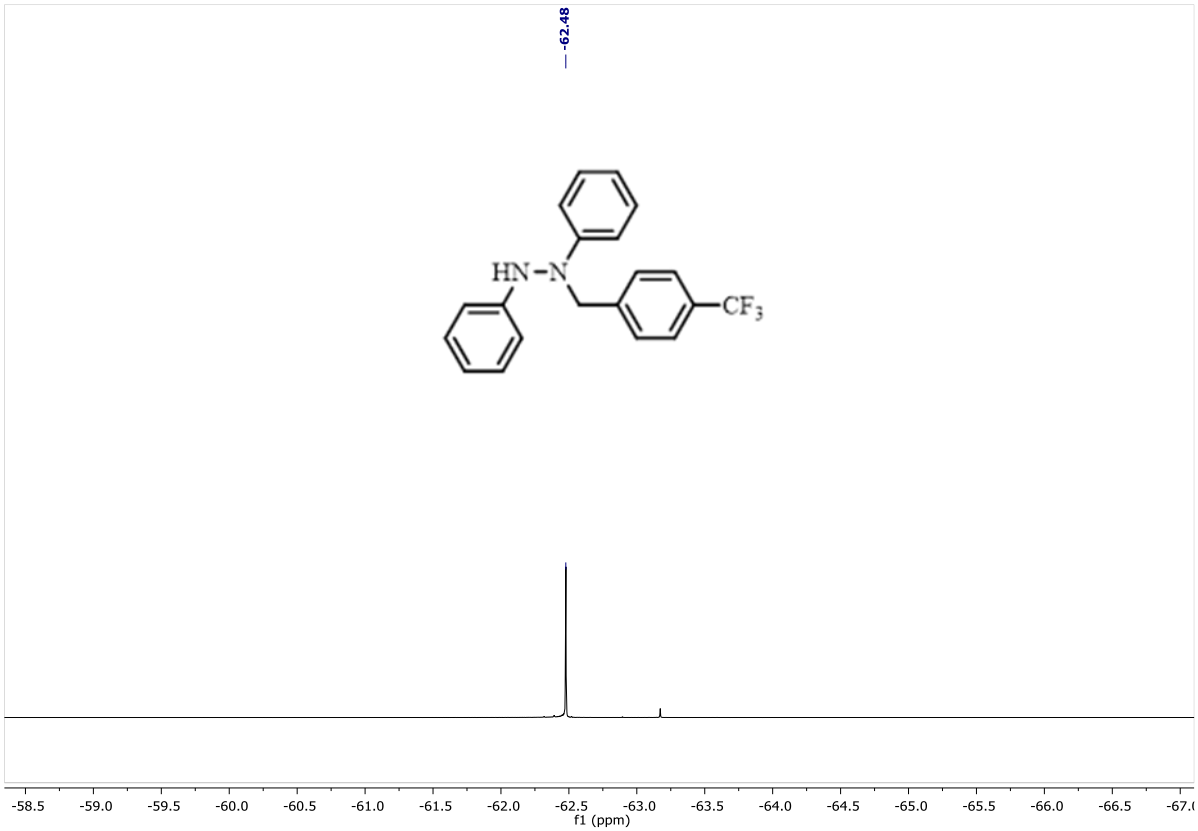


Figure S34: $^{19}F\{^{1}H\}$ NMR Spectrum of **3f** ($CDCl_3$, 471 MHz, 298 K)

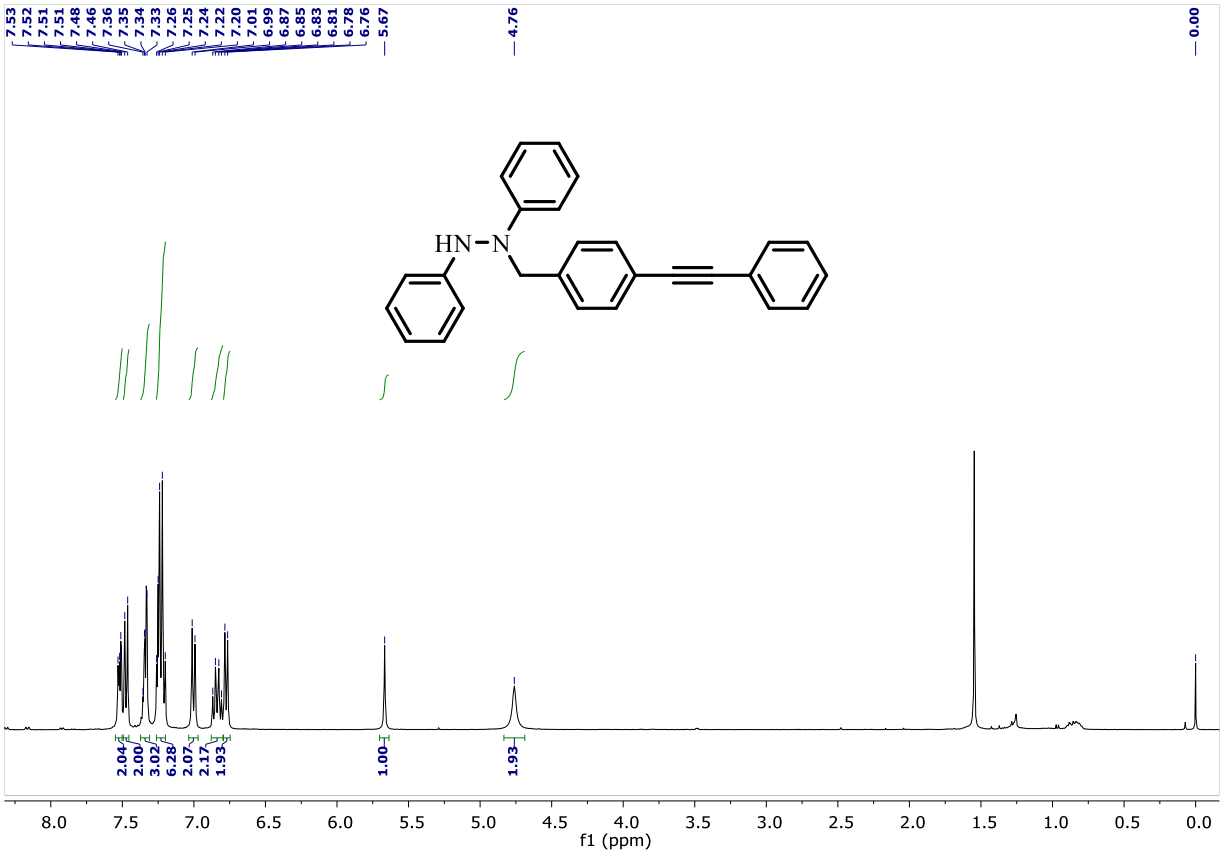


Figure S35: ^{1}H NMR Spectrum of **3g** ($CDCl_3$, 400 MHz, 298 K)

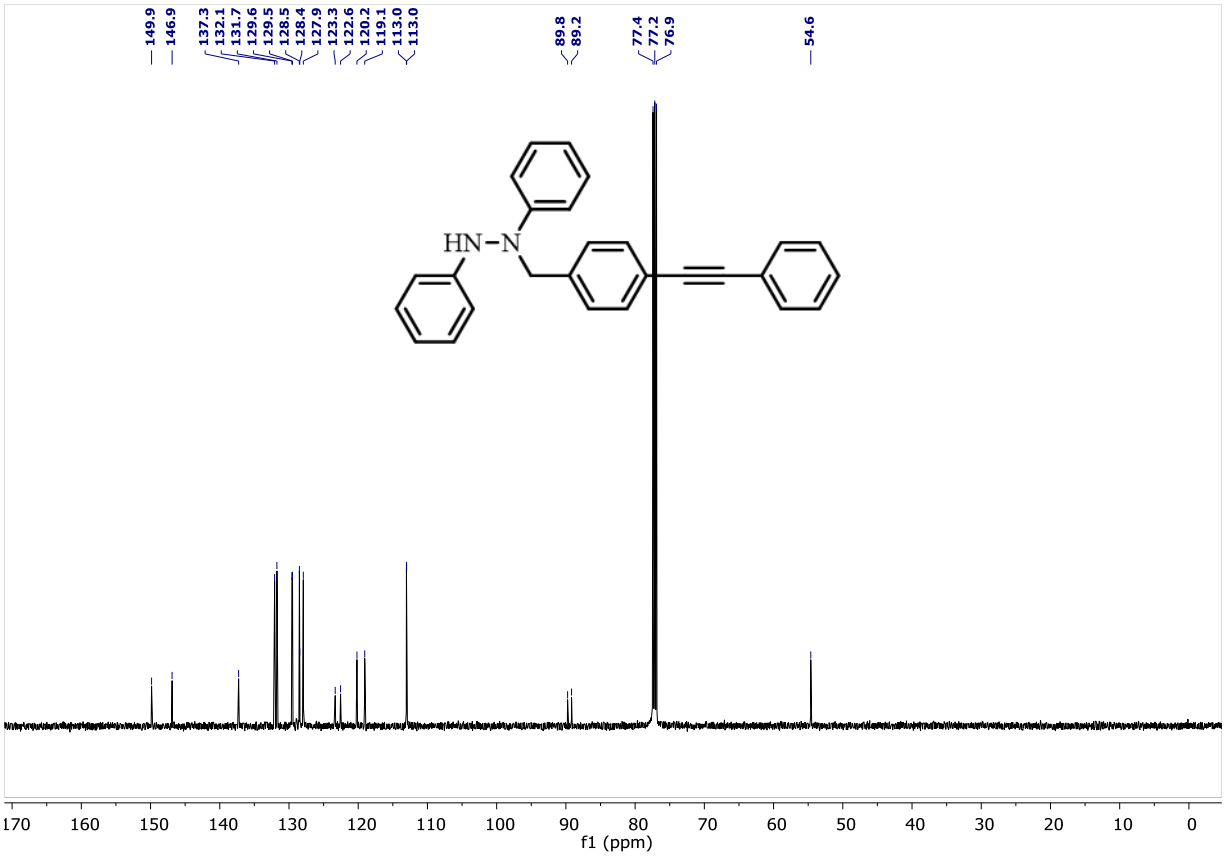


Figure S36: $^{13}C\{^{1}H\}$ NMR Spectrum of **3g** ($CDCl_3$, 126 MHz, 298 K)

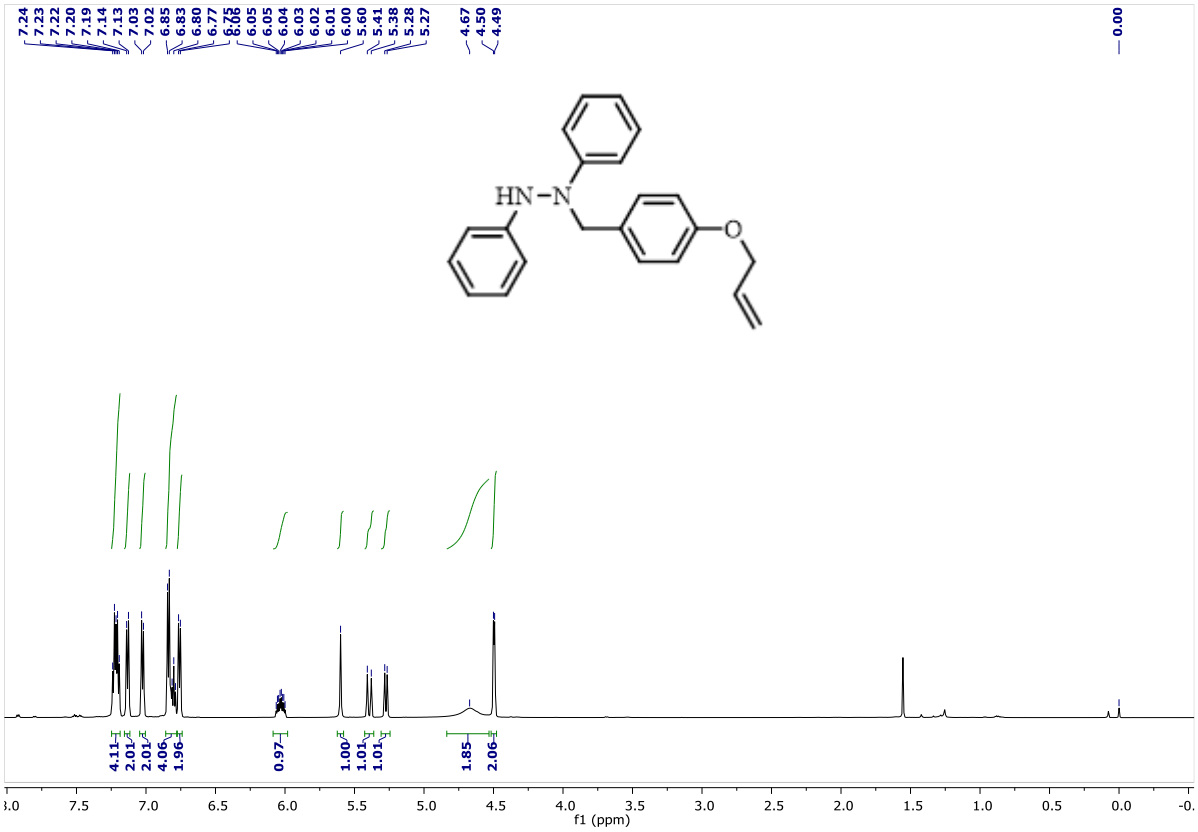


Figure S37: ^{1}H NMR Spectrum of **3h** ($CDCl_3$, 600 MHz, 298 K)

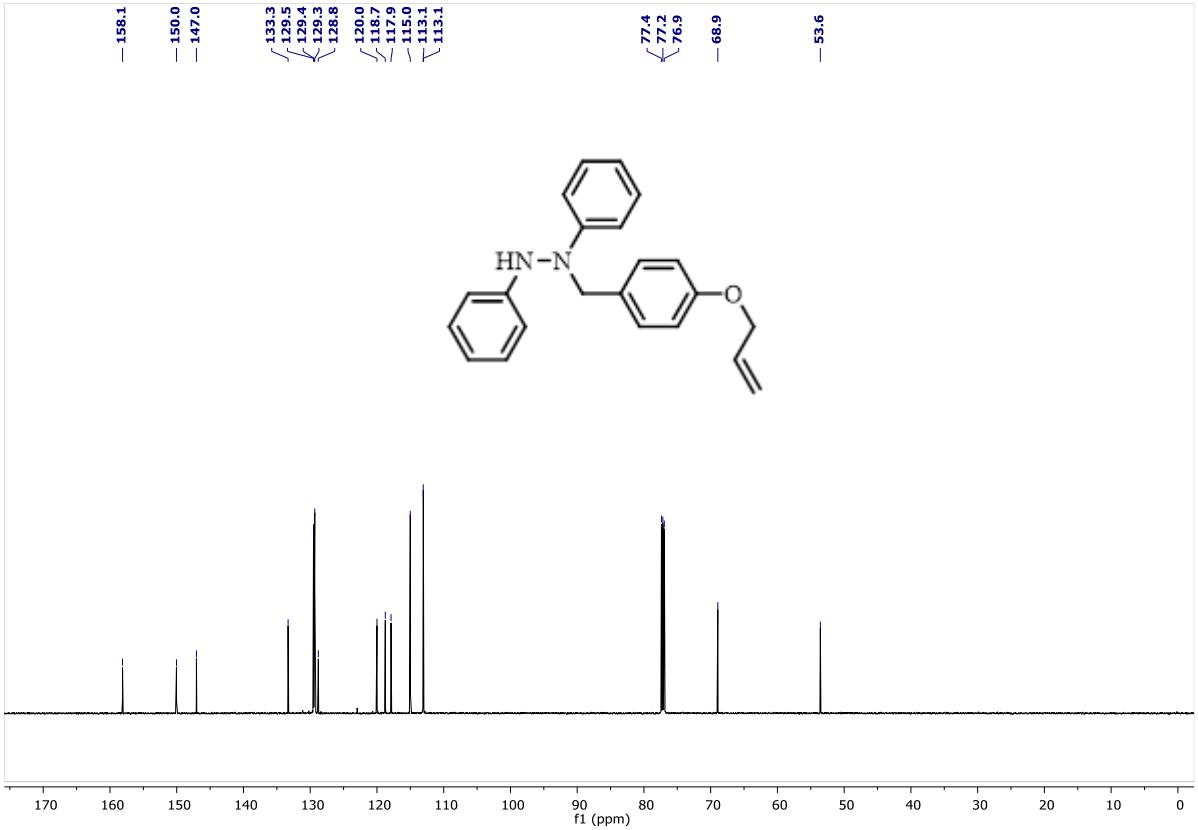


Figure S38: $^{13}C\{^{1}H\}$ NMR Spectrum of **3h** ($CDCl_3$, 151 MHz, 298 K)

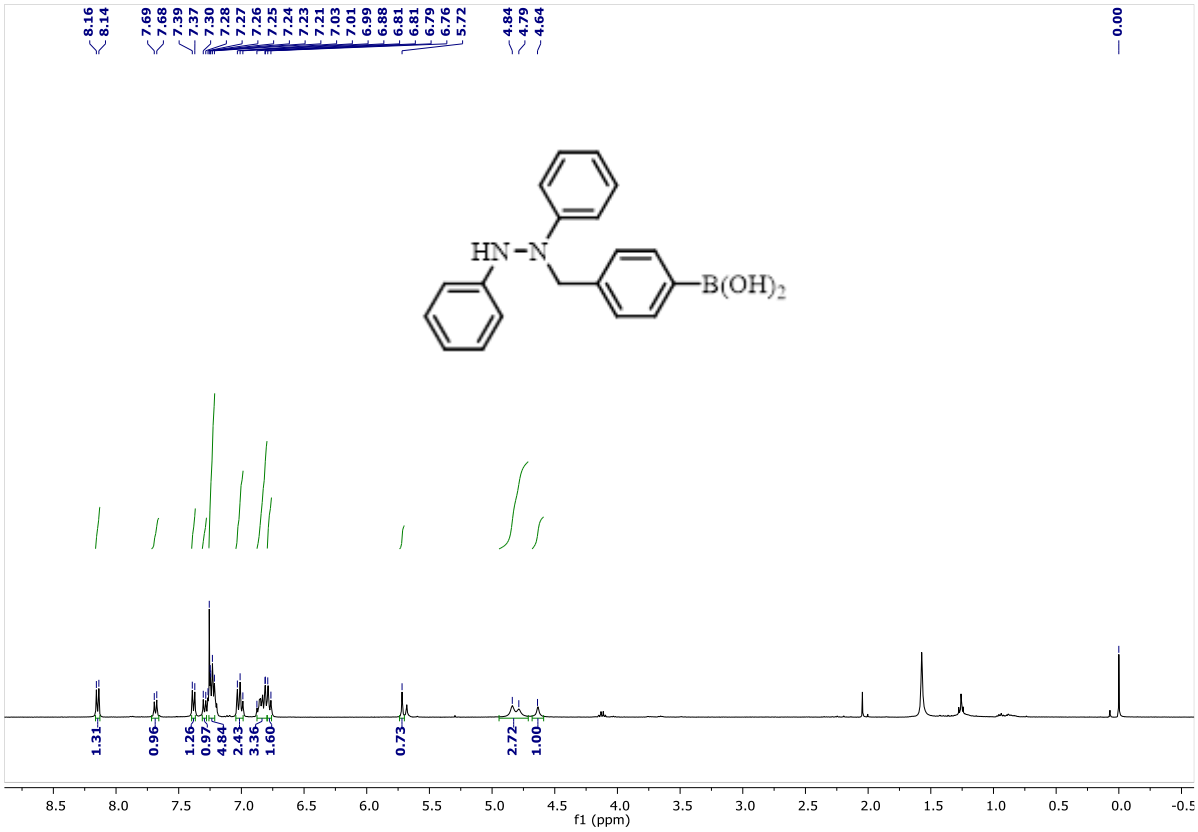


Figure S39: ^{1}H NMR Spectrum of **3i** ($CDCl_3$, 400 MHz, 298 K)

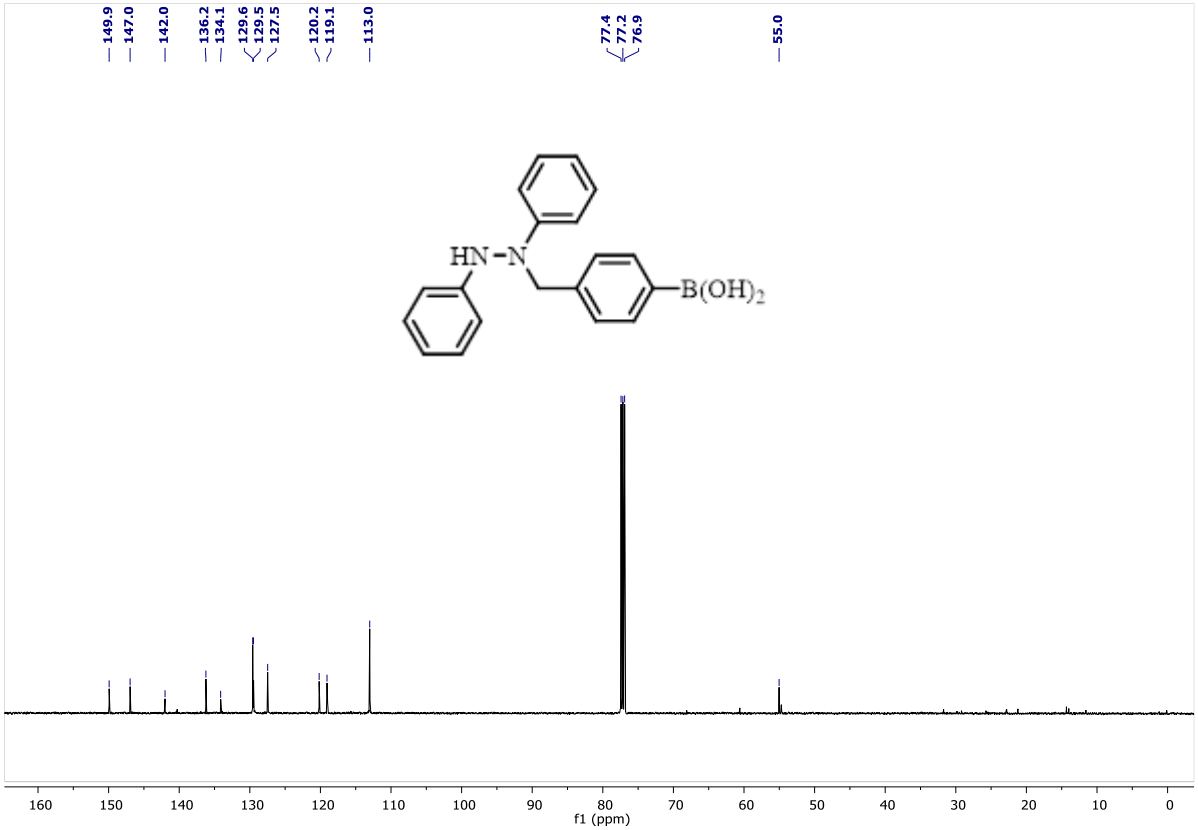


Figure S40: $^{13}C\{^{1}H\}$ NMR Spectrum of **3i** ($CDCl_3$, 126 MHz, 298 K)

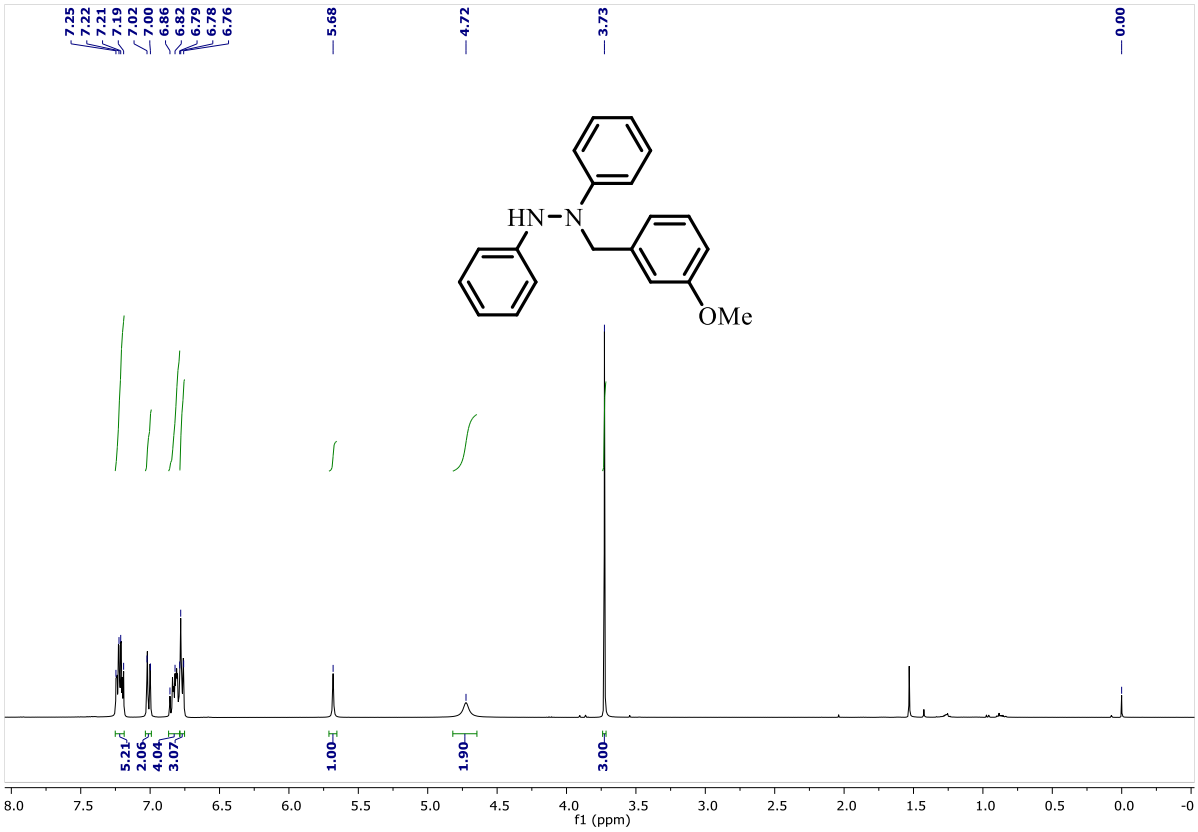


Figure S41: ^{1}H NMR Spectrum of **3j** ($CDCl_3$, 400 MHz, 298 K)

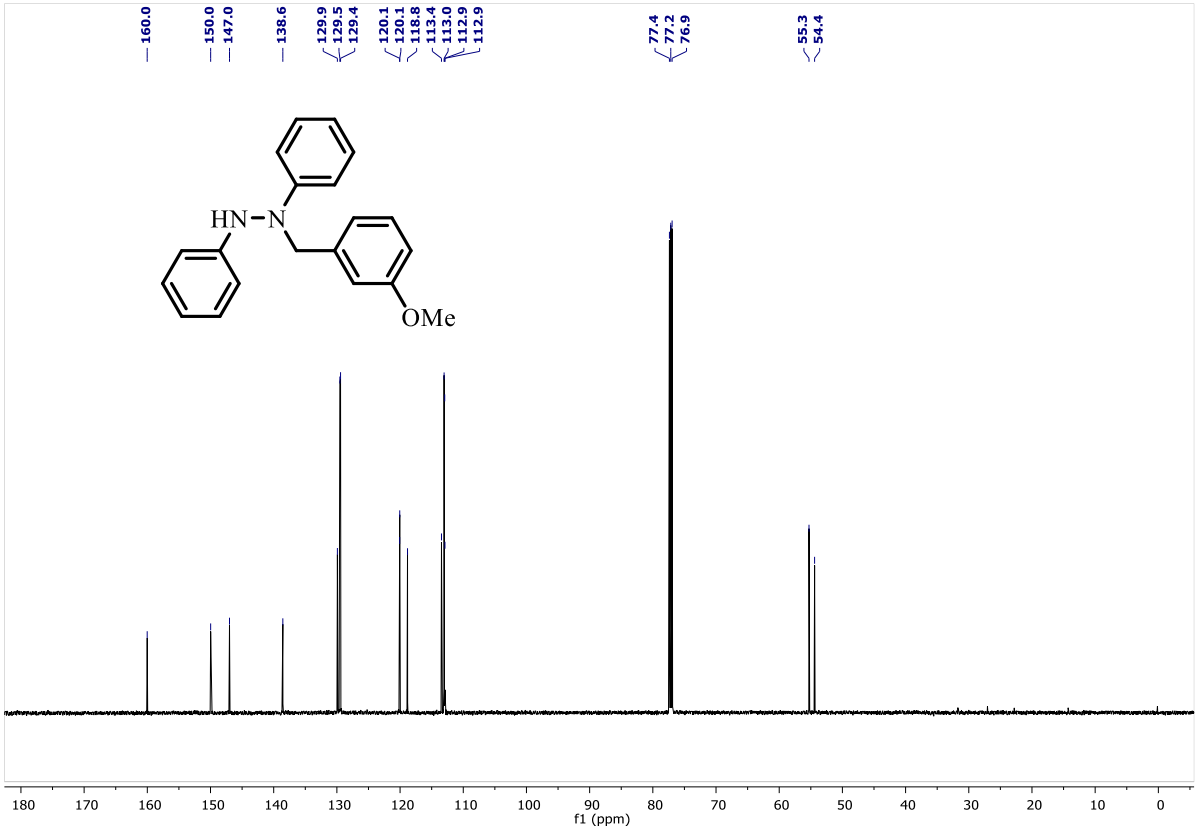


Figure S42: $^{13}C\{^{1}H\}$ NMR Spectrum of **3j** ($CDCl_3$, 151 MHz, 298 K)

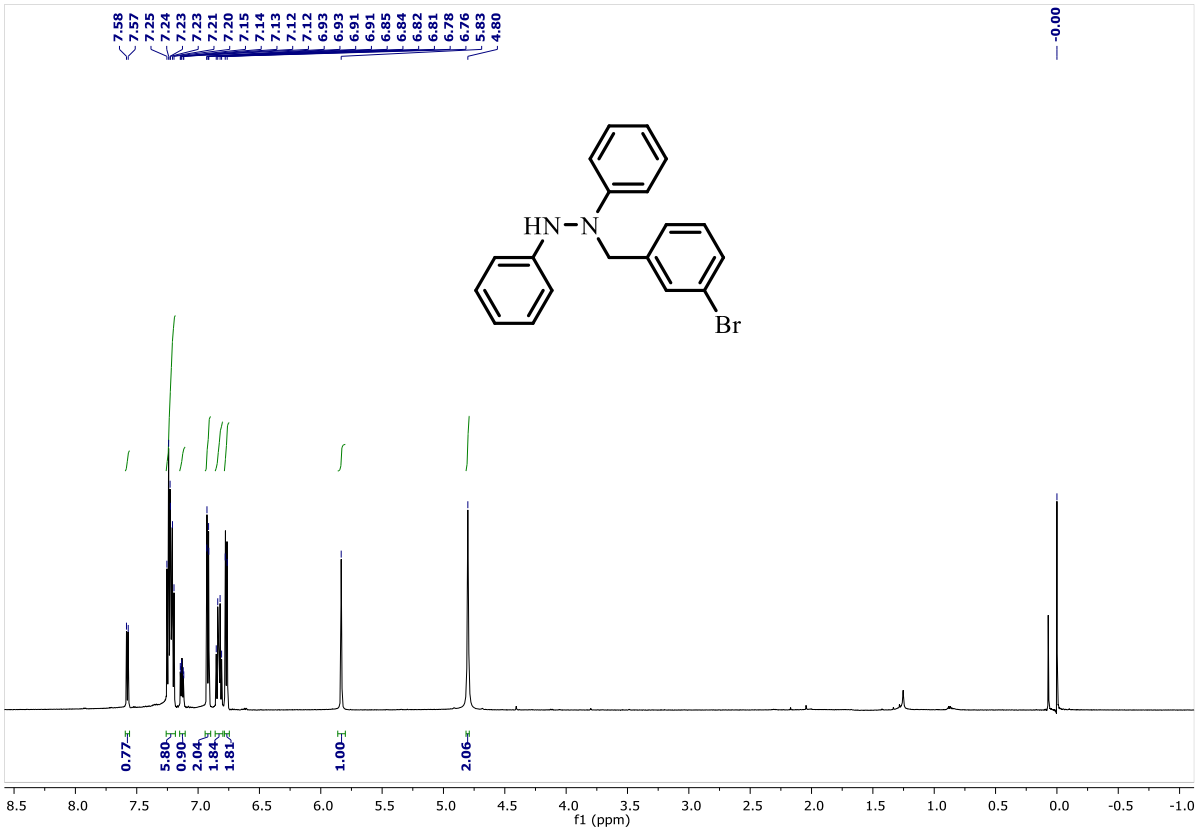


Figure S43: ^{1}H NMR Spectrum of **3k** ($CDCl_3$, 600 MHz, 298 K)

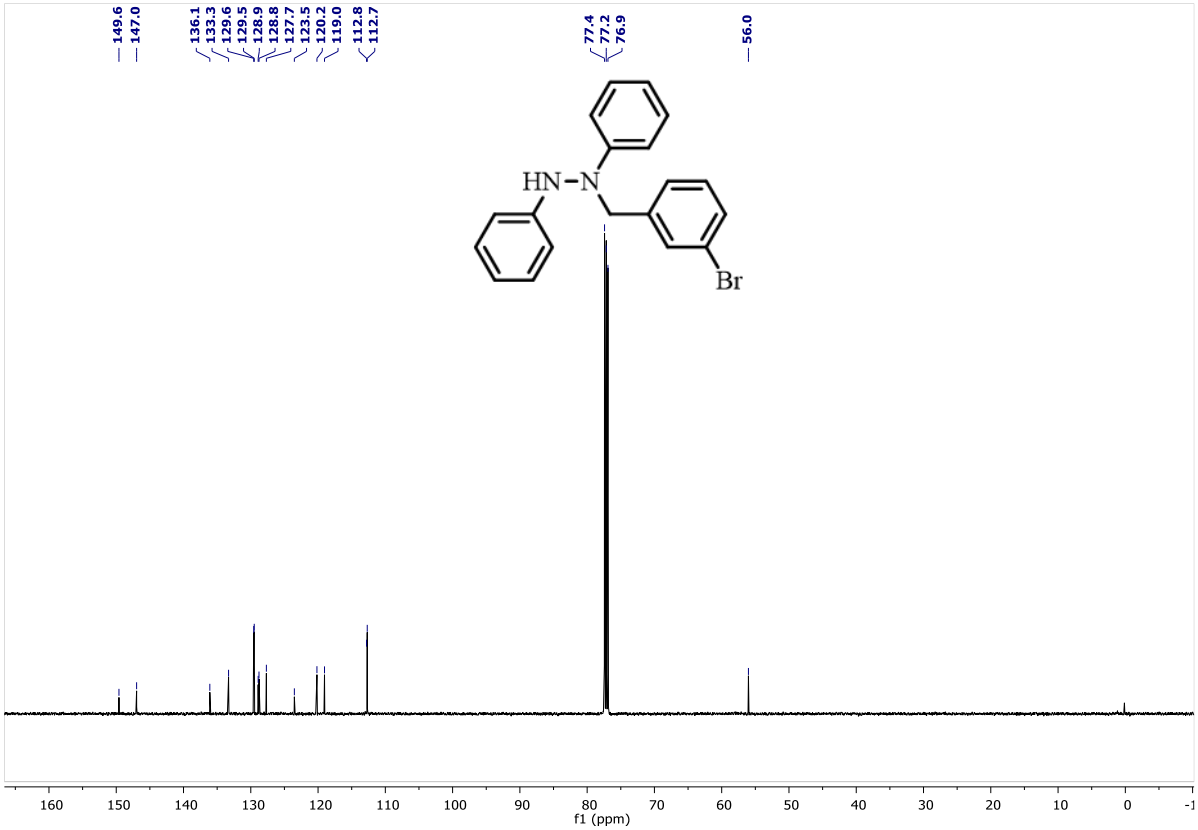


Figure S44: $^{13}C\{^{1}H\}$ NMR Spectrum of **3k** ($CDCl_3$, 126 MHz, 298 K)

