Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-light-mediated defluorinative cyclization of α-fluoro-β-enamino esters catalyzed by 4-CzIPN

Yi-Fan Song,[a] Xiaoyin Niu,*[a,b] Jincan Zhao,[a] Shigang Shen[a] and Xiu-Long Yang*[a]

[a]*Key Laboratory of Chemical Biology of Hebei Province, Key Laboratory of Medicinal Chemistry and Molecular Diagnosis of the Ministry of Education and College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P.R. China.*
[b]*Postdocttoral Reserch Station of Chemistry Affiliated College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P.R. China.*

Corresponding Author
**E-mail*: yangxl@hbu.edu.cn; niuyang0906@126.com

Table of Contents

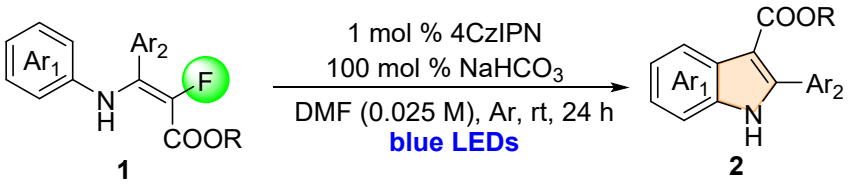
General Information

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR (400 MHz, 101 MHz and 565 MHz, respectively) spectra were measured in $CDCl_3$ recorded on Bruker Avance DPX 400 MHz spectrometer. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. NMR Spectra recorded in $CDCl_3$ were referenced to tetramethylsilane at 0 ppm for ^{1}H or referenced to residual $CHCl_3$ at 77.16 ppm for ^{13}C. The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), *etc*. Photoluminescence spectra were measured on a Horiba Fluoremax-4 PLUS spectrofluorometer (HORIBA Instruments Incorporated, Edison, USA) with a xenon lamp as an excitation light source. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI. Irradiation with blue light was performed using TaoYuan LED (3W, λ_{max} = 440 nm, 145 lm @1200mA).

Substrates Preparation

Aromatic β-ketoesters,[1] α-fluoro-β-enamino esters **1**,[2] *N*-aryl enamine **3**,[3] α-chloro-β-enamino esters **4**[4] and α-bromo-β-enamino esters **5**[4] were synthesized according to the literature and the NMR spectroscopy was consisted with those data.

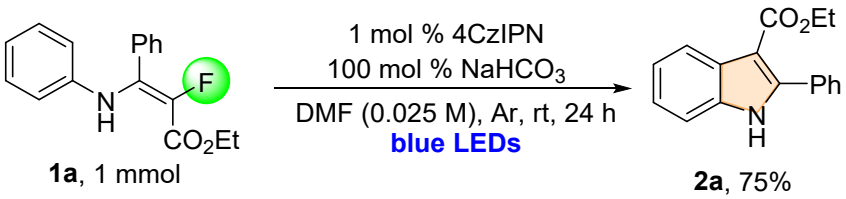
General Experimental Procedure



A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with α-fluoro-β-enamino esters **1** (0.1 mmol), $NaHCO_3$ (0.1 mmol) and 4CzIPN (1 mol%) in DMF (4.0 mL). The mixture was bubbled with a stream of Argon for about 0.5 h. The sample was then irradiated by 3 W blue LEDs (λ_{max} = 440 nm) for 24 h. Upon completion of the

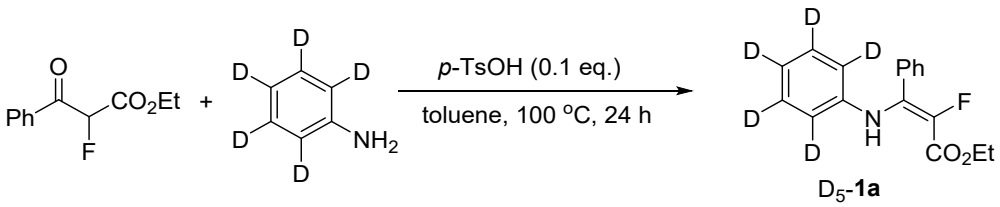
reaction, the solvent was then removed under vacuum (under high vacuum to remove DMF). The residue was purified with chromatography column on silica gel using mixtures of ethyl acetate and petroleum to give the corresponding products. The identity and purity of the product was confirmed by ^{1}H NMR, ^{13}C NMR or ^{19}F NMR spectroscopic analysis.

1 mmol Scale Synthesis of 2a



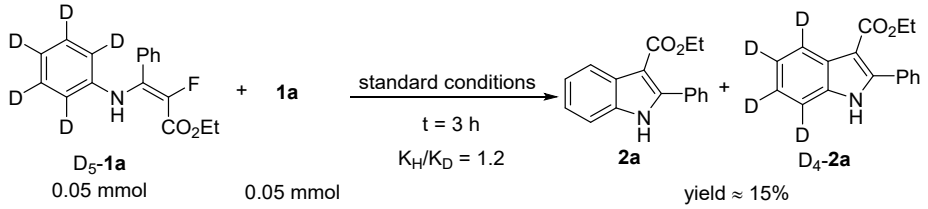
A 100 mL Pyrex tube equipped with a magnetic stir bar was charged with α-fluoro-β-enamino esters **1a** (1 mmol), $NaHCO_3$ (1 mmol) and 4CzIPN (1 mol%) in DMF (40 mL). The mixture was bubbled with a stream of Argon for about 0.5 h. The reaction was stirred and irradiated using a 10 W Kessil blue LED lamp (PR160-456 nm, 25% intensity, 4 cm away) for 24 h. After reaction, the solution was extracted with ethyl acetate. Then the organic phase was combined together and washed with brine and dried over anhydrous sodium sulphate. Upon removal of solvent under vacuum, the residue was purified by chromatography on silica gel to get the products **2a** (199.0 mg, 75%).

The Procedure for Synthesis of D_5-1a



With the preceding procedure[2] above using ethyl 2-fluoro-3-oxo-3-phenylpropanoate (210 mg, 1.0 mmol), aniline-2,3,4,5,6-d_5 (98 mg, 1.0 mmol) and *p*-TsOH (0.1 eq., 0.1 mmol) in toluene (2 mL), desired D_5-**1a** (101 mg, 0.4 mmol, 35%) was obtained as a pale yellow solid (132 mg, 35%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 7.41 – 7.44 (m, 2H), 7.34 – 7.36 (m, 3H), 4.36 (q, J = 7.2 Hz, 2H), 1.39 (q, J = 7.2 Hz, 3H).

Competing Kinetic Isotope Effect (KIE) Experiments



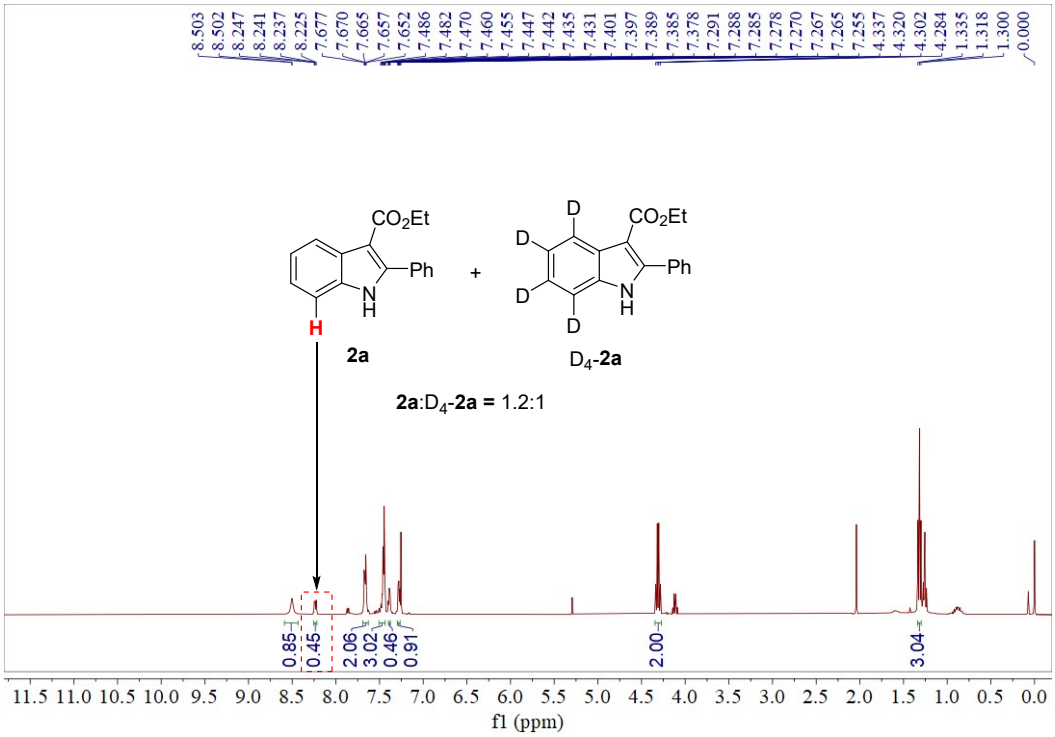


Fig. S1 Intermolecular KIE with D_5-**1a** and **1a**

Spectroscopic Studies

a) UV/Vis absorption spectrum

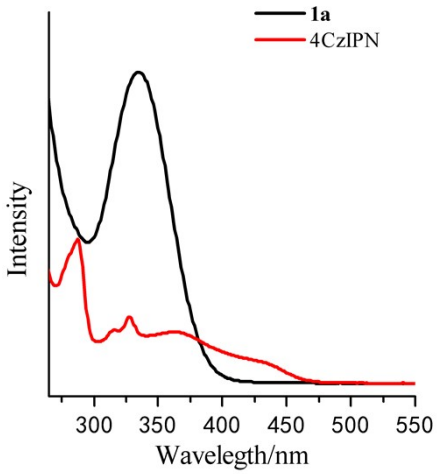


Fig. S2 UV/Vis absorption spectra of 4CzIPN (1×10^{-5} M), α-fluoro-β-enamino esters **1a** (1×10^{-5} M) in DMF.

b) Fluorescence excitation spectrum

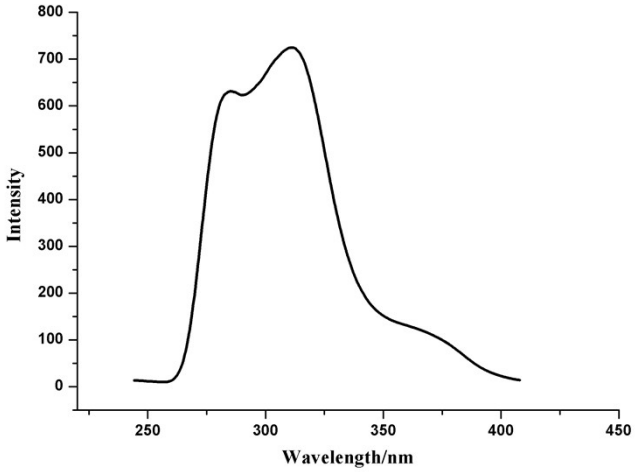


Fig. S3 Excitation spectra of α-fluoro-β-enamino esters **1a** (1×10^{-4} M) in DMF at room temperature.

c) Fluorescence emission spectrum

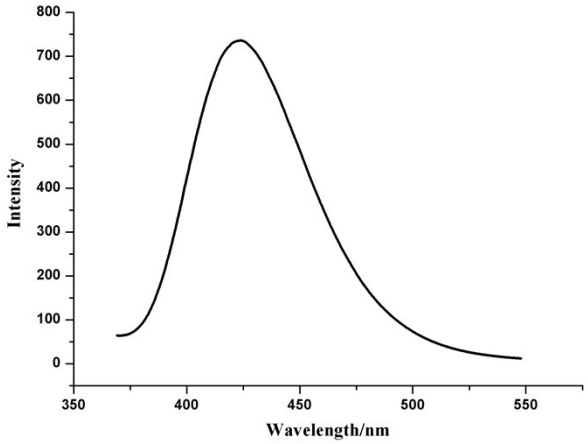


Fig. S4 Emission spectra of α-fluoro-β-enamino esters **1a** (1×10^{-4} M) in DMF at room temperature with excitation at 311 nm.

d) Phosphorescence spectrum

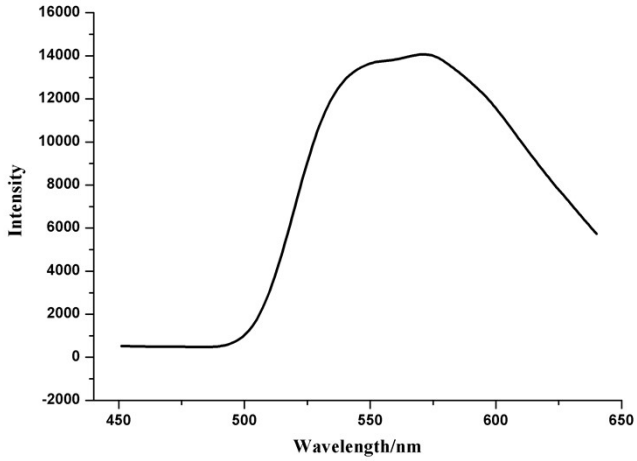


Fig. S5 Phosphorescence spectra of α-fluoro-β-enamino esters **1a** (1×10^{-3} M) in 2-MeTHF glass at 77 K recorded 2 ms pulsed excitation at 335 nm.

e) Fluorescence quenching study of 4CzIPN in DMF

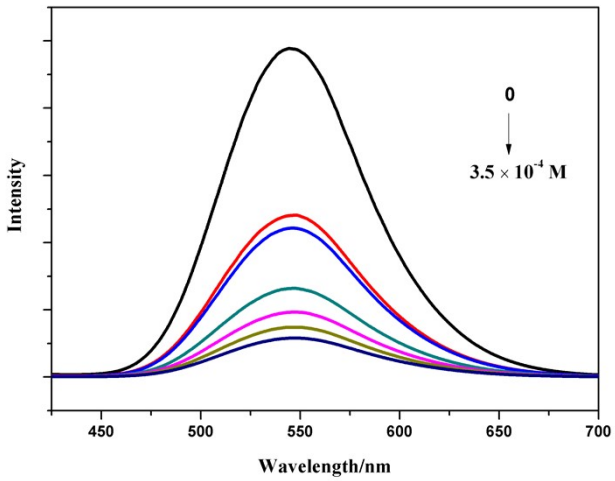


Fig. S6 Luminescence spectra of 4CzIPN (1×10^{-4} M) with α-fluoro-β-enamino esters **1a** (25 mM) in degassed DMF with excitation at 360 nm.

Cyclic Voltammetry Measurements

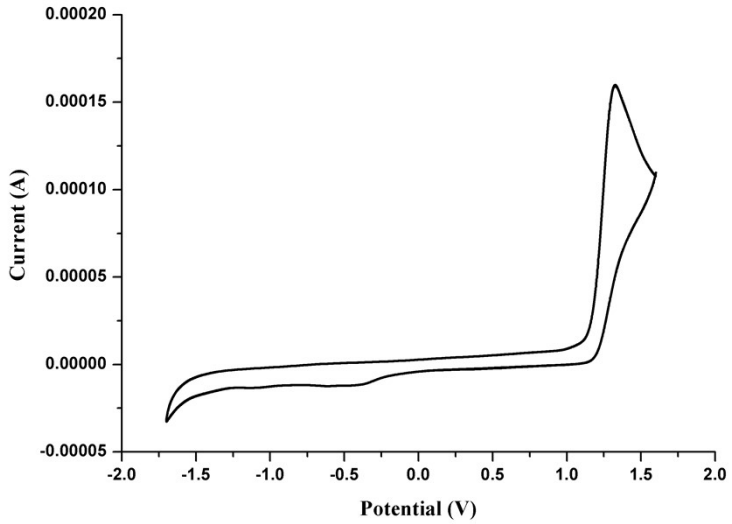


Fig. S7 CV spectra of α-fluoro-β-enamino esters **1a** (5×10^{-3} M) and 0.1 M NBu_4PF_6 in CH_3CN with scan rate 100 mV/s**.**

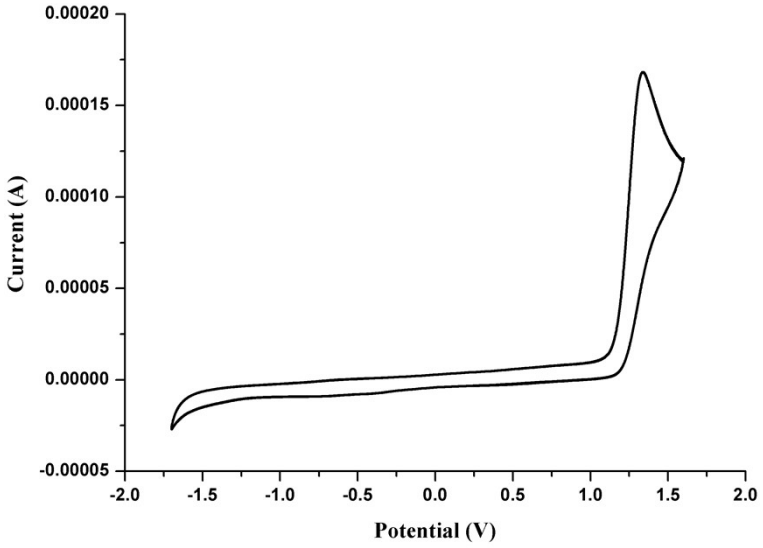


Fig. S8 CV spectra of α-fluoro-β-enamino esters **1a (**5×10^{-3} M**)**, $NaHCO_3$ (5×10^{-3} M) and 0.1 M NBu_4PF_6 in CH_3CN with scan rate 100 mV/s**.**

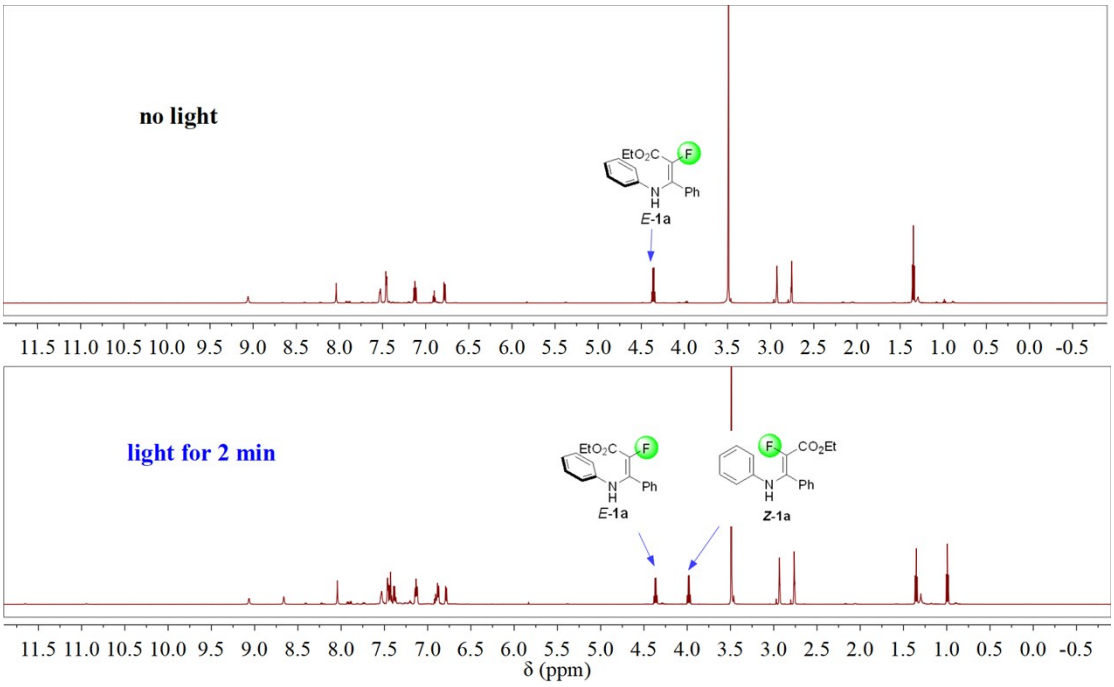


Fig. S9 ^{1}H NMR spectra of the reaction mixture in DMF-d_7 after irradiated by blue LEDs (λmax = 440 nm) for 0 and 2 minutes (DMF-d_7, 600 MHz).

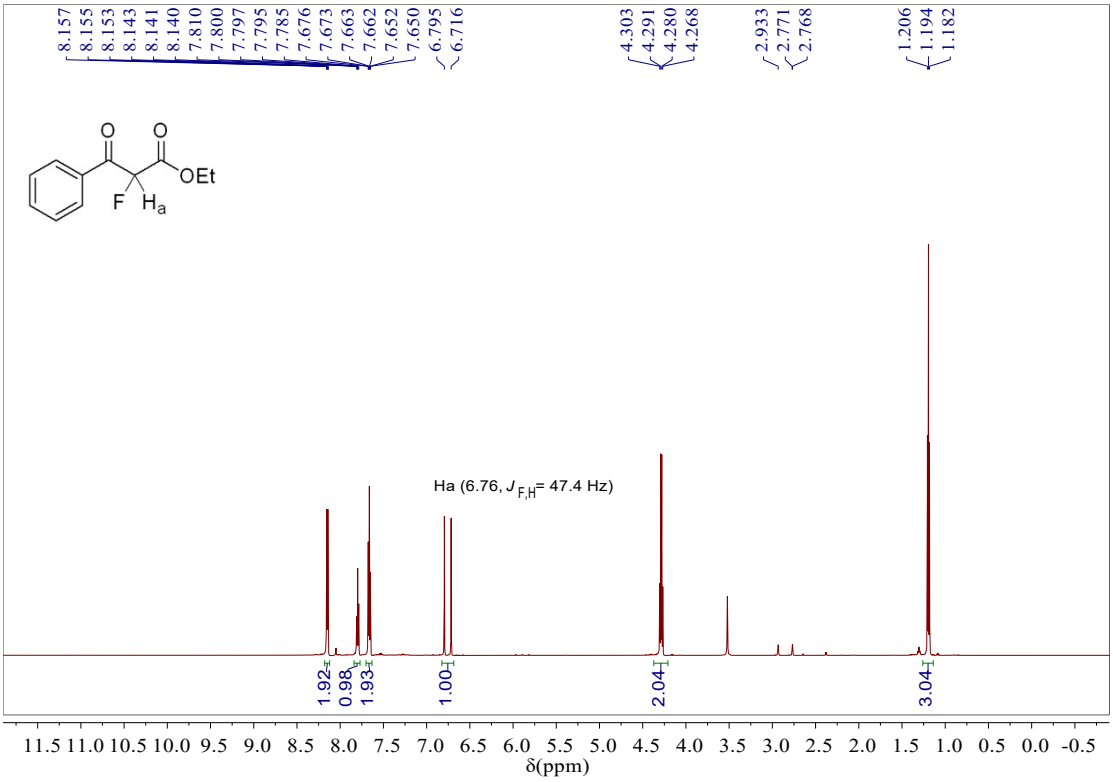
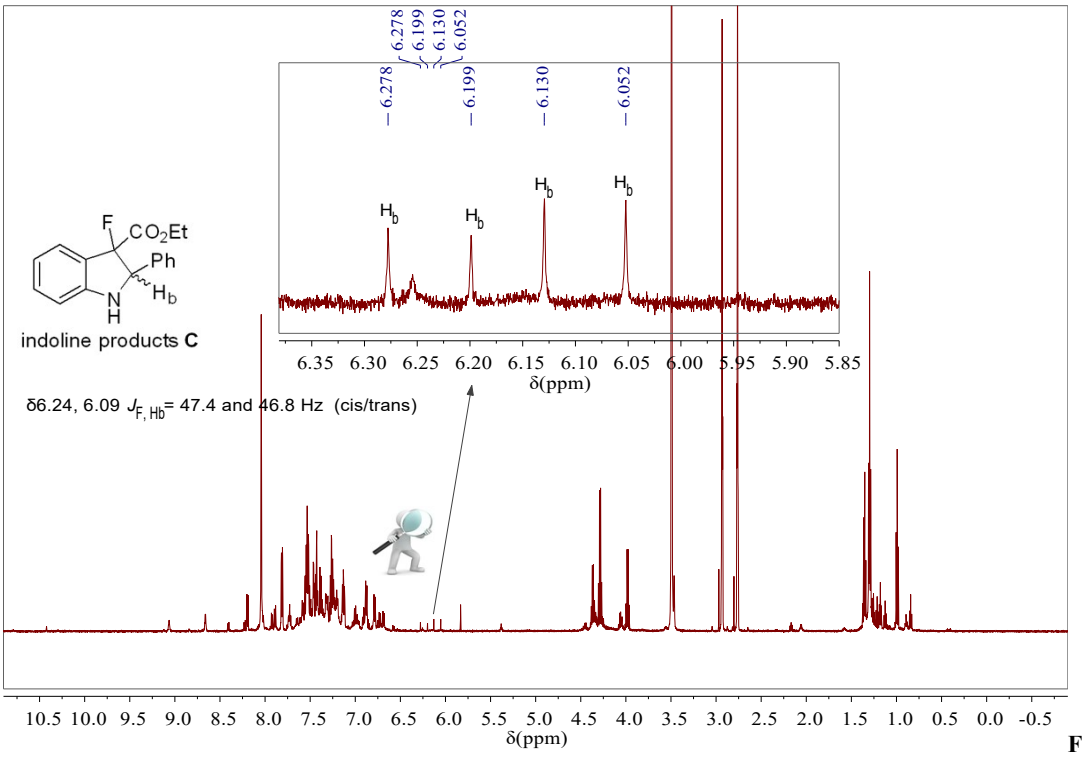


Fig. S10 ^{1}H NMR spectra of ethyl 2-fluoro-3-oxo-3-phenylpropanoate (DMF-d$_7$, 600 MHz).



ig. S11 [1]H NMR spectra of the reaction mixture in DMF-d_7, after irradiated by blue LEDs for 20 minutes (DMF-d_7, 600 MHz)

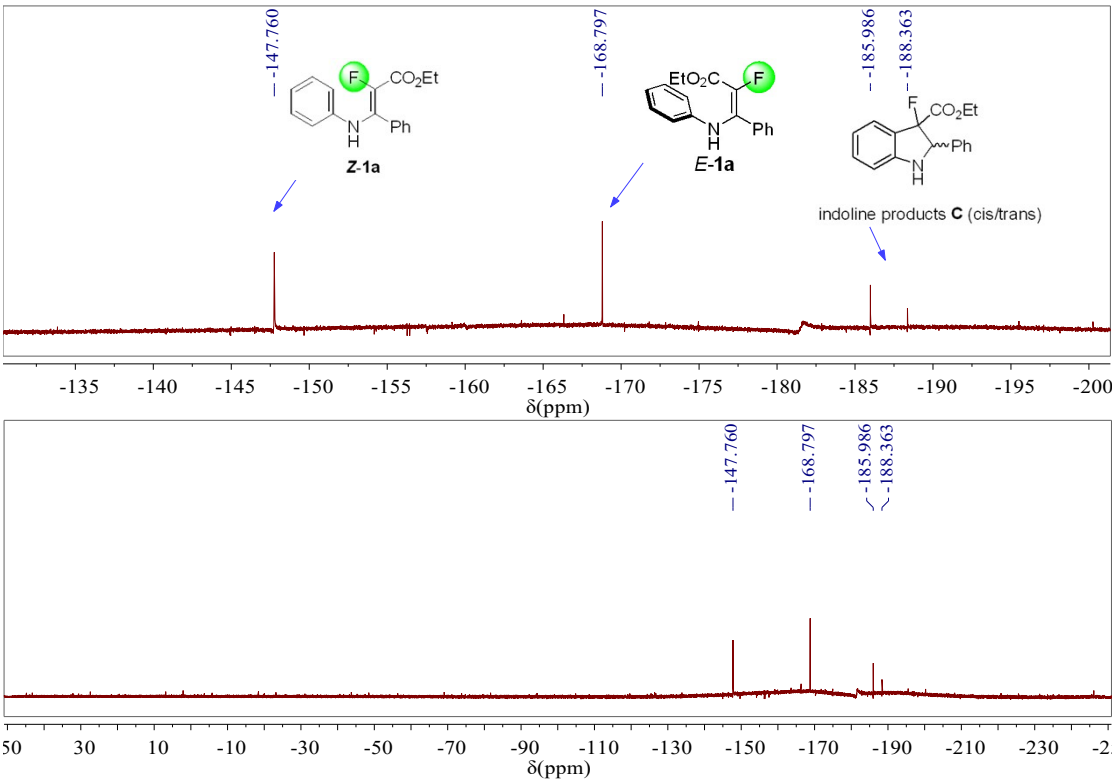
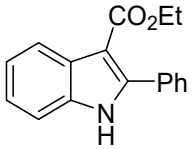


Fig. S12 [19]F NMR spectra of the reaction mixture in DMF-d_7, after irradiated by blue LEDs for 20 minutes (DMF-d_7, 575 MHz)

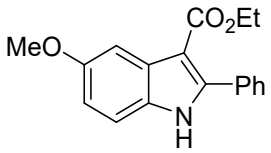
The Spectra Data of Products

Ethyl 2-phenyl-1*H*-indole-3-carboxylate (2a)[5]



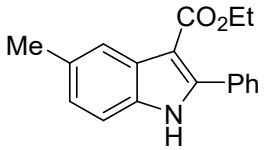
White solid; yield 23.9 mg, 90%; $\mathbf{R}_f$ = 0.34 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.23 (m, 1H), 7.62 – 7.69 (m, 2H), 7.41 – 7.45 (m, 3H), 7.36 (m, 1H), 7.25 – 7.29 (m, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.52, 144.64, 135.25, 132.14, 129.72, 129.29, 128.22, 127.71, 123.31, 122.27, 122.19, 111.16, 104.79, 59.85, 14.43; **ESI-HRMS** Calcd for $C_{17}H_{16}NO_2^+$ $[M+H]^+$ 266.1176, found 266.1181.

Ethyl 2-phenyl-1*H*-indole-3-carboxylate (2b)[5]



Brown solid; yield 26.4 mg, 90%; $\mathbf{R}_f$ = 0.30 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.59 – 7.62 (m, 2H), 7.39 – 7.41 (m, 3H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.63, 155.85, 144.90, 132.30, 130.30, 129.68, 129.66, 129.15, 128.66, 128.13, 113.55, 112.00, 103.68, 59.72, 55.81, 14.36; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_3^+$ $[M+H]^+$ 296.1281, found 296.1285.

