Electronic Supporting Information

Ligand-Assisted Nickel Catalysis Enabling N, N-Dialkylation and Cyclization of Acyl Hydrazides Using Aliphatic Alcohols

Ayanangshu Biswas, Sourav Mandal, Supriya Halder, Bikramaditya Mandal and Debashis Adhikari*

Department of Chemical Sciences, Indian Institute of Science Education and Research

Mohali, SAS Nagar-140306, India: Email: adhikari@iisermohali.ac.in

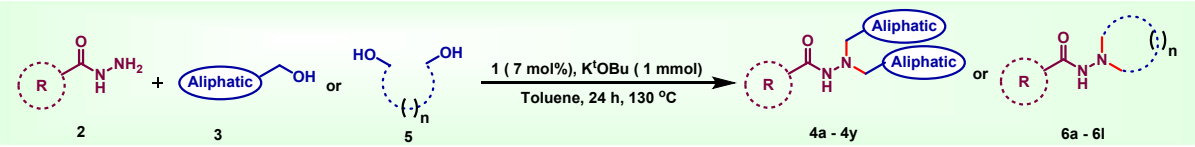
Table of contents

1. General information

Reagent information: All starting materials utilized in this study were procured from commercial suppliers. Potassium *tert*-butoxide, potassium hydroxide, potassium carbonate, sodium hydroxide were purchased from Avra Synthesis Pvt. Ltd., India. Primary and secondary alcohols were purchased from TCI (India) and BLD Pharma. Benzoyl hydrazide was purchased from BLD Pharma. All these chemicals were used without further purification. Glassware was dried overnight at 160 °C. Solvents such as acetonitrile, ethanol, and dichloromethane were used as received (Finar Chemicals). Toluene was dried by heating over sodium with benzophenone as an indicator. For thin layer chromatography (TLC), aluminum foil coated with silica and fluorescent indicator @254 nm (from Merck) was used. Column chromatography was performed using SD Fine silica gel (100-200 mesh) using a gradient of hexane and ethyl acetate as mobile phase.

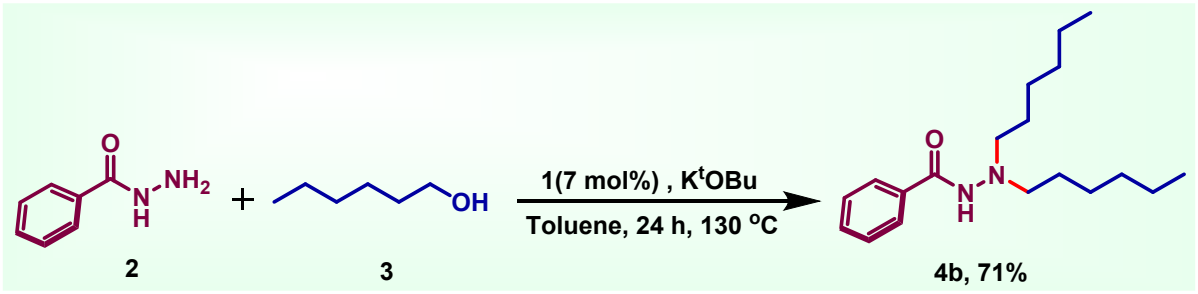
Analytical information: All synthesized products were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopies. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Advance III FT-NMR spectrometer. NMR shifts have been reported as delta (δ) units in parts per million (ppm) and coupling constants (*J*) have been reported in hertz (Hz). Chemical shifts (δ) have been quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (δ 7.26 ppm). Carbon chemical shifts have been internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm). High-resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer.

2. General procedure for N, N-Dialkylation and cyclization of acyl hydrazides by aliphatic alcohols:



A 15 mL pressure tube was charged with 7 mol% of **1**, 1 mmol of acyl hydrazides and KO^{t}Bu (1 mmol) in 2 mL toluene. To it, 2.2 mmol aliphatic alcohol or 1.2 mmol of diol was added under constant stirring of the reaction mixture. The reaction flask was purged with N_2 gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 130 ^{o}C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated in *vacuo*. The residue was purified by column chromatography using ethyl acetate/hexane (10:90) mixture as eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies.

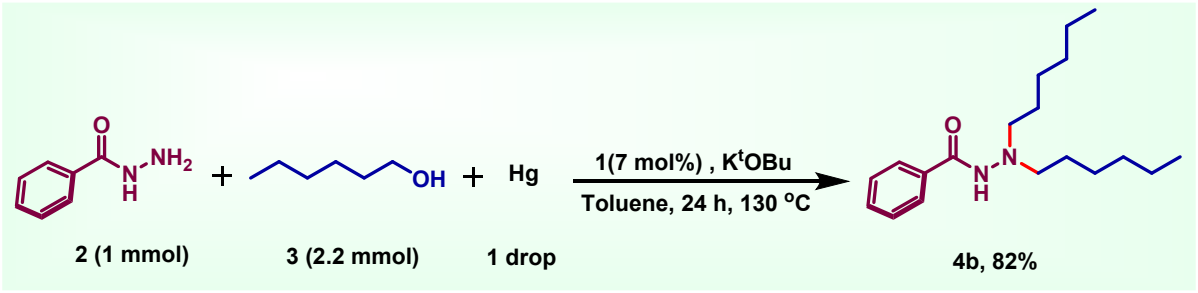
3. Synthetic application: gram-scale synthesis



In a typical reaction, a 30 mL pressure tube was charged with **1** (7 mol%), KO^{t}Bu (822 mg, 7.34 mmol), Benzoyl hydrazide (1 g, 7.34 mmol) and Hexanol (2.028 ml, 16.15 mmol) dissolved in 20 mL toluene under continuous N_2 flushing. The reaction flask was purged with N_2 gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 130 ^{o}C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated *in vacuo.* The residue was purified by column chromatography using an ethyl acetate/hexane (10:90) mixture as an eluent to afford a pure product (1.58 g, 71% yield).

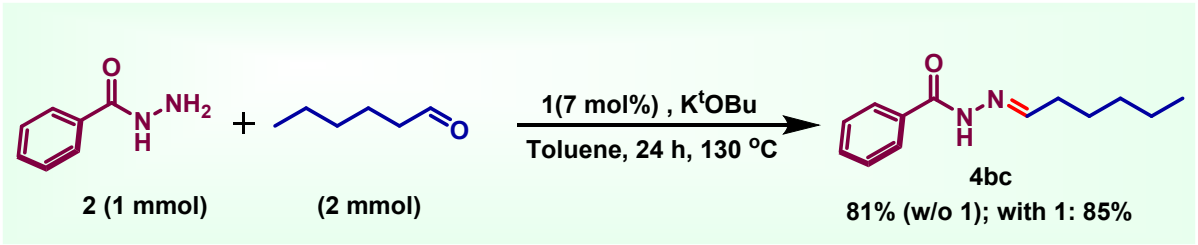
4. Mechanistic studies

4a. Mercury drop test



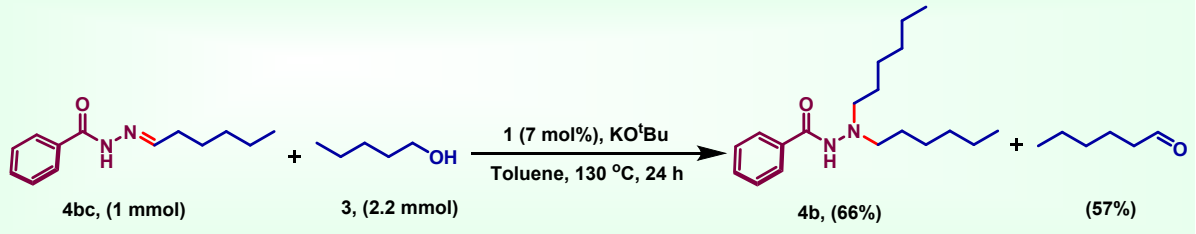
To establish the homogeneity of **1** in N,N-dialkylation of benzoyl hydrazide reaction, we carried out a mercury drop experiment. A 15 mL pressure tube was charged with **1** (7 mol%), KO^{t}Bu (1 mmol), hexanol (2.2 mmol) benzoyl hydrazide (1 mmol), and dissolved in 2 mL toluene. To this reaction mixture, a drop of mercury was added. The reaction flask was purged with an inert gas for a few minutes before closing the flask tightly. The reaction mixture was stirred at 130 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The isolation of the product in 82% yield confirmed that the mercury drop does not have any adverse effect on the reaction outcome. Hence the reaction is homogeneous in nature.

4b. Formation of N'-hexylidenebenzohydrazide



In a typical reaction, a 15 mL pressure tube was charged with KO^{t}Bu (1 mmol), Hexanal (2 mmol), and Benzoyl hydrazide (1 mmol), dissolved in 2 mL toluene. The reaction was performed in the glove box. Then the reaction mixture was stirred at 130 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies.

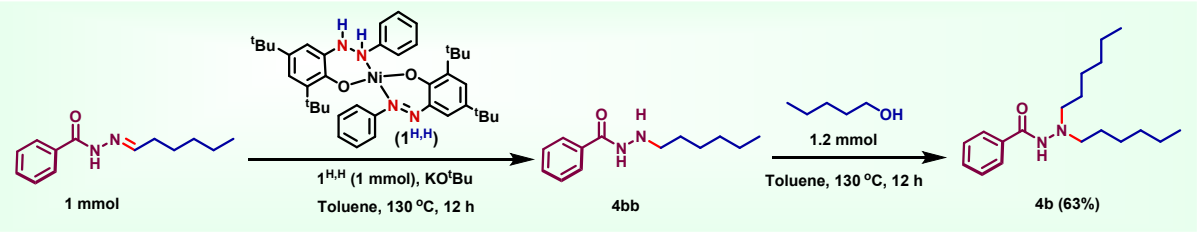
However, such a condensation reaction did not require the catalyst as proved by 81% isolated



yield of **4bc** in the absence of catalyst **1**.

4c. I. Hydrogenation of 4bc in presence of 1

In a typical reaction, a 15 mL pressure tube was charged with **1** (7 mol%), KO^{t}Bu (1 mmol), hexanol (2 mmol), **4bc** (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 130 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using an ethyl acetate/hexane (10:90) mixture as an eluent to afford a pure product. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. The N,N-dialkylated

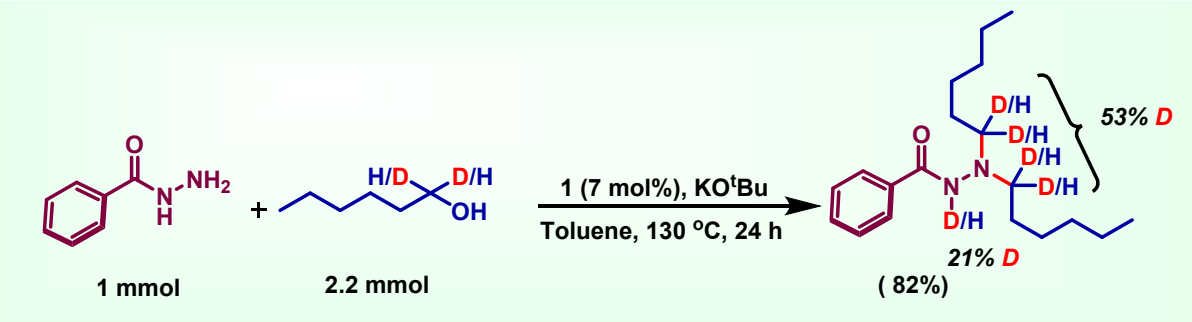


product formation was isolated in 68% yield in the presence of catalyst.

II. Hydrogenation of 4bc starting with $1^{H,H}$

In a typical reaction, a 15 mL pressure tube was charged with **$1^{H,H}$** (1 mmol), KO^{t}Bu (1 mmol), **4bc** (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 130 °C for 12 h to form **4bb**. Further addition of hexanol (1.2 mmol) was followed by stirring at 130 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated *in vacuo.* The residue was purified by column chromatography using an ethyl acetate/hexane

(10:90) mixture as an eluent to afford a pure product. The desired products were fully



characterized by ^{1}H, ^{13}C NMR spectroscopies. The hydrogenated product was isolated in 63% yield.

4d. Deuterium incorporation studies

In a typical reaction, a 15 mL pressure tube was charged with **1** (7 mol%), KO^{t}Bu (1 mmol), deuterated hexanol (2.2 mmol), benzoyl hydrazide (1 mmol), dissolved in 2 mL toluene. The reaction was performed in the glove box, in an inert atmosphere for a few minutes before closing the flask tightly. The reaction mixture was stirred at 130 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated *in vacuo.* The residue was purified by column chromatography using an ethyl acetate/hexane (10:90) mixture as an eluent to afford a deuterium-incorporated pure product in 82% yield.

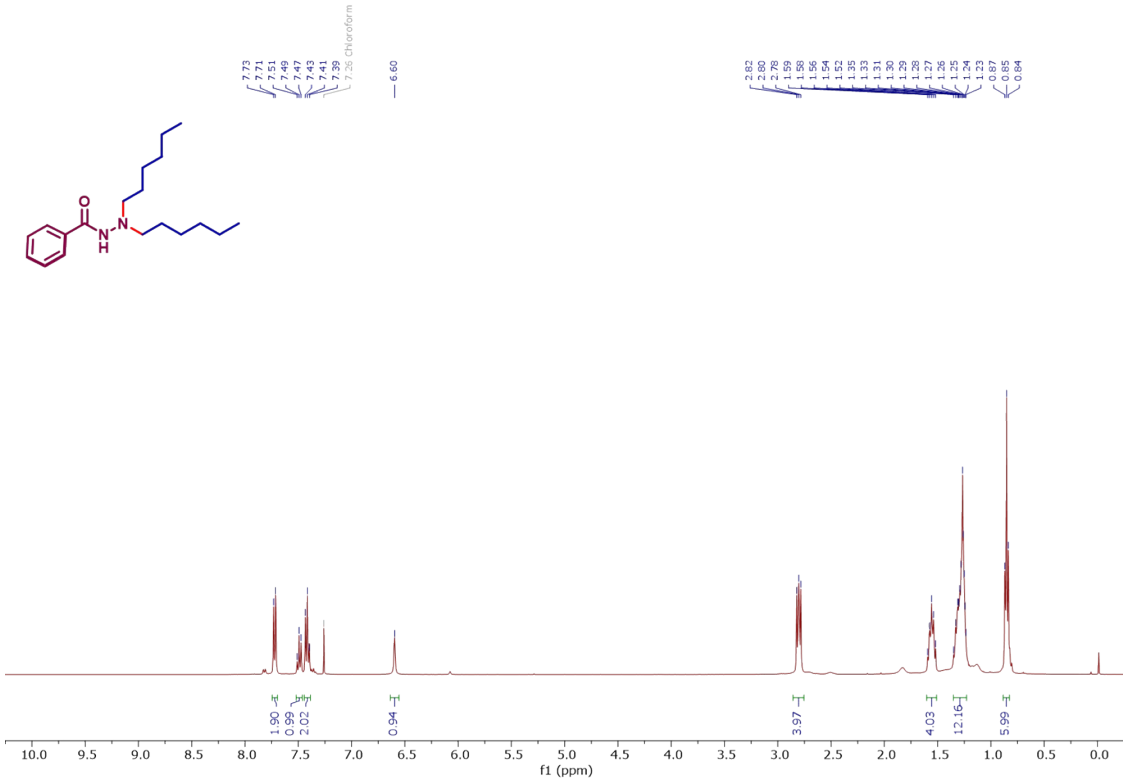


Figure S1. ^{1}H NMR spectrum (400 MHz) of 4b in $CDCl_3$

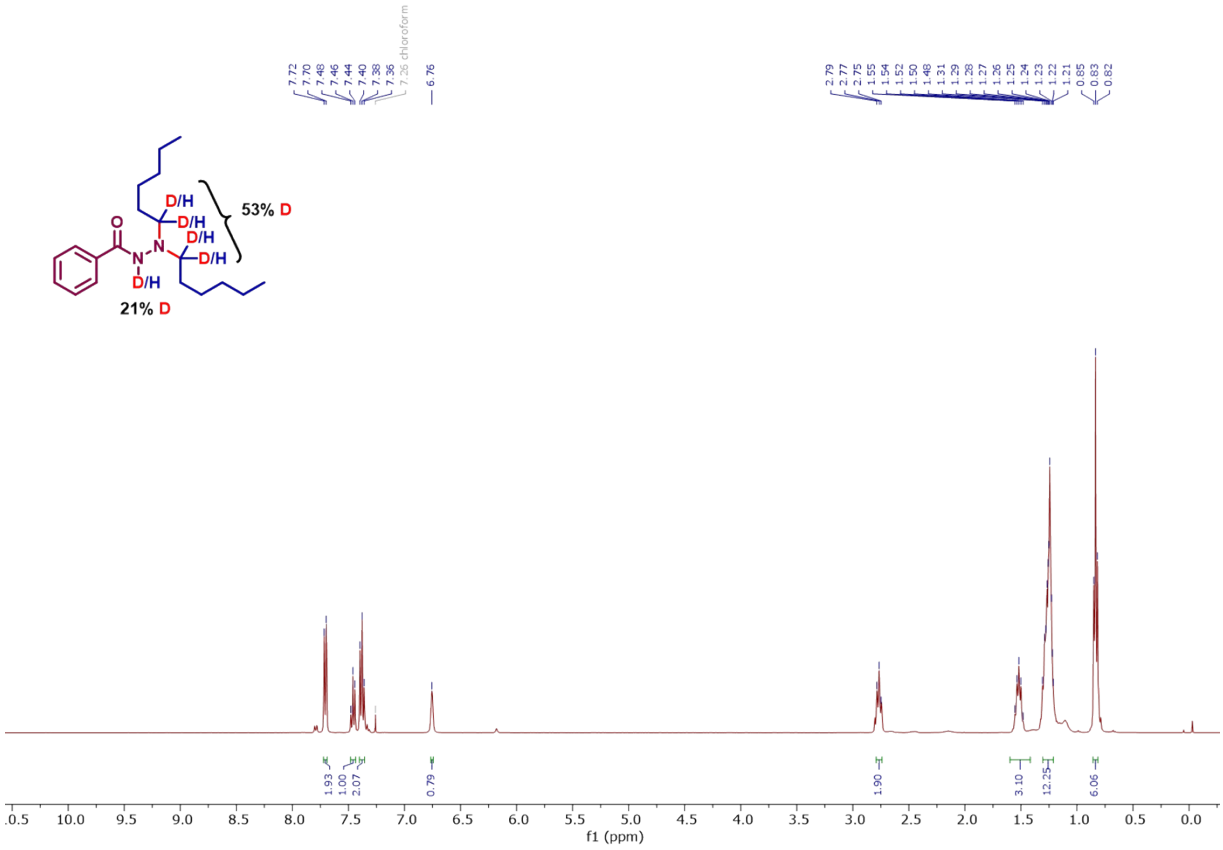
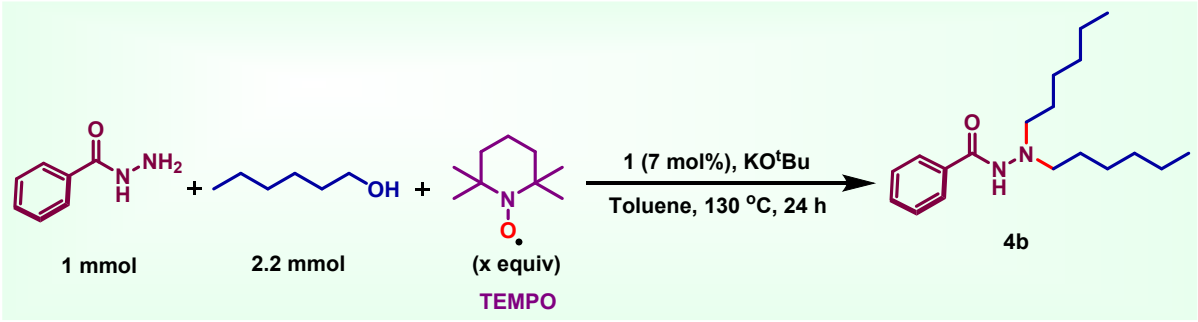


Figure S2. ^{1}H NMR spectrum (400 MHz) of deuterated 4b in $CDCl_3$.

Table S1: The conversion of D-labelled alcohol as monitored by ^{1}H NMR spectroscopy:

	2a	D-incorporation calculation	D-incorporation calculation
Signal δ (ppm)	7.51-7.47	6.76 (1H)	2.79-2.75 (4H)
Integral value	1.00	0.79	1.90
Calculated ratio		(1-0.79) *100 = 21%	[(4-1.90)/4]*100 = 53%



5e. Radical quenching experiment

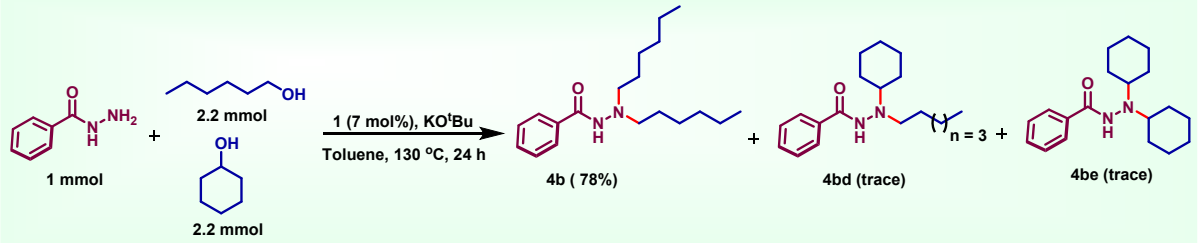
In a typical reaction condition, a 15 mL pressure tube was charged with **1** (7 mol%), KO^{t}Bu (1 mmol), hexanol (2.2 mmol), benzohydrazide (1 mmol), TEMPO (x equiv) dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 130 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated *in vacuo.* The yield of the reaction decreased drastically with the addition of TEMPO, and complete quenching of reaction was observed when it was administered in 2 equivalents. TEMPO-ketyl radical adduct was detected through HRMS (ESI) m/z: $[M + H + K]^+$, Calculated for $C_{15}H_{32}NO_2K$ 298.2148; Found 298.2147**.**

Table S2: Product yield upon varying equivalence of radical quencher

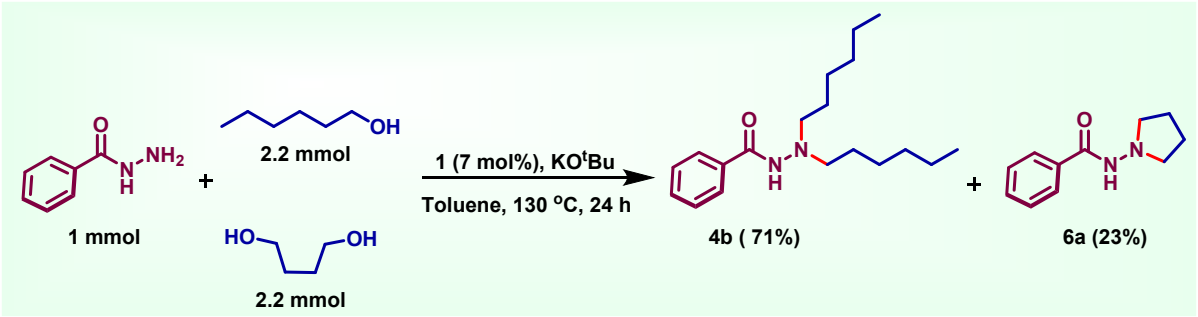
Entry	TEMPO equivalence	Yield (%)
1.	1.5 equiv.	11%

2.	2 equiv.	n.r.

5. Competition experiment:



a) In a typical reaction, a 15 mL pressure tube was charged with **1** (7 mol%), KO^{t}Bu (0.75 mmol), 1-hexanol (2.2 mmol), cyclohexanol (2.2 mmol), benzohydrazide (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 130 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. It resulted in N,N-dihexylbenzohydrazide (**4b**, 78%), N'-cyclohexyl-N'-hexylbenzohydrazide (**4bd**, trace), proving that primary aliphatic alcohols are more reactive and selective than secondary aliphatic alcohols for this transformation.

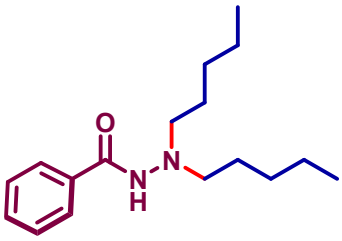


b) In a typical reaction, a 30 mL pressure tube was charged with **1** (7 mol%), KO^{t}Bu (1 mmol), hexan-1-ol (2.2 mmol), butane-1,4-diol (2.2 mmol), benzoyl hydrazide (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 130 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The

desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. It resulted in *N,N*-dihexylbenzohydrazide (**4a**, 71%), and N-(pyrrolidine-1-yl)benzamide (**6a**, 23%), proving that primary aliphatic alcohols are more reactive than 1,n-diol for this transformation

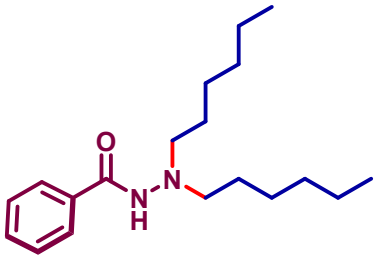
6. Analytical data:

***N′,N′*-dipentylbenzohydrazide (4a):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 227 mg, 82%. The NMR spectroscopic data is in agreement with the literature[3].



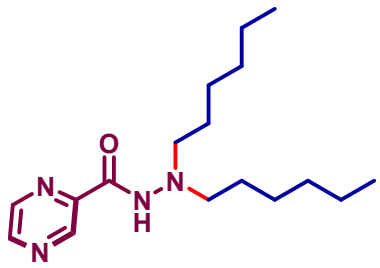
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 2H), 6.57 (s, 1H, NH), 2.81 (t, *J* = 8.1 Hz, 4H), 1.61- 1.53 (m, 4H), 1.33- 1.28 (m, 8H), 0.87 (t, *J* = 8.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 134.2, 131.7, 128.8, 127.1, 58.7, 29.6, 26.8, 22.7, 14.2 ppm.

***N′,N′*-dihexylbenzohydrazide (4b):** Purified by silica gel column chromatography using ethyl acetate/hexane (30:70) mixture as an eluent. White solid. Yield: 265 mg, 87%. The NMR spectroscopic data is in agreement with the literature[3].



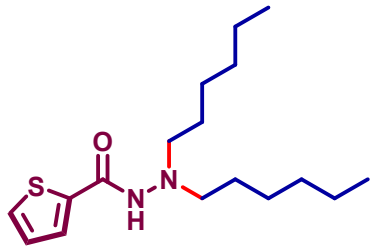
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 2H), 6.80 (s, 1H, NH), 2.80 (t, *J* = 7.9 Hz, 4H), 1.59- 1.52 (m, 4H), 1.35- 1.23 (m, 12H), 0.87 (t, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 134.2, 131.6, 128.7, 127.1, 56.7, 31.9, 27.1, 27.0, 22.7, 14.2 ppm.

***N′,N′*-dihexylpyrazine-2-carbohydrazide(4c):** Purified by silica gel column chromatography using ethyl acetate/hexane (30:70) mixture as an eluent. White solid. Yield: 278 mg, 91%.



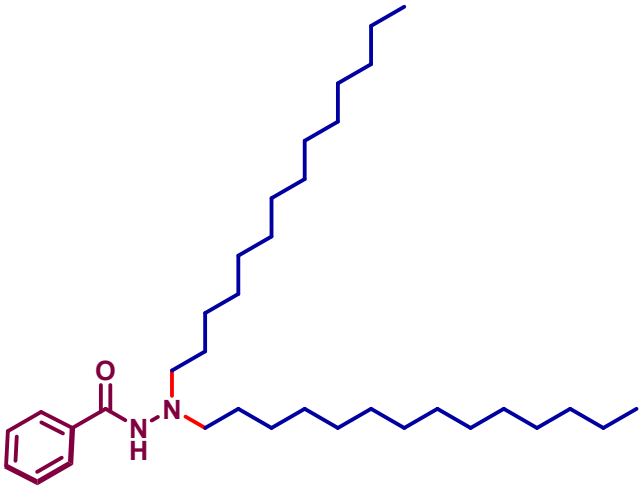
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (s, 1H), 8.71 (d, *J* = 4.1 Hz, 1H), 8.46 (d, *J* = 4.3 Hz, 1H), 8.13 (s, 1H, NH), 2.78 – 2.74 (t, *J* = 7.9, 4H), 1.52 – 1.45 (m, 4H), 1.30 – 1.16 (m, 12H), 0.78 (t, *J* = 7.9 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.3, 147.4, 144.7, 144.4, 142.4, 58.7, 31.7, 26.9, 22.6, 14.0.

***N′,N′*-dihexylthiophene-2-carbohydrazide (4d):** Purified by silica gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White solid. Yield: 215 mg, 69%.



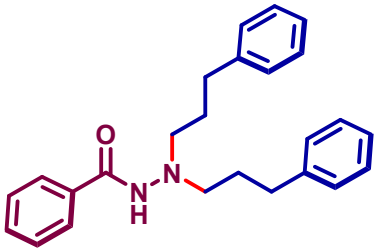
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 5.3 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.06 (dd, *J* = 5.1, 3.8 Hz, 1H), 6.66 (s, 1H, NH), 2.85 – 2.79 (m, 2H), 2.64 – 2.52 (m, 2H), 1.58 – 1.50 (m, 4H), 1.27 – 1.18 (m, 12H), 0.82 (t, *J* = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.5, 135.3, 133.5, 132.6, 126.1, 59.1, 31.7, 27.2, 26.0, 22.7, 22.7, 14.1.

***N′,N′*-ditetradecylbenzohydrazide benzohydrazide (4e):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 476 mg, 90%.



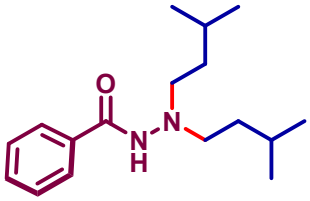
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 6.57 (s, 1H, NH), 2.86 – 2.75 (m, 4H), 1.56 (t, *J* = 7.5 Hz, 4H), 1.24 (d, *J* = 4.7 Hz, 44H), 0.87 (t, *J* = 7.9 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 131.6, 128.7, 127.1, 58.7, 32.1, 29.8, 29.8, 29.7, 29.7, 29.7, 29.5, 27.4, 27.1, 22.8, 14.3.

***N′,N′*-bis(3-phenylpropyl)benzohydrazide(4f):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 309 mg, 83%. The NMR spectroscopic data is in agreement with the literature[2].



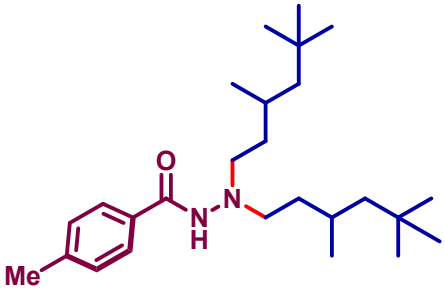
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.27 (t, *J* = 8.1 Hz, 4H), 7.19 (d, *J* = 7.9 Hz, 6H), 6.60 (s, 1H, NH), 2.86 (t, *J* = 8.1 Hz, 4H), 2.73 (t, *J* = 7.9 Hz, 4H), 1.91 (q, *J* = 7.7 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 142.0, 133.9, 131.6, 128.7, 128.5, 128.4, 128.4, 127.0, 125.8, 57.7, 33.4, 28.9 ppm.

***N′,N′*-diisopentylbenzohydrazide(4g):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 243 mg, 88%.



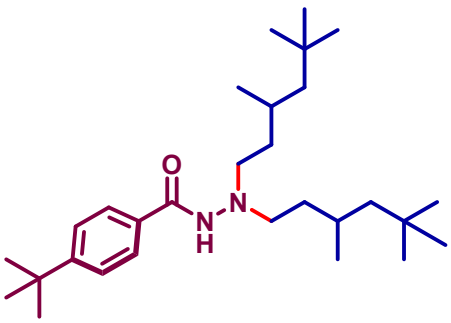
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 6.54 (s, 1H, NH), 2.88 – 2.80 (m, 4H), 1.67 – 1.60 (m, 2H), 1.51 – 1.43 (m, 4H), 0.89 (d, *J* = 7.9 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 134.2, 131.7, 128.8, 127.1, 57.0, 36.0, 26.5, 22.9 ppm.

4-methyl-*N′*,*N′*-bis(3,5,5-trimethylhexyl)benzohydrazide(4h): Purified by silica gel column chromatography using ethyl acetate/hexane (12:88) mixture as an eluent. White solid. Yield: 358 mg, 89%.



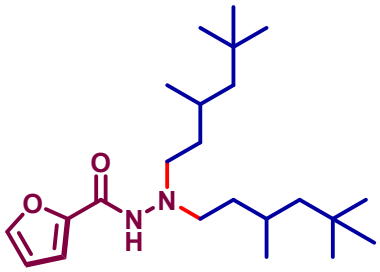
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H, NH), 2.84- 2.76 (m, 4H), 2.34 (s, 3H), 1.59- 1.47 (m, 4H), 1.42- 1.35 (m, 2H), 1.18 (d, *J* = 4.3 Hz, 1H), 1.15 (d, *J* = 4.3 Hz, 1H), 1.02 (d, *J* = 4.2 Hz, 1H), 0.99 (d, *J* = 8.1 Hz, 1H), 0.88 (d, *J* = 7.9 Hz, 6H), 0.83 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 141.8, 131.2, 129.2, 127.0, 56.7, 51.3, 36.4, 31.1, 30.0, 27.6, 27.5, 27.3, 22.8, 21.5, 21.4 ppm.

4-(tert-butyl)-*N′*,*N′*-bis(3,5,5-trimethylhexyl)benzohydrazide (4i): Purified by silica gel column chromatography using ethyl acetate/hexane (12:88) mixture as an eluent. White solid. Yield: 413 mg, 93%.



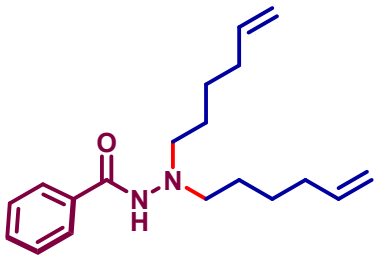
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H, NH), 2.88 – 2.76 (m, 4H), 1.60 – 1.48 (m, 4H), 1.44 – 1.37 (m, 2H), 1.29 (s, 9H), 1.20 (d, *J* = 4.2 Hz, 1H), 1.16 (d, *J* = 4.1 Hz, 1H), 1.03 (d, *J* = 7.9 Hz, 1H), 1.00 (d, *J* = 8.0 Hz, 1H), 0.89 (d, *J* = 7.9 Hz, 6H), 0.84 (s, 18H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 154.9, 131.2, 126.9, 125.5, 56.7, 51.3, 36.4, 34.9, 31.2, 31.1, 30.0, 27.6, 27.6, 22.9, 22.8 ppm.

***N′,N′*-bis(3,5,5-trimethylhexyl)furan-2-carbohydrazide (4j):** Purified by silica gel column chromatography using ethyl acetate/hexane (12:88) mixture as an eluent. White solid. Yield: 306 mg, 81%.



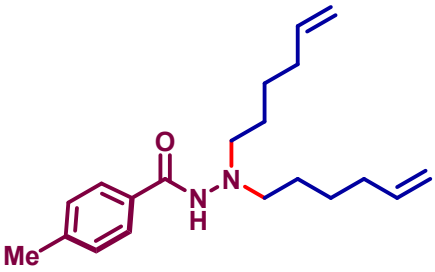
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 4.1 Hz, 1H), 7.12 (d, *J* = 4.2 Hz, 1H), 6.80 (s, 1H, NH), 6.45 (dd, *J* = 4.2, 2.1 Hz, 1H), 2.81 – 2.72 (m, 4H), 1.53 – 1.44 (m, 4H), 1.40 – 1.33 (m, 2H), 1.17 (d, *J* = 4.2 Hz, 1H), 1.14 (d, *J* = 4.0 Hz, 1H), 1.01 (d, *J* = 7.9 Hz, 1H), 0.97 (d, *J* = 8.1 Hz, 1H), 0.87 (d, *J* = 8.0 Hz, 6H), 0.81 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.4, 147.2, 143.9, 114.9, 112.1, 57.0, 51.3, 36.2, 31.9, 30.0, 27.6, 27.5, 22.8 ppm.

***N′,N′*-di(hex-5-en-1-yl)benzohydrazide (4k):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 237 mg, 79%. The NMR spectroscopic data is in agreement with the literature[1].



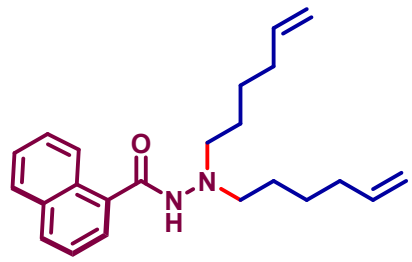
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 6.56 (s, 1H, NH), 5.83 – 5.73 (m, 2H), 5.01 – 4.90 (m, 4H), 2.84 (t, *J* = 8.0 Hz, 4H), 2.06 (q, *J* = 8.1 Hz, 4H), 1.64 – 1.55 (m, 4H), 1.48 – 1.41 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 138.8, 134.2, 131.7, 128.8, 127.1, 114.7, 58.3, 33.7, 26.7, 26.6 ppm.

***N′,N′*-di(hex-5-en-1-yl)-4-methylbenzohydrazide(4l):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 264 mg, 84%.



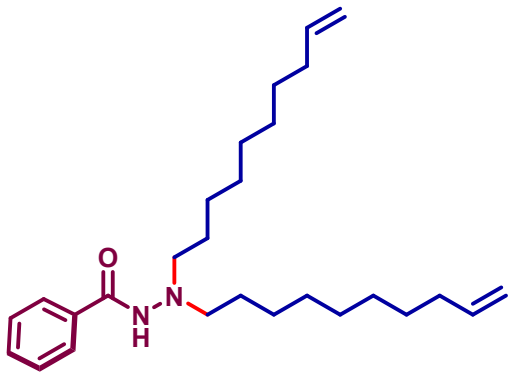
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H, NH), 5.82 – 5.72 (m, 2H), 4.99 – 4.90 (m, 4H), 2.82 (t, *J* = 8.1 Hz, 4H), 2.38 (s, 3H), 2.04 (q, *J* = 8.1 Hz, 4H), 1.60 – 1.53 (m, 4H), 1.46 – 1.39 (m, 4H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.7, 142.1, 138.8, 131.2, 129.4, 127.0, 114.6, 58.2, 33.7, 26.7, 26.6, 21.6 ppm.

