Supporting Information

Palladium-Catalyzed Dearomative Allylic Alkylation of Indoles with Alkynes To Synthesize Indolenines with C3-Quarternary Centers

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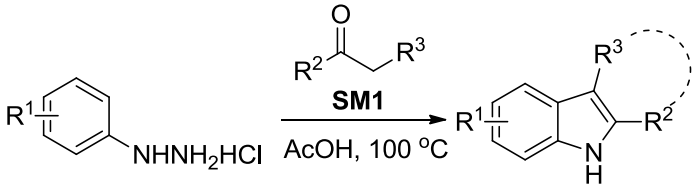
1. General Information

Reagents and Solvents: $Pd(PPh_3)_4$ and Cy_3P are commercially available. Toluene was distilled from sodium metal. 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: ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^{1}H 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. Melting point (m. p.) was measured on a microscopic melting point apparatus.

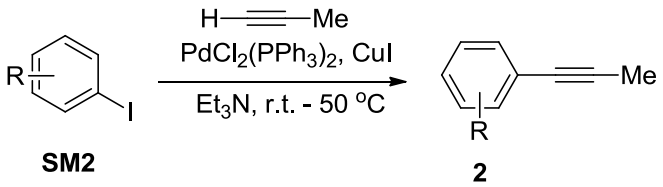
2. Preparation of 3,4-Disubstituted Indoles



Scheme S1. Preparation of 2,3-disubstituted indoles.

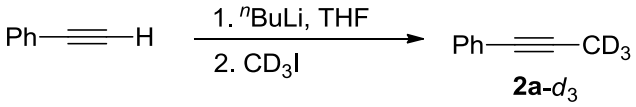
The suspension of substituted phenylhydrazine hydrochloride (40 mmol) in AcOH (40 mL) was heated in 50 ºC for 30 min, then butan-2-one **SM1** (80 mmol, 2 equiv) was added in one portion and the reaction mixture was refluxed for 3 h. After cooling to room temperature, AcOH was removed under vacum and the residue was dissolved in ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give gray residue, which was purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 200:1 to 60:1) to afford the 2,3-disubstituted indoles.

3. Preparation of Alkynes 2



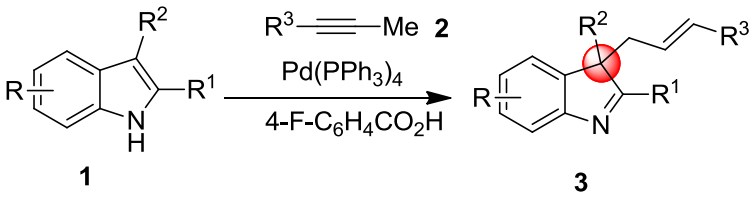
Scheme S2. Preparation of alkynes **2**

Substituted iodobenzene **SM2** (5 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (2 mol %) and CuI (4 mol %) were dissolved in 15 mL Et_3N and the reaction mixture was stirred under argon at r. t.~50 °C for 5 min. Propyne (ca. 5% in tetrahydrofuran, ca. 1 mol/L, purchased from TCI) was added in one portion and the solution was stirred for 5 h to 24 h. After the starting material was consumed completely which was detected by TLC, the reaction mixture was diluted with 60 mL ethyl acetate and filtered through a plug of Celite. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4. The mixture was concentrated *in vacuo* and purified by flash chromatography on silica gel with PE to afford the alkynylation products **2**.



According to the reported procedure:[1] To a flame-dried round-bottom flask under argon was added phenylacetylene (10 mmol, 1.0 equiv) followed by THF (30 mL) and the flask was cooled to -20 °C. *n*-Butyllithium (2.5 M in hexanes, 20 mmol, 2.0 equiv) was added slowly and the reaction was allowed to stir for 1 h. CD_3I (21 mmol, 2.1 equiv) was added at -20 °C and the reaction was allowed to stir at room temperature for 1 h. The reaction was quenched with a saturated solution of ammonium chloride and extracted with ethyl acetate. The organic layers were dried over $MgSO_4$. The mixture was concentrated *in vacuo* and purified by flash chromatography with PE on silica gel to afford **2a**-d_3.

4. General Procedure of Dearomative Allylic Alkylation of Indoles

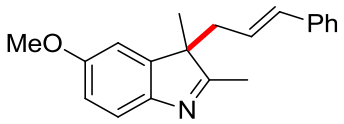


A sealed tube was charged with indoles **1** (0.25 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.025 mmol, 10 mol %), 4-fluorobenzoic acid (0.025 mmol, 10 mol %), alkynes **2** (0.5 mmol, 2.0 equiv) and anhydrous toluene (2.0 mL). The reaction mixture was

[1] Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 16474.

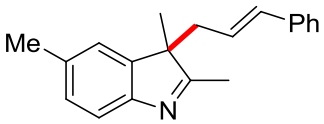
vigorously stirred at 100 ºC (oil temperature) for 24 h under argon. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and filtered through a plug of Celite. The mixture was concentrated *in vacuo* and purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 20:1 to 6:1) to afford the dearomative allylic alkenylated product **3**.

5. Characterization of the Dearomative Allylic Alkylation Products



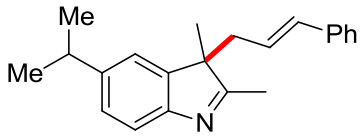
3-cinnamyl-5-methoxy-2,3-dimethyl-3H-indole (3aa)

66.2 mg, 91% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.14 (m, 5H), 6.85 – 6.80 (m, 2H), 6.32 (d, *J* = 15.7 Hz, 1H), 5.65 – 5.54 (m, 1H), 3.78 (s, 3H), 2.71 (dd, *J* = 13.9, 6.5 Hz, 1H), 2.50 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.24 (s, 3H), 1.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 157.8, 148.0, 145.1, 137.0, 133.1, 128.4, 127.3, 126.1, 124.2, 120.1, 112.2, 108.8, 57.8, 55.6, 40.4, 21.9, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{21}NO+H]^+$ 292.1696, found 292.1696.



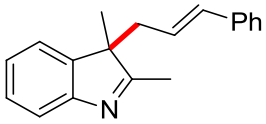
3-cinnamyl-2,3,5-trimethyl-3H-indole (3ba)

55.1 mg, 80% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.09 (m, 7H), 6.33 (d, *J* = 15.7 Hz, 1H), 5.63 – 5.53 (m, 1H), 2.74 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.52 (dd, *J* = 13.9, 8.2 Hz, 1H), 2.39 (s, 3H), 2.26 (s, 3H), 1.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6, 152.2, 143.7, 137.1, 134.8, 133.1, 128.5, 127.3, 126.2, 124.5, 122.8, 119.5, 57.6, 40.5, 22.0, 21.6, 16.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{21}N+H]^+$ 276.1747, found 276.1751.



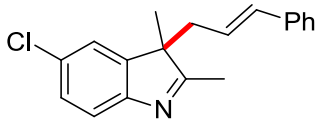
3-cinnamyl-5-isopropyl-2,3-dimethyl-3H-indole (3ca)

61.4 mg, 81% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.06 (m, 7H), 6.22 (d, *J* = 15.7 Hz, 1H), 5.61 – 5.51 (m, 1H), 2.85 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.65 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.39 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.18 (s, 3H), 1.25 (s, 3H), 1.17 (d, *J* = 6.9 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 152.4, 146.0, 143.6, 137.1, 133.2, 128.5, 127.3, 126.2, 125.8, 124.5, 120.1, 119.5, 57.6, 40.5, 34.2, 24.5, 24.3, 21.7, 16.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{22}H_{25}N+H]^+$ 304.2060, found 304.2059.



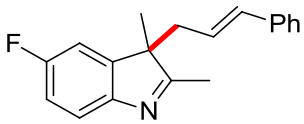
3-cinnamyl-2,3-dimethyl-3H-indole (3da)

50.3 mg, 77% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 11.6, 4.2 Hz, 2H), 7.19 (dt, *J* = 10.9, 8.5 Hz, 6H), 6.32 (d, *J* = 15.7 Hz, 1H), 5.70 – 5.49 (m, 1H), 2.76 (ddd, *J* = 13.9, 6.7, 1.2 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.29 (s, 3H), 1.35 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.6, 154.1, 143.4, 136.9, 133.2, 128.4, 127.8, 127.3, 126.1, 125.1, 124.1, 121.9, 119.9, 57.6, 40.3, 21.6, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{19}N+H]^+$ 262.1590, found 262.1602.



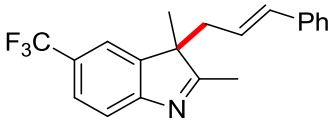
5-chloro-3-cinnamyl-2,3-dimethyl-3H-indole (3ea)

54.0 mg, 73% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 1H), 7.29 – 7.13 (m, 7H), 6.32 (d, *J* = 15.7 Hz, 1H), 5.59 – 5.49 (m, 1H), 2.74 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.54 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.28 (s, 3H), 1.34 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.1, 152.9, 145.4, 136.8, 133.6, 131.0, 128.5, 128.1, 127.5, 126.2, 123.6, 122.5, 120.9, 58.3, 40.3, 21.7, 16.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{18}ClN+H]^+$ 296.1201, found 296.1202.



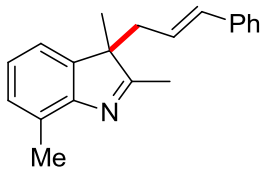
3-cinnamyl-5-fluoro-2,3-dimethyl-3H-indole (3fa)

50.3 mg, 72% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 9.1, 4.6 Hz, 1H), 7.25 – 7.13 (m, 5H), 7.01 – 6.95 (m, 2H), 6.32 (d, *J* = 15.7 Hz, 1H), 5.62–5.52 (m, 1H), 2.72 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.53 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.27 (s, 3H), 1.33 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.3, 162.8, 159.5, 150.3, 145.6, 145.4, 136.9, 133.6, 128.5, 128.3, 127.5, 126.2, 123.6, 120.6, 120.5, 114.6, 114.3, 109.9, 109.5, 58.4, 40.3, 21.7, 16.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{18}FN+H]^+$ 280.1496, found 280.1492.



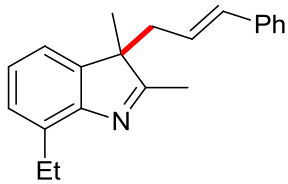
3-cinnamyl-2,3-dimethyl-5-(trifluoromethyl)-3H-indole (3ga)

35.4 mg, 43% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 3H), 7.14 – 7.01 (m, 5H), 6.20 (d, *J* = 15.7 Hz, 1H), 5.42 (dt, *J* = 15.3, 7.7 Hz, 1H), 2.68 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.45 (dd, *J* = 14.0, 8.1 Hz, 1H), 2.22 (s, 3H), 1.26 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 157.1, 144.1, 136.7, 135.0, 133.9, 132.2, 132.1, 128.5, 127.5, 127.4, 127.0, 126.4, 126.2, 125.7, 125.7, 125.6, 125.6, 123.2, 120.1, 119.05, 119.00, 118.95, 118.9, 58.3, 40.2, 21.5, 16.3 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{18}F_3N+H]^+$ 330.1464, found 330.1462.



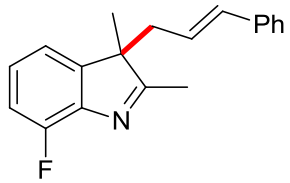
3-cinnamyl-2,3,7-trimethyl-3H-indole (3ha)

49.6 mg, 72% yield, yellow solid, m. p. 62 – 63 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 8H), 6.32 (d, *J* = 15.7 Hz, 1H), 5.69 – 5.59 (m, 1H), 2.73 (dd, *J* = 14.0, 6.7 Hz, 1H), 2.56 – 2.46 (m, 4H), 2.30 (s, 3H), 1.33 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5, 152.7, 143.4, 137.1, 133.1, 129.5, 129.2, 128.5, 127.3, 126.2, 125.0, 124.5, 119.4, 57.8, 40.5, 21.9, 17.0, 16.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{21}N+H]^+$ 276.1747, found 276.1748.



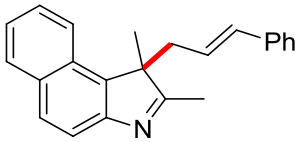
3-cinnamyl-7-ethyl-2,3-dimethyl-3H-indole (3ia)

49.9 mg, 69% yield, yellow solid, m. p. 76 – 78 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 – 7.01 (m, 8H), 6.20 (d, *J* = 15.7 Hz, 1H), 5.57 – 5.47 (m, 1H), 2.89 (dd, *J* = 14.7, 7.3 Hz, 2H), 2.61 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.37 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.19 (s, 3H), 1.21 – 1.18 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.2, 152.2, 143.4, 137.1, 135.8, 133.0, 128.4, 127.4, 127.2, 126.1, 125.1, 124.5, 119.4, 57.7, 40.5, 24.2, 21.7, 16.1, 15.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{23}N+H]^+$ 290.1903, found 290.1908.



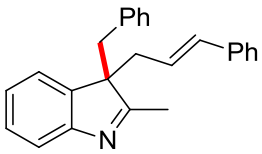
3-cinnamyl-7-fluoro-2,3-dimethyl-3H-indole (3ja)

37.0 mg, 53% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 6H), 7.08 – 6.99 (m, 2H), 6.31 (d, *J* = 15.7 Hz, 1H), 5.70 – 5.51 (m, 1H), 2.79 – 2.72 (m, 1H), 2.54 (dd, *J* = 14.0, 7.9 Hz, 1H), 2.32 (s, 3H), 1.35 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.2, 155.5, 152.2, 147.1, 147.0, 136.9, 133.6, 128.5, 127.5, 126.5, 126.5, 126.2, 123.7, 117.8, 117.7, 115.2, 115.0, 58.6, 40.4, 21.8, 16.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{18}FN+H]^+$ 280.1496, found 280.1497.



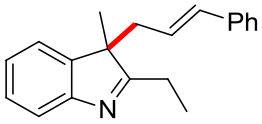
1-cinnamyl-1,2-dimethyl-1H-benzo[e]indole (3ka)

43.6 mg, 56% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.74 (m, 2H), 7.51 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.10 – 7.01 (m, 3H), 6.94 – 6.91 (m, 2H), 6.20 (d, *J* = 15.7 Hz, 1H), 5.26 – 5.16 (m, 1H), 3.22 (dd, *J* = 14.3, 6.2 Hz, 1H), 2.82 (dd, *J* = 14.3, 8.2 Hz, 1H), 2.36 (s, 3H), 1.54 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.9, 151.8, 136.8, 136.3, 132.5, 132.3, 129.8, 129.2, 128.9, 128.3, 127.2, 126.4, 126.1, 124.4, 124.1, 122.5, 119.9, 59.9, 40.2, 22.0, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{23}H_{21}N+H]^+$ 312.1747, found 312.1750.



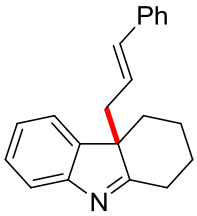
3-benzyl-3-cinnamyl-2-methyl-3H-indole (3la)

54.0 mg, 64% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.11 – 7.01 (m, 10H), 6.73 – 6.61 (m, 2H), 6.23 (d, *J* = 15.7 Hz, 1H), 5.43 – 5.33 (m, 1H), 3.18 (d, *J* = 13.5 Hz, 1H), 2.87 – 2.78 (m, 2H), 2.60 (dd, *J* = 14.0, 8.1 Hz, 1H), 2.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 155.0, 140.8, 136.9, 135.8, 133.3, 129.4, 128.4, 128.0, 127.8, 127.3, 126.7, 126.2, 124.7, 123.8, 123.0, 119.9, 63.0, 42.0, 39.7, 17.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{25}H_{23}N+H]^+$ 338.1903, found 338.1911.



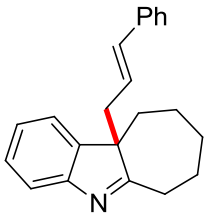
3-cinnamyl-2-ethyl-3-methyl-3H-indole (3ma)

33.7 mg, 49% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.23 (m, 3H), 7.21 – 7.12 (m, 5H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.63 – 5.53 (m, 1H), 2.78 – 2.68 (m, 1H), 2.63 – 2.48 (m, 3H), 1.38 – 1.34 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 154.1, 143.6, 137.1, 133.2, 128.5, 127.9, 127.4, 126.2, 125.1, 124.4, 121.9, 120.1, 57.9, 40.6, 22.6, 21.9, 10.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{21}N+H]^+$ 276.1747, found 276.1750.



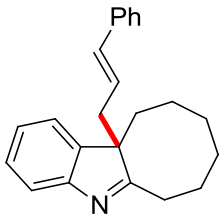
4a-cinnamyl-2,3,4,4a-tetrahydro-1H-carbazole (3na)

41.0 mg, 57% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.25– 7.23 (m, 2H), 7.16– 7.08 (m, 6H), 6.24 (d, *J* = 15.7 Hz, 1H), 5.60 – 5.50 (m, 1H), 2.81 (d, *J* = 11.7 Hz, 1H), 2.71 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.56 – 2.47 (m, 2H), 2.34 (d, *J* = 13.2 Hz, 1H), 2.13 (d, *J* = 11.2 Hz, 1H), 1.81 – 1.60 (m, 2H), 1.41–1.29 (m, 1H), 1.09 (td, *J* = 13.6, 2.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.9, 154.9, 144.7, 137.1, 133.2, 128.5, 127.8, 127.3, 126.2, 124.8, 124.0, 122.1, 120.3, 57.9, 36.7, 30.3, 28.9, 21.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{21}N+H]^+$ 288.1747, found 288.1750.



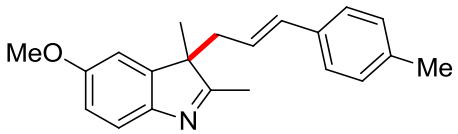
10a-cinnamyl-6,7,8,9,10,10a-hexahydrocyclohepta[b]indole (3oa)

18.1 mg, 24% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.15 (m, 8H), 6.27 (d, *J* = 15.7 Hz, 1H), 5.73 – 5.63 (m, 1H), 2.75 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.68 – 2.59 (m, 2H), 2.51 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.14 – 2.03 (m, 2H), 1.87 – 1.42 (m, 6H), 0.74 (dd, *J* = 24.1, 10.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 155.0, 143.8, 137.2, 133.2, 128.5, 127.9, 127.3, 126.2, 125.0, 124.2, 122.0, 119.9, 62.4, 40.8, 34.9, 31.7, 30.6, 28.7, 24.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{22}H_{23}N+H]^+$ 302.1903, found 302.1909.



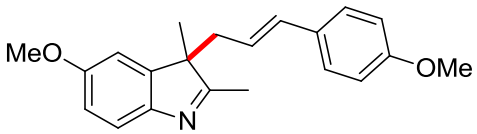
11a-cinnamyl-7,8,9,10,11,11a-hexahydro-6H-cycloocta[b]indole (3pa)

56.0 mg, 71% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.30 (td, *J* = 7.4, 1.7 Hz, 1H), 7.24 (m, 7.24 - 7.11, 7H), 6.23 (d, *J* = 15.7 Hz, 1H), 5.64 – 5.54 (m, 1H), 2.88 – 2.79 (m, 1H), 2.68 – 2.59 (m, 2H), 2.40 (dd, *J* = 13.5, 7.8 Hz, 1H), 2.33 – 2.04 (m, 3H), 1.97 – 1.85 (m, 1H), 1.65 – 1.59 (m, 1H), 1.49 – 1.41 (m, 1H), 1.39 – 1.26 (m, 2H), 1.02 – 0.85 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 155.0, 141.6, 137.1, 133.2, 128.4, 127.8, 127.2, 126.1, 124.8, 124.1, 122.1, 120.0, 62.0, 41.6, 31.4, 30.5, 30.2, 25.7, 25.2, 23.9 ppm. HRMS (ESI) *m/z* calcd for $[C_{23}H_{25}N+H]^+$ 316.2060, found 316.2077.



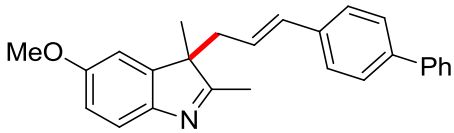
5-methoxy-2,3-dimethyl-3-(3-(p-tolyl)allyl)-3H-indole (3ab)

50.4 mg, 66% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 1H), 7.07 – 7.00 (m, 4H), 6.84 – 6.79 (m, 2H), 6.29 (d, *J* = 15.7 Hz, 1H), 5.61 – 5.51 (m, 1H), 3.78 (s, 3H), 2.70 (dd, *J* = 13.9, 6.5 Hz, 1H), 2.48 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.27 (s, 3H), 2.24 (s, 3H), 1.31 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 157.8, 147.9, 145.2, 137.1, 134.2, 133.0, 129.1, 126.1, 123.1, 120.1, 112.2, 108.8, 57.9, 55.7, 40.5, 21.9, 21.1, 15.9 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{23}NO+H]^+$ 306.1852, found 306.1858.



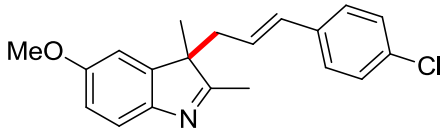
5-methoxy-3-(3-(4-methoxyphenyl)allyl)-2,3-dimethyl-3H-indole (3ac)

56.2 mg, 70% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (dd, *J* = 10.8, 2.4 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.27 (d, *J* = 15.7 Hz, 1H), 5.47 (dt, *J* = 15.3, 7.7 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 2.70 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.48 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.24 (s, 3H), 1.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.5, 159.0, 157.8, 148.0, 145.2, 132.6, 129.9, 127.3, 122.0, 120.1, 113.9, 112.2, 108.8, 58.0, 55.7, 55.3, 40.5, 21.9, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{23}NO_2+H]^+$ 322.1802, found 322.1807.



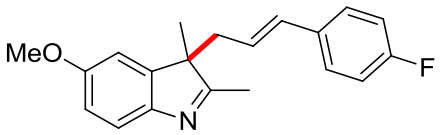
3-(3-([1,1'-biphenyl]-4-yl)allyl)-5-methoxy-2,3-dimethyl-3H-indole (3ad)

66.1 mg, 72% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.28 (m, 5H), 7.23 – 7.19 (m, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.77 – 6.73 (m, 2H), 6.26 (d, *J* = 15.7 Hz, 1H), 5.61 – 5.51 (m, 1H), 3.71 (s, 3H), 2.65 (dd, *J* = 13.9, 6.4 Hz, 1H), 2.44 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.17 (s, 3H), 1.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 157.9, 148.0, 145.1, 140.7, 140.1, 136.1, 132.8, 128.8, 127.3, 127.2, 126.9, 126.6, 124.4, 120.2, 112.3, 108.9, 57.9, 55.7, 40.6, 22.0, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{26}H_{25}NO+H]^+$ 368.2009, found 368.2012.



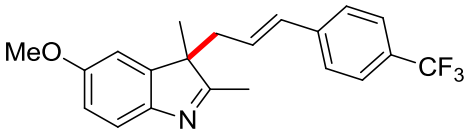
3-(3-(4-chlorophenyl)allyl)-5-methoxy-2,3-dimethyl-3H-indole (3ae)

70.9 mg, 87% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.83 – 6.80 (m, 2H), 6.25 (d, *J* = 15.7 Hz, 1H), 5.67 – 5.44 (m, 1H), 3.80 (s, 3H), 2.72 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.52 (dd, *J* = 14.0, 8.1 Hz, 1H), 2.24 (s, 3H), 1.33 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.2, 157.9, 148.0, 145.0, 135.5, 132.9, 131.9, 128.6, 127.4, 125.0, 120.2, 112.3, 108.8, 57.9, 55.7, 40.5, 22.0, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{20}ClNO+H]^+$ 326.1306, found 326.1311.



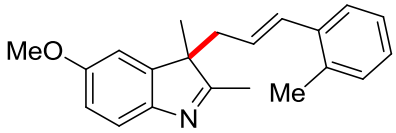
3-(3-(4-fluorophenyl)allyl)-5-methoxy-2,3-dimethyl-3H-indole (3af)

53.4 mg, 69% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 1H), 7.01 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.84 – 6.73 (m, 4H), 6.19 (d, *J* = 15.7 Hz, 1H), 5.44 – 5.34 (m, 1H), 3.72 (s, 3H), 2.63 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.46 (d, *J* = 8.1 Hz, 1H), 2.16 (s, 3H), 1.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 163.8, 160.5, 157.9, 148.0, 145.1, 133.2, 132.0, 127.7, 127.6, 124.0, 124.0, 120.2, 115.5, 115.2, 112.3, 108.8, 57.9, 55.7, 40.5, 22.0, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{20}FNO+H]^+$ 310.1602, found 310.1604.



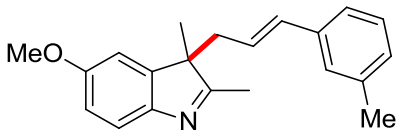
5-methoxy-2,3-dimethyl-3-(3-(4-(trifluoromethyl)phenyl)allyl)-3H-indole (3ag)

71.9 mg, 80% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.0, 3.2 Hz, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.75 – 6.72 (m, 2H), 6.23 (d, *J* = 15.8 Hz, 1H), 5.59 – 5.49 (m, 1H), 3.71 (s, 3H), 2.66 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.48 (dd, *J* = 14.1, 8.2 Hz, 1H), 2.16 (s, 3H), 1.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.0, 158.0, 148.0, 144.9, 140.5, 131.8, 129.3, 128.9, 127.2, 126.6, 126.3, 126.0, 125.5, 125.4, 125.4, 125.3, 122.4, 120.2, 112.3, 108.8, 57.9, 55.7, 40.4, 22.0, 15.9 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{20}F_3NO+H]^+$ 360.1570, found 360.1576.



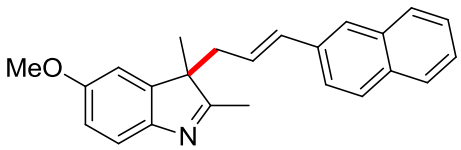
5-methoxy-2,3-dimethyl-3-(3-(o-tolyl)allyl)-3H-indole (3ah)

40.5 mg, 53% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 1H), 7.11 – 7.06 (m, 4H), 6.87 – 6.80 (m, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 5.48 – 5.38 (m, 1H), 3.80 (s, 3H), 2.74 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.56 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.27 (s, 3H), 2.17 (s, 3H), 1.34 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 157.9, 148.1, 145.2, 136.5, 135.1, 131.5, 130.1, 127.3, 126.0, 126.0, 125.7, 120.2, 112.2, 108.9, 58.1, 55.8, 40.8, 22.1, 19.8, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{23}NO+H]^+$ 306.1852, found 306.1849.



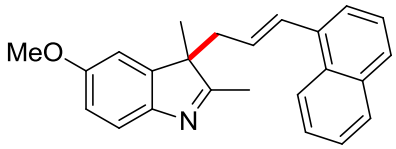
5-methoxy-2,3-dimethyl-3-(3-(m-tolyl)allyl)-3H-indole (3ai)

57.3 mg, 75% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.89 (s, 3H), 6.77 – 6.72 (m, 2H), 6.21 (d, *J* = 15.7 Hz, 1H), 5.56 – 5.46 (m, 1H), 3.71 (s, 3H), 2.63 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.42 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.19 (s, 3H), 2.17 (s, 3H), 1.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 157.8, 148.0, 145.2, 138.0, 137.0, 133.3, 128.4, 128.2, 126.9, 124.0, 123.4, 120.2, 112.3, 108.8, 57.9, 55.7, 40.5, 22.0, 21.4, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{23}NO+H]^+$ 306.1852, found 306.1855.



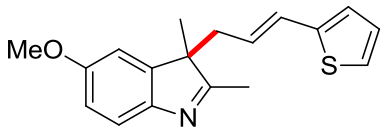
5-methoxy-2,3-dimethyl-3-(3-(naphthalen-2-yl)allyl)-3H-indole (3aj)

60.6 mg, 71% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.42 (s, 1H), 7.36 – 7.25 (m, 4H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.68 – 5.57 (m, 1H), 3.68 (s, 3H), 2.65 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.44 (dd, *J* = 14.0, 8.1 Hz, 1H), 2.16 (s, 3H), 1.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 157.9, 148.0, 145.1, 134.4, 133.5, 133.3, 132.8, 128.1, 127.9, 127.6, 126.2, 125.9, 125.7, 124.6, 123.5, 120.2, 112.3, 108.8, 57.9, 55.7, 40.6, 22.0, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{24}H_{23}NO+H]^+$ 342.1852, found 342.1852.



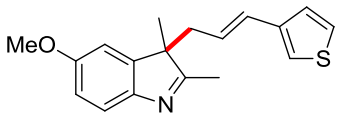
5-methoxy-2,3-dimethyl-3-(3-(naphthalen-1-yl)allyl)-3H-indole (3ak)

52.1 mg, 61% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.32 (m, 3H) 7.23 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 6.7 Hz, 1H), 6.87 (d, *J* = 15.5 Hz, 1H), 6.82 (d, *J* = 2.1 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.49 (dt, *J* = 15.0, 7.3 Hz, 1H), 3.70 (s, 3H), 2.73 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.56 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.21 (s, 3H), 1.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 158.0, 148.1, 145.2, 135.0, 133.5, 131.0, 130.9, 128.4, 127.7, 127.6, 125.9, 125.7, 125.6, 124.1, 124.0, 120.2, 112.3, 108.9, 58.1, 55.8, 40.9, 22.0, 16.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{24}H_{23}NO+H]^+$ 342.1852, found 342.1854.