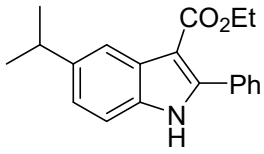
Ethyl 5-methyl-2-phenyl-1*H*-indole-3-carboxylate (2c)[5]



Yellow solid; yield 27.1 mg, 97%; $\mathbf{R}_f$ = 0.39 (PE/EtOAc = 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.03 (s, 1H), 7.61 – 7.64 (m, 2H), 7.41 – 7.44 (m, 3H), 7.24 (m,

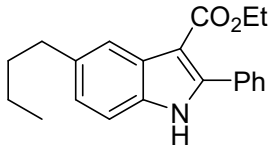
1H), 7.08 (d, *J* = 8.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.59, 144.54, 133.59, 132.36, 131.65, 129.71, 129.18, 128.18, 128.04, 124.86, 121.89, 110.77, 104.37, 59.76, 21.88, 14.44; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_2^+$ $[M+H]^+$ 280.1332, found 280.1337.

Ethyl 5-isopropyl-2-phenyl-1*H*-indole-3-carboxylate (2d) (new compound)



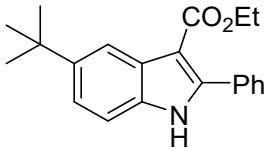
Brown solid; yield 29.7 mg, 97%; **R_f** = 0.43 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.10 (s, 1H), 7.60 –7.62 (m, 2H), 7.40 –7.43 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.10 – 7.16 (m, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.06 (m, 1H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.29 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.63, 144.65, 143.08, 133.87, 132.42, 129.71, 129.16, 128.18, 127.95, 122.52, 119.22, 110.94, 104.59, 59.74, 34.58, 24.73, 14.39; **ESI-HRMS** Calcd for $C_{20}H_{22}NO_2^+$ $[M+H]^+$ 308.1645, found 308.1649.

Ethyl 5-butyl-2-phenyl-1*H*-indole-3-carboxylate (2e) (new compound)



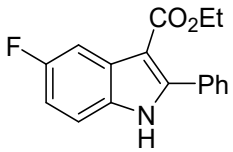
Yellow solid; yield 26.4 mg, 82%; **R_f** = 0.39 (PE/EtOAc = 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.04 (s, 1H), 7.62 (d, *J* = 3.4 Hz, 2H), 7.42 (d, *J* = 1.9 Hz, 3H), 7.29 (s, 1H), 7.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 4.29 (q, *J* = 7.3 Hz, 2H), 2.75 (t, *J* = 7.7 Hz, 2H), 1.68 (t, *J* = 7.7 Hz, 2H), 1.40 (q, *J* = 7.4 Hz, 2H), 1.31 – 1.27 (m, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.59, 144.51, 136.96, 133.74, 132.42, 129.72, 129.19, 128.20, 128.01, 124.38, 121.37, 110.76, 104.53, 59.75, 36.11, 34.53, 22.53, 14.42, 14.17; **ESI-HRMS** Calcd for $C_{21}H_{24}NO_2^+$ $[M+H]^+$ 322.1802, found 322.1808.

Ethyl 5-(tert-butyl)-2-phenyl-1*H*-indole-3-carboxylate (2f)[6]



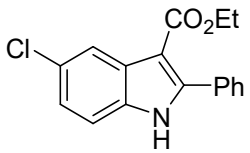
Yellow solid; yield 29.3 mg, 92%; $\mathbf{R_f}$=0.43 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.27 (d, *J* = 0.9 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.38 (q, *J* = 2.6, 1.8 Hz, 3H), 7.35 – 7.26 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.41 (s, 9H), 1.31 – 1.27 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.66, 145.23, 144.74, 133.46, 132.36, 129.69, 129.16, 128.17, 127.59, 121.59, 118.12, 110.67, 104.69, 59.73, 34.99, 31.98, 14.36; **ESI-HRMS** Calcd for $C_{21}H_{24}NO_2^+$ $[M+H]^+$ 322.1802, found 322.1808.

Ethyl 5-fluoro-2-phenyl-1*H*-indole-3-carboxylate (2g)[5]



White solid; yield 27.0 mg, 96%; $\mathbf{R_f}$ = 0.32 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.86 (dd, *J* = 10.1, 2.6 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.43 – 7.37 (m, 3H), 7.26 (d, *J* = 6.1 Hz, 1H), 6.99 (td, *J* = 9.0, 2.6 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.25, 159.34 (d, $^1J_{C,F}$ = 237.5 Hz), 146.14, 131.78 (d, $^3J_{C,F}$ = 7.7 Hz), 129.64, 129.48, 128.50 (d, $^2J_{C,F}$ = 11.2 Hz), 128.25, 112.02, 111.92, 111.68 (d, $^2J_{C,F}$ = 26.4 Hz), 107.59 (d, $^2J_{C,F}$ = 25.5 Hz), 104.98 (d, $^3J_{C,F}$ = 4.5 Hz), 59.98, 14.42; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -121.22 (s, 1F); **ESI-HRMS** Calcd for $C_{17}H_{15}FNO_2^+$ $[M+H]^+$ 284.1081, found 184.1086.

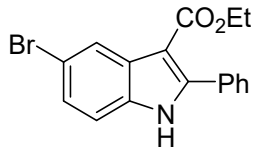
Ethyl 5-chloro-2-phenyl-1*H*-indole-3-carboxylate (2h)[5]



Pale yellow solid; yield 21.9 mg, 73%; $\mathbf{R_f}$ = 0.33 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.19 (s, 1H), 7.64 – 7.57 (m, 2H), 7.43 – 7.38 (m, 3H), 7.24 – 7.18 (m, 2H), 4.32 – 4.22 (m, 2H), 1.30 (td, *J* = 7.1, 2.3 Hz, 3H); **^{13}C NMR** (101

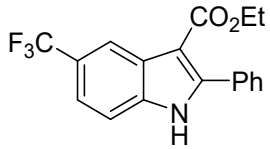
MHz, $CDCl_3$) δ 165.11, 145.76, 133.64, 131.67, 129.67, 129.54, 128.97, 128.84, 128.27, 127.91, 123.65, 121.84, 112.22, 60.05, 14.43; **ESI-HRMS** Calcd for $C_{17}H_{15}ClNO_2^+$ $[M+H]^+$ 300.0786, found 300.0790.

Ethyl 5-bromo-2-phenyl-1*H*-indole-3-carboxylate (2i)[5]



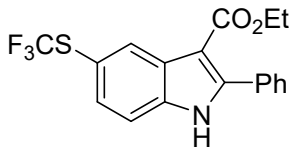
Yellow solid; yield 33.1 mg, 96%; $\mathbf{R_f}$=0.35 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.35 (s, 1H), 7.60 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.41 (dd, *J* = 2.7, 0.9 Hz, 3H), 7.33 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 4.31 – 4.23 (m, 2H), 1.32 – 1.28 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.09, 145.57, 133.91, 131.59, 129.66, 129.55, 129.38, 128.26, 126.23, 124.87, 115.64, 112.64, 104.39, 60.07, 14.42; **ESI-HRMS** Calcd for $C_{17}H_{15}BrNO_2^+$ $[M+H]^+$ 344.0281, found 344.0286.

Ethyl 2-phenyl-5-(trifluoromethyl)-1*H*-indole-3-carboxylate (2j)[5]



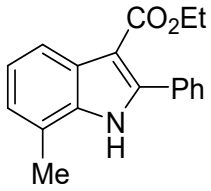
Pale yellow solid; yield 24.6 mg, 74%; $\mathbf{R_f}$ = 0.32 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.54 (d, *J* = 0.8 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.51 – 7.43 (m, 5H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.10, 146.24, 136.64, 131.38, 130.82, 129.66, 128.30, 127.99, 127.17, 124.45 (q, $^2J_{C,F}$ = 31.5 Hz),125.30 (q, $^1J_{C,F}$ = 272.5 Hz), 119.97 (q, $^3J_{C,F}$ = 4.4 Hz) , 111.60, 105.36, 60.23, 14.33; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.69 (s, 3F); **ESI-HRMS** Calcd for $C_{18}H_{15}F_3NO_2^+$ $[M+H]^+$ 344.1049, found 344.1049.

Ethyl 2-phenyl-5-((trifluoromethyl)thio)-1*H*-indole-3-carboxylate (2k) (new compound)



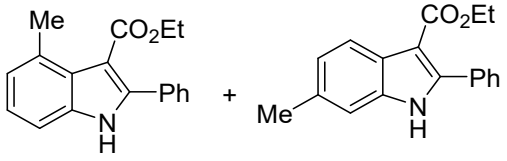
Pale yellow solid; yield 17.6mg, 48%; $\mathbf{R_f}$ = 0.35 (PE/EtOAc =5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.55 (s, 1H), 7.67 – 7.58 (m, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.41 (m, 3H), 7.40 – 7.36 (m, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.13, 146.09, 136.35, 131.46, 131.31, 130.96, 130.0 (q, $^1J_{C,\,F}$ = 306.5 Hz), 129.68, 129.60, 128.41, 128.28, 116.90, 112.24, 104.91, 60.25, 14.33; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -43.55 (s, 3F); **ESI-HRMS** Calcd for $C_{18}H_{15}F_3NO_2S^+$ $[M+H]^+$ 366.0770, found 366.0777.

Ethyl 7-methyl-2-phenyl-1*H*-indole-3-carboxylate (2l)[5]



Pale yellow solid; yield 23.8 mg, 85%; $\mathbf{R_f}$ = 0.43 (PE/EtOAc =5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.43 (dt, *J* = 5.4, 2.9 Hz, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 4.32 – 4.26 (m, 2H), 2.50 (s, 3H), 1.34 – 1.29 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.51, 144.29, 134.81, 132.38, 129.78, 129.25, 128.23, 127.32, 123.93, 122.40, 120.26, 119.98, 105.39, 59.79, 16.66, 14.43; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_2^+$ $[M+H]^+$ 280.1332, found 280.1338.

Ethyl 4-methyl-2-phenyl-1*H*-indole-3-carboxylate (2m) and Ethyl 6-methyl-2-phenyl-1*H*-indole-3-carboxylate (2m')[7]



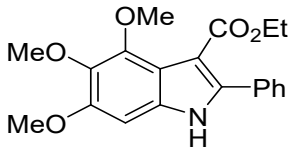
2m **2m'**

2m: **2m'** = 2.0:1

White solid; yield 26.5 mg, 95%; $\mathbf{R_f}$ = 0.33 (PE/EtOAc =8:1); **^{1}H NMR** (400 MHz,

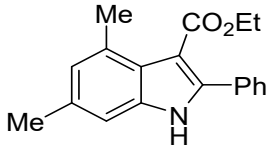
$CDCl_3$) δ 8.49 (s, 3H), 8.08 (d, J = 8.0 Hz, 1H$_{\mathbf{2m}}$), 7.62 – 7.60 (m, 2H$_{\mathbf{2m}}$), 7.53 –7.51 (m, 4H$_{\mathbf{2m+2m'}}$), 7.42 – 7.39 (m, 10H$_{\mathbf{2m+2m'}}$), 7.20 – 7.08 (m, 5H$_{\mathbf{2m+2m'}}$), 6.99 (d, J = 7.2 Hz, 2H$_{\mathbf{2m}}$), 4.27 (q, J = 7.2 Hz, 2H$_{\mathbf{2m'}}$), 4.21 (q, J = 7.2 Hz, 4H$_{\mathbf{2m}}$), 2.66 (s, 6H$_{\mathbf{2m}}$), 2.45 (s, 3H$_{\mathbf{2m'}}$), 1.29 (t, J = 7.2 Hz, 3H$_{\mathbf{2m'}}$), 1.15 (t, J = 7.2 Hz, 6H$_{\mathbf{2m}}$); **^{13}C NMR** (101 MHz, CDCl3) δ 167.10, 165.59, 144.03, 140.90, 135.70, 135.68, 133.24, 132.43, 132.27, 131.54, 129.69, 129.14, 128.84, 128.82, 128.50, 128.18, 125.86, 125.54, 123.92, 123.52, 123.40, 121.89, 111.04, 108.95, 60.66, 59.78, 21.79, 21.25, 14.44, 14.05; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_2^+$ $[M+H]^+$ 280.1332, found 280.1336.

Ethyl 4,5,6-trimethoxy-2-phenyl-1*H*-indole-3-carboxylate (2n)[5]



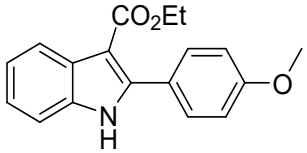
Yellow solid; yield 33.1 mg, 93%; **R$_f$**=0.38 (PE/EtOAc = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.55 – 7.49 (m, 2H), 7.38 (q, J = 7.4, 6.1 Hz, 3H), 6.62 (s, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.00 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.46, 151.97, 146.72, 139.28, 138.47, 132.56, 132.20, 128.61, 128.53, 128.50, 128.49, 114.98, 106.23, 90.04, 61.46, 60.72, 56.26, 14.17; **ESI-HRMS** Calcd for $C_{20}H_{22}NO_5^+$ $[M+H]^+$ 356.1492, found 356.1497.

Ethyl 4,6-dimethyl-2-phenyl-1*H*-indole-3-carboxylate (2o)[8]



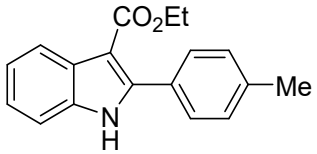
Yellow solid; yield 19.9 mg, 68%; **R$_f$**=0.47 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.52 (d, J = 7.2 Hz, 2H), 7.40 (d, J = 6.9 Hz, 3H), 6.97 (s, 1H), 6.83 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.63 (s, 3H), 2.40 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.02, 140.48, 136.21, 133.31, 132.67, 131.19, 128.84, 128.70, 128.46, 125.47, 123.77, 108.77, 107.27, 60.55, 21.57, 21.21, 14.05; **ESI-HRMS** Calcd for $C_{19}H_{20}NO_2^+$ $[M+H]^+$ 294.1489, found 294.1493.

Ethyl 2-(4-methoxyphenyl)-1*H*-indole-3-carboxylate (2p)[5]



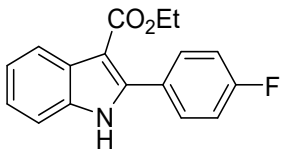
Pale yellow solid; yield 27.2 mg, 92%; $\mathbf{R_f}$ = 0.48 (PE/EtOAc =3:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.19 (d, *J* = 7.1 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.36 – 7.28 (m, 1H), 7.25 (d, *J* = 3.8 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.75, 160.39, 144.87, 135.18, 131.05, 127.79, 124.28, 123.04, 122.15, 122.04, 113.64, 111.10, 104.13, 59.80, 55.42, 14.52; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_3^+$ $[M+H]^+$ 296.1281, found 296.1285.

Ethyl 2-(*p*-tolyl)-1*H*-indole-3-carboxylate (2q)[5]



White solid; yield 24.0 mg, 86%; $\mathbf{R_f}$ = 0.33 (PE/EtOAc =8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.22 – 8.14 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 6.2, 2.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.21 (d, *J* = 4.3 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.32 – 4.23 (m, 2H), 2.35 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.63, 144.96, 139.36, 135.21, 129.56, 129.12, 128.92, 127.76, 123.13, 122.20, 122.07, 111.12, 104.47, 59.80, 21.51, 14.49; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_2^+$ $[M+H]^+$ 280.1332, found 280.1337.

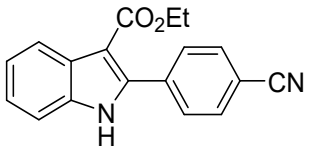
Ethyl 2-(4-fluorophenyl)-1*H*-indole-3-carboxylate (2r)[5]



White solid; yield 23.6 mg, 84%; $\mathbf{R_f}$ = 0.40 (PE/EtOAc =5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.25 – 8.16 (m, 1H), 7.61 (dd, *J* = 7.7, 5.4 Hz, 2H), 7.38 – 7.34

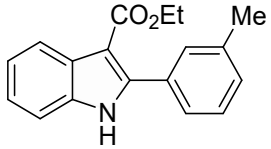
(m, 1H), 7.28 (t, J = 5.5 Hz, 2H), 7.10 (t, J = 8.2 Hz, 2H), 4.29 (q, J = 7.3 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) 165.50, 163.36 (d, $^1J_{C,F}$ = 250.6 Hz), 143.56, 135.24, 131.67 (d, $^3J_{C,F}$ = 8.4 Hz), 128.18 (d, $^4J_{C,F}$ = 3.7 Hz), 127.61, 123.47, 122.32 (2C), 115.32 (d, $^2J_{C,F}$ = 21.9 Hz), 111.15, 104.97, 59.93, 14.46; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -111.60 (s, 1F); **ESI-HRMS** Calcd for $C_{17}H_{15}FNO_2^+$ $[M+H]^+$ 284.1081, found 284.1081.

Ethyl 2-(4-cyanophenyl)-1*H*-indole-3-carboxylate (2s)[9]



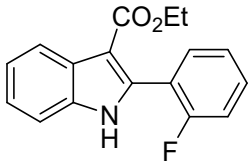
Yellow solid; yield 16.1 mg, 56%; **R_f**=0.34 (PE/EtOAc = 3:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.27–8.17 (m, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.43–7.40 (m, 1H), 7.34–7.29 (m, 2H), 4.33 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.16, 141.74, 136.67, 135.58, 132.77, 131.93, 130.51, 129.38, 127.39, 124.17, 122.70, 122.59, 112.70, 111.37, 60.23, 14.47; **ESI-HRMS** Calcd for $C_{18}H_{15}N_2O_2^+$ $[M+H]^+$ 291.1128, found 291.1130.

Ethyl 2-(*m*-tolyl)-1*H*-indole-3-carboxylate (2t)[10]



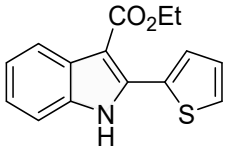
Yellow solid; yield 18.0 mg, 65%; **R_f**=0.42 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.26 – 8.20 (m, 1H), 7.45 (d, J = 6.2 Hz, 2H), 7.37 – 7.25 (m, 5H), 4.30 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.49, 144.76, 137.87, 135.22, 132.10, 130.24, 130.05, 128.15, 127.83, 126.96, 123.25, 122.28, 122.14, 111.07, 104.76, 59.78, 21.55, 14.44; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_2^+$ $[M+H]^+$ 280.1332, found 280.1336.

Ethyl 2-(2-fluorophenyl)-1*H*-indole-3-carboxylate (2u)[11]



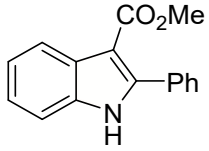
White solid; yield 11.3 mg, 40%; $\mathbf{R_f}$ = 0.31 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.24 (dd, *J* = 6.1, 3.1 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.29 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.25 – 7.14 (m, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.29 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.15, 160.19 (d, $^1J_{C,F}$ = 250.3 Hz), 137.69, 135.43, 132.19 (d, $^4J_{C,F}$ = 2.4 Hz), 131.24 (d, $^3J_{C,F}$ = 8.4 Hz), 127.19, 123.94 (d, $^4J_{C,F}$ = 3.5 Hz), 123.60, 122.23, 122.22, 120.17 (d, $^2J_{C,F}$ = 14.4 Hz), 115.90 (d, $^2J_{C,F}$ = 21.9 Hz), 111.19, 106.84, 59.90, 14.36; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -113.42 (s, 1F); **ESI-HRMS** Calcd for $C_{17}H_{15}FNO_2^+$ $[M+H]^+$ 284.1081, found 284.1082.

Ethyl 2-(thiophen-2-yl)-1*H*-indole-3-carboxylate (2v)[12]



Brown solid; yield 13.5 mg, 50%; $\mathbf{R_f}$ = 0.37 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.24 – 8.17 (m, 1H), 7.88 (d, *J* = 3.1 Hz, 1H), 7.52 (d, *J* = 5.0 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.28 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.48, 139.28, 134.91, 132.22, 128.56, 127.62, 126.35, 125.47, 123.35, 122.32, 122.14, 110.89, 104.68, 59.91, 14.51; **ESI-HRMS** Calcd for $C_{15}H_{14}NO_2S^+$ $[M+H]^+$ 272.0740, found 272.0742.

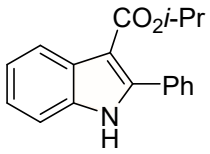
Methyl 2-phenyl-1*H*-indole-3-carboxylate (2w)[13]



Yellow solid; yield 23.7 mg, 94%; $\mathbf{R_f}$=0.37 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.24 – 8.16 (m, 1H), 7.66 – 7.58 (m, 2H), 7.41 (dd, *J* = 7.4, 2.9

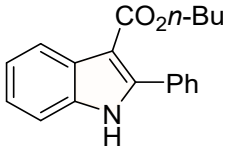
Hz, 3H), 7.37 – 7.32 (m, 1H), 7.27 (d, *J* = 6.3 Hz, 2H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.99, 144.77, 135.28, 132.07, 129.65, 129.33, 128.28, 127.65, 123.35, 122.25, 122.22, 111.20, 104.53, 51.02; **ESI-HRMS** Calcd for $C_{16}H_{14}NO_2^+$ $[M+H]^+$ 252.1019, found 252.1021.

Isopropyl 2-phenyl-1*H*-indole-3-carboxylate (2x)[14]



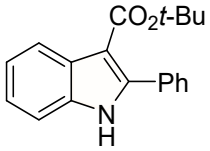
Yellow solid; yield 24.7 mg, 89%; **R_f**=0.43 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.25 – 8.21 (m, 1H), 7.63 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.43 – 7.40 (m, 3H), 7.38 – 7.35 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 5.20 (p, *J* = 6.2 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.01, 144.49, 135.27, 132.28, 130.94, 129.78, 129.23, 128.18, 127.79, 123.27, 122.30, 122.14, 111.12, 67.16, 22.21; **ESI-HRMS** Calcd for $C_{18}H_{18}NO_2^+$ $[M+H]^+$ 280.1332, found 280.1336.

Butyl 2-phenyl-1*H*-indole-3-carboxylate (2y)[14]



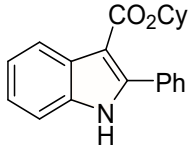
Yellow solid; yield 26.0 mg, 89%; **R_f**=0.43 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.26 – 8.19 (m, 1H), 7.69 – 7.59 (m, 2H), 7.47–7.40 (m, 3H), 7.39–7.35 (m, 1H), 7.31 – 7.25 (m, 2H), 4.24 (t, *J* = 6.6 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.32 (dt, *J* = 14.8, 7.2 Hz, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.59, 144.60, 135.26, 132.29, 129.75, 129.27, 128.23, 127.78, 123.32, 122.30, 122.22, 111.12, 104.96, 63.80, 30.92, 19.46, 13.89; **ESI-HRMS** Calcd for $C_{19}H_{20}NO_2^+$ $[M+H]^+$ 294.1489, found 294.1492.

Tert-butyl 2-phenyl-1*H*-indole-3-carboxylate (2z)[15]



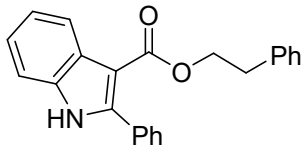
Yellow solid; yield 27.4 mg, 94%; $\mathbf{R_f}$=0.45 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.26 – 8.17 (m, 1H), 7.65 – 7.57 (m, 2H), 7.47 – 7.33 (m, 4H), 7.27 – 7.25 (m, 1H), 7.24 (s, 1H), 1.50 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.72, 143.99, 135.20, 132.61, 129.75, 129.10, 128.24, 127.88, 123.20, 122.22, 122.04, 111.01, 106.43, 80.18, 28.54; **ESI-HRMS** Calcd for $C_{19}H_{19}NNaO_2^+$[M+Na]$^+$ 316.1308, found 316.1308.

Cyclohexyl 2-phenyl-1*H*-indole-3-carboxylate (2aa) (new compound)



Yellow liquid; yield 13.6 mg, 43%; $\mathbf{R_f}$=0.45 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.63 (dd, J = 6.2, 3.0 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.36 (dd, J = 7.2, 1.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 4.98 (tt, J = 8.8, 3.9 Hz, 1H), 1.94 – 1.87 (m, 2H), 1.67 (d, J = 9.4 Hz, 2H), 1.54 – 1.44 (m, 3H), 1.37 – 1.25 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.00, 144.52, 135.27, 132.32, 129.76, 129.20, 128.19, 127.80, 123.24, 122.33, 122.13, 111.13, 105.29, 72.14, 31.94, 25.61, 23.88; **ESI-HRMS** Calcd for $C_{21}H_{22}NO_2^+$ [M+H]$^+$ 320.1645, found 320.1648.

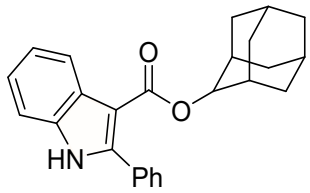
Phenethyl 2-phenyl-1*H*-indole-3-carboxylate (2ab) (new compound)



Yellow solid; yield 26.9 mg, 79%; $\mathbf{R_f}$=0.36 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.43 – 7.39 (m, 3H), 7.34 (d, J = 7.1 Hz, 1H), 7.27 (d, J = 6.8 Hz, 1H), 7.24 – 7.14 (m, 6H), 4.50 – 4.44 (m, 2H), 2.98 (t, J = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.38, 144.72, 138.35, 135.22, 132.17, 130.91, 129.73, 129.36, 129.05, 128.57, 128.28, 127.71,

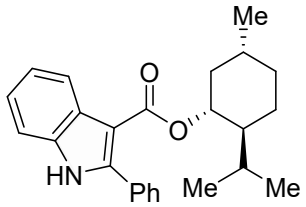
126.52, 123.34, 122.39, 122.20, 111.09, 64.49, 35.31; **ESI-HRMS** Calcd for $C_{23}H_{20}NO_2^+$ $[M+H]^+$ 342.1489, found 342.1490.

Adamantan-2-yl 2-phenyl-1*H*-indole-3-carboxylate (2ac) (new compound)



Yellow solid; yield 32.7 mg, 88%; $\mathbf{R_f}$=0.42 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.33 (d, *J* = 6.9 Hz, 1H), 7.64 (dd, *J* = 6.8, 2.1 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.32 – 7.26 (m, 2H), 5.17 (s, 1H), 2.07 (s, 2H), 1.82 (t, *J* = 20.8 Hz, 8H), 1.71 (s, 2H), 1.49 (d, *J* = 12.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.06, 144.63, 135.22, 132.61, 129.74, 129.22, 128.31, 127.78, 123.28, 122.32, 122.22, 111.10, 105.56, 77.08, 37.66, 36.64, 32.16, 32.09, 27.40, 27.27; **ESI-HRMS** Calcd for $C_{25}H_{26}NO_2^+$ $[M+H]^+$ 372.1958, found 372.1960.

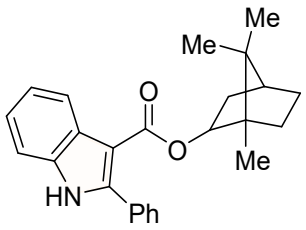
(*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 2-phenyl-1*H*-indole-3-carboxylate (2ad) (new compound)



Yellow liquid; yield 31.8 mg, 85%; R_f=0.33 (PE/EtOAc = 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.44 – 7.40 (m, 3H), 7.39 – 7.35 (m, 1H), 7.27 (d, *J* = 3.8 Hz, 2H), 4.86 (td, *J* = 10.8, 4.2 Hz, 1H), 2.15 (d, *J* = 12.2 Hz, 1H), 1.90 – 1.82 (m, 1H), 1.66 (q, *J* = 4.2 Hz, 2H), 1.47 (s, 1H), 1.35 (t, *J* = 11.6 Hz, 1H), 1.09 – 0.98 (m, 2H), 0.89 (d, *J* = 6.5 Hz, 4H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.70 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.01, 144.54, 135.25, 132.39, 129.85, 129.21, 128.12, 127.84, 123.26, 122.43, 122.18, 111.09, 105.27, 73.57,

47.35, 41.44, 34.50, 31.56, 26.22, 23.52, 22.20, 21.04, 16.40; **ESI-HRMS** Calcd for $C_{25}H_{30}NO_2^+$ $[M+H]^+$ 376.2271, found 376.2271.

(*1R*,*4S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-phenyl-1*H*-indole-3-carboxylate (2ae) (new compound)



Yellow solid; yield 33.9 mg, 91%; $\mathbf{R_f}$=0.43 (PE/EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.33 – 8.23 (m, 1H), 7.61 – 7.57 (m, 2H), 7.43 – 7.39 (m, 3H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.29 – 7.25 (m, 2H), 4.91 (dd, *J* = 7.6, 4.4 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.68 (s, 2H), 1.55 (dd, *J* = 13.0, 3.9 Hz, 1H), 1.25 – 1.06 (m, 2H), 0.87 – 0.80 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.37, 144.69, 135.18, 132.48, 129.78, 129.23, 128.33, 127.67, 123.21, 122.25, 122.06, 111.11, 105.19, 81.20, 48.91, 46.98, 45.16, 39.06, 34.38, 27.20, 20.29, 20.25, 12.05; **ESI-HRMS** Calcd for $C_{25}H_{27}NNaO_2^+$$[M+Na]^+$ 396.1934, found 396.1938.

References

1. (a) J. Hierold and D. W. Lupton, Synthesis of spirocyclic γ-lactones by cascade Beckwith–Dowd ring expansion/cyclization, *Org. Lett.*, 2012, **14**, 3412−3415; (b) S. Meninno, T. Fuoco, C. Tedesco and A. Lattanzi, Straightforward enantioselective access to γ-butyrolactones bearing an all-carbon β-quaternary stereocenter, *Org. Lett.*, 2014, **16**, 4746−4749.
2. Z. Han, Y.-Q. Guan, G. Liu, R. Wang, X. Yin, Q. Zhao, H. Cong, X.-Q. Dong and X. Zhang, Iridium-catalyzed asymmetric hydrogenation of tetrasubstituted α-fluoro-β-enamino esters: Efficient access to chiral α-fluoro-β-amino esters with two adjacent tertiary stereocenters, *Org. Lett.*, 2018, **20**, 6349-6353.
3. (a) T. Lei, W.-Q. Liu, J. Li, M.-Y. Huang, B. Yang, Q.-Y. Meng, B. Chen, C.-H. Tung and L.-Z. Wu, Visible light initiated hantzsch synthesis of 2,5-diaryl-substituted pyrroles at ambient conditions, *Org. Lett.*, 2016, **18**, 2479-2482; (b) S. Würtz, S. Rakshit, J. J. Neumann, T. Dröge and F. Glorius, Palladium-

catalyzed oxidative cyclization of n-aryl enamines: From anilines to indoles, *Angew. Chem. Int. Ed.*, 2008, **47**, 7230-7233.

