Supporting Information

Visible light-activated photocatalyst- and additive-free multi-component reaction driven by cyclopropylamine-based EDA complex in water

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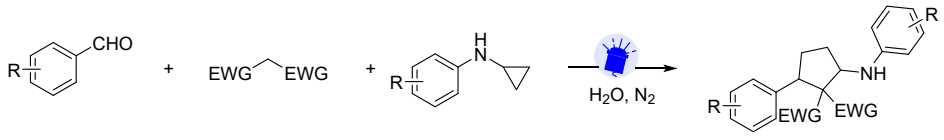
Table of Contents

1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. For reactions that require heating, the heat source is heating mantle. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AMX 500 (500 MHz for ^{1}H, 126 MHz for ^{13}C and 470 MHz for ^{19}F NMR) spectrometer at 25 ^{o}C. The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $CDCl_3$ (δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C NMR). Multiplicities were afforded as: broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of a doublet, td = triplet of a doublet, qd = quartet ofdoublet, ddd = doublet of a doublet of a doublet, m = multiplet. The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. Melting points were determined on a microscopic melting point apparatus and were uncorrected.

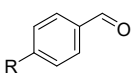
2. General Procedure

2.1 List of the Starting Materials.

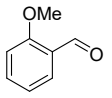


1 2 3 4

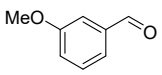
1) Aldehyde:



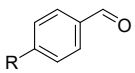
1a, R = H,
1b, R = F,
1c, R = Cl,
1d, R = Br,
1e, R = CN,
1f, R = CF_3,
1g, R = CH_3,
1h, R = *t*-Bu,
1i, R = Ph,
1j, R = OMe,



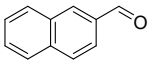
1k



1l



1m, R = COOMe,
1n, R = CH_2COOMe
1o, R = CHO
1p, R = C≡CH



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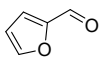

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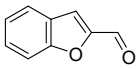
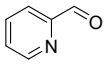
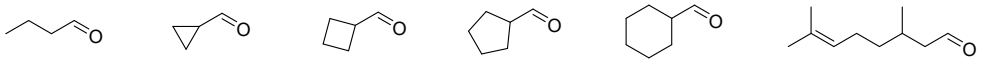


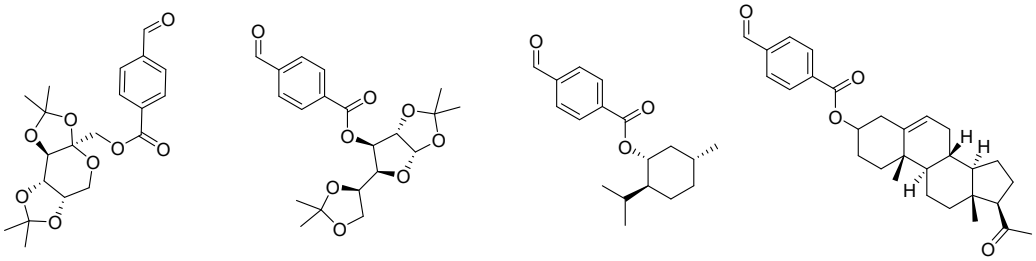
1s



1t

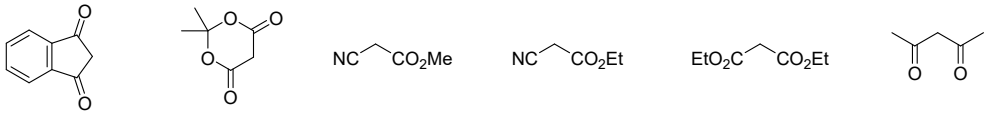


1u **1v** **1w** **1x** **1y** **1z**



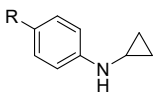
1ba **1ca** **1da** **1ea**

2) Active methylene:

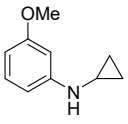


2aa **2ab** **2ac** **2ad** **2ae** **2af**

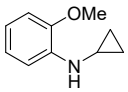
3) Amines:



3ag: R = Cl
3ah: R = CF_3
3ai: R = Me
3aj: R = Et
3ak: R = Ph
3al: R = OMe



3am



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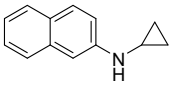

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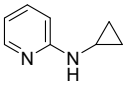
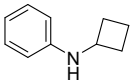
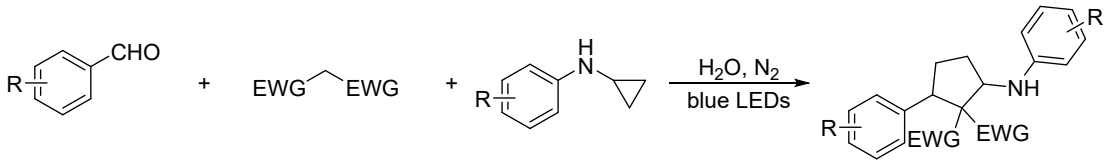


3ap



3b

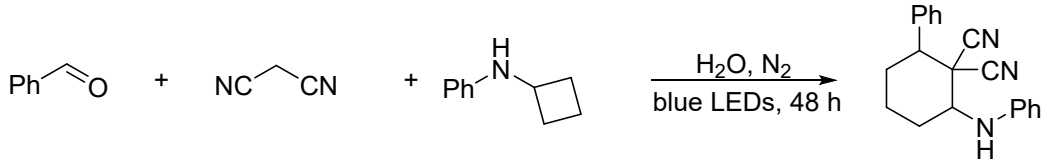
2.2 General procedure for the synthesis of cyclopentylamine.



1 **2** **3** **4**

To a stirred solution of activated methylenes **2** (0.5 mmol, 1.0 equiv) in H_2O (5.0 mL) at room temperature was added aldehydes **1** (0.6 mmol, 1.2 equiv), amines **3** (1 mmol, 2.0 equiv). The reaction mixture was irradiated with blue LED strips (Kessil lamps) at room temperature under an N_2 atmosphere. After completion of the reaction as indicated by TLC analysis, the product was dissolved in ethyl acetate. The aqueous phase was extracted with ethyl acetate (20 mL x 3), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give the crude product. The residue was further purified by flash column chromatography on silica gel to afford the desired product **4**.

2.3 General procedure for the synthesis of cyclohexylamine.

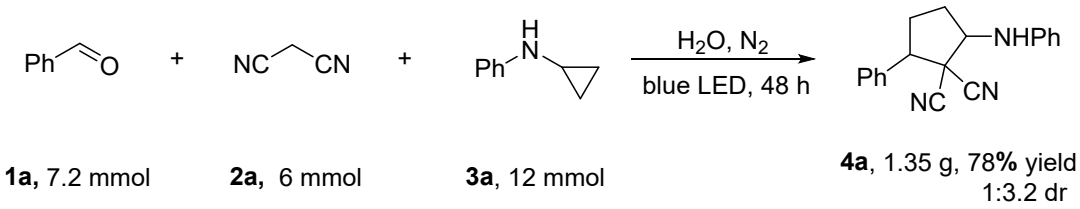


1a **2a** **3b** **6**

To a stirred solution of malononitrile **2a** (0.5 mmol, 1.0 equiv) in H_2O (5.0 mL) at room temperature was added aldehydes **1** (0.6 mmol, 1.2 equiv), cyclobutylamine **3b** (1 mmol, 2.0 equiv). The reaction mixture was irradiated with blue LED strips (Kessil lamps, **Figure S1**) at room temperature under an N_2 atmosphere. After completion of the reaction as indicated by TLC analysis, the product was dissolved in ethyl acetate. The aqueous phase was extracted with ethyl acetate (20 mL x 3), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give the crude product. The residue was further purified by flash column chromatography on silica gel to afford the desired product **6**.

Figure S1

2.4 General procedure for Scale-up reaction.



1a, 7.2 mmol **2a,** 6 mmol **3a**, 12 mmol **4a**, 1.35 g, 78**%** yield 1:3.2 dr

To a stirred solution of activated methylenes **2a** (6 mmol, 1.0 equiv) in H_2O (60.0 mL) at room temperature was added aldehydes **1a** (7.2 mmol, 1.2 equiv), amines **3a** (12 mmol, 2.0 equiv). The reaction mixture was irradiated with blue LED strips (Kessil lamps, Figure S2) at room temperature under an N_2 atmosphere. After completion of the reaction as indicated by TLC analysis, the product was dissolved in ethyl acetate. The aqueous phase was extracted with ethyl acetate three times, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give the crude product. The residue was further purified by flash column chromatography on silica gel to afford the desired product **4a** to yield 78% yield (1.35 g), which was used for the photochemical scale-up reaction.

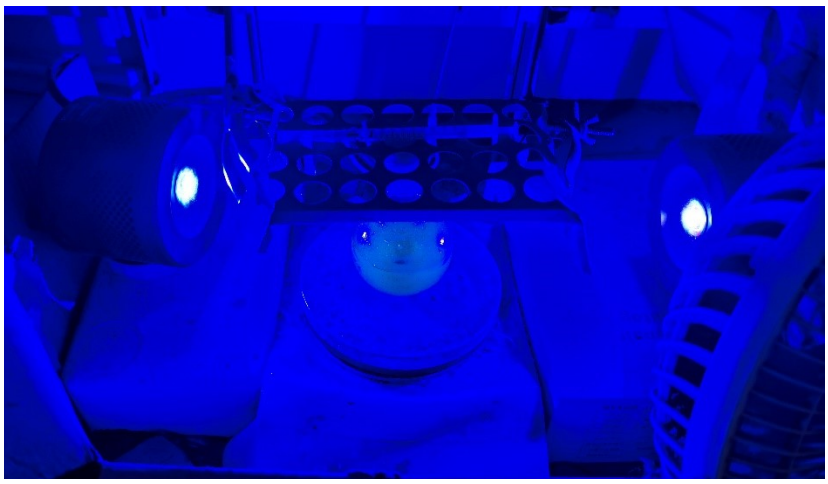
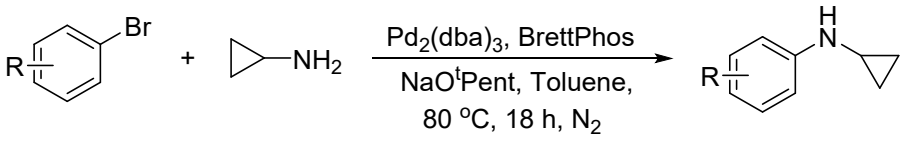


Figure S2

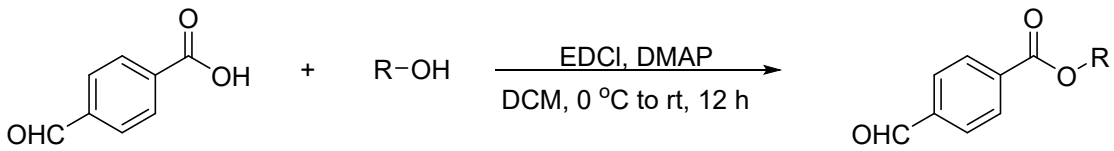
2.5 General procedure for the synthesis of 3ag–3ap[1].



3ag-3ap

To an oven-dried reaction vessel was added aromatic bromide (10.0 mmol, 1.0 equiv), cyclopropylamine (16.0 mmol, 1.6 equiv), $Pd_2(dba)_3$ (91.5 mg, 0.1 mmol, 0.01 equiv), BrettPhos (161.0 mg, 0.3 mmol, 0.03 equiv), sodium tert-pentoxide (3364.5 mg, 30.0 mmol, 3 equiv), and toluene (20 mL) under N_2 atmosphere. The reaction mixture was stirred at 80 °C using a heating aluminum block for 18 h. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a short pad of silica gel, and concentrated in vacuum. Purification of the residue by silica gel column chromatography afforded aryl cyclopropylamines **3ag-3ap.**

2.6 General procedure for the synthesis of 1ba–1ea[2].

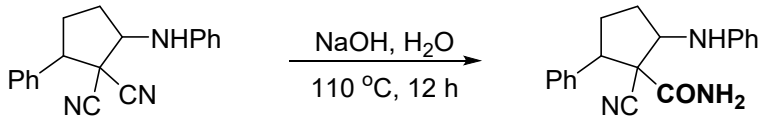


1ba-1ea

1 T. H. Nguyen, S. A. Morris, *Adv. Synth. Catal.,* 2014, **356**, 2831–2837.
2 S. Cao, D. Kim, W. Lee and S. Hong, *Angew. Chem. Int. Ed.,* 2023, **62**, e202312780.

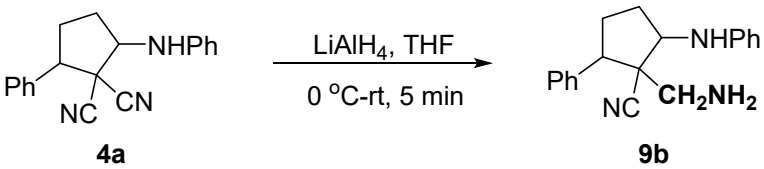
A Schlenk flask was charged with the alcohol (2.0 mmol, 1.0 equiv), EDCI (460.0 mg, 2.4 mmol, 1.2 equiv), DMAP (48.8 mg, 0.4 mmol, 0.2 equiv) and anhydrous DCM (8 mL) under N_2 atmosphere, followed by addition of phydroxybenzaldehyde (330.2 mg, 2.2 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed in vacuum, and the crude residue was purified by silica gel column chromatography (petroleum ether /EtOAc) to afford the crude product **1ba-1ea**.

2.7 General procedure for the synthesis of 9a–9d.

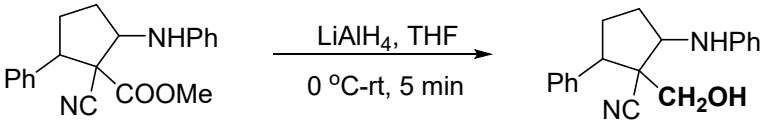


4a **9a**

The sodium hydroxide (3.0 mmol, 15.0 equiv), **4a** (0.2 mmol, 1.0 equiv), and water (2 mL) were added to a 50 ml round-bottom flask. The reaction mixture was stirred at 110 °C for 12 h. After completion of the reaction as indicated by TLC analysis, the reaction was quenched by slow addition of 1 M HCl. The aqueous phase was extracted with ethyl acetate (30 mL x 3), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give the crude product. The residue was further purified by flash column chromatography on silica gel to afford the desired product **9a**.



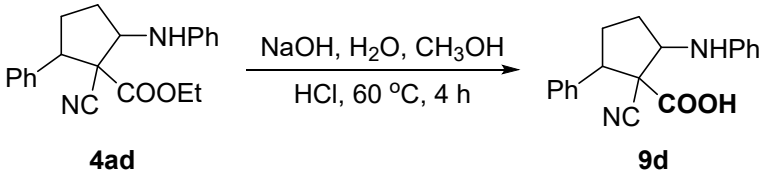
4a **9b**



4ac **9c**

To a 50 ml round-bottom flask was added **4a** (0.2 mmol, 1.0 equiv) and THF (2 mL). The reaction mixture was stirred at 0 °C. Then, $LiAlH_4$ (0.22 mmol, 1.1 equiv) was slowly added to the flask. After completion of the reaction as indicated by TLC analysis, the reaction was quenched with water and dissolved in ethyl acetate. The aqueous phase was extracted with ethyl acetate (30 mL x 3), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give the crude product. The residue

was further purified by flash column chromatography on silica gel to afford the desired product **9b**. The compound **9c** can be obtained as the above procedure for **9b.**

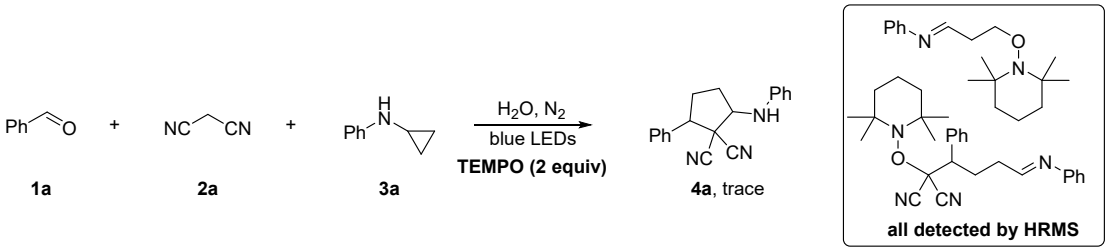


4ad **9d**

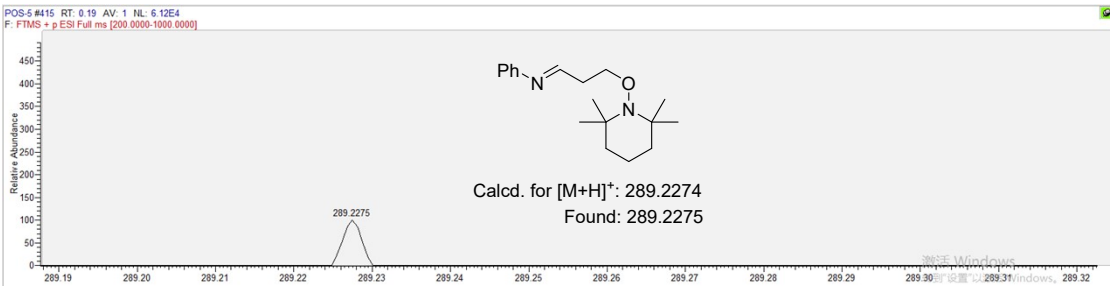
To a 50 ml round-bottom flask was added sodium hydroxide (0.4 mmol, 2.0 equiv), **4ad** (0.2 mmol, 1.0 equiv), water (1 mL) and CH_3OH (1 mL). The reaction mixture was stirred at 60 °C for 4 h. After completion of the reaction as indicated by TLC analysis, the mixture was evaporated under reduced pressure to obtain a crude product. Then, 1 M HCl was added and the organic material was extracted with Et_2O (30 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the desired product **9d**.

3. Mechanistic Study

3.1 Radical trapping experiments



1a **2a** **3a** **4a**, trace **all detected by HRMS**



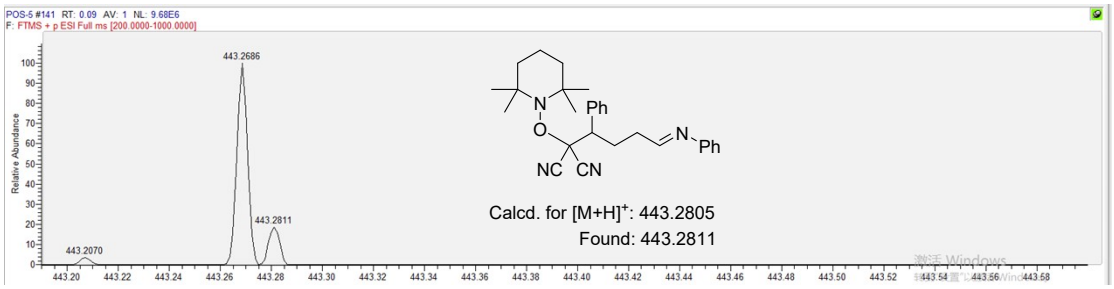
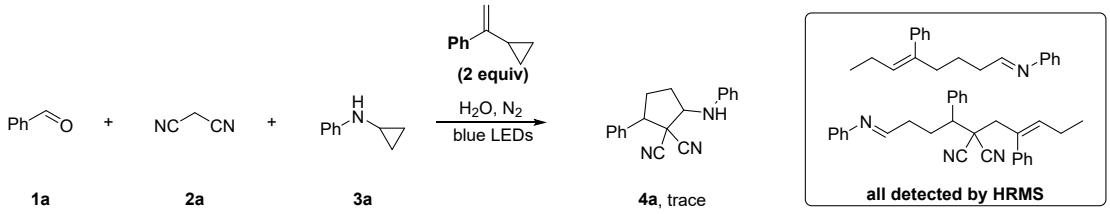


Figure S3

To a stirred solution of **2a** (0.2 mmol, 1.0 equiv) in H_2O (2.0 mL) at room temperature was added aldehydes **1** (0.24 mmol, 1.2 equiv), **3a** (0.4 mmol, 2.0 equiv), and TEMPO (0.4 mmol, 2.0 equiv). The reaction mixture was irradiated with blue LED strips (Kessil lamps) at room temperature under an N_2 atmosphere. The resultant crude solution was measured with high resolution mass spectrometry (HRMS) (Figure S3). **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{18}H_{29}N_2O$: 289.2274, Found: 289.2275. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{28}H_{34}N_4O$: 443.2805, Found: 443.2811.



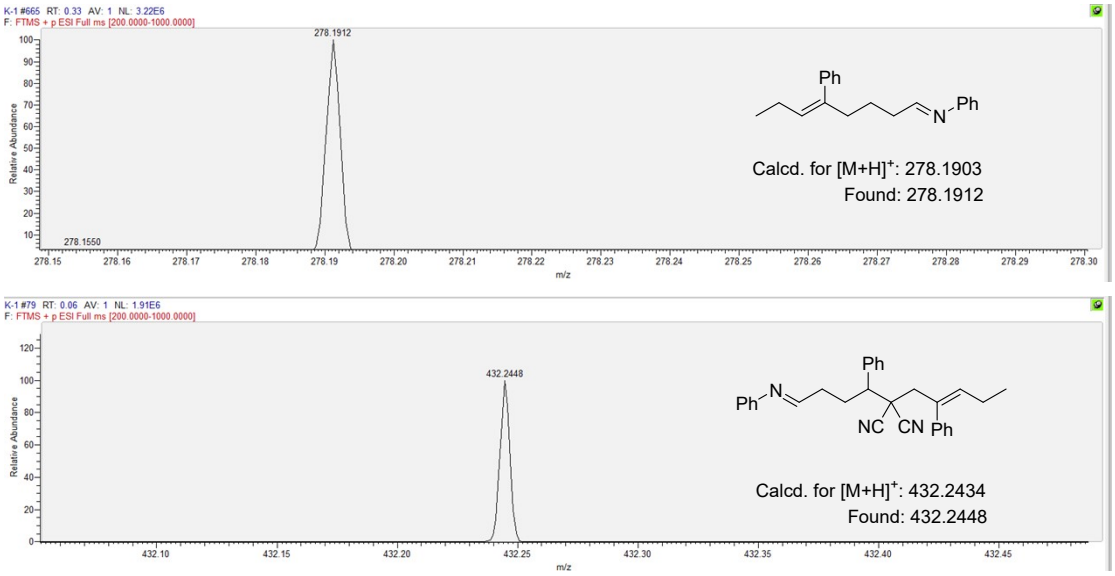
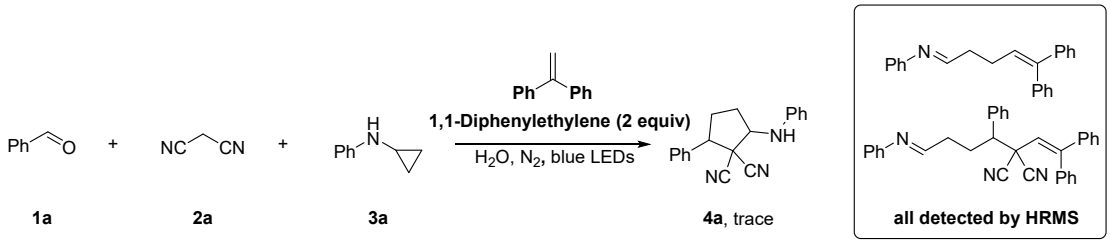


Figure S4

To a stirred solution of activated methylene **2** (0.2 mmol, 1.0 equiv) in H_2O (2.0 mL) at room temperature was added aldehydes **1** (0.24 mmol, 1.2 equiv), (1-cyclopro

pylvinyl) benzene (0.4 mmol, 2.0 equiv), and amines **3** (0.4 mmol, 2.0 equiv)**.** The rea ction mixture was irradiated with blue LED strips (Kessil lamps) at room temperature under an N_2 atmosphere. The resultant crude solution was measured with high resolutio n mass spectrometry (HRMS) **(Figure S4). HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_{20}H_{24}N$ 278.1903, Found 278.1912. **HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_{30}H_{30}N_3$ 432. 2434, Found 432.2448.



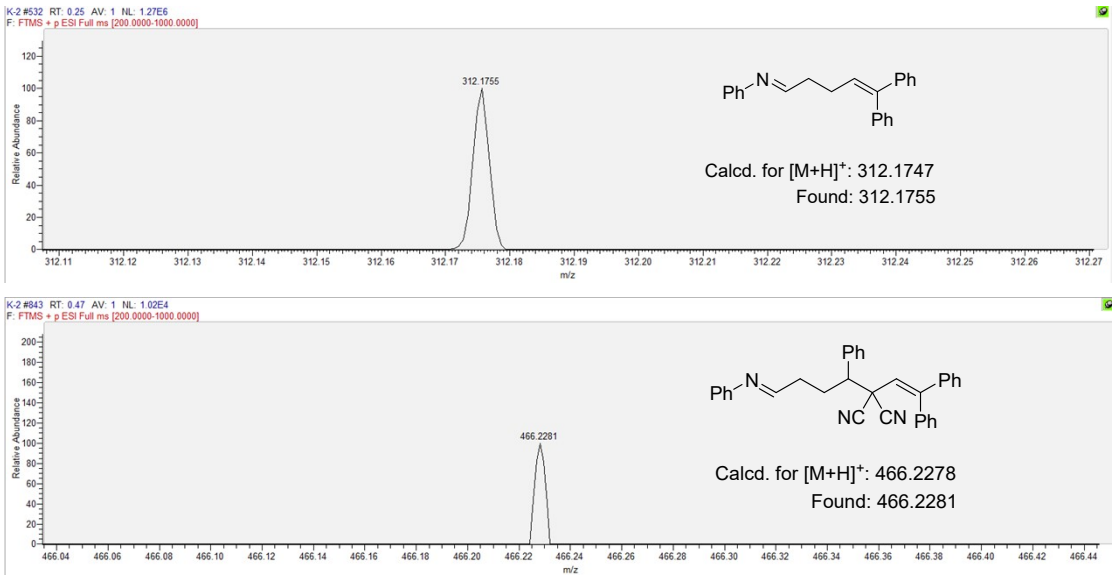


Figure S5

To a stirred solution of activated methylene **2** (0.2 mmol, 1.0 equiv) 1,1-Diphenylethylene (0.4 mmol, 2.0 equiv) in H_2O (2.0 mL) at room temperature was added aldehydes **1** (0.24 mmol, 1.2 equiv), amines **3** (0.4 mmol, 2.0 equiv)**.** The reaction mixture was irradiated with blue LED strips (Kessil lamps) at room temperature under an N_2 atmosphere. The resultant crude solution was measured with high resolution mass spectrometry (HRMS) (Figure S5). **HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_{23}H_{22}N$ 312.1747, Found 312.1755. **HRMS (ESI) m/z:** $[M + H]^+$ Calcd for $C_{33}H_{28}N_3$ 466.2278, Found 466.2281.3.2 UV-vis spectroscopic measurements

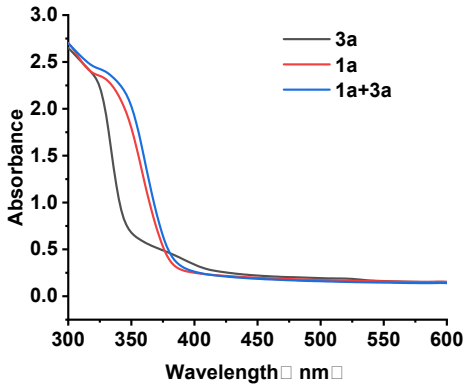


Figure S6

The UV/vis absorption spectra of **3a** (0.02 M) and **1a** (0.02 M) in DMF were recorded in 1 cm path quartz cuvettes by using a SpectraMax M2e Multi-Mode Microplate Reader (Molecular Devices, US) (Figure S6).

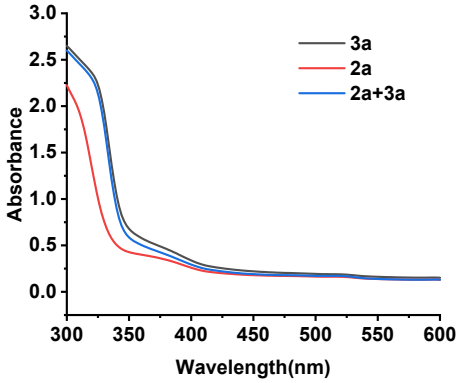


Figure S7

The UV/vis absorption spectra of **3a** (0.02 M) and **2a** (0.02 M) in DMF were recorded in 1 cm path quartz cuvettes by using a SpectraMax M2e Multi-Mode Microplate Reader (Molecular Devices, US) (Figure S7).

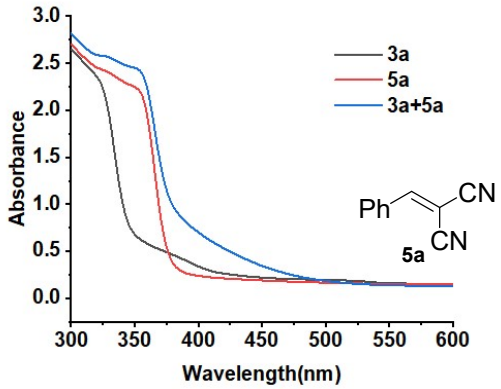


Figure S8

The UV/vis absorption spectra of **3a** (0.02 M) and **5a** (0.02 M) in DMF were recorded in 1 cm path quartz cuvettes by using a SpectraMax M2e Multi-Mode Microplate Reader (Molecular Devices, US) (Figure S8). The results showed that there was a small absorption in the visible light region (>400 nm).

3.3 ^{1}H NMR experiments

^{1}H NMR experiments were performed with the $CDCl_3$ solutions of **3a** and **5a** in different ratios. The ratios of **3a**/**5a** were changed as follows: 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10. (Figure S9).

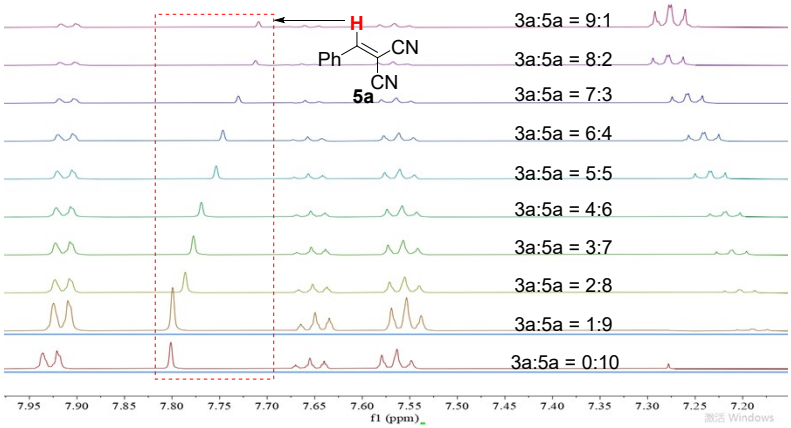
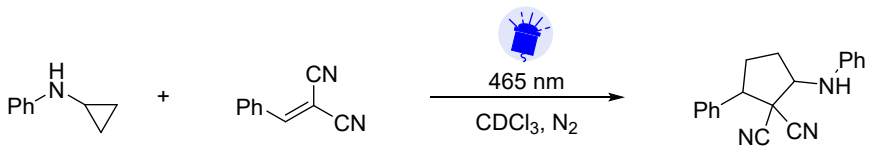


Figure S9

3.4 Light on-off experiments



3a **5a** **4a**

To a stirred solution of lacking electronic alkenes **5a** (0.1 mmol, 1.0 equiv) in $CDCl_3$ (1.0 mL) at room temperature was added amines **3a** (0.2 mmol, 2.0 equiv), The reaction mixture was irradiated with blue LED strips (Kessil lamps) at room temperature under an N_2 atmosphere.

Yield of **4a** was determined by ^1H NMR with dibromomethane as internal standard. (Irradiation: 0-2 h, 4-6 h, 8-10 h, in dark: 2-4 h, 6-8 h) The result indicated that continuous irradiation was indispensable for the reaction to proceed.

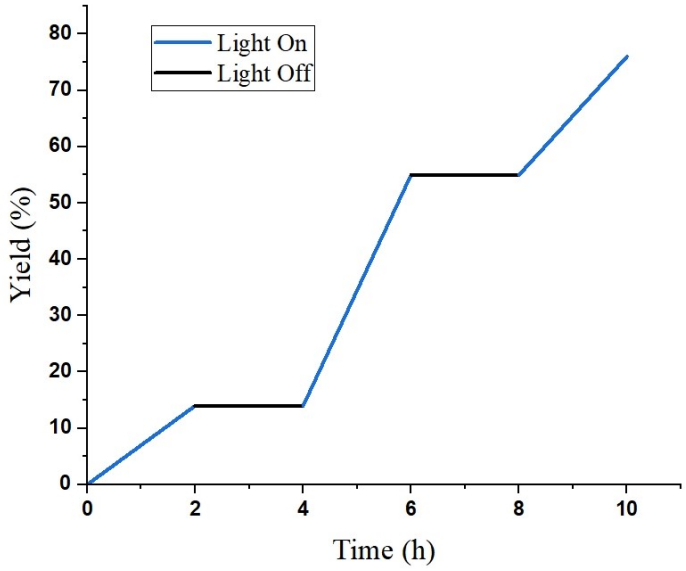


Figure S10

3.5 Quantum yield (Φ) of product 4a

A ferrioxalate actinometer solution was prepared following the Hammond variation of the Hatchard and Parker procedure[3] outlined in the Handbook of Photochemistry[4]. Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The values of the quantum yield of potassium ferrioxalate are related to the concentration and wavelength.

The solutions were prepared and the flask was covered with aluminum foil:

1. Potassium ferrioxalate solution 0.012 M: Potassium ferrioxalate (147.4 mg) and

3 C. G. Hatchard, C. A. Parker, *Proc. R. Soc. (London)*, 1956, *235*, 518.
4 M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, Handbook of Photochemistry, Taylor Francis, **2006**.

69.5 µL of sulfuric acid (96%) were added to a 25 mL volumetric flask and filled to the mark with water.

2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (50 mg in 25 mL).

3. Buffer solution: to a 100 mL volumetric flask, 4.94 g of NaOAc and 1.0 mL of sulfuric acid (96%) were added and filled to the mark with water.

A cuvette was loaded with 1.0 mL of potassium ferrioxalate solution and placed under 40 W Kessil lamp (465 nm). The actinometer solution was irradiated for 60 s. After the irradiation, the actinometer solution was carefully transferred into a 10 mL volumetric flask, then 0.5 mL of phenanthroline solution and 2.0 mL of buffer solution was added and the flask was filled up with water. The absorbance of the final solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The moles of Fe^{2+} formed for the sample was determined using Beer's Law **Equation S1**:

$$mol\left(Fe^{+2}\right) = \frac{V_1 \bullet V_3 \bullet \Delta A\ (510nm)}{10^3 \bullet V_2 \bullet I \bullet \varepsilon\ (510nm)} \quad Equation\ S1$$

Where:

V_1 = Irradiated volume (1 mL).

V_2 = The aliquot of the irradiated solution taken for the estimation of Fe+ ions (1 mL).

V_3 = Final volume of the solution after complexation with 1,10-phenanthroline (10 mL). ε (510 nm) =Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$complex (11100 L $mol^{-1}cm^{-1}$).

l = Optical path-length of the cuvette (1 cm).

ΔA (510 nm) = Difference in absorbance between the irradiated solution and the solution stored in dark (blank).

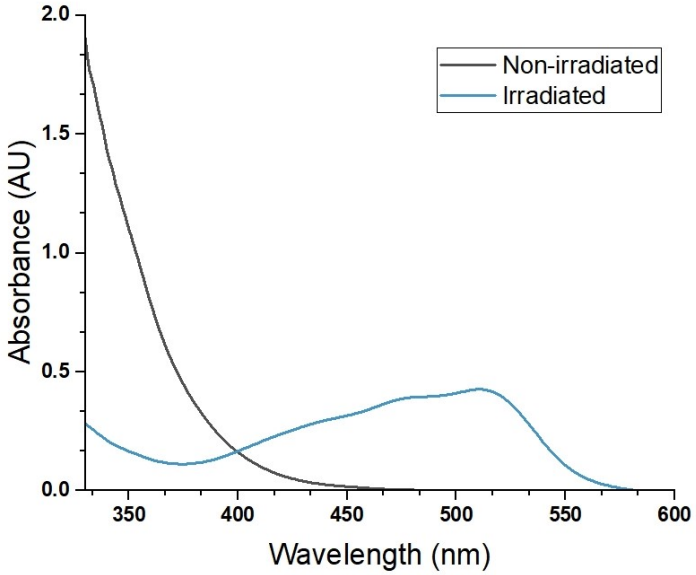


Figure S11. Absorption spectra for irradiated and non-irradiated samples of red $[Fe(phen)_3]^{+2}$

$$mol\left(Fe^{+2}\right) = \frac{1\ ml \bullet 10\ ml \bullet 0.426\ V}{10^3 \bullet 1ml \bullet 1cm \bullet 11100\ L\ mol^{-1}cm^{-1}} = 3.838 \times 10^{-7}\ mol$$

Fraction of light absorbed at 465 nm for the ferrioxalate solution are calculated by

Equation S2.

$$f = 1 - 10^{-A} \quad Equation\ S2$$

Absorption of ferrioxalate solution at 465 nm = 0.372

$$f = 1 - 10^{-0.372} = 0.575$$

The photon flux can be calculated using **Equation S3**.

$$Photon\ flux = \frac{mol\ Fe^{2+}}{\Phi\left(Fe^{+2}\right) \bullet t \bullet f} \quad Equation\ S3$$

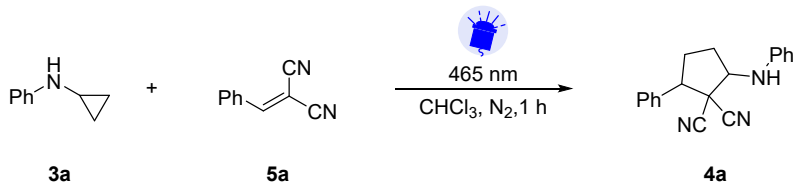
$\Phi(\lambda)$ = The quantum yield for Fe^{2+} formation at 465 nm is 0.92[5]

t = 60 s

$$Photon\ flux = \frac{3.838 \times 10^{-7}}{0.92 \bullet 60s \bullet 0.575} = 1.21 \times 10^{-8} einstein\ s^{-1}$$

5 E. E. Wegner, A. W. Adamson, *J. Am. Chem. Soc.*, 1966, **88**, 394.

Quantum yield determination of photochemical reaction



3a **5a** **4a**

Figure S12

To a stirred solution of lacking electronic alkenes **5a** (0.1 mmol, 1.0 equiv) in $CHCl_3$ (1.0 mL) at room temperature was added amines **3a** (0.2 mmol, 2.0 equiv), The reaction mixture was irradiated with blue LED strips (Kessil lamps) at room temperature under an N_2 atmosphere for 1 hour. After irradiation, product **4a** was determined by ^1H NMR to be 3% yield using dibromomethane as an internal standard. The quantum yield was determined using **Equation S4**.

$$Quantum\ yield\ (reaction\ at\ 465nm) = \frac{mol\ of\ formed\ product}{mol\ of\ photon\ flux \bullet t \bullet f}\ \ Equation\ S4$$

Fraction of light absorbed at 465 nm for the photocatalytic reaction are calculated by

Equation S2.

A = Absorption of photocatalytic reaction (0.297)

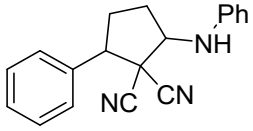
$$f = 1 - 10^{-0.297} = 0.495$$

$$Quantum\ yield\ (reaction\ at\ 465nm) = \frac{3 \times 10^{-6}\ mol}{1.21 \times 10^{-8} einstein\ s^{-1} \bullet 3600s \bullet 0.495} = 0.14$$

The quantum yield studies indicate that this is a non-radical-chain process as evidenced by the Φ value.

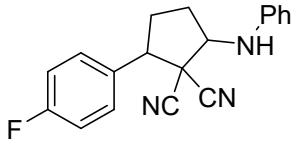
4. Characterization of Products

2-phenyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4a)



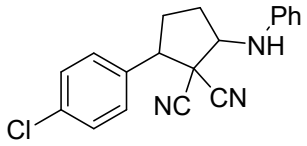
White solid; 129.1 mg, 90% yield; dr 1:6.6; mp 111 – 113 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 – 7.35 (m, 5H), 7.29 – 7.18 (m, 2H), 6.85 (q, *J* = 7.1 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 4.68 (t, *J* = 6.9 Hz, 1H), 4.24 – 4.09 (m, 1H), 3.81 – 3.60 (m, 1H), 2.75 – 2.67 (m, 1H), 2.34 – 2.20 (m, 2H), 1.89 – 1.72 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.92, 134.84, 129.71, 129.09, 128.05, 119.72, 114.91, 114.50, 114.33, 113.73, 65.46, 54.95, 47.83, 33.60, 28.07. **HRMS (ESI-TOF)**: *m/z* [M + H] $^{+}$ calcd for $C_{19}H_{18}N_3$: 288.1495, found: 288.1495.

2-(4-fluorophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4b)



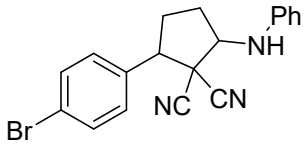
Pink solid; 116.3 mg, 76% yield; dr 1:3.1; mp 136 – 138 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** 1H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.38 (m, 2H), 7.29 – 7.22 (m, 2H), 7.12 (td, *J* = 8.5, 1.4 Hz, 2H), 6.85 (t, *J* = 7.5 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 2H), 4.68 (t, *J* = 7.9 Hz, 1H), 4.15 (s, 1H), 3.69 (td, *J* = 14.0, 12.8, 7.9 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.32 – 2.18 (m, 2H), 1.81 (tdd, *J* = 11.5, 9.9, 8.3, 4.8 Hz, 1H).**^{13}C NMR (126 MHz, $CDCl_3$)**. δ 164.11 (d, *J* = 245.0 Hz), 144.82, 144.75, 130.56 (d, *J* = 3.4 Hz)., 129.81, 129.80, 129.73, 129.65, 120.09, 119.81, 116.21, 116.04, 114.80, 114.51, 114.18, 113.71, 65.37, 65.16, 54.31, 52.92, 49.25, 47.87, 33.60, 30.26, 28.29, 26.27. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -112.38, -112.42. **HRMS (ESI-TOF)**: *m/z* [M + H] $^{+}$ calcd for $C_{19}H_{17}FN_3$: 306.1401, found: 306.1401.

2-(4-chlorophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4c)



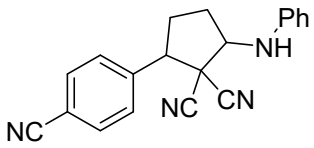
Yellow solid; 130.4 mg, 81% yield; dr 1:3.6; mp 142 – 144 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, CDCl$_3$)** ^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 (d, *J* = 5.5 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.28 – 7.22 (m, 2H), 6.88 – 6.85 (m, 1H), 6.77 – 6.73 (m, 2H), 4.69 (q, *J* = 7.9 Hz, 1H), 4.18 – 4.12 (m, 1H), 3.73 – 3.67 (m, 1H), 2.79 – 2.69 (m, 1H), 2.31 – 2.19 (m, 2H), 1.82 (ddt, *J* = 13.7, 10.6, 8.1 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 144.76, 144.69, 135.19, 135.13, 133.23, 132.91, 129.73, 129.65, 129.36, 129.33, 120.13, 119.86, 115.34, 114.71, 114.52, 114.09, 113.72, 112.23, 65.44, 65.25, 54.34, 52.95, 49.06, 47.71, 33.59, 30.25, 28.11, 26.09. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{19}H_{16}ClN_3$: 322.1105, found: 322.1105.

2-(4-bromophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4d)



Yellow solid; 104.3 mg, 57% yield; dr 1:6.7; mp 111 – 113 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.59 – 7.55 (m, 2H), 7.33 – 7.28 (m, 2H), 7.28 – 7.23 (m, 3H), 6.88 – 6.84 (m, 2H), 6.77 – 6.73 (m, 2H), 4.72 – 4.66 (m, 1H), 4.14 (d, *J* = 9.8 Hz, 1H), 3.68 (dd, *J* = 11.6, 6.8 Hz, 1H), 2.80 – 2.69 (m, 1H), 2.31 – 2.20 (m, 2H), 1.86 – 1.77 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 144.76, 144.69, 133.74, 133.44, 133.11, 132.30, 132.29, 131.83, 129.73, 129.66, 123.33, 123.31, 120.13, 119.85, 114.70, 114.52, 114.08, 113.71, 65.45, 65.27, 54.38, 53.01, 48.98, 47.64, 33.58, 30.24, 28.05, 26.03. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{19}H_{17}BrN_3$: 366.0600, found: 366.0601.

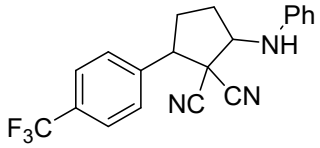
2-(4-cyanophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4e)



White solid; 75.1 mg, 48% yield; dr 1:2.1; mp 173 – 175 ℃; column chromatography

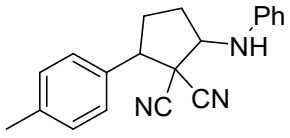
eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 – 7.71 (m, 2H), 7.61 – 7.54 (m, 2H), 7.29 – 7.23 (m, 2H), 6.89 – 6.85 (m, 2H), 6.76 – 6.71 (d, *J* = 1.2 Hz, 1H), 4.82 (q, *J* = 9.4 Hz, 1H), 4.08 (d, *J* = 9.9 Hz, 1H), 3.76 – 3.72 (m, 1H), 2.63 (dtd, *J* = 14.8, 9.1, 6.1 Hz, 1H), 2.35 – 2.26 (m, 2H), 2.01 (dddd, *J* = 14.2, 11.5, 9.3, 5.0 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.61, 144.53, 139.93, 139.67, 132.88, 132.86, 129.77, 129.69, 128.92, 120.30, 118.21, 118.19, 115.04, 114.56, 114.43, 113.78, 113.72, 113.22, 113.16, 111.97, 65.66, 65.50, 54.54, 53.15, 48.70, 47.45, 33.56, 30.18, 27.89, 25.88. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{17}N_4$: 313.1447, found: 313.1447.

2-(phenylamino)-5-(4-(trifluoromethyl)phenyl)cyclopentane-1,1-dicarbonitrile (4f)



Yellow solid; 106.8 mg, 60% yield; dr 1:2.7; mp 175 – 177 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 – 7.67 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.23 (m, 2H), 6.88 – 6.84 (m, 1H), 6.78 – 6.73 (m, 2H), 4.72 (q, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 8.3 Hz, 1H), 3.76 (dd, *J* = 10.4, 8.1 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.34 – 2.27 (m, 2H), 1.89 – 1.79 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.72, 144.65, 138.69, 138.43, 131.29 (q, *J* = 32.4 Hz), 129.75, 129.67, 128.54, 126.08 (q, *J* = 3.5 Hz), 123.85 (q, *J* = 268.96 Hz), 120.21, 119.93, 115.21, 114.57, 114.54, 113.95, 113.72, 112.13, 65.60, 65.44, 54.45, 53.07, 48.85, 47.58, 33.57, 30.21, 28.03, 26.00. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -62.73, -62.76. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{17}F_3N_3$: 356.1369, found: 356.1371.

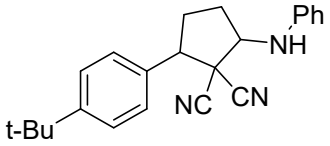
2-(phenylamino)-5-(p-tolyl)cyclopentane-1,1-dicarbonitrile (4g)



White solid; 114.8mg, 76% yield; dr 1:4.3; mp 124 – 126 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.29 (m, 2H), 7.23 (dd, *J* = 8.0, 5.9 Hz, 4H), 6.85 – 6.81 (m, 1H), 6.77 – 6.73 (m, 2H), 4.68 (q,

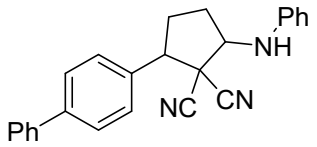
J = 8.1 Hz, 1H), 4.18 – 4.13 (m, 1H), 3.70 (dd, *J* = 10.2, 8.0 Hz, 1H), 2.71 (dddd, *J* = 13.4, 5.7, 4.1, 3.1 Hz, 1H), 2.37 (s, 3H), 2.30 – 2.23 (m, 2H), 1.85 – 1.76 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.92, 139.03, 129.76, 129.69, 127.89, 119.69, 114.99, 114.47, 114.38, 113.72, 65.34, 65.14, 54.74, 53.37, 49.29, 47.90, 33.62, 30.35, 28.13, 26.09, 21.20, 21.18. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{20}N_3$: 302.1651, found: 302.1651.