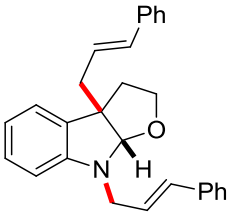
5-methoxy-2,3-dimethyl-3-(3-(thiophen-2-yl)allyl)-3H-indole (3al)

37.9 mg, 51% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 5.0 Hz, 1H), 6.88 – 6.78 (m, 4H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.54 (dt, *J* = 15.2, 7.4 Hz, 1H), 3.80 (s, 3H), 2.66 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.42 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.24 (s, 3H), 1.31 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 157.8, 147.9, 144.9, 142.0, 127.3, 126.3, 125.0, 124.0, 123.8, 120.2, 112.5, 108.8, 57.8, 55.7, 40.2, 21.7, 15.9 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{19}NOS+H]^+$ 298.1260, found 298.1260.



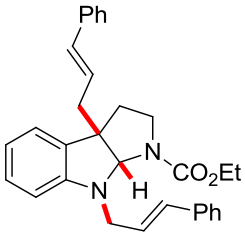
5-methoxy-2,3-dimethyl-3-(3-(thiophen-3-yl)allyl)-3H-indole (3am)

49.8 mg, 67% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 1H), 7.08 – 7.06 (m, 1H), 6.88 (d, *J* = 4.0 Hz, 2H), 6.76 – 6.72 (m, 2H), 6.24 (d, *J* = 15.7 Hz, 1H), 5.42 – 5.31 (m, 1H), 3.72 (s, 3H), 2.64 – 2.57 (m, 1H), 2.39 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.16 (s, 3H), 1.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 157.8, 147.9, 145.1, 139. 6, 127.3, 125.8, 125.0, 124.0, 121.4, 120.1, 112.2, 108.8, 57.8, 55.7, 40.4, 21.9, 15.9 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{19}NOS+H]^+$ 298.1260, found 298.1263.



(3aS,8aS)-3a,8-dicinnamyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (5aa)

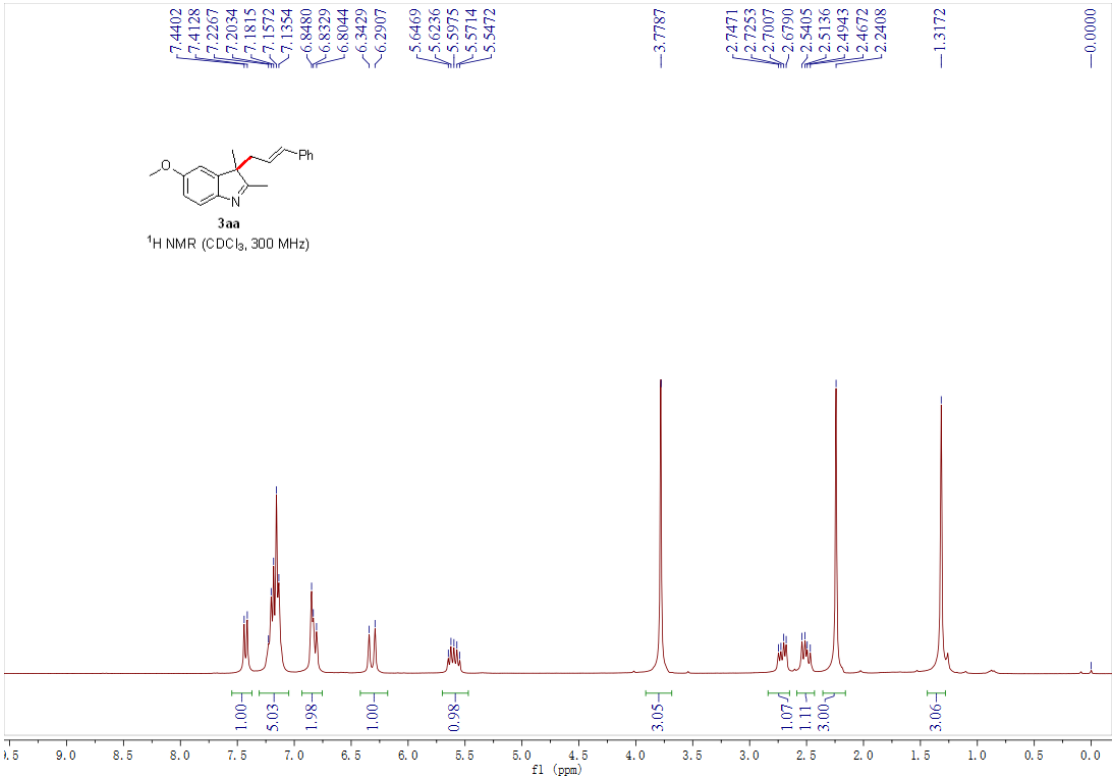
76.7 mg, 78% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 10H), 7.07 (t, *J* = 6.4 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.46 – 6.41 (m, 2H), 6.20 – 6.02 (m, 2H), 5.36 (s, 1H), 4.06 (d, *J* = 5.5 Hz, 2H), 3.97 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.56 – 3.48 (m, 1H), 2.78 (dd, *J* = 13.8, 5.5 Hz, 1H), 2.61 (dd, *J* = 13.8, 8.6 Hz, 1H), 2.24 – 2.10 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 137.4, 136.9, 133.2, 132.5, 131.8, 128.6, 128.6, 128.4, 127.4, 127.3, 126.4, 126.3, 126.1, 126.0, 123.4, 117.5, 105.5, 101.3, 67.0, 56.6, 46.7, 41.9, 40.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{28}H_{27}NO+H]^+$ 394.2165, found 394.2165.

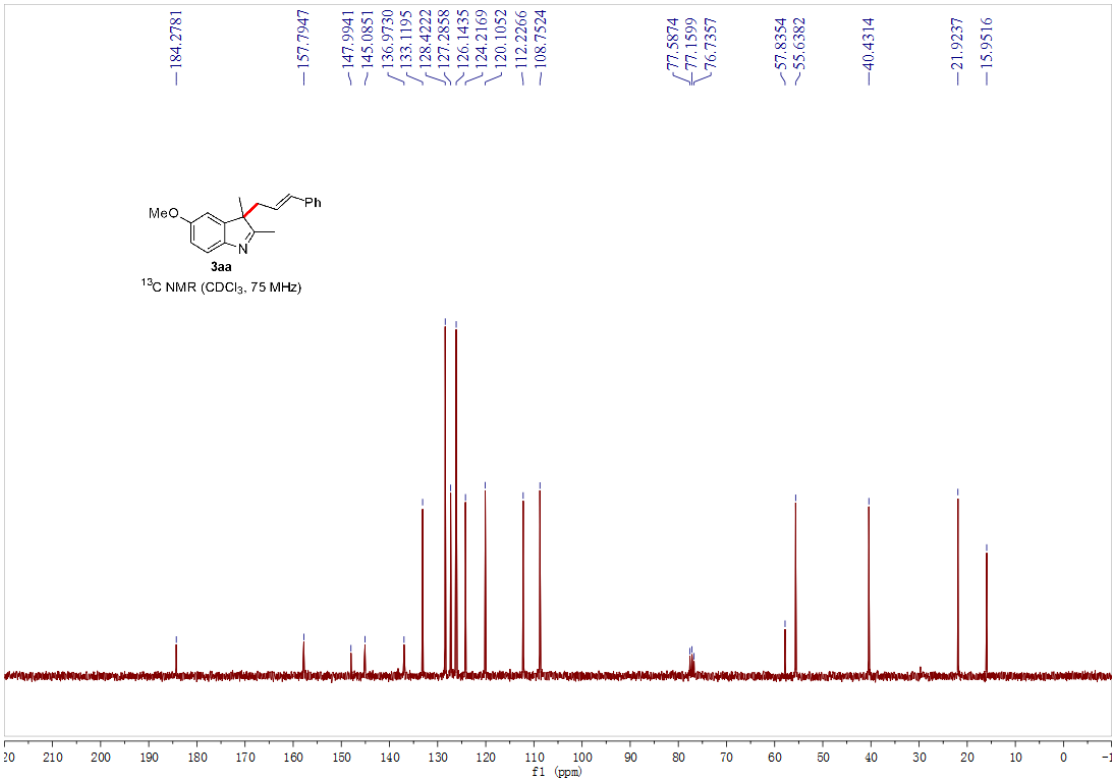


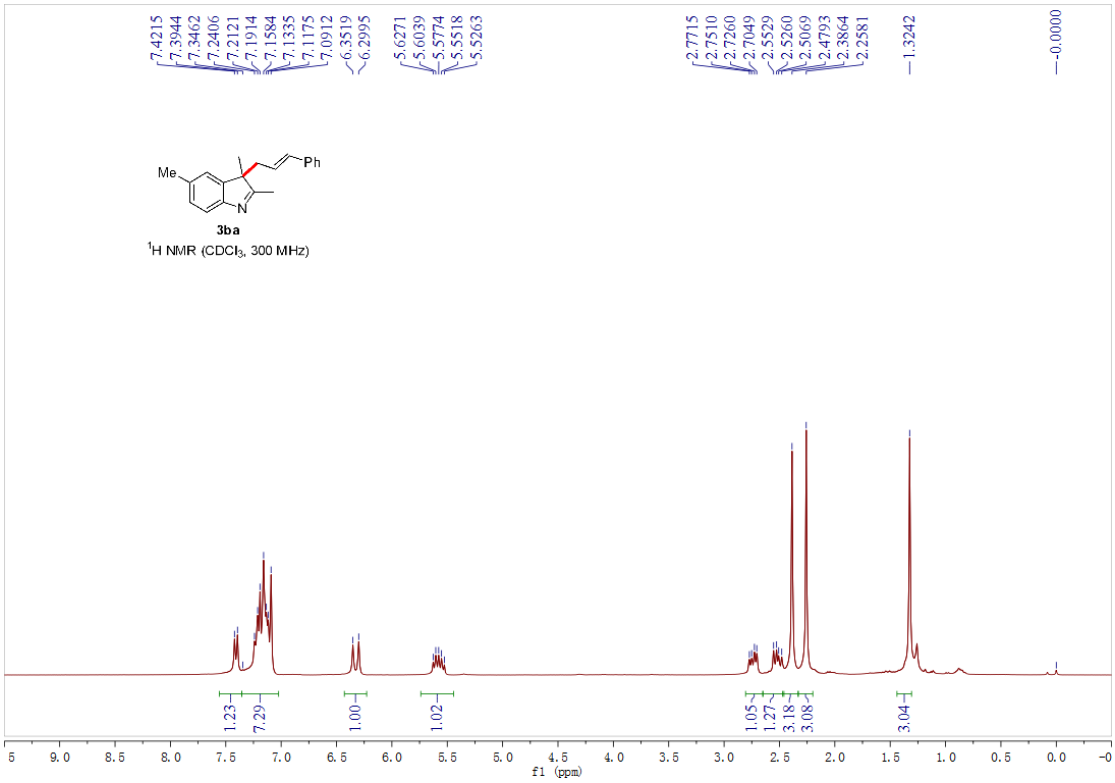
(3aS,8aS)-ethyl 3a,8-dicinnamyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (5ab)

105.7 mg, 91% yield, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 – 6.92 (m, 12H), 6.61 – 6.29 (m, 4H), 6.09 – 5.91 (m, 2H), 5.45 – 5.30 (m, 1H), 4.22 – 3.98 (m, 4H), 3.83 – 3.67 (m, 1H), 3.03 (td, *J* = 10.6, 6.7 Hz, 1H), 2.60 – 2.41 (m, 2H), 2.04 – 1.90 (m, 2H), 1.15 – 1.06 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 150.0, 137.2, 137.1, 136.8, 133.4, 132.2, 132.2, 131.2, 128.5, 128.4, 127.2, 127.1, 126.3, 126.1, 125.4, 122.8, 117.7, 117.4, 106.4, 84.4, 84.0, 61.4, 61.2, 57.4, 56.2, 48.2, 45.4, 42.4, 37.5, 37.2, 14.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{31}H_{32}N_2O_2+H]^+$ 465.2536, found 465.2531.