***N′,N′*-di(hex-5-en-1-yl)-1-naphthohydrazide(4m):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 251 mg, 93%.



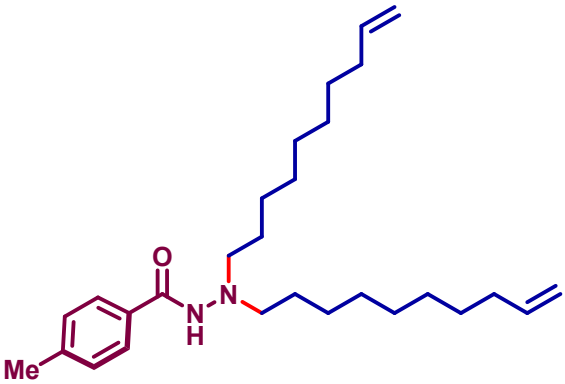
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.43 (t, *J* = 7.9 Hz, 1H), 6.43 (s, 1H, NH), 5.87 – 5.77 (m, 2H), 5.05 – 4.94 (m, 4H), 2.85 (t, *J* = 7.9 Hz, 4H), 2.10 (q, *J* = 7.8 Hz, 4H), 1.73 – 1.65 (m, 4H), 1.54 – 1.47 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.5, 138.8, 133.8, 133.5, 130.8, 130.5, 128.4, 127.4, 126.7, 125.5, 124.8, 124.7, 114.8, 58.5, 33.8, 26.8, 26.6 ppm.

***N′,N′*-di(dec-9-en-1-yl)benzohydrazide(4n):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 330 mg, 80%.



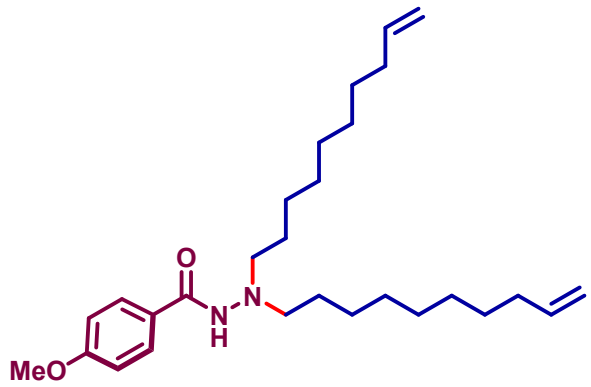
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 2H), 6.71 (s, 1H, NH), 5.83 – 5.72 (m, 2H), 4.99 – 4.88 (m, 4H), 2.83 – 2.76 (m, 4H), 2.03 – 1.97 (m, 4H), 1.58 – 1.50 (m, 4H), 1.35 – 1.23 (m, 20H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.7, 139.2, 134.1, 131.5, 128.6, 127.1, 114.2, 58.6, 33.9, 29.5, 29.4, 29.1, 28.9, 27.3, 27.1 ppm.

***N′,N′*-di(dec-9-en-1-yl)-4-methylbenzohydrazide(4o):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 371 mg, 87%.



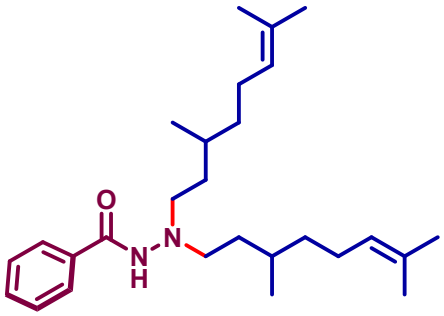
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.66 (s, 1H, NH), 5.83 – 5.72 (m, 2H), 4.99 – 4.88 (m, 4H), 2.83 – 2.74 (m, 4H), 2.36 (s, 3H), 2.02 – 1.97 (m, 4H), 1.57 – 1.50 (m, 4H), 1.33 – 1.22 (m, 20H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.7, 141.9, 139.3, 131.2, 129.3, 127.0, 114.2, 58.6, 33.9, 29.5, 29.5, 29.1, 29.0, 27.3, 27.1, 21.5, 21.4 ppm.

***N′,N′*-di(dec-9-en-1-yl)-4-methoxybenzohydrazide(4p):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 357 mg, 81%.



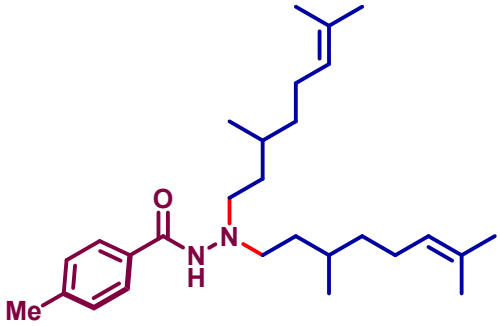
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.56 (s, 1H, NH), 5.83 – 5.73 (m, 2H), 4.99 – 4.89 (m, 4H), 3.83 (s, 3H), 2.83 – 2.75 (m, 4H), 2.01 (t, *J* = 7.9 Hz, 4H), 1.58 – 1.50 (m, 4H), 1.35 – 1.24 (m, 20H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.27, 162.27, 139.31, 128.84, 126.32, 114.21, 113.87, 58.64, 33.89, 29.57, 29.49, 29.16, 28.99, 27.34, 27.13 ppm.

***N′,N′*-bis(3,7-dimethyloct-6-en-1-yl)benzohydrazide (4q):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 375 mg, 91%. The NMR spectroscopic data is in agreement with the literature[1].



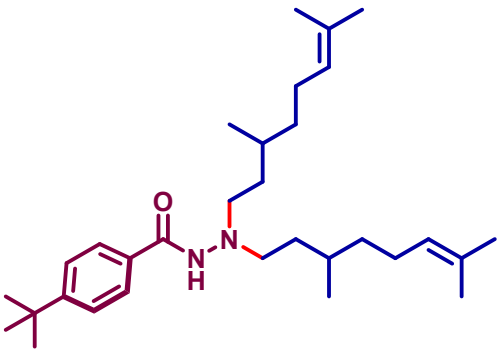
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 6.67 (s, 1H, NH), 5.05 (t, *J* = 8.0 Hz, 2H), 2.90 - 2.76 (m, 4H), 2.01- 1.85 (m, 4H), 1.64 (s, 6H), 1.61 - 1.57 (m, 2H), 1.54 (s, 6H), 1.51 - 1.45 (m, 2H), 1.42 - 1.35 (m, 2H), 1.33 - 1.25 (m, 2H), 1.18 - 1.08 (m, 2H), 0.86 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 134.1, 131.5, 131.2, 128.7, 127.0, 124.8, 124.7, 56.7, 37.2, 34.0, 30.8, 25.8, 25.5, 19.8, 17.7 ppm.

***N′,N′*-bis(3,7-dimethyloct-6-en-1-yl)-4-methylbenzohydrazide (4r):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 348 mg, 82%.



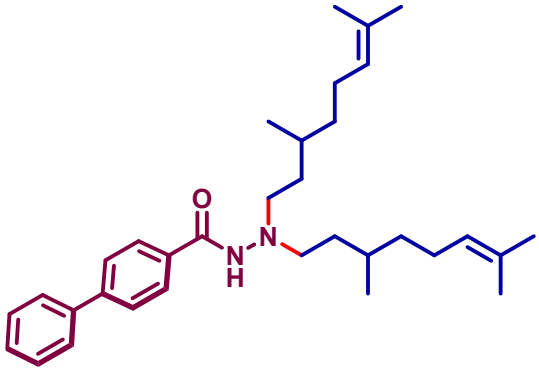
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.62 (s, 1H, NH), 5.05 (t, *J* = 7.9 Hz, 2H), 2.90 – 2.76 (m, 4H), 2.37 (s, 3H), 1.99 – 1.87 (m, 4H), 1.64 (s, 6H), 1.62 – 1.57 (m, 2H), 1.55 (s, 6H), 1.51 – 1.43 (m, 2H), 1.40 – 1.34 (m, 2H), 1.31 – 1.24 (m, 2H), 1.16 – 1.10 (m, 2H), 0.86 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.7, 142.0, 131.2, 131.2, 129.3, 127.0, 124.8, 124.8, 56.7, 37.2, 34.0, 30.8, 25.8, 25.5, 19.8, 17.7 ppm.

4-(tert-butyl)-*N′*,*N′*-bis(3,7-dimethyloct-6-en-1-yl)benzohydrazide (4s): Purified by silica gel column chromatography using ethyl acetate/hexane (30:70) mixture as an eluent. White solid. Yield: 435 mg, 93%.



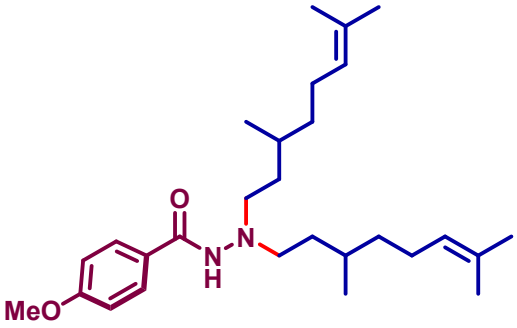
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.65 (s, 1H, NH), 5.05 (t, *J* = 8.0 Hz, 2H), 2.91 – 2.77 (m, 4H), 2.02 – 1.85 (m, 4H), 1.64 (s, 6H), 1.63 – 1.57 (m, 2H), 1.55 (s, 6H), 1.51 – 1.43 (m, 2H), 1.41 – 1.35 (m, 2H), 1.31 (s, 9H), 1.29 – 1.24 (m, 2H), 1.17 – 1.08 (m, 2H), 0.86 (d, *J* = 6.4 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 155.0, 131.2, 131.1, 126.9, 125.6, 124.8, 124.8, 56.7, 37.2, 35.0, 34.0, 31.2, 30.8, 25.8, 25.5, 19.8, 17.7 ppm.

***N′*,*N′*-bis(3,7-dimethyloct-6-en-1-yl)-[1,1'-biphenyl]-4-carbohydrazide (4t):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 420 mg, 86%.



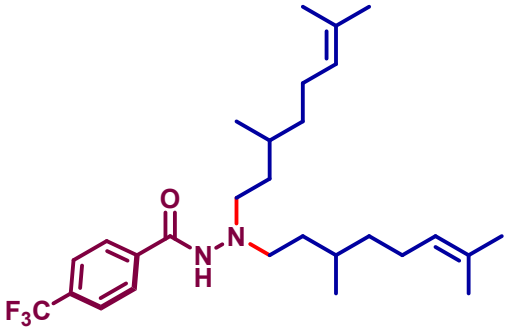
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.59 (dd, *J* = 16.4, 8.2 Hz, 4H), 7.43 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.89 (s, 1H, NH), 5.07 (t, *J* = 8.0 Hz, 2H), 2.95 – 2.81 (m, 4H), 2.02 – 1.89 (m, 4H), 1.66 (s, 6H), 1.64 – 1.58 (m, 2H), 1.56 (s, 6H), 1.53 – 1.46 (m, 2H), 1.44 – 1.39 (m, 2H), 1.37 – 1.28 (m, 2H), 1.20 – 1.11 (m, 2H), 0.88 (d, *J* = 6.4 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.4, 144.3, 140.0, 132.7, 131.1, 128.9, 128.0, 127.6, 127.2, 127.1, 124.8, 124.7, 56.6, 37.2, 34.0, 30.8, 25.7, 25.5, 19.7, 17.7 ppm.

***N′,N′*-bis(3,7-dimethyloct-6-en-1-yl)-4-methoxybenzohydrazide (4u):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 376 mg, 85%.



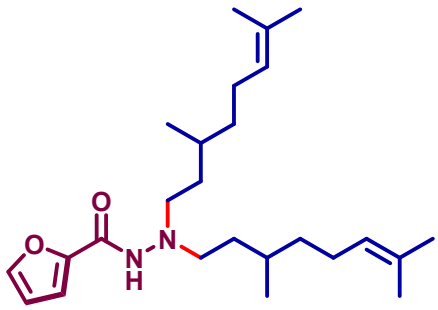
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H, NH), 5.06 (t, *J* = 7.9 Hz, 2H), 3.84 (s, 3H), 2.92 – 2.78 (m, 4H), 2.01 – 1.88 (m, 4H), 1.66 (s, 6H), 1.63 – 1.59 (m, 2H), 1.56 (s, 6H), 1.52 – 1.46 (m, 2H), 1.42 – 1.35 (m, 2H), 1.33 – 1.27 (m, 2H), 1.19 – 1.10 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 162.3, 131.3, 128.8, 126.3, 124.9, 113.9, 56.7, 55.5, 37.3, 34.0, 30.9, 25.8, 25.6, 19.8, 17.7 ppm.

***N′,N′*-bis(3,7-dimethyloct-6-en-1-yl)-4-(trifluoromethyl)benzohydrazide(4v):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 355 mg, 74%.



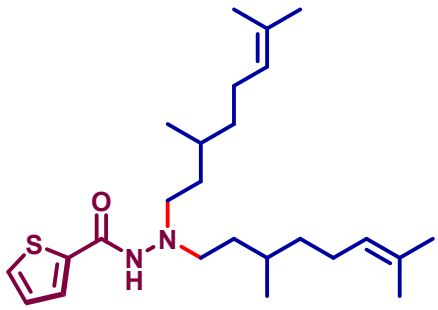
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H, NH), 5.05 (t, *J* = 7.9 Hz, 2H), 2.90 – 2.79 (m, 4H), 1.98 – 1.87 (m, 4H), 1.65 (s, 6H), 1.62 – 1.58 (m, 2H), 1.55 (s, 6H), 1.51 – 1.45 (m, 2H), 1.41 – 1.35 (m, 2H), 1.32 – 1.27 (m, 2H), 1.18 – 1.11 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.4, 137.3, 131.3, 127.5 (q, J_{C-F} = 32 Hz), 125.7 (q, J_{C-F} = 4 Hz), 124.7 (q, J_{C-F} = 270 Hz), 56.5, 37.2, 34.0, 30.7, 25.7, 25.5, 19.7, 17.6. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.01 ppm.

***N′,N′*-bis(3,7-dimethyloct-6-en-1-yl)furan-2-carbohydrazide(4w):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 281 mg, 93%.



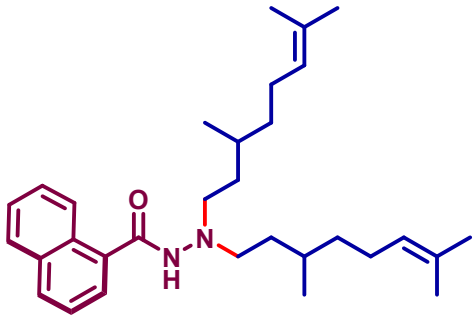
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.14 (d, *J* = 4.3 Hz, 1H), 6.79 (s, 1H, NH), 6.48 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.03 (t, *J* = 7.9 Hz, 2H), 2.84 – 2.73 (m, 4H), 1.96 – 1.89 (m, 4H), 1.64 (s, 6H), 1.61 – 1.56 (m, 2H), 1.54 (s, 6H), 1.49 – 1.42 (m, 2H), 1.39 – 1.34 (m, 2H), 1.30 – 1.25 (m, 2H), 1.15 – 1.09 (m, 2H), 0.85 (d, *J* = 6.5 Hz, 6H)..**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.4, 144.3, 140.0, 132.7, 131.1, 128.9, 128.0, 127.6, 127.2, 127.1, 124.8, 124.8, 56.6, 37.2, 34.0, 30.8, 25.7, 25.5, 19.7, 17.7.

***N′,N′*-bis(3,7-dimethyloct-6-en-1-yl)thiophene-2-carbohydrazide (4x):** Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 255 mg, 61%.



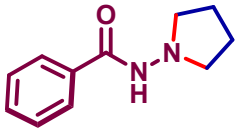
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 6.3 Hz, 1H), 7.51 (d, *J* = 6.4 Hz, 1H), 7.08 – 7.05 (m, 1H), 6.31 (s, 1H, NH), 5.08 (t, *J* = 7.9 Hz, 2H), 3.69 – 3.63 (m, 2H), 2.88 – 2.82 (m, 1H), 2.64 – 2.58 (m, 1H), 1.98 – 1.90 (m, 4H), 1.67 (s, 6H), 1.64 – 1.61 (m, 2H), 1.59 (s, 6H), 1.39 – 1.36 (m, 2H), 1.34 – 1.29 (m, 2H), 1.24 – 1.15 (m, 2H), 1.14 – 1.06 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.4, 135.4, 133.6, 131.4, 126.1, 124.8, 61.3, 40.0, 37.3, 31.0, 29.3, 25.8, 25.8, 25.6, 25.5, 25.4, 19.7, 19.6, 17.7 ppm.

N',N'-bis(3,7-dimethyloct-6-en-1-yl)-1-naphthohydrazide (4y): Purified by silica gel column chromatography using ethyl acetate/hexane (10:90) mixture as an eluent. White solid. Yield: 410 mg, 89%.



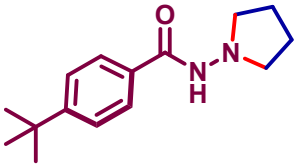
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 1H), 6.39 (s, 1H, NH), 5.10 (t, *J* = 7.9 Hz, 2H), 2.95 – 2.81 (m, 4H), 2.05 – 1.94 (m, 4H), 1.77 – 1.70 (m, 2H), 1.68 (s, 6H), 1.58 (s, 6H), 1.57 – 1.52 (m, 2H), 1.51 – 1.41 (m, 2H), 1.38 – 1.32 (m, 2H), 1.25 – 1.16 (m, 2H), 0.93 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.5, 133.8, 133.6, 131.4, 130.8, 130.5, 128.4, 127.4, 126.7, 125.5, 124.9, 124.8, 124.7, 56.9, 37.4, 34.2, 30.9, 25.9, 25.6, 19.8, 17.8 ppm.

N-(pyrrolidin-1-yl)benzamide (6a): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 133 mg, 71%. The NMR spectroscopic data is in agreement with the literature[3].



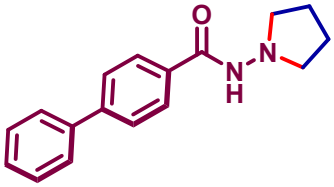
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 6.43 (s, 1H, NH), 3.05 (d, *J* = 7.8 Hz, 4H), 1.96 – 1.92 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 131.7, 128.8, 127.2, 55.4, 22.6 ppm.

4-(tert-butyl)-N-(pyrrolidin-1-yl)benzamide (6b): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 198 mg, 81%. The NMR spectroscopic data is in agreement with the literature[1].



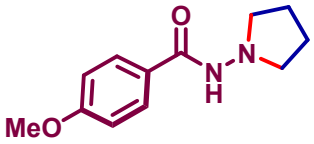
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.46 (s, 1H, NH), 2.99 (t, *J* = 8.0 Hz, 4H), 1.90 – 1.84 (m, 4H), 1.29 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.3, 155.1, 131.0, 127.0, 125.5, 55.4, 35.0, 31.2, 22.4. ppm.

N-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-carboxamide (6c): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 234 mg, 88%.



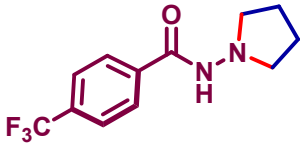
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.65 – 7.55 (m, 4H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.13 – 6.99 (m, 1H), 7.07 (s, 1H, NH), 3.01 (t, *J* = 8.1 Hz, 4H), 1.92 – 1.88 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 144.4, 140.0, 132.6, 129.0, 128.1, 127.7, 127.3, 55.7, 22.3 ppm.

4-methoxy-N-(pyrrolidin-1-yl)benzamide (6d): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 185 mg, 84%. The NMR spectroscopic data is in agreement with the literature[3].



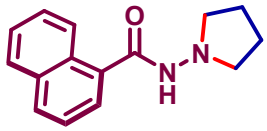
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.32 (s, 1H, NH), 3.82 (s, 3H), 2.99 (t, *J* = 8.0 Hz, 4H), 1.92- 1.87 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9, 162.3, 128.9, 126.2, 113.8, 55.5, 22.4 ppm.

N-(pyrrolidin-1-yl)-4-(trifluoromethyl)benzamide (6e): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 219 mg, 85%.



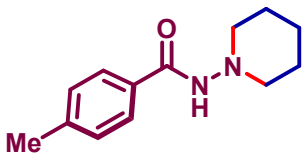
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 6.73 (s, 1H, NH), 2.99 (t, *J* = 8.1 Hz, 4H), 1.91 – 1.85 (m, 4H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.2, 137.3, 133.1, 127.7 (q, $J_{C\text{-}F}$ = 32 Hz), 125.6 (q, $J_{C\text{-}F}$ = 4 Hz), 125.1 (q, $J_{C\text{-}F}$ = 270 Hz), 55.6, 22.3. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.02 ppm.

N-(pyrrolidin-1-yl)-1-naphthamide (6f): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 190 mg, 79%. The NMR spectroscopic data is in agreement with the literature[1].



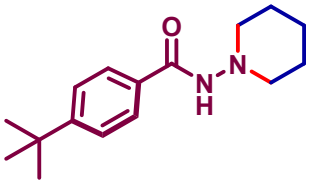
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 7.9 Hz, 1H), 7.85 (dd, *J* = 16.0, 8.0 Hz, 2H), 7.54 – 7.47 (m, 3H), 7.39 (t, *J* = 8.1 Hz, 1H), 6.93 (s, 1H, NH), 3.02 (t, *J* = 8.0 Hz, 4H), 1.91 – 1.87 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.0, 133.7, 133.0, 130.7, 130.4, 128.3, 127.2, 126.5, 125.3, 125.2, 124.7, 55.4, 22.4 ppm.

4-methyl-*N*-(piperidin-1-yl)benzamide (6g): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 166 mg, 76%. The NMR spectroscopic data is in agreement with the literature[3].



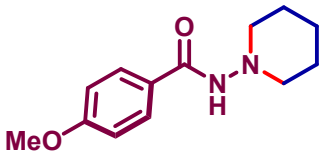
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.80 (s, 1H, NH), 2.86 (t, *J* = 8.1 Hz, 4H), 2.38 (s, 3H), 1.79-1.73 (m, 4H), 1.47-1.41 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.4, 142.0, 131.3, 129.3, 127.1, 57.3, 25.5, 23.4, 21.6 ppm.

4-(tert-butyl)-*N*-(piperidin-1-yl)benzamide (6h): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 223 mg, 86%.



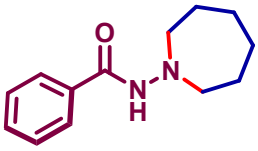
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 1H, NH), 2.83 (t, *J* = 7.9 Hz, 4H), 1.75 – 1.70 (m, 4H), 1.44 – 1.30 (m, 2H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.3, 155.0, 131.2, 127.0, 125.5, 57.2, 35.0, 31.2, 25.4, 23.4 ppm.

4-methoxy-N-(piperidin-1-yl)benzamide (6i): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 150 mg, 65%. The NMR spectroscopic data is in agreement with the literature[3].



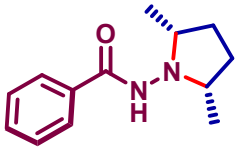
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 6.7 Hz, 2H), 6.70 (s, 1H, NH), 3.84 (s, 3H), 2.85 (t, *J* = 8.0 Hz 4H), 1.80 - 1.73 (m, 4H), 1.47-1.41 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.2, 167.0, 128.9, 126.7, 113.9, 57.4, 26.4, 25.5, 23.4 ppm.

N-(azepan-1-yl)benzamide (6j): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 181 mg, 83%. The NMR spectroscopic data is in agreement with the literature[1].



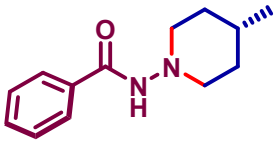
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 2H), 7.29 (s, 1H, NH), 3.18 (t, *J* = 7.9 Hz, 4H), 1.78 - 1.73 (m, 4H), 1.68 - 1.64 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.7, 134.1, 131.5, 128.6, 127.1, 58.2, 27.1, 26.3 ppm.

N-(2,5-dimethylpyrrolidin-1-yl)benzamide (6k): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 167 mg, 77%.



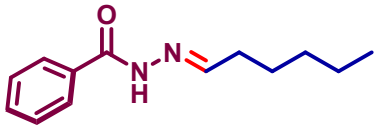
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 6.44 (s, 1H, NH), 2.90 – 2.84 (m, 2H), 1.96 – 1.92 (m, 2H), 1.60 – 1.56 (m, 2H), 1.20 (d, *J* = 6.1 Hz, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.3, 134.3, 131.6, 128.8, 127.1, 28.7, 18.9 ppm.

N-(4-methylpiperidin-1-yl)benzamide (6l): Purified by silica gel column chromatography using ethyl acetate/hexane (40:60) mixture as an eluent. White solid. Yield: 170 mg, 78%.

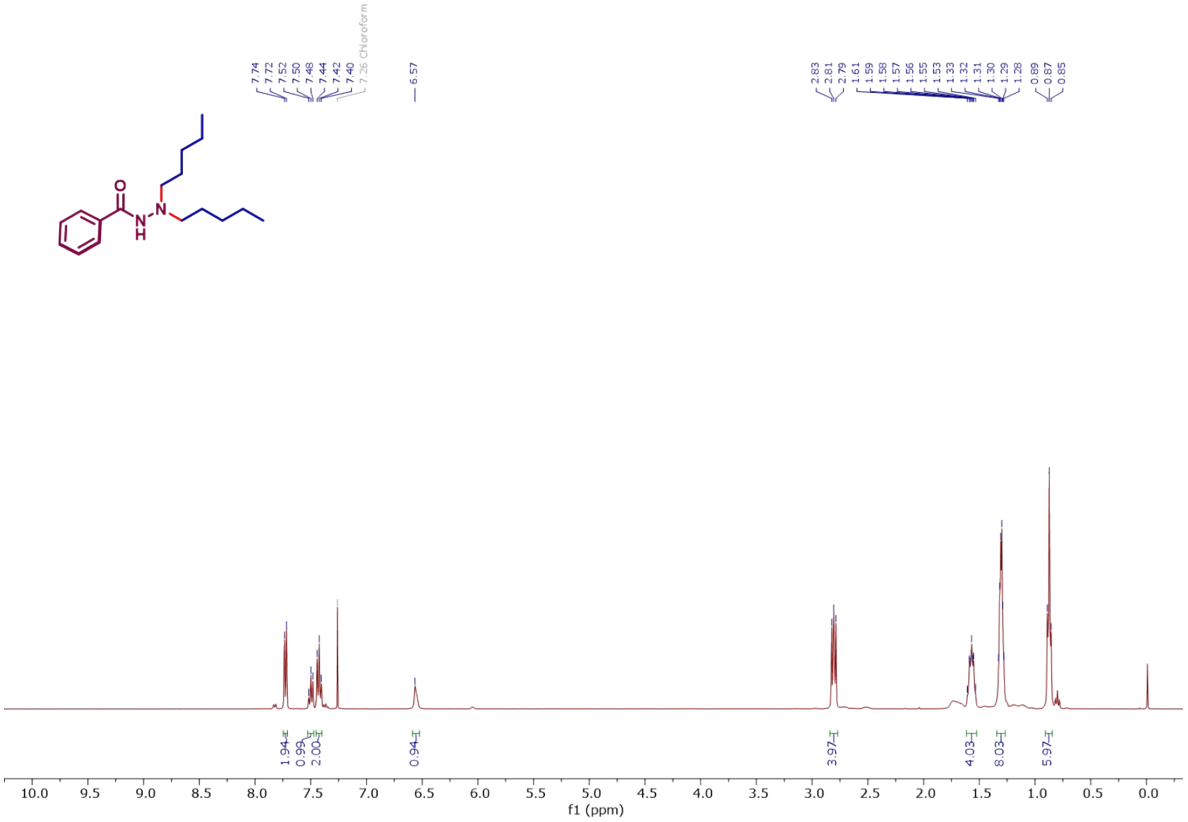


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.92 (s, 1H, NH), 3.23 - 3.19 (m, 2H), 2.51 (t, *J* = 7.9 Hz, 2H), 1.69 - 1.64 (m, 2H), 1.56- 1.49 (m, 2H), 1.47- 1.36 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.5, 134.2, 131.5, 128.6, 127.1, 56.5, 33.6, 29.9, 21.5 ppm.

N'-hexylidenebenzohydrazide (4bc): White solid (yield: 218 mg, 78%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



^{1}H NMR (400 MHz, $CDCl_3$): δ 10.49 (s, 1H, NH), 7.82 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 6.0 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 2.24 (q, *J* = 7.0 Hz, 2H), 1.46 – 1.38 (m, 2H), 1.27 – 1.21 (m, 3H), 0.89 – 0.79 (m, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.8, 153.8, 133.1, 131.6, 128.3, 127.7, 32.6, 31.4, 26.3, 22.4, 13.9.



7. ^{1}H and ^{13}C NMR spectra of synthesized compounds:

Figure S3. ^{1}H NMR spectrum (400 MHz) of 4a in $CDCl_3$

Figure S4. ^{13}C NMR spectrum (100 MHz) of 4a in $CDCl_3$

Figure S5. ^{1}H NMR spectrum (400 MHz) of 4b in $CDCl_3$

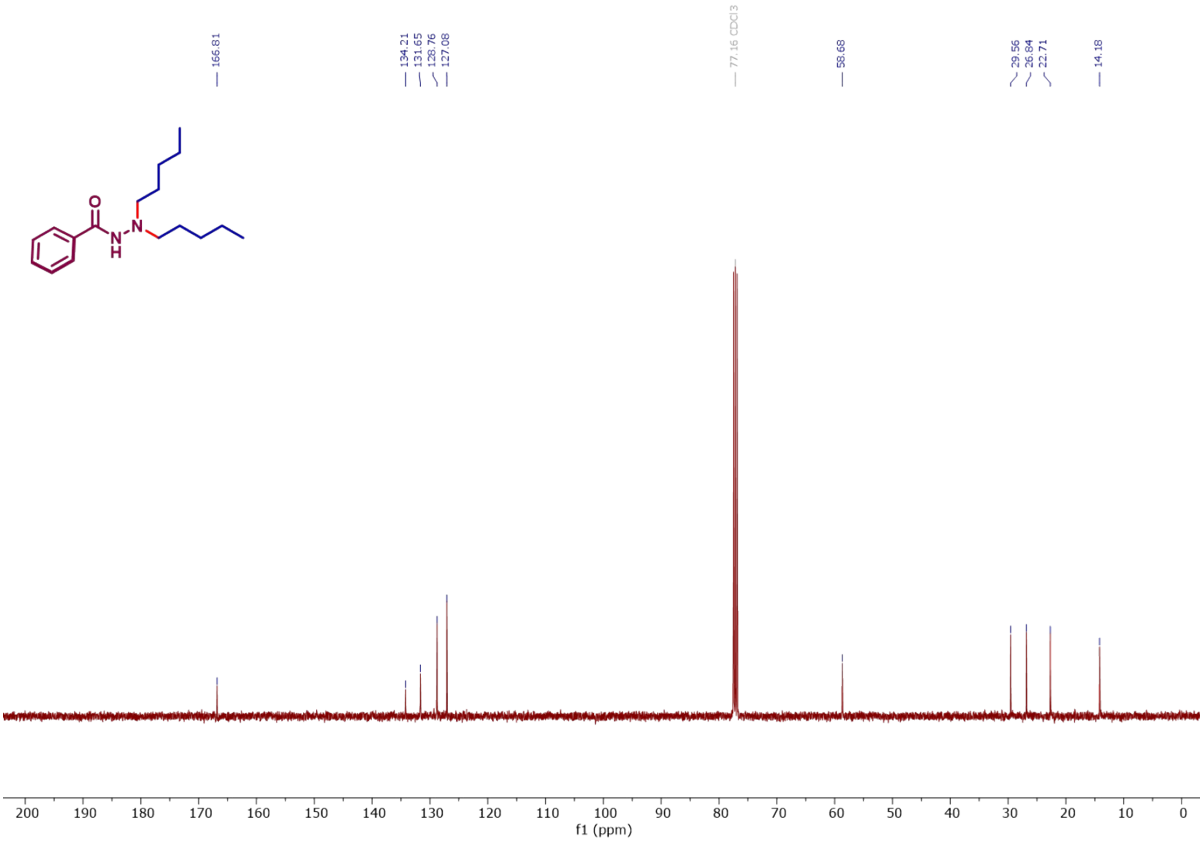
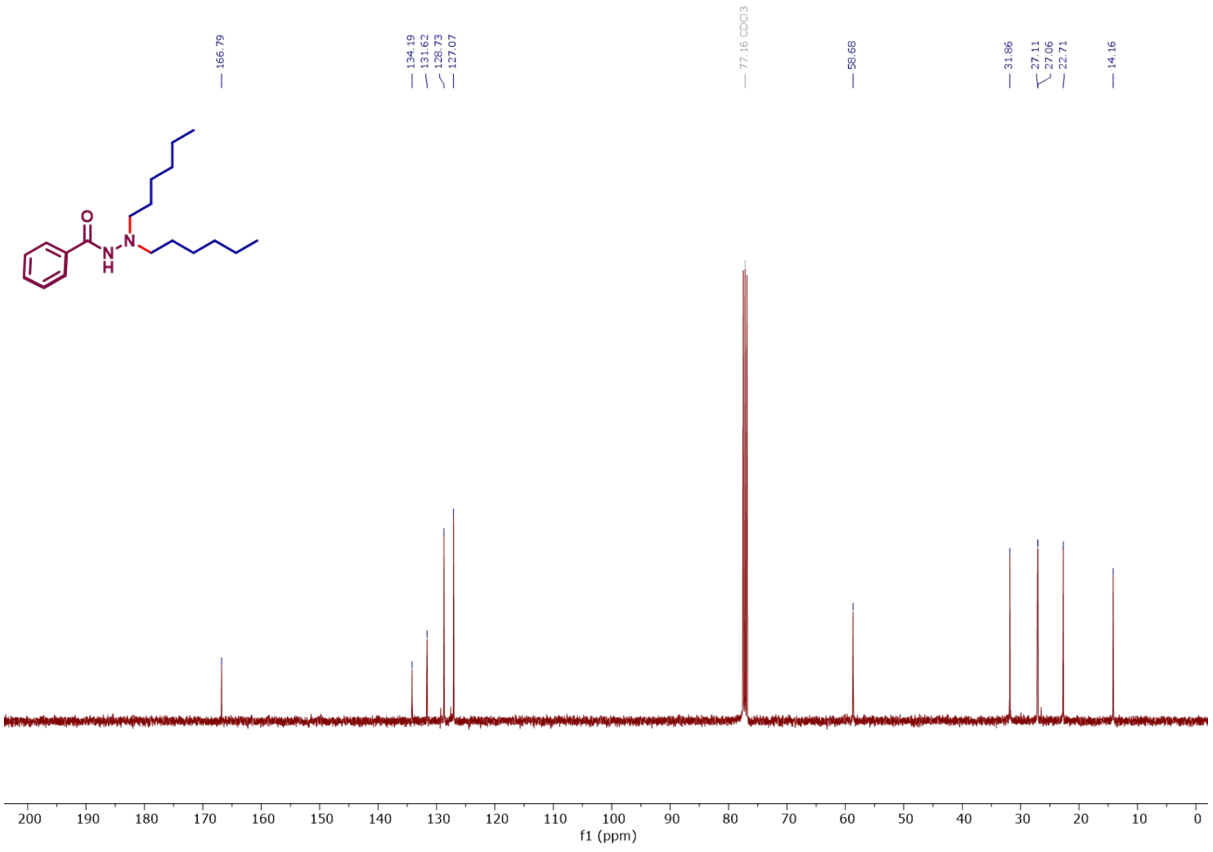