2-(4-(tert-butyl)phenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4h)



White solid; 103.2 mg, 60% yield; dr 1:2.1; mp 53 – 57 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 – 7.42 (m, 3H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.27 – 7.23 (m, 2H), 6.88 – 6.85 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.76 (q, *J* = 8.6 Hz, 1H), 4.07 (d, *J* = 9.2 Hz, 1H), 3.69 (dd, *J* = 10.3, 7.7 Hz, 1H), 2.57 (dtd, *J* = 14.7, 9.1, 6.0 Hz, 1H), 2.25 (tdt, *J* = 13.9, 8.8, 4.7 Hz, 2H), 1.95 (dddd, *J* = 14.1, 11.5, 9.4, 4.9 Hz, 1H), 1.33 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.12, 152.03, 144.97, 144.90, 131.68, 129.69, 129.62, 129.59, 127.77, 127.73, 126.02, 126.00, 119.94, 119.68, 115.66, 115.00, 114.51, 114.46, 113.71, 112.56, 65.37, 65.20, 54.59, 53.23, 49.18, 47.89, 34.68, 33.61, 31.29, 30.29, 28.22, 26.12. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{23}H_{26}N_3$: 344.2121, found: 344.2121.

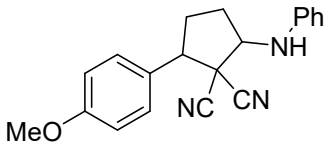
2-([1,1'-biphenyl]-4-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4i)



Yellow solid, 109.2 mg, 60% yield; dr 1:4.8; mp 151 – 154 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 – 7.63 (m, 2H), 7.61 – 7.59 (m, 2H), 7.56 – 7.49 (m, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.26 (dd, *J* = 8.2, 6.8 Hz, 2H), 6.89 – 6.85 (m, 1H), 6.78 – 6.75 (m, 2H), 4.71 (q, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.76 (dd, *J* = 10.8, 7.5 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.35 – 2.28 (m, 2H), 1.88 – 1.79 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ

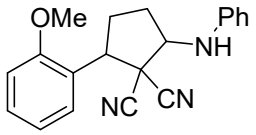
144.90, 141.92, 140.28, 133.73, 129.72, 129.65, 128.88, 128.49, 128.47, 127.77, 127.73, 127.67, 127.15, 120.04, 119.77, 114.93, 114.52, 114.32, 113.82, 113.75, 65.47, 65.28, 54.70, 53.33, 49.16, 47.84, 33.64, 30.33, 28.18, 26.15. **HRMS (ESI-TOF)**: *m/z* $[M + H]^+$ calcd for $C_{25}H_{22}N_3$: 364.1808, found: 364.1808.

2-(4-methoxyphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4j)



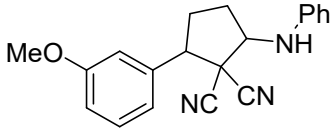
White solid; 138.4 mg, 87% yield; dr 1:6.1; mp 120 – 124 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.32 (m, 2H), 7.27 – 7.22 (m, 2H), 6.96 – 6.92 (m, 2H), 6.87 – 6.82 (m, 1H), 6.74 (dt, *J* = 7.7, 1.1 Hz, 2H), 4.66 (q, *J* = 8.1 Hz, 1H), 4.15 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 3H), 3.71 – 3.66 (m, 1H), 2.70 (dddd, *J* = 13.5, 7.5, 5.1, 4.2 Hz, 1H), 2.28 – 2.20 (m, 2H), 1.84 – 1.74 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.07, 144.94, 129.69, 129.18, 126.75, 119.68, 115.03, 114.43, 113.71, 65.22, 65.00, 55.34, 54.52, 53.15, 49.44, 48.02, 33.60, 30.32, 28.28, 26.23. **HRMS (ESI-TOF)**: *m/z* $[M + H]^+$ calcd for $C_{20}H_{20}N_3O$: 318.1600, found: 318.1600.

2-(2-methoxyphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4k)



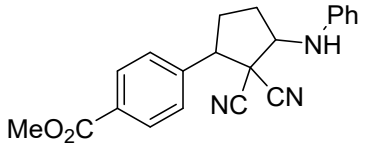
White solid; 143.1 mg, 90% yield; dr 1:8.2; mp 130 – 132 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.33 (m, 1H), 7.28 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.01 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.84 – 6.78 (m, 3H), 4.67 (td, *J* = 10.0, 6.4 Hz, 1H), 4.24 – 4.15 (m, 2H), 3.89 (s, 3H), 2.59 – 2.52 (m, 2H), 2.33 – 2.16 (m, 2H), 1.91 – 1.81 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.55, 145.04, 129.99, 129.62, 127.80, 124.59, 120.74, 119.58, 114.09, 110.87, 65.73, 55.04, 49.11, 45.67, 33.23, 27.25. **HRMS (ESI-TOF)**: *m/z* $[M + H]^+$ calcd for $C_{20}H_{20}N_3O$: 318.1600, found: 318.1600.

2-(3-methoxyphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4l)



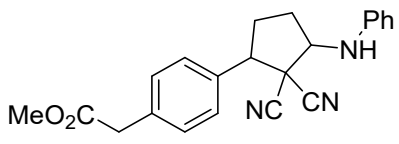
Yellow oil; 49.31 mg, 31% yield; dr 1:1.1; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.07 – 7.04 (m, 1H), 7.01 (dd, *J* = 4.3, 2.1 Hz, 1H), 6.96 – 6.94 (m, 1H), 6.85 (ddd, *J* = 5.1, 2.3, 1.3 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 4.76 (q, *J* = 9.3 Hz, 1H), 4.07 (d, *J* = 10.0 Hz, 1H), 3.83 (s, 3H), 3.72 – 3.67 (m, 1H), 2.62 – 2.53 (m, 1H)), 2.31 – 2.25 (m, 2H), 1.99 – 1.91 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.98, 159.95, 144.89, 144.83, 136.37, 136.00, 130.11, 129.70, 129.62, 120.23, 120.22, 119.99, 119.73, 115.58, 114.90, 114.49, 114.39, 114.35, 114.22, 114.03, 113.92, 113.73, 112.45, 65.46, 65.27, 55.34, 54.85, 53.48, 49.02, 47.72, 33.56, 30.28, 28.07, 26.09. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{20}N_3O$: 318.1600, found: 318.1600.

methyl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate (4m)



White solid; 138.4 mg, 80% yield; dr 1:2.6; mp 153 – 155 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 1.9 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.22 (m, 2H), 6.86 (dd, *J* = 7.9, 2.9 Hz, 2H), 6.76 (s, 1H), 4.71 (q, *J* = 8.1 Hz, 1H), 4.19 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.80 – 3.74 (m, 1H), 2.79 – 2.72 (m, 1H), 2.35 – 2.29 (m, 2H), 1.89 – 1.80 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.50, 166.48, 144.75, 144.69, 139.74, 139.40, 130.93, 130.86, 130.31, 130.25, 129.73, 128.13, 120.15, 119.86, 114.62, 114.55, 114.05, 113.74, 65.61, 65.44, 54.66, 53.26, 52.31, 48.83, 47.54, 33.57, 30.27, 27.99, 26.00. HRMS (ESI - TOF): *m/z* [M + H] $^+$ calcd for $C_{21}H_{20}N_3O_2$: 346.1550, found: 346.1550.

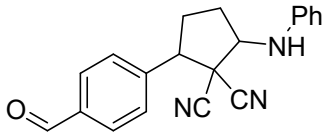
methyl 2-(4-(2,2-dicyano-3-(phenylamino)cyclopentyl)phenyl)acetate (4n)



Yellow oil; 158.5 mg, 88% yield; dr 1:1.2; column chromatography eluent, petroleum

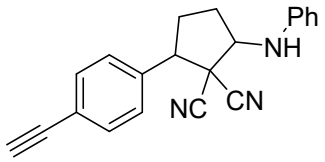
ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 – 7.36 (m, 4H), 7.24 – 7.21 (m, 2H), 6.88 – 6.85 (m, 2H), 6.74 – 6.72 (m, 1H), 4.76 (t, *J* = 9.1 Hz, 1H), 4.19 (s, 1H), 3.71 (s, 3H), 3.68 (d, *J* = 3.7 Hz, 1H), 3.65 (s, 2H), 2.62 – 2.52 (m, 2H), 2.28 – 2.22 (m, 2H), 2.00 – 1.90 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** 171.77, 171.73, 144.91, 144.84, 134.97, 134.88, 133.68, 133.36, 130.01, 129.69, 129.62, 128.29, 119.98, 119.70, 115.53, 114.90, 114.48, 114.26, 113.70, 112.42, 65.43, 65.24, 54.59, 53.23, 52.19, 49.10, 47.79, 40.80, 33.54, 30.26, 28.13, 26.10. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{22}H_{22}N_3O_2$: 360.1706, found: 360.1707.

2-(4-formylphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4o)



Yellow oil; 64.1 mg, 42% yield; dr 1:1.3; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.05 (s, 1H), 7.96 (s, 2H), 7.68 – 7.61 (m, 2H), 7.29 – 7.25 (m, 2H), 6.89 – 6.84 (m, 2H), 6.77 (s, 1H), 4.73 (q, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 3.80 (t, *J* = 9.1 Hz, 1H), 2.82 – 2.74 (m, 1H), 2.36 – 2.30 (m, 2H), 1.91 – 1.82 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 191.60, 191.57, 191.55, 144.70, 144.64, 141.34, 141.03, 136.82, 136.75, 130.33, 130.28, 129.75, 129.67, 128.82, 120.21, 119.93, 115.21, 114.58, 114.56, 113.96, 113.74, 112.12, 65.68, 65.50, 54.74, 53.34, 48.77, 47.50, 33.60, 30.27, 28.01, 26.00. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{17}N_3O$: 316.1444, found: 316.1449.

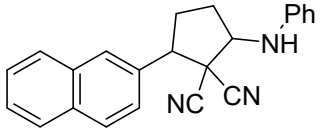
2-(4-ethynylphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4p)



Yellow solid; 50.3 mg, 38% yield; dr 1:1.3; mp 146 – 148 °C; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.24 (dd, *J* = 8.2, 3.8 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 2H), 6.73 (d, *J* = 10.5 Hz, 1H), 4.68 (q, *J* = 8.1 Hz, 1H), 4.13 (t, *J* = 7.9 Hz, 1H), 3.74 – 3.65 (m, 1H), 3.12 (s, 1H), 2.72 (ddt, *J* = 12.3, 7.9, 5.0 Hz, 1H), 2.26 (td, *J* = 8.3, 7.5,

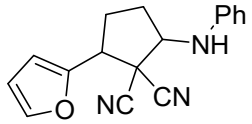
3.7 Hz, 2H), 1.80 (ddd, *J* = 17.6, 11.4, 7.1 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.79, 135.43, 132.78, 129.73, 129.70, 129.37, 128.22, 128.04, 126.78, 123.03, 119.84, 113.74, 113.14, 82.90, 82.86, 78.41, 65.51, 54.70, 47.62, 33.58, 27.98. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{21}H_{17}N_3$: 312.1495 found: 312.1497.

2-(naphthalen-2-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4q)



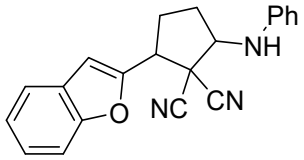
Yellow solid; 101.4 mg, 60% yield; dr 1:4.3; mp 146 – 148 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 – 7.84 (m, 4H), 7.53 (ddd, *J* = 16.0, 7.4, 2.6 Hz, 3H), 7.26 – 7.23 (m, 2H), 6.86 – 6.83 (m, 1H), 6.79 – 6.75 (m, 2H), 4.73 (q, *J* = 8.1 Hz, 1H), 4.20 (d, *J* = 8.4 Hz, 1H), 3.89 (dd, *J* = 12.0, 6.2 Hz, 1H), 2.79 – 2.70 (m, 1H), 2.47 – 2.30 (m, 2H), 1.90 – 1.80 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.90, 133.50, 133.44, 133.26, 132.32, 129.72, 129.65, 128.96, 128.22, 128.20, 127.80, 127.74, 127.36, 126.75, 126.72, 126.67, 125.45, 119.77, 114.95, 114.53, 114.41, 113.77, 65.64, 65.38, 55.11, 53.70, 49.12, 47.74, 33.66, 30.40, 28.22, 26.22. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{23}H_{20}N_3$:338.1651, found: 338.1652.

2-(furan-2-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4r)



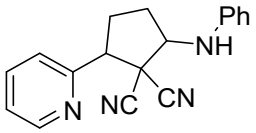
Brown oil; 43.1 mg, 31% yield; dr 1:5.1; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 – 7.47 (m, 1H), 7.27 – 7.22 (m, 2H), 6.84 (dd, *J* = 8.1, 6.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 1.6 Hz, 2H), 4.75 (td, *J* = 8.9, 7.2 Hz, 1H), 4.07 (d, *J* = 8.9 Hz, 1H), 3.93 (dd, *J* = 9.9, 7.2 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.41 – 2.34 (m, 1H), 2.27 – 2.17 (m, 1H), 1.89 – 1.79 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.57, 144.83, 143.54, 129.65, 119.84, 113.96, 110.73, 109.16, 65.02, 48.35, 46.07, 32.64, 26.93. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{17}H1_6N_3O$: 278.1287, found: 278.1288.

2-(benzofuran-2-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4s)



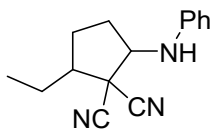
Brown solid; 77.1 mg, 47% yield; dr 1:6.2; mp 148 – 150 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 3H), 6.87 (d, *J* = 8.0 Hz, 3H), 6.82 (s, 1H), 4.77 (q, *J* = 9.4 Hz, 1H), 4.08 (d, *J* = 10.1 Hz, 1H), 3.96 (t, *J* = 9.7 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.51 – 2.42 (m, 1H), 2.41 – 2.33 (m, 1H), 2.05 – 1.95 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.18, 151.77, 144.71, 129.66, 127.67, 125.02, 123.25, 121.31, 120.15, 114.55, 111.51, 105.69, 65.37, 47.60, 46.83, 30.06, 24.91. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{21}H_{18}N_3O$: 328.1444, found: 328.1445.

2-(phenylamino)-5-(pyridin-2-yl)cyclopentane-1,1-dicarbonitrile (4t)



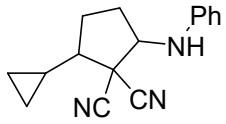
Brown solid; 75.2 mg, 52% yield; dr 1:3.1; mp 152 – 154 ℃; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.71 (dd, *J* = 12.1, 2.4 Hz, 2H), 7.87 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.40 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.90 – 6.83 (m, 3H), 4.82 (q, *J* = 9.3 Hz, 1H), 4.17 (d, *J* = 9.9 Hz, 1H), 3.73 (dt, *J* = 11.7, 6.6 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.36 – 2.26 (m, 2H), 2.07 – 1.96 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.46, 150.37, 149.57, 149.36, 144.75, 144.65, 135.65, 135.37, 130.73, 130.44, 129.74, 129.67, 123.94, 123.91, 120.18, 119.87, 115.07, 114.52, 113.71, 112.12, 65.54, 65.39, 52.57, 51.16, 48.87, 47.57, 33.55, 30.20, 27.93, 25.92. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$calcd for $C_{18}H_{17}N_4$: 289.1447, found: 289.1448.

2-ethyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4u)



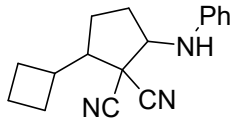
White solid; 73.2 mg, 61% yield; dr 1:1.1; mp 57 – 61 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.28 – 7.19 (m, 2H), 6.83 (t, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.55 (p, *J* = 8.8, 7.9 Hz, 1H), 4.09 – 3.92 (m, 1H), 2.54 – 2.35 (m, 2H), 2.17 – 2.06 (m, 1H), 1.97 – 1.85 (m, 1H), 1.83 – 1.57 (m, 3H), 1.08 (dt, *J* = 15.3, 7.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.05, 129.65, 129.58, 119.83, 119.60, 116.23, 115.01, 114.74, 114.42, 113.79, 112.49, 65.47, 64.90, 52.06, 50.30, 46.77, 45.05, 33.42, 30.24, 28.98, 26.42, 25.26, 24.96, 12.27, 11.89. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{15}H_{18}N_3$: 240.1495, found: 240.1495.

2-cyclopropyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4v)



White solid; 117.2 mg, 93% yield; dr 1:2.9; mp 95 – 97 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 – 7.19 (m, 2H), 6.86 – 6.73 (m, 3H), 4.53 (dt, *J* = 31.9, 8.3 Hz, 1H), 4.00 (s, 1H), 2.55 – 2.33 (m, 1H), 2.17 – 2.00 (m, 1H), 1.92 – 1.56 (m, 3H), 1.04 (pt, *J* = 8.3, 4.1 Hz, 1H), 0.80 – 0.51 (m, 3H), 0.30 – 0.21 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.05, 129.65, 129.58, 119.79, 119.61, 116.39, 115.36, 114.88, 114.42, 114.35, 113.82, 112.85, 65.22, 64.70, 55.87, 54.09, 46.94, 45.39, 33.24, 30.40, 29.08, 26.57, 12.34, 12.19, 4.14, 3.84, 3.74, 2.91. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{16}H_{18}N_3$: 252.1495, found: 252.1495.

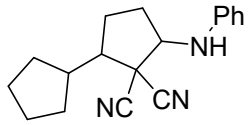
2-cyclobutyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4w)



White solid; 127.8 mg, 87% yield; dr 1:2.1; mp 85 – 87 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.23 (ddd, *J* = 15.9, 7.5, 1.8 Hz, 2H), 6.86 – 6.72 (m, 3H), 4.57 – 4.47 (m, 1H), 4.00 (d, *J* = 39.3 Hz, 1H), 2.68 – 2.51 (m, 2H), 2.49 – 2.31 (m, 1H), 2.31 – 2.08 (m, 2H), 2.07 – 1.92 (m,

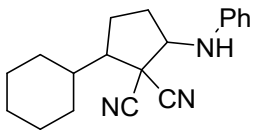
3H), 1.90 – 1.62 (m, 3H), 1.62 – 1.38 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.03, 145.00, 129.64, 129.56, 119.81, 119.61, 116.32, 115.07, 114.85, 114.39, 113.85, 112.54, 65.86, 65.31, 56.32, 54.20, 44.92, 43.26, 38.21, 37.73, 33.37, 30.38, 27.28, 27.21, 27.09, 26.93, 24.70, 18.77, 18.54. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{17}H_{20}N_3$: 266.1652, found: 266.1652.

3-(phenylamino)-[1,1'-bi(cyclopentane)]-2,2-dicarbonitrile (4x)



White solid; 119.1 mg, 85% yield; dr 1:1.4; mp 79 – 81 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.28 – 7.19 (m, 2H), 6.83 (td, *J* = 7.1, 6.6, 2.4 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.56 (t, *J* = 7.7 Hz, 1H), 4.08 (s, 1H), 2.53 – 2.27 (m, 2H), 2.16 – 1.99 (m, 3H), 1.94 – 1.82 (m, 1H), 1.81 – 1.52 (m, 6H), 1.49 – 1.39 (m, 1H), 1.28 – 1.13 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.11, 144.99, 129.67, 129.55, 119.78, 119.54, 116.69, 115.53, 115.02, 114.40, 113.76, 112.75, 66.42, 65.58, 56.80, 53.83, 46.38, 44.55, 44.36, 43.33, 33.94, 31.98, 31.50, 31.39, 31.33, 30.36, 29.76, 27.00, 25.25, 25.21, 24.65, 24.27. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{18}H_{22}N_3$: 280.1808, found: 280.1808.

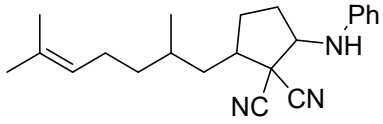
2-cyclohexyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4y)



White solid; 114.7 mg, 78% yield; dr 1:4.1; mp 97 – 99 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.24 (dt, *J* = 9.9, 7.4 Hz, 2H), 6.86 – 6.80 (m, 1H), 6.77 – 6.73 (m, 2H), 4.54 (t, *J* = 8.2 Hz, 1H), 4.10 (s, 1H), 2.47 (dtd, *J* = 13.1, 6.6, 1.7 Hz, 1H), 2.37 – 2.21 (m, 1H), 2.13 (tdd, *J* = 13.2, 6.6, 2.5 Hz, 2H), 1.85 – 1.72 (m, 3H), 1.72 – 1.56 (m, 3H), 1.47 (qd, *J* = 12.4, 6.5 Hz, 1H), 1.39 – 1.25 (m, 2H), 1.24 – 1.12 (m, 2H), 1.08 – 0.94 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.14, 144.95, 129.68, 129.54, 119.77, 119.54, 116.89, 115.52, 115.07, 114.37, 113.78, 112.68, 66.52, 65.83, 57.16, 53.74, 44.97, 43.18, 42.09, 40.53, 33.85,

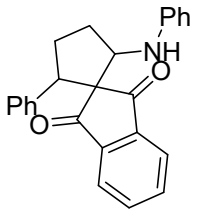
32.30, 31.98, 31.31, 31.01, 30.15, 28.29, 26.08, 25.98, 25.95, 25.83, 25.79, 25.71, 25.63. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{19}H_{24}N_3$: 294.1964, found: 294.1964.

2-(2,6-dimethylhept-5-en-1-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4z)



White solid; 87.4 mg, 52% yield; dr 1:1.2; mp 78 – 81 ℃; column chromatography eluent, petroleum ether/EtOAc = 50:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.28 – 7.19 (m, 2H), 6.88 – 6.80 (m, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.09 (tdp, *J* = 7.2, 4.3, 1.5 Hz, 1H), 4.61 – 4.50 (m, 1H), 4.07 – 3.92 (m, 1H), 2.67 – 2.56 (m, 1H), 2.56 – 2.36 (m, 1H), 2.14 – 1.91 (m, 3H), 1.84 – 1.72 (m, 1H), 1.69 (q, *J* = 1.4 Hz, 3H), 1.68 – 1.62 (m, 1H), 1.61 (s, 3H), 1.55 – 1.13 (m, 4H), 1.02 – 0.90 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.02, 131.69, 129.65, 129.57, 124.25, 124.21, 119.86, 119.84, 119.64, 119.61, 114.44, 114.42, 113.78, 113.76, 65.47, 65.11, 64.77, 64.56, 48.07, 47.95, 47.41, 47.10, 46.47, 46.30, 45.85, 45.31, 39.56, 39.22, 38.79, 38.70, 37.47, 37.35, 36.57, 36.28, 33.64, 33.49, 30.54, 30.40, 30.32, 30.26, 30.18, 29.92, 29.79, 28.96, 27.07, 26.36, 25.75, 25.34, 25.18, 25.12, 20.06, 19.93, 19.20, 19.04, 17.75, 17.74. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{22}H_{30}N_3$:336.2434, found: 336.2434.

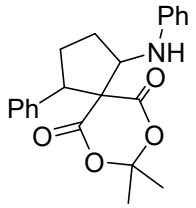
2-phenyl-5-(phenylamino)spiro[cyclopentane-1,2'-indene]-1',3'-dione (4aa)



Yellow solid; 93.2 mg, 51% yield; dr 1:2.6; mp 136 – 138 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.64 (dd, *J* = 5.9, 2.8 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.53 – 7.50 (m, 2H), 7.10 – 7.06 (m, 2H), 7.03 (td, *J* = 8.8, 8.0, 3.2 Hz, 3H), 6.95 – 6.88 (m, 2H), 6.50 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 8.1 Hz, 2H), 4.79 (q, *J* = 8.9 Hz, 1H), 3.87 (dd, *J* = 12.0, 7.7 Hz, 1H), 3.75 (d, *J* = 9.4 Hz, 1H), 2.88 – 2.75 (m, 1H), 2.68 – 2.59 (m, 1H), 2.26 – 2.17 (m, 2H). **^{13}C NMR (126**

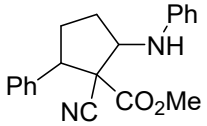
MHz, $CDCl_3$) δ 203.52, 203.41, 202.69, 202.38, 146.47, 146.30, 143.23, 142.59, 142.56, 142.39, 137.61, 137.50, 135.11, 135.02, 134.97, 129.00, 128.93, 128.18, 128.05, 127.93, 127.14, 127.02, 122.46, 122.40, 122.30, 122.17, 118.29, 118.26, 114.40, 114.37, 70.06, 67.18, 62.93, 62.30, 55.45, 53.53, 35.28, 32.41, 29.12, 28.15. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{25}H_{22}NO_2$: 368.1645, found: 368.1645.

8,8-dimethyl-1-phenyl-4-(phenylamino)-7,9-dioxaspiro[4.5]decane-6,10-dione (4ab)



White solid; 54.9 mg, 30% yield; dr 1:2.7; mp 124 – 126 ℃; column chromatography eluent, petroleum ether/EtOAc = 40:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.23 (m, 5H), 7.16 – 7.12 (m, 2H), 6.73 – 6.69 (m, 1H), 6.64 (dd, *J* = 7.0, 1.8 Hz, 2H), 5.11 (td, *J* = 10.1, 8.2 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.95 (d, *J* = 10.7 Hz, 1H), 2.79 (qd, *J* = 12.1, 6.4 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.23 – 2.05 (m, 2H), 1.07 (s, 3H), 0.71 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.97, 169.52, 165.73, 145.87, 145.83, 136.80, 136.74, 129.58, 129.52, 128.92, 128.88, 128.58, 128.34, 128.23, 128.20, 119.20, 118.94, 114.79, 114.56, 106.02, 105.91, 66.45, 66.25, 65.58, 62.24, 59.50, 57.00, 35.12, 32.79, 29.44, 28.80, 28.67, 28.51, 28.35, 28.17. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{22}H_{24}NO_4$: 366.1699, found: 366.1700.

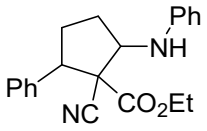
methyl 1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxylate (4ac)



White solid; 96.3 mg, 60% yield; dr 1:1.3; mp 123 – 126 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.31 (m, 5H), 7.21 – 7.18 (m, 2H), 6.75 – 6.72 (m, 2H), 6.68 (dt, *J* = 7.7, 1.1 Hz, 1H), 4.82 (ddd, *J* = 10.2, 8.7, 7.2 Hz, 1H), 4.02 – 3.99 (m, 1H), 3.99 – 3.96 (m, 1H), 3.29 (s, 3H), 2.69 – 2.60 (m, 1H), 2.29 – 2.19 (m, 2H), 1.80 – 1.69 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.12, 167.77, 145.62, 145.11, 136.95, 136.65, 129.41, 129.38, 128.74, 128.68,

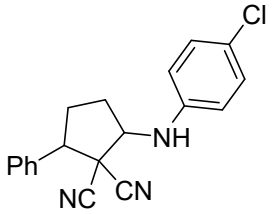
128.21, 128.07, 128.00, 127.86, 119.14, 119.03, 118.91, 116.00, 114.48, 113.78, 65.72, 64.63, 62.21, 59.09, 53.48, 53.03, 52.30, 51.94, 34.42, 30.40, 28.52, 26.52. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{21}N_2O_2$: 321.1597, found: 321.1597.

ethyl 1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxylate (4ad)



White solid; 80.4 mg, 48% yield; dr 1:1.3; mp 83 – 87 ℃; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 5H), 7.21 – 7.16 (m, 2H), 6.74 – 6.72 (m, 2H), 6.70 – 6.67 (m, 1H), 4.84 – 4.79 (m, 1H), 4.06 (d, *J* = 11.1 Hz, 1H), 3.94 – 3.86 (m, 2H), 3.69 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.65 – 2.59 (m, 1H), 2.29 – 2.17 (m, 2H), 1.80 – 1.69 (m, 1H), 0.84 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.53, 167.33, 145.71, 145.33, 137.10, 136.71, 129.37, 129.35, 128.68, 128.66, 128.15, 128.02, 127.99, 127.89, 119.19, 119.07, 118.81, 116.09, 114.47, 113.73, 65.72, 64.29, 63.01, 62.89, 62.43, 59.15, 52.50, 52.00, 34.53, 30.39, 28.48, 26.53, 13.50, 13.28. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{21}H_{23}N_2O$: 335.1754, found: 335.1755.

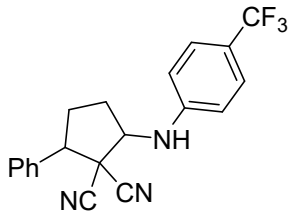
2-((4-chlorophenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4ag)



White solid; 135.3 mg, 84% yield; dr 1:1.1; mp 186 – 189 ℃; column chromatography eluent, petroleum ether/ EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 – 7.41 (m, 5H), 7.20 (d, *J* = 6.6 Hz, 2H), 6.80 – 6.77 (m, 1H), 6.69 – 6.66 (m, 1H), 4.72 (q, *J* = 9.3 Hz, 1H), 4.10 (d, *J* = 10.0 Hz, 1H), 3.75 – 3.70 (m, 1H), 2.64 – 2.54 (m, 1H), 2.32 – 2.27 (m, 2H), 2.01 – 1.91 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.47, 143.40, 134.64, 134.28, 129.61, 129.50, 129.20, 129.13, 128.00, 124.67, 124.50, 115.61, 115.50, 114.84, 114.77, 114.20, 112.28, 65.39, 65.17, 54.98, 53.58, 49.04, 47.64, 33.55, 30.25, 28.04, 26.06, 26.02. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{19}H_{17}ClN_3$:

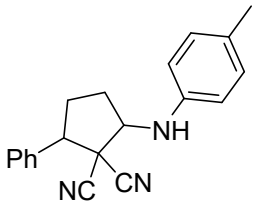
322.1105, found: 322.1104.

2-phenyl-5-((4-(trifluoromethyl)phenyl)amino)cyclopentane-1,1-dicarbonitrile (4ah)



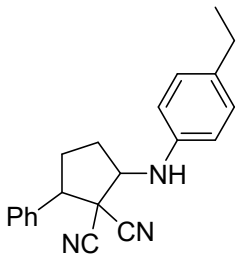
Brown oil; 58.7 mg, 33% yield; dr 1:2.9; column chromatography eluent, petroleum ether/ EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 3.6 Hz, 7H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.71 (q, *J* = 8.1 Hz, 1H), 4.49 (d, *J* = 8.5 Hz, 1H), 3.74 (dt, *J* = 8.4, 6.4 Hz, 1H), 2.81 – 2.71 (m, 1H), 2.36 – 2.28 (m, 2H), 1.90 – 1.79 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** 147.52, 134.50, 129.28, 129.22, 129.17, 128.18, 128.09, 128.02 (q, *J* = 253.83 Hz) 128.00, 127.11 (q, *J* = 3.7 Hz), 114.64, 114.07, 113.36, 113.09, 64.68, 64.06, 55.03, 53.61, 47.67, 33.49, 30.26, 28.04, 25.99. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -61.39. **HRMS (ESI-TOF)**: *m/z* [M + H] $^{+}$ calcd for $C_{20}H_{17}F_3N_3$: 356.1369, found: 356.1369.

2-phenyl-5-(p-tolylamino)cyclopentane-1,1-dicarbonitrile (4ai)



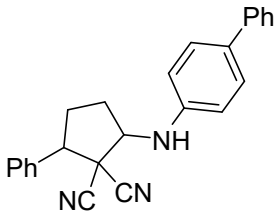
White solid; 105.7 mg, 70% yield; dr 1:12; mp 133 – 136 ℃; column chromatography eluent, petroleum ether/ EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 – 7.36 (m, 5H), 7.08 – 7.01 (m, 2H), 6.81 – 6.75 (m, 2H), 4.73 (q, *J* = 9.4 Hz, 1H), 3.95 (d, *J* = 10.2 Hz, 1H), 3.67 (dd, *J* = 11.6, 8.3 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.49 – 2.38 (m, 1H), 2.31 – 2.20 (m, 4H), 2.00 – 1.89 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.44, 134.55, 130.09, 129.45, 129.08, 128.04, 115.58, 114.85, 112.45, 65.82, 53.56, 49.09, 30.29, 26.08, 20.49. **HRMS (ESI-TOF)**: *m/z* [M + H] $^{+}$ calcd for $C_{20}H_{20}N_3$: 302.1651, found: 302.1650.

2-((4-ethylphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4aj)



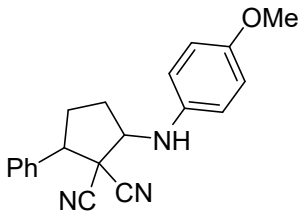
White solid; 132.8 mg, 84% yield; dr 1:9.2; mp 137 – 139 ℃; column chromatography eluent, petroleum ether/ EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 – 7.45 (m, 2H), 7.45 – 7.36 (m, 3H), 7.10 – 7.04 (m, 2H), 6.82 – 6.78 (m, 2H), 4.74 (q, *J* = 9.4 Hz, 1H), 3.96 (d, *J* = 10.1 Hz, 1H), 3.68 (dd, *J* = 11.6, 8.3 Hz, 1H), 2.62 – 2.52 (m, 3H), 2.49 – 2.39 (m, 1H), 2.30 – 2.21 (m, 1H), 2.00 – 1.90 (m, 1H), 1.19 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.66, 135.96, 134.55, 129.08, 128.91, 128.04, 115.58, 114.72, 112.46, 65.77, 53.55, 49.16, 30.34, 28.06, 26.08, 15.80. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{21}H_{22}N_3$: 316.1808, found: 316.1808.

2-([1,1'-biphenyl]-4-ylamino)-5-phenylcyclopentane-1,1-dicarbonitrile (4ak)



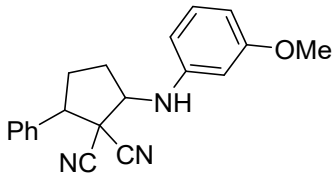
Yellow solid; 163.8 mg, 90% yield; dr 1:3.4; mp 168 – 170 ℃; column chromatography eluent, petroleum ether /EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 – 7.49 (m, 4H), 7.45 – 7.39 (m, 7H), 7.28 (dq, *J* = 7.9, 1.9 Hz, 1H), 6.84 – 6.80 (m, 2H), 4.72 (q, *J* = 8.1 Hz, 1H), 4.24 (d, *J* = 8.4 Hz, 1H), 3.73 (dd, *J* = 10.8, 7.5 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.32 – 2.25 (m, 2H), 1.87 – 1.78 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.30, 140.75, 134.80, 132.65, 129.12, 128.75, 128.36, 128.05, 126.51, 114.04, 65.47, 55.00, 47.85, 33.61, 28.08. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{25}H_{22}N_3$: 364.1808, found: 364.1807.

2-((4-methoxyphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4al)



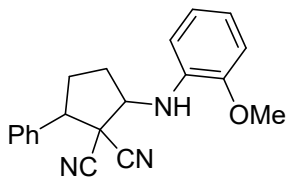
White solid; 127.3 mg, 80% yield; dr 1:6.2; mp 117 – 119 ℃; column chromatography eluent, petroleum ether/EtOAc = 100:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 – 7.35 (m, 5H), 6.86 – 6.80 (m, 4H), 4.66 (q, *J* = 9.4 Hz, 1H), 3.82 (d, *J* = 9.8 Hz, 1H), 3.75 (s, 3H), 3.65 (dd, *J* = 11.6, 8.3 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.48 – 2.37 (m, 1H), 2.30 – 2.21 (m, 1H), 1.99 – 1.89 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.02, 138.58, 134.55, 129.07, 128.02, 116.88, 115.52, 115.03, 112.47, 67.11, 55.68, 53.53, 49.01, 30.21, 26.09. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{20}N_3O$: 318.1601, found: 318.1600.

2-((3-methoxyphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4am)



White solid; 146.2 mg, 92% yield; dr 1:9.3; mp 117 – 119 ℃; column chromatography eluent, petroleum ether/ EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 – 7.38 (m, 5H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.43 – 6.39 (m, 1H), 6.36 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.31 (t, *J* = 2.3 Hz, 1H), 4.67 (q, *J* = 8.2 Hz, 1H), 4.20 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 3H), 3.72 (dd, *J* = 10.4, 7.9 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.31 – 2.23 (m, 2H), 1.86 – 1.74 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.98, 146.33, 134.85, 130.56, 129.08, 128.04, 106.38, 105.15, 99.86, 65.45, 55.23, 55.03, 47.78, 33.55, 28.08. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{20}N_3O$: 318.1601, found: 318.1602.

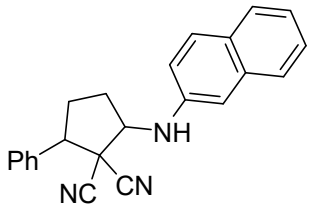
2-((2-methoxyphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4an)



White solid; 144.7 mg, 91% yield; dr 1:4.2; mp 127 – 130 ℃; column chromatography

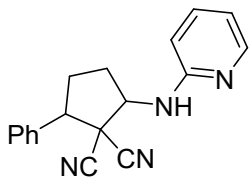
eluent, petroleum ether/ EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 – 7.37 (m, 6H), 6.96 – 6.89 (m, 1H), 6.84 – 6.78 (m, 2H), 4.82 – 4.73 (m, 1H), 4.68 (q, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 3.74 (dd, *J* = 11.0, 7.5 Hz, 1H), 2.79 – 2.71 (m, 1H), 2.34 – 2.26 (m, 2H), 1.95 – 1.84 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.67, 134.97, 134.84, 129.05, 128.07, 121.49, 119.02, 111.41, 110.10, 65.30, 55.61, 54.84, 47.99, 33.65, 28.08. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{20}N_3O$: 318.1601, found: 318.1601.

2-(naphthalen-2-ylamino)-5-phenylcyclopentane-1,1-dicarbonitrile (4ao)



Yellow solid; 101.4 mg, 60% yield; dr 1:1.1; mp 65 – 69 ℃; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.69 (dd, *J* = 9.1, 6.8 Hz, 6H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.45 – 7.37 (m, 10H), 7.29 – 7.24 (m, 2H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.96 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.87 (q, *J* = 9.3 Hz, 1H), 4.79 (q, *J* = 8.1 Hz, 1H), 4.33 (d, *J* = 8.5 Hz, 1H), 4.27 (d, *J* = 9.9 Hz, 1H), 3.72 (t, *J* = 6.3 Hz, 1H), 3.69 (d, *J* = 7.7 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.65 – 2.55 (m, 1H), 2.50 – 2.40 (m, 1H), 2.35 – 2.20 (m, 3H), 2.02 – 1.93 (m, 1H), 1.85 – 1.75 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.59, 142.50, 134.79, 134.70, 134.44, 129.71, 129.60, 129.17, 129.12, 129.10, 128.57, 128.45, 128.07, 128.05, 127.71, 127.69, 126.76, 126.55, 126.41, 123.26, 123.22, 117.74, 117.36, 115.61, 114.95, 114.31, 112.44, 107.61, 106.90, 65.34, 64.89, 55.19, 53.70, 49.11, 47.67, 33.59, 30.35, 28.13, 26.15. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{23}H_{20}N_3$: 338.1652, found: 338.1651.

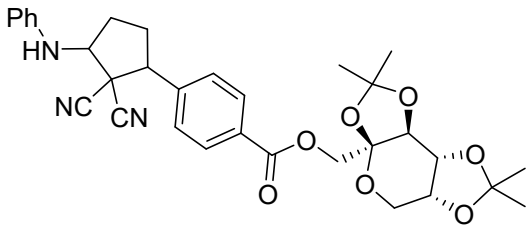
2-phenyl-5-(pyridin-2-ylamino)cyclopentane-1,1-dicarbonitrile (4ap)



Brown oil; 112.7 mg, 78% yield; dr 1:1.9; column chromatography eluent, petroleum

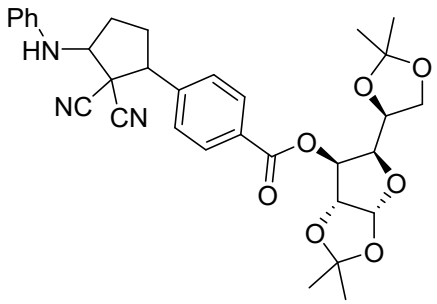
ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.46 – 7.38 (m, 6H), 6.71 (dd, *J* = 7.7, 5.1 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.56 (d, *J* = 9.3 Hz, 1H), 4.89 (d, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 11.5, 8.3 Hz, 1H), 2.58 – 2.49 (m, 1H), 2.32 – 2.23 (m, 2H), 2.04 – 1.93 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.03, 155.99, 148.08, 147.79, 137.76, 137.73, 135.01, 134.75, 129.04, 128.99, 128.92, 128.12, 115.16, 115.05, 115.02, 114.90, 114.87, 113.00, 109.03, 108.56, 62.16, 60.51, 54.97, 53.45, 49.24, 48.09, 32.34, 29.37, 28.27, 26.12. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{18}H_{17}N_4$: 289.1448, found: 289.1448.

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



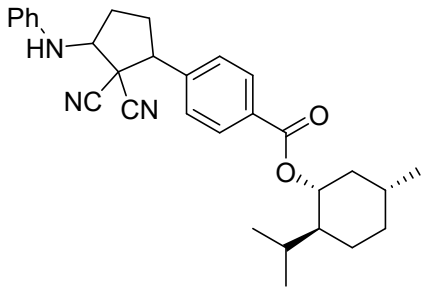
Yellow oil; 160.8 mg, 56% yield; dr 1:1.2; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 8.1 Hz, 3H), 7.53 (dd, *J* = 21.9, 8.2 Hz, 3H), 6.89 – 6.83 (m, 3H), 6.76 (d, *J* = 8.0 Hz, 3H), 4.81 (q, *J* = 9.3 Hz, 1H), 4.75 – 4.62 (m, 5H), 4.46 (q, *J* = 2.4, 1.9 Hz, 2H), 4.38 – 4.32 (m, 3H), 4.29 – 4.24 (m, 2H), 4.20 (d, *J* = 8.4 Hz, 1H), 4.08 (d, *J* = 10.0 Hz, 1H), 3.96 (dd, *J* = 13.0, 1.9 Hz, 2H), 3.83 – 3.73 (m, 4H), 2.81 – 2.71 (m, 1H), 2.67 – 2.57 (m, 1H), 2.51 – 2.40 (m, 1H), 2.36 – 2.27 (m, 2H), 2.06 – 1.94 (m, 1H), 1.91 – 1.81 (m, 1H), 1.55 (s, 6H), 1.45 (s, 6H), 1.39 (s, 6H), 1.34 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.37, 144.72, 144.65, 139.97, 139.63, 130.48, 129.73, 129.65, 128.15, 120.17, 119.88, 114.57, 113.74, 109.21, 108.89, 101.63, 70.79, 70.64, 70.11, 65.70, 65.64, 65.62, 65.46, 61.40, 54.66, 54.65, 53.25, 48.79, 47.50, 33.59, 30.27, 27.99, 27.96, 26.52, 26.00, 25.97, 25.89, 25.59, 25.56, 24.03. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{32}H_{36}N_3O_7$: 574.2548, found: 574.2547.

(3aR,5R,6S,6aR)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate (4ca)



Yellow oil; 152.1 mg, 53% yield; dr 1:1.1; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.2 Hz, 4H), 7.56 (dd, *J* = 22.3, 8.2 Hz, 4H), 7.29 – 7.21 (m, 4H), 6.87 (d, *J* = 8.0 Hz, 3H), 6.76 (d, *J* = 8.0 Hz, 2H), 5.95 (t, *J* = 3.3 Hz, 2H), 5.51 (d, *J* = 2.7 Hz, 2H), 4.81 (q, *J* = 9.3 Hz, 1H), 4.73 (q, *J* = 8.0 Hz, 1H), 4.63 (td, *J* = 3.8, 1.9 Hz, 2H), 4.36 (ddd, *J* = 7.6, 5.2, 2.4 Hz, 2H), 4.32 (dd, *J* = 8.1, 2.9 Hz, 2H), 4.19 (dd, *J* = 8.4, 3.4 Hz, 1H), 4.16 – 4.06 (m, 5H), 3.82 – 3.73 (m, 2H), 2.84 – 2.72 (m, 1H), 2.69 – 2.58 (m, 1H), 2.53 – 2.39 (m, 1H), 2.39 – 2.26 (m, 3H), 2.07 – 1.94 (m, 1H), 1.91 – 1.81 (m, 1H), 1.56 (s, 6H), 1.42 (s, 6H), 1.32 (s, 6H), 1.28 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.63, 164.59, 144.68, 144.61, 140.35, 140.33, 140.01, 130.44, 130.32, 130.25, 129.75, 129.66, 128.31, 120.20, 119.92, 114.60, 114.54, 113.96, 113.72, 112.43, 112.12, 109.51, 105.14, 83.37, 79.94, 72.55, 67.32, 65.62, 65.58, 65.43, 54.68, 54.60, 53.26, 53.24, 48.84, 48.80, 47.54, 47.52, 33.64, 33.59, 30.29, 30.24, 28.01, 27.95, 26.90, 26.74, 26.21, 25.97, 25.93, 25.24. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{32}H_{36}N_3O_7$: 574.2548, found: 574.2547.

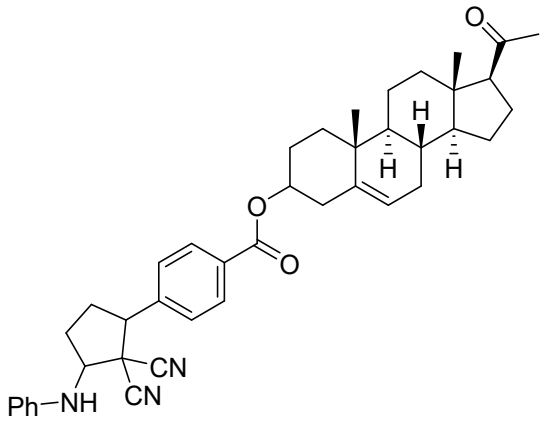
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate(4da)



Green oil; 82.9 mg, 35% yield; dr 1:1.2; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.5 Hz, 4H), 7.55 (d,

J = 8.2 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.25 (dt, *J* = 8.7, 7.3 Hz, 4H), 6.89 – 6.83 (m, 3H), 6.76 (d, *J* = 8.1 Hz, 2H), 4.94 (td, *J* = 10.9, 4.4 Hz, 2H), 4.80 (q, *J* = 9.4 Hz, 1H), 4.72 (d, *J* = 7.9 Hz, 1H), 4.20 (d, *J* = 8.4 Hz, 1H), 4.09 (d, *J* = 10.0 Hz, 1H), 3.80 – 3.72 (m, 2H), 2.81 – 2.71 (m, 1H), 2.66 – 2.56 (m, 1H), 2.46 (dtd, *J* = 13.9, 11.6, 6.1 Hz, 1H), 2.35 – 2.25 (m, 3H), 2.12 (ddd, *J* = 11.9, 5.5, 3.0 Hz, 2H), 2.04 – 1.92 (m, 3H), 1.89 – 1.80 (m, 1H), 1.77 – 1.69 (m, 4H), 1.62 – 1.49 (m, 5H), 1.18 – 1.06 (m, 4H), 0.93 (dd, *J* = 6.8, 3.7 Hz, 13H), 0.80 (dd, *J* = 6.9, 1.7 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.50, 165.47, 144.76, 144.69, 139.46, 139.13, 131.65, 130.29, 129.73, 129.65, 129.65, 128.07, 120.13, 119.85, 114.52, 113.73, 75.17, 65.57, 65.40, 54.66, 54.63, 53.28, 48.87, 48.85, 47.59, 47.56, 47.29, 40.96, 34.31, 33.60, 33.58, 31.48, 30.28, 30.25, 28.04, 26.48, 26.45, 26.01, 23.59, 23.57, 22.06, 20.82, 16.49, 16.47. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{30}H_{36}N_3O_2$: 470.2802, found: 470.2805.

