$Sc(OTf)_3$-catalyzed one-pot two-step approach for spiro-oxindole dihydropyridine derivatives initiated by the *N*-olefination of MBH carbonates

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1. General information

Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or DMSO-d_6 on Bruker 600 MHz instrument (at 600 MHz for ^1H, and at 150 MHz for ^{13}C). Proton chemical shifts are reported in parts per million (δ scale). The ^1H NMR chemical shifts are reported in ppm with the $CDCl_3$ at 7.26 ppm or DMSO-d_6 at 2.50 ppm as standard. The ^{13}C NMR chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.2 ppm, DMSO-d_6: δ = 39.5 ppm). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = doublet of triplet, dt = triplet of doublet), coupling constant(s) (Hz), integration]. High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010 or Waters/Acquity UPLC-Synapt G2HDMS. High-resolution mass spectra were reported for the molecular ion $[M+H]^+$ or $[M+Na]^+$. High performance liquid chromatography (HPLC) was analyzed by chiral column in comparison with authentic racemates, using a Daicel Chiralpak AD Column (250 x 4.6 mm). X-ray diffraction experiment was carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre. UV detection was performed at 254 nm. Column chromatography was performed on silica gel (200-300 mesh) using an eluent of ethyl acetate (EA) and petroleum ether (PE). TLC was performed on glass-backed silica plates; products were visualized using UV light. All reagents and solvents were obtained from commercial sources and used without further purification. Oil baths were used as the heat source. Melting points were recorded on BUCHI Melting Point M-565 instrument.

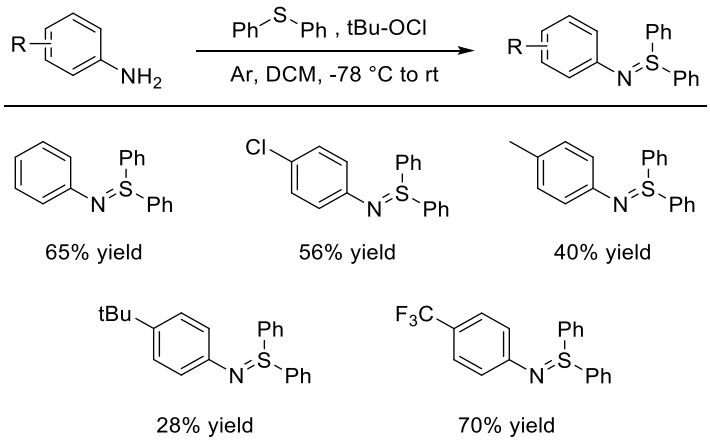
2. Preparation of substrates

Synthesis of MBH carbonates

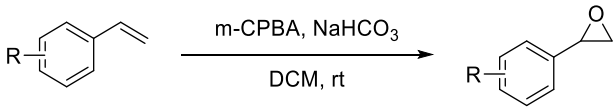
All MBH carbonates were prepared according to the literature procedures.[1]

Synthesis of S,S-diphenyl-N-arylsulfilimines[2]

Under an argon atmosphere, t-BuOCl (2.3 g, 21.0 mmol) was added slowly to a mixture of substituted aniline (20.0 mmol) and diphenyl sulfide (22.0 mmol) in 80 mL DCM at -78 °C. The resulting mixture was stirred at this temperature for 1 h and then for an additional hour at room temperature. After the addition of NEt_3 (4.16 mL, 30 mmol), the resulting mixture was stirred for 10 min. The solvent was evaporated to give crude products. Purification through flash column chromatography using ethyl acetate and petroleum ether as eluent can give S,S-diphenyl-N-arylsulfilimines in 28%-70% yields.

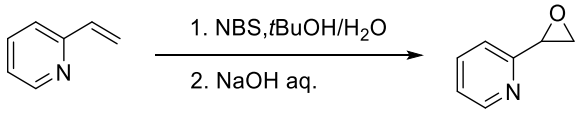


Synthesis of oxiranes[3]



R = 4-Br, 4-Cl, 4-F, 3-Me,2-Me,
2-Naphthylene
Cyclohexan

The styrene derivative (2.0 mmol) was diluted in DCM (10 mL) and mixed with distilled water (10 mL) containing $NaHCO_3$ (1 g). Then, m-CPBA (2.2 mmol) was carefully added. The reaction mixture was stirred at room temperature for 3 h or longer, monitored by TLC. To quench the reaction, aqueous Na_2SO_3 (1.3 g in 10 mL) was added and left to stir for 20 min. The aqueous phase was then extracted with DCM (2 × 10 mL). The combined organic phases were washed with $NaHCO_3$ (2 × 25 mL) and distilled water (25 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give oxiranes.



To solution of 2-vinylpyridine (0.53 g, 5.0 mmol) in tert-Butanol (5 mL) and water (15 mL) was added NBS (6.0 mmol). The mixture was stirred at room temperature for 1 h, then sodium hydroxide was added (3 N, 5 mL). The mixture was stirred at room temperature for 1 h. The crude product was extracted with Ethyl ether (15 mL × 3). The combined organic layers were washed with brine (15 mL × 3), dried over sodium sulfate, concentrated and purified by silica gel chromatography (EtOAc/petroleum ether = 1/3) to give the title compound as a yellow oil (0.45 g, 74% yield).

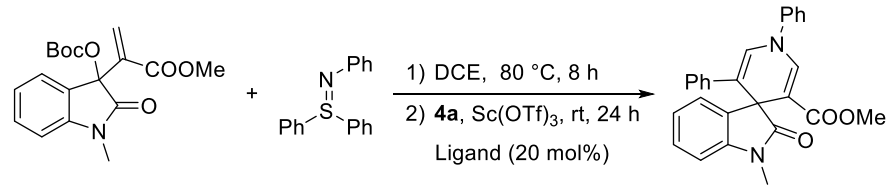
3. References

1 (*a*) X. Tang, Y. Wu, J. Jiang, H. Fang, W.-J. Zhou, W. Huang and G. Zhan, Formal [3+1+1] Carboannulation of Morita-Baylis-Hillman Carbonates with Pyridinium Ylides: Access to Spiro-Cyclopentadiene Oxindoles, *Org. Lett.*, 2021, **23**, 8937-8941; (*b*) Z.-H. Yang, P. Chen, Z.-C. Chen, Z. Chen, W. Du and Y.-C. Chen, A Double Deprotonation Strategy for Cascade Annulations of Palladium-Trimethylenemethanes and Morita-Baylis-Hillman Carbonates to Construct Bicyclo [3.1.0] hexane Frameworks, *Angew. Chem. Int. Ed.*, 2021, **60**, 13913-13917; (*c*) Z.-C. Chen, P. Chen, Z. Chen, Q. Ouyang, H.-P. Liang, W. Du and Y.-C. Chen, Organocatalytic Enantioselective 1,3-Difunctionalizations of Morita-Baylis-Hillman Carbonates, *Org. Lett.*, 2018, **20**, 6279-6283.

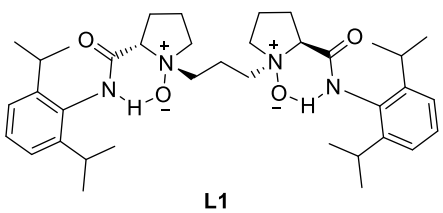
2 X. Tian, L. Song, M. Rudolph, F. Rominger, T. Oeser and A. S. K. Hashmi, Sulfilimines as Versatile Nitrene Transfer Reagents: Facile Access to Diverse Aza-Heterocycles, *Angew. Chem. Int. Ed.*, 2019, **58**, 3589-3593.

3 (*a*) C. E. Paul, D. Tischler, A. Riedel, T. Heine, N. Itoh and F. Hollmann, Nonenzymatic Regeneration of Styrene Monooxygenase for Catalysis, *ACS Catal.*, 2015, **5**, 2961-2965. (*b*) G. He, S.-Y. Zhang, W. A. Nack, R. Pearson, J. Rabb-Lynch and G. Chen, Total Synthesis of Hibispeptin A via Pd-Catalyzed C(sp^3)-H Arylation with Sterically Hindered Aryl Iodides, *Org. Lett*, 2014, **16**, 6488-6491.

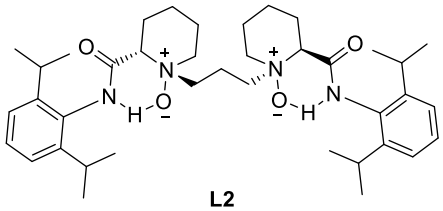
4. Screening of chiral catalysts



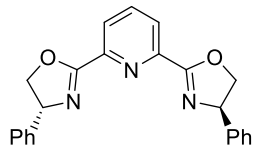
1a **2a** **5a**



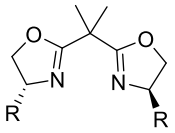
L1



L2



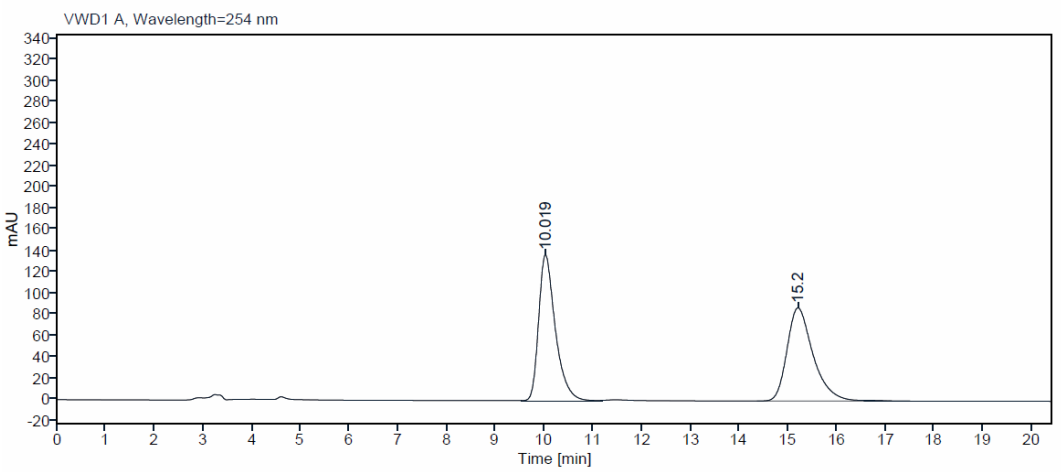
L3



L4, R = Ph
L5, R = *i*pr
L6, R = Bn
L7, R = *t*Bu

Entry	Ligand	Yield (%)[b]	*ee* (%)[c]
1	L1	63	0
2	L2	60	0
3	L3	41	0
4	L4	32	0
5	L5	31	0
6	L6	25	0
7	L7	28	0

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol) were stirred at 80 °C in DCE (1.0 mL) for 8 h, and then **4a** (0.12 mmol), $Sc(OTf)_3$ (0.02 mmol, 20 mol%), Ligand (20 mol%), Na_2SO_4 (50 mg) were added, and the reaction mixture was stirred at room temperature for 24 h. [b]Isolated yield of the product **5a**. [c]The *ee* value was determined by HPLC analysis (Daicel Chiralpak AD, n-hexane/2-propanol = 70:30, 1.0 mL/min, at 254 nm).



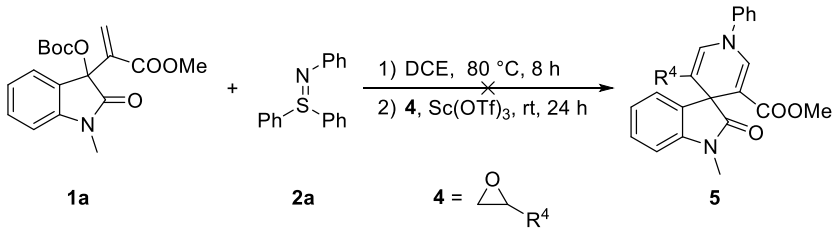
Signal: VWD1 A, Wavelength=254 nm

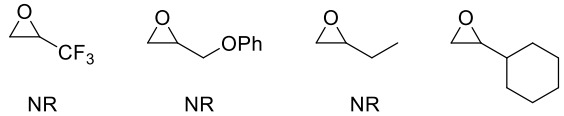
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.019	MM	0.3981	3283.9287	137.4781	50.0872	
15.200	BB	0.5618	3272.4900	87.6010	49.9128	
		Sum	6556.4187			

HPLC spectrogram of compound **5a**

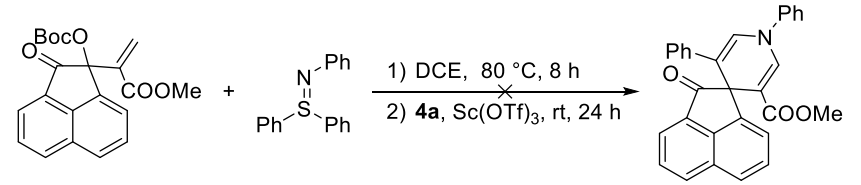
5. Exploration of other substrates

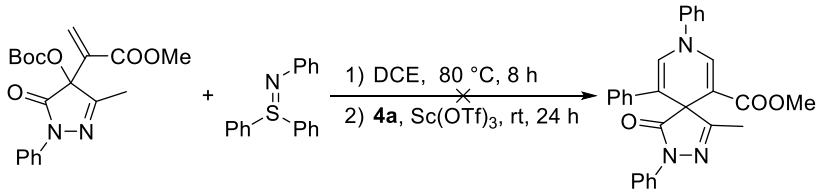
We examined substrates with non-aromatic groups on R^4, such as alkyl, cyclohexyl and trifluoromethyl groups. Unfortunately, these epoxides were inactive, and no products could be obtained.



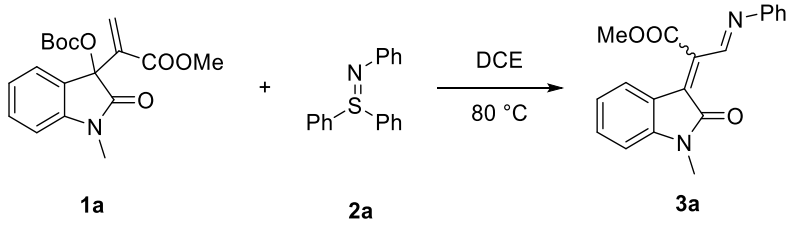


We also tried to enrich the diversity of skeleton of MBH carbonates, including pyrazolone and acenaphthenequinone-based MBH carbonates were examined, but no desired products were obtained.



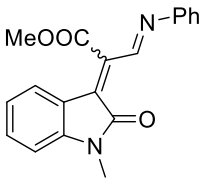


6. Isolation of the *N*-olefination product 3a



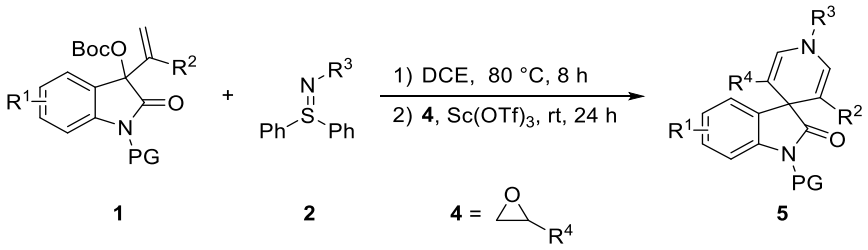
1a **2a** **3a**

In a 25 mL round-bottom flask, Isatin-derived Morita–Baylis–Hillman carbonate **1a** (1.0 mmol) and S,S-diphenyl-N-arylsulfilimine **2a** (1.0 mmol) in DCE (5 mL) was stirred at 80 °C until the reaction completed (monitored by TLC). The mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/5) to give Isatin-derived azadiene **3a** in 81% yield (260 mg). Meanwhile, diphenyl sulfide was recovered in 90% yield.

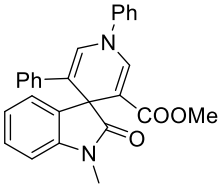


Methyl 2-(1-methyl-2-oxoindolin-3-ylidene)-3-(phenylimino) propanoate (3a): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/5) to give product **3a** as an orange-red solid in 81% yield (260 mg), m. p. 135.2-138.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.28 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.06 (s, 3H), 3.24 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 166.9, 166.8, 155.1, 150.7, 144.6, 138.2, 131.8, 129.1, 127.8, 123.7, 122.8, 121.9, 121.5, 120.1, 108.6, 52.9, 26.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}N_2O_3Na$ 343.1059, found 343.1054.

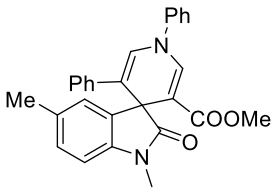
7. General procedure for the synthesis of products 5



Isatin-derived Morita–Baylis–Hillman carbonates **1** (0.1 mmol, 1.0 equiv) and S,S-diphenyl-N-arylsulfilimines **2** (0.12 mmol, 1.2 equiv) were dissolved in 1.0 mL of DCE, and the mixture was stirred at 80 °C for 8 h. Then, oxiranes **4** (0.12 mmol, 1.2 equiv), $Sc(OTf)_3$ (20 mol%) and Na_2SO_4 (50 mg) were added successively and reacted at room temperature for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was directly purified by flash column chromatography on silica gel to give the title products **5**.

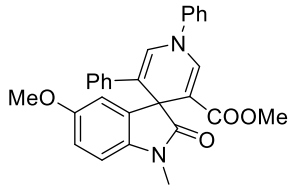


Methyl 1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5a): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5a** as a white solid in 74% yield (31.2 mg), m. p. 184.2-185.8 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.2 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.99 (dt, *J* = 12.6, 7.2 Hz, 3H), 6.72 (d, *J* = 7.2 Hz, 2H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 3.47 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 177.6, 165.3, 142.2, 142.0, 137.5, 135.4, 134.8, 128.8, 128.3, 127.6, 126.6, 126.5, 125.6, 124.6, 123.4, 121.6, 119.21, 119.18, 106.5, 102.6, 52.6, 50.3, 25.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}N_2O_3Na$ 445.1528, found 445.1529.

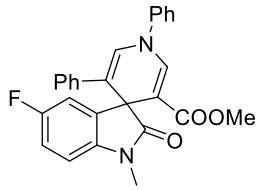


Methyl 1,5-dimethyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5b): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5b** as a white solid in 65% yield (28.5 mg), m. p. 232.3-235.2 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 1.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.16 (s, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.08 – 7.01 (m, 3H), 6.79 (d, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 3.55 (s, 3H), 2.98 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.6, 166.4, 143.3, 140.8, 138.5, 136.6, 135.9, 132.1, 129.8, 129.3, 129.0, 127.6, 127.5, 126.5, 125.6, 125.3,

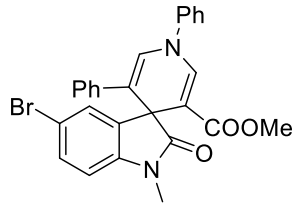
120.4, 120.2, 107.2, 103.7, 53.6, 51.4, 26.3, 21.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1682.



Methyl 5-methoxy-1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5c): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5c** as a white solid in 69% yield (31.3 mg), m. p. 195.5-196.8 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 2H), 6.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.55 (s, 3H), 2.98 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.3, 166.4, 156.2, 143.2, 138.6, 137.2, 136.8, 136.5, 129.8, 129.3, 127.7, 127.6, 126.6, 125.7, 120.3, 120.2, 112.7, 112.0, 107.8, 103.6, 55.8, 54.0, 51.4, 26.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2O_4Na$ 475.1634, found 475.1630.

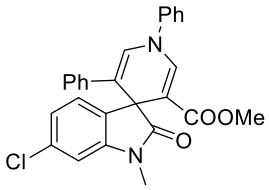


Methyl 5-fluoro-1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5d): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5d** as a white solid in 76% yield (33.5 mg), m. p. 203.4-205.1 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.11 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.91 (td, *J* = 9.0, 2.4 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.53 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.56 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.5, 166.3, 160.4, 158.8, 143.1, 139.1 (d, J_{C-F} = 1.5 Hz), 138.8, 137.3 (d, J_{C-F} = 7.5 Hz), 136.2, 129.9, 129.4, 127.7 (d, J_{C-F} = 3.0 Hz), 126.9, 125.9, 120.3, 119.8, 114.8 (d, J_{C-F} = 22.5 Hz), 112.4 (d, J_{C-F} = 24.0 Hz), 107.9 (d, J_{C-F} = 3.0 Hz), 103.2, 54.1, 51.4, 26.4. ^{19}F NMR (565 MHz, Chloroform-*d*): δ −120.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}FN_2O_3Na$ 463.1434, found 463.1428.

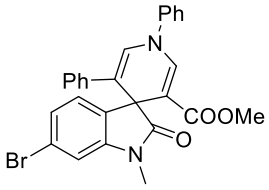


Methyl 5-bromo-1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5e): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5e** as a white solid in 74% yield (36.9 mg), m. p. 211.3-212.6 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H),

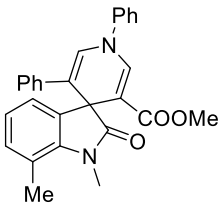
7.37 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.62 (d, *J* = 1.8 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 3.59 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.2, 166.3, 143.1, 142.2, 138.8, 137.8, 136.1, 131.5, 129.9, 129.3, 127.78, 127.76, 127.6, 127.0, 125.9, 120.4, 119.6, 115.2, 109.0, 103.0, 53.8, 51.5, 26.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}BrN_2O_3Na$ 523.0633, found 523.0633.



Methyl 6-chloro-1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5f): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5f** as a white solid in 72% yield (33.0 mg), m. p. 201.7-203.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 1.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.17 – 7.11 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.91 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 2H), 6.50 (d, *J* = 1.8 Hz, 1H), 6.46 (d, *J* = 1.8 Hz, 1H), 3.43 (s, 3H), 2.86 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.7, 166.3, 144.3, 143.1, 138.7, 136.2, 134.3, 134.2, 129.8, 129.3, 127.79, 127.75, 126.9, 125.9, 125.3, 122.5, 120.3, 119.7, 108.3, 103.2, 53.4, 51.4, 26.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}ClN_2O_3Na$ 479.1138, found 479.1137.

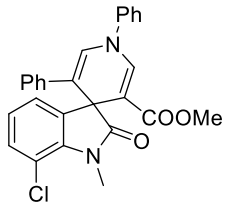


Methyl 6-bromo-1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5g): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5g** as a white solid in 76% yield (38.0 mg), m. p. 189.6-191.3℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 1.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 6.77 (s, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 3.56 (s, 3H), 2.99 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 177.5, 165.3, 143.4, 142.1, 137.7, 135.1, 133.7, 128.8, 128.3, 126.8, 126.7, 125.8, 124.8, 124.6, 124.4, 121.1, 119.3, 118.6, 110.0, 102.1, 52.4, 50.4, 25.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}BrN_2O_3Na$ 523.0633, found 523.0636.

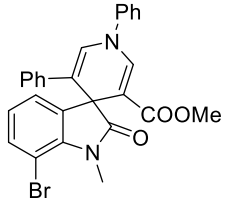


Methyl 1,7-dimethyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5h): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5h** as a white solid in 79% yield (34.5 mg), m. p. 194.7-196.8 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 1.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz,

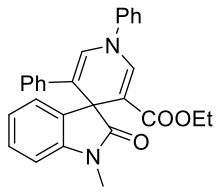
2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 4.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 4.2 Hz, 2H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.56 (d, *J* = 1.8 Hz, 1H), 3.57 (s, 3H), 3.26 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 179.4, 166.4, 143.3, 140.8, 138.4, 136.6, 136.5, 132.3, 129.8, 129.4, 127.57, 127.55, 126.3, 125.6, 122.6, 120.7, 120.2, 119.0, 103.9, 53.1, 51.3, 29.7, 18.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1683.



Methyl 7-chloro-1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5i): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5i** as a white solid in 81% yield (36.9 mg), m. p. 208.6-209.9 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.21 – 7.14 (m, 4H), 7.11 – 7.04 (m, 2H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 2H), 6.50 (d, *J* = 1.8 Hz, 1H), 3.49 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.0, 165.3, 142.1, 138.0, 137.61, 137.59, 135.0, 129.8, 128.8, 128.3, 126.8, 126.7, 125.6, 124.8, 122.3, 122.1, 119.3, 119.0, 114.0, 102.4, 52.6, 50.4, 28.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}ClN_2O_3Na$ 479.1138, found 479.1146.

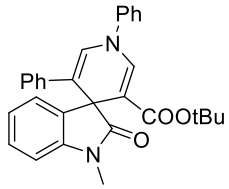


Methyl 7-bromo-1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5j): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5j** as a white solid in 73% yield (36.5 mg), m. p. 208.8-210.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.18 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 2H), 6.50 (d, *J* = 1.2 Hz, 1H), 3.49 (s, 3H), 3.29 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 179.2, 166.3, 143.1, 140.5, 139.0, 138.6, 136.0, 134.1, 129.9, 129.3, 127.9, 127.8, 126.6, 125.9, 123.8, 123.7, 120.3, 120.1, 103.4, 102.1, 53.6, 51.4, 29.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}N_2O_3Na$ 523.0633, found 523.0631.

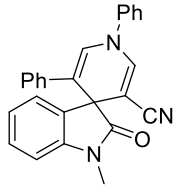


Ethyl 1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5k): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5k** as a white solid in 72% yield (31.6 mg), m. p. 164.9-166.8 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 1.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.23 (q, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.2

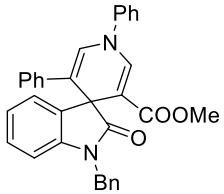
Hz, 1H), 7.10 – 7.02 (m, 3H), 6.79 (d, *J* = 7.8 Hz, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 1.8 Hz, 1H), 4.02 – 3.88 (m, 2H), 2.98 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.7, 166.2, 143.3, 143.1, 138.6, 136.5, 136.1, 129.8, 129.4, 128.5, 127.6, 127.5, 126.6, 125.6, 124.4, 122.7, 120.3, 120.2, 107.4, 103.7, 60.0, 53.7, 26.2, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1688.



Tert-butyl 1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5l): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/5) to give product **5l** as a colorless liquid in 63% yield (29.3 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.8 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.18 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.16 – 7.09 (m, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.68 (d, *J* = 6.6 Hz, 2H), 6.49 – 6.45 (m, 2H), 2.83 (s, 3H), 1.06 (s, 9H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 177.5, 164.9, 142.3, 141.9, 137.5, 135.5, 135.4, 128.7, 128.6, 127.2, 126.39, 126.37, 125.4, 124.3, 123.4, 121.5, 119.4, 118.9, 106.1, 103.6, 79.1, 52.9, 26.8, 24.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{28}N_2O_3Na$ 487.1998, found 487.1989.

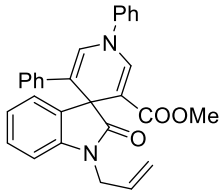


1-methyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carbonitrile (5m): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5m** as a white solid in 58% yield (22.6 mg), m. p. 226.9-227.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (t, *J* = 8.4 Hz, 3H), 7.38 (s, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.80 – 6.76 (m, 2H), 3.15 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 176.5, 142.7, 142.5, 139.5, 136.4, 133.7, 130.0, 129.7, 128.24, 128.16, 127.9, 127.4, 126.4, 125.5, 123.6, 120.4, 117.9, 117.4, 108.5, 85.6, 53.4, 26.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{19}N_3ONa$ 412.1426, found 412.1423.

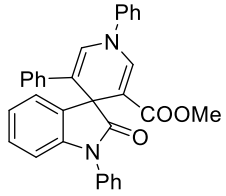


Methyl 1-benzyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5n): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/4) to give product **5n** as a white solid in 73% yield (36.6 mg), m. p. 204.7-206.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 3H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.24 (td, *J* = 7.8, 3.6 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.14 – 7.09 (m, 4H), 7.09 – 7.06 (m, 2H), 6.82 (d, *J* = 7.2 Hz, 2H), 6.70 (d, *J* = 7.2 Hz, 2H), 6.60 (d, *J* = 1.8 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.05 (d, *J* = 16.2 Hz, 1H), 4.48 (d, *J* = 16.8 Hz, 1H),

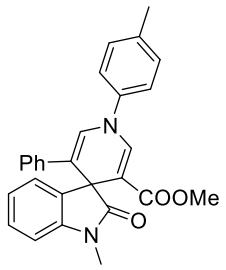
3.54 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.6, 166.5, 143.3, 142.6, 138.6, 136.5, 135.82, 135.78, 130.0, 129.8, 128.6, 128.5, 127.9, 127.7, 127.0, 126.9, 126.8, 125.7, 124.6, 122.7, 120.2, 120.2, 108.8, 103.8, 53.8, 51.3, 44.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{26}N_2O_3Na$ 521.1841, found 521.1833.



Methyl 1-allyl-2-oxo-1',5'-diphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5o): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/5) to give product **5o** as a white solid in 75% yield (33.6 mg), m. p. 121.2-123.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, J = 1.8 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.22 (dt, J = 15.6, 7.8 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 7.07 (dt, J = 15.6, 7.8 Hz, 3H), 6.79 (d, J = 7.8 Hz, 2H), 6.62 (d, J = 7.8 Hz, 1H), 6.57 (d, J = 1.8 Hz, 1H), 5.46 – 5.29 (m, 1H), 4.95 (d, J = 10.2 Hz, 1H), 4.78 (d, J = 17.4 Hz, 1H), 4.36 – 4.29 (m, 1H), 3.99 (dd, J = 16.2, 5.4 Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ178.1, 166.4, 143.3, 142.4, 138.6, 136.4, 135.8, 131.5, 129.9, 129.8, 128.5, 127.7, 127.6, 126.6, 125.7, 124.5, 122.6, 120.3, 120.2, 117.0, 108.6, 103.7, 53.7, 51.3, 42.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{24}N_2O_3Na$ 471.1685, found 471.1683.

