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Supporting Information

Highly diastereoselective synthesis of *cis*-cyclopentane-1,2-diamine derivatives via organophotoredox-catalyzed [3 + 2] cycloadditions

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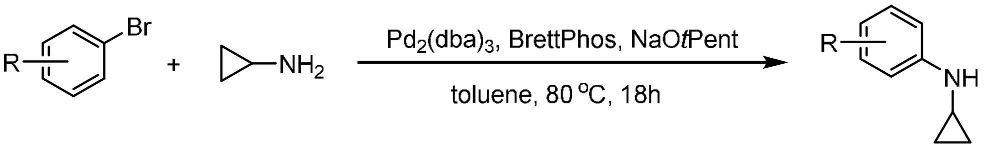
1. General information

All solvents and reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 50 GF254 plates. Flash column chromatography was performed using silica gel (200-300 mesh). Visualization on TLC was achieved by use of UV light (254, 365nm). NMR spectrums were recorded on a Bruker DPX 400 NMR spectrometer at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR. The solvent used for NMR spectroscopy was $CDCl_3$ or DMSO-d_6. Chemical shifts for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were reported as δ in units of parts per million (ppm) downfield from standard tetramethylsilane (0.0), relative to the signal of the solvent ($CDCl_3$ at 7.26 ppm or DMSO-d_6 at 2.50 ppm). Multiplicities were given as s (singlet), d (doublet), dd (doublets of doublet), t (triplet), td (triplet of doublets), tt (triplet of triplets), q (quartet), m (multiplets) or bs (broad single). The number of protons (n) for a given resonance is indicated by nH. Coupling constants were reported as a J value in hertz. A high-resolution mass spectrum (HRMS) was determined by 1290II-6230 TOF using ESI ionization. The X-ray source used for the single crystal X-ray diffraction analysis of compound **3aa** was MoKα (λ = 0.71073). UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 UV-VIS spectrophotometer. Melting points (M.P.) were recorded using SGWX-4A Melting-point Apparatus and were uncorrected.

2. General procedures for the synthesis of substrates

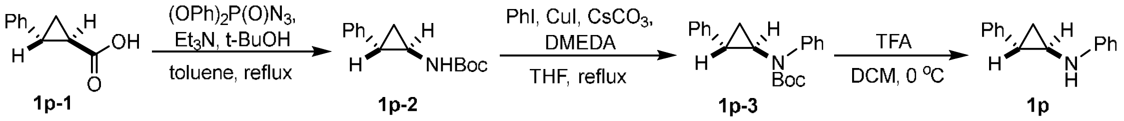
2.1. General procedure 1: Synthesis of *N*-aryl cyclopropylamines (GP1)

Method A (GP1A)[1]



An oven-dried microwave vial was charged with $Pd_2(dba)_3$ (1 mol%) and BrettPhos (3 mol%). The vial was sealed, evacuated and back-filled with nitrogen (3 times). Then toluene (0.5 M), cyclopropylamine (1.6 equiv), the aromatic bromide (1 equiv) and NaO^{t}Pent (45% solution in toluene, 1.5 equiv) were added via syringe to the vial and it was heated at 80 ^{o}C for 18 h. The reaction mixture was then cooled to room temperature, diluted with Et_2O, and filtered through a small pad of silica gel. The filtrate was evaporated under reduced pressure, and the obtained crude residue was subjected to column chromatography with the indicated solvents.

Method B (GP1B)[2]



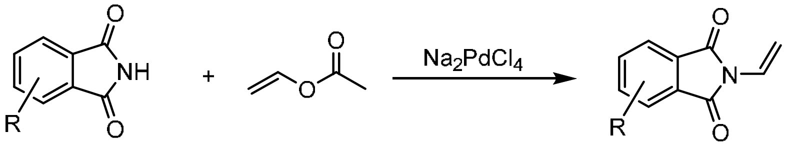
trans-2-Phenyl-1-cyclopropanecarboxylic acid **1p-1** (1 equiv), diphenylphosphoryl azide (1.1 equiv), Et_3N (1.2 equiv) and *tert*-butyl alcohol (10 equiv) were stirred in toluene (0.3 M) at 80-85 ^{o}C for 24 h. The mixture was cooled to room temperature, H_2O was added, and extracted with ethyl acetate three times. The combined organic layers were washed with 1 M HCl, H_2O, saturated $NaHCO_3$, and brine then dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification of the residual mass by silica gel column chromatography (petroleum ether: EtOAc = 5:1) afforded the product, *trans*-*N*-Boc-2-phenylcyclopropylamine **1p-2**, as a yellow solid.

CuI (0.2 equiv), Cs_2CO_3 (2 equiv) and *trans*-*N*-Boc-2-phenylcyclopropylamine **1p-2** (1 equiv) were added to a test tube equipped with a stir bar. After purging with N_2 for a few seconds, the tube was sealed with Teflon screw cap. *N*,*N*'-dimethylethylenediamine (0.4 equiv) and iodobenzene (2 equiv) was added under N_2 followed by the addition of dry THF (0.25 M). The resulting mixture was then heated to reflux for 24 h. After completion, the mixture was cooled to room temperature, diluted with ethyl acetate and filtered over a short pad of silica. Purification of the residual mass by silica gel column chromatography (petroleum ether: EtOAc = 5:1) afforded the product **1p-3** as a colorless oil.

To a solution of the carbamate **1p-3** (1 equiv) in dry CH_2Cl_2 (0.5 M) cooled to 0 °C was added trifluoroacetic acid (4 equiv). The reaction was stirred for 5 h at 0 °C. Upon completion of the reaction, monitored by TLC, was added water. The aqueous layer was basified and then extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuum. Purification of the residual mass by silica gel column chromatography (petroleum ether: EtOAc = 10:1) afforded the product *N*-((1*R*,2*S*)-2-phenylcyclopropyl)aniline **1p** as a yellow oil.

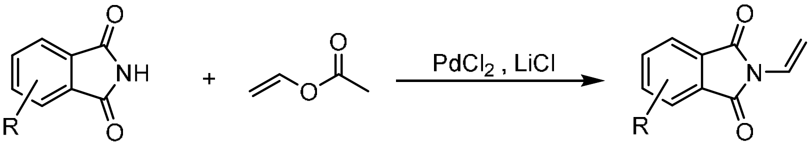
2.3. General procedure 2: Synthesis of *N*-vinylphthalimides (GP2)

Method A (GP2A)[3]



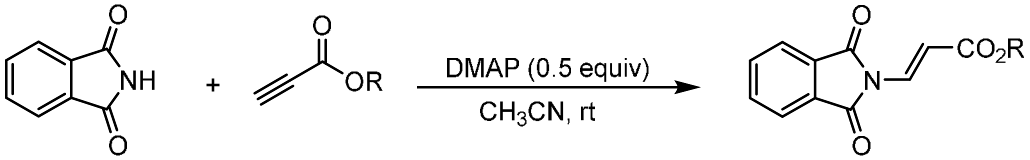
Na_2PdCl_4 (2 mol%) was added to a stirred solution of the corresponding phthalimide (1 equiv) in vinyl acetate (27 equiv) and the mixture was heated under reflux. The solvent was evaporated and the residue was purified by column chromatography to obtain solid compounds.

Method B (GP2B)[3]



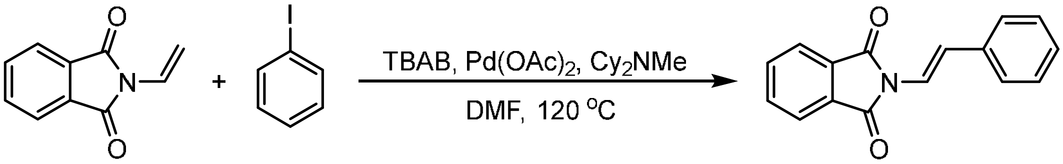
Palladium (II) chloride (10 mol%) and lithium chloride (10 mol% or 1 equiv weighted in a glovebox), was added to a stirred solution of the corresponding phthalimide (1 equiv) in vinyl acetate (27 equiv) and the mixture was heated under reflux. The mixture was cooled down to room temperature and the solvent was evaporated. The residue was purified by column chromatography to obtain solid compounds.

Method C (GP2C)[4]



The phthalimide (1 equiv) and DMAP (0.5 equiv) were dissolved in CH_3CN (0.1 M) under N_2 atmosphere. The propiolate (1.2 equiv) was then slowly added via syringe, and the reaction was stirred until TLC analysis indicated complete consumption of the substrate. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give the product.

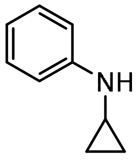
Method D (GP2D)[4]



A mixture of iodobenzene (1 equiv), *N*-vinylphthalimide (1 equiv), Cy_2NMe (1.5 equiv), TBAB (1 equiv) and palladium acetate (0.1 mol%) in DMF (0.5 M) was heated at 120 °C in a round-bottom flask under nitrogen. When full conversion was observed by TLC, the organic layer was extracted with ethyl acetate through stages of extraction with water. The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the product.

3. Characterization data of substrates

3.1. Characterization of *N*-aryl cyclopropylamines



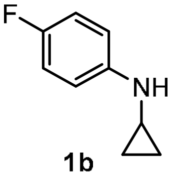
1a

N-Cyclopropylaniline (1a)

Following the **GP1A**, starting from bromobenzene, compound **1a** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.17 (m, 2H), 6.83 – 6.78 (m, 2H), 6.78 – 6.73 (m, 1H), 4.17 (bs, 1H), 2.46 – 2.40 (m, 1H), 0.76 – 0.72 (m, 2H), 0.54 – 0.51 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.81, 129.23, 117.84, 113.26, 25.35, 7.52.



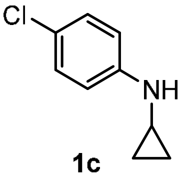
1b

N-Cyclopropyl-4-fluoroaniline (1b)

Following the **GP1A**, starting from 1-bromo-4-fluorobenzene, compound **1b** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[6]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.93 – 6.86 (m, 2H), 6.75 – 6.69 (m, 2H), 4.07 (bs, 1H), 2.44 – 2.34 (m, 1H), 0.76 – 0.67 (m, 2H), 0.54 – 0.45 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.17 (d, *J* = 234.7 Hz), 145.09 (d, *J* = 1.8 Hz), 115.58 (d, *J* = 22.1 Hz), 113.90 (d, *J* = 7.4 Hz), 25.80, 7.45.



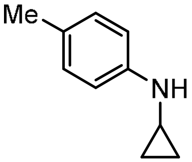
1c

4-Chloro-*N*-cyclopropylaniline (1c)

Following the **GP1A**, starting from 1-bromo-4-chlorobenzene, compound **1c** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[7]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.06 (m, 2H), 6.68 – 6.65 (m, 2H), 4.13 (bs, 1H), 2.38 – 2.33 (m, 1H), 0.71 – 0.67 (m, 2H), 0.48 – 0.44 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.32, 128.96, 122.27, 114.26, 25.34, 7.50.



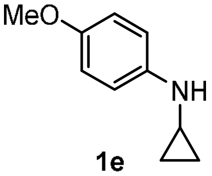
1d

N-Cyclopropyl-4-methylaniline (1d)

Following the **GP1A**, starting from 1-bromo-4-methylbenzene, compound **1d** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[8]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (d, J = 8.2 Hz, 2H), 6.77 – 6.70 (m, 2H), 2.45 – 2.39 (m, 1H), 2.27 (s, 3H), 0.75 – 0.70 (m, 2H), 0.54 – 0.49 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.51, 129.73, 127.05, 113.38, 25.64, 20.54, 7.46.



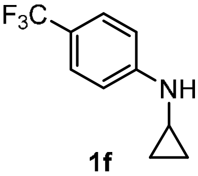
1e

N-Cyclopropyl-4-methoxyaniline (1e)

Following the **GP1A**, starting from 1-bromo-4-methoxybenzene, compound **1e** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[9]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.82 – 6.75 (m, 4H), 3.76 (s, 3H), 2.43 – 2.35 (m, 1H), 0.73 – 0.67 (m, 2H), 0.52 – 0.46 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.45, 143.01, 114.92, 114.31, 55.96, 26.05, 7.39.



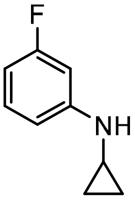
1f

N-Cyclopropyl-4-(trifluoromethyl)aniline (1f)

Following the **GP1A**, starting from 1-bromo-4-(trifluoromethyl)benzene, compound **1f** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[1]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.44 (s, 1H), 2.49 – 2.43 (m, 1H), 0.82 – 0.75 (m, 2H), 0.57 – 0.51 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.35, 126.55 (q, *J* = 3.8 Hz), 125.19 (q, *J* = 270.4 Hz), 119.33 (q, *J* = 32.6 Hz), 112.47, 24.97, 7.67.



1g

N-Cyclopropyl-3-fluoroaniline (1g)

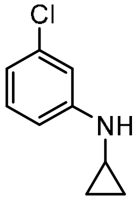
Following the **GP1A**, starting from 1-bromo-3-fluorobenzene, compound **1g** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.06 (m, 1H), 6.55 – 6.48 (m, 2H), 6.44 – 6.39 (m, 1H), 4.27 (bs, 1H), 2.45 – 2.38 (m, 1H), 0.77 – 0.72 (m, 2H), 0.54 – 0.50 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.19 (d, *J* = 242.4 Hz), 150.68 (d, *J* = 10.7 Hz), 130.21 (d, *J* = 10.3 Hz), 109.16 (d, *J* = 2.4 Hz), 104.19 (d, *J* = 21.6 Hz), 99.95 (d, *J* = 25.5 Hz), 25.25, 7.57.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.07.

HRMS (ESI): Calculated for $C_9H_{10}FN$ $[M + H]^+$: 152.0797, found 152.0870.



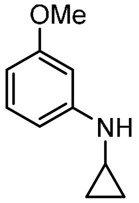
1h

3-Chloro-*N*-cyclopropylaniline (1h)

Following the **GP1A**, starting from 1-bromo-3-chlorobenzene, compound **1h** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[10]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (t, *J* = 8.0 Hz, 1H), 6.80 (t, *J* = 2.1 Hz, 1H), 6.74 – 6.65 (m, 1H), 6.66 – 6.58 (m, 1H), 4.23 (bs, 1H), 2.45 – 2.38 (m, 1H), 0.78 – 0.73 (m, 2H), 0.54 – 0.50 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.98, 135.01, 130.14, 117.66, 112.85, 111.67, 25.18, 7.61.



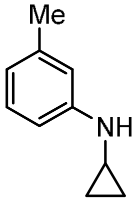
1i

N-Cyclopropyl-3-methoxyaniline (1i)

Following the **GP1A**, starting from 1-bromo-3-methoxybenzene, compound **1i** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[8]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 7.06 (m, 1H), 6.41 – 6.36 (m, 2H), 6.33 – 6.29 (m, 1H), 4.19 (bs, 1H), 3.79 (s, 3H), 2.46 – 2.39 (m, 1H), 0.74 – 0.70 (m, 2H), 0.53 – 0.49 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.87, 150.27, 129.95, 106.51, 102.87, 99.29, 55.21, 25.35, 7.54.



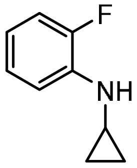
1j

N-Cyclopropyl-3-methylaniline (1j)

Following the **GP1A**, starting from 1-bromo-3-methylbenzen, compound **1j** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[8]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 7.08 (m, 1H), 6.66 – 6.56 (m, 3H), 4.12 (bs, 1H), 2.47 – 2.40 (m, 1H), 2.32 (s, 3H), 0.77 – 0.71 (m, 2H), 0.56 – 0.49 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.85, 139.01, 129.11, 118.80, 114.00, 110.48, 25.39, 21.77, 7.54.



1k

***N*-Cyclopropyl-2-fluoroaniline (1k)**

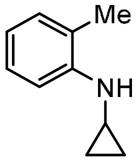
Following the **GP1A**, starting from 1-bromo-2-fluorobenzene, compound **1k** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 – 6.94 (m, 3H), 6.71 – 6.62 (m, 1H), 4.39 (bs, 1H), 2.48 – 2.40 (m, 1H), 0.79 – 0.74 (m, 2H), 0.60 – 0.54 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.41 (d, *J* = 238.4 Hz), 137.22 (d, *J* = 11.2 Hz), 124.58 (d, *J* = 3.5 Hz), 117.11 (d, *J* = 7.0 Hz), 114.36 (d, *J* = 18.2 Hz), 113.35 (d, *J* = 3.5 Hz), 24.85, 7.40.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.95.

HRMS (ESI): Calculated for $C_9H_{10}FN$ $[M + H]^+$: 152.0797, found 152.0869.



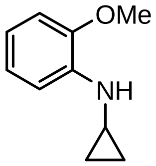
1l

***N*-Cyclopropyl-2-methylaniline (1l)**

Following the **GP1A**, starting from 1-bromo-2-methylbenzen, compound **1l** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[8]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.15 (m, 1H), 7.08 – 7.04 (m, 2H), 6.74 – 6.68 (m, 1H), 2.49 – 2.43 (m, 1H), 2.11 (s, 3H), 0.80 – 0.75 (m, 2H), 0.58 – 0.54 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.80, 130.06, 127.10, 121.76, 117.48, 111.19, 25.42, 17.46, 7.65.



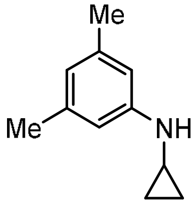
1m

N-Cyclopropyl-2-methoxyaniline (1m)

Following the **GP1A**, starting from 1-bromo-2- methoxybenzene, compound **1m** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[11]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.04 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.91 (td, *J* = 7.5, 1.6 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.75 – 6.69 (m, 1H), 4.67 (bs, 1H), 3.84 (s, 3H), 2.44 – 2.37 (m, 1H), 0.76 – 0.71 (m, 2H), 0.58 – 0.54 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.72, 138.70, 121.32, 117.09, 111.29, 109.40, 55.44, 25.00, 7.27.



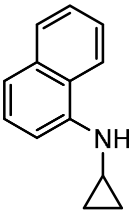
1n

N-Cyclopropyl-3,5-dimethylaniline (1n)

Following the **GP1A**, starting from 1-bromo-3,5-dimethylbenzene, compound **1n** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow oil. Characterization data correspond to the reported values.[7]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.43 (d, *J* = 8.8 Hz, 3H), 4.07 (bs, 1H), 2.45 – 2.39 (m, 1H), 2.27 (s, 6H), 0.75 – 0.70 (m, 2H), 0.53 – 0.47 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.91, 138.93, 119.88, 111.20, 25.42, 21.65, 7.57.

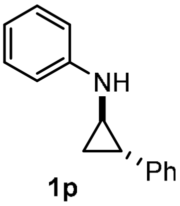

1o

***N*-Cyclopropylnaphthalen-1-amine (1o)**

Following the **GP1A**, starting from 1-bromonaphthalene, compound **1o** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a white solid. Characterization data correspond to the reported values.[8]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.76 (m, 1H), 7.72 – 7.68 (m, 1H), 7.45 – 7.36 (m, 3H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.05 (dd, *J* = 7.5, 1.1 Hz, 1H), 4.85 (bs, 1H), 2.60 – 2.53 (m, 1H), 0.85 – 0.80 (m, 2H), 0.65 – 0.60 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.92, 134.25, 128.71, 126.65, 125.69, 124.72, 123.23, 119.75, 117.82, 105.87, 25.55, 7.61.



1p

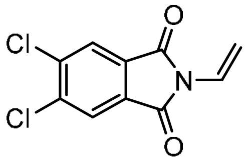
***N*-(1, 2-*trans*)-2-phenylcyclopropyl)aniline (1p)**

Following the **GP1B**, compound **1p** was obtained after purification by silica gel chromatography as a yellow oil. Characterization data correspond to the reported values.[2]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 2H), 7.18 – 7.07 (m, 3H), 7.05 (m, 2H), 6.73 – 6.57 (m, 3H), 4.20 (bs, 1H), 2.55 (m, 1H), 1.97 – 1.86 (m, 1H), 1.25 – 1.11 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.35, 141.65, 129.56, 128.77, 126.17, 126.05, 118.30, 113.49, 36.70, 26.45, 17.80.

3.2. Characterization of *N*-vinylphthalimides



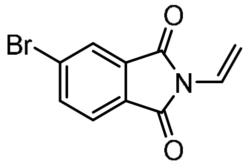
2b

5,6-Dichloro-2-vinylisoindoline-1,3-dione (2b)

Following the **GP2A**, starting from 5,6-dichloroisoindoline-1,3-dione, compound **2b** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 2:1) as a white solid. Characterization data correspond to the reported values.[3]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 2H), 6.83 (dd, J = 16.4, 9.8 Hz, 1H), 6.08 (d, J = 16.4 Hz, 1H), 5.09 (d, J = 9.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.61, 139.67, 130.81, 125.84, 123.71, 105.56.



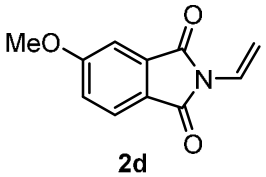
2c

5-Bromo-2-vinylisoindoline-1,3-dione (2c)

Following the **GP2B**, starting from 5-bromoisoindoline-1,3-dione, compound **2c** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a white solid. Characterization data correspond to the reported values.[3]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, J = 1.7 Hz, 1H), 7.88 (dd, J = 7.9, 1.7 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 6.84 (dd, J = 16.4, 9.8 Hz, 1H), 6.08 (d, J = 16.4 Hz, 1H), 5.07 (d, J = 9.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.78, 165.24, 137.68, 133.39, 130.26, 129.62, 127.13, 125.15, 123.78, 105.22.



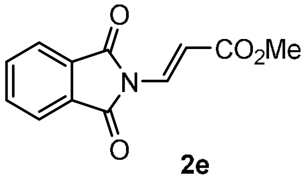
2d

5-Methoxy-2-vinylisoindoline-1,3-dione (2d)

Following the **GP2A**, starting from 5-methoxyisoindoline-1,3-dione, compound **2d** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 2:1) as a white solid. Characterization data correspond to the reported values.[3]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.18 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.85 (dd, *J* = 16.4, 9.9 Hz, 1H), 6.04 (d, *J* = 16.4 Hz, 1H), 5.00 (d, *J* = 9.9 Hz, 1H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.51, 166.37, 165.22, 134.47, 125.54, 124.07, 123.59, 120.62, 108.27, 104.05, 56.28.



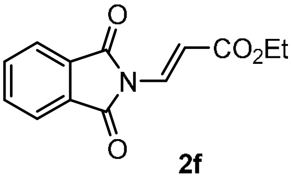
2e

Methyl (*E*)-3-(1,3-dioxoisoindolin-2-yl)acrylate (2e)

Following the **GP2C**, starting from methyl propiolate, compound **2e** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 5:1) as a yellow solid. Characterization data correspond to the reported values.[4]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 3H), 7.84 – 7.80 (m, 2H), 6.98 (d, *J* = 14.7 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.68, 165.60, 135.33, 131.54, 131.30, 124.41, 108.42, 51.90.



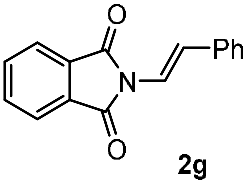
2f

Ethyl (*E*)-3-(1,3-dioxoisoindolin-2-yl)acrylate (2f)

Following the **GP2C**, starting from ethyl propiolate, compound **2f** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 5:1) as a white solid. Characterization data correspond to the reported values.[4]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.91 (m, 3H), 7.83 – 7.79 (m, 2H), 6.97 (dd, *J* = 14.8, 0.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.25, 165.64, 135.30, 131.56, 131.08, 124.40, 108.93, 60.76, 14.45.



2g

(*E*)-2-styrylisoindoline-1,3-dione (2g)

Following the **GP2D**, compound **2g** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid. Characterization data correspond to the reported values.[4]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.87 (m, 2H), 7.77 – 7.74 (m, 2H), 7.65 (d, *J* = 15.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.28 – 7.24 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.49, 135.99, 134.60, 131.73, 128.79, 127.70, 126.27, 123.72, 120.25, 117.63.

4. Optimization of reaction conditions

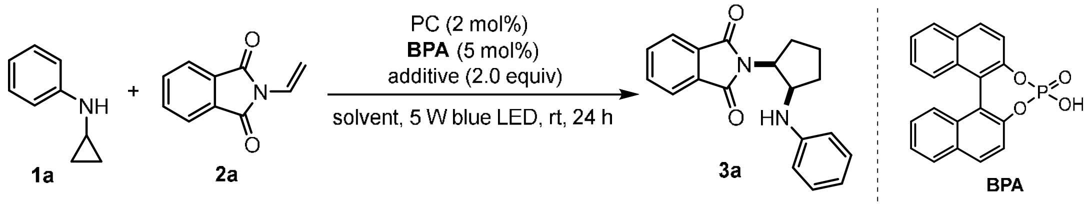


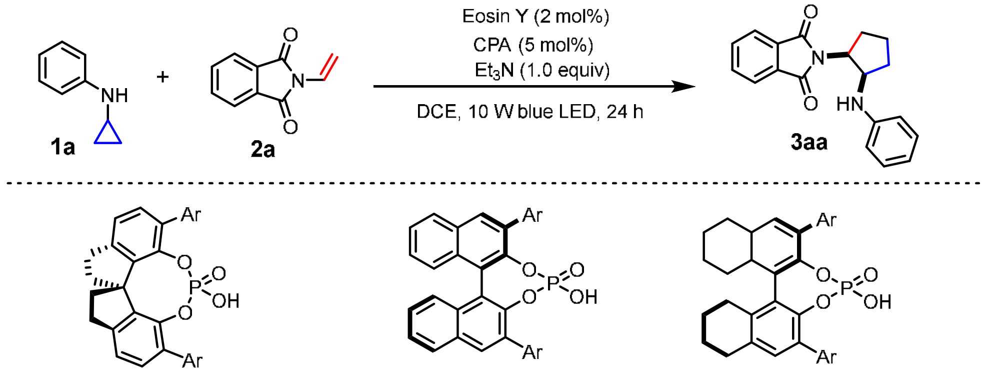
Table S1. Optimization of the reaction conditions

Entry	Ratio (**1a**:**2a**)	Photocatalyst	Additive	Solvent	Yield[h]	Dr[i]
1[a]	1:2	Eosin Y	--	THF (0.2M)	10%	85:15
2	1:2	Eosin Y	--	THF (0.2M)	32%	90:10
3	1:2	Eosin Y	Et_3N	THF (0.2M)	42%	95:5
4	1:2	Eosin Y	DBU	THF (0.2M)	25%	90:10
5	1:2	Eosin Y	DIPEA	THF (0.2M)	41%	94:6
6	1:2	Eosin Y	K_3PO_4	THF (0.2M)	34%	90:10
7	1:2	Eosin Y	Na_3PO_4	THF (0.2M)	33%	90:10
8	1:2	Eosin Y	K_2CO_3	THF (0.2M)	29%	85:15
9	1:2	Eosin Y	Et_3N	DCM (0.2M)	30%	90:10
10	1:2	Eosin Y	Et_3N	DCE (0.2M)	60%	98:2
11	1:2	Eosin Y	Et_3N	CH_3CN (0.2M)	37%	95:5
12	1:2	Eosin Y	Et_3N	Toluene (0.2M)	30%	94:6
13	1:2	Eosin Y	Et_3N	DME (0.2M)	50%	94:6
14	1:2	Eosin Y	Et_3N	EtOAc (0.2M)	24%	97:3
15	1:2	Eosin Y	Et_3N	1,4-dioxane (0.2M)	31%	94:6
16	1:2	Rhodamine B	Et_3N	DCE (0.2M)	21%	95:5
17	1:2	4CzIPN	Et_3N	DCE (0.2M)	24%	93:7
18	1:2	Rose Bengal	Et_3N	DCE (0.2M)	50%	98:2
19	1:2	Thioxanthen-9-one	Et_3N	DCE (0.2M)	23%	96:4

20	1:2	Ir(ppy)$_3$	Et$_3$N	DCE (0.2M)	52%	95:5
21	1:2	Eosin Y	K$_3$PO$_4$	DCE (0.2M)	39%	92:8
22	1:2	Eosin Y	Na$_3$PO$_4$	DCE (0.2M)	42%	90:10
23	1:2	Eosin Y	K$_2$CO$_3$	DCE (0.2M)	35%	87:13
24	1:2	Eosin Y	Et$_3$N	DCE (0.1M)	48%	93:7
25	1:2	Eosin Y	Et$_3$N	DCE (0.4M)	58%	95:5
26	1:3	Eosin Y	Et$_3$N	DCE (0.2M)	53%	95:5
27	1:1	Eosin Y	Et$_3$N	DCE (0.2M)	32%	91:9
28	2:1	Eosin Y	Et$_3$N	DCE (0.2M)	44%	93:7
29[b]	1:2	Eosin Y	Et$_3$N	DCE (0.2M)	61%	95:5
30[c]	1:2	Eosin Y	Et$_3$N	DCE (0.2M)	66%	98:2
31[d]	1:2	Eosin Y	Et$_3$N	DCE (0.2M)	47%	94:6
32[e]	**1:2**	**Eosin Y**	**Et$_3$N**	**DCE (0.2M)**	**75%**	**98:2**
33[f]	1:2	Eosin Y	Et$_3$N	DCE (0.2M)	75%	97:3
34	1:2	--	Et$_3$N	DCE (0.2M)	18%	88:12
35[g]	1:2	Eosin Y	Et$_3$N	DCE (0.2M)	0	--

[a] Without **BPA**. [b] t = 48 h. [c] 1.0 equiv of Et$_3$N was used. [d] 0.5 equiv of Et$_3$N was used. [e] 1.0 equiv of Et$_3$N was used, and the reaction was conducted under 10 W blue LED. [f] 1.0 equiv of Et$_3$N was used, and the reaction was conducted under 15 W blue LED. [g] Without light. [h] Yields of isolated products. [i] Determined by ^{1}H NMR.

5. Optimization of chiral phosphoric acids (CPAs)



5a: Ar = Ph
5b: Ar = 3,5-$(CF_3)_2C_6H_3$
5c: Ar = 2,4,6-$(i\text{Pr})_3C_6H_2$
5d: Ar = 9-anthryl

6a: Ar = Ph
6b: Ar = 2,4,6-$(i\text{Pr})_3C_6H_2$
6c: Ar = 9-anthryl
6d: Ar = 4-PhC_6H_4

7a: Ar = Ph
7b: Ar = 3,5-$(CF_3)_2C_6H_3$
7c: Ar = 2,4,6-$(i\text{Pr})_3C_6H_2$
7d: Ar = 9-anthryl

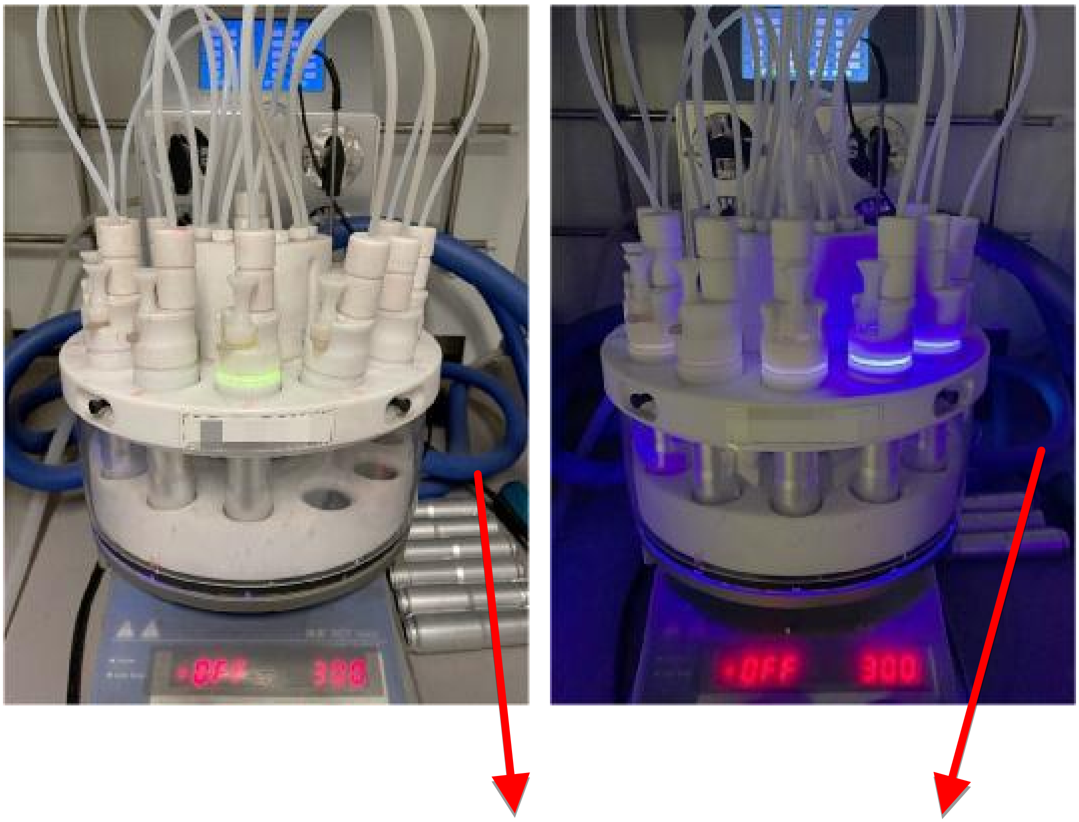
Table S2. Optimization of chiral phosphoric acids (CPAs)

Entry	CPA	Yield[a]	Ee[b]	Dr[c]
1	**5a**	67%	2%	88:12
2	**5b**	62%	3%	85:15
3	**5c**	61%	4%	92:8
4	**5d**	56%	2%	87:13
5	**6a**	71%	0%	95:5
6	**6b**	76%	-5%	98:2
7	**6c**	72%	-2%	94:6
8	**6d**	75%	-3%	96:4
9	**7a**	61%	-1%	90:10
10	**7b**	63%	-4%	89:11
11	**7c**	70%	-8%	94:6
12	**7d**	64%	-3%	93:7

[a] Yields of isolated products. [b] Determined by chiral HPLC analysis. [c] Determined by ^{1}H NMR analysis.

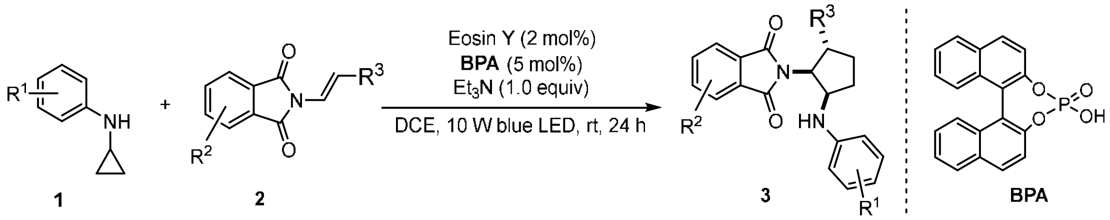
6. Synthesis and characterization of photoredox products

6.1. Photoredox catalysis reaction setup



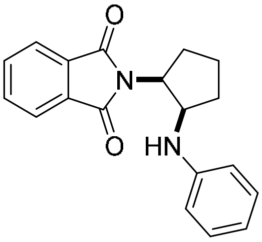
Recirculating liquid in the blue pipeline to maintain the reaction at room temperature

6.2. General procedure 3 for the photoredox [3+2] cycloaddition (GP3)



A Schlenk-tube was charged with Eosin Y (2 mol%), **BPA** (5 mol%), *N*-vinylphthalimide (2.0 equiv) and *N*-aryl cyclopropylamine (1.0 equiv), and then evacuated and backfilled with nitrogen (3 times). Afterwards, anhydrous DCE (0.2 M) and Et$_3$N (1.0 equiv) were added by syringe under nitrogen atmosphere. The tightly sealed tube was then irradiated with a 10 W blue LED. After 24 hours, the mixture was filtered and concentrated under reduced pressure, which was purified by silica gel column chromatography to give the cycloaddition product.

6.3. Characterization data of photoredox products



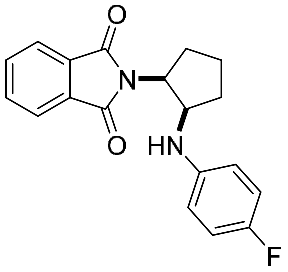
cis-2-(2-(phenylamino)cyclopentyl)isoindoline-1,3-dione (3aa)

Following the **GP3**, starting from *N*-cyclopropylaniline **1a** (26.6 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3aa** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (46.0 mg, 75% yield in 98:2 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.56 (m, 4H), 6.95 – 6.87 (m, 2H), 6.45 – 6.39 (m, 3H), 4.84 (q, *J* = 8.9 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.95 (d, *J* = 8.9 Hz, 1H), 2.61 – 2.47 (m, 1H), 2.28 – 2.17 (m, 1H), 2.11 – 1.87 (m, 3H), 1.63 – 1.47 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.48, 147.17, 133.77, 131.75, 129.09, 122.95, 117.17, 112.67, 56.10, 51.74, 33.73, 28.01, 22.54.

M.P. 192-194 ºC; **IR (film):** γ = 3415, 2969, 1764, 1703, 1601, 1508, 1392, 1377, 1312, 1112, 750, 726 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{18}N_2O_2$ [M + H]$^+$: 307.1441, found 307.1435.



cis-2-(2-((4-fluorophenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ba)

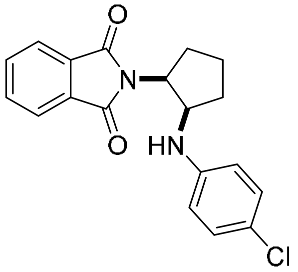
Following the **GP3**, starting from *N*-cyclopropyl-4-fluoroaniline **1b** (30.2 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ba** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (46.1 mg, 71% yield in 96:4 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.23 (m, 4H), 6.55 – 6.44 (m, 1H), 5.87 – 5.81 (m, 1H), 5.81 – 5.72 (m, 2H), 4.49 (q, *J* = 8.9 Hz, 1H), 3.81 – 3.69 (m, 2H), 2.27 – 2.13 (m, 1H), 1.93 – 1.83 (m, 1H), 1.76 – 1.52 (m, 3H), 1.28 – 1.18 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.47, 155.51 (d, *J* = 234.6 Hz), 143.50 (d, *J* = 1.9 Hz), 133.90, 131.69, 122.98, 115.49 (d, *J* = 22.5 Hz), 113.30 (d, *J* = 7.3 Hz), 56.51, 51.63, 33.81, 28.10, 22.58.

^{19}F NMR (376 MHz, Chloroform-d) δ -128.67.

M.P. 176-178 ºC; **IR (film):** γ = 3354, 2973, 2894, 1704, 1509, 1455, 1378, 1216, 1089, 1050, 880, 718 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{17}FN_2O_2$ [M + H]$^+$: 325.1347, found 325.1342.



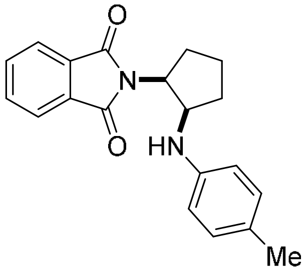
cis-2-(2-((4-chlorophenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ca)

Following the **GP3**, starting from 4-chloro-*N*-cyclopropylaniline **1c** (33.5 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ca** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (47.7 mg, 70% yield in 96:4 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.59 (m, 4H), 6.87 – 6.81 (m, 2H), 6.37 – 6.29 (m, 2H), 4.89 – 4.75 (m, 1H), 4.11 – 3.99 (m, 1H), 3.96 (d, *J* = 9.5 Hz, 1H), 2.60 – 2.45 (m, 1H), 2.28 – 2.17 (m, 1H), 2.10 – 1.84 (m, 3H), 1.61 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.47, 145.75, 133.95, 131.66, 129.10, 123.04, 121.65, 113.67, 56.17, 51.66, 33.69, 28.00, 22.53.

M.P. 201-203 ºC; **IR (film):** γ = 3354, 2973, 1704, 1662, 1379, 1330, 1274, 1089, 1049, 880, 803 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{17}ClN_2O_2$ $[M + H]^+$: 341.1051, found 341.1049.



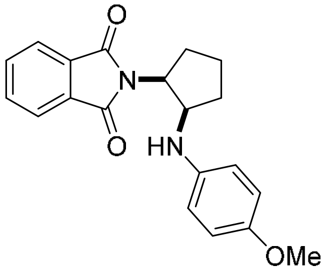
cis-2-(2-(*p*-tolylamino)cyclopentyl)isoindoline-1,3-dione (3da)

Following the **GP3**, starting from *N*-cyclopropyl-4-methylaniline **1d** (29.4 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3da** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (46.8 mg, 73% yield in 96:4 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.56 (m, 4H), 6.73 – 6.68 (m, 2H), 6.37 – 6.31 (m, 2H), 4.81 (q, *J* = 8.9 Hz, 1H), 4.09 (q, *J* = 7.6 Hz, 1H), 3.80 (s, 1H), 2.60 – 2.47 (m, 1H), 2.27 – 2.16 (m, 1H), 2.09 – 1.86 (m, 6H), 1.62 – 1.48 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.51, 144.93, 133.68, 131.83, 129.55, 126.23, 122.91, 112.85, 56.41, 51.82, 33.75, 28.02, 22.54, 20.24.

M.P. 140-142 ºC; **IR (film):** γ = 3382, 2973, 1705, 1519, 1455, 1377, 1089, 1049, 880, 805, 717 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{20}N_2O_2$ [M + H]$^+$: 321.1598, found 321.1592.



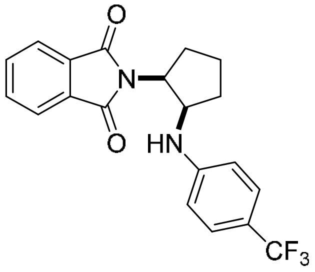
***cis*-2-(2-((4-methoxyphenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ea)**

Following the **GP3**, starting from *N*-cyclopropyl-4-methoxyaniline **1e** (32.6 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ea** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (52.5 mg, 78% yield in 97:3 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.56 (m, 4H), 6.52 – 6.46 (m, 2H), 6.39 – 6.33 (m, 2H), 4.85 – 4.74 (m, 1H), 4.05 (s, 1H), 3.66 (s, 1H), 3.57 (s, 3H), 2.59 – 2.46 (m, 1H), 2.28 – 2.17 (m, 1H), 2.09 – 1.83 (m, 3H), 1.61 – 1.47 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.51, 151.75, 141.45, 133.73, 131.81, 122.92, 114.85, 113.77, 56.71, 55.86, 51.78, 33.85, 28.10, 22.58.