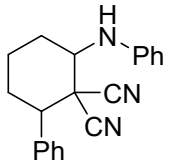
(8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate (4ea)



Yellow solid; 94.3 mg, 30% yield; dr 1:1.7; mp 196 – 199 ℃; column chromatography eluent, petroleum ether/EtOAc = 50:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 – 8.09 (m, 2H), 7.53 (dd, *J* = 22.3, 8.3 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 6.86 (td, *J* = 7.7, 1.5 Hz, 2H), 6.78 – 6.74 (m, 1H), 5.46 – 5.40 (m, 1H), 4.87 (dtt, *J* = 11.6, 8.1, 4.5 Hz, 1H), 4.82 – 4.69 (m, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.83 – 3.72 (m, 1H), 2.83 – 2.59 (m, 1H), 2.55 (t, *J* = 9.0 Hz, 1H), 2.47 (d, *J* = 8.3 Hz, 2H), 2.37 – 2.29 (m, 2H), 2.23 – 2.17 (m, 1H), 2.13 (s, 3H), 2.09 – 1.99 (m, 3H), 1.94 (dt, *J* = 13.4, 3.6 Hz, 1H),

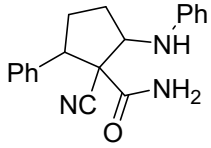
1.77 – 1.63 (m, 4H), 1.62 – 1.46 (m, 5H), 1.30 (q, *J* = 7.0 Hz, 1H), 1.25 – 1.17 (m, 1H), 1.07 (s, 4H), 0.65 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 209.59, 209.54, 165.37, 165.35, 144.68, 139.59, 139.56, 131.49, 130.53, 130.28, 129.72, 129.64, 128.04, 122.58, 120.13, 119.85, 114.54, 113.73, 74.73, 65.56, 65.40, 63.71, 63.68, 56.87, 56.84, 54.66, 53.29, 49.92, 48.87, 47.58, 44.01, 38.82, 38.79, 38.16, 38.08, 37.04, 36.99, 36.68, 34.14, 33.57, 31.94, 31.85, 31.81, 31.58, 30.29, 27.99, 27.85, 27.80, 25.98, 24.51, 22.86, 22.35, 21.08, 19.38, 14.14, 14.08, 13.25. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{41}H_{48}N_3O_3$: 630.3691, found: 630.3690.

2-phenyl-6-(phenylamino)cyclohexane-1,1-dicarbonitrile (6)



Colorless oil; 22.6 mg, 15% yield; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 – 7.38 (m, 5H), 7.25 – 7.21 (m, 2H), 6.87 – 6.79 (m, 3H), 3.96 (ddd, *J* = 11.7, 10.3, 3.9 Hz, 1H), 3.76 (d, *J* = 10.3 Hz, 1H), 3.11 (dd, *J* = 12.7, 3.2 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.14 – 1.97 (m, 3H), 1.74 – 1.63 (m, 1H), 1.62 – 1.55 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.40, 137.20, 129.53, 128.98, 128.37, 119.94, 115.11, 114.78, 113.23, 60.46, 50.60, 49.78, 30.05, 27.41, 24.04. **HRMS (ESI-TOF)**: *m/z* [M + H] $^+$ calcd for $C_{20}H_{20}N_3$: 302.1651, found: 302.1651.

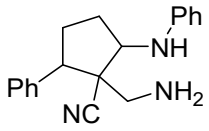
1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxamide (9a)



White solid; 17.1 mg, 28% yield; mp 147 – 149 ℃; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.30 (m, 5H), 7.18 – 7.14 (m, 2H), 6.78 – 6.70 (m, 3H), 5.92 (s, 1H), 5.39 (s, 1H), 4.78 (q, *J* = 9.4 Hz, 1H), 4.01 – 3.92 (m, 2H), 2.62 – 2.52 (m, 1H), 2.45 – 2.34 (m, 1H), 2.28 – 2.18 (m, 1H), 1.94 – 1.85 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.33, 145.81, 136.89, 129.43, 128.67, 128.12, 128.01, 118.87, 117.99, 113.96, 63.43, 63.19, 51.40, 31.02,

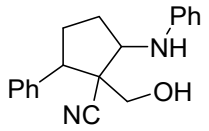
26.68. **HRMS (ESI-TOF)**: *m/z* [M + H] $^{+}$ calcd for $C_{19}H_{20}N_3O$: 306.1601, found: 306.1600.

1-(aminomethyl)-2-phenyl-5-(phenylamino)cyclopentane-1-carbonitrile (9b)



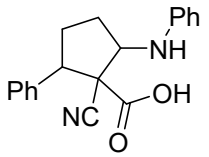
Yellow oil; 22.2 mg, 38% yield; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 7.15 (t, *J* = 7.7 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 2H), 3.85 (d, *J* = 6.3 Hz, 1H), 3.54 (d, *J* = 9.7 Hz, 1H), 3.23 (dt, *J* = 11.1, 5.9 Hz, 1H), 3.18 – 3.05 (m, 2H), 2.18 – 2.04 (m, 2H), 1.65 – 1.45 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.89, 136.31, 129.46, 129.35, 129.12, 127.84, 117.64, 112.79, 111.85, 111.78, 46.40, 43.32, 30.22, 29.71, 26.95. **HRMS (ESI-TOF)**: *m/z* [M + H] $^{+}$ calcd for $C_{19}H_{22}N_3$: 292.1808, found: 292.1808.

1-(hydroxymethyl)-2-phenyl-5-(phenylamino)cyclopentane-1-carbonitrile (9c)



White solid; 29.3 mg, 50% yield; mp 174 – 176 ℃; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 4.4 Hz, 4H), 7.32 (q, *J* = 4.2 Hz, 1H), 7.24 (dd, *J* = 9.1, 6.5 Hz, 2H), 6.83 (dd, *J* = 12.3, 7.7 Hz, 3H), 4.42 (t, *J* = 7.9 Hz, 1H), 3.86 (d, *J* = 11.6 Hz, 2H), 3.69 (d, *J* = 11.6 Hz, 1H), 3.51 (dd, *J* = 12.5, 6.3 Hz, 1H), 2.73 (s, 1H), 2.62 – 2.52 (m, 1H), 2.27 – 2.09 (m, 2H), 1.71 – 1.59 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.62, 137.80, 129.74, 128.68, 128.64, 127.90, 121.44, 119.55, 113.96, 63.48, 62.37, 53.24, 48.71, 34.17, 28.66. **HRMS (ESI-TOF)**: *m/z* [M + H] $^{+}$ calcd for $C_{19}H_{21}N_2O$: 293.1648, found: 293.1648.

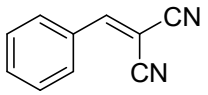
1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxylic acid (9d)



Yellow oil; 33.1 mg, 54% yield; column chromatography eluent, petroleum

ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.28 (m, 5H), 7.17 – 7.07 (m, 2H), 6.77 – 6.68 (m, 3H), 6.23 (s, 2H), 4.77 (t, *J* = 9.2 Hz, 1H), 3.83 (dd, *J* = 11.8, 8.5 Hz, 1H), 2.61 – 2.52 (m, 1H), 2.44 – 2.34 (m, 1H), 2.30 – 2.19 (m, 1H), 1.98 – 1.88 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.44, 145.37, 136.36, 129.41, 128.83, 128.35, 127.85, 119.49, 114.28, 64.61, 62.51, 52.23, 30.41, 27.02. **HRMS (ESI-TOF)**: *m/z* $[M + H]^+$ calcd for $C_{19}H_{22}N_2O_2$: 307.1441, found: 307.1445.

2-benzylidenemalononitrile(10)



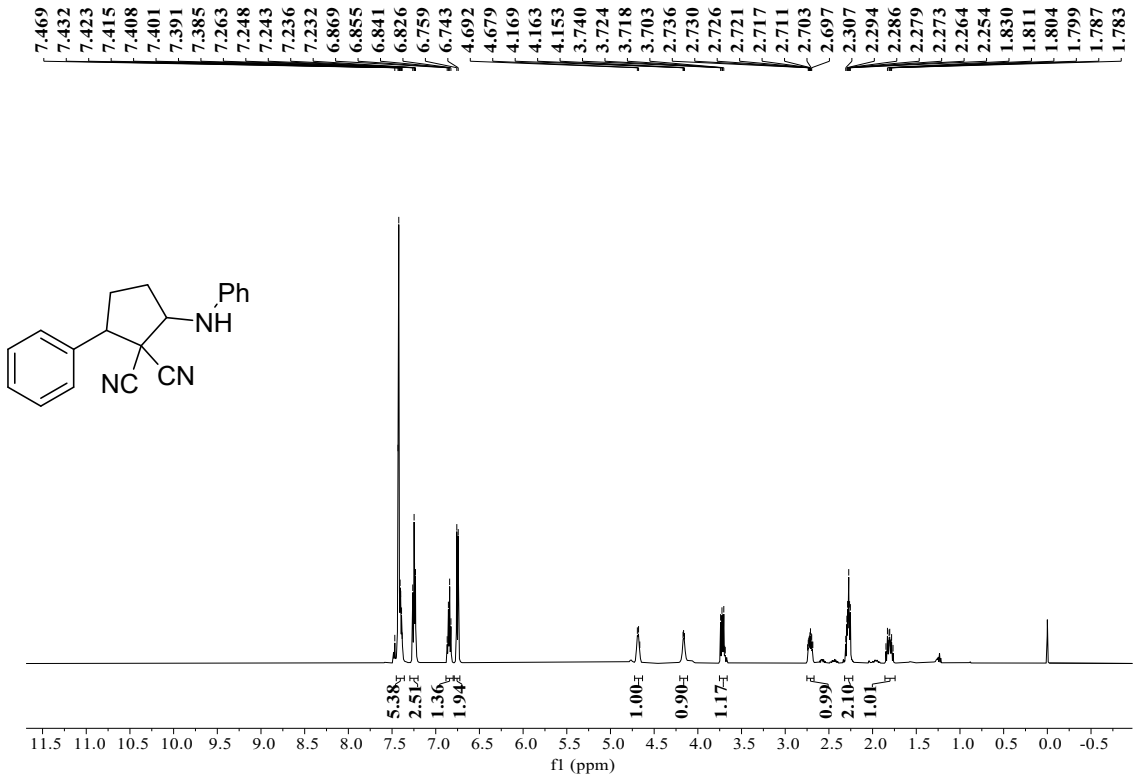
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 2H), 7.79 (d, J = 2.0 Hz, 1H), 7.64 (dd, J = 8.5, 6.5 Hz, 1H), 7.57 – 7.53 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.97, 134.67, 130.96, 130.76, 129.67, 113.73, 112.57, 82.91.

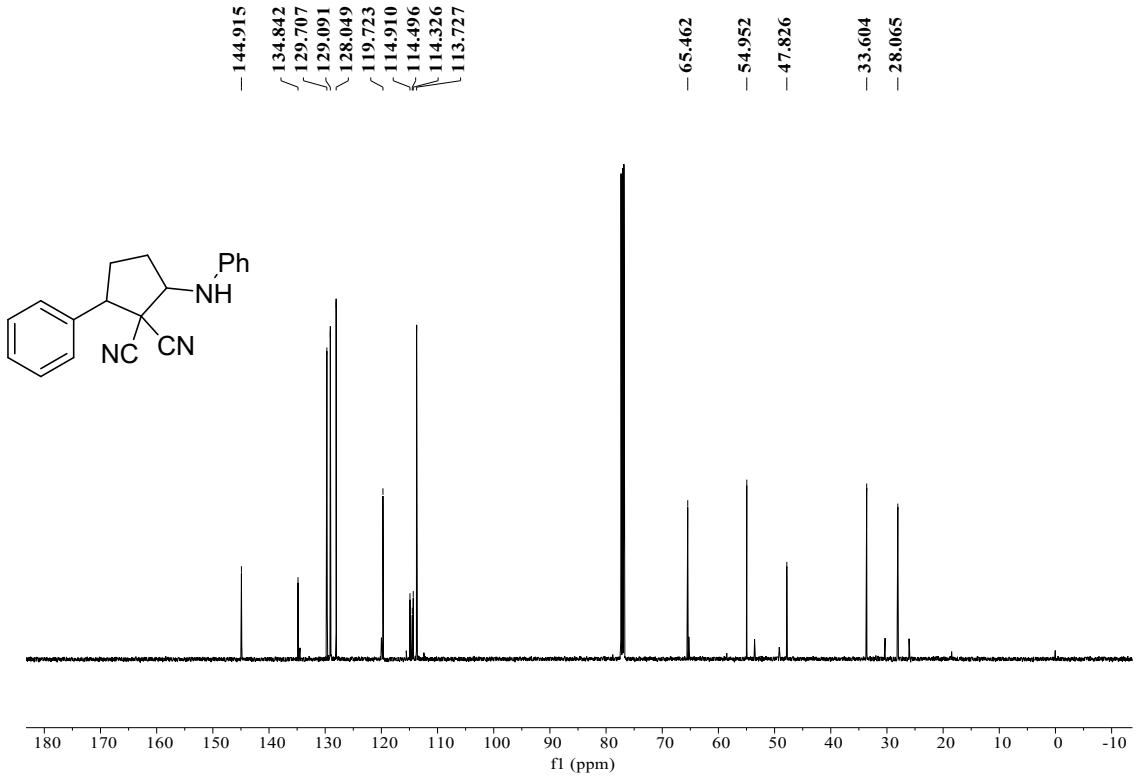
5. ^{1}H and ^{13}C NMR Spectra

2-phenyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4a)

^{1}H NMR (500 MHz, $CDCl_3$)

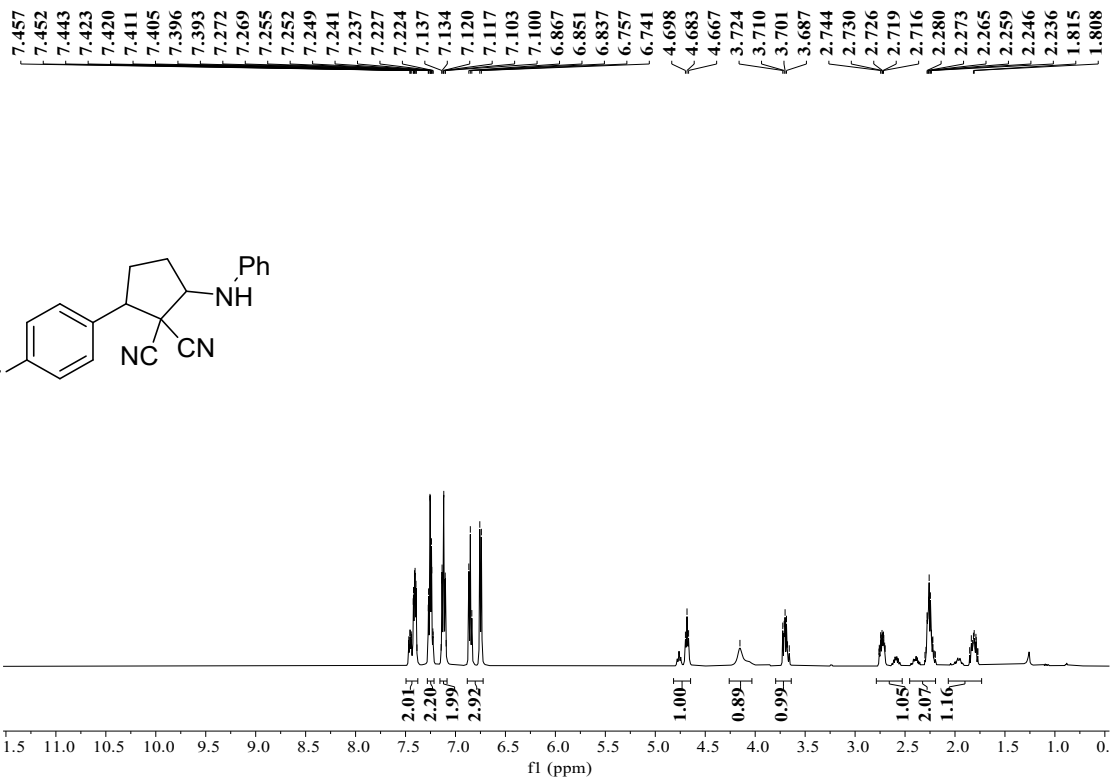


^{13}C NMR (126 MHz, $CDCl_3$)

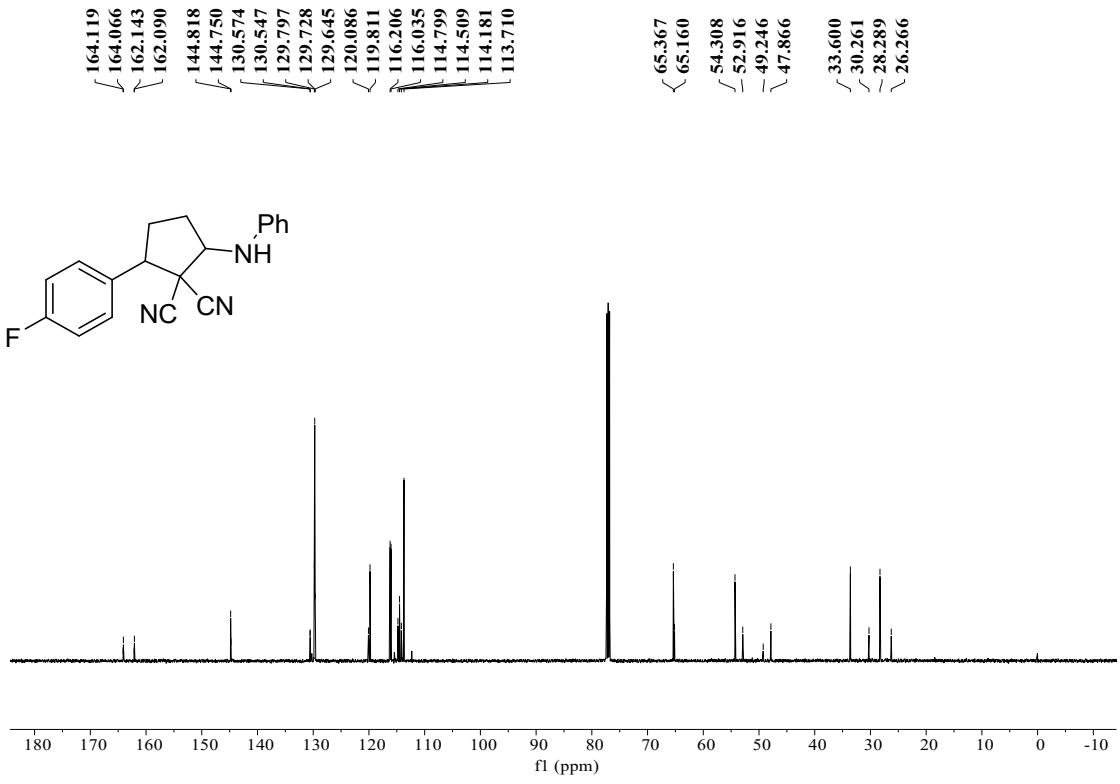


2-(4-fluorophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4b)

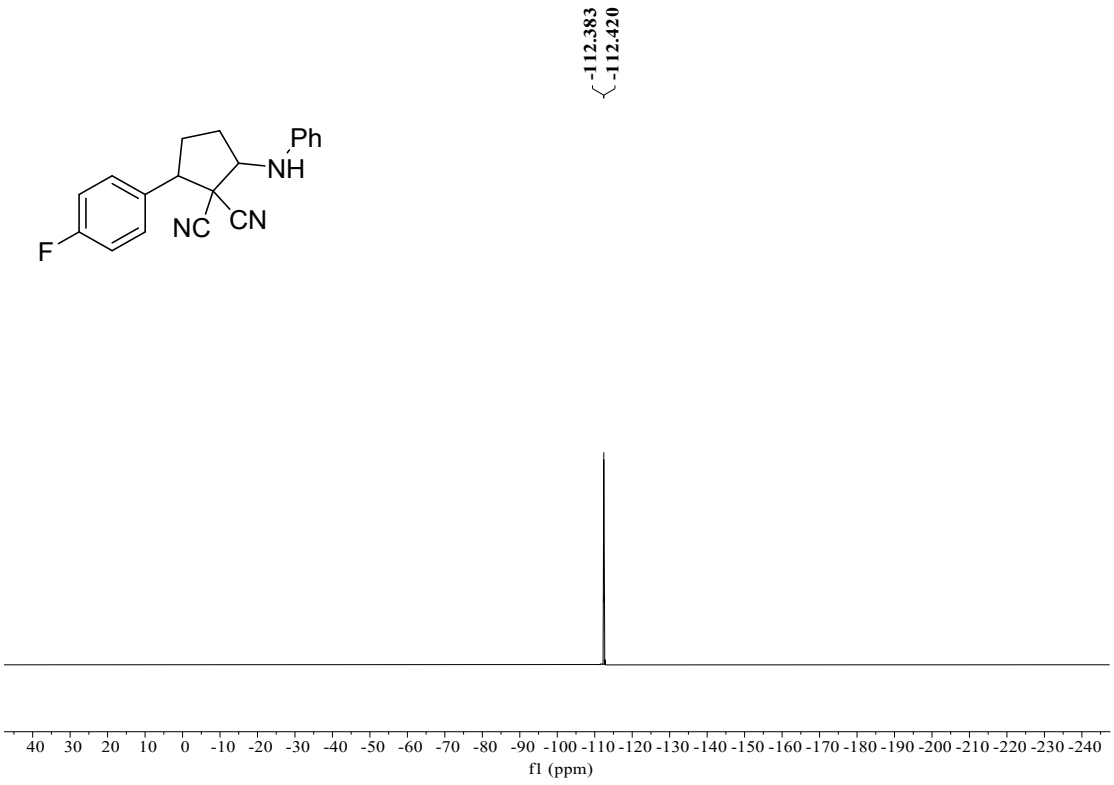
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

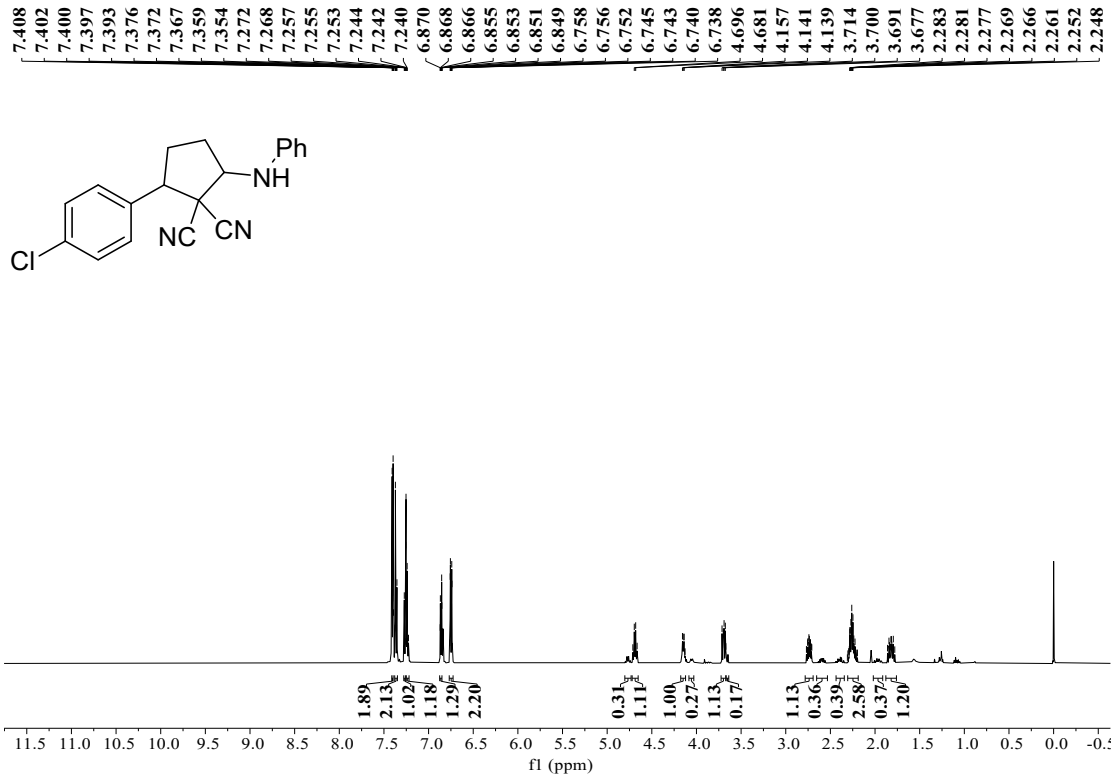


^{19}F NMR (470 MHz, $CDCl_3$)

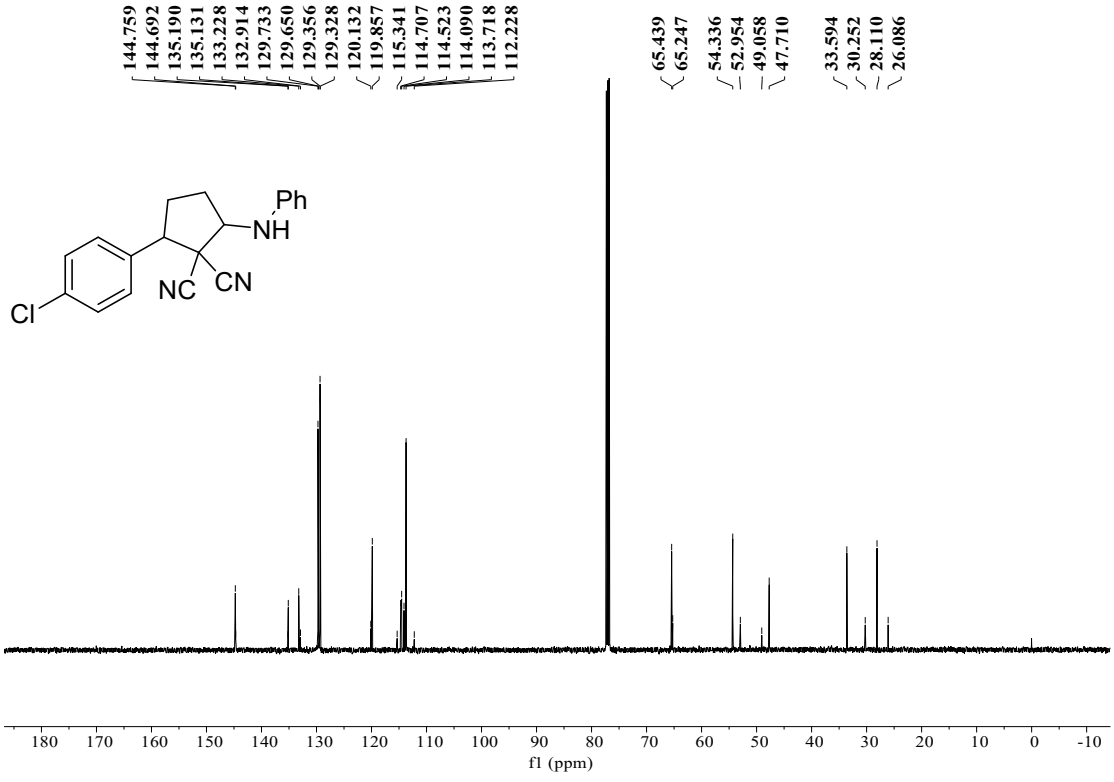


2-(4-chlorophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile(4c)

^{1}H NMR (500 MHz, $CDCl_3$)

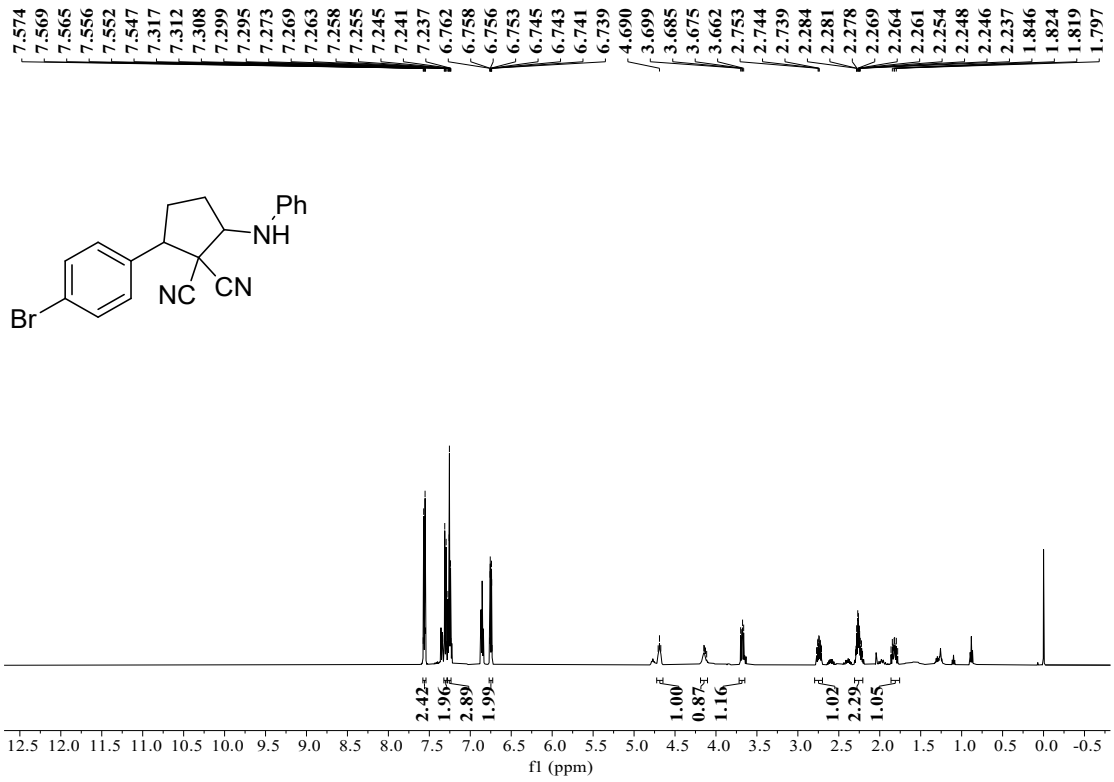


^{13}C NMR (126 MHz, $CDCl_3$)

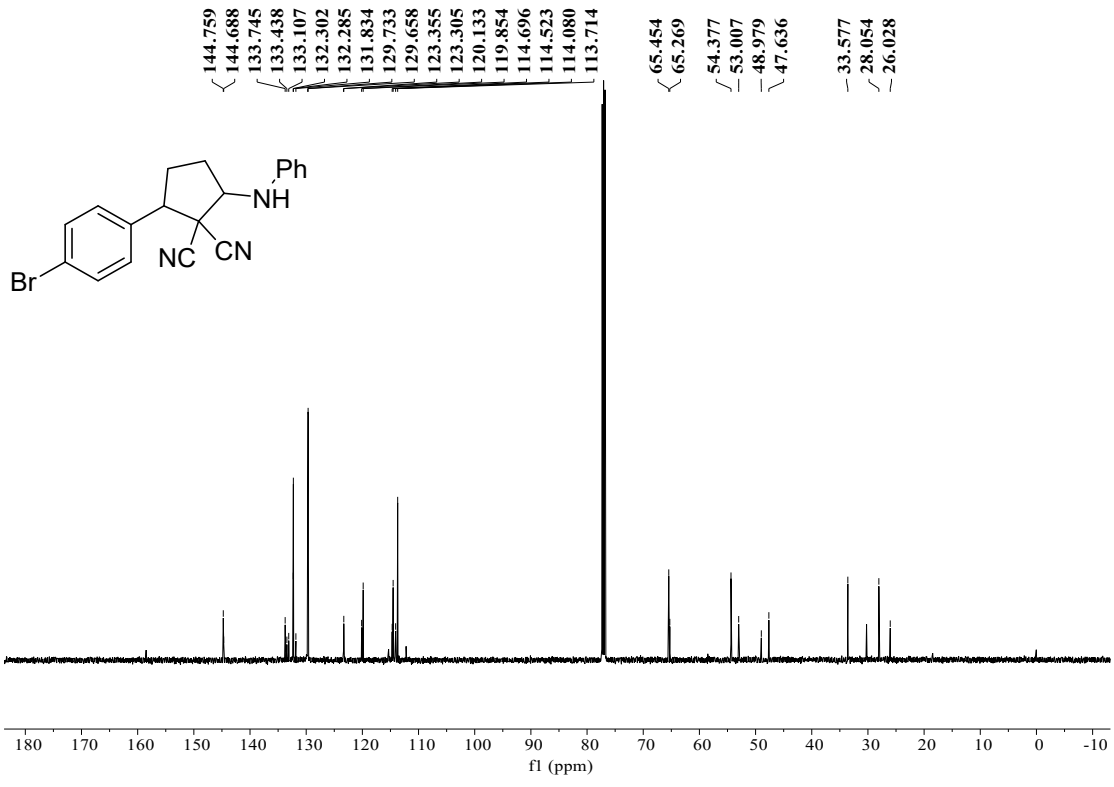


2-(4-bromophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4d)

^{1}H NMR (500 MHz, $CDCl_3$)

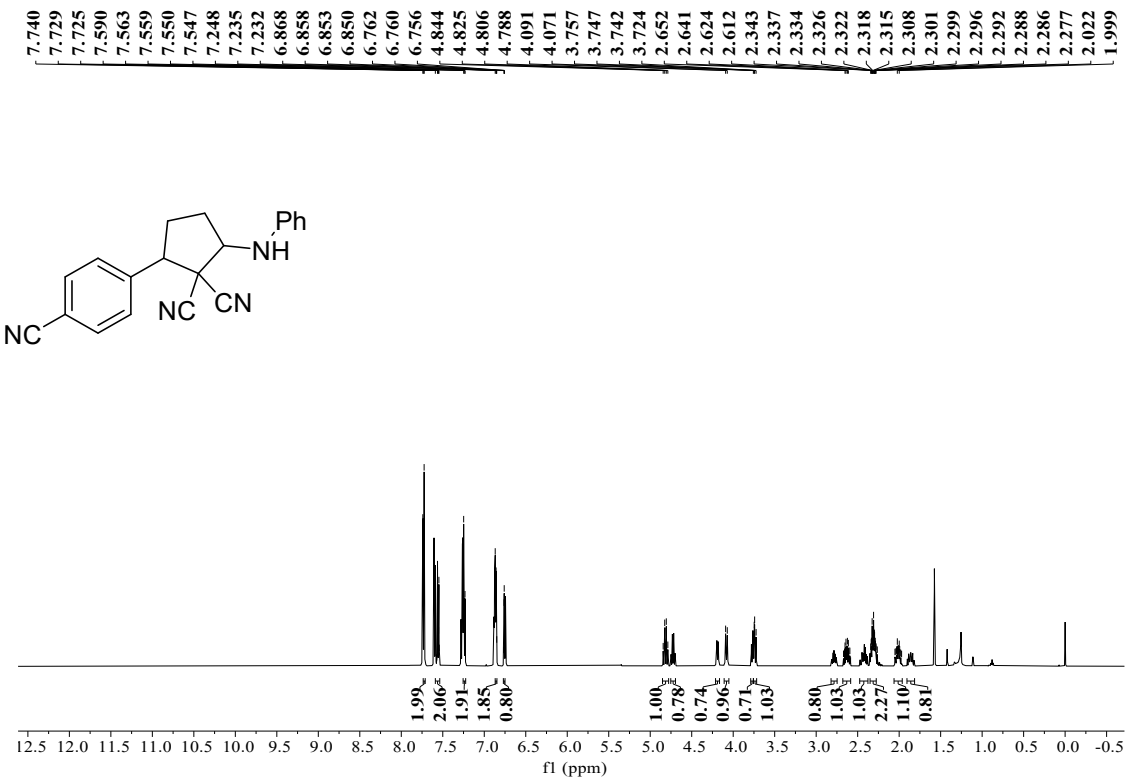


^{13}C NMR (126 MHz, $CDCl_3$)

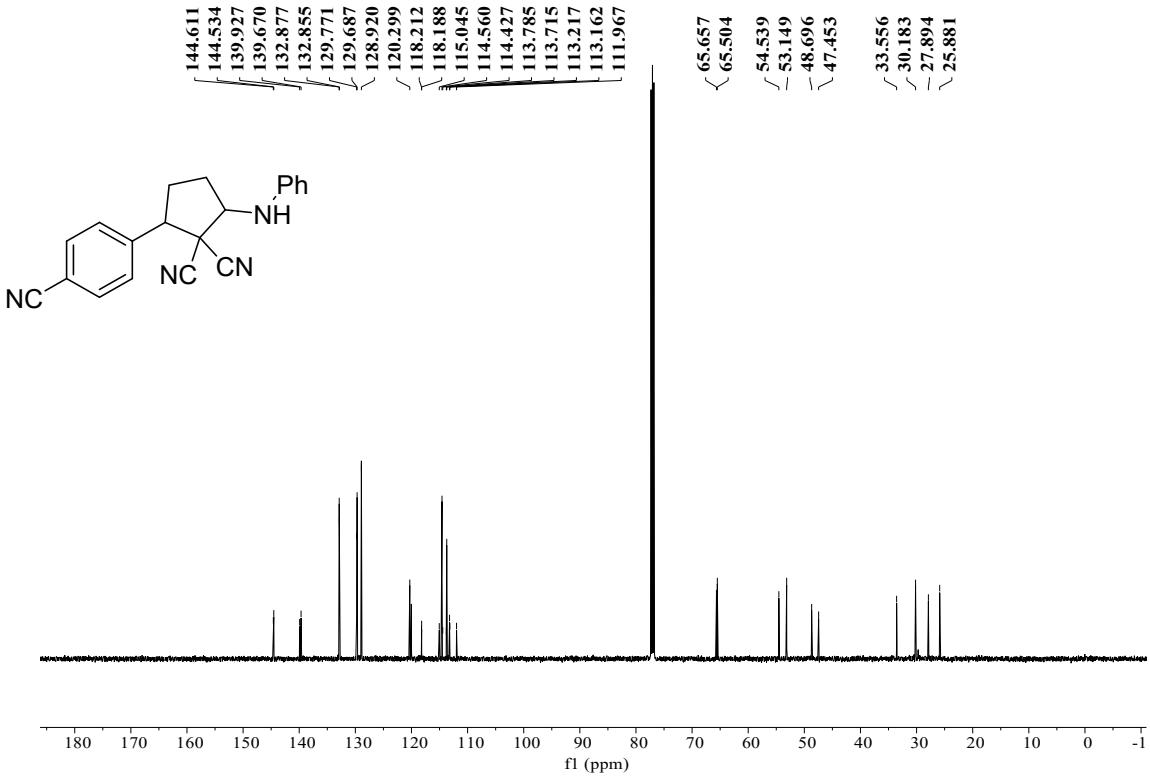


2-(4-cyanophenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4e)

^{1}H NMR (500 MHz, $CDCl_3$)

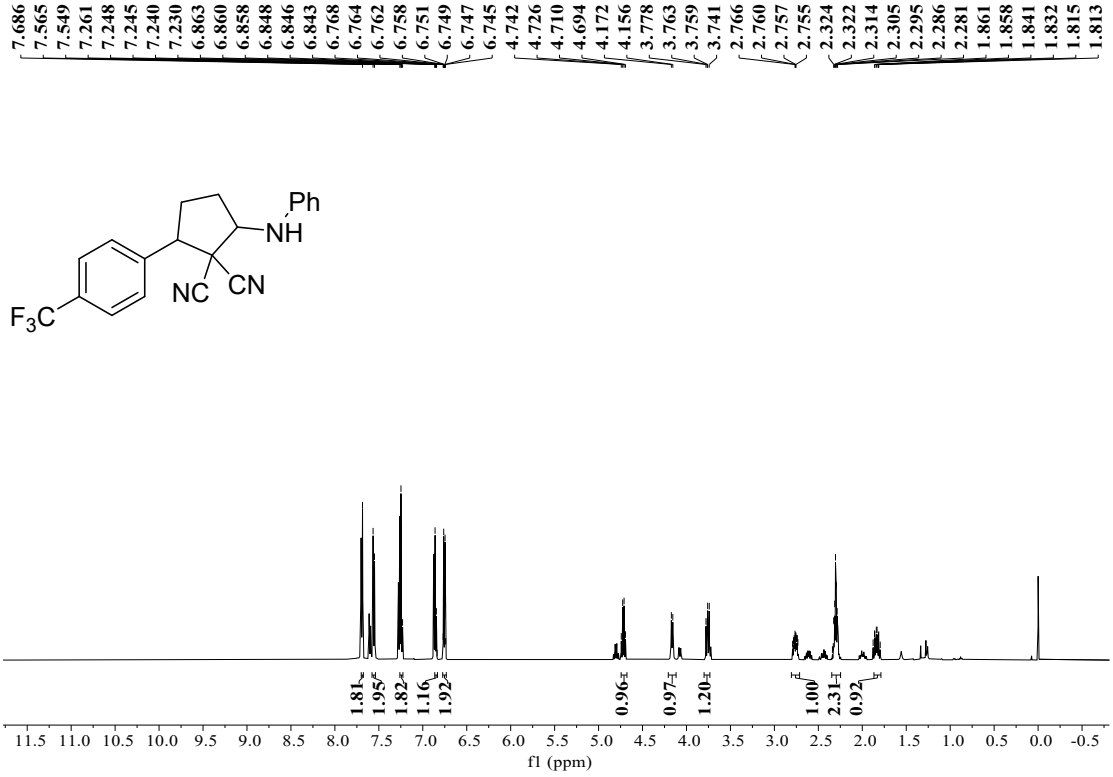


^{13}C NMR (126 MHz, $CDCl_3$)

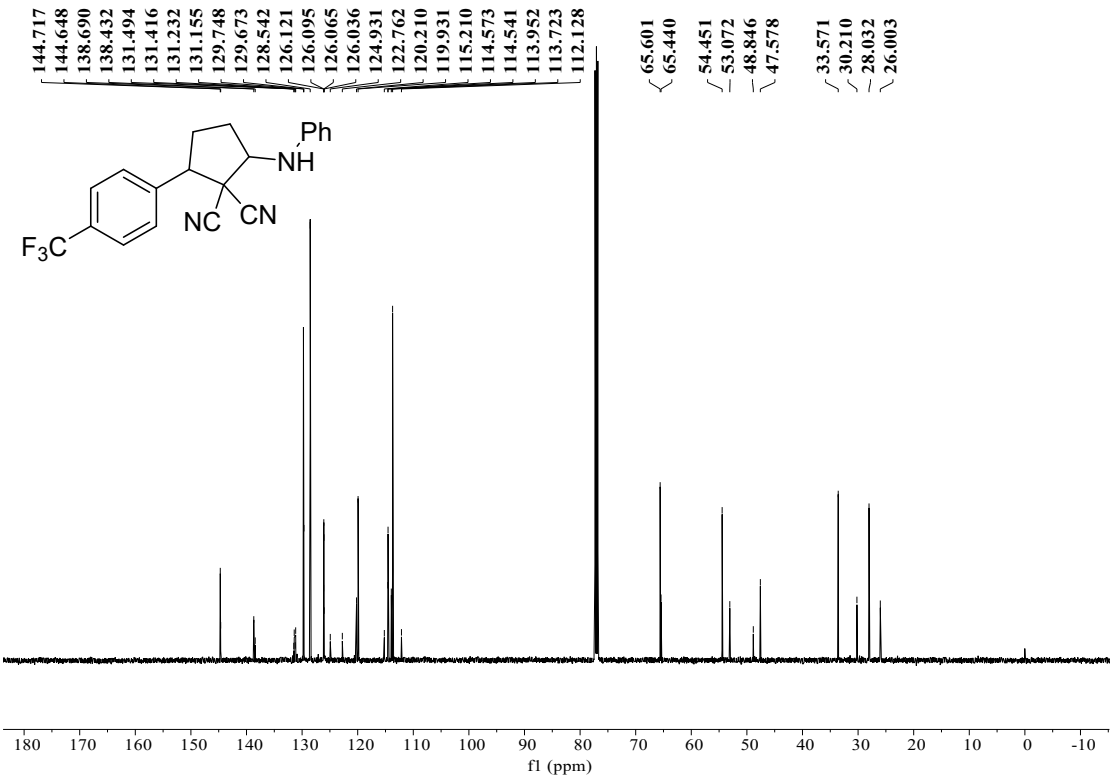


2-(phenylamino)-5-(4-(trifluoromethyl)phenyl)cyclopentane-1,1-dicarbonitrile (4f)

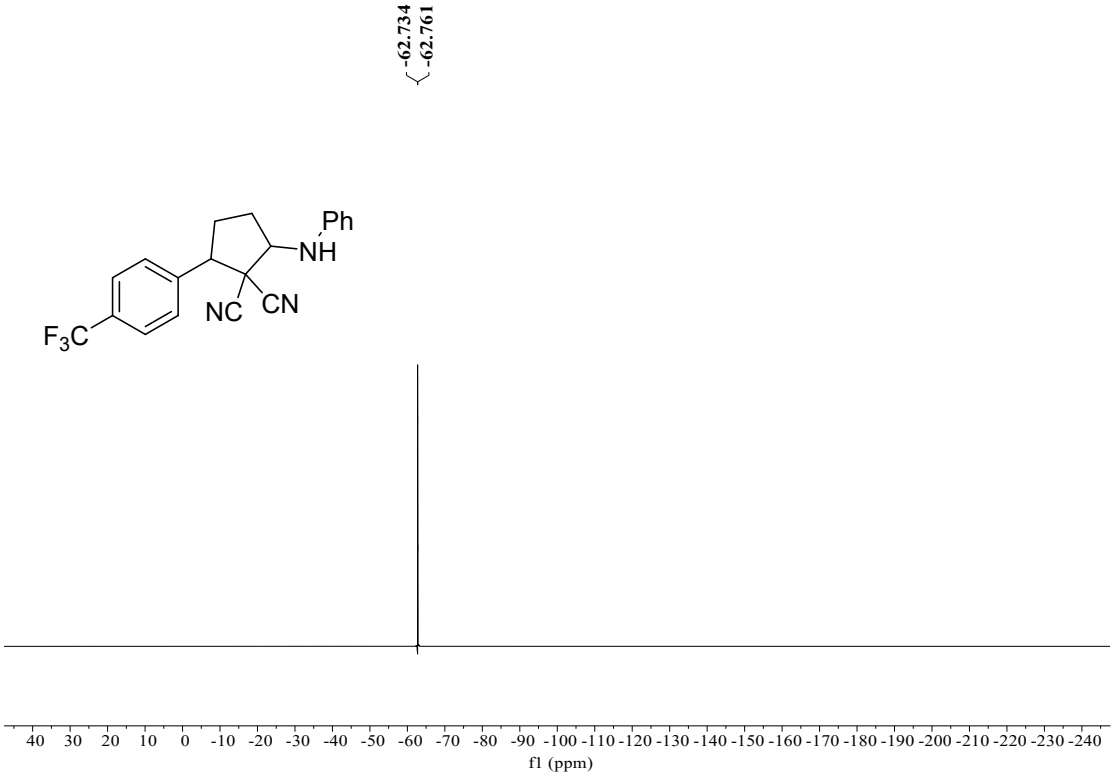
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

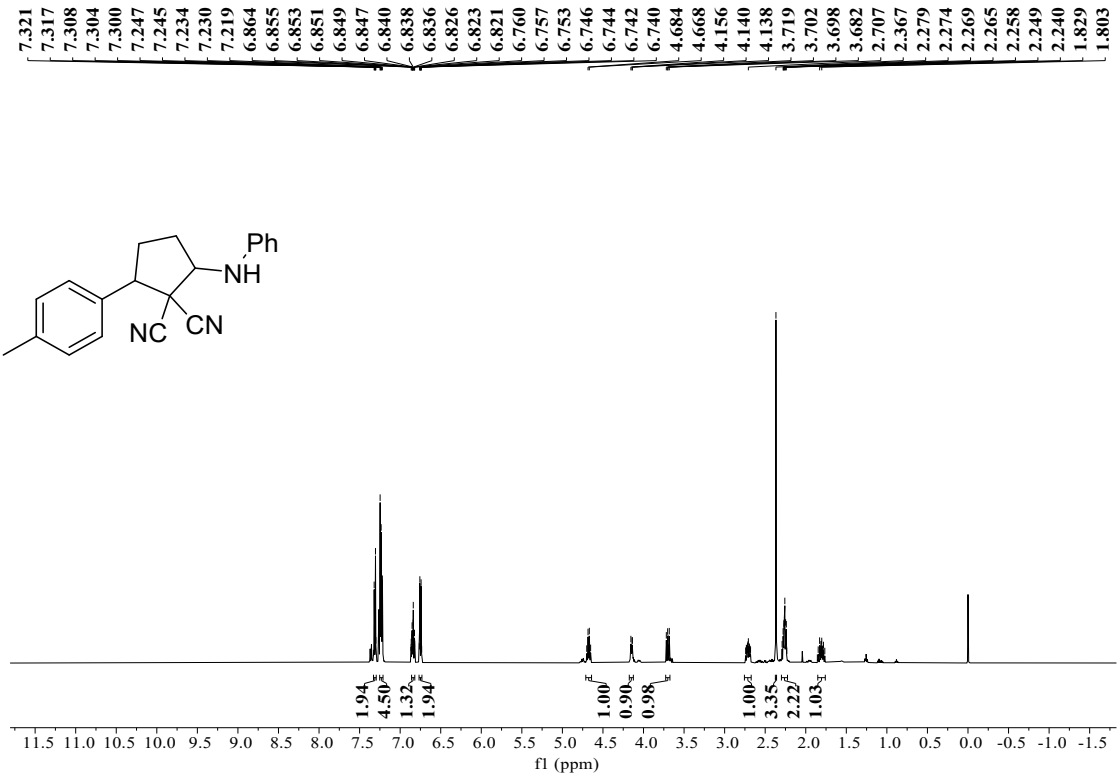


^{19}F NMR (470 MHz, $CDCl_3$)