4. C. Qiu, H. Yu, C. Qiu, F. Li, T. Suo, C. Wang, S. Bie and Z. Li, Metal-free halogenation of *N*-substituted enaminoesters and enaminones: A facile access to functionalized α,α-dihaloimines, *Synthesis*, 2020, **52**, 1301-1314.

5. C.-J. Wu, Q.-Y. Meng, T. Lei, J.-J. Zhong, W.-Q. Liu, L.-M. Zhao, Z.-J. Li, B. Chen, C.-H. Tung and L.-Z. Wu, An oxidant-free strategy for indole synthesis via intramolecular c–c bond construction under visible light irradiation: Cross-coupling hydrogen evolution reaction, *ACS Catal.*, 2016, **6**, 4635-4639.

6. W.-Q. Liu, T. Lei, Z.-Q. Song, X.-L. Yang, C.-J. Wu, X. Jiang, B. Chen, C.-H. Tung and L.-Z. Wu, Visible light promoted synthesis of indoles by single photosensitizer under aerobic conditions, *Org. Lett.*, 2017, **19**, 3251-3254.

7. Z. He, W. Liu and Z. Li, I_2-Catalyzed indole formation via oxidative cyclization of *N*-aryl enamines, *Chemistry – An Asian Journal*, 2011, **6**, 1340-1343.

8. S. Tang, X. Gao and A. Lei, Electrocatalytic intramolecular oxidative annulation of *N*-aryl enamines into substituted indoles mediated by iodides, *Chem. Commun.*, 2017, **53**, 3354-3356.

9. J. H. Kim and S.-g. Lee, Palladium-catalyzed intramolecular trapping of the blaise reaction intermediate for tandem one-pot synthesis of indole derivatives, *Org. Lett.*, 2011, **13**, 1350-1353.

10. Y. Li, J. Peng, X. Chen, B. Mo, X. Li, P. Sun and C. Chen, Copper-catalyzed synthesis of multisubstituted indoles through tandem Ullmann-type C–N formation and cross-dehydrogenative coupling reactions, *J. Org. Chem.*, 2018, **83**, 5288-5294.

11. F.-Z. Hu, S.-H. Zhao, H. Chen, S.-W. Yu, X.-Y. Xu, W.-C. Yuan and X.-M. Zhang, Facile synthesis of 2,3-disubstituted indoles by NBS/CuCl mediated oxidative cyclization of *N*-aryl enamines, *ChemistrySelect*, 2017, **2**, 1409-1412.

12. S. Tanimori, H. Ura and M. Kirihata, Copper-catalyzed synthesis of 2,3-disubstituted indoles, *Eur. J. Org. Chem.*, 2007, **2007**, 3977-3980.

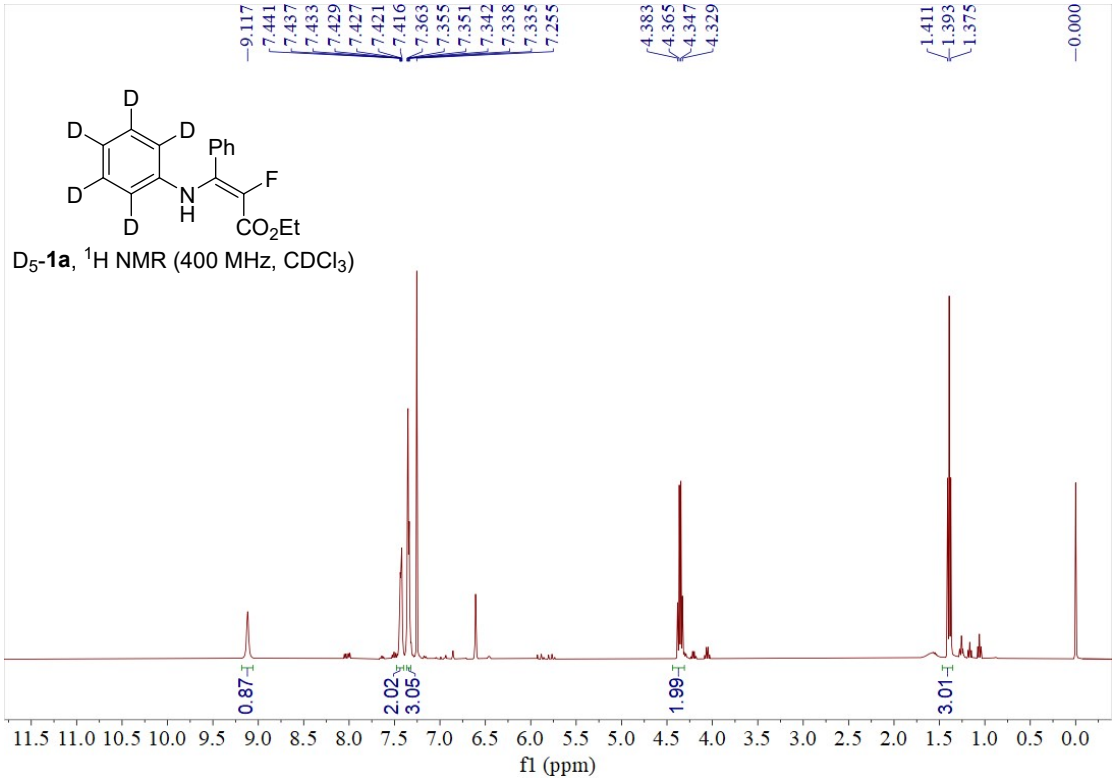
13. J. J. Neumann, S. Rakshit, T. Dröge, S. Würtz and F. Glorius, Exploring the oxidative cyclization of substituted *N*-aryl enamines: Pd-catalyzed formation of indoles from anilines, *Chem. Eur. J.*, 2011, **17**, 7298-7303.

14. P. Sun, J. Yang, Z. Song, Y. Cai, Y. Liu, C. Chen, X. Chen and J. Peng, Copper-mediated one-pot synthesis of indoles through sequential hydroamination and cross-dehydrogenative coupling reaction, *Synthesis*,

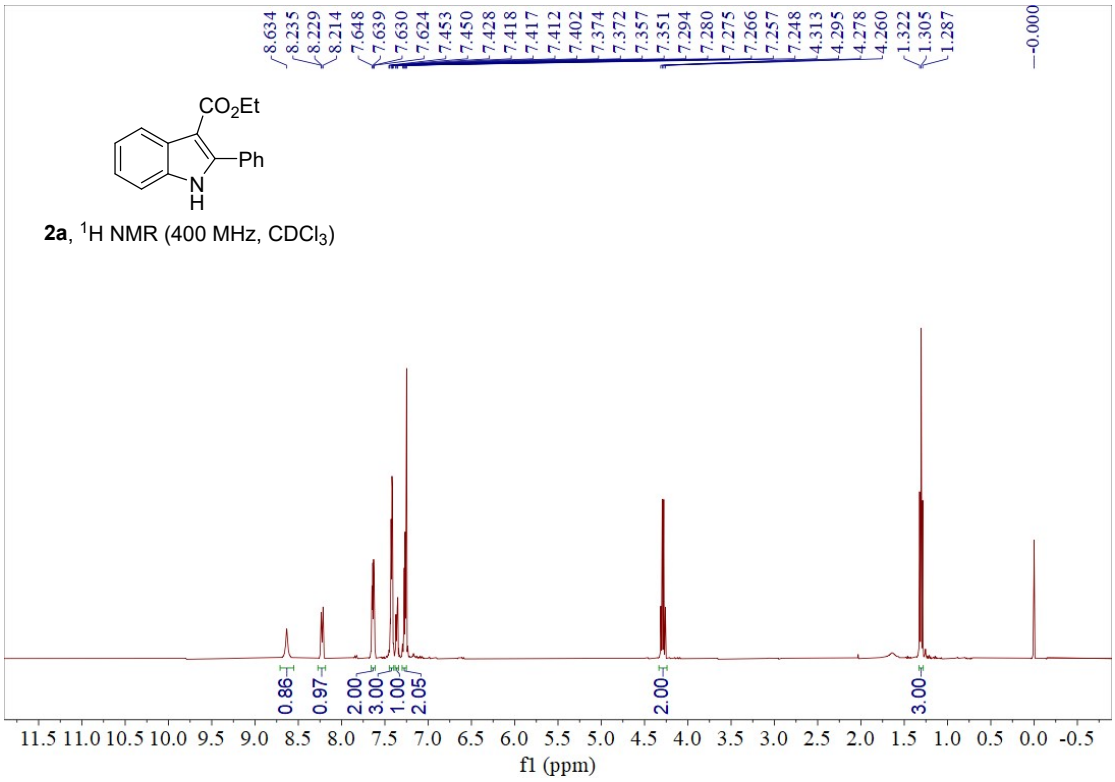
2020, **52**, 75-84.

15. K. Kim, H. Y. Kim and K. Oh, Aerobic oxidation approaches to indole-3-carboxylates: a tandem cross coupling of Amines–intramolecular Mannich–oxidation sequence, *Org. Lett.*, 2019, **21**, 6731-6735.

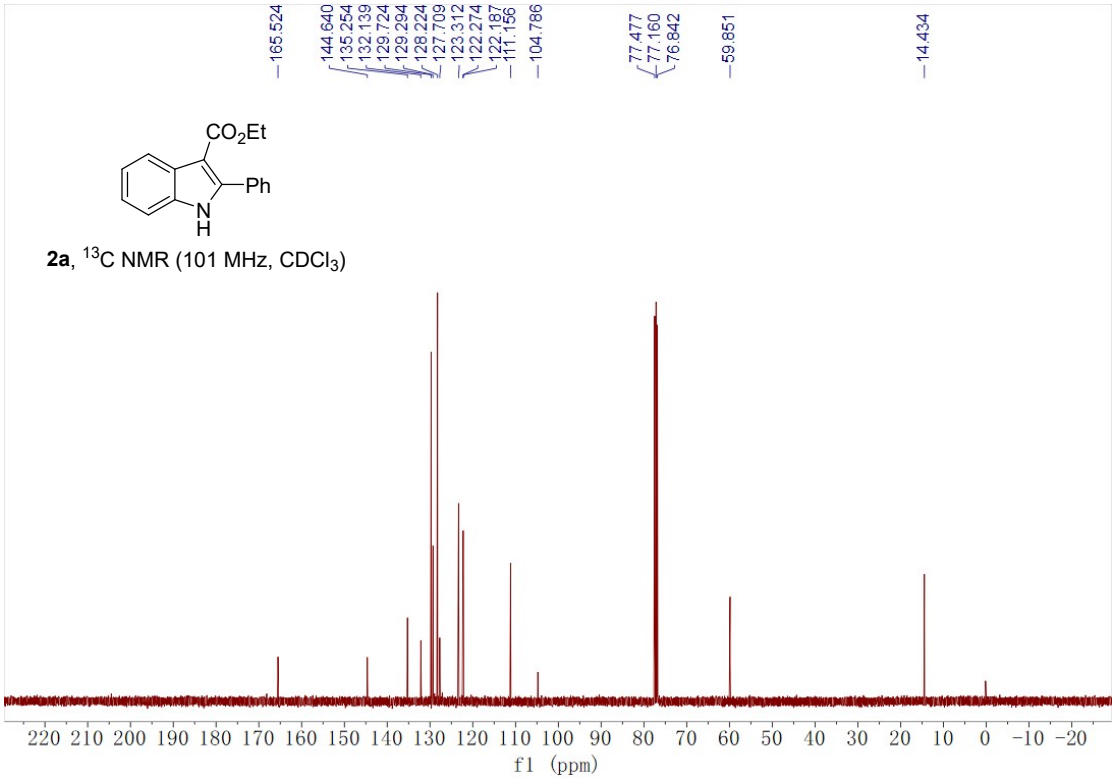
The NMR Spectra of Starting Materials



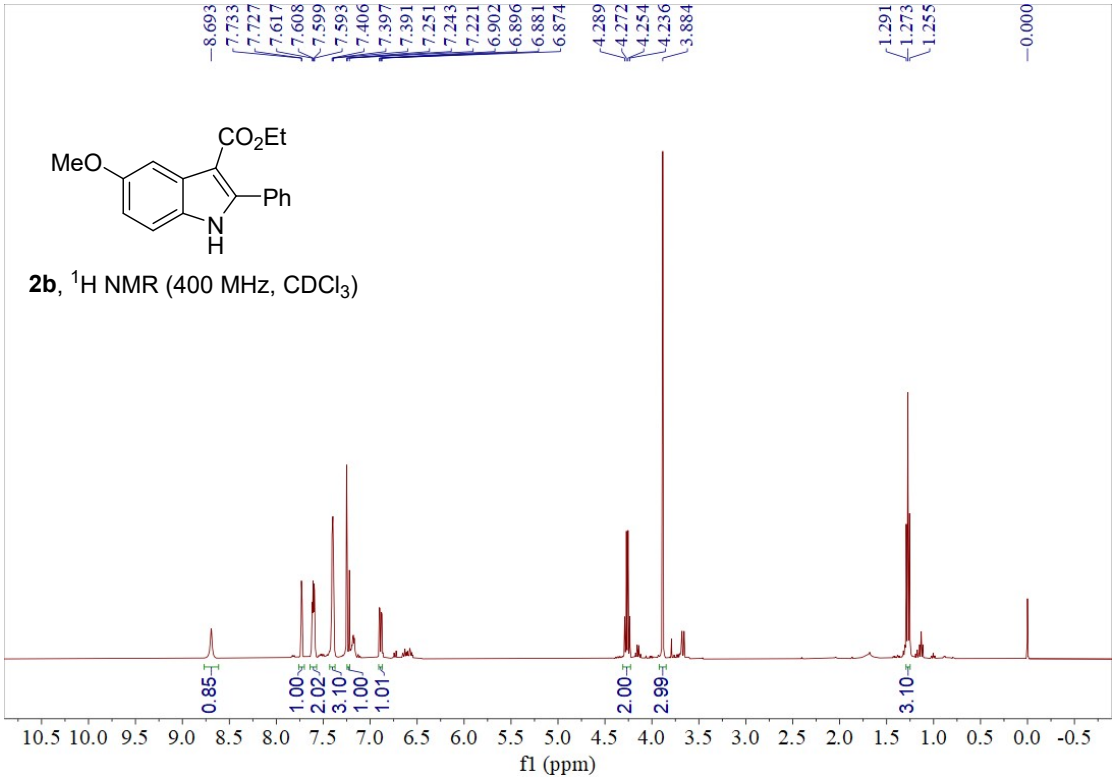
The NMR Spectra of Products



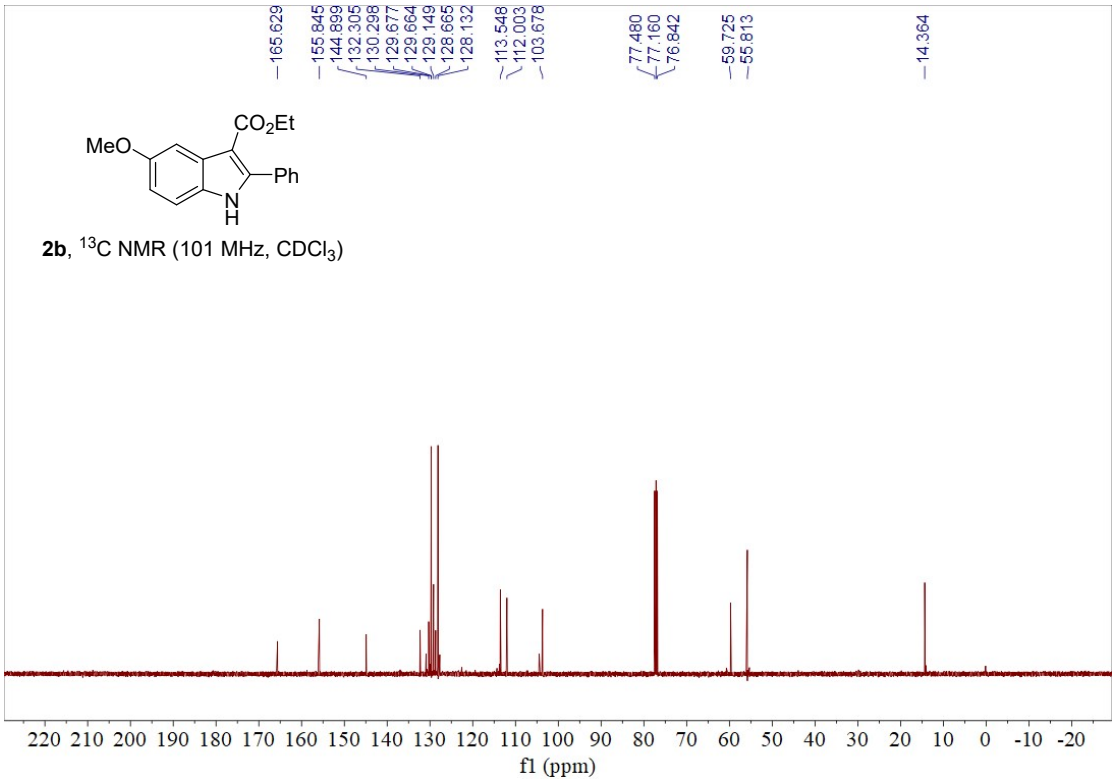
2a, ^{1}H NMR (400 MHz, $CDCl_3$)



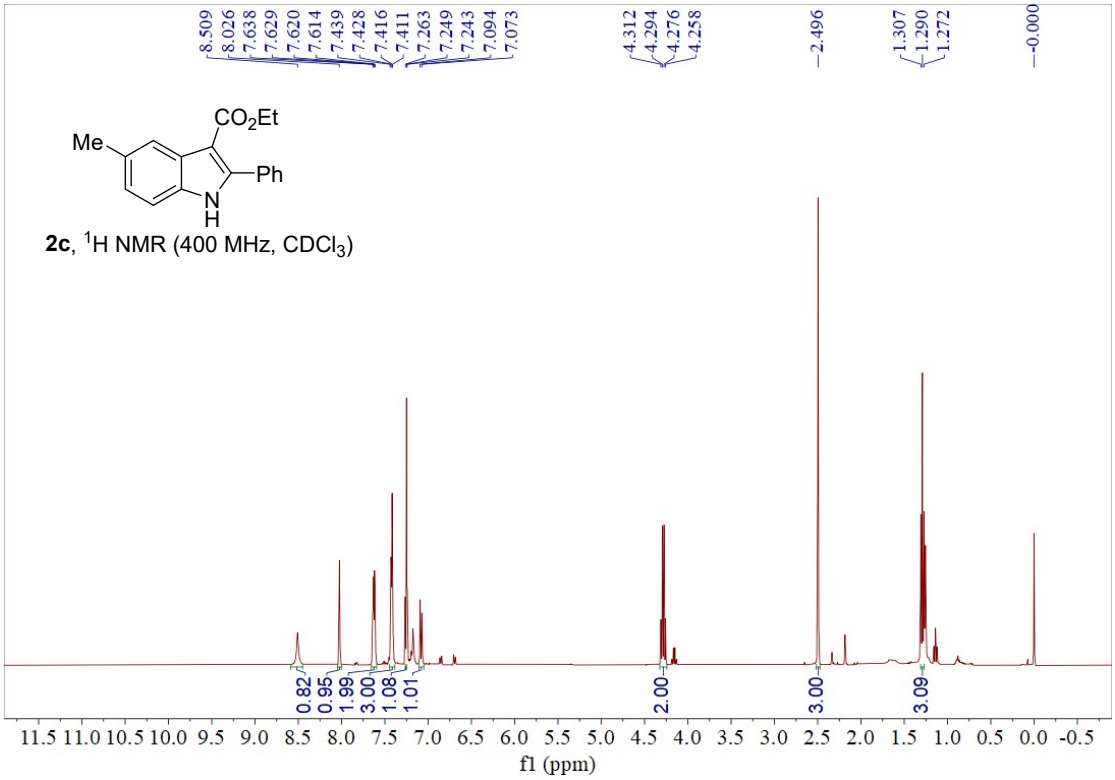
2a, ^{13}C NMR (101 MHz, $CDCl_3$)



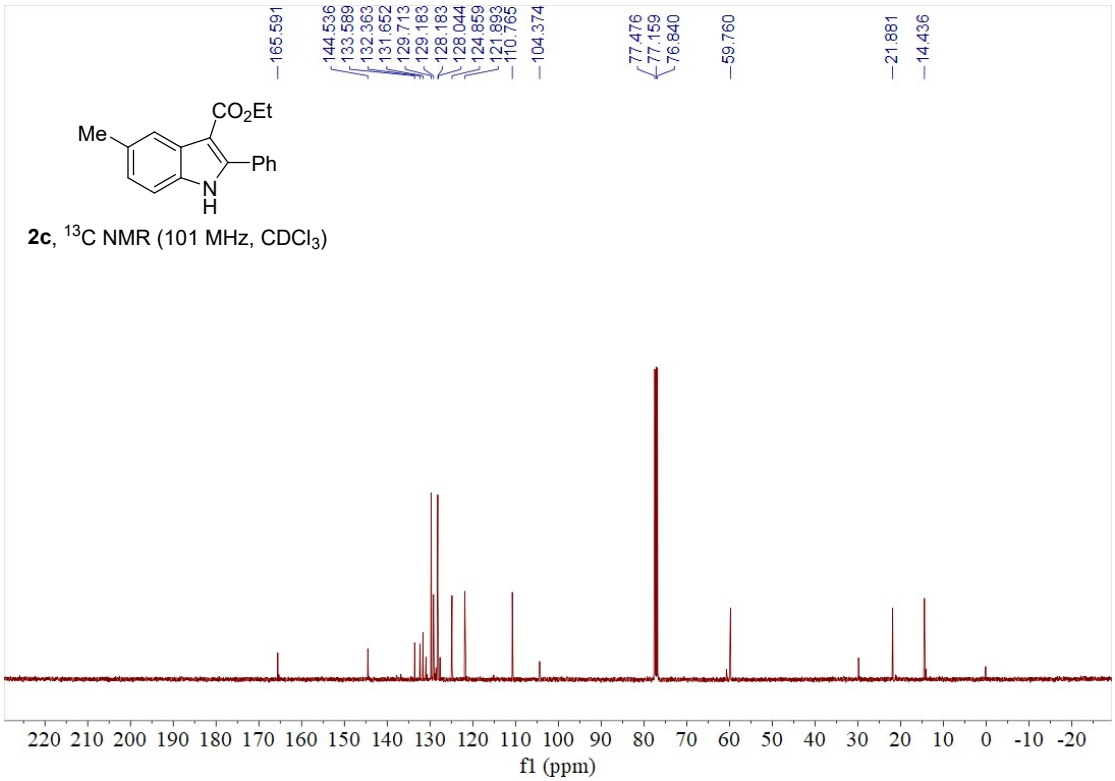
2b, ^{1}H NMR (400 MHz, $CDCl_3$)



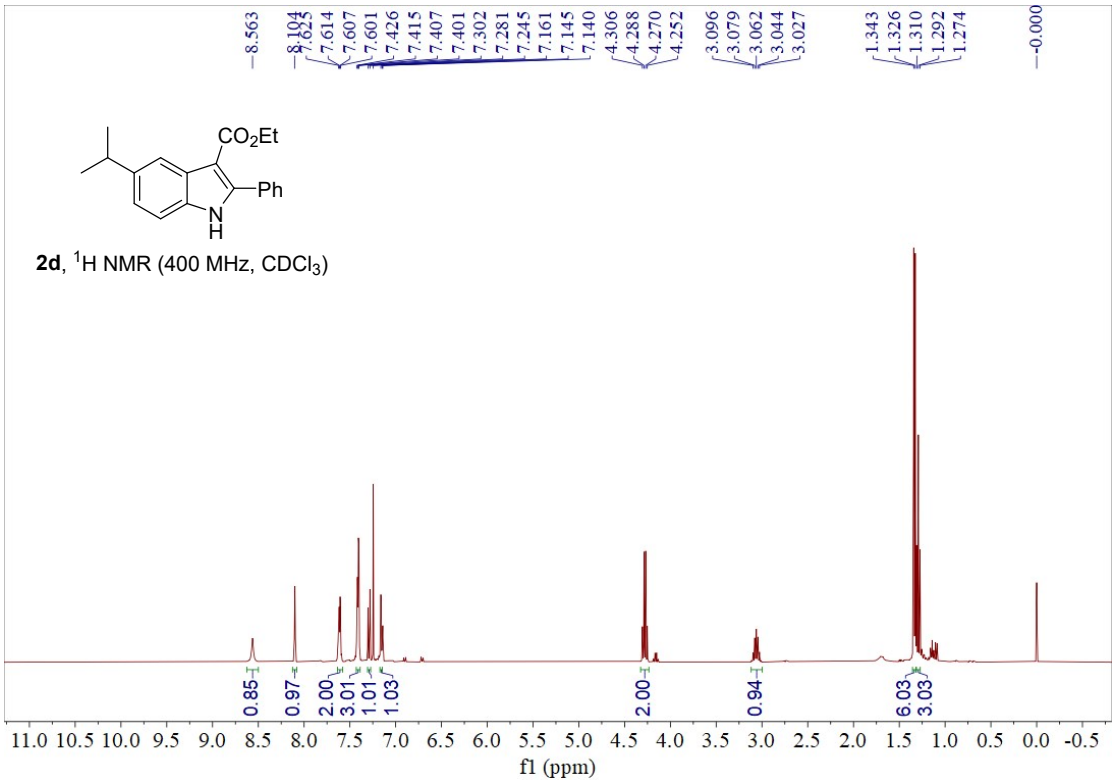
2b, ^{13}C NMR (101 MHz, $CDCl_3$)



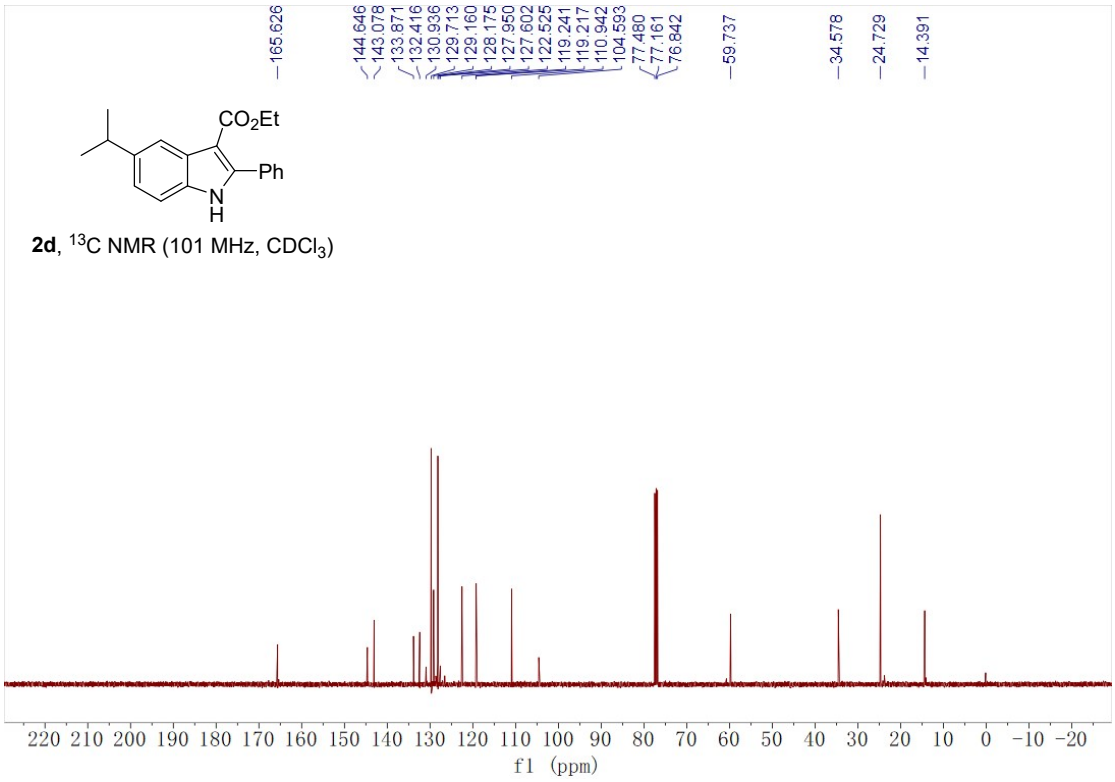
2c, ^{1}H NMR (400 MHz, $CDCl_3$)



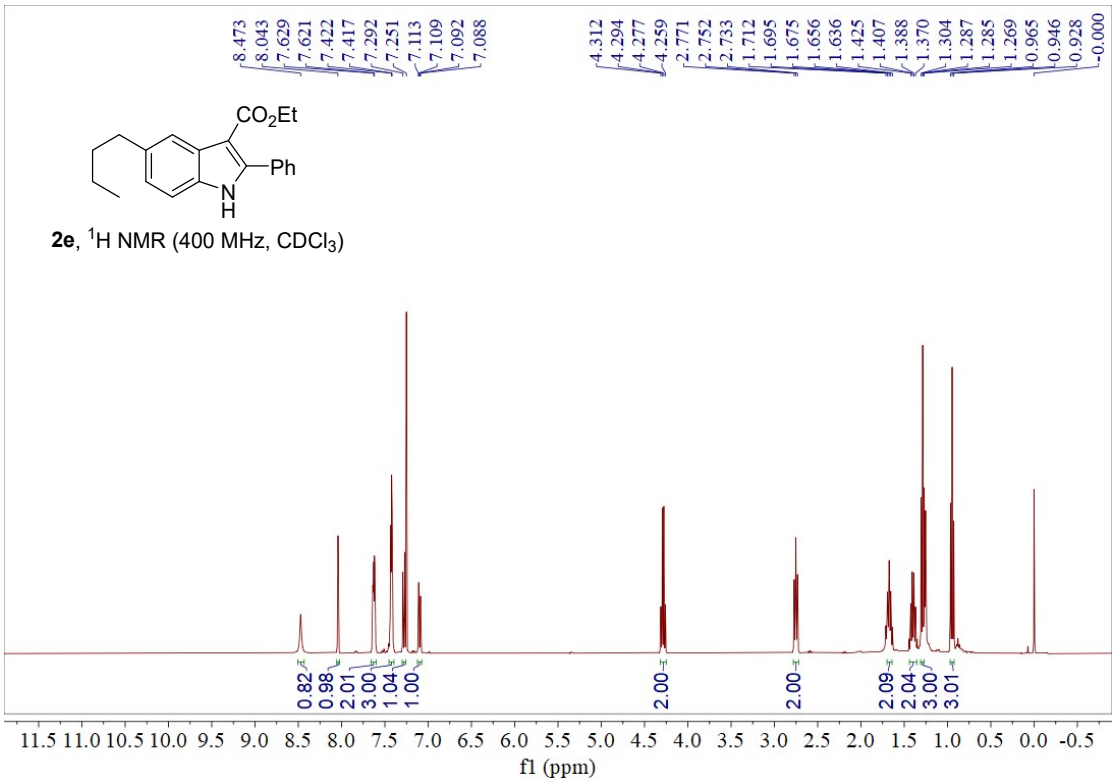
2c, ^{13}C NMR (101 MHz, $CDCl_3$)



