Supporting Information

Palladium-Catalyzed Imidoylative Spirocyclization of 3-(2-Isocyanoethyl)indoles

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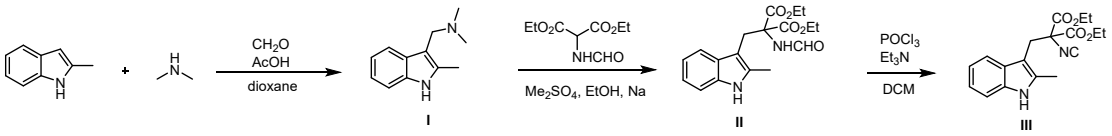
Contents

1. General considerations

The reactions were carried out under air or argon atmosphere. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) in $CDCl_3$ as solvent and recorded in ppm relative to internal standard tetramethylsilane. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectroscopic data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI. The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purificationunless otherwise specified. Products were purified by flash chromatography on 200-300 mesh silica gels, SiO_2.

2. Experimental section

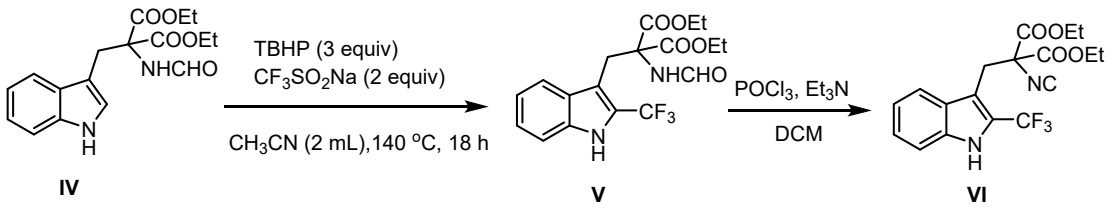
Synthesis of starting materials:



Step 1: In a two-necked round bottom flask equipped with a dropping funnel, 2.1 mL formaldehyde (37 wt% in water, 28 mmol) were dissolved in 24 mL dioxane together with 2 mL H_2O and 26 mL glacial acetic acid. The flask was immersed in an ice bath and dimethylamine (40 wt% in water, 3.47 mL, 28 mmol) was added at once. To this mixture, 26 mmol of the desired indole, dissolved in 24 mL dioxane, were added dropwise. After the addition of the indole, the mixture was allowed to stir for 2 h at 0 °C, then for 12 h at rt. The mixture was then diluted with 32 mL water and 1.5 g of Celite was added. After stirring for 10 minutes, the mixture was filtered off over Celite and the filtrate was treated with 2N NaOH. The precipitate was recovered by filtration, washed with water and dried under vacuum to afford the product **I**.[1]

Step 2: Sodium (0.23 g, 10 mmol) was dissolved in absolute ethanol (30 mL). diethyl 2-formamidomalonate (1.74 g, 10 mmol) and ethyl formamidomalonate **I** (2.03 g, 10 mmol) were added to this solution followed by the slow addition of dimethyl sulfate (2.52 g). The solution was allowed to stand at room temperature for 4 h, and the white precipitate that formed was poured into water, filtered, and dried. The yield of the title compound **II** was 90-99%.[2]

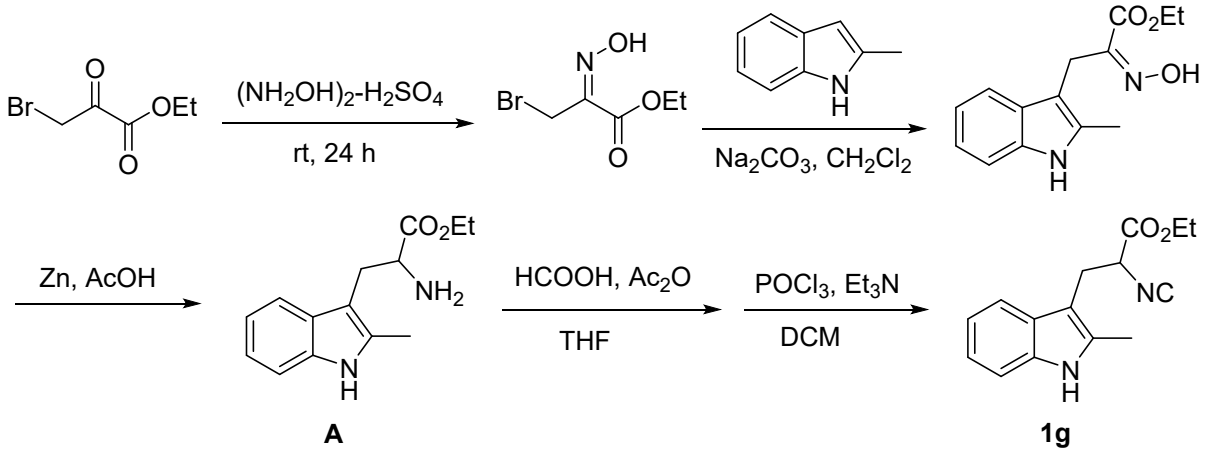
Step 3: **II** (3 mmol, 1.0 equiv) was dissolved in dry DCM (30 mL) and Et_3N (4 equiv), cooled to -20 °C. To mixture $POCl_3$ (1.2 equiv) was added, dropwise slowly. The reaction mixture was stirred for 2 h. Then, 10 mL of H_2O was added slowly to the reaction mixture at -20 °C The crude reaction mixture was extracted with DCM (100 mL×3) and washed with brine (100 mL). The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to afford the product **III** as a colourless oil in 90-98% yield.[3]



IV **V** **VI**

Similar procedures (**IV**) according to the above general procedure (step 1, step 2). **IV** (0.3 mmol), CF_3SO_2Na (0.6 mmol, 2 equiv), TBHP (0.9 mmol, 3 equiv) and CH_3CN (2 mL) were added into a sealed Pyrex test tube stirred at 140 °C under air. The reaction was stopped about 18 h and cooled to room temperature. Then, the crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum ether as the developing solvent to give the products **V**.[4]

Similar procedures (**VI**) according to the above general procedure (step 3), and the substrate **VI** was obtained as colorless oil.



A **1g**

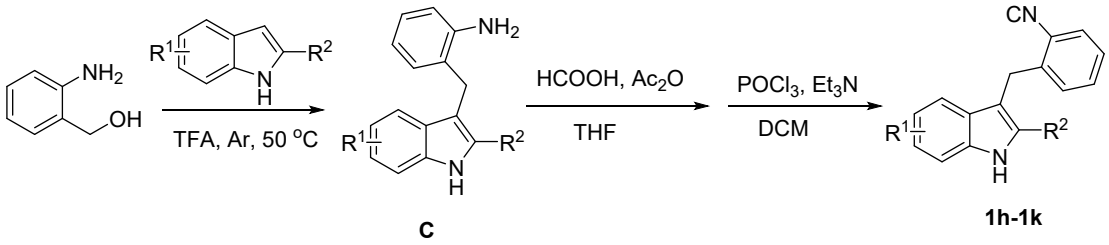
Step 1: A solution of hydroxylamine sulfate (0.5 g, 3.1 mmol) in water (3.0 mL) was added to a solution of ethylbromopyruvate (90%) (0.65 g, 3.0 mmol) in $CHCl_3$ (1.0 mL). The two-phase system was rapidly stirred for 24 h at room temperature. The mixture was extracted with $CHCl_3$ (30 mL). The combined extracts were dried over Na_2SO_4 and concentrated to give the title compound (0.62 g, 99%) as a white solid.

Step 2: A solution of 3-bromo-2-hydrox-yimino-propionic acid ethyl ester (0.38 g, 1.8 mmol) in CH_2Cl_2 (2.0 mL) was slowly added dropwise to a stirring mixture of 2-methyl-1*H*-indole (0.24 g, 1.8 mmol) and Na_2CO_3 (1.05 g, 9.9 mmol) in CH_2Cl_2 (3.0 mL) at room temperature. The mixture was stirred for 20 h, filtered through celite and concentrated to give the title compound (0.41 g, 87%).

Step 3: Zinc powder (0.39 g, 6.0 mmol) was added portionwise to a stirred solution of ethyl(*Z*)-2-(hydroxyimino)-3-(2-methyl-1H-indol-3-yl)-propanoate (0.39 g, 1.5 mmol) in acetic acid (10 mL) over 30 min. After stirring overnight, the mixture was filtered through celite and concentrated. The residue was dissolved in HCl (1.0 M) and reevaporated to give the title compound (0.35 g, 95%).

Step 4: A mixture of HCO_2H (3.5 equiv), Ac_2O (1.5 equiv) was stirred at rt for 30 min. To this mixture, a solution of **A** (1.4 mmol, 1.0 equiv) in THF was added slowly. After completion of the reaction, the reaction was quenched by adding saturated aqueous $NaHCO_3$. The organic layer was seperated, and the aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The combined organic phase was washed with brine (40 mL), dried over $MgSO_4$. The concentrated residue was used for next step without further purification. The product was dissolved in dry DCM (30 mL) and Et_3N (4.0 equiv), cooled to -20 ^oC. To mixture $POCl_3$ (1.2 equiv) was added, dropwise slowly. The reaction mixture was stirred for 2 h. Then, 10 mL of H_2O was

added slowly to the reaction mixture at -20 °C The crude reaction mixture was extracted with DCM (100 mL×3) and washed with brine (100 mL). The organic phase was concentrated in vacuo and the residue was purified by silica gel flash column chromatography to afford the product **1g** (1.05 mmol, 75%) as a colorless liquid.

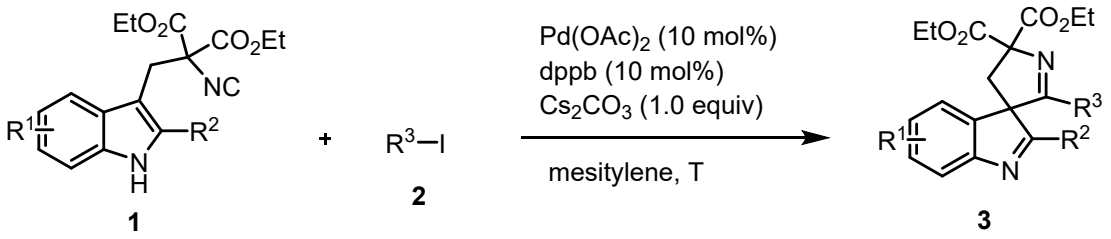


Step 1: To a solution of (2-aminophenyl)methanol (9.8 mmol) and 2-methyl-1*H*-indole (12.74 mmol) in 1,2-dichloroethane (40 mL). After degassing with argon and four evacuation/backfill cycles with argon, trifluoroacetic acid (3.92 mmol) was added dropwise, then the mixture was heated with heating mantle and stirred at 50 °C. When the reaction was complete as monitored by TLC, aqueous solution of saturated Na_2CO_3 was added, concentrated under reduced pressure, dilute hydrochloric acid was added, and the mixture was extracted with dichloromethane three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated, and the resulting mixture was purified by column chromatography on silica gel to afford the product 2-((2-methyl-1H-indol-3-yl)methyl)aniline (1.618 g, 70%)

Step 2: A mixture of HCO_2H (3.5 equiv), Ac_2O (1.5 equiv) was stirred at rt for 30 min. To this mixture, a solution of **C** (1.0 equiv) in THF was added slowly. After completion of the reaction, the reaction was quenched by adding saturated aqueous $NaHCO_3$. The organic layer was seperated, and the aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The combined organic phase was washed with brine (40 mL), dried over $MgSO_4$. The concentrated residue was used for next step without further purification. The product was dissolved in dry DCM (30 mL) and Et_3N (4.0 equiv), cooled to -20 °C. To mixture $POCl_3$ (1.2 equiv) was added, dropwise slowly. The reaction mixture was stirred for 2 h. Then, 10 mL of H_2O was added slowly to the reaction mixture at -20 °C The crude reaction mixture was extracted with DCM (100 mL×3) and washed with brine (100 mL). The organic phase was concentrated in *vacuo* and the residue was purified by silica gel flash column chromatography to

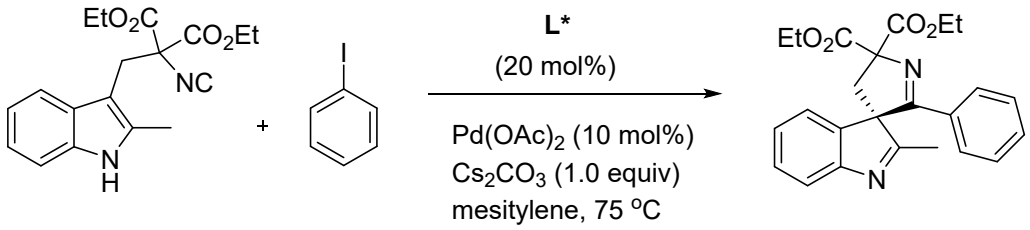
afford the product **1h-1k** as a colourless oil.

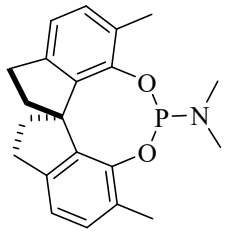
General procedure for the spirocyclization reaction



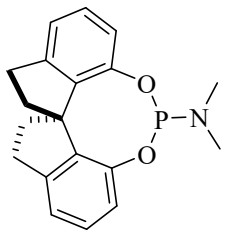
To a mixture of R^3I (0.15 mmol), $Pd(OAc)_2$ (10 mol%), dppb (10 mol%), Cs_2CO_3 (0.1 mmol) in mesitylene (1 mL) was added of **1** (1.0 mol) in mesitylene (1 mL) via a syringe pump during a period of 1.5 h under Ar at 75 °C. The reaction mixture was quenched with water and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under *vaccuo.* The residue was purified by silica gel flash column chromatography to afford the product **3**.

Ligand screening for enantioselective synthesis of spiroindolines

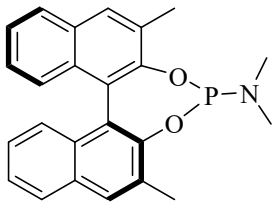




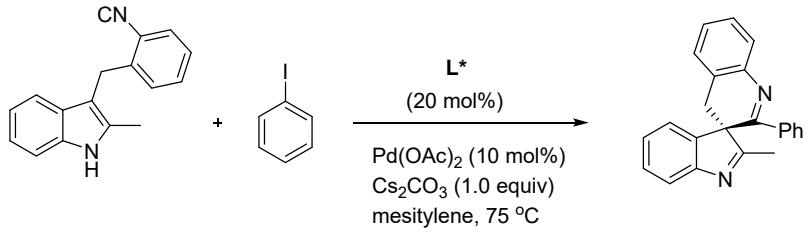
95% yield, 49% ee

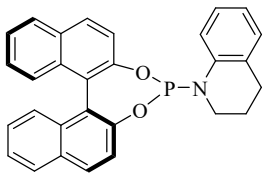


70% yield, 25% ee



40% yield, 0% ee





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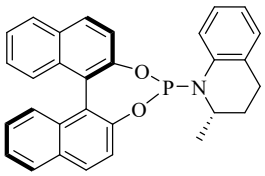
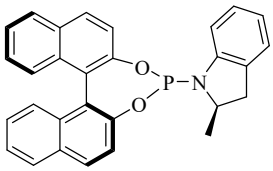
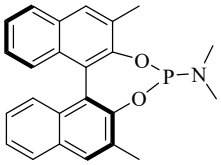


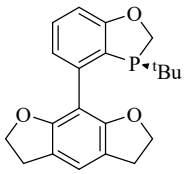
54% yield, 43% ee



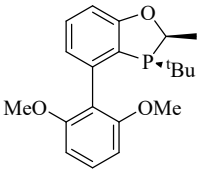
48% yield, 59% ee



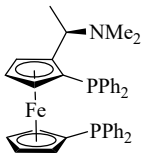
57% yield, 36% ee



5% yield, 65% ee



9% yield, 33% ee



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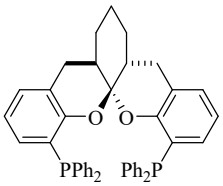
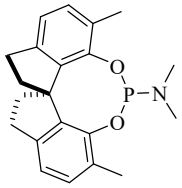
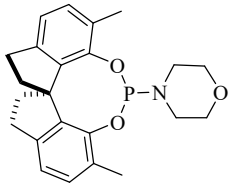


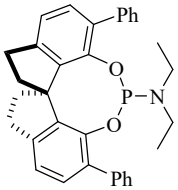
3% yield, 3% ee



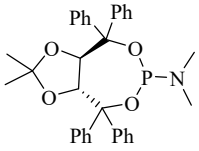
86% yield, 85% ee



65% yield, 80% ee



9% yield, 24% ee



8% yield, 50% ee

References:

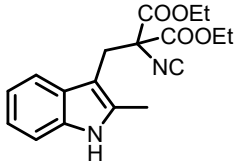
(1) S. Li, S. Zard, *Org. Lett.* 2013, **15**, 5898–5901.

(2) T. Hagen, K. Narayanan, J. Names, J. Cook, *J. Org. Chem.* 1989, **54**, 2170−2178.

(3) S. Tang, S. Yang, H. Sun, Y. Zhou, J. Li, Q. Zhu, *Org. Lett.* 2018, **20**, 1832−1836.

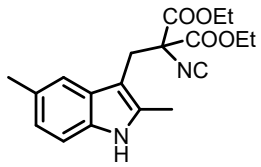
(4) J. Xie, Z. Wang, G. Jiang, *RSC Adv.*, 2019, **9**, 35098−35101.

3. Characterization data



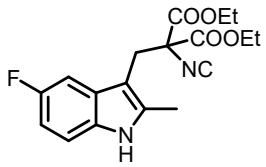
diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (1a):

Prepared from diethyl 2-formamido-2-((2-methyl-1H-indol-3-yl)methyl)malonate (1.04 g, 3 mmol, 1.0 equiv) and Et_3N (1.21 g, 12 mmol, 4.0 equiv), and $POCl_3$ (0.34 ml, 3.6 mmol, 1.2 equiv) according to the general procedure. The product **1a** was isolated as colorless oil (905 mg, 2.76 mmol, 92% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.04 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.10-7.02 (m, 2H), 4.22 (q, J = 7.1 Hz, 4H), 3.70 (s, 2H), 2.46 (s, 3H), 1.20 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.3, 163.5, 135.1, 134.9, 128.3, 121.3, 119.4, 118.2, 110.3, 102.7, 70.0, 63.7, 31.5, 13.6, 12.6. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{18}H_{21}N_2O_4$: 329.1496, found: 329.1491.



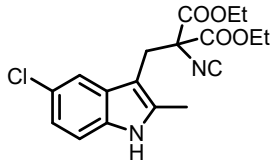
diethyl 2-((2,5-dimethyl-1H-indol-3-yl)methyl)-2-isocyanomalonate (1b):

Prepared from diethyl 2-((2,5-dimethyl-1H-indol-3-yl)methyl)-2-formamidomalonate (1.08 g, 3 mmol, 1.0 equiv) and Et_3N (1.21 g, 12 mmol, 4.0 equiv), and $POCl_3$ (0.34 ml, 3.6 mmol, 1.2 equiv) according to the general procedure. The product **1b** was isolated as colorless oil (902 mg, 2.64 mmol, 88% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 7.00 (d, J = 8.2 Hz, 1H), 6.84 (dd, J = 8.3, 1.2 Hz, 1H), 4.19 (q, J = 7.1 Hz, 4H), 3.65 (s, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 1.18 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.0, 163.1, 135.0, 133.3, 128.9, 127.8, 122.2, 117.4, 109.9, 101.4, 69.9, 63.4, 31.3, 21.2, 13.3, 12.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{19}H_{23}N_2O_4$: 343.1652, found: 343.1654.



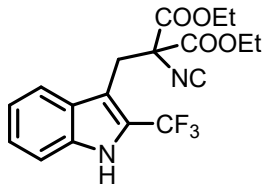
diethyl 2-((5-fluoro-2-methyl-1H-indol-3-yl)methyl)-2-isocyanomalonate (1c):

Prepared from diethyl 2-((5-fluoro-2-methyl-1H-indol-3-yl)methyl)-2-formamidomalonate (1.09 g, 3 mmol, 1.0 equiv) and Et_3N (1.21 g, 12 mmol, 4.0 equiv), and $POCl_3$ (0.34 ml, 3.6 mmol, 1.2 equiv) according to the general procedure. The product **1c** was isolated as colorless oil (913 mg, 2.64 mmol, 88% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 7.07 (dd, J = 10.0, 2.4 Hz, 1H), 7.02 (dd, J = 8.7, 4.5 Hz, 1H), 6.75 (td, J = 9.1, 2.6 Hz, 1H), 4.27-4.22 (m, 4H), 3.64 (s, 2H), 2.37 (s, 3H), 1.23 (t, J= 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.0, 163.3, 157.6 (d, J = 232.1 Hz), 137.0, 131.5, 128.5 (d, J = 9.8 Hz), 110.9 (d, J = 9.6 Hz), 109.0 (d, J = 25.9 Hz), 102.9 (d, J = 24.1 Hz), 102.4 (d, J = 4.3 Hz), 70.0, 63.7, 31.3, 13.5, 12.3. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{18}H_{20}FN_2O_4$: 347.1402, found: 347.1400.



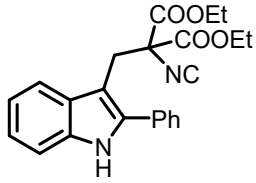
diethyl 2-((5-chloro-2-methyl-1H-indol-3-yl)methyl)-2-isocyanomalonate (1d):

Prepared from diethyl 2-((5-chloro-2-methyl-1H-indol-3-yl)methyl)-2-formamidomalonate (1.14 g, 3 mmol, 1.0 equiv) and Et_3N (1.21 g, 12 mmol, 4.0 equiv), and $POCl_3$ (0.34 ml, 3.6 mmol, 1.2 equiv) according to the general procedure. The product **1d** was isolated as colorless oil (958 mg, 2.52 mmol, 84% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.06 (d, J = 8.6 Hz, 1H), 6.98 (dd, J = 8.6, 1.9 Hz, 1H), 4.30-4.24 (m, 4H), 3.64 (s, 2H), 2.43 (s, 3H), 1.27 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.1, 163.5, 136.7, 133.4, 129.3, 125.1, 121.3, 117.3, 111.4, 102.3, 70.1, 63.9, 31.2, 13.6, 12.6. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{18}H_{20}ClN_2O_4$: 363.1106, found: 363.1113.



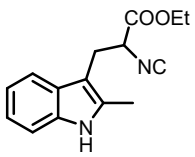
diethyl 2-isocyano-2-((2-(trifluoromethyl)-1H-indol-3-yl)methyl)malonate (1e):

Prepared from diethyl 2-formamido-2-((2-(trifluoromethyl)-1H-indol-3-yl)methyl)malonate (0.40 g, 1.0 mmol, 1.0 equiv) and Et_3N (0.40 g, 4.0 mmol, 4.0 equiv), and $POCl_3$ (0.11 ml, 1.2 mmol, 1.2 equiv) according to the general procedure. The product **1e** was isolated as colorless oil (357 mg, 0.93 mmol, 93% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 9.01, 7.62 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.25-7.21 (m, 1H), 7.15-7.11 (m, 1H), 4.29-4.24 (m, 4H), 3.90 (s, 2H), 1.22 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.1, 135.3, 126.8, 124.9, 124.0 (q, J = 36.7 Hz), 121.5 (q, J = 267.9 Hz), 120.7, 120.2, 117.5, 108.2, 108.2, 69.6, 64.0, 30.1, 13.5. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{18}H_{18}F_3N_2O_4$: 383.1213, found: 383.1214.



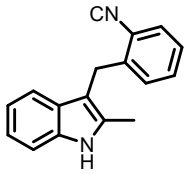
diethyl 2-isocyano-2-((2-phenyl-1H-indol-3-yl)methyl)malonate (1f):

Prepared from diethyl 2-formamido-2-((2-phenyl-1H-indol-3-yl)methyl)malonate (0.41 g, 1.0 mmol, 1.0 equiv) and Et_3N (0.40 g, 4.0 mmol, 4.0 equiv), and $POCl_3$ (0.11 ml, 1.2 mmol, 1.2 equiv) according to the general procedure. The product **1f** was isolated as colorless oil (323 mg, 0.83 mmol, 83% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.56-7.54 (m, 2H), 7.45-7.32 (m, 4H), 7.20-7.10 (m, 2H), 4.12-4.04 (m, 2H), 4.00-3.92 (m, 4H), 1.12 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.0, 163.7, 137.7, 135.5, 132.7, 128.8, 128.8, 128.7, 128.0, 122.3, 119.7, 119.3, 111.0, 103.0, 69.6, 63.4, 30.5, 13.5. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{23}H_{23}N_2O_4$: 391.1652, found: 391.1649.



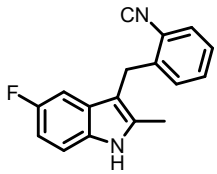
ethyl 2-isocyano-3-(2-methyl-1H-indol-3-yl)propanoate (1g):

The product **1g** was isolated as a colorless liquid (192.2 mg, 0.75 mmol, 75% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.00 (s, 1H), 7.49 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.19-7.11 (m, 2H), 4.51 (dd, J = 8.6, 5.0 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.48-3.42 (m, 1H), 3.34 (dd, J = 14.6, 8.6 Hz, 1H), 2.49 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.7, 160.2, 135.2, 133.8, 127.8, 121.5, 119.6, 117.3, 110.5, 104.7, 62.7, 57.2, 28.9, 13.9, 11.9. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{15}H_{17}N_2O_2$: 257.1285, found: 257.1282.



3-(2-isocyanobenzyl)-2-methyl-1H-indole (1h):

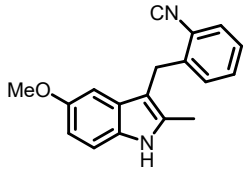
The product **1h** was isolated as a colorless liquid (197 mg, 0.80 mmol, 80% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.75 (s, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.18 (dd, J = 23.4, 9.3 Hz, 4H), 7.02 (t, J = 7.2 Hz, 1H), 6.92 (t, J = 7.0 Hz, 1H), 4.28 (s, 2H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.2, 137.8, 135.3, 132.4, 129.5, 129.3, 128.6, 126.7, 126.6, 125.9, 121.2, 119.4, 118.1, 110.3, 107.9, 26.3, 11.8. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{17}H_{15}N_2$: 247.1230, found: 247.1227.



5-fluoro-3-(2-isocyanobenzyl)-2-methyl-1H-indole (1i):

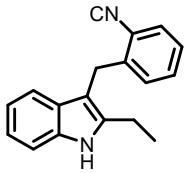
The product **1i** was isolated as a colorless liquid (208 mg, 0.80 mmol, 80% yield). (new compound) **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.90 (s, 1H), 7.41-7.38 (m, 1H), 7.21 (ddd, J = 8.3, 4.9, 3.4 Hz, 3H), 7.05-7.02 (m, 1H), 6.92 (dd, J = 9.8, 2.5 Hz, 1H), 6.88- 6.82 (m, 1H), 4.14 (s, 2H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.3, 157.8 (d, J = 232.6 Hz), 137.4, 134.5 (d, J = 3.6 Hz), 131.7, 129.4 (d, J = 4.4

Hz), 129.1, 129.0, 126.9, 126.8, 110.9, 110.8, 109.2 (d, J = 26.0 Hz), 108.1 (d, J = 4.3 Hz), 103.2 (d, J = 25.5 Hz), 26.4, 11.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -124.57. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{17}H_{14}FN_2$: 265.1136, found: 265.1131.



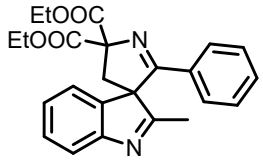
3-(2-isocyanobenzyl)-5-methoxy-2-methyl-1H-indole (1j):

The product **1j** was isolated as colorless oil (180 mg, 0.76 mmol, 75% yield). (new compound) **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.83 (s, 1H), 7.42-7.37 (m, 1H), 7.23-7.16 (m, 3H), 7.09-.04 (m, 1H), 6.79 (dd, J = 5.5, 2.3 Hz, 2H), 4.16 (s, 2H), 3.78 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.2, 154.0, 137.7, 133.3, 130.4, 129.5, 129.3, 129.1, 126.7, 126.7, 125.9, 110.9, 110.8, 107.8, 100.6, 55.9, 26.4, 11.9. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{18}H_{17}N_2O$: 277.1335, found: 277.1327.



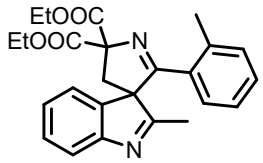
2-ethyl-3-(2-isocyanobenzyl)-1H-indole (1k):

The product **1k** was isolated as colorless oil (198 mg, 0.76 mmol, 76% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H), 7.44-7.41 (m, 1H), 7.36 (d, J = 8.7 Hz, 2H), 7.22-7.16 (m, 3H), 7.11-7.05 (m, 2H), 4.25 (s, 2H), 2.80 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.3, 138.5, 138.0, 135.5, 129.5, 129.5, 128.7, 126.8, 126.7, 126.0, 121.3, 119.5, 118.4, 110.6, 106.9, 26.2, 19.6, 14.2. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{18}H_{17}N_2$: 261.1386, found: 265.1131.



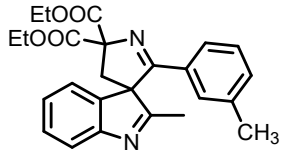
diethyl 2-methyl-2'-phenylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3a)：

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3a** was isolated as colorless oil (39.6 mg, 0.098 mmol, 98% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.34-7.28 (m, 4H), 7.21-7.14 (m, 3H), 7.45-7.36 (m, 4H), 3.23 (d, J = 14.7 Hz, 1H), 2.85 (d, J = 14.7 Hz, 1H), 2.23 (s, 3H), 1.37 (q, J = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.0, 174.7, 169.8，169.3, 154.6, 141.9, 131.6, 131.5, 129.0, 128.5, 127.9, 126.6, 122.7, 120.6, 85.9, 75.0, 62.7, 62.6, 40.2, 16.4, 16.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{25}N_2O_4$: 405.1809, found: 405.1806.



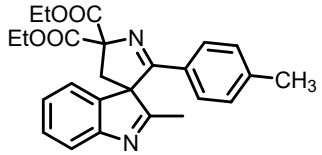
diethyl 2-methyl-2'-(o-tolyl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3b):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-iodo-2-methylbenzene (32.7 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3b** was isolated as colorless oil (28.8 mg, 0.069 mmol, 69% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.50 (d, J = 8.3 Hz, 1H), 7.37-7.33 (m, 2H), 7.23-7.19 (m, 1H), 7.14-7.11 (m, 2H), 6.82-6.77 (m, 1H), 6.33 (d, J = 7.8 Hz, 1H), 4.43-4.37 (m, 4H), 6.45 (d, J = 14.7 Hz, 1H), 2.92 (d, J = 14.7 Hz, 1H), 2.51 (s, 3H), 2.28 (s, 3H), 1.38 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 180.3, 176.2, 169.8, 169.4, 154.9, 141.0, 137.9, 131.4, 131.0, 129.9, 129.0, 126.4, 126.1, 125.3, 122.4, 120.3, 87.1, 62.6, 38.9, 20.9, 16.6, 14.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{25}H_{27}N_2O_4$: 419.1965, found: 419.1971.



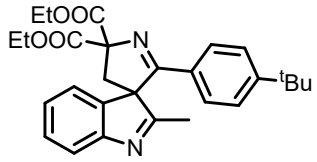
diethyl 2-methyl-2'-(m-tolyl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3c):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-iodo-3-methylbenzene (32.7 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3c** was isolated as colorless oil (37.2 mg, 0.089 mmol, 89% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.7 Hz, 1H), 7.41-7.38 (m, 2H), 7.27 (d, J = 5.3 Hz, 1H), 7.21-7.17 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 6.99 (t, J = 7.7 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 4.43-4.36 (m, 4H), 3.23 (d, J = 14.7 Hz, 1H), 2.84 (d, J = 14.7 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 1.37 (q, J = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.0, 174.8, 169.8, 169.3, 154.6, 142.0, 138.2, 132.5, 131.3, 129.0, 128.7, 128.4, 126.6, 124.6, 122.6, 120.5, 85.8, 74.9, 62.7, 62.6, 40.1, 21.1, 16.4, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{25}H_{27}N_2O_4$: 419.1965, found: 419.1967.



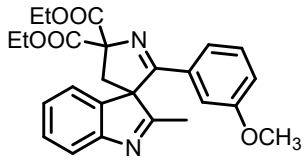
diethyl 2-methyl-2'-(p-tolyl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3d):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-iodo-4-methylbenzene (32.7 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3d** was isolated as colorless oil (40.1 mg, 0.096 mmol, 96% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.54 (d, J = 7.7 Hz, 1H), 7.73-7.28 (m, 1H), 7.18 (d, J = 7,7 Hz, 1H), 7.13-7.08 (m, 3H), 6.85 (d, J = 8.1 Hz, 2H), 4.35-4.27 (m, 4H), 3.14 (d, J = 14.7 Hz, 1H), 2.75 (d, J = 14.7 Hz, 1H), 2.17 (s, 3H), 2.14 (s, 3H), 1.29 (td, J = 7.2, 5.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.1, 174.4, 169.8, 269.4, 154.7, 142.2, 142.1, 129.2, 128.9, 128.8, 127.9, 126.5, 122.6, 120.5, 85.8, 74.9, 62.6, 62.5, 40.2, 21.3, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{25}H_{27}N_2O_4$: 419.1965, found: 419.1967.



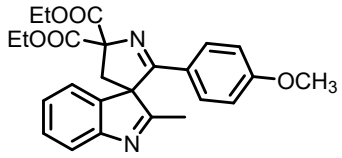
diethyl 2'-(4-(tert-butyl)phenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3e):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-(tert-butyl)-4-iodobenzene (39.0 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3e** was isolated as colorless oil (33.1 mg, 0.072 mmol, 72% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.29-7.24 (m, 4H), 7.21-7.16 (m, 3H), 4.41-4.35 (m, 4H), 3.22 (d, J = 14.7 Hz, 1H), 2.83 (d, J = 14.7 Hz, 1H), 2.23(s, 3H), 1.37 (q, J = 6.5 Hz, 6H), 1.21 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.3, 174.6, 169.8, 169.4, 155.1, 154.6, 142.2, 128.9, 128.6, 127.7, 126.5, 125.5, 122.5, 120.5, 85.8, 74.8, 62.6, 62.5, 40.3, 30.9, 16.4, 14.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{28}H_{33}N_2O_4$: 461.2435, found: 461.2438.



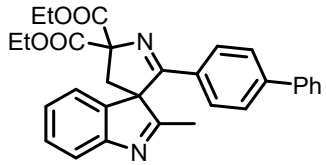
diethyl 2'-(3-methoxyphenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3f):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-iodo-3-methoxybenzene (35.1 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3f** was isolated as colorless oil (33.5 mg, 0.077 mmol, 77% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.7 Hz, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.31-7.29 (m, 1H), 7.23-7.19 (m, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.90-6.85 (m, 2H), 6.79-6.78 (m, 1H), 4.44-4.35 (m, 4H), 3.57 (s, 3H), 3.24 (d, J = 14.7 Hz, 1H), 2.85 (d, J = 14.7 Hz, 1H), 2.23 (s, 3H), 1.37 (q, J = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.1, 174.6, 169.7, 169.2, 159.3, 154.6, 142.1, 132.6, 129.5, 129.0, 126.6, 122.7, 120.5, 120.3, 118.7, 111.7, 85.8, 75.0, 62.7, 62.6, 55.1, 40.1, 16.4, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{25}H_{27}N_2O_5$: 435.1914, found: 435.1916.



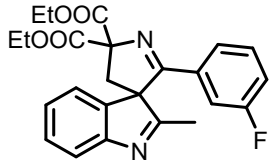
diethyl 2'-(4-methoxyphenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3g):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-iodo-4-methoxybenzene (35.1 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3g** was isolated as colorless oil (17.8 mg, 0.041 mmol, 41% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.55 (d, J = 7.7 Hz, 1H), 7.31 (td, J = 7.6, 1.1 Hz, 1H), 7.21-7.18 (m, 3H), 7.11 (t, J = 7.5 Hz, 1H), 6.58 (d, J = 8.9 Hz, 2H), 4.35-4.27 (m, 4H), 3.65 (s, 3H), 3.14 (d, J = 14.6 Hz, 1H), 2.49 (d, J = 14.6 Hz, 1H), 2.15 (s, 3H), 1.29 (q, J = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.4, 173.7, 170.0, 169.5, 162.3, 154.6, 142.3, 129.8, 128.9, 126.6, 124.1, 122.7, 120.6, 113.9, 85.7, 74.8, 62.6, 62.5, 55.2, 40.4, 16.3, 14.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{25}H_{27}N_2O_5$: 435.1914, found: 435.1906.



