Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of *N*-β-Aminoacrylate Substituted Indoles *via* ^{t}BuOK Catalyzed Addition of Indoles to Ketenimines

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1) General Information

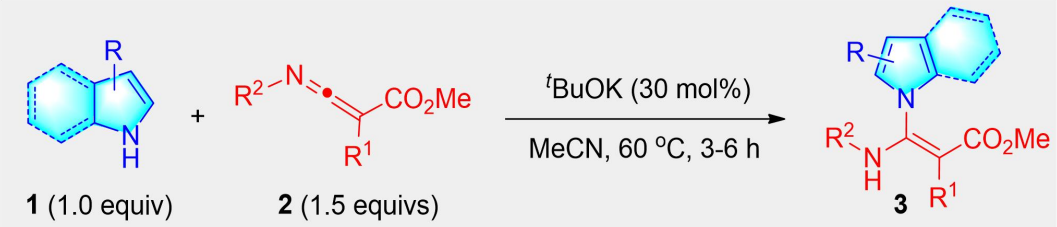
Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

Anhydrous solvents such as CH_2Cl_2, CH_3CN, THF, toluene, and EtOAc, and the catalysts such as Et_3N, DABCO, DBU, ^{t}BuOLi, ^{t}BuONa, and ^{t}BuOK were purchased from Energy Chemical. Unless otherwise stated, all purchased reagents were used without further purification. The; All reactions involving air- or moisture-sensitive compounds were carried out under nitrogen atmosphere in dried Schlenk tube. The ketenimines **1**[1] was prepared using the literature procedures.

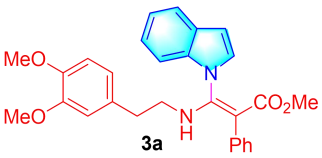
References

[1] (a) P. Lu and Y. Wang, *Chem. Soc. Rev.*, **2012**, *41*, 5687; (b) G.-S. Chen, S.-J. Chen, J. Luo, X.-Y. Mao, A. S.-C. Chan, R. W.-Y. Sun and Y.-L. Liu, *Angew. Chem. Int. Ed.*, **2020**, *59*, 614; (c) J. Luo, G.-S. Chen, S.-J. Chen, Z.-D. Li, Y.-L. Zhao and Y.-L. Liu, *Adv. Synth. Catal.* **2020**, *362*, 3635.

2) General Procedure and Spectral Data of Products 3.

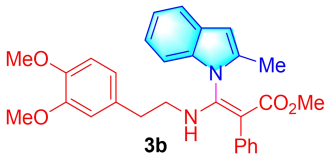


To a 10.0 mL Schlenk tube were successively added ^{t}BuOK (30 mol%), indole or pyrrole **1** (0.10 mmol), anhydrous MeCN (1.0 mL) and ketenimines **2** (0.15 mmol). The reaction mixture was stirred vigorously at 60 °C for 3-6 h under N_2 atmosphere till full consumption of **1**. The reaction mixture was then concentrated by rotary vaporation, and the residue was subjected to column chromatography using petroleum ether/ethyl acetate (from 20:1-3:1) as eluent to afford the desired products **3**.



3a

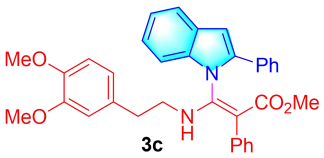
The reaction was run at 60 °C for 3 h, affording product **3a** as a yellow solid (91% yield, 41.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.70 (t, J = 6.8 Hz, 2H), 2.92-3.01 (m, 1H), 3.12-3.19 (m, 1H), 3.71 (s, 3H), 3.79 (s, 3H), 3.86 (s, 3H), 6.20 (dd, J = 3.2, 0.8 Hz, 1H), 6.30 (d, J = 3.2 Hz, 1H), 6.48 (d, J = 2.0 Hz, 1H), 6.59 (dd, J = 8.0, 2.0 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.80-6.82 (m, 2H), 6.91-6.95 (m, 3H), 7.08-7.12 (m, 1H), 7.18-7.23 (m, 1H), 7.35 (dd, J = 8.4, 0.8 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 9.23 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 154.1, 148.8, 147.6, 135.8, 135.4, 130.9, 130.5, 128.3, 127.8, 127.3, 125.8, 122.8, 120.82, 120.76, 112.0, 111.2, 111.1, 103.7, 97.0, 55.9, 55.6, 51.4, 45.5, 37.1; HRMS (ESI): Exact mass calcd for $C_{28}H_{28}N_2O_4Na$ $[M+Na]^+$: 479.1941, Found: 479.1952.



3b

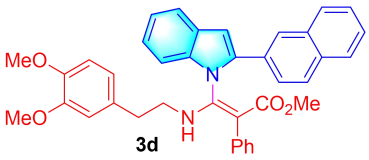
The reaction was run at 60 °C for 3 h, affording product **3b** as a yellow solid (91% yield, 42.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H), 2.62-2.66 (m, 2H), 2.83-2.90 (m, 2H), 3.71 (s, 3H), 3.77 (s, 3H), 3.84 (s, 3H), 6.07 (s, 1H), 6.39 (s, 1H), 6.55 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.85-6.93 (m, 5H), 7.05 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 9.41 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 152.3, 148.8, 147.6, 136.7, 135.6, 134.9, 130.8, 130.4, 128.1, 127.1, 125.9, 121.6, 120.5, 120.4, 119.6, 111.7, 111.1, 110.4, 102.2, 98.4, 55.8, 55.6,

51.4, 44.8, 36.7, 12.6; HRMS (ESI): Exact mass calcd for $C_{29}H_{30}N_2O_4Na$ $[M+Na]^+$: 493.2098, Found: 493.2108.



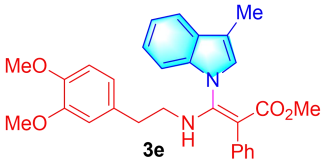
3c

The reaction was run at 60 °C for 6 h, affording product **3c** as a yellow solid (48% yield, 25.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.84 (t, *J* = 6.8 Hz, 2H), 3.26-3.38 (m, 2H), 3.61 (s, 3H), 3.84 (s, 3H), 3.87 (s, 3H), 6.18 (dd, *J* = 8.0, 1.2 Hz, 2H), 6.42 (d, *J* = 0.4 Hz, 1H), 6.68-6.72 (m, 4H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.86 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.01-7.04 (m, 2H), 7.13-7.17 (m, 1H), 7.20-7.25 (m, 3H), 7.27-7.29 (m, 1H), 7.34 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 9.57 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 152.8, 148.9, 147.7, 139.7, 137.9, 134.4, 131.7, 131.0, 130.3, 128.2, 128.1, 127.6, 127.2, 126.7, 125.6, 123.0, 121.1, 120.8, 120.6, 112.2, 111.3, 111.1, 103.7, 97.5, 55.9, 55.8, 51.2, 45.4, 36.0; HRMS (ESI): Exact mass calcd for $C_{34}H_{32}N_2O_4Na$ $[M+Na]^+$: 555.2254, Found: 555.2246.



3d

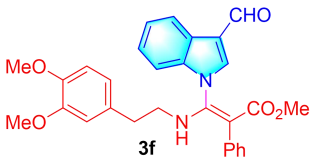
The reaction was run at 60 °C for 6 h, affording product **3d** as a yellow solid (37% yield, 21.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (t, *J* = 6.8 Hz, 2H), 3.38-3.43 (m, 2H), 3.56 (s, 3H), 3.83 (s, 3H), 3.88 (s, 3H), 6.12 (d, *J* = 7.6 Hz, 2H), 6.54 (s, 1H), 6.65 (t, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 7.16-7.19 (m, 2H), 7.25-7.28 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.48-7.50 (m, 2H), 7.53-7.55 (m, 2H), 7.67-7.71 (m, 2H), 7.82-7.85 (m, 1H), 9.62 (t, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 152.9, 148.9, 147.7, 139.7, 138.1, 134.3, 133.0, 132.6, 130.9, 130.3, 129.2, 128.3, 127.6, 126.7, 126.3, 126.20, 126.17, 125.7, 125.2, 123.1, 121.2, 120.7, 120.6, 112.1, 111.2, 111.1, 104.2, 97.5, 55.8, 55.7, 51.2, 45.4, 36.0; HRMS (ESI): Exact mass calcd for $C_{38}H_{34}N_2O_4Na$ $[M+Na]^+$: 605.2411, Found: 605.2396.



3e

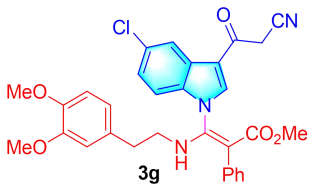
The reaction was run at 60 °C for 3 h, affording product **3e** as a yellow solid (88% yield, 41.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (d, *J* = 1.2 Hz, 3H), 2.69 (td, *J* = 6.8, 2.4 Hz, 2H), 2.95-3.03 (m, 1H), 3.11-3.19 (m, 1H), 3.71 (s, 3H), 3.78 (s, 3H), 3.86 (s, 3H), 6.05 (d, *J* = 1.2 Hz, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 6.59 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.79-6.81 (m, 2H), 6.91-6.94 (m, 3H), 7.07-7.11 (m, 1H), 7.15-7.19 (m, 1H), 7.28 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.37-7.39 (m, 1H), 9.19 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.4, 148.8, 147.6, 136.0, 135.6, 131.0, 130.5, 128.9, 127.2, 125.6,

125.1, 122.7, 120.8, 120.2, 118.7, 113.0, 111.9, 111.2, 111.0, 96.6, 55.9, 55.6, 51.3, 45.6, 37.1, 9.2; HRMS (ESI): Exact mass calcd for $C_{29}H_{30}N_2NaO_4$ $[M+Na]^+$: 493.2098, Found: 493.2108.



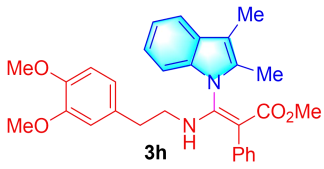
3f

The reaction was run at 60 °C for 4 h, affording product **3f** as a yellow solid (69% yield, 33.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66-2.77 (m, 2H), 2.85-2.91 (m, 1H), 3.22-3.27 (m, 1H), 3.74 (s, 3H), 3.79 (s, 3H), 3.88 (s, 3H), 6.45 (s, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.57 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.74-6.80 (m, 3H), 6.91-6.95 (m, 3H), 7.28-7.40 (m, 3H), 8.14 (d, *J* = 7.6 Hz, 1H), 9.21-9.23 (m, 1H), 9.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.8, 170.5, 152.4, 148.9, 147.8, 138.7, 137.1, 134.3, 130.7, 130.2, 127.8, 126.5, 125.1, 124.2, 123.6, 122.2, 121.1, 119.5, 112.1, 111.3, 111.2, 97.9, 56.0, 55.6, 51.6, 45.7, 37.3; HRMS (ESI): Exact mass calcd for $C_{29}H_{28}N_2O_5Na$ $[M+Na]^+$: 507.1890, Found: 507.1834.



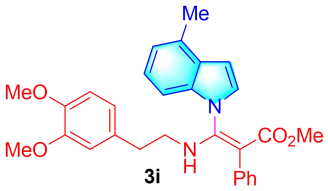
3g

The reaction was run at 60 °C for 6 h, affording product **3g** as a yellow solid (69% yield, 38.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67-2.80 (m, 2H), 2.84-2.94 (m, 1H), 3.17 (d, *J* = 18.8 Hz, 1H), 3.35-3.42 (m, 1H), 3.55 (d, *J* = 18.8 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 3.92 (s, 3H), 6.04 (s, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 6.67-6.70 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.94-7.02 (m, 3H), 7.32-7.33 (m, 2H), 8.16-8.17 (m, 1H), 9.18 (dd, *J* = 9.2, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 170.3, 151.9, 149.1, 147.9, 136.0, 135.0, 134.3, 131.2, 130.14, 130.11, 128.4, 127.9, 126.8, 126.1, 125.8, 122.2, 121.9, 114.8, 113.9, 112.6, 112.4, 111.4, 98.0, 56.2, 55.7, 51.8, 45.9, 37.9, 28.8; HRMS (ESI): Exact mass calcd for $C_{31}H_{28}ClN_3O_5Na$ $[M+Na]^+$: 580.1615, Found: 580.1613.



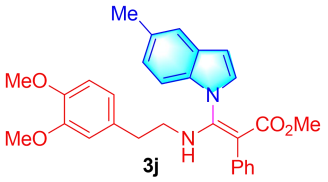
3h

The reaction was run at 60 °C for 4 h, affording product **3h** as a yellow solid (78% yield, 37.8 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.03 (s, 3H), 2.59-2.67 (m, 2H), 2.76-2.84 (m, 1H), 2.86-2.95 (m, 1H), 3.70 (s, 3H), 3.76 (s, 3H), 3.84 (s, 3H), 6.36 (d, *J* = 2.0 Hz, 1H), 6.54 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.84-6.86 (m, 2H), 6.89-6.92 (m, 3H), 7.05 (td, *J* = 8.0, 1.6 Hz, 1H), 7.11 (td, *J* = 7.2, 1.6 Hz, 1H), 7.16-7.19 (m, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 9.41 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 152.8, 148.8, 147.5, 135.8, 135.1, 131.3, 130.9, 130.5, 128.9, 127.0, 125.7, 121.6, 120.5, 119.8, 117.8, 111.7, 111.1, 110.2, 109.1, 98.3, 55.8, 55.6, 51.3, 44.8, 36.8, 10.2, 8.6; HRMS (ESI): Exact mass calcd for $C_{30}H_{32}N_2NaO_4$ $[M+Na]^+$: 507.2254, Found: 507.2244.



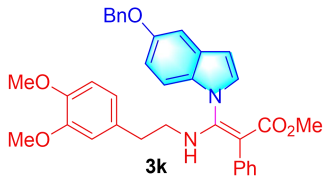
3i

The reaction was run at 60 °C for 5 h, affording product **3i** as a yellow solid (83% yield, 39.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.69 (t, *J* = 6.8 Hz, 2H), 2.90-2.95 (m, 1H), 3.11-3.16 (m, 1H), 3.71 (s, 3H), 3.79 (s, 3H), 3.86 (s, 3H), 6.20 (d, *J* = 3.2 Hz, 1H), 6.29 (d, *J* = 3.6 Hz, 1H), 6.47 (s, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.82-6.83 (m, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.95-6.96 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 9.23 (t, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.2, 148.8, 147.6, 135.6, 135.5, 130.9, 130.5, 130.2, 128.1, 127.3, 127.1, 125.7, 122.9, 121.1, 120.8, 112.0, 111.1, 108.8, 102.2, 96.9, 55.9, 55.6, 51.4, 45.5, 37.1, 18.6; HRMS (ESI): Exact mass calcd for $C_{29}H_{30}N_2O_4Na$ $[M+Na]^+$: 493.2098, Found: 493.2111.



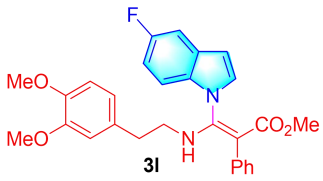
3j

The reaction was run at 60 °C for 4 h, affording product **3j** as a yellow solid (85% yield, 40.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.69 (t, *J* = 6.4 Hz, 2H), 2.92-2.98 (m, 1H), 3.13-3.18 (m, 1H), 3.71 (s, 3H), 3.79 (s, 3H), 3.86 (s, 3H), 6.10 (d, *J* = 3.2 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 6.47 (s, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.80-6.81 (m, 2H), 6.94-6.95 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 9.21 (t, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.3, 148.7, 147.6, 135.6, 134.2, 130.9, 130.5, 130.1, 128.6, 127.9, 127.4, 125.7, 124.4, 120.8, 120.6, 112.0, 111.0, 110.9, 103.3, 96.7, 55.9, 55.6, 51.3, 45.6, 37.1, 21.3; HRMS (ESI): Exact mass calcd for $C_{29}H_{30}N_2O_4Na$ $[M+Na]^+$: 493.2098, Found: 493.2106.



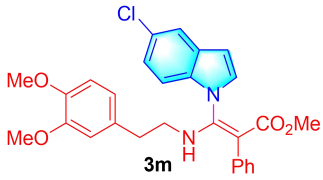
3k

The reaction was run at 60 °C for 3 h, affording product **3k** as a yellow solid (94% yield, 52.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (t, *J* = 6.8 Hz, 2H), 2.92-3.01 (m, 1H), 3.13-3.18 (m, 1H), 3.69 (s, 3H), 3.79 (s, 3H), 3.85 (s, 3H), 5.03 (s, 2H), 6.09 (d, *J* = 3.2 Hz, 1H), 6.24 (d, *J* = 3.6 Hz, 1H), 6.50 (s, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.80-6.81 (m, 2H), 6.91-6.98 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 9.17 (t, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.2, 154.0, 148.7, 147.6, 137.4, 135.5, 131.0, 130.9, 130.5, 128.9, 128.5, 128.4, 127.8, 127.5, 127.3, 125.7, 120.8, 113.3, 112.01, 111.96, 111.1, 103.9, 103.5, 96.8, 70.5, 55.9, 55.6, 51.3, 45.6, 37.1; HRMS (ESI): Exact mass calcd for $C_{35}H_{34}N_2O_5Na$ $[M+Na]^+$: 585.2360, Found: 585.2364.



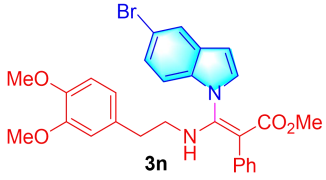
3l

The reaction was run at 60 °C for 6 h, affording product **3l** as a yellow solid (72% yield, 34.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (t, *J* = 6.8 Hz, 2H), 2.92-3.00 (m, 1H), 3.09-3.17 (m, 1H), 3.71 (s, 3H), 3.81 (s, 3H), 3.87 (s, 3H), 6.15 (d, *J* = 3.2 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 6.59 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.75-6.81 (m, 3H), 6.90-6.96 (m, 4H), 7.09 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.24 (dd, *J* = 9.2, 4.4 Hz, 1H), 9.19 (t, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 158.3 (d, *J* = 235 Hz), 153.7, 148.8, 147.6, 135.3, 132.2, 130.8, 130.4, 129.4, 128.7 (d, *J* = 10.1 Hz), 127.4, 125.9, 120.8, 112.0, 111.8 (d, *J* = 9.5 Hz), 111.1, 111.0 (d, *J* = 25.9 Hz), 105.8 (d, *J* = 23.5 Hz), 103.7 (d, *J* = 4.4 Hz), 97.2, 55.9, 55.6, 51.4, 45.5, 37.1; HRMS (ESI): Exact mass calcd for $C_{28}H_{27}FN_2O_4Na$ $[M+Na]^+$: 497.1847, Found: 497.1859.



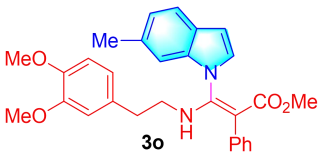
3m

The reaction was run at 60 °C for 5 h, affording product **3m** as a yellow solid (74% yield, 36.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67-2.71 (m, 2H), 2.89-2.98 (m, 1H), 3.07-3.15 (m, 1H), 3.71 (s, 3H), 3.80 (s, 3H), 3.86 (s, 3H), 6.13 (d, *J* = 3.2 Hz, 1H), 6.30 (d, *J* = 3.6 Hz, 1H), 6.48 (d, *J* = 1.2 Hz, 1H), 6.58 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.75-6.79 (m, 3H), 6.95-6.96 (m, 3H), 7.14 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.24 (d, *J* = 9.2 Hz, 1H), 7.42 (d, *J* = 1.6 Hz, 1H), 9.17 (t, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ170.6, 153.6, 148.9, 147.8, 135.3, 134.3, 130.9, 130.5, 129.4, 129.2, 127.6, 126.5, 126.0, 123.2, 121.0, 120.4, 112.3, 112.1, 111.2, 103.3, 97.3, 56.0, 55.7, 51.6, 45.6, 37.3; HRMS (ESI): Exact mass calcd for $C_{28}H_{28}ClN_2O_4$ $[M+H]^+$: 491.1732, Found: 491.1723.



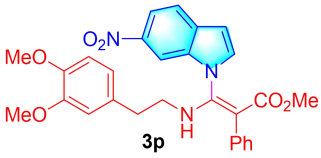
3n

The reaction was run at 60 °C for 5 h, affording product **3n** as a yellow solid (82% yield, 43.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67-2.71 (m, 2H), 2.88-2.97 (m, 1H), 3.07-3.14 (m, 1H), 3.71 (s, 3H), 3.80 (s, 3H), 3.86 (s, 3H), 6.13 (d, *J* = 3.6 Hz, 1H), 6.28 (d, *J* = 3.2 Hz, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 6.58 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.75-6.79 (m, 3H), 6.94-6.96 (m, 3H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.26-7.29 (m, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 9.17 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ170.6, 153.4, 148.8, 147.7, 135.1, 134.4, 130.7, 130.4, 129.9, 129.0, 127.4, 126.0, 125.7, 123.3, 120.8, 114.0, 112.6, 111.9, 111.1, 103.2, 97.4, 55.9, 55.6, 51.5, 45.5, 37.1; HRMS (ESI): Exact mass calcd for $C_{28}H_{27}BrN_2O_4Na$ $[M+Na]^+$: 557.1046, Found: 557.1054.



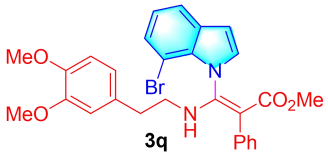
3o

The reaction was run at 60 °C for 4 h, affording product **3o** as a yellow solid (79% yield, 37.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.94-3.02 (m, 1H), 3.14-3.21 (m, 1H), 3.71 (s, 3H), 3.79 (s, 3H), 3.85 (s, 3H), 6.14 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.24 (d, *J* = 3.2 Hz, 1H), 6.49 (d, *J* = 2.0 Hz, 1H), 6.59 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.80-6.83 (m, 2H), 6.92-6.95 (m, 4H), 7.16 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 9.24 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ170.8, 154.3, 148.8, 147.6, 136.2, 135.6, 132.7, 131.0, 130.5, 127.3, 127.2, 126.1, 125.7, 122.5, 120.8, 120.3, 112.1, 111.23, 111.17, 103.6, 96.9, 55.9, 55.6, 51.3, 45.6, 37.2, 21.8; HRMS (ESI): Exact mass calcd for $C_{29}H_{30}N_2O_4Na$ $[M+Na]^+$: 493.2098, Found: 493.2109.



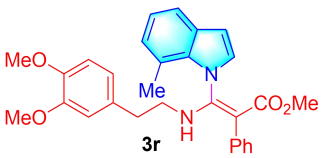
3p

The reaction was run at 60 °C for 3 h, affording product **3p** as a yellow solid (83% yield, 41.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69-2.79 (m, 2H), 2.90-2.99 (m, 1H), 3.17-3.25 (m, 1H), 3.73 (s, 3H), 3.80 (s, 3H), 3.87 (s, 3H), 6.32 (d, *J* = 3.2 Hz, 1H), 6.53-6.56 (m, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.76-6.78 (m, 3H), 6.91-6.92 (m, 3H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.98 (dd, *J* = 8.8, 1.2 Hz, 1H), 8.25 (s, 1H), 9.18 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 152.2, 148.8, 147.7, 143.8, 134.8, 134.3, 133.3, 132.8, 130.5, 130.3, 127.5, 126.2, 120.8, 120.7, 116.3, 112.0, 111.1, 108.0, 104.3, 98.1, 55.9, 55.6, 51.6, 45.6, 37.2; HRMS (ESI): Exact mass calcd for $C_{28}H_{27}N_3O_6Na$ $[M+Na]^+$: 524.1792, Found: 524.1786.



3q

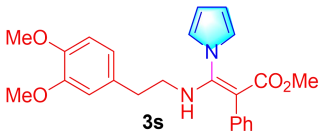
The reaction was run at 60 °C for 5 h, affording product **3q** as a yellow solid (70% yield, 37.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68-2.77 (m, 3H), 3.14-3.19 (m, 1H), 3.68 (s, 3H), 3.82 (s, 3H), 3.85 (s, 3H), 6.28 (d, *J* = 3.6 Hz, 1H), 6.49 (d, *J* = 3.2 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 6.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.91-6.96 (m, 4H), 7.00-7.03 (m, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 9.35 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 153.5, 148.8, 147.6, 135.1, 133.2, 130.9, 130.9, 130.5, 129.6, 127.3, 127.2, 125.9, 121.7, 120.7, 120.2, 111.9, 111.1, 104.3, 104.0, 98.1, 55.9, 55.7, 51.3, 44.9, 36.4; HRMS (ESI): Exact mass calcd for $C_{28}H_{27}BrN_2O_4Na$ $[M+Na]^+$: 557.1046, Found: 557.1050.