Figure S6. ^{13}C NMR spectrum (100 MHz) of 4b in $CDCl_3$



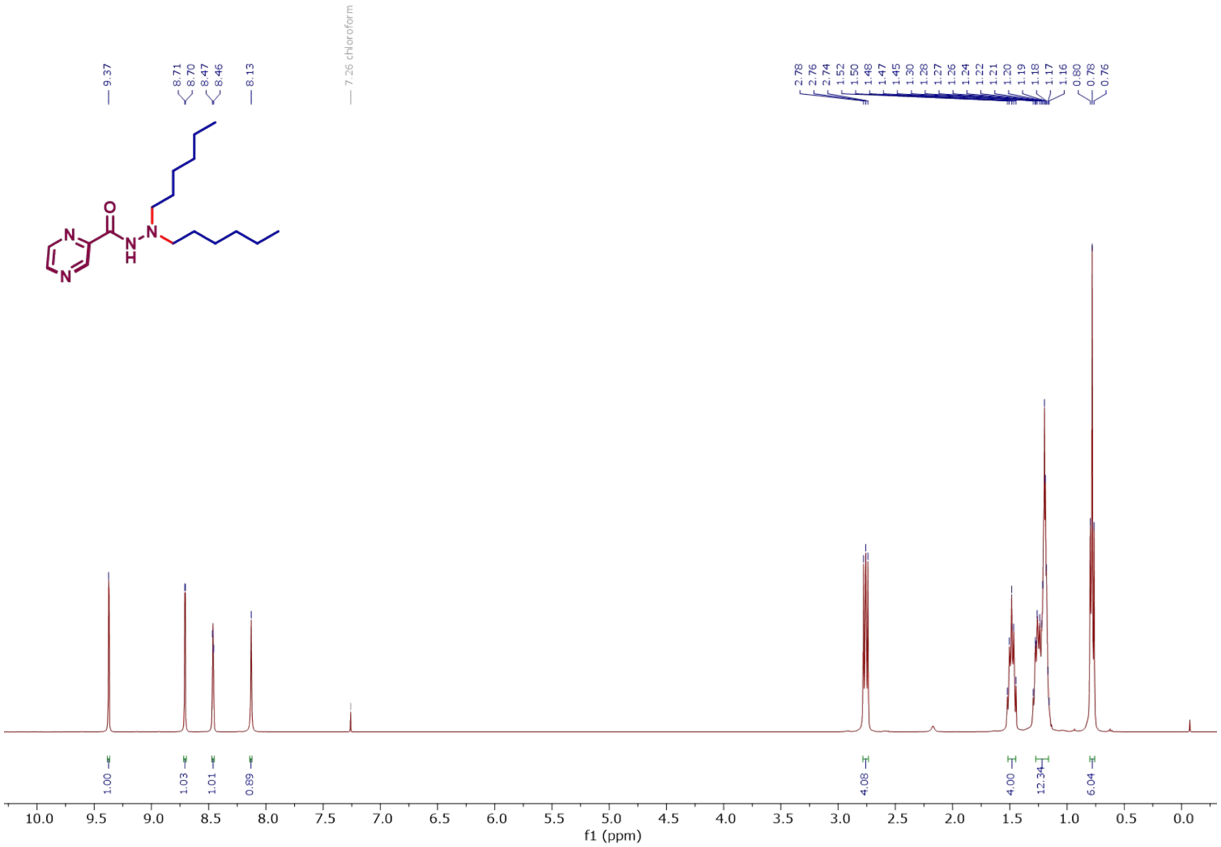


Figure S7. ^{1}H NMR spectrum (400 MHz) of 4c in $CDCl_3$

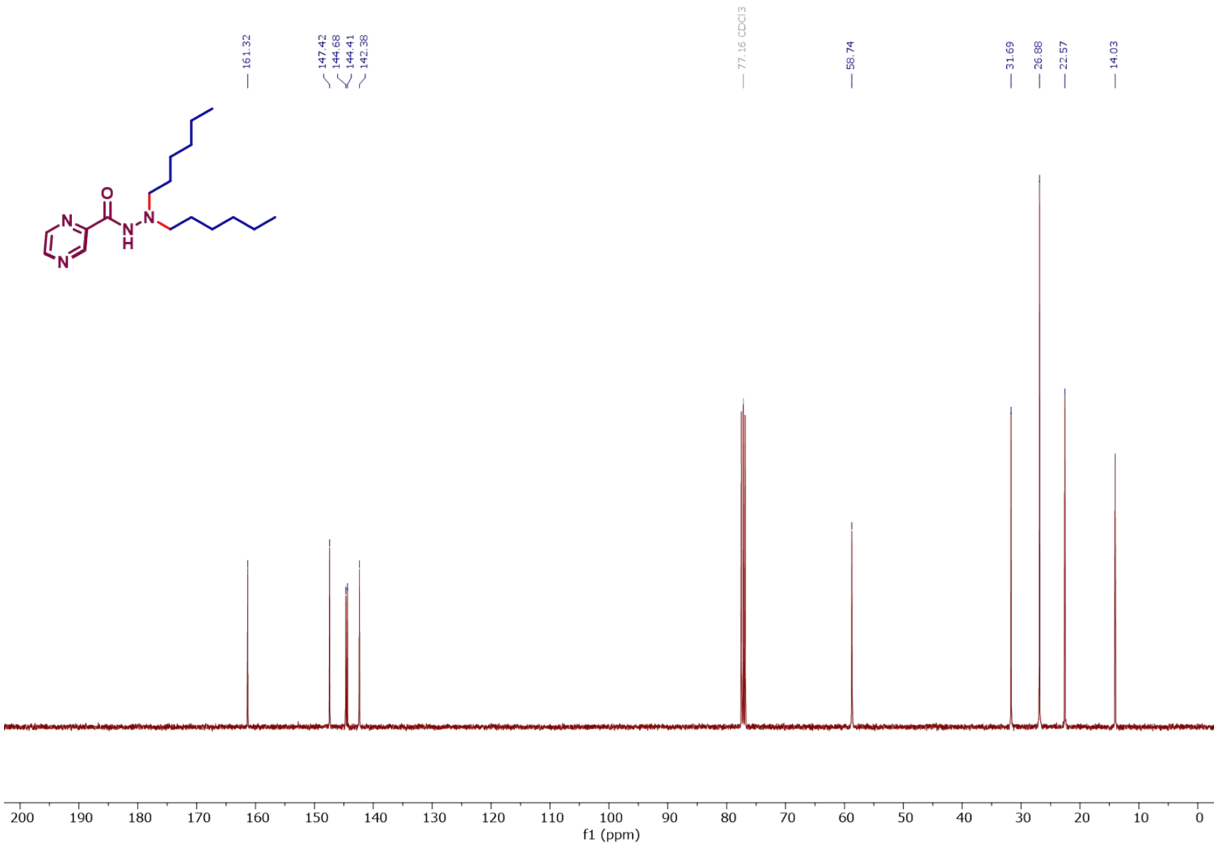


Figure S8. ^{13}C NMR spectrum (100 MHz) of 4c in $CDCl_3$

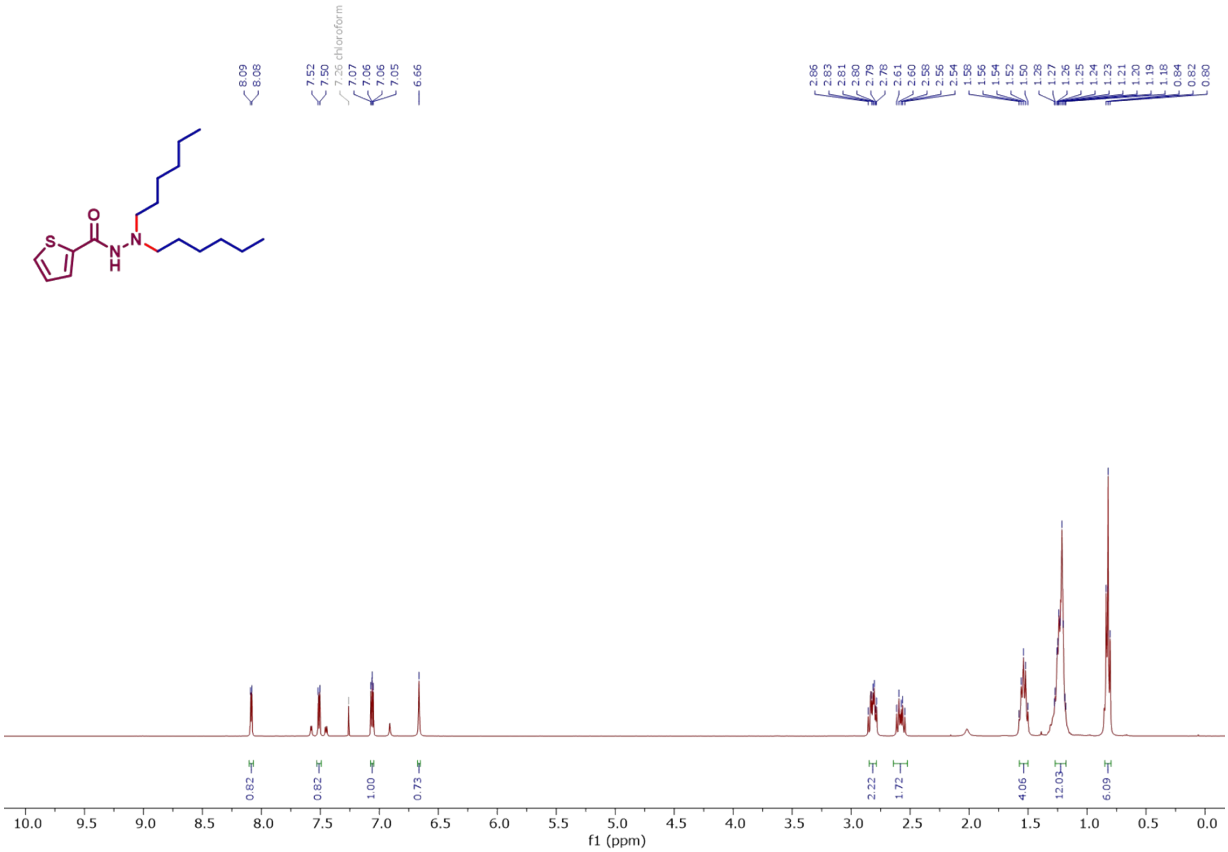


Figure S9. ^{1}H NMR spectrum (400 MHz) of 4d in $CDCl_3$

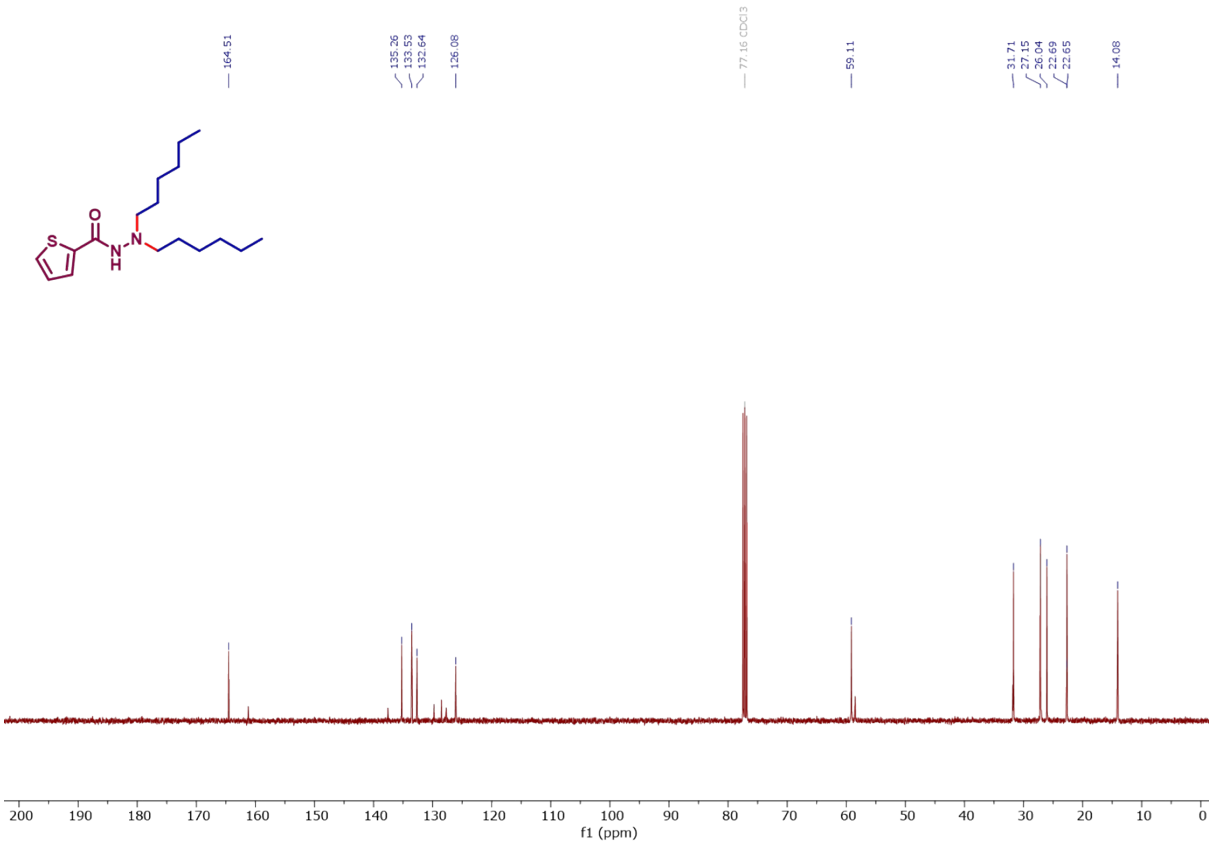


Figure S10. ^{13}C NMR spectrum (100 MHz) of 4d in $CDCl_3$

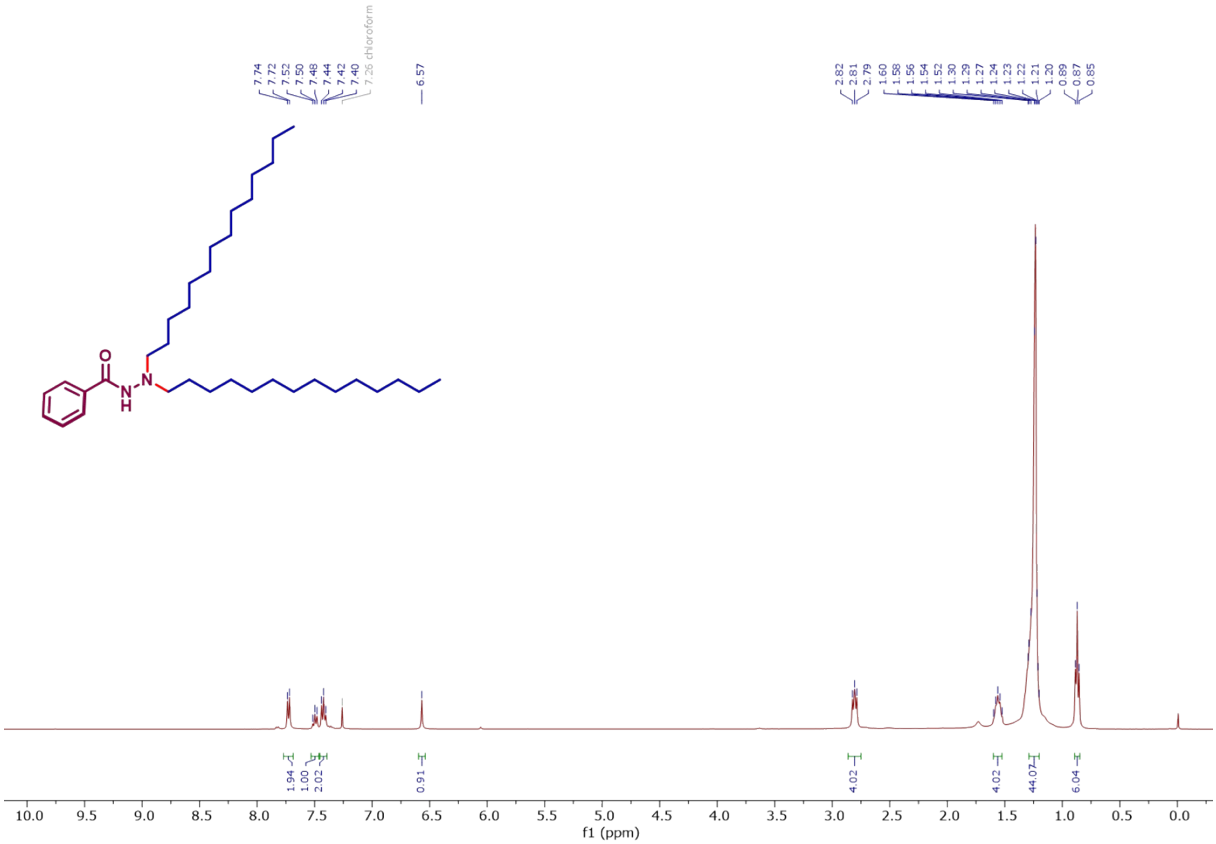


Figure S11. ^{1}H NMR spectrum (400 MHz) of 4e in $CDCl_3$

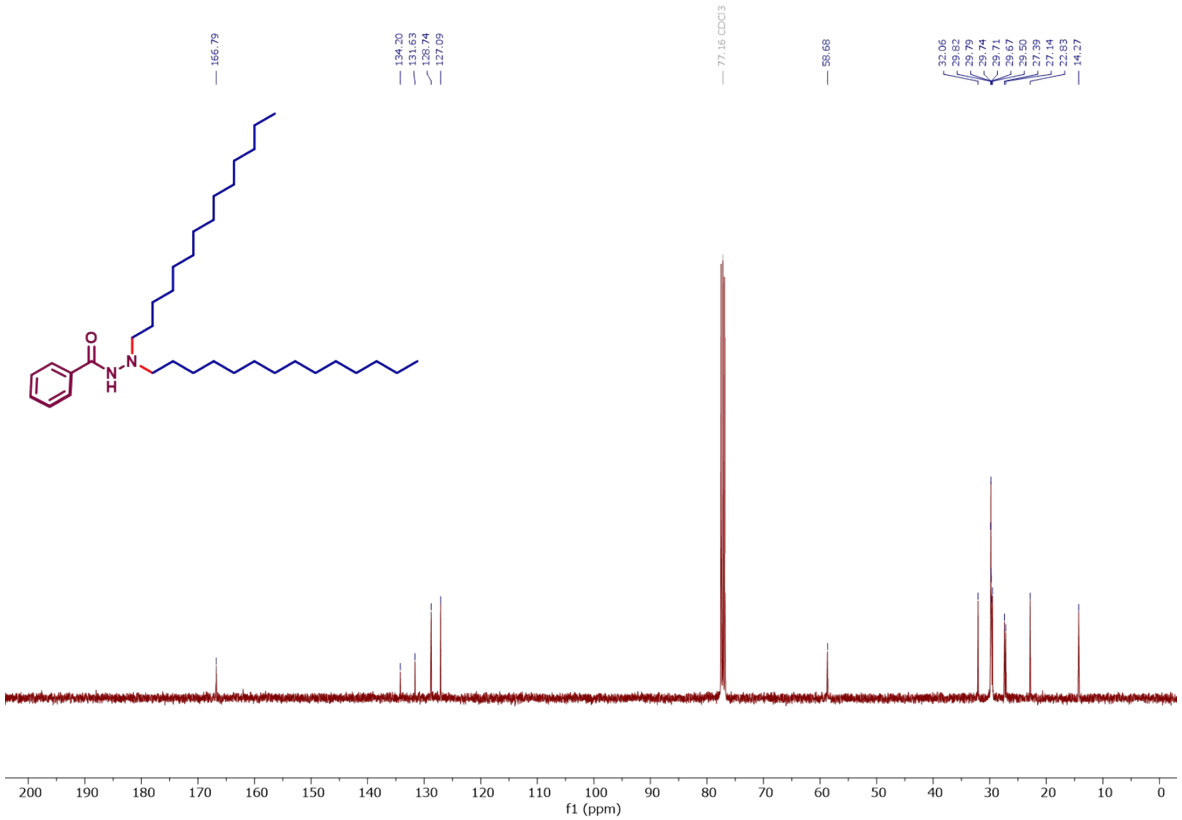
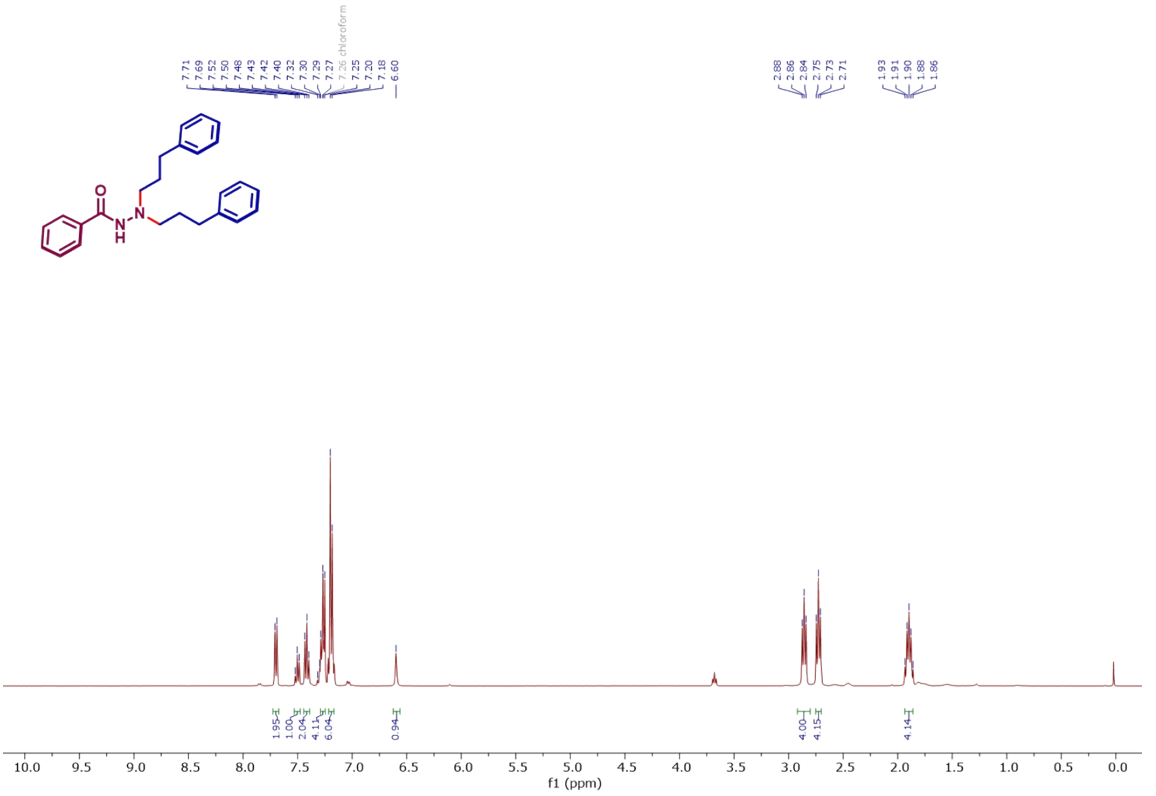


Figure S12. ^{13}C NMR spectrum (100 MHz) of 4e in $CDCl_3$



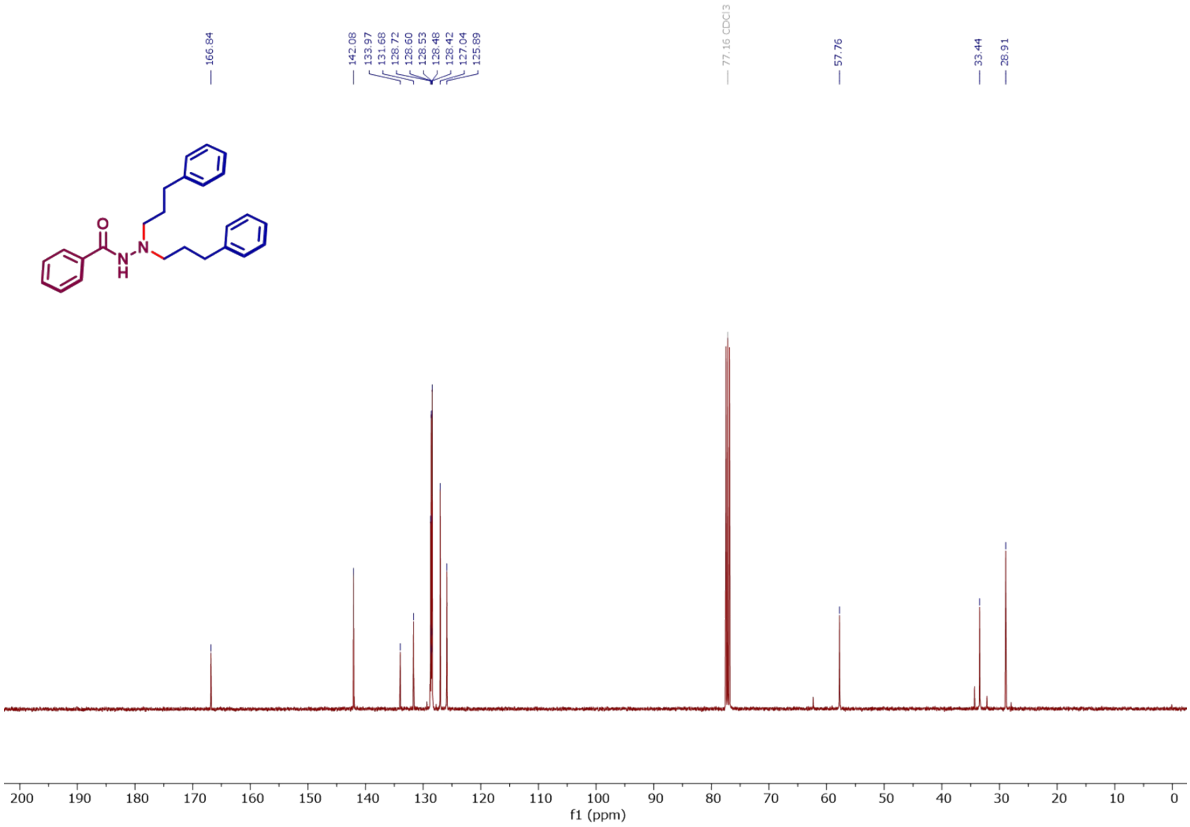


Figure S13. ^{1}H NMR spectrum (400 MHz) of 4f in $CDCl_3$

Figure S14. ^{13}C NMR spectrum (100 MHz) of 4f in $CDCl_3$

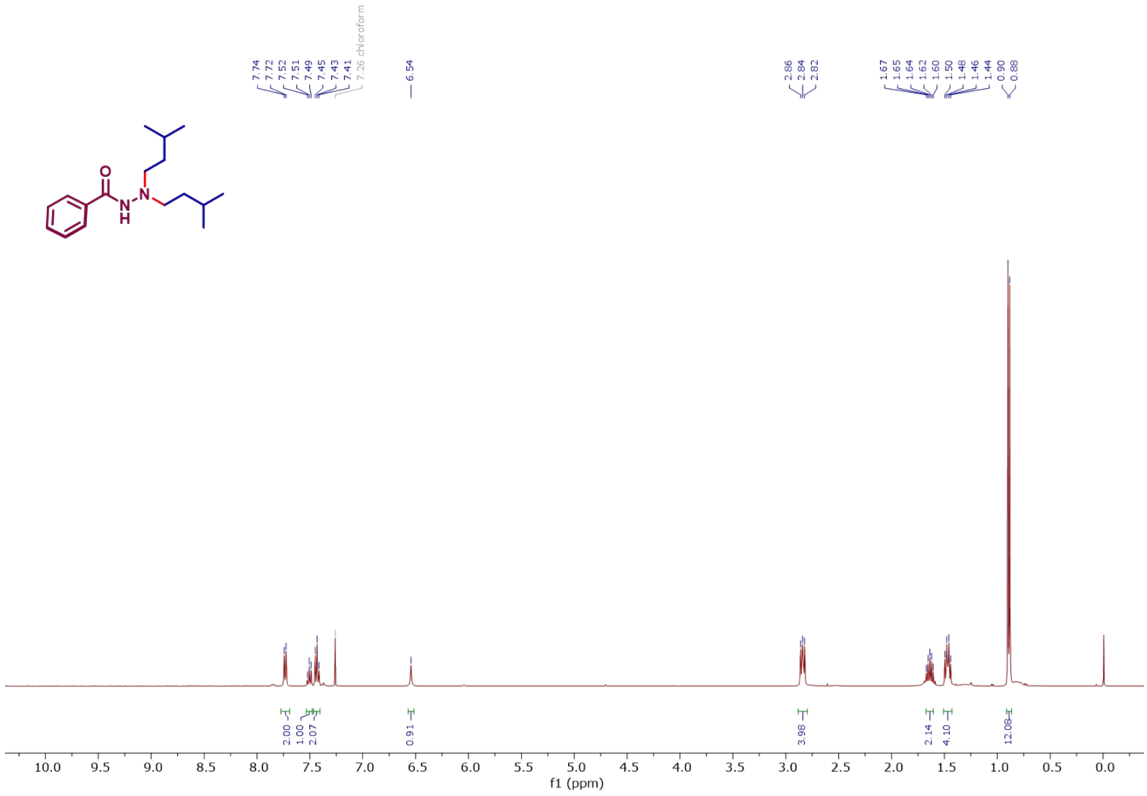
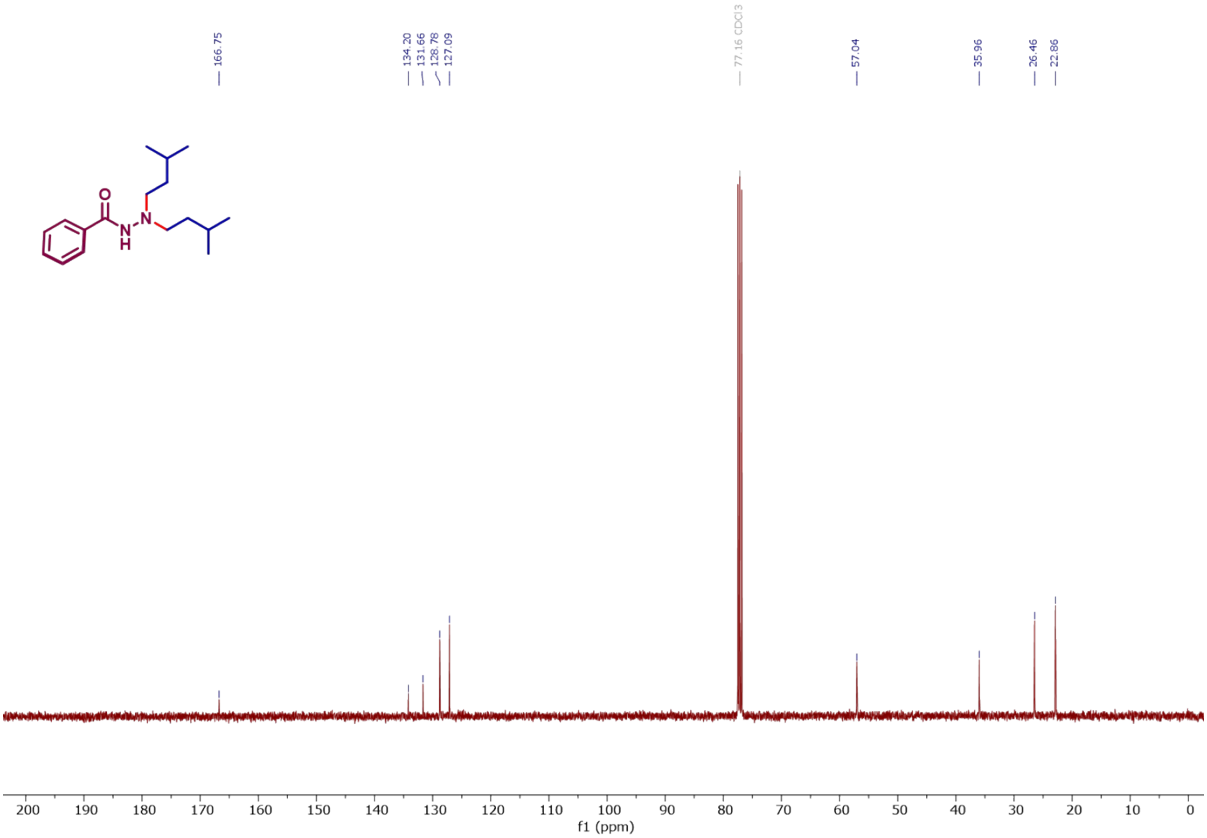


Figure S15. ^{1}H NMR spectrum (400 MHz) of 4g in $CDCl_3$



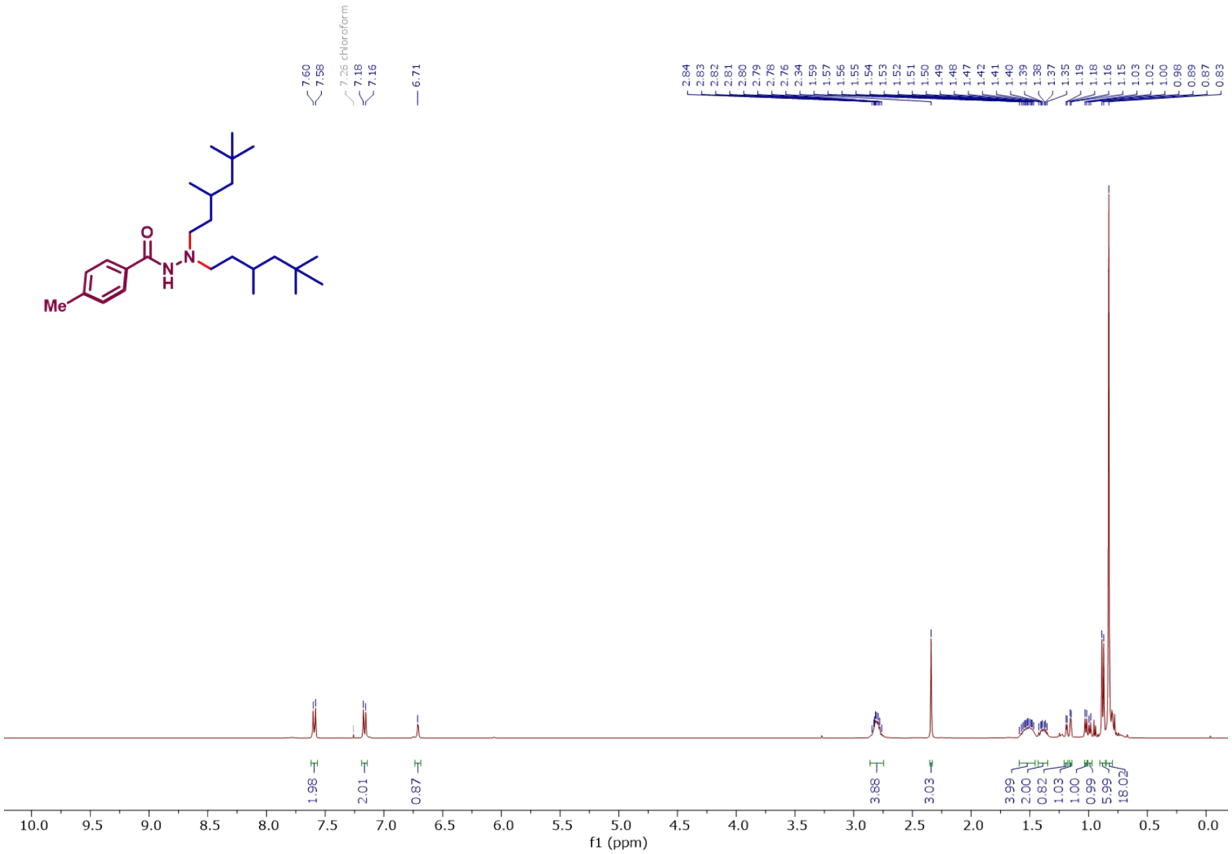
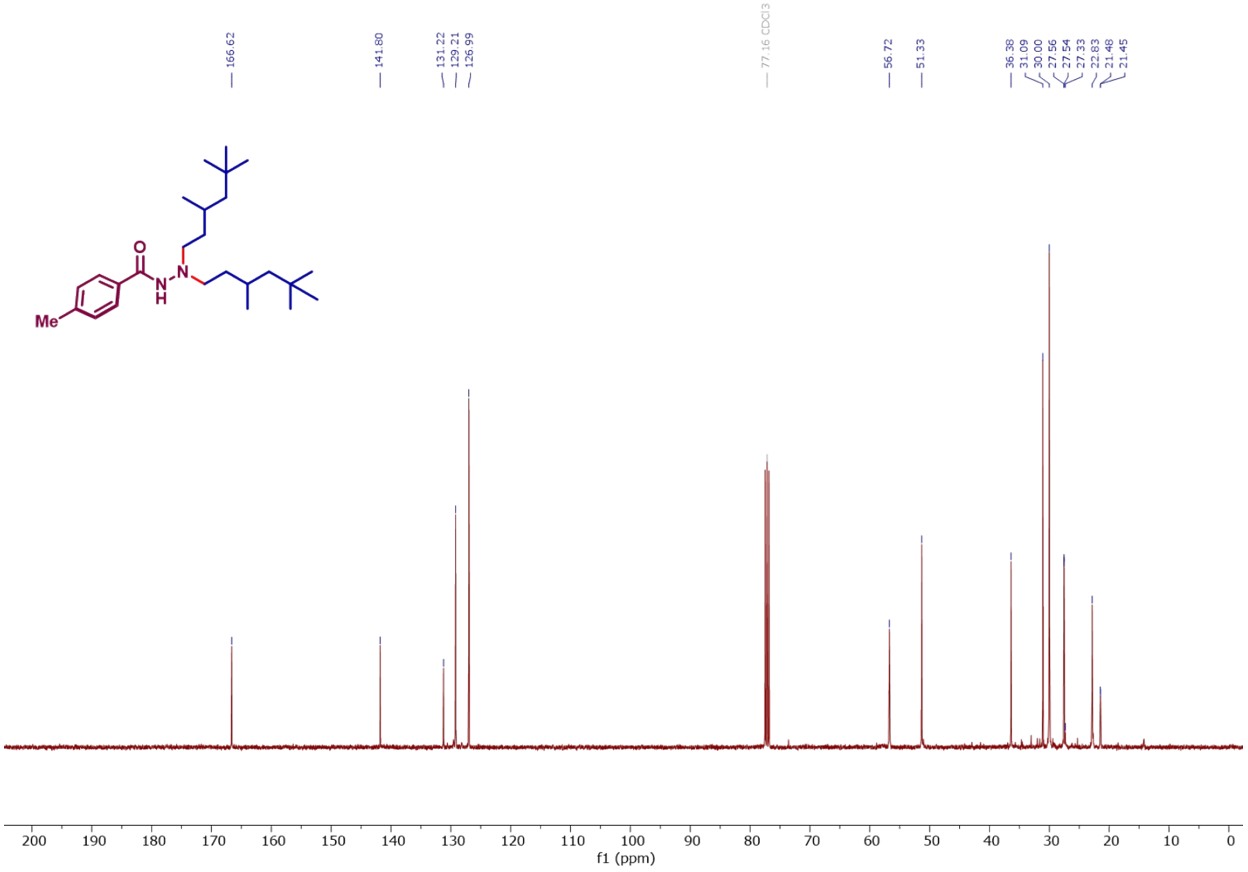