6. ^{1}H and ^{13}C NMR Spectra of Title Compounds



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7.3462
7.2406
7.2121
7.1914
7.1584
7.1335
7.1175
7.0912
6.3519
6.2995
5.6271
5.6039
5.5774
5.5518
5.5263
2.7715
2.7510
2.7260
2.7049
2.5529
2.5260
2.5069
2.4793
2.3864
2.2581
1.3242
-0.0000
Me
Ph
N
3ba
1H NMR (CDCl3, 300 MHz)
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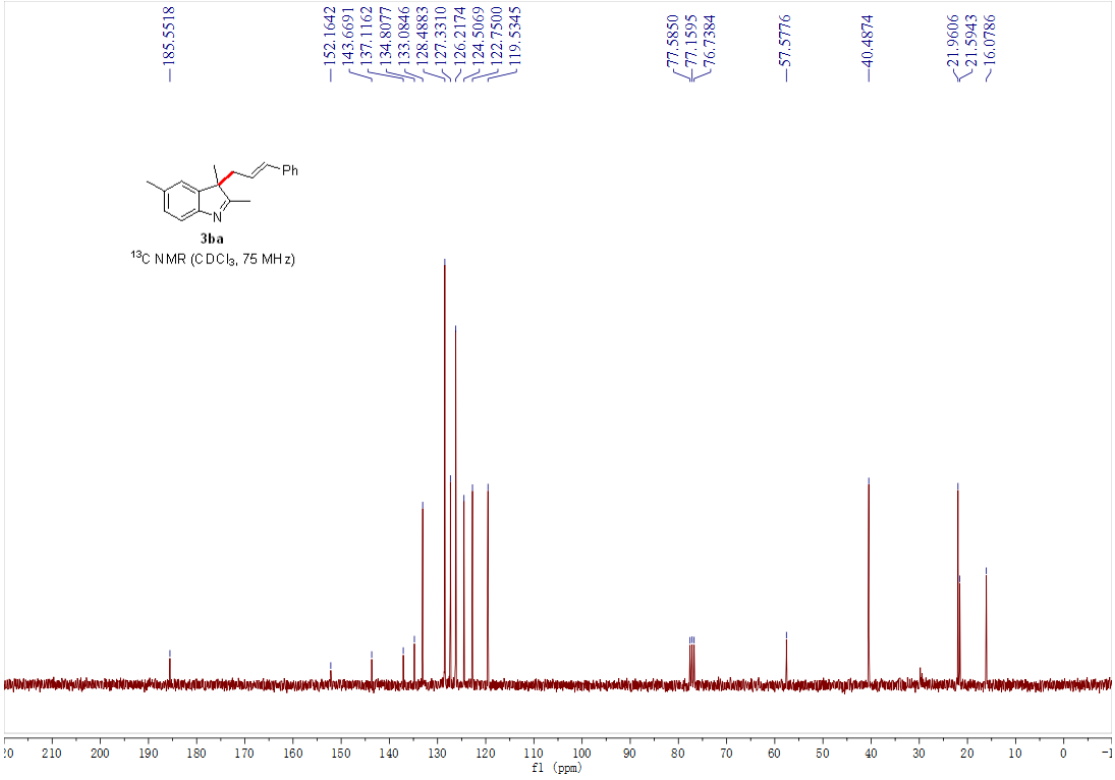
7.29
1.00
1.02
1.05
1.27
3.18
3.08
3.04
f1 (ppm)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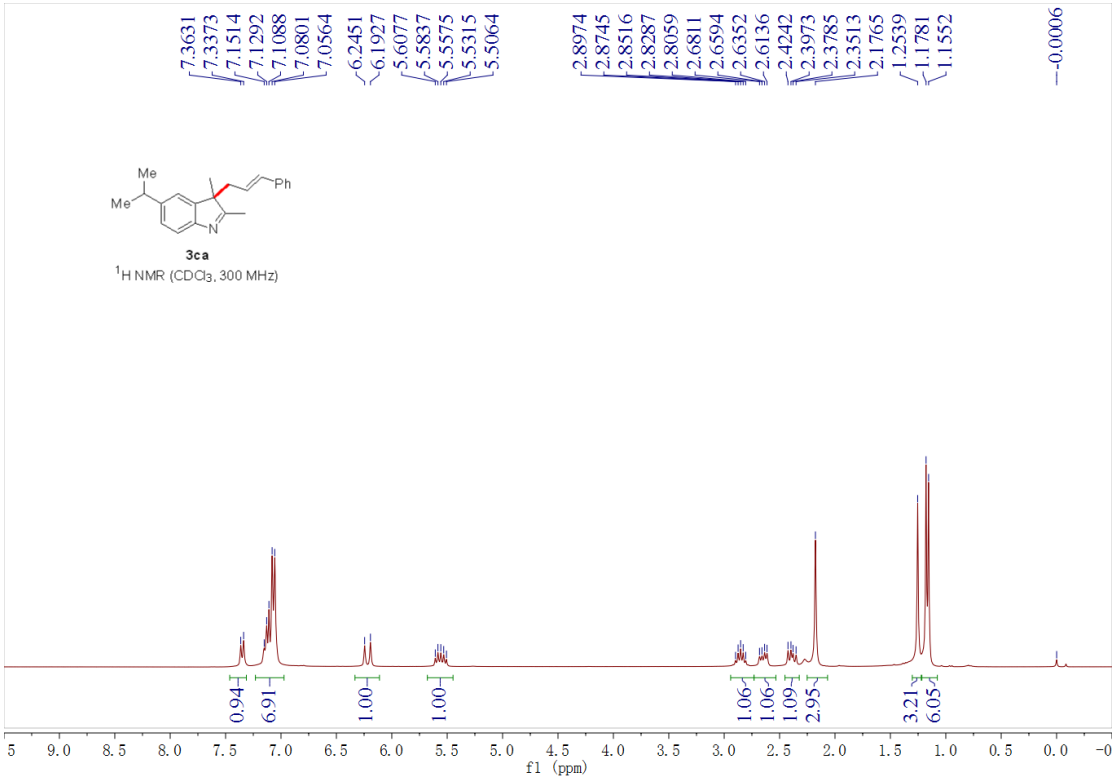
143.6691
137.1162
134.8077
133.0846
128.4883
127.3310
126.2174
124.5069
122.7500
119.5345
77.5850
77.1595
76.7384
57.5776
40.4874
21.9606
21.5943
16.0786
Ph
N
3ba
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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7.1514
7.1292
7.1088
7.0801
7.0564
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6.1927
5.6077
5.5837
5.5575
5.5315
5.5064
2.8974
2.8745
2.8516
2.8287
2.8059
2.6811
2.6594
2.6352
2.6136
2.4242
2.3973
2.3785
2.3513
2.1765
1.2539
1.1781
1.1552
-0.0006
Me
Me
Ph
N
3ca
1H NMR (CDCl3, 300 MHz)
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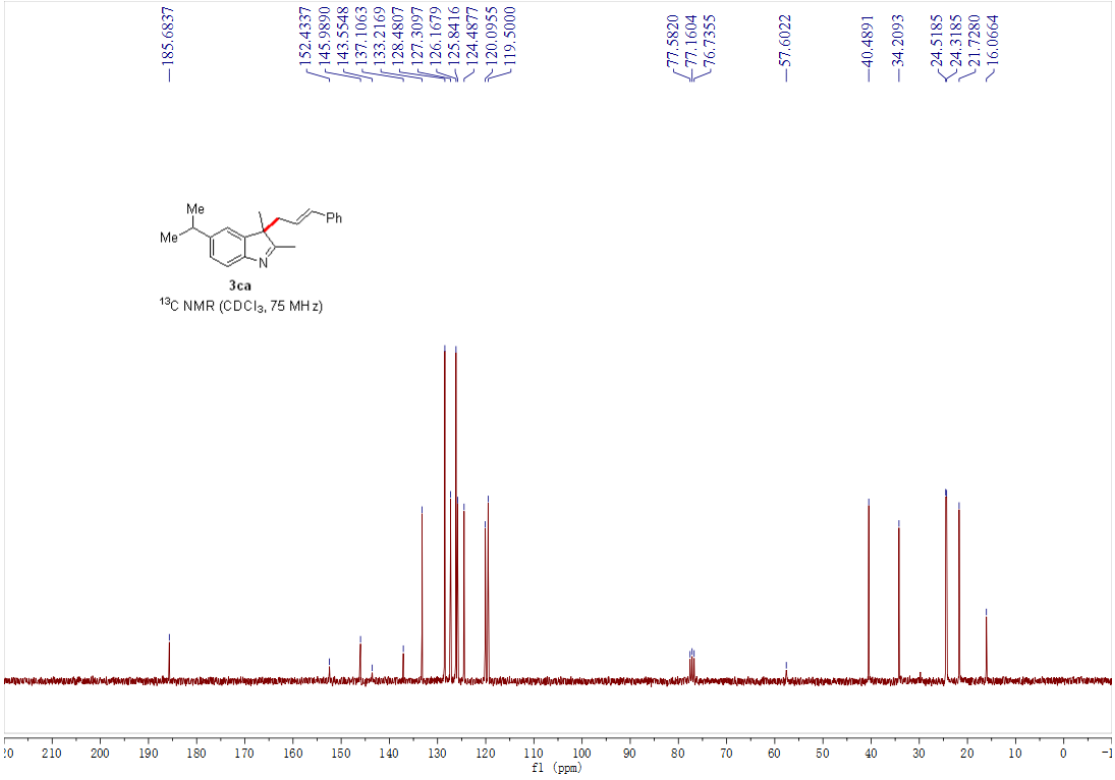
1.00
1.06
1.06
1.09
2.95
3.21
6.05
f1 (ppm)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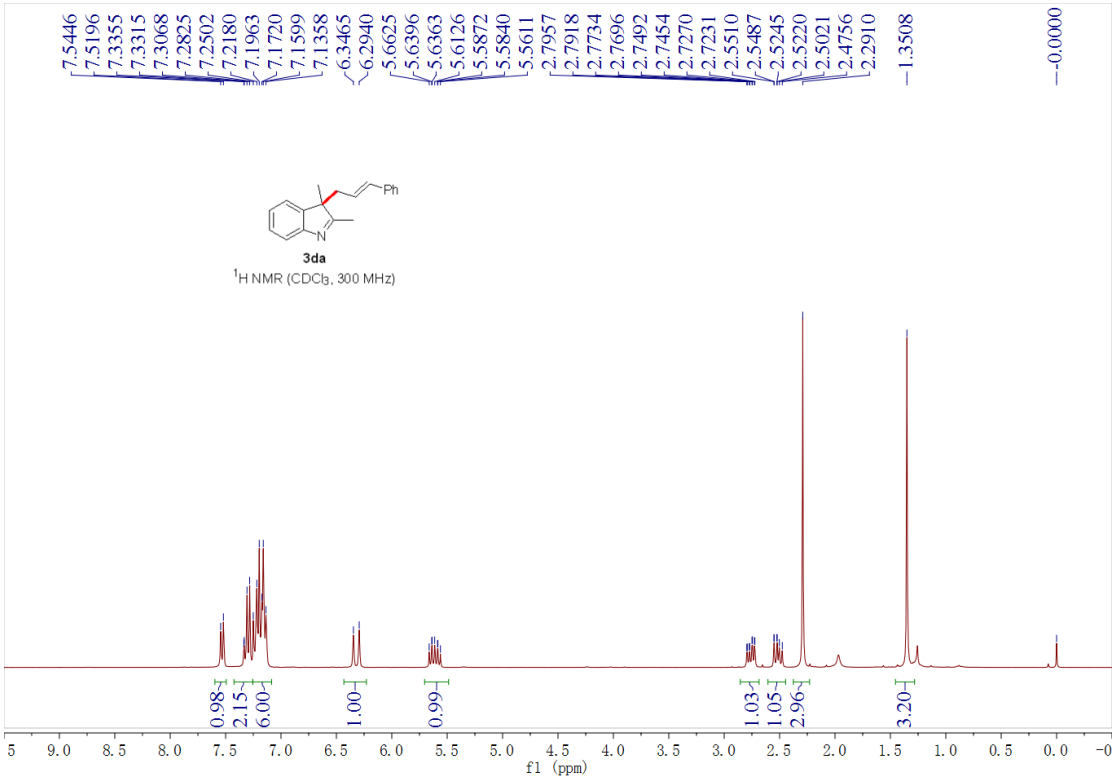
143.5548
137.1063
133.2169
128.4807
127.3097
126.1679
125.8416
124.4877
120.0955
119.5000
77.5820
77.1604
76.7355
57.6022
40.4891
34.2093
24.5185
24.3185
21.7280
16.0664
Me
Me
Ph
N
3ca
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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7.3068
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7.2180
7.1963
7.1720
7.1599
7.1358
6.3465
6.2940
5.6625
5.6396
5.6363
5.6126
5.5872
5.5840
5.5611
2.7957
2.7918
2.7734
2.7696
2.7492
2.7454
2.7270
2.7231
2.5510
2.5487
2.5245
2.5220
2.5021
2.4756
2.2910
1.3508
0.0000
Ph
N
3da
1H NMR (CDCl3, 300 MHz)
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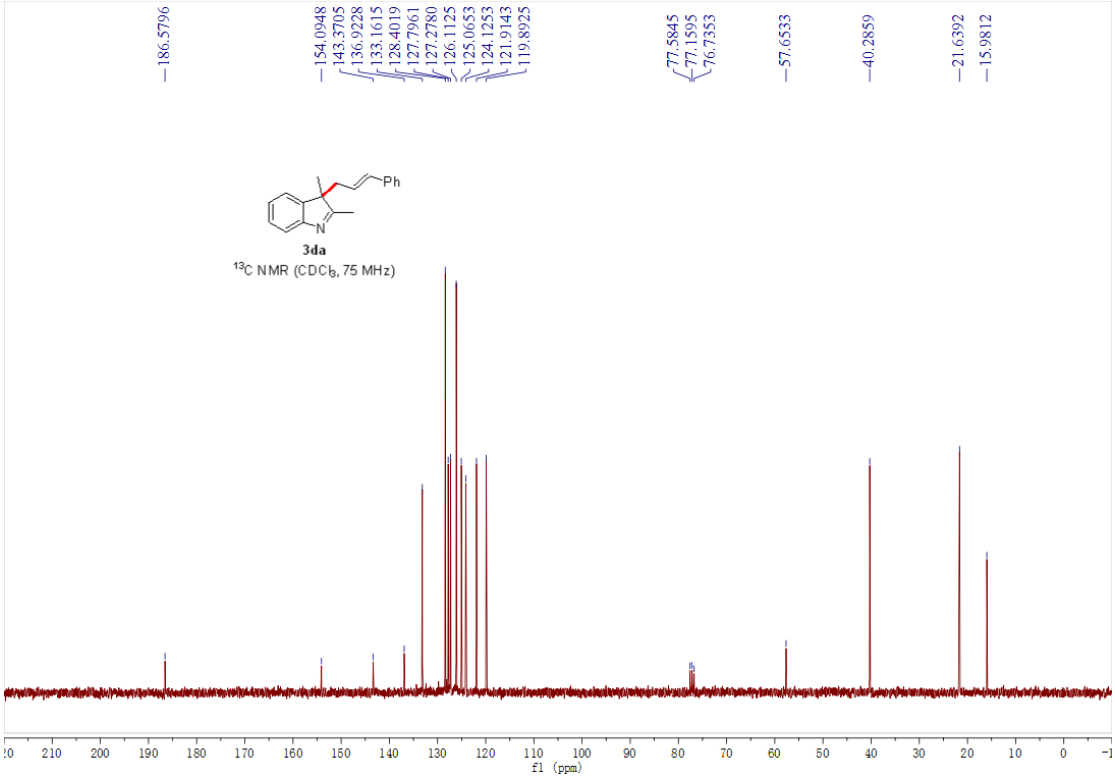
2.15
6.00
1.00
0.99
1.03
1.05
2.96
3.20
f1 (ppm)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143.3705
136.9228
133.1615
128.4019
127.7961
127.2780
126.1125
125.0653
124.1253
121.9143
119.8925
77.5845
77.1595
76.7353
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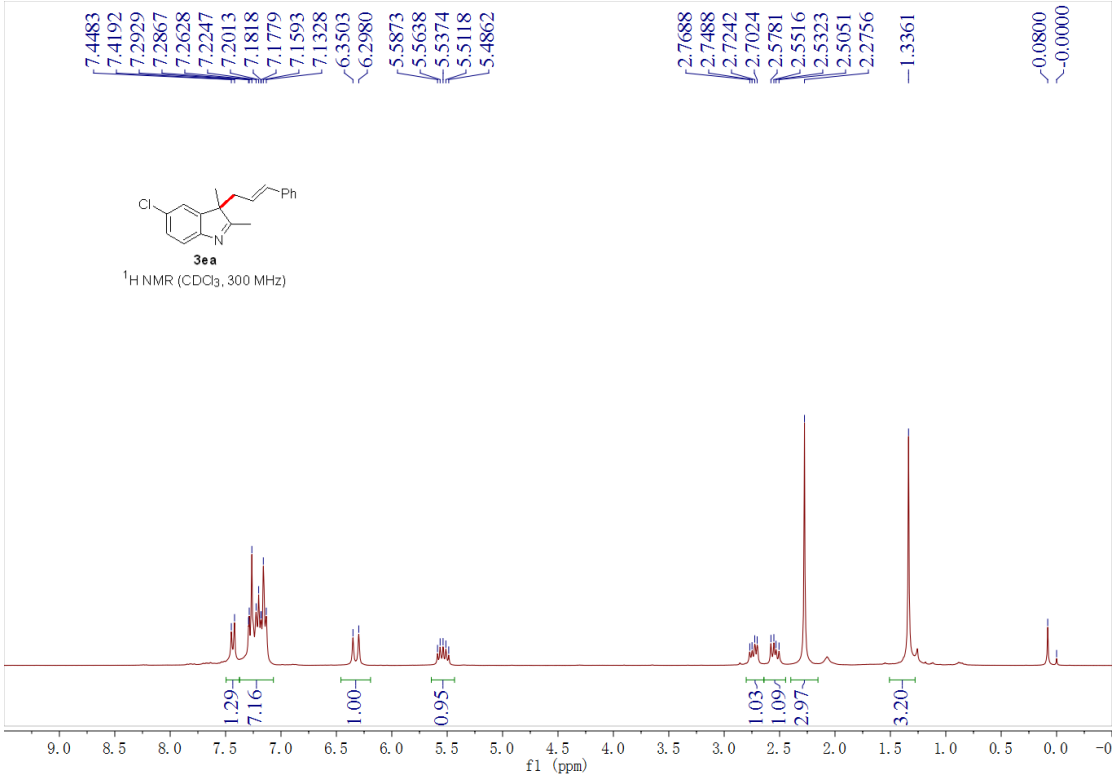
40.2859
21.6392
15.9812
Ph
N
3da
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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7.2867
7.2628
7.2247
7.2013
7.1818
7.1779
7.1593
7.1328
6.3503
6.2980
5.5873
5.5638
5.5374
5.5118
5.4862
2.7688
2.7488
2.7242
2.7024
2.5781
2.5516
2.5323
2.5051
2.2756
1.3361
0.0800
-0.0000
Cl
Ph
N
3ea
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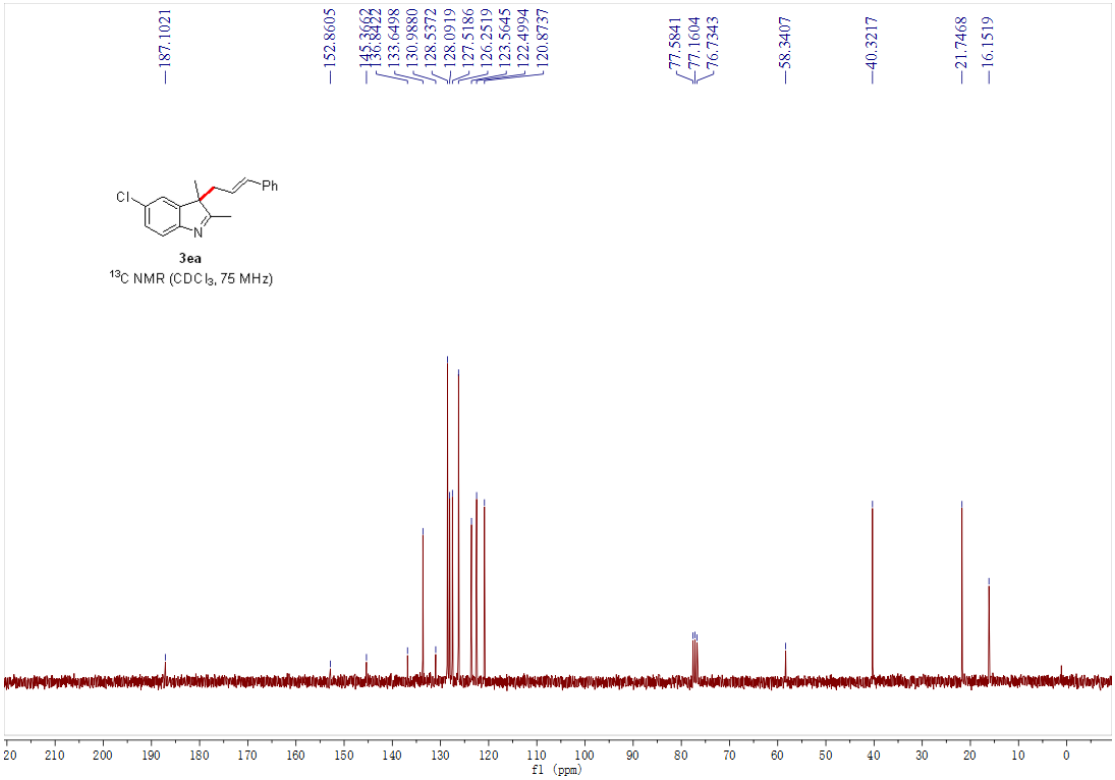
1.00
0.95
1.03
1.09
2.97
3.20
f1 (ppm)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130.9880
128.5372
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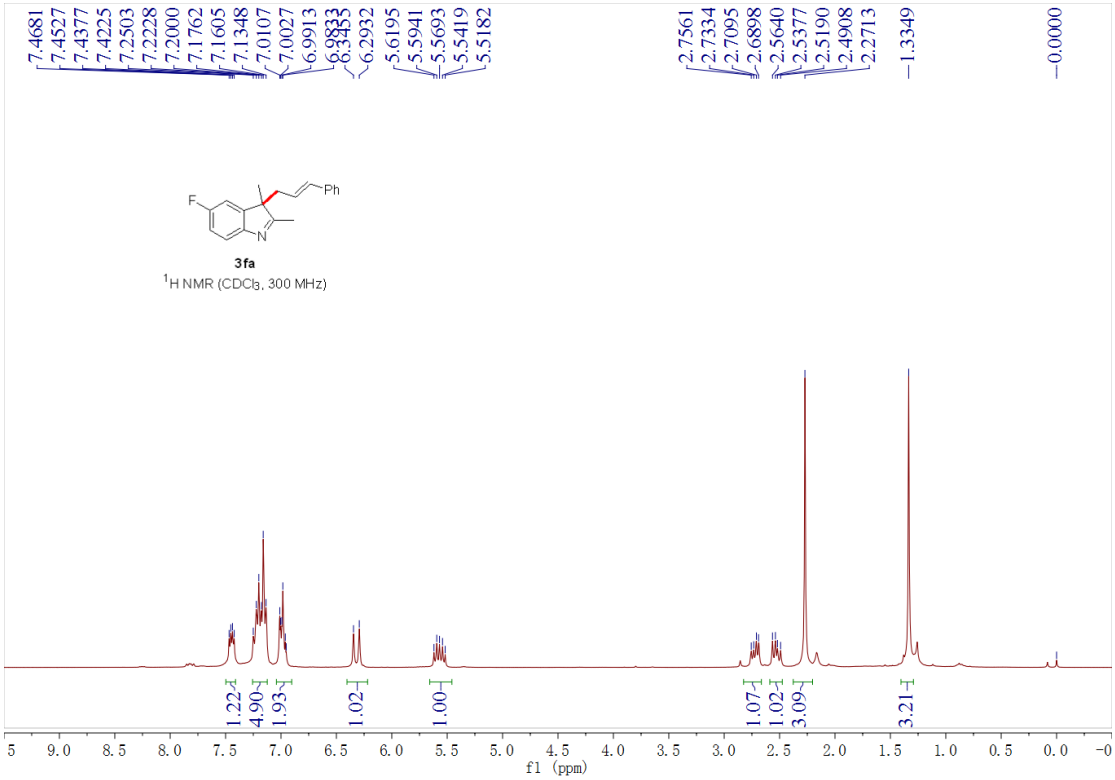
123.5645
122.4994
120.8737
77.5841
77.1604
76.7343
58.3407
40.3217
21.7468
16.1519
Cl
Ph
N
3ea
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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7.0107
7.0027
6.9913
6.9833
6.9453
6.2932
5.6195
5.5941
5.5693
5.5419
5.5182
2.7561
2.7334
2.7095
2.6898
2.5640
2.5377
2.5190
2.4908
2.2713
1.3349
0.0000
F
Ph
N
3fa
1H NMR (CDCl3, 300 MHz)
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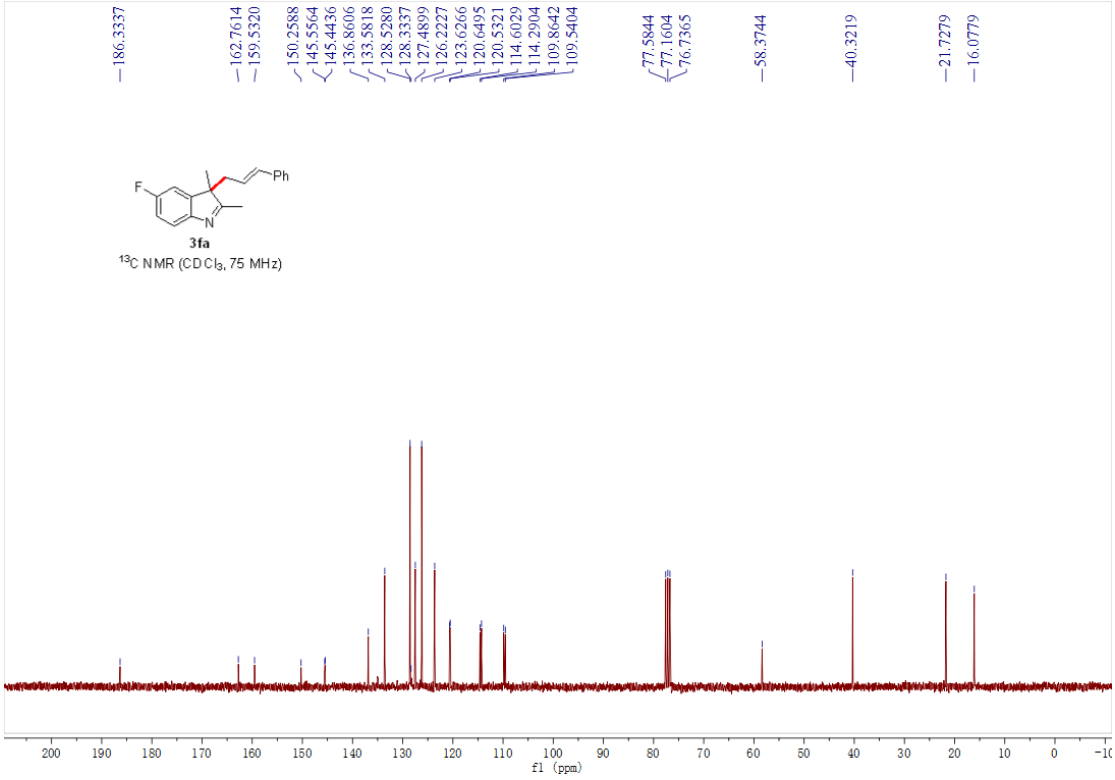
1.93
1.02
1.00
1.07
1.02
3.09
3.21
f1 (ppm)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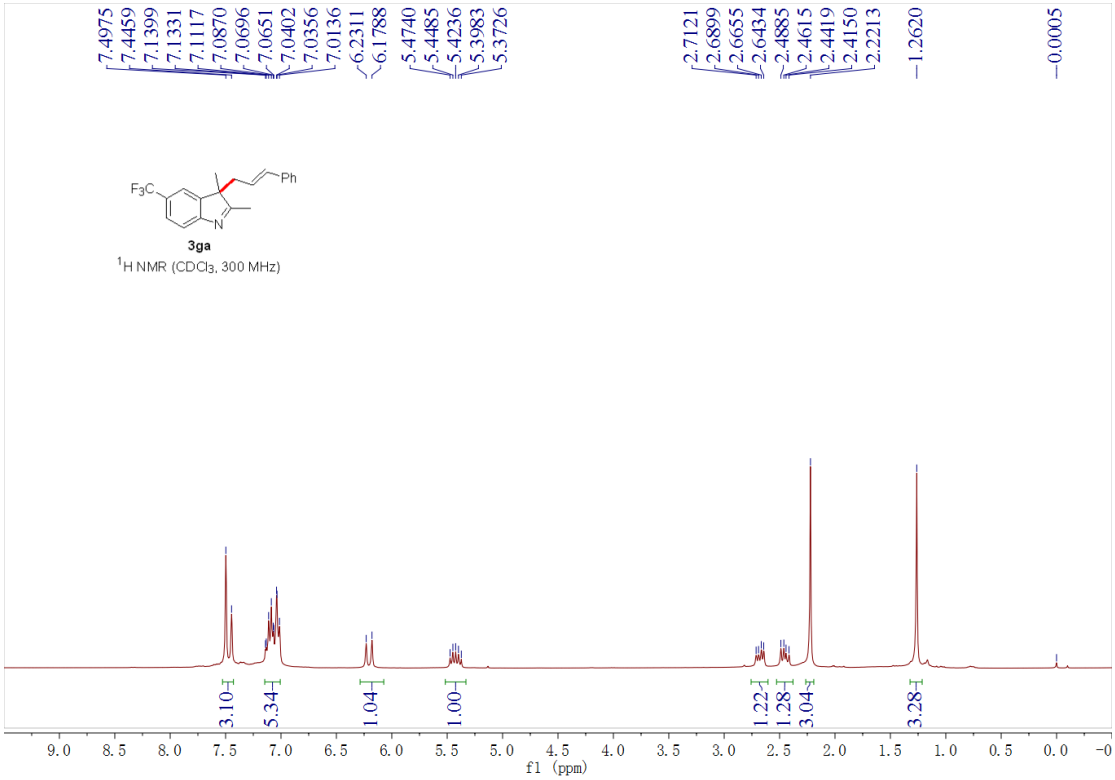
159.5320
150.2588
145.5564
145.4436
136.8606
133.5818
128.5280
128.3337
127.4899
126.2227
123.6266
120.6495
120.5321
114.6029
114.2904
109.8642
109.5404
77.5844
77.1604
76.7365
58.3744
40.3219
21.7279
16.0779
F
Ph
N
3fa
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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7.0136
6.2311
6.1788
5.4740
5.4485
5.4236
5.3983
5.3726
2.7121
2.6899
2.6655
2.6434
2.4885
2.4615
2.4419
2.4150
2.2213
1.2620
0.0005
F3C
Ph
N
3ga
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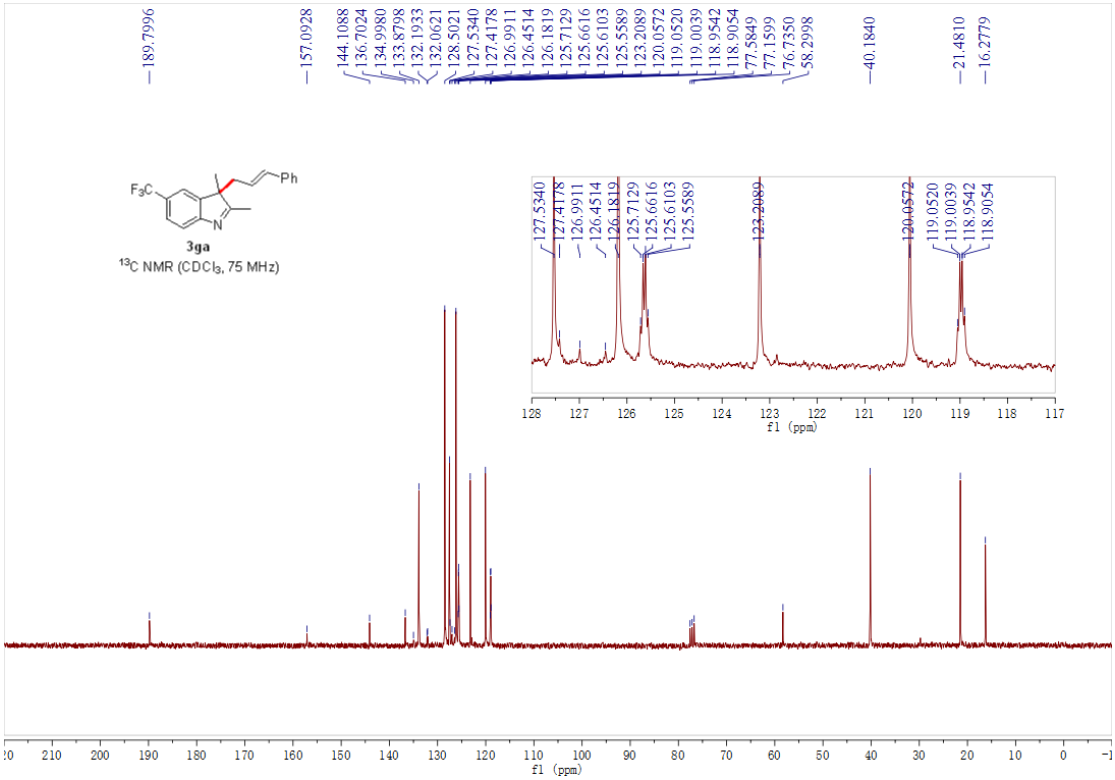
1.04
1.00
1.22
1.28
3.04
3.28
f1 (ppm)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128.5021
127.5340
127.4178
126.9911
126.4514
126.1819
125.7129
125.6616
125.6103
125.5589
123.2089
120.0572
119.0520
119.0039
118.9542
118.9054
77.5849
77.1599
76.7350
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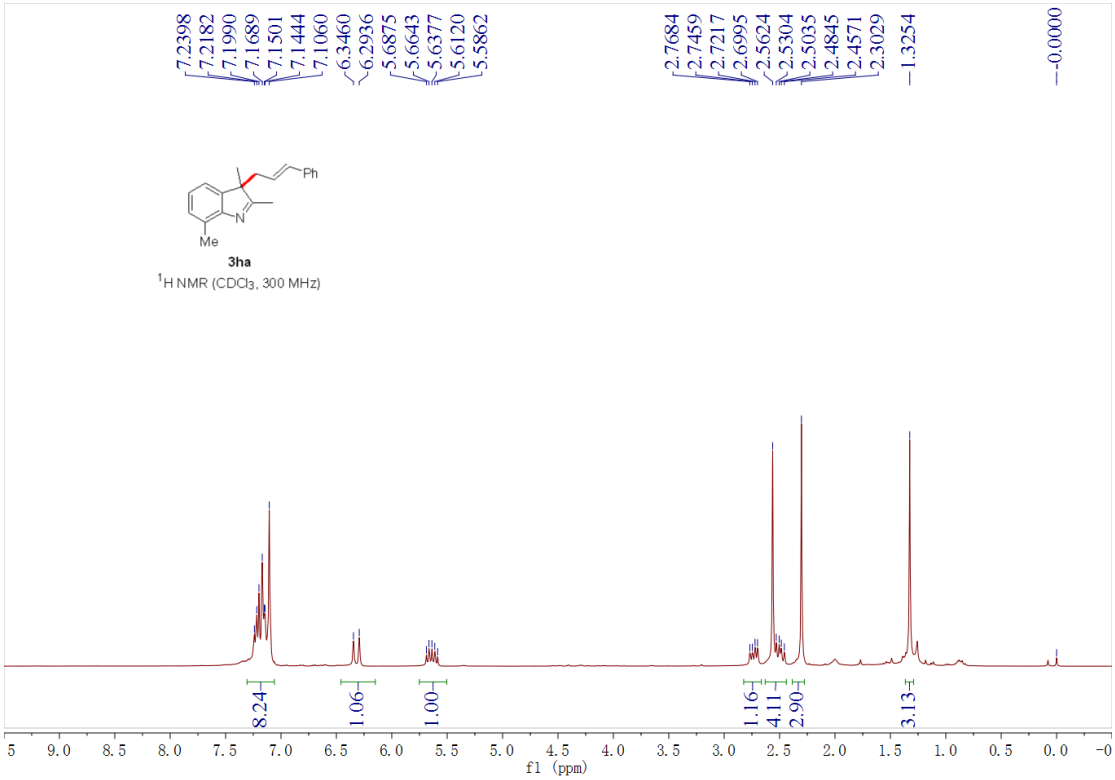
16.2779
F3C
Ph
N
3ga
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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5.6377
5.6120
5.5862
2.7684
2.7459
2.7217
2.6995
2.5624
2.5304
2.5035
2.4845
2.4571
2.3029
1.3254
0.0000
Ph
N
Me
3ha
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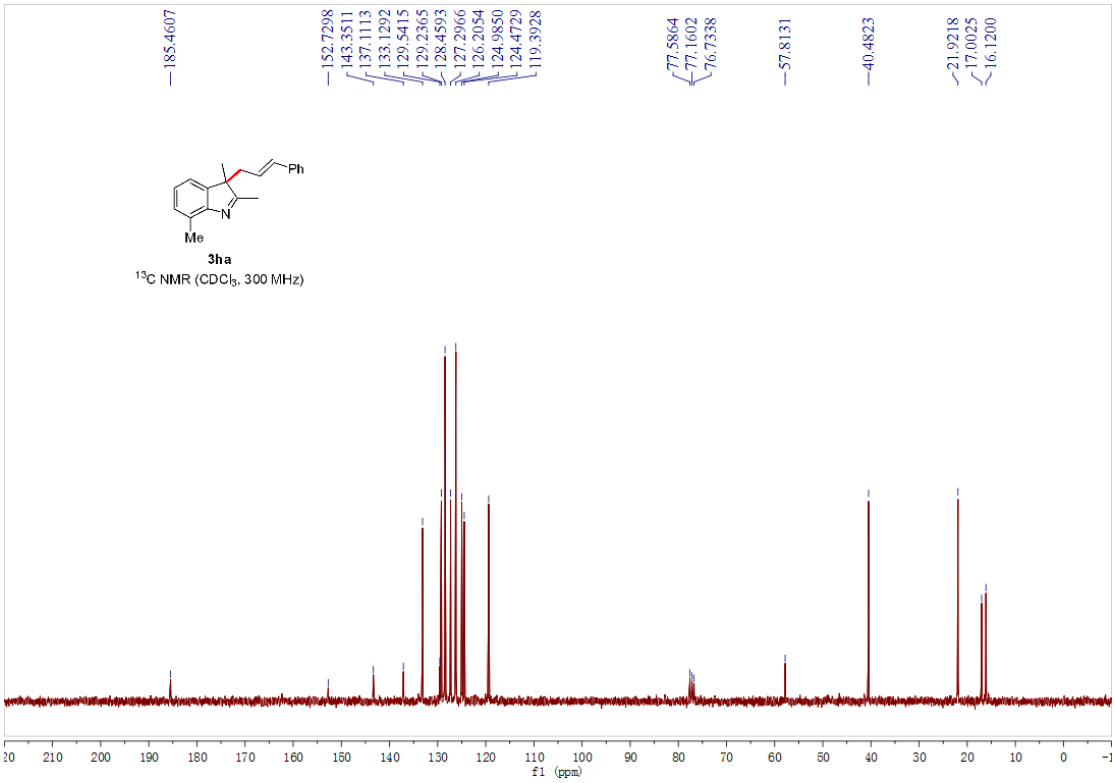
1.00
1.16
4.11
2.90
3.13
f1 (ppm)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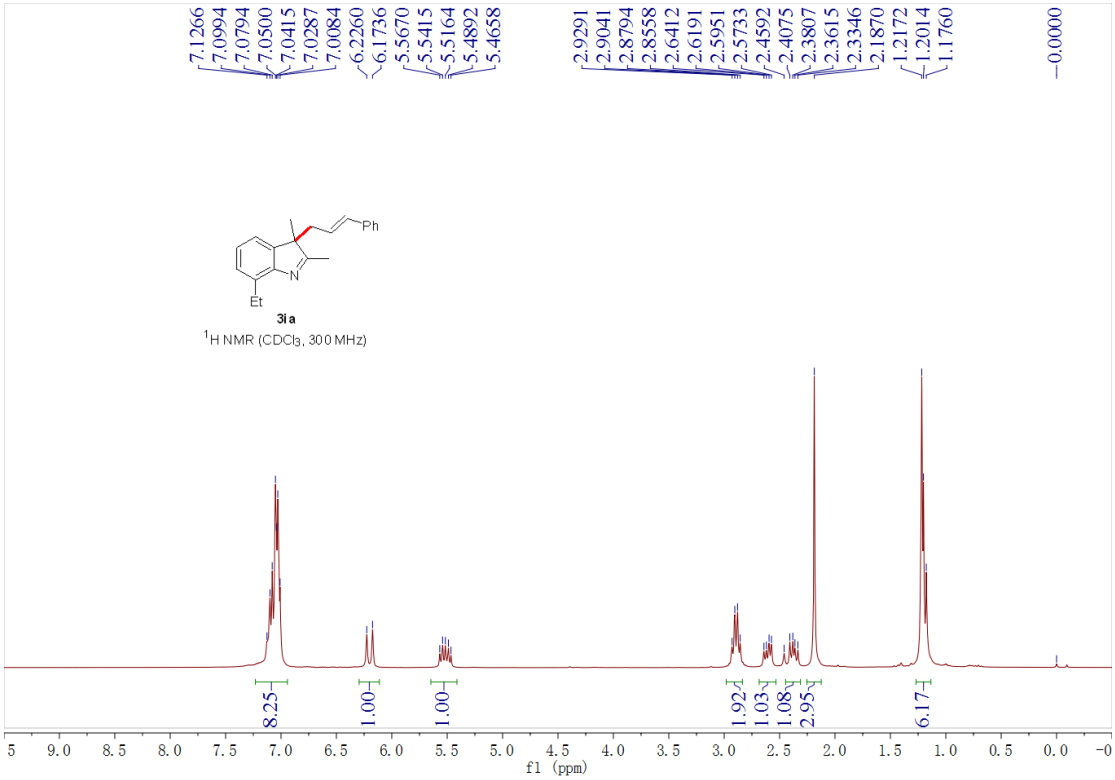
124.9850
124.4729
119.3928
77.5864
77.1602
76.7338
57.8131
40.4823
21.9218
17.0025
16.1200
Ph
N
Me
3ha
13C NMR (CDCl3, 300 MHz)
f1 (ppm)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5.4892
5.4658
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2.9041
2.8794
2.8558
2.6412
2.6191
2.5951
2.5733
2.4592
2.4075
2.3807
2.3615
2.3346
2.1870
1.2172
1.2014
1.1760
0.0000
Ph
N
Et
3ia
1H NMR (CDCl3, 300 MHz)
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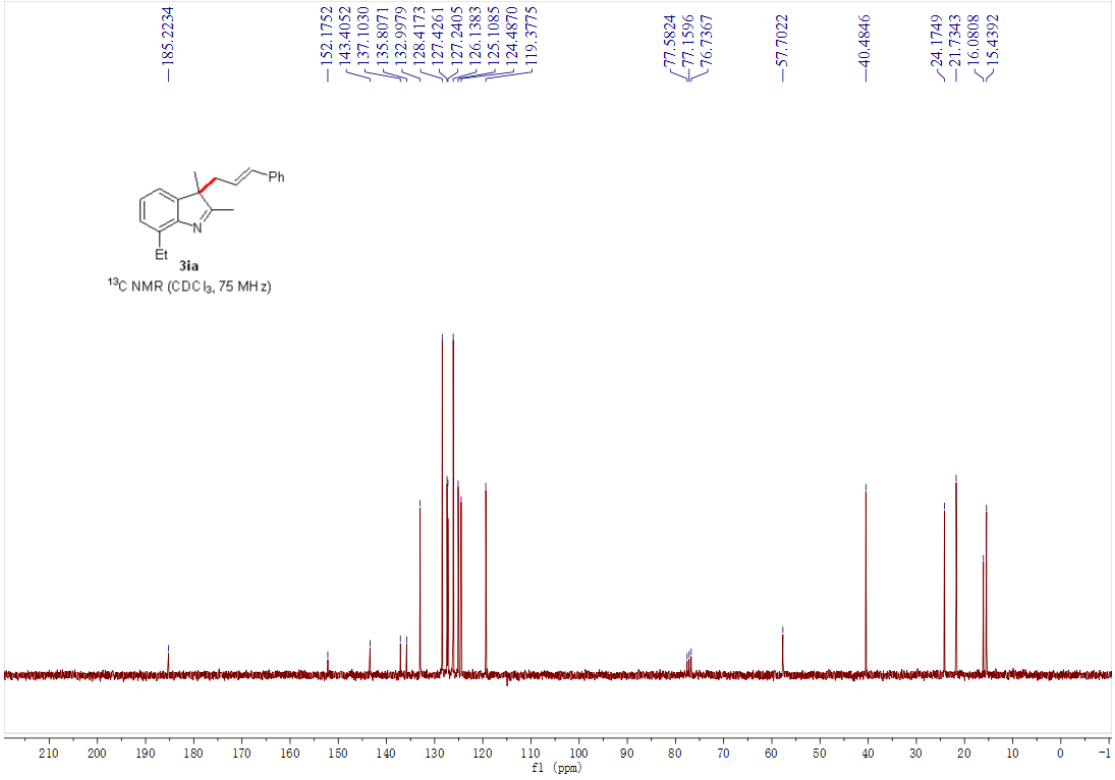
1.00
1.00
1.92
1.03
1.08
2.95
6.17
f1 (ppm)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137.1030
135.8071
132.9979
128.4173
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127.2405
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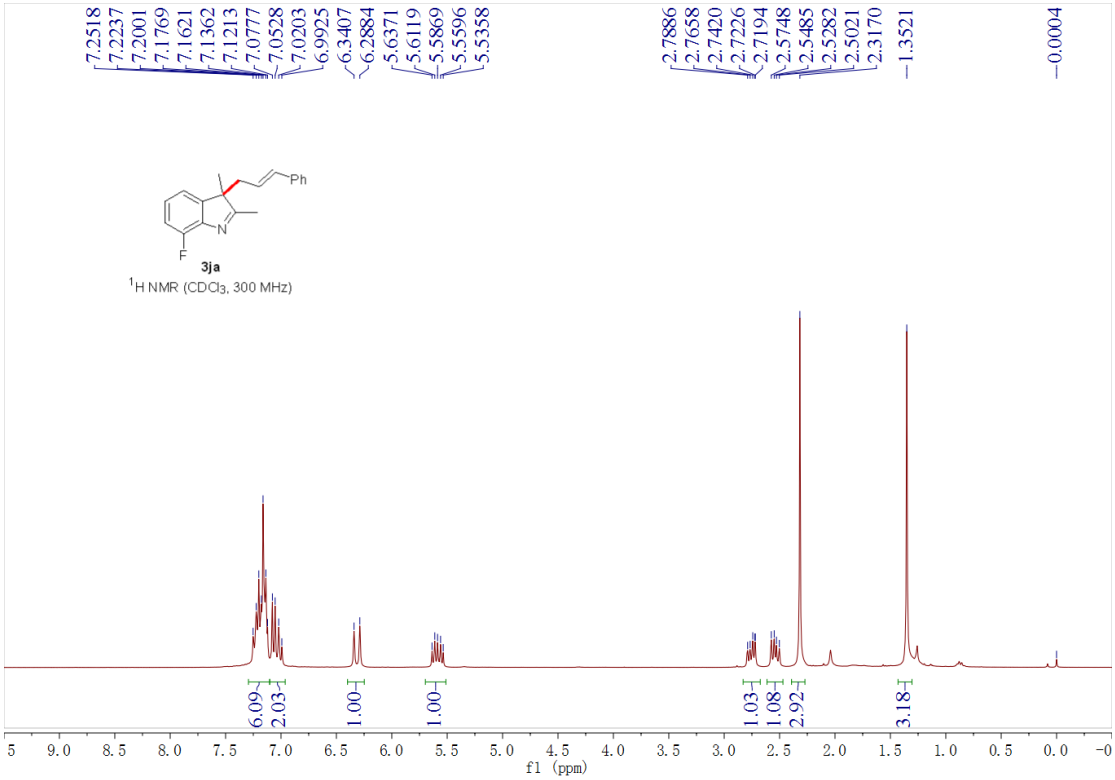
125.1085
124.4870
119.3775
77.5824
77.1596
76.7367
57.7022
40.4846
24.1749
21.7343
16.0808
15.4392
Ph
N
Et
3ia
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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7.2237
7.2001
7.1769
7.1621
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7.1213
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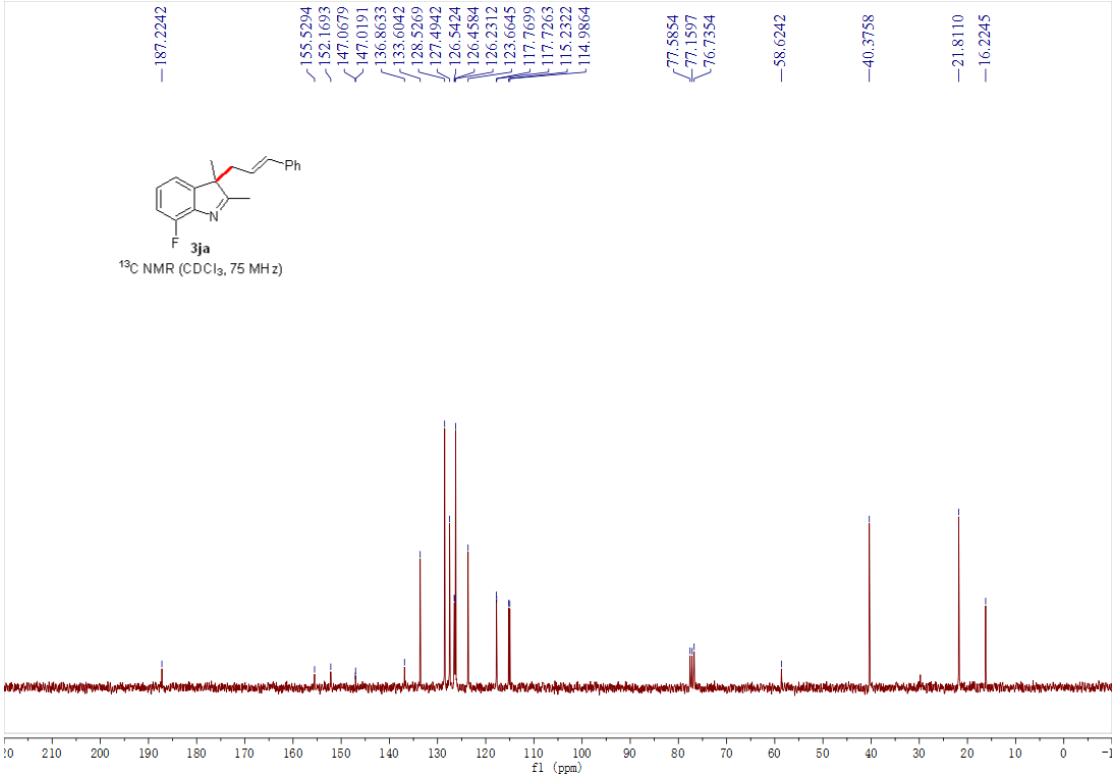
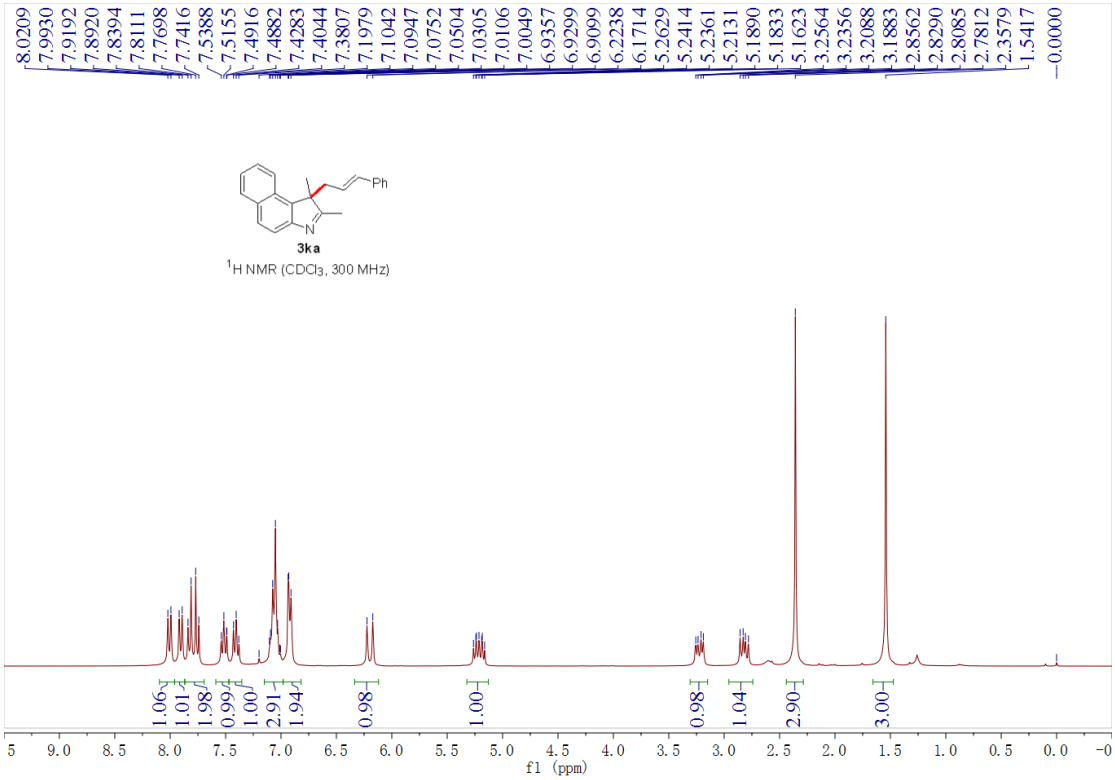
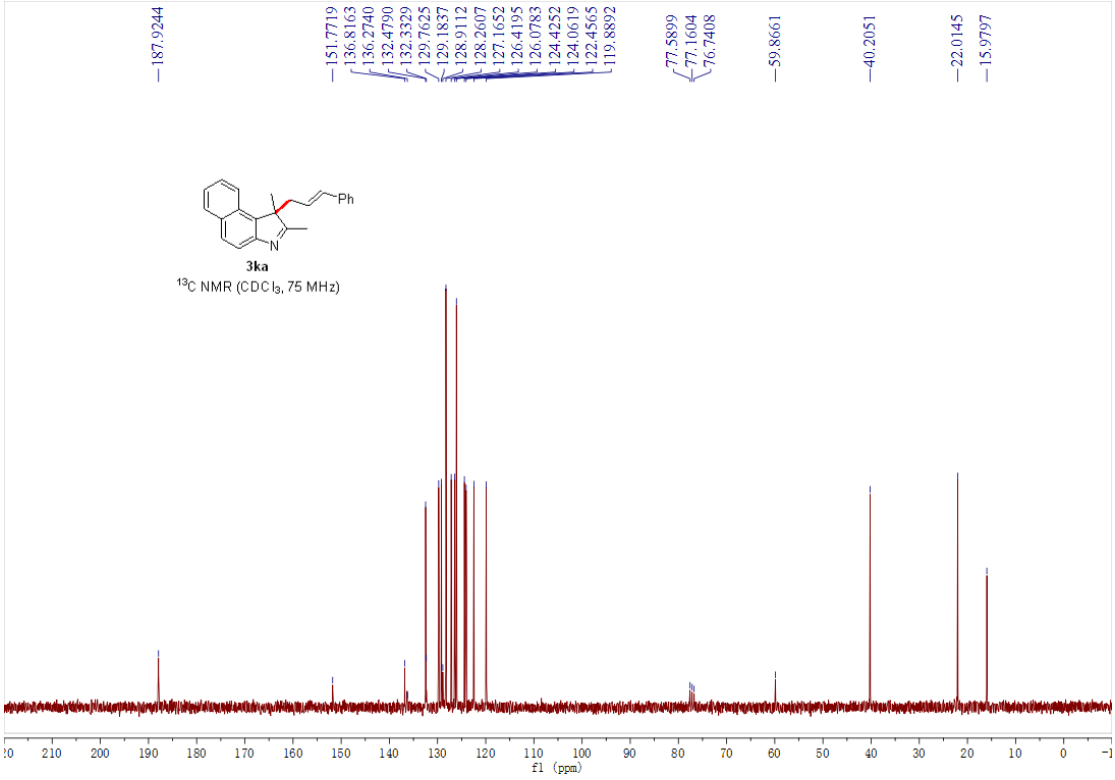
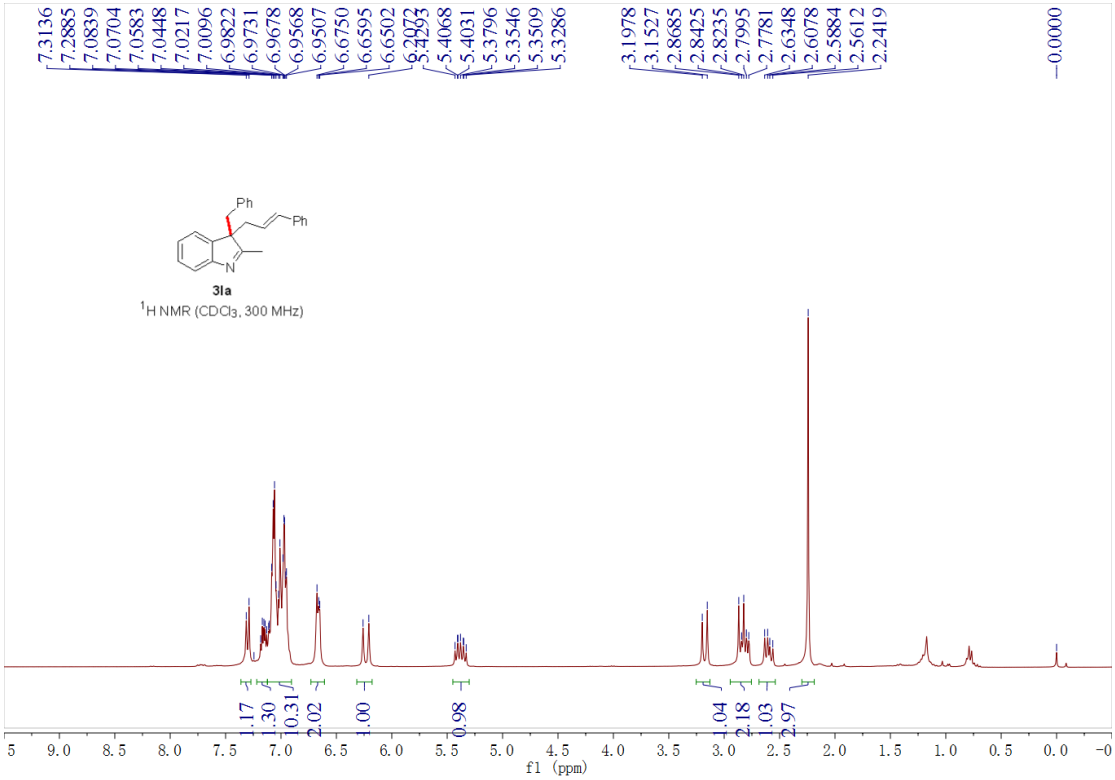
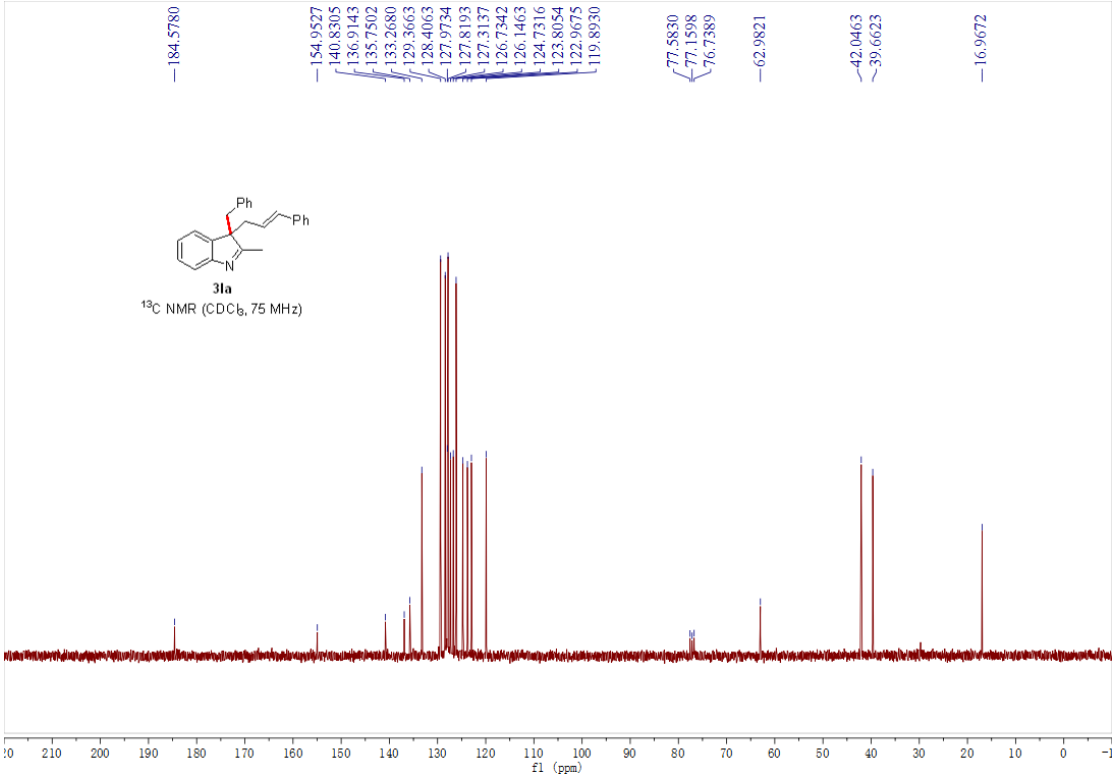
6.9925
6.3407
6.2884
5.6371
5.6119
5.5869
5.5596
5.5358
2.7886
2.7658
2.7420
2.7226
2.7194
2.5748
2.5485
2.5282
2.5021
2.3170
1.3521
0.0004
Ph
N
F
3ja
^{1}H NMR ($CDCl_3$, 300 MHz)
6.09
2.03
1.00
1.00
1.03
1.08
2.92
3.18
f1 (ppm)