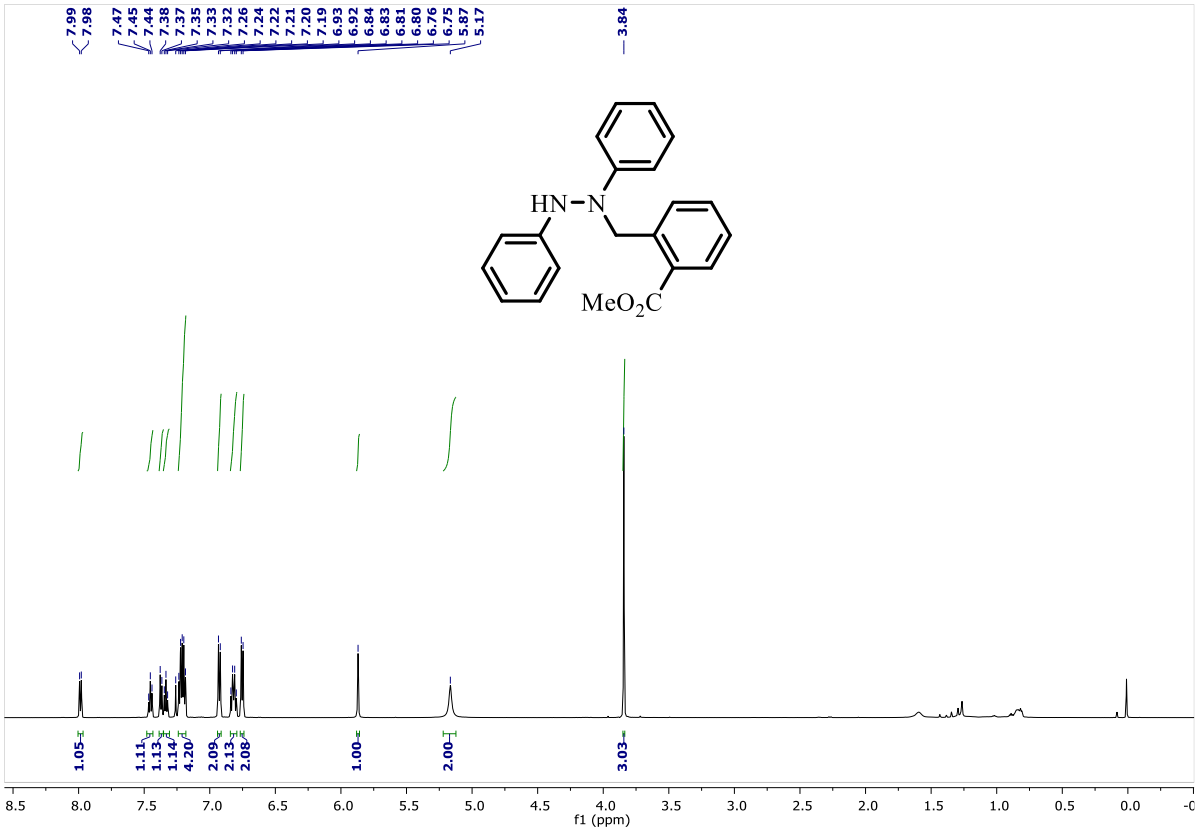


Figure S45: ^{1}H NMR Spectrum of **3l** ($CDCl_3$, 600 MHz, 298 K)

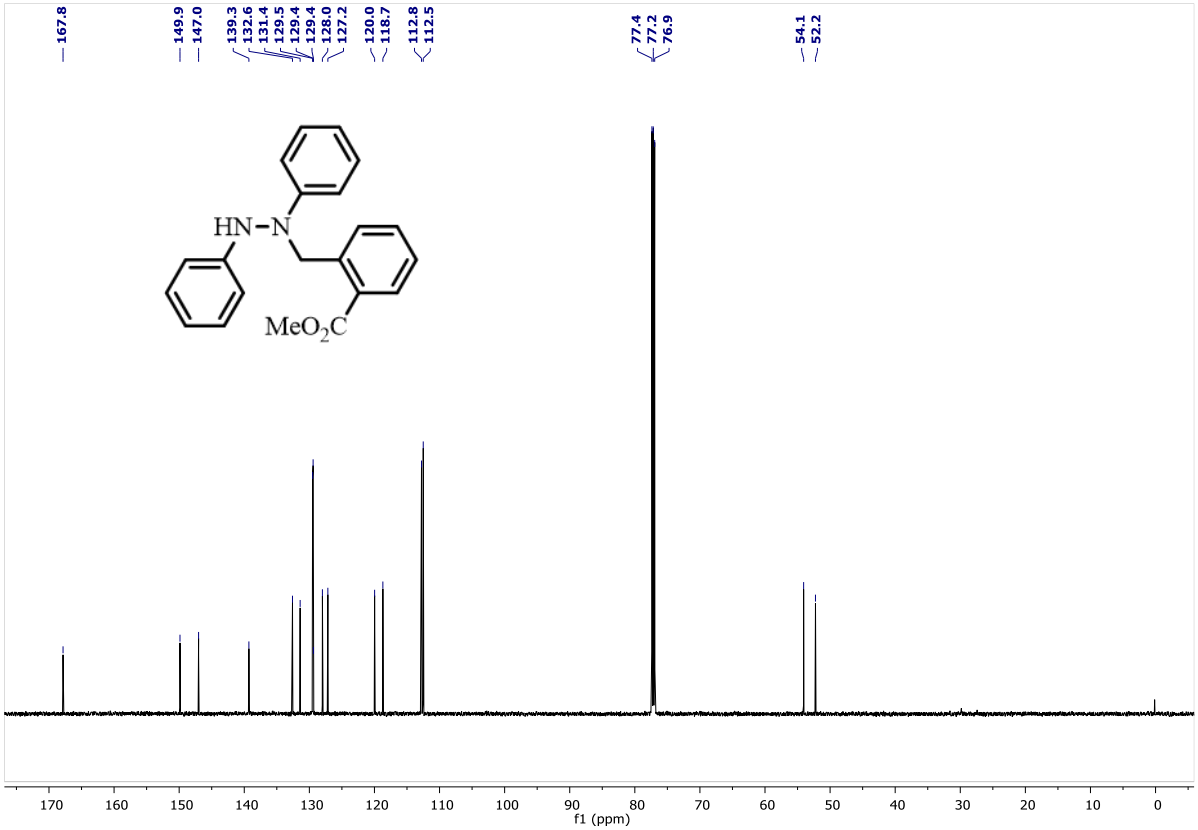


Figure S46: $^{13}C\{^{1}H\}$ NMR Spectrum of **3l** ($CDCl_3$, 151 MHz, 298 K)

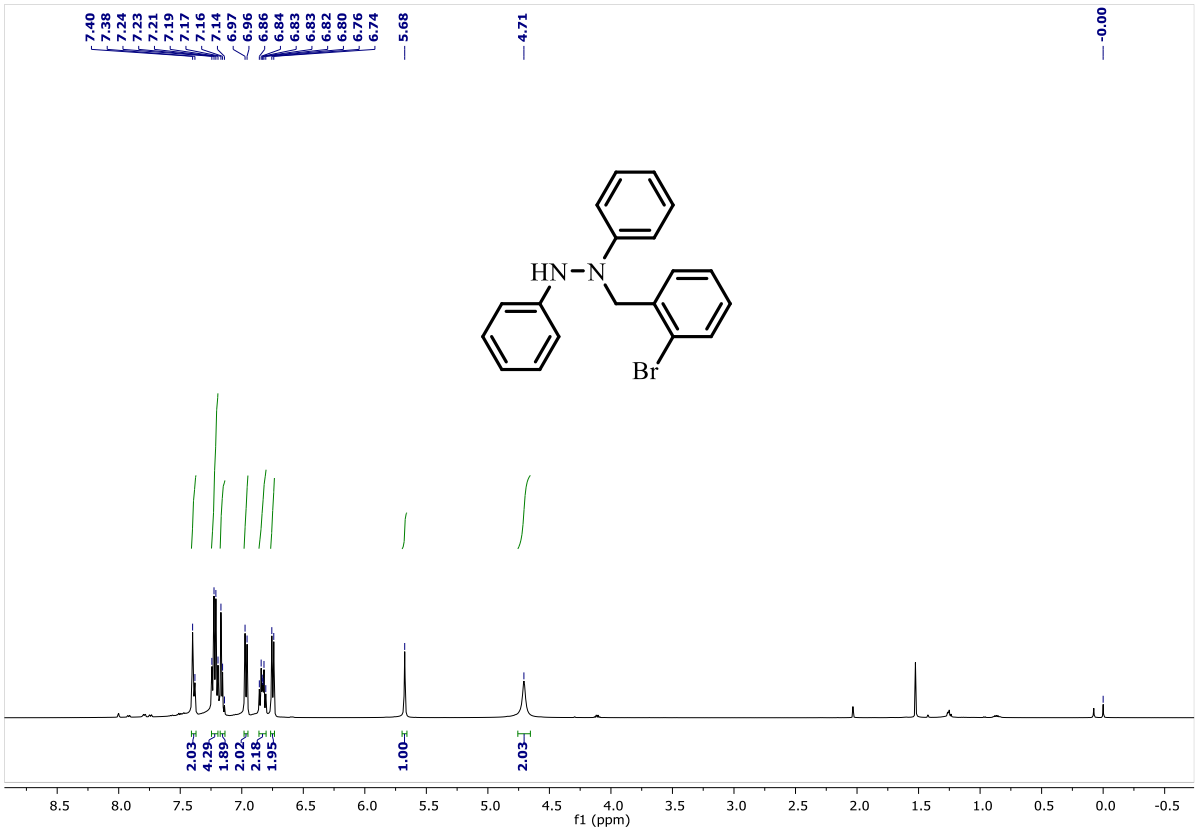


Figure S47: ^{1}H NMR Spectrum of **3m** ($CDCl_3$, 500 MHz, 298 K)

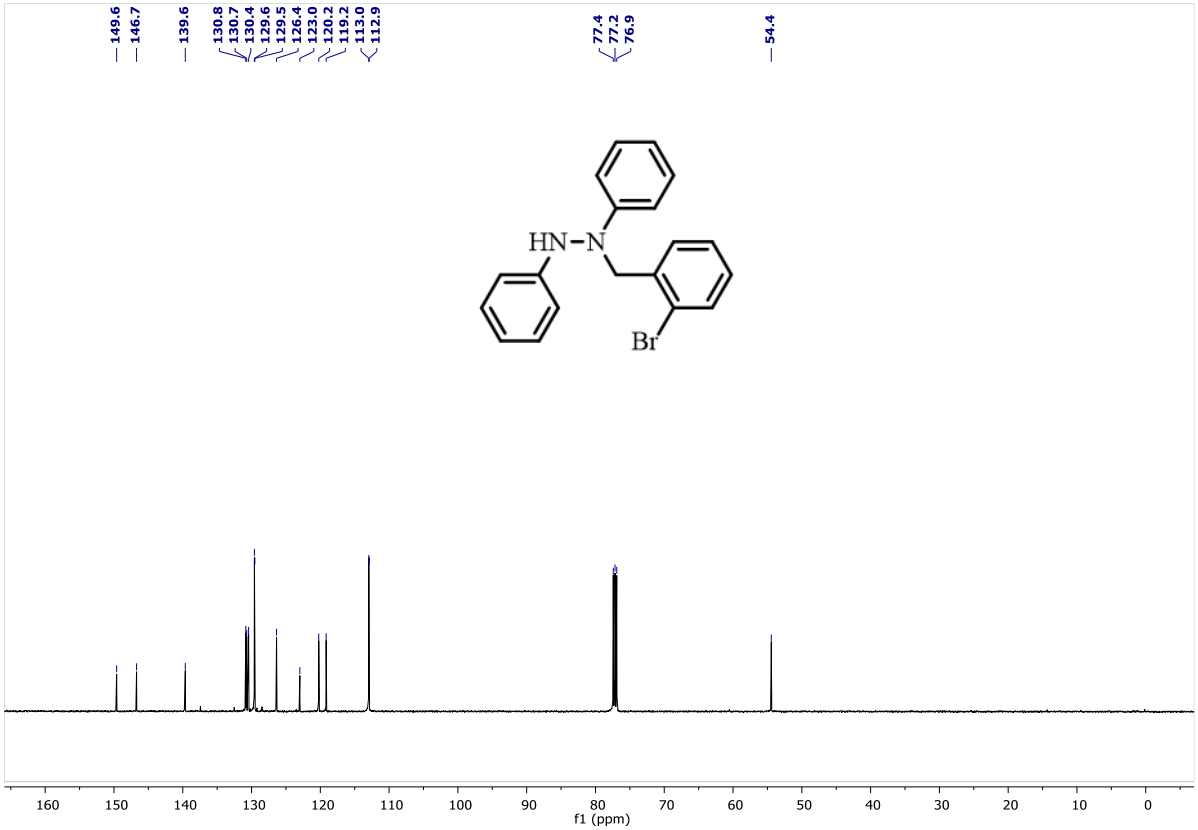


Figure S48: $^{13}C\{^{1}H\}$ NMR Spectrum of **3m** ($CDCl_3$, 126 MHz, 298 K)

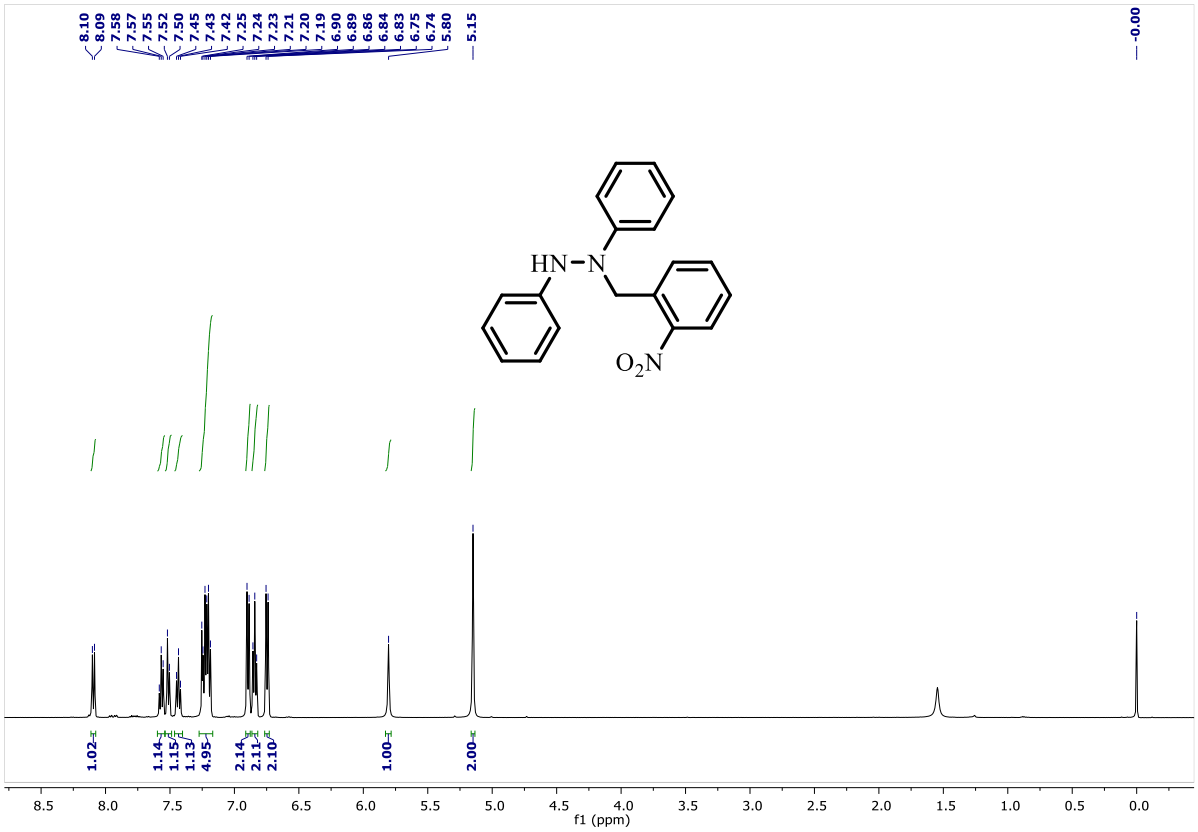


Figure S49: ^{1}H NMR Spectrum of **3n** ($CDCl_3$, 500 MHz, 298 K)

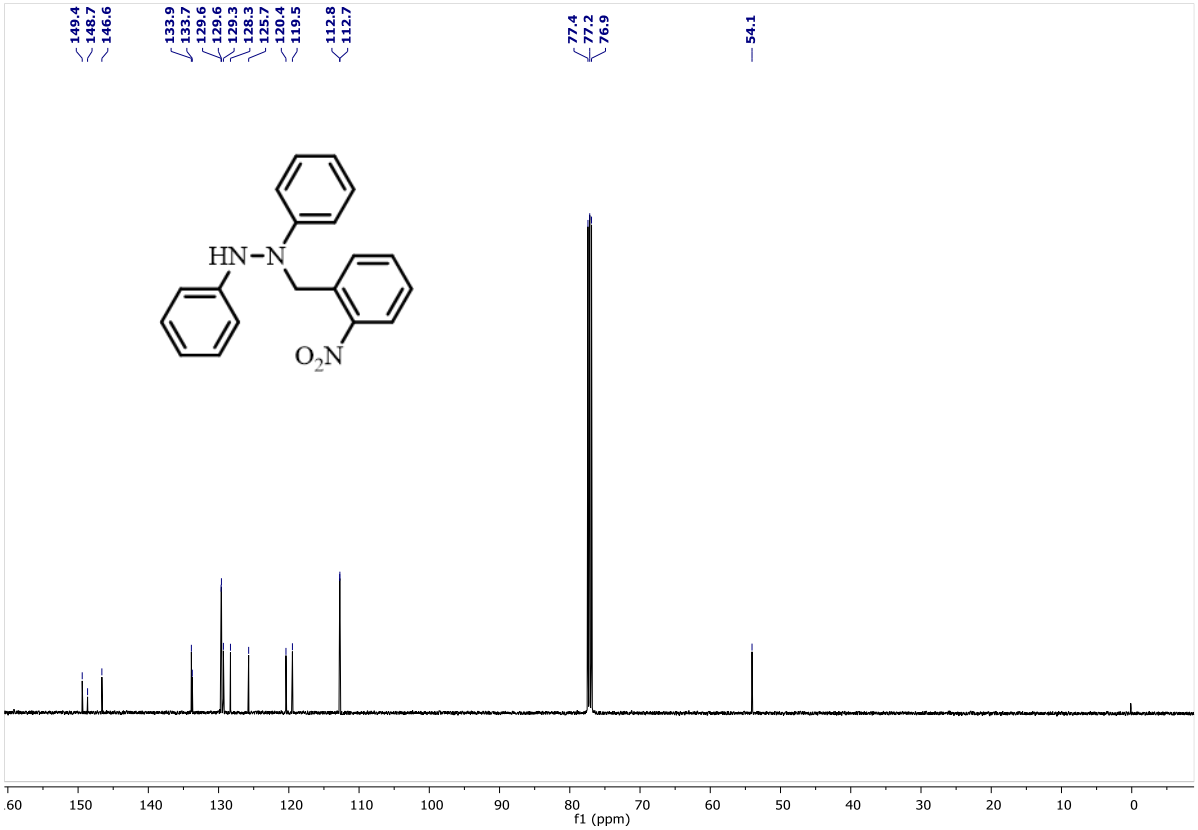


Figure S50: $^{13}C\{^{1}H\}$ NMR Spectrum of **3n** ($CDCl_3$, 126 MHz, 298 K)

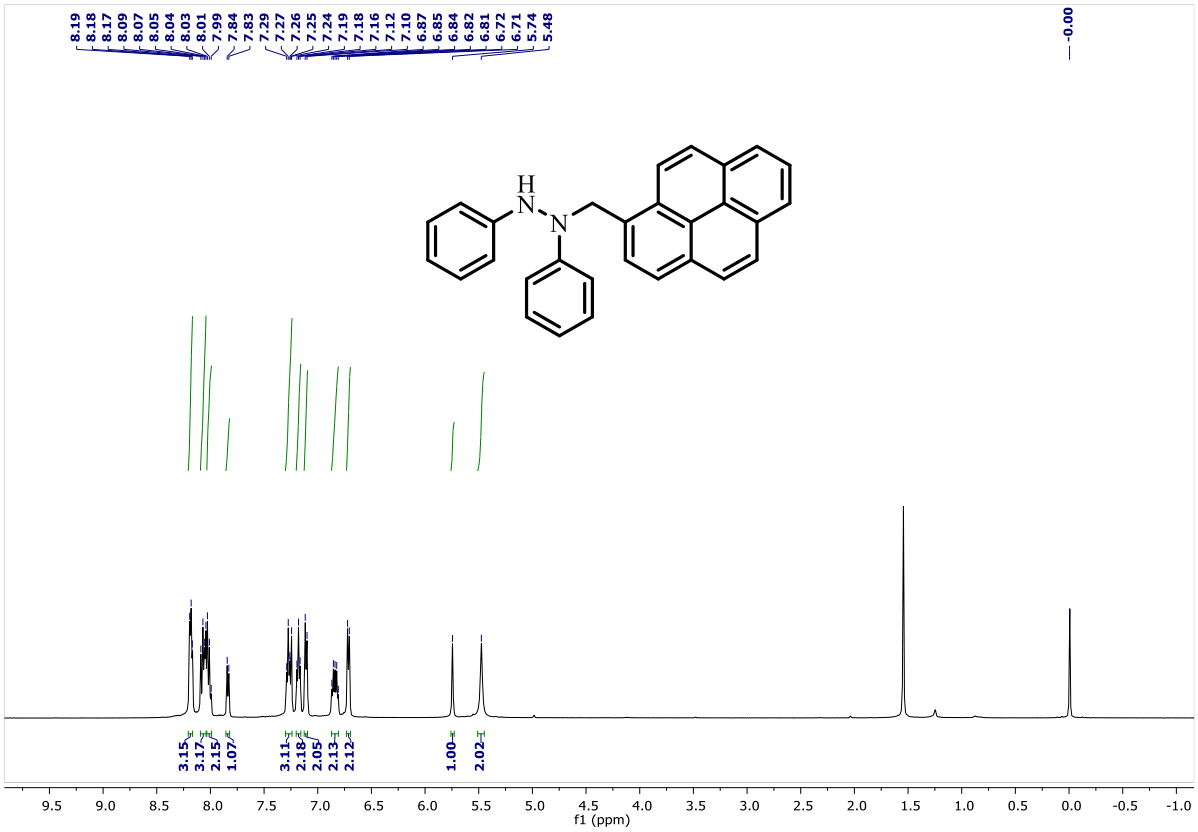


Figure S51: ^{1}H NMR Spectrum of **3o** ($CDCl_3$, 500 MHz, 298 K)

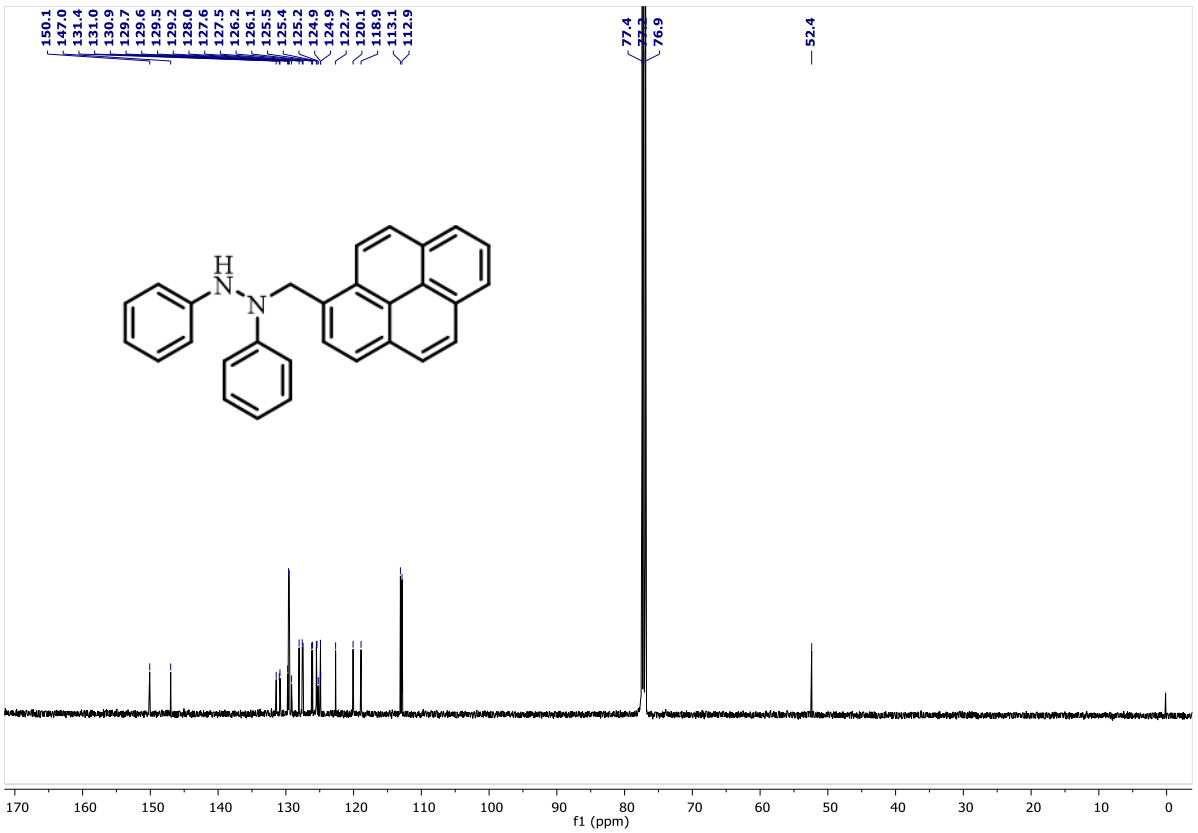


Figure S52: $^{13}C\{^{1}H\}$ NMR Spectrum of **3o** ($CDCl_3$, 126 MHz, 298 K)

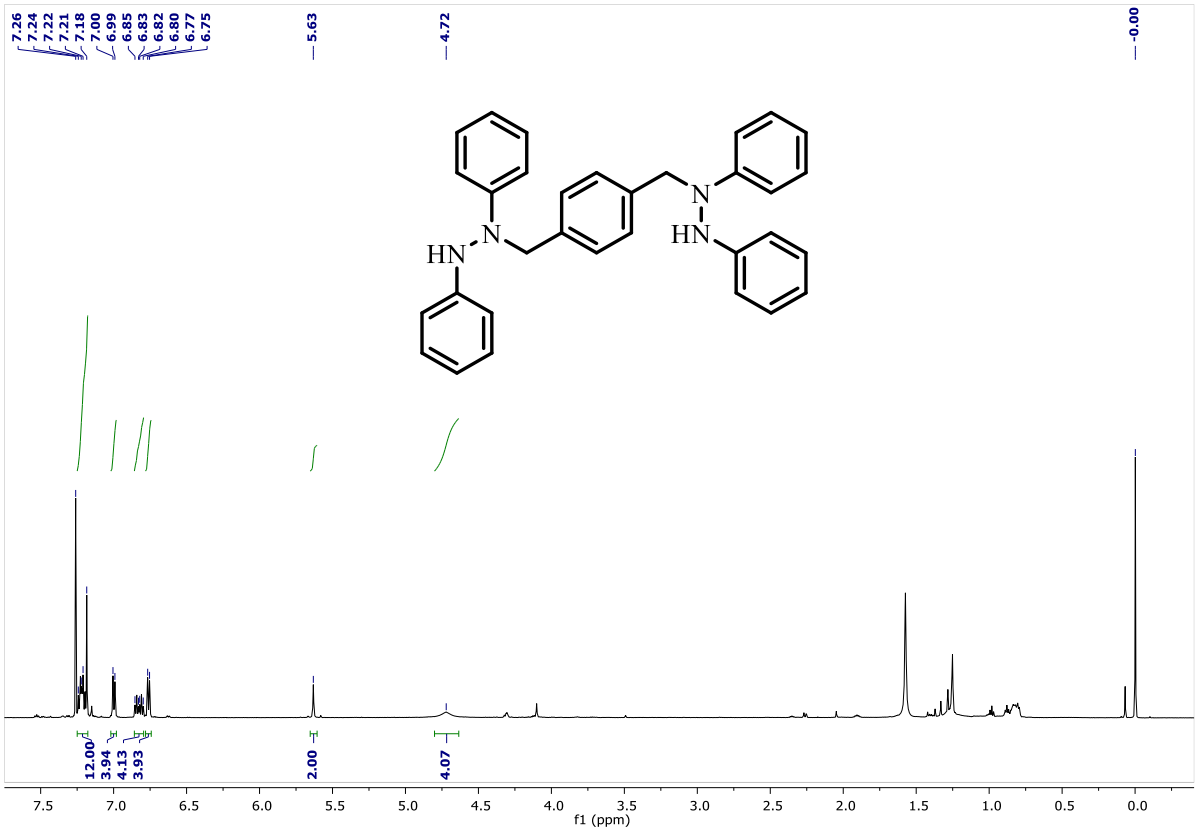


Figure S53: ^{1}H NMR Spectrum of **3p** ($CDCl_3$, 600 MHz, 298 K)

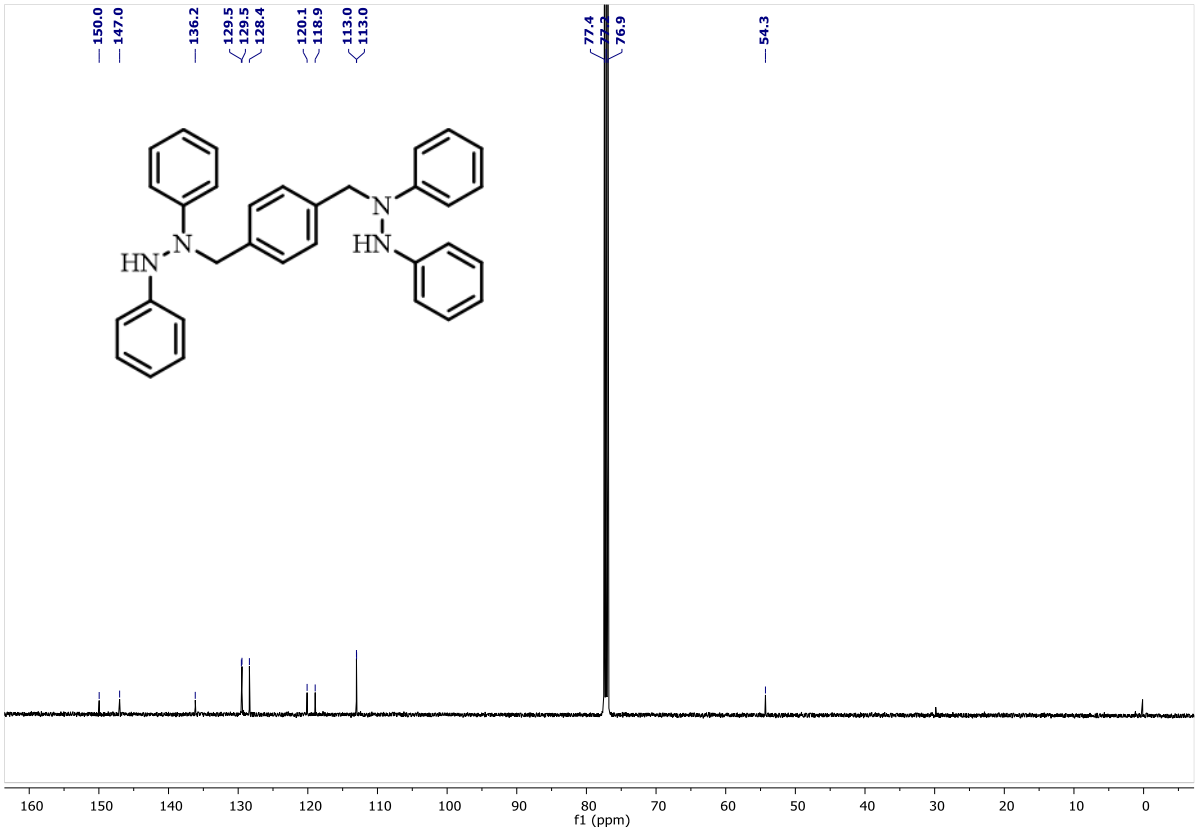


Figure S54: $^{13}C\{^{1}H\}$ NMR Spectrum of **3p** ($CDCl_3$, 126 MHz, 298 K)

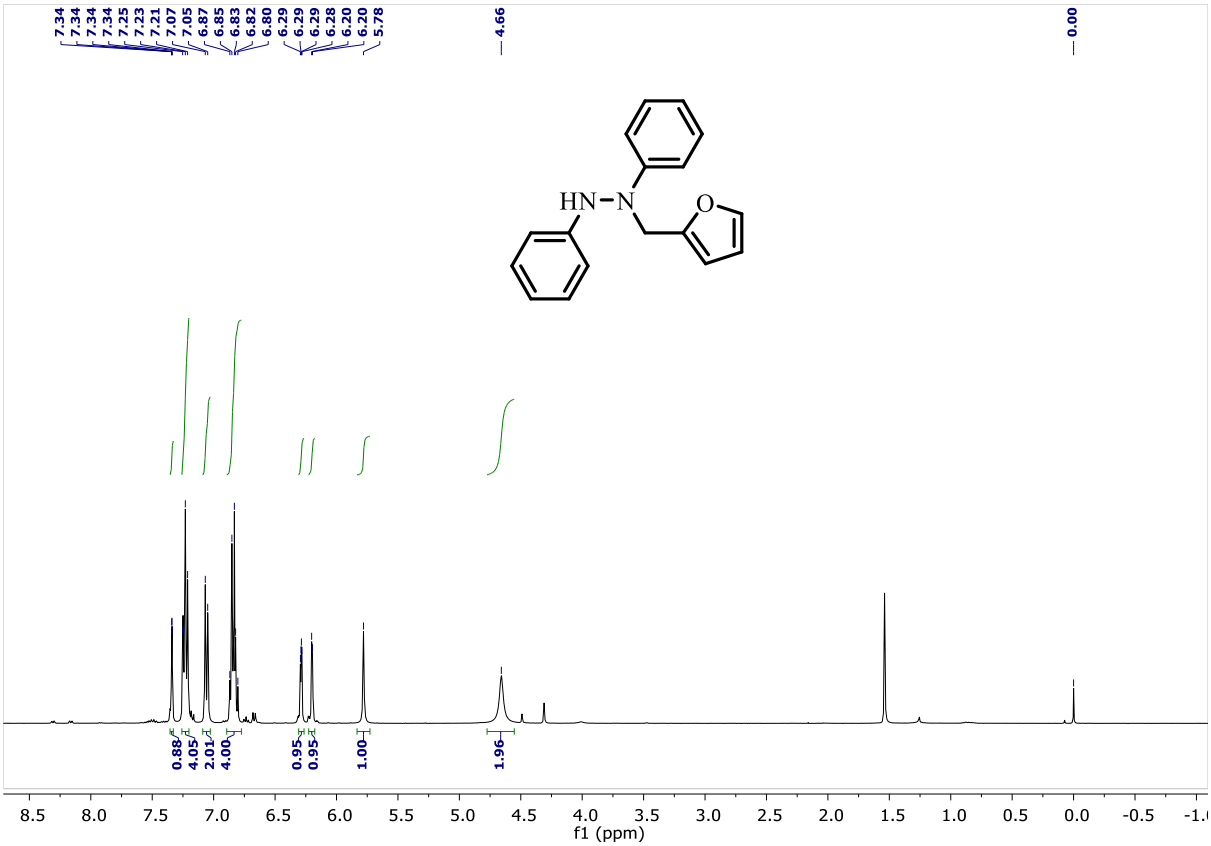


Figure S55: ^{1}H NMR Spectrum of **3q** ($CDCl_3$, 400 MHz, 298 K)