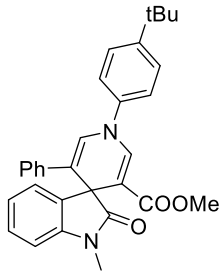


Methyl 2-oxo-1,1',5'-triphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5p): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5p** as a white solid in 74% yield (35.9 mg), m. p. 203.6-204.1 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (d, J = 1.8 Hz, 1H), 7.43 (dq, J = 14.4, 7.8, 7.2 Hz, 5H), 7.32 (dd, J = 13.2, 7.8 Hz, 3H), 7.23 (dt, J = 18.6, 7.2 Hz, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.16 – 7.10 (m, 3H), 7.05 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.8 Hz, 2H), 6.64 (s, 1H), 6.53 (d, J = 7.8 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 177.8, 166.5, 143.3, 143.2, 138.7, 136.4, 135.6, 134.9, 129.9, 129.8, 129.5, 128.6, 127.9, 127.8, 127.7, 126.8, 126.4, 125.7, 124.8, 123.1, 120.4, 120.3, 108.7, 103.8, 53.9, 51.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{24}N_2O_3Na$ 507.1685, found 507.1686.

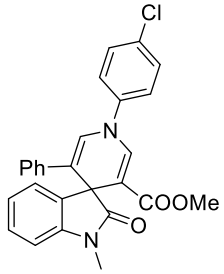


Methyl 1-methyl-2-oxo-5'-phenyl-1'-(p-tolyl)-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5q): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5q** as a white solid in 64% yield (27.9 mg), m. p. 239.5-241.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 6.6 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.2 Hz,

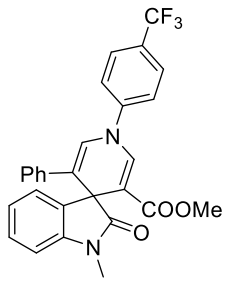
1H), 7.06 (dt, *J* = 15.0, 7.8 Hz, 3H), 6.79 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 1.8 Hz, 1H), 3.54 (s, 3H), 3.01 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.8, 166.5, 143.0, 141.0, 138.8, 136.6, 136.0, 135.6, 130.3, 129.3, 128.6, 127.6, 127.5, 126.9, 124.4, 122.7, 120.3, 120.0, 107.5, 103.1, 53.6, 51.3, 26.3, 20.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1695.



Methyl 1'-(4-(tert-butyl)phenyl)-1-methyl-2-oxo-5'-phenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5r): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5r** as a white solid in 70% yield (33.5 mg), m. p. 203.7-205.3 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 1.8 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.06 (dt, *J* = 13.8, 6.0 Hz, 3H), 6.79 (d, *J* = 6.6 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 1.8 Hz, 1H), 3.54 (s, 3H), 3.01 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.8, 166.4, 148.9, 143.1, 140.8, 138.8, 136.6, 136.0, 129.3, 128.6, 127.6, 127.5, 126.8, 126.6, 124.4, 122.7, 120.01, 119.97, 107.5, 103.2, 53.6, 51.3, 34.5, 31.4, 26.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{30}N_2O_3Na$ 501.2154, found 501.2156.

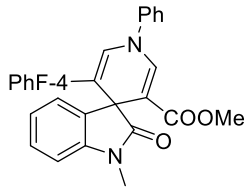


Methyl 1'-(4-chlorophenyl)-1-methyl-2-oxo-5'-phenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5s): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5s** as a white solid in 72% yield (32.8 mg), m. p. 273.8-275.2°C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.10 – 7.02 (m, 3H), 6.78 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 3.54 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.5, 166.2, 143.1, 141.8, 138.1, 136.2, 135.6, 131.1, 129.9, 129.3, 128.7, 127.7, 127.6, 126.2, 124.4, 122.7, 121.4, 120.7, 107.6, 104.2, 53.5, 51.4, 26.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}ClN_2O_3Na$ 479.1138, found 479.1131.

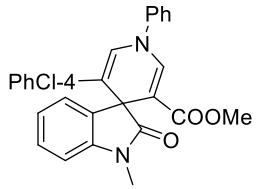


Methyl 1-methyl-2-oxo-5'-phenyl-1'-(4-(trifluoromethyl)phenyl)-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5t): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5t** as a white solid in 76% yield (37.4 mg), m. p. 233.5-234.5 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.2

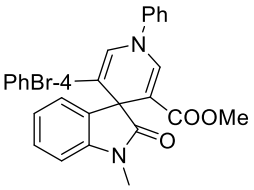
Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.99 (q, *J* = 7.2 Hz, 3H), 6.71 (d, *J* = 6.6 Hz, 2H), 6.57 – 6.54 (m, 2H), 3.48 (s, 3H), 2.92 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.2, 166.0, 145.6, 143.2, 137.4, 136.0, 135.3, 129.3, 128.9, 127.8, 127.7, 127.4, 127.1 (q, J_{C-F} = 4.5 Hz), 125.5, 124.8, 124.3, 123.0, 122.7, 121.4, 119.6, 107.6, 105.3, 53.6, 51.5, 26.3. ^{19}F NMR (565 MHz, Chloroform-*d*): δ −62.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{21}F_3N_2O_3Na$ 513.1402, found 513.1405.



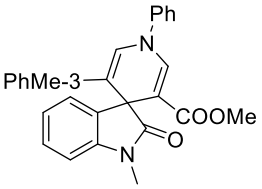
Methyl 5'-(4-fluorophenyl)-1-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5u): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5u** as a white solid in 71% yield (31.0 mg), m. p. 178.1-180.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.23 – 7.13 (m, 4H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.71 – 6.64 (m, 4H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 3.47 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.6, 166.3, 163.1, 161.4, 143.2, 143.0, 138.6, 135.6, 132.4 (d, J_{C-F} = 3.0 Hz), 131.2 (d, J_{C-F} = 7.5 Hz), 129.8, 128.8, 126.8, 125.8, 124.4, 122.8, 120.3, 119.2, 114.6, 114.4, 107.6, 103.6, 53.7, 51.4, 26.3. ^{19}F NMR (565 MHz, Chloroform-*d*): δ −114.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}FN_2O_3Na$ 463.1434, found 463.1430.



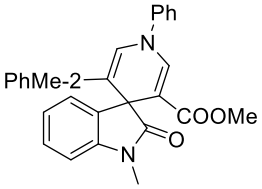
Methyl 5'-(4-chlorophenyl)-1-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5v): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5v** as a white solid in 76% yield (34.8 mg), m. p. 189.4-192.3 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.2 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.14 (m, 4H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 1.2 Hz, 1H), 3.47 (s, 3H), 2.96 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.5, 166.3, 143.2, 143.0, 138.6, 135.6, 135.0, 133.6, 130.7, 129.9, 128.8, 127.9, 127.0, 125.9, 124.4, 122.8, 120.3, 119.0, 107.7, 103.7, 53.5, 51.4, 26.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{21}ClN_2O_3Na$ 479.1138, found 479.1136.



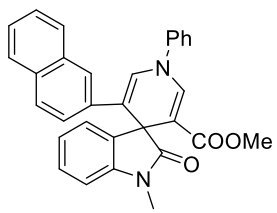
Methyl 3'-(4-bromophenyl)-1-methyl-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyridine]-5'-carboxylate (5w): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5w** as a white solid in 79% yield (39.5 mg), m. p. 208.6-209.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 1.8 Hz, 1H), 7.28 (t, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 3H), 6.42 (d, *J* = 1.8 Hz, 1H), 3.40 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.5, 166.3, 143.1, 143.0, 138.5, 135.6, 135.5, 131.0, 130.8, 129.9, 128.9, 127.0, 125.9, 124.4, 122.8, 121.8, 120.3, 118.9, 107.7, 103.8, 53.4, 51.4, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}BrN_2O_3$ 501.0814, found 501.0811.



Methyl 1-methyl-2-oxo-1'-phenyl-5'-(m-tolyl)-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5x): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5x** as a white solid in 73% yield (32.0 mg), m. p. 144.3-145.2 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.63 (s, 1H), 6.60 (d, *J* = 1.8 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 3.54 (s, 3H), 3.02 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.7, 166.4, 143.3, 143.2, 138.5, 137.2, 136.5, 136.0, 130.0, 129.8, 128.6, 128.3, 127.5, 126.5, 126.1, 125.7, 124.4, 122.7, 120.3, 120.2, 107.4, 103.6, 53.5, 51.3, 26.3, 21.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1680.

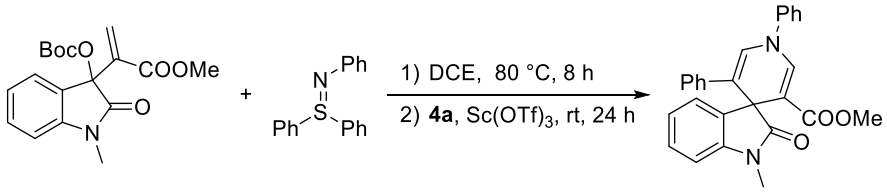


Methyl 1-methyl-2-oxo-1'-phenyl-5'-(o-tolyl)-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5y): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5y** as a white solid in 70% yield (30.7 mg), m. p. 199.4-201.5 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.8 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.15 – 7.02 (m, 5H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 4.8 Hz, 2H), 6.67 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.32 (d, *J* = 1.8 Hz, 1H), 3.40 (s, 3H), 2.80 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.6, 166.4, 143.3, 143.0, 138.8, 137.5, 135.4, 135.0, 130.4, 130.1, 129.8, 128.7, 127.6, 127.2, 125.6, 124.6, 124.4, 122.3, 120.1, 117.5, 107.4, 103.7, 54.1, 51.3, 26.2, 20.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2O_3Na$ 459.1685, found 459.1687.



Methyl 1-methyl-5'-(naphthalen-2-yl)-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxylate (5z): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give product **5z** as a white solid in 68% yield (32.0 mg), m. p. 203.1-205.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 9.6 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.41 – 7.35 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 3H), 7.26 – 7.21 (m, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.89 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 3.56 (s, 3H), 2.97 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.7, 166.4, 143.3, 143.2, 138.6, 136.0, 134.2, 132.8, 132.6, 129.8, 128.7, 128.3, 128.0, 127.4, 127.2, 127.11, 127.07, 125.90, 125.88, 125.7, 124.5, 122.8, 120.3, 120.1, 107.6, 103.8, 53.6, 51.4, 26.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{24}N_2O_3Na$ 495.1685, found 495.1691.

8. Scale-up synthesis of product 5a

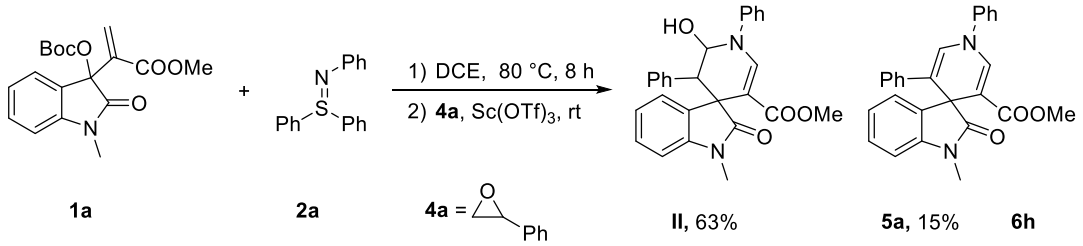


1a **2a** **5a,** 72%

Isatin-derived Morita–Baylis–Hillman carbonate **1a** (2.0 mmol, 1.0 equiv) and S,S-diphenyl-N-arylsulfilimine **2a** (2.4 mmol, 1.2 equiv) were dissolved in 10.0 mL of DCE, and the mixture was stirred at 80 °C for 8 h. Then, 2-phenyloxirane **4a** (2.4 mmol, 1.2 equiv), $Sc(OTf)_3$ (20 mol%) and Na_2SO_4 (1.0 g) were added successively and reacted at room temperature for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated and the residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1/3) to give the title product **5a** in 72% yield (609 mg).

9. Mechanistic studies

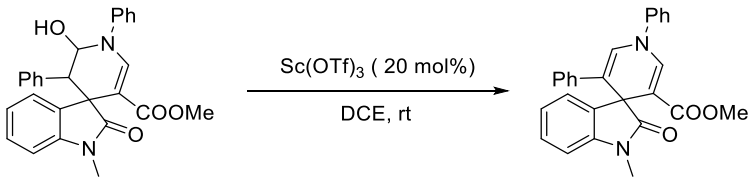
Intermediate compound II conversion experiment



1a **2a** **4a** = **II,** 63% **5a,** 15% **6h**

II, 0% **5a,** 71% **24h**

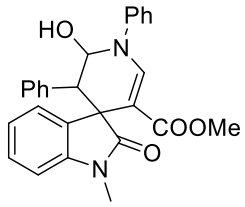
In order to explore the reaction mechanism, we monitored the model reaction. The formation of intermediate **II** and product **5a** was observed after the second-step reaction proceeding 6 h. The intermediate **II** and product **5a** could be isolated in 63% and 15% yields, respectively. After another 18 h, the intermediate disappeared and was completely transformed into desired product in 71% yield. NMR and HR-MS roughly confirmed the chemical structure of intermediate **II**.



II **5a,** 88%

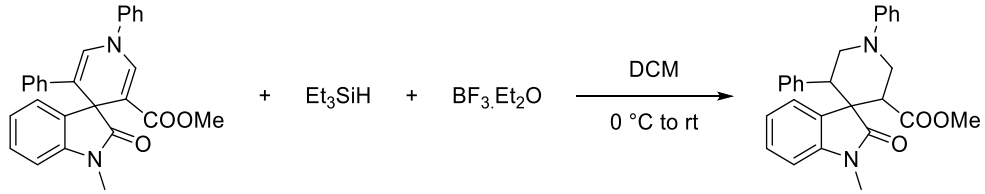
In addition, we also isolated pure intermediate **II** and found that it could be further converted into product **5a** in 88% yield. A solution of **II** (0.1 mmol), $Sc(OTf)_3$ (20 mol %) and

Na_2SO_4 (50 mg) in DCE (1.0 mL) was stirred at room temperature. After 12 h, the reaction mixture was concentrated and directly purified by flash column chromatography on silica gel to give the title product **5a** in 88% yield.



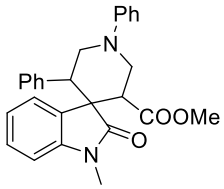
Methyl 2'-hydroxy-1-methyl-2-oxo-1',3'-diphenyl-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyridine]-5'-carboxylate (II): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/3) to give intermediate **II** as a white solid in 88% yield (37.3 mg), m. p. 135.8-139.4 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.67 (d, *J* = 12.0 Hz, 1H), 7.40 (d, *J* = 4.2 Hz, 4H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.19 – 7.08 (m, 5H), 7.06 (q, *J* = 8.4 Hz, 3H), 6.52 (d, *J* = 7.8 Hz, 1H), 5.43 (d, *J* = 12.0 Hz, 1H), 3.62 (s, 1H), 3.49 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 179.1, 166.2, 144.6, 143.9, 142.4, 134.6, 133.3, 129.62, 129.57, 128.2, 127.7, 127.6, 124.3, 123.1, 121.7, 118.8, 108.1, 102.2, 82.7, 53.6, 52.6, 51.1, 26.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{24}N_2O_4Na$ 463.1634, found 463.1634.

10. Synthetic transformation of product 5a

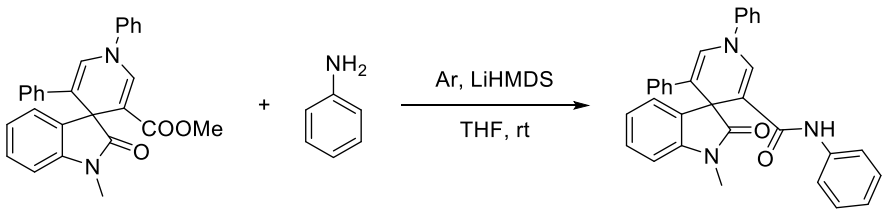


5a **6,** 55%

Product **5a** (42.2 mg, 0.1 mmol) was dissolved in DCM (1 mL) at 0 °C, Et_3SiH (23.2 mg, 32.0 μL, 0.2 mmol) and $BF_3 \cdot Et_2O$ (28.4 mg, 54.0 μL, 0.2 mmol) was added. Then, the reaction was stirred at room temperature for 6 h. Then the mixture was quenched by saturated $NaHCO_3$ solution (1.0 mL) and extracted with DCM (2 × 10 mL). The organic phase was dried and concentrated. Then the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/3) to give product **6** in 97% total yield with 4:2:1 dr. The major isomer of product **6** could be isolated as a pure compound in 55% yield.



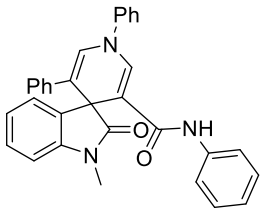
Methyl 1-methyl-2-oxo-1',5'-diphenylspiro[indoline-3,4'-piperidine]-3'-carboxylate (major isomer of 6): white solid, 55% yield (23.4 mg), m. p. 198.4-200.3 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.04 (dt, *J* = 12.6, 7.2 Hz, 2H), 6.97 (t, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 7.2 Hz, 2H), 6.51 (d, *J* = 7.8 Hz, 1H), 4.25 – 4.19 (m, 1H), 3.77 – 3.74 (m, 1H), 3.73 – 3.70 (m, 1H), 3.70 – 3.65 (m, 1H), 3.62 (t, *J* = 12.6 Hz, 1H), 3.57 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.36 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 177.8, 170.7, 150.5, 144.5, 136.7, 129.4, 128.6, 128.3, 127.7, 127.4, 127.2, 125.0, 121.7, 120.2, 116.7, 107.9, 54.2, 51.8, 50.0, 48.9, 47.0, 46.2, 25.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}N_2O_3$ 427.2022, found 427.2013.



5a **7,** 89%

An oven-dried vial equipped with a stir bar was charged with **5a** (0.1 mmol), aniline (1.2 equiv) placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles. THF (0.25 M) and LiHMDS (2.0 M in THF, 2.2 equiv) were added with vigorous stirring

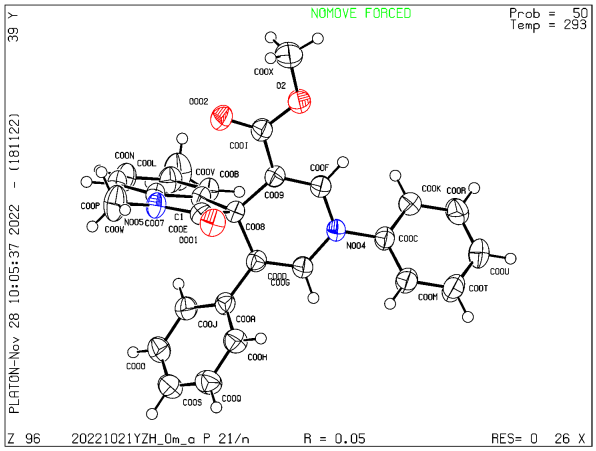
at room temperature, and the reaction mixture was stirred for 15 h at room temperature. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 5 mL), extracted with ethyl acetate (3 × 10 mL), the organic layers were combined, washed with water (1 × 5 mL), brine (1 × 5 mL), dried over Na_2SO_4 and concentrated. Purification by chromatography on silica gel (EtOAc/petroleum ether = 1/2) to give compound **7**.



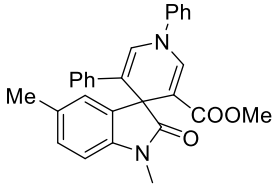
1-methyl-2-oxo-N,1',5'-triphenyl-1'H-spiro[indoline-3,4'-pyridine]-3'-carboxamide (7): The residue was purified by a silica gel flash chromatography (EtOAc/petroleum ether = 1/2) to give product **7** as a white solid in 89% yield (43.0 mg), m. p. 269.9-271.3 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.77 (s, 1H), 8.02 (d, J = 1.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.24 – 7.16 (m, 3H), 7.13 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.2 Hz, 2H), 7.00 (t, J = 7.2 Hz, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.84 (s, 1H), 6.79 (d, J = 7.2 Hz, 3H). 2.92 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 178.6, 165.0, 143.6, 143.3, 139.9, 137.5, 136.5, 134.4, 130.2, 129.1, 128.9, 128.6, 128.0, 127.7, 126.8, 125.4, 124.1, 123.2, 122.6, 120.2, 120.1, 119.0, 109.5, 108.1, 53.3, 26.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{25}N_3O_2Na$ 506.1844, found 506.1844.

11. X-ray crystal structure of product 5b

To a 10 mL tube containing **5b** (30.0 mg) was added a mixture of solvent (n-hexane/ethyl acetate = 1:1, v/v) (6.0 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by X-ray single crystal diffraction. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre.



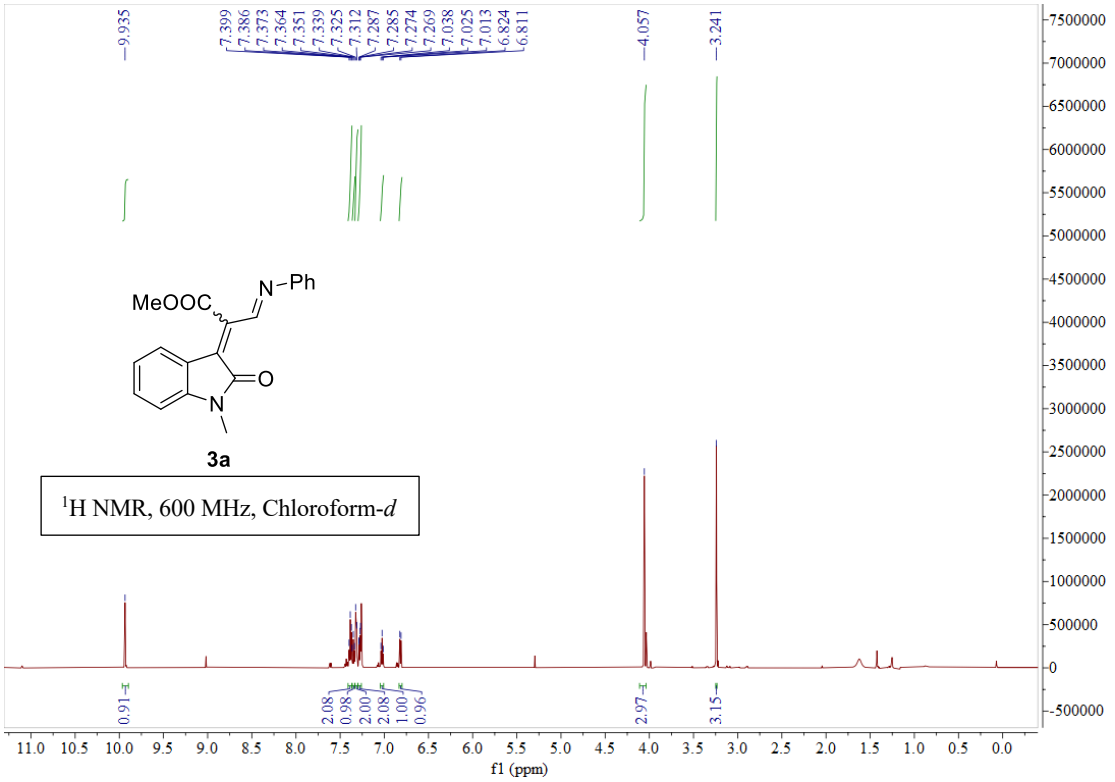
(ellipsoid contour probability 50%)

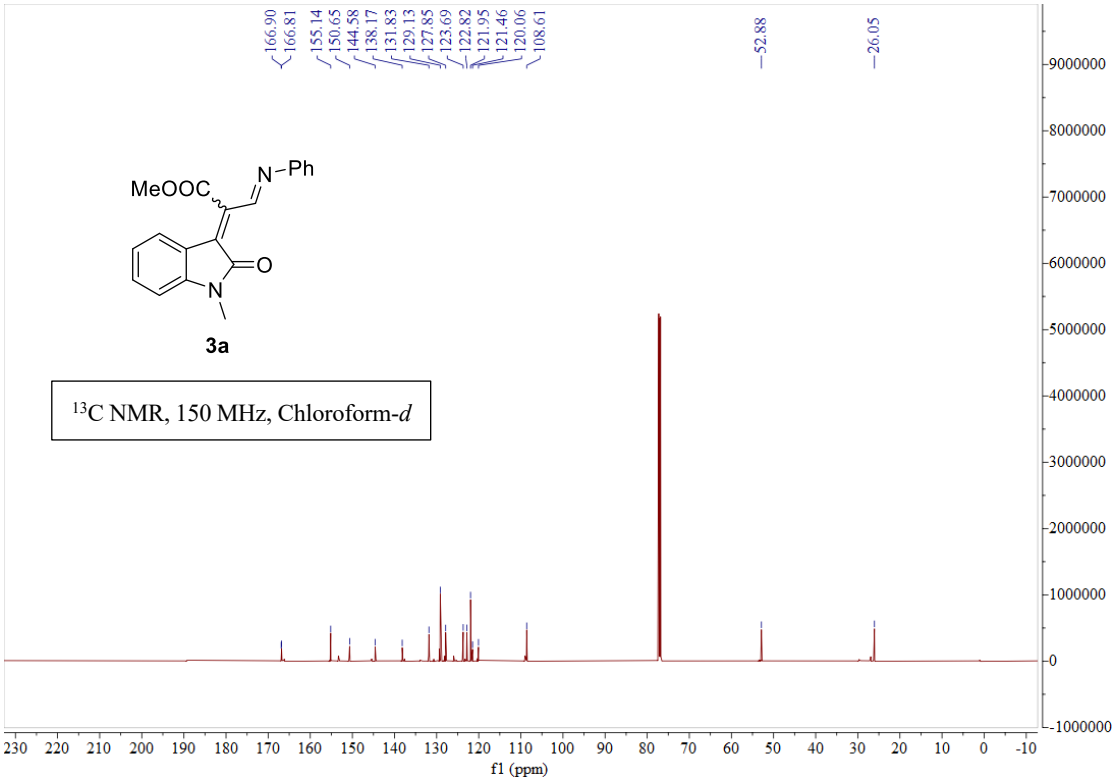


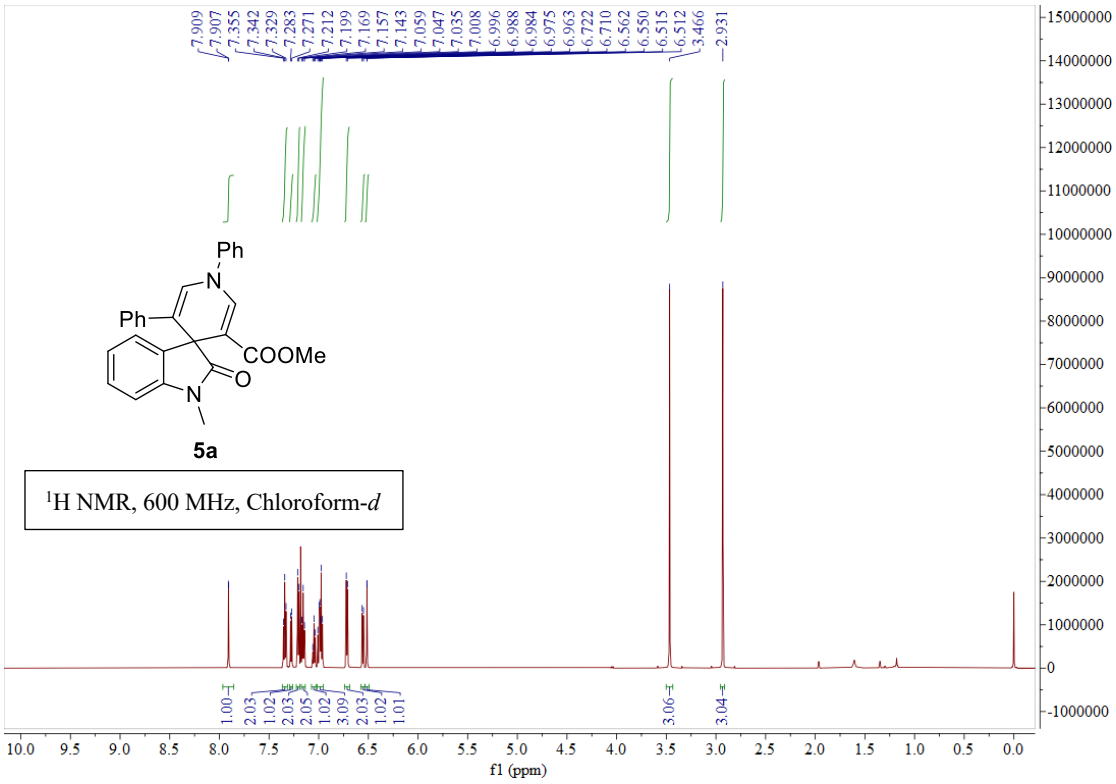
5b

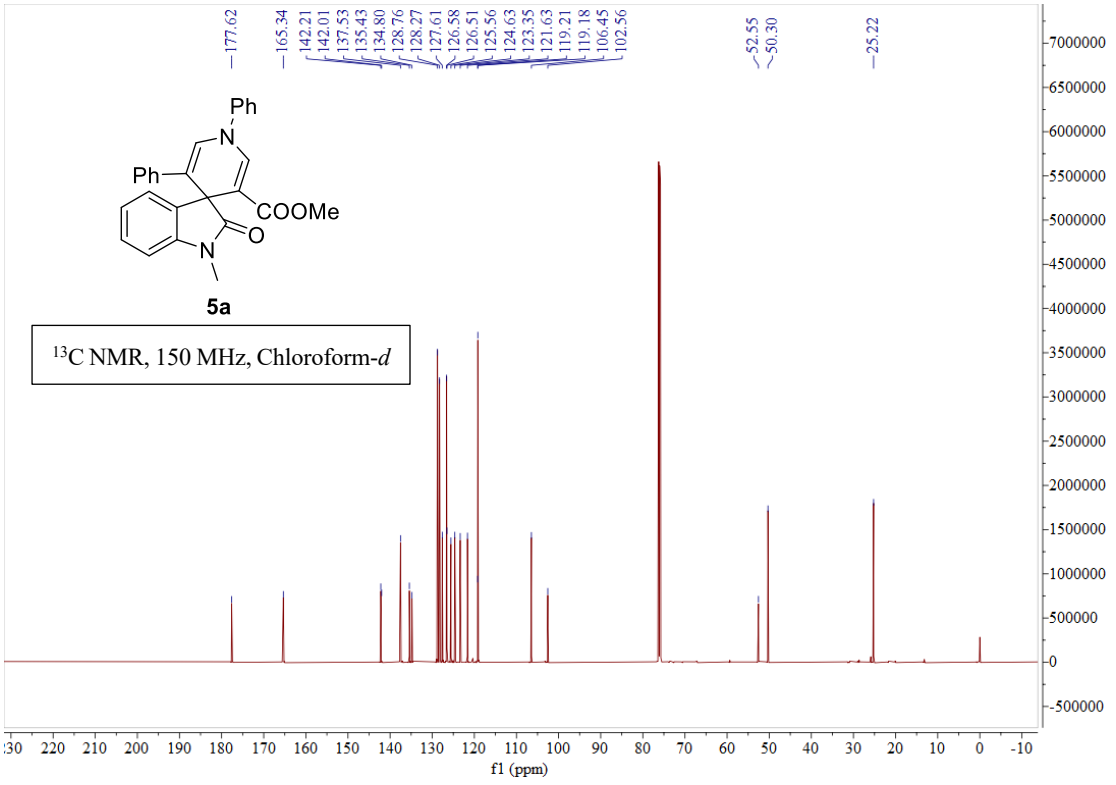
Identification code	20221021YZH
Chemical formula	$C_{28}H_{24}N_2O_3$
Formula weight	436.49 g/mol
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 11.7238(3) Å α = 90° b = 13.4171(3) Å β = 99.1520(10)° c = 15.0267(4) Å γ = 90°
Volume	2333.60(10) $Å^3$
Z	4
Density (calculated)	1.242 g/cm^3
Absorption coefficient	0.650 mm^{-1}
F(000)	920
Theta range for data collection	4.44 to 68.16°
Index ranges	-14<=h<=13, -16<=k<=15, -17<=l<=18
Reflections collected	32293
Independent reflections	4257 [R(int) = 0.0676]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4257 / 0 / 301
Goodness-of-fit on F^2	1.042
Δ/σmax	0.048
Final R indices	3288 data; I>2σ(I) R1 = 0.0534, wR2 = 0.1332 all data R1 = 0.0697, wR2 = 0.1502
Weighting scheme	$w=1/[\sigma^2(Fo^2)+(0.0805P)^2+0.6854P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.243 and -0.258 $eÅ^{-3}$
R.M.S. deviation from mean	0.052 $eÅ^{-3}$