M.P. 157-159 ºC; **IR (film):** γ = 3391, 2970, 2927, 1705, 1512, 1393, 1375, 1236, 1088, 1044, 879, 717 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{20}N_2O_3$ [M + H]$^+$: 337.1547, found 337.1538.



cis-2-(2-((4-(trifluoromethyl)phenyl)amino)cyclopentyl)isoindoline-1,3-dione (3fa)

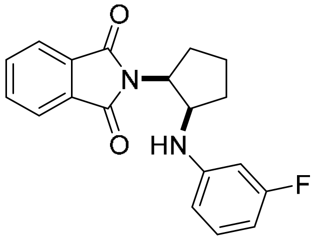
Following the **GP3**, starting from *N*-cyclopropyl-4-(trifluoromethyl)aniline **1f** (40.2 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3fa** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (57.7 mg, 77% yield in 95:5 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.57 (m, 4H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.42 (d, *J* = 8.5 Hz, 2H), 4.88 – 4.78 (m, 1H), 4.30 (d, *J* = 9.2 Hz, 1H), 4.18 – 4.08 (m, 1H), 2.62 – 2.50 (m, 1H), 2.30 – 2.20 (m, 1H), 2.10 – 1.88 (m, 3H), 1.63 – 1.54 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.48, 149.70, 134.00, 131.55, 126.44 (q, *J* = 3.8 Hz), 124.86 (q, *J* = 270.4 Hz), 123.03, 118.65 (q, *J* = 32.6 Hz), 111.88, 55.78, 51.77, 33.58, 27.82, 22.52.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.23.

M.P. 147-149 ºC; **IR (film):** γ = 3391, 2963, 2872, 1770, 1704, 1615, 1533, 1375, 1327, 1111, 1066, 827, 717 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{17}F_3N_2O_2$ [M + H]$^+$: 375.1315, found 375.1310.



***cis*-2-(2-((3-fluorophenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ga)**

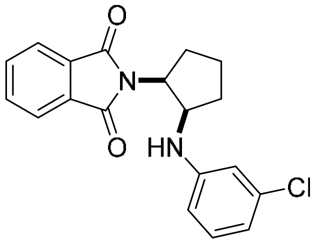
Following the **GP3**, starting from *N*-cyclopropyl-3-fluoroaniline **1g** (30.2 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ga** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (46.1 mg, 71% yield in 96:4 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.58 (m, 4H), 6.87 – 6.80 (m, 1H), 6.20 – 6.15 (m, 1H), 6.14 – 6.07 (m, 2H), 4.82 (q, *J* = 8.8 Hz, 1H), 4.09 (d, *J* = 26.4 Hz, 2H), 2.59 – 2.47 (m, 1H), 2.26 – 2.18 (m, 1H), 2.09 – 1.87 (m, 3H), 1.64 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.44, 163.89 (d, *J* = 242.9 Hz), 148.96 (d, *J* = 10.7 Hz), 133.93, 131.66, 130.22 (d, *J* = 10.1 Hz), 123.03, 108.35 (d, *J* = 2.2 Hz), 103.56 (d, *J* = 21.7 Hz), 99.48 (d, *J* = 25.3 Hz), 56.09, 51.69, 33.52, 27.85, 22.45.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.11.

M.P. 175-177 ºC; **IR (film):** γ = 3404, 2966, 1771, 1702, 1620, 1531, 1396, 1340, 1151, 1069, 994, 874, 721 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{17}FN_2O_2$ [M + H]$^+$: 325.1347, found 325.1342.



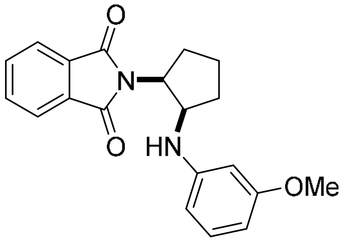
***cis*-2-(2-((3-chlorophenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ha)**

Following the **GP3**, starting from 3-chloro-*N*-cyclopropylaniline **1h** (33.5 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ha** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (46.3 mg, 68% yield in 95:5 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.60 (m, 4H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.41 – 6.34 (m, 2H), 6.29 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.86 – 4.78 (m, 1H), 4.11 – 4.03 (m, 2H), 2.59 – 2.50 (m, 1H), 2.26 – 2.19 (m, 1H), 2.07 – 1.88 (m, 3H), 1.62 – 1.52 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.47, 148.35, 134.83, 133.95, 131.64, 130.12, 123.06, 117.00, 112.63, 110.83, 56.03, 51.77, 33.54, 27.81, 22.47.

M.P. 180-182 ºC; **IR (film):** γ = 3397, 2963, 2866, 1772, 1703, 1598, 1469, 1393, 1377, 1066, 874, 719 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{17}ClN_2O_2$ $[M + H]^+$: 341.1051, found 341.1049.



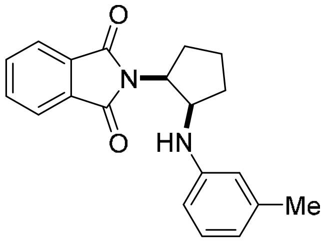
cis-2-(2-((3-methoxyphenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ia)

Following the **GP3**, starting from *N*-cyclopropyl-3-methoxyaniline **1i** (32.6 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ia** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (50.5 mg, 75% yield in 97:3 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 2H), 7.61 – 7.57 (m, 2H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.05 – 5.95 (m, 3H), 4.82 (q, *J* = 8.8 Hz, 1H), 4.14 – 4.05 (m, 1H), 3.96 (d, *J* = 9.2 Hz, 1H), 3.62 (s, 3H), 2.59 – 2.49 (m, 1H), 2.26 – 2.19 (m, 1H), 2.08 – 1.89 (m, 3H), 1.61 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.50, 160.58, 148.58, 133.75, 131.76, 129.89, 122.93, 105.69, 103.04, 98.36, 56.16, 55.01, 51.76, 33.70, 27.97, 22.54.

M.P. 143-145 ºC; **IR (film):** γ = 3397, 2957, 2870, 1769, 1704, 1614, 1393, 1374, 1211, 1162, 1069, 824, 717 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{20}N_2O_3$ [M + H]$^+$: 337.1547, found 337.1552.



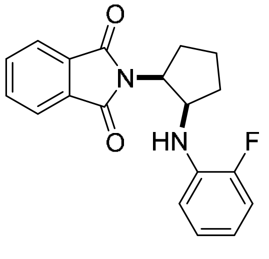
***cis*-2-(2-(m-tolylamino)cyclopentyl)isoindoline-1,3-dione (3ja)**

Following the **GP3**, starting from *N*-cyclopropyl-3-methylaniline **1j** (29.4 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ja** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (46.8 mg, 73% yield in 96:4 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.64 (m, 2H), 7.61 – 7.57 (m, 2H), 6.82 – 6.77 (m, 1H), 6.26 – 6.21 (m, 3H), 4.85 – 4.78 (m, 1H), 4.16 – 4.08 (m, 1H), 3.87 (d, *J* = 8.7 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.26 – 2.19 (m, 1H), 2.08 – 1.89 (m, 6H), 1.62 – 1.51 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.49, 147.20, 138.76, 133.68, 131.77, 128.99, 122.85, 118.07, 113.66, 109.97, 56.12, 51.79, 33.76, 27.96, 22.56, 21.44.

M.P. 140-142 ºC; **IR (film):** γ = 3400, 2964, 2919, 1771, 1704, 1605, 1532, 1469, 1395, 1067, 873, 764, 719, 695 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{20}N_2O_2$ [M + H]$^+$: 321.1598, found 321.1601.



***cis*-2-(2-((2-fluorophenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ka)**

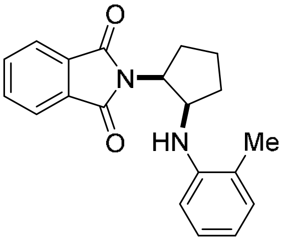
Following the **GP3**, starting from *N*-cyclopropyl-2-fluoroaniline **1k** (30.2 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ka** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (42.2 mg, 65% yield in 95:5 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.67 (m, 2H), 7.63 – 7.59 (m, 2H), 6.86 – 6.81 (m, 1H), 6.67 – 6.59 (m, 2H), 6.40 – 6.34 (m, 1H), 4.85 (q, *J* = 8.8 Hz, 1H), 4.20 (dd, *J* = 9.5, 3.2 Hz, 1H), 4.13 – 4.05 (m, 1H), 2.62 – 2.52 (m, 1H), 2.28 – 2.20 (m, 1H), 2.11 – 1.99 (m, 3H), 1.64 – 1.53 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.32, 151.19 (d, *J* = 238.6 Hz), 135.73 (d, *J* = 11.4 Hz), 133.88, 131.71, 124.61 (d, *J* = 3.4 Hz), 123.05, 116.51 (d, *J* = 7.0 Hz), 114.27 (d, *J* = 18.6 Hz), 112.52 (d, *J* = 3.3 Hz), 56.04, 51.68, 33.60, 27.92, 22.51.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -136.74.

M.P. 164-166 ºC; **IR (film):** γ = 3421, 2968, 2927, 1764, 1704, 1617, 1521, 1393, 1335, 1067, 877, 719, 643 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{17}FN_2O_2$ $[M + H]^+$: 325.1347, found 325.1362.



cis-2-(2-(*o*-tolylamino)cyclopentyl)isoindoline-1,3-dione (3la)

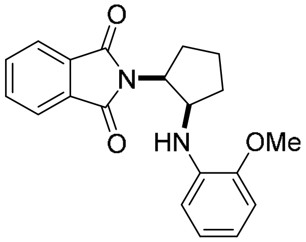
Following the **GP3**, starting from *N*-cyclopropyl-2-methylaniline **1l** (29.4 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3la** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (48.1 mg, 75% yield in 98:2 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.58 (m, 4H), 6.97 (td, *J* = 7.8, 1.7 Hz, 1H), 6.77 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.52 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.41 (td, *J* = 7.3, 1.2

Hz, 1H), 4.88 (q, *J* = 8.8 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 1H), 3.98 (s, 1H), 2.68 – 2.58 (m, 1H), 2.27 – 2.19 (m, 1H), 2.10 – 1.95 (m, 6H), 1.68 – 1.57 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.53, 145.13, 133.90, 131.80, 130.02, 127.16, 122.95, 121.67, 116.63, 109.86, 55.73, 51.99, 33.55, 27.65, 22.40, 17.42.

M.P. 154-156 ºC; **IR (film):** γ = 3354, 2971, 1704, 1514, 1451, 1378, 1323, 1274, 1088, 1050, 880, 718 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{20}N_2O_2$ [M + H]$^+$: 321.1598, found 321.1601.



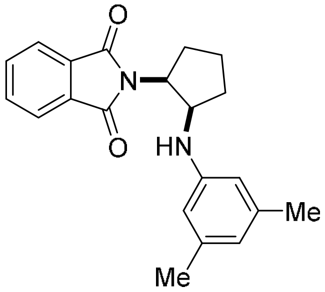
***cis*-2-(2-((2-methoxyphenyl)amino)cyclopentyl)isoindoline-1,3-dione (3ma)**

Following the **GP3**, starting from *N*-cyclopropyl-2-methoxyaniline **1m** (32.6 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3ma** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (48.4 mg, 72% yield in 97:3 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.62 – 7.56 (m, 2H), 6.73 (td, *J* = 7.6, 1.5 Hz, 1H), 6.57 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.46 – 6.33 (m, 2H), 4.85 (q, *J* = 8.8 Hz, 1H), 4.39 (d, *J* = 9.8 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.48 (s, 3H), 2.59 – 2.48 (m, 1H), 2.29 – 2.20 (m, 1H), 2.12 – 1.99 (m, 3H), 1.60 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.19, 146.54, 137.34, 133.61, 131.88, 122.81, 121.39, 116.57, 111.09, 109.32, 56.49, 55.24, 51.27, 33.78, 28.16, 22.79.

M.P. 177-179 ºC; **IR (film):** γ = 3354, 2974, 2891, 1706, 1455, 1379, 1089, 1049, 880, 803 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{20}N_2O_3$ [M + H]$^+$: 337.1547, found 337.1550.



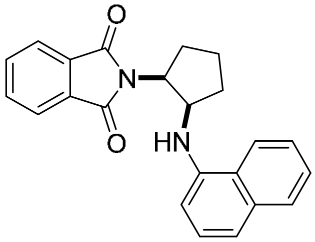
cis-2-(2-((3,5-dimethylphenyl)amino)cyclopentyl)isoindoline-1,3-dione (3na)

Following the **GP3**, starting from *N*-cyclopropyl-3,5-dimethylaniline **1n** (32.5 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3na** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (50.2 mg, 75% yield in 97:3 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 4H), 6.03 (d, *J* = 9.7 Hz, 3H), 4.79 (q, *J* = 8.9 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.77 (d, *J* = 9.2 Hz, 1H), 2.62 – 2.49 (m, 1H), 2.26 – 2.19 (m, 1H), 2.06 – 1.86 (m, 9H), 1.61 – 1.48 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.57, 147.28, 138.69, 133.63, 131.82, 122.79, 119.14, 111.02, 56.15, 51.90, 33.83, 27.95, 22.62, 21.35.

M.P. 202-204 ºC; **IR (film):** γ = 3392, 2972, 2926, 1702, 1600, 1455, 1379, 1337, 1274, 1088, 1049, 880, 717 cm^{-1}; **HRMS (ESI):** Calculated for $C_{21}H_{22}N_2O_2$ [M + H]$^+$: 335.1754, found 335.1759.



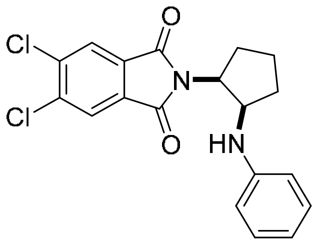
cis-2-(2-(naphthalen-1-ylamino)cyclopentyl)isoindoline-1,3-dione (3oa)

Following the **GP3**, starting from *N*-cyclopropylnaphthalen-1-amine **1o** (36.7 mg, 0.2 mmol) and 2-vinylisoindoline-1,3-dione **2a** (69.3 mg, 0.4 mmol), compound **3oa** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 20:1) as a yellow solid (55.6 mg, 78% yield in 98:2 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.47 – 7.43 (m, 2H), 7.35 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 5.03 – 4.90 (m, 2H), 4.33 – 4.25 (m, 1H), 2.74 – 2.64 (m, 1H), 2.29 – 2.21 (m, 1H), 2.17 – 2.01 (m, 3H), 1.69 – 1.61 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.66, 142.49, 134.30, 133.78, 131.59, 128.41, 126.63, 125.50, 124.61, 123.10, 122.92, 120.24, 116.92, 104.52, 56.35, 52.03, 33.06, 27.51, 22.30.

M.P. 192-194 ºC; **IR (film):** γ = 3354, 2972, 1768, 1704, 1580, 1532, 1378, 1275, 1088, 1049, 880, 717 cm^{-1}; **HRMS (ESI):** Calculated for $C_{23}H_{20}N_2O_2$ $[M + H]^+$: 357.1598, found 357.1603.



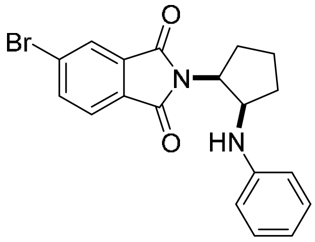
***cis*-5,6-dichloro-2-(2-(phenylamino)cyclopentyl)isoindoline-1,3-dione (3ab)**

Following the **GP3**, starting from *N*-cyclopropylaniline **1a** (26.6 mg, 0.2 mmol) and 5,6-dichloro-2-vinylisoindoline-1,3-dione **2b** (96.8 mg, 0.4 mmol), compound **3ab** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (53.3 mg, 71% yield in 95:5 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (s, 2H), 6.95 – 6.90 (m, 2H), 6.45 (t, *J* = 7.3 Hz, 1H), 6.41 – 6.37 (m, 2H), 4.80 (q, *J* = 8.9 Hz, 1H), 4.15 – 4.07 (m, 1H), 3.78 (d, *J* = 9.0 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.29 – 2.22 (m, 1H), 2.08 – 1.88 (m, 3H), 1.60 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.46, 146.94, 138.58, 130.82, 129.21, 125.02, 117.41, 112.57, 55.97, 52.17, 33.94, 28.12, 22.67.

M.P. 190-192 ºC; **IR (film):** γ = 3354, 2973, 2927, 1773, 1708, 1602, 1506, 1370, 1310, 1089, 1049, 881, 743, 602 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{16}Cl_2N_2O_2$ [M + H]$^+$: 375.0662, found 375.0665.



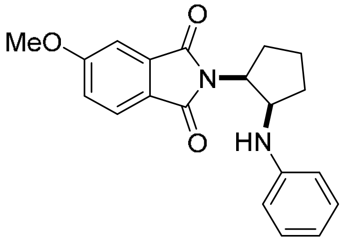
cis-5-bromo-2-(2-(phenylamino)cyclopentyl)isoindoline-1,3-dione (3ac)

Following the **GP3**, starting from *N*-cyclopropylaniline **1a** (26.6 mg, 0.2 mmol) and 5-bromo-2-vinylisoindoline-1,3-dione **2c** (100.8 mg, 0.4 mmol), compound **3ac** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (52.4 mg, 68% yield in 96:4 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.77 (m, 1H), 7.74 – 7.70 (m, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 6.94 – 6.90 (m, 2H), 6.46 – 6.39 (m, 3H), 4.81 (q, *J* = 8.9 Hz, 1H), 4.11 (s, 1H), 3.83 (s, 1H), 2.56 – 2.46 (m, 1H), 2.28 – 2.21 (m, 1H), 2.07 – 1.90 (m, 3H), 1.60 – 1.52 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.60, 168.12, 147.01, 136.76, 133.33, 130.22, 129.16, 128.59, 126.28, 124.33, 117.31, 112.60, 56.00, 51.92, 33.85, 28.07, 22.61.

M.P. 160-162 ºC; **IR (film):** γ = 3397, 2972, 1707, 1601, 1419, 1374, 1090, 1048, 880, 738, 692 cm^{-1}; **HRMS (ESI):** Calculated for $C_{19}H_{17}BrN_2O_2$ [M + H]$^+$: 385.0546, found 385.0548.



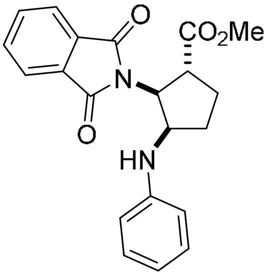
cis-5-methoxy-2-(2-(phenylamino)cyclopentyl)isoindoline-1,3-dione (3ad)

Following the **GP3**, starting from *N*-cyclopropylaniline **1a** (26.6 mg, 0.2 mmol) and 5-methoxy-2-vinylisoindoline-1,3-dione **2d** (81.3 mg, 0.4 mmol), compound **3ad** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (49.8 mg, 74% yield in 96:4 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.3 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.48 – 6.42 (m, 3H), 4.80 (q, *J* = 8.9 Hz, 1H), 4.12 – 4.05 (m, 1H), 3.97 (s, 1H), 3.87 (s, 3H), 2.57 – 2.47 (m, 1H), 2.24 – 2.17 (m, 1H), 2.07 – 1.91 (m, 3H), 1.60 – 1.52 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.24, 169.18, 164.47, 147.18, 134.29, 129.05, 124.63, 123.68, 119.56, 117.07, 112.61, 107.66, 56.06, 56.04, 51.64, 33.59, 27.92, 22.41.

M.P. 130-132 ºC; **IR (film):** γ = 3394, 2971, 1703, 1602, 1490, 1390, 1371, 1286, 1092, 1050, 880, 749, 693 cm^{-1}; **HRMS (ESI):** Calculated for $C_{20}H_{20}N_2O_3$ [M + H]$^+$: 337.1547, found 337.1551.



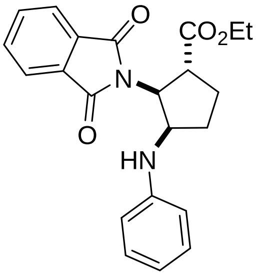
methyl-2-(1,3-dioxoisoindolin-2-yl), *trans*-3-(phenylamino)cyclopentane, *trans*-1-carboxylate (3ae)

Following the **GP3**, starting from *N*-cyclopropylaniline **1a** (26.6 mg, 0.2 mmol) and methyl (*E*)-3-(1,3-dioxoisoindolin-2-yl)acrylate **2e** (92.5 mg, 0.4 mmol), compound **3ae** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (50.3 mg, 69% yield in 85:15 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.59 (m, 4H), 6.94 – 6.88 (m, 2H), 6.47 – 6.39 (m, 3H), 5.06 (t, *J* = 9.1 Hz, 1H), 4.29 – 4.18 (m, 1H), 3.96 – 3.79 (m, 2H), 3.64 (s, 3H), 2.40 – 2.24 (m, 2H), 2.07 – 1.96 (m, 1H), 1.89 – 1.78 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.38, 169.15, 146.72, 133.97, 131.61, 129.21, 123.19, 117.58, 112.70, 55.82, 54.18, 52.23, 45.26, 33.28, 26.42.

M.P. 215-217 ºC; **IR (film):** γ = 3394, 2951, 1771, 1732, 1707, 1602, 1507, 1379, 1207, 1079, 750, 718, 693 cm^{-1}; **HRMS (ESI):** Calculated for $C_{21}H_{20}N_2O_4$ [M + H]$^+$: 365.1496, found 365.1499.



ethyl-2-(1,3-dioxoisoindolin-2-yl), *trans* -3-(phenylamino)cyclopentane, *trans* -1-carboxylate (3af)

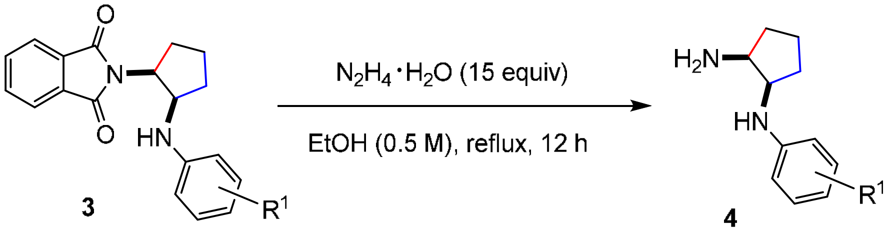
Following the **GP3**, starting from *N*-cyclopropylaniline **1a** (26.6 mg, 0.2 mmol) and ethyl (*E*)-3-(1,3-dioxoisoindolin-2-yl)acrylate **2f** (98.1 mg, 0.4 mmol), compound **3af** was obtained after purification by silica gel chromatography (petroleum ether: EtOAc = 10:1) as a yellow solid (57.5 mg, 76% yield in 88:12 dr).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.58 (m, 4H), 6.96 – 6.88 (m, 2H), 6.48 – 6.39 (m, 3H), 5.07 – 4.99 (m, 1H), 4.27 – 4.19 (m, 1H), 4.14 – 4.04 (m, 2H), 3.94 (s, 1H), 3.88 – 3.80 (m, 1H), 2.40 – 2.23 (m, 2H), 2.06 – 1.96 (m, 1H), 1.89 – 1.78 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).

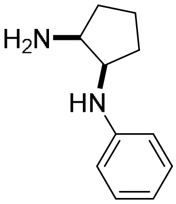
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.82, 169.14, 146.76, 133.97, 131.63, 129.20, 123.15, 117.54, 112.68, 60.94, 55.78, 54.20, 45.36, 33.20, 26.16, 14.18.

M.P. 220-222 ºC; **IR (film):** γ = 3395, 2964, 1771, 1731, 1708, 1602, 1507, 1378, 1204, 1030, 750, 718, 693 cm^{-1}; **HRMS (ESI):** Calculated for $C_{22}H_{22}N_2O_4$ [M + H]$^+$: 379.1653 , found 379.1656.

7. Deprotection of product 3



To a stirred solution of **3** (0.2 mmol, 1 equiv) in EtOH (0.4 mL) was added hydrazine hydrate (w=80%, 0.18 mL, 15 equiv). The mixture was refluxed for 12 h. After completion of the reaction, as indicated by TLC, the mixture was combined with aqueous $NaHCO_3$ and extracted with DCM. Then, the combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After concentration, the residue was purified by silica gel chromatography to give the deprotected product **4**.



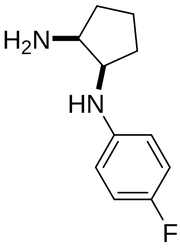
***cis*-*N*^{1}-phenylcyclopentane-1,2-diamine (4a)**

Deprotected product **4a** was obtained after purification by silica gel chromatography (DCM: MeOH = 10:1) as a white solid (26.8 mg, 76% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.09 – 7.00 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 6.49 (t, *J* = 7.2 Hz, 1H), 5.41 (d, *J* = 6.5 Hz, 1H), 3.52 – 3.41 (m, 1H), 3.34 – 3.28 (m, 1H), 2.94 (bs, 2H), 1.88 – 1.75 (m, 2H), 1.73 – 1.64 (m, 1H), 1.59 – 1.40 (m, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 148.64, 128.85, 115.37, 112.38, 57.04, 52.33, 32.27, 29.14, 19.98.

M.P. 97-99 ºC; **IR (film):** γ = 3354, 2973, 2893, 1379, 1089, 1049, 880, 429 cm^{-1}; **HRMS (ESI):** Calculated for $C_{11}H_{16}N_2$ $[M + H]^+$: 177.1386, found 177.1384.



cis-N¹-(4-fluorophenyl)cyclopentane-1,2-diamine (4b)

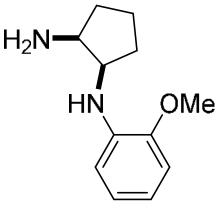
Deprotected product **4b** was obtained after purification by silica gel chromatography (DCM: MeOH = 10:1) as a white solid (28.7 mg, 74% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.94 – 6.82 (m, 2H), 6.63 – 6.54 (m, 2H), 5.37 (d, *J* = 6.6 Hz, 1H), 3.45 – 3.37 (m, 1H), 3.33 – 3.27 (m, 1H), 2.90 (bs, 2H), 1.88 – 1.74 (m, 2H), 1.72 – 1.63 (m, 1H), 1.57 – 1.39 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 154.04 (d, *J* = 230.3 Hz), 145.35, 115.11 (d, *J* = 21.8 Hz), 112.99 (d, *J* = 7.3 Hz), 57.54, 52.27, 32.27, 29.07, 19.92.

^{19}F NMR (376 MHz, DMSO-d_6) δ -130.24.

M.P. 76-78 ºC; **IR (film):** γ = 3323, 2972, 2865, 1384, 1074, 820, 428 cm^{-1}; **HRMS (ESI):** Calculated for $C_{11}H_{15}FN_2$ [M + H]$^+$: 194.1219, found 194.1216.



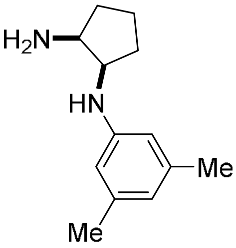
cis-N¹-(2-methoxyphenyl)cyclopentane-1,2-diamine (4c)

Deprotected product **4c** was obtained after purification by silica gel chromatography (DCM: MeOH = 10:1) as a white solid (33.8 mg, 82% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.81 – 6.71 (m, 2H), 6.57 – 6.48 (m, 2H), 5.10 (d, *J* = 5.9 Hz, 1H), 3.77 (s, 3H), 3.47 – 3.40 (m, 1H), 3.35 – 3.29 (m, 1H), 1.93 – 1.80 (m, 2H), 1.73 – 1.65 (m, 1H), 1.55 – 1.41 (m, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 146.46, 137.86, 121.02, 115.13, 109.66, 109.55, 56.22, 55.19, 52.48, 32.88, 29.80, 20.35.

M.P. 81-83ºC; **IR (film):** γ = 3356, 2983, 2892, 1377, 1086, 1049, 843, 432, 413 cm^{-1}; **HRMS (ESI):** Calculated for $C_{12}H_{18}N_2O$ [M + H]$^+$: 206.1419, found 206.1417.



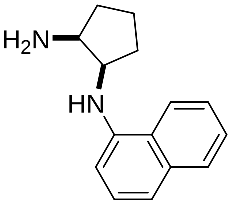
cis-*N*^{1}-(3,5-dimethylphenyl)cyclopentane-1,2-diamine (4d)

Deprotected product **4d** was obtained after purification by silica gel chromatography (DCM: MeOH = 10:1) as a white solid (30.6 mg, 75% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 6.26 – 6.13 (m, 3H), 5.23 (d, *J* = 6.6 Hz, 1H), 3.48 – 3.40 (m, 1H), 3.32 – 3.27 (m, 1H), 3.14 (bs, 2H), 2.12 (s, 6H), 1.87 – 1.74 (m, 2H), 1.72 – 1.62 (m, 1H), 1.58 – 1.38 (m, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 148.59, 137.52, 117.44, 110.40, 57.06, 52.24, 32.28, 29.20, 21.23, 19.93.

M.P. 107-109 ºC; **IR (film):** γ = 3350, 2963, 2853, 1383, 1096, 1052, 860 cm^{-1}; **HRMS (ESI):** Calculated for $C_{13}H_{20}N_2$ [M + H]$^+$: 205.1699, found 205.1695.



cis-*N*^{1}-(naphthalen-1-yl)cyclopentane-1,2-diamine (4e)

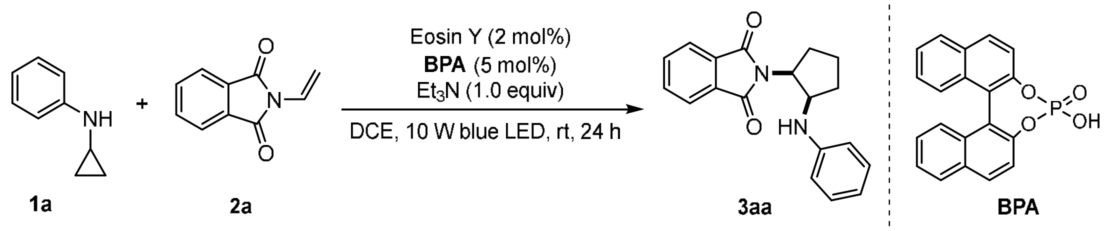
Deprotected product **4e** was obtained after purification by silica gel chromatography (DCM: MeOH = 10:1) as a yellow oil (36.2 mg, 80% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.46 – 7.39 (m, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.02 (d, *J* = 5.4 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.51 – 3.45 (m, 1H), 2.97 (bs, 2H), 2.04 – 1.97 (m, 1H), 1.94 – 1.86 (m, 1H), 1.78 – 1.70 (m, 2H), 1.60 – 1.50 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 143.57, 134.05, 128.04, 126.87, 125.60, 124.05, 123.15, 121.22, 115.35, 103.86, 56.52, 52.39, 32.71, 29.53, 20.53.

M.P. 97-99 ºC; **IR (film):** γ = 3345, 2923, 2852, 1580, 1522, 1474, 1408, 1396, 1102, 767, 426, 416 cm^{-1}; **HRMS (ESI):** Calculated for $C_{15}H_{18}N_2$ [M + H]$^+$: 227.1543, found 227.1540.

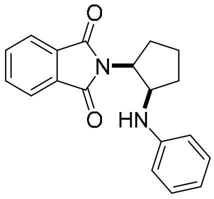
8. Reaction at 1 mmol scale



A Schlenk-tube was charged with Eosin Y (13.8 mg, 2 mol%), **BPA** (17.4 mg, 5 mol%), *N*-vinylphthalimide **2a** (346.3 mg, 2.0 mmol) and *N*-Cyclopropylaniline **1a** (133.09 mg, 1.0 mmol), and then evacuated and backfilled with nitrogen (3 times). Afterwards, anhydrous DCE (5.0 mL, 0.2 M) and Et_3N (101.09 mg, 1.0 equiv) were added by syringe under nitrogen atmosphere. The tightly sealed tube was then irradiated with a 10 W blue LED. After 24 hours, the mixture was filtered and concentrated under reduced pressure, which was purified by silica gel column chromatography (petroleum ether: EtOAc = 10:1) to give the product **3aa** as a yellow solid (208.3 mg, 68 % yield in 95:5 dr).

9. X-Ray Structure and Crystal Data of 3aa

Crystallisation of **3aa** was obtained from the mixed solution of dichloromethane and hexane maintained at room temperature for a week. The single crystal of product **3aa** was determined by X-ray diffraction analysis (Bruker APEX-II CCD diffractometer). The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2306450).



3aa

≡

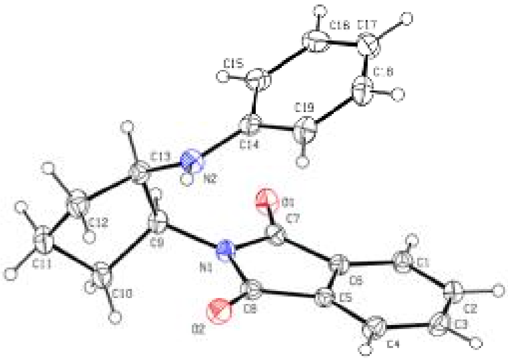


Table 1 Crystal data and structure refinement for mo_230411_XY_0 (3aa).

Identification code	mo_230411_XY_0
Empirical formula	$C_{19}H_{18}N_2O_2$
Formula weight	306.35
Temperature/K	170.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.0152(3)
b/Å	9.9594(3)
c/Å	11.9574(4)
α/°	90
β/°	92.5640(10)
γ/°	90
Volume/Å^3	1548.41(8)

Z	4
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	0.086
F(000)	648.0
Crystal size/mm^3	0.45 × 0.35 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.152 to 55.062
Index ranges	$-16 \leq h \leq 15$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	23366
Independent reflections	3555 [R_{int} = 0.0467, R_{sigma} = 0.0285]
Data/restraints/parameters	3555/0/208
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1100
Final R indexes [all data]	R_1 = 0.0645, wR_2 = 0.1212
Largest diff. peak/hole / e Å^{-3}	0.39/-0.44

10. UV-Vis Absorption spectra

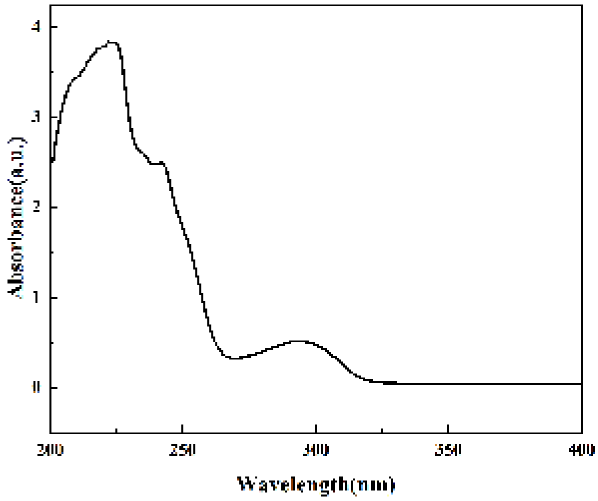


Figure S1. UV-Vis absorption spectra of **3aa**.

11. Stern−Volmer quenching experiments

A Shimadzu RF-6000 Spectro Fluorescencephotometer was used to record the emission intensities. All the solutions were excited at 440 nm and the emission intensity at 578 nm was observed. In a typical experiment, the emission spectrum of a 2×10^{-4} M solution of Eosin Y in DCE was collected. Then, appropriate amount of quencher was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 578 nm.

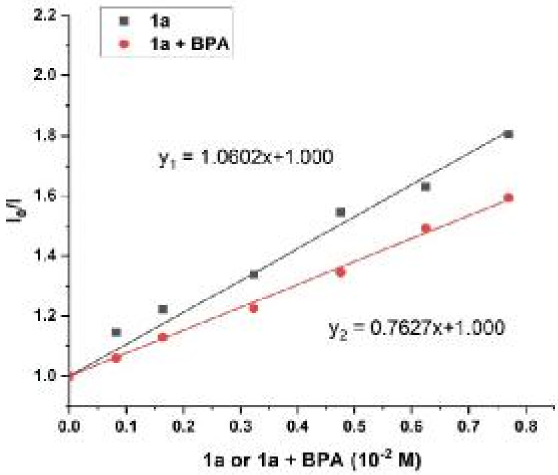


Figure. S1. Stern–Volmer quenching experiments of Eosin Y with **1a** or **1a** + **BPA**.

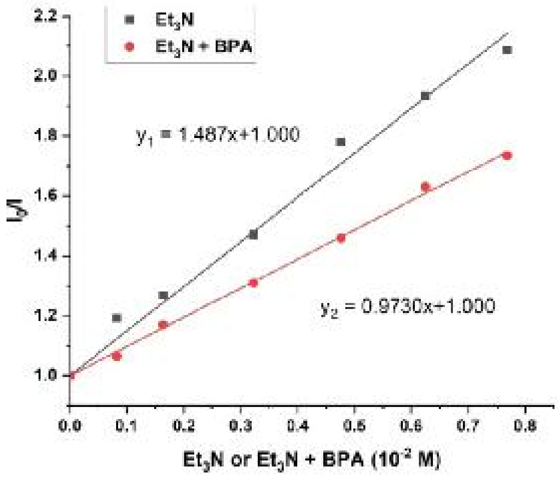


Figure. S2. Stern–Volmer quenching experiments of Eosin Y with Et_3N or Et_3N + **BPA**.

12. NMR Experiments

NMR experiments were performed on a Bruker DPX 400 NMR spectrometer at 400 MHz for ^{1}H NMR, 162 MHz for ^{31}P NMR. The solvent used for NMR spectroscopy was DMSO-d_6. Chemical shifts for ^{1}H NMR spectra were reported as δ in units of parts per million (ppm) downfield from standard tetramethylsilane (0.0), relative to the signal of the solvent (DMSO-d_6 at 2.50 ppm).

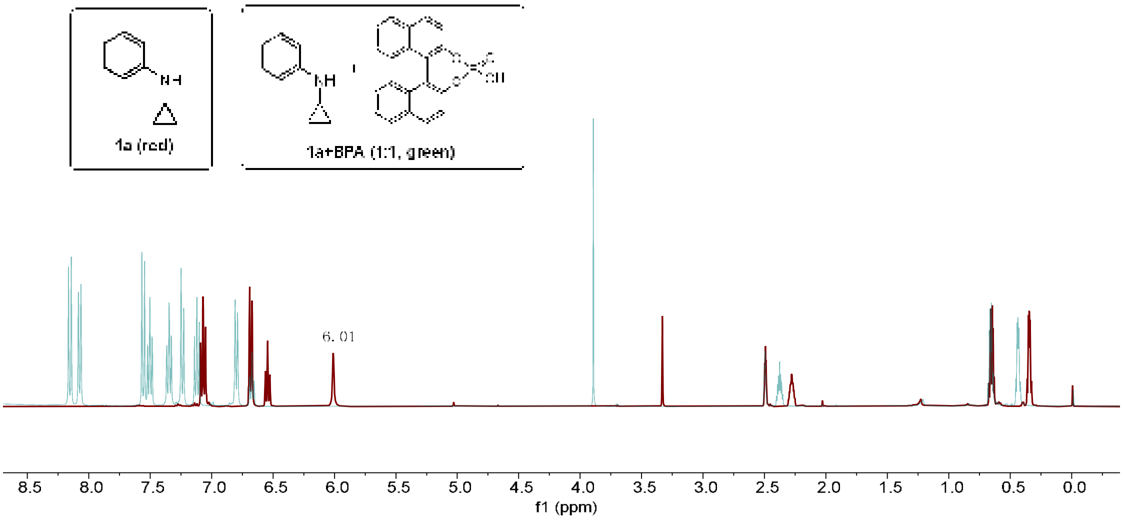
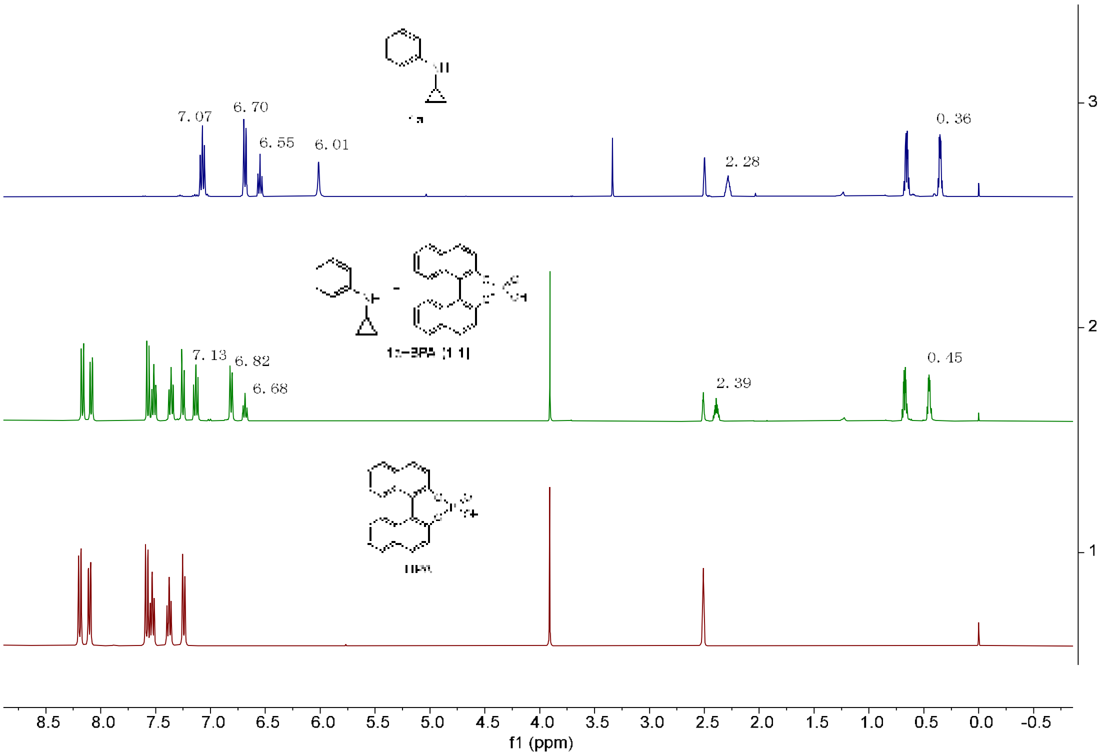


Figure S4. Comparison of ^{1}H NMR chemical shift between **1a** and **1a+BPA** (1:1).

Comment: The **1a/BPA** system has a significant effect on the chemical shifts of **1a** and **BPA**. For **1a**, the chemical shifts of the hydrogen atoms of the aryl and alkyl moieties have changed. Due to the formation of hydrogen bonds between 1a and BPA, the peak of the amine hydrogen atoms (at 6.01 ppm in **1a**) did not appear in the **1a/BPA** system (see Figure S4 and Figure S5). In addition, the chemical shifts in ^{31}P NMR spectra of the phosphorus atoms of **BPA** have changed from 2.66 ppm (**BPA**) to 2.91 ppm (**1a+BPA**) (see Figure S6).



