**Supporting information**

# Eutectogels-catalyzed for one-pot multi-component reaction: Access to pyridine and chromene derivatives

Phat Ngoc Nguyen,[a,b] Linh Ho Thuy Nguyen,[b,c] Tan Le Hoang Doan,[b,c] Phuong Hoang Tran[a,b] and Hai Truong Nguyen[a,b*]

[a] Department of Organic Chemistry, Faculty of Chemistry, University of Science, Ho Chi Minh City, 700000, Vietnam. Email: ngthai@hcmus.edu.vn

[b] Vietnam National University-Ho Chi Minh City, 700000, Vietnam.

[c] Center for Innovative Materials and Architectures, Vietnam National University – Ho Chi Minh City, 721337, Vietnam.

*Corresponding author:

Hai Truong Nguyen: phone number: +84-908-108-824; e-mail: ngthai@hcmus.edu.vn

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## Section S1. Chemical and equipment

### 2.1. Chemical

Benzaldehyde (99%), 4-methoxybenzaldehyde (98%), 4-chlorobenzaldehyde (98%), 4-fluorobenzaldehyde (98%), 2-chlorobenzaldehyde (99%), 2-fluorobenzaldehyde (97%), 4-bromobenzaldehyde (99%), 4-methylbenzaldehyde (97%), 2-furaldehyde (99%), ammonium acetate (97%) were purchased from Sigma-Aldrich. 1,3-cyclohexadione (97%), acetophenone (98%), malononitrile (99%), and dimedone (99%) were acquired from Acros.

Ethyl acetate (for analysis EMSURE ACS,ISO,Reag. Ph Eur) and Acetone (for analysis EMPARTA ACS) was acquired from Merck. Thin-layer chromatography (TLC) was conducted using aluminium plates (F-254) covered with silica gel. The experiment included the use of silica gel (230–400 mesh, Merck) for column chromatography.

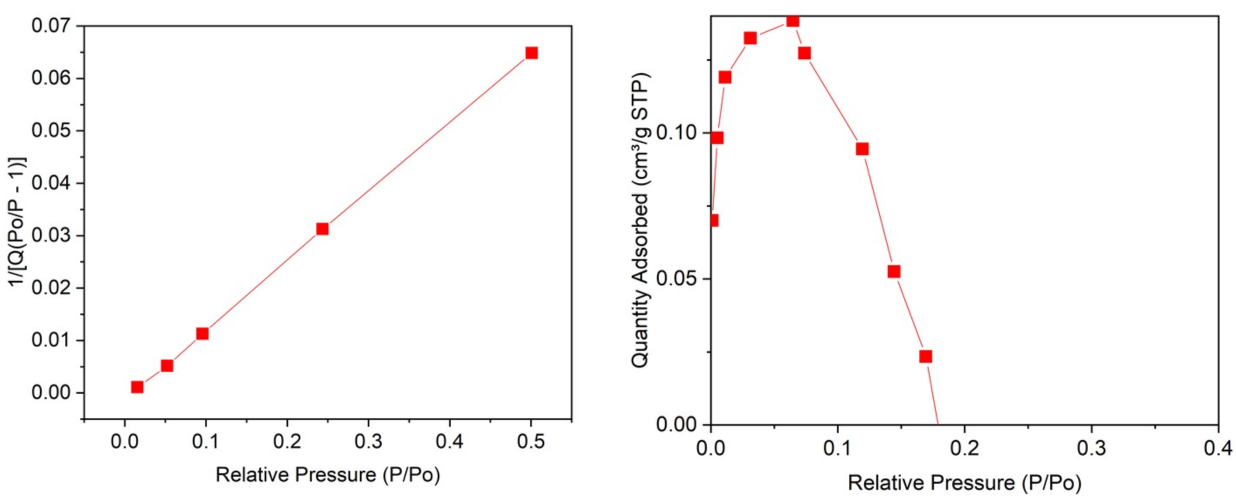
### 2.2. Techniques for analysis

The $^{1}$H-NMR and $^{13}$C-NMR spectra were acquired utilizing a Bruker Avance 500 MHz instrument in DMSO-$d_6$, with the solvent peaks serving as the system's internal standard. The boiling points were determined utilizing a Buchi B-545 melting point apparatus. Fourier-transform infrared (FTIR) spectra were acquired using a Bruker E400 FT-IR spectrometer. A Q-500 thermal gravimetric analyzer was used to conduct thermogravimetric analysis (TGA). The experimental procedure included exposing the sample to a temperature gradient at a rate of 5 °C per minute, while maintaining a controlled airflow. The refining process included the acquisition of Powder X-ray diffraction (P-XRD) data using a Bruker D8 Advance instrument. The data was obtained by employing Ni-filtered Cu K (λ = 1.54059) radiation. The shape and structure of the material were examined with a Hitachi S-4800 scanning electron microscopy (SEM) in combination with an XZS-107T digital microscope and an NHV-CAM camera, aided by the eScope software. The $N_2$ isotherm was measured and analyzed using the Quantachrome NOVA 3200e system, which operated at a temperature of 77 K. The EMAX energy EX-400 EDX device was used to perform an examination using energy-dispersive X-ray spectroscopy (EDX). The high-resolution mass spectra were acquired using a Bruker micrOTOF-QII mass spectrometer, which was operated in positive electrospray ionization mode and had an ionization energy of 80 electron volts (eV).

**Table S1.** The investigation of the mechanism pathway through control reactions

| Entry | Substance 1 | Substance 2 | Product isolated |
|---|---|---|---|
| 1 | Benzaldehyde | Malononitrile | + |
| 2 | Benzaldehyde | Cyclohexanone | - |
| 3 | Benzaldehyde | Ammonium acetate | - |
| 4 | Malononitrile | Cyclohexanone | - |
| 5 | Malononitrile | Ammonium acetate | - |
| 6 | Cyclohexanone | Ammonium acetate | - |

Reaction condition: substance 1 (1 mmol) and substance 2 (1 mmol) within 15 minutes at 80 °C; “+”: Reaction; “-”: No reaction.



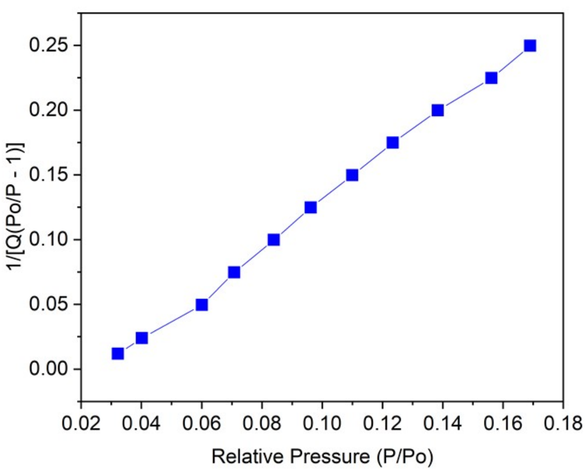

Multipoint BET plot

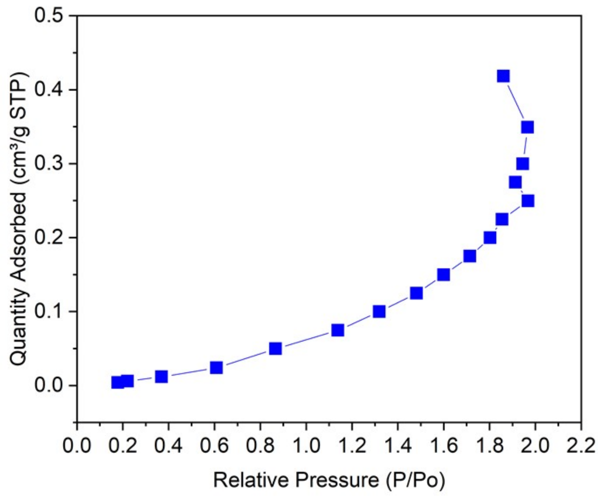
$N_2$ adsorption–desorption isotherms

BET surface area: 0.5751 ± 0.0044 m²/g.

Pore Volume: 0.000008 cm³/g

**Fig. S1.** BET of ETG-Acetamide fresh.




Multipoint BET plot　　　　　　　$N_2$ adsorption–desorption isotherms

BET surface area: 7.3835 ± 0.1136 m²/g

**Fig. S2.** BET of ETG-Acetamide reusable (after 3 times).

**Section S2. NMR data**

*2-Amino-4-phenyl-5,6,7,8-tetrahydroquinoline-3-carbonitrile*[1-5] ***(1a)***

With 71%, the pale yellow powder was produced. $R_f$ = 0.59 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 242-244 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.55-1.60 (m, 2H), 1.70-1.75 (m, 2H), 2.19 (t, $J$ = 6.5 Hz, 2H), 2.70 (t, $J$ = 6.5 Hz, 2H), 5.64 (s, 2H), 7.26-7.28 (m, 2H), 7.44–7.46, (m, 1H), 7.48-7.51 (m, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 22.1, 22.4, 25.8, 32.8, 88.0, 116.7, 118.3, 128.0, 128.5, 128.6, 136.4, 153.9, 157.9, 160.9 ppm.

*2-Amino-4-(4-methoxyphenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile*[2, 4-7] ***(2a)***

With 47%, the pale yellow powder was produced. $R_f$ = 0.51 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 239-240 °C; $^1$H-NMR (500 MHz, DMSO): $\delta$ = 1.55-1.59 (m, 2H), 1.70-1.75 (m, 2H), 2.23 (t, $J$ = 6.5 Hz, 2H), 2.69 (t, $J$ = 6.5 Hz, 2H), 3.81 (s, 3H), 6.51 (s, 2H), 7.04 (d, $J$ = 8.5 Hz, 2H), 7.22 (d, $J$ = 8.5 Hz, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO): $\delta$ = 22.1, 22.5, 25.9, 32.8, 55.1, 88.3, 113.9, 116.9, 118.6, 128.5, 129.6, 153.7, 157.9, 159.3, 160.8 ppm.

*2-Amino-4-(4-chlorophenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile*[2-7] ***(3a)***

With 33%, the yellow powder was produced. $R_f$ = 0.53 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 266-268 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.56-1.61 (m, 2H), 1.71-1.75 (m, 2H), 2.19 (t, *J* = 6.5 Hz, 2H), 2.70 (t, *J* = 6.5 Hz, 2H), 6.60 (s, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 22.0, 22.4, 25.8, 32.8, 87.8, 116.5, 118.2, 128.7, 130.1, 133.4, 135.2, 152.7, 157.9, 161.1 ppm.

*2-Amino-4-(4-fluorophenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile*[5] ***(4a)***

With 58%, the pale yellow powder was produced. $R_f$ = 0.52 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 259-260 °C; $^1$H-NMR (500 MHz, DMSO): $\delta$ = 1.56-1.61 (m, 2H), 1.71-1.75 (m, 2H), 2.19 (t, *J* = 6.5 Hz, 2H), 2.70 (t, *J* = 6.5 Hz, 2H), 6.58 (s, 2H), 7.33-7.37 (m, 4H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 22.1, 22.4, 25.8, 32.8, 88.1, 115.7 (d, *J* = 21.3 Hz), 116.6, 118.4, 130.5 (d, *J* = 8.8 Hz), 132.7 (d, *J* = 2.5 Hz), 153.0, 157.9, 161.0, 162.1 (d, *J* = 243.8 Hz) ppm.

*2-Amino-4-(2-chlorophenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile*[5, 6] ***(5a)***

With 46%, the pale yellow powder was produced. $R_f$ = 0.59 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 259-251 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.57-1.63 (m, 2H), 1.70–1.75 (m, 2H), 2.03–2.14 (m, 2H), 2.66–2.77 (m, 2H), 6.66 (s, 2H), 7.31–7.32 (m, 1H), 7.48–7.50 (m, 2H), 7.62–7.63 (m, 1H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 22.1, 22.2, 25.2, 32.7, 87.9, 116.1, 118.5, 127.7, 129.6, 129.9, 130.5, 131.0, 135.2, 151.3, 157.8, 161.3 ppm.

*2-Amino-4-(2-fluorophenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile* ***(6a)***

With 44%, the yellow powder was produced. $R_f$ = 0.58 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 254-256 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.58–1.63 (m, 2H), 1.71-1.76 (m, 2H), 2.09–2.24 (m, 2H), 2.66–2.77 (m, 2H), 6.66 (s, 2H), 7.33–7.39 (m, 3H), 7.52–

7.56 (m, 1H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 22.0, 22.2, 25.3, 32.7, 88.3, 115.9 (d, $J$ = 21.3 Hz), 116.2, 118.9, 123,6 (d, $J$ = 17.5 Hz), 124.9 (d, $J$ = 2.5 Hz), 129.6 (d, $J$ = 2.5 Hz), 131.3 (d, $J$ = 8.8 Hz), 148.0, 157.8, 158.2 (d, $J$ = 242.5 Hz), 161.3 ppm.

*2-Amino-4-(4-bromophenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile*[4, 5] *(7**a**)*

With 53%, the pale yellow powder was produced. $R_f$= 0.53 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 299-301 °C; $^{1}$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.58–1.62 (m, 2H), 1.71–1.75 (m, 2H), 2.19 (t, $J$ = 6.5 Hz, 2H), 2.70 (t, $J$ = 6.5 Hz, 2H), 6.61 (s, 2H), 7.27 (d, $J$ = 8.5 Hz, 2H), 7.70 (d, $J$ = 8.5 Hz, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 22.0, 22.4, 25.8, 32.8, 87.7, 116.5, 118.1, 122.1, 130.4, 131.6, 135.6, 152.7, 157.9, 161.1 ppm.

*2-Amino-4-(p-tolyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile*[4, 6, 7] ***(8a)***

With 44%, the pale yellow powder was produced. $R_f$ = 0.57 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 258-260 °C; $^{1}$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.54–1.59 (m, 2H), 1.70–1.75 (m, 2H), 2.20 (t, $J$ = 6.5 Hz, 2H), 2.37 (s, 3H), 2.69 (t, $J$ = 6.5 Hz, 2H), 6.52 (s, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 20.8, 22.1, 22.5, 25.9, 32.8, 88.1, 116.7, 118.4, 128.0, 129.1, 133.4, 137.9, 154.0, 157.9, 160.8 ppm.

*2-Amino-4-(furan-2-yl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile* ***(9a)***

With 48%, the yellow powder was produced. $R_f$ = 0.58 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 216-218 °C; $^{1}$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 0.78-0.82 (m. 2H), 0.88-0.92 (m, 2H), 1.68 (t, $J$ = 6.0 Hz, 2H), 1.86 (t, $J$ = 6.5 Hz, 2H), 5.74 (s, 2H), 5.86 (dd, $J$ = 1.5 Hz & 3.5 Hz, 1H), 6.06 (d, $J$ = 3.5 Hz, 1H), 7.08 (d, $J$ = 1.5 Hz, 1H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 21.9, 22.5, 26.1, 33.0, 85.7, 111.7, 113.7, 116.9, 118.3, 141.1, 144.5, 147.4, 158.5, 161.7 ppm.

*2-Amino-4,6-diphenylnicotinonitrile*[2-4, 8-10] ***(10a)***

With 15%, the white powder was produced. $R_f$ = 0.84 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 186-187 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 7.01 (s, 2H), 7.28 (s, 1H), 7.48-7.51 (m, 3H), 7.54-7.58 (m, 3H), 7.68 (dd, $J$ = 2.0 Hz & 8.0 Hz, 2H), 8.12-8.14 (m, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 86.7, 109.3, 117.0, 127.3, 128.4, 128.7, 129.6, 130.1, 137.0, 137.6, 154.9, 158.6, 160.9 ppm.

*2-Amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile*[2, 8-10] ***(11a)***

With 12%, the white powder was produced. $R_f$ = 0.78 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 188-190 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 3.84 (s, 3H), 6.95 (s, 2H), 7.11 (d, $J$ = 8.5 Hz, 2H), 7.25 (s, 1H), 7.47-7.49 (m, 3H), 7.66 (d, $J$ = 8.5 Hz, 2H), 8.12 (dd, $J$ = 2.5 & 7.5 Hz, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 55.3, 86.4, 109.0, 114.2, 117.3, 127.2, 128.6, 129.1, 129.8, 130.0, 137.7, 154.5, 158.5, 160.4, 161.0 ppm.

*2-Amino-4-(4-chlorophenyl)-6-phenylnicotinonitrile*[2-4, 8-10] ***(12a)***

With 46%, the white powder was produced. $R_f$ = 0.84 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 185-186 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 7.05 (s, 2H), 7.29 (s, 1H), 7.48-7.51 (m, 3H), 7.63 (d, $J$ = 8.5 Hz, 2H), 7.72 (d, $J$ = 8.5 Hz, 2H), 8.12-8.14 (m, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 86.5, 109.1, 116.8, 127.3, 128.6, 128.7, 130.1, 130.3, 134.5, 135.8, 137.5, 153.6, 158.7, 160.8 ppm.

*2-Amino-4-(4-fluorophenyl)-6-phenylnicotinonitrile*[9, 10] ***(13a)***

With 19%, the white powder was produced. $R_f$ = 0.84 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 164-166 °C; ; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 7.0 (s, 2H), 7.28 (s, 1H), 7.38-7.43 (m, 2H), 7.48-7.51 (m, 3H), 7.73-7.77 (m, 2H), 8.12-8.14 (m, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 86.6, 109.3, 115.7 (d, $J$ = 22.5 Hz), 117.0, 127.3, 128.6, 130.1, 130.8 (d, $J$ = 8.8 Hz), 133.4 (d, $J$ = 2.5 Hz), 137.5, 153.8, 158.7, 160.8, 162.9 (d, $J$ = 245.0 Hz) ppm.

*2-Amino-6-phenyl-4-(4-bromophenyl)nicotinonitrile*[4, 8, 10] ***(14a)***

With 36%, the white powder was produced. $R_f$ = 0.84 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 183-185 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 7.05 (s, 2H), 7.28 (s, 1H), 7.48-7.51 (m, 3H), 7.64 (d, $J$ = 8.5 Hz, 2H), 7.77 (d, $J$ = 8.5 Hz, 2H), 8.12-8.14 (m, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 86.4, 109.1, 116.8, 123.2, 127.3, 128.6, 130.2, 130.5, 131.7, 136.1, 137.5, 153.7, 158.8, 160.8 ppm.

*2-Amino-6-phenyl-4-(p-tolyl)nicotinonitrile*[2-4, 8-10] ***(15a)***

With 31%, the white powder was produced. $R_f$ = 0.84 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 181-183 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 2.40 (s, 3H), 6.97 (s, 2H), 7.25 (s, 1H), 7.37 (d, $J$ = 7.5 Hz, 2H), 7.47-7.50 (m, 3H), 7.59 (d, $J$ = 7.5 Hz, 2H), 8.11-8.13 (m, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 20.8, 86.5, 109.1, 117.1, 127.2, 128.2, 128.6, 129.3, 130.0, 134.1, 137.6, 139.3, 154.8, 158.5, 160.9 ppm.

*2.4.16. 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile*[11-17] ***(16b)***

With 50%, the pale yellow powder was produced. $R_f$ = 0.52 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 233-234 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 0.96 (s, 3H), 1.04 (s, 3H), 2.11 (d, $J$ = 16.0 Hz, 1H), 2.26 (d, $J$ = 16.0 Hz, 1H), 2.48 - 2.58 (m, 2H), 4.17 (s, 1H), 7.00 (s, 2H), 7.14 (d, $J$ = 7.5 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.28 (t, $J$ = 7.5 Hz, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 26.8, 28.4, 31.8, 35.6, 50.0, 58.3, 112.7, 119.7, 126.5, 127.1, 128.3, 144.7, 158.5, 162.5, 195.6 ppm.

*2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile*[11, 12, 16, 17] ***(17b)***

With 14%, the pale yellow powder was produced. $R_f$ = 0.48 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 200-202 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 0.94 (s, 3H), 1.03 (s, 3H), 2.08 (d, *J* = 16.0 Hz, 1H), 2.24 (d, *J* = 16.0 Hz, 1H), 2.45–2.45 (m, 2H), 3,71 (s, 3H), 4.12 (s, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.95 (s, 2H), 7.05 (d, *J* = 8.5 Hz, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 26.8, 28.4, 31.8, 34.7, 50.0, 55.0, 58.6, 113.0, 113.7, 119.8, 128.2, 136.8, 157.9, 158.4, 162.1, 195.0 ppm.

*2-Amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile*[11, 13-17] ***(18b)***

With 75%, the pale yellow powder was produced. $R_f$ = 0.48 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 184-185 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 0.94 (s, 3H), 1.03 (s, 3H), 2.11 (d, *J* = 16.0 Hz, 1H), 2.25 (d, *J* = 16.0 Hz, 1H), 2.47–2.54 (m, 2H), 3,71 (s, 3H), 4.20 (s, 1H), 7.03 (s, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 7.16–7.19 (m, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO): $\delta$ = 26.8, 28.3, 31.8, 34.9, 50.0, 58.1, 112.6, 115.0 (d, *J* = 21.3 Hz), 119.6, 129.0 (d, *J* = 7.5 Hz), 140.9 (d, *J* = 2.5 Hz), 158.5, 160.9 (d, *J* = 241.3 Hz), 162.5, 195.7 ppm.

*2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile*[11, 16, 17] ***(19b)***

With 7%, the pale yellow powder was produced. $R_f$ = 0.51 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 213-215 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 0.98 (s, 3H), 1.04 (s, 3H), 2.08 (d, *J* = 16.0 Hz, 1H), 2.25 (d, *J* = 16.0 Hz, 1H), 2.47 – 2.57 (m, 2H), 4.69 (s, 1H), 7.03 (s, 2H), 7.16–7.22 (m, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 26.9, 28.4, 31.8, 32.8, 49.9, 56.8, 111.8, 119.2, 127.4, 128.2, 129.4, 130.0, 132.1, 141.6, 158.7, 163.1, 195.5 ppm.

*2-Amino-4-(2-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-*

*carbonitrile*[16] ***(20b)***

With 42%, the yellow powder was produced. $R_f$ = 0.52 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 237-239 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 0.96 (s, 3H), 1.04 (s, 3H), 2.08 (d, *J* = 16.0 Hz, 1H), 2.27 (d, *J* = 16.0 Hz, 1H), 2.45–2.57 (m, 2H), 4.45 (s, 1H), 7.03 (s, 2H), 7.09–7.13 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.21–7.25 (m, 1H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 26.6, 28.5, 29.8, 31.8, 49.9, 56.7, 111.4, 115.4 (d, *J* = 21.3 Hz), 119,5, 124,4 (d, *J* = 2.5 Hz), 128.6 (d, *J = 7.5 Hz*), 129.7 (d, *J* = 3.8 Hz), 131.2 (d, *J* = 12.5 Hz), 158.8, 159.9 (d, *J* = 245.0 Hz), 163.1, 195.6 ppm.

*2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile*[11, 13, 15-17] ***(21b)***

With 8%, the pale yellow powder was produced. $R_f$ = 0.53 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 232-234 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.00 (s, 6H), 2.33 (s, 2H), 2.83 (s, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.73 (s, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 27.7, 31.6, 46.9, 52.4, 90.8, 115.3, 115.6, 121.3, 129.5, 130.8, 137.3, 155.6, 160.3, 168.1, 194.0 ppm.