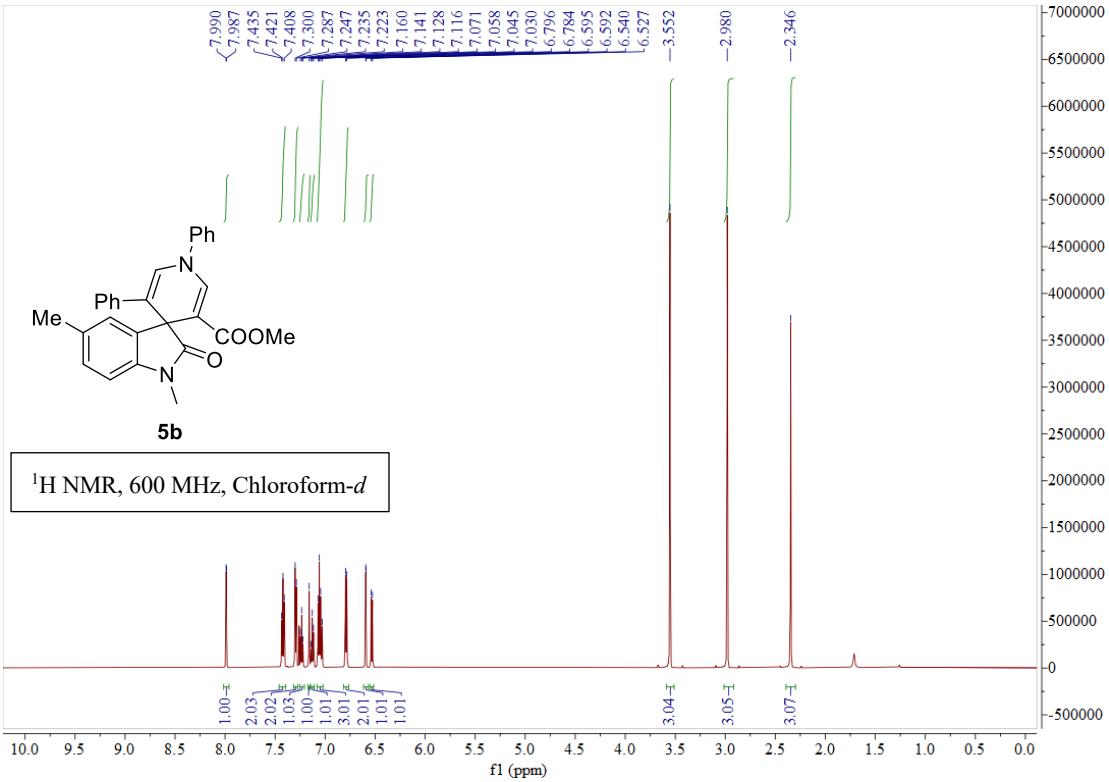
12. ^{1}H NMR and ^{13}C NMR spectra





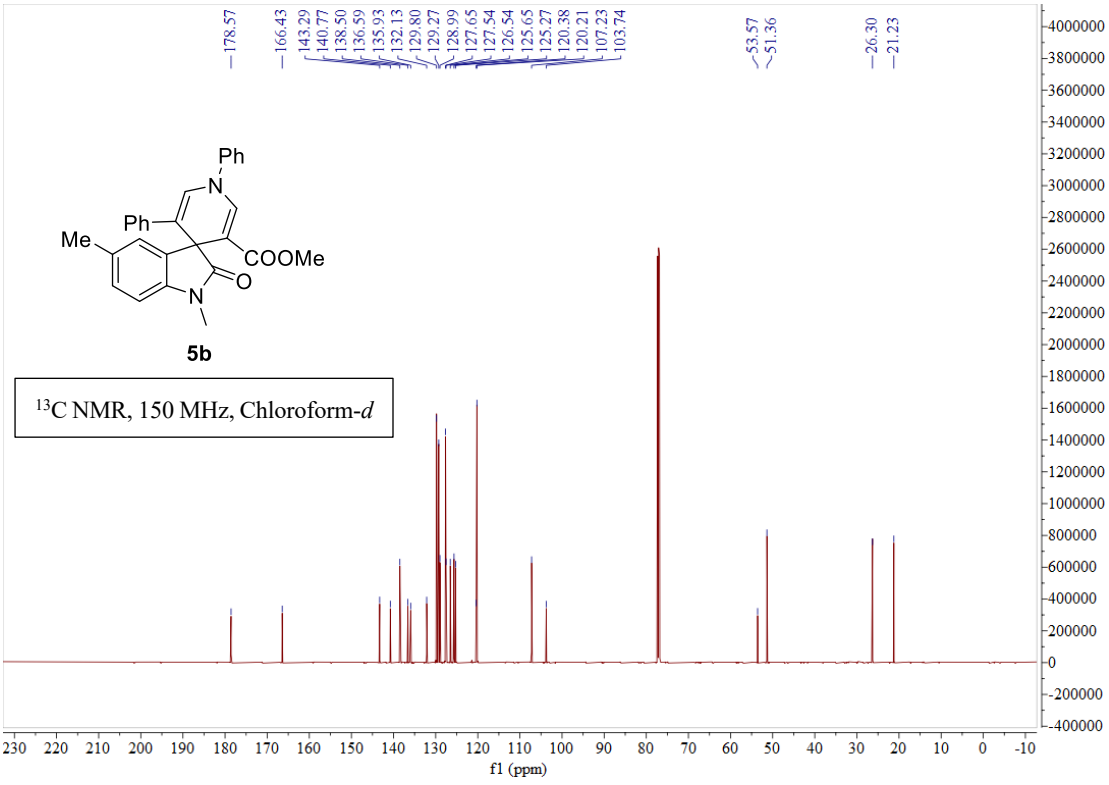

7.909
7.907
7.355
7.342
7.329
7.283
7.271
7.212
7.199
7.169
7.157
7.143
7.059
7.047
7.035
7.008
6.996
6.988
6.984
6.975
6.963
6.722
6.710
6.562
6.550
6.515
6.512
3.466
2.931
Ph
N
Ph
COOMe
O
N
5a
1H NMR, 600 MHz, Chloroform-d
1.00
2.03
1.02
2.03
2.05
1.02
3.09
2.03
1.02
1.01
3.06
3.04
f1 (ppm)


177.62
165.34
142.21
142.01
137.53
135.43
134.80
128.76
128.27
127.61
126.58
126.51
125.56
124.63
123.35
121.63
119.21
119.18
106.45
102.56
52.55
50.30
25.22
Ph
N
Ph
COOMe
O
N
5a
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



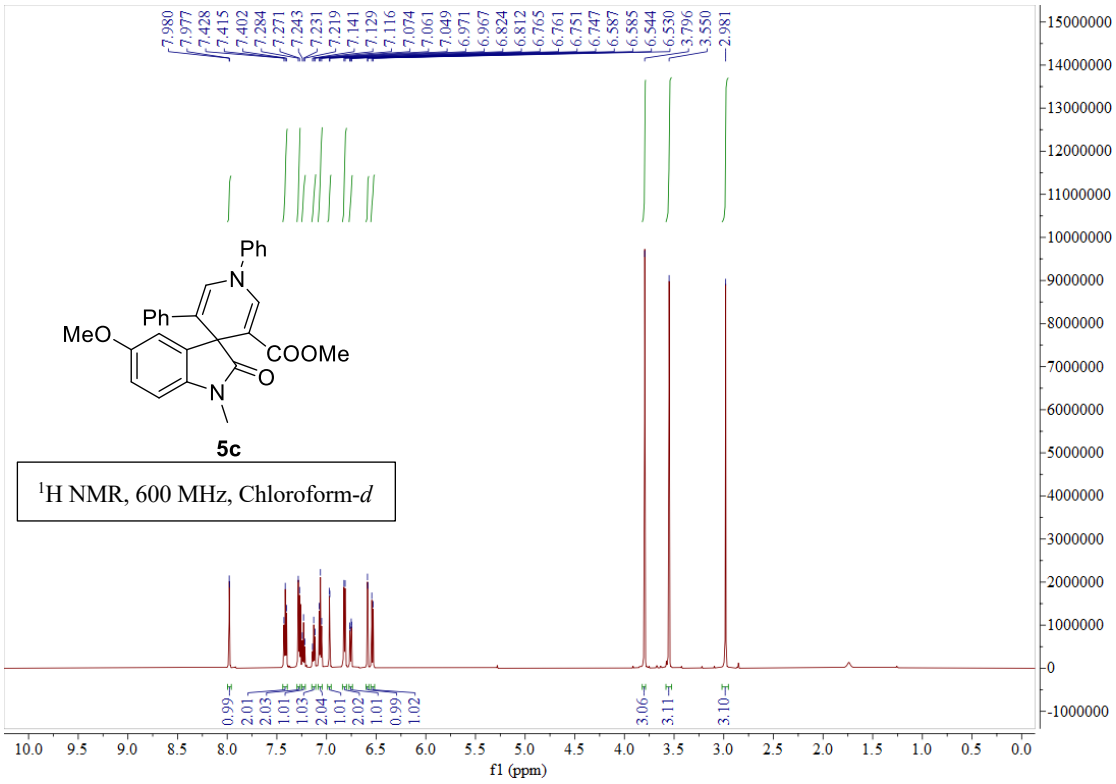
5b

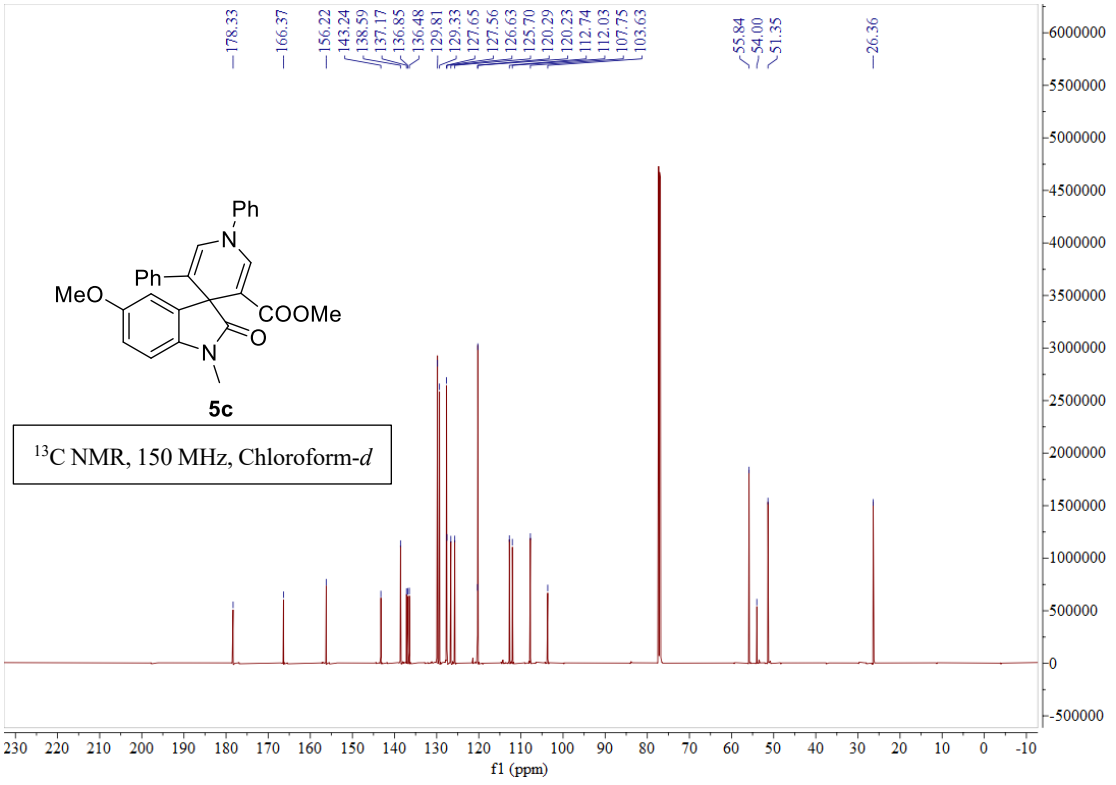
^{1}H NMR, 600 MHz, Chloroform-*d*

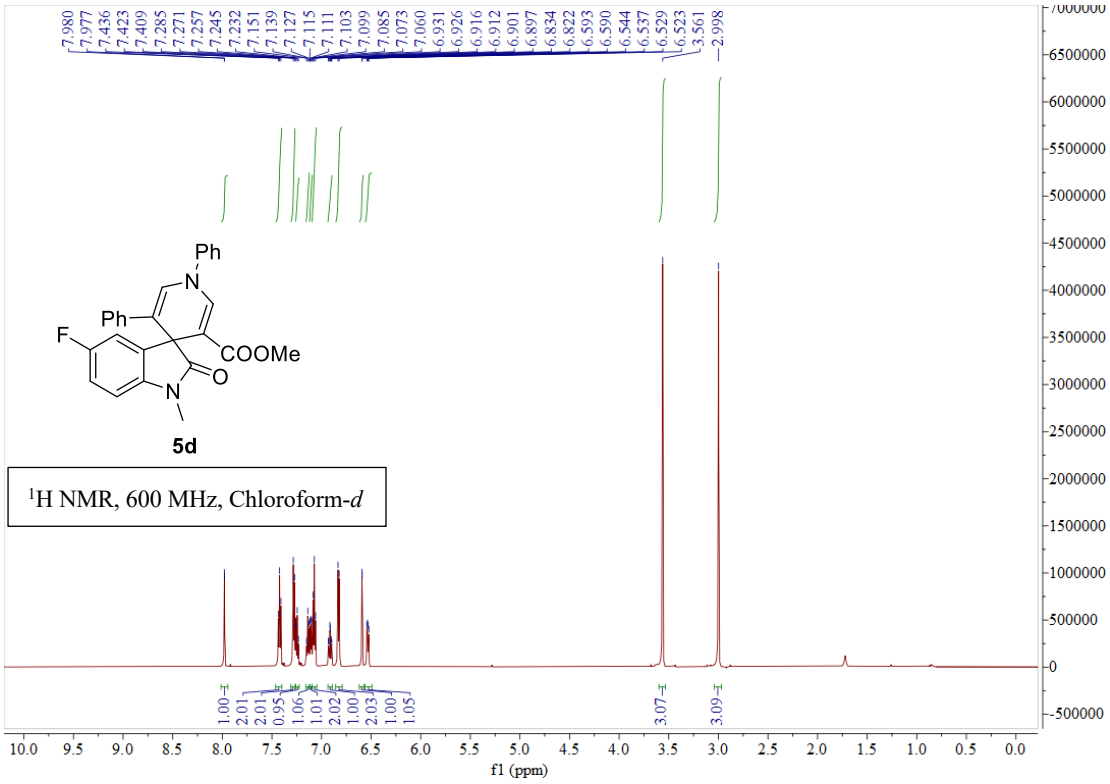


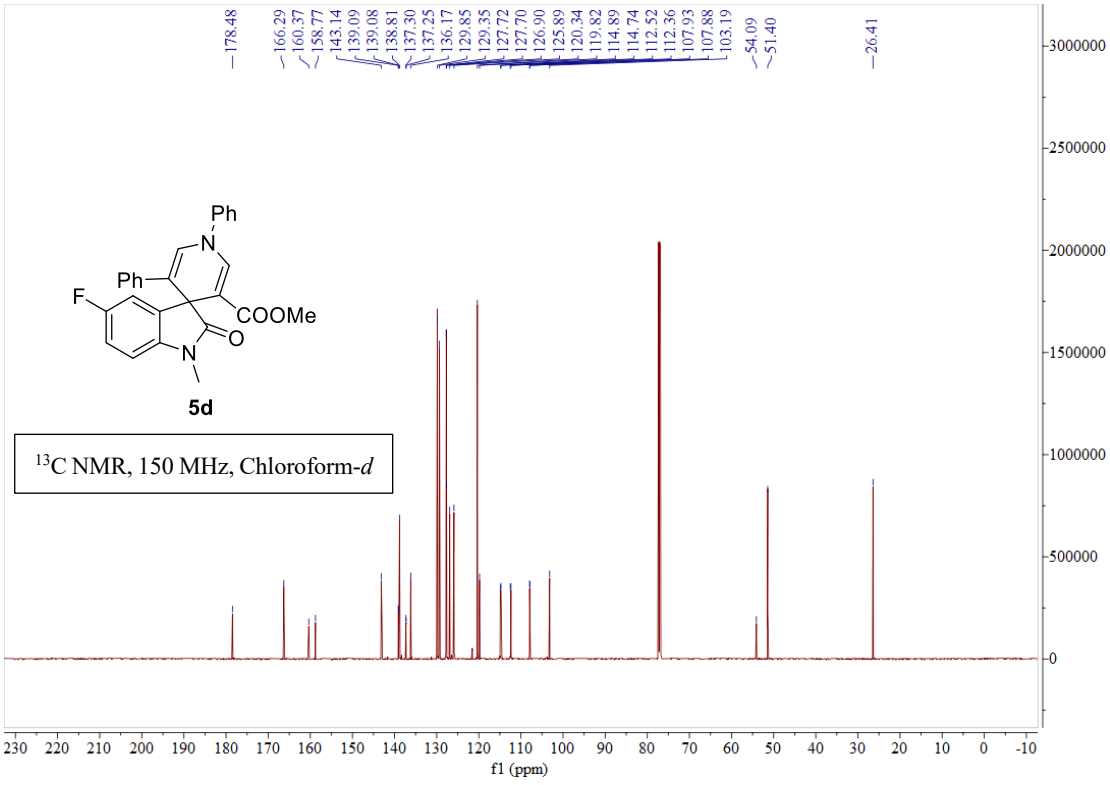
5b

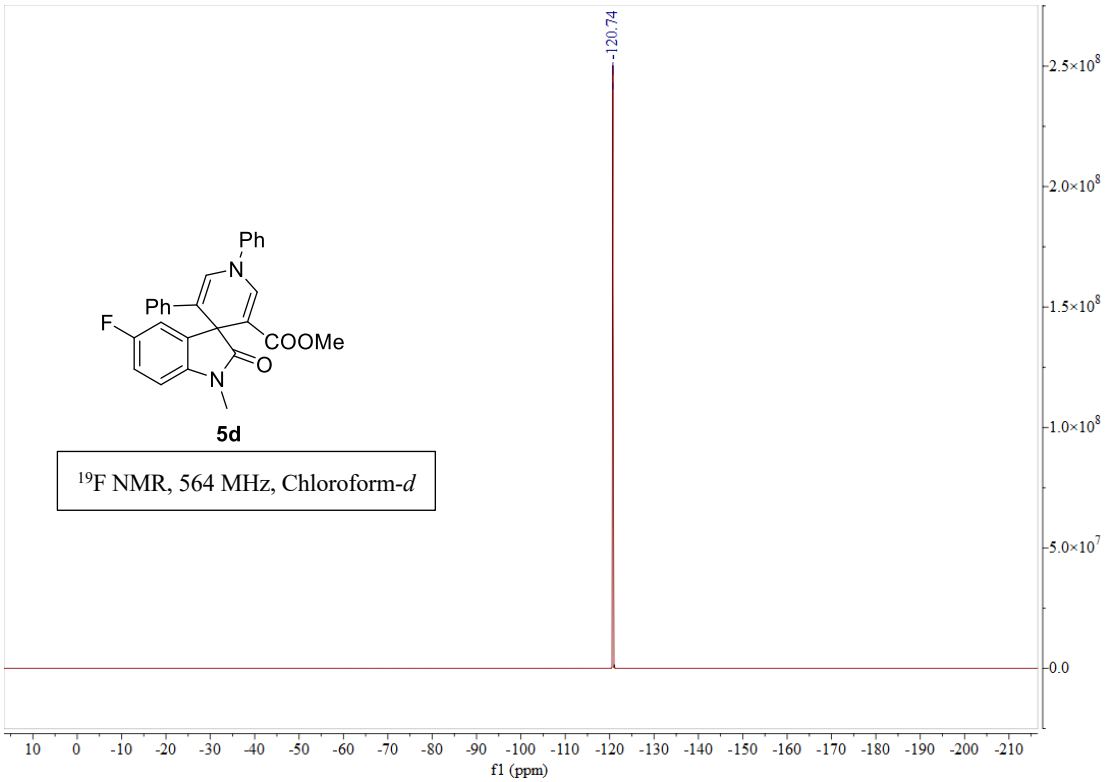
^{13}C NMR, 150 MHz, Chloroform-*d*


7.980
7.977
7.428
7.415
7.402
7.284
7.271
7.243
7.231
7.219
7.141
7.129
7.116
7.074
7.061
7.049
6.971
6.967
6.824
6.812
6.765
6.761
6.751
6.747
6.587
6.585
6.544
6.530
3.796
3.550
2.981
Ph
N
Ph
MeO
COOMe
O
N
5c
[1]H NMR, 600 MHz, Chloroform-d
0.99
2.01
2.03
1.01
1.03
2.04
1.01
2.02
1.01
0.99
1.02
3.06
3.11
3.10
f1 (ppm)


178.33
166.37
156.22
143.24
138.59
137.17
136.85
136.48
129.81
129.33
127.65
127.56
126.63
125.70
120.29
120.23
112.74
112.03
107.75
103.63
55.84
54.00
51.35
26.36
Ph
N
Ph
MeO
COOMe
O
N
5c
[13]C NMR, 150 MHz, Chloroform-d
f1 (ppm)

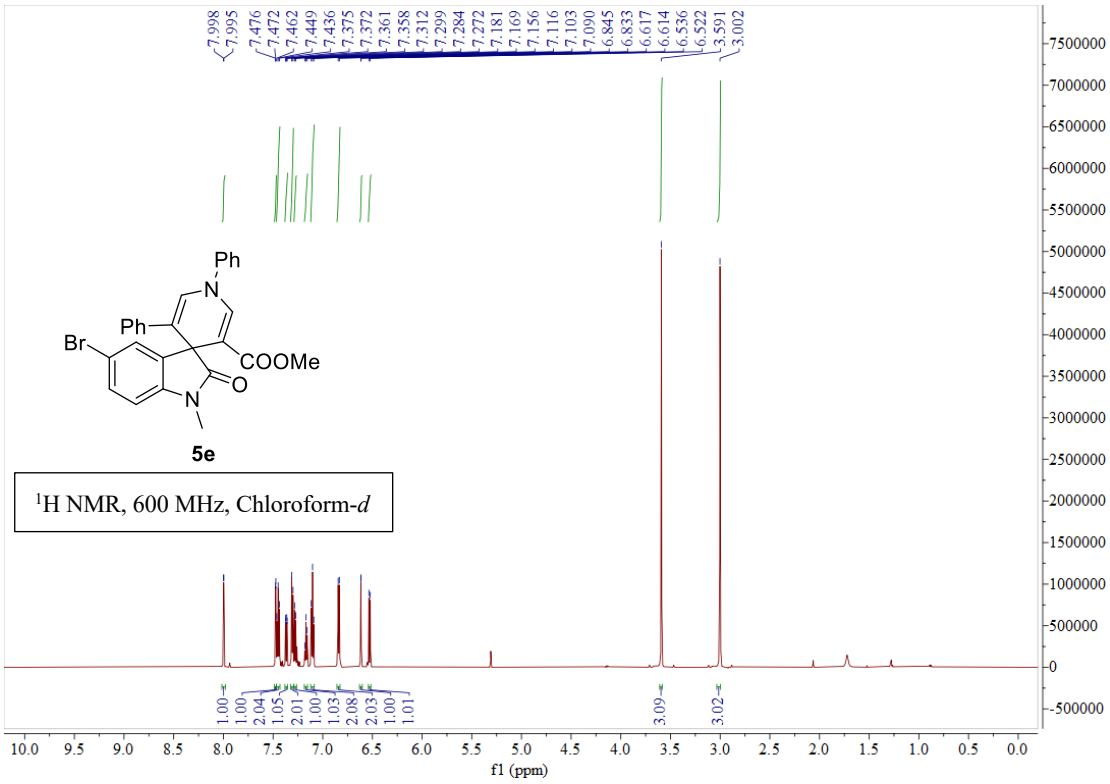

Ph
N
Ph
F
COOMe
O
N
5d
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)