Figure S16. ^{13}C NMR spectrum (100 MHz) of 4g in $CDCl_3$

Figure S17. ^{1}H NMR spectrum (400 MHz) of 4h in $CDCl_3$

Figure S18. ^{13}C NMR spectrum (100 MHz) of 4h in $CDCl_3$



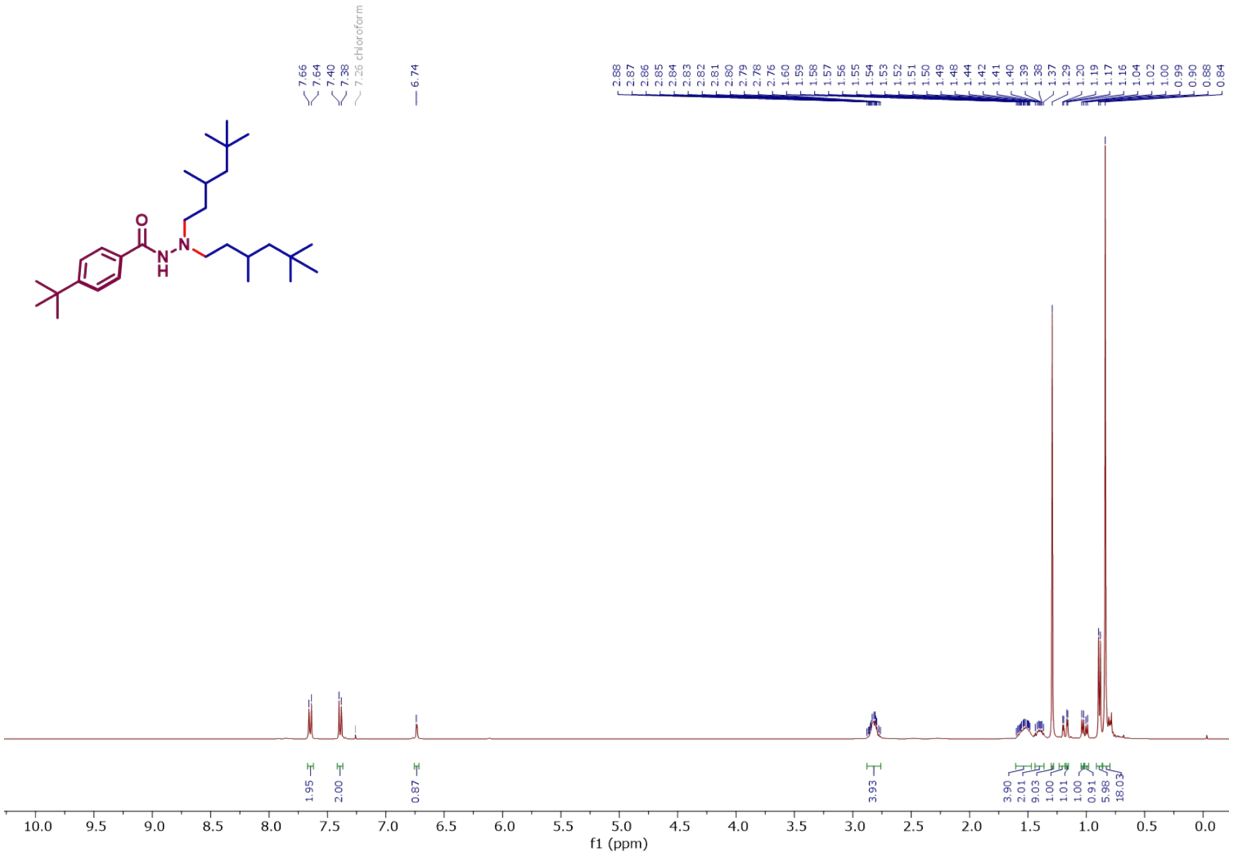
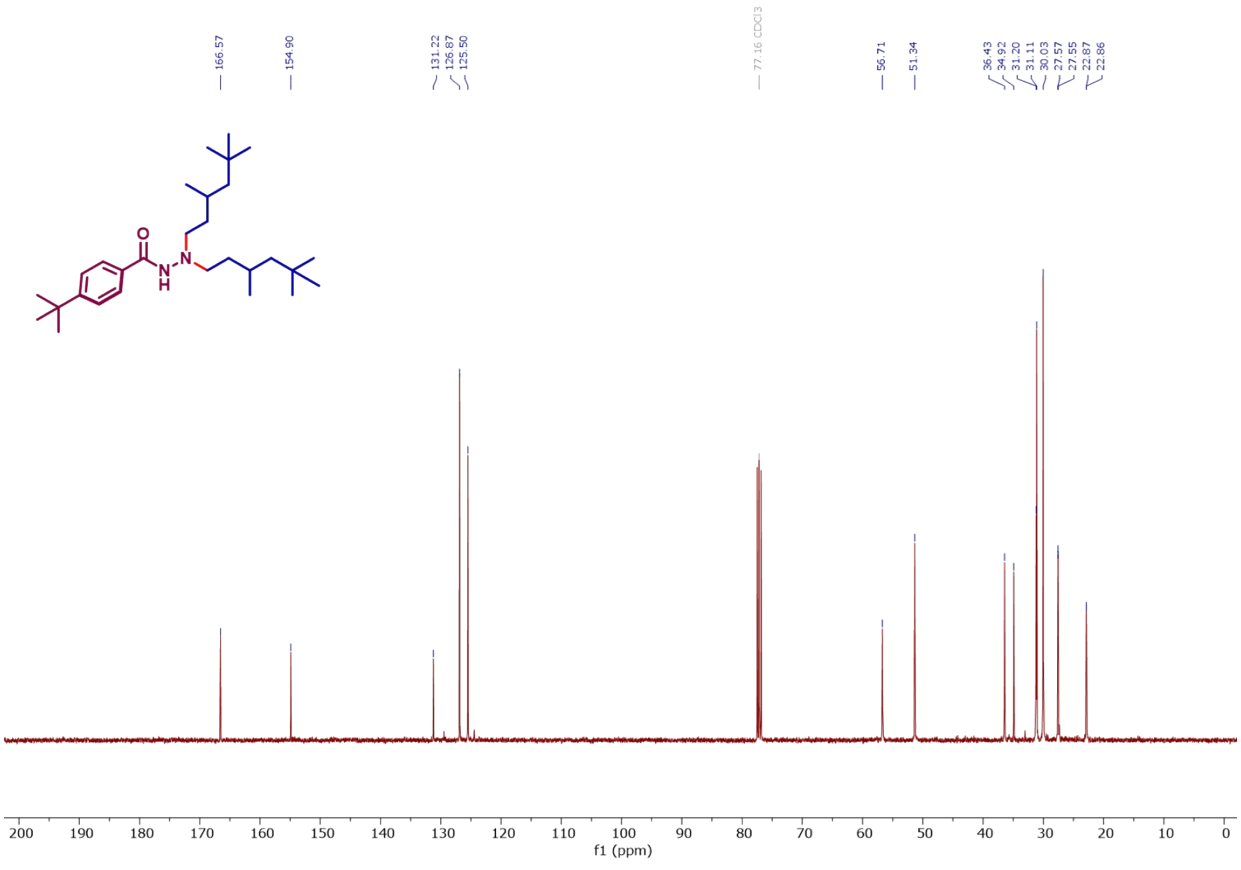


Figure S19. ^{1}H NMR spectrum (400 MHz) of 4i in $CDCl_3$

Figure S20. ^{13}C NMR spectrum (100 MHz) of 4i in $CDCl_3$



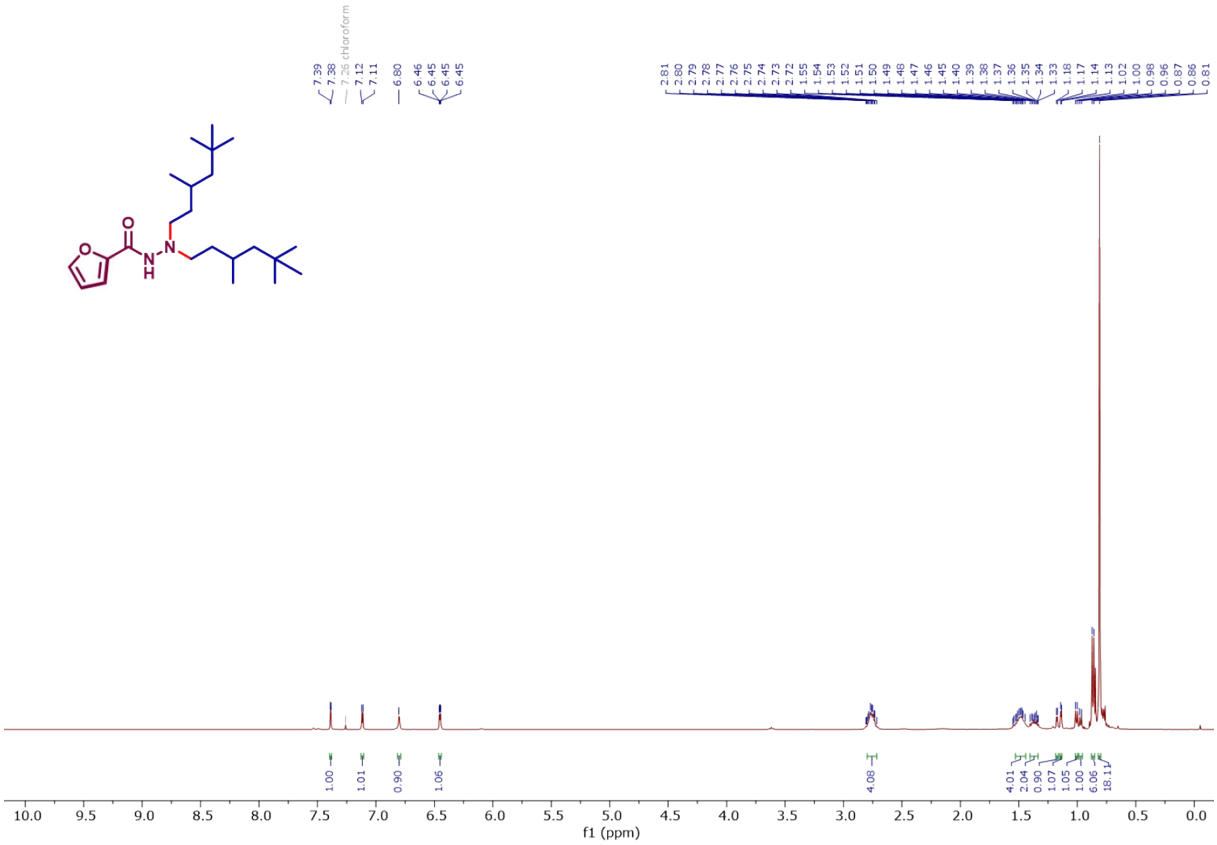


Figure S21. ^{1}H NMR spectrum (400 MHz) of 4j in $CDCl_3$

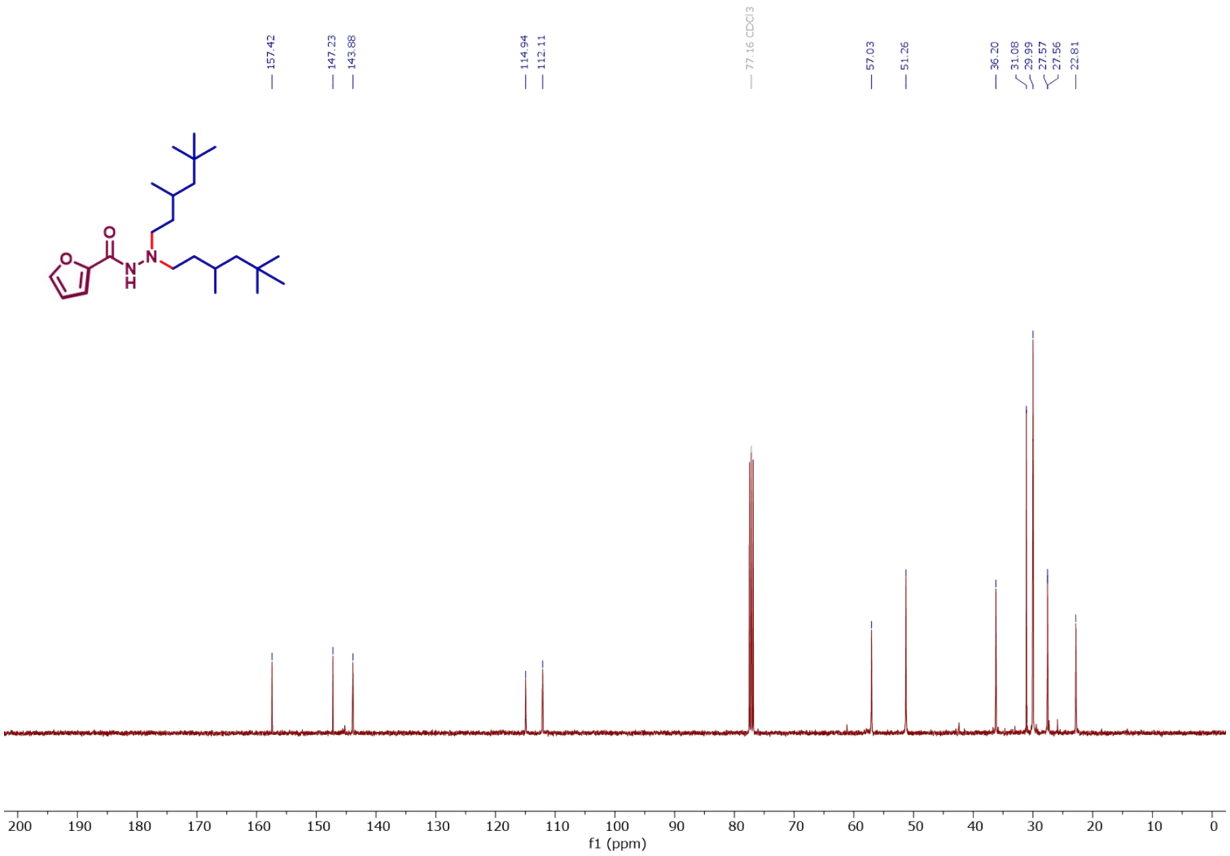


Figure S22. ^{13}C NMR spectrum (100 MHz) of 4j in $CDCl_3$

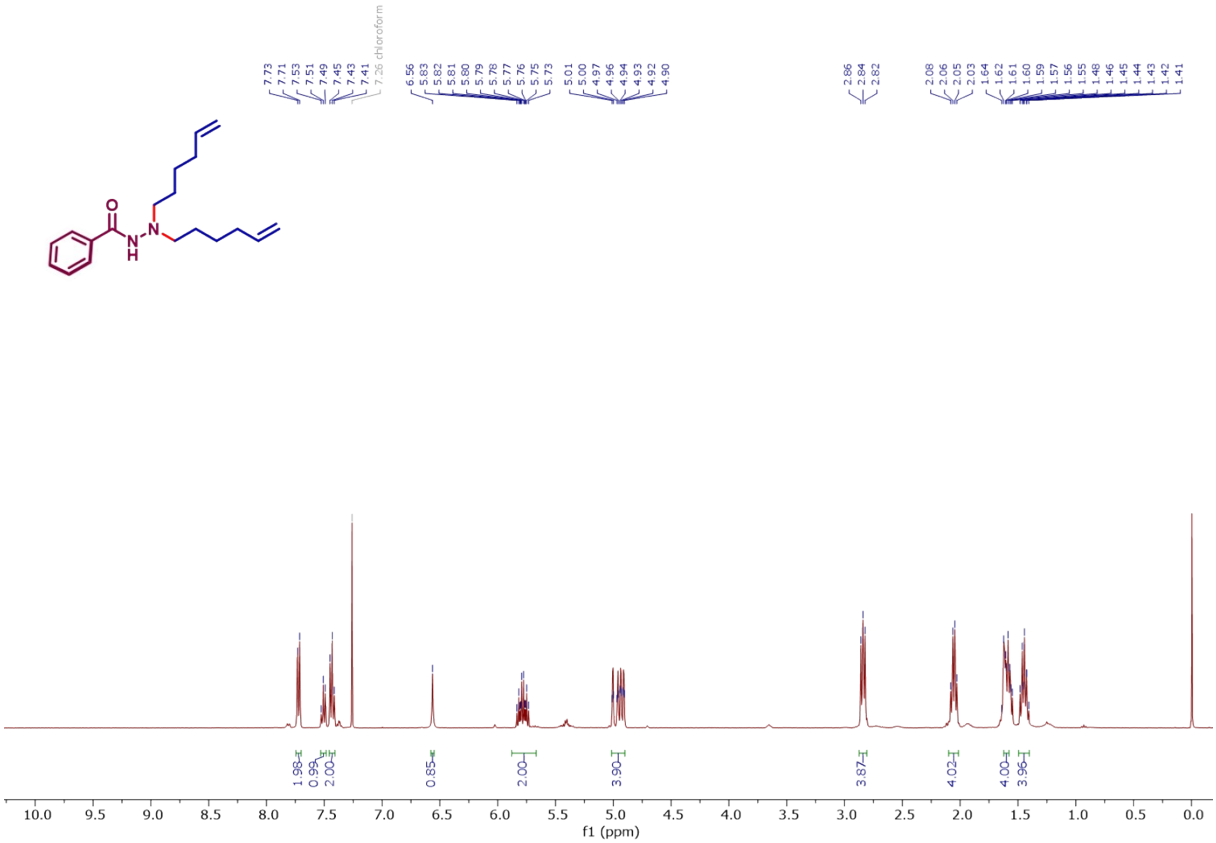


Figure S23. ^{1}H NMR spectrum (400 MHz) of 4k in $CDCl_3$

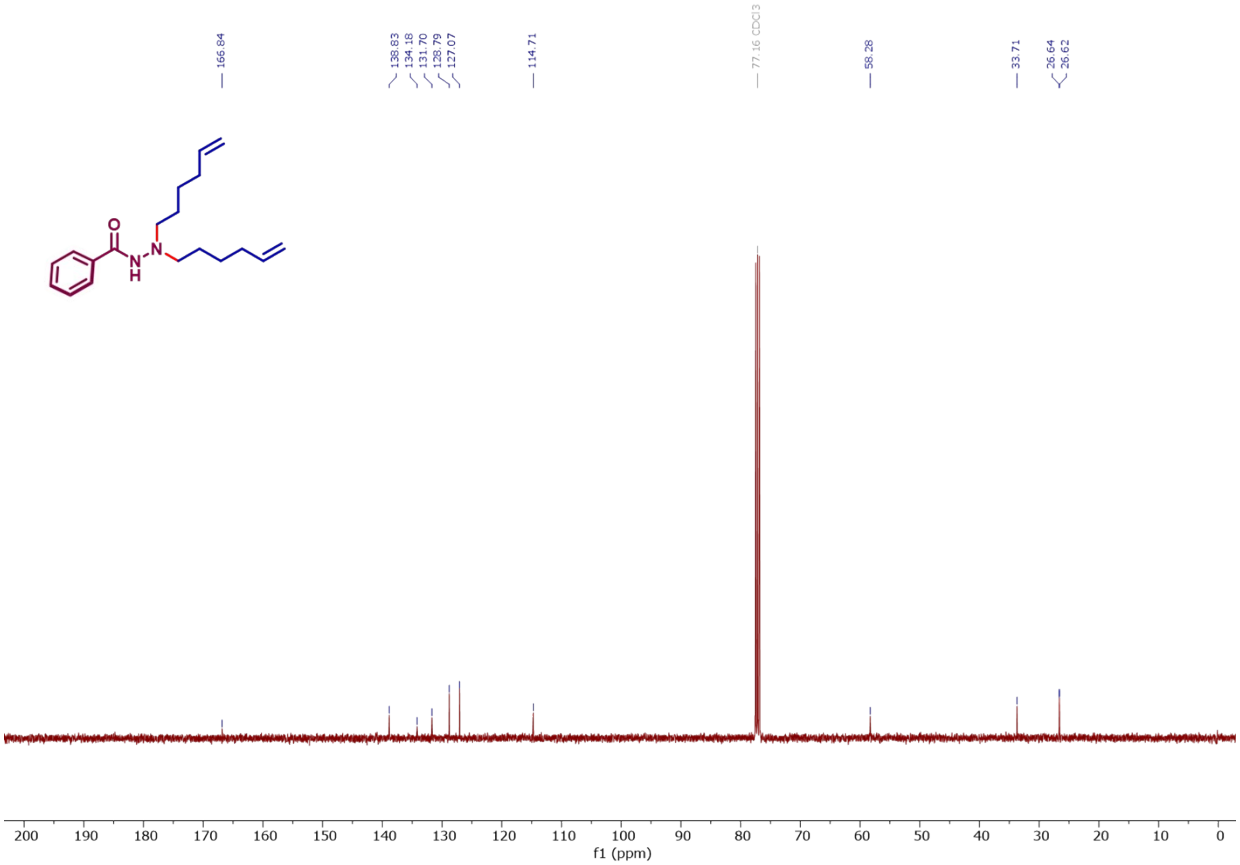


Figure S24. ^{13}C NMR spectrum (100 MHz) of 4k in $CDCl_3$

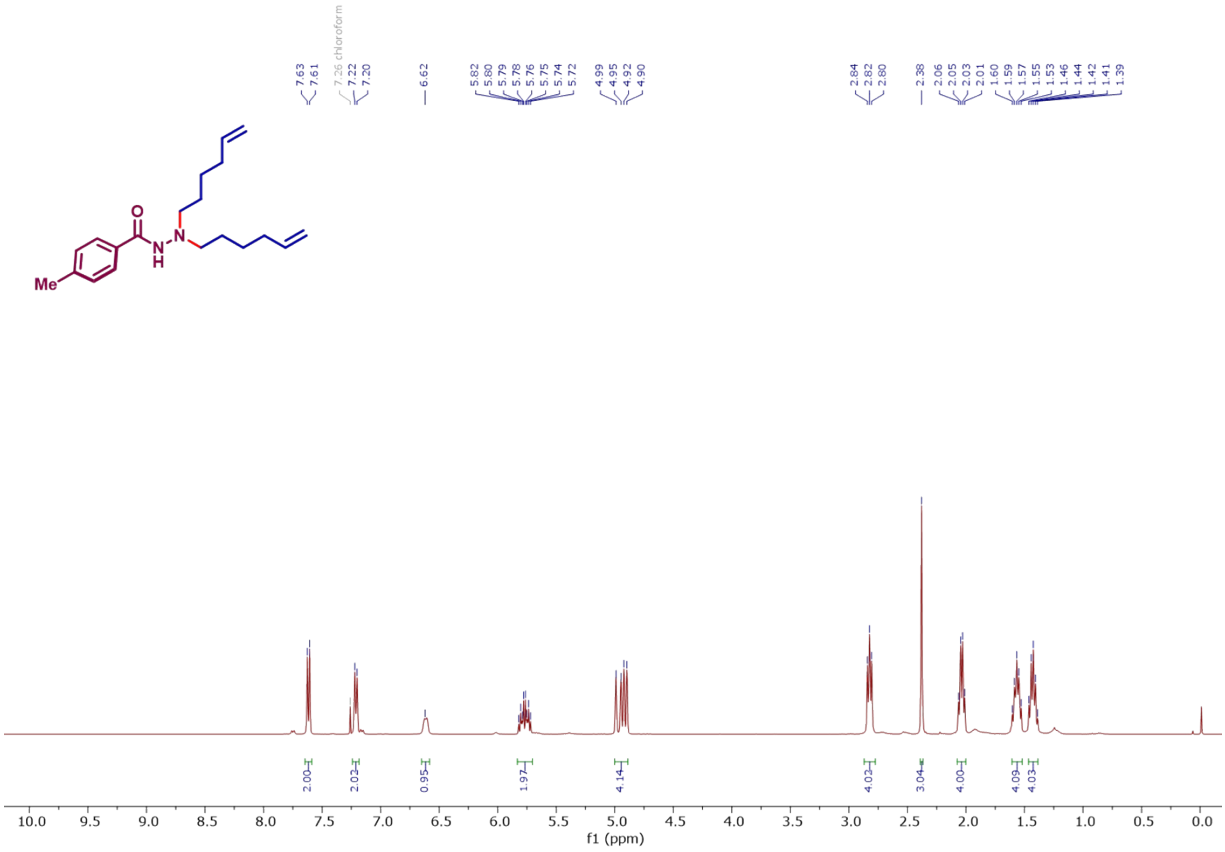


Figure S25. ^{1}H NMR spectrum (400 MHz) of 4l in $CDCl_3$

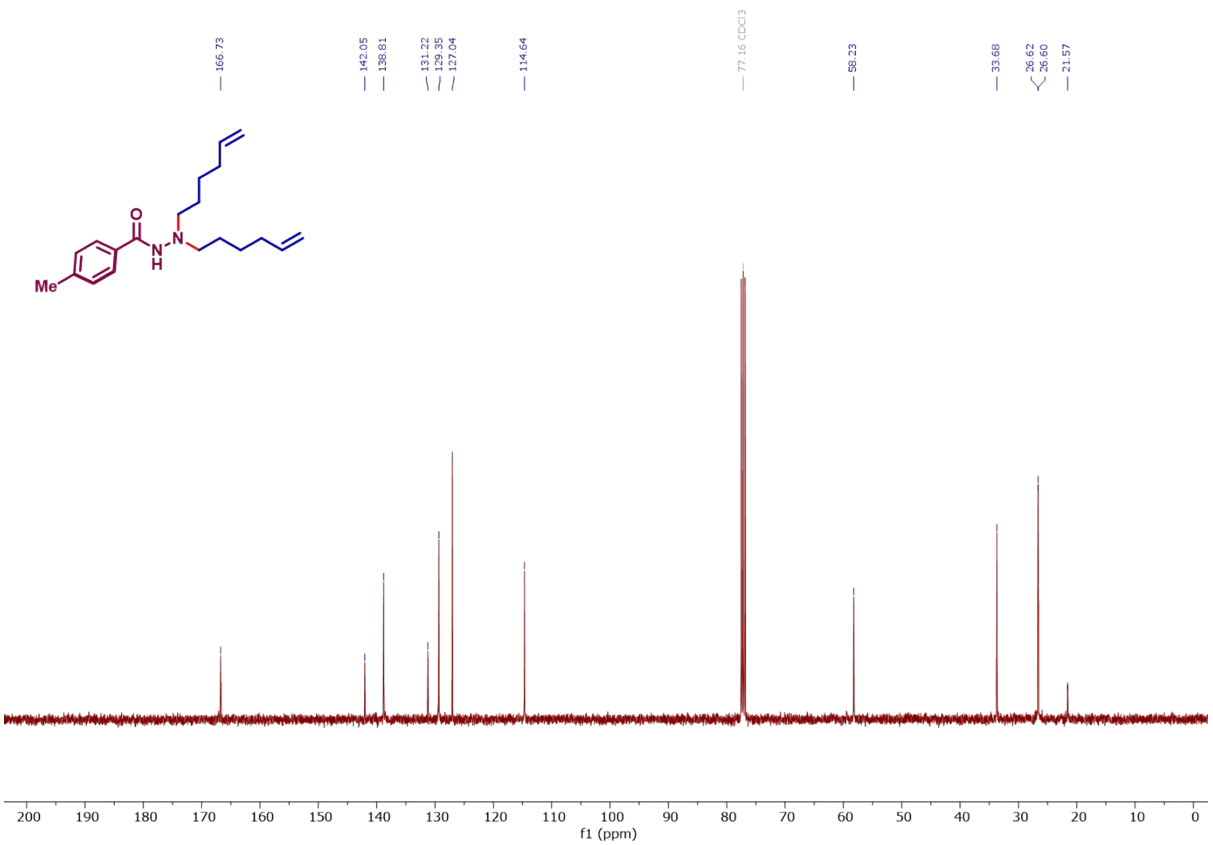


Figure S26. ^{13}C NMR spectrum (100 MHz) of 4l in $CDCl_3$

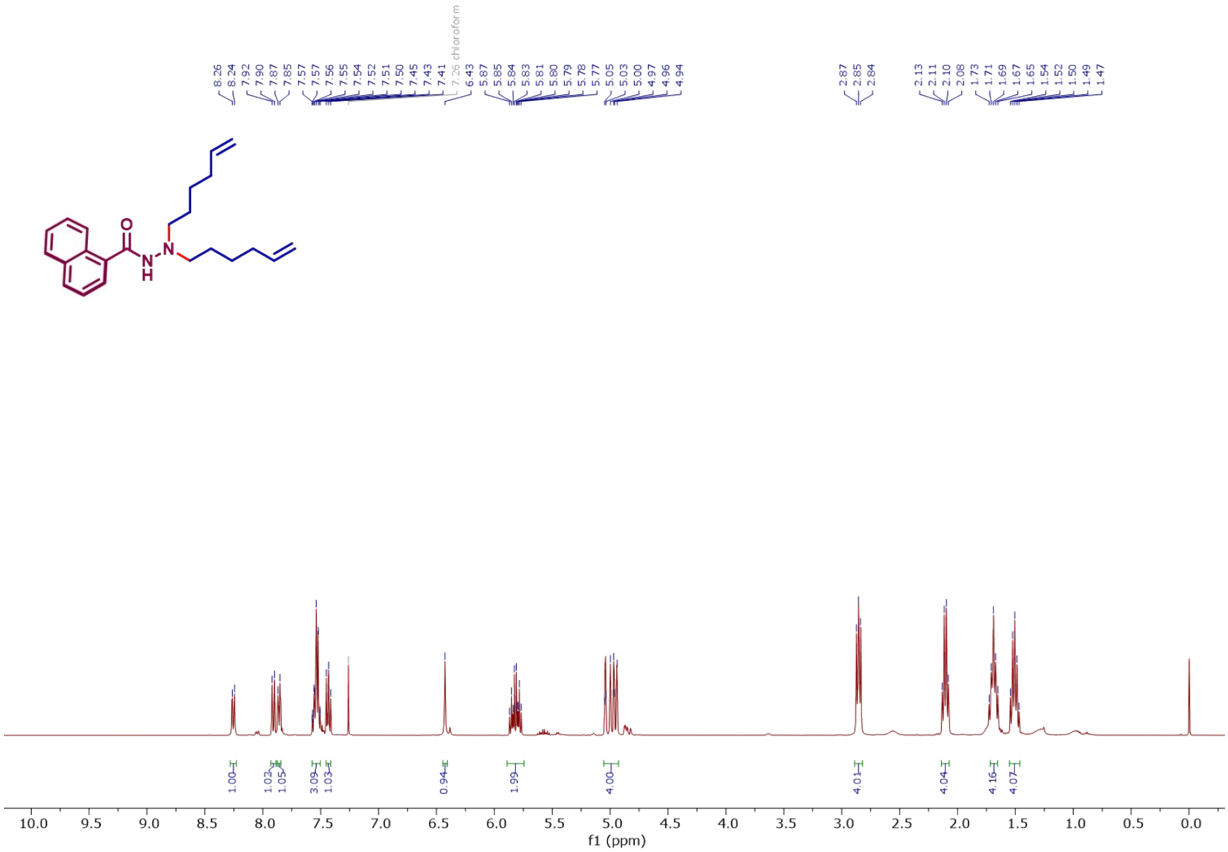


Figure S27. ^{1}H NMR spectrum (400 MHz) of 4m in $CDCl_3$

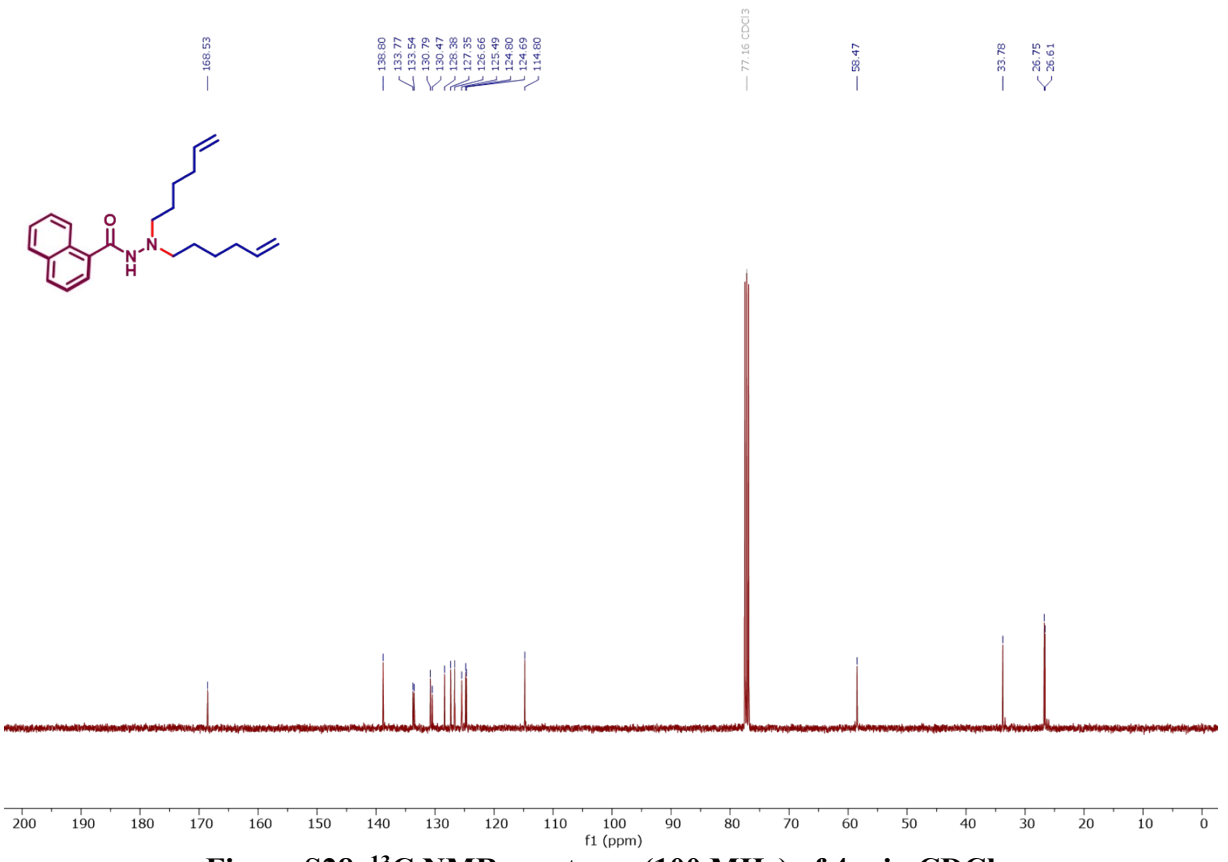


Figure S28. ^{13}C NMR spectrum (100 MHz) of 4m in $CDCl_3$

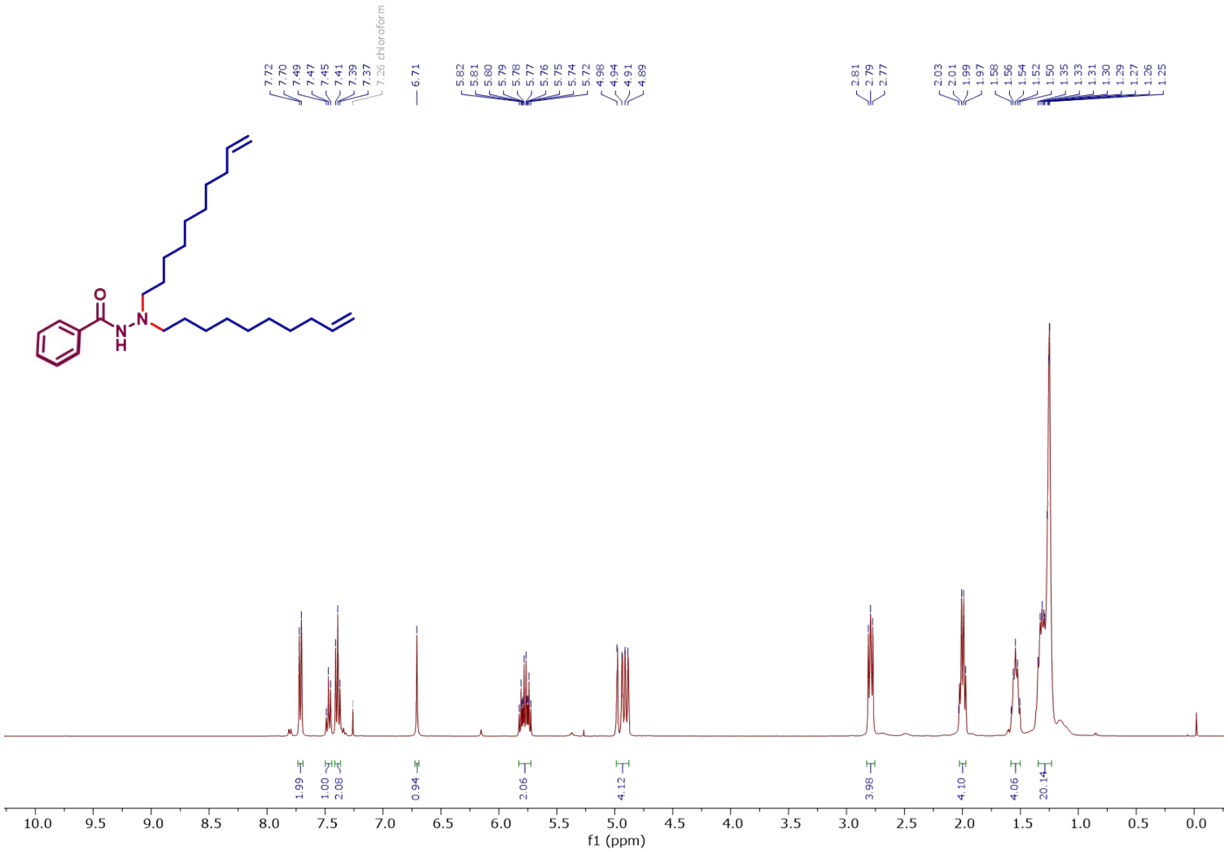


Figure S29. ^{1}H NMR spectrum (400 MHz) of 4n in $CDCl_3$

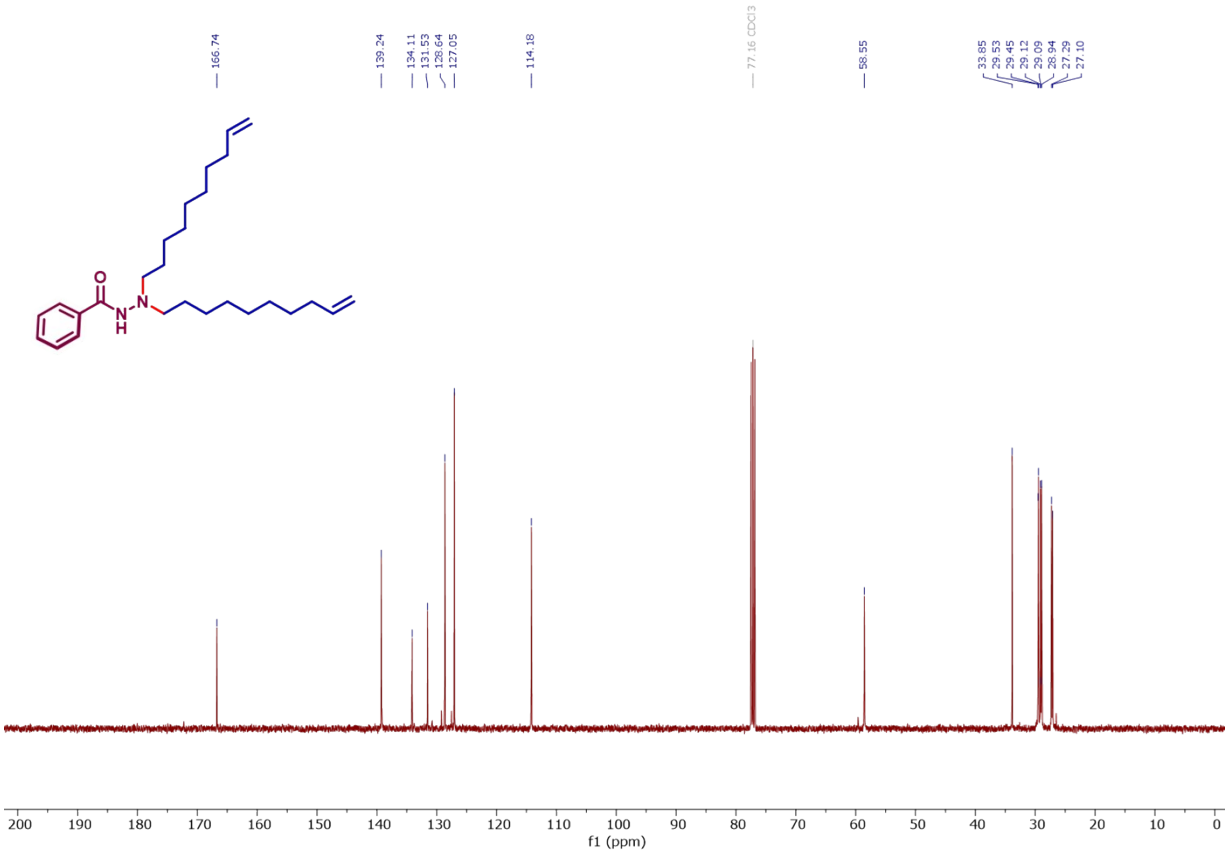
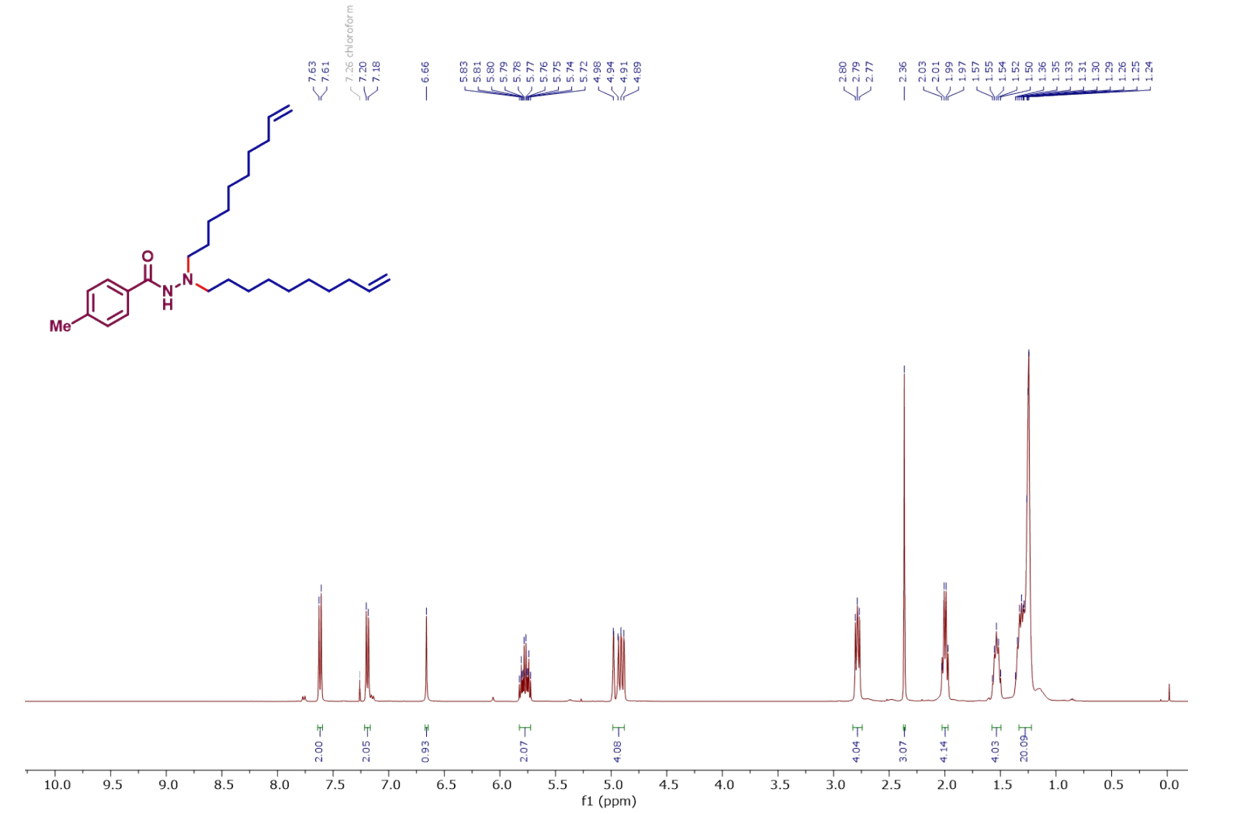


