Supporting Information

Accessing 1,3-Dienes via Palladium-Catalyzed Allylic Alkylation of Pronucleophiles with Skipped Enynes

Shang Gao,[+] Hao Liu,[+] Chi Yang, Zhiyuan Fu, Hequan Yao* and Aijun Lin*

State Key Laboratory of Natural Medicines (SKLNM) and Department of Medicinal Chemistry, School of Pharmacy, China Pharmaceutical University, Nanjing, 210009, P. R. China

Fax: (+86)-25-8327-1042; e-mail: ajlin@cpu.edu.cn; hyao@cpu.edu.cn; cpuhyao@126.com

([+]These authors contributed equally to this work)

Contents

1. General Information

Reagents and Solvents: $Pd(PPh_3)_4$ and $PhCO_2H$ were commercially available. PE refers to petroleum ether b. p. 60-90 °C and EA refers to ethyl acetate. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

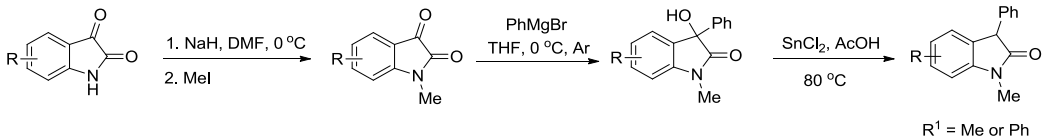
Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

Data collection: ^1H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) or BRUKER AV-500 (500 MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^1H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.16 ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Infrared (IR) spectra were recorded using a thin film supported on KBr disks. Melting point (m. p.) was measured on a microscopic melting point apparatus.

2. Preparation of the Substrates

2.1 Preparation of Pronucleophiles

Substituted oxindoles were prepared according to the reported literature[1] as the following procedures:



Substituted isatins (20.0 mmol) were dissolved in anhydrous DMF (30 mL), and the resultant solution was cooled to 0 °C, whereupon sodium hydride (60% dispersion in oil, 0.95 g, 24.0 mmol) was added in one portion and stirred for 5 min. Iodomethane (1.87 mL, 30.0 mmol) was added and the reaction was stirred at 0 °C for 30 min. The reaction mixture was then poured into saturated aqueous NH_4Cl and extracted with EA (4 x 30 mL). The combined organic layers were washed with water and brine, then dried

1. Trost, B. M.; Xie, J.; Sieber, J. D. *J. Am. Chem. Soc.* **2011**, *133*, 20611.

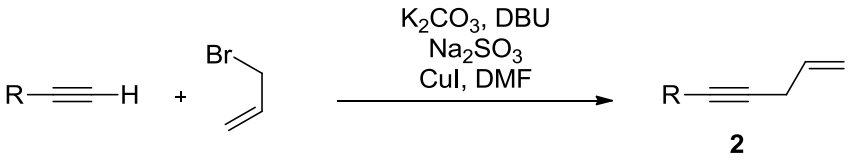
over Na_2SO_4, filtered, and concentrated to give the crude substituted *N*-methyl isatins, which was used without further purification, R_f = 0.50 (PE : EA = 1 : 1).

The crude substituted *N*-methyl isatins (20.0 mmol) were dissolved in anhydrous THF (30 mL) and cooled to 0 °C followed by dropwise addition of a 2.0 M solution of PhMgBr in THF (12.0 mL, 24.0 mmol). Then, the ice-bath was removed, and the reaction was stirred under argon atmosphere for 30 min at which point TLC analysis indicated consumption of the starting material. The reaction mixture was poured into saturated aqueous NH_4Cl (20 mL), and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated to give the crude alcohol, R_f = 0.45 (PE : EA = 1 : 1).

The crude alcohol (5.0 mmol) was dissolved in 30 mL of glacial acetic acid and $SnCl_2$•2 H_2O (10.0 mmol) was added. The reaction mixture was stirred at 80 °C for 2 h at which point TLC analysis indicated consumption of the starting material. Next, the solution was cooled to room temperature, concentrated *in vacuo*, and then diluted with EA (100 mL). The solution was washed with water (3 x 20 mL) and brine (30 mL). The organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography with EA/PE to afford the oxindoles as solid.

2.2 Preparation of Skipped Enynes

Skipped enynes **2** were prepared according to the reported literature:[2]

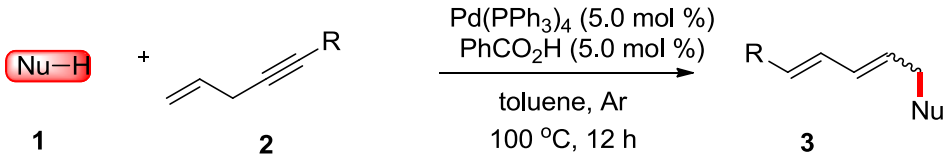


2

A mixture of allyl bromide (2.6 mL, 30 mmol, 1.5 equiv), substituted terminal alkynes (20 mmol, 1.0 equiv), Na_2SO_3 (1.26 g, 10 mmol, 0.5 equiv), CuI (76 mg, 0.4 mmol, 0.02 equiv) and K_2CO_3 (2.78 g, 1.0 equiv) in DMF (10 mL) and DBU (8 drops) were stirred at room temperature for 5-24 h until the terminal alkynes were consumed completely. The reaction was quenched with aqueous solution of 1 M HCl and the mixture was extracted with Et_2O three times. The combined organic layer was washed with 1 M HCl, brine and dried over Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure at room temperature. The crude mixture was purified by flash column chromatography on silica gel with PE as eluent to afford **2**. (Note: DMF was used here as solvent to prepared **2** instead of DMSO).

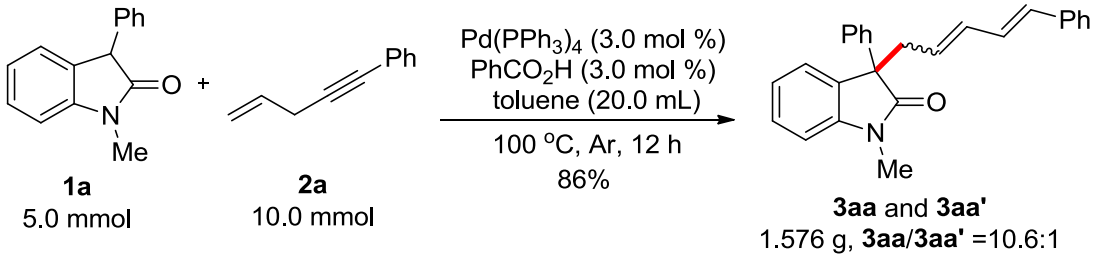
2. Bieber, L. W.; da Silva, M. F. *Tetrahedron Lett.* **2007**, *48*, 7088.

3. General Procedure of Allylic Alkylation of Pronucleophiles with Skipped Enynes



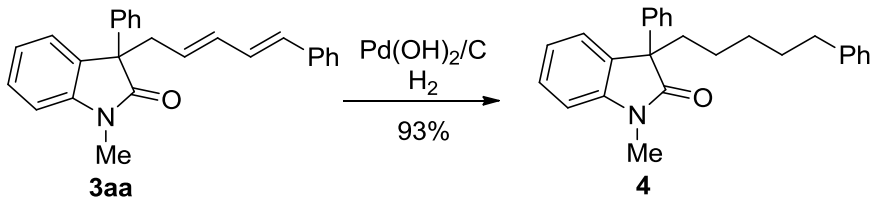
A 10 mL sealed tube was charged with pronucleophiles **1** (0.25 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.025 mmol, 5.0 mol %), benzoic acid (0.025 mmol, 5.0 mol %), skipped enynes **2** (0.50 mmol, 2.0 equiv), toluene (1.0 mL) and a stir bar. The sealed tube was then filled with argon and sealed upon completion of this manipulation. The reaction mixture was vigorously stirred at 100 °C for 12 h under argon. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and filtered through a plug of Celite. The reaction solution was then concentrated *in vacuo* and purified with flash column chromatography (PE/EA = 20:1) to afford a mixture of stereoisomers of compound **3** and the *E*/*Z* ratio was determined by ^{1}H NMR. The mixture of stereoisomers was separated by a second flash column (eluted with PE/EA = 20:1) to afford the major stereoisomer.

Procedures for gram-scale synthesis of **3aa**:

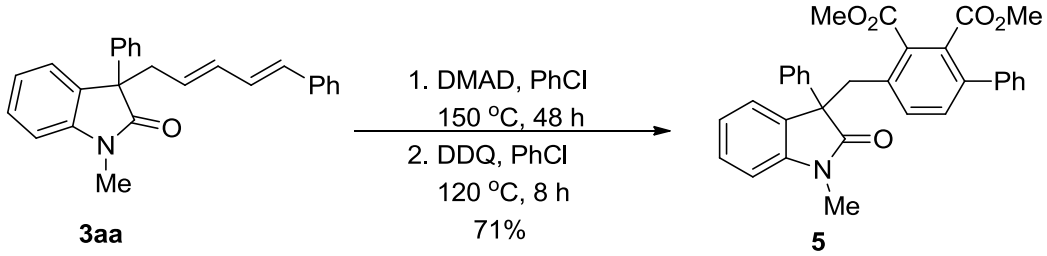


A 100 mL sealed tube was charged with **1a** (5.0 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.150 mmol, 5.0 mol %), benzoic acid (0.150 mmol, 3.0 mol %), skipped enynes **2** (10.0 mmol, 2.0 equiv), toluene (20 mL) and a stir bar. The sealed tube was then filled with argon and sealed upon completion of this manipulation. The reaction mixture was vigorously stirred at 100 °C for 12 h under argon. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (40 mL) and filtered through a plug of Celite. The residue was washed with ethyl acetate. The combined organic solution was then concentrated *in vacuo* and purified with flash column chromatography (PE/EA = 20:1) to afford a mixture of **3aa** and **3aa'** (1.576 g) and the *E*/*Z* ratio was determined by ^{1}H NMR. The mixture of stereoisomers was separated by a second flash column (eluted with PE/EA = 20:1) to afford **3aa**.

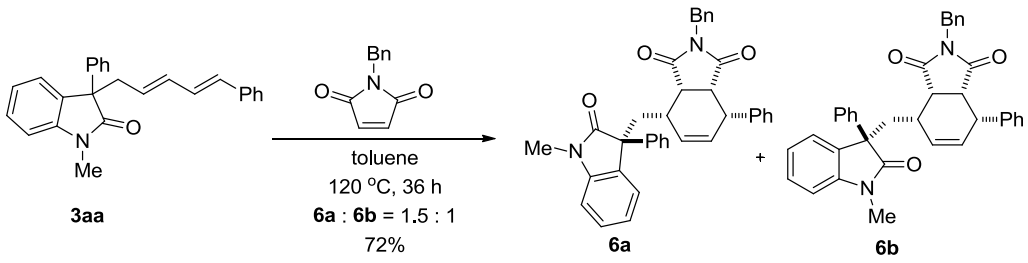
4. Derivation of the Allylic Alkylated Product 3aa



Reduction of 3aa: To the solution of **3aa** (73.0 mg, 0.2 mmol) in 2.0 mL methanol was added 10% $Pd(OH)_2/C$, and the solution was stirred at room temperature under a balloon of H_2 overnight. The reaction mixture was filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **4** as a colorless oil.

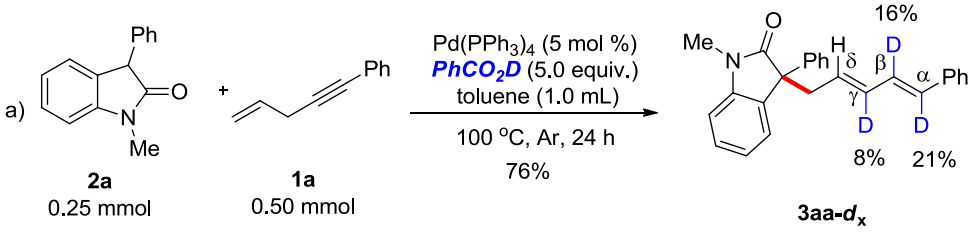


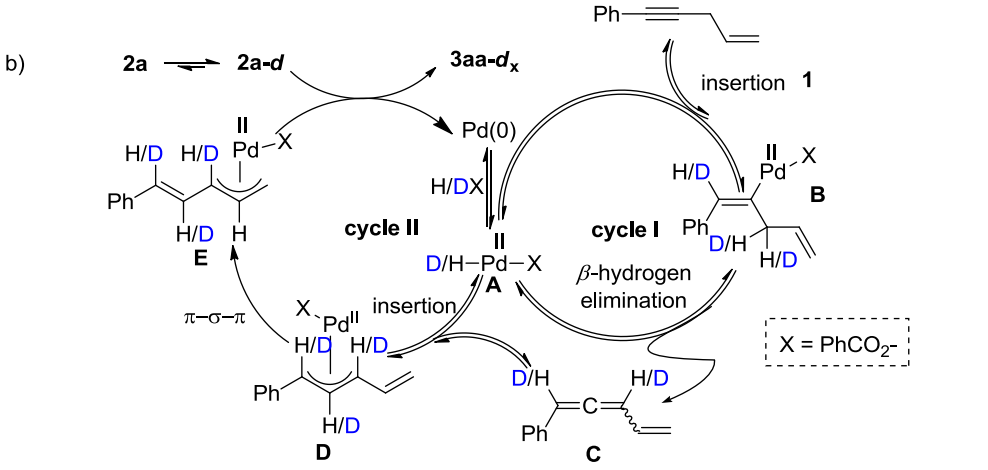
Cascade Diels-Alder/oxidation of 3aa: To the solution of **3aa** (73.0 mg, 0.2 mmol, 1.0 equiv) in 2.0 mL PhCl was added dimethyl acetylenedicarboxylate (0.6 mmol, 3.0 equiv) and the reaction mixture was stirred in 150 °C under argon atmosphere for 48 h. DDQ was then added and the resulting solution was stirred for 8 h at 120 °C. The reaction solution was then concentrated *in vacuo* and purified with flash column chromatography (PE/EA = 6:1~2:1) to afford compound **5** as white solid.

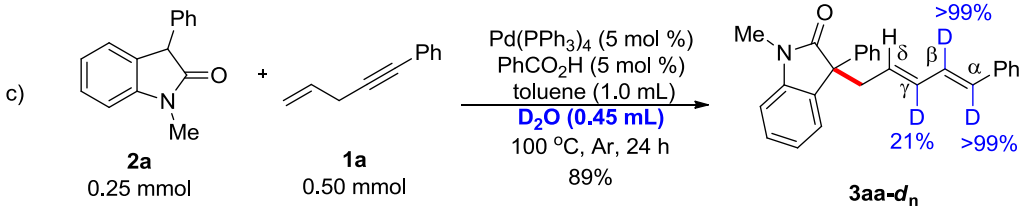


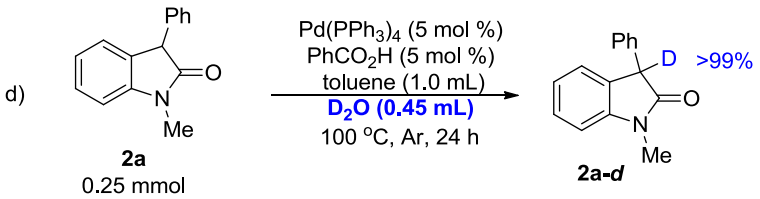
Diels-Alder reaction of 3aa with *N*-benzylmaleimide: To the solution of **3aa** (73.0 mg, 0.2 mmol, 1.0 equiv) in 2.0 mL toluene was added *N*-benzylmaleimide (0.22 mmol, 1.1 equiv) and the reaction mixture was stirred in 120 °C under argon atmosphere for 36 h. The reaction solution was then concentrated *in vacuo* and purified with flash column chromatography (PE/EA = 6:1~2:1) to afford compound **6a** and **6b** as white solid.

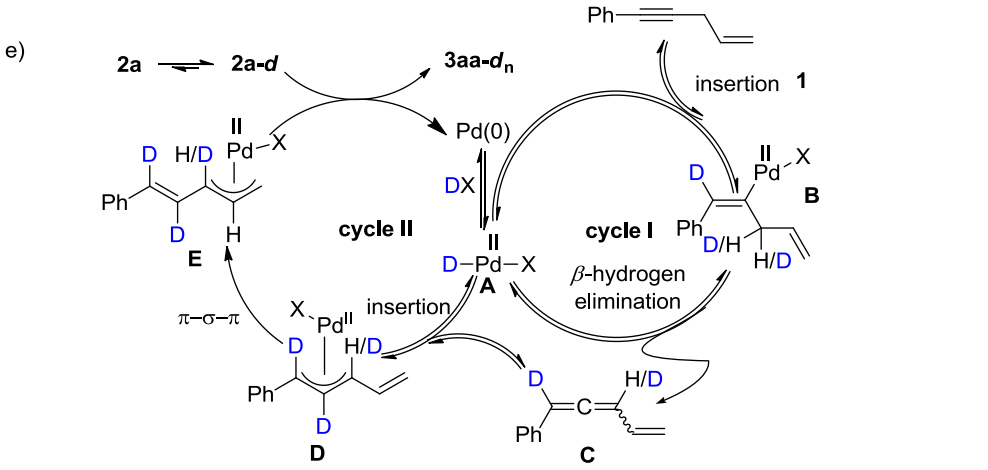
5. Deuterated-Labeling Experiment[a]





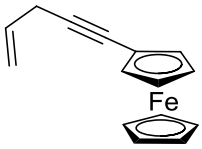






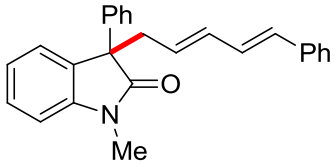
[a] The extent of deuterium incorporation was determined using ^{1}H NMR spectroscopy.

6. Characterization of the Title Compounds



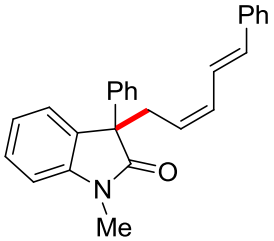
pent-4-en-1-yn-1-ylferrocene (2l)

Isolated yield: 83%, 4.15 g, 16.6 mmol. Brown solid, m. p. 40–41 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 – 5.84 (m, 1H), 5.40 (d, *J* = 16.9 Hz, 1H), 5.16 (d, *J* = 9.7 Hz, 1H), 4.39 (s, 2H), 4.20 – 4.15 (m, 7H), 3.09 (d, *J* = 3.3 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.0, 116.1, 82.7, 80.9, 71.3, 69.9, 68.4, 66.2, 24.0 ppm. IR (KBr) υ 3093, 2914, 1105, 1001, 819 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{15}H_{14}{}^{56}Fe]^+$ 250.0439, found 250.0439.



1-methyl-3-phenyl-3-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)indolin-2-one (3aa)

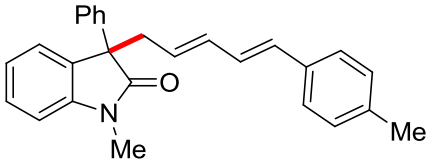
Total isolated yield: 93%, 85.0 mg, 0.23 mmol, 2*E*/2*Z* = 8.2:1. Purified **3aa**, yellow solid, m. p. 104–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.35 – 7.23 (m, 8H), 7.19 – 7.16 (m, 1H), 7.14 – 7.09 (m, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.53 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.18 (dd, *J* = 15.0, 10.3 Hz, 1H), 5.39 (ddd, *J* = 15.0, 8.4, 6.5 Hz, 1H), 3.18 – 3.13 (m, 4H), 3.04 (dd, *J* = 13.8, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 143.9, 139.4, 137.3, 134.7, 131.7, 131.6, 128.7, 128.6, 128.4, 128.3, 127.5, 127.5, 127.2, 126.3, 125.3, 122.6, 108.4, 56.7, 41.2, 26.5 ppm. IR (KBr) υ 3055, 3024, 2930, 1714, 1699, 1614, 1470, 1373, 989, 752, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{23}NO+H]^+$ 366.1852, found 366.1858.



1-methyl-3-phenyl-3-((2Z,4E)-5-phenylpenta-2,4-dien-1-yl)indolin-2-one (3aa')

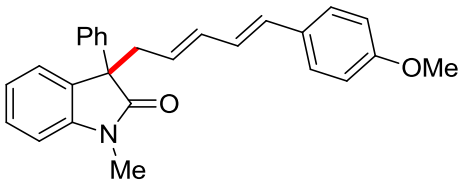
Purified **3aa'**, yellow solid, 55–57 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.33 – 7.18 (m, 9H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 15.4, 11.2 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.08 (t, *J* = 11.0 Hz, 1H), 5.14 (dt, *J* = 10.1, 7.8 Hz, 1H), 3.33 (dd, *J* = 15.1, 9.6 Hz, 1H), 3.30 – 3.15 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 144.0, 139.7, 137.6, 133.5, 132.0, 128.73, 128.70, 128.5, 128.5, 127.7, 127.5, 127.3, 126.7, 125.8, 125.4, 124.3, 122.7, 108.4, 56.4, 36.3, 26.6 ppm. IR (KBr) υ 3055, 3024, 2930, 1714, 1611, 1491, 1472, 1373, 696 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{23}NO+H]^+$ 366.1852, found 366.1858.



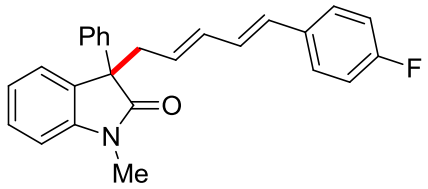
1-methyl-3-phenyl-3-((2E,4E)-5-(p-tolyl)penta-2,4-dien-1-yl)indolin-2-one (3ab)

Total isolated yield: 89%, 84.4 mg, 0.22 mmol, 2*E*/2*Z* = 7.6:1. Purified **3ab**, yellow solid, 84–86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.35 – 7.27 (m, 4H), 7.25 – 7.23 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.13- 7.05 (m, 3H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.49 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.34 (d, *J* = 15.7 Hz, 1H), 6.17 (dd, *J* = 15.0, 10.2 Hz, 1H), 5.35 (ddd, *J* = 14.9, 8.4, 6.5 Hz, 1H), 3.18 – 3.13 (m, 4H), 3.03 (dd, *J* = 13.7, 8.6 Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 143.9, 139.4, 137.3, 134.9, 134.5, 131.7, 131.5, 129.4, 128.7, 128.4, 127.7, 127.6, 127.5, 127.2, 126.2, 125.3, 122.6, 108.4, 56.8, 41.2, 26.5, 21.3 ppm. IR (KBr) υ 3053, 3022, 2920, 1714, 1612, 1495, 1472, 1373, 1348, 752, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{25}NO+H]^+$ 380.2009, found 380.2014.



3-((2E,4E)-5-(4-methoxyphenyl)penta-2,4-dien-1-yl)-1-methyl-3-phenylindolin-2-one (3ac)

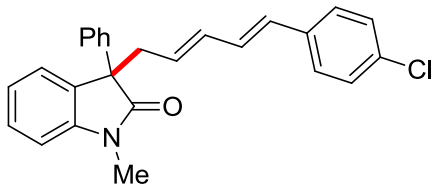
Total isolated yield: 88%, 87.0 mg, 0.22 mmol, 2*E*/2*Z* = 7.4:1. Purified **3ac**, yellow solid, m. p. 100–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.35 - 7.22 (m, 7H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.41 (dd, *J* = 15.5, 9.6 Hz, 1H), 6.32 (d, *J* = 15.5 Hz, 1H), 6.15 (dd, *J* = 15.0, 9.6 Hz, 1H), 5.38 – 5.28 (m, 1H), 3.76 (s, 3H), 3.18 – 3.12 (m, 4H), 3.03 (dd, *J* = 13.7, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 159.2, 143.9, 139.5, 134.9, 131.7, 131.1, 130.1, 128.6, 128.3, 127.5, 127.5, 127.2, 127.0, 126.7, 125.3, 122.6, 114.1, 108.4, 56.8, 55.4, 41.2, 26.5 ppm. IR (KBr) υ 3055, 3026, 2953, 1715, 1611, 1614, 1491, 1470, 831, 752, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{25}NO_2+H]^+$ 396.1958, found 396.1961.



3-((2E,4E)-5-(4-fluorophenyl)penta-2,4-dien-1-yl)-1-methyl-3-phenylindolin-2-one (3ad)

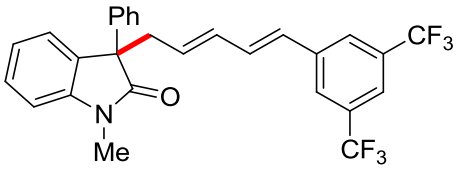
Total isolated yield: 96%, 92.0 mg, 0.24 mmol, 2*E*/2*Z* = 8.0:1. Purified **3ad**, yellow

solid, m. p. 94–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.23 (m, 9H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.44 (dd, *J* = 15.6, 10.0 Hz, 1H), 6.32 (d, *J* = 15.6 Hz, 1H), 6.16 (dd, *J* = 15.0, 10.0 Hz, 1H), 5.43 – 5.33 (m, 1H), 3.25 – 3.10 (m, 4H), 3.04 (dd, *J* = 13.7, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 162.2 (d, *J* = 245 Hz), 143.8, 139.4, 134.5, 133.5 (d, *J* = 3.4 Hz), 131.6, 130.3, 128.7, 128.39, 128.36, 127.8, 127.6 (d, *J* = 7.8 Hz), 127.2, 125.3, 122.6, 115.6 (d, *J* = 21 Hz), 108.4, 56.7, 41.2, 26.5 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.4 ppm. IR (KBr) υ 3055, 3024, 2930, 1714, 1612, 1470, 1373, 1227, 837, 754, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{22}FNO+H]^+$ 384.1758, found 384.1763.



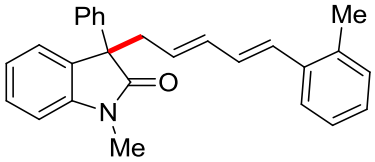
3-((2E,4E)-5-(4-chlorophenyl)penta-2,4-dien-1-yl)-1-methyl-3-phenylindolin-2-one (3ae)

Total isolated yield: 96%, 96.0 mg, 0.24 mmol, 2*E*/2*Z* = 7.1:1. Purified **3ae**, yellow solid, 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.27 – 7.20 (m, 6H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.49 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.30 (d, *J* = 15.6 Hz, 1H), 6.16 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.45 – 5.35 (m, 1H), 3.18 – 3.12 (m, 4H), 3.05 (dd, *J* = 13.8, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 143.8, 139.4, 135.8, 134.4, 132.9, 131.6, 130.2, 129.2, 129.0, 128.8, 128.7, 128.4, 127.5, 127.4, 127.2, 125.3, 122.6, 108.4, 56.6, 41.2, 26.5 ppm. IR (KBr) υ 3055, 3026, 2927, 1714, 1611, 1489, 1470, 1348, 1090, 827, 752, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{22}ClNO+H]^+$ 400.1463, found 400.1468.



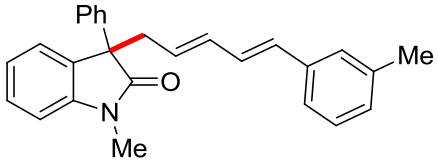
3-((2E,4E)-5-(3,5-bis(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)-1-methyl-3-phenylindolin-2-one (3af)

Total isolated yield: 90%, 112.8 mg, 0.22 mmol, 2*E*/2*Z* = 6.6:1. Purified **3af**, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73– 7.65 (m, 3H), 7.44 – 7.38 (m, 2H), 7.35 – 7.24 (m, 5H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.66 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.60 – 5.50 (m, 1H), 3.22 – 3.16 (m, 4H), 3.10 (dd, *J* = 13.8, 8.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 143.9, 139.5, 139.3, 133.7, 132.3, 131.9 (q, *J* = 32.9 Hz), 131.88, 131.3, 128.8, 128.6, 128.3, 127.6, 127.2, 125.94, 125.91, 125.3 (t, *J* =28.5 Hz), 122.7, 121.6, 120.5 (penta, *J* = 3.7 Hz), 108.5, 56.6, 41.2, 26.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.0 ppm. IR (neat) υ 3055, 3027, 1714, 1614, 1381, 1278, 1177, 1130, 989, 895, 754, 698 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{28}H_{21}F_6NO+H]^+$ 502.1600, found 502.1608.



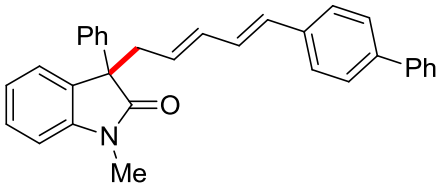
1-methyl-3-phenyl-3-((2E,4E)-5-(o-tolyl)penta-2,4-dien-1-yl)indolin-2-one (3ag)

Total isolated yield: 57%, 54.1 mg, 0.14 mmol, 2*E*/2*Z* = 9.0:1. Purified **3ag**, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 3H), 7.34 – 7.24 (m, 5H), 7.15 - 7.09 (m, 4H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.45 (dd, *J* = 15.4, 10.2 Hz, 1H), 6.23 (dd, *J* = 15.0, 10.2 Hz, 1H), 5.37 (ddd, *J* = 14.9, 8.5, 6.4 Hz, 1H), 3.19 – 3.13 (m, 4H), 3.06 (dd, *J* = 13.7, 8.7 Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 143.9, 139.4, 136.1, 135.6, 135.1, 131.7, 130.5, 129.7, 129.1, 128.7, 128.4, 128.1, 127.5, 127.4, 127.2, 126.1, 125.3, 124.9, 122.6, 108.4, 56.8, 41.2, 26.5, 19.9 ppm. IR (neat) υ 3055, 3022, 2930, 1714, 1610, 1491, 1373, 1346, 989, 750, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{25}NO+H]^+$ 380.2009, found 380.2016.



1-methyl-3-phenyl-3-((2E,4E)-5-(m-tolyl)penta-2,4-dien-1-yl)indolin-2-one (3ah)

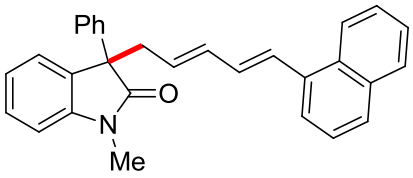
Total isolated yield: 89%, 84.4 mg, 0.22 mmol, 2*E*/2*Z* = 8.8:1. Purified **3ah**, faint yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.20 (m, 5H), 7.18 – 7.05 (m, 4H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.52 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.34 (d, *J* = 15.7 Hz, 1H), 6.17 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.37 (ddd, *J* = 14.9, 8.4, 6.5 Hz, 1H), 3.24 – 3.11 (m, 4H), 3.04 (dd, *J* = 13.7, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 143.8, 139.4, 138.1, 137.2, 134.8, 131.7, 128.7, 128.5, 128.4, 128.4, 128.3, 128.1, 127.5, 127.2, 126.9, 125.3, 123.5, 122.6, 108.4, 56.7, 41.2, 26.5, 21.5 ppm. IR (neat) υ 3055, 3022, 2918, 1714, 1610, 1491, 1472, 1373, 989, 752, 694 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{25}NO+H]^+$ 380.2009, found 380.2012.



3-((2E,4E)-5-([1,1'-biphenyl]-4-yl)penta-2,4-dien-1-yl)-1-methyl-3-phenylindolin-2-one (3ai)

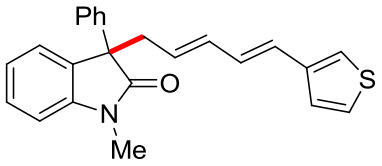
Total isolated yield: 95%, 104.9 mg, 0.24 mmol, 2*E*/2*Z* = 7.7:1. Purified **3ai**, yellow solid, m. p. 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.37 (m, 5H), 7.34 – 7.20 (m, 7H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.57 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.20 (dd, *J* = 14.9, 10.4 Hz, 1H), 5.40 (dt, *J* = 14.9, 7.5 Hz, 1H), 3.17 – 3.13 (m, 4H),

3.05 (dd, *J* = 13.6, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 143.9, 140.7, 140.1, 139.4, 136.4, 134.8, 131.7, 131.1, 128.9, 128.7, 128.7, 128.4, 128.4, 127.5, 127.4, 127.3, 127.2, 126.9, 126.7, 125.3, 122.6, 108.4, 56.7, 41.2, 26.5 ppm. IR (KBr) υ 3055, 3026, 2928, 1714, 1699, 1478, 1472, 1373, 989, 758, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{32}H_{27}NO+H]^+$ 442.2165, found 442.2170.



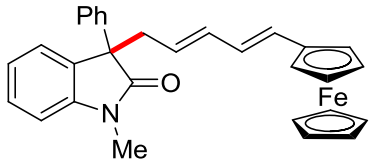
1-methyl-3-((2E,4E)-5-(naphthalen-1-yl)penta-2,4-dien-1-yl)-3-phenylindolin-2-one (3aj)

Total isolated yield: 62%, 64.4 mg, 0.15 mmol, 2*E*/2*Z* = 7.2:1. Purified **3aj**, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.52 - 7.46 (m, 2H), 7.46 -7.26 (m, *J* = 7.7 Hz, 3H), 7.38 - 7.24 (m, 5H), 7.19 - 7.11 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.61 (dd, *J* = 15.3, 10.5 Hz, 1H), 6.35 (dd, *J* = 15.0, 10.6 Hz, 1H), 5.49 – 5.39 (m, 1H), 3.28 – 3.17 (m, 4H), 3.10 (dd, *J* = 13.7, 8.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 143.9, 139.4, 135.0, 134.6, 133.8, 131.7, 131.4, 131.1, 128.7, 128.7, 128.7, 128.4, 128.2, 127.9, 127.5, 127.2, 126.1, 125.8, 125.6, 125.4, 123.6, 123.1, 122.7, 108.4, 56.8, 41.3, 26.6 ppm. IR (neat) υ 3055, 2928, 1714, 1611, 1495, 1470, 1373, 989, 752, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{30}H_{25}NO+H]^+$ 416.2009, found 416.2016.



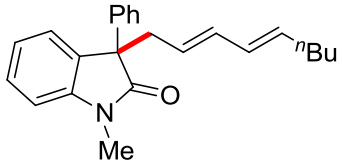
1-methyl-3-phenyl-3-((2E,4E)-5-(thiophen-3-yl)penta-2,4-dien-1-yl)indolin-2-one (3ak)

Total isolated yield: 94%, 87.3 mg, 0.23 mmol, 2*E*/2*Z* = 5.9:1. Purified **3ak**, faint yellow solid, m. p. 105–107 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.21 (m, 5H), 7.21 – 7.19 (m, 1H), 7.13 – 7.078 (m, 2H), 7.06 - 7.05 (m, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.42 – 6.30 (m, 2H), 6.12 (dd, *J* = 14.5, 7.2 Hz, 1H), 5.35 (ddd, *J* = 15.0, 8.5, 6.4 Hz, 1H), 3.17 – 3.12 (m, 4H), 3.02 (dd, *J* = 13.7, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 143.8, 140.1, 139.4, 134.6, 131.6, 128.7, 128.6, 128.4, 127.8, 127.5, 127.2, 126.1, 125.7, 125.3, 124.8, 122.6, 121.9, 108.4, 56.7, 41.2, 26.5 ppm. IR (KBr) υ 3055, 3026, 1707, 1609, 1491, 1470, 1371, 746, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{24}H_{21}NOS+H]^+$ 372.1417, found 372.1420.



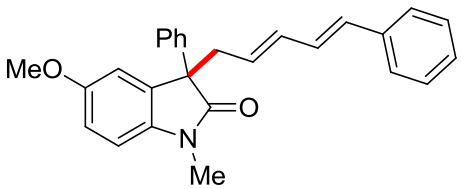
3-((2E,4E)-5-(ferrocenyl)penta-2,4-dien-1-yl)-1-methyl-3-phenylindolin-2-one (3al)

Total isolated yield: 96%, 113.6 mg, 0.24 mmol, 2*E*/2*Z* = 7.6:1. Purified **3al**, brown solid, m. p. 141–143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.36 – 7.23 (m, 6H), 7.14 – 7.09 (m, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.14 – 6.02 (m, 3H), 5.23 (ddd, *J* = 14.7, 8.4, 6.3 Hz, 1H), 4.26 (t, *J* = 1.4 Hz, 2H), 4.18 (t, *J* = 1.7 Hz, 2H), 4.05 (s, 5H), 3.19 (s, 3H), 3.11 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.98 (dd, *J* = 13.6, 8.5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 143.9, 139.5, 135.1, 131.8, 129.8, 128.6, 128.3, 127.4, 127.2, 126.4, 125.3, 125.1, 122.5, 108.3, 83.1, 69.4, 69.3, 68.9, 66.9, 66.5, 56.8, 41.3, 26.5 ppm. IR (KBr) υ 3055, 3024, 2927, 1714, 1611, 1493, 1470, 985, 817, 752, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{30}H_{27}NO^{56}Fe+H]^+$ 474.1515, found 474.1517.



1-methyl-3-((2E,4E)-nona-2,4-dien-1-yl)-3-phenylindolin-2-one (3am)

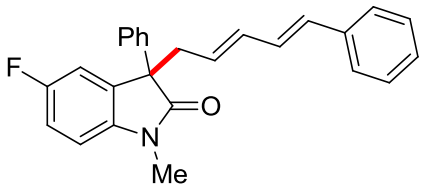
Total isolated yield: 77%, 66.4 mg, 0.19 mmol, 2*E*/2*Z* = 6.6:1. Purified **3am**, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.21 (m, 8H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 5.98 (dd, *J* = 15.0, 10.3 Hz, 1H), 5.78 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.56 – 5.46 (m, 1H), 5.11 (ddd, *J* = 14.9, 8.4, 6.3 Hz, 1H), 3.18(s, 3H), 3.09 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.94 (dd, *J* = 13.7, 8.6 Hz, 1H), 1.98 (q, *J* = 6.7 Hz, 2H), 1.35 – 1.23 (m, 5H), 0.86 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 143.9, 139.5, 134.8, 134.3, 131.8, 129.7, 128.6, 128.3, 127.4, 127.2, 125.4, 124.7, 122.5, 108.3, 56.8, 41.1, 32.3, 31.5, 26.5, 22.3, 14.0 ppm. IR (neat) υ 3055, 3020, 2955, 2926, 1717, 1611, 1493, 1470, 989, 752, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{24}H_{27}NO+H]^+$ 346.2165, found 346.2172.



5-methoxy-1-methyl-3-phenyl-3-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)indolin-2-one (3ba)

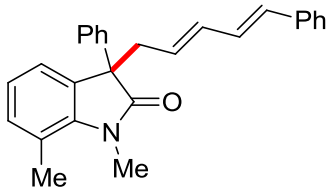
Total isolated yield: 74%, 73.1 mg, 0.18 mmol, 2*E*/2*Z* = 13.4:1. Purified **3ba**, white solid, m. p. 66–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 10H), 7.20 – 7.15 (m, 1H), 6.88 – 6.85 (m, 2H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.55 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.20 (dd, *J* = 15.0, 10.3 Hz, 1H), 5.44 – 5.35 (m, 1H), 3.78

(s, 3H), 3.18 – 3.11 (m, 4H), 3.04 (dd, *J* = 13.8, 8.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 156.0, 139.4, 137.5, 137.4, 134.8, 133.1, 131.6, 128.7, 128.7, 128.3, 127.5, 127.5, 127.2, 126.3, 115.1, 112.7, 108.7, 57.2, 55.9, 41.1, 26.6 ppm. IR (KBr) υ 3057, 3022, 2934, 2833, 1714, 1600, 1361, 1470, 1288, 804, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{25}NO_2+H]^+$ 396.1958, found 396.1963.