Ph
N
Ph
F
COOMe
O
N
5d
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



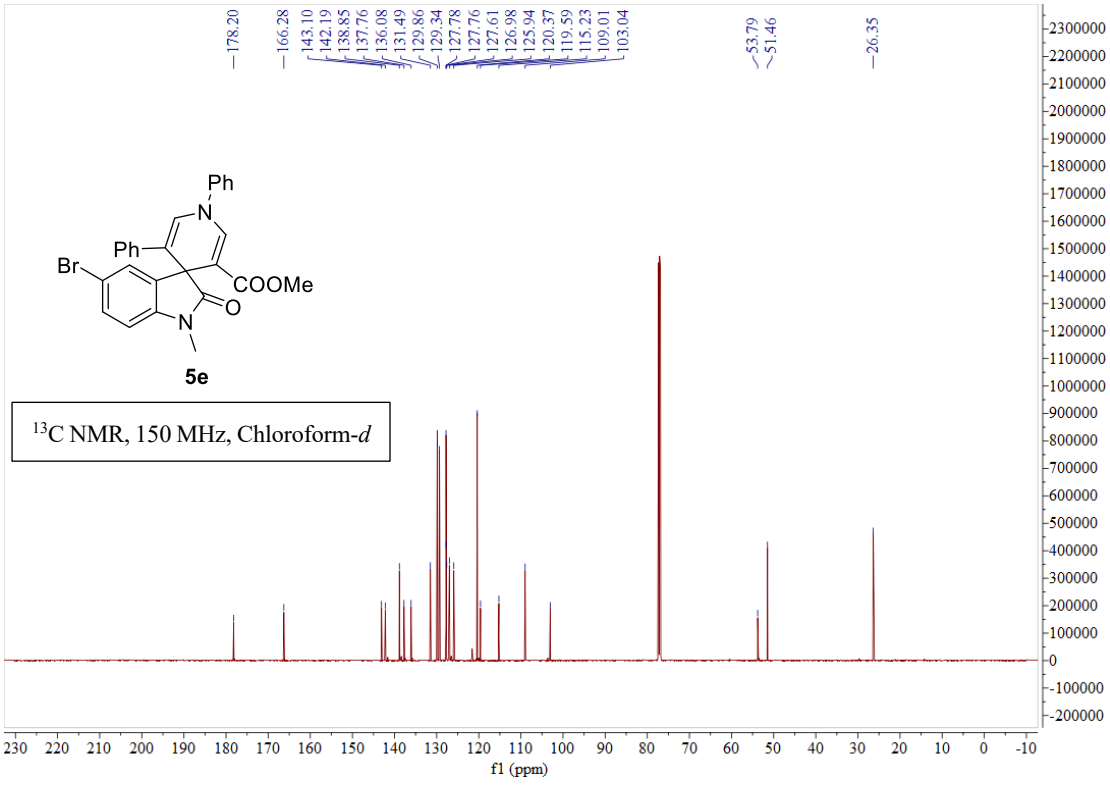
5d

^{19}F NMR, 564 MHz, Chloroform-*d*



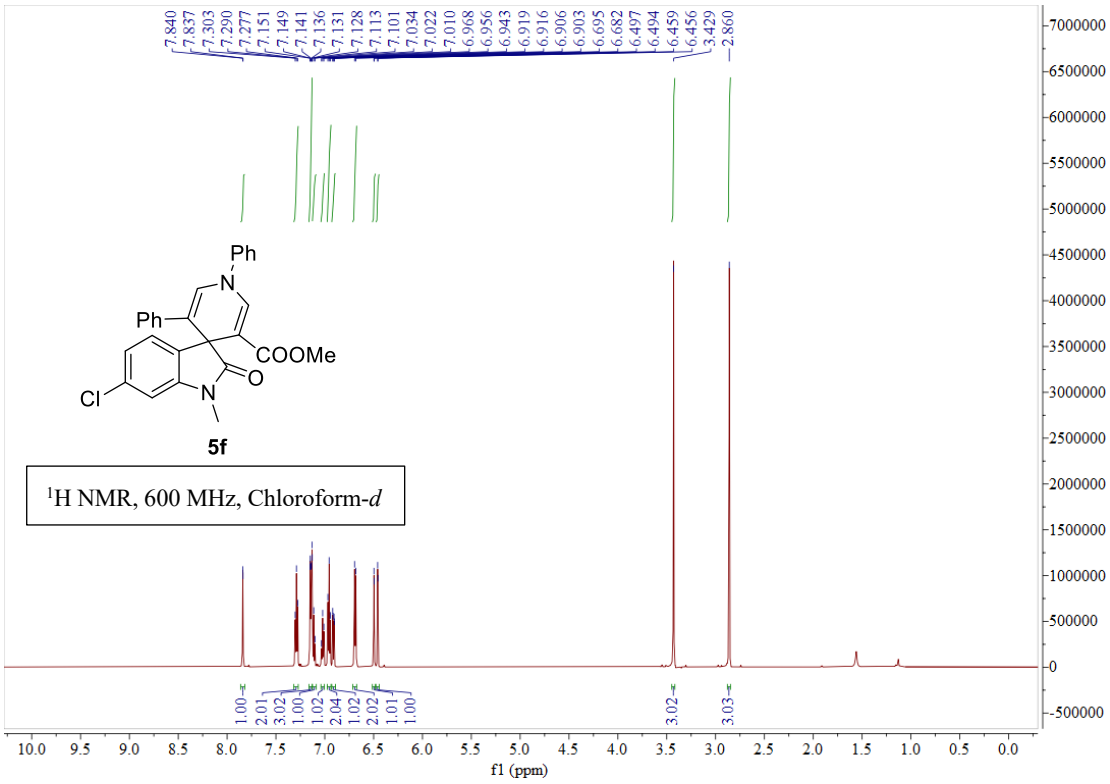
5e

^{1}H NMR, 600 MHz, Chloroform-*d*



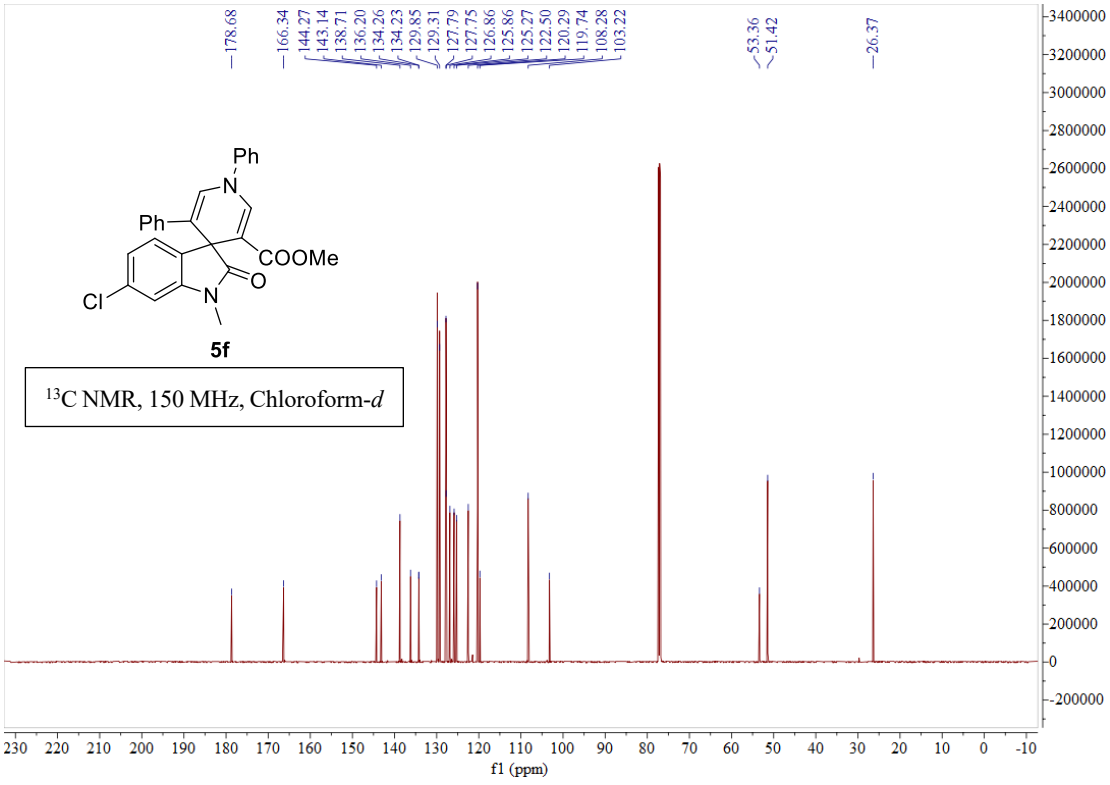
5e

^{13}C NMR, 150 MHz, Chloroform-*d*



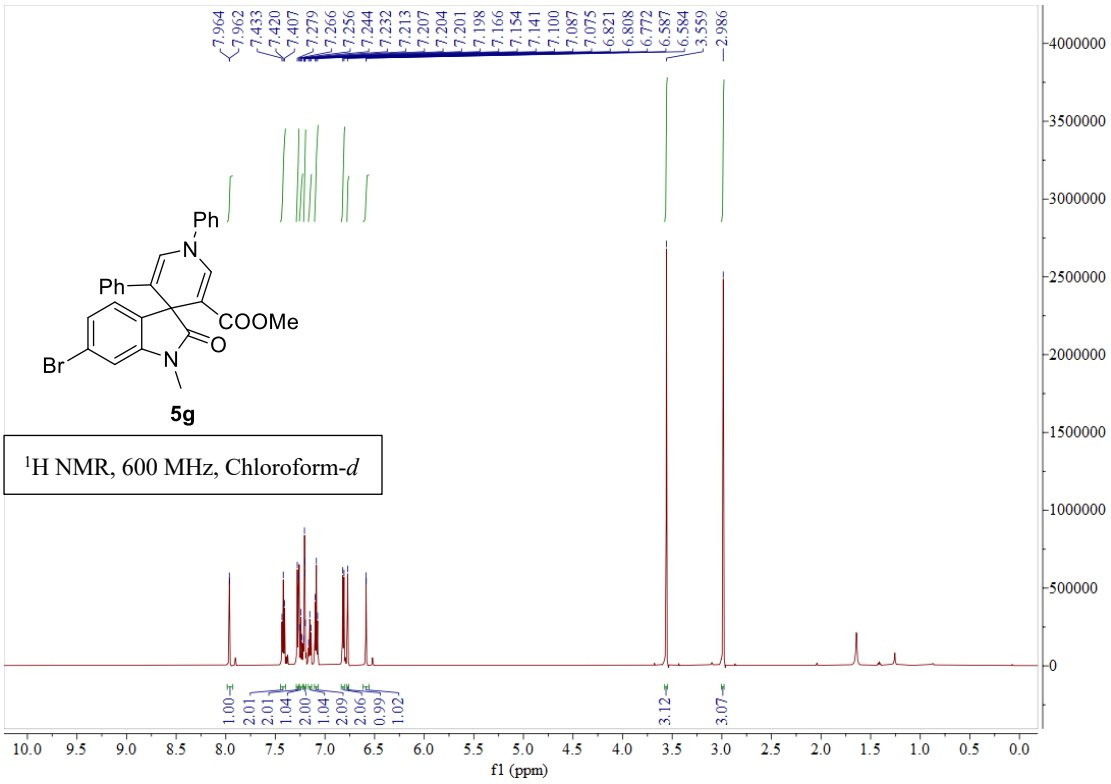
5f

^{1}H NMR, 600 MHz, Chloroform-*d*



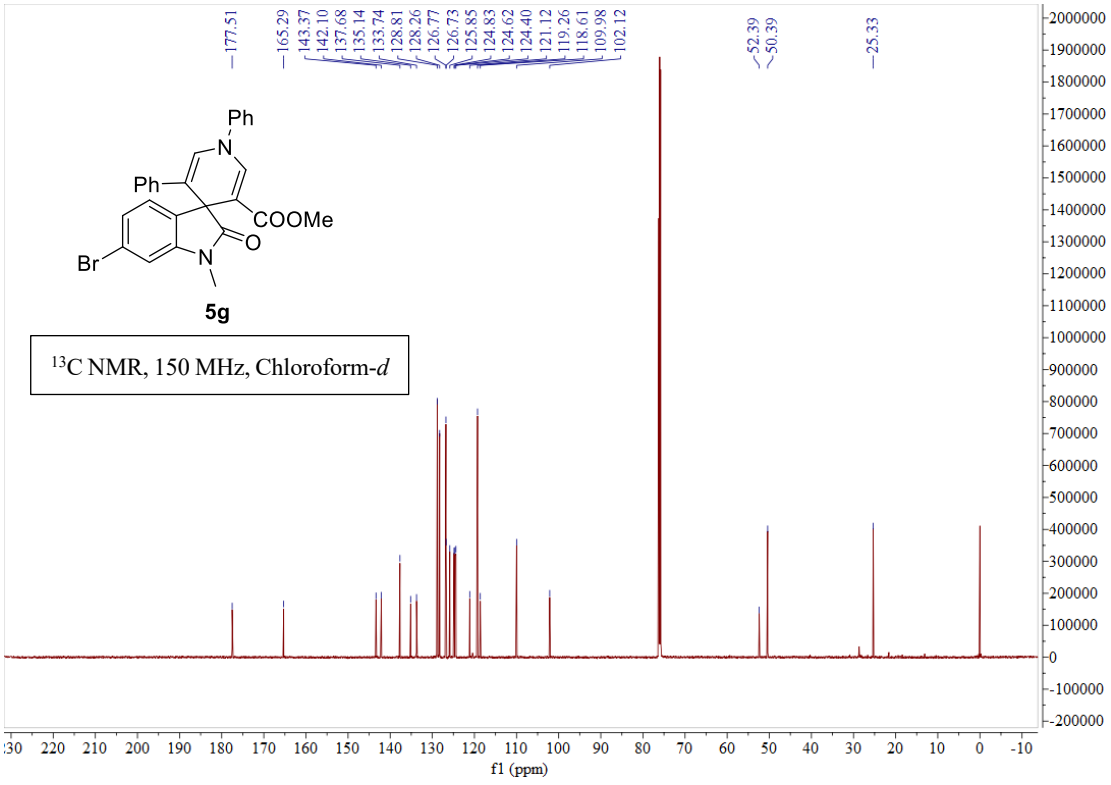
5f

^{13}C NMR, 150 MHz, Chloroform-*d*



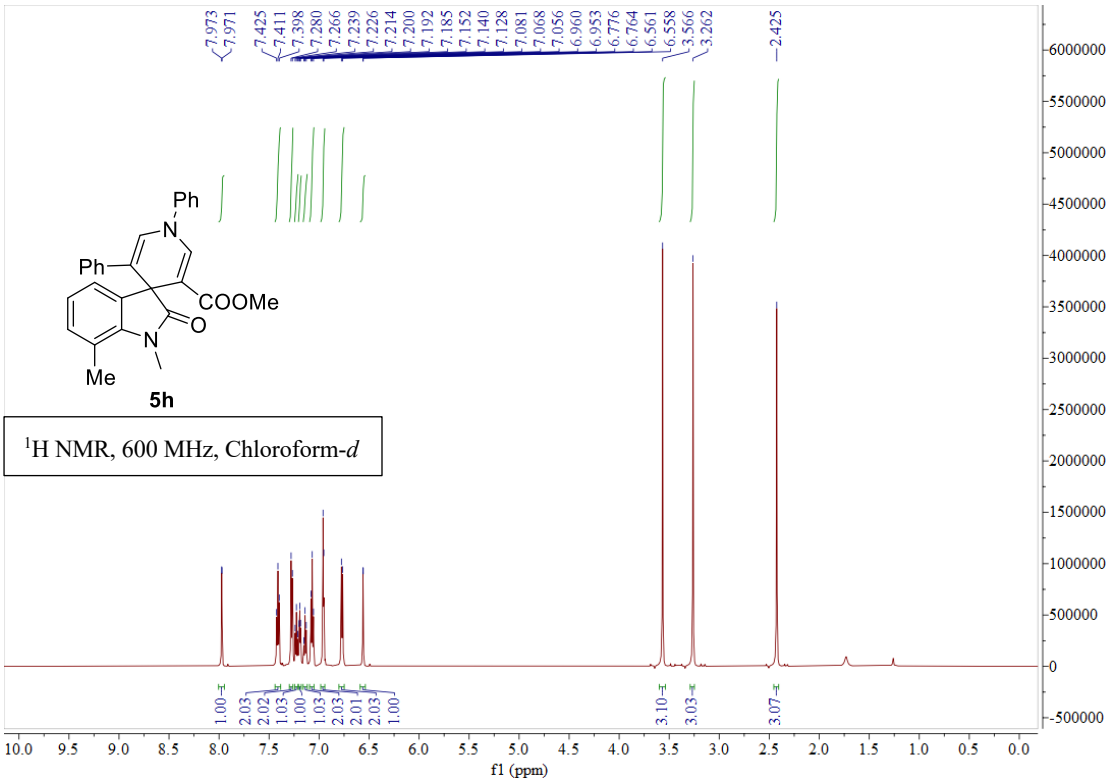
5g

^{1}H NMR, 600 MHz, Chloroform-*d*

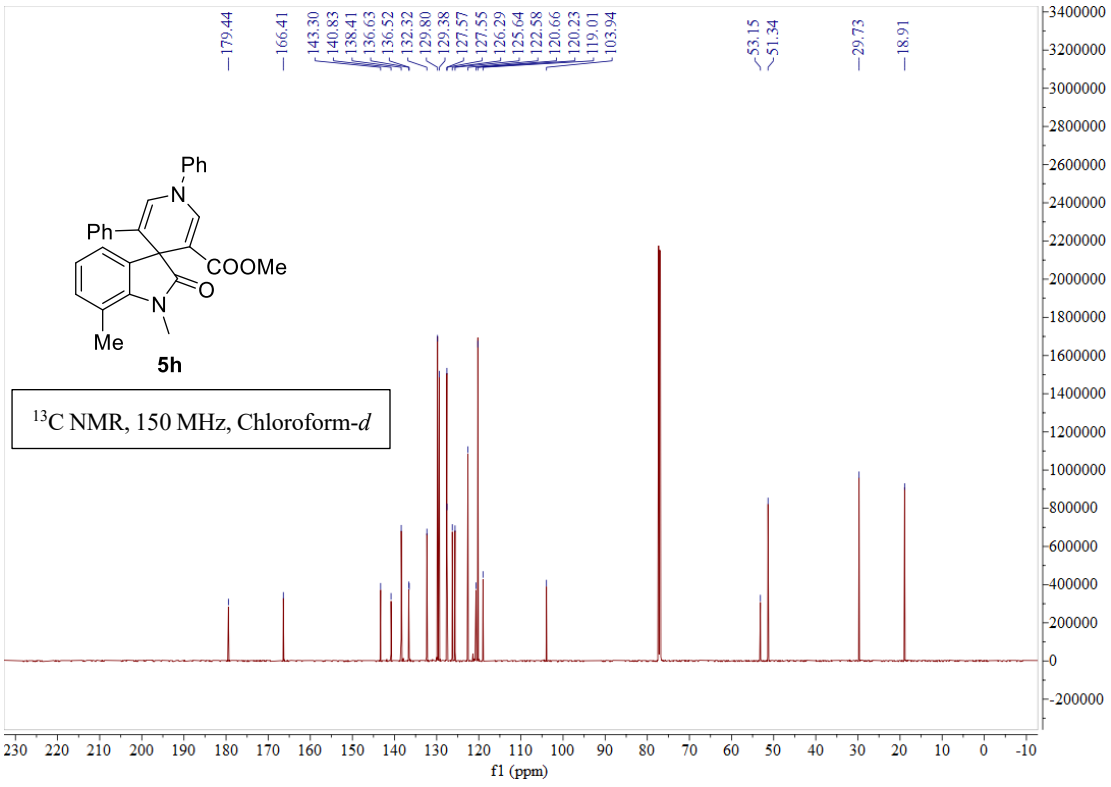


5g

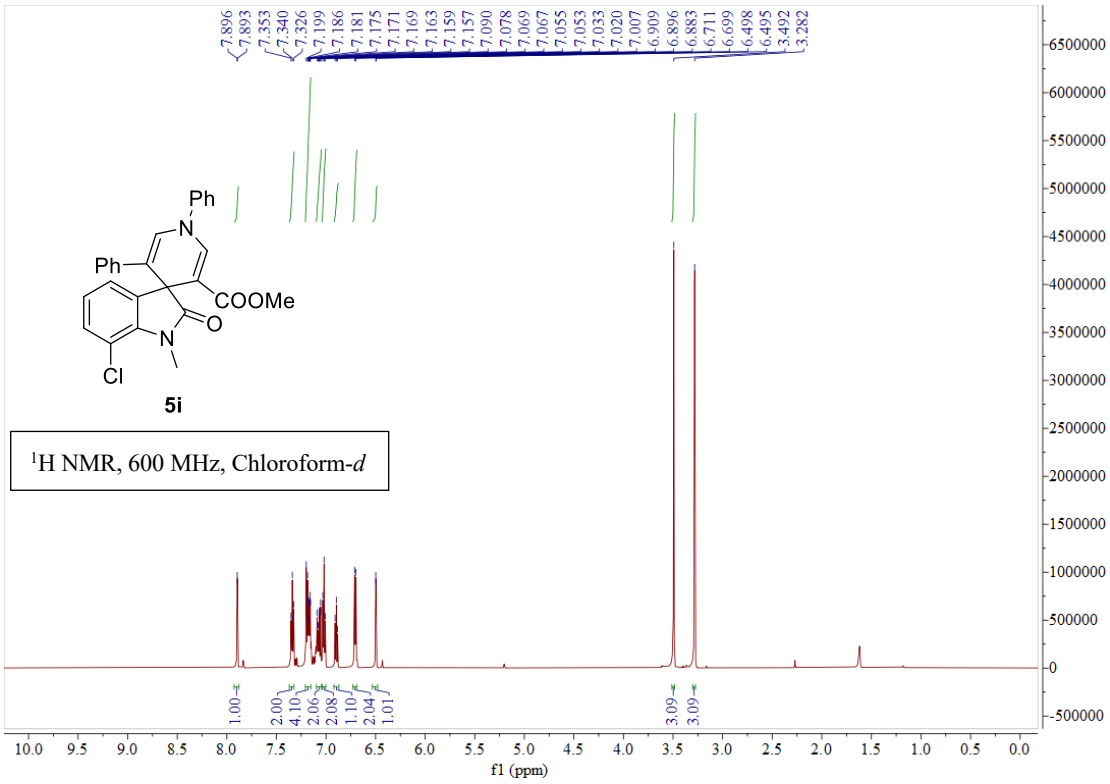
^{13}C NMR, 150 MHz, Chloroform-*d*



^{1}H NMR, 600 MHz, Chloroform-*d*

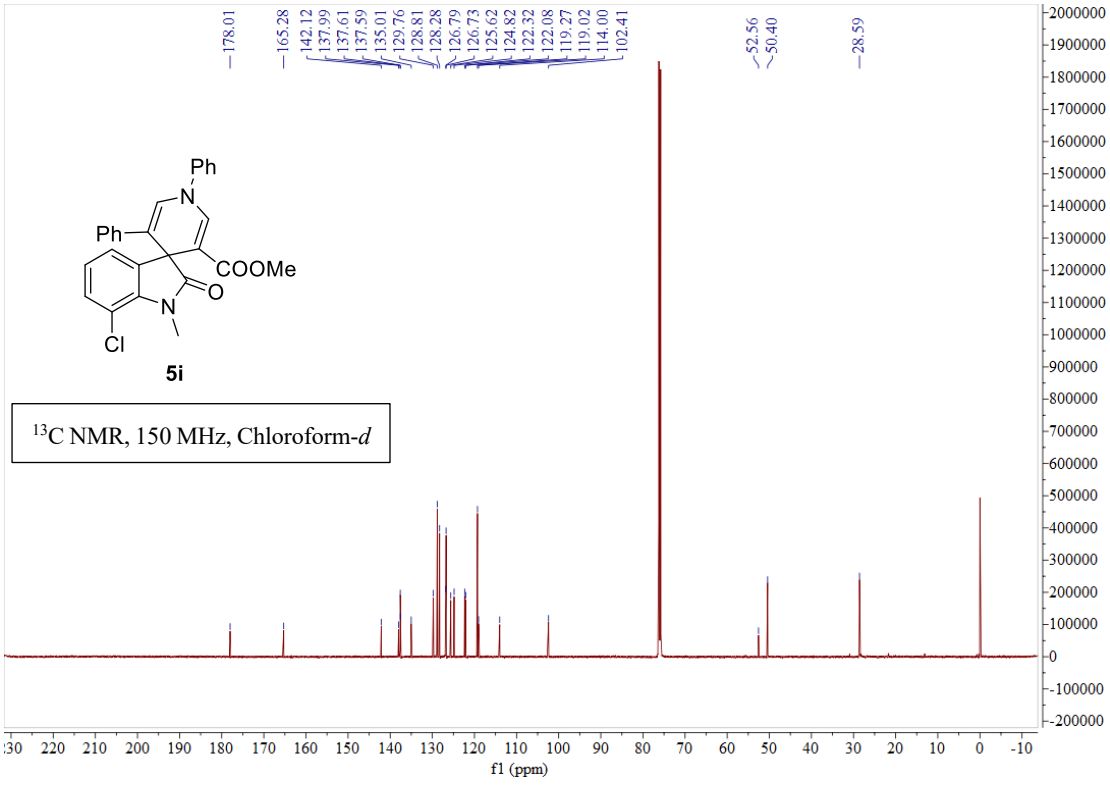


^{13}C NMR, 150 MHz, Chloroform-*d*



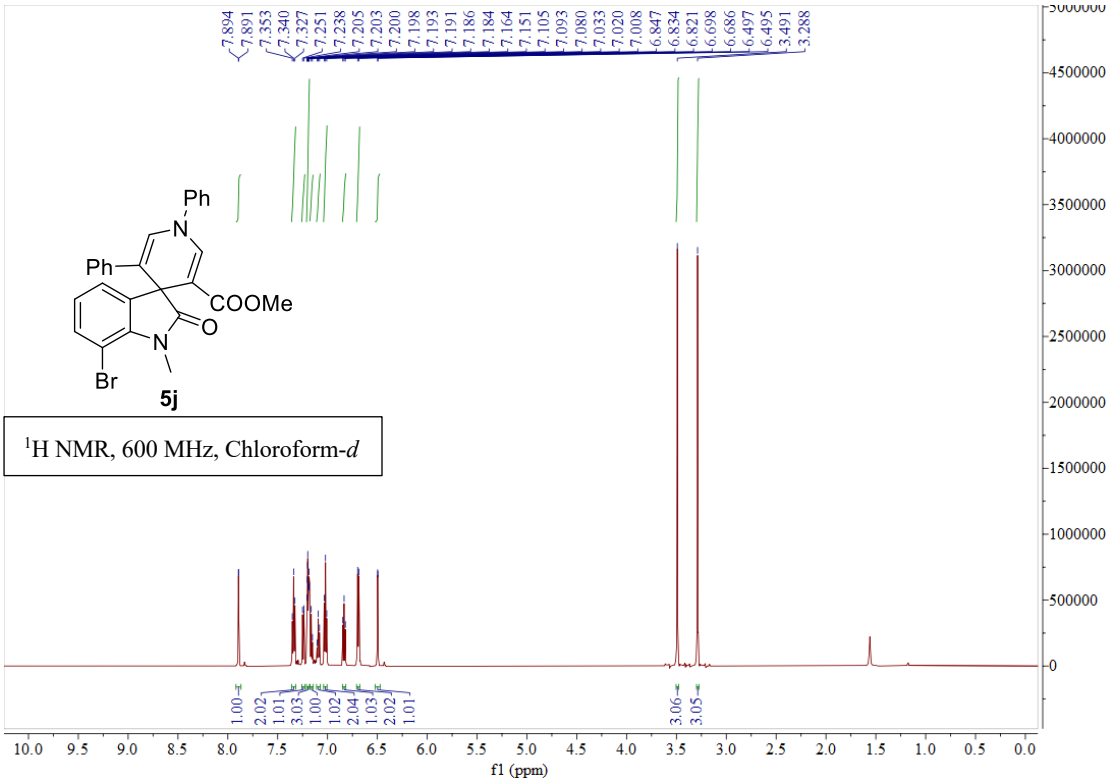
5i

^{1}H NMR, 600 MHz, Chloroform-*d*

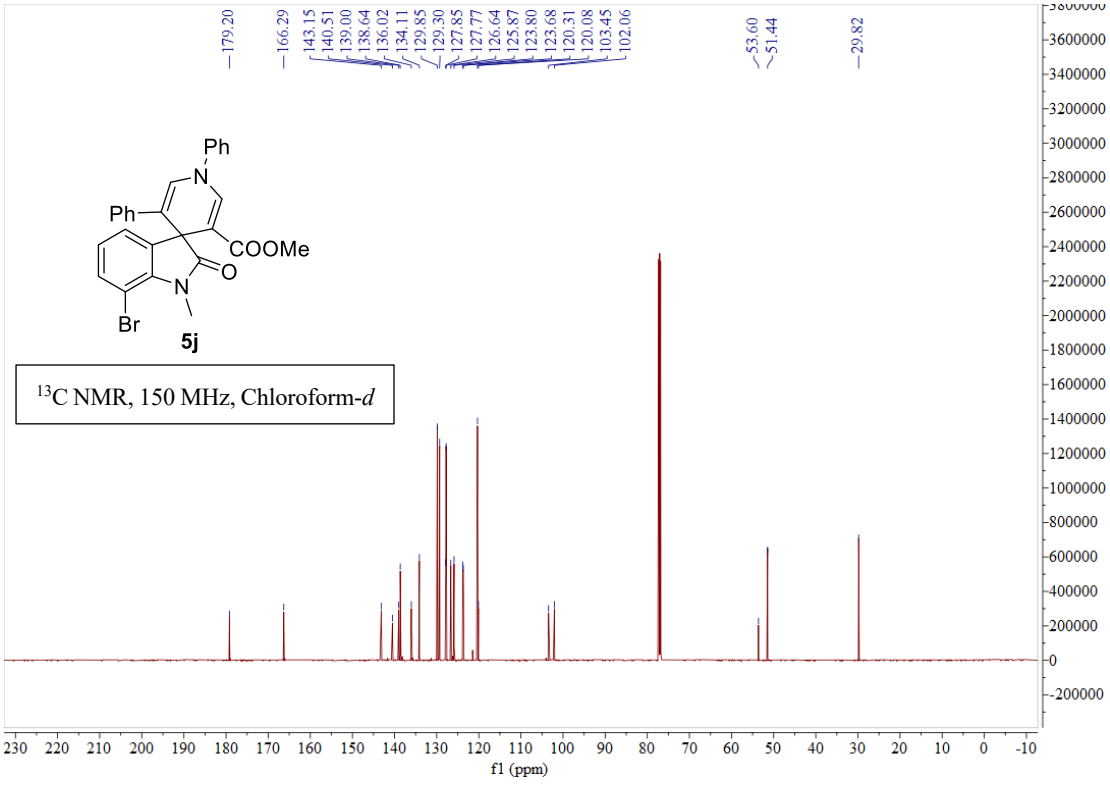


5i

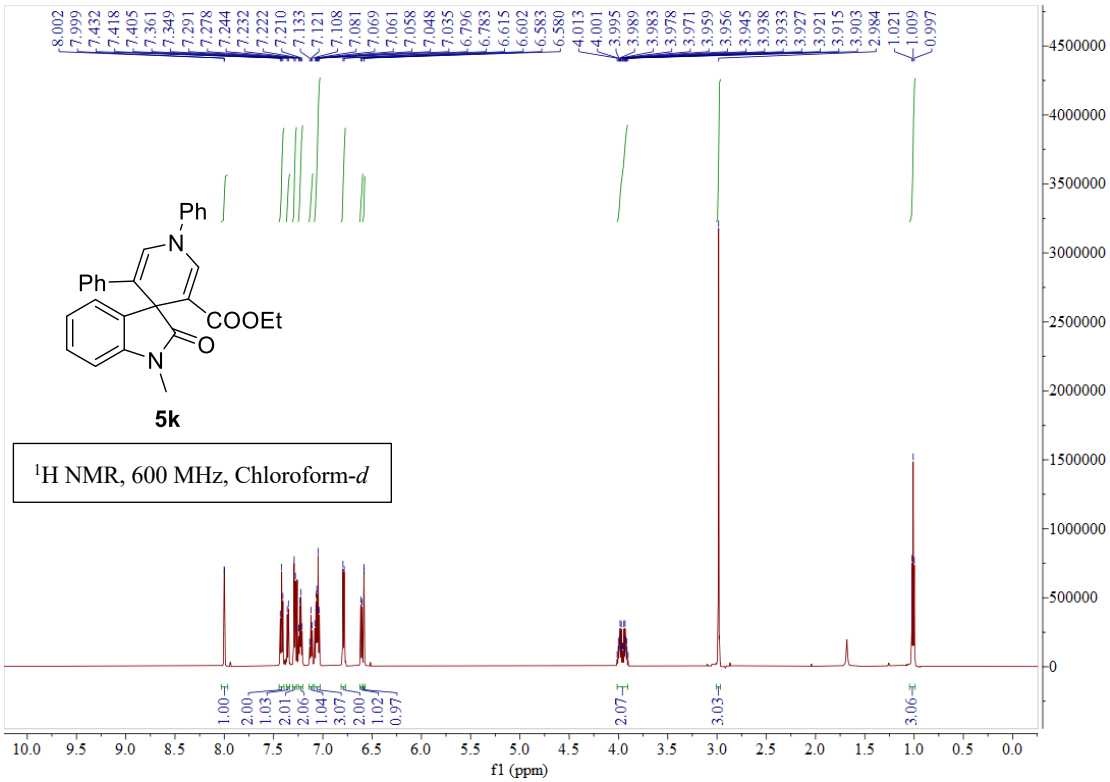
^{13}C NMR, 150 MHz, Chloroform-*d*

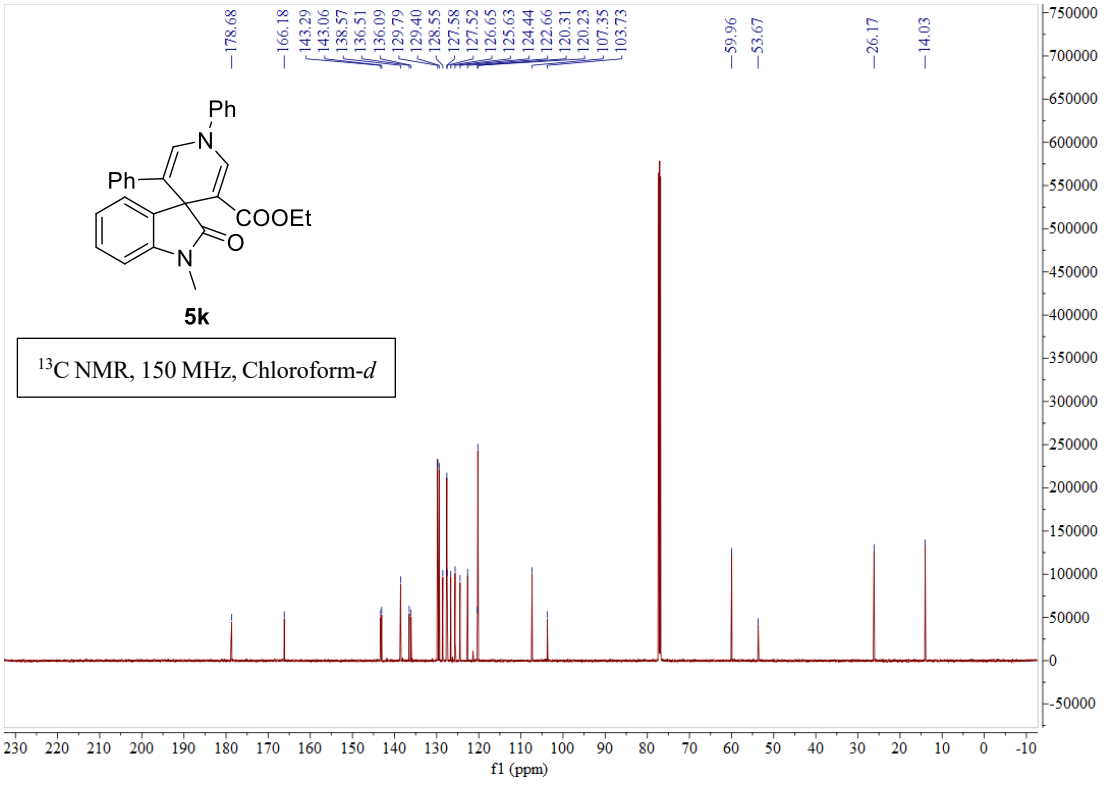


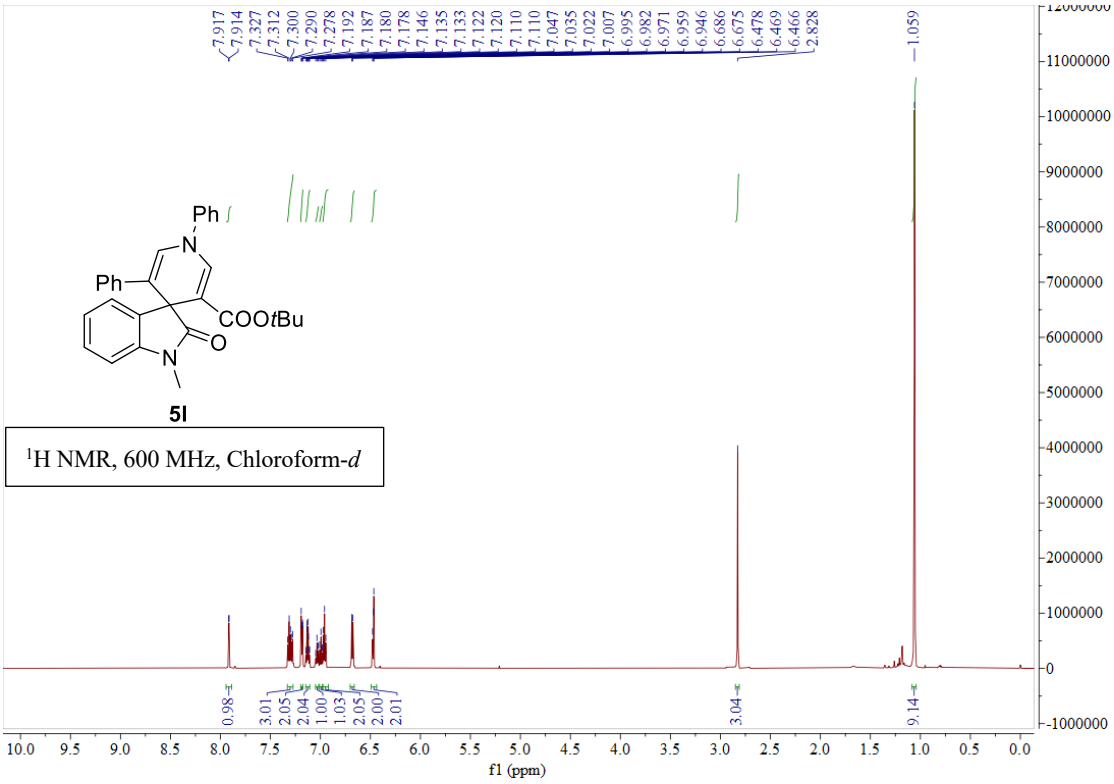
^{1}H NMR, 600 MHz, Chloroform-*d*



^{13}C NMR, 150 MHz, Chloroform-*d*

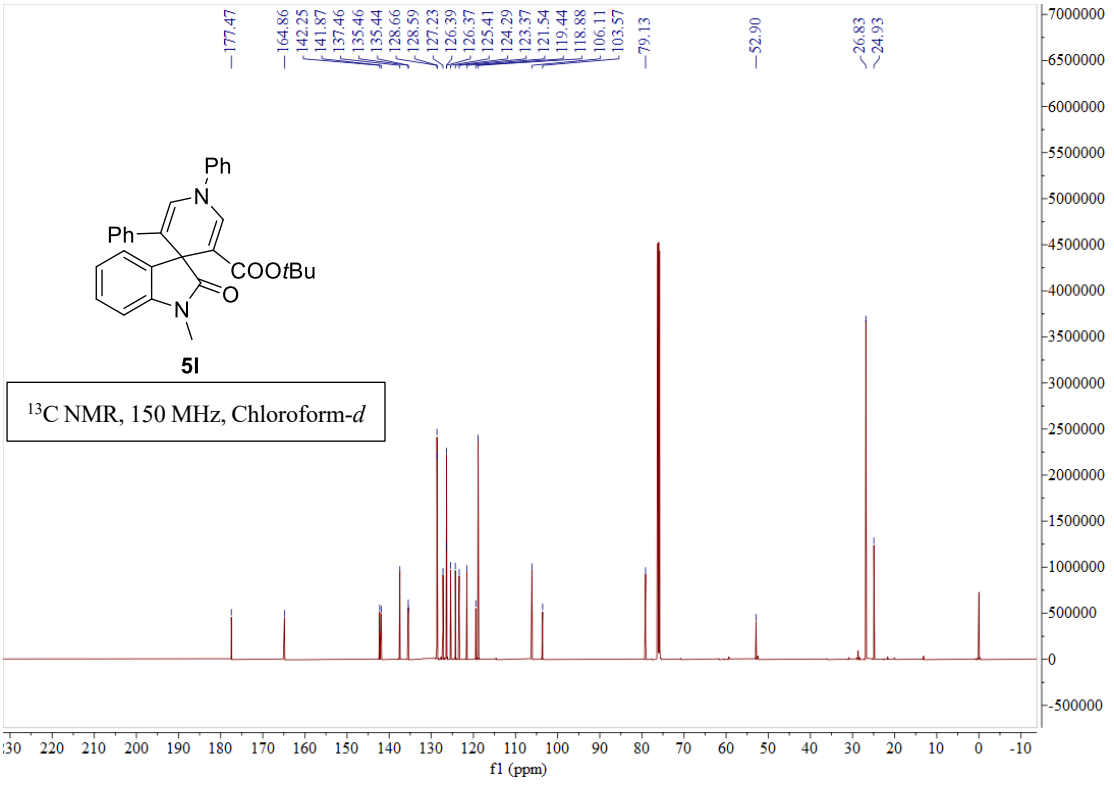

8.002
7.999
7.432
7.418
7.405
7.361
7.349
7.291
7.278
7.244
7.232
7.222
7.210
7.133
7.121
7.108
7.081
7.069
7.061
7.058
7.048
7.035
6.796
6.783
6.615
6.602
6.583
6.580
4.013
4.001