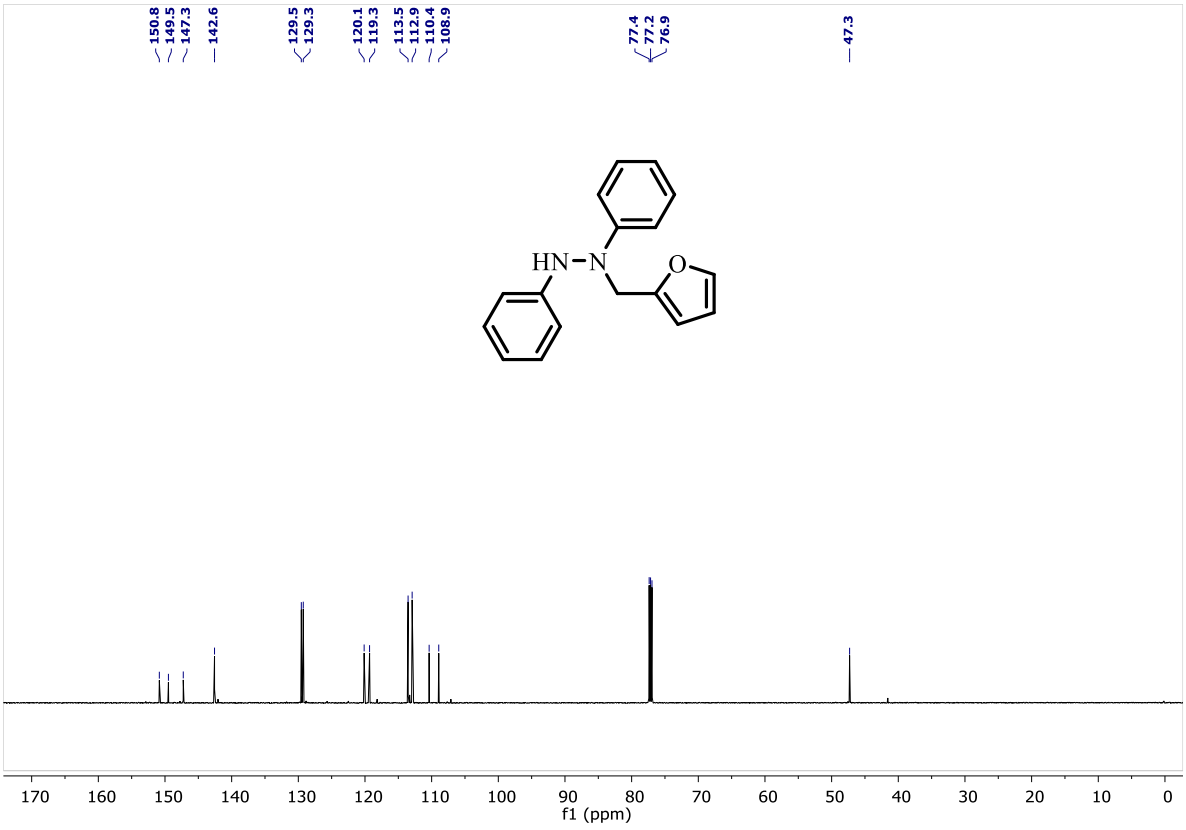


Figure S56: $^{13}C\{^{1}H\}$ NMR Spectrum of **3q** ($CDCl_3$, 151 MHz, 298 K)

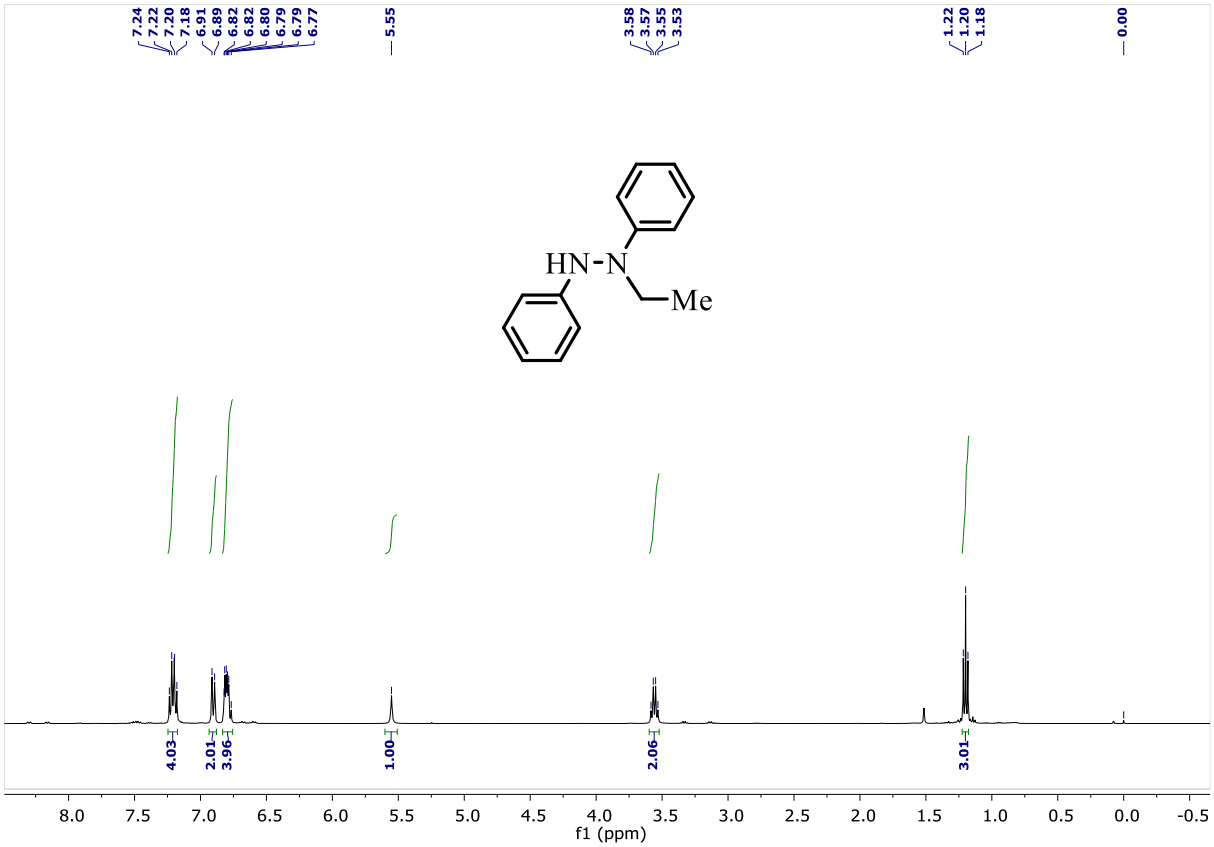


Figure S57: ^{1}H NMR Spectrum of **3r** ($CDCl_3$, 400 MHz, 298 K)

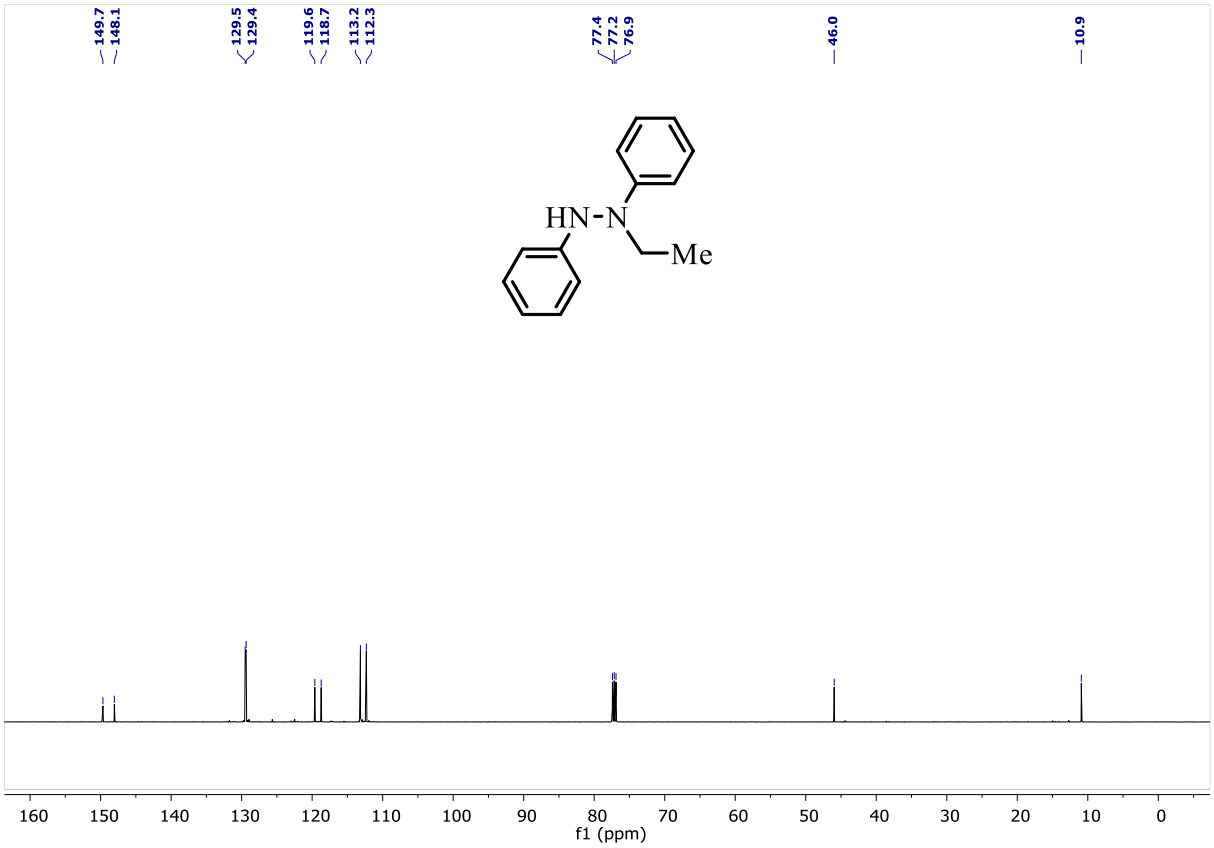


Figure S58: $^{13}C\{^{1}H\}$ NMR Spectrum of **3r** ($CDCl_3$, 126 MHz, 298 K)

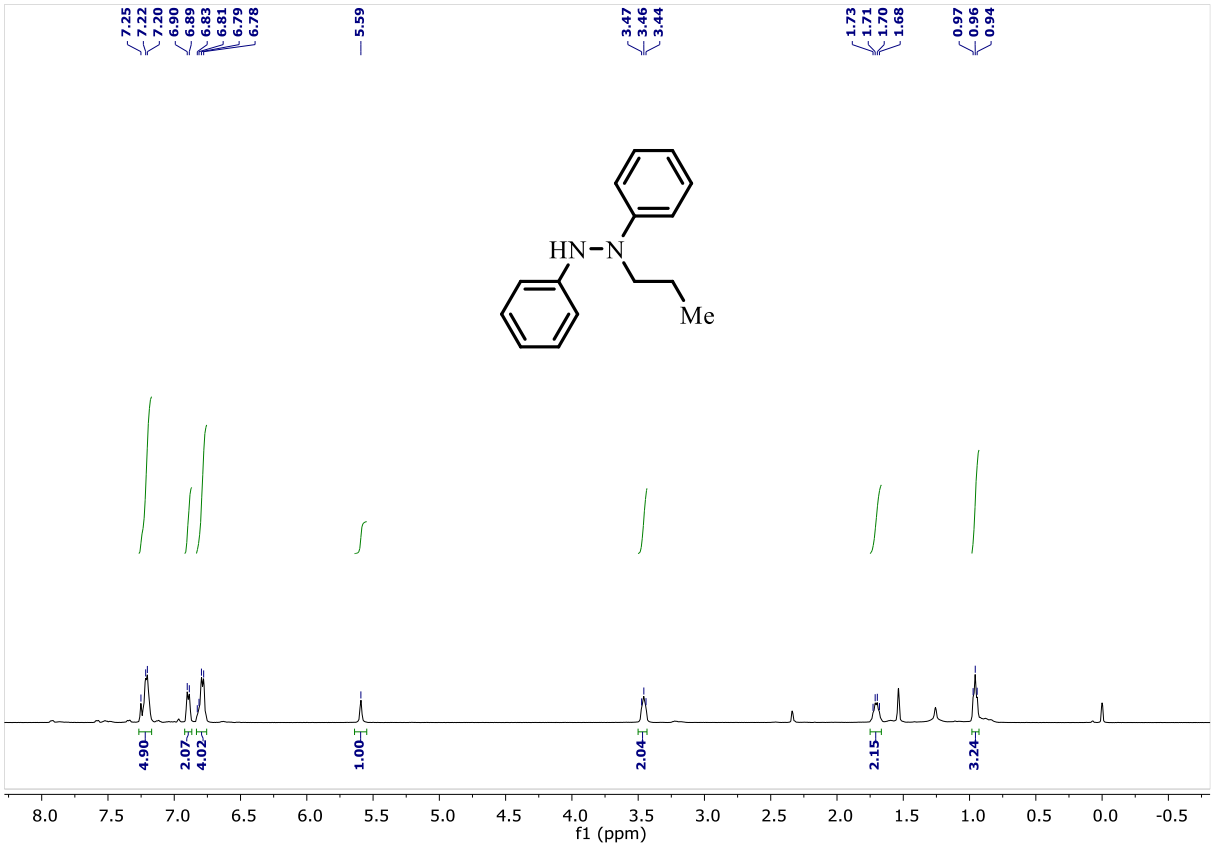


Figure S59: ^{1}H NMR Spectrum of **3s** ($CDCl_3$, 500 MHz, 298 K)

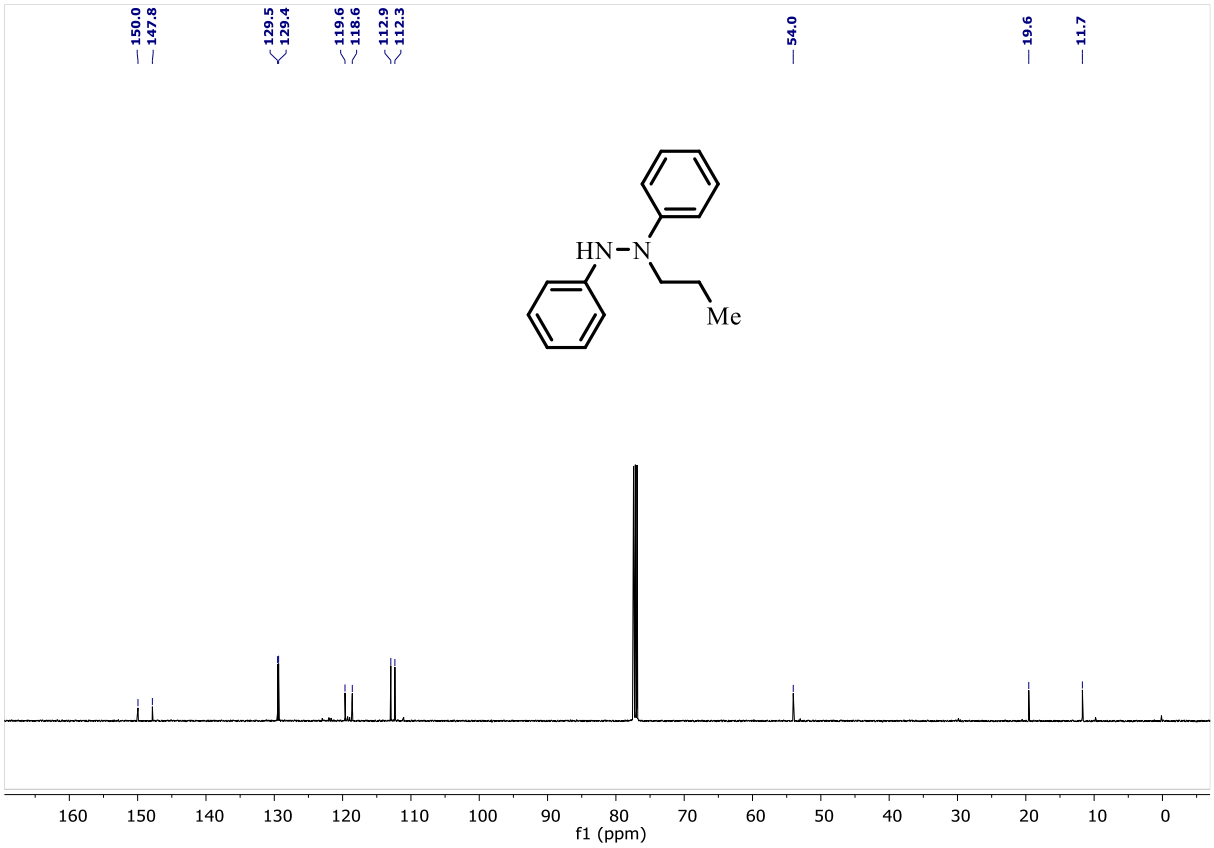


Figure S60: $^{13}C\{^{1}H\}$ NMR Spectrum of **3s** ($CDCl_3$, 126 MHz, 298 K)

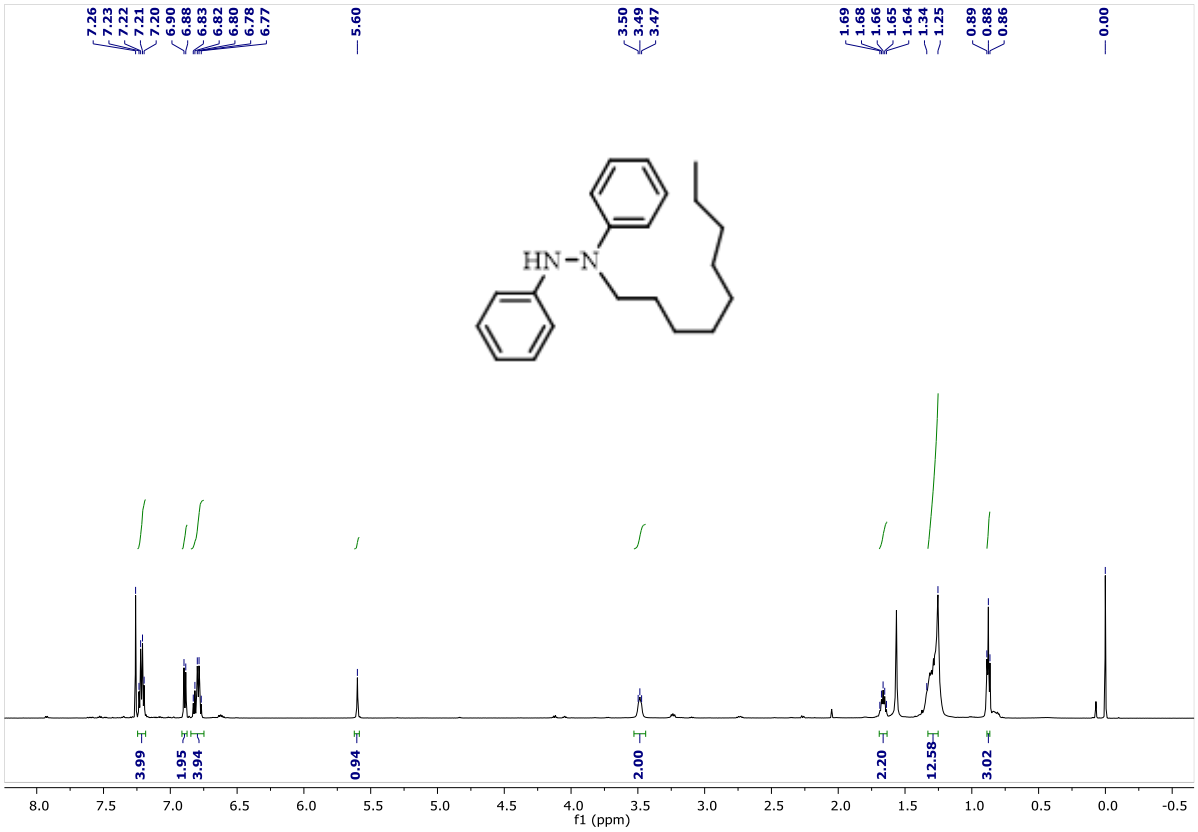


Figure S61: ^{1}H NMR Spectrum of **3t** ($CDCl_3$, 600 MHz, 298 K)

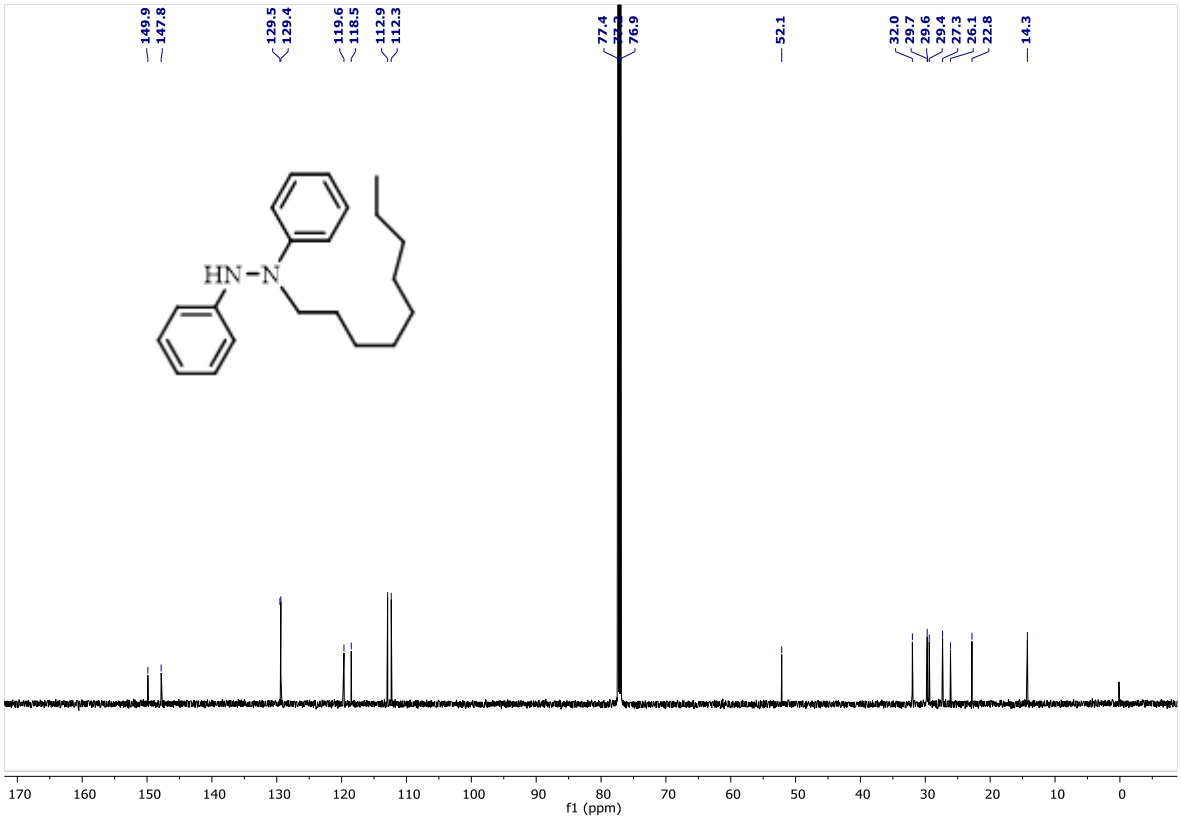


Figure S62: $^{13}C\{^{1}H\}$ NMR Spectrum of **3t** ($CDCl_3$, 151 MHz, 298 K)

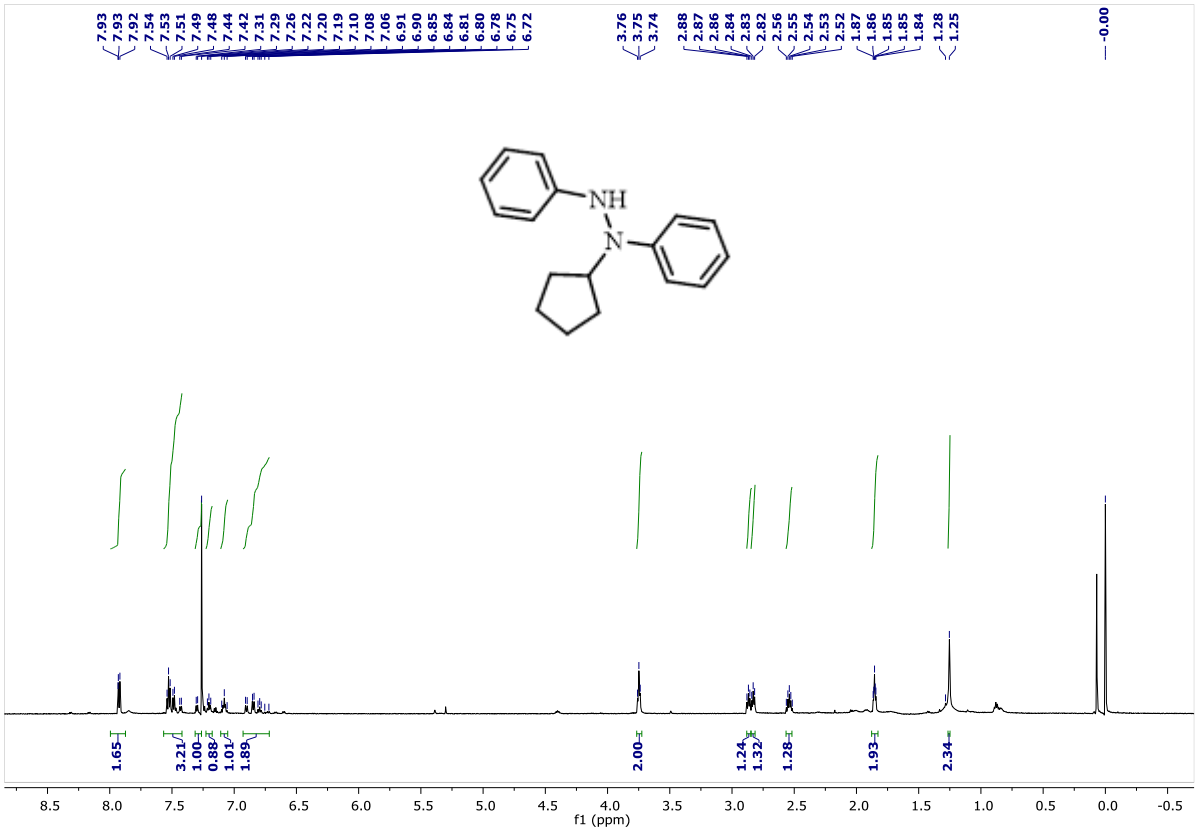


Figure S63: ^{1}H NMR Spectrum of **3u** ($CDCl_3$, 600 MHz, 298 K)

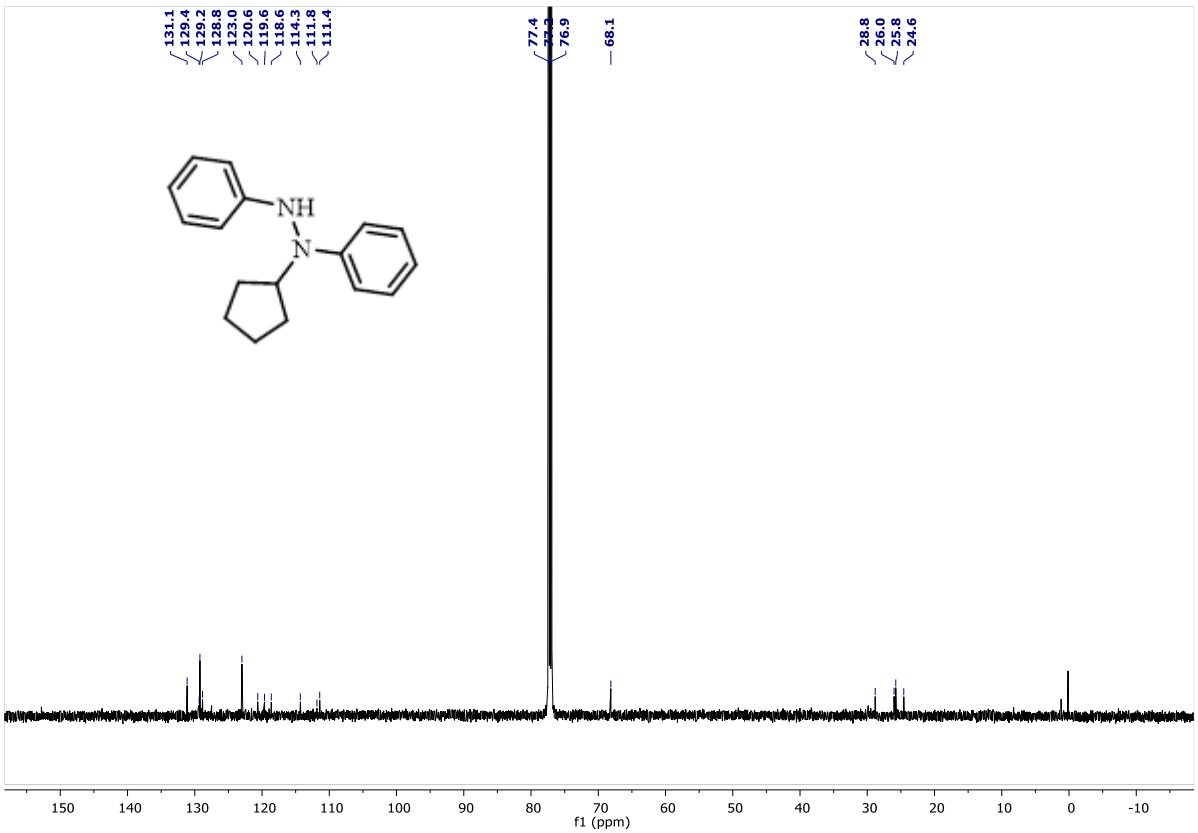


Figure S64: $^{13}C\{^{1}H\}$ NMR Spectrum of **3u** ($CDCl_3$, 151 MHz, 298 K)

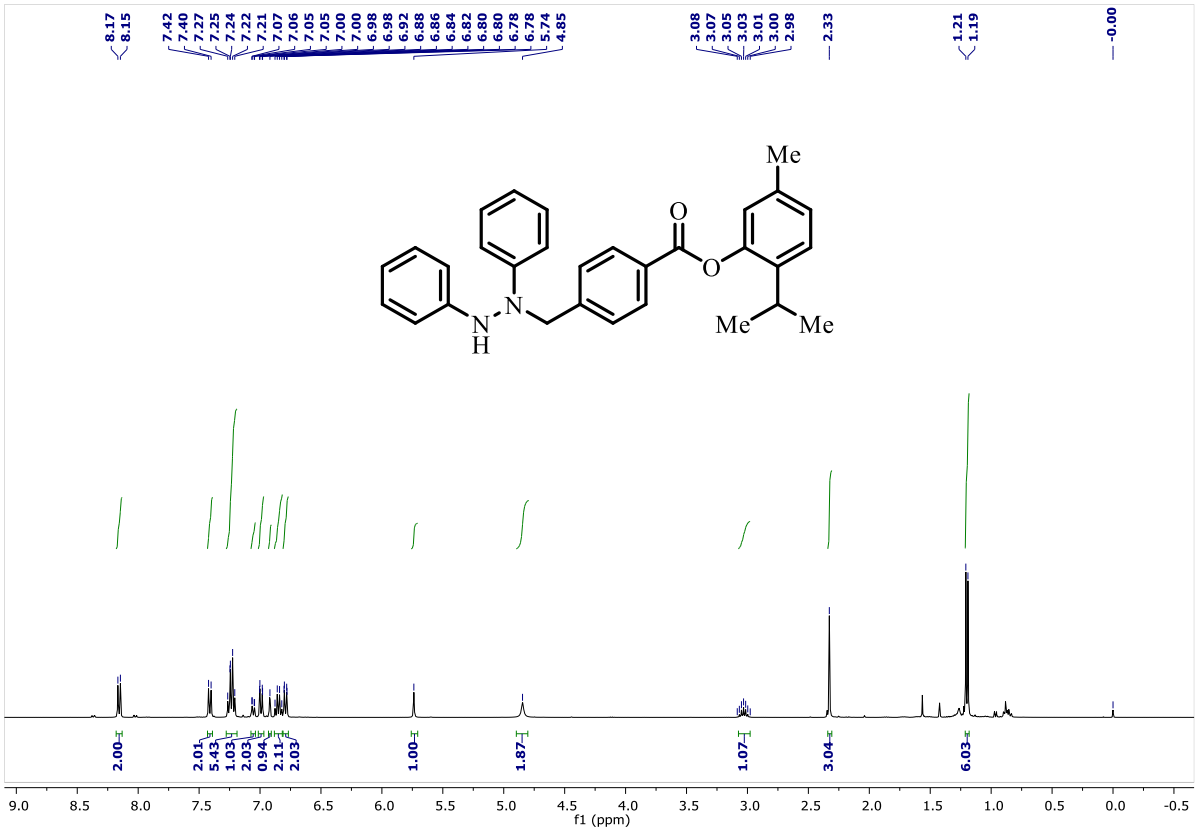


Figure S65: ^{1}H NMR Spectrum of **3aa** ($CDCl_3$, 400 MHz, 298 K)

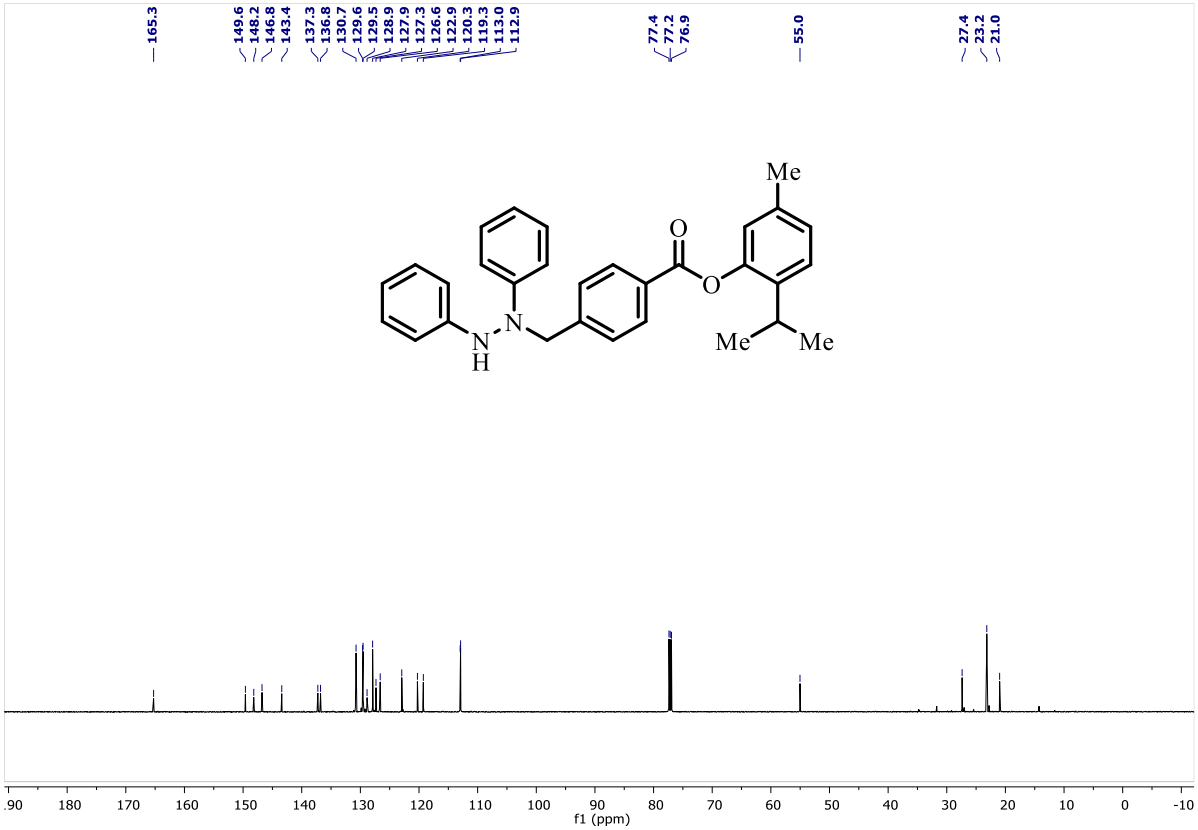


Figure S66: $^{13}C\{^{1}H\}$ NMR Spectrum of **3aa** ($CDCl_3$, 151 MHz, 298 K)