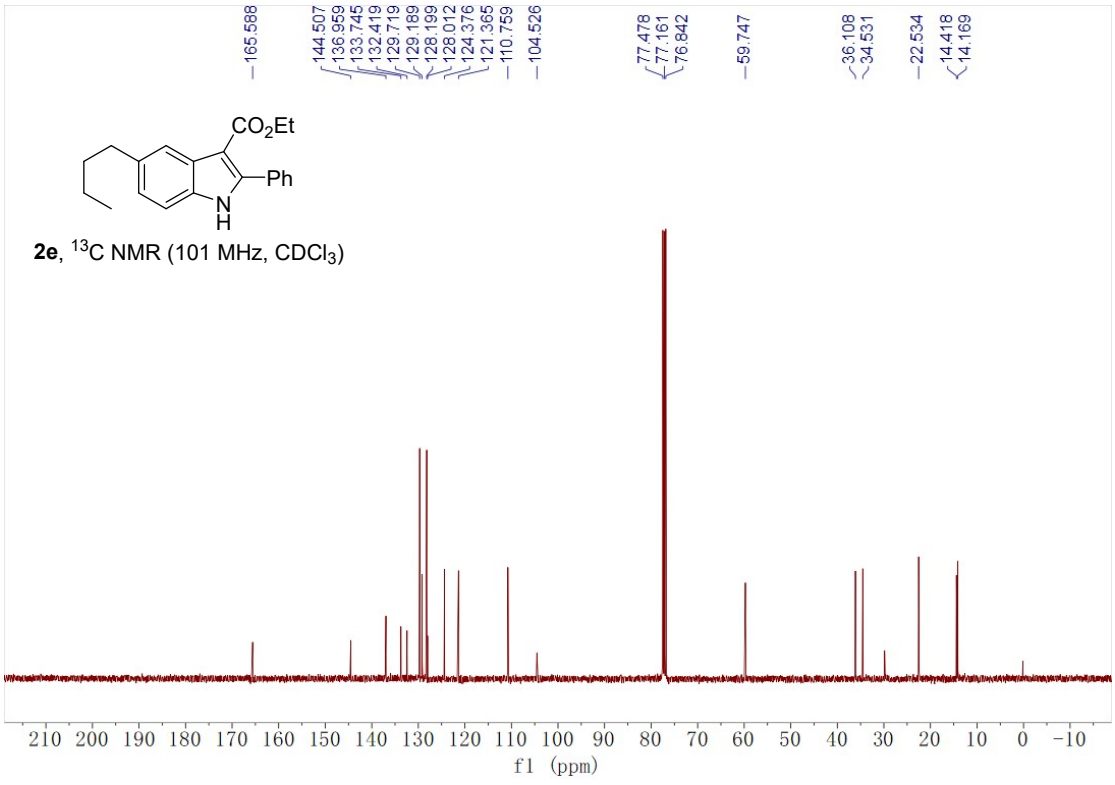
2d, ^{1}H NMR (400 MHz, $CDCl_3$)



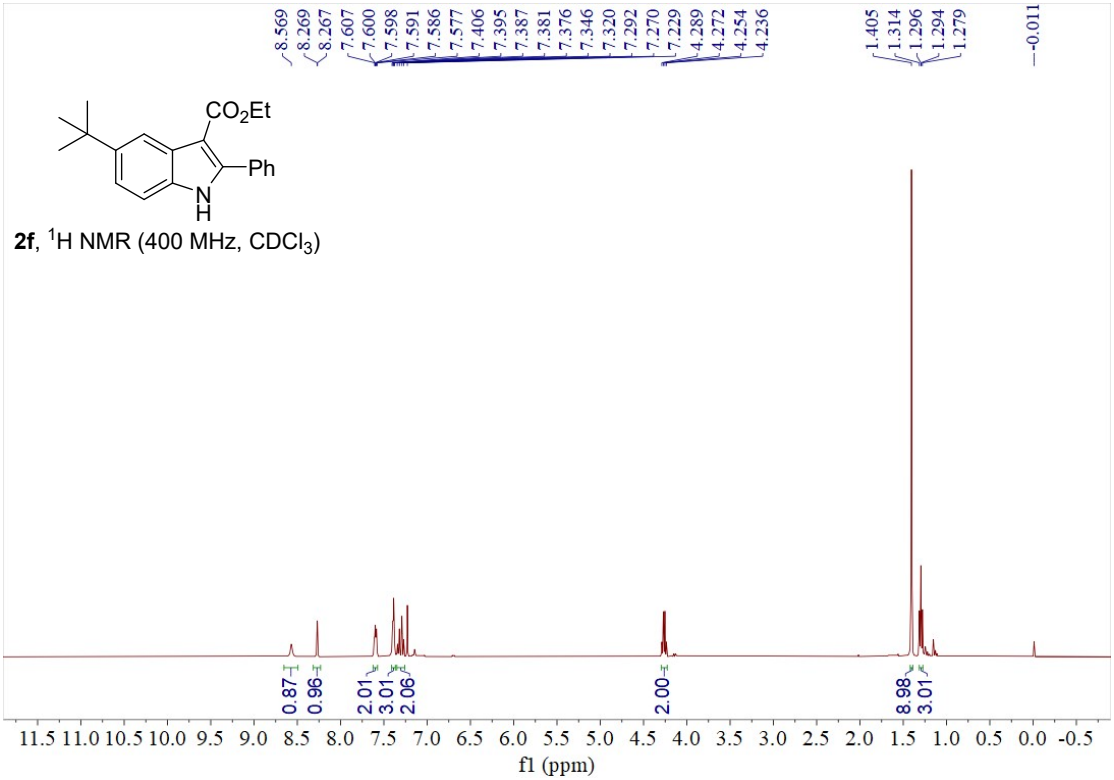
2d, ^{13}C NMR (101 MHz, $CDCl_3$)



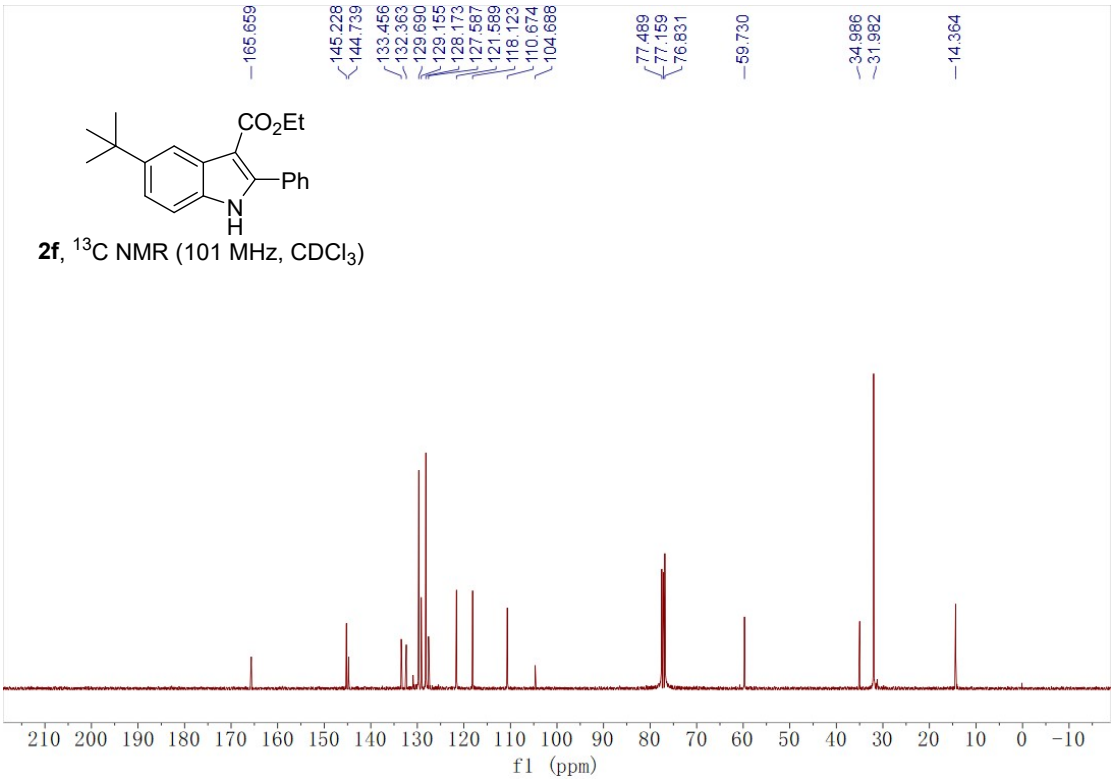
2e, ^{1}H NMR (400 MHz, $CDCl_3$)



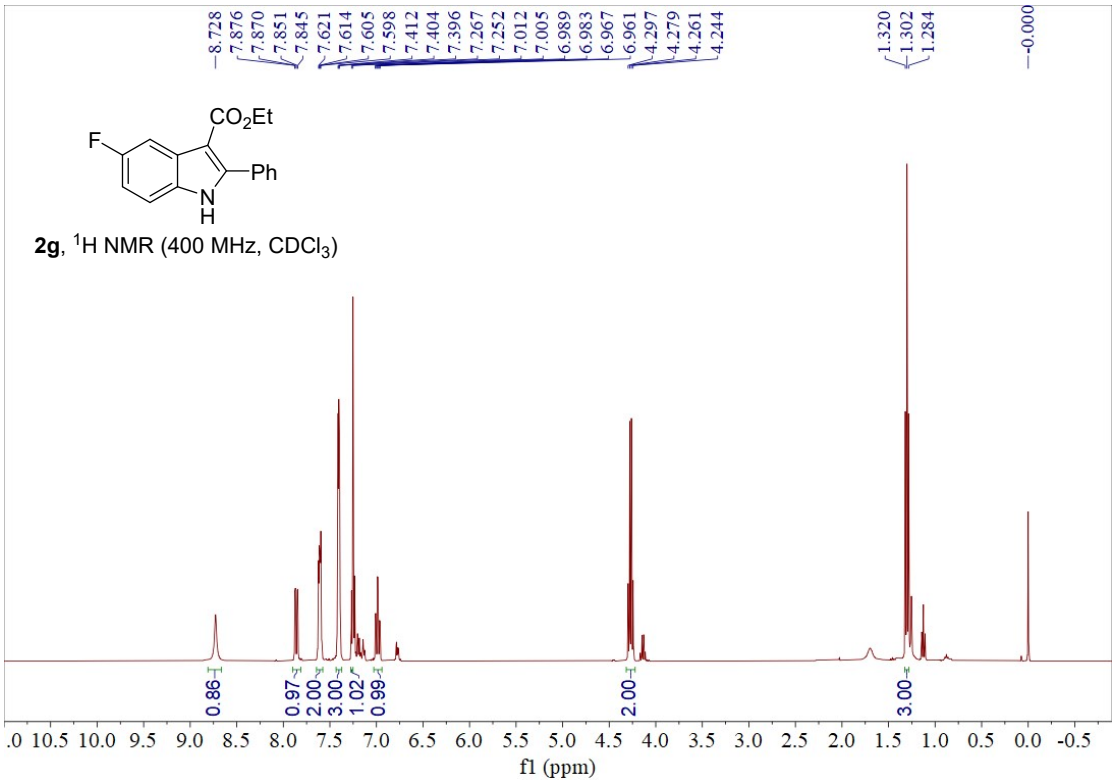
2e, ^{13}C NMR (101 MHz, $CDCl_3$)



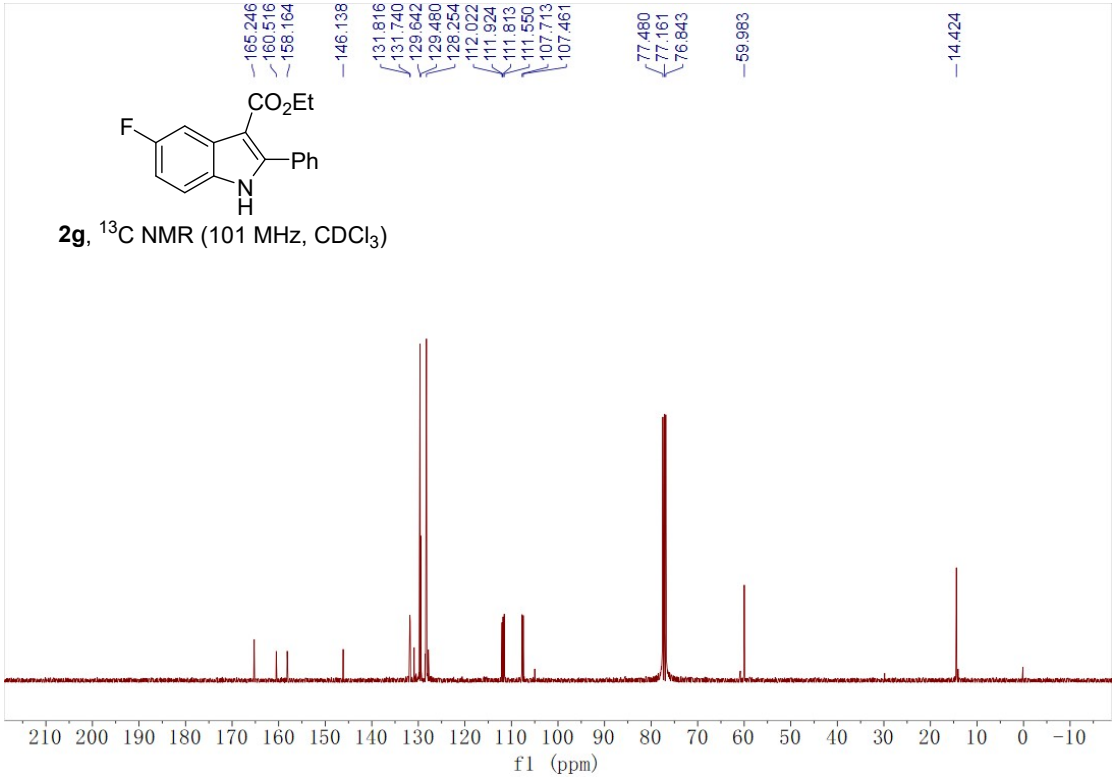
2f, ^{1}H NMR (400 MHz, $CDCl_3$)



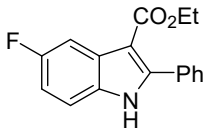
2f, ^{13}C NMR (101 MHz, $CDCl_3$)



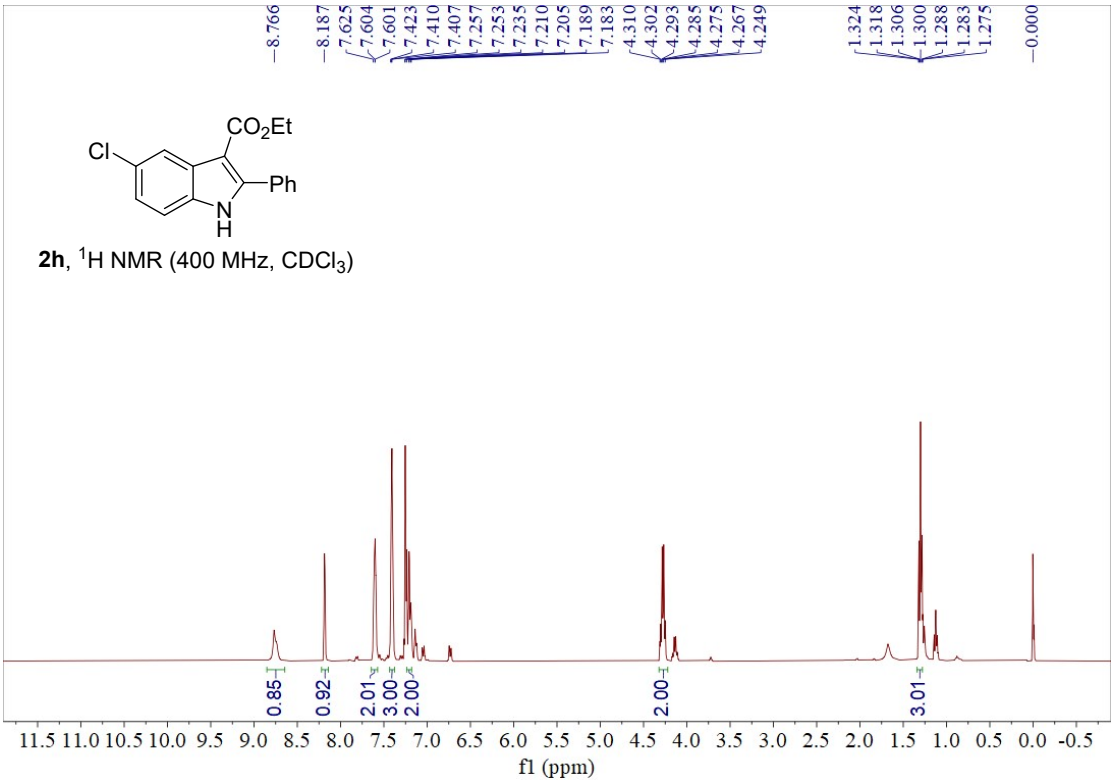
2g, ^{1}H NMR (400 MHz, $CDCl_3$)



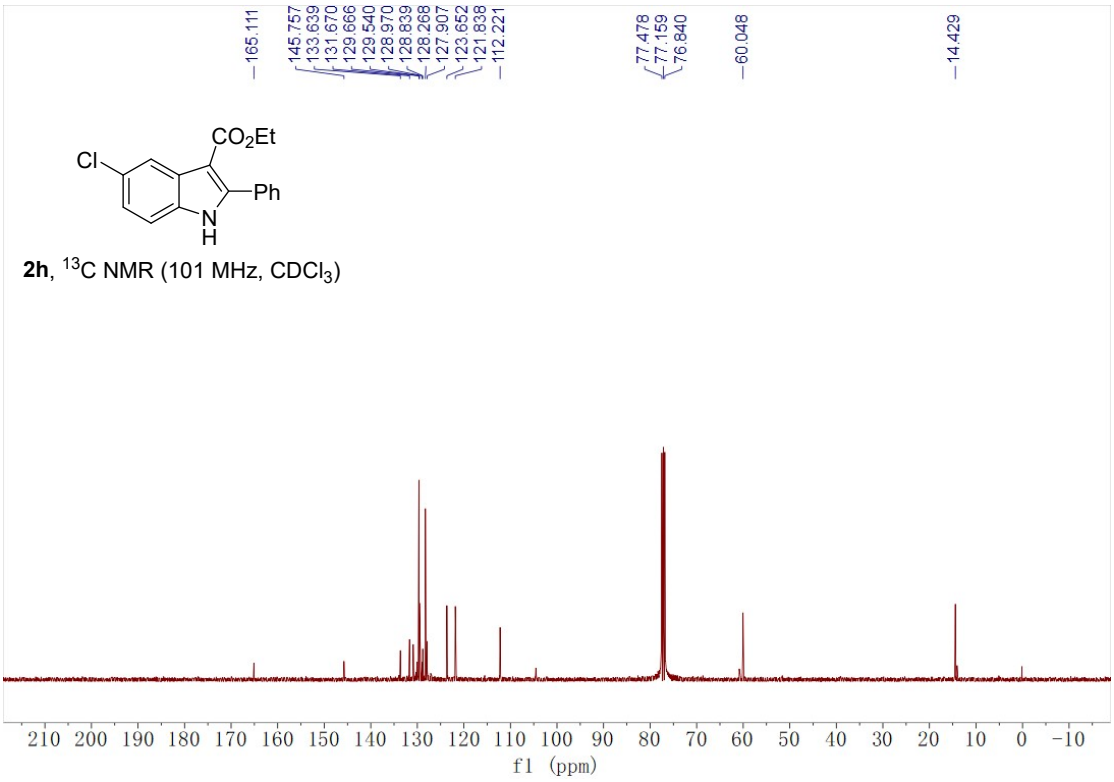
2g, ^{13}C NMR (101 MHz, $CDCl_3$)



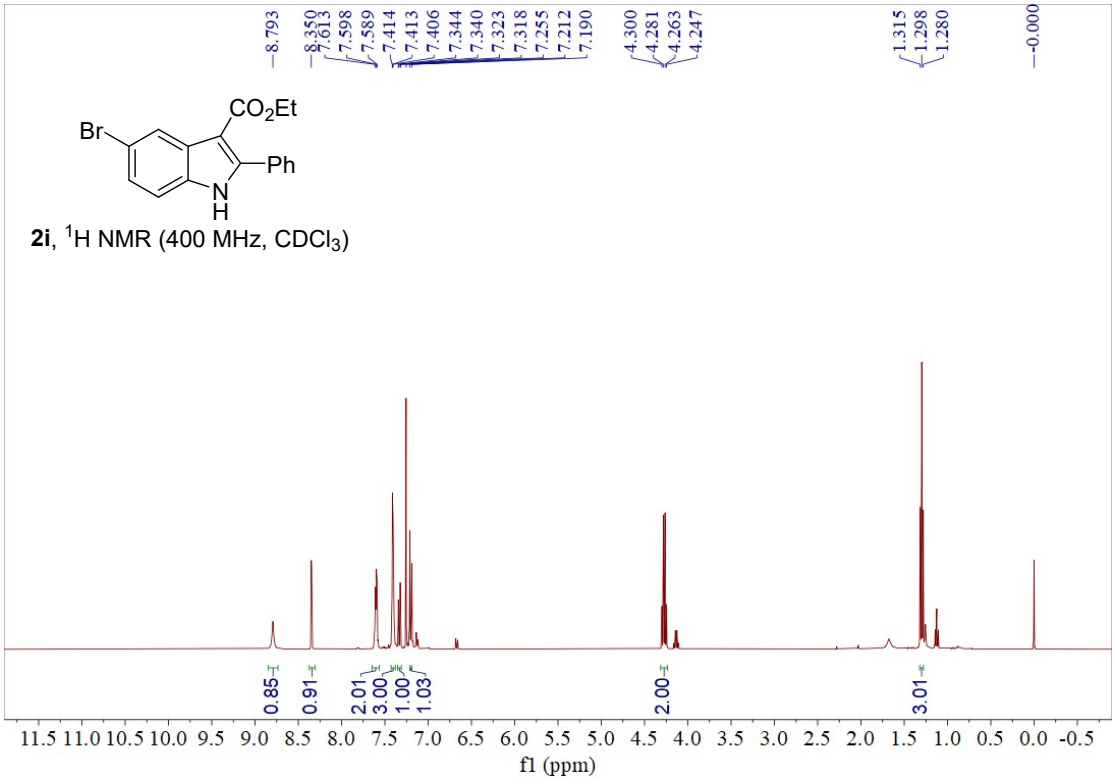
2g, ^{19}F NMR (565 MHz, $CDCl_3$)



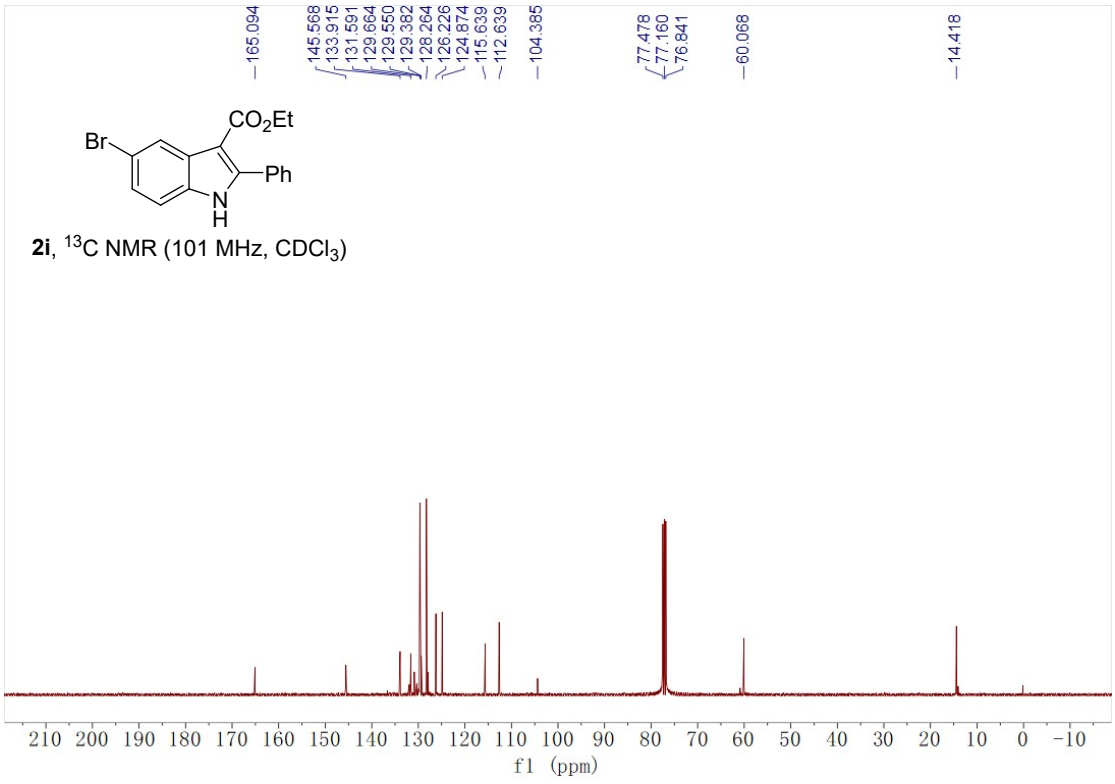
2h, ^{1}H NMR (400 MHz, $CDCl_3$)



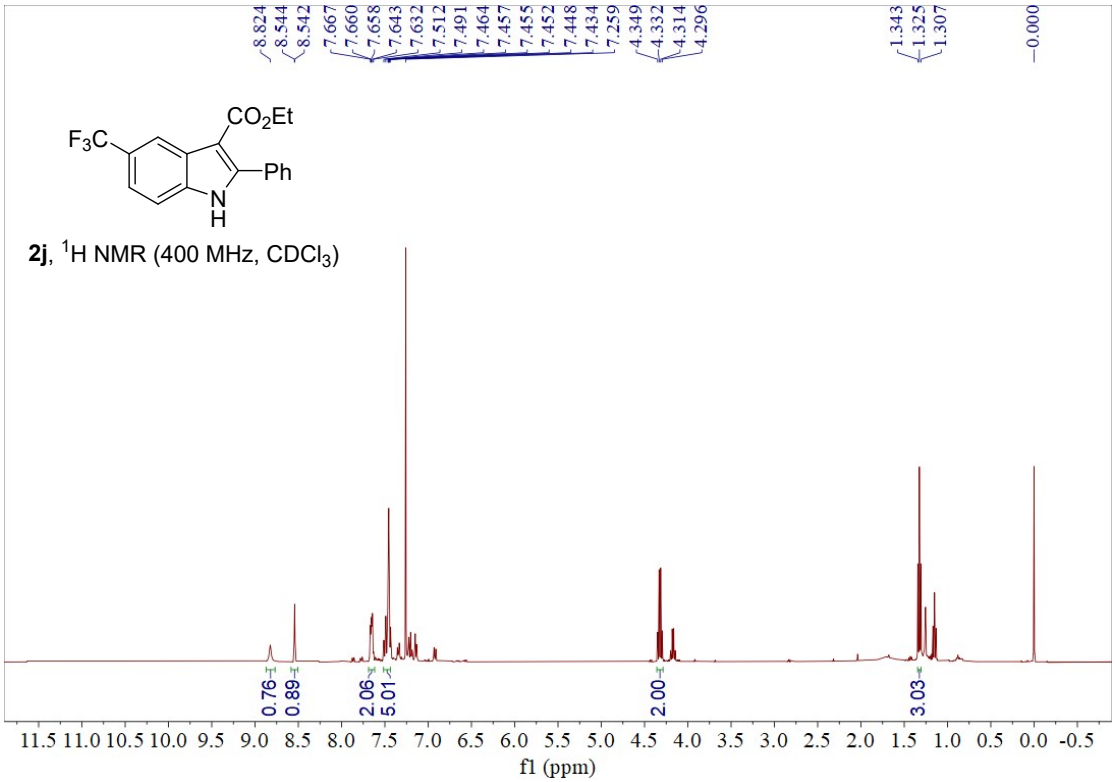
2h, ^{13}C NMR (101 MHz, $CDCl_3$)



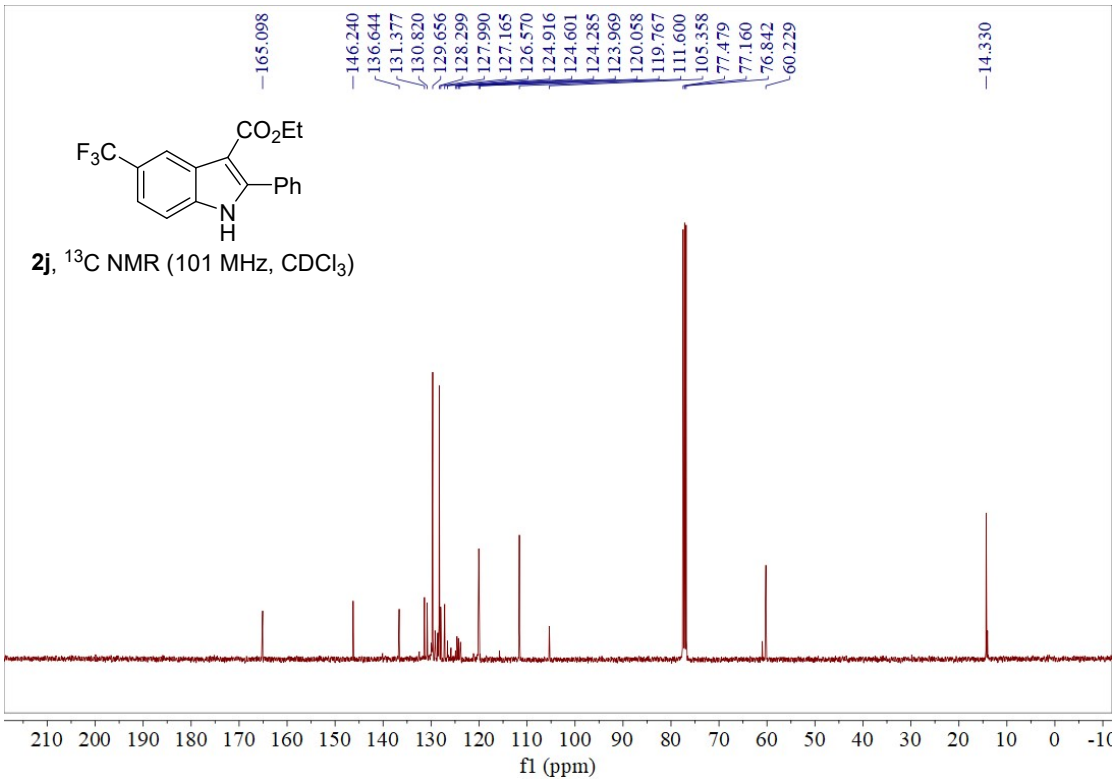
2i, ^{1}H NMR (400 MHz, $CDCl_3$)