3.995
3.989
3.983
3.978
3.971
3.959
3.956
3.945
3.938
3.933
3.927
3.921
3.915
3.903
2.984
1.021
1.009
0.997
Ph
N
Ph
COOEt
O
N
5k
1H NMR, 600 MHz, Chloroform-d
1.00
2.00
1.03
2.01
2.06
1.04
3.07
2.00
1.02
0.97
2.07
3.03
3.06
f1 (ppm)


178.68
166.18
143.29
143.06
138.57
136.51
136.09
129.79
129.40
128.55
127.58
127.52
126.65
125.63
124.44
122.66
120.31
120.23
107.35
103.73
59.96
53.67
26.17
14.03
Ph
N
Ph
COOEt
O
N
5k
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



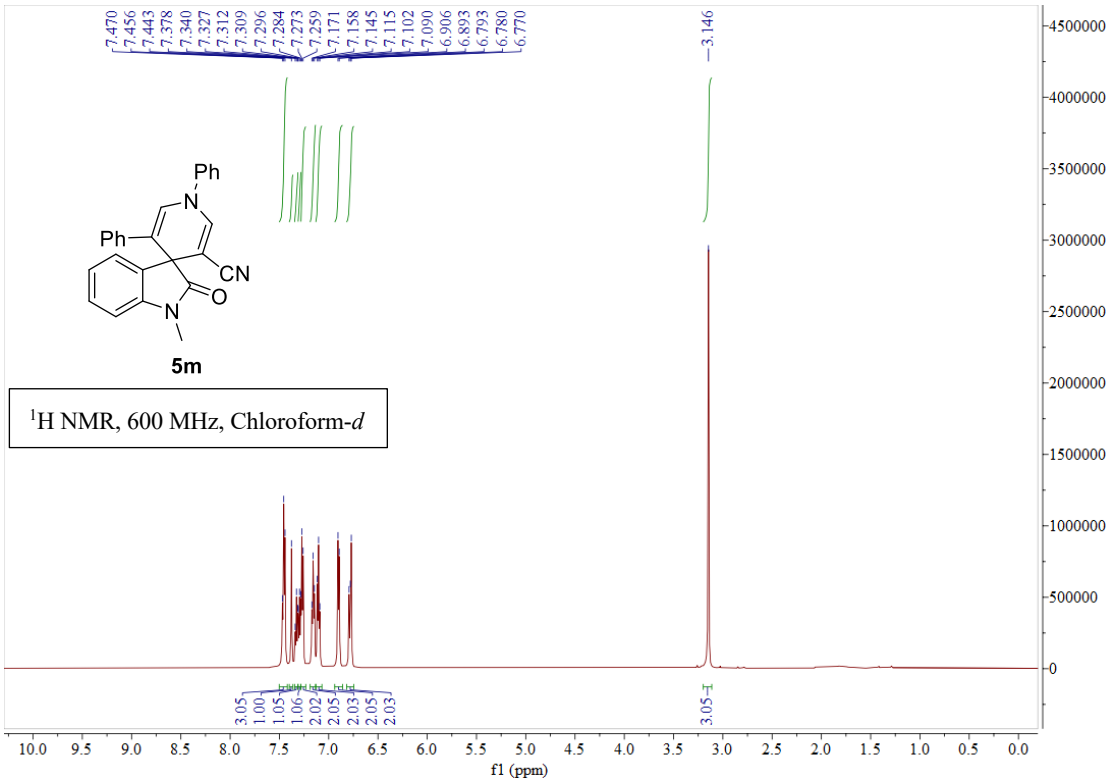
5l

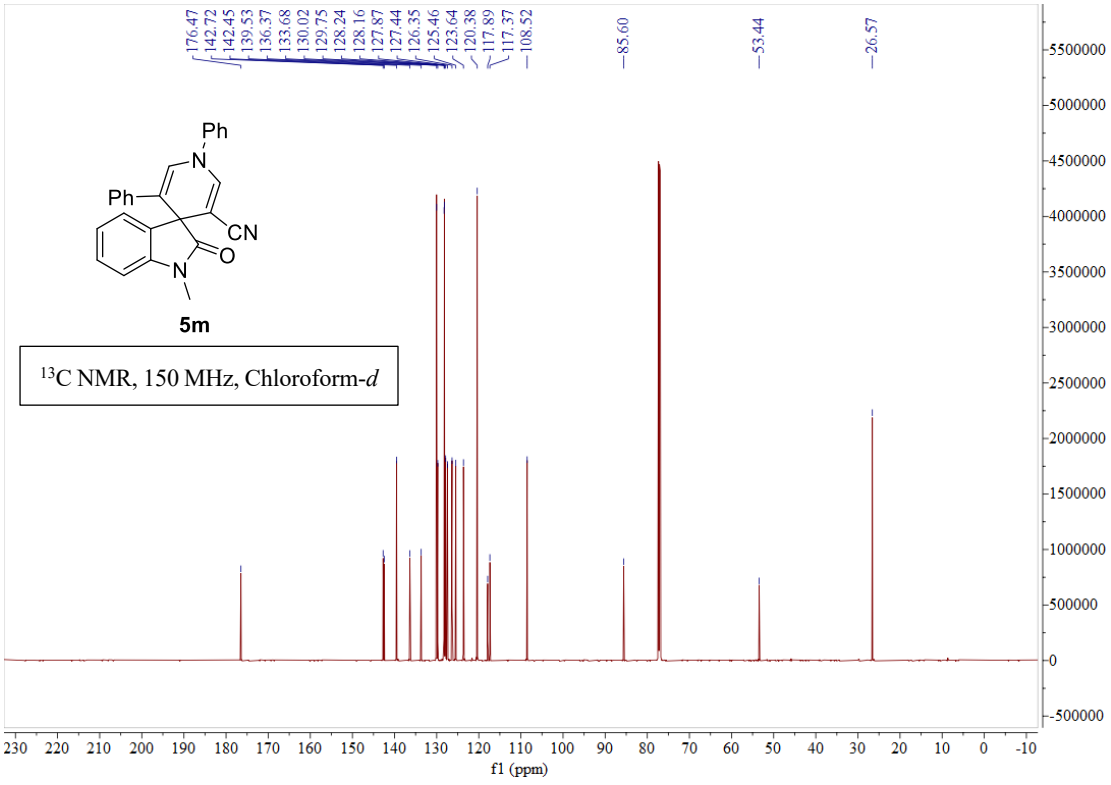
^{1}H NMR, 600 MHz, Chloroform-*d*

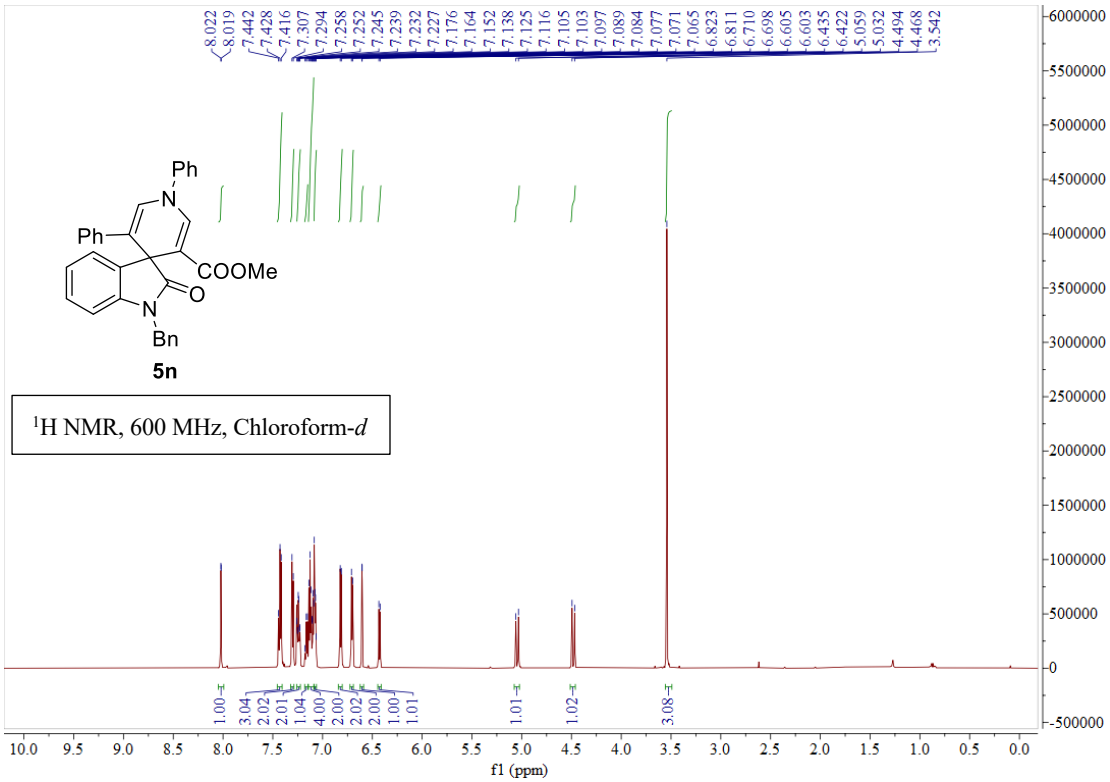


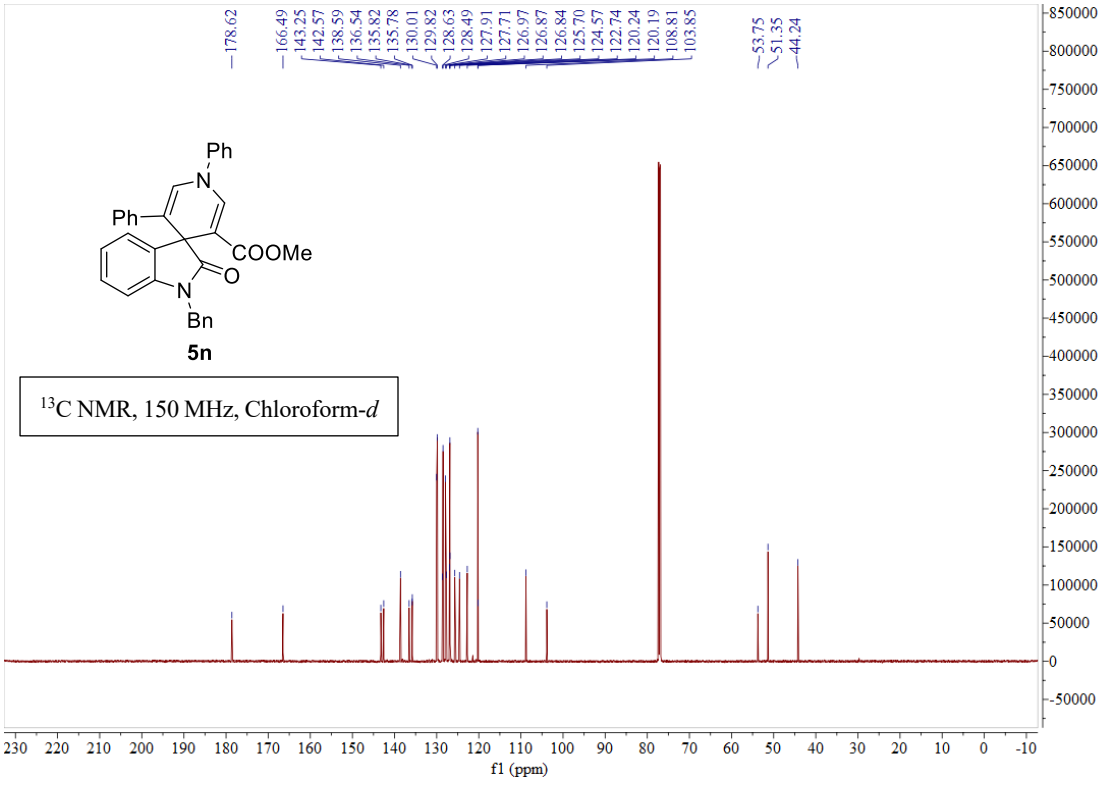
5l

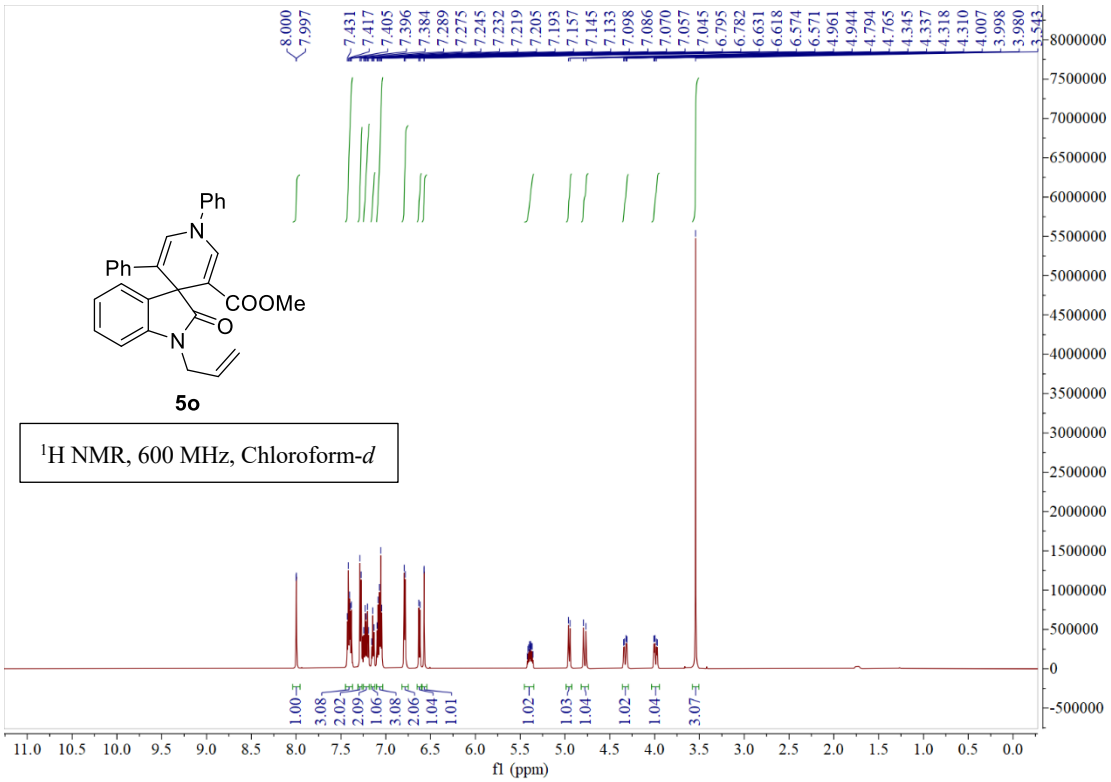
^{13}C NMR, 150 MHz, Chloroform-*d*


7.470
7.456
7.443
7.378
7.340
7.327
7.312
7.309
7.296
7.284
7.273
7.259
7.171
7.158
7.145
7.115
7.102
7.090
6.906
6.893
6.793
6.780
6.770
3.146
Ph
N
Ph
CN
O
N
5m
[1]H NMR, 600 MHz, Chloroform-d
3.05
1.00
1.05
1.06
2.02
2.05
2.03
2.05
2.03
3.05
f1 (ppm)


176.47
142.72
142.45
139.53
136.37
133.68
130.02
129.75
128.24
128.16
127.87
127.44
126.35
125.46
123.64
120.38
117.89
117.37
108.52
85.60
53.44
26.57
Ph
N
Ph
CN
O
N
5m
[13]C NMR, 150 MHz, Chloroform-d
f1 (ppm)

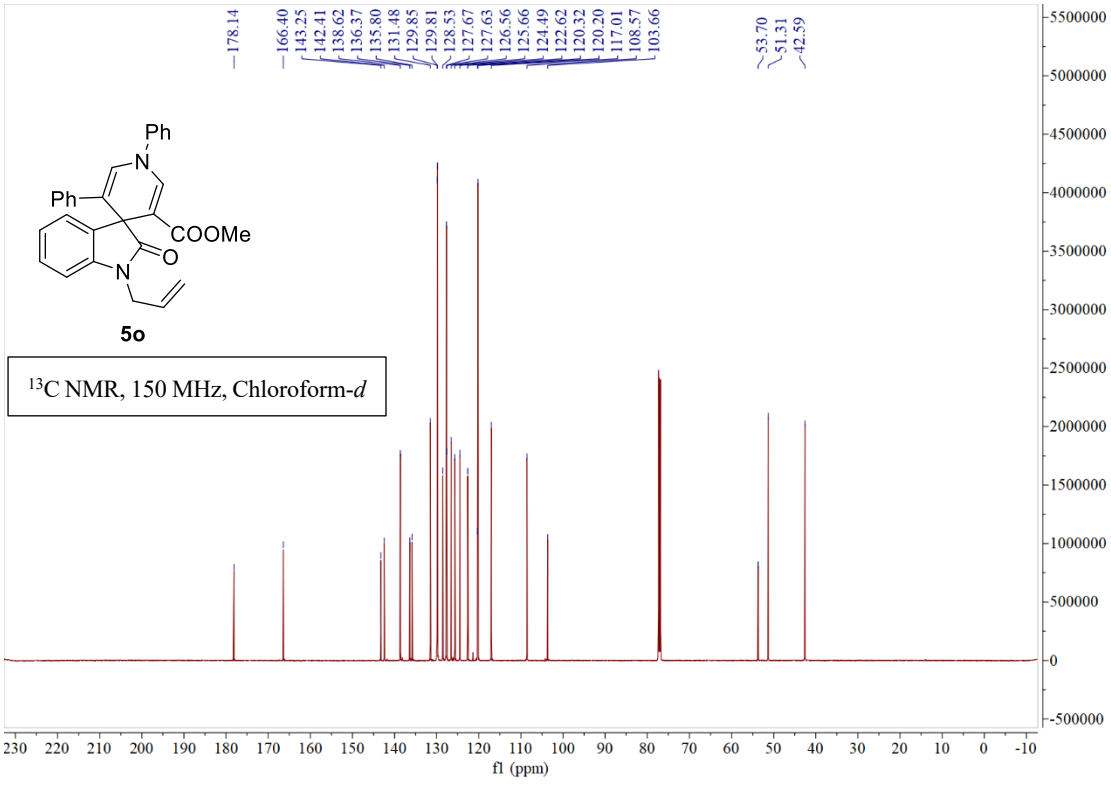

Ph
N
Ph
COOMe
O
N
Bn
5n
[1]H NMR, 600 MHz, Chloroform-d
f1 (ppm)


Ph
N
Ph
COOMe
O
N
Bn
5n
[13]C NMR, 150 MHz, Chloroform-d
f1 (ppm)