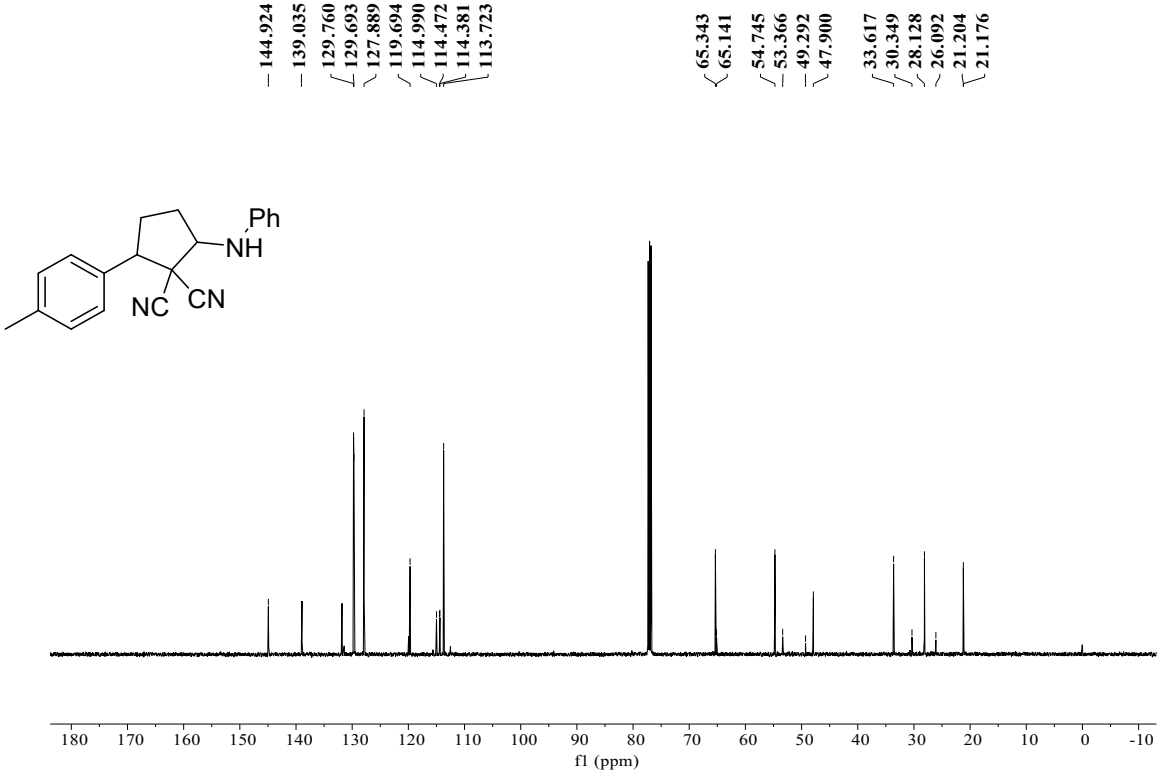


2-(phenylamino)-5-(p-tolyl)cyclopentane-1,1-dicarbonitrile (4g)

^{1}H NMR (500 MHz, $CDCl_3$)

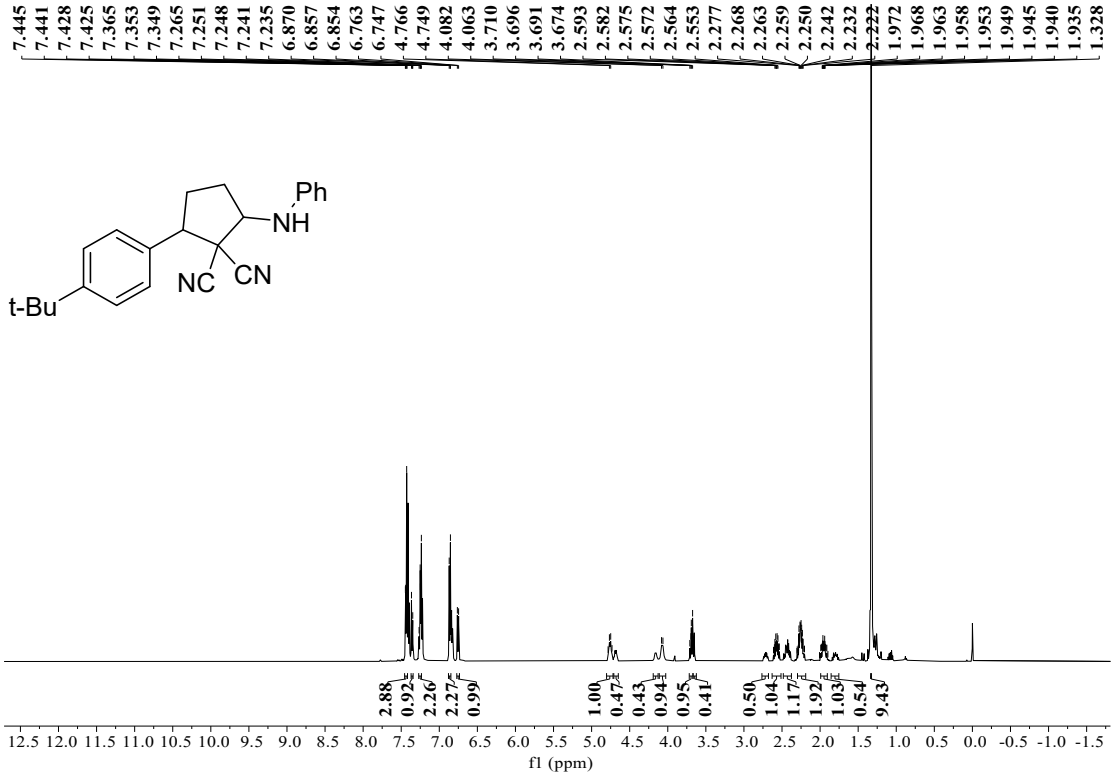


^{13}C NMR (126 MHz, $CDCl_3$)

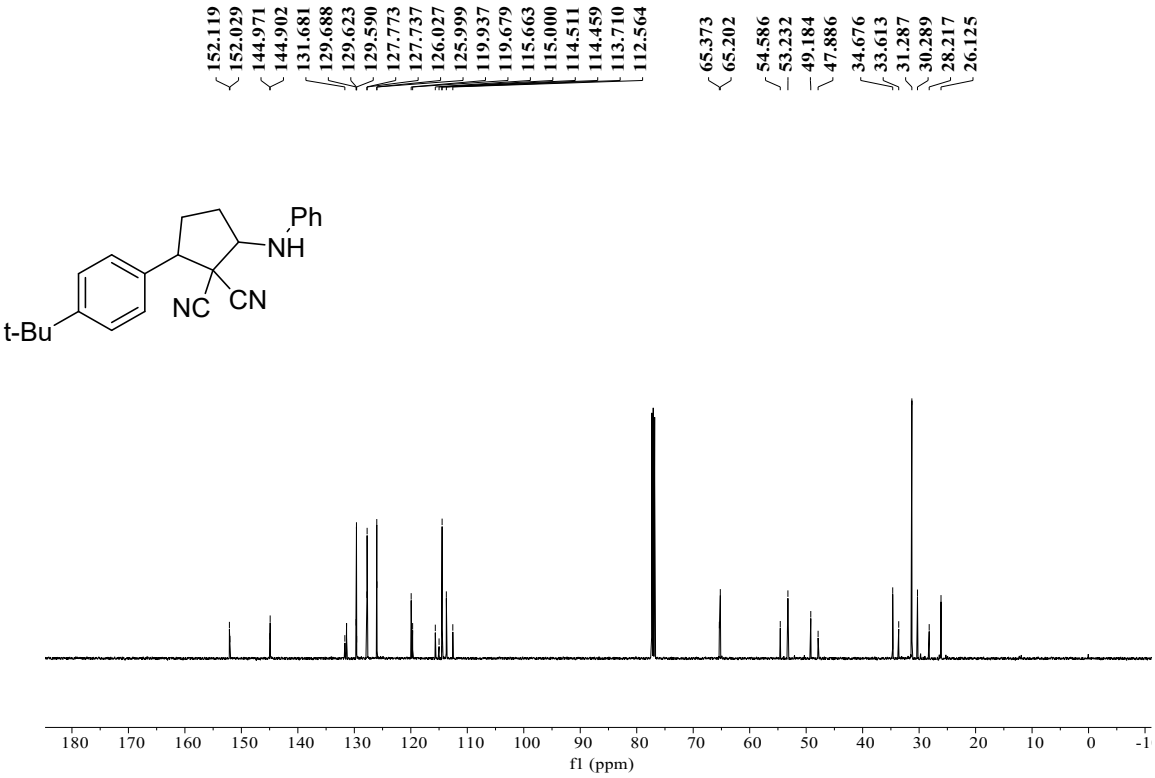


2-(4-(tert-butyl)phenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4h)

^{1}H NMR (500 MHz, $CDCl_3$)

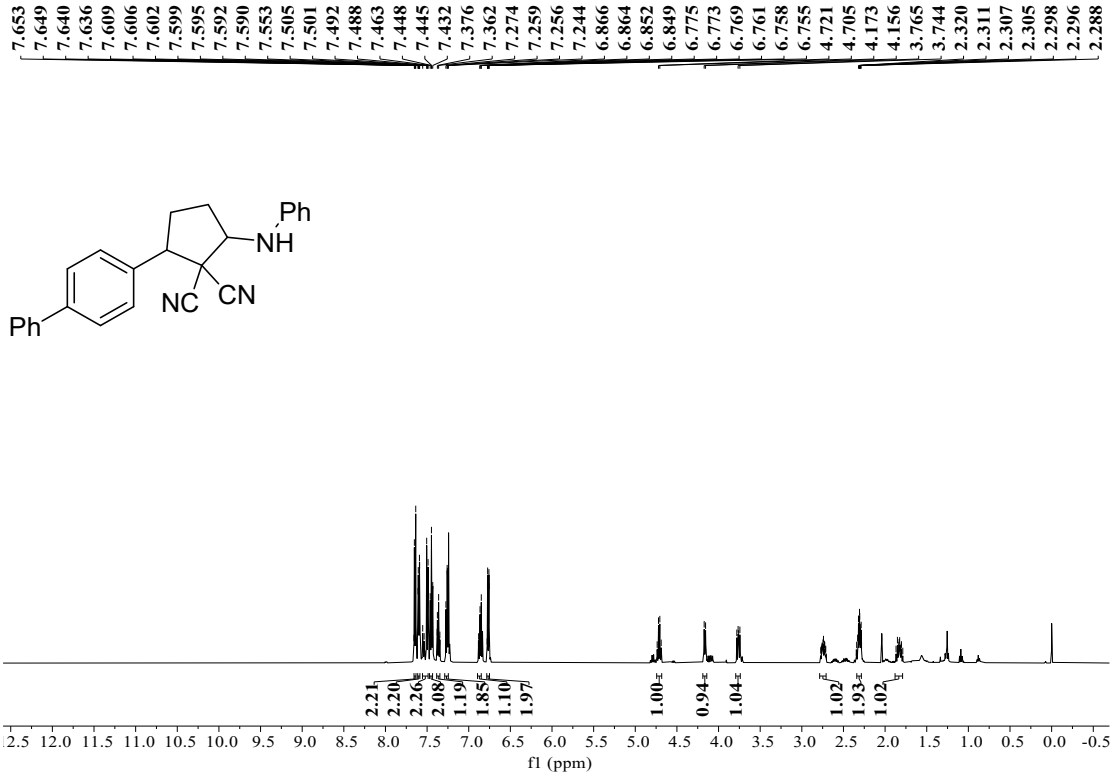


^{13}C NMR (126 MHz, $CDCl_3$)

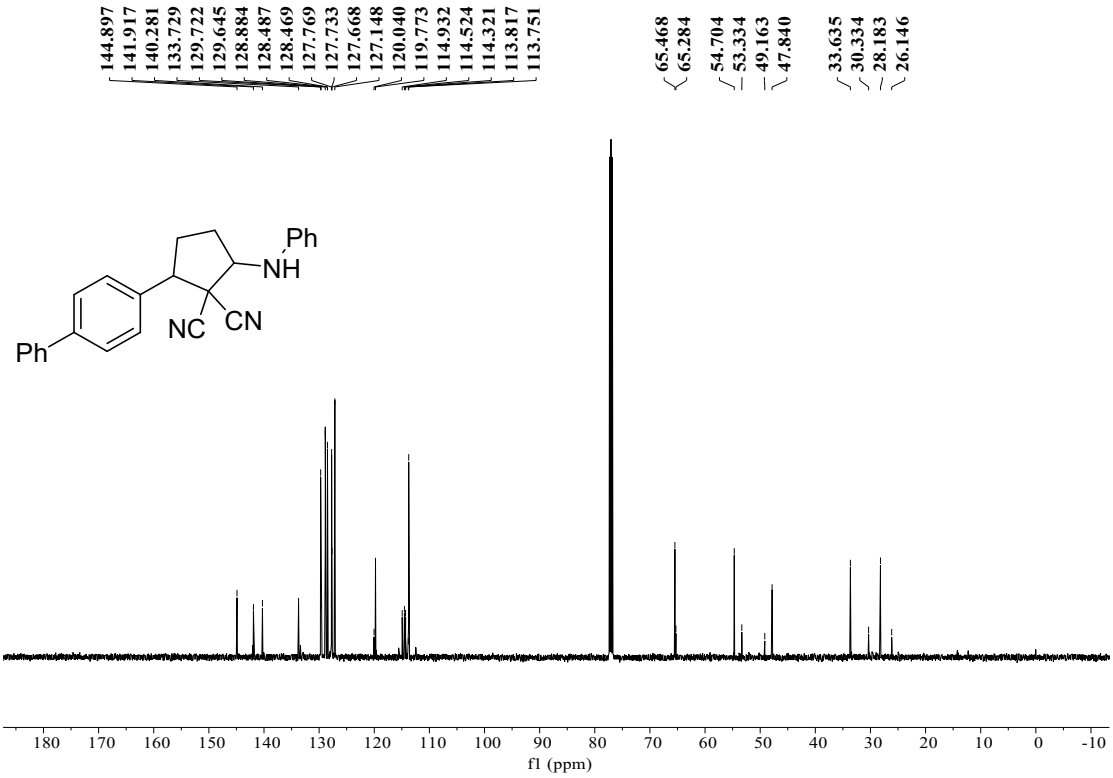


2-([1,1'-biphenyl]-4-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4i)

^{1}H NMR (500 MHz, $CDCl_3$)

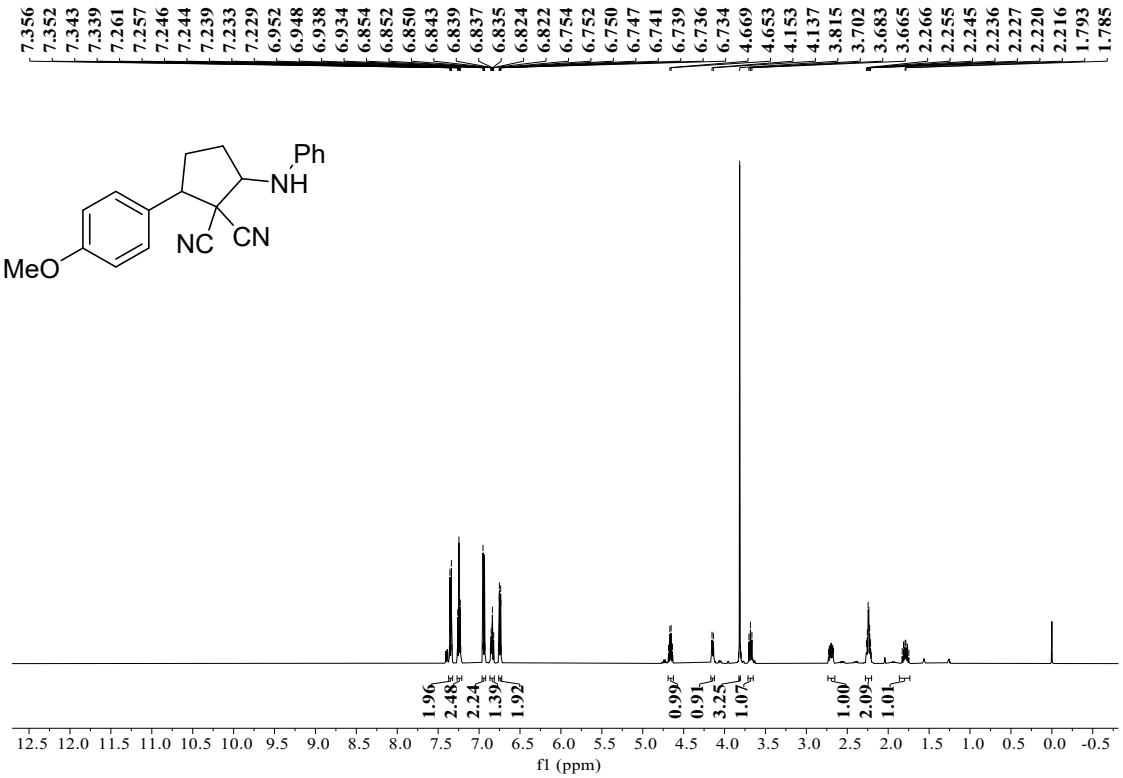


^{13}C NMR (126 MHz, $CDCl_3$)

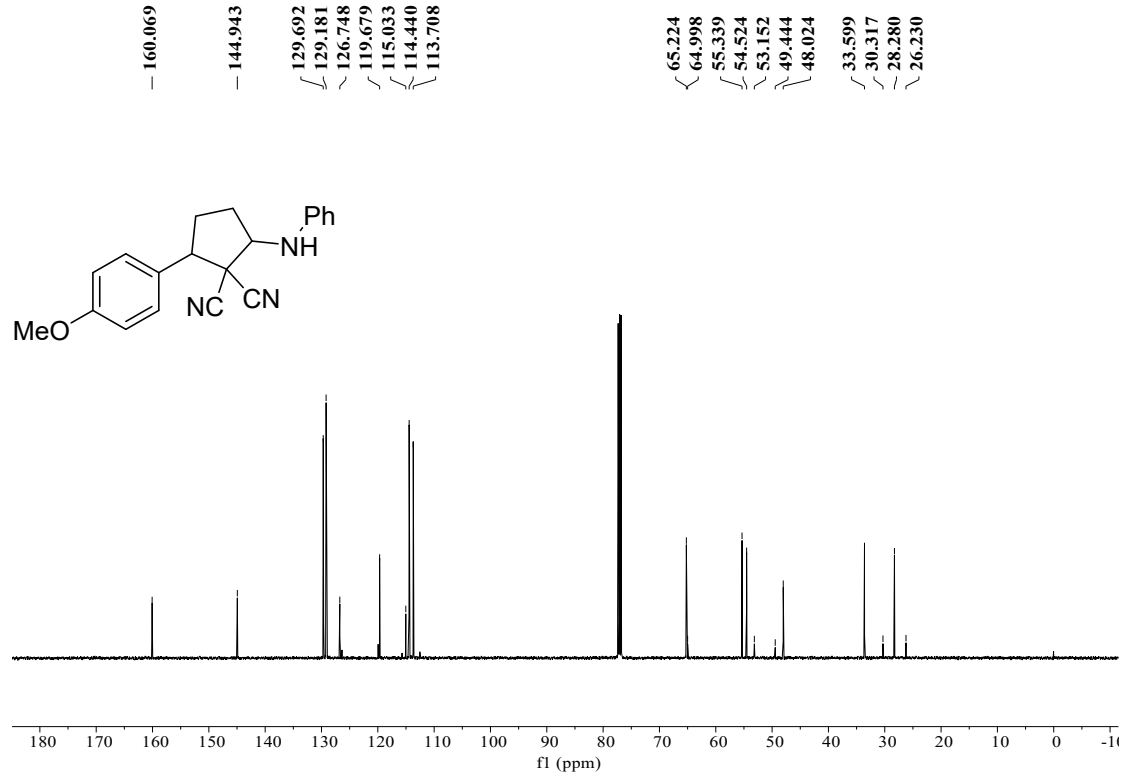


2-(4-methoxyphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4j)

^{1}H NMR (500 MHz, $CDCl_3$)

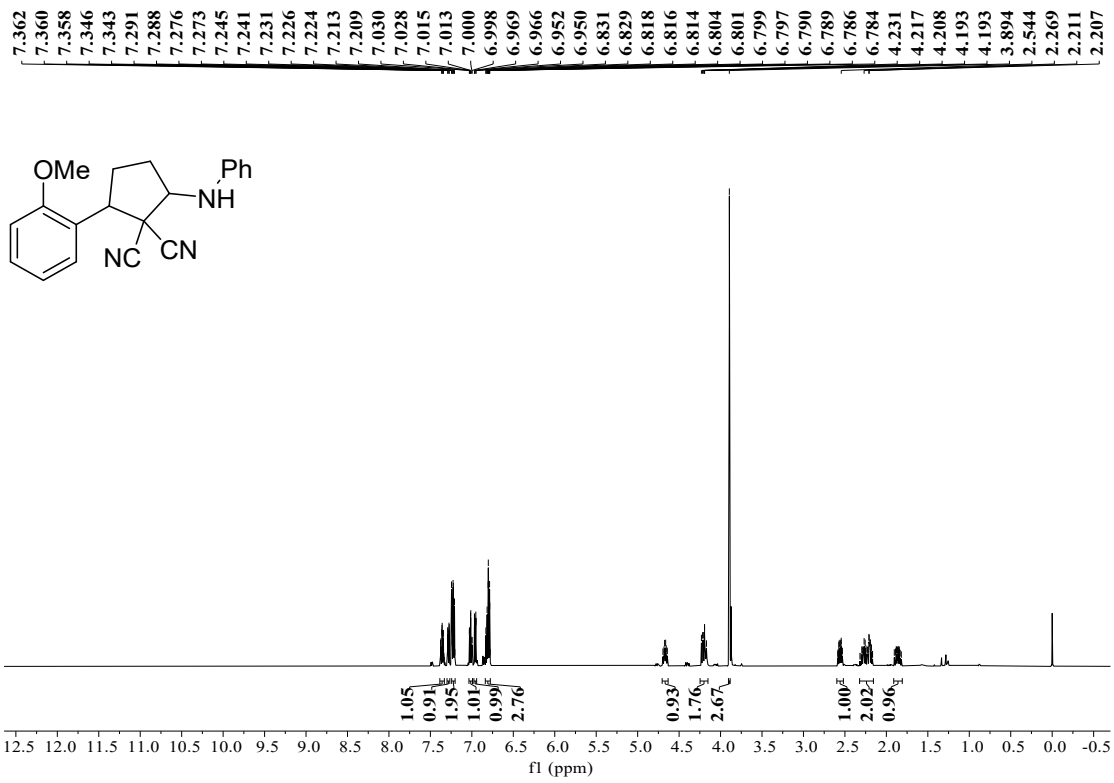


^{13}C NMR (126 MHz, $CDCl_3$)

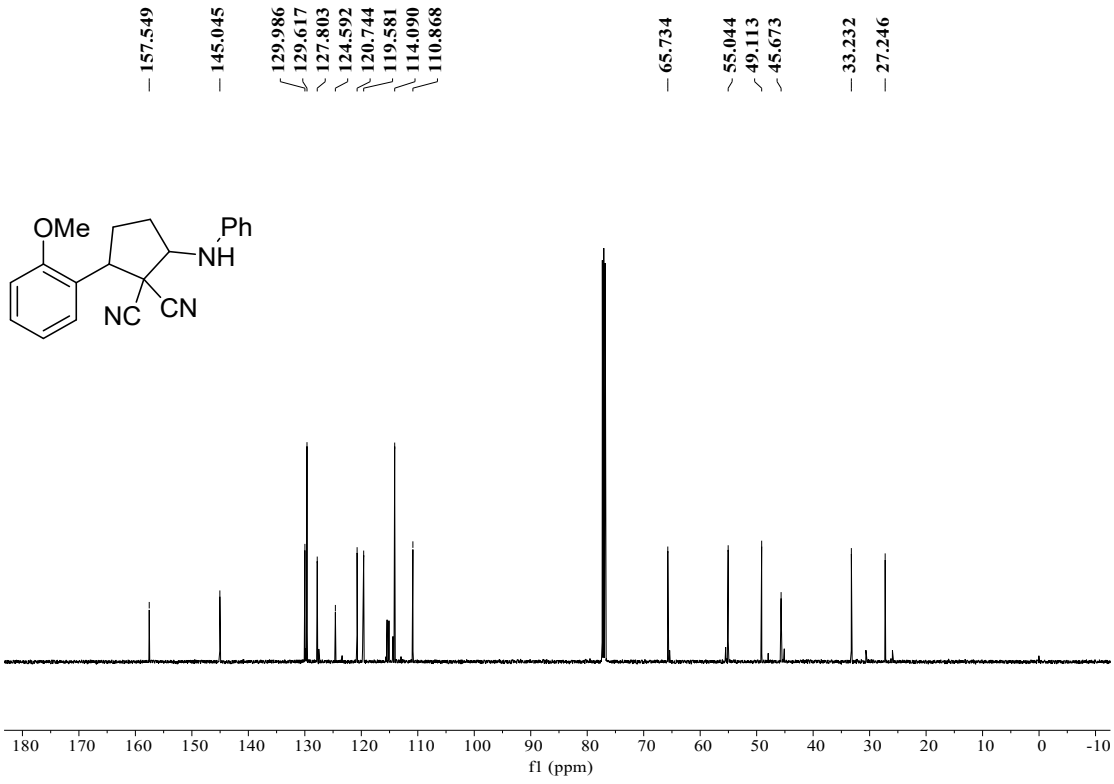


2-(2-methoxyphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4k)

^{1}H NMR (500 MHz, $CDCl_3$)

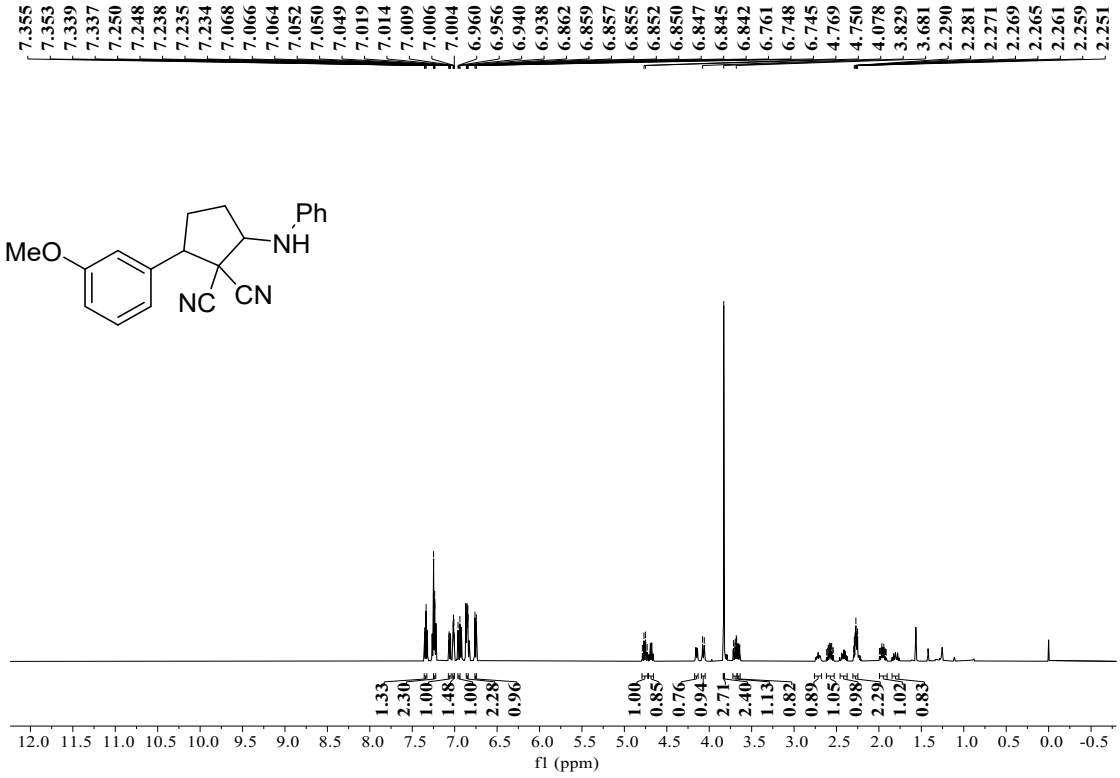


^{13}C NMR (126 MHz, $CDCl_3$)

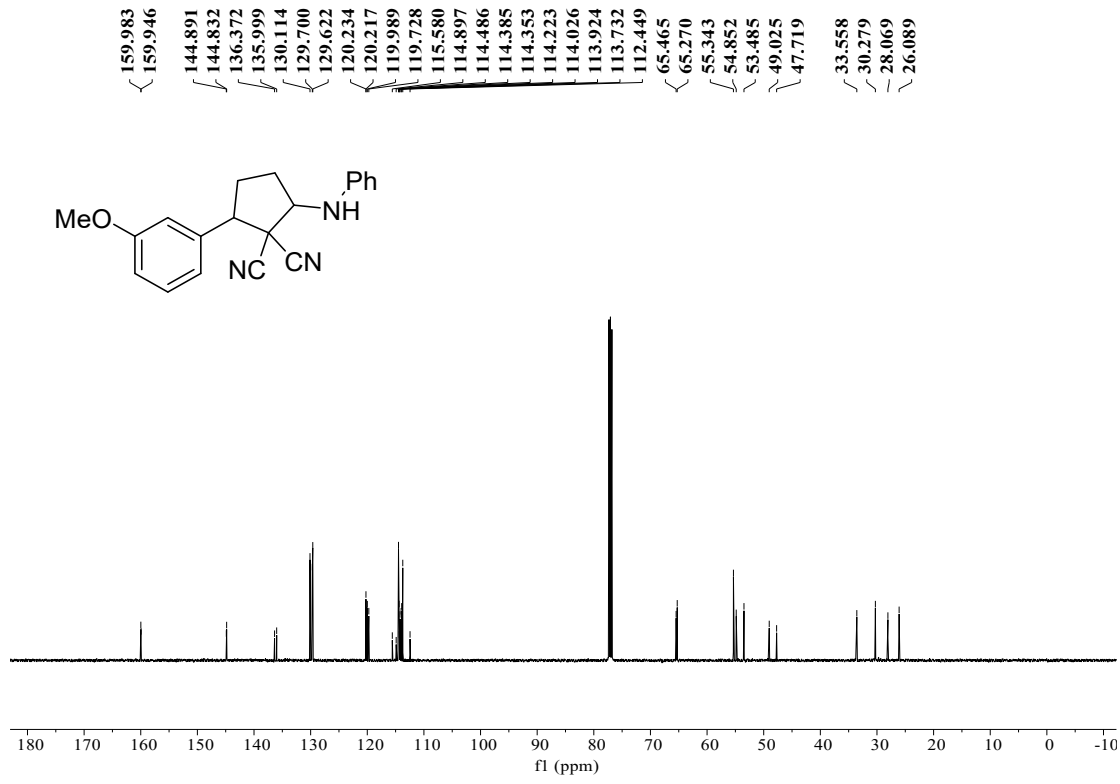


2-(3-methoxyphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4l)

^{1}H NMR (500 MHz, $CDCl_3$)

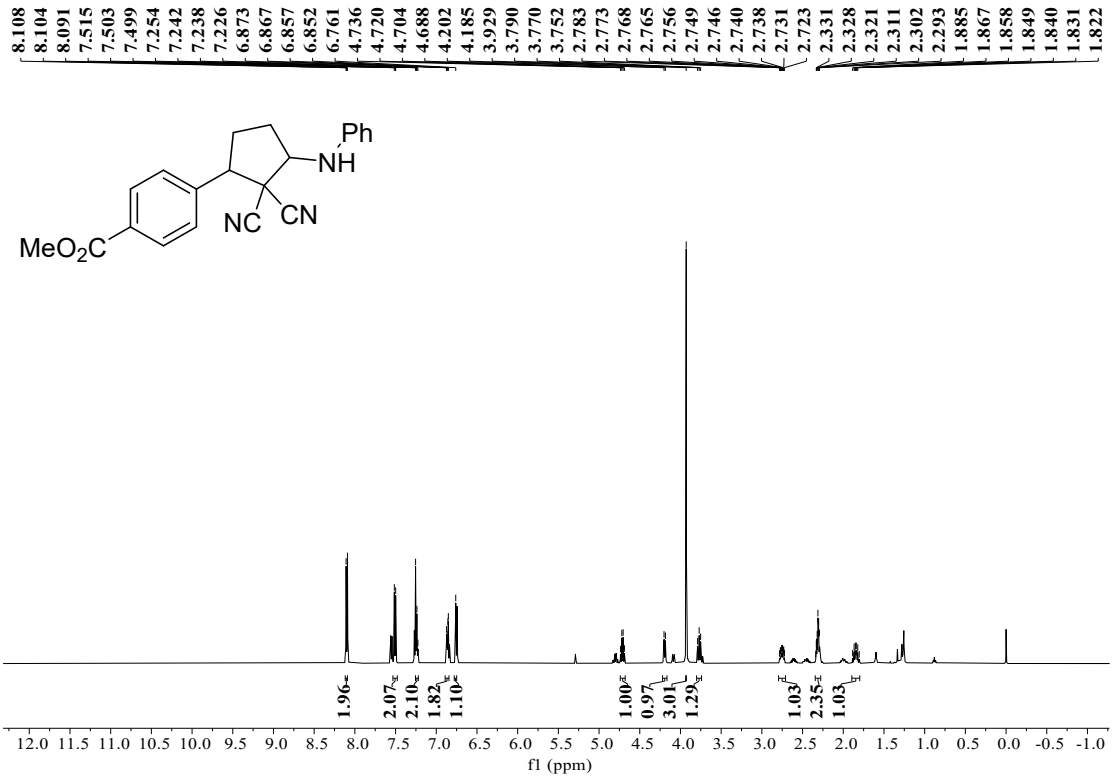


^{13}C NMR (126 MHz, $CDCl_3$)

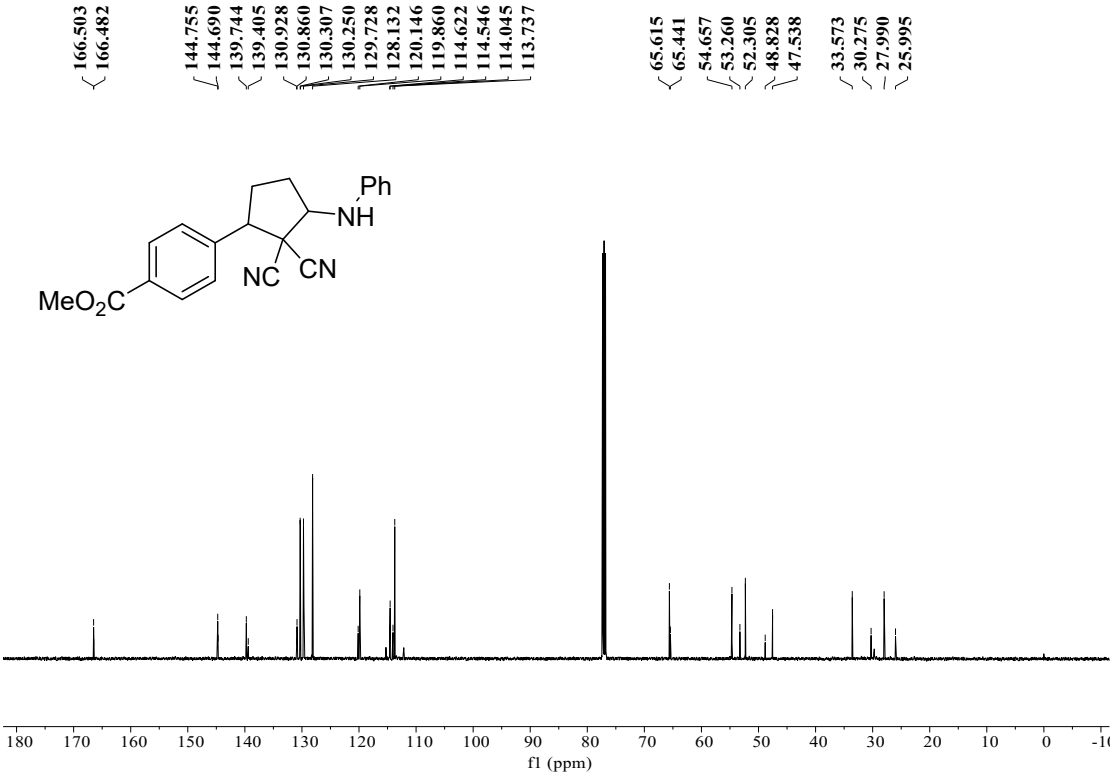


methy-l4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate(4m)

^{1}H NMR (500 MHz, $CDCl_3$)

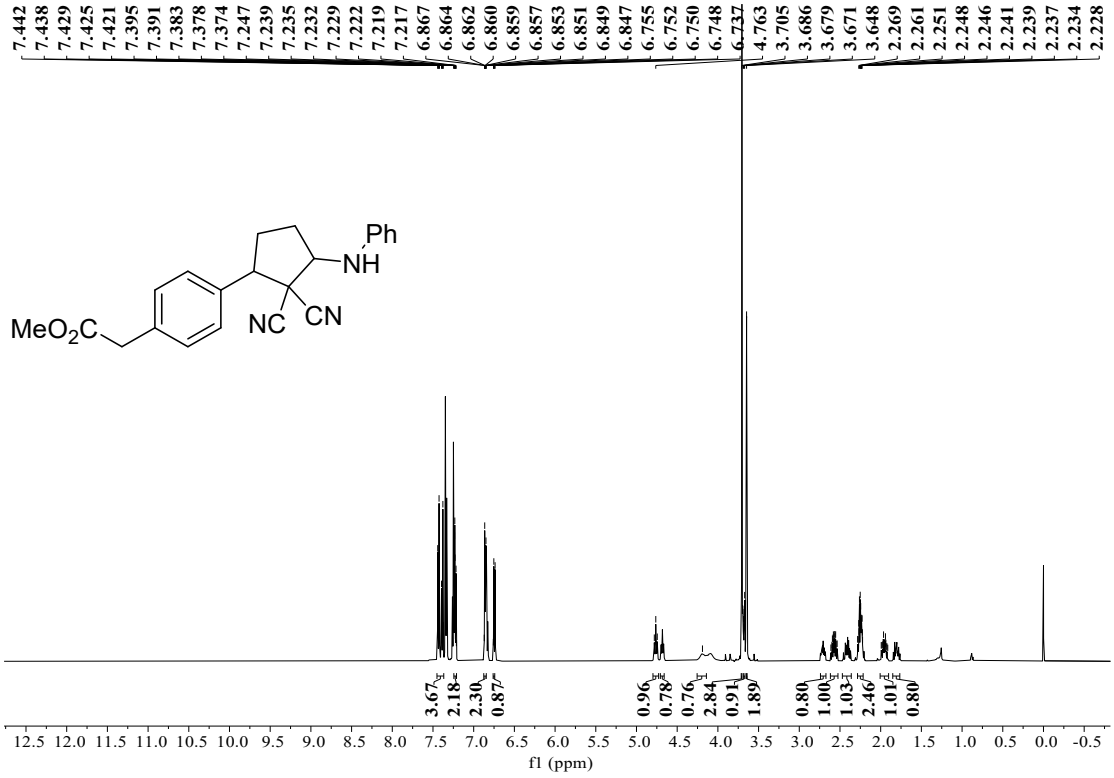


^{13}C NMR (126 MHz, $CDCl_3$)

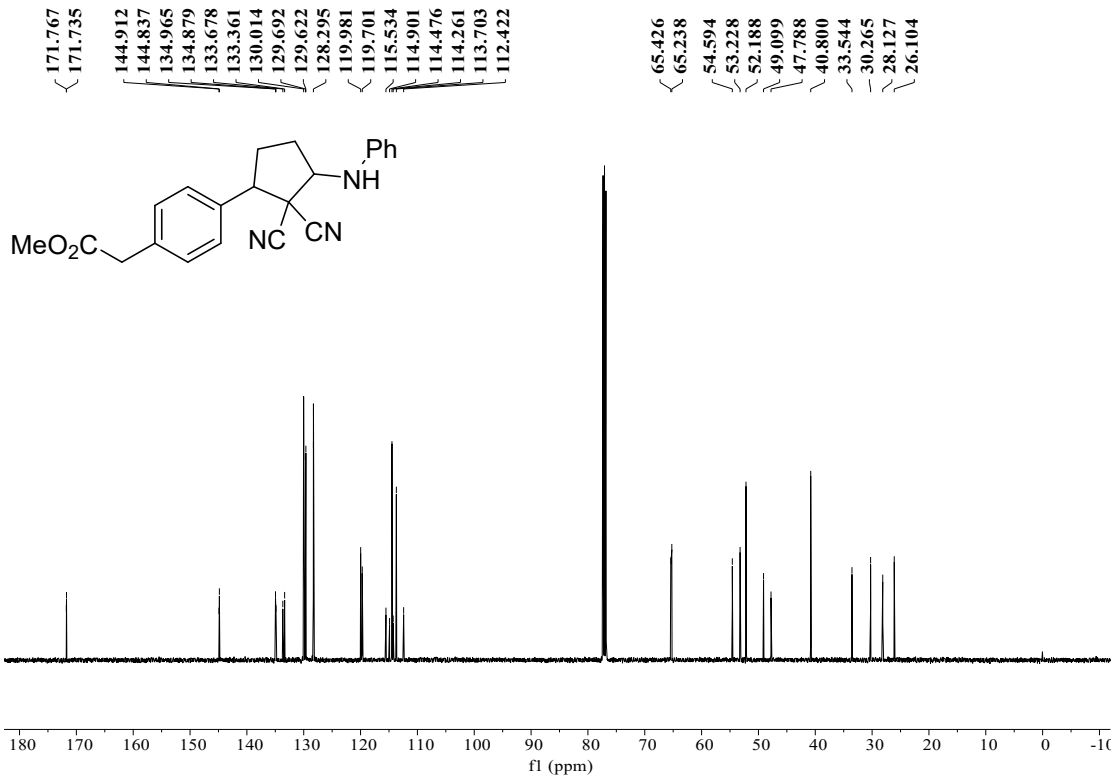


methyl 2-(4-(2,2-dicyano-3-(phenylamino)cyclopentyl)phenyl)acetate (4n)

^{1}H NMR (500 MHz, $CDCl_3$)

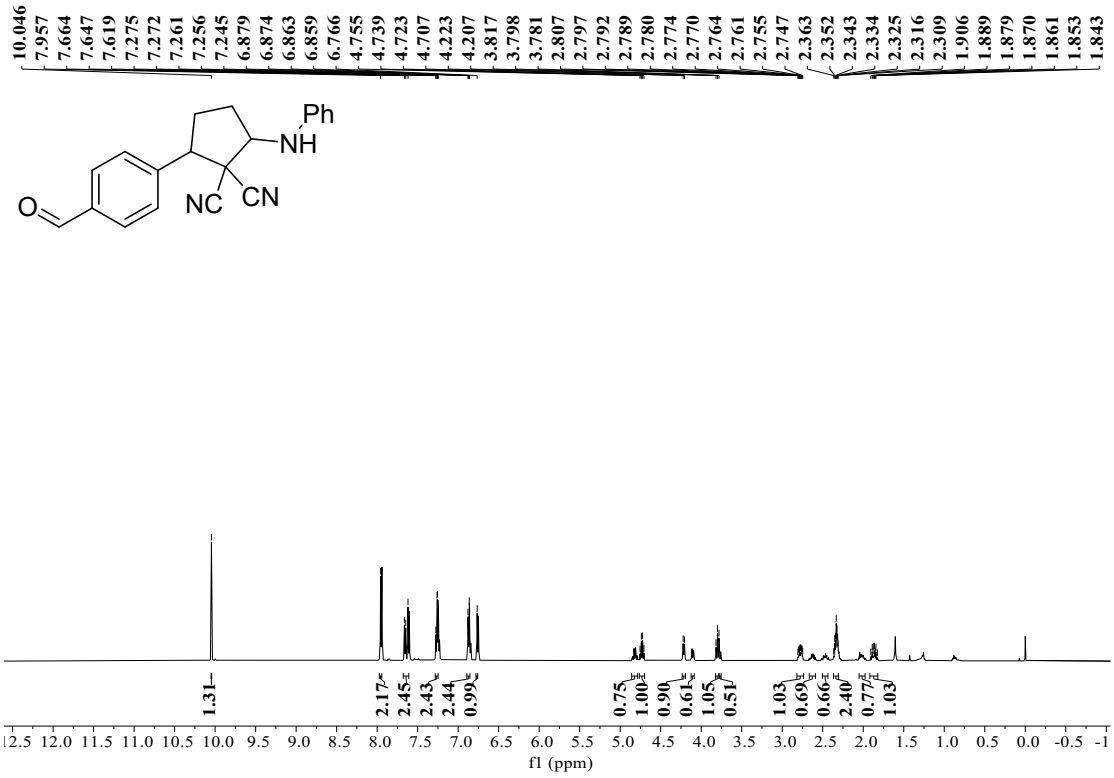


^{13}C NMR (126 MHz, $CDCl_3$)

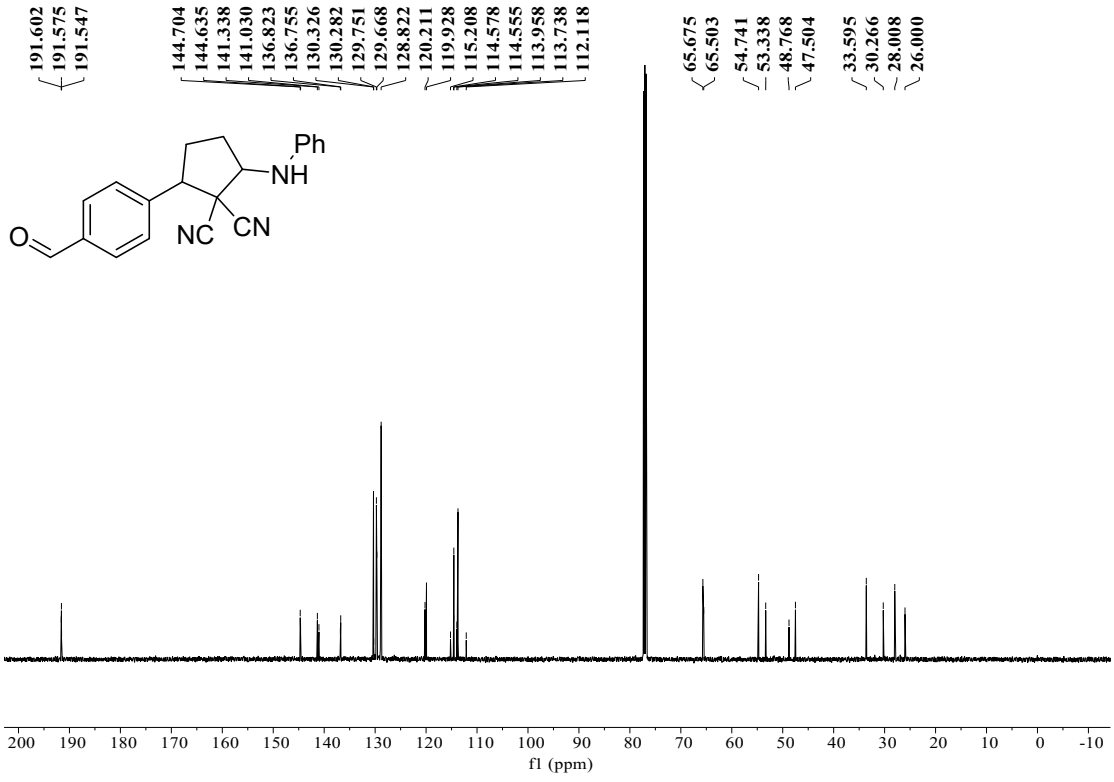


2-(4-formylphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4o)

^{1}H NMR (500 MHz, $CDCl_3$)