Figur S5. Influence of **1a/BPA** system on chemical shift of **1a** and **BPA** hydrogen atom.

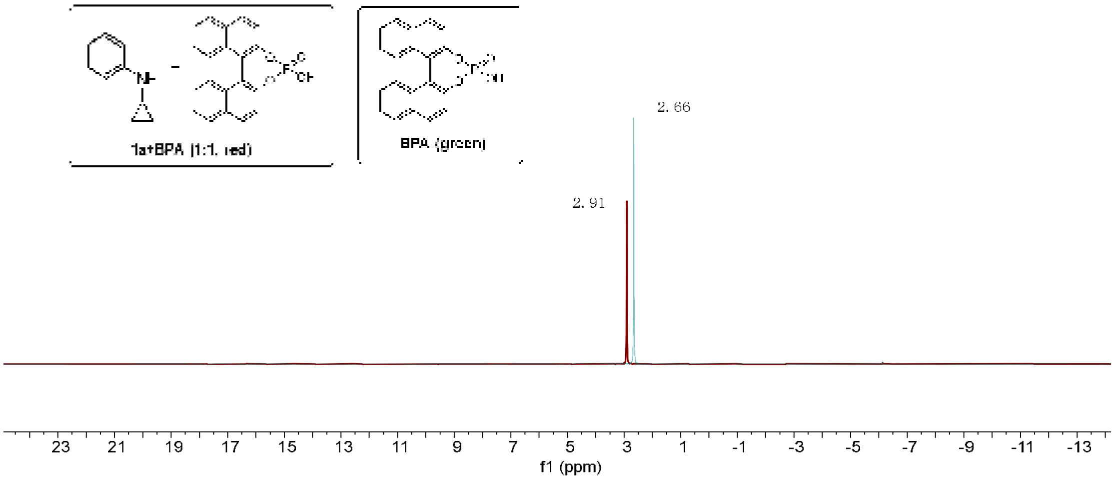
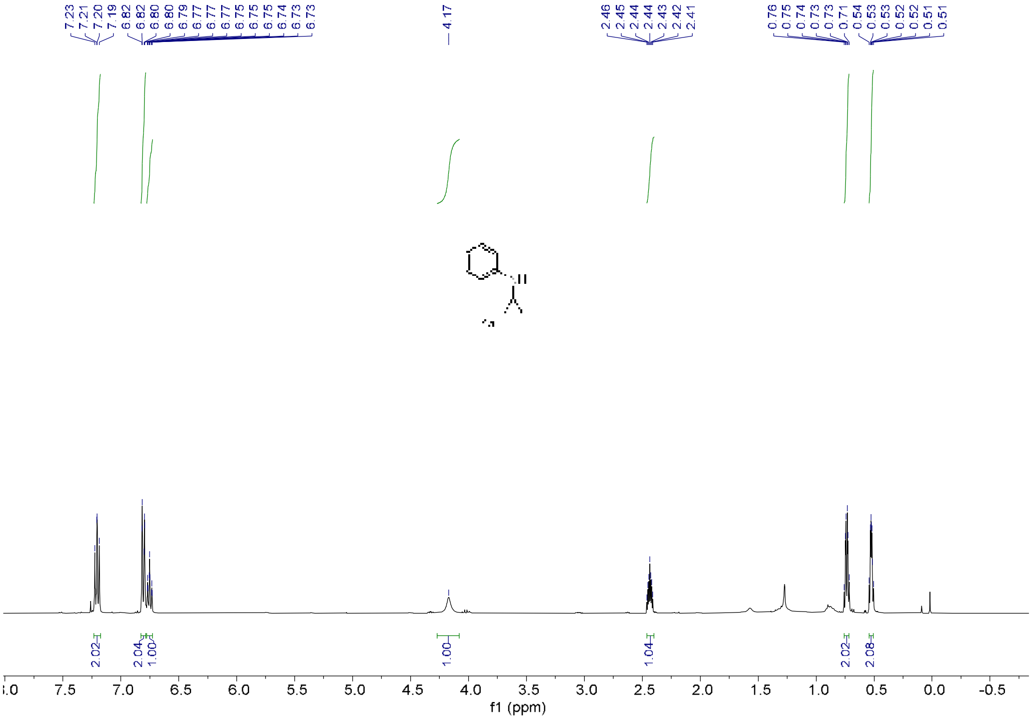


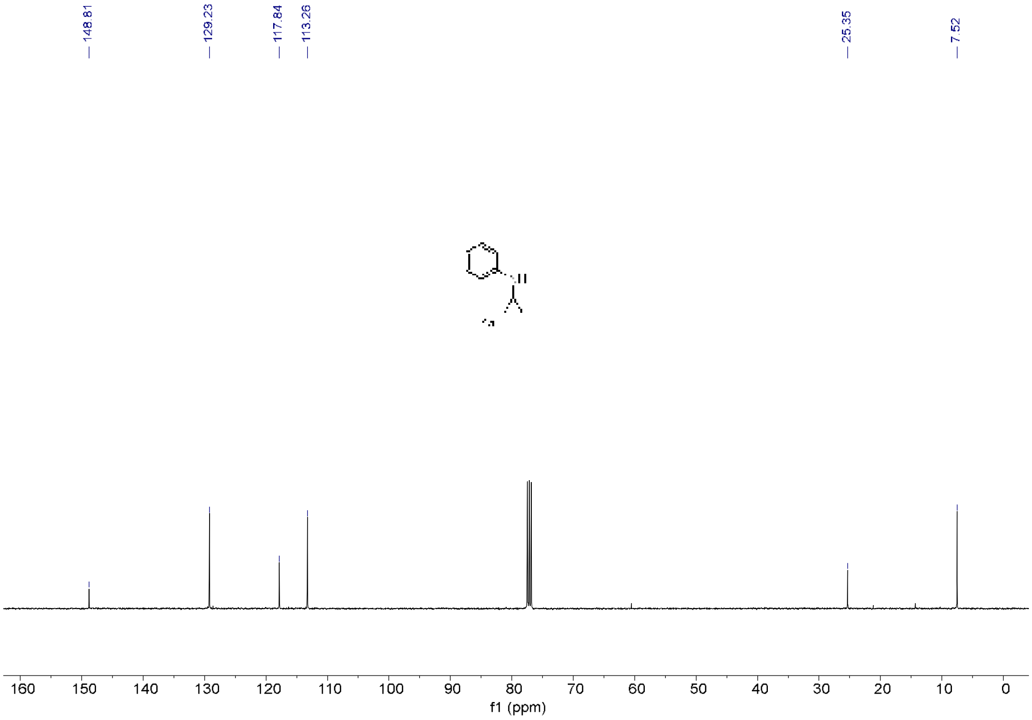
Figure S6. Comparison of ^{31}P NMR chemical shift between **BPA** and **1a+BPA** (1:1).

13. Copies of NMR spectra

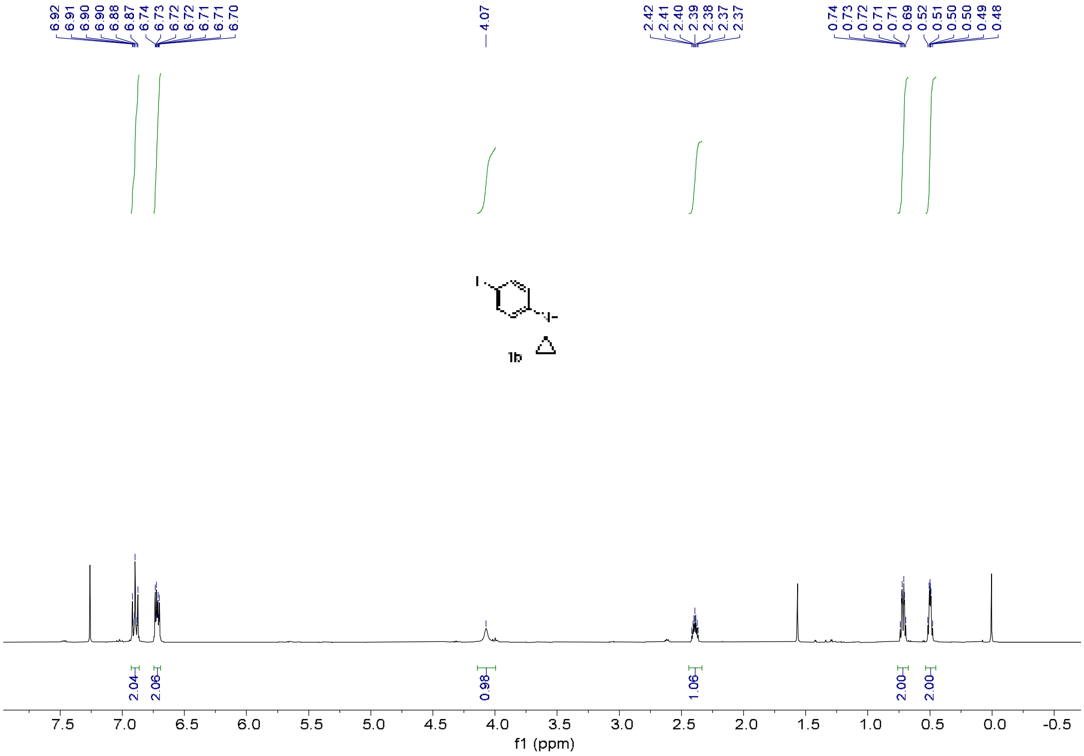
^{1}H NMR (400 MHz, CDCl$_3$) of **1a**



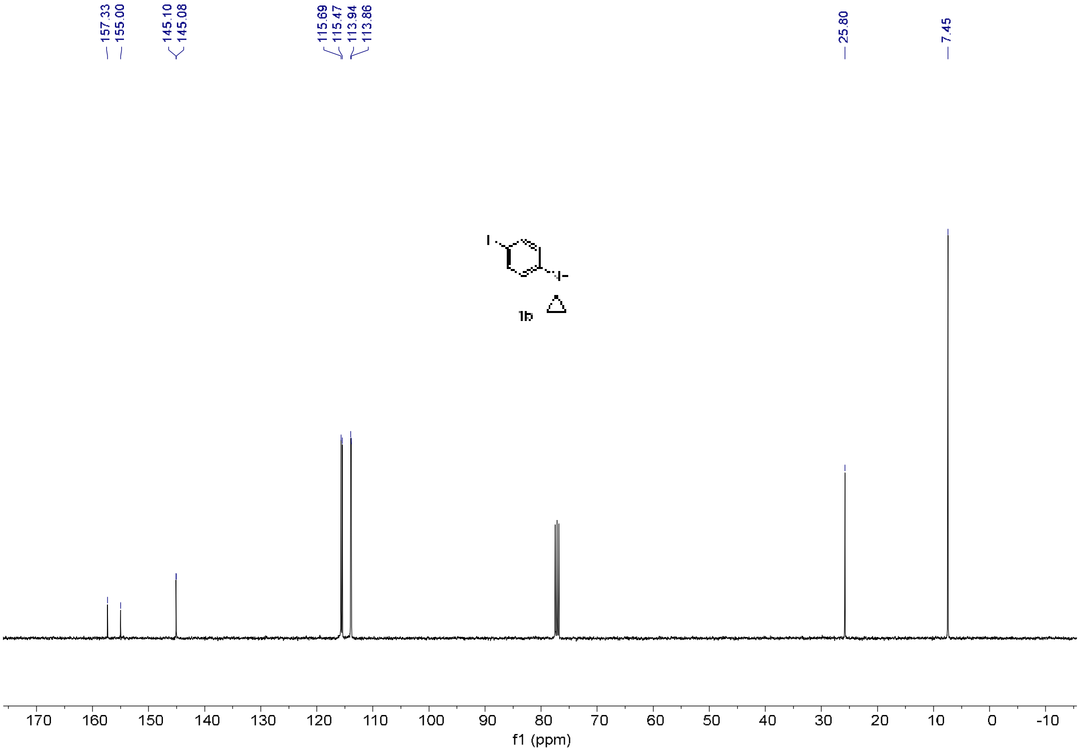
^{13}C NMR (101 MHz, CDCl$_3$) of **1a**



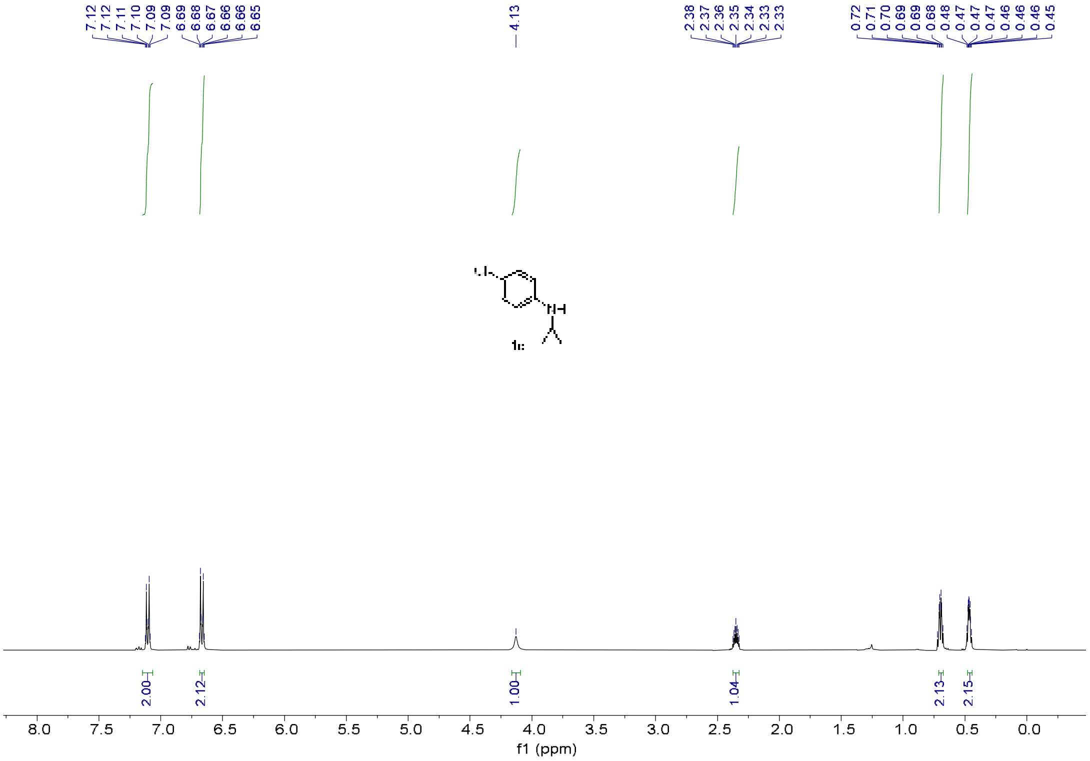
^{1}H NMR (400 MHz, CDCl$_3$) of **1b**



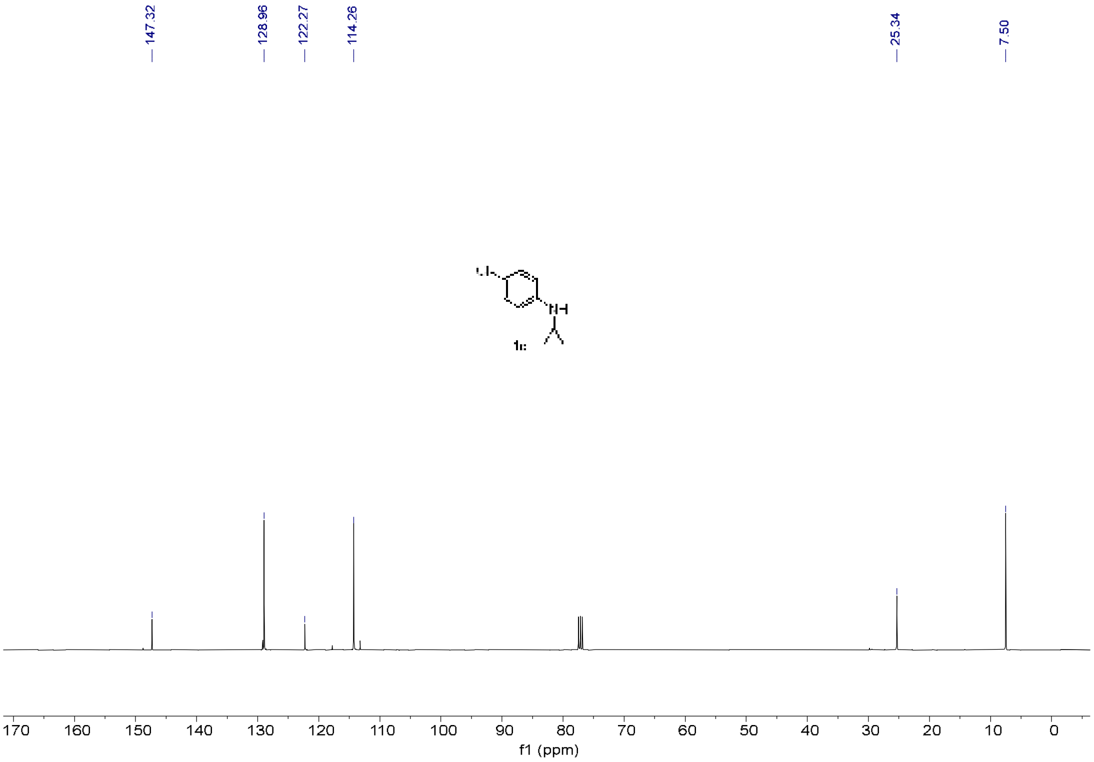
^{13}C NMR (101 MHz, CDCl$_3$) of **1b**



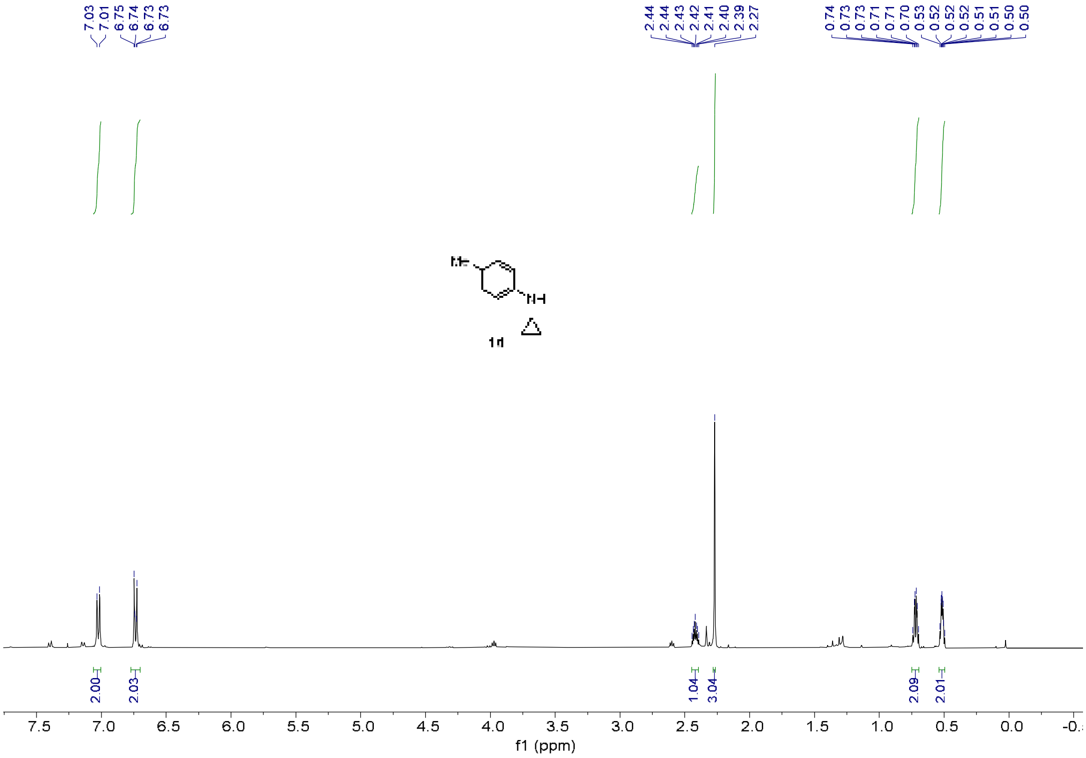
^{1}H NMR (400 MHz, CDCl$_3$) of **1c**



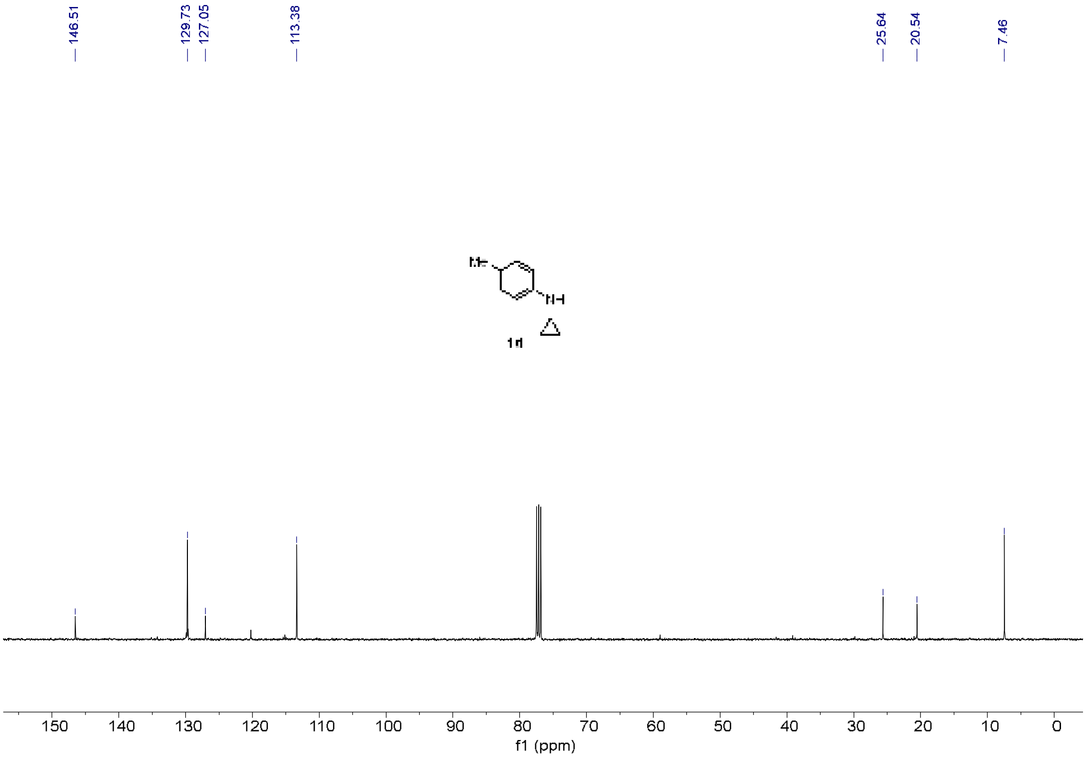
^{13}C NMR (101 MHz, CDCl$_3$) of **1c**



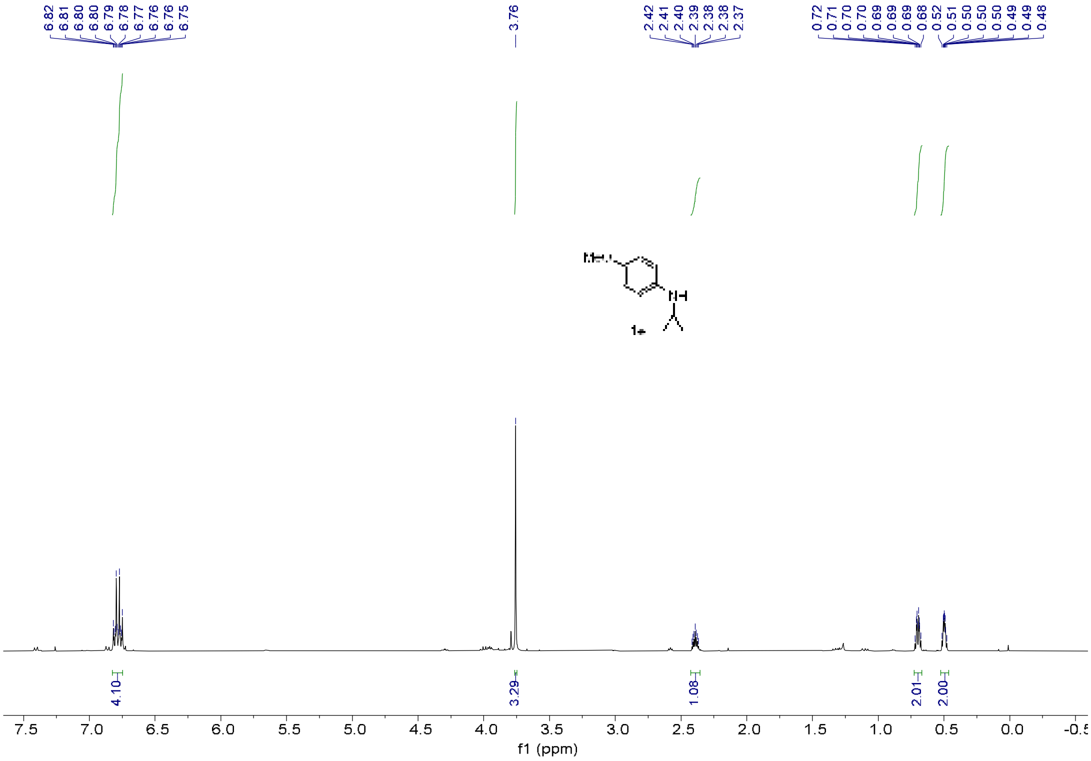
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



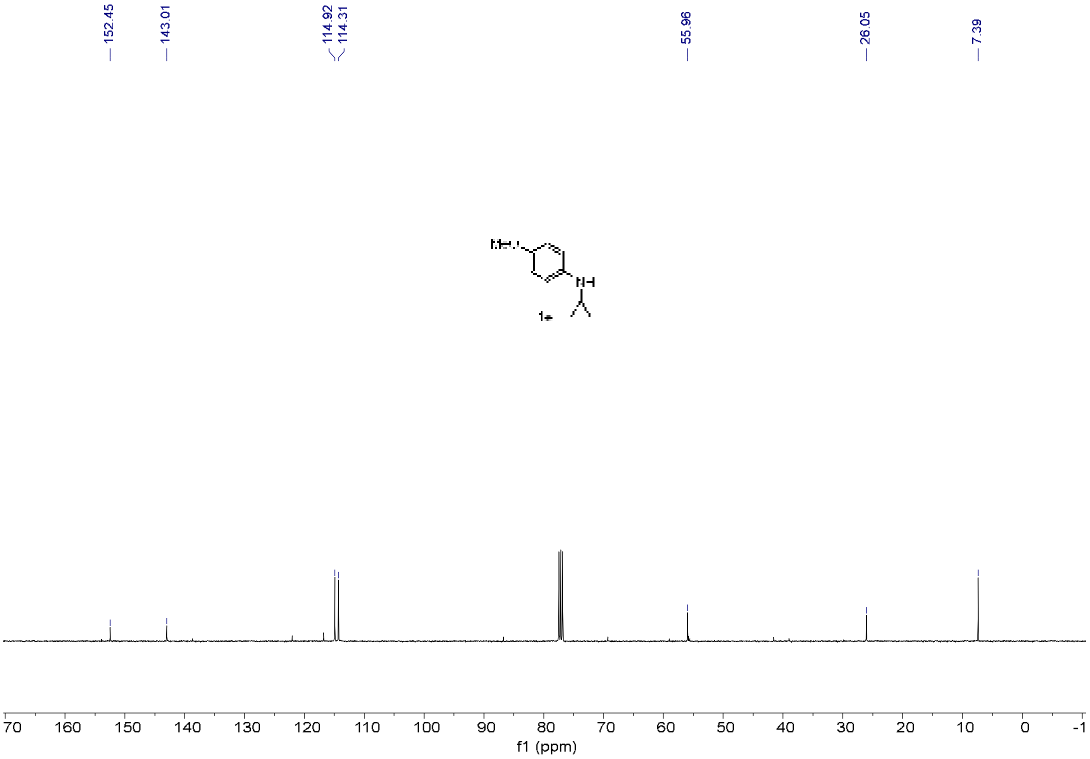
^{13}C NMR (101 MHz, $CDCl_3$) of **1d**



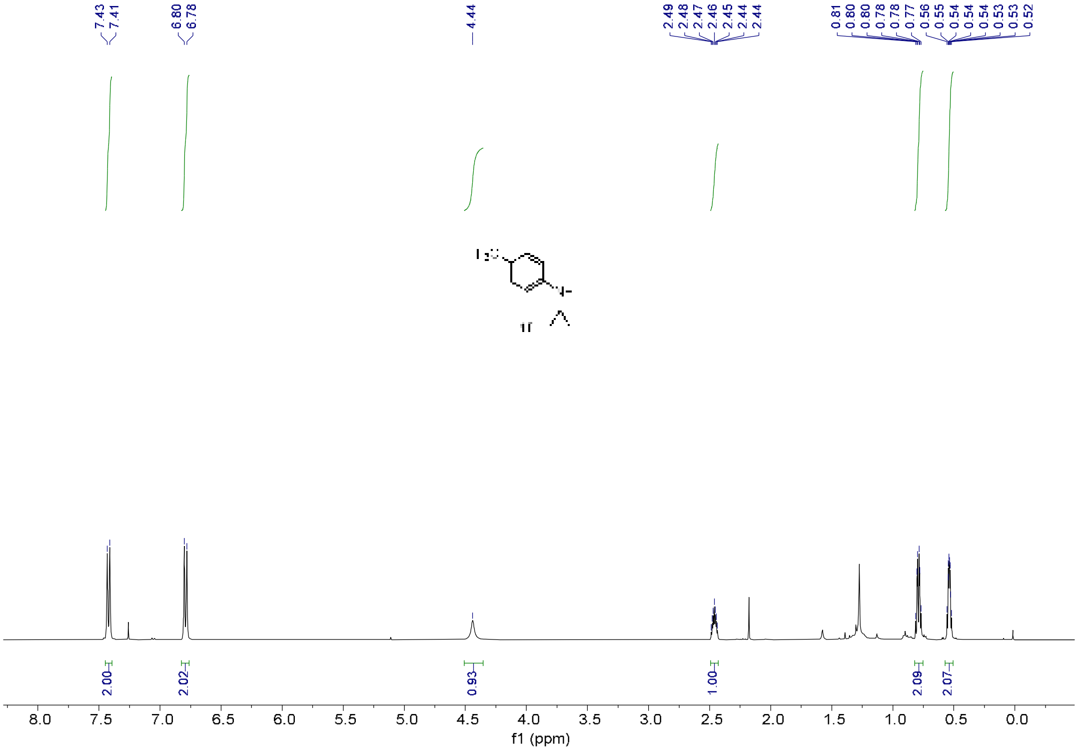
^{1}H NMR (400 MHz, CDCl$_3$) of **1e**



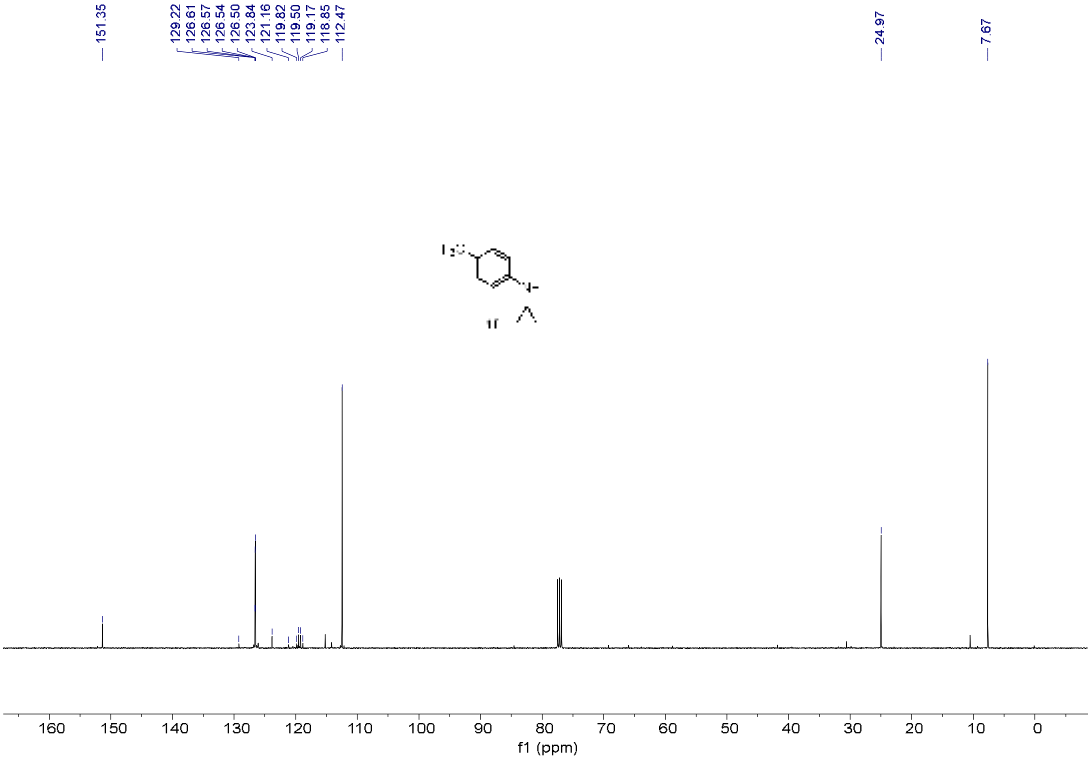
^{13}C NMR (101 MHz, CDCl$_3$) of **1e**



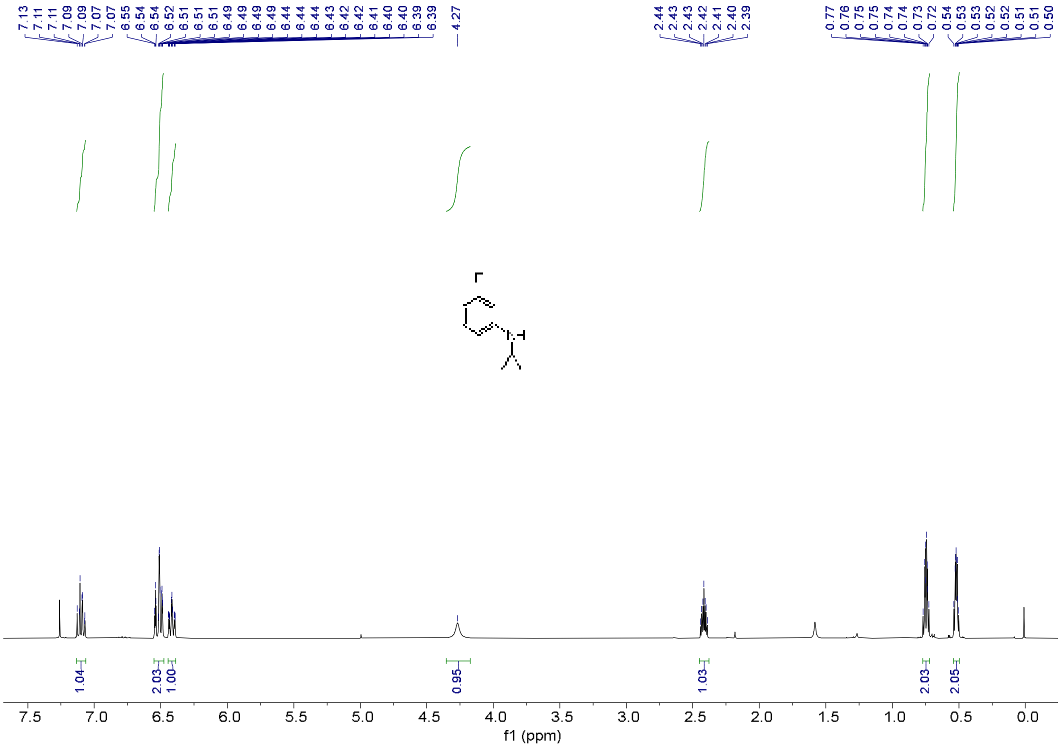
^{1}H NMR (400 MHz, CDCl$_3$) of **1f**



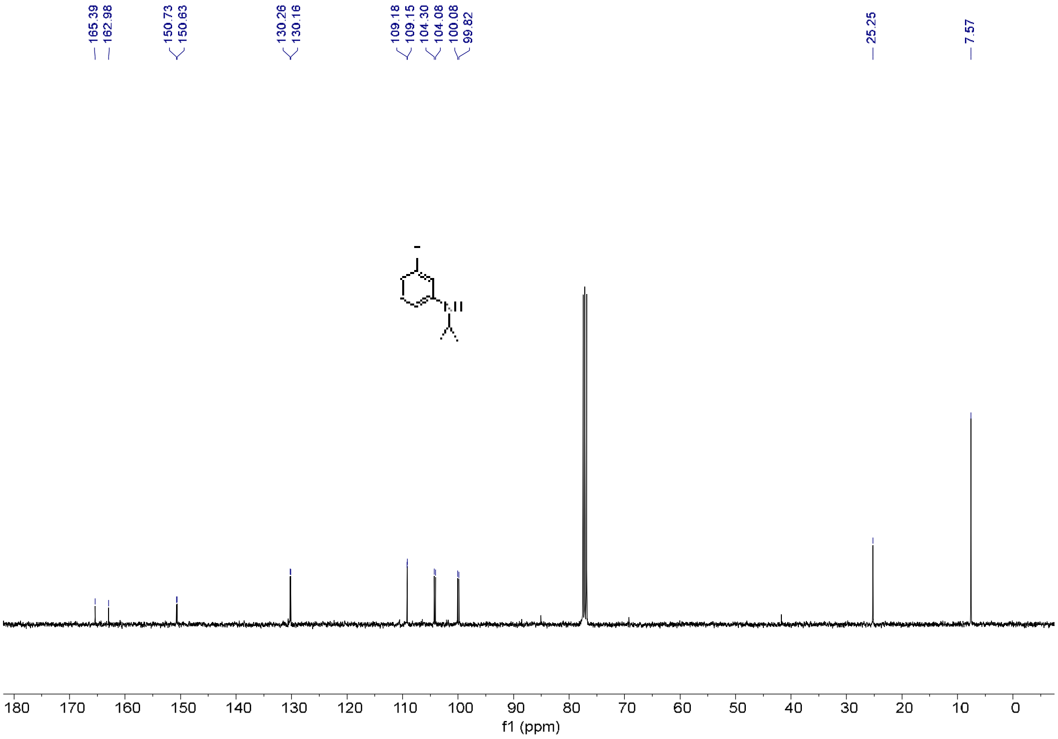
^{13}C NMR (101 MHz, CDCl$_3$) of **1f**



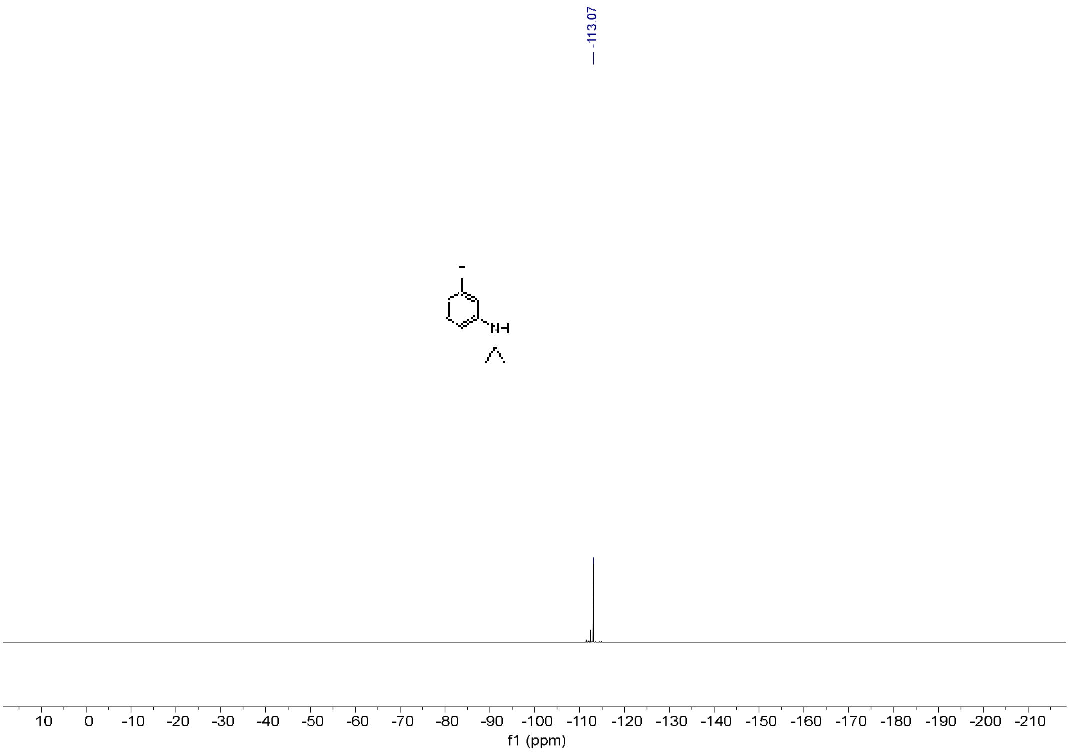
^{1}H NMR (400 MHz, CDCl$_3$) of **1g**



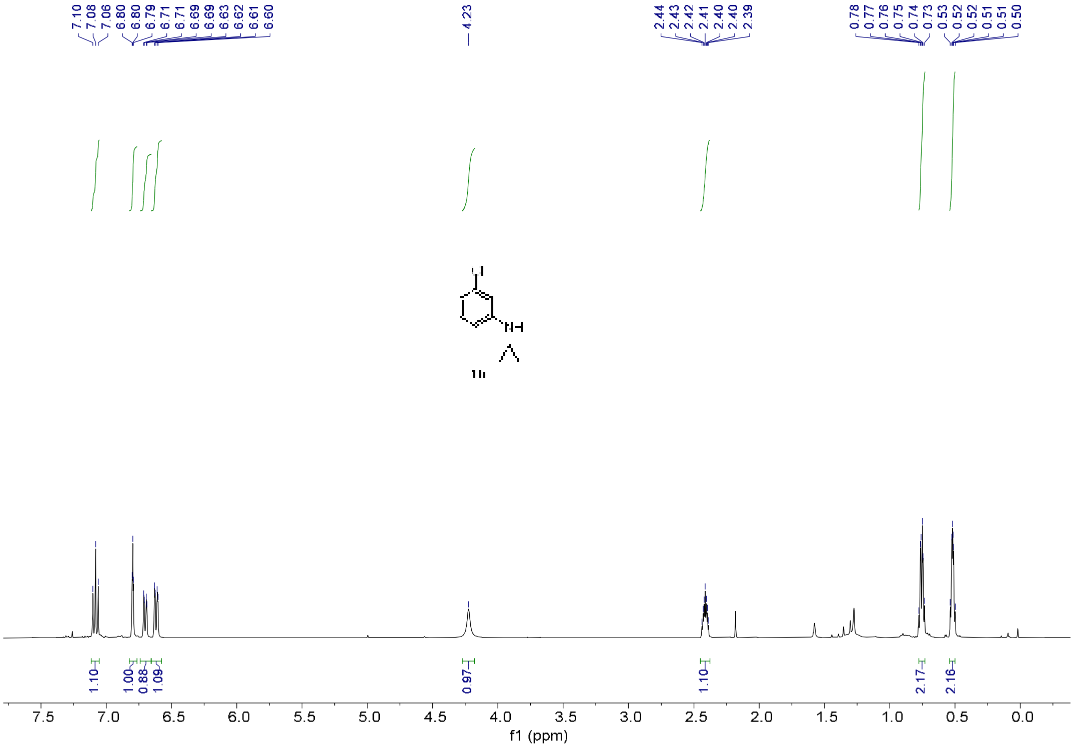
^{13}C NMR (101 MHz, CDCl$_3$) of **1g**