3r

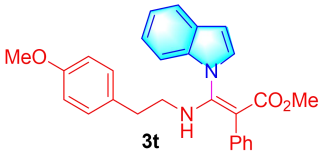
The reaction was run at 60 °C for 4 h, affording product **3r** as a yellow solid (74% yield, 34.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 2.62-2.72 (m, 3H), 2.95-3.00 (m, 1H), 3.70 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 6.25 (d, *J* = 3.2 Hz, 1H), 6.36 (d, *J* = 3.2 Hz, 1H), 6.45 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.92-7.02 (m, 7H),

7.31 (d, J = 7.6 Hz, 1H), 9.42 (t, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 155.4, 148.8, 147.6, 135.3, 135.0, 130.83, 130.81, 128.9, 128.4, 127.4, 125.8, 125.2, 121.5, 120.9, 120.7, 118.8, 111.9, 111.1, 103.8, 97.7, 55.9, 55.6, 51.3, 44.7, 36.7, 17.8; HRMS (ESI): Exact mass calcd for $C_{29}H_{30}N_2O_4Na$ [M+Na]$^+$: 493.2098, Found: 493.2111.



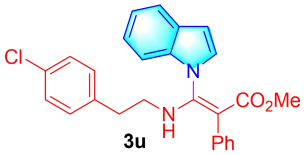
3s

The reaction was run at 60 °C for 3 h, affording product **3s** as a yellow solid (98% yield, 39.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (t, J = 6.8 Hz, 2H), 3.17 (dd, J = 13.2, 6.8 Hz, 2H), 3.68 (s, 3H), 3.87 (s, 6H), 5.95 (t, J = 2.4 Hz, 2H), 6.28 (t, J = 2.0 Hz, 2H), 6.63-6.68 (m, 2H), 6.80 (d, J = 8.4 Hz, 1H), 6.93-6.95 (m, 2H), 7.04-7.12 (m, 3H), 9.05 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 155.6, 148.8, 147.6, 135.7, 131.0, 130.7, 127.3, 125.7, 121.4, 120.8, 112.11, 111.2, 109.4, 96.1, 55.9, 55.7, 51.2, 45.5, 37.2; HRMS (ESI): Exact mass calcd for $C_{24}H_{26}N_2O_4Na$ [M+Na]$^+$: 429.1785, Found: 429.1790.



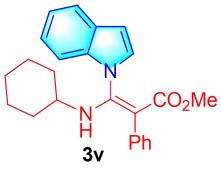
3t

The reaction was run at 60 °C for 3 h, affording product **3t** as a yellow solid (96% yield, 40.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (t, J = 7.2 Hz, 2H), 2.91-3.00 (m, 1H), 3.11-3.17 (m, 1H), 3.73 (s, 3H), 3.79 (s, 3H), 6.22 (d, J = 3.2 Hz, 1H), 6.37 (d, J = 3.6 Hz, 1H), 6.79-6.85 (m, 4H), 6.94-6.97 (m, 5H), 7.11 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 9.20 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 158.3, 154.0, 135.8, 135.5, 130.5, 130.3, 129.8, 128.3, 127.7, 127.3, 125.7, 122.8, 120.8, 120.7, 113.9, 111.2, 103.8, 97.1, 55.2, 51.3, 45.4, 36.5; HRMS (ESI): Exact mass calcd for $C_{27}H_{26}N_2O_3Na$ [M+Na]$^+$: 449.1836, Found: 449.1826.

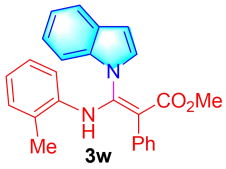


3u

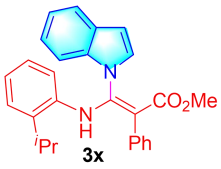
The reaction was run at 60 °C for 3 h, affording product **3u** as a yellow solid (97% yield, 41.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73 (t, J = 6.8 Hz, 2H), 2.93-3.01 (m, 1H), 3.11-3.17 (m, 1H), 3.72 (s, 3H), 6.23 (d, J = 3.2 Hz, 1H), 6.36 (d, J = 3.6 Hz, 1H), 6.82-6.83 (m, 2H), 6.94-6.96 (m, 5H), 7.11 (t, J = 7.6 Hz, 1H), 7.19-7.23 (m, 3H), 7.35 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 9.18 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 153.9, 136.8, 135.8, 135.4, 132.4, 130.5, 130.3, 128.6, 128.3, 127.6, 127.4, 125.8, 122.9, 120.8, 111.1, 104.0, 97.4, 51.4, 45.0, 36.8; HRMS (ESI): Exact mass calcd for $C_{26}H_{23}ClN_2O_2Na$ [M+Na]$^+$: 453.1340, Found: 453.1342.



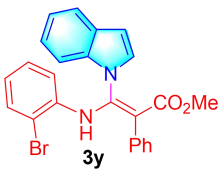
The reaction was run at 60 °C for 5 h, affording product **3v** as a yellow solid (67% yield, 25.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05-1.12 (m, 2H), 1.29-1.36 (m, 2H), 1.37-1.46 (m, 2H), 1.61-1.70 (m, 3H), 1.78-1.83 (m, 1H), 2.81-2.86 (m, 1H), 3.72 (s, 3H), 6.27 (dd, J = 3.6, 0.8 Hz, 1H), 6.67 (d, J = 3.2 Hz, 1H), 6.84-6.88 (m, 2H), 6.92-6.95 (m, 3H), 7.08-7.12 (m, 1H), 7.18-7.22 (m, 1H), 7.44-7.48 (m, 2H), 9.14 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 153.5, 136.1, 135.6, 130.5, 128.3, 127.8, 127.2, 125.7, 122.8, 120.73, 120.67, 111.1, 104.0, 97.3, 52.2, 51.3, 35.0, 33.3, 25.3, 24.3, 24.1; HRMS (ESI): Exact mass calcd for $C_{24}H_{26}N_2O_2Na$ $[M+Na]^+$: 397.1886, Found: 397.1888.



The reaction was run at 60 °C for 3 h, affording product **3w** as a yellow solid (99% yield, 37.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 3H), 3.78 (s, 3H), 5.99 (d, J = 8.4 Hz, 1H), 6.29 (d, J = 3.2 Hz, 1H), 6.61 (t, J = 8.0 Hz, 1H), 6.71 (d, J = 3.6 Hz, 1H), 6.77 (t, J = 7.6 Hz, 1H), 6.97-7.04 (m, 7H), 7.10 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 10.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 149.4, 137.4, 135.1, 135.0, 130.7, 130.5, 128.9, 128.5, 127.52, 127.48, 126.4, 126.1, 123.8, 122.6, 120.8, 120.5, 119.6, 111.6, 105.2, 99.4, 51.8, 18.4; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}N_2O_2Na$ $[M+Na]^+$: 405.1574, Found: 405.1570.

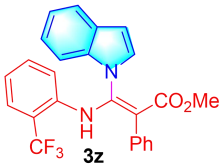


The reaction was run at 60 °C for 3 h, affording product **3x** as a yellow solid (99% yield, 40.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (d, J = 6.4 Hz, 6H), 3.51-3.58 (sep, J = 6.8 Hz, 1H), 3.79 (s, 3H), 6.17 (d, J = 8.0 Hz, 1H), 6.26 (d, J = 3.6 Hz, 1H), 6.61 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 3.2 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 6.93-7.03 (m, 7H), 7.19 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 10.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 150.1, 140.2, 135.8, 135.2, 135.1, 130.7, 128.4, 127.7, 127.4, 126.0, 125.9, 125.6, 124.8, 122.4, 121.2, 120.7, 120.5, 111.7, 105.1, 99.4, 51.8, 28.1; HRMS (ESI): Exact mass calcd for $C_{27}H_{26}N_2O_2Na$ $[M+Na]^+$: 433.1886, Found: 433.1880.



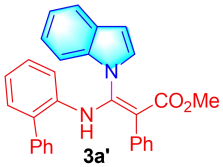
The reaction was run at 60 °C for 3 h, affording product **3y** as a yellow solid (94% yield, 41.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.00 (s, 1H), 6.30 (s, 1H), 6.66-6.69 (m, 3H), 7.00-7.05 (m, 6H), 7.31-7.37 (m, 3H), 7.48 (s, 1H), 10.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 147.7, 137.3, 135.1, 134.6, 132.7, 130.7, 128.5, 127.8, 127.6, 127.5, 126.3, 124.5, 123.0,

121.0, 120.6, 120.2, 115.6, 111.7, 105.5, 101.0, 52.0; HRMS (ESI): Exact mass calcd for $C_{24}H_{19}BrN_2O_2Na$ $[M+Na]^+$: 469.0522, Found: 469.0526.



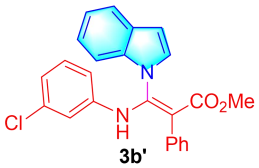
3z

The reaction was run at 60 °C for 6 h, affording product **3z** as a yellow solid (78% yield, 34 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.17-6.19 (m, 1H), 6.31 (d, *J* = 3.2 Hz, 1H), 6.74 (d, *J* = 3.2 Hz, 1H), 6.90-6.92 (m, 2H), 6.95-7.04 (m, 7H), 7.33-7.36 (m, 2H), 7.53-7.55 (m, 1H), 11.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 147.8, 137.2, 135.1, 134.5, 132.4, 130.6, 128.5, 127.6, 127.5, 126.4, 123.2, 122.9, 121.4, 121.2, 121.0, 120.9 (*J* = 29.5 Hz), 120.6, 111.6, 105.8, 102.1, 52.1; HRMS (ESI): Exact mass calcd for $C_{25}H_{19}F_3N_2O_2Na$ $[M+Na]^+$: 459.1291, Found: 459.1276.



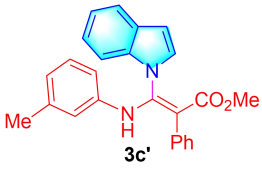
3a'

The reaction was run at 60 °C for 5 h, affording product **3a'** as a yellow solid (95% yield, 42.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 6.21 (d, *J* = 3.2 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 6.48 (d, *J* = 3.2 Hz, 1H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.89-6.93 (m, 3H), 6.97-7.03 (m, 5H), 7.13-7.16 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 6.8 Hz, 1H), 7.54- 7.61(m, 4H), 10.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 148.8, 139.0, 136.1, 135.14, 135.08, 134.8, 130.61, 130.58, 129.4, 128.7, 128.5, 127.8, 127.6, 127.4, 126.0, 124.1, 122.4, 121.0, 120.8, 120.4, 112.0, 105.0, 100.1, 51.7; HRMS (ESI): Exact mass calcd for $C_{30}H_{24}N_2O_2Na$ $[M+Na]^+$: 467.1730, Found: 467.1720.



3b'

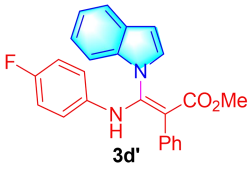
The reaction was run at 60 °C for 3 h, affording product **3b'** as a yellow solid (97% yield, 39.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.26 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.34 (d, *J* = 3.2 Hz, 1H), 6.53 (t, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 3.2 Hz, 1H), 6.78-6.81 (m, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.98-7.01 (m, 3H), 7.03-7.08 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.39-7.41 (m, 1H), 10.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 148.3, 140.3, 135.0, 134.5, 130.6, 129.9, 128.6, 127.6, 127.2, 126.4, 123.5, 123.0, 121.1, 120.7, 120.1, 117.7, 111.7, 105.7, 100.8, 51.9; HRMS (ESI): Exact mass calcd for $C_{24}H_{19}ClN_2O_2Na$ $[M+Na]^+$: 425.1027, Found: 425.1023.



3c'

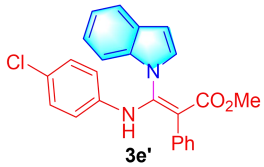
The reaction was run at 60 °C for 3 h, affording product **3c'** as a yellow solid (98% yield, 37.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3H), 3.79 (s, 3H), 6.22 (d, *J* = 8.0 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.40 (s, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 3.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.98-7.07 (m, 7H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 10.88 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 149.0, 138.8, 138.7, 135.1, 134.9, 130.7, 128.7, 128.5, 127.4, 126.1, 124.4, 122.7, 120.9, 120.8, 120.5, 116.8, 111.9, 105.2, 99.5, 51.7, 21.2; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}N_2O_2Na$ $[M+Na]^+$: 405.1573, Found: 405.1573.



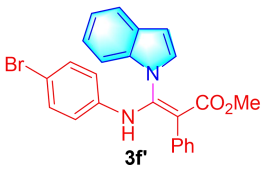
3d'

The reaction was run at 60 °C for 3 h, affording product **3d'** as a yellow solid (97% yield, 37.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.30 (d, *J* = 2.8 Hz, 1H), 6.50-6.53 (m, 2H), 6.66-6.71 (m, 3H), 6.98-7.08 (m, 7H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 10.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 159.2 (d, *J* = 242 Hz), 149.2, 135.01, 134.98, 134.96, 134.7, 130.6, 128.4, 127.5, 127.4, 126.2, 122.8, 121.9 (d, *J* = 8.1 Hz), 121.0, 120.6, 115.7 (d, *J* = 22.6 Hz), 111.8, 105.4, 99.6, 51.8; HRMS (ESI): Exact mass calcd for $C_{24}H_{19}FN_2O_2Na$ $[M+Na]^+$: 409.1323, Found: 409.1319.



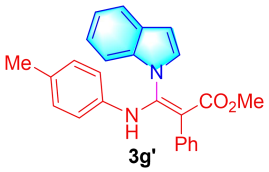
3e'

The reaction was run at 60 °C for 3 h, affording product **3e'** as a yellow solid (98% yield, 39.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.32 (d, *J* = 2.8 Hz, 1H), 6.41 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 3.2 Hz, 1H), 6.92-7.07 (m, 9H), 7.30 (d, *J* = 8.3 hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 10.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 148.5, 137.6, 134.9, 134.6, 130.6, 129.0, 128.8, 128.5, 127.5, 127.2, 126.3, 123.0, 121.1, 120.7, 111.7, 105.6, 100.3, 51.9; HRMS (ESI): Exact mass calcd for $C_{24}H_{19}ClN_2O_2Na$ $[M+Na]^+$: 425.1027, Found: 425.1025.



3f'

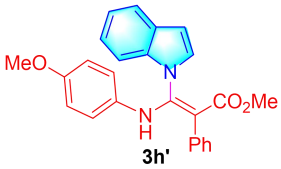
The reaction was run at 60 °C for 3 h, affording product **3f'** as a yellow solid (96% yield, 42.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.32 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.34-6.36 (m, 2H), 6.69 (d, *J* = 3.6 Hz, 1H), 6.97-7.00 (m, 2H), 7.01-7.06 (m, 5H), 7.08-7.10 (m, 2H), 7.30 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38-7.41 (m, 1H), 10.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 148.4, 138.2, 134.9, 134.5, 132.0, 130.6, 128.5, 127.6, 127.2, 126.3, 123.0, 121.4, 121.1, 120.7, 116.4, 111.7, 105.6, 100.5, 51.9; HRMS (ESI): Exact mass calcd for $C_{24}H_{19}BrN_2O_2Na$ $[M+Na]^+$: 469.0522, Found: 469.0519.



3g'

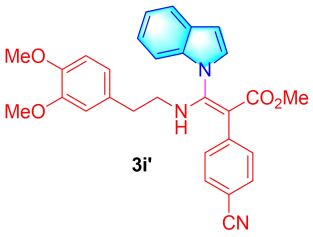
The reaction was run at 60 °C for 3 h, affording product **3g'** as a yellow solid (98% yield, 37.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 3.78 (s, 3H), 6.30 (dd, *J* = 3.2, 0.3 Hz, 1H), 6.43 (d, *J* = 8.3 Hz, 2H), 6.72 (d, *J* = 3.2 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.97-7.06 (m, 7H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 10.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 149.3, 136.3, 135.1, 135.0, 133.3, 130.7, 129.5, 128.4, 127.5, 127.4, 126.0, 122.7,

120.8, 120.5, 120.2, 111.9, 105.1, 99.1, 51.7, 20.6; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}N_2O_2Na$ $[M+Na]^+$: 405.1573, Found: 405.1574.



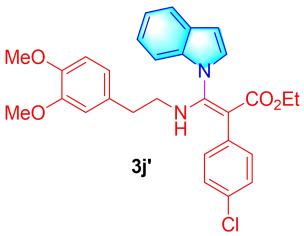
3h'

The reaction was run at 60 °C for 3 h, affording product **3h'** as a yellow solid (94% yield, 37.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.78 (s, 3H), 6.29 (d, *J* = 3.2 Hz, 1H), 6.54 (s, 4H), 6.73 (d, *J* = 3.2 Hz, 1H), 6.98-7.08 (m, 7H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 10.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 156.1, 149.7, 135.03, 134.98, 131.9, 130.7, 128.3, 127.5, 127.4, 126.0, 122.6, 122.0, 120.7, 120.4, 114.1, 111.9, 105.0, 98.7, 55.1, 51.6; HRMS (ESI): Exact mass calcd for $C_{25}H_{22}N_2O_3Na$ $[M+Na]^+$: 421.1523, Found: 421.1528.



3i'

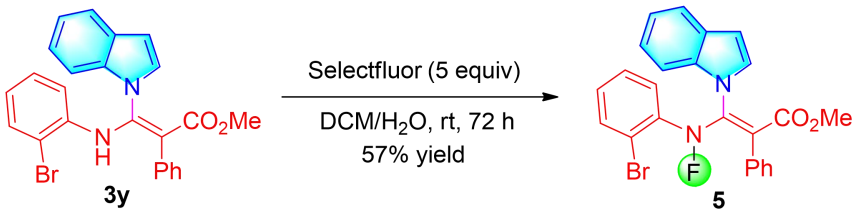
The reaction was run at 60 °C for 6 h, affording product **3i'** as a yellow solid (83% yield, 39.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.71 (t, *J* = 7.2 Hz, 2H), 3.00-3.08 (m, 1H), 3.19-3.25 (m, 1H), 3.72 (s, 3H), 3.79 (s, 3H), 3.86 (s, 3H), 6.24 (s, 2H), 6.49 (s, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.17-7.22 (m, 3H), 7.25-7.26 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 9.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 154.5, 148.8, 147.7, 141.0, 135.6, 131.1, 130.9, 130.6, 128.3, 127.2, 123.3, 121.3, 121.1, 120.8, 119.1, 112.0, 111.1, 110.9, 108.9, 104.7, 95.4, 55.9, 55.6, 51.4, 45.7, 36.9; HRMS (ESI): Exact mass calcd for $C_{29}H_{27}N_3O_4Na$ $[M+Na]^+$: 504.1894, Found: 504.1903.



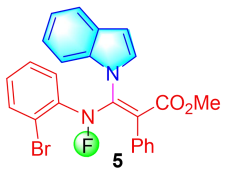
3j'

The reaction was run at 60 °C for 5 h, affording product **3j'** as a yellow solid (89% yield, 44.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, *J* = 7.6 Hz, 3H), 2.69 (t, *J* = 6.8 Hz, 2H), 2.91-3.00 (m, 1H), 3.10-3.18 (m, 1H), 3.78 (s, 3H), 3.85 (s, 3H), 4.12-4.28 (m, 2H), 6.24 (s, 1H), 6.29 (s, 1H), 6.47 (s, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 6.71-6.76 (m, 3H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 9.26 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 154.0, 148.8, 147.6, 135.7, 134.2, 131.7, 131.3, 130.8, 128.3, 127.6, 127.4, 122.9, 120.9, 120.8, 112.0, 111.09, 111.06, 104.1, 96.1, 60.0, 55.9, 55.6, 45.5, 37.1, 14.4; HRMS (ESI): Exact mass calcd for $C_{29}H_{29}ClN_2O_4Na$ $[M+Na]^+$: 527.1708, Found: 527.1711.

3) Synthetic Transformation of Product 3y.



To a 5.0 mL vial was successively added **3y** (0.1 mmol. 1.0 equiv), DCM/H_2O (v/v = 1:1, 2 mL), and selectfluor (0.50 mmol, 5 equiv). The vial was capped and the reaction mixture was allowed to stir at room temperature for 72 h. Upon completion, the mixture was extracted with DCM (5 mL * 3), and the combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent in vacuo, the residue was purified by silica gel chromatography eluting with petroleum ether/ethyl acetate (5:1 to 2:1) to afford compound **5** (26.4 mg, pale-yellow solid).

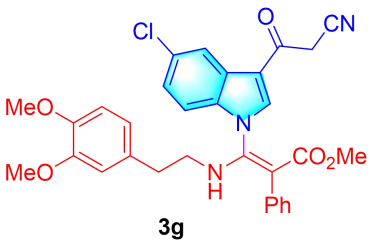


Chemical Formula: $C_{24}H_{18}BrFN_2O_2$
Exact Mass: 464.0536

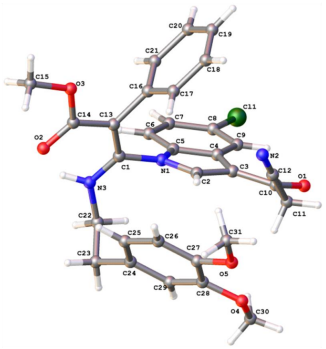
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.18 (d, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 3.2 Hz, 1H), 6.77-6.83 (m, 2H), 6.98-7.04 (m, 4H), 7.39-7.42 (m, 4H), 7.54-7.57 (m, 1H), 7.71-7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1 (d, *J* = 26.8 Hz), 144.4, 134.7, 134.0, 133.8, 133.1, 129.4, 128.3, 128.3, 127.6, 126.9, 125.9 (d, *J* = 9.0 Hz), 125.5 (d, *J* = 4.7 Hz), 123.1, 121.4, 120.6, 119.6, 118.2, 112.3, 106.2, 53.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.9; HRMS (ESI): Exact mass calcd for $C_{24}H_{18}BrFN_2O_2Na$ $[M+Na]^+$: 487.0428, Found: 487.0440.

4) X-Ray crystallographic data for compound 3g.

Data intensity of **3g** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 149.99(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number 2249124 (**3g**).



3g



X-Ray structure of product **3g**

Crystal data.

Formula weight	558.01
Empirical formula	$C_{31}H_{28}ClN_3O_5$
Temperature/K	149.99(10)
Space group	P-1
Crystal system	triclinic
a/Å	8.9246(6)
b/Å	9.5581(6)
c/Å	19.710(3)
α/°	79.501(7)
β/°	79.413(8)
γ/°	85.021(5)
Volume/Å^3	1622.6(3)
Z	2
ρ_{calc}g/cm^3	1.142
μ/mm^{-1}	1.366
F(000)	584.0
Reflections collected	10860
Independent reflections	6395 [R_{int} = 0.0518, R_{sigma} = 0.0679]
Final R indexes [I>=2σ (I)]	R_1 = 0.1272, wR_2 = 0.3391
Final R indexes [all data]	R_1 = 0.1408, wR_2 = 0.3533

5) DFT Calculation Results.

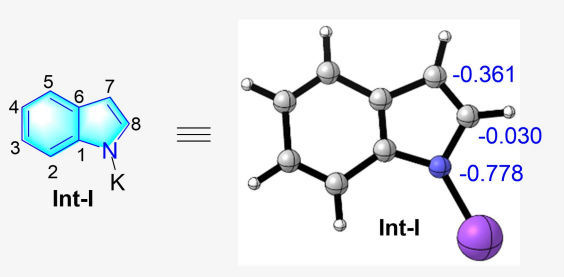


Figure S1. The calculated NBO net charges of *N*1, C2 and C3 atoms of indole anion intermediate **Int-I**.

Redundant internal coordinates found in file.

C, 0, 2.4376263591, -0.4693175229, 0.

C, 0, 1.0094560996, -0.5418907503, 0.

C, 0, 0.2460740235, 0.6394996451, 0.

C, 0, 0.887225519, 1.8665534559, 0.

C, 0, 2.294396899, 1.9379297536, 0.

C, 0, 3.0649405543, 0.7878886019, 0.

C, 0, 2.8808436419, -1.8237706974, 0.

C, 0, 1.734609945, -2.5911823119, 0.

H, 0, -0.8518256986, 0.6261934537, 0.

H, 0, 0.3028088925, 2.7820959674, 0.

H, 0, 2.7753395583, 2.911584529, 0.

H, 0, 4.1501209338, 0.8572353118, 0.

H, 0, 3.9016392874, -2.1808275035, 0.

H, 0, 1.6736263196, -3.6746906662, 0.

N, 0, 0.5858934973, -1.8499766815, 0.