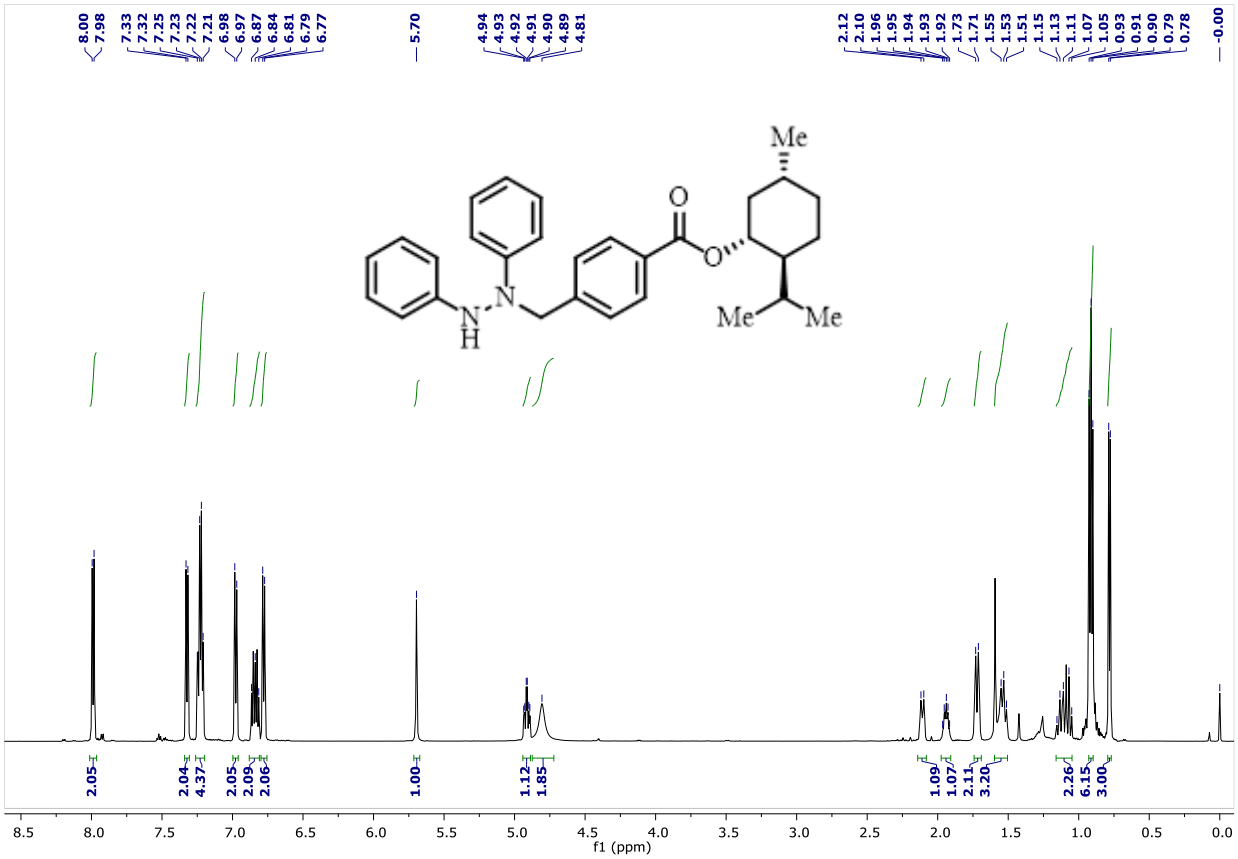


Figure S67: ^{1}H NMR Spectrum of **3ab** ($CDCl_3$, 600 MHz, 298 K)

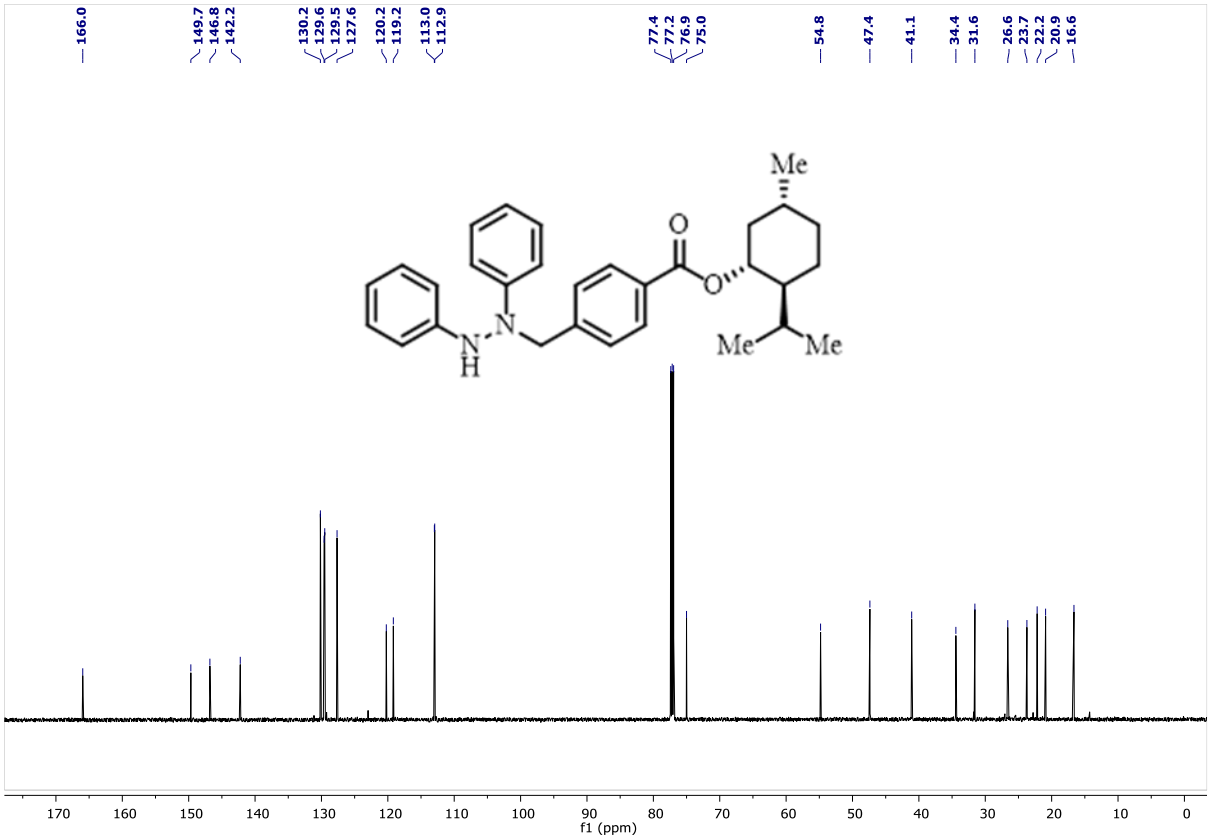


Figure S68: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ab** ($CDCl_3$, 151 MHz, 298 K)

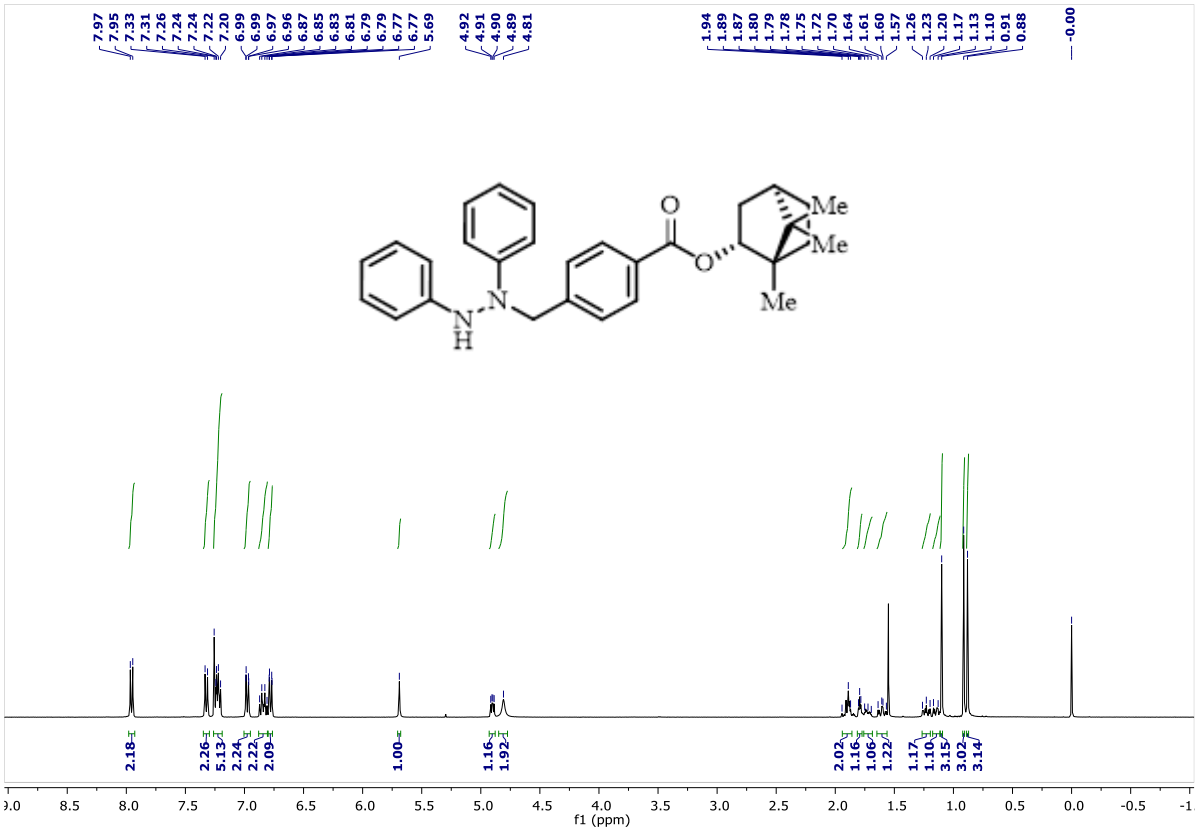


Figure S69: ^{1}H NMR Spectrum of **3ac** ($CDCl_3$, 400 MHz, 298 K)

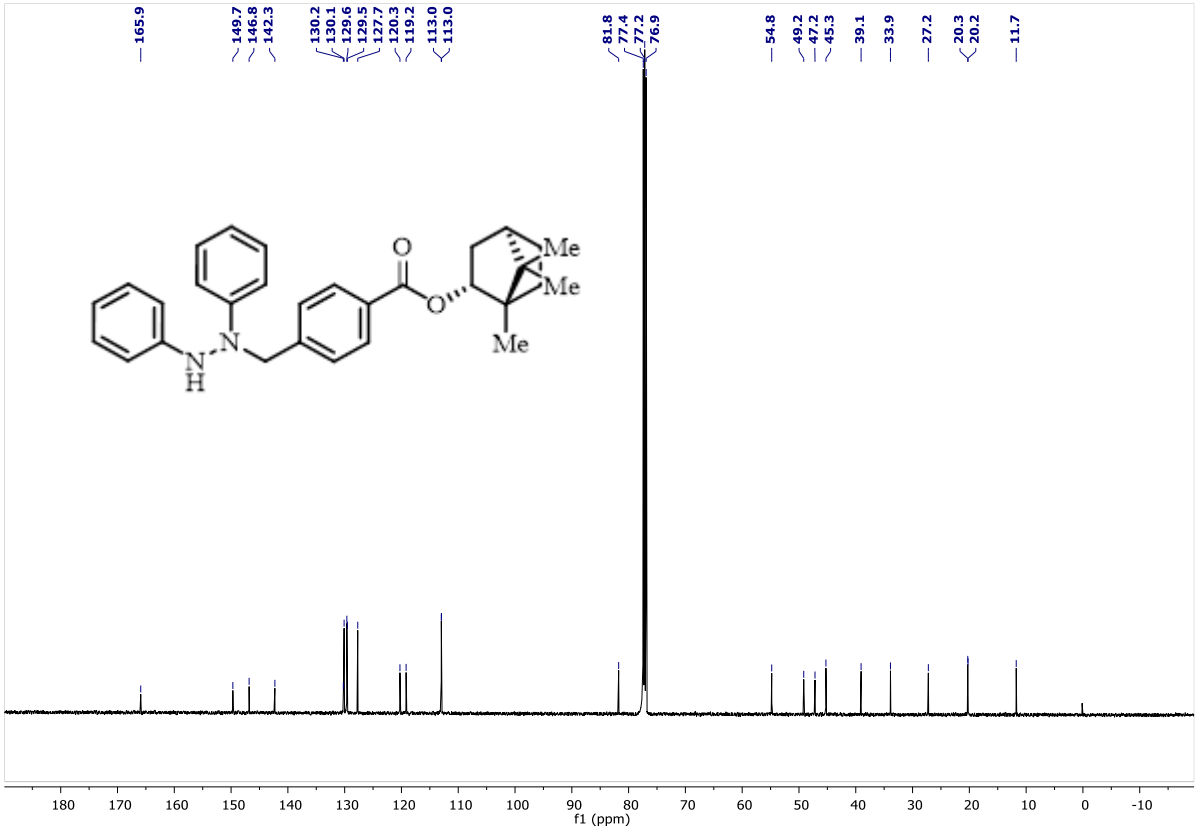


Figure S70: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ac** ($CDCl_3$, 126 MHz, 298 K)

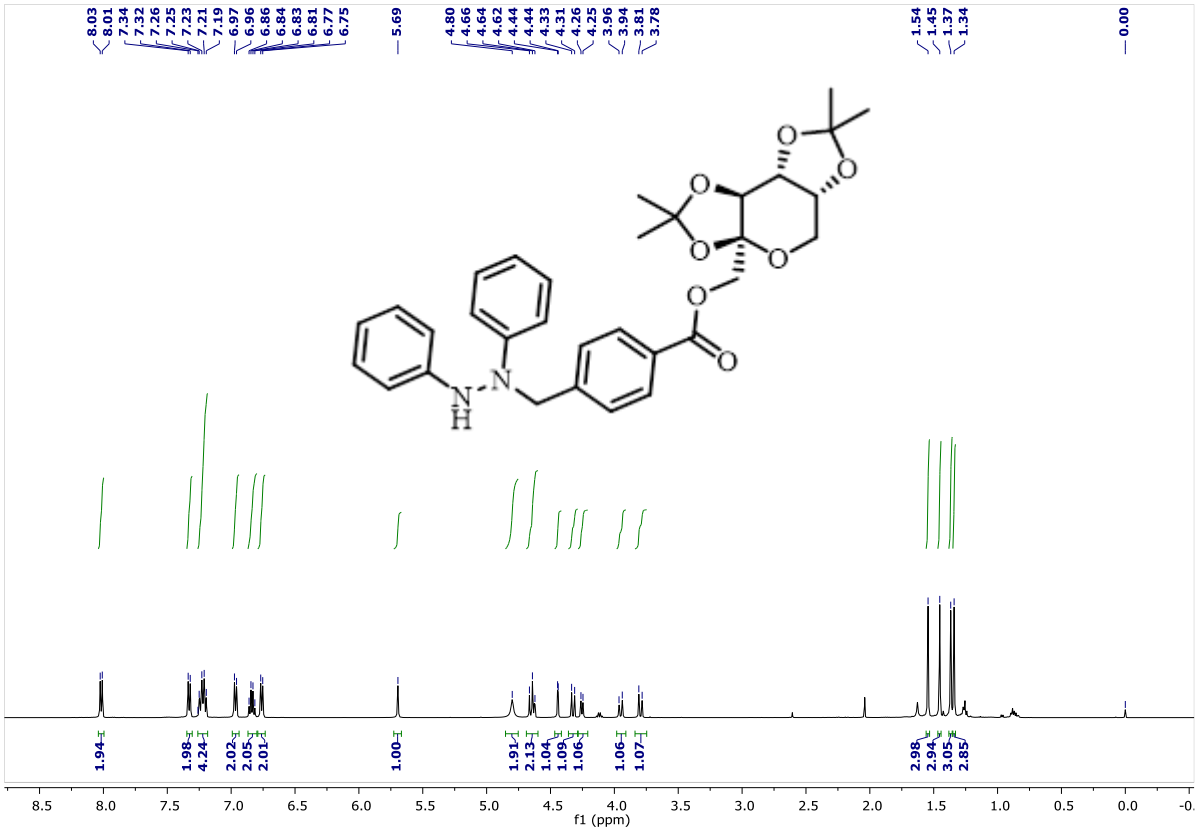


Figure S71: ^{1}H NMR Spectrum of **3ad** ($CDCl_3$, 500 MHz, 298 K)

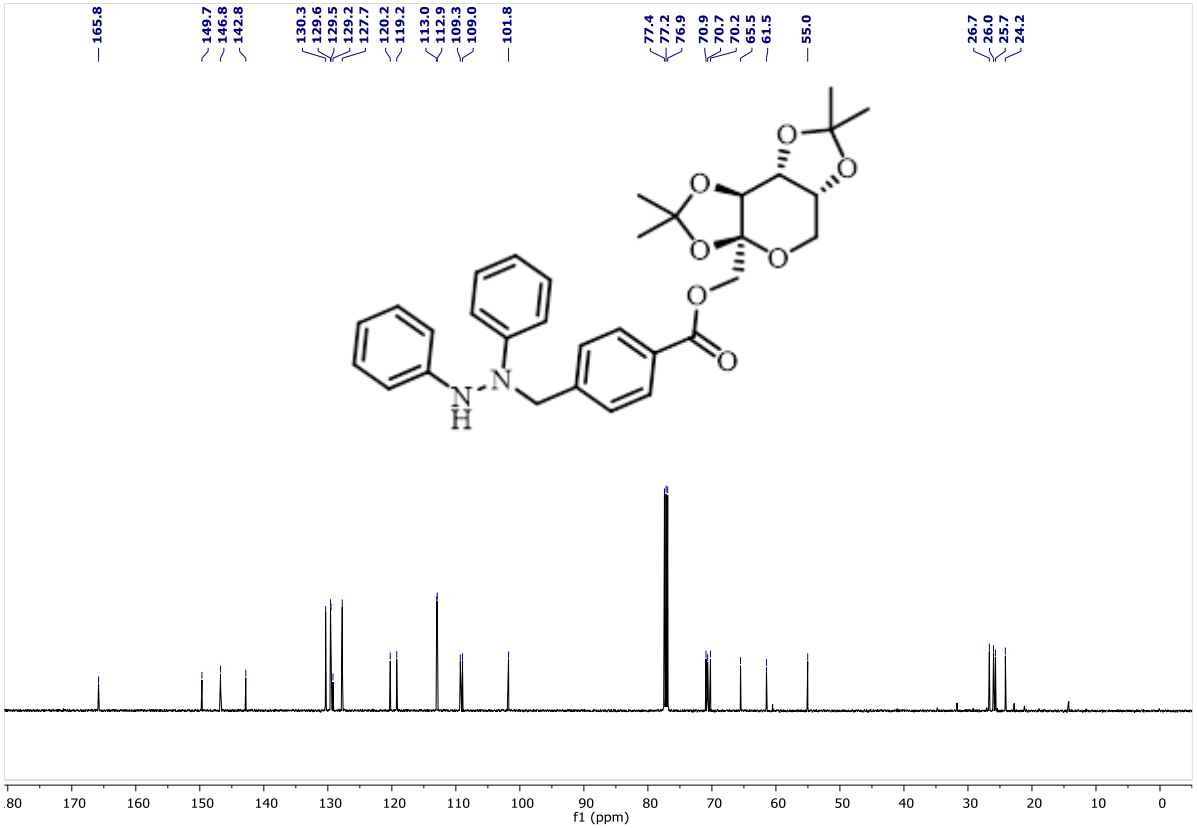


Figure S72: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ad** ($CDCl_3$, 126 MHz, 298 K)

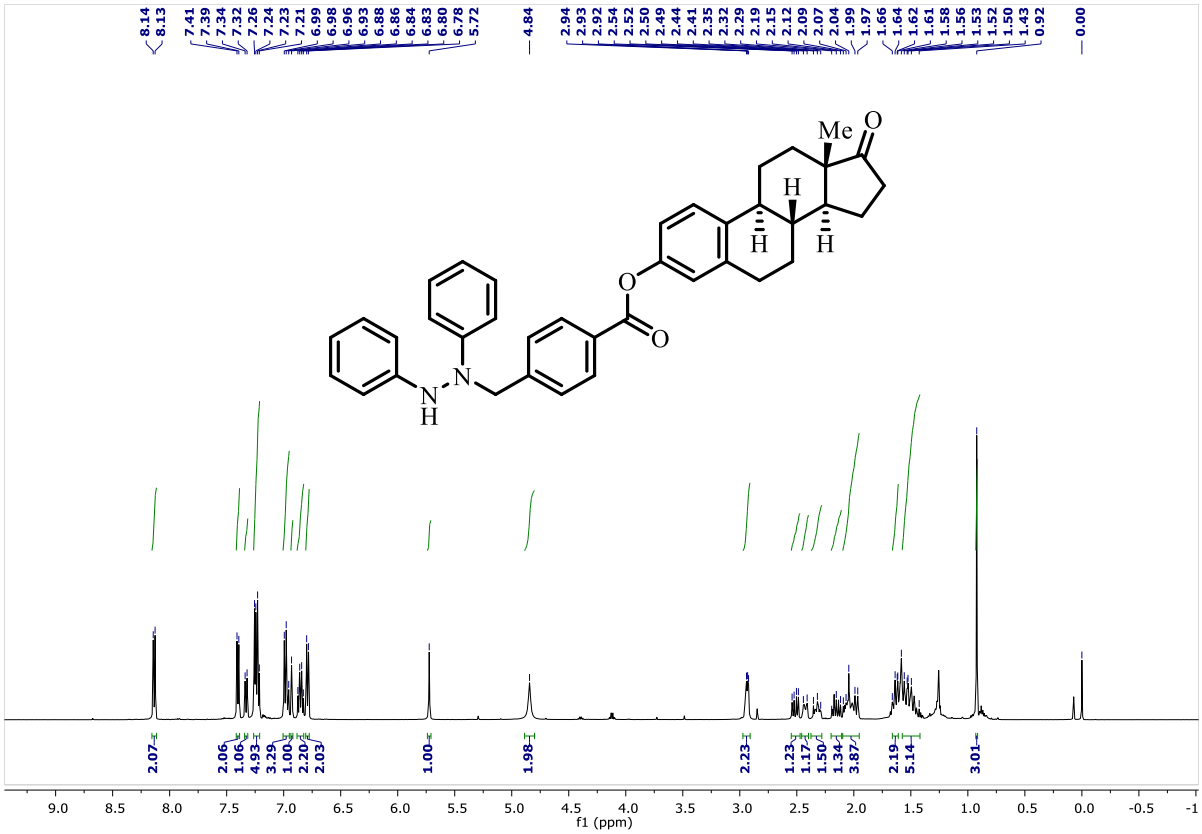


Figure S73: ^{1}H NMR Spectrum of **3ae** ($CDCl_3$, 500 MHz, 298 K)

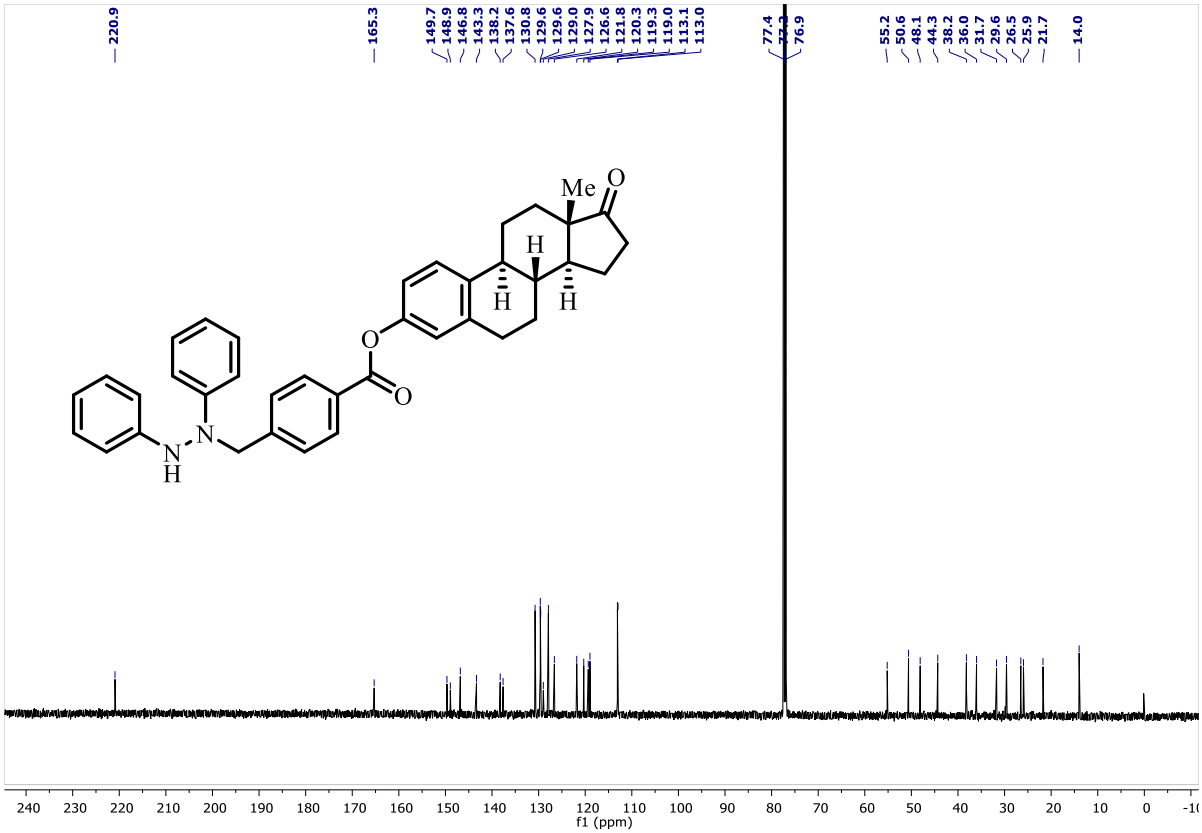


Figure S74: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ae** ($CDCl_3$, 126 MHz, 298 K)

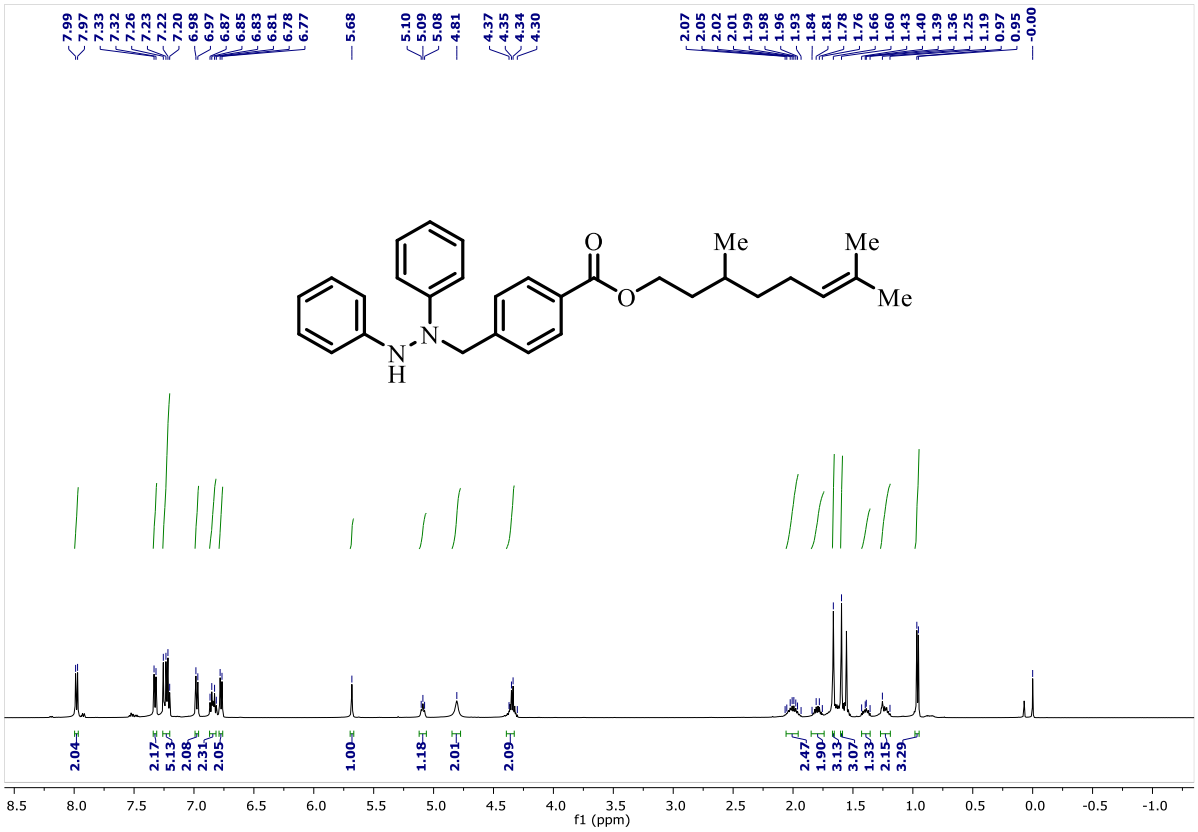


Figure S75: ^{1}H NMR Spectrum of **3af** ($CDCl_3$, 500 MHz, 298 K)

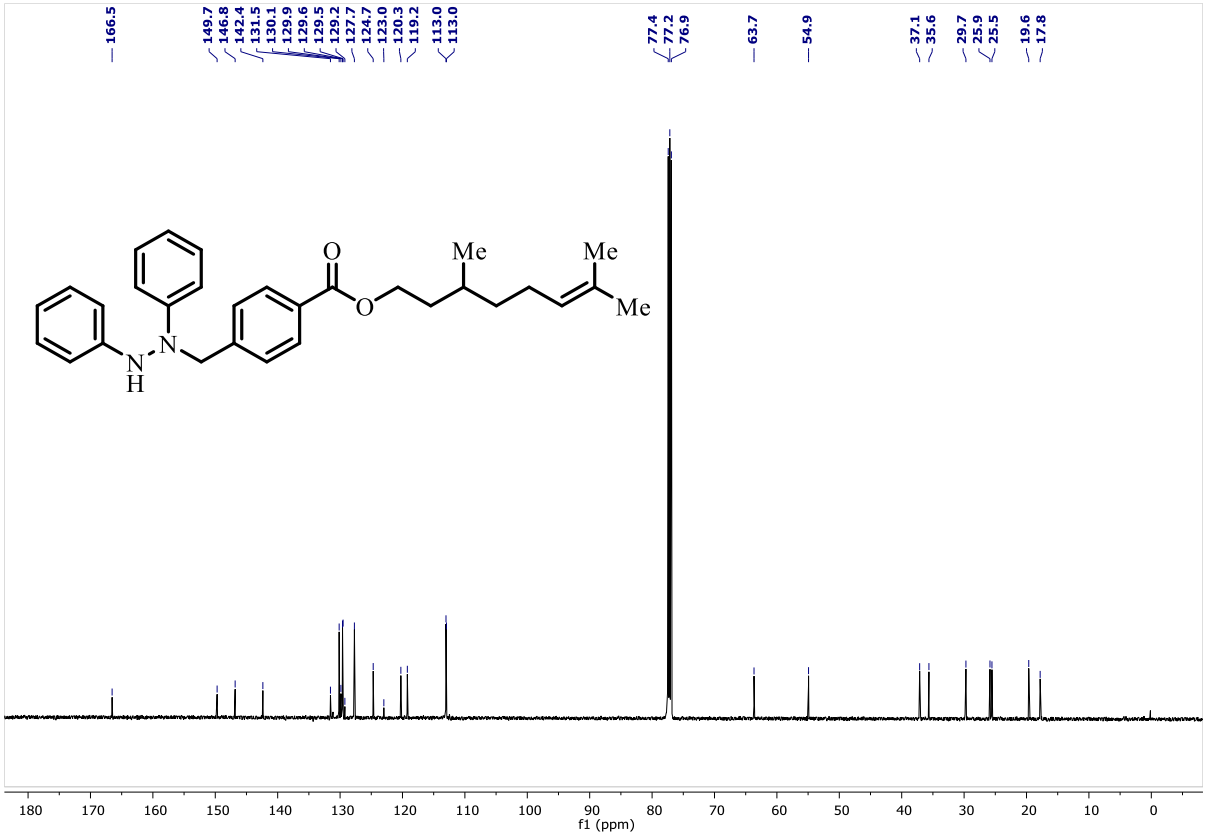


Figure S76: $^{13}C\{^{1}H\}$ NMR Spectrum of **3af** ($CDCl_3$, 126 MHz, 298 K)

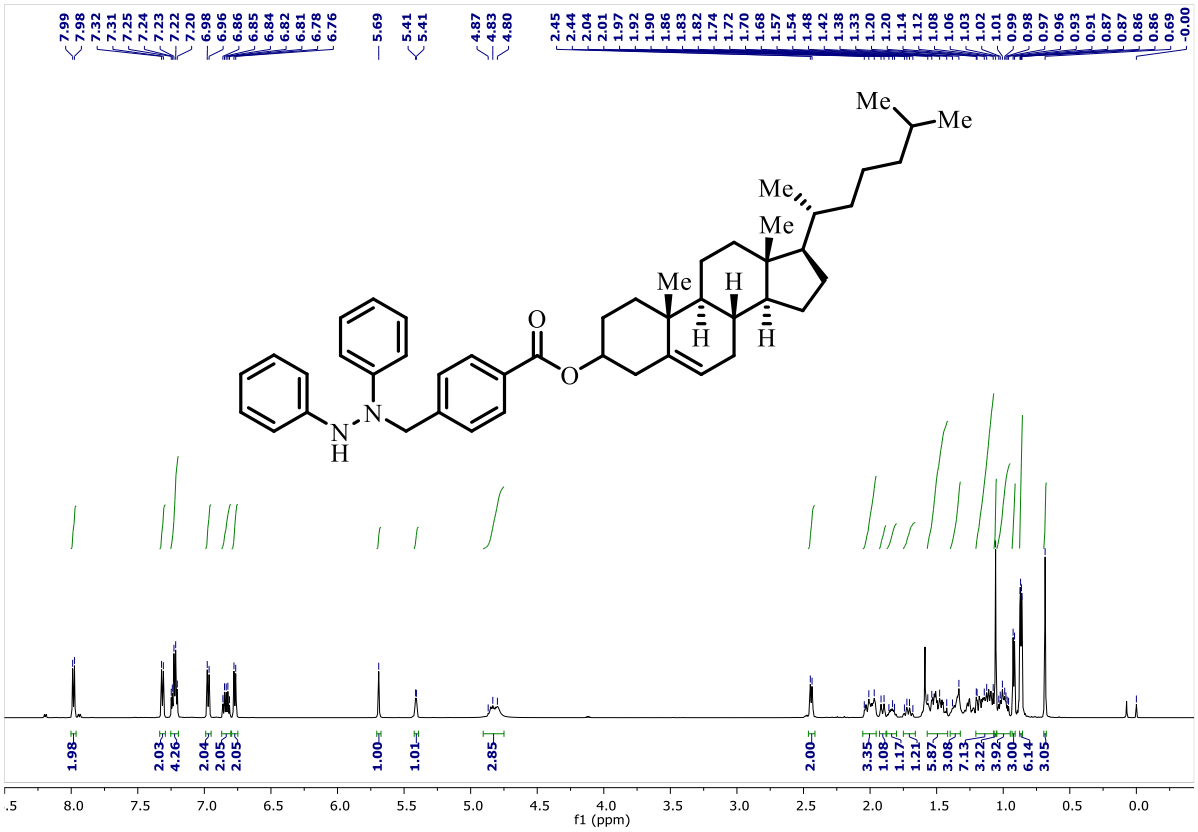


Figure S77: ^{1}H NMR Spectrum of **3ag** ($CDCl_3$, 600 MHz, 298 K)