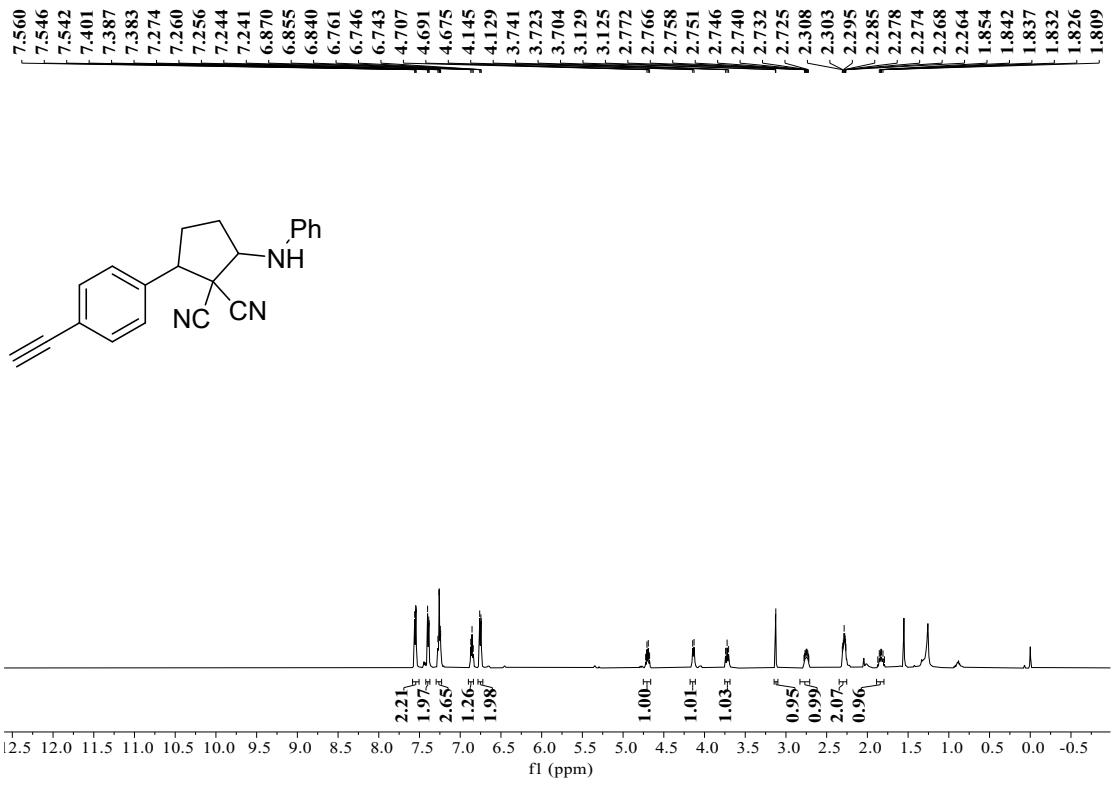


^{13}C NMR (126 MHz, $CDCl_3$)

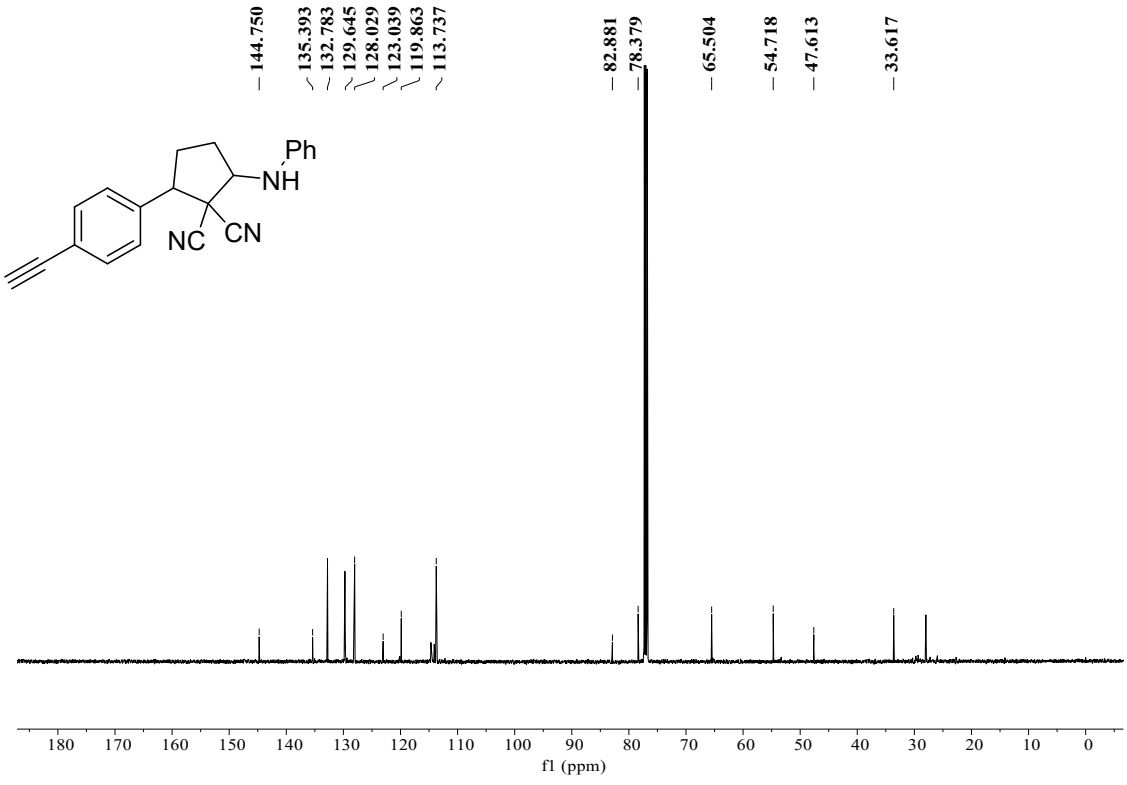


2-(4-ethynylphenyl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4p)

^{1}H NMR (500 MHz, $CDCl_3$)

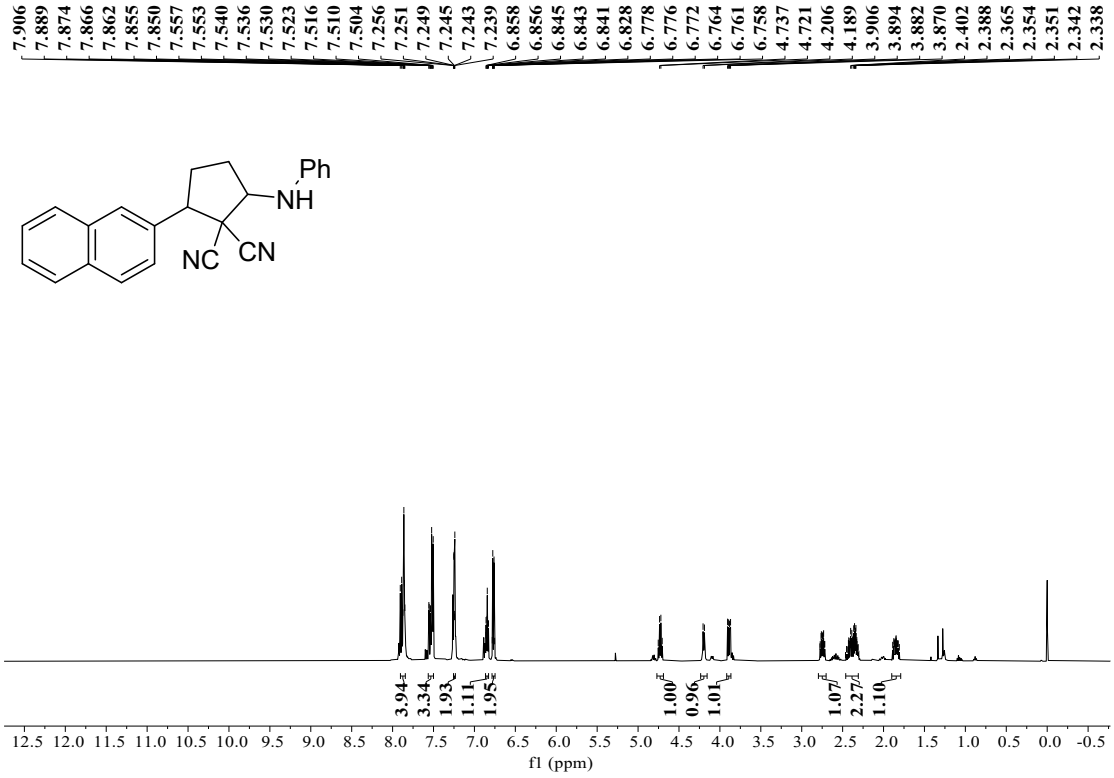


^{13}C NMR (126 MHz, CDCl3)

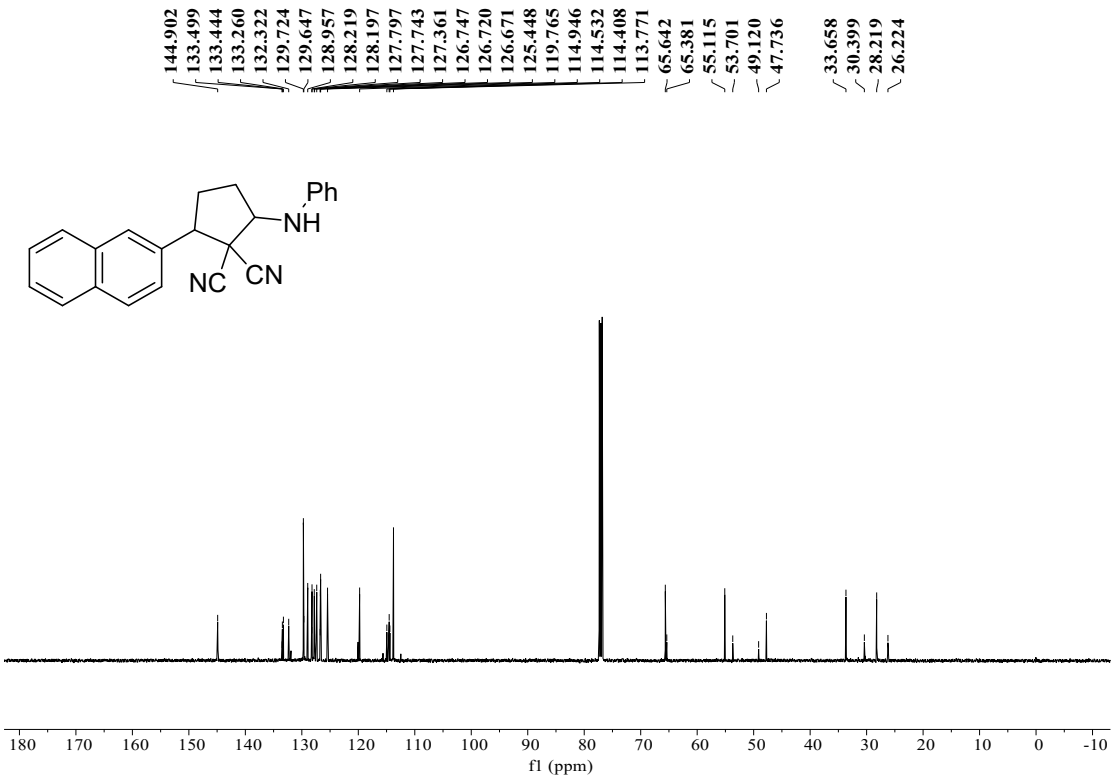


2-(naphthalen-2-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4q)

^{1}H NMR (500 MHz, $CDCl_3$)

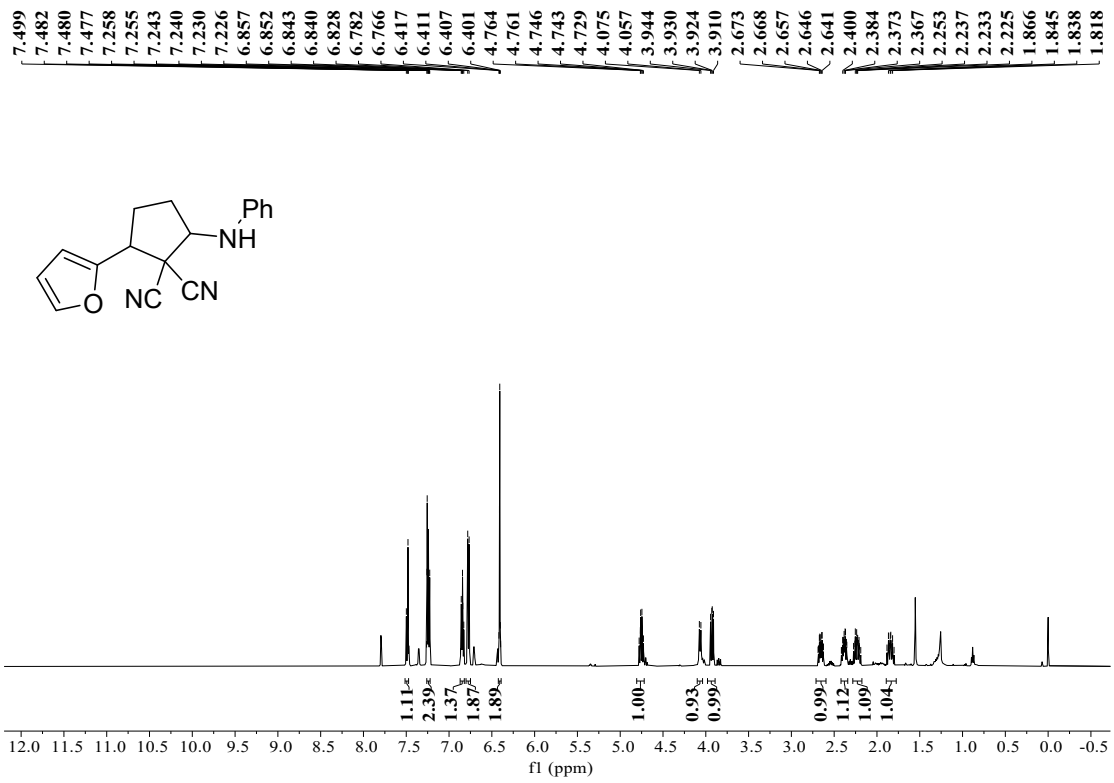


^{13}C NMR (126 MHz, $CDCl_3$)

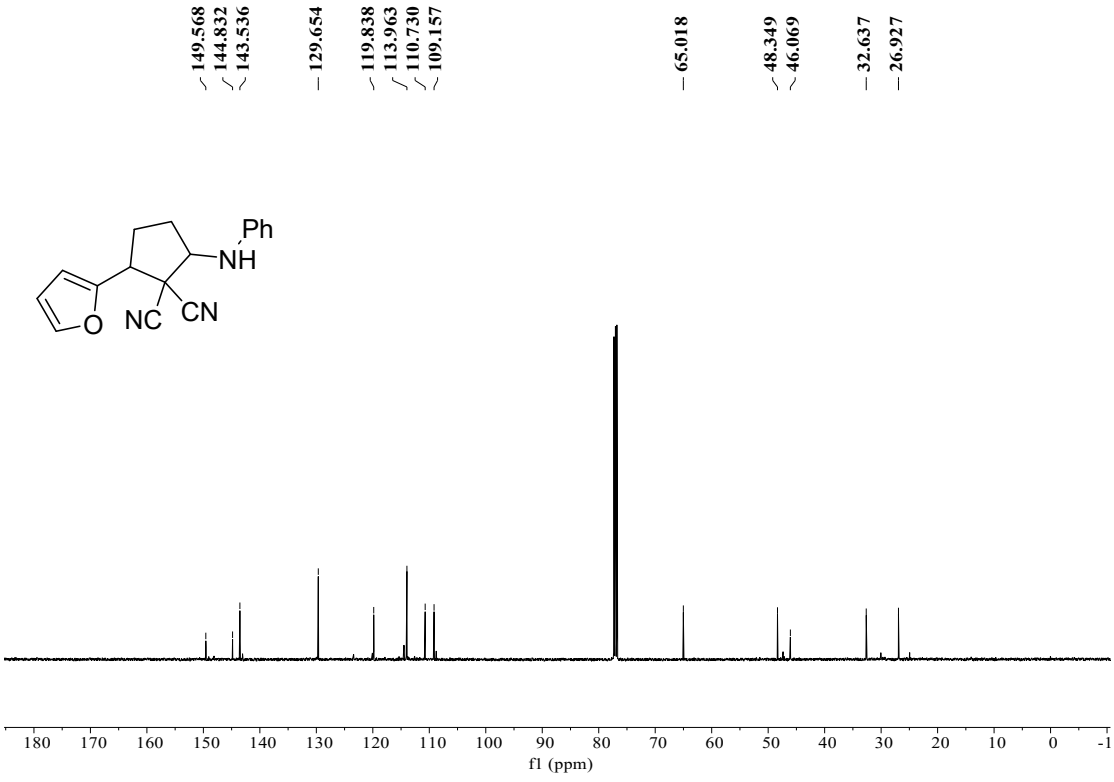


2-(furan-2-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4r)

^{1}H NMR (500 MHz, $CDCl_3$)

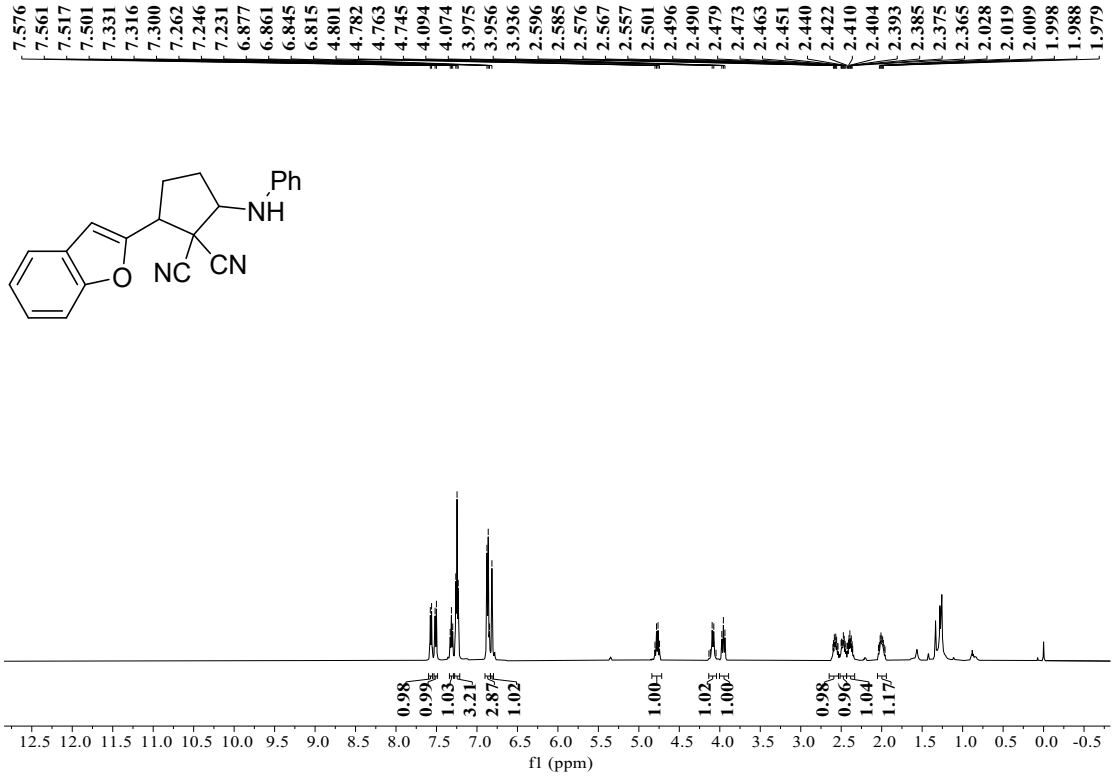


^{13}C NMR (126 MHz, $CDCl_3$)

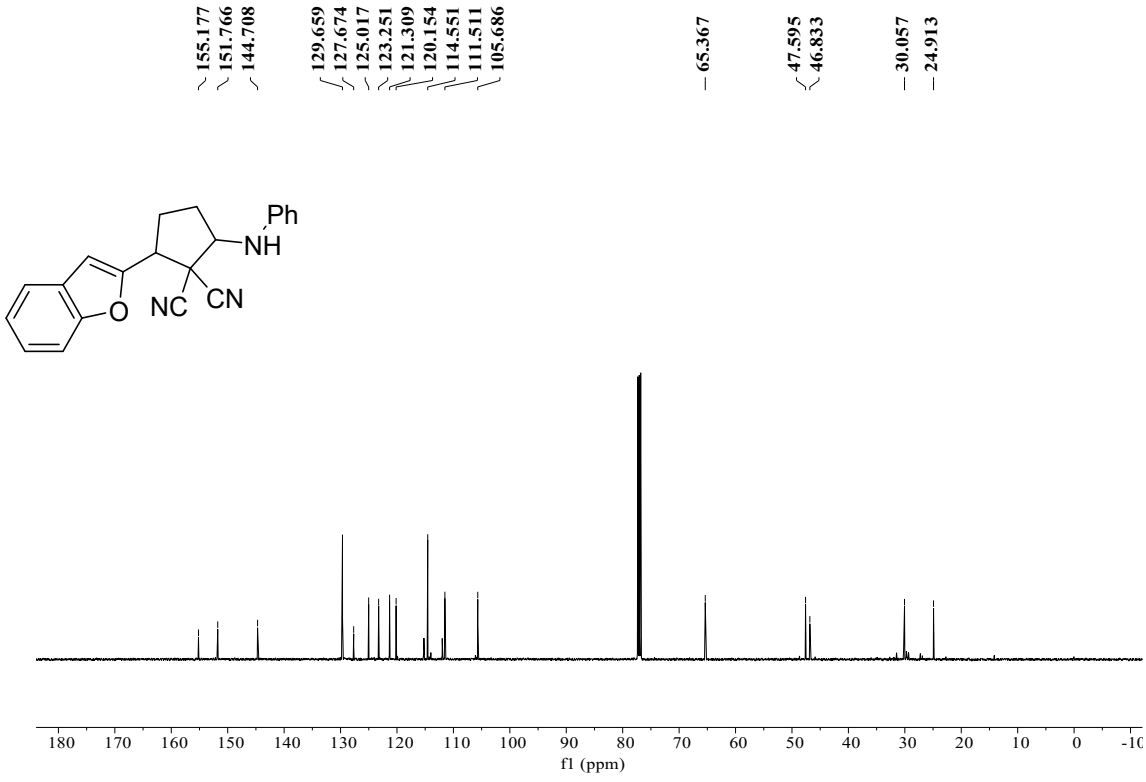


2-(benzofuran-2-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4s)

^{1}H NMR (500 MHz, $CDCl_3$)

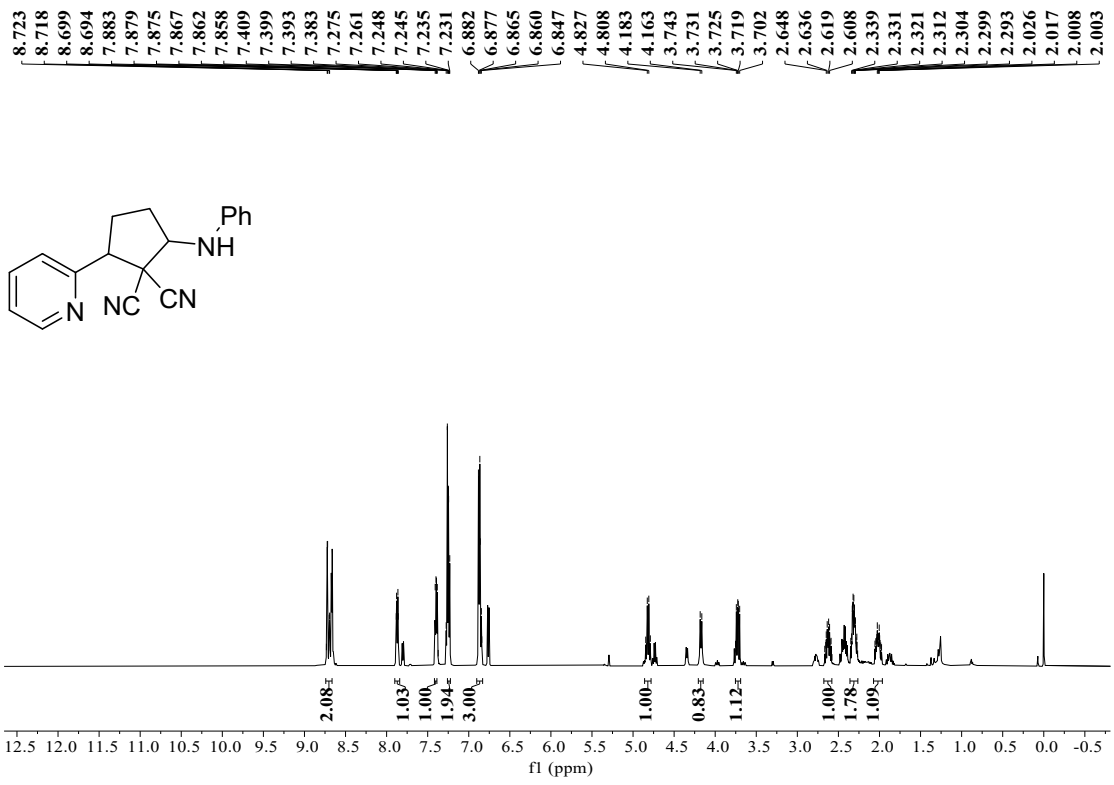


^{13}C NMR (126 MHz, $CDCl_3$)

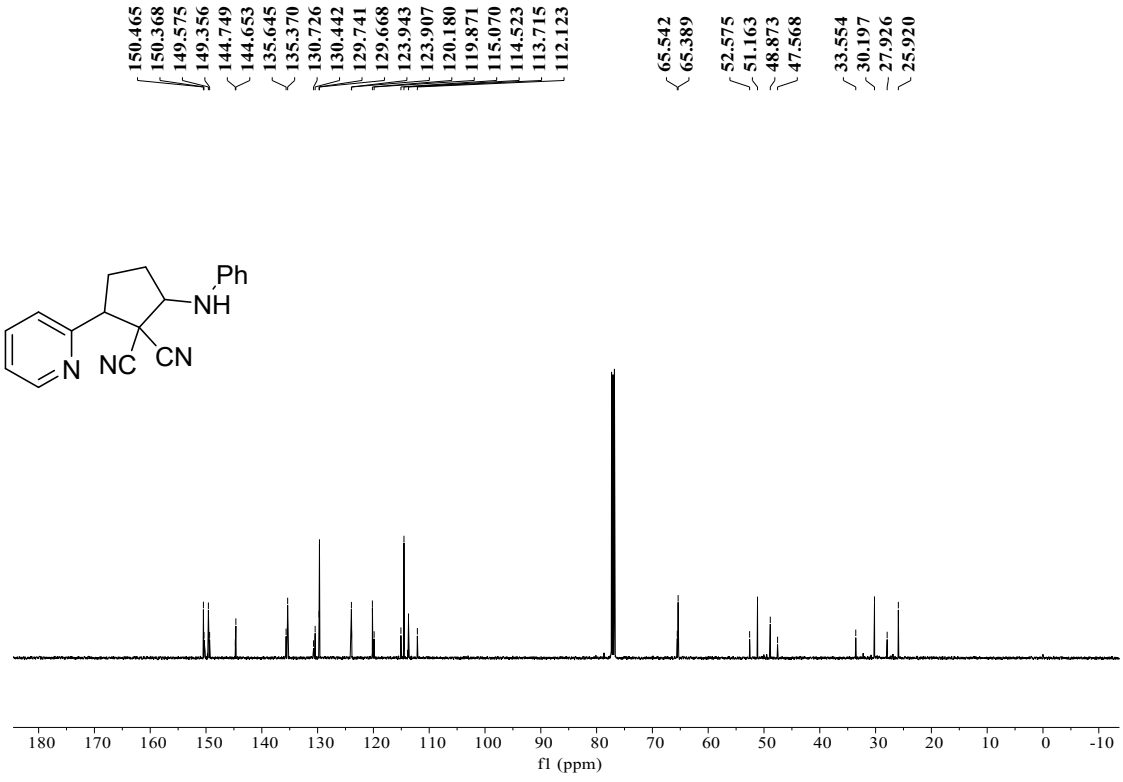


2-(phenylamino)-5-(pyridin-2-yl)cyclopentane-1,1-dicarbonitrile (4t)

^{1}H NMR (500 MHz, $CDCl_3$)

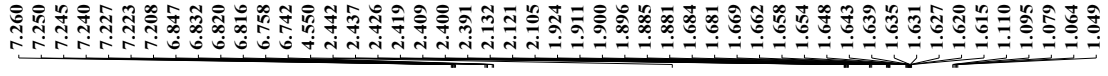


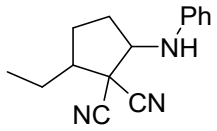
^{13}C NMR (126 MHz, $CDCl_3$)

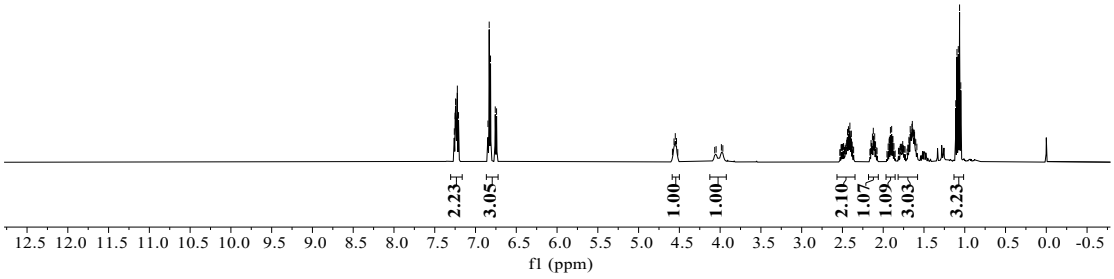


2-ethyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4u)

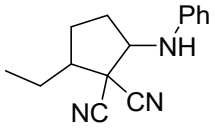
^{1}H NMR (500 MHz, $CDCl_3$)

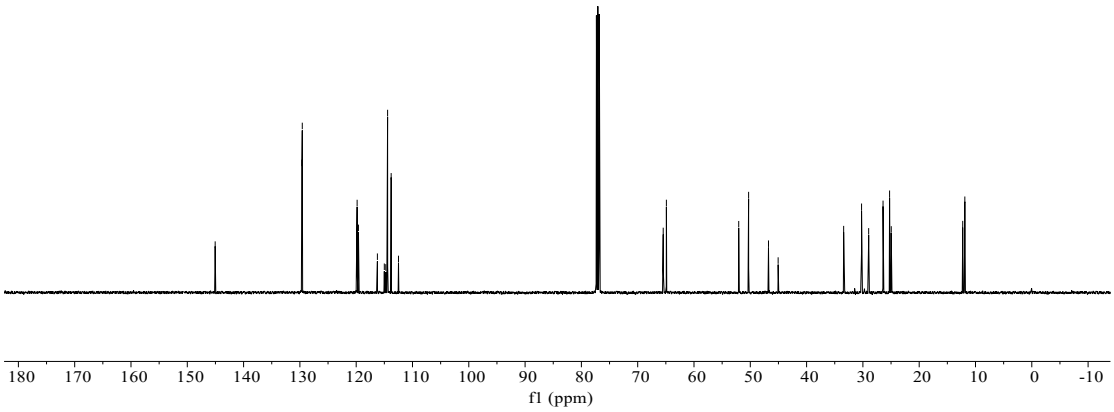






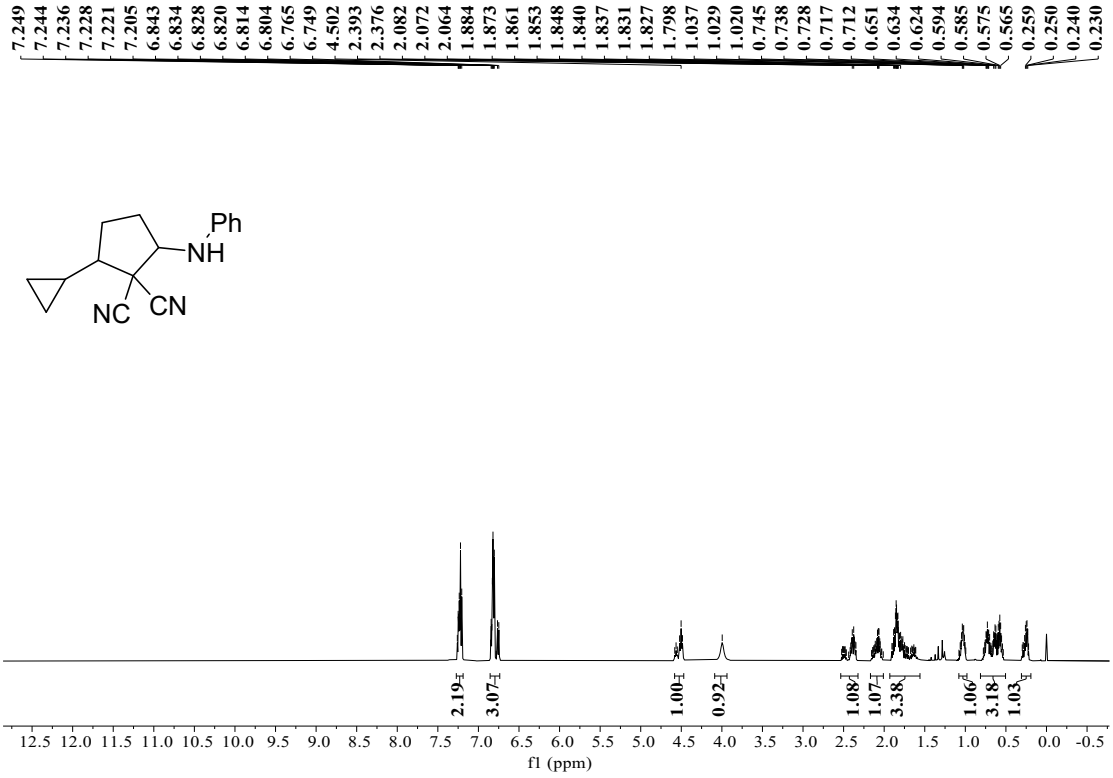
^{13}C NMR (126 MHz, $CDCl_3$)



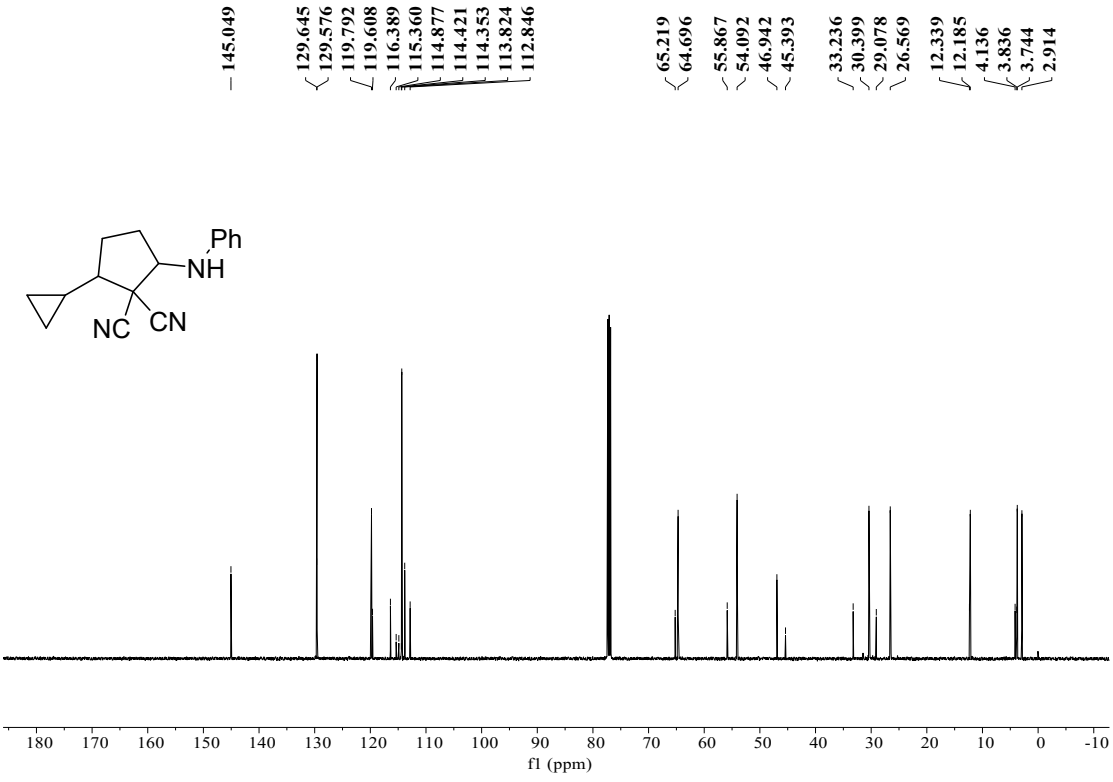


2-cyclopropyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4v)

^{1}H NMR (500 MHz, $CDCl_3$)

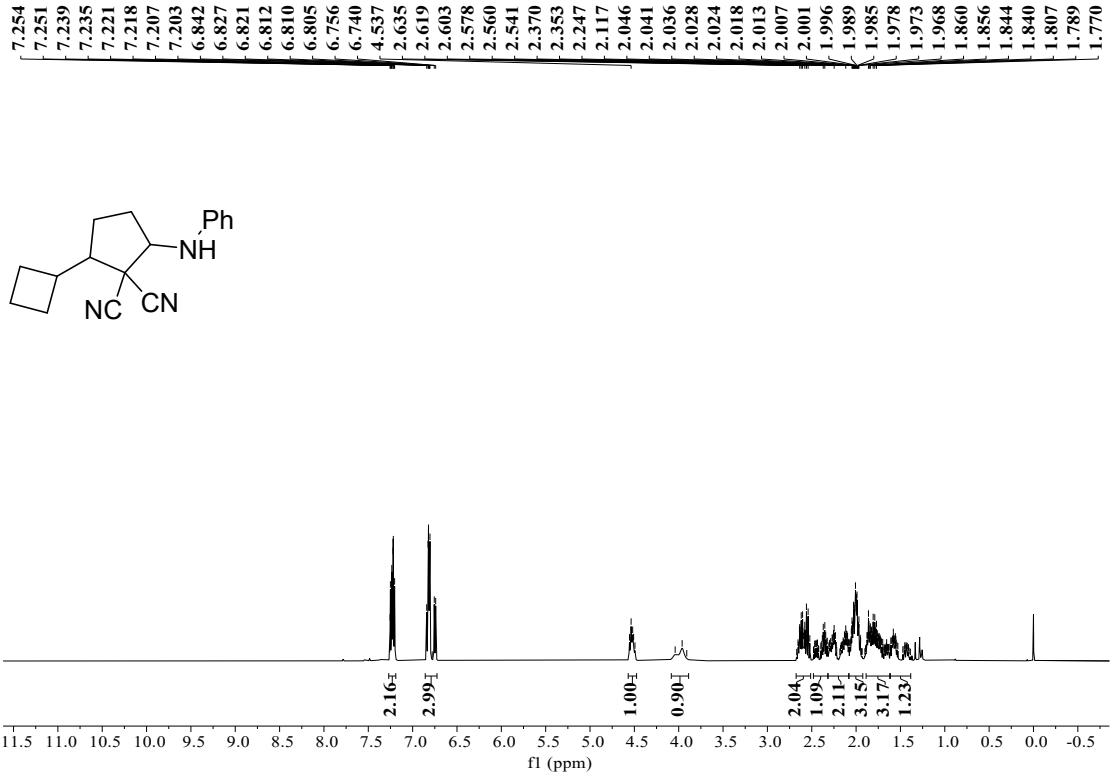


^{13}C NMR (126 MHz, $CDCl_3$)

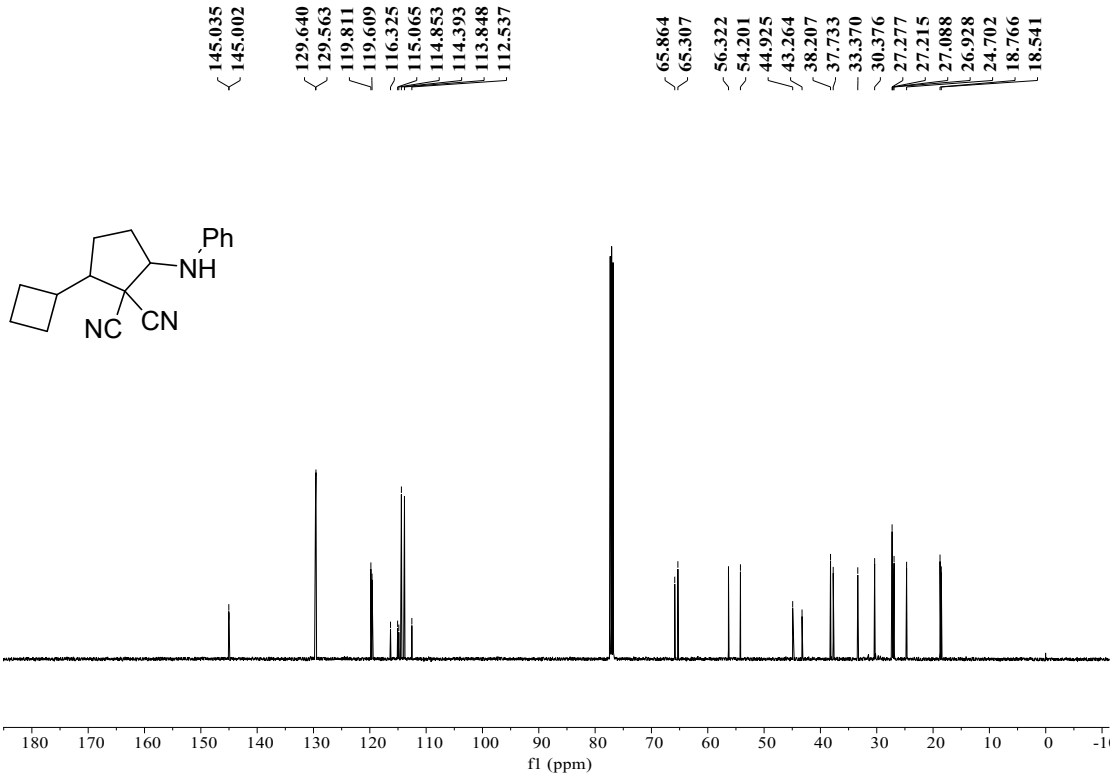


2-cyclobutyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4w)

^{1}H NMR (500 MHz, $CDCl_3$)

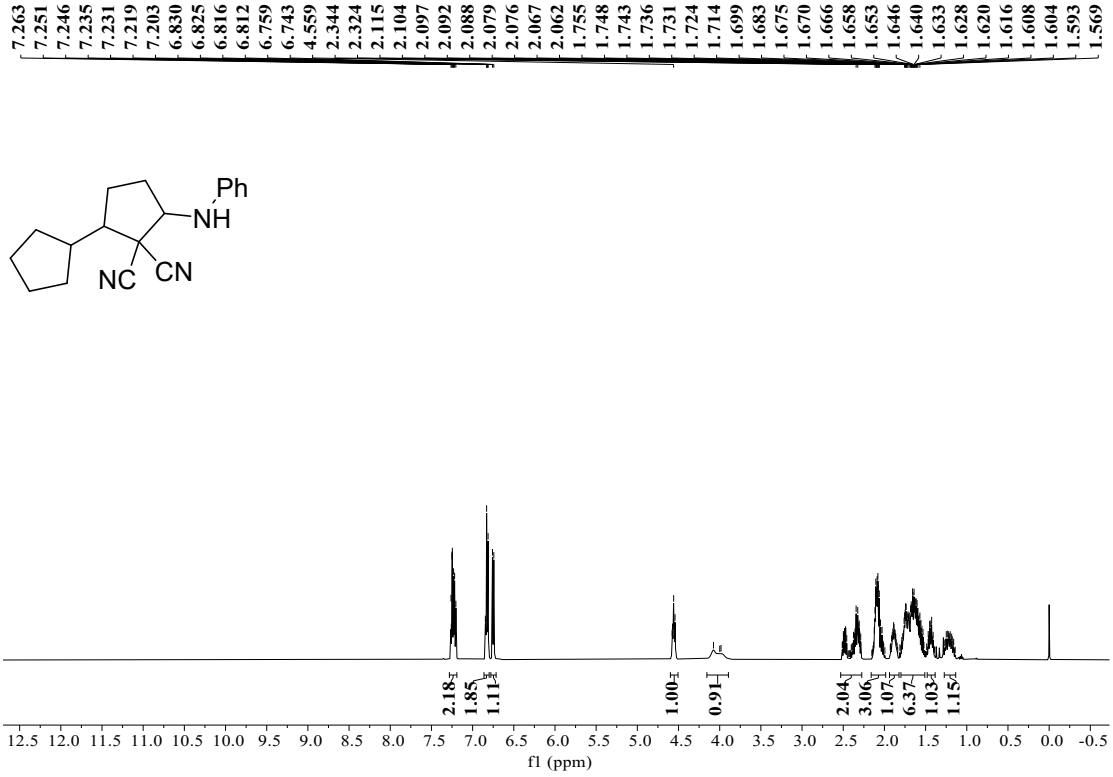


^{13}C NMR (126 MHz, $CDCl_3$)

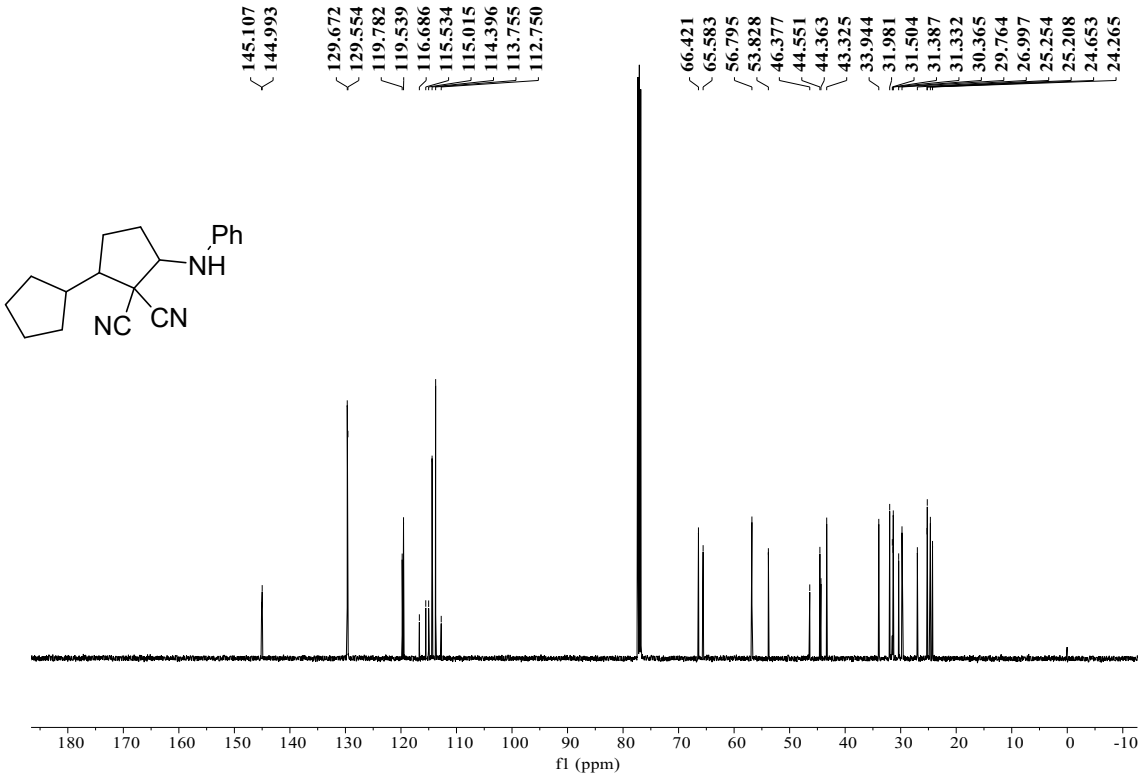


3-(phenylamino)-[1,1'-bi(cyclopentane)]-2,2-dicarbonitrile (4x)

^{1}H NMR (500 MHz, $CDCl_3$)