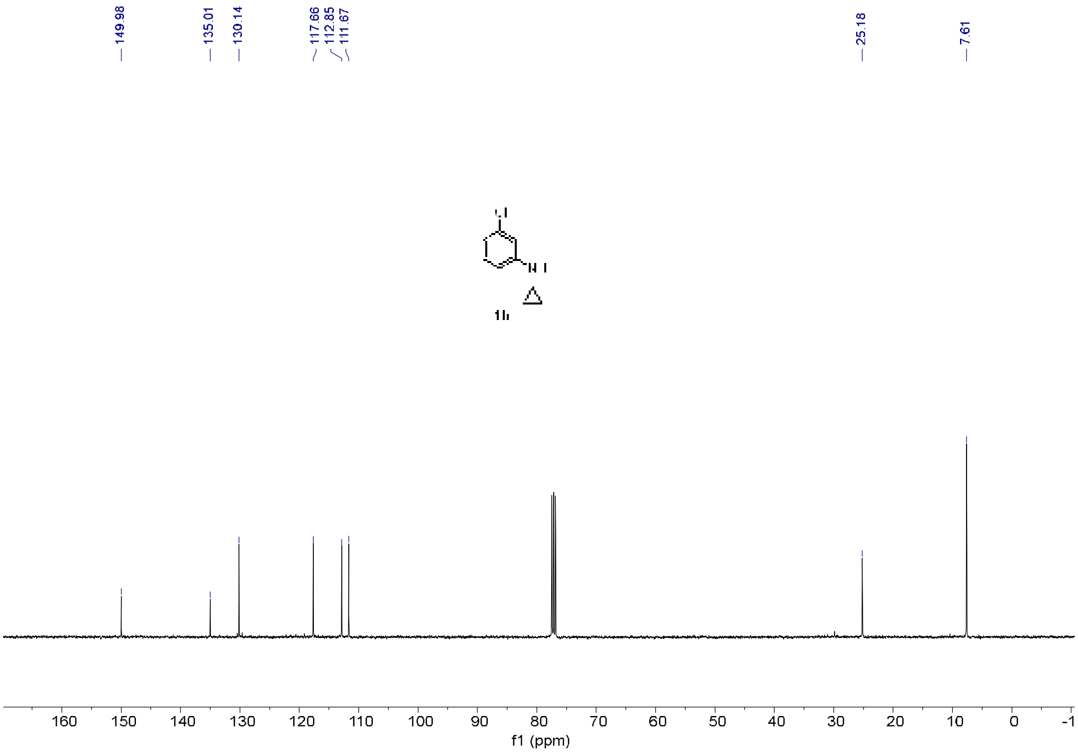
^{19}F NMR (376 MHz, CDCl$_3$) of **1g**



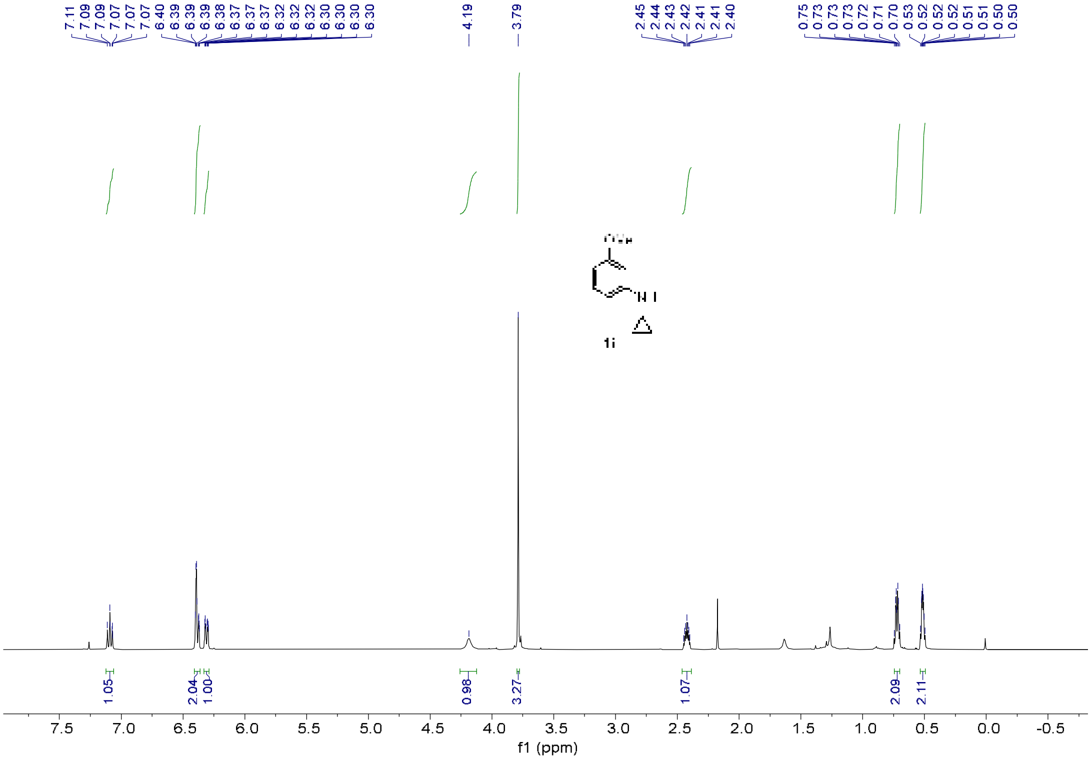
^{1}H NMR (400 MHz, CDCl$_3$) of **1h**



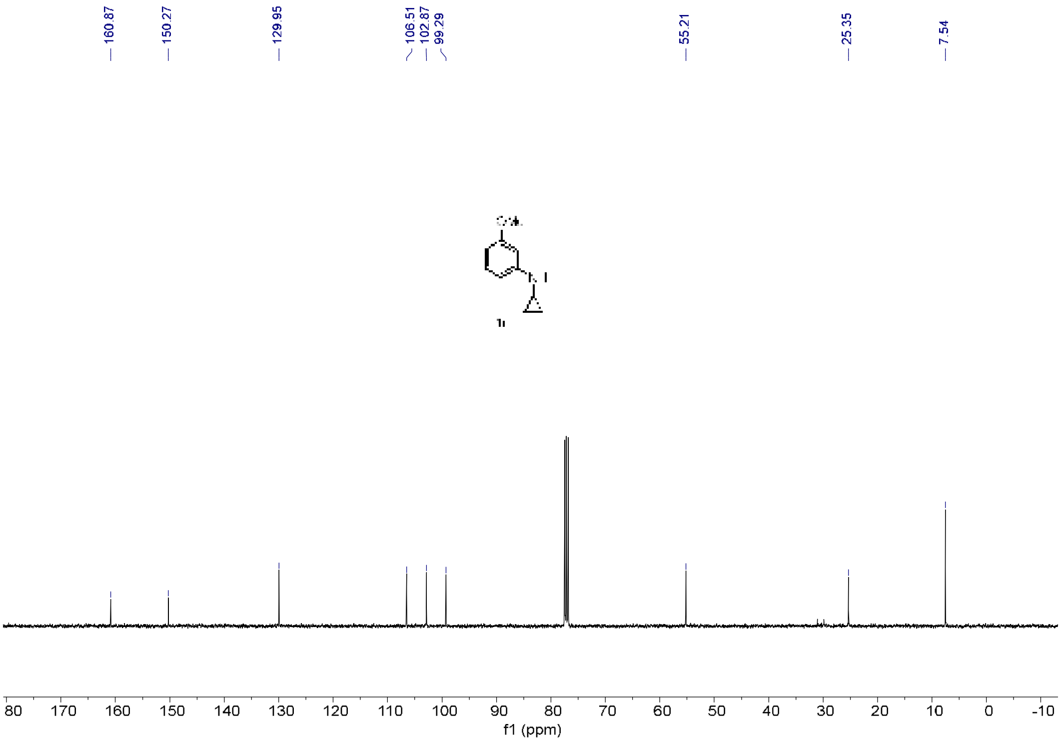
^{13}C NMR (101 MHz, CDCl$_3$) of **1h**



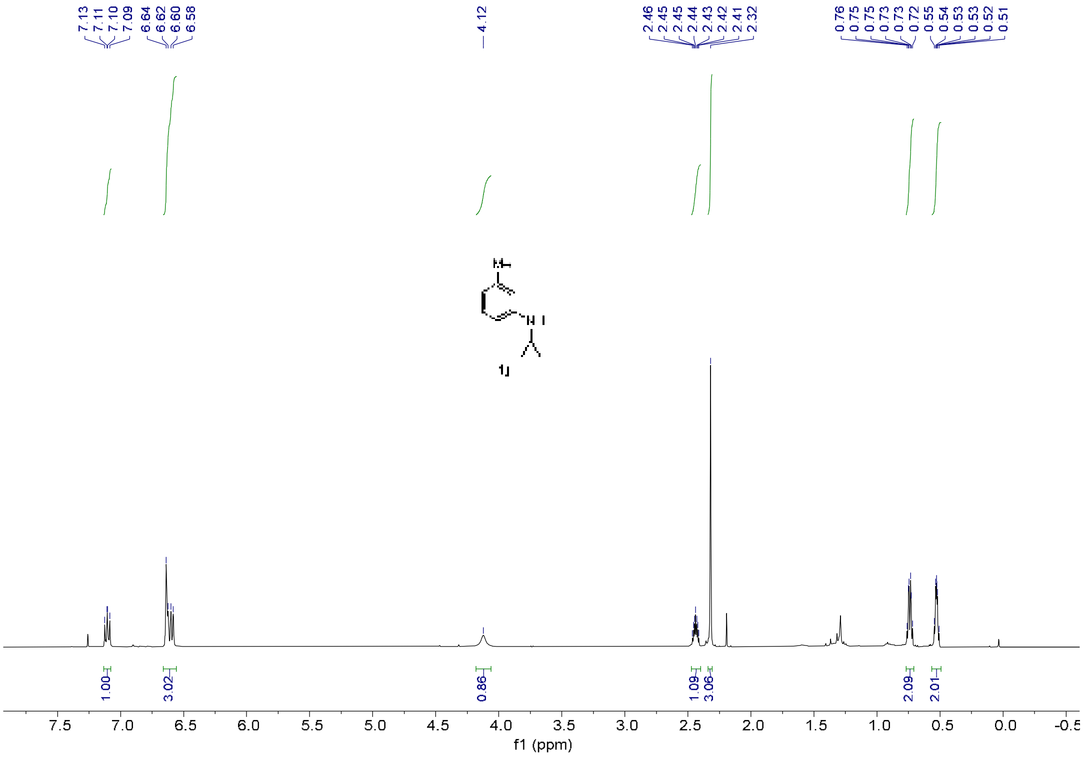
^{1}H NMR (400 MHz, CDCl$_3$) of **1i**



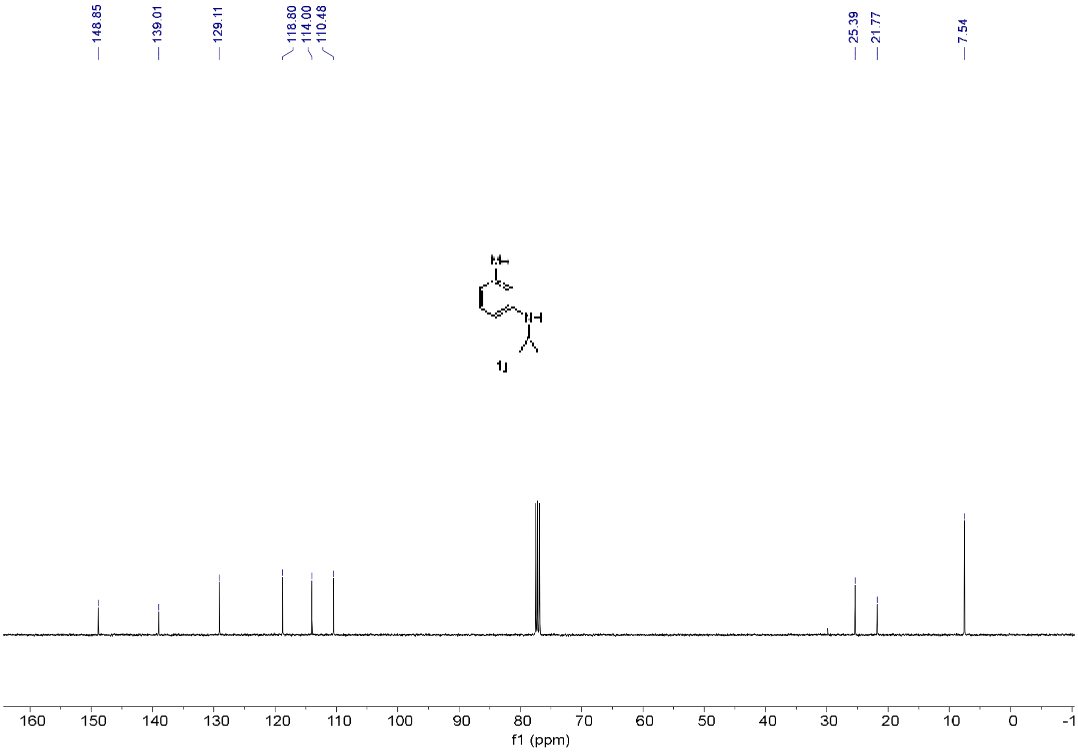
^{13}C NMR (101 MHz, CDCl$_3$) of **1i**



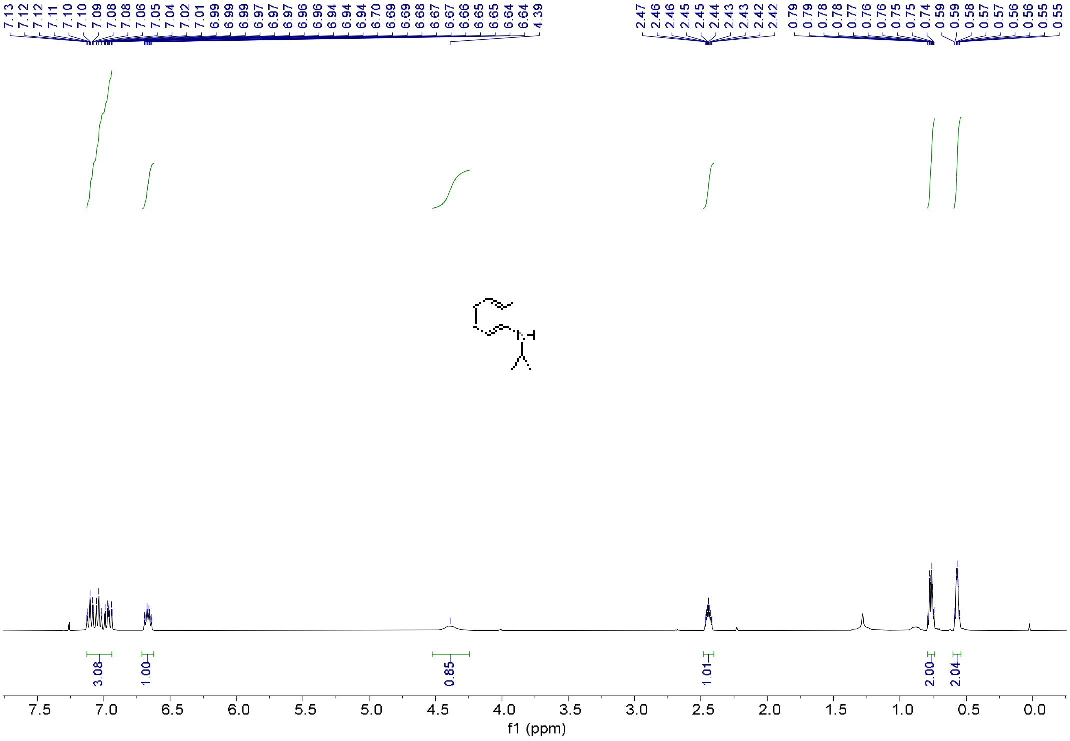
^{1}H NMR (400 MHz, CDCl$_3$) of **1j**



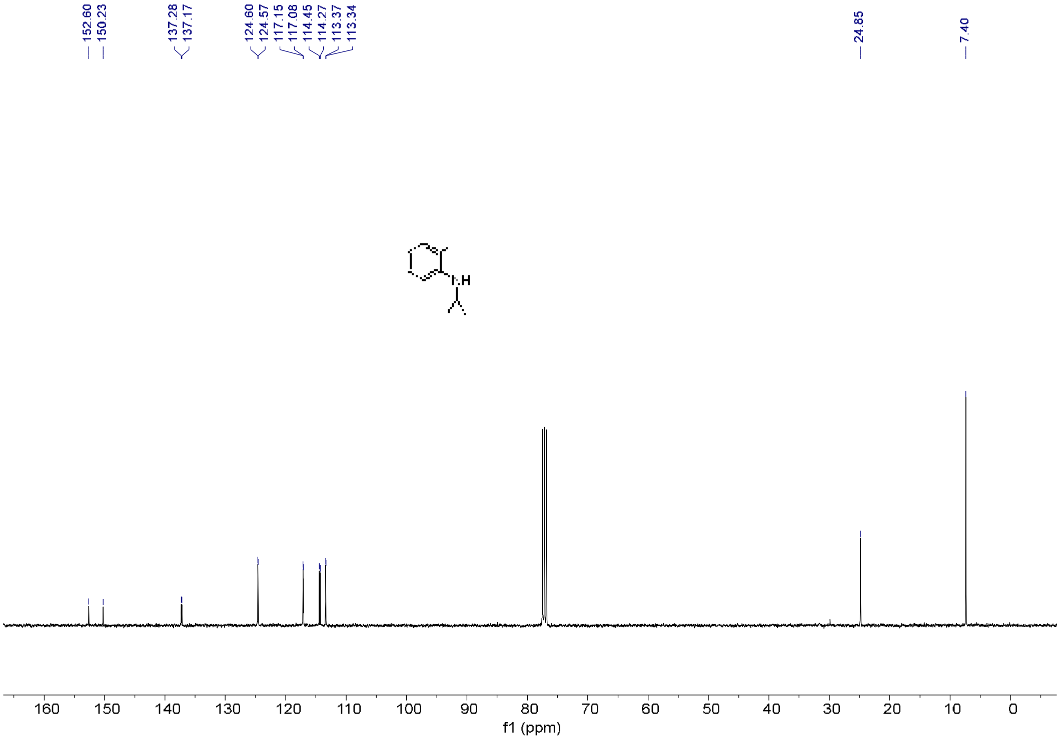
^{13}C NMR (101 MHz, CDCl$_3$) of **1j**



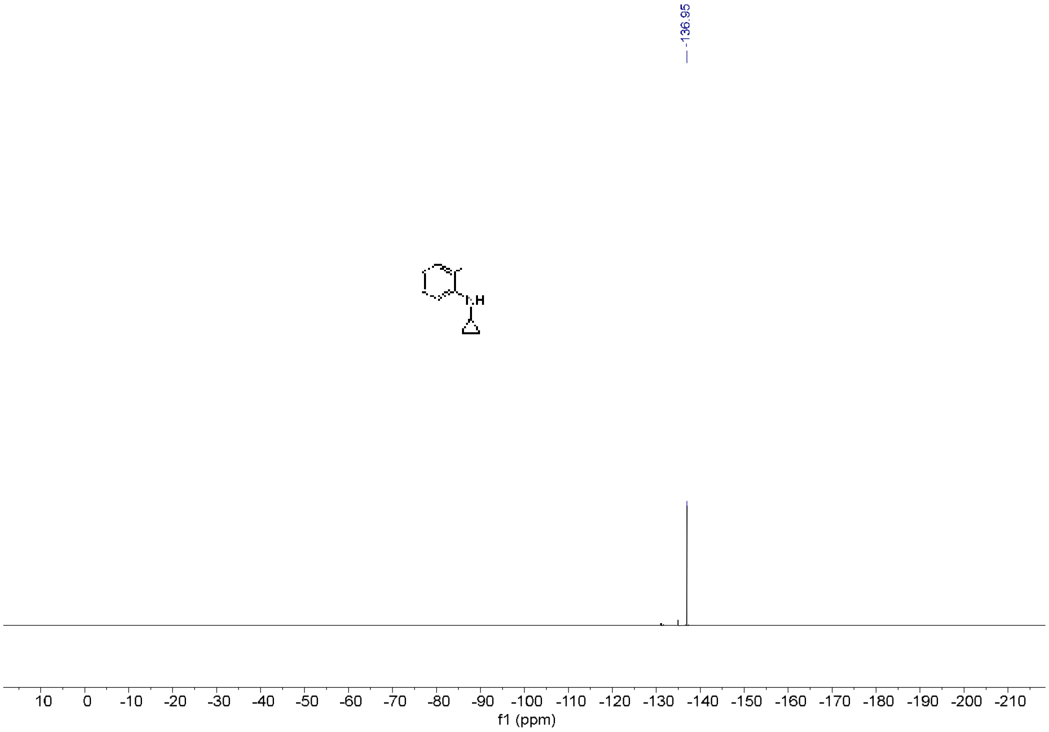
^{1}H NMR (400 MHz, CDCl$_3$) of **1k**



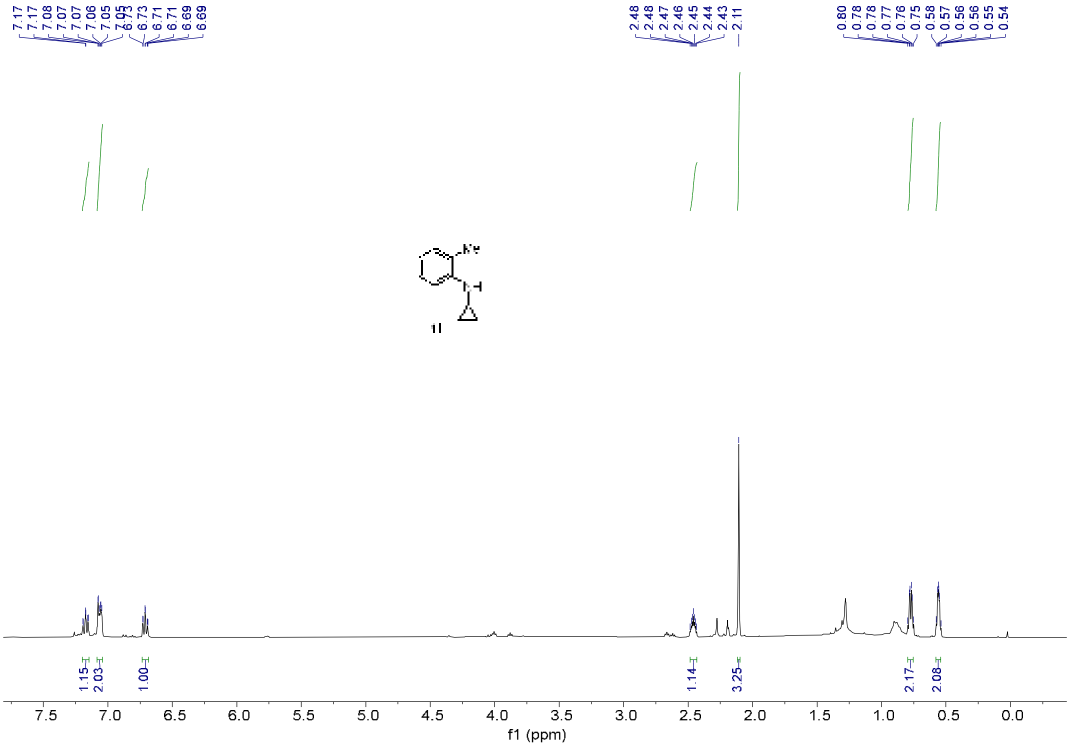
^{13}C NMR (101 MHz, CDCl$_3$) of **1k**



^{19}F NMR (376 MHz, CDCl$_3$) of **1k**



^{1}H NMR (400 MHz, CDCl$_3$) of **1l**



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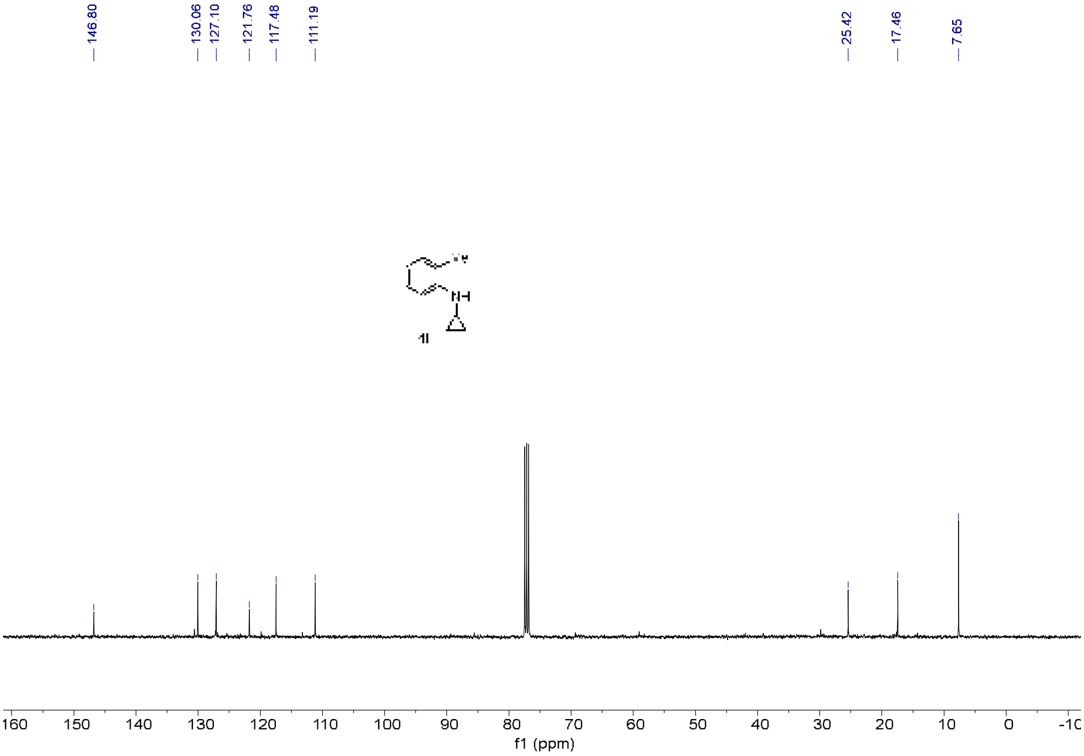
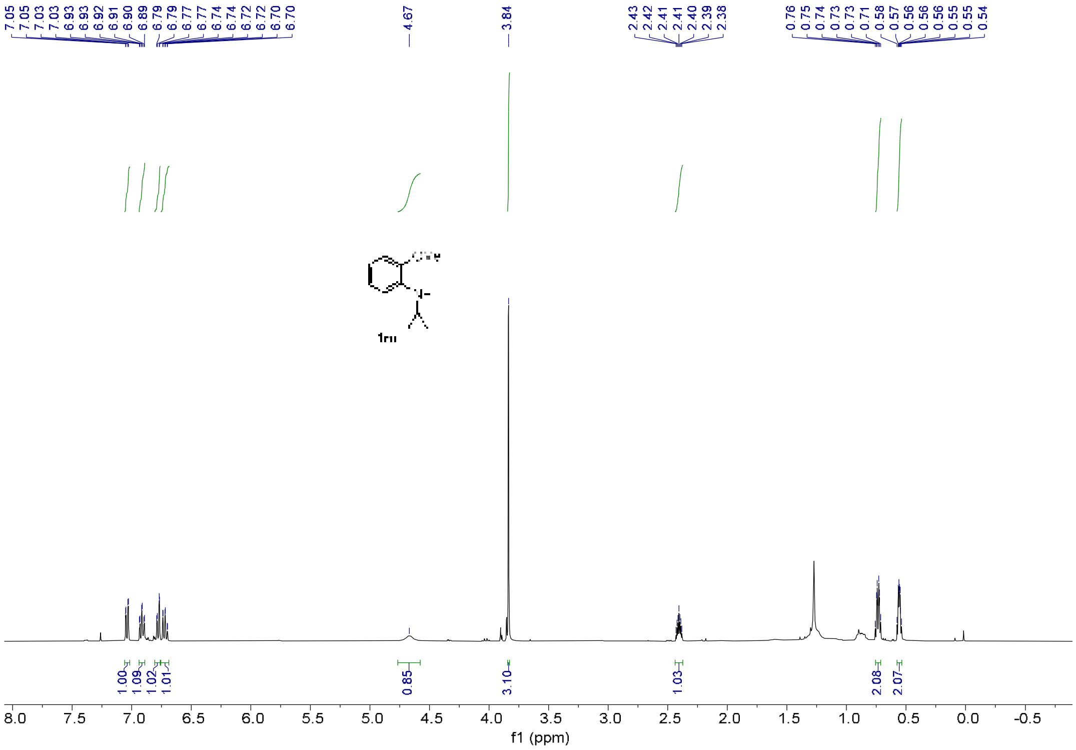
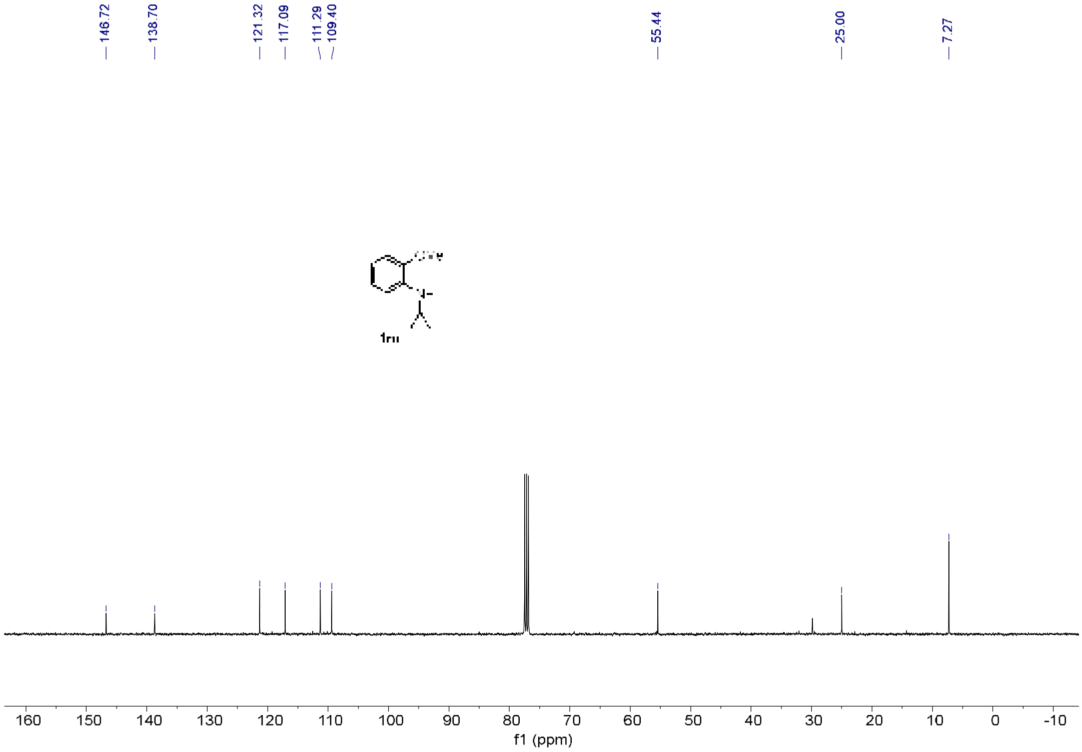


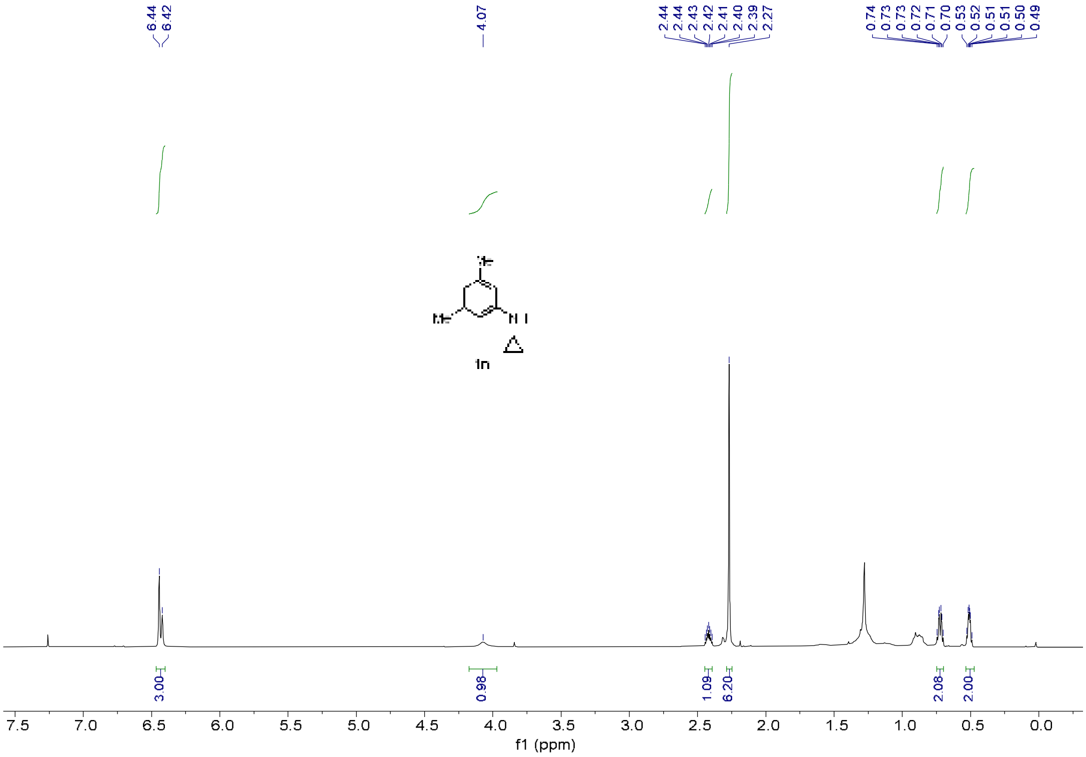
^{1}H NMR (400 MHz, CDCl$_3$) of **1m**



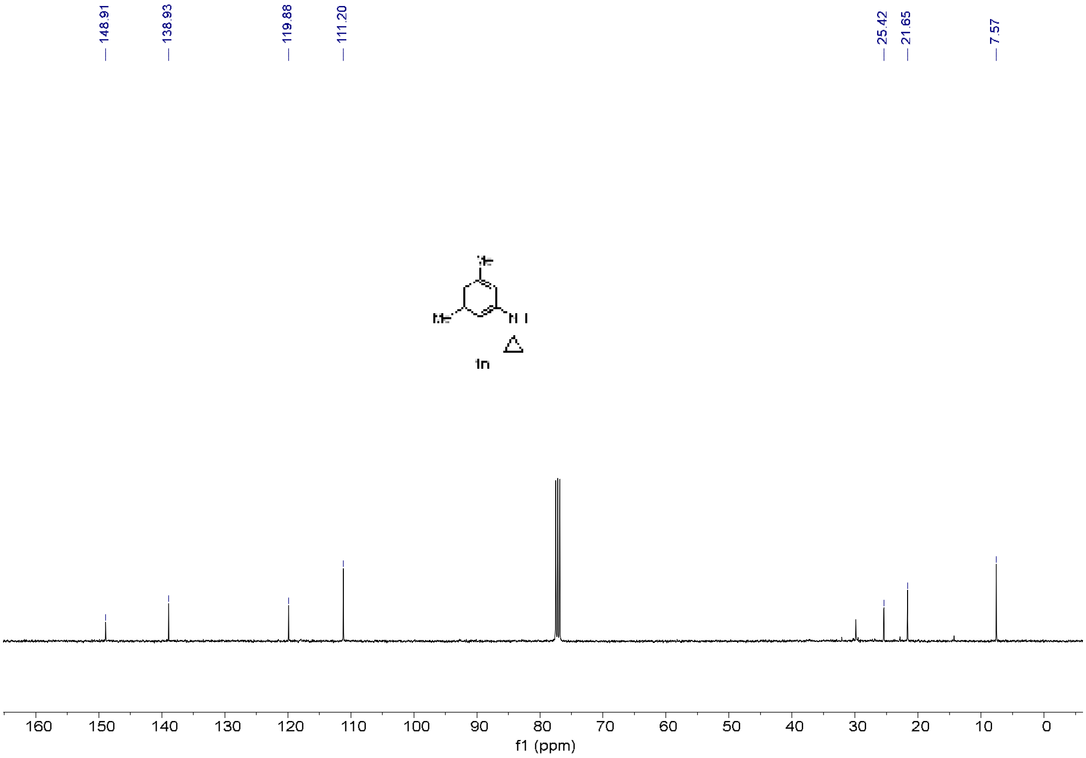
^{13}C NMR (101 MHz, CDCl$_3$) of **1m**



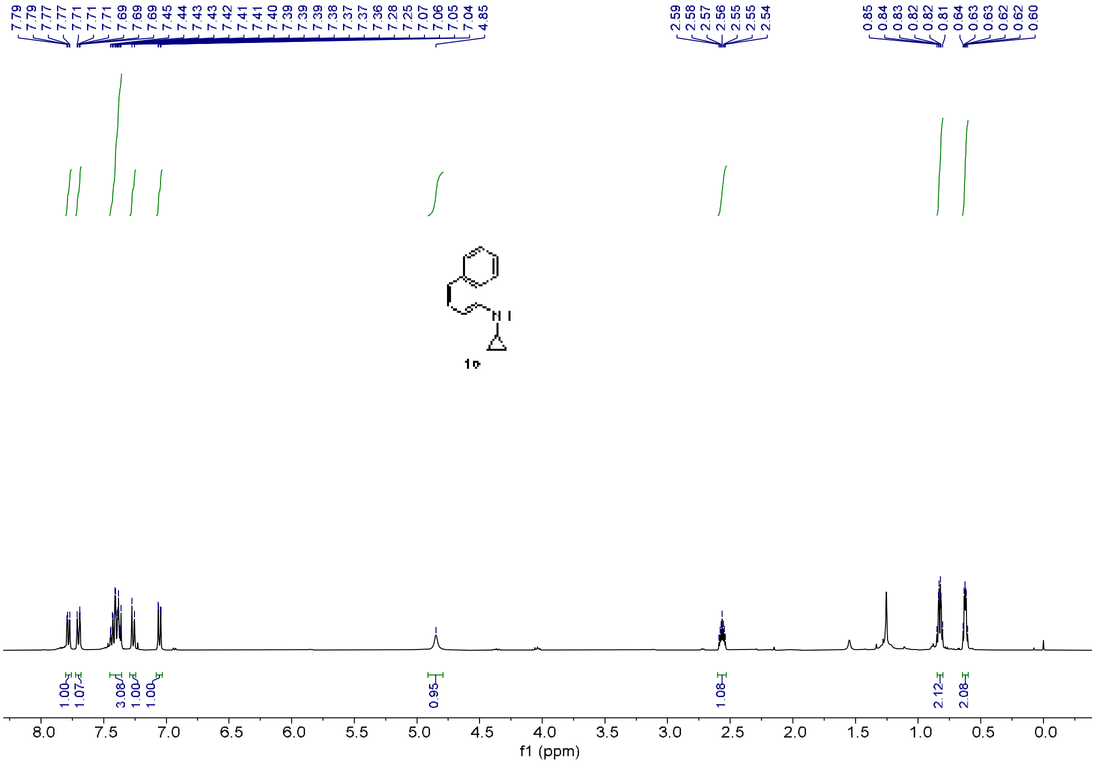
^{1}H NMR (400 MHz, CDCl$_3$) of **1n**



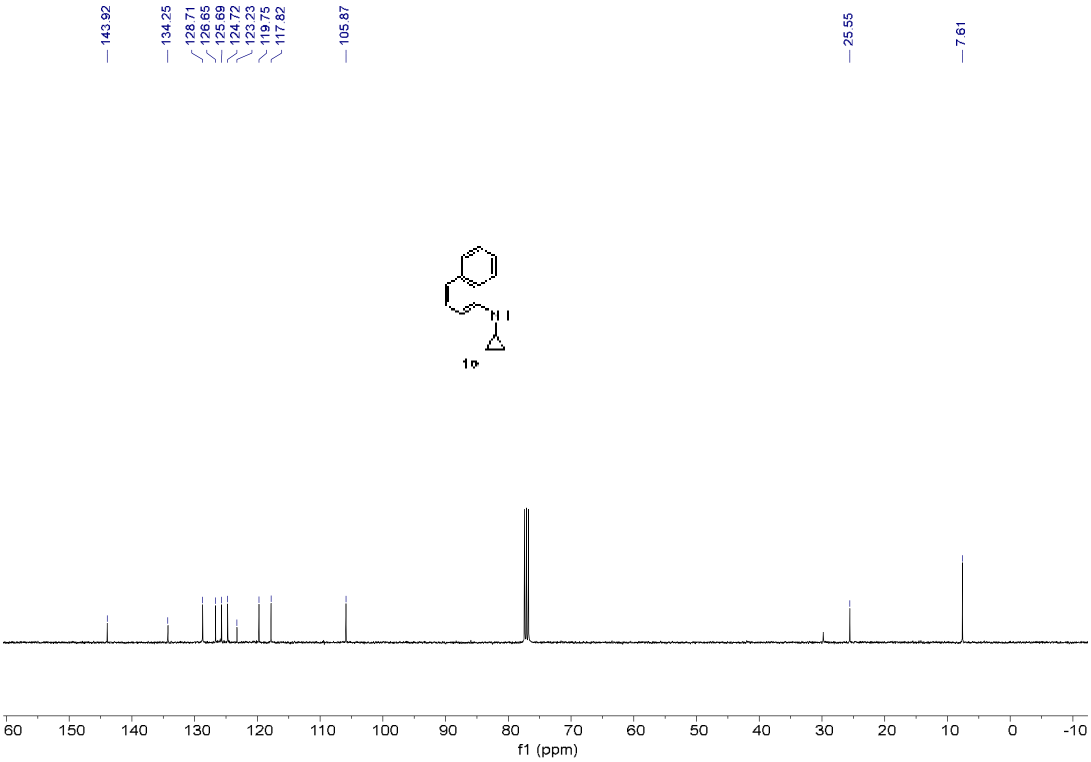
^{13}C NMR (101 MHz, CDCl$_3$) of **1n**