*2-Amino-7,7-dimethyl-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile*[11, 15-17] ***(22b)***

With 6%, the pale yellow powder was produced. $R_f$ = 0.57 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 200-202 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 1.00 (s, 6H), 2.32 (s, 2H), 2.36 (s, 3H), 2.83 (s, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 2H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 20.9, 27.7, 31.6, 47.0, 52.6, 91.1, 115.5, 116.0, 127.3, 128.4, 135.0, 137.1, 156.9, 160.3, 167.9, 193.9 ppm.

*2-Amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile*[12, 17] ***(23b)***

With 28%, the pale yellow powder was produced. $R_f$ = 0.49 (*n*-Hexane-Ethyl acetate = 5:5); Mp. = 218-220 °C; $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ = 0.98 (s, 3H), 1.04 (s, 3H), 2.17 (d, $J$ = 16.0 Hz, 1H), 2.29 (d, $J$ = 16.0 Hz, 1H), 2.43-2.54 (m, 2H), 4.32 (s, 1H), 6.05 (d, $J$ = 3.0 Hz, 1H), 6.32 (dd, $J$ = 2.0 Hz & 3.0 Hz, 1H), 7.48 (d, $J$ = 2.0 Hz, 1H) ppm. $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ = 26.6, 28.4, 29.0, 31.8, 49.9, 55.4, 105.1, 110.4, 110.5, 119.6, 141.8, 155.7, 159.3, 163.6, 195.4 ppm.