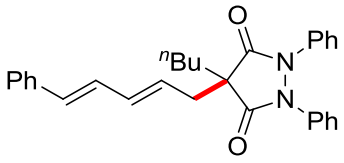
5-fluoro-1-methyl-3-phenyl-3-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)indolin-2-one (3ca)

Total isolated yield: 78%, 74.7 mg, 0.19 mmol, 2*E*/2*Z* = 7.2:1. Purified **3ca**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 11H), 7.07 – 7.01 (m, 2H), 6.81 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.54 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.19 (dd, *J* = 15.0, 10.2 Hz, 1H), 5.37 (dt, *J* = 15.0, 7.5 Hz, 1H), 3.18 (s, 3H), 3.18 – 3.03 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 159.3 (d, *J* = 239.2 Hz), 140.0, 139.9, 137.3, 135.1, 133.5 (d, *J* = 7.9 Hz), 132.0, 128.8, 128.7, 128.5, 127.7, 127.6 (d, *J* = 5.5 Hz), 127.1, 126.4, 114.7 (d, *J* = 23.4 Hz), 113. 3(d, *J* = 24.7 Hz), 108.8 (d, *J* = 8.0 Hz), 57.3, 41.1, 26.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -94.1 ppm. IR (neat) υ 3059, 3024, 2924, 1714, 1273, 991, 810, 698 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{22}FNO+H]^+$ 384.1758, found 384.1765.



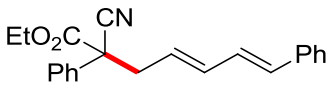
1,7-dimethyl-3-phenyl-3-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)indolin-2-one (3da)

Total isolated yield: 83%, 78.7 mg, 0.21 mmol, 2*E*/2*Z* = 8.3:1. Purified **3da**, yellow solid, m. p. 45–47 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.32 – 7.24 (m, 7H), 7.18 (qt, *J* = 6.8, 1.2 Hz, 1H), 7.08 – 6.96 (m, 2H), 7.03 – 6.95 (m, 1H), 6.56 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.19 (dd, *J* = 15.0, 10.3 Hz, 1H), 5.43 – 5.33 (m, 1H), 3.47 (d, *J* = 3.5 Hz, 3H), 3.16 – 3.03 (m, 2H), 2.59 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 141.8, 139.9, 137.4, 134.7, 132.4, 132.1, 131.5, 128.8, 128.7, 128.5, 127.5, 127.4, 127.2, 126.3, 123.3, 122.5, 119.9, 56.2, 41.3, 29.9, 19.4 ppm. IR (KBr) υ 2920, 2851, 1705, 1611, 1506, 1456, 1361, 736, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{27}H_{25}NO+H]^+$ 380.2009, found 380.2011.



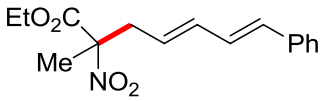
4-butyl-1,2-diphenyl-4-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)pyrazolidine-3,5-dione (3ea)

Total isolated yield: 78%, 87.8 mg, 0.19 mmol, 2*E*/2*Z* = 4.6:1. Purified **3ea**, yellow solid, m. p. 86–88 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.18 (m, 13H), 7.16 – 7.09 (m, 2H), 6.61 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.33 (dd, *J* = 15.1, 10.3 Hz, 1H), 5.67 (dt, *J* = 15.3, 7.8 Hz, 1H), 2.71 (d, *J* = 7.8 Hz, 2H), 1.96 – 1.91 (m, 2H), 1.42 – 1.30 (m, 4H), 0.85 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 137.2, 135.8, 135.5, 132.7, 129.0, 128.7, 128.1, 127.7, 126.9, 126.4, 126.3, 122.9, 55.4, 39.5, 35.3, 27.1, 27.0, 22.8, 13.8 ppm. IR (KBr) υ 3024, 2957, 2926, 1720, 1595, 1491, 991, 756, 691 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{30}H_{30}N_2O_2+H]^+$ 451.2380, found 451.2382.



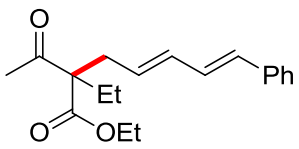
(4E,6E)-ethyl 2-cyano-2,7-diphenylhepta-4,6-dienoate (3fa)

Total isolated yield: 97%, 80.4 mg, 0.24 mmol, 2*E*/2*Z* = 7.6:1. Purified **3fa**, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.49 – 7.39 (m, 5H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.76 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.55 (d, *J* = 15.7 Hz, 1H), 6.42 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.76 (dt, *J* = 15.0, 7.5 Hz, 1H), 4.36 – 4.20 (m, 2H), 3.26 (dd, *J* = 14.1, 7.9 Hz, 1H), 2.97 (dd, *J* = 14.1, 7.1 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 137.0, 136.5, 134.2, 133.1, 129.3, 129.0, 128.7, 128.1, 127.8, 126.5, 126.2, 125.8, 118.2, 63.4, 54.5, 41.7, 13.9 ppm. IR (neat) υ 3026, 2981, 1743, 1678, 1449, 1030, 991, 856, 694 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{21}NO_2+Na]^+$ 354.1465, found 354.1469.



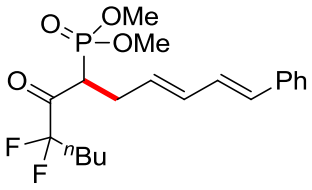
(4E,6E)-ethyl 2-methyl-2-nitro-7-phenylhepta-4,6-dienoate (3ga)

Total isolated yield: 89%, 64.3 mg, 0.22 mmol, 2*E*/2*Z* = 4.4:1. Purified **3ga**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 4H), 7.22 – 7.20 (m, 1H), 6.72 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.31 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.61 (dt, *J* = 15.1, 7.6 Hz, 1H), 4.28 (q, *J* = 6.9 Hz, 2H), 3.08 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.95 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.78 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 137.0, 136.7, 133.2, 128.7, 127.9, 127.9, 126.5, 124.6, 92.4, 63.0, 40.2, 21.3, 14.0 ppm. IR (neat) υ 2984, 2940, 1749, 1557, 1448, 1386, 1252, 752, 700 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{16}H_{19}NO_4+H]^+$ 290.1387, found 290.1383.



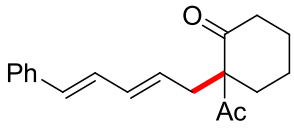
***(4E,6E)-ethyl 2-acetyl-2-ethyl-7-phenylhepta-4,6-dienoate* (3ha)**

Total isolated yield: 53%, 39.8 mg, 0.13 mmol, 2*E*/2*Z* = 3.3:1. Purified **3ha**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 6H), 6.70 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.24 (dd, *J* = 15.1, 10.3 Hz, 1H), 5.57 (dt, *J* = 15.1, 7.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.76 – 2.61 (m, 2H), 2.14 (s, 3H), 2.00 – 1.86 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.87, 172.14, 137.41, 134.32, 131.66, 128.74, 128.71, 128.48, 127.55, 126.40, 77.58, 77.16, 76.74, 64.23, 61.40, 34.62, 26.97, 24.71, 14.28, 8.30 ppm. IR (neat) υ 3055, 2928, 1697, 1647, 1495, 1589, 1489, 1471, 1435, 765, 704 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{19}H_{24}O_3+Na]^+$ 323.1618, found 323.1617.



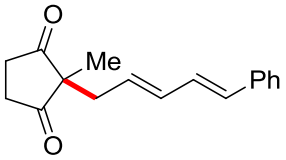
dimethyl ((1E,3E)-8,8-difluoro-7-oxo-1-phenyldodeca-1,3-dien-6-yl)phosphonate (3ia)

Total isolated yield: 72%, 72.0 mg, 0.18 mmol, 2*E*/2*Z* = 3.7:1. Purified **3ia**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.23 – 7.18 (m, 1H), 6.67 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.24 (dd, *J* = 15.0, 10.3 Hz, 1H), 5.62 (dt, *J* = 14.9, 7.3 Hz, 1H), 3.92 (ddd, *J* = 22.7, 10.2, 4.4 Hz, 1H), 3.80 (dd, *J* = 11.1, 5.1 Hz, 6H), 2.93 – 2.70 (m, 2H), 2.04 – 1.89 (m, 2H), 1.45 – 1.32 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 196.84 (td, *J* = 33.3, 6.1 Hz), 137.1, 133.9, 132.4, 129.2 (d, *J* = 14.9 Hz) , 128.6, 128.0, 127.6, 126.4, 118.1 (t, *J* = 251.7 Hz), 53.7 (d, *J* = 6.6 Hz), 53.4 (d, *J* = 7.0 Hz), 45.7 (d, *J* = 127.5 Hz), 32.2 (t, *J* = 22.7 Hz), 31.1 (d, *J* = 4.8 Hz), 23.1 (t, *J* = 4.0 Hz), 22.4, 13.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -104.9 (tAB, J = 273.5, 17.7 Hz), 106.3 (tAB, J = 273.5, 17.7 Hz) ppm. IR (neat) υ 3054, 3026, 1749, 1734, 1716, 1683, 1489, 754, 700 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{20}H_{27}F_2O_4P+H]^+$ 401.1688, found 401.1692.



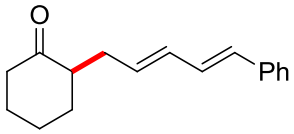
2-acetyl-2-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)cyclohexanone (3ja)

Total isolated yield: 67%, 47.3 mg, 0.17 mmol, 2*E*/2*Z* = 3.8:1. Purified **3ja**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 6.70 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.20 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.61 (dt, *J* = 15.1, 7.6 Hz, 1H), 2.67 (dd, *J* = 14.6, 7.7 Hz, 1H), 2.56 – 2.46 (m, 3H), 2.34 – 2.28 (m, 1H), 2.11 (s, 3H), 2.05 – 1.97 (m, 1H), 1.78 – 1.64 (m, 3H), 1.56 – 1.46 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.8, 206.2, 137.3, 134.3, 131.7, 128.7, 128.7, 127.6, 126.4, 68.1, 42.0, 38.0, 34.3, 27.2, 26.5, 22.3 ppm. IR (neat) υ 3024, 2941, 2864, 1715, 1694, 1495, 1360, 1312, 991, 748, 692 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{19}H_{22}O_2+Na]^+$ 305.1512, found 305.1528.



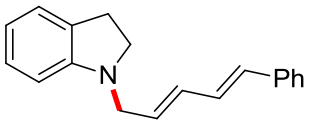
2-methyl-2-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)cyclopentane-1,3-dione (3ka)

Total isolated yield: 93%, 59.1 mg, 0.23 mmol, 2*E*/2*Z* = 4.5:1. Purified **3ka**, yellow solid, m. p. 66–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 6.66 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.21 (dd, *J* = 15.0, 10.3 Hz, 1H), 5.56 (dt, *J* = 15.3, 7.8 Hz, 1H), 2.81 – 2.61 (m, 4H), 2.44 (d, *J* = 7.8 Hz, 2H), 1.13 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.4, 137.1, 135.3, 132.6, 128.7, 128.1, 127.7, 126.8, 126.4, 57.2, 39.2, 35.5, 19.0 ppm. IR (KBr) υ 3022, 2928, 1719, 1499, 1417, 1317, 1070, 991, 748, 692 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{17}H_{18}O_2+H]^+$ 255.1380, found 255.1384.



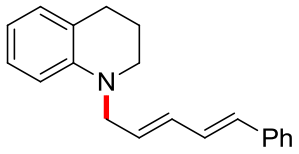
2-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)cyclohexanone (3la)

Total isolated yield: 60%, 36.0 mg, 0.15 mmol, 2*E*/2*Z* = 6.7:1. Purified **3la**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.1 Hz, 1H), 6.74 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.79 (dt, *J* = 15.0, 7.4 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.44 – 2.23 (m, 3H), 2.18 – 2.00 (m, 3H), 1.94 –1.81 (m, 1H), 1.75 – 1.63 (m, 2H), 1.46 –1.32 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.6, 137.7, 133.1, 132.4, 130.6, 129.2, 128.7, 127.3, 126.3, 50.9, 42.3, 33.7, 33.0, 28.1, 25.2 ppm. IR (neat) υ 2932, 2859, 1705, 1449, 1128, 968, 750, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{17}H_{20}O+H]^+$ 241.1587, found 241.1592.



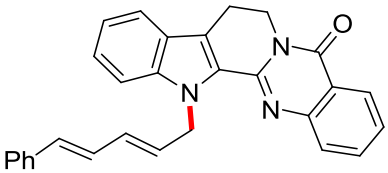
1-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)indoline (3ma)

Total isolated yield: 97%, 63.3 mg, 0.24 mmol, 2*E*/2*Z* = 6.9:1. Mixtures of **3ma** and **3ma'**, brown liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 - 7.18 (m, 1H), 7.07 (t, *J* = 8.2 Hz, 2H), 6.78 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.56 – 6.51 (m, 2H), 6.42 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.88 (dt, *J* = 15.0, 6.3 Hz, 1H), 3.79 (d, *J* = 6.2 Hz, 2H), 3.34 (t, *J* = 8.3 Hz, 2H), 2.95 (t, *J* = 8.2 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) (major) δ 152.2, 137.3, 133.0, 132.1, 130.2, 128.7, 128.4, 127.6, 127.4, 126.4, 124.6, 117.9, 107.6, 53.4, 51.4, 46.51, 28.7 ppm. IR (neat) υ 3055, 3024, 2922, 1604, 1487, 1470, 1024, 989, 746, 692 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{19}H_{29}N+H]^+$ 262.1590, found 262.1589.



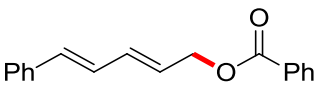
1-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)-1,2,3,4-tetrahydroquinoline (3na)

Total isolated yield: 96%, 66.0 mg, 0.24 mmol, 2*E*/2*Z* = 6.1:1. Mixtures of **3na** and **3na'**, brown liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 7.21 – 7.13 (m, 1H), 7.15-7.10 (m, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.76 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.62 – 6.56 (m, 2H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.32 (dd, *J* = 15.2, 10.5 Hz, 1H), 5.82 (dt, *J* = 15.2, 5.4 Hz, 1H), 3.93 (d, *J* = 5.1 Hz, 2H), 3.26 (t, *J* = 5.6 Hz , 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.00 – 1.92 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 137.4, 131.7, 131.6, 130.1, 129.1, 128.7, 128.5, 127.5, 127.2, 126.3, 122.6, 116.0, 111.5, 53.2, 49.3, 28.2, 22.4 ppm. IR (neat) υ 3024, 2926, 2841, 1601, 1504, 989, 746 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{20}H_{21}N+H]^+$ 276.1747, found 276.1746.



13-((2E,4E)-5-phenylpenta-2,4-dien-1-yl)-7,8-dihydroindolo[2',3':3,4]pyrido[2,1-b]quinazolin-5(13H)-one (3oa)

Total isolated yield: 57%, 61.2 mg, 0.14 mmol, 2*E*/2*Z* = 5.3:1. Purified **3oa**, yellow soild, m. p. 174–176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.46 – 7.16 (m, 3H), 7.35 – 7.11 (m, 6H), 6.71 (dd, *J* = 15.5, 10.4 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.33 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.09 (dt, *J* = 12.1, 5.7 Hz, 1H), 5.66 (d, *J* = 5.5 Hz, 2H), 4.55 (t, *J* = 6.6 Hz, 2H), 3.18 (t, *J* = 6.6 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 147.5, 145.5, 140.2, 137.3, 134.2, 132.7, 132.3, 130.2, 128.7, 128.3, 127.7, 127.4, 127.2, 126.4, 126.4, 125.5, 124.6, 121.1, 120.6, 120.2, 119.7, 110.9, 46.9, 41.0, 20.0 ppm. IR (KBr) υ 3057, 3024, 2926, 1668, 1587, 1537, 989, 772, 692 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{29}H_{23}N_3O+H]^+$ 430.1914, found 430.1912.

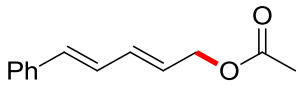


(2E,4E)-5-phenylpenta-2,4-dien-1-yl benzoate (3pa)[3]

Total isolated yield: 67%, 44.3 mg, 0.17 mmol, 2*E*/2*Z* = 6.4:1. Purified **3pa**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.38 (m, 4H), 7.31 (t, *J* = 6.8 Hz, 2H), 7.24 – 7.20 (m, 1H), 6.79 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.67 – 6.53 (m, 2H), 5.99 (dt, *J* = 14.1, 6.3 Hz, 1H), 4.90 (d, *J* = 6.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 137.1, 134.7, 134.0, 133.1, 130.4, 129.8, 128.8, 128.5, 127.9, 127.9, 127.1, 126.6, 65.3 ppm. IR (neat) υ 2924, 2850, 1716, 1450,

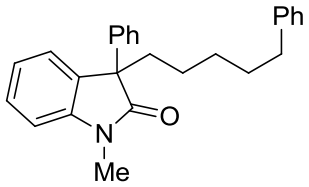
3 Known products, see: Zhang, Y.; Li, Z.; Liu, Z.-Q. *Org. Lett.* **2012**, *14*, 1838.

1271, 1115, 1026, 968, 750, 711 cm^{-1}.



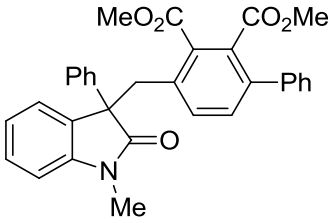
(2E,4E)-5-phenylpenta-2,4-dien-1-yl acetate (3qa)

Total isolated yield: 61%, 30.8 mg, 0.15 mmol, 2*E*/2*Z* = 7.6:1. Purified **3ra**, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.37 – 7.322 (m, 2H), 7.29 – 7.23 (m, 1H), 6.80 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.48 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.91 (dd, *J* = 15.2, 6.5 Hz, 1H), 4.68 (d, *J* = 6.5 Hz, 1H), 2.11 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 137.1, 134.7, 133.9, 128.8, 128.0, 127.8, 127.0, 126.6, 64.9, 21.1 ppm. IR (neat) υ 2918, 1732, 1250, 1074, 966, 750, 692 cm^{-1}.



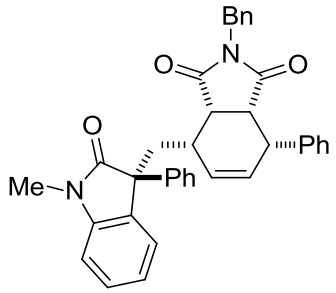
1-methyl-3-phenyl-3-(5-phenylpentyl)indolin-2-one (4)

Isolated yield: 93%, 68.7 mg, 0.18 mmol. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 9H), 7.16 – 7.13 (m, 1H), 7.10 (t, *J* = 7.8 Hz, 3H), 6.88 (d, *J* = 7.7 Hz, 1H), 3.20 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.36 (td, *J* = 12.7, 4.4 Hz, 1H), 2.17 (td, *J* = 12.8, 4.2 Hz, 1H), 1.56 – 1.445 (m, 2H), 1.35 – 1.05 (m, 4H), 0.98 – 0.83 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.7, 144.0, 142.6, 140.4, 132.4, 128.6, 128.4, 128.3, 128.2, 127.3, 126.9, 125.7, 124.8, 122.6, 108.3, 56.8, 37.9, 35.9, 31.1, 29.4, 26.4, 24.4 ppm. IR (neat) υ 3057, 3024, 2930, 2857, 1614, 1371, 1253, 1126, 916, 750, 696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{27}NO+H]^{+}$ 370.2165, found 370.2174.



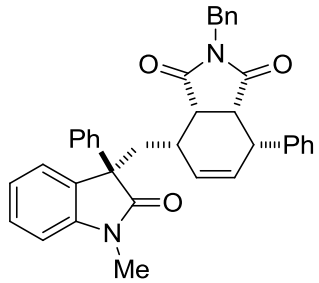
dimethyl 4-((1-methyl-2-oxo-3-phenylindolin-3-yl)methyl)-[1,1'-biphenyl]-2,3-dicarboxylate (5)

Isolated yield: 71%, 71.8 mg, 0.14 mmol. White solid, m. p. 190–192 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.1 Hz, 2H), 7.36 – 7.26 (m, 6H), 7.25 – 7.14 (m, 6H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 4.02 (AB, *J* = 13.6 Hz, 2H), 3.72 (s, 3H), 3.52 (s, 3H), 3.07 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 169.1, 167.8, 143.6, 139.7, 139.2, 134.6, 132.9, 132.6, 132.3, 131.1, 130.4, 128.7, 128.5, 128.4, 128.2, 127.8, 127.6, 127.4, 126.0, 122.4, 108.3, 57.9, 52.5, 52.3, 39.3, 26.4 ppm. IR (KBr) υ 3061, 3028, 2947, 1715, 1612, 1495, 1472, 1213, 1128, 764, 698 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{32}H_{27}NO_5+H]^{+}$ 506.1962, found 506.1972.



(±)-(3aS,4S,7R,7aR)-2-benzyl-4-(((S)-1-methyl-2-oxo-3-phenylindolin-3-yl)methyl)-7-phenyl-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione (6a)

Total isolated yield of **6a** and **6b**: 72%, 0.14 mmol (**6a**:**6b** = 1.5:1, 47.8 mg **6a** was isolated). Purified **6a**, white solid, 194–196 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 2H), 7.41 – 7.30 (m, 13H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.08 – 7.05 (m, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.11 – 6.00 (m, 2H), 4.52 (AB, *J* = 14.1 Hz, 2H), 3.29 – 3.10 (m, 5H), 3.14 (dd, *J* = 10.6, 5.3 Hz, 2H), 2.84 (dd, *J* = 8.2, 5.8 Hz, 1H), 2.06 – 2.05 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 176.9, 175.4, 143.9, 140.2, 138.8, 135.9, 134.4, 131.8, 130.1, 128.7, 128.7, 128.6, 128.6, 128.5, 128.2, 127.8, 127.5, 127.1, 127.0, 125.0, 122.9, 108.4, 56.6, 46.8, 45.4, 42.1, 41.5, 39.4, 33.5, 26.5 ppm. IR (KBr) υ 3059, 3032, 2922, 2851, 1771, 1608, 1495, 1471, 1396, 989, 754, 698 cm^{-1}. HRMS (ESI) calcd for $[C_{37}H_{32}N_2O_3+H]^+$ 553.2486, found 553.2482.



(±)-(3aS,4S,7R,7aR)-2-benzyl-4-(((R)-1-methyl-2-oxo-3-phenylindolin-3-yl)methyl)-7-phenyl-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione (6b)

Total isolated yield of **6a** and **6b**: 72% (**6a**:**6b** = 1.5:1, 31.8 mg **6b** was isolated). Purified **6b**, white solid, 216–218 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.34 – 7.22 (m, 13H), 7.13 – 7.08 (dd, *J* = 10.9, 4.1 Hz, 1H), 7.02 – 6.99 (m, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.80 (AB, *J* = 9.2, 1H), 5.31 (dt, *J* = 9.3, 3.2 Hz, 1H), 4.48 (q, *J* = 14.1 Hz, 2H), 3.35 (s, 1H), 3.30 (dd, *J* = 14.5, 2.4 Hz, 1H), 3.24 (s, 3H), 3.21 – 3.01 (m, 3H), 2.25 (brs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 177.2, 175.5, 143.7, 140.4, 138.8, 136.0, 133.9, 132.2, 129.5, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.6, 127.1, 126.9, 125.4, 122.9, 108.7, 57.1, 46.8, 46.2, 42.2, 41.6, 39.5, 34.2, 26.6 ppm. IR (KBr) υ 2920, 2851, 1716, 1541,1396, 752, 696 cm^{-1}. HRMS (ESI) calcd for $[C_{37}H_{32}N_2O_3+Na]^+$ 575.2305, found 575.2313.

7. X-Ray Crystallography Data

7.1 X-Ray Crystallography Data of 3aa

Computing details

Cell refinement: *SAINT* v7.68A (Bruker, 2009); data reduction: *SAINT* v7.68A (Bruker, 2009); program(s) used to solve structure: ShelXT (Sheldrick, 2015); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

References

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Crystal data of **3aa**

$C_{26}H_{23}NO$	$F(000) = 776$
$M_r = 365.45$	$D_x = 1.233$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.934$ (2) Å	Cell parameters from 1023 reflections
$b = 22.154$ (4) Å	$\theta = 2.3–19.3°$
$c = 8.9741$ (18) Å	$\mu = 0.07$ mm^{-1}
$\beta = 94.349$ (5)°	$T = 205$ K
$V = 1969.3$ (7) Å^3	Block, colourless
$Z = 4$	0.26 × 0.16 × 0.13 mm

Data collection

Bruker APEX-II CCD diffractometer	2278 reflections with $I > 2\sigma(I)$

graphite	R_{int} = 0.081
ϕ and ω scans	θ_{max} = 27.6°, θ_{min} = 1.8°
Absorption correction: multi-scan *SADABS2008*/1 (Bruker,2008) was used for absorption correction. wR2(int) was 0.0886 before and 0.0569 after correction. The Ratio of minimum to maximum transmission is 0.8726. The λ/2 correction factor is 0.0015.	*h* = -12→12
T_{min} = 0.651, T_{max} = 0.746	*k* = -28→26
15889 measured reflections	*l* = -10→11
4474 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.062	H-atom parameters constrained
$wR(F^2)$ = 0.182	$w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.99	$(\Delta/\sigma)_{max} < 0.001$
4474 reflections	$\Delta\rangle_{max}$ = 0.35 e Å^{-3}
254 parameters	$\Delta\rangle_{min}$ = -0.23 e Å^{-3}
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.82451 (19)	0.47660 (7)	0.3353 (2)	0.0479 (5)
N1	0.9193 (2)	0.38254 (9)	0.3613 (2)	0.0379 (5)
C24	0.8933 (2)	0.32436 (10)	0.3016 (3)	0.0345 (6)
C6	0.7572 (2)	0.41782 (10)	0.0279 (3)	0.0364 (6)
C26	0.8288 (2)	0.42337 (11)	0.3015 (3)	0.0377 (6)
C19	0.7848 (3)	0.32661 (11)	0.1961 (3)	0.0380 (6)
C7	0.7341 (2)	0.39074 (10)	0.1811 (3)	0.0356 (6)
C13	0.3216 (2)	0.36655 (11)	0.8354 (3)	0.0404 (6)
C8	0.5859 (2)	0.39660 (12)	0.2196 (3)	0.0414 (6)
H8A	0.5617	0.4395	0.2186	0.050*
H8B	0.5282	0.3766	0.1411	0.050*
C11	0.4423 (3)	0.36806 (12)	0.6004 (3)	0.0435 (7)
H11	0.4823	0.3308	0.6271	0.052*
C9	0.5560 (3)	0.37063 (12)	0.3667 (3)	0.0435 (7)
H9	0.5972	0.3336	0.3939	0.052*
C12	0.3585 (3)	0.39177 (12)	0.6937 (3)	0.0447 (7)
H12	0.3186	0.4289	0.6652	0.054*
C3	0.8097 (3)	0.46502 (12)	-0.2517 (3)	0.0490 (7)
H3	0.8270	0.4813	-0.3451	0.059*
C10	0.4769 (3)	0.39481 (12)	0.4620 (3)	0.0440 (7)
H10	0.4397	0.4329	0.4375	0.053*
C25	1.0298 (3)	0.39685 (12)	0.4696 (3)	0.0468 (7)
H25A	1.0203	0.3740	0.5604	0.070*
H25B	1.0285	0.4397	0.4921	0.070*
H25C	1.1146	0.3865	0.4291	0.070*
C14	0.3424 (3)	0.30619 (12)	0.8730 (3)	0.0472 (7)
H14	0.3838	0.2804	0.8070	0.057*
C23	0.9587 (3)	0.27132 (12)	0.3422 (3)	0.0492 (7)
H23	1.0334	0.2707	0.4131	0.059*
C20	0.7374 (3)	0.27455 (12)	0.1290 (3)	0.0497 (7)
H20	0.6641	0.2755	0.0564	0.060*

C18	0.2660 (3)	0.40379 (13)	0.9397 (3)	0.0512 (7)
H18	0.2522	0.4449	0.9175	0.061*
C1	0.8871 (3)	0.42551 (13)	-0.0130 (3)	0.0530 (8)
H1	0.9600	0.4146	0.0545	0.064*
C15	0.3028 (3)	0.28369 (13)	1.0067 (3)	0.0533 (8)
H15	0.3142	0.2425	1.0291	0.064*
C5	0.6534 (3)	0.43412 (13)	-0.0754 (3)	0.0552 (8)
H5	0.5635	0.4296	-0.0515	0.066*
C21	0.8004 (3)	0.21958 (12)	0.1706 (3)	0.0576 (8)
H21	0.7676	0.1832	0.1277	0.069*
C22	0.9089 (3)	0.21899 (13)	0.2735 (3)	0.0588 (9)
H22	0.9512	0.1820	0.2984	0.071*
C16	0.2469 (3)	0.32139 (15)	1.1067 (4)	0.0569 (8)
H16	0.2195	0.3059	1.1971	0.068*
C2	0.9129 (3)	0.44903 (13)	-0.1517 (3)	0.0569 (8)
H2	1.0026	0.4539	-0.1764	0.068*
C17	0.2312 (3)	0.38165 (14)	1.0745 (4)	0.0584 (8)
H17	0.1965	0.4078	1.1446	0.070*
C4	0.6804 (3)	0.45709 (14)	-0.2141 (3)	0.0592 (8)
H4	0.6082	0.4673	-0.2833	0.071*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0613 (12)	0.0336 (10)	0.0483 (12)	0.0022 (9)	-0.0003 (9)	-0.0031 (8)
N1	0.0384 (11)	0.0399 (12)	0.0347 (13)	0.0002 (10)	-0.0026 (10)	0.0010 (9)
C24	0.0373 (13)	0.0334 (13)	0.0339 (15)	0.0007 (11)	0.0095 (11)	0.0029 (11)
C6	0.0409 (14)	0.0324 (13)	0.0356 (15)	-0.0033 (11)	0.0014 (12)	0.0016 (11)
C26	0.0404 (14)	0.0362 (14)	0.0368 (16)	0.0008 (11)	0.0057 (12)	0.0031 (11)
C19	0.0420 (14)	0.0371 (14)	0.0356 (15)	-0.0010 (11)	0.0081 (12)	0.0010 (11)
C7	0.0340 (13)	0.0383 (13)	0.0343 (15)	0.0009 (11)	0.0026 (11)	0.0009 (11)
C13	0.0345 (13)	0.0452 (15)	0.0416 (16)	0.0025 (12)	0.0032 (12)	0.0020 (12)
C8	0.0391 (14)	0.0485 (15)	0.0363 (16)	0.0035 (12)	0.0017 (12)	0.0051 (12)

C11	0.0430 (14)	0.0420 (15)	0.0455 (17)	0.0019 (12)	0.0035 (13)	0.0063 (12)
C9	0.0388 (14)	0.0475 (16)	0.0448 (17)	0.0038 (12)	0.0066 (13)	0.0084 (13)
C12	0.0445 (15)	0.0456 (15)	0.0443 (17)	0.0036 (13)	0.0043 (13)	0.0067 (13)
C3	0.0651 (19)	0.0452 (16)	0.0375 (16)	-0.0081 (14)	0.0095 (14)	0.0047 (13)
C10	0.0425 (15)	0.0452 (15)	0.0449 (17)	0.0052 (12)	0.0076 (13)	0.0074 (13)
C25	0.0414 (15)	0.0590 (17)	0.0388 (17)	-0.0062 (13)	-0.0040 (12)	0.0033 (13)
C14	0.0566 (17)	0.0428 (15)	0.0427 (17)	0.0023 (13)	0.0073 (14)	0.0001 (13)
C23	0.0530 (17)	0.0483 (17)	0.0471 (18)	0.0150 (14)	0.0088 (14)	0.0104 (13)
C20	0.0571 (17)	0.0469 (16)	0.0461 (18)	-0.0078 (14)	0.0098 (14)	-0.0081 (13)
C18	0.0478 (16)	0.0486 (16)	0.058 (2)	0.0084 (13)	0.0119 (15)	0.0024 (14)
C1	0.0419 (16)	0.072 (2)	0.0457 (19)	0.0046 (14)	0.0048 (14)	0.0091 (15)
C15	0.0624 (18)	0.0461 (16)	0.0514 (19)	-0.0057 (14)	0.0040 (16)	0.0100 (14)
C5	0.0418 (16)	0.071 (2)	0.052 (2)	-0.0087 (14)	-0.0021 (14)	0.0180 (15)
C21	0.084 (2)	0.0359 (16)	0.055 (2)	-0.0066 (15)	0.0205 (18)	-0.0081 (14)
C22	0.089 (2)	0.0395 (16)	0.051 (2)	0.0173 (16)	0.0258 (18)	0.0056 (14)
C16	0.0475 (17)	0.077 (2)	0.0478 (19)	-0.0005 (16)	0.0150 (14)	0.0133 (16)
C2	0.0482 (17)	0.068 (2)	0.057 (2)	-0.0015 (15)	0.0164 (15)	0.0065 (16)
C17	0.0489 (17)	0.069 (2)	0.059 (2)	0.0123 (15)	0.0147 (15)	-0.0015 (16)
C4	0.0607 (19)	0.069 (2)	0.0461 (19)	-0.0070 (16)	-0.0079 (15)	0.0154 (15)

Geometric parameters (Å, º)

O1—C26	1.219 (3)	C3—C4	1.364 (4)
N1—C24	1.412 (3)	C10—H10	0.9400
N1—C26	1.357 (3)	C25—H25A	0.9700
N1—C25	1.445 (3)	C25—H25B	0.9700
C24—C19	1.381 (3)	C25—H25C	0.9700
C24—C23	1.378 (3)	C14—H14	0.9400
C6—C7	1.534 (3)	C14—C15	1.383 (4)
C6—C1	1.378 (4)	C23—H23	0.9400
C6—C5	1.381 (4)	C23—C22	1.387 (4)
C26—C7	1.556 (3)	C20—H20	0.9400
C19—C7	1.510 (3)	C20—C21	1.406 (4)

C19—C20	1.368 (3)	C18—H18	0.9400
C7—C8	1.543 (3)	C18—C17	1.373 (4)
C13—C12	1.460 (4)	C1—H1	0.9400
C13—C14	1.391 (4)	C1—C2	1.391 (4)
C13—C18	1.393 (4)	C15—H15	0.9400
C8—H8A	0.9800	C15—C16	1.374 (4)
C8—H8B	0.9800	C5—H5	0.9400
C8—C9	1.490 (4)	C5—C4	1.390 (4)
C11—H11	0.9400	C21—H21	0.9400
C11—C12	1.333 (4)	C21—C22	1.365 (4)
C11—C10	1.440 (4)	C22—H22	0.9400
C9—H9	0.9400	C16—H16	0.9400
C9—C10	1.319 (4)	C16—C17	1.373 (4)
C12—H12	0.9400	C2—H2	0.9400
C3—H3	0.9400	C17—H17	0.9400
C3—C2	1.357 (4)	C4—H4	0.9400
C24—N1—C25	124.3 (2)	N1—C25—H25A	109.5
C26—N1—C24	111.2 (2)	N1—C25—H25B	109.5
C26—N1—C25	124.5 (2)	N1—C25—H25C	109.5
C19—C24—N1	109.8 (2)	H25A—C25—H25B	109.5
C23—C24—N1	127.5 (2)	H25A—C25—H25C	109.5
C23—C24—C19	122.7 (2)	H25B—C25—H25C	109.5
C1—C6—C7	119.6 (2)	C13—C14—H14	119.6
C1—C6—C5	117.1 (2)	C15—C14—C13	120.7 (3)
C5—C6—C7	123.3 (2)	C15—C14—H14	119.6
O1—C26—N1	125.5 (2)	C24—C23—H23	121.6
O1—C26—C7	126.2 (2)	C24—C23—C22	116.8 (3)
N1—C26—C7	108.2 (2)	C22—C23—H23	121.6
C24—C19—C7	109.4 (2)	C19—C20—H20	120.6
C20—C19—C24	119.7 (2)	C19—C20—C21	118.8 (3)
C20—C19—C7	130.8 (2)	C21—C20—H20	120.6

C6—C7—C26	108.48 (19)	C13—C18—H18	119.3
C6—C7—C8	112.2 (2)	C17—C18—C13	121.3 (3)
C19—C7—C6	112.1 (2)	C17—C18—H18	119.3
C19—C7—C26	101.28 (19)	C6—C1—H1	119.2
C19—C7—C8	112.1 (2)	C6—C1—C2	121.6 (3)
C8—C7—C26	110.0 (2)	C2—C1—H1	119.2
C14—C13—C12	122.5 (2)	C14—C15—H15	119.9
C14—C13—C18	117.7 (3)	C16—C15—C14	120.2 (3)
C18—C13—C12	119.8 (2)	C16—C15—H15	119.9
C7—C8—H8A	108.5	C6—C5—H5	119.6
C7—C8—H8B	108.5	C6—C5—C4	120.8 (3)
H8A—C8—H8B	107.5	C4—C5—H5	119.6
C9—C8—C7	115.1 (2)	C20—C21—H21	120.0
C9—C8—H8A	108.5	C22—C21—C20	120.0 (3)
C9—C8—H8B	108.5	C22—C21—H21	120.0
C12—C11—H11	117.3	C23—C22—H22	119.0
C12—C11—C10	125.5 (3)	C21—C22—C23	122.0 (3)
C10—C11—H11	117.3	C21—C22—H22	119.0
C8—C9—H9	117.0	C15—C16—H16	120.0
C10—C9—C8	125.9 (3)	C17—C16—C15	119.9 (3)
C10—C9—H9	117.0	C17—C16—H16	120.0
C13—C12—H12	116.3	C3—C2—C1	120.5 (3)
C11—C12—C13	127.3 (2)	C3—C2—H2	119.7
C11—C12—H12	116.3	C1—C2—H2	119.7
C2—C3—H3	120.6	C18—C17—H17	120.0
C2—C3—C4	118.8 (3)	C16—C17—C18	120.0 (3)
C4—C3—H3	120.6	C16—C17—H17	120.0
C11—C10—H10	117.1	C3—C4—C5	121.2 (3)
C9—C10—C11	125.8 (2)	C3—C4—H4	119.4
C9—C10—H10	117.1	C5—C4—H4	119.4

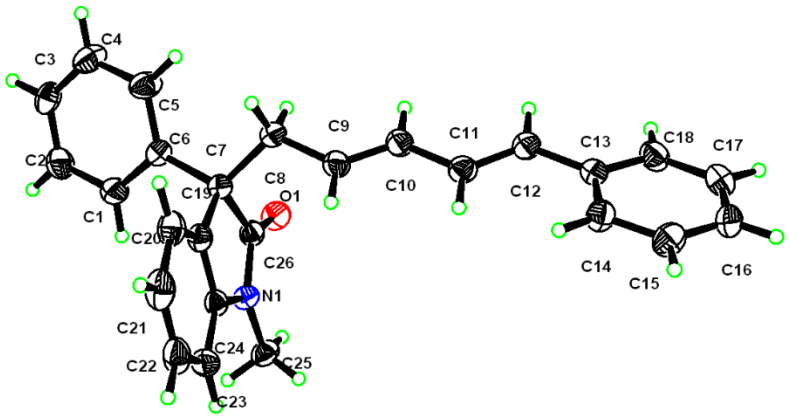


Figure S1. X-ray crystal structure of compound **3aa**

7.2 X-Ray Crystallography Data of 6a

Computing details

Cell refinement: *SAINT* v8.34A (Bruker, 2013); data reduction: *SAINT* v8.34A (Bruker, 2013); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

References

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

(cu_2017209_0m_a)