K, 0, -1.5405555717, -1.6918457947, 0

Mulliken charges:

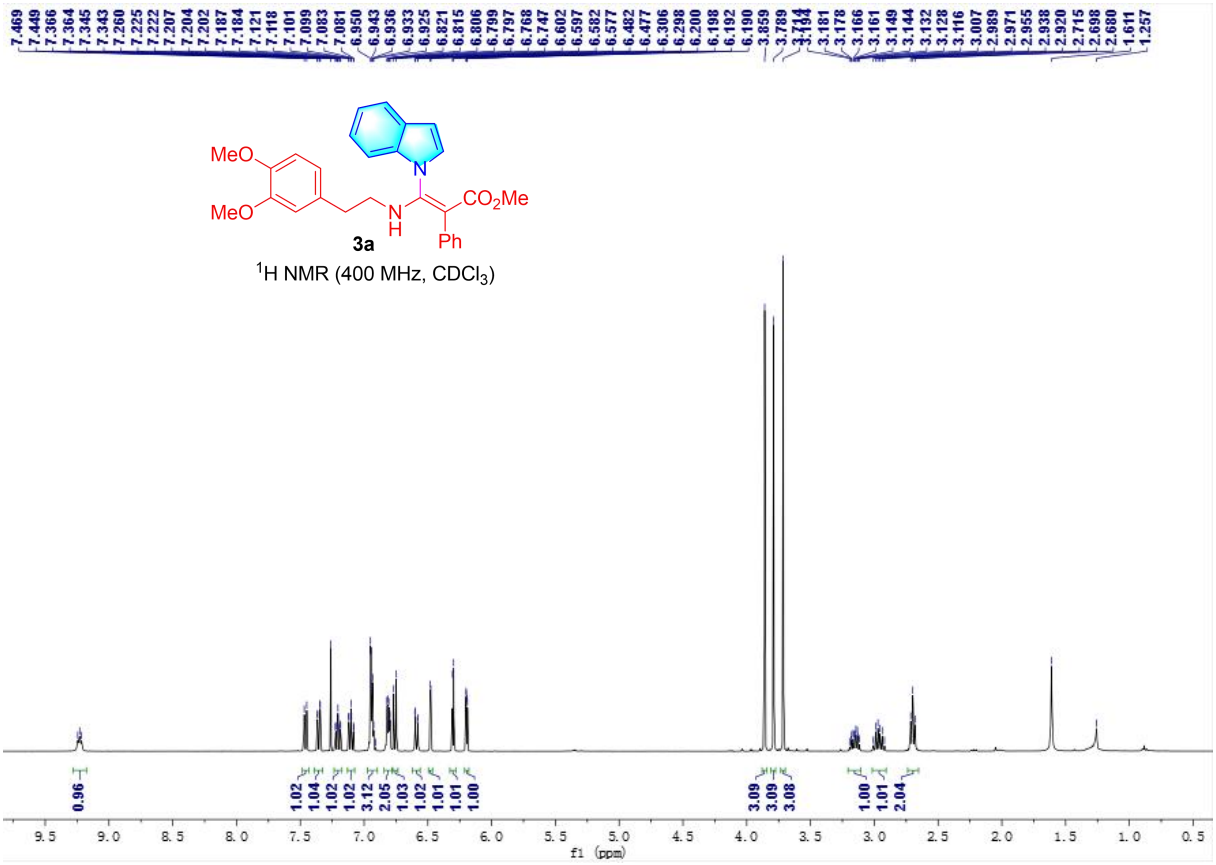
1	C	0.071130
2	C	0.277162
3	C	-0.213879
4	C	-0.193611
5	C	-0.184178
6	C	-0.206853
7	C	-0.262559

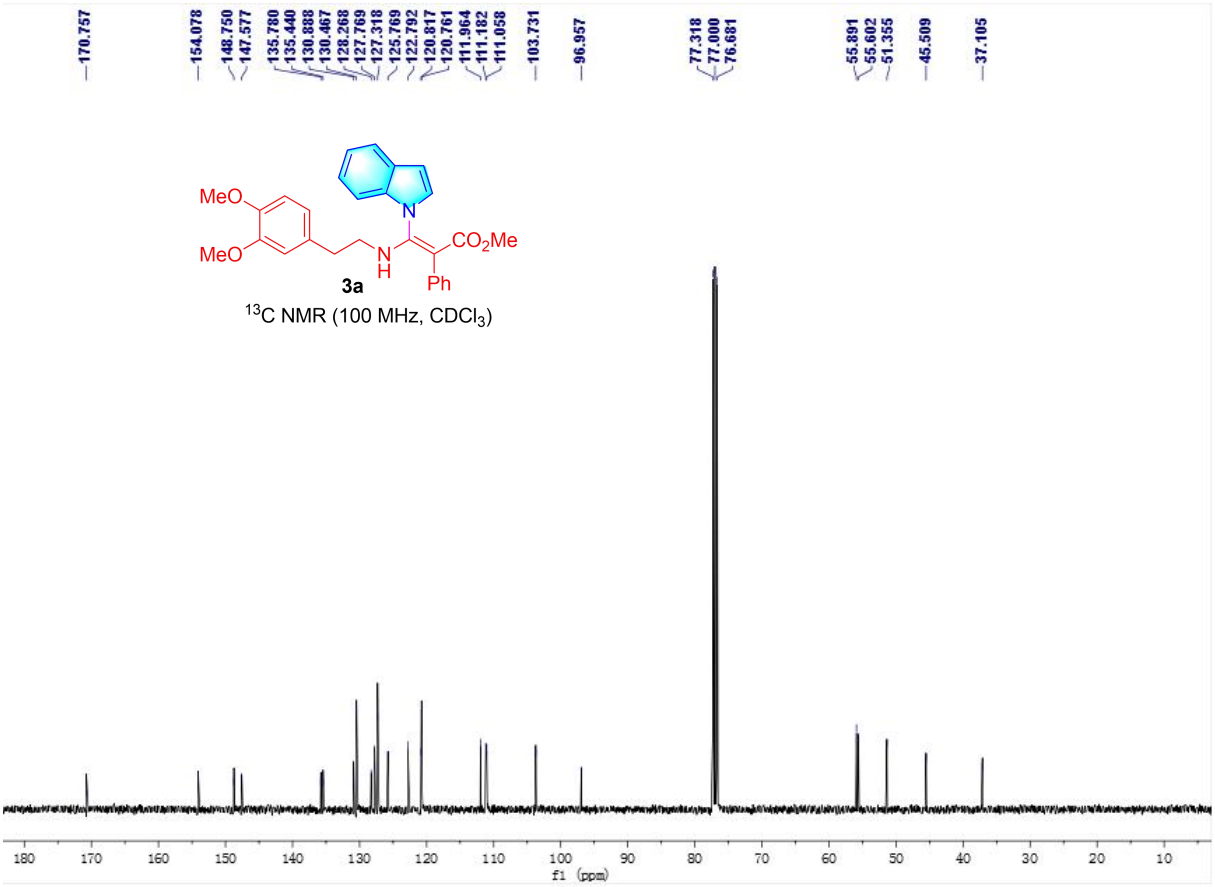
8	C	-0.013316
9	H	0.093472
10	H	0.132461
11	H	0.133925
12	H	0.140763
13	H	0.131572
14	H	0.128539
15	N	-0.718867
16	K	0.684239

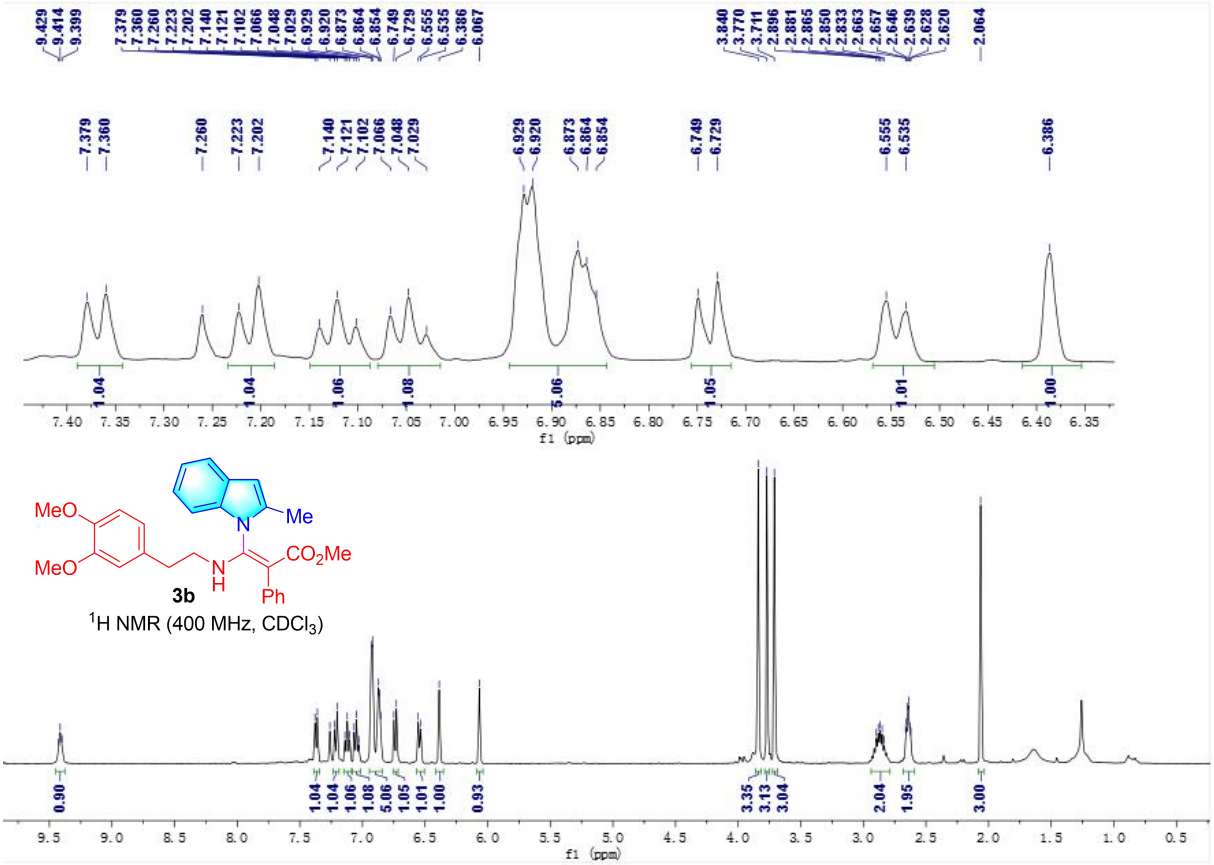
Summary of Natural Population Analysis:

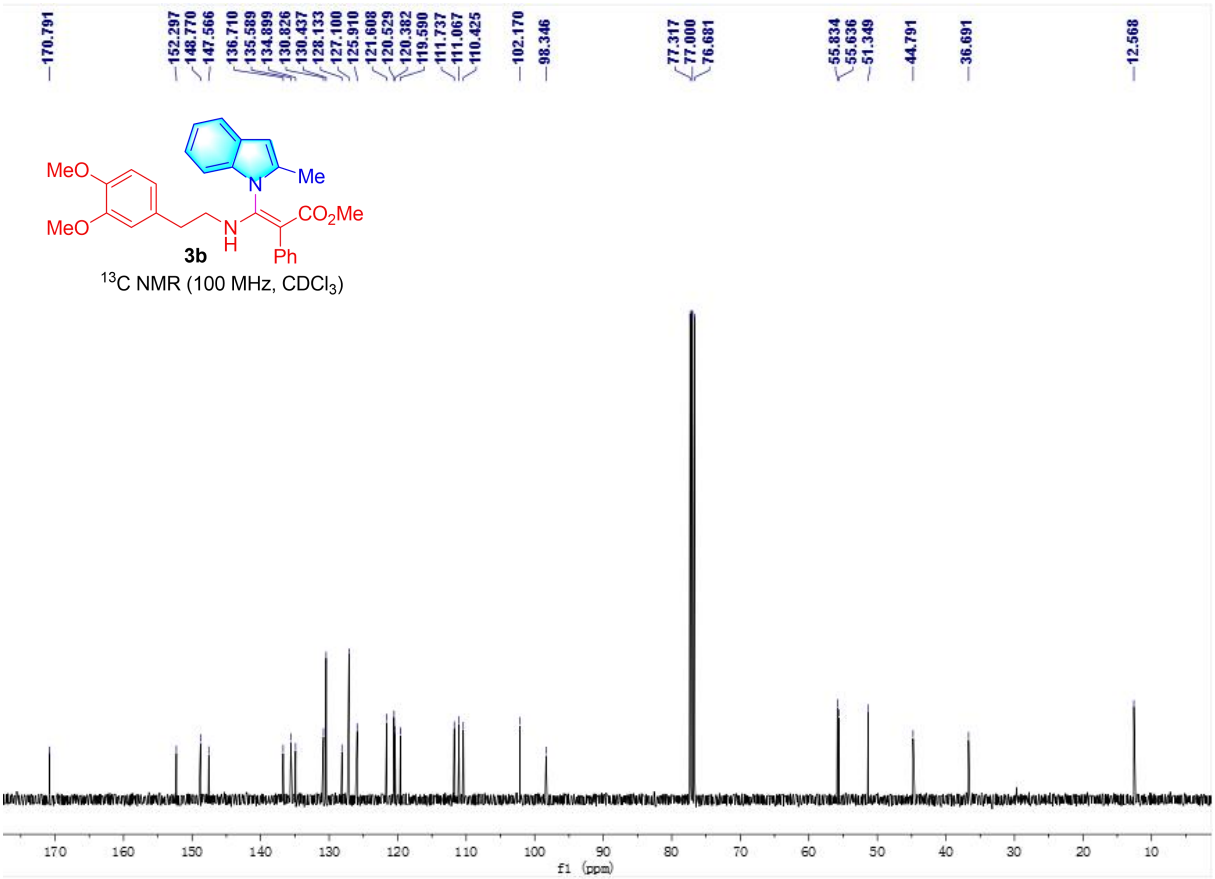
Atom	No	Charge	Core	Valence	Rydberg	Total
C	1	-0.11676	1.99906	4.10296	0.01474	6.11676
C	2	0.13183	1.99906	3.85114	0.01797	5.86817
C	3	-0.29337	1.99903	4.28283	0.01151	6.29337
C	4	-0.26762	1.99914	4.25336	0.01512	6.26762
C	5	-0.28340	1.99914	4.27034	0.01392	6.28340
C	6	-0.22111	1.99906	4.20918	0.01288	6.22111
C	7	-0.36135	1.99902	4.35022	0.01211	6.36135
C	8	-0.03046	1.99921	4.00832	0.02293	6.03046
H	9	0.16581	0.00000	0.83321	0.00097	0.83419
H	10	0.22989	0.00000	0.76936	0.00075	0.77011
H	11	0.23195	0.00000	0.76734	0.00072	0.76805
H	12	0.23261	0.00000	0.76644	0.00095	0.76739
H	13	0.23377	0.00000	0.76573	0.00051	0.76623
H	14	0.21154	0.00000	0.78796	0.00050	0.78846
N	15	-0.77850	1.99947	5.76533	0.01369	7.77850
K	16	0.91518	9.99751	0.08306	0.00425	10.08482
* Total *		0.00000	27.98969	43.86677	0.14353	72.00000

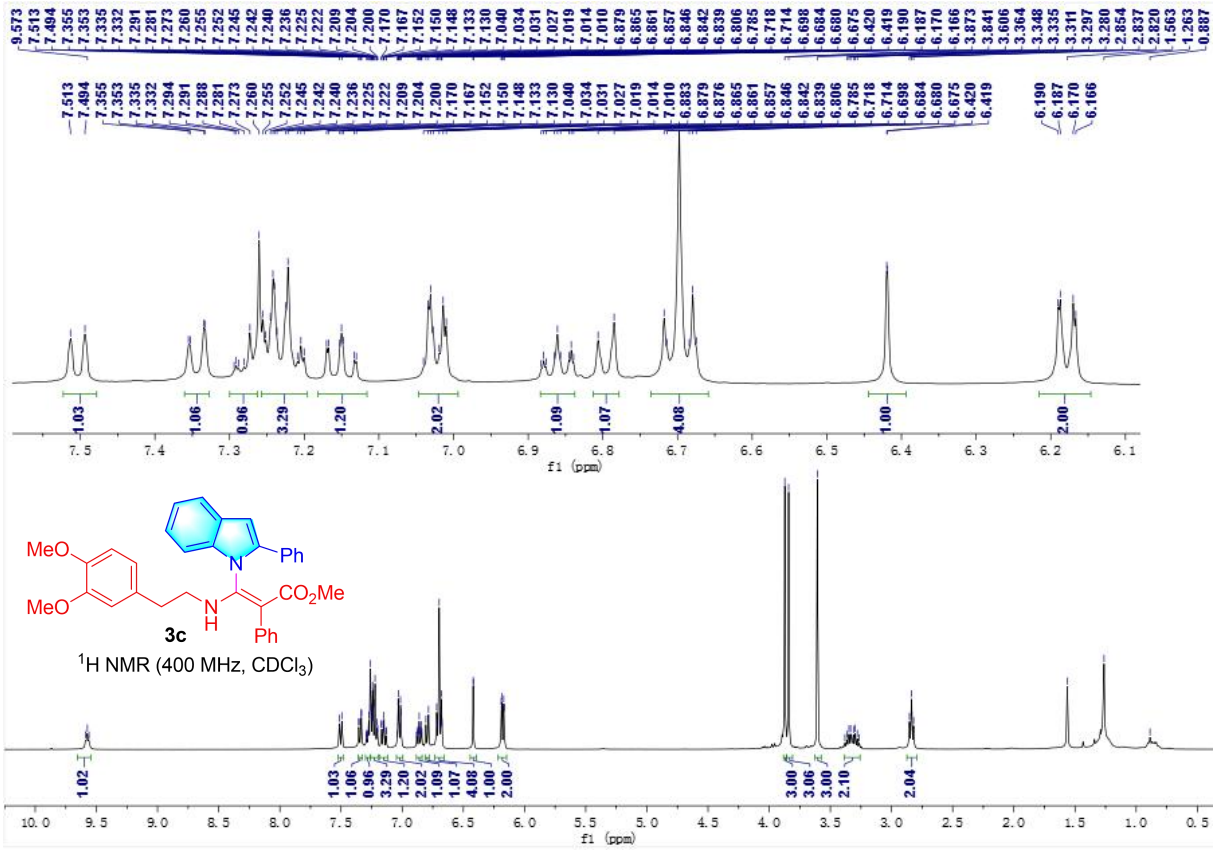
6) Copies of ^{1}H NMR and ^{13}C NMR Spectra of Products 3 and 5.

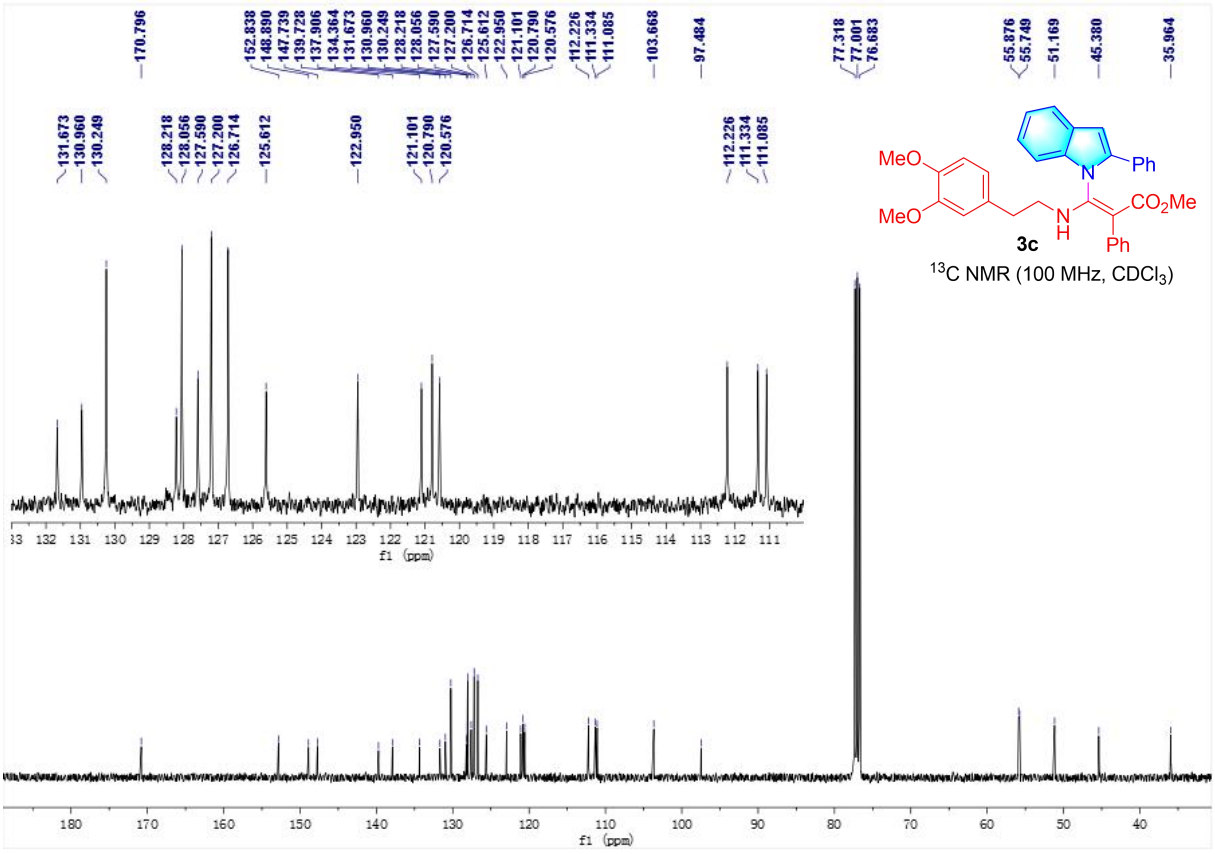


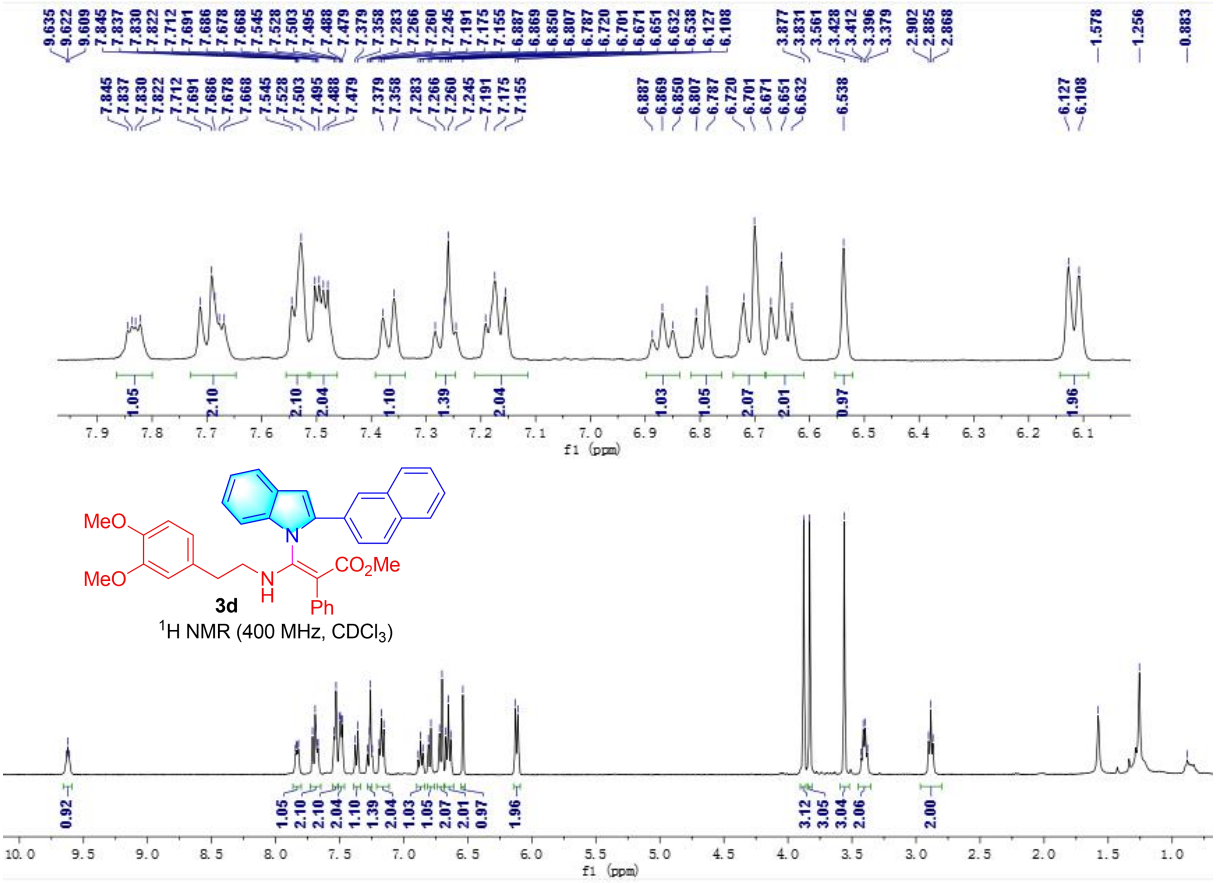


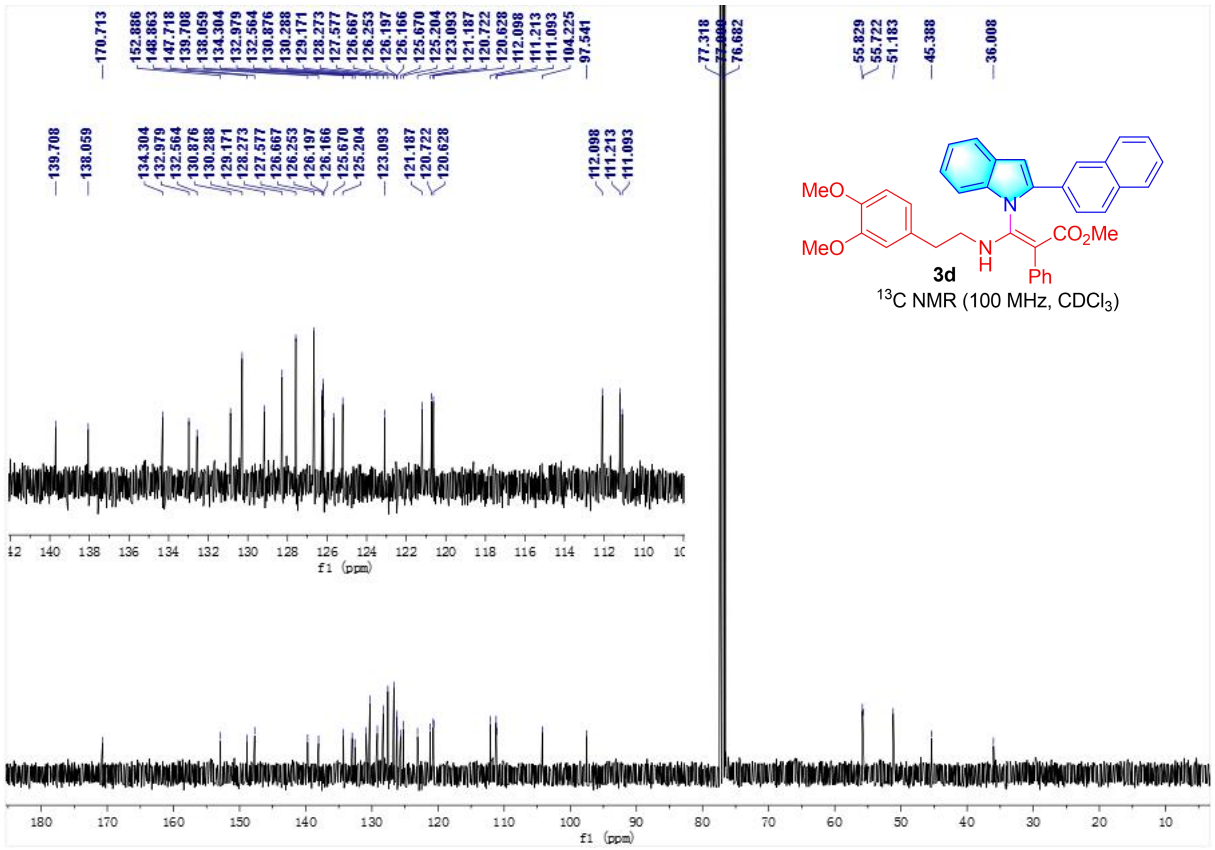

MeO
MeO
N
Me
N
H
CO2Me
Ph
3b
1H NMR (400 MHz, CDCl3)
f1 (ppm)