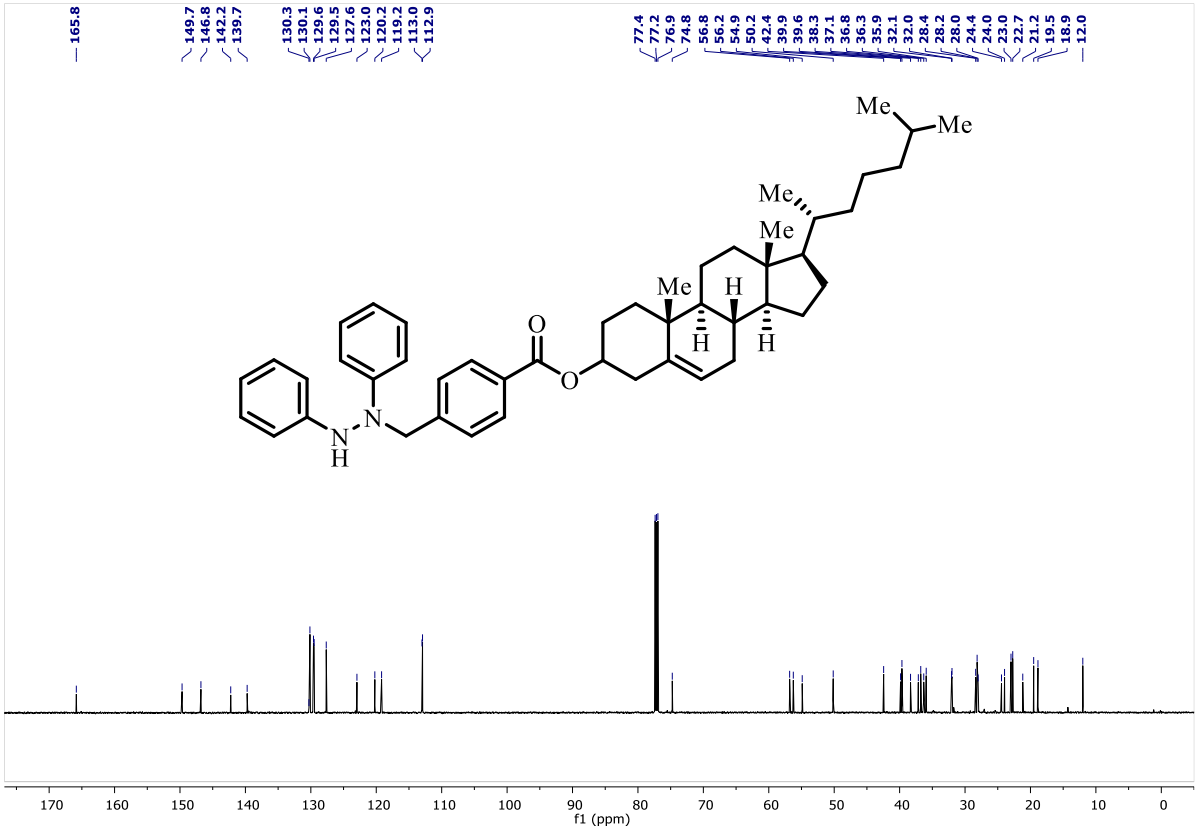


Figure S78: ^{13}C{^{1}H} NMR Spectrum of **3ag** ($CDCl_3$, 151 MHz, 298 K)

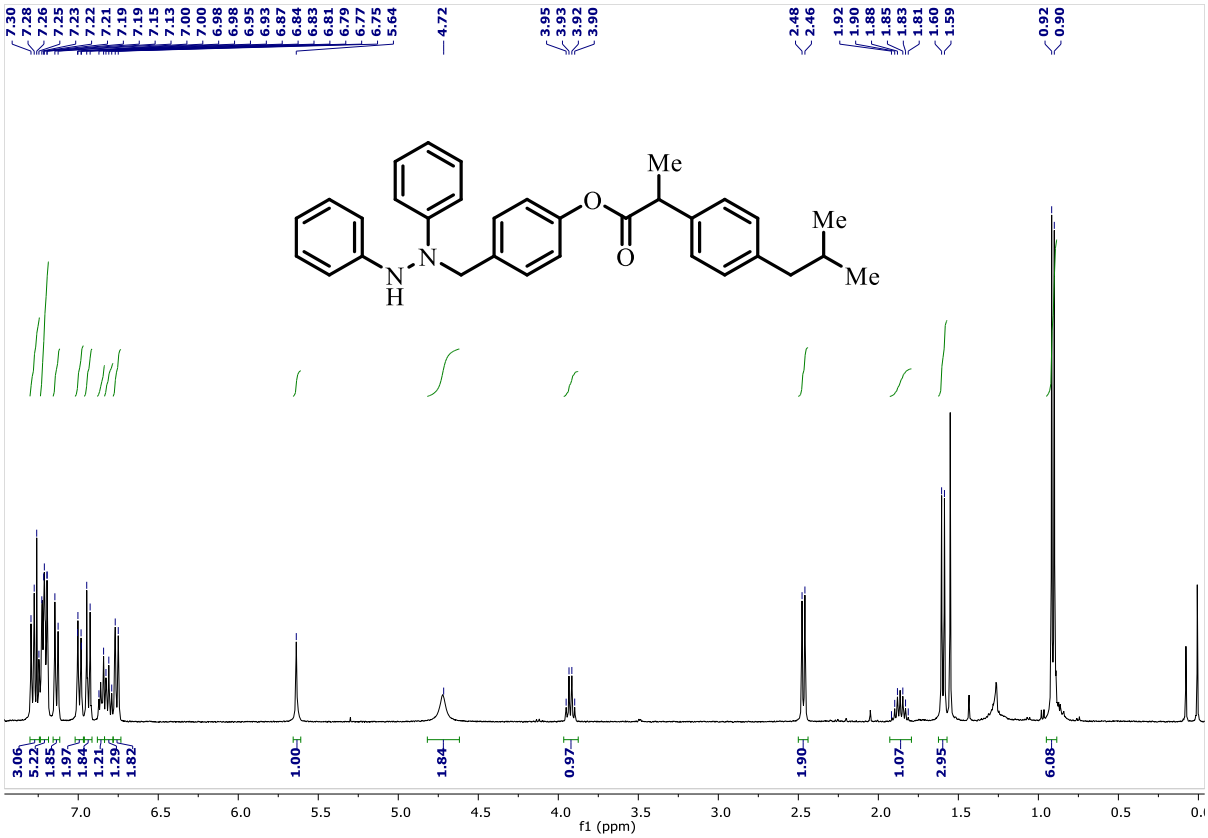


Figure S79: ^{1}H NMR Spectrum of **3ah** ($CDCl_3$, 400 MHz, 298 K)

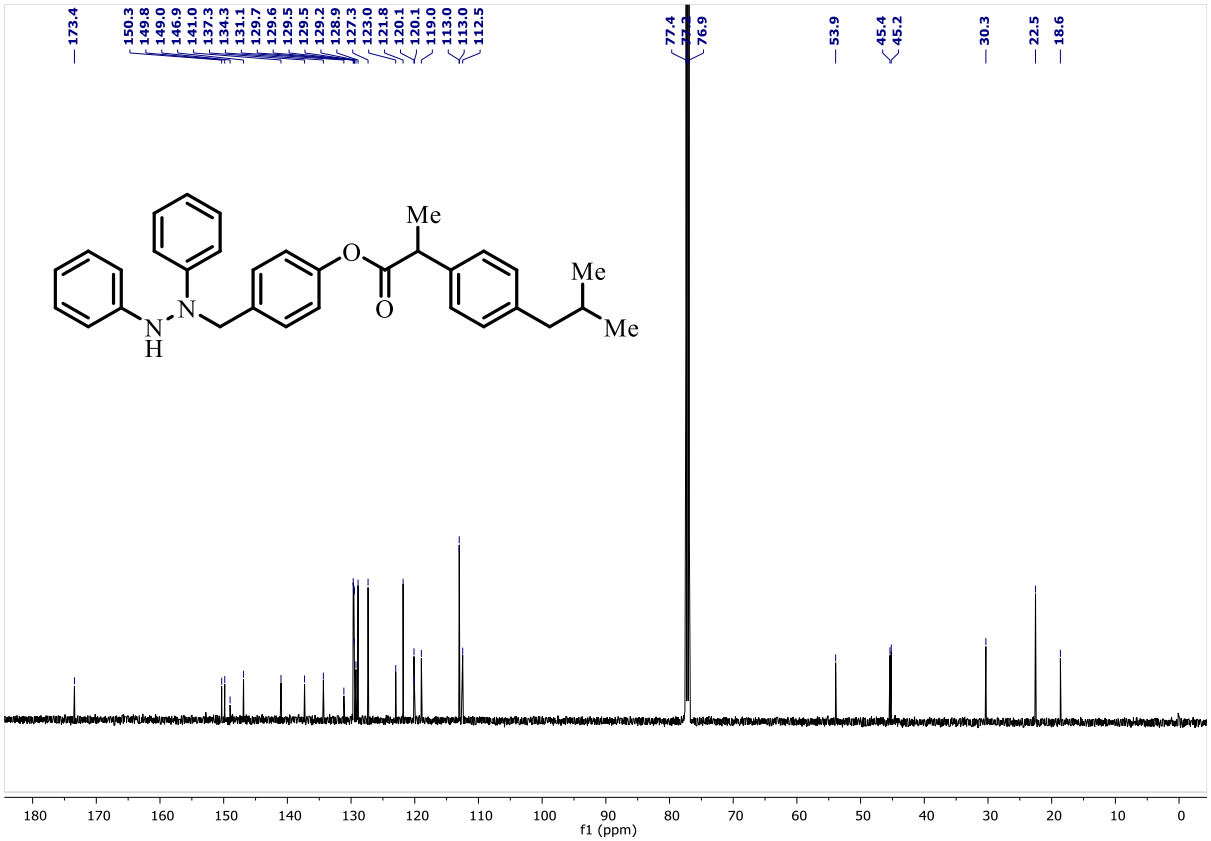


Figure S80: $^{13}C\{^{1}H\}$ NMR Spectrum of **3ah** ($CDCl_3$, 126 MHz, 298 K)

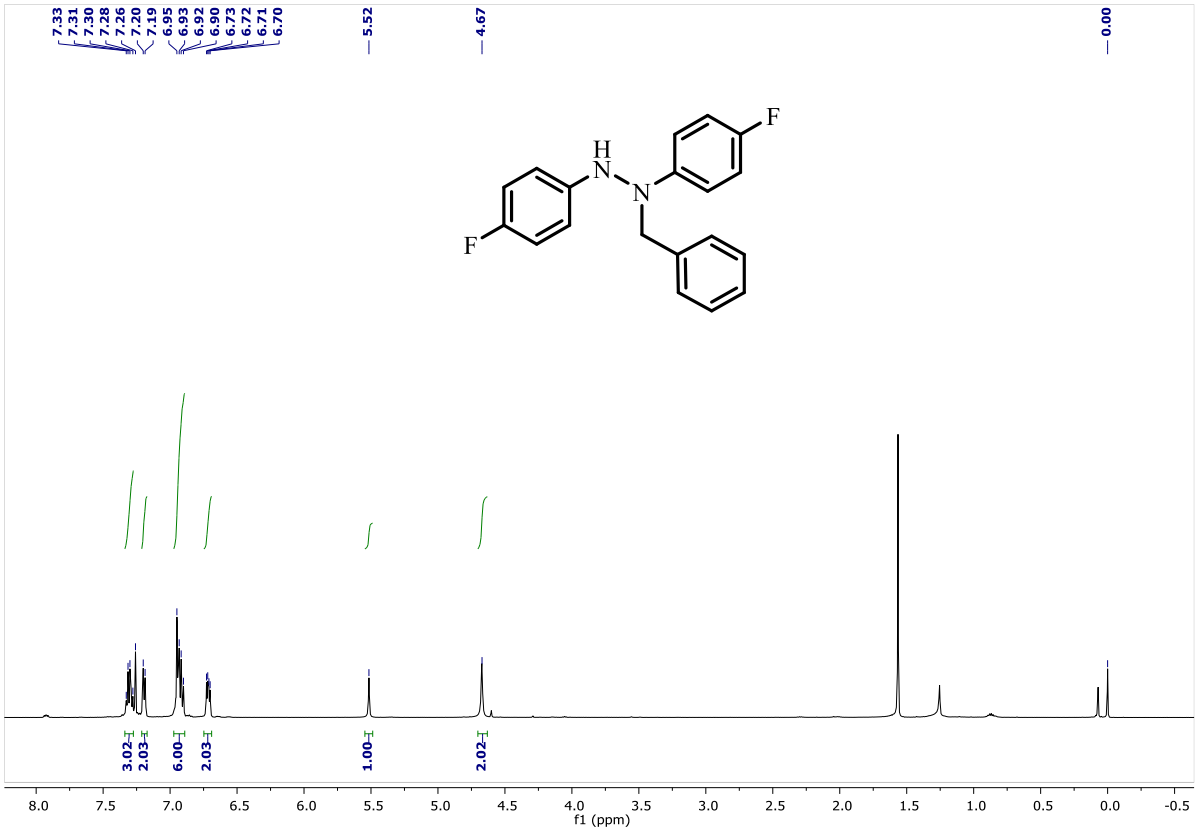


Figure S81: ^{1}H NMR Spectrum of **4a** ($CDCl_3$, 500 MHz, 298 K)

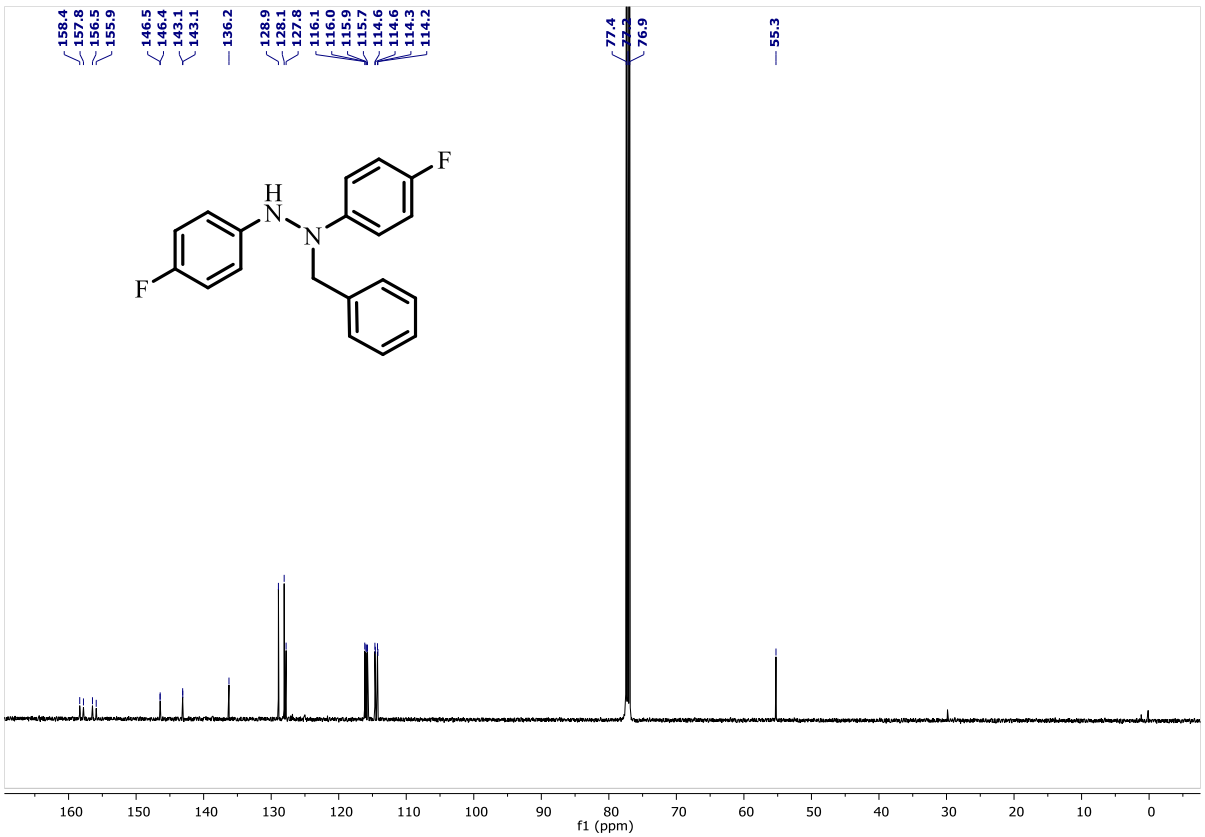


Figure S82: $^{13}C\{^{1}H\}$ NMR Spectrum of **4a** ($CDCl_3$, 126 MHz, 298 K)

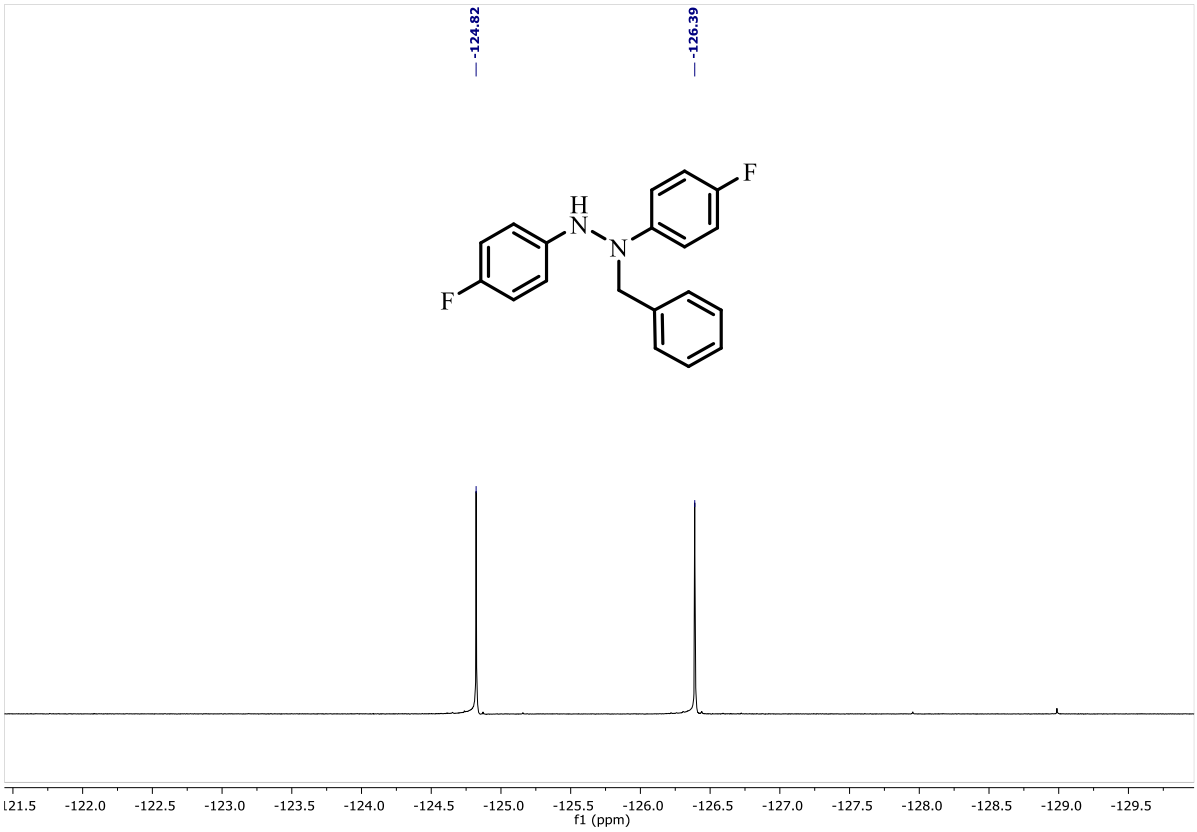


Figure S83: $^{19}F\{^{1}H\}$ NMR Spectrum of **4a** ($CDCl_3$, 471 MHz, 298 K)

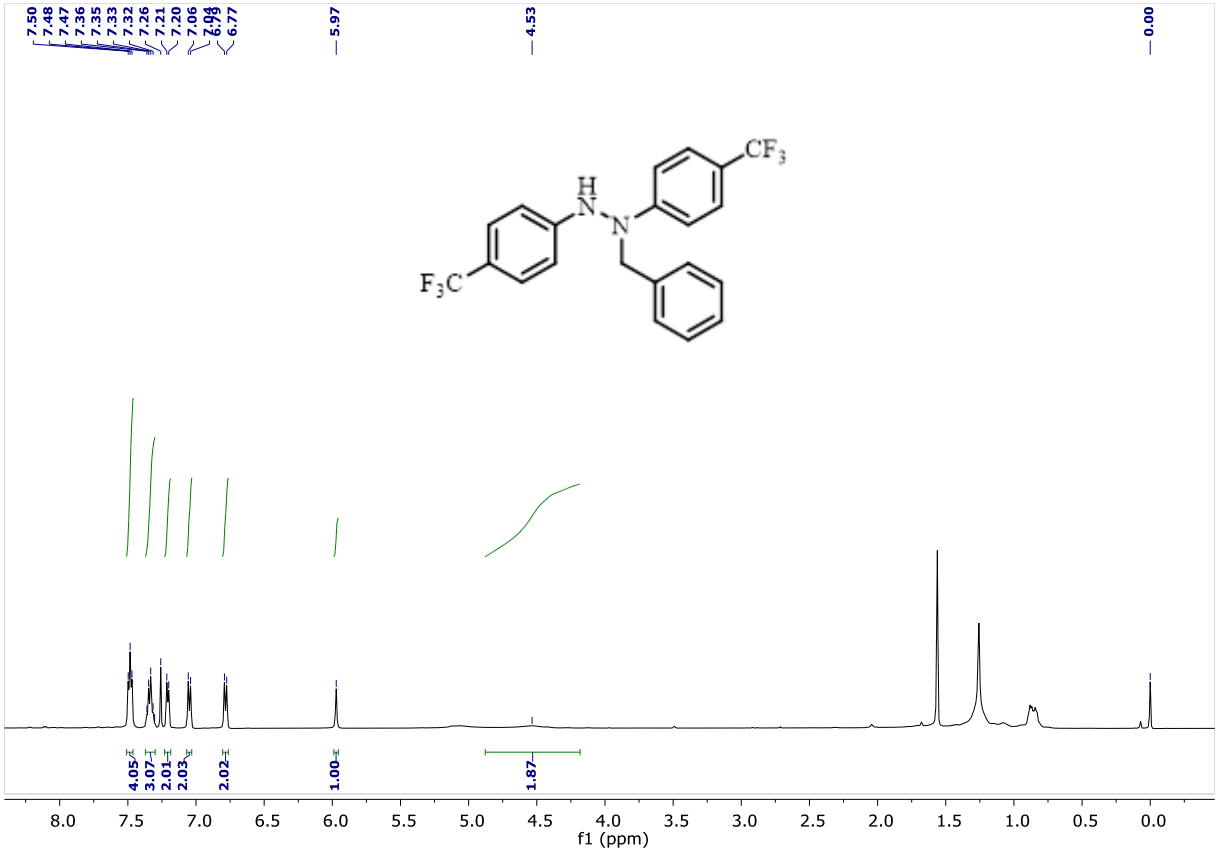


Figure S84: ^{1}H NMR Spectrum of **4b** ($CDCl_3$, 500 MHz, 298 K)

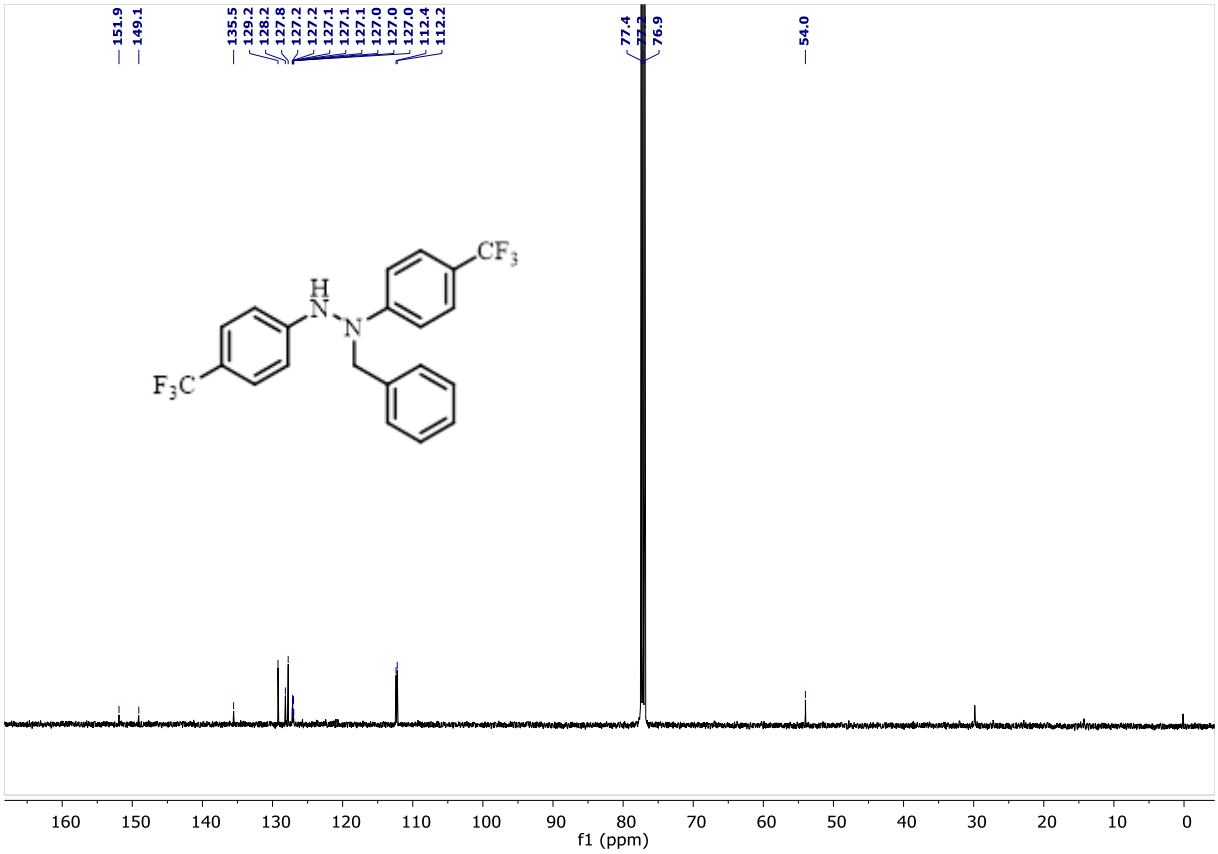


Figure S85: $^{13}C\{^{1}H\}$ NMR Spectrum of **4b** ($CDCl_3$, 126 MHz, 298 K)

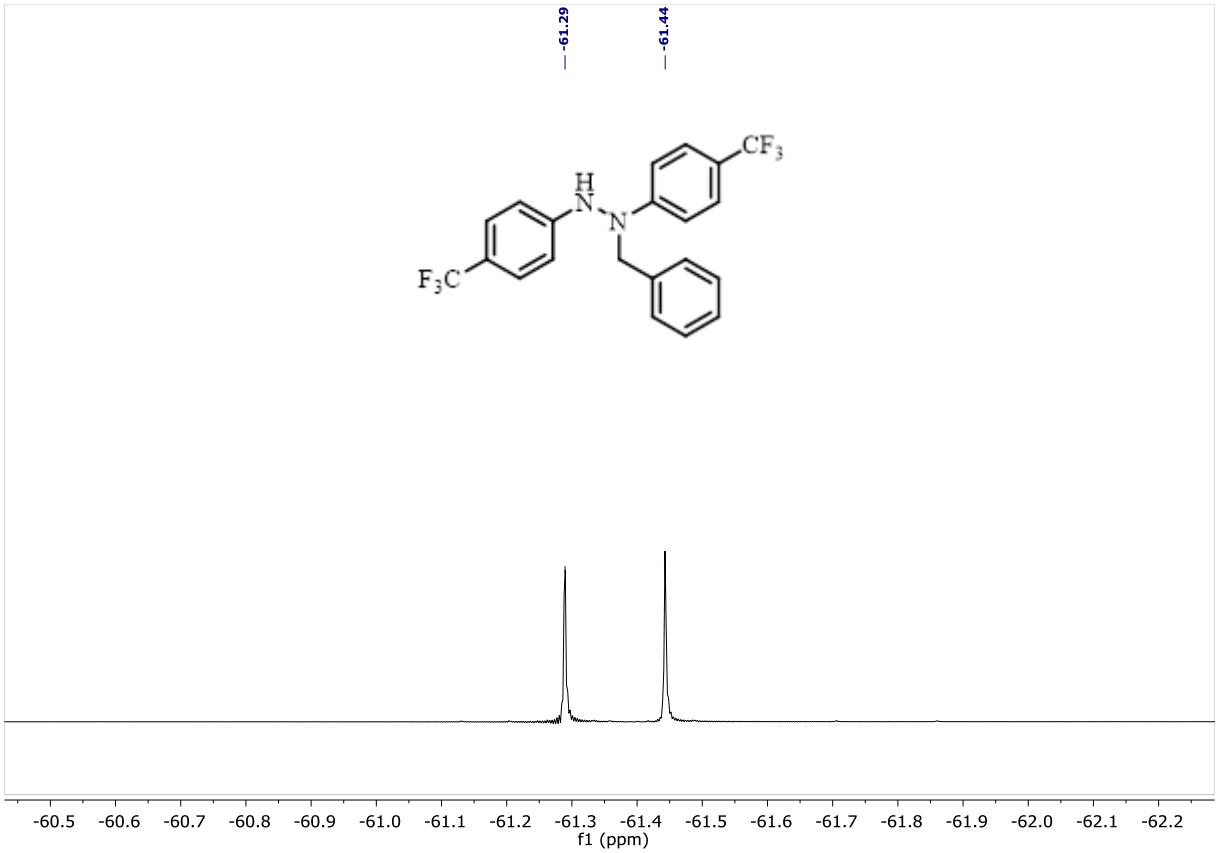


Figure S86: $^{19}F\{^{1}H\}$ NMR Spectrum of **4b** ($CDCl_3$, 471 MHz, 298 K)

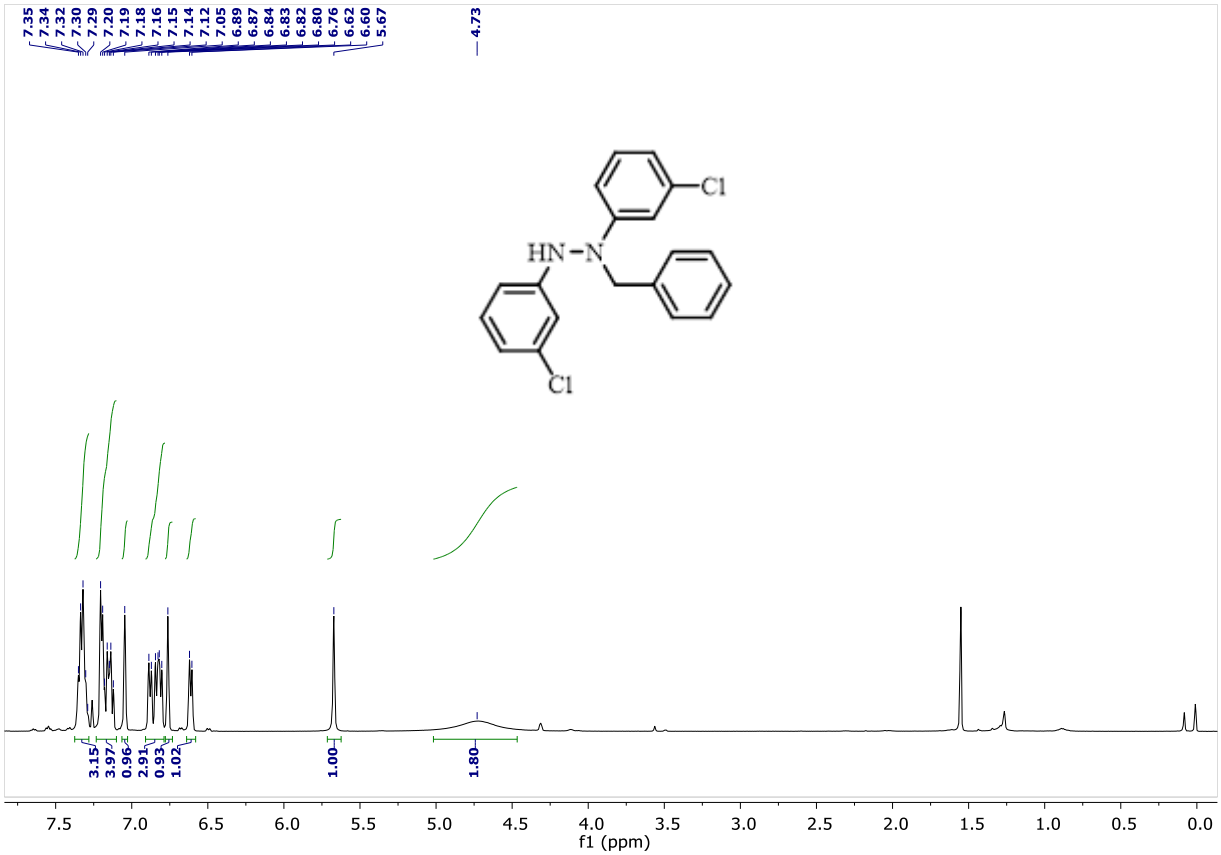


Figure S87: ^{1}H NMR Spectrum of **4c** ($CDCl_3$, 500 MHz, 298 K)