Crystal data

$C_{37}H_{32}N_2O_3$	$Z = 2$

M_r = 552.64	F(000) = 584
Triclinic, $P\bar{1}$	D_x = 1.299 Mg m^{-3}
a = 7.3961 (5) Å	Cu $K\alpha$ radiation, λ = 1.54178 Å
b = 14.159 (2) Å	Cell parameters from 826 reflections
c = 14.7965 (10) Å	θ = 38.5–68.3°
α = 113.245 (5)°	μ = 0.65 mm^{-1}
β = 93.815 (2)°	T = 205 K
γ = 94.009 (4)°	Block, colourless
V = 1412.7 (3) Å^3	0.28 × 0.12 × 0.08 mm

Data collection

Bruker APEX-II CCD diffractometer	3916 reflections with $I > 2\sigma(I)$
ϕ and ω scans	R_{int} = 0.027
Absorption correction: multi-scan *SADABS2014*/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.0732 before and 0.0386 after correction. The Ratio of minimum to maximum transmission is 0.8758. The λ/2 correction factor is 0.00150.	θ_{max} = 61.2°, θ_{min} = 5.6°
T_{min} = 0.660, T_{max} = 0.754	h = -8→8
13633 measured reflections	k = -16→16
4140 independent reflections	l = -16→16

Refinement

Refinement on F^2	7 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.040	H-atom parameters constrained
$wR(F^2)$ = 0.107	$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 0.3071P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.11	$(\Delta/\sigma)_{max}$ = 0.001
4140 reflections	$\Delta\rangle_{max}$ = 0.20 e Å^{-3}

380 parameters	$\Delta\rangle_{min}$ = -0.31 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O3	0.00044 (13)	0.09252 (8)	0.87073 (7)	0.0342 (3)
O1	0.85758 (13)	0.33551 (8)	0.70942 (8)	0.0369 (3)
O2	0.52245 (13)	0.30788 (8)	0.98446 (8)	0.0390 (3)
N2	0.28086 (14)	0.18252 (9)	0.93201 (8)	0.0254 (3)
N1	0.64848 (16)	0.35802 (9)	0.60062 (9)	0.0311 (3)
C21	0.11680 (17)	0.22271 (10)	0.81314 (10)	0.0259 (3)
H21	-0.0002	0.2530	0.8150	0.031*
C23	0.37821 (17)	0.27013 (10)	0.93484 (10)	0.0267 (3)
C13	0.49859 (18)	0.41504 (10)	0.60568 (11)	0.0289 (3)
C24	0.11645 (17)	0.15764 (10)	0.87274 (10)	0.0255 (3)
C15	0.72834 (18)	0.37662 (10)	0.69261 (10)	0.0273 (3)
C17	0.39926 (18)	0.32780 (11)	0.79335 (10)	0.0281 (3)
H17	0.3206	0.3433	0.7452	0.034*
C8	0.48283 (18)	0.47803 (10)	0.70351 (10)	0.0270 (3)
C16	0.54554 (19)	0.41917 (11)	0.84254 (10)	0.0299 (3)
H16A	0.6432	0.3984	0.8766	0.036*
H16B	0.4922	0.4757	0.8926	0.036*
C7	0.62945 (18)	0.45970 (10)	0.76938 (10)	0.0270 (3)

C22	0.27431 (17)	0.30890 (10)	0.86607 (10)	0.0258 (3)
H22	0.2240	0.3739	0.9057	0.031*
C20	0.15006 (18)	0.15564 (11)	0.70272 (10)	0.0284 (3)
H20	0.1202	0.1975	0.6648	0.034*
C37	0.57157 (19)	0.02602 (12)	0.86711 (11)	0.0330 (3)
H37	0.6468	0.0889	0.8913	0.040*
C18	0.46934 (19)	0.22551 (11)	0.73767 (10)	0.0304 (3)
H18	0.5946	0.2207	0.7322	0.036*
C6	0.77331 (18)	0.55204 (11)	0.82324 (10)	0.0285 (3)
C19	0.35012 (19)	0.14286 (11)	0.69671 (10)	0.0301 (3)
H19	0.3892	0.0771	0.6643	0.036*
C31	0.34289 (19)	0.11674 (11)	0.98050 (10)	0.0297 (3)
H31A	0.2431	0.0976	1.0124	0.036*
H31B	0.4435	0.1545	1.0315	0.036*
C1	0.7776 (2)	0.64047 (11)	0.80431 (12)	0.0351 (3)
H1	0.6853	0.6466	0.7607	0.042*
C32	0.40564 (18)	0.02078 (11)	0.90493 (10)	0.0276 (3)
C9	0.3411 (2)	0.53879 (12)	0.72649 (12)	0.0359 (4)
H9	0.3285	0.5817	0.7925	0.043*
C36	0.6267 (2)	-0.05992 (13)	0.79465 (12)	0.0396 (4)
H36	0.7394	-0.0556	0.7699	0.048*
C29	-0.0395 (2)	-0.12683 (12)	0.60919 (12)	0.0414 (4)
H29	-0.0053	-0.1887	0.6113	0.050*
C33	0.2968 (2)	-0.07263 (11)	0.86849 (11)	0.0339 (3)
H33	0.1846	-0.0774	0.8935	0.041*
C5	0.9122 (2)	0.54543 (12)	0.88827 (11)	0.0362 (3)
H5	0.9123	0.4859	0.9018	0.043*
C10	0.2165 (2)	0.53540 (13)	0.64980 (14)	0.0460 (4)
H10	0.1186	0.5761	0.6644	0.055*
C25	0.02541 (18)	0.05604 (11)	0.65518 (10)	0.0285 (3)
C30	0.0735 (2)	-0.03634 (12)	0.65705 (11)	0.0347 (3)
H30	0.1846	-0.0371	0.6914	0.042*

C3	1.0527 (2)	0.71249 (12)	0.91330 (12)	0.0406 (4)
H3	1.1469	0.7665	0.9434	0.049*
C12	0.3780 (2)	0.41174 (12)	0.52896 (12)	0.0404 (4)
H12	0.3915	0.3696	0.4629	0.048*
C4	1.0494 (2)	0.62508 (13)	0.93298 (12)	0.0411 (4)
H4	1.1414	0.6197	0.9772	0.049*
C2	0.9167 (2)	0.72004 (12)	0.84915 (13)	0.0412 (4)
H2	0.9181	0.7796	0.8356	0.049*
C26	-0.1417 (2)	0.05514 (12)	0.60583 (11)	0.0350 (3)
H26	-0.1783	0.1171	0.6051	0.042*
C34	0.3521 (2)	-0.15884 (12)	0.79570 (12)	0.0401 (4)
H34	0.2778	-0.2220	0.7715	0.048*
C28	-0.2027 (2)	-0.12690 (13)	0.55814 (12)	0.0464 (4)
H28	-0.2781	-0.1890	0.5238	0.056*
C11	0.2354 (2)	0.47338 (14)	0.55356 (14)	0.0483 (4)
H11	0.1503	0.4725	0.5030	0.058*
C27	-0.2542 (2)	-0.03549 (14)	0.55794 (12)	0.0440 (4)
H27	-0.3668	-0.0349	0.5249	0.053*
C14	0.7086 (2)	0.28512 (14)	0.51078 (12)	0.0459 (4)
H14A	0.6190	0.2251	0.4816	0.069*
H14B	0.8246	0.2638	0.5260	0.069*
H14C	0.7227	0.3175	0.4645	0.069*
C35	0.5169 (2)	-0.15215 (13)	0.75846 (12)	0.0408 (4)
H35	0.5539	-0.2106	0.7084	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0292 (5)	0.0374 (6)	0.0354 (6)	-0.0050 (4)	0.0039 (4)	0.0152 (5)
O1	0.0335 (5)	0.0378 (6)	0.0460 (7)	0.0141 (4)	0.0051 (4)	0.0220 (5)
O2	0.0333 (6)	0.0460 (6)	0.0380 (6)	-0.0097 (5)	-0.0086 (5)	0.0214 (5)
N2	0.0249 (6)	0.0282 (6)	0.0246 (6)	0.0028 (4)	0.0015 (4)	0.0122 (5)
N1	0.0352 (6)	0.0311 (6)	0.0285 (7)	0.0126 (5)	0.0073 (5)	0.0113 (6)

C21	0.0234 (6)	0.0277 (7)	0.0269 (7)	0.0063 (5)	0.0016 (5)	0.0107 (6)
C23	0.0267 (7)	0.0290 (7)	0.0226 (7)	0.0026 (5)	0.0035 (5)	0.0084 (6)
C13	0.0287 (7)	0.0265 (7)	0.0337 (8)	0.0038 (5)	0.0036 (6)	0.0142 (7)
C24	0.0241 (7)	0.0277 (7)	0.0229 (7)	0.0050 (5)	0.0046 (5)	0.0075 (6)
C15	0.0268 (7)	0.0267 (7)	0.0329 (8)	0.0049 (5)	0.0058 (5)	0.0159 (6)
C17	0.0312 (7)	0.0289 (7)	0.0265 (7)	0.0034 (6)	0.0029 (5)	0.0136 (6)
C8	0.0267 (7)	0.0247 (7)	0.0332 (8)	0.0025 (5)	0.0048 (6)	0.0151 (6)
C16	0.0334 (7)	0.0298 (7)	0.0282 (8)	0.0020 (6)	0.0044 (6)	0.0134 (7)
C7	0.0285 (7)	0.0263 (7)	0.0284 (7)	0.0044 (5)	0.0042 (6)	0.0130 (6)
C22	0.0278 (7)	0.0233 (7)	0.0266 (7)	0.0050 (5)	0.0039 (5)	0.0099 (6)
C20	0.0331 (7)	0.0296 (7)	0.0240 (7)	0.0047 (6)	0.0009 (5)	0.0124 (6)
C37	0.0324 (7)	0.0352 (8)	0.0323 (8)	0.0010 (6)	0.0027 (6)	0.0150 (7)
C18	0.0299 (7)	0.0333 (8)	0.0295 (8)	0.0044 (6)	0.0079 (6)	0.0134 (7)
C6	0.0289 (7)	0.0286 (7)	0.0276 (7)	0.0040 (6)	0.0088 (6)	0.0098 (6)
C19	0.0354 (8)	0.0296 (7)	0.0255 (7)	0.0068 (6)	0.0074 (6)	0.0100 (6)
C31	0.0323 (7)	0.0352 (8)	0.0267 (7)	0.0052 (6)	0.0028 (6)	0.0175 (7)
C1	0.0351 (8)	0.0313 (8)	0.0407 (9)	0.0043 (6)	0.0060 (6)	0.0158 (7)
C32	0.0304 (7)	0.0320 (7)	0.0255 (7)	0.0039 (6)	-0.0005 (5)	0.0174 (6)
C9	0.0330 (8)	0.0323 (8)	0.0450 (9)	0.0094 (6)	0.0097 (6)	0.0165 (7)
C36	0.0395 (8)	0.0483 (9)	0.0340 (9)	0.0104 (7)	0.0092 (6)	0.0178 (8)
C29	0.0506 (9)	0.0286 (8)	0.0439 (9)	0.0063 (7)	0.0216 (7)	0.0103 (7)
C33	0.0325 (7)	0.0345 (8)	0.0401 (9)	0.0028 (6)	0.0018 (6)	0.0212 (7)
C5	0.0336 (8)	0.0418 (8)	0.0385 (9)	-0.0001 (6)	0.0032 (6)	0.0224 (7)
C10	0.0319 (8)	0.0438 (9)	0.0678 (12)	0.0132 (7)	0.0033 (7)	0.0269 (9)
C25	0.0324 (7)	0.0312 (7)	0.0207 (7)	0.0045 (6)	0.0041 (5)	0.0088 (6)
C30	0.0351 (8)	0.0352 (8)	0.0352 (8)	0.0069 (6)	0.0072 (6)	0.0147 (7)
C3	0.0366 (8)	0.0373 (8)	0.0382 (9)	-0.0059 (6)	0.0105 (7)	0.0055 (7)
C12	0.0441 (9)	0.0400 (8)	0.0358 (9)	0.0049 (7)	-0.0043 (7)	0.0151 (7)
C4	0.0320 (8)	0.0540 (10)	0.0352 (9)	-0.0034 (7)	0.0020 (6)	0.0171 (8)
C2	0.0433 (9)	0.0288 (8)	0.0503 (10)	0.0009 (6)	0.0124 (7)	0.0140 (7)
C26	0.0365 (8)	0.0398 (8)	0.0273 (8)	0.0057 (6)	0.0007 (6)	0.0120 (7)
C34	0.0475 (9)	0.0291 (8)	0.0427 (9)	0.0012 (6)	-0.0071 (7)	0.0157 (7)

C28	0.0467 (9)	0.0407 (9)	0.0363 (9)	-0.0098 (7)	0.0114 (7)	0.0003 (8)
C11	0.0395 (9)	0.0507 (10)	0.0566 (11)	0.0080 (7)	-0.0115 (8)	0.0257 (9)
C27	0.0353 (8)	0.0557 (10)	0.0327 (9)	-0.0036 (7)	-0.0019 (6)	0.0114 (8)
C14	0.0565 (10)	0.0460 (9)	0.0348 (9)	0.0206 (8)	0.0134 (7)	0.0121 (8)
C35	0.0544 (10)	0.0383 (8)	0.0290 (8)	0.0160 (7)	0.0019 (7)	0.0112 (7)

Geometric parameters (Å, º)

O3—C24	1.2048 (16)	C31—H31B	0.9800
O1—C15	1.2144 (17)	C31—C32	1.507 (2)
O2—C23	1.2121 (16)	C1—H1	0.9400
N2—C23	1.3744 (18)	C1—C2	1.388 (2)
N2—C24	1.3879 (17)	C32—C33	1.385 (2)
N2—C31	1.4615 (17)	C9—H9	0.9400
N1—C13	1.4053 (18)	C9—C10	1.397 (2)
N1—C15	1.3635 (19)	C36—H36	0.9400
N1—C14	1.446 (2)	C36—C35	1.376 (2)
C21—H21	0.9900	C29—H29	0.9400
C21—C24	1.5059 (19)	C29—C30	1.377 (2)
C21—C22	1.5445 (18)	C29—C28	1.380 (3)
C21—C20	1.579 (2)	C33—H33	0.9400
C23—C22	1.5243 (19)	C33—C34	1.381 (2)
C13—C8	1.387 (2)	C5—H5	0.9400
C13—C12	1.380 (2)	C5—C4	1.379 (2)
C15—C7	1.545 (2)	C10—H10	0.9400
C17—H17	0.9900	C10—C11	1.369 (3)
C17—C16	1.5266 (19)	C25—C30	1.389 (2)
C17—C22	1.5519 (19)	C25—C26	1.390 (2)
C17—C18	1.505 (2)	C30—H30	0.9400
C8—C7	1.5138 (19)	C3—H3	0.9400
C8—C9	1.377 (2)	C3—C4	1.378 (2)
C16—H16A	0.9800	C3—C2	1.375 (2)
C16—H16B	0.9800	C12—H12	0.9400

C16—C7	1.5543 (19)	C12—C11	1.391 (2)
C7—C6	1.5319 (19)	C4—H4	0.9400
C22—H22	0.9900	C2—H2	0.9400
C20—H20	0.9900	C26—H26	0.9400
C20—C19	1.507 (2)	C26—C27	1.377 (2)
C20—C25	1.5108 (19)	C34—H34	0.9400
C37—H37	0.9400	C34—C35	1.383 (3)
C37—C32	1.391 (2)	C28—H28	0.9400
C37—C36	1.376 (2)	C28—C27	1.376 (3)
C18—H18	0.9400	C11—H11	0.9400
C18—C19	1.319 (2)	C27—H27	0.9400
C6—C1	1.385 (2)	C14—H14A	0.9700
C6—C5	1.394 (2)	C14—H14B	0.9700
C19—H19	0.9400	C14—H14C	0.9700
C31—H31A	0.9800	C35—H35	0.9400
C23—N2—C24	113.01 (11)	N2—C31—C32	109.52 (11)
C23—N2—C31	125.25 (11)	H31A—C31—H31B	108.2
C24—N2—C31	121.66 (11)	C32—C31—H31A	109.8
C13—N1—C14	125.41 (13)	C32—C31—H31B	109.8
C15—N1—C13	111.34 (12)	C6—C1—H1	119.7
C15—N1—C14	123.19 (12)	C6—C1—C2	120.61 (14)
C24—C21—H21	110.1	C2—C1—H1	119.7
C24—C21—C22	104.18 (10)	C37—C32—C31	120.05 (13)
C24—C21—C20	110.41 (11)	C33—C32—C37	118.81 (14)
C22—C21—H21	110.1	C33—C32—C31	121.07 (13)
C22—C21—C20	111.69 (11)	C8—C9—H9	120.6
C20—C21—H21	110.1	C8—C9—C10	118.72 (15)
O2—C23—N2	124.20 (13)	C10—C9—H9	120.6
O2—C23—C22	127.32 (13)	C37—C36—H36	120.0
N2—C23—C22	108.48 (11)	C35—C36—C37	119.99 (15)
C8—C13—N1	109.58 (12)	C35—C36—H36	120.0

C12—C13—N1	128.12 (14)	C30—C29—H29	119.9
C12—C13—C8	122.29 (13)	C30—C29—C28	120.18 (15)
O3—C24—N2	123.34 (12)	C28—C29—H29	119.9
O3—C24—C21	128.54 (12)	C32—C33—H33	119.8
N2—C24—C21	108.10 (11)	C34—C33—C32	120.47 (14)
O1—C15—N1	124.88 (14)	C34—C33—H33	119.8
O1—C15—C7	126.82 (13)	C6—C5—H5	119.6
N1—C15—C7	108.28 (11)	C4—C5—C6	120.83 (14)
C16—C17—H17	107.2	C4—C5—H5	119.6
C16—C17—C22	114.02 (11)	C9—C10—H10	119.7
C22—C17—H17	107.2	C11—C10—C9	120.67 (15)
C18—C17—H17	107.2	C11—C10—H10	119.7
C18—C17—C16	115.22 (12)	C30—C25—C20	122.20 (12)
C18—C17—C22	105.43 (11)	C30—C25—C26	118.23 (13)
C13—C8—C7	109.24 (11)	C26—C25—C20	119.56 (13)
C9—C8—C13	119.71 (13)	C29—C30—C25	120.84 (14)
C9—C8—C7	130.91 (13)	C29—C30—H30	119.6
C17—C16—H16A	108.8	C25—C30—H30	119.6
C17—C16—H16B	108.8	C4—C3—H3	120.3
C17—C16—C7	113.93 (11)	C2—C3—H3	120.3
H16A—C16—H16B	107.7	C2—C3—C4	119.36 (14)
C7—C16—H16A	108.8	C13—C12—H12	121.4
C7—C16—H16B	108.8	C13—C12—C11	117.20 (16)
C15—C7—C16	111.62 (11)	C11—C12—H12	121.4
C8—C7—C15	101.46 (11)	C5—C4—H4	119.8
C8—C7—C16	111.35 (11)	C3—C4—C5	120.46 (15)
C8—C7—C6	114.55 (11)	C3—C4—H4	119.8
C6—C7—C15	105.86 (11)	C1—C2—H2	119.7
C6—C7—C16	111.45 (11)	C3—C2—C1	120.53 (15)
C21—C22—C17	112.85 (11)	C3—C2—H2	119.7
C21—C22—H22	109.6	C25—C26—H26	119.6
C23—C22—C21	103.81 (10)	C27—C26—C25	120.75 (15)

C23—C22—C17	111.29 (11)	C27—C26—H26	119.6
C23—C22—H22	109.6	C33—C34—H34	120.0
C17—C22—H22	109.6	C33—C34—C35	119.99 (14)
C21—C20—H20	106.1	C35—C34—H34	120.0
C19—C20—C21	109.50 (11)	C29—C28—H28	120.2
C19—C20—H20	106.1	C27—C28—C29	119.55 (14)
C19—C20—C25	114.60 (12)	C27—C28—H28	120.2
C25—C20—C21	113.81 (11)	C10—C11—C12	121.40 (15)
C25—C20—H20	106.1	C10—C11—H11	119.3
C32—C37—H37	119.6	C12—C11—H11	119.3
C36—C37—H37	119.6	C26—C27—H27	119.8
C36—C37—C32	120.71 (14)	C28—C27—C26	120.41 (15)
C17—C18—H18	120.9	C28—C27—H27	119.8
C19—C18—C17	118.13 (12)	N1—C14—H14A	109.5
C19—C18—H18	120.9	N1—C14—H14B	109.5
C1—C6—C7	121.86 (13)	N1—C14—H14C	109.5
C1—C6—C5	118.21 (13)	H14A—C14—H14B	109.5
C5—C6—C7	119.78 (12)	H14A—C14—H14C	109.5
C20—C19—H19	120.6	H14B—C14—H14C	109.5
C18—C19—C20	118.85 (13)	C36—C35—C34	120.03 (15)
C18—C19—H19	120.6	C36—C35—H35	120.0
N2—C31—H31A	109.8	C34—C35—H35	120.0
N2—C31—H31B	109.8		

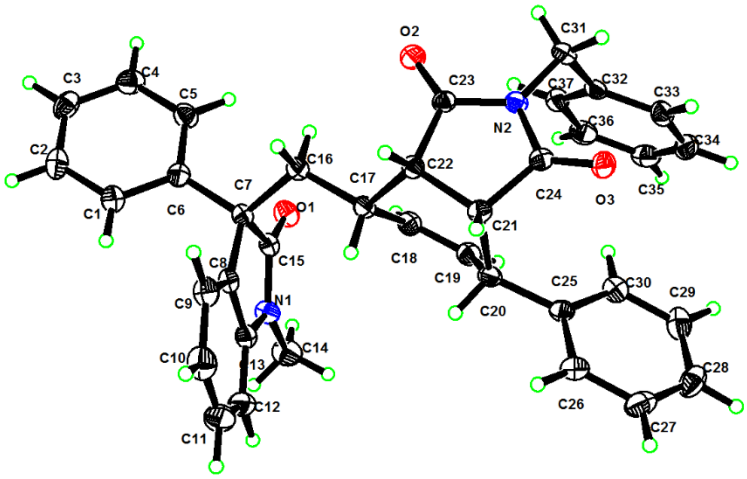
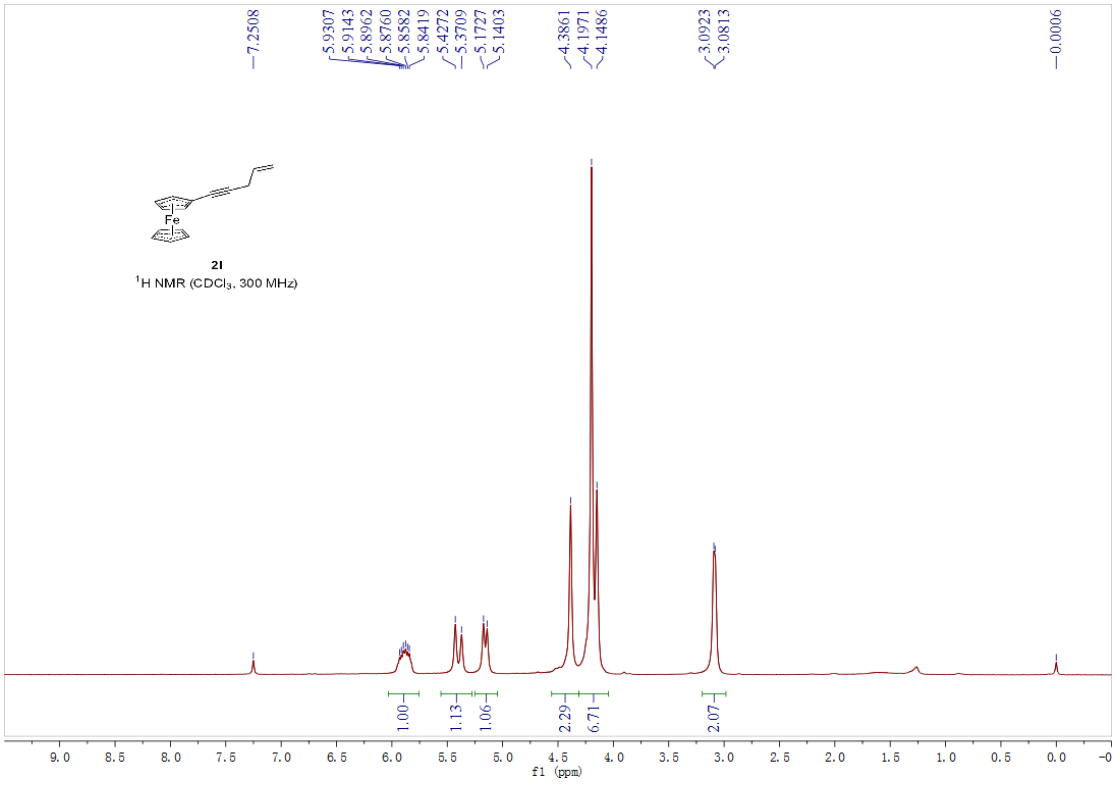
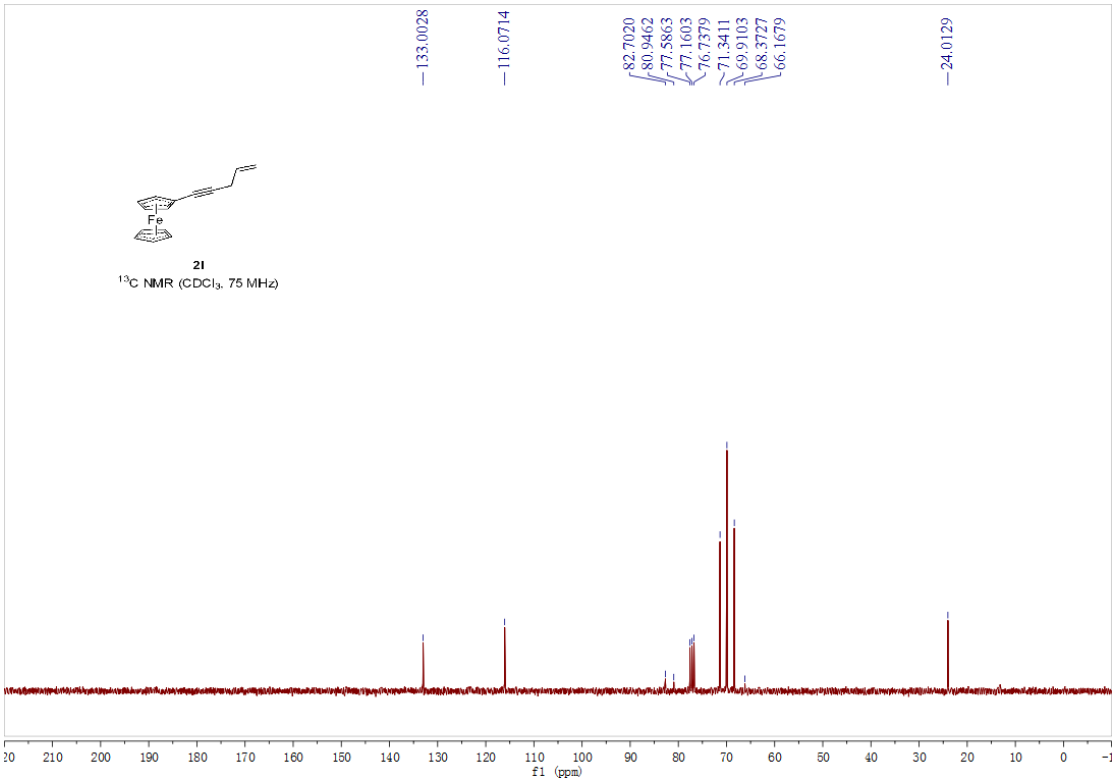


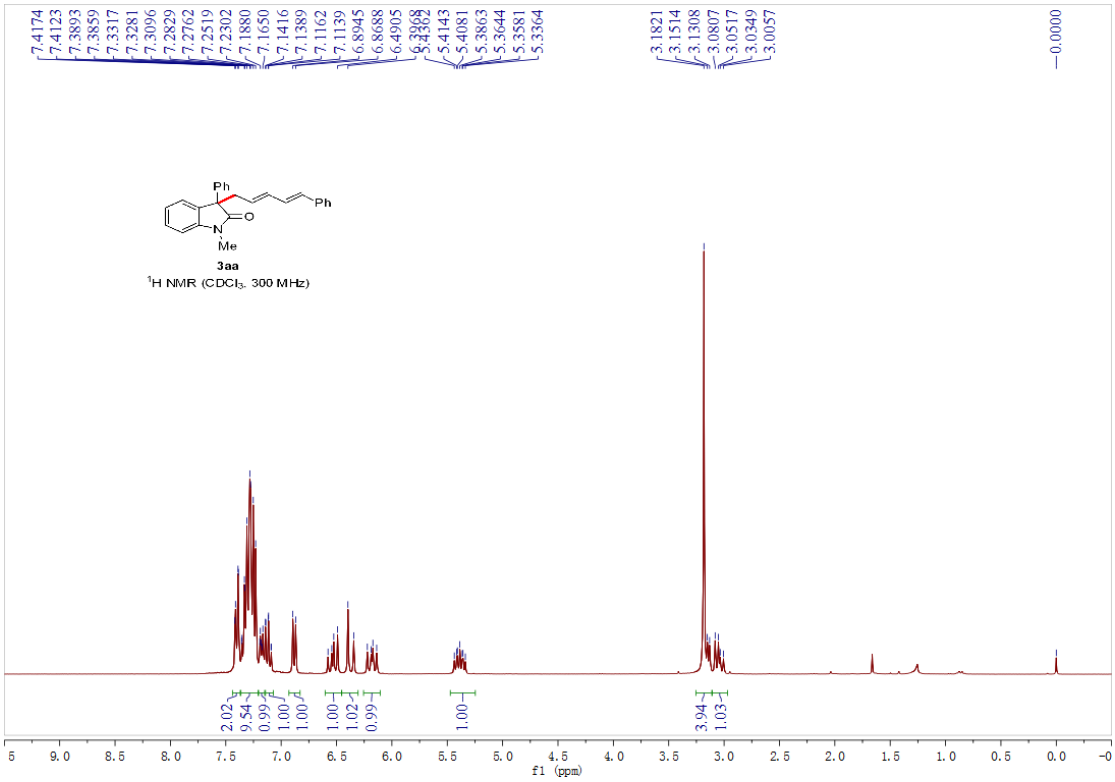
Figure S2. X-ray crystal structure of compound **6a**

8. ^{1}H, ^{13}C and ^{19}F NMR Spectra of the Title Compounds

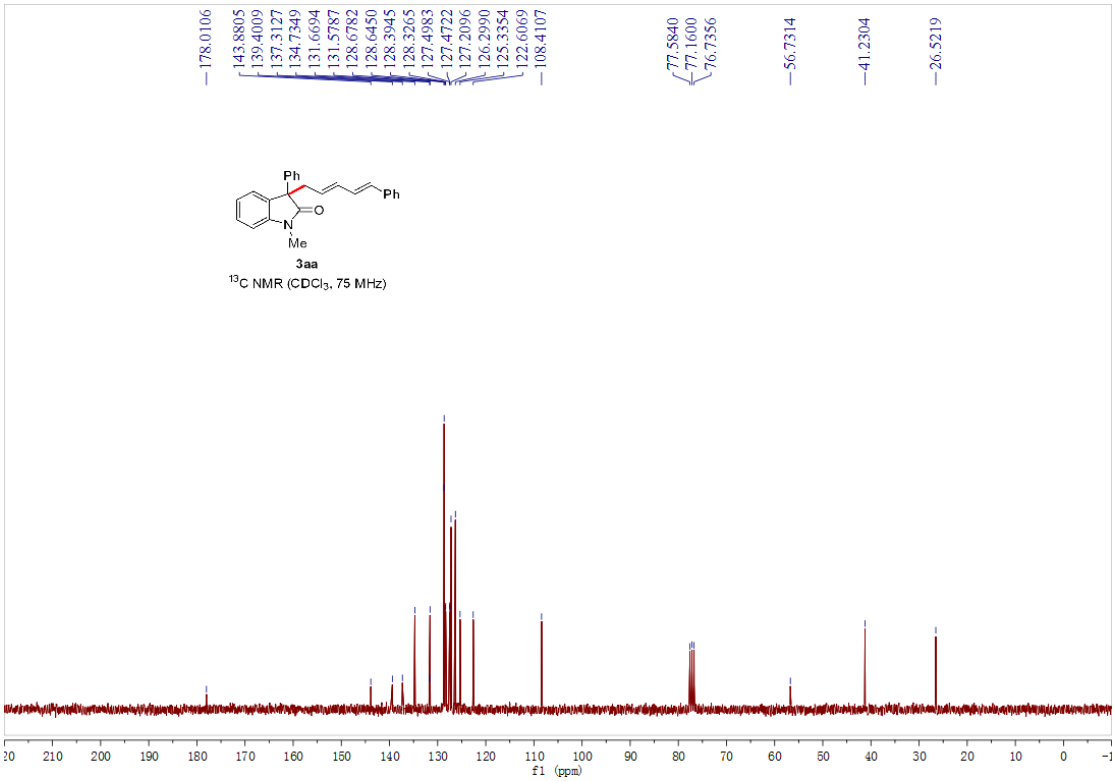




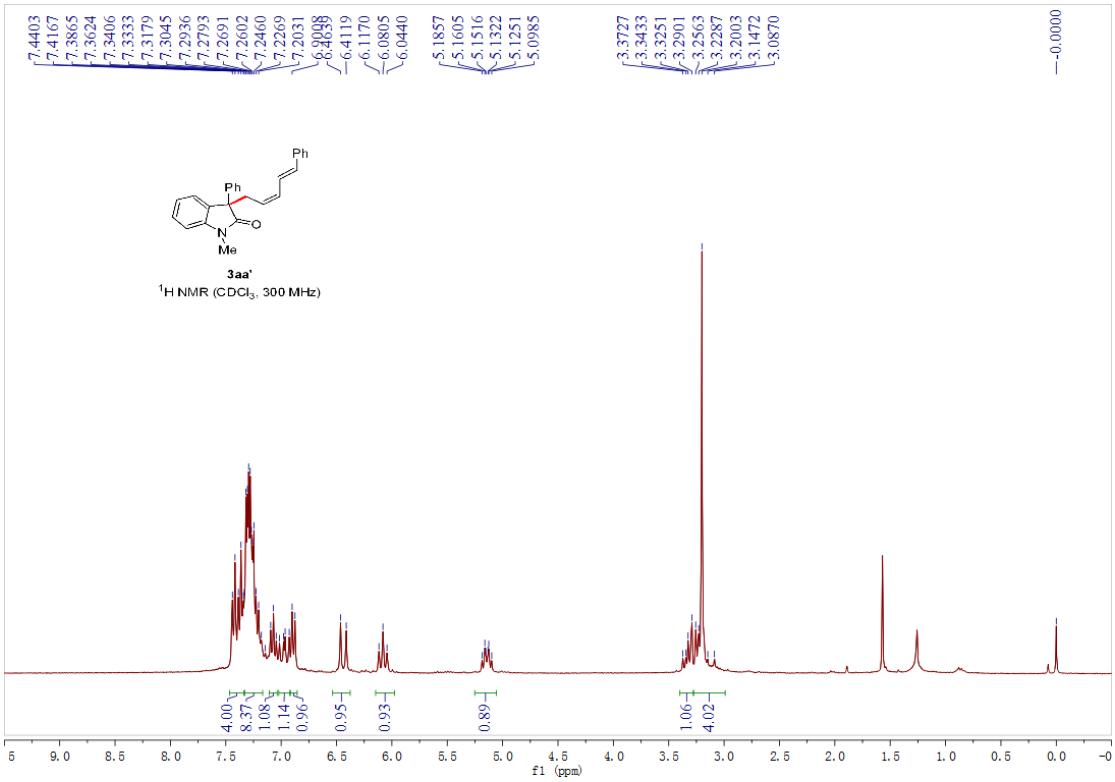
^{1}H NMR spectrum of purified **3aa**



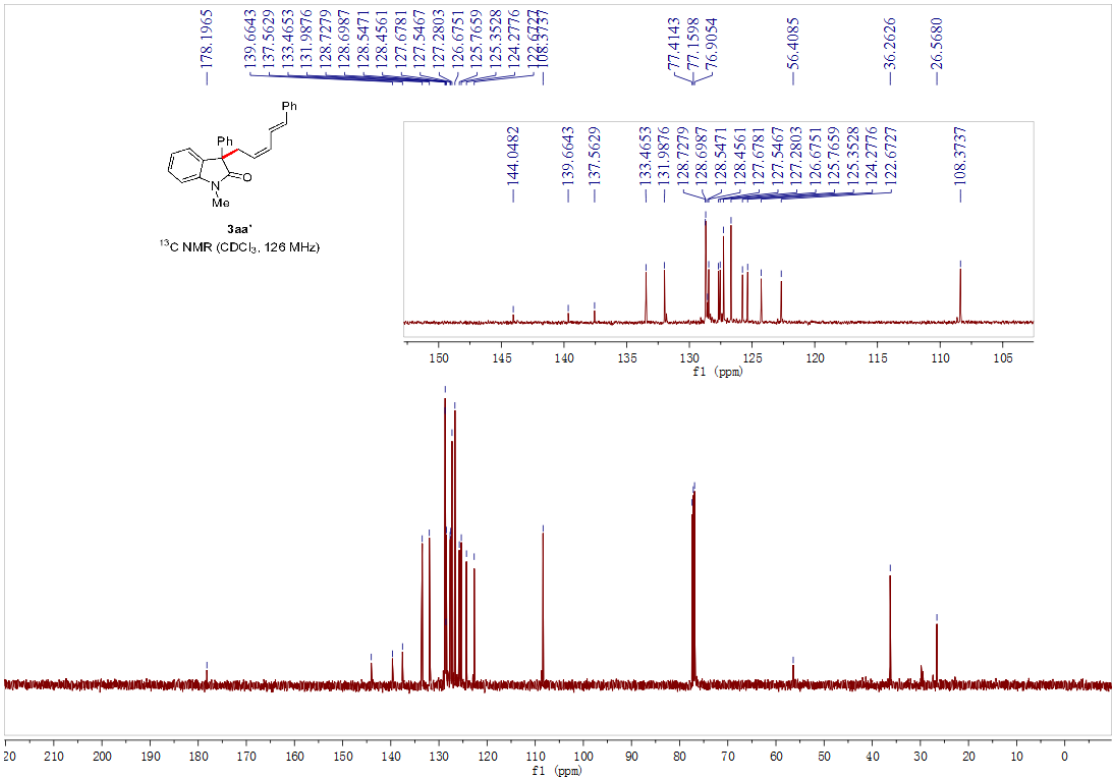
^{13}C NMR spectrum of purified **3aa**



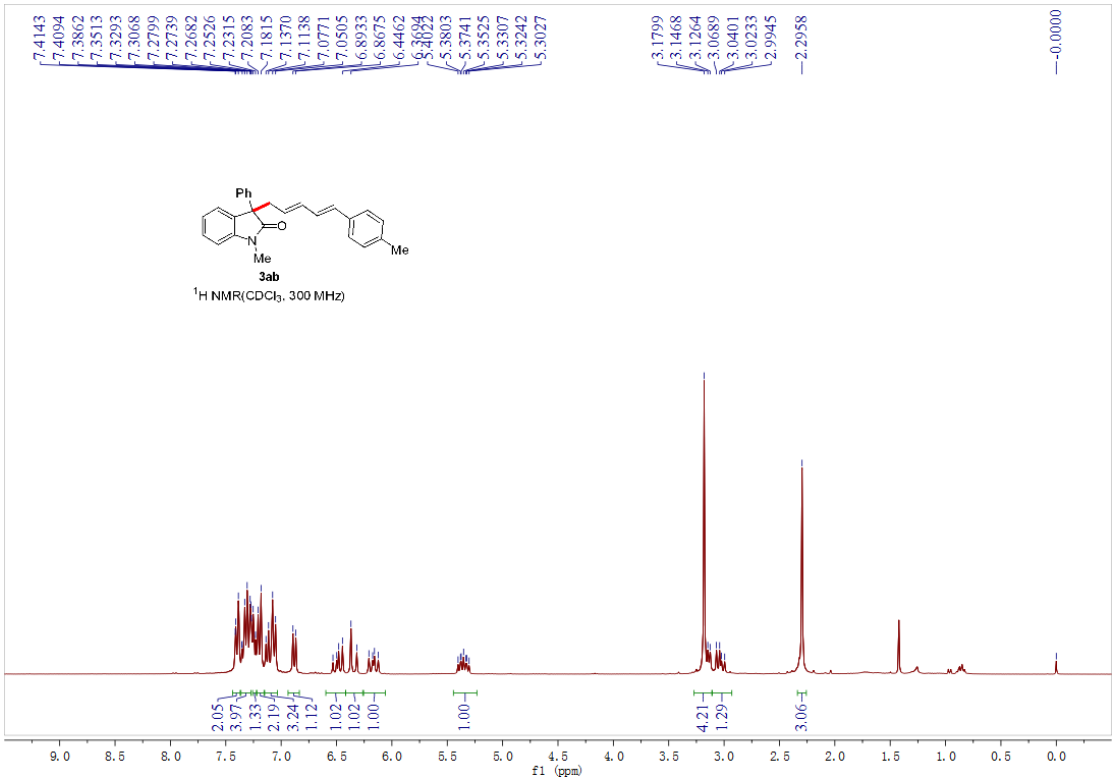
^{1}H NMR spectrum of purified **3aa'**



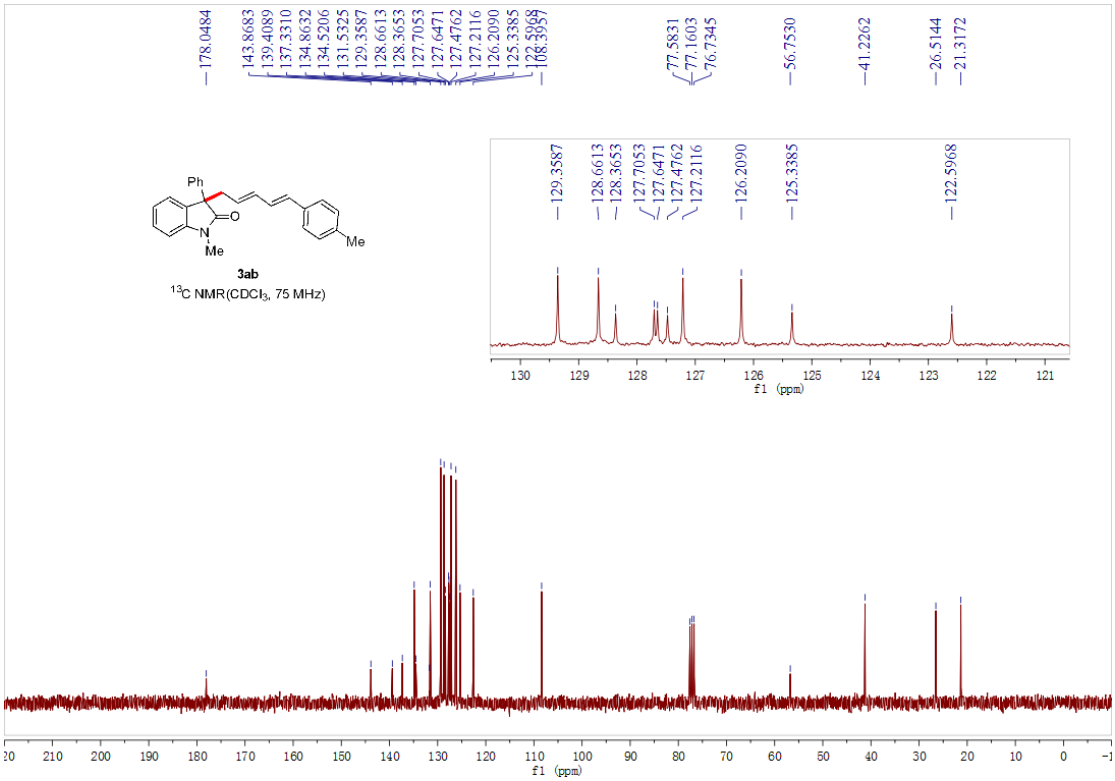
^{13}C NMR spectrum of purified **3aa'**



