Electronic Supplementary Information for:

Visible-Light-Induced Dearomative 1,4-Carbamoylpyridinylation of Nonactivated Naphthalenes

Cheng-An Jin,[a,b] Hao Liu,[a] Bo-Wen Xie,[a] Ren-Xiao Liang*[a] and Yi-Xia Jia*[c]

[a] *College of Chemical Engineering, State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, China.*

[b] *College of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing, 312000, China.*

[c] *School of Chemistry and Chemical Engineering, Tianjin University of Technology*

**E-mails: liangrx@zjut.edu.cn; yxjia@zjut.edu.cn*

1. General information

Unless otherwise noted, commercial reagents were used without additional purification. Anhydrous DCM, MeCN, and DMF were freshly distilled over CaH_2. All the reactions were carried out under argon atmosphere using standard Schlenk technique unless otherwise noted. NMR spectra were acquired on Brucker AVANCE 400 or 500 MHz spectrometer for ^{1}H, ^{13}C and ^{19}F, respectively. Chemical shifts are reported in ppm (δ) from TMS with the solvent resonance as internal standard and reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), etc. HRMS data were recorded on a Thermo Scientific LTQ Orbitrap XL or Agilent 6210 TOF LC/MS mass spectrometer. GCMS data were recorded on an Agilent 7890B-5977B GC/MS mass spectrometer. UV-vis absorption spectra were measured using a Shimadzu UV-2600 spectrophotometer. Fluorescence quenching experiments were conducted on a Hitachi F-4500 fluorescence spectrometer. Single crystal X-ray diffraction analysis was performed using a Bruker D8 Venture. Melting points were determined in open capillaries without correction. Reactions were monitored by thin-layer chromatography on silica gel plates (60 F-254) under ultraviolet light (254 and 365 nm) or by dipping the plates in $KMnO_4$ stain. Flash column chromatography was performed using silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents for purification purposes.

2. Photo-catalyzed reaction apparatus

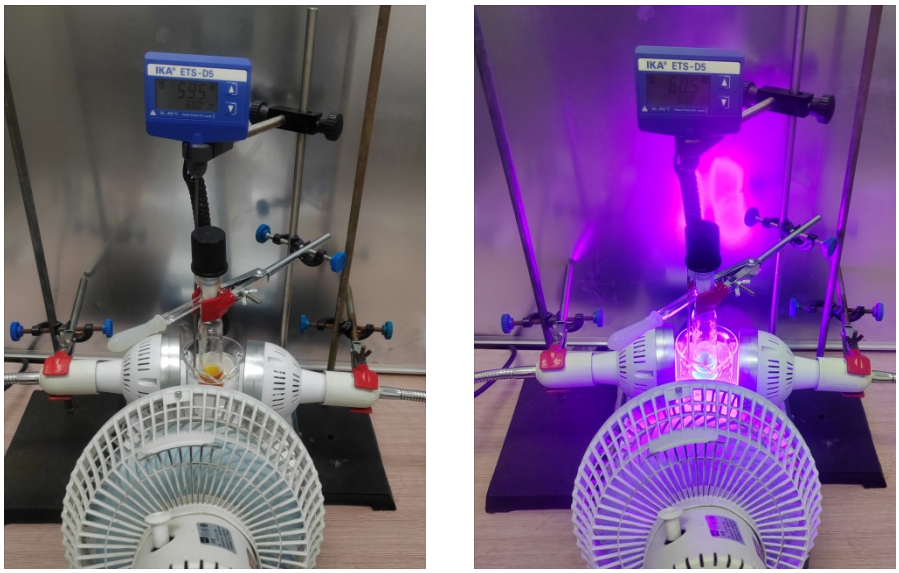


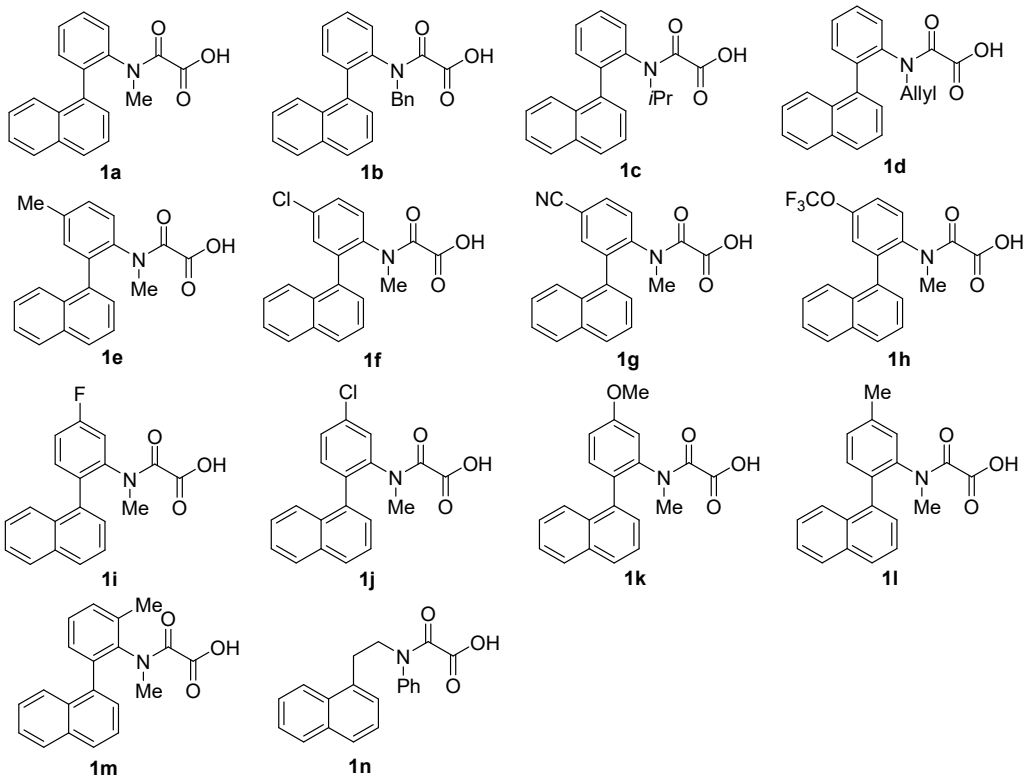
Figure S1. The setting-up reaction.

The photo-catalyzed reaction apparatus was shown in **Figure S1.** LEDs Manufacturer: Xuzhou Ai Jia electronic technology Co. LTD. Relevant parameters of LEDs: a) broadband source: λ = 400–410 nm; b) peak wavelength of light source: λ_{max} = 403.7 nm; c) half width: Δ λ_d = 13.8 nm; d) power P = 198.6 mW. Material of the irradiation vessel: borosilicate reaction tube (25 mL) and quartz beaker (100 mL). Heating medium and method: immerse the reaction tube in a quartz beaker filled with silicone oil and conduct the photocatalytic reaction at 60 °C. Distance between light source and irradiation vessel: ~3 cm. No filter was used. The small electric fan is used to cool the lamp.

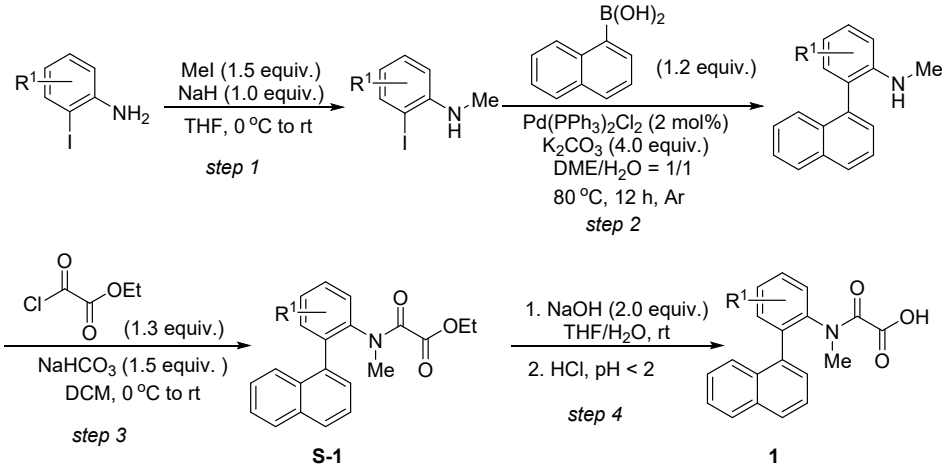
3. Synthesis and characterization of starting materials

3.1 Procedures for the preparation of oxamic acids

The oxamic acids used in this work:



Procedure A : For synthesis of 1a, 1e–1m



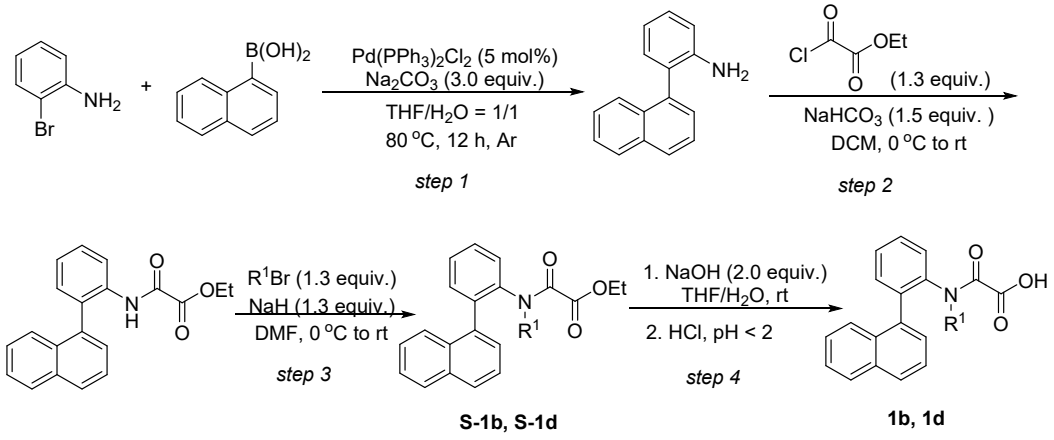
Step 1:[1] To a solution of 2-iodoanilines (10 mmol) in dry THF (0.4 M) at 0 °C was added NaH (60% in mineral oil, 1.0 equiv.) in portions. After stirring at 0 °C for 30 min, MeI (1.5 equiv.) was added drop-wise to the reaction mixture, which was allowed to stir at room temperature. When the reaction was completed (monitored by TLC), the reaction system was quenched by water and extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography flash chromatography on silica gel eluenting with petroleum ether to afford the related 2-iodo-*N*-methylanilines.

Step 2:[2] A 100 mL Schlenk tube with a magnetic stir bar was charged with K_2CO_3 (4.0 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), 2-iodo-*N*-methylanilines (1.0 equiv.), 1-naphthylboronic acid (1.2 equiv.). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, distilled water and DME were introduced into the tube via syringe under argon atmosphere. The resulting mixture was heated at 80 °C (oil bath) for 12 h. Afterwards the resulting solution was filtered through a plug of Celite and the residue was washed with ethyl acetate (30 mL). The filtrate was extracted with ethyl acetate (2 × 30 mL). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography eluting with ethyl acetate and petroleum ether to afford the corresponding *N*-methyl-2-(naphthalen-1-yl)aniline derivatives.

Step 3:[3] To a stirred solution of *N*-methyl-2-(naphthalen-1-yl)aniline derivatives (1.0 equiv.) and $NaHCO_3$ (1.5 equiv.) in DCM at 0 °C was added the solution of ethyl 2-chloro-2-oxoacetate (1.3 equiv.) in DCM (10 mL) dropwise. The reaction mixture was stirred at room temperature overnight. When the reaction was completed, 20 mL H_2O was added. The layers were separated, and the aqueous layer was re-extracted with DCM (2 × 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography flash chromatography on silica gel eluting with petroleum ether/EtOAc (v/v = 10:1) to afford to the key intermediates **S-1a**, and **S-1e** to **S-1m**.

Step 4: To a solution of oxamic esters **S-1** (1.0 equiv) in THF, was added NaOH (2.0 equiv.), dissolved in deionized water (~1:1 THF/water). The resulting mixture was stirred at room temperature for 2~5 hours until the starting ester was consumed according to TLC analysis. The reaction mixture was then diluted with an equivalent amount of deionized water and EtOAc. The layers were separated, and the aqueous layer was washed with EtOAc (× 2) before being acidified to pH < 2 by the drop-wise addition of 3 M aqueous HCl. Thereafter, the aqueous layer was re-extracted with EtOAc for three times, the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the appropriate oxamic acids **1**, which was used without further purification.

Procedure B: For synthesis of 1b and 1d



Step 1:[4] A 100 mL Schlenk tube with a magnetic stir bar was charged with Na_2CO_3 (30 mmol, 3.0 equiv.), $Pd(PPh_3)_2Cl_2$ (5 mol%), 2-bromoaniline (10 mmol, 1.0 equiv.),

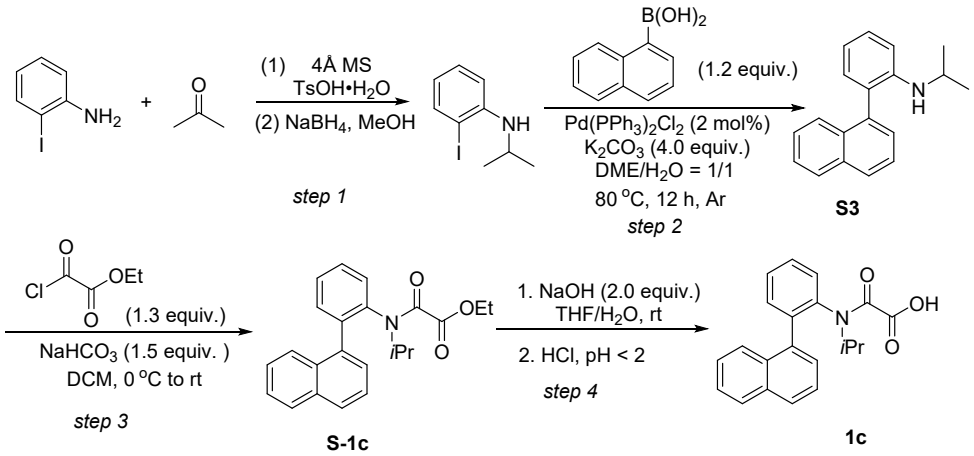
and 1-naphthylboronic acid (15 mmol, 1.5 equiv.). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, distilled water (15 mL) and THF (15 mL) were introduced into the tube via syringe under argon atmosphere. The mixture was heated at 80 °C (oil bath) for 12 h. Afterwards the resulting solution was filtered through a plug of Celite and the residue was washed with ethyl acetate (30 mL). The filtrate was extracted with ethyl acetate (2 × 30 mL). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford the corresponding 2-(naphthalen-1-yl)aniline.

Step 2:[3] To a stirred solution of 2-(naphthalen-1-yl)aniline (1.0 equiv.) and $NaHCO_3$ (1.5 equiv.) in DCM (10 mL) at 0 °C was added the solution of ethyl 2-chloro-2-oxoacetate (1.3 equiv.) in DCM (10 mL) dropwise. The resulting mixture was stirred at room temperature overnight. When the reaction was completed, 20 mL H_2O was added. The layers were separated, and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure to get the ethyl 2-((2-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate, and it was directly used in the next step without further purification.

Step 3: A round-bottom flask was charged with oxamic esters **S1** (1.0 equiv.) and DMF (0.2 M). The reaction mixture was allowed to stir at an ice bath for 15 min, NaH (60%, 1.3 equiv.) was then added in portions, and stirring for additional 30 min. Subsequently, BnBr or allyl bromide (1.3 equiv.) was added to the reaction mixture dropwise. The resulting reaction mixture was allowed to stir at room temperature. Upon reaction completion, the reaction was quenched with NH_4Cl solution. The mixture was extracted with ethyl acetate three times. The combined organic phases were washed with saturated NaCl solution, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by column chromatography to afford the key intermediates **S-1b** or **S-1d**.

Step 4: To a solution of oxamic esters **S-1b** or **S-1d** (1.0 equiv.) in THF, was added NaOH (2.0 equiv.), dissolved in deionized water (~1:1 THF/water). The resulting mixture was stirred at room temperature for 2~5 h until the starting ester was completely consumed according to TLC analysis. The reaction mixture was then diluted with an equivalent amount of deionized water and EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc before being acidified to pH < 2 by the dropwise addition of 3 M aqueous HCl. Thereafter, the aqueous layer was extracted with EtOAc (× 3), the combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to give the appropriate oxamic acids which was used without further purification.

Procedure C: For synthesis of 1c



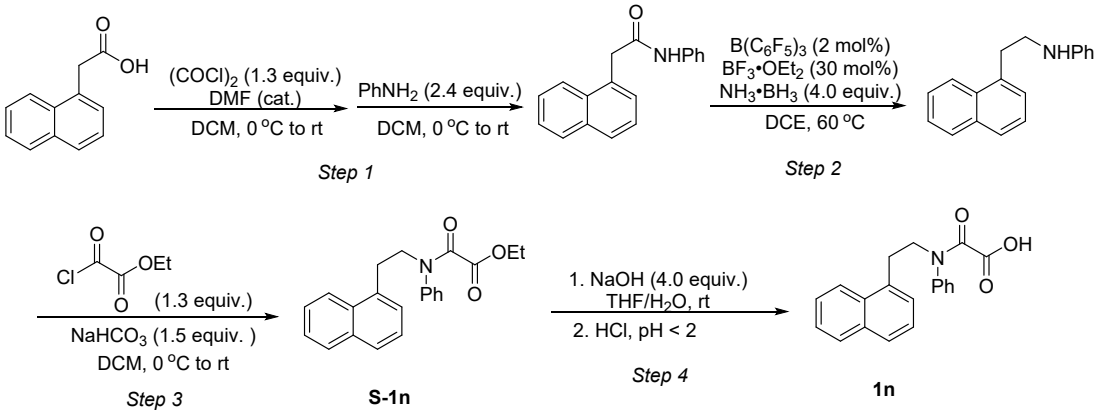
Step 1:[5] To a solution of 2-iodoaniline (1.0 equiv.) in dry acetone (5 mL/mmol) in a round bottom flask were added TsOH·H_2O (0.2 equiv.) and 4 Å molecular sieves (2.0 g/mmol). The resulting mixture was stirred at 50 °C (oil bath) for 48 h. After cooling to room temperature, the mixture was filtered and the filtrate was evaporated to give the crude imine. It was solubilized in methanol and cool to 0 °C. $NaBH_4$ (3.0 equiv.) was added and stirred overnight. 1 M aqueous NaOH solution was added and stirred for 10 min. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using ethyl acetate and petroleum ether mixture as an eluent to afford the 2-iodo-*N*-isopropylaniline.

Step 2:[1] A 100 mL Schlenk tube with a magnetic stir bar was charged with K_2CO_3 (4.0 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), 2-iodo-*N*-isopropylaniline (1.0 equiv.), and 1-naphthylboronic acid (1.2 equiv). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, DME/H_2O (1:1, ~0.3 M) was introduced into the tube via syringe under argon atmosphere. The mixture was heated at 80 °C (oil bath) for 12 h. Afterwards the resulting solution was filtered through a plug of Celite and the residue was washed with ethyl acetate (30 mL). The filtrate was extracted with ethyl acetate (2 × 30 mL). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography as eluting with ethyl acetate and petroleum ether to afford *N*-isopropyl-2-(naphthalen-1-yl)aniline.

Step 3:[3] To a stirred solution of *N*-isopropyl-2-(naphthalen-1-yl)aniline (1.0 equiv.) and $NaHCO_3$ (1.5 equiv.) in DCM (0.5 M) at 0 °C was added the solution of ethyl 2-chloro-2-oxoacetate (1.3 equiv.) in DCM (0.5 M) dropwise. The resulting mixture was stirred at room temperature overnight. When the reaction was completed, 20 mL H_2O was added. The layers were separated, and the aqueous layer was re-extracted with DCM (2 × 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified with column chromatography to afford the key intermediates **S-1c**.

Step 4: To a solution of oxamic esters **S-1c** (1.0 equiv.) in THF, was added NaOH (2.0 equiv.), dissolved in deionized water (~1:1 THF/water). The resulting mixture was stirred at room temperature for 5 hours until the starting ester was completely consumed according to TLC analysis. The reaction mixture was then diluted with an equivalent amount of deionized water and EtOAc. The layers were separated, and the aqueous layer was washed with EtOAc (× 2) before being acidified to pH < 2 by the dropwise addition of 3 M aqueous HCl. Thereafter, the aqueous layer was re-extracted with EtOAc (× 3), the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the oxamic acid **1c** which was used without further purification.

Procedure D: For synthesis of 1n



Step 1:[6] To a 100 mL flask equipped with a stirring bar were charged with the 2-(naphthalen-1-yl)acetic acid (5.0 mmol, 1.0 equiv.) and DCM (10 mL). Oxalyl chloride (6.5 mmol,1.3 equiv.) was added dropwise at 0 °C, followed by two drops of DMF as the catalyst. The mixture was slowly warmed up to room temperature and stirred for additional 2 h. Then, the solvent was removed under reduced pressure and the residue was dissolved in 10 mL DCM. The aniline (12 mmol, 2.4 equiv.) was added drop-wise at 0 °C and the mixture was slowly warmed to room temperature. After stirring for 2 h, 25 mL H_2O was added, and the mixture was extracted by EtOAc (3 × 25 mL). The combined organic phase was washed with brine (25 mL) and dried over Na_2SO_4. After removal of Na_2SO_4 and solvent, the residue was purified by silica gel chromatography eluting with hexane/acetone to give the 2-(naphthalen-1-yl)- *N*-phenylacetamide.

Step 2:[7] To a Schlenk tube were charged with 2-(naphthalen-1-yl)-*N*-phenylacetamide (1.0 equiv.), $B(C_6F_5)_3$ (2 mol %), $NH_3{\cdot}BH_3$ (4.0 equiv.), $BF_3{\cdot}OEt_2$ (30 mol%), and DCE (0.17 M). Then the reaction mixture was stirred at 60 °C (oil bath) for 24 h. After cooling to ambient temperature, the mixture was diluted with EtOAc. Then aqueous NaOH was added to the reaction mixture, which was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4, then filtered and evaporated under reduced pressure. After the removal of volatile materials by rotary evaporation, the resultant mixture was purified by silica gel column chromatography using a mixture of ethyl acetate and petroleum ether to give the product *N*-(2-(naphthalen-1-yl)ethyl)aniline.

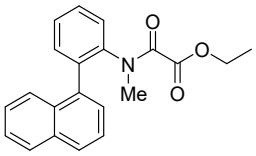
Step 3:[3] To a stirred solution of *N*-(2-(naphthalen-1-yl)ethyl)aniline (1.0 equiv.) and $NaHCO_3$ (1.5 equiv.) in DCM (0.5 M) at 0 °C, ethyl 2-chloro-2-oxoacetate (1.3 equiv.) in DCM (0.5 M) was added drop-wise to the mixture. The reaction mixture was stirred at room temperature overnight until the aniline was consumed according to TLC analysis. After the reaction completed, 20 mL H_2O was added. The layers were separated, and the aqueous layer was re-extracted with DCM (2 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by column chromatography to afford the key intermediates **S-1n**.

Step 4: To a solution of oxamic esters **S-1n** (1.0 equiv.) in THF, was added NaOH (2.0 equiv.), dissolved in deionized water (~2:1 THF/water). The resulting mixture was stirred at room temperature for about 5 h until the starting ester was consumed according to TLC analysis. The reaction mixture was then diluted with an equivalent amount of deionized water and EtOAc. The layers were separated, and the aqueous layer was washed with EtOAc (× 2) before being acidified to pH < 2 by the drop-wise addition of 3 M aqueous HCl. Thereafter, the aqueous layer was re-extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the oxamic acid **1n** which was used without further purification.

*Of note, to display clear peaks in the spectra, the characteristics for the corresponding esters **S-1** of the acid substrates **1** were provided.*

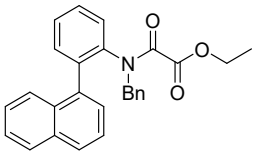
*Moreover, since several isomers (theoretically four isomers) could be obtained for synthesis of the naphthalene substrates due to C-C and/or C-N bond atropisomerisms, numerous peaks were observed in the NMR spectra. In order to better present the characterization of these compounds, all peaks of ^{1}H NMR spectra were recorded with the isomeric ratios indicated (e.g. major isomer:other isomers = 3.8:1 for compound **S-1a**), while the major peaks of ^{13}C NMR spectra were recorded as the NMR data.*

ethyl 2-(methyl(2-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate (S-1a)



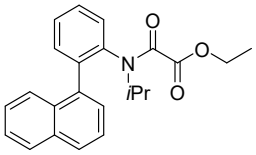
General procedure A was followed. White solid, Mp = 89-91 °C; 89% yield (for the last step); Major isomer : other isomers = 3.8:1. *All peaks were recorded for the ^{1}H NMR spectrum*: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 13.5, 8.2 Hz, 2.00H), 7.78 (q, *J* = 6.1 Hz, 0.90H), 7.62 (d, *J* = 8.6 Hz, 0.90H), 7.58 – 7.36 (m, 6.25H), 7.36 – 7.28 (m, 0.90H), 4.17 (q, *J* = 7.2 Hz, 1.73H), 3.99 (dq, *J* = 14.7, 8.3 Hz, 0.14H), 3.77 – 3.60 (m, 0.13H), 2.98 (s, 0.38H), 2.67 (s, 0.24H), 2.56 (s, 2.38H), 1.22 (t, *J* = 7.1 Hz, 0.24H), 1.15 (t, *J* = 7.1 Hz, 2.38H), 1.00 (t, *J* = 7.3 Hz, 0.38H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum*: ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.8, 161.9, 140.3, 137.4, 135.0, 133.9, 133.2, 131.8, 128.6, 128.5, 128.4, 128.1, 127.3, 126.5, 126.4, 125.9, 125.8, 125.0, 61.9, 35.0, 13.8. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{19}NNaO_3^+$ ([M+Na]$^+$): 356.1257, found 356.1265.

ethyl 2-(benzyl(2-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate (S-1b)



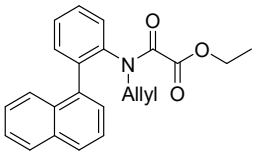
General procedure B was followed. White solid, Mp = 170-172 °C; 64% yield (for the last step); Major isomer : other isomers = 10:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.88 (m, 3.10H), 7.70 (dd, *J* = 8.9, 3.6 Hz, 1.00H), 7.60 (td, *J* = 7.6, 2.7 Hz, 1.00H), 7.59 – 7.47 (m, 2.09H), 7.48 – 7.39 (m, 2.16H), 7.26 – 7.15 (m, 4.07H), 7.01 – 6.91 (m, 2.67H), 5.15 (dd, *J* = 14.6, 3.9 Hz, 0.09H), 5.02 (dd, *J* = 14.6, 4.2 Hz, 0.91H), 4.17 (tq, *J* = 7.1, 3.4 Hz, 1.81H), 4.02 (td, *J* = 7.1, 3.4 Hz, 0.12H), 3.93 (dd, *J* = 14.2, 4.3 Hz, 0.11H), 3.67 (ddd, *J* = 10.6, 7.2, 3.2 Hz, 0.10H), 3.12 (ddd, *J* = 14.5, 4.8, 2.1 Hz, 0.92H), 1.13 (t, *J* = 7.2 Hz, 2.76H), 1.02 (td, *J* = 7.2, 2.4 Hz, 0.24H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.7, 162.2, 137.7, 137.5, 135.5, 134.8, 134.1, 133.2, 131.7, 130.4, 129.0, 128.8, 128.5, 128.4, 128.3, 128.1, 127.6, 127.5, 126.6, 126.0, 125.9, 125.0, 61.9, 49.8, 13.8. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{23}NNaO_3^+$ ([M+Na]$^+$): 432.1570, found 432.1578.

ethyl 2-(isopropyl(2-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate (S-1c)



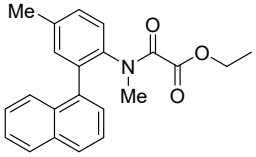
General procedure C was followed. Colorless oil; 63% yield (for the last step); Major isomer : other isomers = 14:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 7.2, 1.2 Hz, 0.90H), 7.94 – 7.85 (m, 2.17H), 7.62 (dd, *J* = 8.4, 1.3 Hz, 1.00H), 7.56 (dd, *J* = 8.3, 7.1 Hz, 1.00H), 7.52 – 7.45 (m, 3.00H), 7.45 – 7.38 (m, 2.20H), 7.31 – 7.26 (m, 1.00H), 4.37 – 4.26 (m, 0.13H), 4.12 (qd, *J* = 7.1, 2.4 Hz, 1.87H), 3.80 – 3.64 (m, 0.07H), 3.55 – 3.27 (m, 1H), 1.12 (t, *J* = 7.1 Hz, 2.81H), 1.05 (t, *J* = 7.2 Hz, 0.19H), 0.85 (d, *J* = 6.8 Hz, 2.81H), 0.79 (d, *J* = 6.7 Hz, 0.19H), 0.54 (d, *J* = 7.0 Hz, 2.80H), 0.31 (d, *J* = 6.7 Hz, 0.20H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.8, 162.1, 139.6, 138.4, 135.6, 133.9, 133.4, 132.1, 130.2, 128.6, 128.4, 128.3, 128.1, 128.0, 126.4, 125.7, 125.6, 125.0, 61.6, 54.8, 18.8, 18.5, 13.8. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{23}NNaO_3^+$ ([M+Na]$^+$): 384.1570, found 384.1580.

ethyl 2-(allyl(2-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate (S-1d)



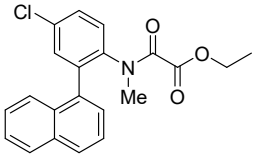
General procedure B was followed. White solid, Mp = 119-120 °C; 72% yield (for the last step); Major isomer : other isomers = 9:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.79 (m, 2.00H), 7.79 – 7.73 (m, 1.00H), 7.51 (d, *J* = 8.5 Hz, 0.98H), 7.48 – 7.36 (m, 2.96H), 7.35 – 7.33 (m, 2.46H), 7.30 (td, *J* = 7.4, 2.1 Hz, 1.03H), 7.21 – 7.15 (m, 1.03H), 5.78 – 5.56 (m, 0.10H), 5.47 – 5.39 (m, 0.91H), 4.86 (d, *J* = 10.1 Hz, 0.10H), 4.82 (dd, *J* = 10.2, 1.4 Hz, 0.90H), 4.67 – 4.55 (m, 0.90H), 4.41 (dd, *J* = 14.9, 5.0 Hz, 0.10H), 4.18 (dt, *J* = 14.8, 5.1Hz, 1.81H), 4.07 (q, *J* = 6.7 Hz, 1.81H), 3.90 (dq, *J* = 10.8, 7.1 Hz, 0.10H), 3.70 – 3.46 (m, 0.12H), 3.33 (dd, *J* = 15.0, 7.4 Hz, 0.10H), 2.74 – 2.60 (m, 0.90H), 1.04 (t, *J* = 7.1 Hz, 2.70H), 0.91 (t, *J* = 7.1 Hz, 0.30H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.7, 161.8, 138.0, 137.6, 134.8, 134.0, 133.2, 131.8, 131.0, 130.0, 128.7, 128.4, 128.2, 127.4, 126.4, 125.9, 125.8, 125.0, 119.2, 61.9, 49.3, 13.8. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{21}NNaO_3^+$ ([M+Na]$^+$): 382.1414, found 382.1422.

ethyl 2-(methyl(4-methyl-2-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate (S-1e)



General procedure A was followed. Yellow oil; 88% yield (for the last step); Major isomer : other isomers = 4:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 14.7, 7.5 Hz, 2.09H), 7.81 (dd, *J* = 7.2, 1.3 Hz, 0.71H), 7.70 – 7.63 (m, 0.86H), 7.52 (dd, *J* = 8.3, 7.0 Hz, 0.85H), 7.50 – 7.44 (m, 1.19H), 7.42 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 0.97H), 7.33 – 7.26 (m, 0.65H), 7.26 – 7.18 (m, 2.51H), 4.18 (q, *J* = 7.1 Hz, 1.72H), 4.03 (qd, *J* = 7.2, 2.8 Hz, 0.19H), 3.70 (dq, *J* = 10.7, 7.1 Hz, 0.12H), 2.95 (s, 0.38H), 2.67 (s, 0.21H), 2.55 (s, 2.35H), 2.41 (s, 0.36H), 2.40 (s, 2.55H), 2.33 (s, 0.07H), 1.24 – 1.12 (m, 2.57H), 1.02 (t, *J* = 7.1 Hz, 0.49H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.9, 162.0, 138.4, 137.7, 137.1, 135.2, 133.9, 133.7, 131.9, 129.1, 128.6, 128.3, 127.9, 127.3, 126.4, 125.9, 125.8, 125.2, 61.8, 35.0, 21.1, 13.9. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{21}NNaO_3^+$ ([M+Na]$^+$): 370.1414, found 370.1423.

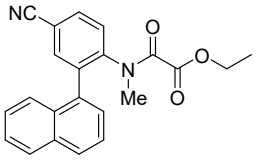
ethyl 2-((4-chloro-2-(naphthalen-1-yl)phenyl)(methyl)amino)-2-oxoacetate (S-1f)



General procedure A was followed. Yellow oil; 86% yield (for the last step); Major isomer : other isomers = 3.3:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H

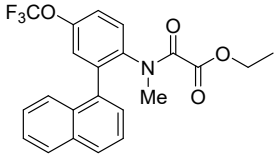
NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.73 (m, 1.98H), 7.71 – 7.62 (m, 0.78H), 7.52 – 7.46 (m, 0.88H), 7.44 – 7.31 (m, 4.26H), 7.28 (dd, *J* = 8.4, 2.5 Hz, 0.92H), 7.16 (d, *J* = 8.5 Hz, 1.00H), 4.09 (q, *J* = 7.2 Hz, 1.70H), 3.87 (dq, *J* = 10.5, 7.0 Hz, 0.15H), 3.53 (dq, *J* = 10.9, 7.2 Hz, 0.15H), 2.85 (s, 0.40H), 2.54 (s, 0.30H), 2.42 (s, 2.30H), 1.17 – 1.01 (m, 2.60H), 0.88 (t, *J* = 7.2 Hz, 0.40H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.5, 161.6, 139.2, 139.0, 134.2, 133.8, 133.7, 133.0, 131.5, 129.4, 128.9, 128.8, 128.5, 127.3, 126.8, 126.1, 125.7, 124.6, 62.1, 35.1, 13.9. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{18}ClNNaO_3^+$ ([M+Na]$^+$): 390.0867, found 390.0877.

ethyl 2-((4-cyano-2-(naphthalen-1-yl)phenyl)(methyl)amino)-2-oxoacetate (S-1g)



General procedure A was followed. Yellow solid, Mp = 117-119 °C; 76% yield (for the last step); Major isomer : other isomers = 2.3:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 2.06H), 7.81 – 7.66 (m, 2.90H), 7.58 – 7.35 (m, 5.09H), 4.25 – 4.10 (m, 1.67H), 3.89 (dt, *J* = 10.2, 5.1 Hz, 0.17H), 3.52 (t, *J* = 8.9 Hz, 0.17H), 2.99 (s, 0.50H), 2.65 (s, 0.40H), 2.55 (s, 2.10H), 1.23 – 1.12 (m, 2.51H), 0.94 (t, *J* = 7.1 Hz, 0.50H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.0, 161.1, 144.7, 138.7, 136.7, 133.9, 132.8, 132.3, 131.2, 129.4, 129.0, 128.9, 127.4, 127.2, 126.4, 125.7, 124.2, 117.8, 112.4, 62.4, 35.1, 13.8. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{18}N_2NaO_3^+$ ([M+Na]$^+$): 381.1210, found 381.1219.

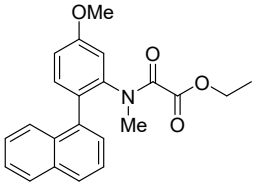
ethyl 2-(methyl(2-(naphthalen-1-yl)-4-(trifluoromethoxy)phenyl)amino)-2-oxoacetate (S-1h)



General procedure A was followed. Colorless oil; 75% yield (for the last step); Major isomer : other isomers = 3.1:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.84 (m, 2.03H), 7.79 (dd, *J* = 7.2, 1.2 Hz, 0.90H), 7.62 – 7.50 (m, 2.88H), 7.50 – 7.44 (m, 1.51H), 7.39 (d, *J* = 8.6 Hz, 0.98H), 7.34 (d, *J* = 2.8 Hz, 1.06H), 7.32 – 7.27 (m, 0.90H), 4.26 – 4.16 (m, 1.72H), 3.97 (dq, *J* = 10.9, 7.1 Hz, 0.13H), 3.62 (dq, *J* = 10.7, 7.2 Hz, 0.13H), 3.02 (s, 0.40H), 2.68 (s, 0.33H), 2.56 (s, 2.27H), 1.22 (t, *J* = 7.2 Hz, 0.34H), 1.17 (t, *J* = 7.1 Hz, 2.32H), 0.98 (t, *J* = 7.2 Hz, 0.38H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.5, 161.7, 148.5, 139.6, 139.0, 133.9, 133.5, 131.5, 129.7, 129.1, 128.8, 127.2, 126.9, 126.1, 125.7, 125.4, 124.4, 120.6,120.4 (q, *J* = 258.3 Hz), 62.1, 34.9, 13.6. *Peaks of the major isomer were recorded for the ^{19}F NMR spectrum:* ^{19}F NMR (471 MHz, Chloroform-*d*) δ -57.9.

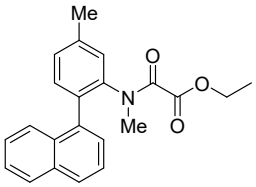
HRMS *m/z* (ESI+): Calculated for $C_{22}H_{18}F_3NNaO_4^+$ ([M+Na]$^+$): 440.1080, found 440.1089.

ethyl 2-((5-methoxy-2-(naphthalen-1-yl)phenyl)(methyl)amino)-2-oxoacetate (S-1i)



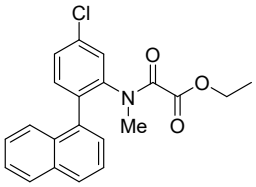
General procedure A was followed. White solid, Mp = 109-110 °C; 71% yield (for the last step); Major isomer : other isomers = 3.3:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 19.8, 8.3 Hz, 2.09H), 7.75 (dt, *J* = 7.2, 1.7 Hz, 0.77H), 7.65 (d, *J* = 8.4 Hz, 0.86H), 7.56 – 7.46 (m, 1.97H), 7.43 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1.10H), 7.34 (d, *J* = 8.4 Hz, 1.05H), 7.01 (dd, *J* = 8.5, 2.7 Hz, 0.97H), 6.97 – 6.93 (m, 0.20H), 6.88 (t, *J* = 2.4 Hz, 0.81H), 4.21 (qd, *J* = 7.2, 1.6 Hz, 1.70H), 4.05 (q, *J* = 7.1 Hz, 0.11H), 3.97 (dt, *J* = 13.9, 8.4 Hz, 0.15H), 3.92 – 3.85 (m, 2.92H), 3.80 (s, 0.12H), 3.63 (d, *J* = 7.9 Hz, 0.13H), 3.35 (s, 0.12H), 2.99 (s, 0.36H), 2.66 (s, 0.22H), 2.55 (s, 2.30H), 1.22 (t, *J* = 7.1 Hz, 0.30H), 1.18 (t, *J* = 7.1 Hz, 2.26H), 1.04 (t, *J* = 7.1 Hz, 0.15H), 0.99 (t, *J* = 7.1 Hz, 0.36H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.8, 162.0, 159.4, 141.0, 134.8, 133.92, 133.90, 132.1, 129.2, 128.6, 128.2, 127.6, 126.3, 125.8, 125.8, 125.1, 113.9, 113.6, 61.9, 55.6, 34.9, 13.8. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{21}NNaO_4^+$ ([M+Na]$^+$): 386.1363, found 386.1370.

ethyl 2-(methyl(5-methyl-2-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate (S-1j)



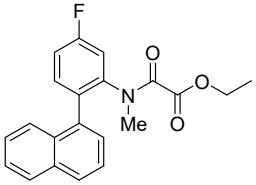
General procedure A was followed. Colorless oil; 76% yield (for the last step); Major isomer : other isomers = 3.2:1. *All peaks were recorded for the ^{1}H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.84 (m, 2.08H), 7.78 (dd, *J* = 7.2, 1.3 Hz, 0.78H), 7.68 – 7.62 (m, 0.85H), 7.56 – 7.45 (m, 2.01H), 7.42 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 1.01H), 7.37 – 7.26 (m, 2.12H), 7.16 (d, *J* = 1.8 Hz, 0.80H), 4.26 – 4.14 (m, 1.70H), 4.07 – 3.93 (m, 0.20H), 3.69 – 3.57 (m, 0.12H), 3.34 (s, 0.10H), 2.99 (s, 0.36H), 2.67 (s, 0.25H), 2.55 (s, 2.29H), 2.47 (s, 0.25H), 2.45 (s, 0.35H), 2.43 (s, 2.28H), 2.35 (s, 0.10H), 1.22 (t, *J* = 7.1 Hz, 0.22H), 1.15 (t, *J* = 7.1 Hz, 2.30H), 1.00 (dt, *J* = 9.2, 7.1 Hz, 0.48H). *Peaks of the major isomer were recorded for the ^{13}C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.8, 162.0, 140.1, 138.6, 135.1, 134.2, 133.9, 133.0, 132.0, 129.0, 128.6, 128.2, 127.4, 126.4, 125.8, 125.8, 125.1, 61.8, 34.9, 21.0, 13.8. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{21}NNaO_3^+$ ([M+Na]$^+$): 370.1414, found 370.1423.

ethyl 2-((5-chloro-2-(naphthalen-1-yl)phenyl)(methyl)amino)-2-oxoacetate (S-1k)



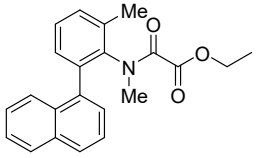
General procedure A was followed. White solid, Mp = 104-105 °C; 85% yield (for the last step); Major isomer : other isomers = 3:1. *All peaks were recorded for the [1]H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.84 (m, 1.98H), 7.83 – 7.72 (m, 0.90H), 7.59 (d, *J* = 8.3 Hz, 0.86H), 7.55 – 7.39 (m, 4.26H), 7.39 – 7.31 (m, 1.73H), 4.33 – 4.12 (m, 1.70H), 4.07 – 3.96 (m, 0.15H), 3.70 – 3.56 (m, 0.15H), 2.96 (s, 0.43H), 2.67 (s, 0.30H), 2.54 (s, 2.23H), 1.30 – 1.14 (m, 2.55H), 1.01 (t, *J* = 7.1 Hz, 0.45H). *Peaks of the major isomer were recorded for the [13]C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.5, 161.6, 141.4, 136.0, 134.2, 133.9, 133.8, 133.7, 131.6, 128.8, 128.7, 128.5, 128.3, 127.4, 126.7, 126.1, 125.8, 124.7, 62.2, 34.9, 13.9. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{18}ClNNaO_3^+$ ([M+Na]$^+$): 390.0867, found 390.0875.

ethyl 2-((5-fluoro-2-(naphthalen-1-yl)phenyl)(methyl)amino)-2-oxoacetate (S-1l)



General procedure A was followed. Colorless oil; 88% yield (for the last step); Major isomer : other isomers = 3:1. *All peaks were recorded for the [1]H NMR spectrum:* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 12.8, 8.5 Hz, 2.00H), 7.82 – 7.70 (m, 0.90H), 7.58 (d, *J* = 8.4 Hz, 0.86H), 7.49 (ddd, *J* = 15.3, 8.0, 4.2 Hz, 1.93H), 7.45 – 7.36 (m, 2.11H), 7.18 (tdd, *J* = 9.4, 6.5, 4.0 Hz, 1.27H), 7.09 (dd, *J* = 8.9, 2.7 Hz, 0.75H), 4.28 – 4.12 (m, 1.70H), 3.96 (dt, *J* = 14.1, 7.1 Hz, 0.15H), 3.58 (dq, *J* = 14.5, 7.2 Hz, 0.15H), 2.99 (s, 0.45H), 2.66 (s, 0.30H), 2.54 (s, 2.25H), 1.25 – 1.13 (m, 2.55H), 0.97 (t, *J* = 7.1 Hz, 0.45H). *Peaks of the major isomer were recorded for the [13]C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.4, 161.73 (d, *J* = 250.0 Hz), 161.6, 141.5 (d, *J* = 9.4 Hz), 134.4 (d, *J* = 8.8 Hz), 134.1, 133.9, 133.5 (d, *J* = 3.7 Hz), 131.9, 128.7, 128.6, 127.6, 126.6, 126.0, 125.8, 124.8, 115.6 (d, *J* = 4.6 Hz), 115.4 (d, *J* = 2.7 Hz), 62.1, 34.9, 13.8. *Peaks of the major isomer were recorded for the [19]F NMR spectrum:* ^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.3. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{18}FNNaO_3^+$ ([M+Na]$^+$): 374.1163, found 374.1171.

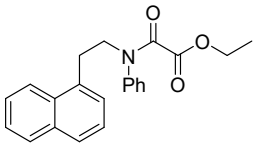
ethyl 2-(methyl(2-methyl-6-(naphthalen-1-yl)phenyl)amino)-2-oxoacetate (S-1m)



General procedure A was followed. White solid, Mp = 143-144 °C; 76% yield (for the last step); Major isomer : other isomers = 2.8:1. *All peaks were recorded for the [1]H*

NMR spectrum: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.80 (m, 2.00H), 7.75 (dd, *J* = 7.1, 1.2 Hz, 0.70H), 7.55 – 7.42 (m, 2.32H), 7.41 – 7.31 (m, 3.66H), 7.28 – 7.25 (m, 0.37H), 7.24 – 7.16 (m, 0.95H), 4.26 – 4.10 (m, 1.57H), 3.79 (dd, *J* = 10.7, 7.1 Hz, 0.21H), 3.36 (dd, *J* = 10.7, 7.2 Hz, 0.22H), 3.27 (s, 0.58H), 3.23 (s, 0.10H), 2.72 (s, 0.08H), 2.58 (s, 2.22H), 2.42 (s, 0.62H), 2.36 (s, 2.01H), 2.34 (s, 0.22H), 2.30 (s, 0.11H), 1.25 (t, *J* = 7.1 Hz, 0.24H), 1.15 (t, *J* = 7.1 Hz, 2.07H), 0.92 (t, *J* = 7.1 Hz, 0.11H), 0.77 (t, *J* = 7.2 Hz, 0.58H). *Peaks of the major isomer were recorded for the* ^{13}*C NMR spectrum:* ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.2, 161.5, 139.1, 139.0, 136.8, 135.5, 133.6, 132.3, 130.6, 130.2, 128.5, 128.4, 128.2, 127.1, 126.1, 125.8, 125.7, 125.4, 61.8, 34.9, 18.1, 13.7. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{21}NNaO_3^+$ ([M+Na]$^+$): 370.1414, found 370.1419.

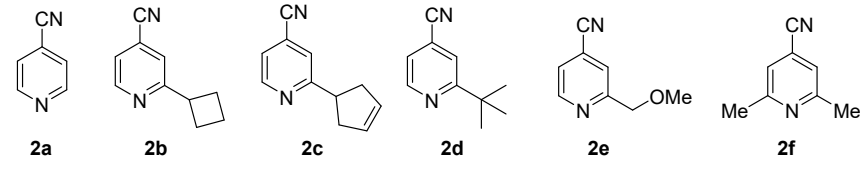
ethyl 2-((2-(naphthalen-1-yl)ethyl)(phenyl)amino)-2-oxoacetate (S-1n)



General procedure D was followed. White solid, Mp = 136-138 °C; 85% yield (for the last step); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 – 8.06 (m, 1H), 7.81 (dd, *J* = 8.03, 1.54 Hz, 1H), 7.71 (d, *J* = 8.09 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.39 – 7.32 (m, 4H), 7.29 (dd, *J* = 7.02, 1.33 Hz, 1H), 7.21 – 7.16 (m, 2H), 4.10 – 4.05 (m, 2H), 4.01 (q, *J* = 7.15 Hz, 2H), 3.42 – 3.36 (m, 2H), 0.98 (t, *J* = 7.15 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.5, 161.8, 140.3, 134.2, 133.9, 132.0, 129.6, 128.8, 128.6, 127.5, 127.4, 126.9, 126.4, 125.7, 125.5, 123.7, 61.7, 50.2, 30.9, 13.6. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{21}NNaO_3^+$ ([M+Na]$^+$): 370.1414, found 370.1423.

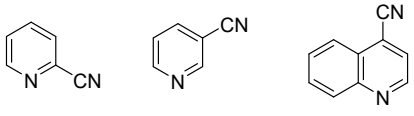
3.2 Procedure for the preparation of cyanopyridines

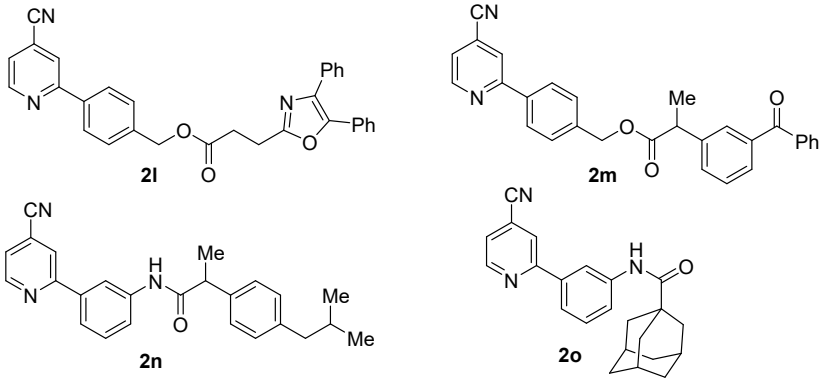
The cyanopyridines used in this work:



2a **2b** **2c** **2d** **2e** **2f** **2g** **2h** **2i** **2j** **2k**

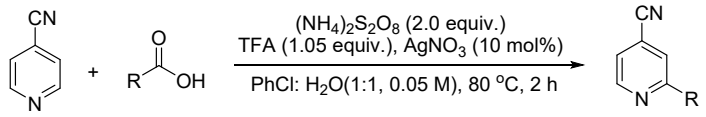
unsuccessful substrates:





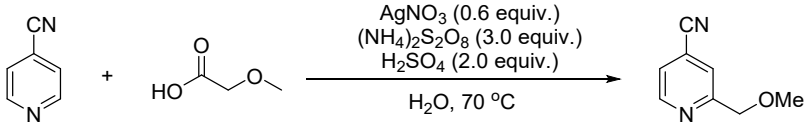
2a, **2f** and **2p-2o** were purchased from commercial sources and used without further purification.

Procedure E: For synthesis of 2b-2d



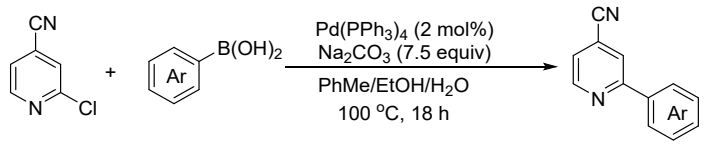
Cyanopyridines **2b-2d** were prepared according to the literature procedures[8]. To the solution of 4-cyanopyridine (1.0 equiv.) in PhCl/H_2O (1:1, 0.05 M) was added alkyl carboxylic acid (2.8 equiv.), $(NH_4)_2S_2O_8$ (2.0 equiv.), TFA (1.05 equiv.), and $AgNO_3$ (10 mol%). The resulting mixture was stirred at 80 °C in an oil bath for 2 h. Then the reaction mixture was cooled to 0 °C and NaOH (8 M) was added slowly until pH 9~10. The mixture was filtered through a pad of Celite and extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residue was purified by flash chromatography on silica gel to afford corresponding cyanopyridines.

Procedure F: For synthesis of 2e



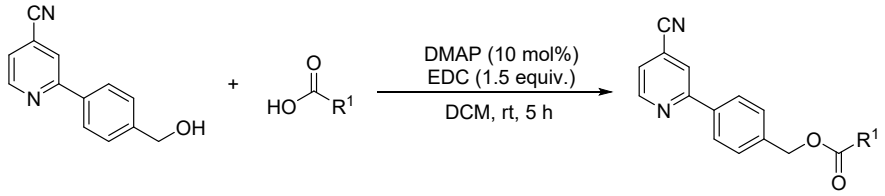
2-(methoxymethyl)isonicotinonitrile **2e** was prepared according to the literature procedure [9]. To the solution of 4-cyanopyridine (10 mmol) in H_2O (15 mL) was added 2-methoxyacetic acid (1.0 equiv.), sulfuric acid (2.0 equiv.), and $AgNO_3$ (0.6 equiv.). Then, slowly add a solution of ammonium persulfate (3.0 equiv.) in 10 mL H_2O. The resulting mixture was stirred at 70 °C in an oil bath, and monitored by GCMS. After most of the 4-cyanopyridine was vanished, the reaction mixture was cooled to 0 °C, then neutralize the reaction with sodium bicarbonate and extract the reaction mixture with ethyl acetate (3×30 mL). Combine the organic extracts and wash with water (2×25 mL).The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residue was purified by flash chromatography on silica gel to afford the 2-(methoxymethyl)isonicotinonitrile **2e**.