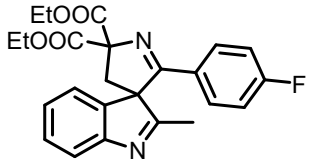
diethyl 2'-([1,1'-biphenyl]-4-yl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3h):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 4-iodo-1,1'-biphenyl (42.0 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3h** was isolated as colorless oil (40.4 mg, 0.084 mmol, 84% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.65 (d, J = 7.7 Hz, 1H), 7.49-7.47 (m, 2H), 7.43-7.36 (m, 7H), 7.33-7.29 (m, 2H), 7.20 (td, J = 7.4, 1.0 Hz, 1H), 4.45-4.34 (m, 4H), 3.25 (d, J = 14.7 Hz, 1H), 2.87 (d, J = 14.7 Hz, 1H), 2.26 (s, 3H), 1.38 (td, J = 7.1, 6.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.0, 174.2, 169.8, 169.3, 154.7, 144.3, 142.0, 139.8, 130.3, 129.0, 128.8, 128.4, 127.9, 127.1, 127.0, 126.6, 122.7, 120.6, 85.9, 74.9, 62.6, 62.6, 40.3, 16.4, 14.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{30}H_{29}N_2O_4$: 481.2122, found: 481.2124.



diethyl 2'-(3-fluorophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3i):

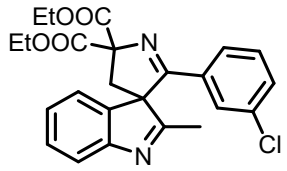
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-fluoro-3-iodobenzene (33.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3i** was isolated as colorless oil (38.0 mg, 0.090 mmol, 90% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 7.7 Hz, 1H), 7.42 (td, J = 7.6, 1.2 Hz, 1H), 7.28 (s, 1H), 7.23-7.19 (m, 2H), 7.13-7.08 (m, 1H), 7.05-7.00 (m, 1H), 6.87 (d, J = 7.8 Hz, 1H), 4.45-4.36 (m, 4H), 3.25 (d, J = 14.8 Hz, 1H), 2.86 (d, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.38 (q, J = 6.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.5, 173.7 (d, J = 2.7 Hz), 169.5, 169.1, 162.4 (d, J = 245.5 Hz), 154.6, 141.5, 133.4 (d, J = 7.8 Hz), 130.1 (d, J = 7.9 Hz), 129.2, 126.7, 123.3 (d, J = 3.1 Hz), 122.6, 120.7, 118.7 (d, J = 21.1 Hz), 115.0 (d, J = 23.2 Hz), 85.8, 62.8, 62.7, 40.1, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{24}N_2O_4$: 423.1715, found: 423.1714.



diethyl 2'-(4-fluorophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3j):

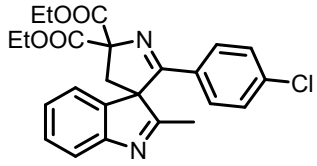
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-fluoro-4-iodobenzene (33.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3j** was isolated as colorless oil (34.2 mg, 0.081 mmol, 81% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 7.7 Hz, 1H), 7.41 (td, J = 7.6, 1.3 Hz, 1H), 7.33-7.28 (m, 3H), 7.22-7.18 (m, 1H), 6.85 (t, J = 8.7 Hz， 1H), 4.42-4.36 (m,4H), 3.24 (d, J = 14.8 Hz, 1H), 2.85 (d, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.37 (q, J = 6.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.8, 173.5, 169.7, 169.2, 164.7 (d, J = 251.6 Hz), 154.5, 141.7, 130.2 (d, J = 8.8 Hz), 129.1, 127.6 (d, J = 3.2 Hz), 126.7, 122.6, 120.7, 115.6 (d, J = 21.6 Hz), 85.7, 74.8, 62.7, 62.6, 40.2, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for

$C_{24}H_{24}N_2O_4$: 423.1715, found: 423.1720.



diethyl 2'-(3-chlorophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3k):

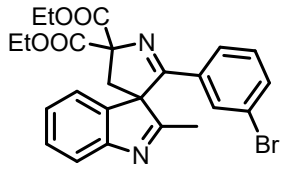
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-chloro-3-iodobenzene (35.8 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3k** was isolated as colorless oil (30.3 mg, 0.069 mmol, 69% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.65-7.63 (m, 2H), 7.42 (td, J = 7.5, 1.2 Hz, 1H), 7.31-7.26 (m, 3H), 7.21 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 4.45-4.36 (m, 4H), 3.24 (d, J = 14.8 Hz, 1H), 2.86 (d, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.38 (q, J = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.4, 173.6, 169.5, 169.0, 154.6, 141.4, 134.7, 133.0, 131.7, 129.8, 129.3, 128.3, 126.8, 125.4, 122.6, 120.7, 85.9, 74.8, 62.8, 62.7, 40.1, 16.4, 14.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{24}ClN_2O_4$: 439.1419, found: 439.1418.



diethyl 2'-(4-chlorophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3l):

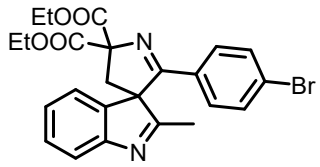
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-chloro-4-iodobenzene (35.8 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3l** was isolated as colorless oil (34.6 mg, 0.079 mmol, 79% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.55 (d, J = 7.7 Hz, 1H), 7.32 (td, J = 7.6, 1.0 Hz, 1H), 7.20-7.15 (m, 3H), 7.14-7.09 (m, 1H), 7.07-7.04 (m, 2H), 4.36-4.27 (m, 4H), 3.15 (d, J = 14.7 Hz, 1H), 2.77 (d, J = 14.7 Hz, 1H), 2.14 (s, 3H), 1.29 (td, J = 7.1, 5.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.6, 173.6, 169.6, 169.1, 154.7, 141.6, 138.0, 129.9, 129.2, 129.2, 128.8, 126.7, 122.6, 120.7, 85.9, 74.9, 62.7, 62.6, 40.2, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$)

calculated for $C_{24}H_{24}ClN_2O_4$: 439.1419, found: 439.1418.



diethyl 2'-(3-bromophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3m):

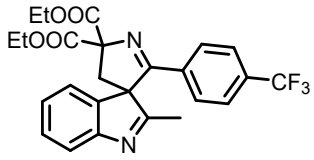
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-bromo-3-iodobenzene (42.4 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3m** was isolated as colorless oil (39.6 mg, 0.082 mmol, 82% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.83 (t, J = 1.8 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.46-7.40 (m, 2H), 7.28 (s, 1H), 7.23-7.19 (m, 1H), 6.97 (t, J = 7.9 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 4.45-4.36 (m, 4H), 3.26 (d, J = 14.7 Hz, 1H), 2.86 (d, J = 14.7 Hz, 1H), 2.23 (s, 3H), 1.38 (q, J = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.4, 173.5, 169.5, 169.0, 154.6, 141.4, 134.6, 133.2, 131.1, 130.0, 129.3, 126.7, 125.8, 122.8, 122.6, 120.7, 85.8, 74.8, 62.8, 62.7, 40.1, 16.4, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{24}BrN_2O_4$: 483.0914, found: 483.0911.



diethyl 2'-(4-bromophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3n):

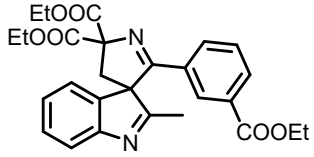
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-bromo-4-iodobenzene (42.4 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3n** was isolated as colorless oil (39.2 mg, 0.081 mmol, 81% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.62(d, J = 7.7 Hz, 1H), 7.40 (td, J = 7.6, 1.3 Hz, 1H), 7.31-7.28 (m, 2H), 7.26-7.25 (m, 1H), 7.21-7.19 (m,1H), 7.17-7.15 (m, 2H), 4.43-4.35 (m, 4H), 3.23 (d, J = 14.8 Hz, 1H), 2.85 (d, J = 14.8 Hz, 1H), 2.22(s, 3H), 1.37 (td, J = 7.1, 5.5 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.6, 173.8, 169.6, 169.1, 154.6, 141.6, 131.8, 130.3, 129.4, 129.2, 126.7, 126.6, 122.6, 120.7, 85.9, 74.8, 62.7, 62.7, 40.2, 16.3, 14.0.

HRMS (ESI) ([M+H]$^+$) calculated for $C_{24}H_{24}BrN_2O_4$: 483.0914, found: 483.0916.



diethyl 2-methyl-2'-(4-(trifluoromethyl)phenyl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3o):

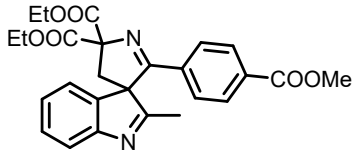
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-iodo-4-(trifluoromethyl)benzene (40.8 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3o** was isolated as colorless oil (43.9 mg, 0.093 mmol, 93% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.65 (d, J = 7.8 Hz, 1H), 7.45-7.40 (m, 5H), 7.29-2.27 (m, 1H), 7.23-7.20 (m, 1H), 4.45-4.37 (m, 4H), 3.26 (d, J = 14.8 Hz, 1H), 2.89 (d, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.38 (q, J = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.3, 173.7, 169.4, 168.9, 154.6, 141.3, 134.6, 133.1 (q, J = 32.5), 129.4, 128.2, 127.5, 126.8, 125.5 (q, J = 3.6 Hz), 123.5 (q, J = 270.9 Hz), 122.6, 120.8, 86.0, 74.9, 62.8, 62.8, 40.1, 16.4, 14.0. **HRMS (ESI)** ([M+H]$^+$) calculated for $C_{25}H_{24}F_3N_2O_4$: 473.1683, found: 473.1675.



diethyl 2'-(3-(ethoxycarbonyl)phenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3p):

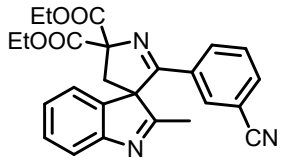
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and ethyl 3-iodobenzoate (41.4 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3p** was isolated as colorless oil (40.5 mg, 0.085 mmol, 85% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 7.8 Hz, 1H), 7.86 (s, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.51-7.49 (m, 1H), 7.45-7.41 (m, 1H), 7.31-7.28 (m, 2H), 7.24-7.20 (m, 1H), 4.46-4.37 (m, 4H), 4.28 (q, J = 7.1 Hz, 2H), 3.27 (d, J = 14.7 Hz, 1H), 2.88 (d, J = 14.7 Hz, 1H), 2.21 (s, 3H), 1.41-1.36 (m, 6H), 1.33 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.3, 174.2, 169.6, 169.1, 165.5, 154.8, 141.5, 132.5, 131.9, 131.7, 130.9, 129.2, 128.9, 128.7,

126.7, 122.6, 120.7, 86.0, 75.0, 62.7, 62.7, 61.1, 40.1, 16.3, 14.2, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{27}H_{29}N_2O_6$: 477.2020, found: 477.2019.



diethyl 2'-(4-(methoxycarbonyl)phenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3q):

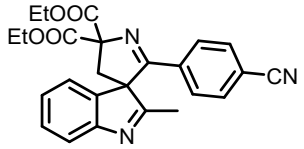
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3q** was isolated as white solid (38.8 mg, 0.084 mmol, 84% yield): mp 86−87 °C. (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 7.7 Hz, 1H), 7.33 (td, J = 7.6, 1.2 Hz, 1H), 7.29-7.26 (m, 2H), 7.19 (d, J = 7.4 Hz, 1H), 7.12 (td, J = 7.4, 0.7 Hz, 1H), 4.37-4.20 (m, 4H), 3.78 (s, 3H), 3.17 (d, J = 14.7 Hz, 1H), 2.80 (d, J = 14.7 Hz, 1H), 2.15 (s, 3H), 1.33-1.28 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.3, 174.2, 169.5, 169.0, 166.1, 154.8, 141.5, 135.4, 132.7, 129.6, 129.3, 127.8, 126.7, 122.6, 120.7, 86.1, 75.0, 62.8, 62.7, 52.2, 40.1, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{26}H_{27}N_2O_6$: 463.1864, found: 463.1857.



diethyl 2'-(3-cyanophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3r):

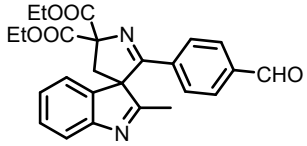
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 3-iodobenzonitrile (34.4 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3r** was isolated as colorless oil (40.8 mg, 0.095 mmol, 95% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.87 (s, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.5, 1.3 Hz, 1H), 7.27-7.20 (m, 4H), 4.46-4.34 (m, 4H), 3.27 (d, J = 14.8 Hz, 1H), 2.98 (d, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.39 (q, J = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 180.9, 173.0, 169.3, 168.8, 154.6, 140.9, 134.6, 132.5, 131.8, 131.4, 129.5, 129.5,

126.9, 122.6, 120.9, 117.7, 113.1, 85.9, 74.7, 72.9, 62.8, 40.0, 16.4, 14.0. **HRMS (ESI)** ([M+H]$^+$) calculated for $C_{25}H_{24}N_3O_4$: 430.1761, found: 430.1763.



diethyl 2'-(4-cyanophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3s):

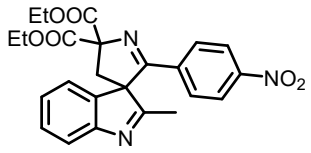
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 4-iodobenzonitrile (34.4 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3s** was isolated as colorless oil (37.8 mg, 0.088 mmol, 88% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 7.8 Hz, 1H), 7.47-7.38 (m, 5H), 7.27-7.25 (m, 1H), 7.23-7.19 (m, 1H), 4.45-4.36 (m, 4H), 3.26 (d, J = 14.8 Hz, 1H), 2.89 (d, J = 14.8 Hz, 1H), 2.22 (s, 3H), 1.38 (td, J = 7.1, 5.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.0, 173.4, 169.3, 168.8, 154.7, 141.1, 135.4, 132.2, 129.5, 126.9, 122.6, 120.9, 117.9, 115.0, 86.1, 74.9, 62.8, 62.8, 40.1, 16.3, 14.0. **HRMS (ESI)** ([M+H]$^+$) calculated for $C_{25}H_{24}N_3O_4$: 430.1761, found: 430.1769.



diethyl 2'-(4-formylphenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3t):

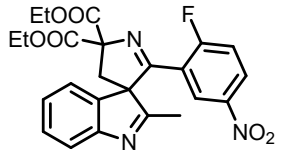
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 4-iodobenzaldehyde (34.8 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3t** was isolated as colorless oil (34.6 mg, 0.080 mmol, 80% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 9.23 (s, 1H), 7.69-7.64 (m, 3H), 7.46-7.40 (m, 3H), 7.29-7.27 (m, 1H), 7.21 (t, J = 7.4 Hz, 1H), 4.44-4.37 (m, 4H), 3.26 (d, J = 14.8 Hz, 1H), 2.89 (d, J = 14.8 Hz, 1H), 2.24 (s, 3H), 1.38 (q, J = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 191.4, 181.2, 174.0, 169.4, 168.9, 154.7, 141.3, 138.0, 136.6, 129.6, 129.4, 128.5, 126.8, 122.6, 120.8, 86.1, 75.0, 62.8, 62.8, 40.1, 16.4, 14.0. **HRMS (ESI)** ([M+H]$^+$) calculated for

$C_{25}H_{25}N_2O_5$: 433.1758, found: 433.1756.



diethyl 2-methyl-2'-(4-nitrophenyl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3u):

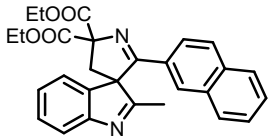
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-iodo-4-nitrobenzene (37.4 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3u** was isolated as colorless oil (38.7 mg, 0.086 mmol, 86% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 7.7 Hz, 1H), 7.47-7.41 (m, 3H), 7.28-7.26 (m, 1H), 7.22 (t, J = 7.4 Hz, 1H), 4.47-4.37 (m, 4H), 3.27 (d, J = 14.8 Hz, 1H), 2.91 (d, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.39 (q, J = 6.5 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 180.8, 173.2, 169.2, 168.8, 154.7, 149.5, 141.0, 137.0, 129.6, 128.9, 126.9, 123.6, 122.6, 120.9, 86.2, 75.0, 62.9, 62.8, 40.1, 16.4, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{24}N_3O_6$: 450.1660, found: 450.1653.



diethyl 2'-(2-fluoro-5-nitrophenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3v):

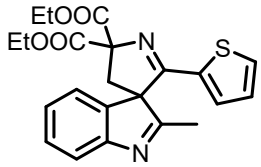
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 1-fluoro-2-iodo-4-nitrobenzene (40.1 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3v** was isolated as colorless oil (41.1 mg, 0.088 mmol, 88% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.17-8.13 (m, 1H), 7.54-7.51 (m, 2H), 7.45-7.40 (m, 2H), 7.32-7.28 (m, 1H), 7.14 (t, J = 9.0 Hz, 1H), 4.47-4.39 (m, 4H), 3.31 (d, J = 14.9 Hz, 1H), 3.03 (d, J = 14.9 Hz, 1H), 2.30 (s, 3H), 1.40 (td, J = 7.1, 0.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 178.8, 170.7 (d, J = 3.3 Hz), 168.9, 161.9, 163.2 (d, J = 263.3 Hz), 155.3, 143.5, 139.1, 129.87, 127.5 (d, J = 10.4 Hz), 126.8, 125.3 (d, J = 4.1 Hz), 122.6, 121.2 (d, J = 15.7 Hz), 120.7, 117.4 (d, J = 24.6 Hz), 87.4, 77.0, 63.0, 63.0,

38.4, 16.4, 16.3, 14.0, 14,0. **HRMS (ESI)** ([M+H]$^+$) calculated for $C_{24}H_{23}FN_3O_6$: 468.1565, found: 468.1568.



diethyl 2-methyl-2'-(naphthalen-2-yl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3w):

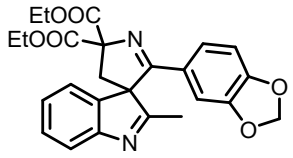
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 2-iodonaphthalene (38.1 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3w** was isolated as colorless oil (19.5 mg, 0.043 mmol, 43% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.73-7.62 (m, 4H), 7.57 (d, J = 7.0 Hz, 1H), 7.48-7.37 (m, 3H), 7.30 (d, J = 7.0 Hz, 1H), 7.19 (td, J = 7.5, 0.8 Hz, 1H), 4.47-4.38 (m, 4H), 3.29 (d, J = 14.7 Hz, 1H), 2.90 (d, J = 14.7 Hz, 1H), 2.26 (s, 3H), 1.39 (q, J = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.2, 174.5, 169.8, 169.4, 154.7, 142.2, 134.7, 132.5, 129.1, 129.1, 128.9, 128.6, 128.2, 127.7, 127.4, 126.7, 126.4, 124.7, 122.7, 120.6, 86.0, 75.0, 62.7, 62.7, 40.3, 16.4, 14.1. **HRMS (ESI)** ([M+H]$^+$) calculated for $C_{28}H_{27}N_2O_4$: 455.1965, found: 455.1963.



diethyl 2-methyl-2'-(thiophen-2-yl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3x):

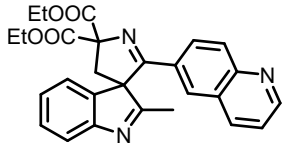
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 2-iodothiophene (31.5 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3x** was isolated as colorless oil (30.4 mg, 0.074 mmol, 74% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.7 Hz, 1H), 7.43-7.39 (m, 1H), 7.35 (d, J = 5.0 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 6.77 (t, J = 4.4 Hz, 1H), 6.53 (d, J = 5.8 Hz, 1H), 4.43-4.35 (m, 4H), 3.25 (d, J = 14.8 Hz, 1H), 2.90 (d, J = 14.8 Hz, 1H), 2.26 (s, 3H), 1.37 (td, J = 7.1, 2.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.8, 169.6, 169.2, 168.7,

154.8, 141.6, 134.5, 131.1, 129.9, 129.2, 127.9, 126.6, 122.8, 120.4, 86.1, 74.8, 62.6, 62.6, 40.1, 16.2, 14.0, 14.0. **HRMS (ESI)** ([M+H]$^+$) calculated for $C_{22}H_{23}N_2O_4S$: 411.1373, found: 411.1375.



diethyl 2'-(benzo[d][1,3]dioxol-5-yl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3y):

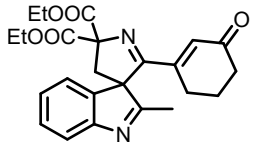
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 5-iodobenzo[d][1,3]dioxole (37.2 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3y** was isolated as colorless oil (34.1 mg, 0.076 mmol, 76% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.62 (d, J = 7.7 Hz, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.27 (d, J = 8.3 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 1.7 Hz, 1H), 6.59 (dd, J = 8.2, 1.8 Hz, 1H), 6.51 (d, J = 8.2 Hz, 1H), 5.90 (s, 2H), 4.44-4.34 (m, 4H), 3.22 (d, J = 14.7 Hz, 1H), 2.80 (d, J = 14.7 Hz, 1H), 2.23 (s, 3H), 1.37 (q, J = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.2, 173.5, 169.9, 169.4, 154.5, 150.5, 147.9, 142.2, 129.0, 126.6, 125.6, 122.9, 122.6, 120.6, 108.2, 108.0, 101.4, 85.5, 74.7, 62.6, 62.5, 40.4, 16.3, 14.0. **HRMS (ESI)** ([M+H]$^+$) calculated for $C_{25}H_{25}N_2O_6$: 449.1707, found: 449.1711.



diethyl 2-methyl-2'-(quinolin-6-yl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3z):

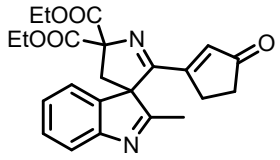
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 7-iodoquinoline (38.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3z** was isolated as colorless oil (34.6 mg, 0.076 mmol, 76% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 8.88-8.87 (m, 1H), 7.95-7.86 (m, 3H), 7.70 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 1.7 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.34-7.31 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 4.48-4.39 (m, 4H), 3.30 (d, J = 14.7 Hz, 1H), 2.92 (d, J = 14.7 Hz, 1H), 2.26 (s, 3H), 1.40 (q, J = 7.2

Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.8, 174.0, 169.6, 169.1, 154.7, 151,8, 149.3, 141.8, 137.1, 129.8, 129.6, 129.3, 128.5, 128.3, 127.5, 126.8, 122.7, 120.7, 86.0, 75.0, 62.8, 62.7, 40.2, 16.4, 14.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{27}H_{26}N_3O_4$: 456.1918, found: 456.1913.



diethyl 2-methyl-2'-(3-oxocyclohex-1-en-1-yl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3aa):

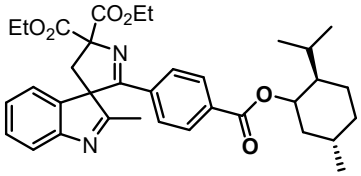
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 3-iodocyclohex-2-en-1-one (33.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3aa** was isolated as colorless oil (37.6 mg, 0.089 mmol, 89% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.59 (d, J = 7.7 Hz, 1H), 7.41-7.36 (m, 1H), 7.20 (d, J = 3.9 Hz, 2H), 5.36 (s, 1H), 4.43-4.33 (m, 4H), 3.25 (d, J = 11.0 Hz, 1H), 2.77 (d, J = 11.0 Hz, 1H), 2.65-2.62 (m, 2H), 2.31-2.27 (m, 2H), 2.25 (s, 3H), 1.96-1.89 (m, 2H), 1.38-1.33 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 199.4, 180.5, 175.2, 169.1, 168.6, 154.4, 150.5, 141.2, 130.3, 129.4, 126.7, 122.1, 121.0, 86.1, 74.5, 62.9, 62.8, 40.0, 37.5, 26.6, 21.9, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{27}N_2O_5$: 423.1914, found: 423.1911.



diethyl 2-methyl-2'-(3-oxocyclopent-1-en-1-yl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3ab):

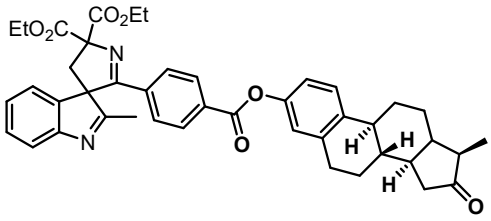
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and 3-iodocyclopent-2-en-1-one (31.2 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ab** was isolated as colorless oil (31.5 mg, 0.077 mmol, 77% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.59 (d, J = 7.7 Hz, 1H), 7.42-7.38 (m, 1H), 7.23-7.19 (m, 2H), 5.51 (t, J = 1.84 Hz, 1H), 4.45-4.35 (m, 4H), 3.20 (d, J = 14.9 Hz, 1H), 3.02-2.92 (m, 2H), 2.86 (d, J = 14.9 Hz, 1H), 2.36-2.33 (m, 2H), 2.24 (s, 3H), 1.37 (td, J = 7.1, 1.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 209.4, 180.3, 172.2, 169.0, 168.5, 154.7, 140.8, 134.8,

129.6, 126.8, 122.4, 120.9, 86.9, 74.9, 63.0, 62.9, 39.4, 34.4, 28.9, 16.2, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{23}H_{25}N_2O_5$: 409.1758, found: 409.1752.



diethyl 2'-(4-((((2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3ac):

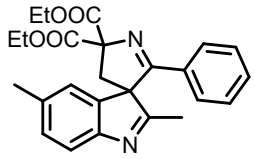
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and (2R,5S)-2-isopropyl-5-methylcyclohexyl 4-iodobenzoate (57.9 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ac** was isolated as colorless oil (45.8 mg, 0.078 mmol, 78% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.83 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 7.7 Hz, 1H), 7.44-7.39 (m, 1H), 7.38-7.34 (m, 2H), 7.29-7.27 (m, 1H), 7.23-7.18 (m, 1H), 4.91-4.83 (m, 1H), 4.46-4.37 (m, 4H), 3.25 (dd, J = 14.7, 5.0 Hz, 1H), 2.87 (dd, J = 14.7, 6.6 Hz, 1H), 2.22 (d, J = 6.6 Hz, 3H), 2.04 (d, J = 12.0 Hz, 1H), 1.88-1.83 (m, 1H), 1.70 (d, J = 11.4 Hz, 2H), 1.53-1.45 (m, 2H), 1.38 (td, J = 13.3, 6.8 Hz, 6H), 1.10-1.00 (m, 2H), 0.91-0.86 (m, 7H), 0.73 (dd, J = 6.9, 2.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.5, 181.4, 174.2, 174.1, 169.5, 169.5, 169.1, 169.0, 165.1, 154.7, 141.6, 141.6, 135.1, 133.4, 133.4, 129.6, 129.2, 127.8, 126.7, 122.6, 120.7, 86.0, 75.1, 75.0, 62.8, 62.7, 47.1, 47.1, 40.8, 40.1, 34.2, 31.4, 26.4, 26.3, 23.5, 23.4, 22.0, 20.7, 20.7, 16.4, 16.4, 16.3, 14.1. **HRMS (APCI)** ($[M+H]^+$) calculated for $C_{35}H_{43}N_2O_6$: 587.3116, found: 587.3111.



diethyl 2-methyl-2'-(4-((((8S,9S,14S,17R)-17-methyl-16-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)phenyl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3ad):

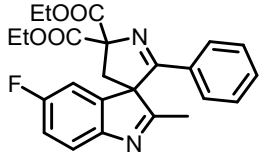
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and (8S,9S,14S,17R)-17-methyl-16-oxo-

7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-iodobenzoate (75.0 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ad** was isolated as colorless oil (52.6 mg, 0.075 mmol, 75% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.98 (d, J = 8.6 Hz), 7.64 (d, J = 7.7 Hz, 1H), 7.43-7.41 (m, 3H), 7.32-7.27 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.92-6.87 (m, 2H), 4.47-4.37 (m, 4H), 3.27 (d, J = 14.7 Hz, 1H), 3.92-2.88 (m, 3H), 2.51 (dd, J = 19.1, 8.8 Hz, 1H), 2.43-2.39 (m, 1H), 2.32-2.28 (m, 1H), 2.25 (s, 3H), 2.19-2.15 (m, 1H), 2.10-1.95 (m, 3H), 1.66-1.60 (m, 2H), 1.57-1.45 (m, 4H), 1.39 (td, 13.2, 7.1 Hz, 6H), 0.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.2, 174.12, 169.4, 169.0, 164.5, 154.7, 148.5, 141.4, 138.0, 137.5, 135.9, 132.1, 130.2, 129.3, 128.0, 126.7, 126.4, 122.6, 121.4, 120.7, 118.6, 86.1, 75.0, 62.8, 62.7, 50.3, 47.9, 44.1, 40.0, 37.9, 35.8, 31.5, 29.3, 26.2, 25.7, 21.5, 16.4, 14.0, 13.8. **HRMS (APCI)** ($[M+H]^+$) calculated for $C_{43}H_{45}N_2O_7$: 701.3221, found: 701.3223.



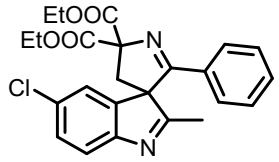
diethyl 2,5-dimethyl-2'-phenylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3ae):

Prepared from diethyl 2-((2,5-dimethyl-1H-indol-3-yl)methyl)-2-isocyanomalonate (34.2 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ae** was isolated as colorless oil (38.1 mg, 0.091 mmol, 91% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.50 (d, J = 7.8 Hz, 1H), 7.34-7.31 (m, 3H), 7.20-7.15 (m, 3H), 7.06 (s, 1H), 4.44-4.35 (m, 4H), 3.23 (d, J = 14.7 Hz, 1H), 2.83 (d, J = 14.7 Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H), 1.38 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 180.9, 174.8, 169.8, 169.3, 152.4, 142.1, 136.6, 131.6, 131.5, 129.6, 128.5, 127.9, 123.3, 120.1, 85.8, 74.8, 62.7, 62.6, 40.4, 21.4, 16.3, 14.1, 14.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{25}H_{27}N_2O_4$: 419.1965, found: 419.1960.



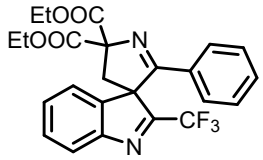
diethyl 5-fluoro-2-methyl-2'-phenylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3af):

Prepared from diethyl 2-((5-fluoro-2-methyl-1H-indol-3-yl)methyl)-2-isocyanomalonate (34.6 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3af** was isolated as colorless oil (35.5 mg, 0.084 mmol, 84% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.56 (dd, J = 8.5, 4.6 Hz, 1H), 7.36-7.31 (m, 3H), 7.19 (t, J = 7.5 Hz, 2H), 7.08 (td, J = 8.9, 2.6 Hz, 1H), 7.02 (dd, J = 7.8, 2.5 Hz, 1H), 4.44-4.35 (m, 4H), 3.23 (d, J = 14.8 Hz, 1H), 2.82 (d, J = 14.8 Hz, 1H), 2.21 (s, 3H), 1.38 (td, J = 7.1, 2.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.8 (d, J = 3.6 Hz), 174.0, 169.6, 169.1, 161.6 (d, J = 244.7 Hz), 150.7 (d, J = 2.4 Hz), 143.7 (d, J = 9.1 Hz), 131.8, 131.3, 128.6, 127.8, 121.3 (d, J = 8.7 Hz), 115.7 (d, J = 23.7 Hz), 110.6 (d, J = 25.2 Hz), 85.9, 62.7, 62.7, 40.2, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{24}FN_2O_4$: 423.1715, found: 423.1712.



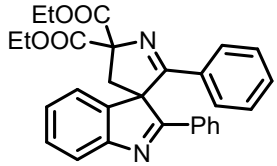
diethyl 5-chloro-2-methyl-2'-phenylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3ag):

Prepared from diethyl 2-((5-chloro-2-methyl-1H-indol-3-yl)methyl)-2-isocyanomalonate (36.3 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ag** was isolated as colorless oil (37.7 mg, 0.086 mmol, 86% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.55 (d, J = 8.2 Hz, 1H), 7.38-7.30 (m, 4H), 7.26 (d, J = 2.0 Hz, 1H), 7.19 (t, J = 7.7 Hz, 2H), 4.45-4.35 (m, 4H), 3.24 (d, J = 14.8 Hz, 1H), 2.82 (d, J = 14.8 Hz, 1H), 2.22 (s, 3H), 1.38 (td, J = 7.1, 2.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.5, 173.8, 169.6, 169.1, 153.2, 143.6, 132.3, 131.8, 131.2, 129.2, 128.6, 127.8, 123.2, 121.4, 85.9, 75.1, 62.8, 62.7, 40.2, 16.4, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{24}ClN_2O_4$: 439.1419, found: 439.1417.



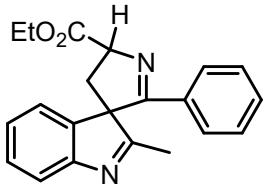
diethyl 2'-phenyl-2-(trifluoromethyl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3ah):

Prepared from diethyl 2-isocyano-2-((2-(trifluoromethyl)-1H-indol-3-yl)methyl)malonate (38.2 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ah** was isolated as colorless oil (43.1 mg, 0.094 mmol, 94% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.87 (d, J =7.8 Hz, 1H), 7.55-7.51 (m, 1H), 7.47-7.40 (m, 2H), 7.34-7.30 (m, 1H), 7.18-7.13 (m, 4H), 4.44-4.35 (m, 4H), 3.55 (d, J = 14.9 Hz, 1H), 3.01 (d, J = 14.9 Hz, 1H), 1.37 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.1, 169.5, 168.6, 168.5 (q, J = 34.8 Hz), 151.6, 141.6, 131.8, 131.4, 130.0, 129.8, 128.5, 127.5, 123.5, 123.0, 119.9 (q, J = 274.0 Hz), 86.4, 72.9, 62.9, 62.7, 38.5, 14.0, 13.9. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{22}F_3N_2O_4$: 459.1526, found: 459.1525.



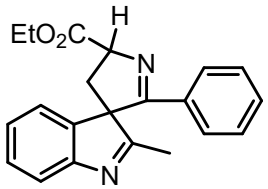
diethyl 2,2'-diphenylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3ai):

Prepared from diethyl 2-isocyano-2-((2-phenyl-1H-indol-3-yl)methyl)malonate (39.0 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ai** was isolated as white solid (45.3mg, 0.097 mmol, 97% yield): mp 95−97 ^{o}C. (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.94 (d, J = 6.7 Hz, 2H), 7.78 (d, J = 7.7 Hz, 1H), 7.44-7.36 (m, 6H), 7.29 (d, J = 7.3 Hz, 1H), 7.24-7.18 (m, 2H), 7.11 (t, J = 7.8 Hz, 2H), 4.44-4.30 (m, 4H), 3.28 (d, J = 14.4 Hz, 1H), 2.96 (d, J = 14.4 Hz, 1H), 1.38-1.31 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 178.1, 176.1, 169.7, 169.1, 153.9, 142.2, 131.7, 131.6, 131.6, 131.3, 129.2, 128.8, 128.5, 128.4, 128.1, 126.9, 122.6, 121.4, 86.0, 73.2, 62.6, 62.5, 41.9, 14.0, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{29}H_{27}N_2O_4$: 467.1965, found: 467.1966.



ethyl 2-methyl-2'-phenyl-4',5'-dihydrospiro[indole-3,3'-pyrrole]-5'-carboxylate(3aj):

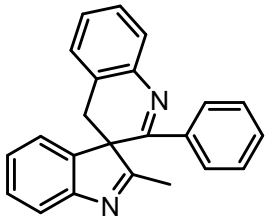
Prepared from diethyl ethyl 2-isocyano-3-(2-methyl-1H-indol-3-yl)propanoate (25.6 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3aj** was isolated as colorless oil (16.0 mg, 49% yield). (new compound). **^{1}HNMR** (500 MHz, $CDCl_3$) δ: 7.67 (d, J = 7.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.24 (t, J = 7.3 Hz, 1H), 7.24-7.14 (m, 7H), 5.27 (t, J = 8.0 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.82 (dd, J = 13.5, 8.0 Hz, 1H), 2.43 (dd, J = 13.5, 8.0 Hz, 1H), 2.27 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 183.2, 172.8, 171.8, 153.2, 141.4, 131.7, 131.4, 129.1, 128.6, 127.4, 126.7, 121.7, 120.7, 74.4, 73.2, 61.8, 38.2, 16.5, 14.2. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{21}H_{21}N_2O_2$: 333.1598, found: 333.1592.



ethyl 2-methyl-2'-phenyl-4',5'-dihydrospiro[indole-3,3'-pyrrole]-5'-carboxylate(3aj'):

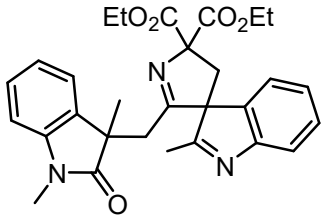
Prepared from diethyl ethyl 2-isocyano-3-(2-methyl-1H-indol-3-yl)propanoate (25.6 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3aj'** was isolated as colorless oil (15.9 mg, 48% yield). (new compound). **^{1}HNMR** (500 MHz, $CDCl_3$) δ: 7.67 (d, J = 7.7 Hz, 1H), 7.43 -7.36 (m, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.22 (d, J = 7.7 Hz, 3H), 7.15 (t, J = 7.7 Hz, 2H), 5.23 (dd, J = 8.5, 6.8 Hz, 1H), 4.34 (q, J = 7.0 Hz, 2H), 2.76 (dd, J = 14.1, 8.8 Hz, 1H), 2.65 (dd, J = 14.1, 6.6 Hz, 1H), 2.29 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 182.6, 172.9, 171.9, 153.5, 141.8, 131.8,

131.4, 129.0, 128.6, 127.5, 127.0, 123.0, 120.3, 74.6, 73.0, 61.8, 38.0, 16.3, 14.2. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{21}H_{21}N_2O_2$: 333.1598, found: 333.1592.



2-methyl-2'-phenyl-4'H-spiro[indole-3,3'-quinoline] (3ak):

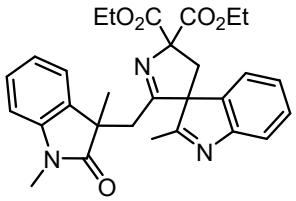
Prepared from 3-(2-isocyanobenzyl)-2-methyl-1H-indole (24.6 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ak** was isolated as colorless oil (27.7 mg, 0.086 mmol, 86% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.65 (dd, J = 13.4, 7.7 Hz, 2H), 7.44-7.29 (m, 3H), 7.22 (d, J = 15.3 Hz, 3H), 7.12 (dd, J = 19.7, 7.3 Hz, 3H), 6.97 (t, J = 7.9 Hz, 1H), 6.75 (d, J = 7.4 Hz, 1H), 3.46 (d, J = 15.7 Hz, 1H), 2.52 (d, J = 15.7 Hz, 1H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 184.5, 164.2, 153.8, 144.0, 140.6, 138.7, 130.2, 128.9, 128.5, 128.4, 128.0, 127.8, 127.2, 126.3, 125.8, 124.2, 122.6, 120.9, 61.4, 34.8, 17.5. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{23}H_{19}N_2$: 323.1543, found: 323.1536.



diethyl 2'-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (5a):

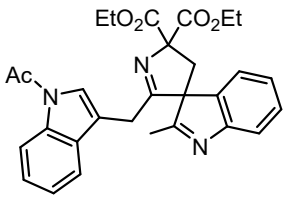
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and *N*-(2-iodophenyl)-*N*-methylmethacrylamide (45.2 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **5a** was isolated as colorless oil (19.8 mg, 0.040 mmol, 40% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.55 (d, J = 7.4 Hz, 1H), 7.37 (td, J = 7.4, 1.2 Hz, 1H), 7.26-7.17 (m, 3H), 7.11 (d, J = 7.0 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 7.8

Hz, 1H), 4.35-4.29 (m, 2H), 4.12-3.99 (m, 2H), 3.19 (s, 3H), 2.82 (d, *J* = 15.0 Hz, 1H), 2.73 (d, *J* = 15.0 Hz, 1H), 2.28 (d, *J* = 18.2 Hz, 1H), 2.01 (d, *J* = 18.2 Hz, 1H), 1.94 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.21-1.17 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ*: 178.0, 179.8, 175.2, 169.2, 168.9, 155.1, 144.7, 139.6, 133.6, 129.0, 127.7, 126.6, 122.6, 121.8, 121.6, 120.1, 107.8, 87.2, 62.3, 61.9, 45.6, 37.5, 36.1, 26.4, 24.2, 16.3, 14.1, 14.0. **HRMS (APCI)** ($[M+H]^+$) calculated for $C_{29}H_{32}N_3O_5$: 502.2336, found: 502.2344.