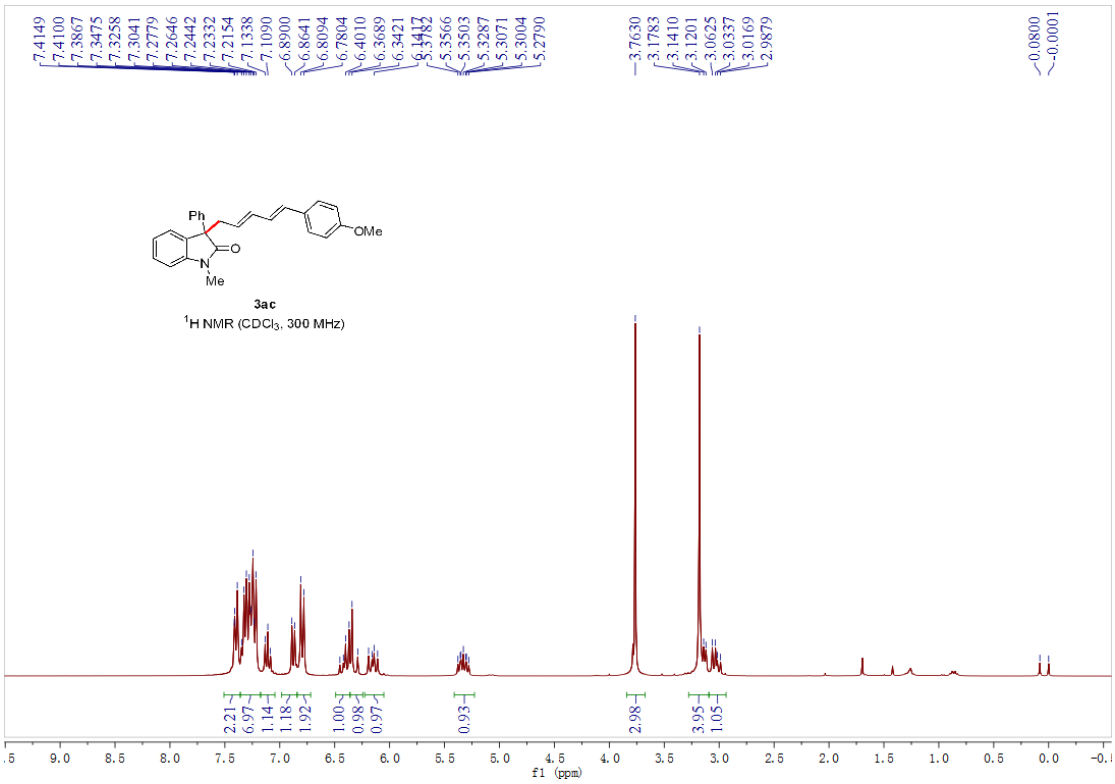
^{1}H NMR spectrum of purified **3ab**



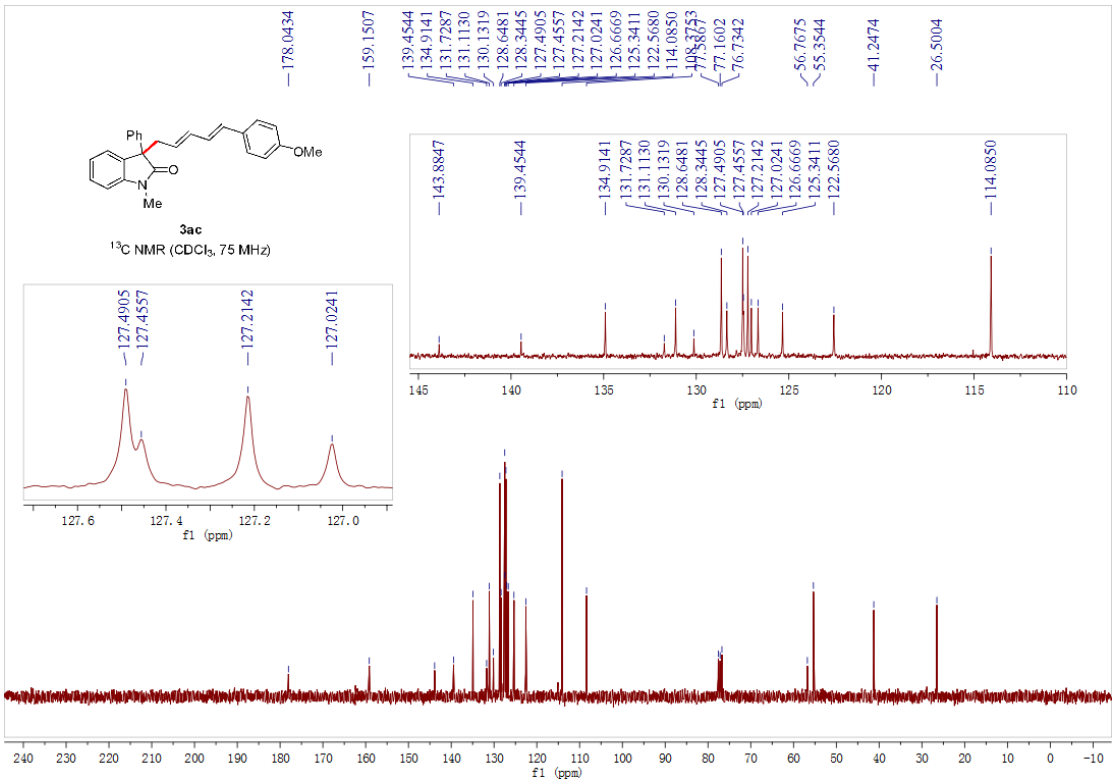
^{13}C NMR spectrum of purified **3ab**



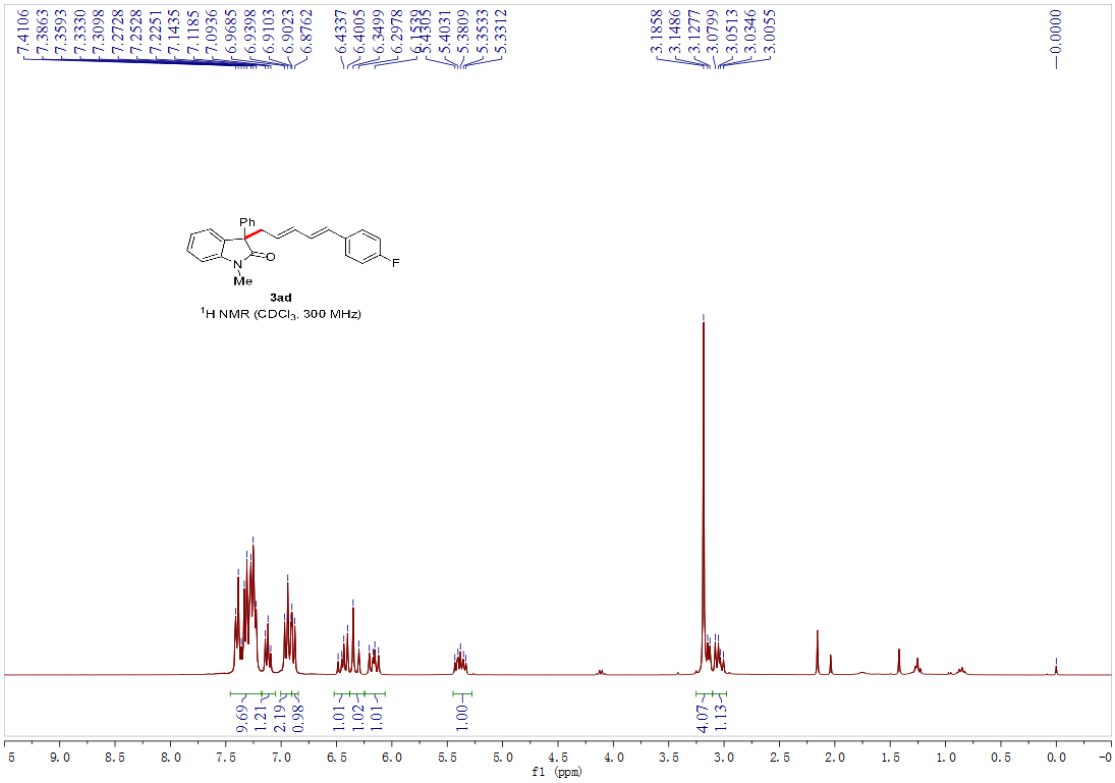
^{1}H NMR spectrum of purified **3ac**



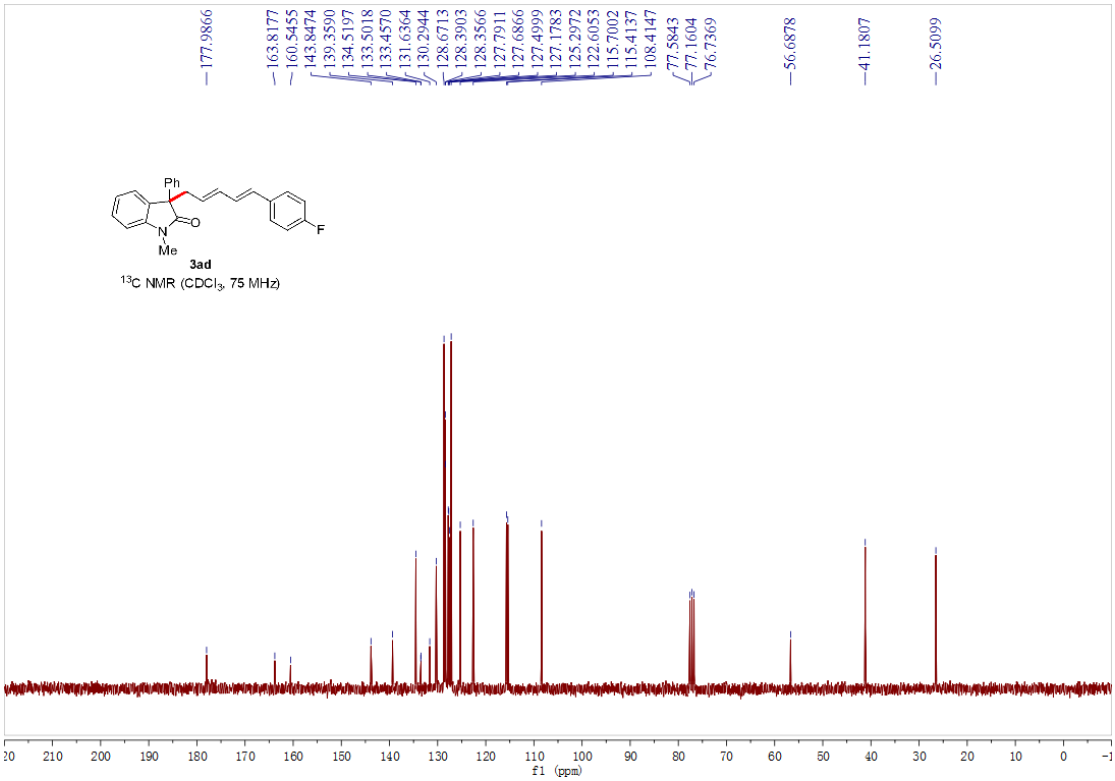
^{13}C NMR spectrum of purified **3ac**



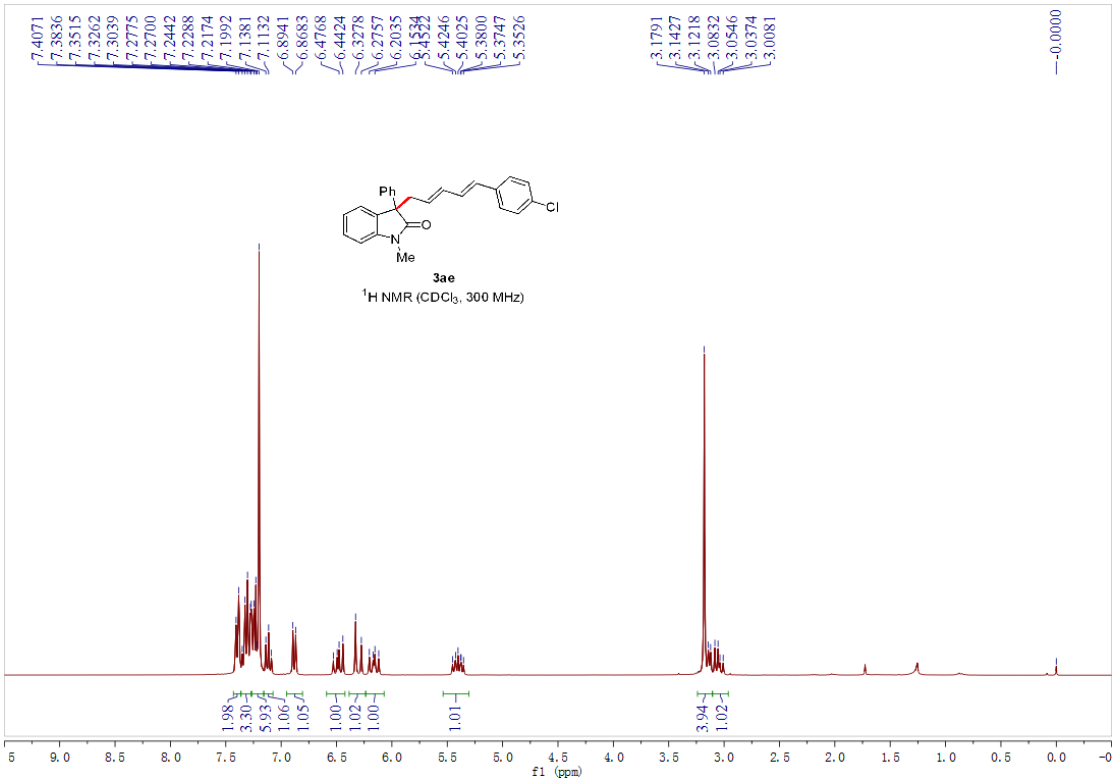
^{1}H NMR spectrum of purified **3ad**



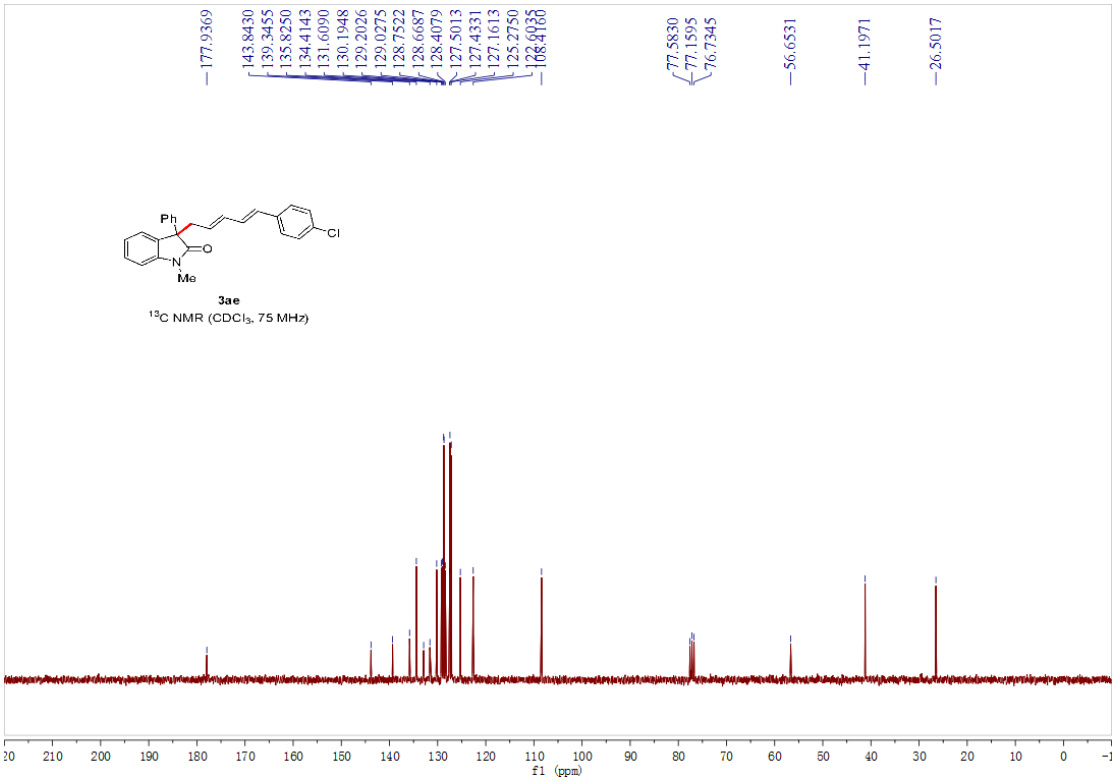
^{13}C NMR spectrum of purified **3ad**



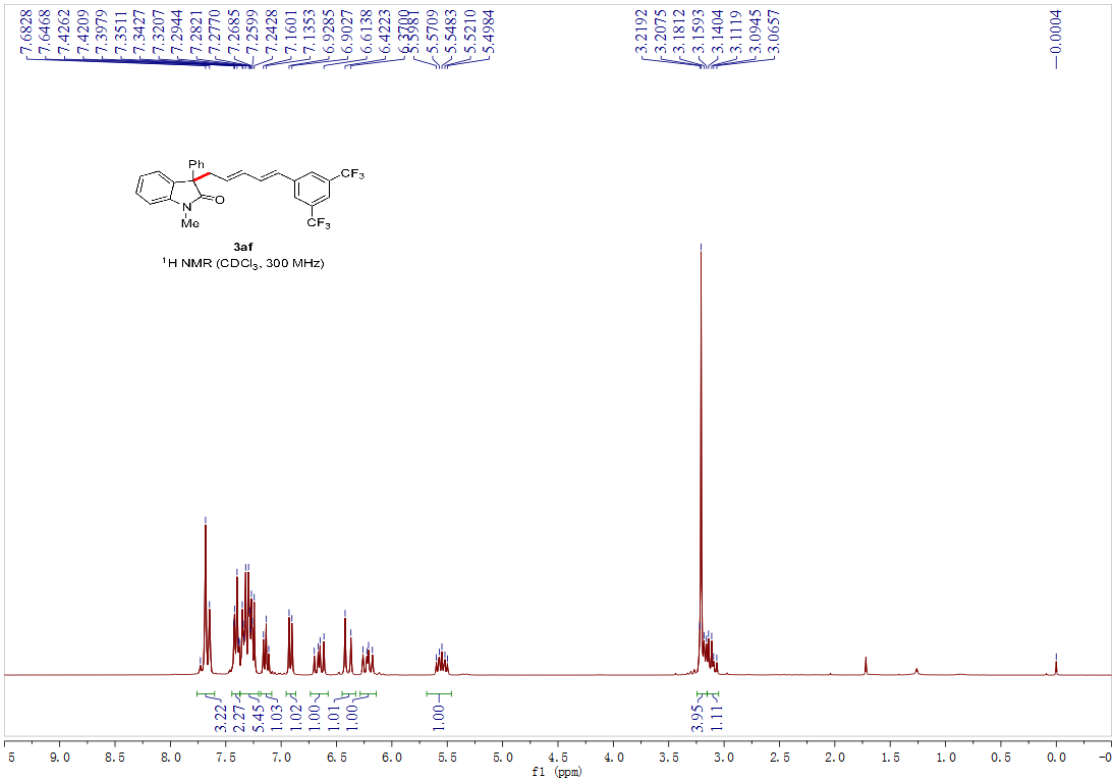
^{1}H NMR spectrum of purified **3ae**



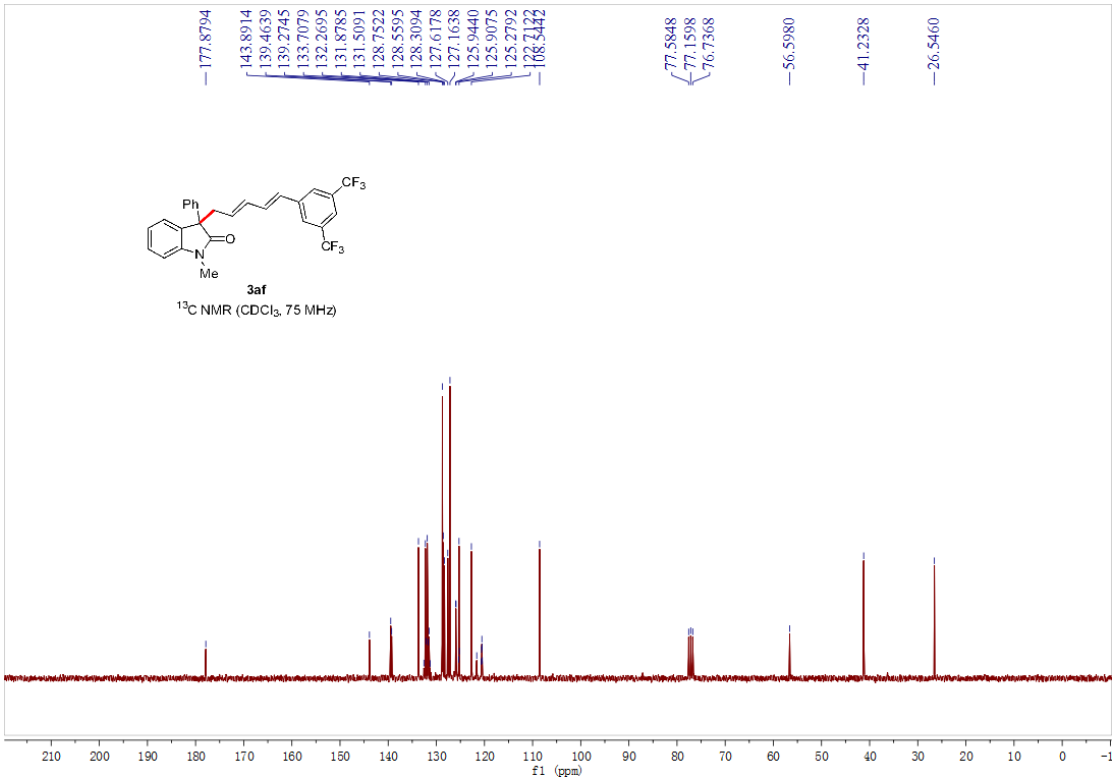
^{13}C NMR spectrum of purified **3ae**



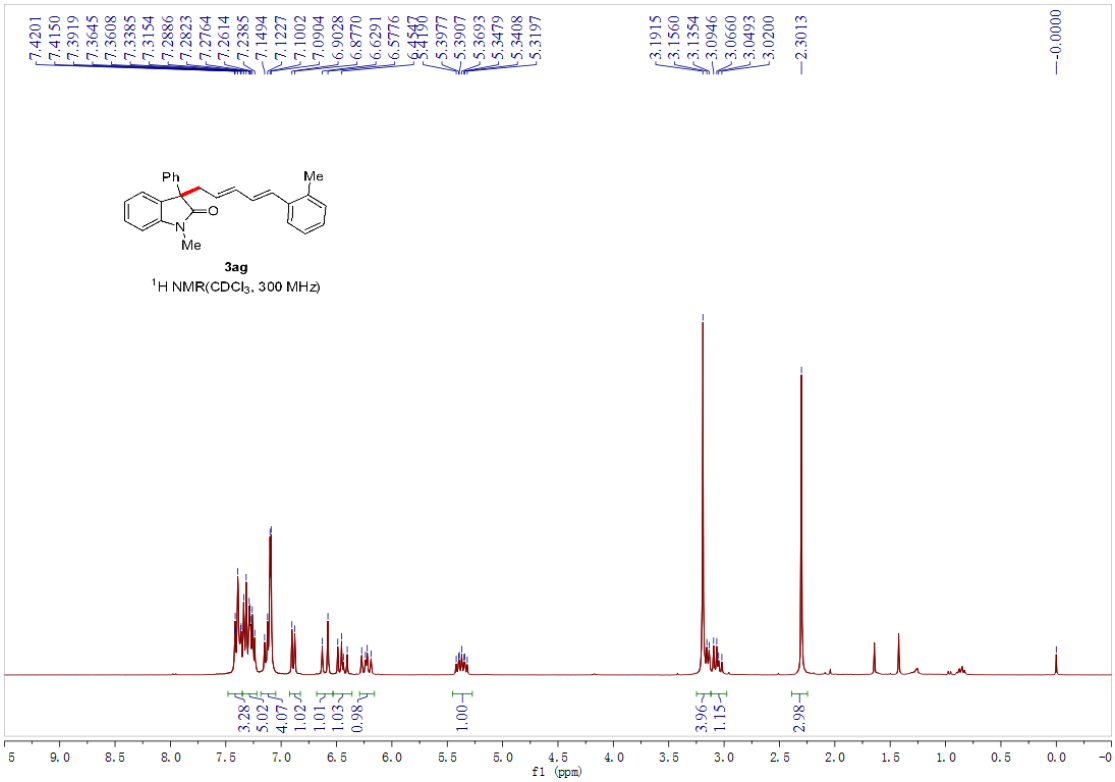
^{1}H NMR spectrum of purified **3af**



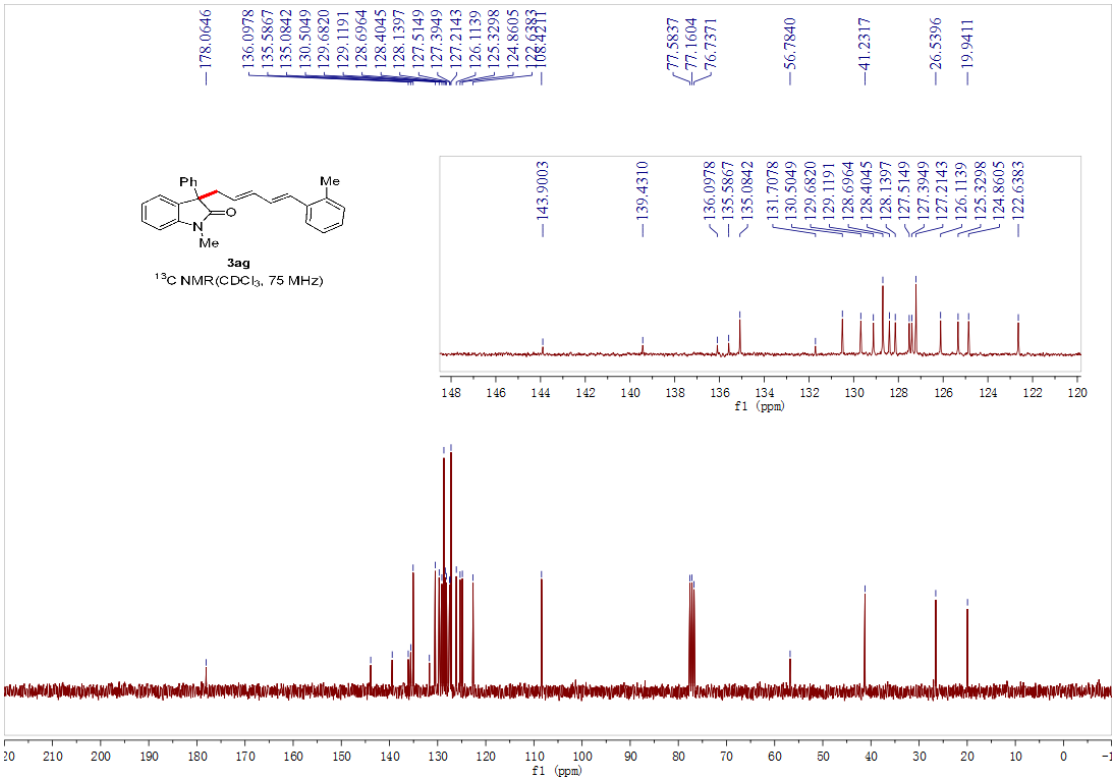
^{13}C NMR spectrum of purified **3af**



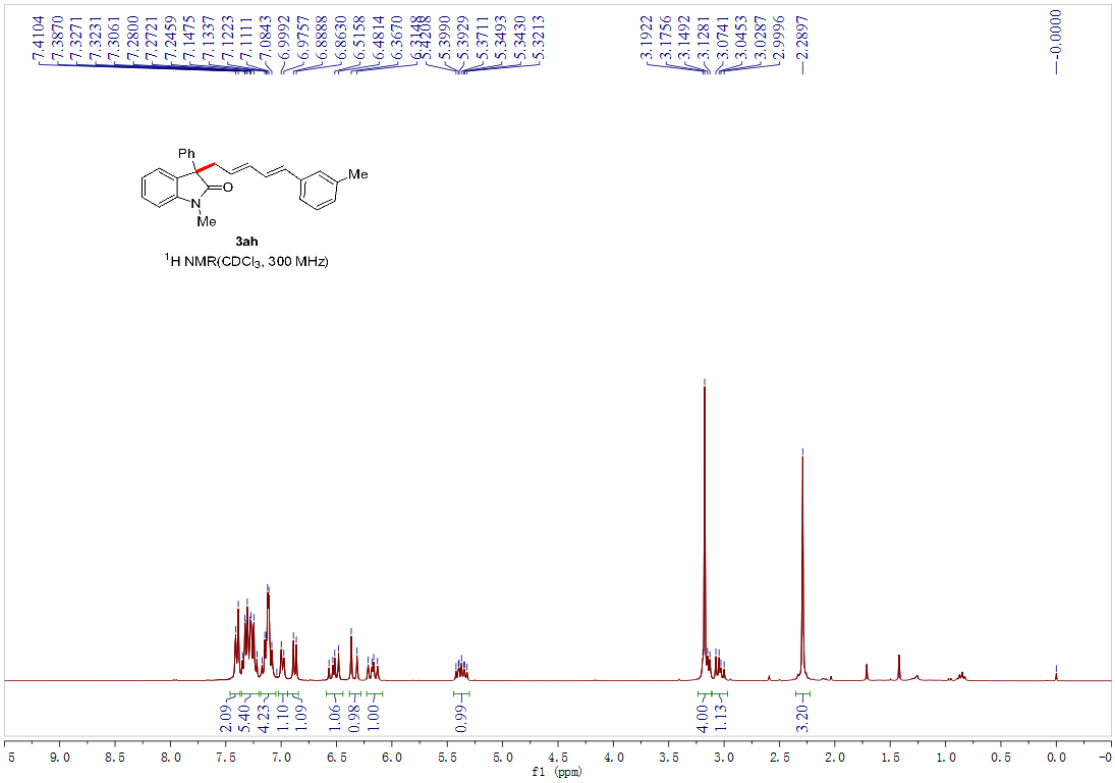
^{1}H NMR spectrum of purified **3ag**



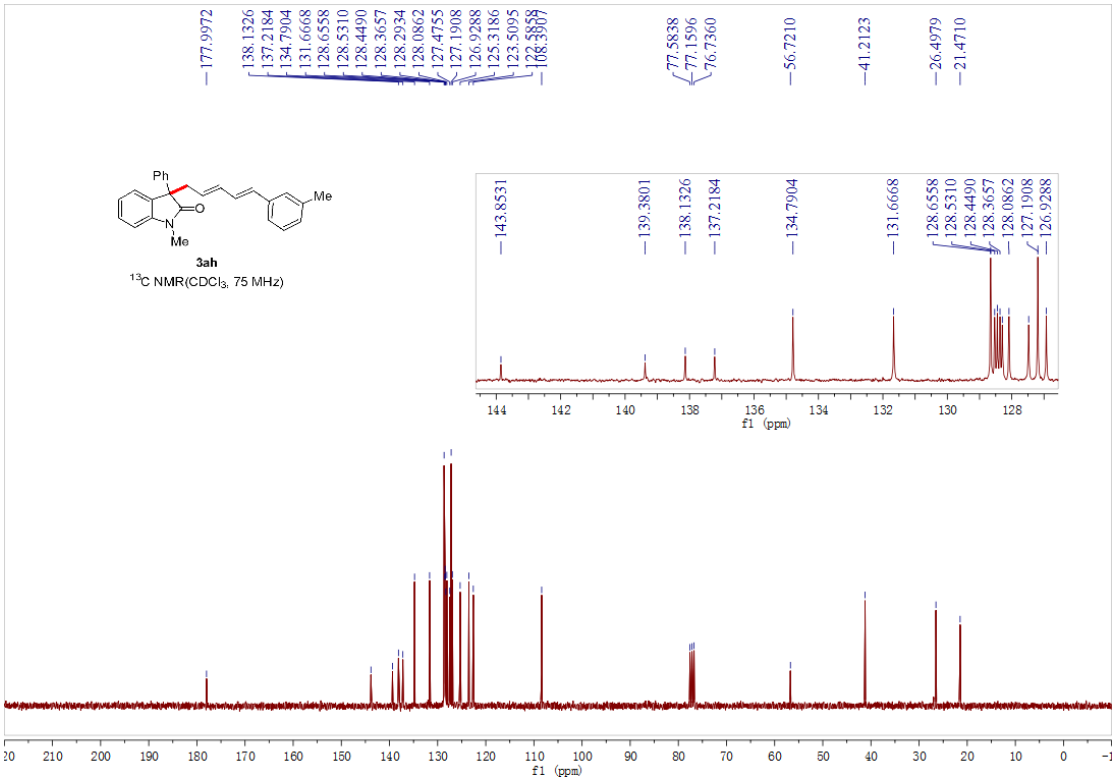
^{13}C NMR spectrum of purified **3ag**



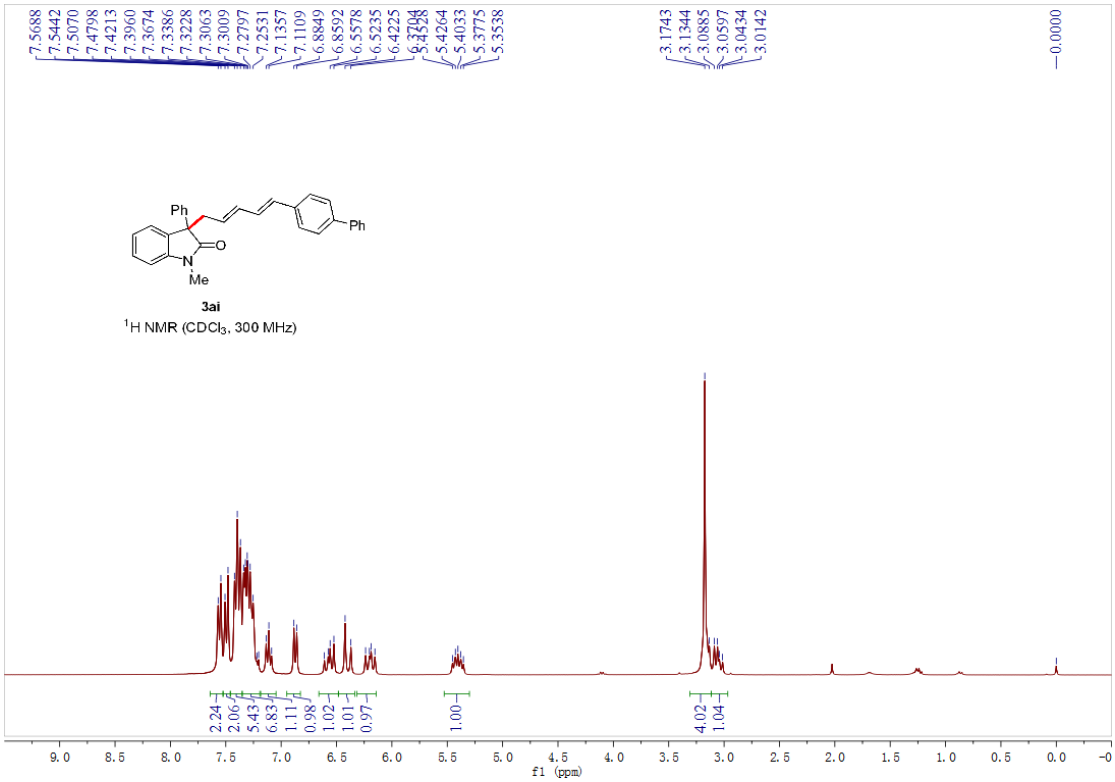