Procedure G: For synthesis of 2g-2j



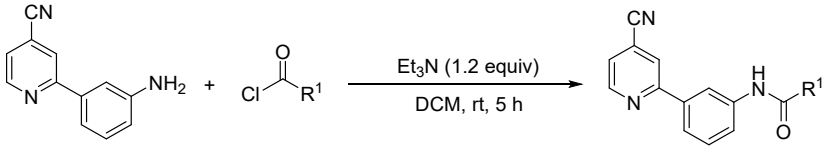
According to the previous reference[10], a 100 mL Schlenk tube with a magnetic stir bar was charged with 2-chloroisonicotinonitrile (5.0 mmol, 1.0 equiv.), aryl boronic acids (1.2 equiv.), $Pd(PPh_3)_4$ (2 mol%), and Na_2CO_3 (7.5 equiv.). Then, the tube was evacuated and back-filled with argon for three times. Degassed toluene (15 mL, 0.33 M), EtOH (3.9 mL, 1.33 M) and H_2O (15 mL, 0.33 M) were added via syringe under argon atmosphere. The resulting mixture was stirred vigorously at 100 ºC (oil bath) for 18 h under argon atmosphere and then allowed to cool to room temperature. The crude reaction mixture was poured into a separatory funnel containing brine (50 mL) and extracted with EtOAc (3 × 25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel diluting with petroleum ether/ethyl acetate to afford the corresponding cyanopyridines.

Procedure H: For synthesis of 2l and 2m



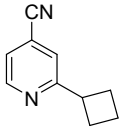
A mixture of carboxylic acid compound (2.5 mmol), DMAP (10 mol%), and 2-(hydroxymethyl)isonicotinonitrile (2.5 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature for 5 h. The resulting mixture was added to H_2O. The organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated reduced pressure. The residue was purified by column chromatography on silica gel diluting with petroleum ether/ethyl acetate to give the corresponding cyanopyridines.

Procedure I: For synthesis of 2n and 2o



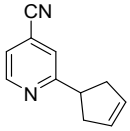
A mixture of 2-(hydroxymethyl)isonicotinonitrile (2.5 mmol) and NEt_3 (1.2 equiv.) in dry CH_2Cl_2 (10 mL) was stirred in an ice-water bath. The resulting mixture was added to acyl chloride dropwise. The solution was allowed to room temperature and stirred for 3 h. Then, the reaction system was diluted with 30 mL of CH_2Cl_2, washed with H_2O, and then the organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel diluting with petroleum ether/ethyl acetate to give the corresponding cyanopyridines.

2-cyclobutylisonicotinonitrile (2b)



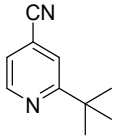
General procedure E was followed. Yellow oil; 52% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 5.0 Hz, 1H), 7.33 (s, 1H), 7.28 (d, *J* = 4.6 Hz, 1H), 3.66 (p, *J* = 8.7 Hz, 1H), 2.38 – 2.21 (m, 4H), 2.11 – 1.95 (m, 1H), 1.92 – 1.82 (m, 1H). Known compound, the NMR data is consistent with literature report.[8]

2-(cyclopent-3-en-1-yl)isonicotinonitrile (2c)



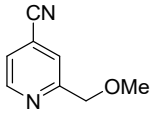
General procedure E was followed. Yellow oil; 30% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 5.0 Hz, 1H), 7.41 (s, 1H), 7.32 (dd, *J* = 5.0, 1.5 Hz, 1H), 5.76 (s, 2H), 3.69 (tt, *J* = 9.3, 6.3 Hz, 1H), 2.91 – 2.81 (m, 2H), 2.63 – 2.54 (m, 2H). Known compound, the NMR data is consistent with literature report. [8]

2-(tert-butyl)isonicotinonitrile (2d)



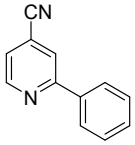
General procedure E was followed. Yellow oil; 62% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (dt, *J* = 4.9, 1.0 Hz, 1H), 7.56 (t, *J* = 1.2 Hz, 1H), 7.33 (dd, *J* = 4.9, 1.4 Hz, 1H), 1.38 (s, 9H). Known compound, the NMR data is consistent with literature report. [11]

2-(methoxymethyl)isonicotinonitrile (2e)



General procedure F was followed. Yellow oil; 32% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.66 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.40 (ddd, *J* = 5.0, 1.6, 0.8 Hz, 1H), 4.60 (s, 2H), 3.49 (s, 3H). Known compound, the NMR data is consistent with literature report. [9]

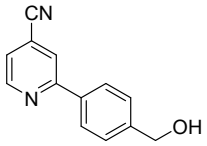
2-phenylisonicotinonitrile (2g)



General procedure G was followed. White solid, Mp = 76-77 °C; 75% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (dd, *J* = 5.0, 1.0 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.97

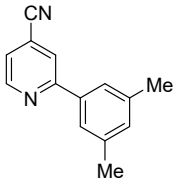
(t, *J* = 1.2 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.47 (dd, *J* = 5.0, 1.4 Hz, 1H). Known compound, the NMR data is consistent with literature report.[12]

2-(4-(hydroxymethyl)phenyl)isonicotinonitrile (2h)



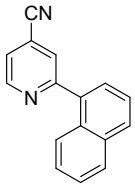
General procedure G was followed. White solid, Mp = 99-100 °C; 68% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (dd, *J* = 7.4, 4.2 Hz, 1H), 8.02 – 7.87 (m, 3H), 7.54 – 7.36 (m, 3H), 4.73 (s, 2H), 2.88 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.4, 150.6, 143.3, 136.3, 127.4, 127.1, 123.2, 122.1, 121.2, 116.7, 64.5. HRMS *m/z* (ESI+): Calculated for $C_{13}H_{11}N_2O^+$ ([M+H]$^+$) 211.0866, found 211.0874.

2-(3,5-dimethylphenyl)isonicotinonitrile (2i)



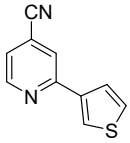
General procedure G was followed. Yellow solid, Mp = 74-75 °C; 60% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.76 (dd, *J* = 5.03, 0.96 Hz, 1H), 7.85 (t, *J* = 1.21 Hz, 1H), 7.52 (d, *J* = 1.63 Hz, 2H), 7.35 (dd, *J* = 5.01, 1.45 Hz, 1H), 7.05 (s, 1H), 2.33 (s, 6H). Known compound, the NMR data is consistent with literature report.[13]

2-(naphthalen-1-yl)isonicotinonitrile (2j)



General procedure G was followed. Yellow solid, Mp = 81-82 °C; 72% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (dd, *J* = 5.0, 1.0 Hz, 1H), 8.08 – 7.87 (m, 3H), 7.83 (t, *J* = 1.2 Hz, 1H), 7.64 – 7.48 (m, 5H). Known compound, the NMR data is consistent with literature report.[12]

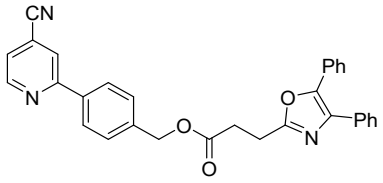
2-(thiophen-3-yl)isonicotinonitrile (2k)



General procedure G was followed. Yellow solid, Mp = 94-96 °C; 60% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.96 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.77 (dd, *J* = 1.4, 1.0 Hz, 1H), 7.63 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.41 (dd, *J* = 5.1,

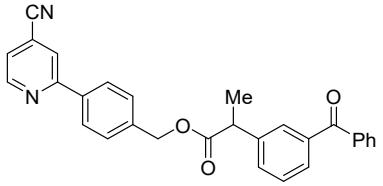
3.0 Hz, 1H), 7.34 (dd, *J* = 5.0, 1.4 Hz, 1H). Known compound, the NMR data is consistent with literature report.[14]

4-(4-cyanopyridin-2-yl)benzyl 3-(4,5-diphenyloxazol-2-yl)propanoate (2l)



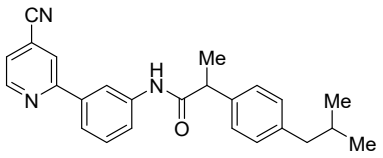
General procedure H was followed. White solid, Mp = 101-102 °C; 87% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.81 (t, *J* = 1.2 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.59 – 7.51 (m, 2H), 7.49 – 7.26 (m, 9H), 5.24 (s, 2H), 3.23 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 161.6, 158.1, 150.6, 145.5, 138.0, 137.0, 135.1, 132.4, 128.9, 128.7, 128.6, 128.5, 128.5, 128.1, 127.9, 127.1, 126.5, 123.2, 121.9, 121.2, 116.7, 65.9, 31.1, 23.5. HRMS *m/z* (ESI+): Calculated for $C_{31}H_{24}N_3O_3^+$ ([M+H]$^+$) 486.1812, found 486.1818.

4-(4-cyanopyridin-2-yl)benzyl 2-(3-benzoylphenyl)propanoate (2m)



General procedure H was followed. Colorless oil, 82% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.90 (t, *J* = 1.2 Hz, 1H), 7.80 – 7.77 (m, 3H), 7.69 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.50 – 7.43 (m, 4H), 7.40 – 7.34 (m, 2H), 5.22 – 5.17 (m, 2H), 3.91 (q, *J* = 7.1 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.4, 173.7, 158.1, 150.6, 140.6, 138.0, 137.9, 137.4, 137.1, 132.5, 131.6, 130.1, 129.2, 129.1, 128.6, 128.4, 128.3, 127.1, 123.3, 121.9, 121.2, 116.7, 65.9, 45.4, 18.4. HRMS *m/z* (ESI+): Calculated for $C_{29}H_{23}N_2O_3^+$ ([M+H]$^+$) 447.1703, found 447.1712.

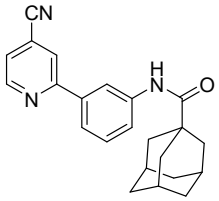
***N*-(3-(4-cyanopyridin-2-yl)phenyl)-2-(4-isobutylphenyl)propanamide (2n)**



General procedure I was followed. White solid, Mp = 122-123 °C; 86% yield; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.04 (t, *J* = 2.0 Hz, 1H), 7.81 (dd, *J* = 2.6, 1.4 Hz, 1H), 7.59 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.37 – 7.27 (m, 3H), 7.21 – 7.18 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 3.65 (q, *J* = 7.1 Hz, 1H), 2.39 (d, *J* = 7.2 Hz, 2H), 1.78 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.52 (d, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.0, 158.1, 150.5, 141.2, 138.9, 137.9, 137.9, 130.0, 129.7, 127.4, 123.4, 122.6, 122.2, 121.4, 121.3, 118.1,

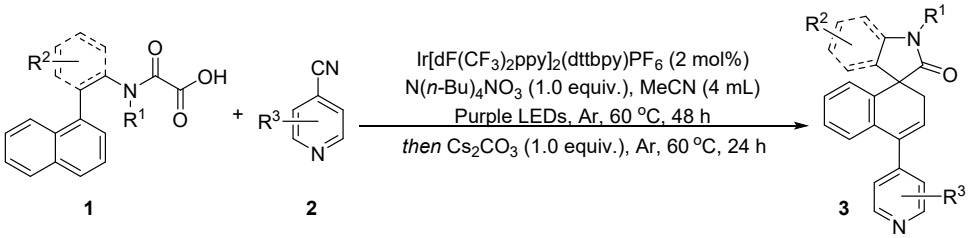
116.6, 47.8, 45.0, 30.2, 22.4, 18.5. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{26}N_3O^+$ ($[M+H]^+$) 384.2071, found 384.2077.

***N*-(3-(4-cyanopyridin-2-yl)phenyl)adamantane-1-carboxamide (2o)**



General procedure I was followed. White solid, Mp = 150-151 °C; 80% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (dd, *J* = 4.9, 0.9 Hz, 1H), 8.25 (t, *J* = 2.0 Hz, 1H), 7.93 (t, *J* = 1.2 Hz, 1H), 7.75 – 7.63 (m, 2H), 7.53 (s, 1H), 7.47 – 7.36 (m, 2H), 2.09 (q, *J* = 3.1 Hz, 3H), 1.98 (d, *J* = 2.9 Hz, 6H), 1.82 – 1.68 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.4, 158.1, 150.5, 139.0, 137.9, 129.7, 123.4, 122.4, 122.1, 121.6, 121.3, 118.4, 116.6, 41.6, 39.3, 36.4, 28.1. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{24}N_3O^+$ ($[M+H]^+$) 358.1914, found 358.1920.

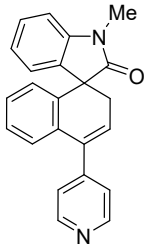
4. General procedure for the photo-catalyzed dearomative difunctionalization reaction



1 **2** **3**

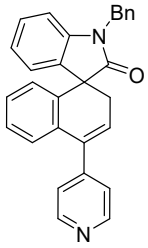
To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer were charged with aryl oxamic acids **1** (0.2 mmol, 1.0 equiv.), cyanopyridines **2** (1.0 mmol, 5.0 equiv.), N(*n*-Bu)$_4$NO$_3$ (0.2 mmol, 1.0 equiv.), and Ir[dF(CF$_3$)$_2$ppy]$_2$(dttbpy)PF$_6$ (2 mol%). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, MeCN (4 mL) was introduced into the tube via syringe under argon atmosphere. Afterward, the tube was sealed and the mixture was stirred at 60 °C under irradiation of purple LED lamp (λ= 400–410 nm). After 48 h, the tube was taken out and cooled to room temperature. Under argon atmosphere, Cs_2CO_3 (1.0 equiv.) was added, and the tube was sealed. Then, the reaction was stirred at 60 °C for additional 24 h. When the reaction was completed, the solution was diluted with 20 mL H_2O, then extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with 20 mL brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel diluting with petroleum ether/ethyl acetate to give the target product **3**.

1-methyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3a)



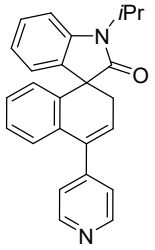
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 65% yield; Pale yellow solid, M.P. = 217-218 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.62 (m, 2H), 7.44 – 7.36 (m, 2H), 7.29 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.22 – 7.06 (m, 3H), 7.00 – 6.90 (m, 2H), 6.89 – 6.82 (m, 1H), 6.17 (dd, *J* = 6.0, 3.4 Hz, 1H), 3.36 (s, 3H), 3.17 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.64 (dd, *J* = 17.1, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 150.1, 148.0, 141.8, 138.8, 136.0, 133.5, 132.9, 128.9, 128.5, 127.8, 126.3, 126.1, 125.7, 123.5, 122.8, 108.6, 51.9, 33.8, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{18}N_2NaO^+$ ([M+Na]$^+$) 361.1311, found 361.1320.

1-benzyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3b)



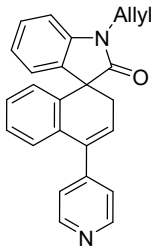
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 59% yield; Pale yellow solid, M.P. = 182-183 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 – 8.66 (m, 2H), 7.44 (dt, *J* = 4.4, 1.2 Hz, 2H), 7.40 – 7.27 (m, 6H), 7.23 – 7.14 (m, 3H), 7.12 (dd, *J* = 7.0, 2.1 Hz, 1H), 6.92 (ddd, *J* = 9.0, 7.2, 1.4 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.19 (dd, *J* = 5.9, 3.6 Hz, 1H), 5.05 (s, 2H), 3.22 (dd, *J* = 17.1, 3.6 Hz, 1H), 2.72 (dd, *J* = 17.1, 5.9 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 149.9, 148.3, 141.1, 138.8, 136.0, 135.9, 133.4, 133.02, 129.0, 128.9, 128.5, 127.9, 127.8, 127.3, 126.4, 126.2, 125.7, 123.6, 123.6, 122.9, 109.7, 51.9, 44.0, 34.1. HRMS *m/z* (ESI+): Calculated for $C_{29}H_{23}N_2O^+$ ([M+H]$^+$) 415.1805, found 415.1806.

1-isopropyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3c)



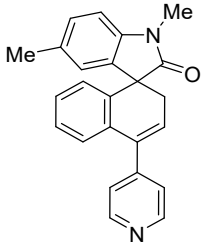
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 56% yield; Pale yellow solid, M.P. = 204-205 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.62 (m, 2H), 7.49 – 7.36 (m, 2H), 7.30 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.23 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.16 (pd, *J* = 7.4, 1.7 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.91 (td, *J* = 7.5, 1.0 Hz, 1H), 6.87 – 6.80 (m, 1H), 6.16 (dd, *J* = 6.0, 3.5 Hz, 1H), 4.78 (p, *J* = 7.0 Hz, 1H), 3.15 (dd, *J* = 17.1, 3.5 Hz, 1H), 2.63 (dd, *J* = 17.2, 6.0 Hz, 1H), 1.58 (dd, *J* = 7.0, 2.8 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.9, 149.7, 148.4, 140.5, 138.6, 136.4, 134.1, 132.8, 128.9, 128.2, 127.7, 126.3, 126.0, 125.9, 123.7, 123.6, 122.2, 110.3, 51.5, 44.1, 33.9, 19.7, 19.5. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{23}N_2O^+$ ([M+H]$^+$) 367.1805, found 367.1811.

1-allyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3d)



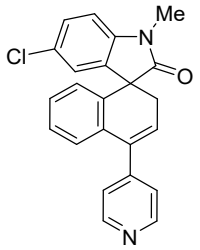
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 40% yield; Pale yellow solid, M.P. =172-173 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.61 (m, 2H), 7.46 – 7.40 (m, 2H), 7.30 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.21 – 7.13 (m, 2H), 7.09 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.89 – 6.85 (m, 1H), 6.17 (dd, *J* = 5.9, 3.6 Hz, 1H), 5.92 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 5.33 – 5.24 (m, 2H), 4.54 – 4.40 (m, 2H), 3.17 (dd, *J* = 17.1, 3.6 Hz, 1H), 2.67 (dd, *J* = 17.1, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.9, 149.7, 148.5, 141.2, 138.8, 136.1, 133.5, 133.0, 131.4, 129.0, 128.5, 127.9, 126.4, 126.2, 125.9, 123.7, 123.6, 122.9, 117.8, 109.6, 51.9, 42.6, 34.1. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{21}N_2O^+$ ([M+H]$^+$) 365.1648, found 365.1657.

1,5-dimethyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3e)



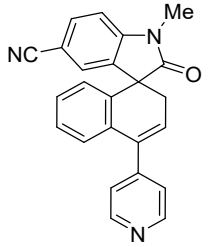
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 59% yield; Pale yellow solid, M.P. =172-173 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 – 8.65 (m, 2H), 7.49 – 7.43 (m, 2H), 7.21 – 7.12 (m, 2H), 7.11 – 7.04 (m, 3H), 6.88 – 6.79 (m, 2H), 6.18 (dd, *J* = 5.9, 3.6 Hz, 1H), 3.32 (s, 3H), 3.14 (dd, *J* = 17.2, 3.6 Hz, 1H), 2.65 (dd, *J* = 17.2, 5.9 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.1, 149.3, 149.0, 139.5, 138.5, 136.2, 133.5, 132.8, 132.4, 128.9, 128.8, 127.8, 126.3, 126.2, 124.3, 123.7, 108.4, 51.9, 33.8, 26.6, 21.2. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{21}N_2O^+$ ([M+H]$^+$) 353.1648, found 353.1652.

5-chloro-1-methyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3f)



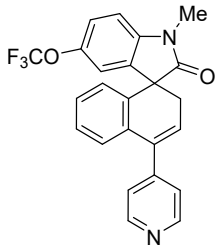
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 61% yield; Pale yellow solid, M.P. = 226-227 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 – 8.64 (m, 2H), 7.48 – 7.41 (m, 2H), 7.27 – 7.19 (m, 3H), 7.16 (td, *J* = 7.5, 1.7 Hz, 1H), 7.08 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.88 – 6.80 (m, 2H), 6.18 (dd, *J* = 5.9, 3.5 Hz, 1H), 3.33 (s, 3H), 3.15 (dd, *J* = 17.2, 3.5 Hz, 1H), 2.63 (dd, *J* = 17.1, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.7, 149.3, 148.7, 140.5, 138.7, 135.2, 134.9, 132.7, 129.1, 128.5, 128.2, 128.1, 126.4, 126.1, 125.8, 124.0, 123.7, 109.6, 52.0, 33.7, 26.7. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{18}ClN_2O^+$ ([M+H]$^+$) 373.1102, found 373.1108.

1-methyl-2-oxo-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalene]-5-carbonitrile (3g)



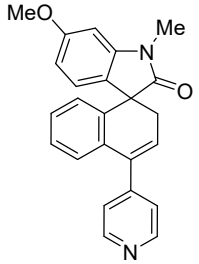
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 39% yield; Pale yellow solid, M.P. = 271-272 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.66 (m, 2H), 7.62 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.25 – 7.11 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.80 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.16 (dd, *J* = 6.0, 3.4 Hz, 1H), 3.38 (s, 3H), 3.17 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.62 (dd, *J* = 17.1, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.9, 150.2, 147.4, 145.8, 139.0, 134.5, 134.3, 133.8, 132.8, 129.1, 128.5, 126.9, 126.7, 125.9, 124.7, 123.4, 118.9, 109.1, 106.0, 51.6, 33.6, 26.9. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{18}N_3O^+$ ([M+H]$^+$) 364.1444, found 364.1456.

1-methyl-4'-(pyridin-4-yl)-5-(trifluoromethoxy)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3h)



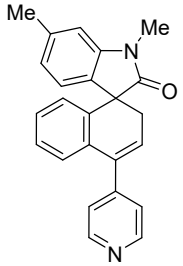
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 60% yield; Pale yellow solid, M.P. = 169-171 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 – 8.62 (m, 2H), 7.42 – 7.36 (m, 2H), 7.26 – 7.14 (m, 4H), 7.11 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.17 (dd, *J* = 6.0, 3.4 Hz, 1H), 3.37 (s, 3H), 3.19 (dd, *J* = 17.1, 3.5 Hz, 1H), 2.66 (dd, *J* = 17.2, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.9, 150.2, 147.7, 144.71, 144.69, 140.5, 139.0, 135.1, 134.7, 132.9, 129.0, 128.2, 126.5, 126.0, 125.1, 123.3, 121.4, 120.4 (q, *J* = 255.0 Hz), 109.0, 52.1, 33.6, 26.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.2. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{18}F_3N_2O_2^+$ ([M+H]$^+$) 423.1315, found 423.1321.

6-methoxy-1-methyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3i)



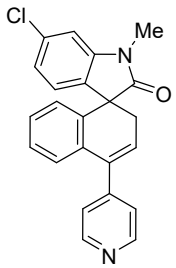
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 65% yield; Pale yellow solid, M.P. = 220-221 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 – 8.65 (m, 2H), 7.42 – 7.36 (m, 2H), 7.20 – 7.07 (m, 4H), 6.88 – 6.82 (m, 1H), 6.50 (d, *J* = 2.3 Hz, 1H), 6.44 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.16 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.80 (s, 3H), 3.33 (s, 3H), 3.13 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.61 (dd, *J* = 17.0, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.8, 160.4, 150.1, 148.1, 143.2, 138.7, 136.4, 132.9, 128.8, 127.7, 126.2, 125.9, 125.8, 125.6, 124.1, 123.4, 106.5, 96.5, 55.6, 51.6, 33.9, 26.6; HRMS *m/z* (ESI+): Calculated for $C_{24}H_{21}N_2O_2^+$ ([M+H]$^+$) 369.1598, found 369.1603.

1,6-dimethyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3j)



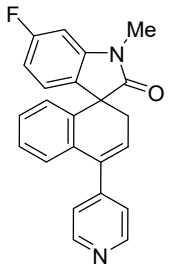
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 34% yield; Pale yellow solid, M.P. = 239-240 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 – 8.61 (m, 2H), 7.43 – 7.37 (m, 2H), 7.20 – 7.07 (m, 4H), 6.88 – 6.82 (m, 1H), 6.79 – 6.72 (m, 2H), 6.16 (dd, *J* = 6.1, 3.5 Hz, 1H), 3.34 (s, 3H), 3.15 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.62 (dd, *J* = 17.1, 6.1 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.5, 150.0, 148.1, 141.9, 138.7, 136.3, 132.9, 130.6, 128.9, 127.7, 126.2, 126.0, 125.8, 123.5, 123.3, 123.2, 109.5, 51.8, 33.9, 26.6, 21.8. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{21}N_2O^+$ ([M+H]$^+$) 353.1648, found 353.1656.

6-chloro-1-methyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3k)



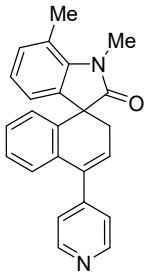
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 53% yield; Pale yellow solid, M.P. = 220-221 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 – 8.64 (m, 2H), 7.43 – 7.37 (m, 2H), 7.22 – 7.12 (m, 3H), 7.09 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.86 – 6.79 (m, 1H), 6.15 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.33 (s, 3H), 3.14 (dd, *J* = 17.1, 3.5 Hz, 1H), 2.61 (dd, *J* = 17.1, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.1, 149.9, 148.1, 143.2, 138.8, 135.5, 134.3, 132.8, 131.7, 129.0, 128.0, 126.4, 126.0, 125.5, 124.4, 123.5, 122.6, 109.3, 51.6, 33.7, 26.7. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{18}ClN_2O^+$ ([M+H]$^+$) 373.1102, found 373.1112.

6-fluoro-1-methyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3l)



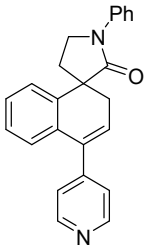
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 52% yield; Pale yellow solid, M.P. = 214-215 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 – 8.66 (m, 2H), 7.42 – 7.36 (m, 2H), 7.23 – 7.08 (m, 4H), 6.87 – 6.80 (m, 1H), 6.70 – 6.57 (m, 2H), 6.16 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.33 (s, 3H), 3.14 (dd, *J* = 17.1, 3.5 Hz, 1H), 2.61 (dd, *J* = 17.1, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.5, 163.2 (d, *J* = 245.7 Hz), 150.1, 147. 9, 143.5 (d, *J* = 11.1 Hz), 138.8, 135.8, 132.9, 128.9, 128.8, 127.9, 126.4, 125.9, 125.4 (d, *J* = 4.1 Hz), 124.51 (d, *J* = 9.6 Hz), 123.4, 108.8 (d, *J* = 22.2 Hz), 97.4 (d, *J* = 28.2 Hz), 51.6, 33.9, 26.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.6. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{18}FN_2O^+$ ([M+H]$^+$) 357.1398, found 357.1403.

1,7-dimethyl-4'-(pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3m)



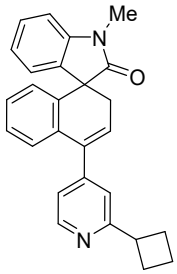
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 27% yield; Pale yellow solid, M.P. = 241-243 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.60 (m, 2H), 7.44 – 7.37 (m, 2H), 7.20 – 7.07 (m, 4H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.14 (dd, *J* = 5.9, 3.5 Hz, 1H), 3.63 (s, 3H), 3.14 (dd, *J* = 17.2, 3.5 Hz, 1H), 2.69 – 2.58 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.1, 150.0, 148.1, 139.6, 138.7, 136.3, 134.2, 132.9, 132.2, 128.8, 127.7, 126.3, 125.7, 123.5, 122.7, 121.5, 120.1, 51.2, 34.3, 29.9, 19.3. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{21}N_2O^+$ ([M+H]$^+$) 353.1648, found 353.1657.

1'-phenyl-4-(pyridin-4-yl)-2H-spiro[naphthalene-1,3'-pyrrolidin]-2'-one (3n)



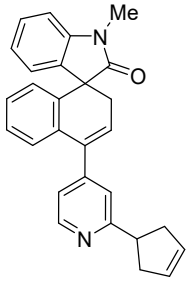
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 19% yield; Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 – 8.62 (m, 2H), 7.85 – 7.80 (m, 2H), 7.52 – 7.45 (m, 2H), 7.42 – 7.38 (m, 2H), 7.29 – 7.22 (m, 3H), 7.16 – 7.05 (m, 2H), 6.28 (dd, *J* = 6.8, 2.7 Hz, 1H), 3.93 – 3.84 (m, 2H), 3.18 (dd, *J* = 17.0, 2.7 Hz, 1H), 2.57 (dd, *J* = 17.1, 6.8 Hz, 1H), 2.40 (dt, *J* = 12.6, 7.9 Hz, 1H), 2.30 (ddd, *J* = 12.7, 6.3, 4.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.2, 149.2, 148.8, 139.2, 137.9, 137.9, 132.2, 129.0, 128.6, 127.4, 127.2, 126.1, 125.2, 125.0, 123.7, 120.0, 50.3, 45.0, 33.3, 32.9. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{21}N_2O^+$ ([M+H]$^+$) 353.1648, found 353.1653.

4'-(2-cyclobutylpyridin-4-yl)-1-methyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3o)



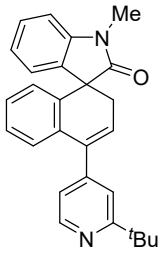
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 43% yield; Pale yellow solid, M.P. = 170-172 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.29 (ddd, *J* = 7.8, 6.8, 1.3 Hz, 1H), 7.21 – 7.10 (m, 3H), 7.08 (s, 2H), 6.99 – 6.92 (m, 2H), 6.86 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.13 (dd, *J* = 6.1, 3.4 Hz, 1H), 3.36 (s, 3H), 3.16 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.66 – 2.52 (m, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 165.2, 149.4, 148.2, 141.8, 139.1, 136.0, 133.6, 133.1, 128.7, 128.5, 127.8, 126.4, 126.0, 125.3, 123.5, 122.8, 120.8, 120.7, 108.5, 52.0, 42.1, 33.8, 28.5, 26.6, 18.3. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{25}N_2O^+$ ([M+H]$^+$) 393.1961, found 353.1972.

4'-(2-(cyclopent-3-en-1-yl)pyridin-4-yl)-1-methyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3p)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 31% yield; Pale yellow solid, M.P. = 172-174 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.25 (dd, *J* = 5.1, 1.7 Hz, 1H), 7.23 – 7.11 (m, 3H), 7.01 – 6.92 (m, 2H), 6.87 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.18 (dd, *J* = 6.0, 3.4 Hz, 1H), 5.82 (s, 2H), 3.76 (tt, *J* = 9.3, 6.9 Hz, 1H), 3.38 (s, 3H), 3.18 (dd, *J* = 17.0, 3.4 Hz, 1H), 2.99 – 2.86 (m, 2H), 2.77 – 2.69 (m, 2H), 2.65 (dd, *J* = 17.1, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 166.5, 149.2, 148.6, 141.9, 139.0, 136.0, 133.5, 133.1, 129.6, 129.1, 128.8, 128.5, 127.8, 126.4, 126.1, 125.4, 123.5, 122.8, 121.3, 121.0, 108.6, 52.0, 45.0, 40.2, 33.8, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{28}H_{25}N_2O^+$ ([M+H]$^+$) 405.1961, found 405.1971.

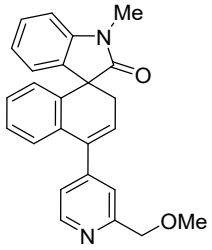
4'-(2-(tert-butyl)pyridin-4-yl)-1-methyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3q)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 40% yield; Pale yellow solid, M.P. = 171-172 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.44 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.21 – 7.10 (m, 4H), 6.97 – 6.91 (m, 2H), 6.88 – 6.82 (m, 1H), 6.16 (dd, *J* = 6.1, 3.3 Hz, 1H), 3.36 (s, 3H), 3.18 (dd, *J* = 17.0, 3.4 Hz, 1H), 2.63 (dd, *J* = 17.0, 6.1 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.4, 169.9, 148.7, 148.1, 141.8, 139.3, 136.0, 133.6, 133.2, 128.7, 128.5, 127.8, 126.4, 126.0, 125.2,

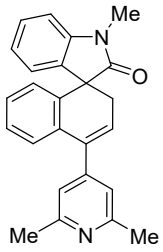
123.5, 122.8, 120.5, 118.8, 108.6, 52.0, 37.5, 33.8, 30.3, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{27}N_2O^+$ ([M+H]$^+$) 395.2118, found 395.2127.

4'-(2-(methoxymethyl)pyridin-4-yl)-1-methyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3r)



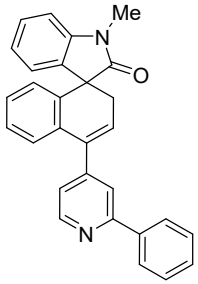
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 50% yield; Pale yellow solid, M.P. = 145-146 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.31 – 7.23 (m, 3H), 7.17 – 7.09 (m, 2H), 7.06 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.96 – 6.86 (m, 2H), 6.86 – 6.79 (m, 1H), 6.16 (dd, *J* = 6.1, 3.4 Hz, 1H), 4.64 (s, 2H), 3.49 (s, 3H), 3.32 (s, 3H), 3.14 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.60 (dd, *J* = 17.1, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 158.6, 149.1, 141.8, 138.8, 136.0, 133.5, 132.9, 128.9, 128.5, 127.8, 126.3, 126.1, 125.9, 123.5, 122.8, 122.3, 121.0, 108.6, 75.3, 58.9, 52.0, 33.8, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{23}N_2O_2^+$ ([M+H]$^+$) 383.1754, 383.1761.

4'-(2,6-dimethylpyridin-4-yl)-1-methyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3s)



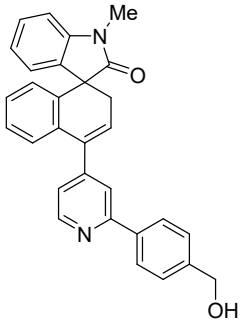
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 49% yield; Pale yellow solid, M.P. = 206-208 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.40 (m, 2H), 7.32 (td, *J* = 7.4, 1.5 Hz, 1H), 7.29 – 7.22 (m, 4H), 7.12 – 7.05 (m, 2H), 7.02 – 6.96 (m, 1H), 6.26 (dd, *J* = 6.0, 3.4 Hz, 1H), 3.50 (s, 3H), 3.29 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.74 (m, 7H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 157.9, 148.8, 141.8, 139.0, 135.9, 133.6, 133.2, 128.7, 128.4, 127.8, 126.4, 126.0, 124.9, 123.5, 122.8, 120.1, 108.5, 52.0, 33.8, 26.6, 24.5. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{23}N_2O^+$ ([M+H]$^+$) 367.1805, found 367.1812.

1-methyl-4'-(2-phenylpyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3t)



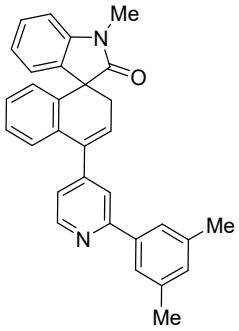
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 44% yield; Pale yellow solid, M.P. = 214-215 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 5.0 Hz, 1H), 8.11 – 7.99 (m, 2H), 7.84 (s, 1H), 7.53 – 7.41 (m, 3H), 7.37 – 7.26 (m, 3H), 7.23 – 7.13 (m, 3H), 6.99 – 6.85 (m, 3H), 6.23 (dd, *J* = 6.0, 3.4 Hz, 1H), 3.36 (s, 3H), 3.20 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.66 (dd, *J* = 17.1, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 157.9, 149.9, 148.9, 141.9, 139.3, 139.0, 136.0, 133.5, 133.1, 129.1, 128.9, 128.8, 128.5, 127.9, 127.1, 126.4, 126.1, 125.6, 123.5, 122.9, 121.9, 120.3, 108.6, 52.0, 33.8, 26.6; HRMS *m/z* (ESI+): Calculated for $C_{29}H_{23}N_2O^+$ ([M+H]$^+$) 415.1805, found 415.1817.

4'-(2-(4-(hydroxymethyl)phenyl)pyridin-4-yl)-1-methyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3u)



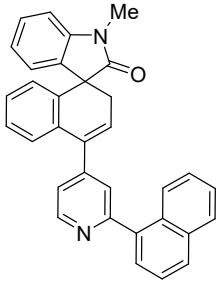
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 46% yield; Pale yellow solid, M.P. = 206-208 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 5.1 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.88 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.31 (m, 3H), 7.26 – 7.17 (m, 3H), 7.05 – 6.95 (m, 2H), 6.91 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.28 (dd, *J* = 5.9, 3.5 Hz, 1H), 4.77 (s, 2H), 3.39 (s, 3H), 3.21 (dd, *J* = 17.1, 3.6 Hz, 1H), 2.89 (s, 1H), 2.71 (dd, *J* = 17.1, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.2, 157.4, 149.5, 149.4, 142.4, 141.9, 138.9, 137.9, 136.0, 133.5, 132.9, 128.9, 128.5, 127.9, 127.3, 126.3, 126.2, 125.9, 123.5, 122.9, 122.1, 120.5, 108.6, 64.7, 52.0, 33.8, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{25}N_2O_2^+$ ([M+H]$^+$) 445.1911, found 445.1918.

4'-(2-(3,5-dimethylphenyl)pyridin-4-yl)-1-methyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3v)



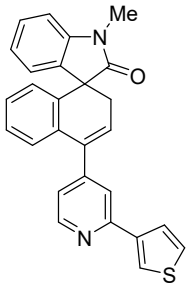
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 40% yield; Pale yellow solid, M.P. = 224-225 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.65 (d, *J* = 1.6 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.29 (td, *J* = 7.7, 1.3 Hz, 1H), 7.23 – 7.13 (m, 3H), 7.09 (s, 1H), 6.99 – 6.92 (m, 2H), 6.90 – 6.84 (m, 1H), 6.23 (dd, *J* = 6.0, 3.4 Hz, 1H), 3.37 (s, 3H), 3.20 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.66 (dd, *J* = 17.1, 6.0 Hz, 1H), 2.41 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 158.2, 149.8, 148.8, 141.9, 139.2, 139.1, 138.4, 136.0, 133.5, 133.1, 130.8, 128.9, 128.5, 127.9, 126.4, 126.1, 125.6, 124.9, 123.5, 122.9, 121.8, 120.4, 108.6, 52.0, 33.8, 26.6, 21.4. HRMS *m/z* (ESI+): Calculated for $C_{31}H_{27}N_2O^+$ ([M+H]$^+$) 443.2118, found 443.2129.

1-methyl-4'-(2-(naphthalen-1-yl)pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3w)



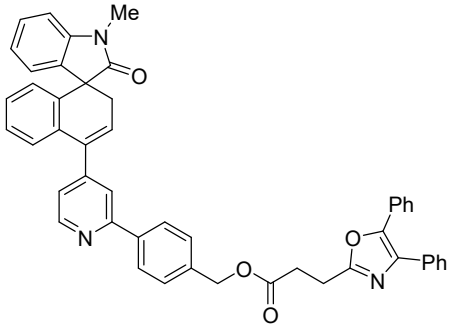
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 64% yield; Pale yellow solid, M.P. = 253-254 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (dd, *J* = 5.0, 0.8 Hz, 1H), 8.26 – 8.18 (m, 1H), 7.96 – 7.90 (m, 2H), 7.74 – 7.66 (m, 2H), 7.60 – 7.49 (m, 3H), 7.47 (dd, *J* = 5.1, 1.7 Hz, 1H), 7.34 – 7.21 (m, 4H), 7.16 (td, *J* = 7.4, 1.6 Hz, 1H), 6.97 – 6.90 (m, 2H), 6.87 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.27 (dd, *J* = 6.1, 3.4 Hz, 1H), 3.36 (s, 3H), 3.20 (dd, *J* = 17.1, 3.4 Hz, 1H), 2.65 (dd, *J* = 17.1, 6.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 159.6, 149.8, 148.5, 141.8, 138.9, 138.3, 136.1, 134.0, 133.5, 133.0, 131.2, 129.1, 128.9, 128.5, 128.4, 127.9, 127.6, 126.6, 126.4, 126.2, 125.9, 125.6, 125.3, 124.7, 123.5, 122.9, 121.8, 108.6, 52.0, 33.8, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{33}H_{25}N_2O^+$ ([M+H]$^+$) 465.1961, found 465.1971.

1-methyl-4'-(2-(thiophen-3-yl)pyridin-4-yl)-2'H-spiro[indoline-3,1'-naphthalen]-2-one (3x)



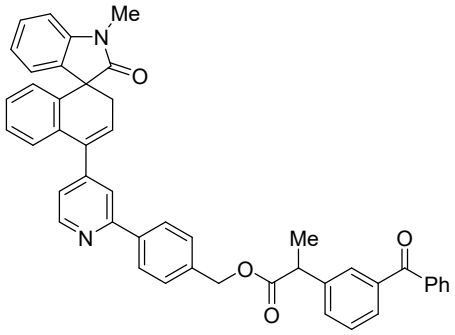
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 43% yield; Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.98 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.41 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.33 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.17 (dddd, *J* = 10.0, 8.6, 6.2, 4.0 Hz, 3H), 7.00 – 6.92 (m, 2H), 6.87 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.22 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.36 (s, 3H), 3.19 (dd, *J* = 17.1, 3.5 Hz, 1H), 2.66 (dd, *J* = 17.1, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.2, 153.8, 149.7, 149.0, 141.9, 138.9, 136.0, 133.5, 133.0, 128.9, 128.5, 127.9, 126.4, 126.3, 126.3, 126.2, 125.6, 124.0, 123.5, 122.9, 121.7, 120.1, 108.6, 52.0, 33.8, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{21}N_2OS^+$ ([M+H]$^+$) 421.1369, found 421.1378.

4-(4-(1-methyl-2-oxo-2'H-spiro[indoline-3,1'-naphthalen]-4'-yl)pyridin-2-yl)benzyl-3-(4,5-diphenyloxazol-2-yl)propanoate (3y)



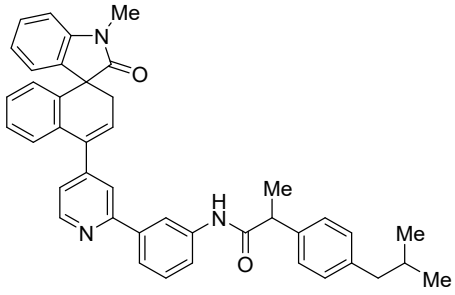
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 49% yield; Pale yellow solid, M.P. = 104-105 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.69 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.73 – 7.69 (m, 1H), 7.56 – 7.52 (m, 2H), 7.49 – 7.46 (m, 2H), 7.41 – 7.37 (m, 2H), 7.30 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.28 – 7.19 (m, 8H), 7.14 – 7.06 (m, 3H), 6.91 – 6.84 (m, 2H), 6.81 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.16 (dd, *J* = 6.0, 3.5 Hz, 1H), 5.17 (s, 2H), 3.29 (s, 3H), 3.17 – 3.10 (m, 3H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.60 (dd, *J* = 17.1, 6.0 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 179.2, 171.9, 161.7, 149.6, 145.5, 141.9, 138.9, 136.9, 136.1, 135.1, 133.5, 133.0, 132.5, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.0, 127.9, 127.9, 127.3, 126.5, 126.3, 126.2, 125.9, 123.5, 122.9, 122.2, 120.4, 108.6, 66.2, 52.0, 33.9, 31.2, 26.6, 23.5. HRMS *m/z* (ESI+): Calculated for $C_{48}H_{38}N_3O_4^+$ ([M+H]$^+$) 720.2857, found 720.2866.

4-(4-(1-methyl-2-oxo-2'H-spiro[indoline-3,1'-naphthalen]-4'-yl)pyridin-2-yl)benzyl-2-(3-benzoylphenyl)propanoate (3z)



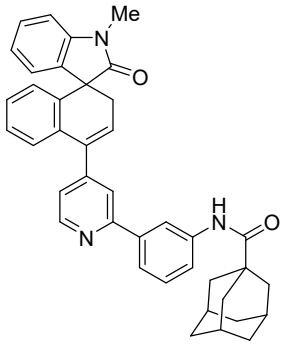
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 40% yield; Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 5.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.84 – 7.77 (m, 4H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.57 (dd, *J* = 7.7, 4.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 3H), 7.41 – 7.29 (m, 5H), 7.25 – 7.14 (m, 3H), 7.02 – 6.94 (m, 2H), 6.93 – 6.86 (m, 1H), 6.25 (dd, *J* = 6.0, 3.5 Hz, 1H), 5.21 (s, 2H), 3.90 (q, *J* = 7.1 Hz, 1H), 3.38 (s, 3H), 3.21 (dd, *J* = 17.1, 3.5 Hz, 1H), 2.70 (dd, *J* = 17.1, 6.0 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.4, 179.2, 173.8, 157.2, 149.7, 149.2, 141.9, 140.7, 138.9, 137.9, 137.5, 136.9, 136.0, 133.5, 133.0, 132.5, 131.6, 130.0, 129.3, 129.0, 128.9, 128.6, 128.5, 128.3, 128.3, 127.9, 127.3, 126.3, 126.2, 125.8, 123.5, 122.9, 122.2, 120.4, 108.6, 66.3, 51.9, 45.4, 33.8, 26.6, 18.4. HRMS *m/z* (ESI+): Calculated for $C_{46}H_{37}N_2O_4^+$ ([M+H]$^+$) 681.2748, found 681.2756.

2-(4-isobutylphenyl)-N-(3-(4-(1-methyl-2-oxo-2'H-spiro[indoline-3,1'-naphthalen]-4'-yl)pyridin-2-yl)phenyl)propanamide (3aa)



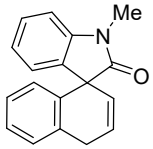
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 50% yield; Pale yellow solid, M.P. = 105-107 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 – 8.67 (m, 1H), 7.95 (q, *J* = 2.0 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.68 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.51 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.20 – 7.11 (m, 5H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.22 (dd, *J* = 5.9, 3.6 Hz, 1H), 3.73 (q, *J* = 7.1 Hz, 1H), 3.35 (s, 3H), 3.17 (dd, *J* = 17.1, 3.5 Hz, 1H), 2.67 (dd, *J* = 17.1, 5.9 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.86 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.59 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 179.2, 172.9, 157.1, 149.4, 149.3, 141.9, 141.1, 139.4, 138.8, 138.8, 138.1, 136.0, 133.5, 133.0, 129.9, 129.5, 128.9, 128.6, 127.9, 127.5, 126.3, 126.2, 126.0, 123.5, 122.9, 122.7, 122.3, 120.7, 120.6, 118.1, 108.6, 52.0, 47.8, 45.0, 33.8, 30.2, 26.6, 22.4, 18.6. HRMS *m/z* (ESI+): Calculated for $C_{42}H_{40}N_3O_2^+$ ([M+H]$^+$) 618.3115, found 618.3123.

(3r,5r,7r)-N-(3-(4-(1-methyl-2-oxo-2'H-spiro[indoline-3,1'-naphthalen]-4'-yl)pyridin-2-yl)phenyl)adamantane-1-carboxamide (3ab)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 46% yield; Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (dd, *J* = 5.1, 0.7 Hz, 1H), 8.11 (t, *J* = 1.9 Hz, 1H), 7.90 (ddd, *J* = 8.1, 2.3, 1.0 Hz, 1H), 7.86 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.74 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.59 (s, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.22 – 7.12 (m, 3H), 6.98 (td, *J* = 7.6, 1.0 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.86 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.24 (dd, *J* = 5.9, 3.6 Hz, 1H), 3.35 (s, 3H), 3.17 (dd, *J* = 17.1, 3.6 Hz, 1H), 2.68 (dd, *J* = 17.1, 5.9 Hz, 1H), 2.10 (t, *J* = 6.2 Hz, 3H), 1.98 (d, *J* = 2.9 Hz, 6H), 1.80 – 1.71 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.2, 176.3, 157.0, 149.6, 149.2, 142.0, 139.2, 138.9, 138.8, 136.0, 133.5, 133.0, 129.6, 128.9, 128.6, 127.9, 126.3, 126.2, 126.1, 123.5, 122.9, 122.6, 122.3, 121.1, 120.6, 118.4, 108.6, 51.9, 41.6, 39.3, 36.5, 33.8, 28.2, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{40}H_{38}N_3O_2^+$ ([M+H]$^+$) 592.2959, found 592.2967.

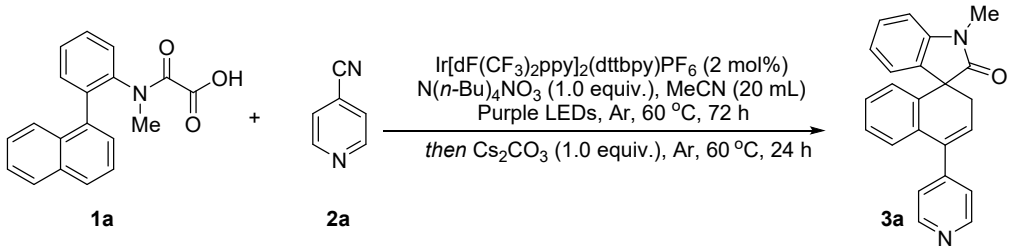
1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4)



White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (ddd, *J* = 7.80, 6.94, 1.95 Hz, 1H), 7.25 (ddd, *J* = 7.21, 1.58, 0.73 Hz, 1H), 7.18 (td, *J* = 7.42, 1.33 Hz, 1H), 7.07 – 6.98 (m, 3H), 6.93 (dt, *J* = 7.77, 0.82 Hz, 1H), 6.55 (dd, *J* = 7.87, 1.31 Hz, 1H), 6.33 (ddd, *J* = 9.91, 4.21, 3.14 Hz, 1H), 5.57 (ddd, *J* = 9.86, 2.59, 1.72 Hz, 1H), 3.79 (dt, *J* = 21.80, 2.93 Hz, 1H), 3.58 (ddd, *J* = 21.74, 4.37, 1.70 Hz, 1H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.3, 143.7, 135.8, 134.3, 134.2, 128.8, 128.4, 128.1, 127.3, 126.8, 126.6, 125.4, 124.8, 123.3, 108.1, 54.7, 30.1, 26.7.

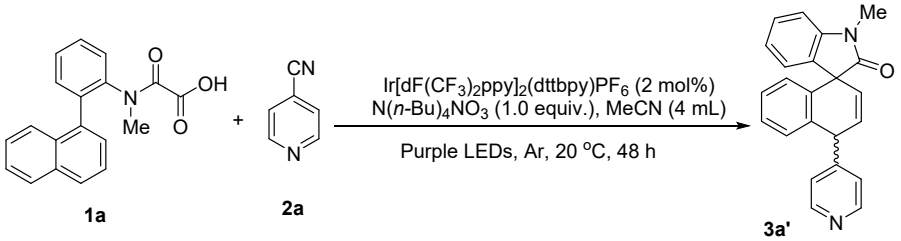
5. Scale-up reaction and mechanistic investigations

5.1 The scale-up reaction



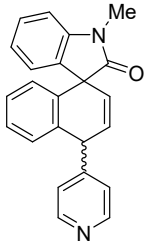
To a 100 mL oven-dried Schlenk tube equipped with a magnetic stirrer was added aryl oxamic acid **1a** (1.0 mmol, 1.0 equiv.), 4-cyanopyridine **2a** (5.0 mmol, 5.0 equiv.), $N(n\text{-}Bu)_4NO_3$ (1.0 mmol, 1.0 equiv.), and $Ir[dF(CF_3)_2ppy]_2(dttbpy)PF_6$ (2 mol%). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, MeCN (20 mL) was introduced into the tube via syringe under argon atmosphere. Afterward, the tube was sealed and the mixture was stirred at 60 °C under the irradiation of four 20 W purple LED lamp (λ= 400–410 nm). After 72 hours of reaction, the bottle was taken out and cooled to room temperature. Under argon atmosphere, Cs_2CO_3 (1.0 mmol, 1.0 equiv.) was added and stirred at 60 °C for additional 24 hours. Then, the reaction solution was diluted with 20 mL H_2O, then extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with 20 mL brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel diluting with petroleum ether/ethyl acetate to give the target product **3a** (192.7 mg, 57% yield).

5.2 Alkene tautomerization of 3a'

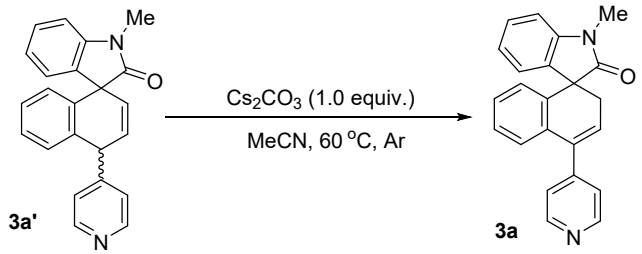


To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer were added aryl oxamic acid **1a** (0.2 mmol, 1.0 equiv.), 4-cyanopyridine **2a** (1.0 mmol, 5.0 equiv.), $N(n\text{-}Bu)_4NO_3$ (0.2 mmol, 1.0 equiv.), and $Ir[dF(CF_3)_2ppy]_2(dttbpy)PF_6$ (2 mol%, 4.6 mg). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, MeCN (4 mL) was introduced into the tube via syringe under argon atmosphere. Afterward, the tube was sealed and the mixture was stirred at 20 °C under the irradiation of purple LED lamp (λ= 400–410 nm) for 48 h. Then, the reaction mixture was diluted with 20 mL H_2O, and then extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with 20 mL brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel diluting with petroleum ether/ethyl acetate to give the target product **3a'**.