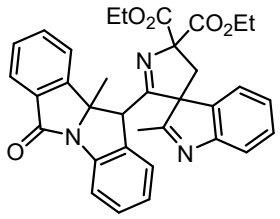
diethyl 2'-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (5a'):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and *N*-(2-iodophenyl)-*N*-methylmethacrylamide (45.2 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **5a'** was isolated as colorless oil (12.1 mg, 0.024 mmol, 24% yield). (new compound). **^{1}HNMR** (500 MHz, $CDCl_3$) *δ*: 7.55 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.21 (dq, *J* = 13.0, 7.1, 6.6 Hz, 3H), 7.11 (d, *J* = 7.0 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.31 (qd, *J* = 7.1, 1.4 Hz, 2H), 4.12-3.98 (m, 2H), 3.19 (s, 3H), 2.88-2.68 (m, 2H), 2.28 (d, *J* = 18.3 Hz, 1H), 2.01 (d, *J* = 18.3 Hz, 1H), 1.93 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ*: 180.3, 180.2, 174.9, 169.1, 169.0, 155.3, 144.6, 139.6, 133.1, 129.1, 127.5, 126.2, 122.8, 122.0, 121.6, 120.2, 107.7, 87.2, 62.2, 62.0, 45.7, 37.5, 35.6, 26.4, 24.3, 16.1, 14.1, 14.0. **HRMS (APCI)** ($[M+H]^+$) calculated for $C_{29}H_{32}N_3O_5$: 502.2336, found: 502.2344.



diethyl 2'-((1-acetyl-1H-indol-3-yl)methyl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (5b):

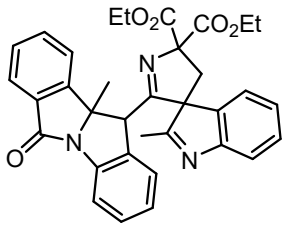
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and *N*-(2-iodophenyl)-*N*-(propa-1,2-dien-1-yl)acetamide (44.9 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **5b** was isolated as colorless oil (35.0 mg, 0.070 mmol, 70% yield). (new compound). **^{1}HNMR** (500 MHz, $CDCl_3$) δ: 8.31 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.31-7.25 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 6.95-6.90 (m, 2H), 6.87 (s, 1H), 4.41-4.35 (m, 4H), 3.43 (d, J = 15.3 Hz, 1H), 3.28 (d, J = 15.3 Hz, 1H), 3.05 (d, J = 15.2 Hz, 1H), 2.86 (d, J = 15.2 Hz, 1H), 2.48 (s, 3H), 2.02 (s, 3H), 1.37-1.34 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 179.9, 177.6, 169.5, 169.2, 168.3, 155.2, 139.9, 135.5, 129.7, 128.8, 126.0, 125.3, 124.2, 123.3, 122.7, 119.8, 119.2, 116.4, 115.4, 86.7, 62.7, 62.7, 38.2, 26.7, 23.8, 16.2, 14.1. **HRMS (APCI)** ($[M+H]^+$) calculated for $C_{29}H_{30}N_3O_5$: 500.2180, found: 500.2178.



diethyl 2-methyl-2'-(10b-methyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (5c)：

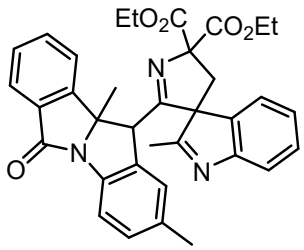
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and (2-bromophenyl)(2-methyl-1H-indol-1-yl)methanone (47.1 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **5c** was isolated as colorless oil (34.8 mg, 0.062 mmol, 62% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.82 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.60 (td, J = 7.5, 1.0 Hz, 1H), 7.53 (td, J = 7.6, 1.2 Hz, 1H), 7.49 (td, J = 6.7, 1.2 Hz, 1H), 7.44 (td, J = 7.4, 0.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.30-7.27 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.02-7.01 (m, 2H), 4.05-3.95 (m, 3H), 3.85-3.81 (m, 1H), 2.93-2.89 (m, 2H), 2.44 (d, J = 14.9 Hz, 1H), 2.02 (s, 3H), 1.24 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 179.6, 175.7, 169.2, 168.1, 166.9, 155.9, 147.2, 139.2, 138.7, 135.1, 134.9, 131.6, 129.6, 129.2, 128.3, 126.0, 125.9, 124.0, 123.6, 123.3, 122.6, 120.6, 117.8, 86.9, 77.7, 75.3, 62.3, 61.8, 48.8, 36.9, 27.2, 17.7, 13.7, 13.6. **HRMS (ESI)** ($[M+H]^+$) calculated for

$C_{34}H_{32}N_3O_5$: 562.2336, found: 562.2338.



diethyl 2-methyl-2'-(10b-methyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)spiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (5c')：

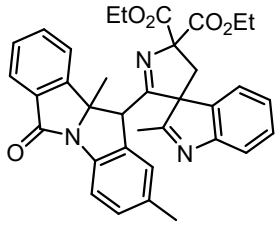
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and (2-bromophenyl)(2-methyl-1H-indol-1-yl)methanone (47.1 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **5c'** was isolated as colorless oil (18.0 mg, 0.032 mmol, 32% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 6.9 Hz, 1H), 7,57-7.50 (m, 2H), 7.48-7.42 (m, 3H), 7.40-7.36 (m, 1H), 7.23-7.20 (m, 1H), 7.11 (td, J = 7.4, 0.8 Hz, 1H), 7.11 (td, J = 7.4, 0.8 Hz, 1H), 6.81(td, J = 7.6, 1.0 Hz, 1H), 6.48 (d, J = 7.3 Hz, 1H), 6.10 (d, J = 7.5 Hz, 1H), 4.20-4.10 (m, 3H), 4.01-3.94 (m, 1H), 3.62 (s, 1H), 2.80 (d, J = 14.9 Hz, 1H), 2.46 (d, J = 14.9 Hz, 1H), 2.28 (s, 3H), 1.47 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 179.2, 176.7, 168.7, 168.6, 165.9, 155.3, 147.2, 138.5, 137.7, 135.3, 133.9, 131.6, 129.4, 129.3, 128.5, 126.7, 126.3, 124.4, 123.9, 123.2, 120.1, 116.7, 86.6, 75.2, 62.3, 62.2, 51.0, 37.8, 28.7, 17.4, 13.9, 13.8. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{34}H_{32}N_3O_5$: 562.2336, found: 562.2338.



diethyl 2'-(2,10b-dimethyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (5d):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and (2-bromophenyl)(2,5-dimethyl-1H-indol-1-yl)methanone (49.2 mg, 0.15 mmol, 1.5 equiv) according to the general procedure.

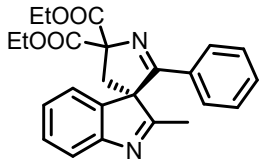
The product **5d** was isolated as colorless oil (25.9 mg, 0.045 mmol, 45% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.81 (d, J = 7.5 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.61-7.57 (m, 2H), 7.54-7.50 (m, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 7.3 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 6.72 (s, 1H), 4.07-3.97 (m, 3H), 3.87-3.83 (m, 1H), 2.95 (s, 1H), 2.86 (d, J = 14.9 Hz, 1H), 2.45 (d, J = 15.0 Hz, 1H), 2.28 (s, 3H), 2.00 (s, 3H), 1.25 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 1.03 (t, J = 7.0 Hz, 3H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 179.6, 176.1, 169.1, 168.3, 166.7, 155.8, 147.2, 139.4, 136.4, 135.0, 134.8, 133.2, 131.5, 129.7, 129.6, 128.2, 126.8, 126.0, 123.9, 123.1, 122.7, 120.6, 117.3, 86.8, 75.5, 62.3, 61.8, 49.1, 37.0, 27.4, 21.1, 17.6, 13.8, 13.6. **HRMS (APCI)** ($[M+H]^+$) calculated for $C_{35}H_{34}N_3O_5$: 576.2493, found: 576.2490



diethyl 2'-(2,10b-dimethyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)-2-methylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (5d'):

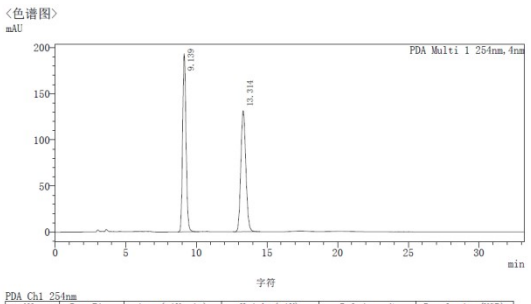
Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and (2-bromophenyl)(2,5-dimethyl-1H-indol-1-yl)methanone (49.2 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **5d'** was isolated as colorless oil (14.4 mg, 0.025 mmol, 25% yield). (new compound). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.85 (d, J = 7.5 Hz, 1H), 7.56-7.48 (m, 3H), 7.44-7.35 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 7.4 Hz, 1H), 5.64 (s, 1H), 4.18-4.07 (m, 3H), 3.96-3.90 (m, 1H), 3.47 (s, 1H), 2.88 (d, J = 14.6 Hz, 1H), 2.42 (d, J = 14.6 Hz, 1H), 2.31, (s, 3H), 2.14, (s, 3H), 1.45 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 179.5, 176.3, 168.9, 168.5, 166.0, 155.3, 147.4, 138.0, 135.9, 135.4, 134.3, 132.7, 131.5, 129.6, 129.3, 128.3, 127.4, 126.1, 124.3, 124.2, 122.6, 120.3, 116.5, 86.7, 75.3,

62.3, 62.1, 50.6, 37.7, 28.4, 21.1, 17.3, 13.8, 13.7. **HRMS (APCI)** ($[M+H]^+$) calculated for $C_{35}H_{34}N_3O_5$: 576.2493, found: 576.2490



diethyl (R)-2-methyl-2'-phenylspiro[indole-3,3'-pyrrole]-5',5'(4'H)-dicarboxylate (3a'):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3a'** was isolated as colorless oil (38.4 mg, 0.095 mmol, 95% yield). (new compound). $[\alpha]_D^{25}$ = +55.3 (c = 0.11 in $CHCl_3$, 49% ee). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.34-7.28 (m, 4H), 7.21-7.14 (m, 3H), 7.45-7.36 (m, 4H), 3.23 (d, J = 14.7 Hz, 1H), 2.85 (d, J = 14.7 Hz, 1H), 2.23 (s, 3H), 1.37 (q, J = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 182.0, 174.7, 169.8，169.3, 154.6, 141.9, 131.6, 131.5, 129.0, 128.5, 127.9, 126.6, 122.7, 120.6, 85.9, 75.0, 62.7, 62.6, 40.2, 16.4, 16.1. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{25}N_2O_4$: 405.1809, found: 405.1806. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 10/1, 1.0 mL/min, λ = 254 nm, t (major) = 13.2 min, t (minor) = 9.1 min.



PDA Ch1 254nm

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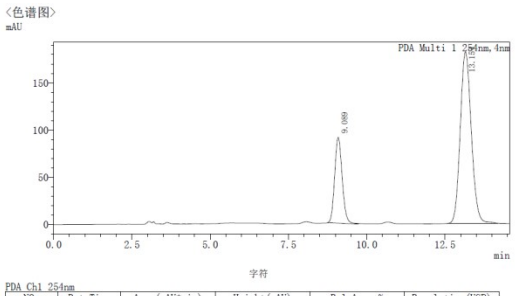
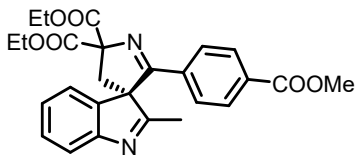
1	9.139	3255614	192583	50.027	0.450
2	13.314	3252115	131122	49.973	0.658
总计		6507729	323706	100.000	



PDA Ch1 254nm

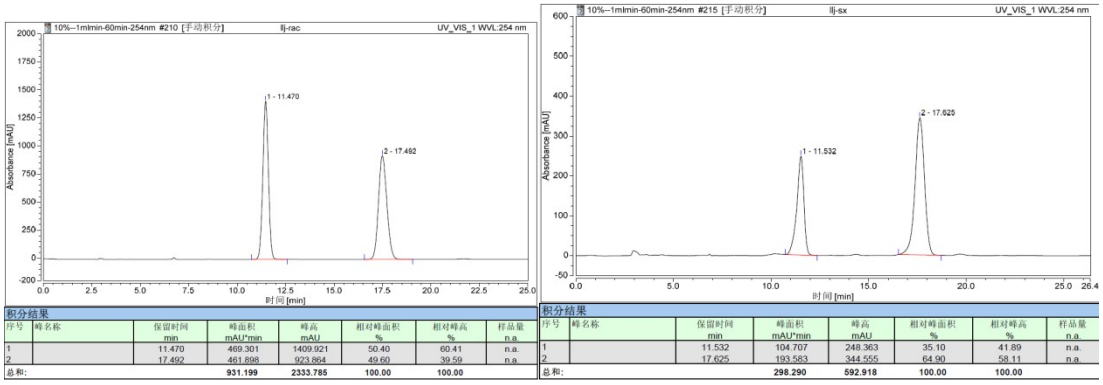
NO.	Ret.Time	Area(uAU*min)	Height(uAU)	Rel.Area %	Resolution(USP)
1	9.089	1614396	90918	25.332	0.445
2	13.194	4463914	181717	74.668	0.650
总计		5978309	272635	100.000	

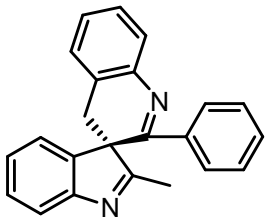


diethyl (R)-2'-(4-(methoxycarbonyl)phenyl)-2-methylspiro[indole-3,3'-pyrrole]-

5',5'(4'H)-dicarboxylate (3q'):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (32.8 mg, 0.1 mmol, 1.0 equiv) and methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3q'** was isolated as colorless oil (37.0 mg, 0.080 mmol, 80% yield): mp 86-87 °C. (new compound). $[\alpha]_D^{25}$ = +35.3 (c = 0.1 in $CHCl_3$, 30% ee). **^{1}HNMR** (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 7.7 Hz, 1H), 7.33 (td, J = 7.6, 1.2 Hz, 1H), 7.29-7.26 (m, 2H), 7.19 (d, J = 7.4 Hz, 1H), 7.12 (td, J = 7.4, 0.7 Hz, 1H), 4.37-4.20 (m, 4H), 3.78 (s, 3H), 3.17 (d, J = 14.7 Hz, 1H), 2.80 (d, J = 14.7 Hz, 1H), 2.15 (s, 3H), 1.33-1.28 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 181.3, 174.2, 169.5, 169.0, 166.1, 154.8, 141.5, 135.4, 132.7, 129.6, 129.3, 127.8, 126.7, 122.6, 120.7, 86.1, 75.0, 62.8, 62.7, 52.2, 40.1, 16.3, 14.0. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{26}H_{27}N_2O_6$: 463.1864, found: 463.1857. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 10/1, 1.0 mL/min, λ = 254 nm, t (major) = 17.6 min, t (minor) = 11.5 min.

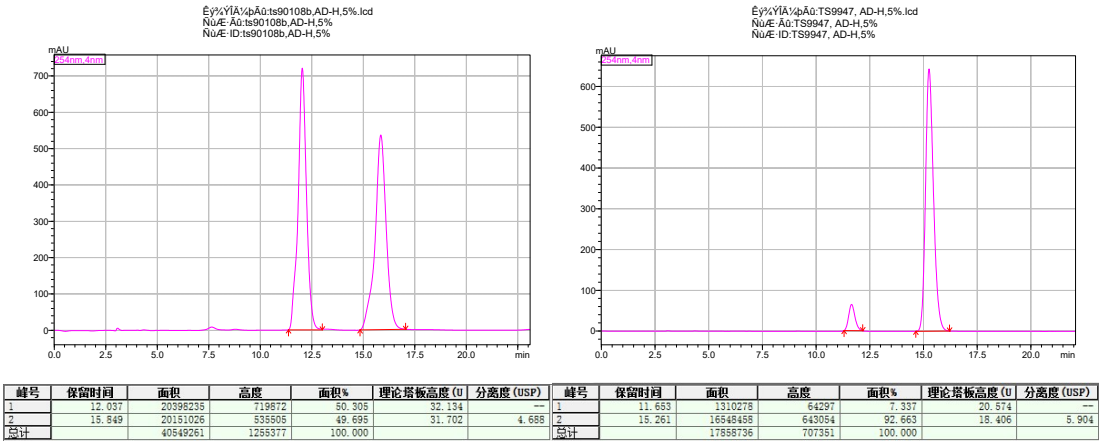




(R)-2-methyl-2'-phenyl-4'H-spiro[indole-3,3'-quinoline] (3ak'):

Prepared from 3-(2-isocyanobenzyl)-2-methyl-1H-indole (24.6 mg, 0.1 mmol, 1.0 equiv) and iodobenzene (30.6 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **3ak'** was isolated as colorless oil (27.7 mg, 0.086 mmol, 86% yield). (new compound). $[\alpha]_D^{25}$ = +65.3 (c = 0.15 in $CHCl_3$, 85% ee). **^{1}HNMR** (400

MHz, $CDCl_3$) δ: 7.65 (dd, J = 13.4, 7.7 Hz, 2H), 7.44-7.29 (m, 3H), 7.22 (d, J = 15.3 Hz, 3H), 7.12 (dd, J = 19.7, 7.3 Hz, 3H), 6.97 (t, J = 7.9 Hz, 1H), 6.75 (d, J = 7.4 Hz, 1H), 3.46 (d, J = 15.7 Hz, 1H), 2.52 (d, J = 15.7 Hz, 1H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 184.5, 164.2, 153.8, 144.0, 140.6, 138.7, 130.2, 128.9, 128.5, 128.4, 128.0, 127.8, 127.2, 126.3, 125.8, 124.2, 122.6, 120.9, 61.4, 34.8, 17.5. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{23}H_{19}N_2$: 323.1543, found: 323.1536. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 15.3 min, t (minor) = 11.7 min.



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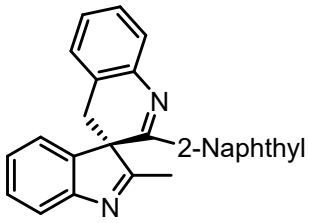
1	12.037	20398235	719872	50.305	32.134	--
2	15.849	20151026	535505	49.695	31.702	4.688
总计		40549261	1255377	100.000		

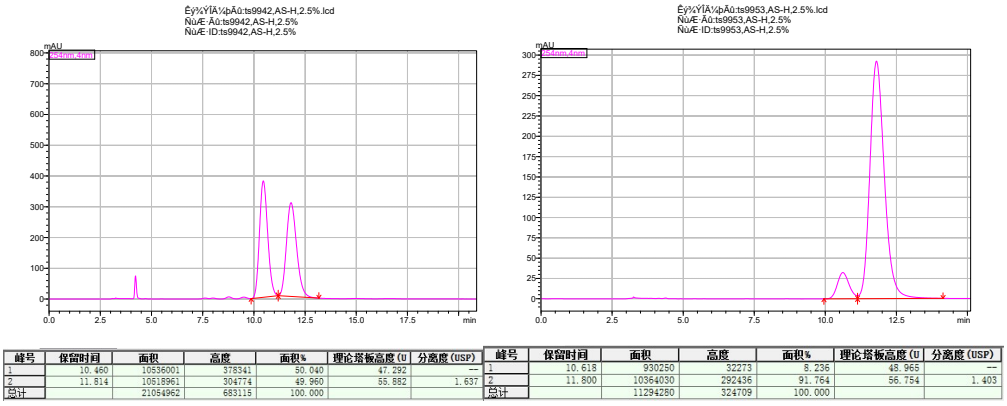
峰号	保留时间	面积	高度	面积%	理论塔板高度(U	分离度(USP)
1	11.653	1310278	64297	7.337	20.574	--
2	15.261	16548458	643054	92.663	18.406	5.904
总计		17858736	707351	100.000		



(R)-2-methyl-2'-(naphthalen-1-yl)-4'H-spiro[indole-3,3'-quinoline] (6a):

Prepared from diethyl 2-isocyano-2-((2-methyl-1H-indol-3-yl)methyl)malonate (24.6 mg, 0.1 mmol, 1.0 equiv) and methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **6a** was isolated as colorless oil (15.4 mg, 0.063 mmol, 63% yield). (new compound). $[\alpha]_D^{25}$ = +31.8 (c = 0.40 in $CHCl_3$, 84% ee). **^{1}HNMR** (500 MHz, $CDCl_3$) δ: 7.74-7.60 (m, 6H), 7.45-7.34 (m, 4H), 7.33-7.13 (m, 3H), 7.08 (d, J = 7.4 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 7.4 Hz, 1H), 3.45 (d, J = 15.7 Hz, 1H), 2.56 (d, J = 15.7 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 184.5, 164.1, 154.1, 144.1, 141.0, 136.1, 134.1, 132.8, 129.0, 128.9,

128.5, 128.2, 128.0, 127.8, 127.5, 127.3, 127.1, 126.4, 126.3, 125.9, 124.3, 123.6, 122.7, 121.0, 61.6, 35.1, 17.6. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{27}H_{21}N_2$: 373.1699, found: 373.1695. The enantiomeric ratio was determined by Daicel Chiralcel AS-H (0.46 cm × 25 cm), Hexanes/IPA = 97.5/2.5, 1.0 mL/min, λ = 254 nm, t (major) = 11.8 min, t (minor) = 10.6 min.



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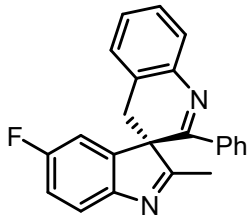
1	10.460	10536001	378341	50.040	47.292	--
2	11.814	10518961	304774	49.960	55.882	1.637
总计		21054962	683115	100.000		

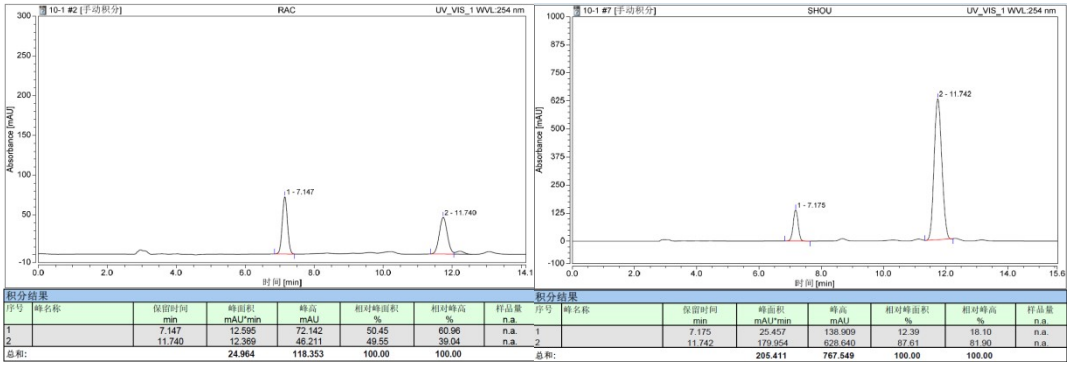
峰号	保留时间	面积	高度	面积%	理论塔板高度(U	分离度(USP)
1	10.618	930250	32273	8.236	48.965	--
2	11.800	10364030	292436	91.764	56.754	1.403
总计		11294280	324709	100.000		



(R)-5-fluoro-2-methyl-2'-phenyl-4'H-spiro[indole-3,3'-quinoline] (6b):

Prepared from 5-fluoro-3-(2-isocyanobenzyl)-2-methyl-1H-indole (26.4 mg, 0.1 mmol, 1.0 equiv) and methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **6b** was isolated as colorless oil (22.4 mg, 0.066 mmol, 66% yield). (new compound). $[\alpha]_D^{25}$ = +10.1 (c = 0.40 in $CHCl_3$, 85% ee). **^{1}HNMR** (500 MHz, $CDCl_3$) δ: 7.61-7.54 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.31-7.28 (m, 1H), 7.21 (dd, J = 9.7, 6.8 Hz, 3H), 7.12-6.99 (m, 4H), 6.40 (dd, J = 7.9, 2.5 Hz, 1H), 3.41 (d, J = 15.7 Hz, 1H), 2.50 (d, J = 15.8 Hz, 1H), 2.03 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 184.4, 163.4, 160.9 (d, J = 195.0 Hz),150.0, 143.8, 142.4 (d, J = 7.2 Hz), 138.5, 130.4, 128.7, 128.6, 128.0, 127.3, 126.2, 123.7, 121.6 (d, J = 7.2 Hz), 115.7 (d, J = 18.8 Hz), 110.4 (d, J = 20.2 Hz), 61.7, 34.8, 17.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -123.75. **HRMS (ESI)** ($[M+H_3O]^+$) calculated for $C_{23}H_{20}FN_2O$: 359.1554, found: 359.1545. The enantiomeric ratio was determined by Daicel Chiralcel AD-H

(0.46 cm × 25 cm), Hexanes/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 11.8 min, t (minor) = 7.1 min.

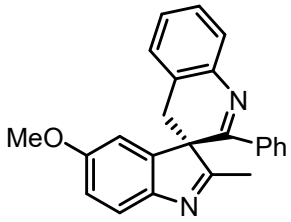


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.147	12.595	72.142	50.45	60.96	n.a.
2		11.740	12.369	46.211	49.55	39.04	n.a.
总和:			24.964	118.353	100.00	100.00	

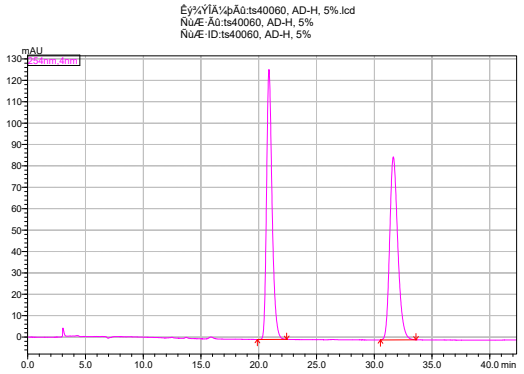
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		7.175	25.457	138.909	12.39	18.10	n.a.
2		11.742	179.954	628.640	87.61	81.90	n.a.
总和:			205.411	767.549	100.00	100.00	

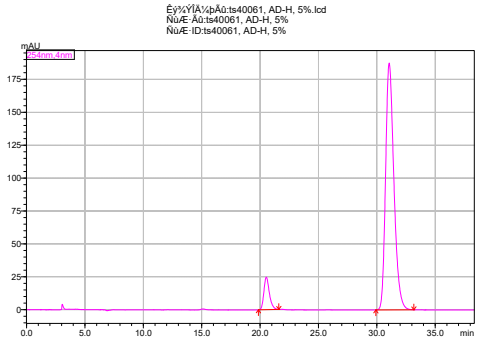


(R)-5-methoxy-2-methyl-2'-phenyl-4'H-spiro[indole-3,3'-quinoline] (6c):

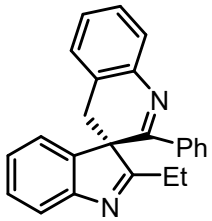
Prepared from 3-(2-isocyanobenzyl)-5-methoxy-2-methyl-1H-indole (27.6 mg, 0.1 mmol, 1.0 equiv) and methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **6c** was isolated as colorless oil (24.6 mg, 0.070 mmol, 70% yield). (new compound). $[\alpha]_D^{25}$ = +58.6 (c = 0.10 in $CHCl_3$, 84% ee). **^{1}HNMR** (500 MHz, $CDCl_3$) δ: 7.59 (d, J = 7.7 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.31-7.06 (m, 8H), 6.91 (t, J = 8.2 Hz, 1H), 3.78 (s, 2H), 3.47 (d, J = 16.4 Hz, 1H), 2.89 (d, J = 16.4 Hz, 1H), 2.01 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 184.7, 165.2, 160.0, 154.1, 145.1, 140.9, 138.9, 130.4, 129.1, 128.7, 128.7, 126.5, 126.0, 122.8, 121.1, 116.3, 114.1, 112.2, 62.0, 55.7, 34.4, 17.7. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{21}N_2O$: 353.1648, found: 353.1641. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 31.0 min, t (minor) = 20.5 min.



峰号	保留时间	面积	高度	面积%	理论塔板高度(U	分离度(USP)
1	20.885	4186870	126141	50.025	15.685	--
2	31.647	4182692	85532	49.975	15.097	10.133
总计		8369562	211673	100.000		



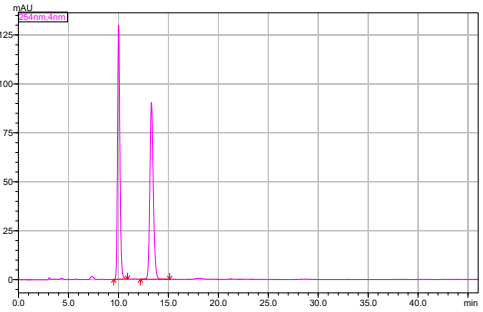
峰号	保留时间	面积	高度	面积%	理论塔板高度(U	分离度(USP)
1	20.534	810677	24720	8.048	15.996	--
2	31.059	9261823	187448	91.952	16.059	9.866
总计		10072500	212168	100.000		



(R)-2-ethyl-2'-phenyl-4'H-spiro[indole-3,3'-quinoline] (6d):

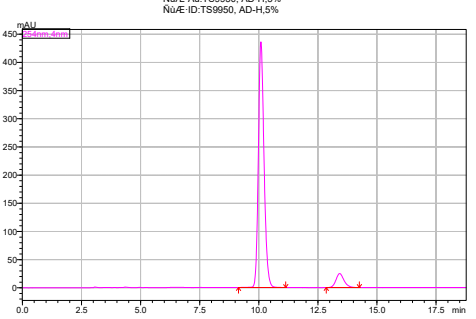
Prepared from 2-ethyl-3-(2-isocyanobenzyl)-1H-indole (26.0 mg, 0.1 mmol, 1.0 equiv) and methyl 4-iodobenzoate (39.3 mg, 0.15 mmol, 1.5 equiv) according to the general procedure. The product **6d** was isolated as colorless oil (25.2 mg, 0.075 mmol, 75% yield). (new compound). $[\alpha]_D^{25}$ = +40.3 (c = 0.1 in $CHCl_3$, 85% ee). **^{1}HNMR** (500 MHz, $CDCl_3$) δ: 7.71 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.44-7.33 (m, 2H), 7.32-7.27 (m, 1H), 7.24-7.20 (m, 3H), 7.16- 7.05 (m, 3H), 6.99-6.95 (m, 1H), 6.74 (d, J = 7.3 Hz, 1H), 3.47 (d, J = 15.7 Hz, 1H), 2.58-2.39 (m, 2H), 2.25-2.15 (m, 1H), 1.12 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 188.8, 164.6, 154.1, 144.1, 140.6, 139.0, 130.1, 128.9, 128.4, 128.4, 128.0, 127.7, 127.3, 126.3, 125.8, 124.4, 122.6, 121.1, 61.7 35.0, 24.4, 10.6. **HRMS (ESI)** ($[M+H]^+$) calculated for $C_{24}H_{21}N_2$: 337.1699, found: 337.1694. The enantiomeric ratio was determined by Daicel Chiralcel AD-H (0.46 cm × 25 cm), Hexanes/IPA = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 13.4 min, t (minor) = 10.1 min.

Êý¾ÝÎÄ¼þÃû:ts9944, AD-H,5%.lcd
Ñù±¾Ãû:ts9944, AD-H,5%
Ñù±¾ID:ts9944, AD-H,5%



峰号	保留时间	面积	高度	面积%	理论塔板高度(U	分离度(USP)
1	10.020	2139213	129535	49.786	17.673	--
2	13.304	2157632	90383	50.214	20.399	6.221
总计		4296844	219918	100.000		

Êý¾ÝÎÄ¼þÃû:TS9950, AD-H,5%.lcd
Ñù±¾Ãû:TS9950, AD-H,5%
Ñù±¾ID:TS9950, AD-H,5%

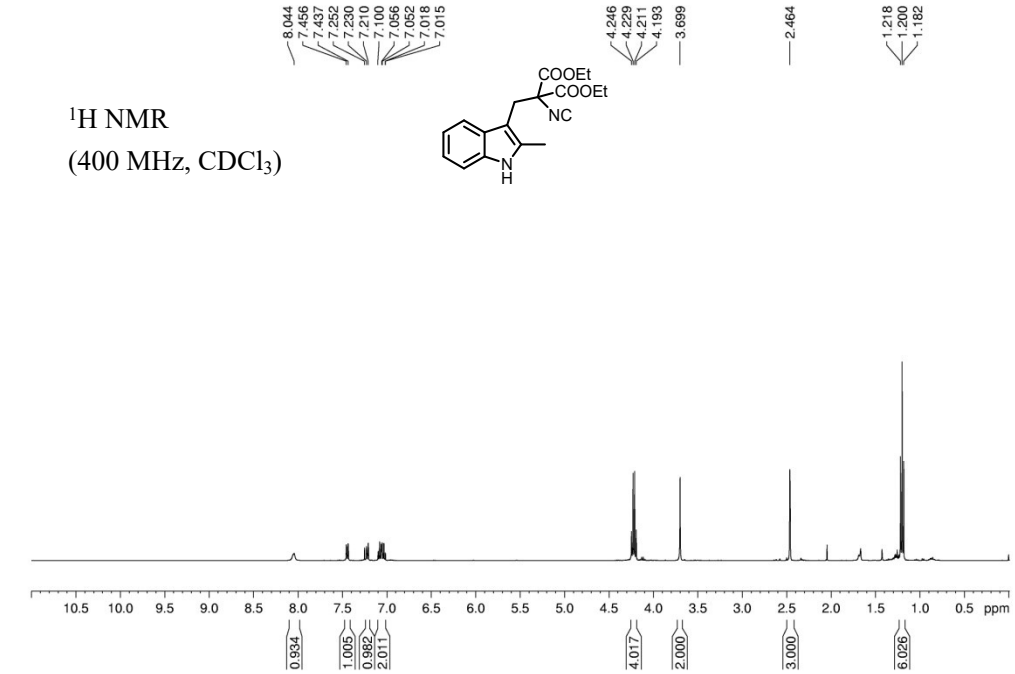


峰号	保留时间	面积	高度	面积%	理论塔板高度(U	分离度(USP)
1	10.090	7260438	435718	92.463	17.929	--
2	13.422	591856	24889	7.537	20.142	6.266
总计		7852294	460607	100.000		

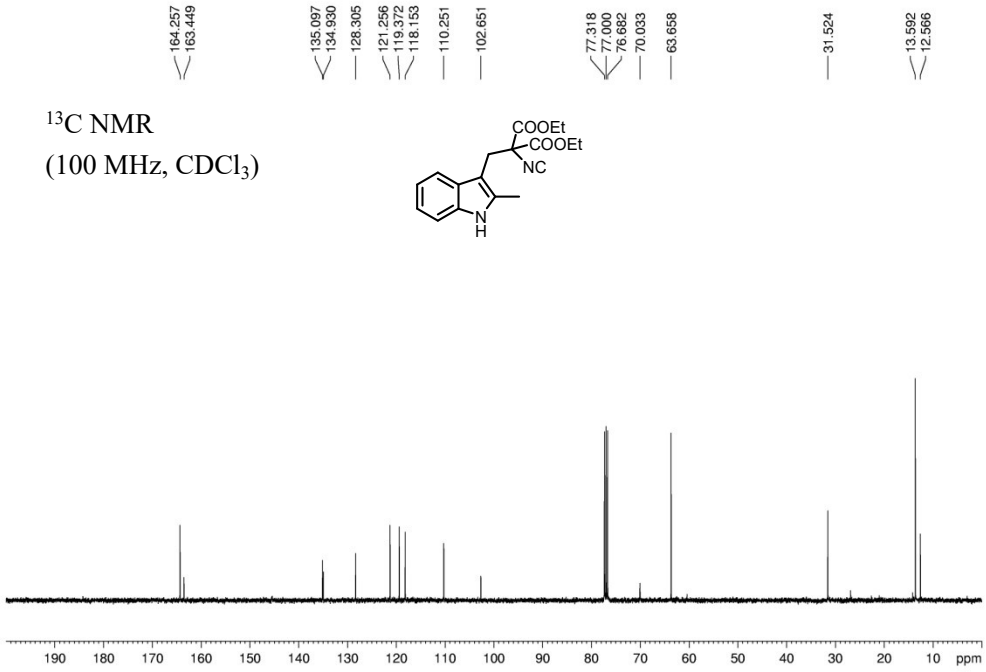
4. ^{1}H and ^{13}C NMR spectra of all products

(1a)

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

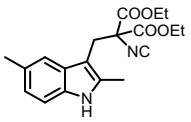


^{13}C NMR
(100 MHz, $CDCl_3$)

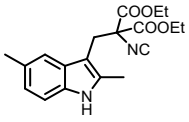


(1b)

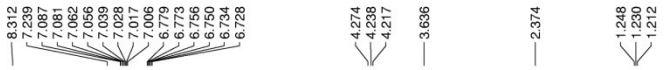
^{1}H NMR
(400 MHz, $CDCl_3$)



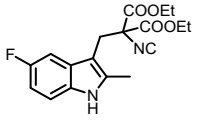
^{13}C NMR
(100 MHz, $CDCl_3$)

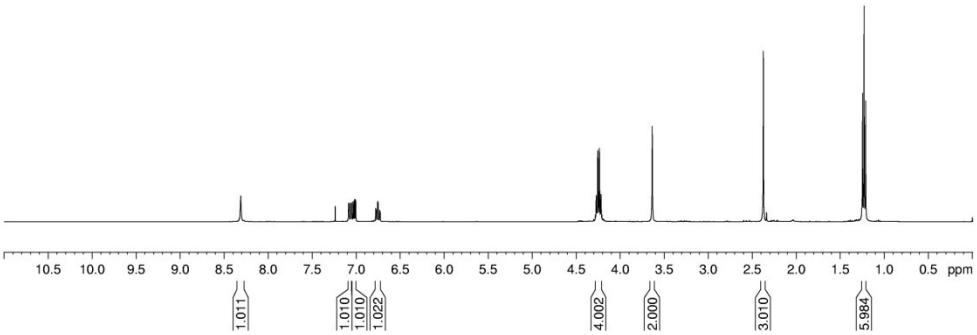


(1c)

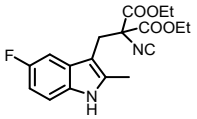


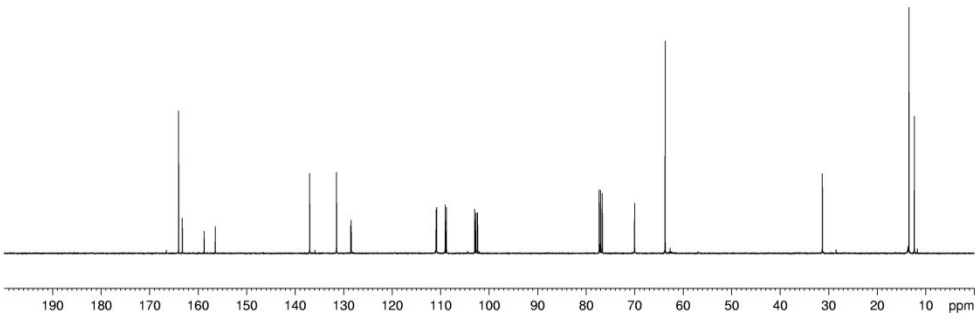
^{1}H NMR
(400 MHz, $CDCl_3$)