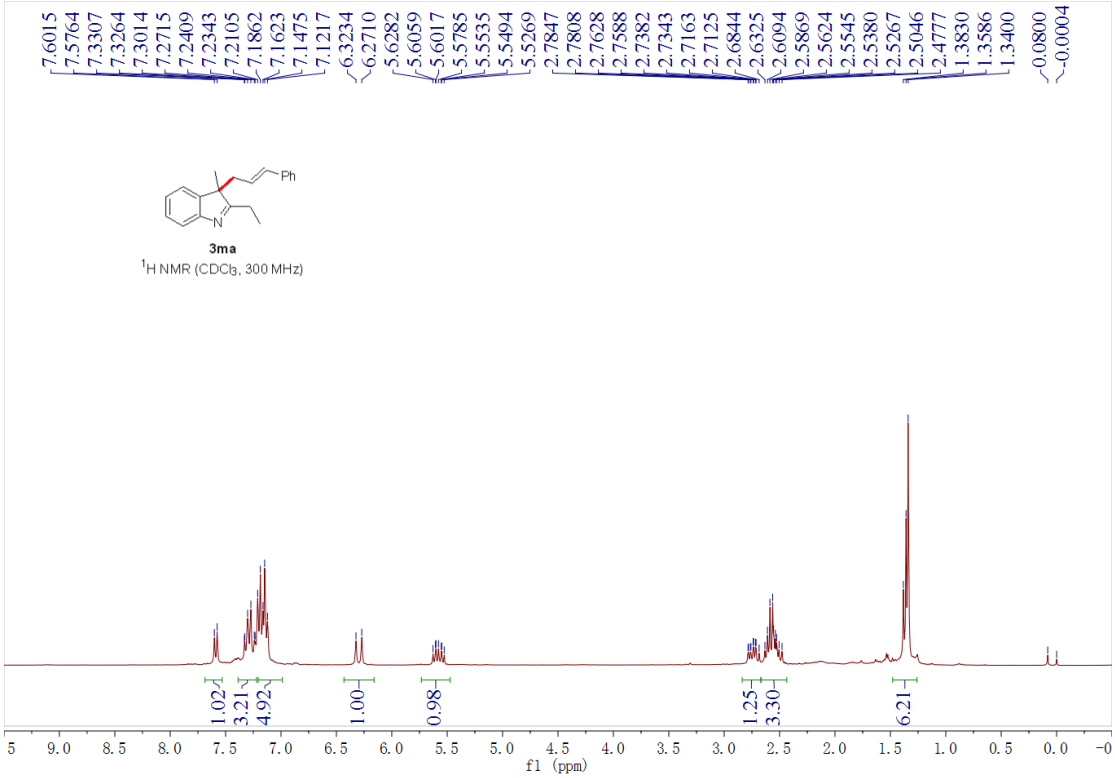

187.2242
155.5294
152.1693
147.0679
147.0191
136.8633
133.6042
128.5269
127.4942
126.5424
126.4584
126.2312
123.6645
117.7699
117.7263
115.2322
114.9864
77.5854
77.1597
76.7354
58.6242
40.3758
21.8110
16.2245
Ph
N
F
3ja
^{13}C NMR ($CDCl_3$, 75 MHz)
f1 (ppm)

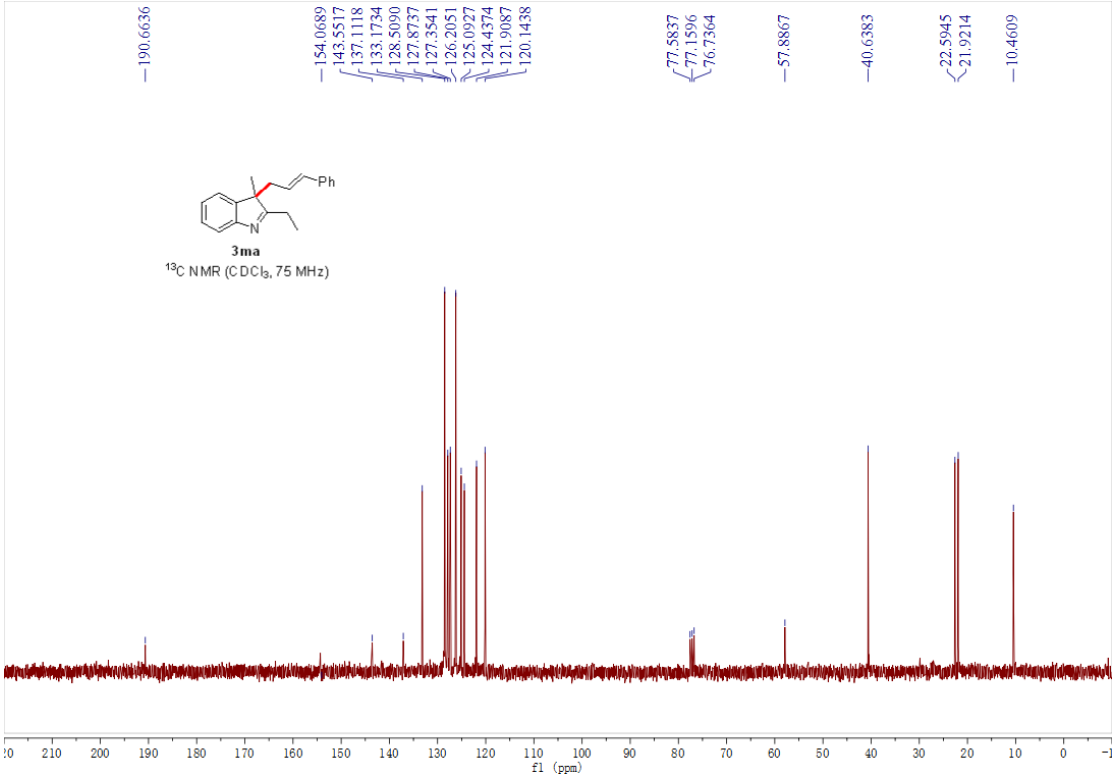

8.0209
7.9930
7.9192
7.8920
7.8394
7.8111
7.7698
7.7416
7.5388
7.5155
7.4916
7.4882
7.4283
7.4044
7.3807
7.1979
7.1042
7.0947
7.0752
7.0504
7.0305
7.0106
7.0049
6.9357
6.9299
6.9099
6.2238
6.1714
5.2629
5.2414
5.2361
5.2131
5.1890
5.1833
5.1623
3.2564
3.2356
3.2088
3.1883
2.8562
2.8290
2.8085
2.7812
2.3579
1.5417
0.0000
Ph
N
3ka
1H NMR (CDCl3, 300 MHz)
1.06
1.01
1.98
0.99
1.00
2.91
1.94
0.98
1.00
0.98
1.04
2.90
3.00
f1 (ppm)

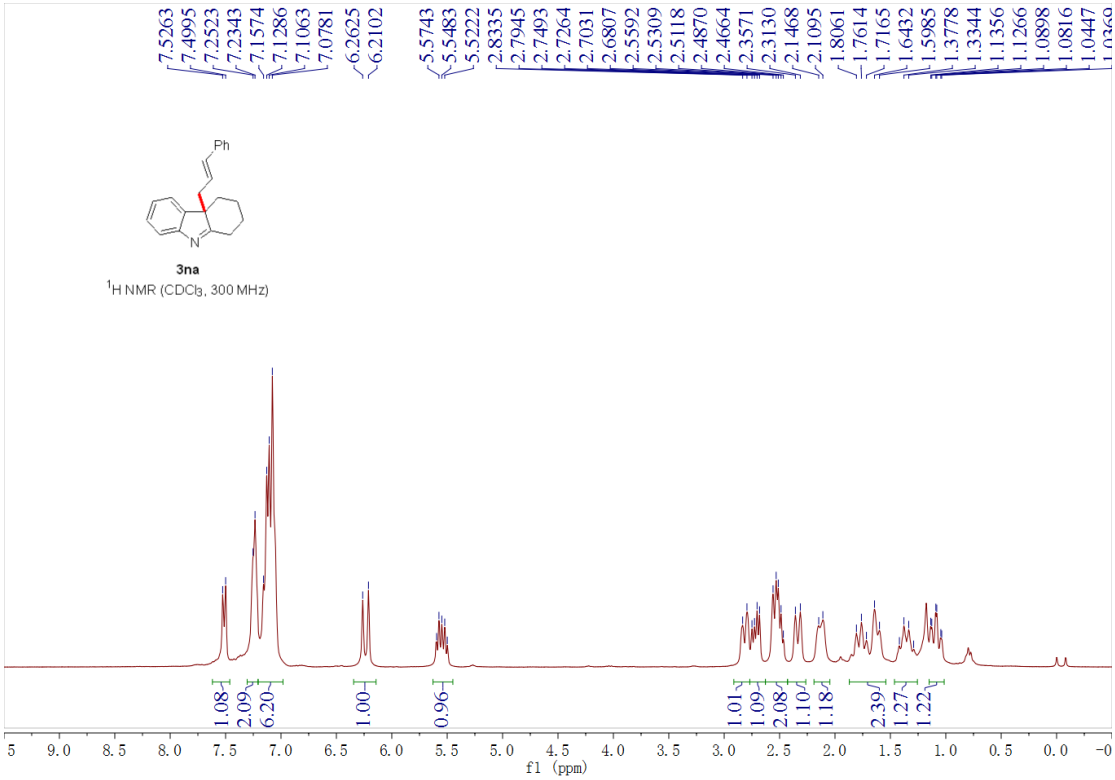

187.9244
151.7719
136.8163
136.2740
132.4790
132.3329
129.7625
129.1837
128.9112
128.2607
127.1652
126.4195
126.0783
124.4252
124.0619
122.4565
119.8892
77.5899
77.1604
76.7408
59.8661
40.2051
22.0145
15.9797
Ph
N
3ka
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

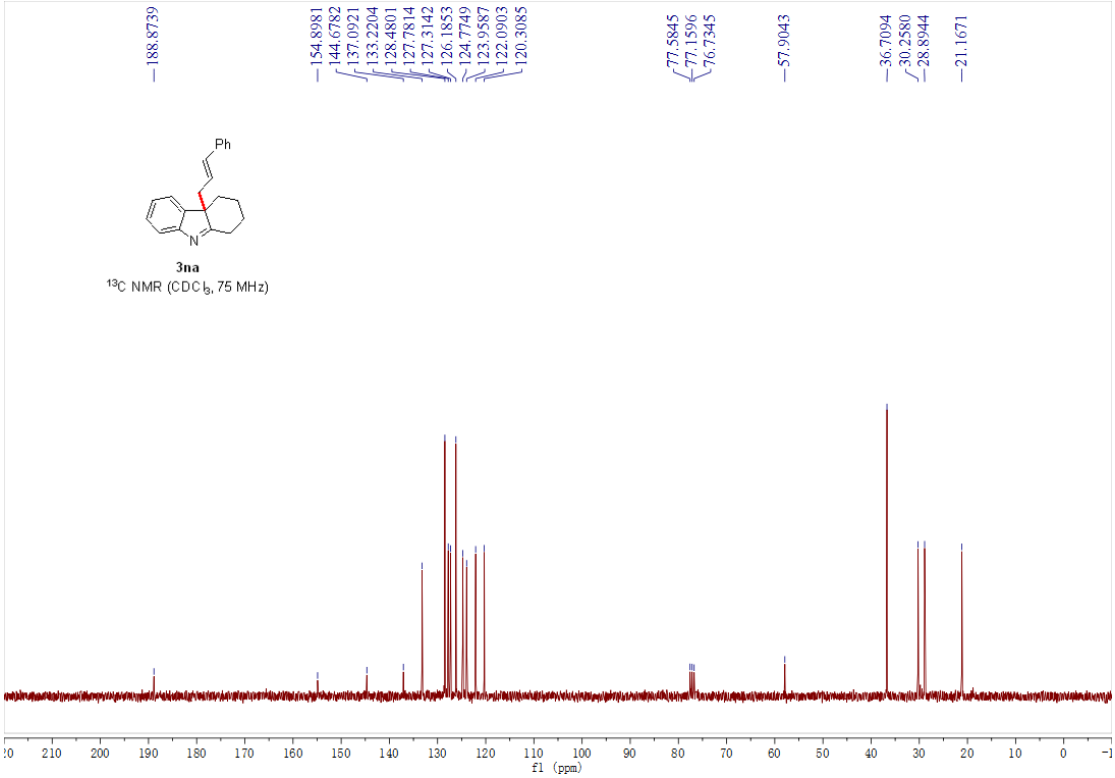

7.3136
7.2885
7.0839
7.0704
7.0583
7.0448
7.0217
7.0096
6.9822
6.9731
6.9678
6.9568
6.9507
6.6750
6.6595
6.6502
5.4068
5.4031
5.3796
5.3546
5.3509
5.3286
3.1978
3.1527
2.8685
2.8425
2.8235
2.7995
2.7781
2.6348
2.6078
2.5884
2.5612
2.2419
0.0000
Ph
Ph
N
3la
1H NMR (CDCl3, 300 MHz)
1.17
1.30
10.31
2.02
1.00
0.98
1.04
2.18
1.03
2.97
f1 (ppm)