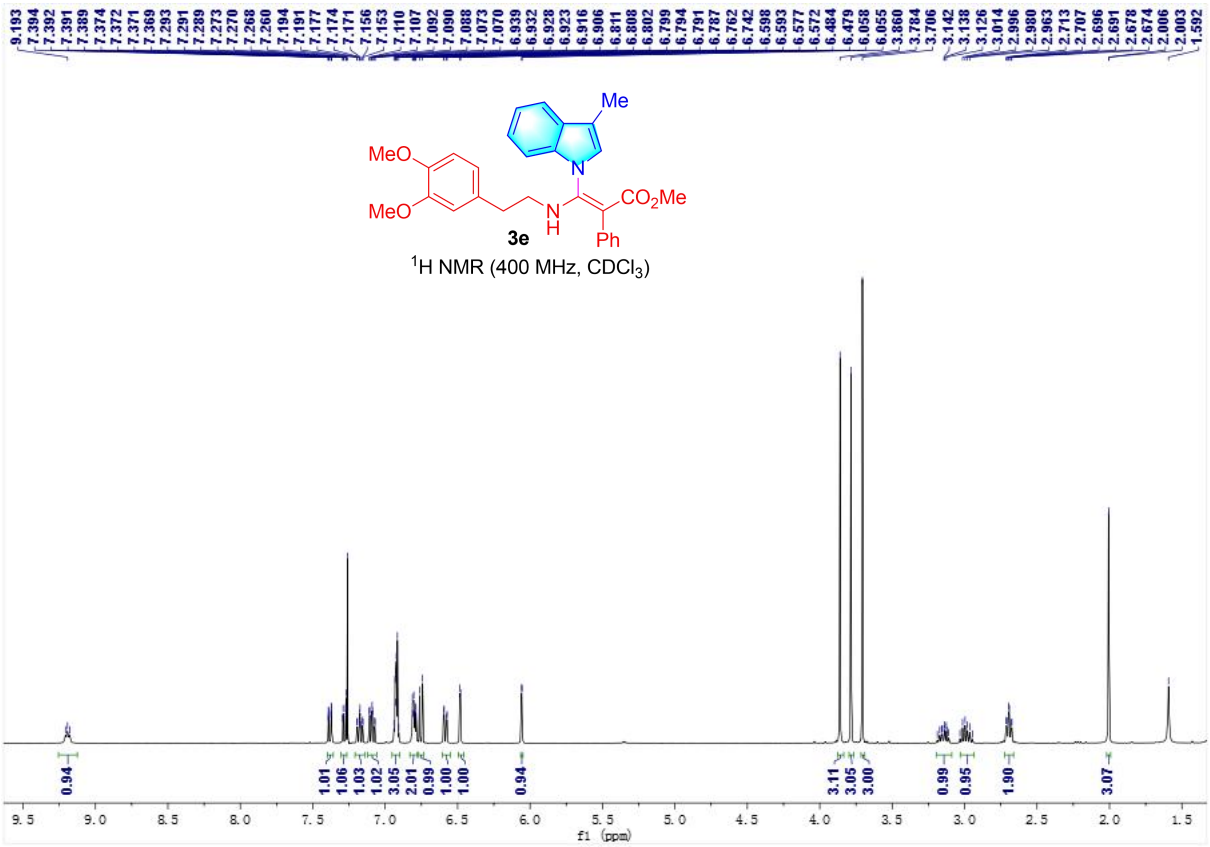

MeO
MeO
N
Me
N
H
CO2Me
Ph
3b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

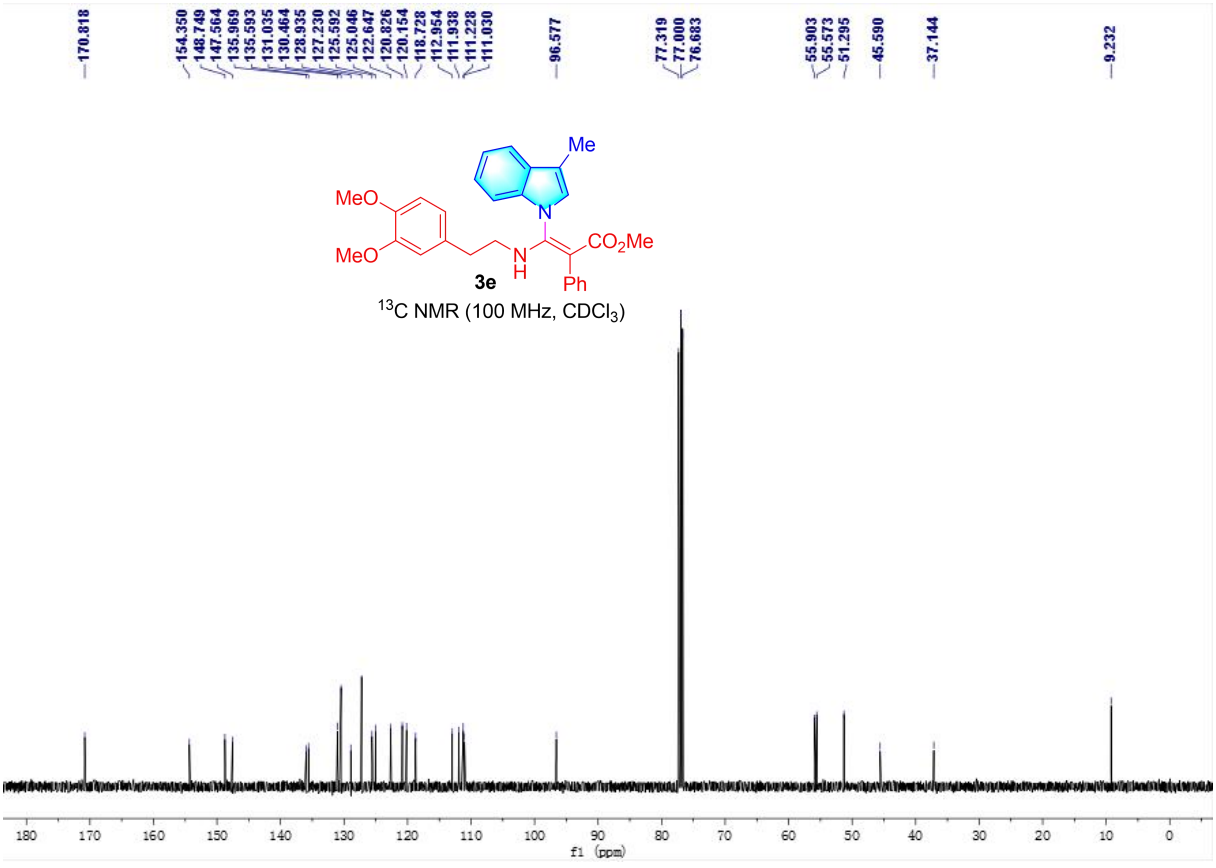

MeO
MeO
N
Ph
CO2Me
N
H
Ph
3c
1H NMR (400 MHz, CDCl3)


MeO
MeO
N
Ph
CO2Me
N
H
Ph
3c
13C NMR (100 MHz, CDCl3)


MeO
MeO
N
H
CO2Me
Ph
3d
1H NMR (400 MHz, CDCl3)


MeO
MeO
N
H
CO2Me
Ph
3d
13C NMR (100 MHz, CDCl3)


Me
MeO
MeO
N
N
H
CO2Me
Ph
3e
1H NMR (400 MHz, CDCl3)
f1 (ppm)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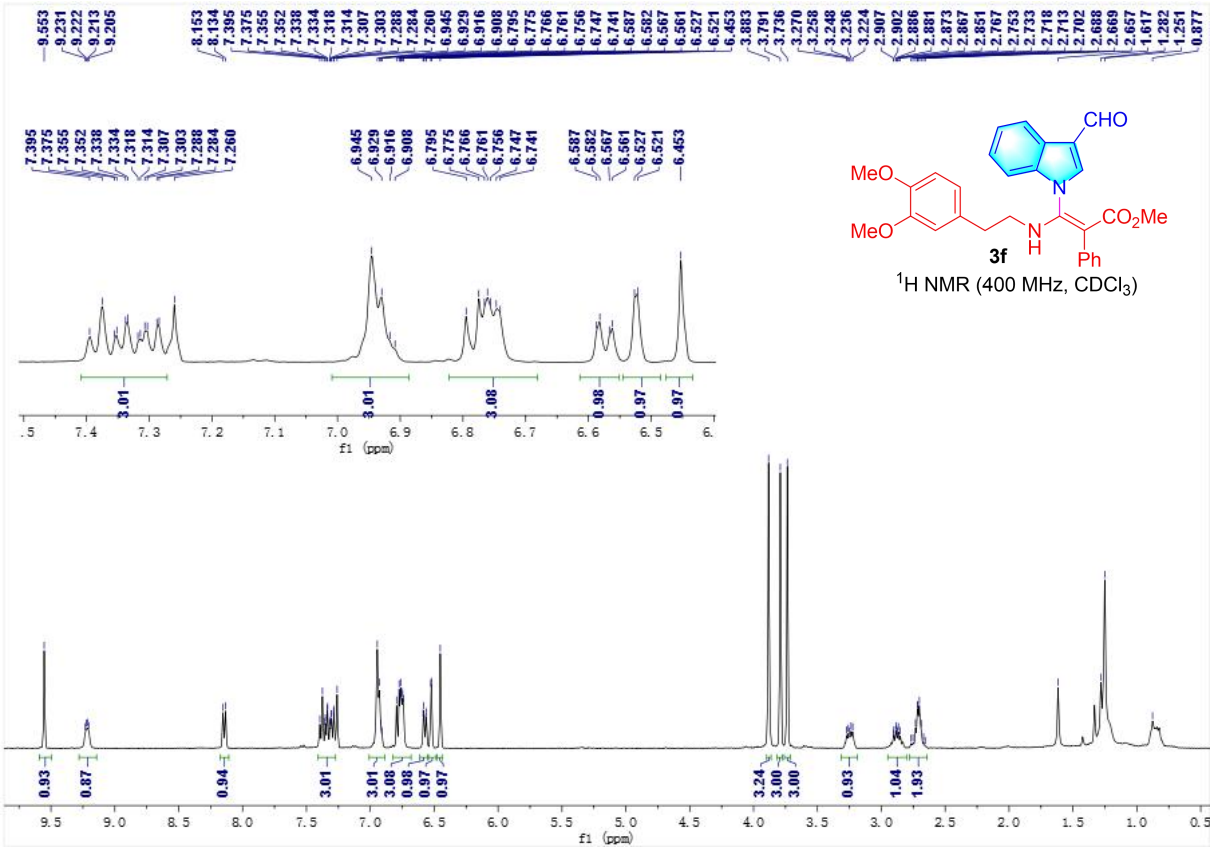
MeO
MeO
N
N
H
CO2Me
Ph
3e
13C NMR (100 MHz, CDCl3)
f1 (ppm)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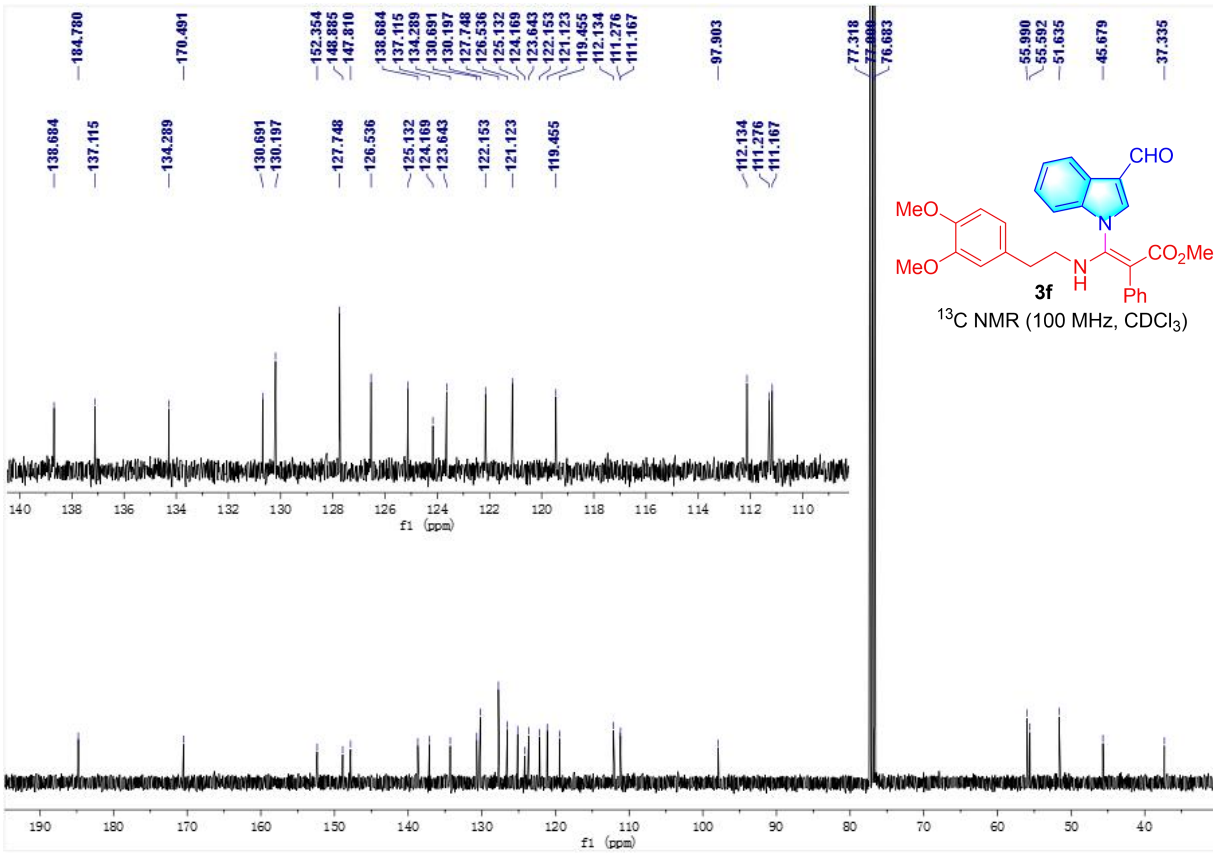
MeO
CHO
N
N
H
CO2Me
Ph
3f
1H NMR (400 MHz, CDCl3)
f1 (ppm)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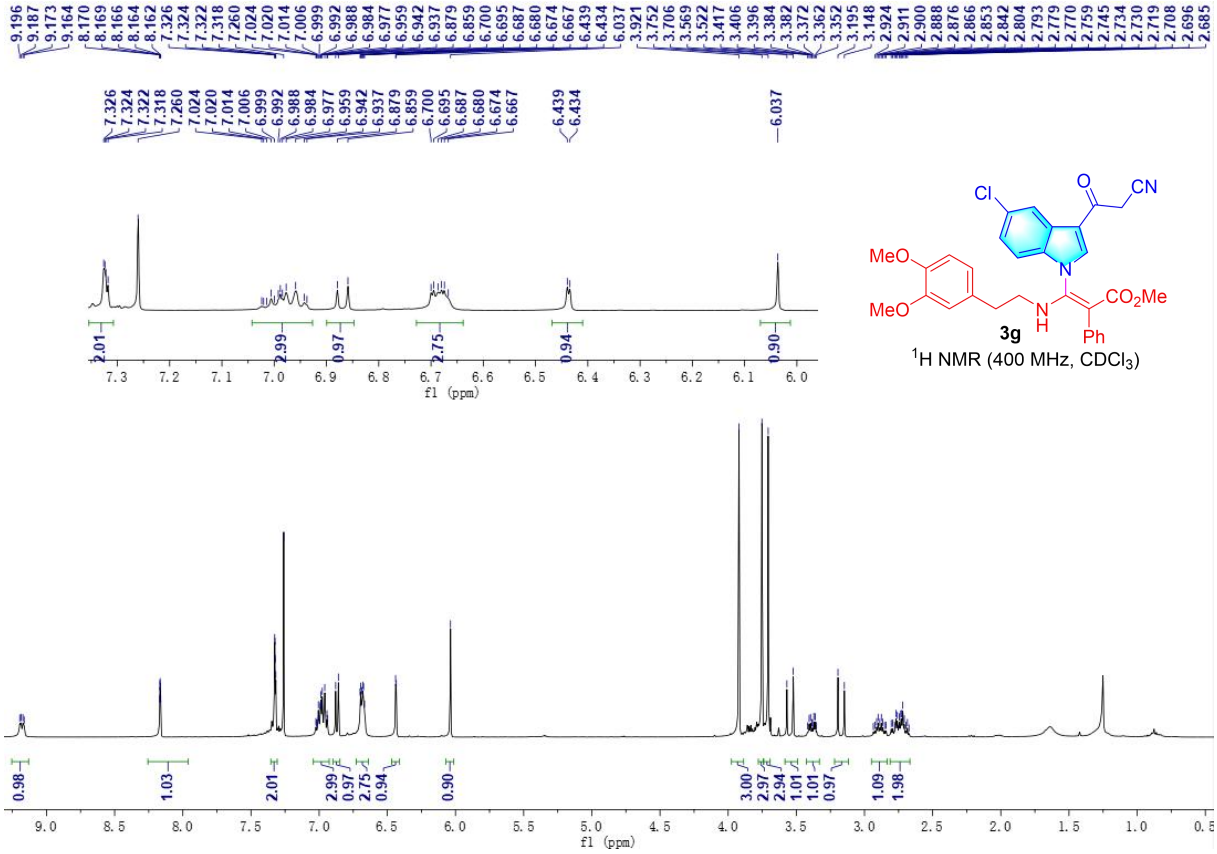
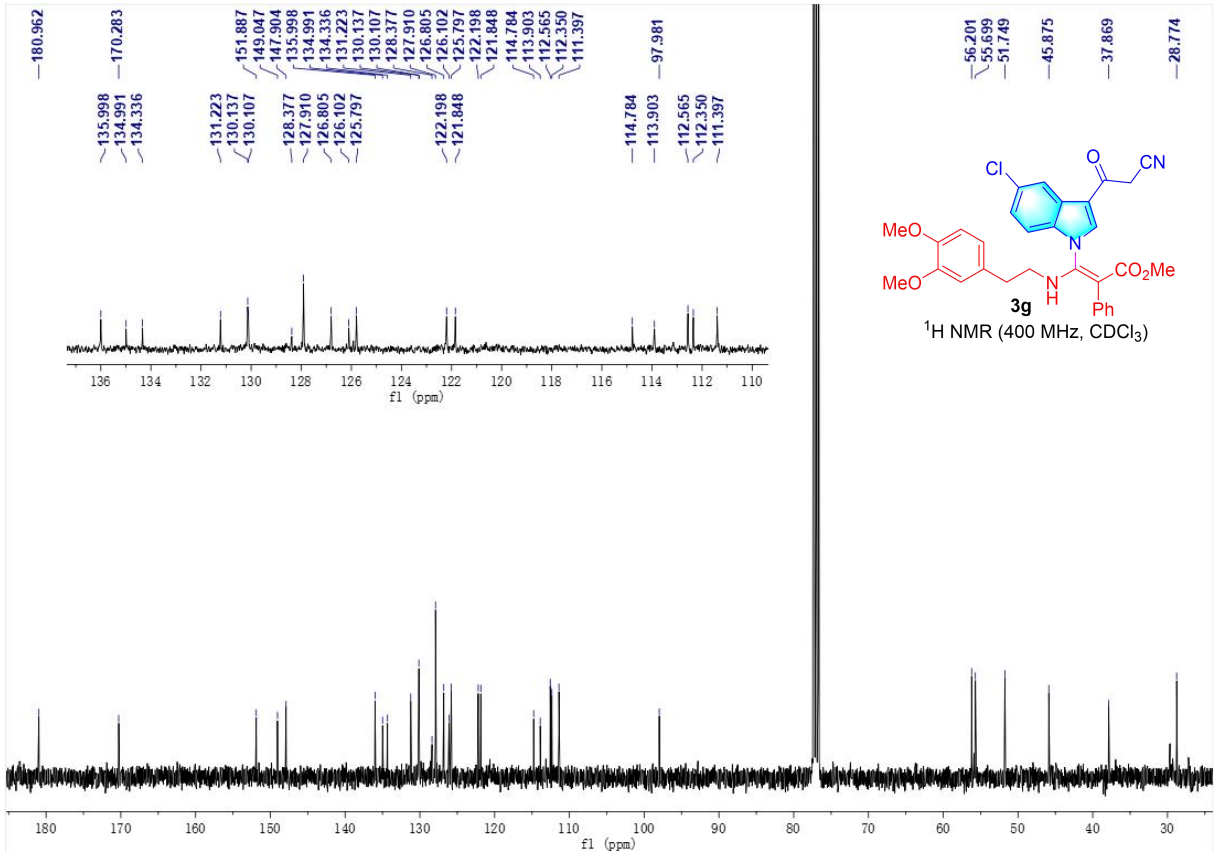
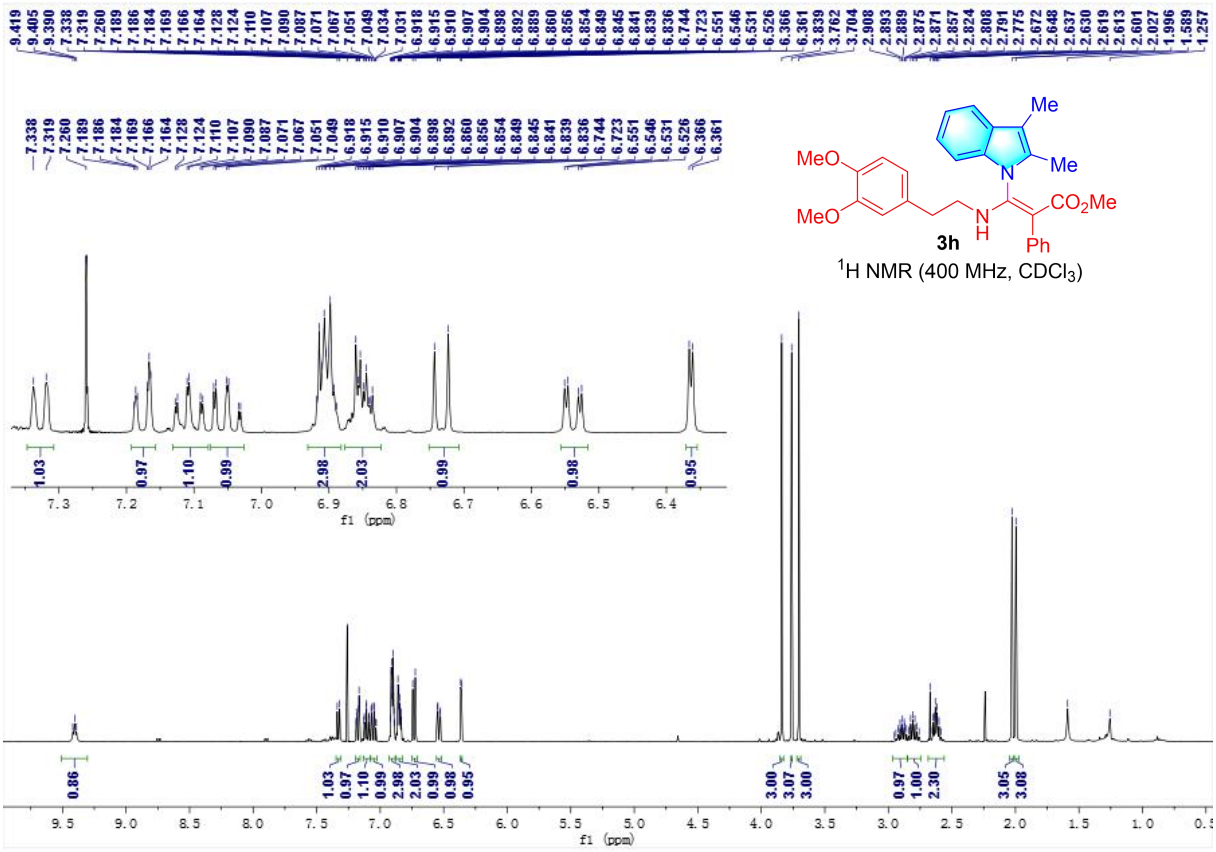
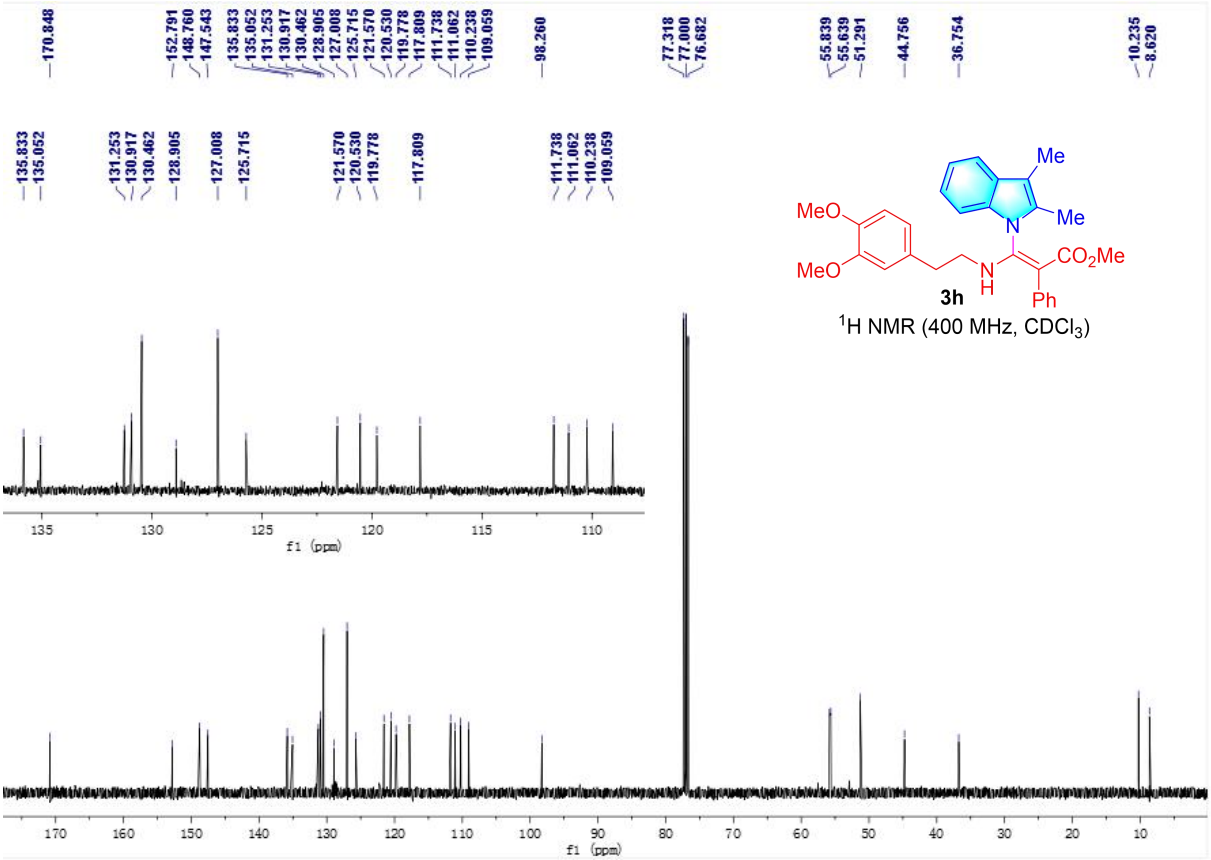
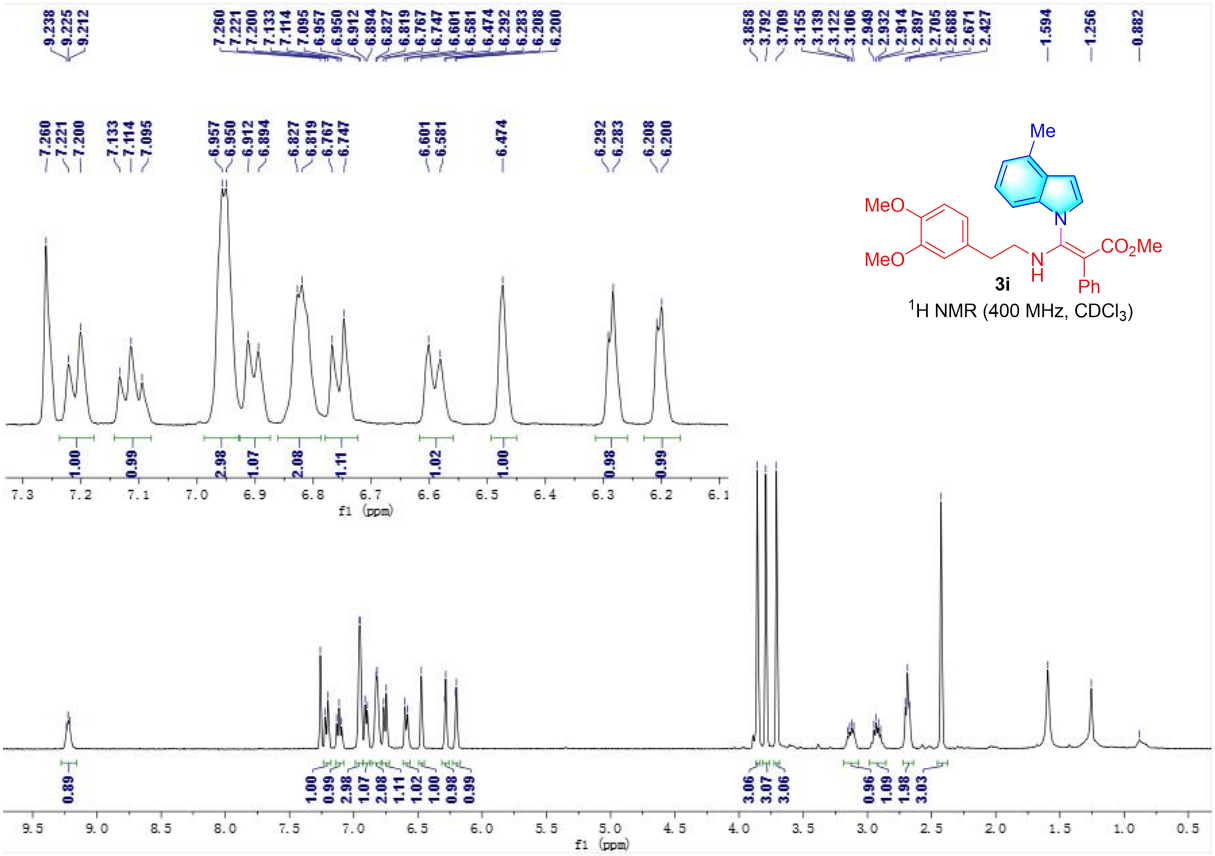
MeO
CHO
N
N
H
CO2Me
Ph
3f
13C NMR (100 MHz, CDCl3)
f1 (ppm)