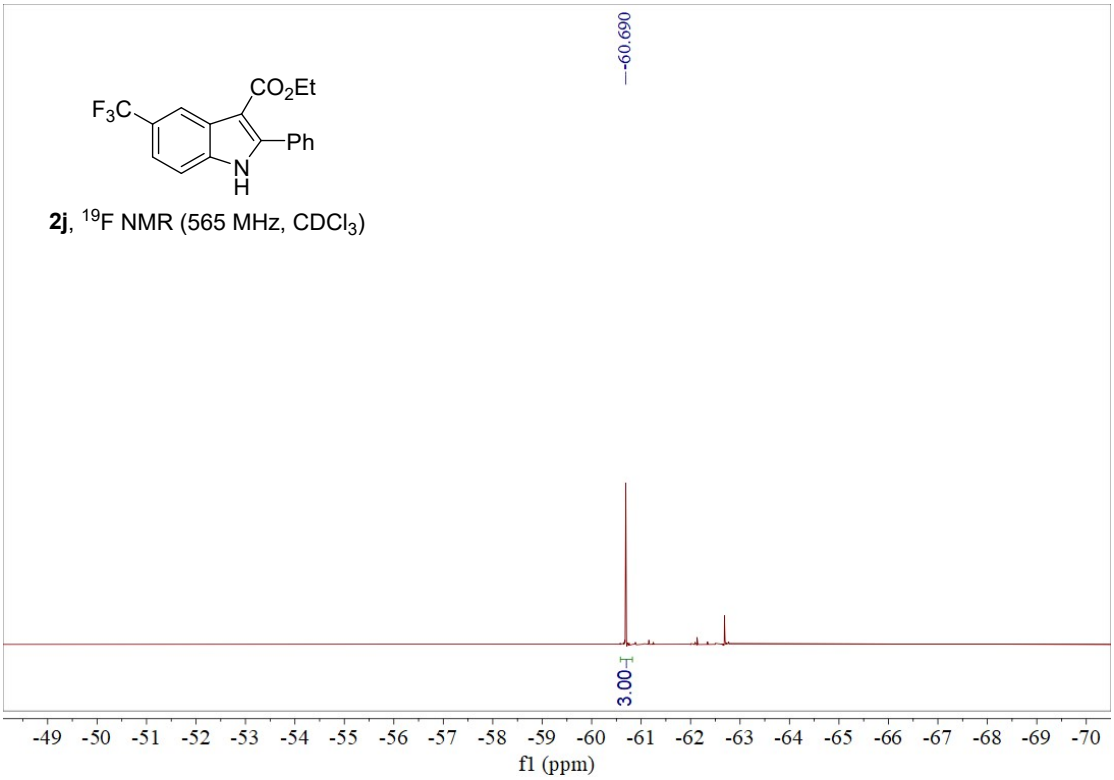
2i, ^{13}C NMR (101 MHz, $CDCl_3$)



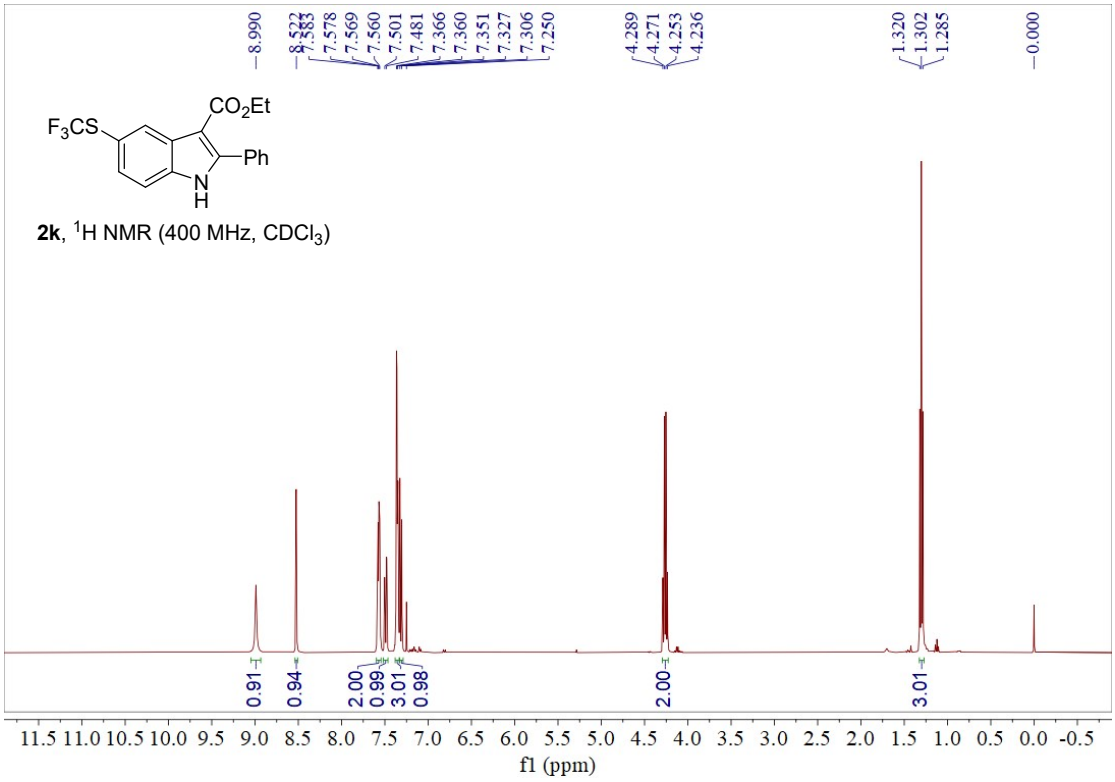
2j, ^{1}H NMR (400 MHz, $CDCl_3$)

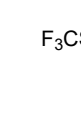


2j, ^{13}C NMR (101 MHz, $CDCl_3$)



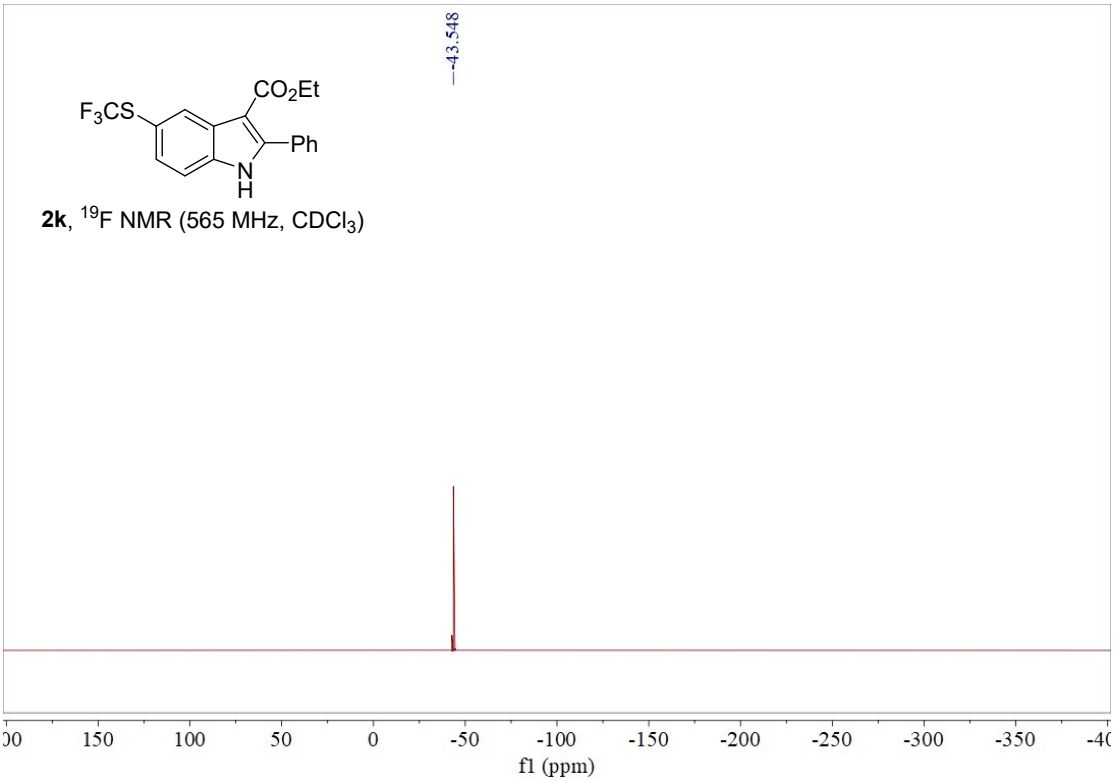
2j, ^{19}F NMR (565 MHz, $CDCl_3$)



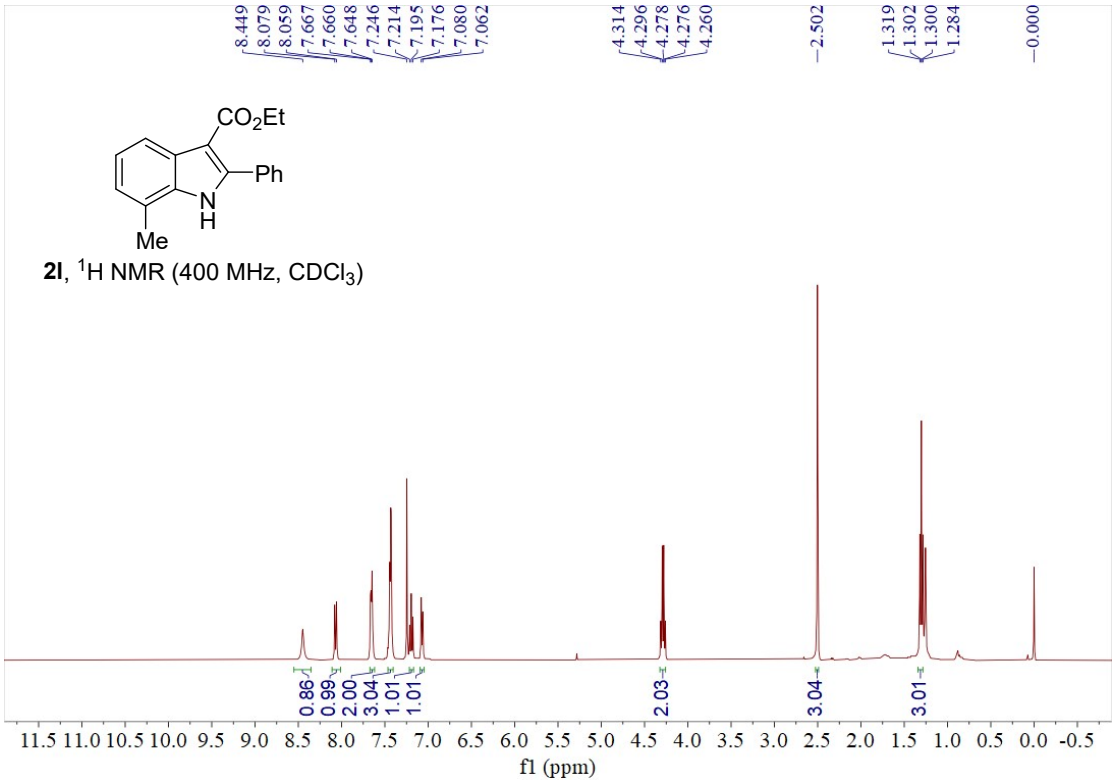


2k, ^{1}H NMR (400 MHz, $CDCl_3$)

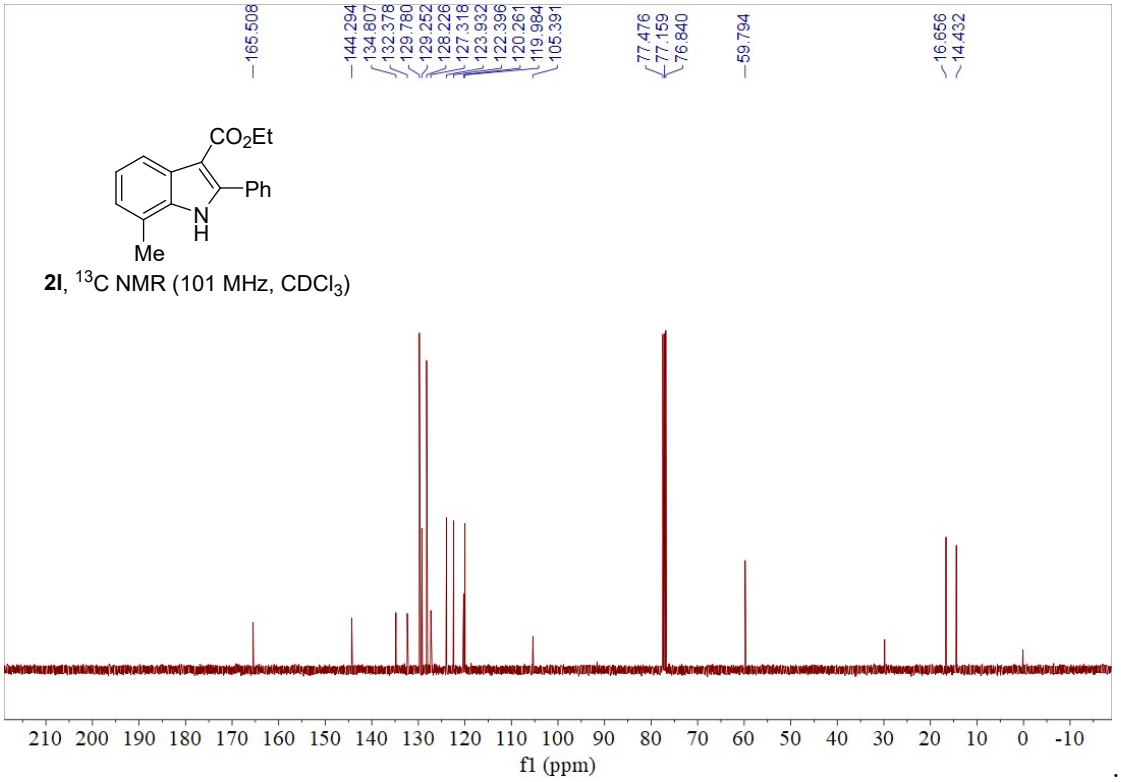
2k, ^{13}C NMR (101 MHz, $CDCl_3$)



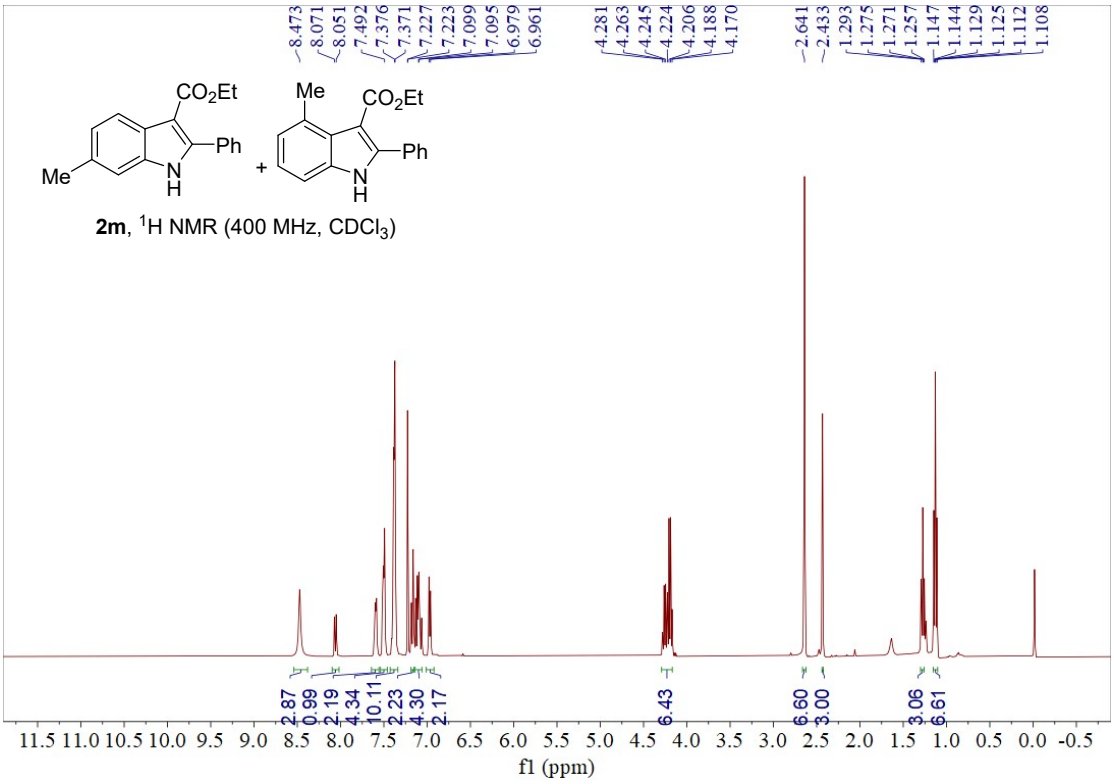
2k, ^{19}F NMR (565 MHz, $CDCl_3$)



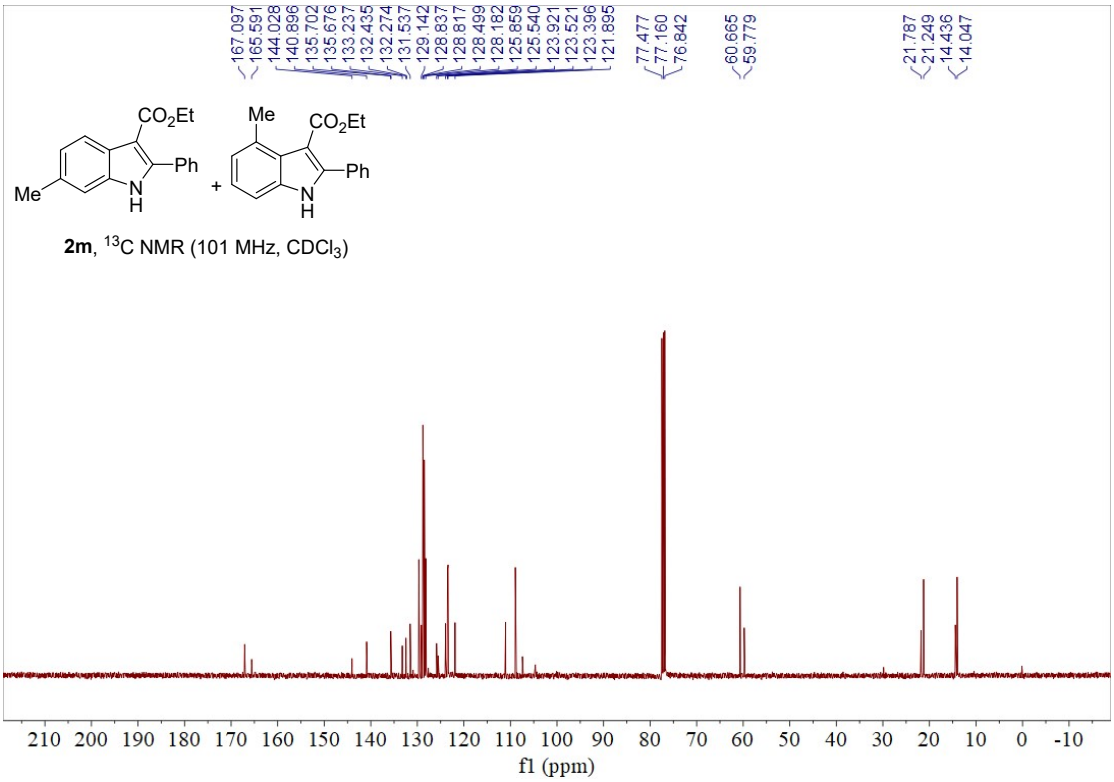
2l, ^{1}H NMR (400 MHz, $CDCl_3$)



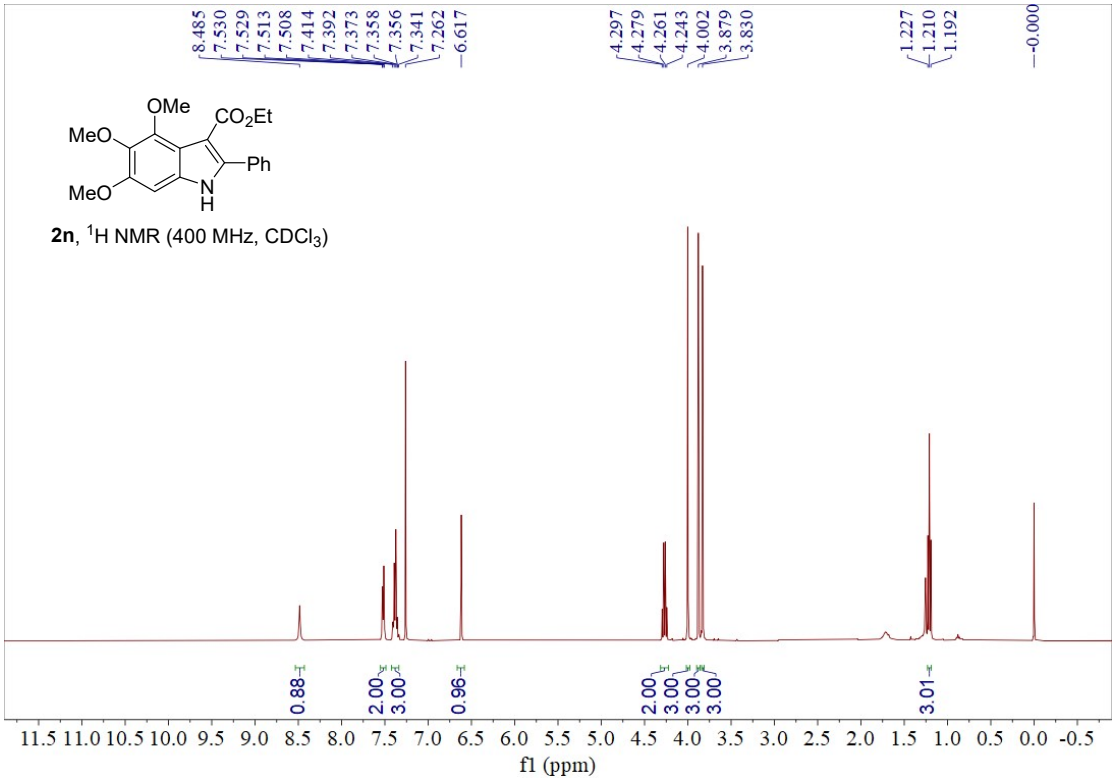
2l, ^{13}C NMR (101 MHz, $CDCl_3$)



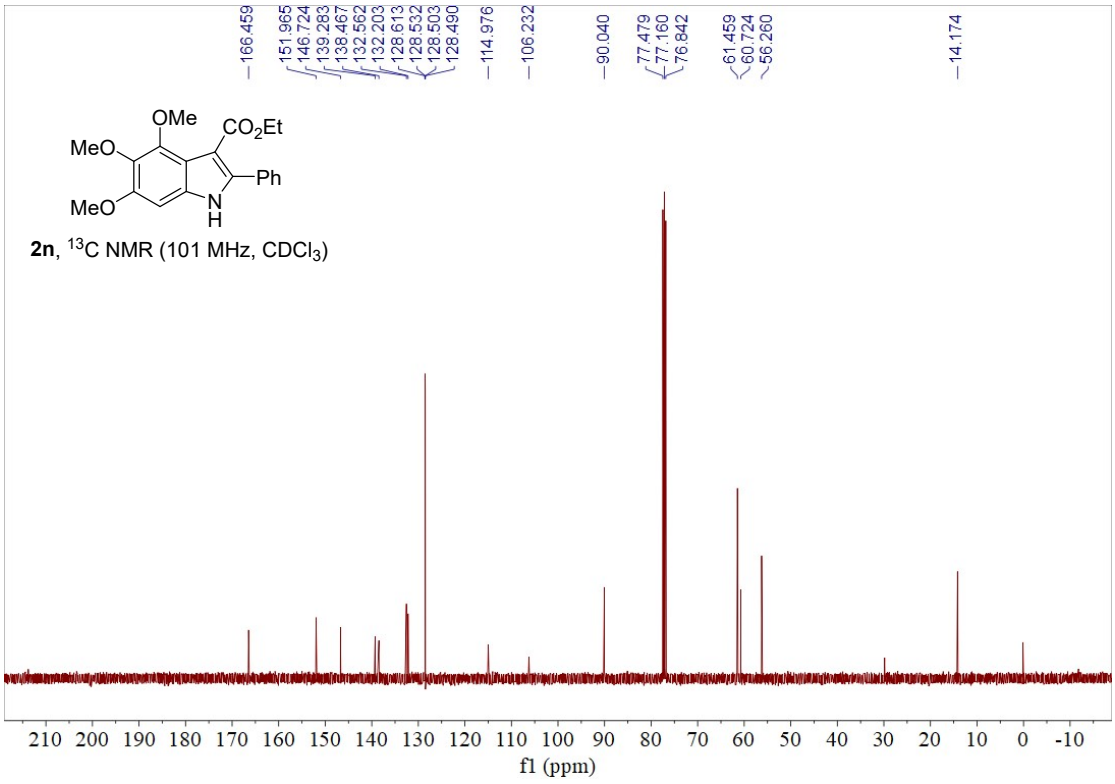
2m, ^{1}H NMR (400 MHz, $CDCl_3$)



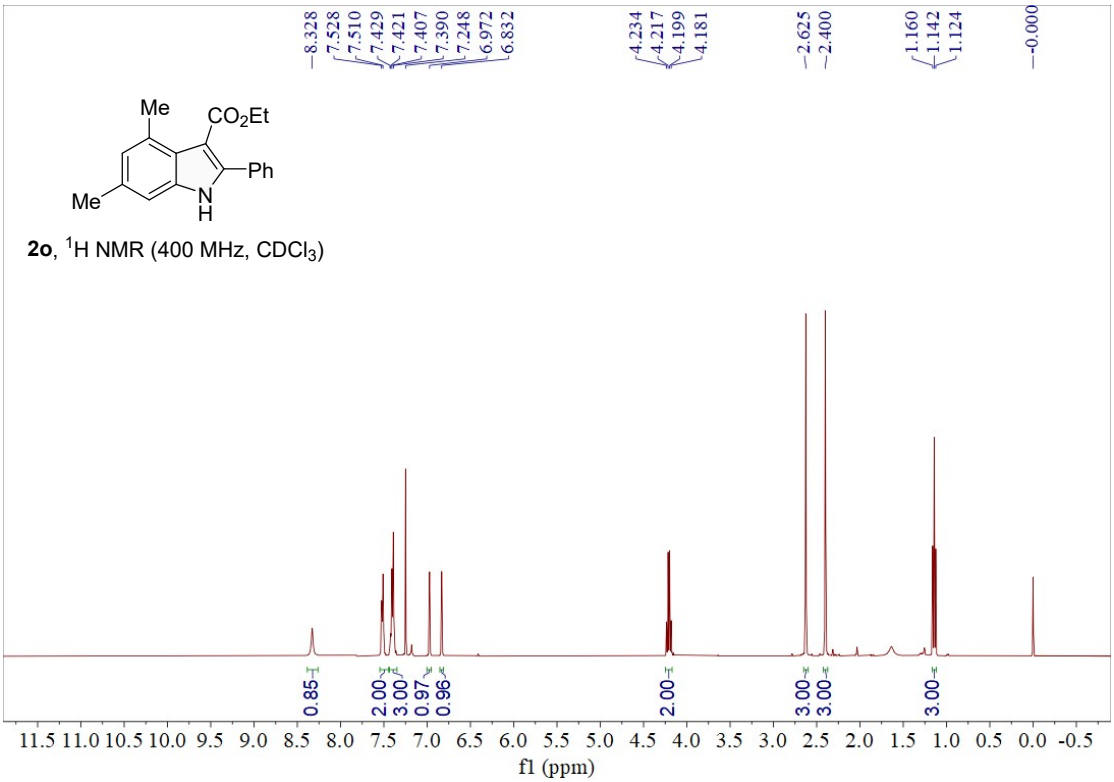
2m, ^{13}C NMR (101 MHz, $CDCl_3$)