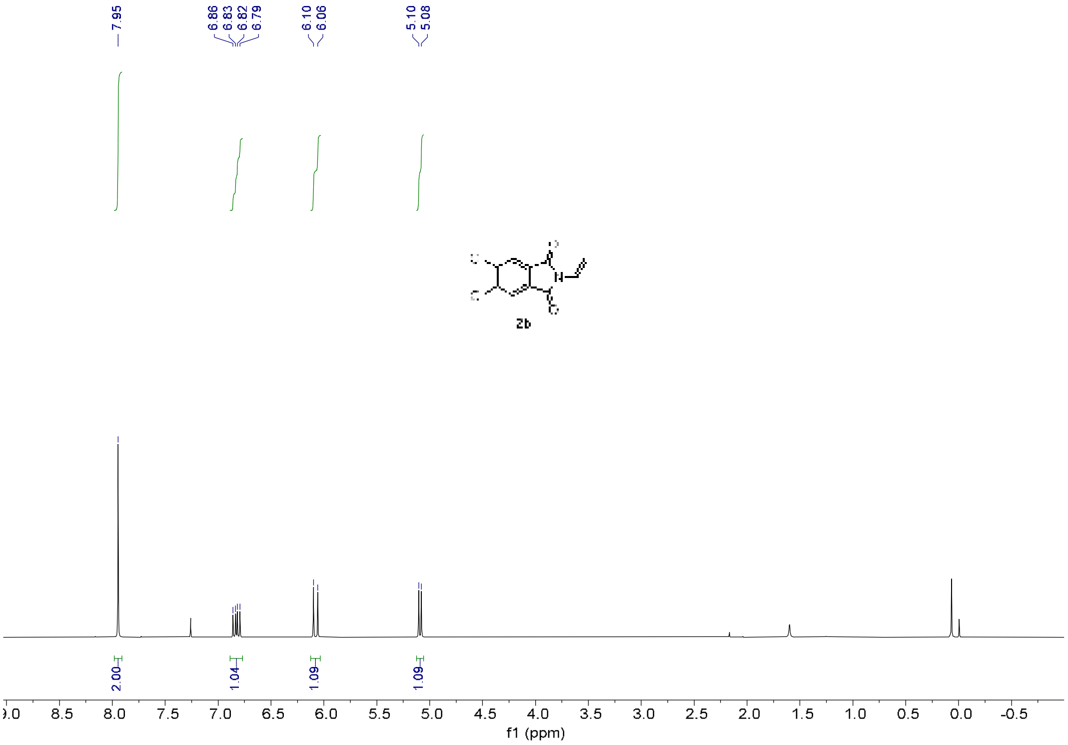
^{1}H NMR (400 MHz, $CDCl_3$) of **1o**



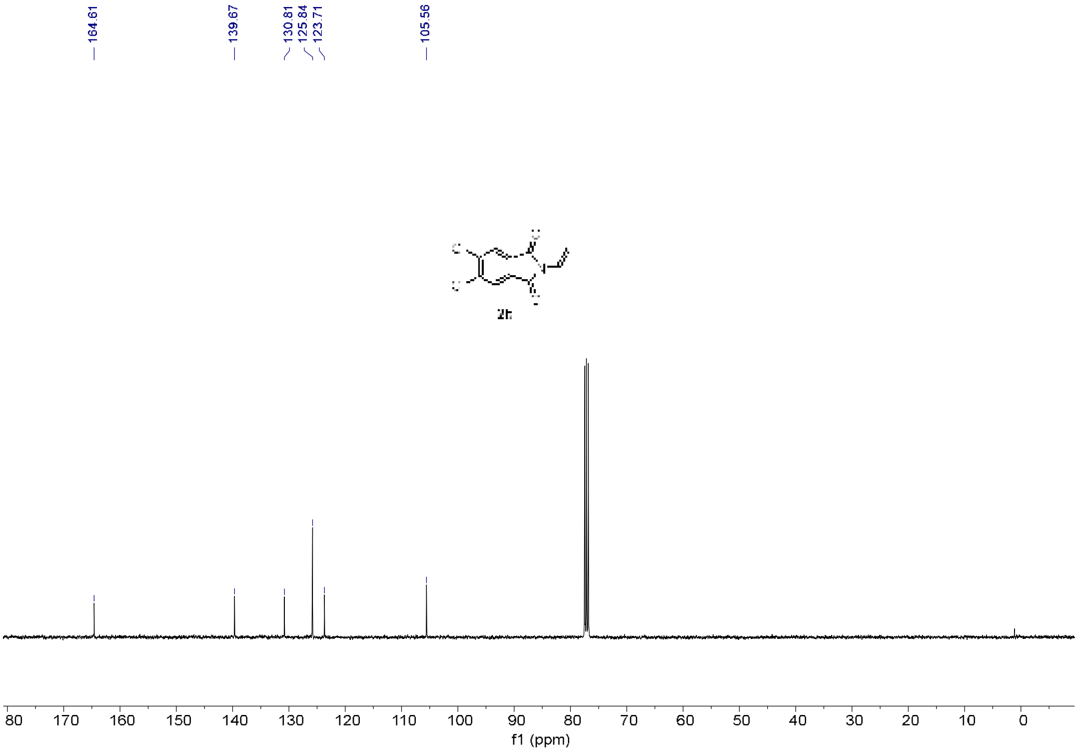
^{13}C NMR (101 MHz, $CDCl_3$) of **1o**



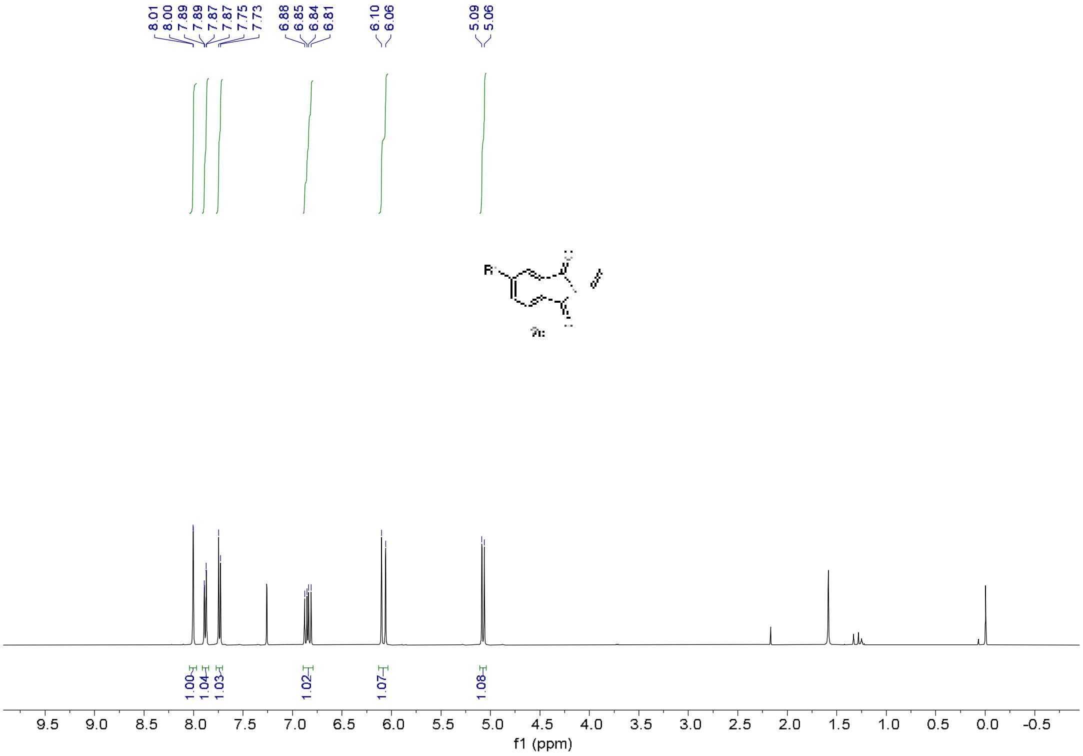
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



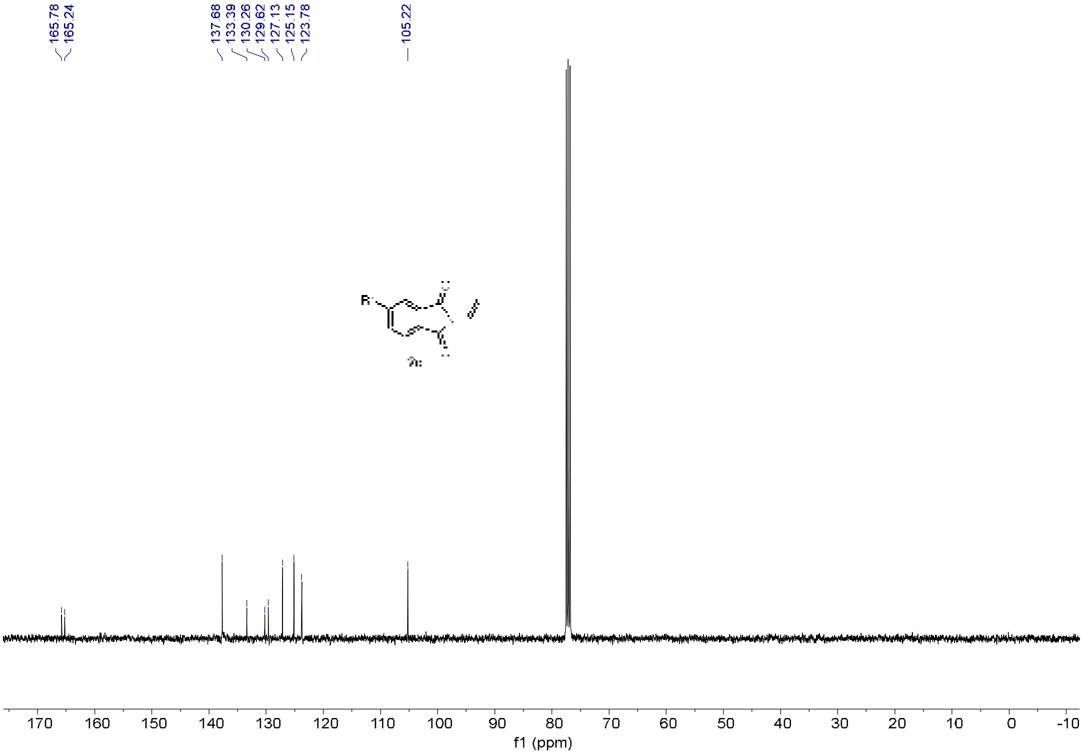
^{13}C NMR (101 MHz, $CDCl_3$) of **2b**



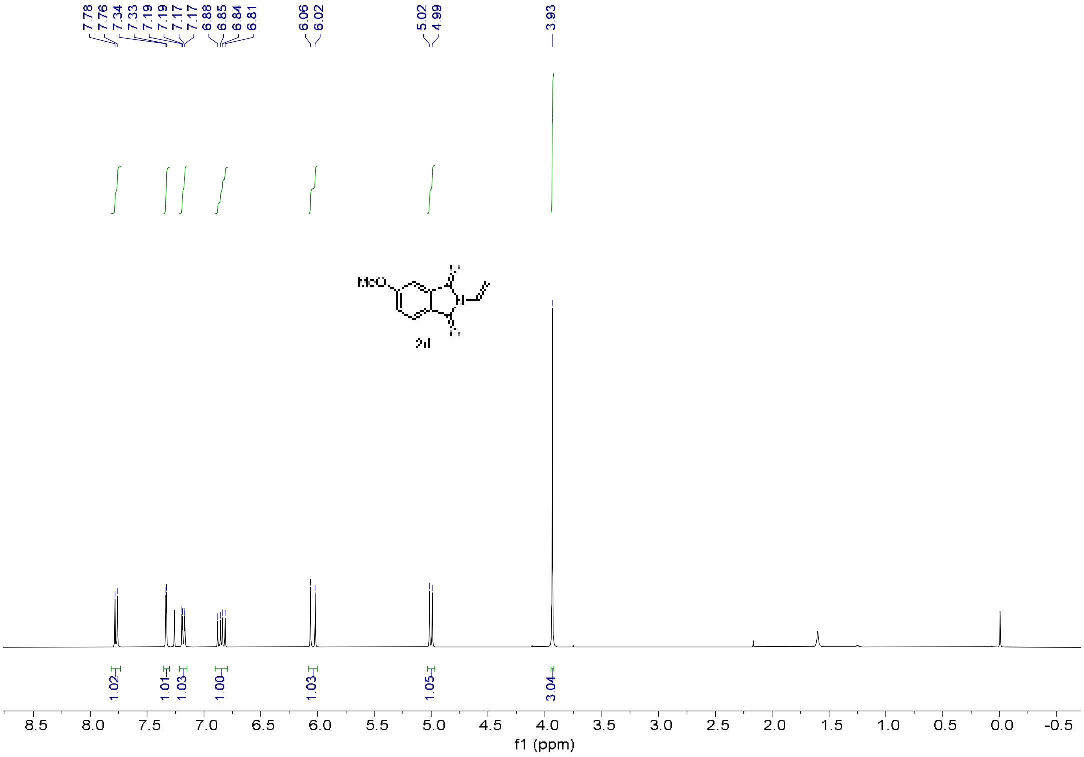
^{1}H NMR (400 MHz, CDCl$_3$) of **2c**



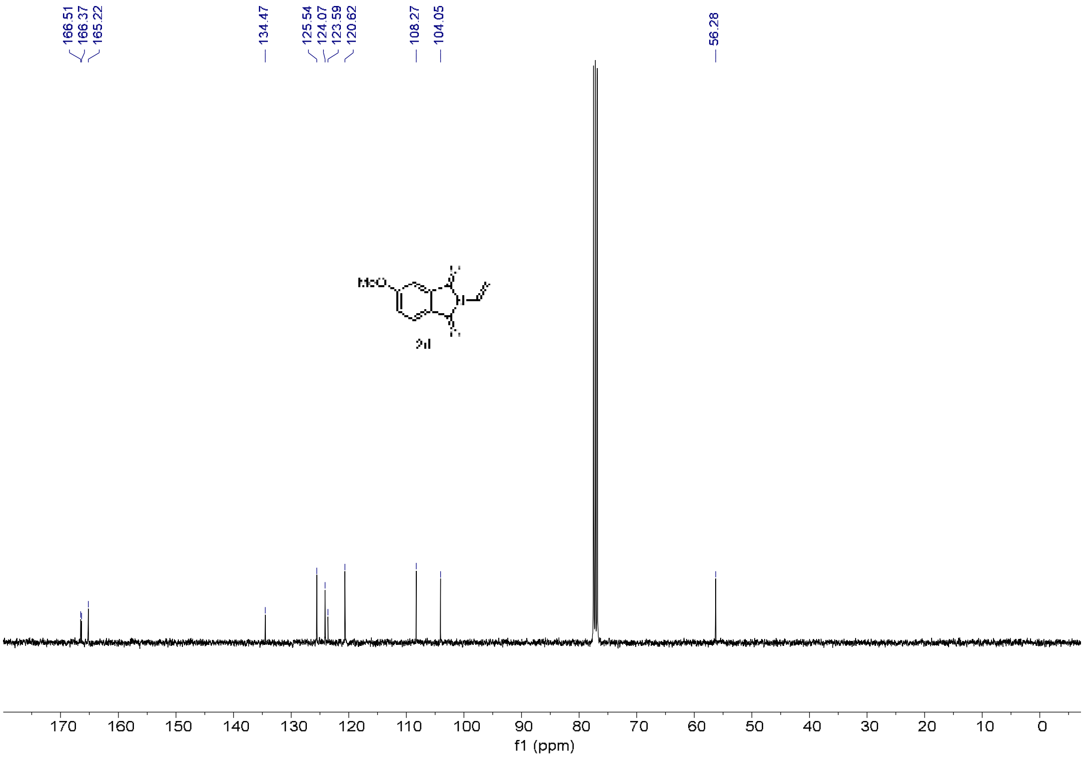
^{13}C NMR (101 MHz, CDCl$_3$) of **2c**



^{1}H NMR (400 MHz, CDCl$_3$) of **2d**



^{13}C NMR (101 MHz, CDCl$_3$) of **2d**



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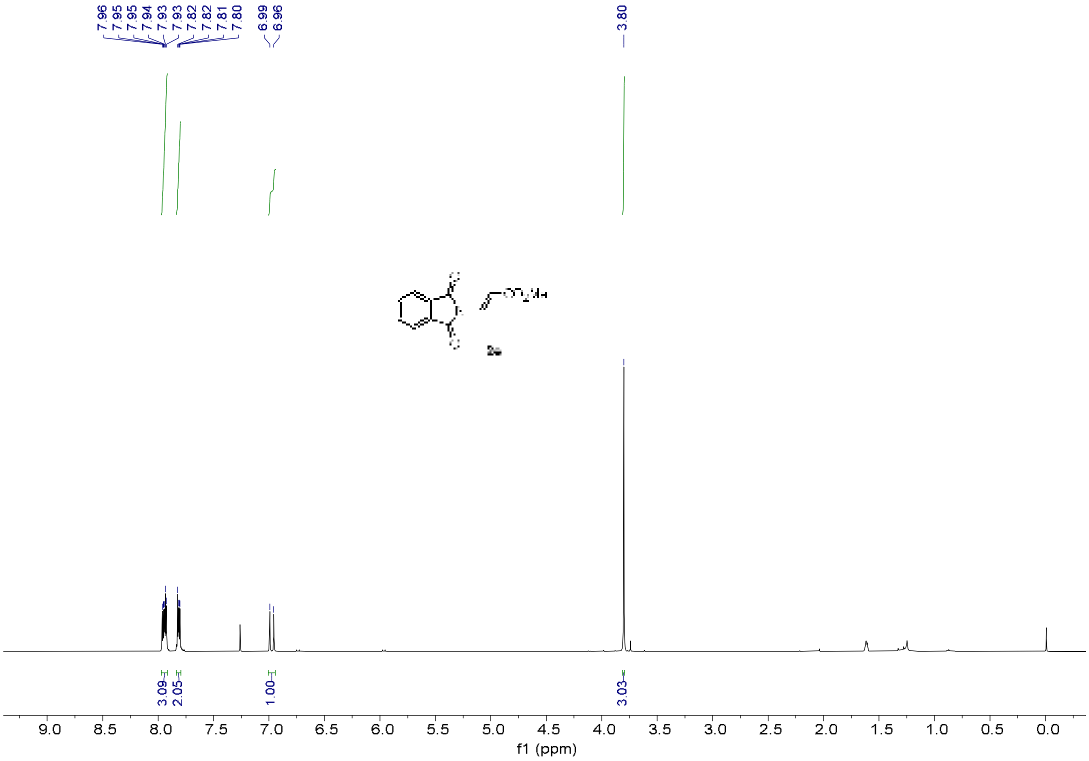
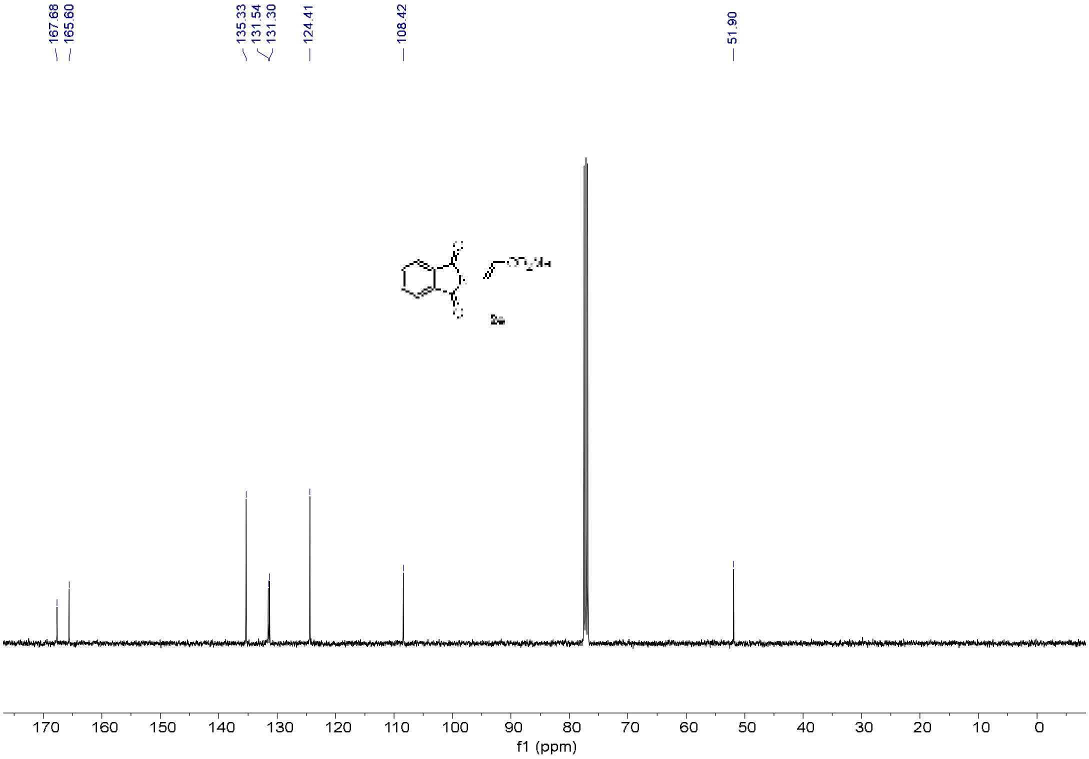
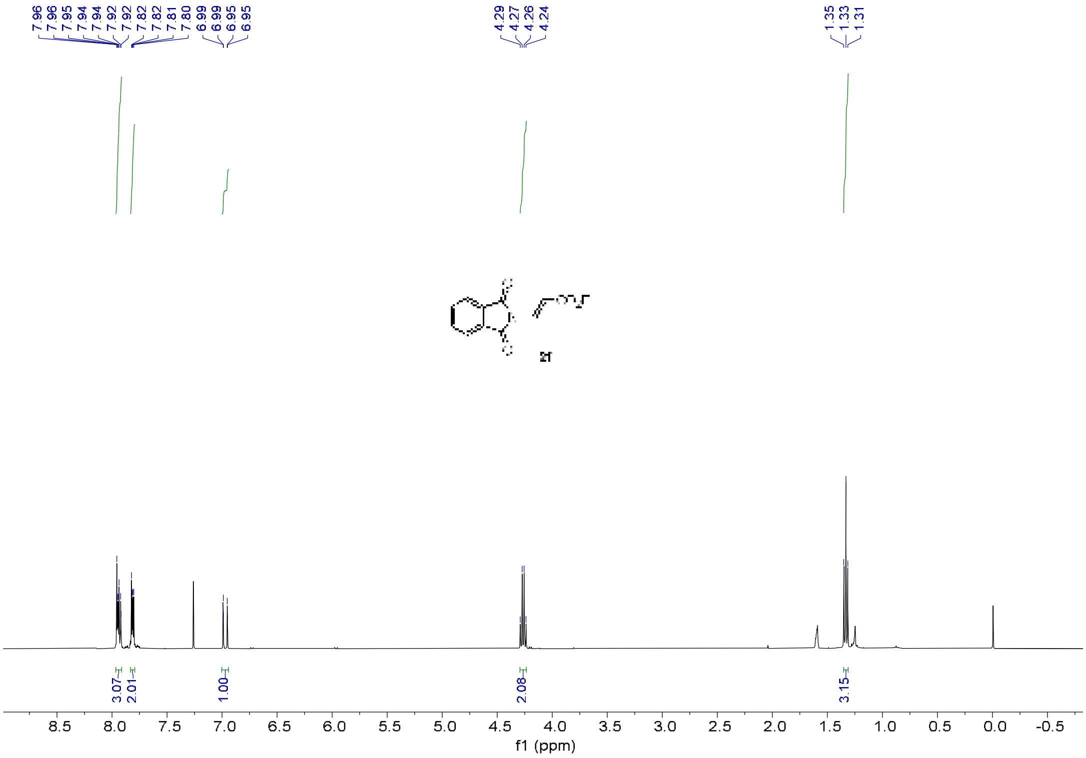


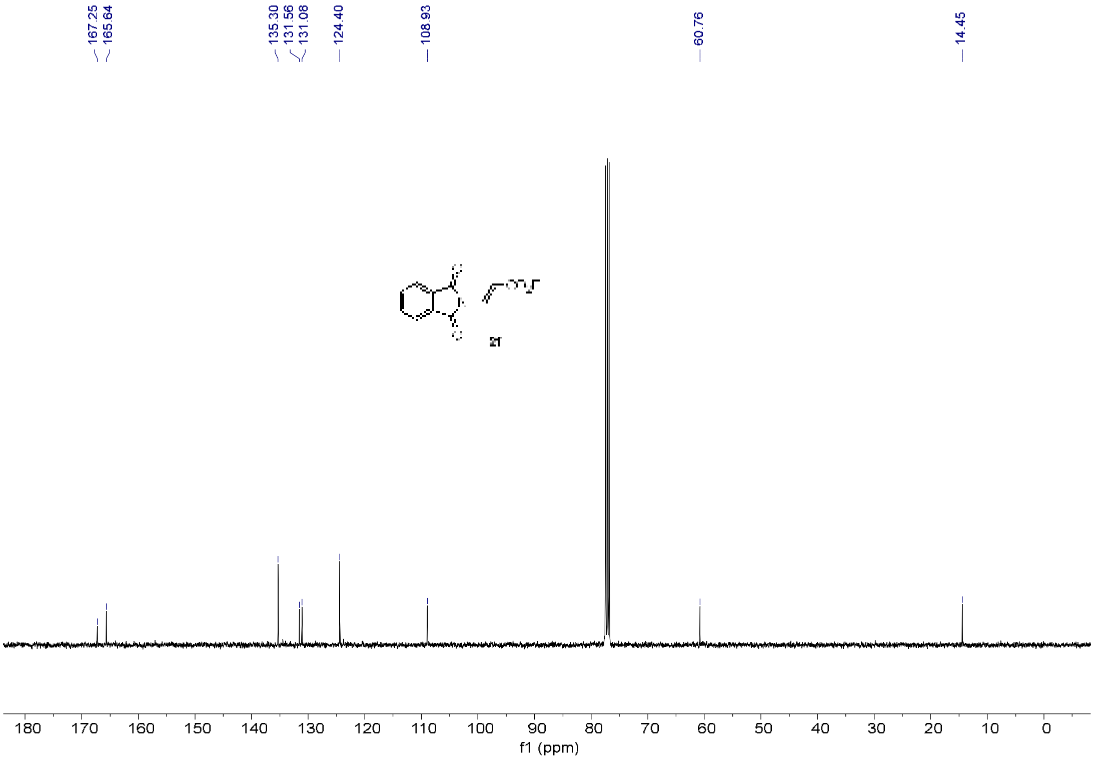
^{13}C NMR (101 MHz, CDCl$_3$) of **2e**



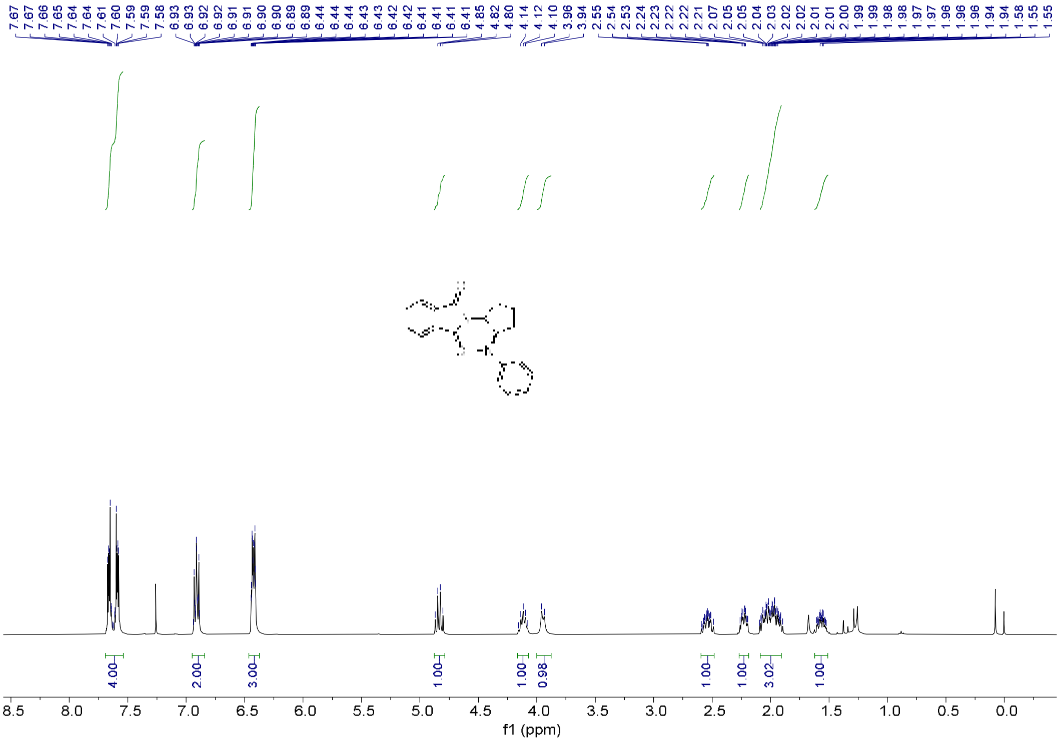
^{1}H NMR (400 MHz, CDCl$_3$) of **2f**



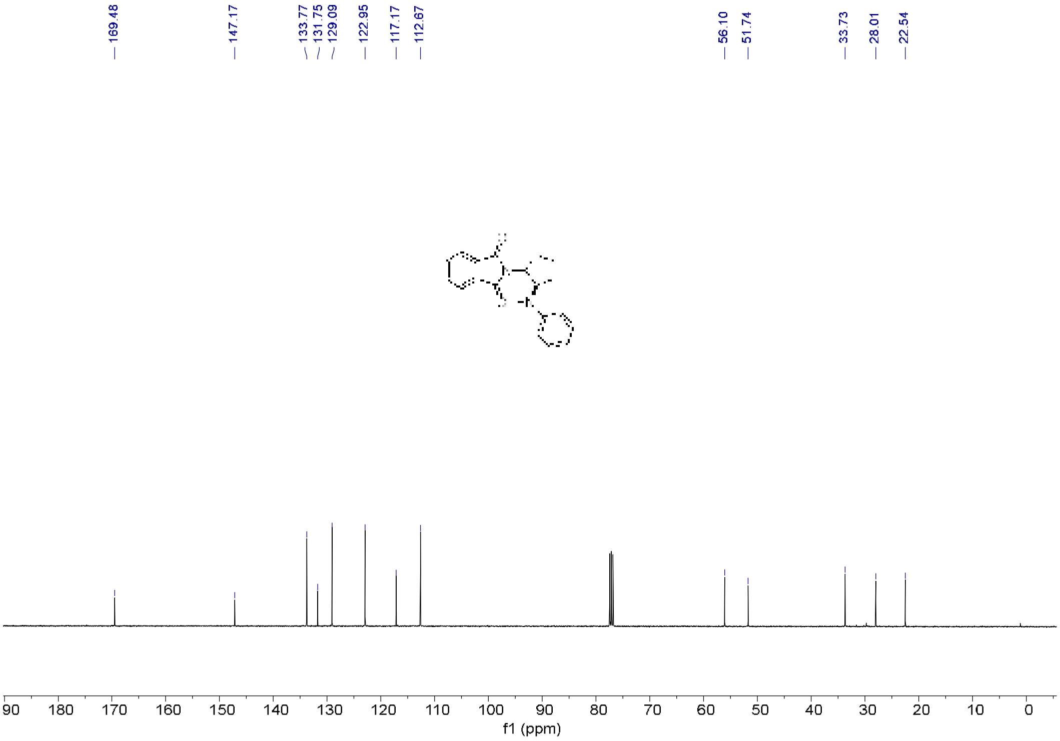
^{13}C NMR (101 MHz, CDCl$_3$) of **2f**



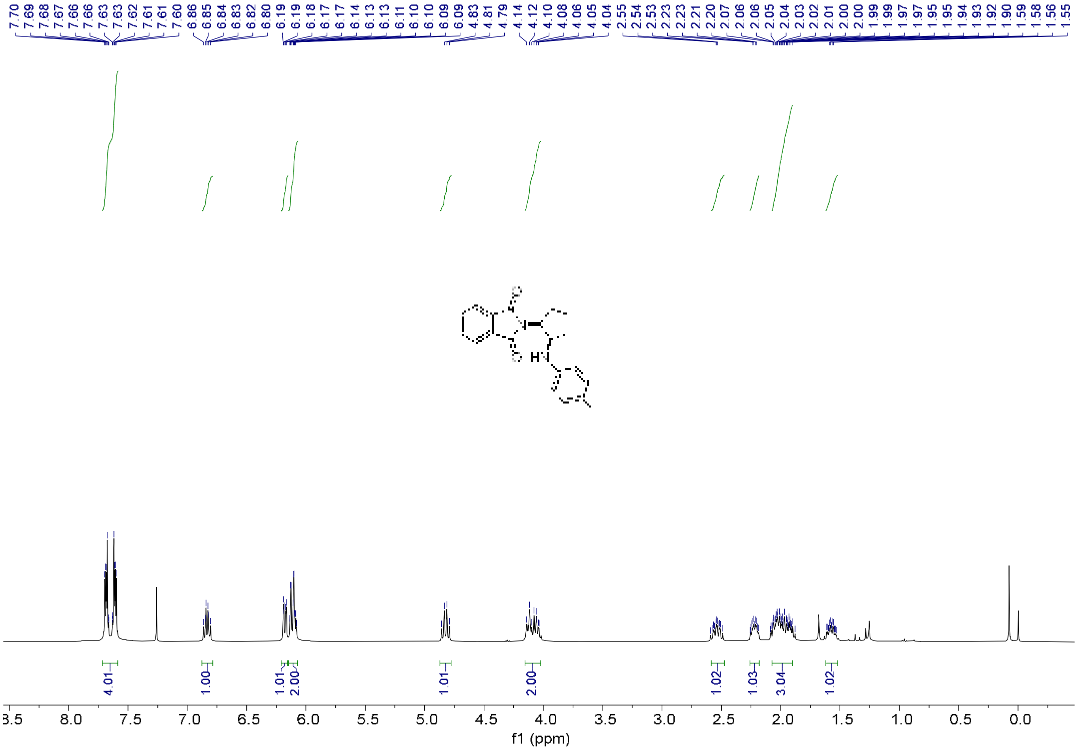
^{1}H NMR (400 MHz, CDCl$_3$) of **3aa**



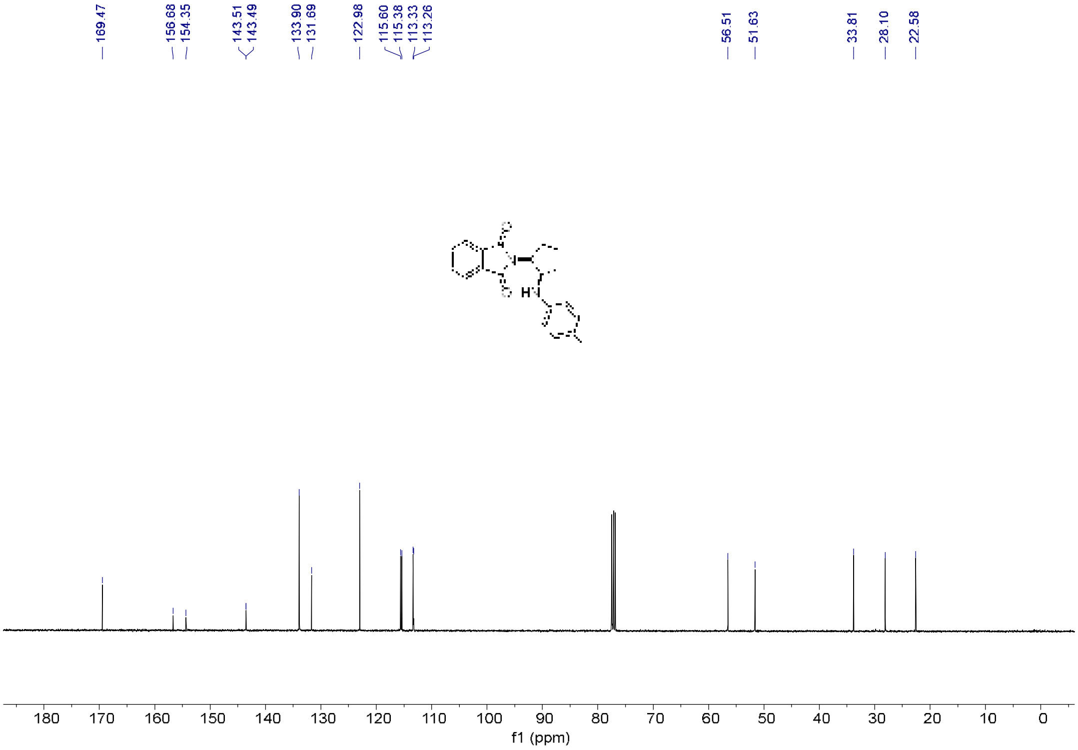
^{13}C NMR (101 MHz, CDCl$_3$) of **3aa**



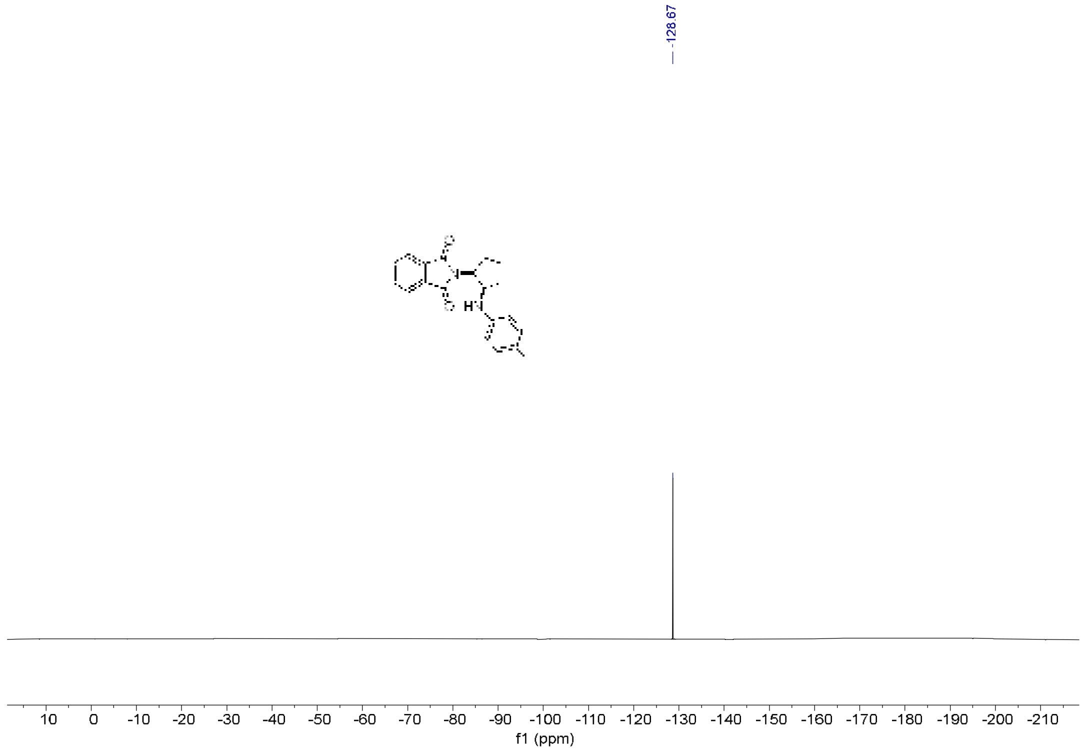
^{1}H NMR (400 MHz, CDCl$_3$) of **3ba**



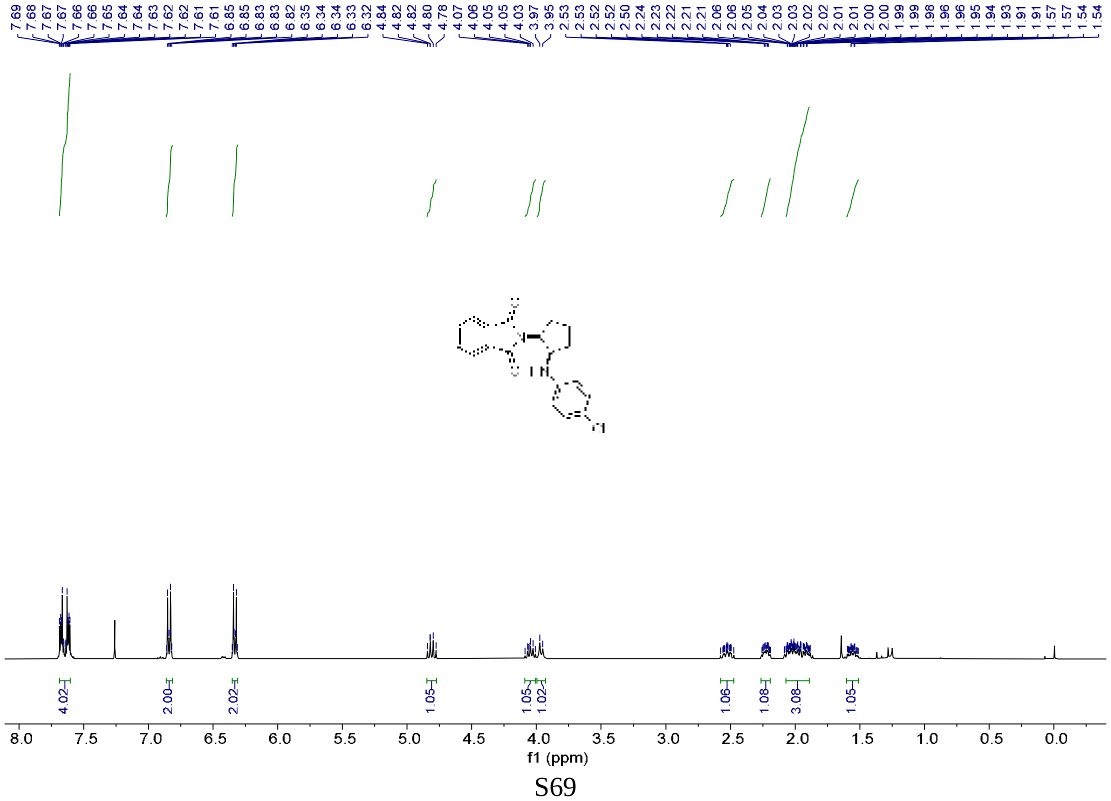
^{13}C NMR (101 MHz, CDCl$_3$) of **3ba**