**Section S3. NMR spectral**

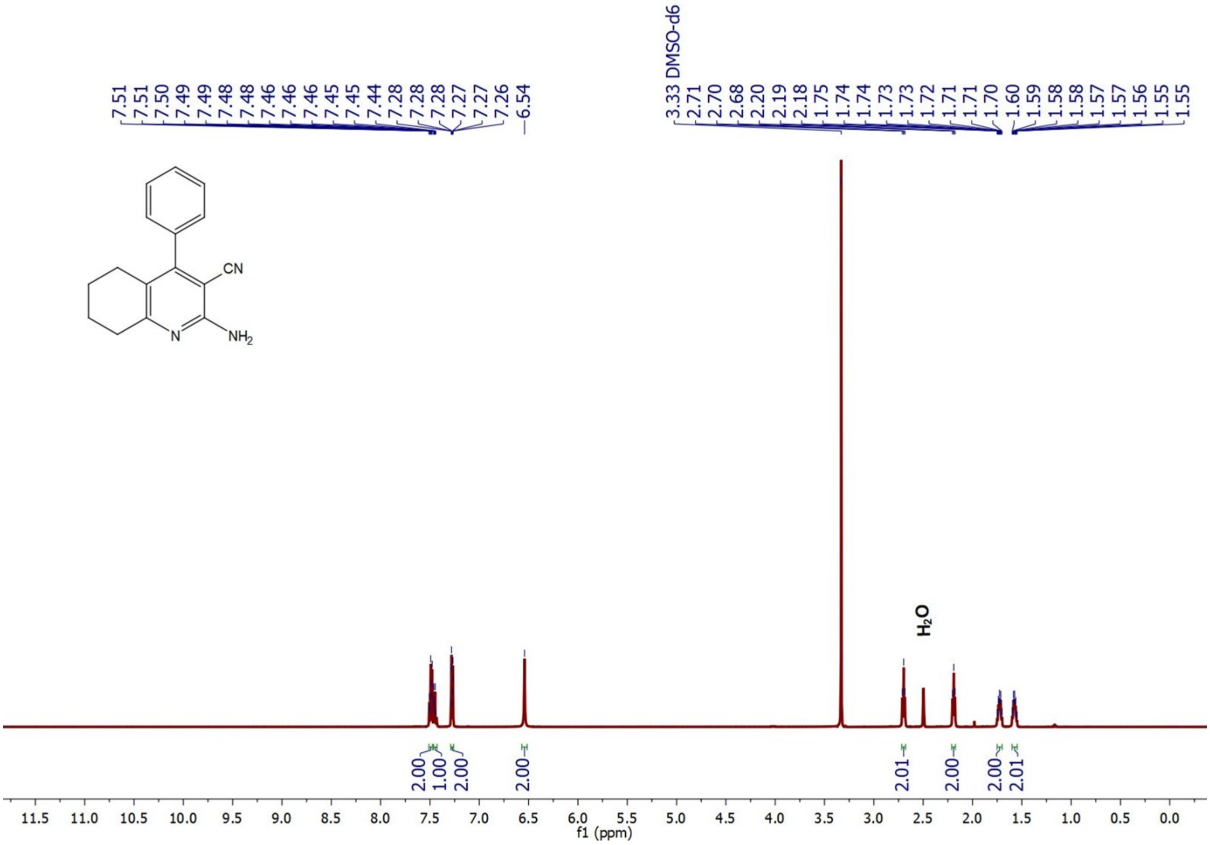



**Figure S2-1.1.** $^{1}H$–NMR spectrum of 1a

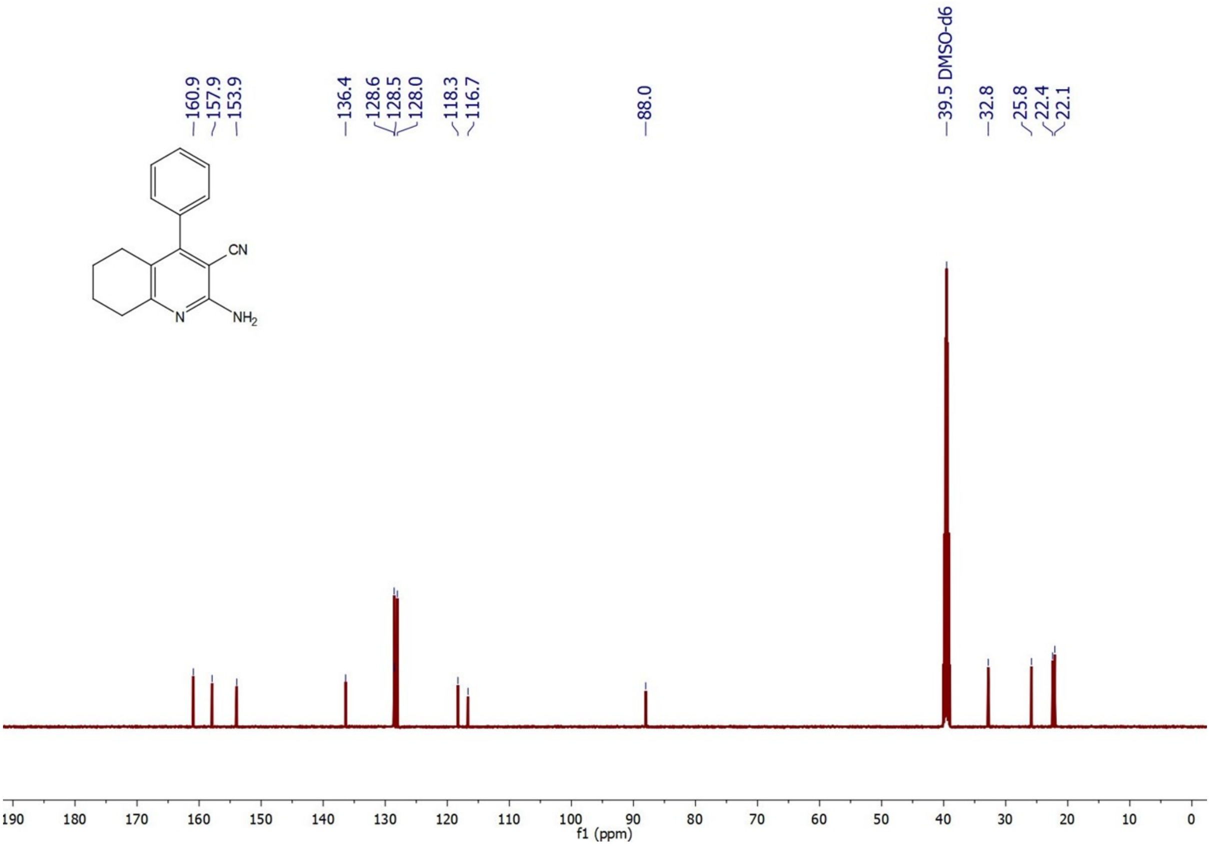



**Figure S2-1.2.** $^{13}C$–NMR spectrum of 1a

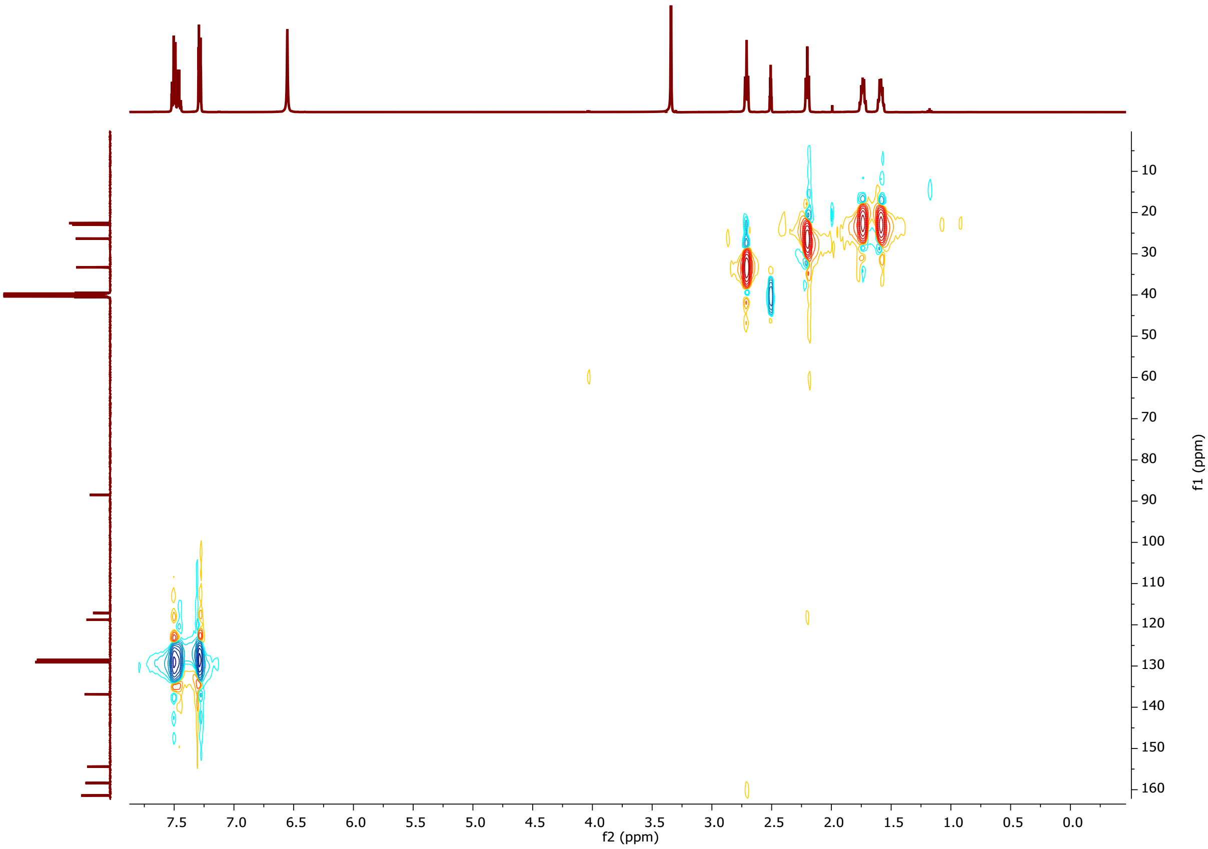



**Figure S2-1.3.** HSQC spectrum of 1a

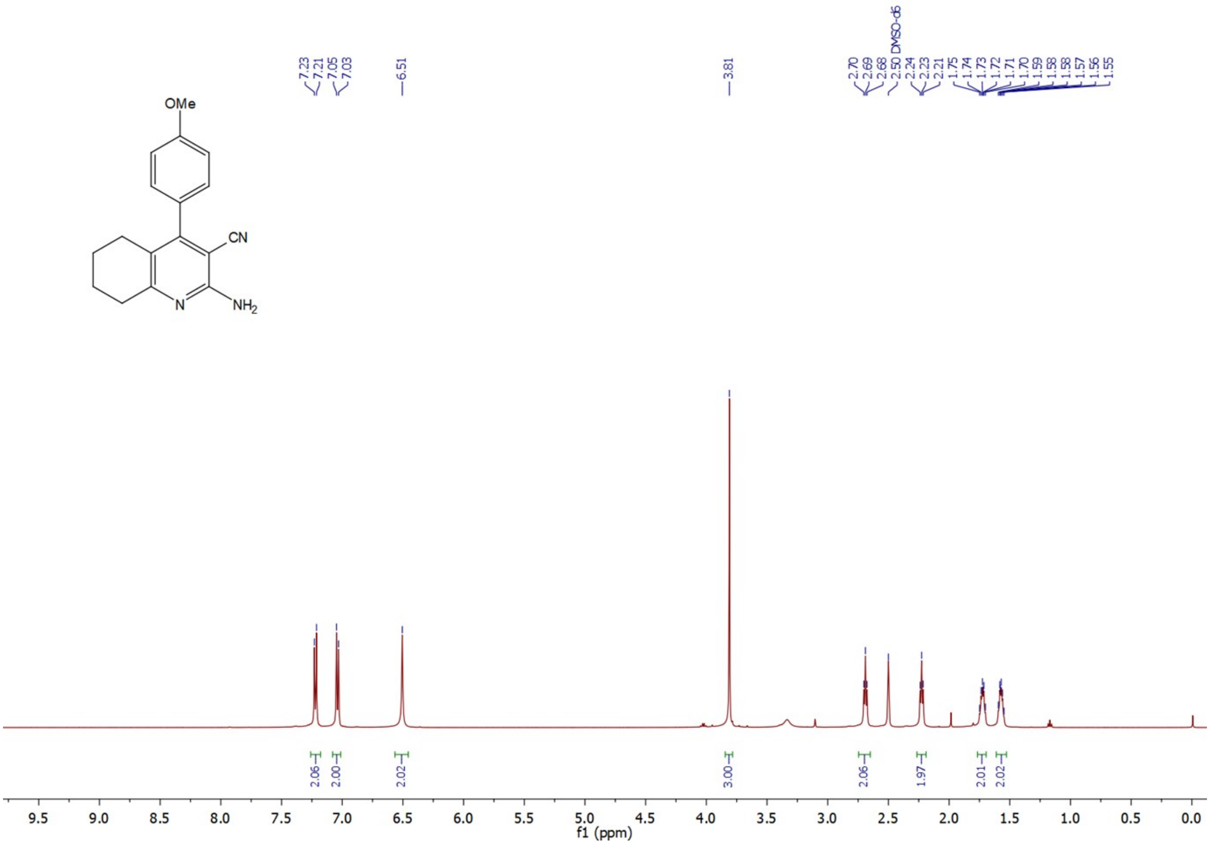



**Figure S2-2.1.** $^{1}$H –NMR spectrum of 2a

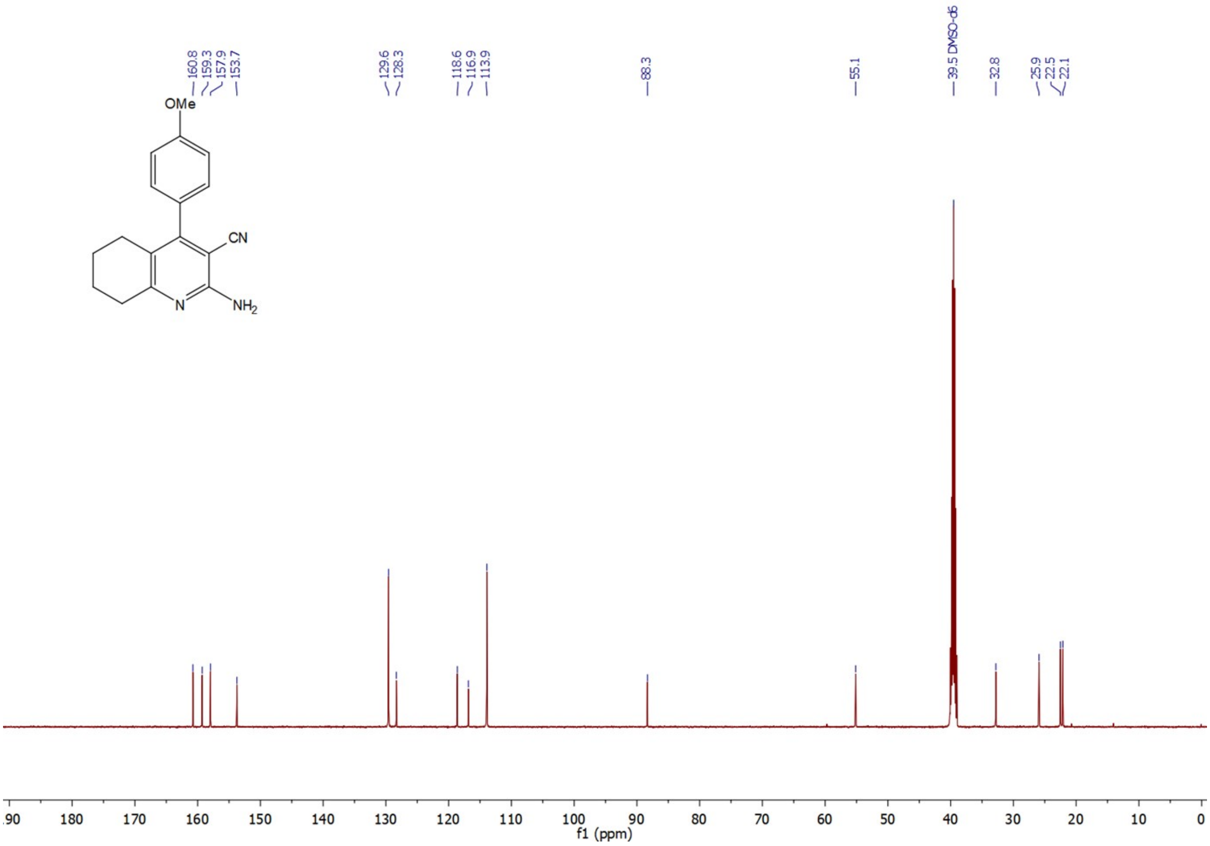



**Figure S2-2.2.** $^{13}C$–NMR spectrum of 2a

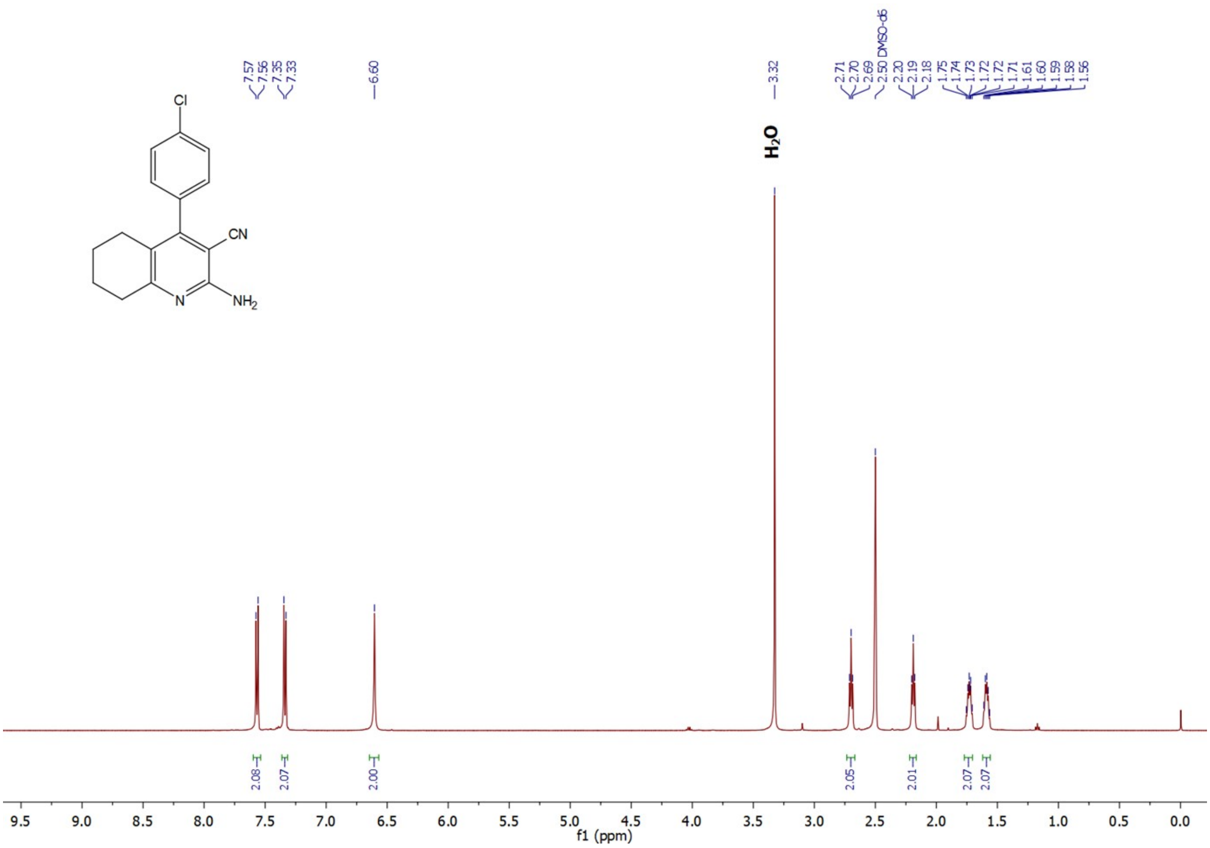



**Figure S2-3.1.** $^{1}H$–NMR spectrum of 3a

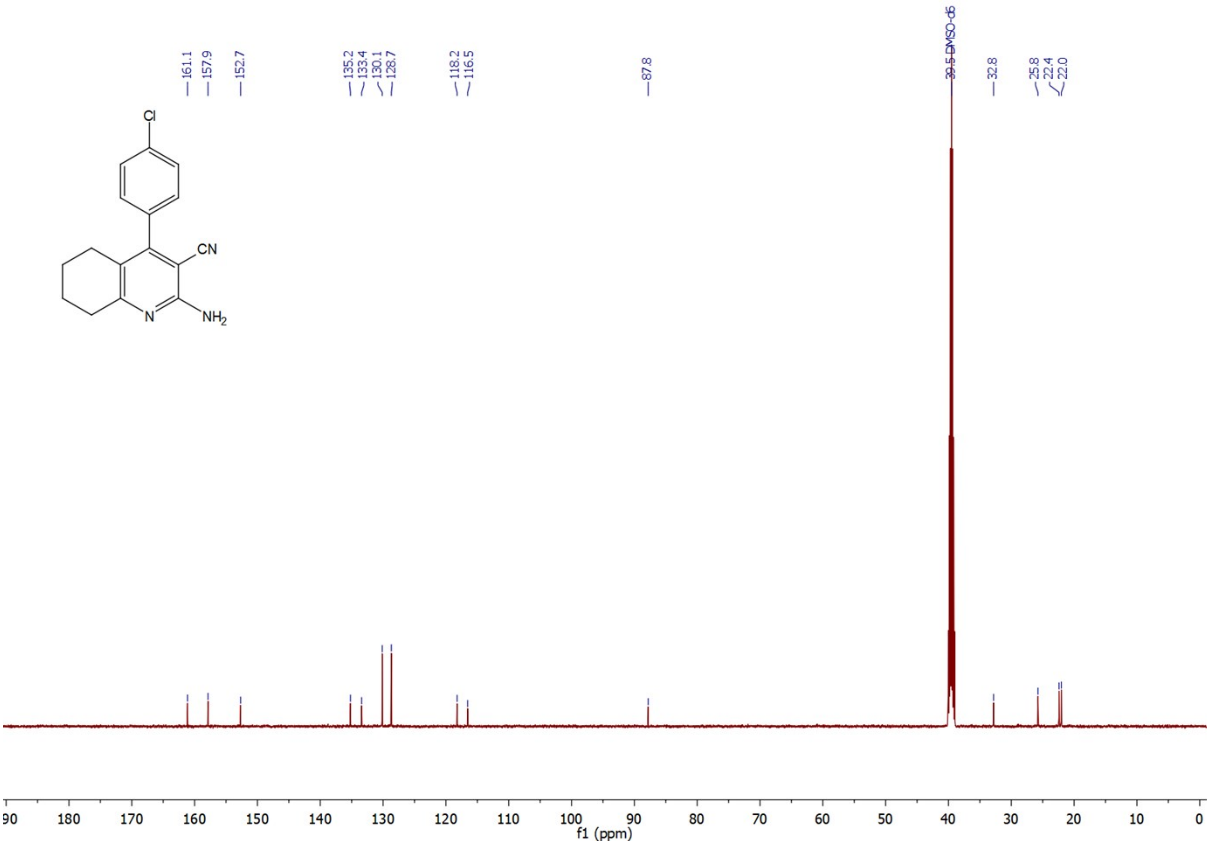


**Figure S2-3.2.** $^{13}$C–NMR spectrum of 3a

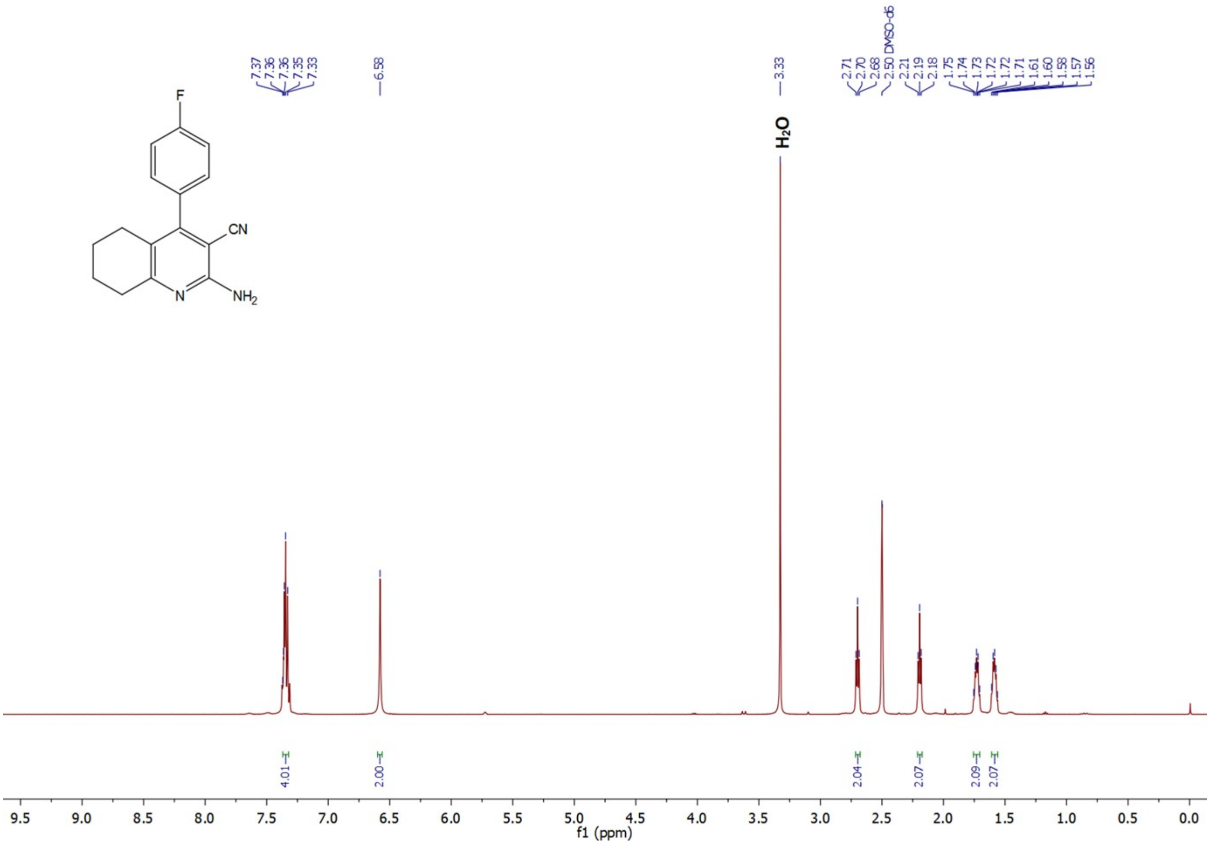


**Figure S2-4.1.** $^{1}$H–NMR spectrum of 4a

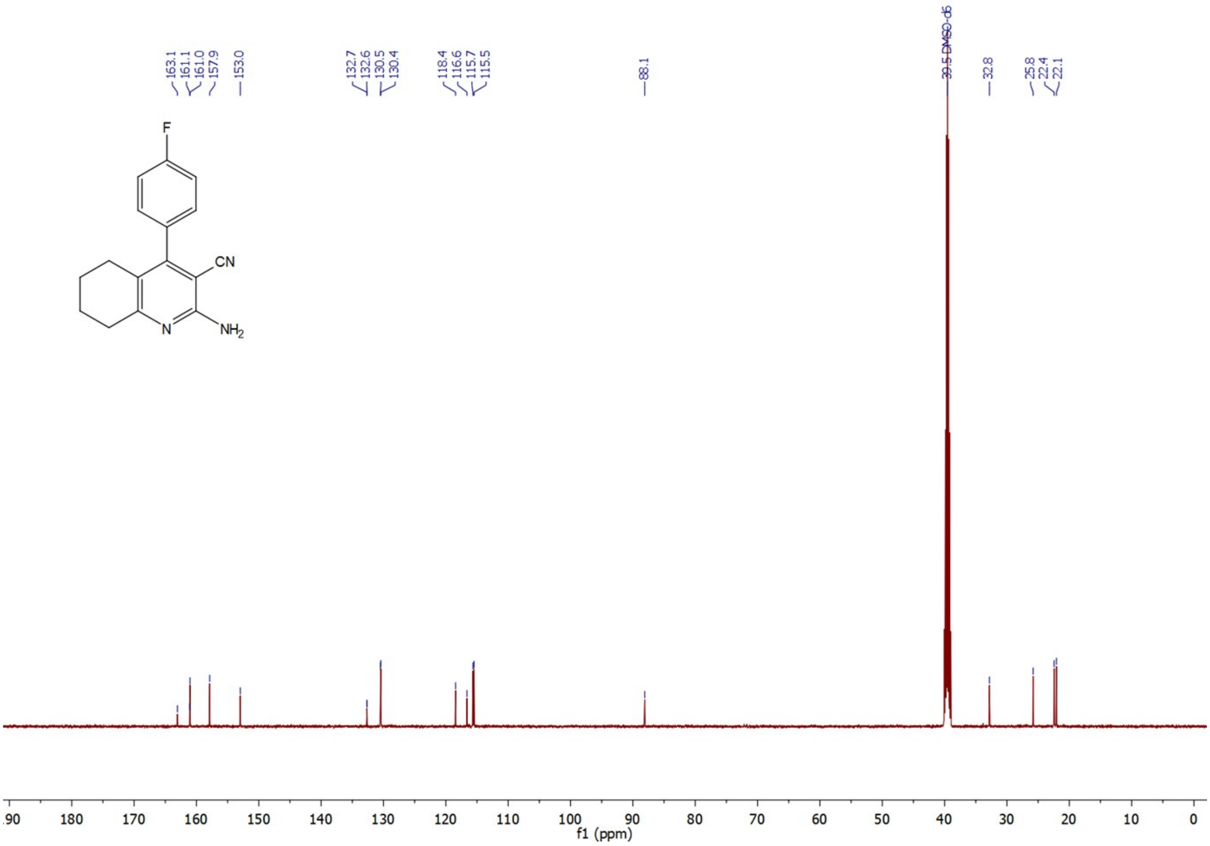