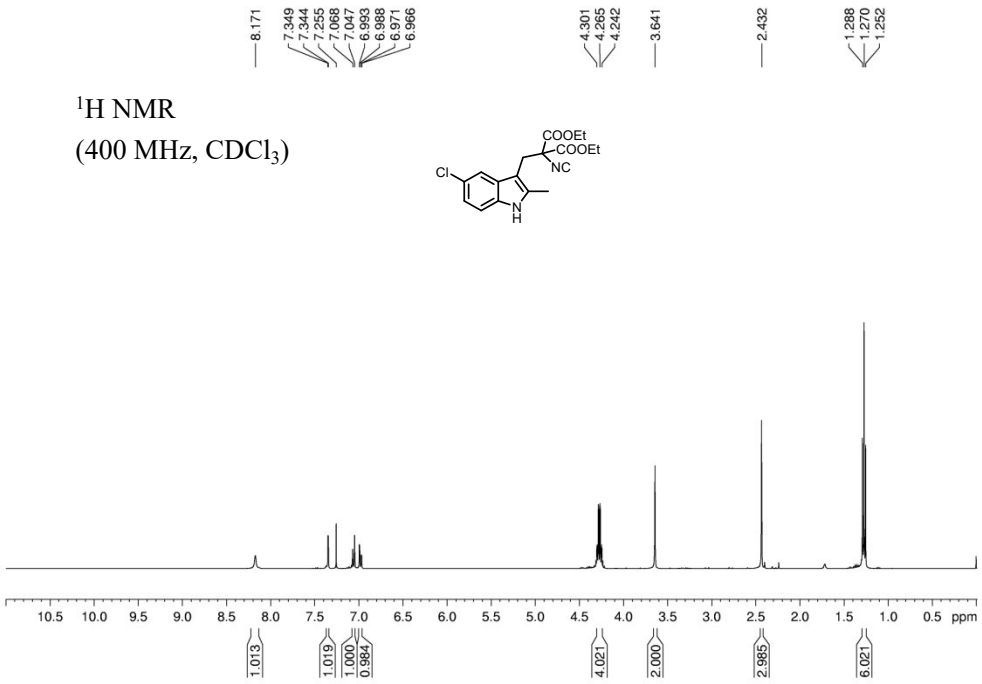


^{13}C NMR
(100 MHz, $CDCl_3$)

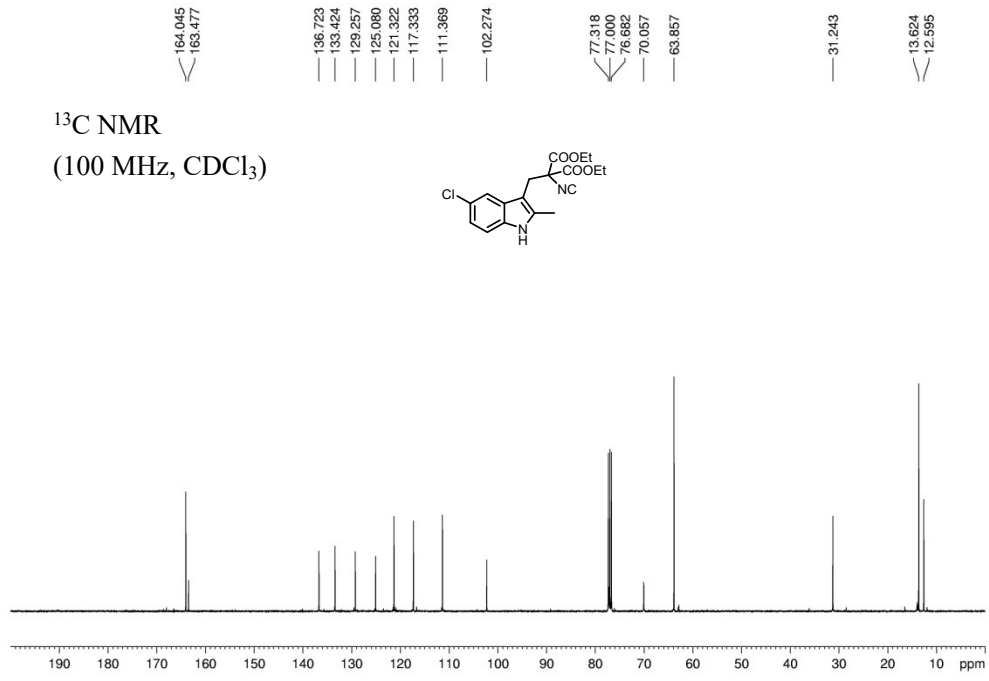




(1d)



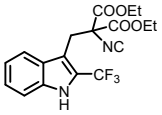
^{1}H NMR
(400 MHz, $CDCl_3$)

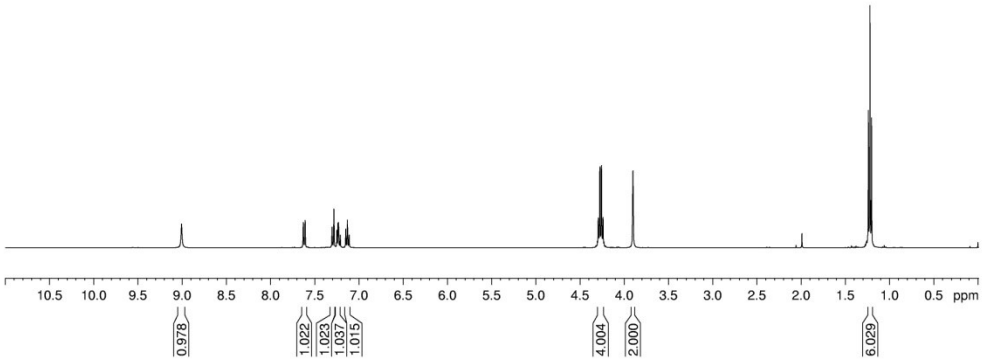


^{13}C NMR
(100 MHz, $CDCl_3$)

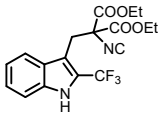
(1e)

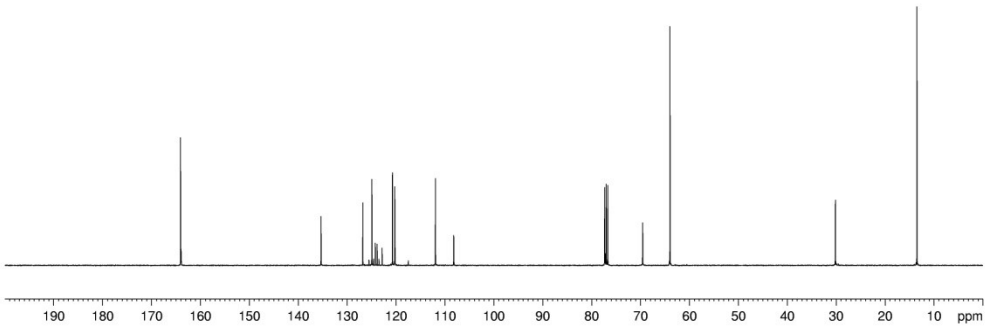
^{1}H NMR
(400 MHz, $CDCl_3$)



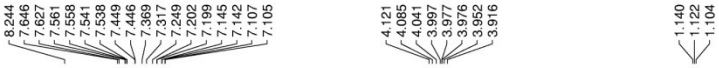


^{13}C NMR
(100 MHz, $CDCl_3$)

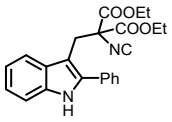


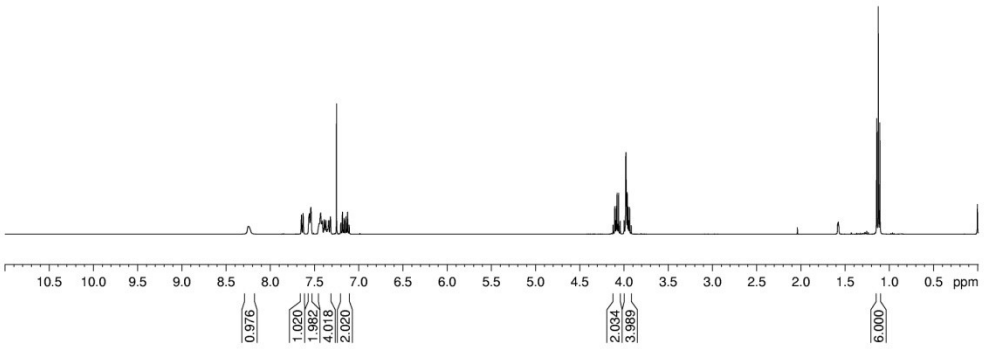


（1f）

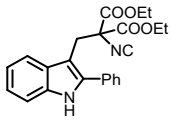


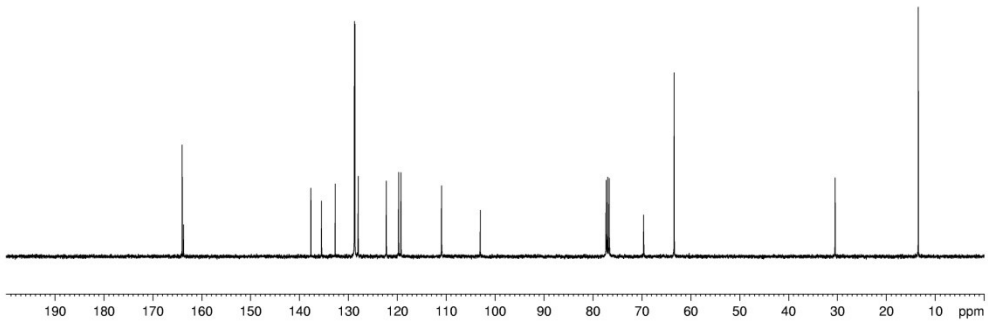
^{1}H NMR
(400 MHz, $CDCl_3$)



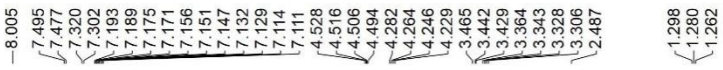


^{13}C NMR
(100 MHz, $CDCl_3$)

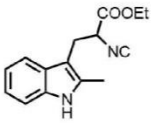


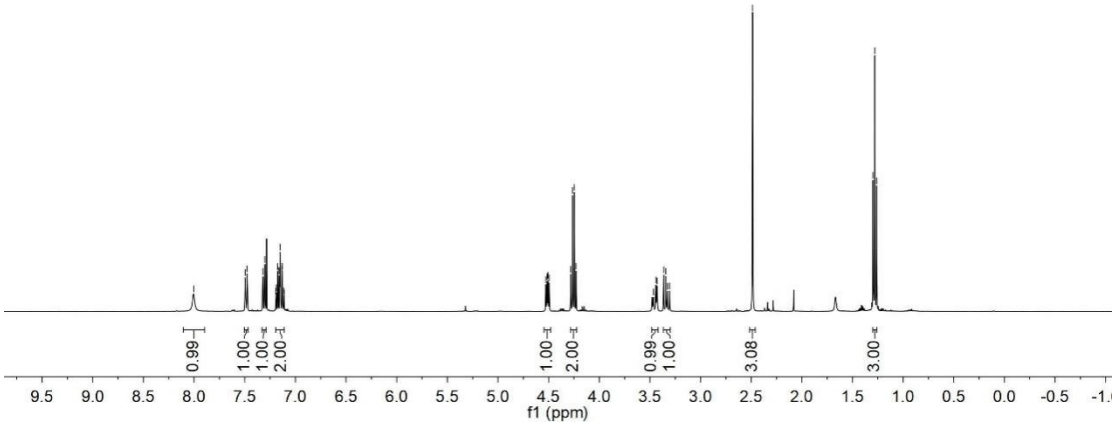


(1g)

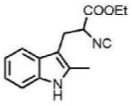


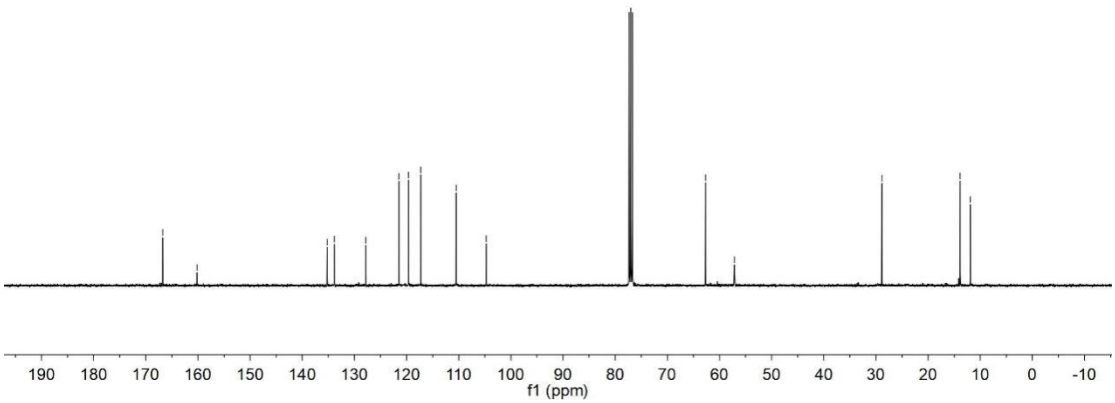
^{1}H NMR
(400 MHz, $CDCl_3$)





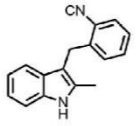
^{13}C NMR
(100 MHz, $CDCl_3$)

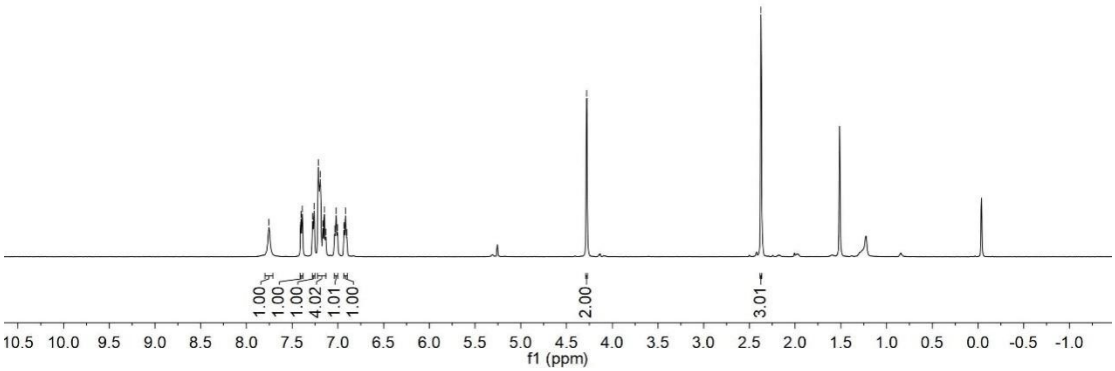




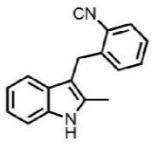
(1h)

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

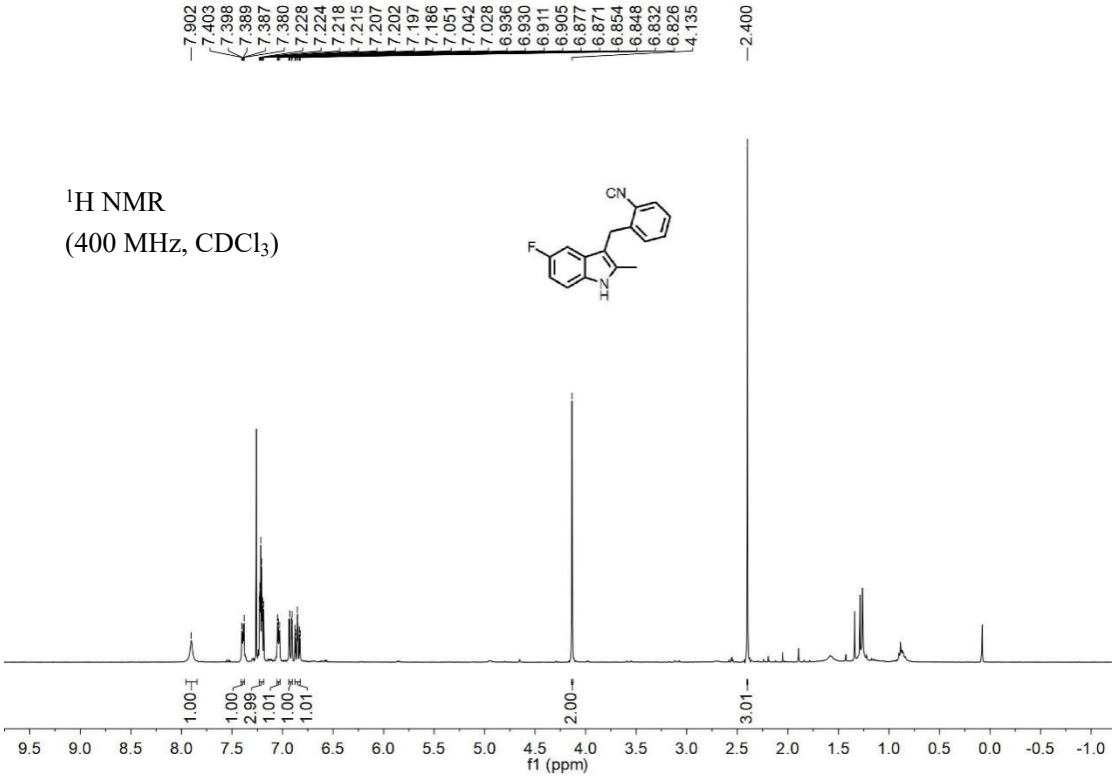




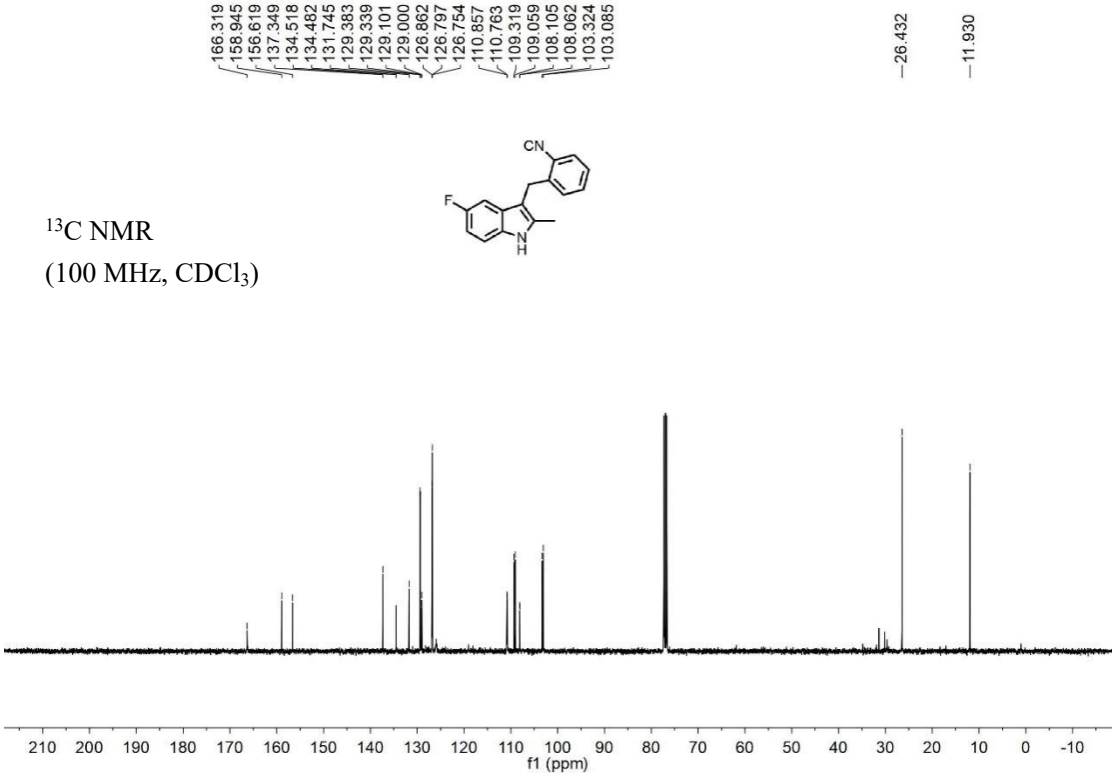
^{13}C NMR
(100 MHz, $CDCl_3$)



(1i)



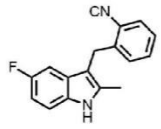
^{1}H NMR
(400 MHz, $CDCl_3$)



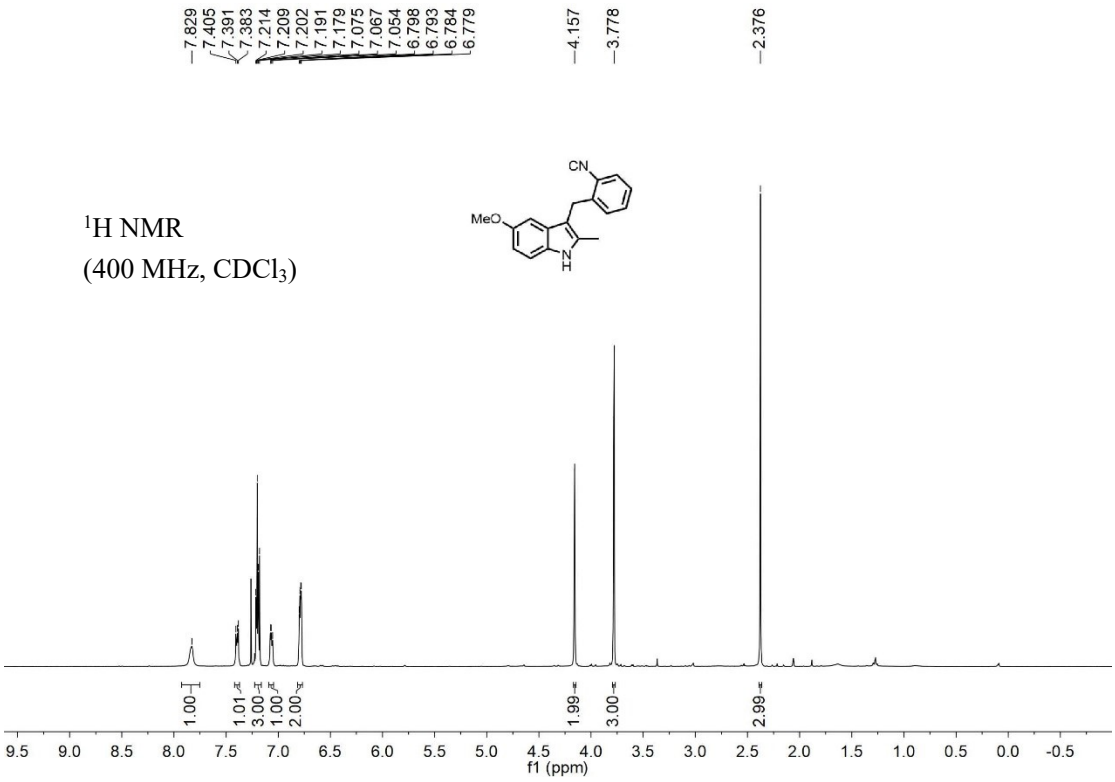
^{13}C NMR
(100 MHz, $CDCl_3$)

^{19}F NMR

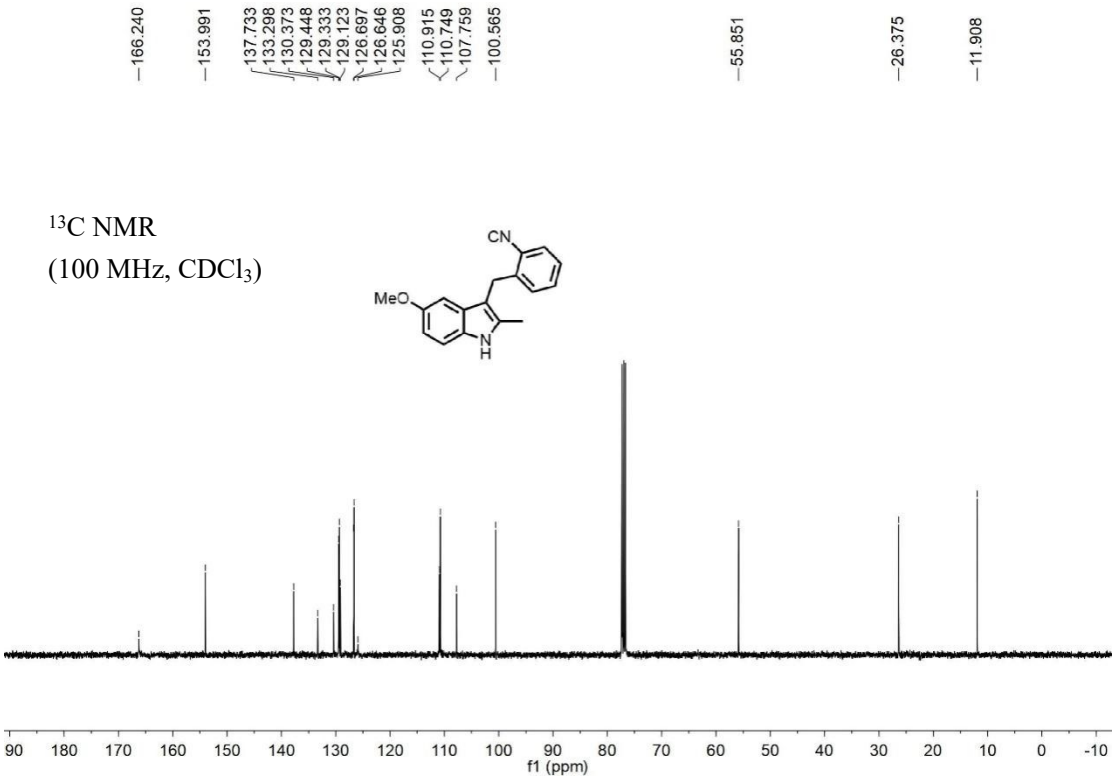
(376 MHz, $CDCl_3$)



(1j)



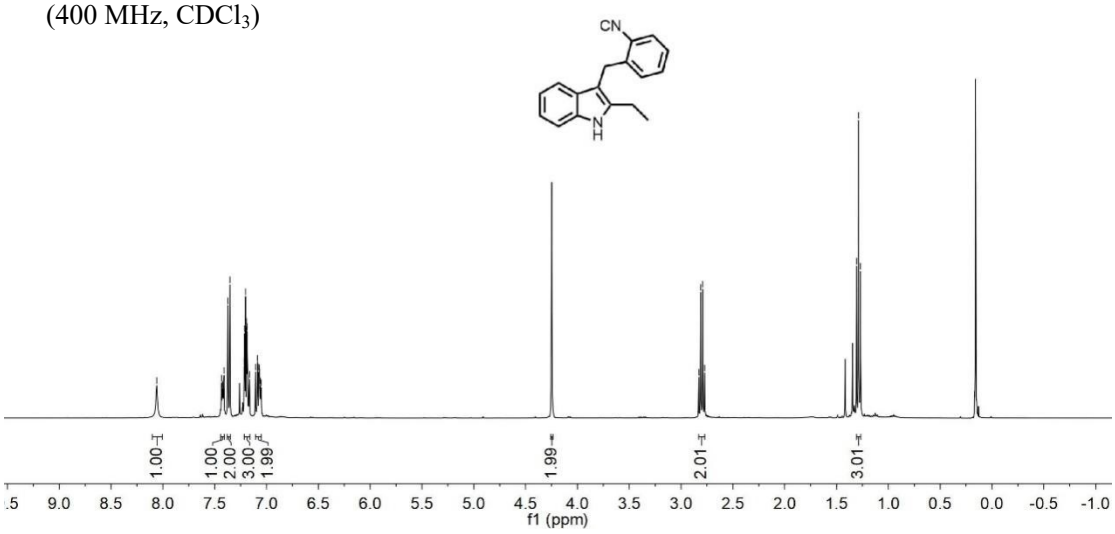
^{1}H NMR
(400 MHz, $CDCl_3$)



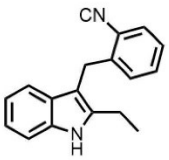
^{13}C NMR
(100 MHz, $CDCl_3$)

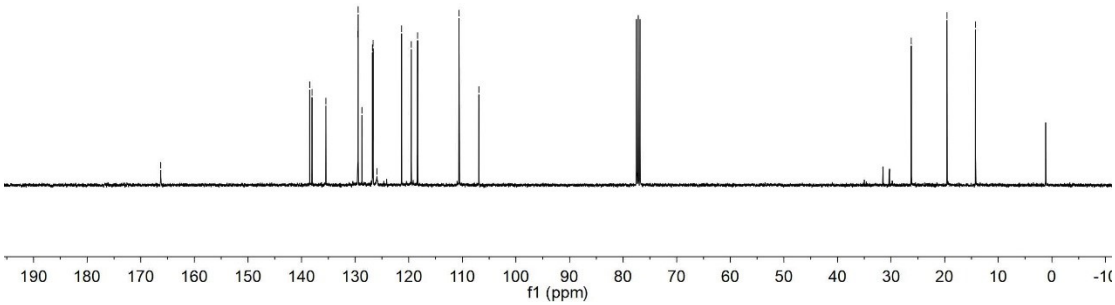
(1k)

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

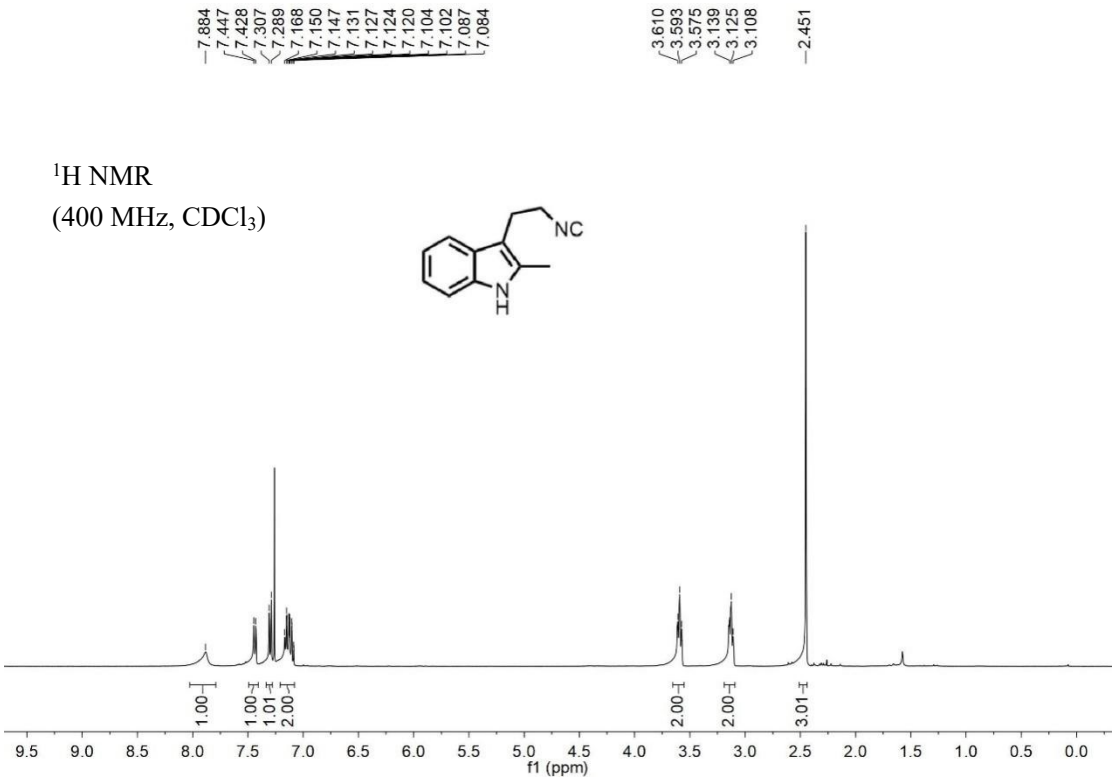


^{13}C NMR
(100 MHz, $CDCl_3$)

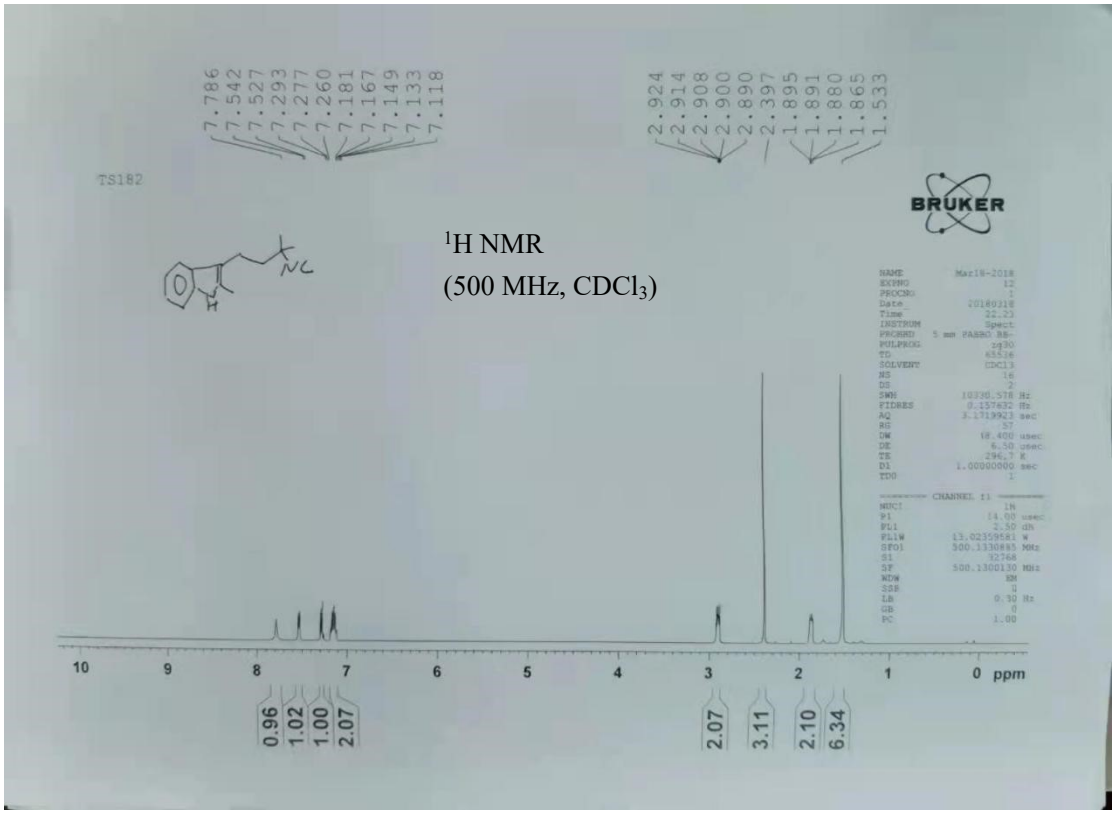




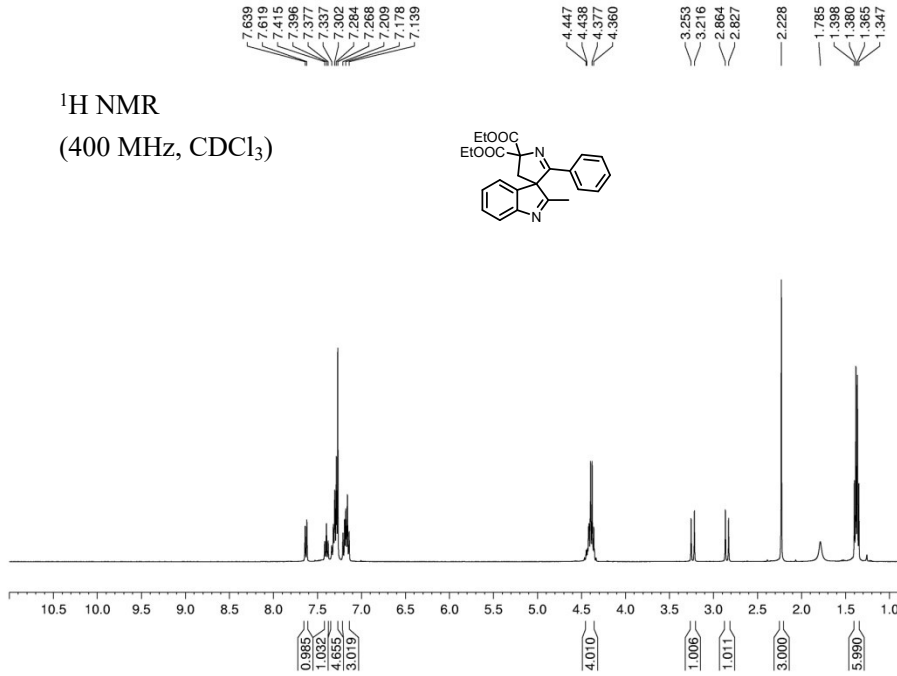
(1l)


7.884
7.447
7.428
7.307
7.289
7.168
7.150
7.147
7.131
7.127
7.124
7.120
7.104
7.102
7.087
7.084
3.610
3.593
3.575
3.139
3.125
3.108
2.451
^{1}H NMR
(400 MHz, $CDCl_3$)
NC
H
1.00
1.00
1.01
2.00
2.00
2.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

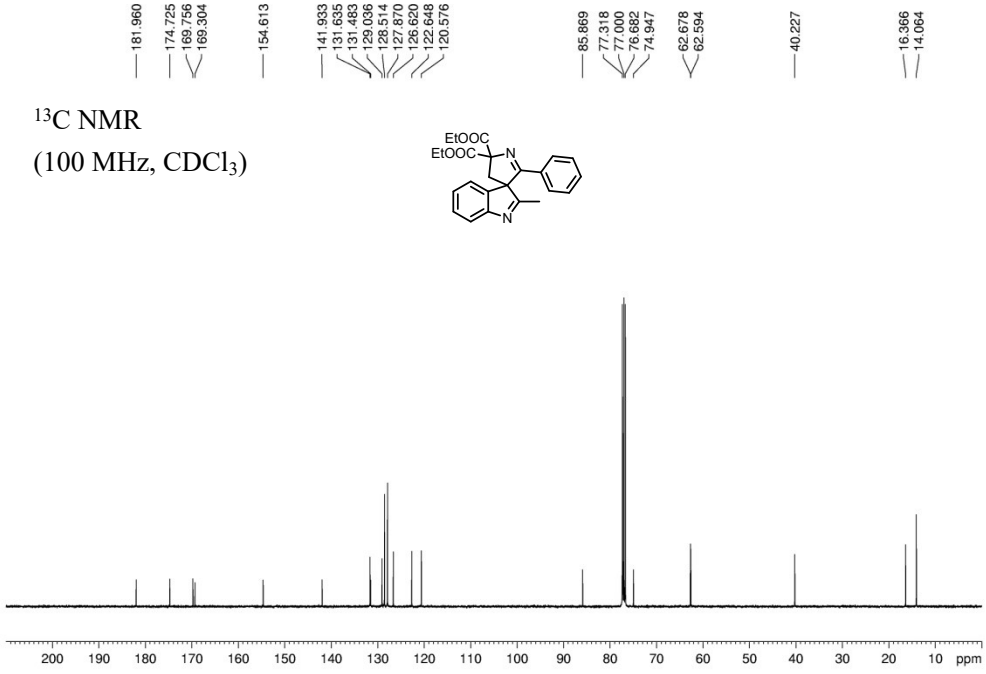
(1m)


7.786
7.542
7.527
7.293
7.277
7.260
7.181
7.167
7.149
7.133
7.118
2.924
2.914
2.908
2.900
2.890
2.397
1.895
1.891
1.880
1.865
1.533
TS182
BRUKER
NC
H
^{1}H NMR
(500 MHz, $CDCl_3$)
10 9 8 7 6 5 4 3 2 1 0 ppm
0.96
1.02
1.00
2.07
2.07
3.11
2.10
6.34

(3a)

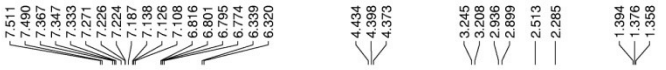


^{1}H NMR
(400 MHz, $CDCl_3$)