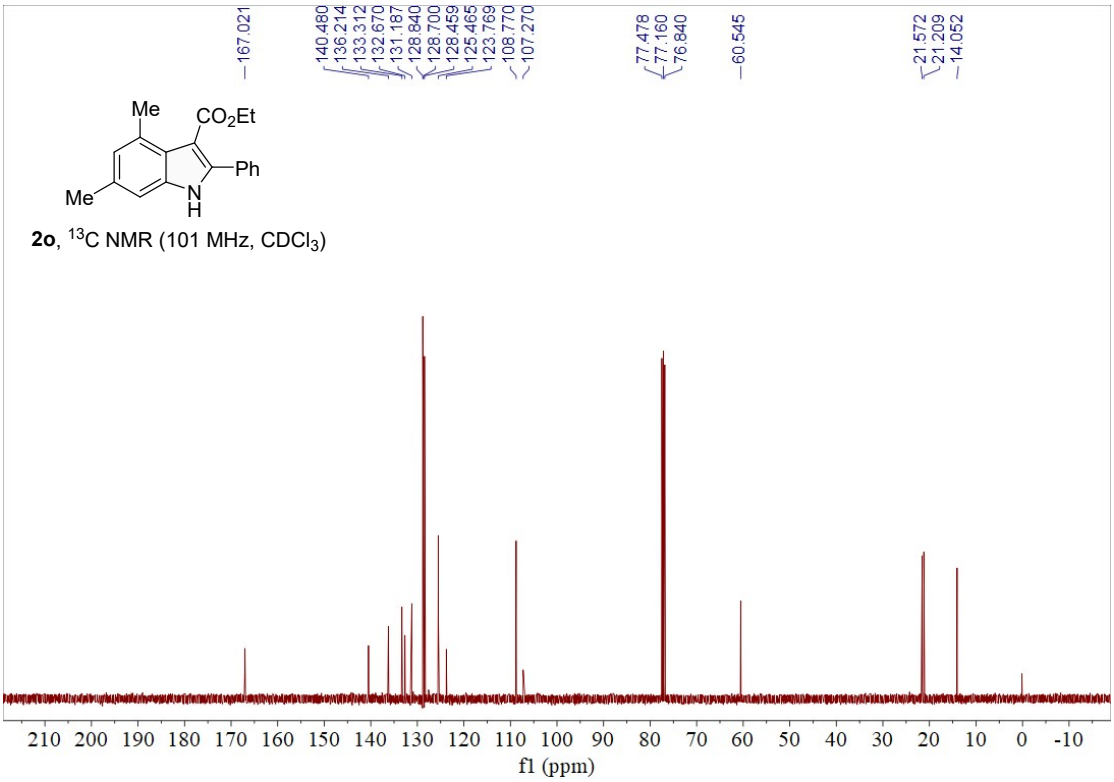
2n, ^{1}H NMR (400 MHz, $CDCl_3$)



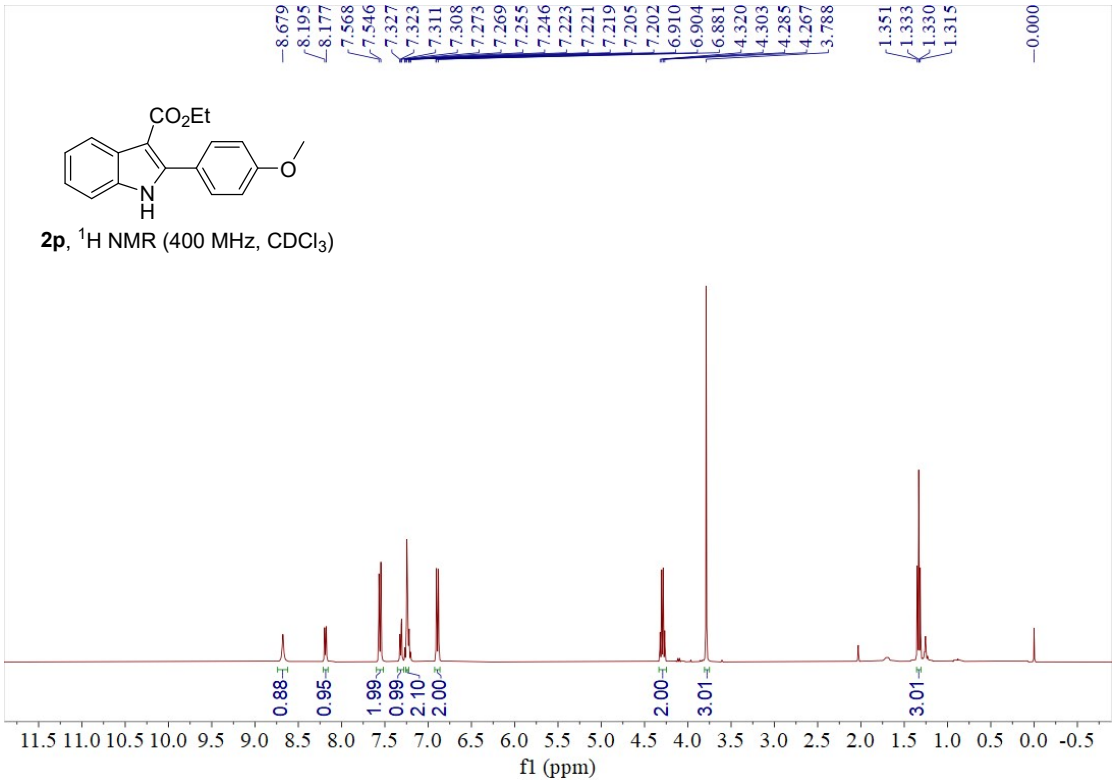
2n, ^{13}C NMR (101 MHz, $CDCl_3$)



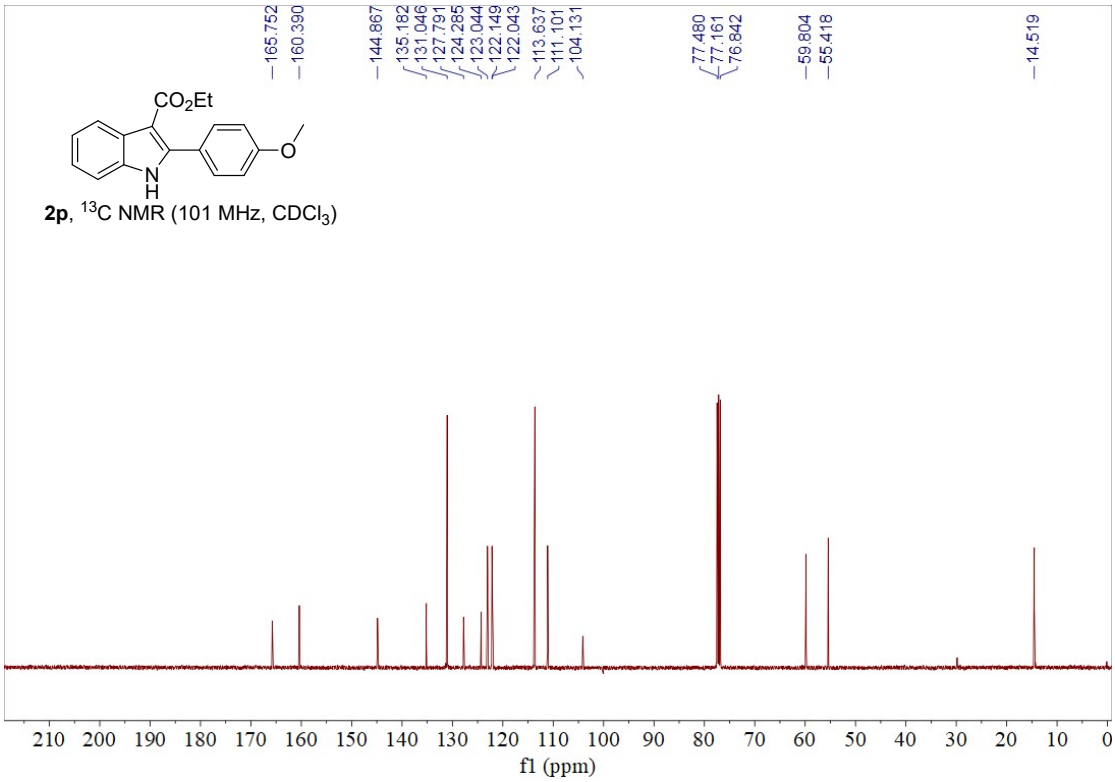
2o, ^{1}H NMR (400 MHz, $CDCl_3$)



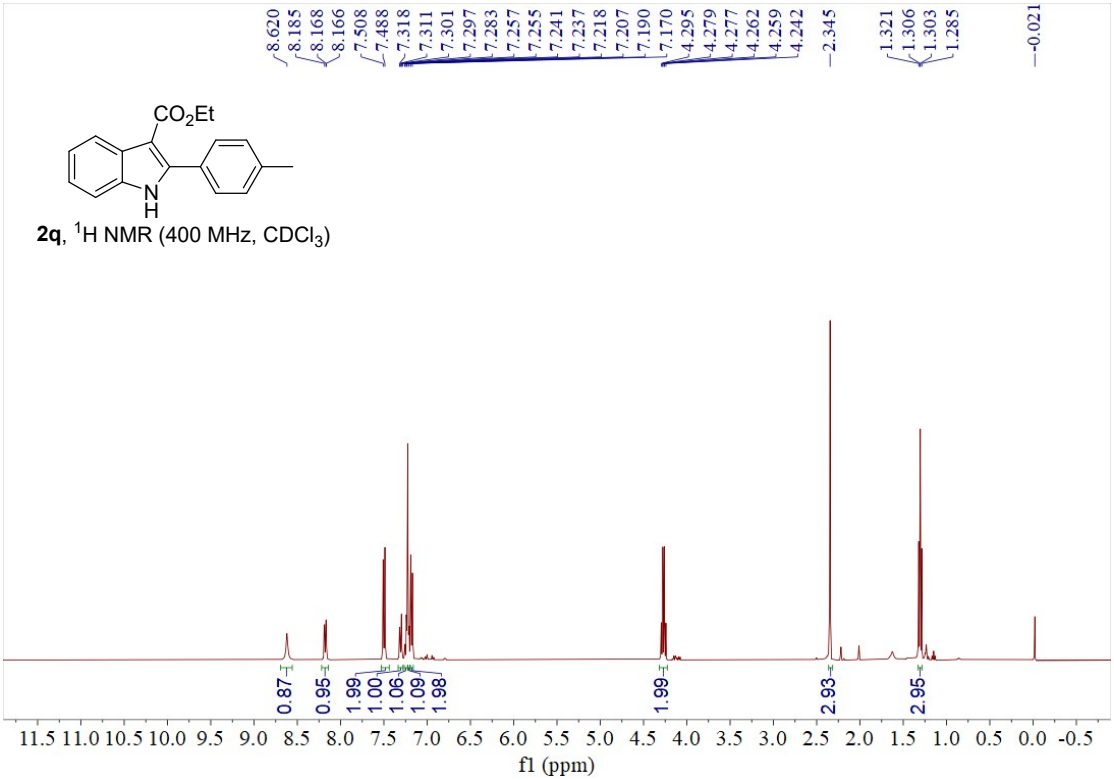
2o, ^{13}C NMR (101 MHz, $CDCl_3$)



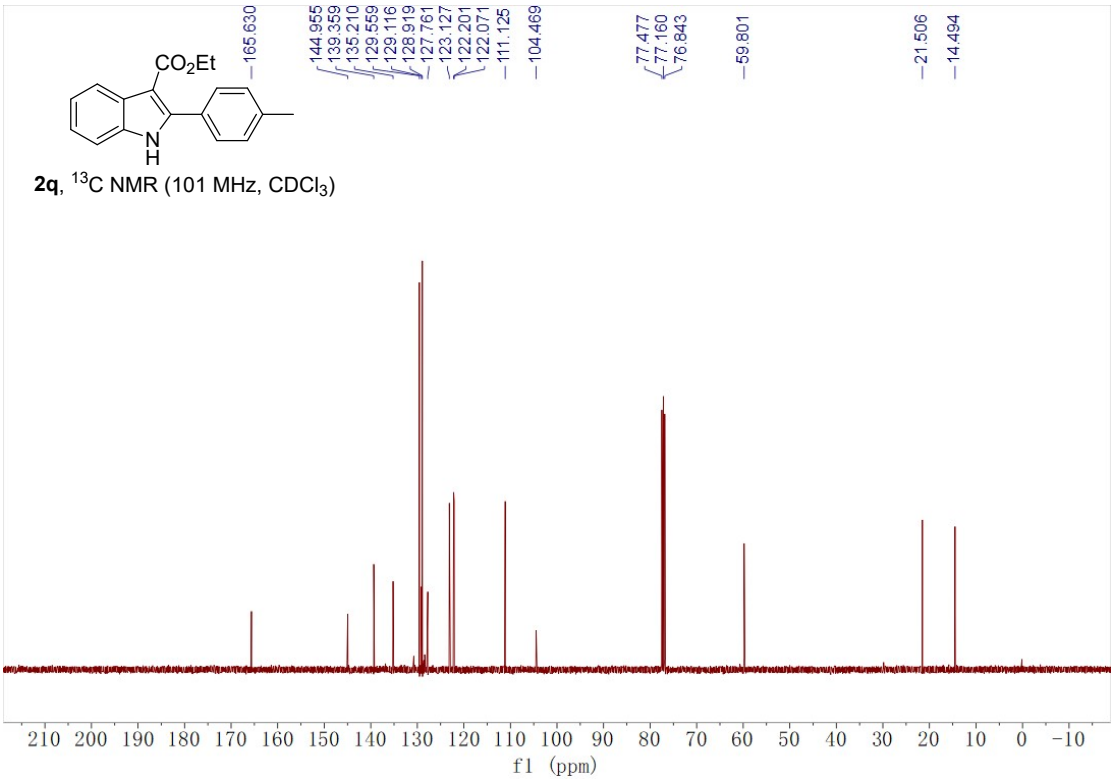
2p, ^{1}H NMR (400 MHz, $CDCl_3$)



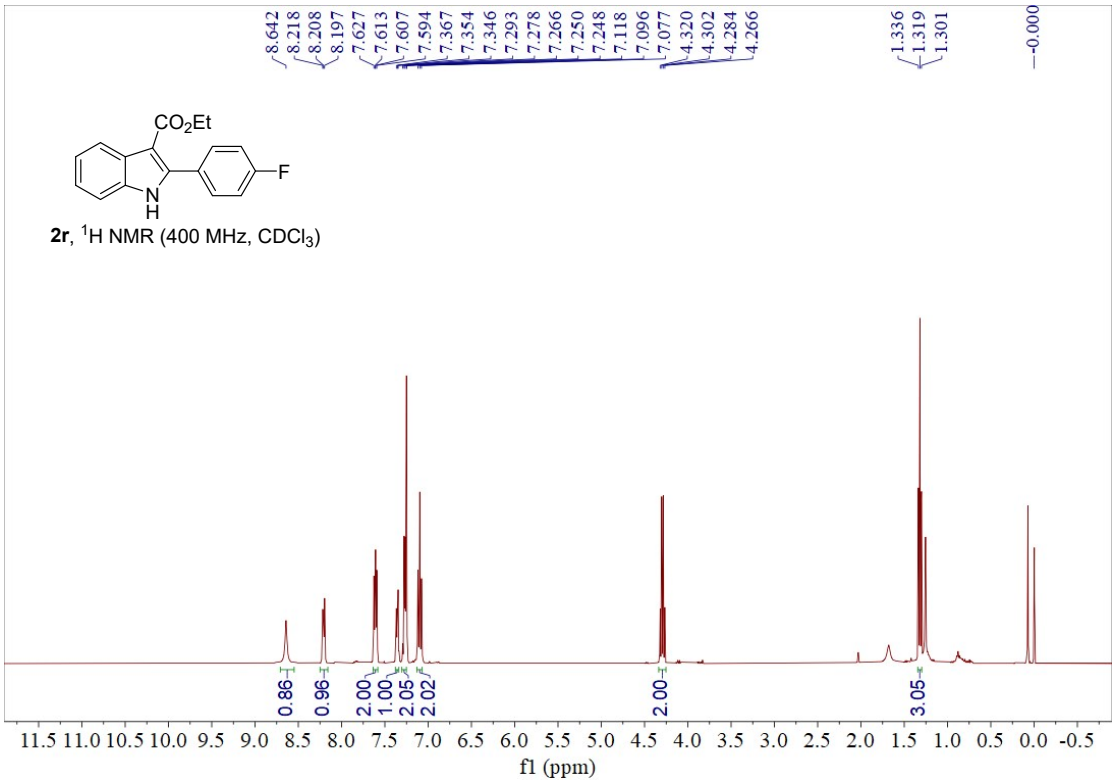
2p, ^{13}C NMR (101 MHz, $CDCl_3$)



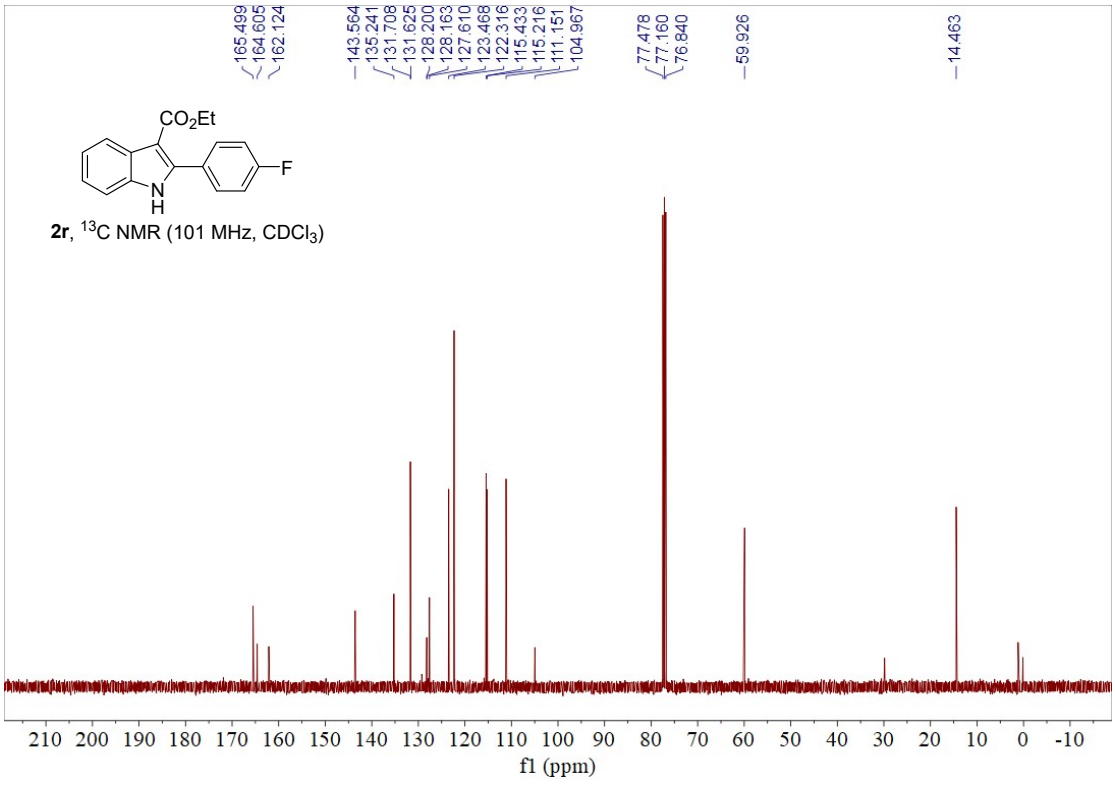
2q, ^{1}H NMR (400 MHz, $CDCl_3$)



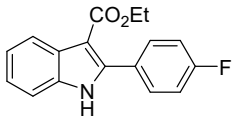
2q, ^{13}C NMR (101 MHz, $CDCl_3$)



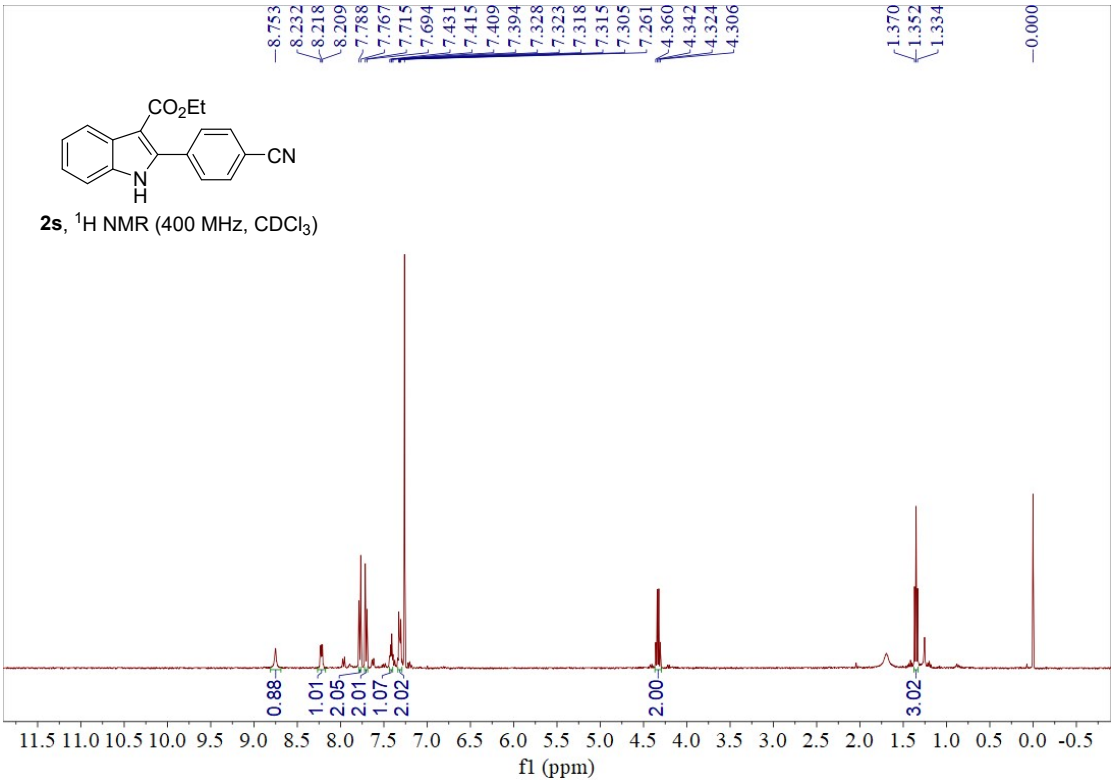
2r, ^{1}H NMR (400 MHz, $CDCl_3$)



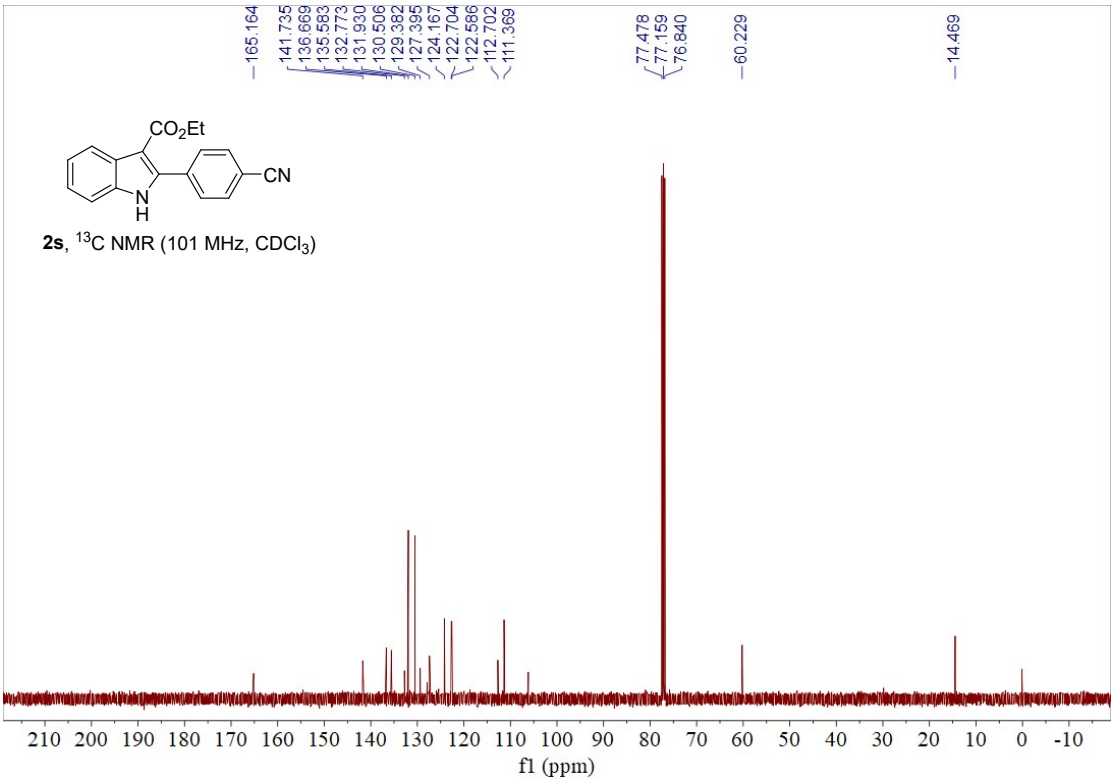
2r, ^{13}C NMR (101 MHz, $CDCl_3$)



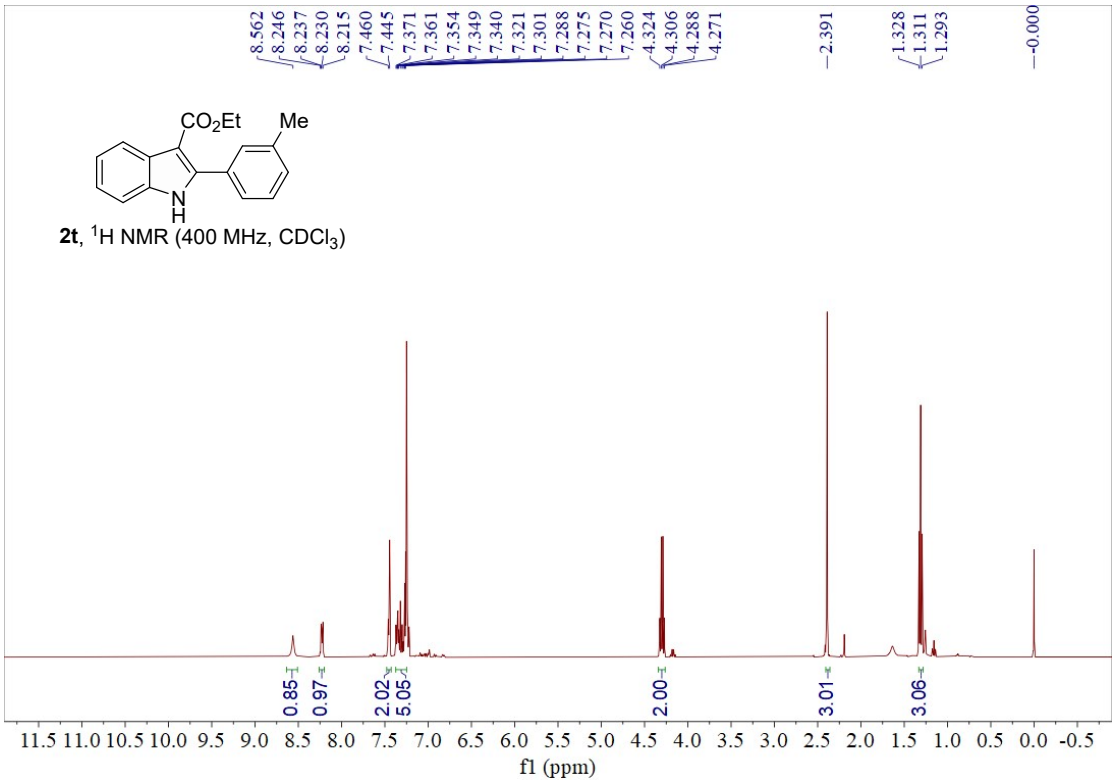
2r, ^{19}F NMR (565 MHz, $CDCl_3$)



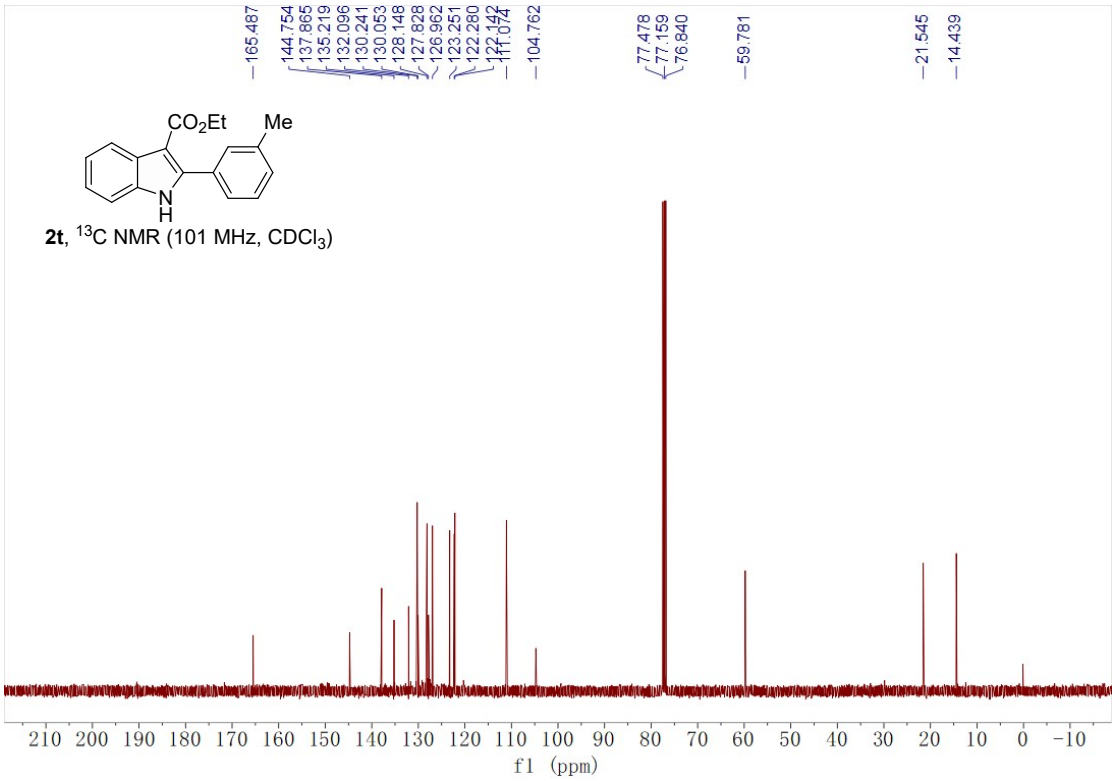
2s, ^{1}H NMR (400 MHz, $CDCl_3$)