^{1}H NMR spectrum of purified **3ah**



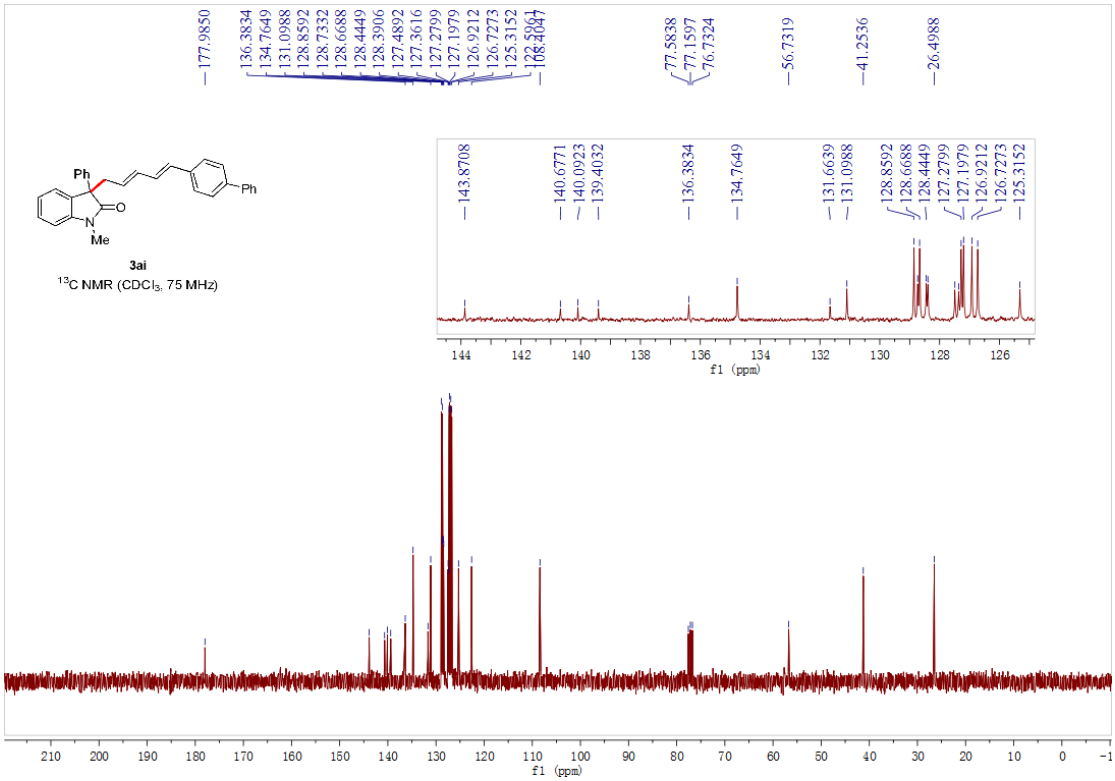
^{13}C NMR spectrum of purified **3ah**



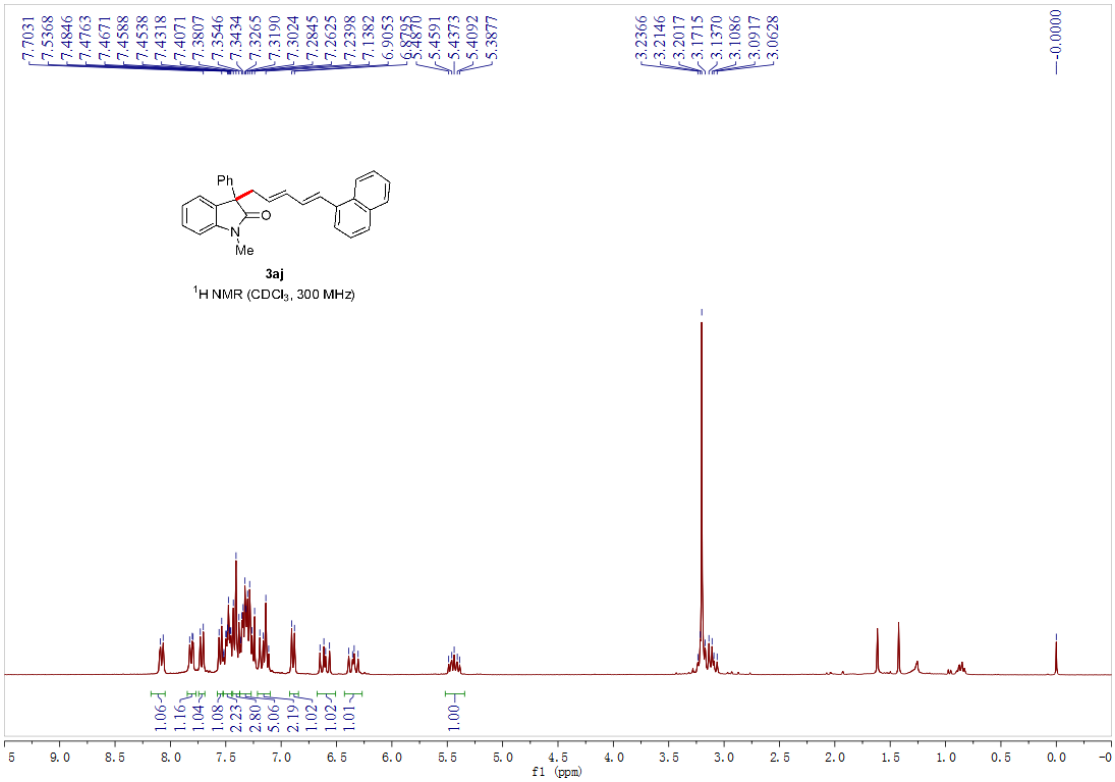
^{1}H NMR spectrum of purified **3ai**



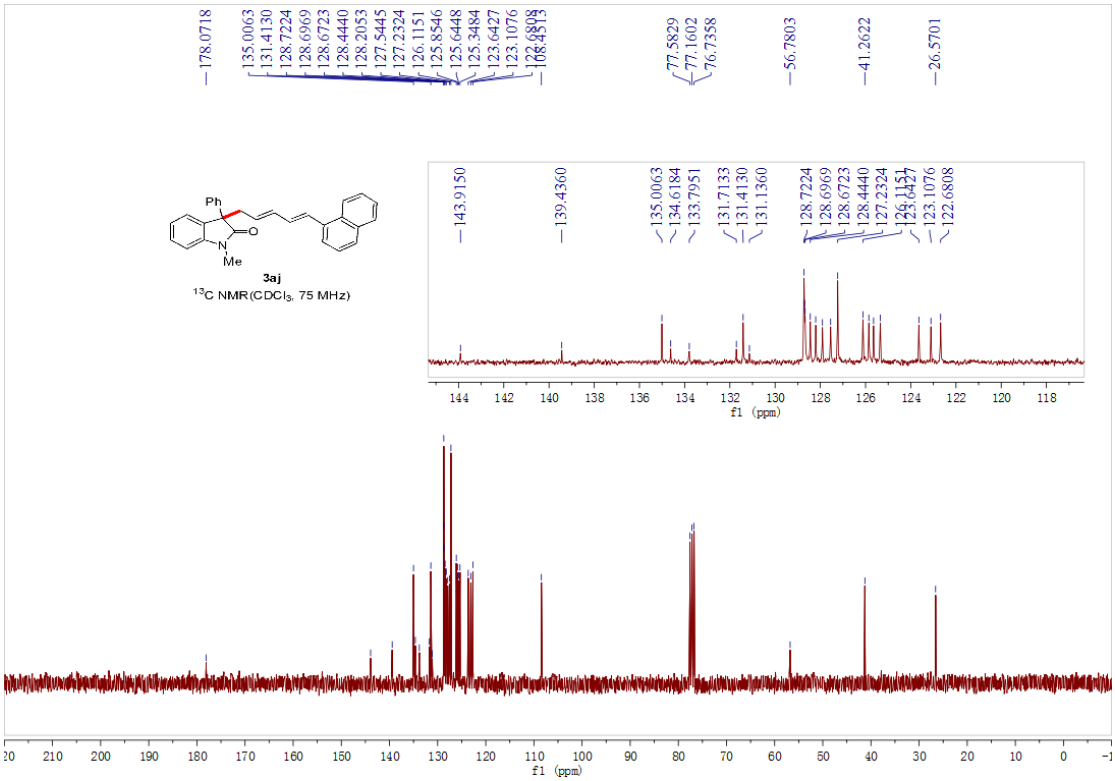
^{13}C NMR spectrum of purified **3ai**



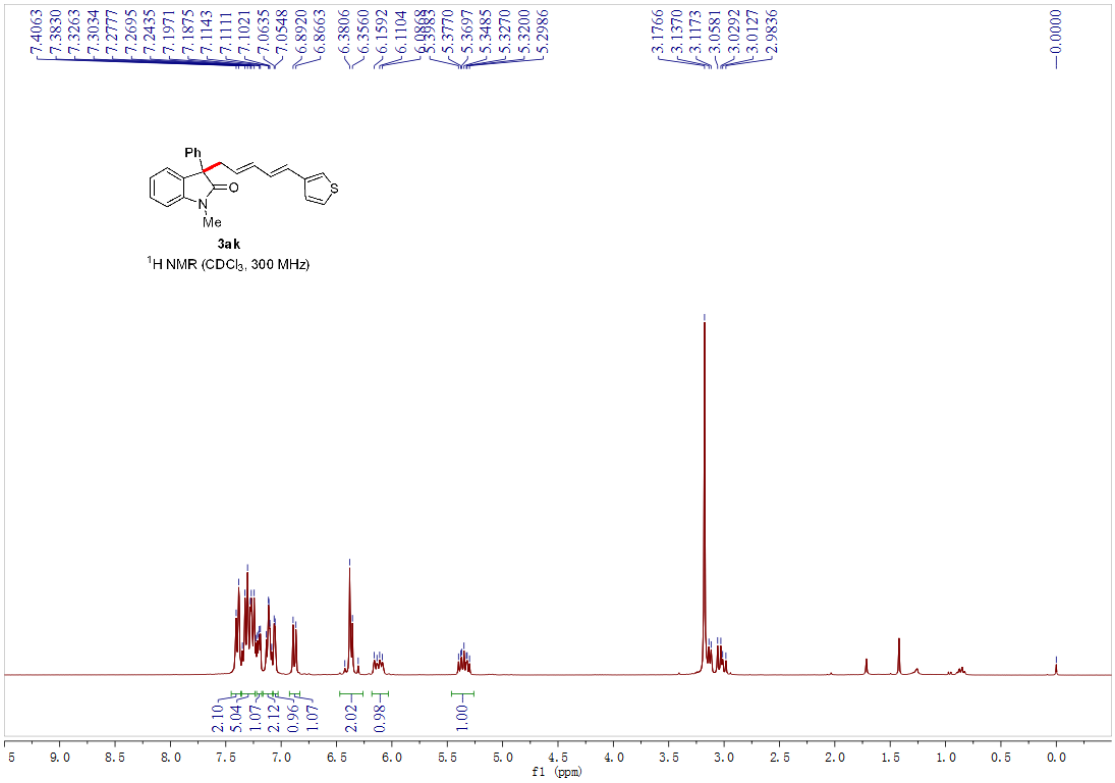
^{1}H NMR spectrum of purified **3aj**



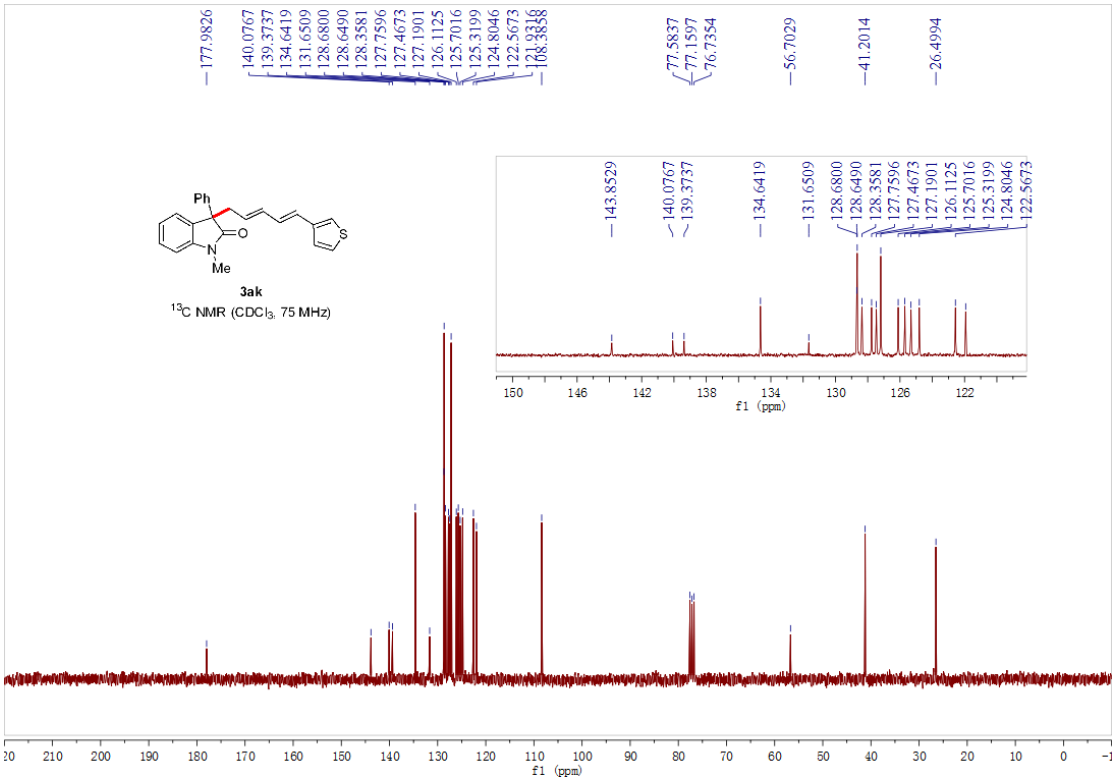
^{13}C NMR spectrum of purified **3aj**



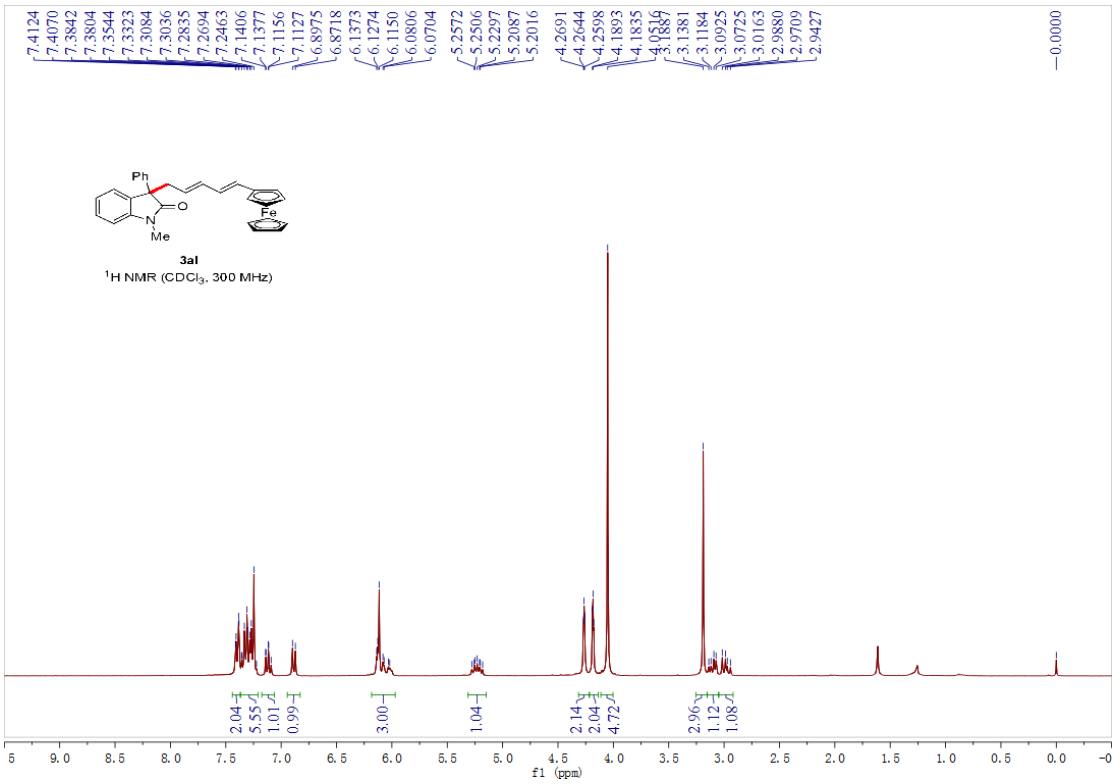
^{1}H NMR spectrum of purified **3ak**



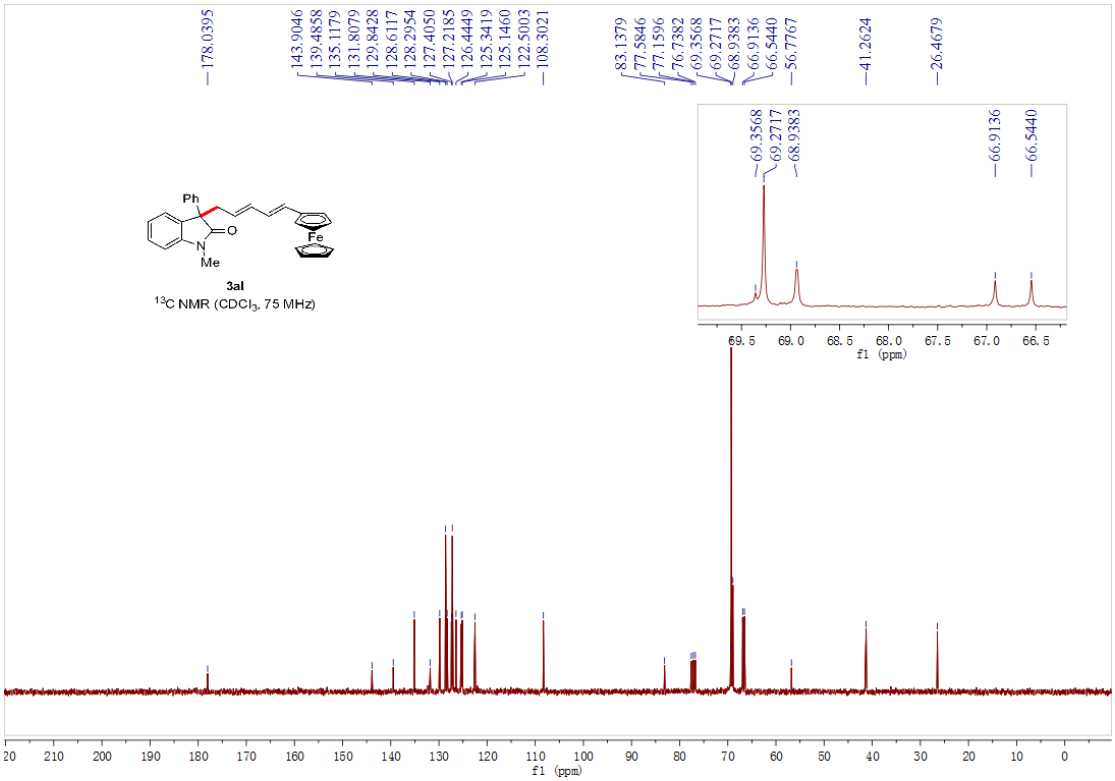
^{13}C NMR spectrum of purified **3ak**



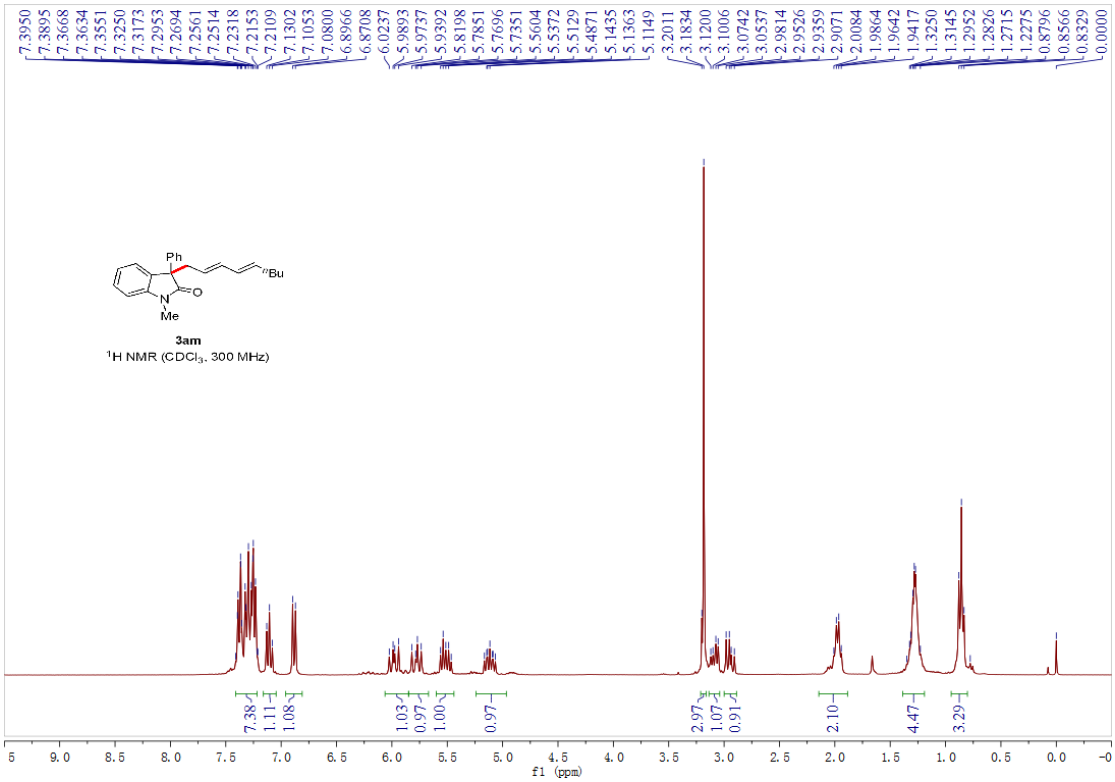
^{1}H NMR spectrum of purified **3al**



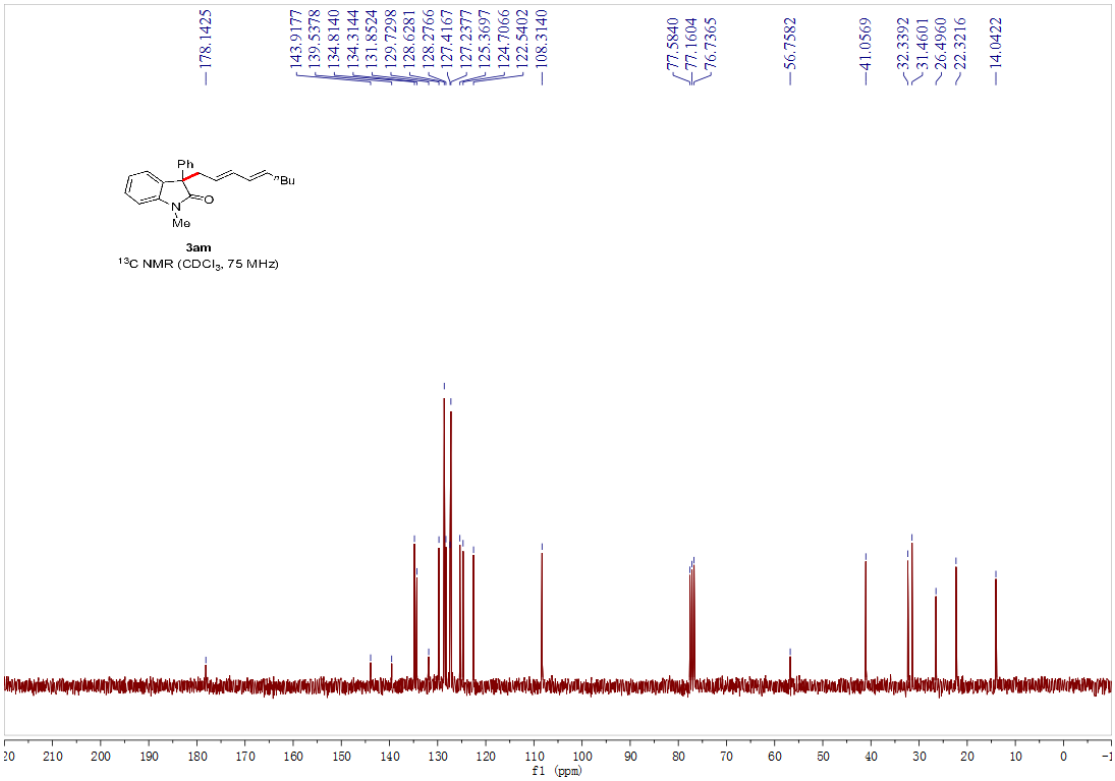
^{13}C NMR spectrum of purified **3al**



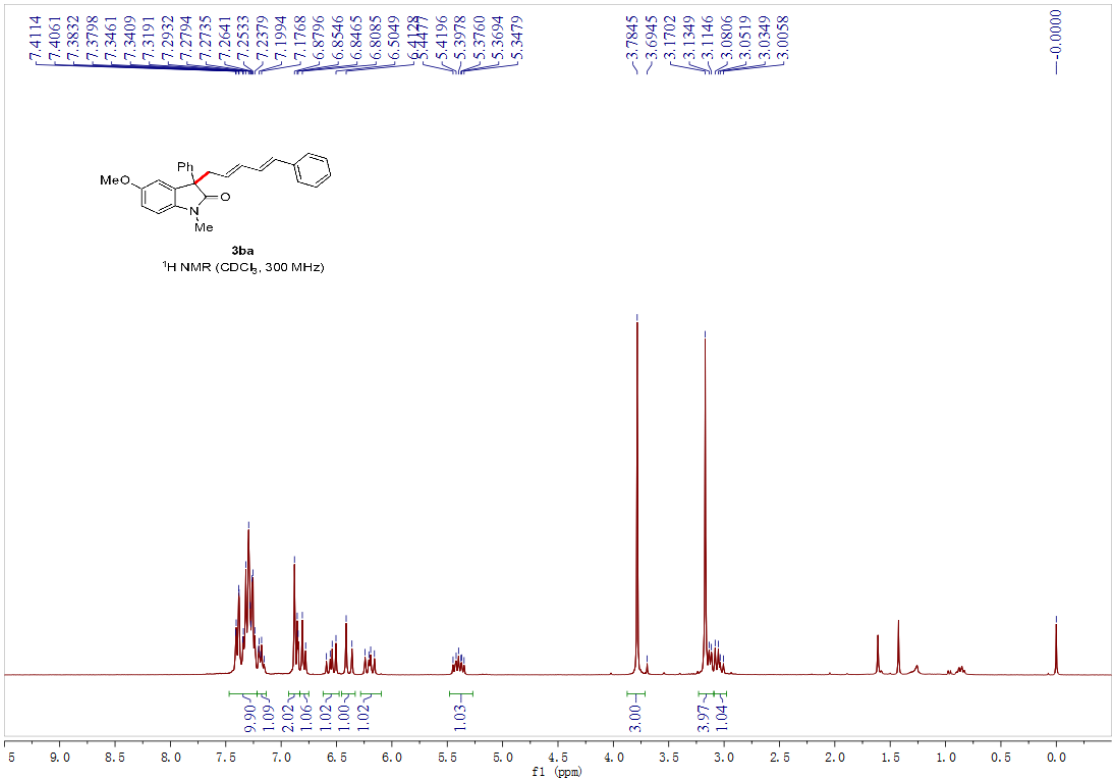
^{1}H NMR spectrum of purified **3am**



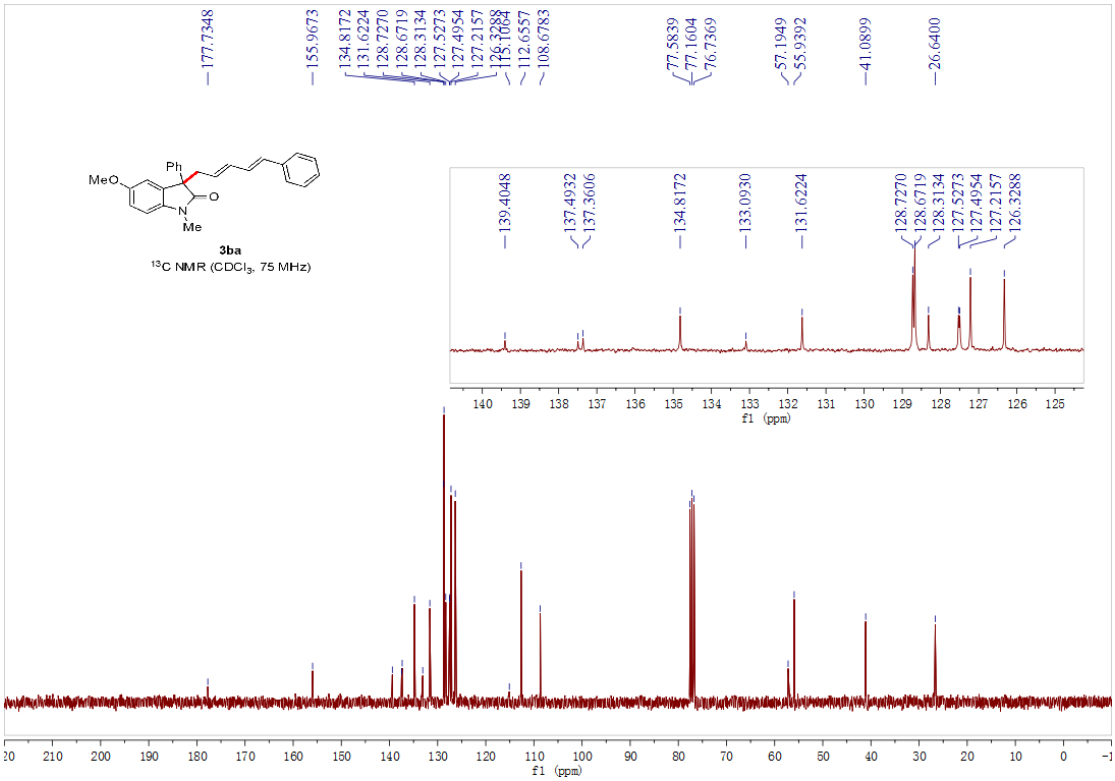
^{13}C NMR spectrum of purified **3am**



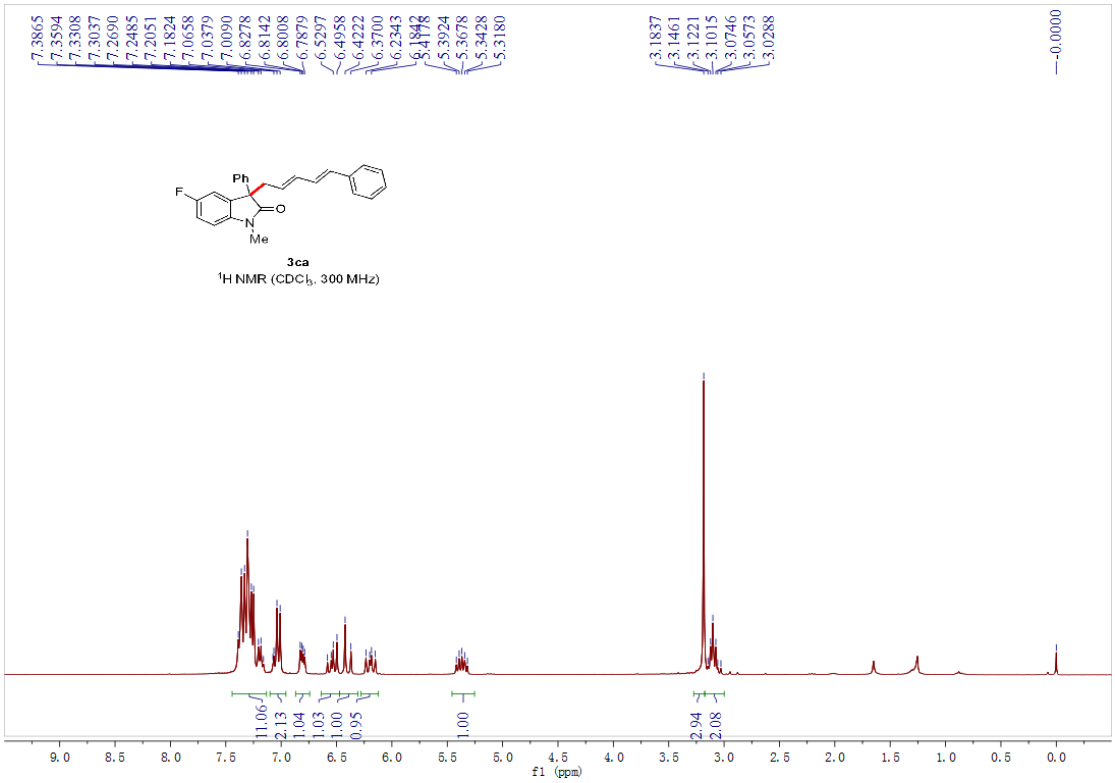
^{1}H NMR spectrum of purified **3ba**



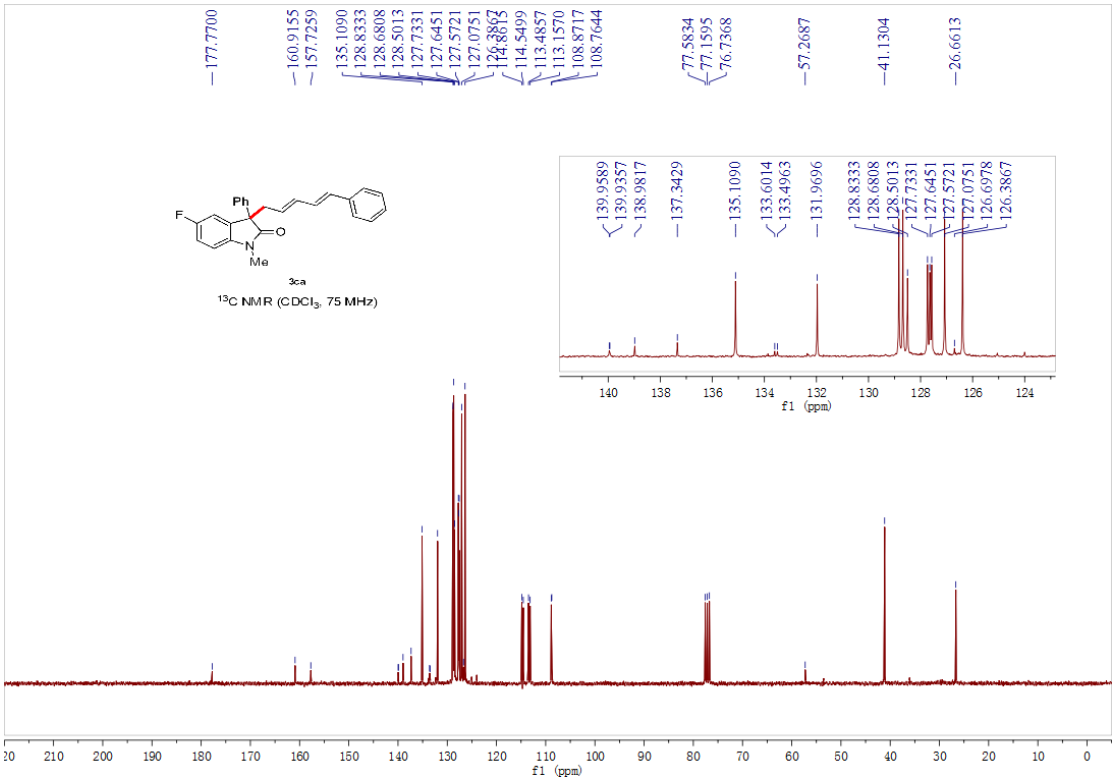