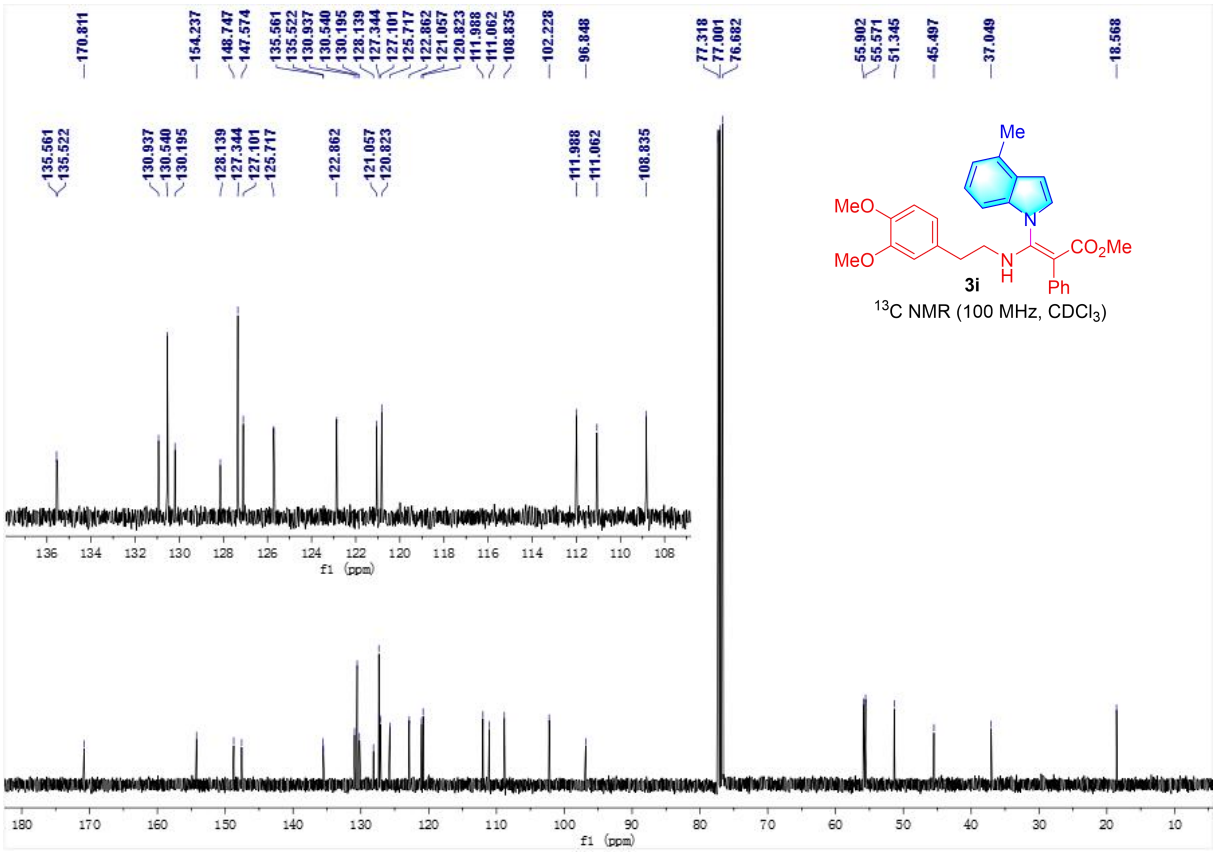

Cl
O
CN
MeO
MeO
N
N
H
CO2Me
Ph
3g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

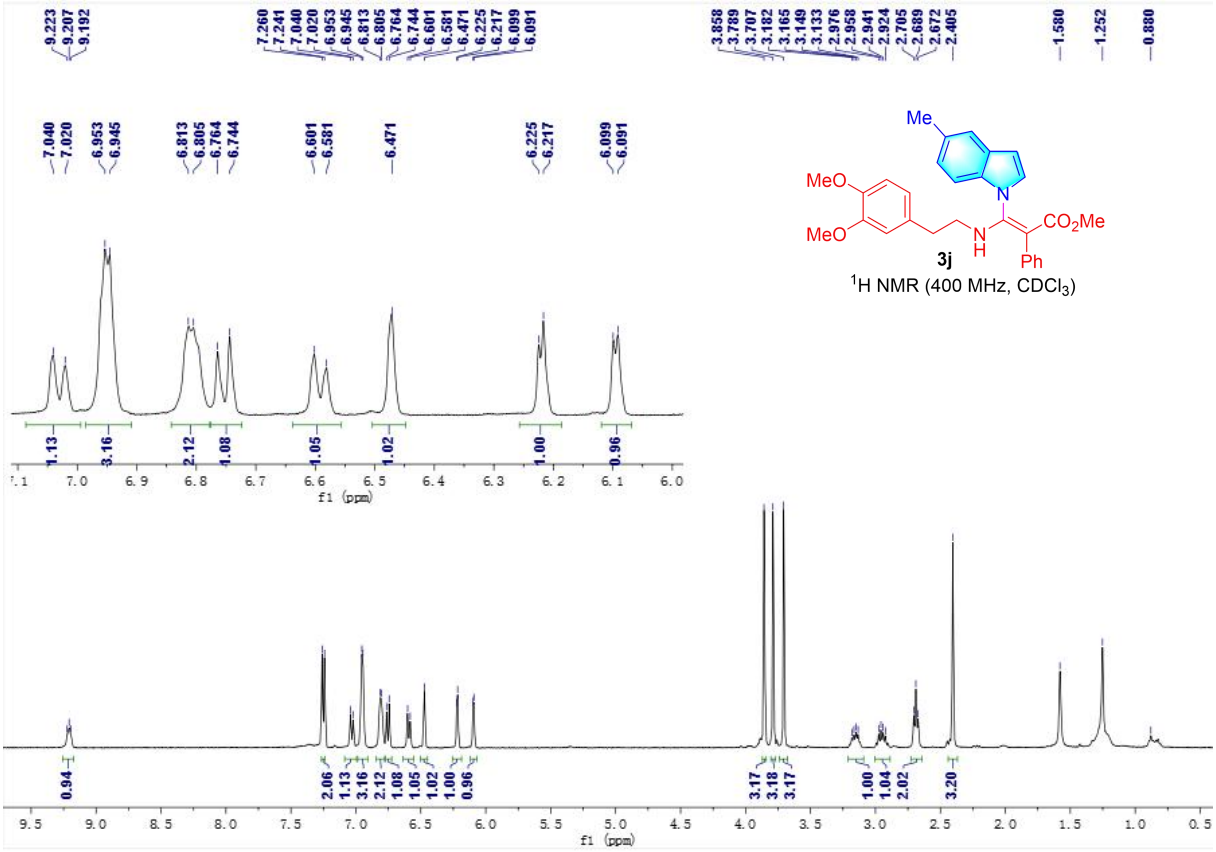

Cl
O
CN
MeO
MeO
N
N
H
CO2Me
Ph
3g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

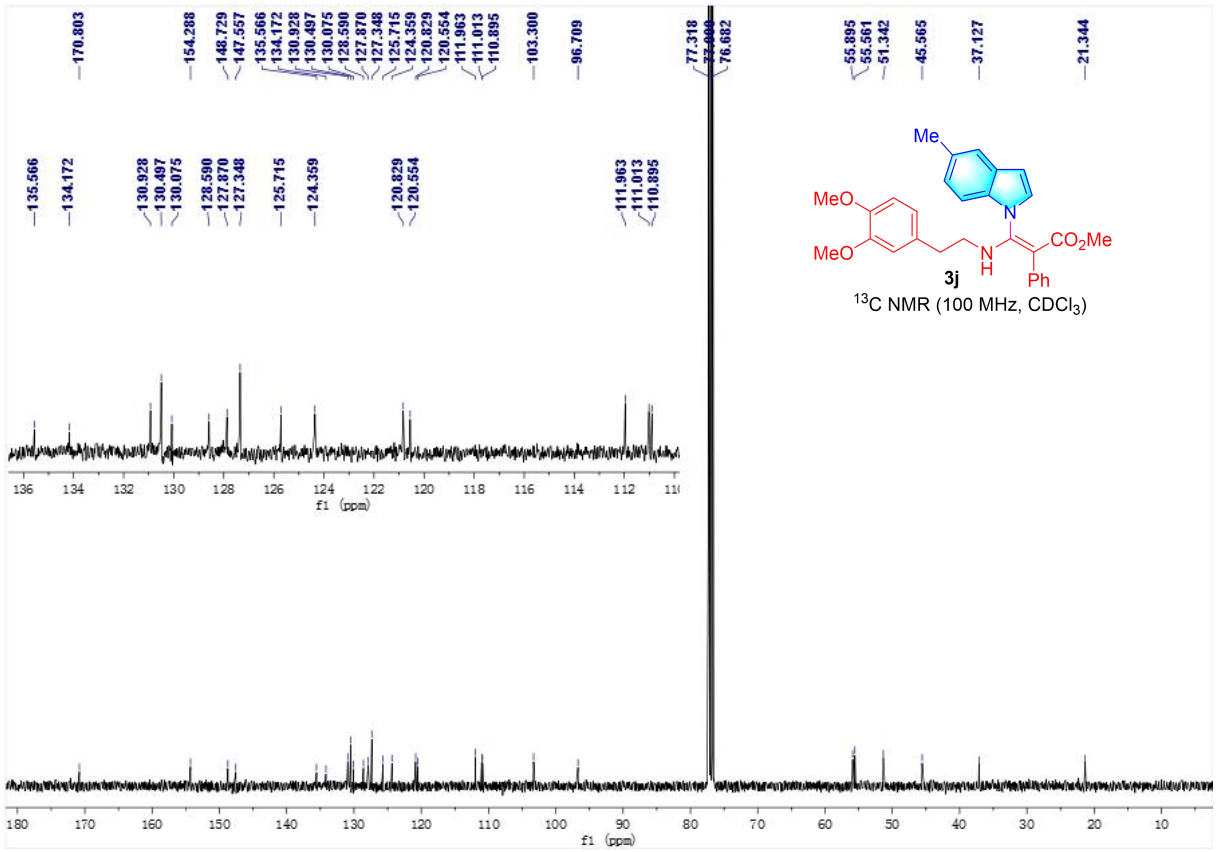

MeO
MeO
Me
Me
N
N
H
CO2Me
Ph
3h
1H NMR (400 MHz, CDCl3)
f1 (ppm)

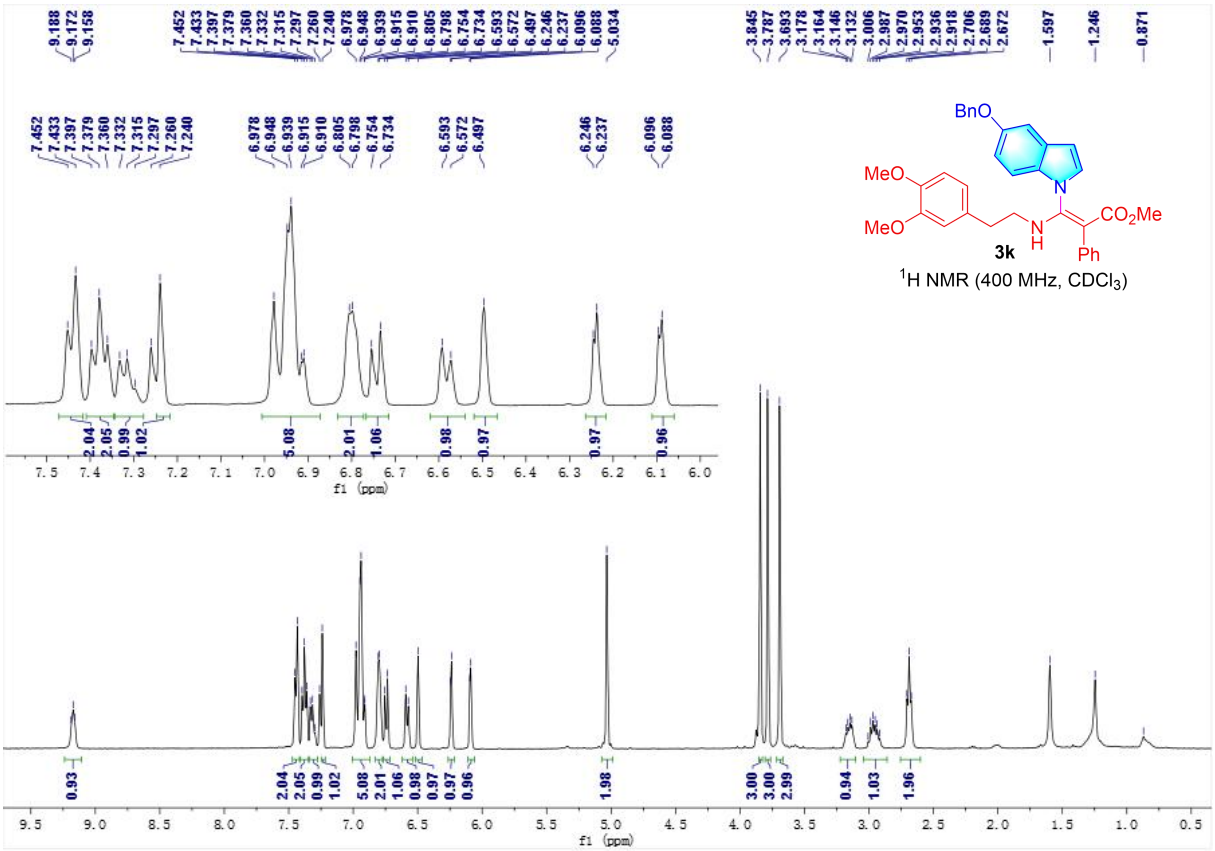

MeO
MeO
Me
Me
N
N
H
CO2Me
Ph
3h
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
MeO
MeO
N
N
H
CO2Me
Ph
3i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

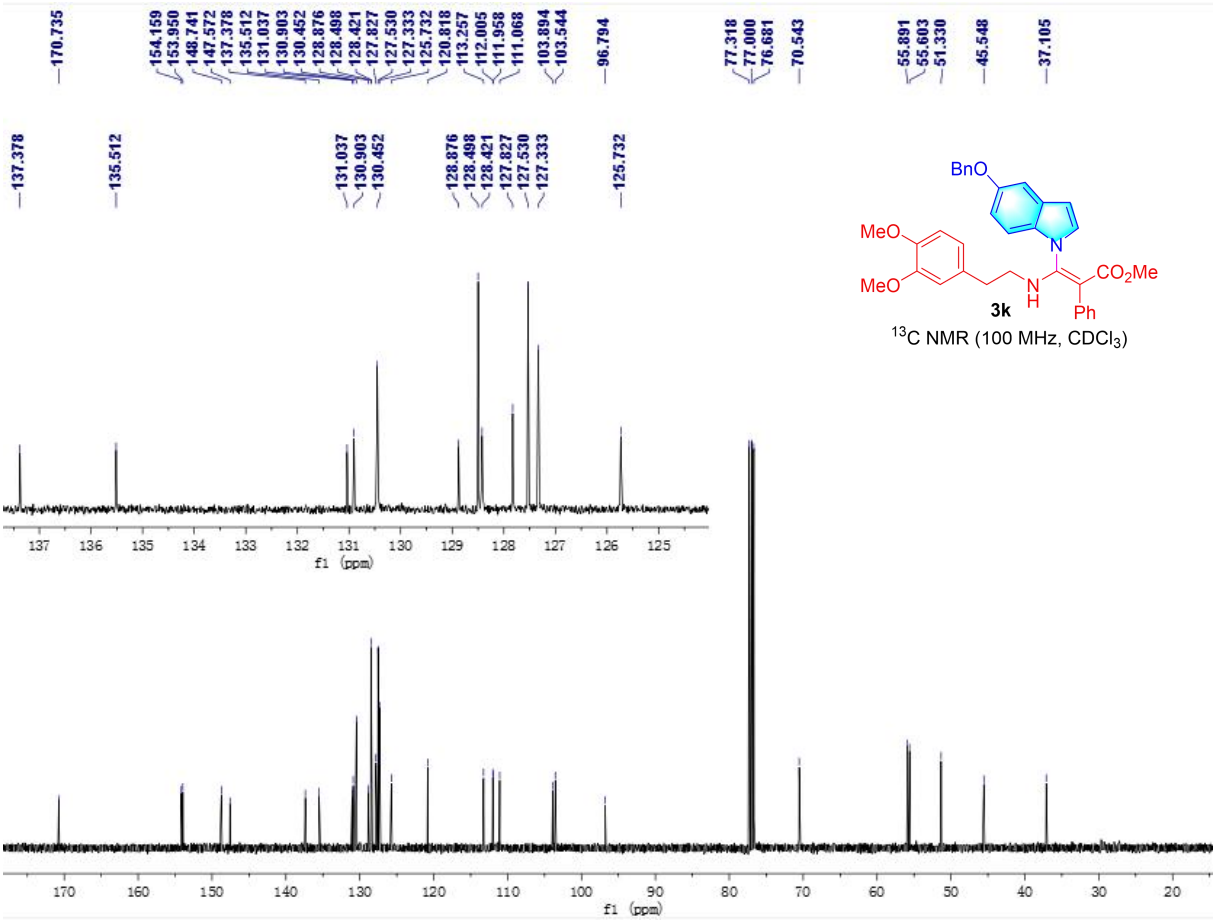

Me
MeO
MeO
N
N
H
CO2Me
Ph
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)