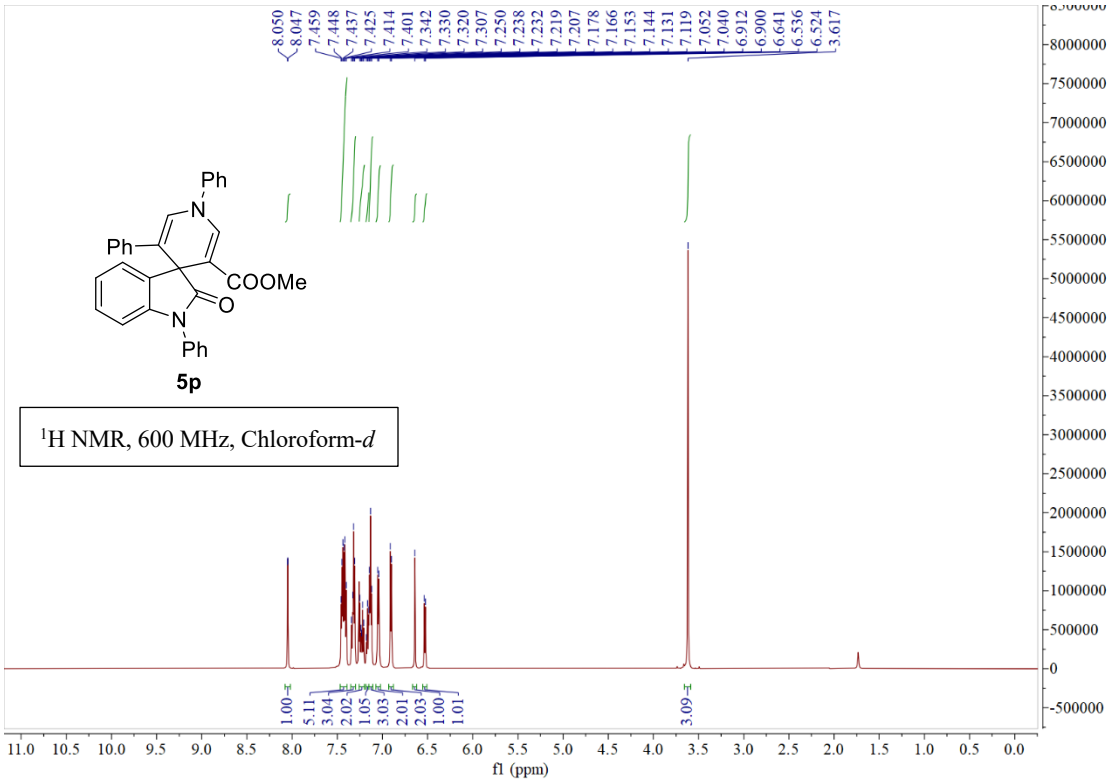
5o

^{1}H NMR, 600 MHz, Chloroform-*d*



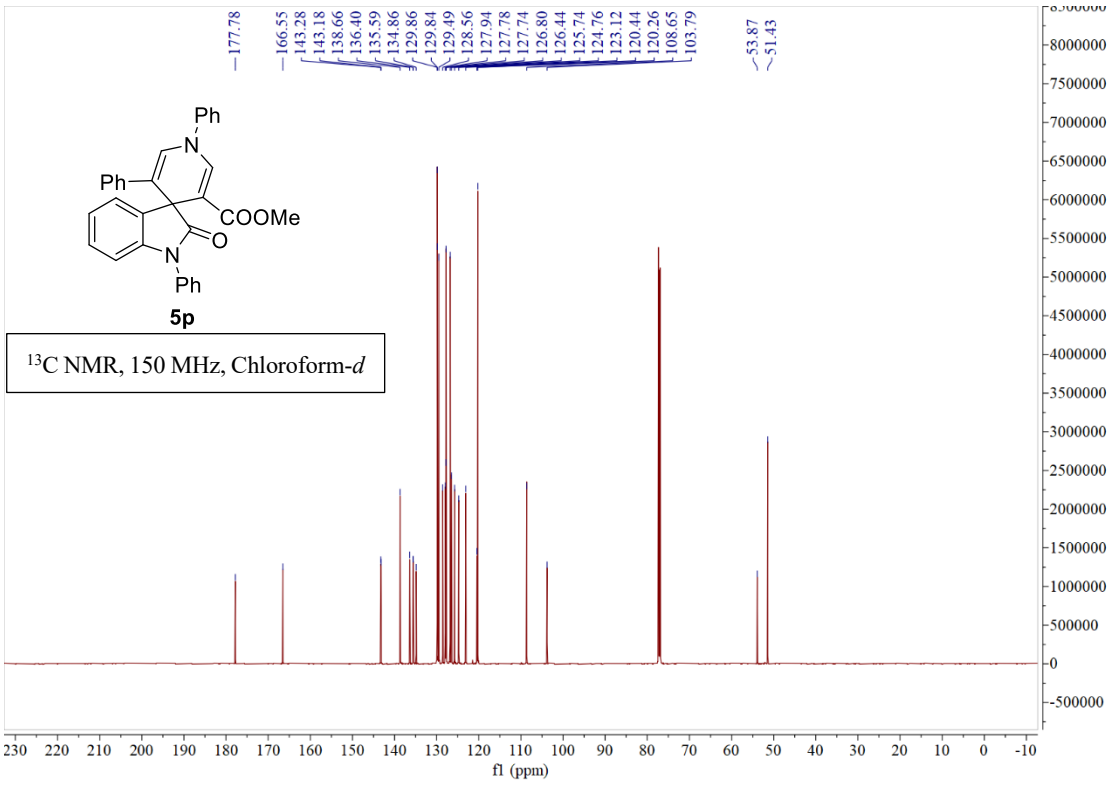
5o

^{13}C NMR, 150 MHz, Chloroform-*d*



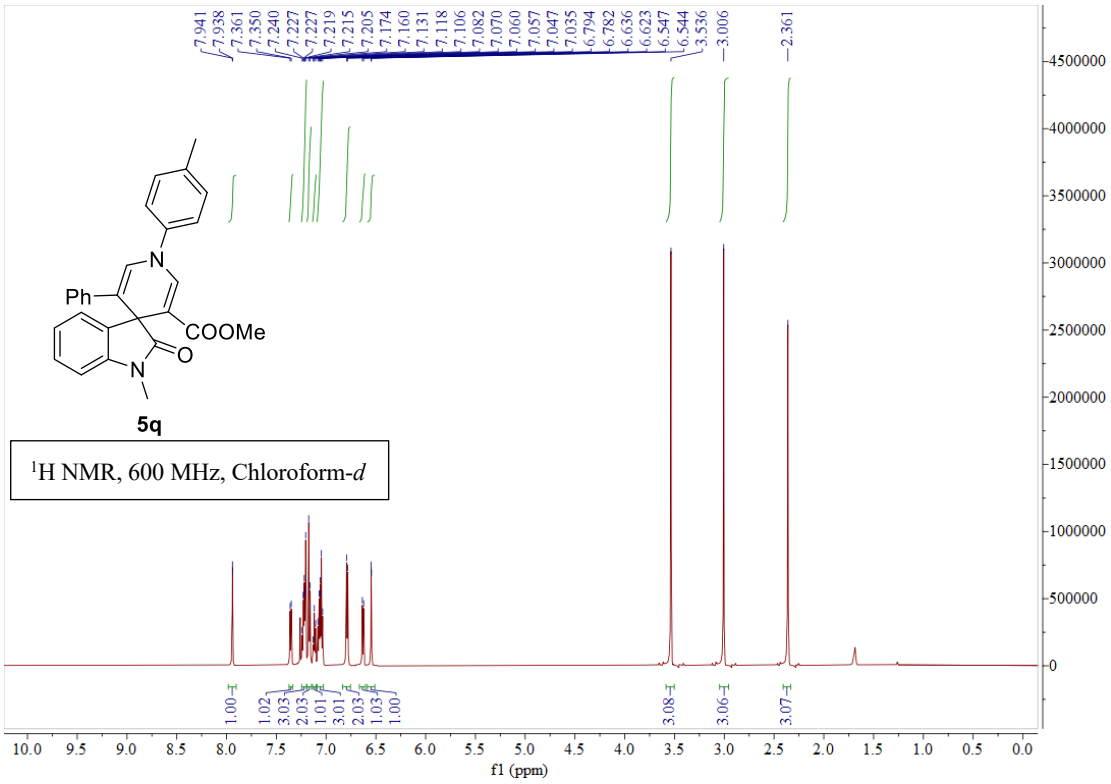
5p

^{1}H NMR, 600 MHz, Chloroform-*d*



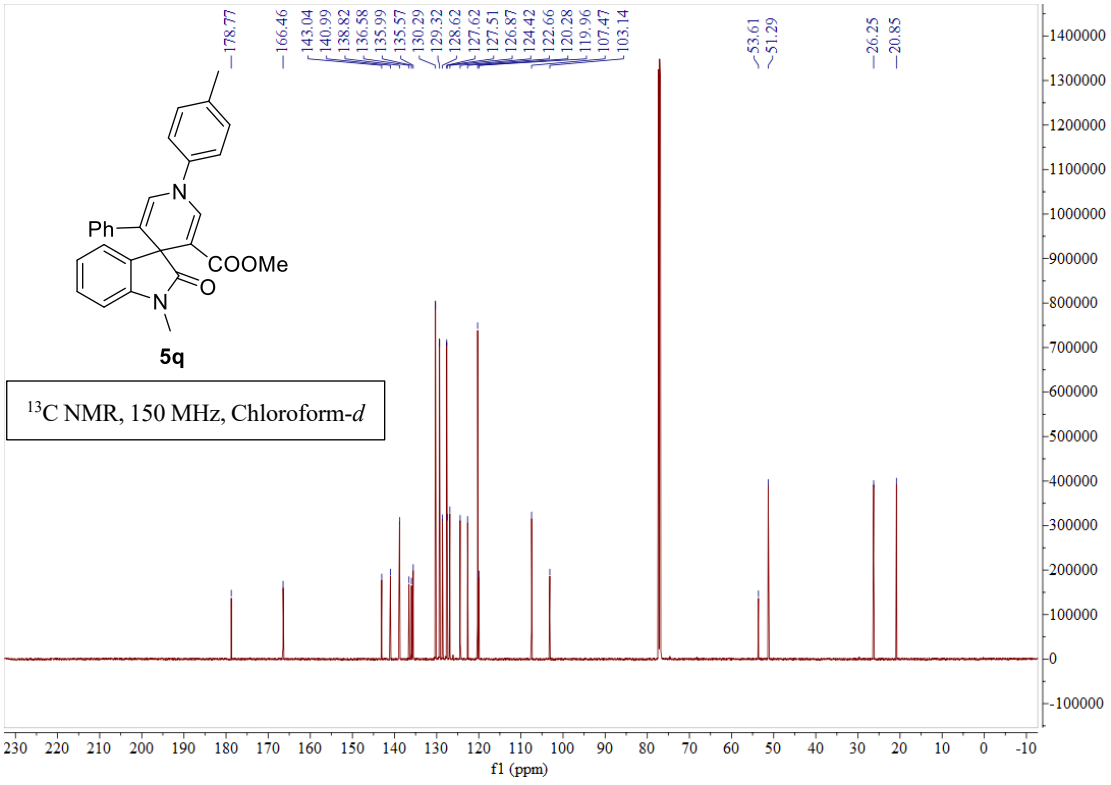
5p

^{13}C NMR, 150 MHz, Chloroform-*d*



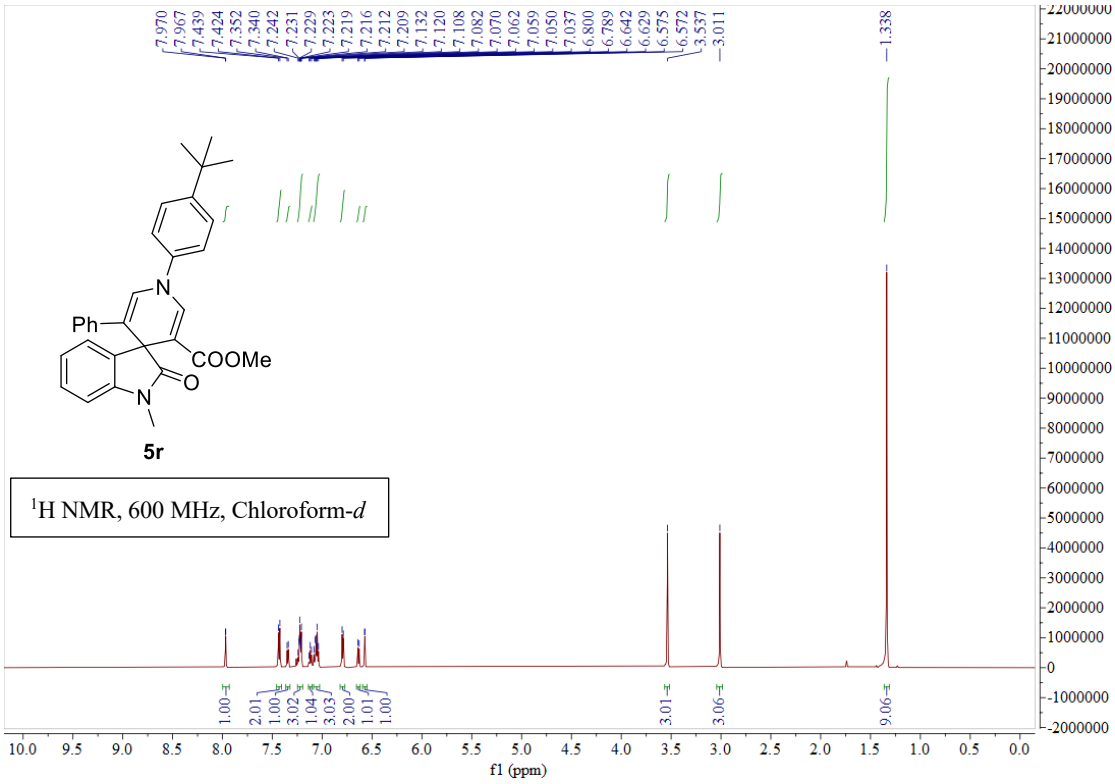
5q

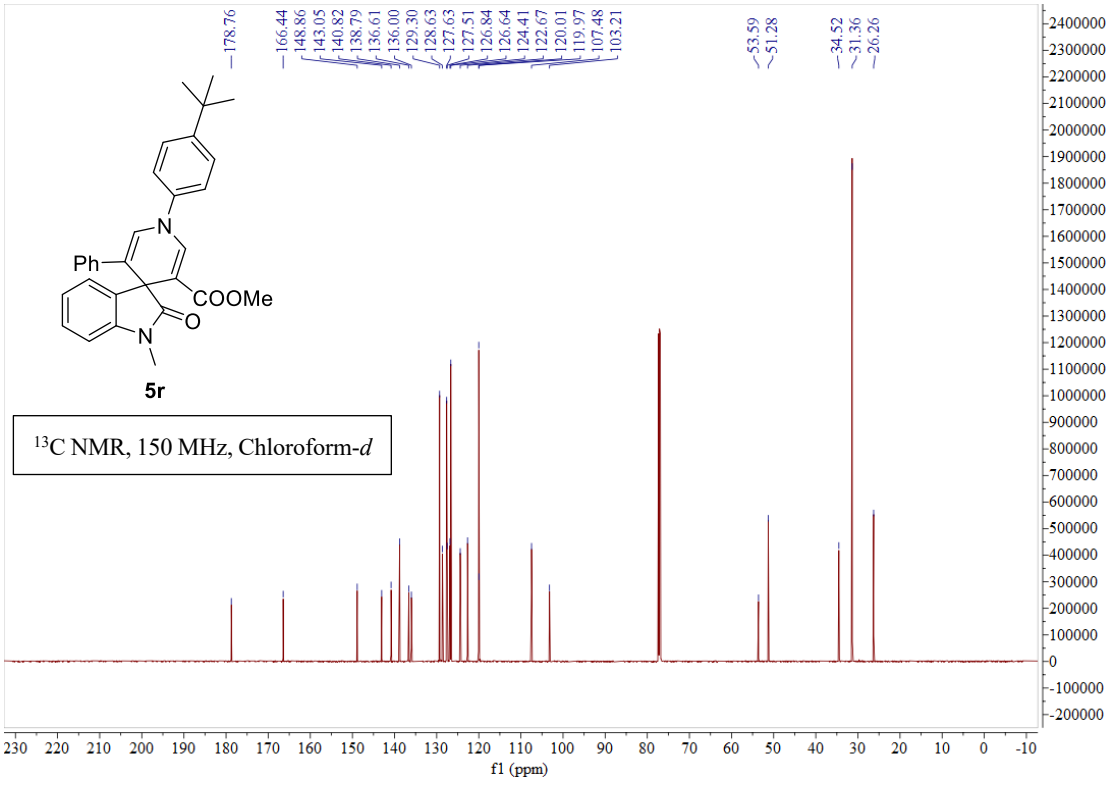
^{1}H NMR, 600 MHz, Chloroform-*d*

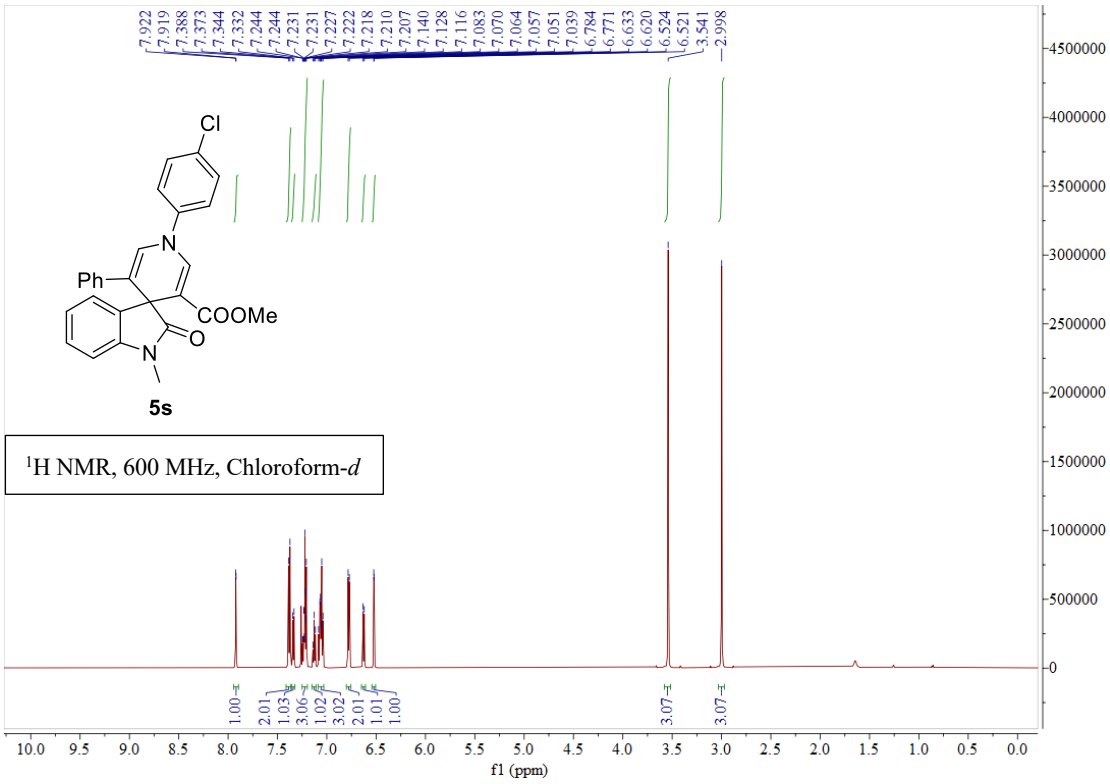


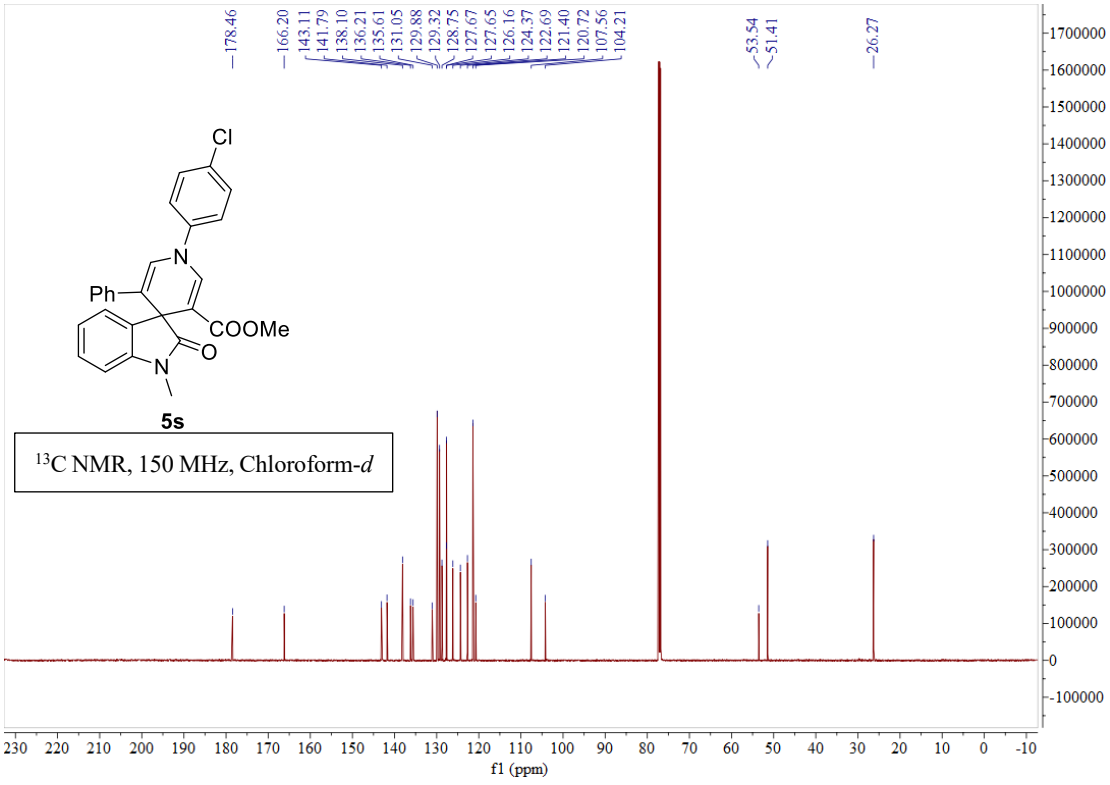
5q

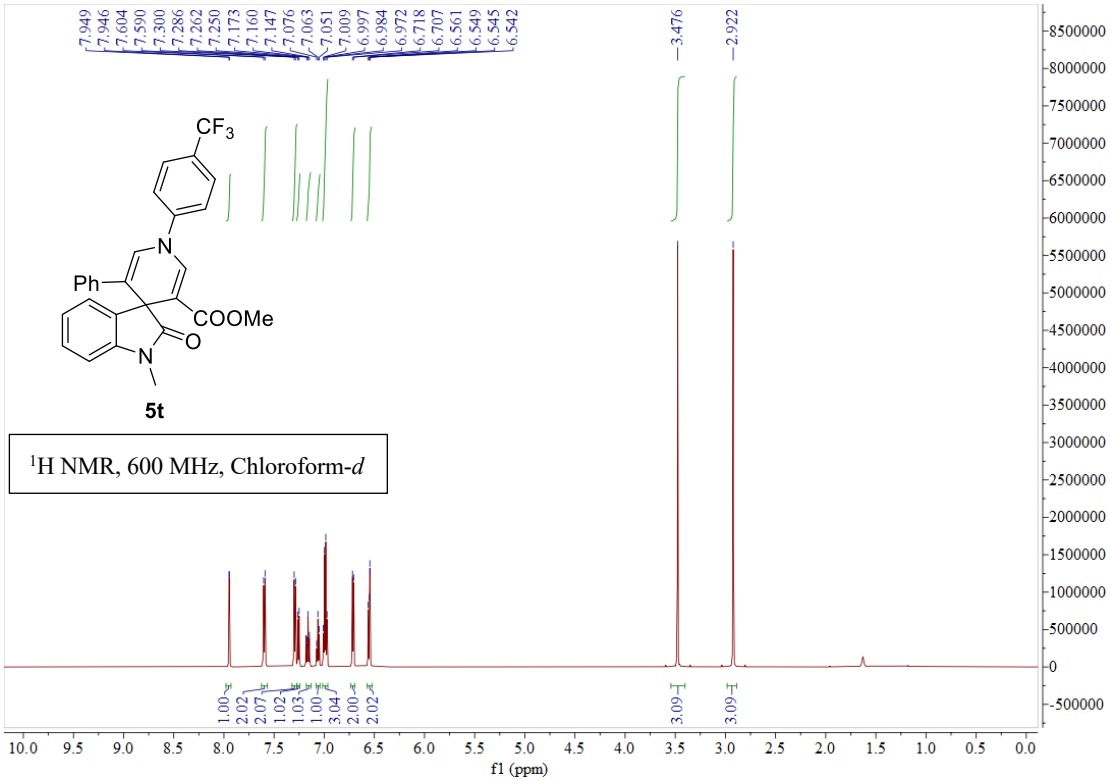
^{13}C NMR, 150 MHz, Chloroform-*d*


7.970
7.967
7.439
7.424
7.352
7.340
7.242
7.231
7.229
7.223
7.219
7.216
7.212
7.209
7.132
7.120
7.108
7.082
7.070
7.062
7.059
7.050
7.037
6.800
6.789
6.642
6.629
6.575
6.572
3.537
3.011
1.338
Ph
COOMe
O
N
N
5r
[1]H NMR, 600 MHz, Chloroform-d
1.00
2.01
1.00
3.02
1.04
3.03
2.00
1.01
1.00
3.01
3.06
9.06
f1 (ppm)


178.76
166.44
148.86
143.05
140.82
138.79
136.61
136.00
129.30
128.63
127.63
127.51
126.84
126.64
124.41
122.67
120.01
119.97
107.48
103.21
53.59
51.28
34.52
31.36
26.26
Ph
COOMe
O
N
N
5r
[13]C NMR, 150 MHz, Chloroform-d
f1 (ppm)

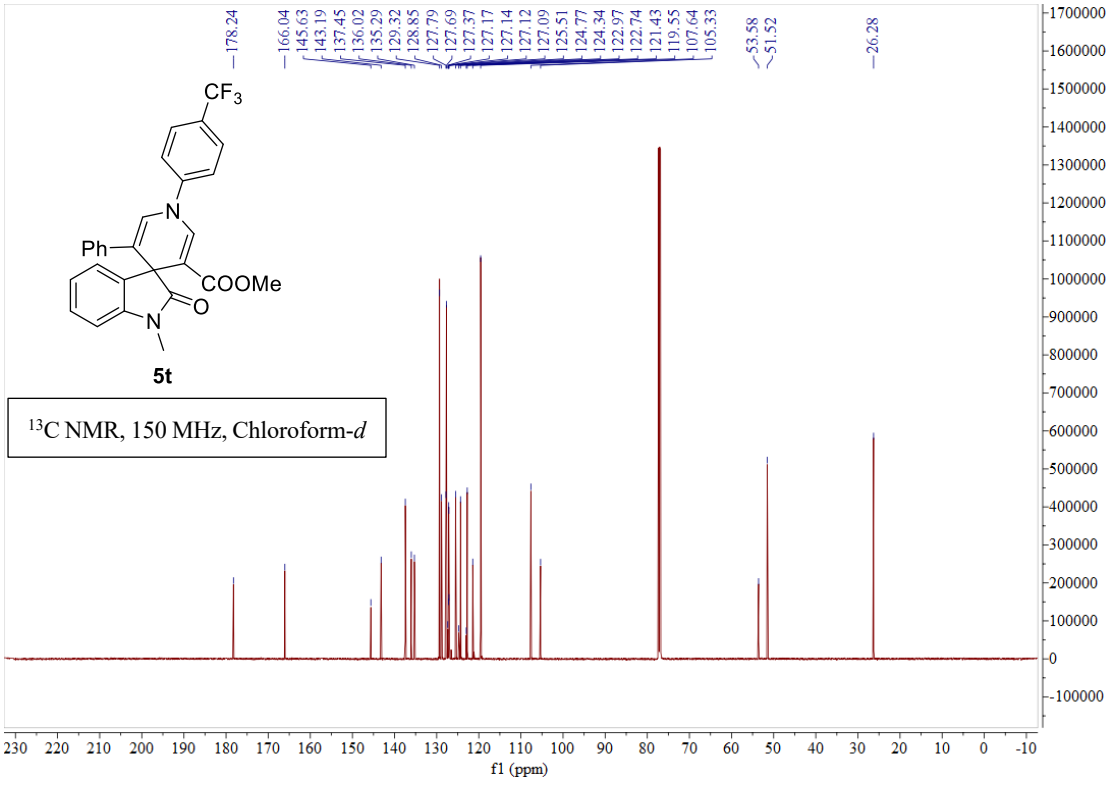

7.922
7.919
7.388
7.373
7.344
7.332
7.244
7.244
7.231
7.231
7.227
7.222
7.218
7.210
7.207
7.140
7.128
7.116
7.083
7.070
7.064
7.057
7.051
7.039
6.784
6.771
6.633
6.620
6.524
6.521
3.541
2.998
Cl
N
Ph
COOMe
O
N
5s
1H NMR, 600 MHz, Chloroform-d
1.00
2.01
1.03
3.06
1.02
3.02
2.01
1.01
1.00
3.07
3.07
f1 (ppm)


178.46
166.20
143.11
141.79
138.10
136.21
135.61
131.05
129.88
129.32
128.75
127.67
127.65
126.16
124.37
122.69
121.40
120.72
107.56
104.21
53.54
51.41
26.27
Cl
N
Ph
COOMe
O
N
5s
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)