Figure S30. ^{13}C NMR spectrum (100 MHz) of 4n in $CDCl_3$



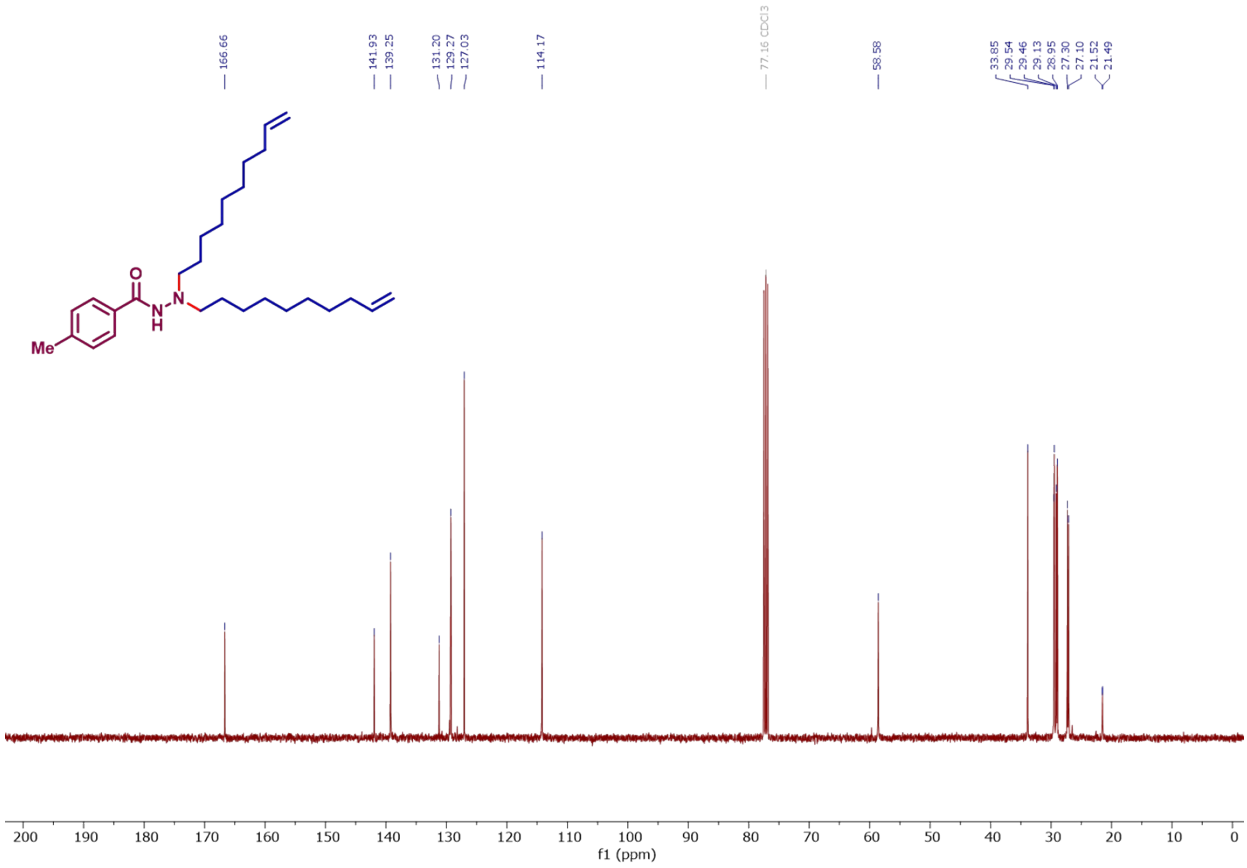


Figure S31. ^{1}H NMR spectrum (400 MHz) of 4o in $CDCl_3$

Figure S32. ^{13}C NMR spectrum (100 MHz) of 4o in $CDCl_3$

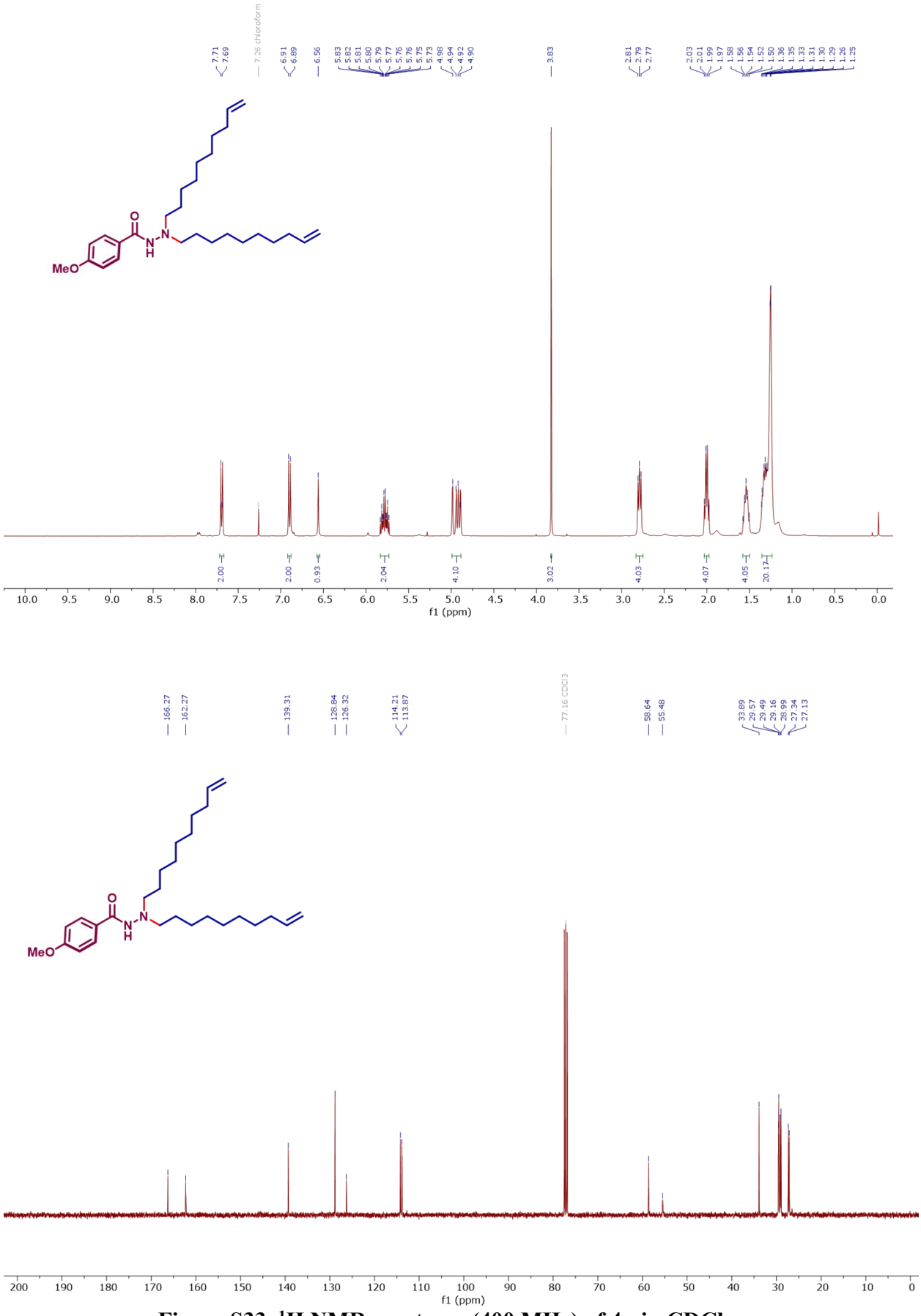


Figure S33. ^{1}H NMR spectrum (400 MHz) of 4p in $CDCl_3$

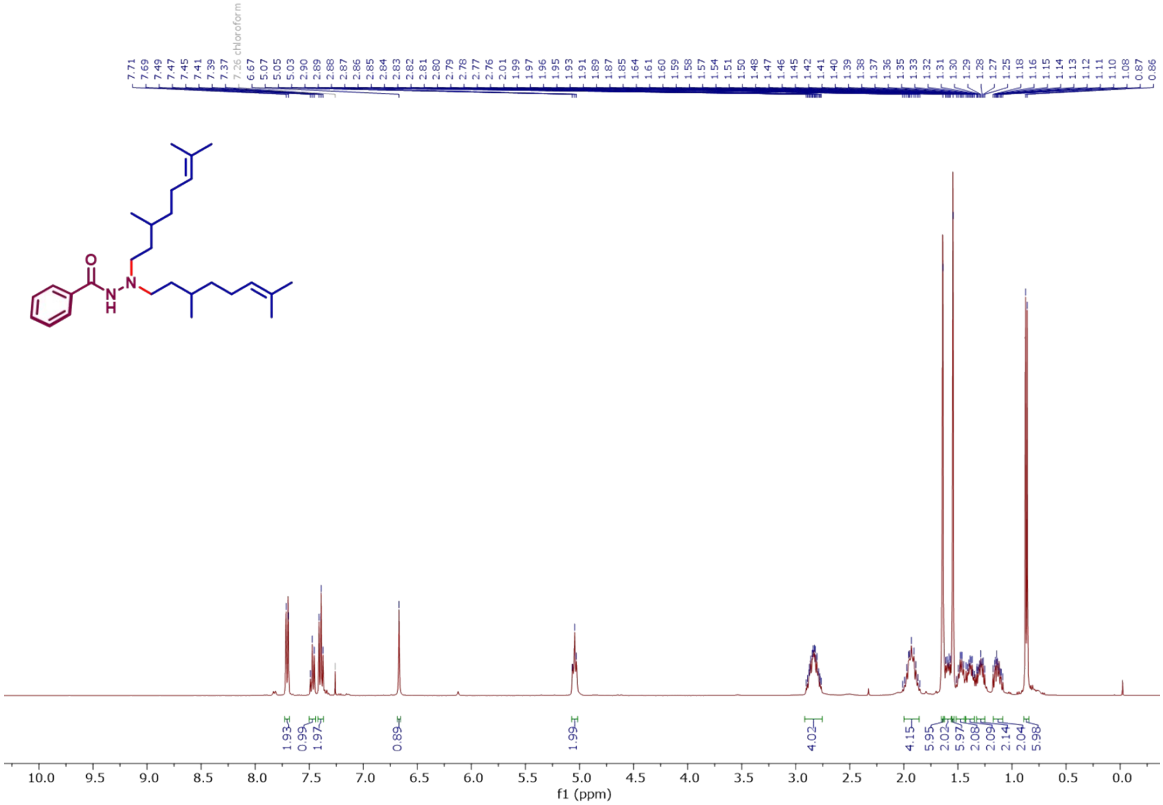


Figure S34. ^{13}C NMR spectrum (100 MHz) of 4p in $CDCl_3$

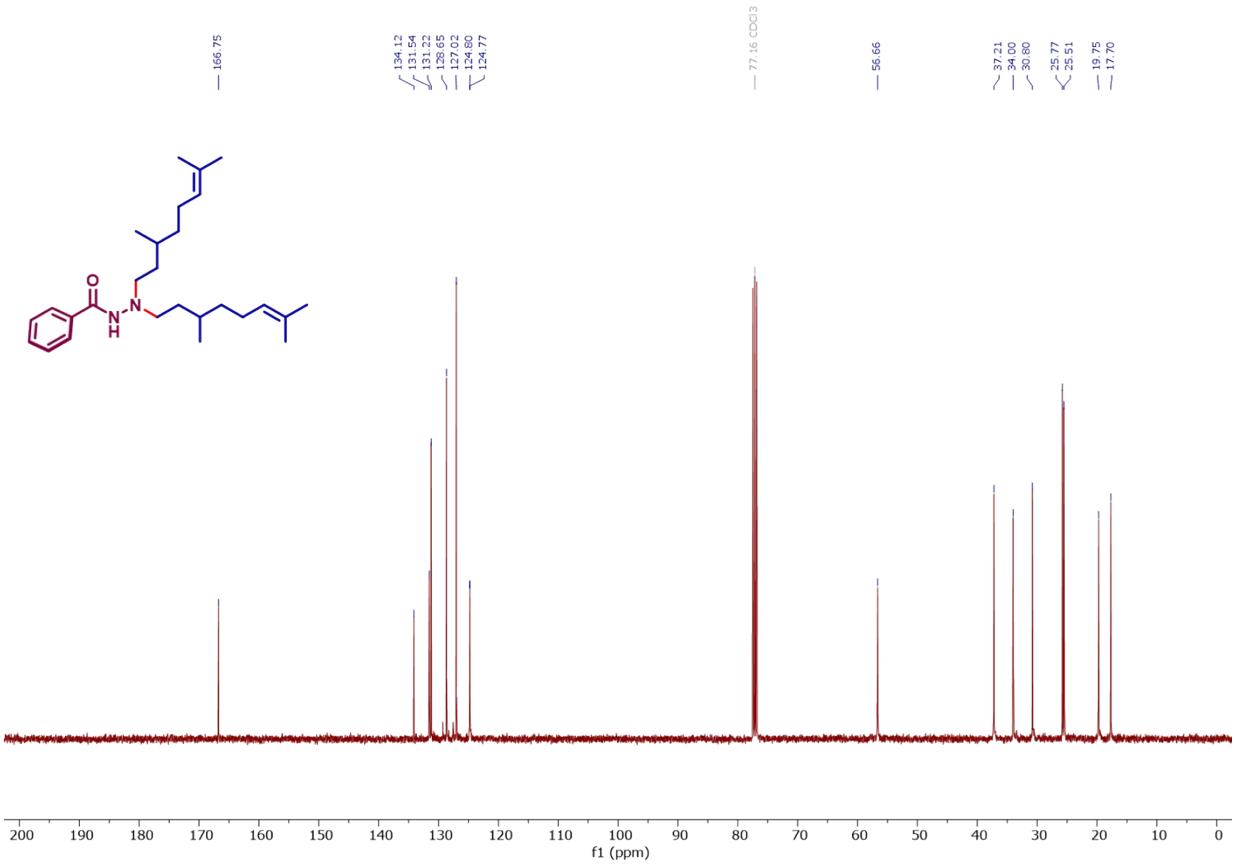


Figure S35. ^{1}H NMR spectrum (400 MHz) of 4q in $CDCl_3$

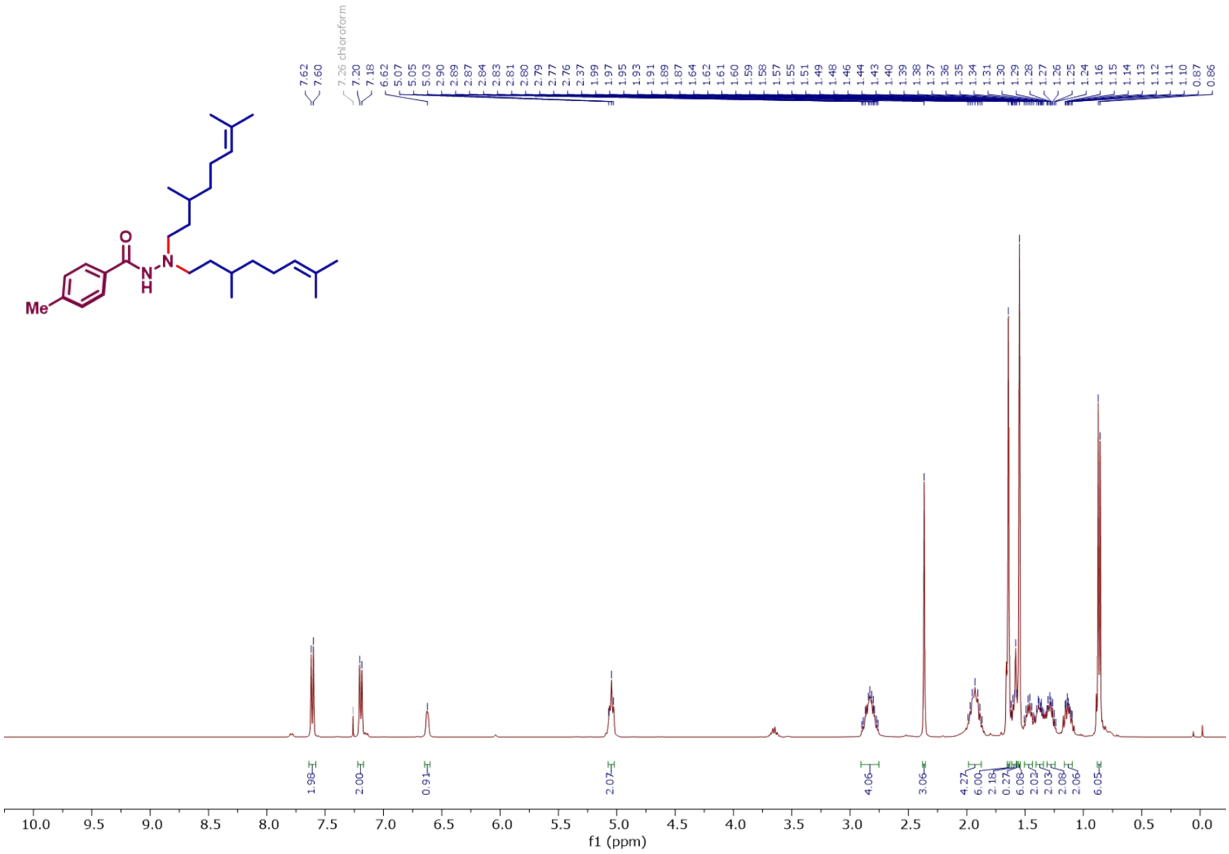


Figure S36. ^{13}C NMR spectrum (100 MHz) of 4q in $CDCl_3$

Figure S37. ^{1}H NMR spectrum (400 MHz) of 4r in $CDCl_3$

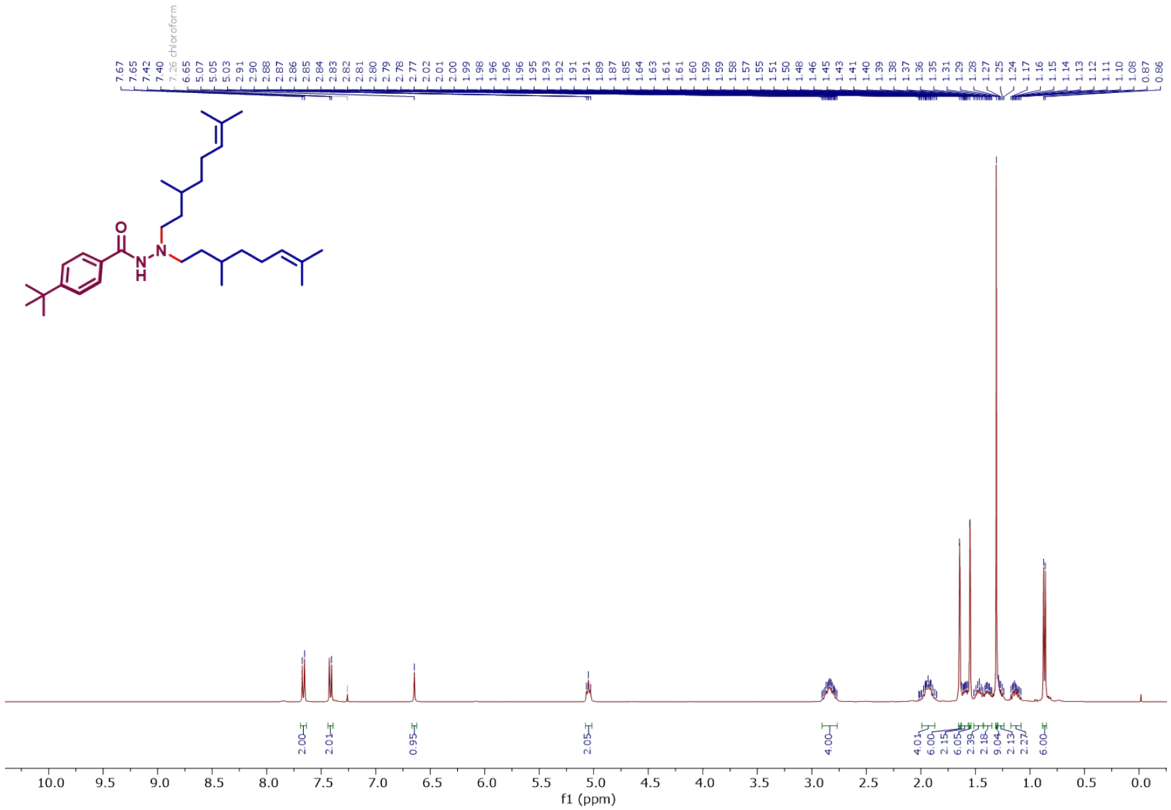


Figure S38 ^{13}C NMR spectrum (100 MHz) of 4r in $CDCl_3$

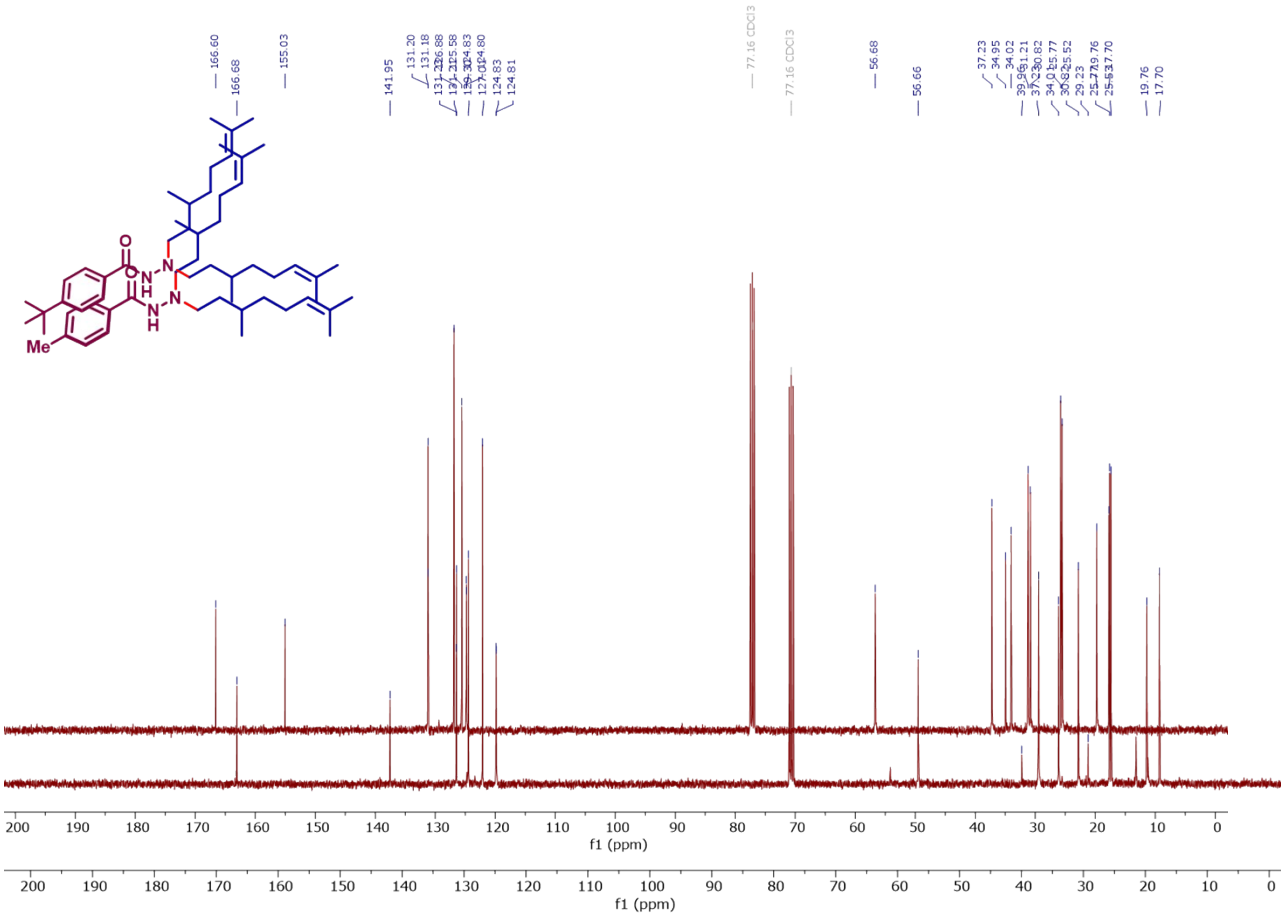


Figure S39. ^{1}H NMR spectrum (400 MHz) of 4s in $CDCl_3$

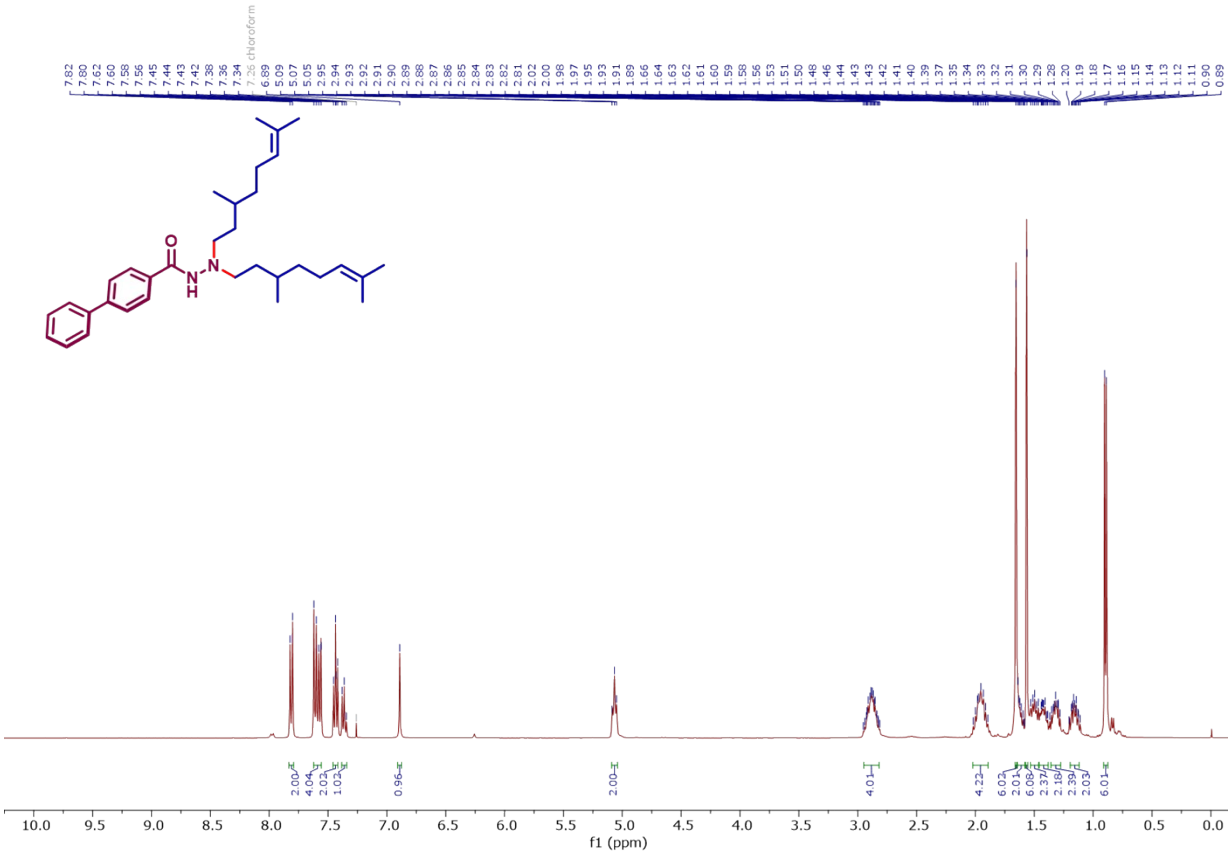
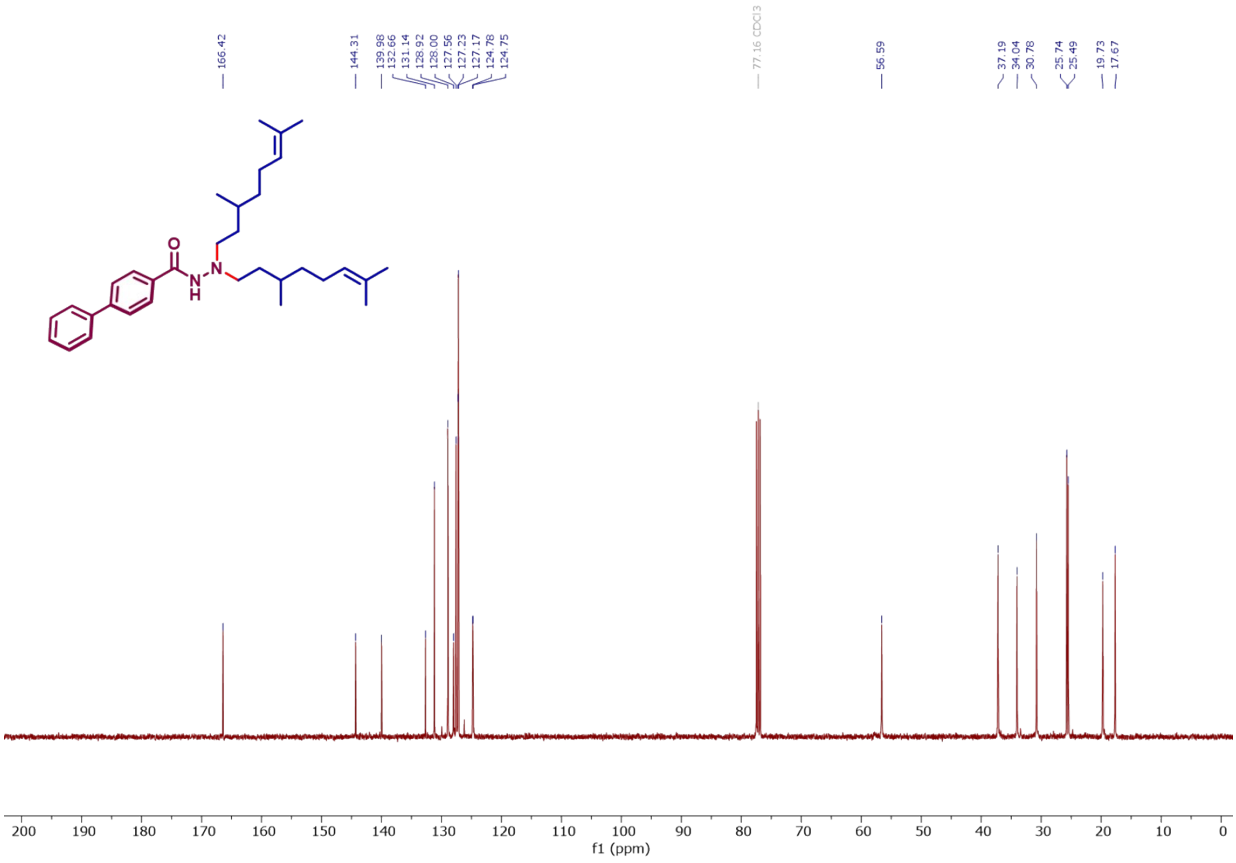


Figure S40. ^{13}C NMR spectrum (100 MHz) of 4s in $CDCl_3$

Figure S41. ^{1}H NMR spectrum (400 MHz) of 4t in $CDCl_3$

Figure S42. ^{13}C NMR spectrum (100 MHz) of 4t in $CDCl_3$



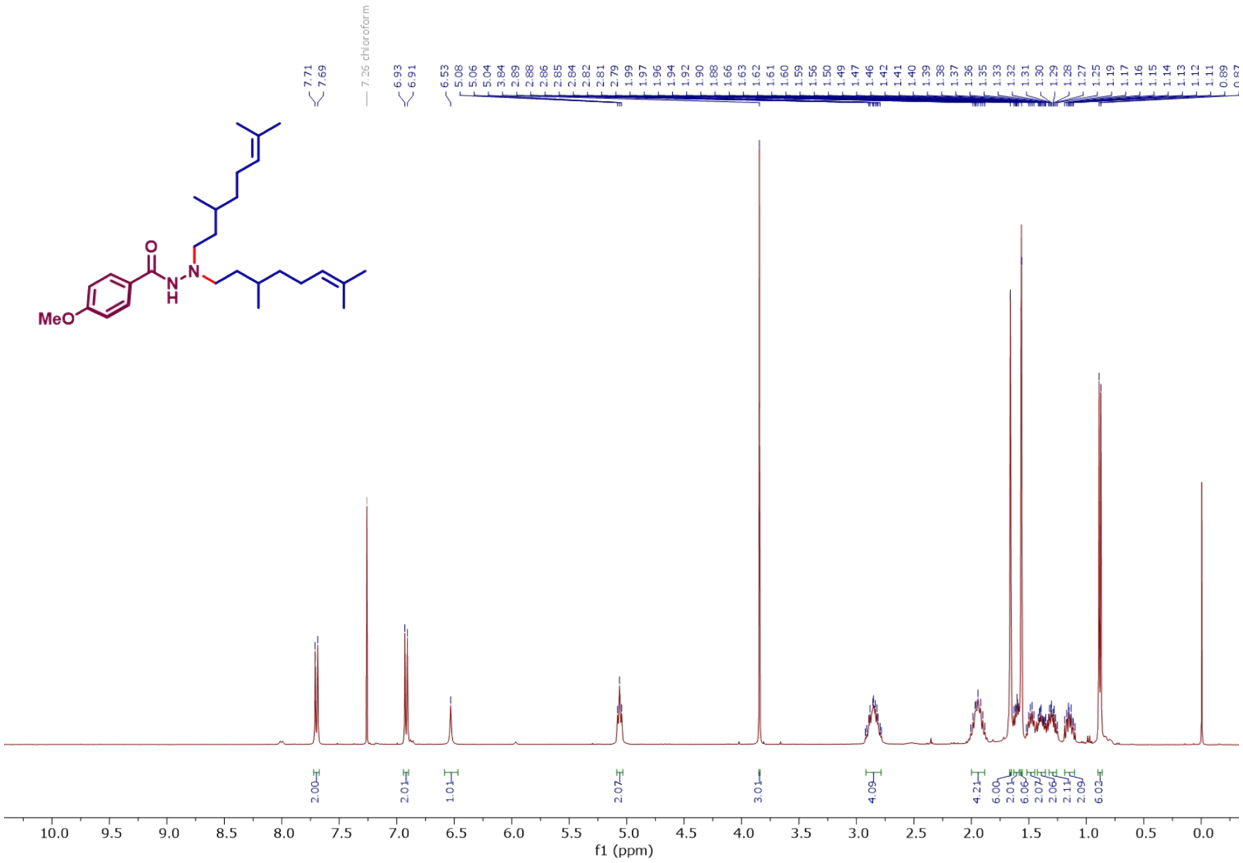
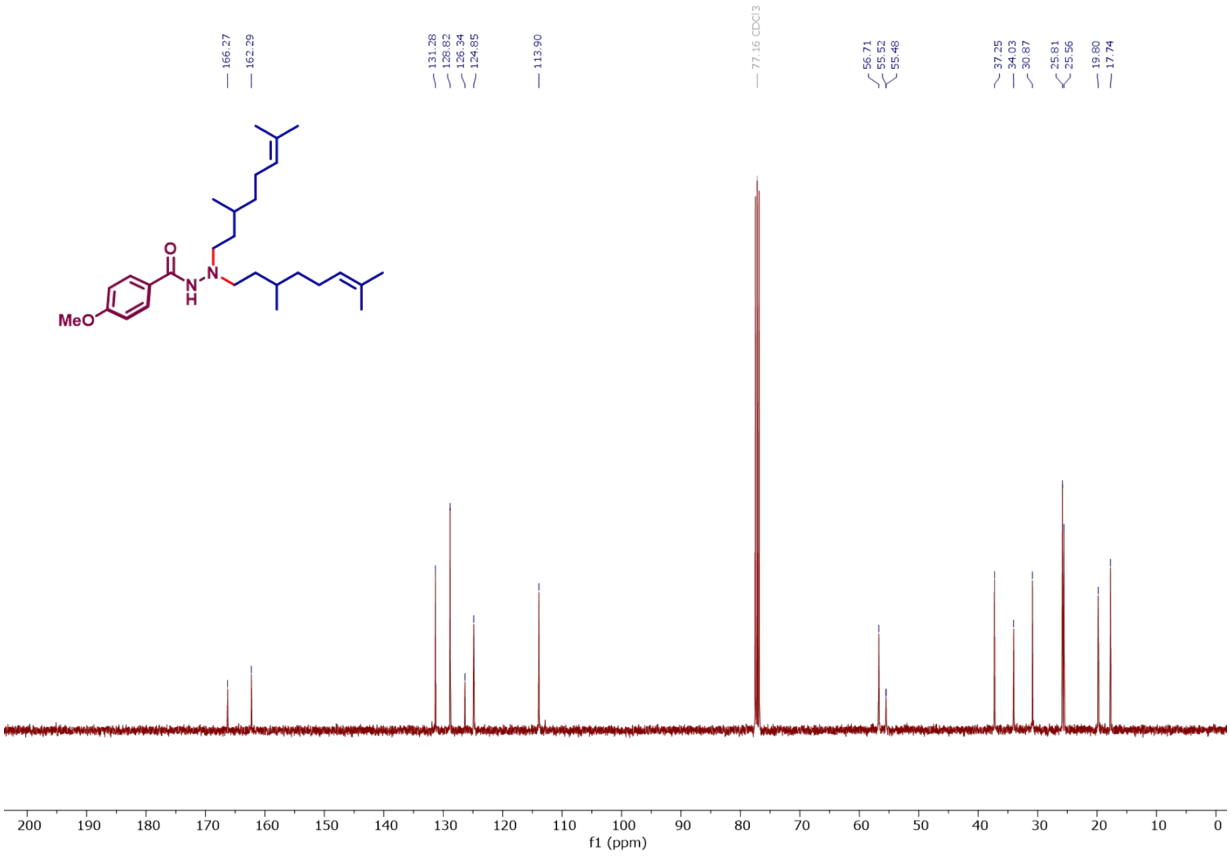