Me
MeO
MeO
N
H
N
CO2Me
Ph
3j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

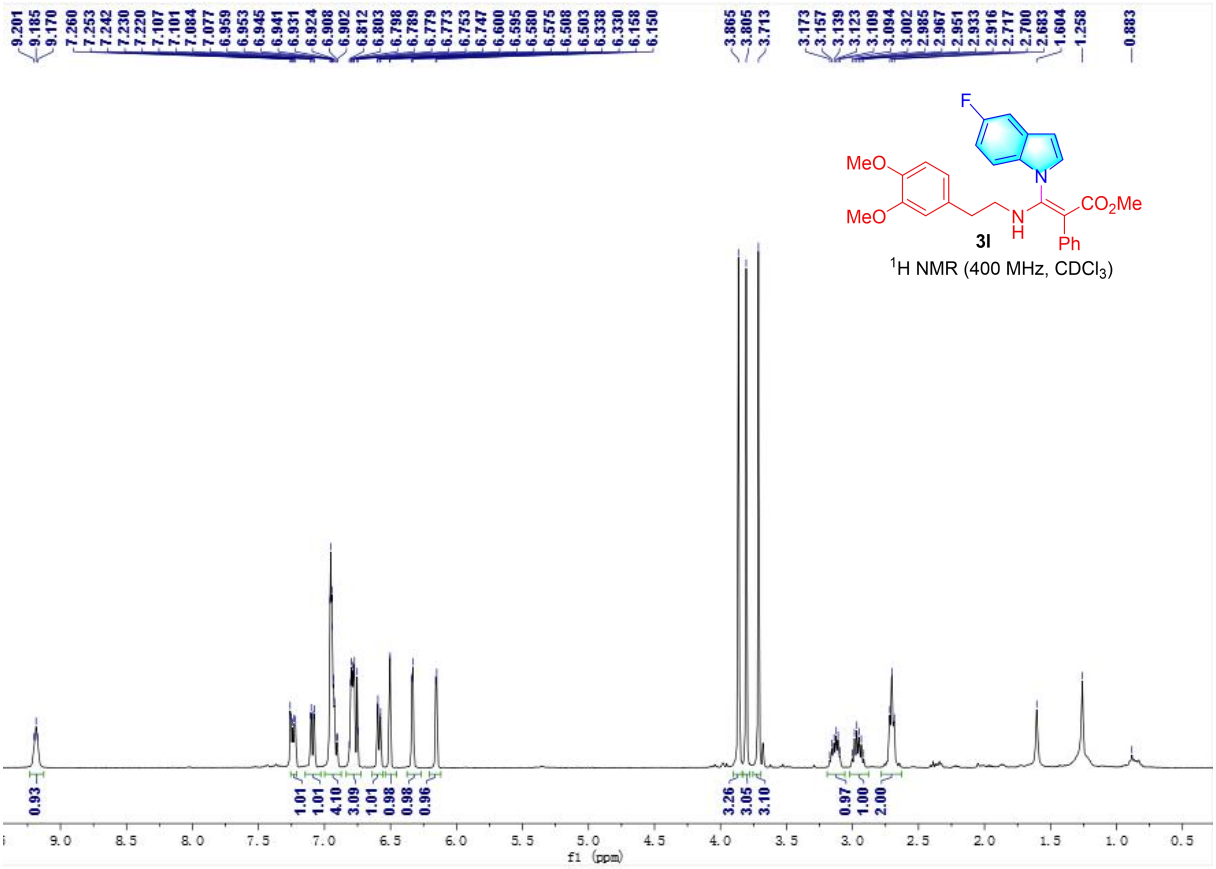

Me
MeO
MeO
N
H
N
CO2Me
Ph
3j
13C NMR (100 MHz, CDCl3)
f1 (ppm)



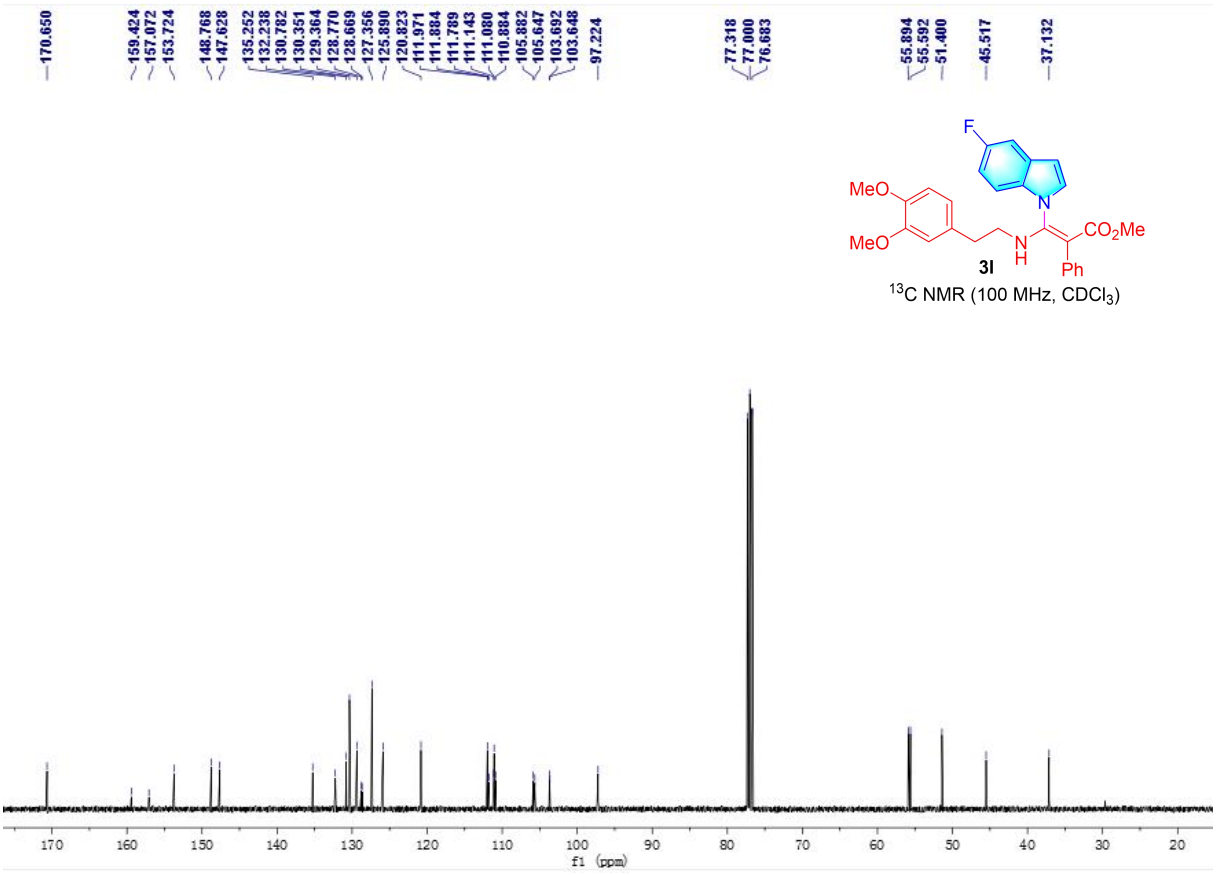
^{1}H NMR (400 MHz, $CDCl_3$)



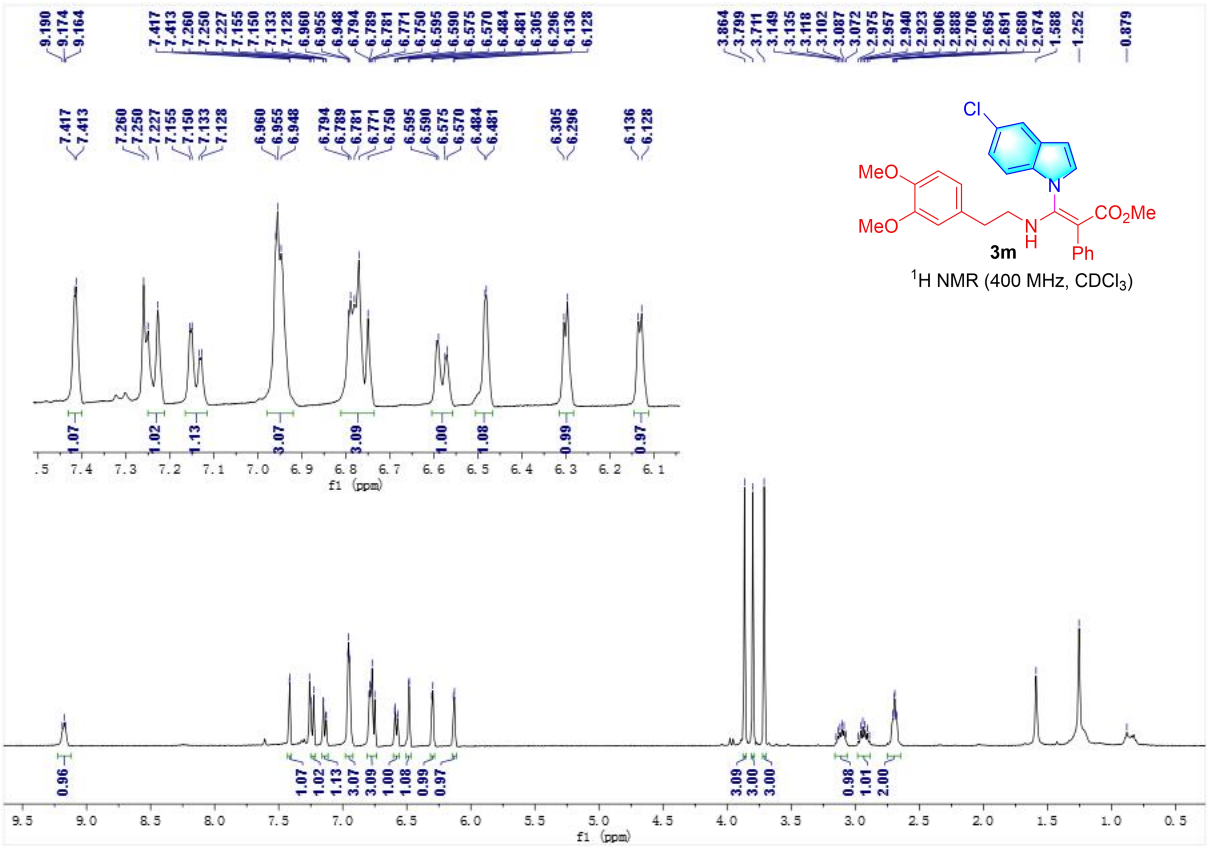
^{13}C NMR (100 MHz, $CDCl_3$)



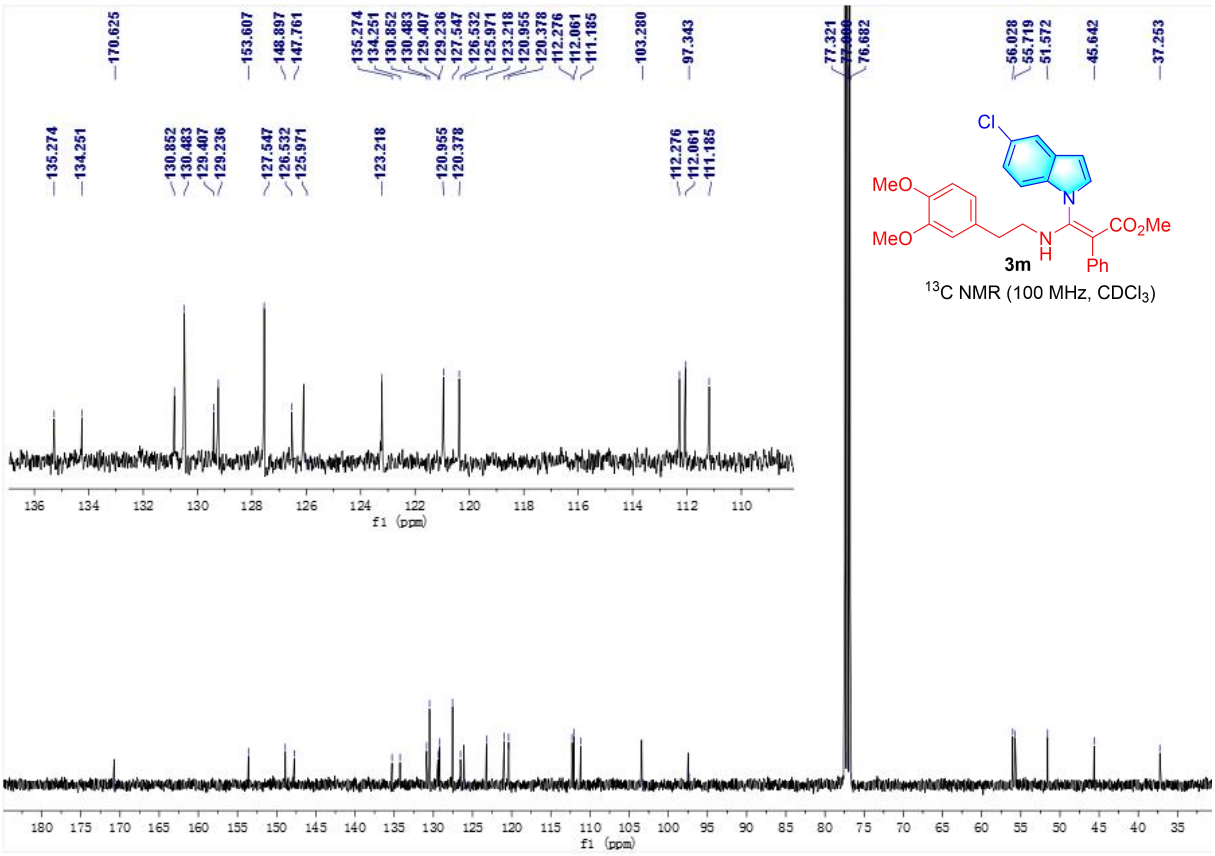
^{1}H NMR (400 MHz, $CDCl_3$)



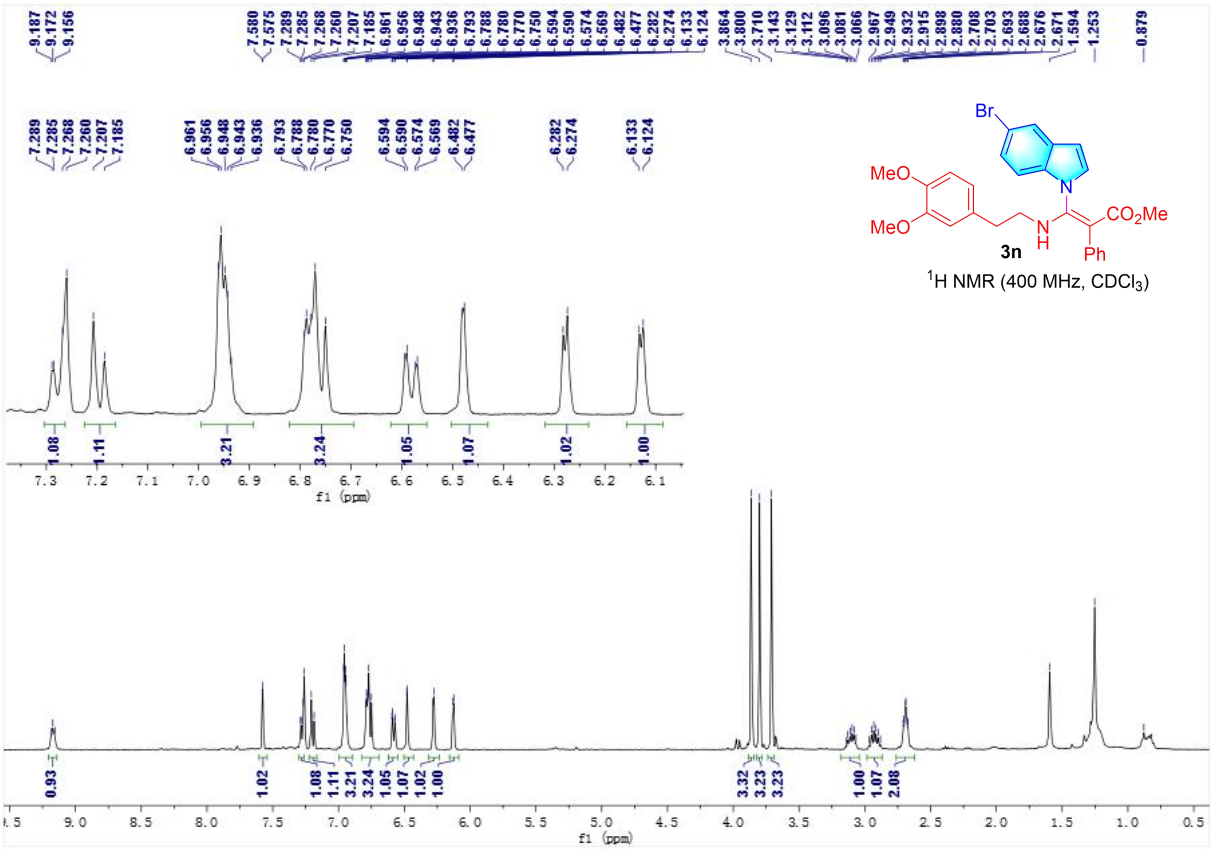
^{13}C NMR (100 MHz, $CDCl_3$)

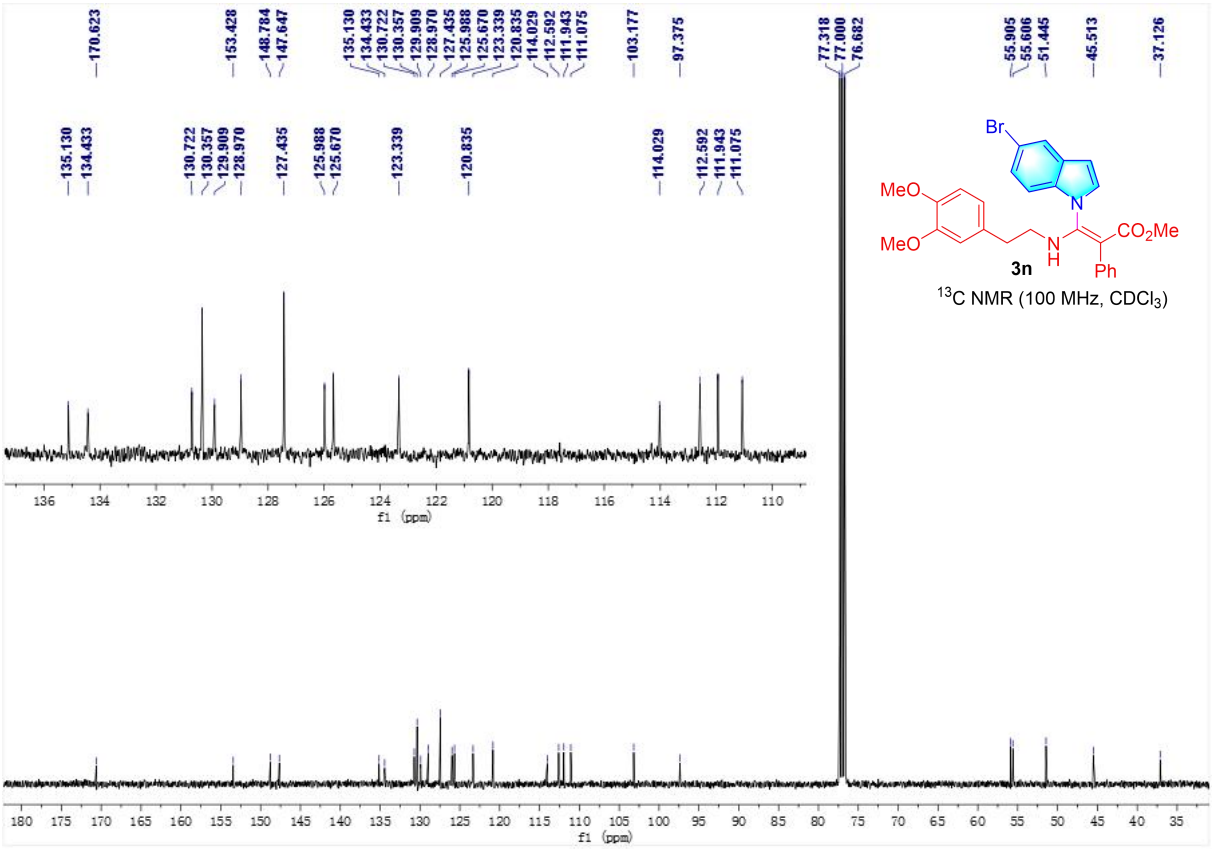


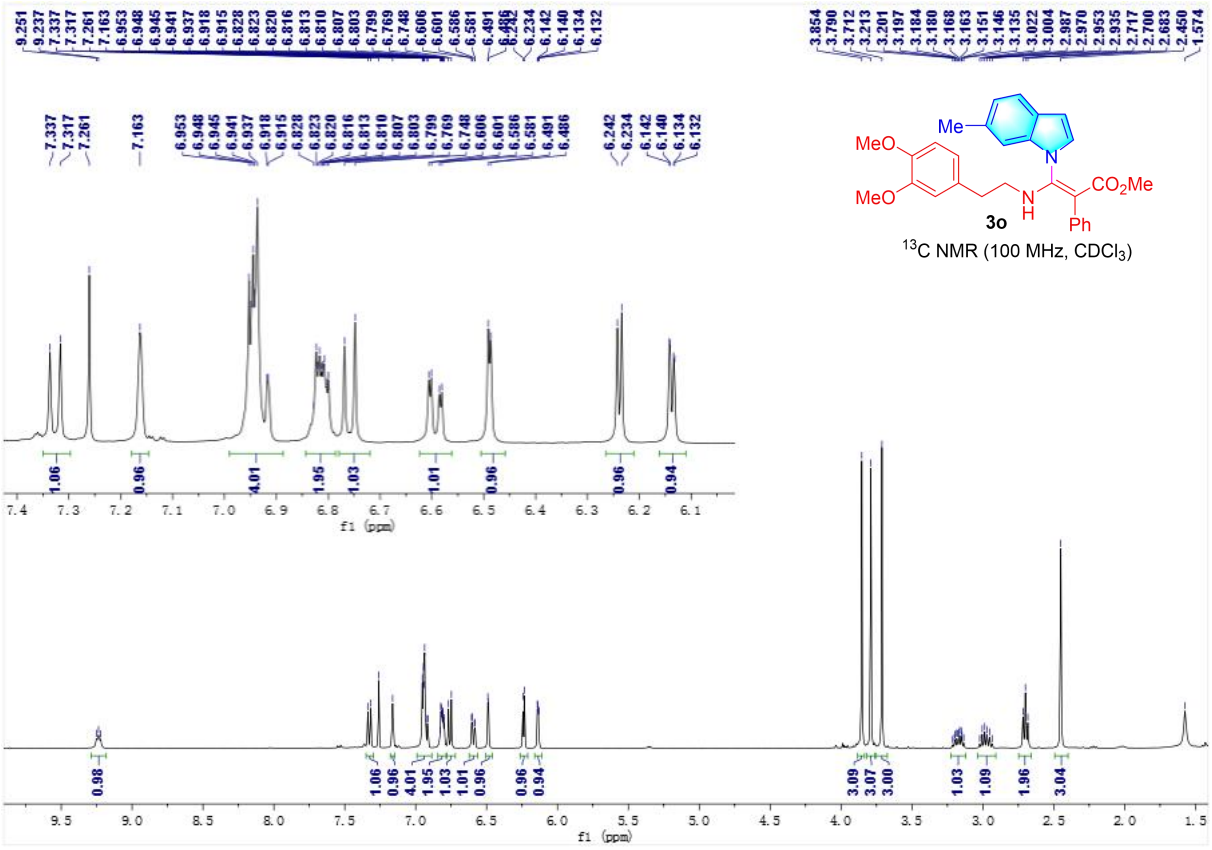
^{1}H NMR (400 MHz, $CDCl_3$)