1-methyl-4'-(pyridin-4-yl)-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3a')

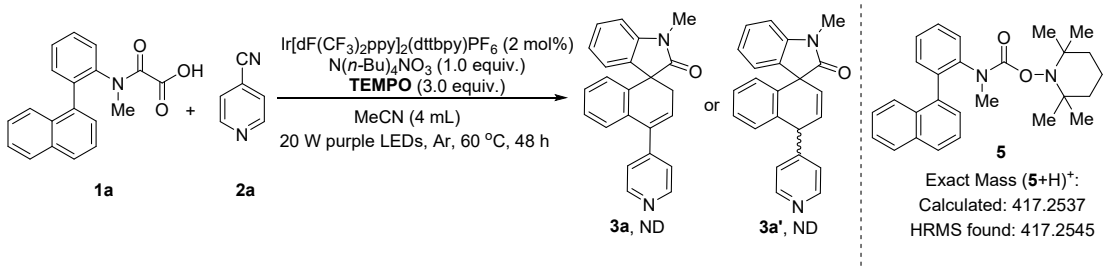


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether1:3 (v/v); 49% yield; dr = 2.6:1, Pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 – 8.57 (m, 1.42H), 8.58 – 8.53 (m, 0.54H), 7.76 – 7.59 (m, 0.38H), 7.39 – 7.33 (m, 0.96H), 7.25 – 7.19 (m, 1.51H), 7.15 – 7.07 (m, 2.44H), 7.07 – 7.00 (m, 1.71H), 6.95 (dd, *J* = 16.0, 7.8 Hz, 1.96H), 6.64 – 6.52 (m, 1.00H), 6.16 (dd, *J* = 9.9, 3.0 Hz, 1.00H), 5.65 (dd, *J* = 9.9, 2.5 Hz, 0.72H), 5.59 (dd, *J* = 9.9, 1.8 Hz, 0.28H), 4.99 (d, *J* = 2.9 Hz, 0.72H), 4.91 – 4.74 (m, 0.28H), 3.32 (s, 0.72H), 3.28 (s, 2.28H). ^{13}C NMR (100 MHz, Chloroform-d) δ 177.6, 154.2, 154.0, 150.1, 149.3, 143.9, 143.7, 135.7, 135.6, 135.5, 135.0, 133.8, 133.3, 130.8, 129.8, 129.6, 129.5, 128.9, 127.9, 127.8, 127.5, 127.3, 127.0, 125.1, 124.8, 124.72, 124.69, 124.2, 123.54, 123.48, 108.4, 108.3, 54.7, 54.4, 45.6, 44.6, 26.9, 26.8. HRMS *m/z* (ESI+): Calculated for $C_{23}H_{19}N_2O^+$ ([M+H]$^+$) 339.1492, found 339.1498.

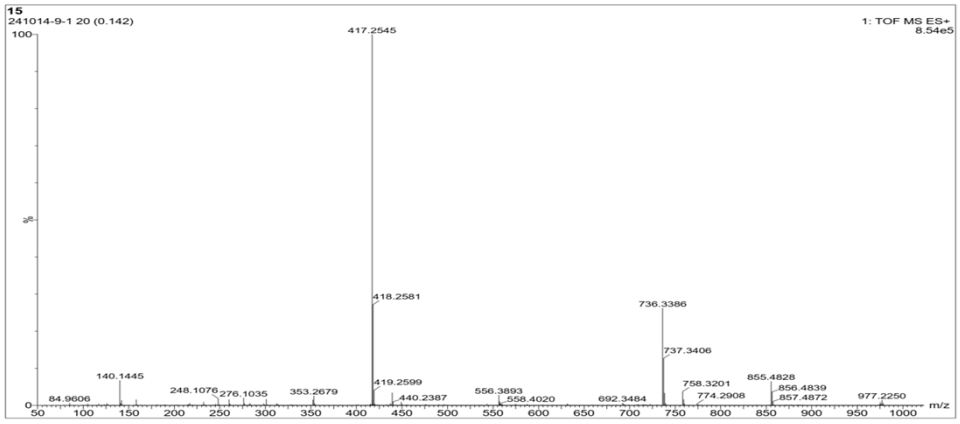


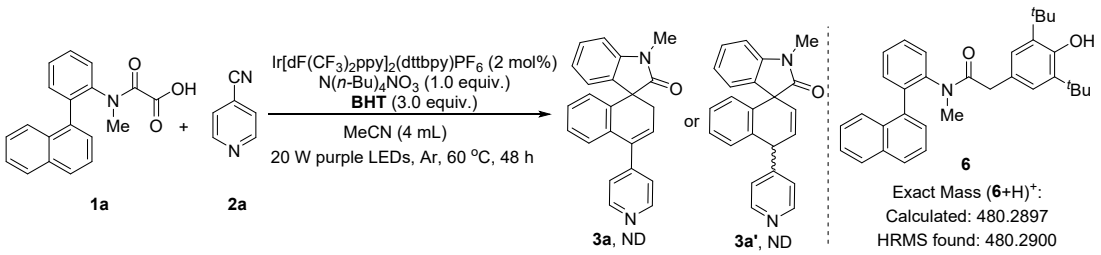
To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer was charged with Cs_2CO_3 (0.1 mmol, 1.0 equiv.). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, the solution of **3a'** (0.1 mmol, 1.0 equiv.) in MeCN (2 mL) was introduced into the tube via syringe under argon atmosphere. Afterward, the tube was sealed and the mixture was stirred at 60 °C for 24 h. Then, the reaction mixture was diluted with 10 mL H_2O, and then extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with 20 mL brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel diluting with petroleum ether/ethyl acetate to give the target product **3a** (31.1 mg, 92% yield).

5.3 Radical trapping experiments

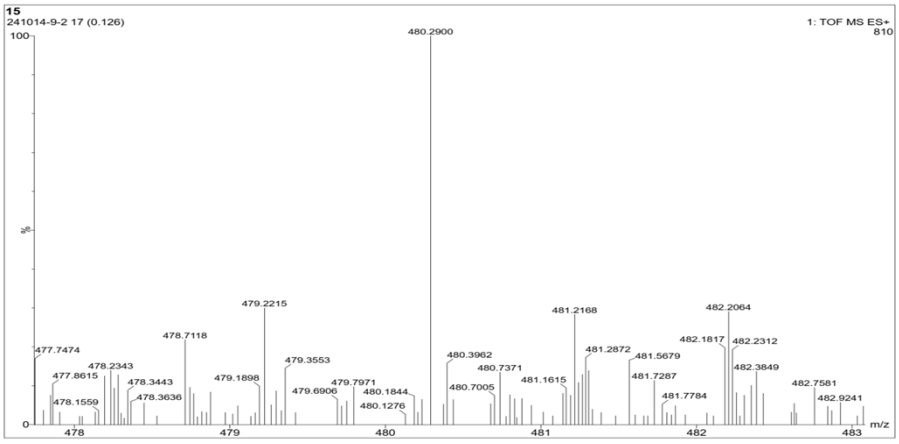


To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer were added aryl oxamic acid **1a** (0.2 mmol, 1.0 equiv.), 4-cyanopyridine **2a** (1.0 mmol, 5.0 equiv.), $N(n\text{-}Bu)_4NO_3$ (0.2 mmol, 1.0 equiv.), TEMPO (0.6 mmol, 3.0 equiv.), and $Ir[dF(CF_3)_2ppy]_2(dttbpy)PF_6$ (2 mol%, 4.6 mg). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, MeCN (4 mL) was introduced into the tube via syringe under argon atmosphere. Afterward, the tube was sealed and the mixture was stirred at 60 °C under the irradiation of purple LED lamp (λ= 400–410 nm). After 48 h, the tube was taken out and cooled to room temperature. Then, the reaction solution was analyzed by HRMS. The formation of TEMPO-trapped carbamoyl adduct **5** was detected by HRMS. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{31}N_2O_2^+$ ($[M+H]^+$) 417.2537, found 417.2545.





To a 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer were added aryl oxamic acid **1a** (0.2 mmol, 1.0 equiv.), 4-cyanopyridine **2a** (1.0 mmol, 5.0 equiv.), $N(n\text{-}Bu)_4NO_3$ (0.2 mmol, 1.0 equiv.), BHT (0.6 mmol, 3.0 equiv.), and $Ir[dF(CF_3)_2ppy]_2(dttbpy)PF_6$ (2 mol%, 4.6 mg). Then, the tube was evacuated and back-filled with argon for three times. Subsequently, MeCN (4 mL) was introduced into the tube via syringe under argon atmosphere. Afterward, the tube was sealed and the mixture was stirred at 60 °C under the irradiation of purple LED lamp (λ= 400–410 nm). After 48 hours, the tube was taken out and cooled to room temperature. Then, the reaction solution was analyzed by HRMS. The formation of BHT-trapped carbamoyl adduct **6** was detected by HRMS. HRMS *m/z* (ESI+): Calculated for $C_{26}H_{31}N_2O_2^+$ ($[M+H]^+$) 480.2897, found 480.2900.



5.4 Stern-Volmer Fluorescence quenching experiments

Emission intensities were recorded using a F-4500 FL spectrophotometer, and the results shown in **Figure S2**. First, the emission intensity of fluoresce solutions was observed at 489 nm. The solutions were irradiated at 380 nm and fluorescence was measured from 400 nm to 650 nm. In a typical experiment, the emission spectrum of a 2×10^{-5} M solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ with different concentration of **1a** (**2a**) in degassed anhydrous MeCN and the linear relationship between I_0/I and the increasing concentration of **1a** (**2a**) from 0 M to 4.0×10^{-2} M.

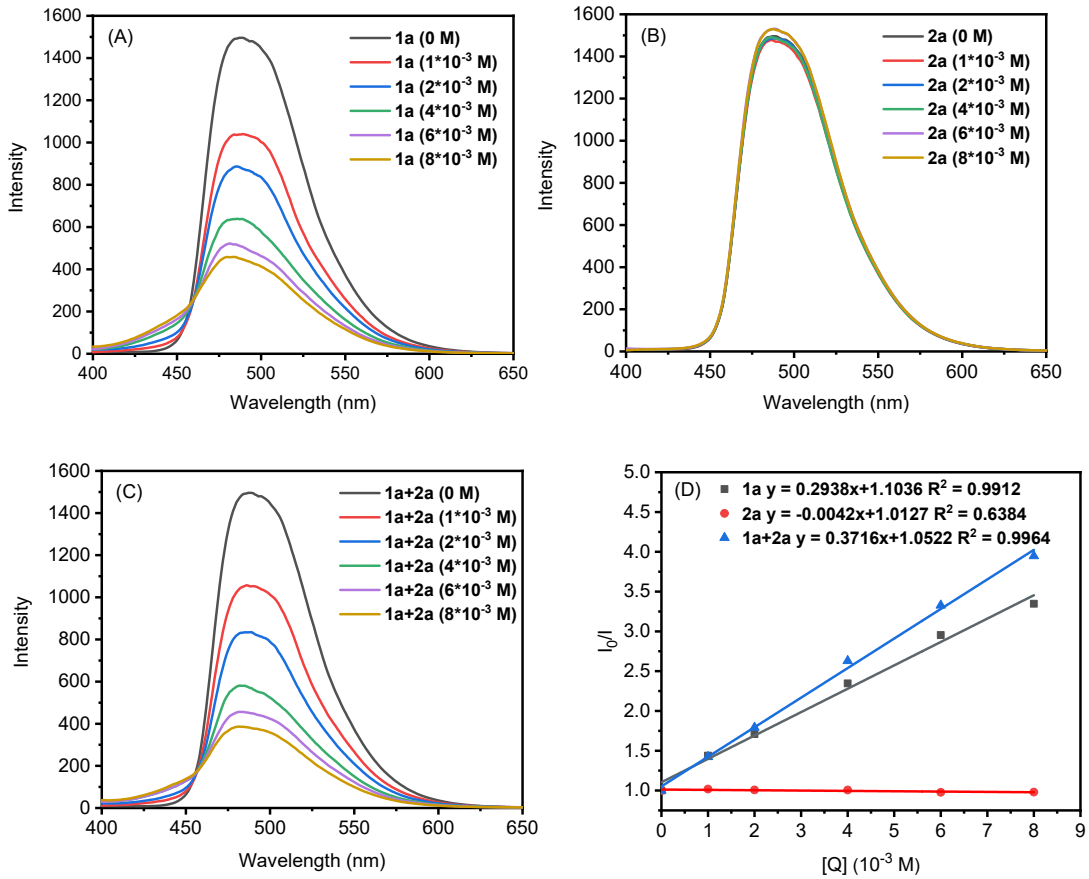


Figure S2. (A) The emission spectrum of a 2×10^{-5} M solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ with different concentration of **1a**; (B) The emission

spectrum of a 2×10^{-5} M solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ with different concentration of **2a**; (C) The emission spectrum of a 2×10^{-5} M solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ with different concentration of **1a** and **2a**; (D) The linear relationship between I_0/I (I_0 and I are the fluorescence intensities before and after adding the various concentrations of **1a**, **2a**, or **1a**+**2a**, respectively) and the concentration of **1a**, **2a**, or **1a**+**2a**.

5.5 Characterization with UV-Vis spectroscopy

UV-visible absorption spectra were collected on a Shimadzu UV-2600 spectrophotometer, and shown in **Figure S3**. Upon comparison, only the photocatalyst demonstrates strong absorption in the visible light region around 400 nm.

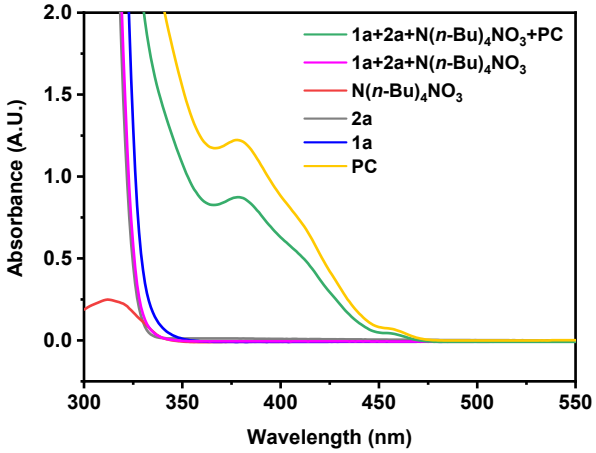


Figure S3. Absortion spectra of **1a** (0.05 M), **2a** (0.25 M), $N(n\text{-}Bu)_4NO_3$ (0.05 M), the mixture of **1a**+**2a**+$N(n\text{-}Bu)_4NO_3$ and the mixture of **1a**+**2a**+$N(n\text{-}Bu)_4NO_3$ +PC in MeCN. PC: $(Ir[dF(CF_3)_2ppy]_2(dttbpy)PF_6)$.

5.6 Cyclic voltammetry experiments

The cyclic voltammetry experiments were conducted on an electrochemical workstation (METROHM, Autolab) with a three-electrode system. The working electrode was a glassy carbon disk (diameter, 3 mm), the counter electrode was a platinum wire, and the reference electrode was an Ag/AgCl electrode. The glass carbon electrode was polished by Al_2O_3 powder (0.05 μm) before each CV experiments cyclic voltammetry. The cyclic voltammetry experiments were recorded in an electrolyte of $n\text{-}Bu_4NPF_6$ (0.1 M) in degassed MeCN at 25 °C. The cyclic voltammetry was scanned from 0 V, and the scan rate was 0.10 V/s.

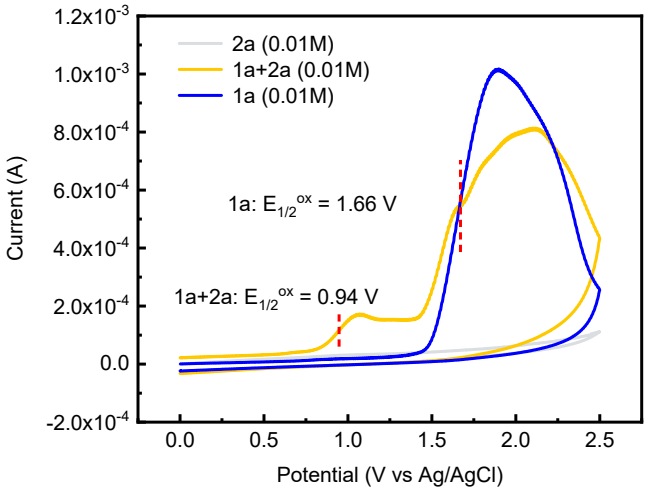


Figure S4. CV of **1a** (0.01 M in CH_3CN), **2a** (0.01 M in CH_3CN), and **1a**+**2a** (0.01 M in CH_3CN). The scan rate was 0.10 V/s, ranging from 0 V to 2.5 V.

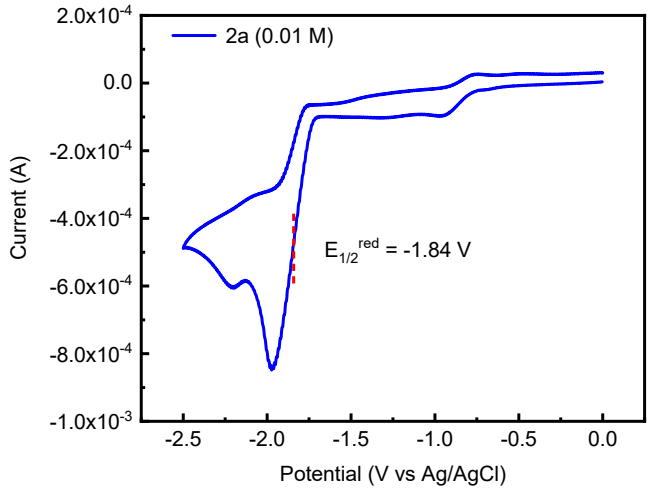
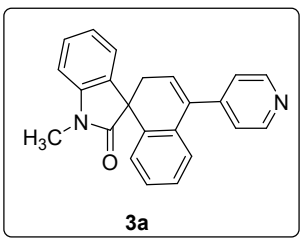
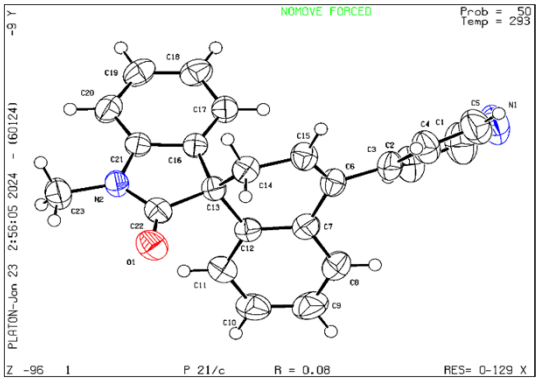


Figure S5. CV of **2a** (0.01 M in CH_3CN). The scan rate was 0.10 V/s, ranging from -2.5 V to 0 V.

6. Crystal report of compound 3a

Crystal report of compound **3a** (CCDC number: 2376866):





checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1

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                  alpha=90        beta=95.914(15)     gamma=90
Temperature:      293 K

                 Calculated                Reported
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Space group      P 21/c                    P 21/c
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C23 H18 N2 O              C23 H18 N2 O
Sum formula      C23 H18 N2 O              C23 H18 N2 O
Mr               338.39                    338.39
Dx,g cm-3        1.290                     1.290
Z                4                         4
Mu (mm-1)        0.080                     0.080
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F000'            712.27
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Nref             4025                      4025
Tmin,Tmax        0.990,0.992
Tmin'            0.984

Correction method= Not given

Data completeness= 1.000           Theta(max)= 27.578

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Click on the hyperlinks for more details of the test.
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Alert level C

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PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     11.116 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         8 Report
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PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          1 Check
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Alert level G

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PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         17 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.9 Low
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged     Please Check
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........       3.13 Note
             Predicted wR2: Based on SigI**2  7.48 or SHELX Weight 23.89
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
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  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 11 ALERT level G = General information/check it is not something unexpected

  5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  2 ALERT type 2 Indicator that the structure model may be wrong or deficient
  7 ALERT type 3 Indicator that the structure quality may be low
  2 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/01/2024; check.def file version of 05/01/2024

7. References

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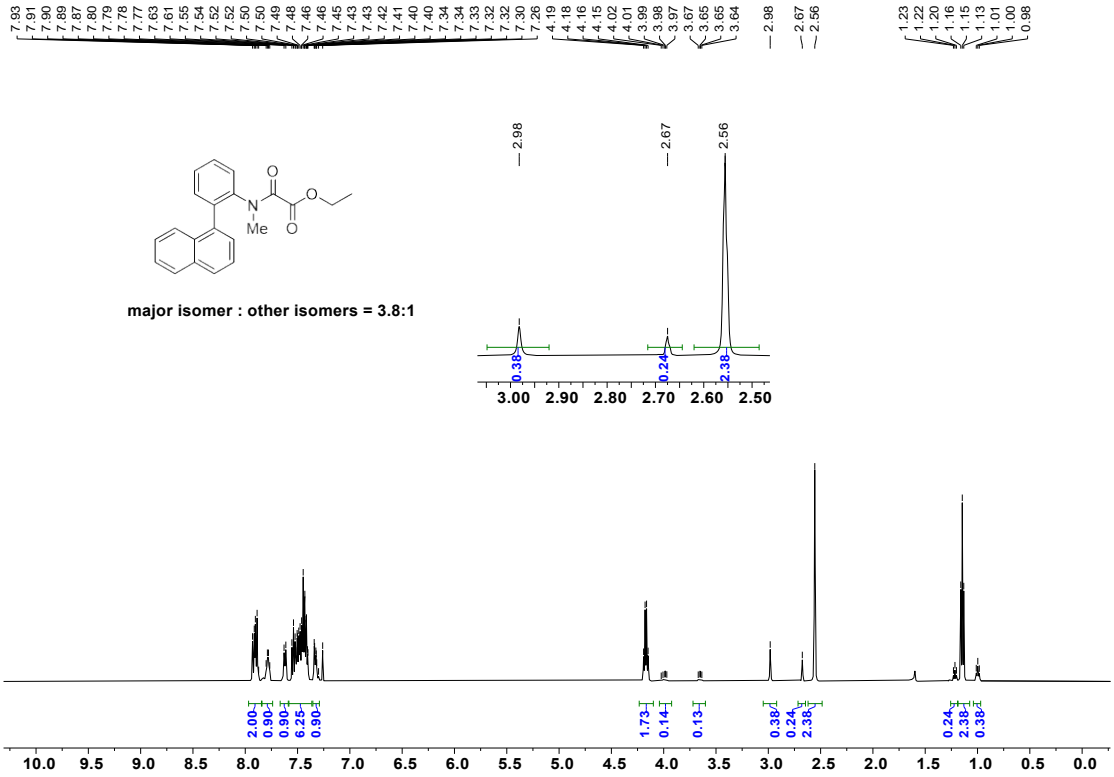
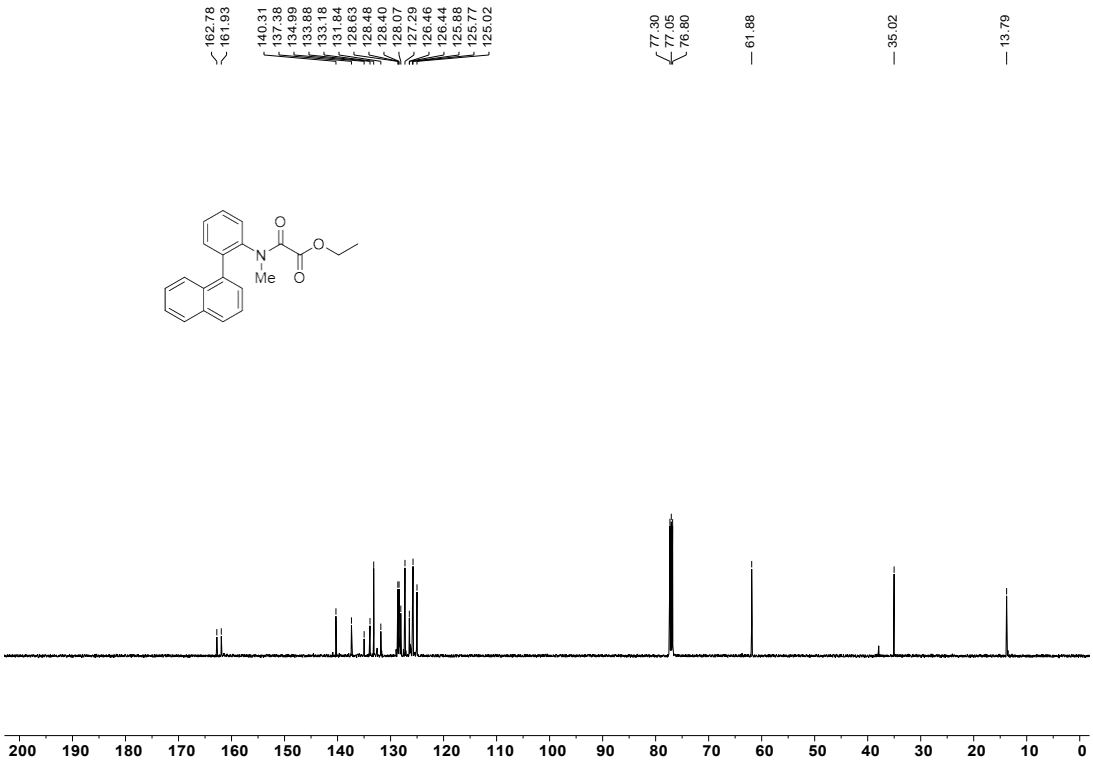
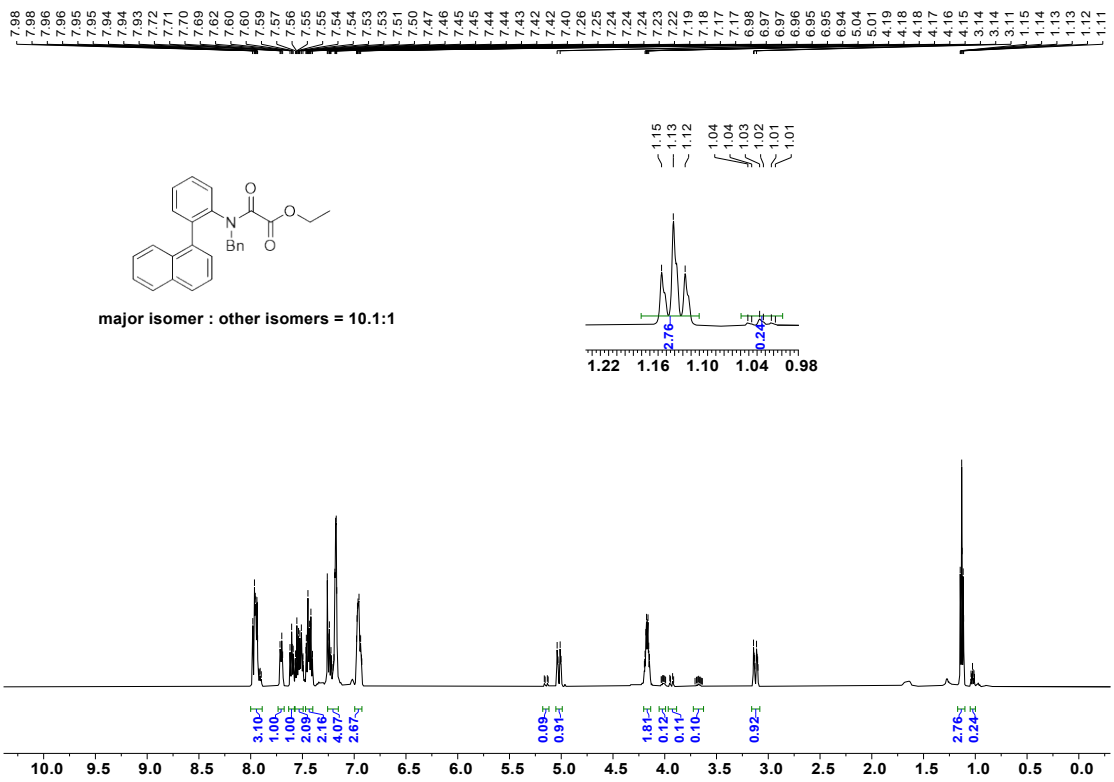
8. Copies of NMR spectra



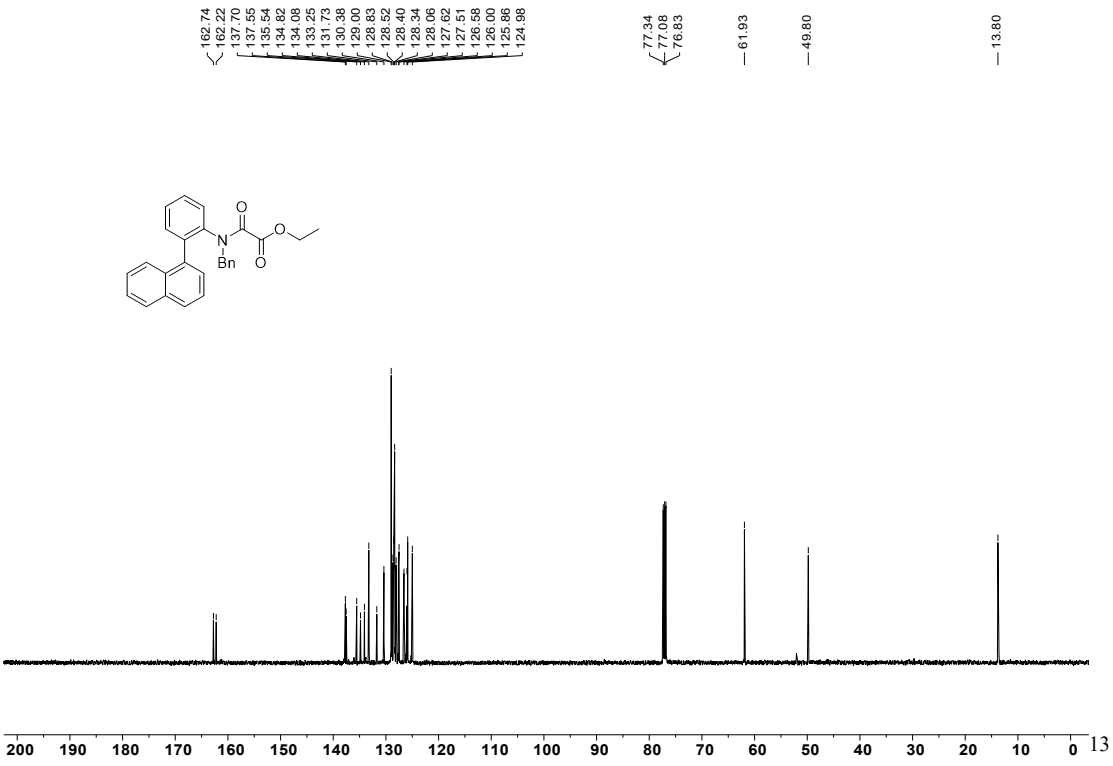
^{1}H NMR spectrum of compound **S-1a** (500 MHz, Chloroform-*d*)



^{13}C NMR spectrum of compound **S-1a** (125 MHz, Chloroform-*d*)



^{1}H NMR spectrum of compound **S-1b** (500 MHz, Chloroform-*d*)



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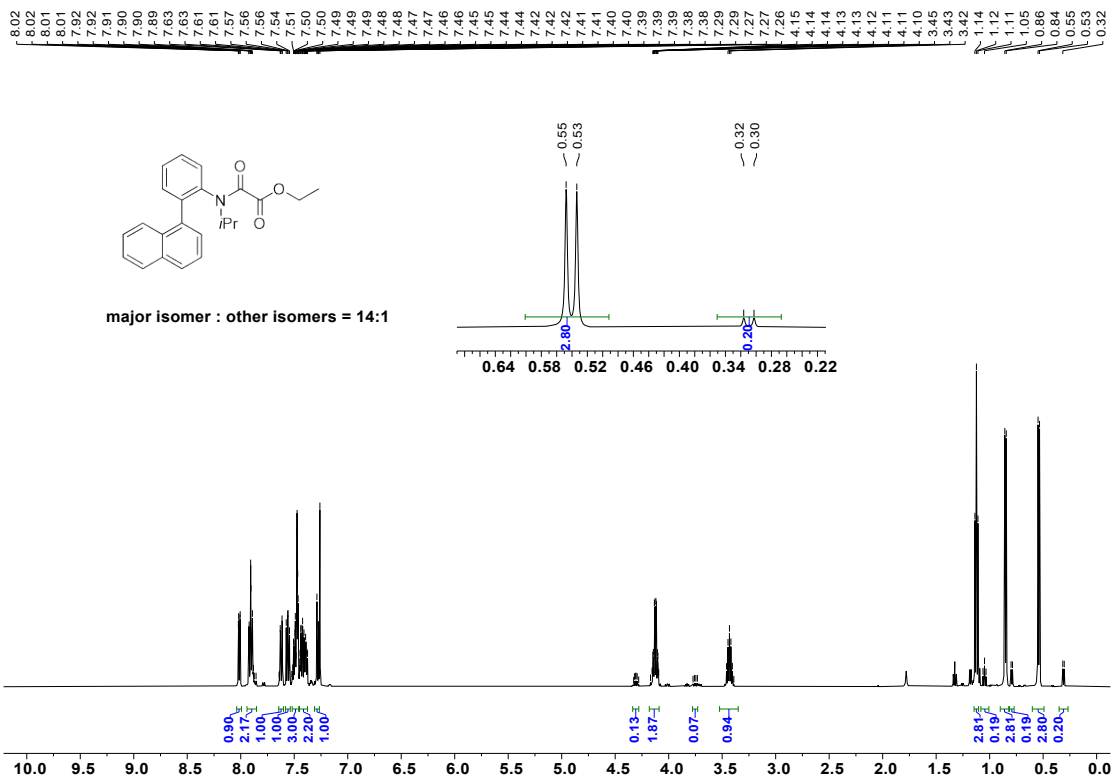
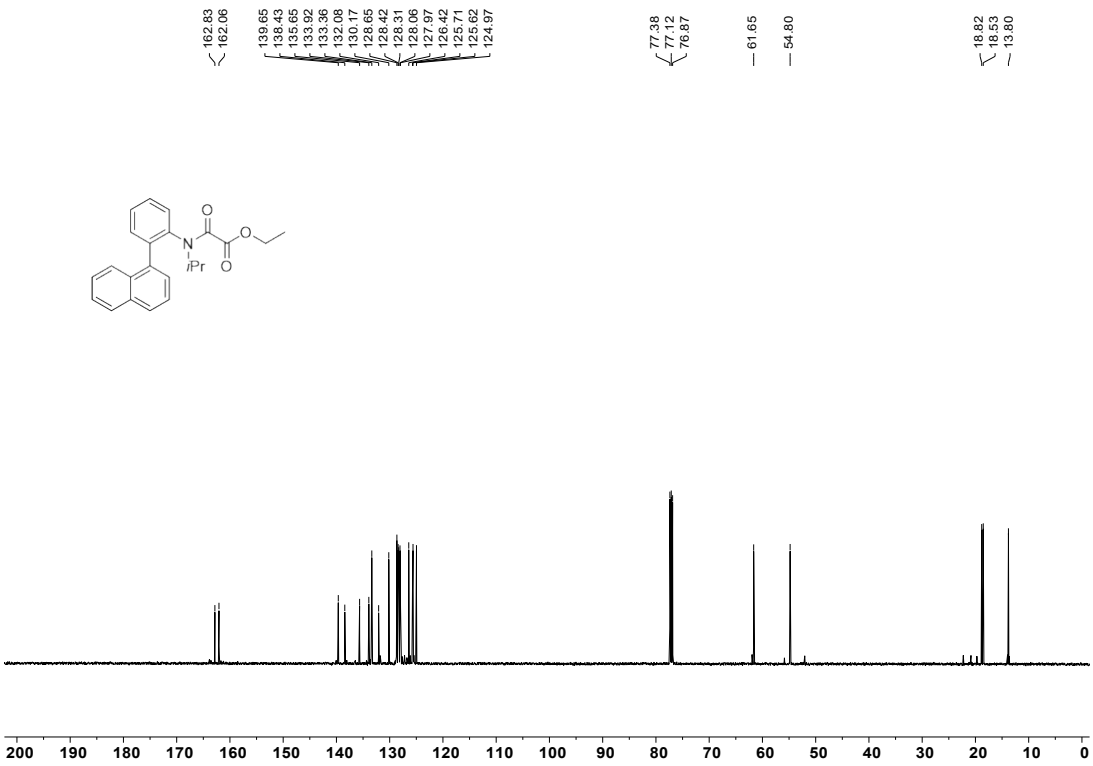


^{1}H NMR spectrum of compound **S-1c** (500 MHz, Chloroform-*d*)



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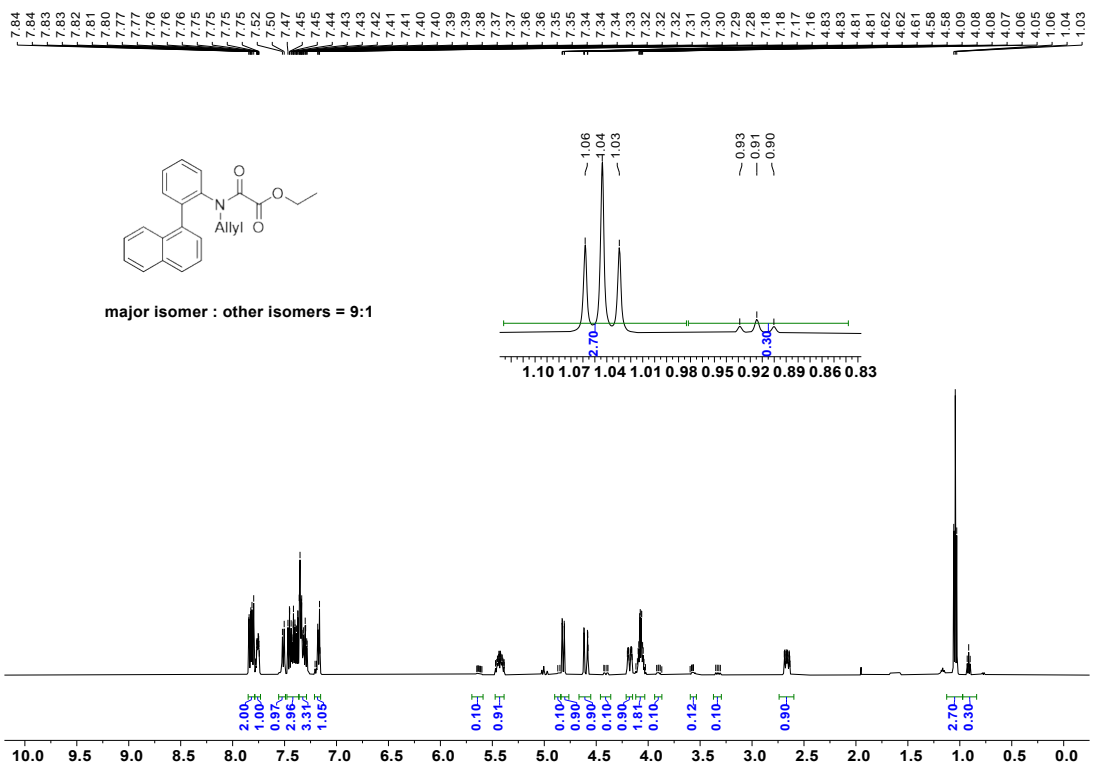
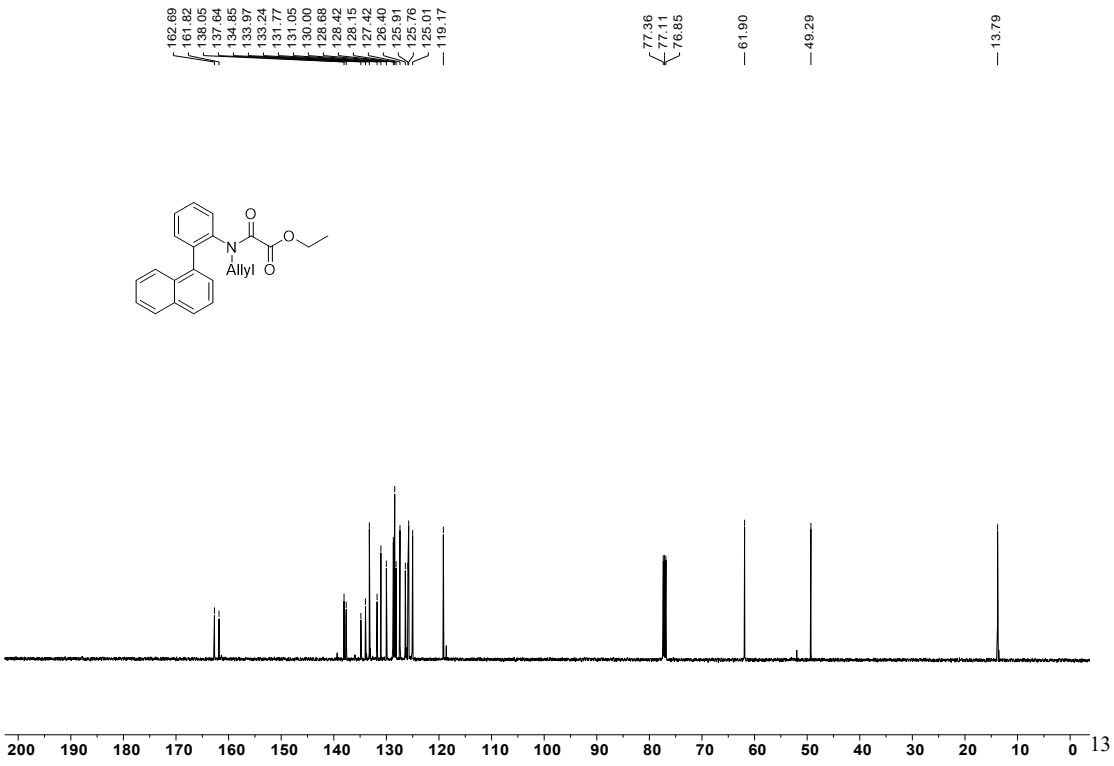


^{1}H NMR spectrum of compound **S-1d** (500 MHz, Chloroform-*d*)



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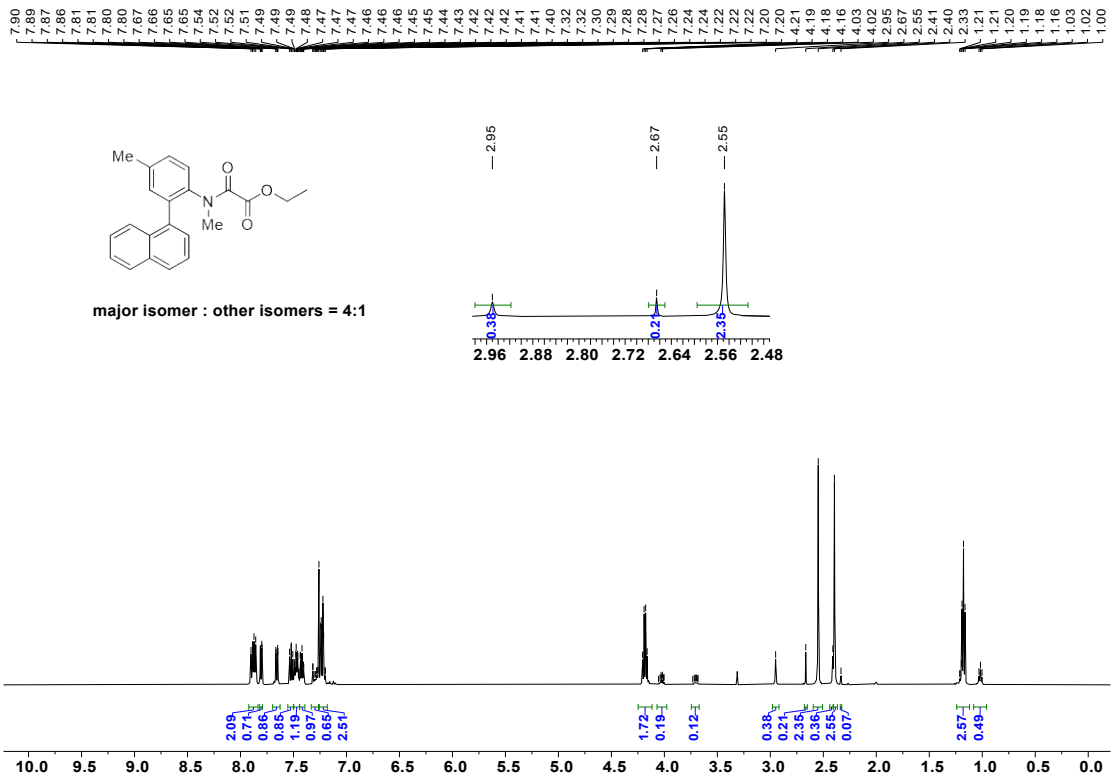

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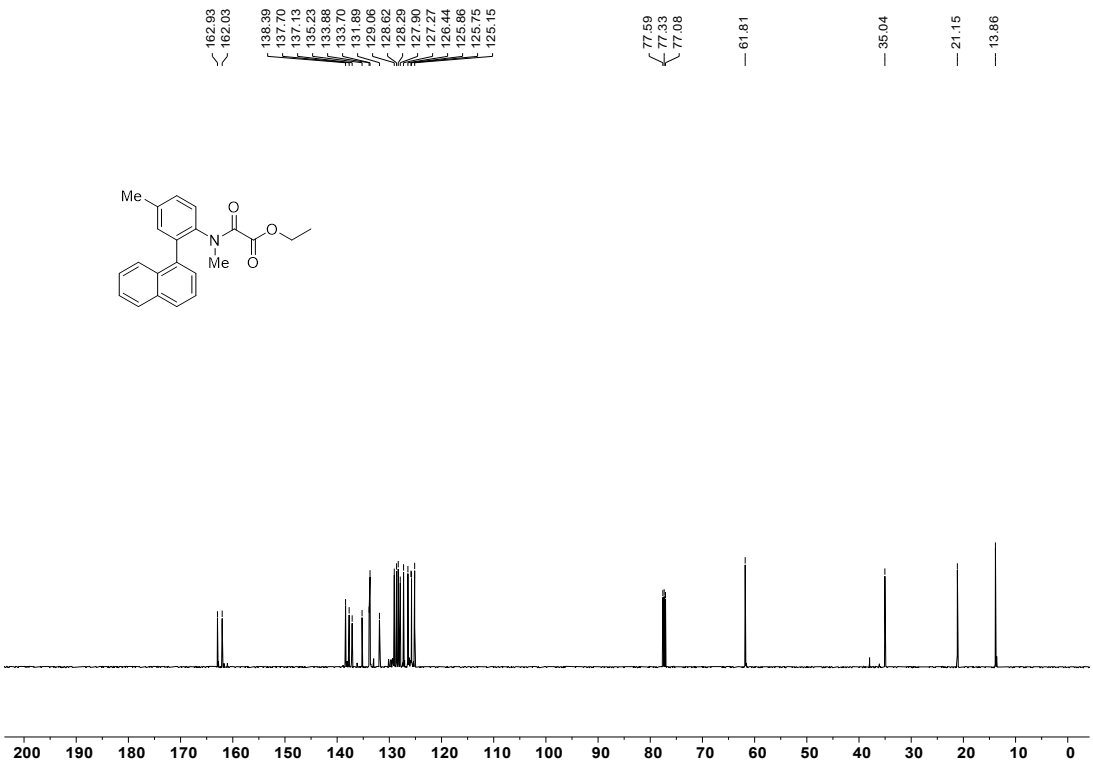

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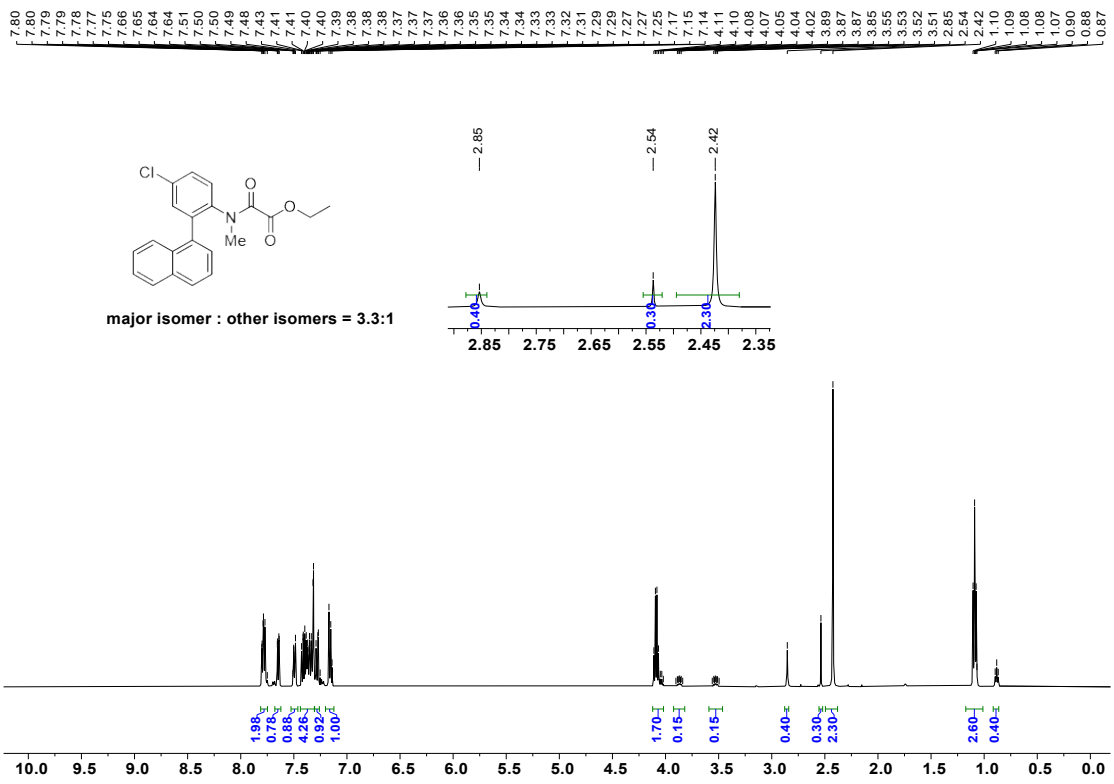

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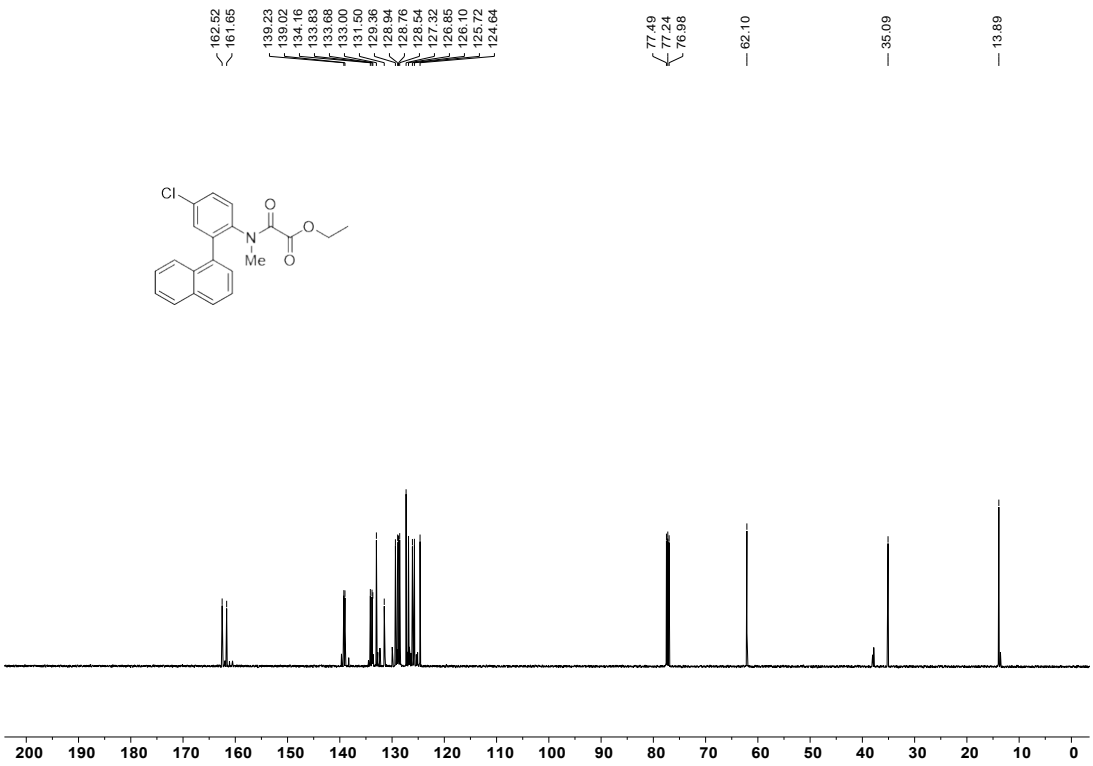