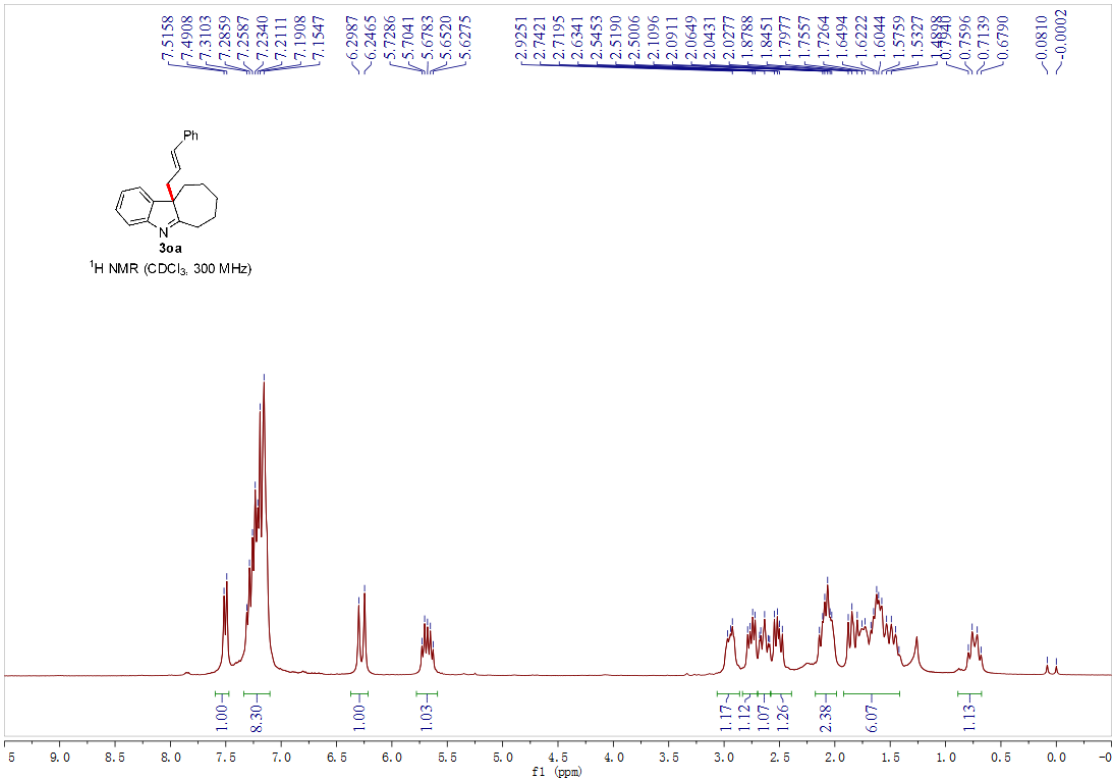

184.5780
154.9527
140.8305
136.9143
135.7502
133.2680
129.3663
128.4063
127.9734
127.8193
127.3137
126.7342
126.1463
124.7316
123.8054
122.9675
119.8930
77.5830
77.1598
76.7389
62.9821
42.0463
39.6623
16.9672
Ph
Ph
N
3la
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

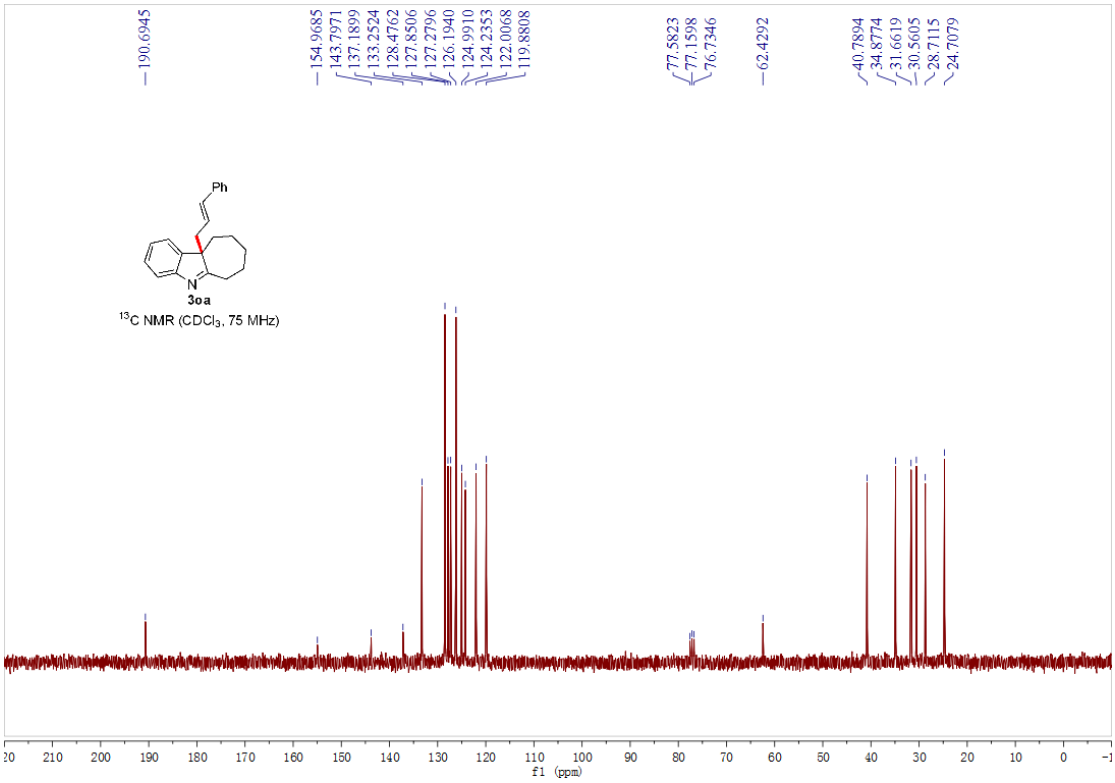

7.6015
7.5764
7.3307
7.3264
7.3014
7.2715
7.2409
7.2343
7.2105
7.1862
7.1623
7.1475
7.1217
6.3234
6.2710
5.6282
5.6059
5.6017
5.5785
5.5535
5.5494
5.5269
2.7847
2.7808
2.7628
2.7588
2.7382
2.7343
2.7163
2.7125
2.6844
2.6325
2.6094
2.5869
2.5624
2.5545
2.5380
2.5267
2.5046
2.4777
1.3830
1.3586
1.3400
0.0800
-0.0004
Ph
N
3ma
1H NMR (CDCl3, 300 MHz)
1.02
3.21
4.92
1.00
0.98
1.25
3.30
6.21
f1 (ppm)

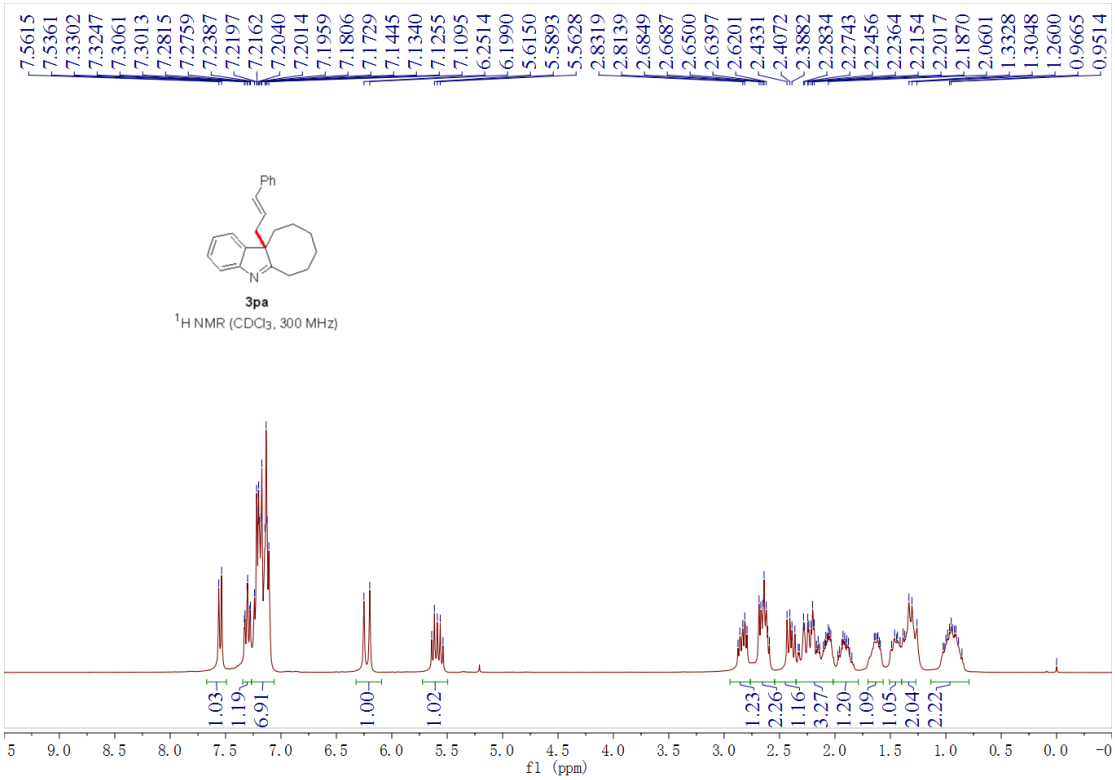

190.6636
154.0689
143.5517
137.1118
133.1734
128.5090
127.8737
127.3541
126.2051
125.0927
124.4374
121.9087
120.1438
77.5837
77.1596
76.7364
57.8867
40.6383
22.5945
21.9214
10.4609
Ph
N
3ma
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

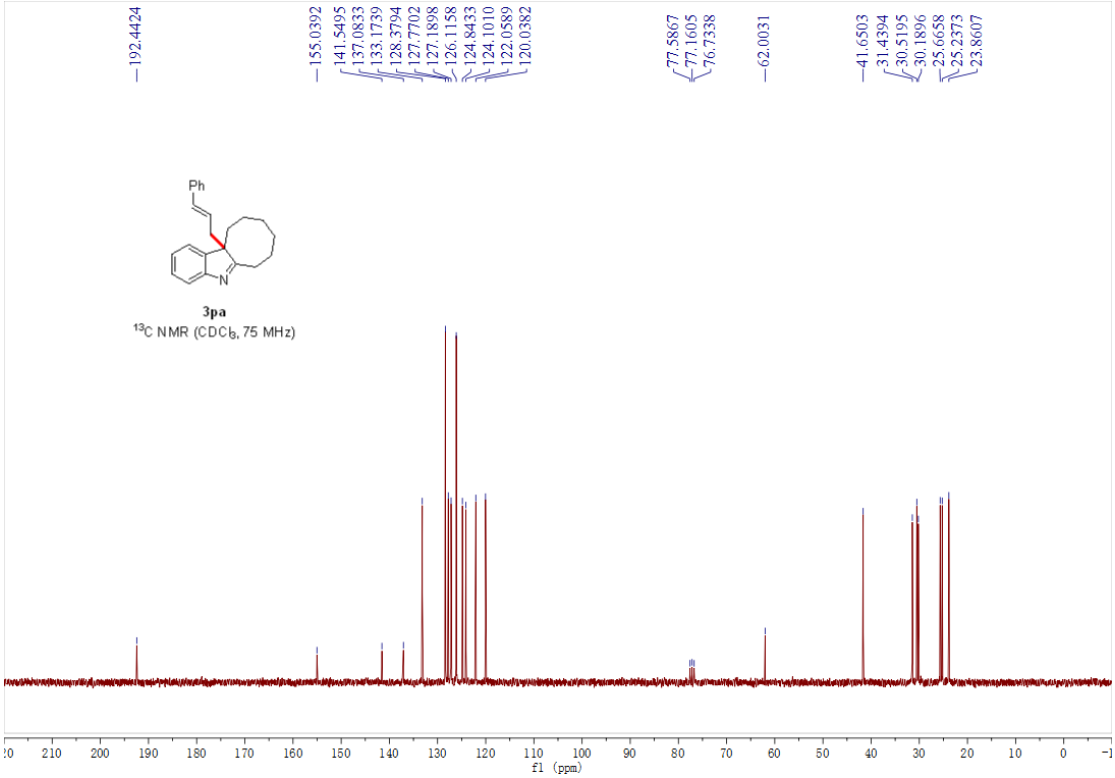

7.5263
7.4995
7.2523
7.2343
7.1574
7.1286
7.1063
7.0781
6.2625
6.2102
5.5743
5.5483
5.5222
2.8335
2.7945
2.7493
2.7264
2.7031
2.6807
2.5592
2.5309
2.5118
2.4870
2.4664
2.3571
2.3130
2.1468
2.1095
1.8061
1.7614
1.7165
1.6432
1.5985
1.3778
1.3344
1.1356
1.1266
1.0898
1.0816
1.0447
Ph
N
3na
1H NMR (CDCl3, 300 MHz)
1.08
2.09
6.20
1.00
0.96
1.01
1.09
2.08
1.10
1.18
2.39
1.27
1.22
f1 (ppm)

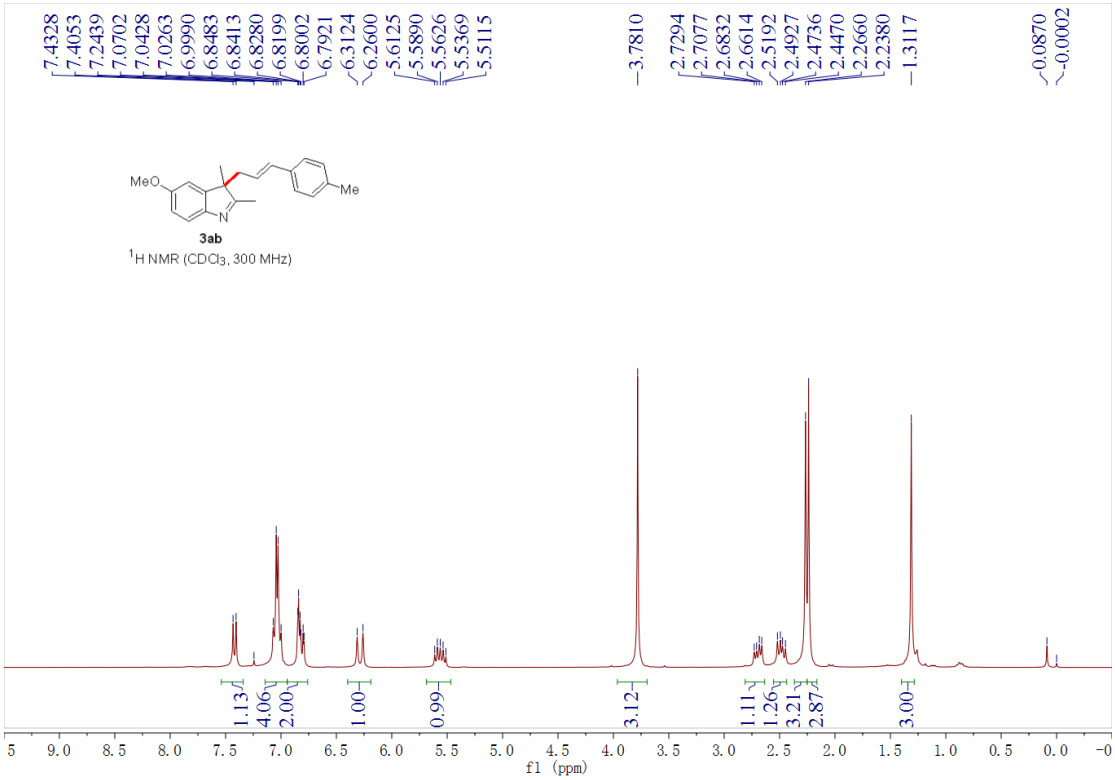

188.8739
154.8981
144.6782
137.0921
133.2204
128.4801
127.7814
127.3142
126.1853
124.7749
123.9587
122.0903
120.3085
77.5845
77.1596
76.7345
57.9043
36.7094
30.2580
28.8944
21.1671
Ph
N
3na
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

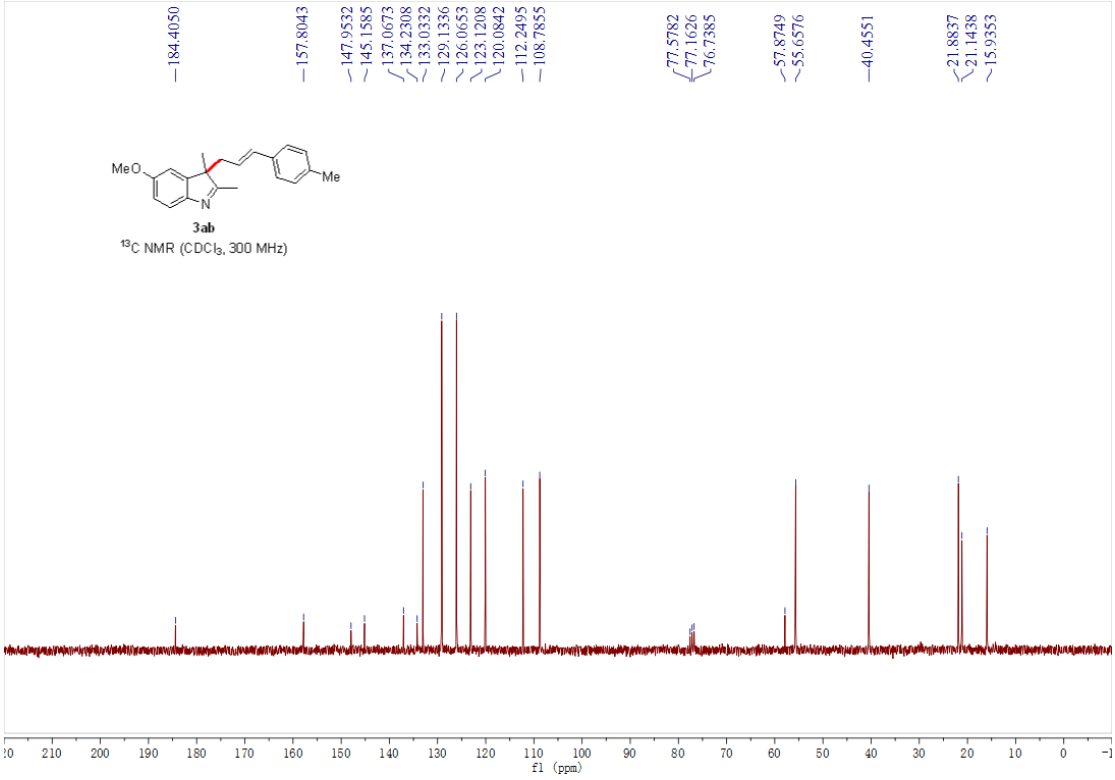

Ph
N
3oa
1H NMR (CDCl3, 300 MHz)
f1 (ppm)


Ph
N
3oa
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.5615
7.5361
7.3302
7.3247
7.3061
7.3013
7.2815
7.2759
7.2387
7.2197
7.2162
7.2040
7.2014
7.1959
7.1806
7.1729
7.1445
7.1340
7.1255
7.1095
6.2514
6.1990
6.1150
5.5893
5.5628
2.8319
2.8139
2.6849
2.6687
2.6500
2.6397
2.6201
2.4331
2.4072
2.3882
2.2834
2.2743
2.2456
2.2364
2.2154
2.2017
2.1870
2.0601
1.3328
1.3048
1.2600
0.9665
0.9514
Ph
N
3pa
1H NMR (CDCl3, 300 MHz)
1.03
1.19
6.91
1.00
1.02
1.23
2.26
1.16
3.27
1.20
1.09
1.05
2.04
2.22
f1 (ppm)


192.4424
155.0392
141.5495
137.0833
133.1739
128.3794
127.7702
127.1898
126.1158
124.8433
124.1010
122.0589
120.0382
77.5867
77.1605
76.7338
62.0031
41.6503
31.4394
30.5195
30.1896
25.6658
25.2273
23.8607
Ph
N
3pa
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.4328
7.4053
7.2439
7.0702
7.0428
7.0263
6.9990
6.8483
6.8413
6.8280
6.8199
6.8002
6.7921
6.3124
6.2600
5.6125
5.5890
5.5626
5.5369
5.5115
3.7810
2.7294
2.7077
2.6832
2.6614
2.5192
2.4927
2.4736
2.4470
2.2660
2.2380
1.3117
0.0870
-0.0002
MeO
Me
N
3ab
1H NMR (CDCl3, 300 MHz)
1.13
4.06
2.00
1.00
0.99
3.12
1.11
1.26
3.21
2.87
3.00
f1 (ppm)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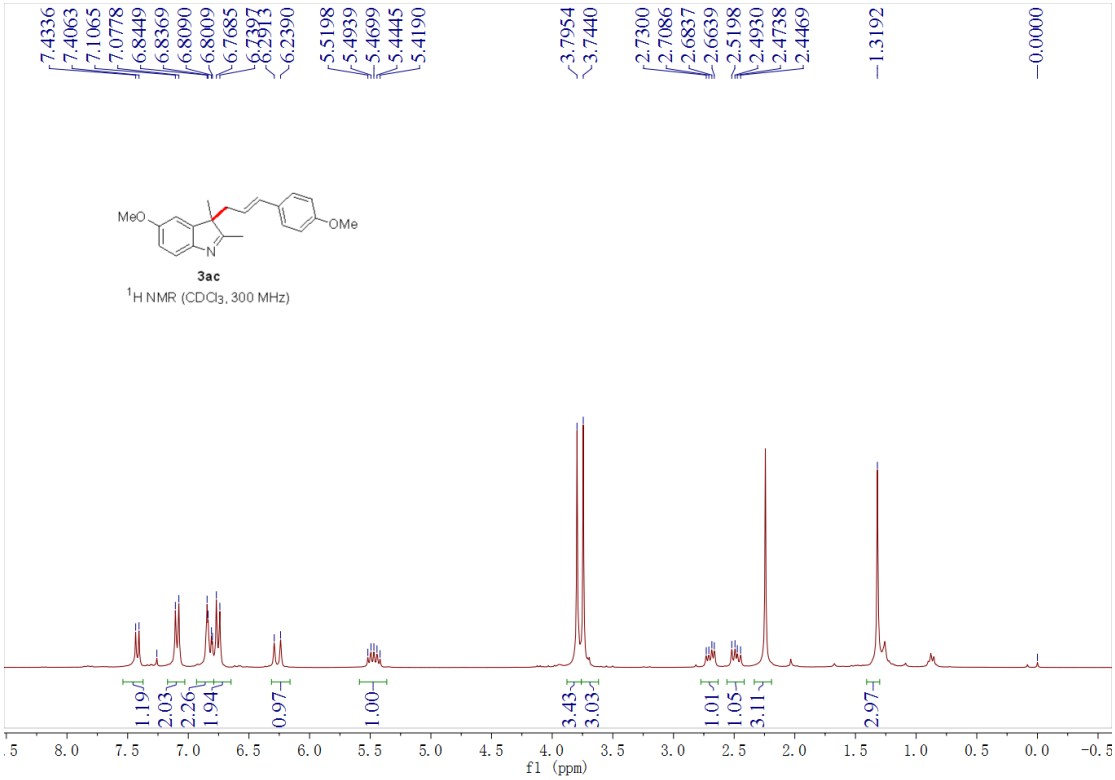
147.9532
145.1585
137.0673
134.2308
133.0332
129.1336
126.0653
123.1208
120.0842
112.2495
108.7855
77.5782
77.1626
76.7385
57.8749
55.6576
40.4551
21.8837
21.1438
15.9353
MeO
Me
N
3ab
13C NMR (CDCl3, 300 MHz)
f1 (ppm)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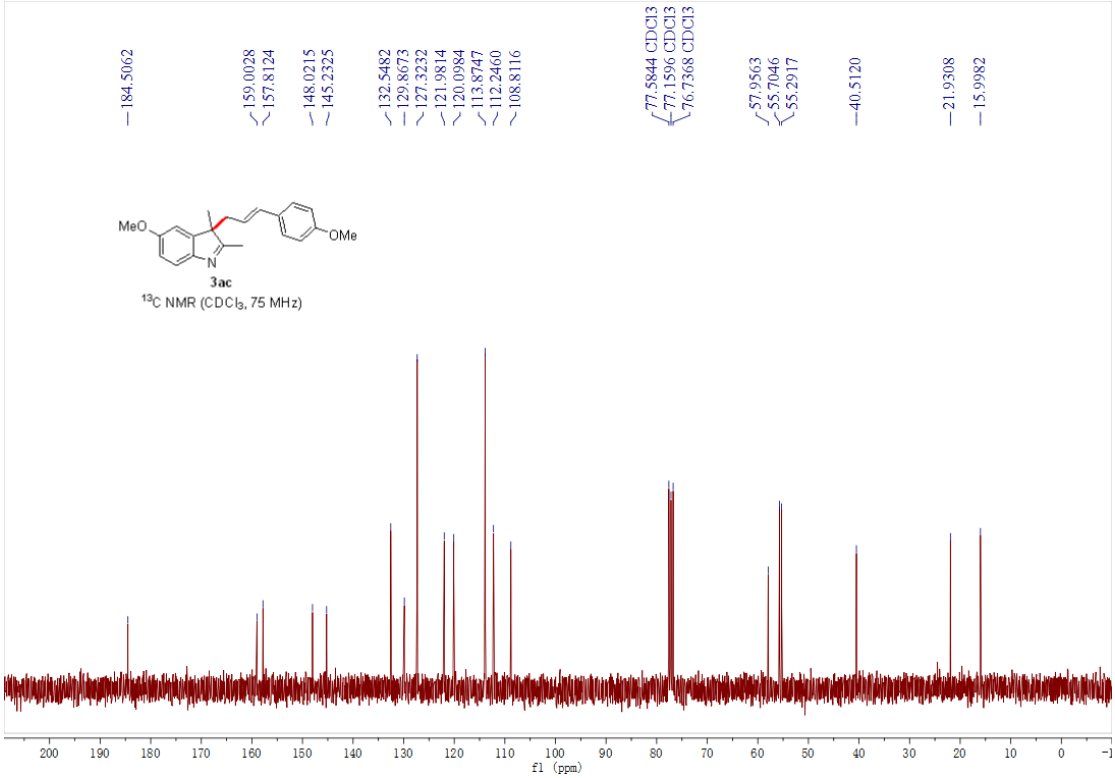
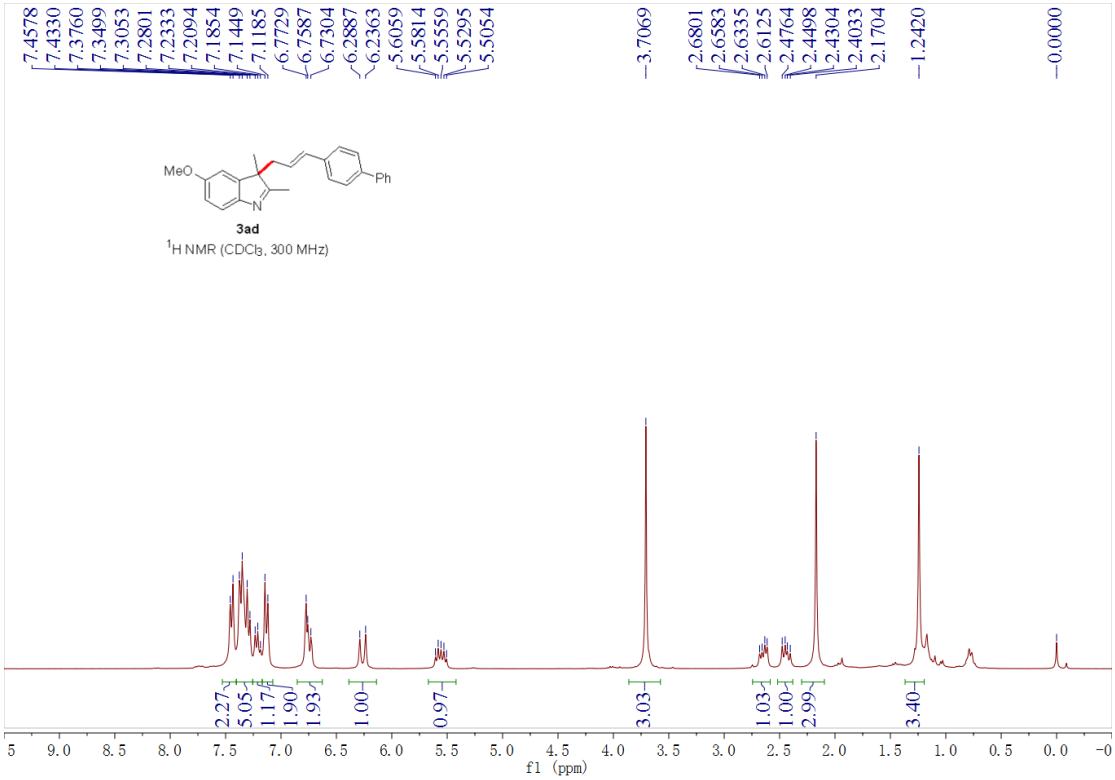
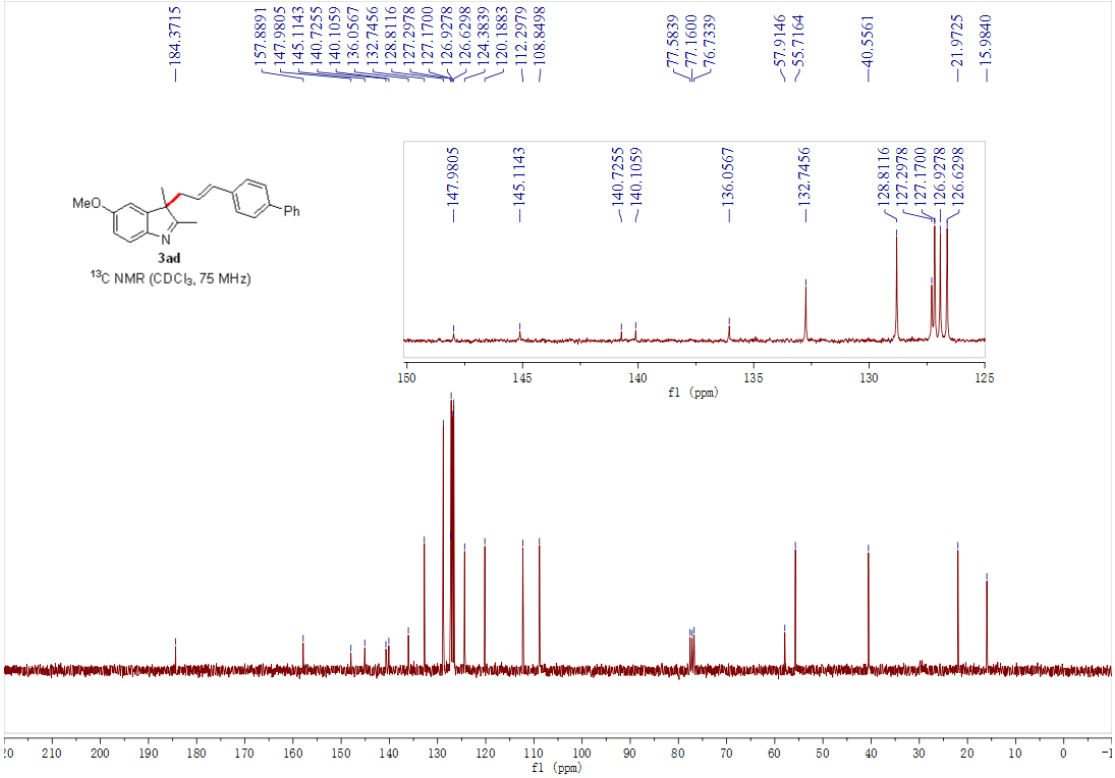
7.4063
7.1065
7.0778
6.8449
6.8369
6.8090
6.8009
6.7685
6.7397
6.2913
6.2390
5.5198
5.4939
5.4699
5.4445
5.4190
3.7954
3.7440
2.7300
2.7086
2.6837
2.6639
2.5198
2.4930
2.4738
2.4469
1.3192
0.0000
MeO
OMe
N
3ac
1H NMR (CDCl3, 300 MHz)
1.19
2.03
2.26
1.94
0.97
1.00
3.43
3.03
1.01
1.05
3.11
2.97
f1 (ppm)