Figure S43. ^{1}H NMR spectrum (400 MHz) of 4u in $CDCl_3$

Figure S44. ^{13}C NMR spectrum (100 MHz) of 4u in $CDCl_3$



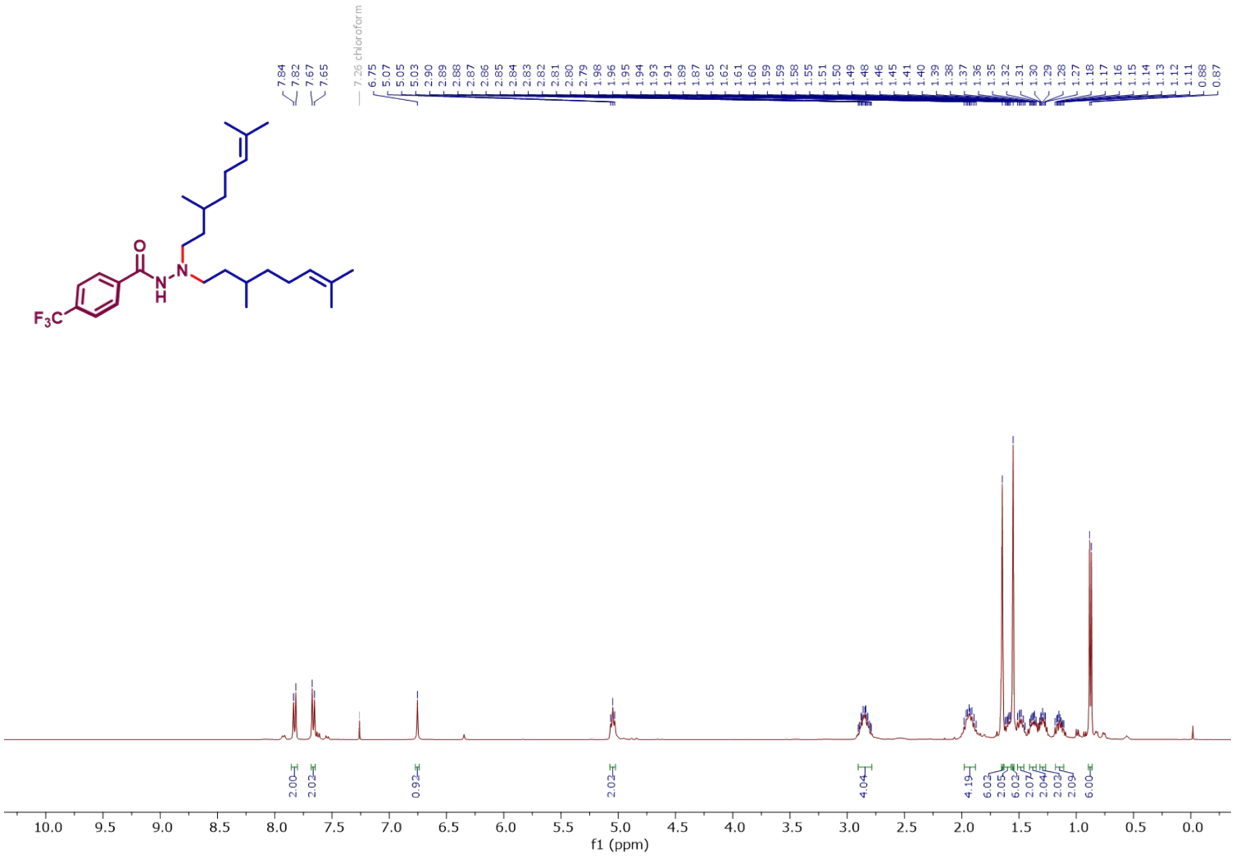


Figure S45. ^{1}H NMR spectrum (400 MHz) of 4v in $CDCl_3$

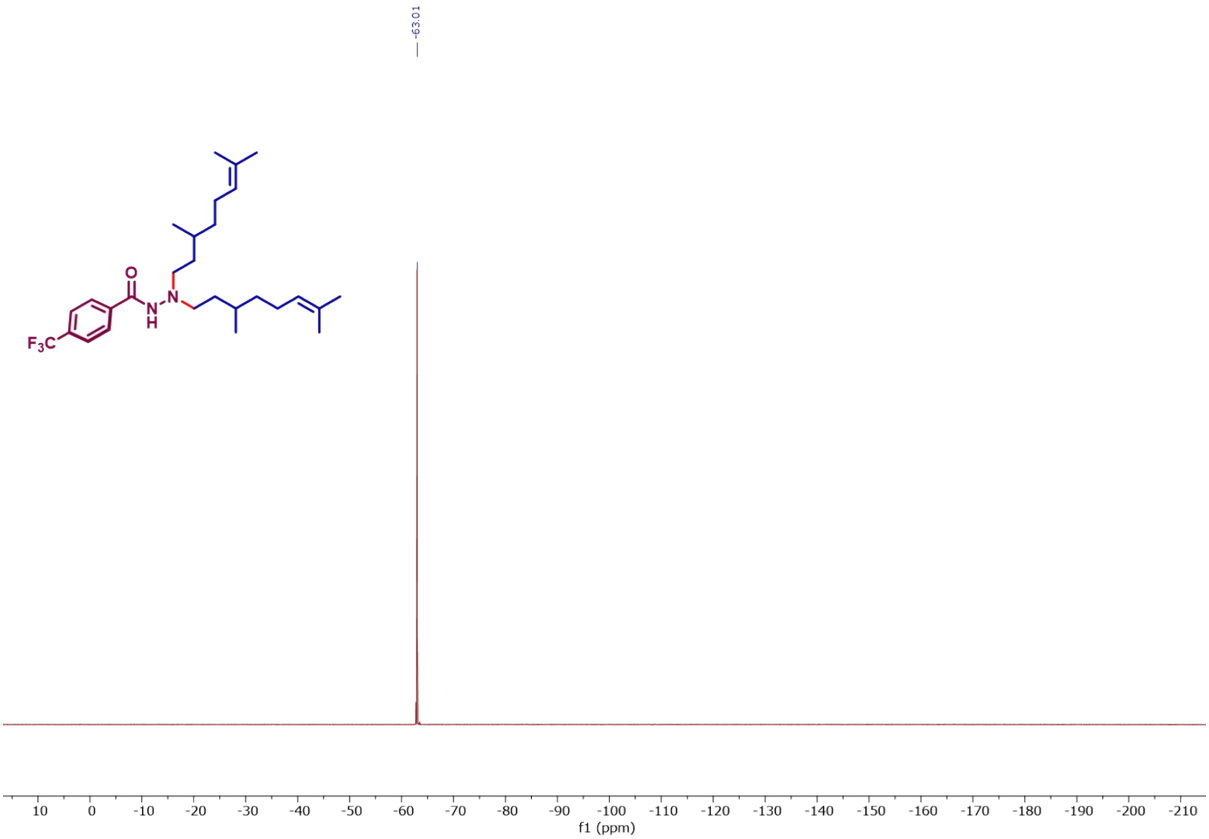


Figure S46. ^{13}C NMR spectrum (100 MHz) of 4v in $CDCl_3$

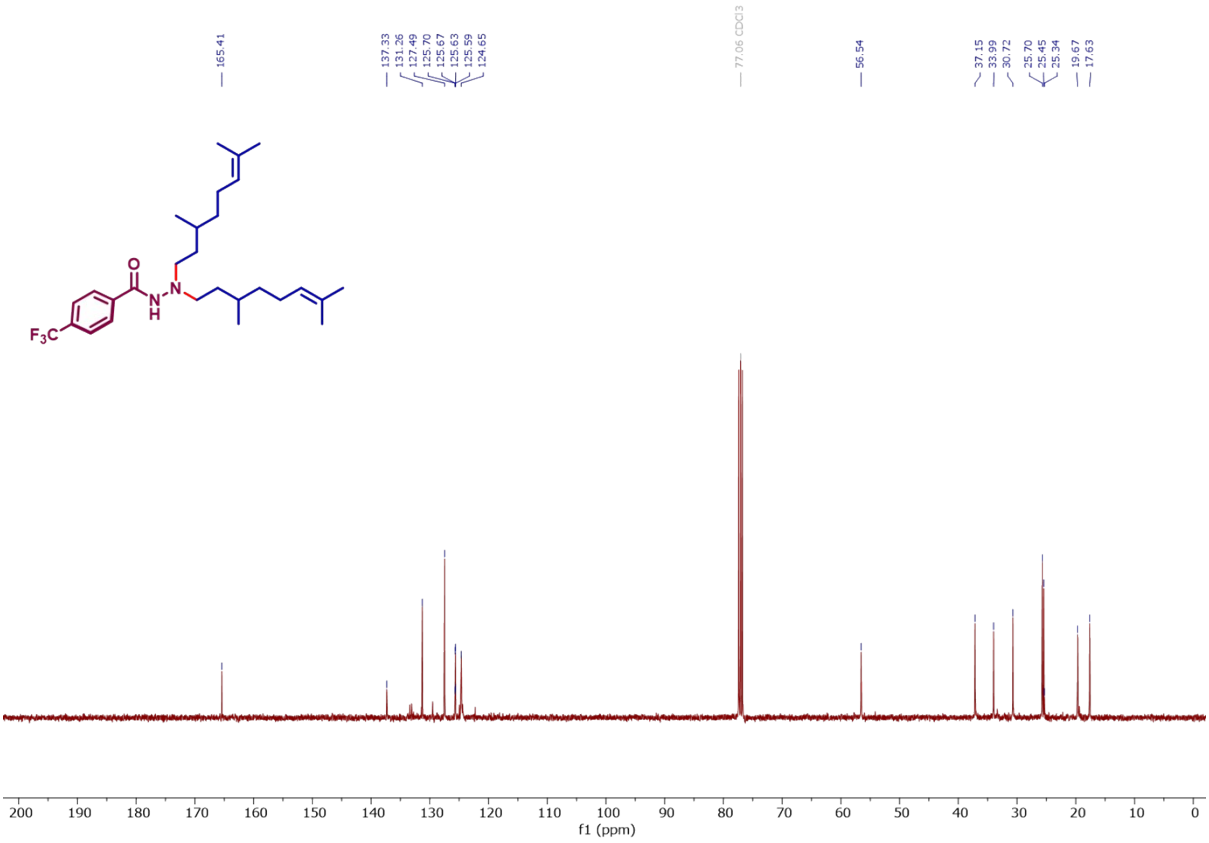


Figure S47. ^{19}F NMR spectrum (376 MHz) of 4v in $CDCl_3$

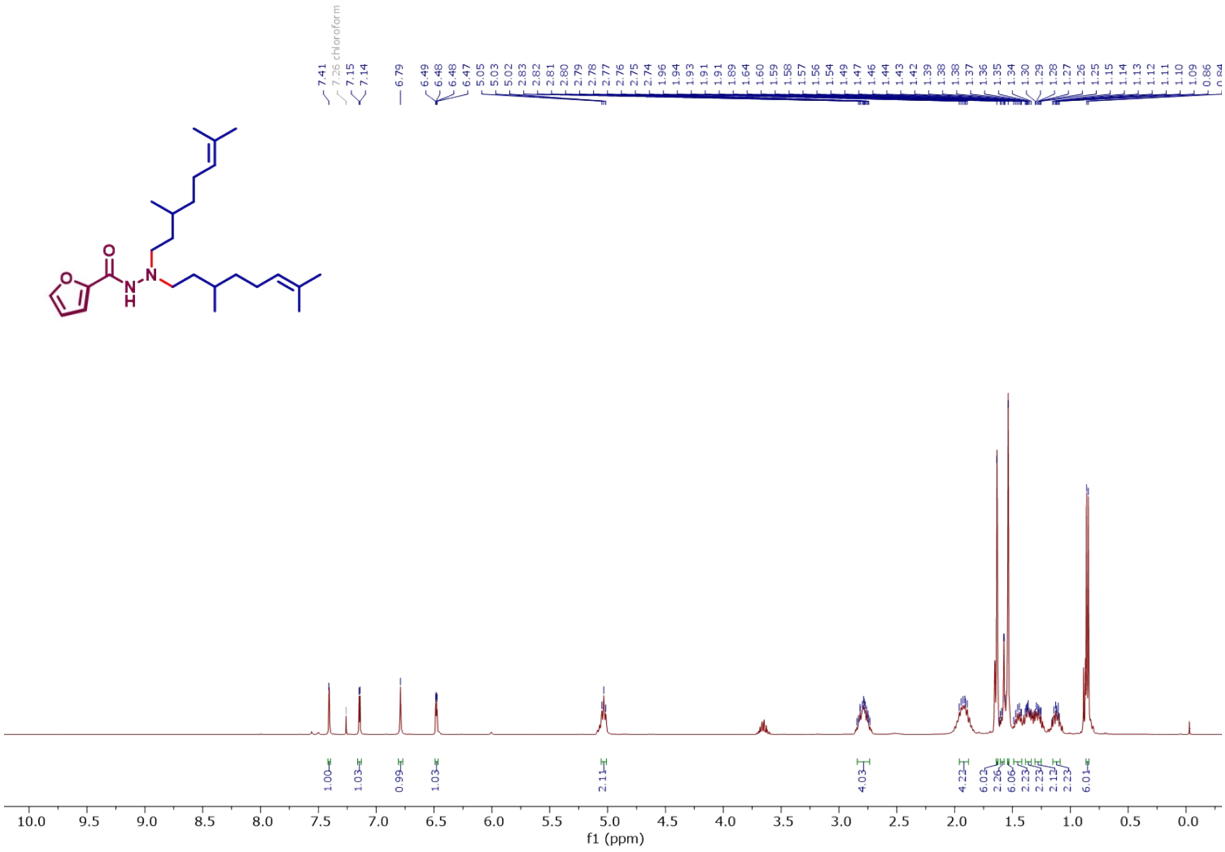
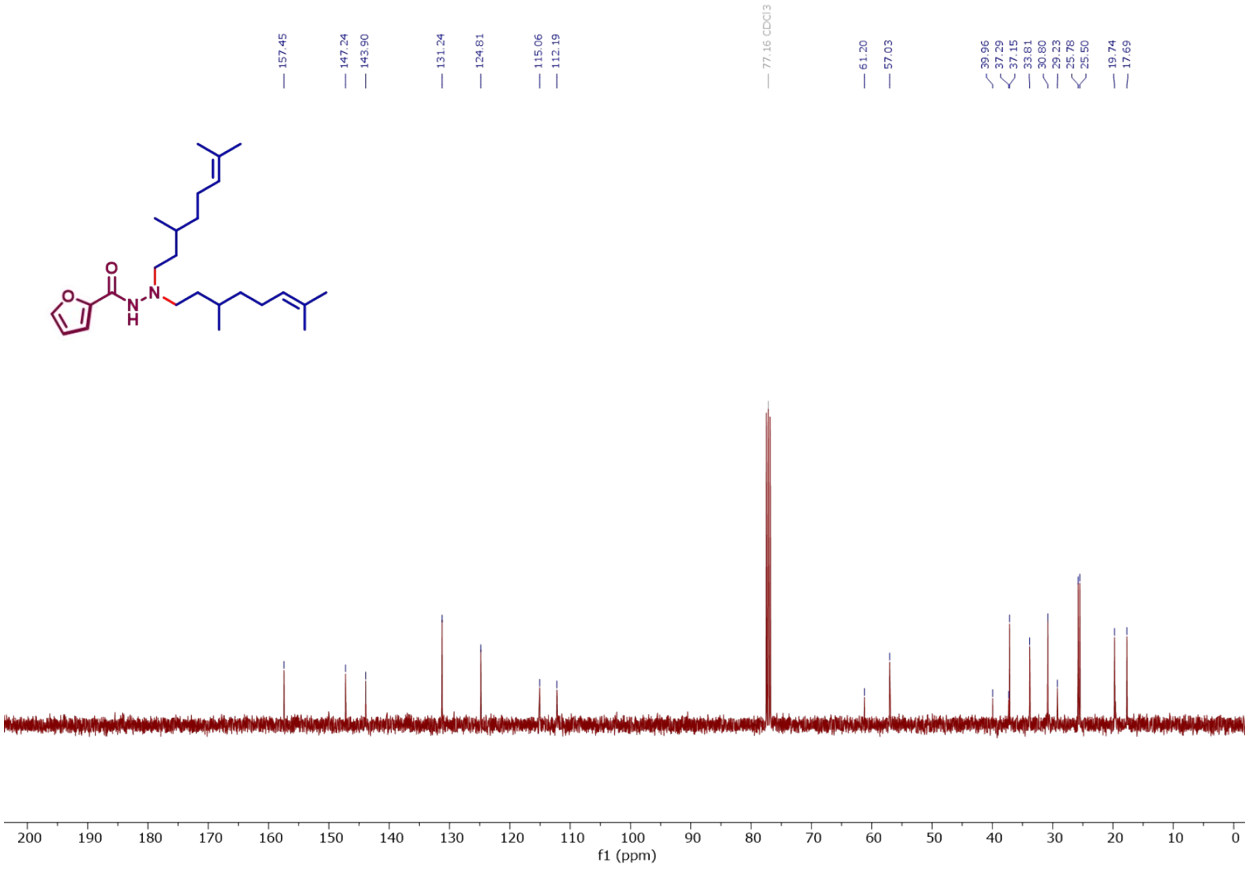