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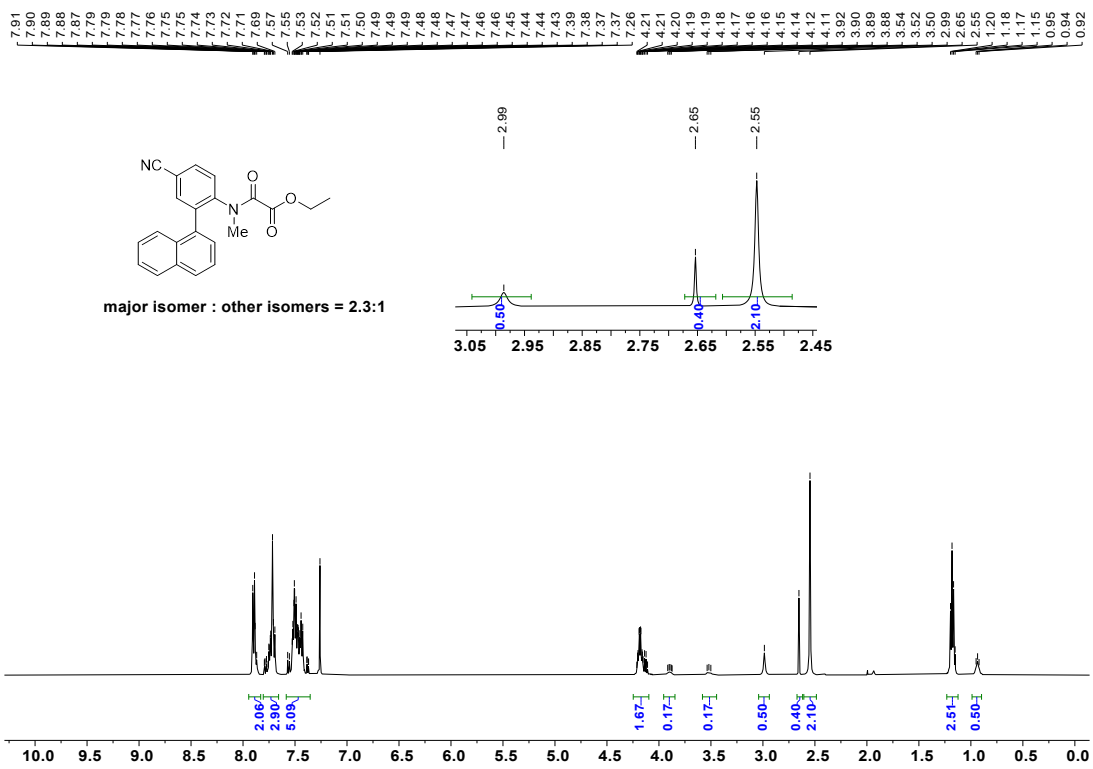

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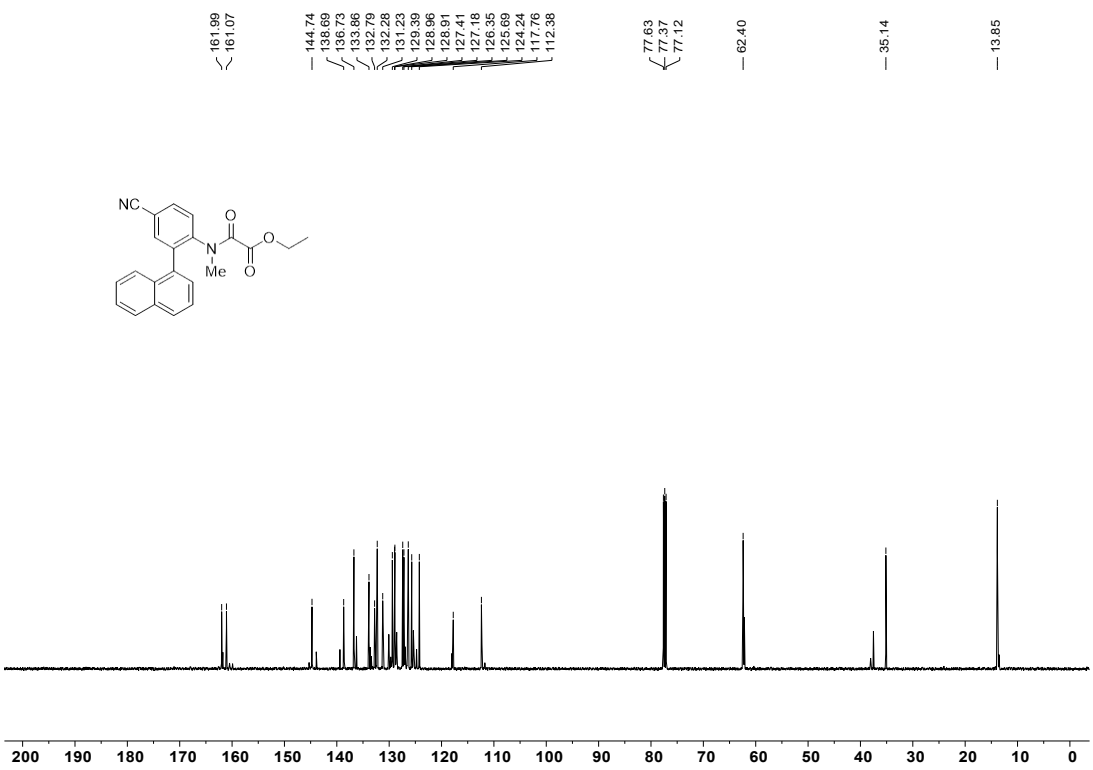

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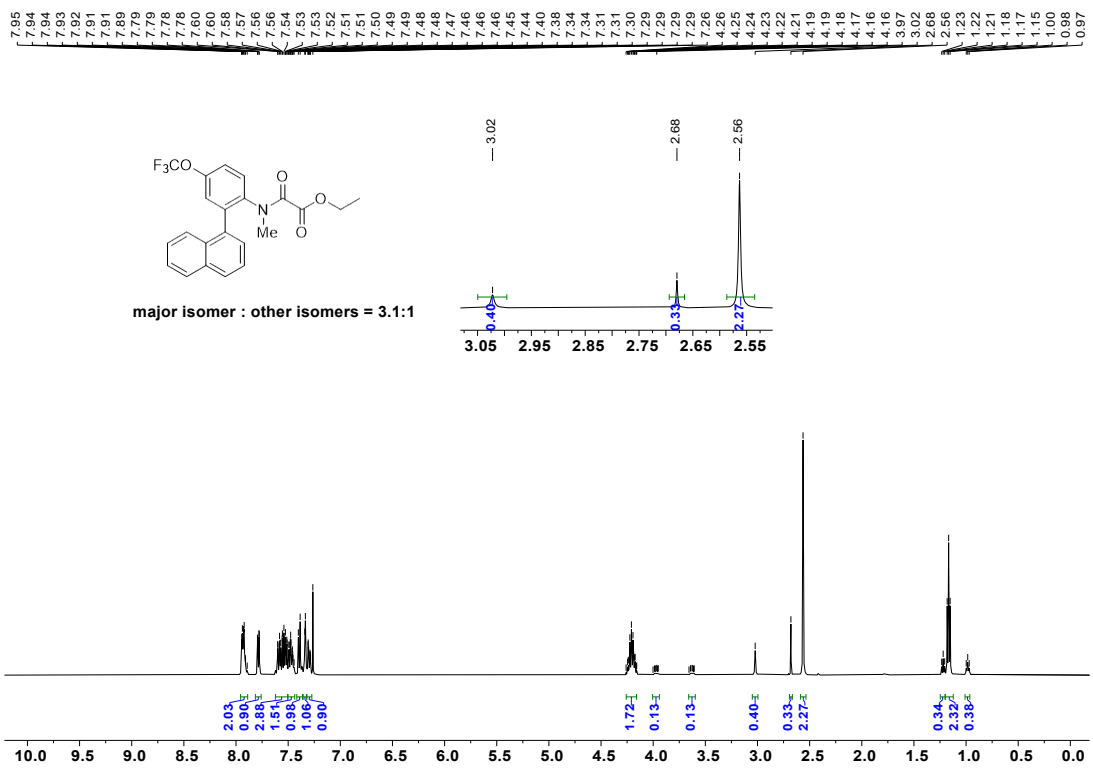
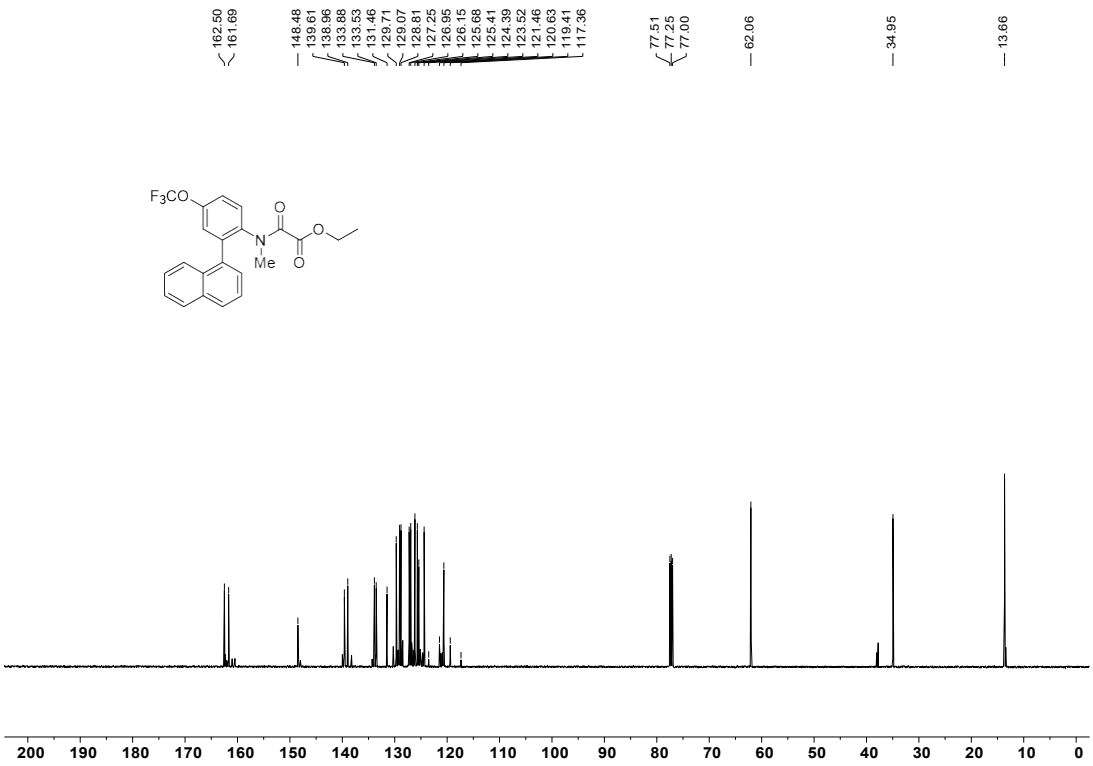
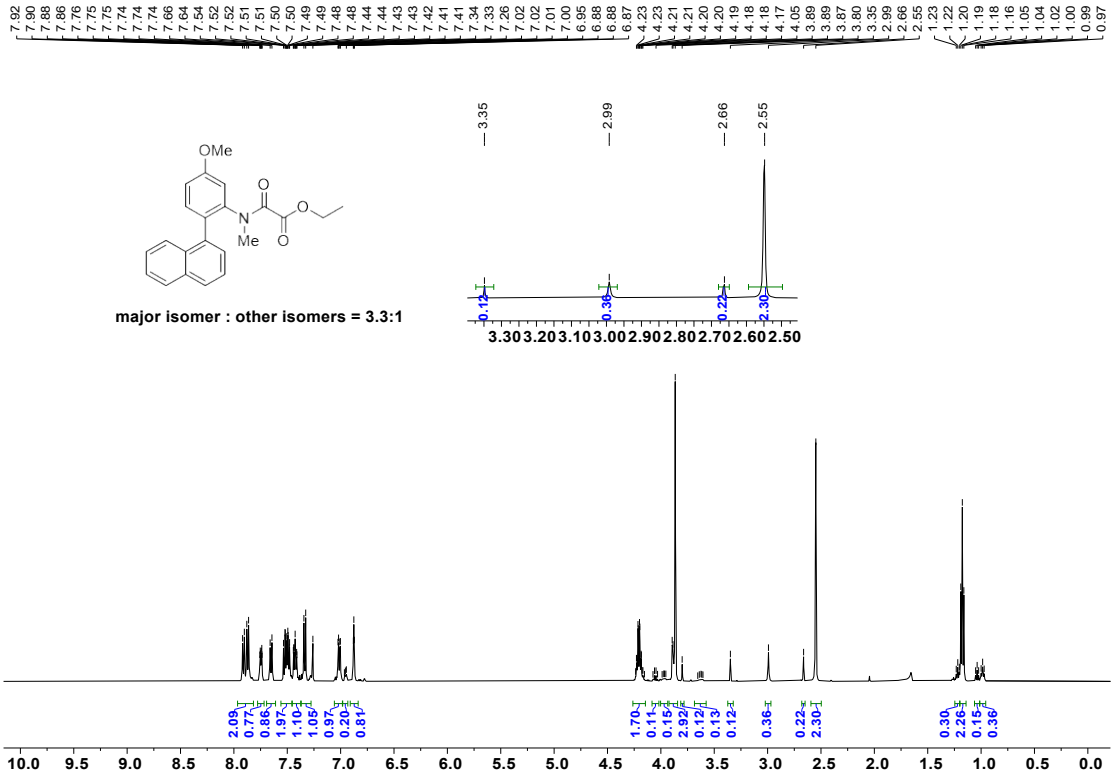


^{1}H NMR spectrum of compound **S-1h** (500 MHz, Chloroform-*d*)



^{13}C NMR spectrum of compound **S-1h** (125 MHz, Chloroform-*d*)

^{19}F NMR spectrum of compound **S-1h** (471 MHz, Chloroform-*d*)



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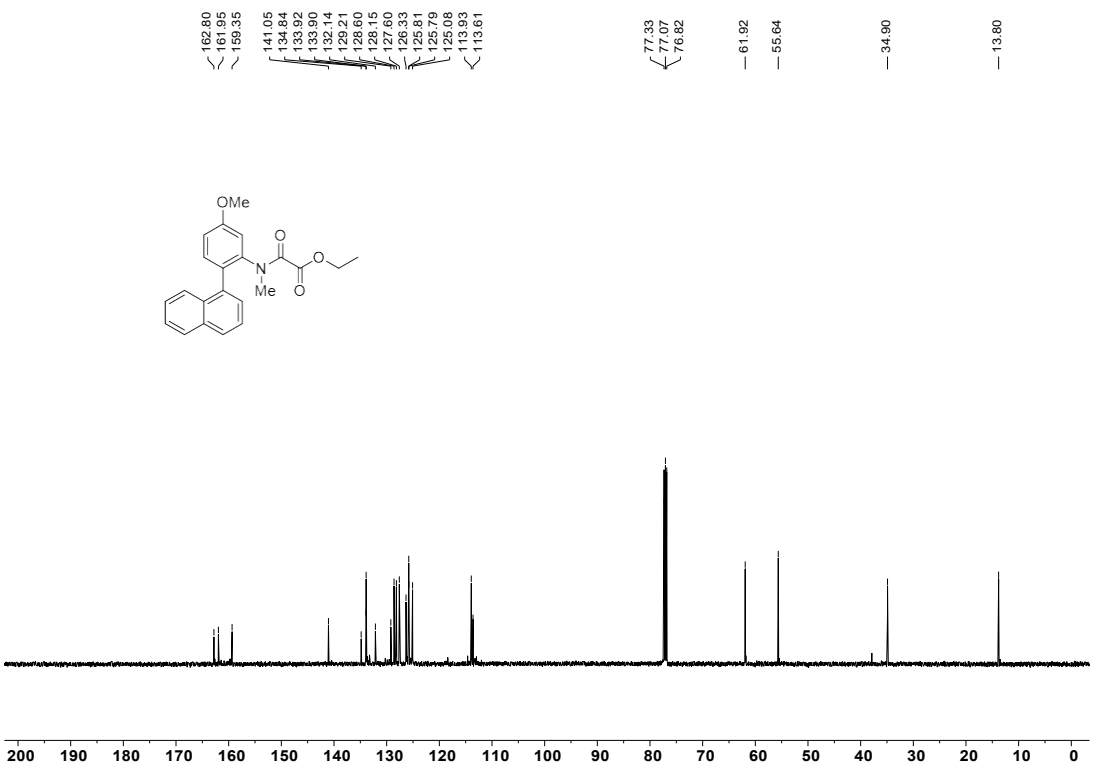

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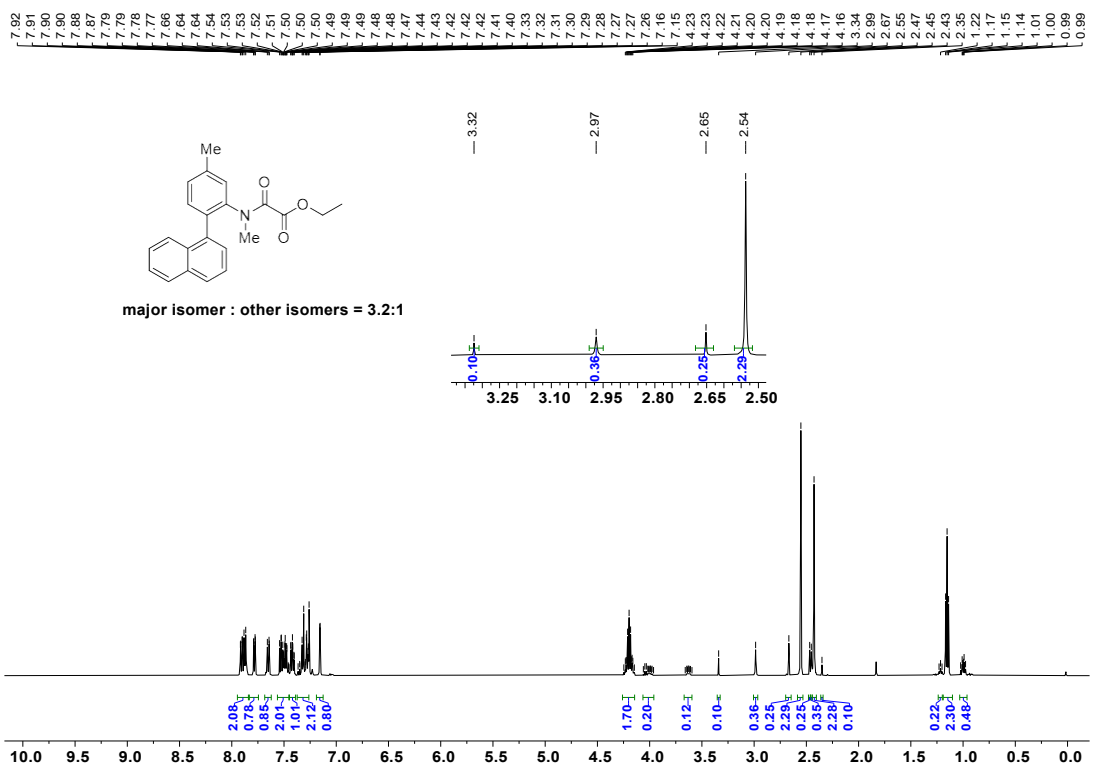

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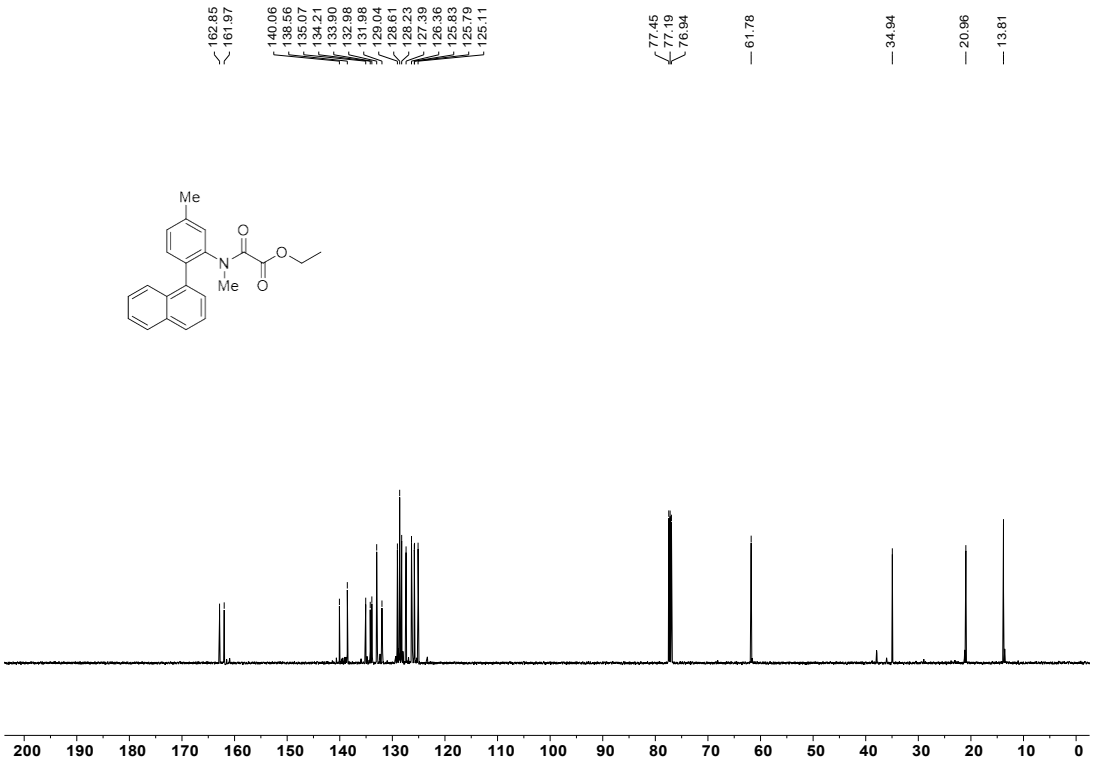

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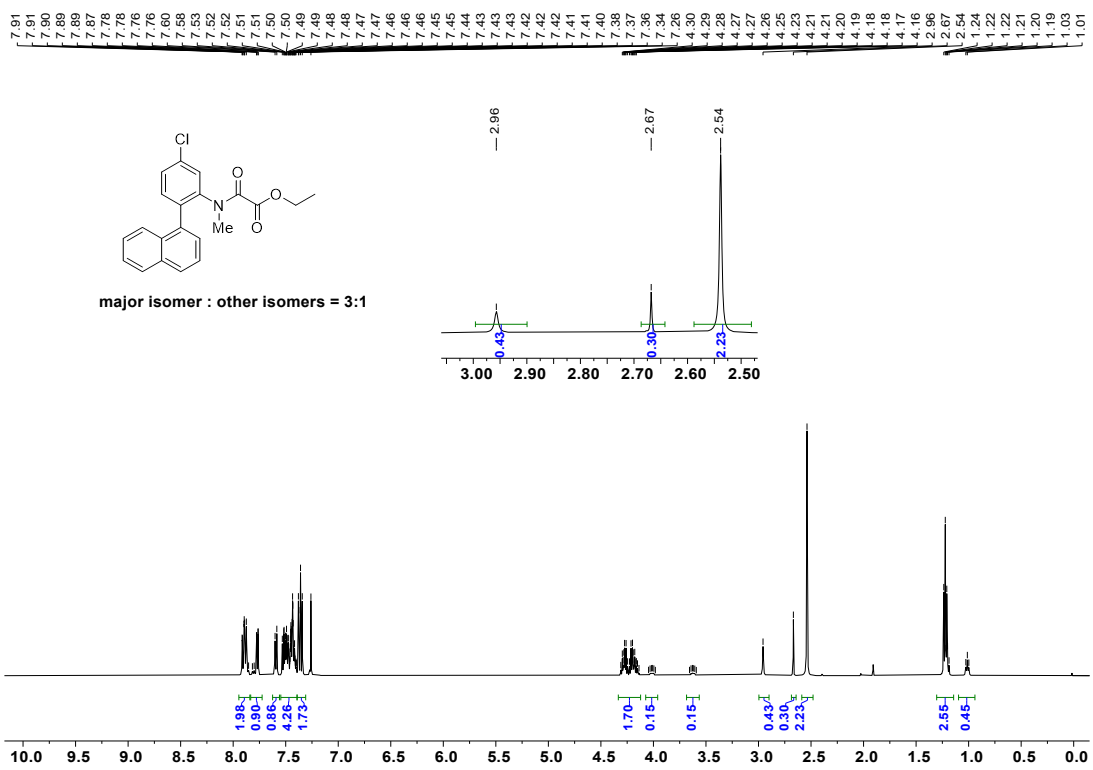

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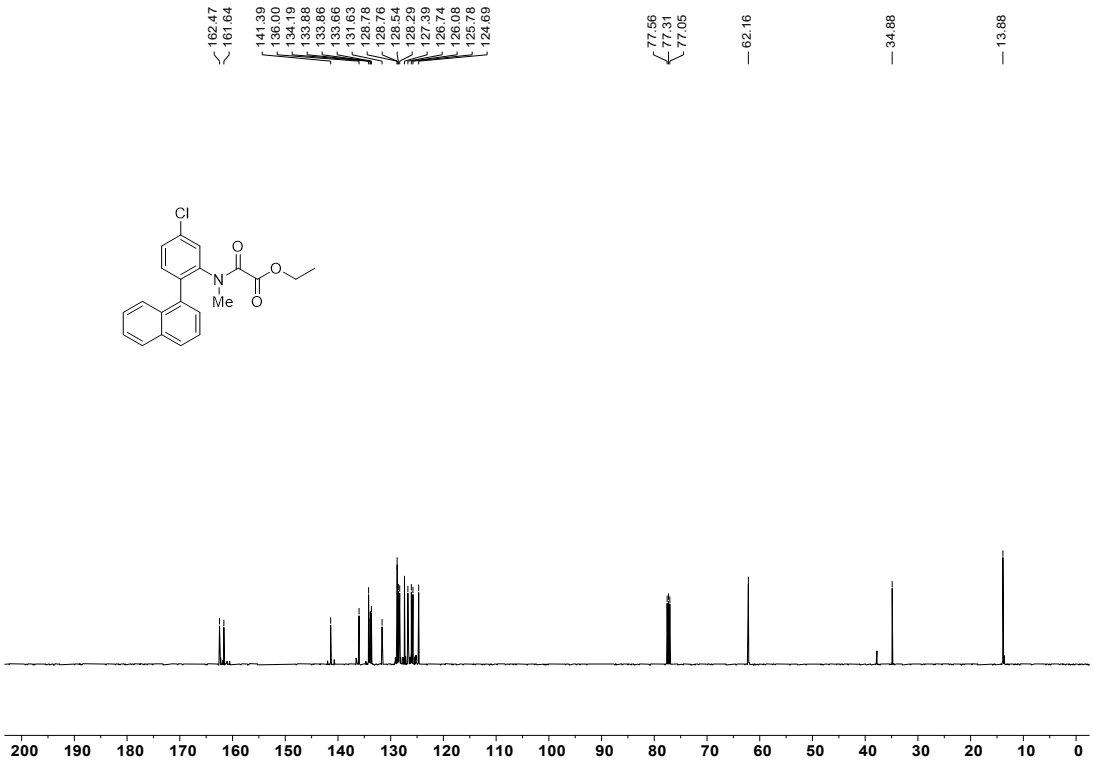

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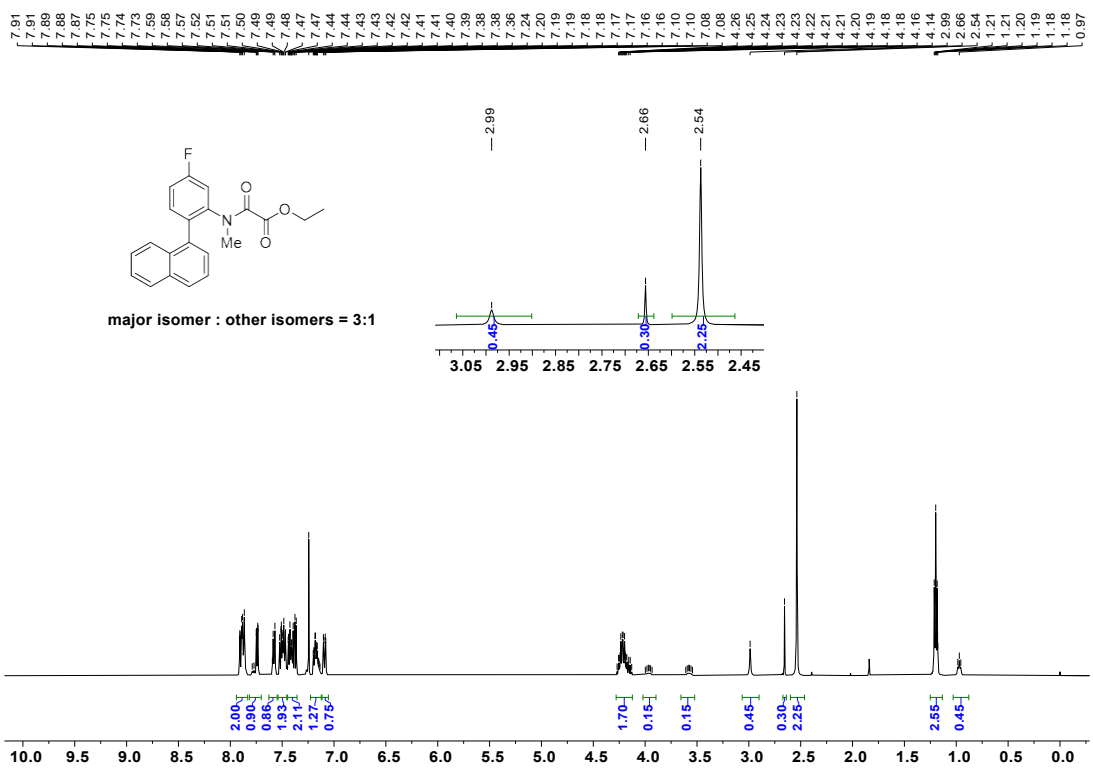

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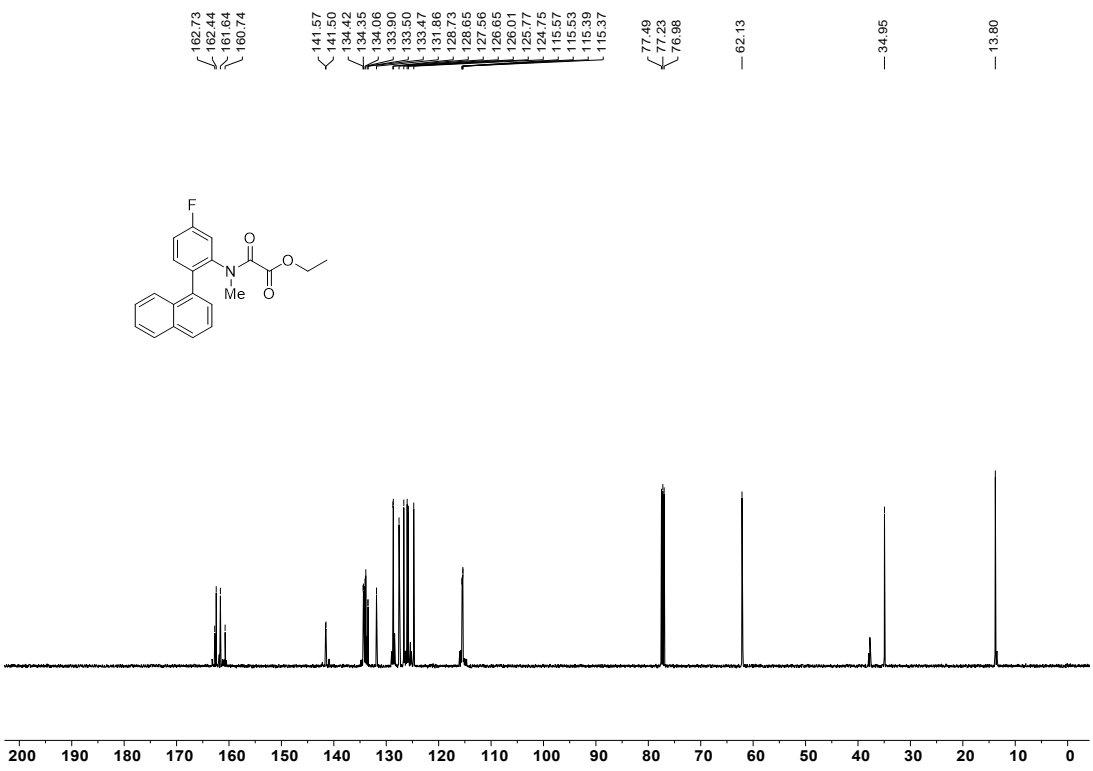

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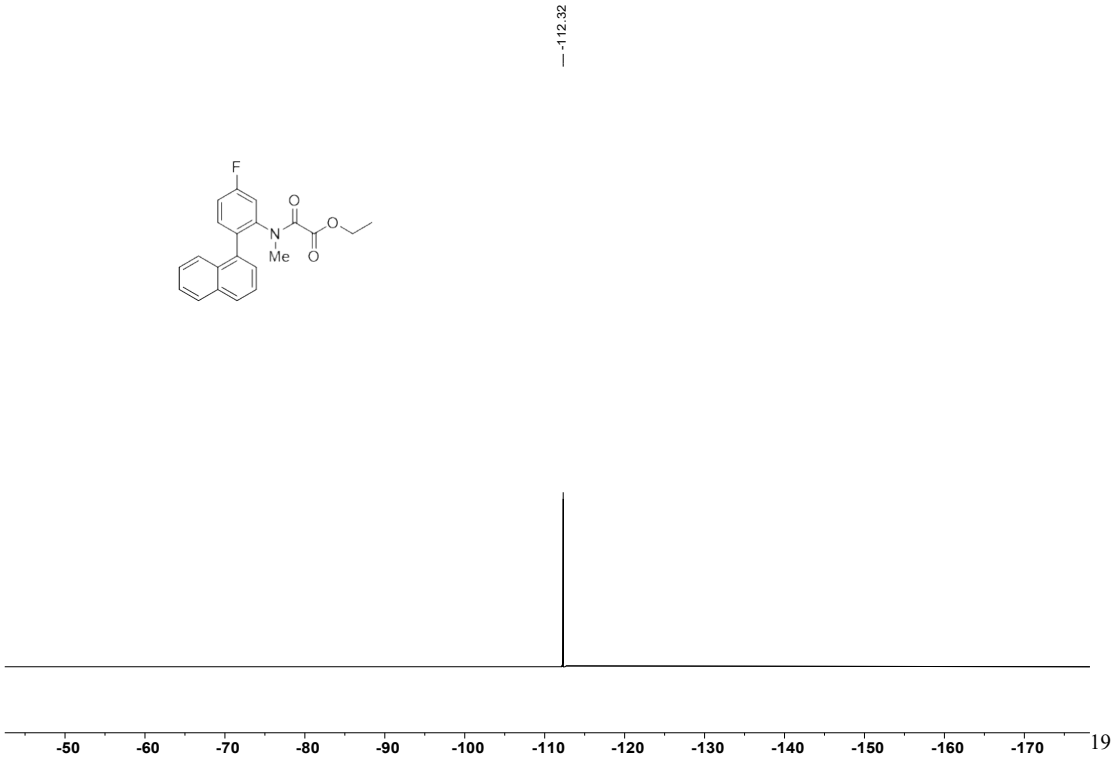

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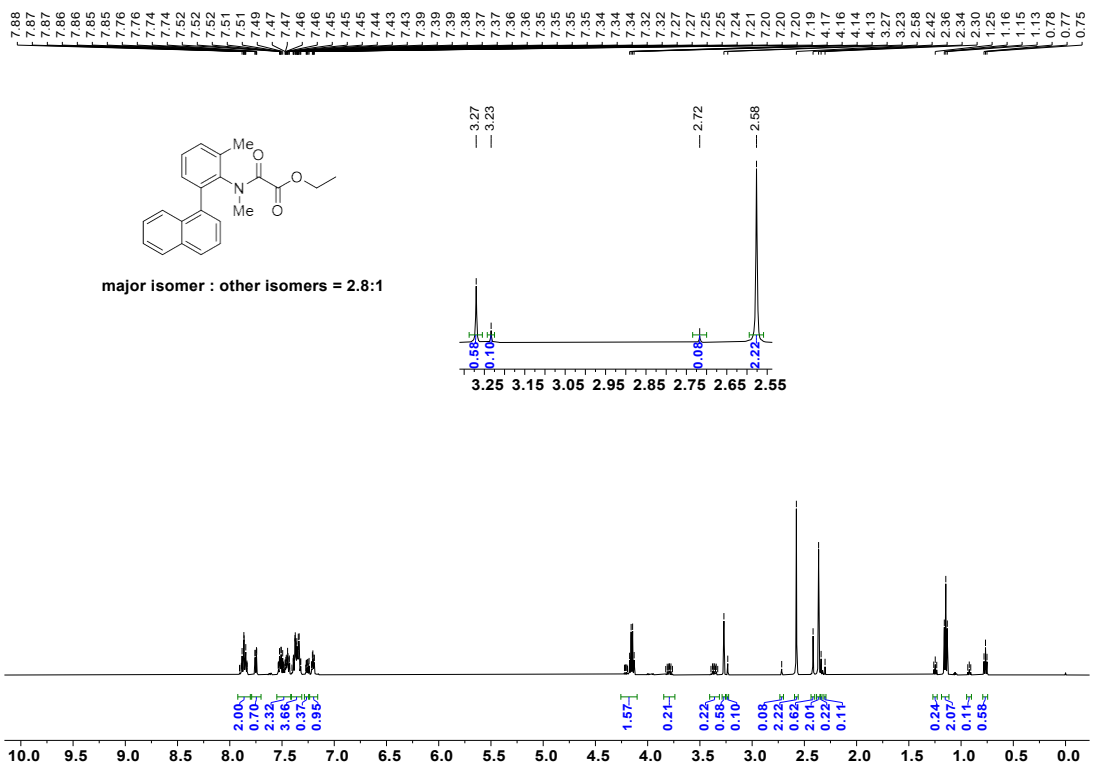

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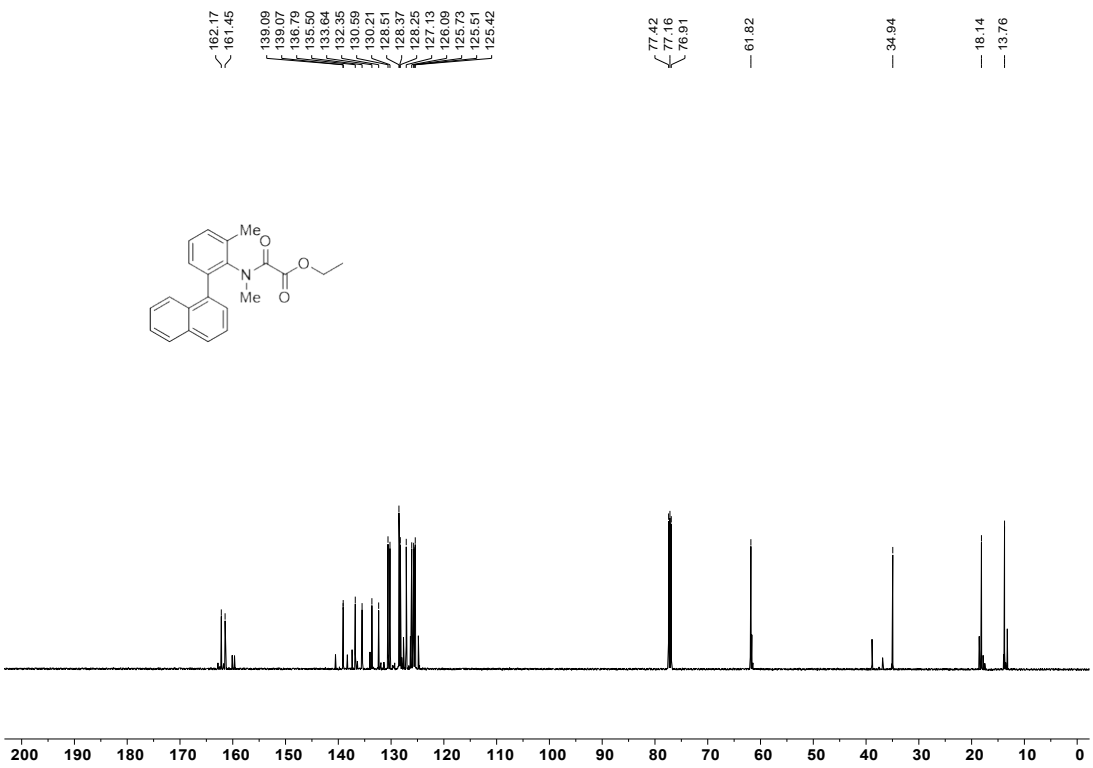

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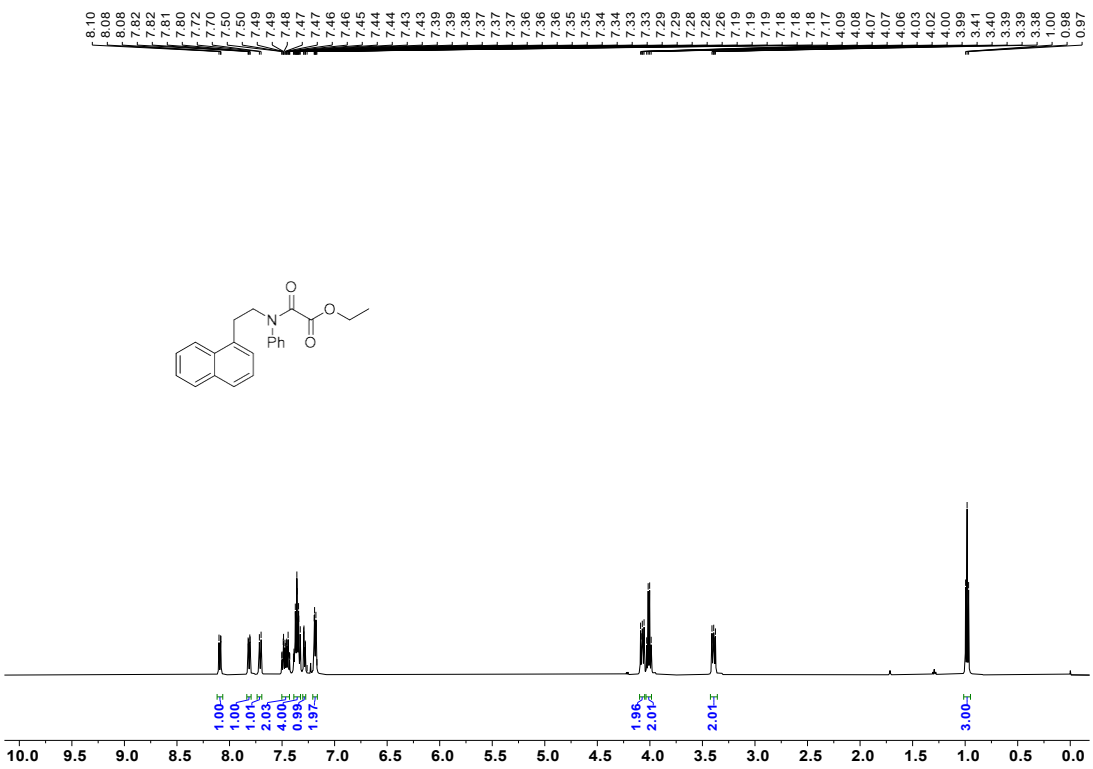

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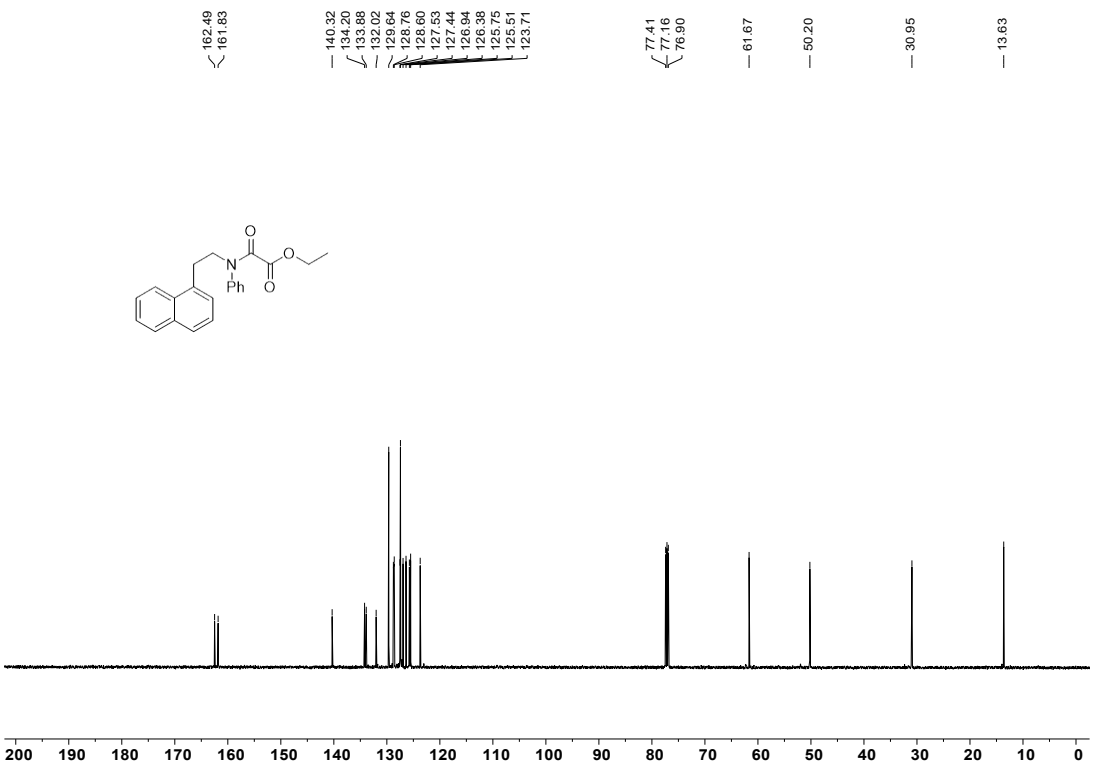

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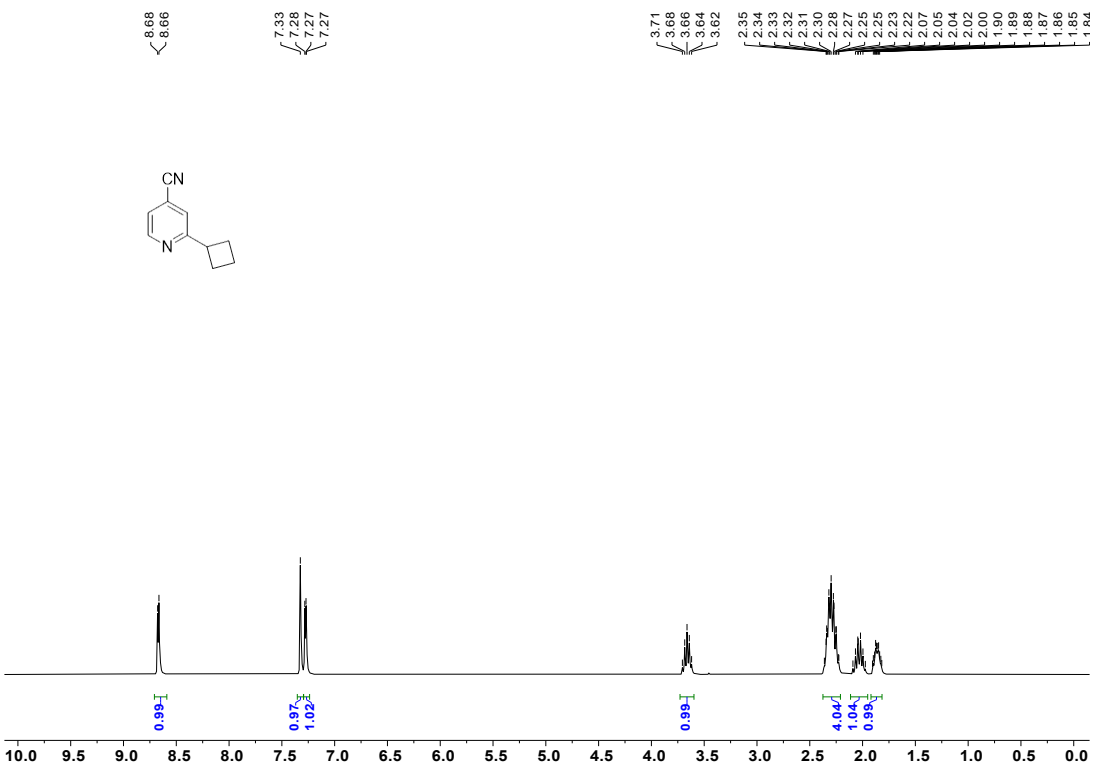

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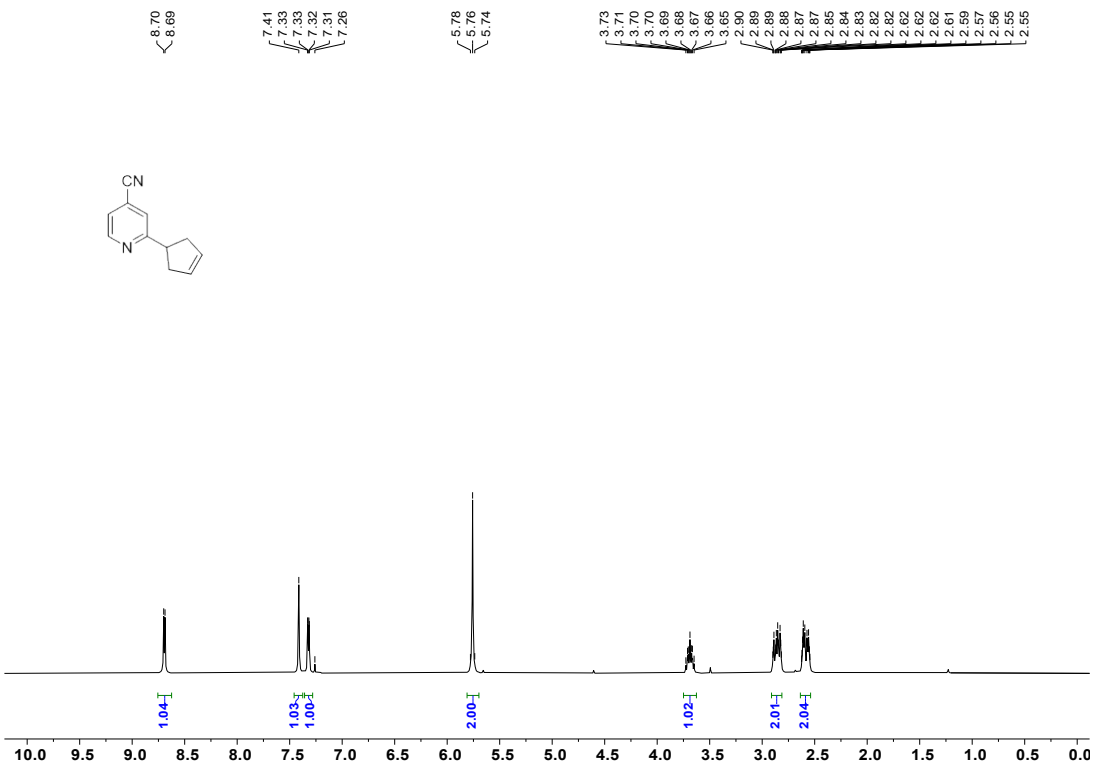

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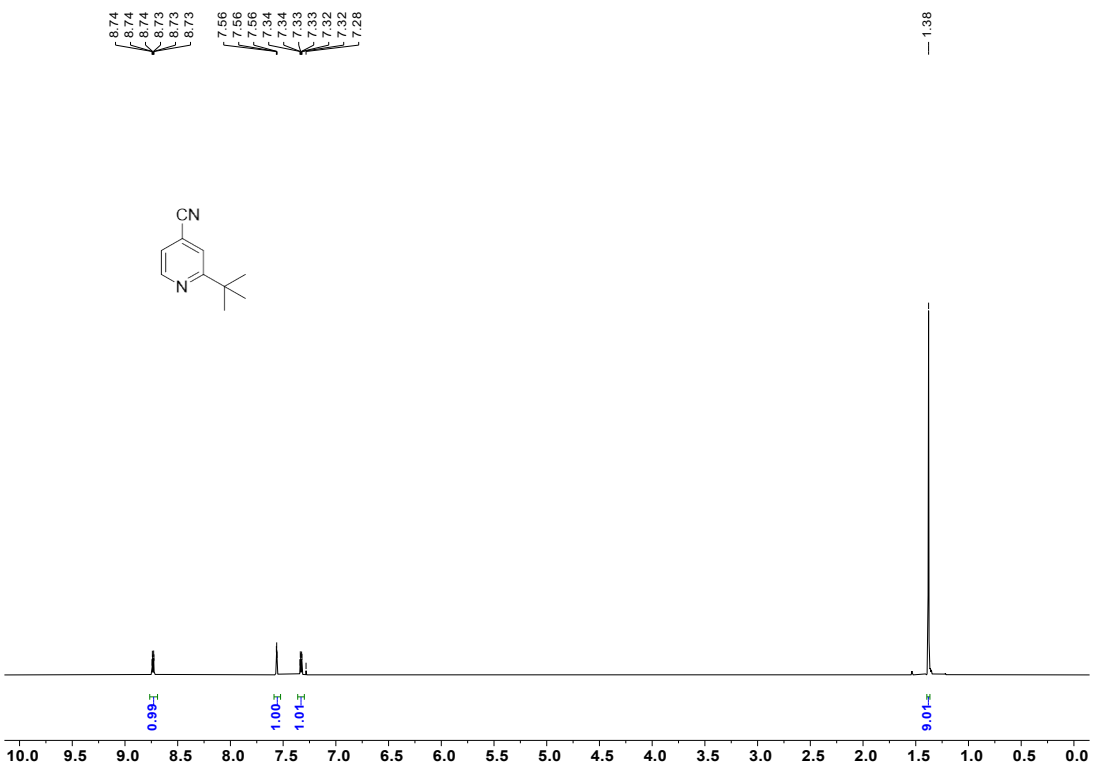