184.5062
159.0028
157.8124
148.0215
145.2325
132.5482
129.8673
127.3232
121.9814
120.0984
113.8747
112.2460
108.8116
77.5844 CDCl3
77.1596 CDCl3
76.7368 CDCl3
57.9563
55.7046
55.2917
40.5120
21.9308
15.9982
MeO
OMe
N
3ac
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.4578
7.4330
7.3760
7.3499
7.3053
7.2801
7.2333
7.2094
7.1854
7.1449
7.1185
6.7729
6.7587
6.7304
6.2887
6.2363
5.6059
5.5814
5.5559
5.5295
5.5054
3.7069
2.6801
2.6583
2.6335
2.6125
2.4764
2.4498
2.4304
2.4033
2.1704
1.2420
0.0000
MeO
Ph
N
3ad
1H NMR (CDCl3, 300 MHz)
2.27
5.05
1.17
1.90
1.93
1.00
0.97
3.03
1.03
1.00
2.99
3.40
f1 (ppm)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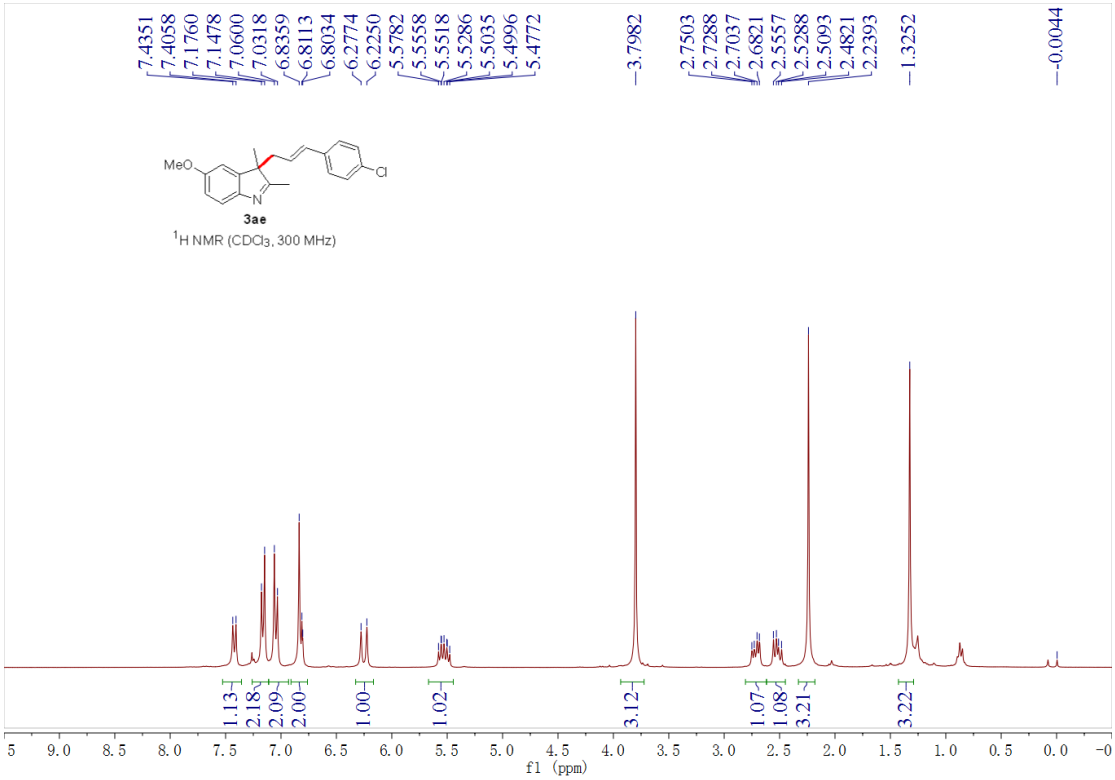
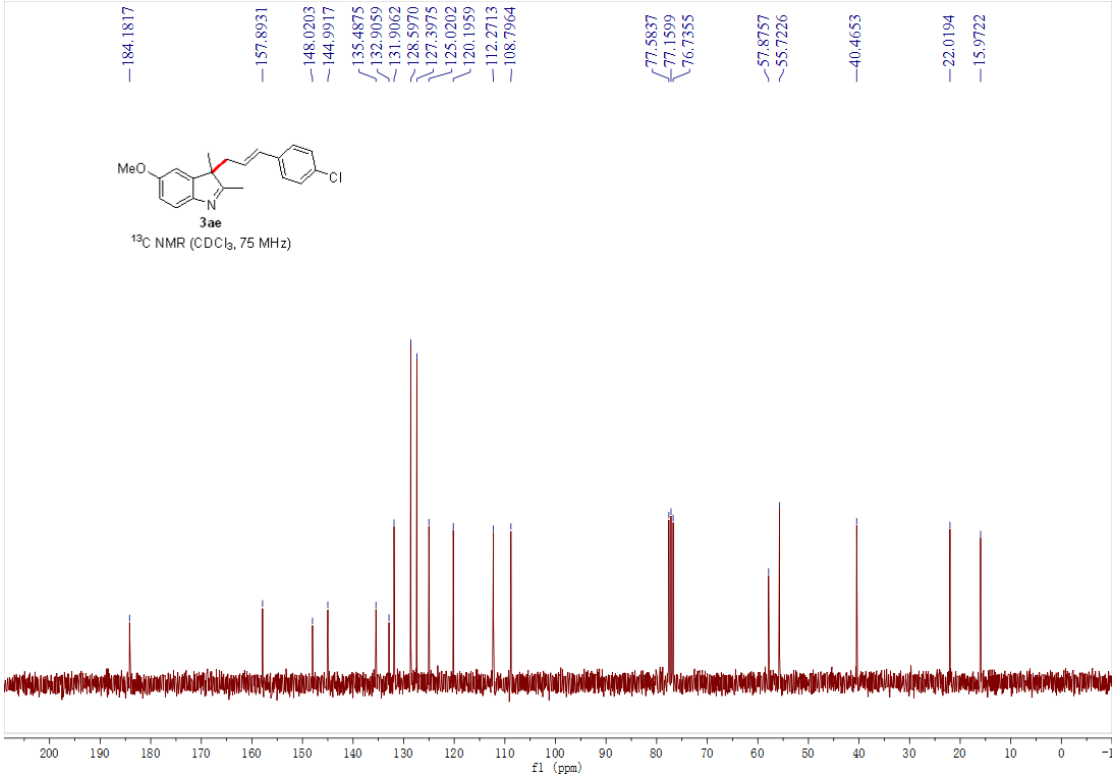
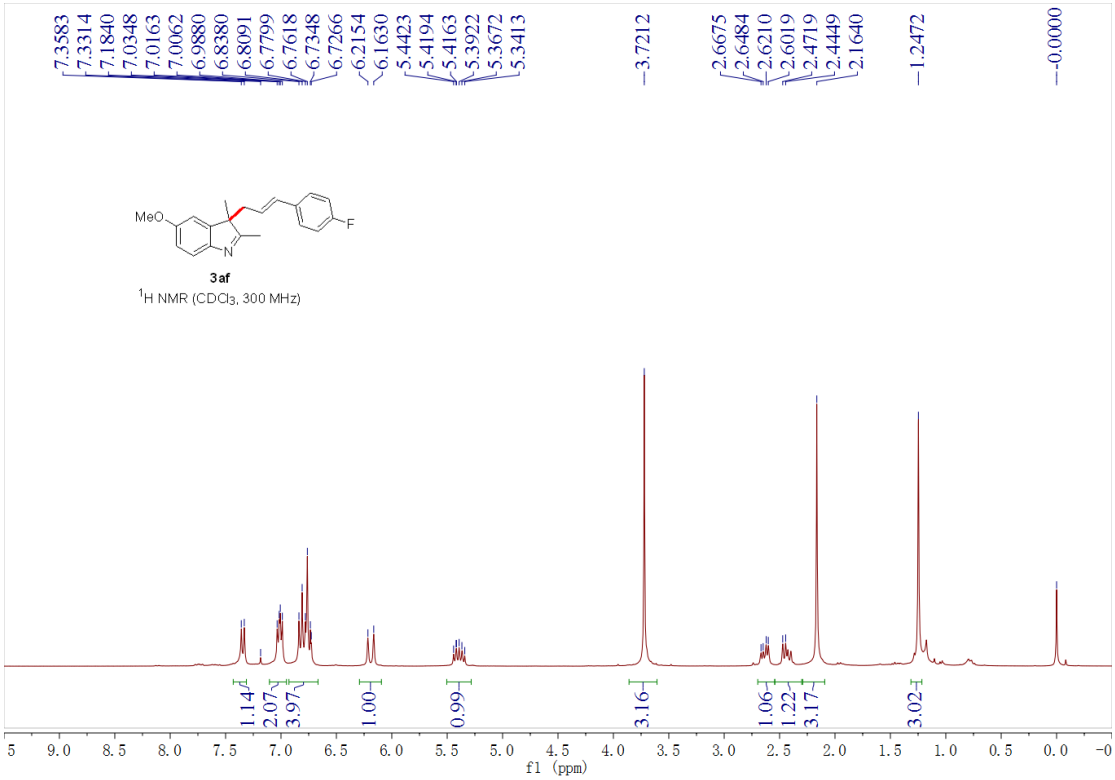
157.8891
147.9805
145.1143
140.7255
140.1059
136.0567
132.7456
128.8116
127.2978
127.1700
126.9278
126.6298
124.3839
120.1883
112.2979
108.8498
77.5839
77.1600
76.7339
57.9146
55.7164
40.5561
21.9725
15.9840
MeO
Ph
N
3ad
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.4351
7.4058
7.1760
7.1478
7.0600
7.0318
6.8359
6.8113
6.8034
6.2774
6.2250
5.5782
5.5558
5.5518
5.5286
5.5035
5.4996
5.4772
3.7982
2.7503
2.7288
2.7037
2.6821
2.5557
2.5288
2.5093
2.4821
2.2393
1.3252
-0.0044
MeO
Cl
N
3ae
1H NMR (CDCl3, 300 MHz)
1.13
2.18
2.09
2.00
1.00
1.02
3.12
1.07
1.08
3.21
3.22
f1 (ppm)


184.1817
157.8931
148.0203
144.9917
135.4875
132.9059
131.9062
128.5970
127.3975
125.0202
120.1959
112.2713
108.7964
77.5837
77.1599
76.7355
57.8757
55.7226
40.4653
22.0194
15.9722
MeO
Cl
N
3ae
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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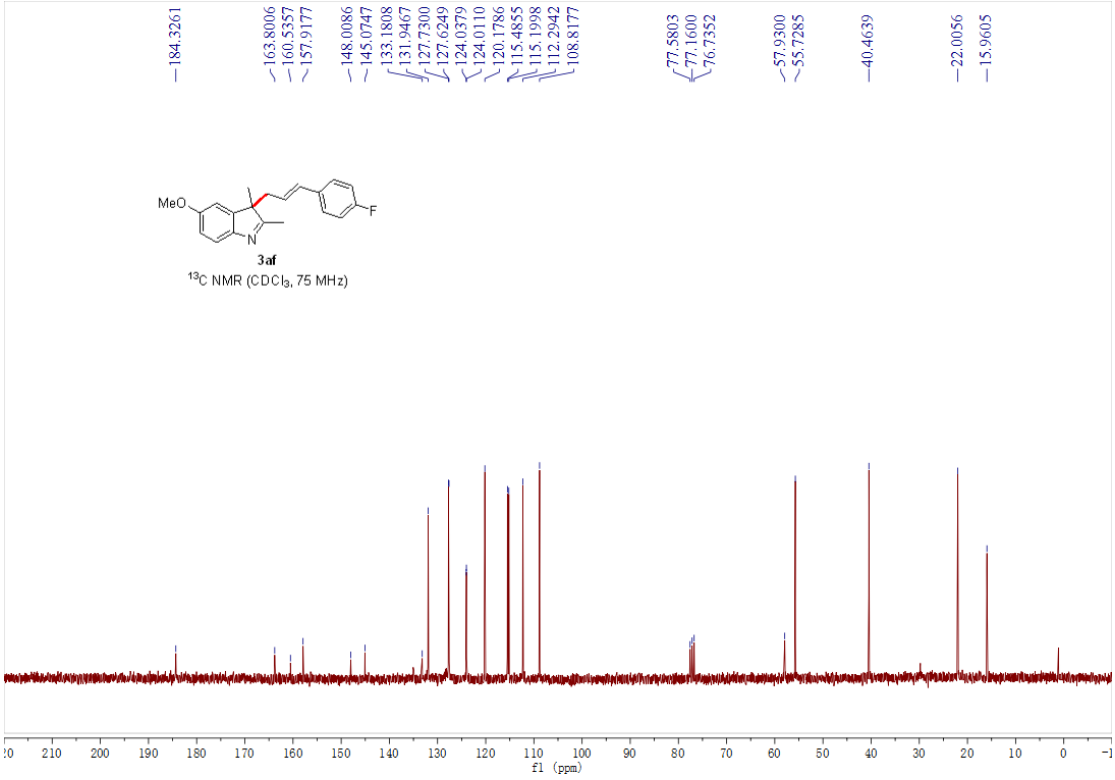
7.3314
7.1840
7.0348
7.0163
7.0062
6.9880
6.8380
6.8091
6.7799
6.7618
6.7348
6.7266
6.2154
6.1630
5.4423
5.4194
5.4163
5.3922
5.3672
5.3413
3.7212
2.6675
2.6484
2.6210
2.6019
2.4719
2.4449
2.1640
1.2472
0.0000
MeO
F
N
3af
1H NMR (CDCl3, 300 MHz)
1.14
2.07
3.97
1.00
0.99
3.16
1.06
1.22
3.17
3.02
f1 (ppm)


184.3261
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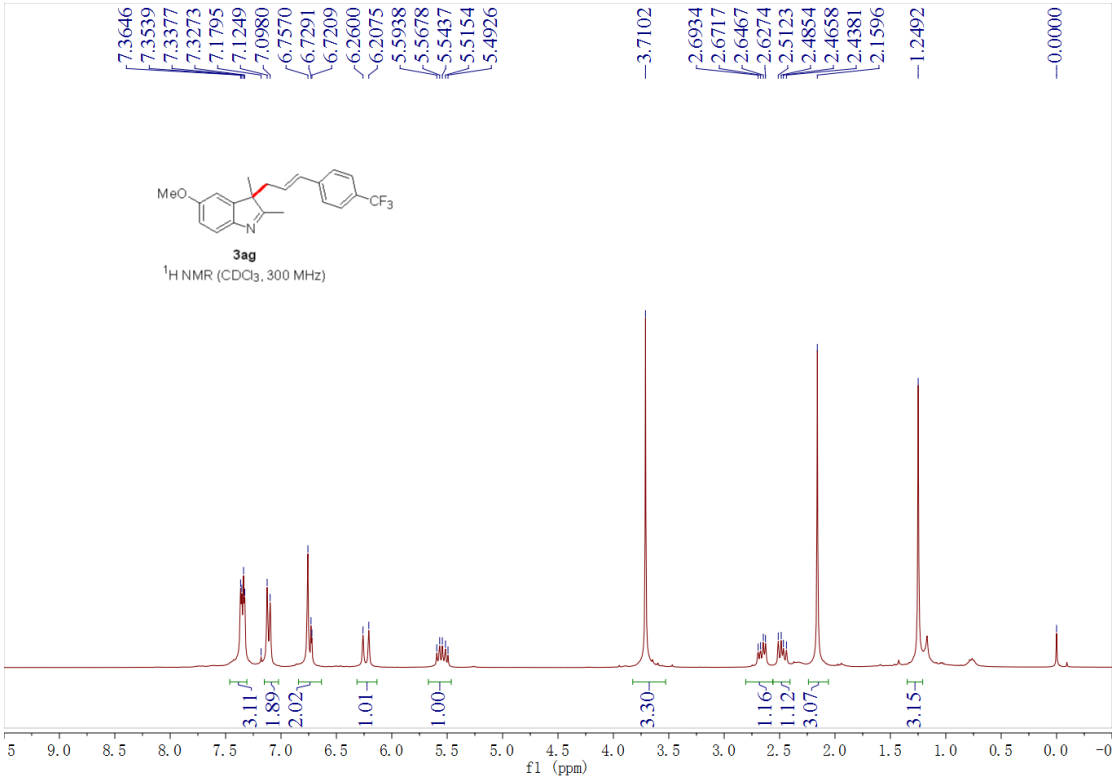
160.5357
157.9177
148.0086
145.0747
133.1808
131.9467
127.7300
127.6249
124.0379
124.0110
120.1786
115.4855
115.1998
112.2942
108.8177
77.5803
77.1600
76.7352
57.9300
55.7285
40.4639
22.0056
15.9605
MeO
F
N
3af
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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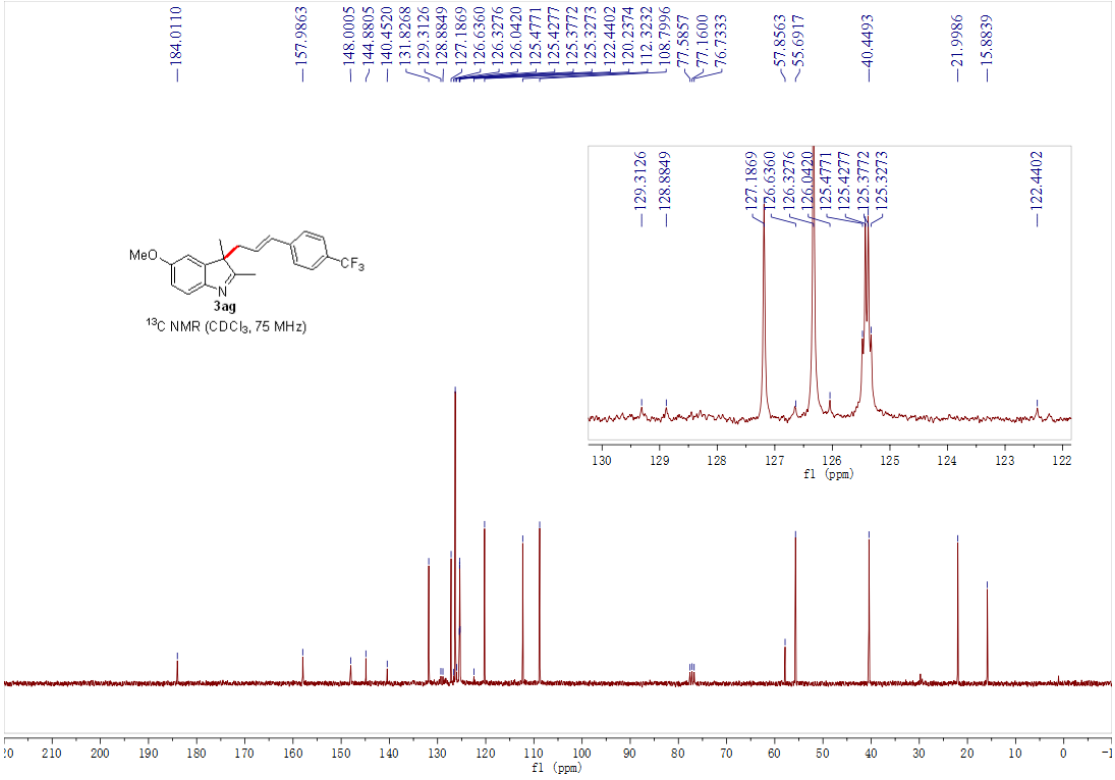
7.3539
7.3377
7.3273
7.1795
7.1249
7.0980
6.7570
6.7291
6.7209
6.2600
6.2075
5.5938
5.5678
5.5437
5.5154
5.4926
3.7102
2.6934
2.6717
2.6467
2.6274
2.5123
2.4854
2.4658
2.4381
2.1596
1.2492
0.0000
MeO
CF3
N
3ag
1H NMR (CDCl3, 300 MHz)
3.11
1.89
2.02
1.01
1.00
3.30
1.16
1.12
3.07
3.15
f1 (ppm)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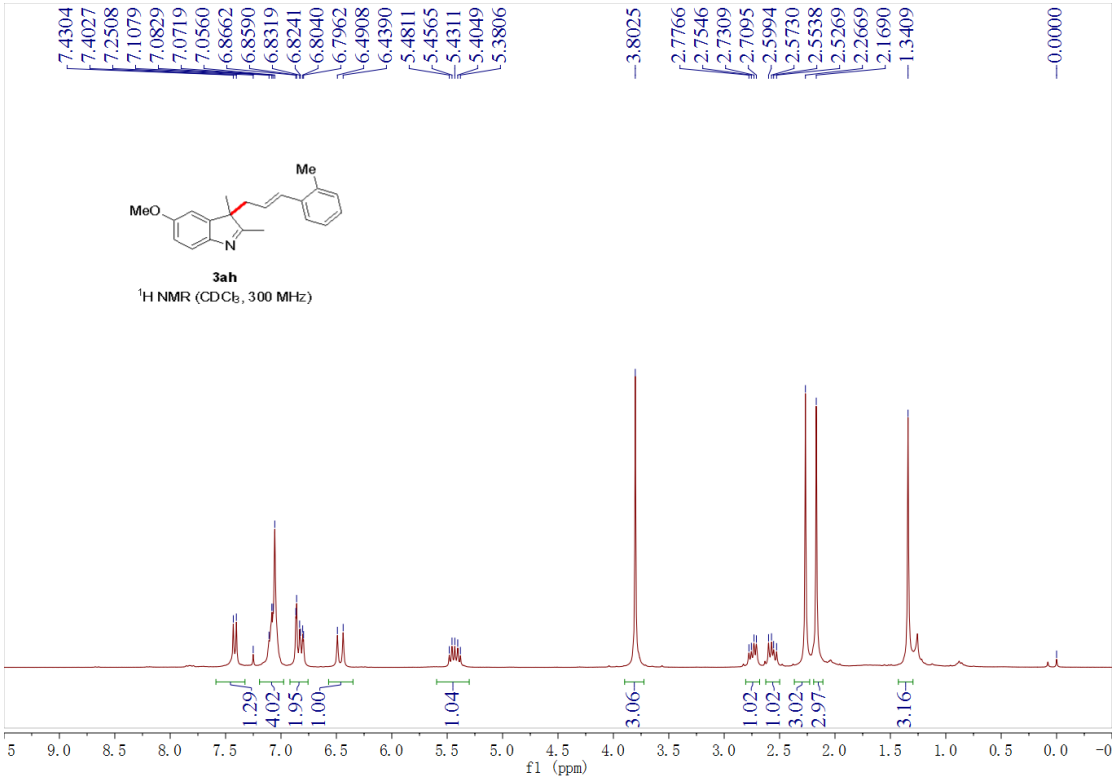
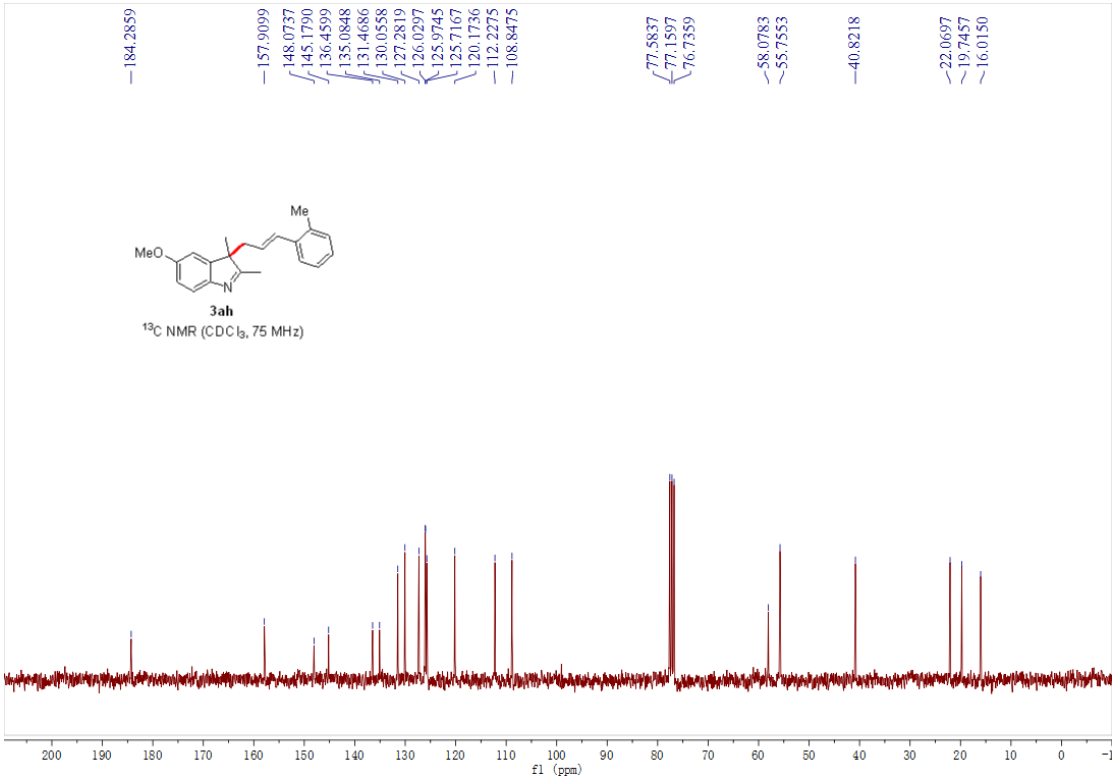
157.9863
148.0005
144.8805
140.4520
131.8268
129.3126
128.8849
127.1869
126.6360
126.3276
126.0420
125.4771
125.4277
125.3772
125.3273
122.4402
120.2374
112.3232
108.7996
77.5857
77.1600
76.7333
57.8563
55.6917
40.4493
21.9986
15.8839
MeO
CF3
N
3ag
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.4304
7.4027
7.2508
7.1079
7.0829
7.0719
7.0560
6.8662
6.8590
6.8319
6.8241
6.8040
6.7962
6.4908
6.4390
5.4811
5.4565
5.4311
5.4049
5.3806
3.8025
2.7766
2.7546
2.7309
2.7095
2.5994
2.5730
2.5538
2.5269
2.2669
2.1690
1.3409
0.0000
Me
MeO
N
3ah
1H NMR (CDCl3, 300 MHz)
1.29
4.02
1.95
1.00
1.04
3.06
1.02
1.02
3.02
2.97
3.16
f1 (ppm)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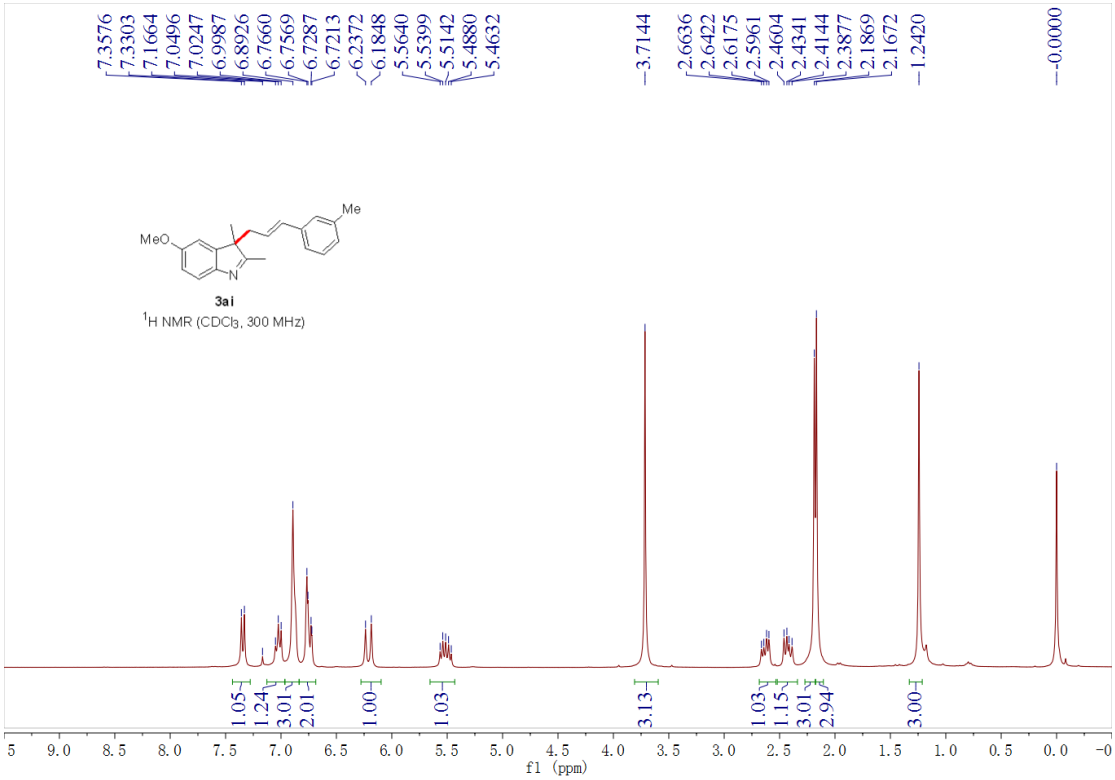
157.9099
148.0737
145.1790
136.4599
135.0848
131.4686
130.0558
127.2819
126.0297
125.9745
125.7167
120.1736
112.2275
108.8475
77.5837
77.1597
76.7359
58.0783
55.7553
40.8218
22.0697
19.7457
16.0150
Me
MeO
N
3ah
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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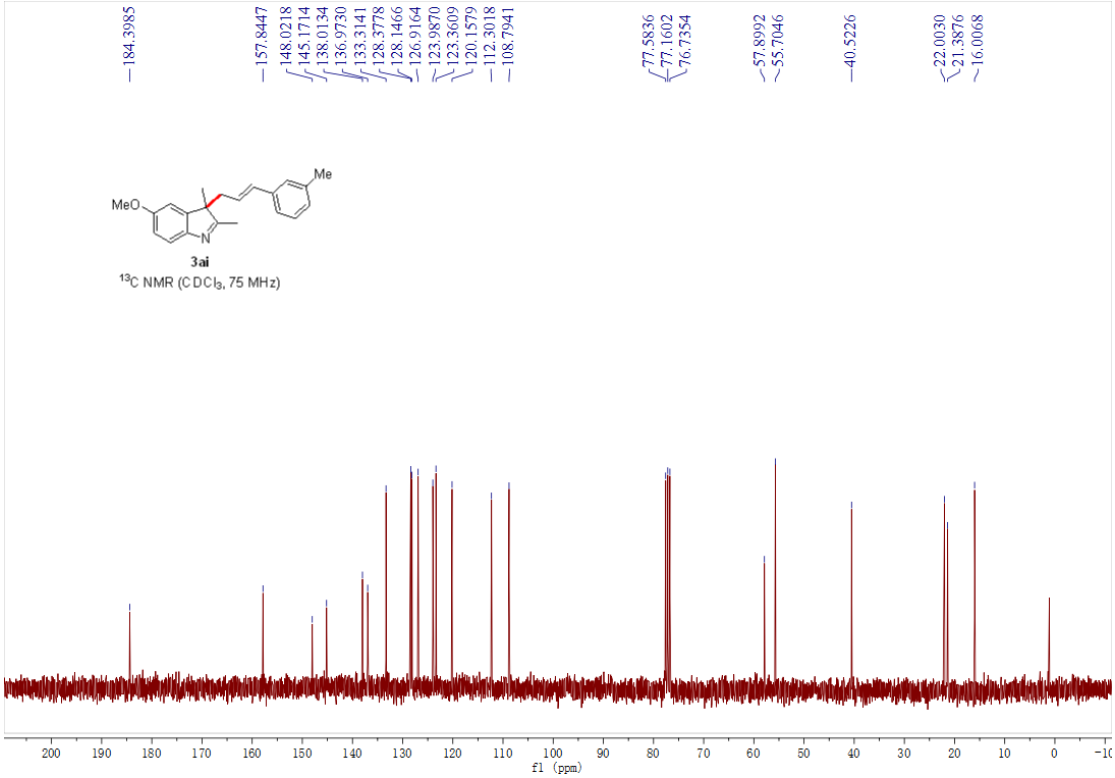
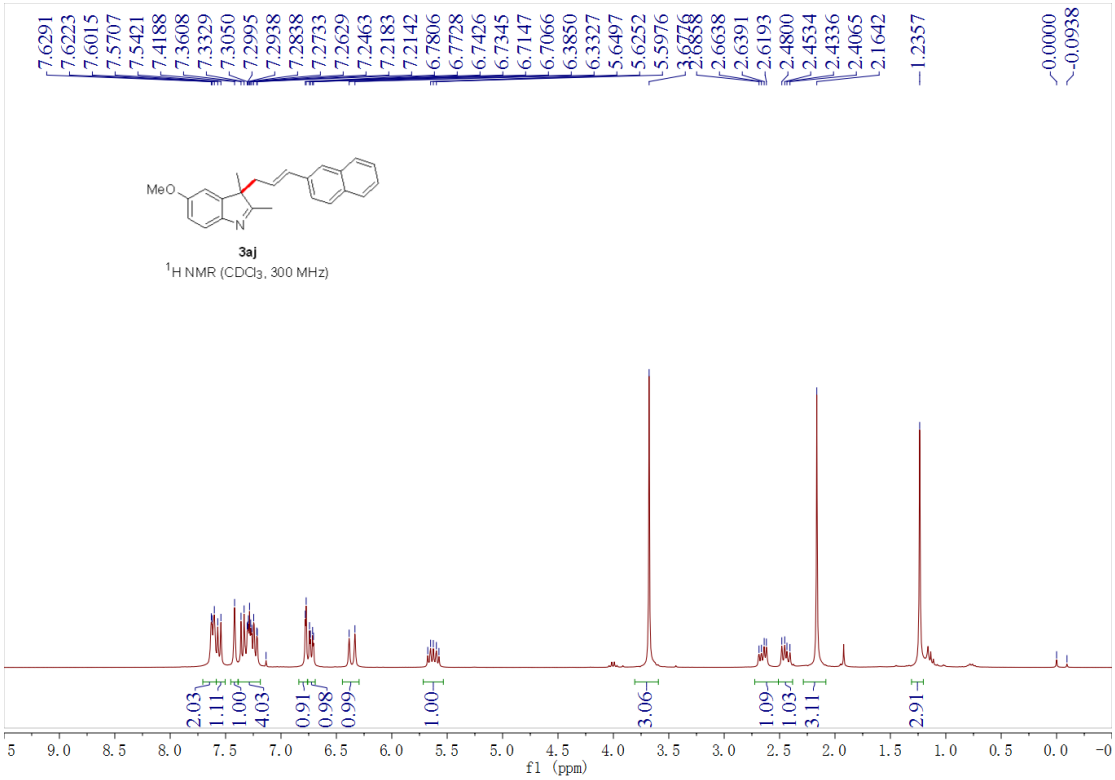
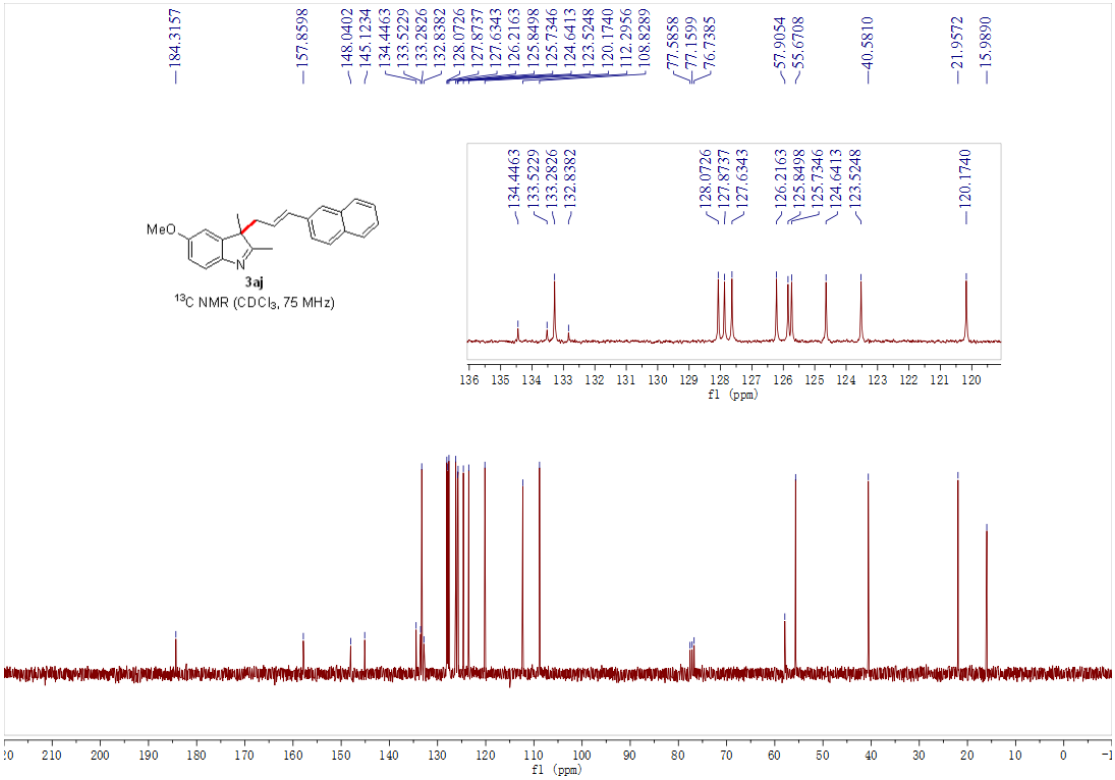
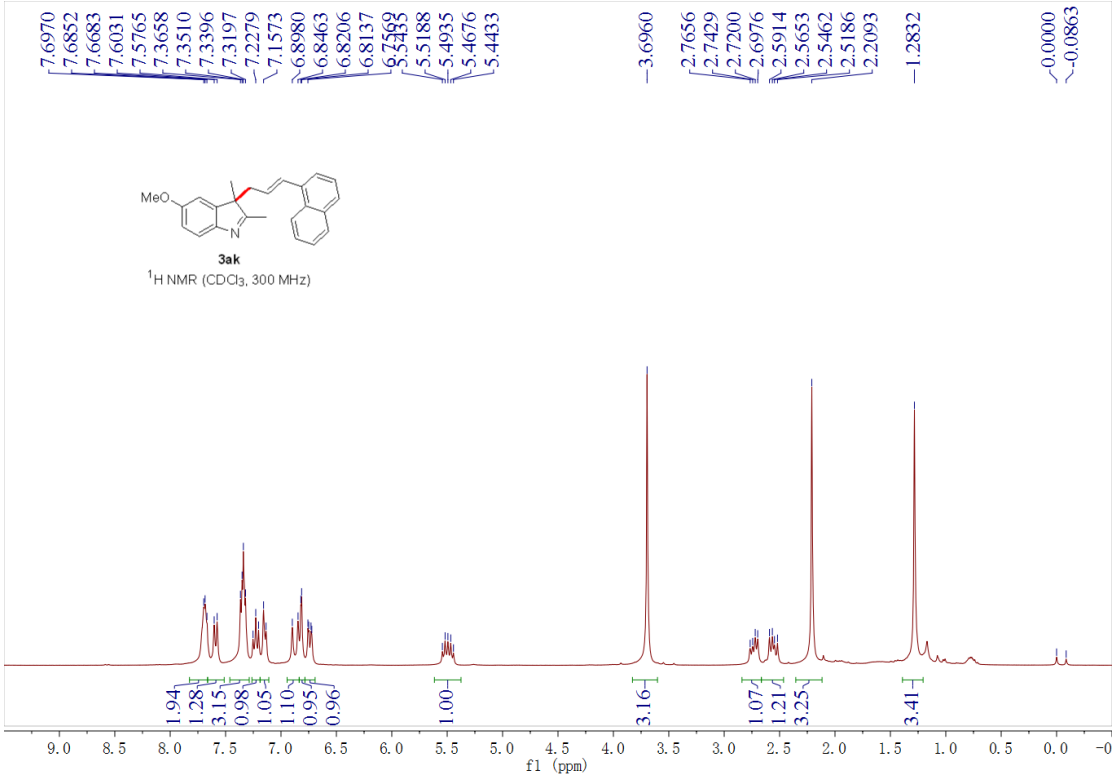
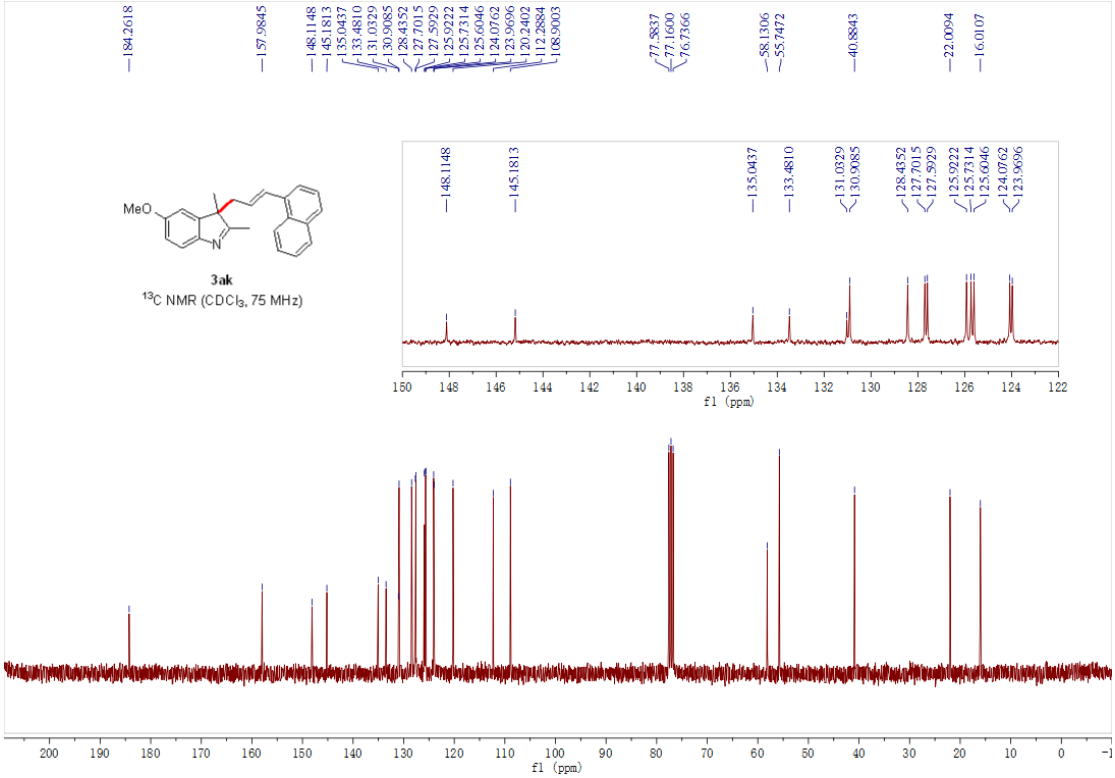
7.3303
7.1664
7.0496
7.0247
6.9987
6.8926
6.7660
6.7569
6.7287
6.7213
6.2372
6.1848
5.5640
5.5399
5.5142
5.4880
5.4632
3.7144
2.6636
2.6422
2.6175
2.5961
2.4604
2.4341
2.4144
2.3877
2.1869
2.1672
1.2420
-0.0000
MeO
Me
N
3ai
1H NMR (CDCl3, 300 MHz)
1.05
1.24
3.01
2.01
1.00
1.03
3.13
1.03
1.15
3.01
2.94
3.00
f1 (ppm)