^{13}C NMR spectrum of purified **3ba**



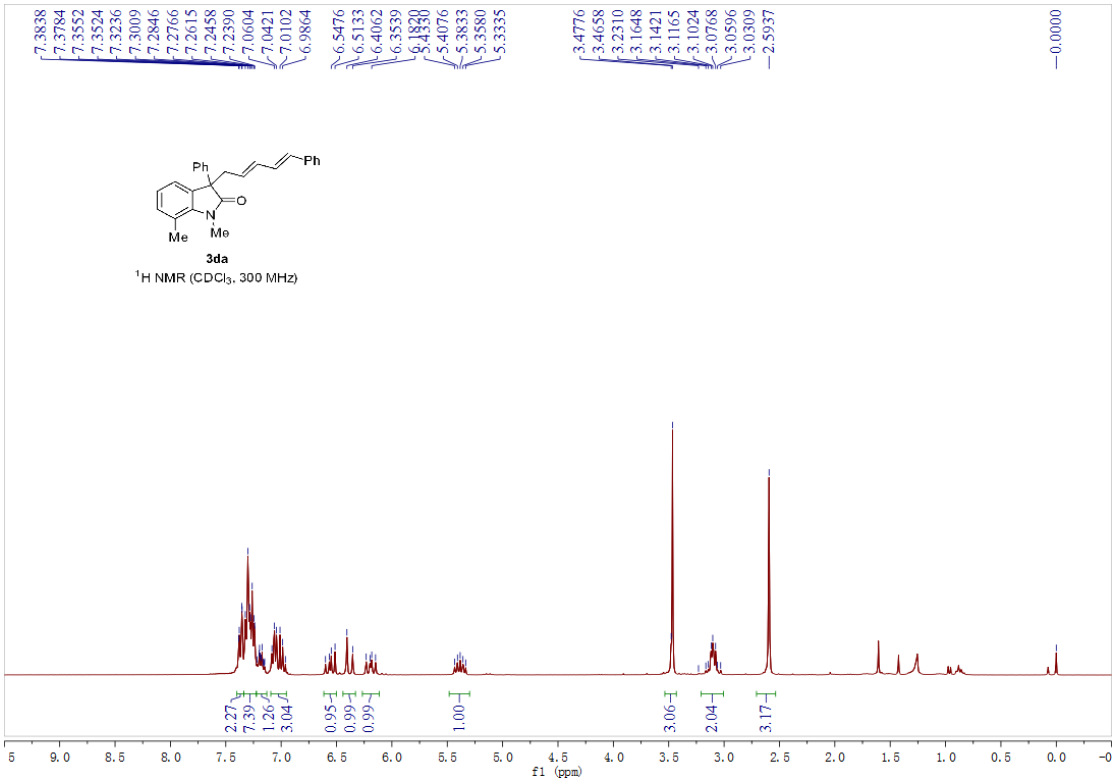
^{1}H NMR spectrum of purified **3ca**



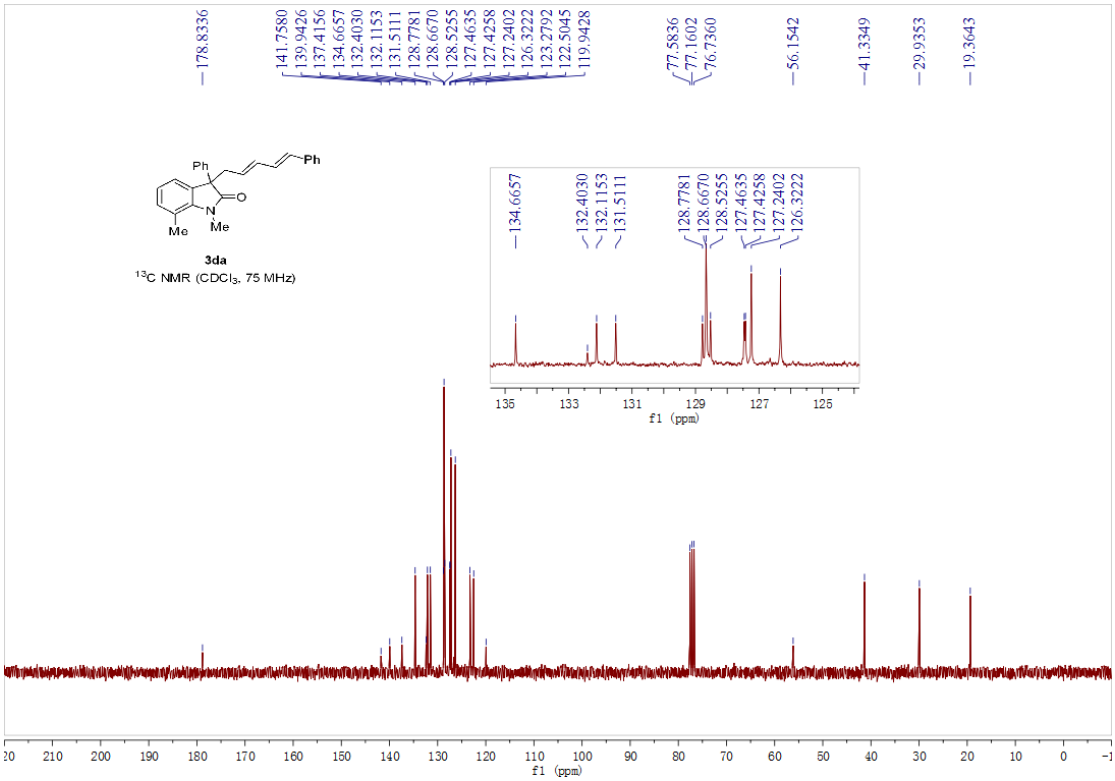
^{13}C NMR spectrum of purified **3ca**



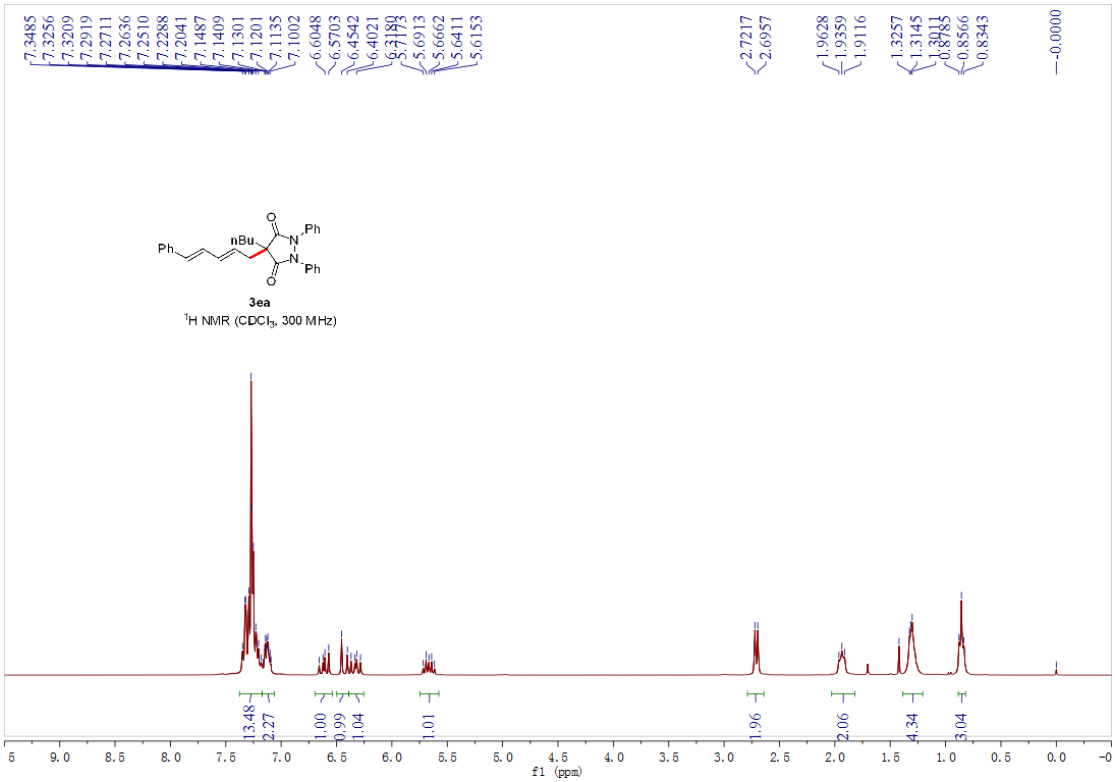
^{1}H NMR spectrum of purified **3da**



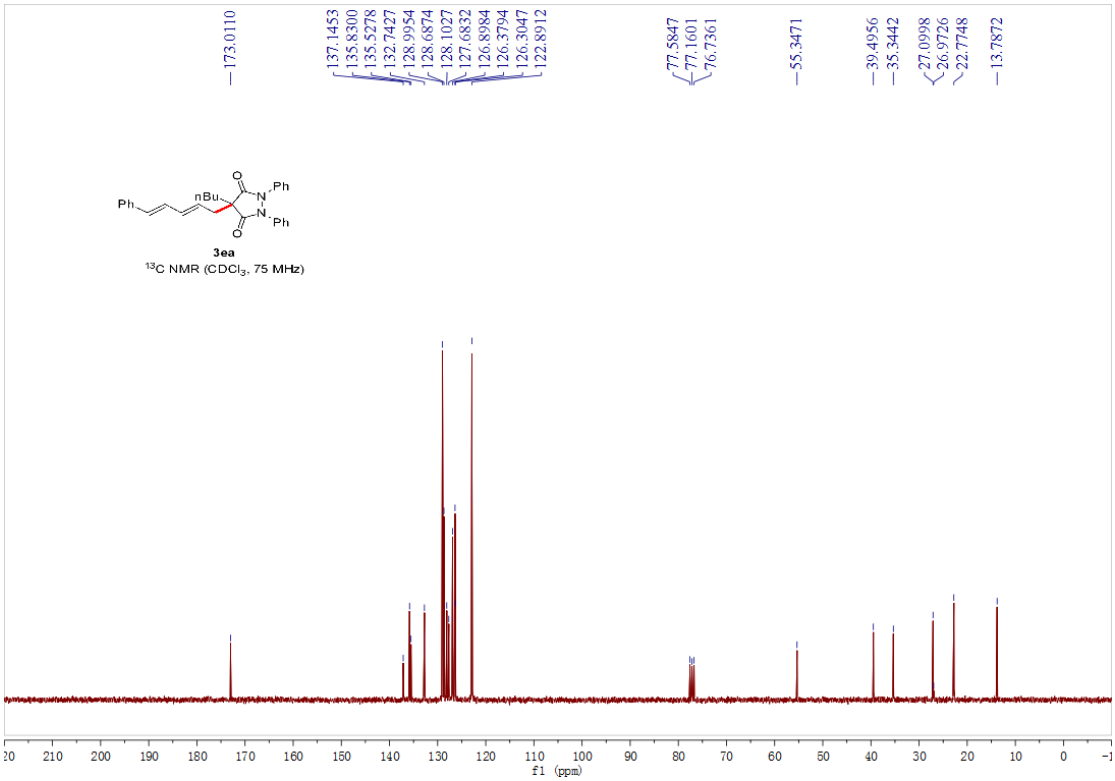
^{13}C NMR spectrum of purified **3da**



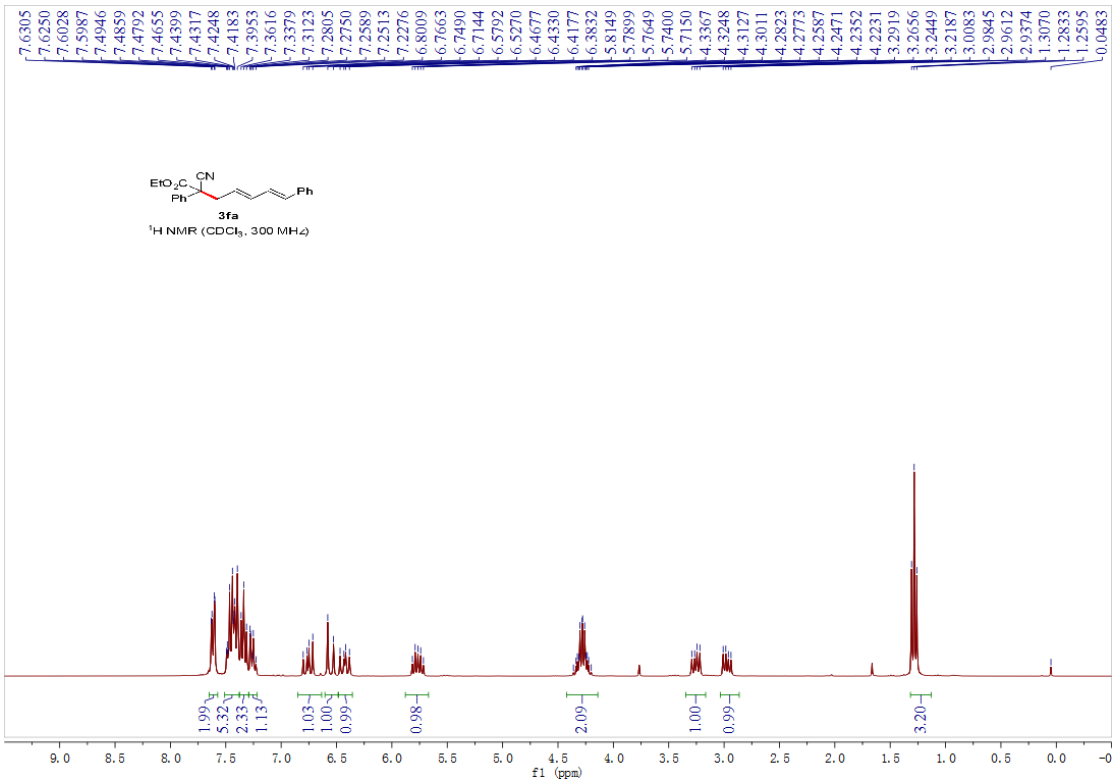
^{1}H NMR spectrum of purified **3ea**



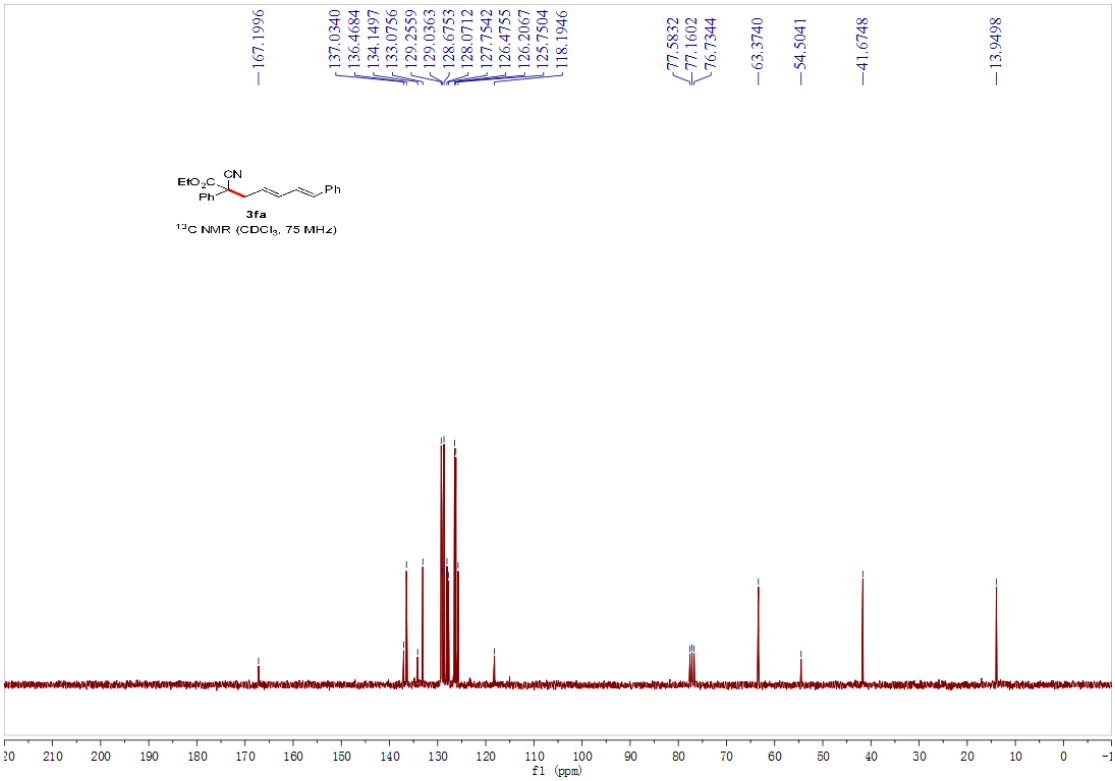
^{13}C NMR spectrum of purified **3ea**



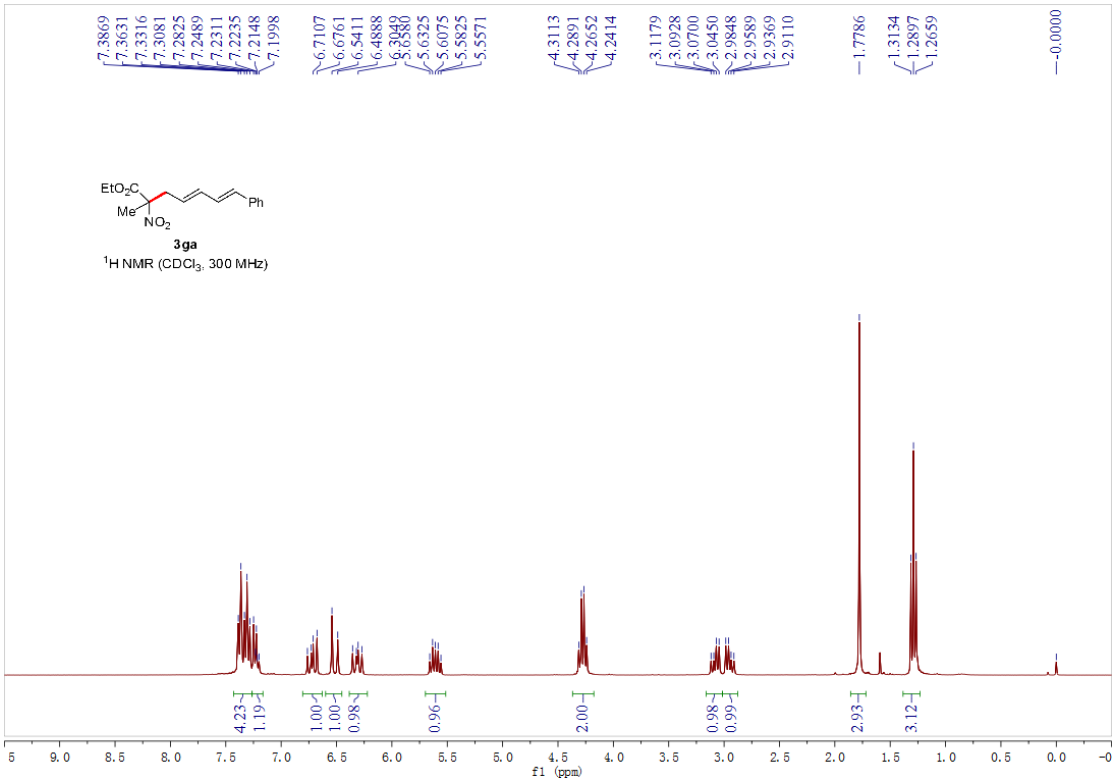
^{1}H NMR spectrum of purified **3fa**



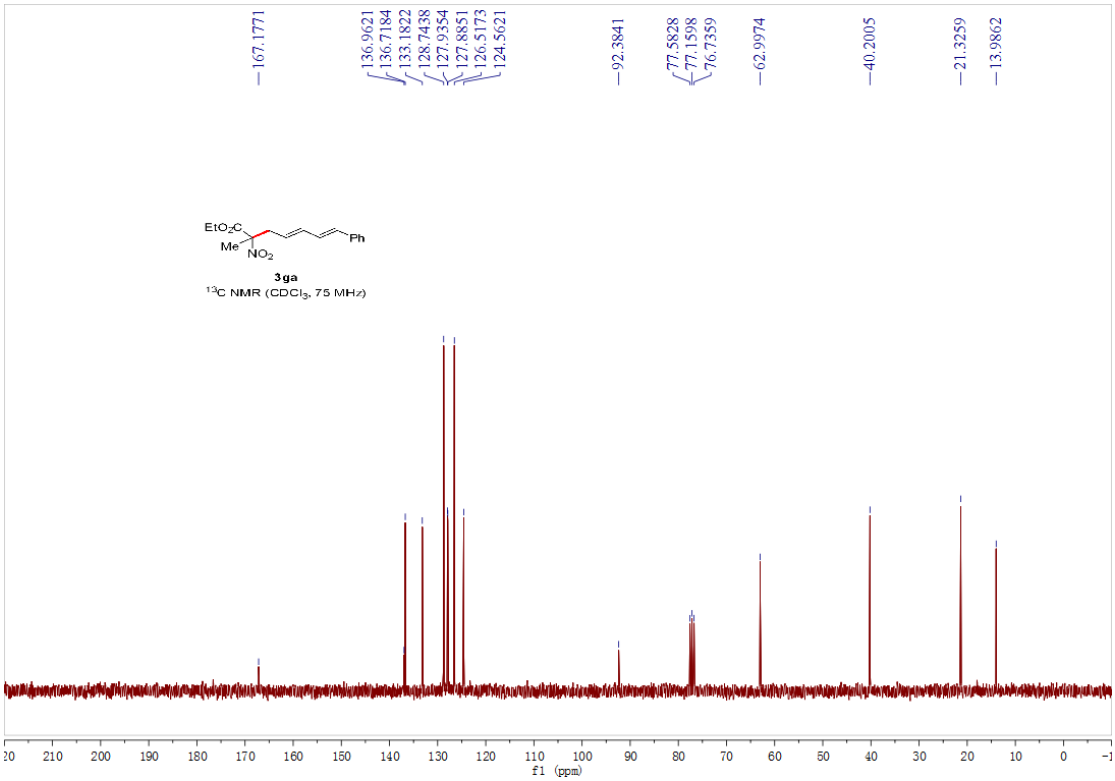
^{13}C NMR spectrum of purified **3fa**



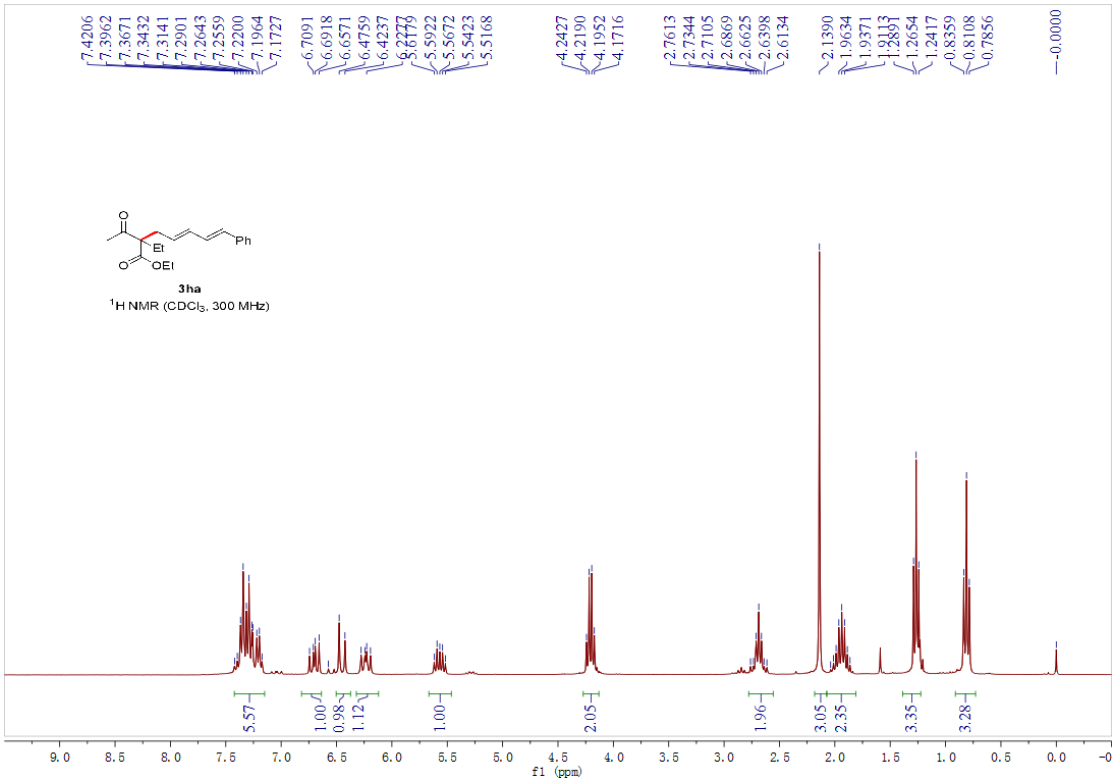
^{1}H NMR spectrum of purified **3ga**



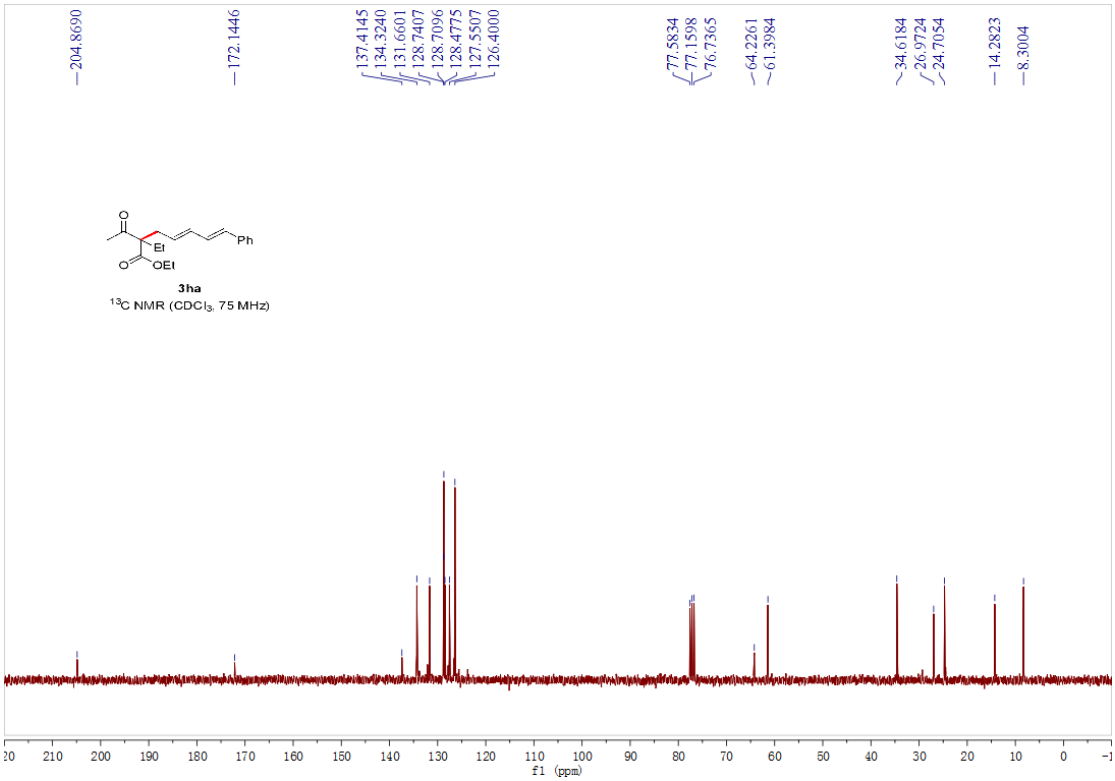
^{13}C NMR spectrum of purified **3ga**



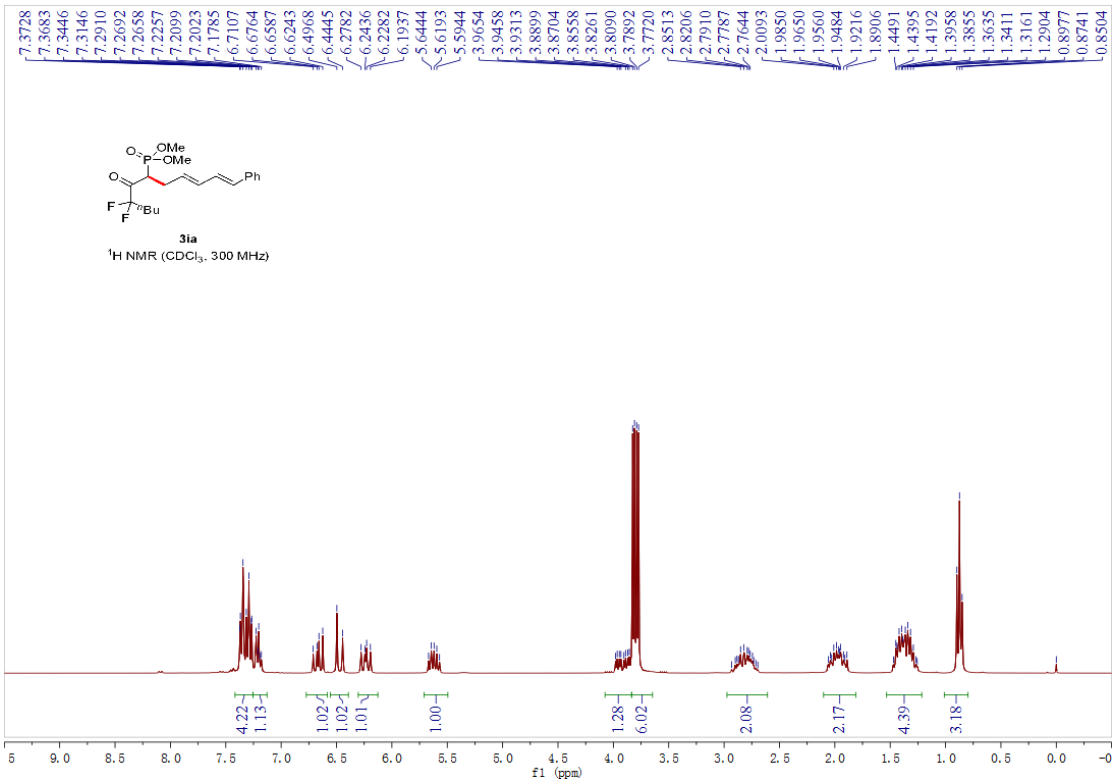
^{1}H NMR spectrum of purified **3ha**



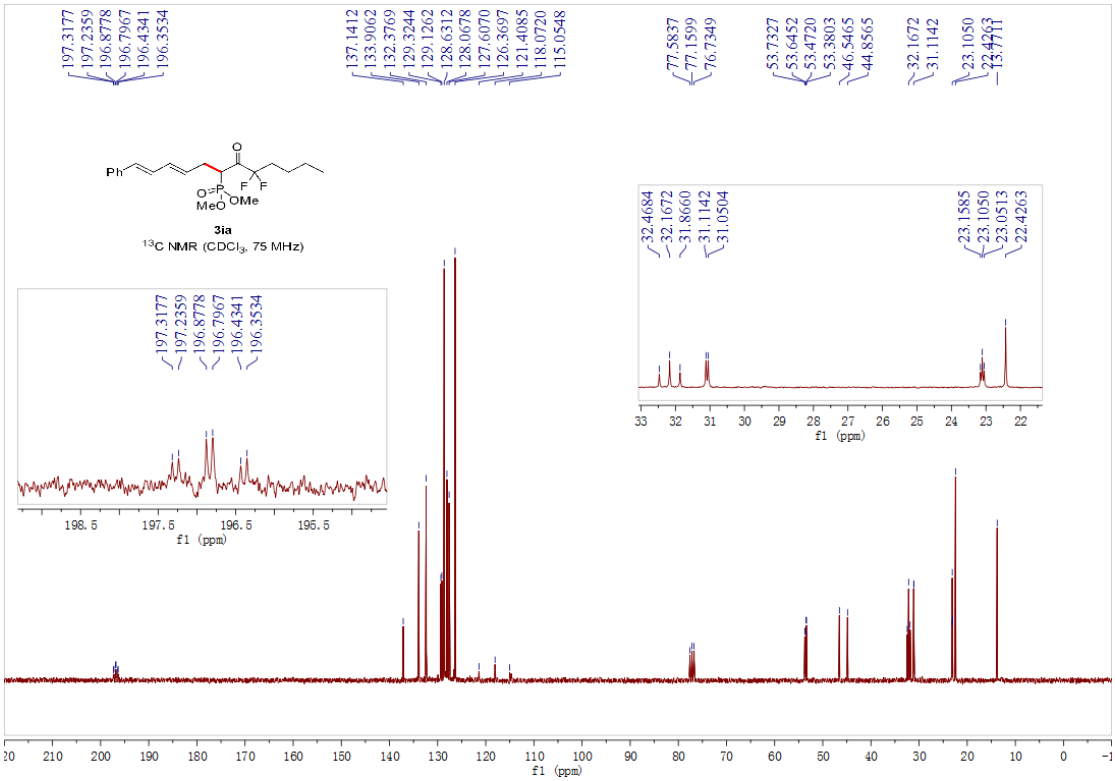
^{13}C NMR spectrum of purified **3ha**