**Figure S2-4.2.** $^{13}C$–NMR spectrum of 4a

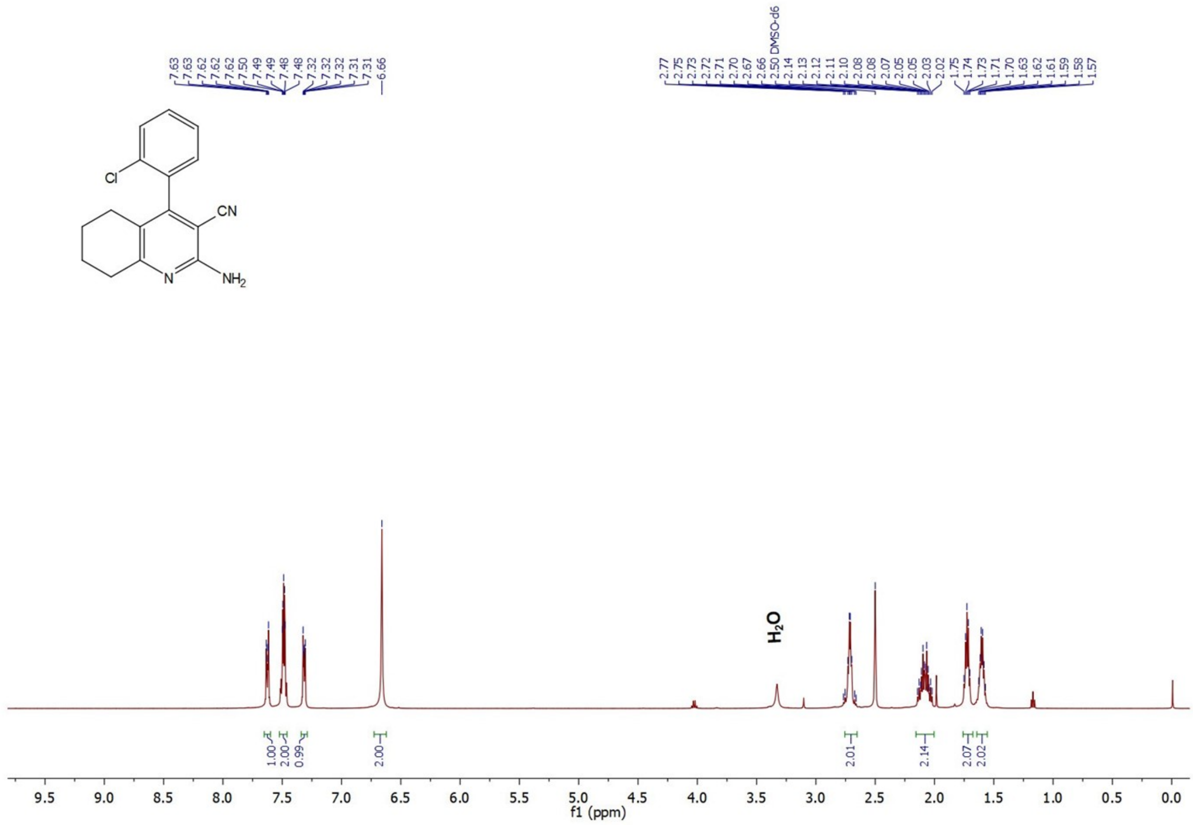



**Figure S2-5.1.** $^{1}H$–NMR spectrum of 5a

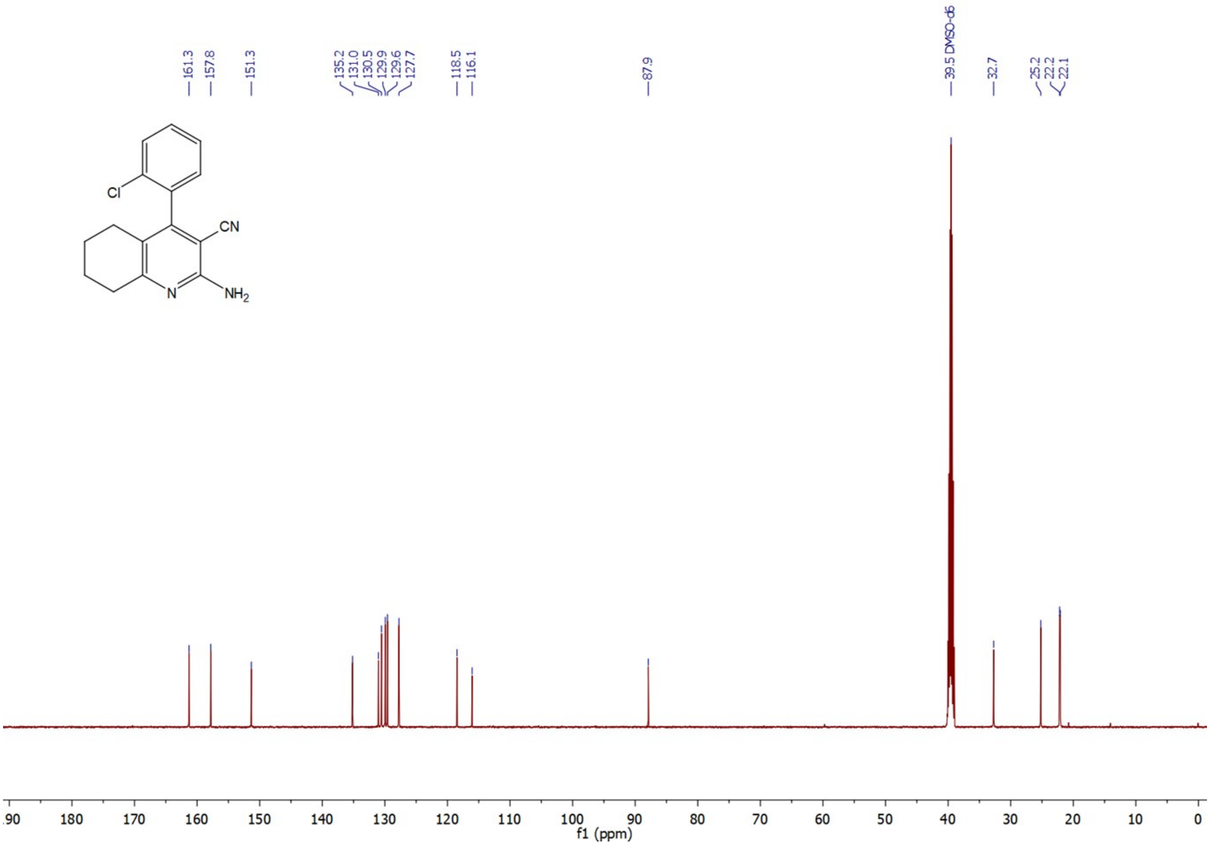


**Figure S2-5.2.** $^{13}$C–NMR spectrum of 5a

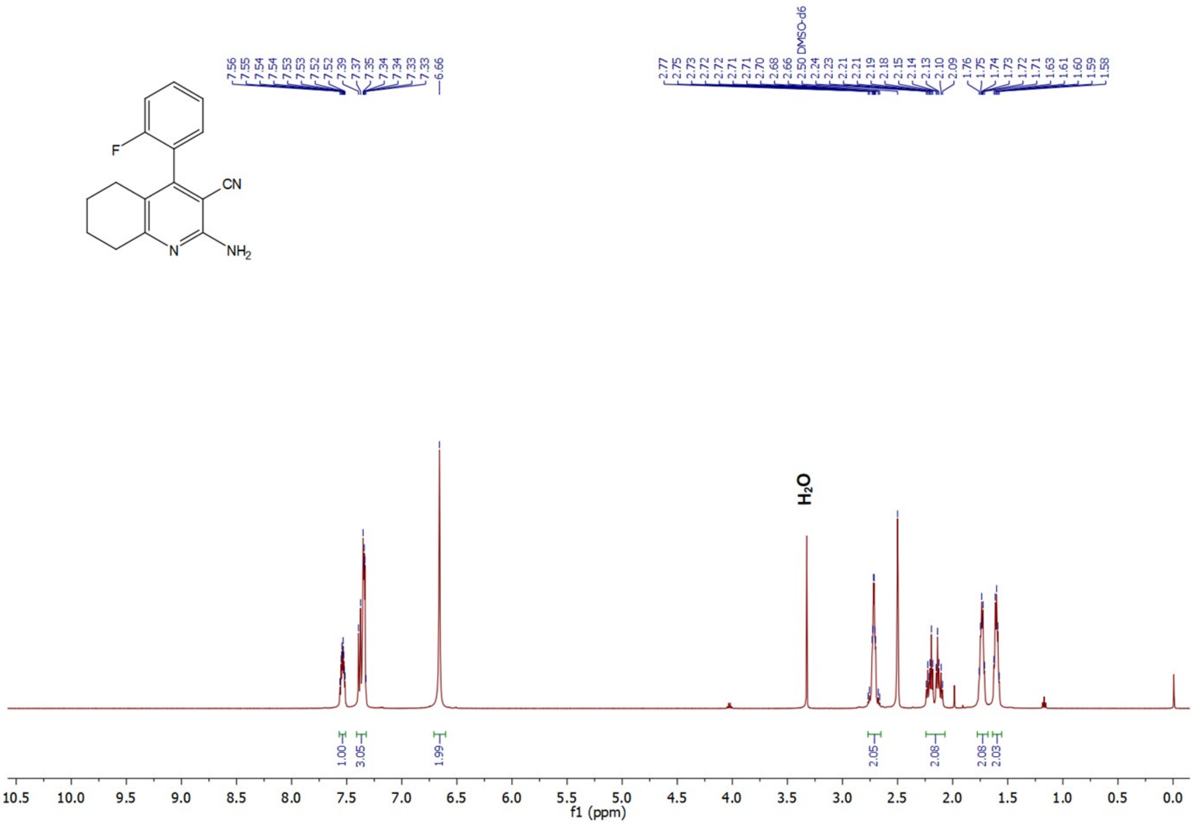


**Figure S2-6.1.** $^{1}$H–NMR spectrum of 6a

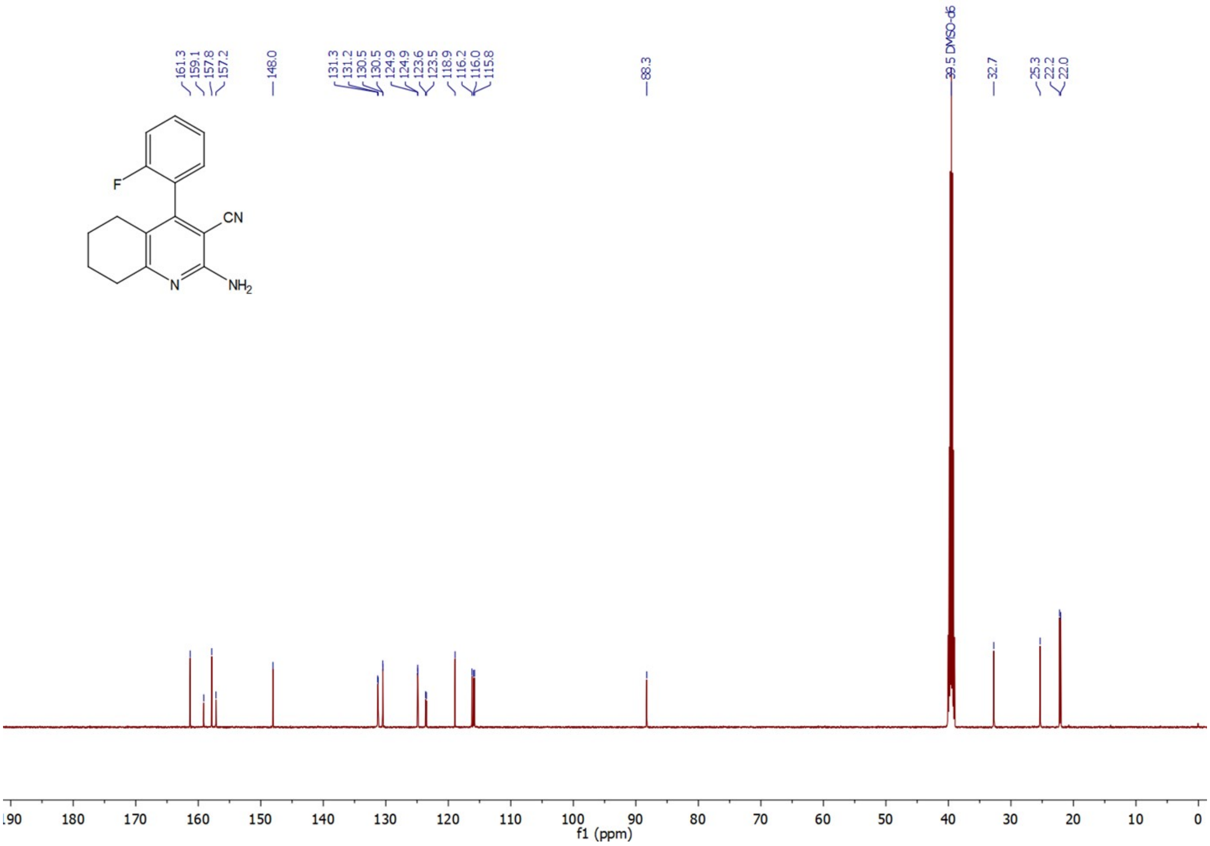


**Figure S2-6.2.** $^{13}C$–NMR spectrum of 6a

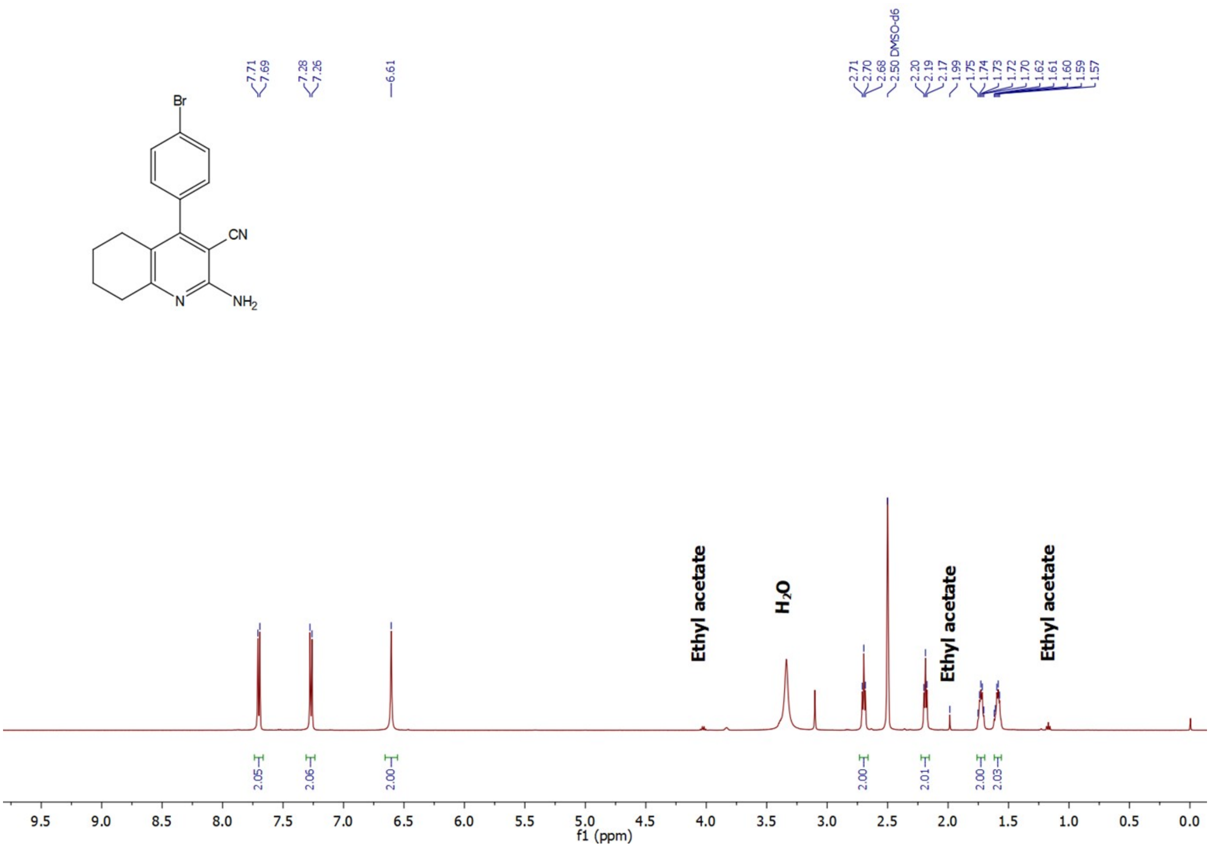



**Figure S2-7.1.** $^{1}H$–NMR spectrum of 7a

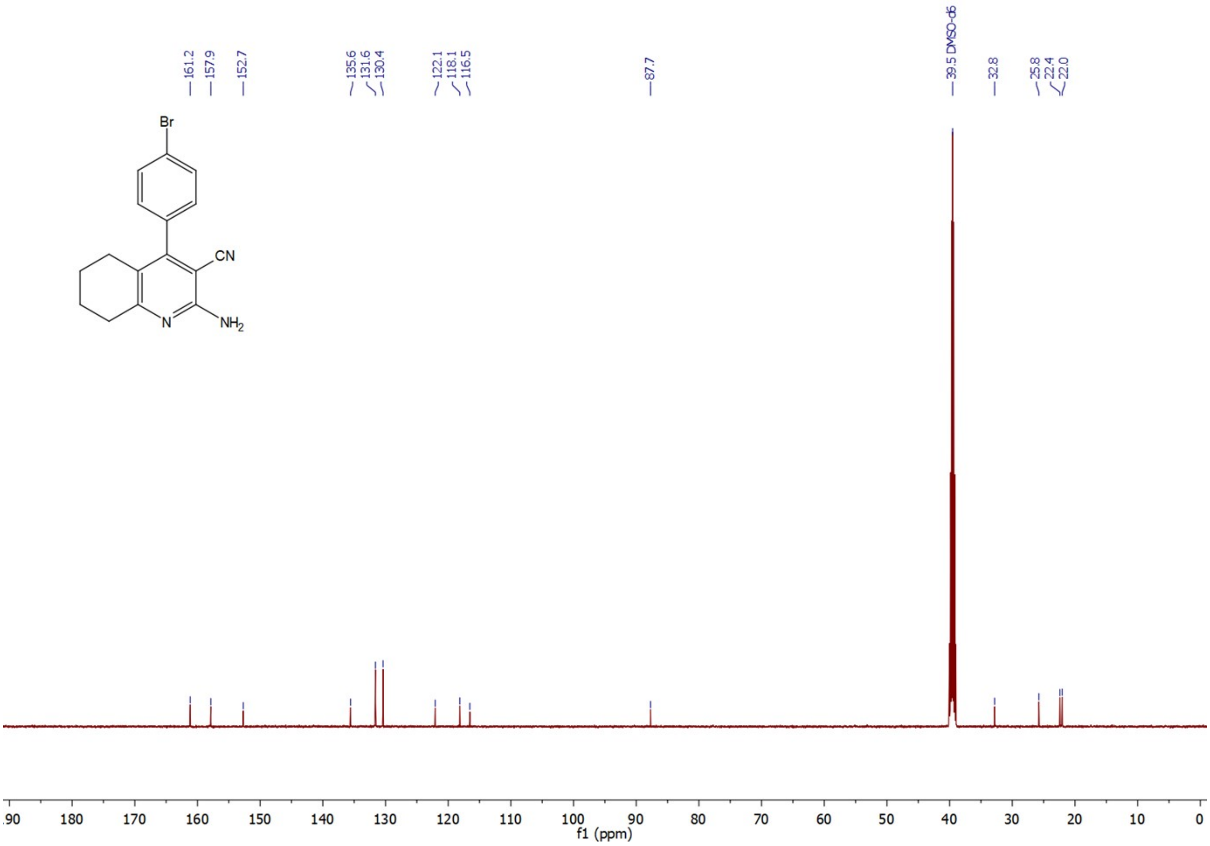



**Figure S2-7.2.** $^{13}$C–NMR spectrum of 7a

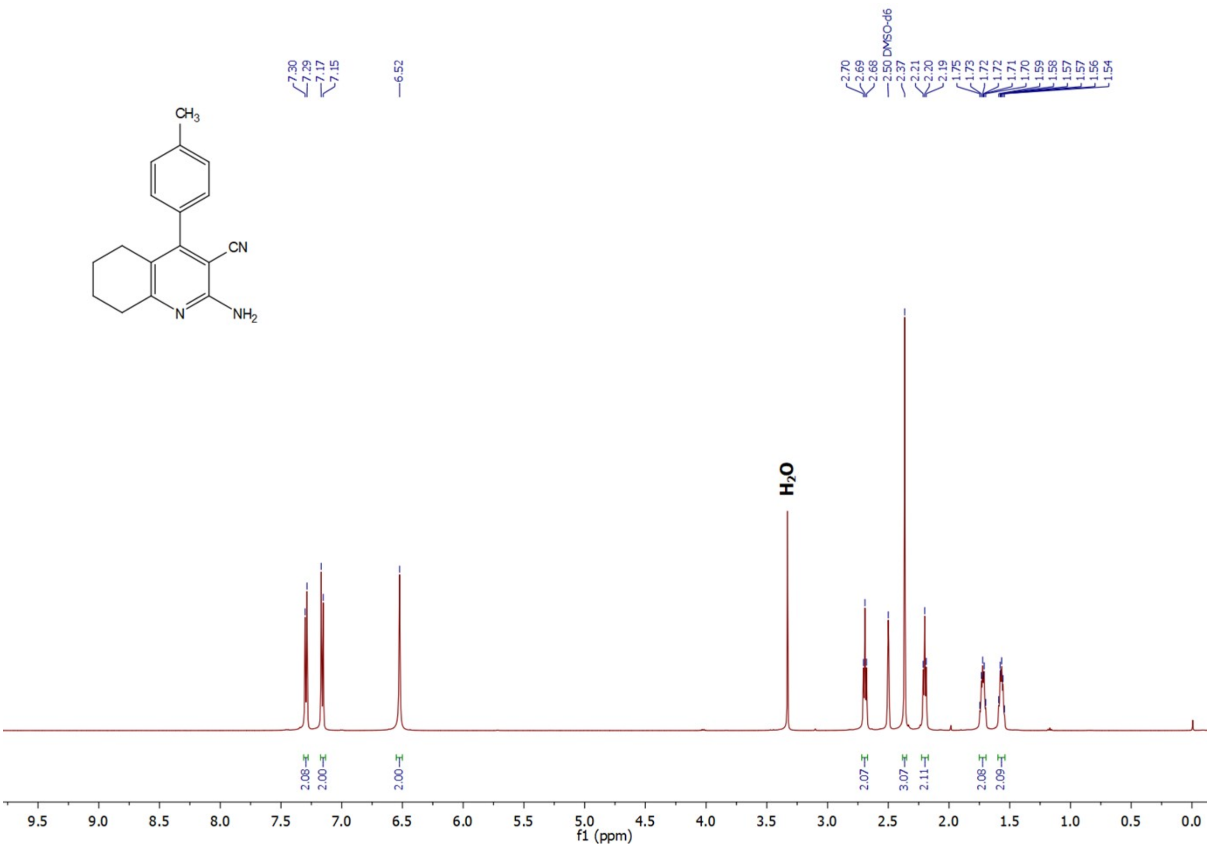



**Figure S2-8.1.** $^{1}$H–NMR spectrum of 8a

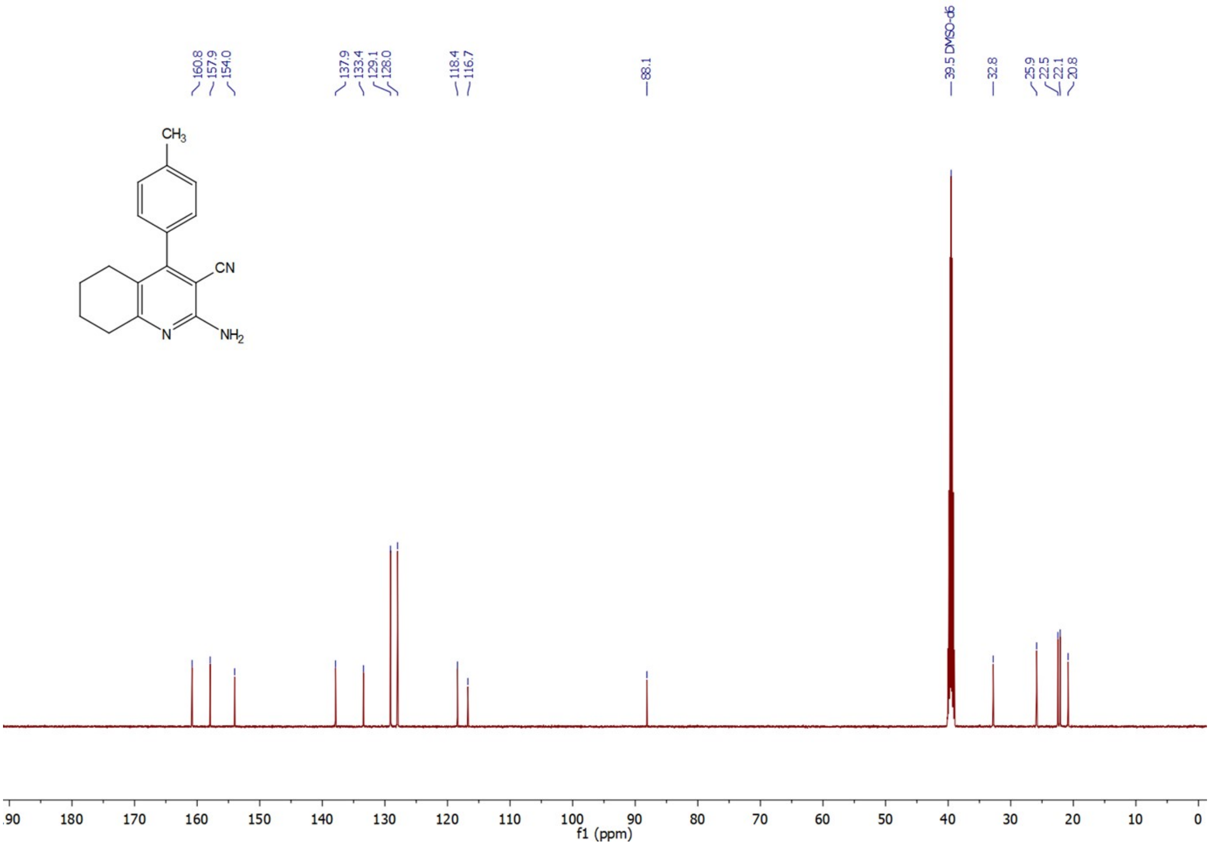