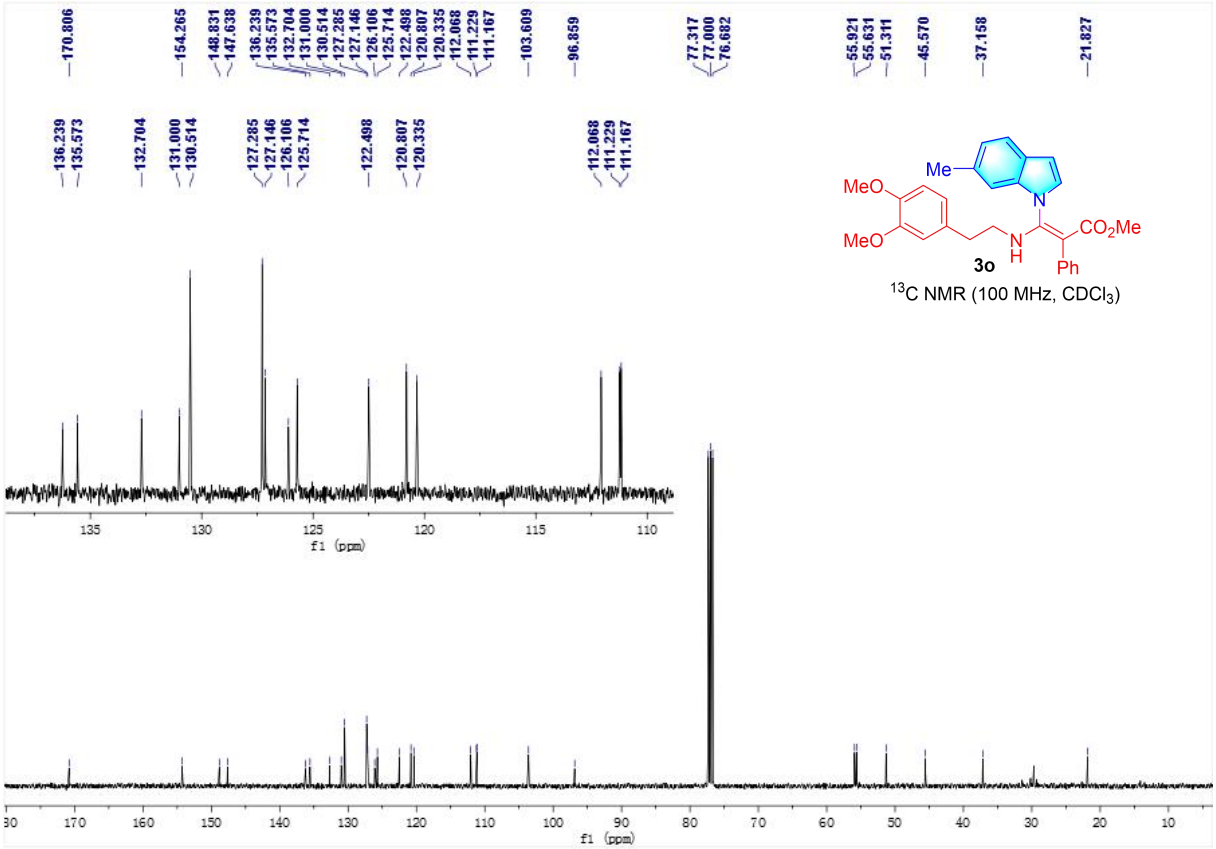


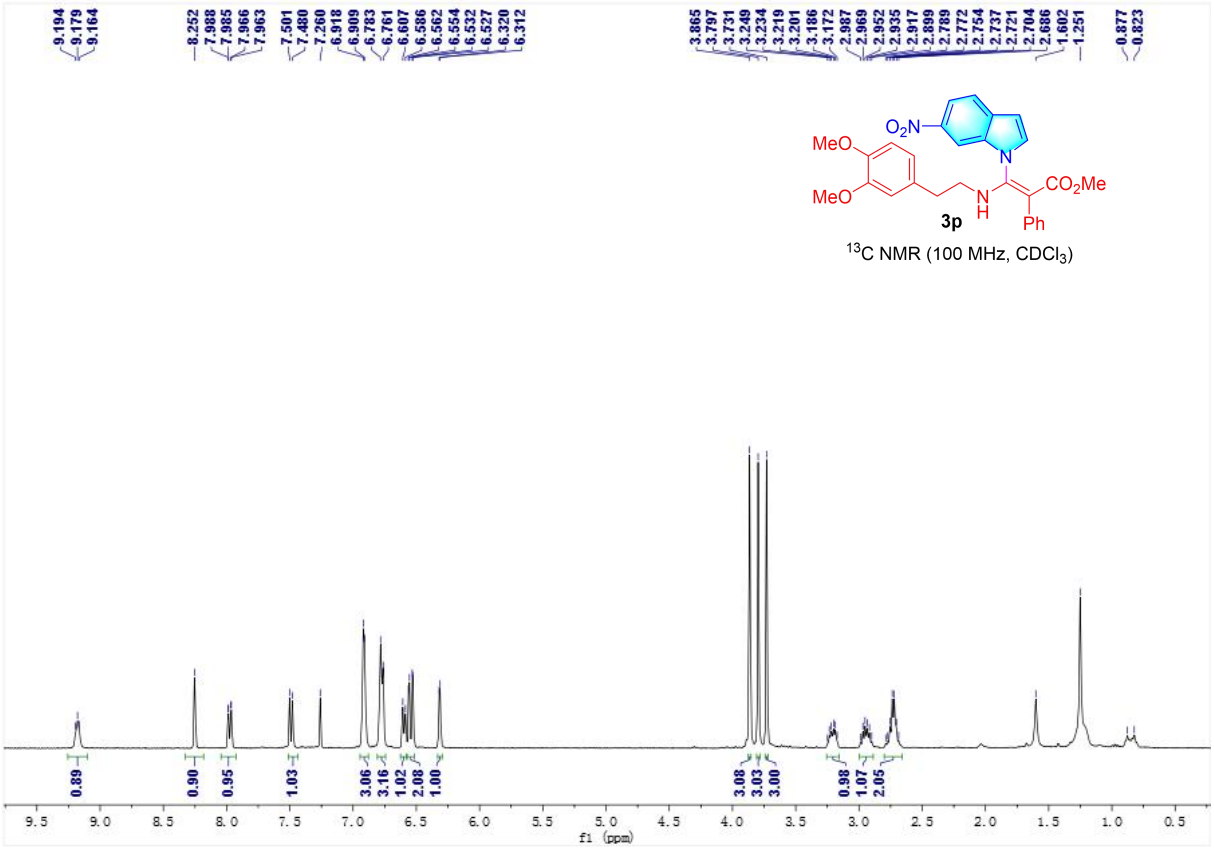
^{13}C NMR (100 MHz, $CDCl_3$)


Br
MeO
MeO
N
H
N
CO2Me
Ph
3n
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Br
MeO
MeO
N
H
N
CO2Me
Ph
3n
13C NMR (100 MHz, CDCl3)
f1 (ppm)


Me
MeO
MeO
N
N
H
CO2Me
Ph
3o
13C NMR (100 MHz, CDCl3)
f1 (ppm)


Me
MeO
MeO
N
N
H
CO2Me
Ph
3o
13C NMR (100 MHz, CDCl3)
f1 (ppm)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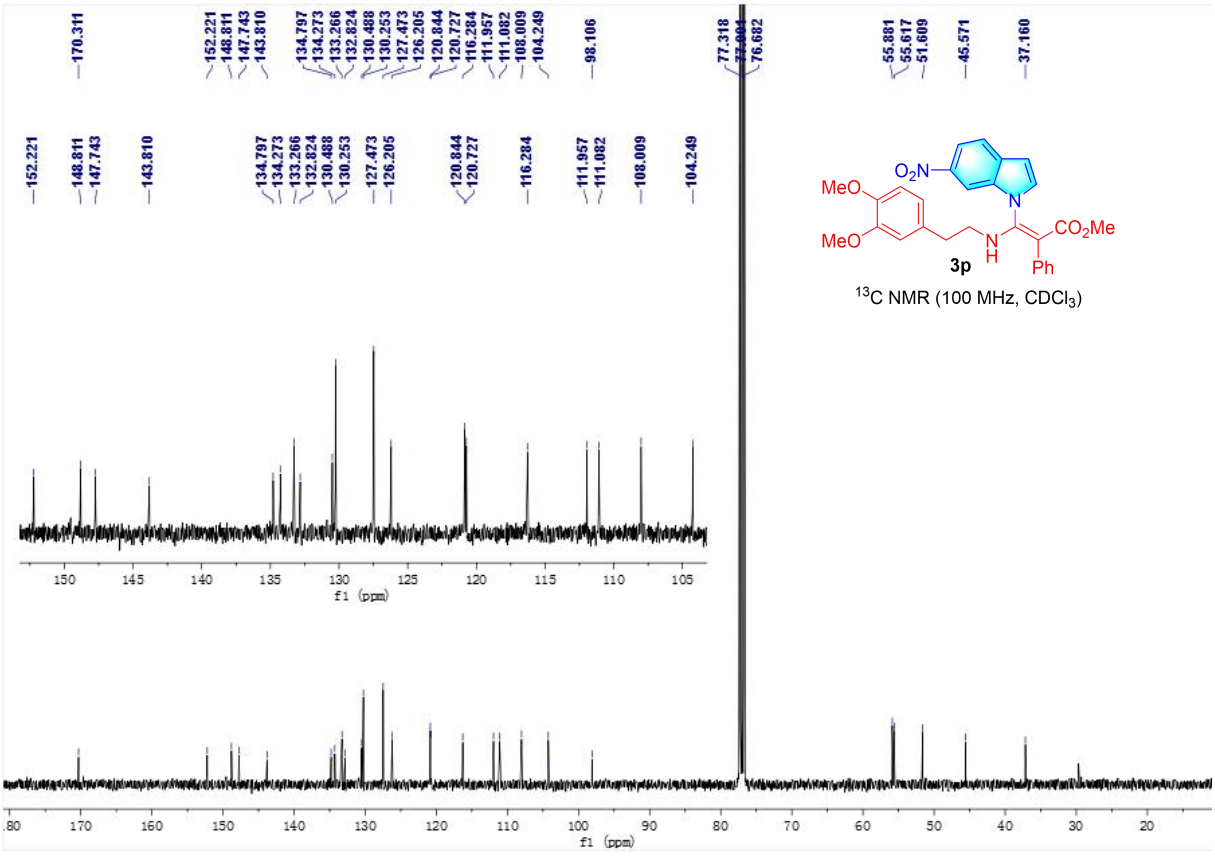
9.164
8.252
7.988
7.985
7.966
7.963
7.501
7.480
7.260
6.918
6.909
6.783
6.761
6.607
6.586
6.562
6.554
6.532
6.527
6.320
6.312
3.865
3.797
3.731
3.249
3.234
3.219
3.201
3.186
3.172
2.987
2.969
2.952
2.935
2.917
2.899
2.789
2.772
2.754
2.737
2.721
2.704
2.686
1.602
1.251
0.877
0.823
0.89
0.90
0.95
1.03
3.06
3.16
1.02
2.08
1.00
3.08
3.03
3.00
0.98
1.07
2.05
f1 (ppm)
MeO
MeO
O2N
N
N
H
CO2Me
Ph
3p
13C NMR (100 MHz, CDCl3)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147.743
143.810
134.797
134.273
133.266
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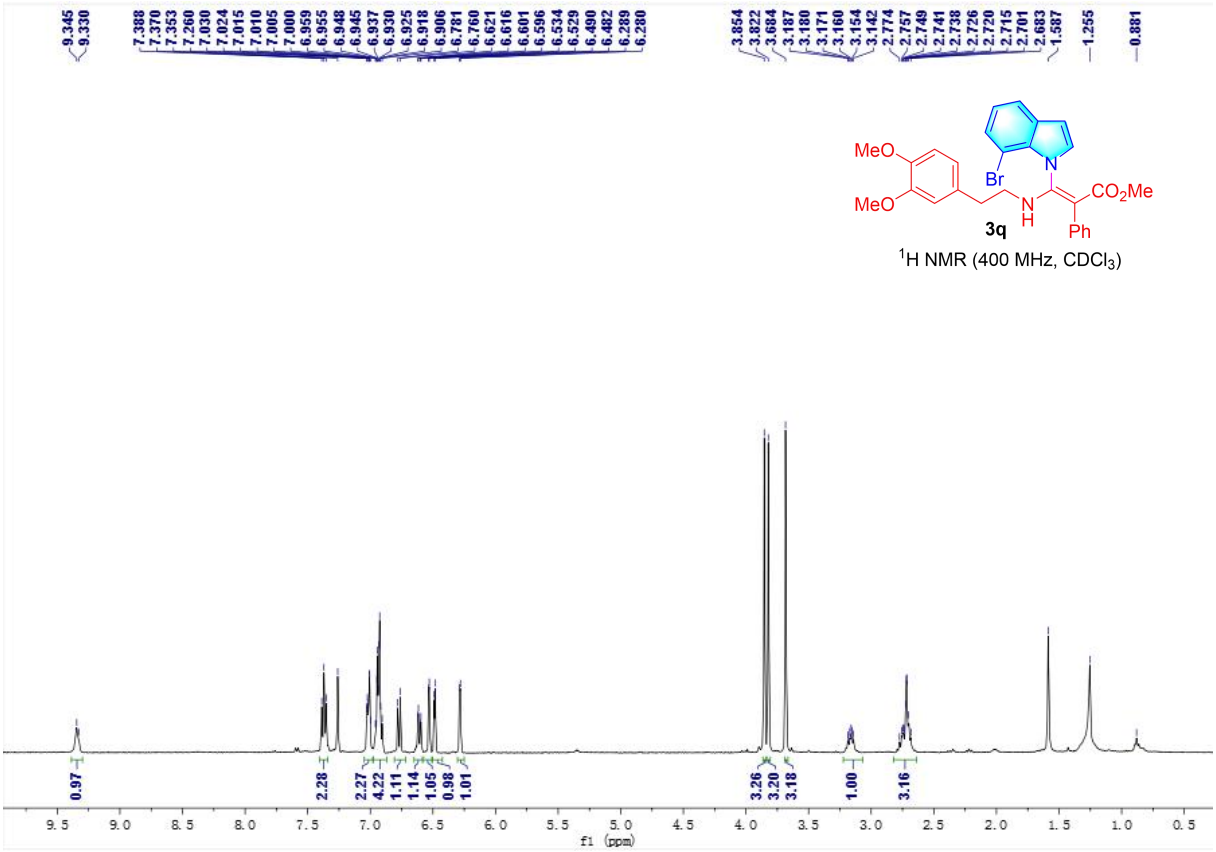
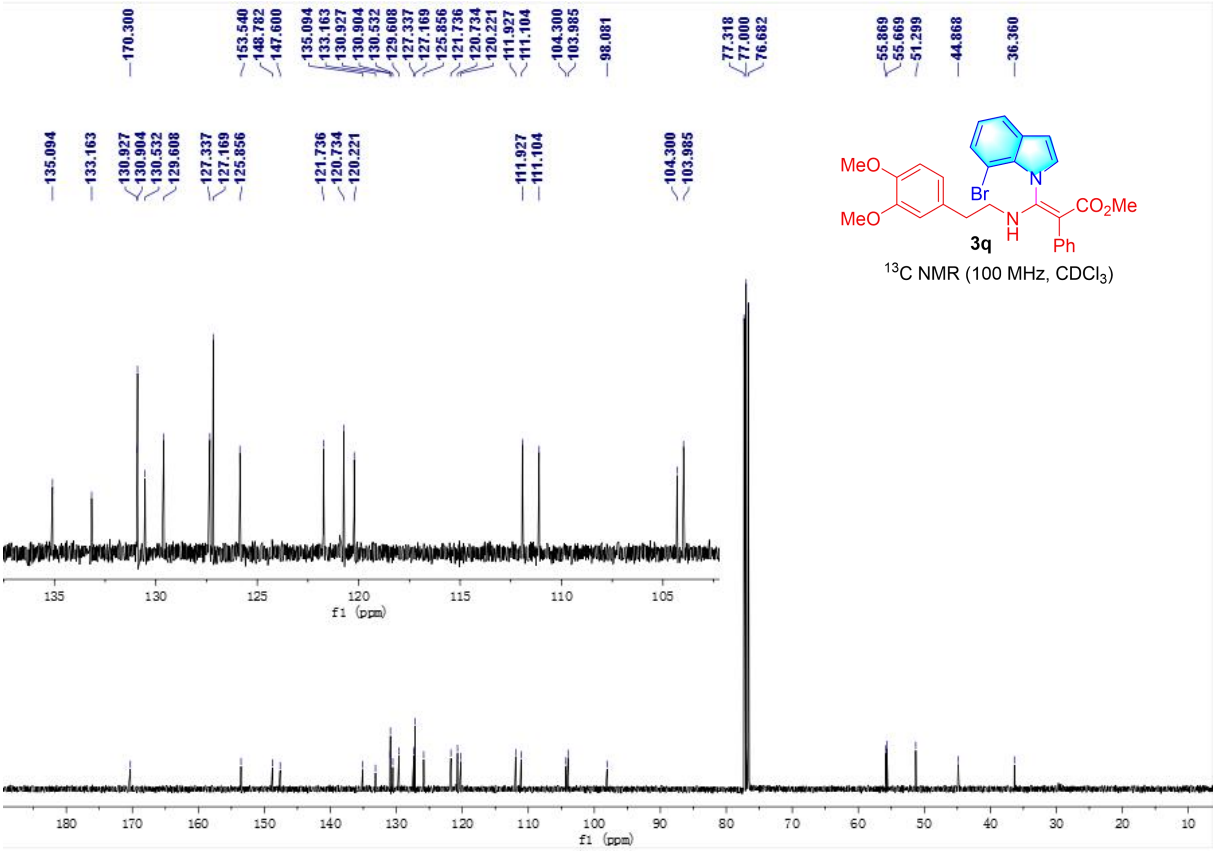
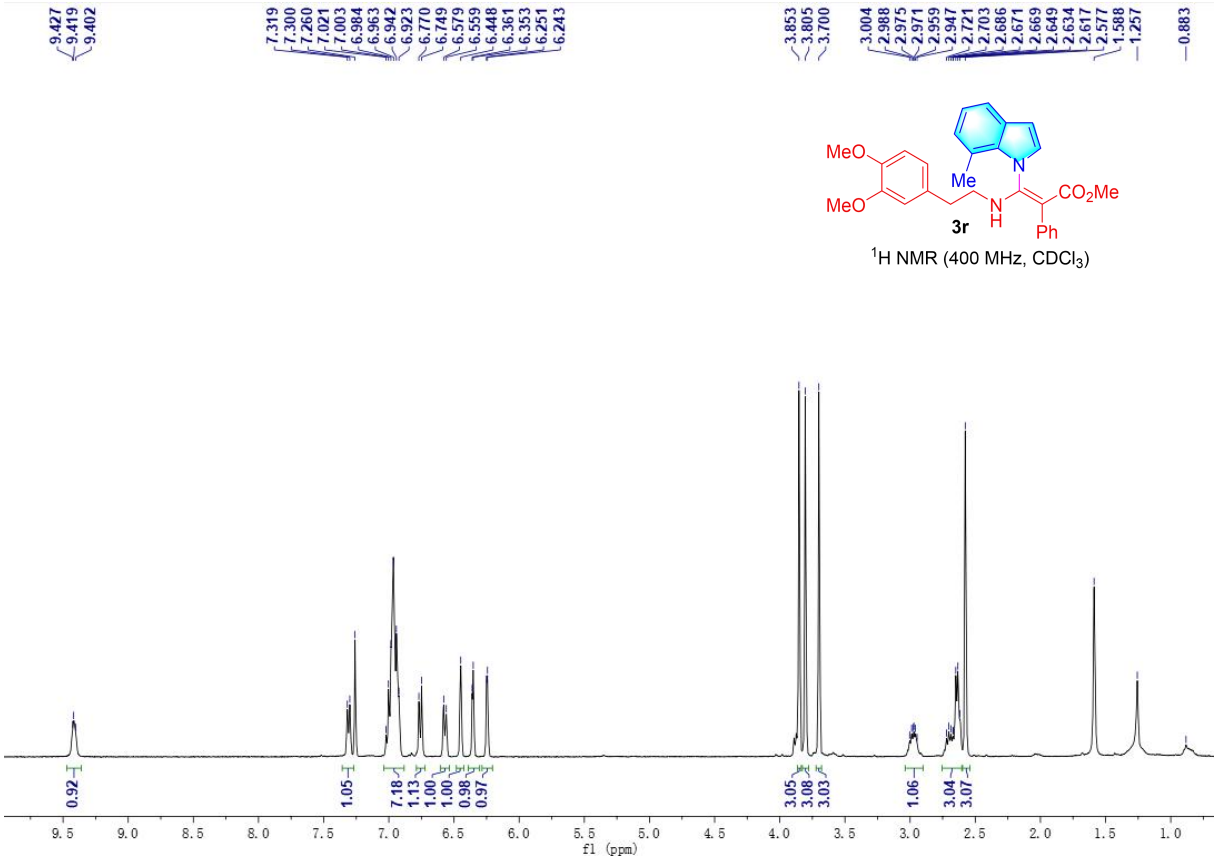
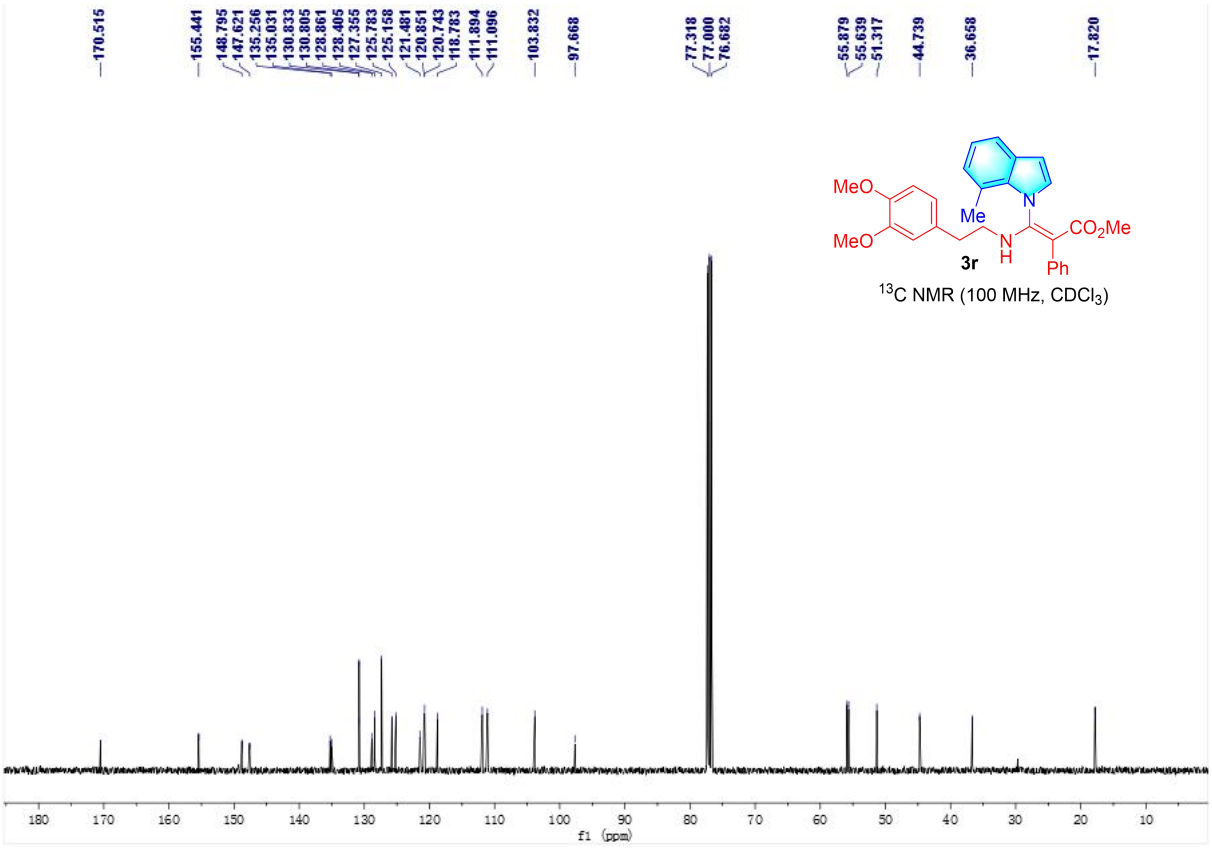
130.488
130.253
127.473
126.205
120.844
120.727
116.284
111.957
111.082
108.009
104.249
98.106
77.318
76.682
55.881
55.617
51.609
45.571
37.160
f1 (ppm)
MeO
MeO
O2N
N
N
H
CO2Me
Ph
3p
13C NMR (100 MHz, CDCl3)