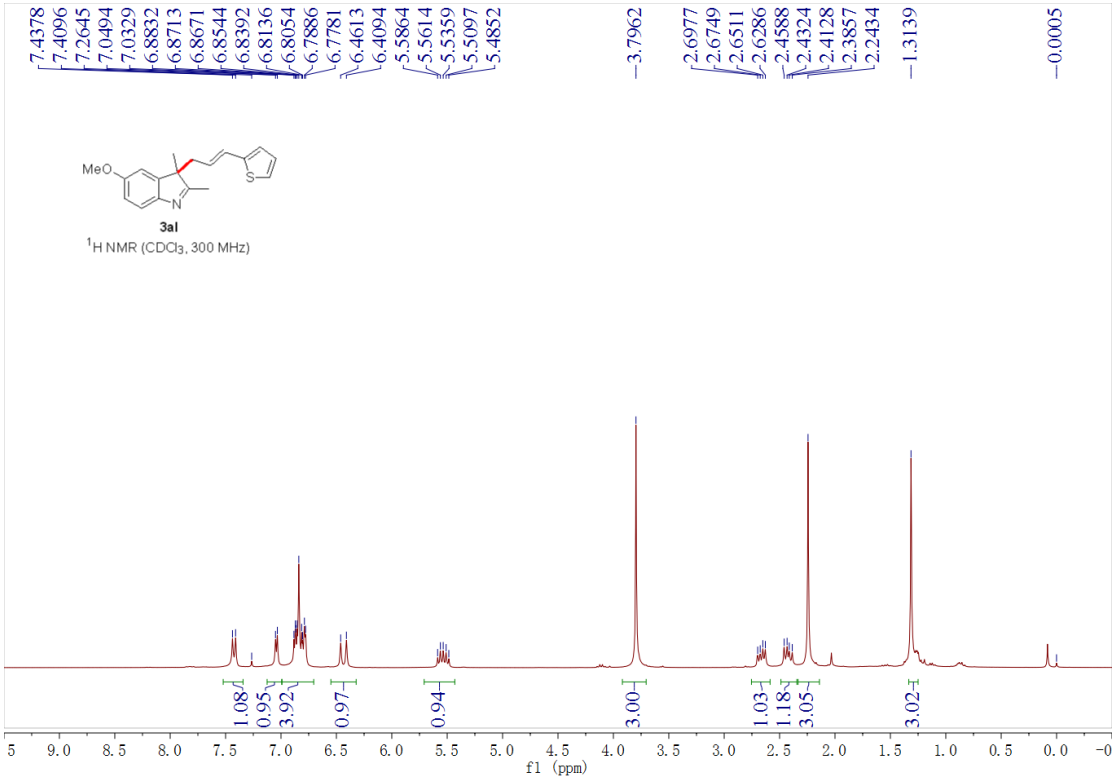

184.3985
157.8447
148.0218
145.1714
138.0134
136.9730
133.3141
128.3778
128.1466
126.9164
123.9870
123.3609
120.1579
112.3018
108.7941
77.5836
77.1602
76.7354
57.8992
55.7046
40.5226
22.0030
21.3876
16.0068
MeO
Me
N
3ai
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

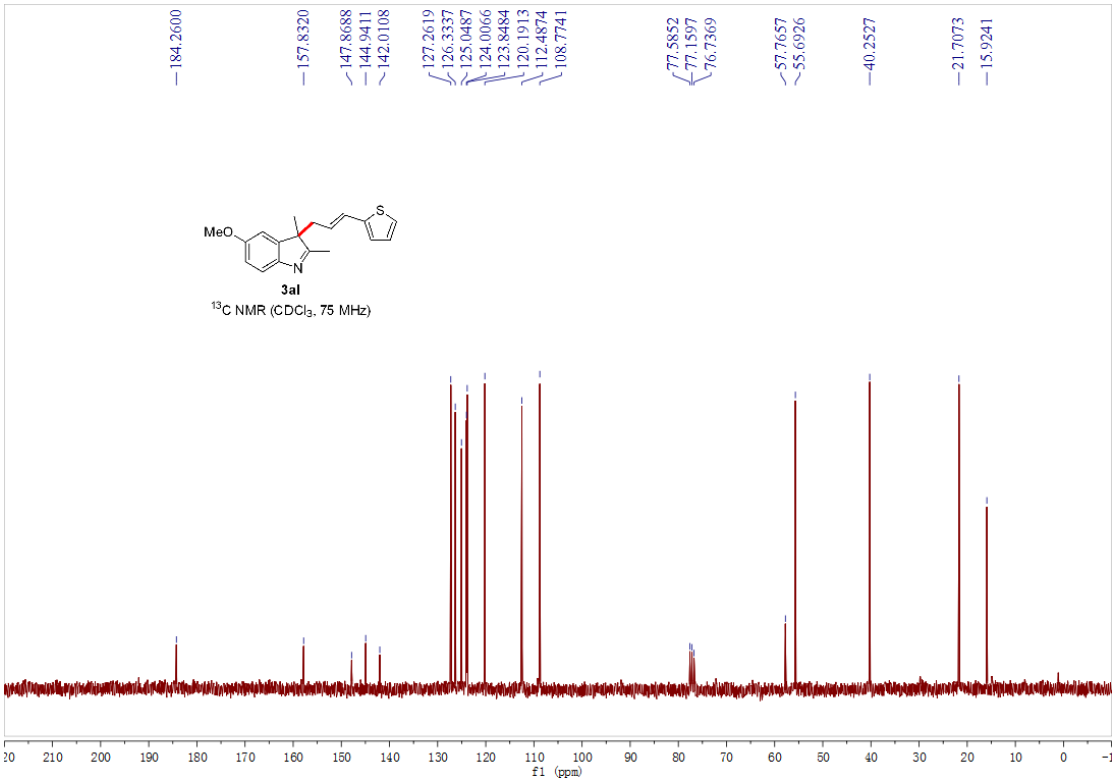

MeO
N
3aj
1H NMR (CDCl3, 300 MHz)
f1 (ppm)

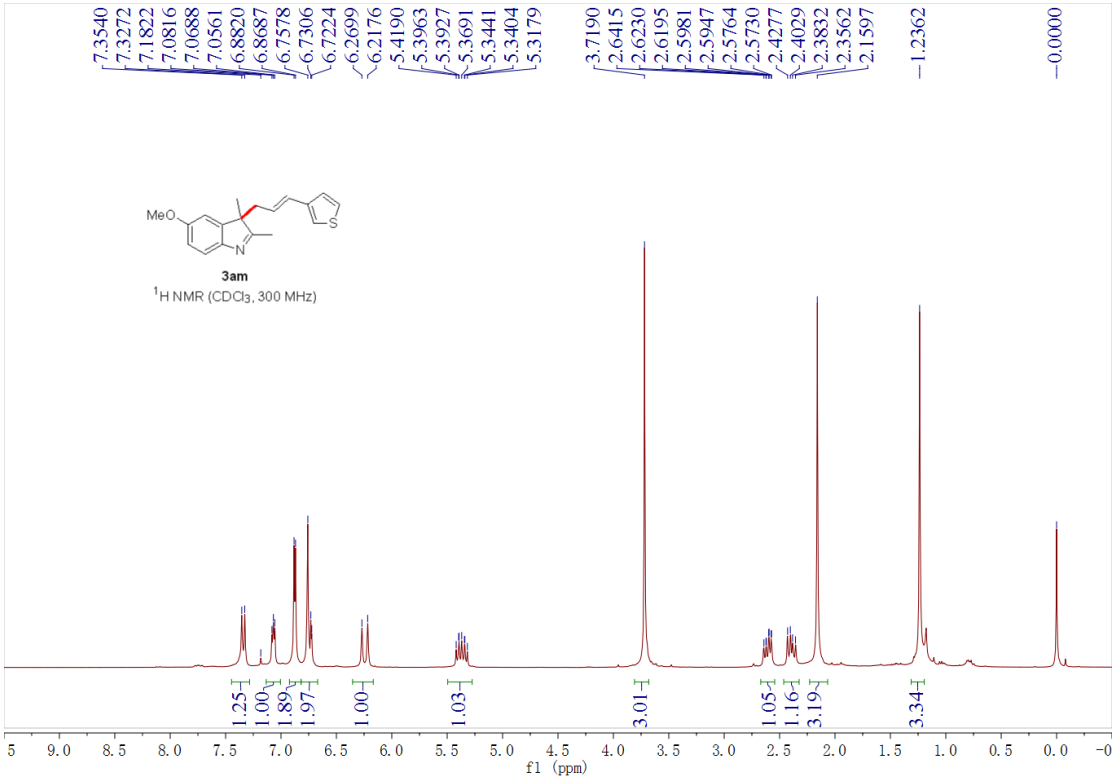

MeO
N
3aj
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

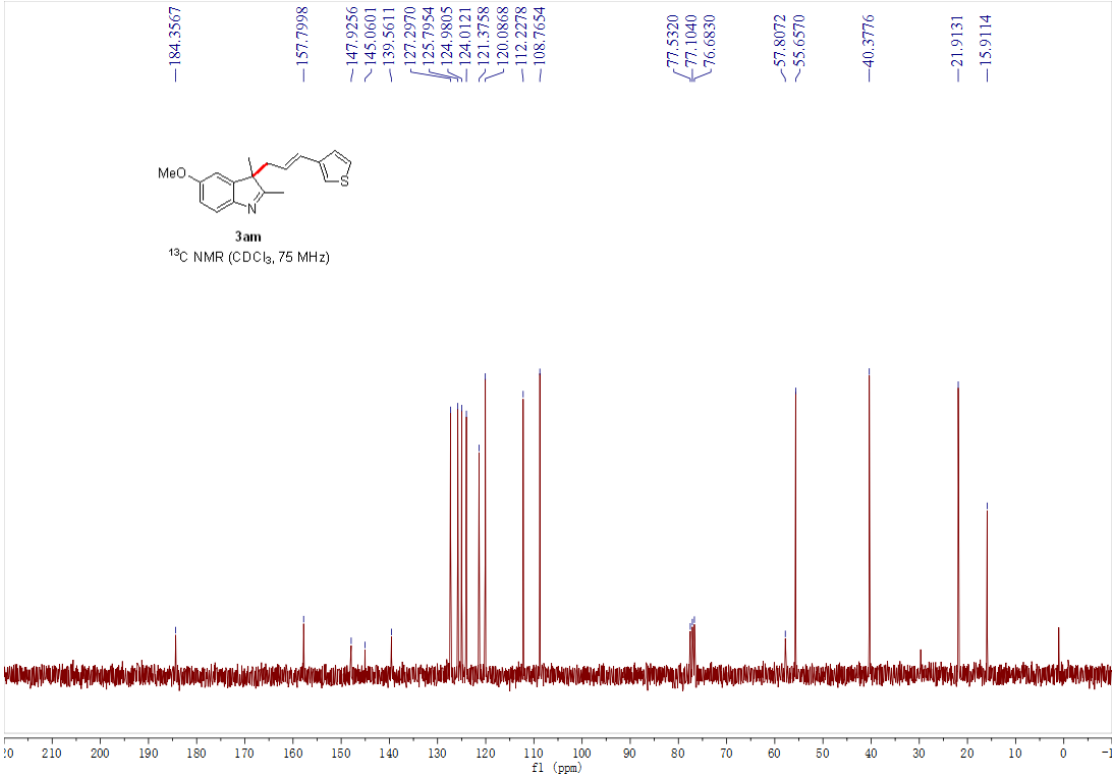

7.6970
7.6852
7.6683
7.6031
7.5765
7.3658
7.3510
7.3396
7.3197
7.2279
7.1573
6.8980
6.8463
6.8206
6.8137
6.7569
5.5435
5.5188
5.4935
5.4676
5.4433
3.6960
2.7656
2.7429
2.7200
2.6976
2.5914
2.5653
2.5462
2.5186
2.2093
1.2832
0.0000
-0.0863
MeO
N
3ak
1H NMR (CDCl3, 300 MHz)
1.94
1.28
3.15
0.98
1.05
1.10
0.95
0.96
1.00
3.16
1.07
1.21
3.25
3.41
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


184.2618
157.9845
148.1148
145.1813
135.0437
133.4810
131.0329
130.9085
128.4352
127.7015
127.5929
125.9222
125.7314
125.6046
124.0762
123.9696
120.2402
112.2884
108.9003
77.5837
77.1600
76.7366
58.1306
55.7472
40.8843
22.0094
16.0107
MeO
N
3ak
13C NMR (CDCl3, 75 MHz)
150 148 146 144 142 140 138 136 134 132 130 128 126 124 122
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.4378
7.4096
7.2645
7.0494
7.0329
6.8832
6.8713
6.8671
6.8544
6.8392
6.8136
6.8054
6.7886
6.7781
6.4613
6.4094
5.5864
5.5614
5.5359
5.5097
5.4852
3.7962
2.6977
2.6749
2.6511
2.6286
2.4588
2.4324
2.4128
2.3857
2.2434
1.3139
0.0005
MeO
N
S
3al
^{1}H NMR ($CDCl_3$, 300 MHz)
1.08
0.95
3.92
0.97
0.94
3.00
1.03
1.18
3.05
3.02
f1 (ppm)


184.2600
157.8320
147.8688
144.9411
142.0108
127.2619
126.3337
125.0487
124.0066
123.8484
120.1913
112.4874
108.7741
77.5852
77.1597
76.7369
57.7657
55.6926
40.2527
21.7073
15.9241
MeO
N
S
3al
^{13}C NMR ($CDCl_3$, 75 MHz)
f1 (ppm)


7.3540
7.3272
7.1822
7.0816
7.0688
7.0561
6.8820
6.8687
6.7578
6.7306
6.7224
6.6699
6.2176
5.4190
5.3963
5.3927
5.3691
5.3441
5.3404
5.3179
3.7190
2.6415
2.6230
2.6195
2.5981
2.5947
2.5764
2.5730
2.4277
2.4029
2.3832
2.3562
2.1597
1.2362
0.0000
MeO
N
S
3am
1H NMR (CDCl3, 300 MHz)
1.25
1.00
1.89
1.97
1.00
1.03
3.01
1.05
1.16
3.19
3.34
f1 (ppm)