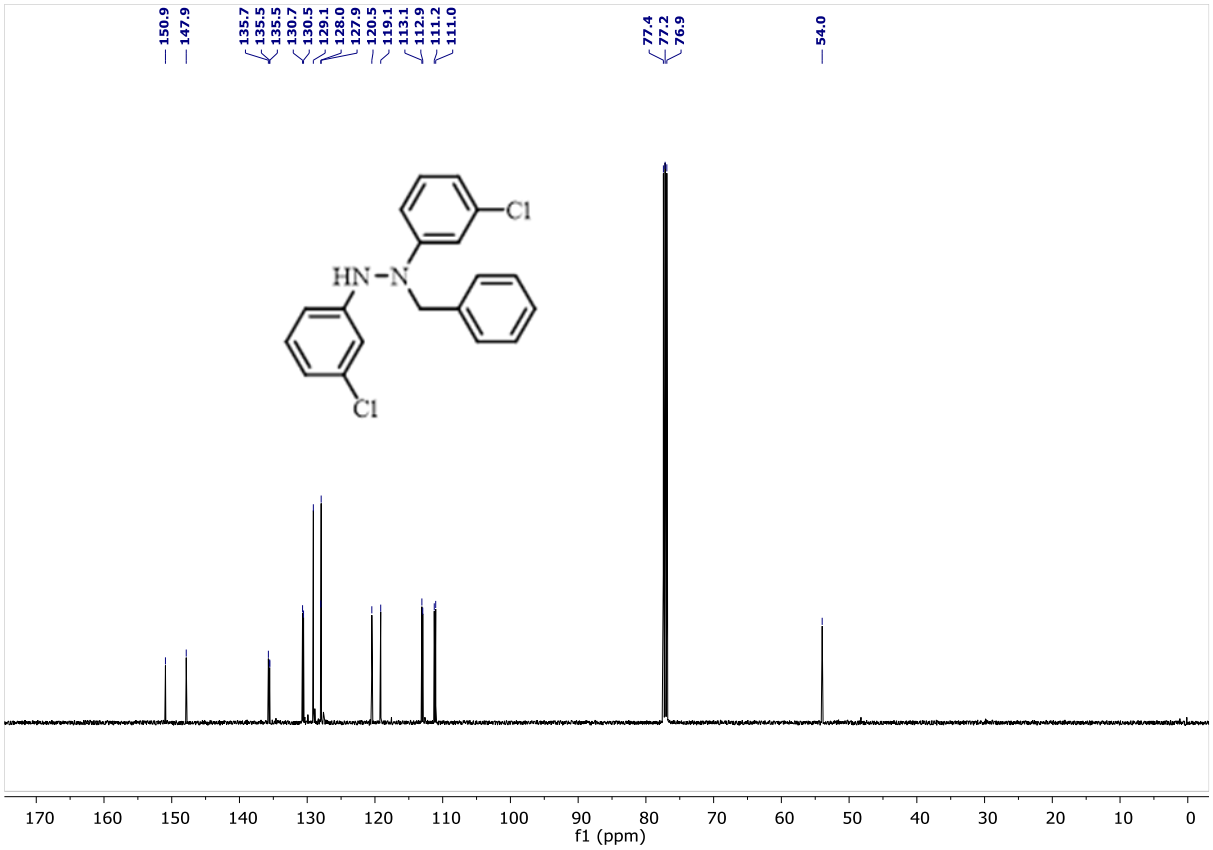


Figure S88: $^{13}C\{^{1}H\}$ NMR Spectrum of **4c** ($CDCl_3$, 126 MHz, 298 K)

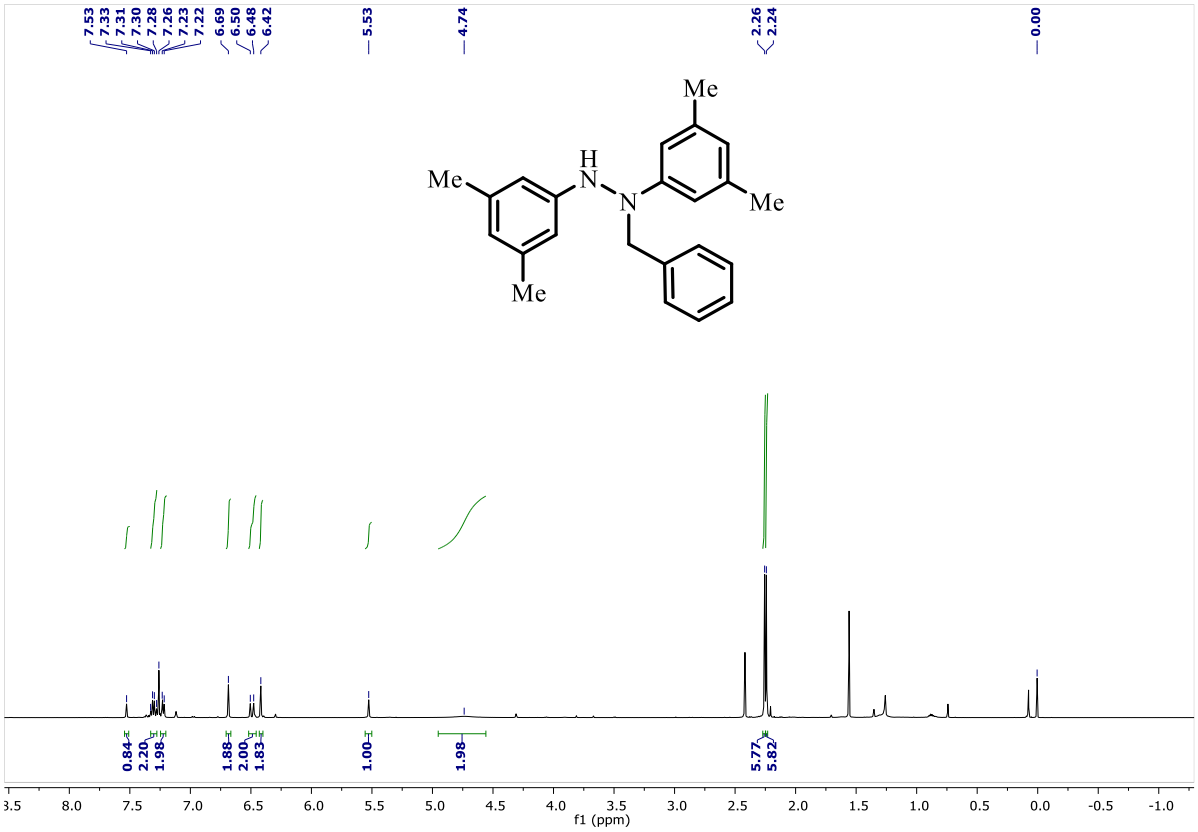


Figure S89: ^{1}H NMR Spectrum of **4d** ($CDCl_3$, 500 MHz, 298 K)

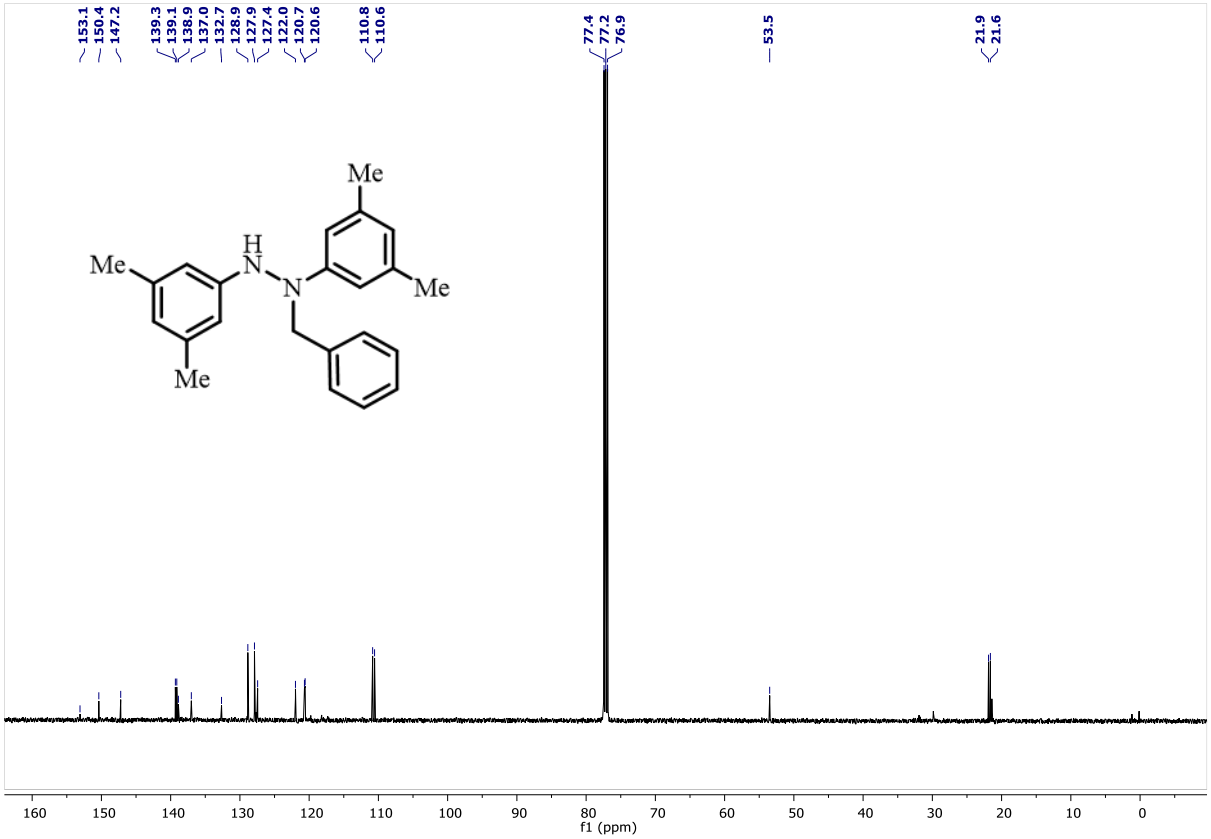


Figure S90: $^{13}C\{^{1}H\}$ NMR Spectrum of **4d** ($CDCl_3$, 126 MHz, 298 K)

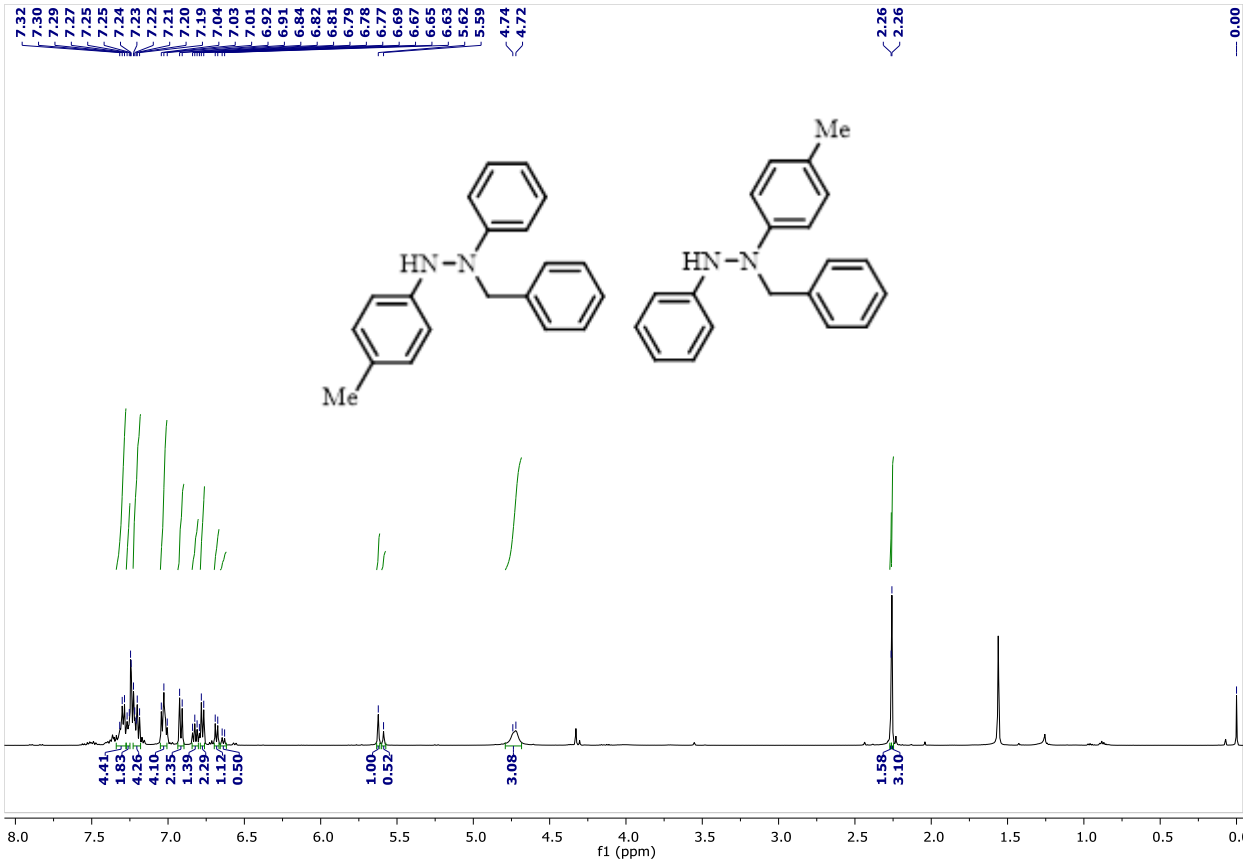


Figure S91: ^{1}H NMR Spectrum of **4e-1 + 4e-2** ($CDCl_3$, 500 MHz, 298 K)

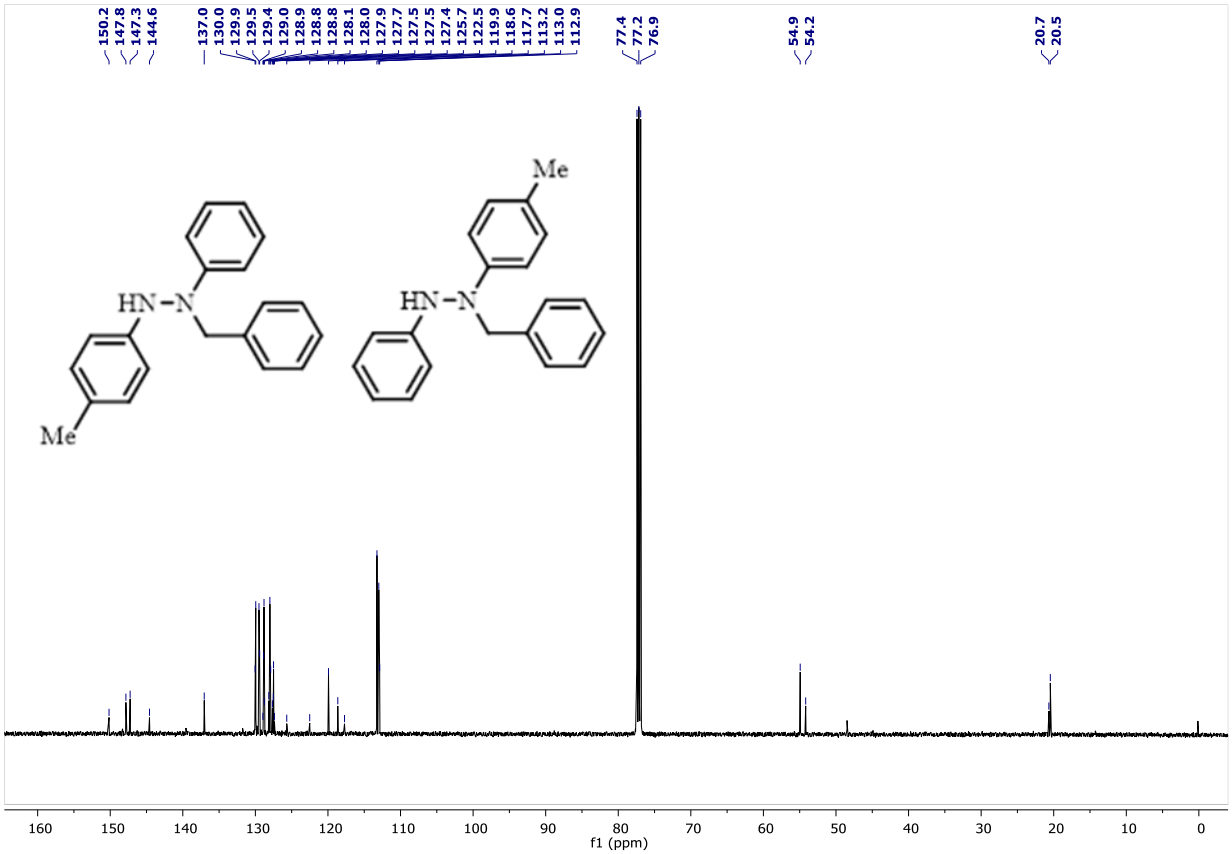


Figure S92: $^{13}C\{^{1}H\}$ NMR Spectrum of **4e-1 + 4e-2** ($CDCl_3$, 126 MHz, 298 K)

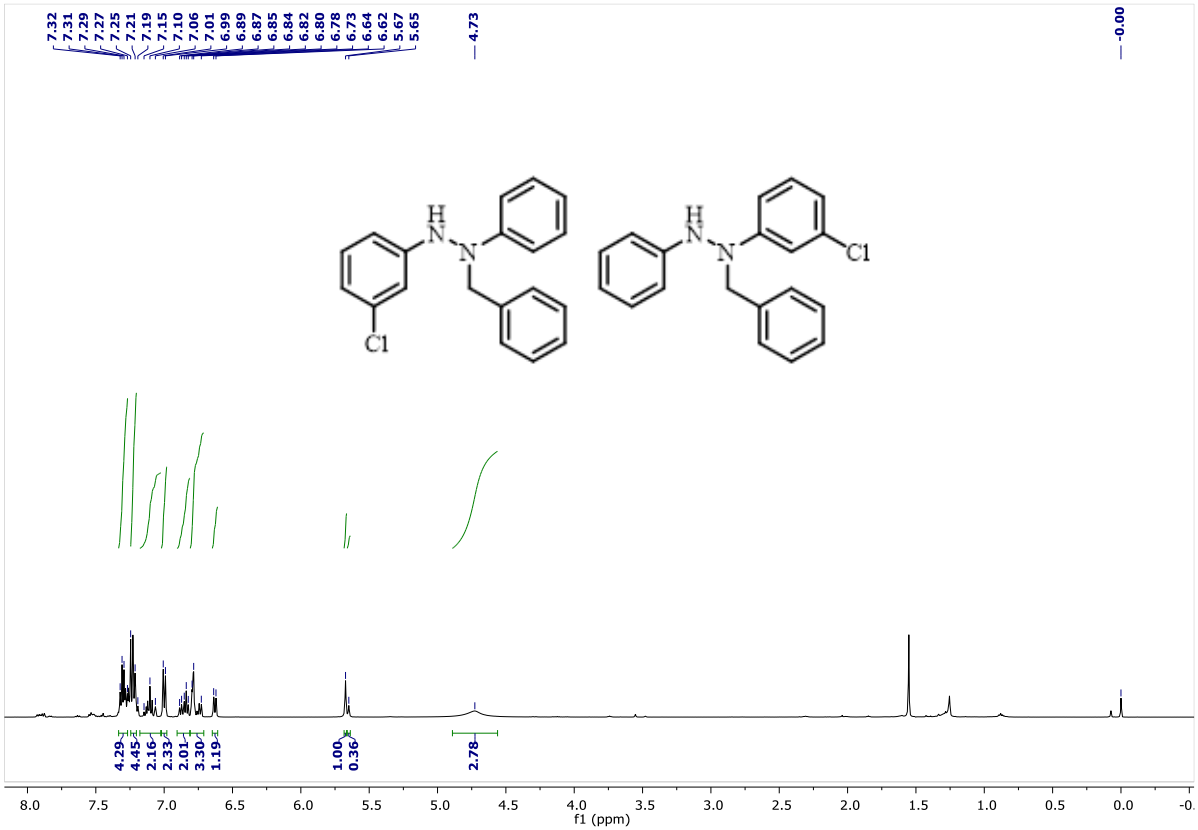


Figure S93: ^{1}H NMR Spectrum of **4f-1** + **4f-2** ($CDCl_3$, 500 MHz, 298 K)

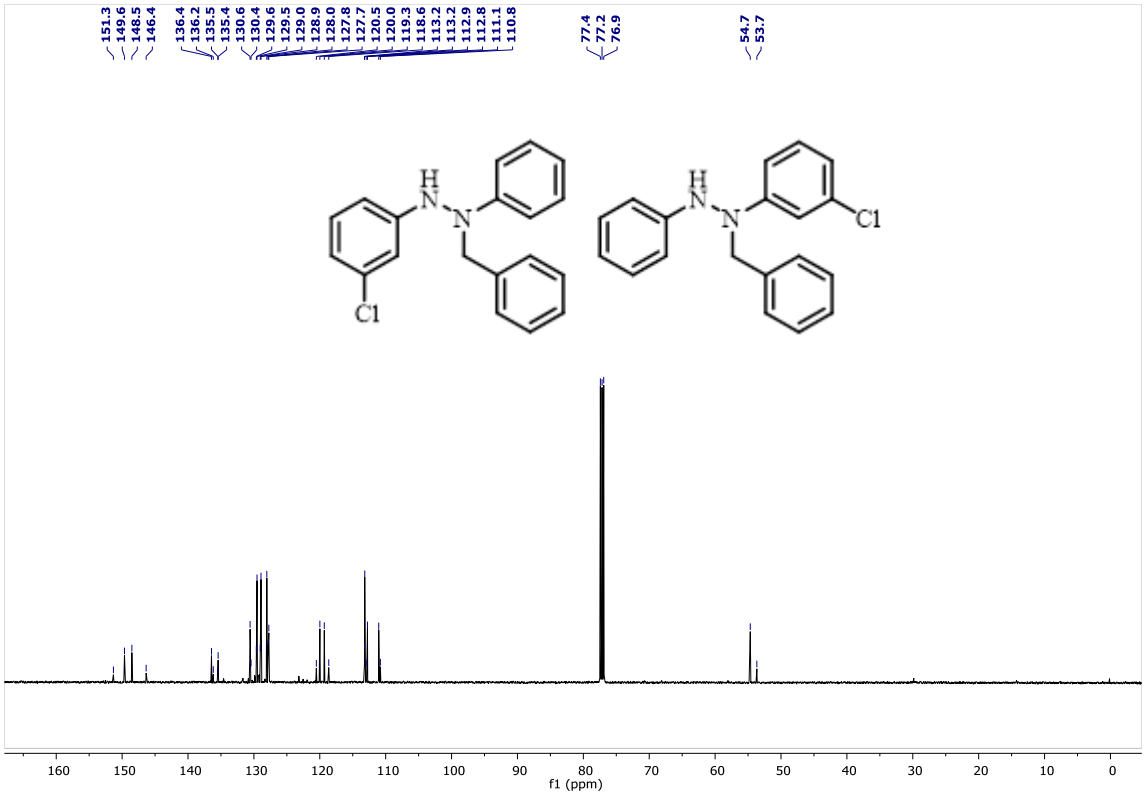


Figure S94: $^{13}C\{^{1}H\}$ NMR Spectrum of **4f-1** + **4f-2** ($CDCl_3$, 126 MHz, 298 K)

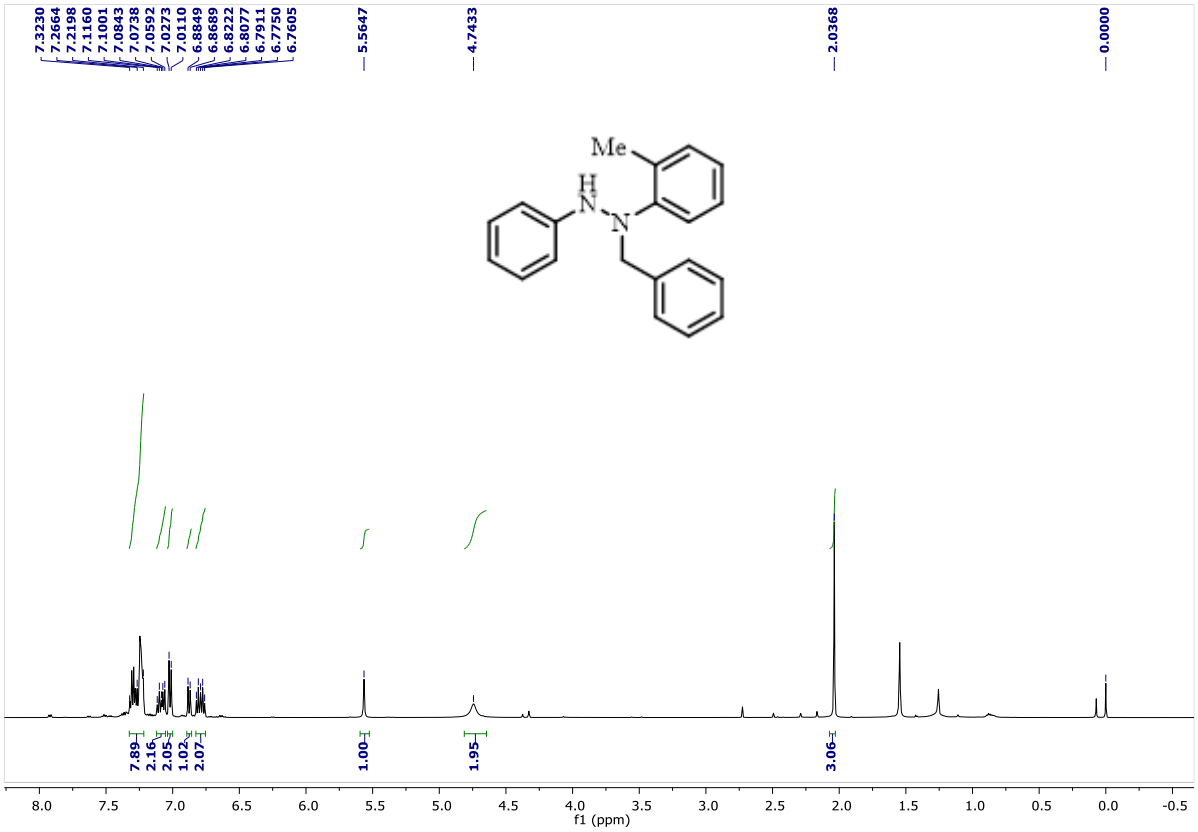


Figure S95: ^{1}H NMR Spectrum of **4g** ($CDCl_3$, 500 MHz, 298 K)

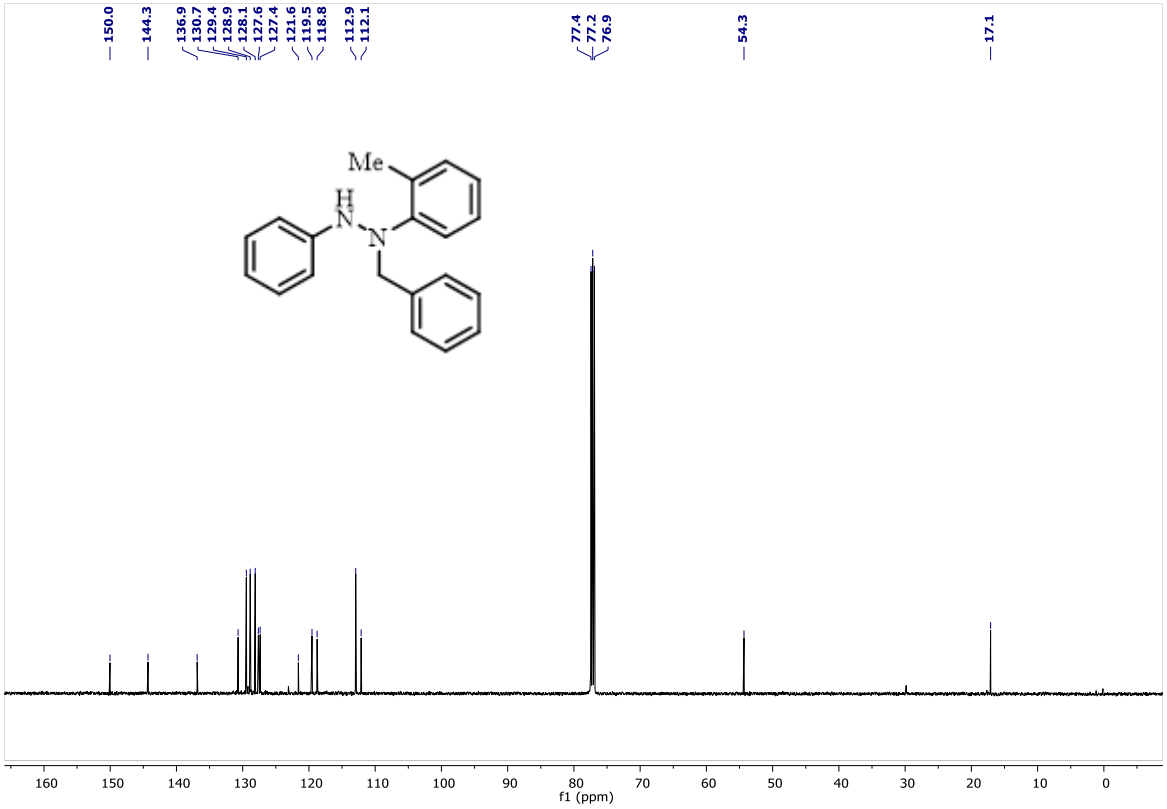


Figure S96: $^{13}C\{^{1}H\}$ NMR Spectrum of **4g** ($CDCl_3$, 126 MHz, 298 K)

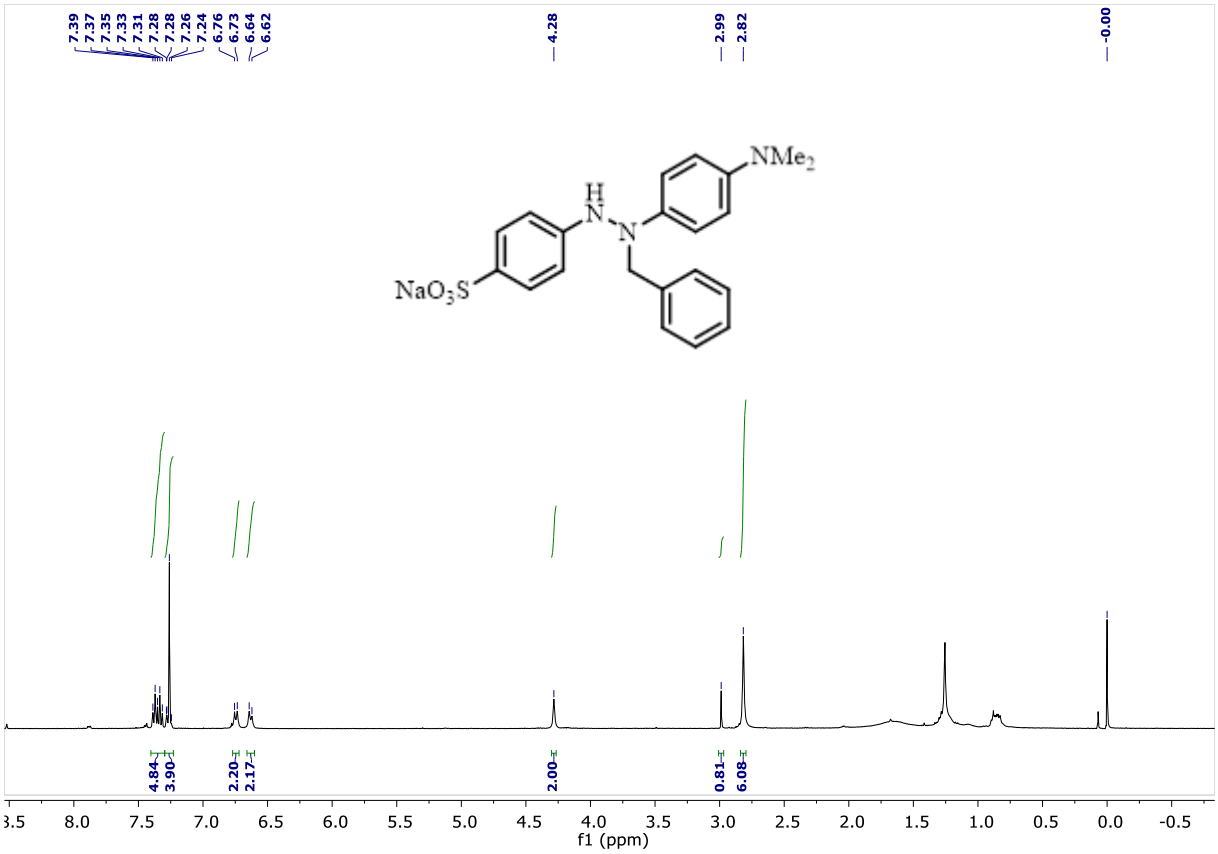


Figure S97: ^{1}H NMR Spectrum of **4h** ($CDCl_3$, 400 MHz, 298 K)

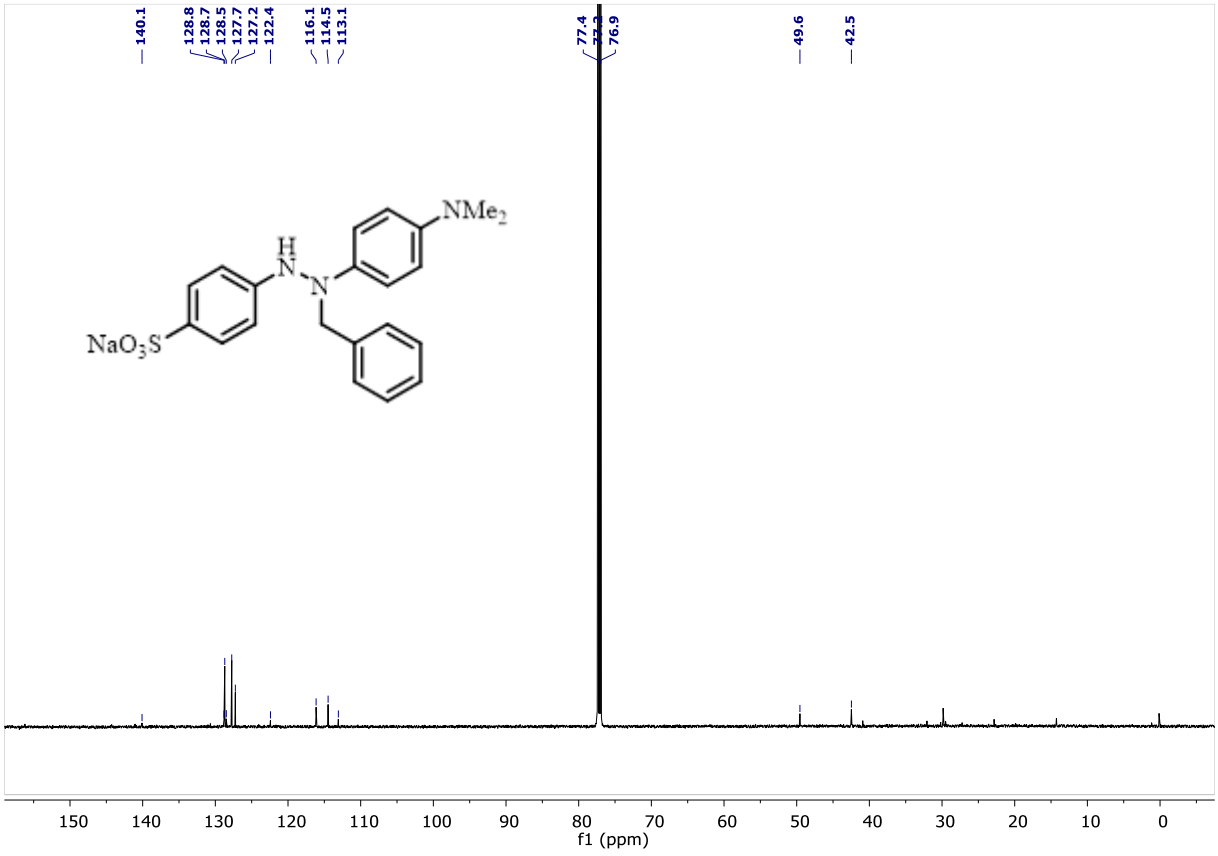


Figure S98: $^{13}C\{^{1}H\}$ NMR Spectrum of **4h** ($CDCl_3$, 151 MHz, 298 K)