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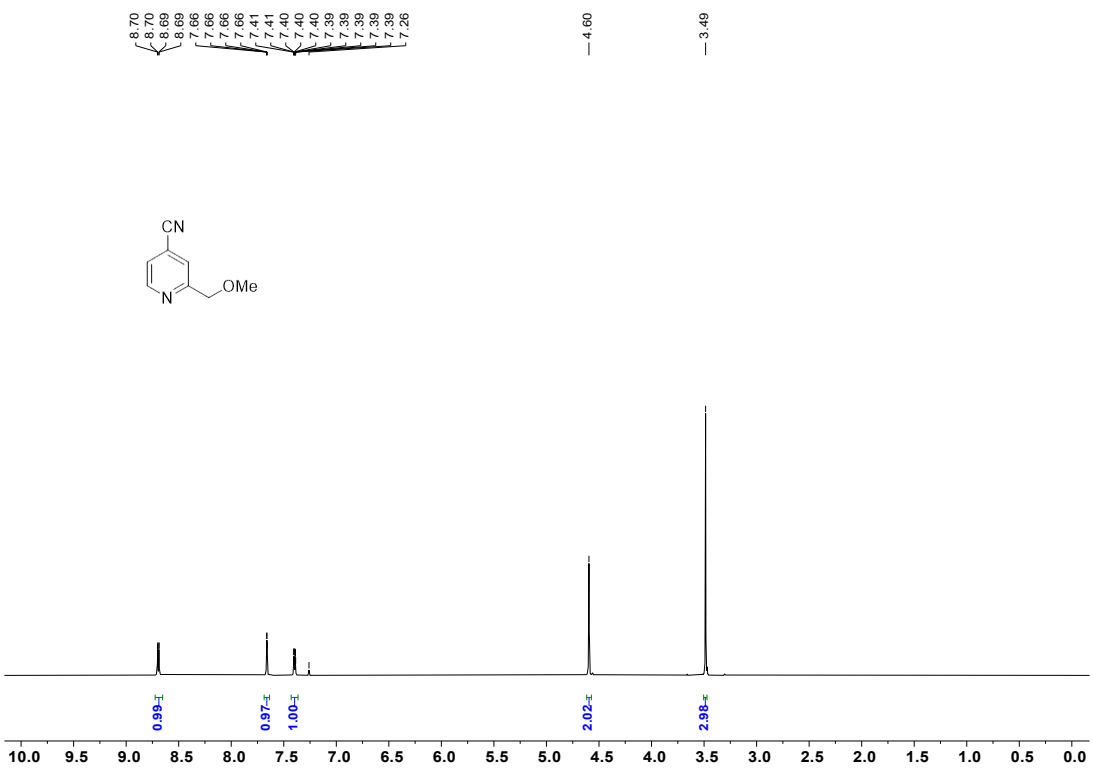

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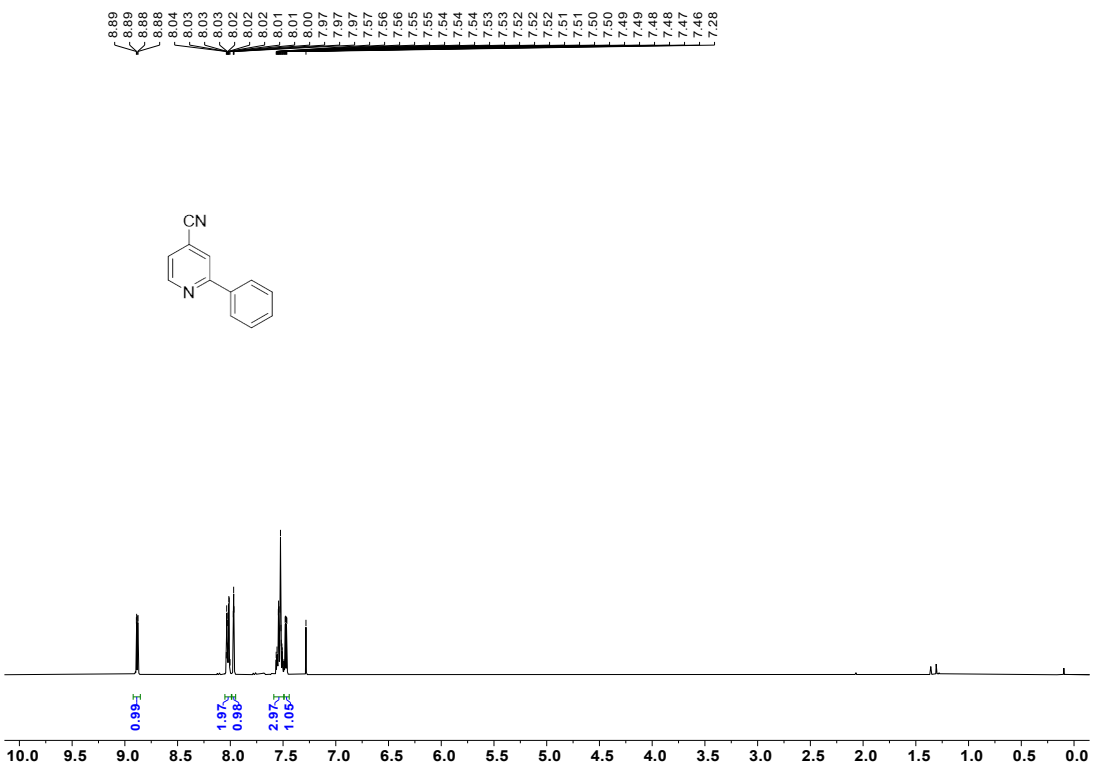

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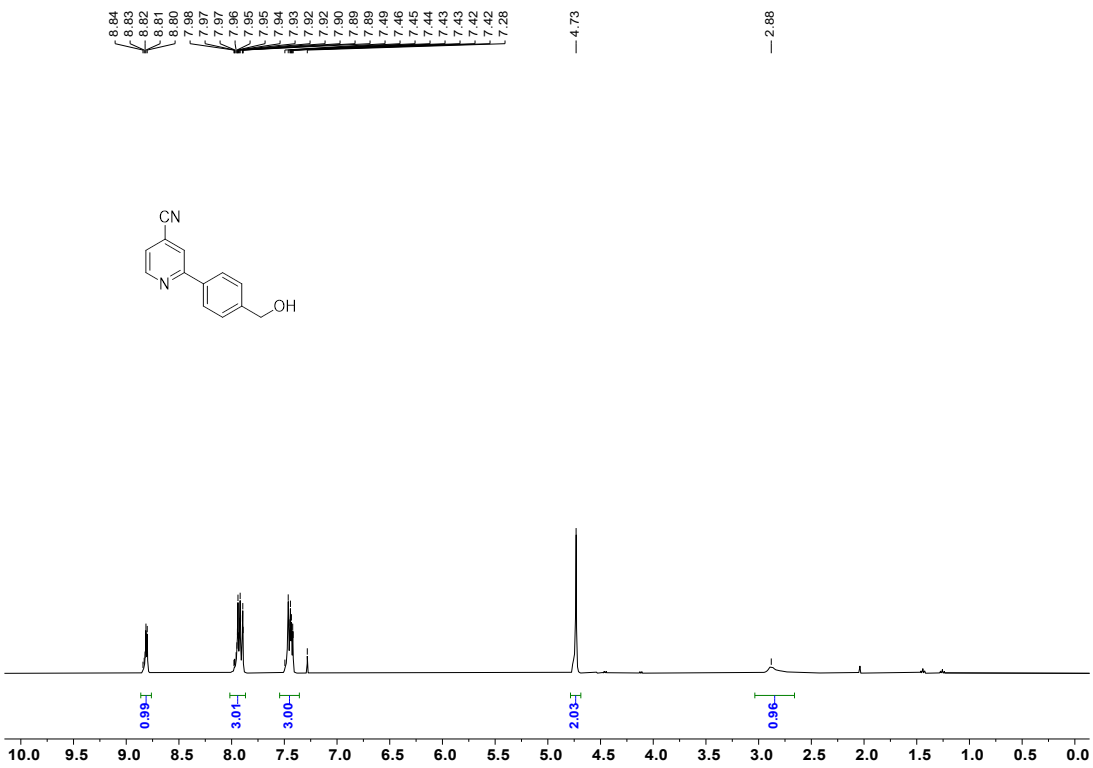

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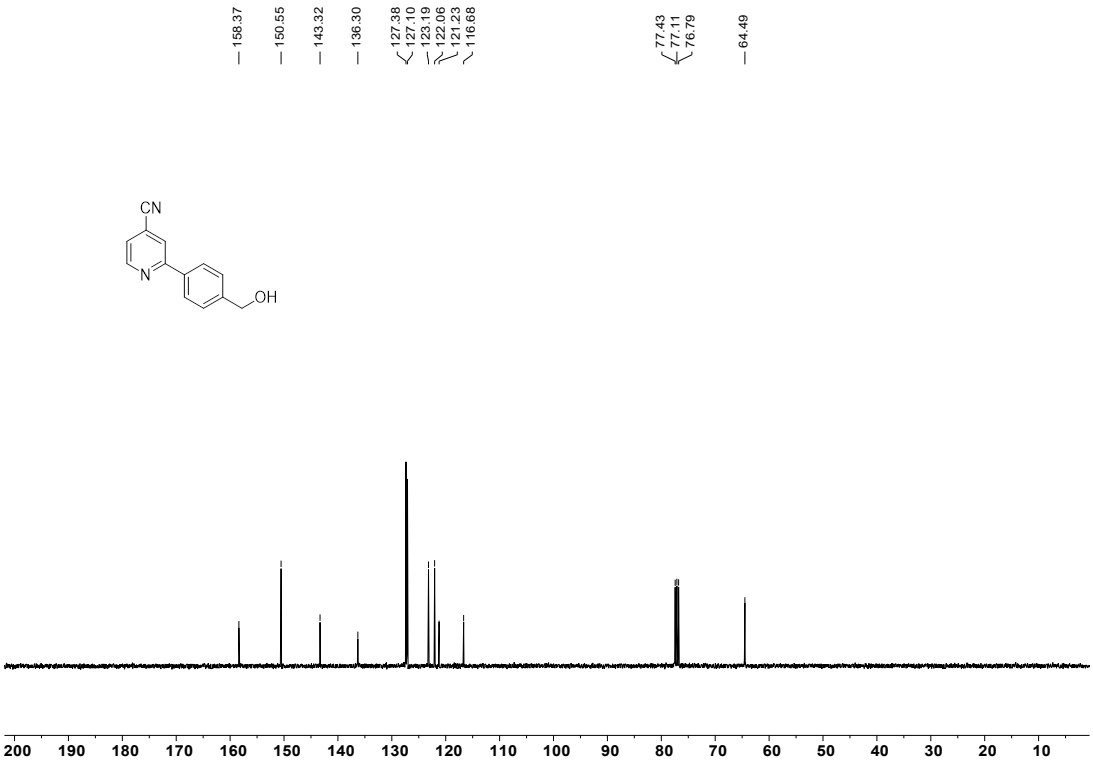

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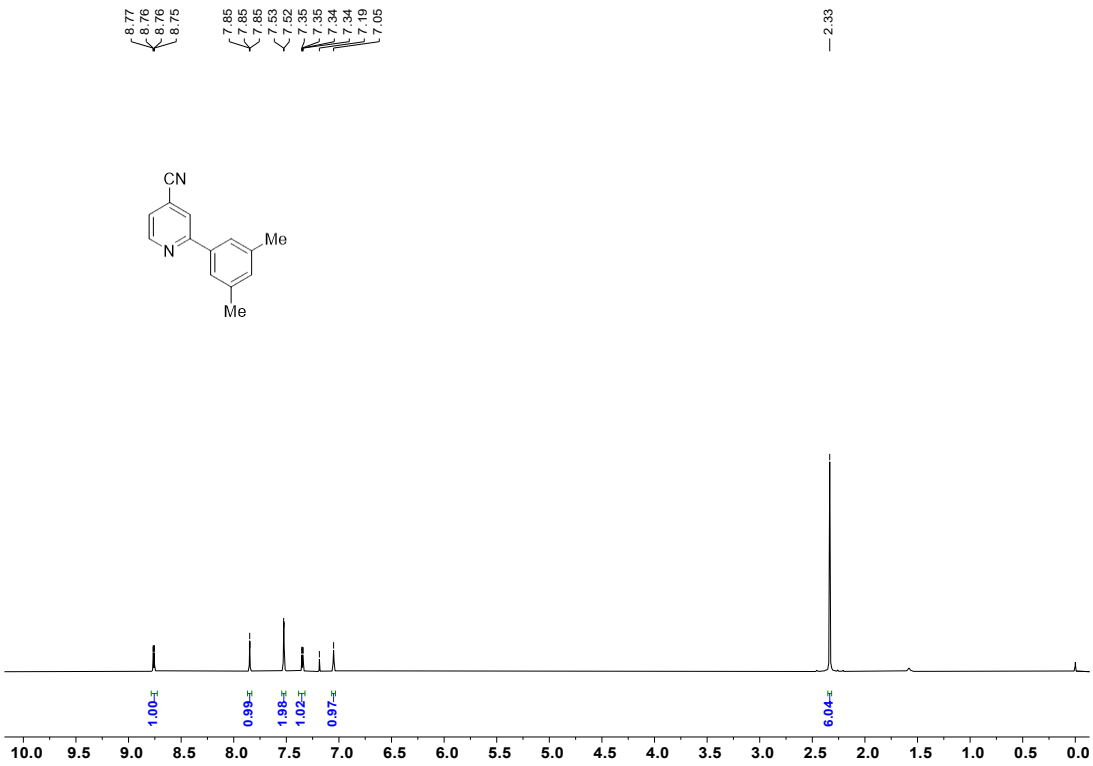

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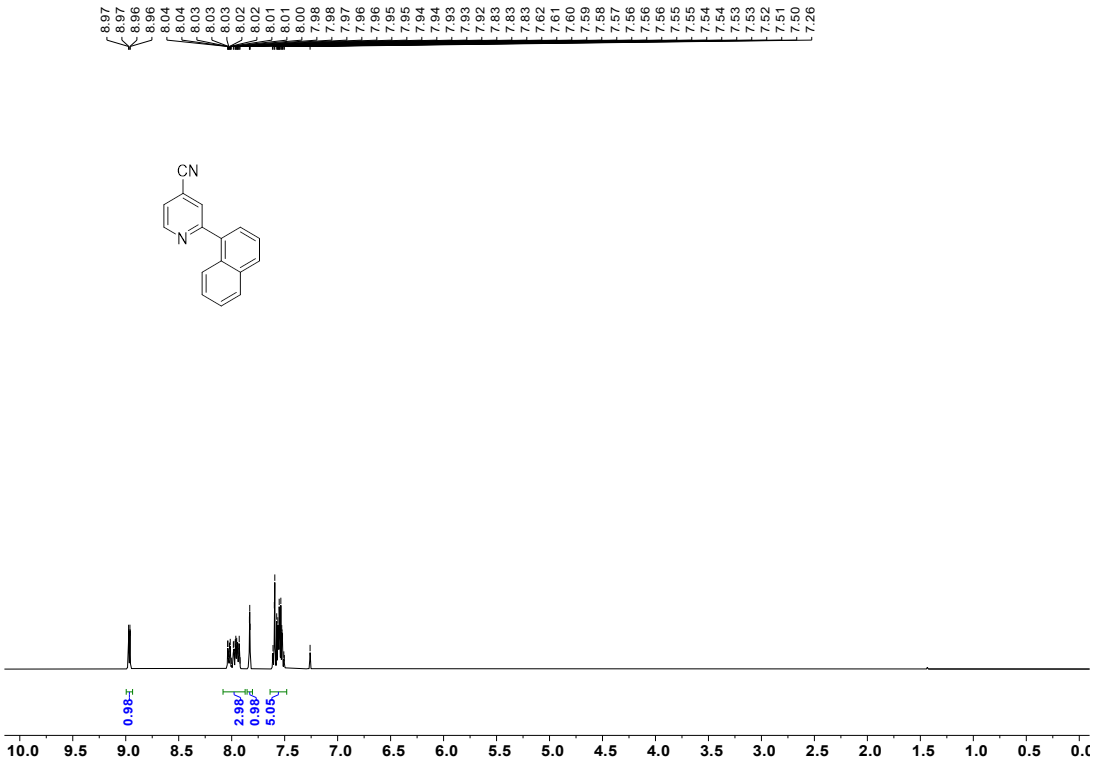

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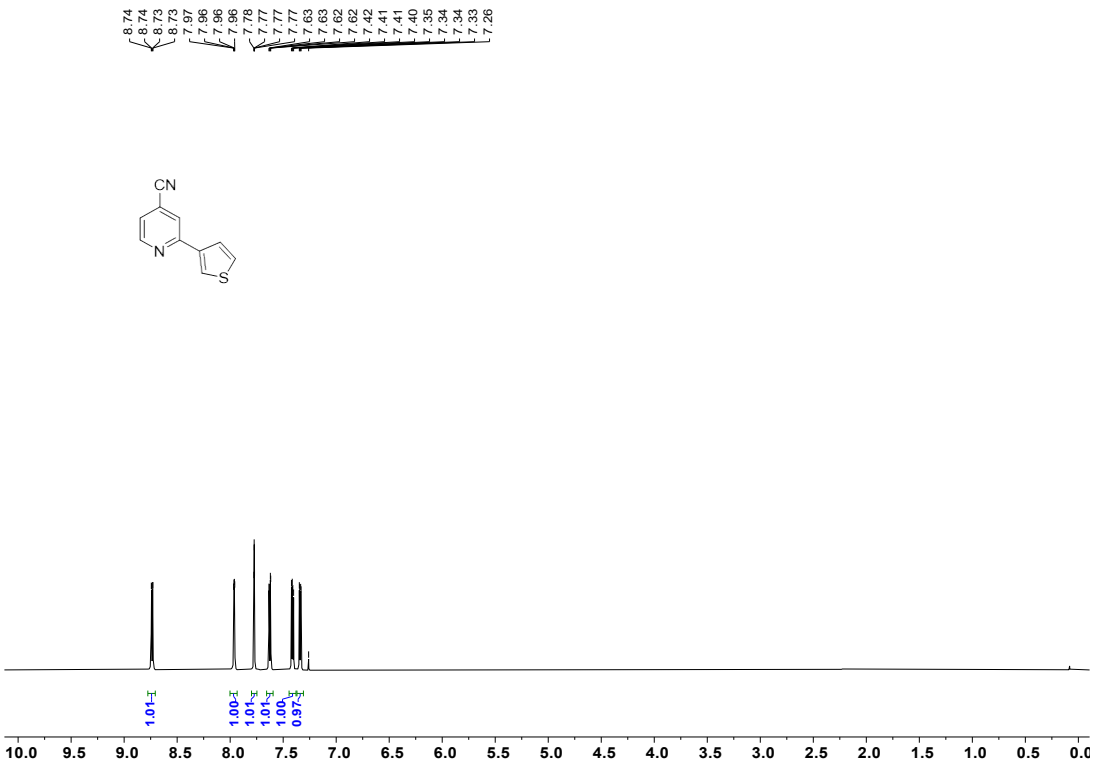

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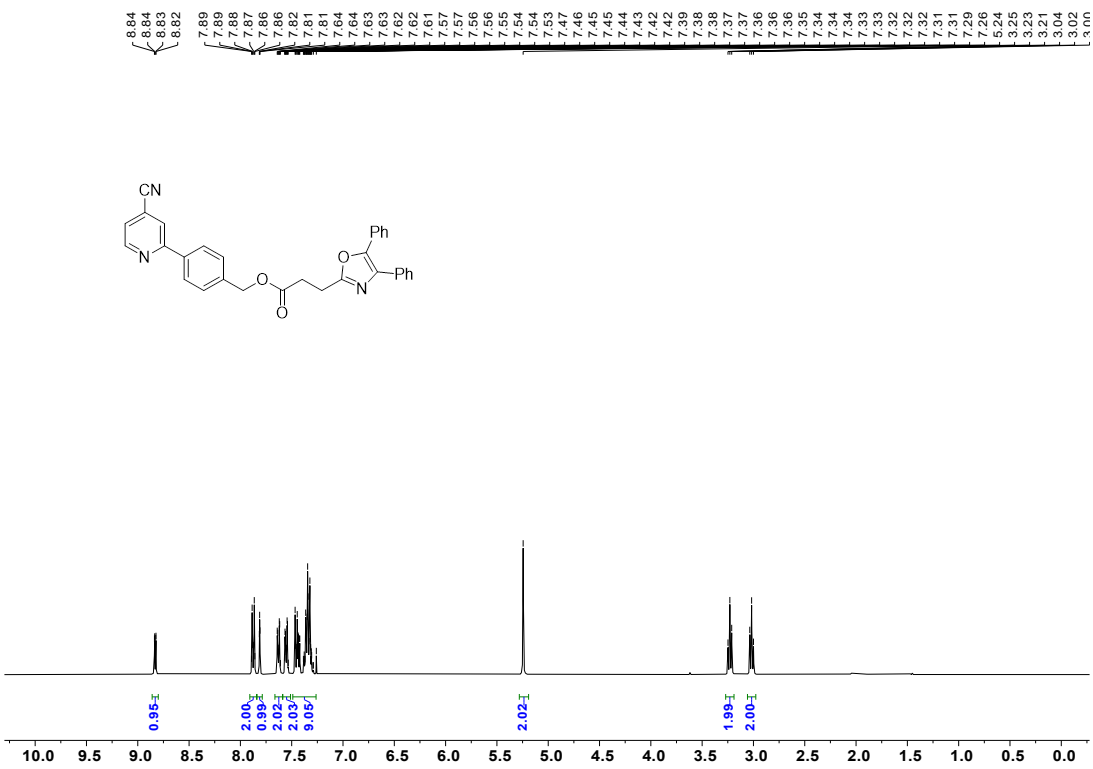

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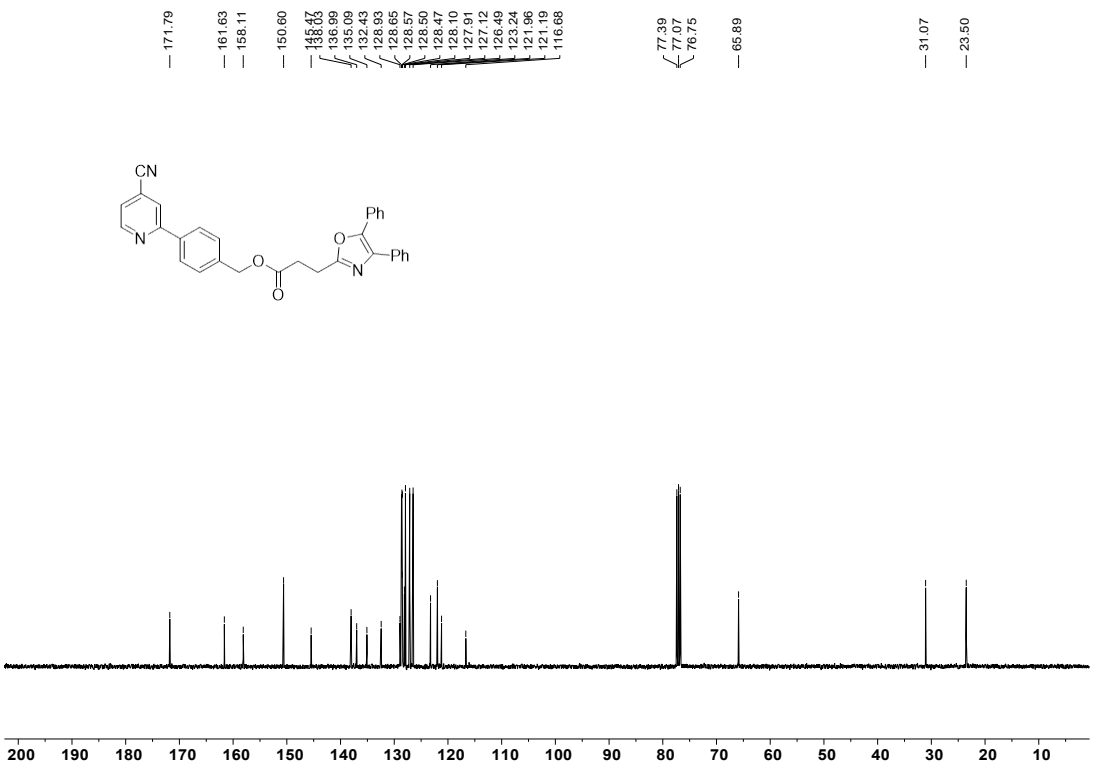

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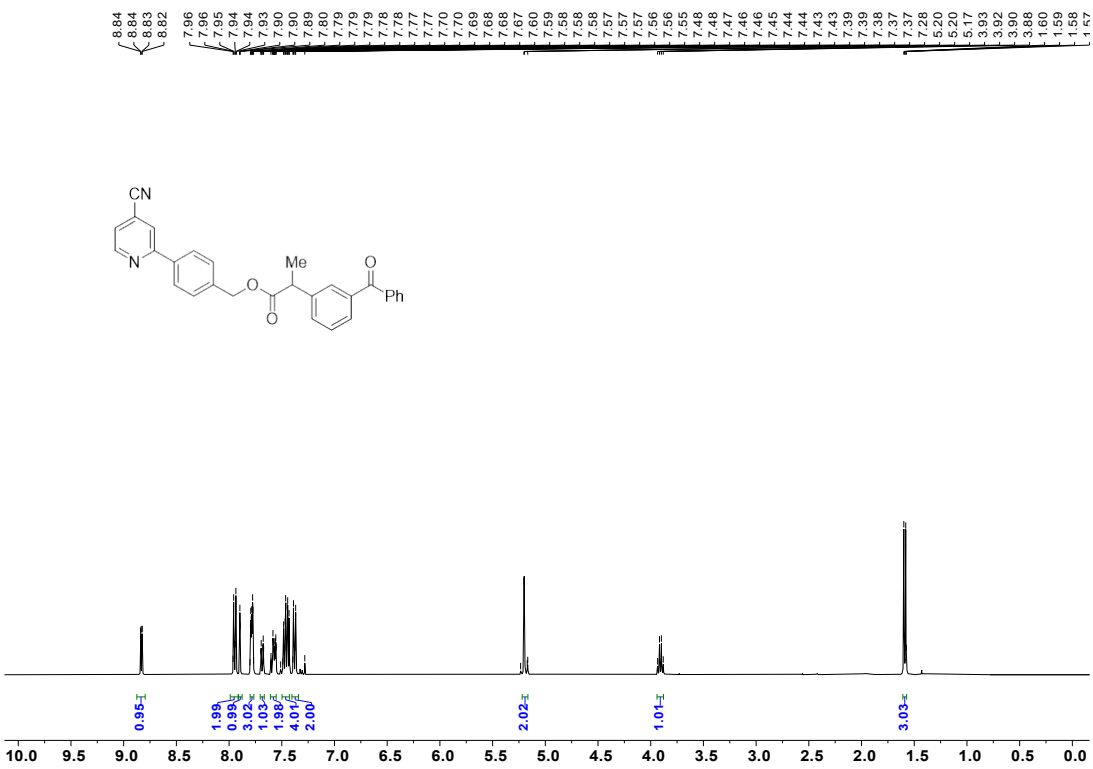

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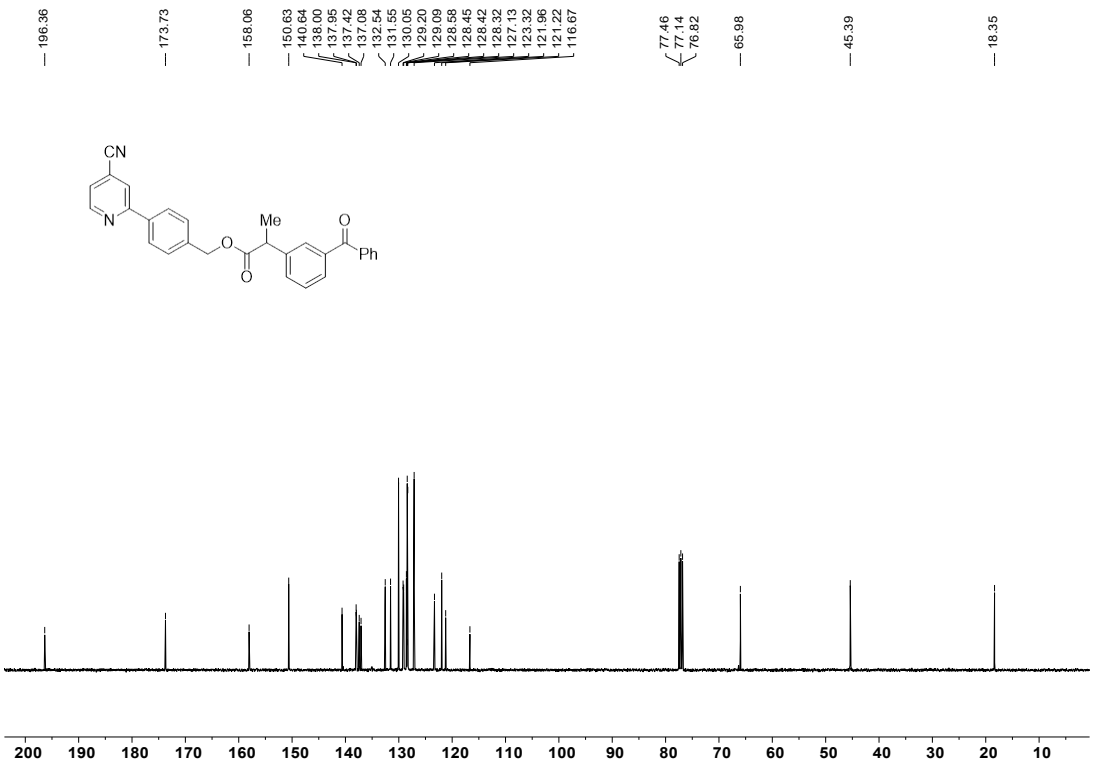
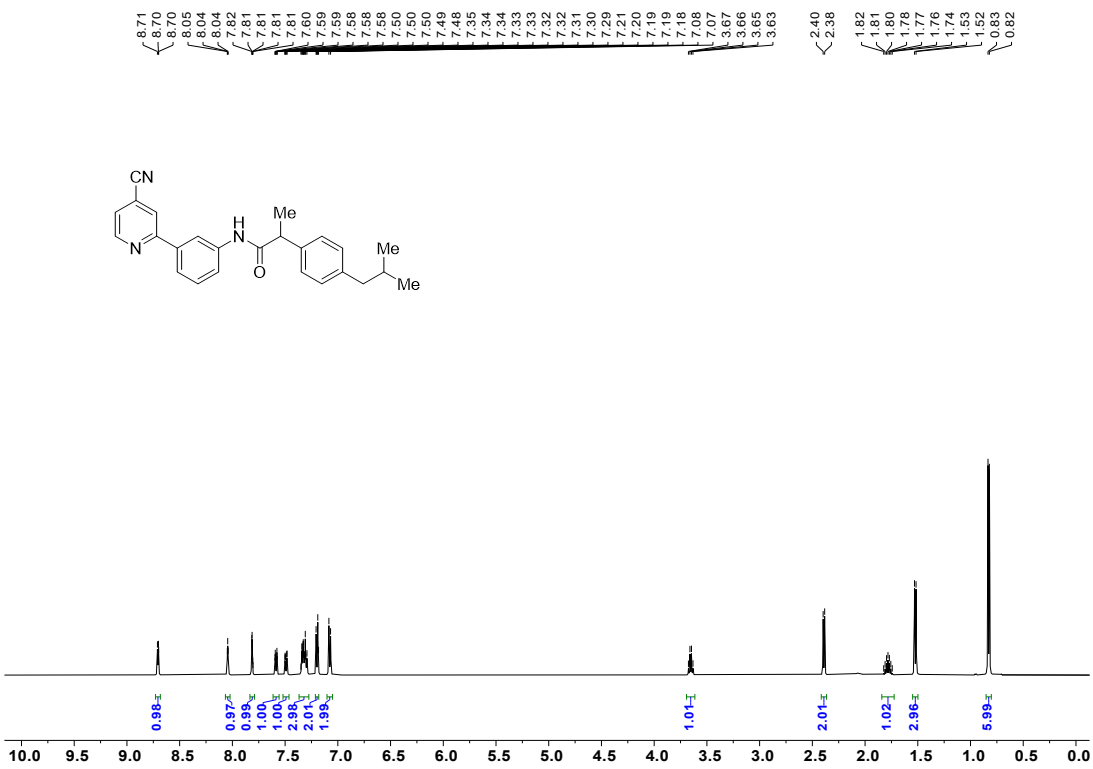
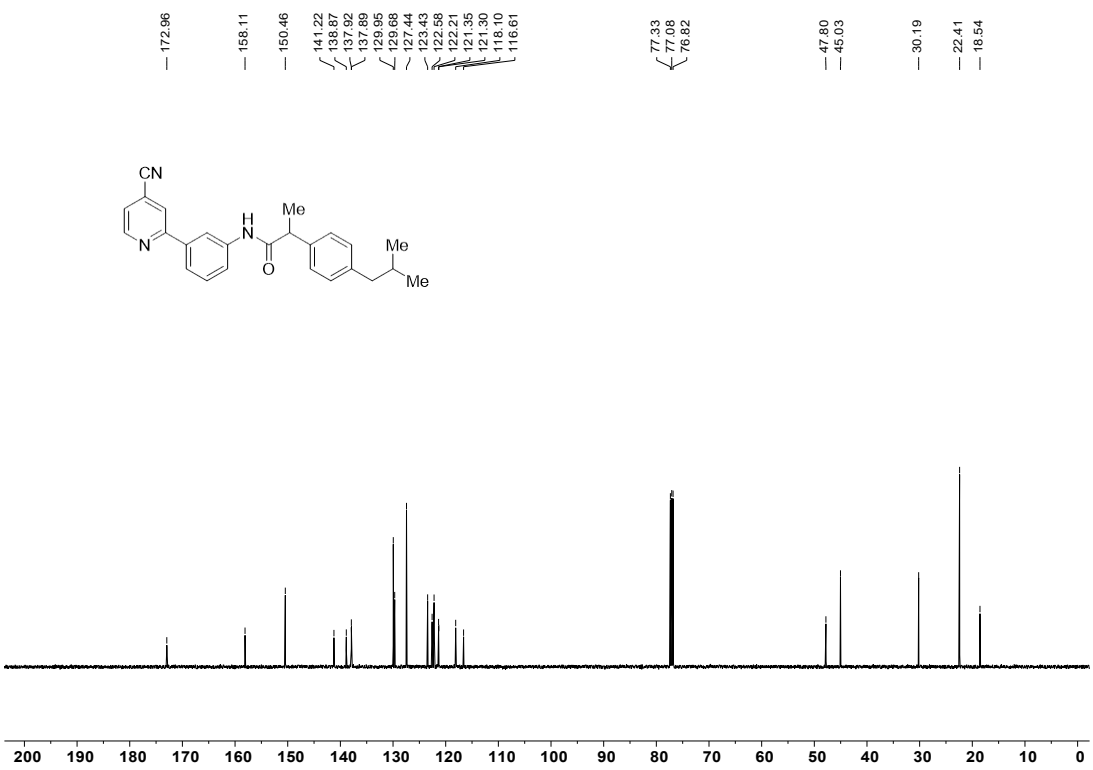


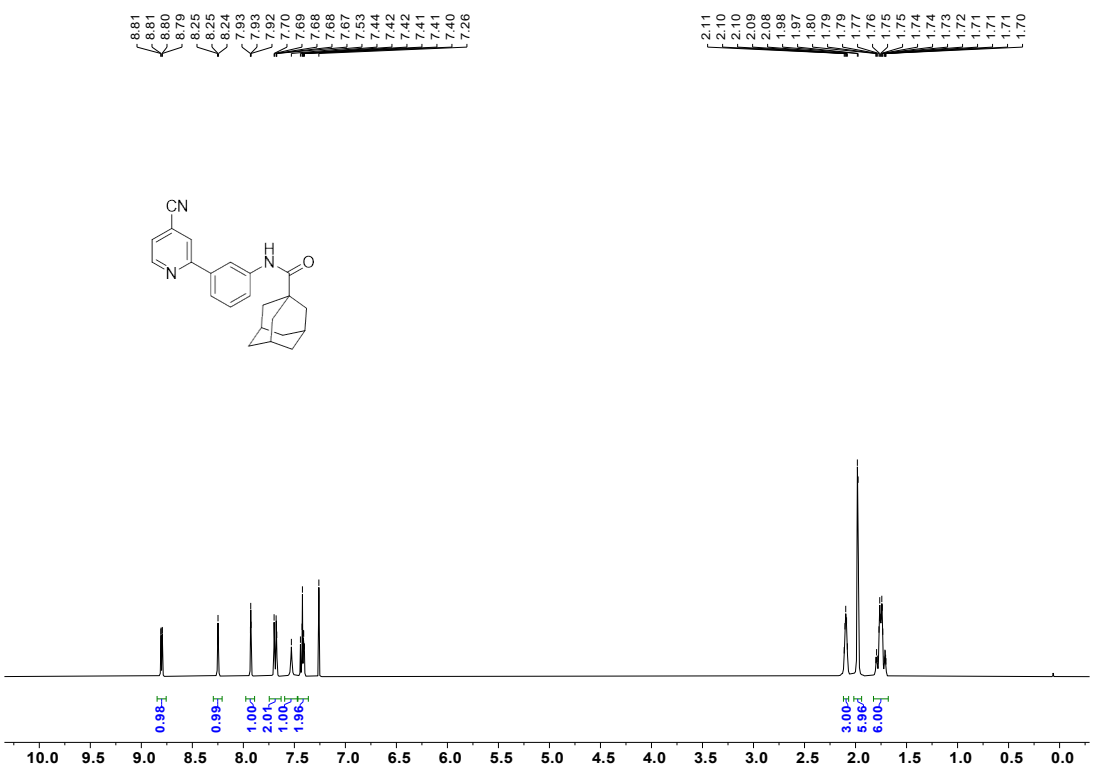
^{13}C NMR spectrum of compound **2m** (100 MHz, Chloroform-*d*)



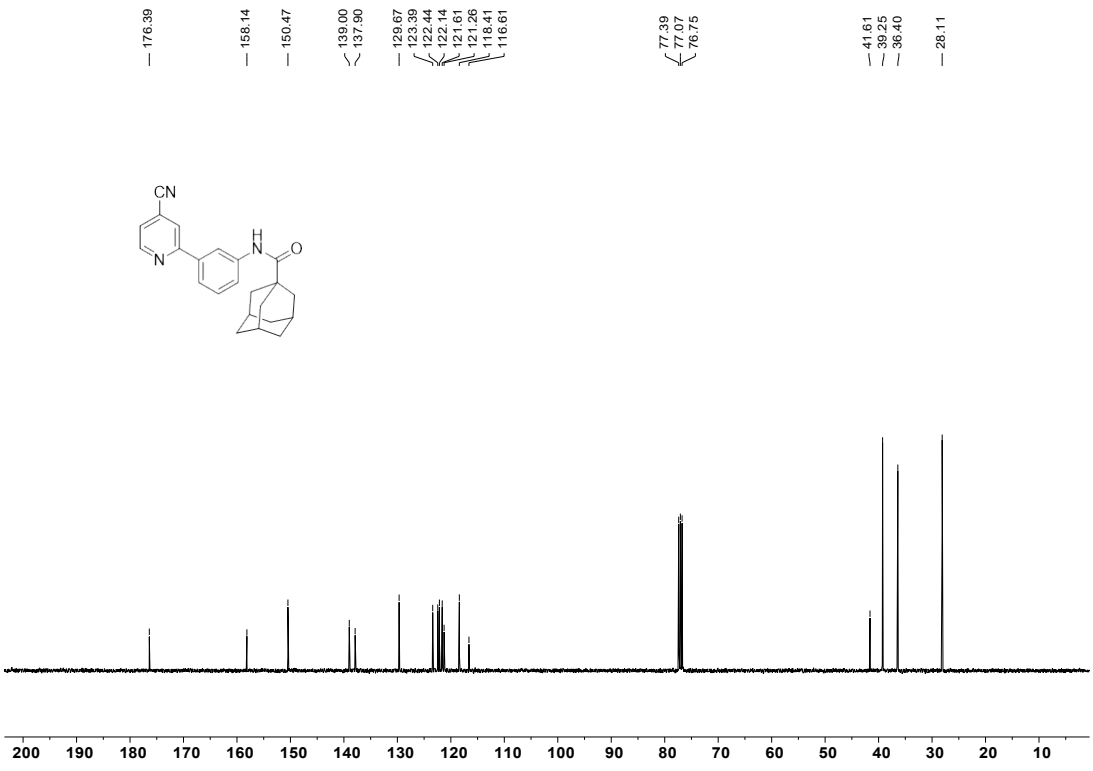
^{1}H NMR spectrum of compound **2n** (500 MHz, Chloroform-*d*)



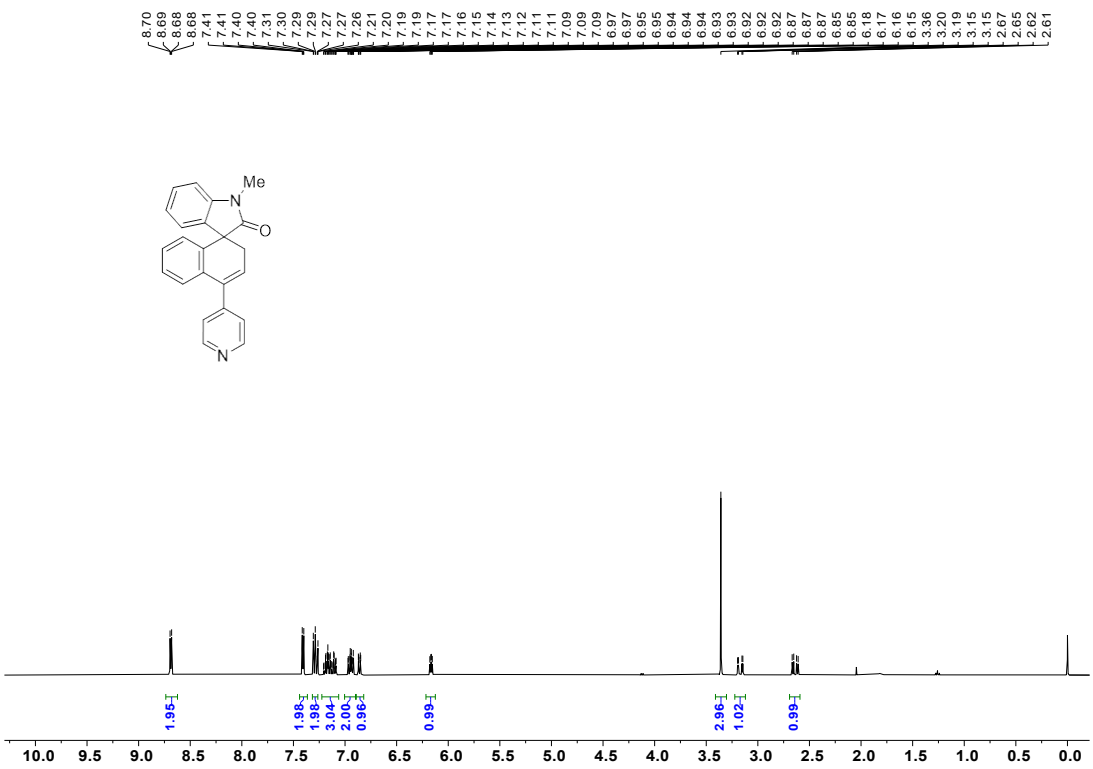
^{13}C NMR spectrum of compound **2n** (125 MHz, Chloroform-*d*)



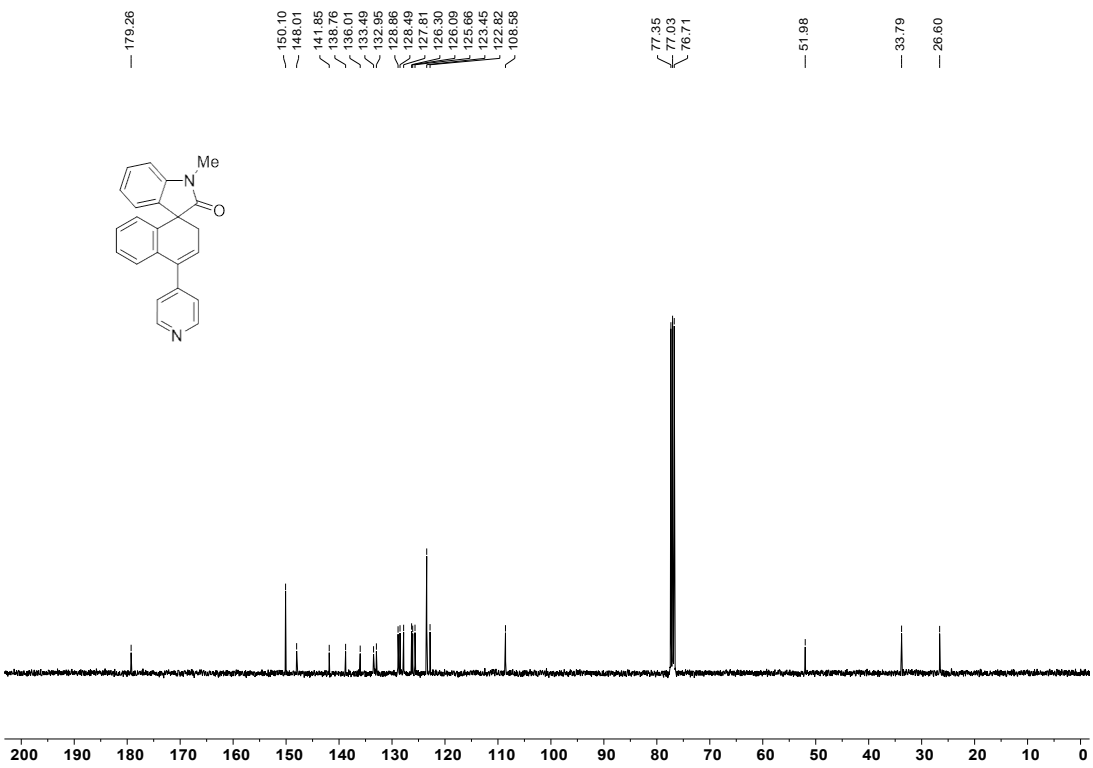
^{1}H NMR spectrum of compound **2o** (400 MHz, Chloroform-*d*)



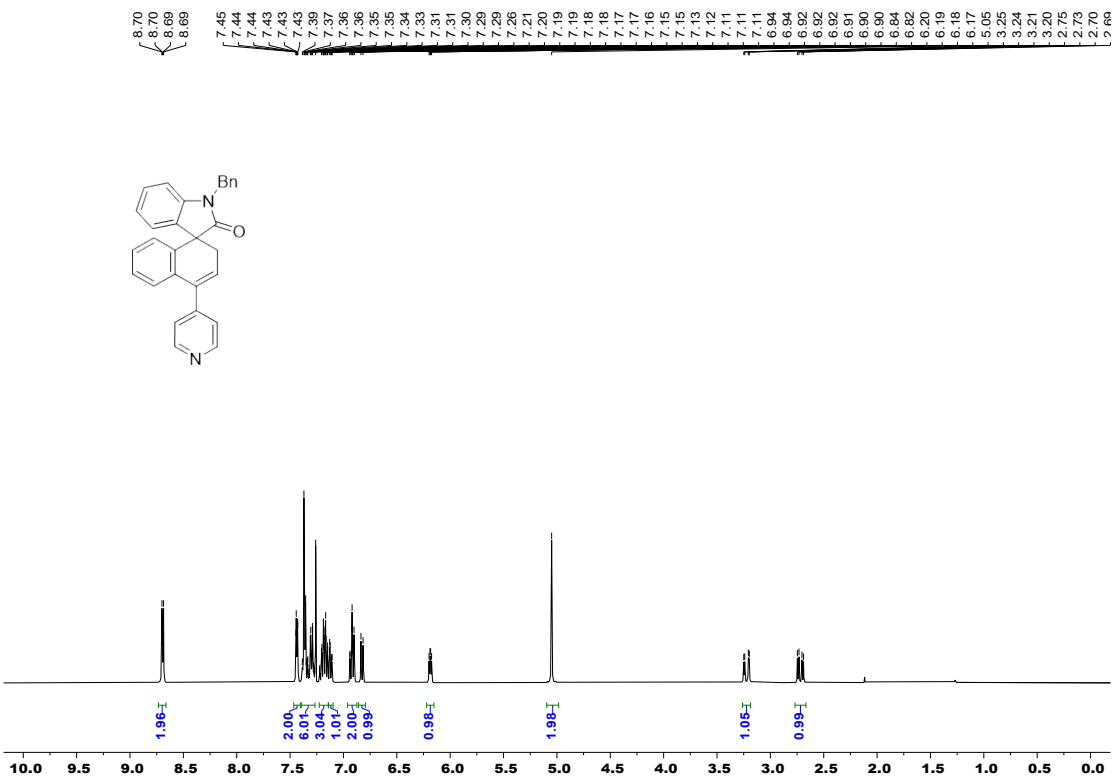
^{13}C NMR spectrum of compound **2o** (100 MHz, Chloroform-*d*)



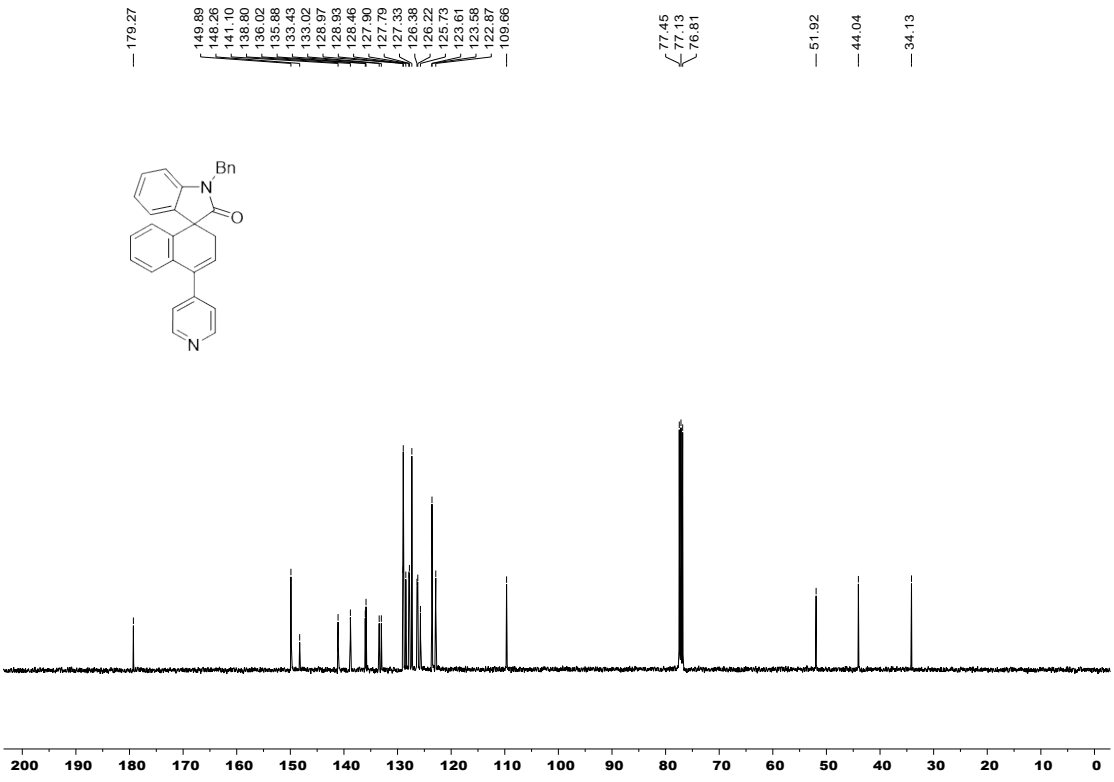
^{1}H NMR spectrum of compound **3a** (400 MHz, Chloroform-*d*)



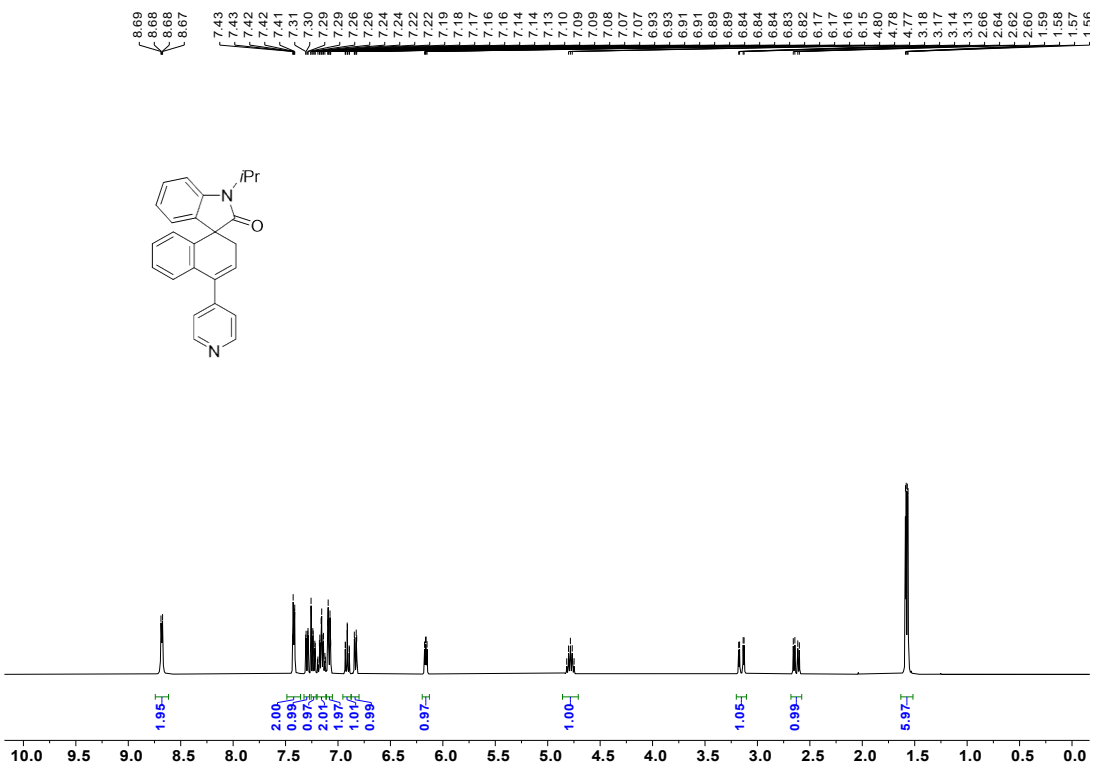
^{13}C NMR spectrum of compound **3a** (100 MHz, Chloroform-*d*)