184.3567
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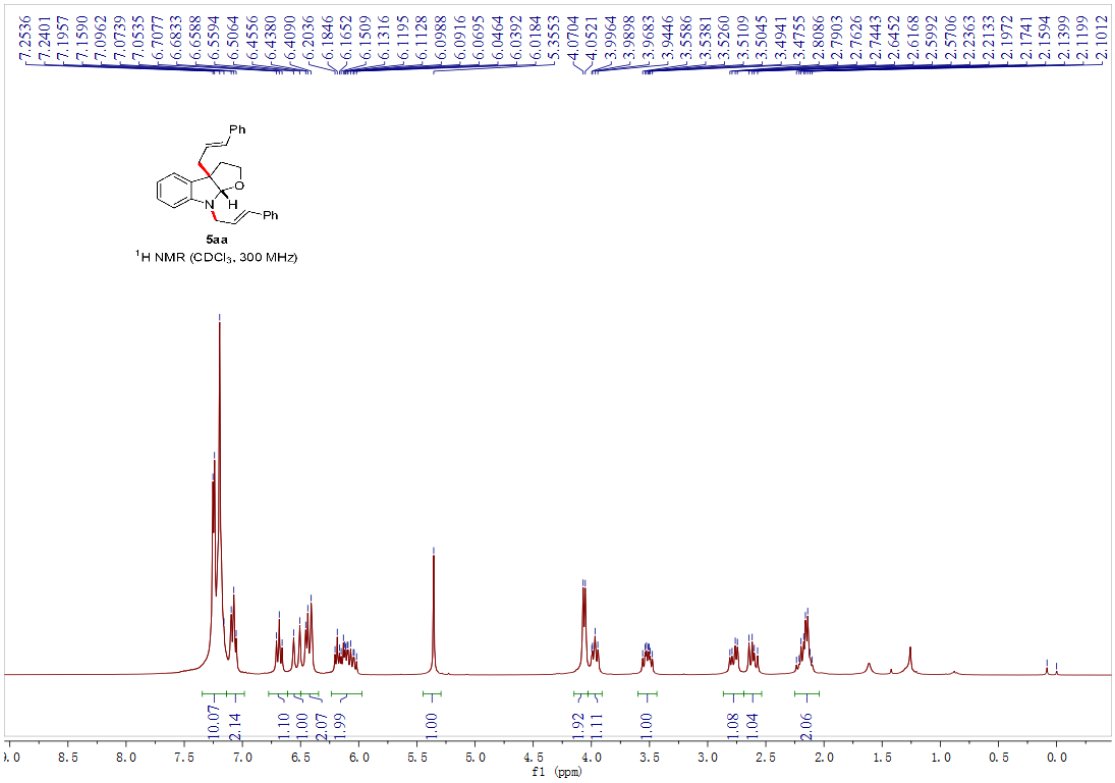
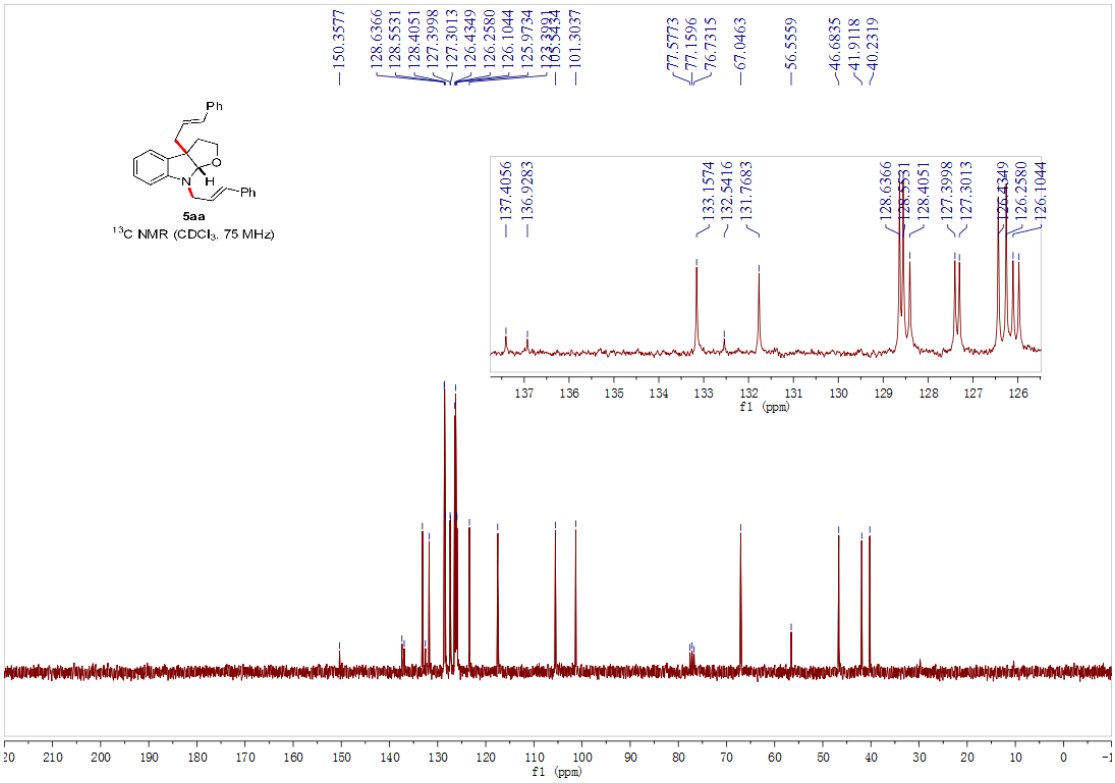
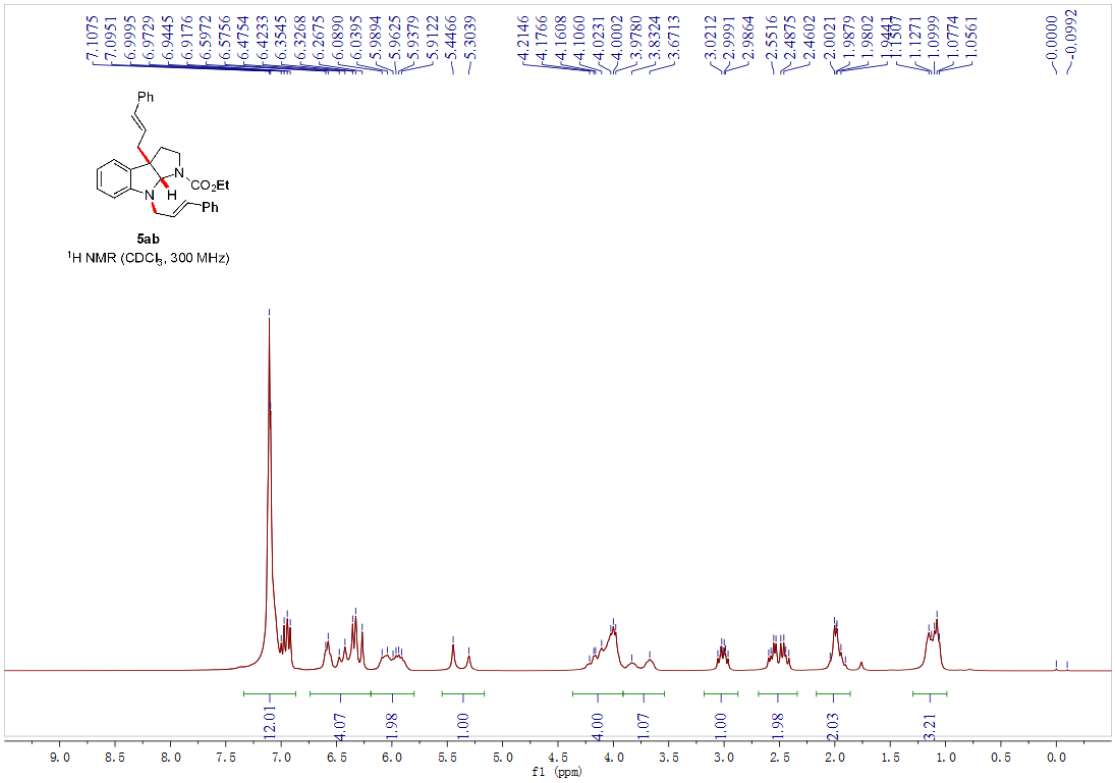
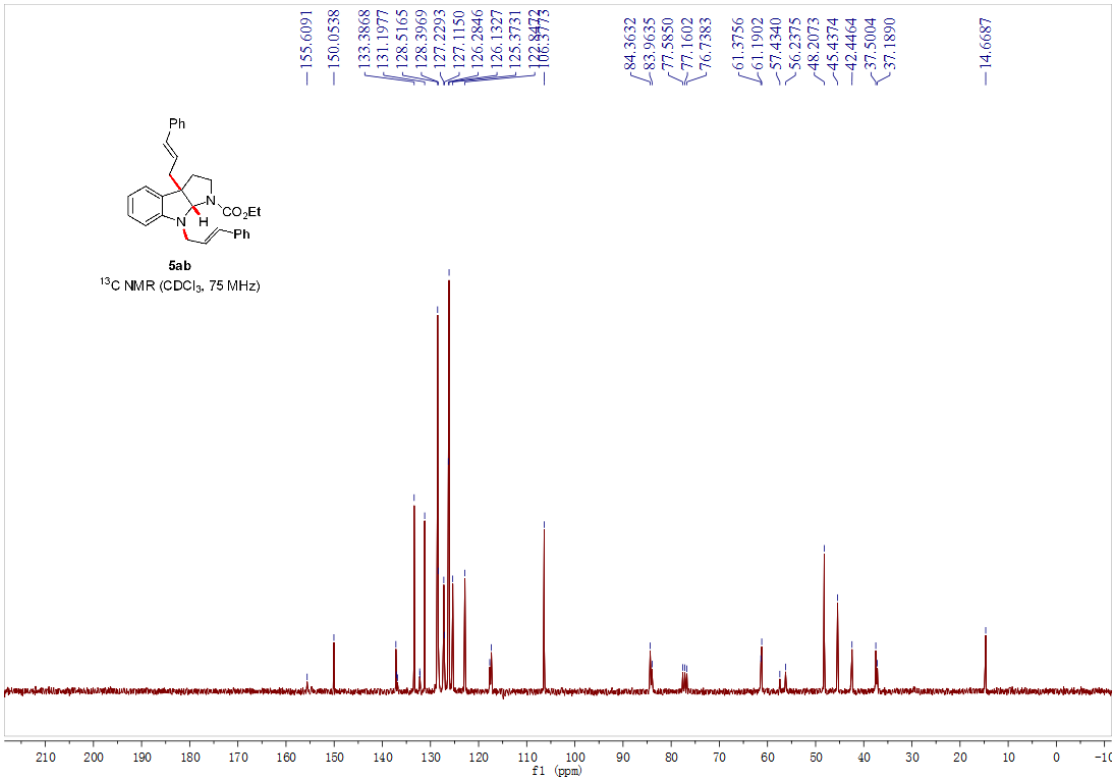
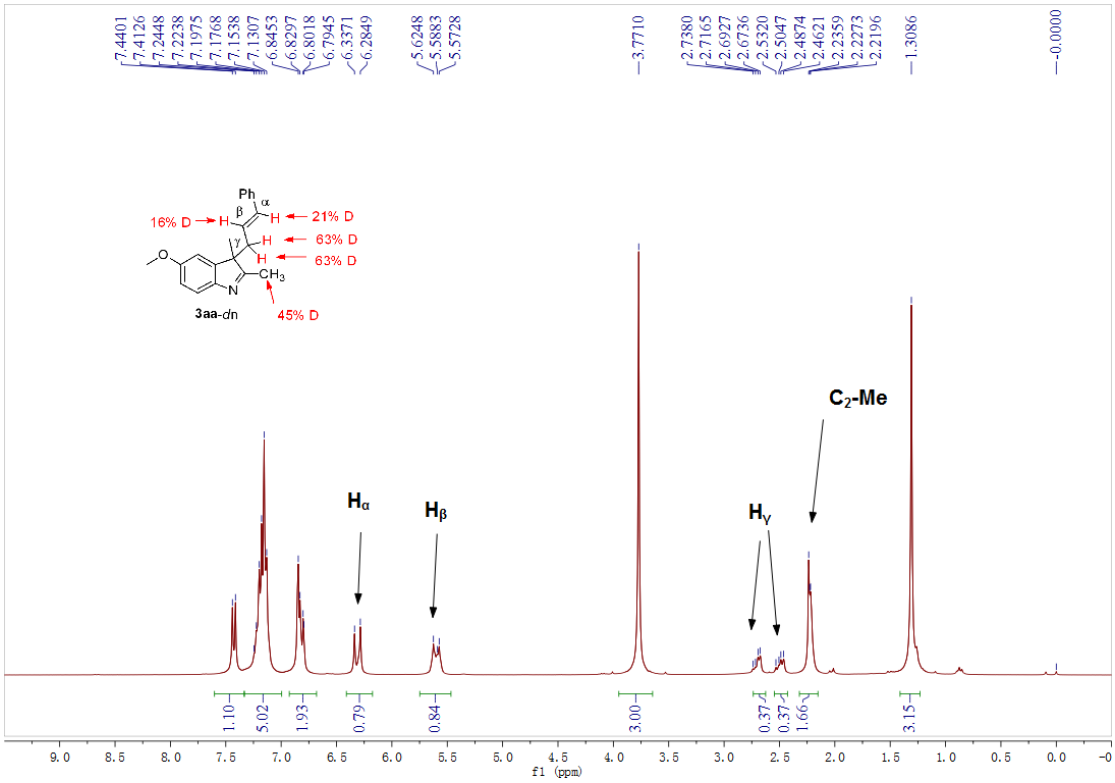
147.9256
145.0601
139.5611
127.2970
125.7954
124.9805
124.0121
121.3758
120.0868
112.2278
108.7654
77.5320
77.1040
76.6830
57.8072
55.6570
40.3776
21.9131
15.9114
MeO
N
S
3am
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

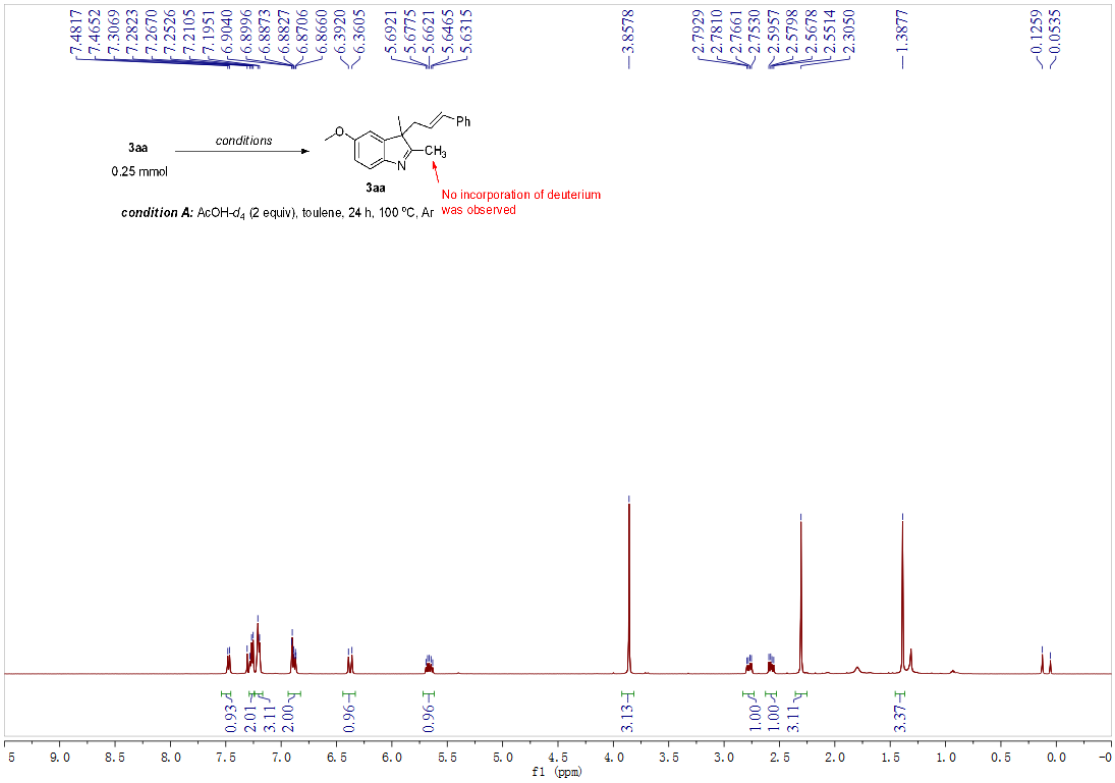

5aa
^{1}H NMR ($CDCl_3$, 300 MHz)
f1 (ppm)

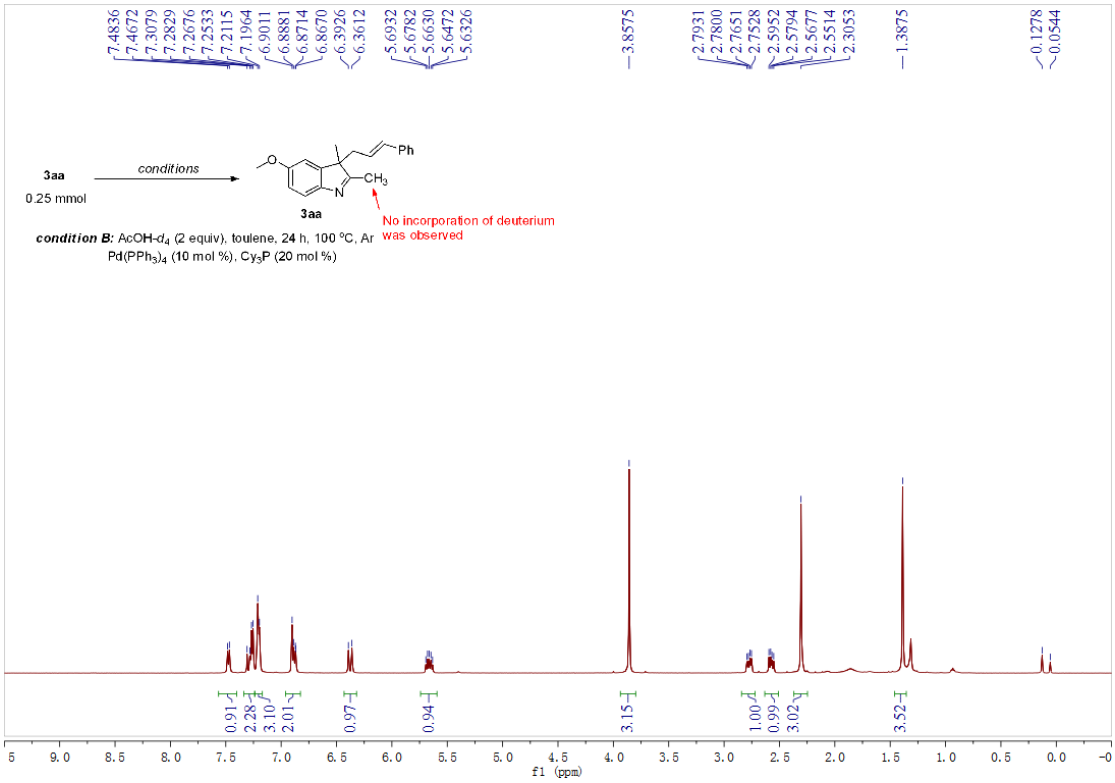

5aa
^{13}C NMR ($CDCl_3$, 75 MHz)
f1 (ppm)

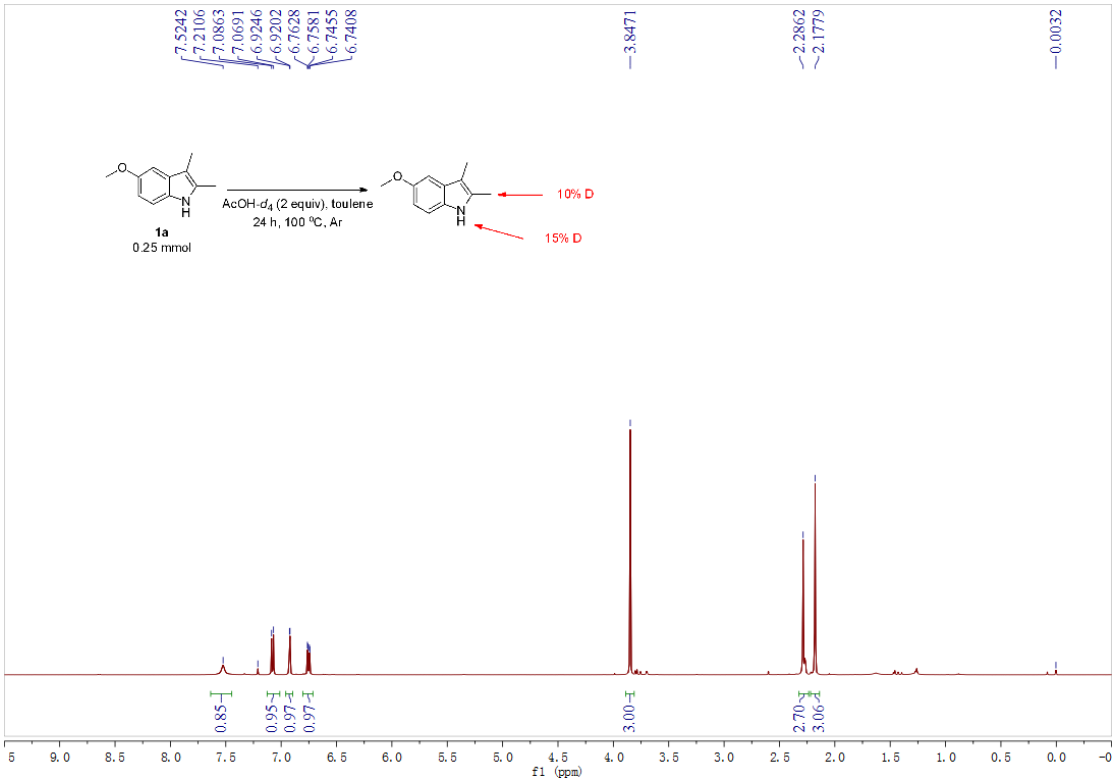

5ab
¹H NMR (CDCl₃, 300 MHz)
f1 (ppm)

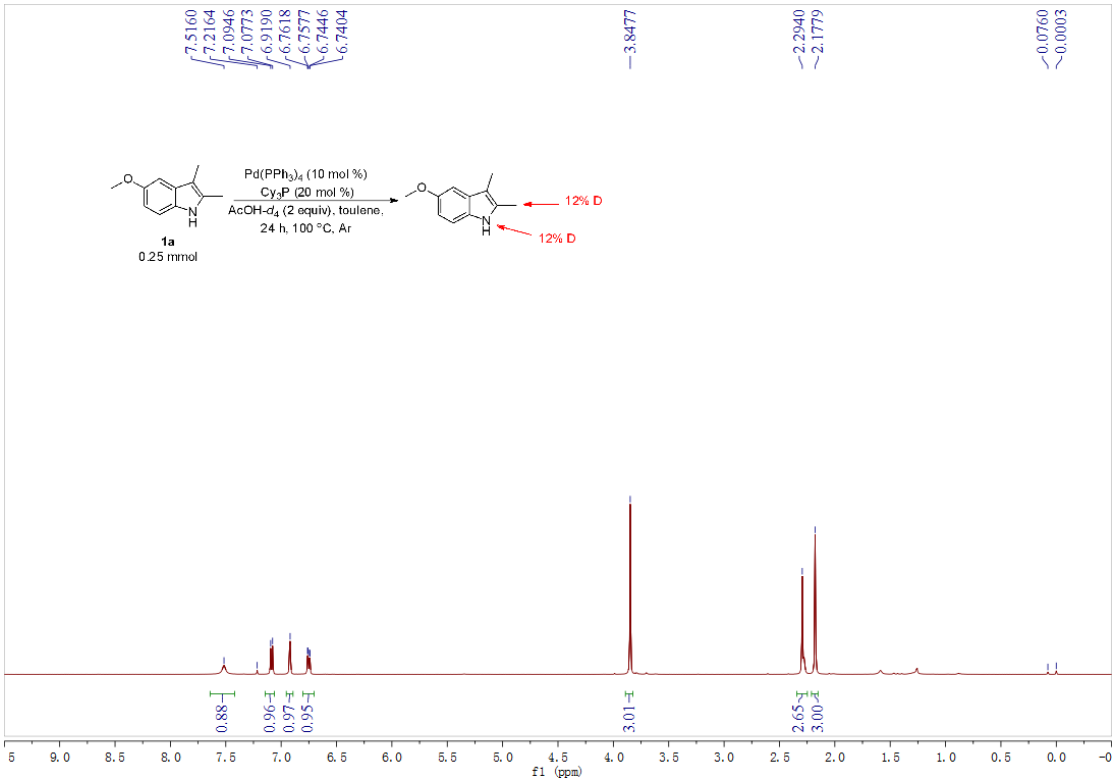

5ab
¹³C NMR (CDCl₃, 75 MHz)
f1 (ppm)

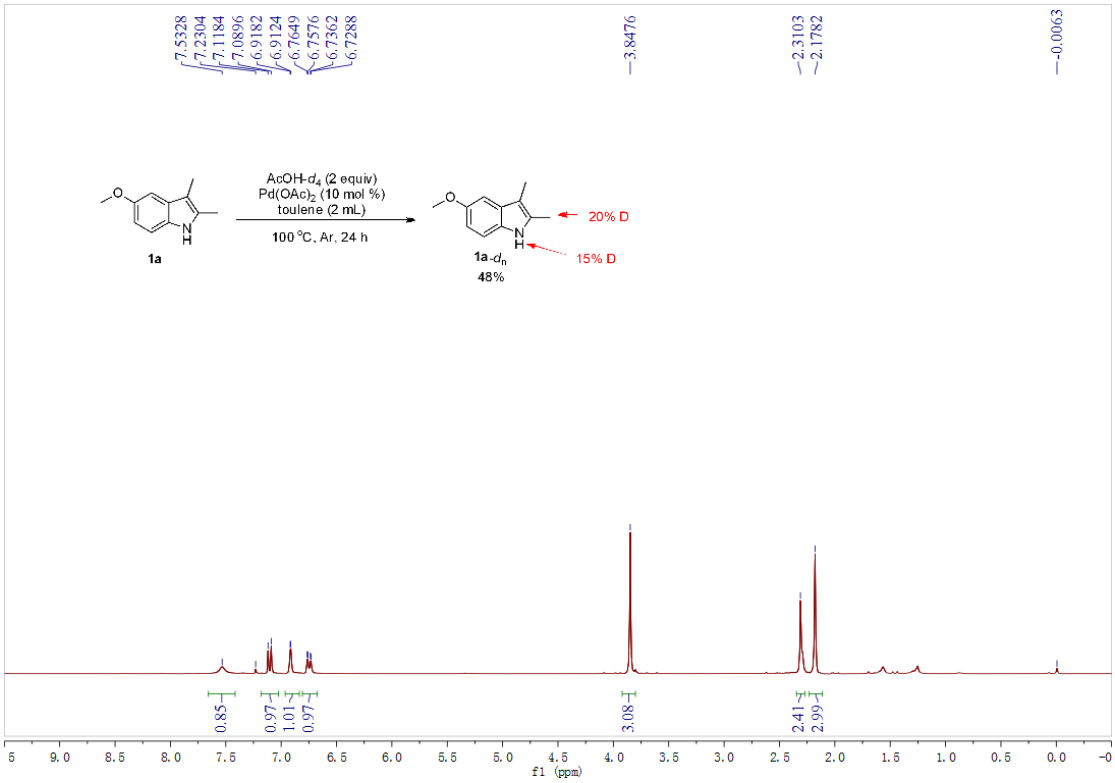

7.4401
7.4126
7.2448
7.2238
7.1975
7.1768
7.1538
7.1307
6.8453
6.8297
6.8018
6.7945
6.3371
6.2849
5.6248
5.5883
5.5728
3.7710
2.7380
2.7165
2.6927
2.6736
2.5320
2.5047
2.4874
2.4621
2.2359
2.2273
2.2196
1.3086
0.0000
Ph
α
β
γ
16% D
H
21% D
63% D
63% D
CH3
N
O
3aa-dn
45% D
Hα
Hβ
Hγ
C2-Me
1.10
5.02
1.93
0.79
0.84
3.00
0.37
0.37
1.66
3.15
f1 (ppm)


7.4817
7.4652
7.3069
7.2823
7.2670
7.2526
7.2105
7.1951
6.9040
6.8996
6.8873
6.8827
6.8706
6.8660
6.3920
6.3605
5.6921
5.6775
5.6621
5.6465
5.6315
3.8578
2.7929
2.7810
2.7661
2.7530
2.5957
2.5798
2.5678
2.5514
2.3050
1.3877
0.1259
0.0535
3aa
0.25 mmol
conditions
Ph
CH3
N
O
3aa
No incorporation of deuterium was observed
condition A: AcOH-d4 (2 equiv), toulene, 24 h, 100 °C, Ar
0.93
2.01
3.11
2.00
0.96
0.96
3.13
1.00
1.00
3.11
3.37
f1 (ppm)


3aa
0.25 mmol
conditions
Ph
CH3
3aa
No incorporation of deuterium was observed
condition B: AcOH-d4 (2 equiv), toulene, 24 h, 100 °C, Ar
Pd(PPh3)4 (10 mol %), Cy3P (20 mol %)
f1 (ppm)


1a
0.25 mmol
AcOH-d4 (2 equiv), toulene
24 h, 100 °C, Ar
10% D
15% D
f1 (ppm)


7.5160
7.2164
7.0946
7.0773
6.9190
6.7618
6.7577
6.7446
6.7404
3.8477
2.2940
2.1779
0.0760
0.0003
Pd(PPh3)4 (10 mol %)
Cy3P (20 mol %)
AcOH-d4 (2 equiv), toulene,
24 h, 100 °C, Ar
1a
0.25 mmol
12% D
12% D
0.88
0.96
0.97
0.95
3.01
2.65
3.00
f1 (ppm)


7.5328
7.2304
7.1184
7.0896
6.9182
6.9124
6.7649
6.7576
6.7362
6.7288
3.8476
2.3103
2.1782
-0.0063
AcOH-d4 (2 equiv)
Pd(OAc)2 (10 mol %)
toulene (2 mL)
100 °C, Ar, 24 h
1a
1a-dn
48%
20% D
15% D
0.85
0.97
1.01
0.97
3.08
2.41
2.99
f1 (ppm)