Figure S48. ^{1}H NMR spectrum (400 MHz) of 4w in $CDCl_3$

Figure S49. ^{13}C NMR spectrum (100 MHz) of 4w in $CDCl_3$



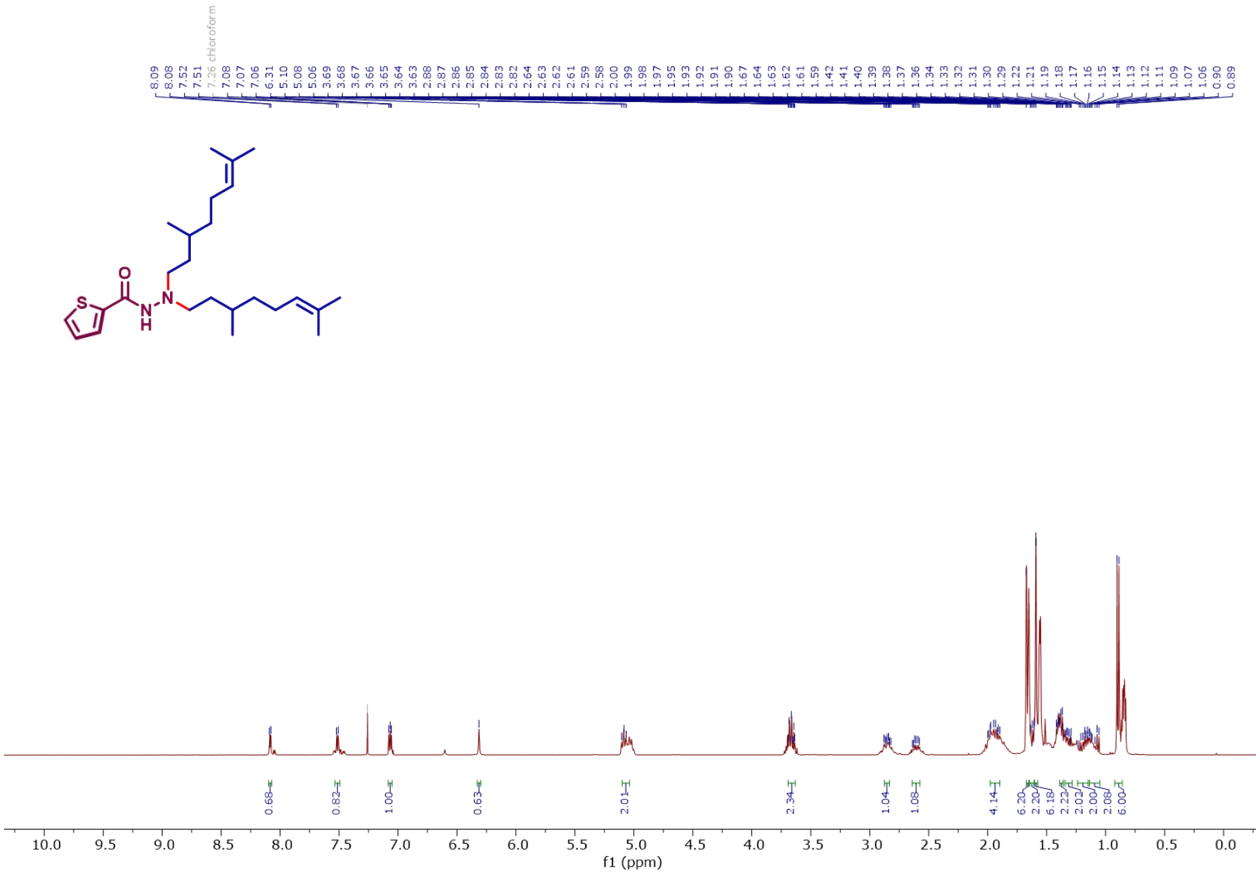


Figure S50. ^{1}H NMR spectrum (400 MHz) of 4x in $CDCl_3$

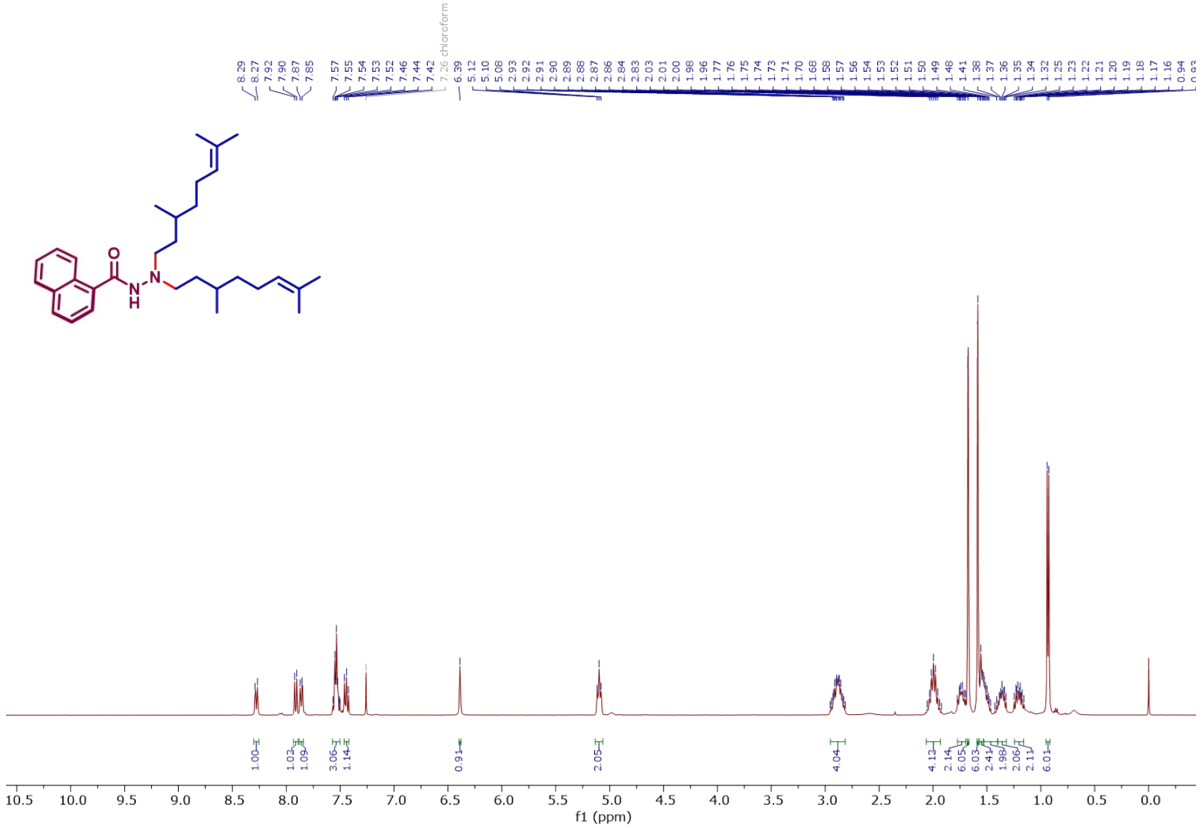


Figure S51. ^{13}C NMR spectrum (100 MHz) of 4x in $CDCl_3$

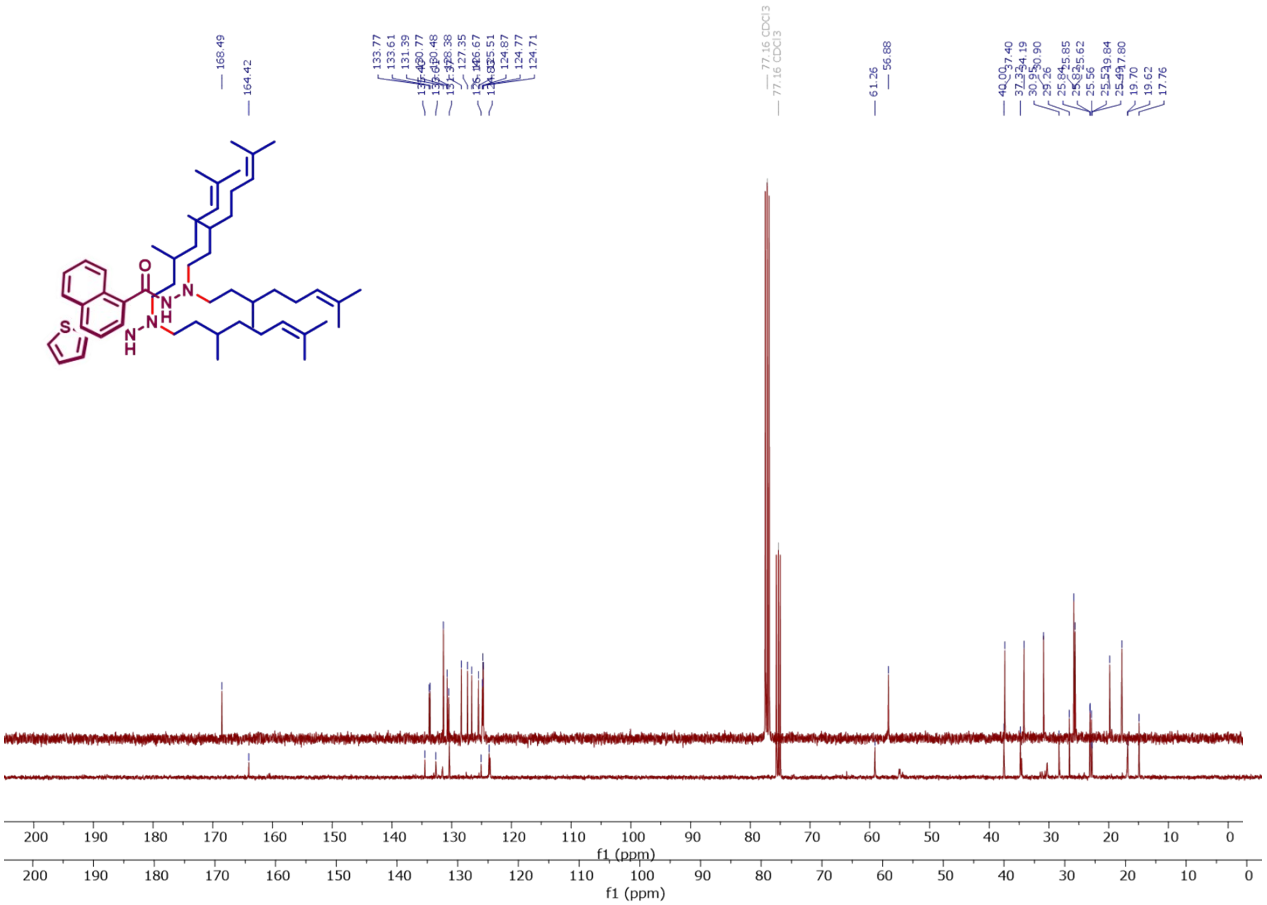


Figure S52. ^{1}H NMR spectrum (400 MHz) of 4y in $CDCl_3$

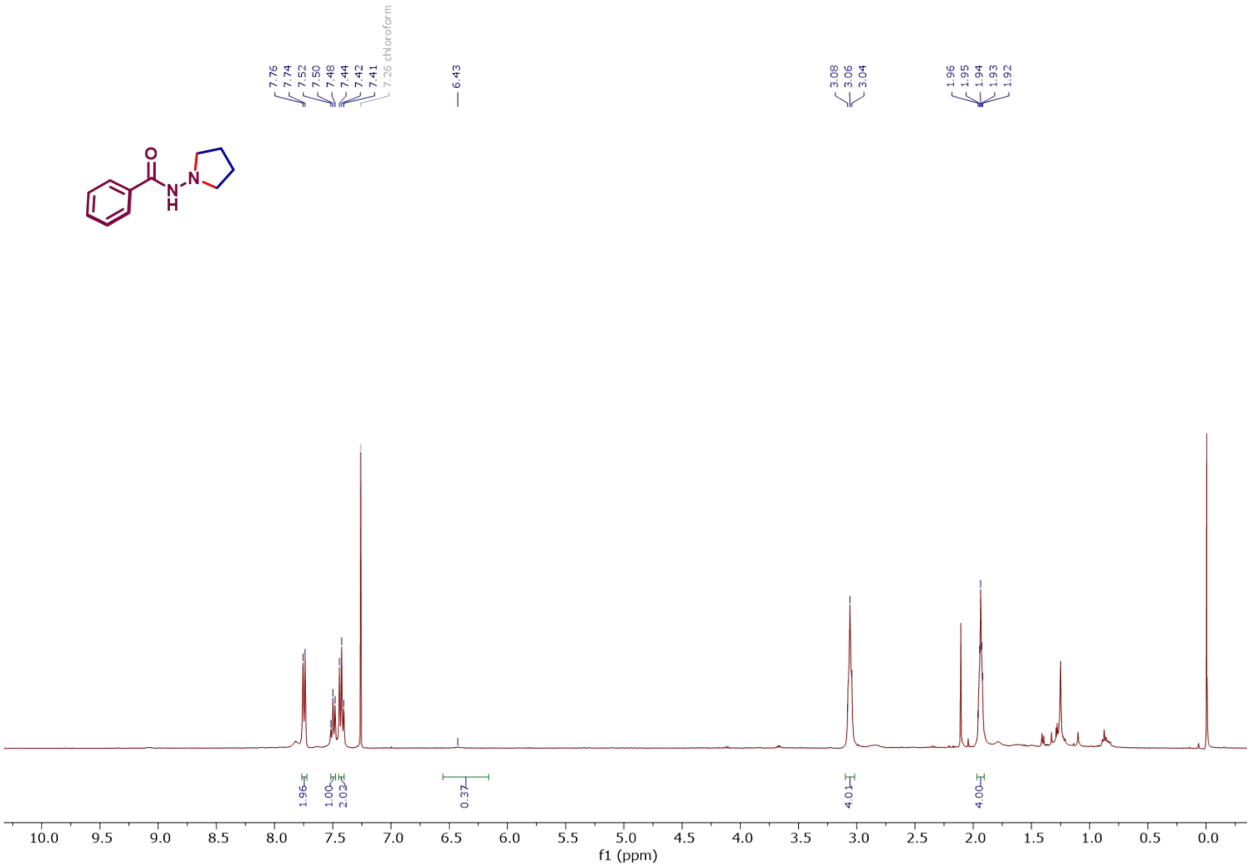


Figure S53. ^{13}C NMR spectrum (100 MHz) of 4y in $CDCl_3$

Figure S54. ^{1}H NMR spectrum (400 MHz) of 6a in $CDCl_3$

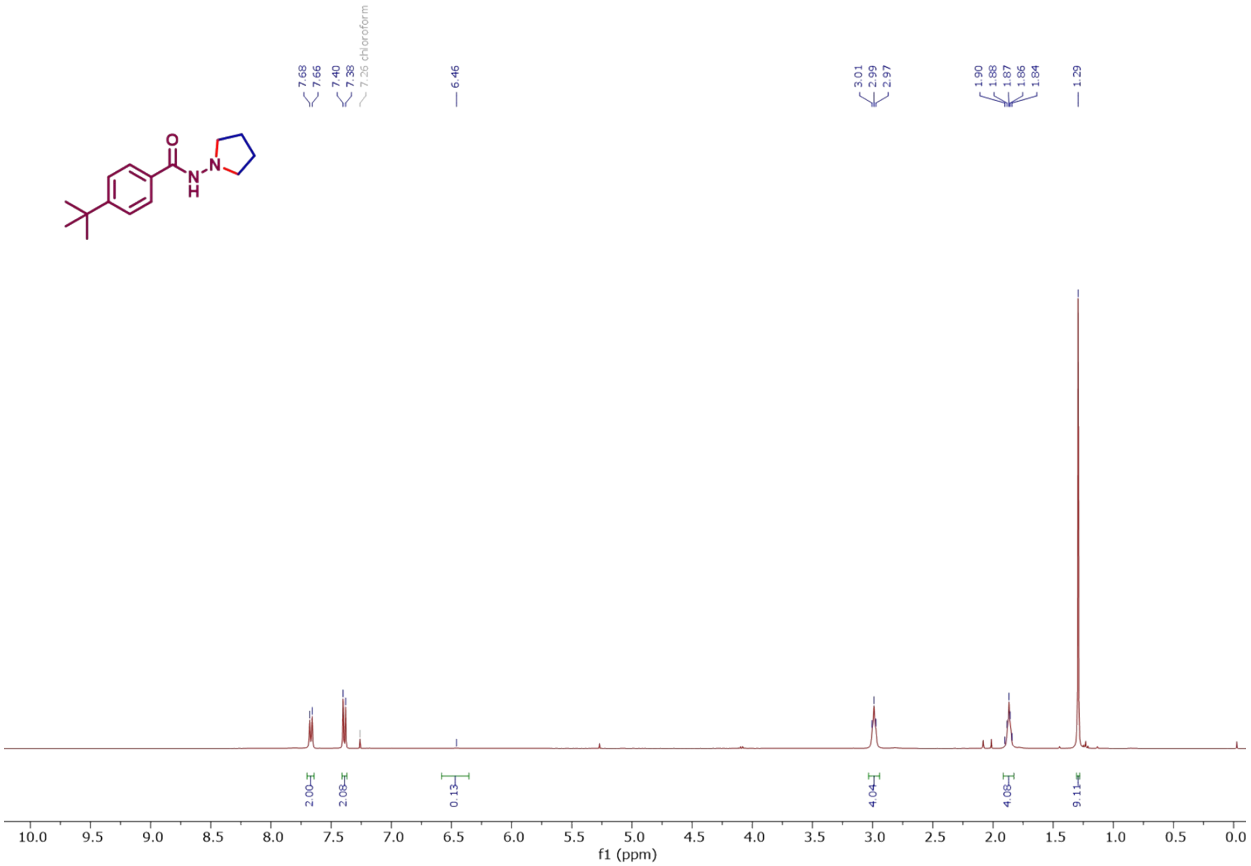


Figure S55. ^{13}C NMR spectrum (100 MHz) of 6a in $CDCl_3$

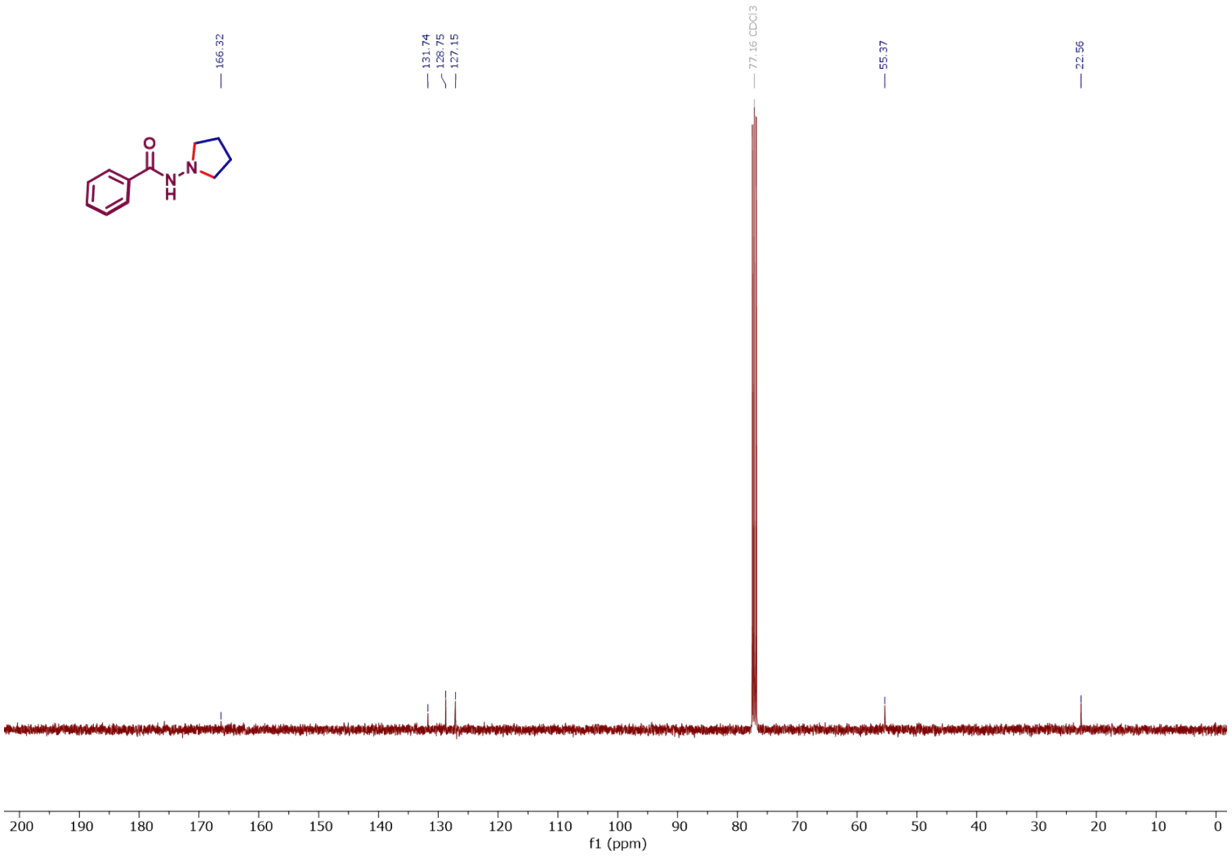


Figure S56. ^{1}H NMR spectrum (400 MHz) of 6b in $CDCl_3$

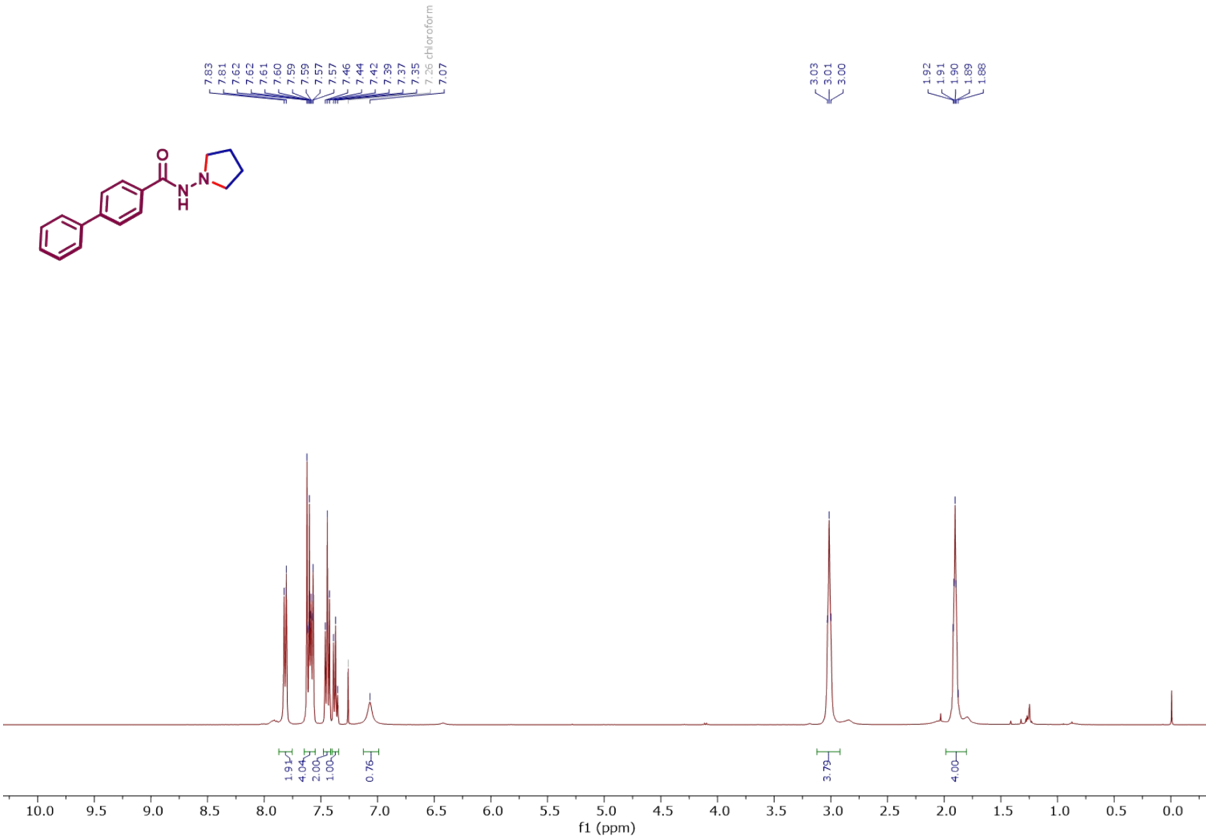


Figure S57. ^{13}C NMR spectrum (100 MHz) of 6b in $CDCl_3$

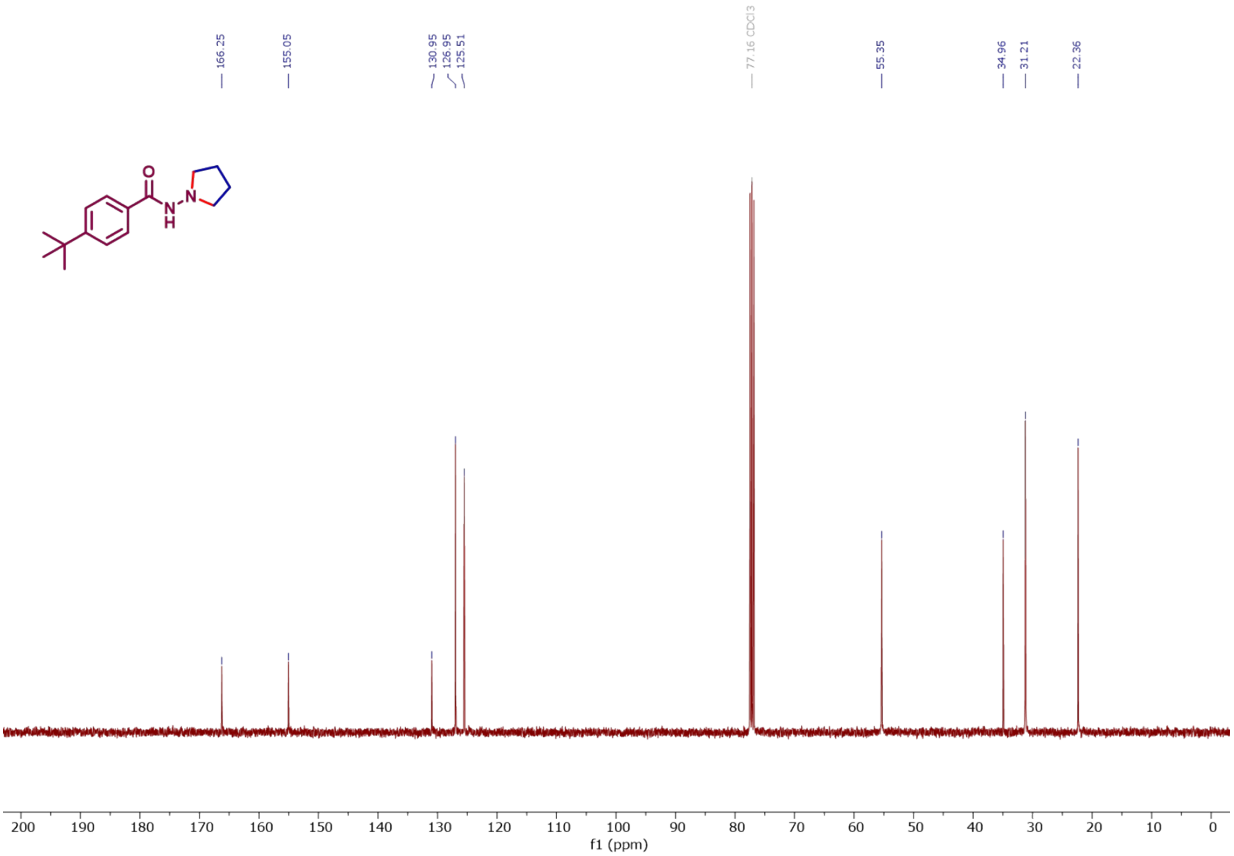
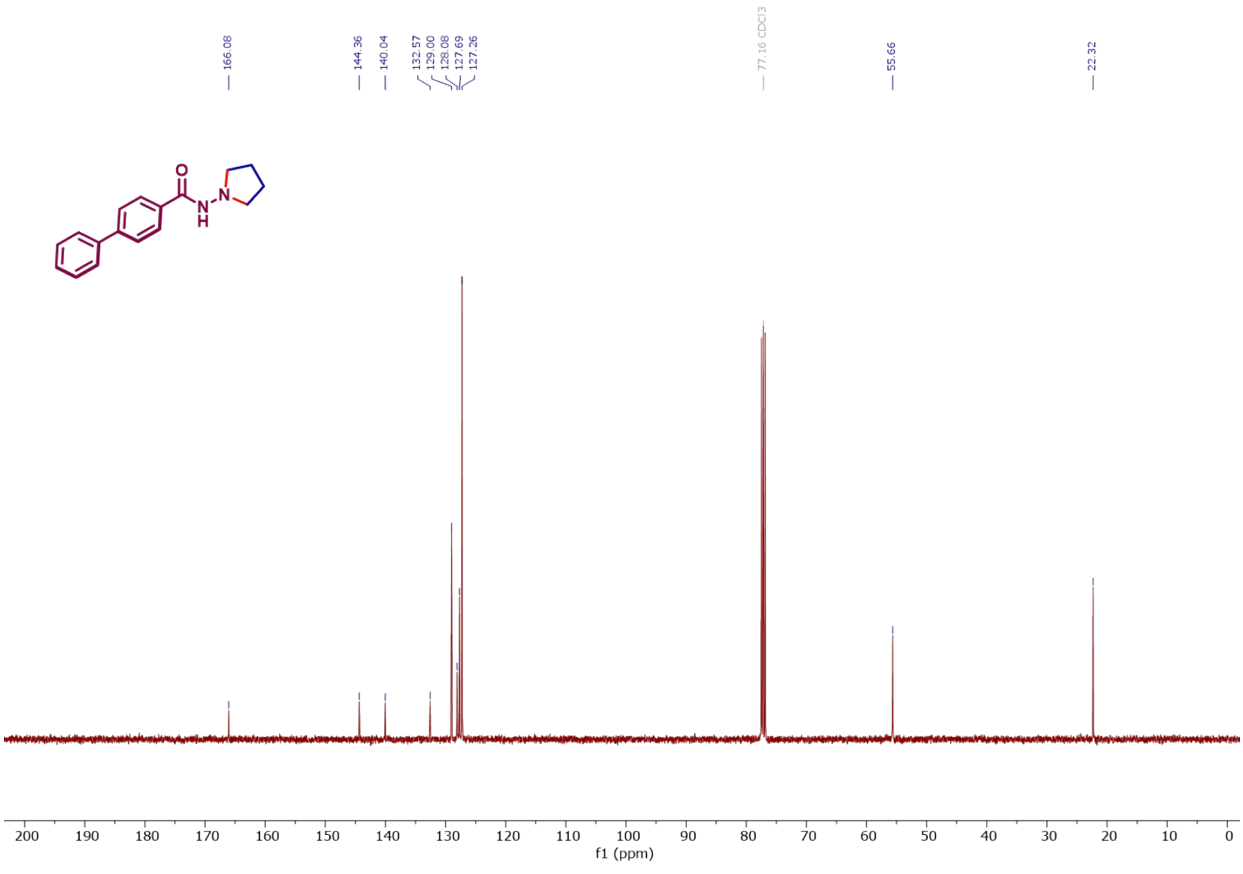


Figure S58. ^{1}H NMR spectrum (400 MHz) of 6c in $CDCl_3$

Figure S59. ^{13}C NMR spectrum (100 MHz) of 6c in $CDCl_3$



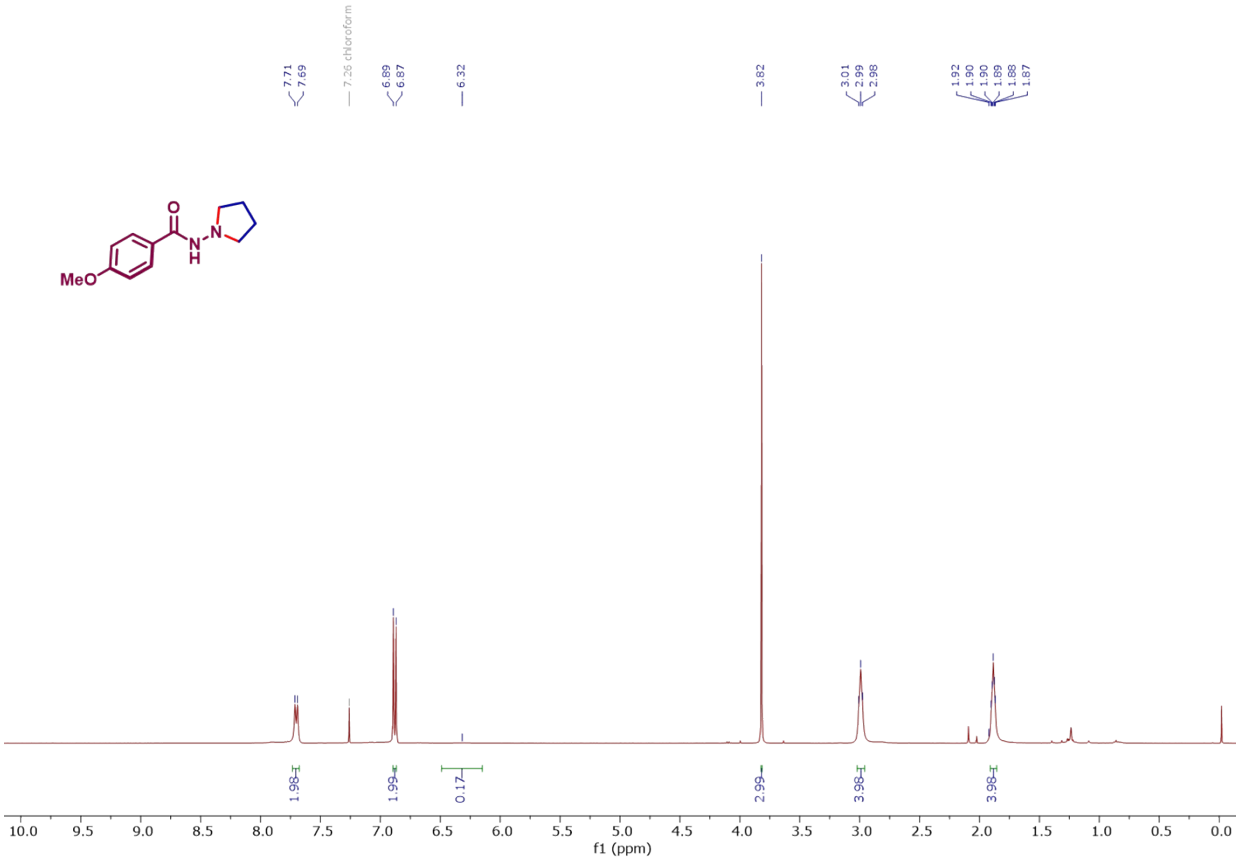
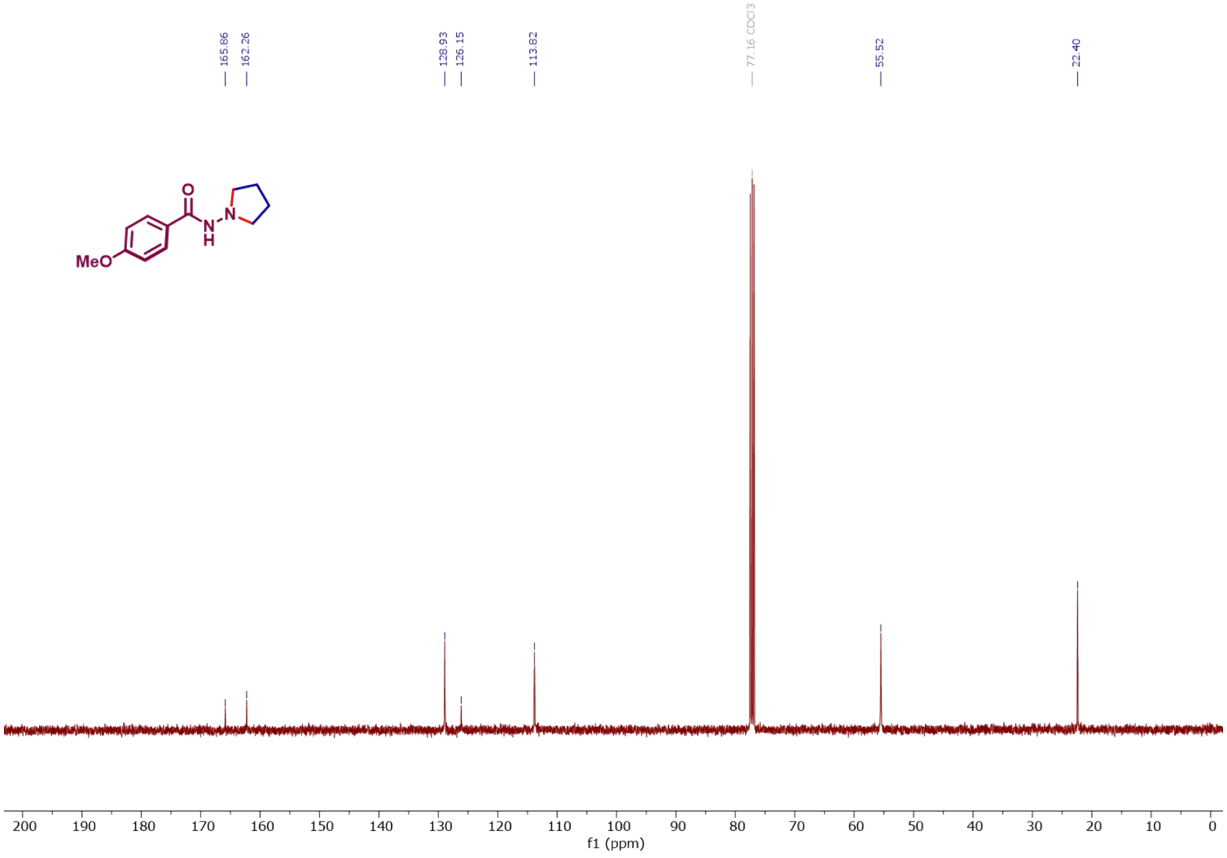