**Figure S2-8.2.** $^{13}C$–NMR spectrum of 8a

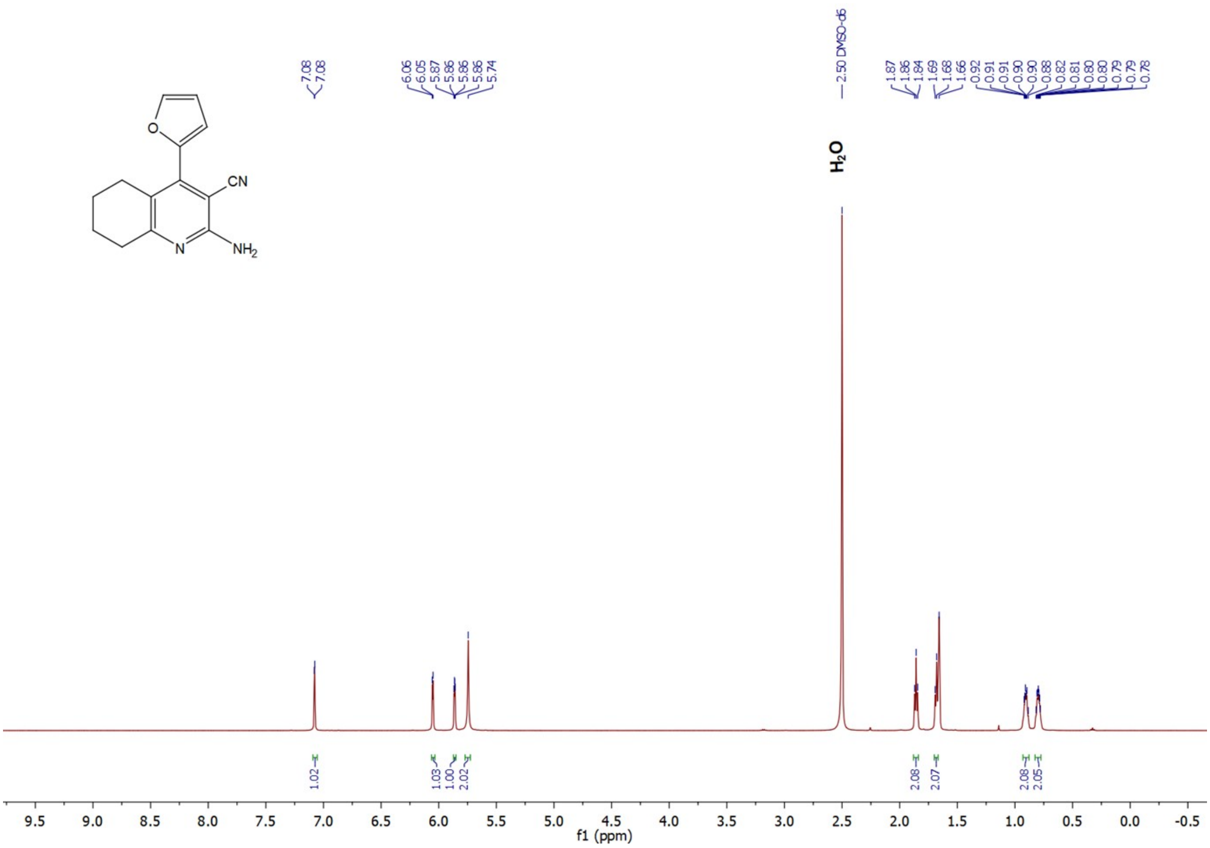



**Figure S2-9.1.** $^{1}H$–NMR spectrum of 9a

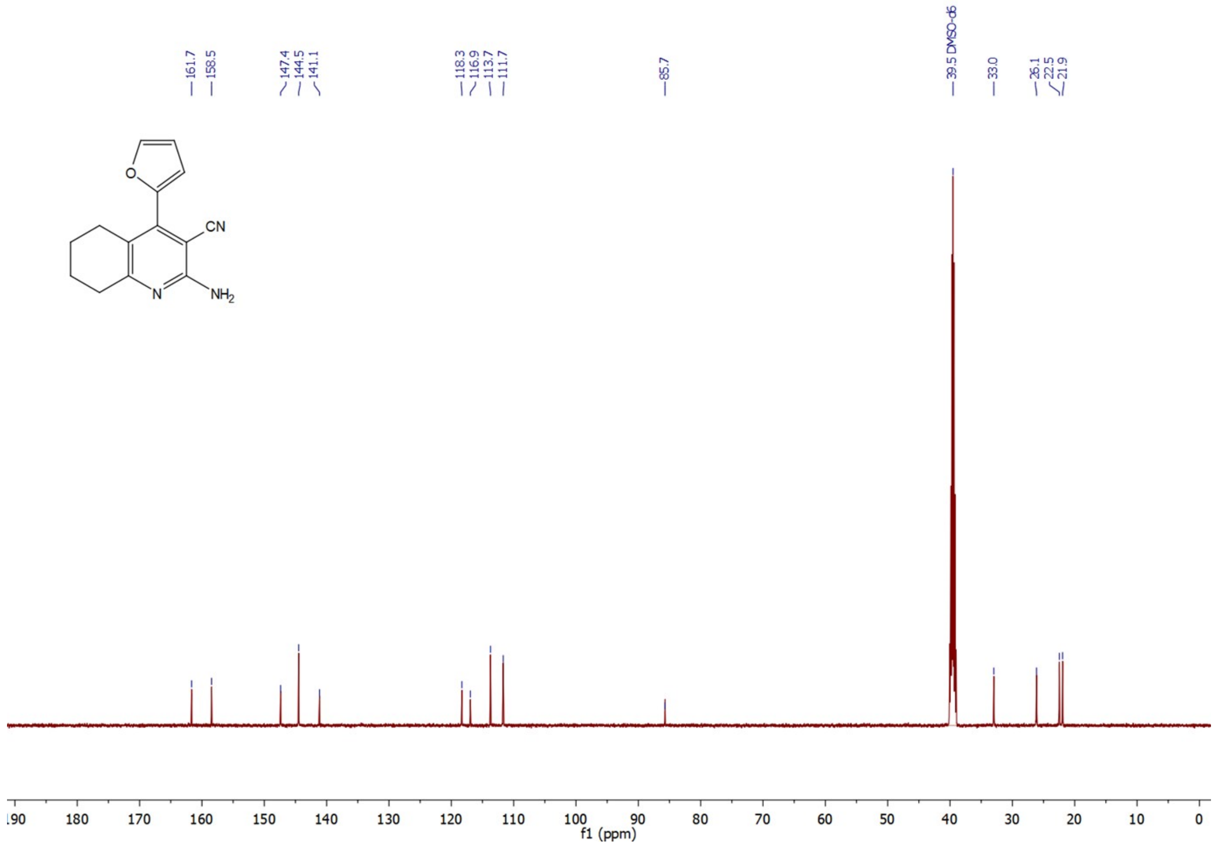



**Figure S2-9.2.** $^{13}$C–NMR spectrum of 9a

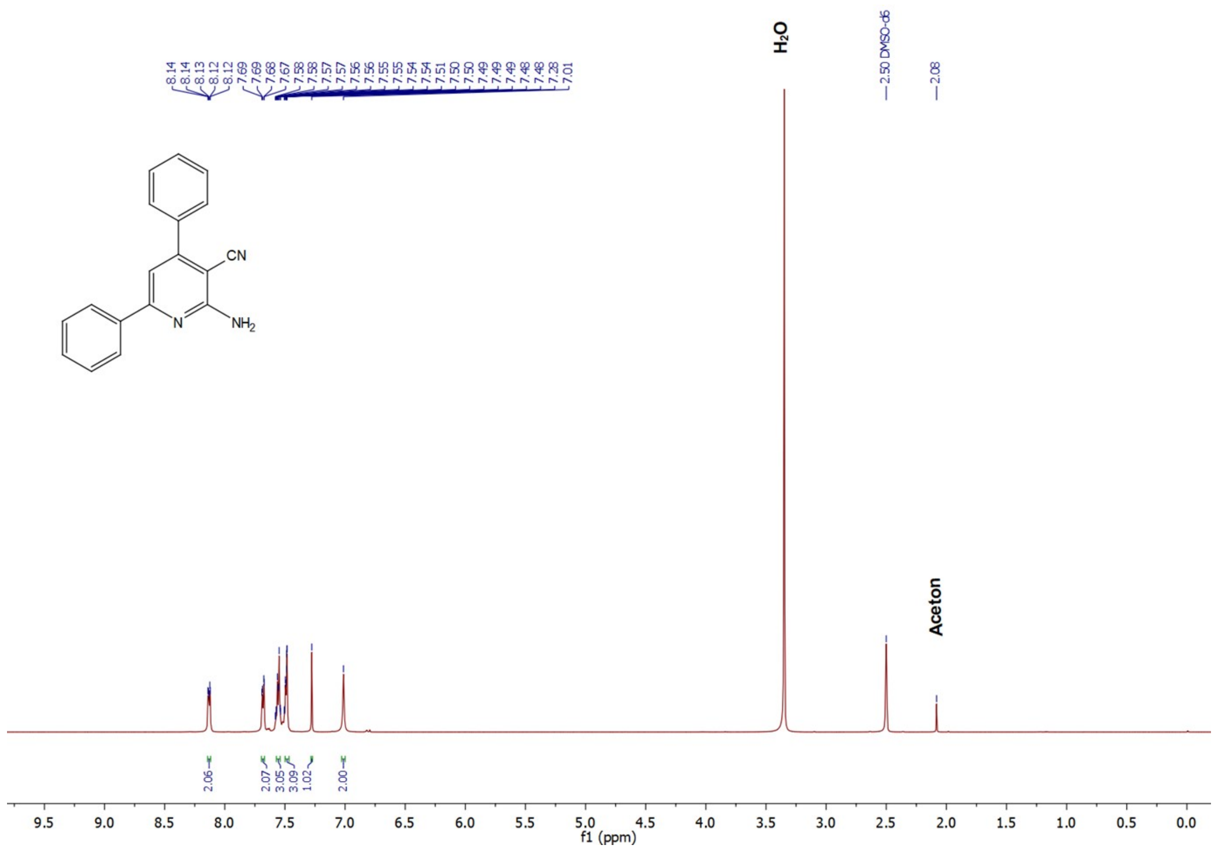



**Figure S2-10.1.** $^{1}$H–NMR spectrum of 10a

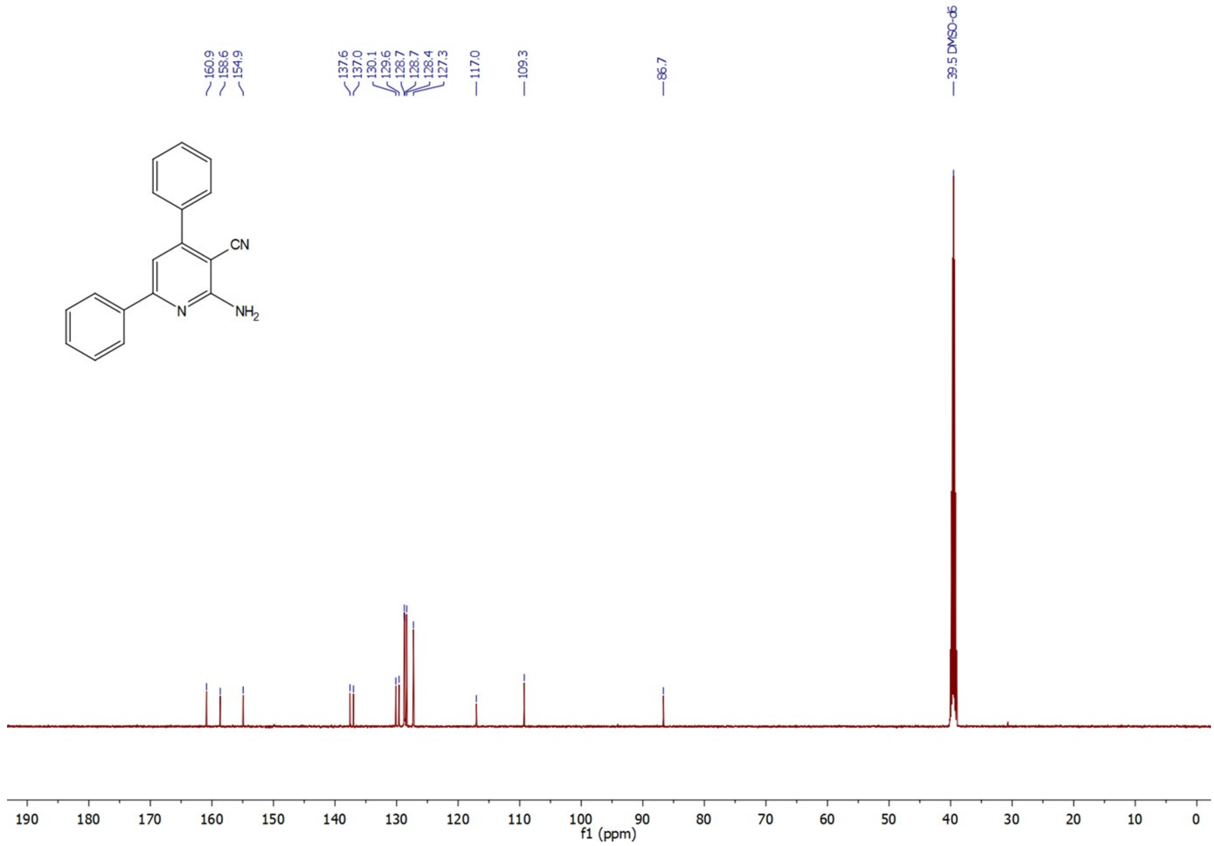


**Figure S2-10.2.** $^{13}$C–NMR spectrum of 10a

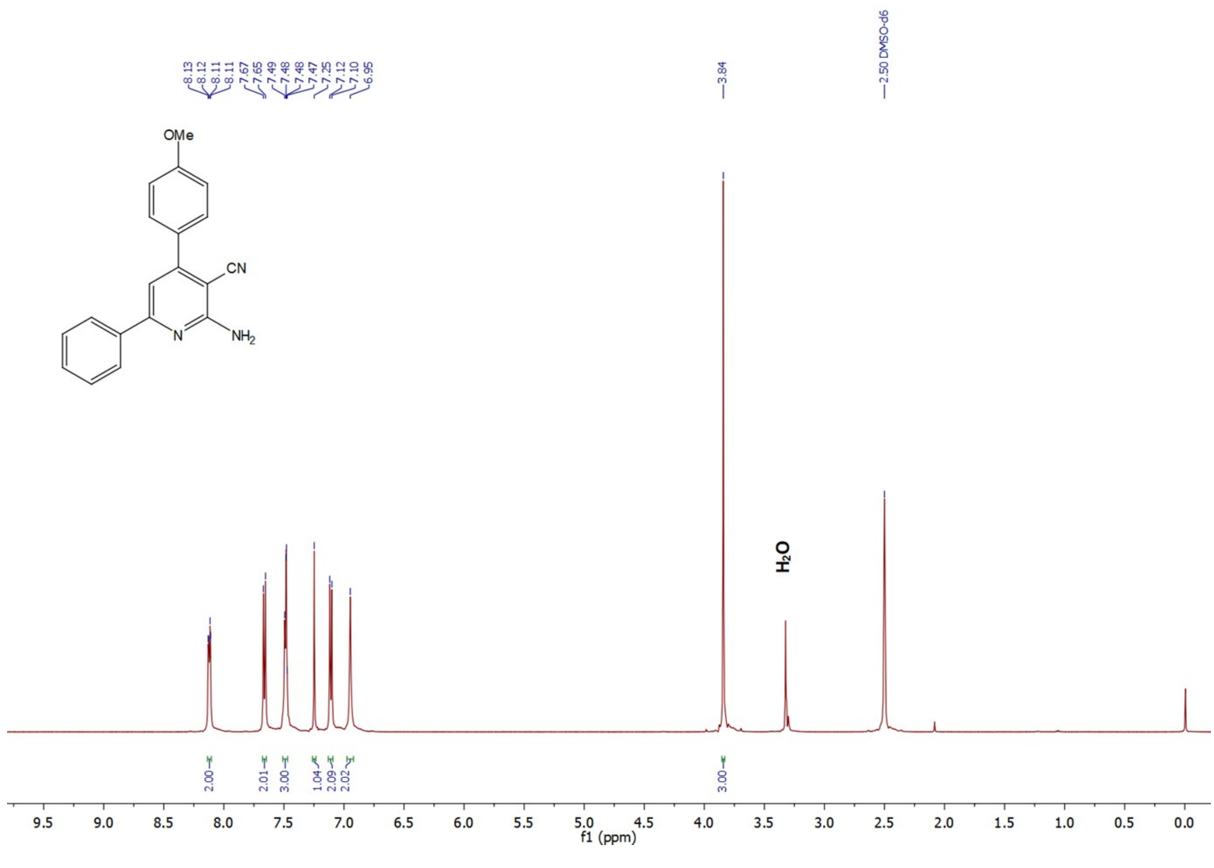


**Figure S2-11.1.** $^{1}$H–NMR spectrum of 11a

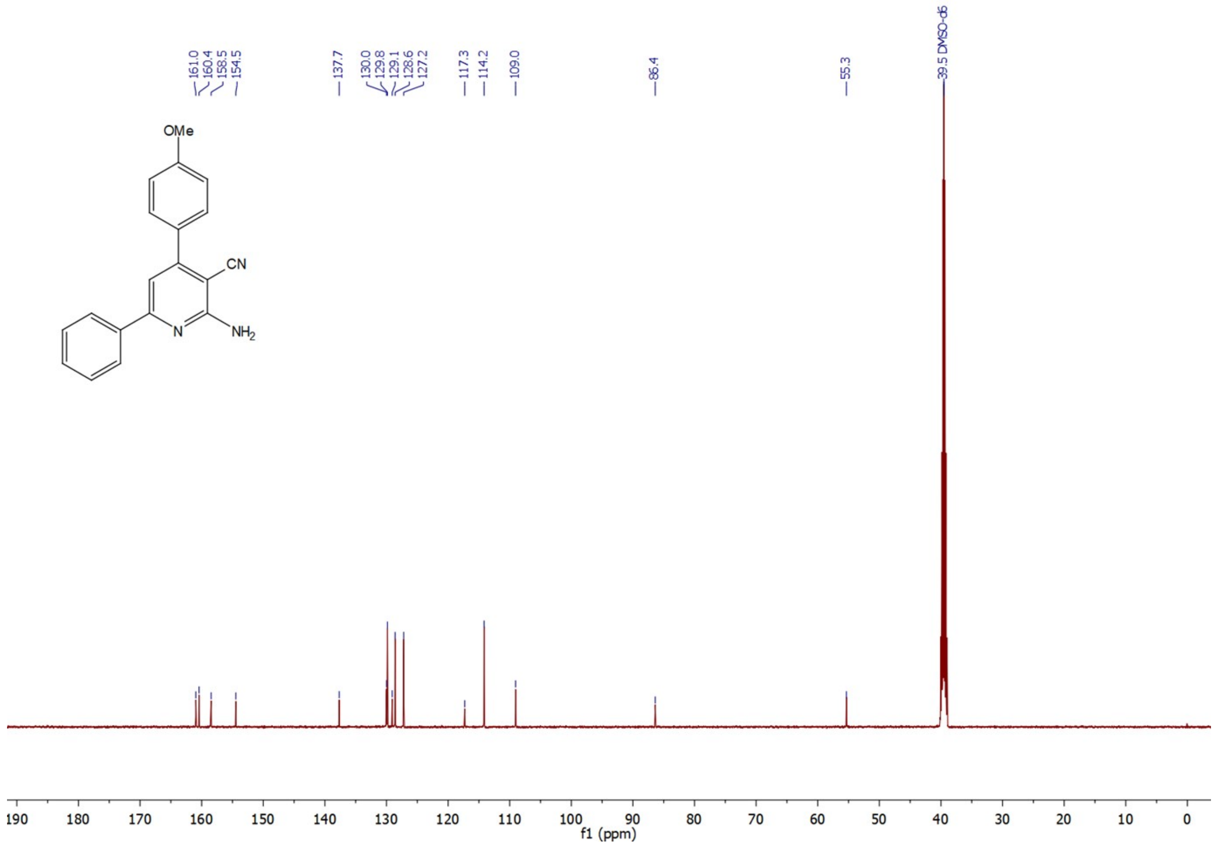


**Figure S2-11.2.** $^{13}C$–NMR spectrum of 11a

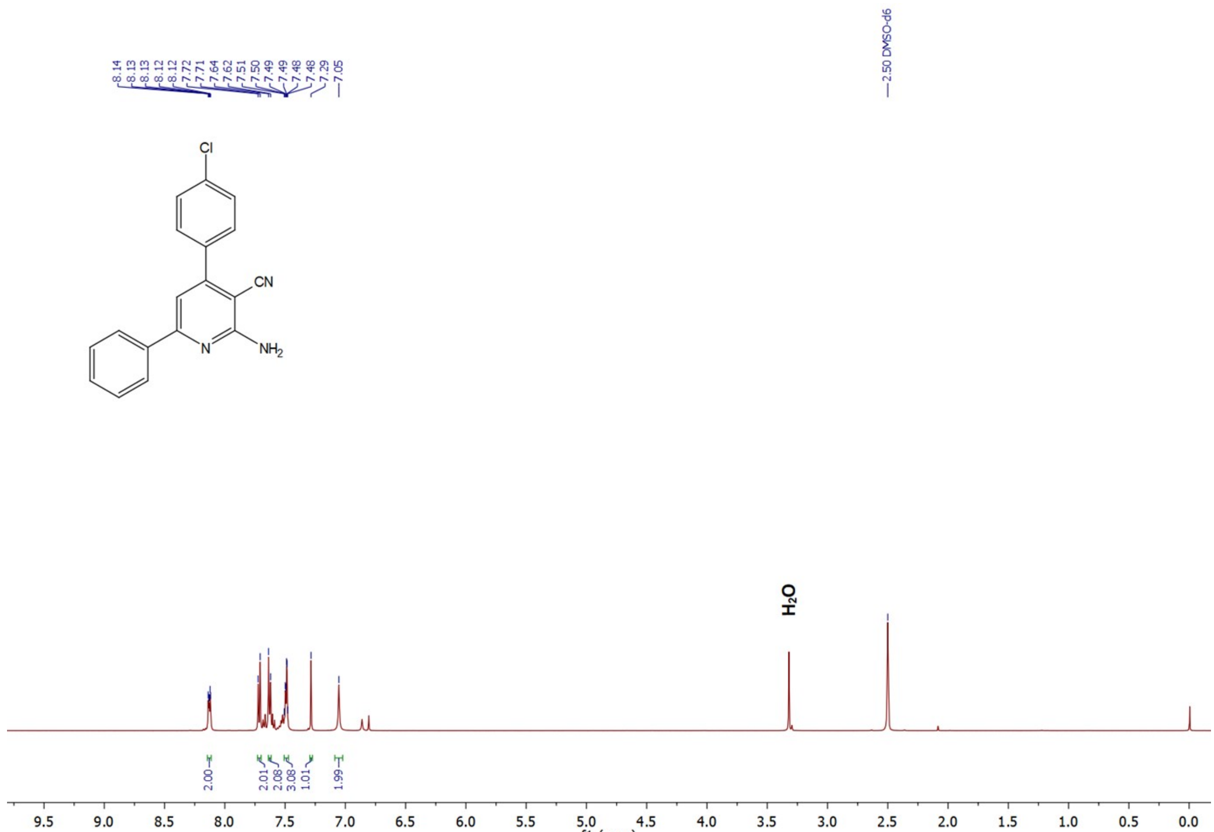


**Figure S2-12.1.** $^{1}H$–NMR spectrum of 12a

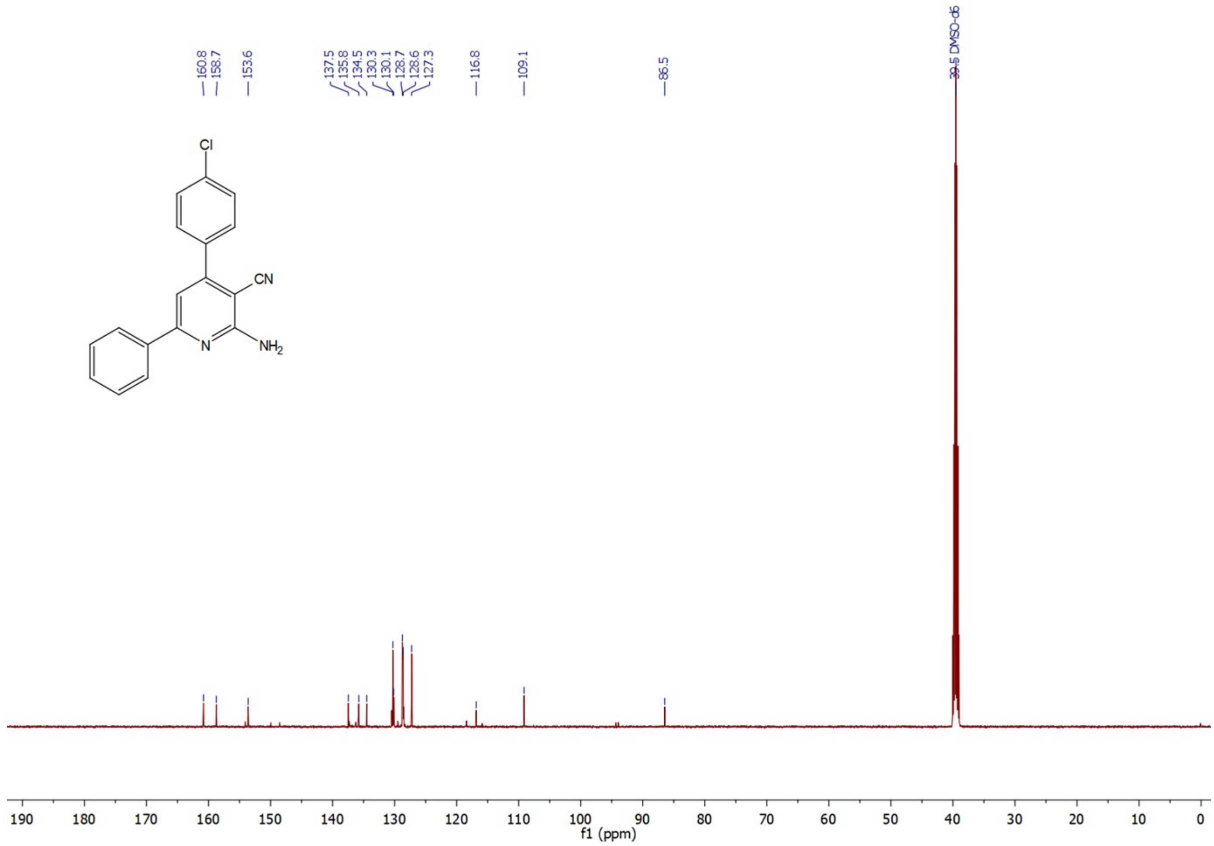