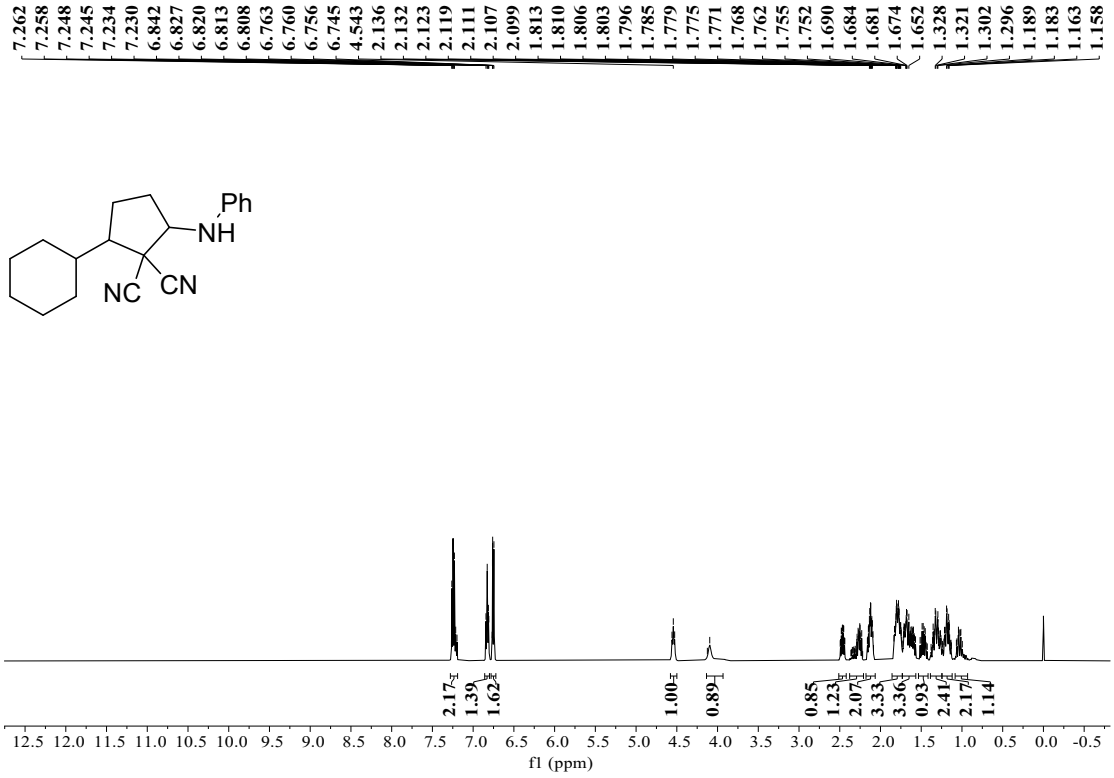


^{13}C NMR (126 MHz, $CDCl_3$)

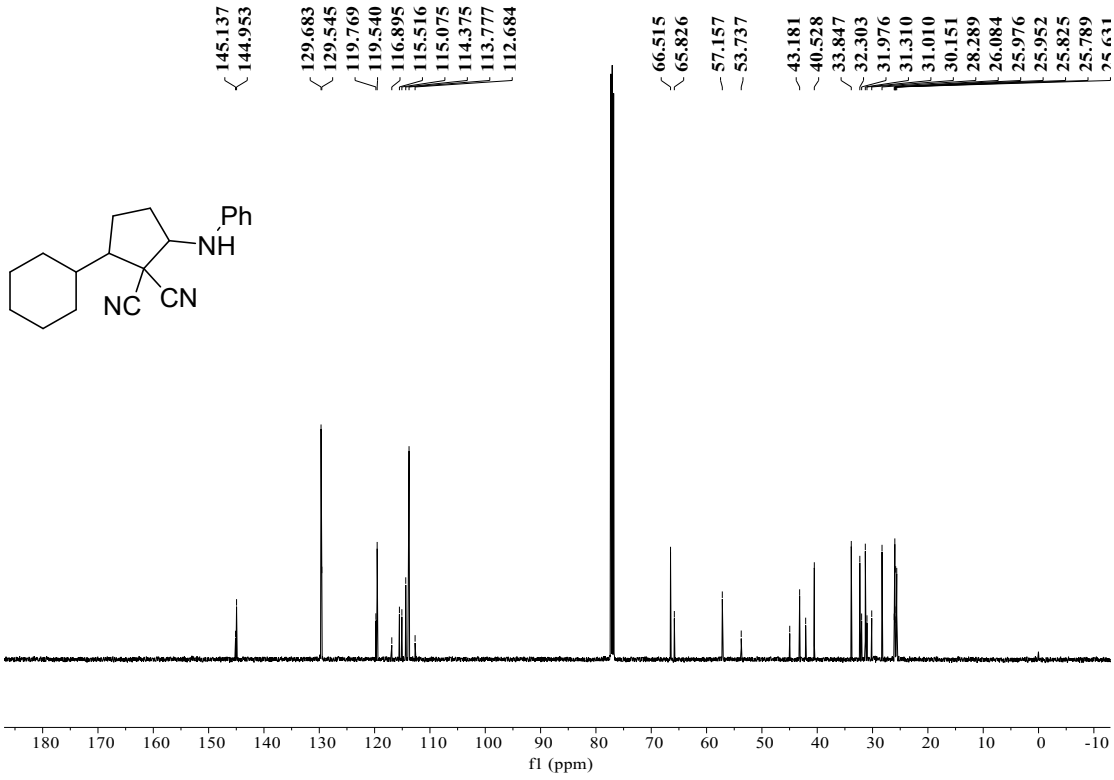


2-cyclohexyl-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4y)

^{1}H NMR (500 MHz, $CDCl_3$)

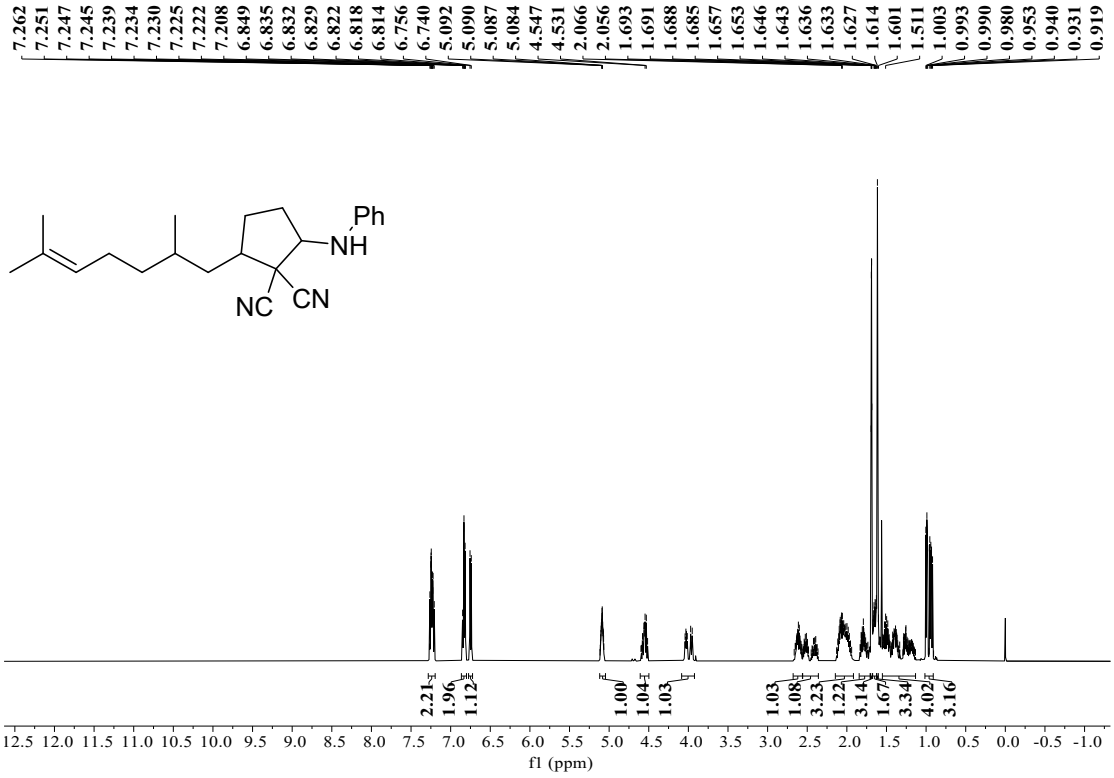


^{13}C NMR (126 MHz, $CDCl_3$)

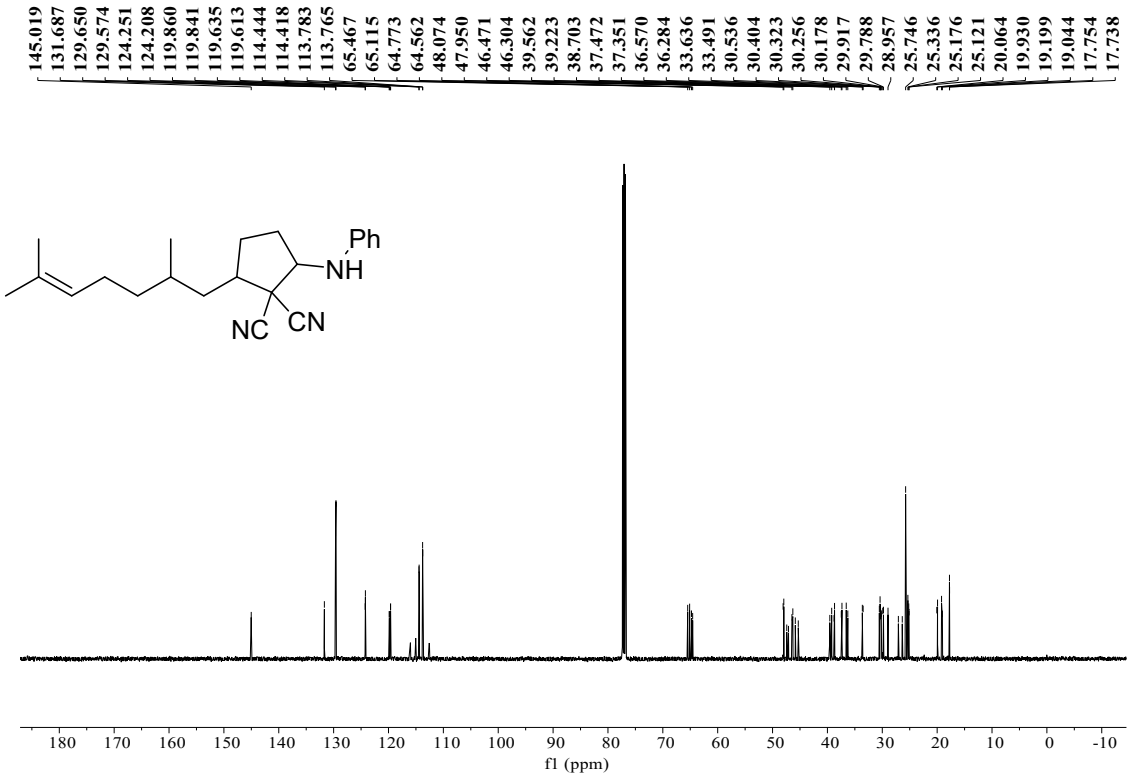


2-(2,6-dimethylhept-5-en-1-yl)-5-(phenylamino)cyclopentane-1,1-dicarbonitrile (4z)

^{1}H NMR (500 MHz, $CDCl_3$)

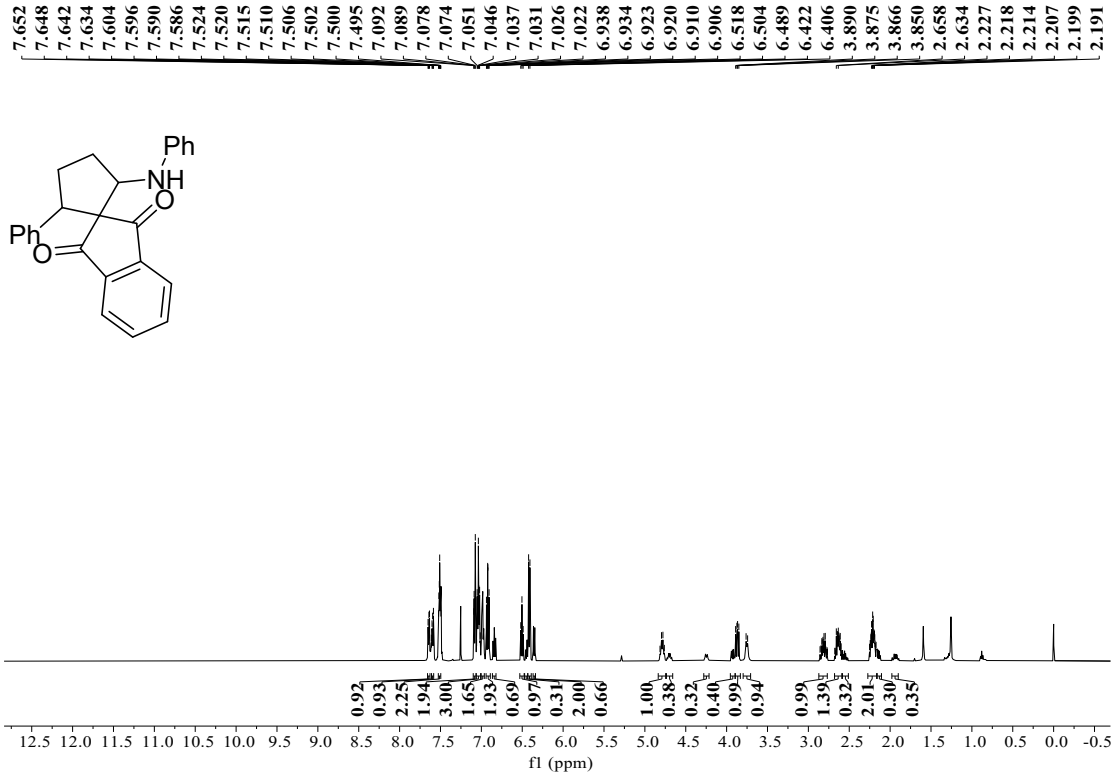


^{13}C NMR (126 MHz, $CDCl_3$)

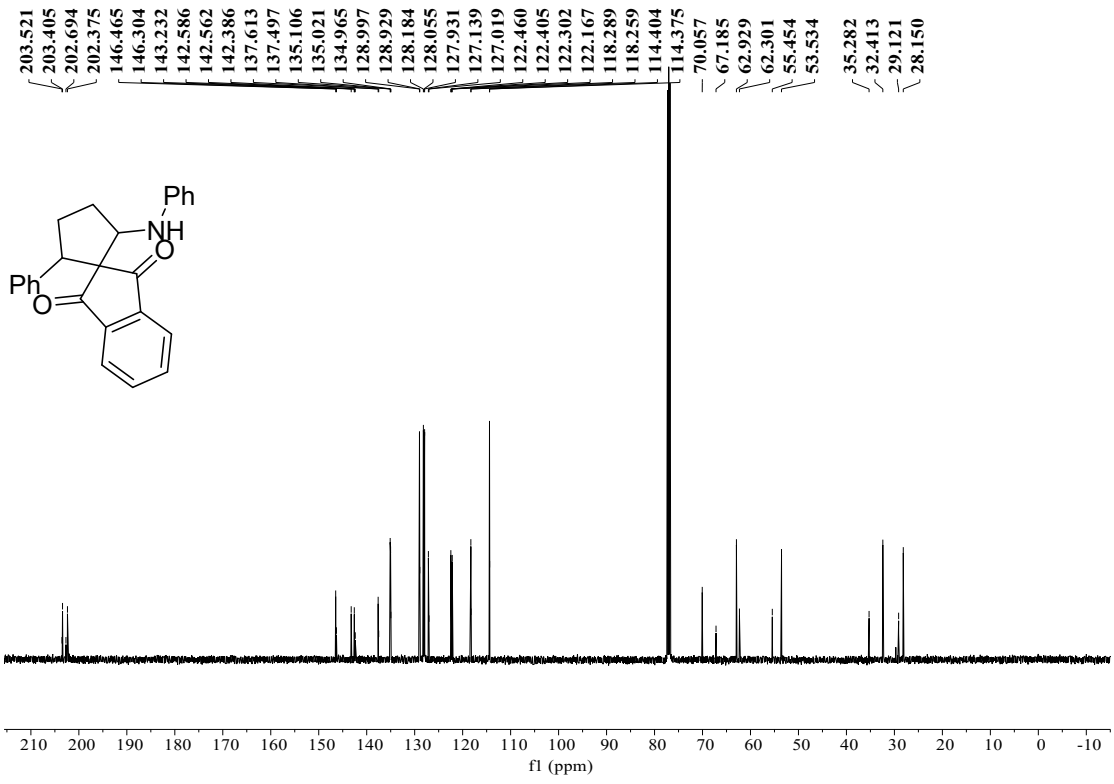


2-phenyl-5-(phenylamino)spiro[cyclopentane-1,2'-indene]-1',3'-dione (4aa)

^{1}H NMR (500 MHz, $CDCl_3$)

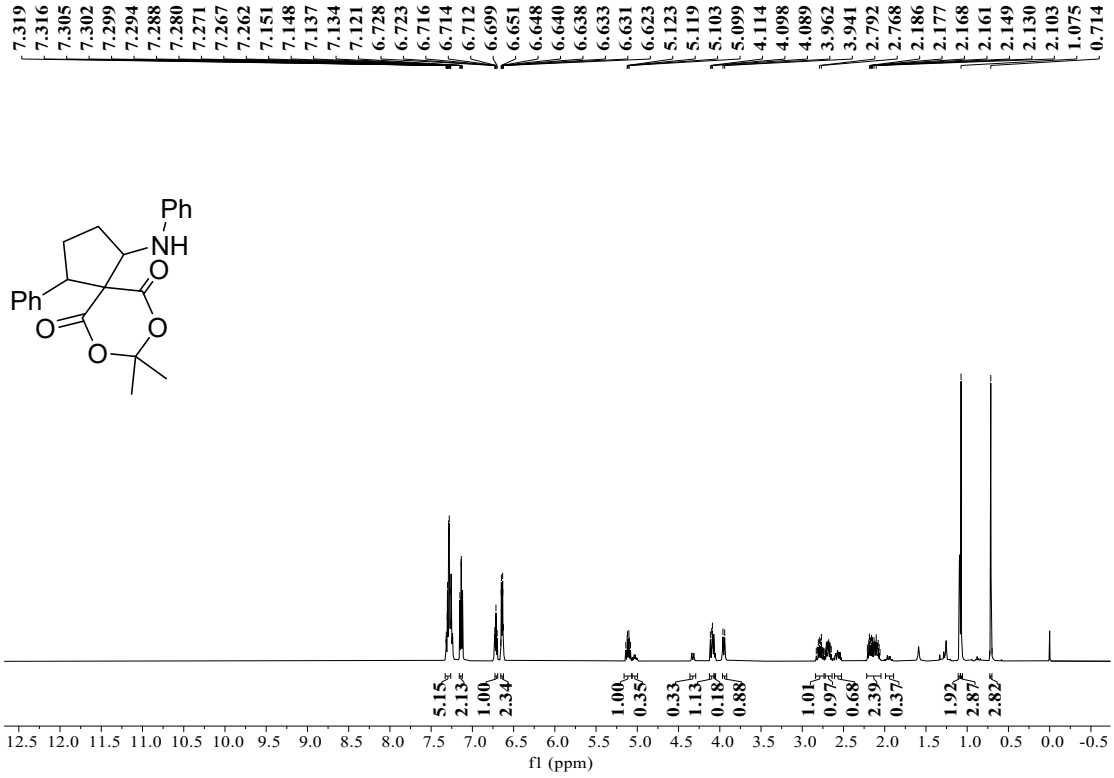


^{13}C NMR (126 MHz, $CDCl_3$)

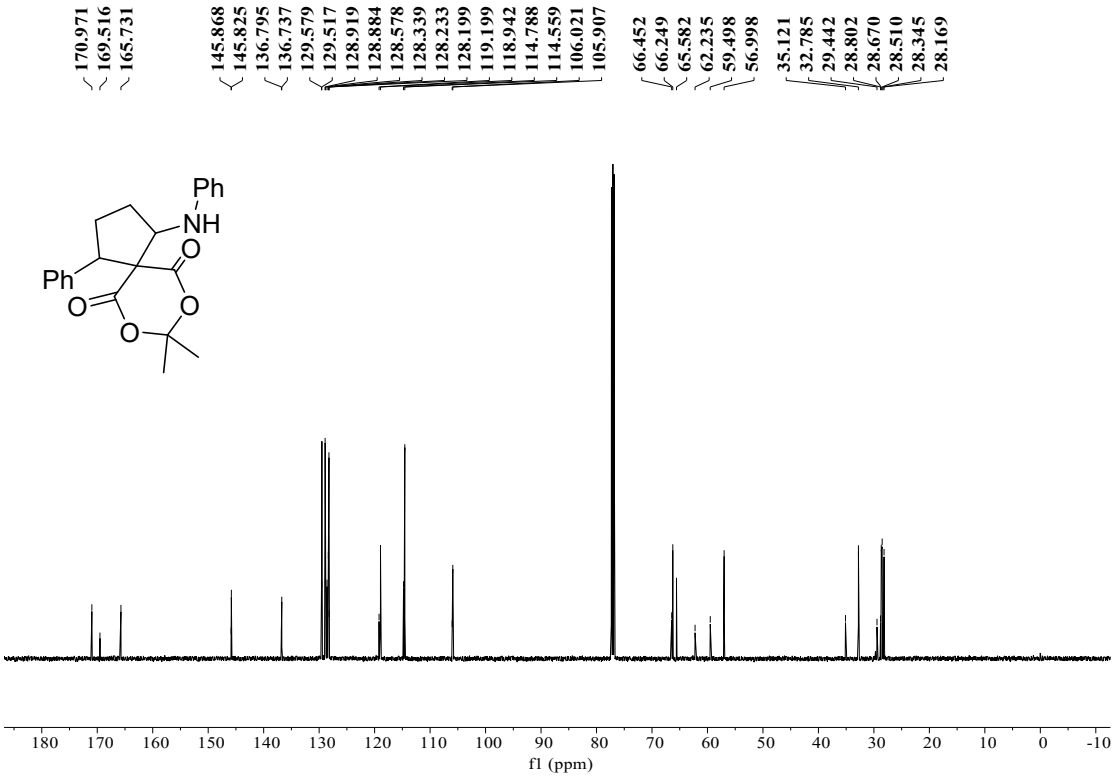


8,8-dimethyl-1-phenyl-4-(phenylamino)-7,9-dioxaspiro[4.5]decane-6,10-dione (4ab)

^{1}H NMR (500 MHz, $CDCl_3$)

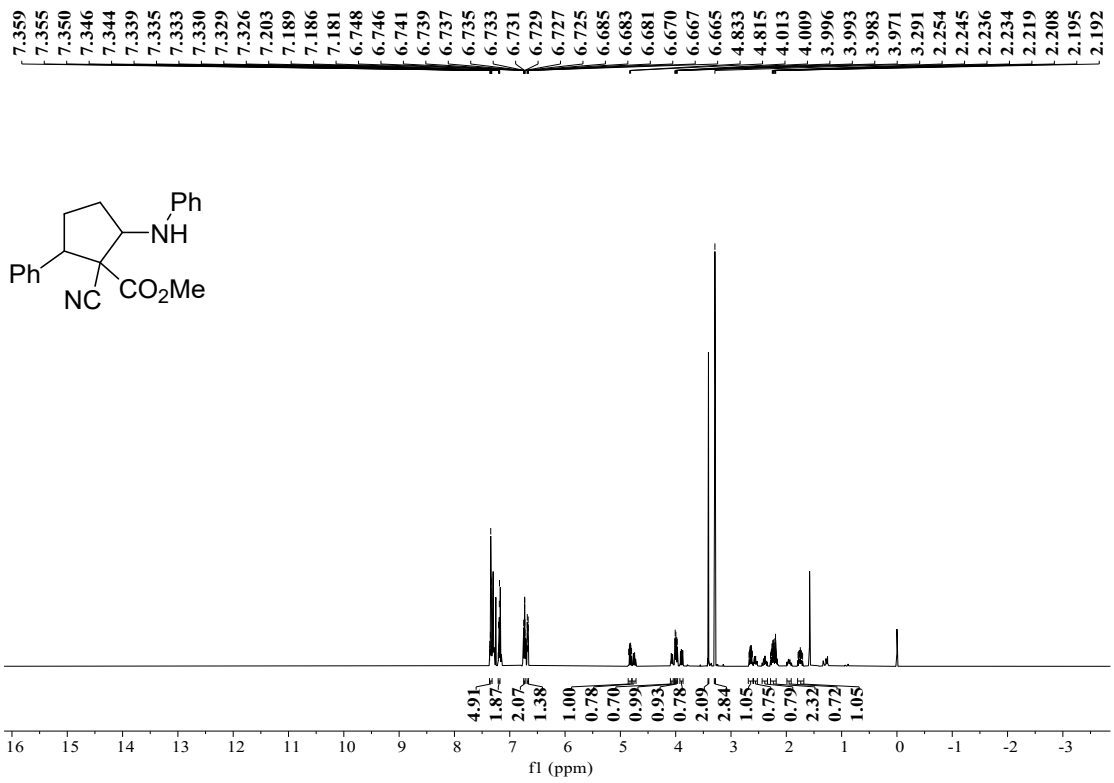


^{13}C NMR (126 MHz, $CDCl_3$)

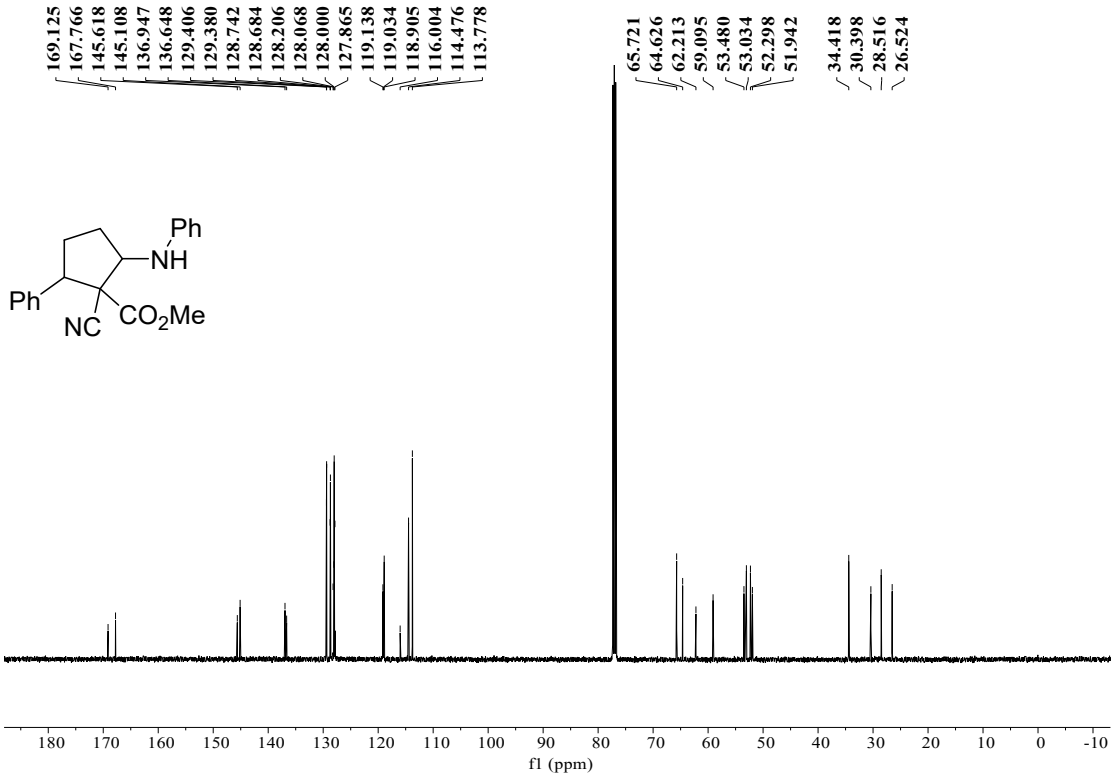


methyl 1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxylate (4ac)

^{1}H NMR (500 MHz, $CDCl_3$)

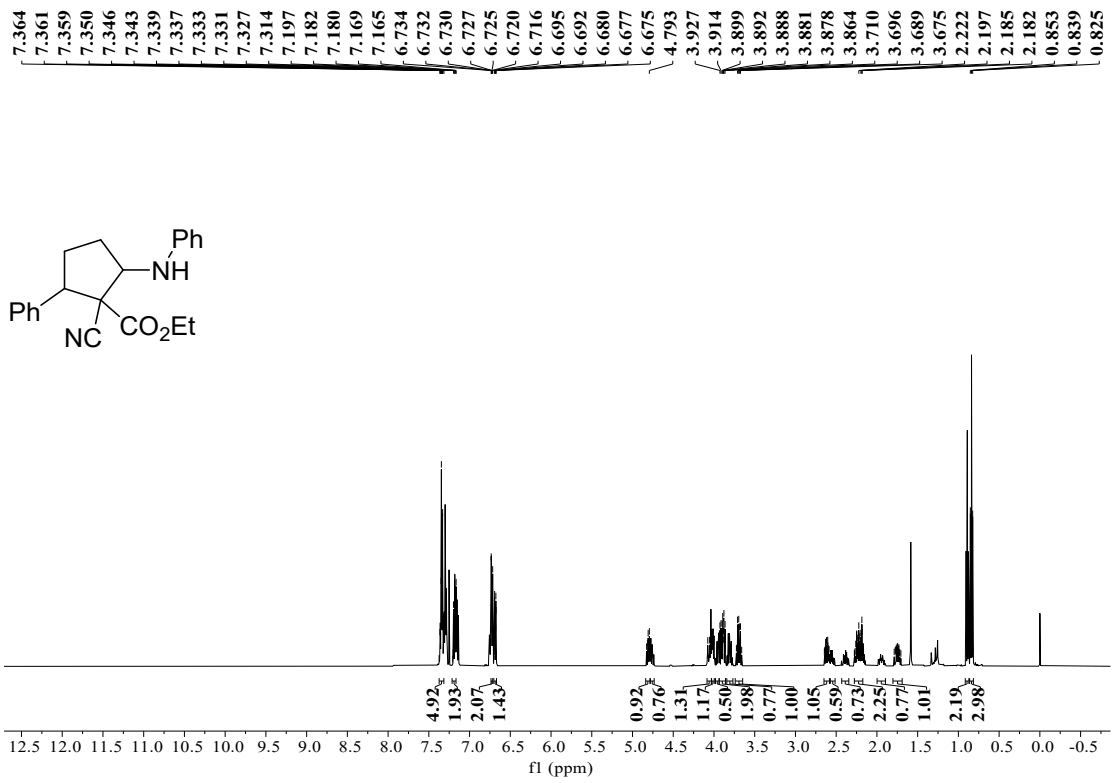


^{13}C NMR (126 MHz, $CDCl_3$)

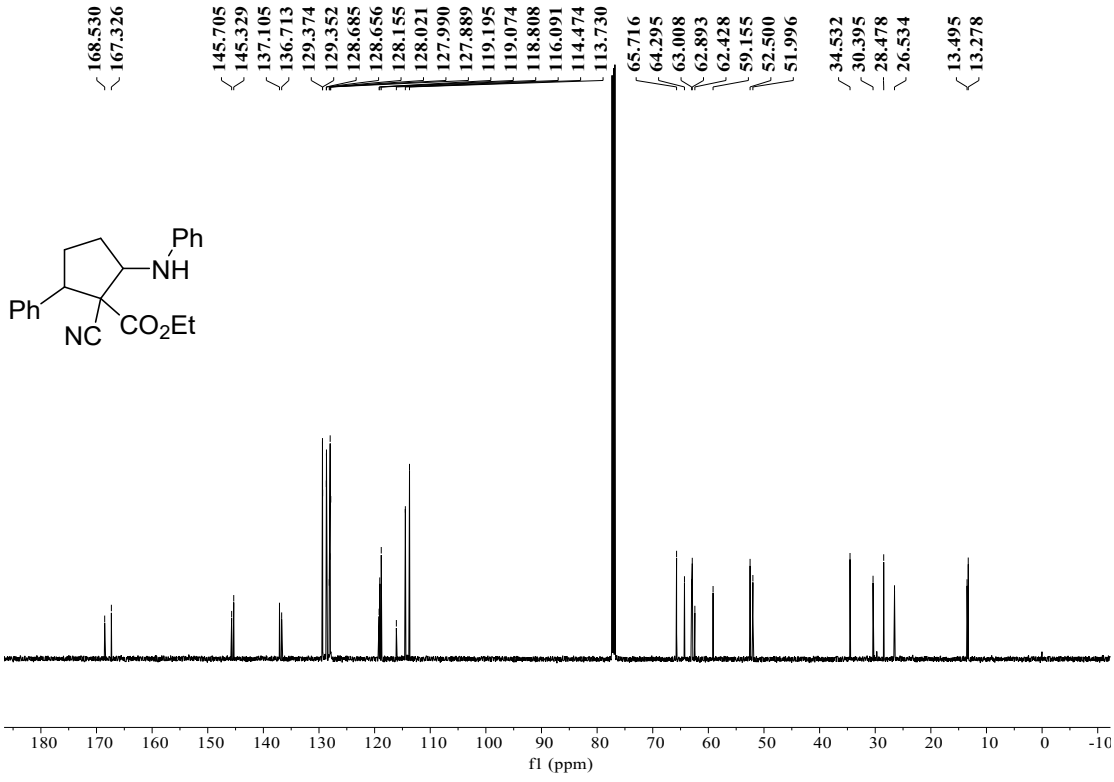


ethyl 1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxylate (4ad)

^{1}H NMR (500 MHz, $CDCl_3$)

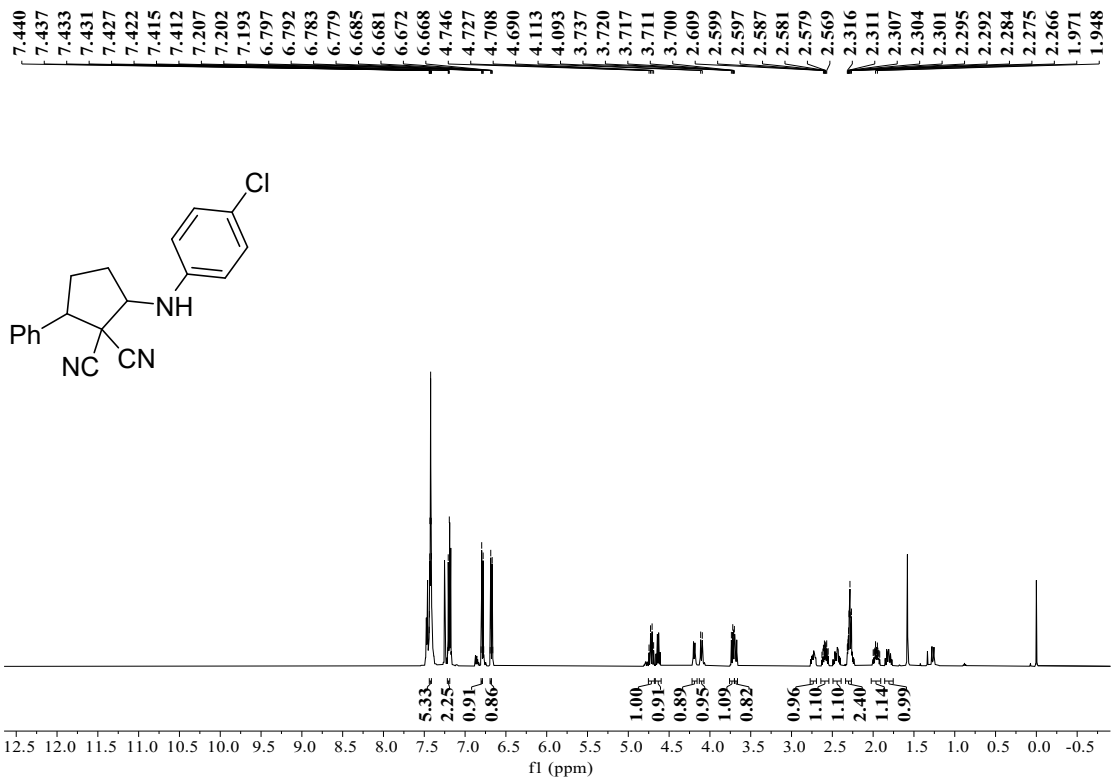


^{13}C NMR (126 MHz, $CDCl_3$)

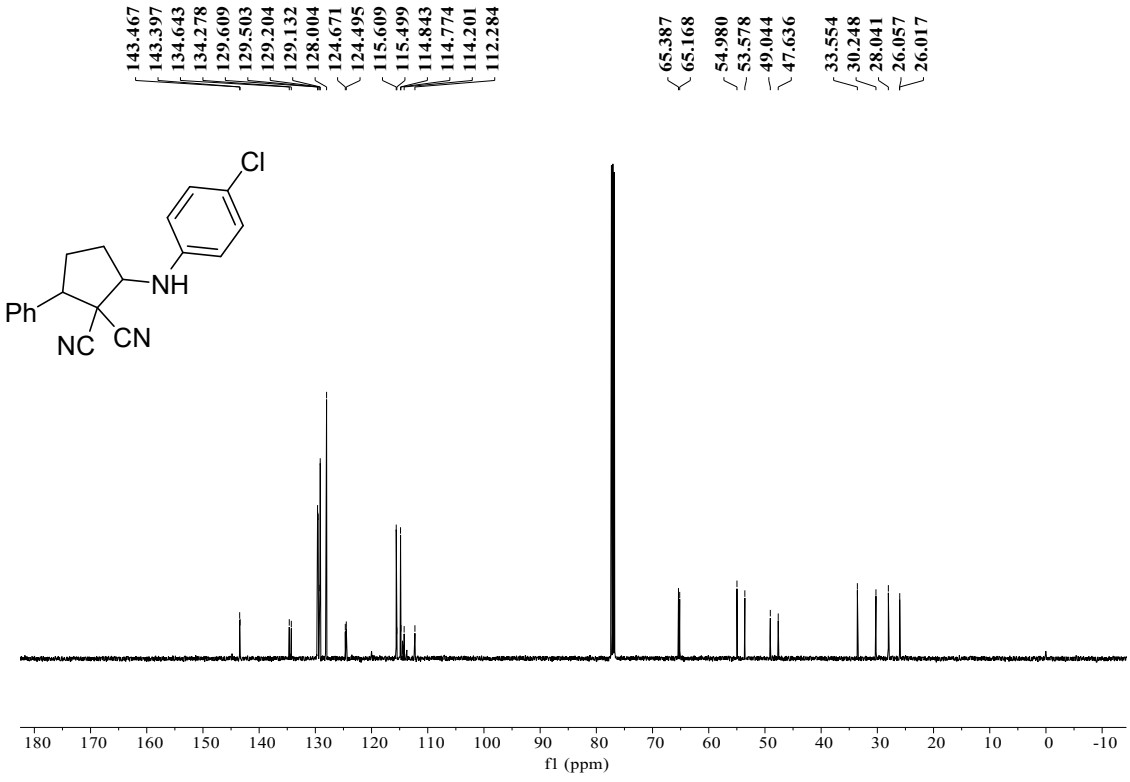


2-((4-chlorophenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4ag)

^{1}H NMR (500 MHz, $CDCl_3$)

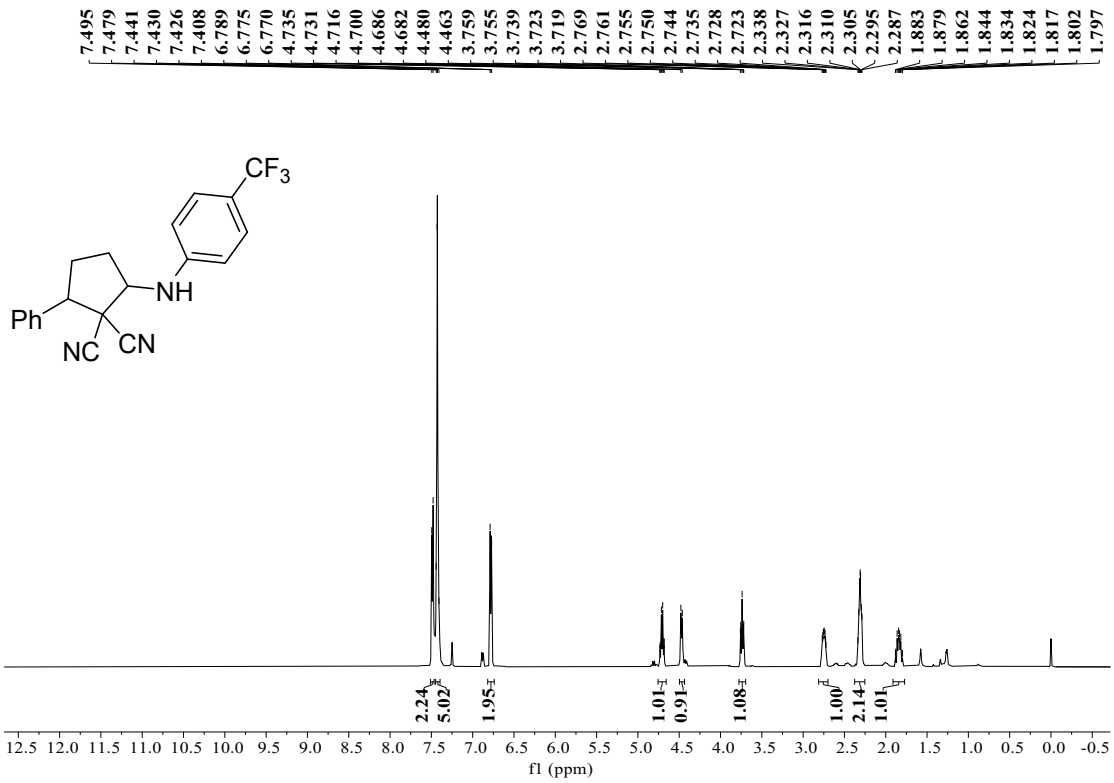


^{13}C NMR (126 MHz, $CDCl_3$)

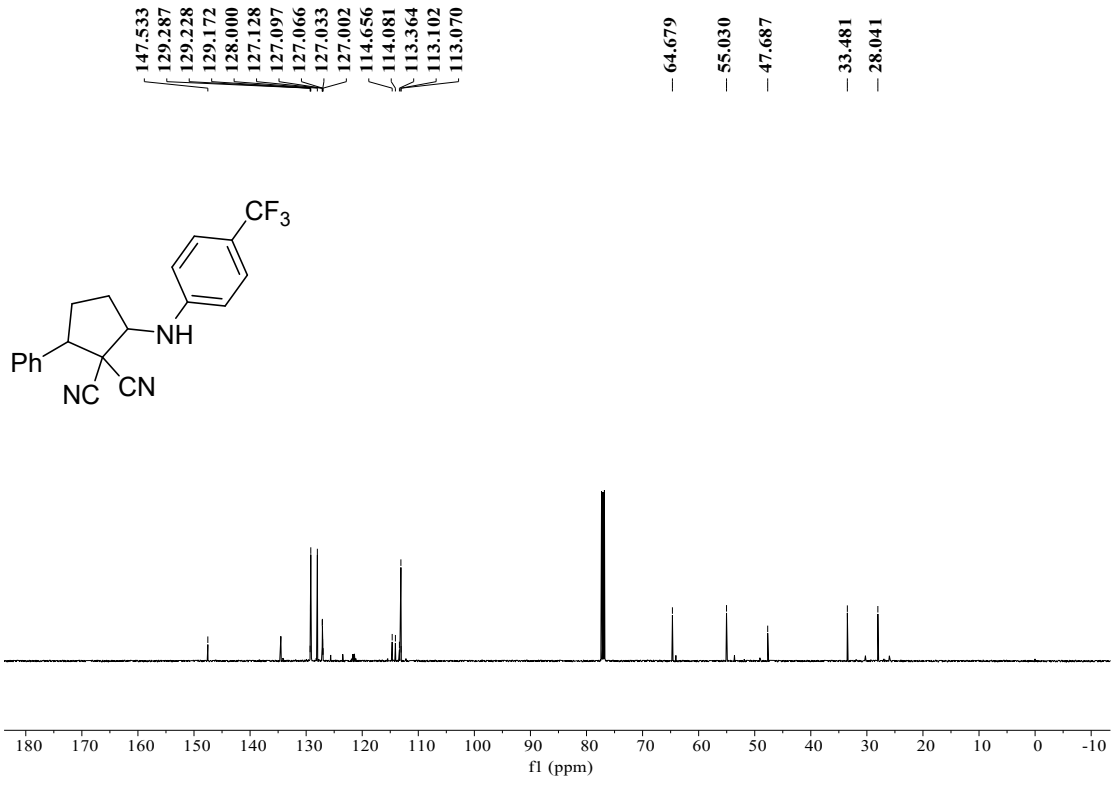


2-phenyl-5-((4-(trifluoromethyl)phenyl)amino)cyclopentane-1,1-dicarbonitrile (4ah)

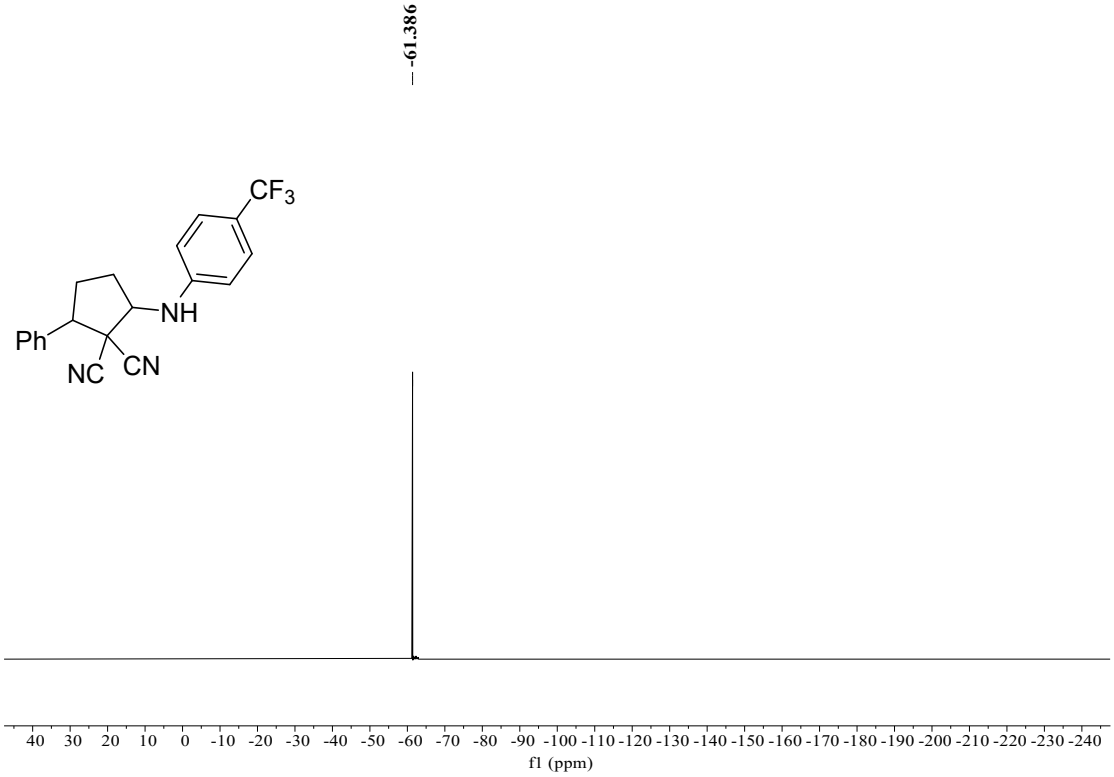
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

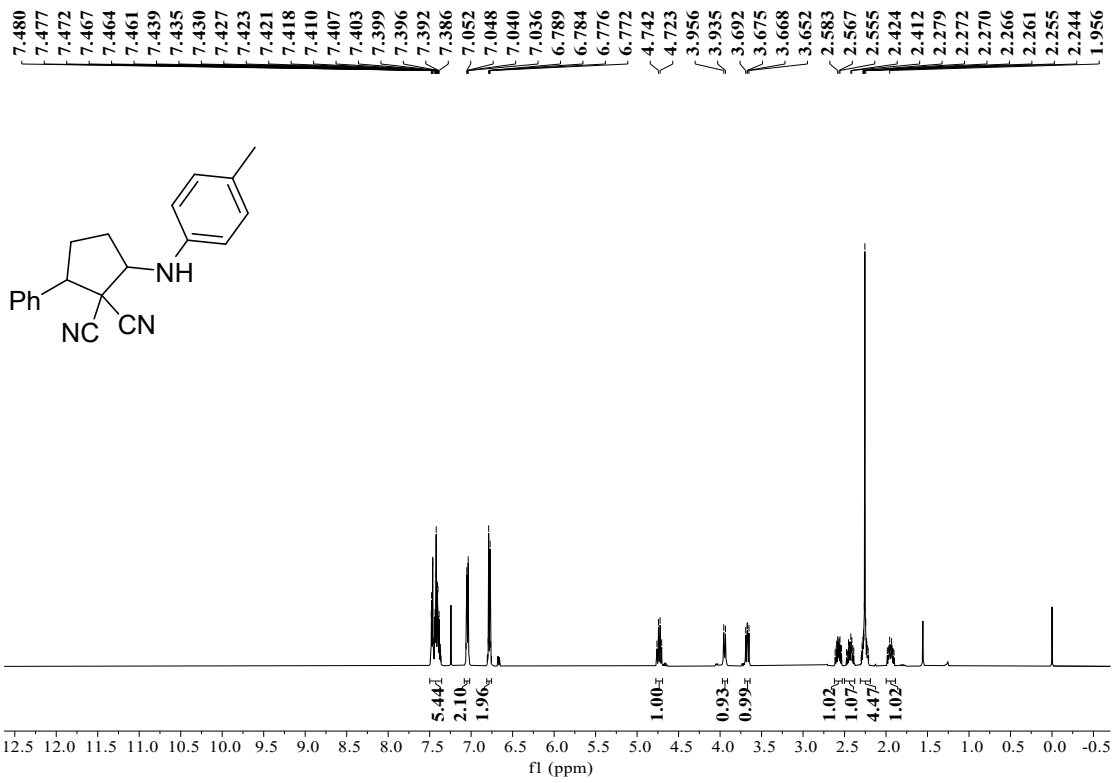


^{19}F NMR (470 MHz, $CDCl_3$)