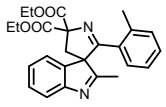


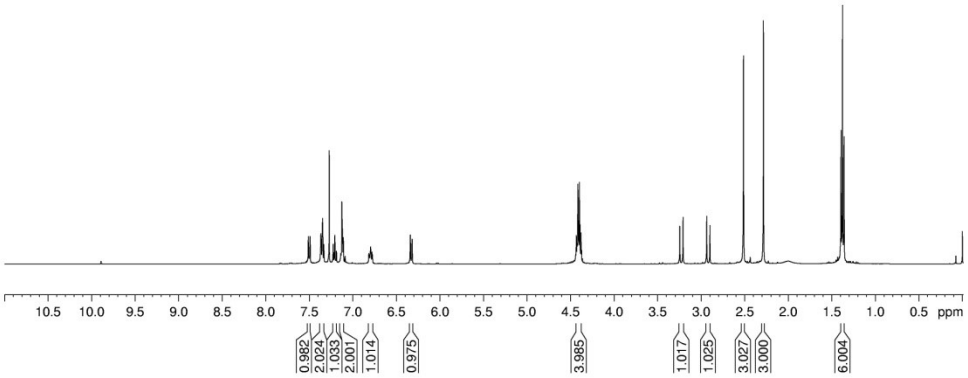
^{13}C NMR
(100 MHz, $CDCl_3$)

(3b)

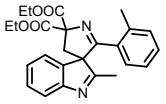


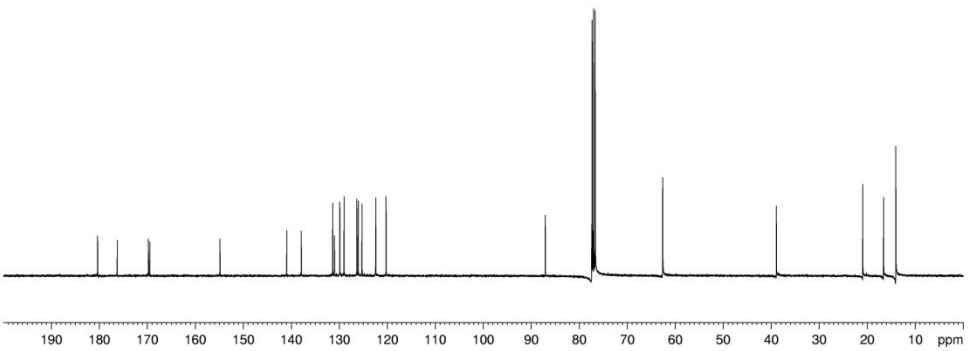
^{1}H NMR
(400 MHz, $CDCl_3$)



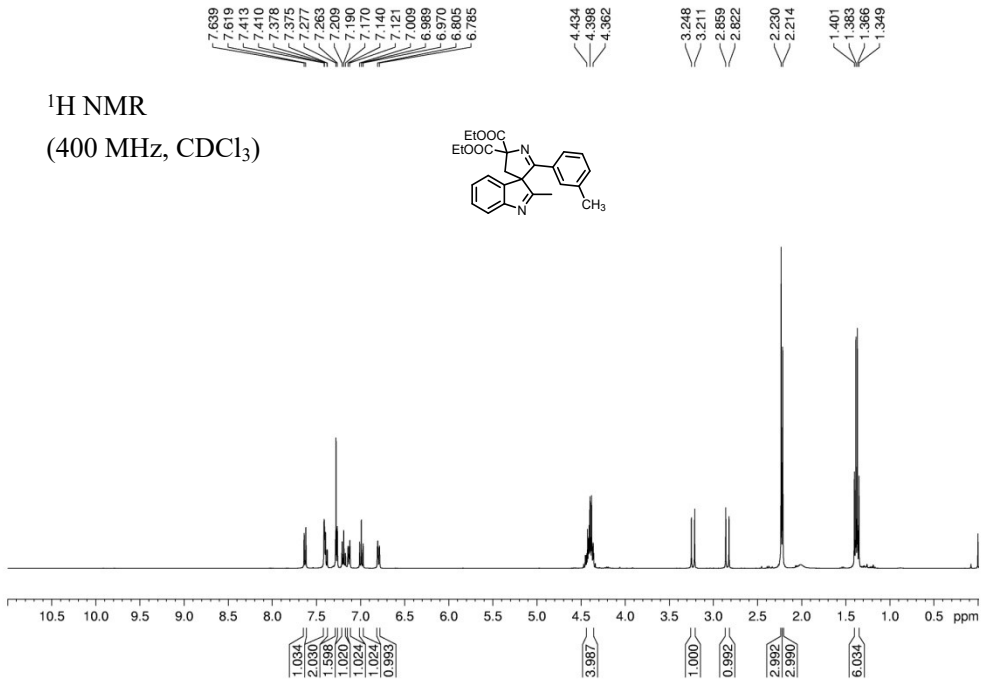


^{13}C NMR
(100 MHz, $CDCl_3$)

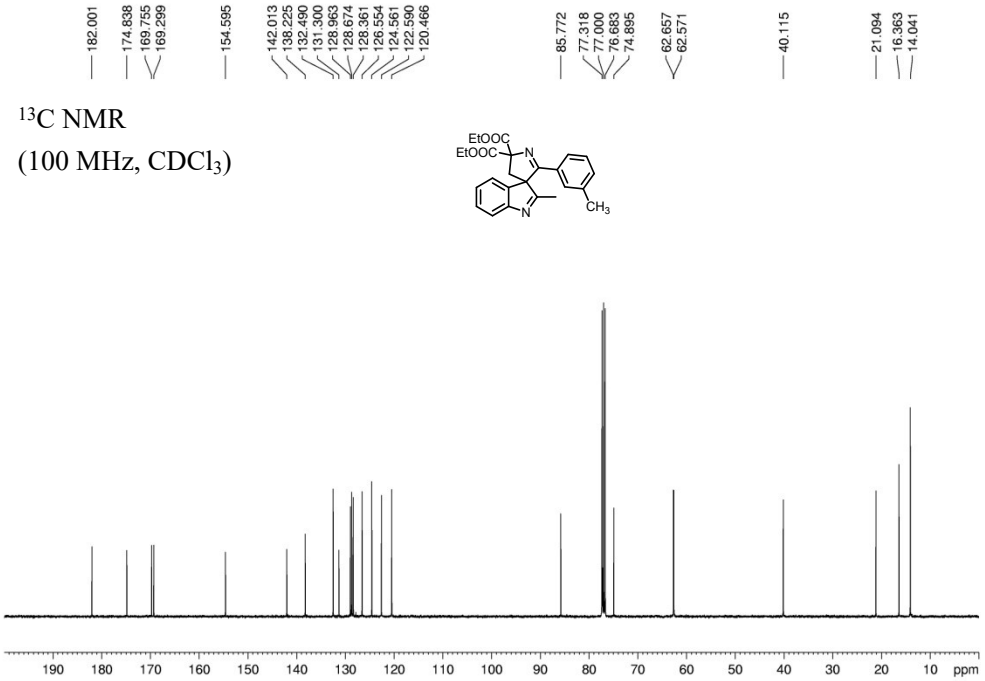




(3c)

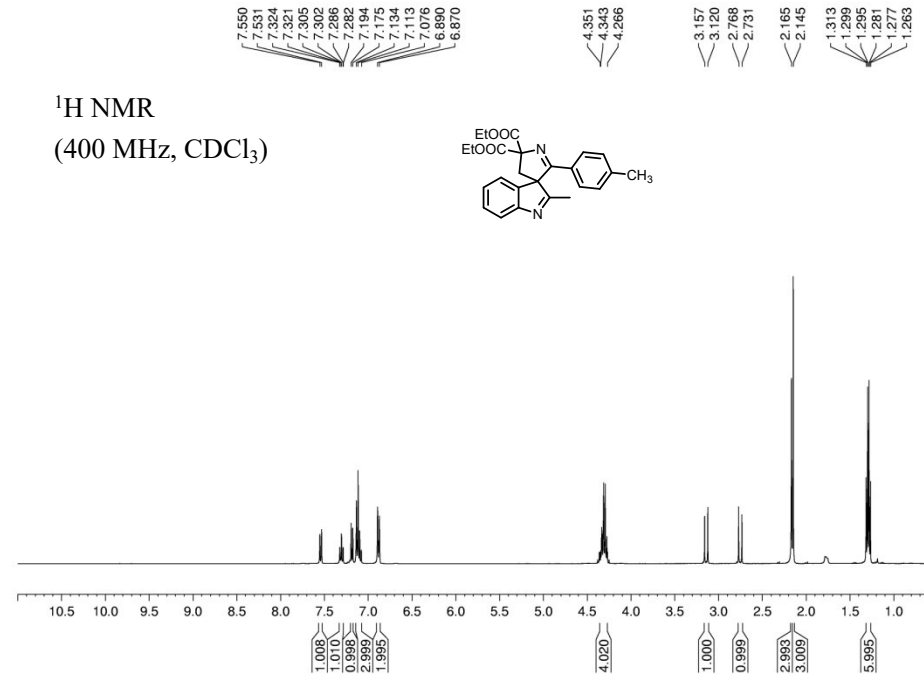


^{1}H NMR
(400 MHz, $CDCl_3$)

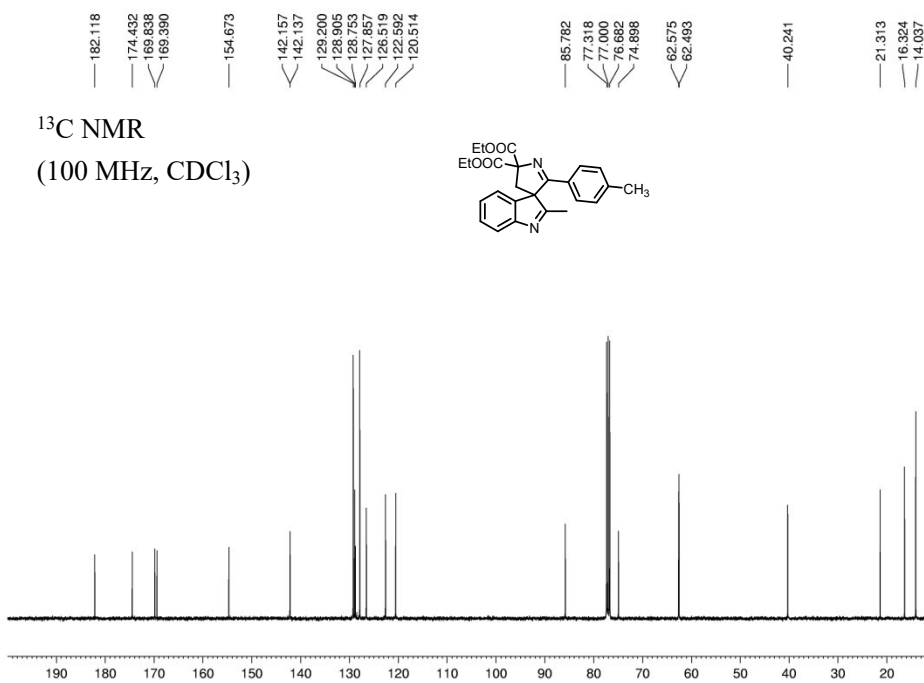


^{13}C NMR
(100 MHz, $CDCl_3$)

(3d)

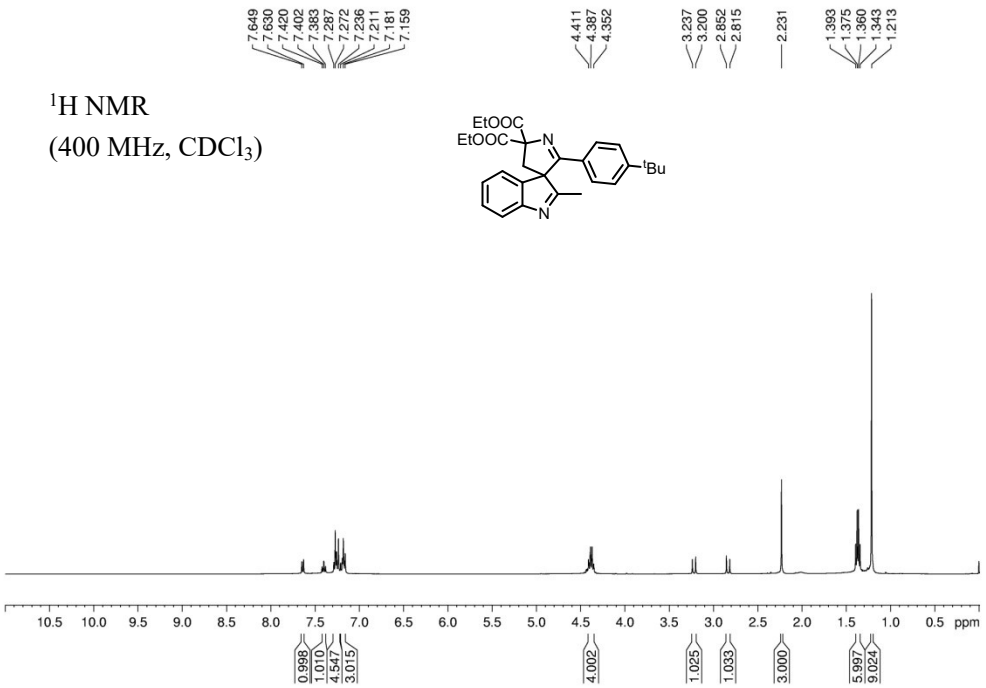


^{1}H NMR
(400 MHz, $CDCl_3$)

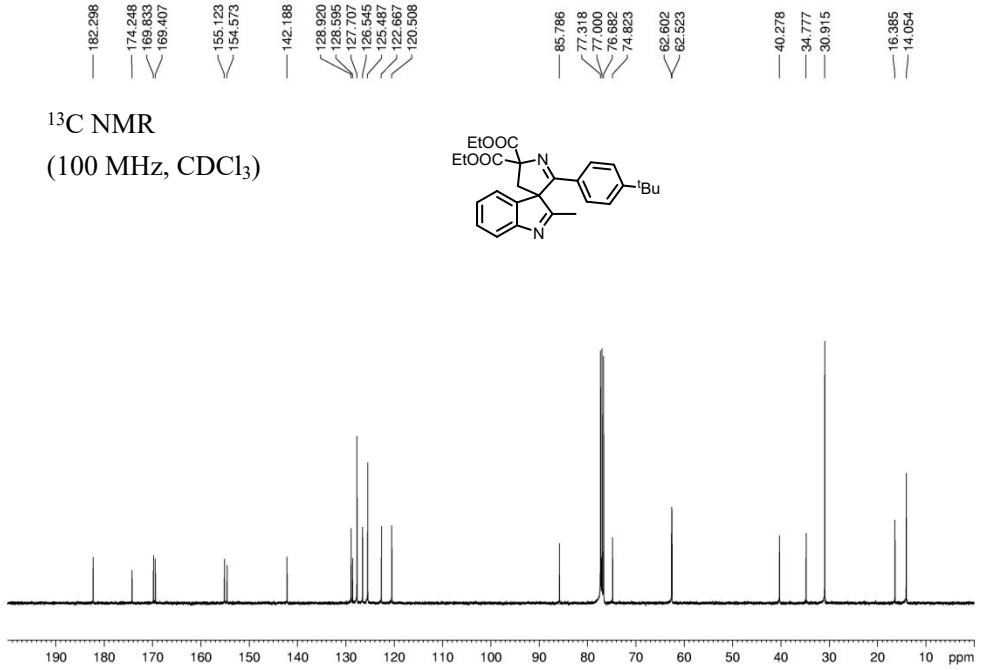


^{13}C NMR
(100 MHz, $CDCl_3$)

(3e)



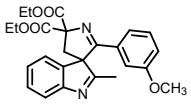
^{1}H NMR
(400 MHz, $CDCl_3$)

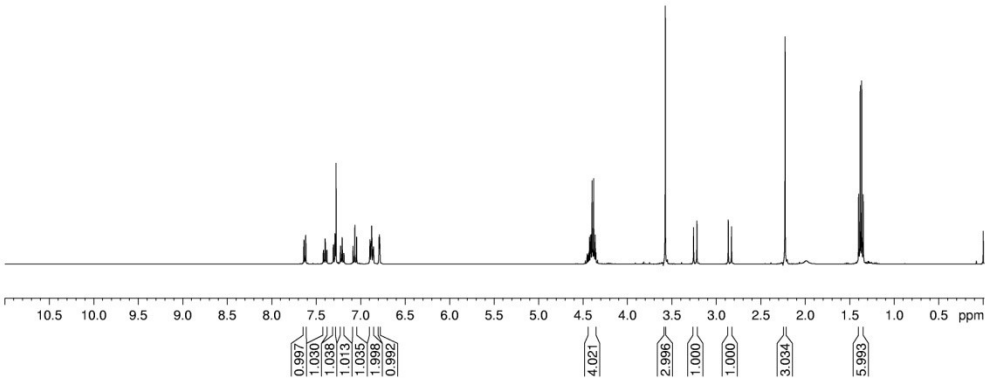


^{13}C NMR
(100 MHz, $CDCl_3$)

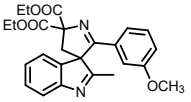
(3f)

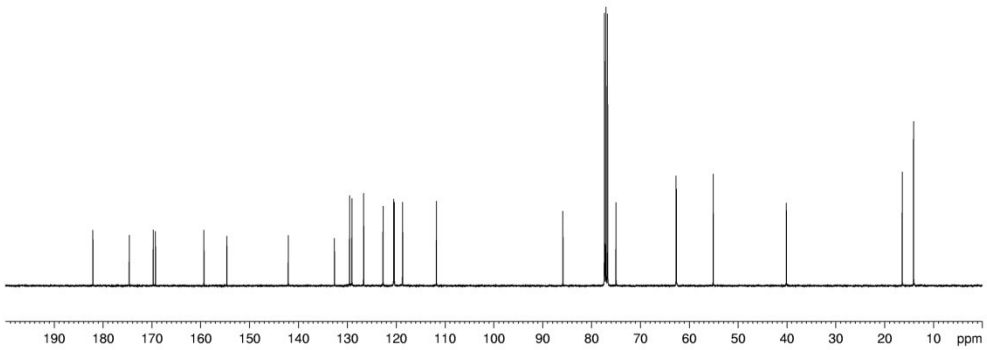
^{1}H NMR
(400 MHz, $CDCl_3$)





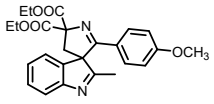
^{13}C NMR
(100 MHz, $CDCl_3$)

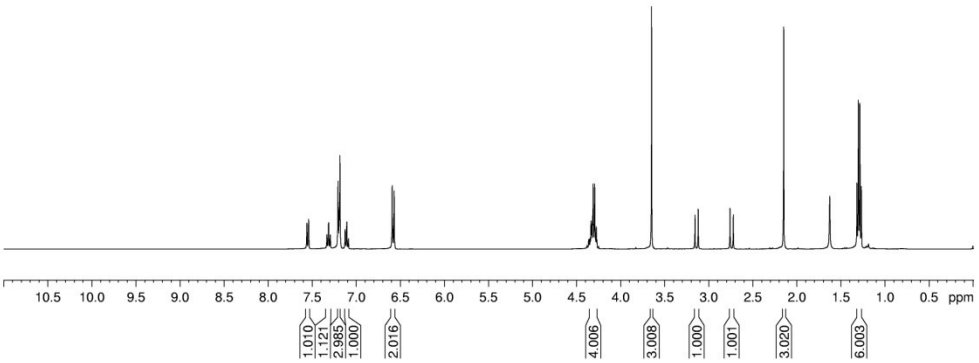




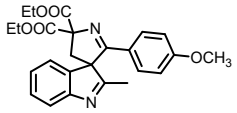
(3g)

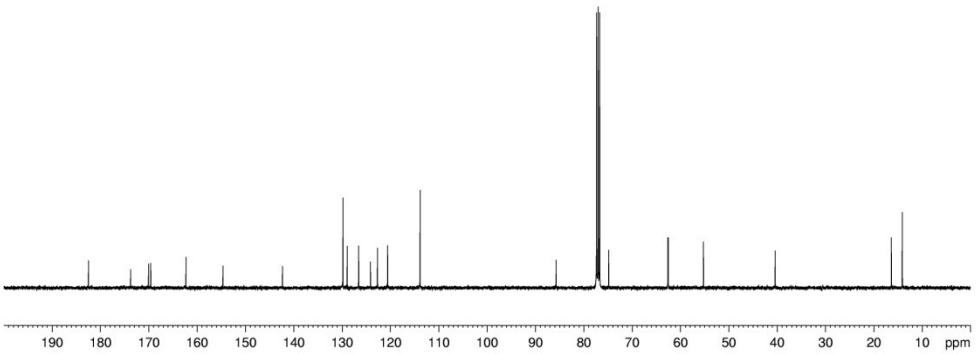
^{1}H NMR
(400 MHz, $CDCl_3$)



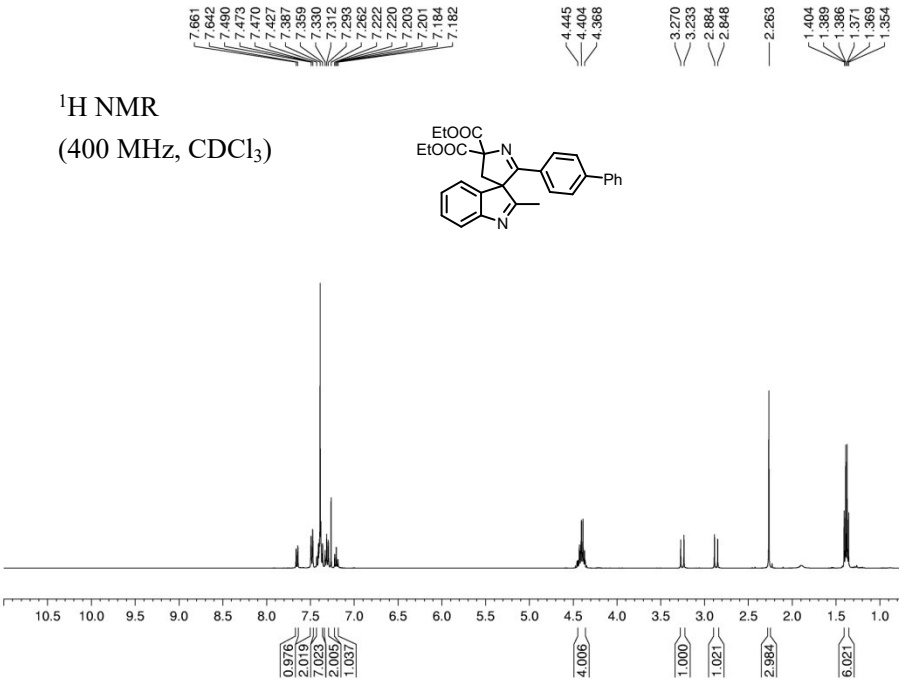


^{13}C NMR
(100 MHz, $CDCl_3$)

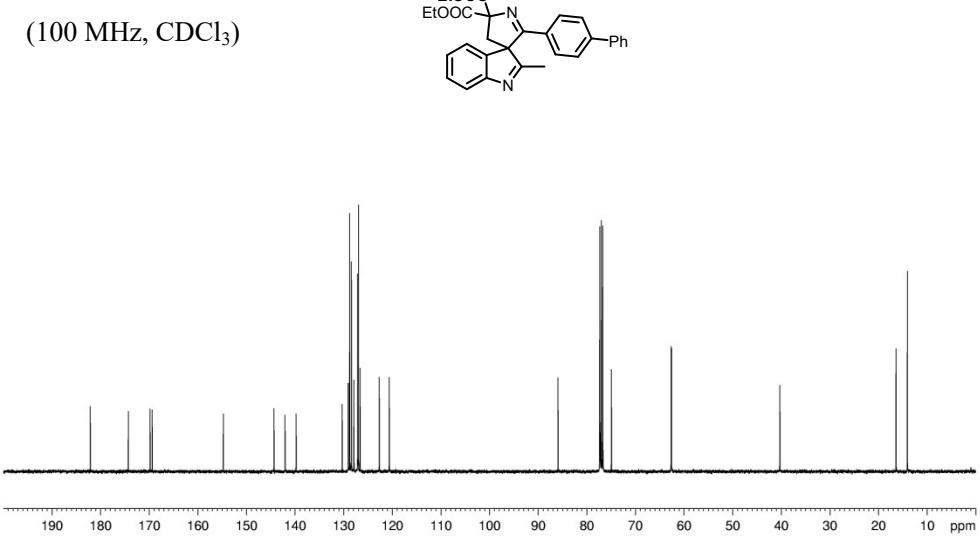




(3h)

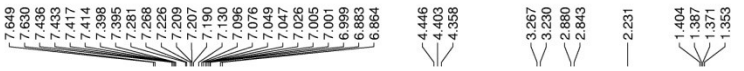


^{1}H NMR
(400 MHz, $CDCl_3$)

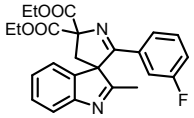


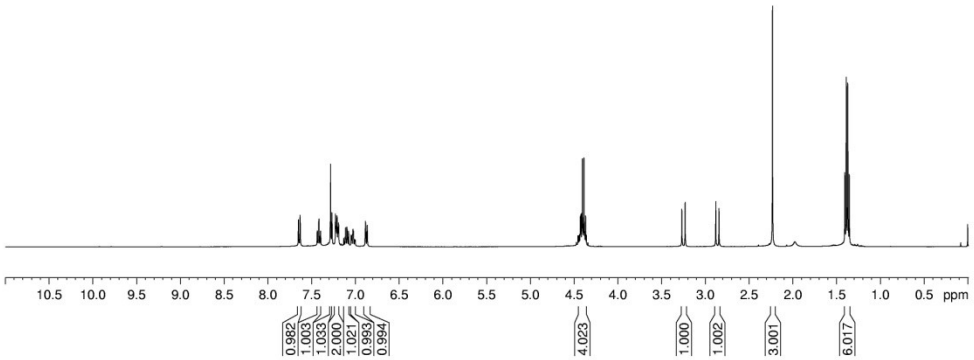
^{13}C NMR
(100 MHz, $CDCl_3$)

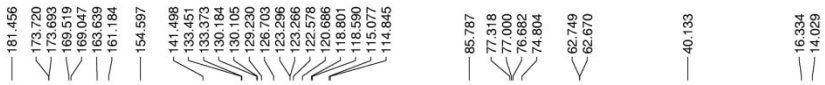
(3i)



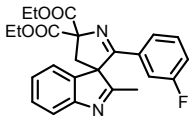
^{1}H NMR
(400 MHz, $CDCl_3$)

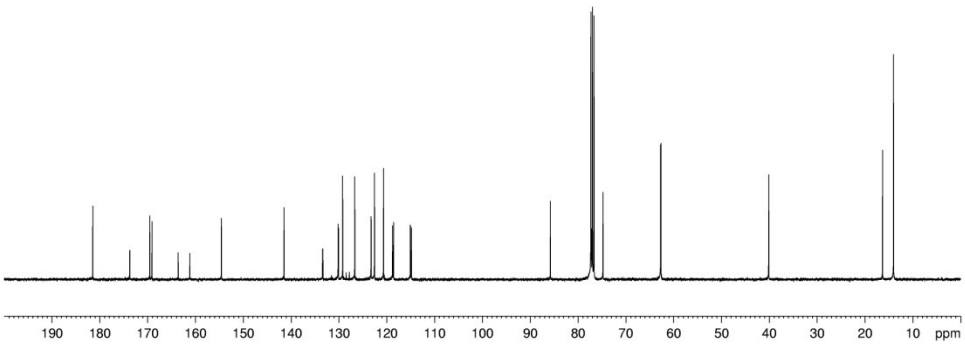






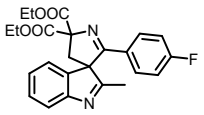
^{13}C NMR
(100 MHz, $CDCl_3$)

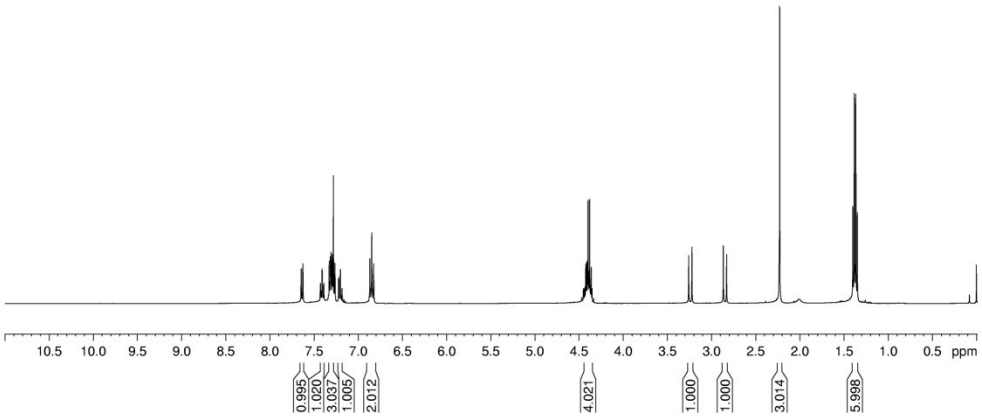




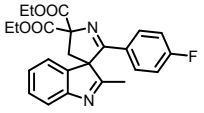
(3j)

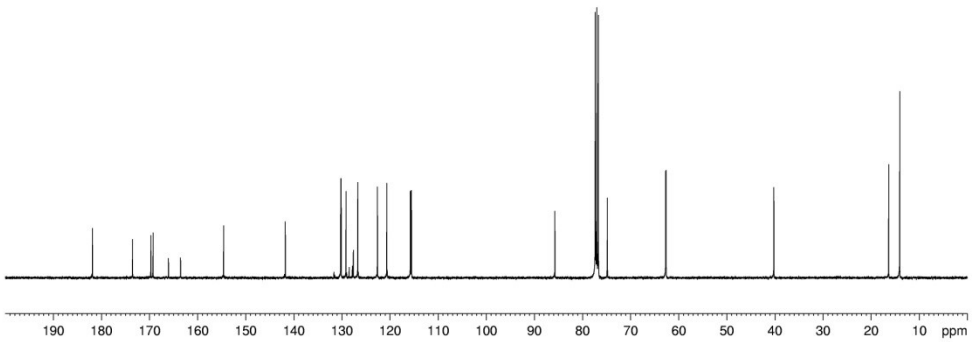
^{1}H NMR
(400 MHz, $CDCl_3$)





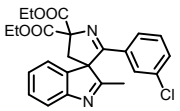
^{13}C NMR
(100 MHz, $CDCl_3$)

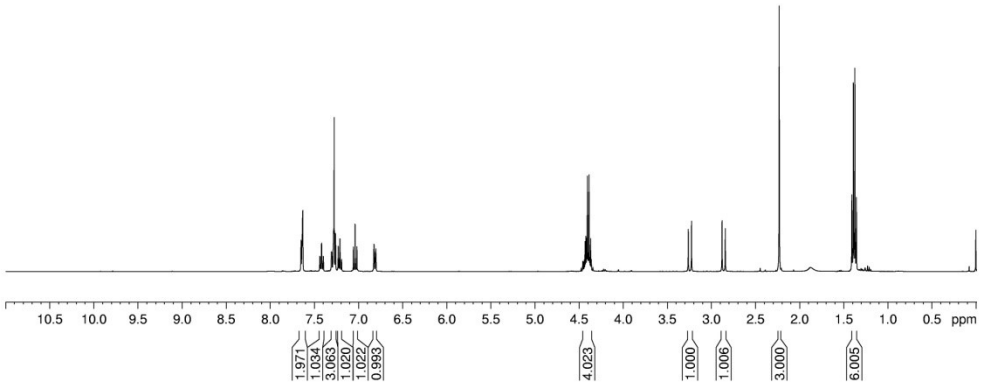




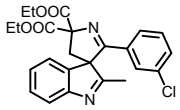
(3k)

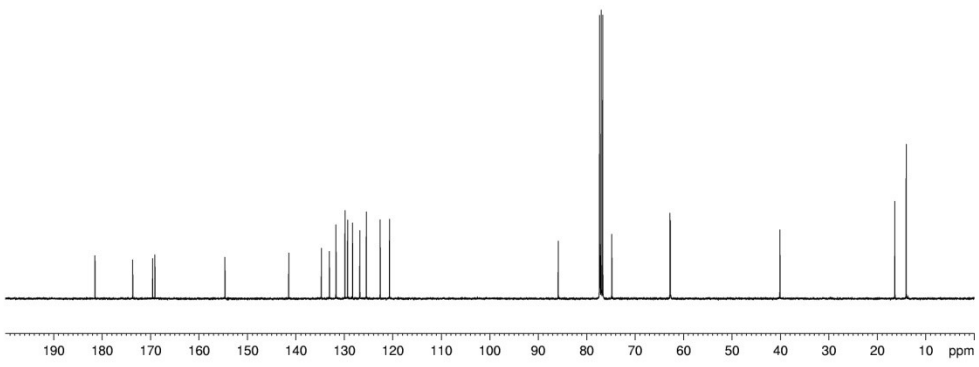
^{1}H NMR
(400 MHz, $CDCl_3$)





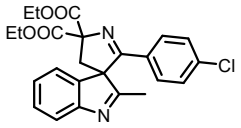
^{13}C NMR
(100 MHz, $CDCl_3$)

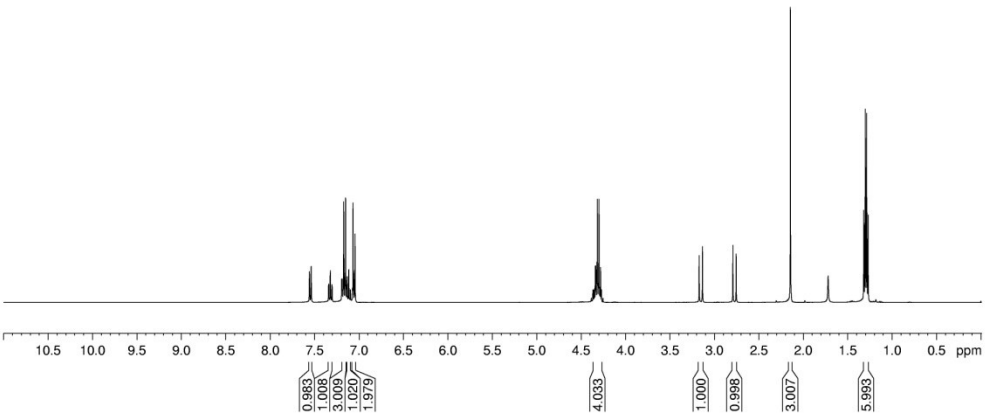




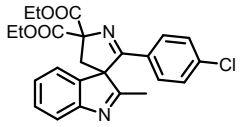
(3l)

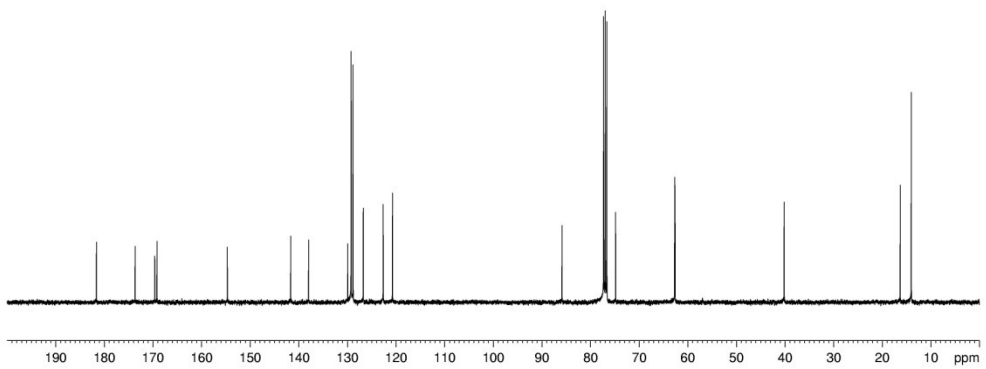
^{1}H NMR
(400 MHz, $CDCl_3$)





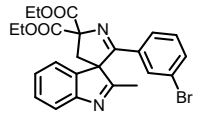
^{13}C NMR
(100 MHz, $CDCl_3$)

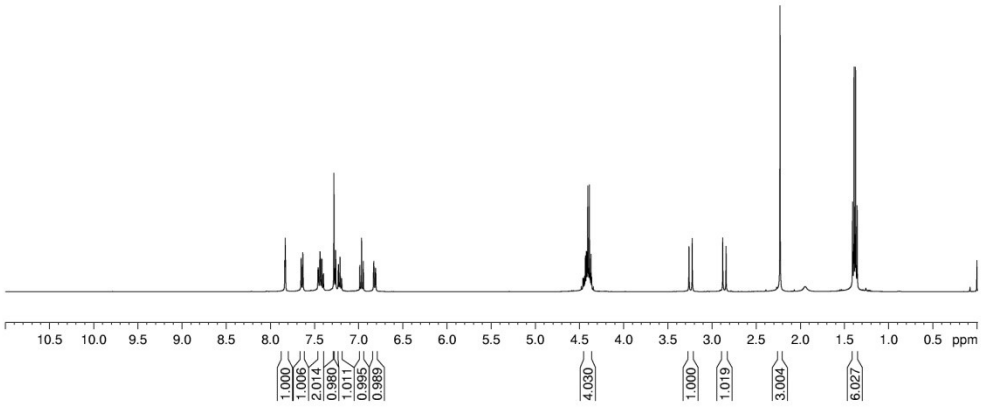




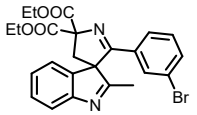
(3m)

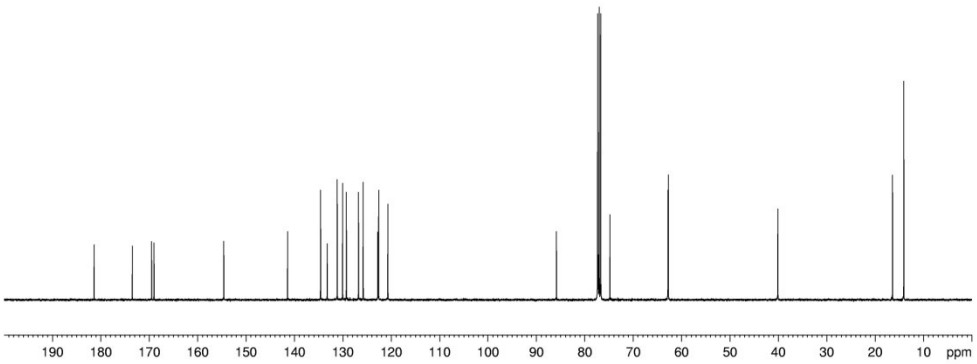
^{1}H NMR
(400 MHz, $CDCl_3$)