Figure S60. ^{1}H NMR spectrum (400 MHz) of 6d in $CDCl_3$

Figure S61. ^{13}C NMR spectrum (100 MHz) of 6d in $CDCl_3$



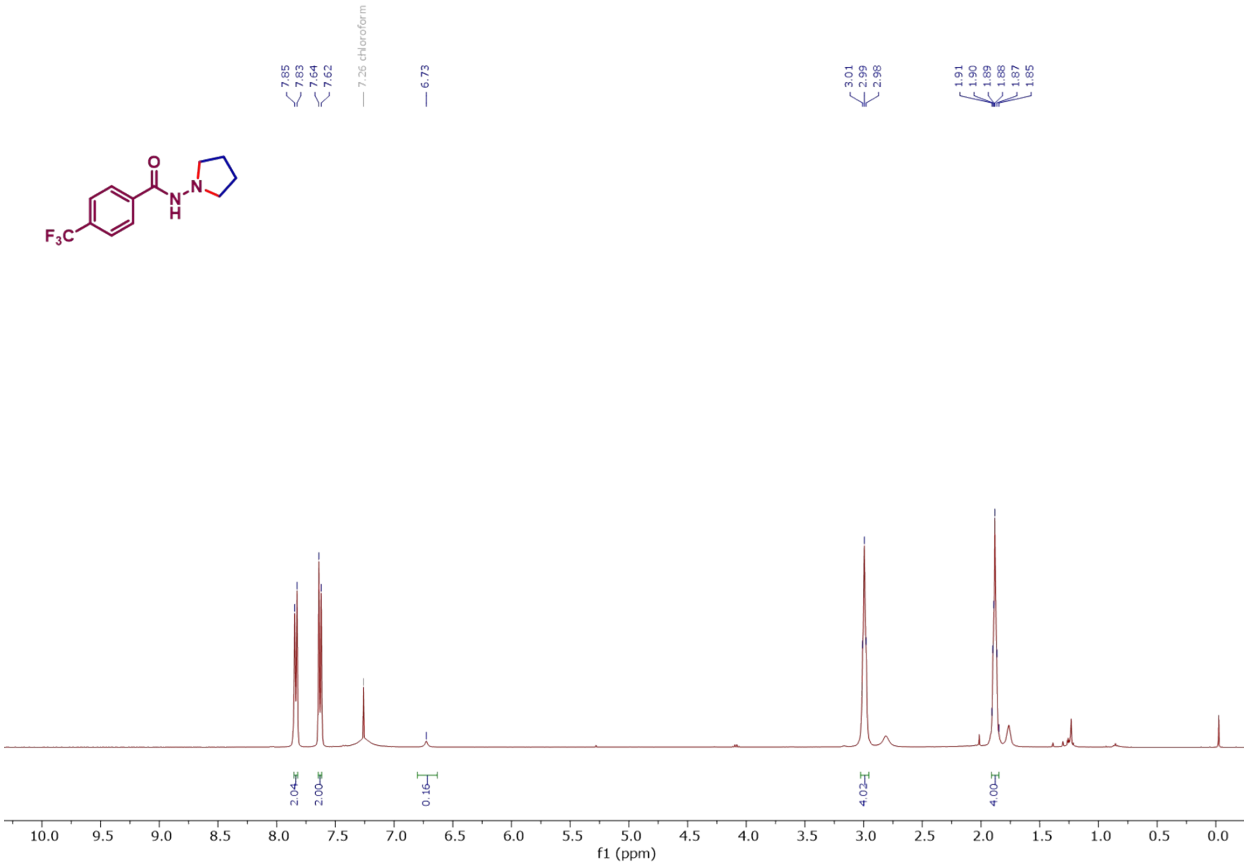


Figure S62. ^{1}H NMR spectrum (400 MHz) of 6e in $CDCl_3$

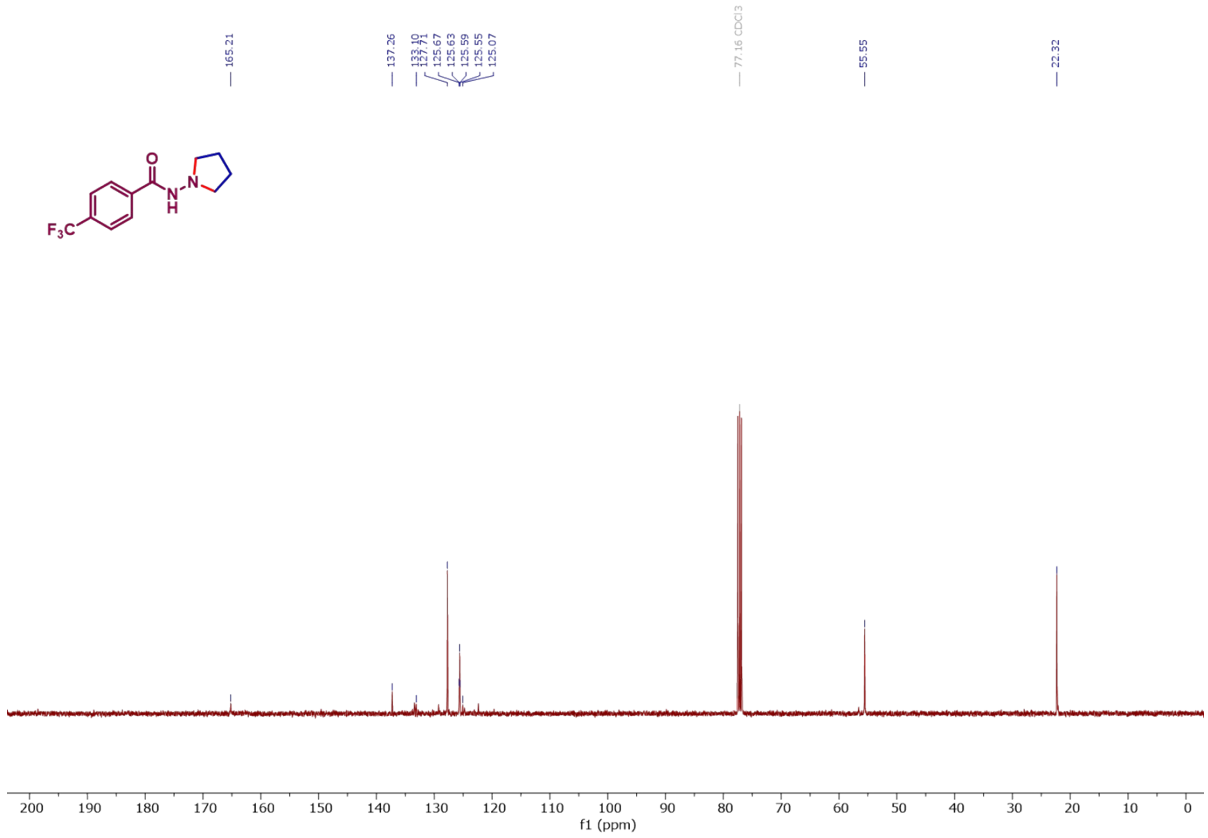


Figure S63. ^{13}C NMR spectrum (100 MHz) of 6e in $CDCl_3$

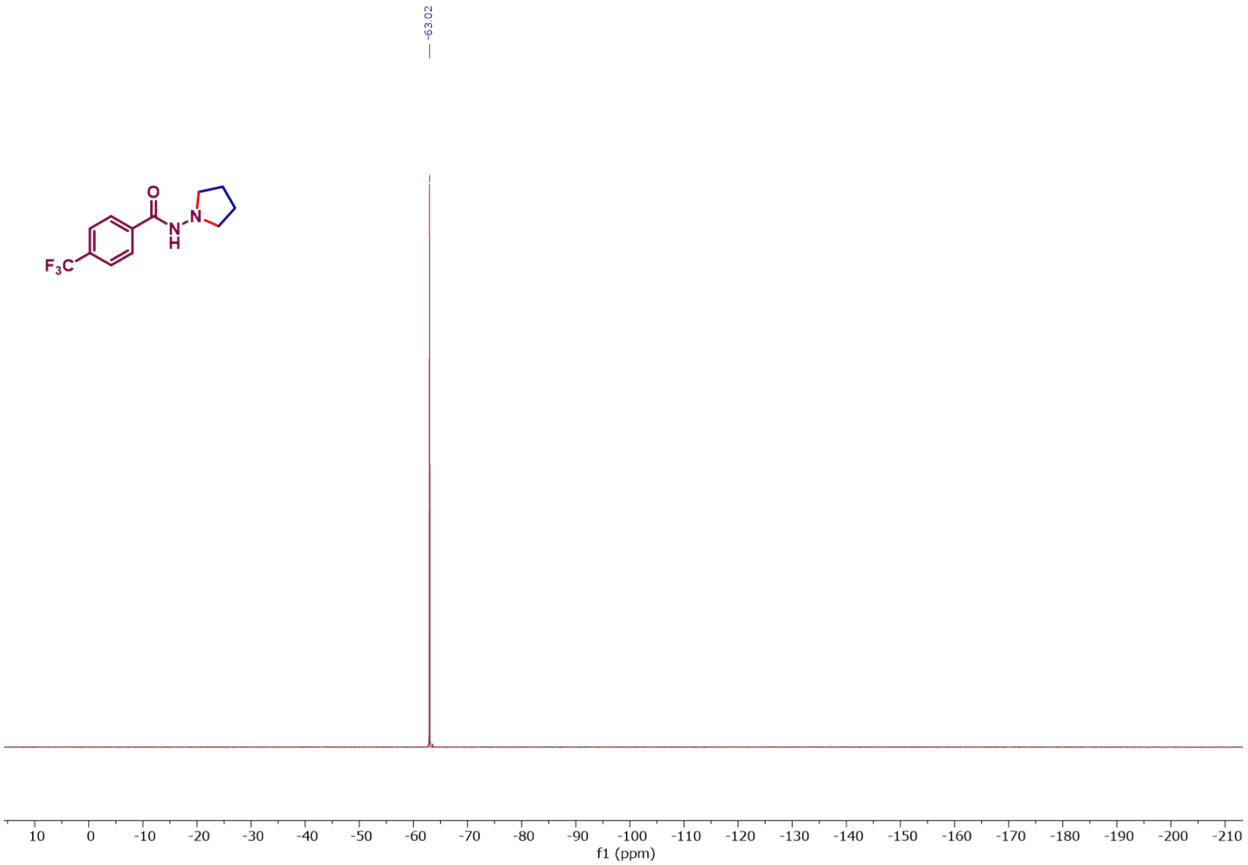


Figure S64. ^{19}F NMR spectrum (376 MHz) of 6e in $CDCl_3$

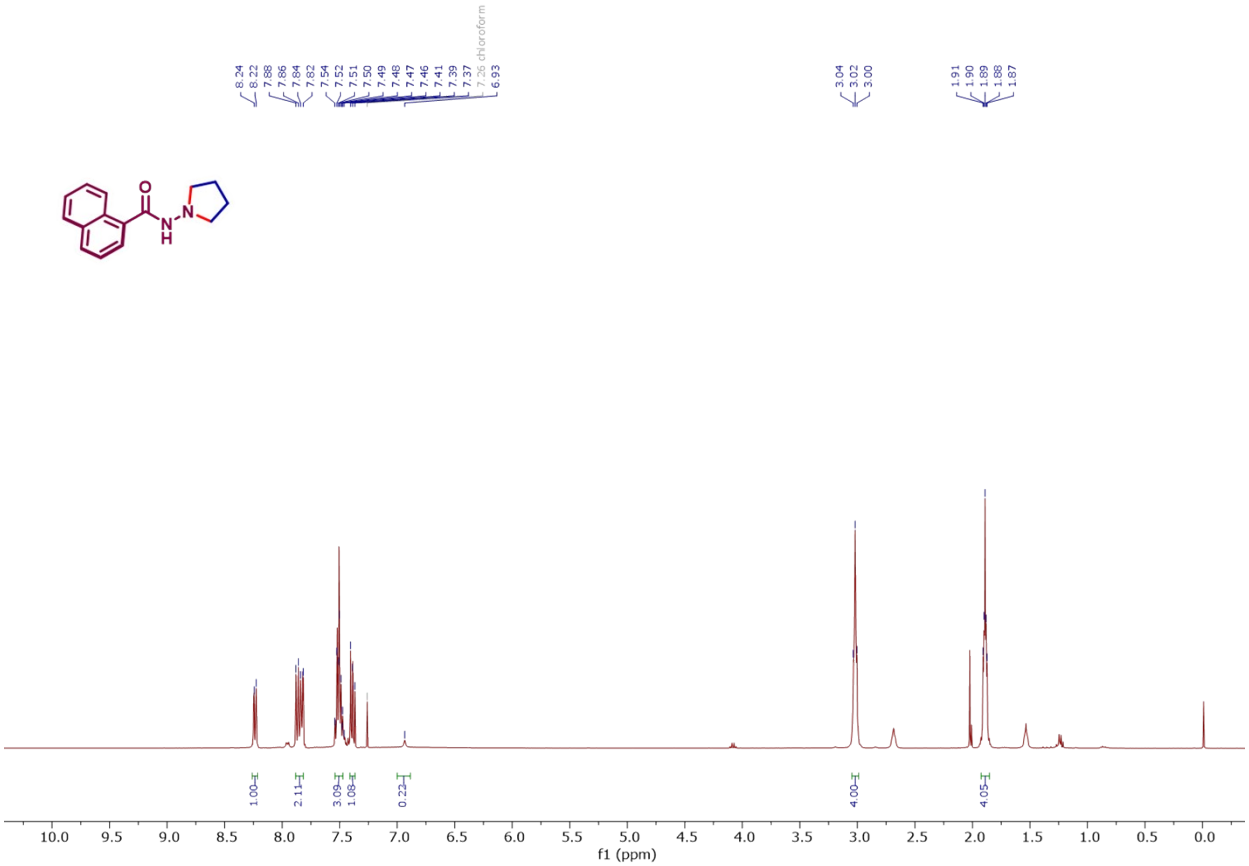


Figure S65. ^{1}H NMR spectrum (400 MHz) of 6f in $CDCl_3$

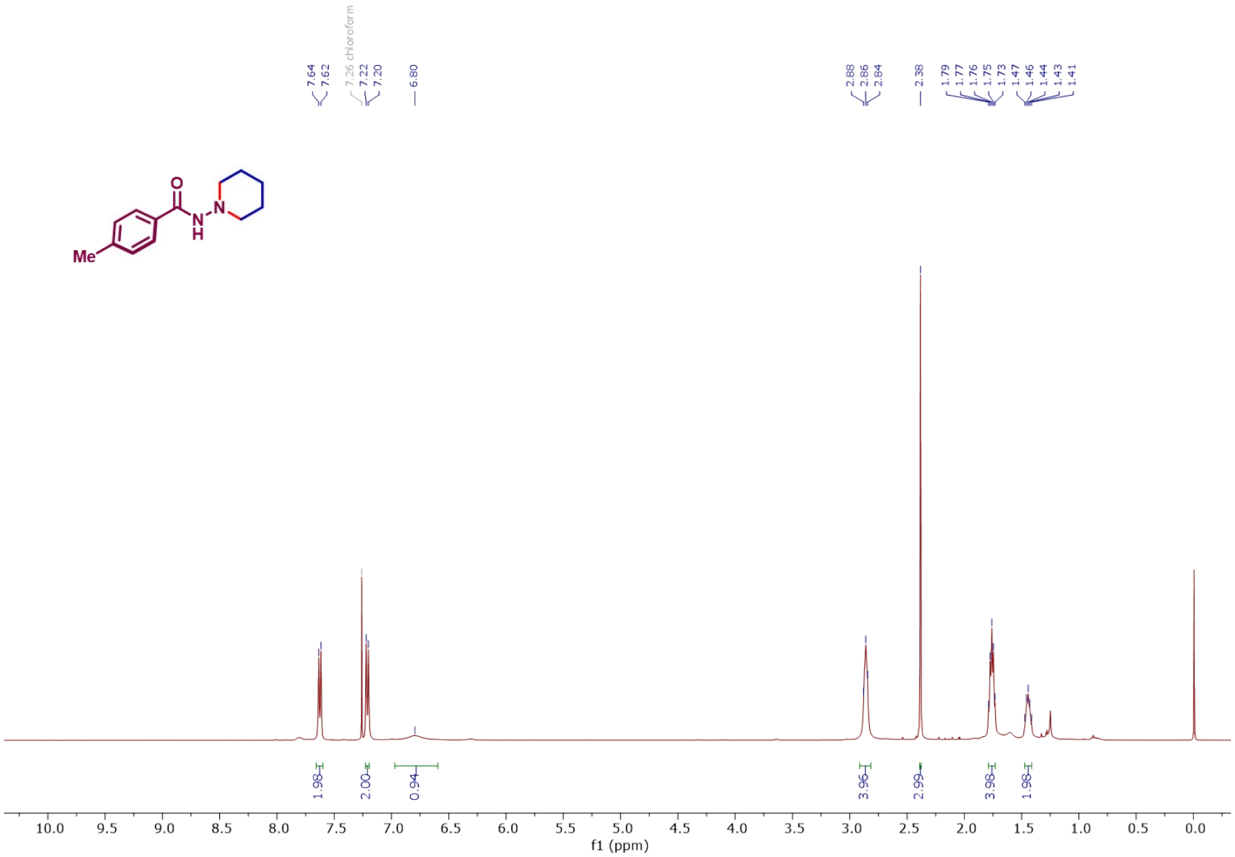


Figure S66. ^{13}C NMR spectrum (100 MHz) of 6f in $CDCl_3$

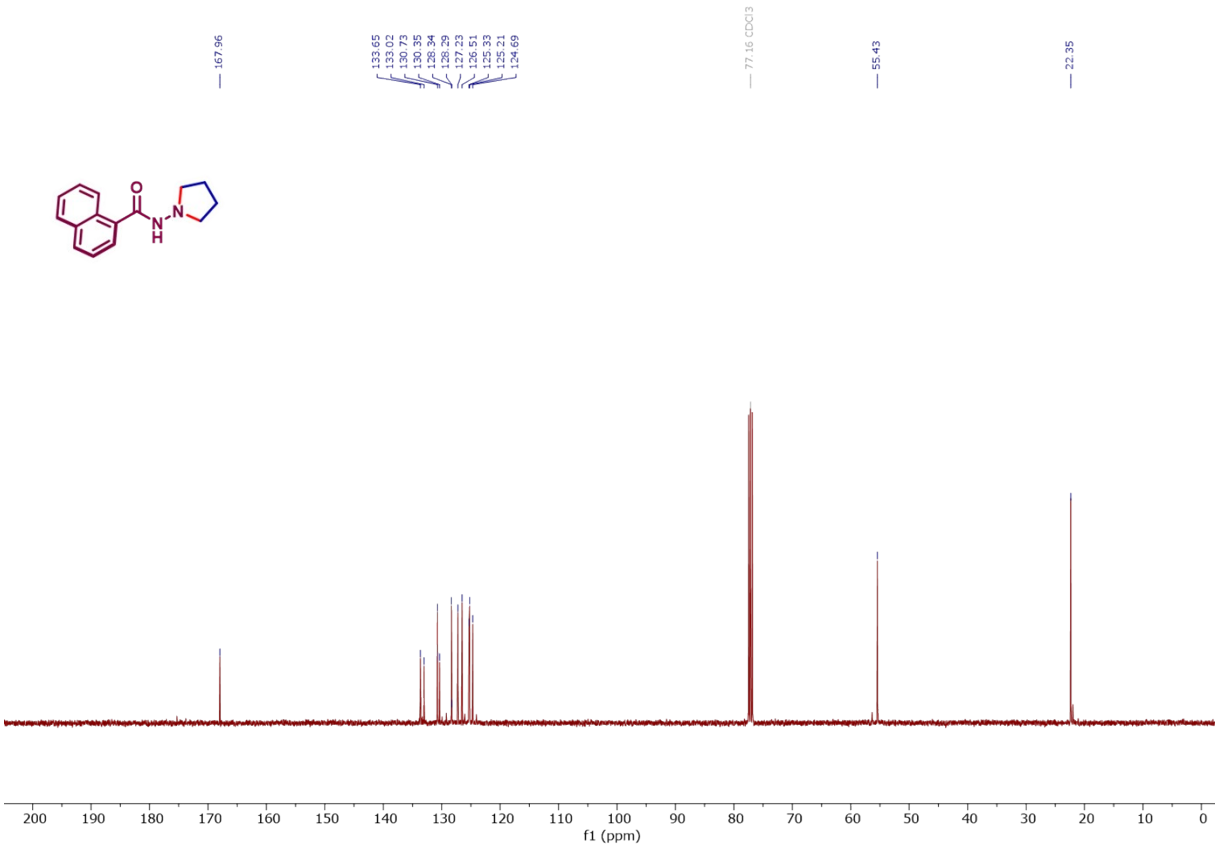


Figure S67. ^{1}H NMR spectrum (400 MHz) of 6g in $CDCl_3$

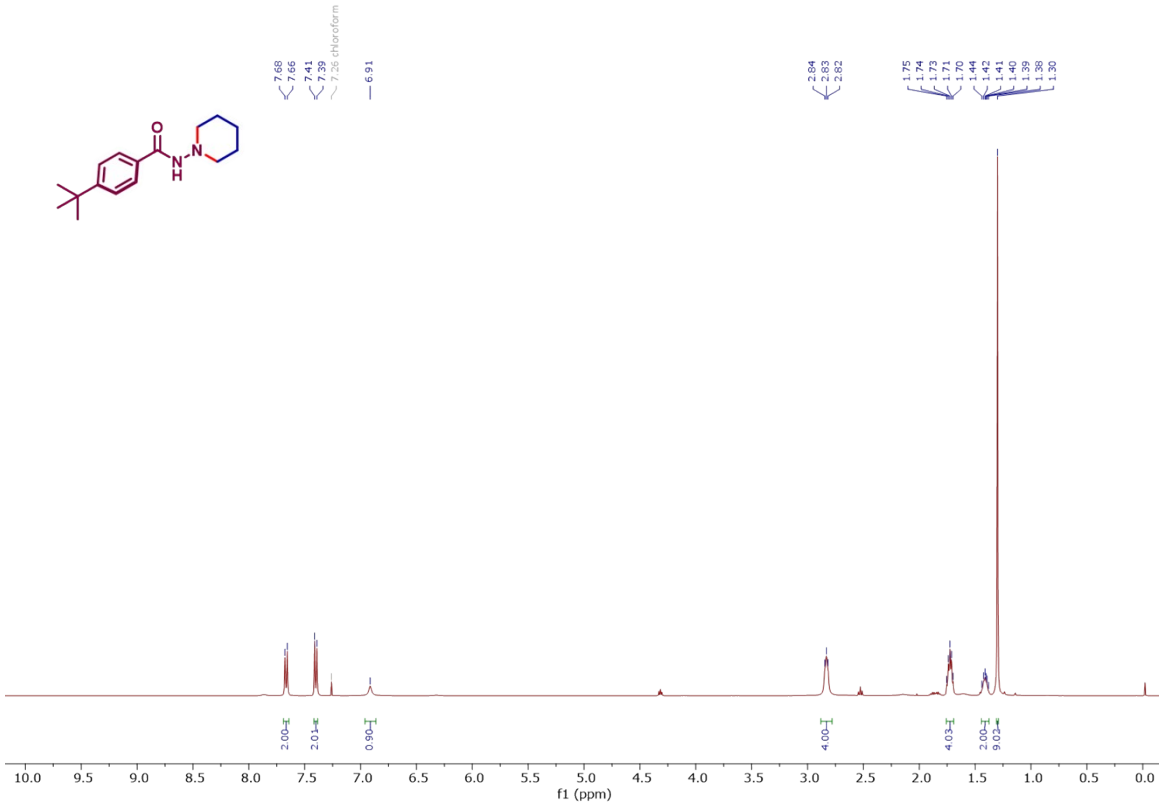


Figure S68. ^{13}C NMR spectrum (100 MHz) of 6g in $CDCl_3$

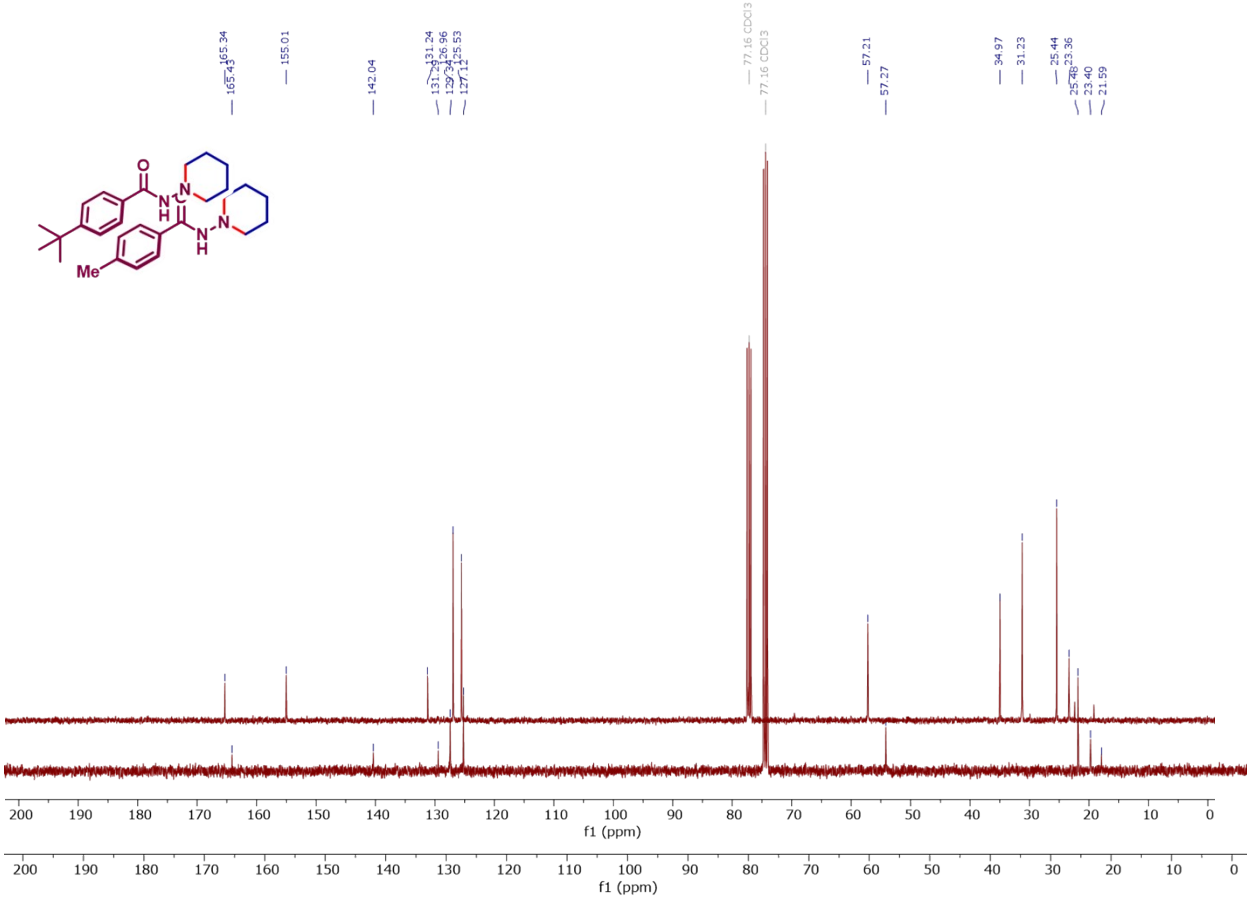


Figure S69. ^{1}H NMR spectrum (400 MHz) of 6h in $CDCl_3$

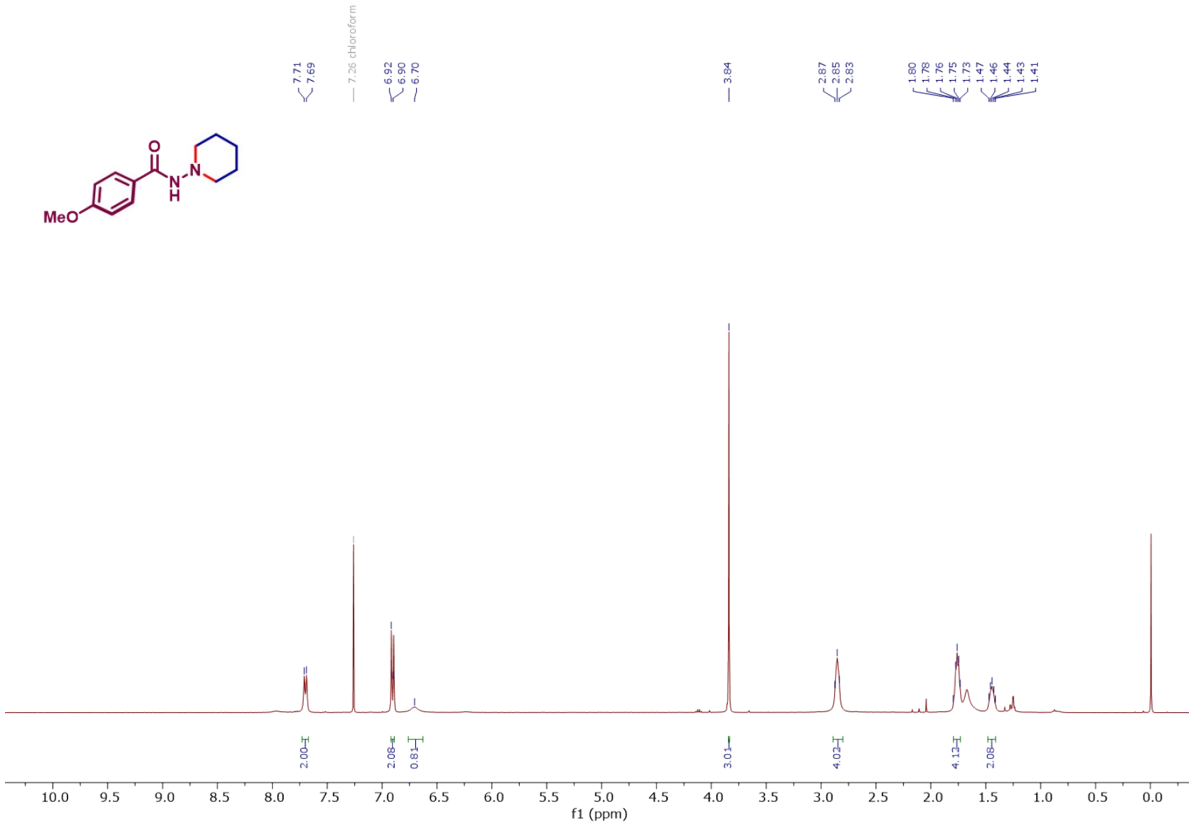


Figure S70. ^{13}C NMR spectrum (100 MHz) of 6h in $CDCl_3$

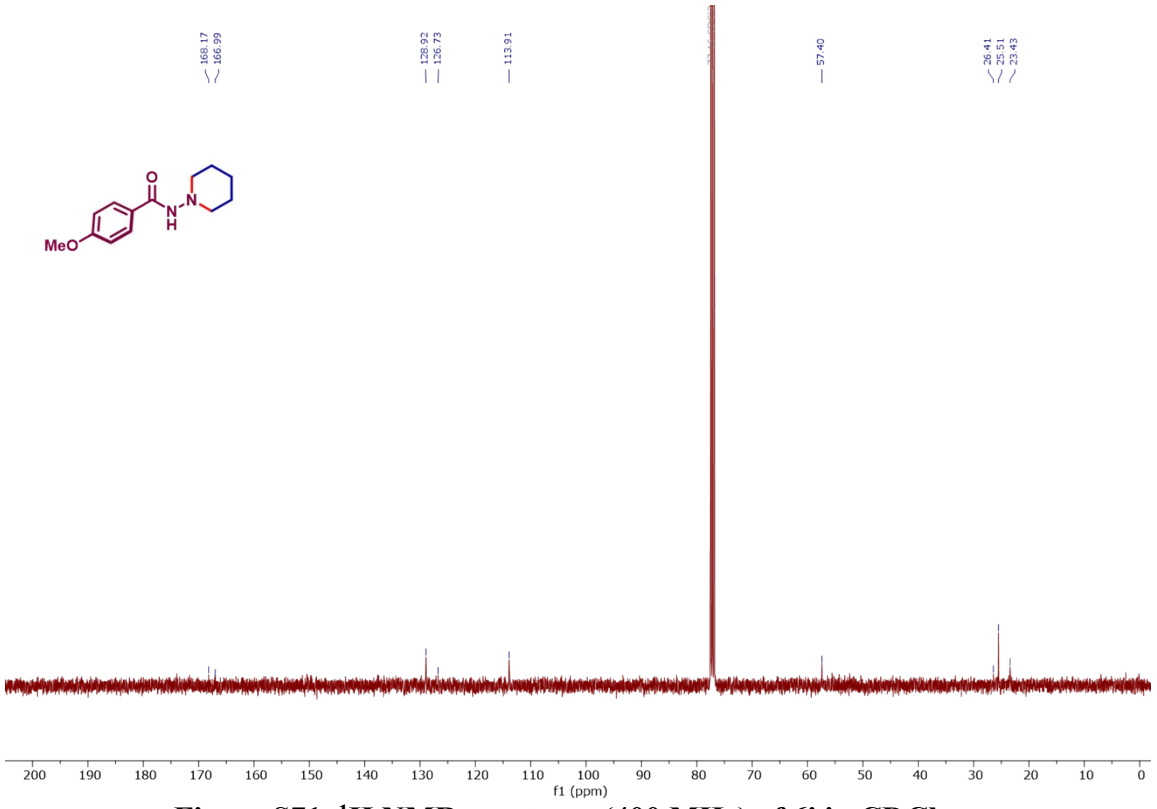
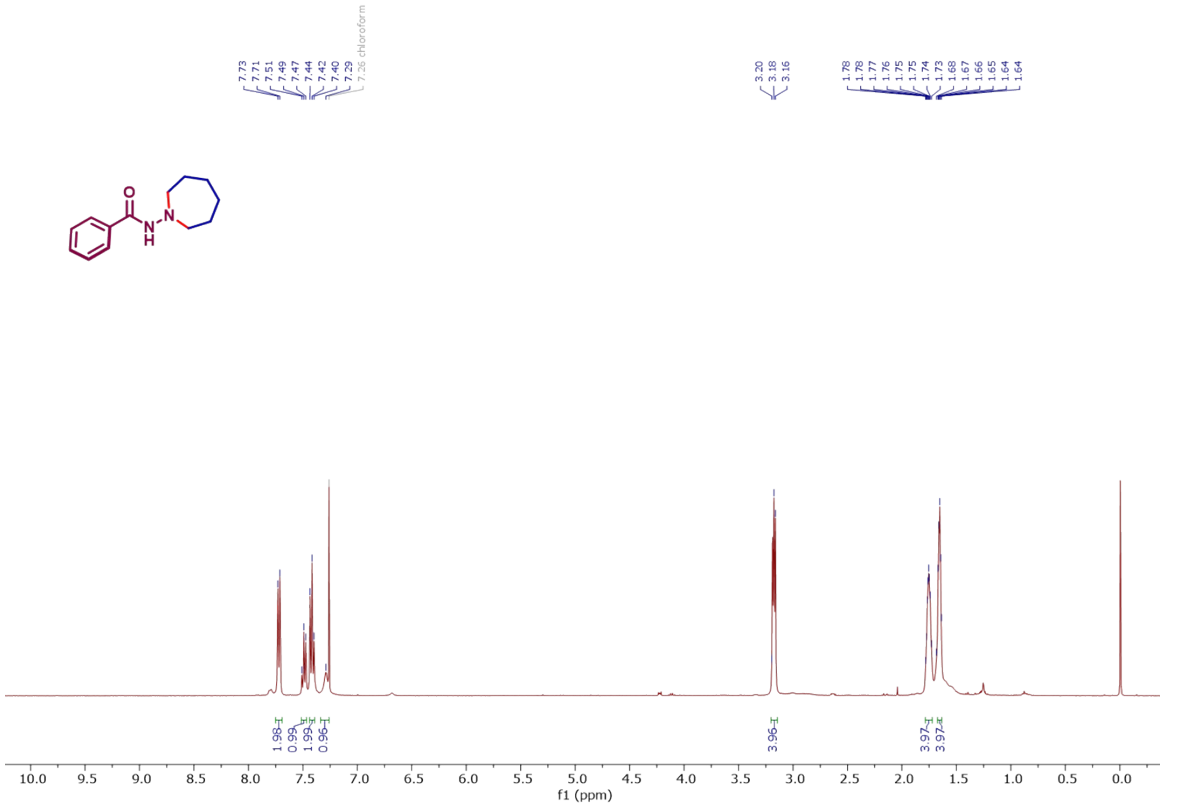


Figure S71. ^{1}H NMR spectrum (400 MHz) of 6i in $CDCl_3$



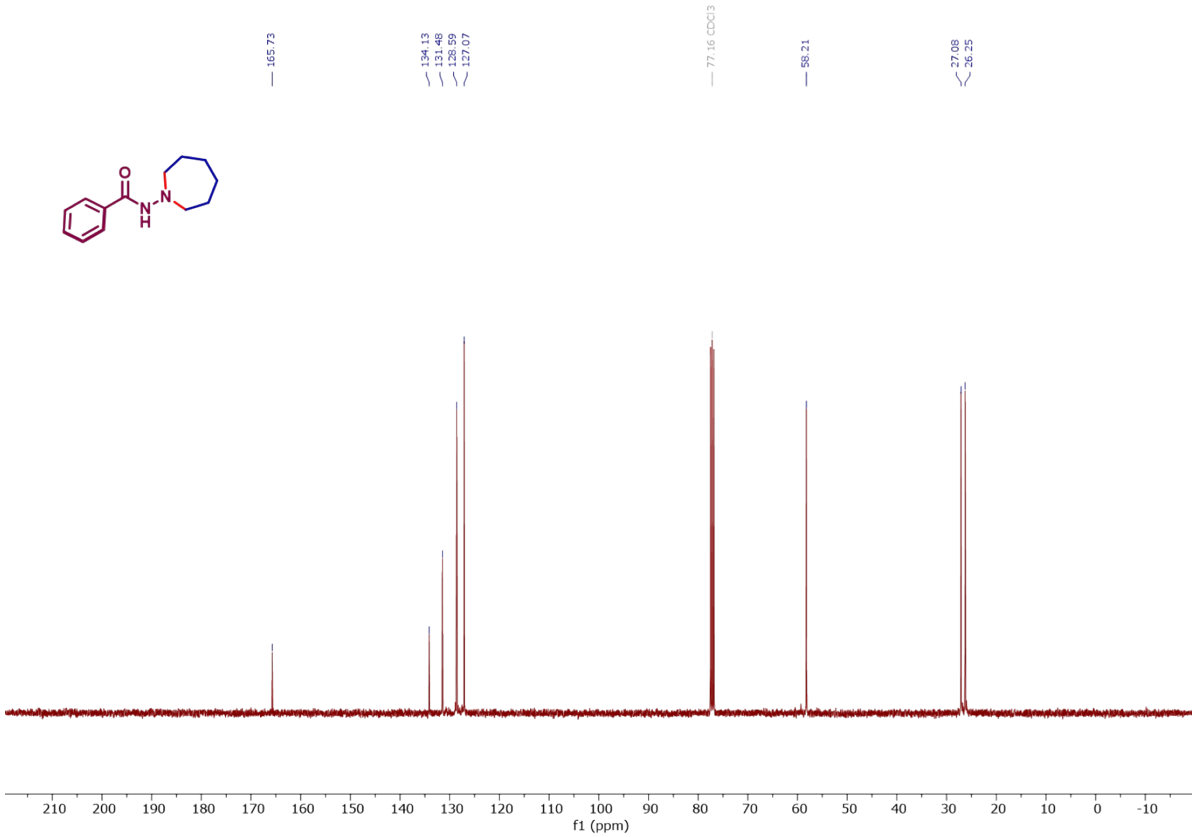


Figure S72. ^{13}C NMR spectrum (100 MHz) of 6i in $CDCl_3$

Figure S73. ^{1}H NMR spectrum (400 MHz) of 6j in $CDCl_3$

Figure S74. ^{13}C NMR spectrum (100 MHz) of 6j in $CDCl_3$

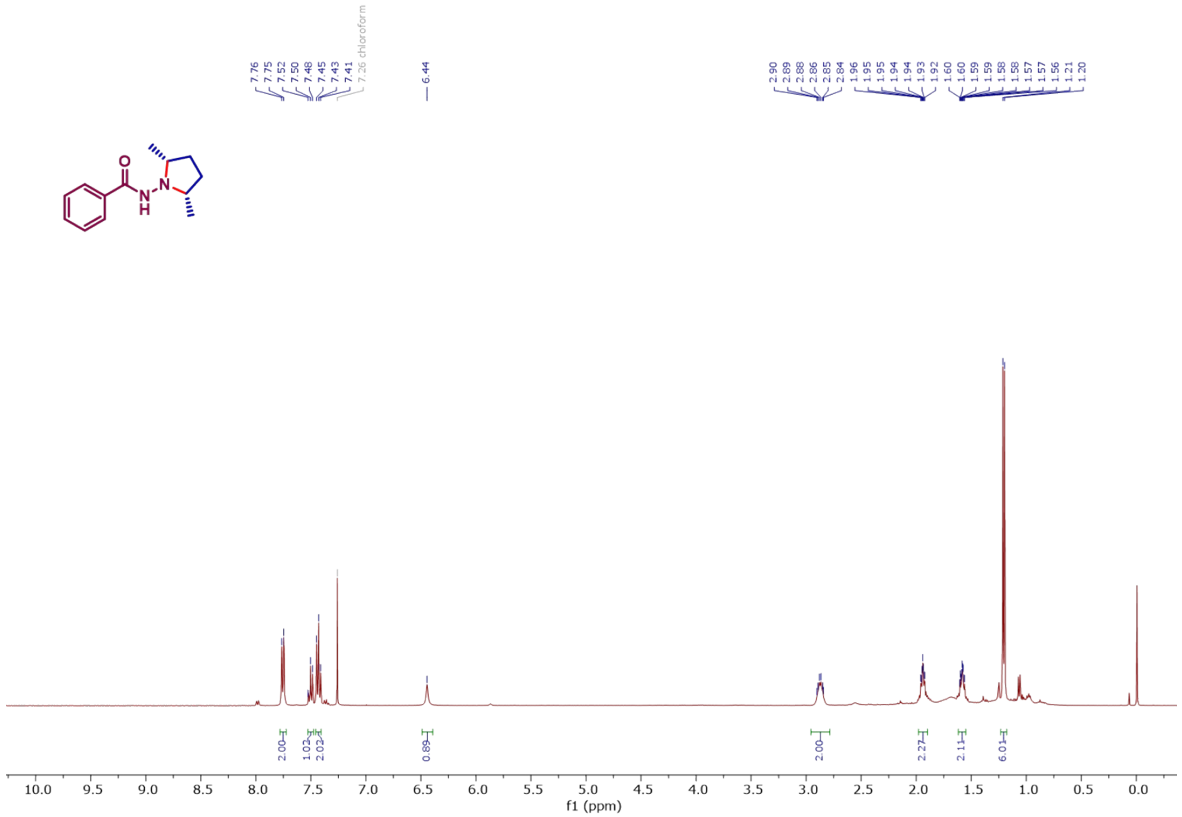


Figure S75. ^{1}H NMR spectrum (400 MHz) of 6k in $CDCl_3$

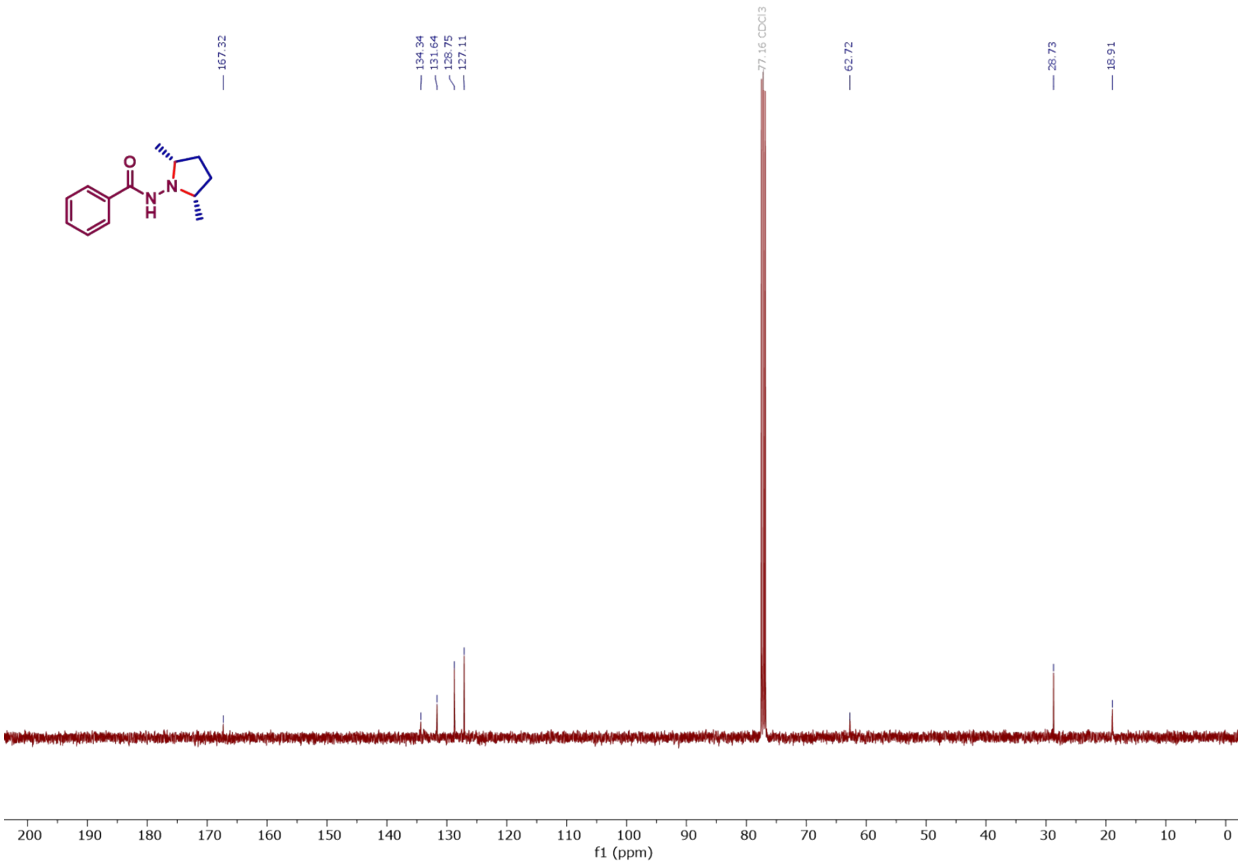


Figure S76. ^{13}C NMR spectrum (100 MHz) of 6k in $CDCl_3$

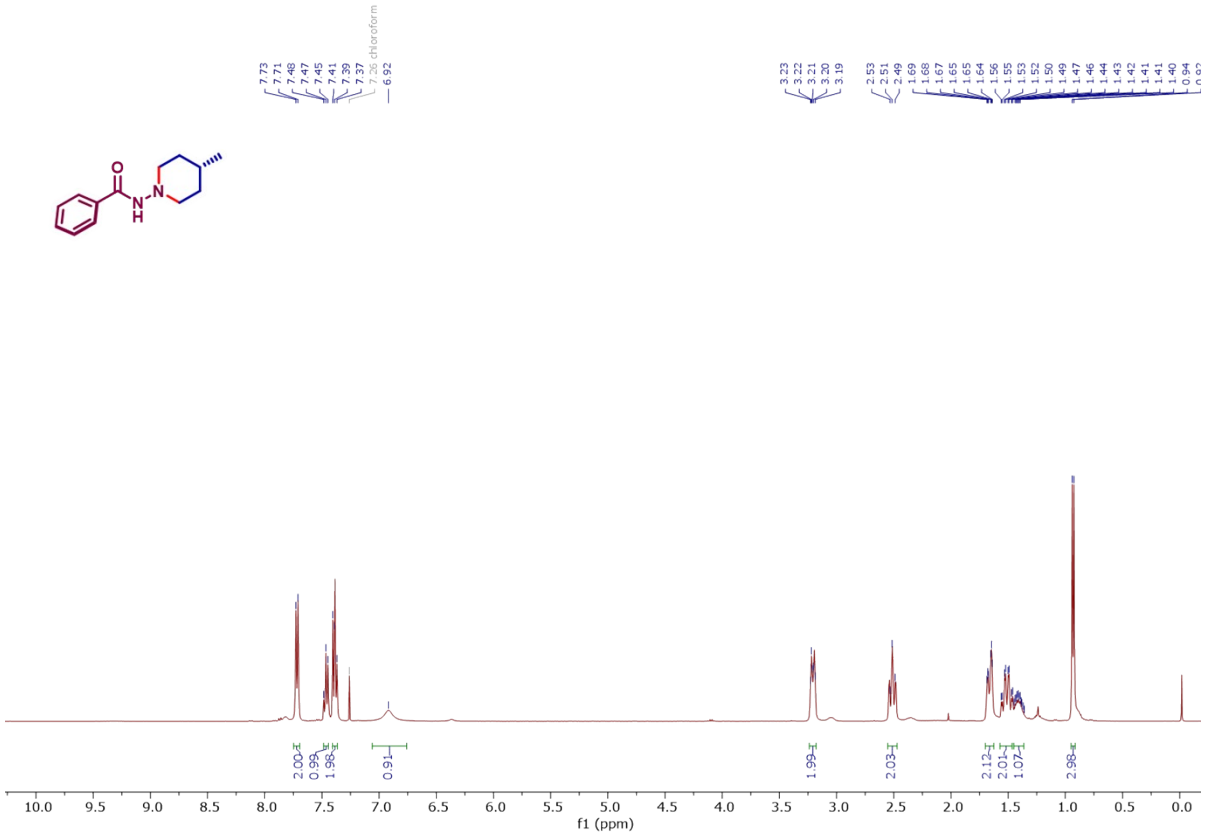


Figure S77. ^{1}H NMR spectrum (400 MHz) of 6l in $CDCl_3$

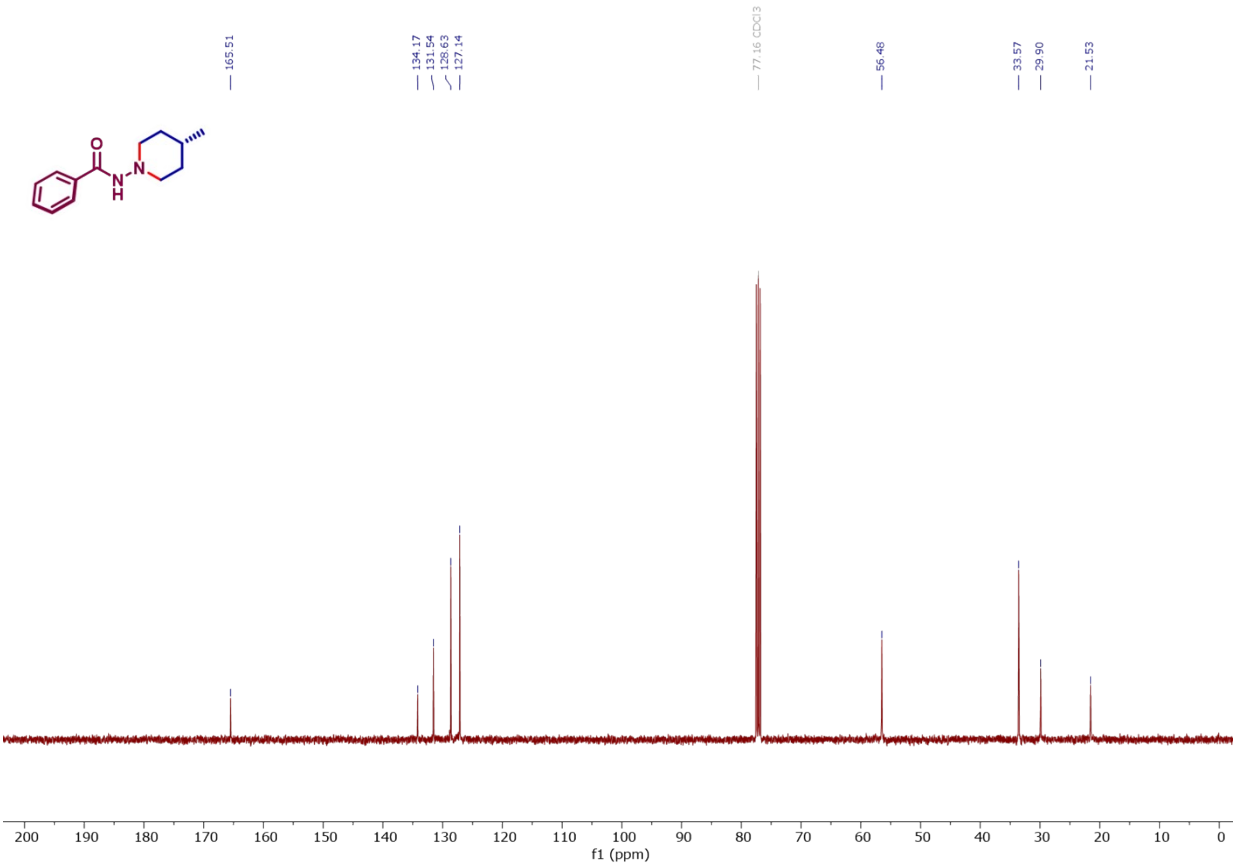


Figure S78. ^{13}C NMR spectrum (100 MHz) of 6l in $CDCl_3$

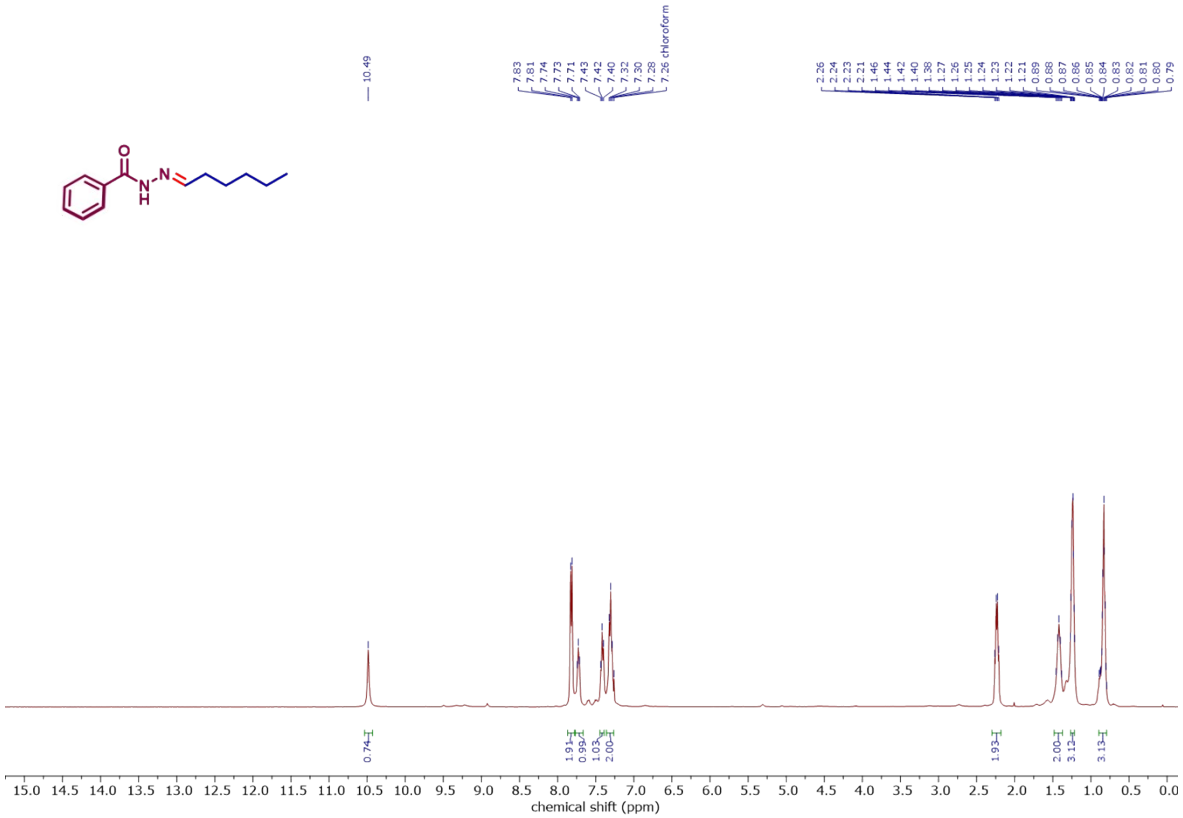


Figure S79. ^{1}H NMR spectrum (400 MHz) of 4bc in $CDCl_3$

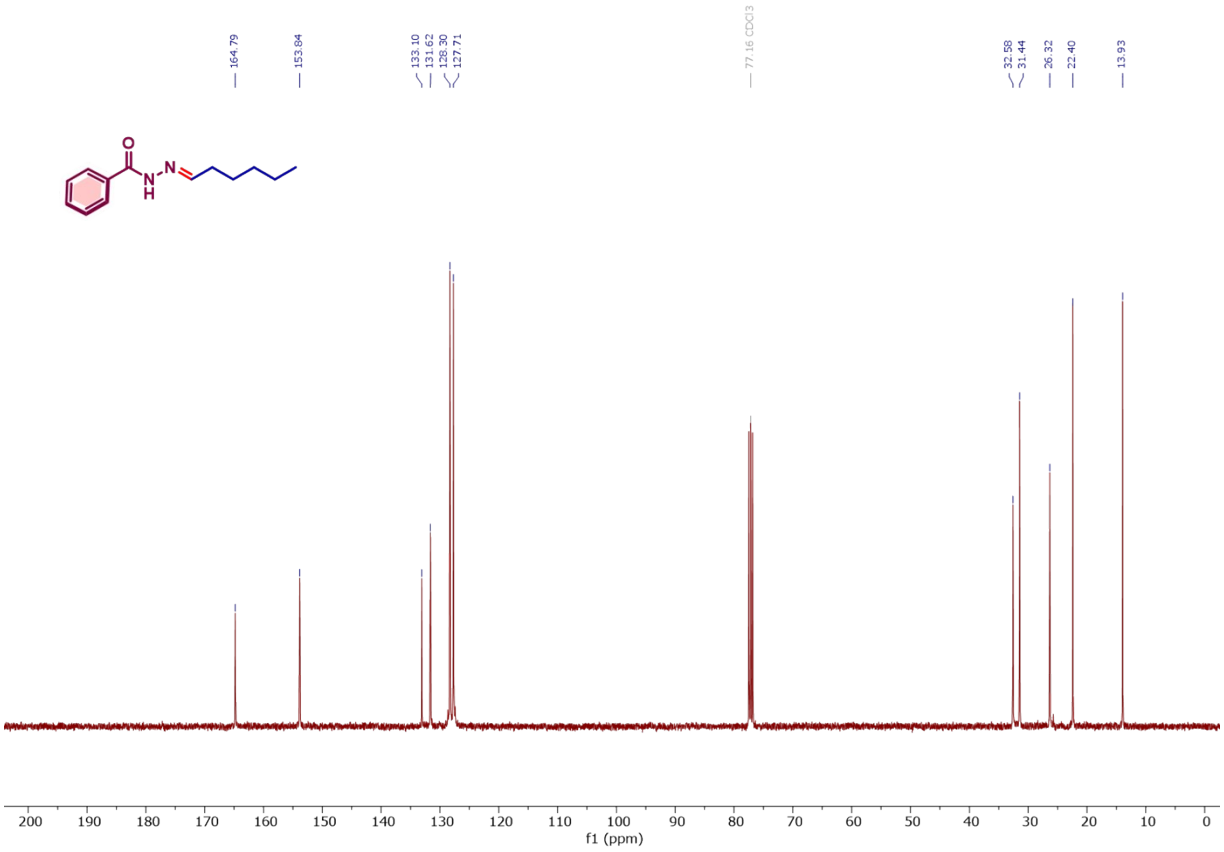


Figure S80. ^{13}C NMR spectrum (100 MHz) of 4bc in $CDCl_3$

8. References:

1. S. Thiyagarajan and C. Gunanathan, *Org. Lett.*, 2020, **22**, 6617.

2. N. Joly, L. Bettoni, S. Gaillard, A. Poater and J.-L. Renaud, *J. Org. Chem.*, 2021, **86**, 6813.

3. R. Babu, S. S. Padhy, G. Sivakumar and E. Balaraman, *Catal. Sci. Technol.*, 2023, **13**, 2763.