**Figure S2-12.2.** $^{13}C$–NMR spectrum of 12a

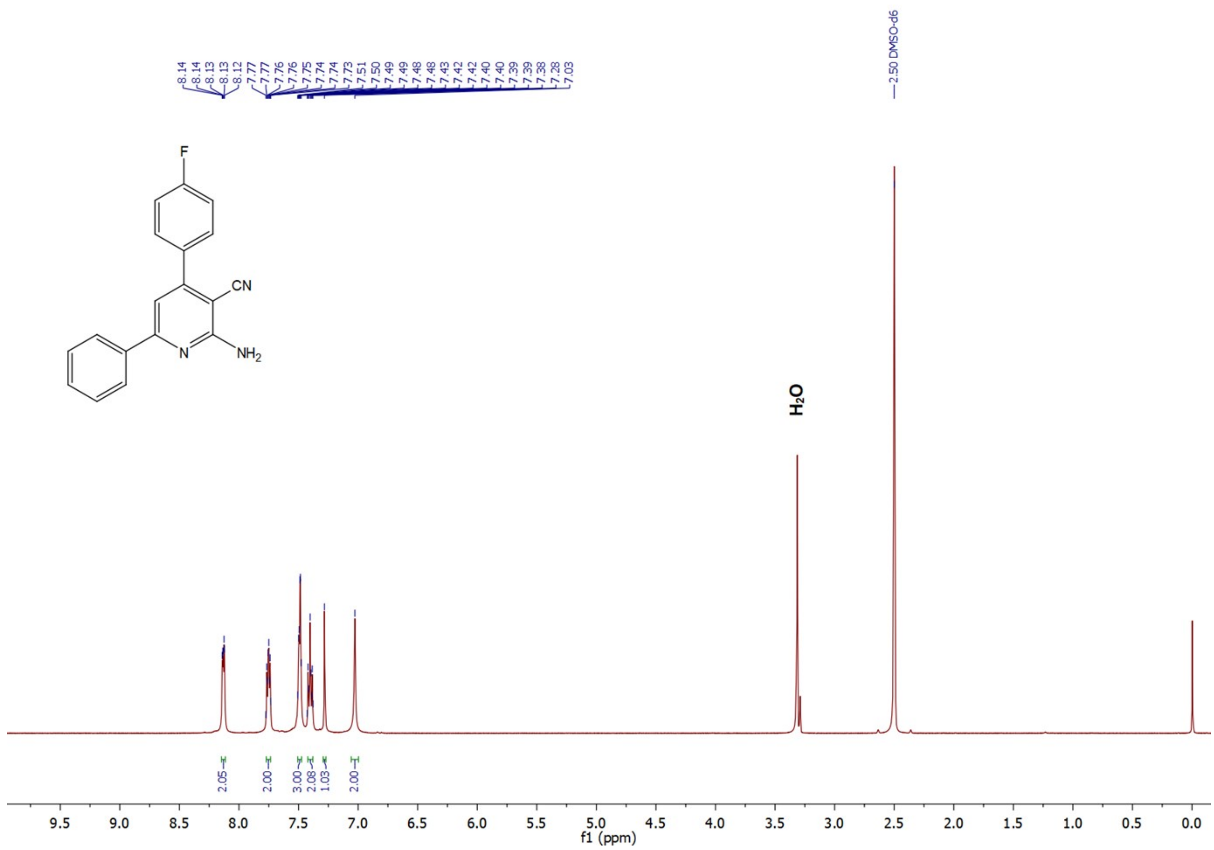


**Figure S2-13.1.** $^{1}H$–NMR spectrum of 13a

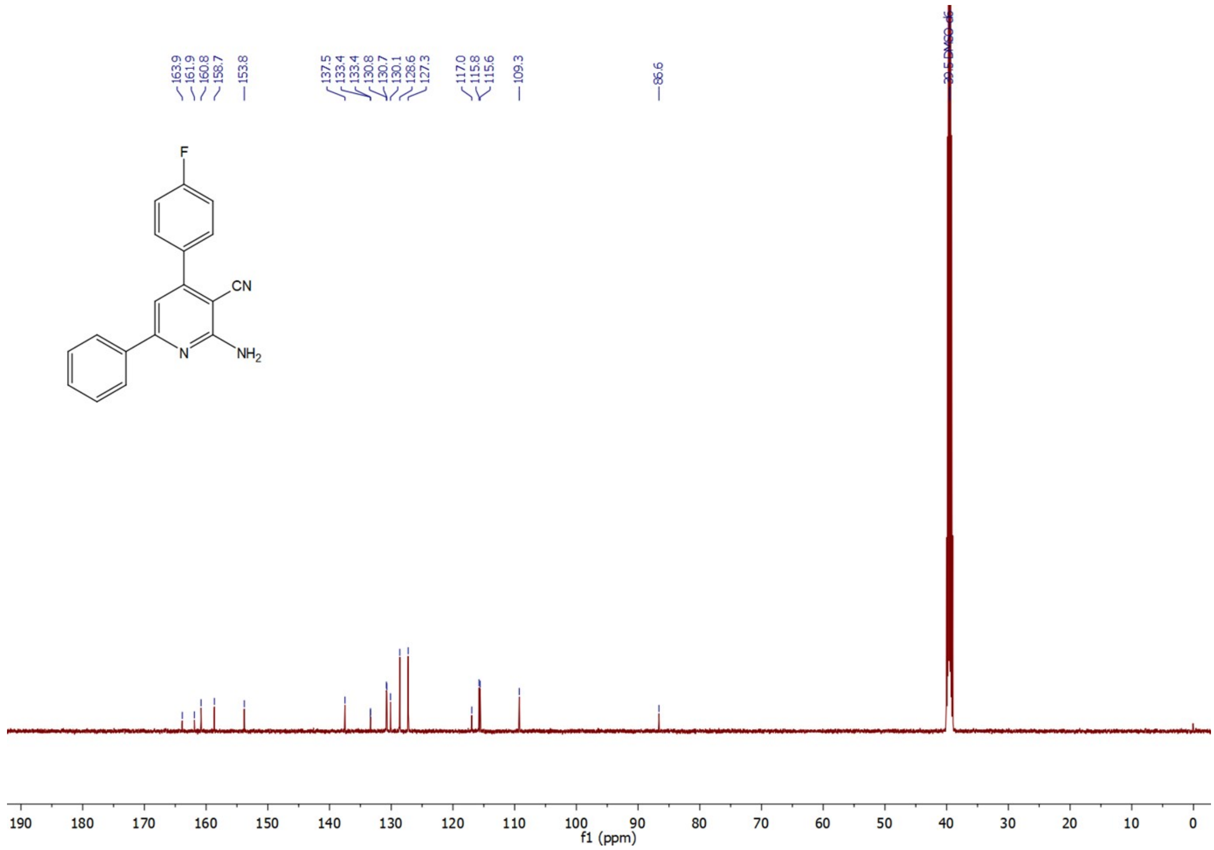


**Figure S2-13.2.** $^{13}$C–NMR spectrum of 13a

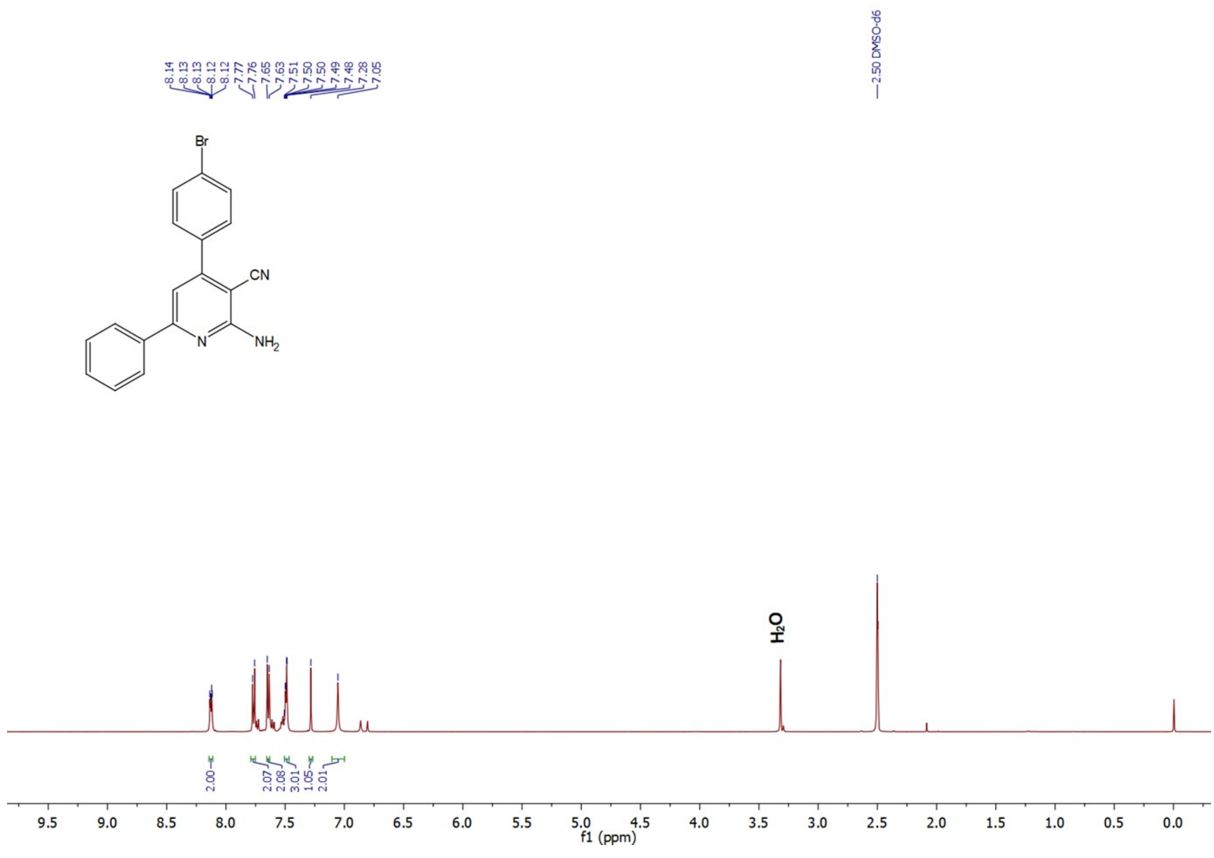


**Figure S2-14.1.** $^{1}$H–NMR spectrum of 14a

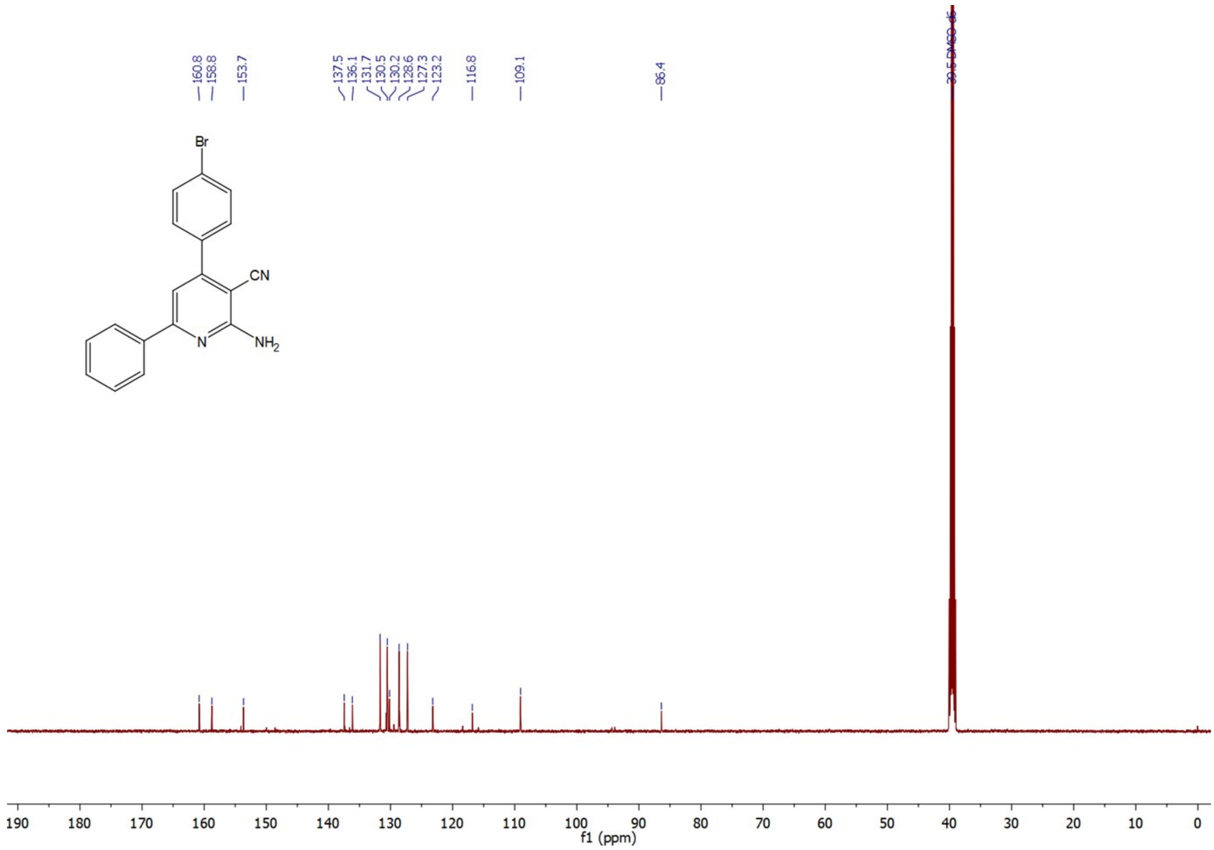



**Figure S2-14.2.** $^{13}$C–NMR spectrum of 14a

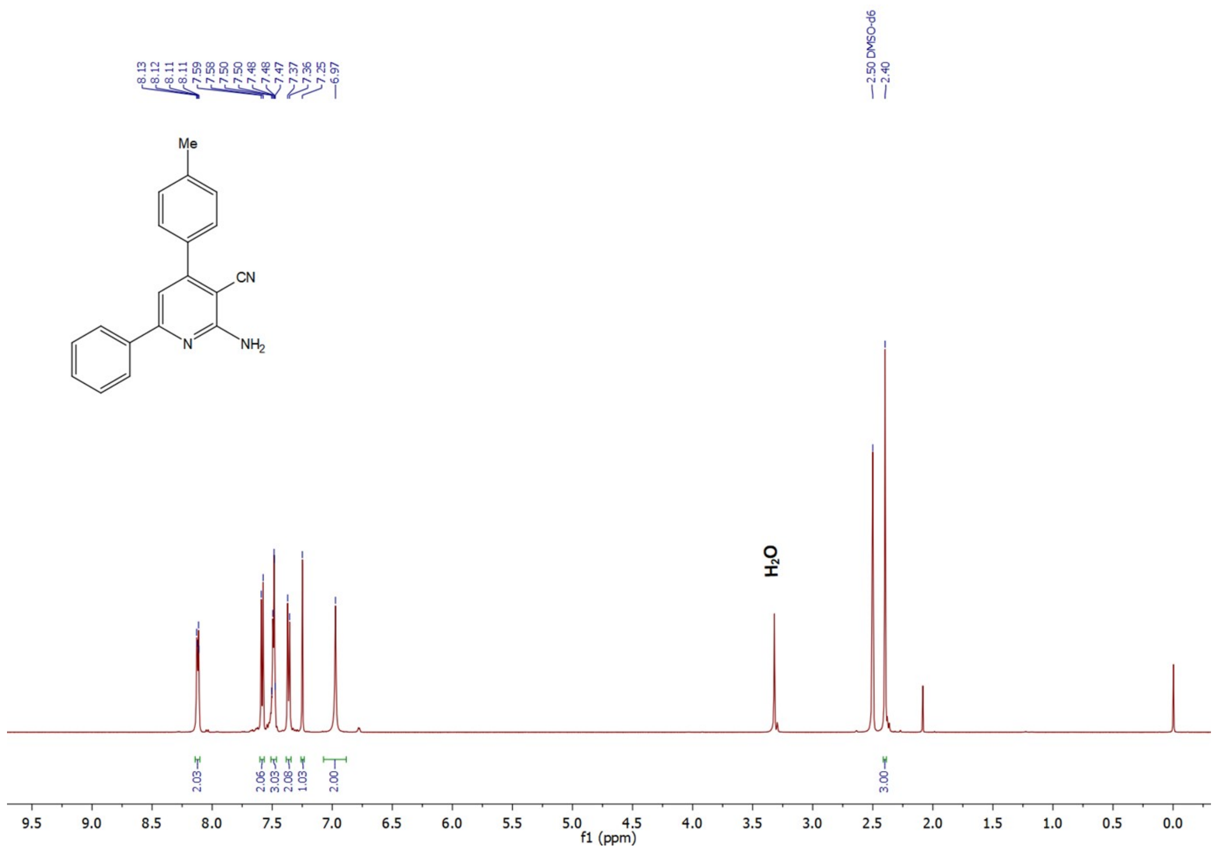



**Figure S2-15.1.** $^{1}$H–NMR spectrum of 15a

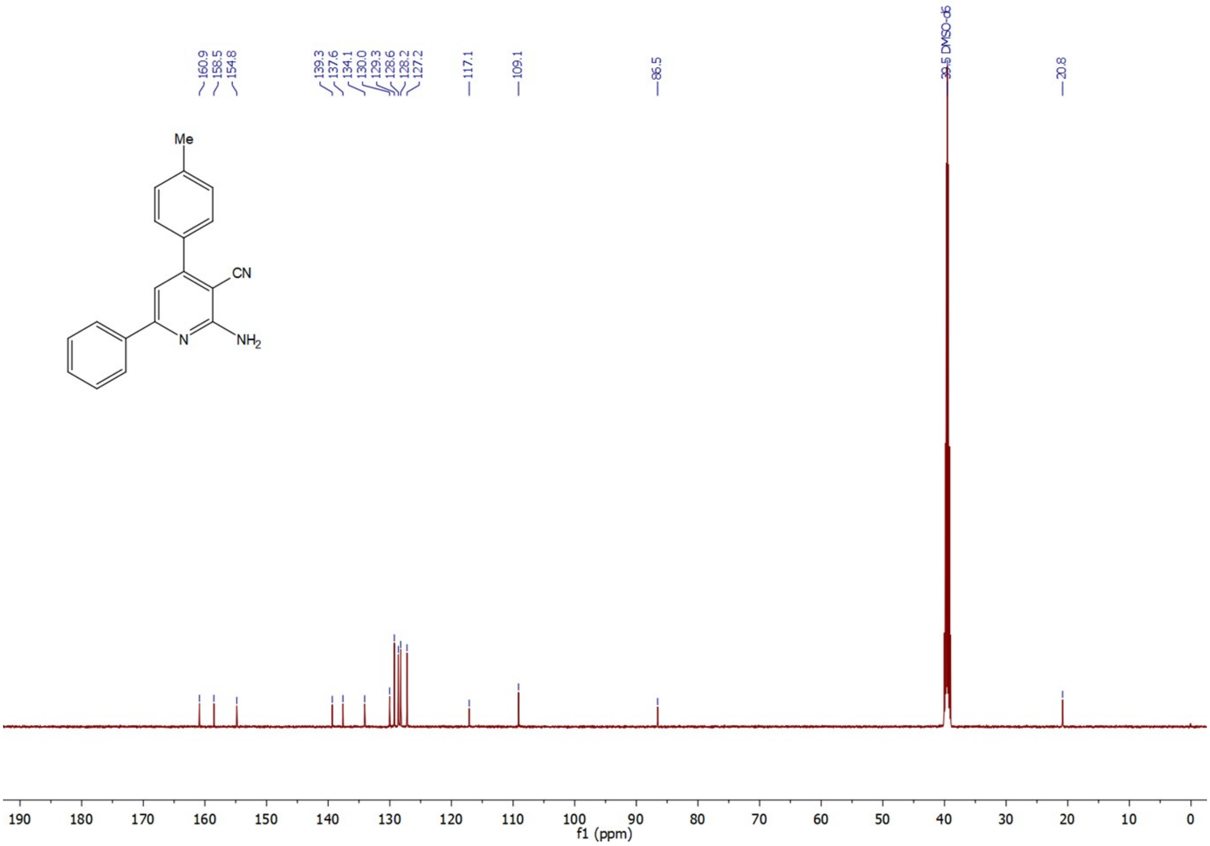



**Figure S2-15.2.** $^{13}$C–NMR spectrum of 15a

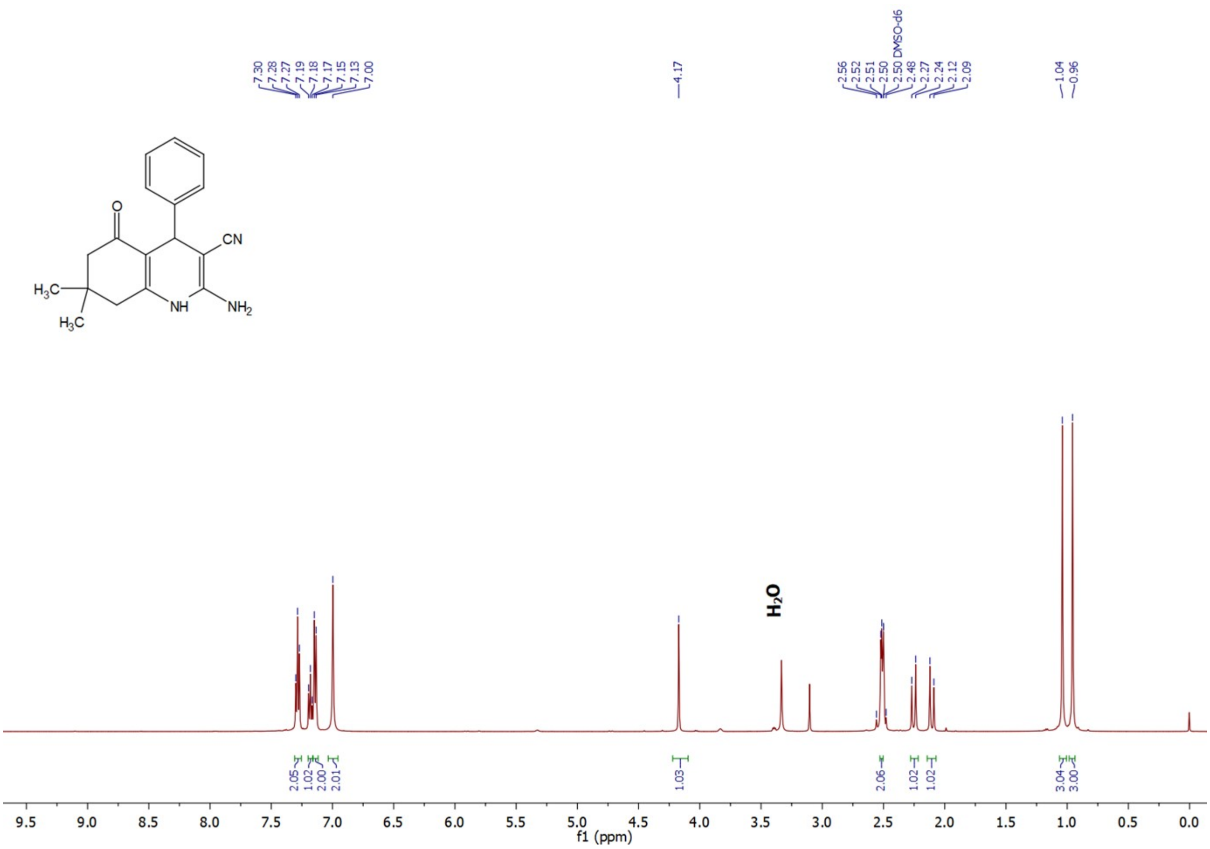



**Figure S2-16.1.** $^{1}$H–NMR spectrum of 16b

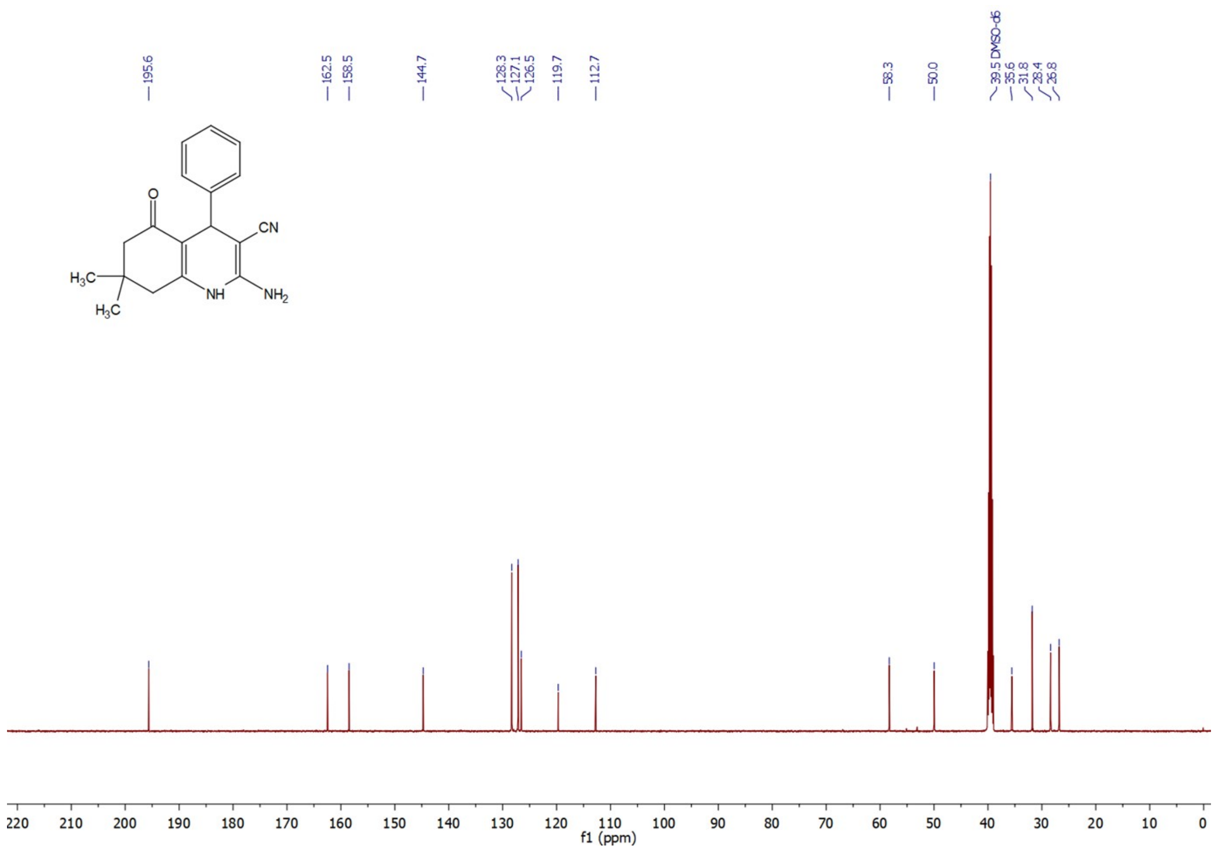