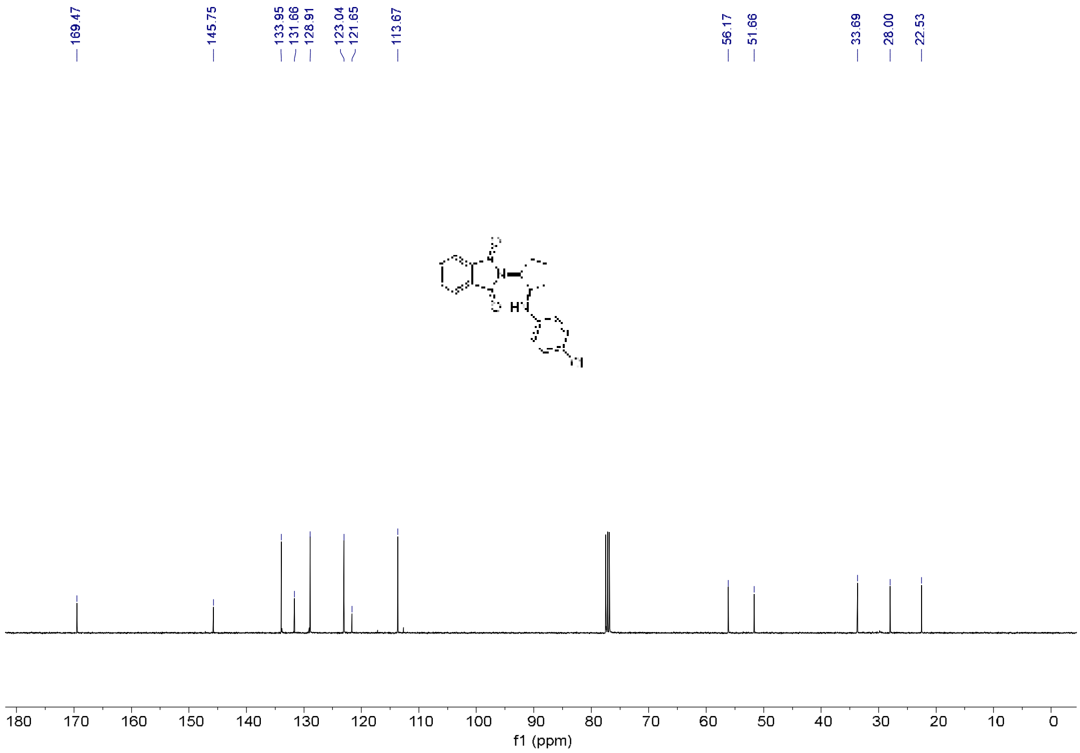
^{19}F NMR (376 MHz, CDCl$_3$) of **3ba**



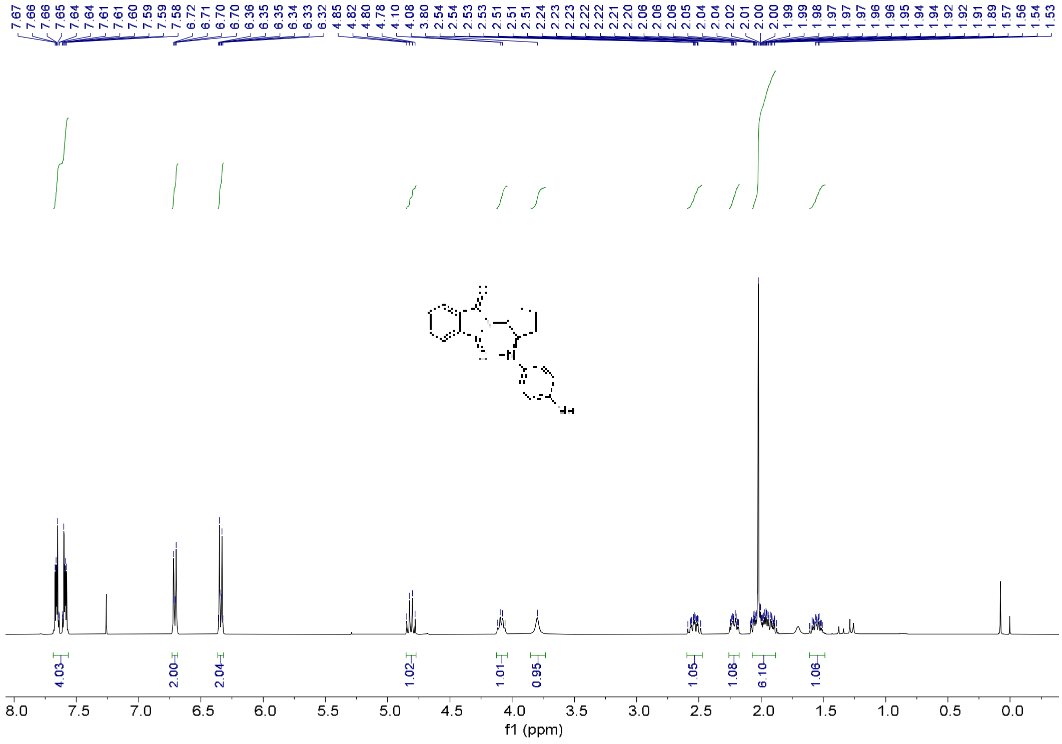
^{1}H NMR (400 MHz, CDCl$_3$) of **3ca**



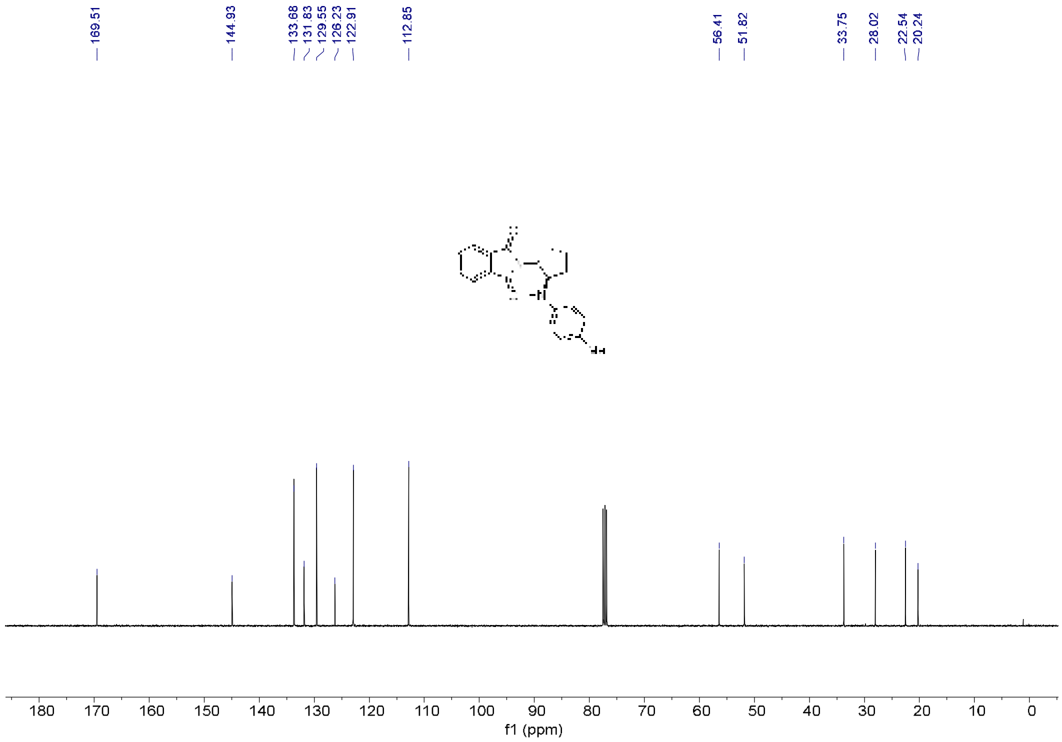
^{13}C NMR (101 MHz, CDCl$_3$) of **3ca**



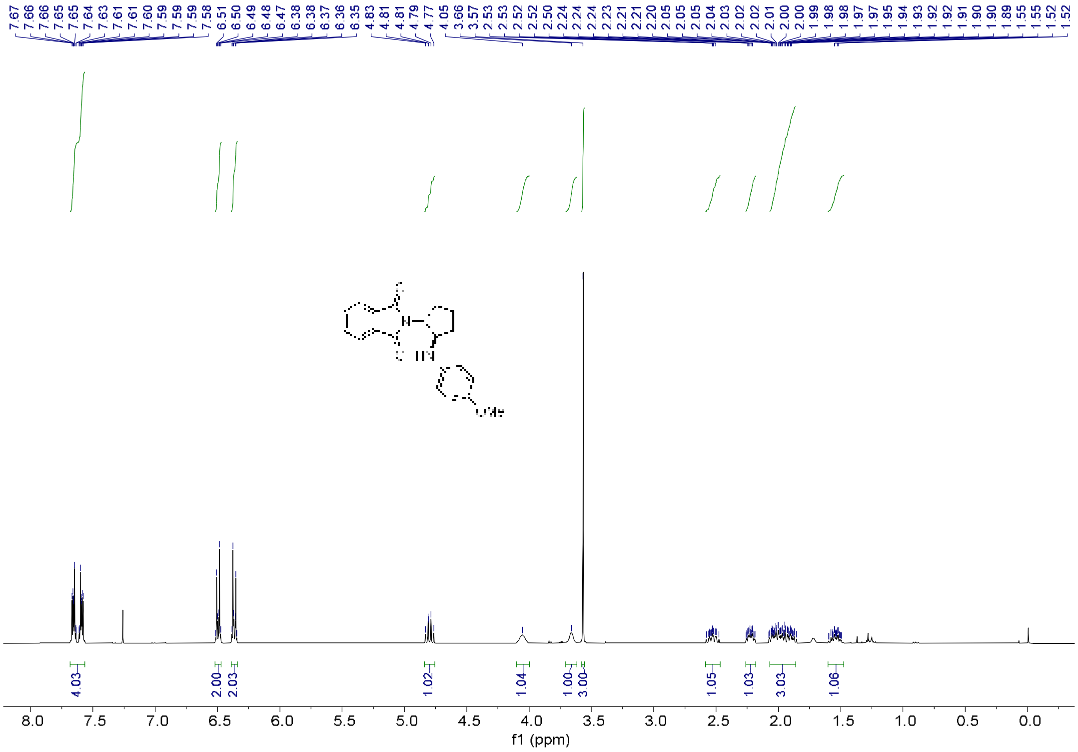
^{1}H NMR (400 MHz, CDCl$_3$) of **3da**



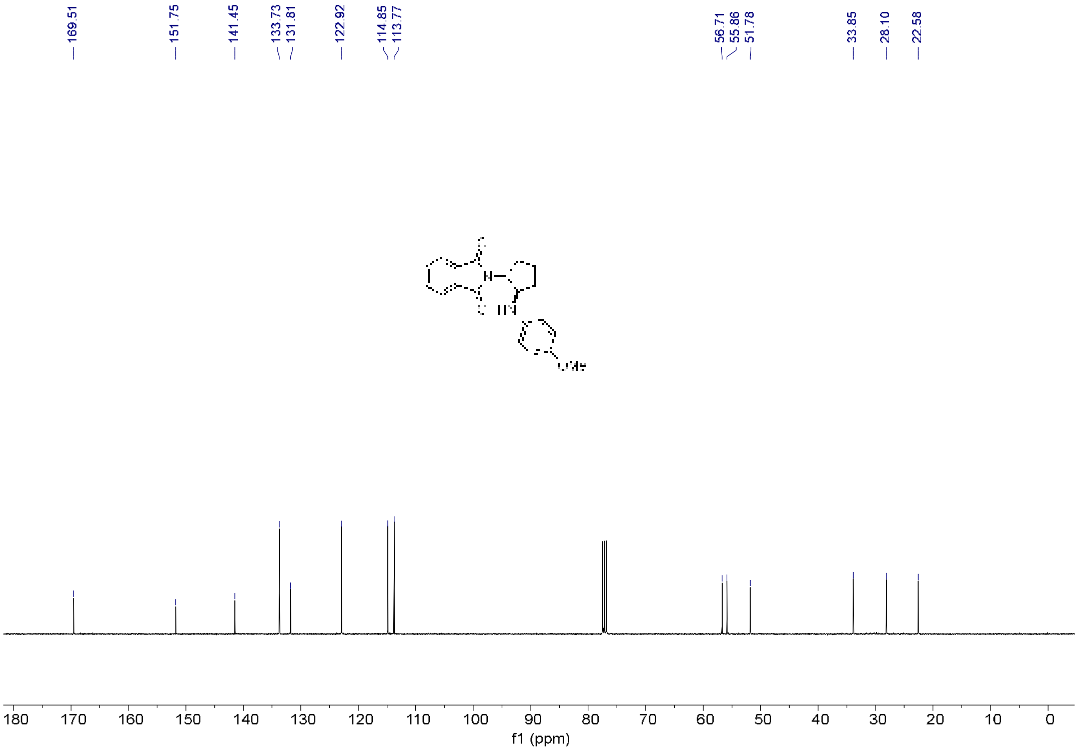
^{13}C NMR (101 MHz, $CDCl_3$) of **3da**



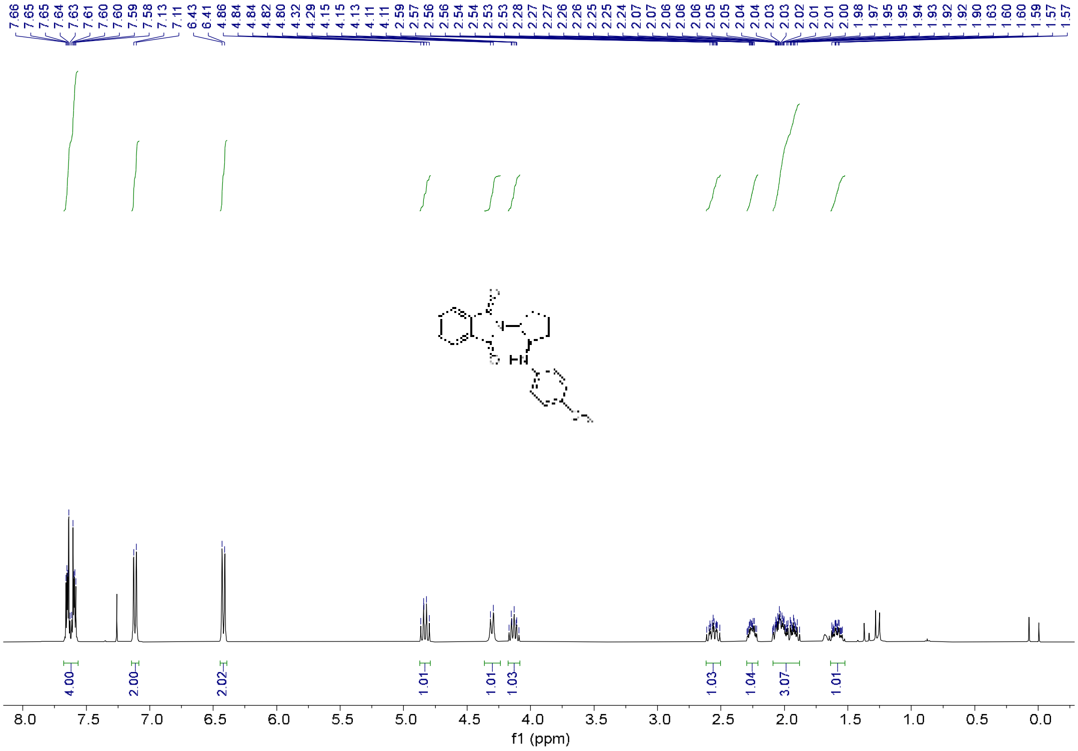
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



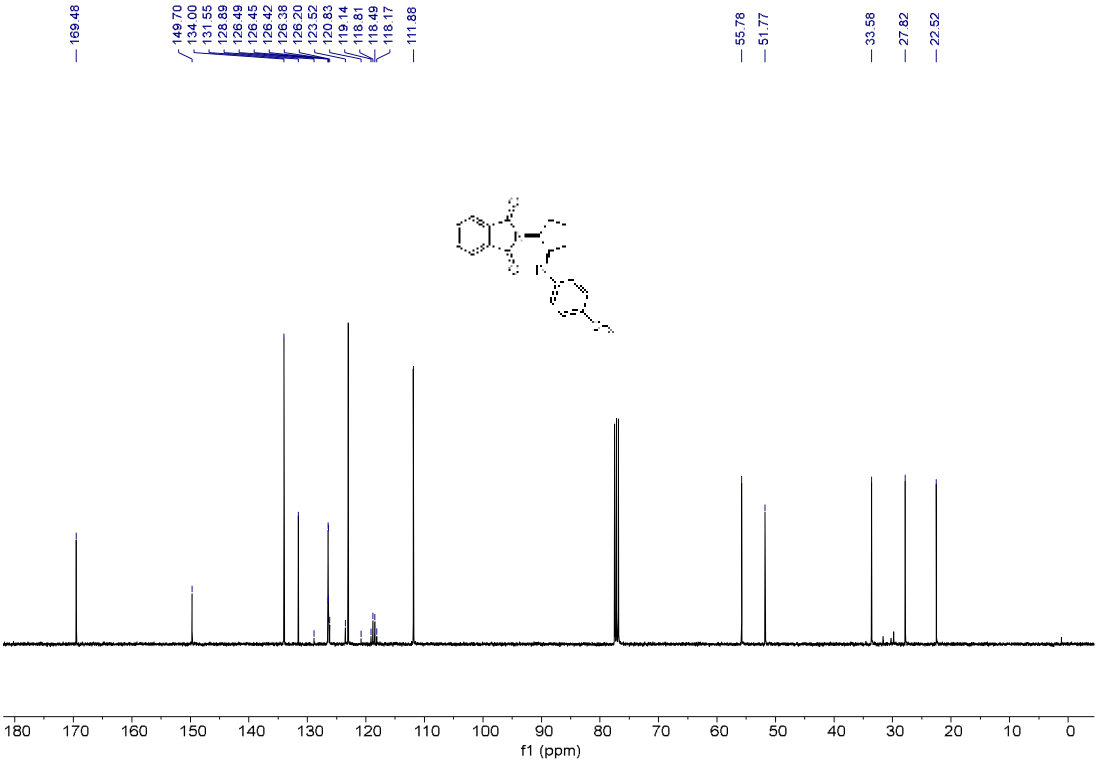
^{13}C NMR (101 MHz, CDCl$_3$) of **3ea**



^{1}H NMR (400 MHz, CDCl$_3$) of **3fa**

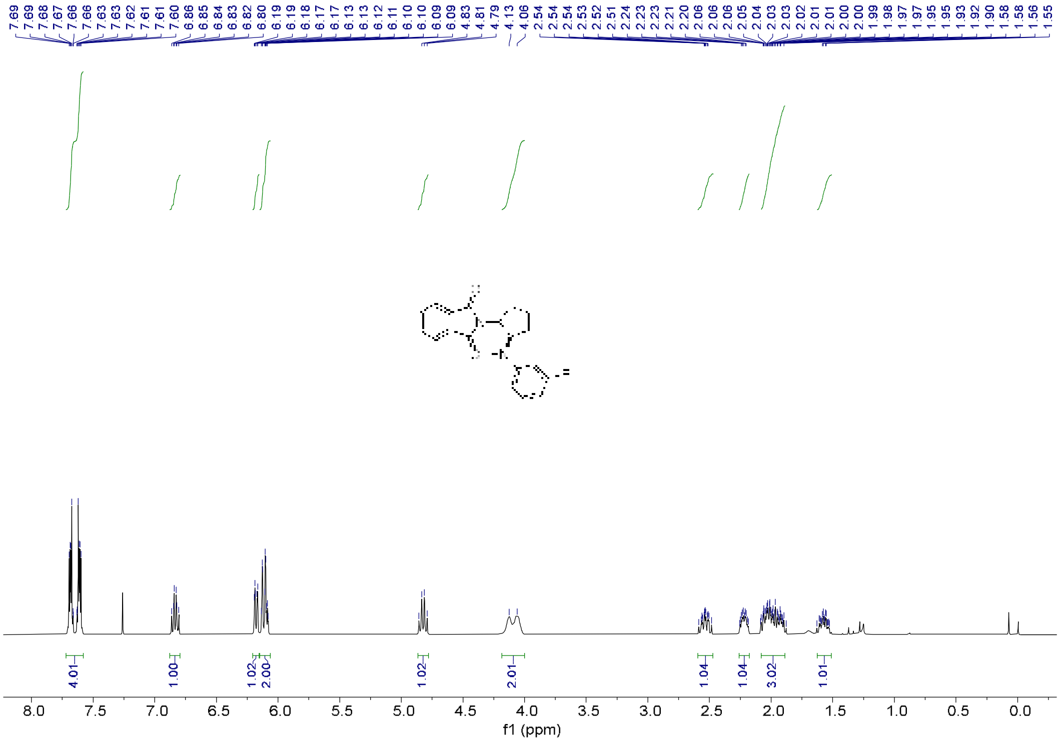


^{13}C NMR (101 MHz, CDCl$_3$) of **3fa**



^{19}F NMR (376 MHz, CDCl$_3$) of **3fa**

^{1}H NMR (400 MHz, CDCl$_3$) of **3ga**



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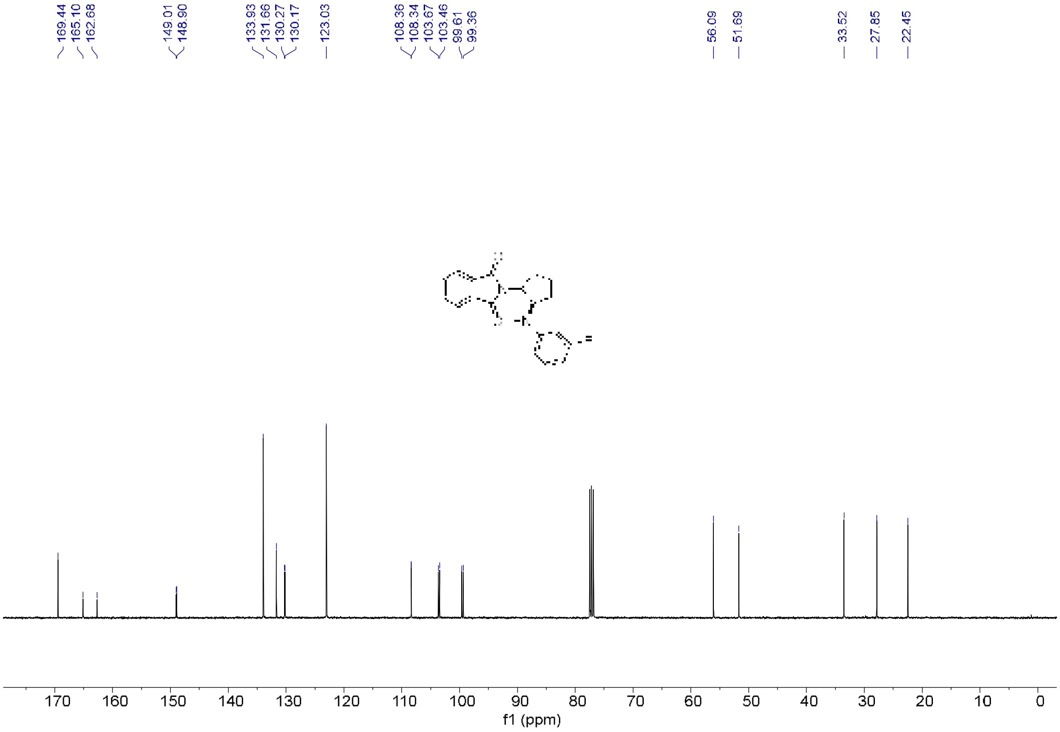

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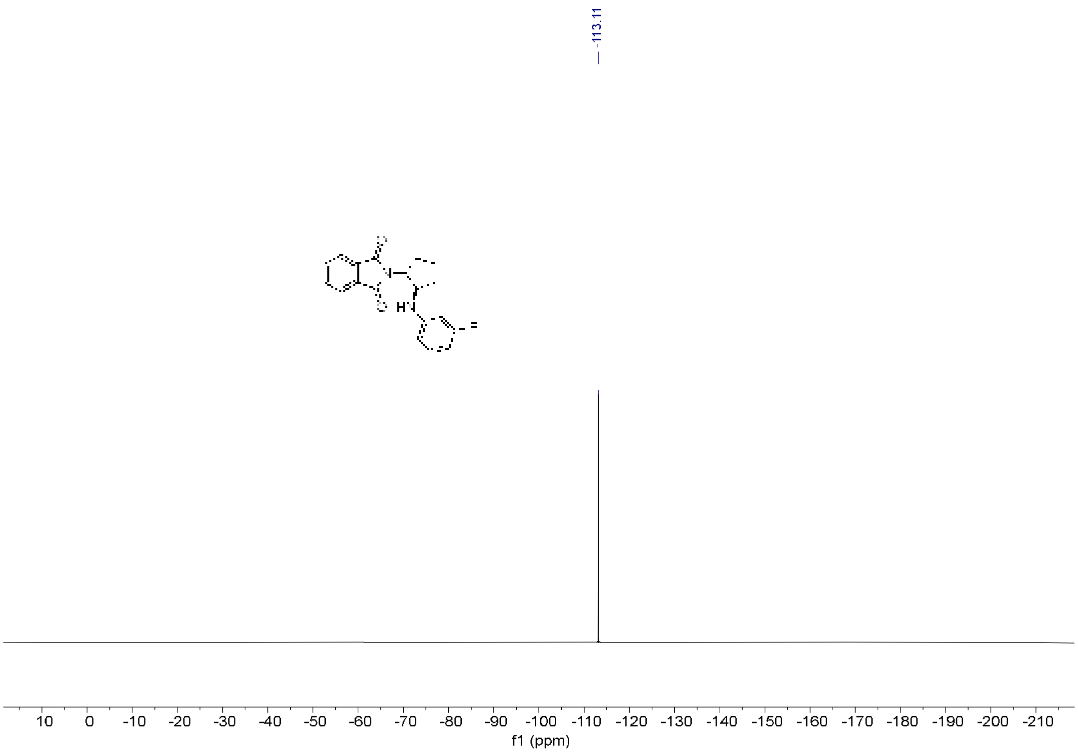
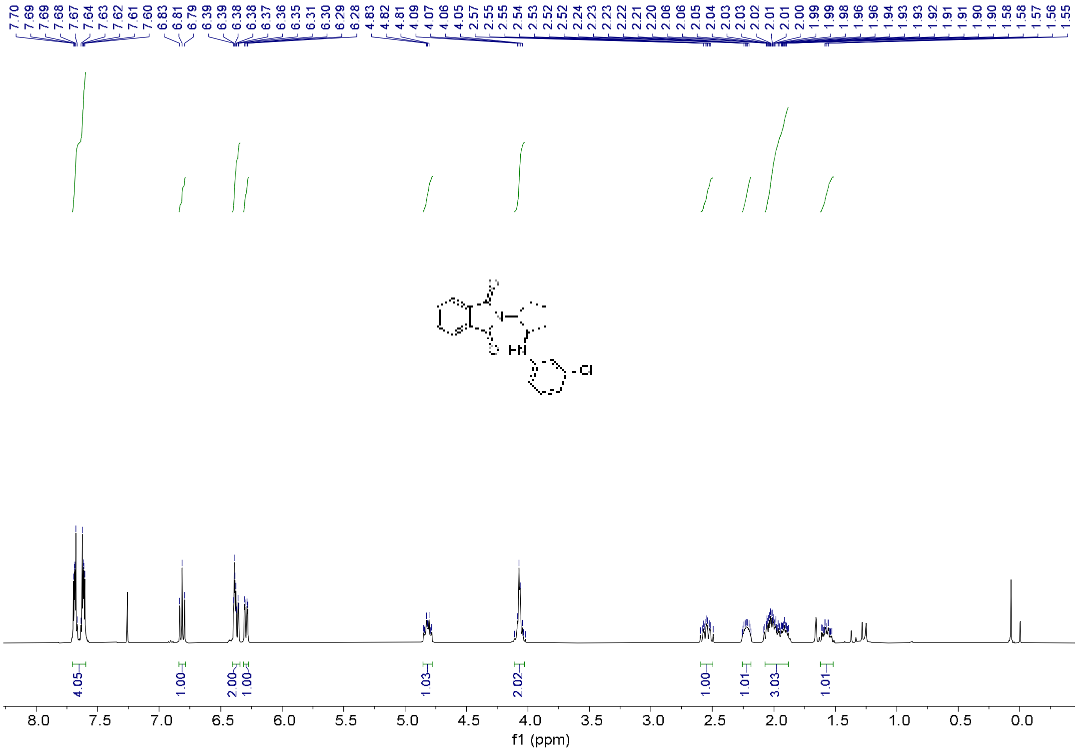
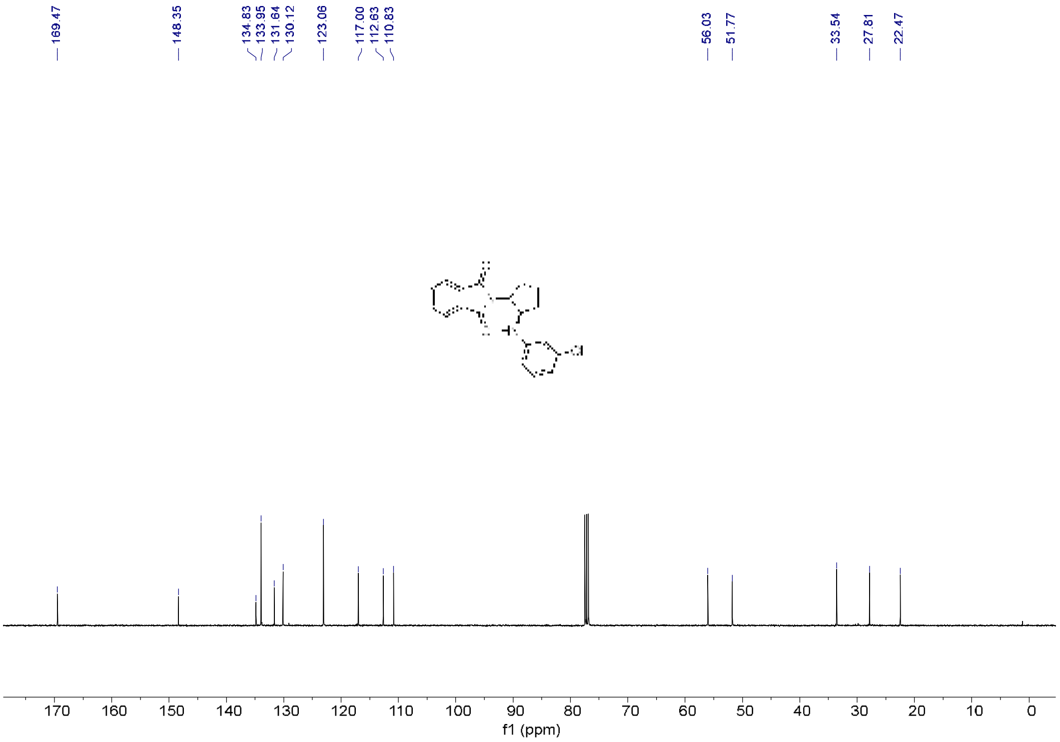


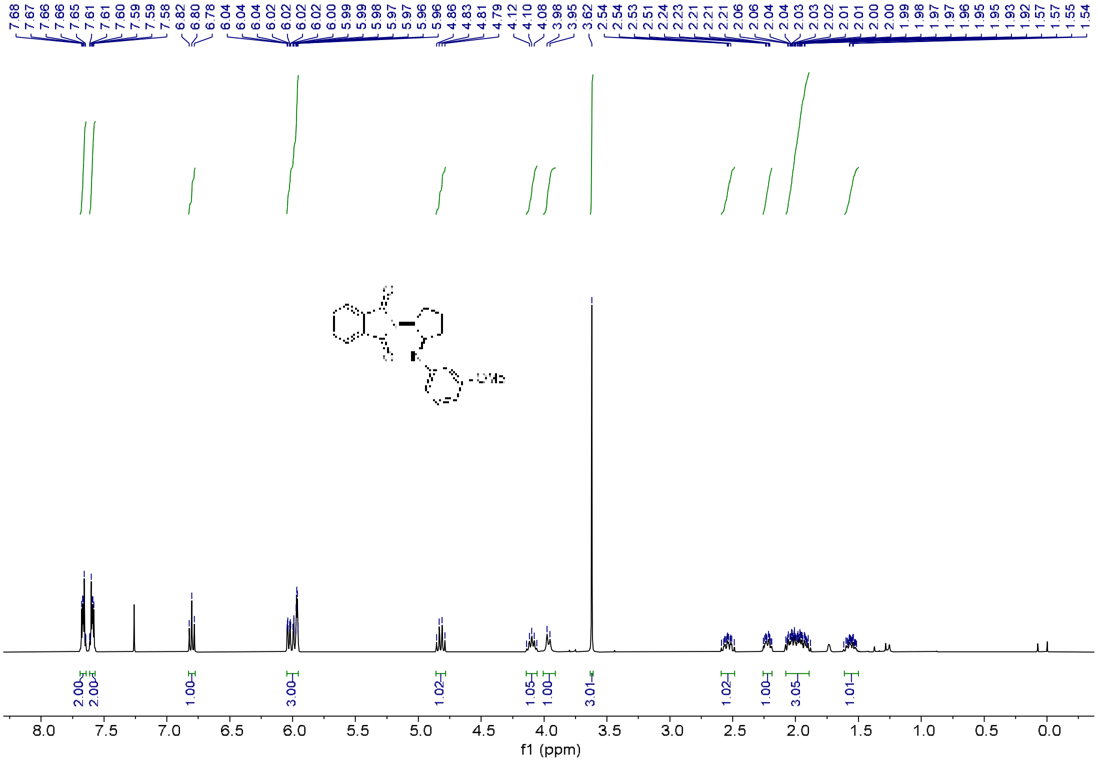
^{1}H NMR (400 MHz, CDCl$_3$) of **3ha**



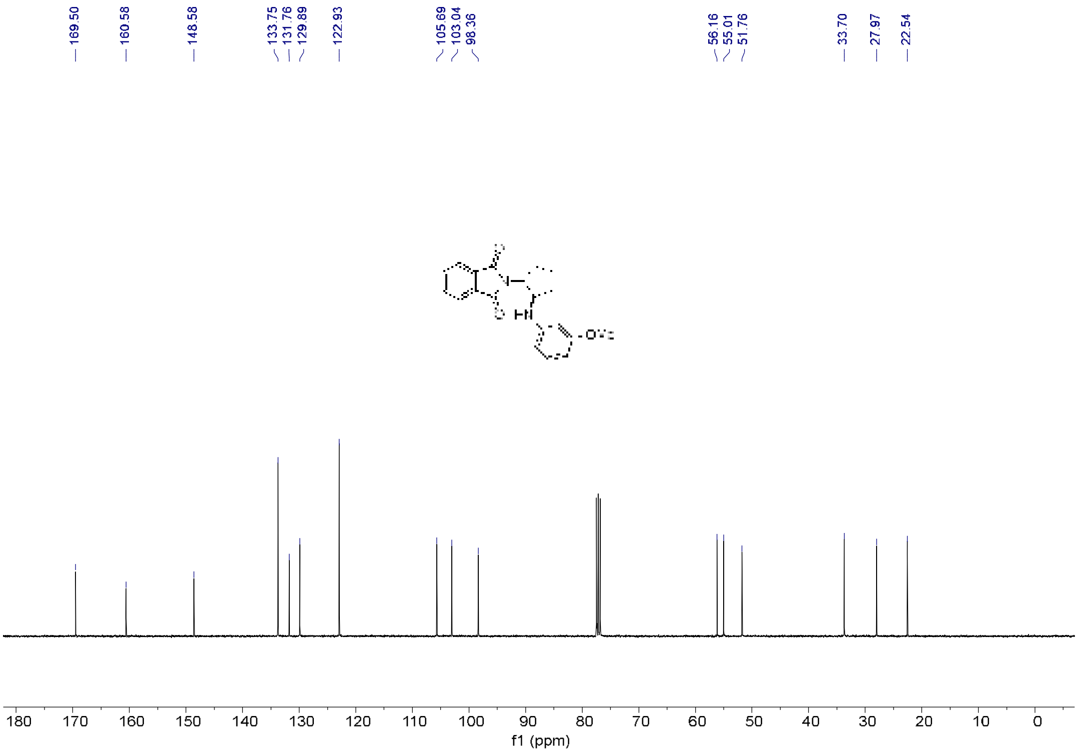
^{13}C NMR (101 MHz, CDCl$_3$) of **3ha**



^{1}H NMR (400 MHz, CDCl$_3$) of **3ia**



^{13}C NMR (101 MHz, CDCl$_3$) of **3ia**



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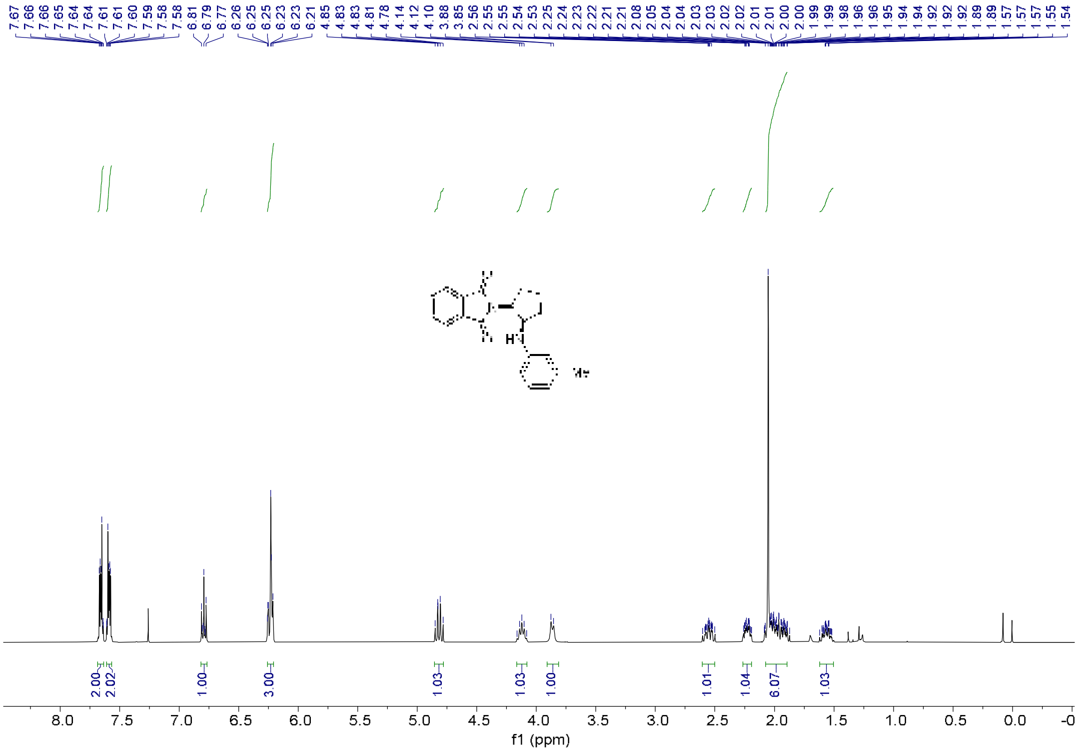
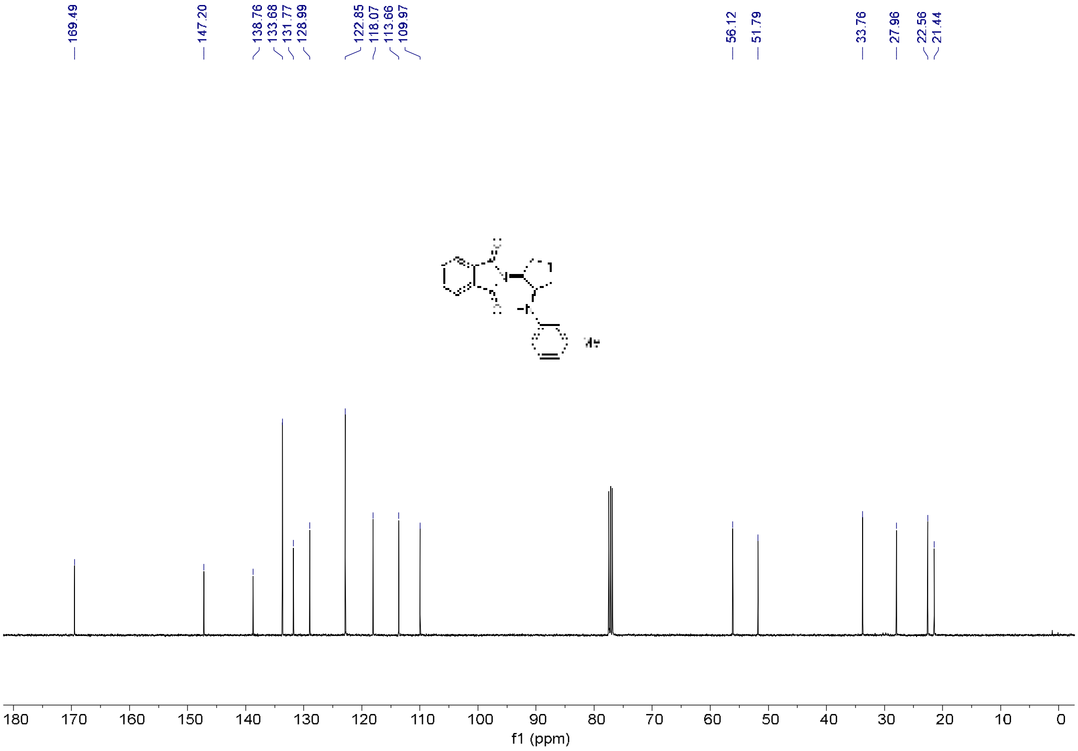