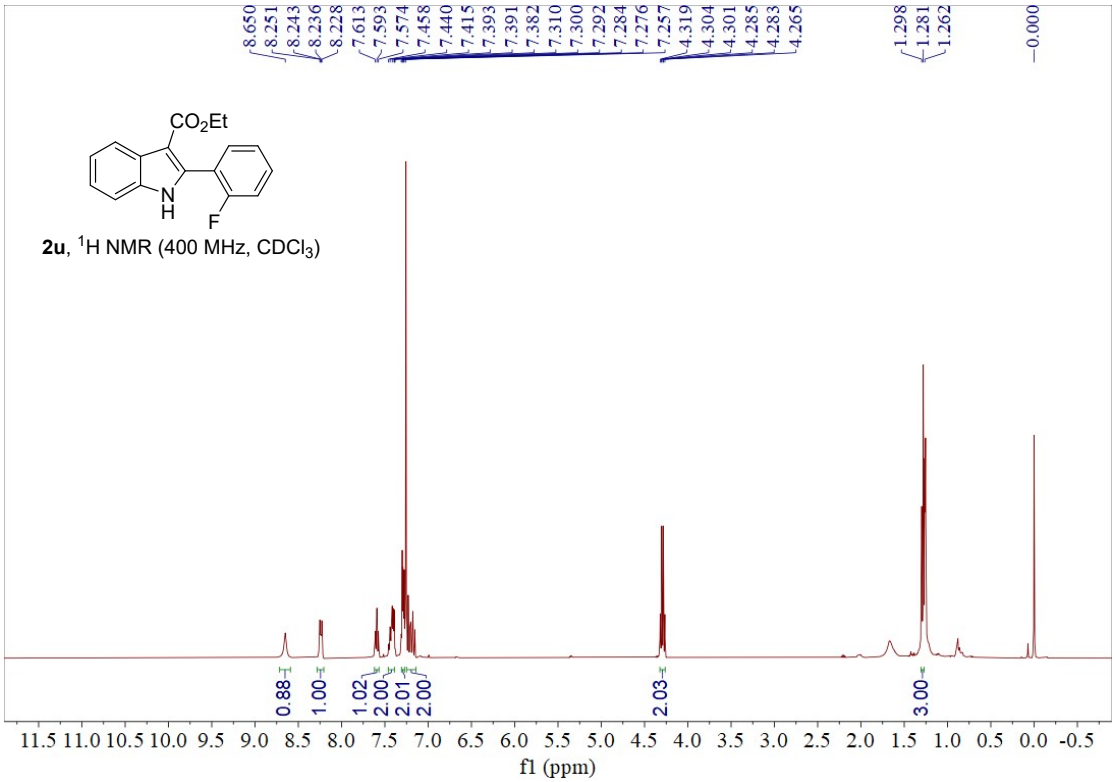
2s, ^{13}C NMR (101 MHz, $CDCl_3$)



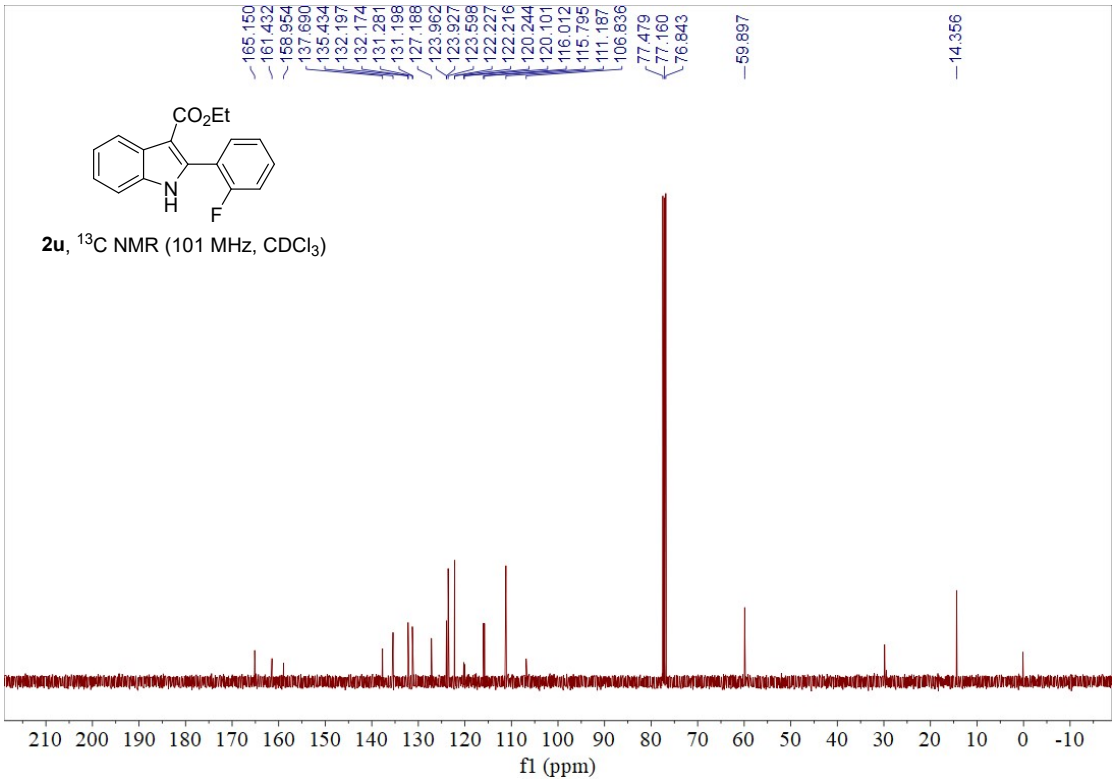
2t, ^{1}H NMR (400 MHz, $CDCl_3$)



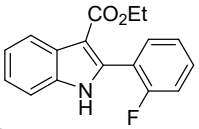
2t, ^{13}C NMR (101 MHz, $CDCl_3$)



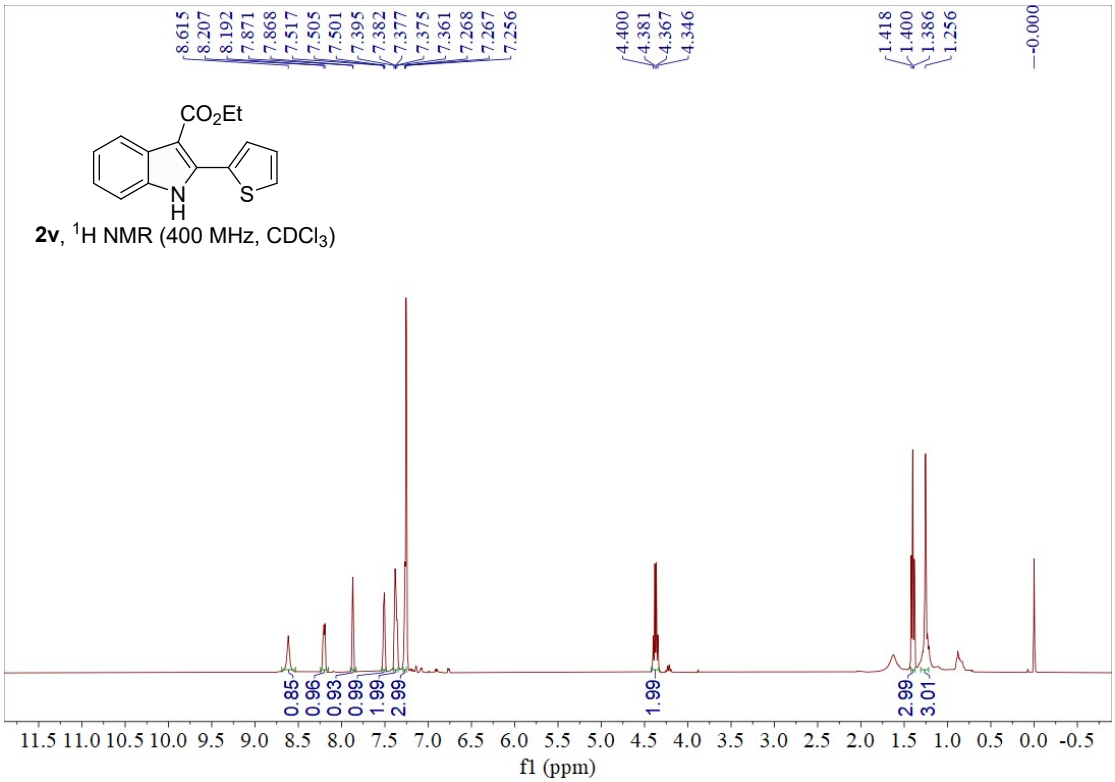
2u, ^{1}H NMR (400 MHz, $CDCl_3$)



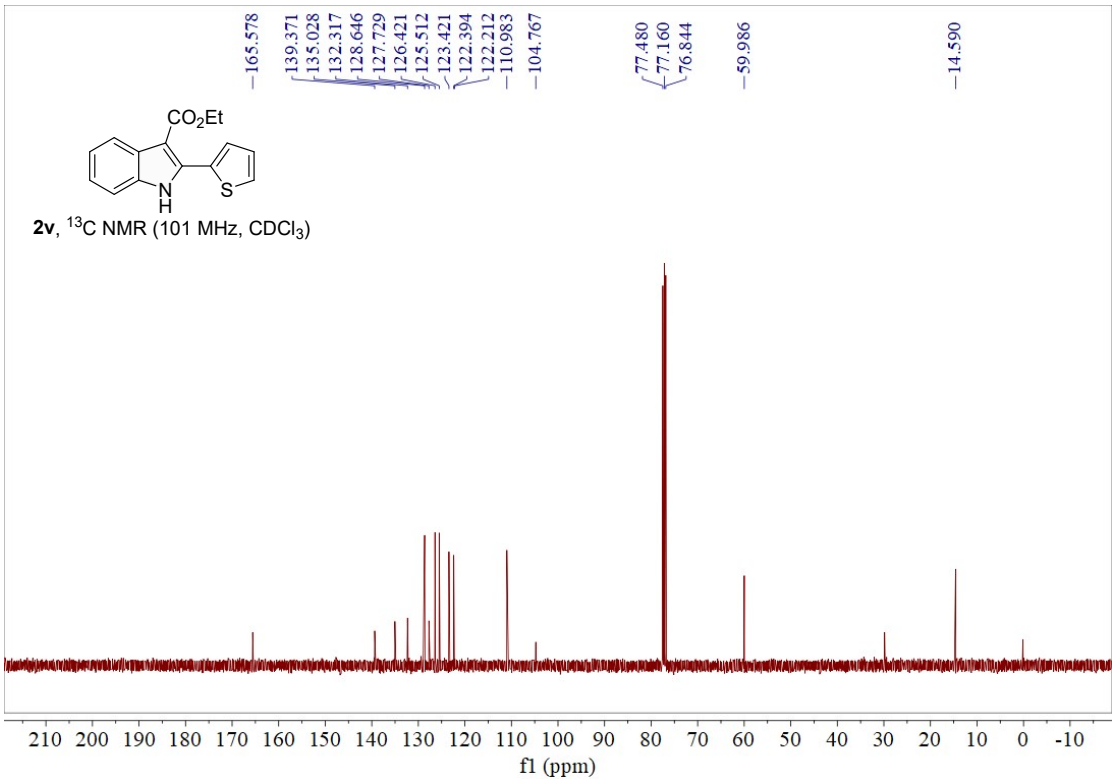
2u, ^{13}C NMR (101 MHz, $CDCl_3$)



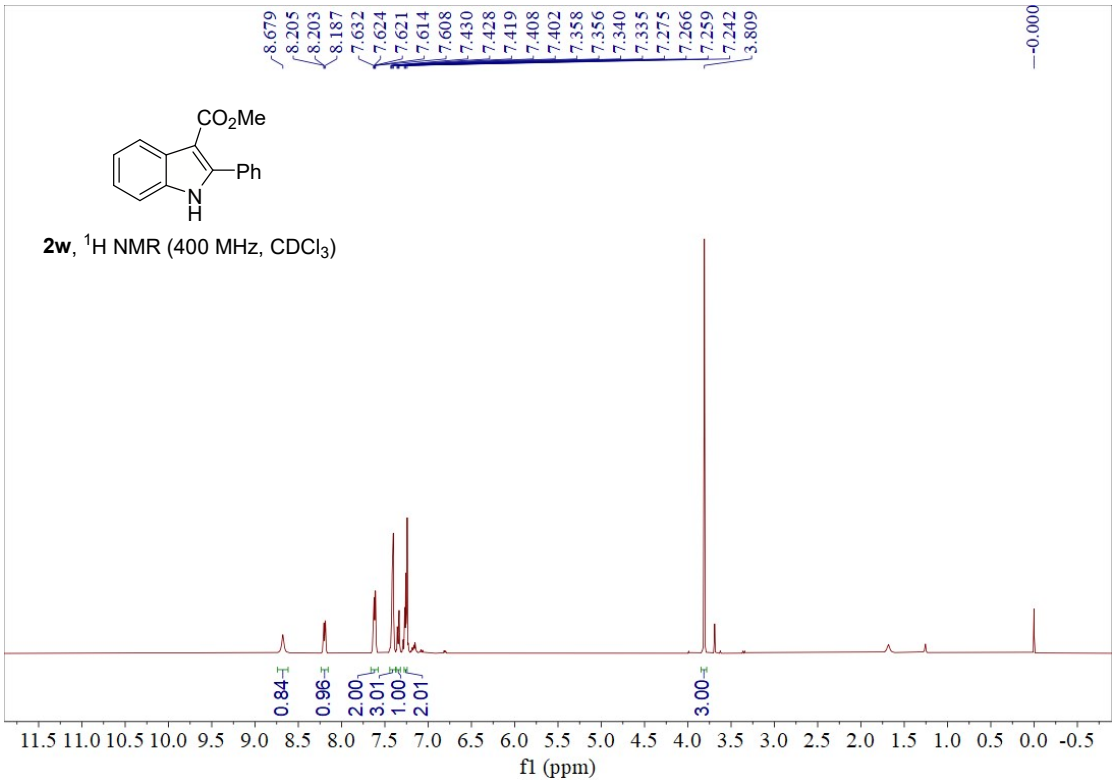
2u, ^{19}F NMR (565 MHz, $CDCl_3$)



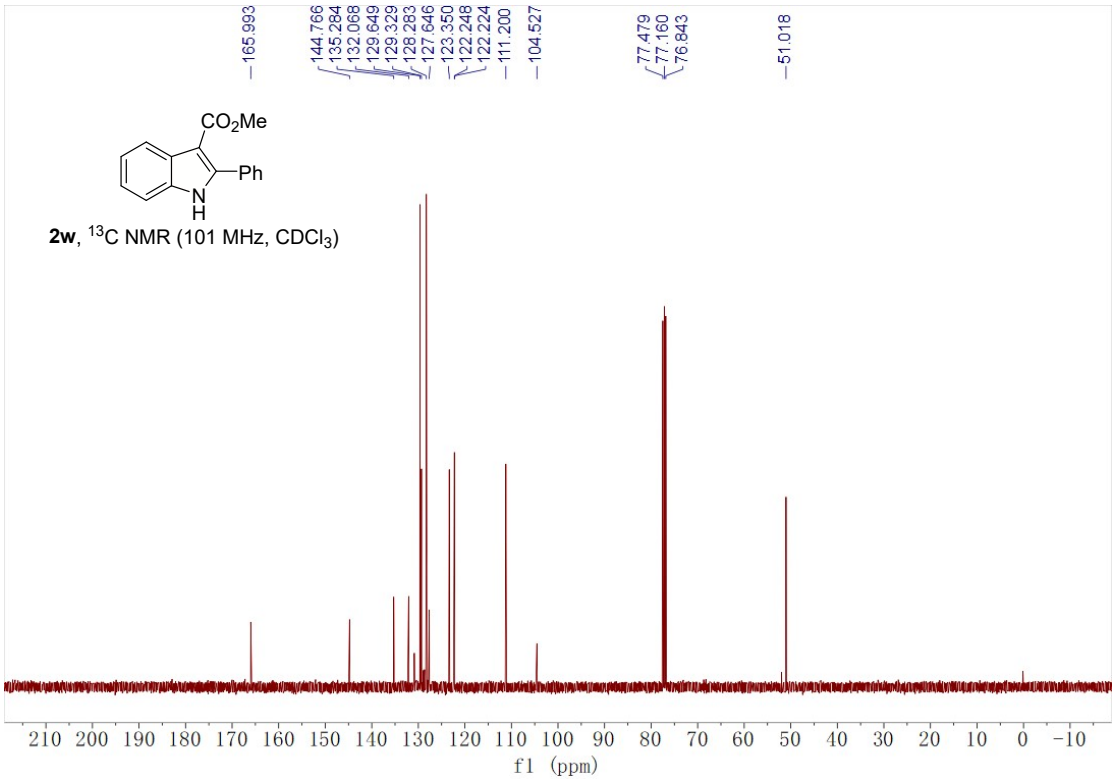
2v, ^{1}H NMR (400 MHz, $CDCl_3$)



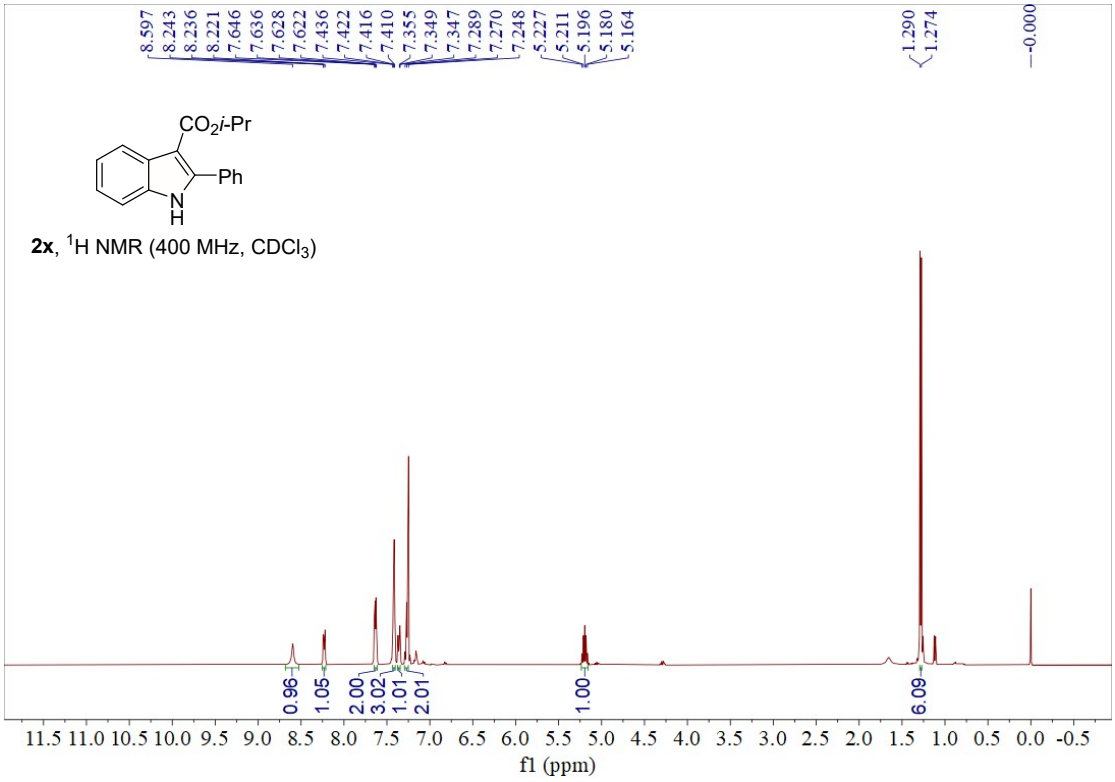
2v, ^{13}C NMR (101 MHz, $CDCl_3$)



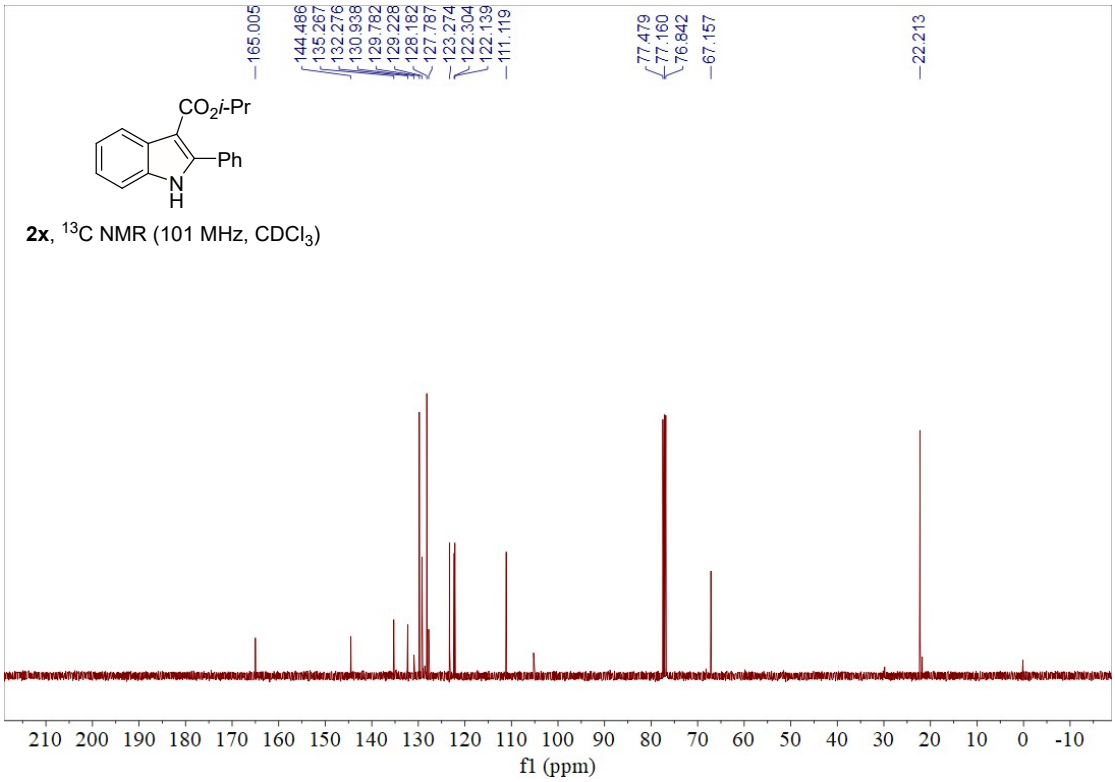
2w, ^{1}H NMR (400 MHz, $CDCl_3$)



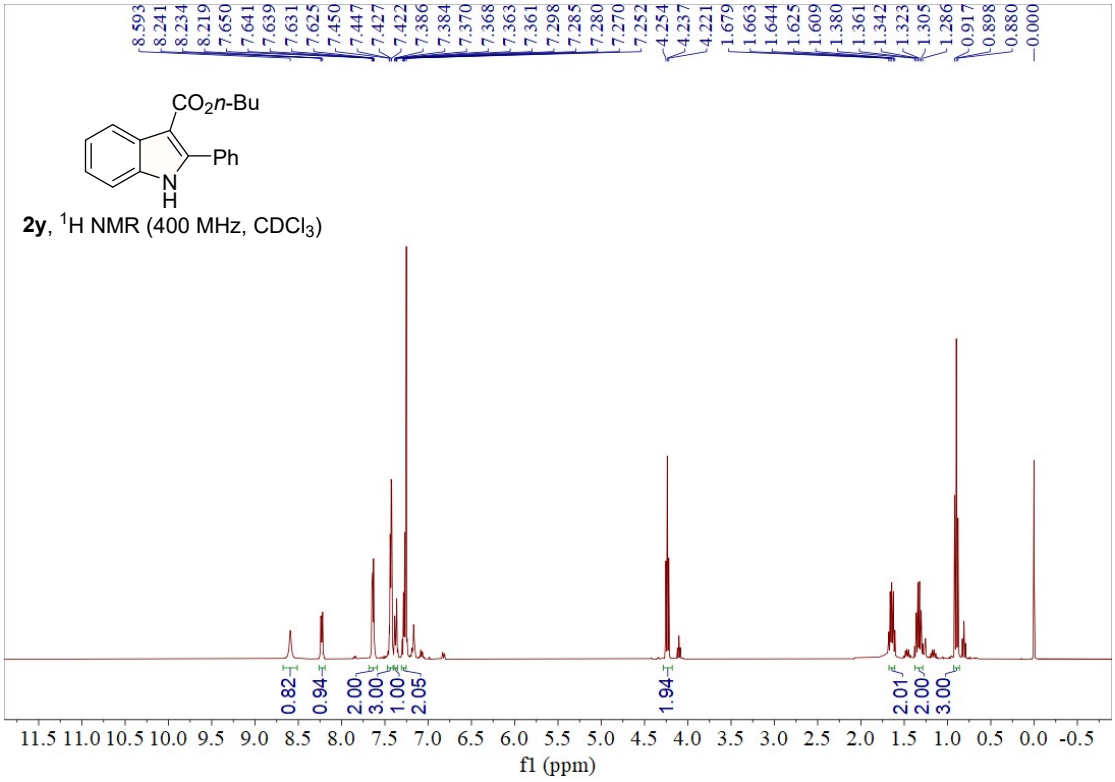
2w, ^{13}C NMR (101 MHz, $CDCl_3$)



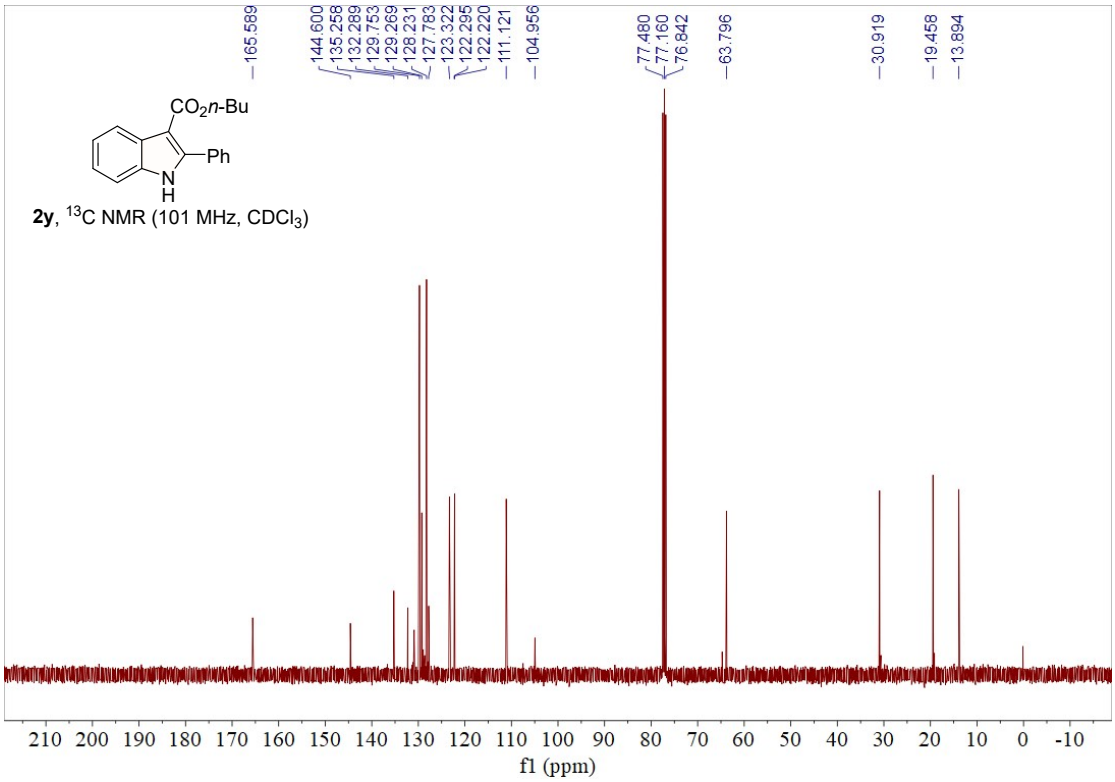
2x, ^{1}H NMR (400 MHz, $CDCl_3$)



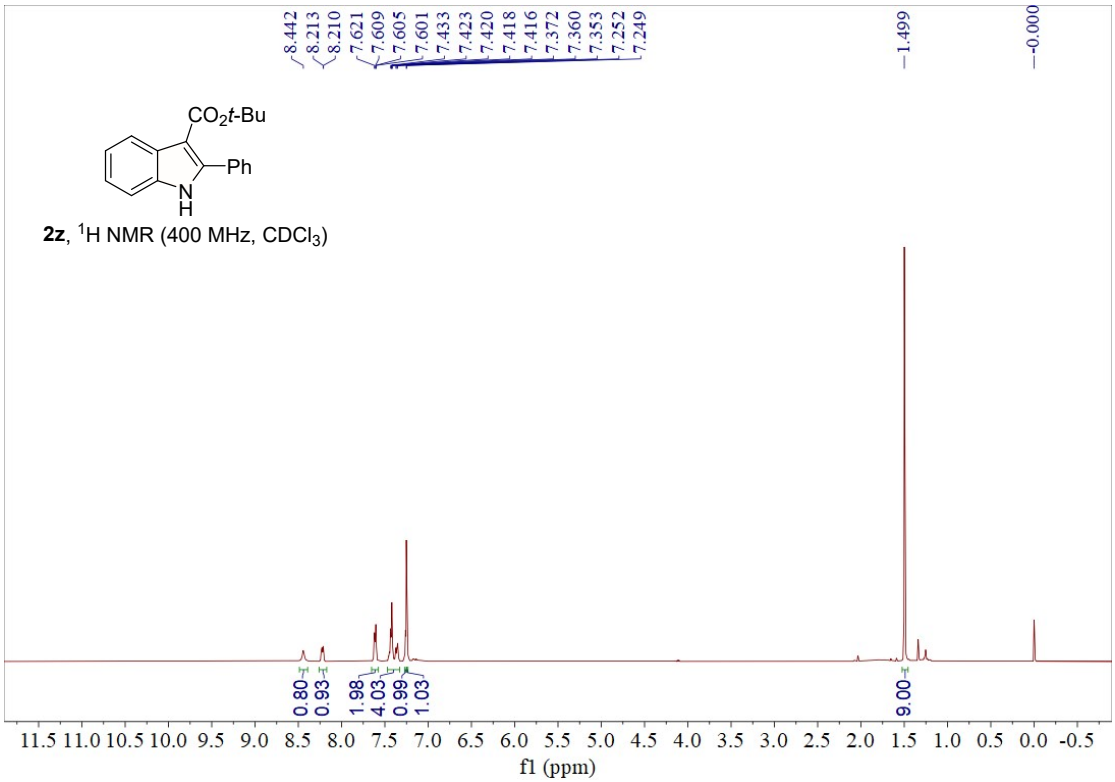
2x, ^{13}C NMR (101 MHz, $CDCl_3$)