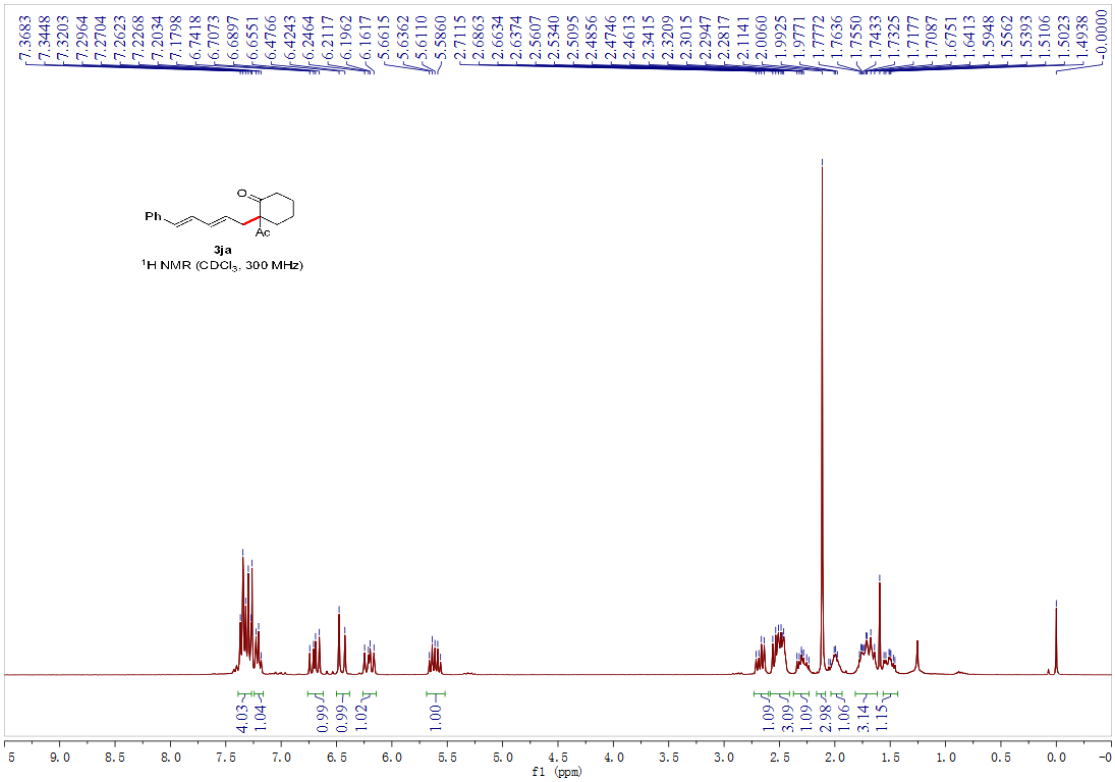
^{1}H NMR spectrum of purified **3ia**



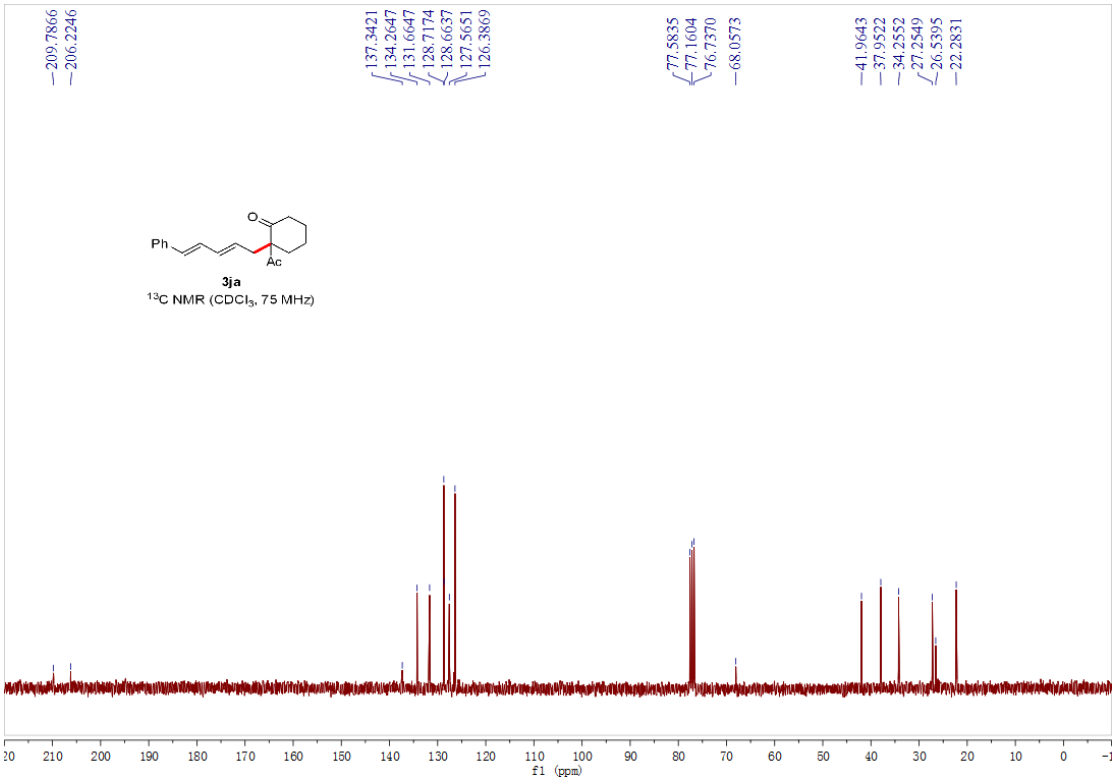
^{13}C NMR spectrum of purified **3ia**



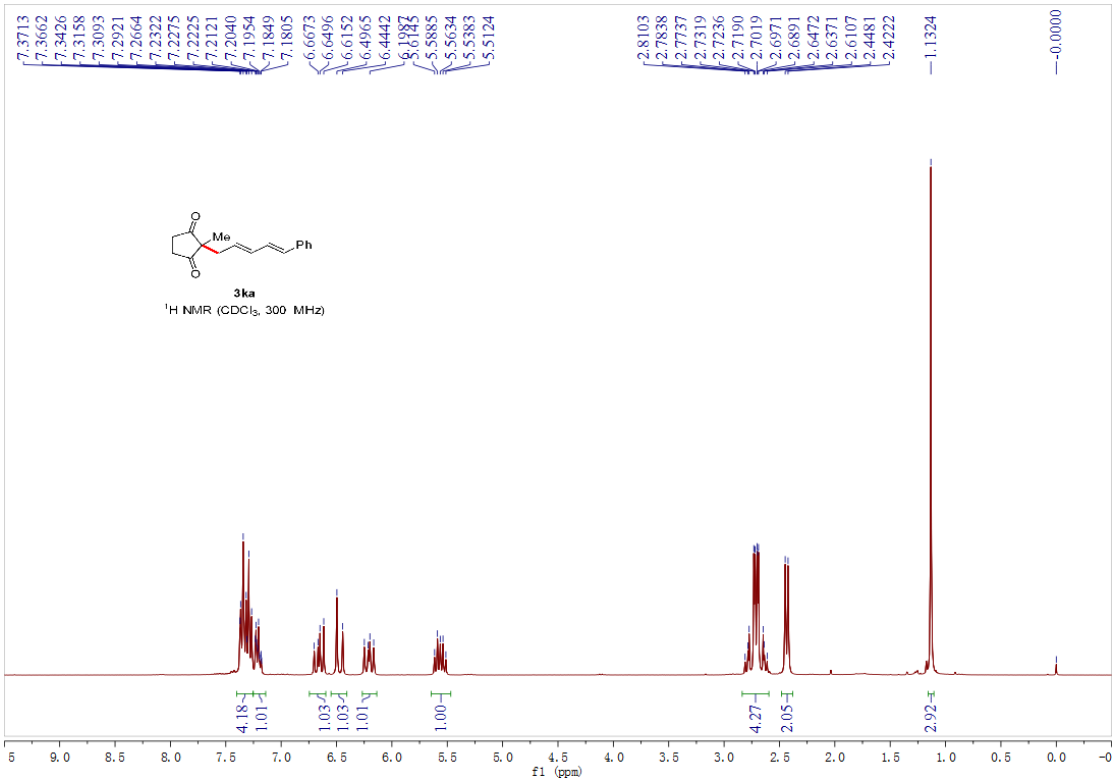
^{1}H NMR spectrum of purified **3ja**



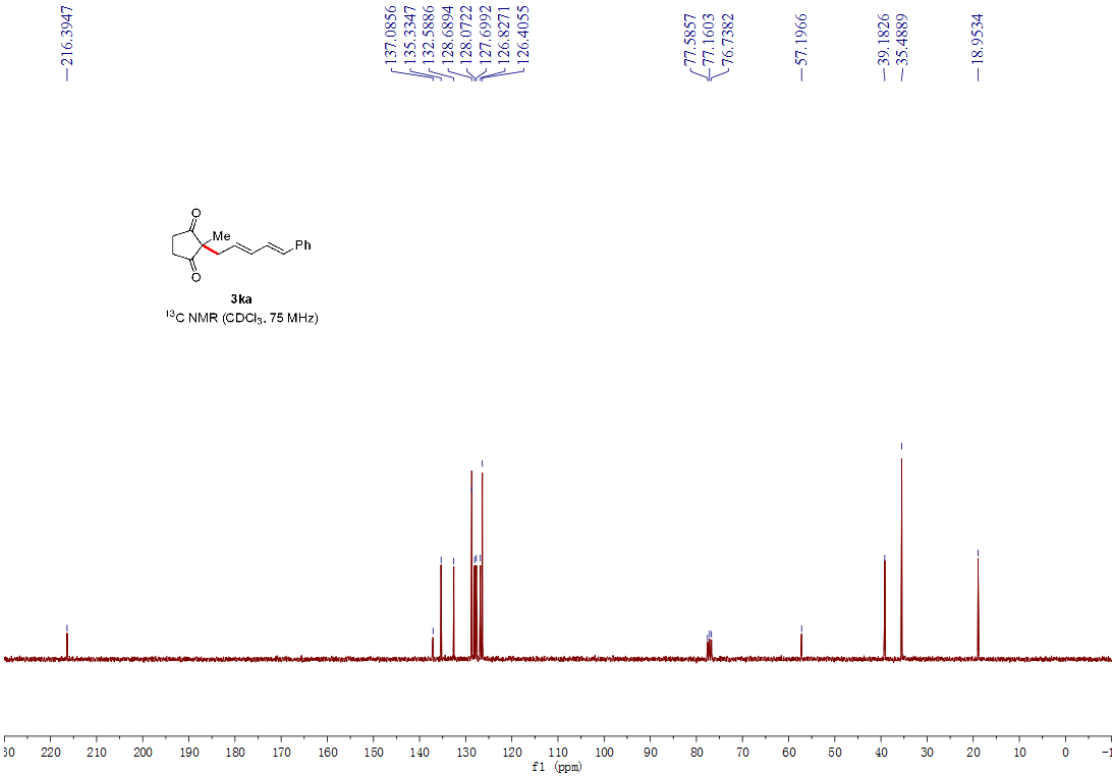
^{13}C NMR spectrum of purified **3ja**



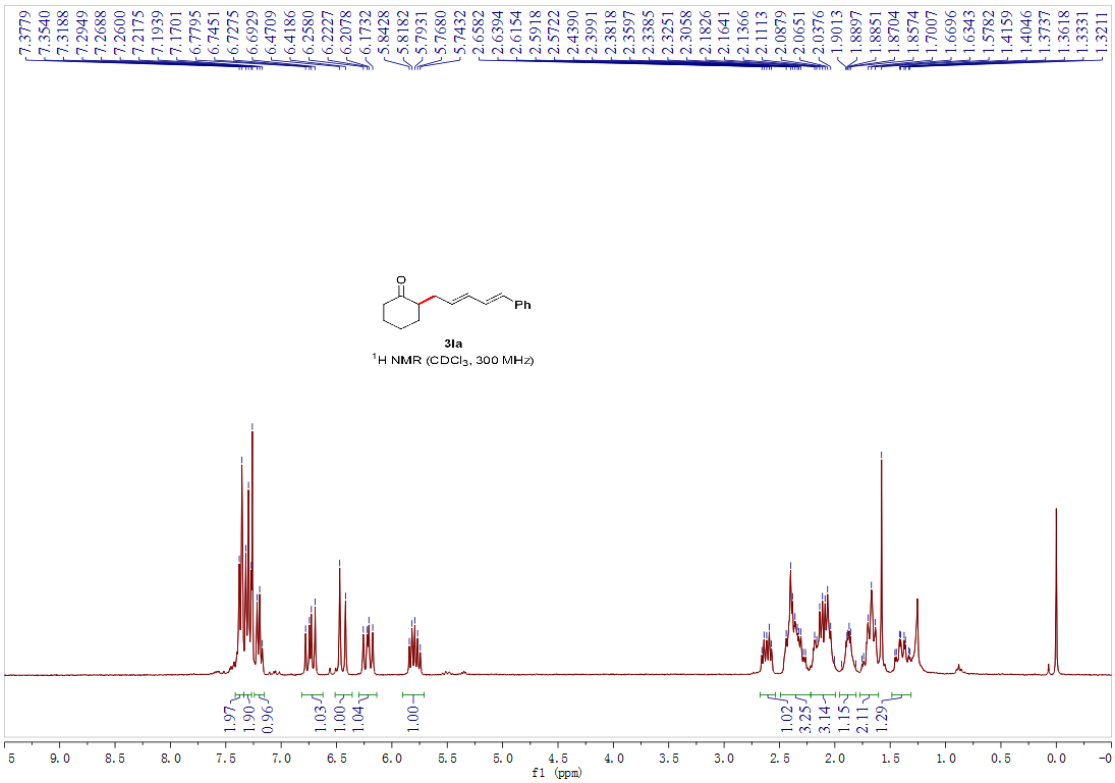
^{1}H NMR spectrum of purified **3ka**



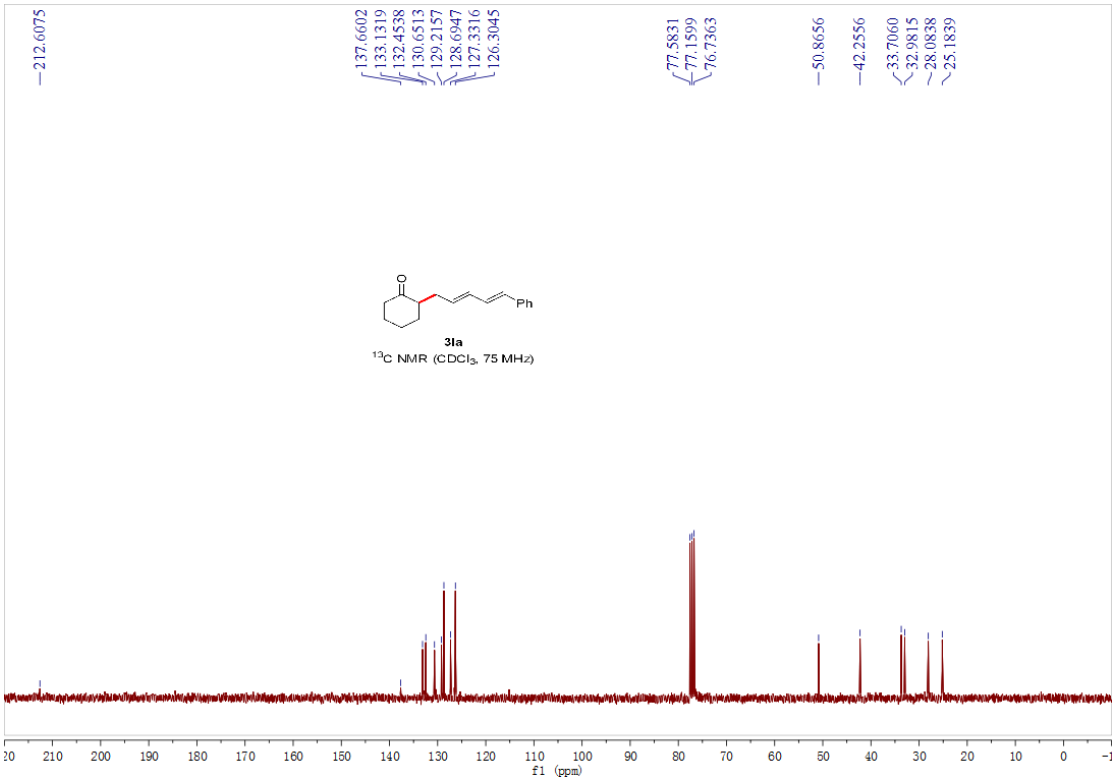
^{13}C NMR spectrum of purified **3ka**



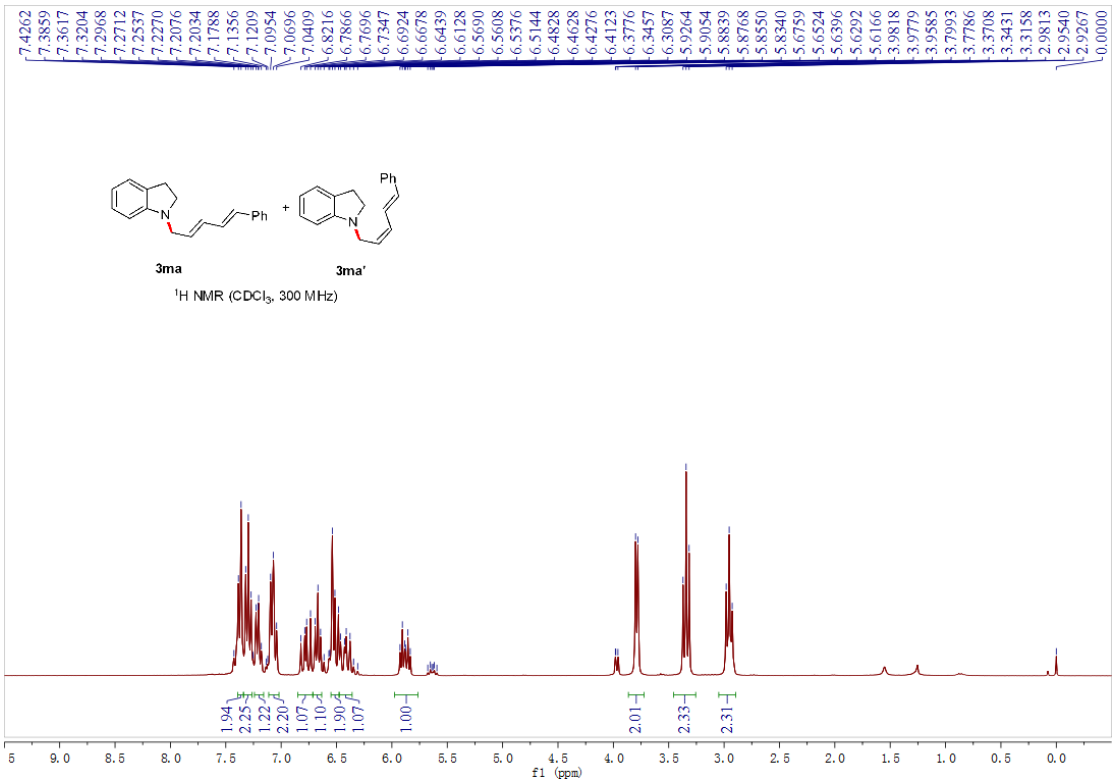
^{1}H NMR spectrum of purified **3la**



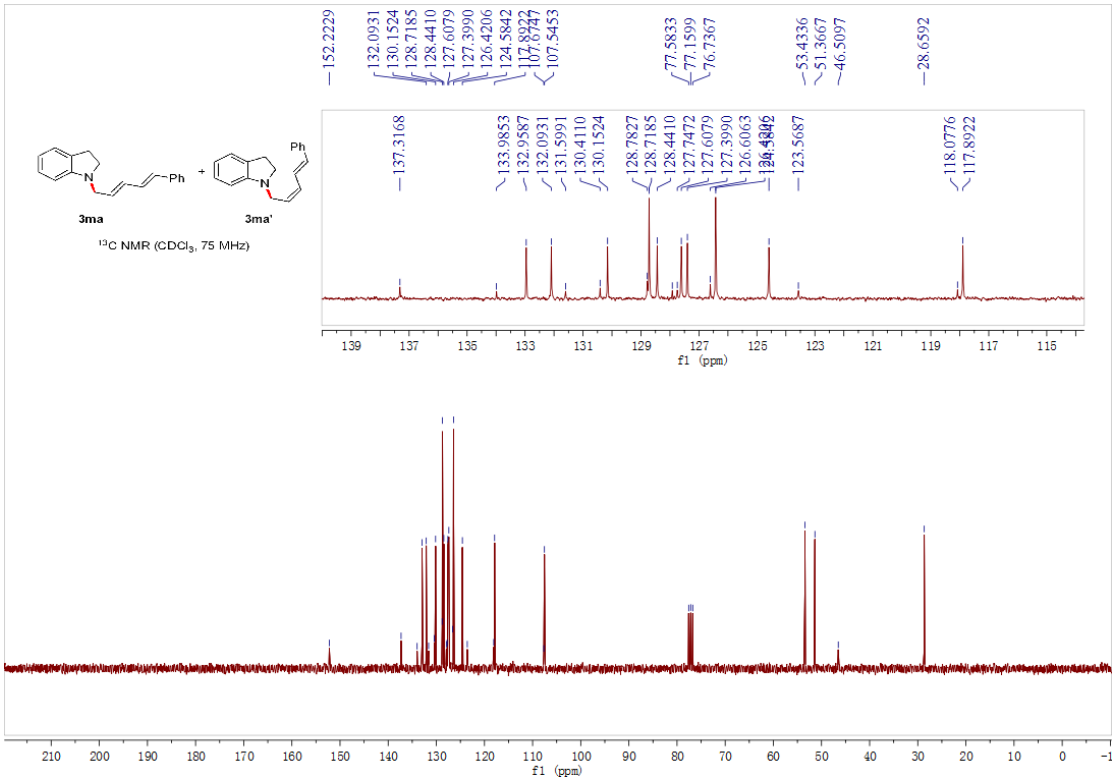
^{13}C NMR spectrum of purified **3la**



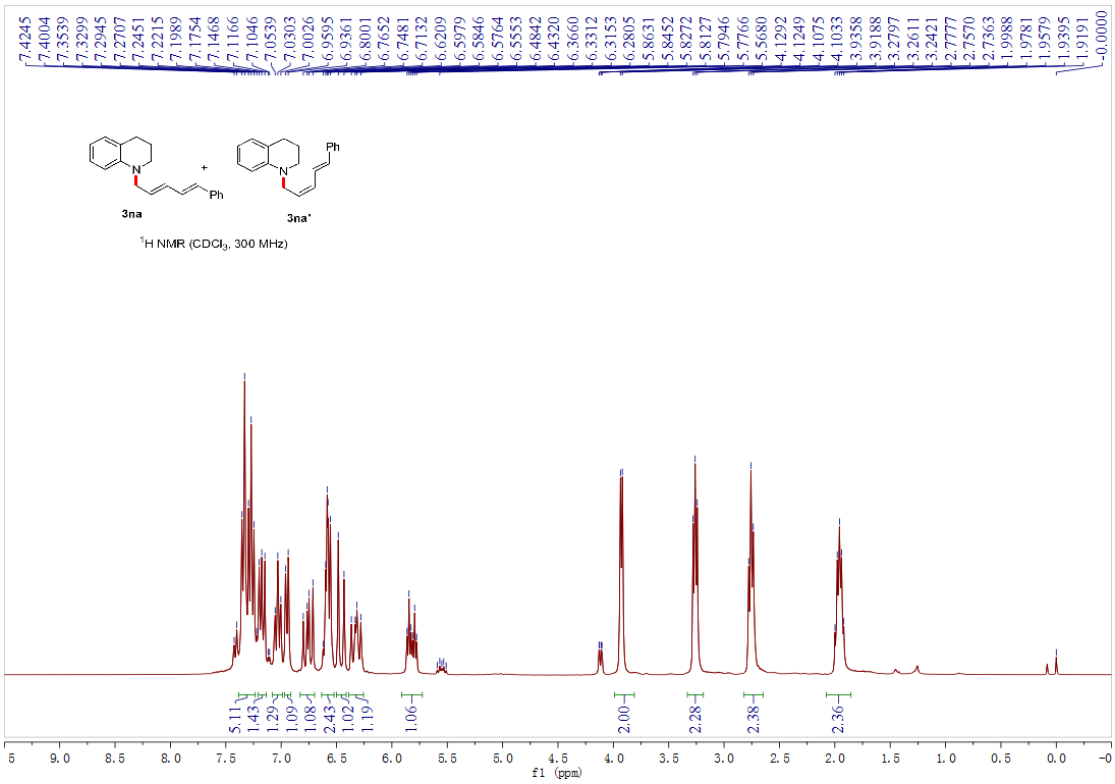
^{1}H NMR spectrum of the mixture of **3ma** and **3ma'**



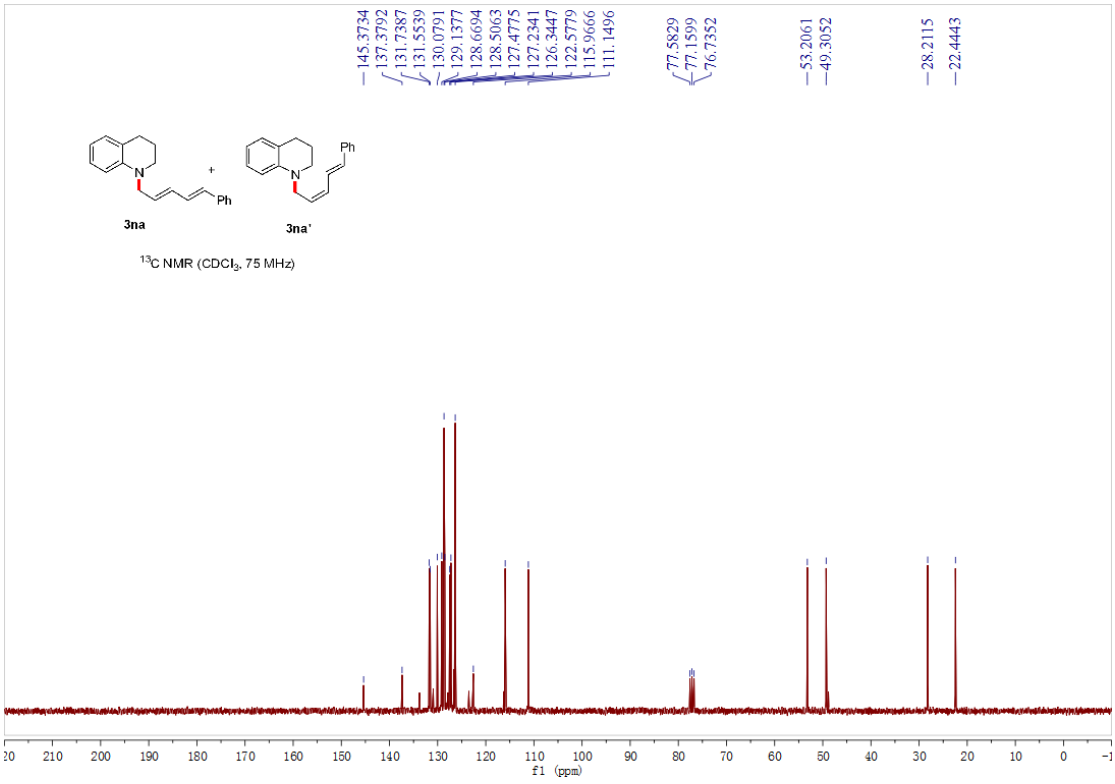
^{13}C NMR spectrum of the mixture of **3ma** and **3ma'**



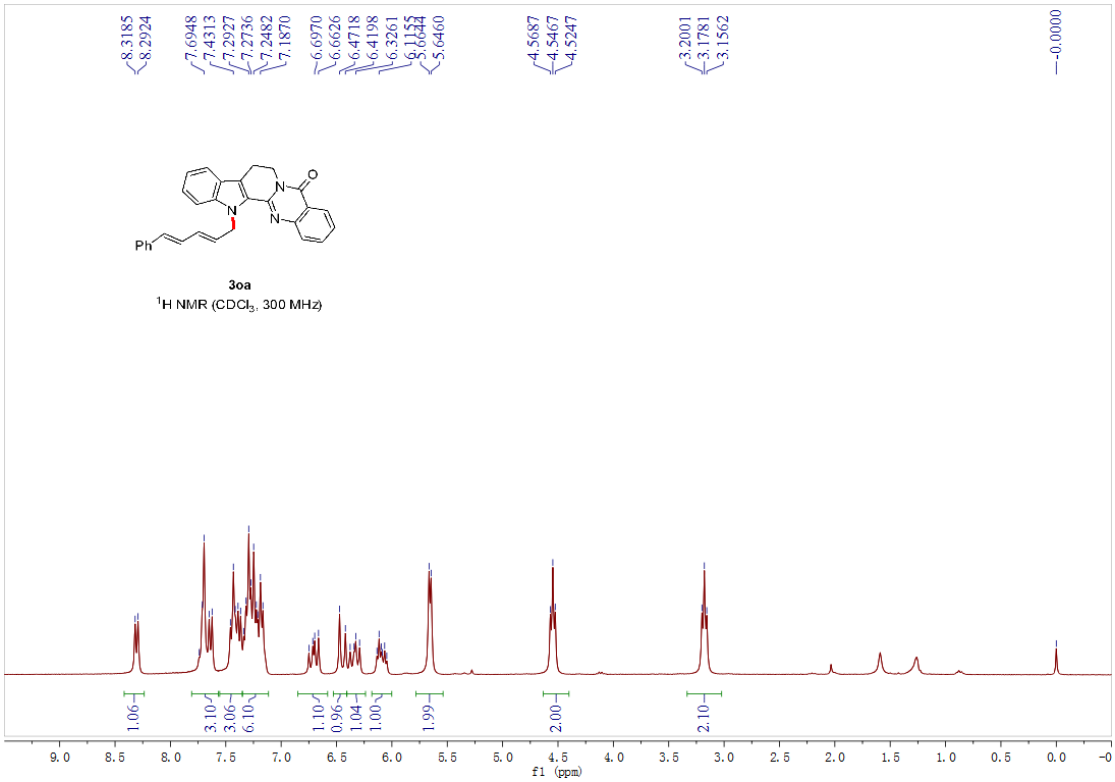
^{1}H NMR spectrum of the mixture of **3na** and **3na'**



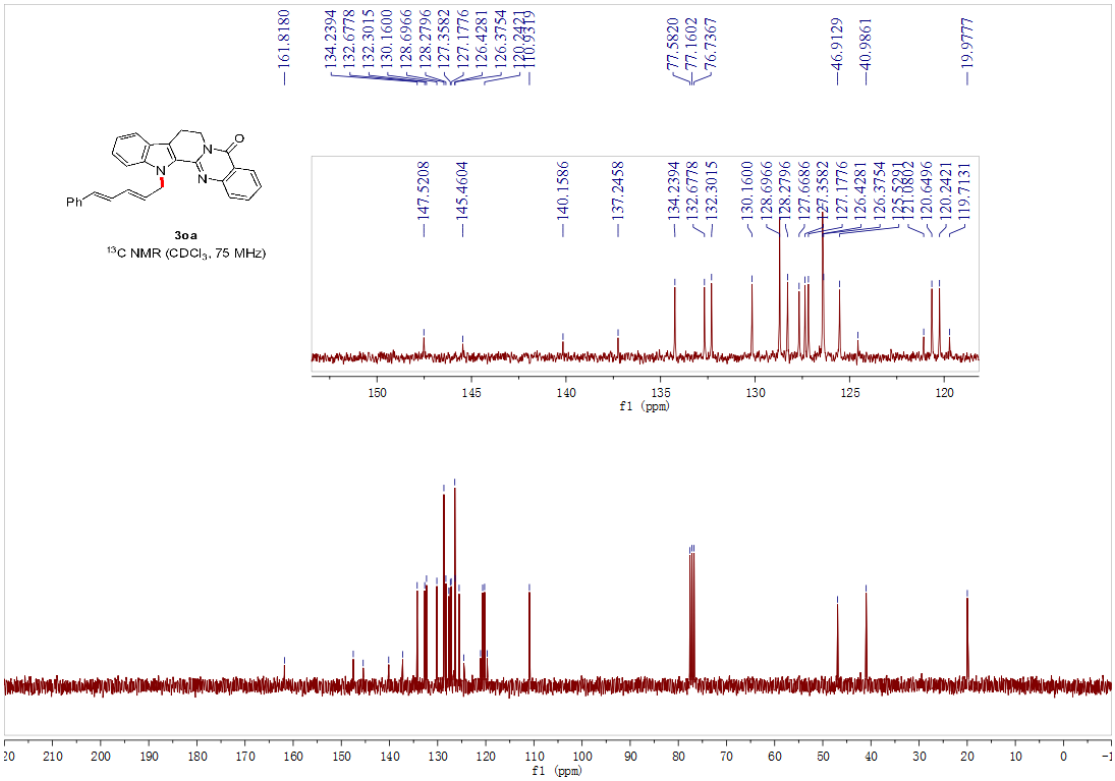
^{13}C NMR spectrum of the mixture of **3na** and **3na'**