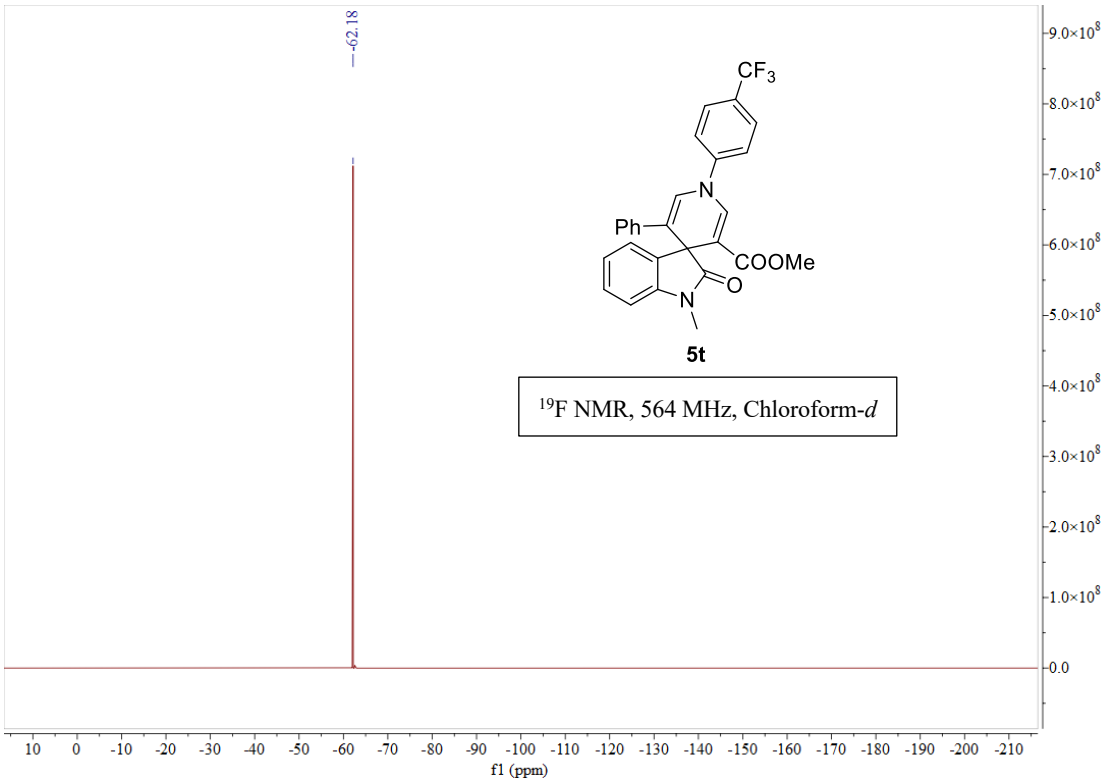
5t

^{1}H NMR, 600 MHz, Chloroform-*d*



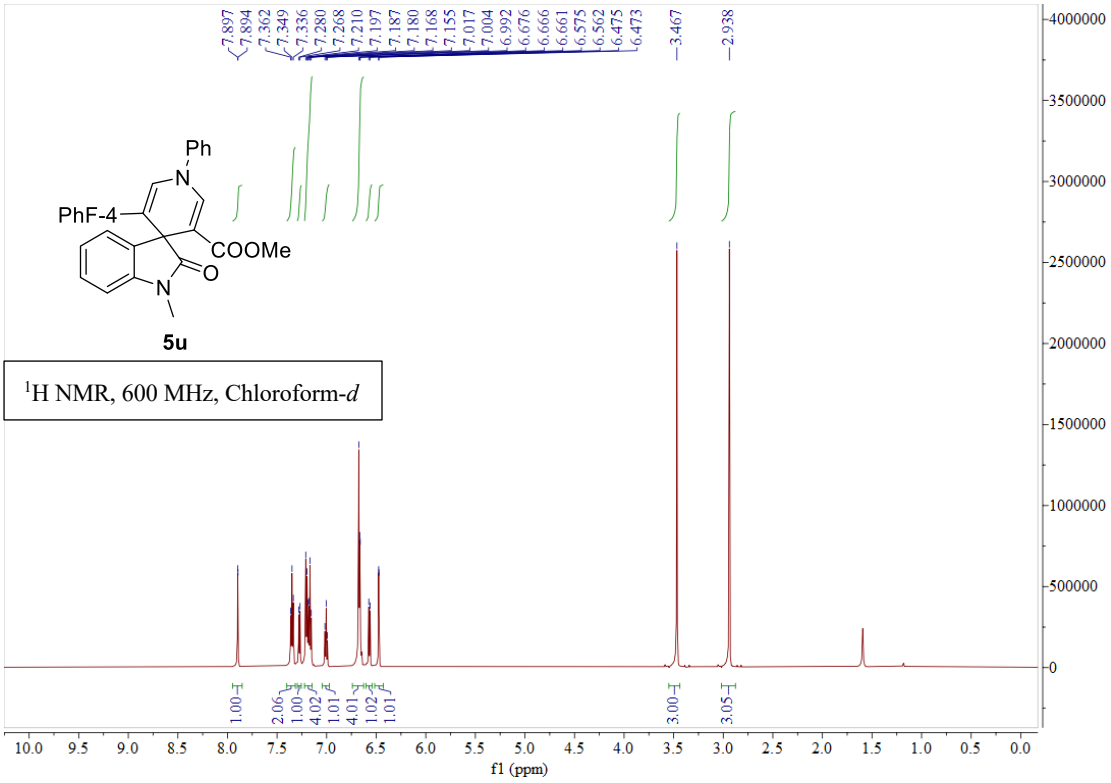
5t

^{13}C NMR, 150 MHz, Chloroform-*d*

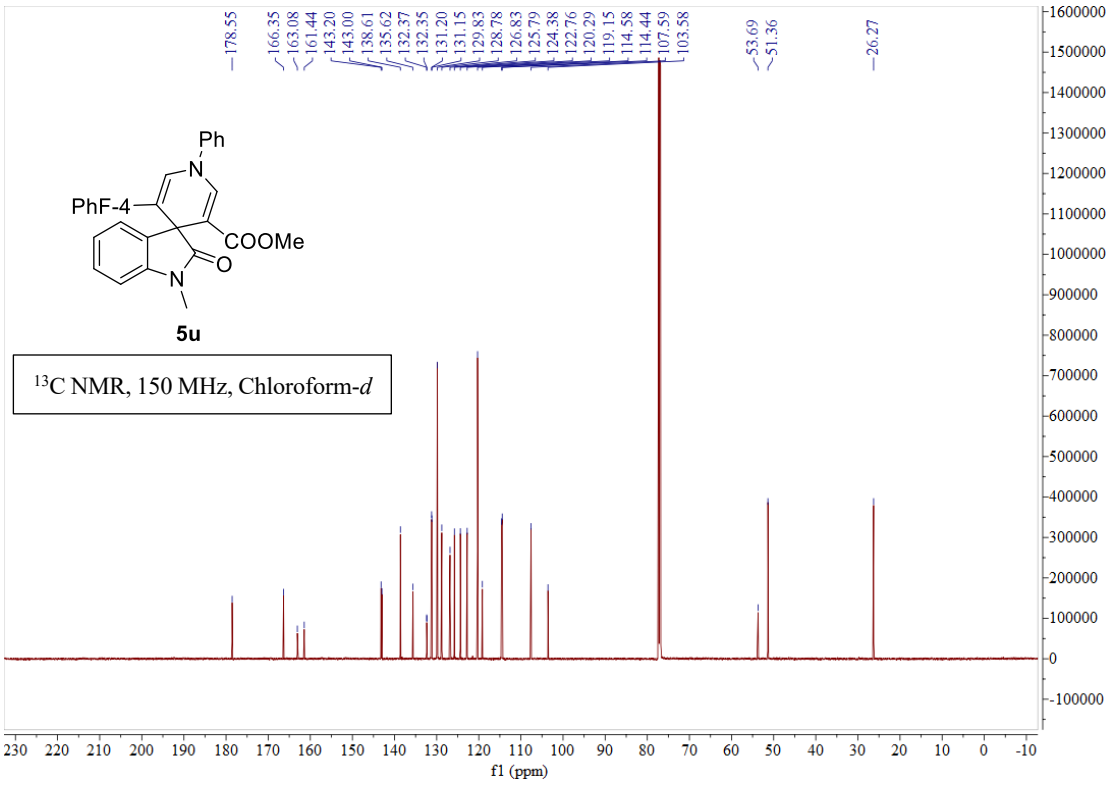


5t

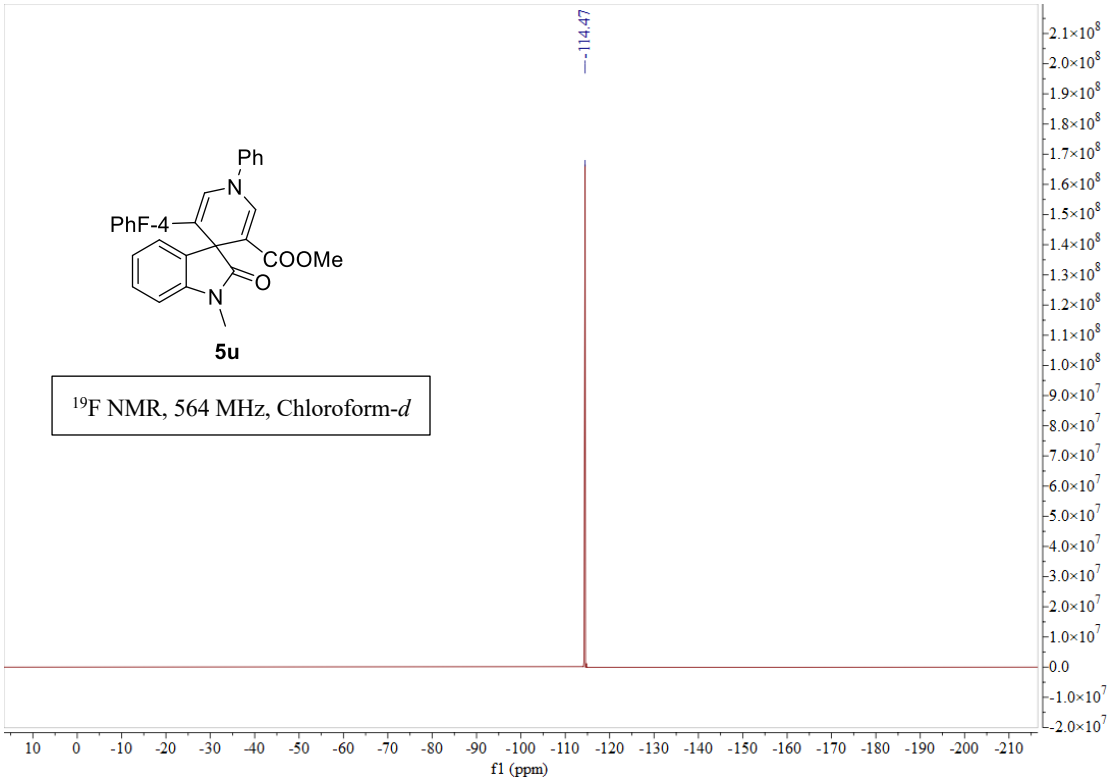
^{19}F NMR, 564 MHz, Chloroform-*d*



^{1}H NMR, 600 MHz, Chloroform-*d*

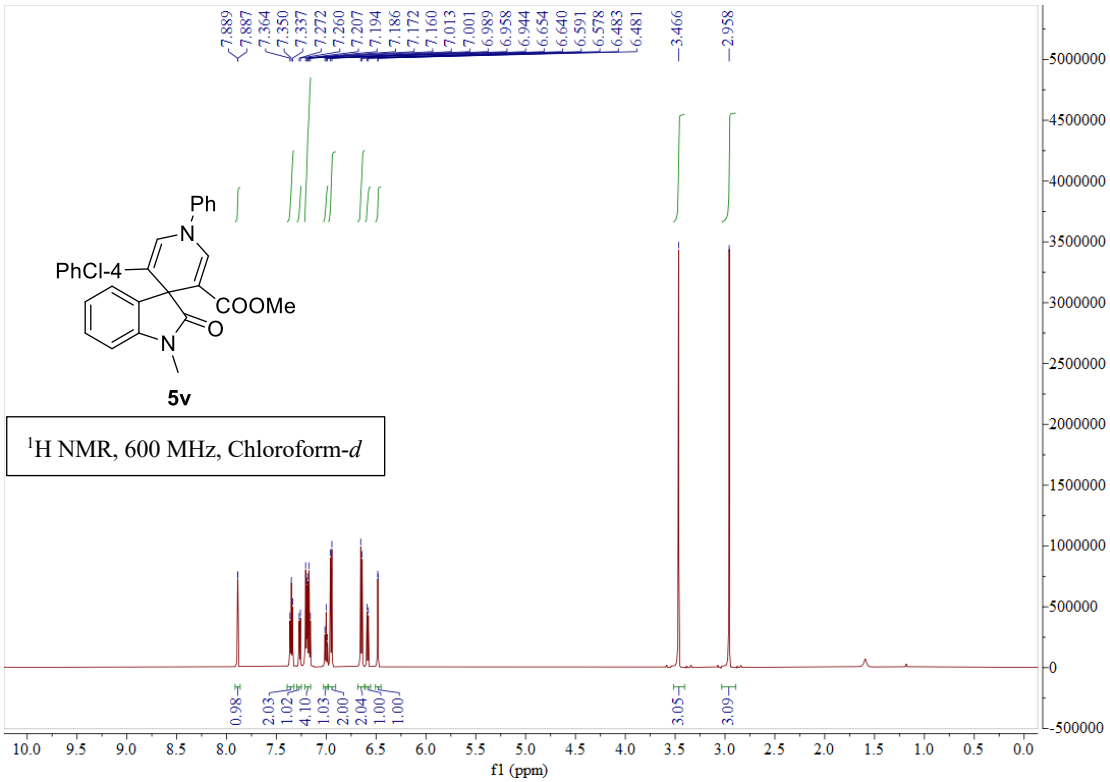


^{13}C NMR, 150 MHz, Chloroform-*d*

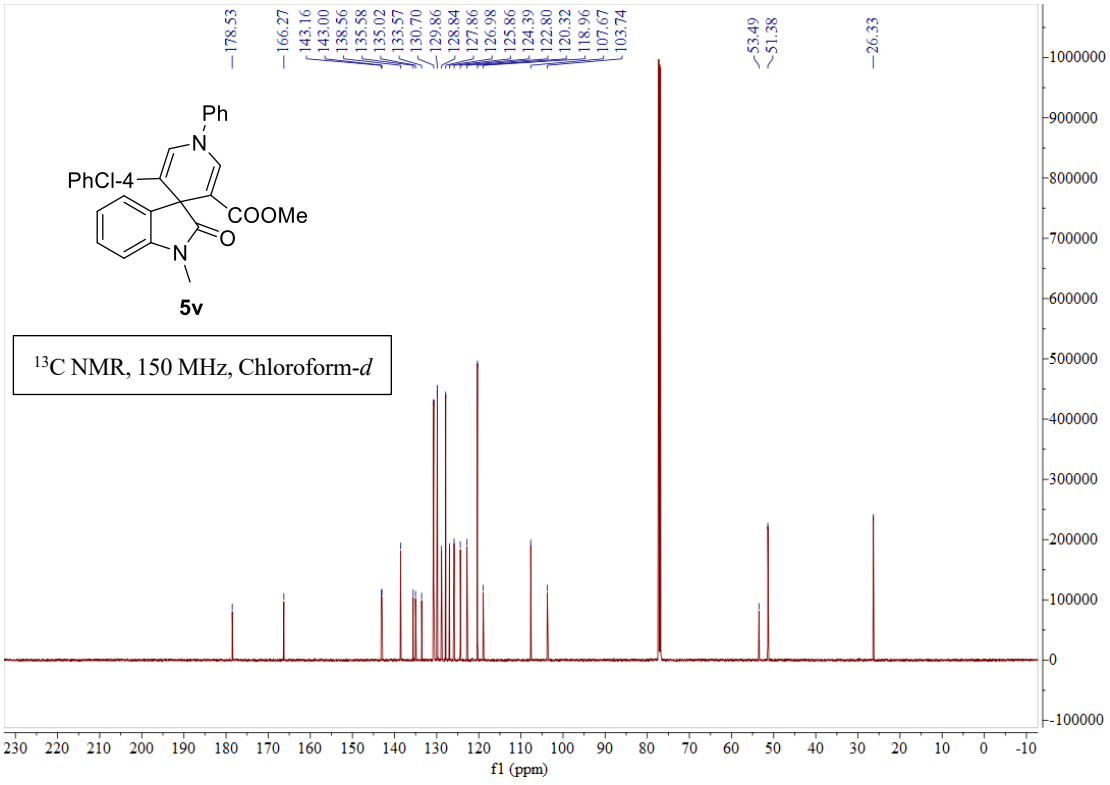


5u

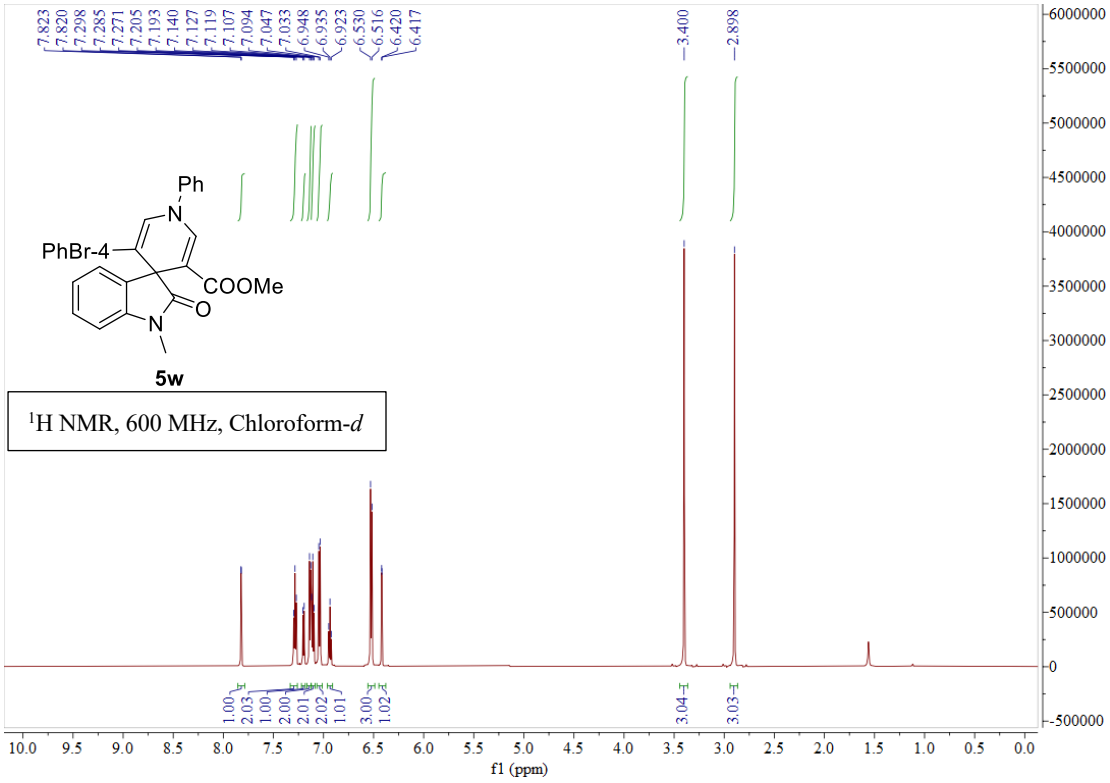
^{19}F NMR, 564 MHz, Chloroform-*d*



^{1}H NMR, 600 MHz, Chloroform-*d*

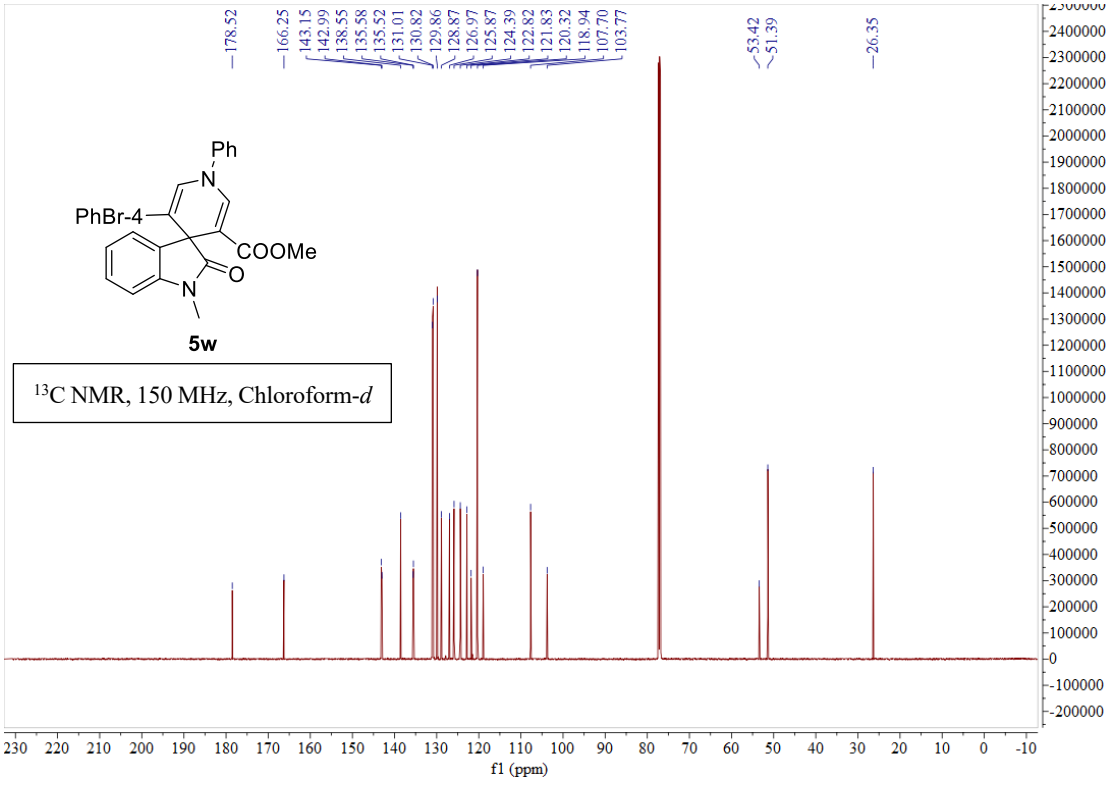


^{13}C NMR, 150 MHz, Chloroform-*d*



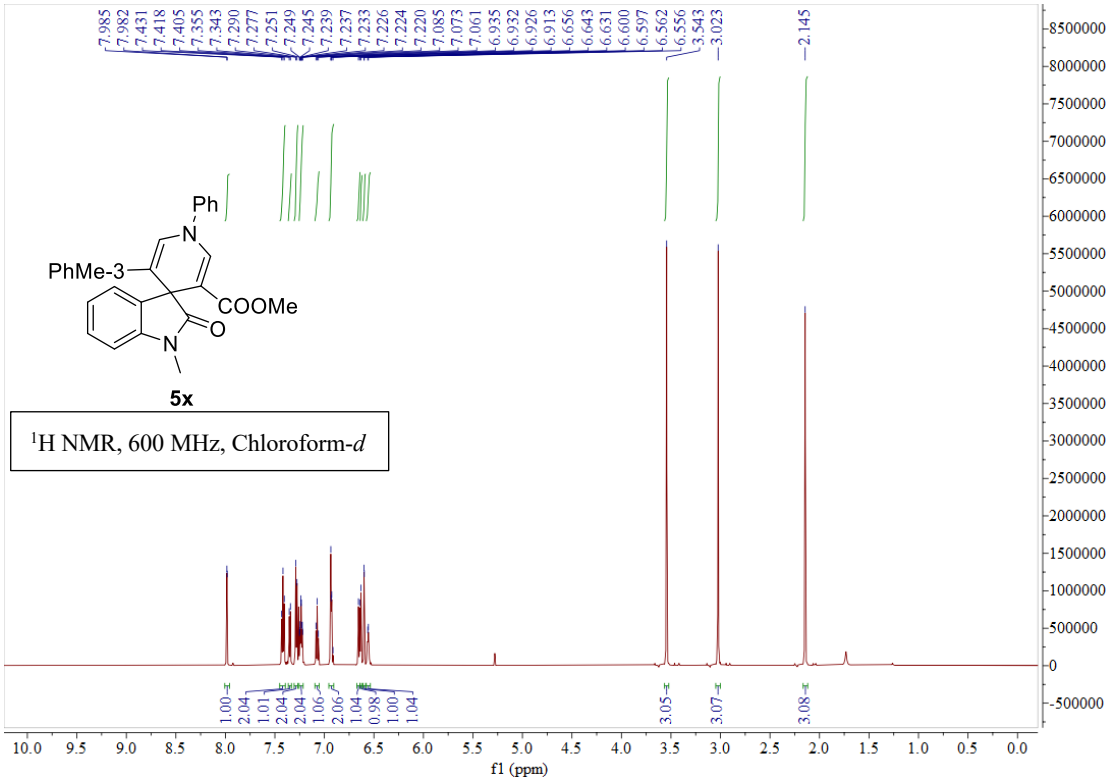
5w

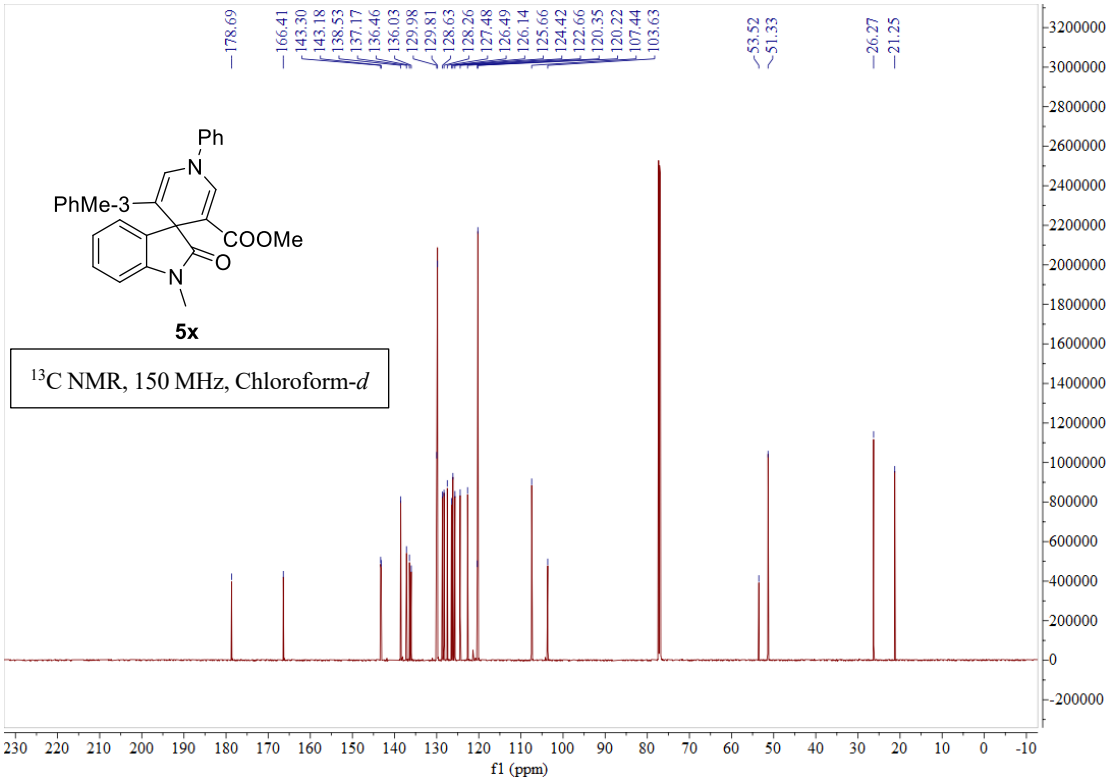
^{1}H NMR, 600 MHz, Chloroform-*d*

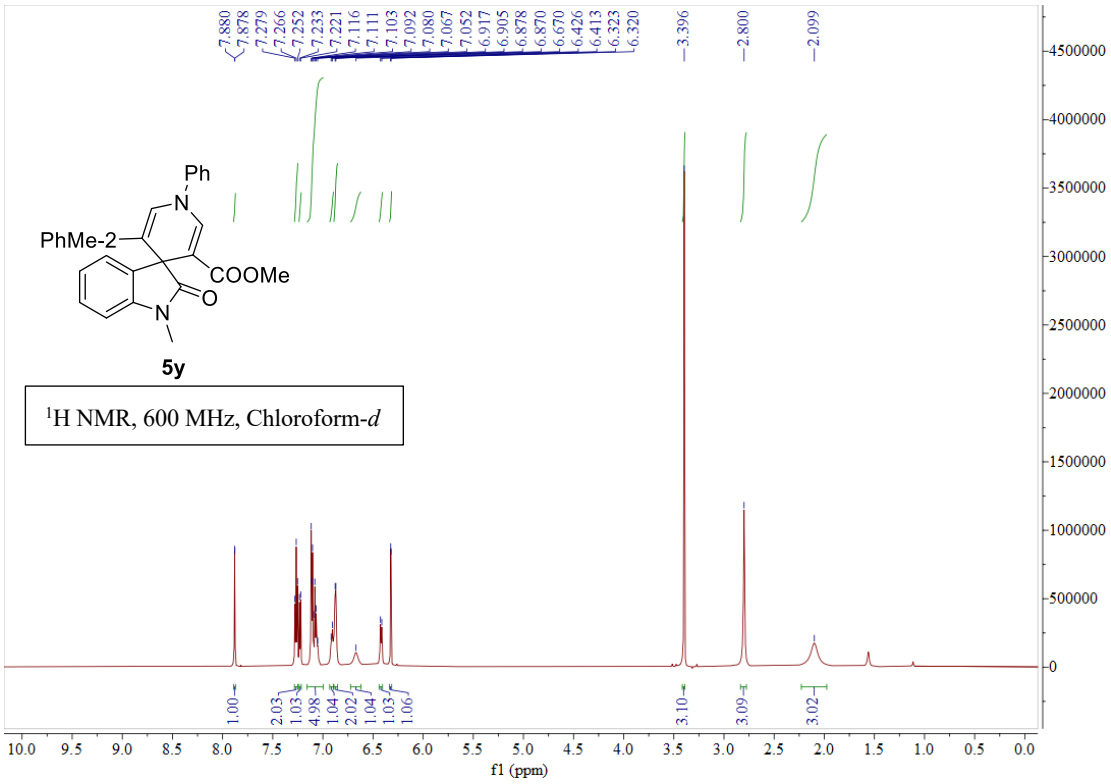


5w

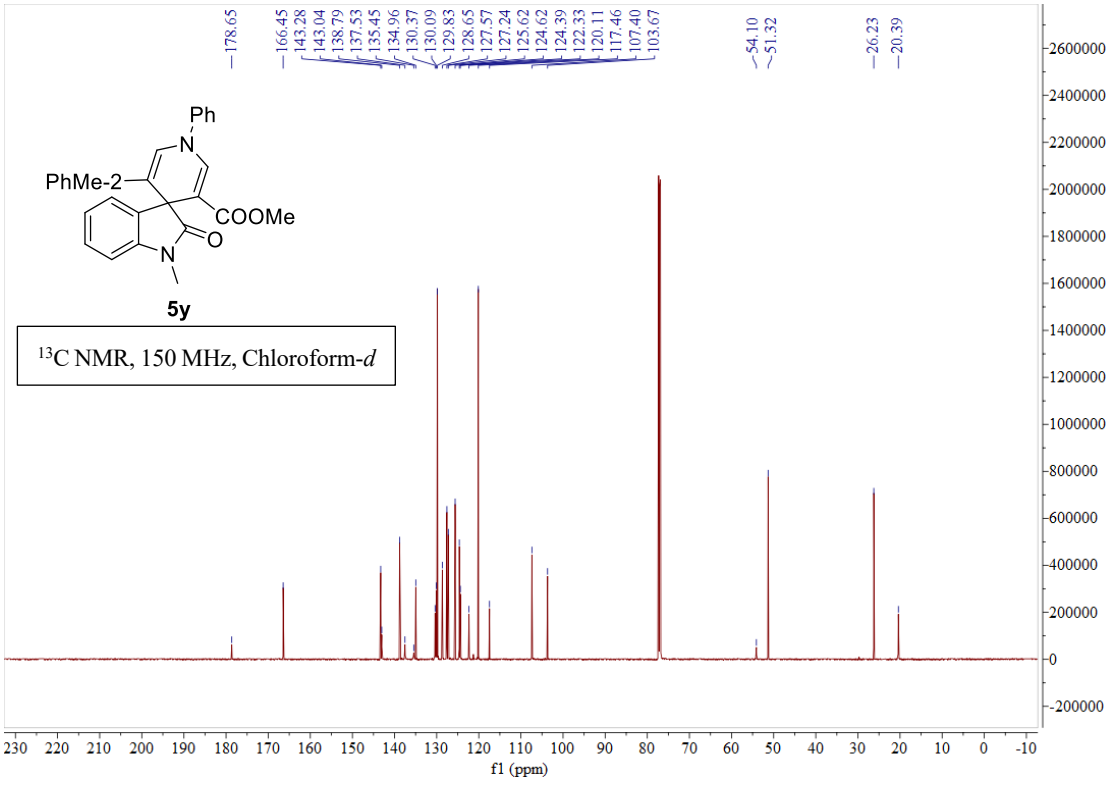
^{13}C NMR, 150 MHz, Chloroform-*d*


Ph
N
PhMe-3
COOMe
O
N
5x
[1]H NMR, 600 MHz, Chloroform-d
f1 (ppm)