**Figure S2-16.2.** $^{13}$C–NMR spectrum of 16b

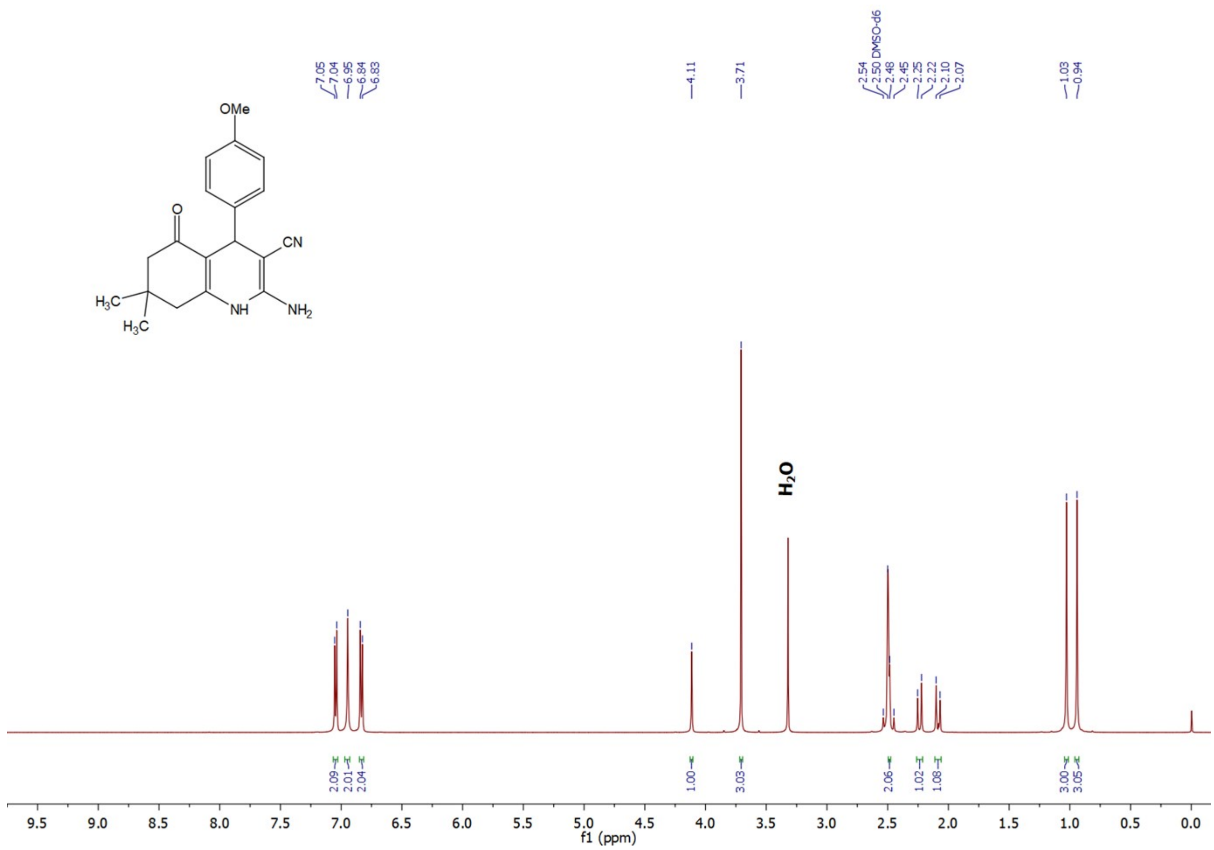


**Figure S2-17.1.** $^{1}$H–NMR spectrum of 17b

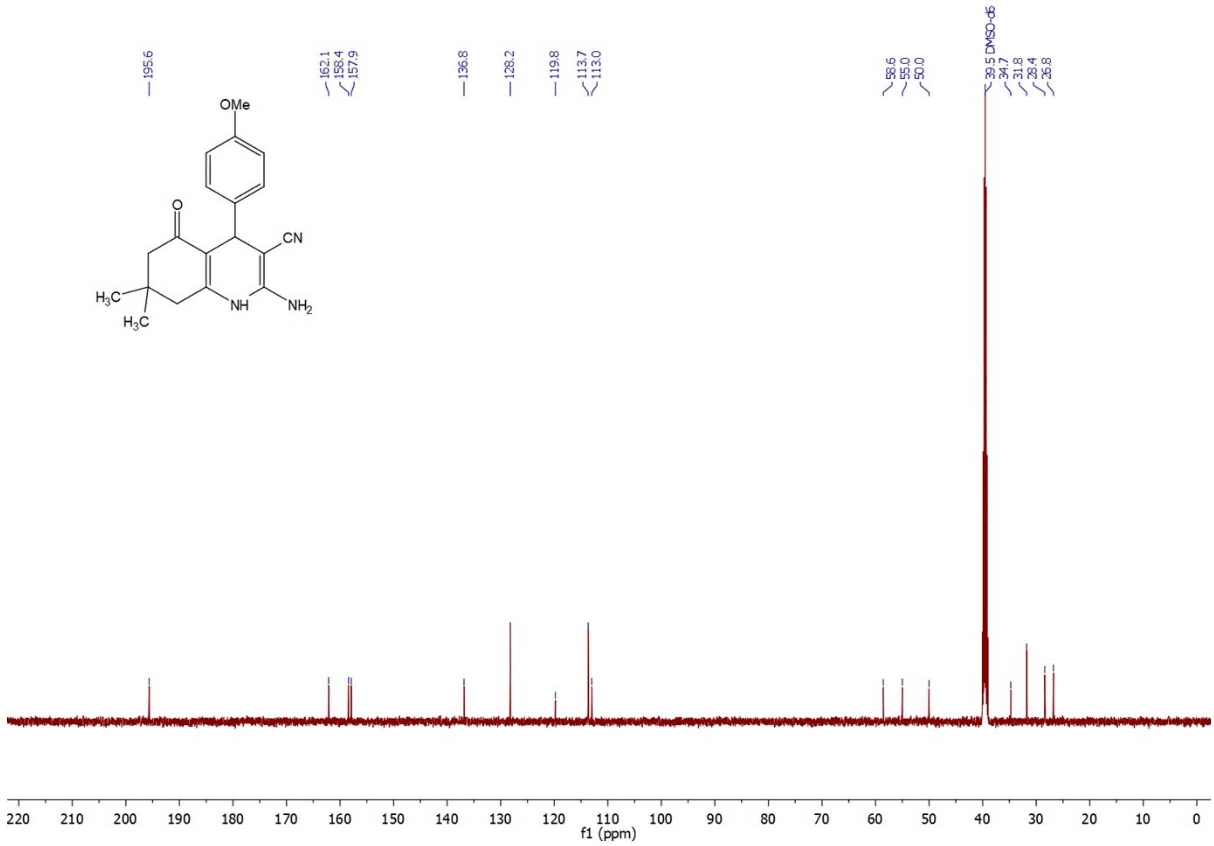


**Figure S2-17.2.** $^{13}C$–NMR spectrum of 17b

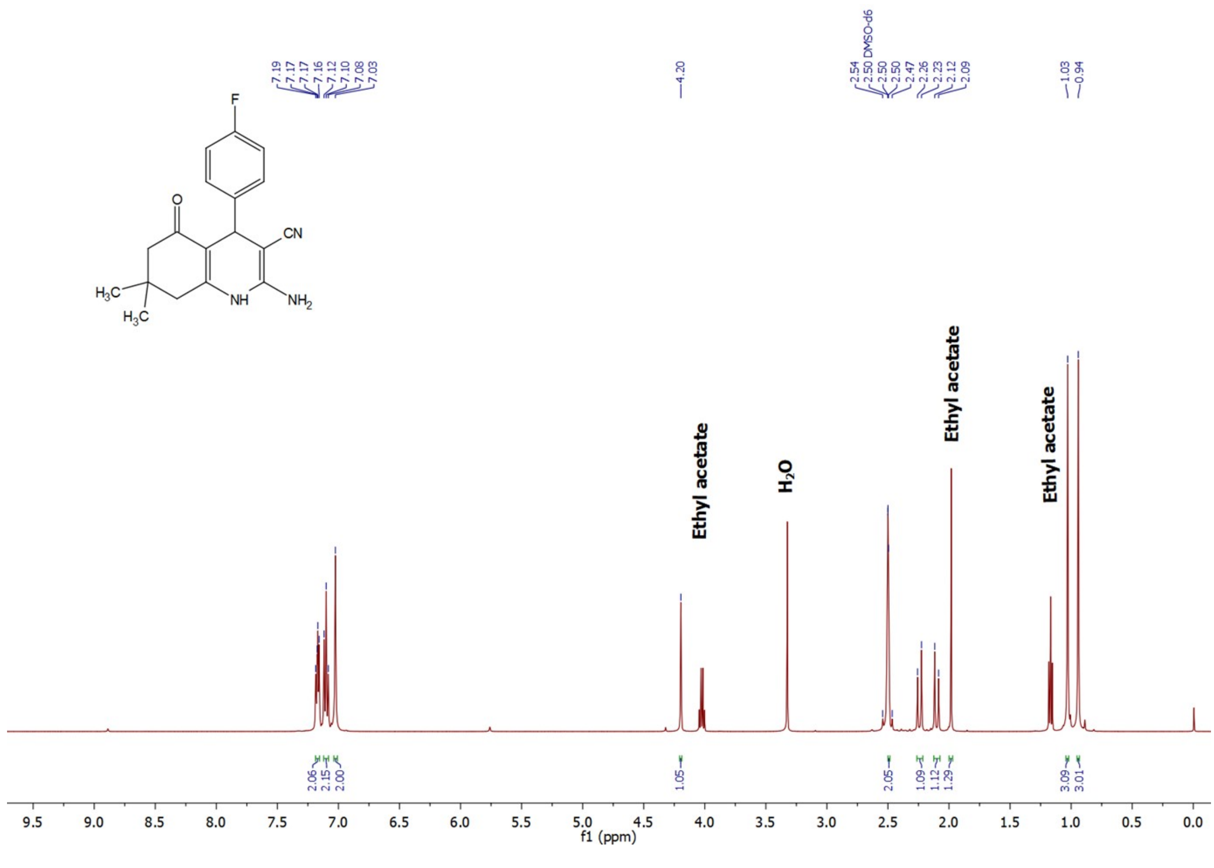



**Figure S2-18.1.** $^{1}H$–NMR spectrum of 18b

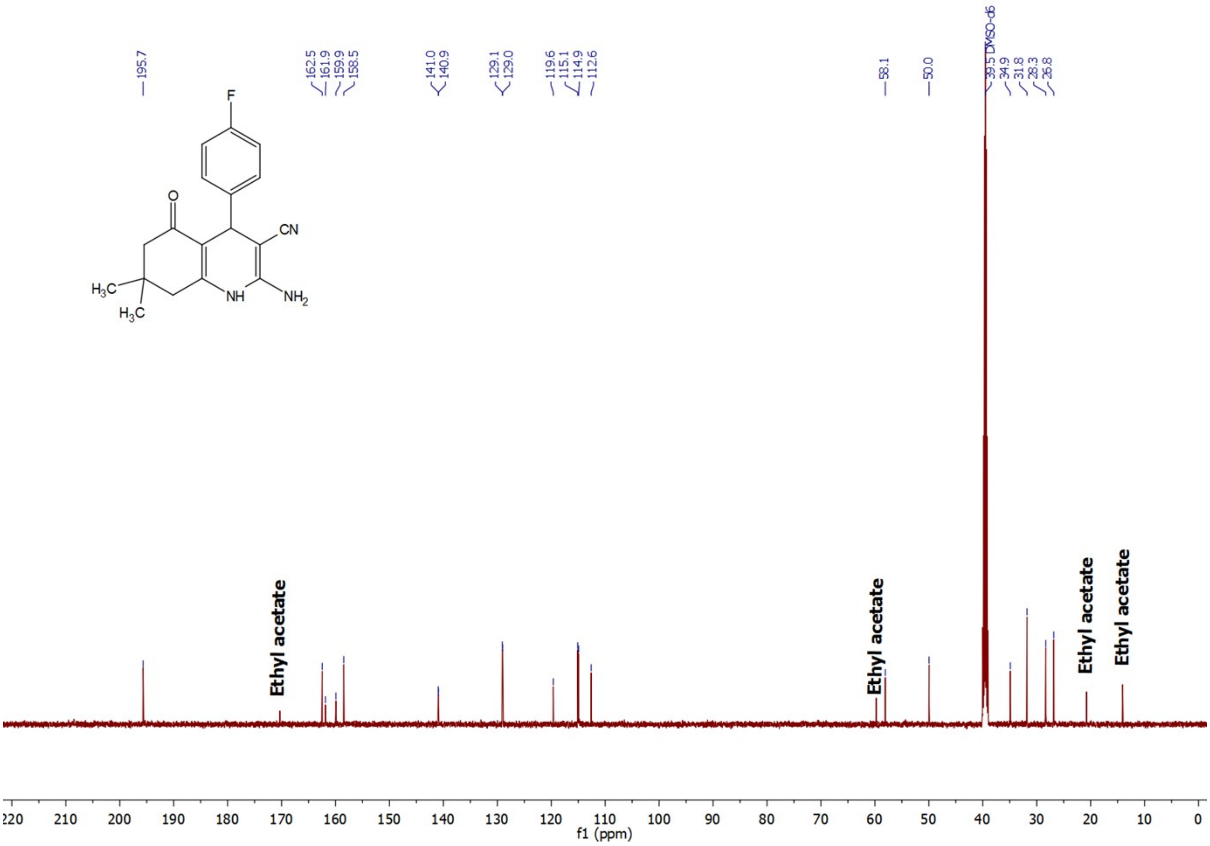



**Figure S2-18.2.** $^{13}C$–NMR spectrum of 18b

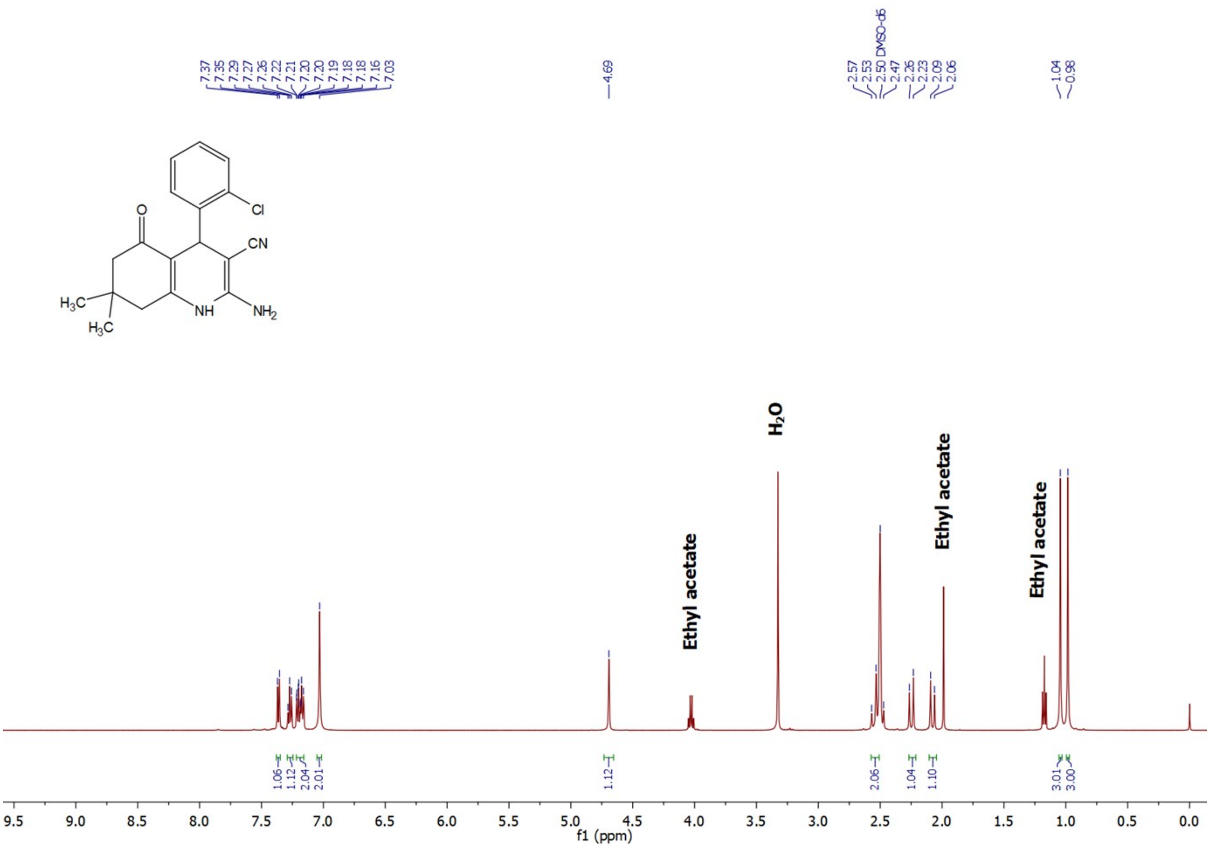



**Figure S2-19.1.** $^{1}H$–NMR spectrum of 19b

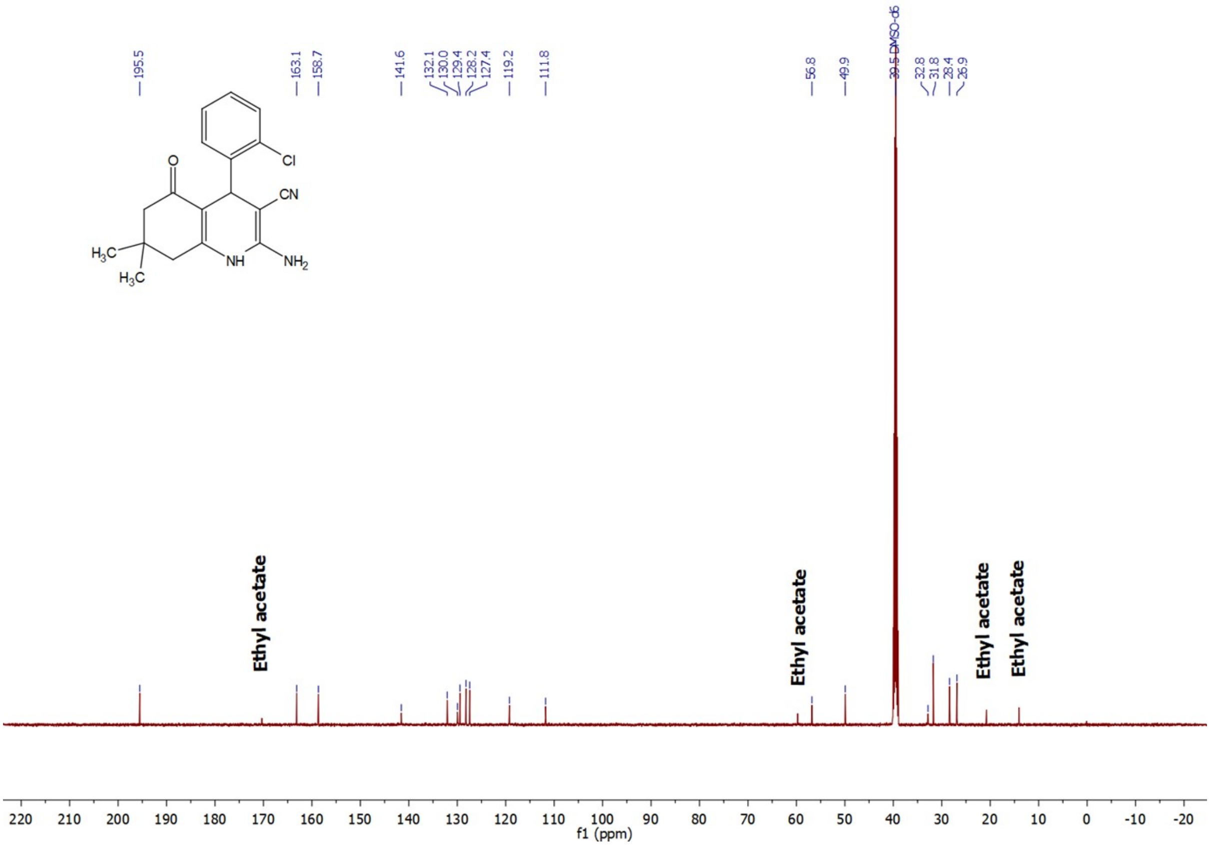



**Figure S2-19.2.** $^{13}C$–NMR spectrum of 19b

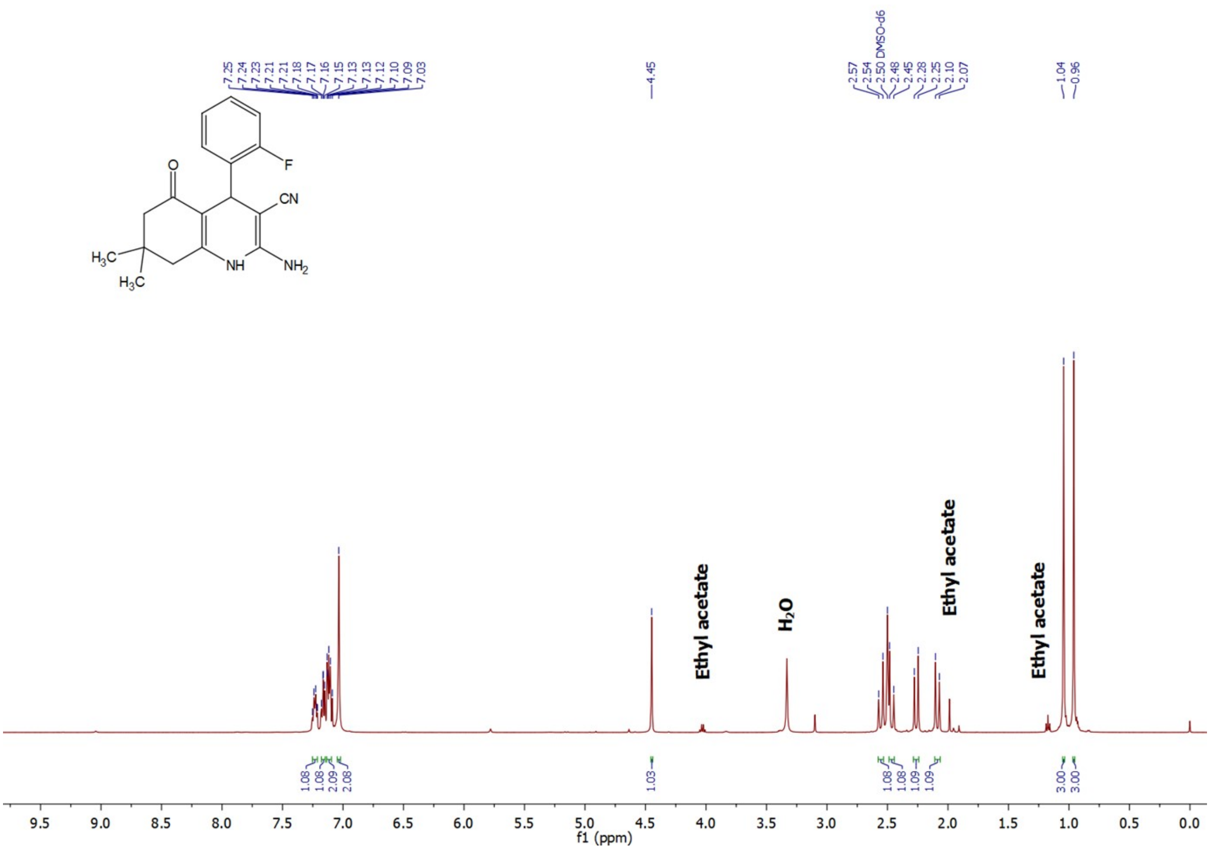



**Figure S2-20.1.** $^{1}H$–NMR spectrum of 20b

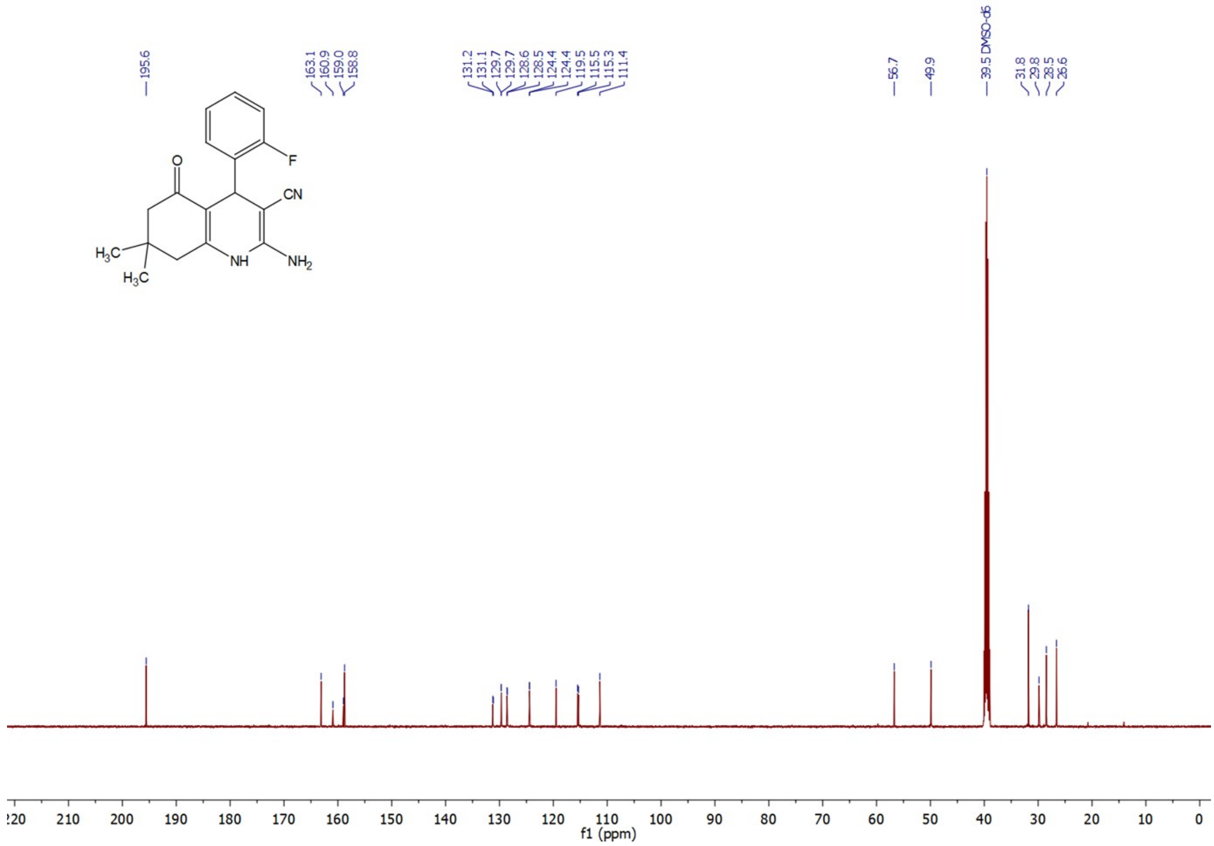