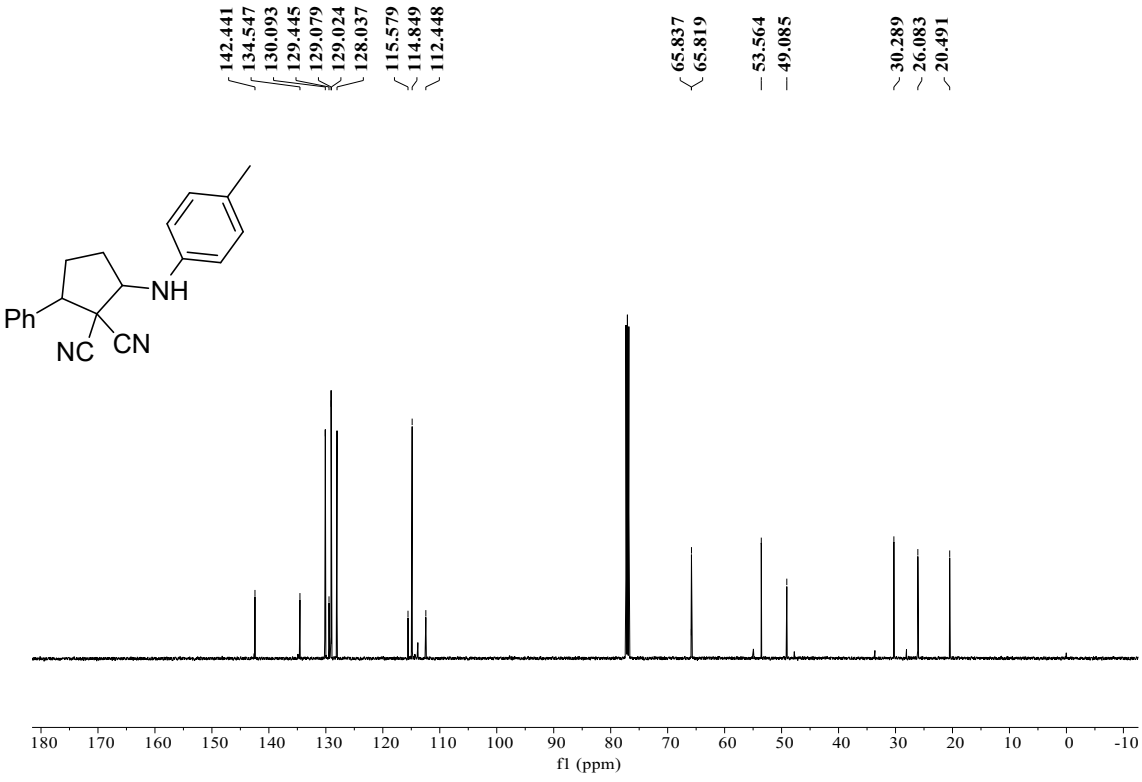


2-phenyl-5-(p-tolylamino)cyclopentane-1,1-dicarbonitrile (4ai)

^{1}H NMR (500 MHz, $CDCl_3$)

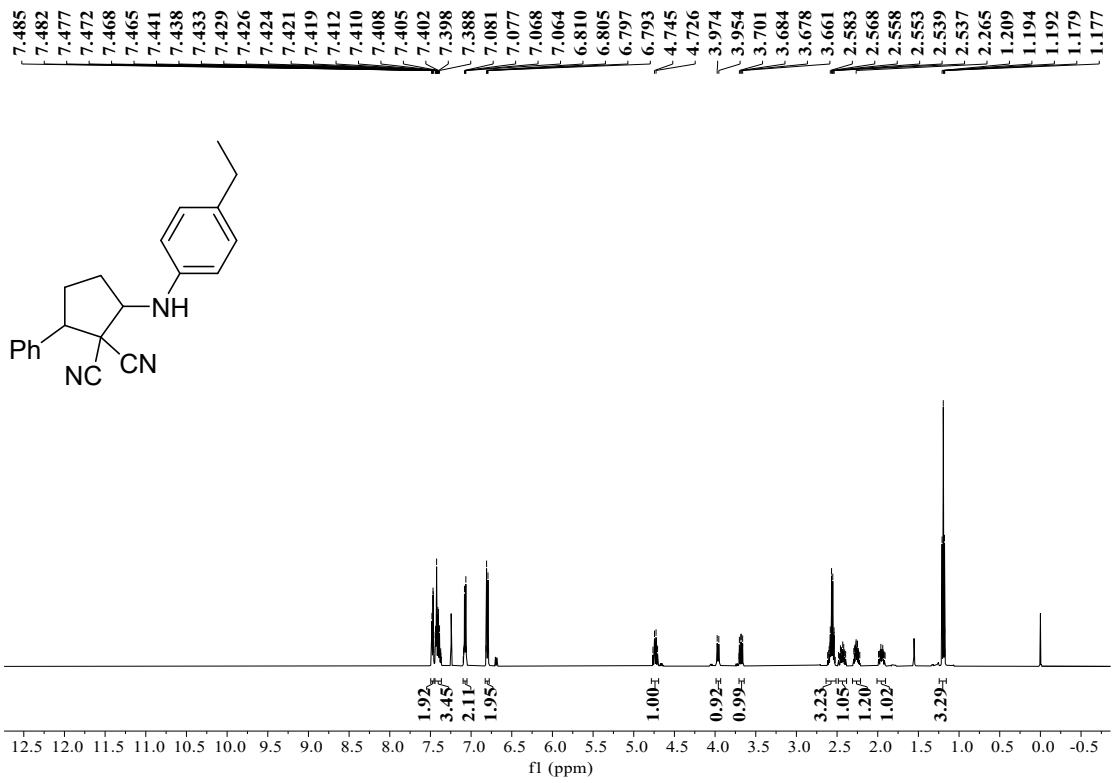


^{13}C NMR (126 MHz, $CDCl_3$)

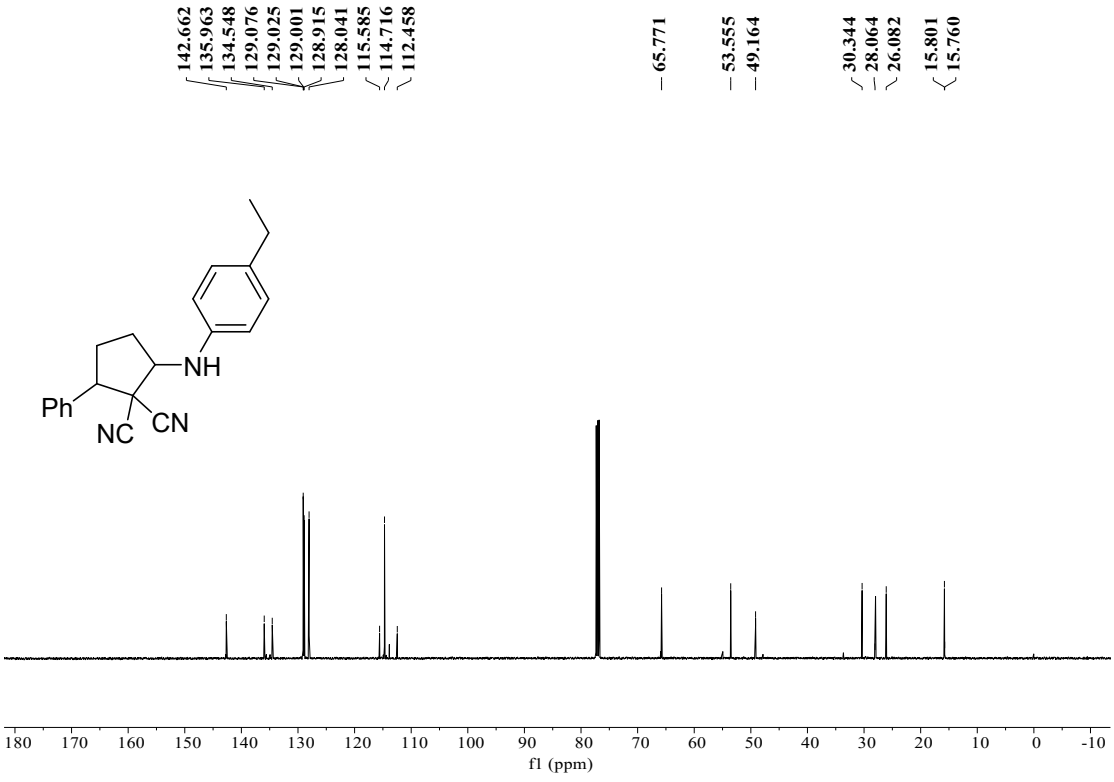


2-((4-ethylphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4aj)

^{1}H NMR (500 MHz, $CDCl_3$)

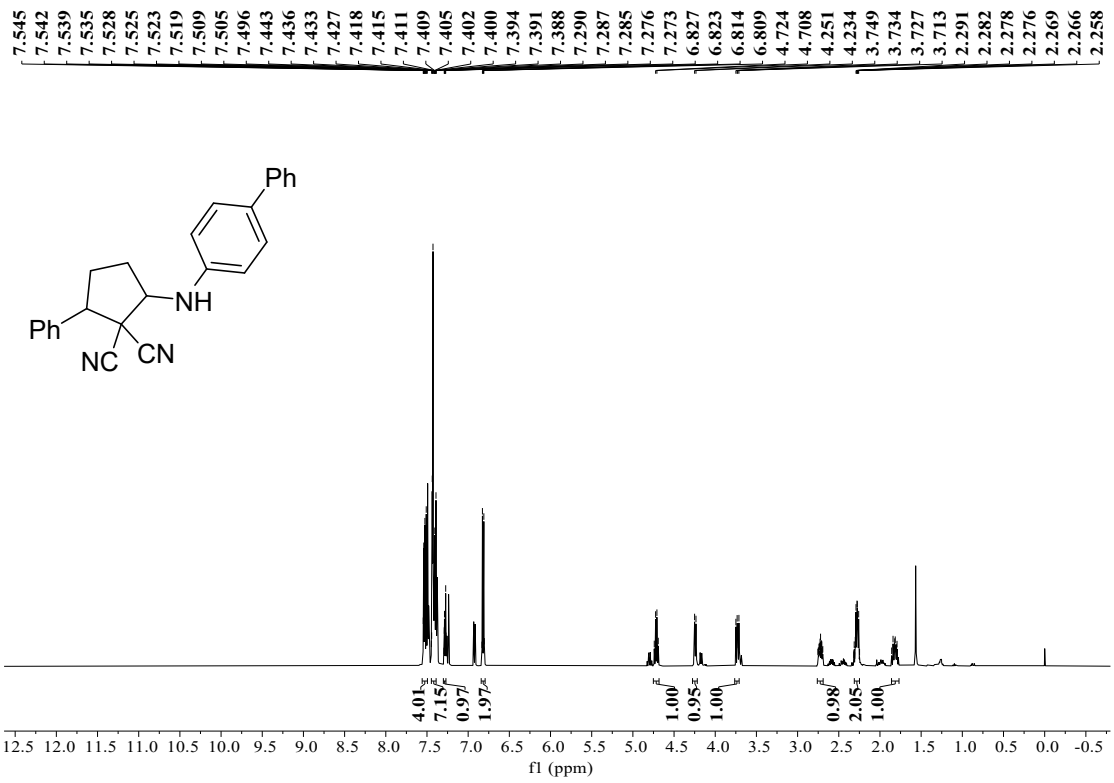


^{13}C NMR (126 MHz, $CDCl_3$)

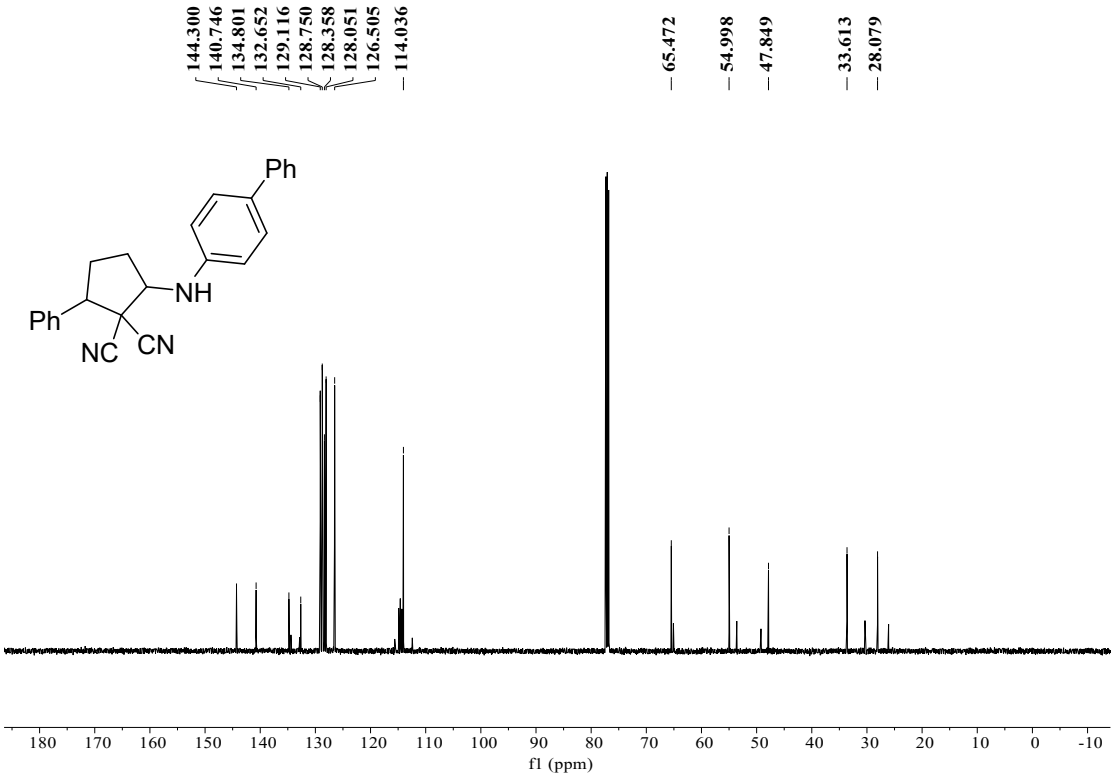


2-([1,1'-biphenyl]-4-ylamino)-5-phenylcyclopentane-1,1-dicarbonitrile (4ak)

^{1}H NMR (500 MHz, $CDCl_3$)

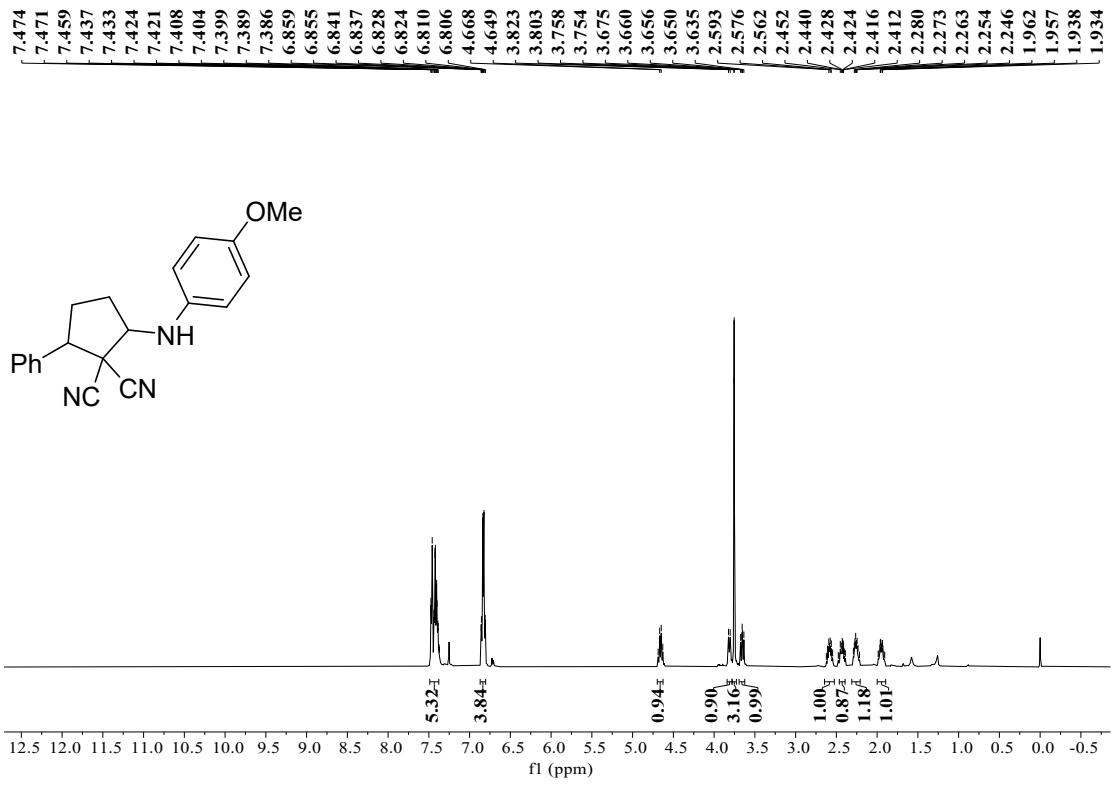


^{13}C NMR (126 MHz, $CDCl_3$)

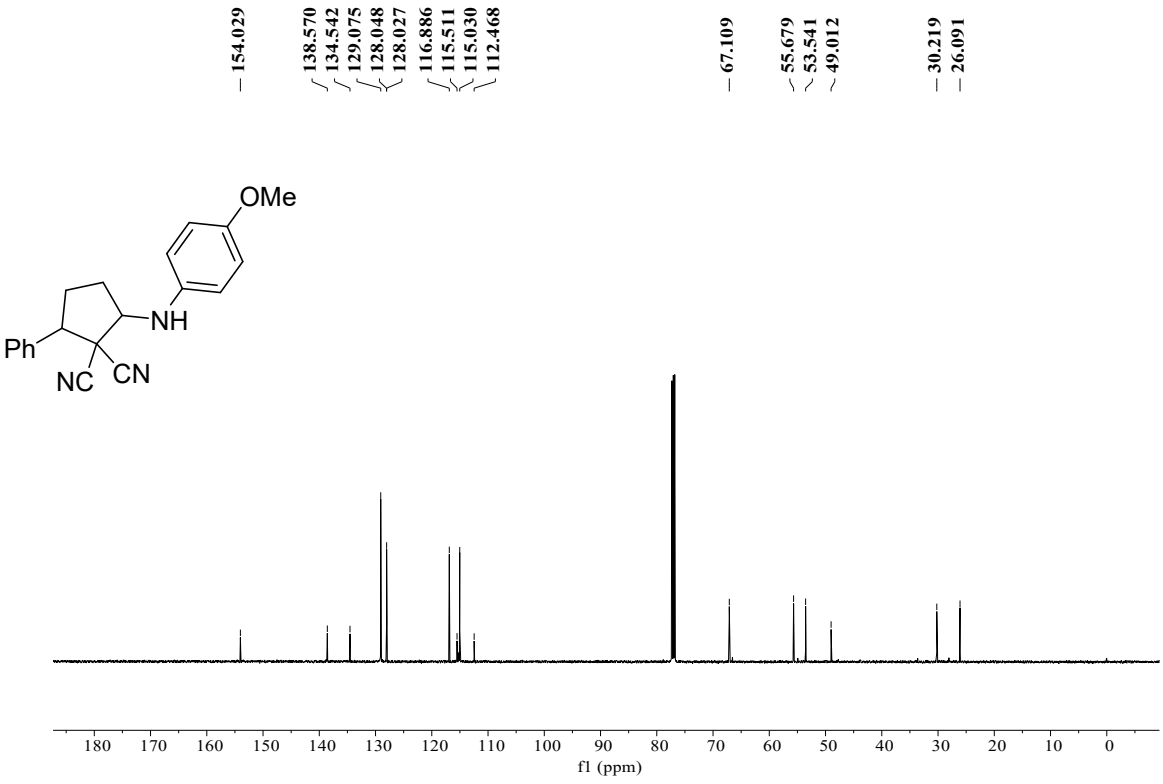


2-((4-methoxyphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4al)

^{1}H NMR (500 MHz, $CDCl_3$)

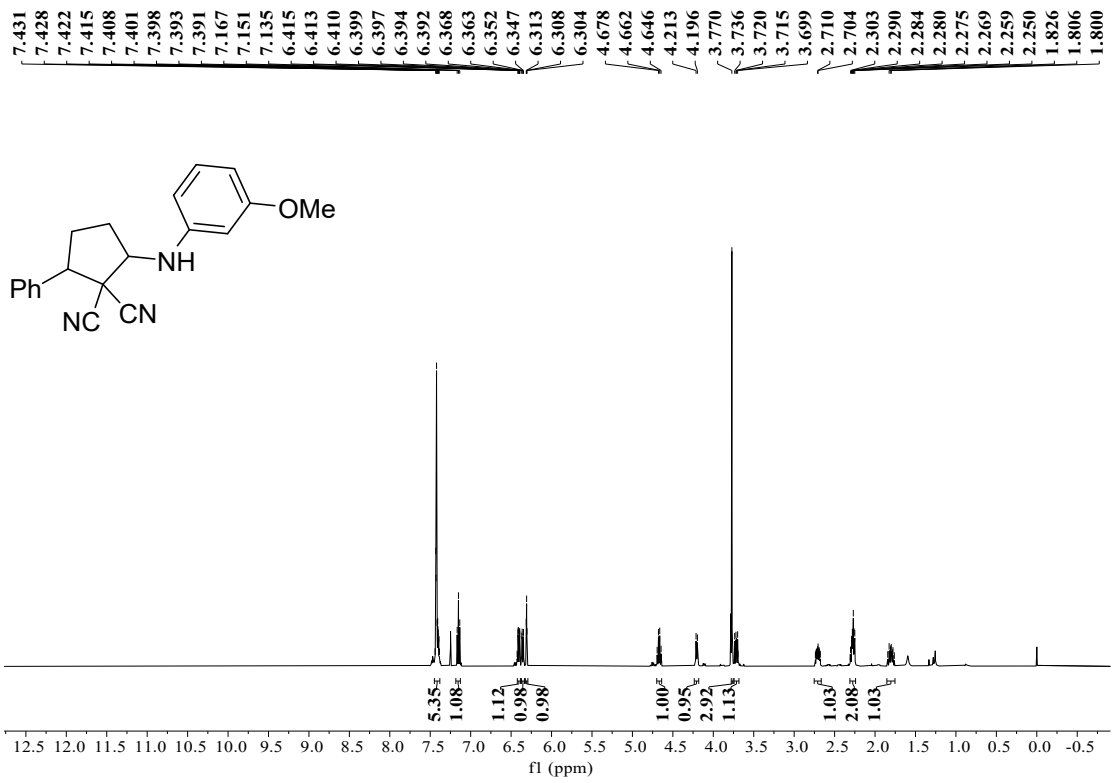


^{13}C NMR (126 MHz, $CDCl_3$)

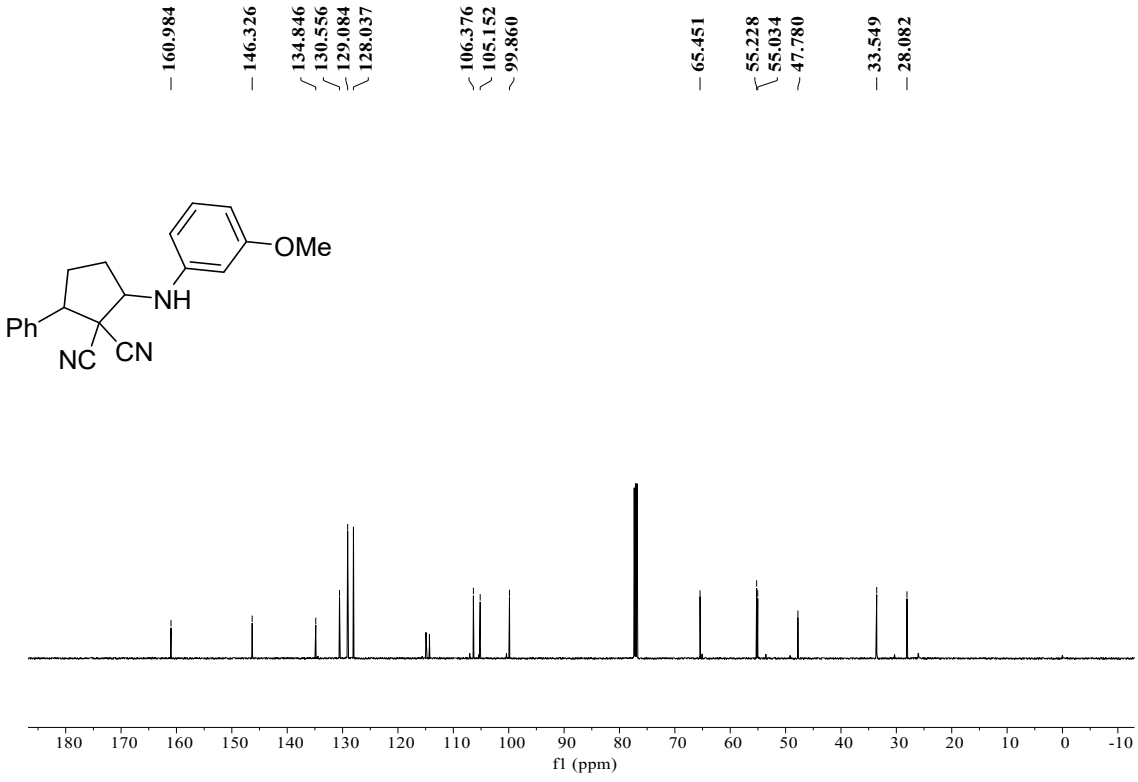


2-((3-methoxyphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4am)

^{1}H NMR (500 MHz, $CDCl_3$)

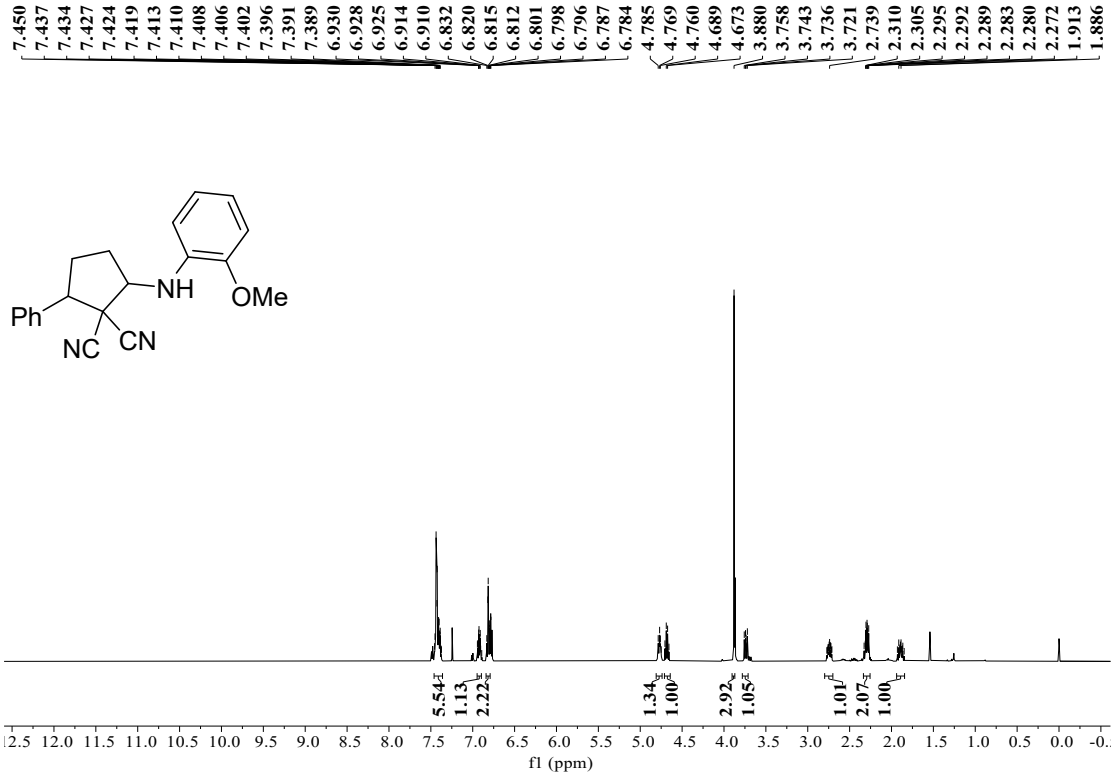


^{13}C NMR (126 MHz, $CDCl_3$)

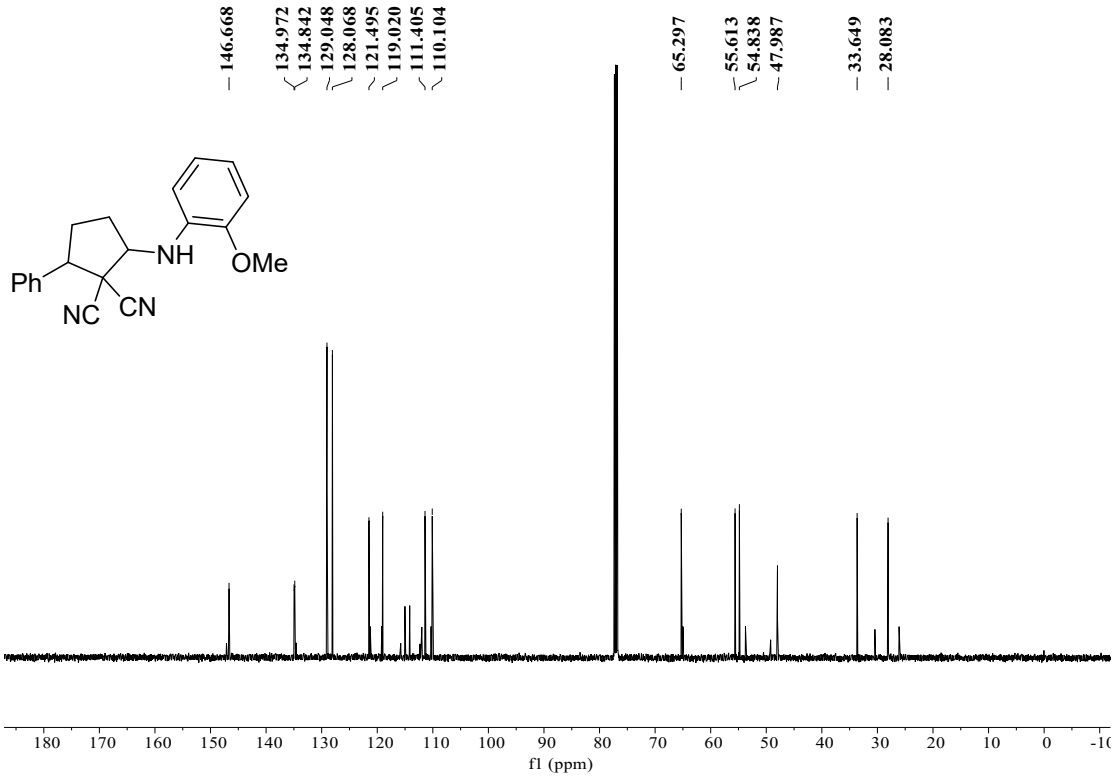


2-((2-methoxyphenyl)amino)-5-phenylcyclopentane-1,1-dicarbonitrile (4an)

^{1}H NMR (500 MHz, $CDCl_3$)

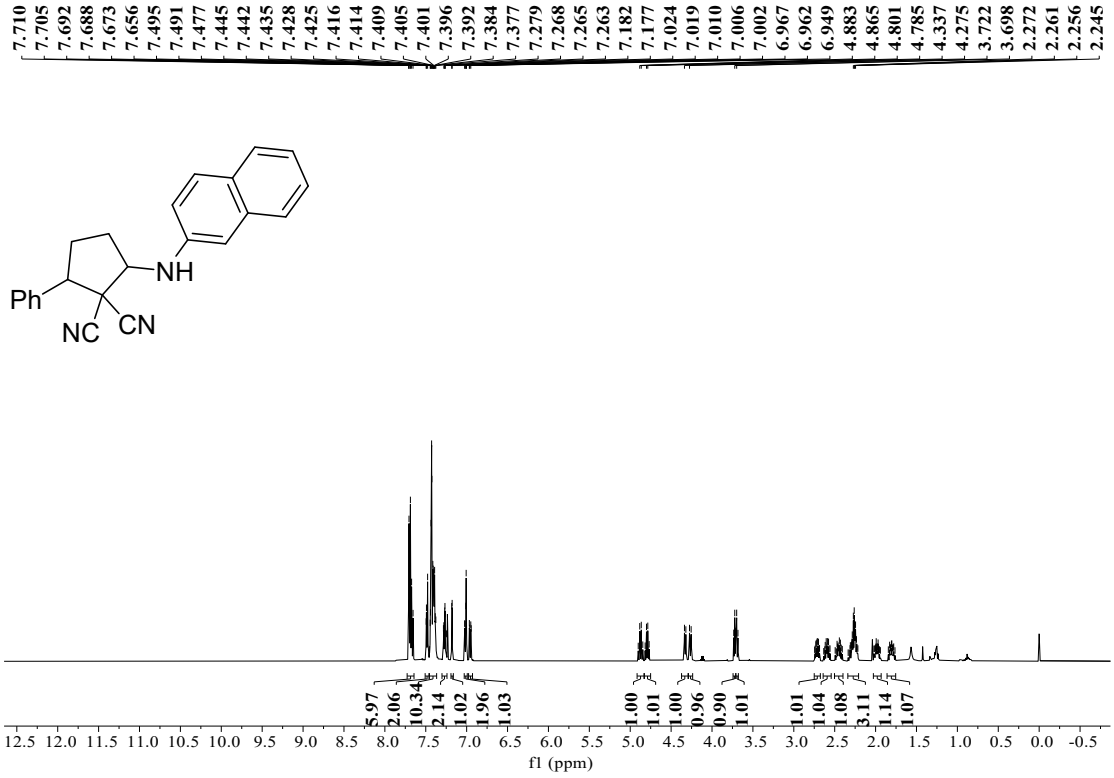


^{13}C NMR (126 MHz, $CDCl_3$)

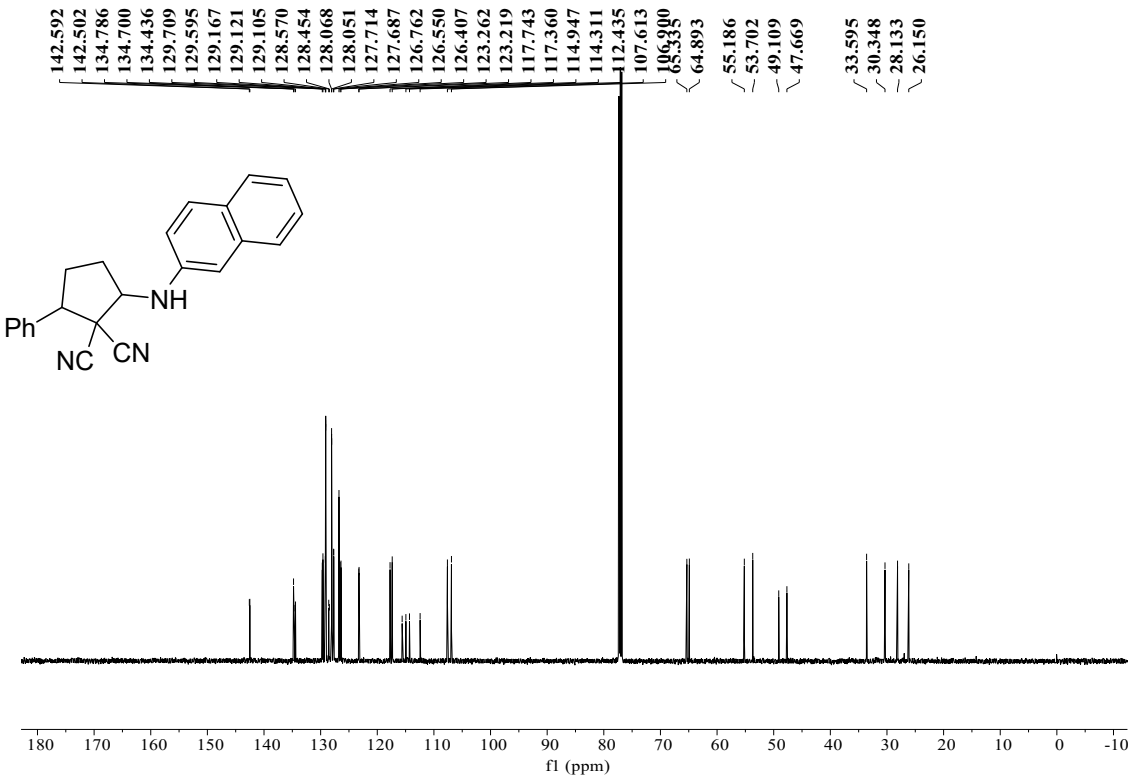


2-(naphthalen-2-ylamino)-5-phenylcyclopentane-1,1-dicarbonitrile (4ao)

^{1}H NMR (500 MHz, $CDCl_3$)

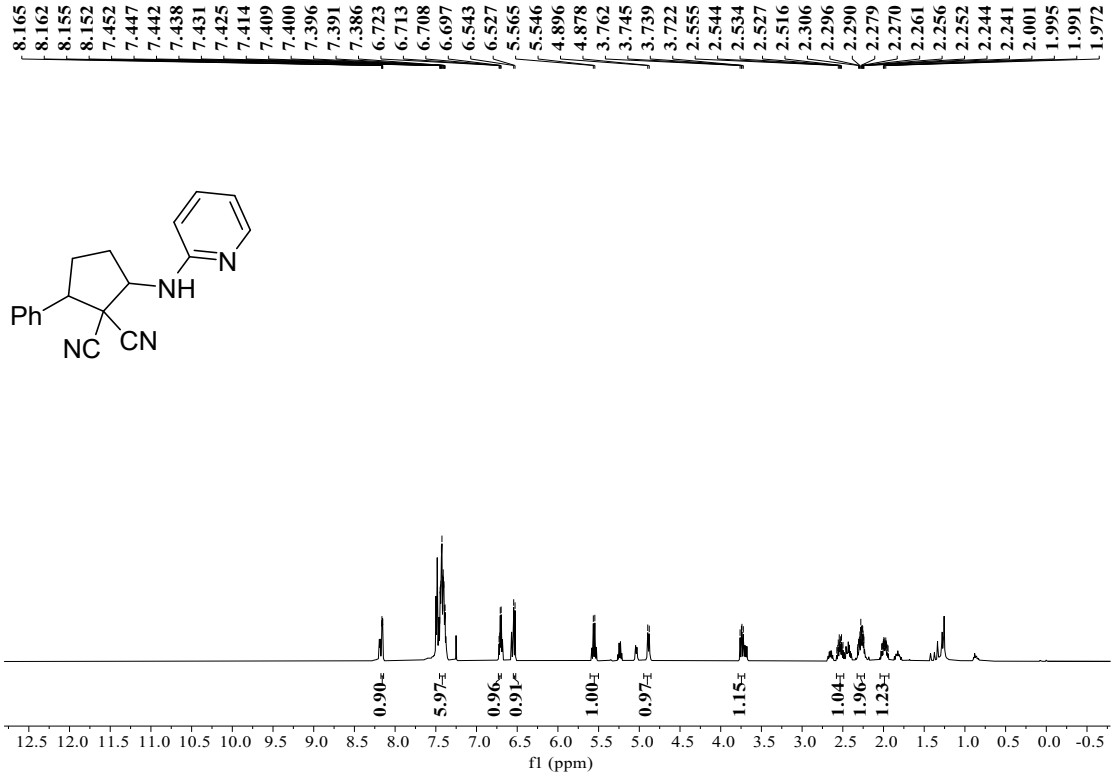


^{13}C NMR (126 MHz, $CDCl_3$)

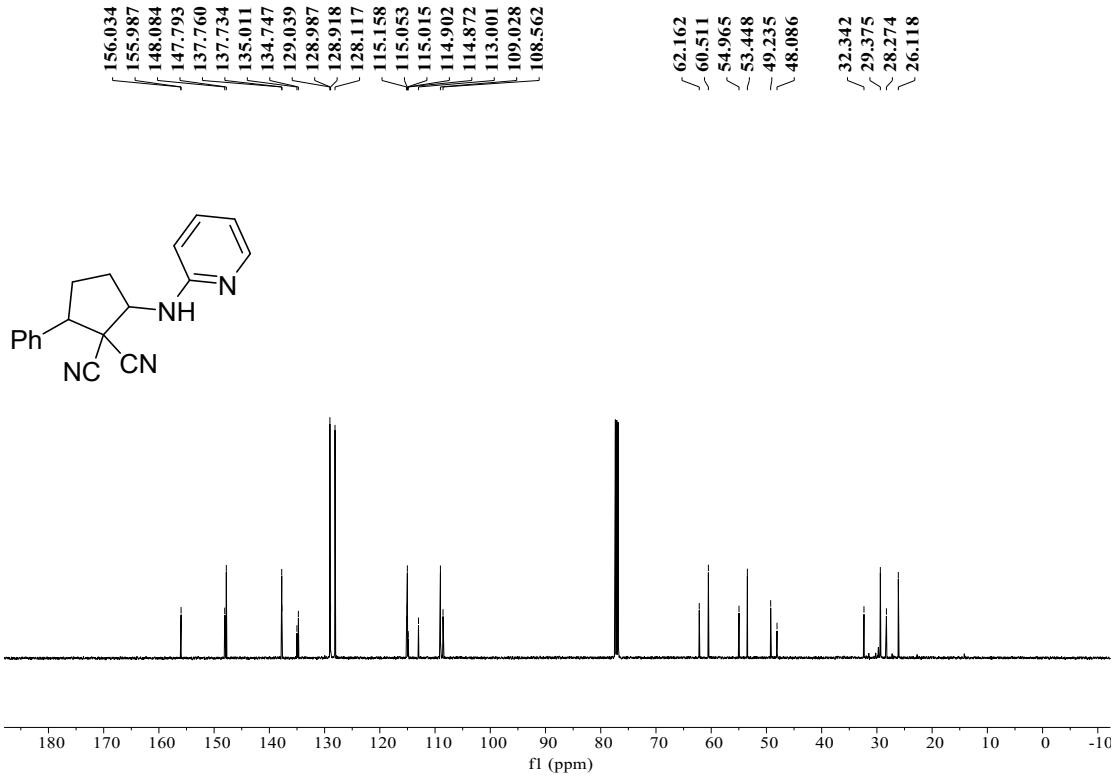


2-phenyl-5-(pyridin-2-ylamino)cyclopentane-1,1-dicarbonitrile (4ap)

^{1}H NMR (500 MHz, $CDCl_3$)

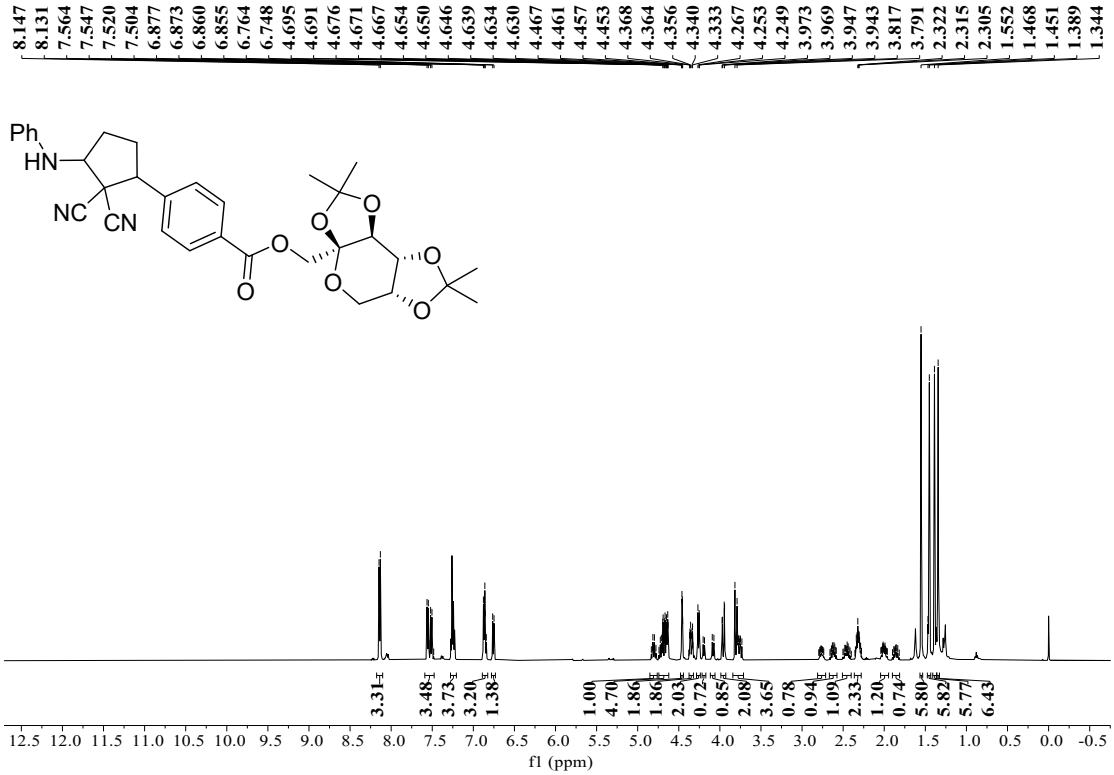


^{13}C NMR (126 MHz, $CDCl_3$)

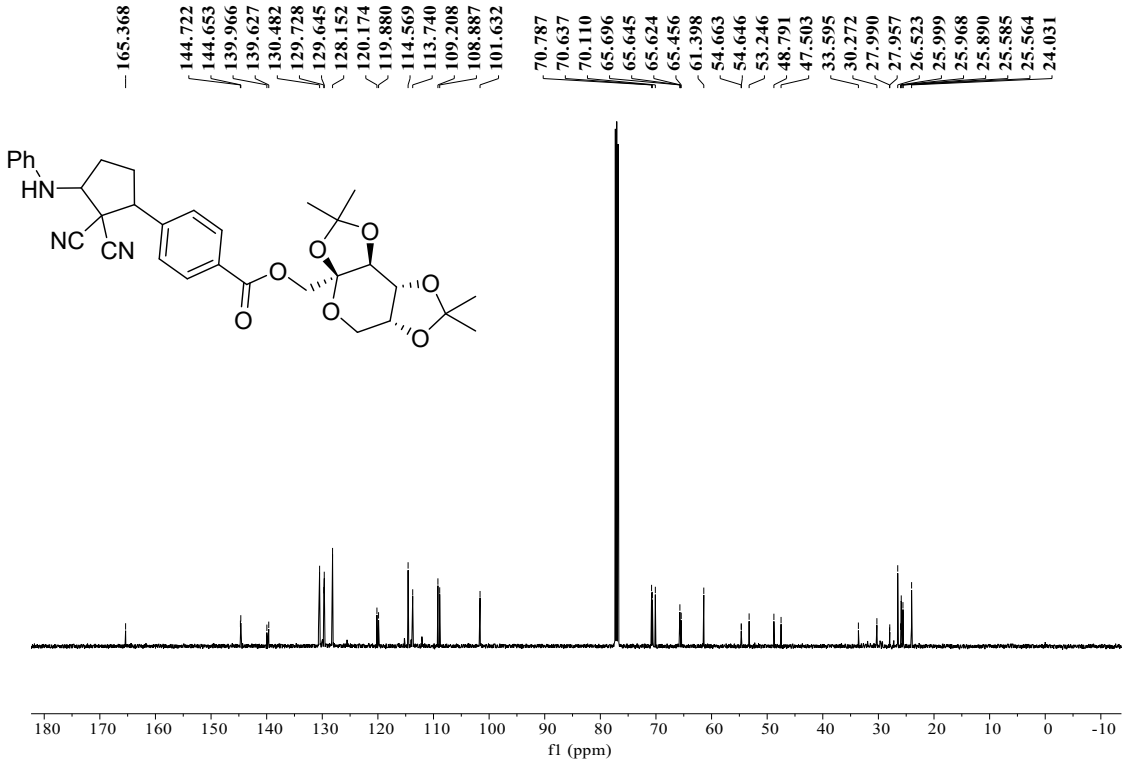


((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate (4ba)