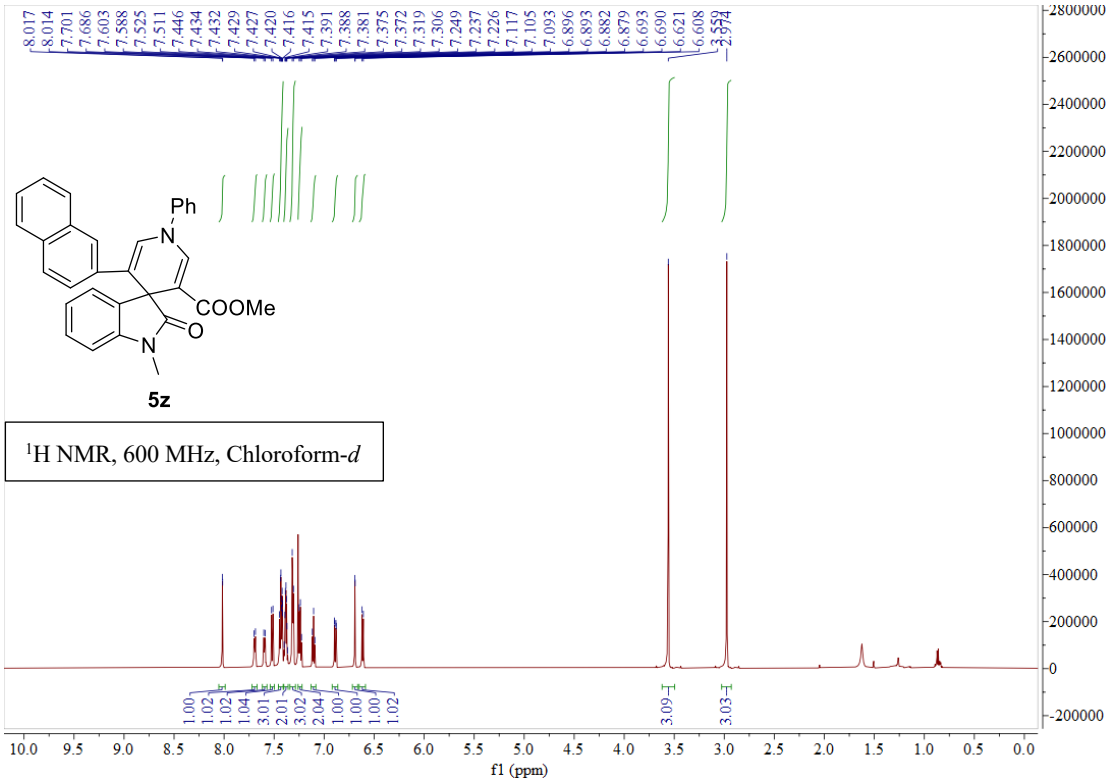

Ph
N
PhMe-3
COOMe
O
N
5x
[13]C NMR, 150 MHz, Chloroform-d
f1 (ppm)

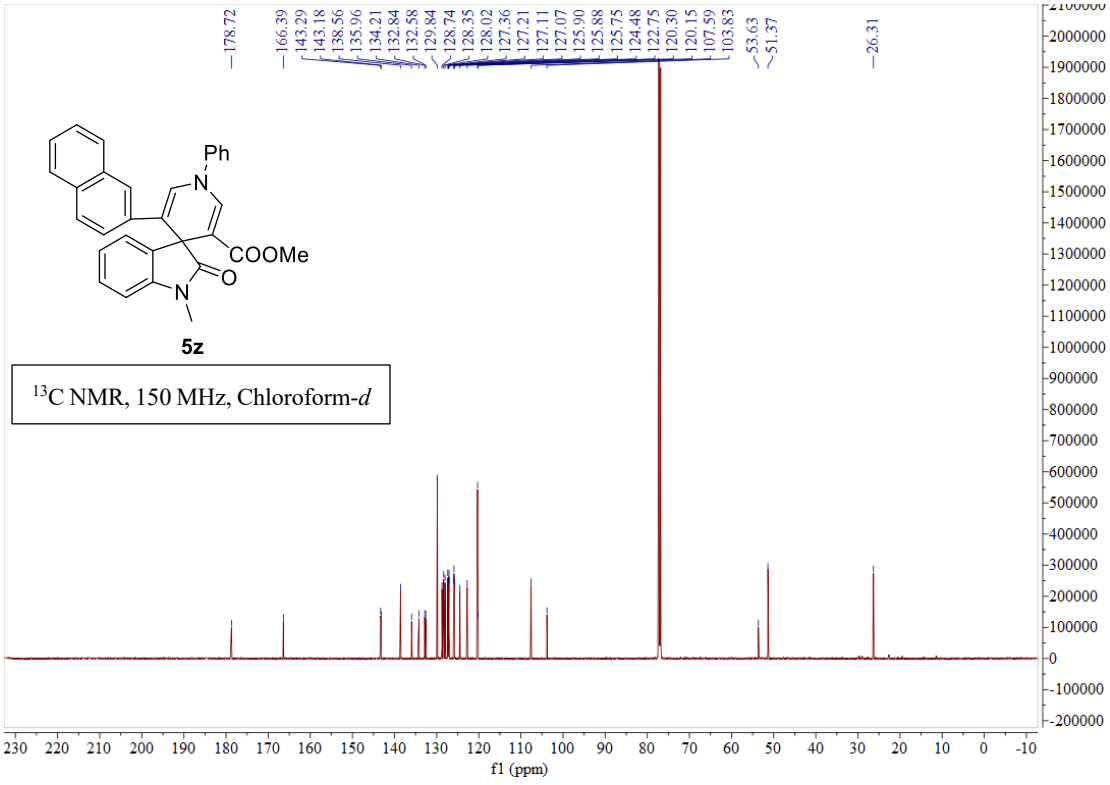


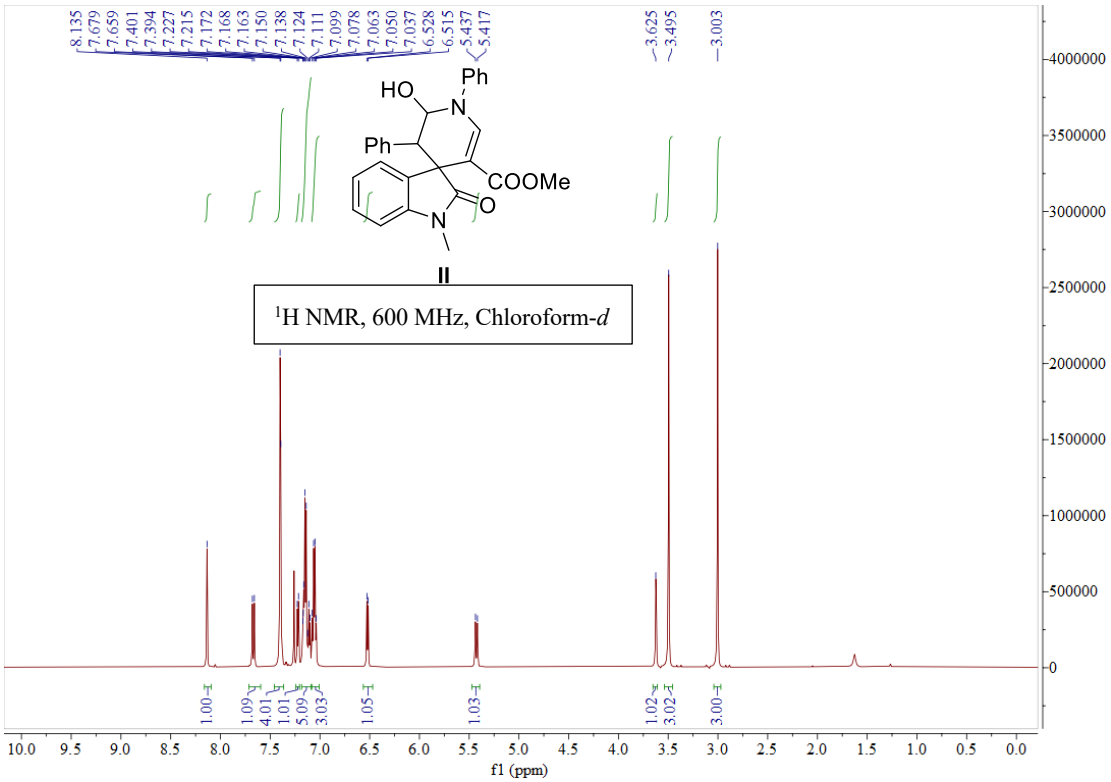
^{1}H NMR, 600 MHz, Chloroform-*d*

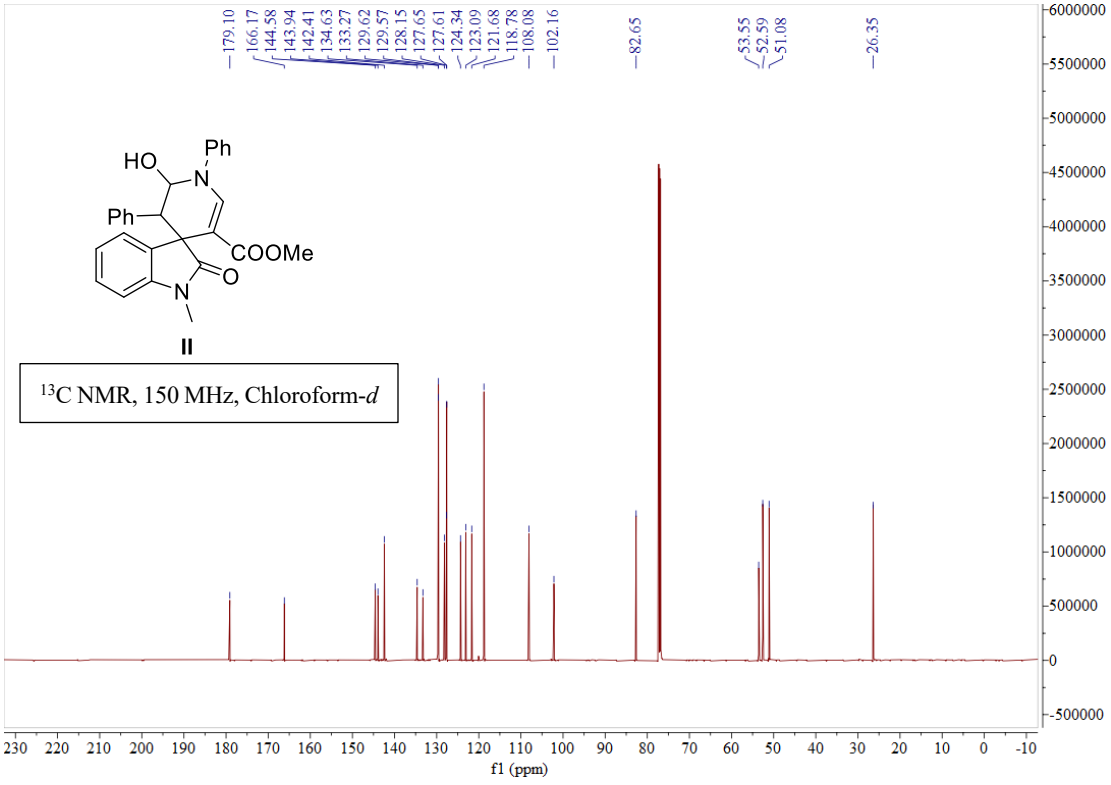


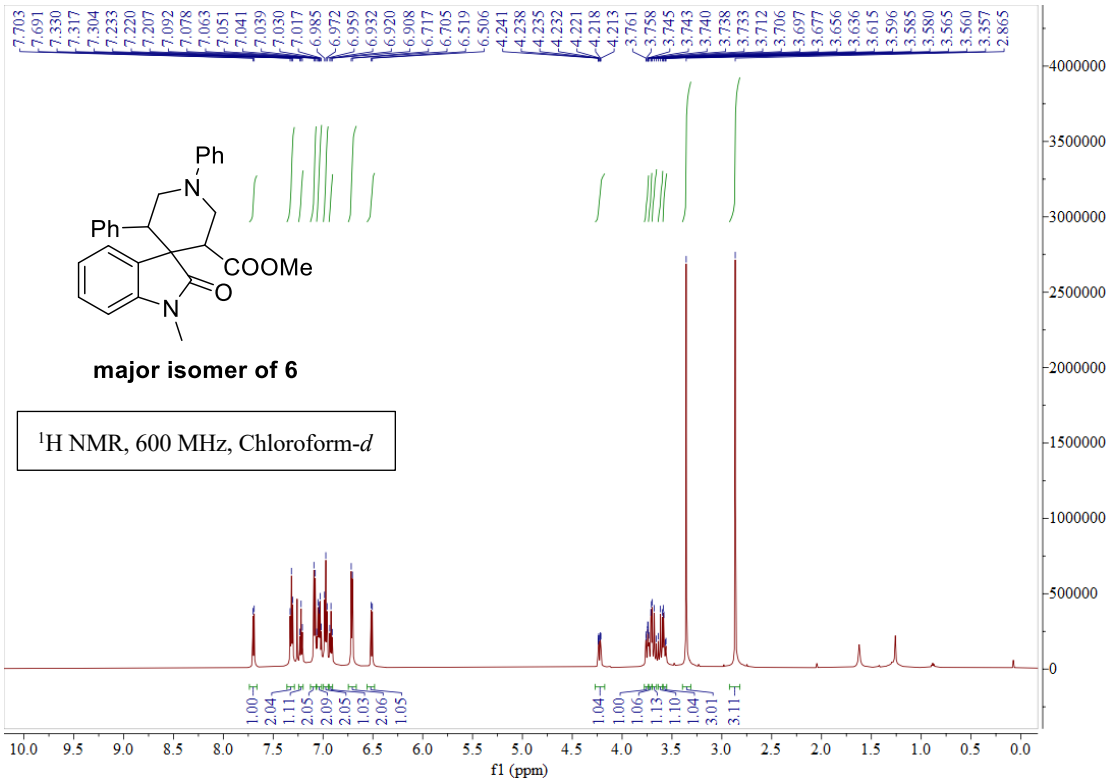
^{13}C NMR, 150 MHz, Chloroform-*d*

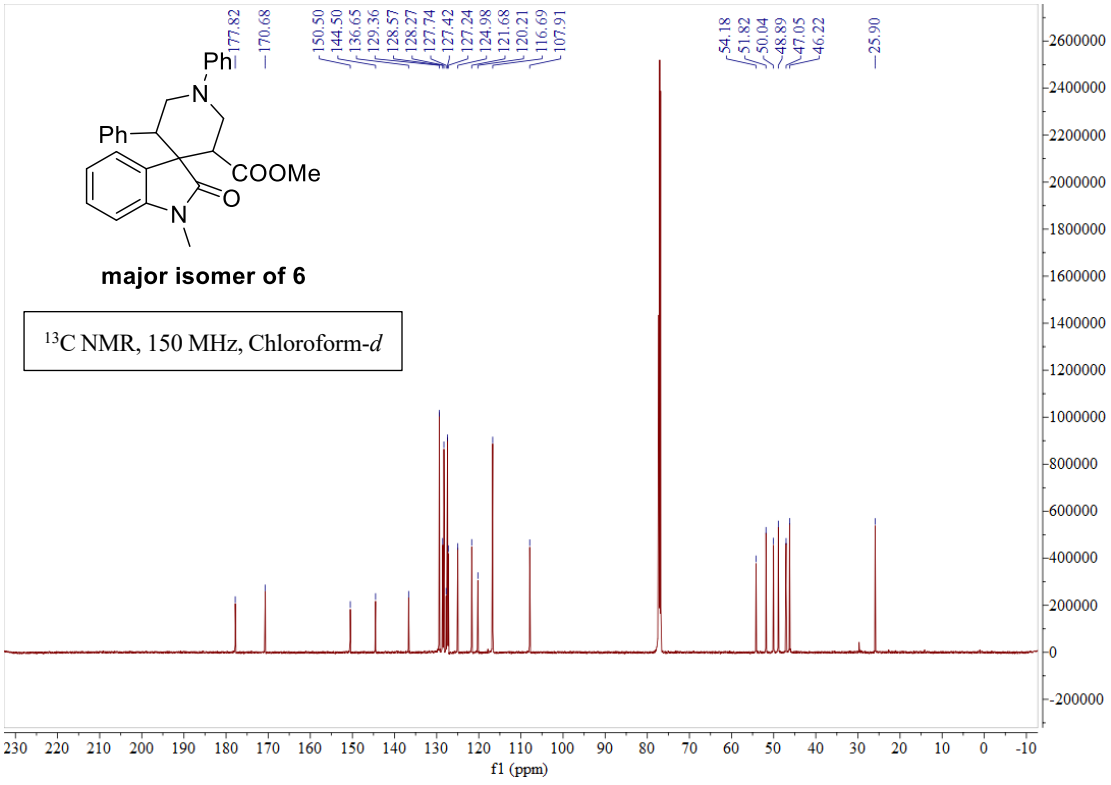

Ph
N
COOMe
O
N
5z
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)

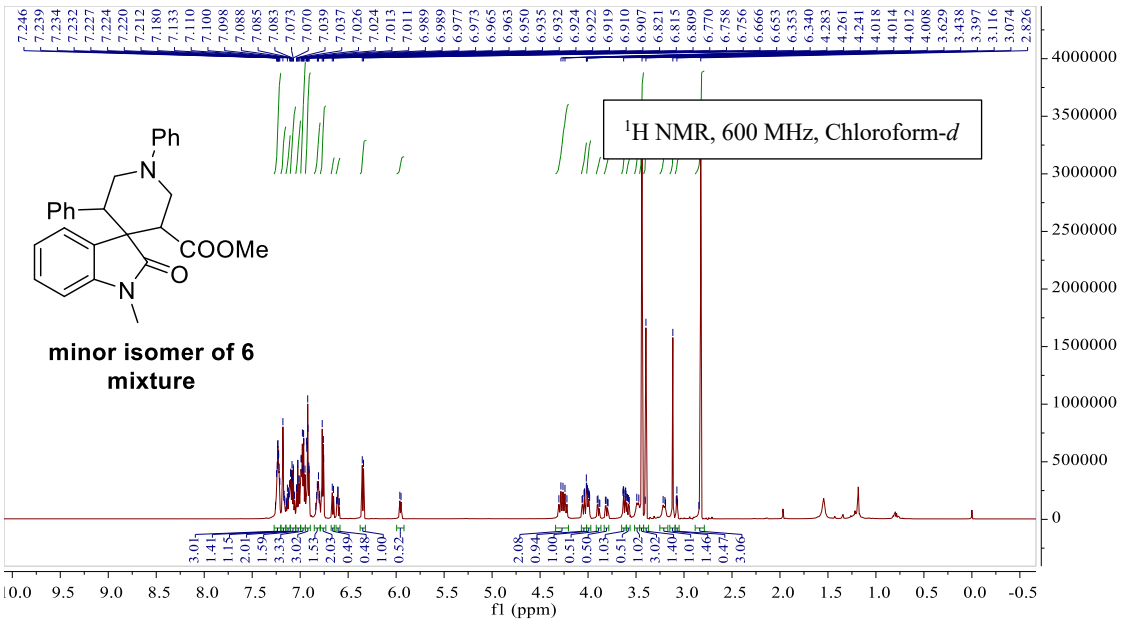

Ph
N
COOMe
O
N
5z
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)

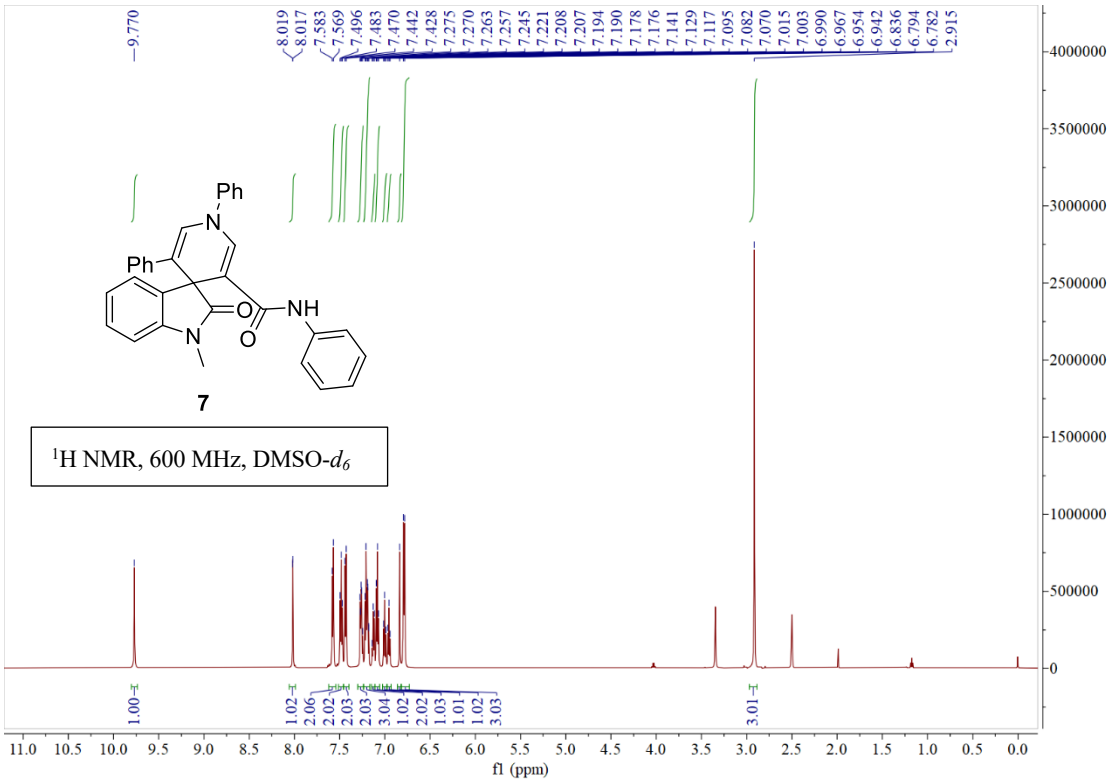

8.135
7.679
7.659
7.401
7.394
7.227
7.215
7.172
7.168
7.163
7.150
7.138
7.124
7.111
7.099
7.078
7.063
7.050
7.037
6.528
6.515
5.437
5.417
3.625
3.495
3.003
HO
Ph
N
Ph
COOMe
O
N
II
1H NMR, 600 MHz, Chloroform-d
1.00
1.09
4.01
1.01
5.09
3.03
1.05
1.03
1.02
3.02
3.00
f1 (ppm)


179.10
166.17
144.58
143.94
142.41
134.63
133.27
129.62
129.57
128.15
127.65
127.61
124.34
123.09
121.68
118.78
108.08
102.16
82.65
53.55
52.59
51.08
26.35
HO
Ph
N
Ph
COOMe
O
N
II
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)


major isomer of 6
1H NMR, 600 MHz, Chloroform-d
f1 (ppm)

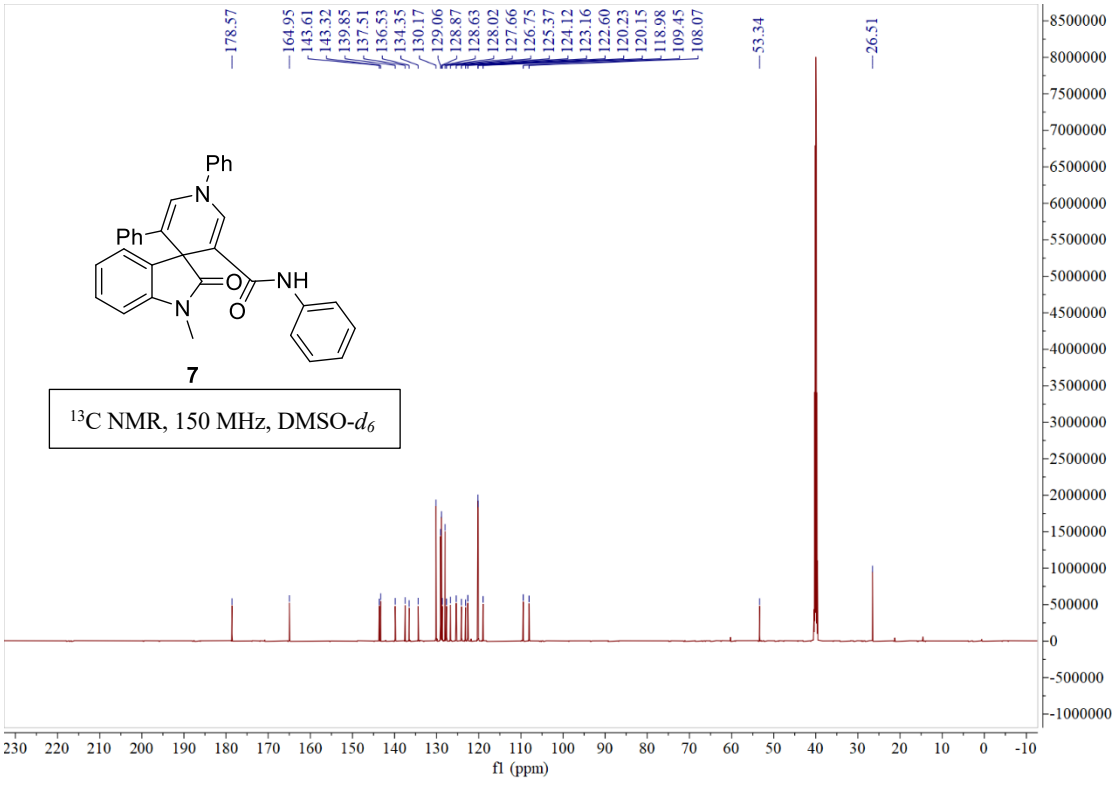

major isomer of 6
13C NMR, 150 MHz, Chloroform-d
f1 (ppm)


Ph
N
Ph
COOMe
O
N
minor isomer of 6 mixture
^{1}H NMR, 600 MHz, Chloroform-*d*
f1 (ppm)



7

^{1}H NMR, 600 MHz, DMSO-d_6



7

^{13}C NMR, 150 MHz, DMSO-d_6