**Figure S2-20.2.** $^{13}$C–NMR spectrum of 20b

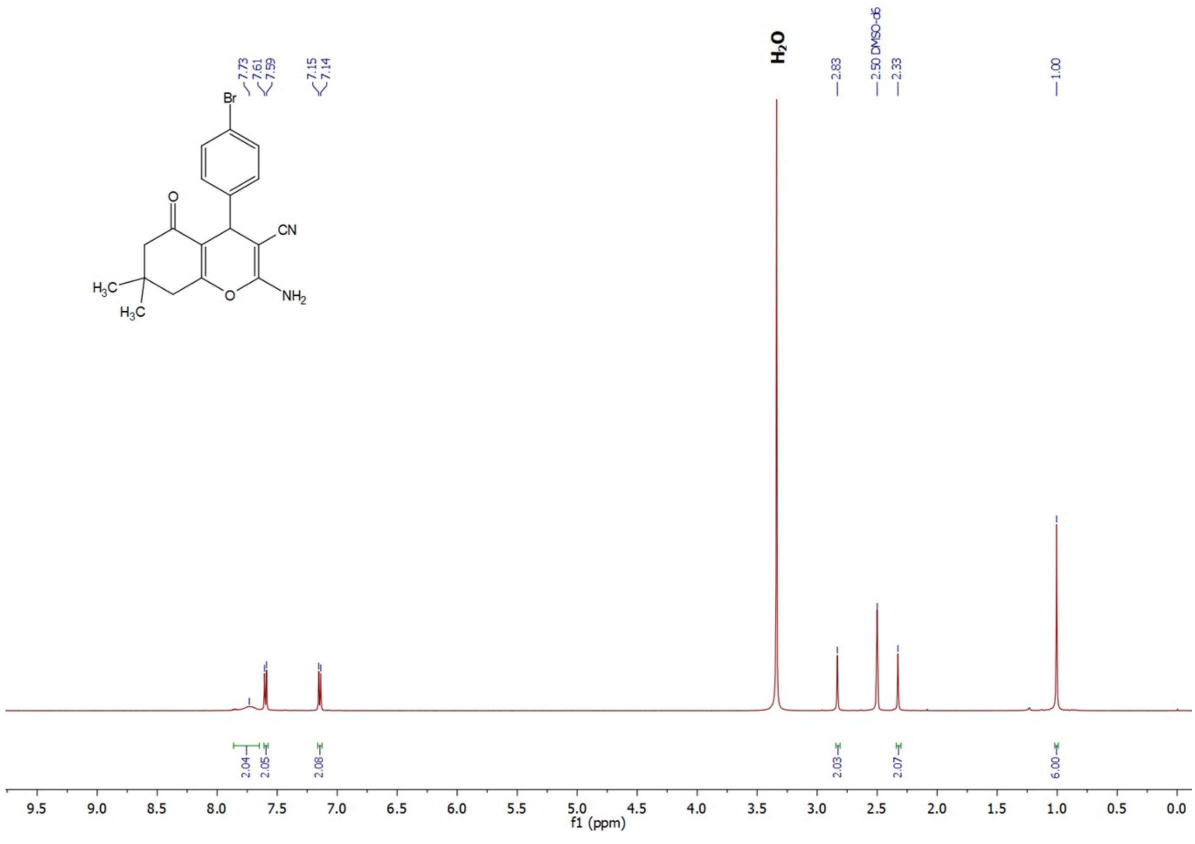



**Figure S2-21.1.** $^{1}$H–NMR spectrum of 21b

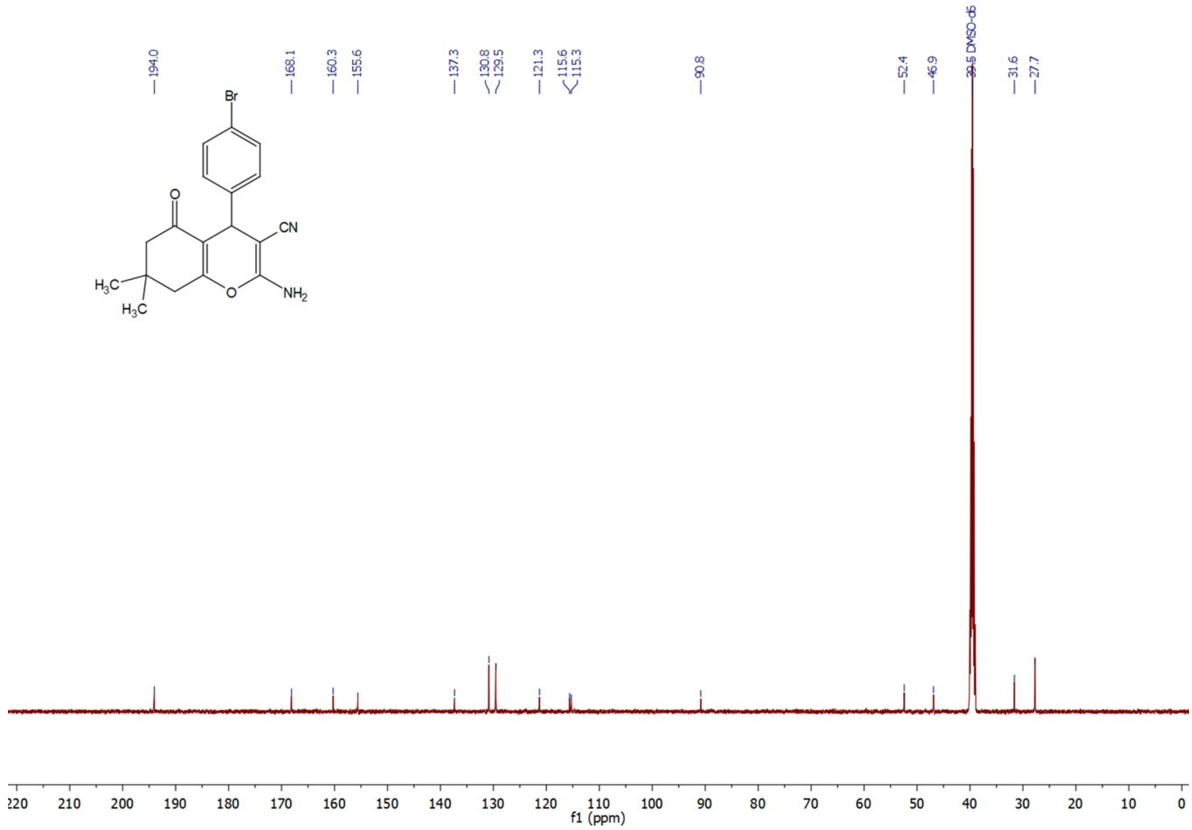



**Figure S2-21.2.** $^{13}C$–NMR spectrum of 21b

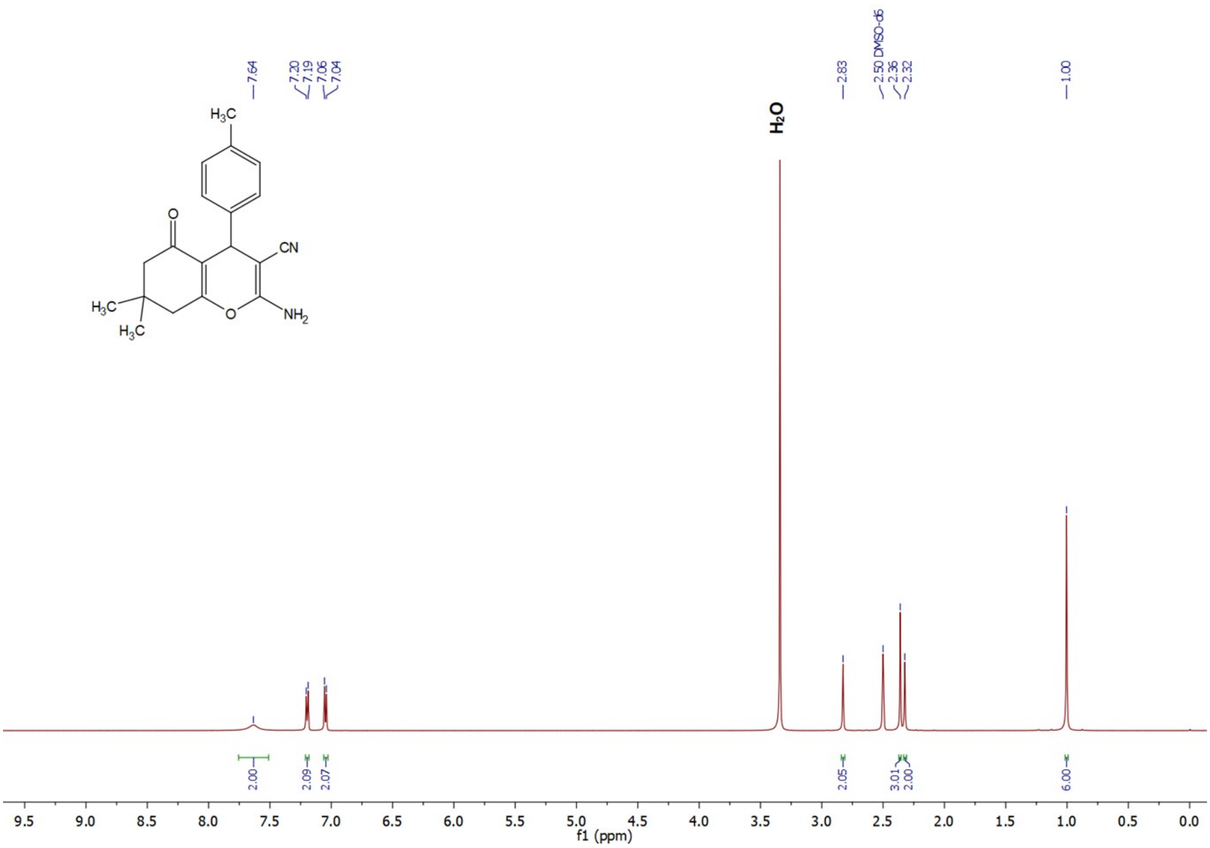



**Figure S2-22.1.** $^{1}H$–NMR spectrum of 22b

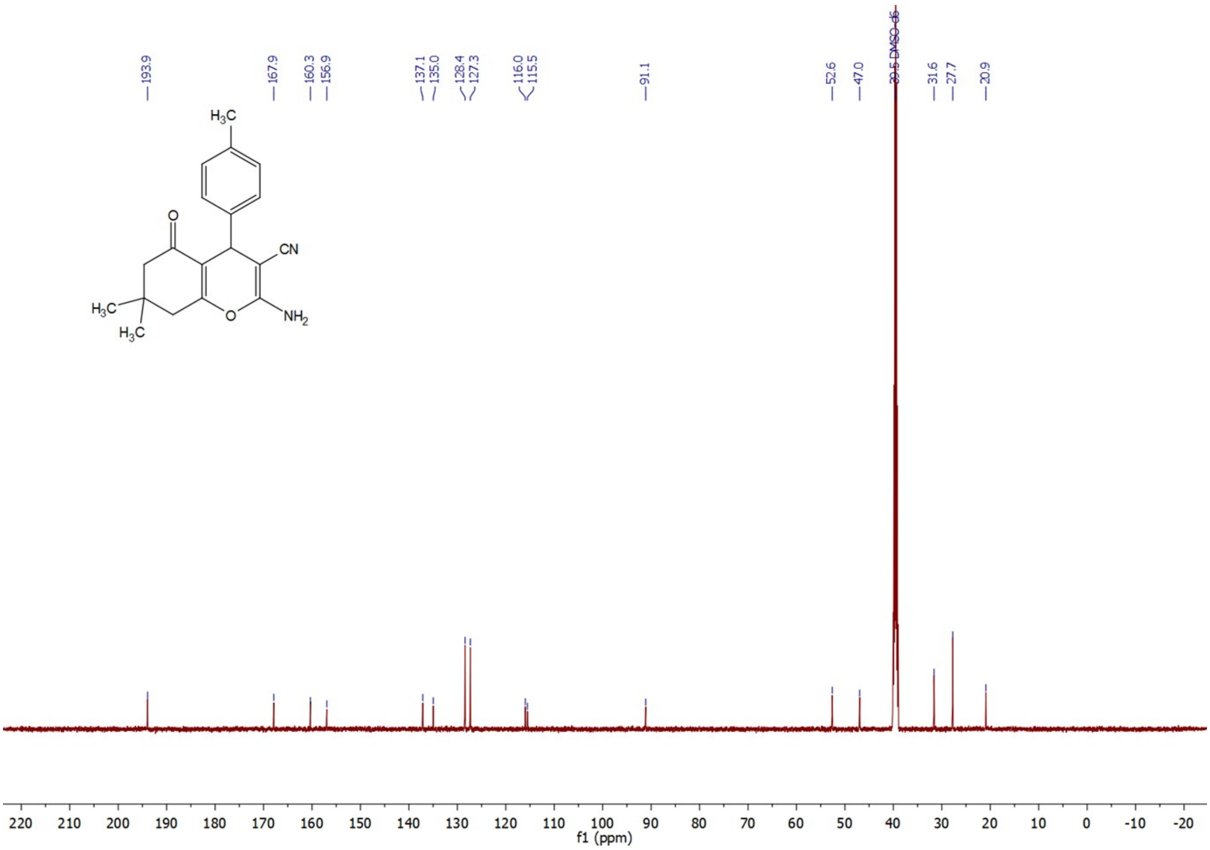



**Figure S2-22.2.** $^{13}C$–NMR spectrum of 22b

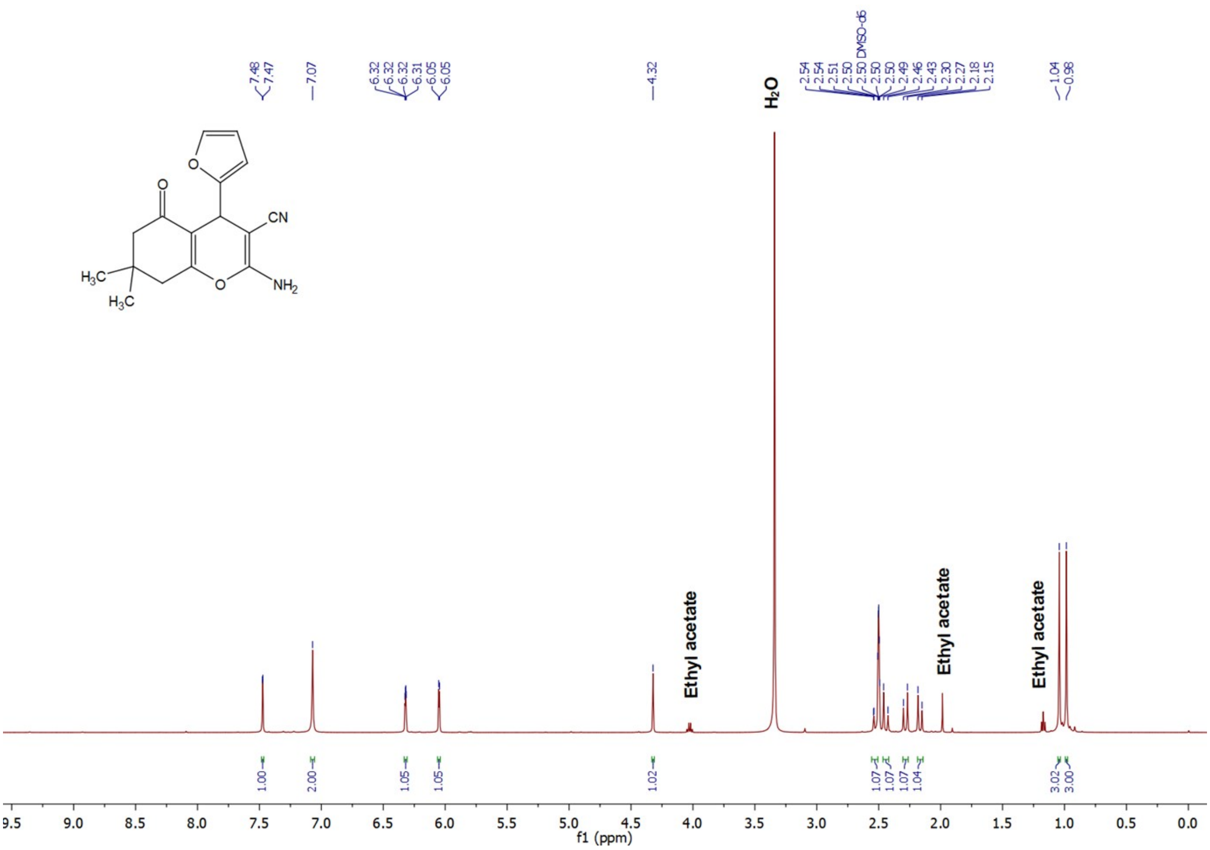



**Figure S2-23.1.** $^{1}H$–NMR spectrum of 23b

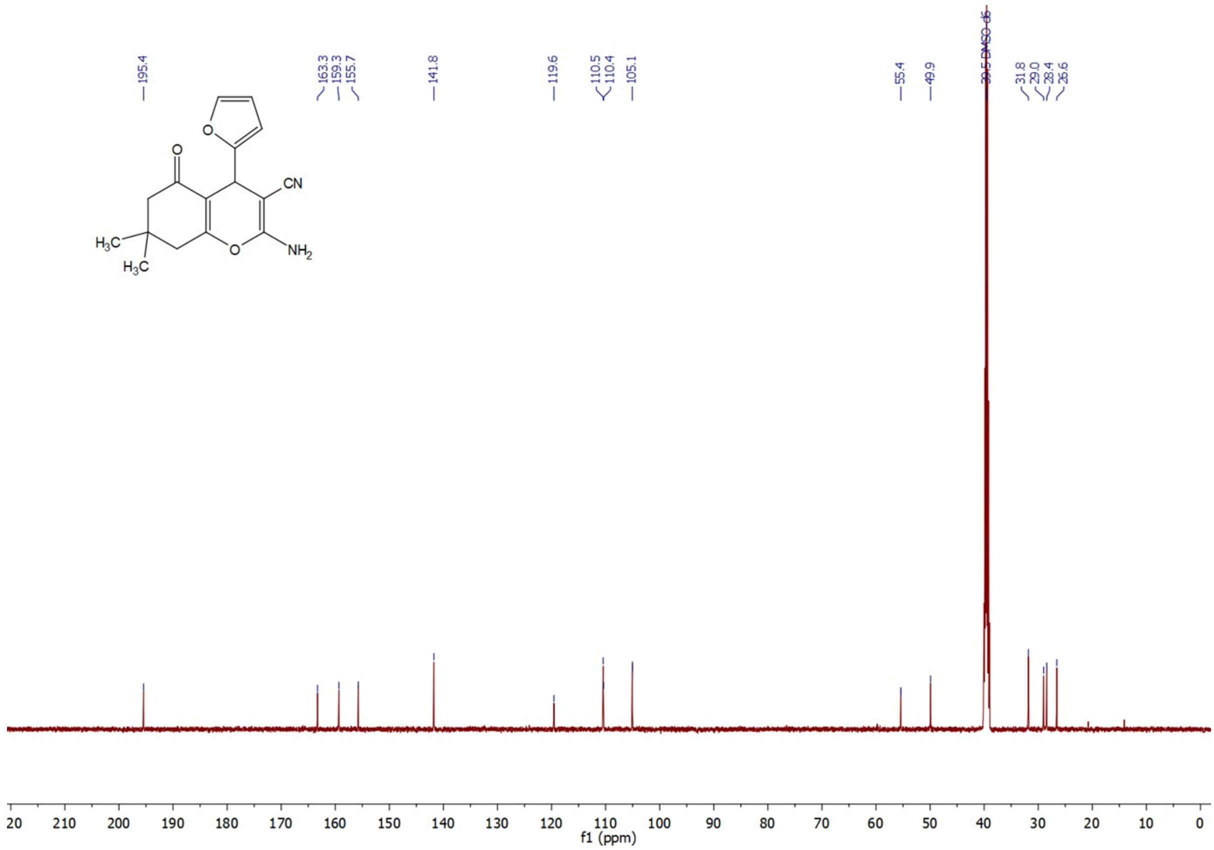


**Figure S2-23.2.** $^{13}C$–NMR spectrum of 23b

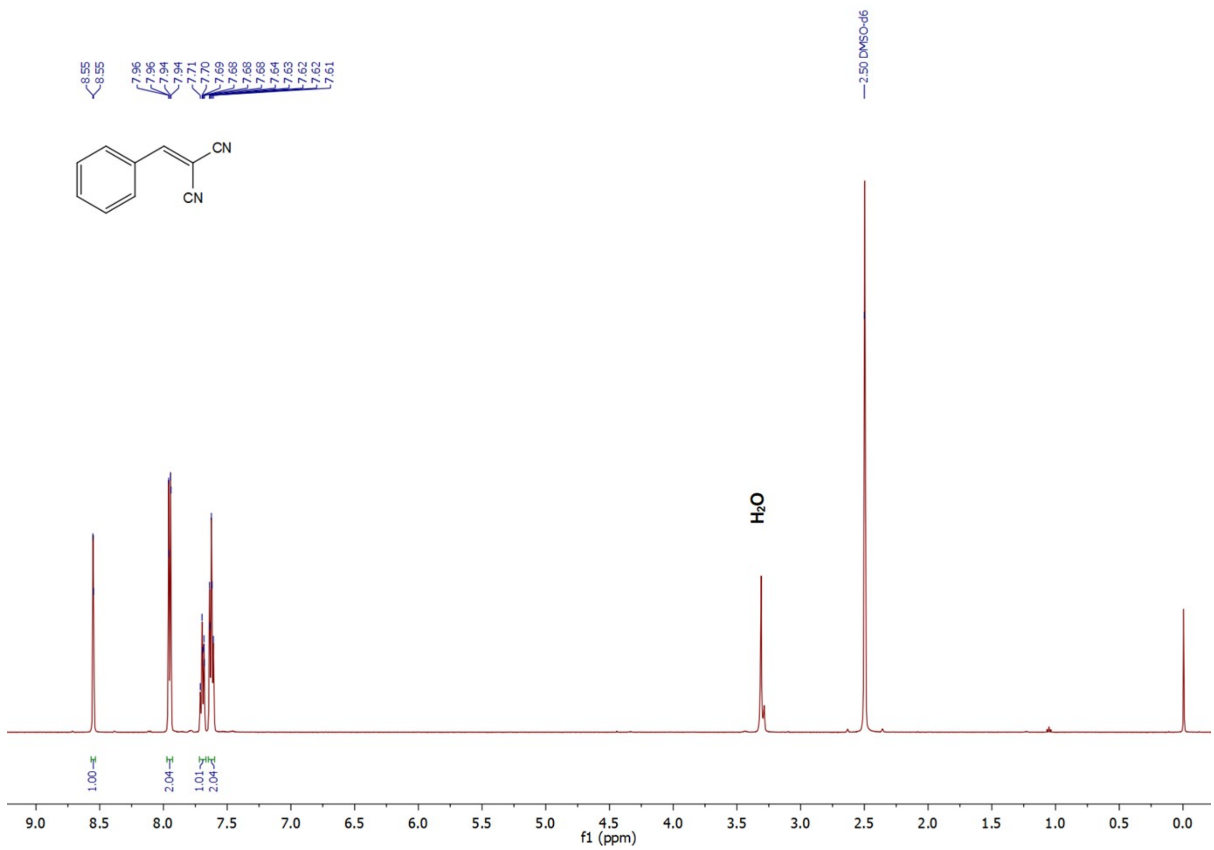


**Figure S2-24.1.** $^{1}H$–NMR spectrum of 2-benzylidenemalononitrile

**Section S4. References**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