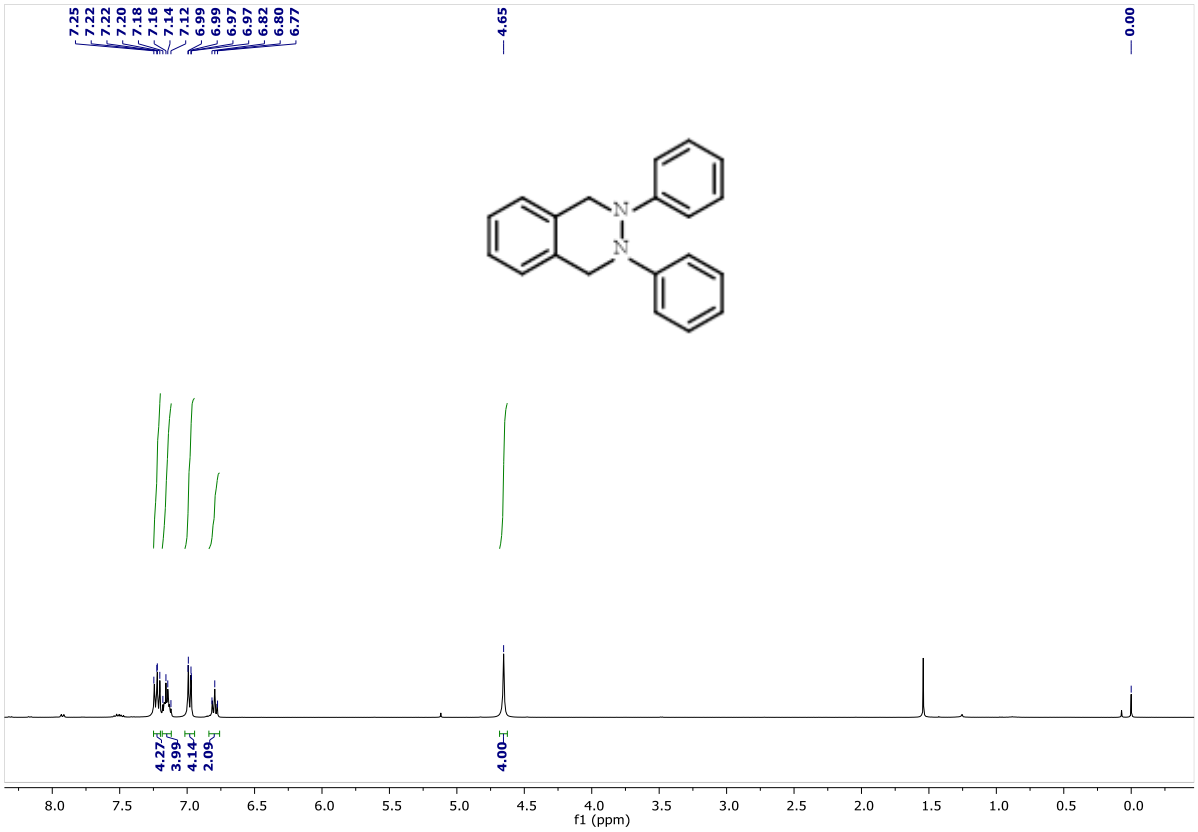


Figure S99: ^{1}H NMR Spectrum of **5a** ($CDCl_3$, 400 MHz, 298 K)

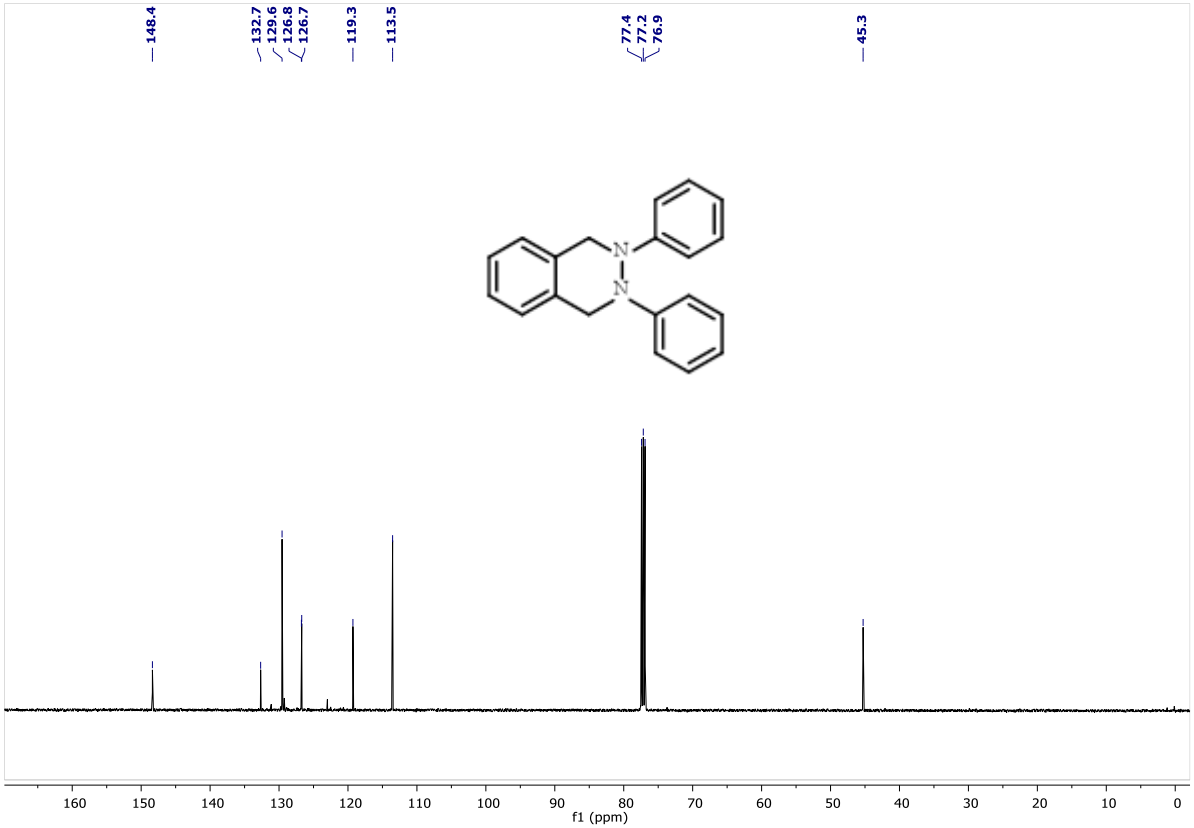


Figure S100: $^{13}C\{^{1}H\}$ NMR Spectrum of **5a** ($CDCl_3$, 126 MHz, 298 K)

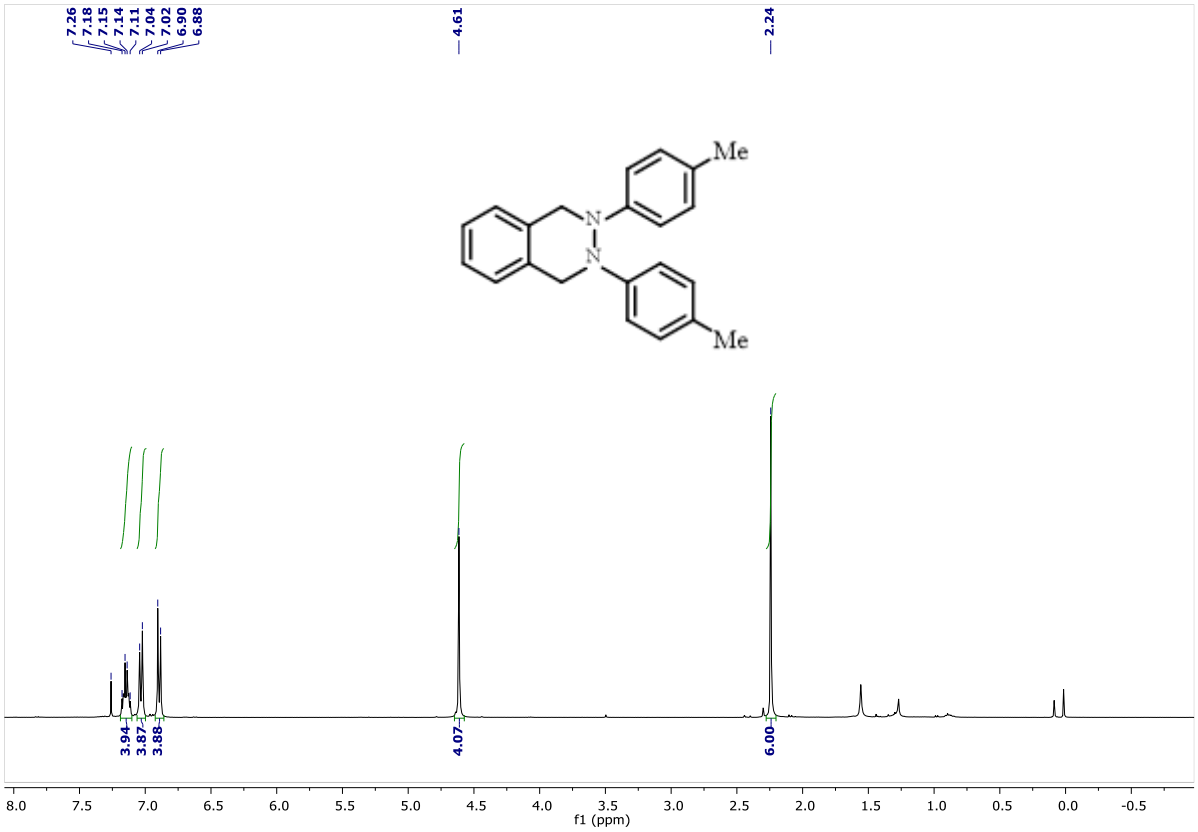


Figure S101: ^{1}H NMR Spectrum of **5b** ($CDCl_3$, 400 MHz, 298 K)

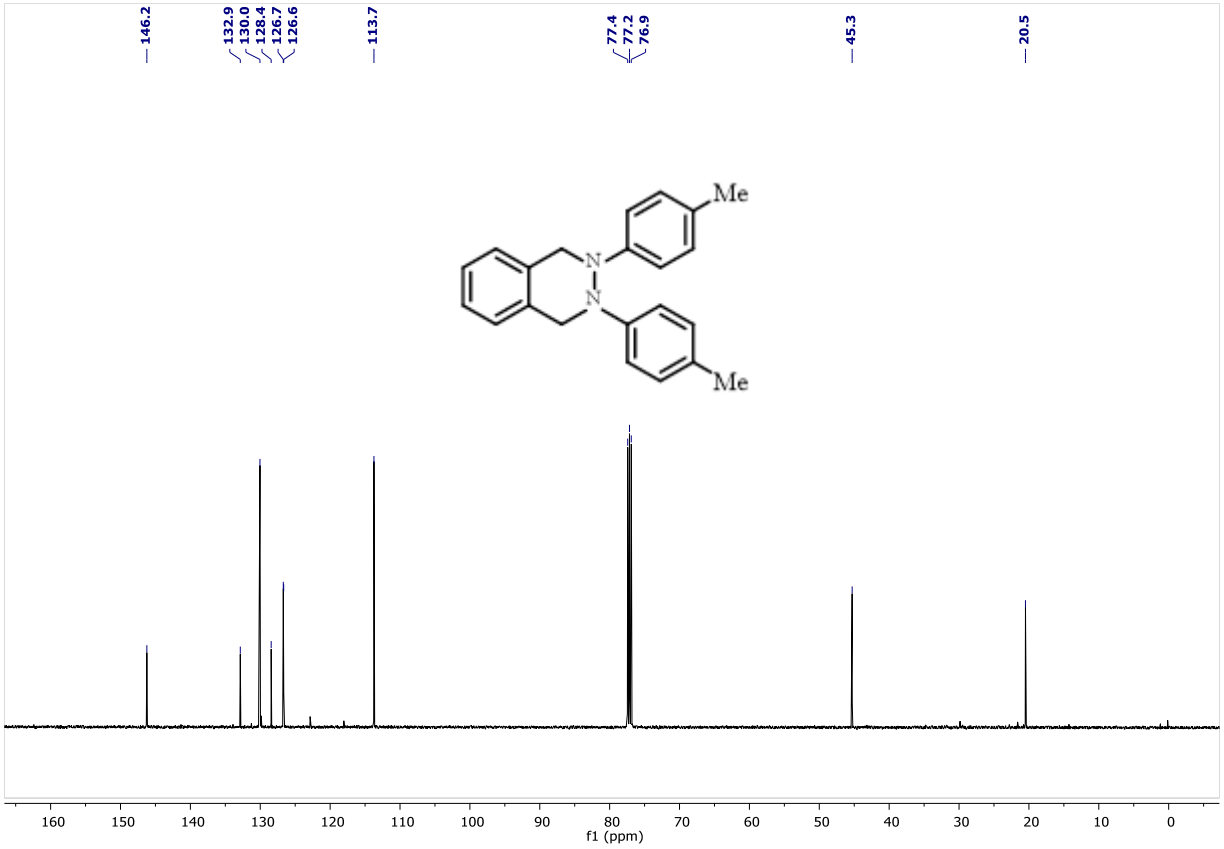


Figure S102: ^{13}C{^{1}H} NMR Spectrum of **5b** ($CDCl_3$, 126 MHz, 298 K)

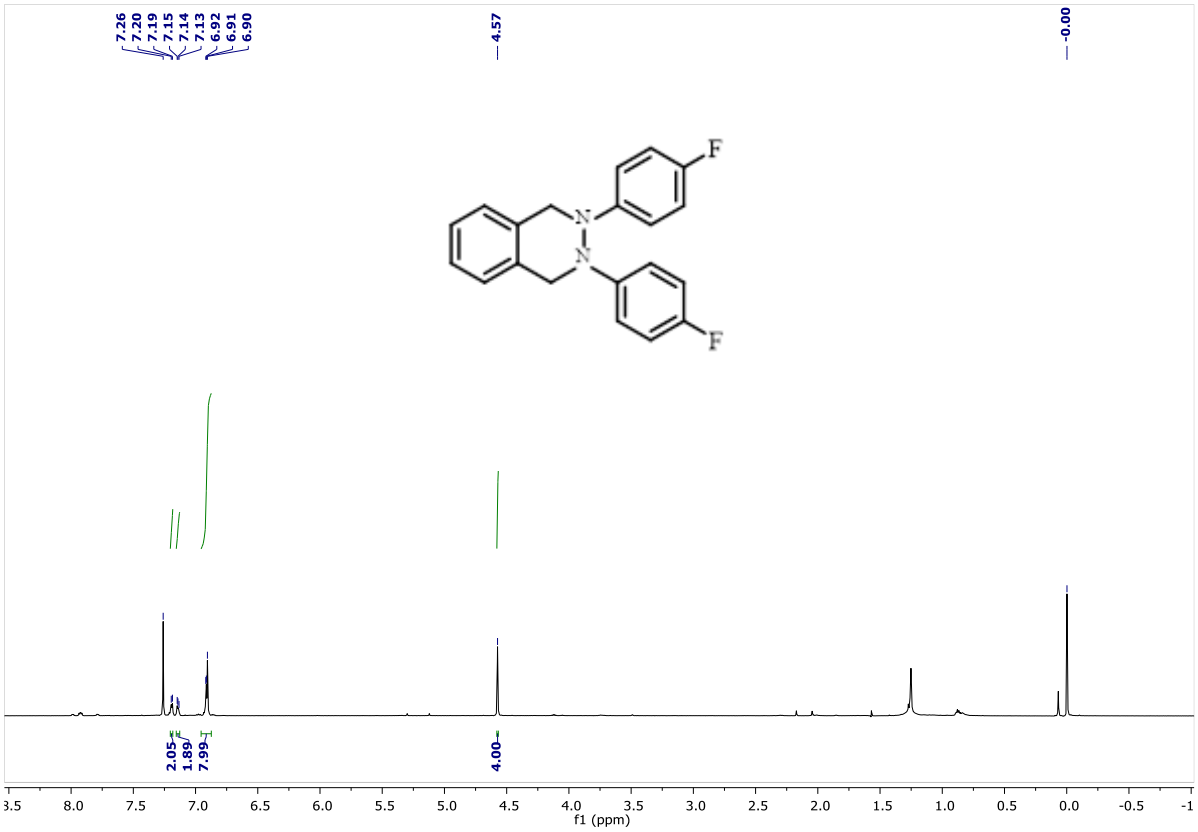


Figure S103: ^{1}H NMR Spectrum of **5c** ($CDCl_3$, 600 MHz, 298 K)

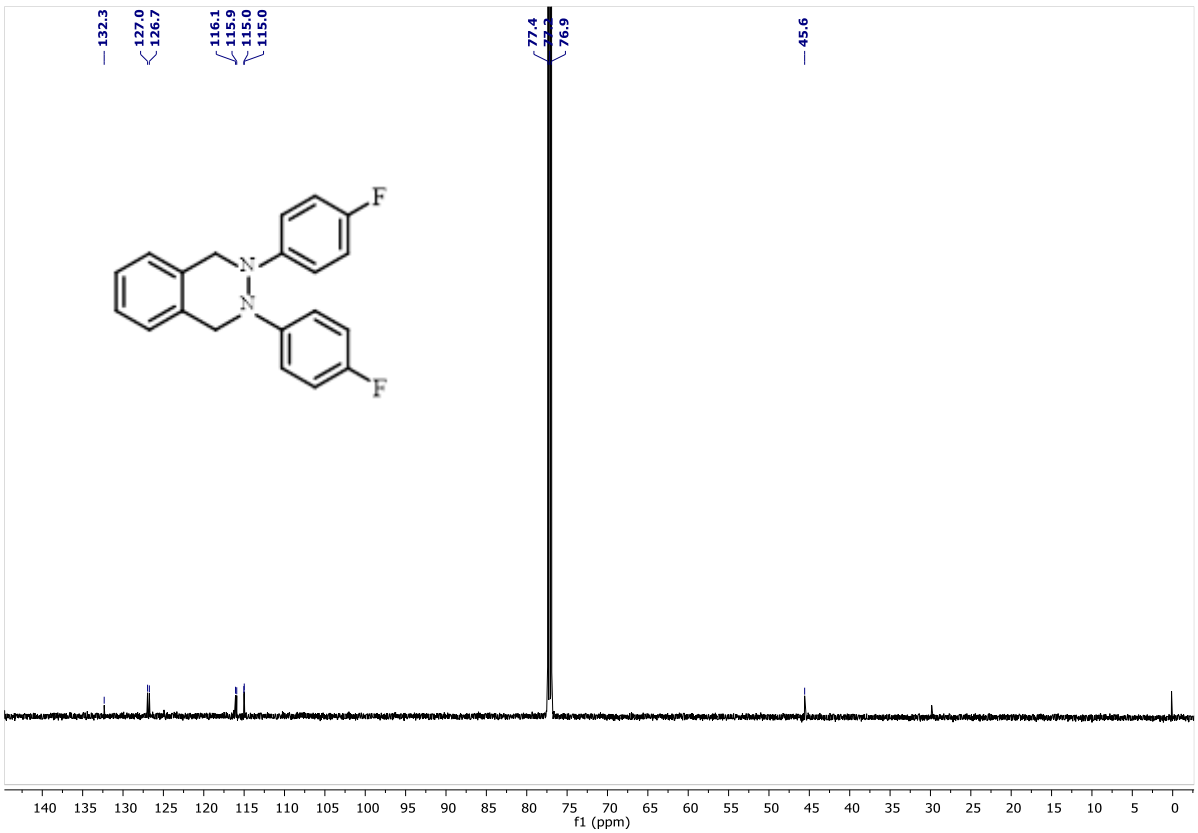


Figure S104: $^{13}C\{^{1}H\}$ NMR Spectrum of **5c** ($CDCl_3$, 151 MHz, 298 K)

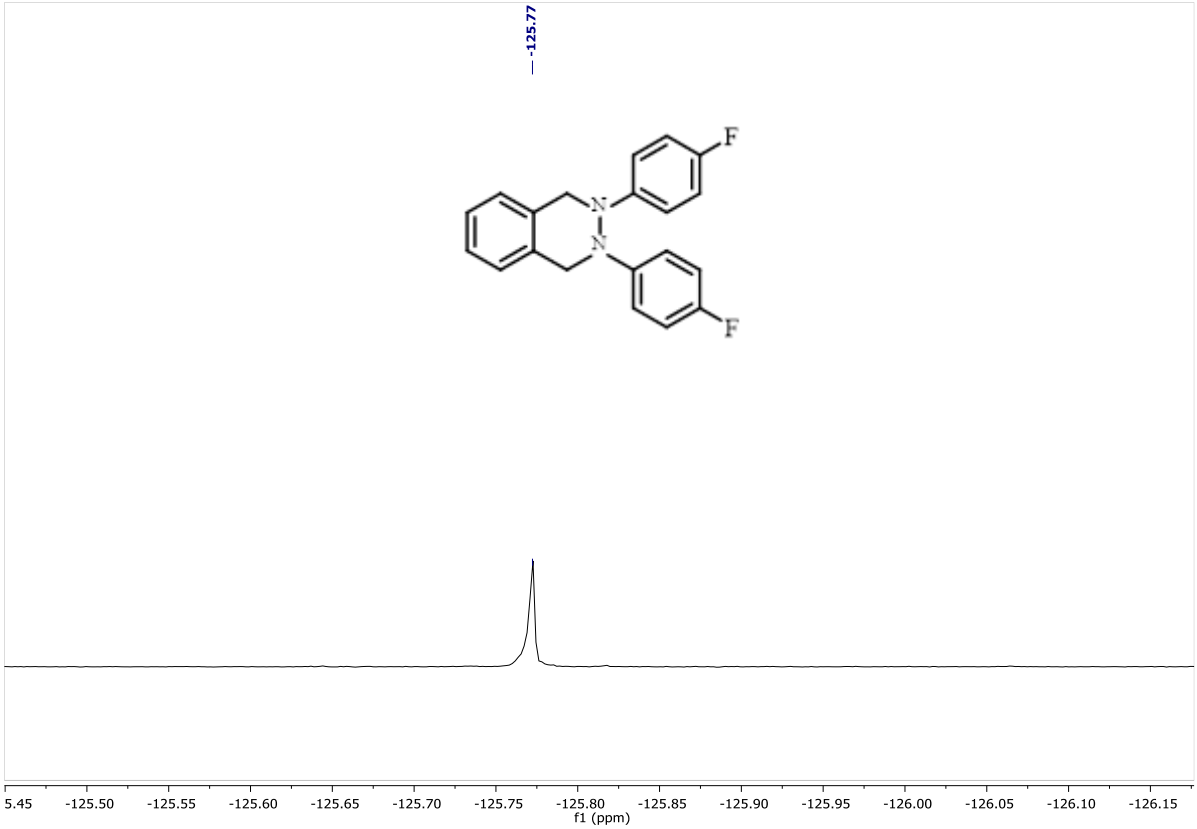


Figure S105: $^{19}F\{^{1}H\}$ NMR Spectrum of **5c** ($CDCl_3$, 565 MHz, 298 K)

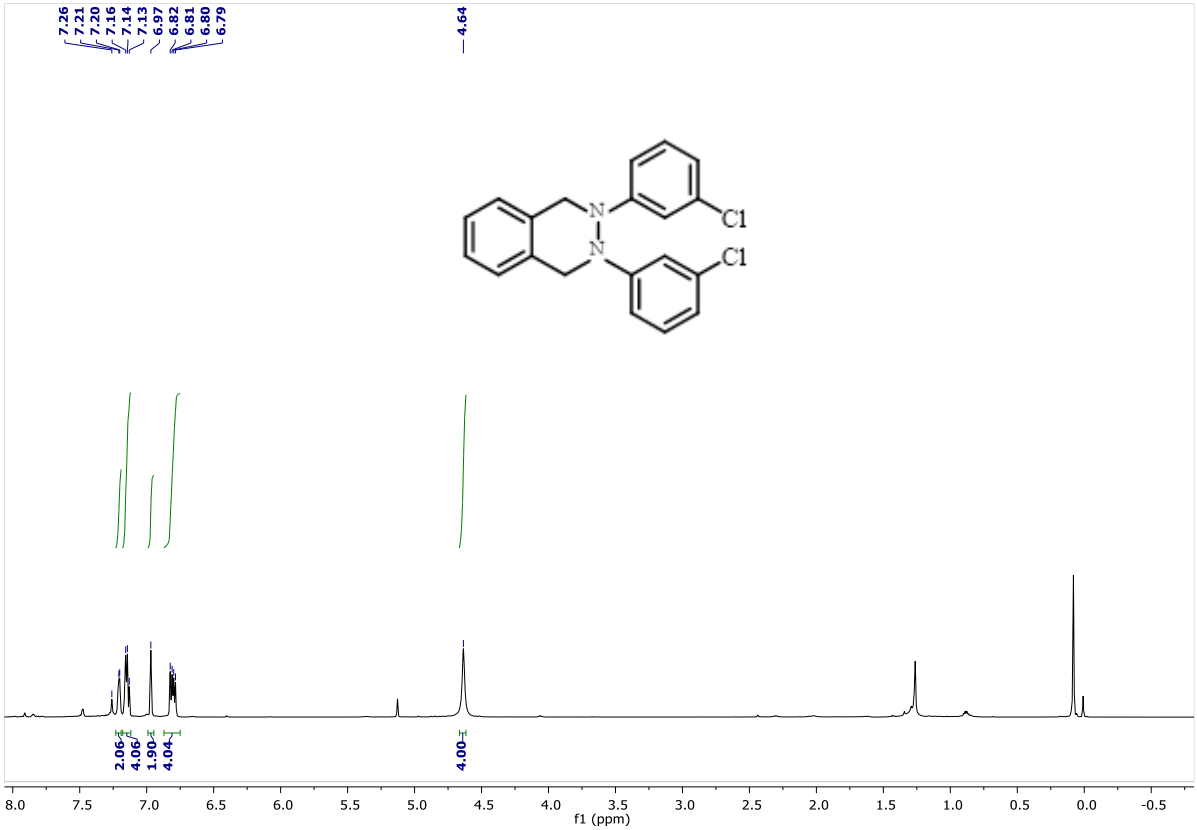


Figure S106: ^{1}H NMR Spectrum of **5d** ($CDCl_3$, 600 MHz, 298 K)

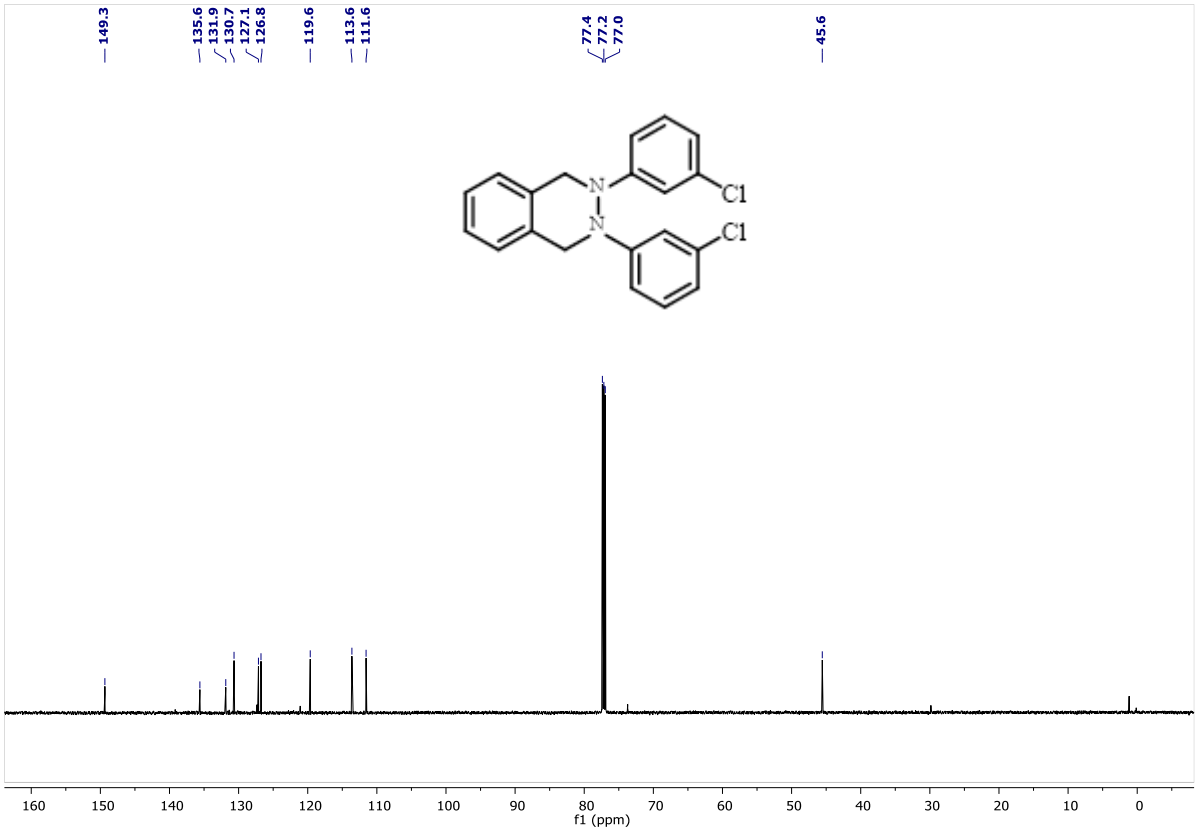


Figure S107: $^{13}C\{^{1}H\}$ NMR Spectrum of **5d** ($CDCl_3$, 151 MHz, 298 K)

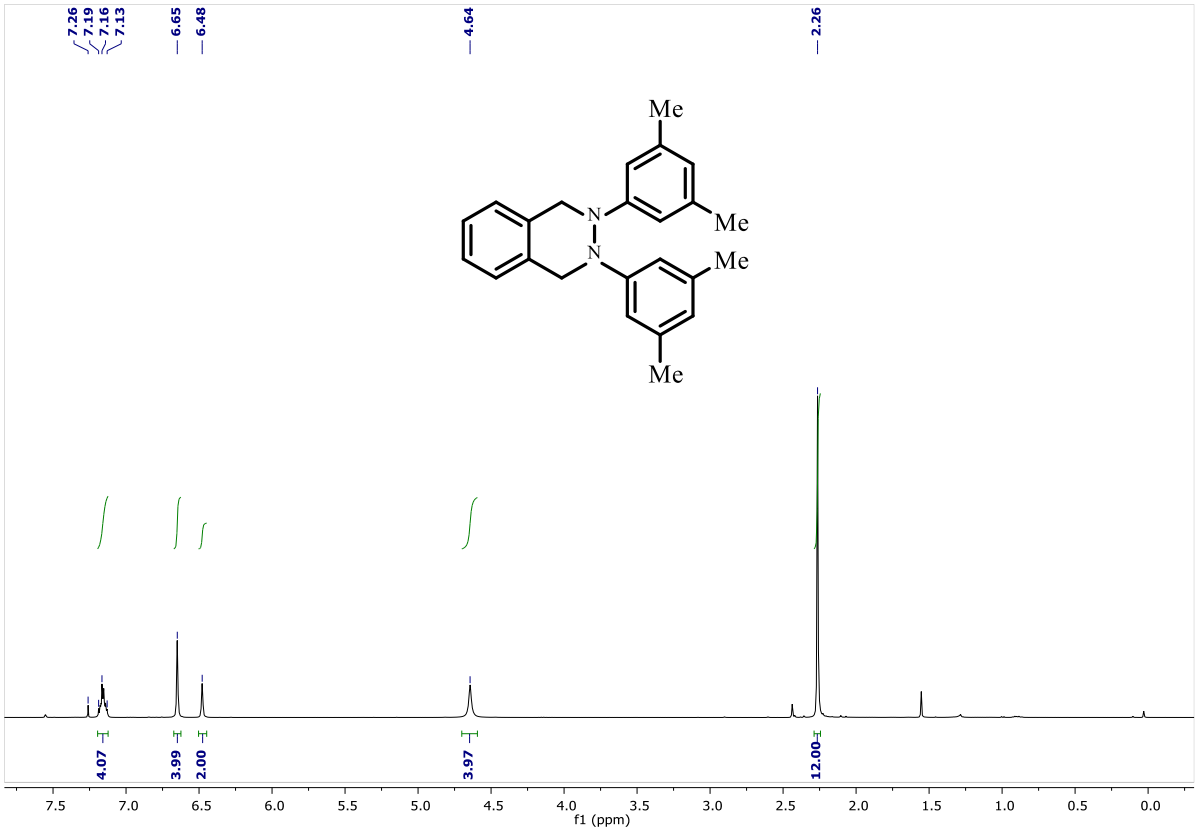


Figure S108: ^{1}H NMR Spectrum of **5e** ($CDCl_3$, 400 MHz, 298 K)

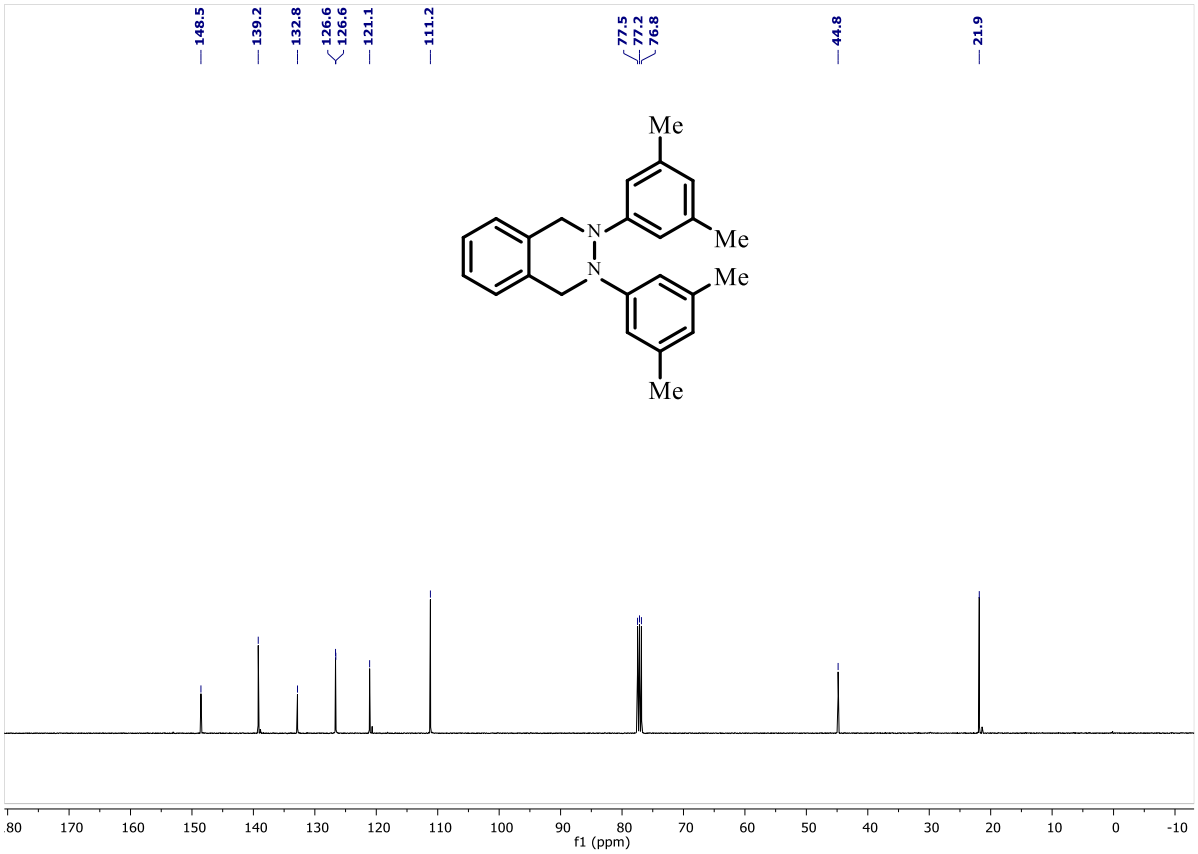


Figure S109: $^{13}C\{^{1}H\}$ NMR Spectrum of **5e** ($CDCl_3$, 101 MHz, 298 K)