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





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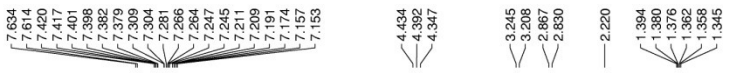
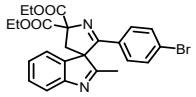
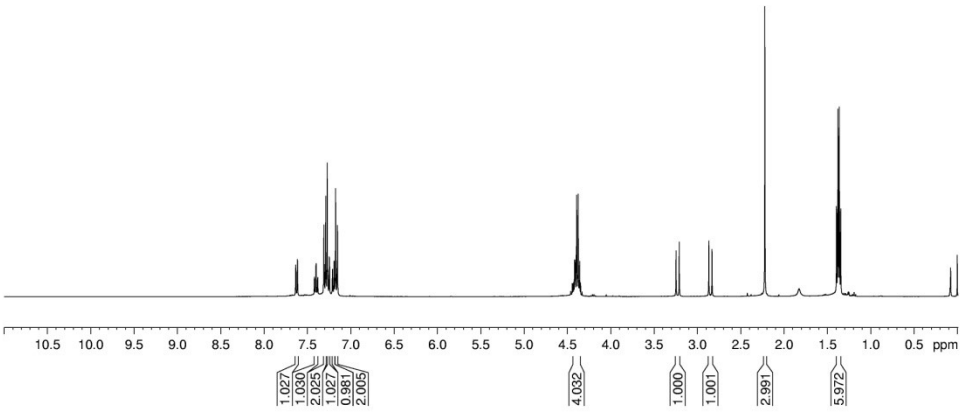
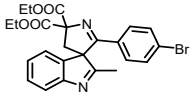


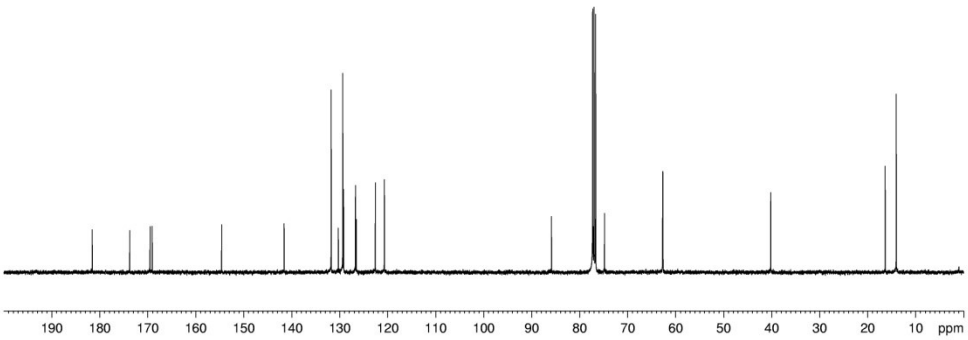
^{1}H NMR
(400 MHz, $CDCl_3$)



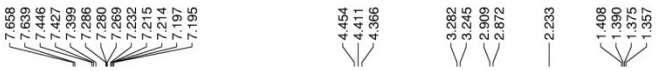


^{13}C NMR
(100 MHz, $CDCl_3$)

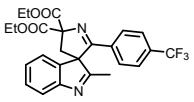


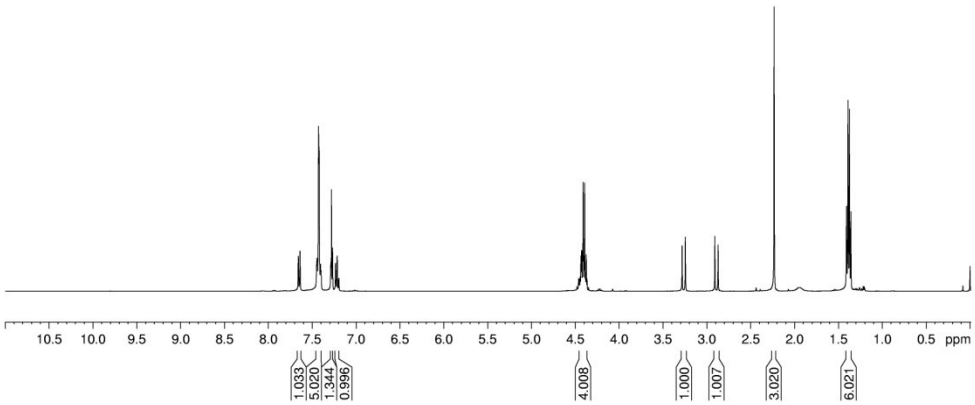


(3o)

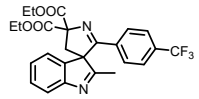


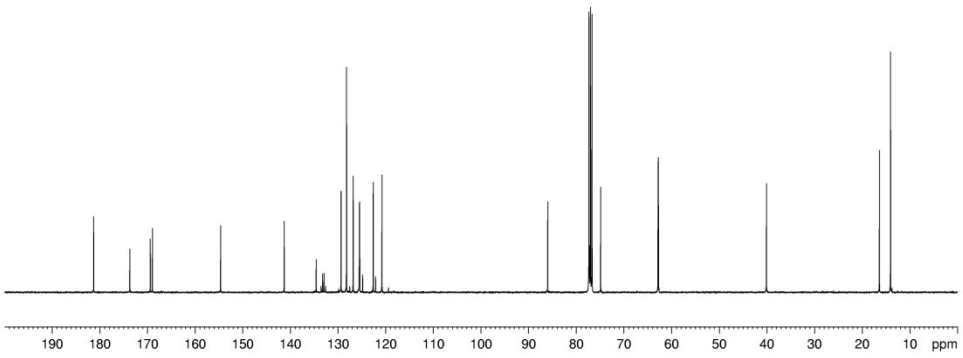
^{1}H NMR
(400 MHz, $CDCl_3$)





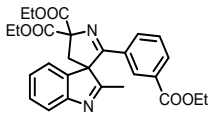
^{13}C NMR
(100 MHz, $CDCl_3$)

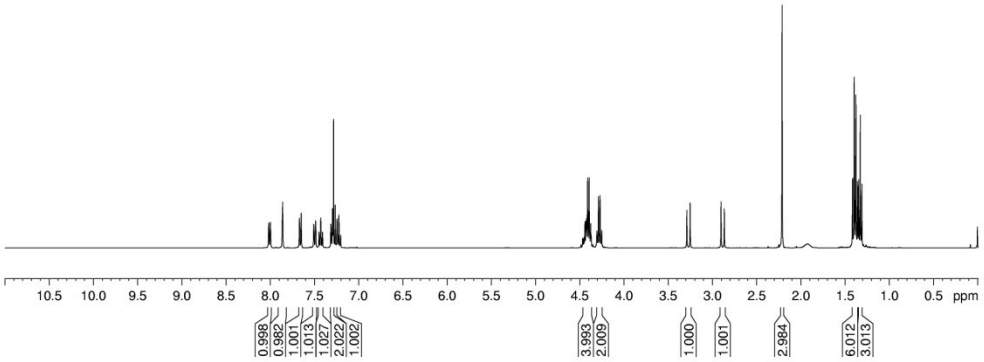




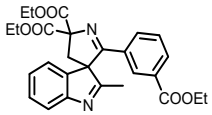
(3p)

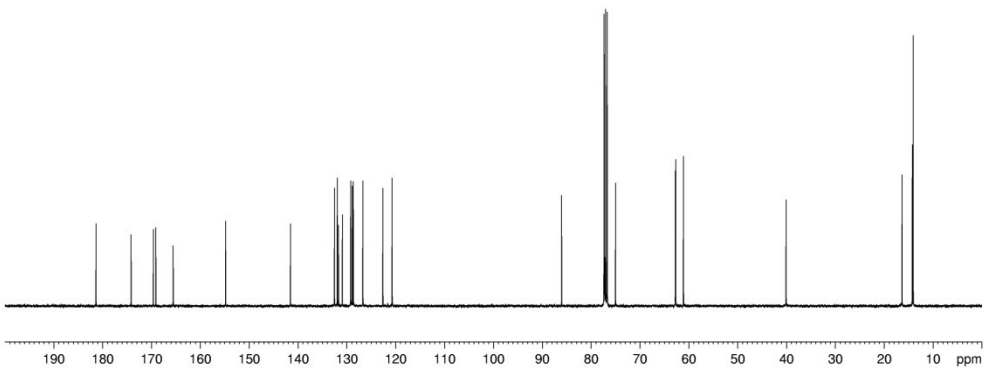
^{1}H NMR
(400 MHz, $CDCl_3$)





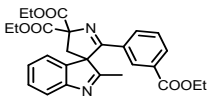
^{13}C NMR
(100 MHz, $CDCl_3$)

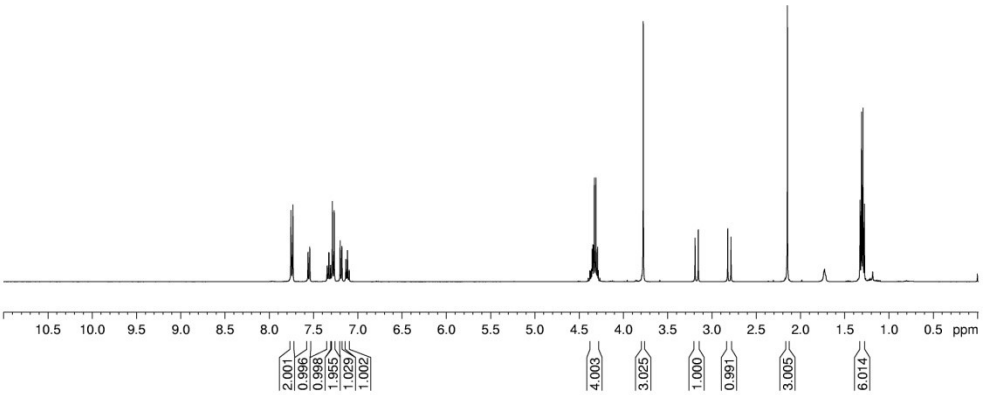




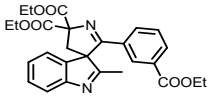
(3q)

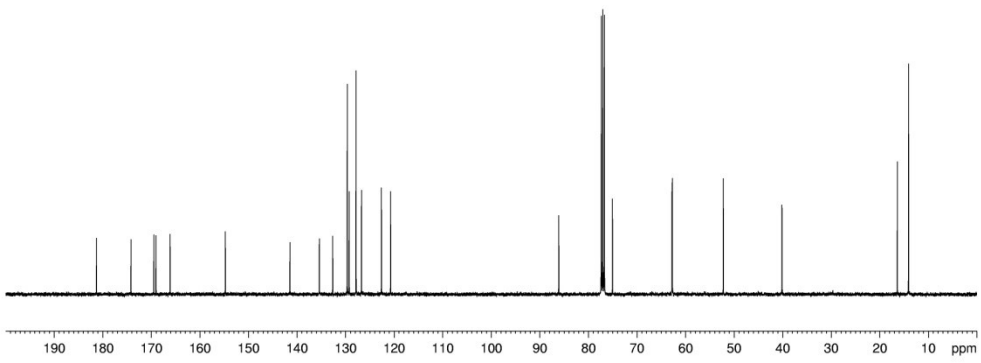
^{1}H NMR
(400 MHz, $CDCl_3$)



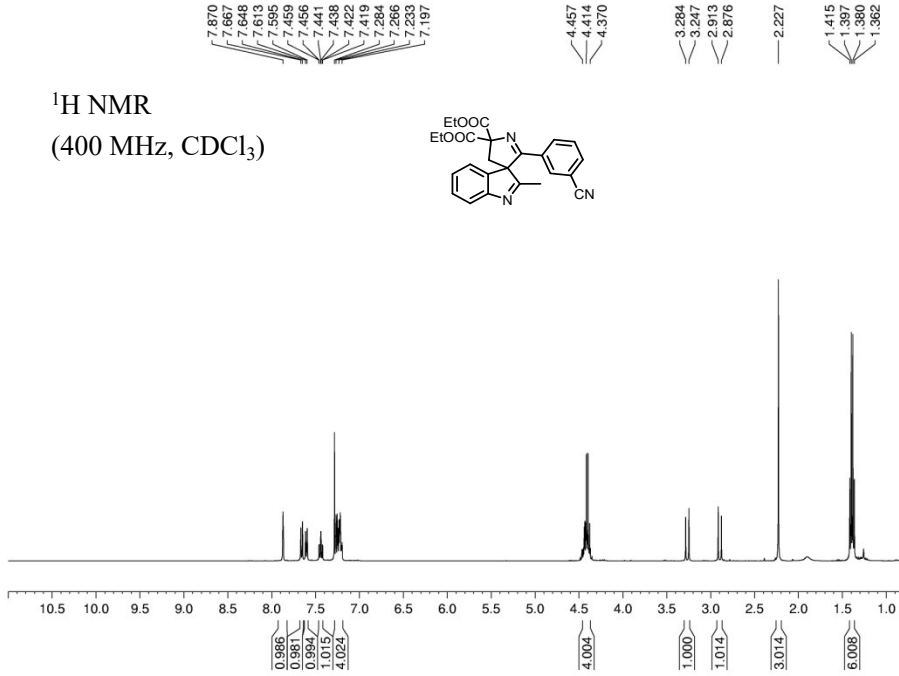


^{13}C NMR
(100 MHz, $CDCl_3$)

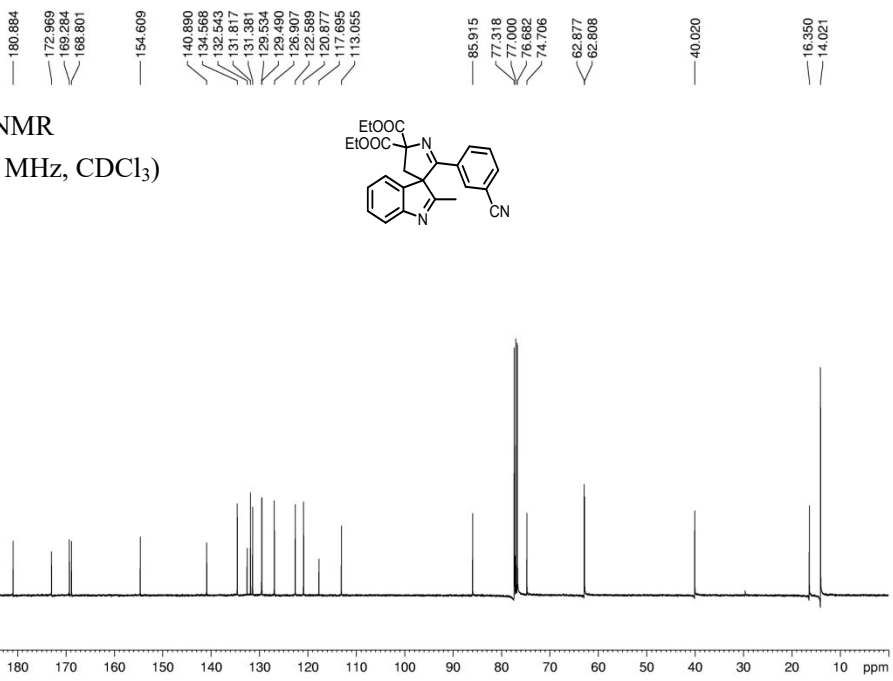




(3r)



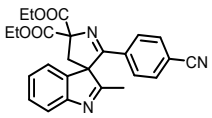
^{1}H NMR
(400 MHz, $CDCl_3$)



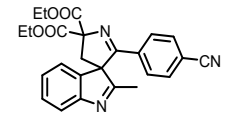
^{13}C NMR
(100 MHz, $CDCl_3$)

(3s)

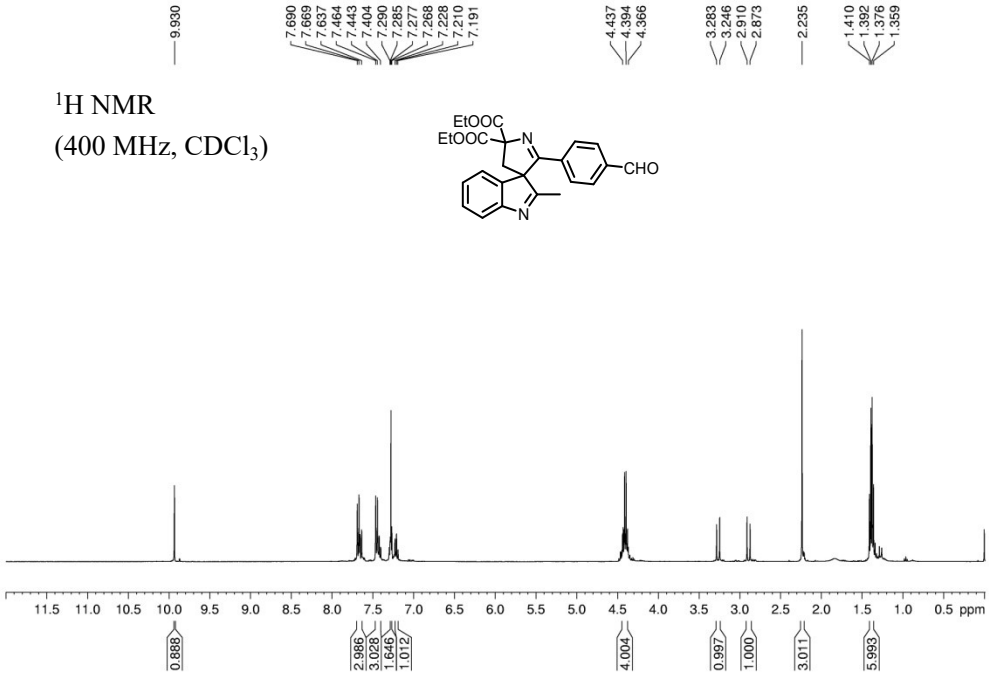
^{1}H NMR
(400 MHz, $CDCl_3$)



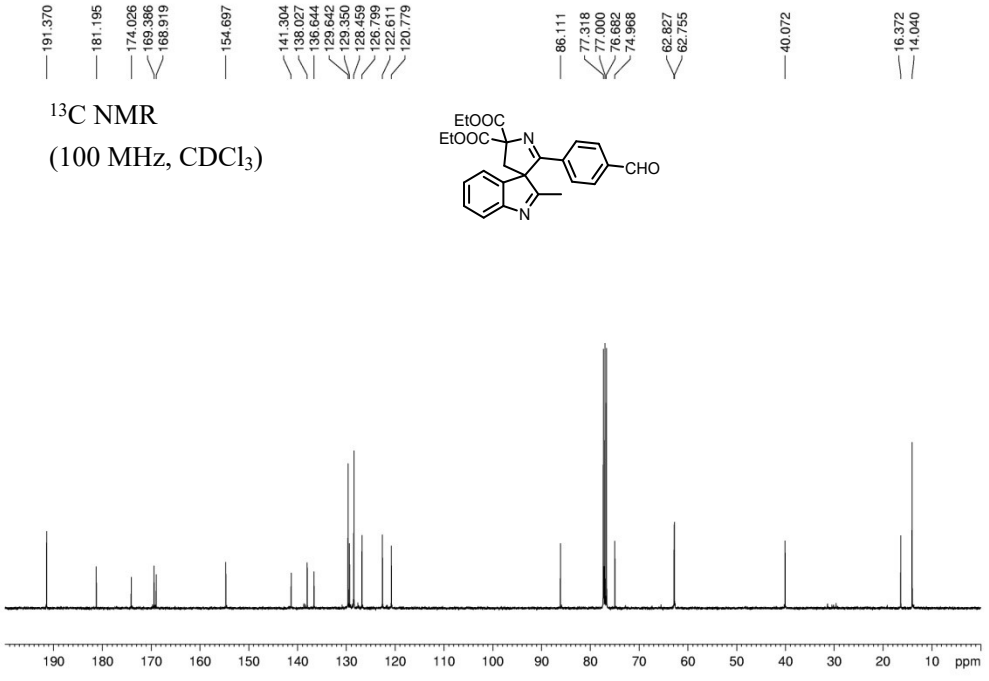
^{13}C NMR
(100 MHz, $CDCl_3$)



(3t)

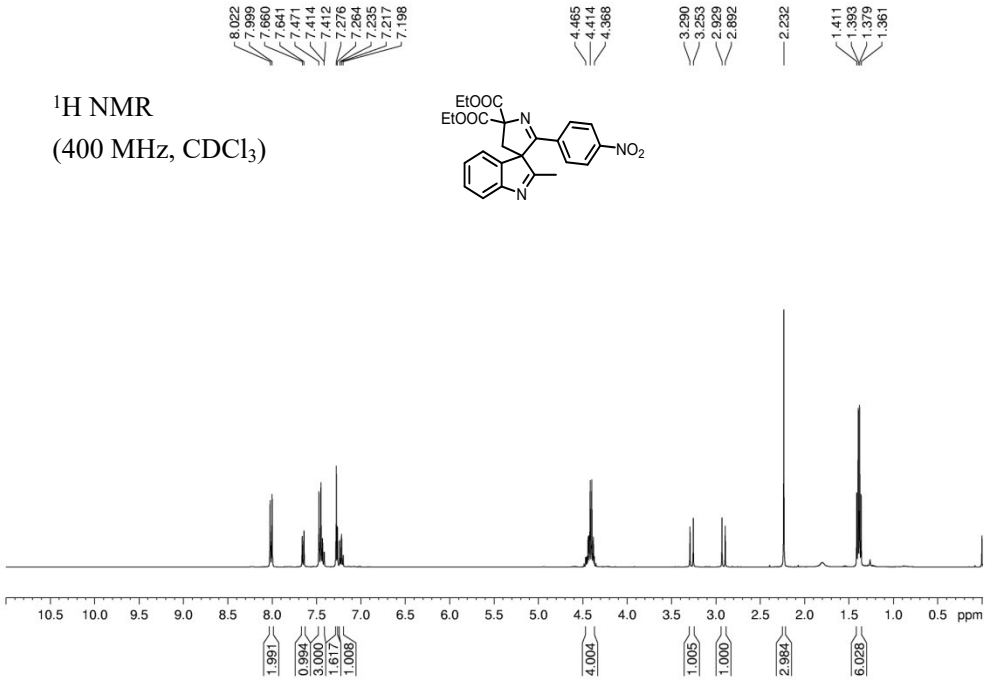


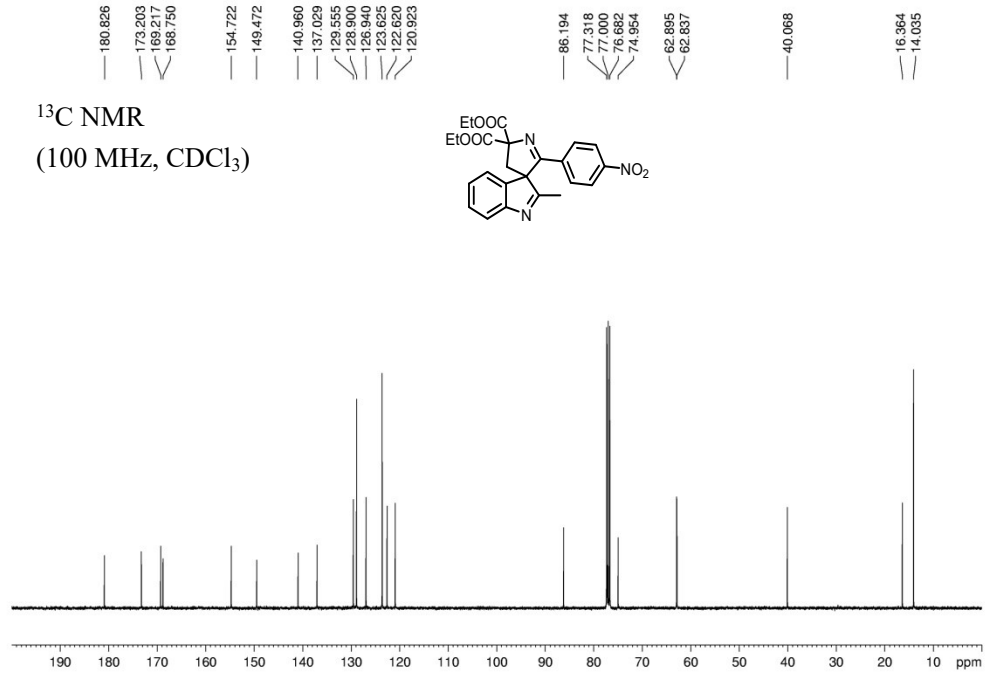
^{1}H NMR
(400 MHz, $CDCl_3$)



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

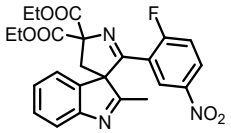
(3u)

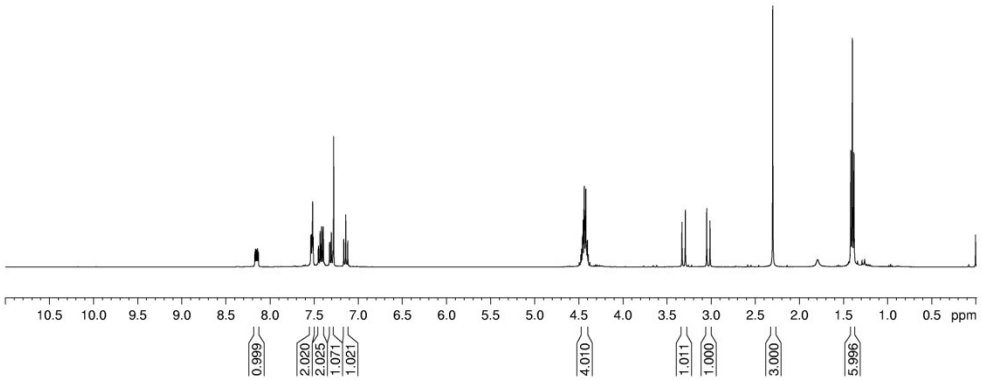

8.022
7.999
7.660
7.641
7.471
7.414
7.412
7.276
7.264
7.235
7.217
7.198
4.465
4.414
4.368
3.290
3.253
2.929
2.892
2.232
1.411
1.393
1.379
1.361
1H NMR
(400 MHz, CDCl3)
EtOOC
EtOOC
N
NO2
N
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.991
0.994
3.000
1.617
1.008
4.004
1.005
1.000
2.984
6.028


180.826
173.203
169.217
168.750
154.722
149.472
140.960
137.029
129.555
128.900
126.940
123.625
122.620
120.923
86.194
77.318
77.000
76.682
74.954
62.895
62.837
40.068
16.364
14.035
13C NMR
(100 MHz, CDCl3)
EtOOC
EtOOC
N
NO2
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

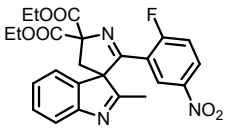
(3v)

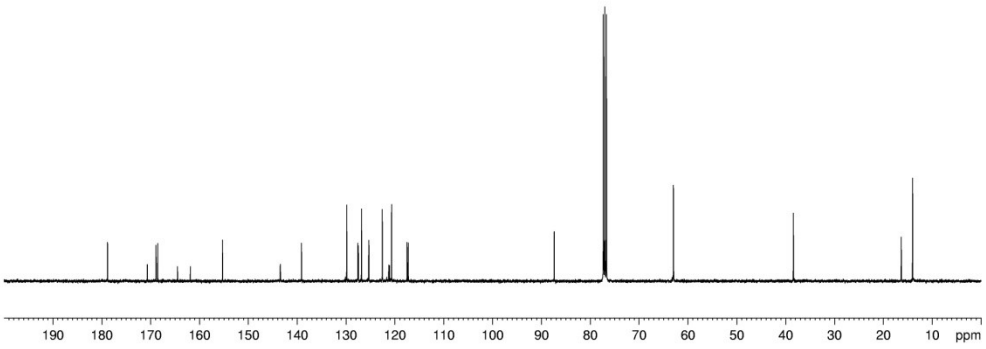
^{1}H NMR
(400 MHz, $CDCl_3$)



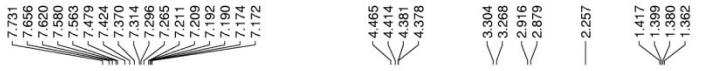


^{13}C NMR
(100 MHz, $CDCl_3$)

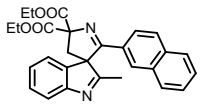


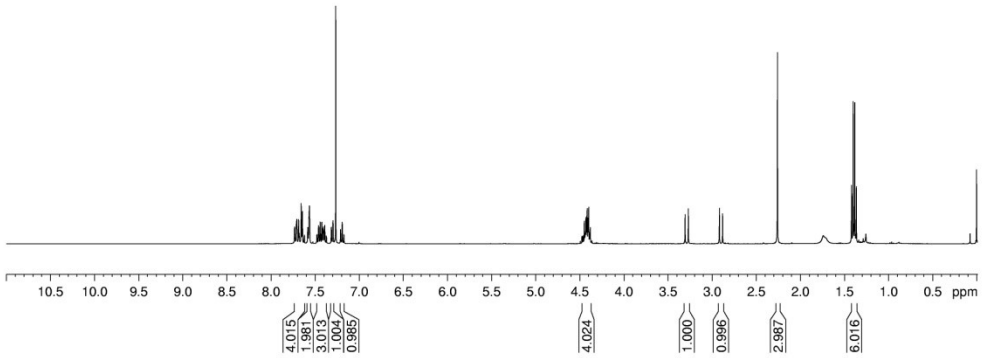


(3w)

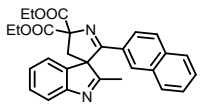


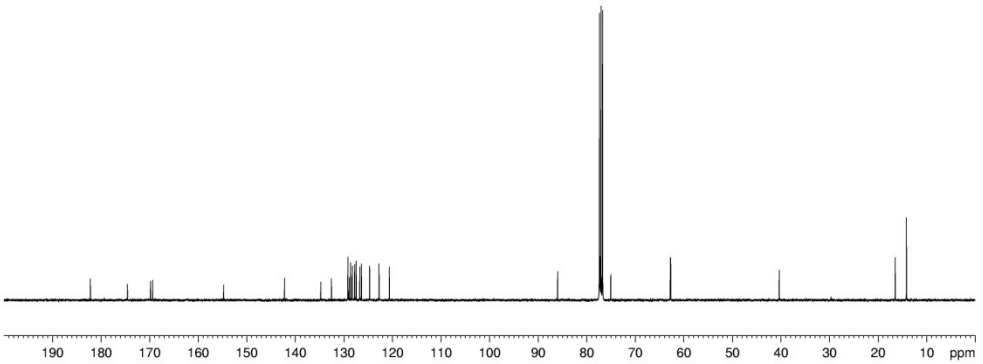
^{1}H NMR
(400 MHz, $CDCl_3$)



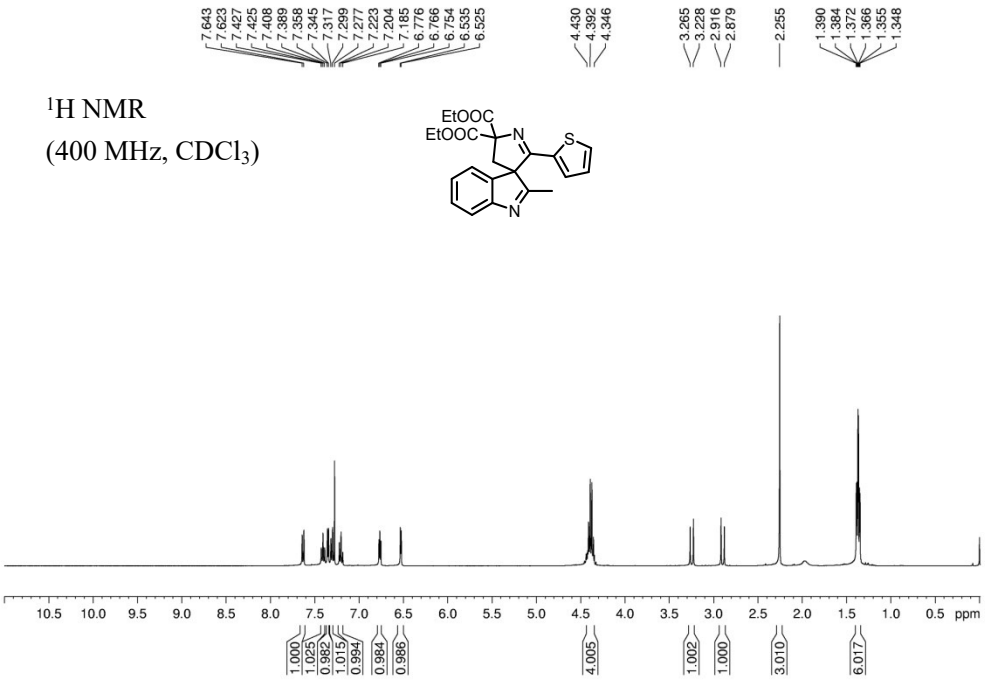


^{13}C NMR
(100 MHz, $CDCl_3$)

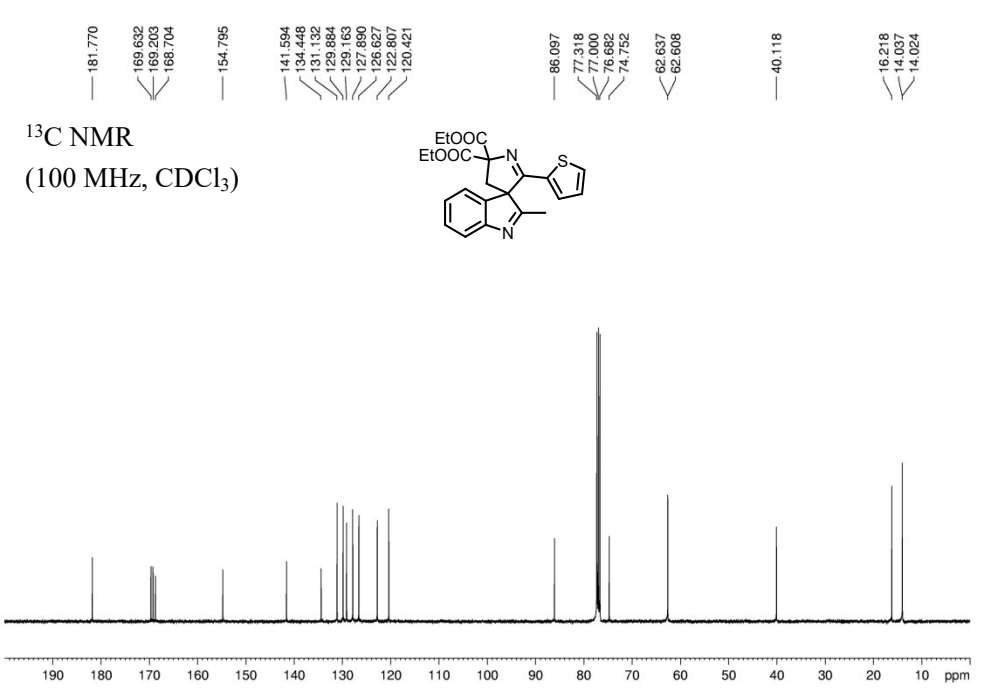




(3x)



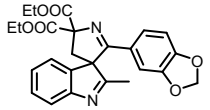
^{1}H NMR
(400 MHz, $CDCl_3$)

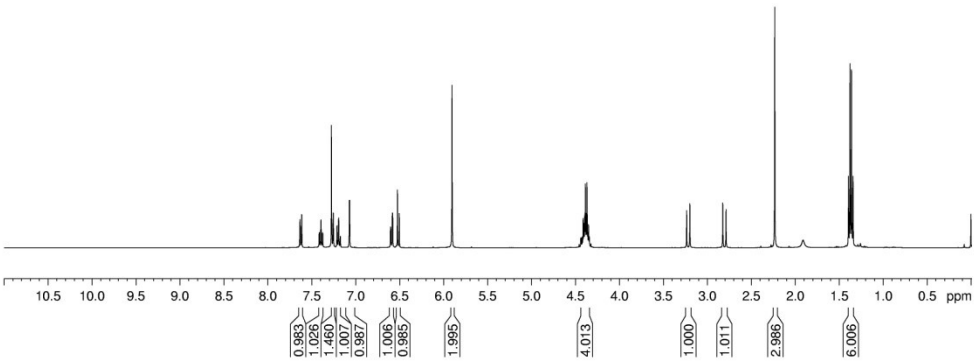


^{13}C NMR
(100 MHz, $CDCl_3$)

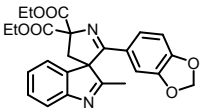
(3y)

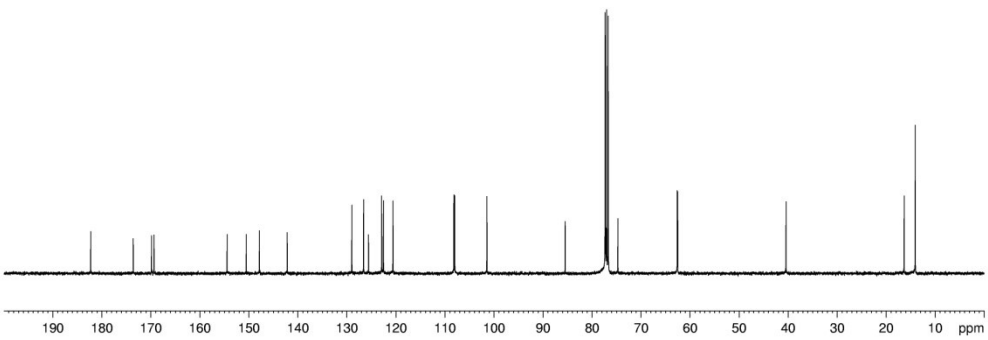
^{1}H NMR
(400 MHz, $CDCl_3$)





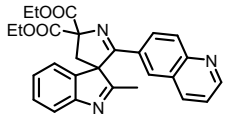
^{13}C NMR
(100 MHz, $CDCl_3$)

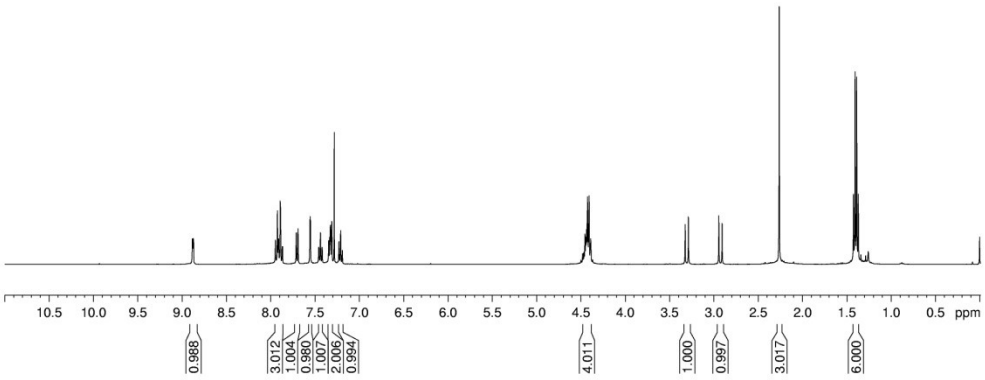




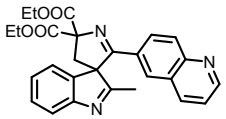
(3z)

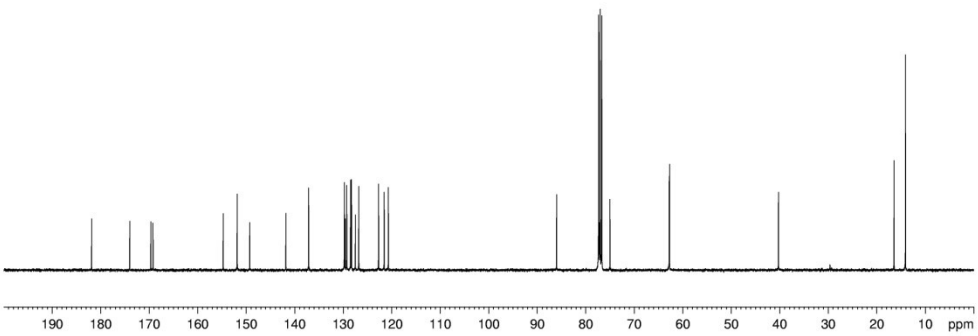
^{1}H NMR
(400 MHz, $CDCl_3$)