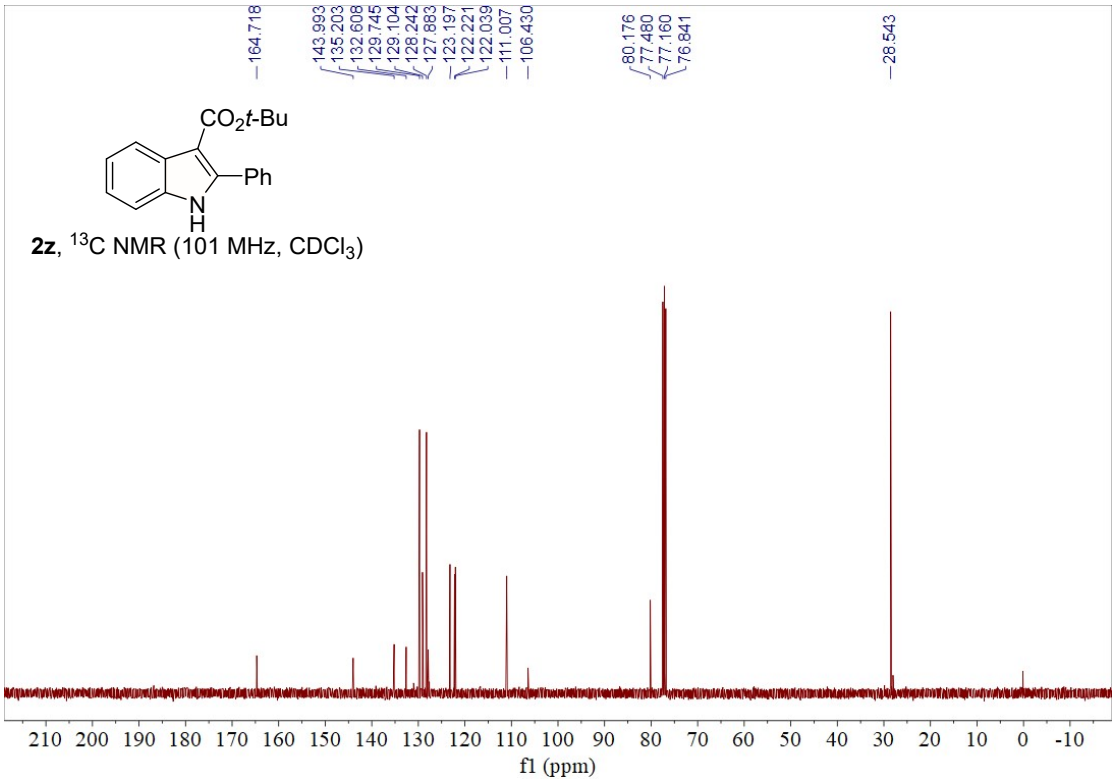
2y, ^{1}H NMR (400 MHz, $CDCl_3$)



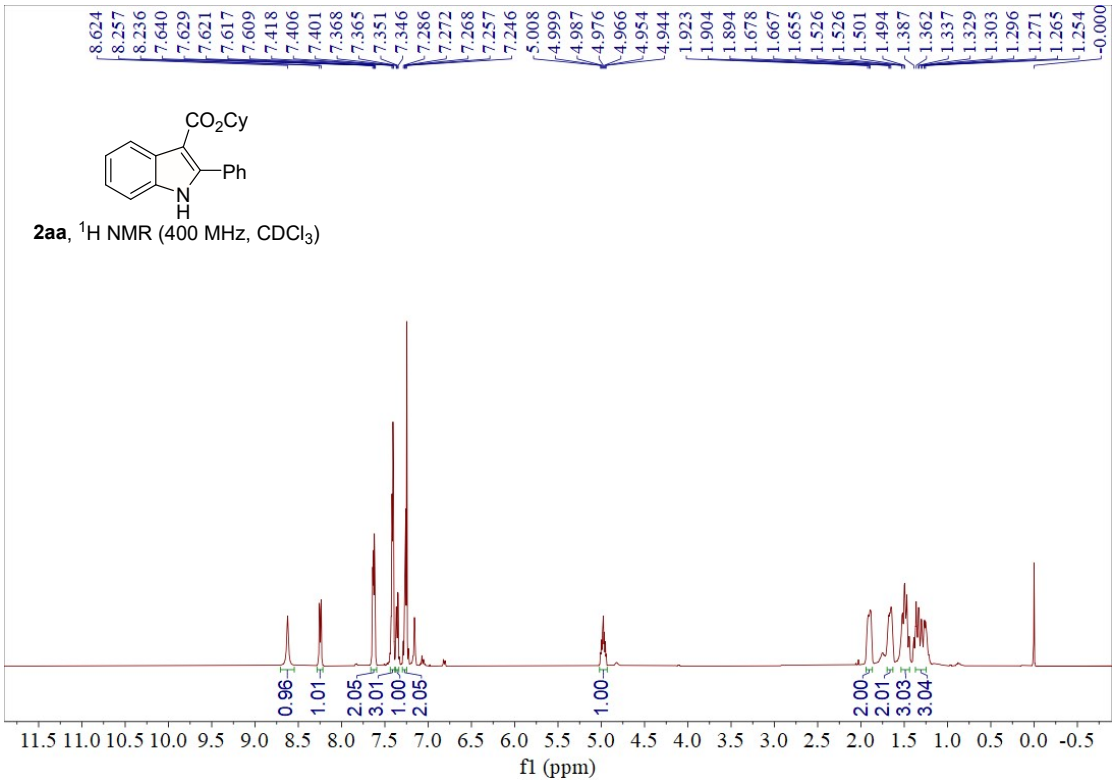
2y, ^{13}C NMR (101 MHz, $CDCl_3$)



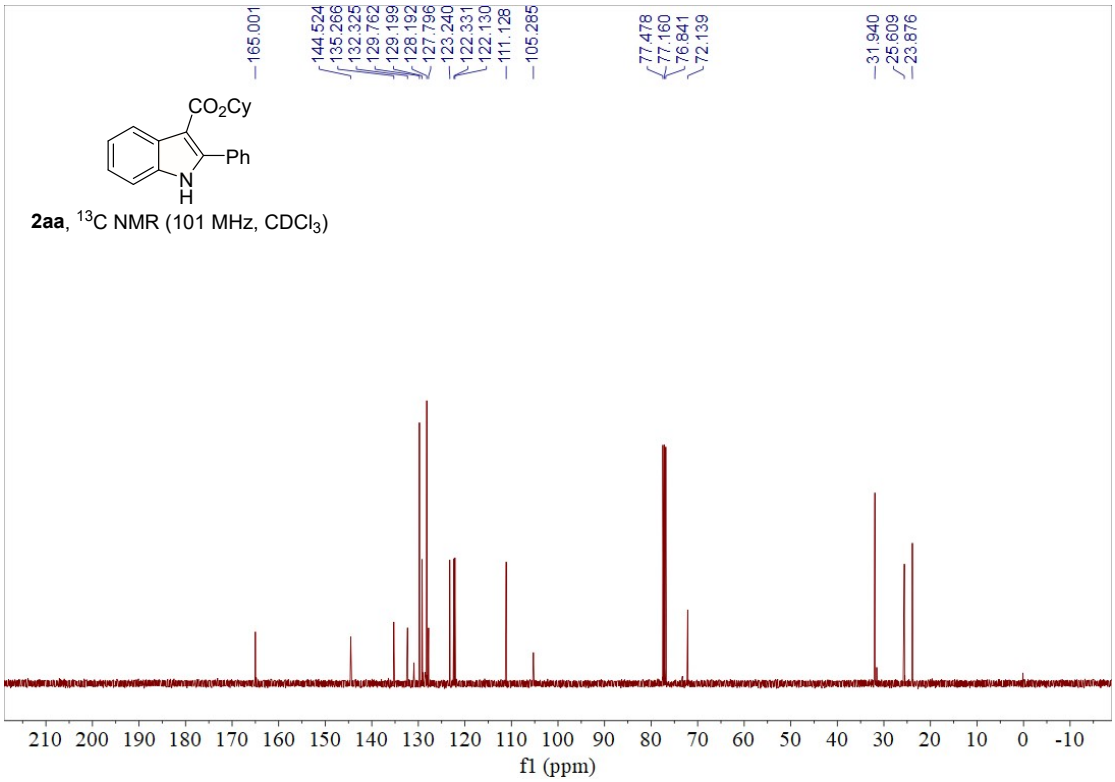
2z, ^{1}H NMR (400 MHz, $CDCl_3$)



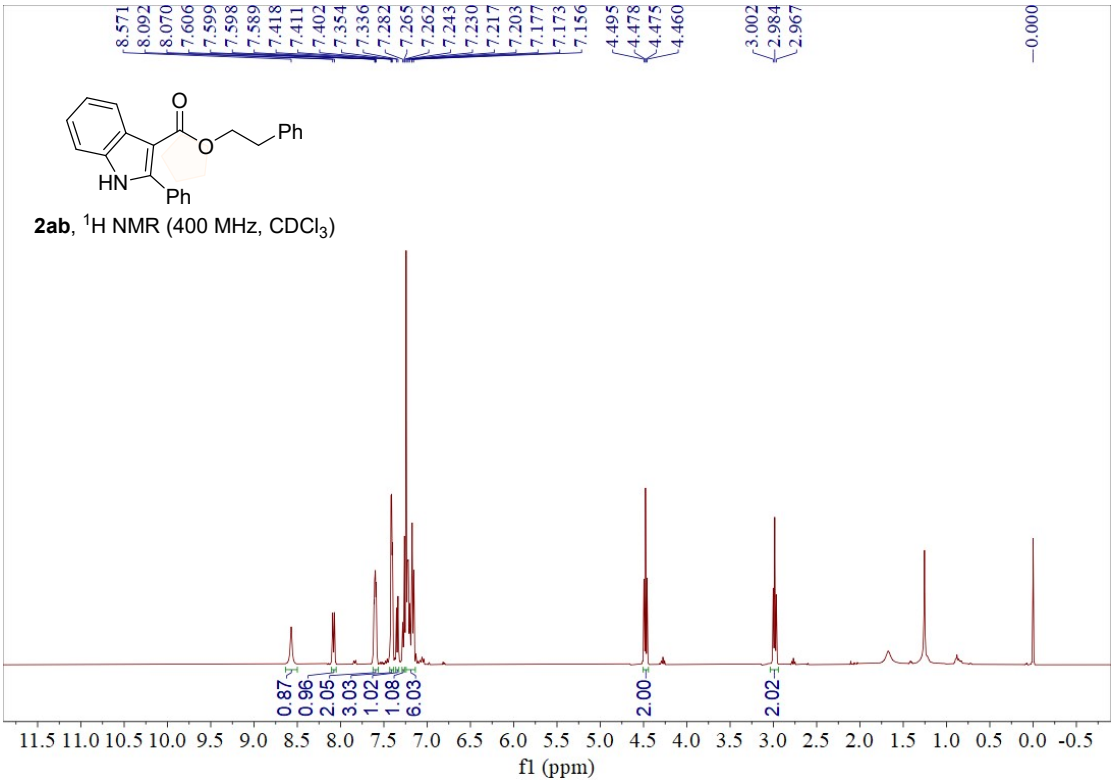
2z, ^{13}C NMR (101 MHz, $CDCl_3$)



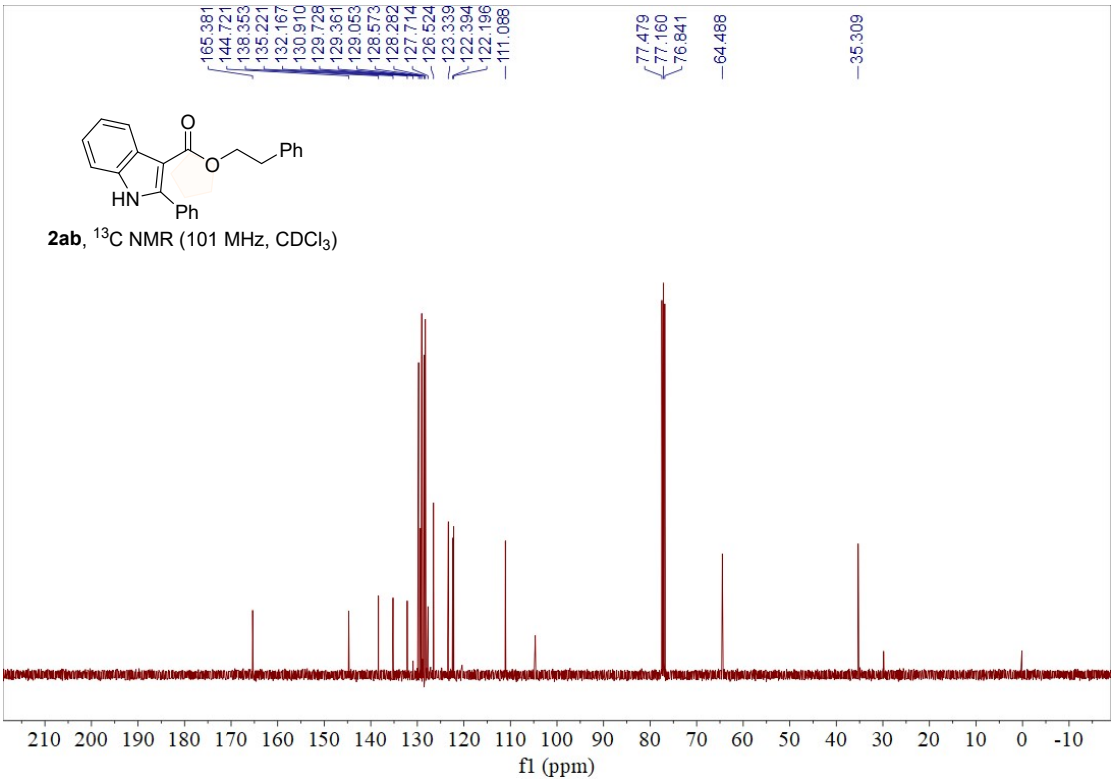
2aa, ^{1}H NMR (400 MHz, $CDCl_3$)



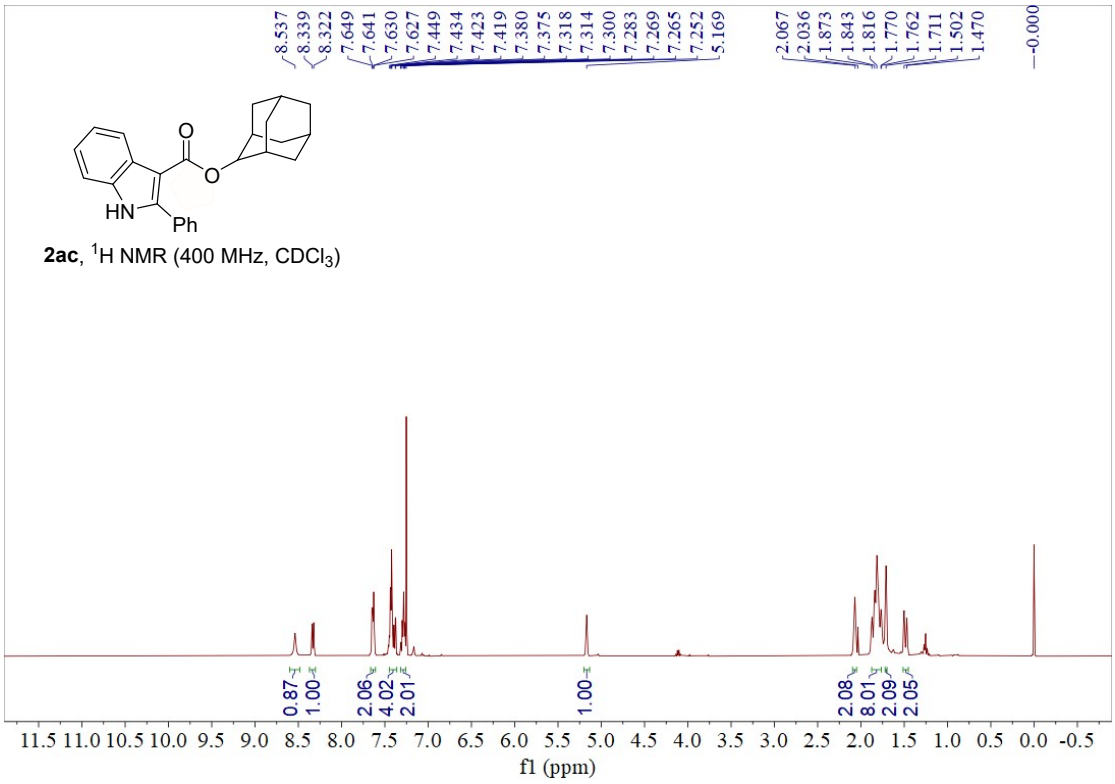
2aa, ^{13}C NMR (101 MHz, $CDCl_3$)



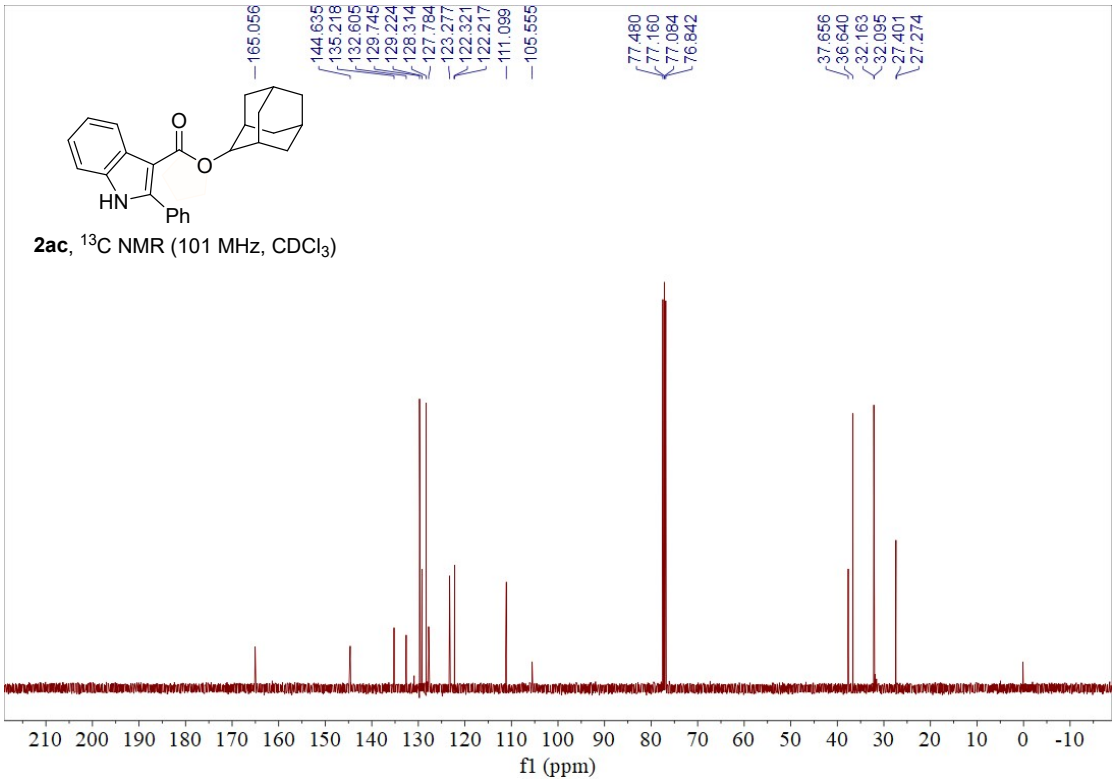
2ab, ^{1}H NMR (400 MHz, $CDCl_3$)



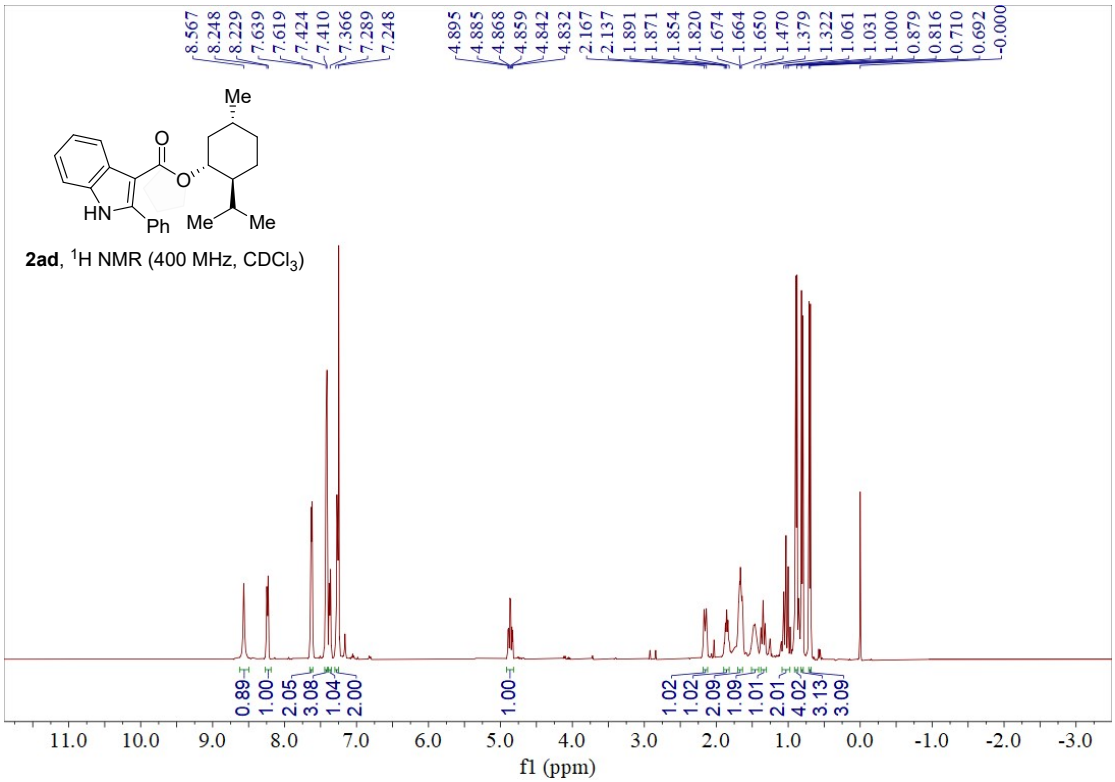
2ab, ^{13}C NMR (101 MHz, $CDCl_3$)



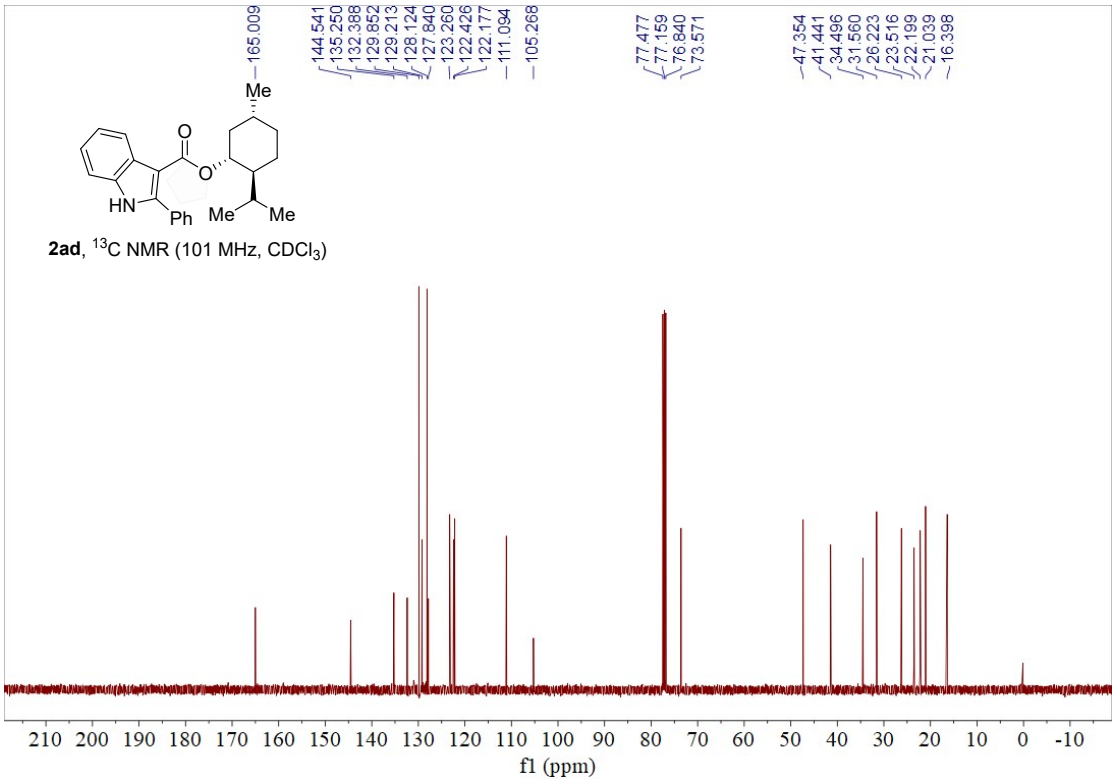
2ac, ^{1}H NMR (400 MHz, $CDCl_3$)



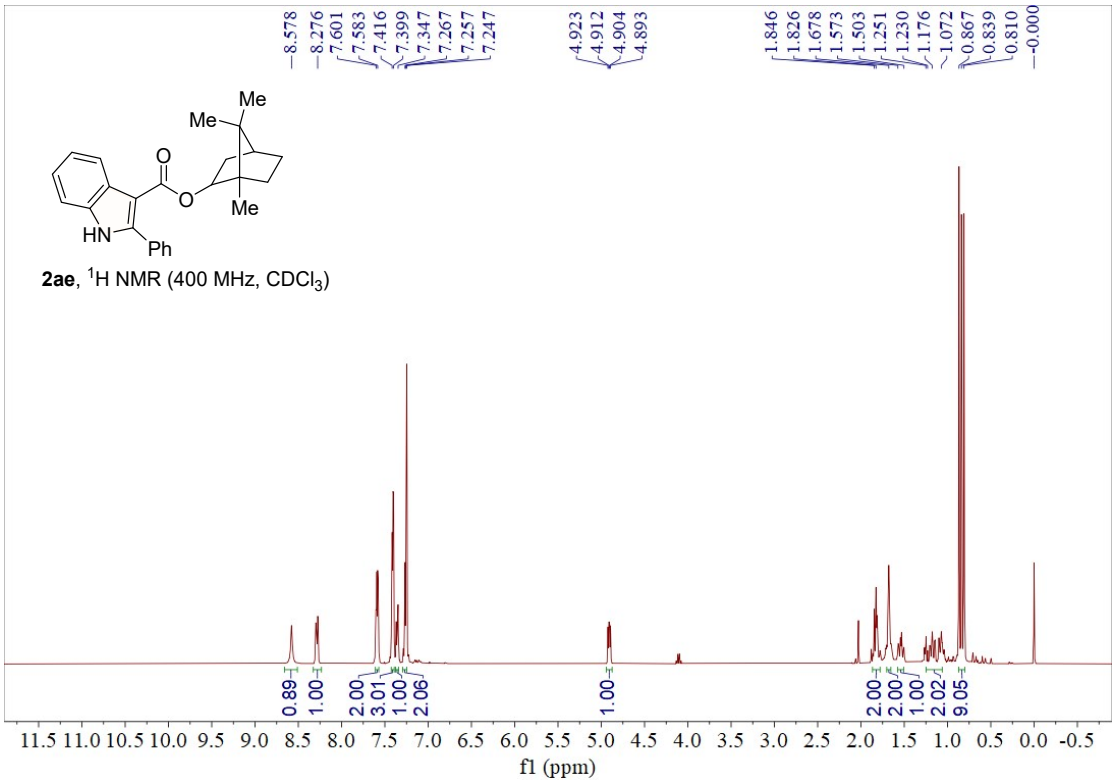
2ac, ^{13}C NMR (101 MHz, $CDCl_3$)



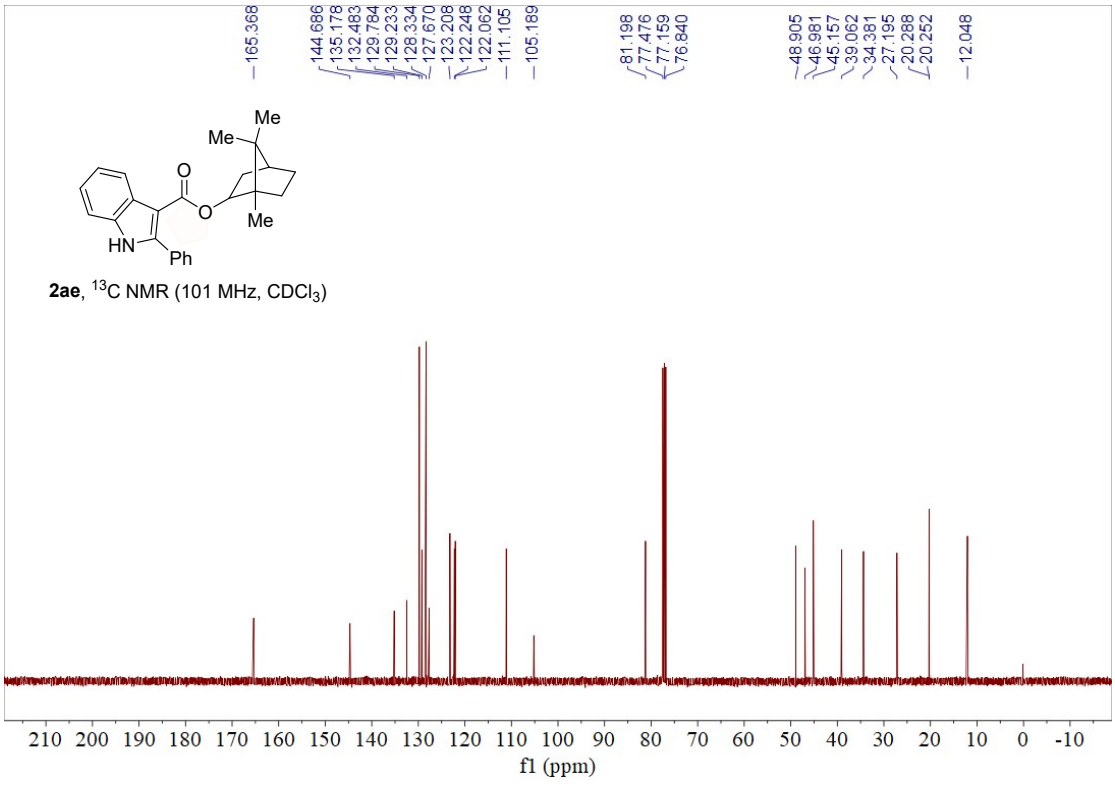
2ad, ^{1}H NMR (400 MHz, $CDCl_3$)



2ad, ^{13}C NMR (101 MHz, $CDCl_3$)



2ae, ^{1}H NMR (400 MHz, $CDCl_3$)



2ae, ^{13}C NMR (101 MHz, $CDCl_3$)