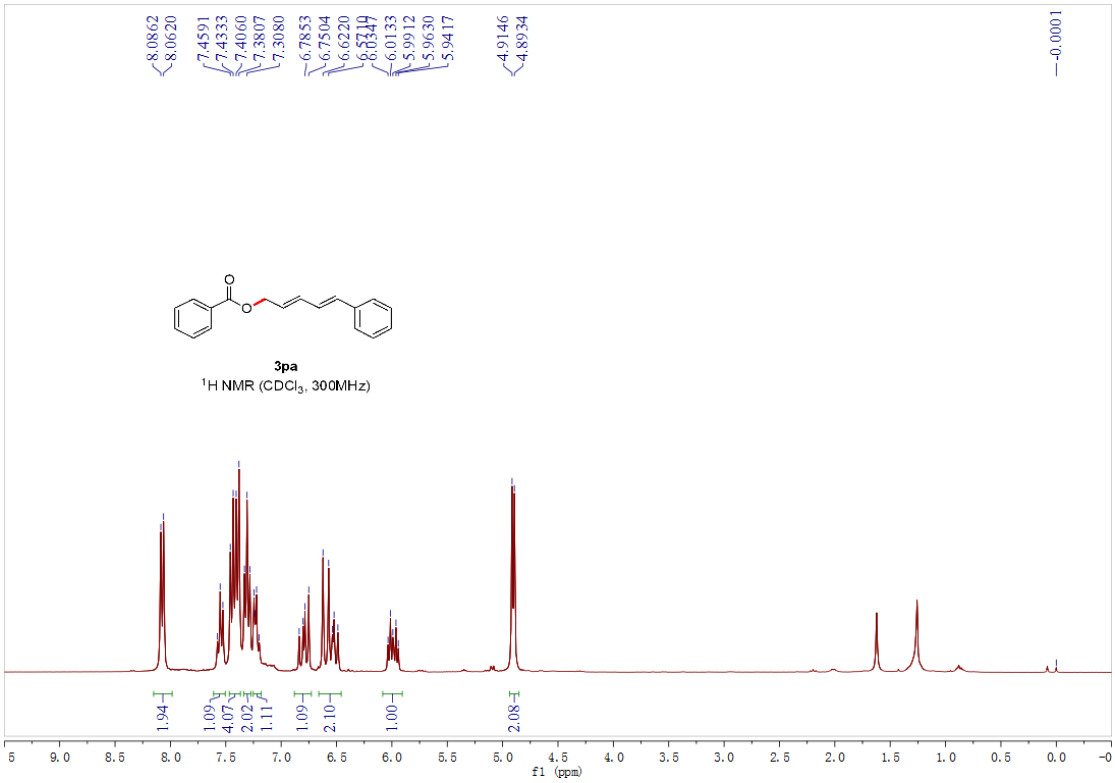
^{1}H NMR spectrum of purified **3oa**



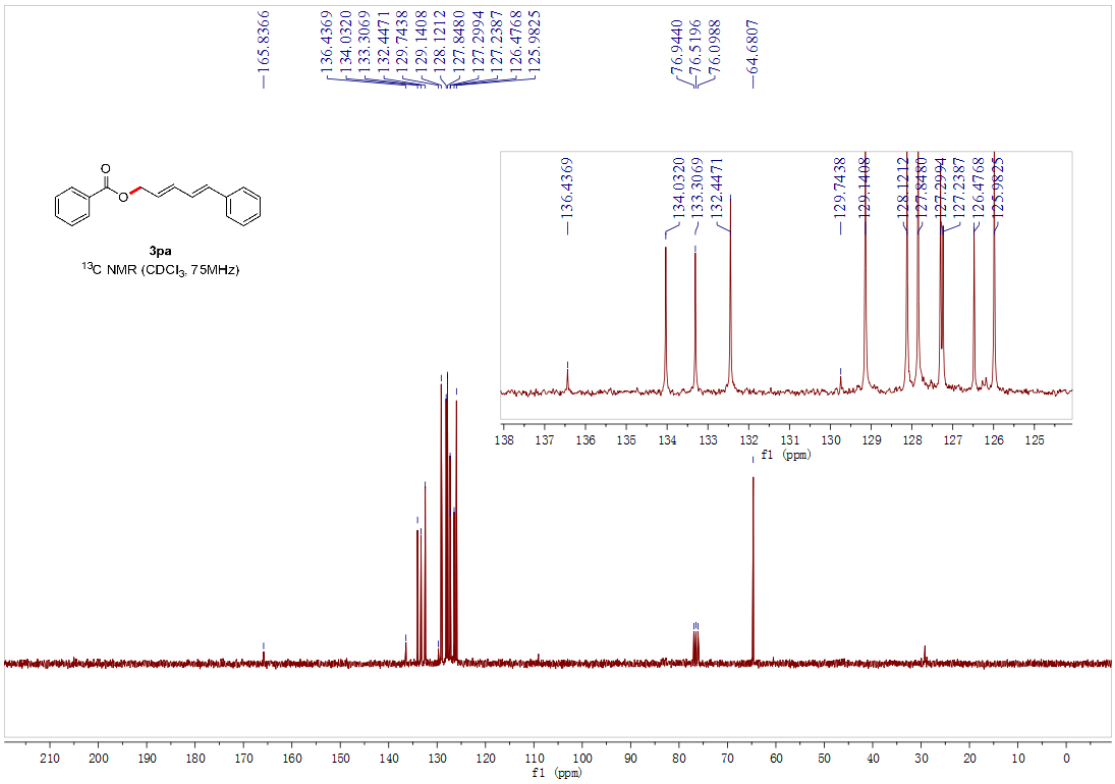
^{13}C NMR spectrum of purified **3oa**



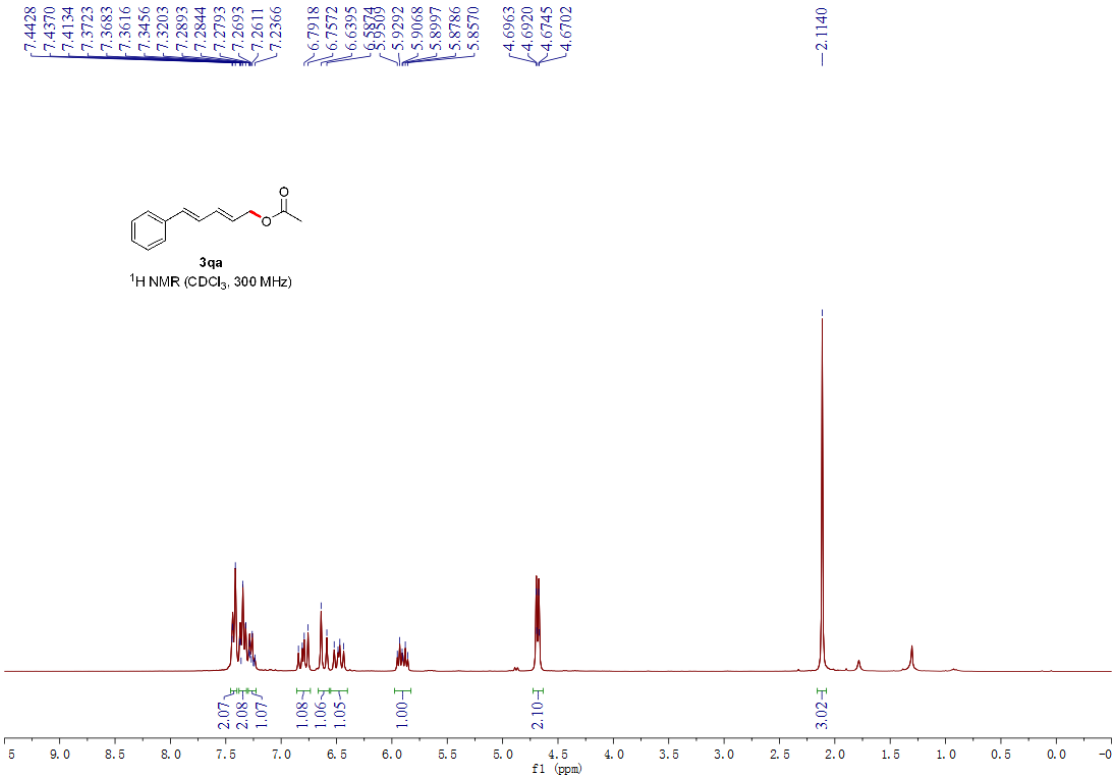
^{1}H NMR spectrum of purified **3pa**



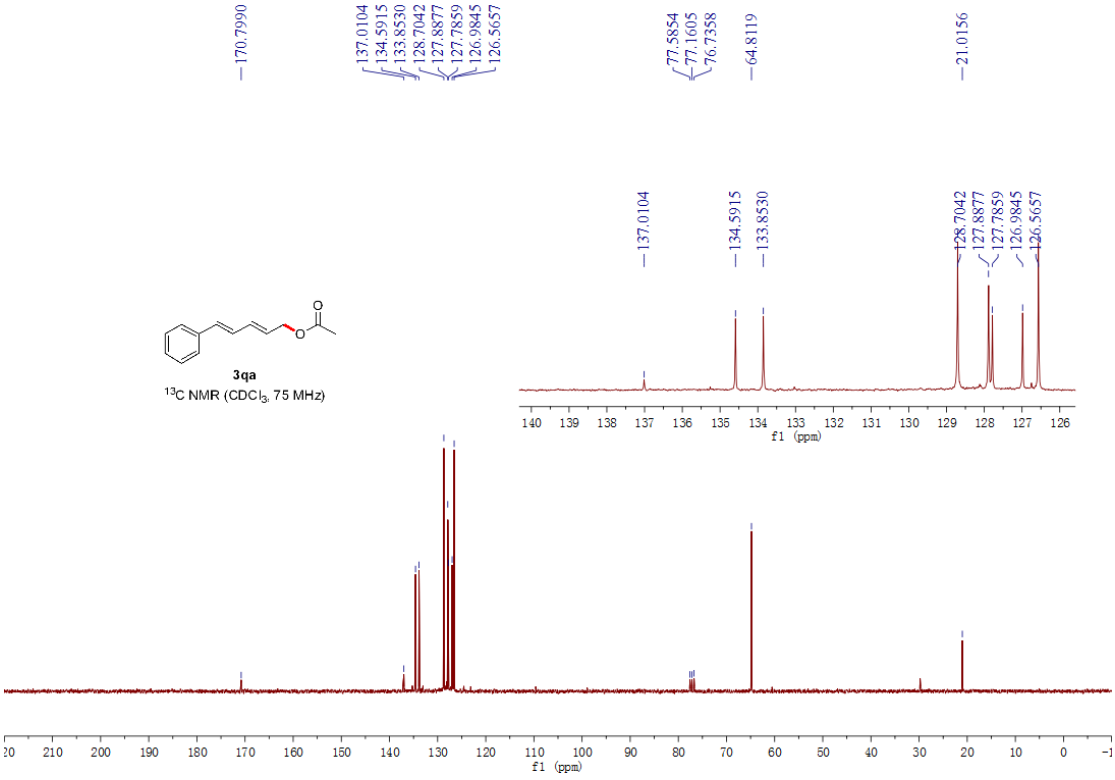
^{13}C NMR spectrum of purified **3pa**

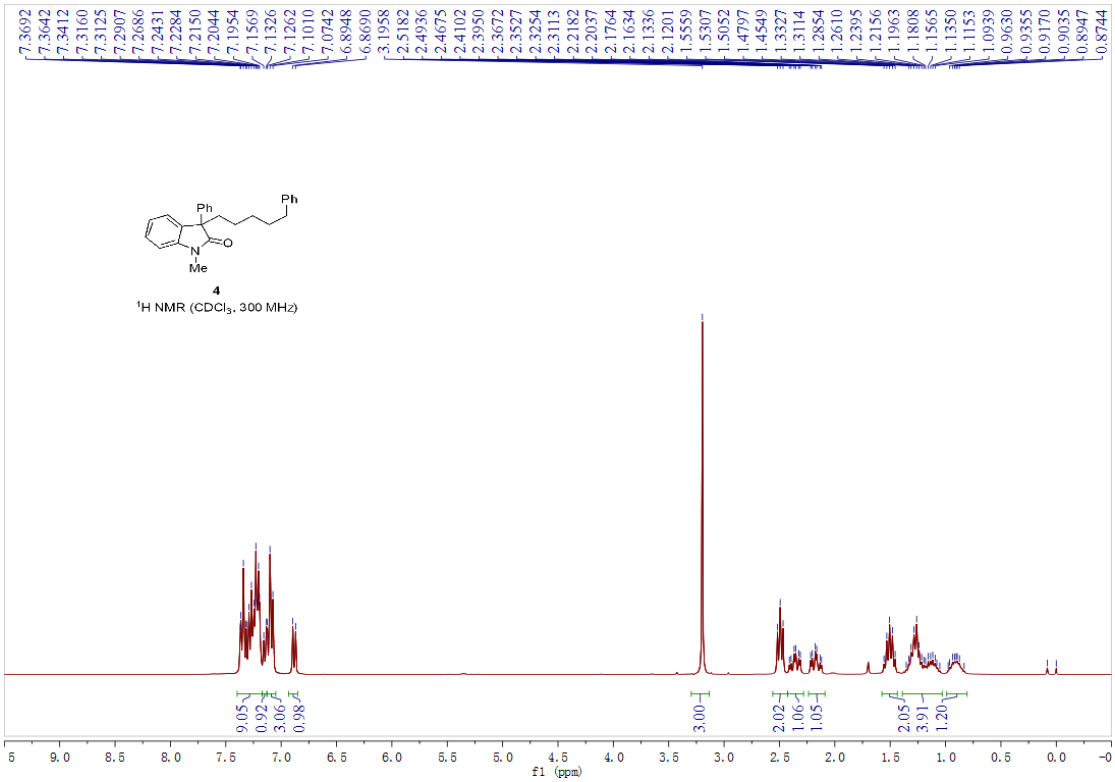


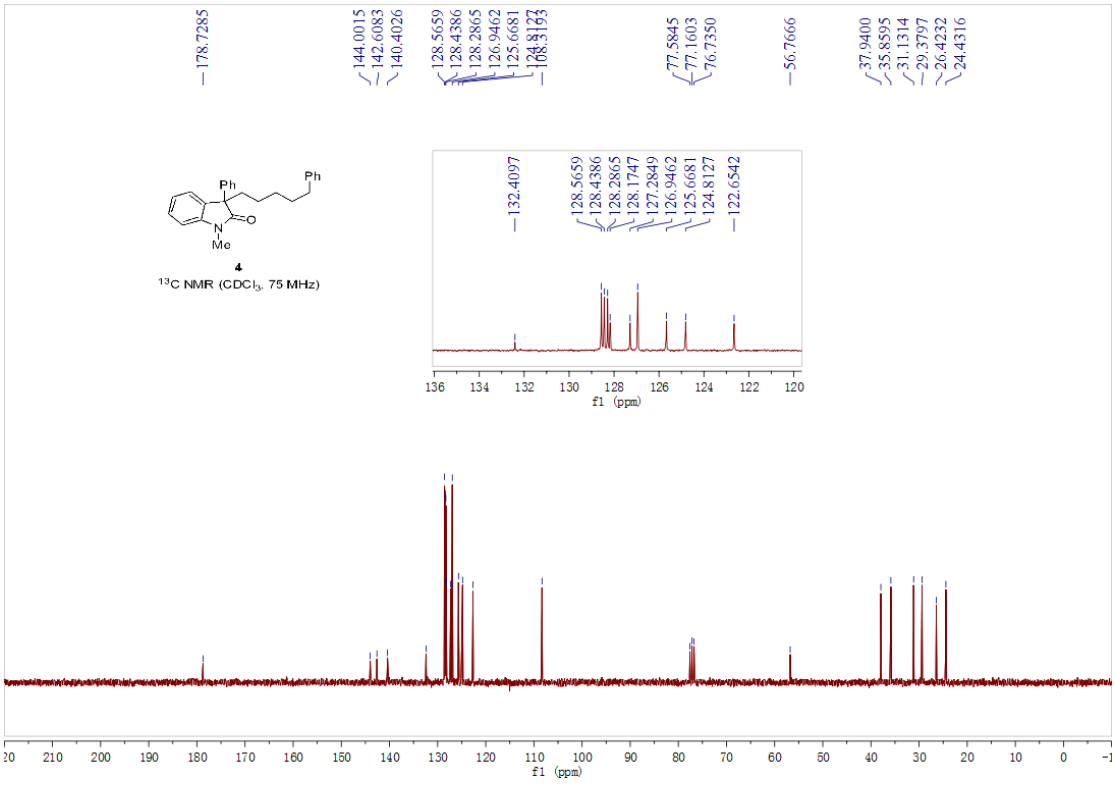
^{1}H NMR spectrum of purified **3qa**

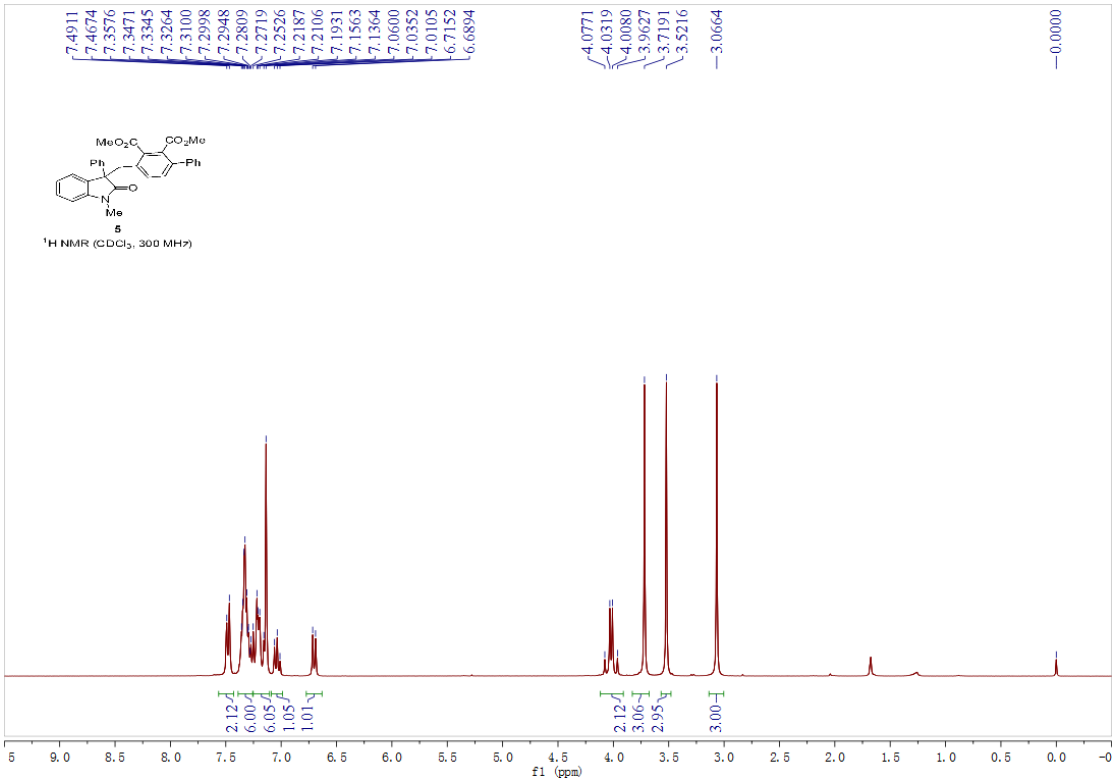


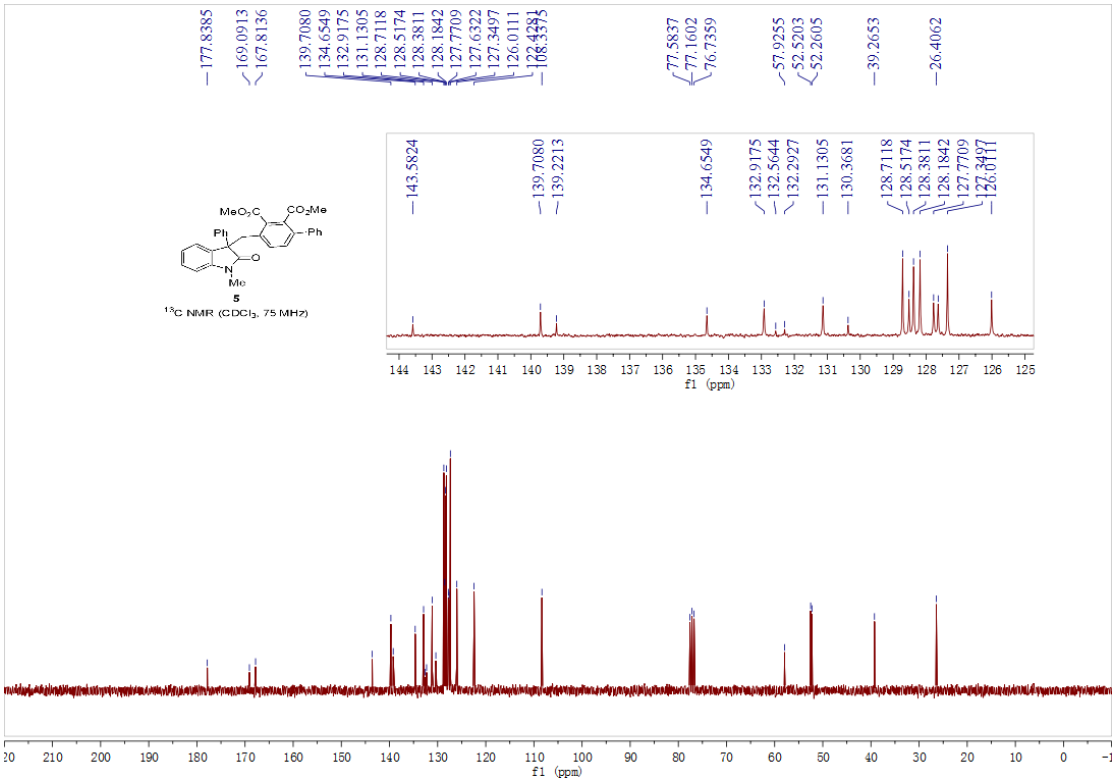
^{13}C NMR spectrum of purified **3qa**

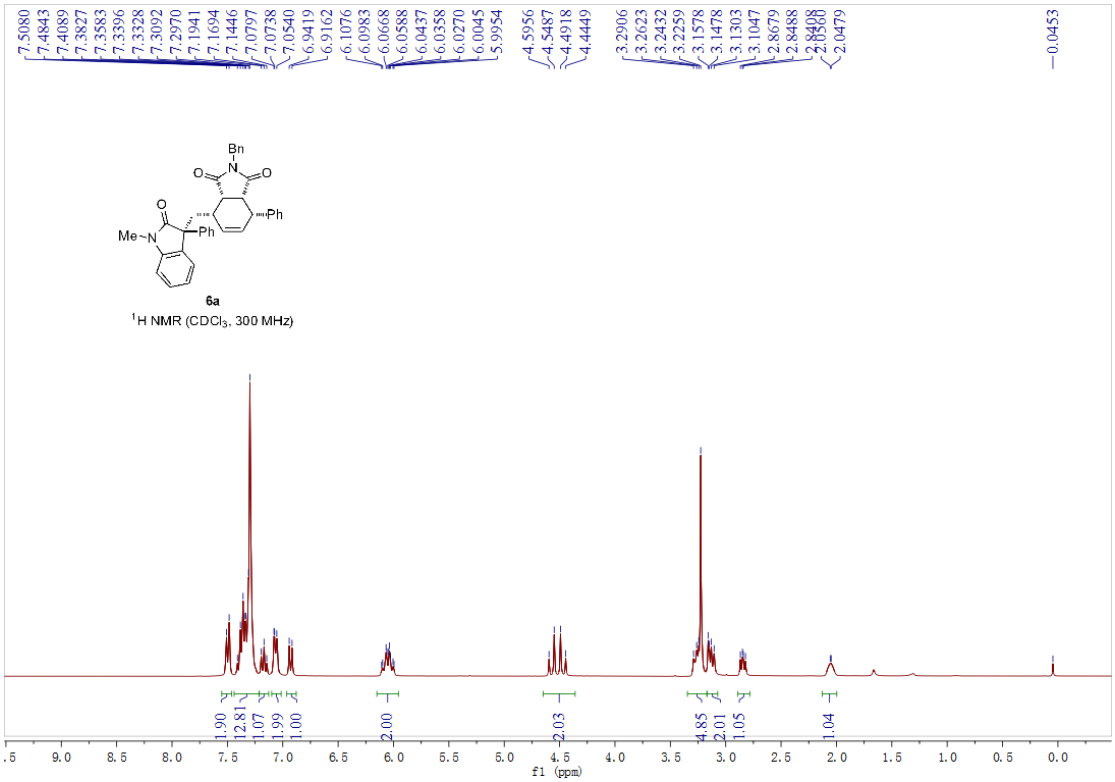


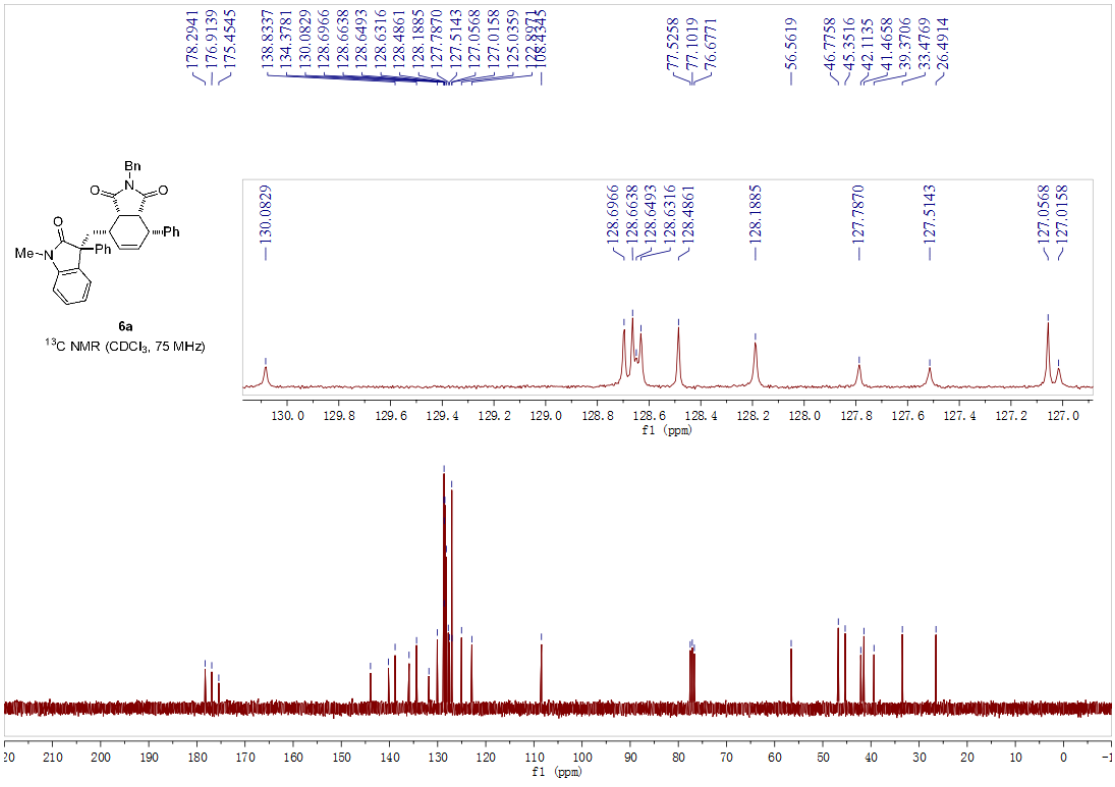

Ph
Ph
O
N
Me
4
1H NMR (CDCl3, 300 MHz)
f1 (ppm)

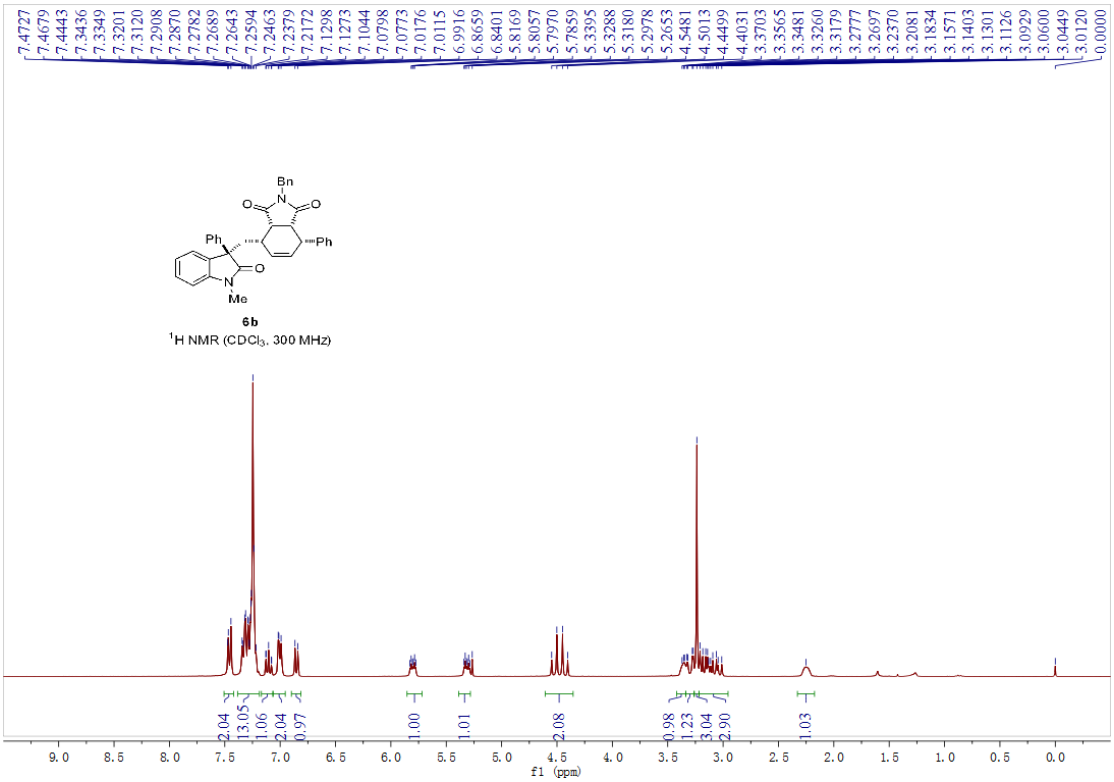

Ph
Ph
O
N
Me
4
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.4911
7.4674
7.3576
7.3471
7.3345
7.3264
7.3100
7.2998
7.2948
7.2809
7.2719
7.2526
7.2187
7.2106
7.1931
7.1563
7.1364
7.0600
7.0352
7.0105
6.7152
6.6894
4.0771
4.0319
4.0080
3.9627
3.7191
3.5216
3.0664
0.0000
MeO2C
CO2Me
Ph
Ph
O
N
Me
5
1H NMR (CDCl3, 300 MHz)
2.12
6.00
6.05
1.05
1.01
2.12
3.06
2.95
3.00
f1 (ppm)


177.8385
169.0913
167.8136
139.7080
134.6549
132.9175
131.1305
128.7118
128.5174
128.3811
128.1842
127.7709
127.6322
127.3497
126.0111
122.4281
108.3375
77.5837
77.1602
76.7359
57.9255
52.5203
52.2605
39.2653
26.4062
143.5824
139.7080
139.2213
134.6549
132.9175
132.5644
132.2927
131.1305
130.3681
128.7118
128.5174
128.3811
128.1842
127.7709
127.3497
126.0111
MeO2C
CO2Me
Ph
Ph
O
N
Me
5
13C NMR (CDCl3, 75 MHz)
f1 (ppm)
f1 (ppm)

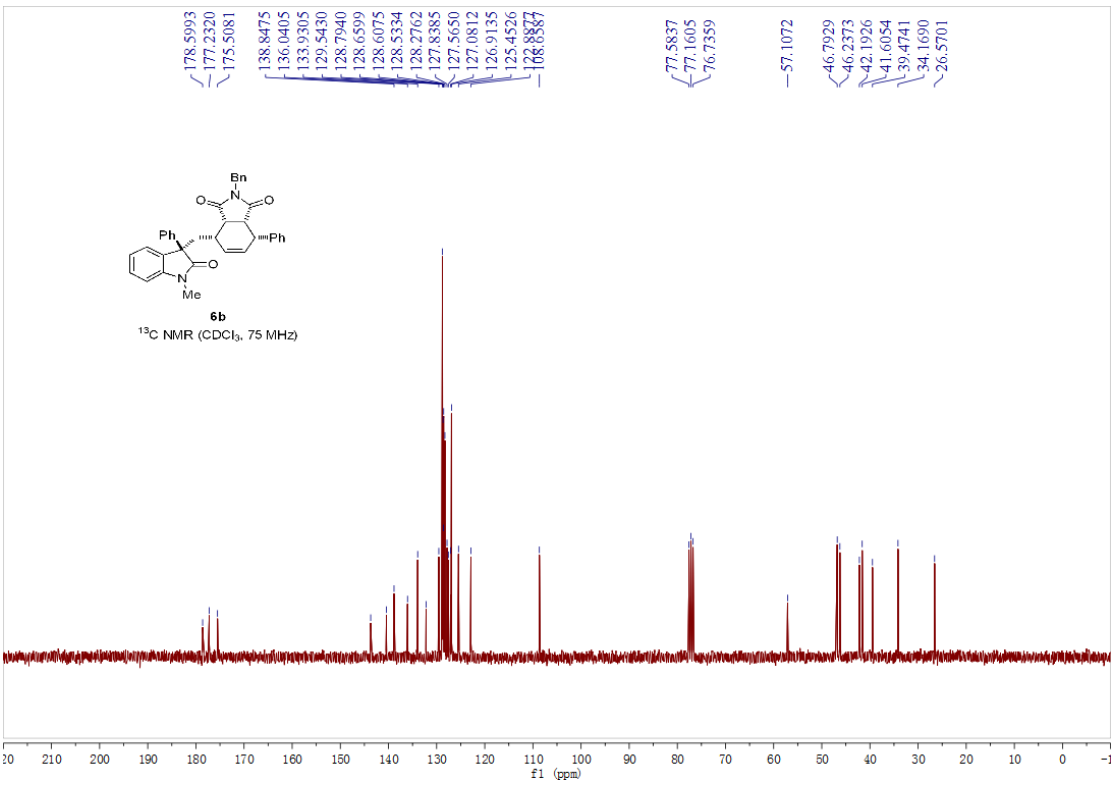

7.5080
7.4843
7.4089
7.3827
7.3583
7.3396
7.3328
7.3092
7.2970
7.1941
7.1694
7.1446
7.0797
7.0738
7.0540
6.9419
6.9162
6.1076
6.0983
6.0668
6.0588
6.0437
6.0358
6.0270
6.0045
5.9954
4.5956
4.5487
4.4918
4.4449
3.2906
3.2623
3.2432
3.2259
3.1578
3.1478
3.1303
3.1047
2.8679
2.8488
2.8408
2.0560
2.0479
0.0453
Bn
Me
Ph
Ph
6a
1H NMR (CDCl3, 300 MHz)
1.90
12.81
1.07
1.99
1.00
2.00
2.03
4.85
2.01
1.05
1.04
f1 (ppm)


178.2941
176.9139
175.4545
138.8337
134.3781
130.0829
128.6966
128.6638
128.6493
128.6316
128.4861
128.1885
127.7870
127.5143
127.0568
127.0158
125.0359
122.8971
108.4345
77.5258
77.1019
76.6771
56.5619
46.7758
45.3516
42.1135
41.4658
39.3706
33.4769
26.4914
Bn
Me
Ph
Ph
6a
13C NMR (CDCl3, 75 MHz)
130.0829
128.6966
128.6638
128.6493
128.6316
128.4861
128.1885
127.7870
127.5143
127.0568
127.0158
f1 (ppm)



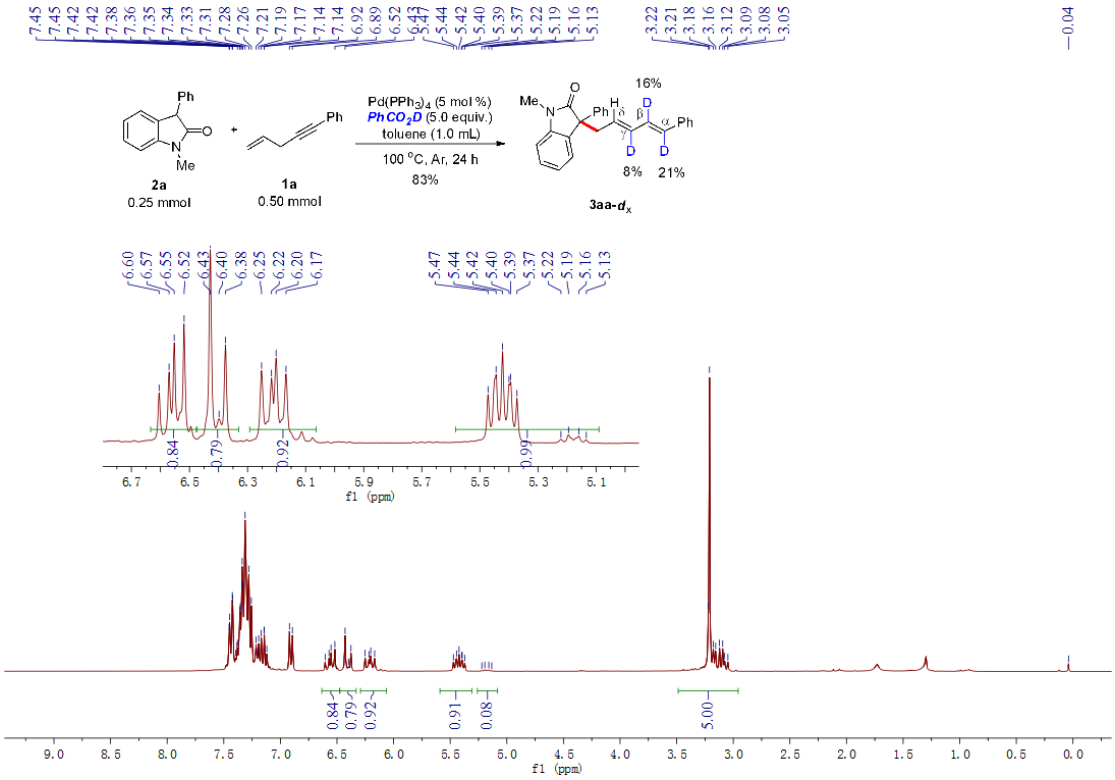
6b

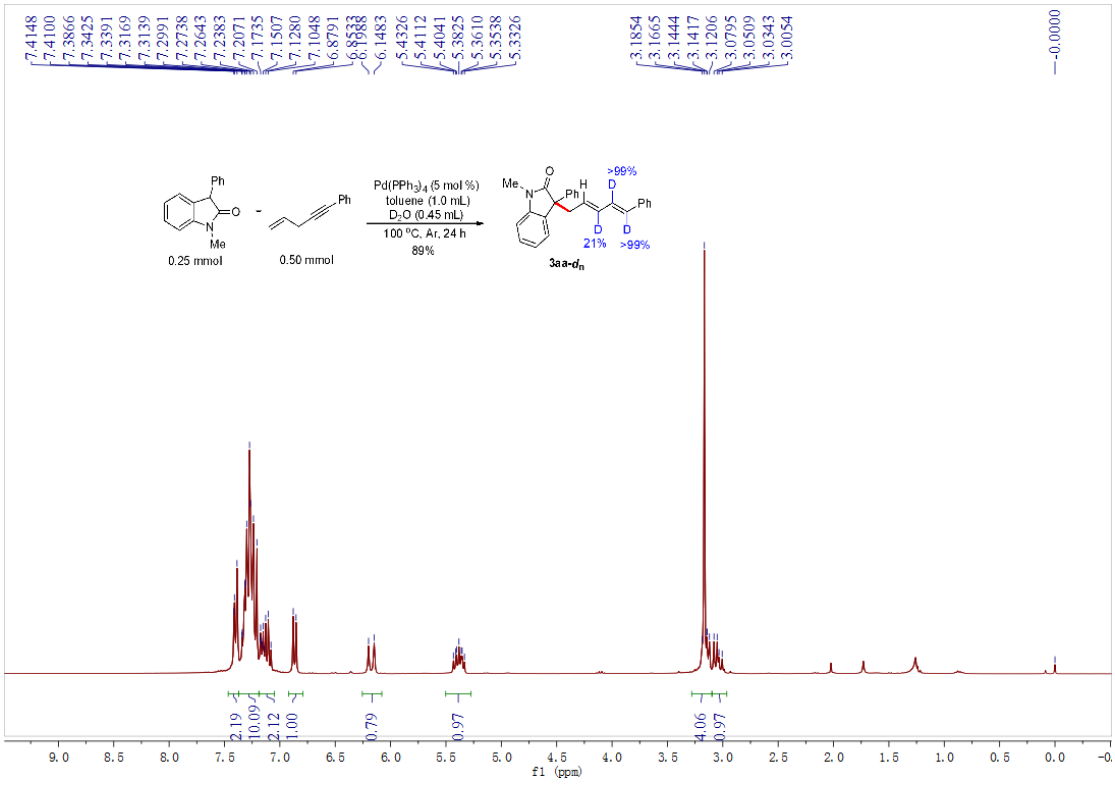
^{1}H NMR ($CDCl_3$, 300 MHz)



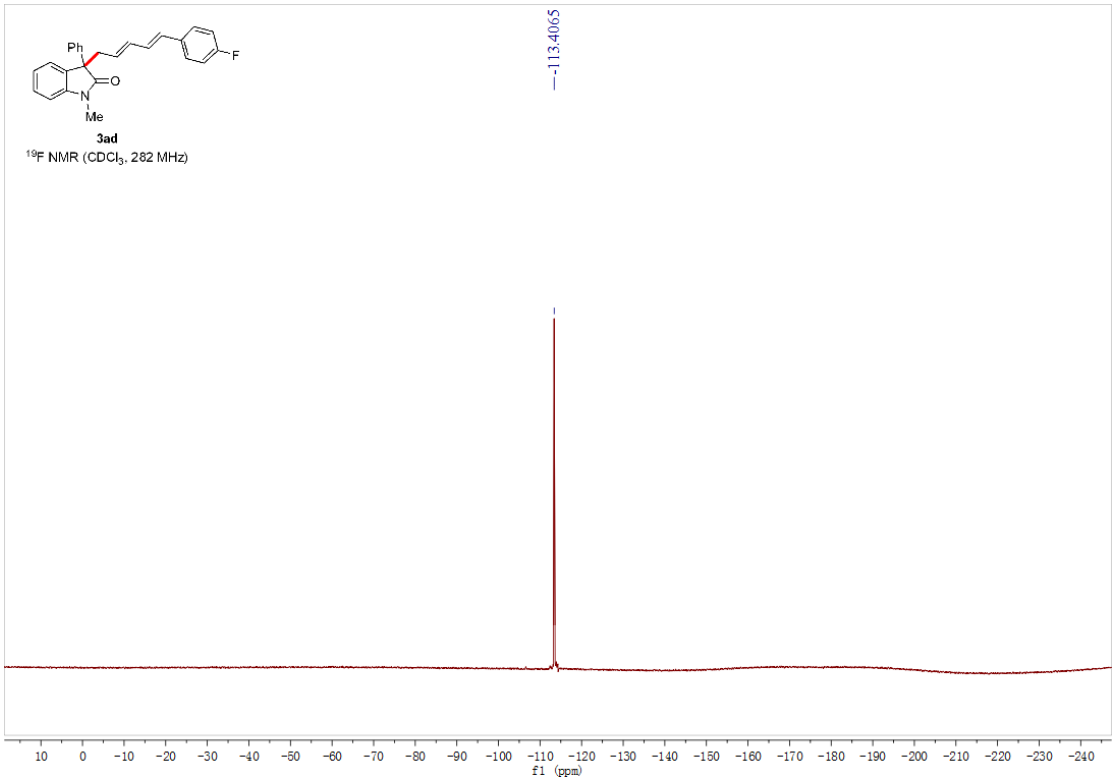
6b

^{13}C NMR ($CDCl_3$, 75 MHz)

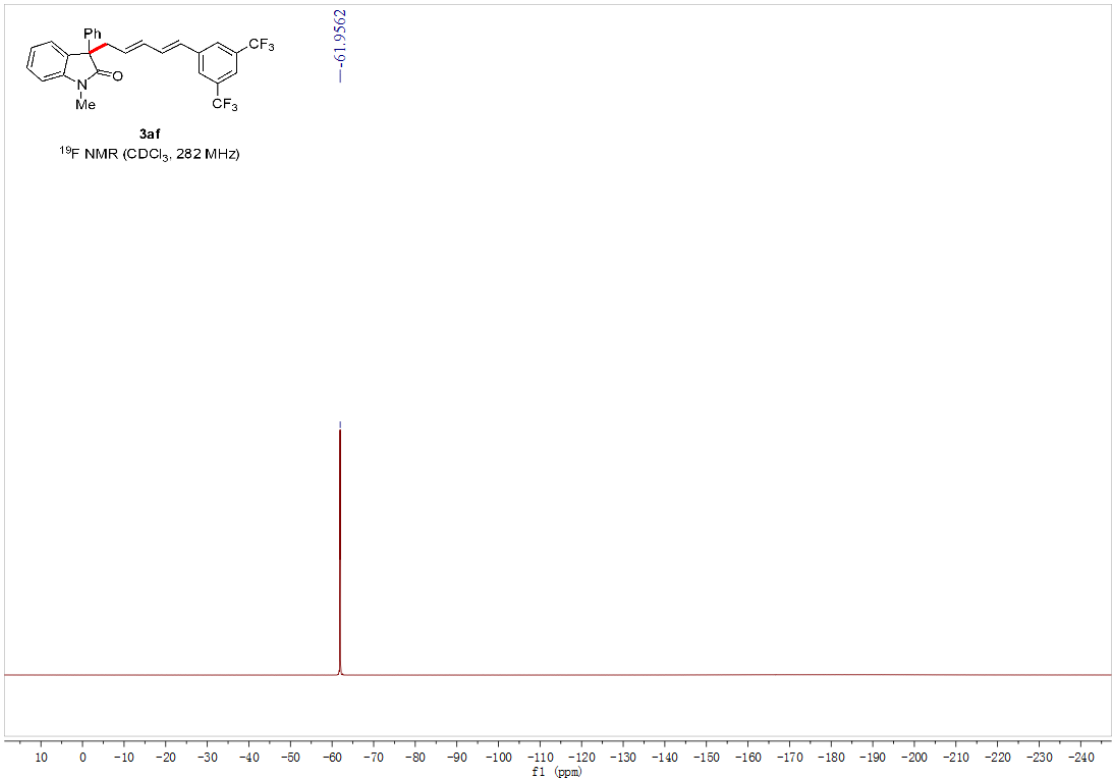

Pd(PPh3)4 (5 mol %)
PhCO2D (5.0 equiv.)
toluene (1.0 mL)
100 °C, Ar, 24 h
83%
2a
0.25 mmol
1a
0.50 mmol
16%
8% 21%
3aa-dx
f1 (ppm)


Pd(PPh3)4 (5 mol %)
toluene (1.0 mL)
D2O (0.45 mL)
100 °C, Ar, 24 h
89%
0.25 mmol
0.50 mmol
>99%
21%
>99%
3aa-dn
f1 (ppm)

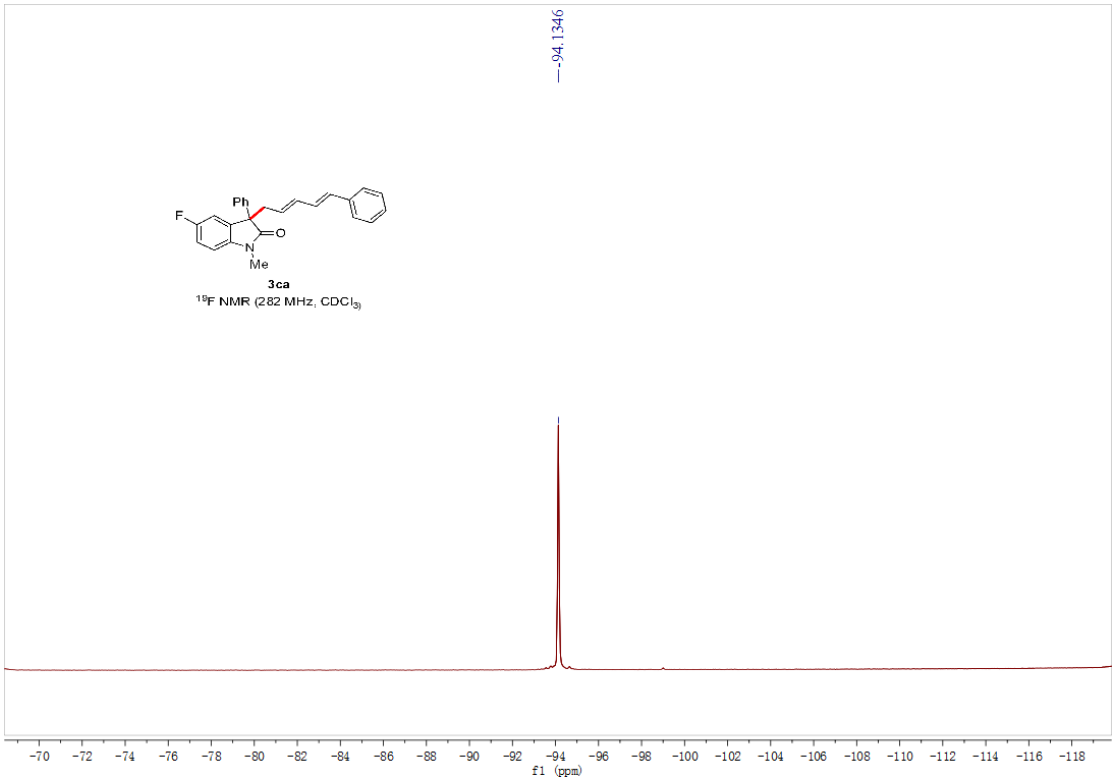
^{19}F NMR spectrum of purified **3ad**



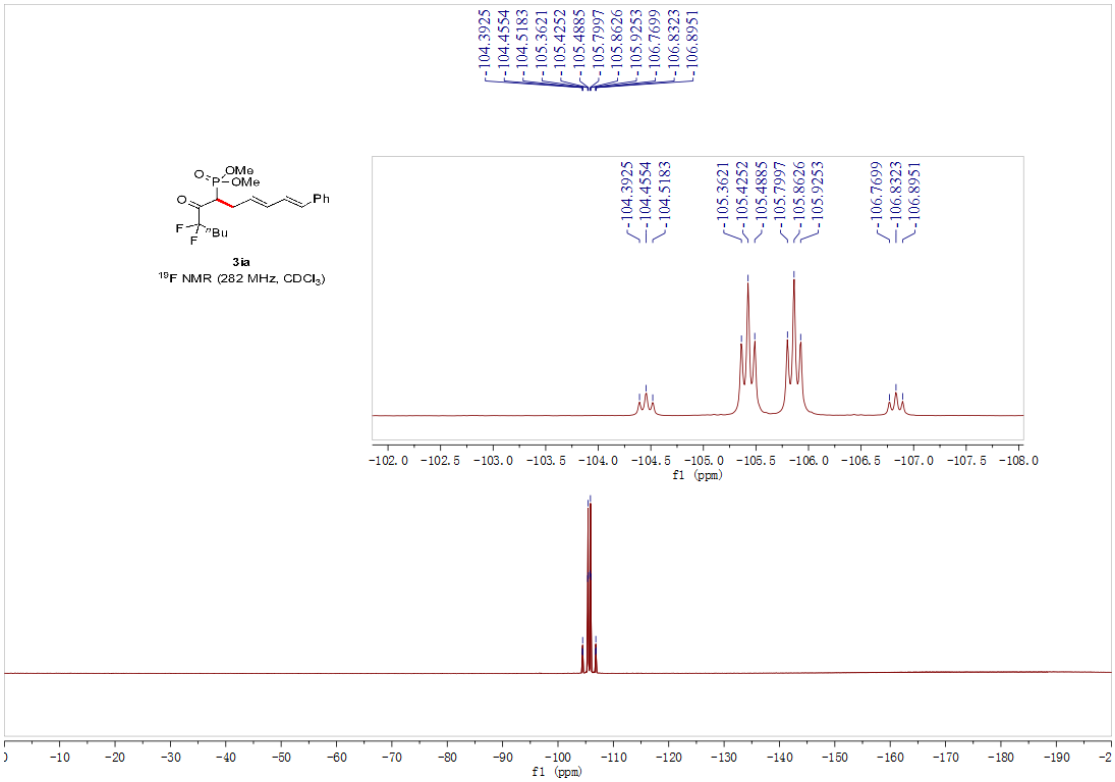
^{19}F NMR spectrum of purified **3af**



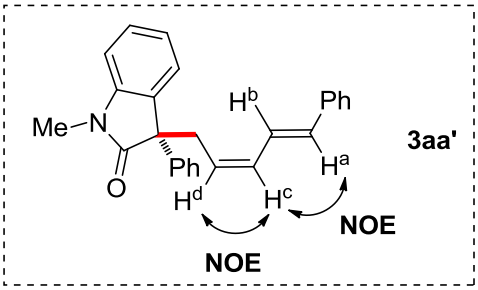
^{19}F NMR spectrum of purified **3ca**

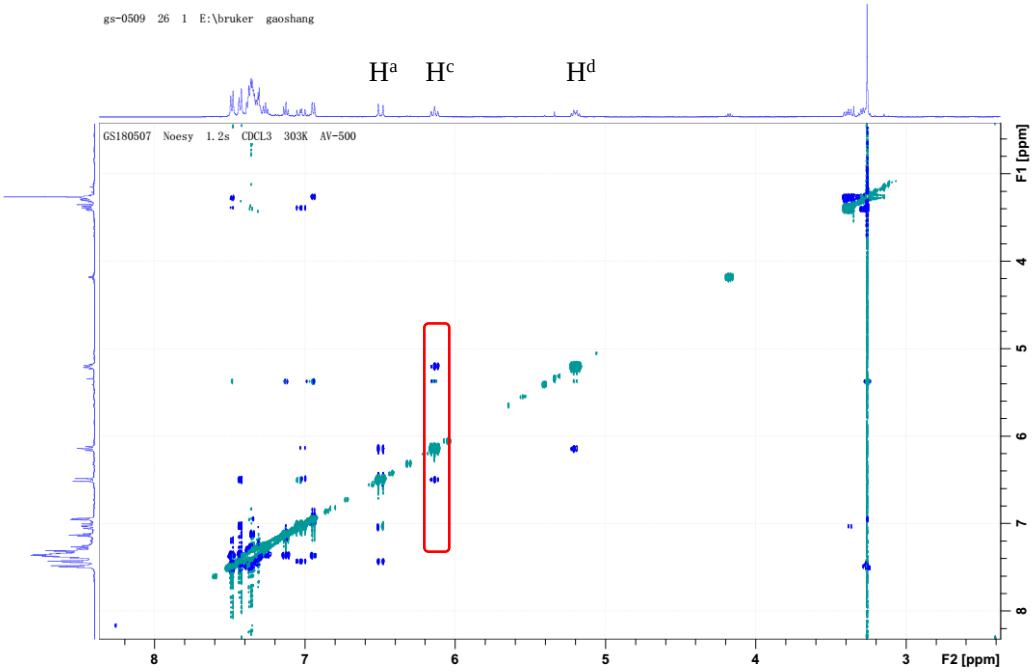


^{19}F NMR spectrum of purified **3ia**



NOE of 3aa'


Me
N
O
Ph
H^d
H^b
Ph
H^c
H^a
NOE
NOE
3aa'


gs-0509 26 1 E:\bruker gaoshang
H^a H^c H^d
GS180507 Noesy 1.2s CDCL3 303K AV-500
F1 [ppm]
F2 [ppm]
8
7
6
5
4
3