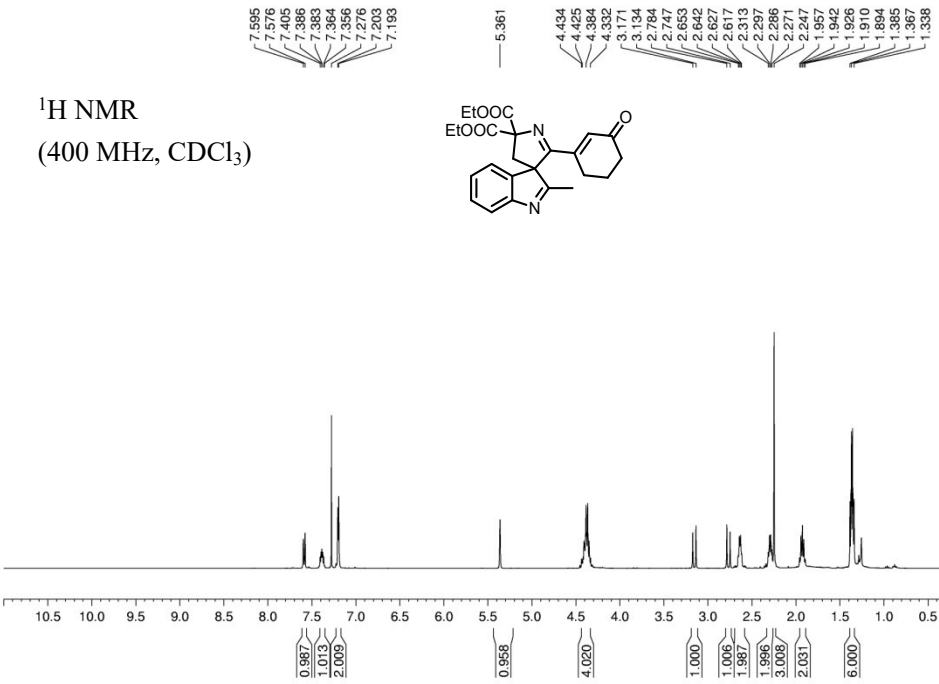


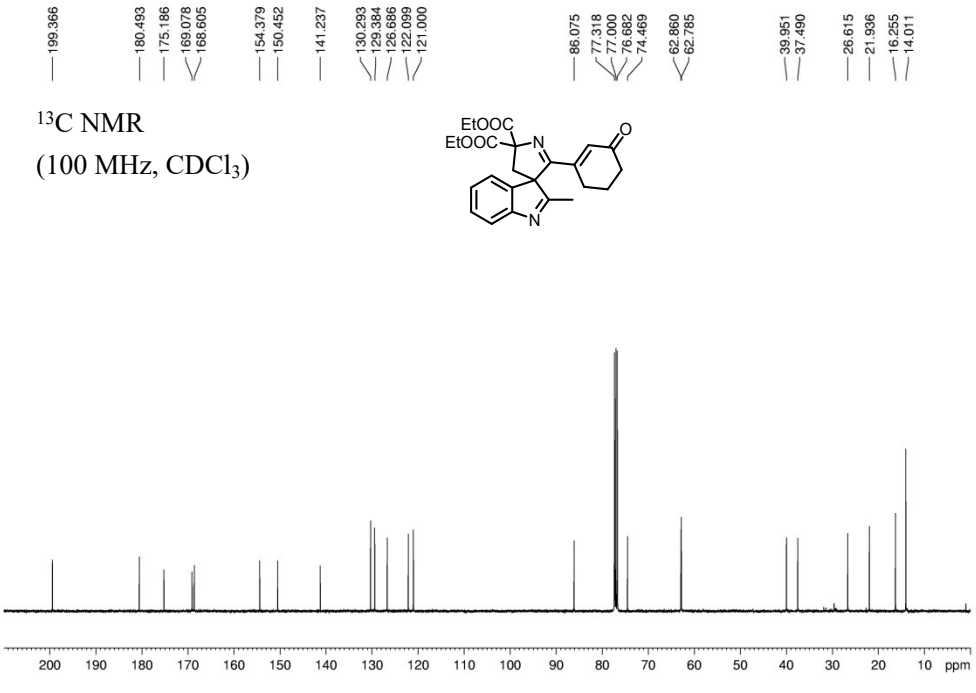
^{13}C NMR
(100 MHz, $CDCl_3$)



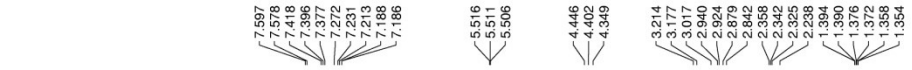


(3aa)

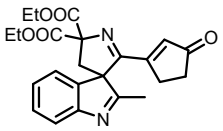

7.595
7.576
7.405
7.386
7.383
7.364
7.356
7.276
7.203
7.193
5.361
4.434
4.425
4.384
4.332
3.171
3.134
2.784
2.747
2.653
2.642
2.627
2.617
2.313
2.297
2.286
2.271
2.247
1.957
1.942
1.926
1.910
1.894
1.385
1.367
1.338
^{1}H NMR
(400 MHz, $CDCl_3$)
EtOOC
EtOOC
N
O
N
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.987
1.013
2.009
0.958
4.020
1.000
1.006
1.987
1.996
3.008
2.031
6.000

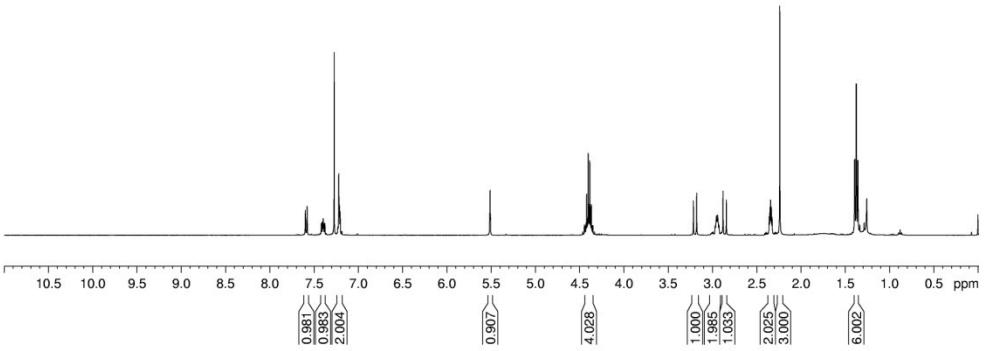

199.366
180.493
175.186
169.078
168.605
154.379
150.452
141.237
130.293
129.384
126.686
122.099
121.000
86.075
77.318
77.000
76.682
74.469
62.860
62.785
39.951
37.490
26.615
21.936
16.255
14.011
^{13}C NMR
(100 MHz, $CDCl_3$)
EtOOC
EtOOC
N
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

(3ab)

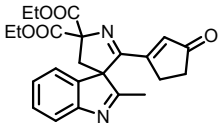


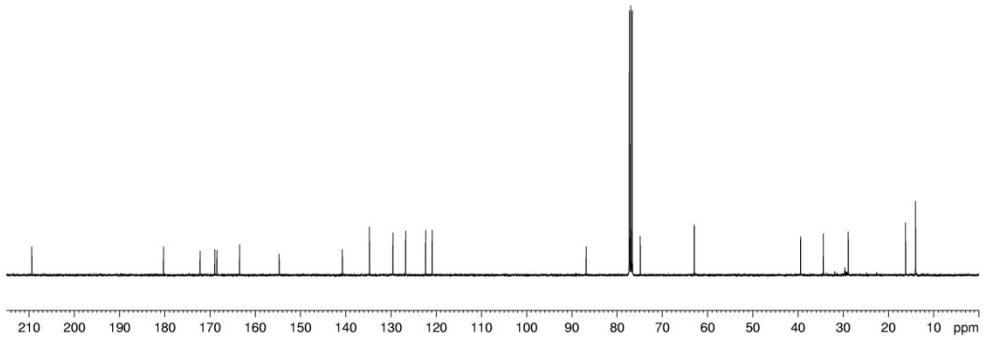
^{1}H NMR
(400 MHz, $CDCl_3$)





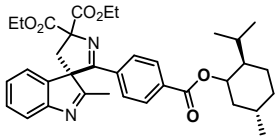
^{13}C NMR
(100 MHz, $CDCl_3$)

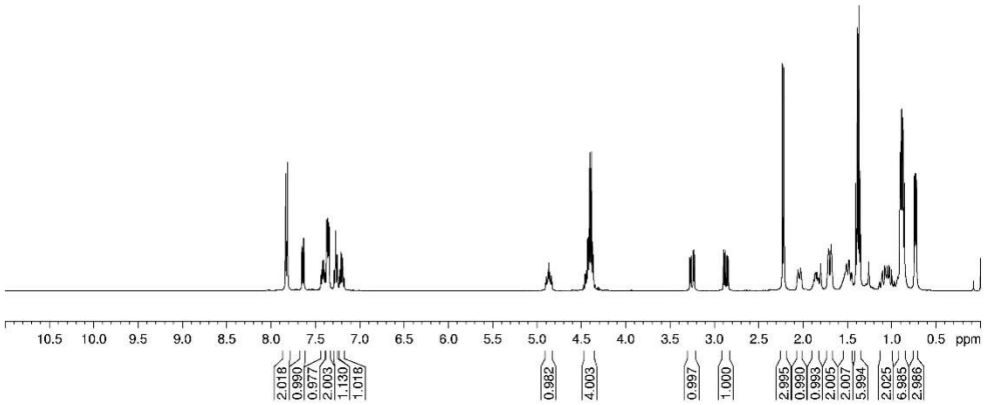




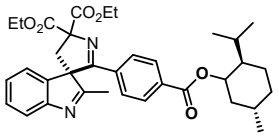
(3ac)

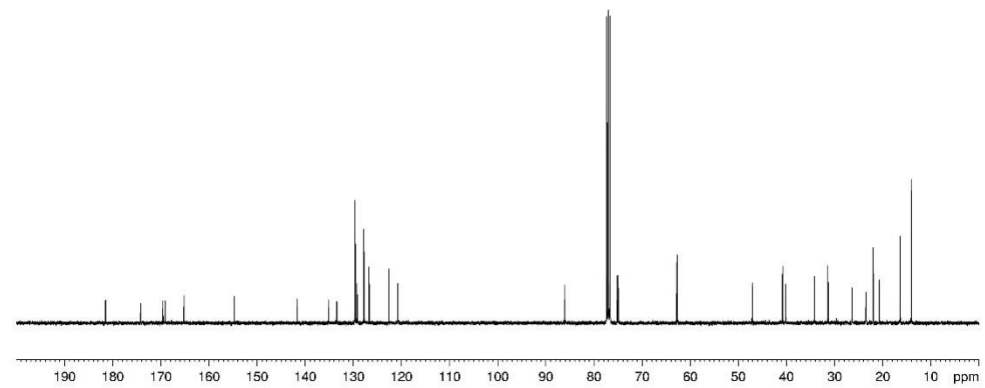
^{1}H NMR
(400 MHz, $CDCl_3$)





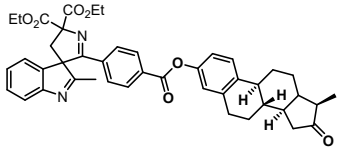
^{13}C NMR
(100 MHz, $CDCl_3$)

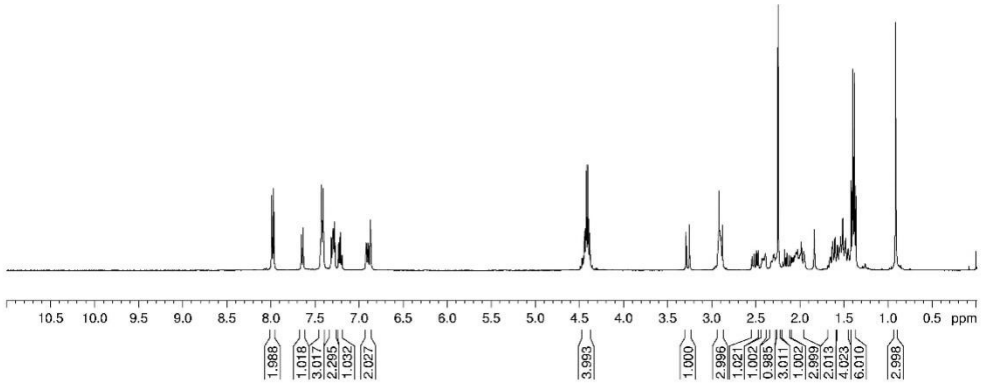




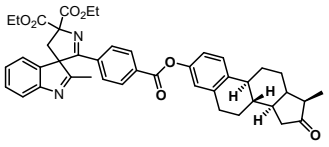
(3ad)

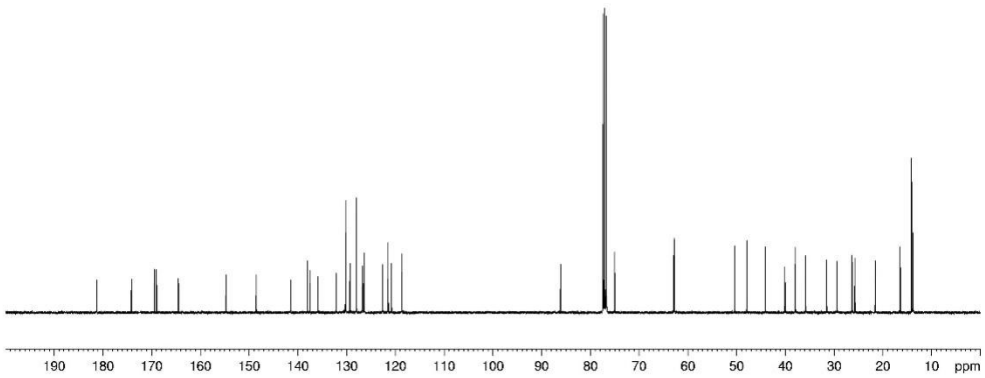
^{1}H NMR
(400 MHz, $CDCl_3$)





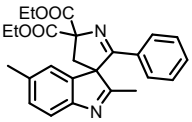
^{13}C NMR
(100 MHz, $CDCl_3$)



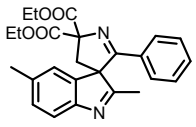


(3ae)

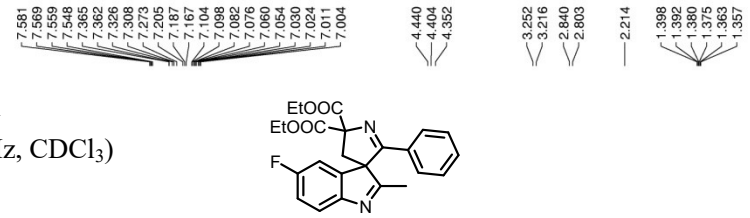
^{1}H NMR
(400 MHz, $CDCl_3$)



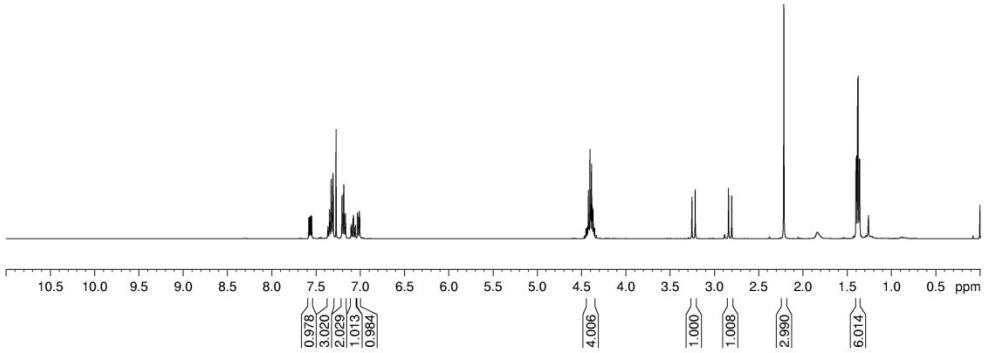
^{13}C NMR
(100 MHz, $CDCl_3$)



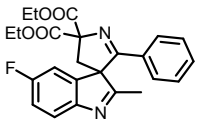
(3af)

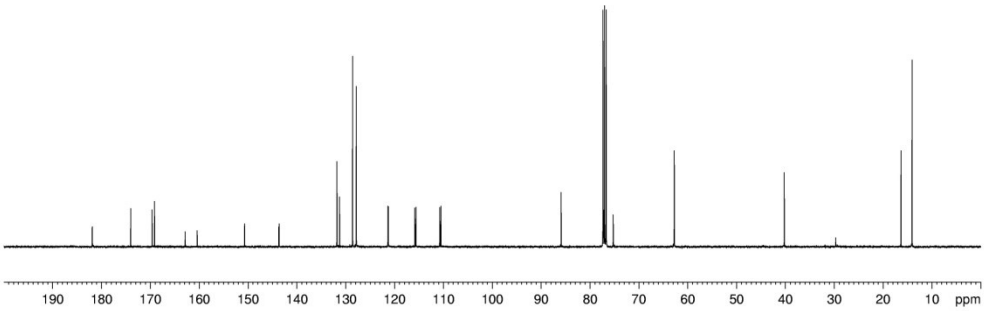


^{1}H NMR
(400 MHz, $CDCl_3$)

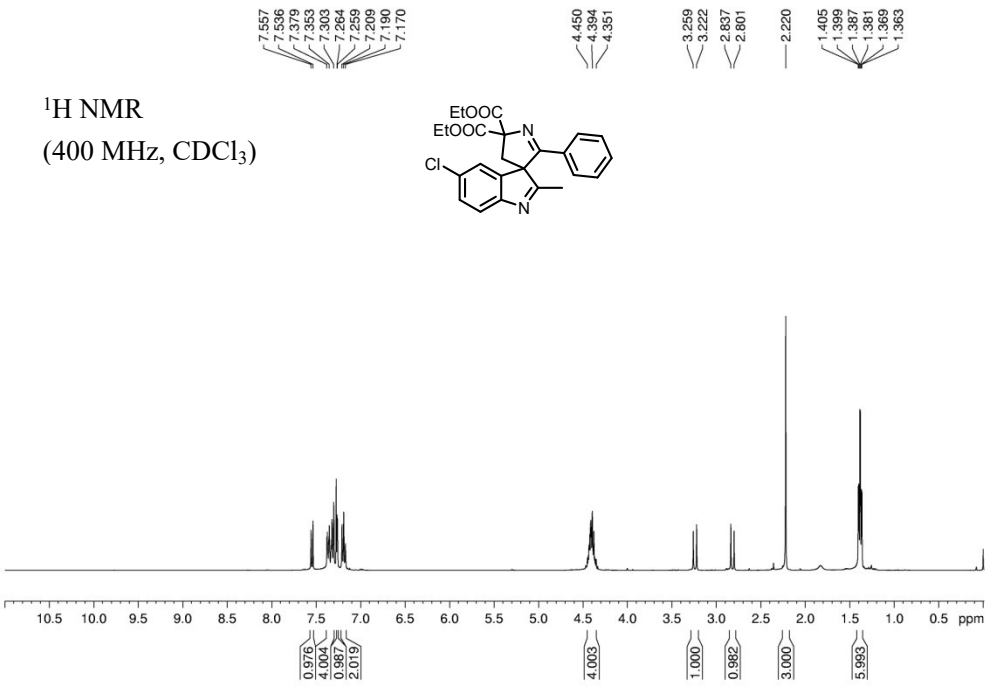


^{13}C NMR
(100 MHz, $CDCl_3$)

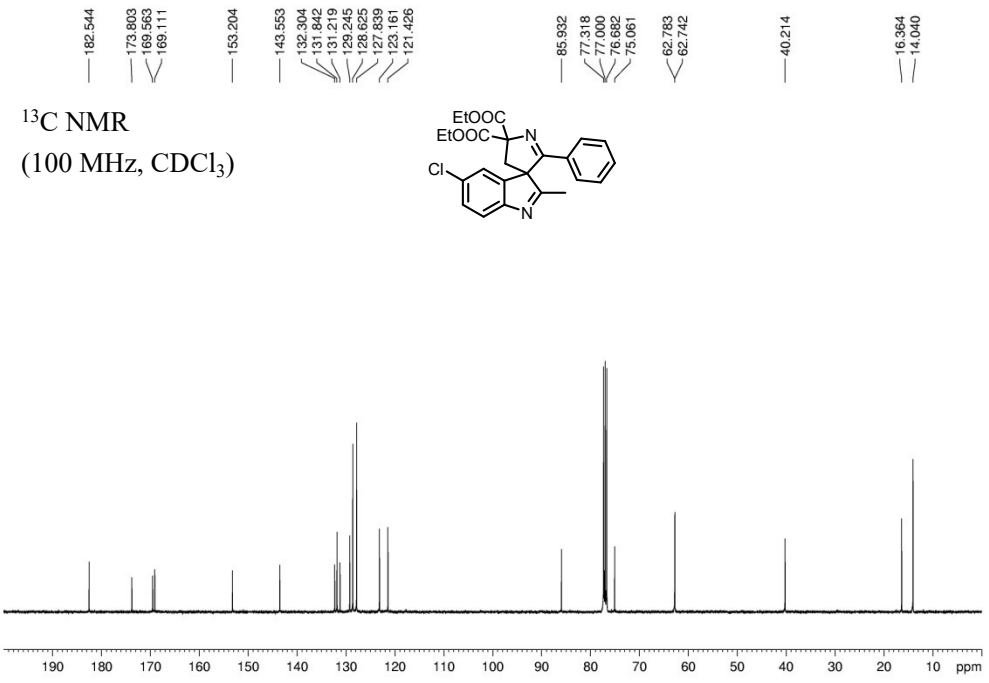




(3ag)



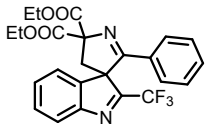
^{1}H NMR
(400 MHz, $CDCl_3$)

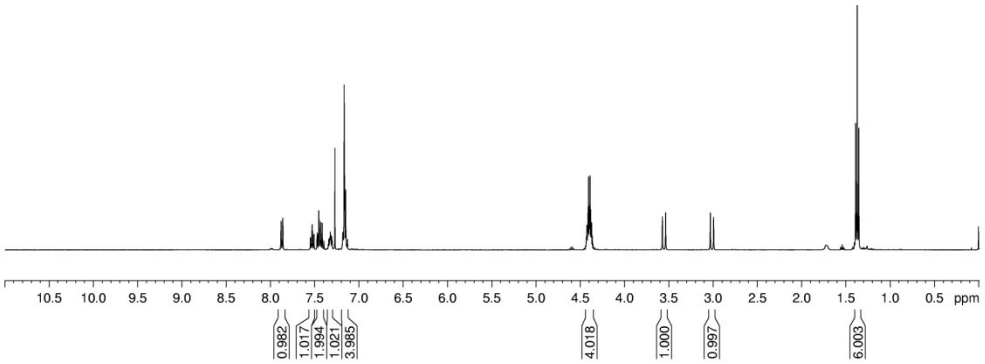


^{13}C NMR
(100 MHz, $CDCl_3$)

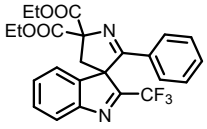
(3ah)

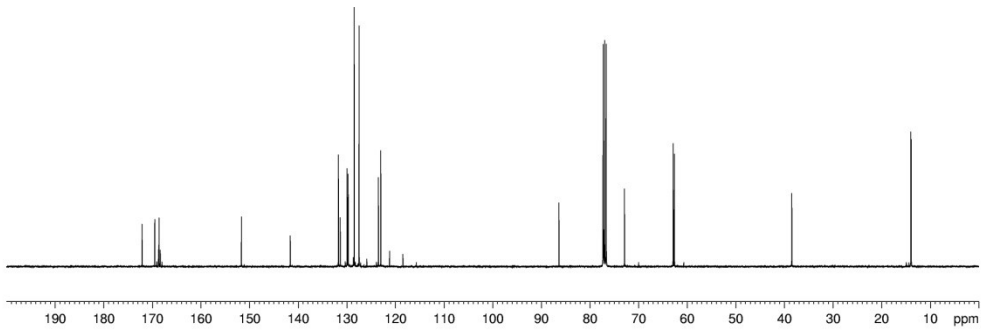
^{1}H NMR
(400 MHz, $CDCl_3$)





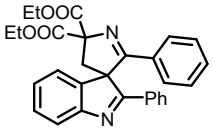
^{13}C NMR
(100 MHz, $CDCl_3$)

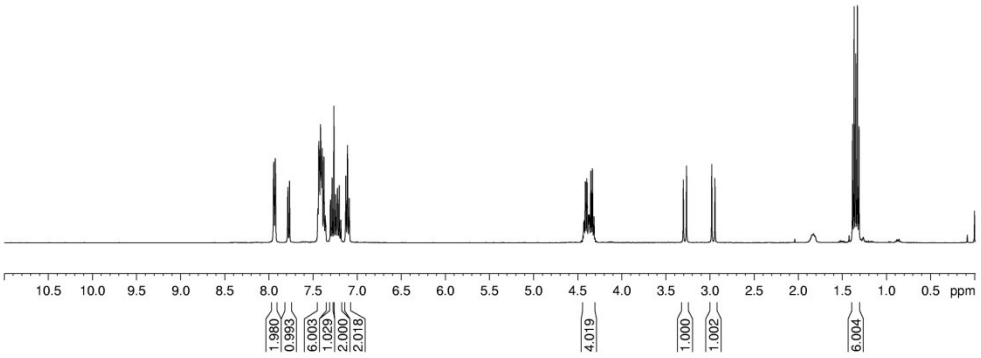




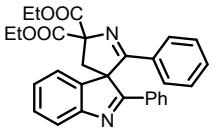
(3ai)

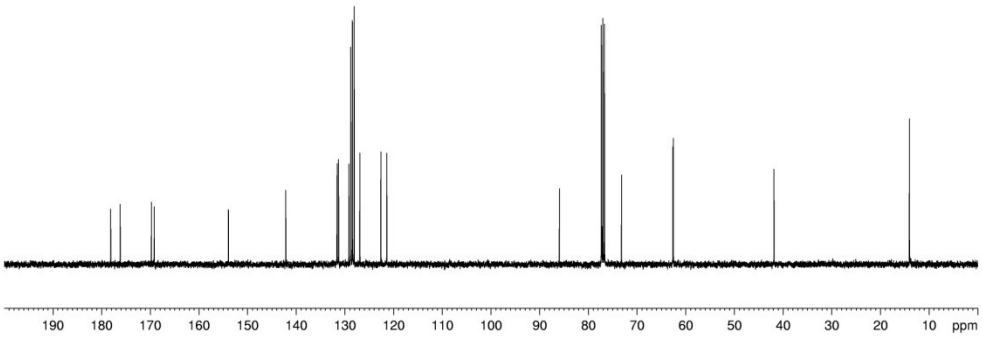
^{1}H NMR
(400 MHz, $CDCl_3$)





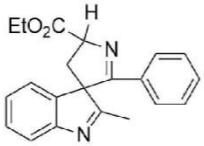
^{13}C NMR
(100 MHz, $CDCl_3$)

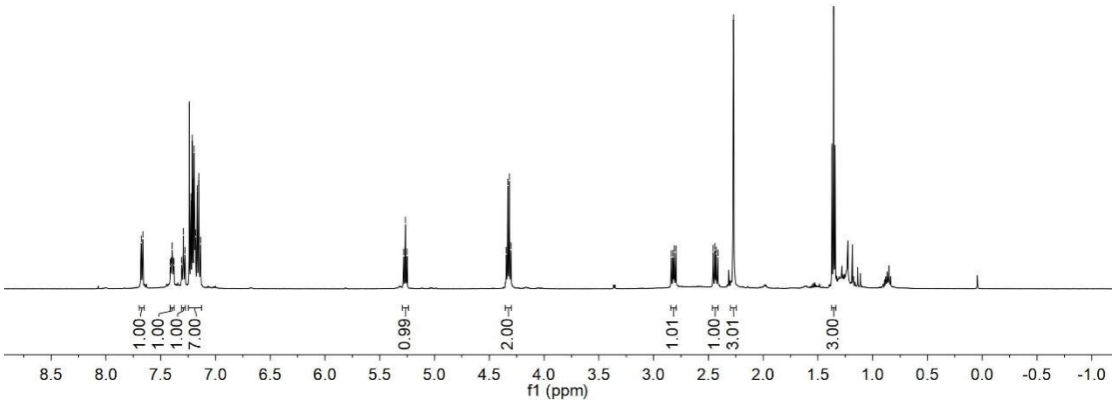




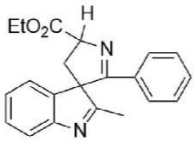
(3aj)

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



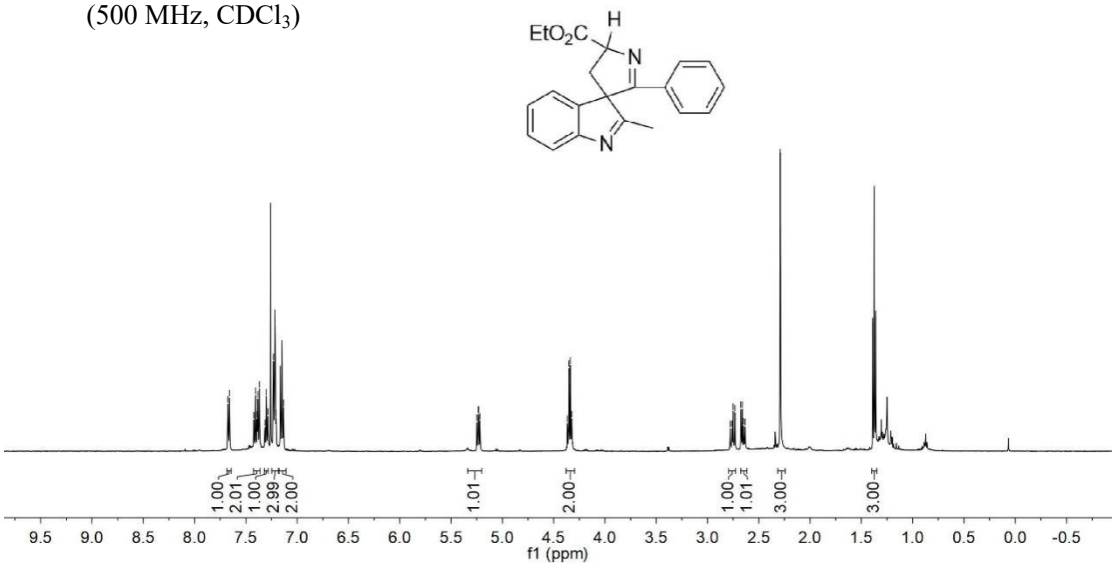


^{13}C NMR
(125 MHz, $CDCl_3$)

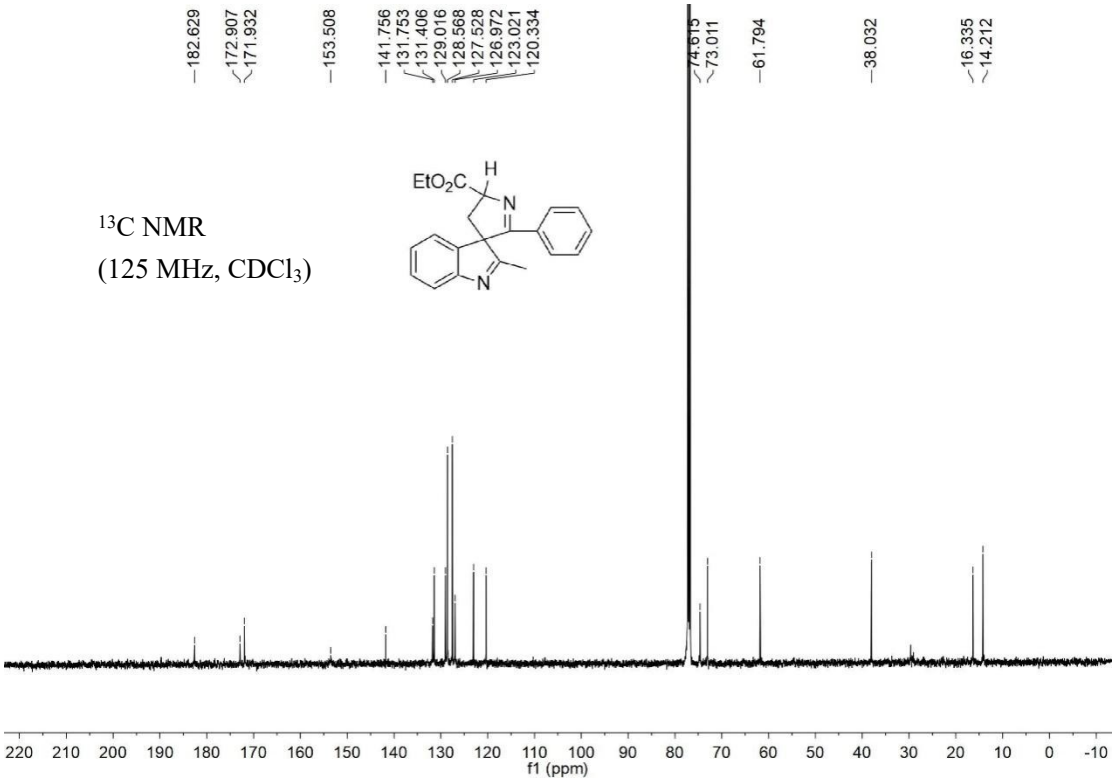


(3aj')

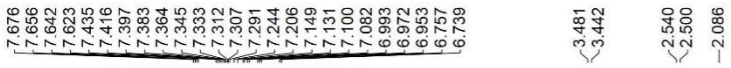
^{1}H NMR
(500 MHz, $CDCl_3$)



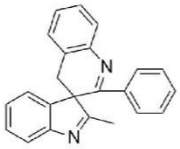
^{13}C NMR
(125 MHz, $CDCl_3$)

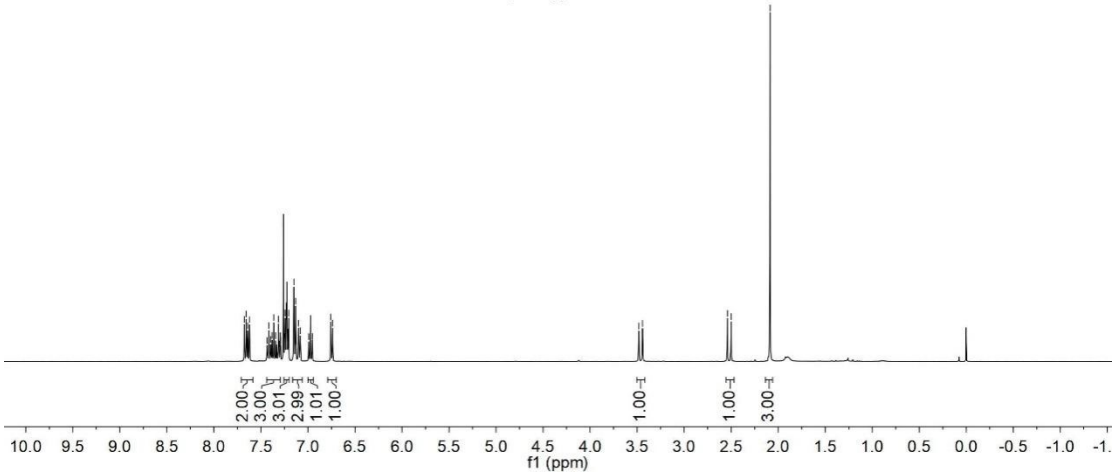


(3ak)

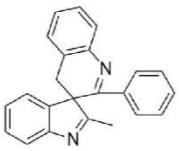


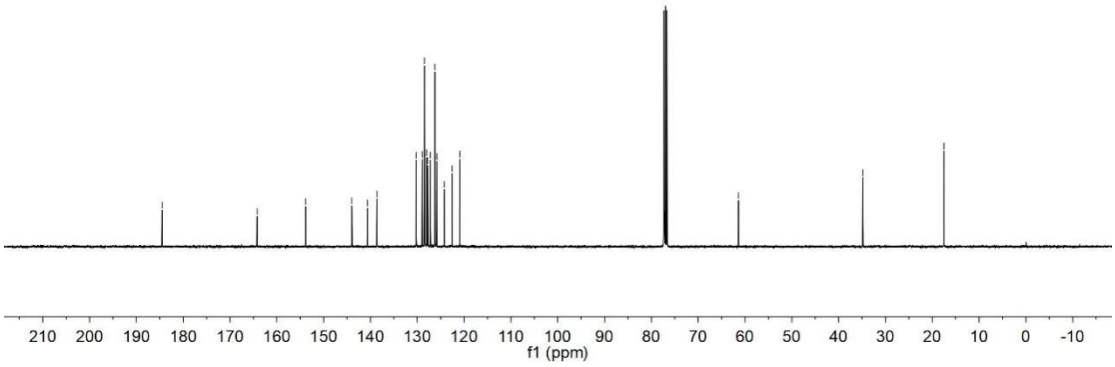
^{1}H NMR
(400 MHz, $CDCl_3$)



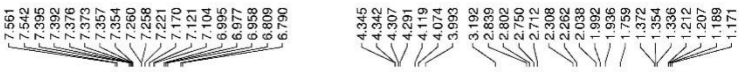


^{13}C NMR
(100 MHz, $CDCl_3$)

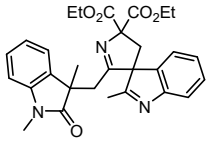


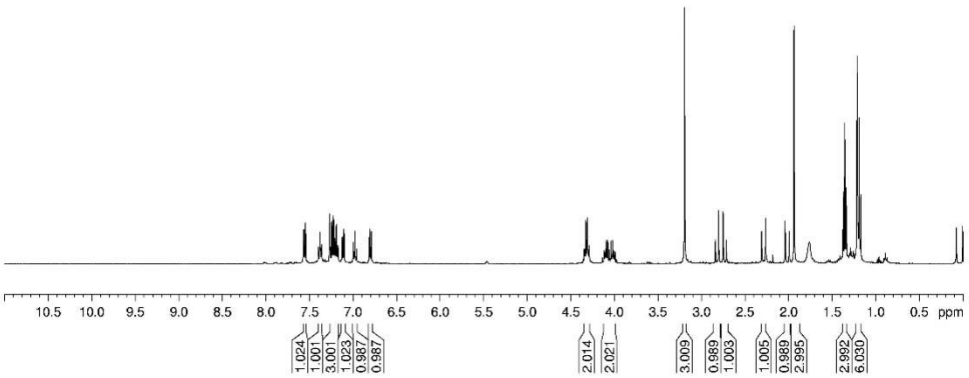


(5a)