^{13}C NMR (101 MHz, CDCl$_3$) of **3ja**



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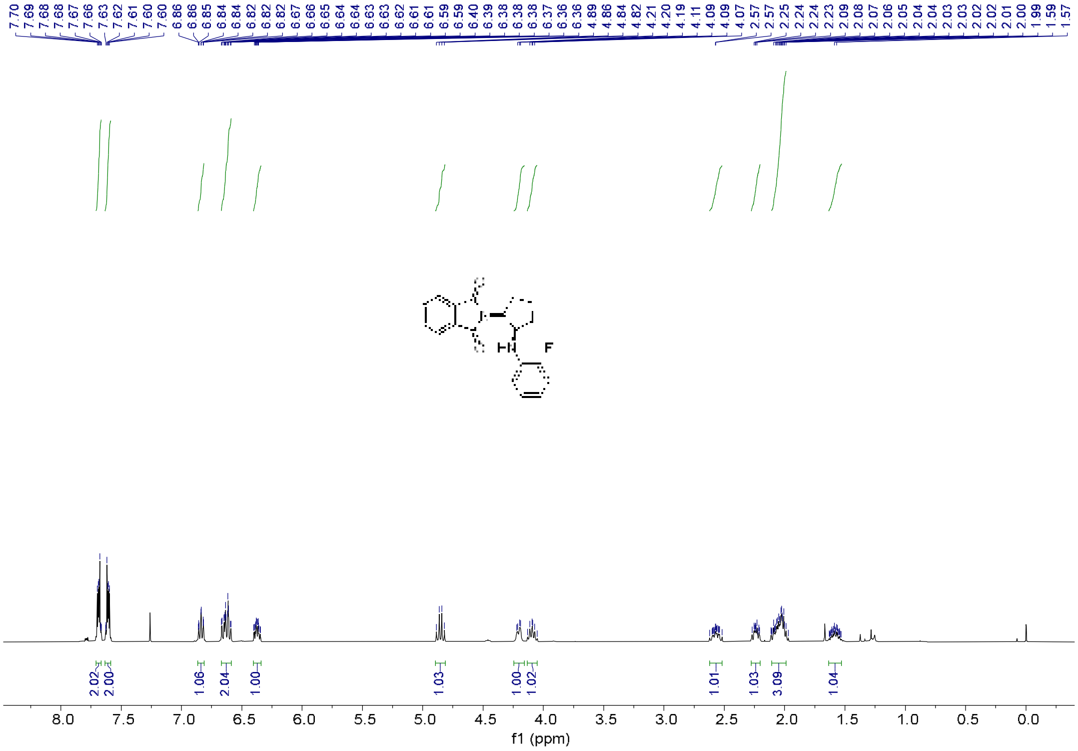
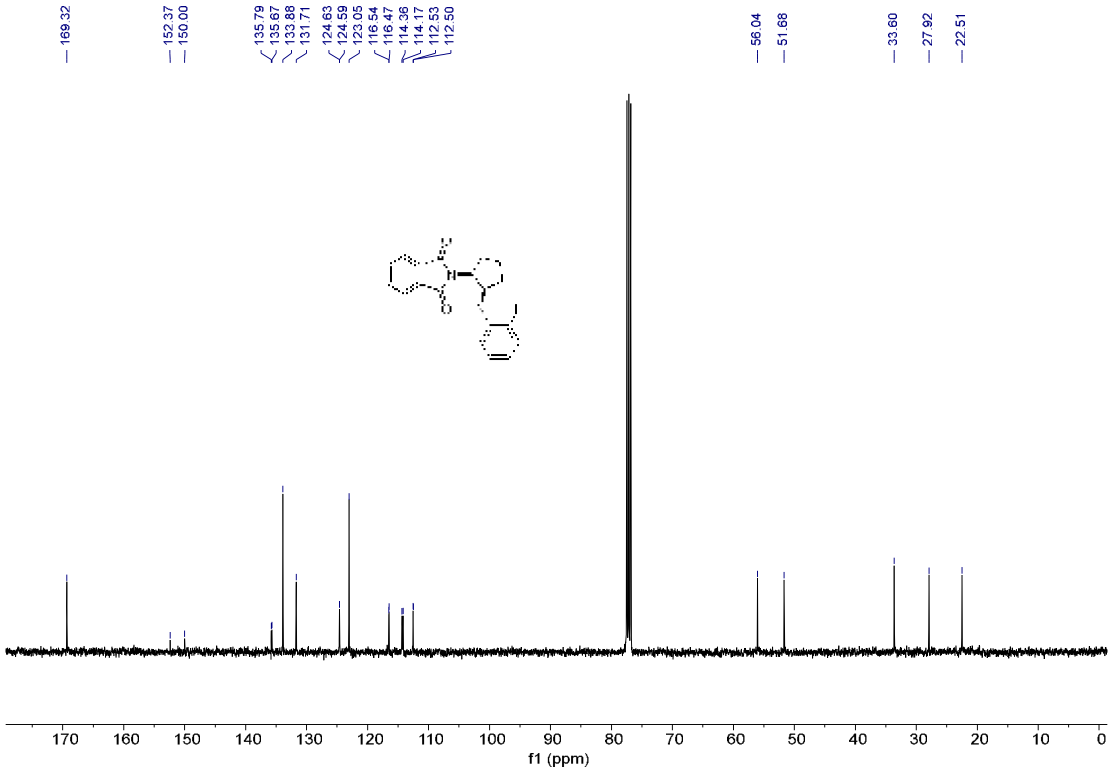
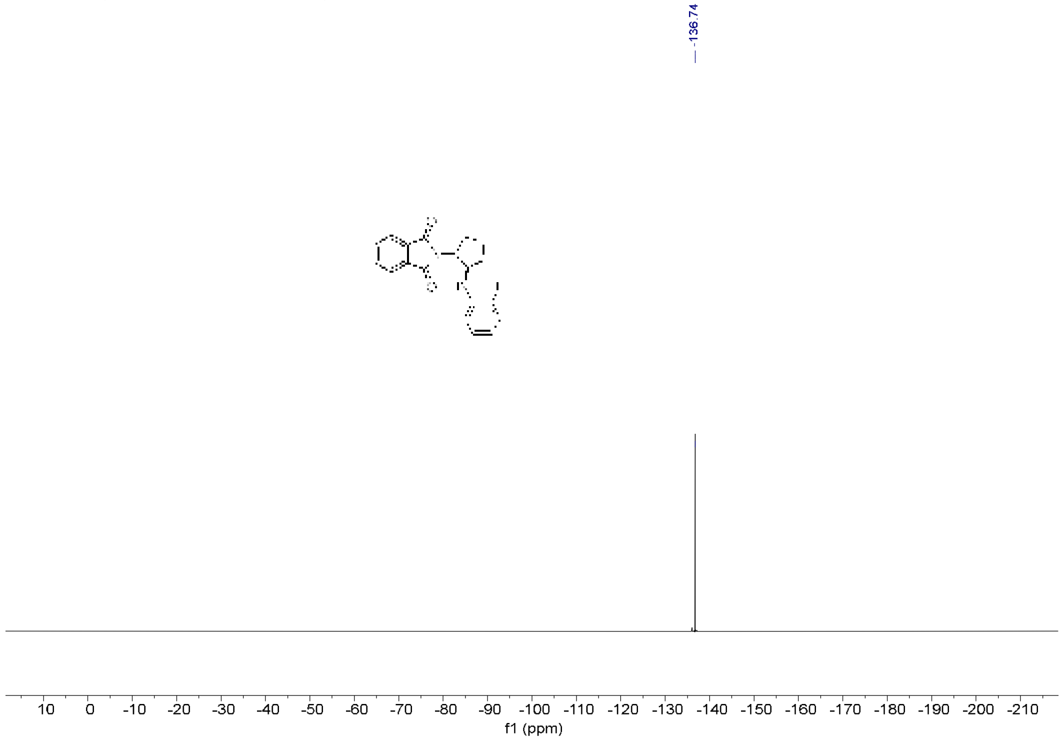


^{13}C NMR (101 MHz, CDCl$_3$) of **3ka**



^{19}F NMR (376 MHz, CDCl$_3$) of **3ka**



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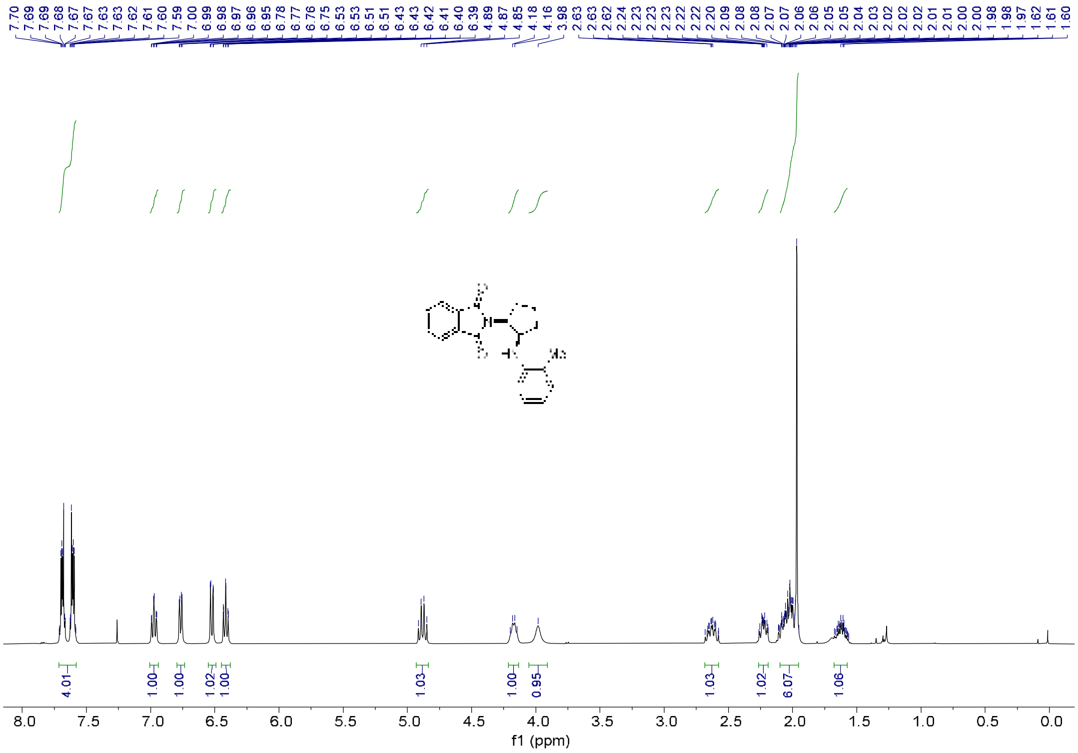

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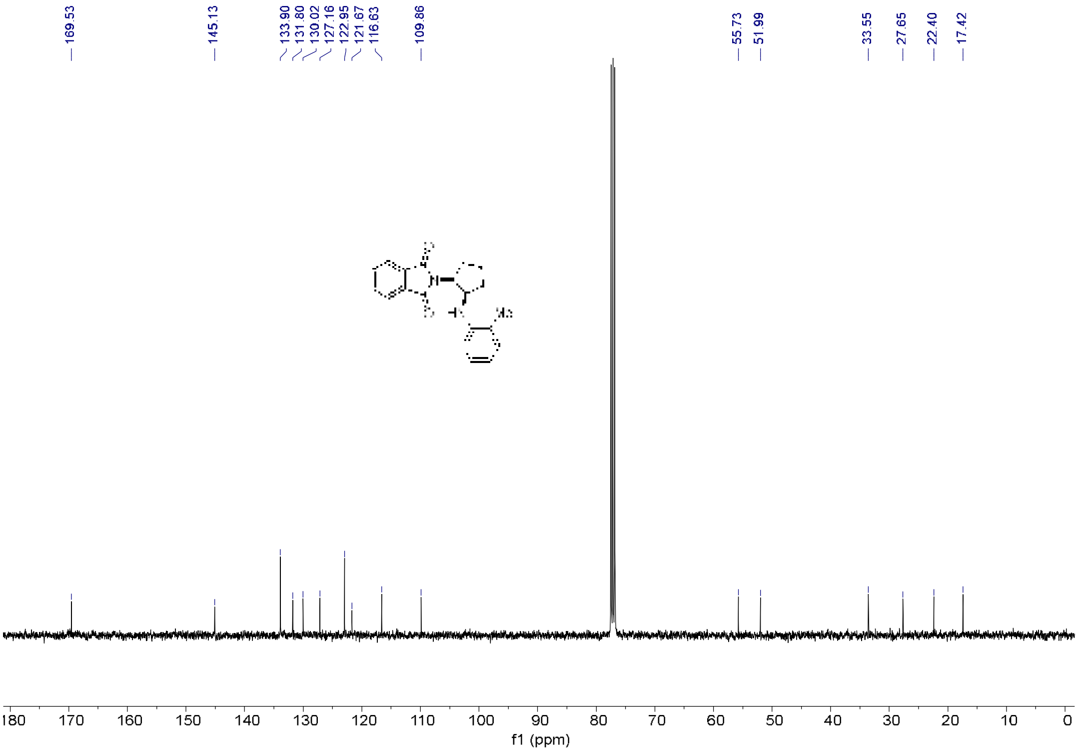

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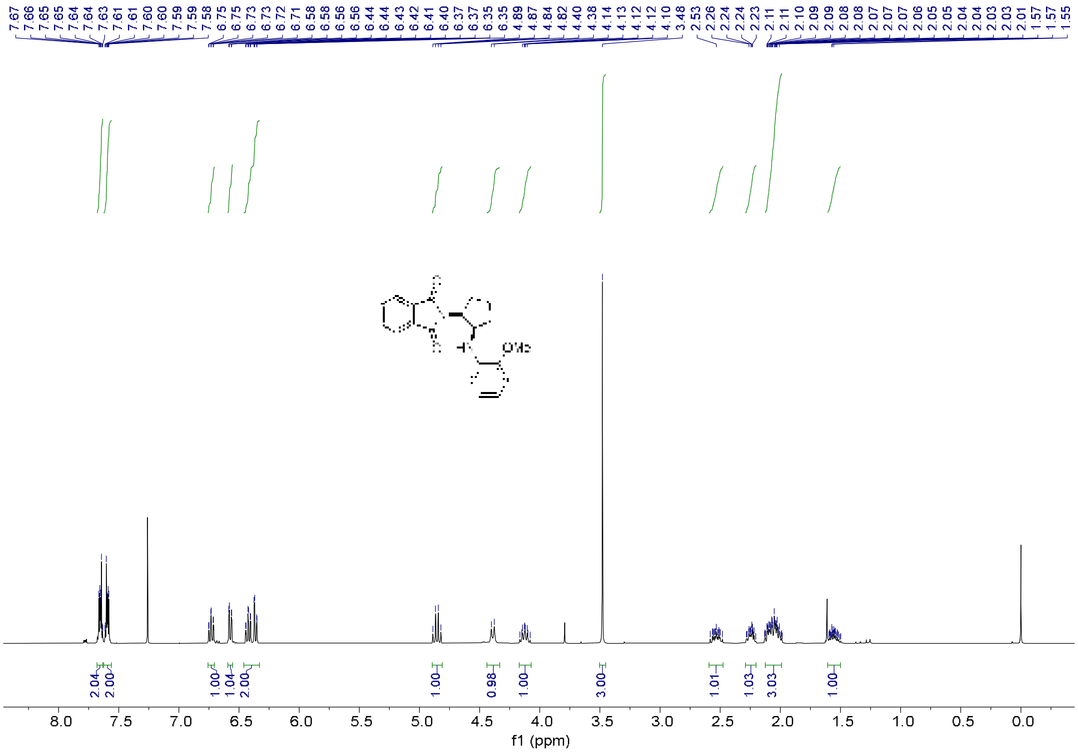
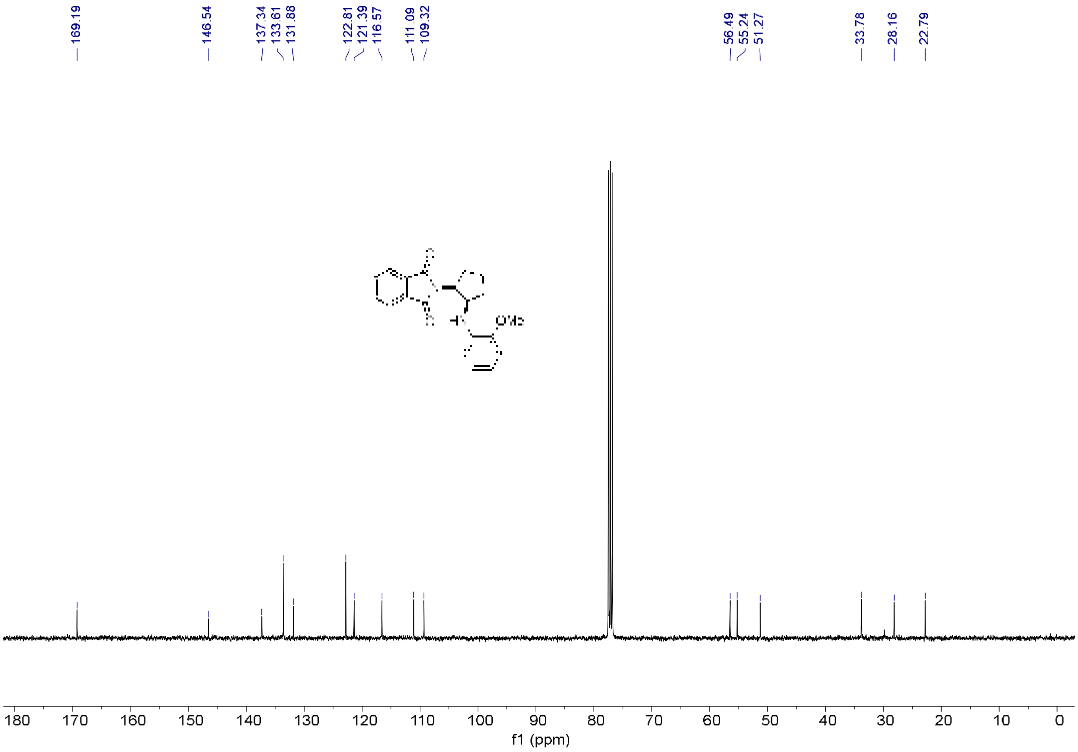


^{13}C NMR (101 MHz, CDCl$_3$) of **3ma**



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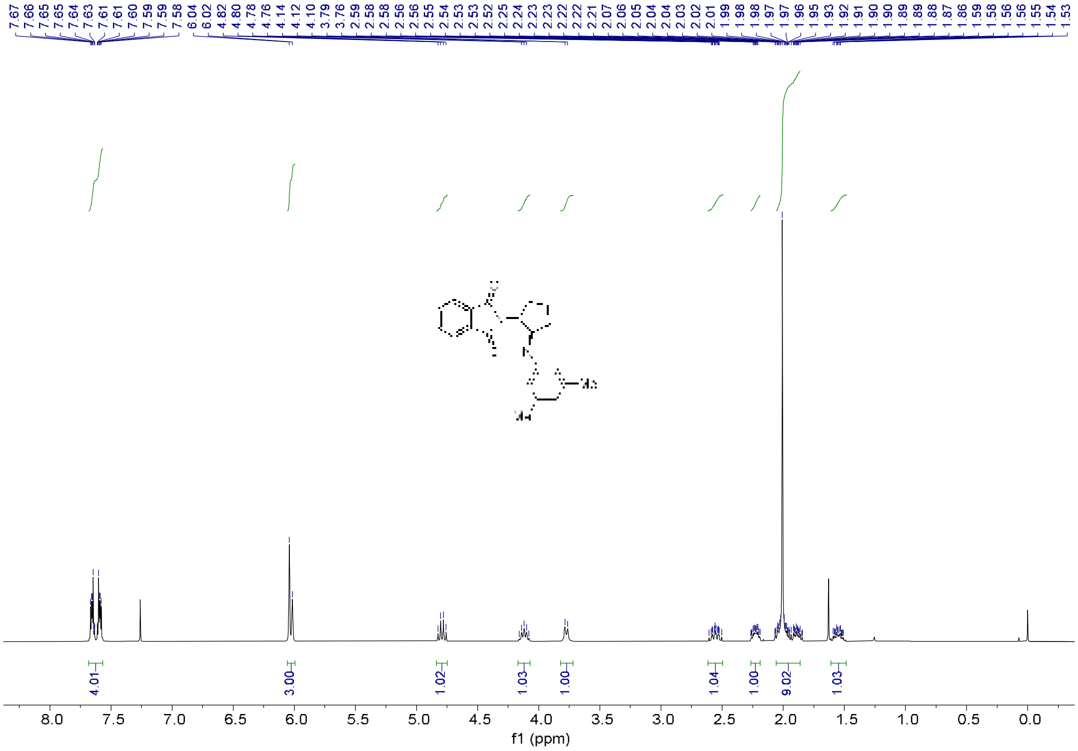
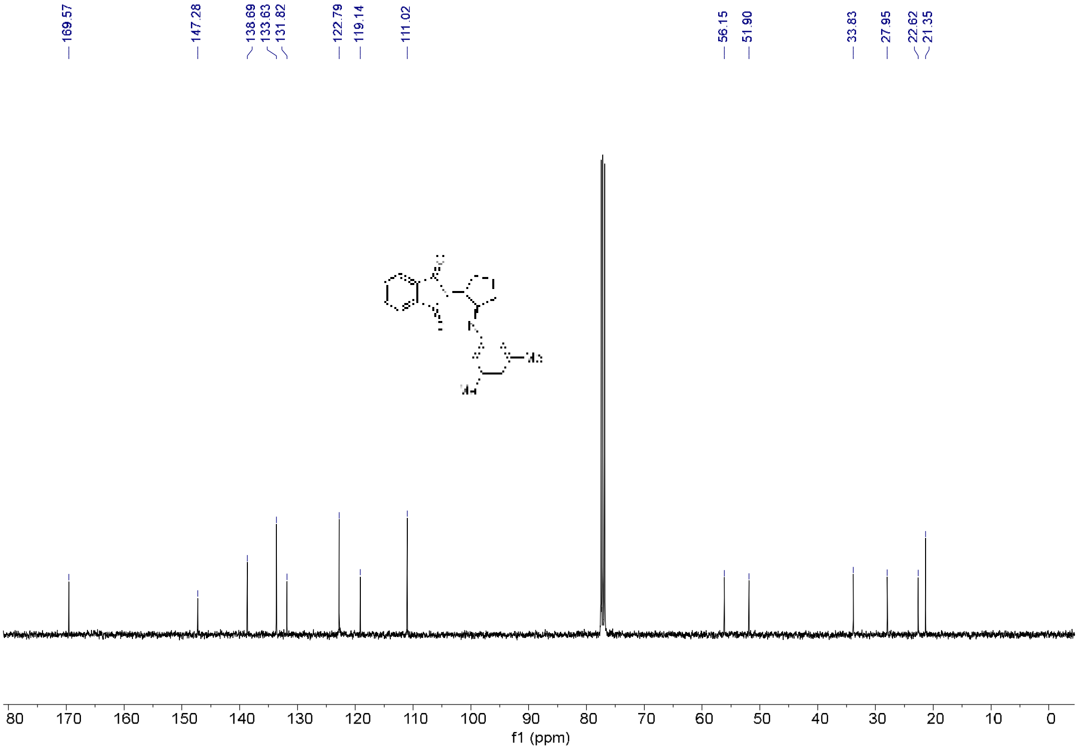


^{13}C NMR (101 MHz, CDCl$_3$) of **3na**



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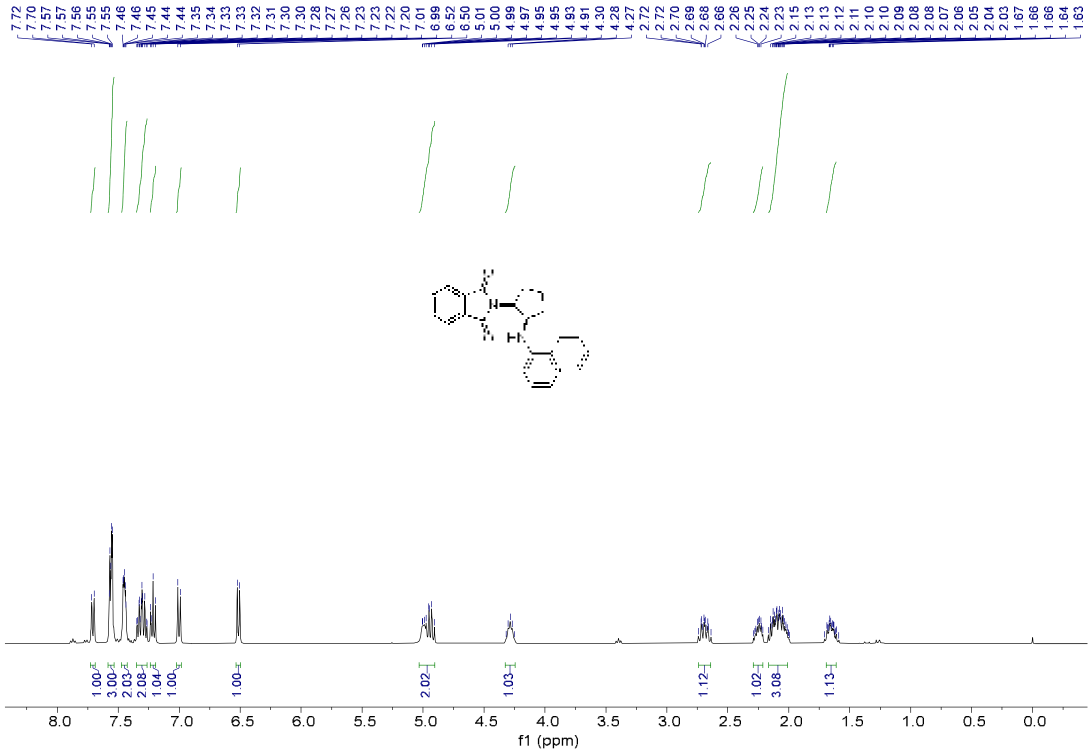
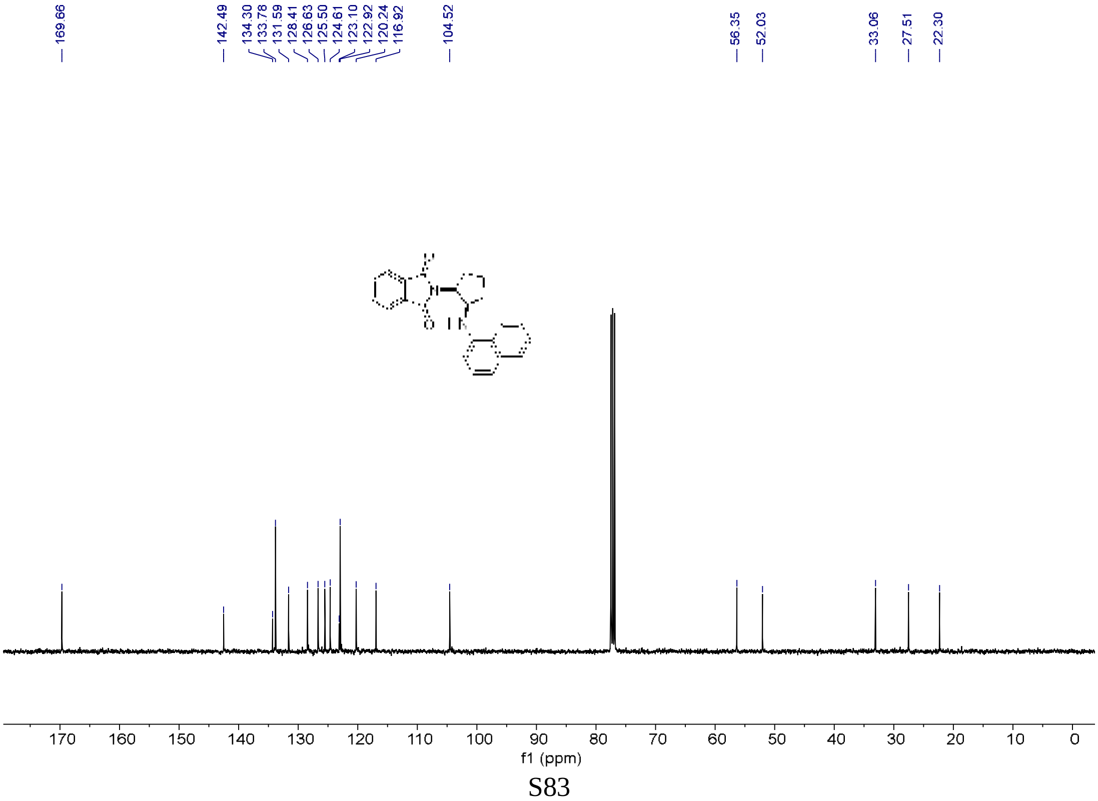
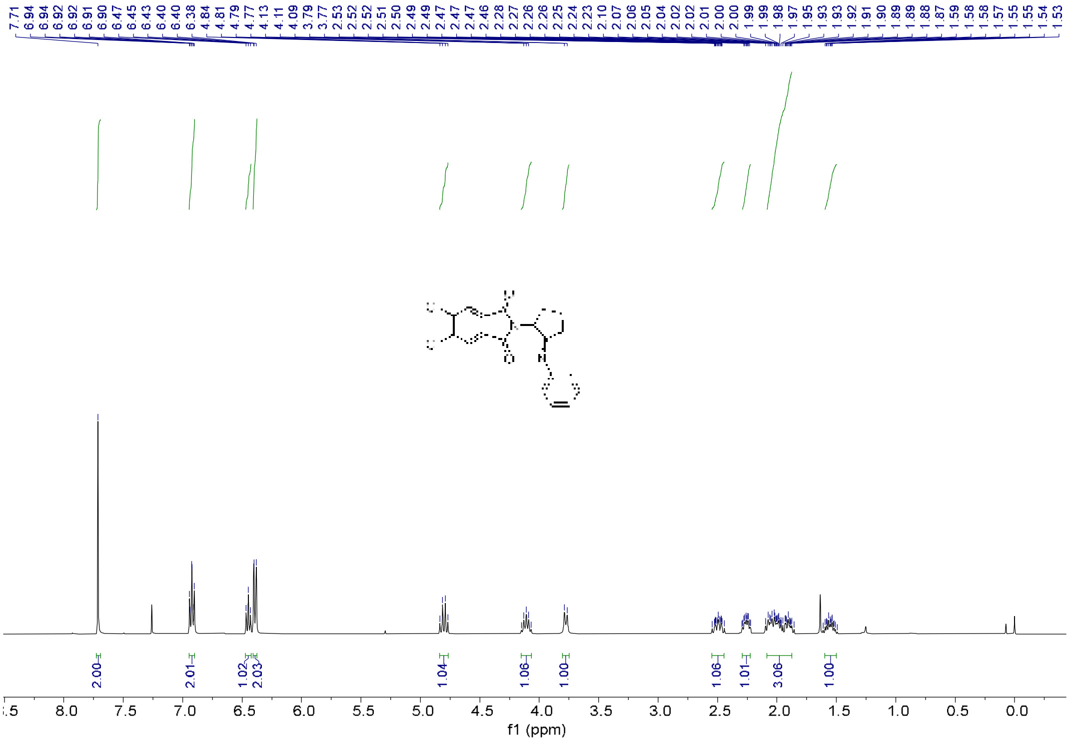


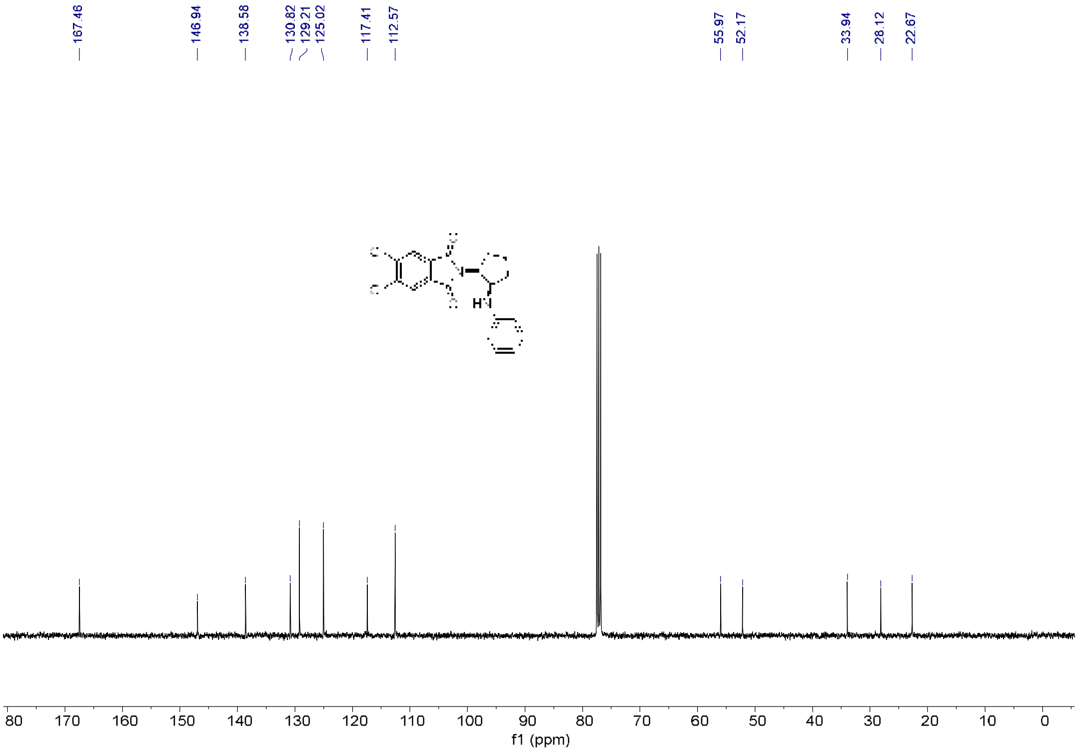
^{13}C NMR (101 MHz, CDCl$_3$) of **3oa**



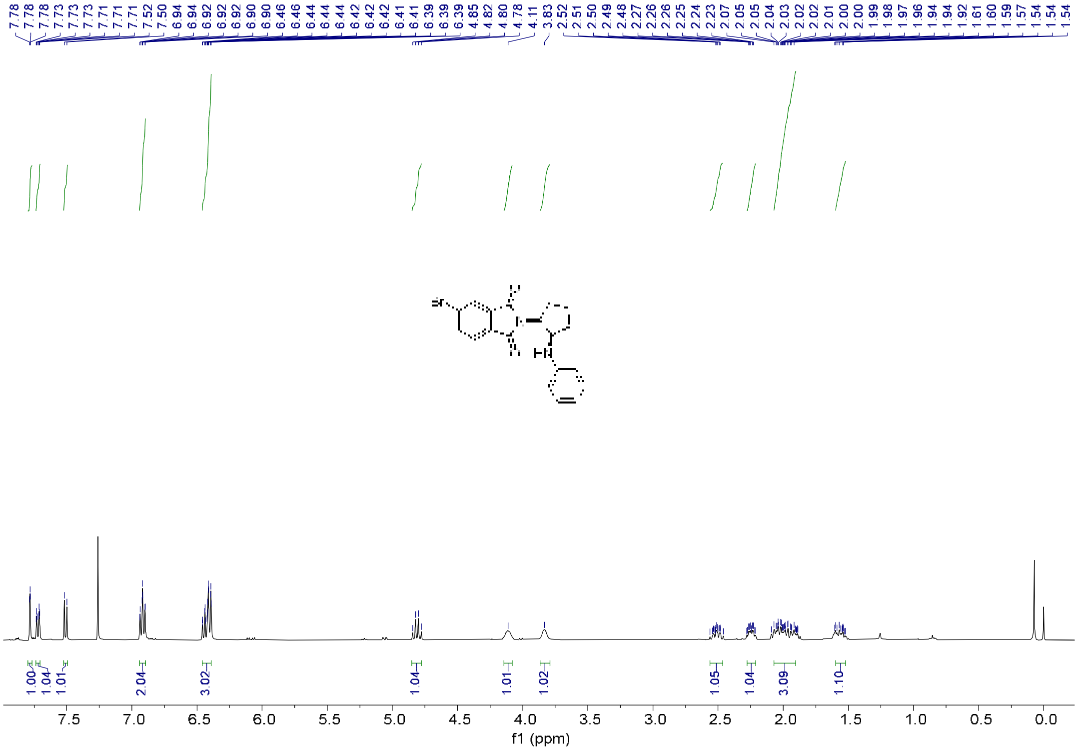
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



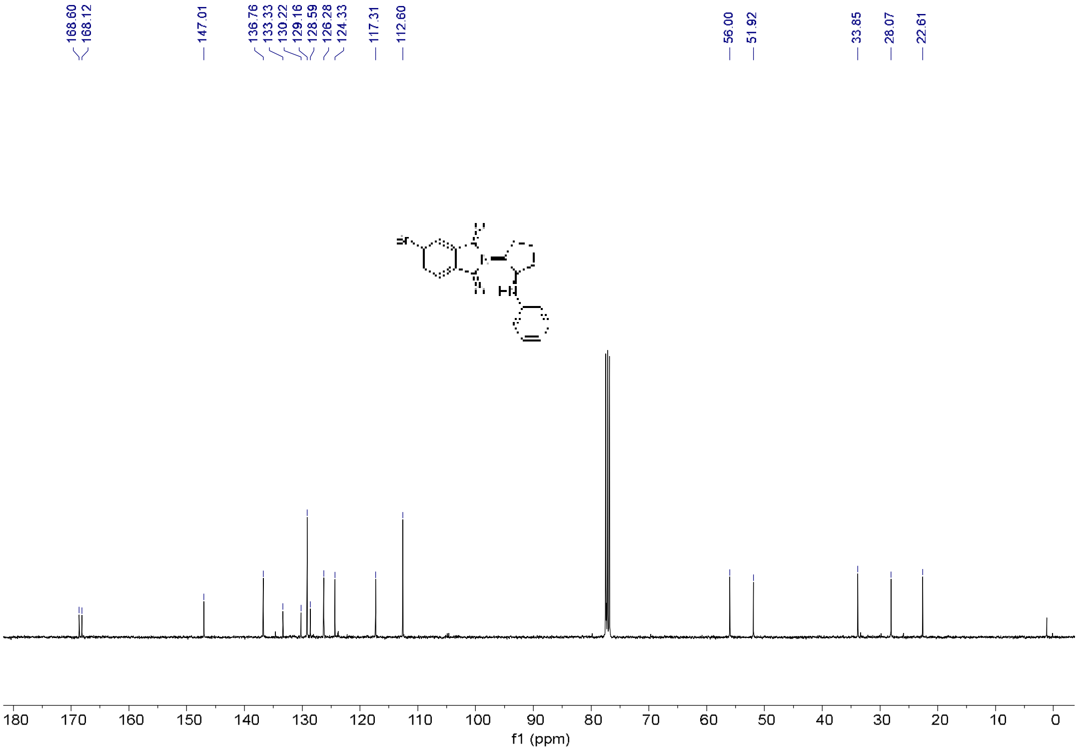
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



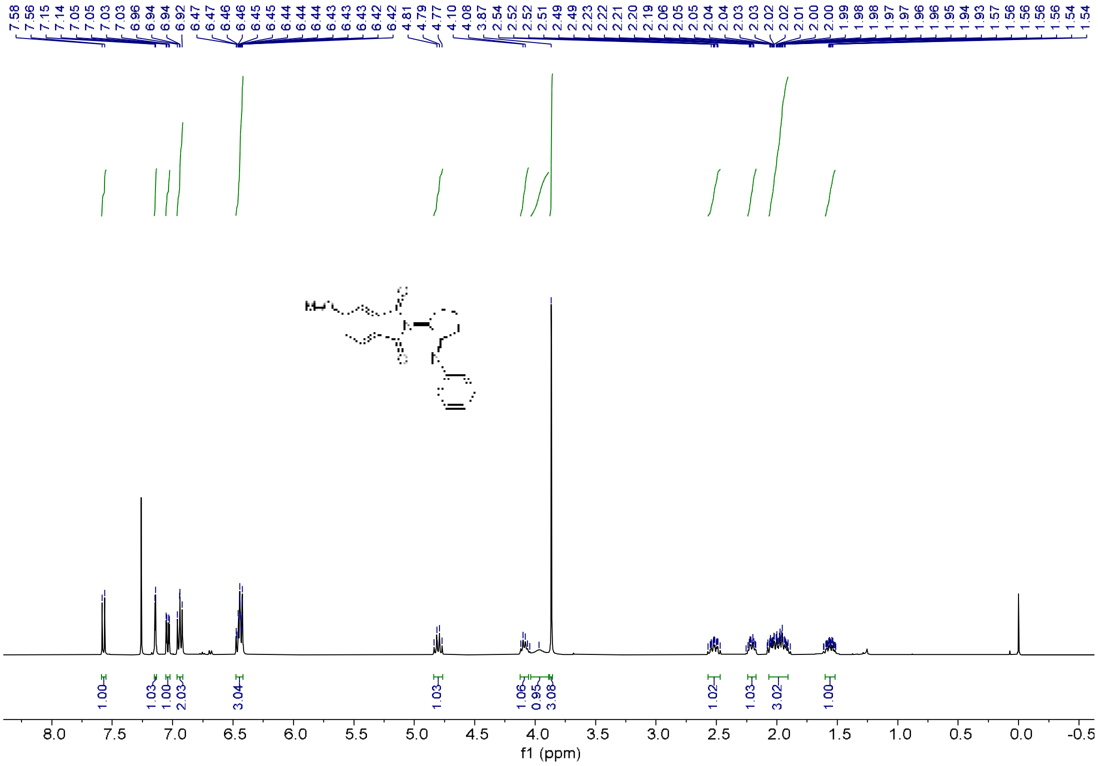
^{1}H NMR (400 MHz, CDCl$_3$) of **3ac**