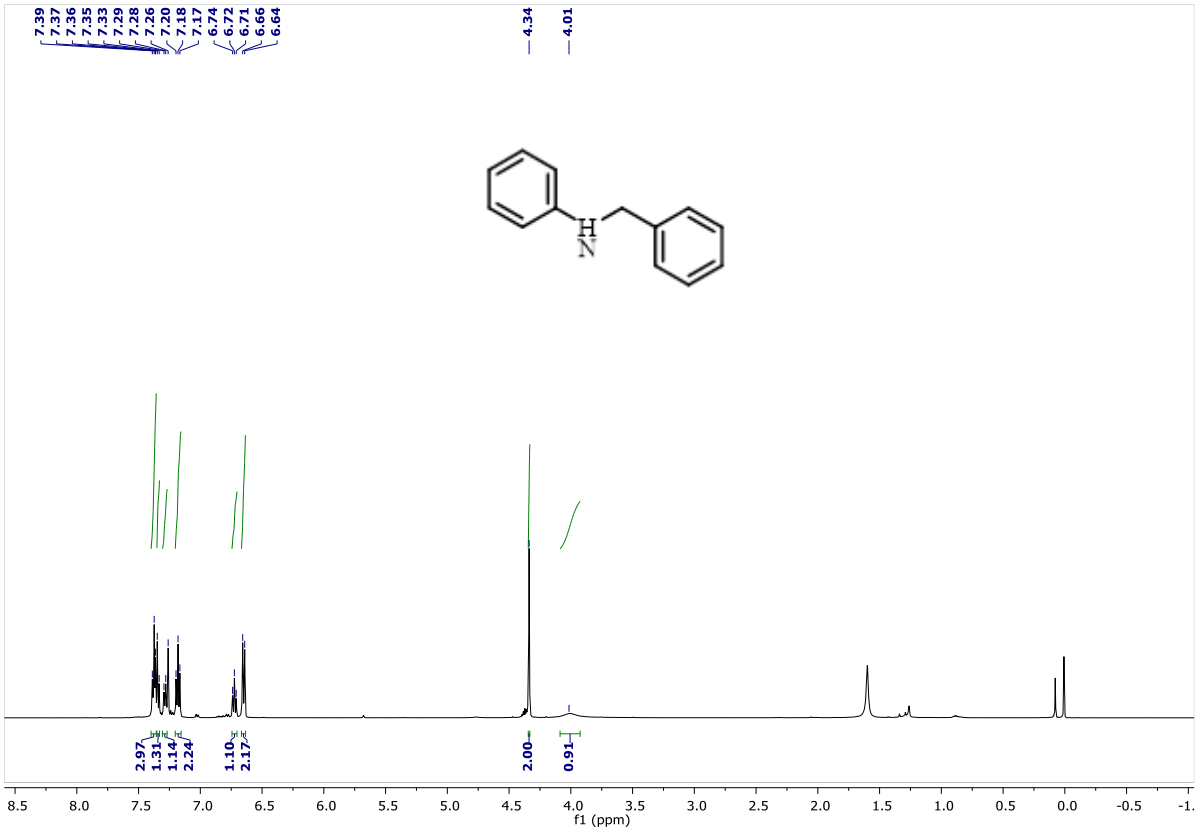


Figure S110: ^{1}H NMR Spectrum of **6a** ($CDCl_3$, 500 MHz, 298 K)

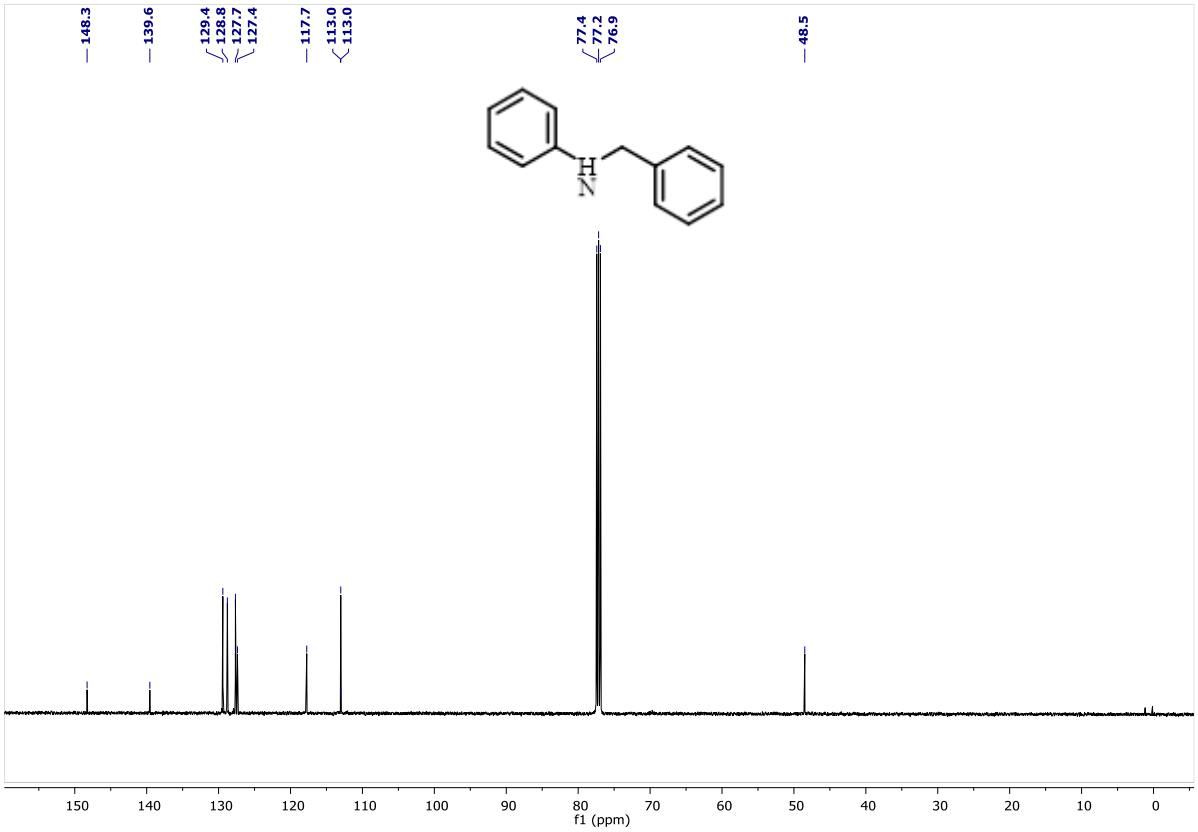


Figure S111: $^{13}C\{^{1}H\}$ NMR Spectrum of **6a** ($CDCl_3$, 126 MHz, 298 K)

Figure S112: ^{1}H NMR Spectrum of **6b** ($CDCl_3$, 500 MHz, 298 K)

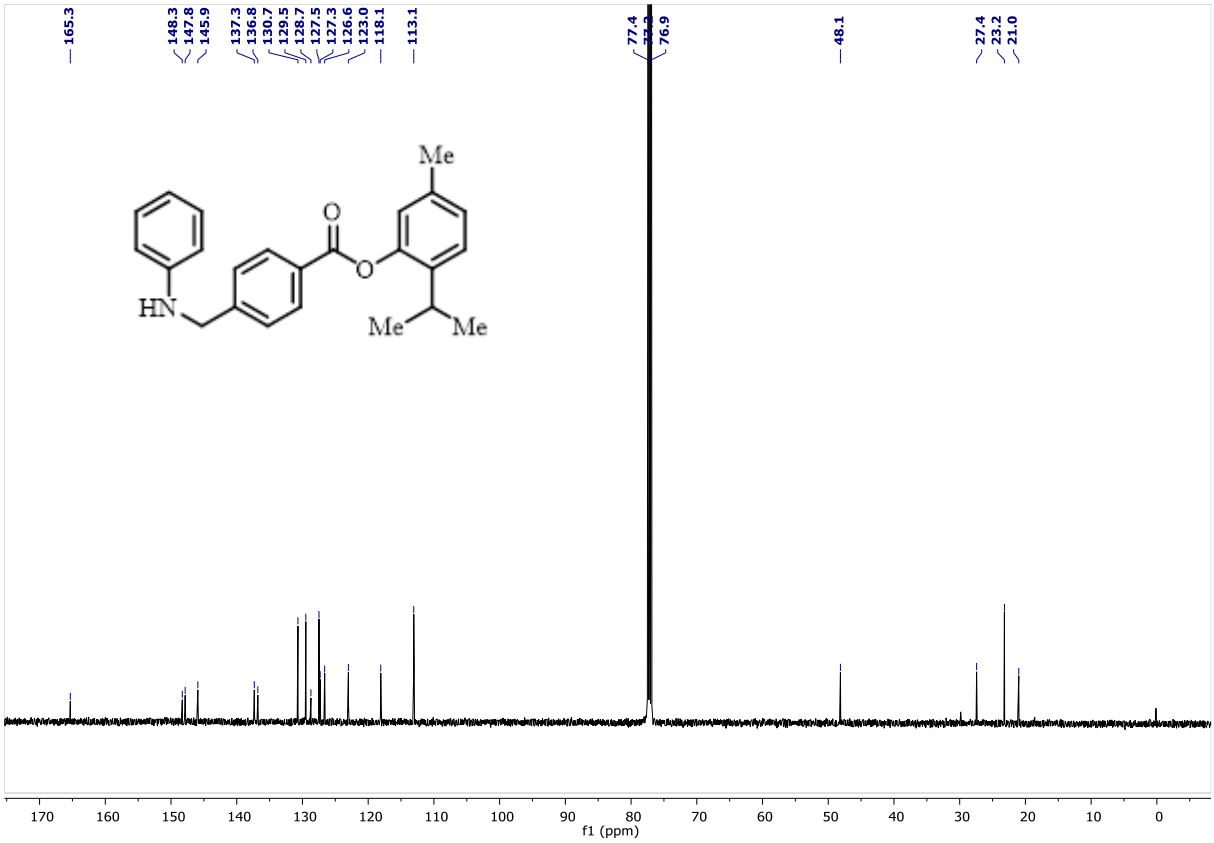


Figure S113: $^{13}C\{^{1}H\}$ NMR Spectrum of **6b** ($CDCl_3$, 126 MHz, 298 K)

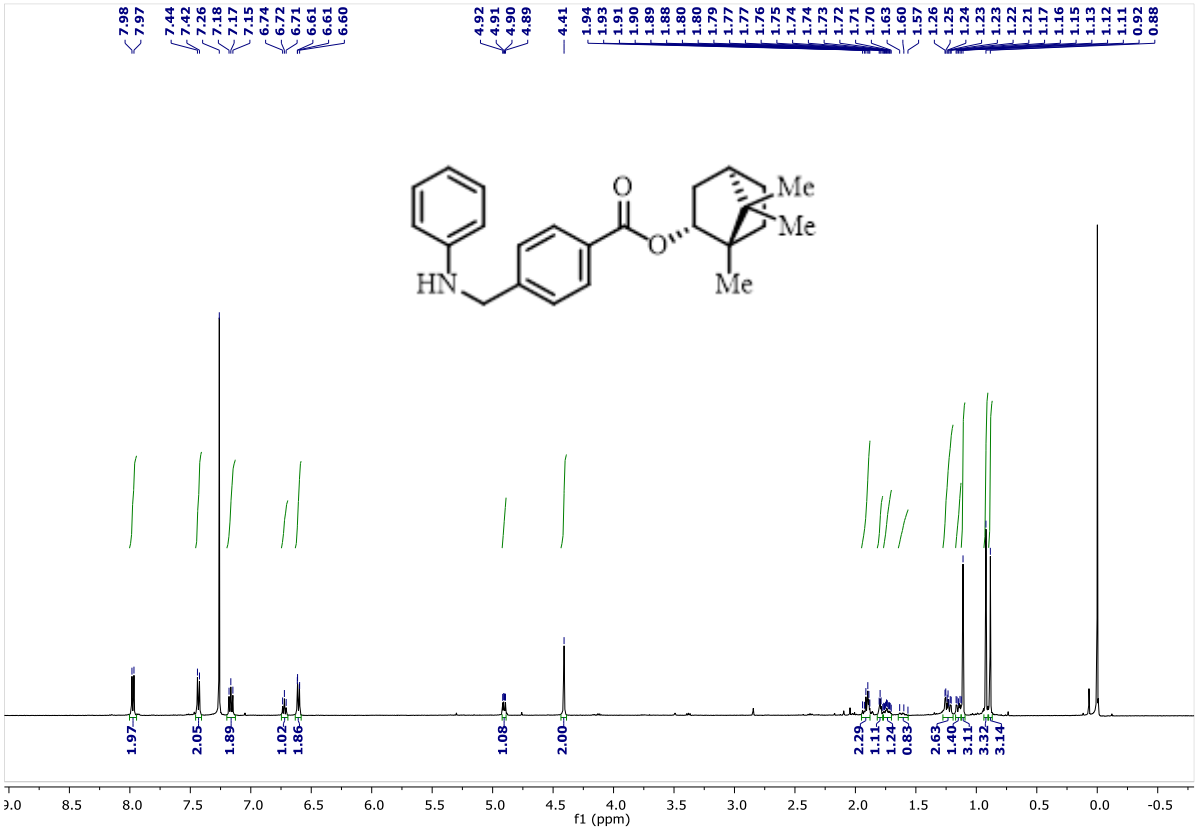


Figure S114: ^{1}H NMR Spectrum of **6c** ($CDCl_3$, 500 MHz, 298 K)

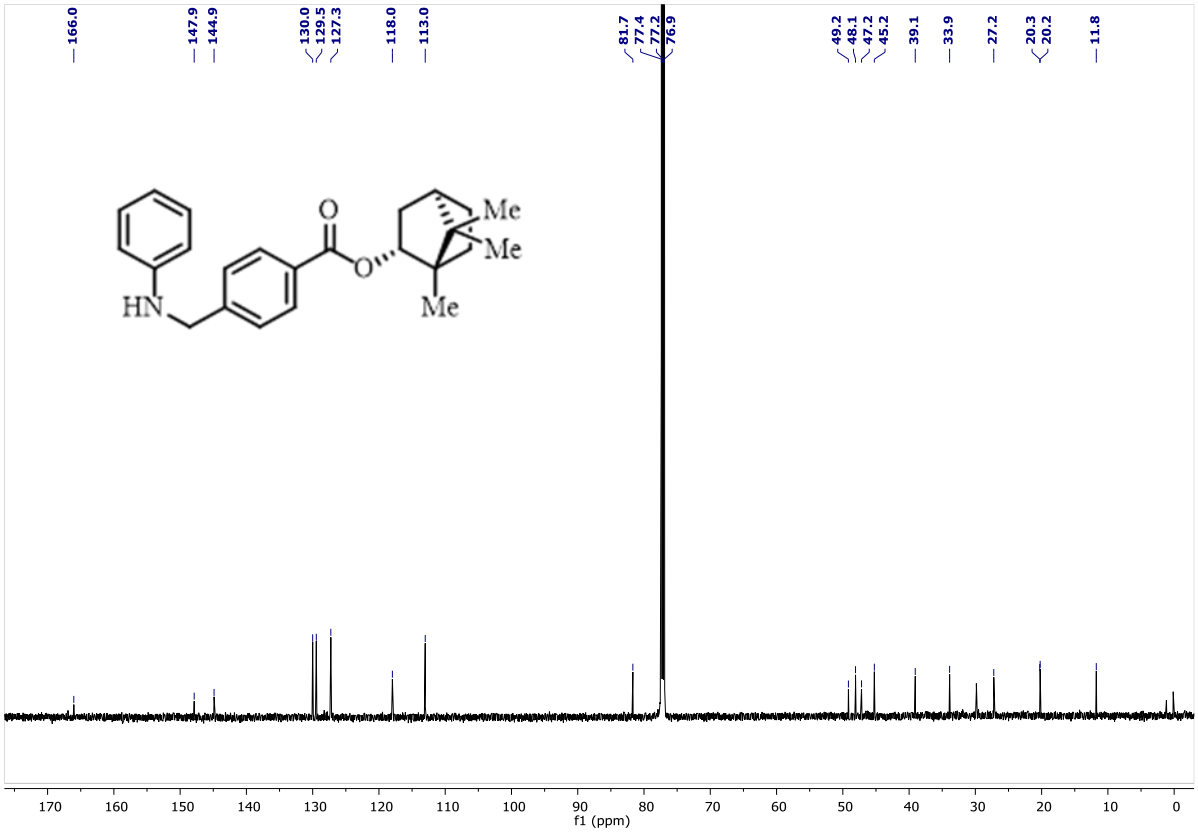


Figure S115: $^{13}C\{^{1}H\}$ NMR Spectrum of **6c** ($CDCl_3$, 151 MHz, 298 K)

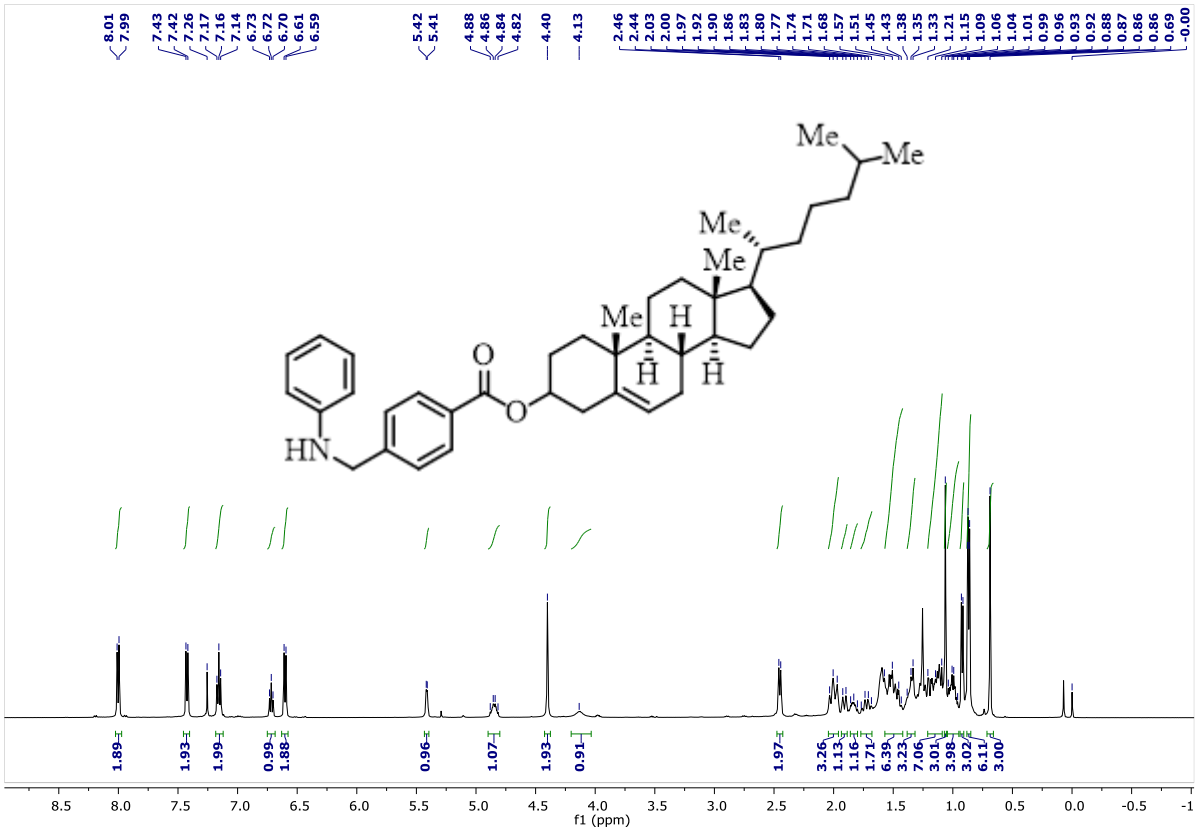


Figure S116: ^{1}H NMR Spectrum of **6d** ($CDCl_3$, 500 MHz, 298 K)

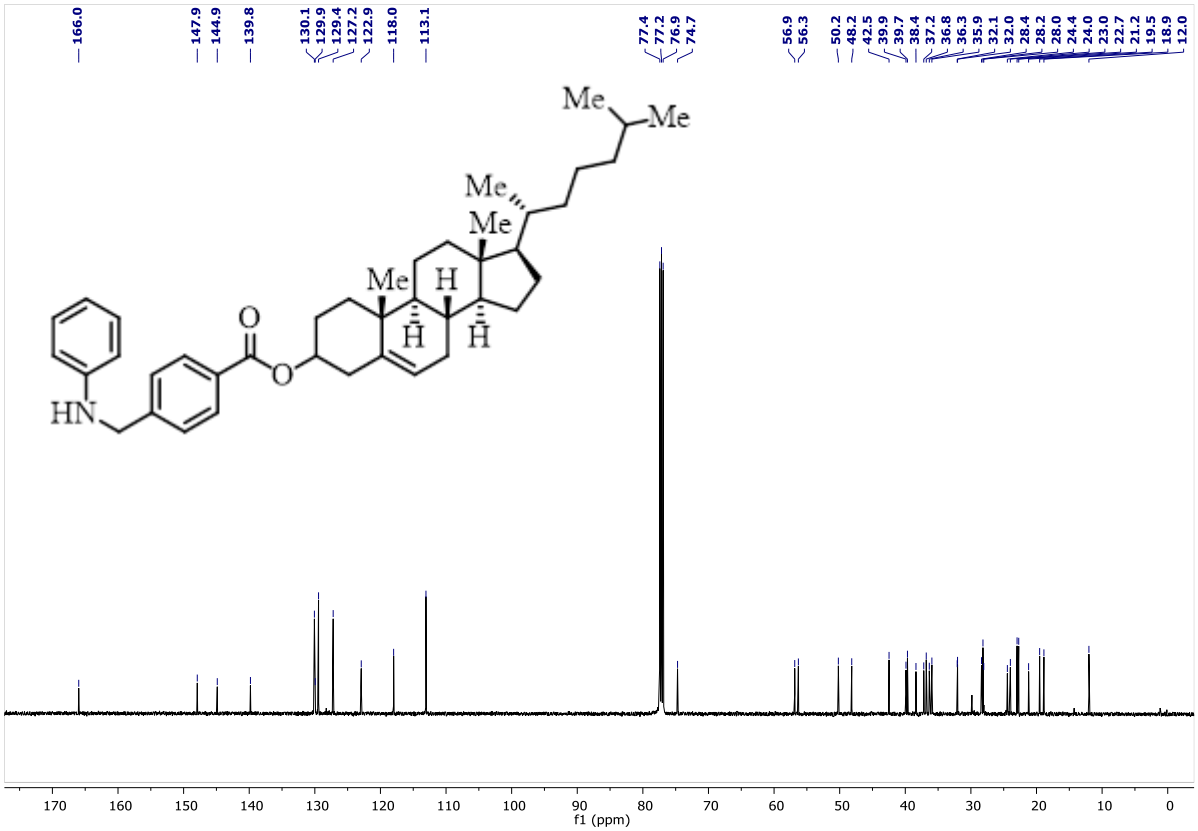


Figure S117: $^{13}C\{^{1}H\}$ NMR Spectrum of **6d** ($CDCl_3$, 126 MHz, 298 K)

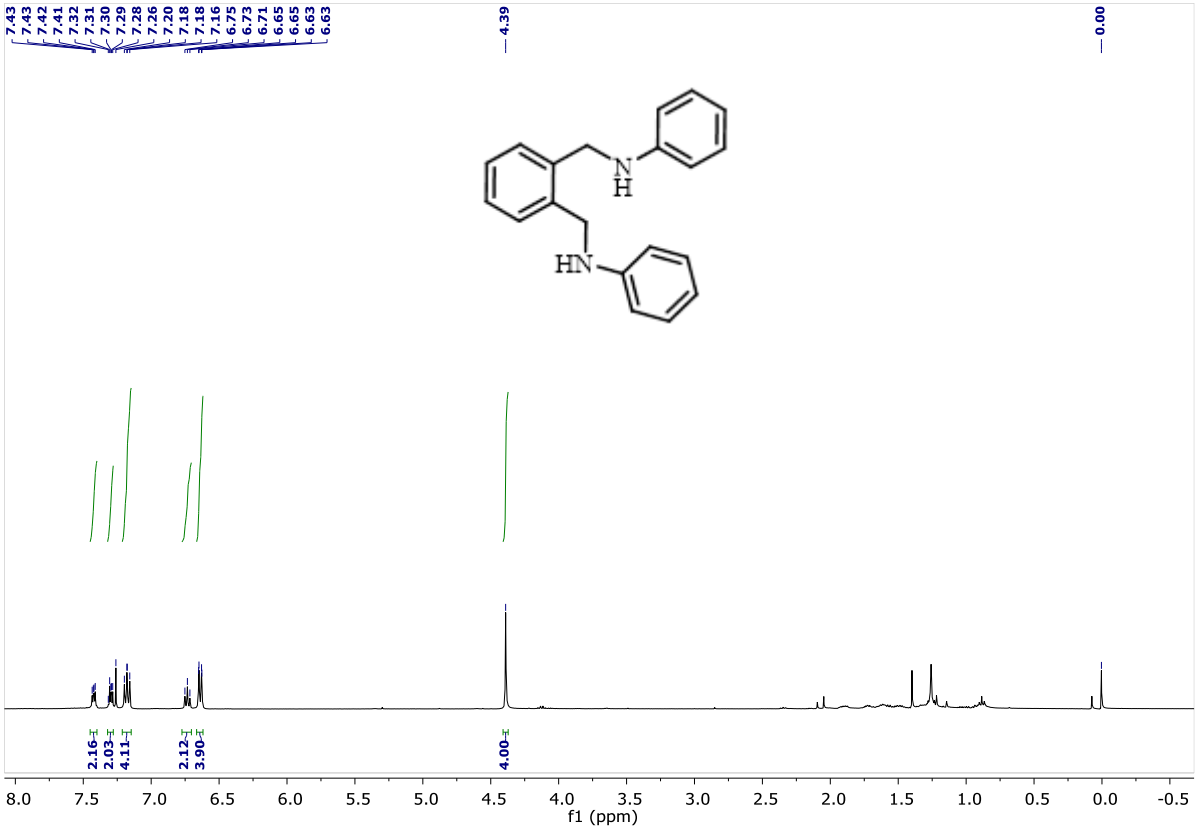


Figure S118: ^{1}H NMR Spectrum of **7** ($CDCl_3$, 400 MHz, 298 K)

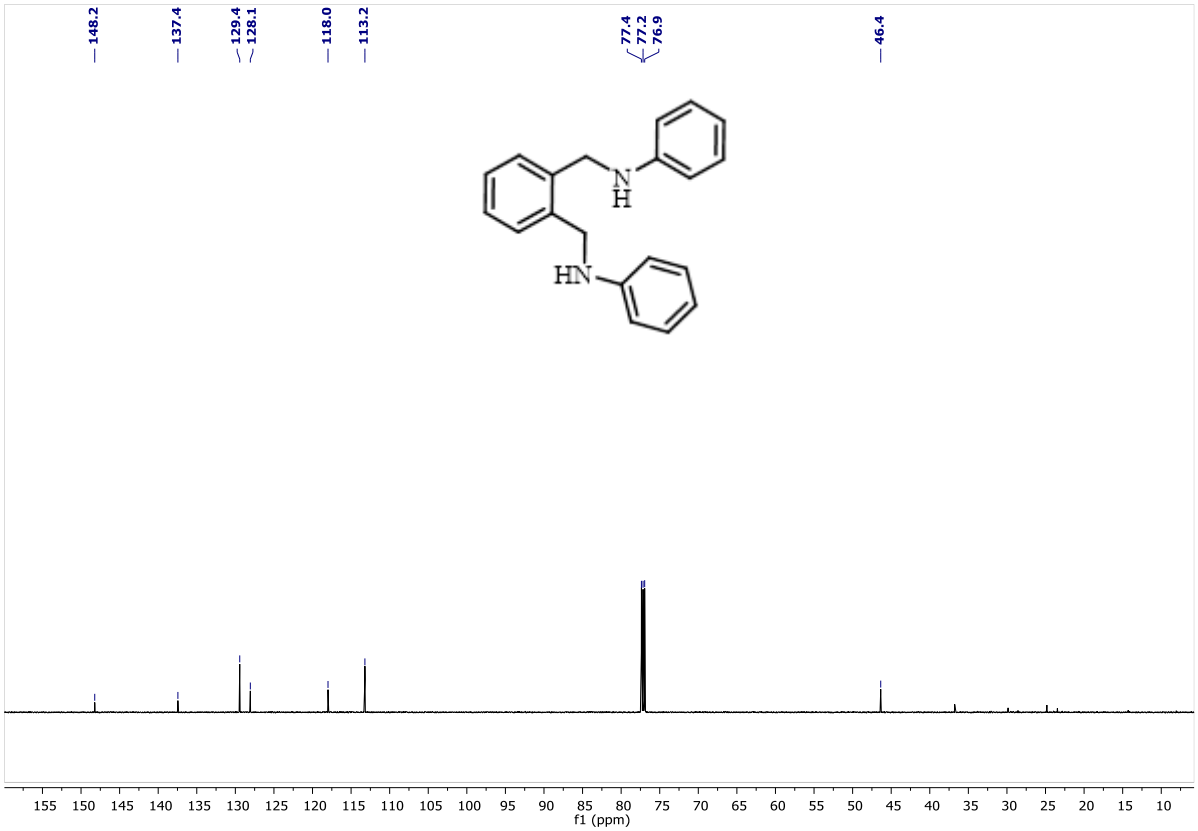


Figure S119: $^{13}C\{^{1}H\}$ NMR Spectrum of **7** ($CDCl_3$, 151 MHz, 298 K)

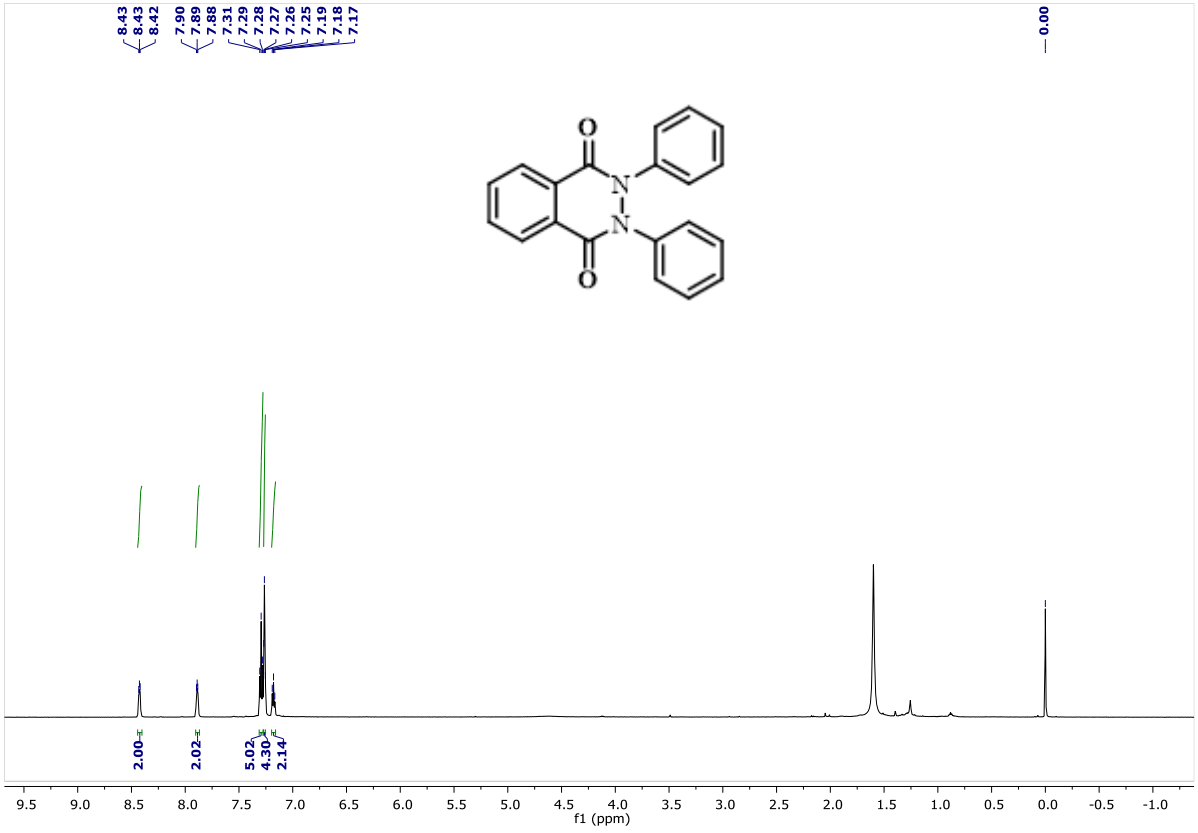


Figure S120: ^{1}H NMR Spectrum of **8** ($CDCl_3$, 600 MHz, 298 K)

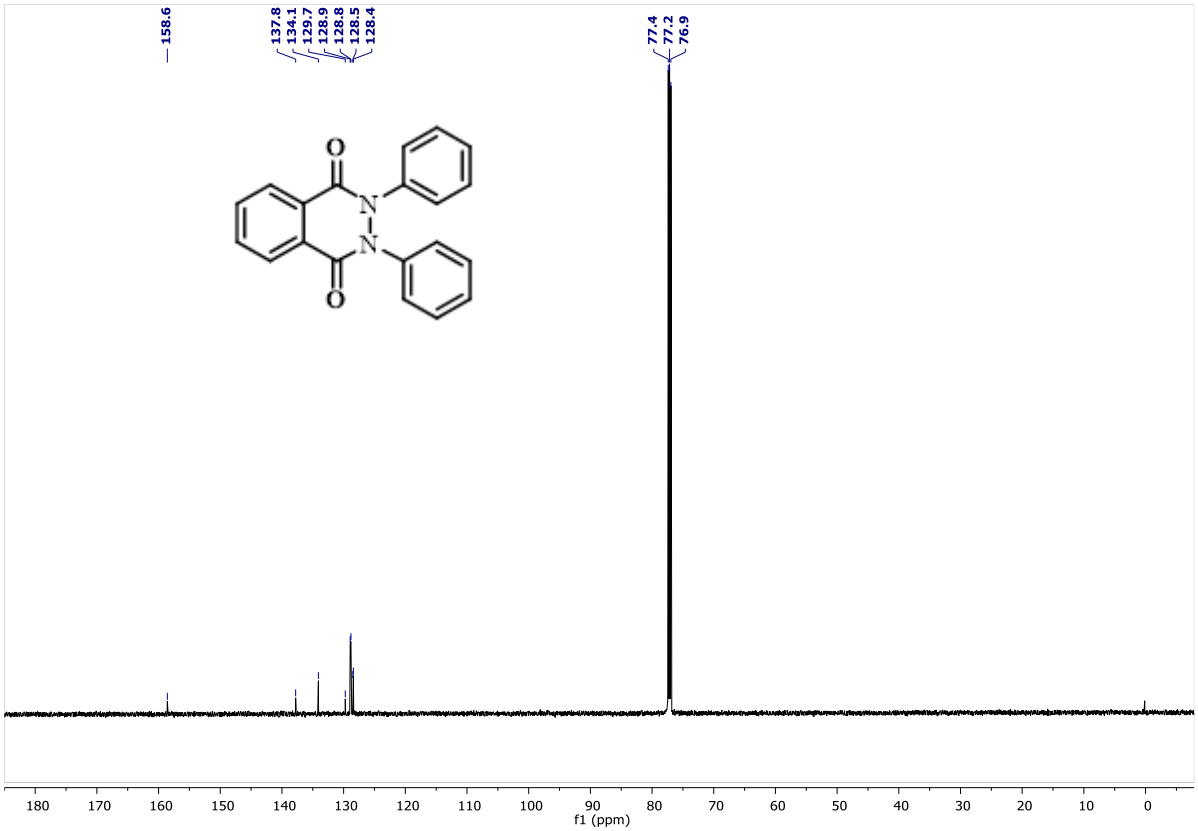


Figure S121: $^{13}C\{^{1}H\}$ NMR Spectrum of **8** ($CDCl_3$, 151 MHz, 298 K)

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