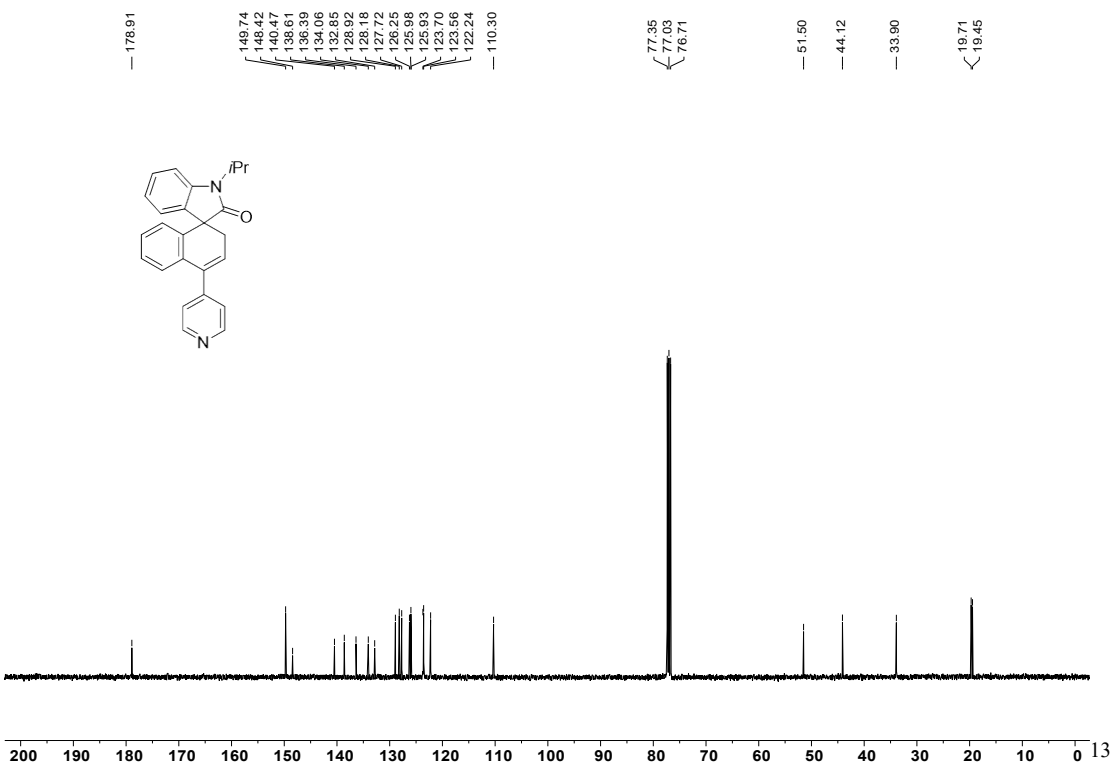
^{1}H NMR spectrum of compound **3b** (400 MHz, Chloroform-*d*)



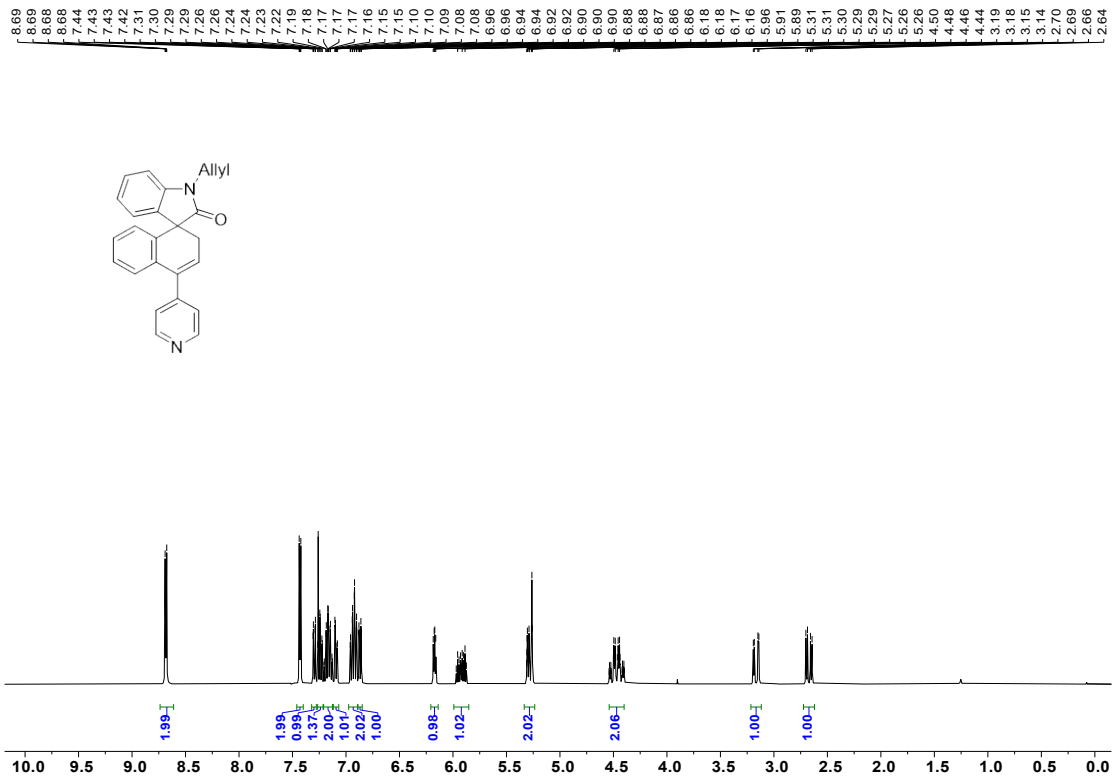
^{13}C NMR spectrum of compound **3b** (100 MHz, Chloroform-*d*)



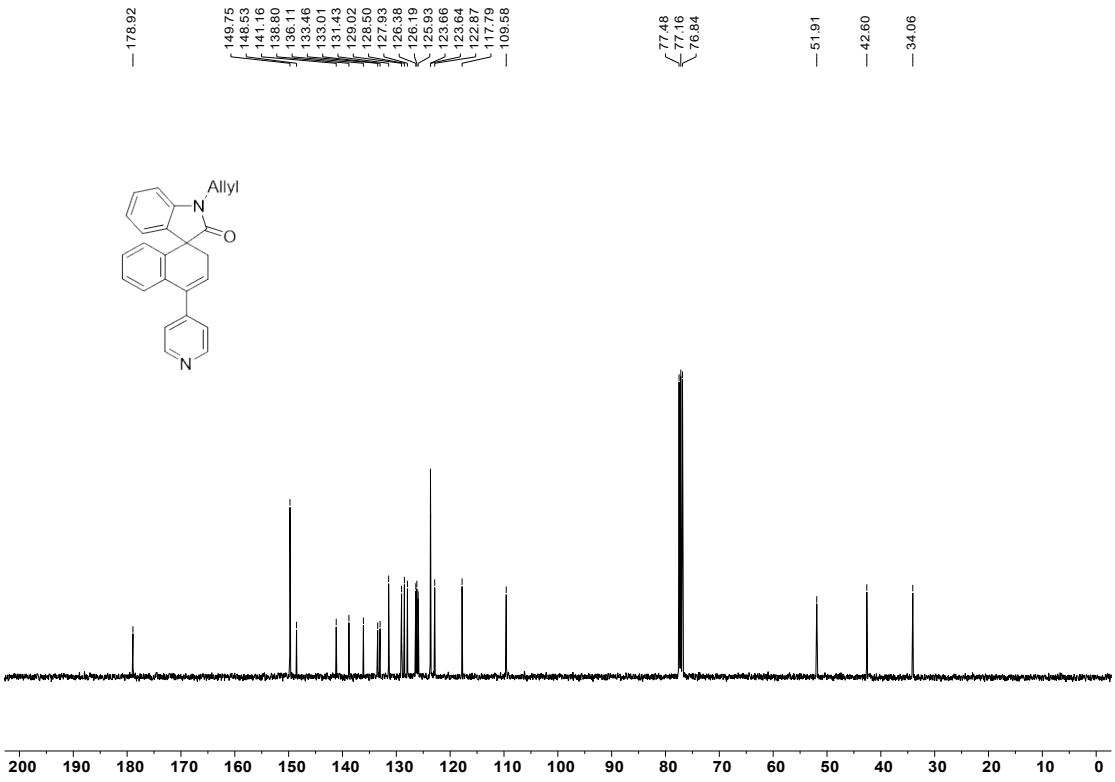
^{1}H NMR spectrum of compound **3c** (400 MHz, Chloroform-*d*)



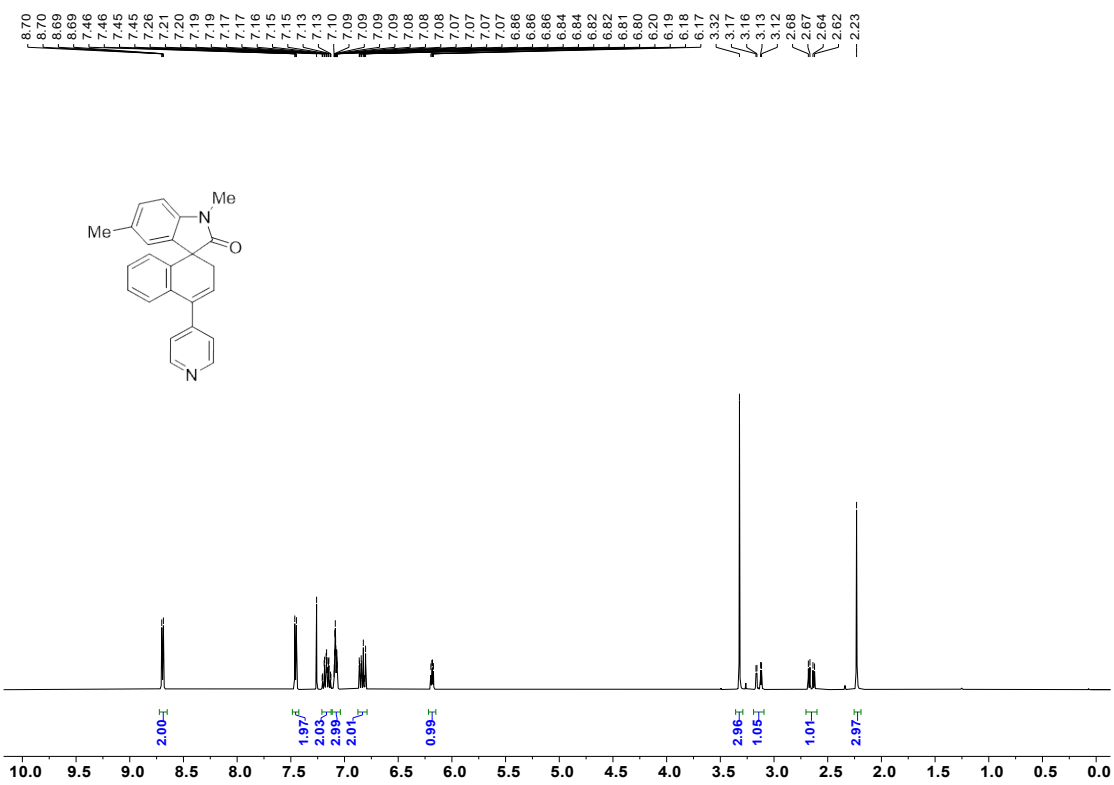
C NMR spectrum of compound **3c** (100 MHz, Chloroform-*d*)



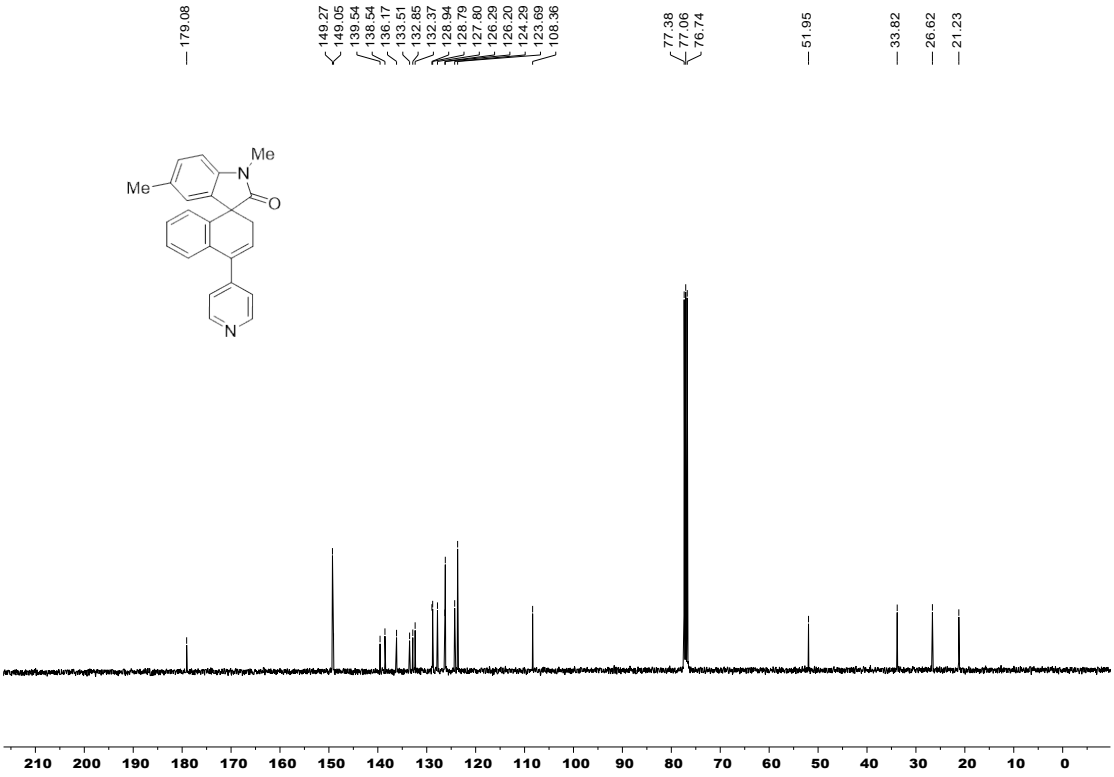
^{1}H NMR spectrum of compound **3d** (400 MHz, Chloroform-*d*)



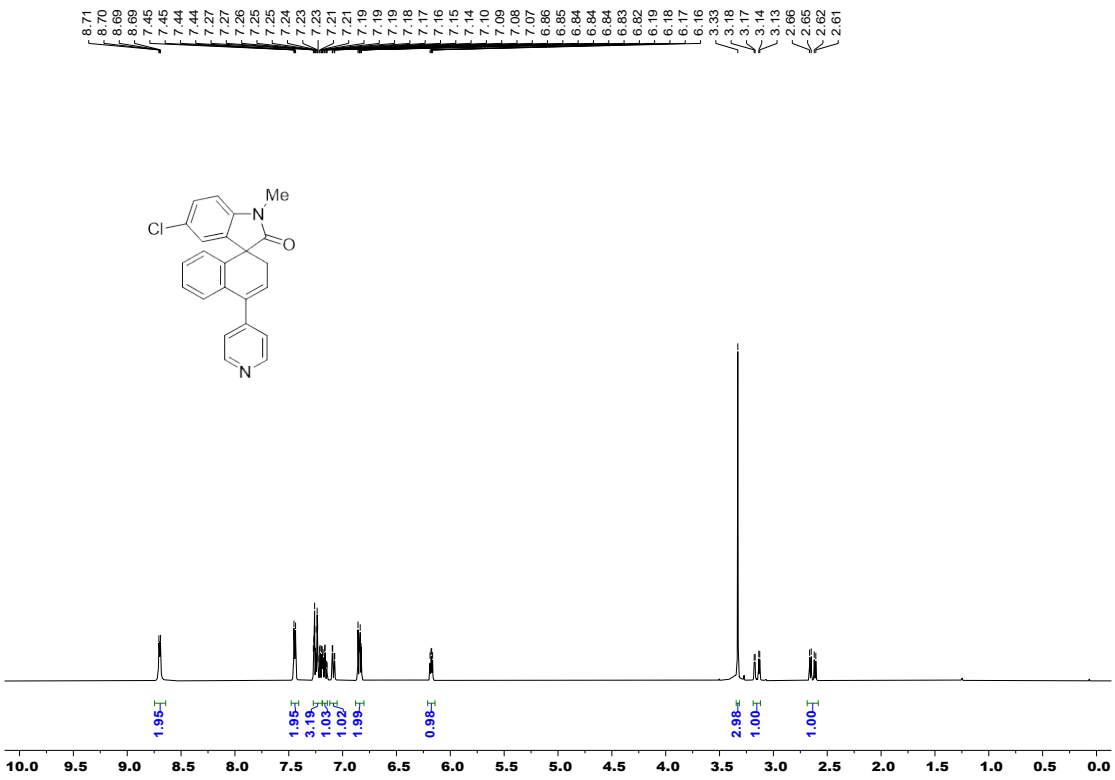
^{13}C NMR spectrum of compound **3d** (100 MHz, Chloroform-*d*)



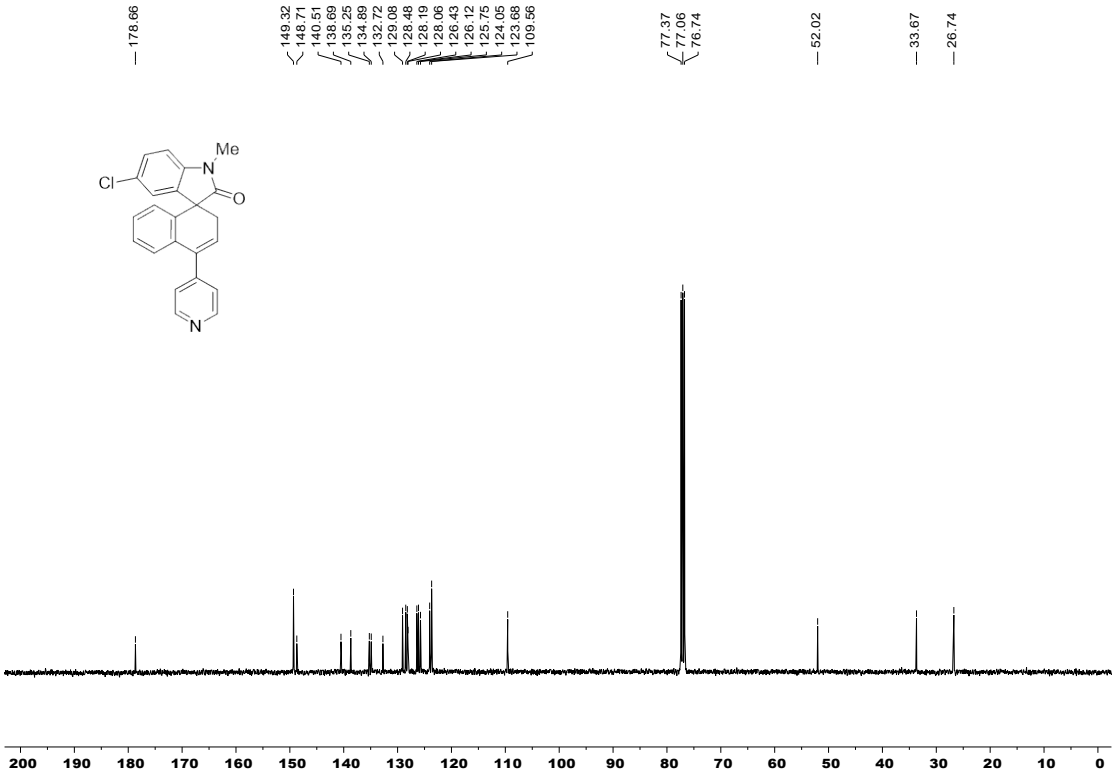
^{1}H NMR spectrum of compound **3e** (400 MHz, Chloroform-*d*)



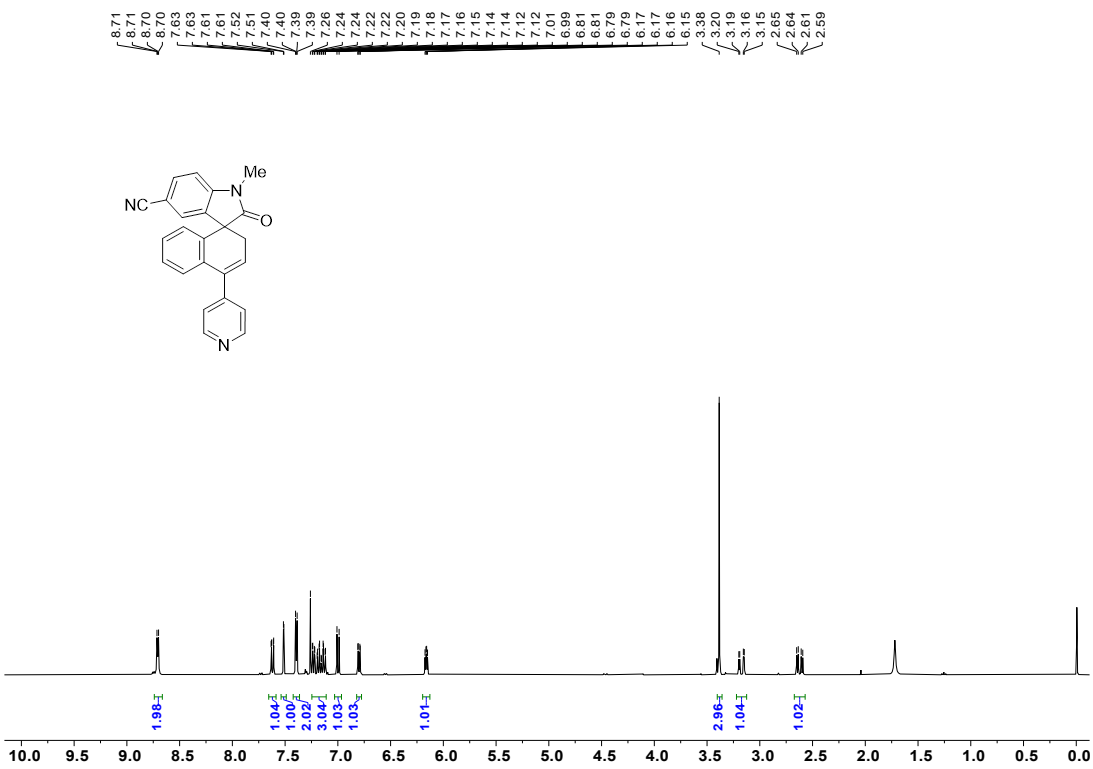
^{13}C NMR spectrum of compound **3e** (100 MHz, Chloroform-*d*)



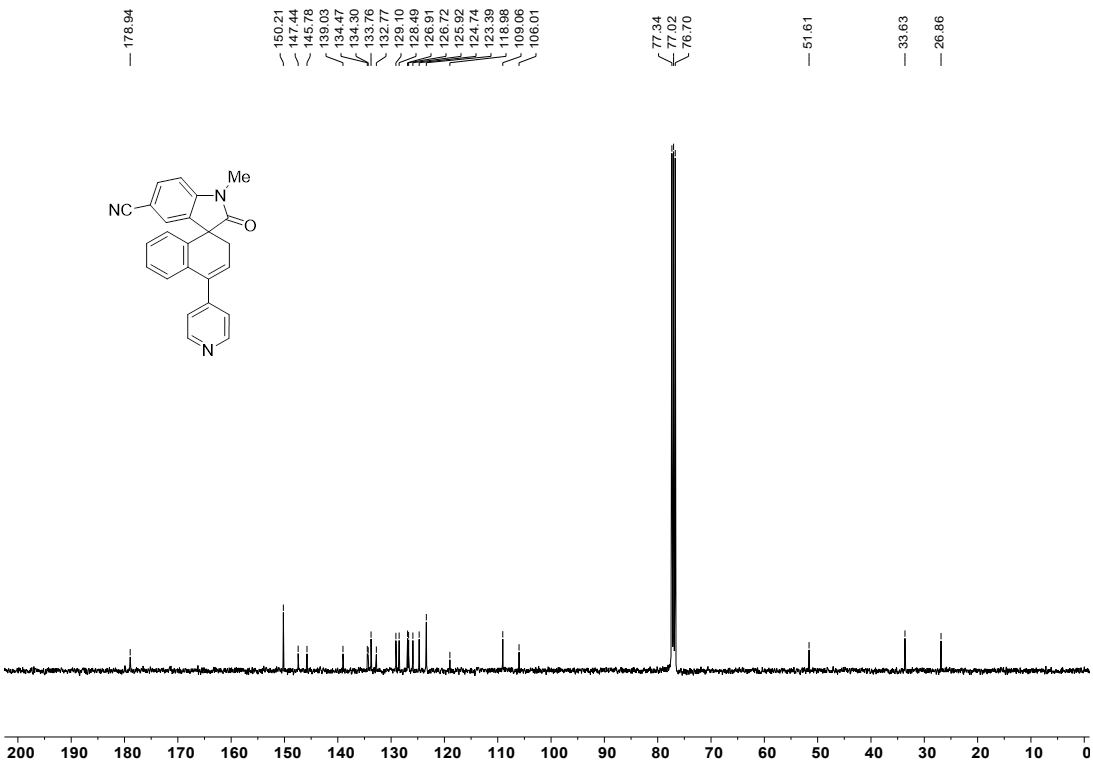
^{1}H NMR spectrum of compound **3f** (400 MHz, Chloroform-*d*)



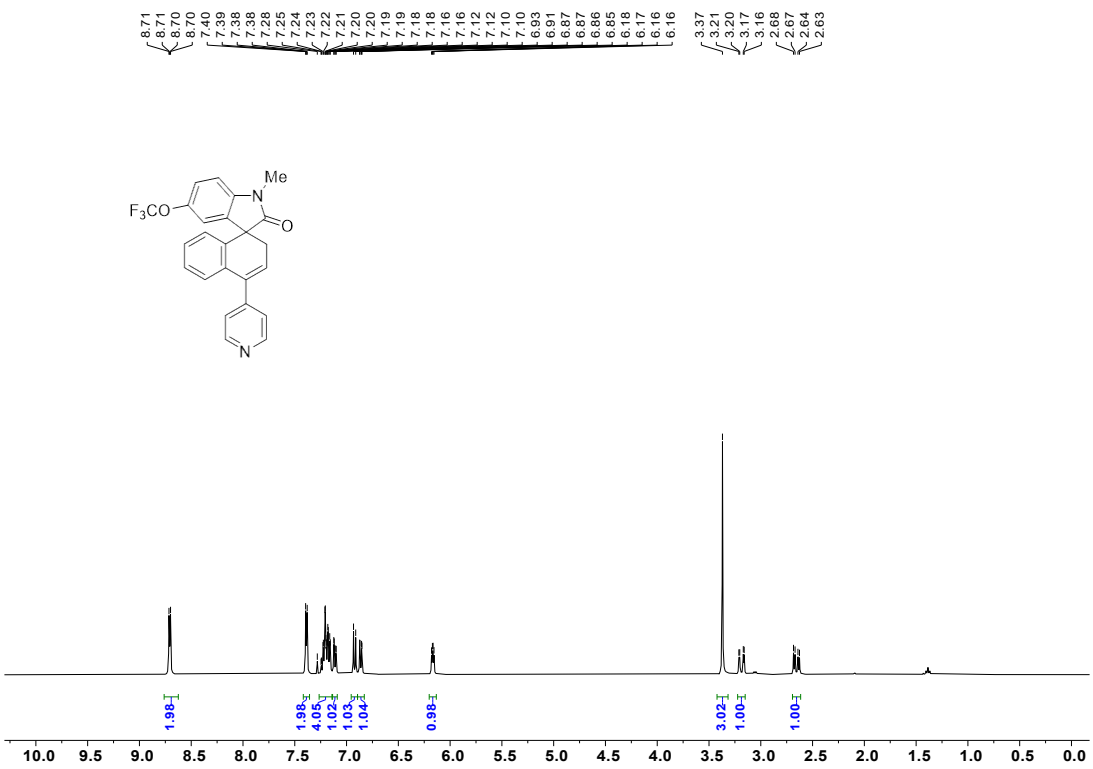
^{13}C NMR spectrum of compound **3f** (100 MHz, Chloroform-*d*)



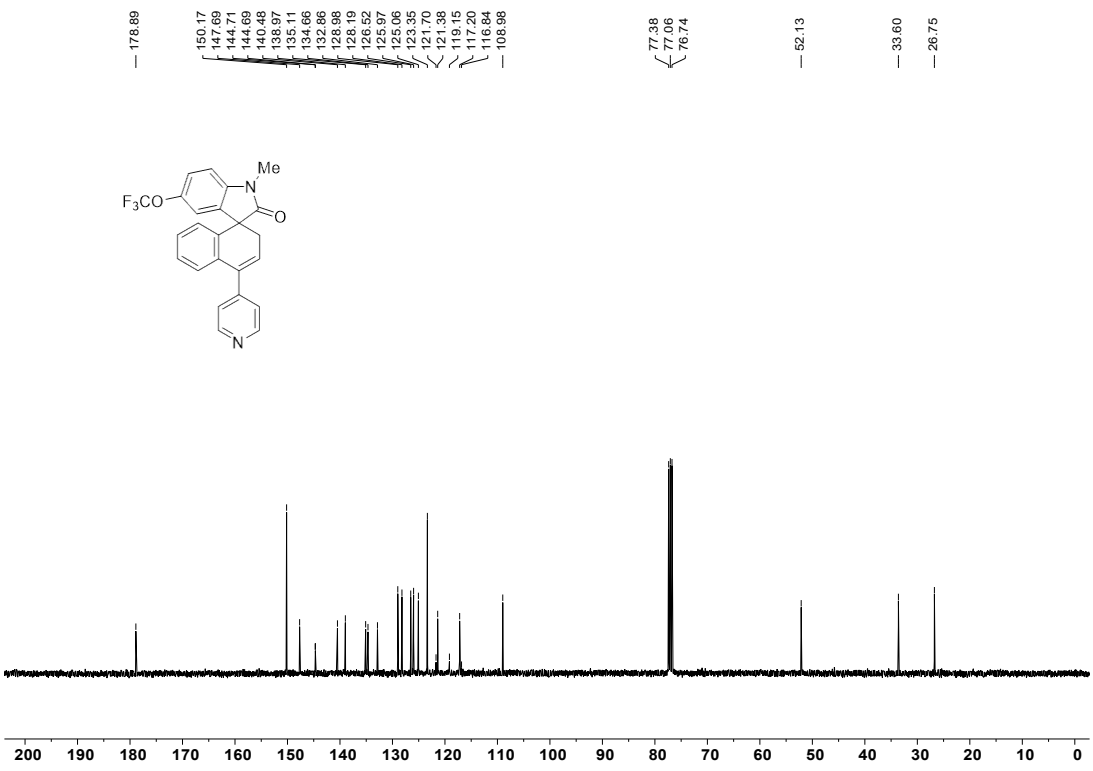
^{1}H NMR spectrum of compound **3g** (400 MHz, Chloroform-*d*)



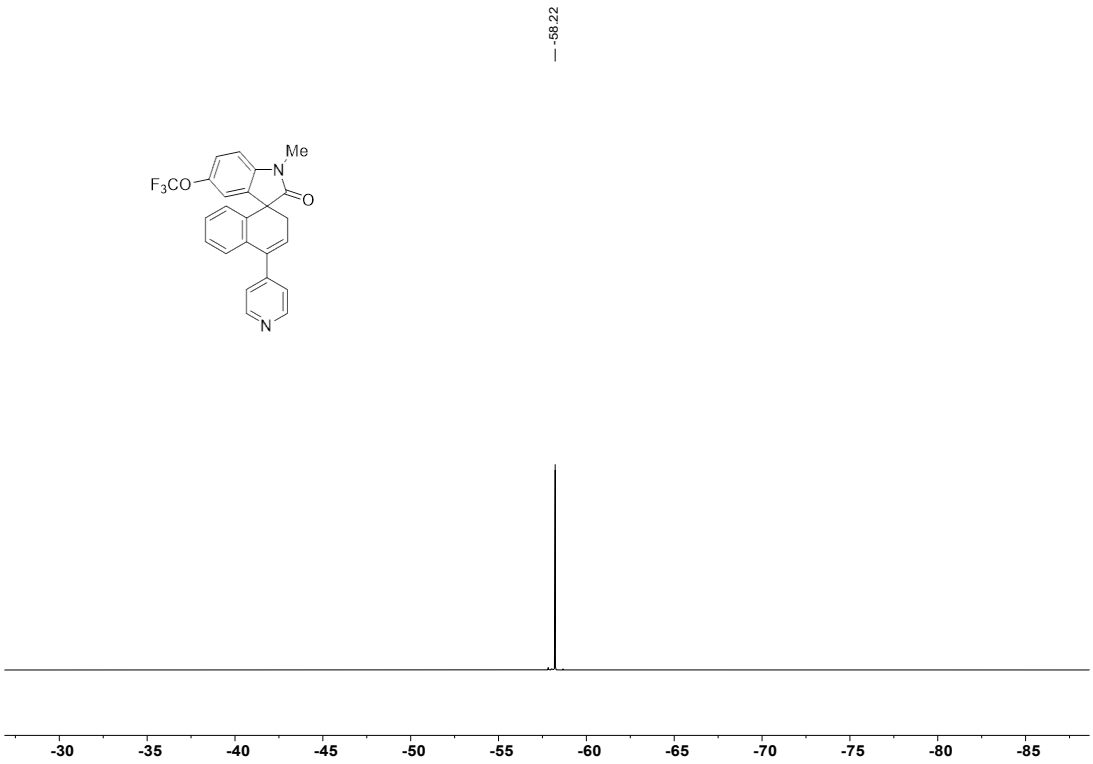
^{13}C NMR spectrum of compound **3g** (100 MHz, Chloroform-*d*)



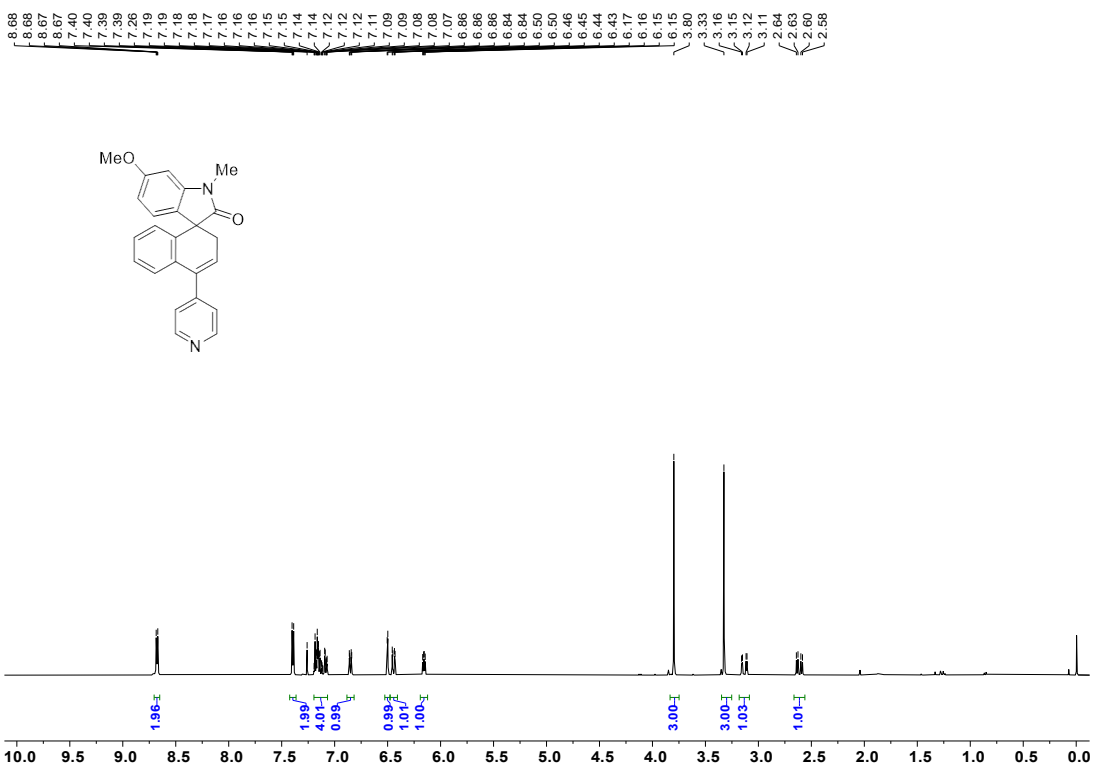
^{1}H NMR spectrum of compound **3h** (400 MHz, Chloroform-*d*)



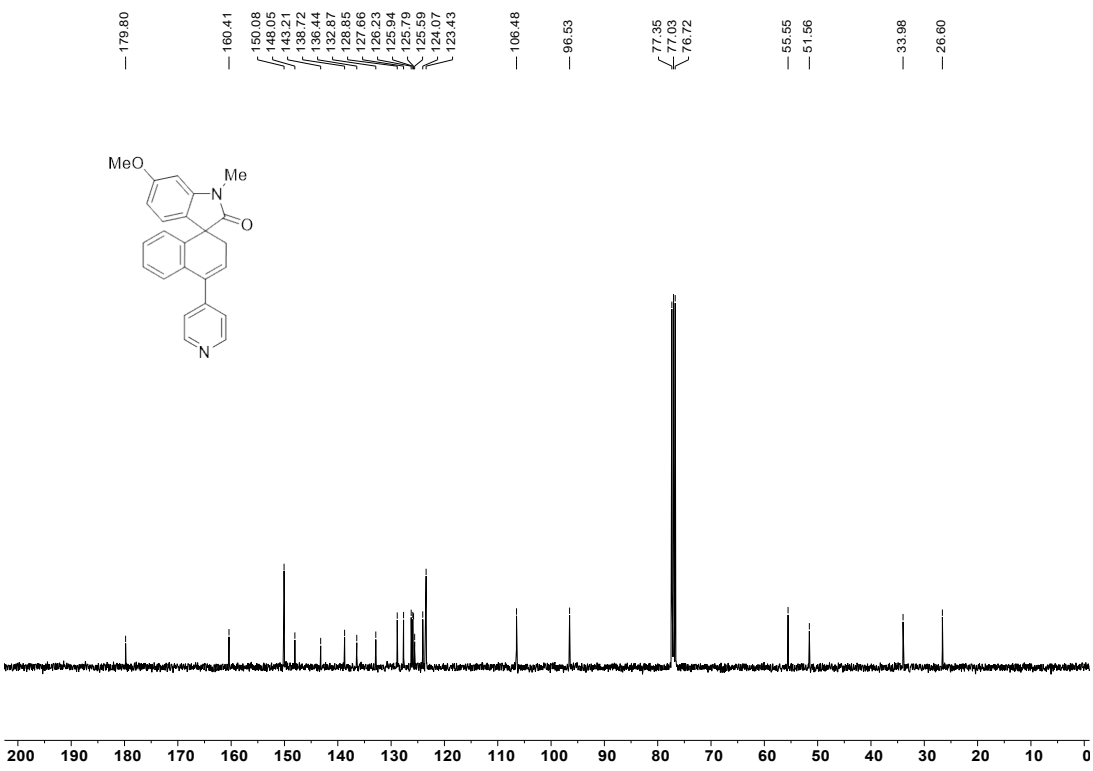
^{13}C NMR spectrum of compound **3h** (100 MHz, Chloroform-*d*)



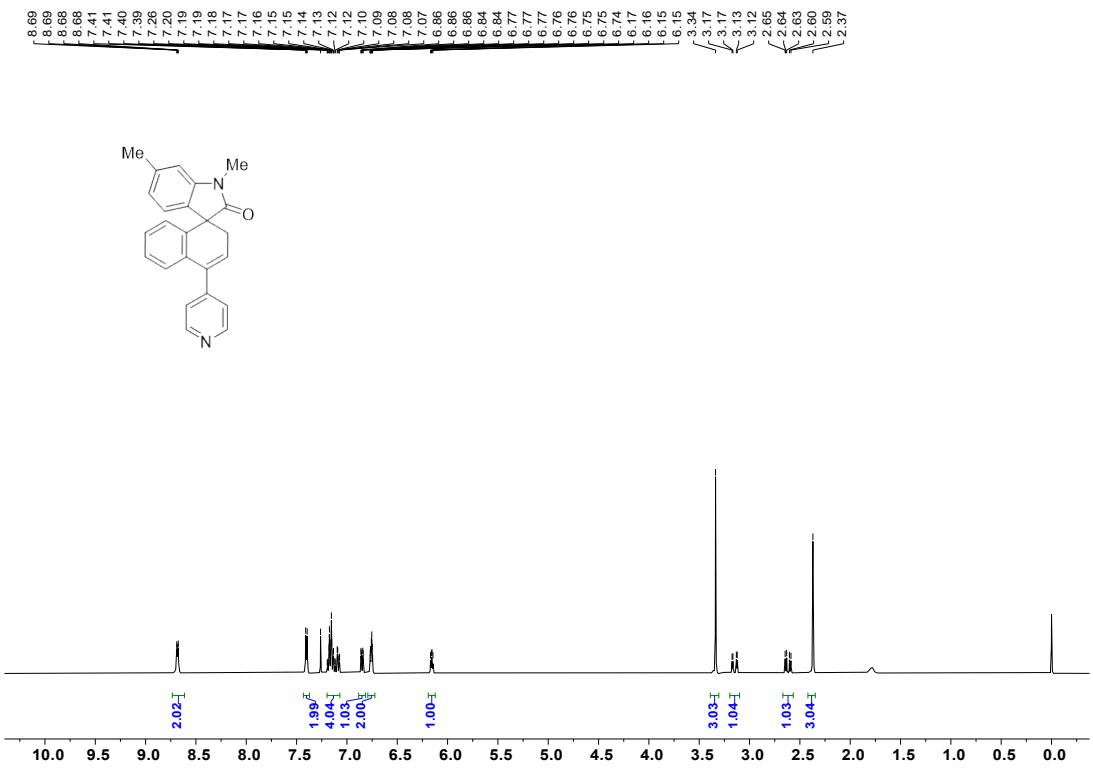
^{19}F NMR spectrum of compound **3h** (376 MHz, Chloroform-*d*)



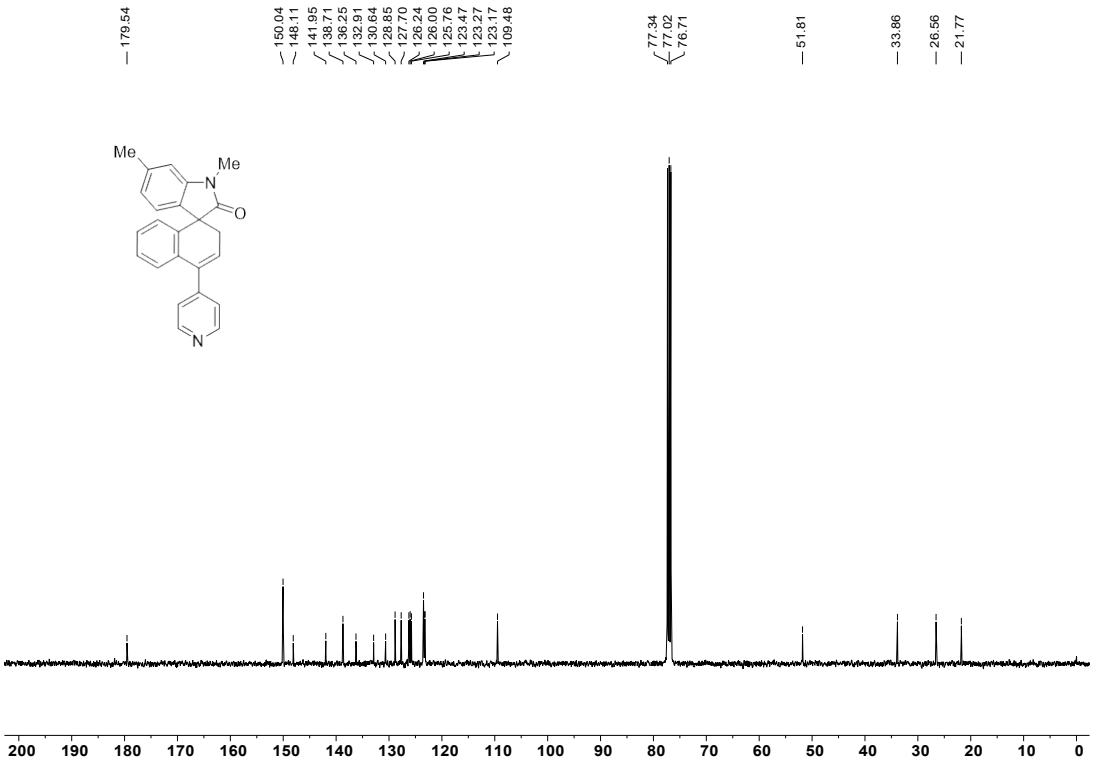
^{1}H NMR spectrum of compound **3i** (400 MHz, Chloroform-*d*)



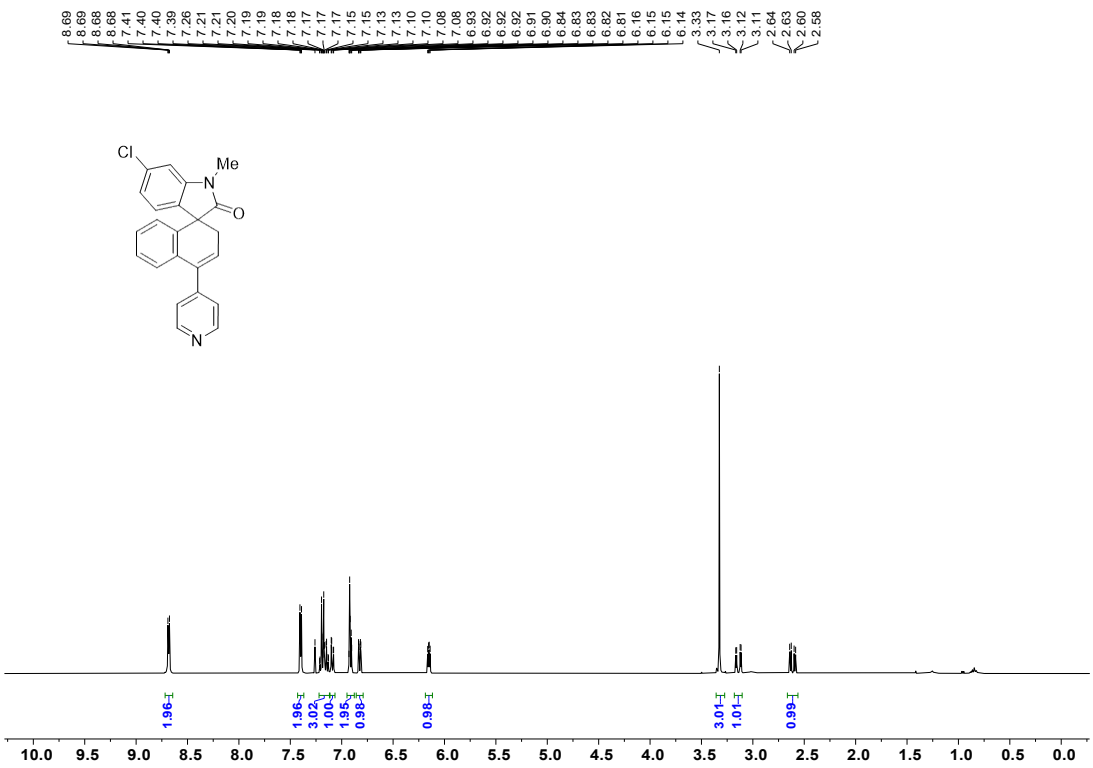
^{13}C NMR spectrum of compound **3i** (100 MHz, Chloroform-*d*)



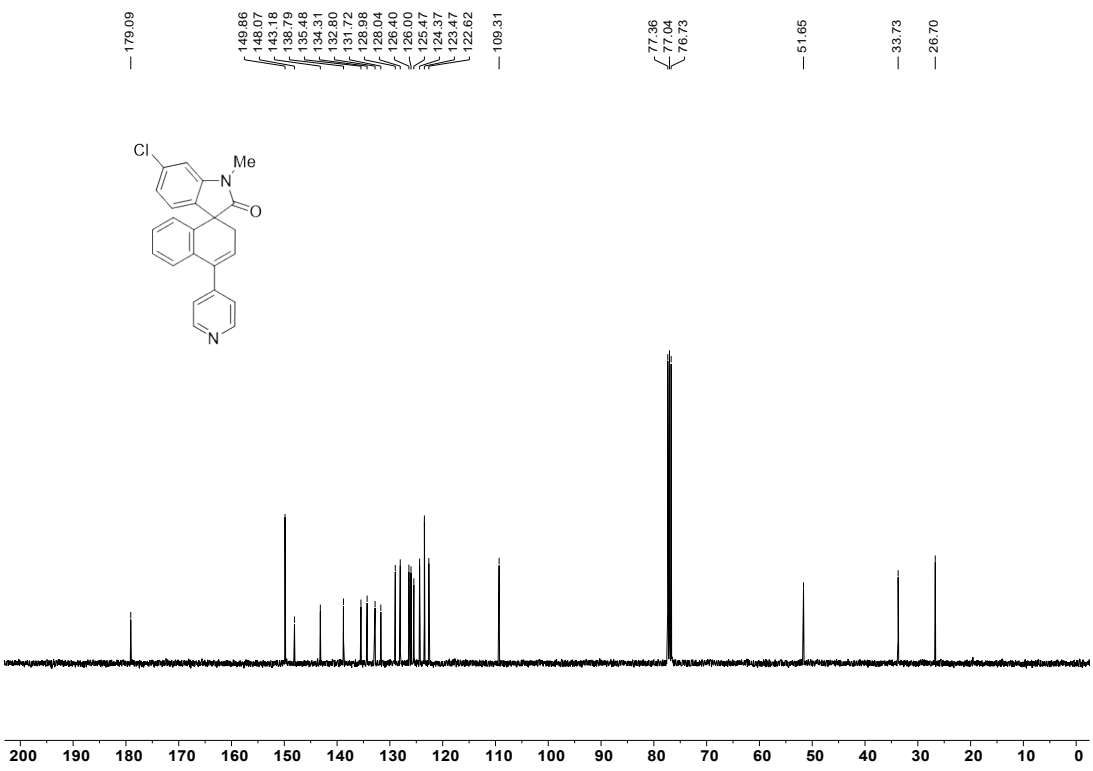
^{1}H NMR spectrum of compound **3j** (400 MHz, Chloroform-*d*)



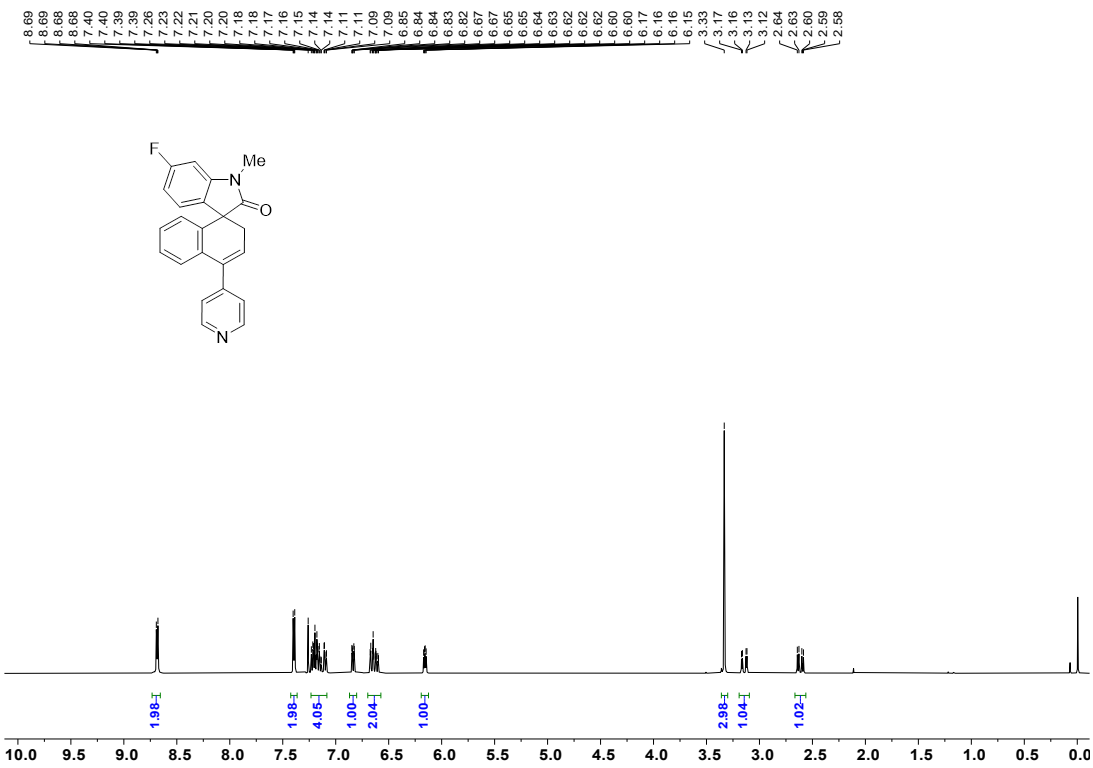
^{13}C NMR spectrum of compound **3j** (100 MHz, Chloroform-*d*)