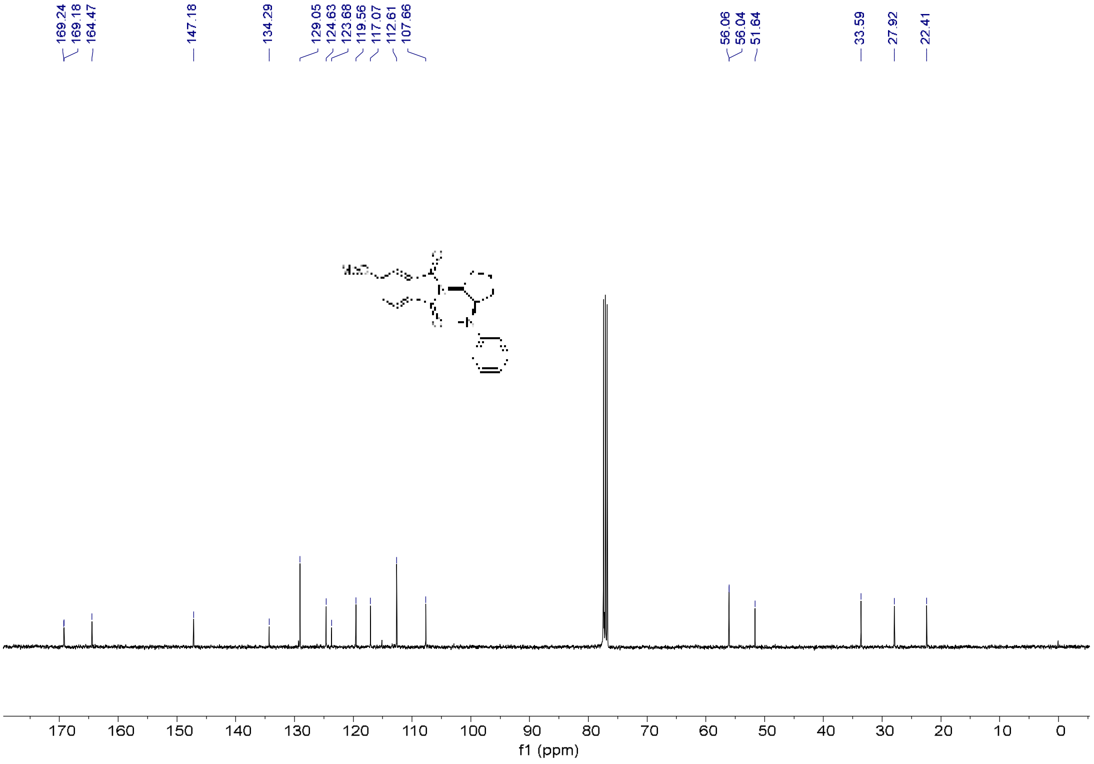
^{13}C NMR (101 MHz, CDCl$_3$) of **3ac**



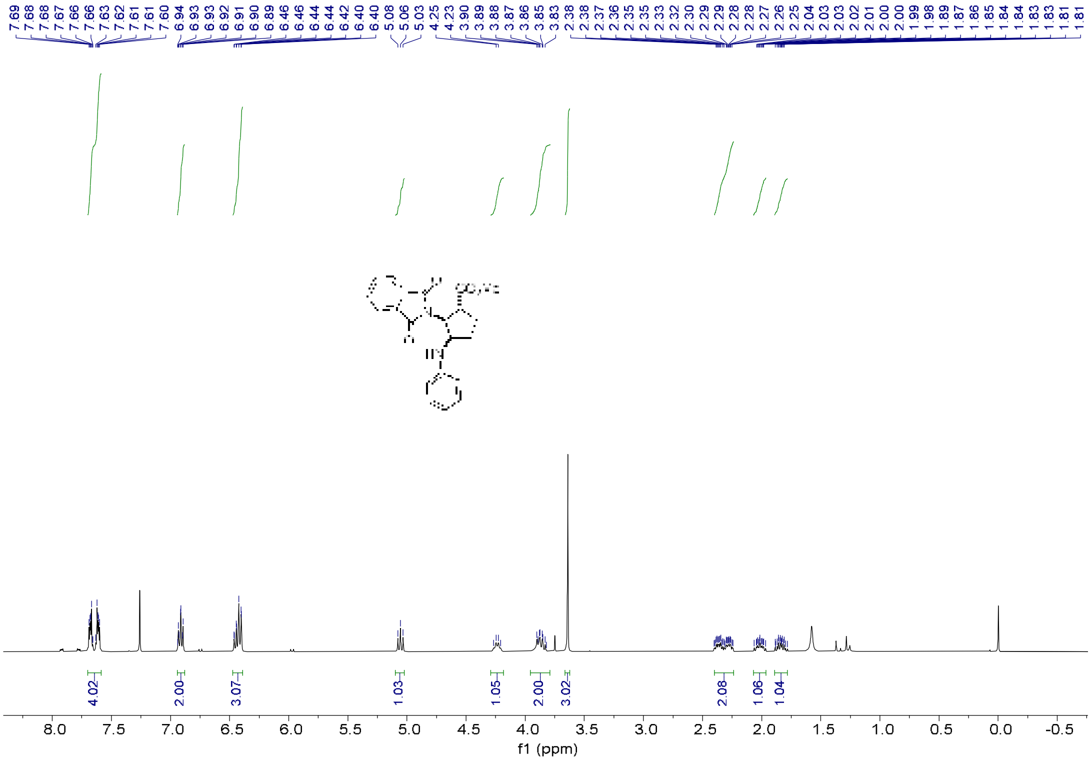
^{1}H NMR (400 MHz, CDCl$_3$) of **3ad**



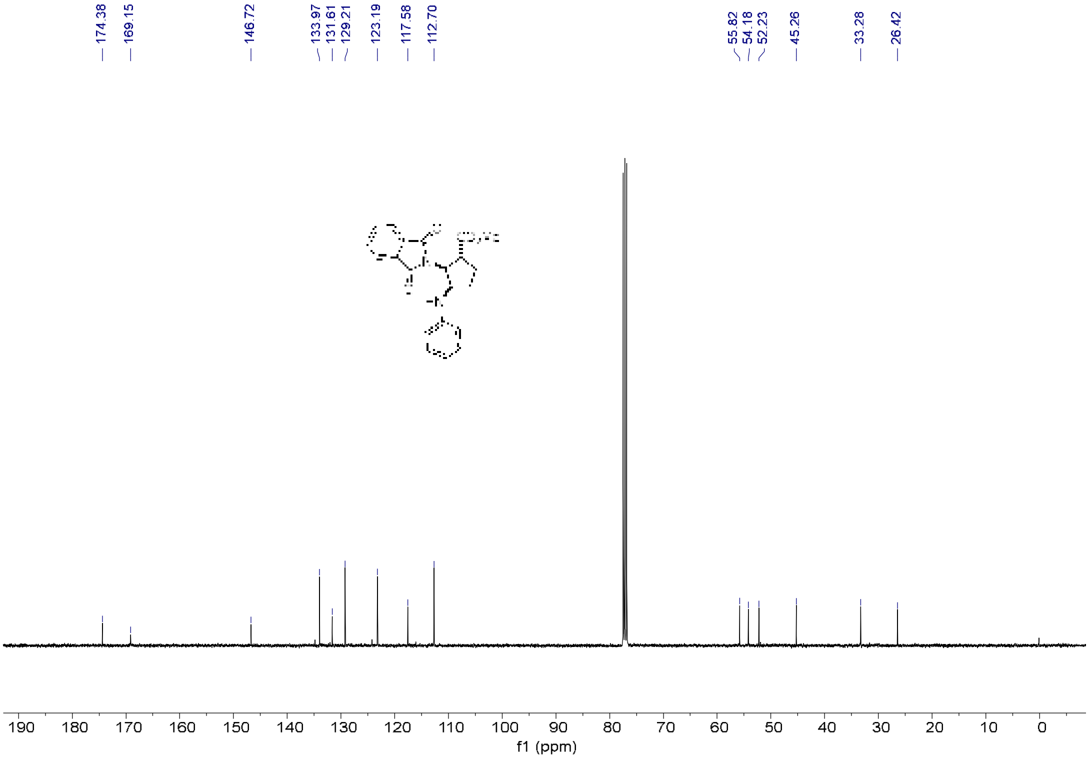
^{13}C NMR (101 MHz, CDCl$_3$) of **3ad**



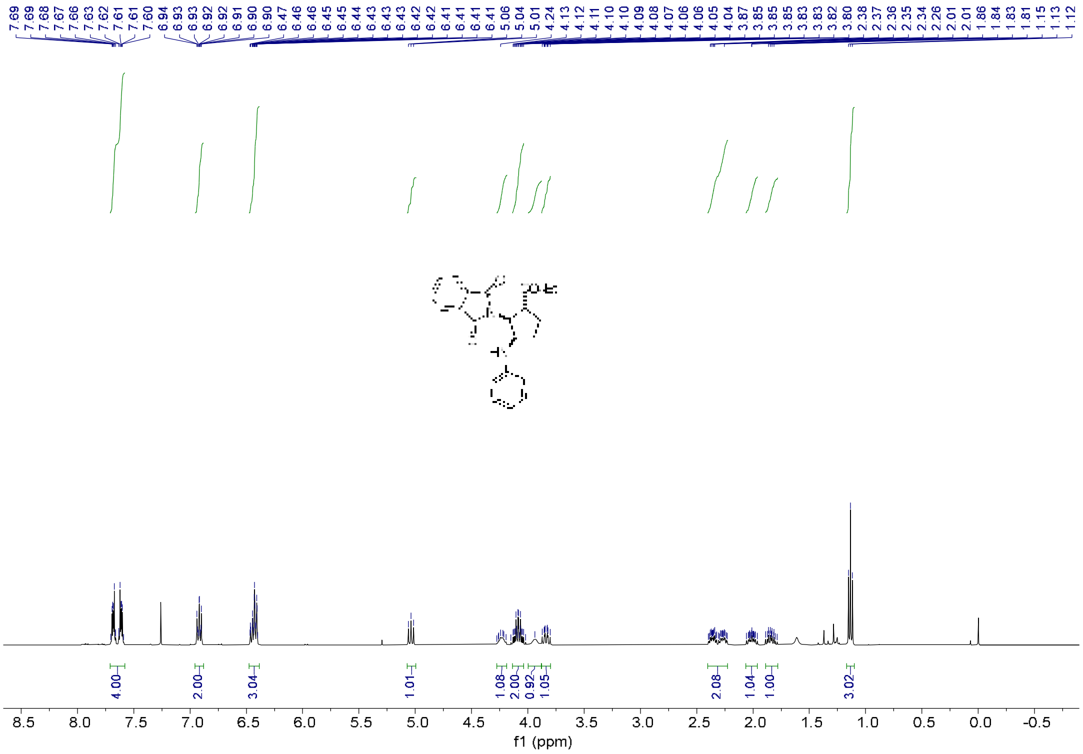
^{1}H NMR (400 MHz, CDCl$_3$) of **3ae**



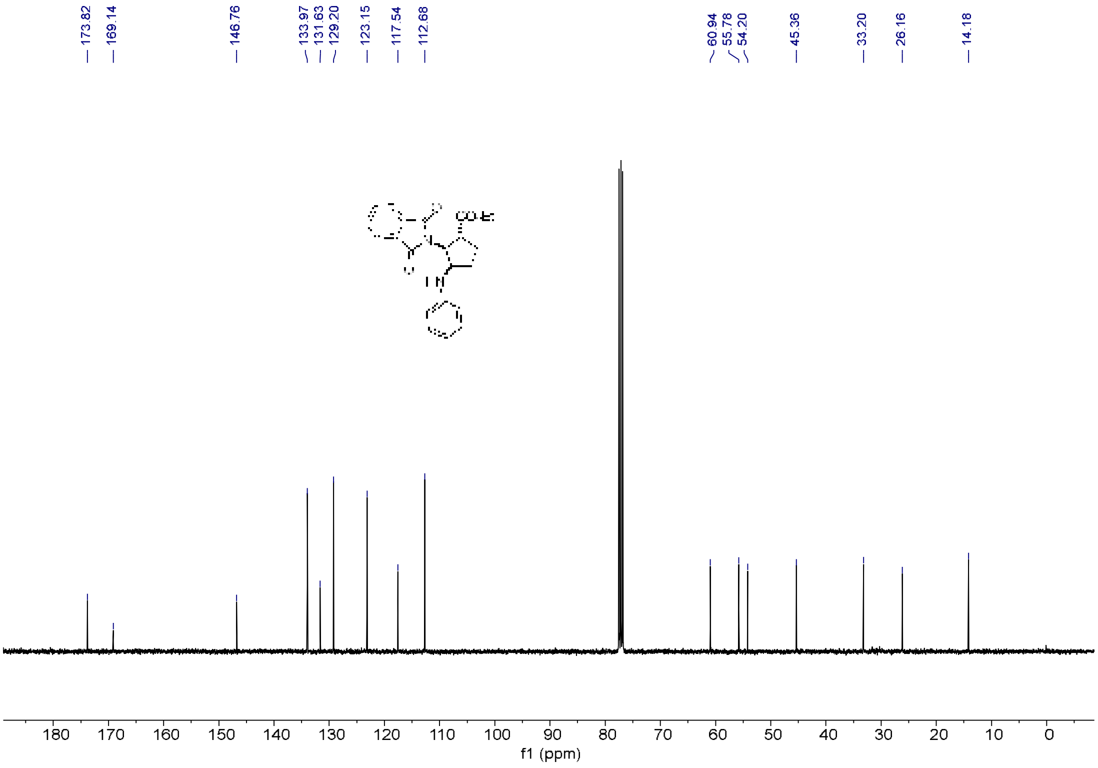
^{13}C NMR (101 MHz, CDCl$_3$) of **3ae**



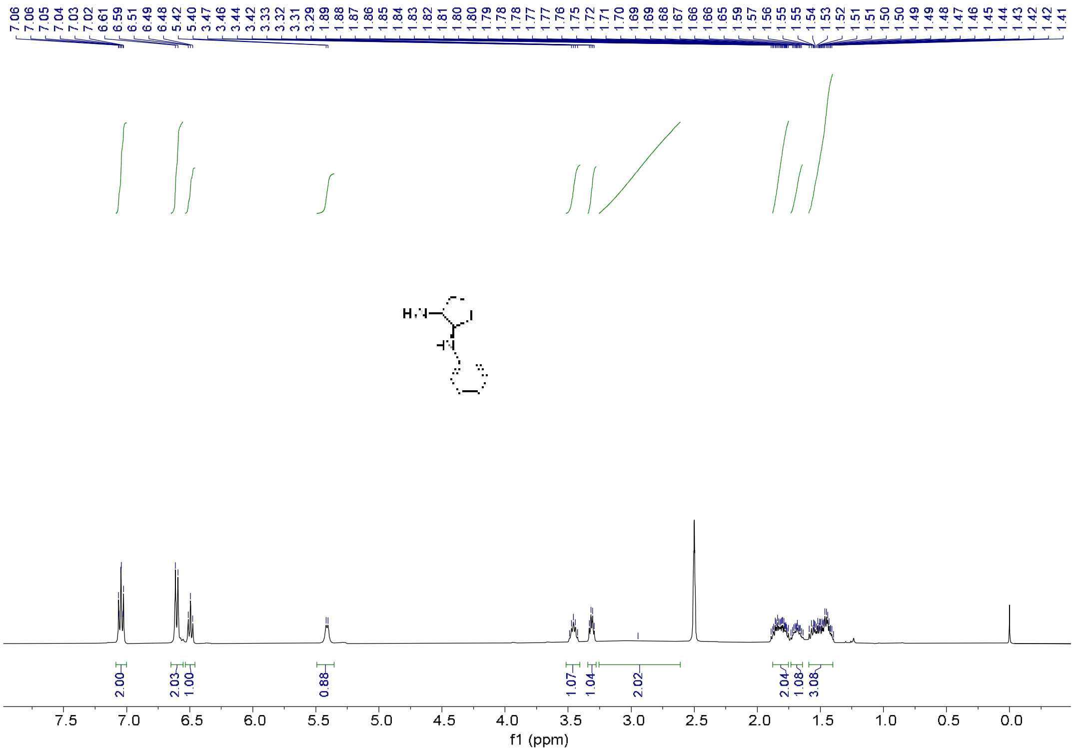
^{1}H NMR (400 MHz, CDCl$_3$) of **3af**



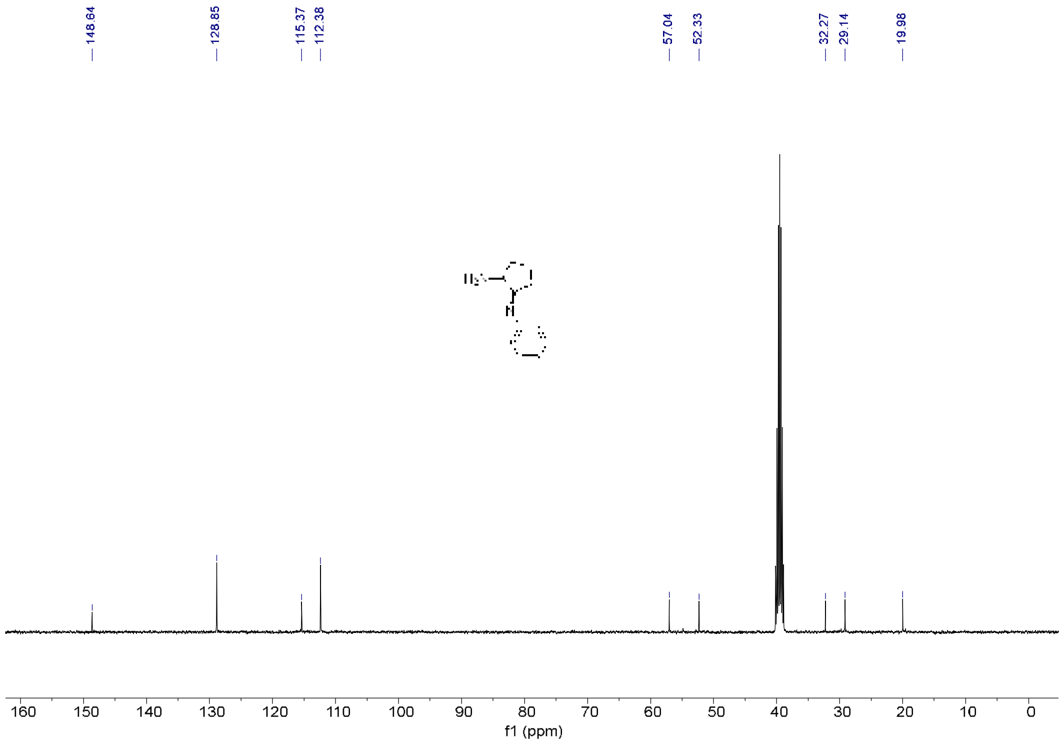
^{13}C NMR (101 MHz, CDCl$_3$) of **3af**



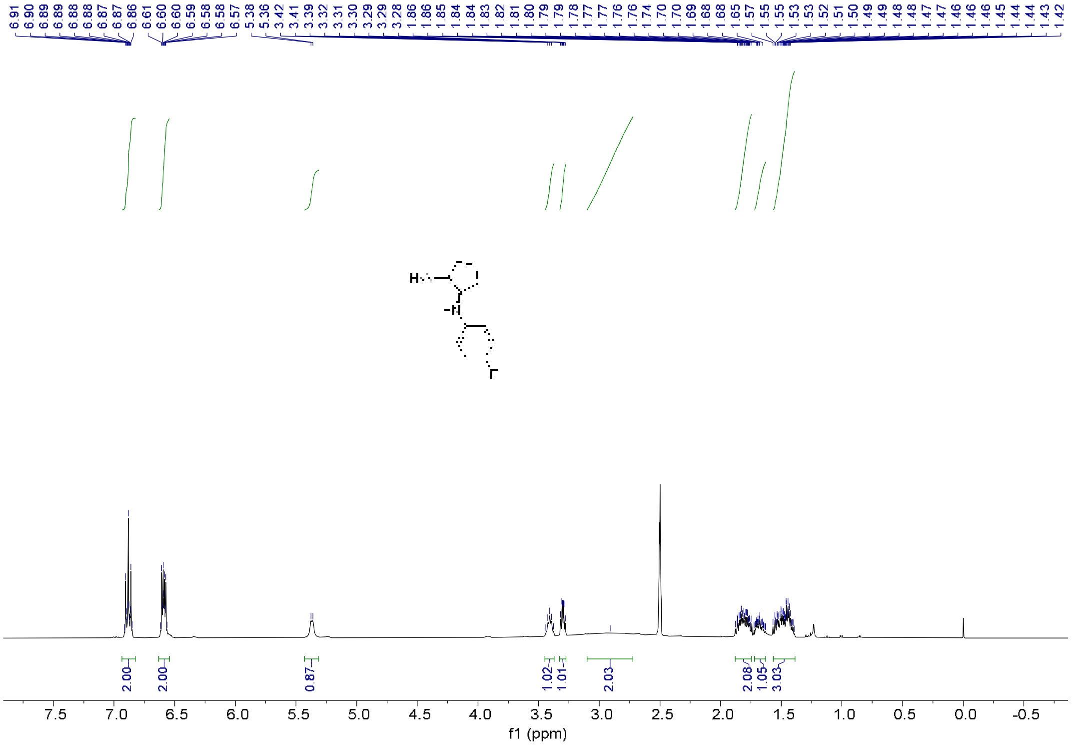
^{1}H NMR (400 MHz, DMSO-d_6) of **4a**



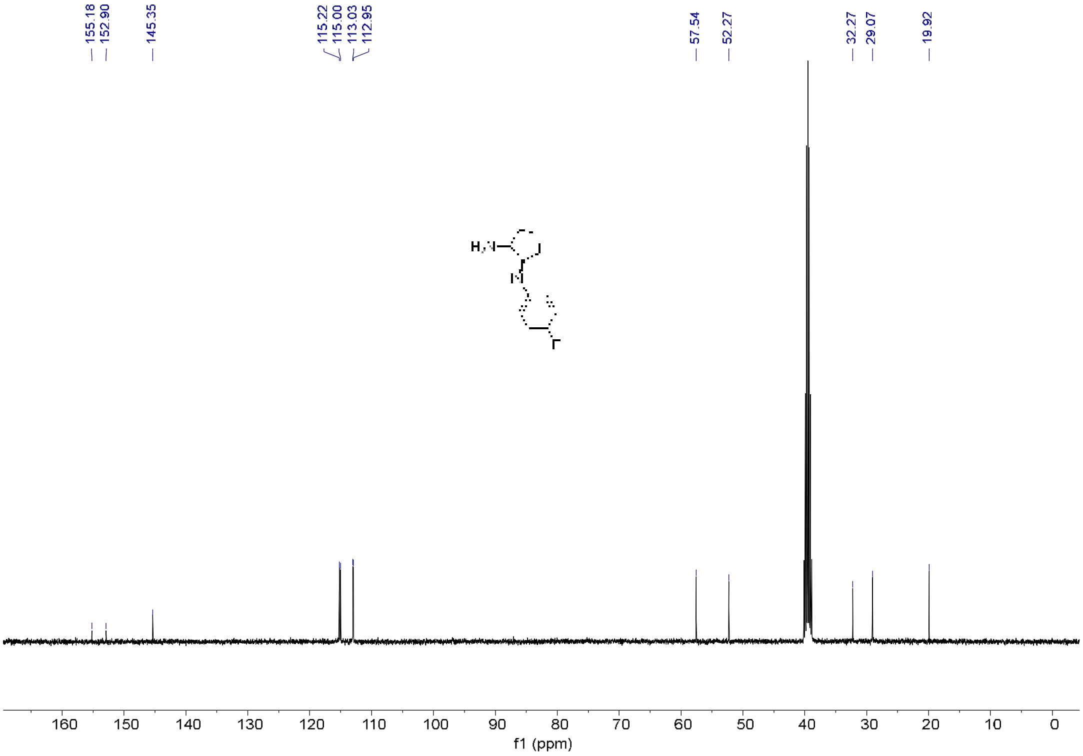
^{13}C NMR (101 MHz, DMSO-d_6) of **4a**



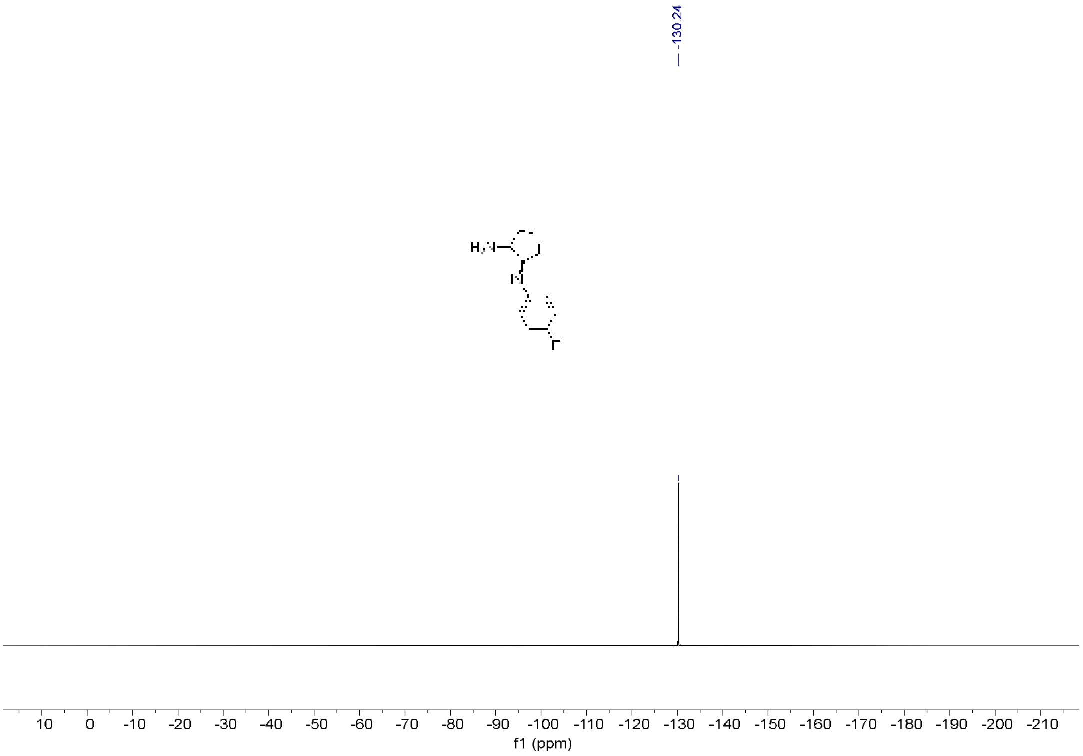
^{1}H NMR (400 MHz, DMSO-d_6) of **4b**



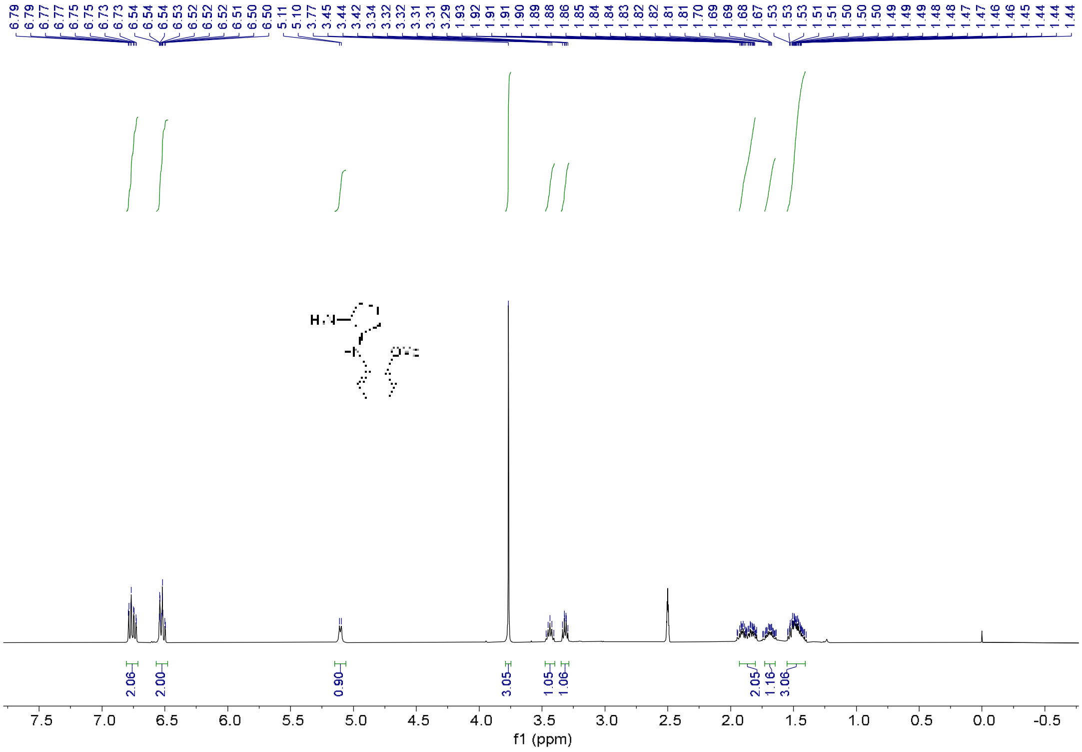
^{13}C NMR (101 MHz, DMSO-d_6) of **4b**



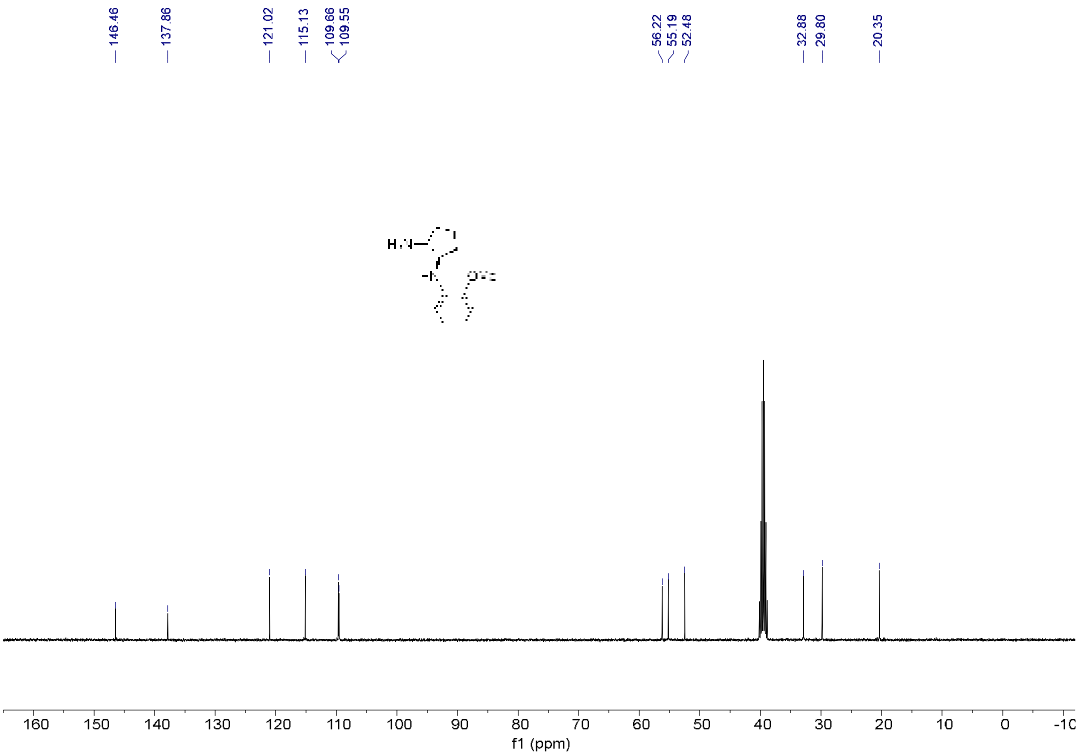
^{19}F NMR (376 MHz, DMSO-d_6) of **4b**



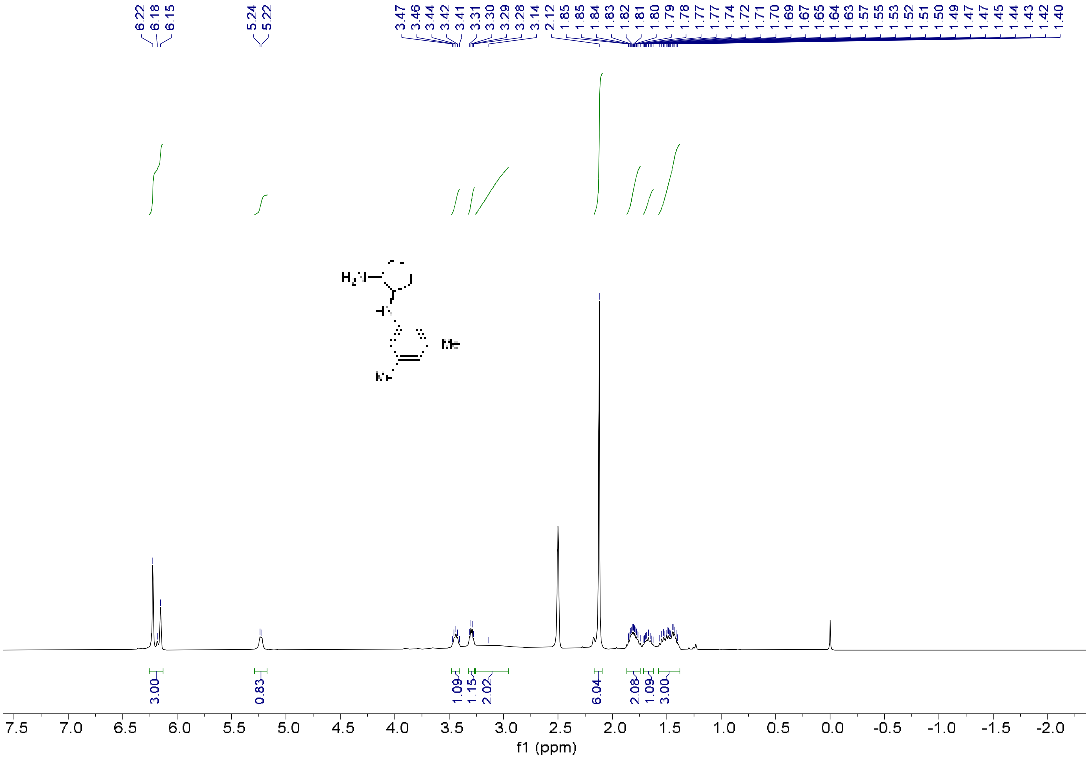
^{1}H NMR (400 MHz, DMSO-d_6) of **4c**



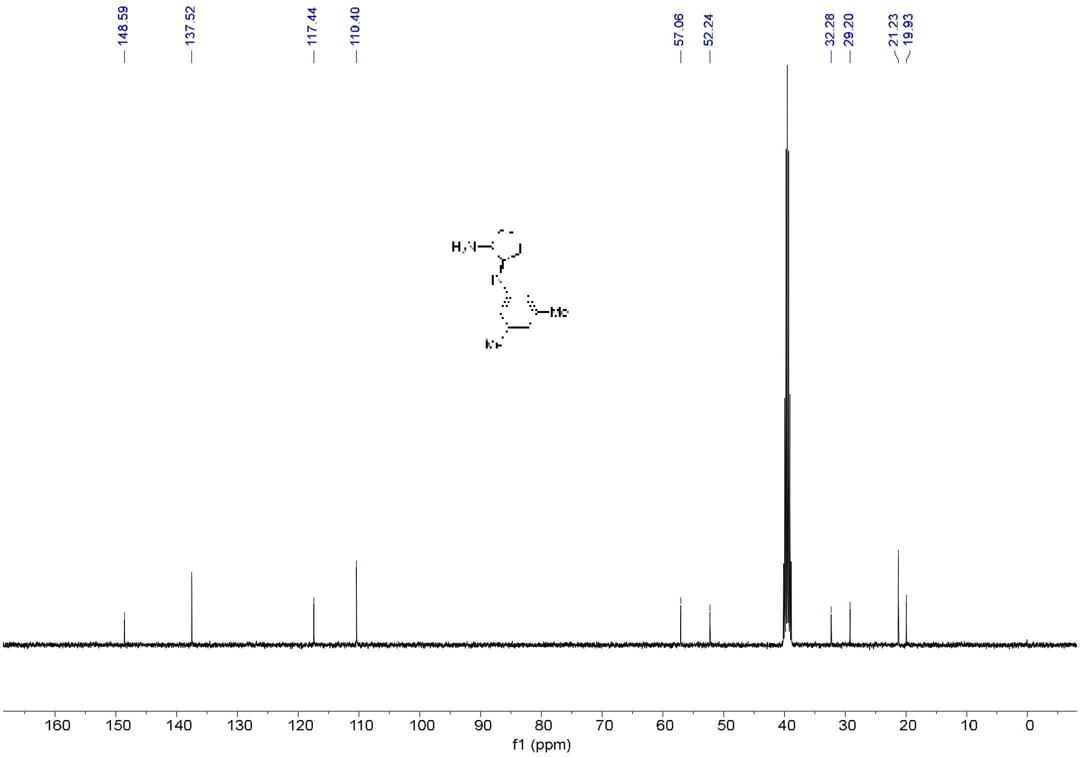
^{13}C NMR (101 MHz, DMSO-d_6) of **4c**



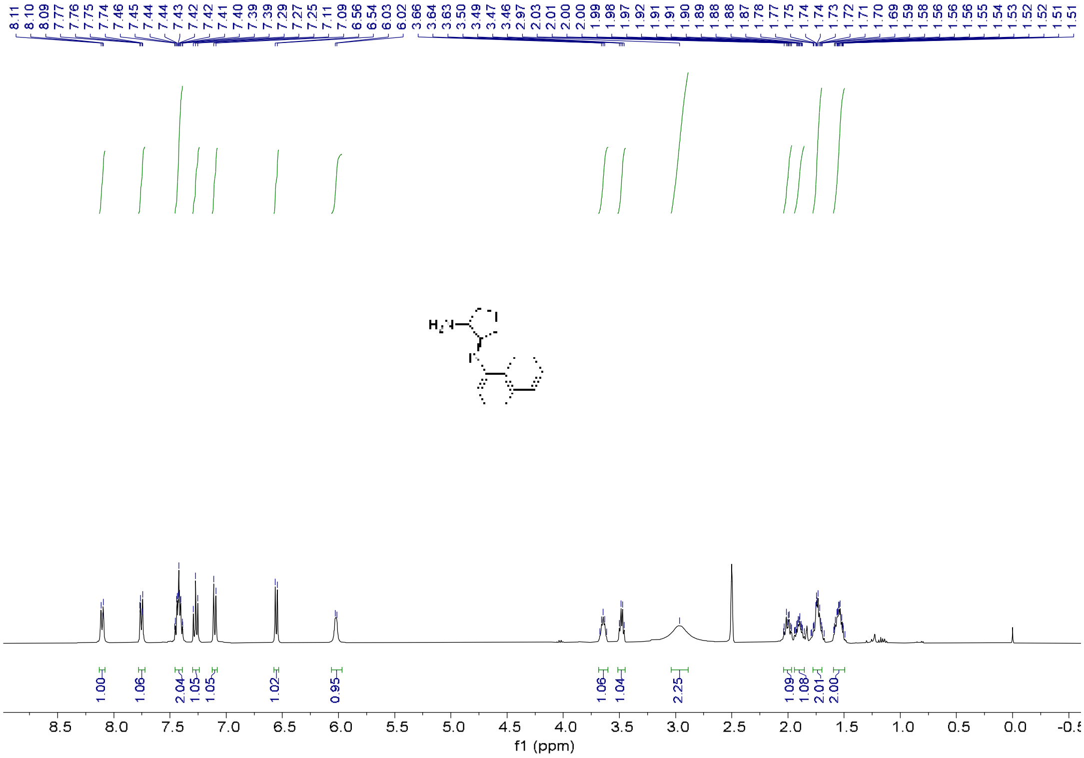
^{1}H NMR (400 MHz, DMSO-d_6) of **4d**



^{13}C NMR (101 MHz, DMSO-d_6) of **4d**



^{1}H NMR (400 MHz, DMSO-d_6) of **4e**



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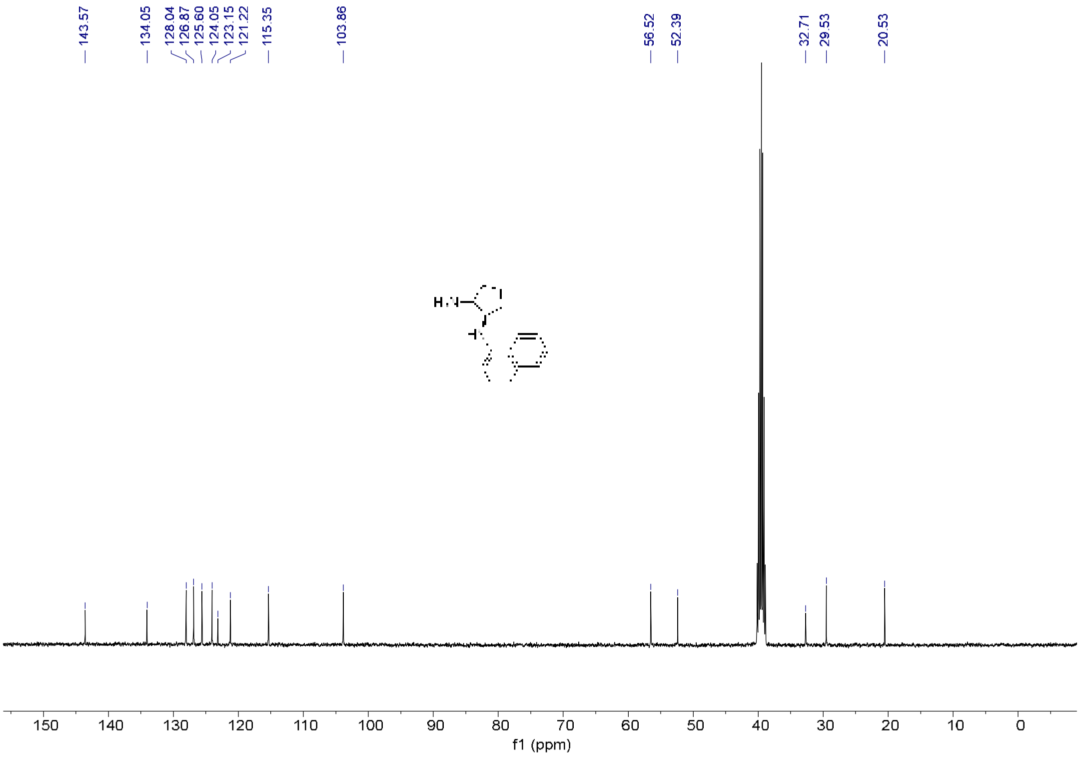

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