^{1}H NMR (500 MHz, $CDCl_3$)

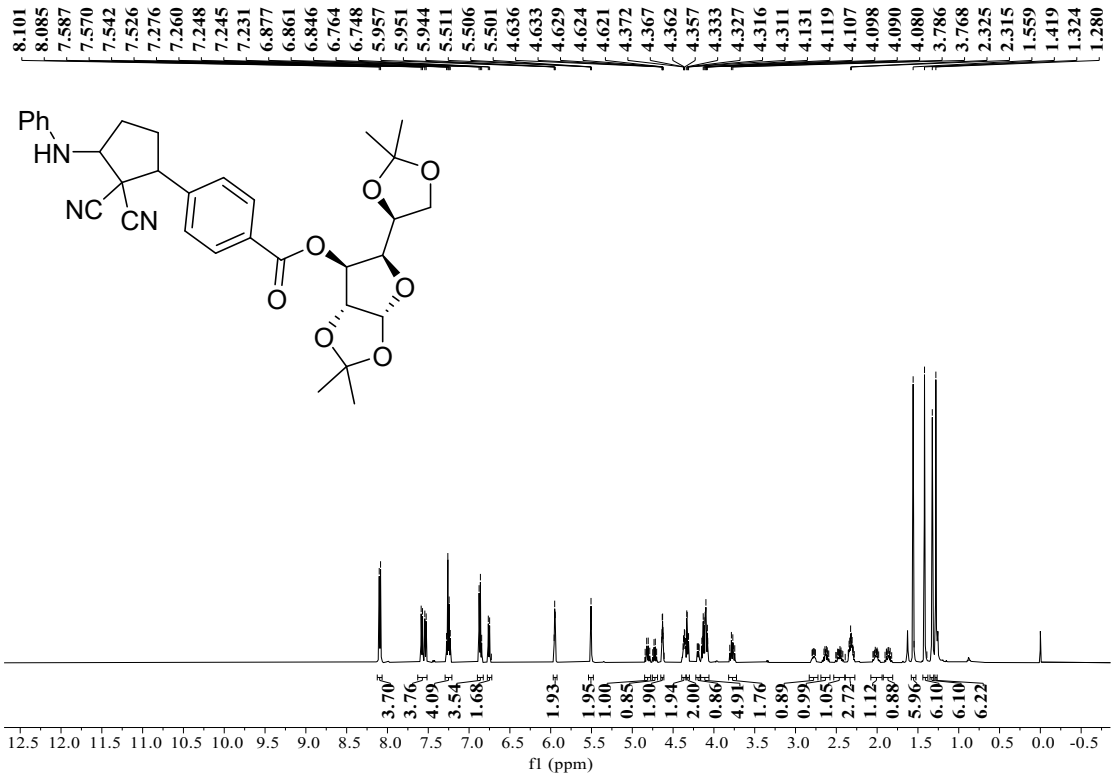


^{13}C NMR (126 MHz, $CDCl_3$)

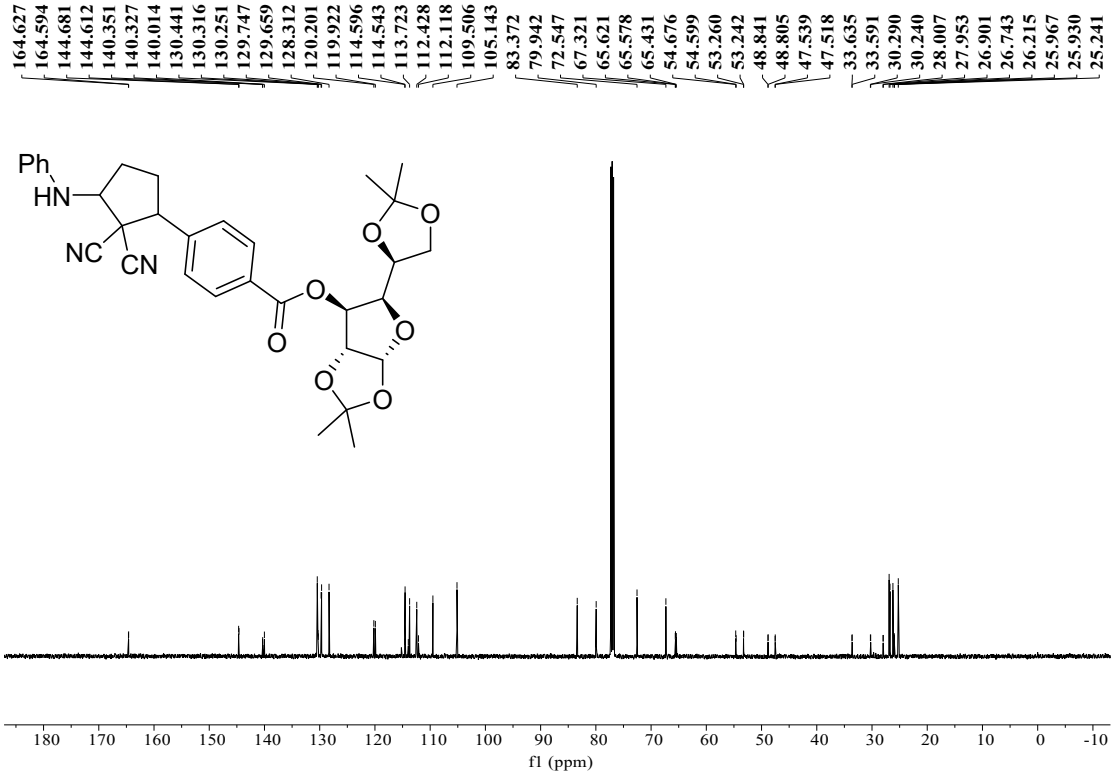


(3aR,5R,6S,6aR)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro [2,3-d][1,3]dioxol-6-yl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate (4ca)

^{1}H NMR (500 MHz, $CDCl_3$)

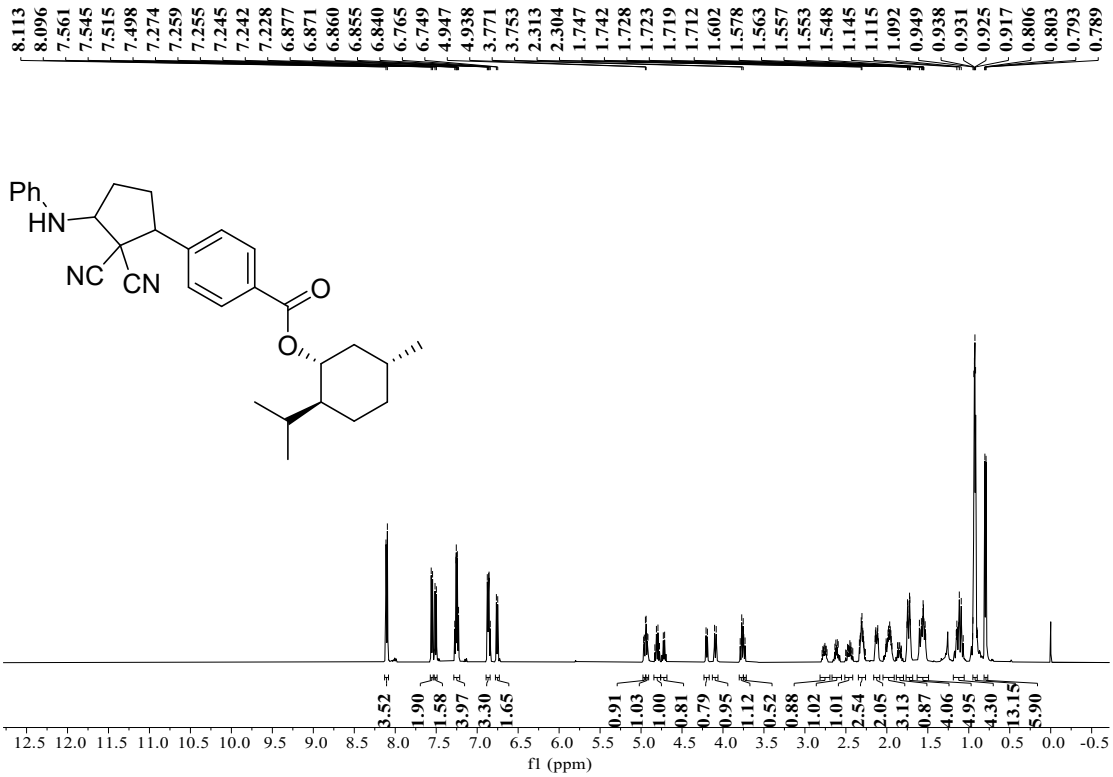


^{13}C NMR (126 MHz, $CDCl_3$)

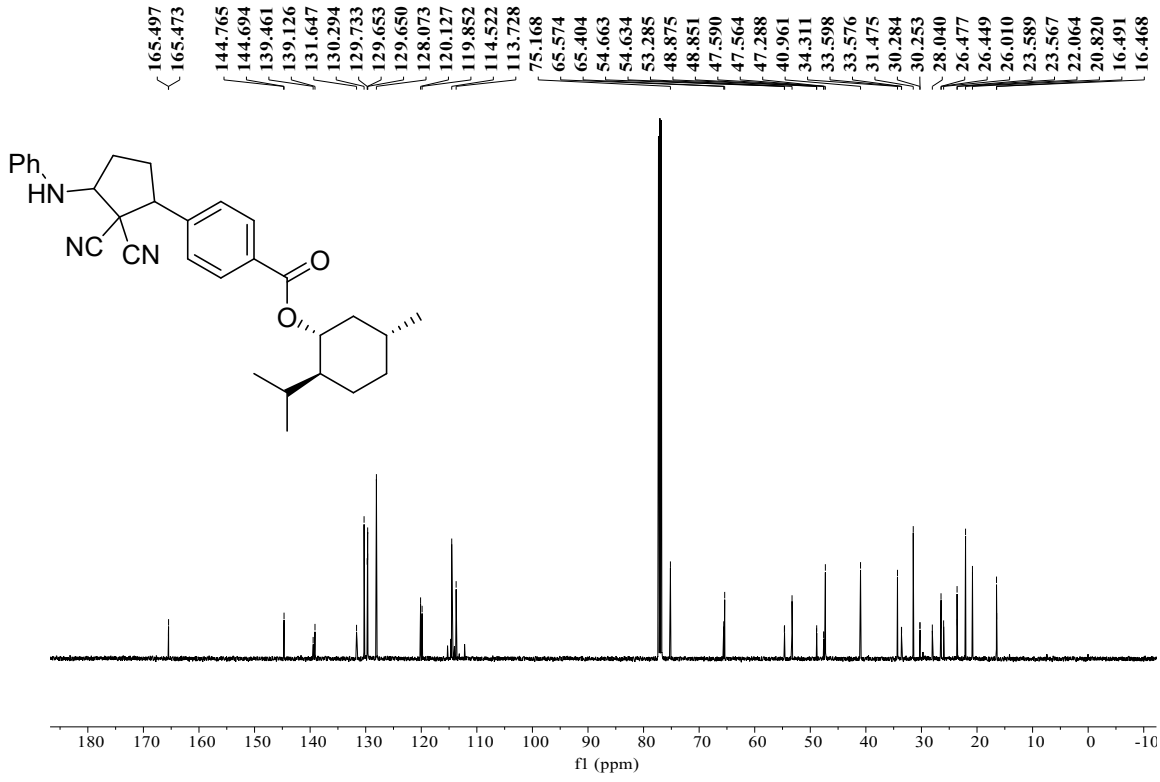


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate(4da)

^{1}H NMR (500 MHz, $CDCl_3$)

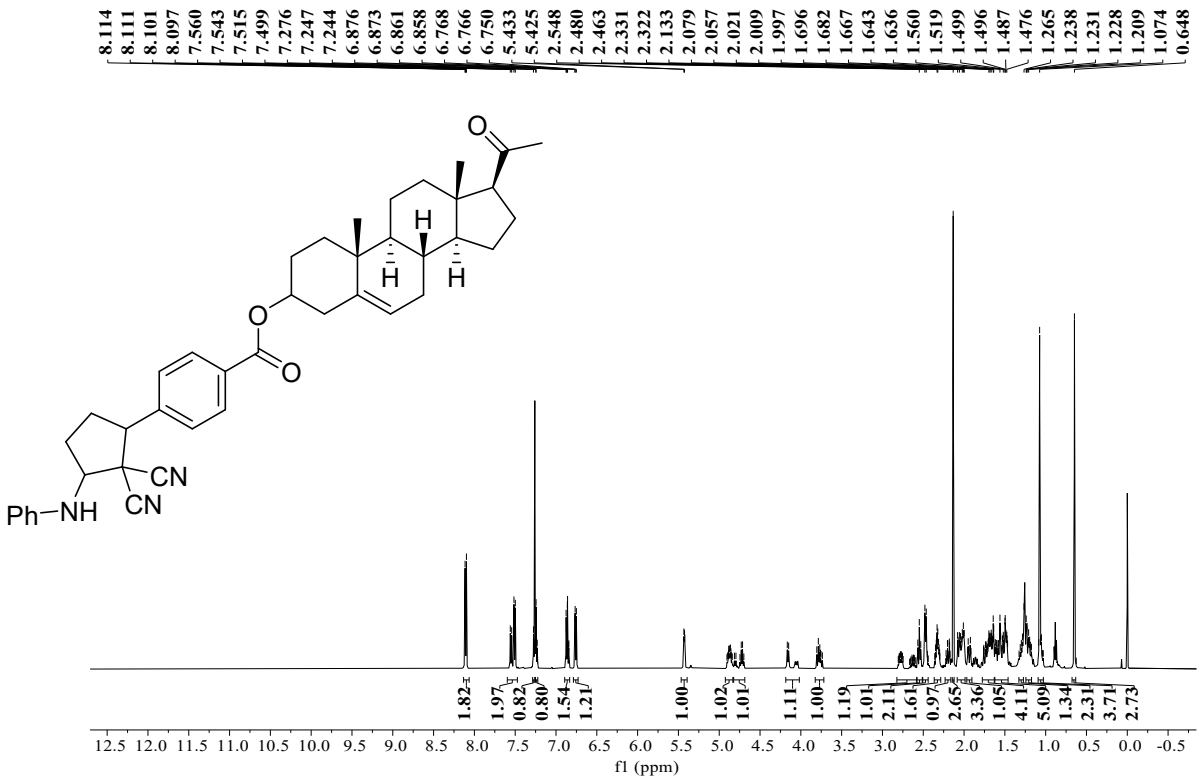


^{13}C NMR (126 MHz, $CDCl_3$)

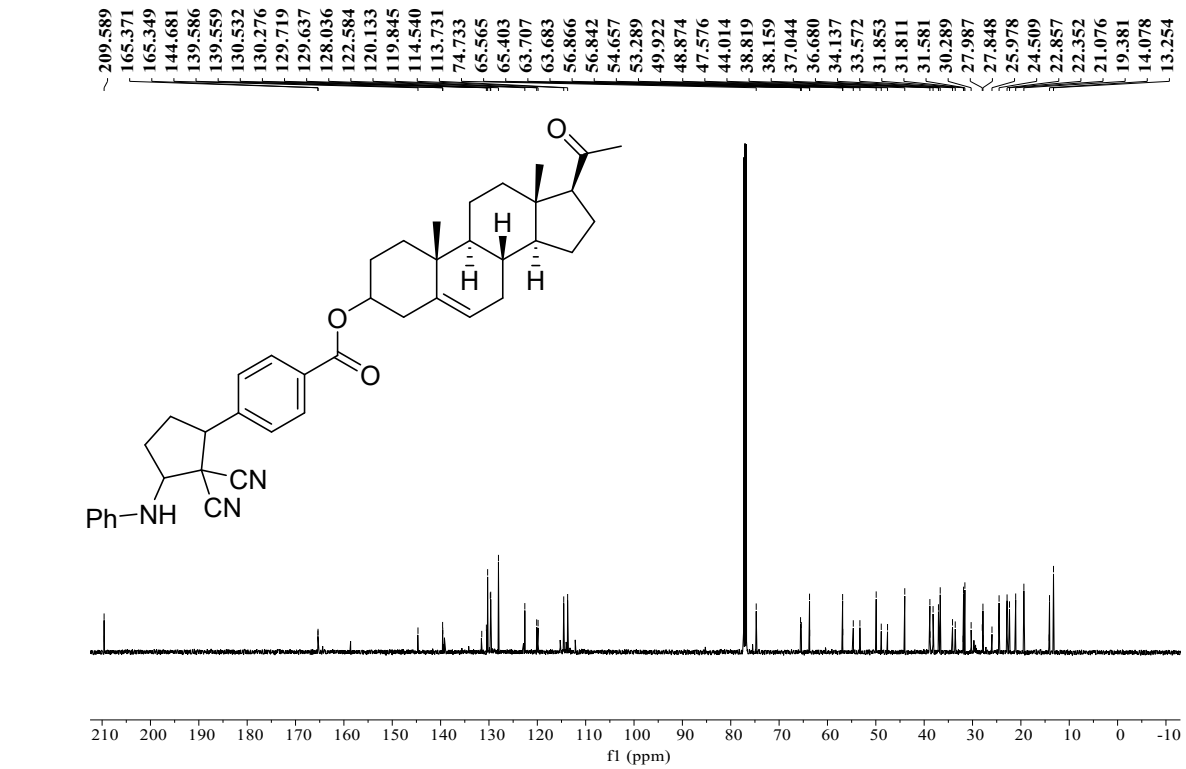


(8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(2,2-dicyano-3-(phenylamino)cyclopentyl)benzoate (4ea)

^{1}H NMR (500 MHz, $CDCl_3$)

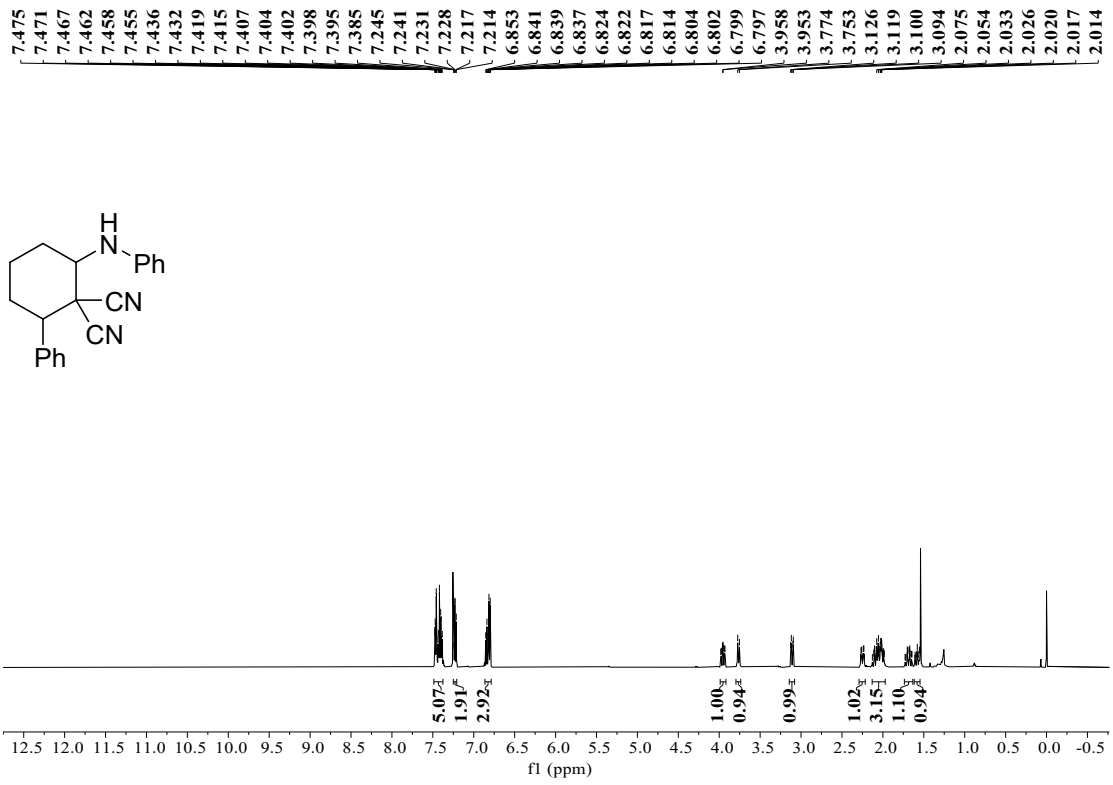


^{13}C NMR (126 MHz, $CDCl_3$)

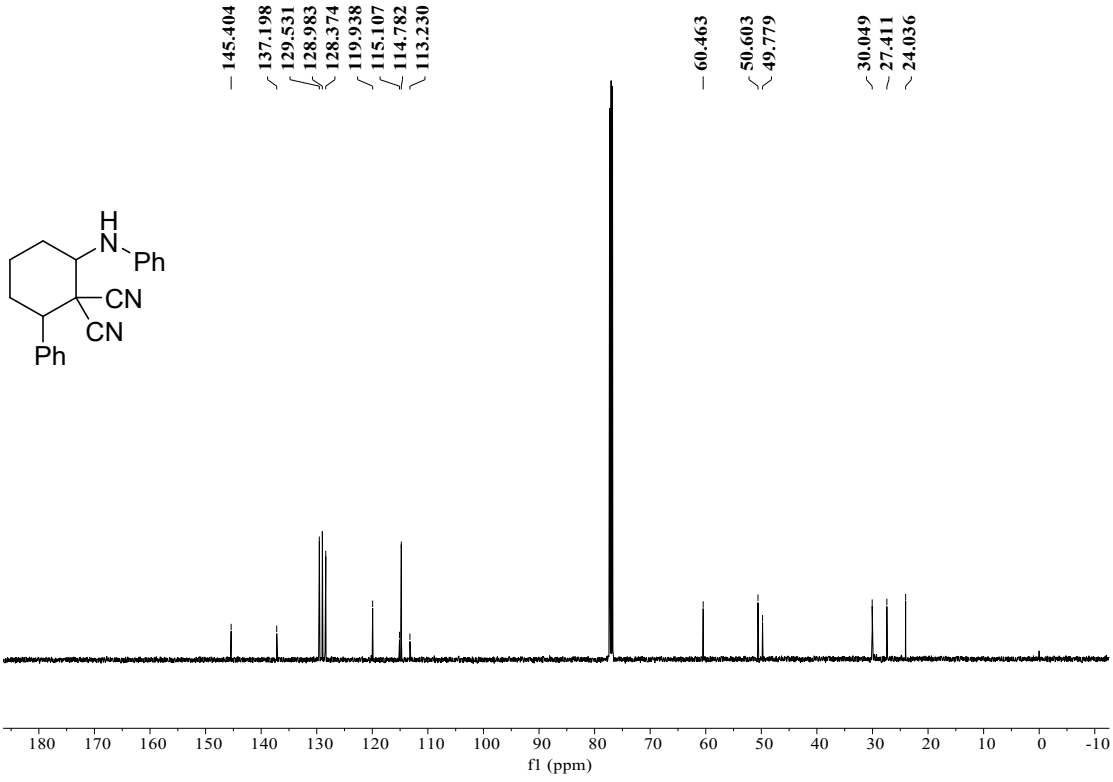


2-phenyl-6-(phenylamino)cyclohexane-1,1-dicarbonitrile (6)

^{1}H NMR (500 MHz, $CDCl_3$)

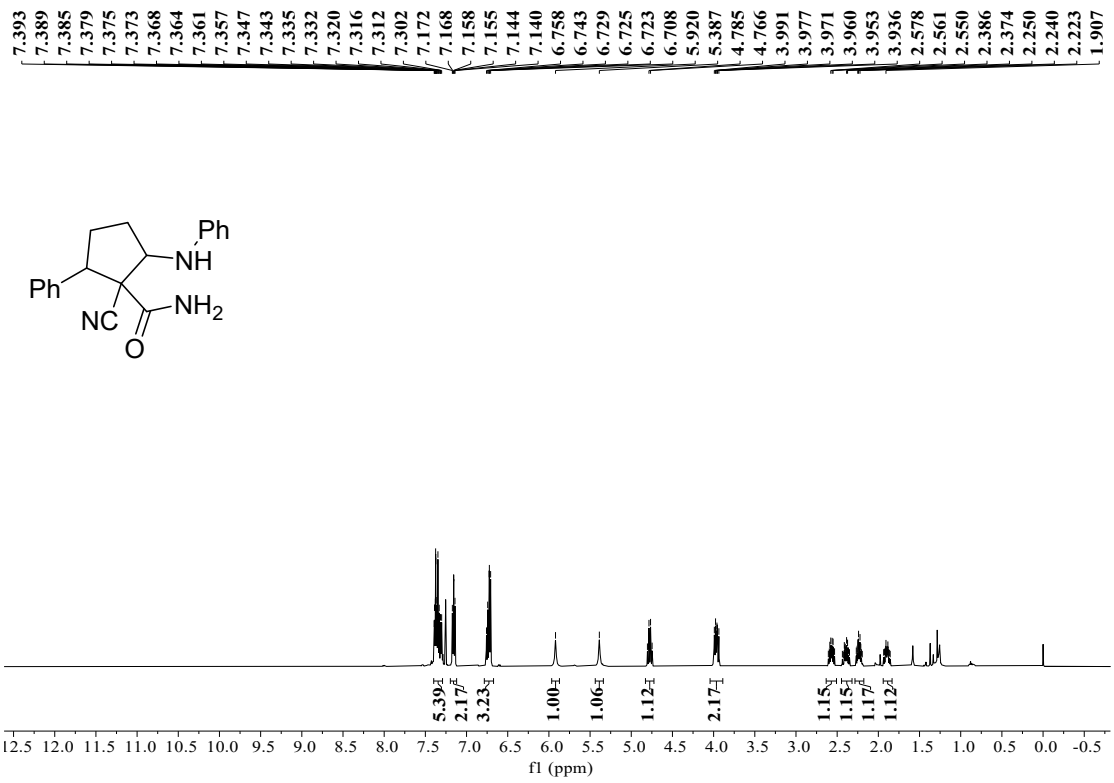


^{13}C NMR (126 MHz, $CDCl_3$)

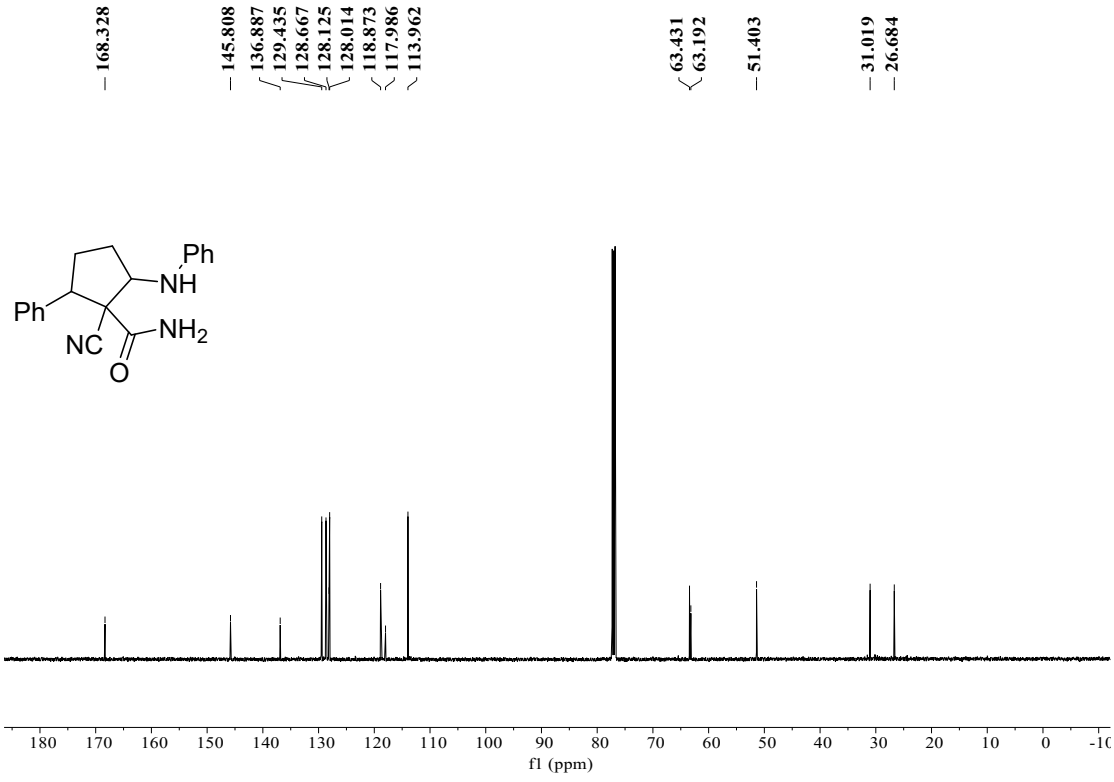


1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxamide (9a)

^{1}H NMR (500 MHz, $CDCl_3$)

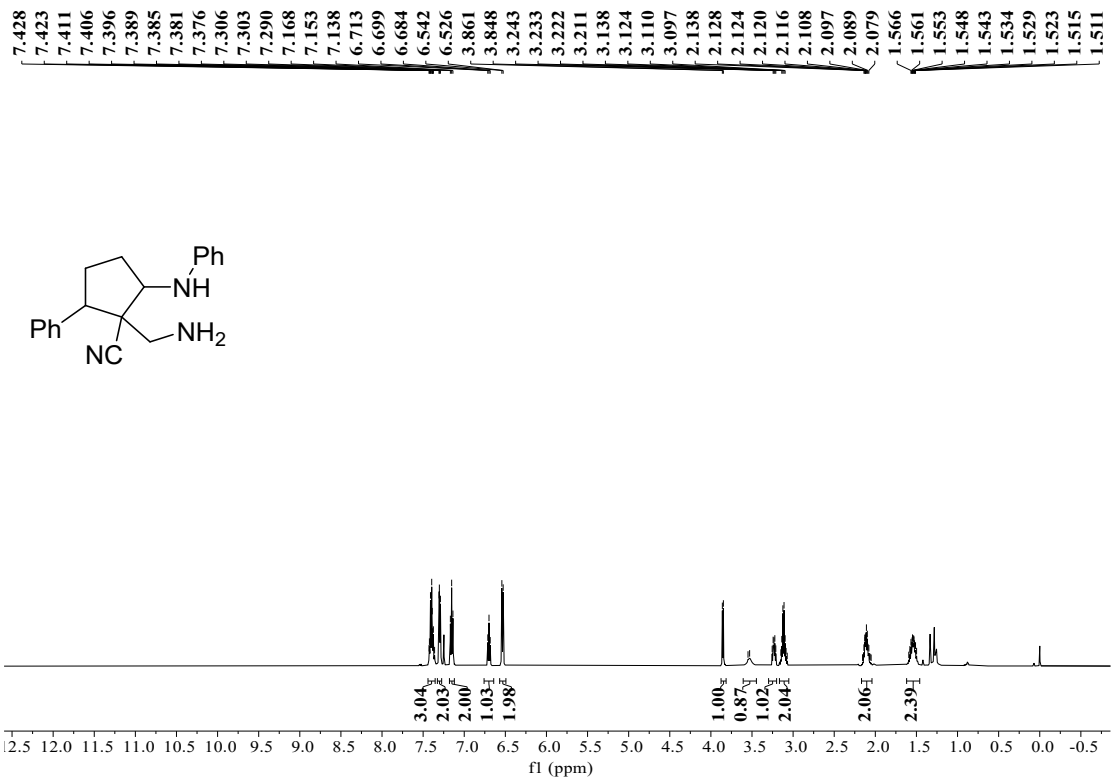


^{13}C NMR (126 MHz, $CDCl_3$)

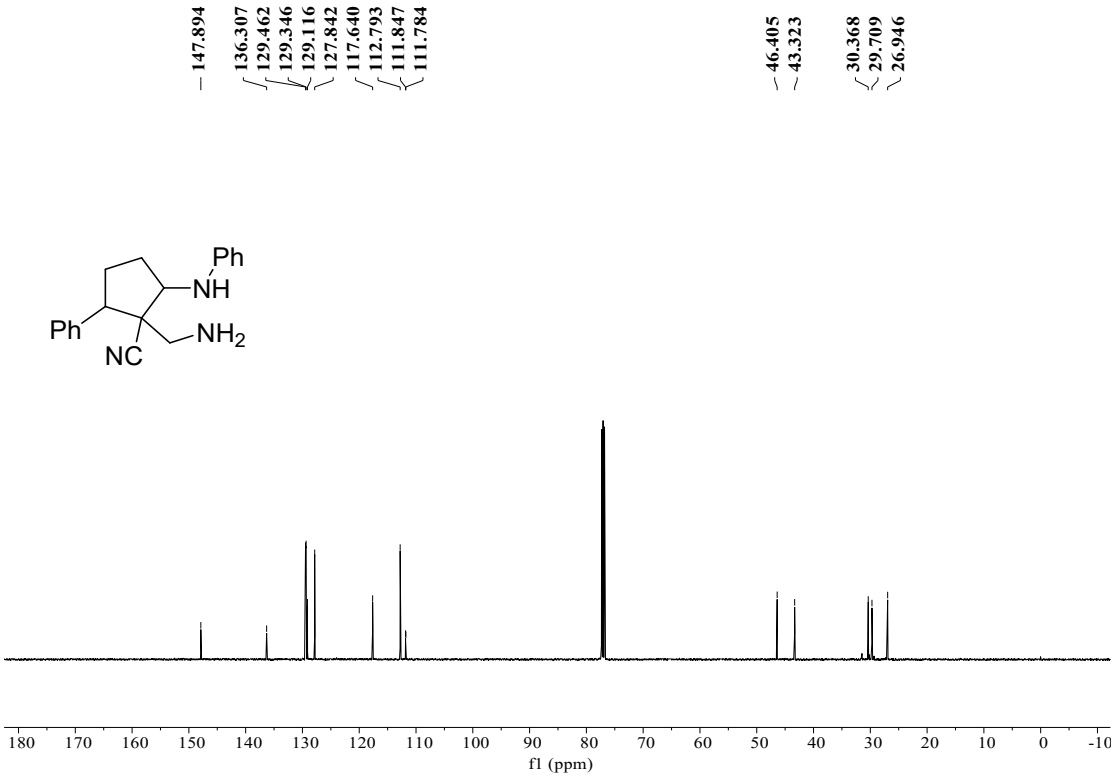


1-(aminomethyl)-2-phenyl-5-(phenylamino)cyclopentane-1-carbonitrile (9b)

^{1}H NMR (500 MHz, $CDCl_3$)

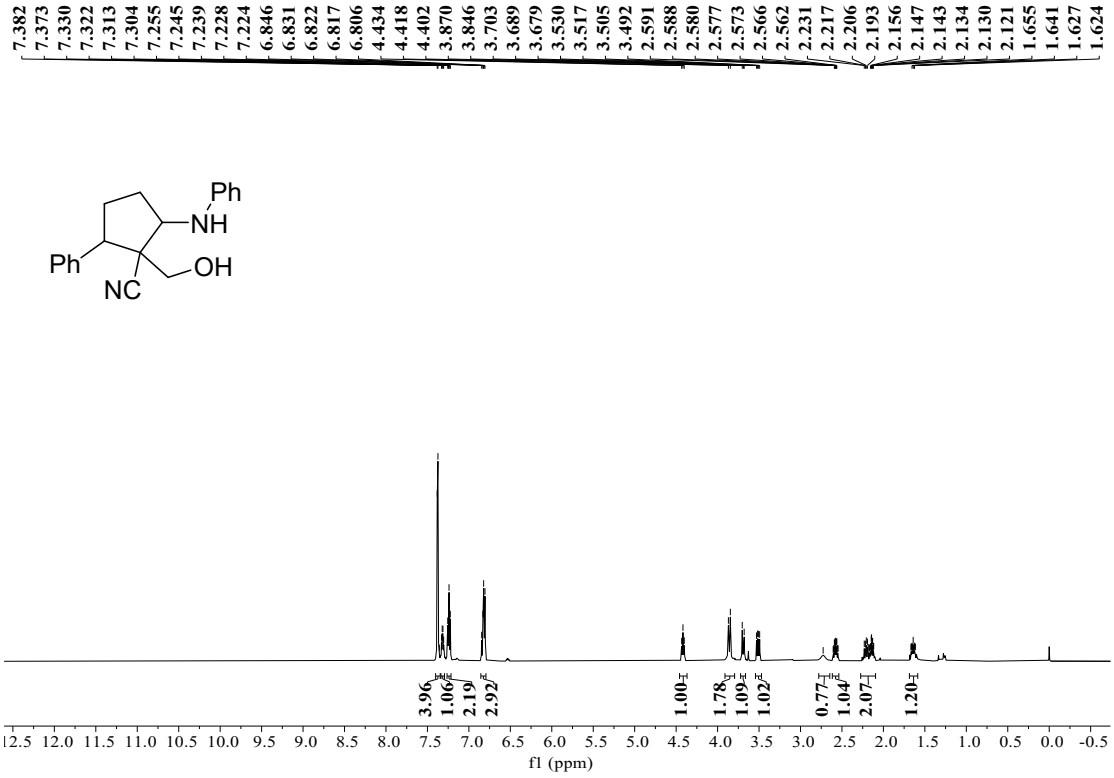


^{13}C NMR (126 MHz, $CDCl_3$)

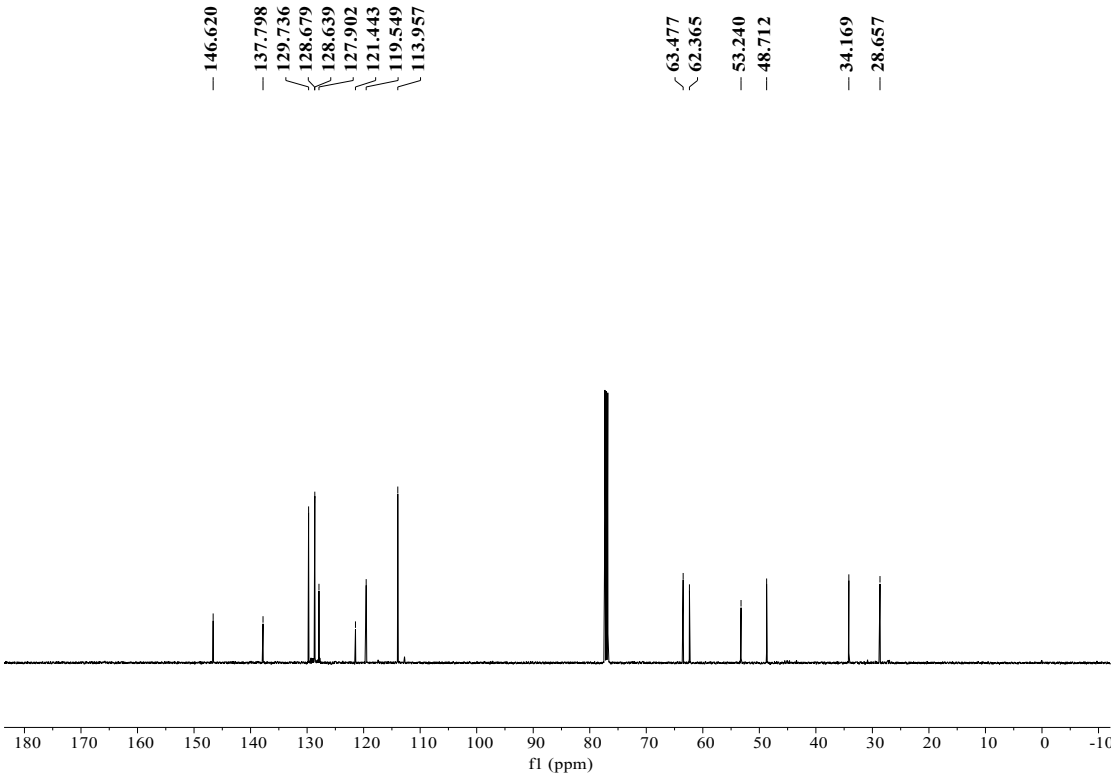


1-(hydroxymethyl)-2-phenyl-5-(phenylamino)cyclopentane-1-carbonitrile (9c)

^{1}H NMR (500 MHz, $CDCl_3$)

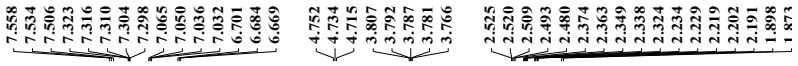


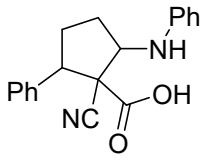
^{13}C NMR (126 MHz, $CDCl_3$)

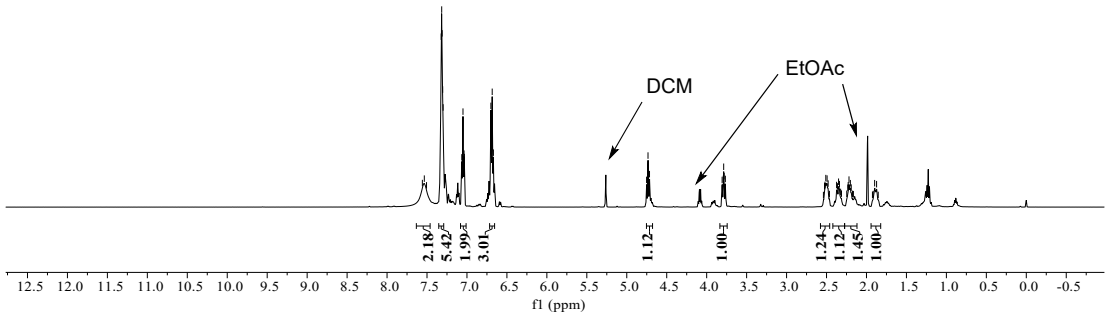


1-cyano-2-phenyl-5-(phenylamino)cyclopentane-1-carboxylic acid (9d)

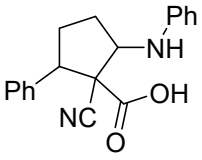
^{1}H NMR (500 MHz, $CDCl_3$)

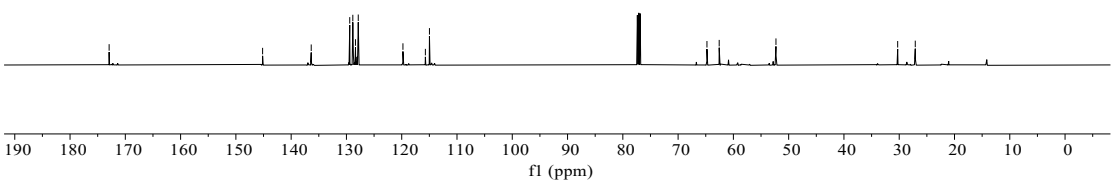






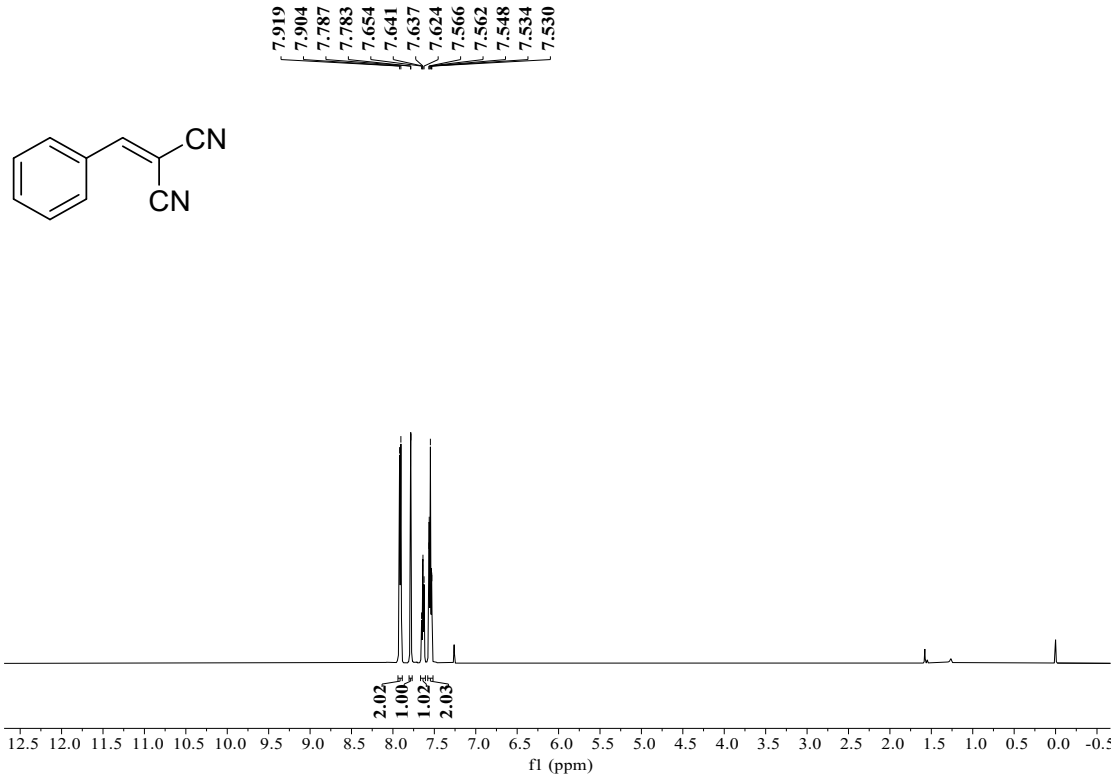
^{13}C NMR (126 MHz, $CDCl_3$)



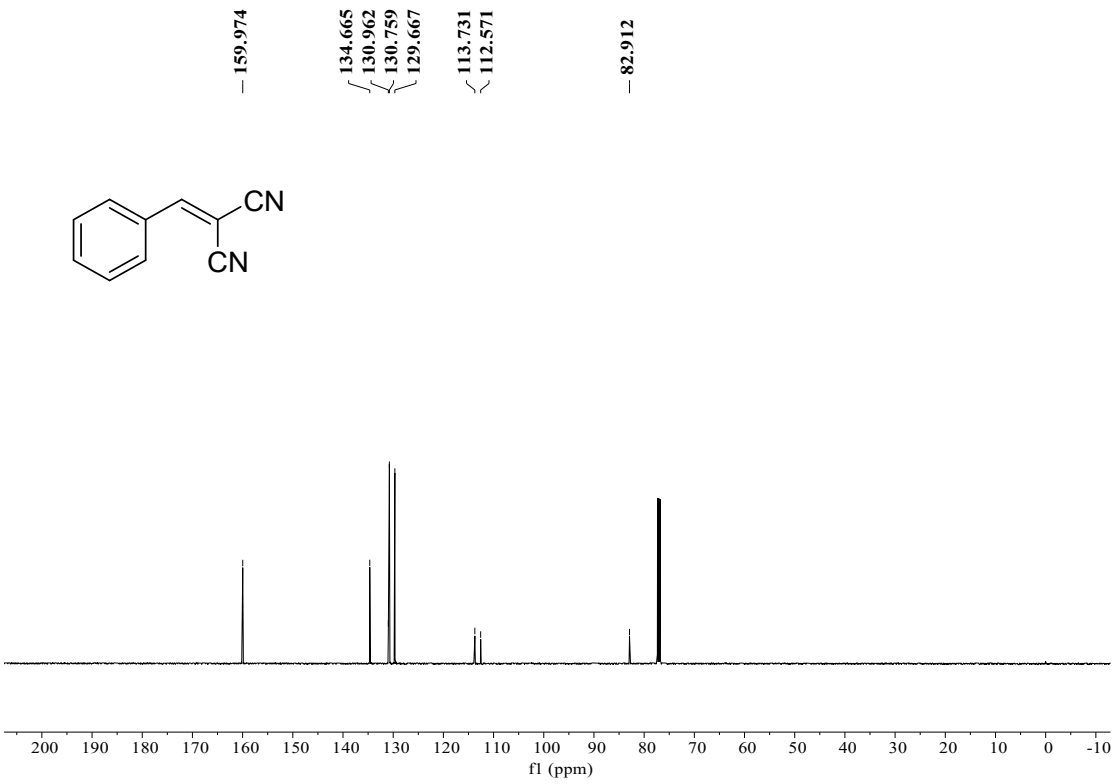


2-benzylidenemalononitrile(5a)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)


159.974
134.665
130.962
130.759
129.667
113.731
112.571
82.912
CN
CN
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)