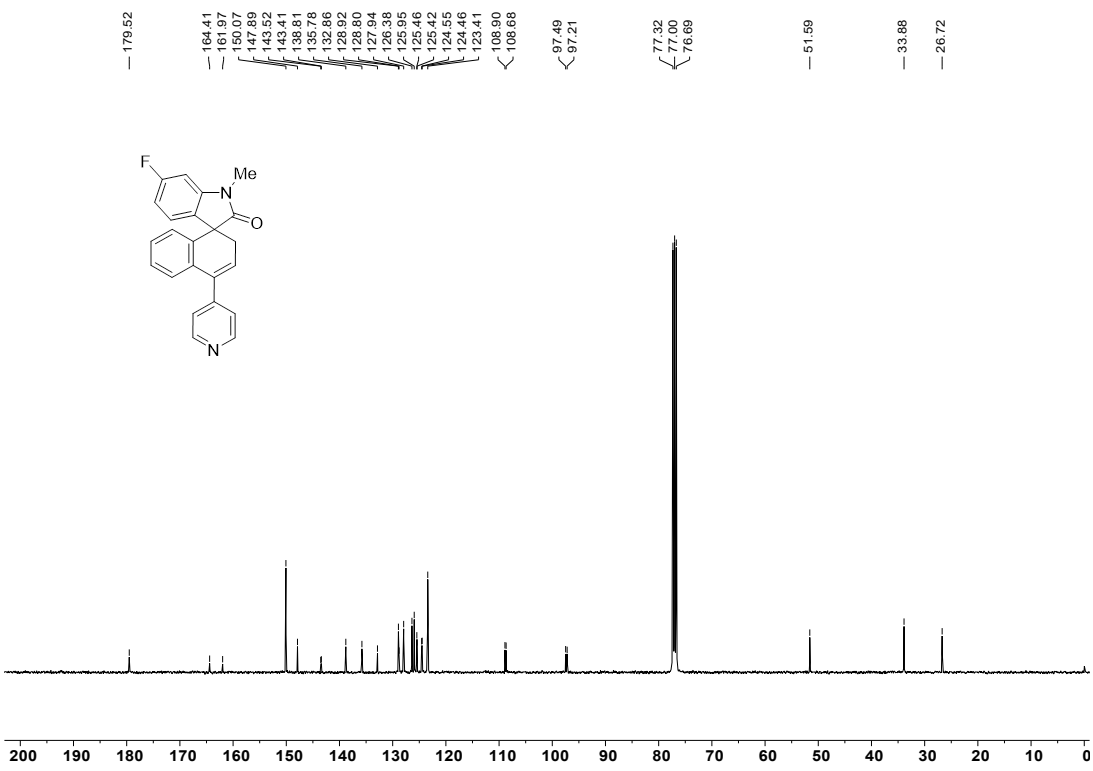
^{1}H NMR spectrum of compound **3k** (400 MHz, Chloroform-*d*)



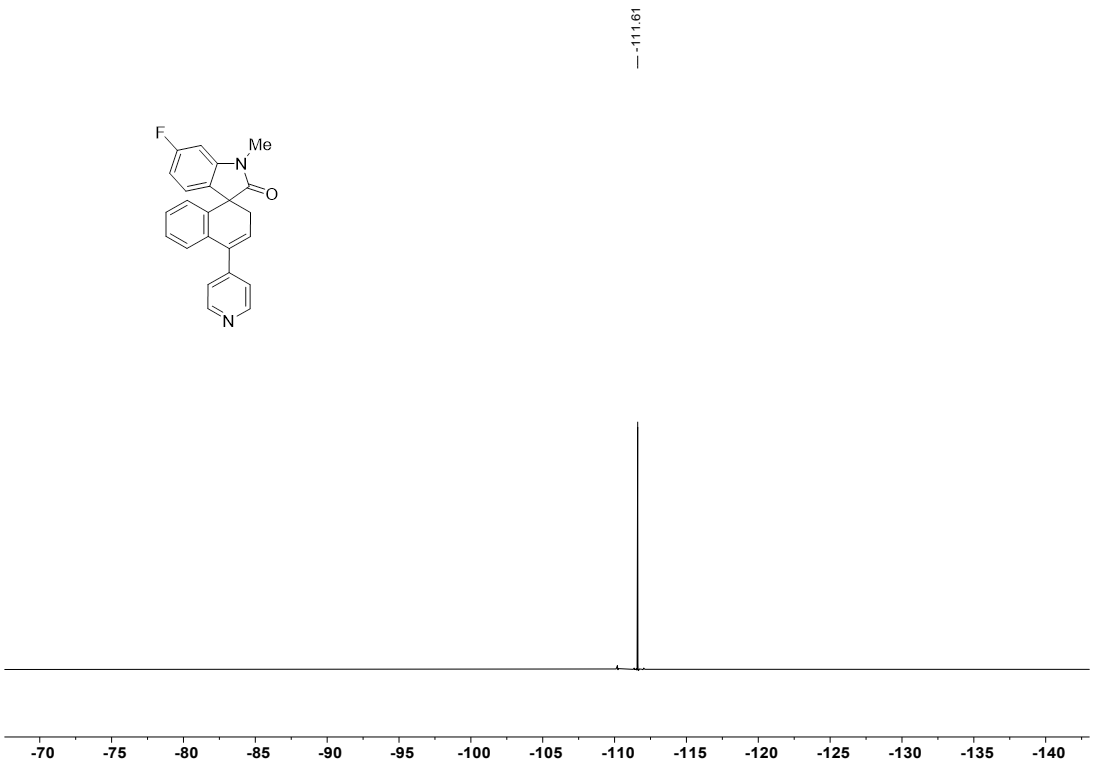
^{13}C NMR spectrum of compound **3k** (400 MHz, Chloroform-*d*)



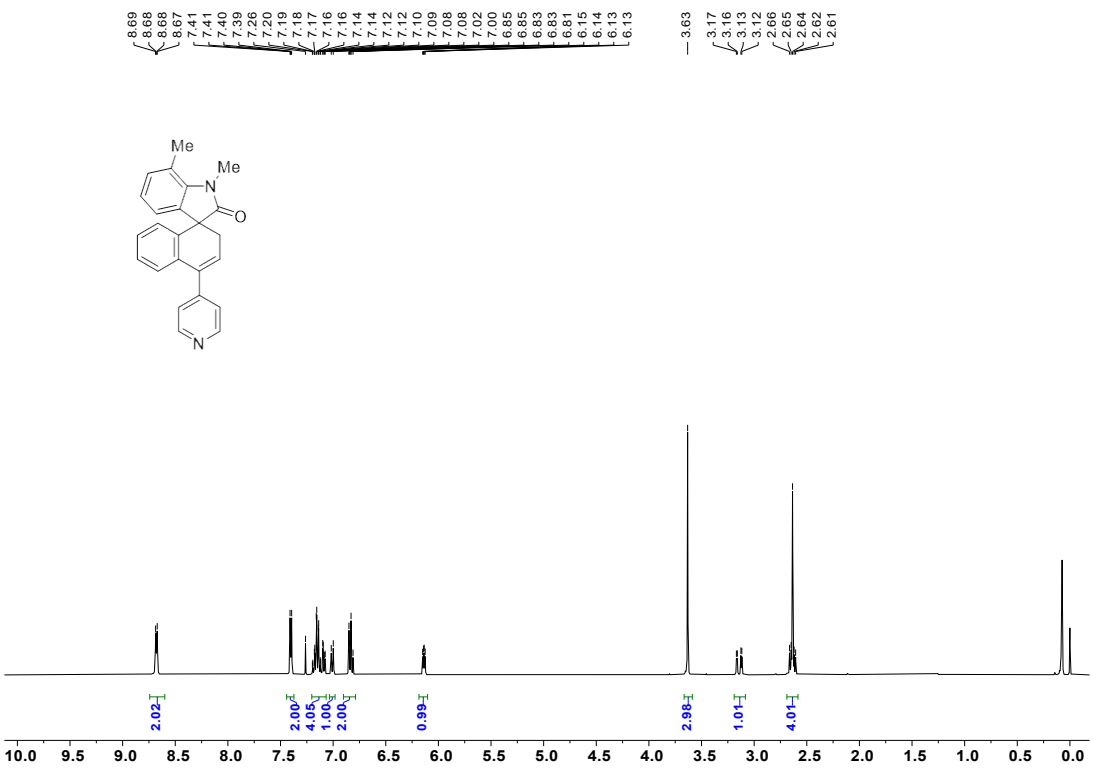
^{1}H NMR spectrum of compound **3l** (400 MHz, Chloroform-*d*)



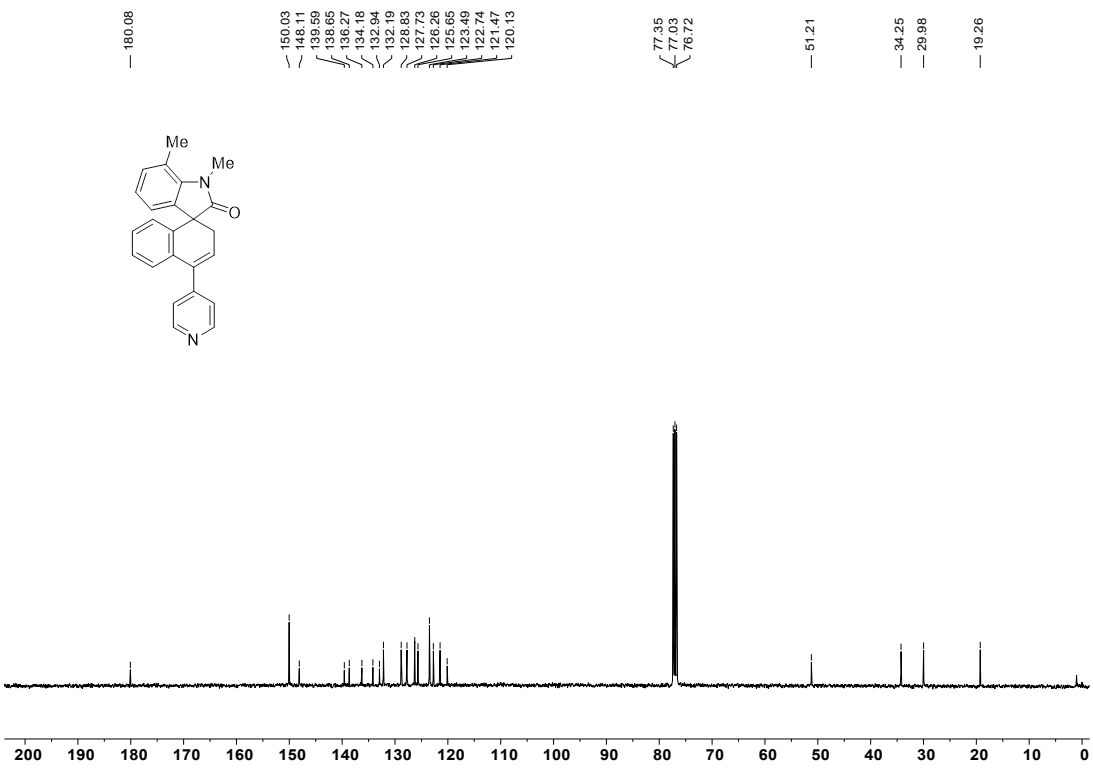
^{13}C NMR spectrum of compound **3l** (100 MHz, Chloroform-*d*)



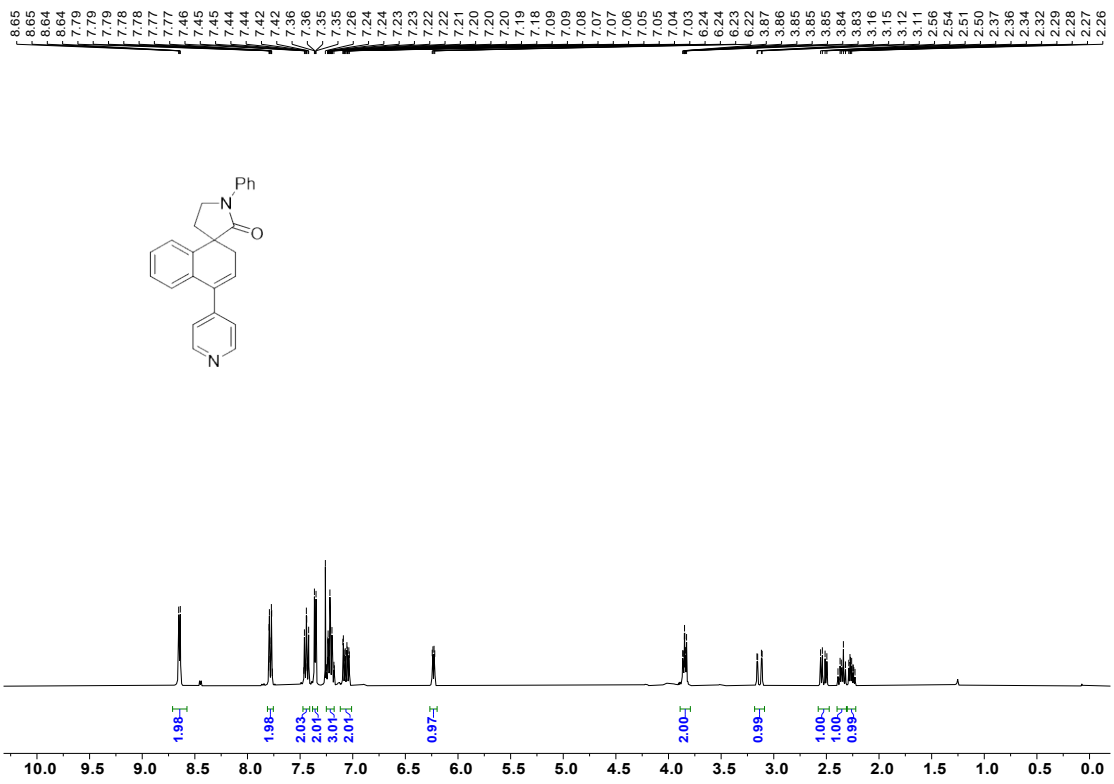
^{19}F NMR spectrum of compound **3l** (376 MHz, Chloroform-*d*)



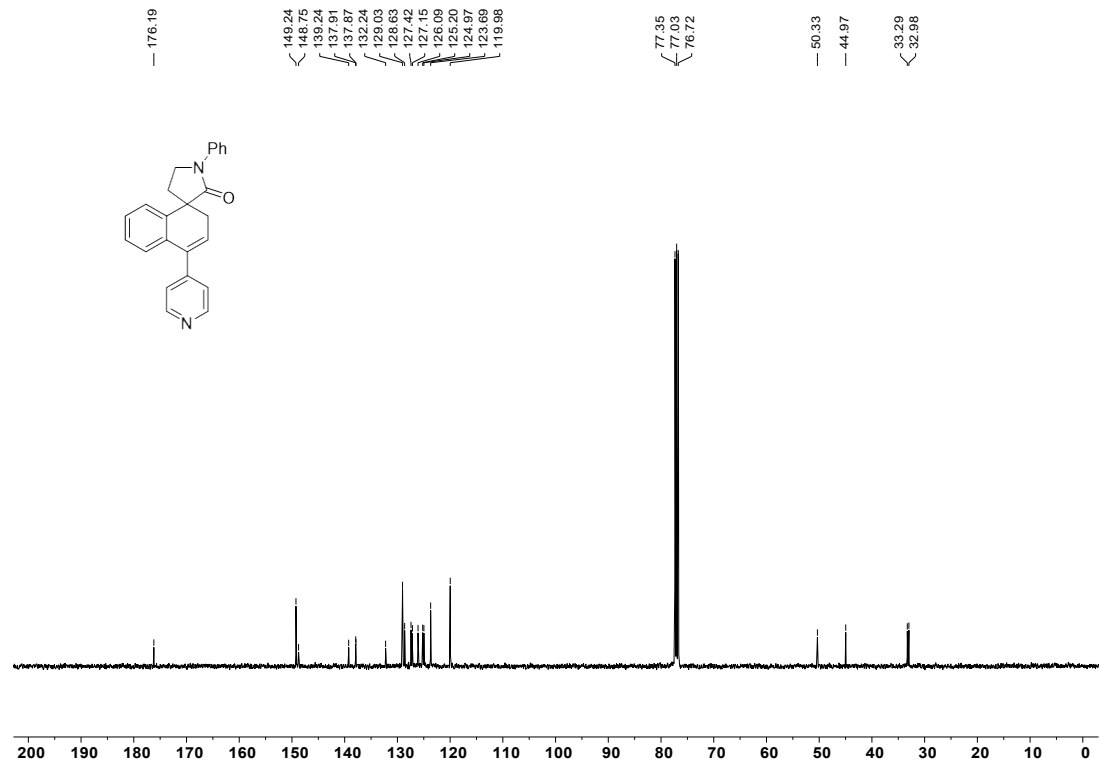
^{1}H NMR spectrum of compound **3m** (400 MHz, Chloroform-*d*)



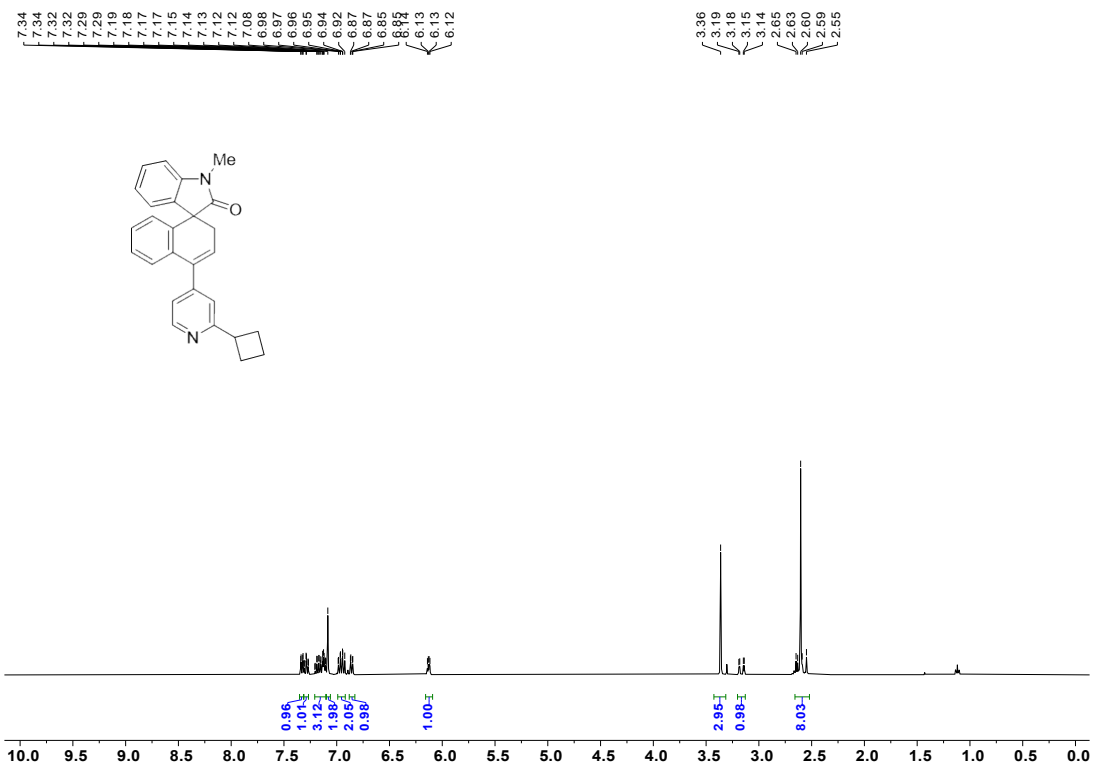
^{13}C NMR spectrum of compound **3m** (100 MHz, Chloroform-*d*)



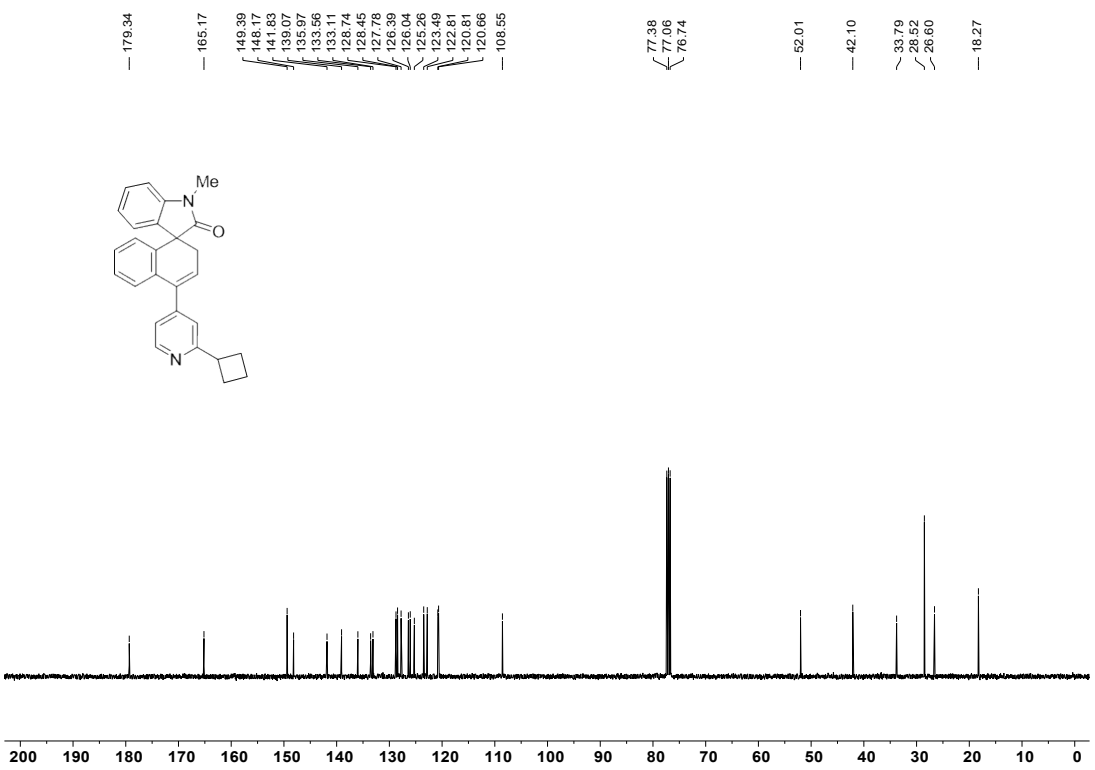
^{1}H NMR spectrum of compound **3n** (400 MHz, Chloroform-*d*)



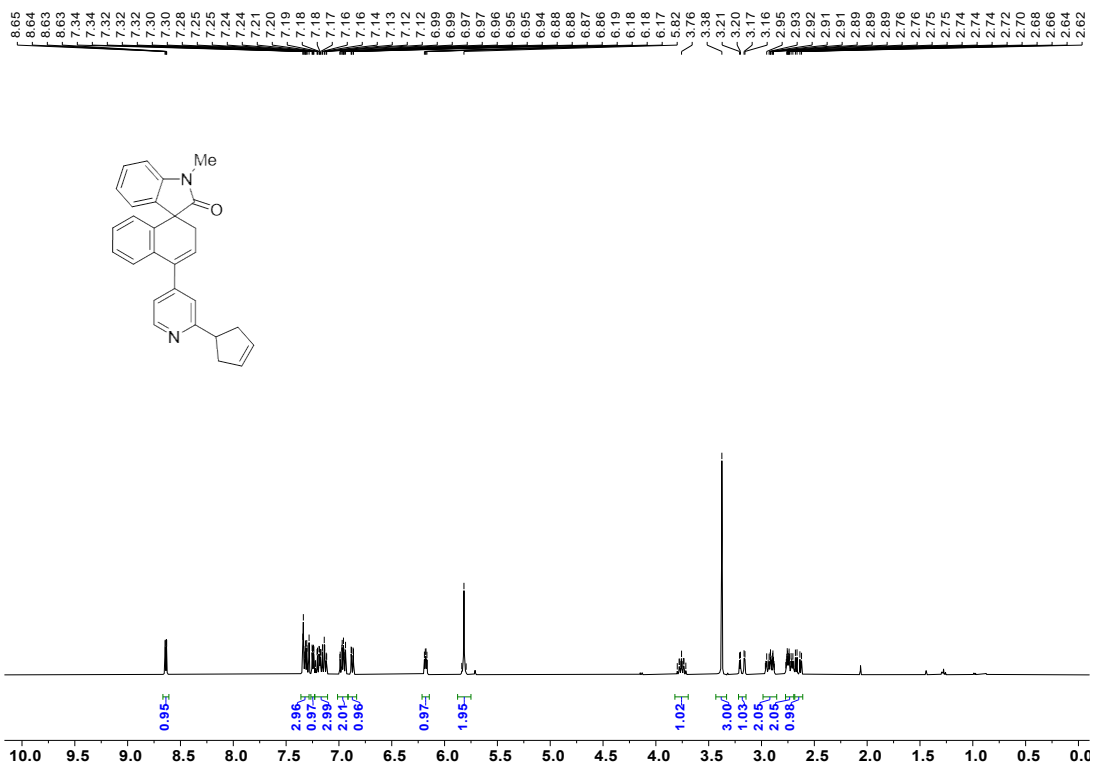
^{13}C NMR spectrum of compound **3n** (100 MHz, Chloroform-*d*)



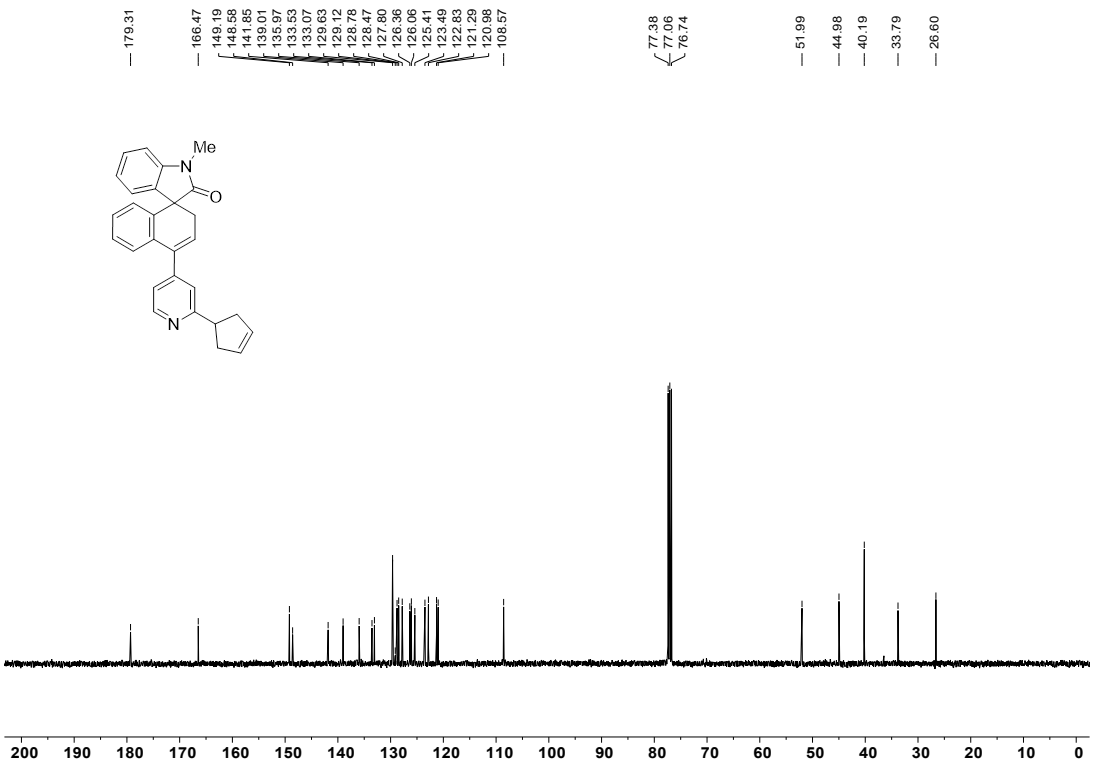
^{1}H NMR spectrum of compound **3o** (400 MHz, Chloroform-*d*)



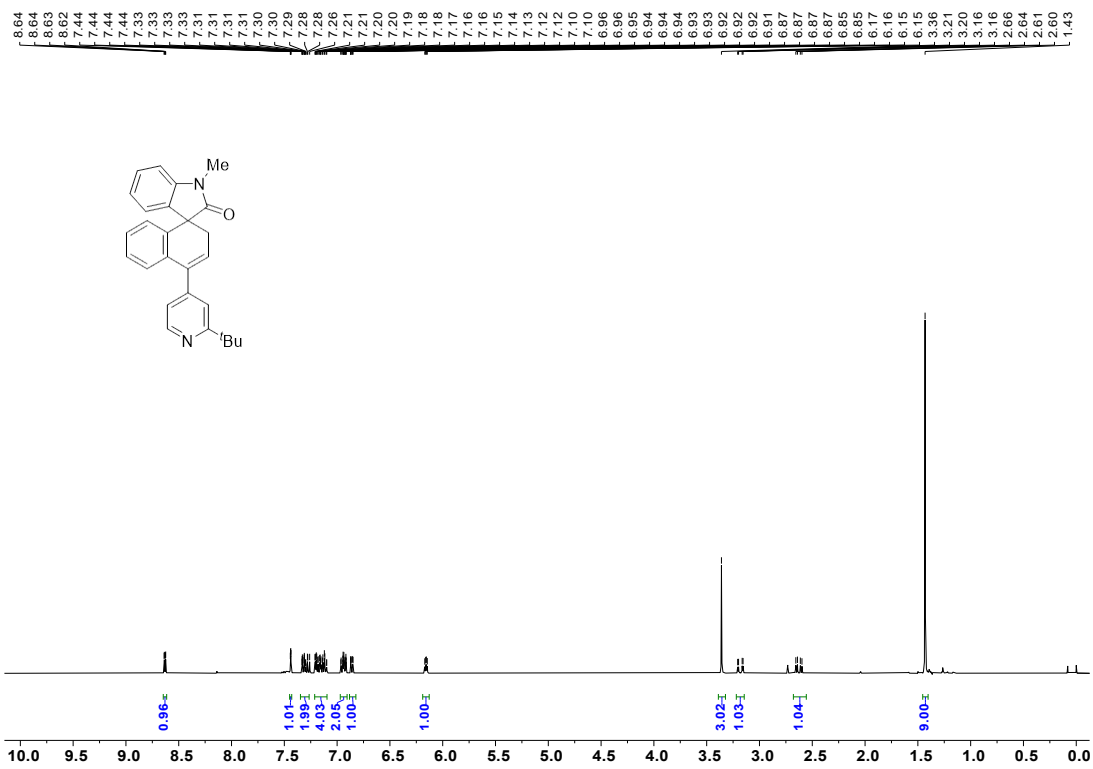
^{13}C NMR spectrum of compound **3o** (100 MHz, Chloroform-*d*)



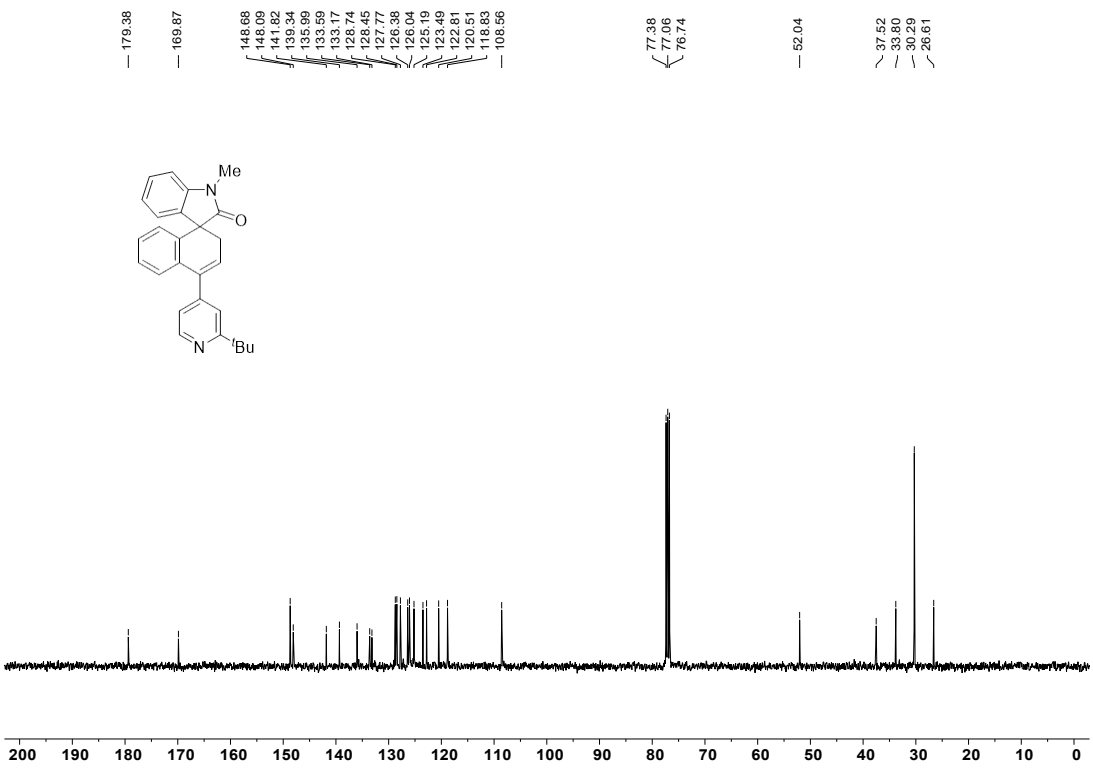
^{1}H NMR spectrum of compound **3p** (400 MHz, Chloroform-*d*)



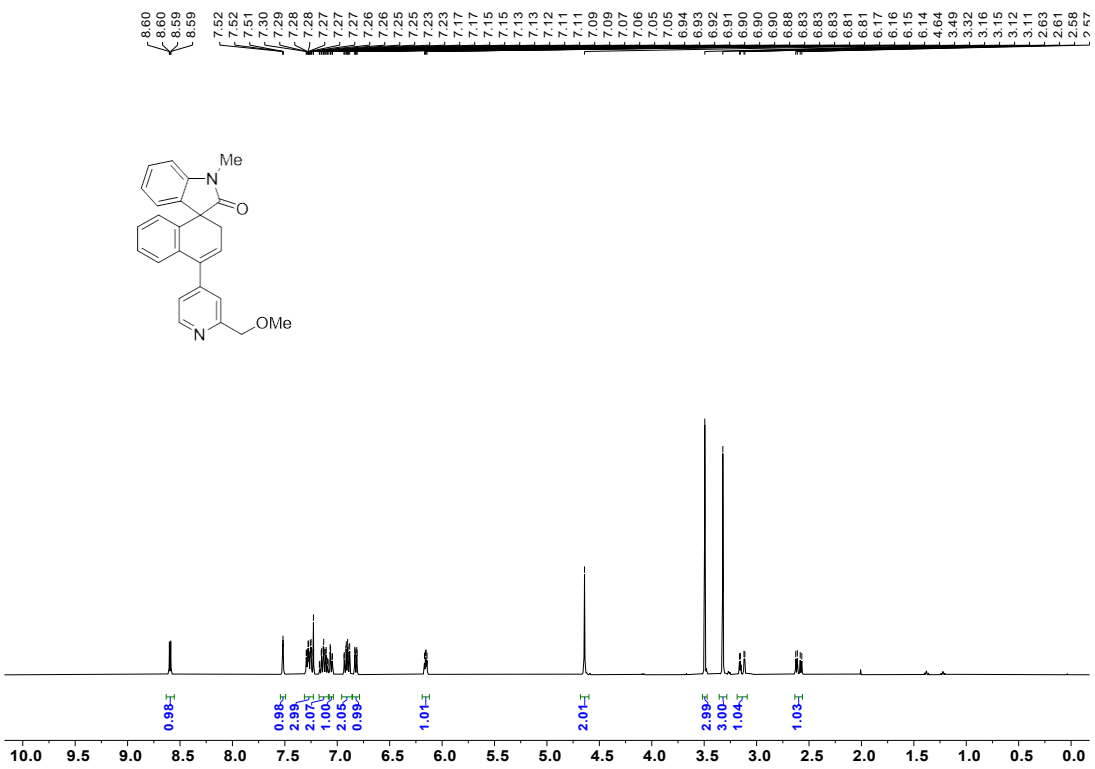
^{13}C NMR spectrum of compound **3p** (100 MHz, Chloroform-*d*)



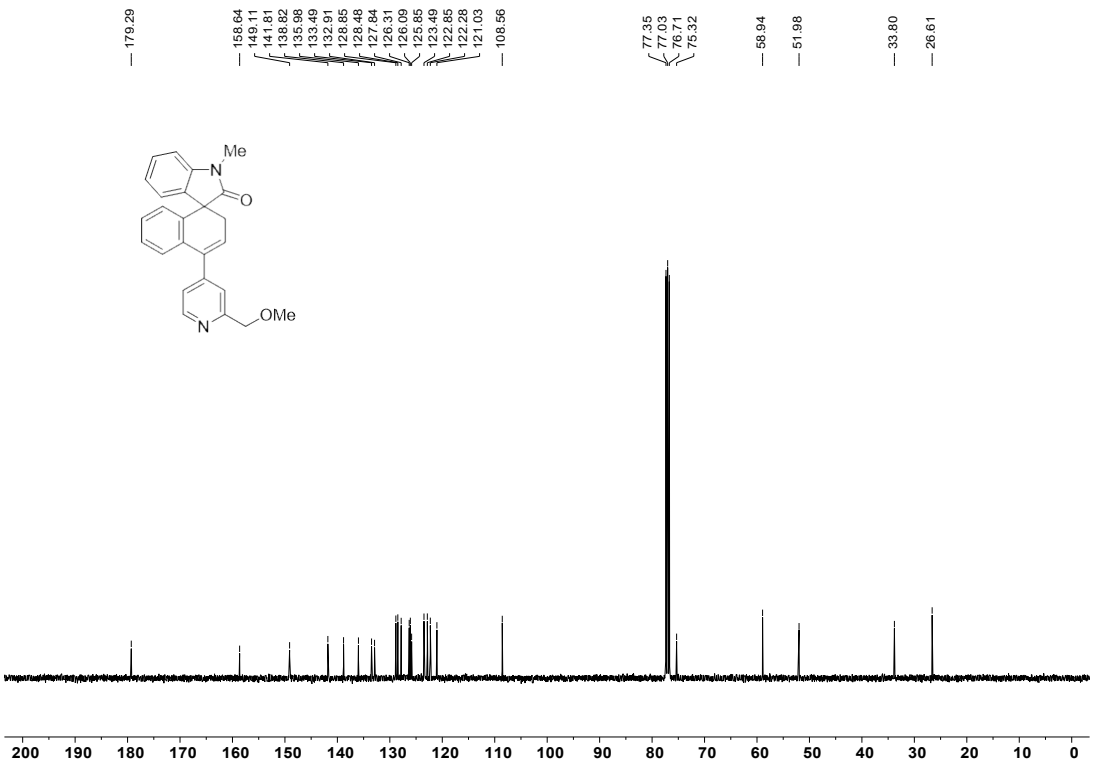
^{1}H NMR spectrum of compound **3q** (400 MHz, Chloroform-*d*)



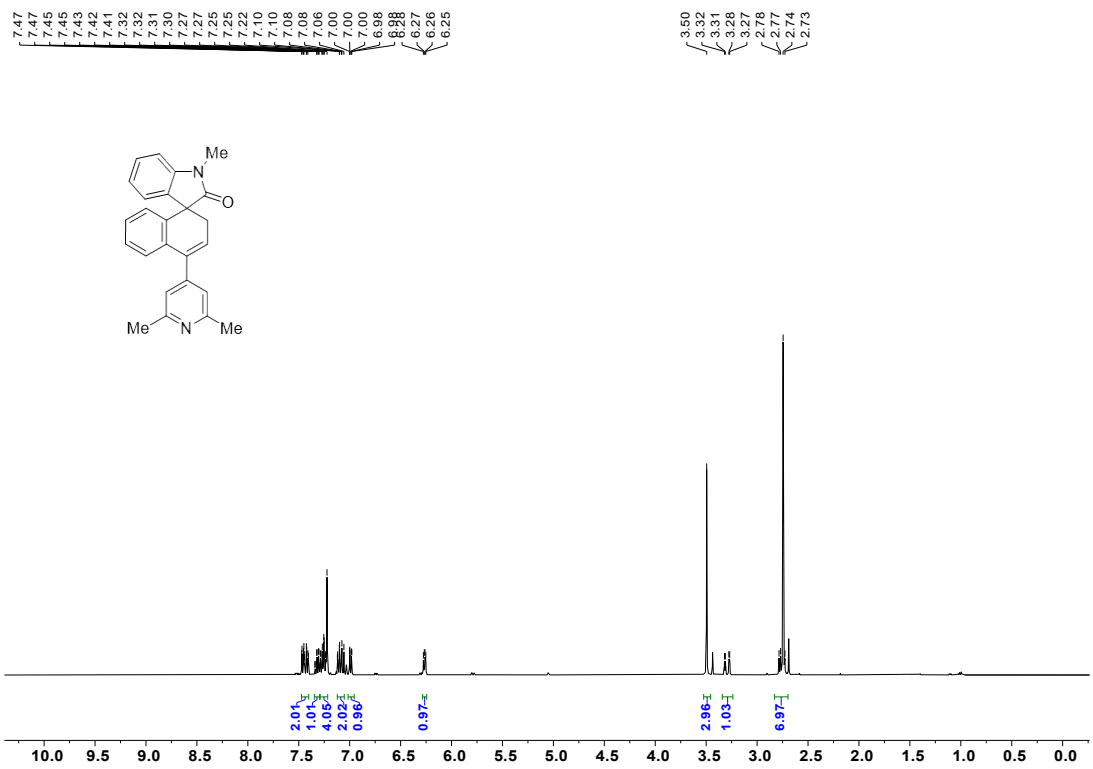
^{13}C NMR spectrum of compound **3q** (100 MHz, Chloroform-*d*)



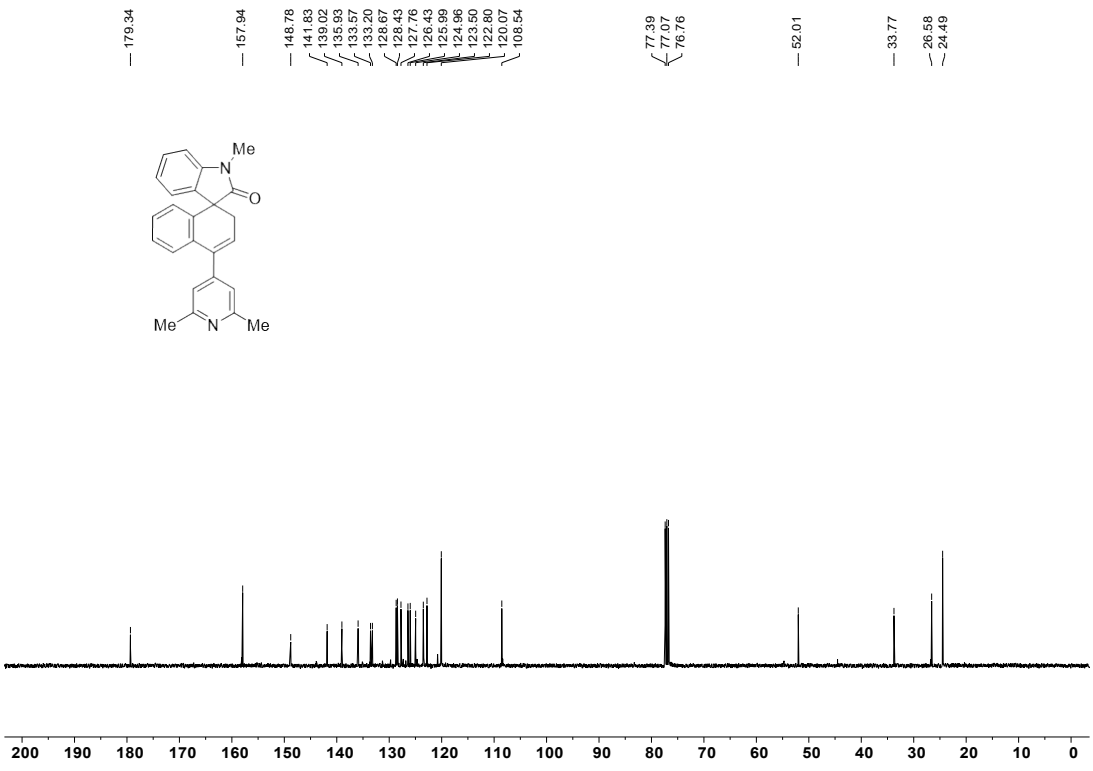
^{1}H NMR spectrum of compound **3r** (400 MHz, Chloroform-*d*)



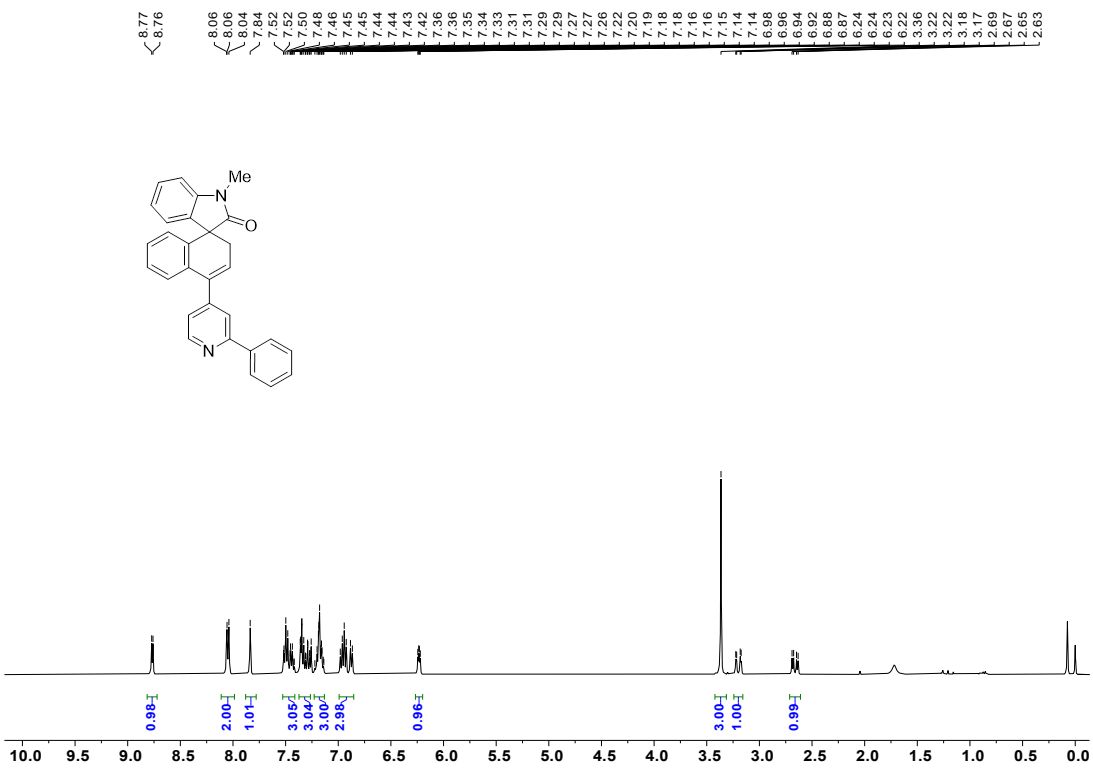
^{13}C NMR spectrum of compound **3r** (100 MHz, Chloroform-*d*)



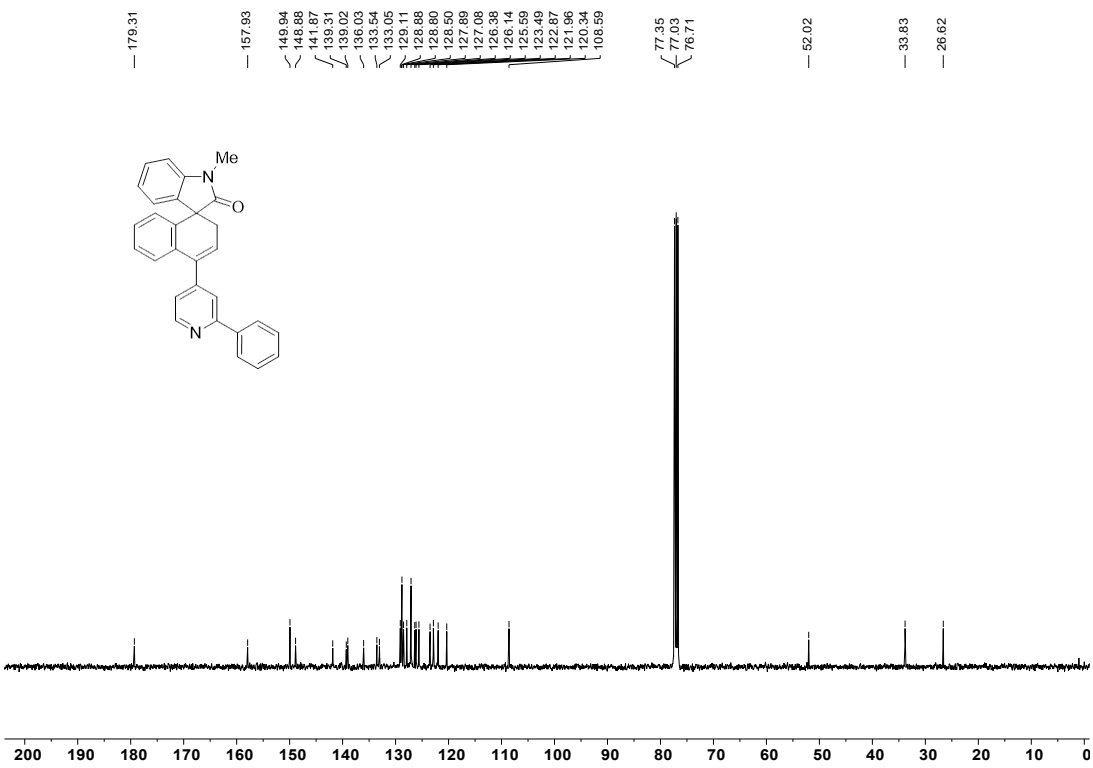
^{1}H NMR spectrum of compound **3s** (400 MHz, Chloroform-*d*)



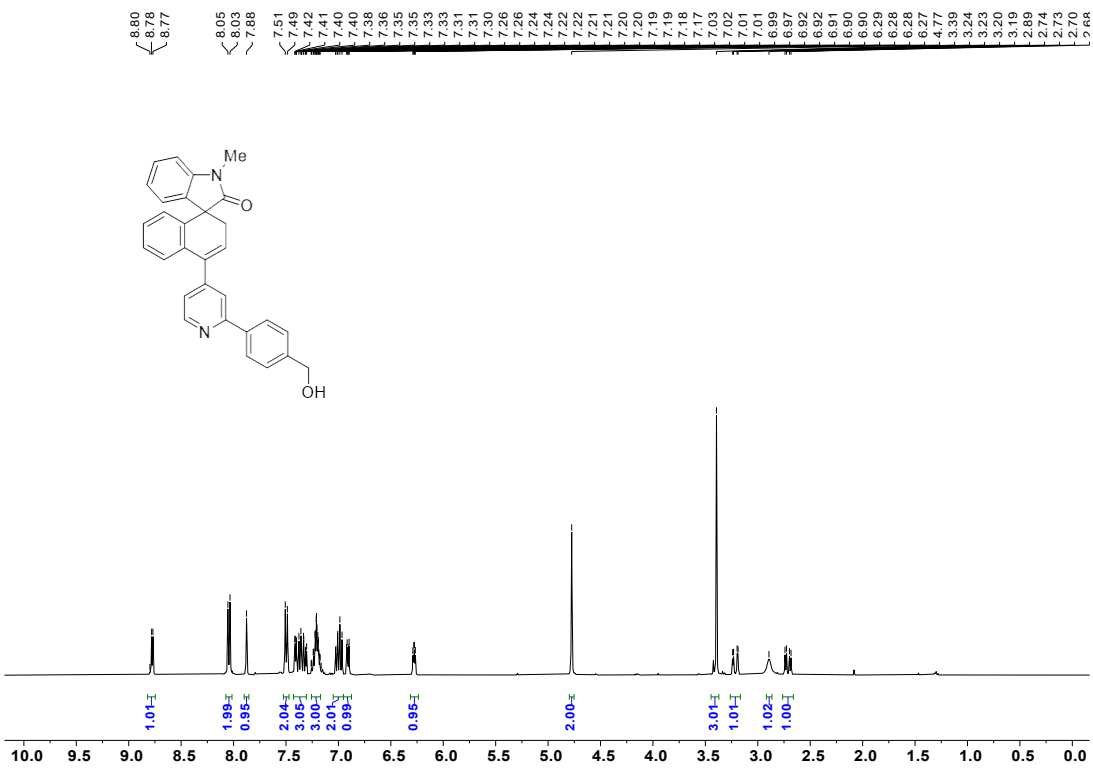
^{13}C NMR spectrum of compound **3s** (100 MHz, Chloroform-*d*)