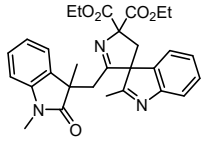


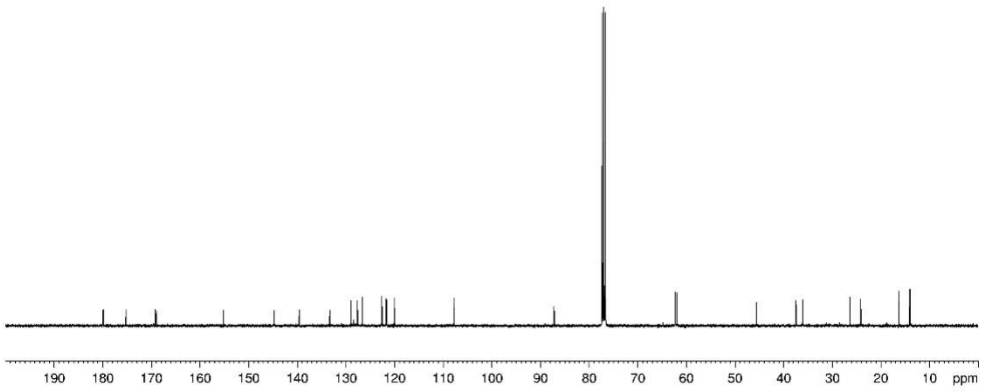
^{1}H NMR
(400 MHz, $CDCl_3$)





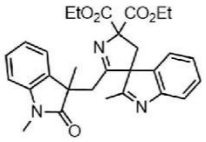
^{13}C NMR
(100 MHz, $CDCl_3$)

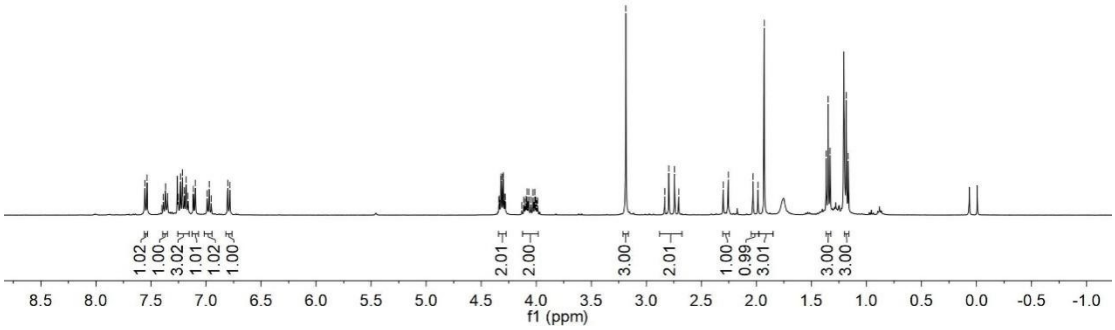




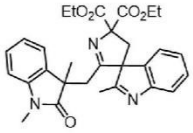
(5a')

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



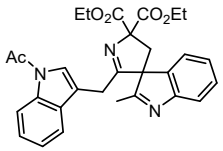


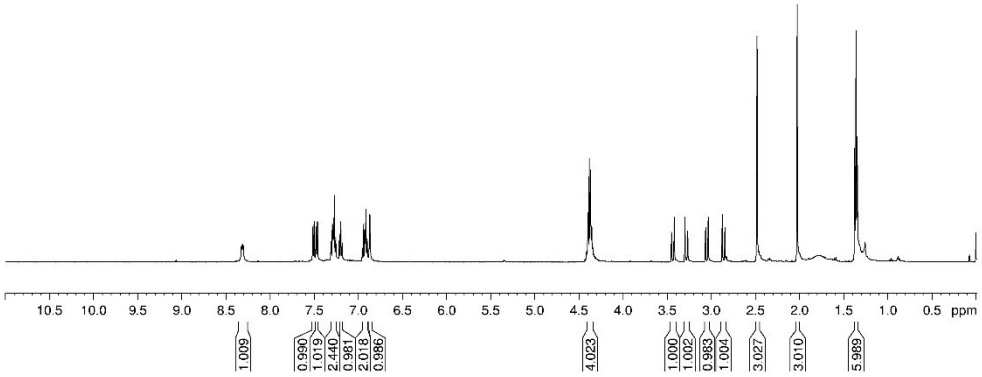
^{13}C NMR
(100 MHz, $CDCl_3$)

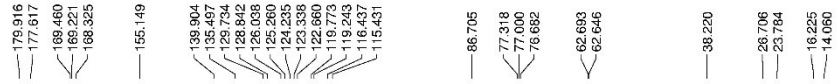


(5b)

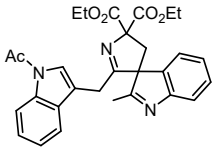
^{1}H NMR
(500 MHz, $CDCl_3$)

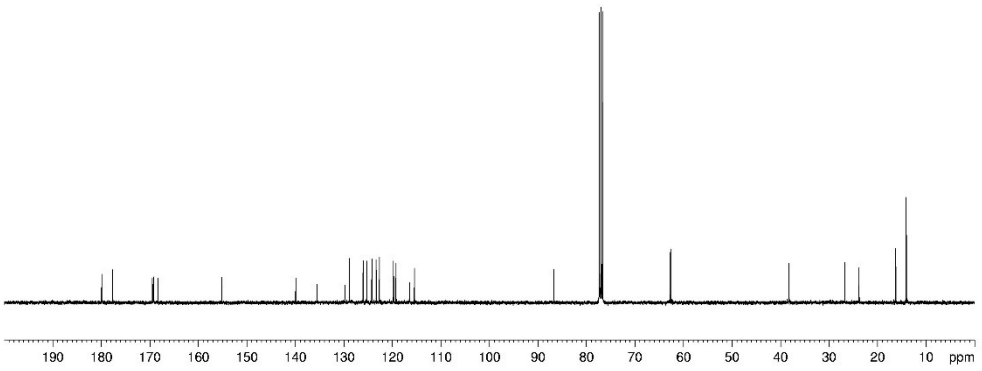




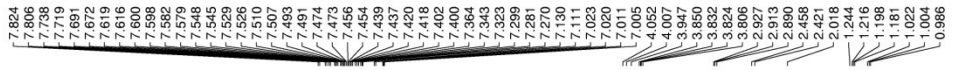


^{13}C NMR
(100 MHz, $CDCl_3$)

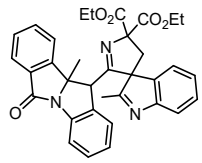


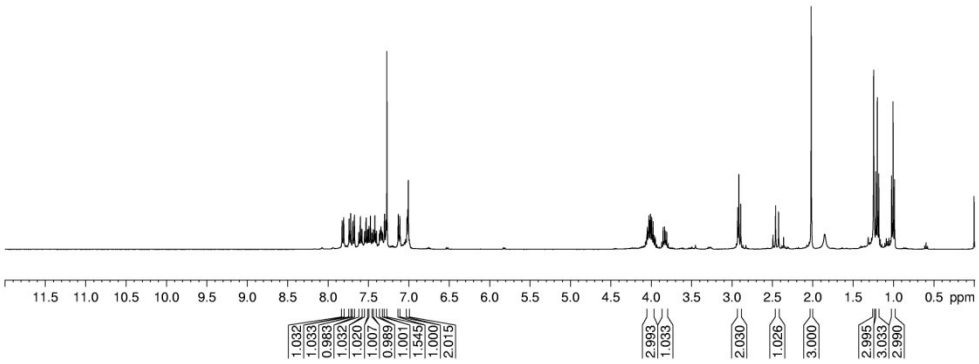


(5c)

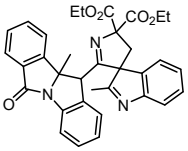


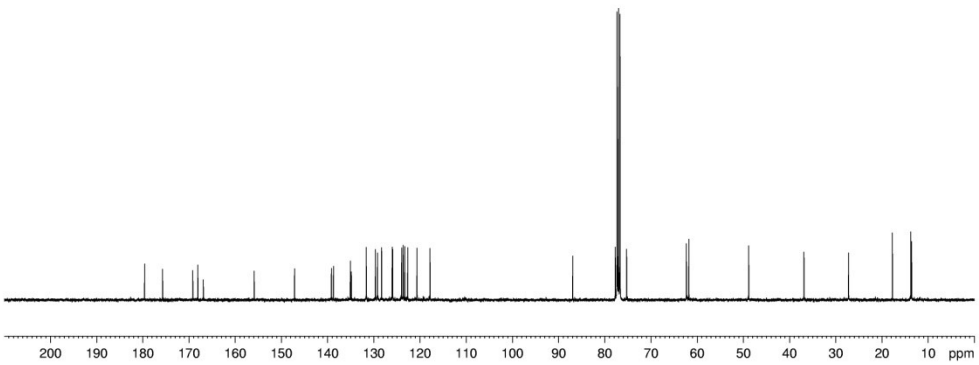
^{1}H NMR
(400 MHz, $CDCl_3$)



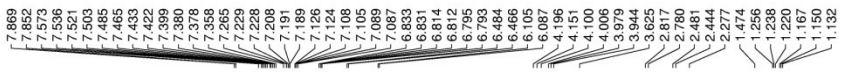


^{13}C NMR
(100 MHz, $CDCl_3$)

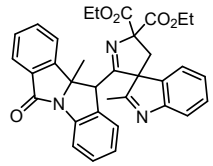


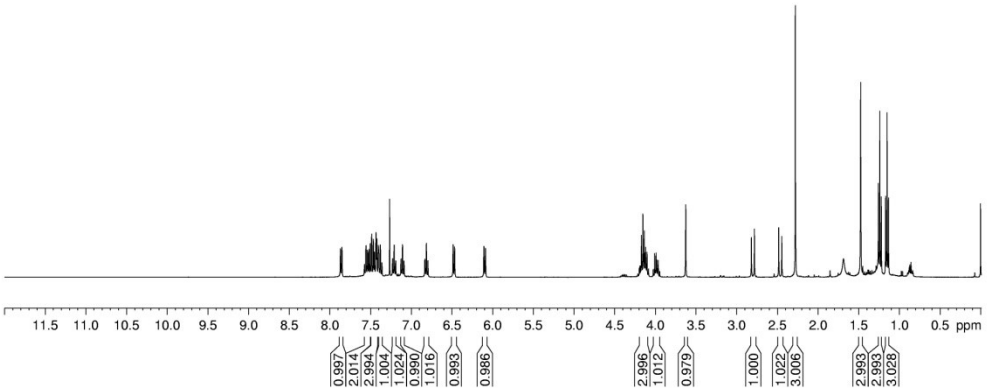


(5c')

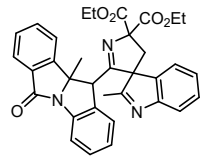


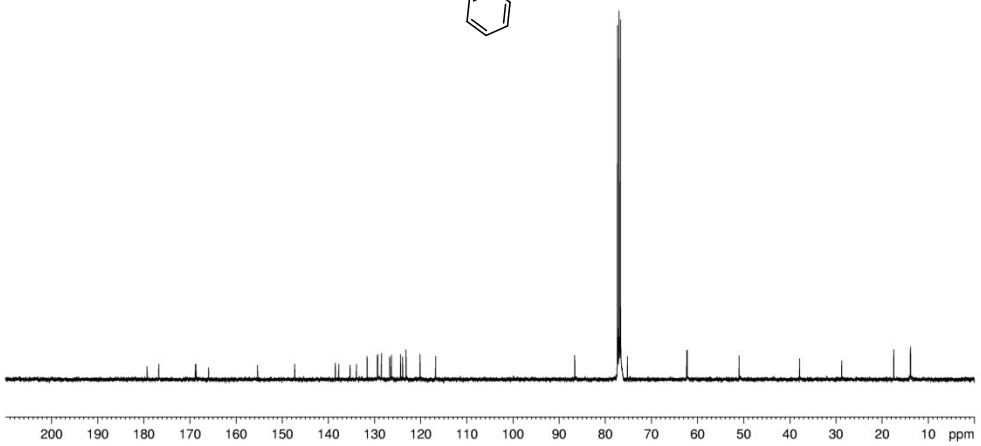
^{1}H NMR
(400 MHz, $CDCl_3$)



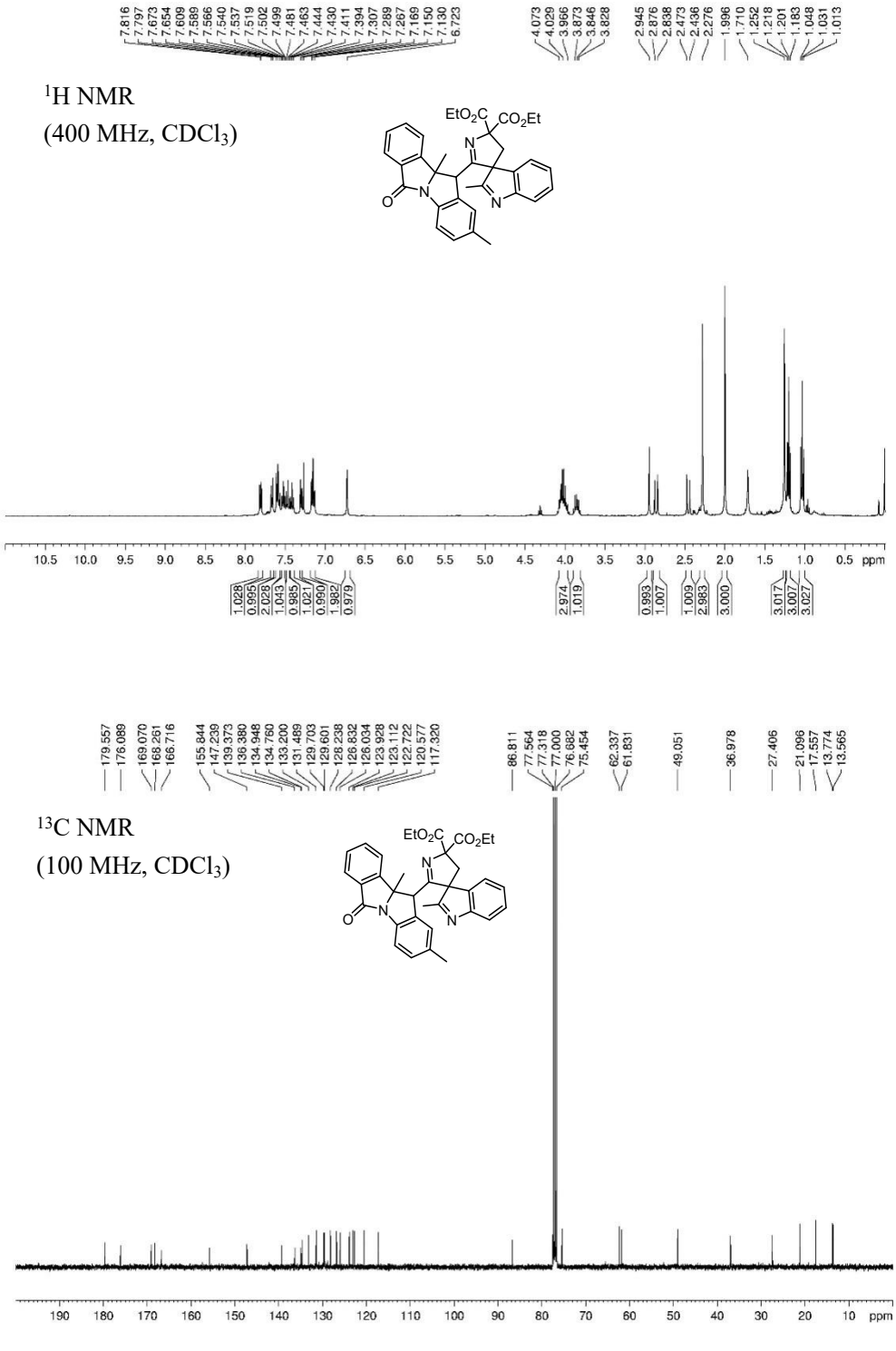


^{13}C NMR
(100 MHz, $CDCl_3$)





(5d)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7.673
7.654
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7.589
7.566
7.540
7.537
7.519
7.502
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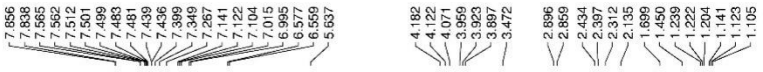
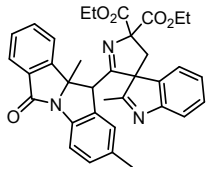
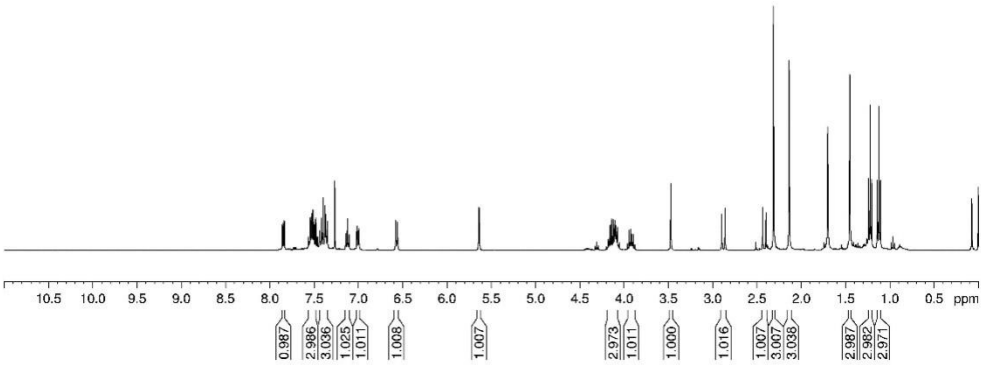
7.481
7.463
7.444
7.430
7.411
7.394
7.307
7.289
7.267
7.169
7.150
7.130
6.723
4.073
4.029
3.966
3.873
3.846
3.828
2.945
2.876
2.838
2.473
2.436
2.276
1.996
1.710
1.252
1.218
1.201
1.183
1.048
1.031
1.013
^{1}H NMR
(400 MHz, $CDCl_3$)
EtO_2C
CO_2Et
N
O
N
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.028
0.995
2.028
1.043
0.985
1.021
0.990
1.982
0.979
2.974
1.019
0.993
1.007
1.009
2.983
3.000
3.017
3.007
3.027
179.557
176.089
169.070
168.261
166.716
155.844
147.239
139.373
136.380
134.948
134.760
133.200
131.489
129.703
129.601
128.238
126.832
126.034
123.928
123.112
122.722
120.577
117.320
86.811
77.564
77.318
77.000
76.682
75.454
62.337
61.831
49.051
36.978
27.406
21.096
17.557
13.774
13.565
^{13}C NMR
(100 MHz, $CDCl_3$)
EtO_2C
CO_2Et
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

(5d')

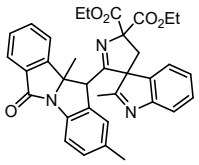


^{1}H NMR
(400 MHz, $CDCl_3$)

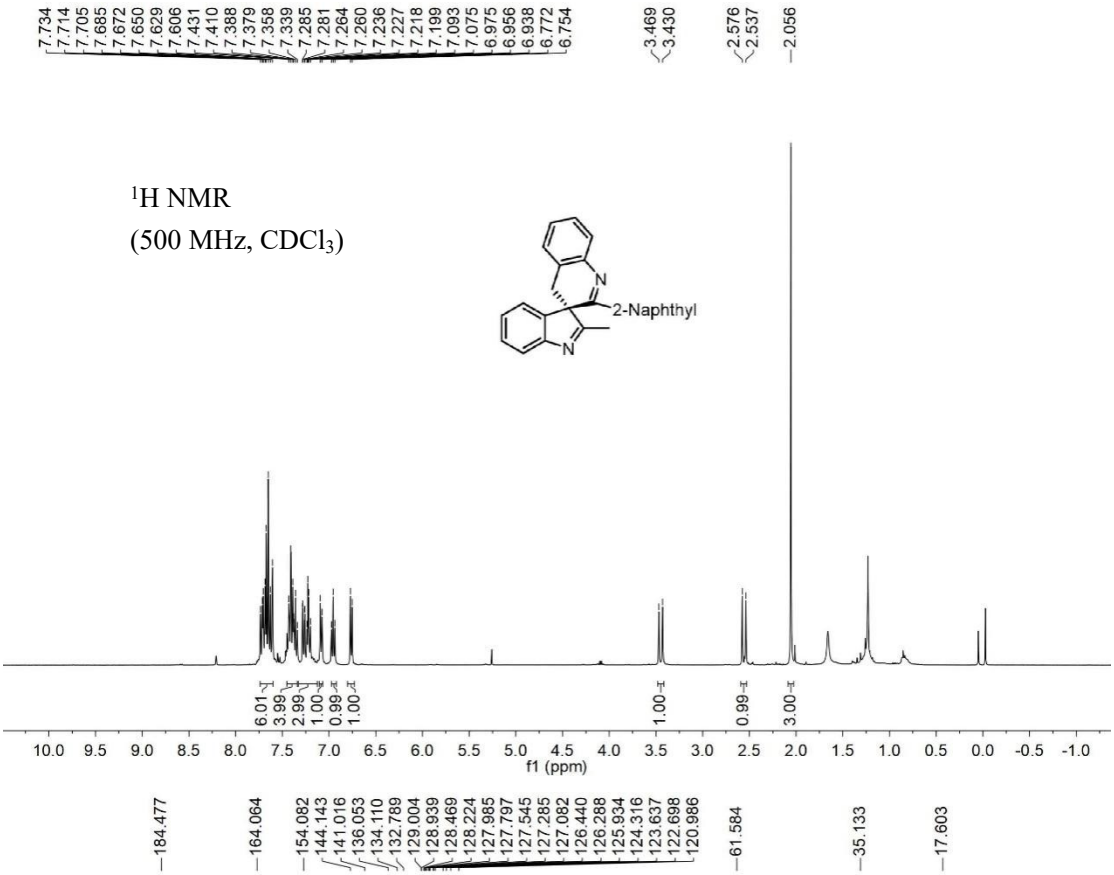


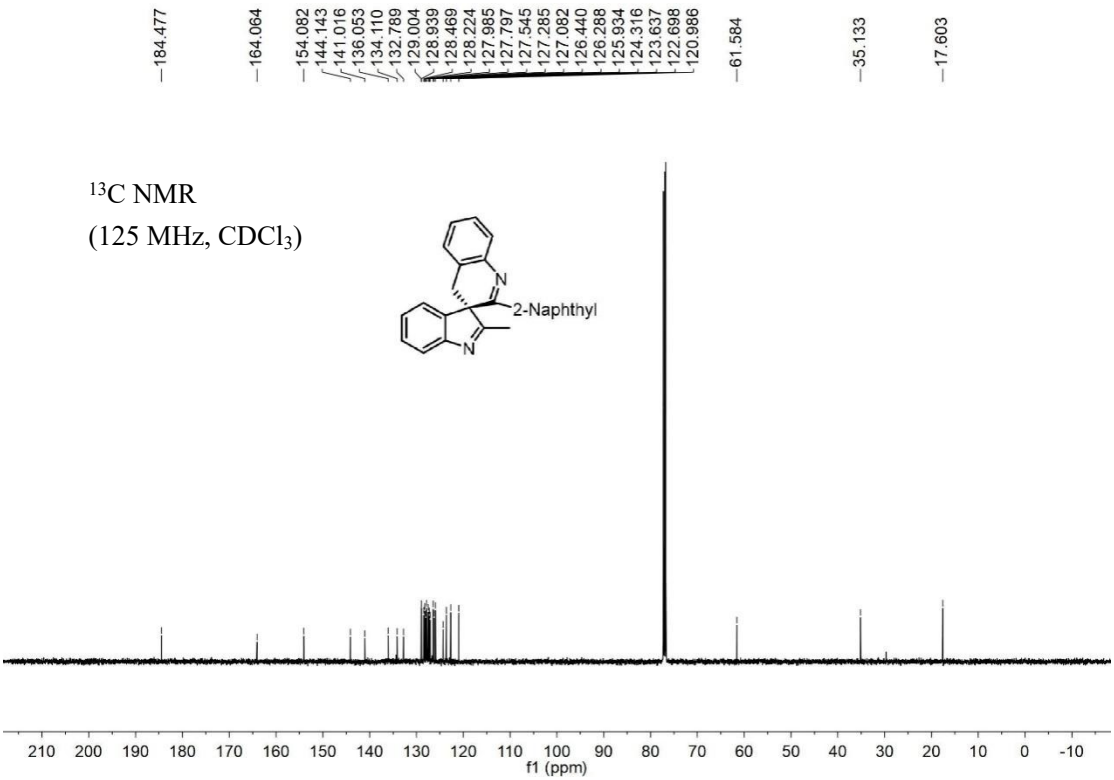


^{13}C NMR
(100 MHz, $CDCl_3$)

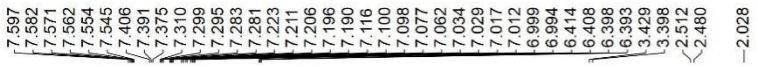


(6a)

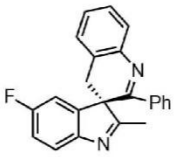

7.734
7.714
7.705
7.685
7.672
7.650
7.629
7.606
7.431
7.410
7.388
7.379
7.358
7.339
7.285
7.281
7.264
7.260
7.236
7.227
7.218
7.199
7.093
7.075
6.975
6.956
6.938
6.772
6.754
3.469
3.430
2.576
2.537
2.056
^{1}H NMR
(500 MHz, $CDCl_3$)
2-Naphthyl
6.01
3.99
2.99
1.00
0.99
1.00
1.00
0.99
3.00
f1 (ppm)

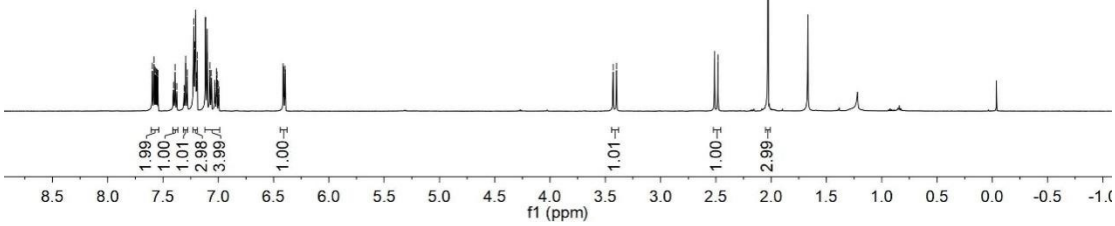

184.477
164.064
154.082
144.143
141.016
136.053
134.110
132.789
129.004
128.939
128.469
128.224
127.985
127.797
127.545
127.285
127.082
126.440
126.288
125.934
124.316
123.637
122.698
120.986
61.584
35.133
17.603
^{13}C NMR
(125 MHz, $CDCl_3$)
2-Naphthyl
f1 (ppm)

(6b)

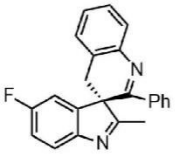


^{1}H NMR
(500 MHz, $CDCl_3$)

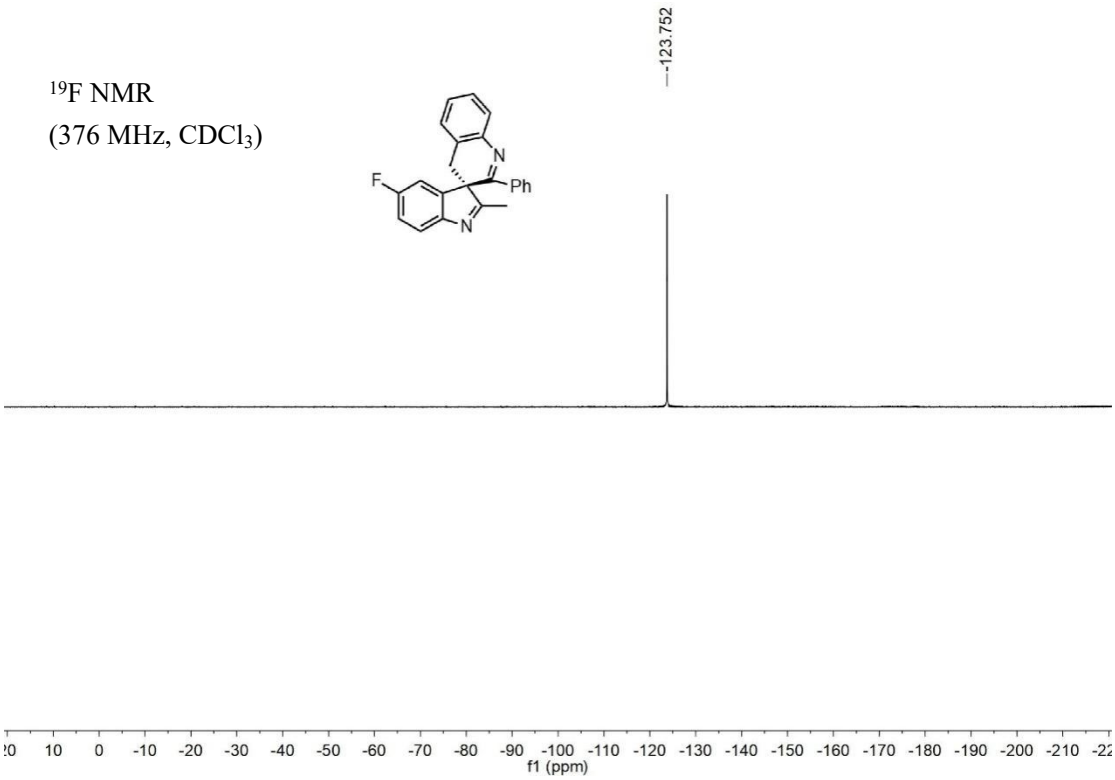




^{13}C NMR
(125 MHz, $CDCl_3$)

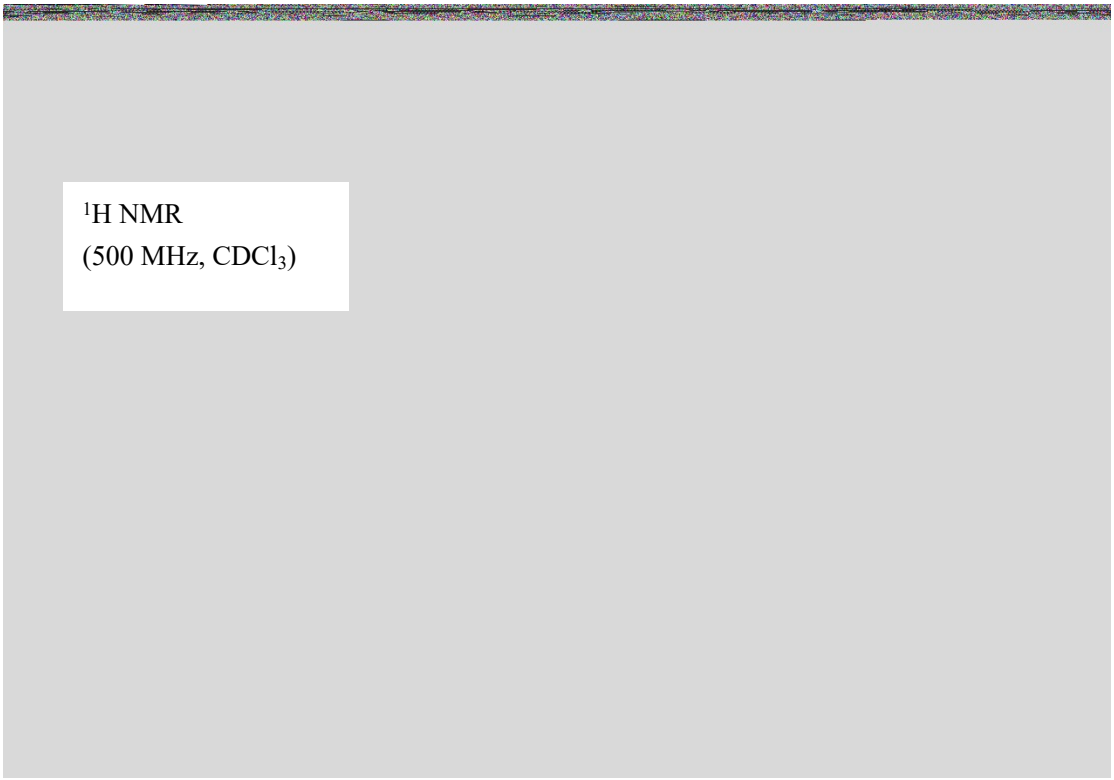


^{19}F NMR
(376 MHz, $CDCl_3$)

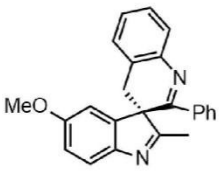


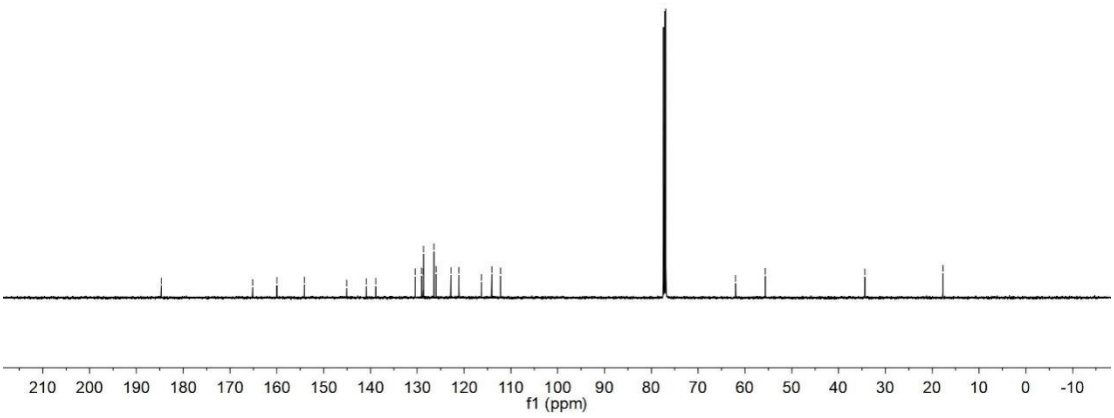
(6c)

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



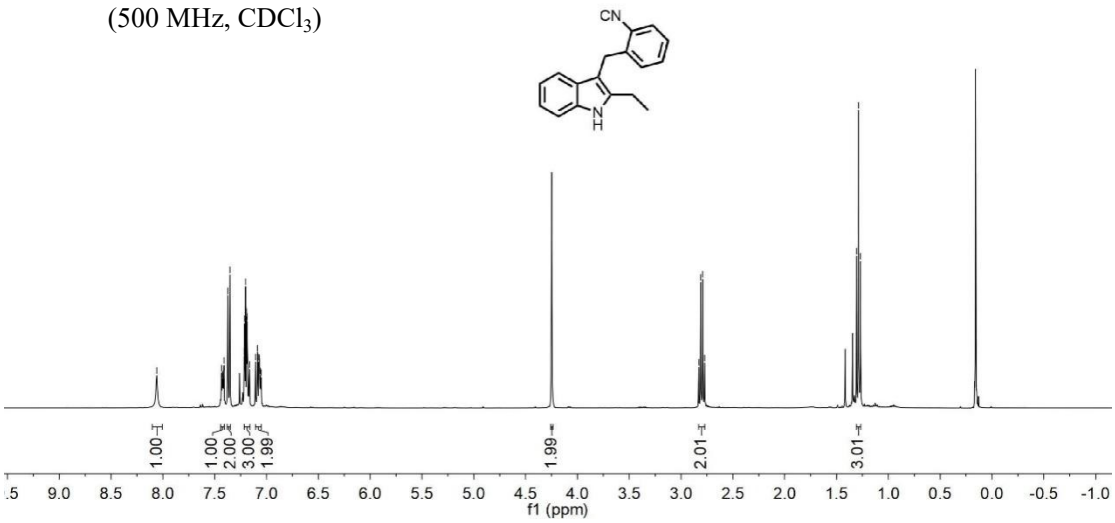
^{13}C NMR
(125 MHz, $CDCl_3$)





(6d)

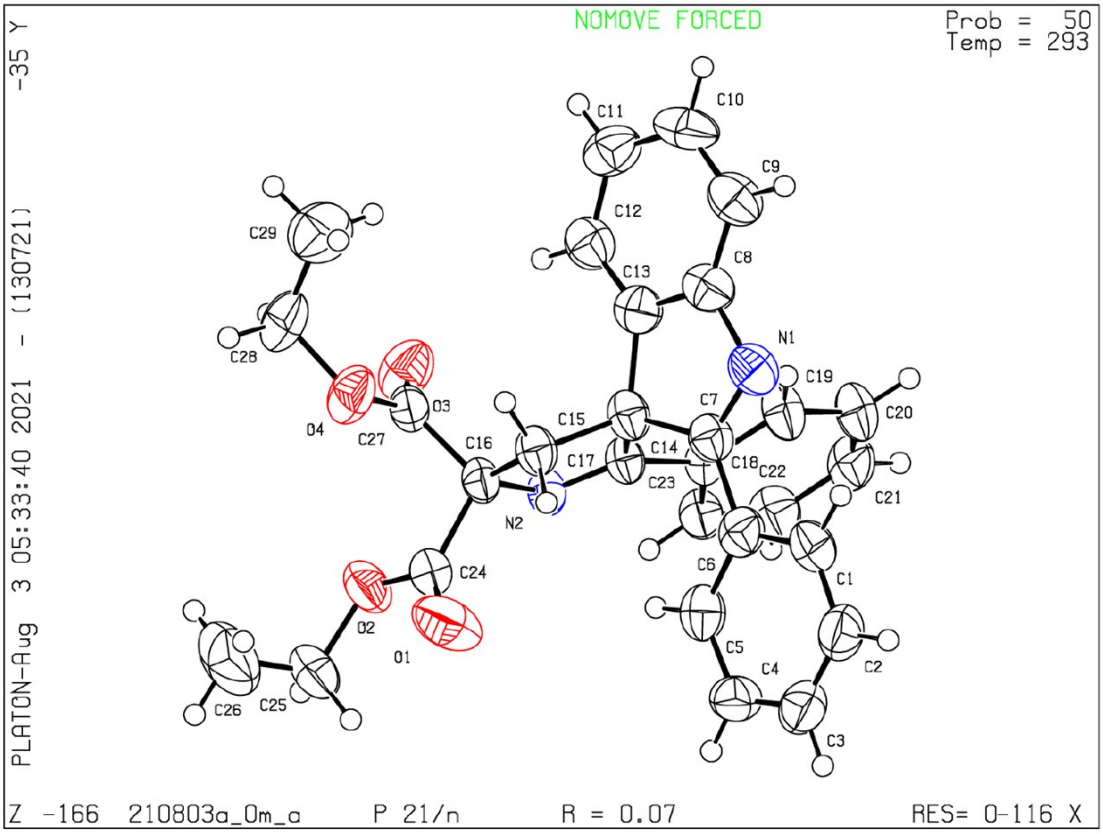
^{1}H NMR
(500 MHz, $CDCl_3$)



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

7. X-ray Crystallographic Data

X-ray Crystallographic Data of *(rac)*-3ai (CCDC: 2103272)



X-ray Crystallographic Data of *(R)*-3q (CCDC: 2103303)