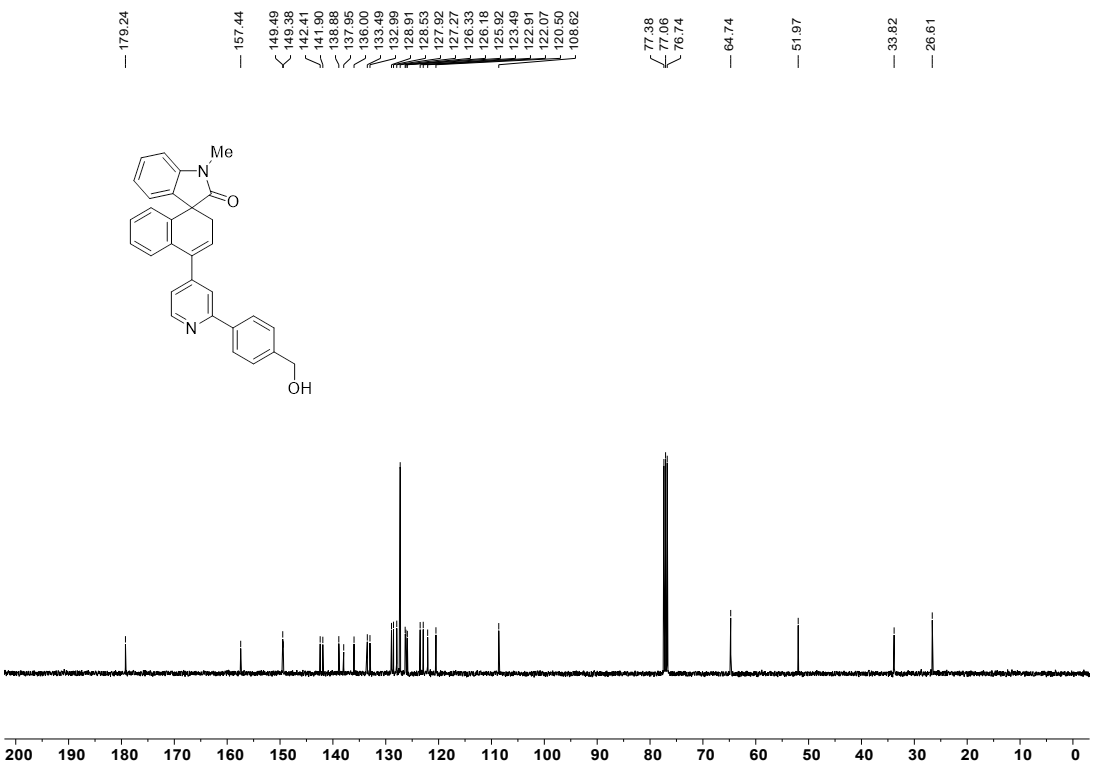
^{1}H NMR spectrum of compound **3t** (400 MHz, Chloroform-*d*)



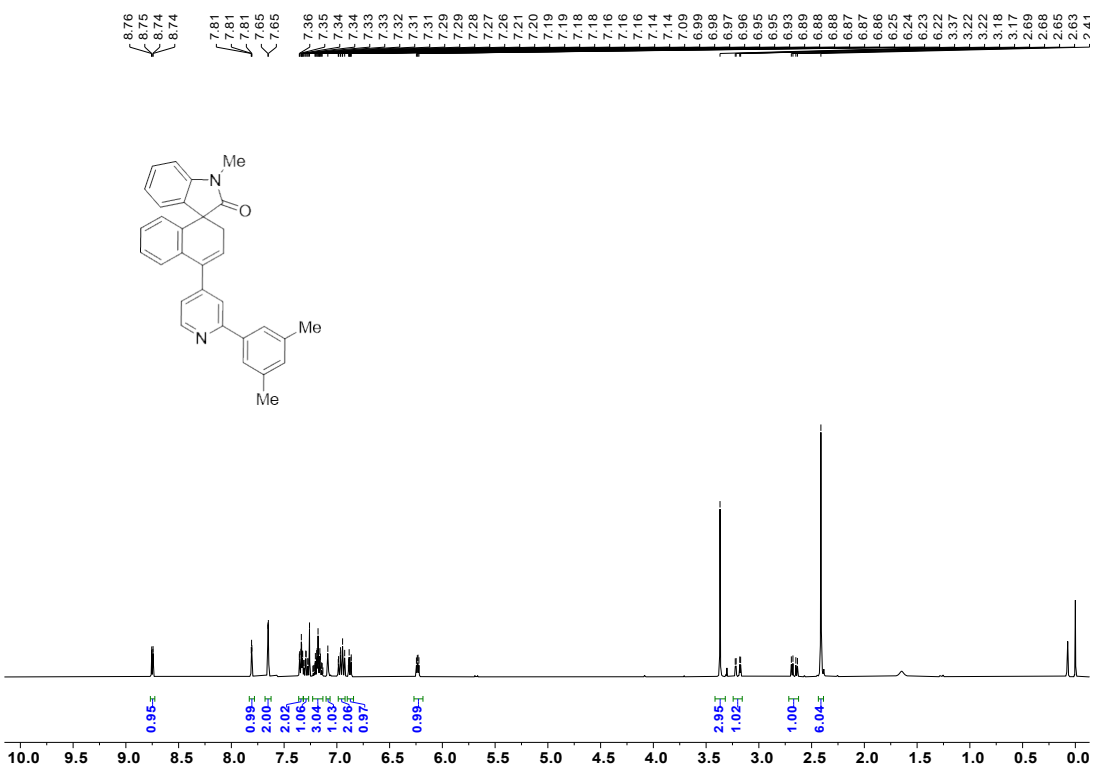
^{13}C NMR spectrum of compound **3t** (100 MHz, Chloroform-*d*)



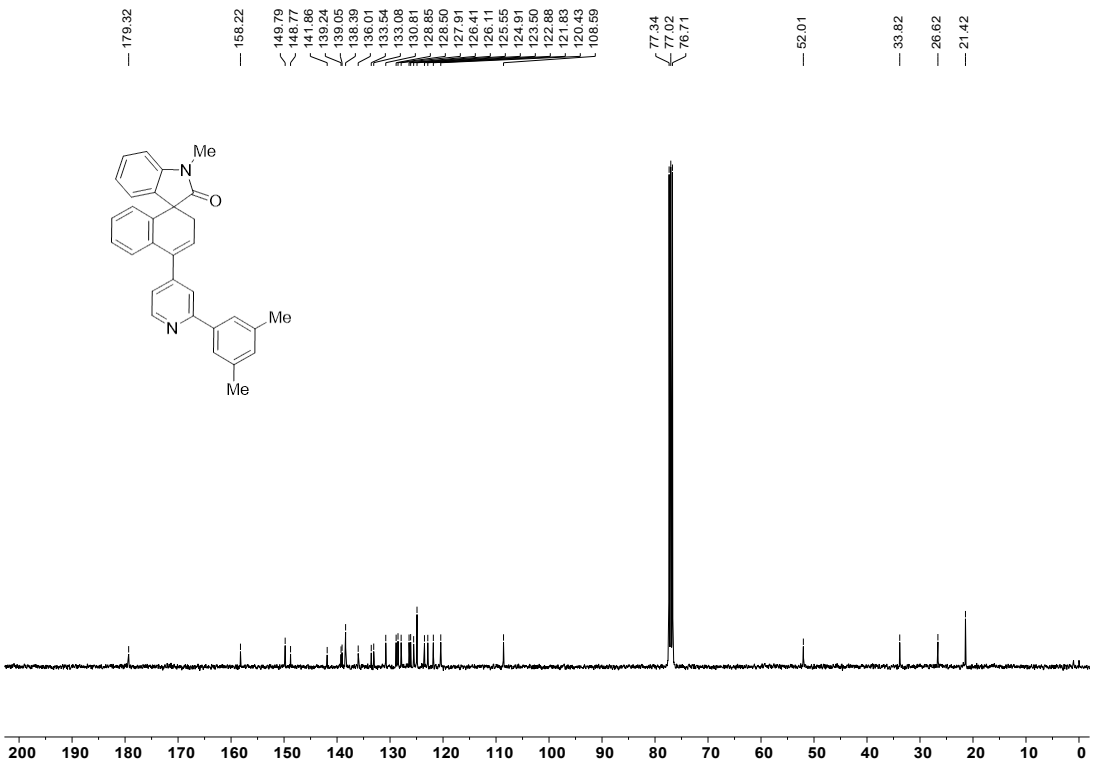
^{1}H NMR spectrum of compound **3u** (400 MHz, Chloroform-*d*)



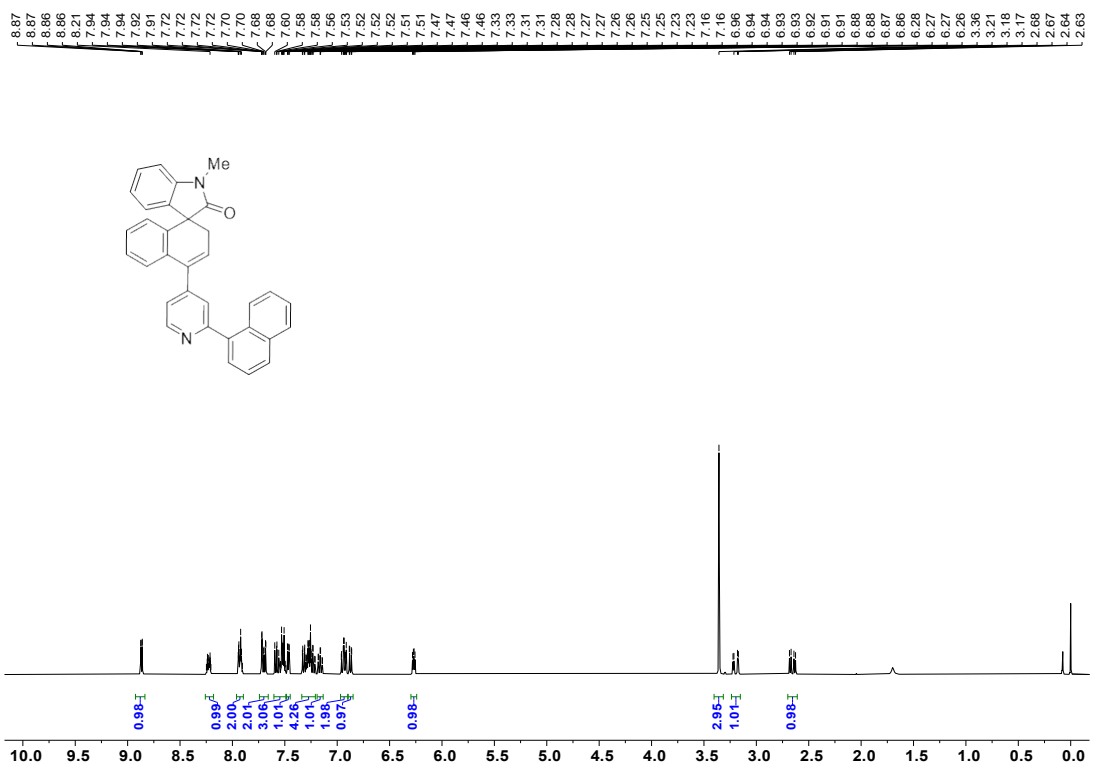
^{13}C NMR spectrum of compound **3u** (100 MHz, Chloroform-*d*)



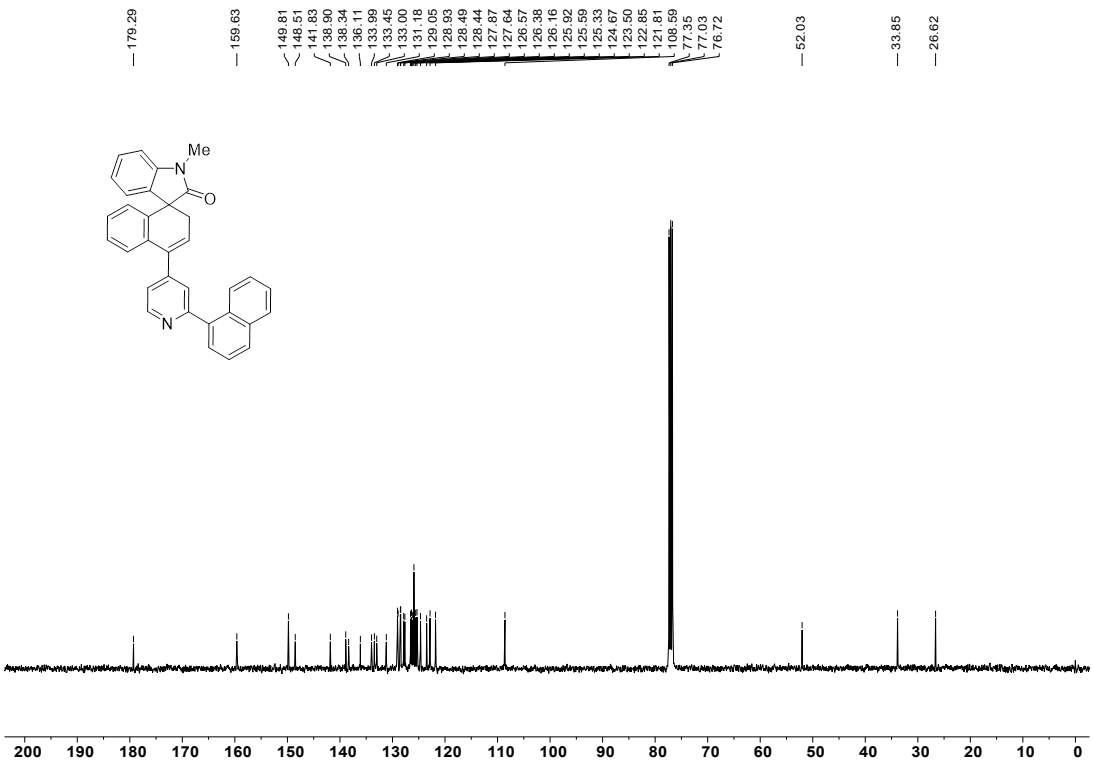
^{1}H NMR spectrum of compound **3v** (400 MHz, Chloroform-*d*)



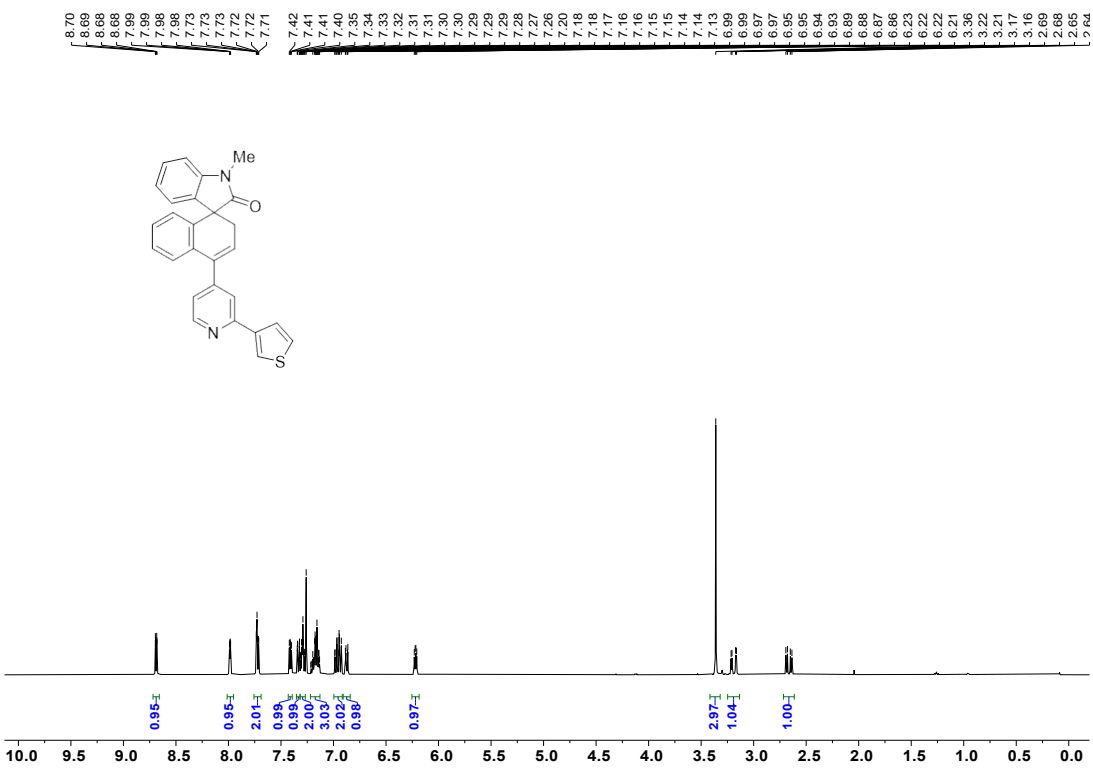
^{13}C NMR spectrum of compound **3v** (100 MHz, Chloroform-*d*)



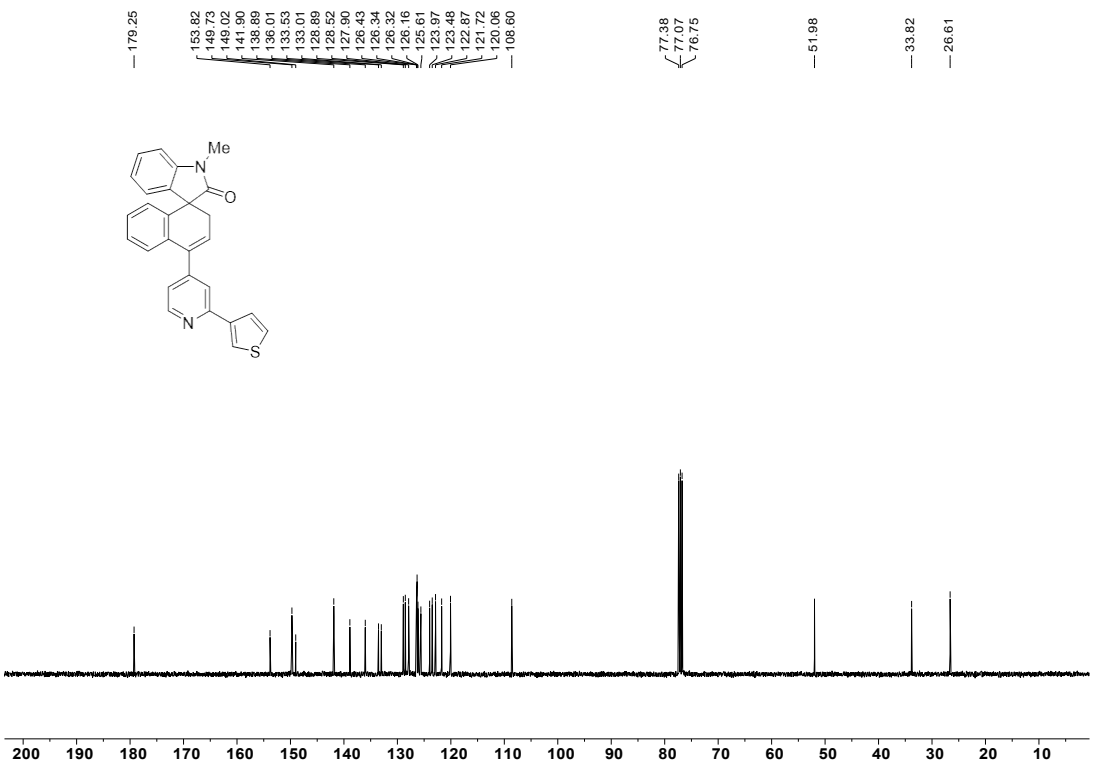
^{1}H NMR spectrum of compound **3w** (400 MHz, Chloroform-*d*)



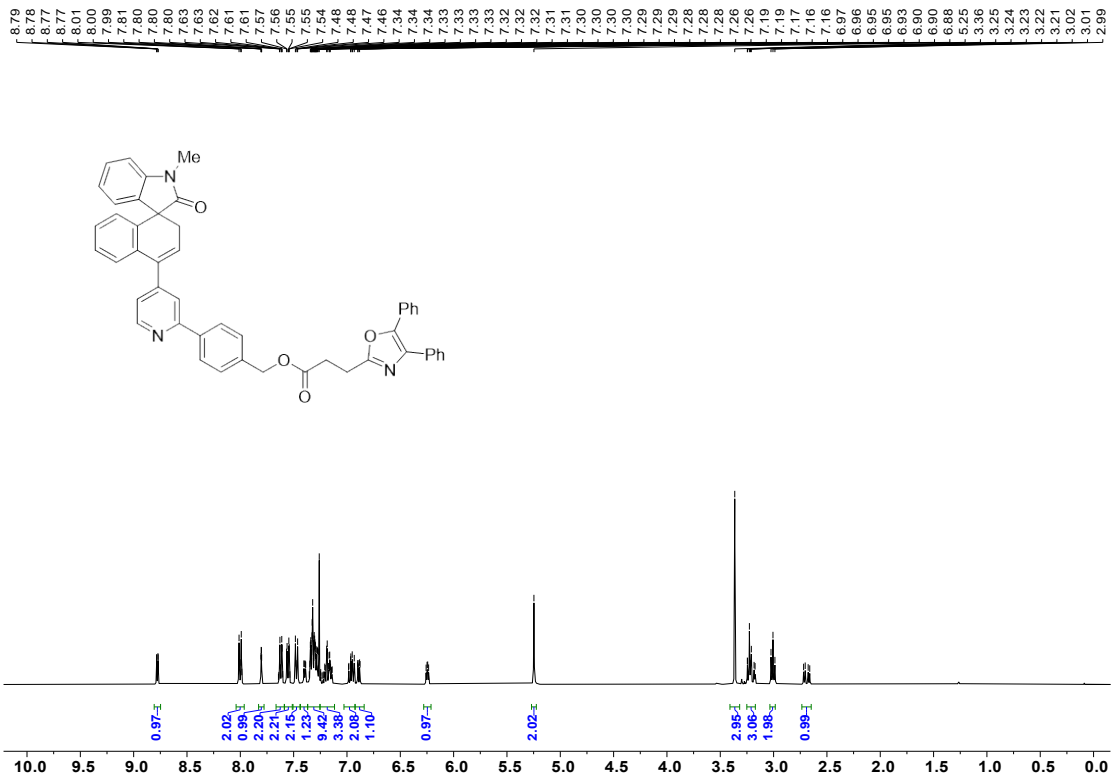
^{13}C NMR spectrum of compound **3w** (100 MHz, Chloroform-*d*)



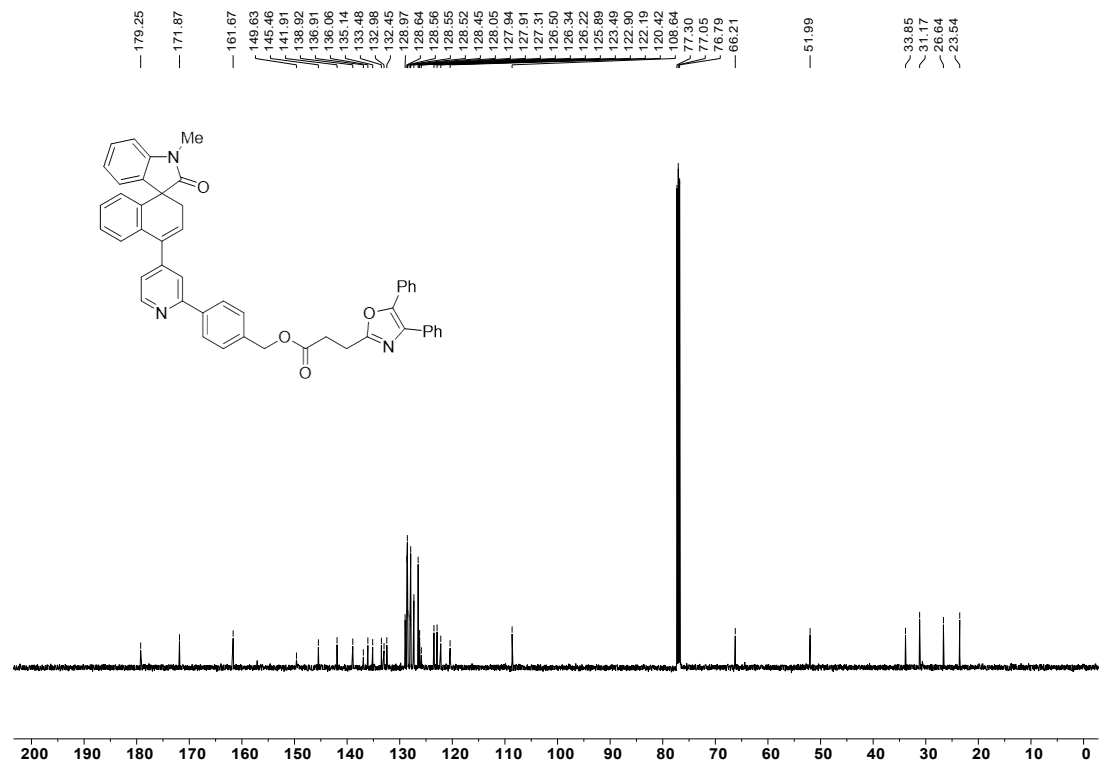
^{1}H NMR spectrum of compound **3x** (400 MHz, Chloroform-*d*)



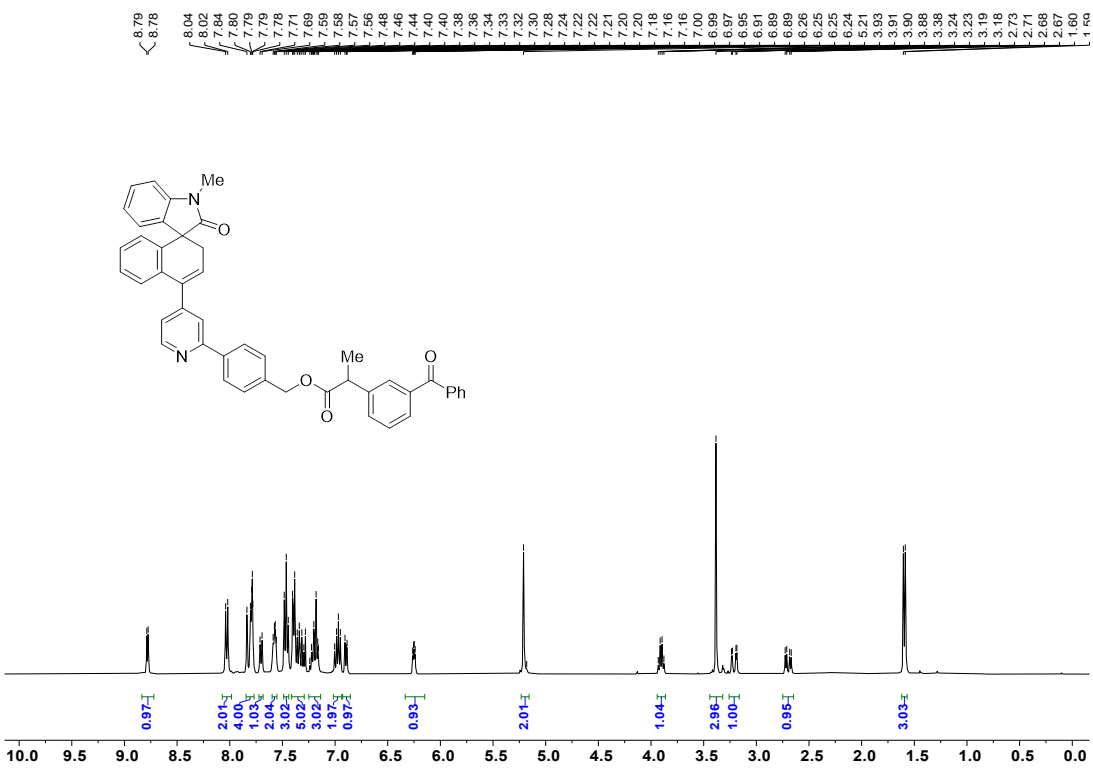
^{13}C NMR spectrum of compound **3x** (100 MHz, Chloroform-*d*)



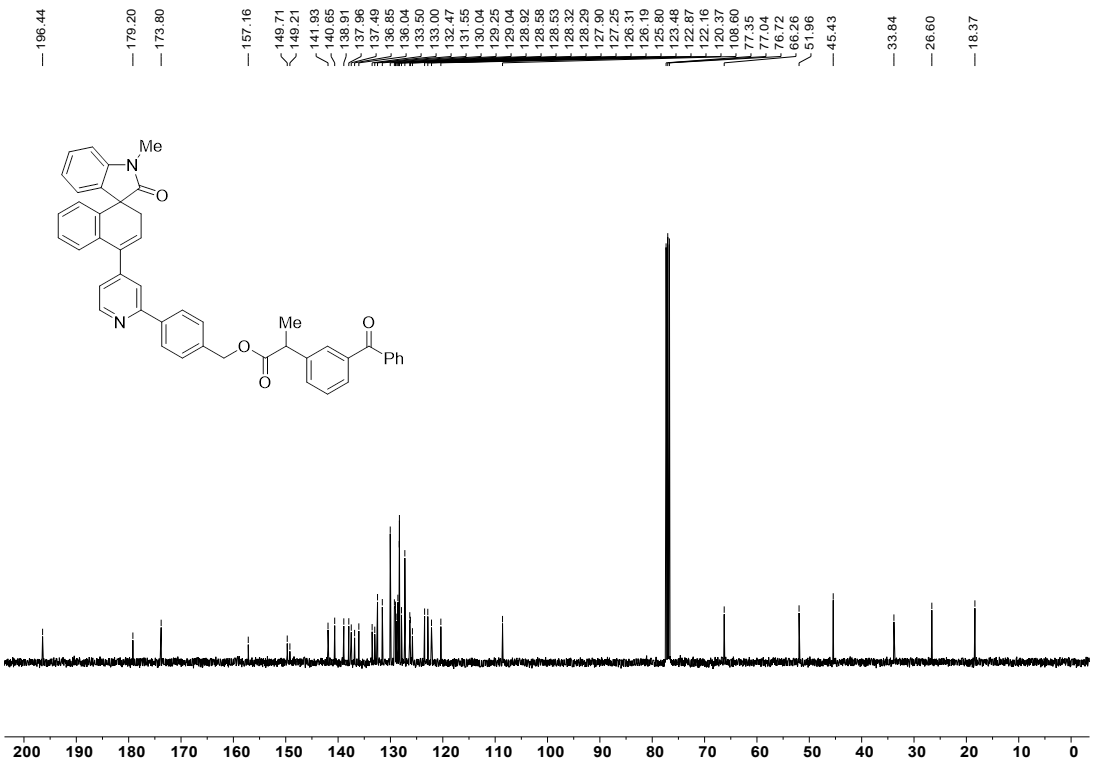
^{1}H NMR spectrum of compound **3y** (400 MHz, Chloroform-*d*)



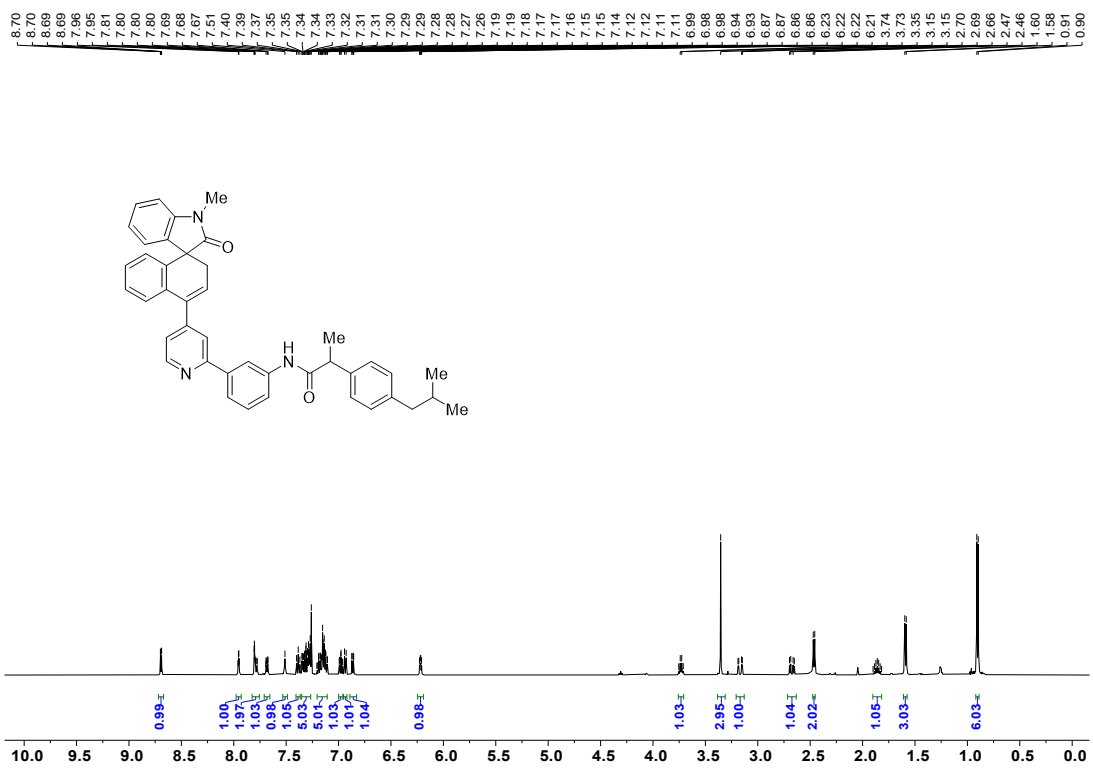
^{13}C NMR spectrum of compound **3y** (125 MHz, Chloroform-*d*)



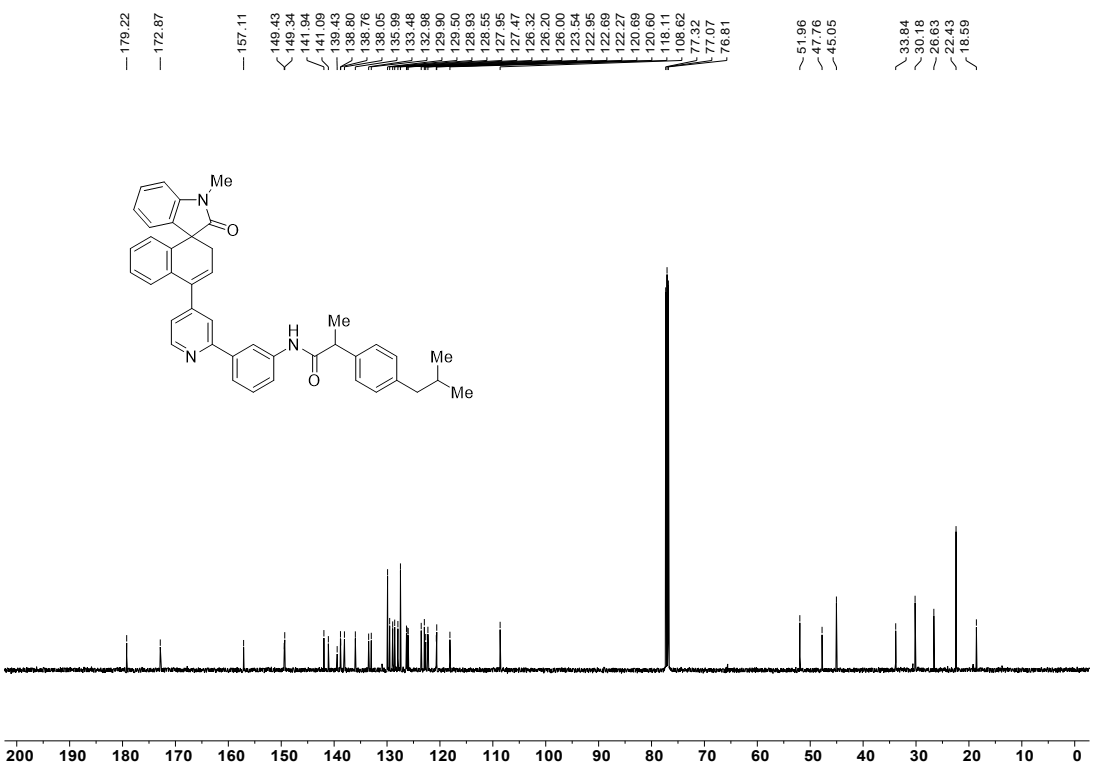
^{1}H NMR spectrum of compound **3z** (400 MHz, Chloroform-*d*)



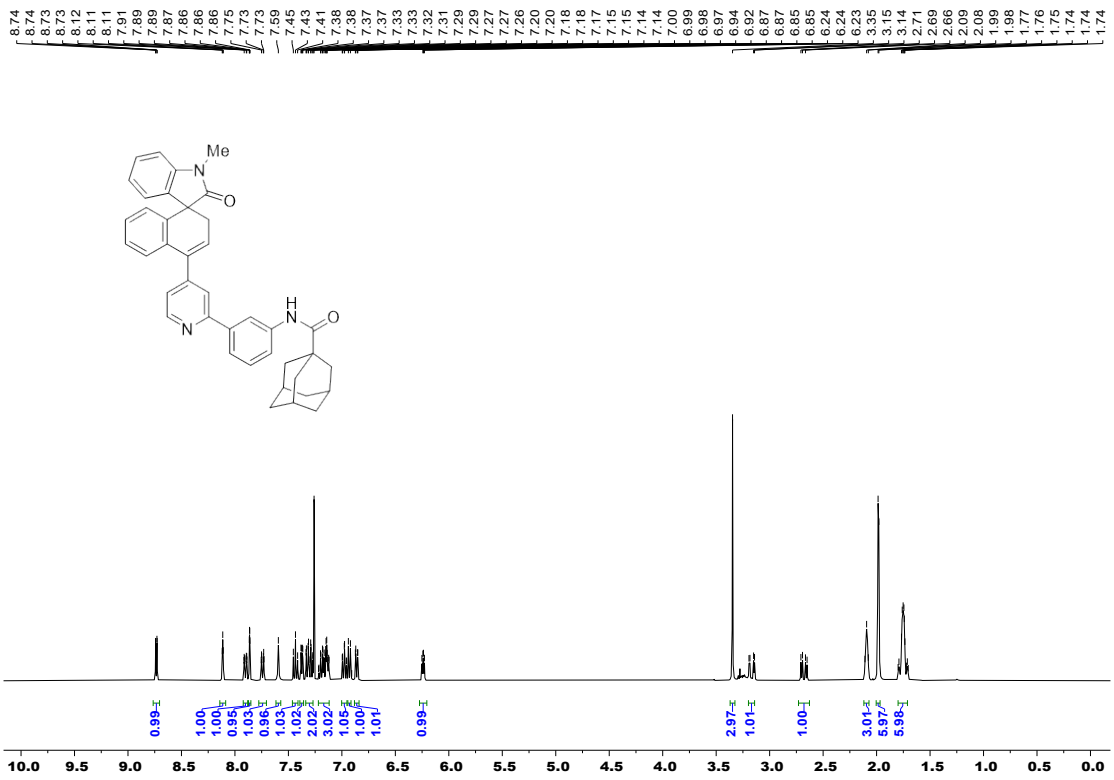
^{13}C NMR spectrum of compound **3z** (100 MHz, Chloroform-*d*)



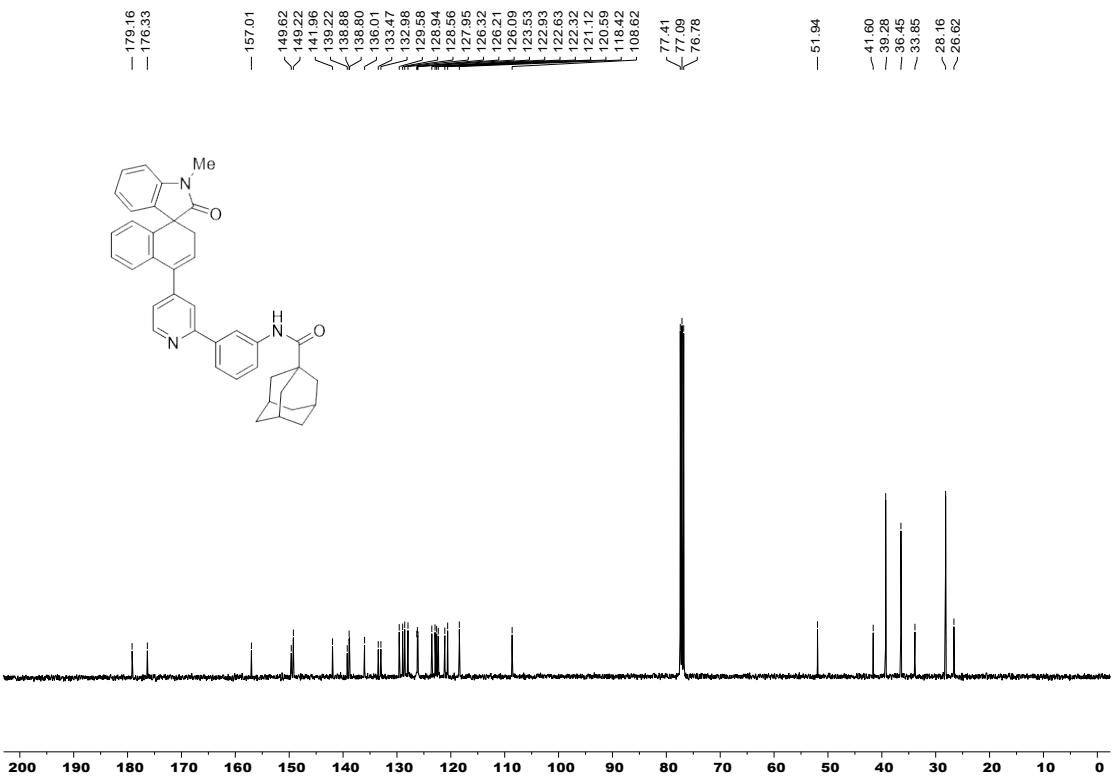
^{1}H NMR spectrum of compound **3aa** (500 MHz, Chloroform-*d*)



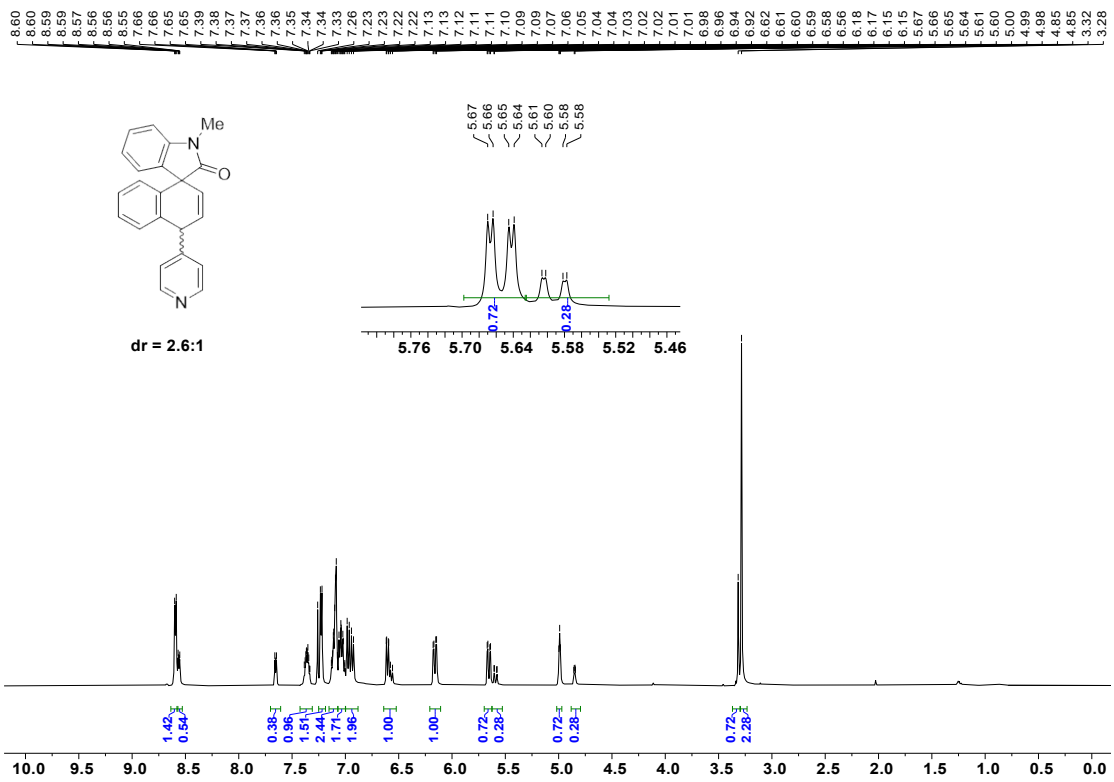
^{13}C NMR spectrum of compound **3aa** (125 MHz, Chloroform-*d*)



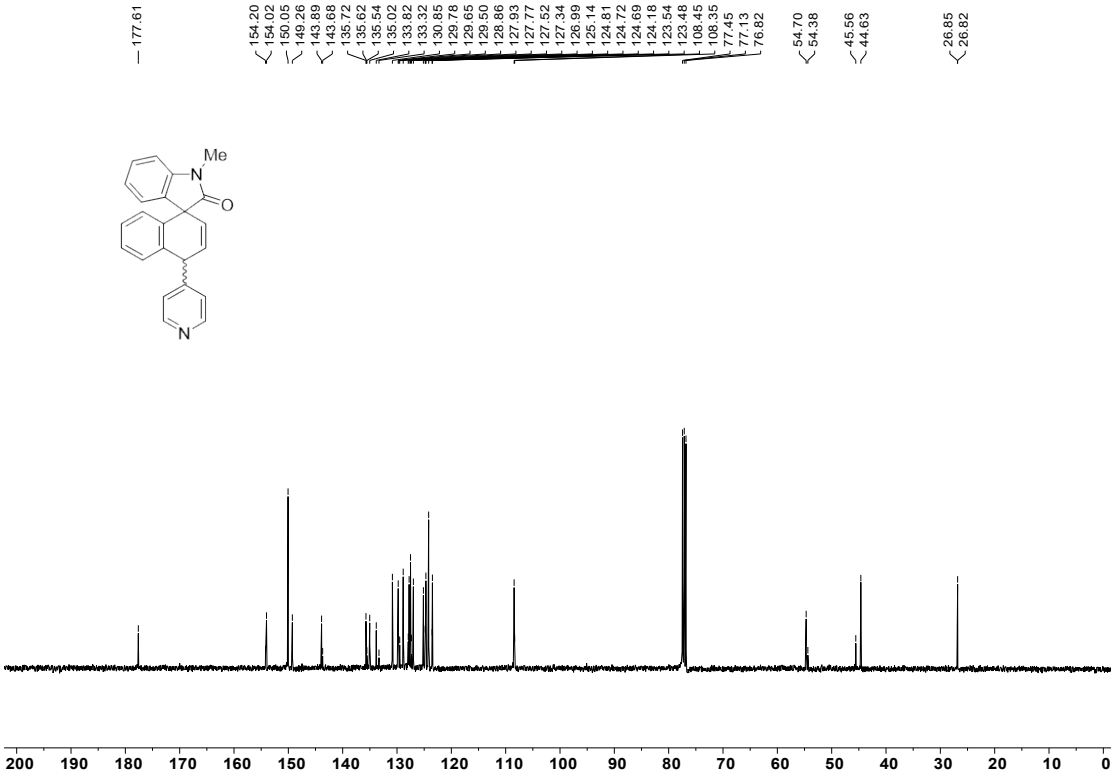
^{1}H NMR spectrum of compound **3ab** (400 MHz, Chloroform-*d*)



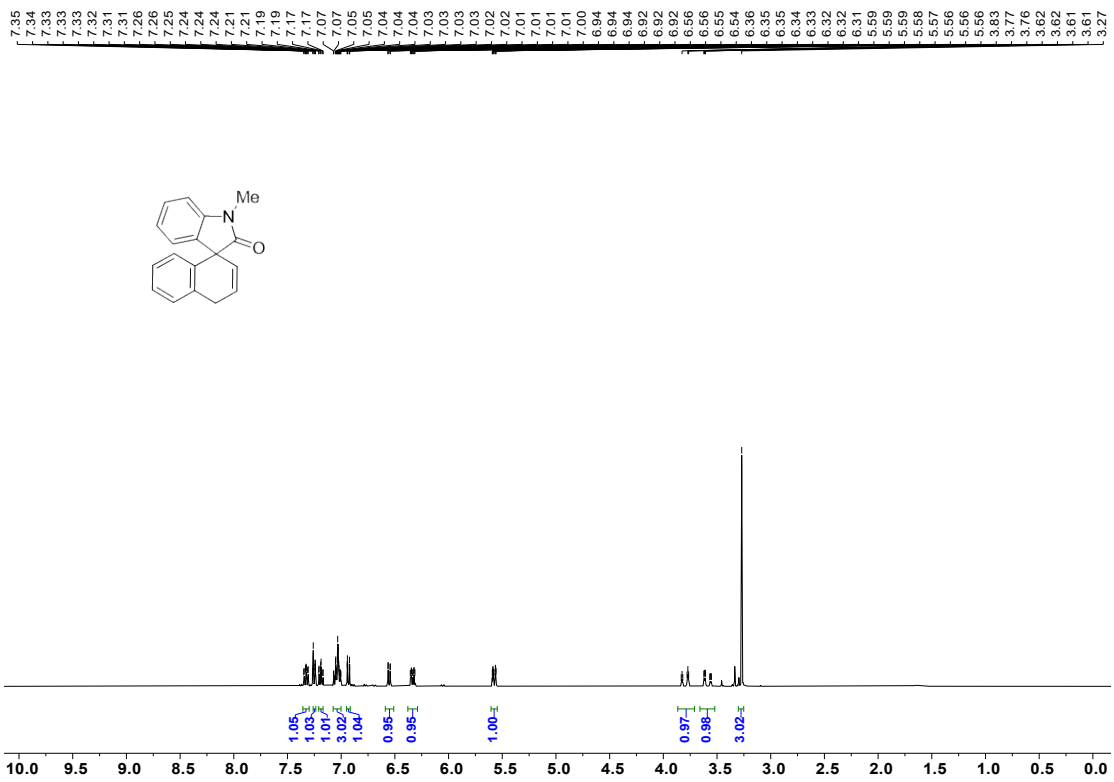
^{13}C NMR spectrum of compound **3ab** (100 MHz, Chloroform-*d*)



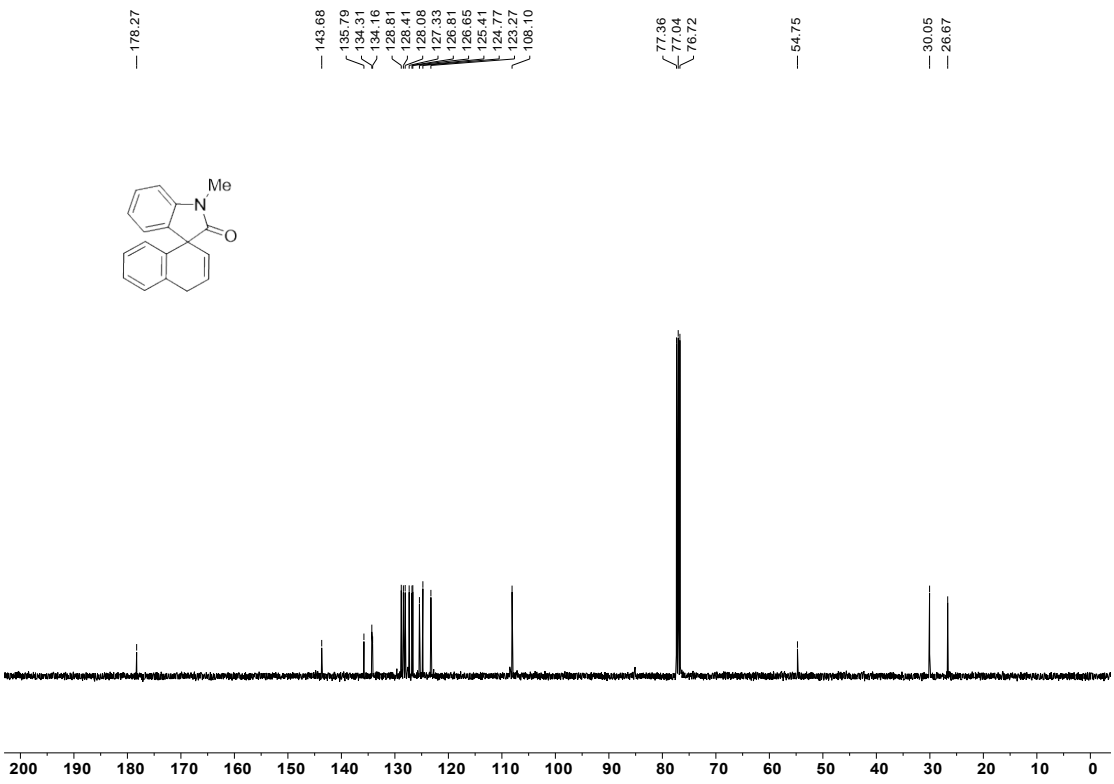
^{1}H NMR spectrum of compound **3a'** (400 MHz, Chloroform-*d*)



^{13}C NMR spectrum of compound **3a'** (100 MHz, Chloroform-*d*)



^{1}H NMR spectrum of compound **4** (400 MHz, Chloroform-*d*)



^{13}C NMR spectrum of compound **4** (100 MHz, Chloroform-*d*)