MeO
MeO
Br
N
N
H
CO2Me
Ph
3q
1H NMR (400 MHz, CDCl3)
f1 (ppm)

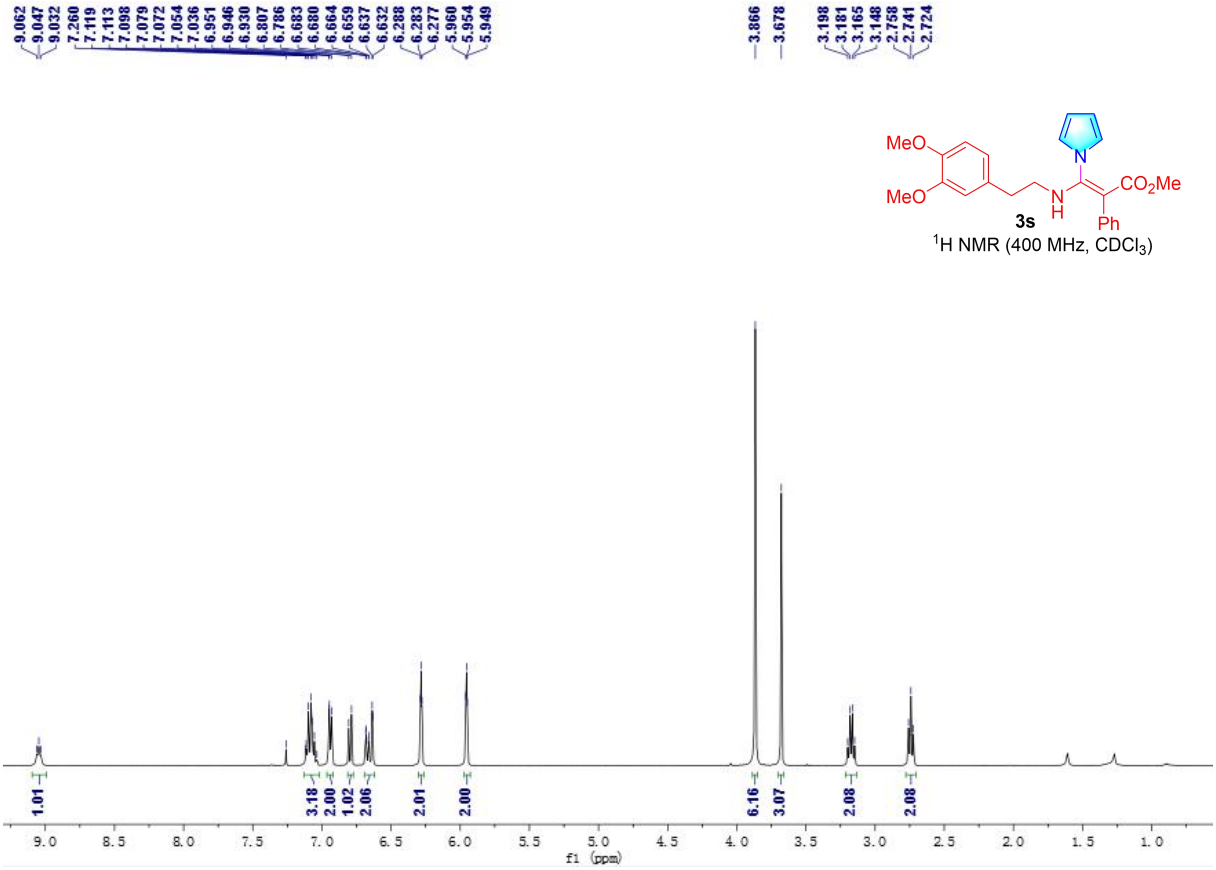

MeO
MeO
Br
N
N
H
CO2Me
Ph
3q
13C NMR (100 MHz, CDCl3)
f1 (ppm)



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



^{13}C NMR (100 MHz, $CDCl_3$)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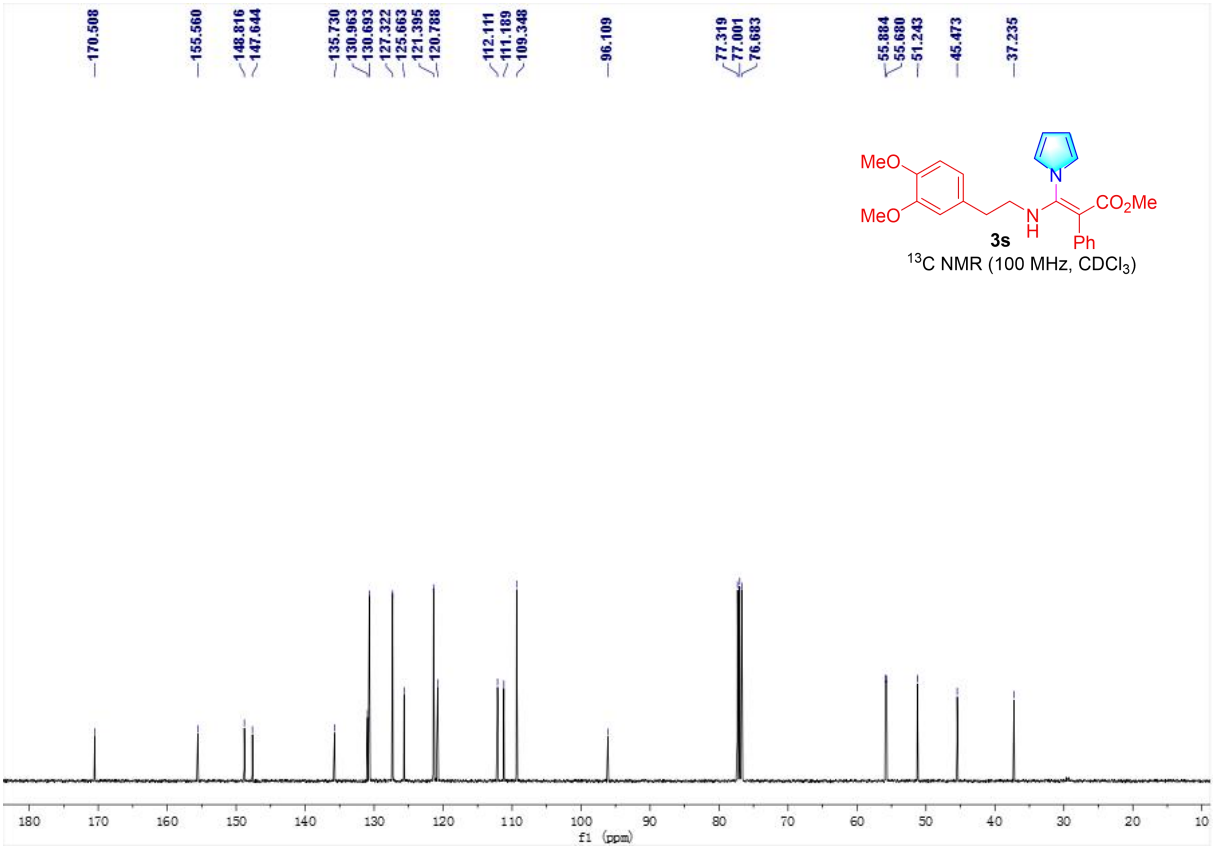
7.260
7.119
7.113
7.098
7.079
7.072
7.054
7.036
6.951
6.946
6.930
6.807
6.786
6.683
6.680
6.664
6.659
6.637
6.632
6.288
6.283
6.277
5.960
5.954
5.949
3.866
3.678
3.198
3.181
3.165
3.148
2.758
2.741
2.724
MeO
MeO
N
H
N
CO2Me
Ph
3s
1H NMR (400 MHz, CDCl3)
1.01
3.18
2.00
1.02
2.06
2.01
2.00
6.16
3.07
2.08
2.08
f1 (ppm)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148.816
147.644
135.730
130.963
130.693
127.322
125.663
121.395
120.788
112.111
111.189
109.348
96.109
77.319
77.001
76.683
55.884
55.680
51.243
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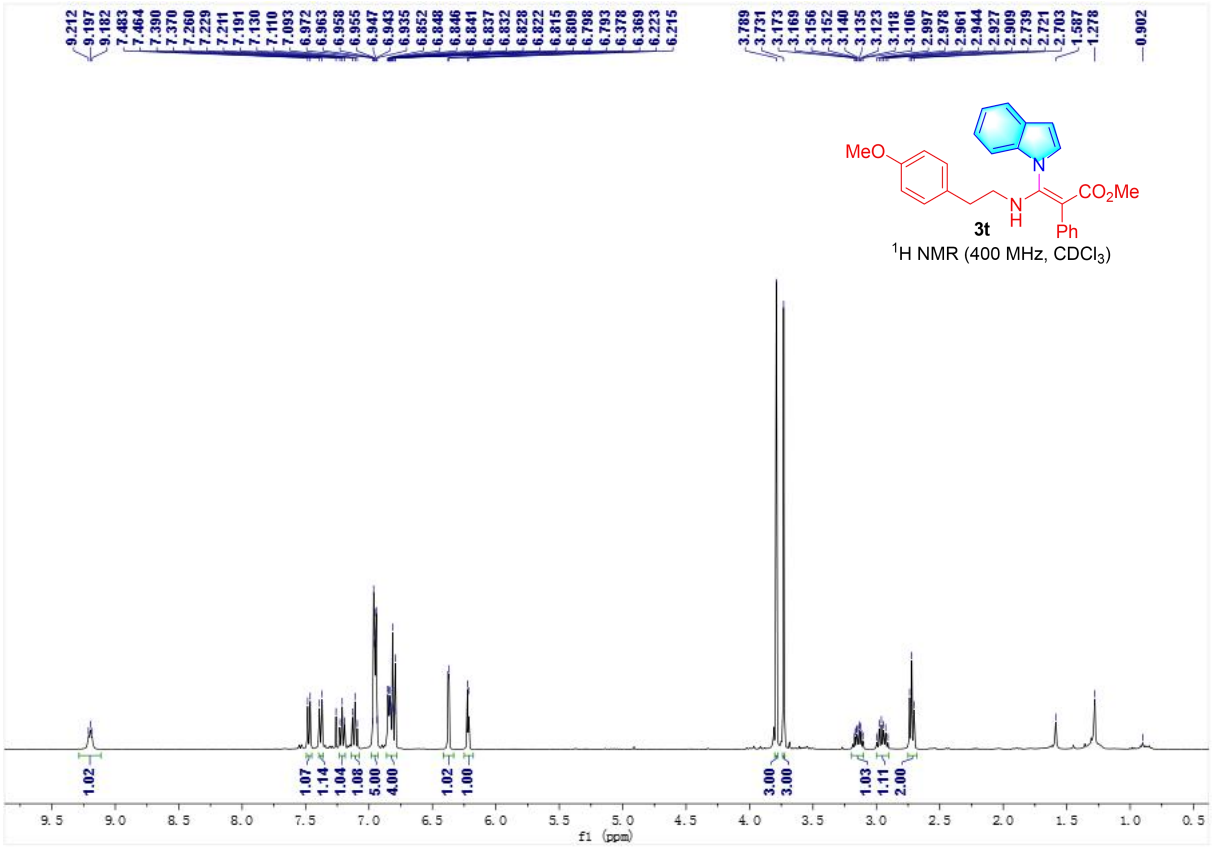
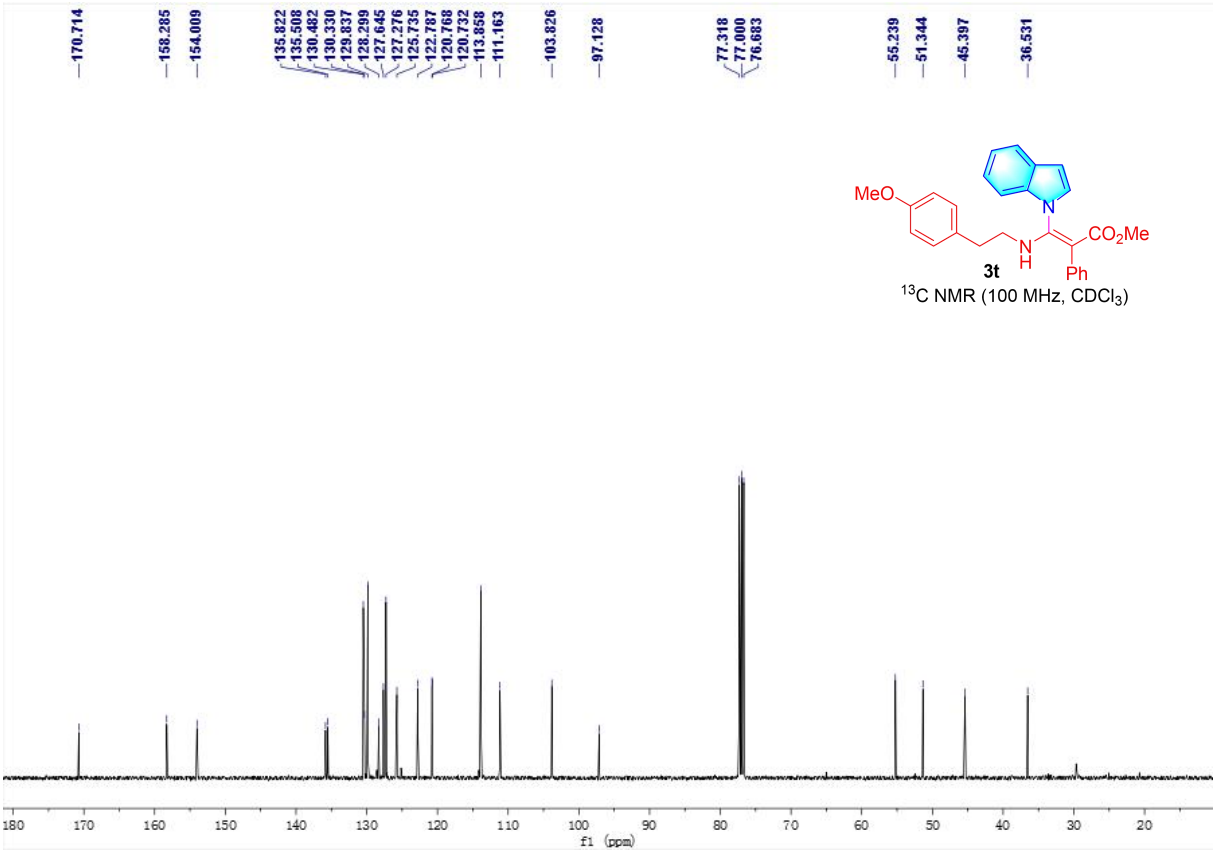
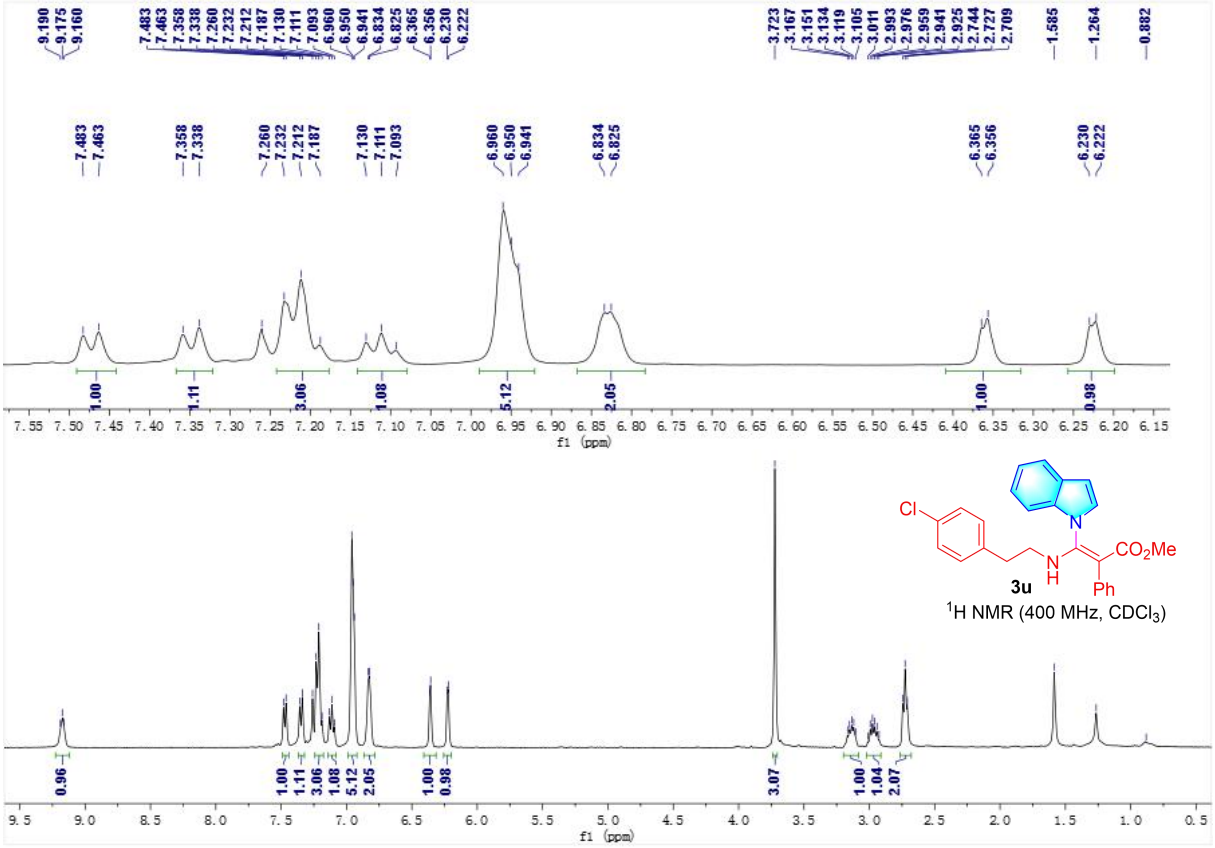
MeO
MeO
N
H
N
CO2Me
Ph
3s
13C NMR (100 MHz, CDCl3)
f1 (ppm)


MeO
N
N
H
CO2Me
Ph
3t
1H NMR (400 MHz, CDCl3)
f1 (ppm)


MeO
N
N
H
CO2Me
Ph
3t
13C NMR (100 MHz, CDCl3)
f1 (ppm)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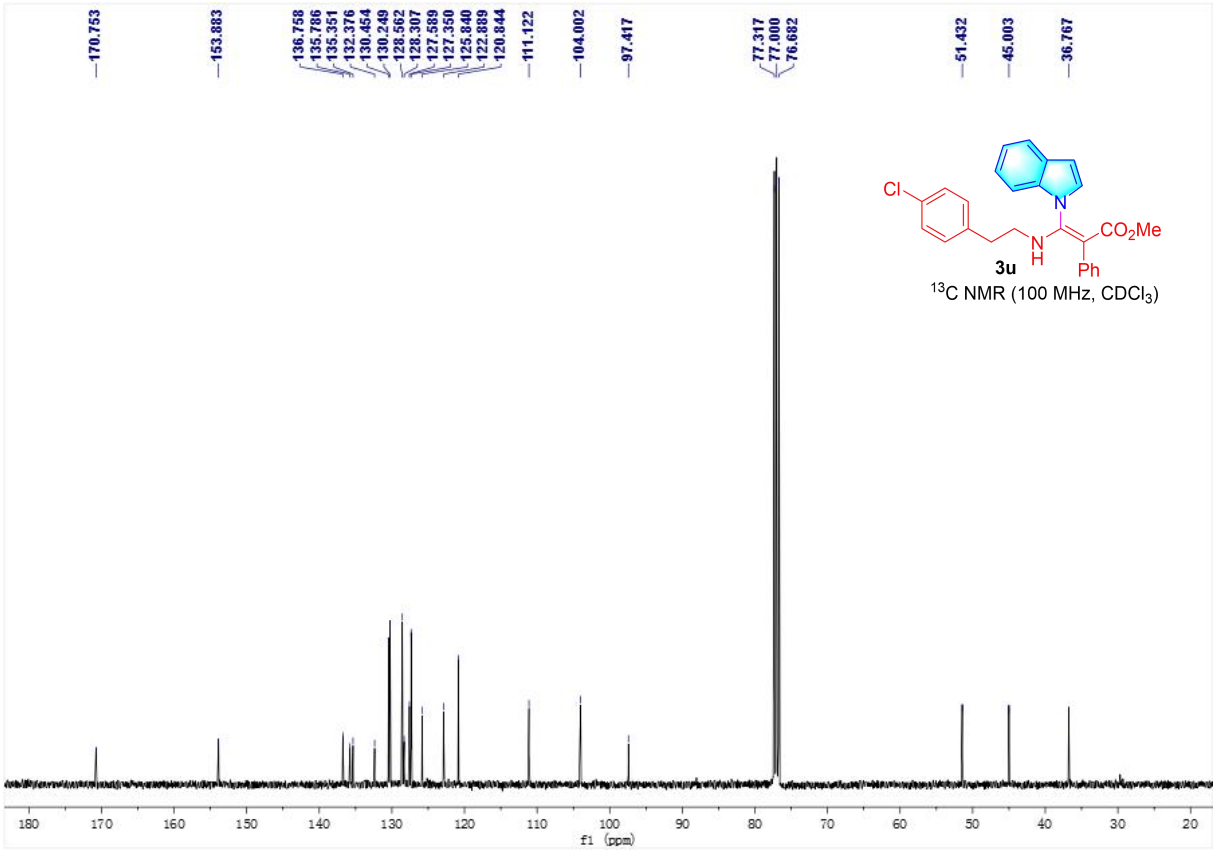
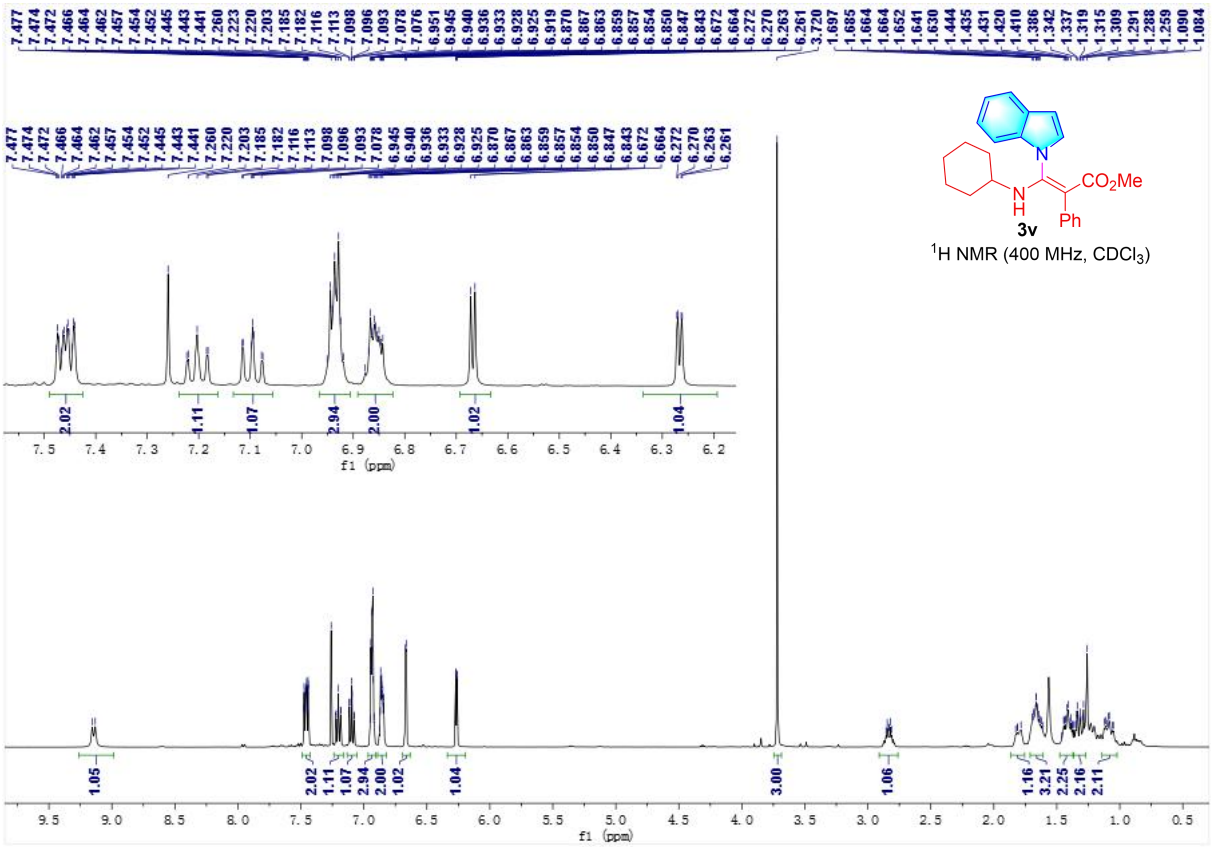
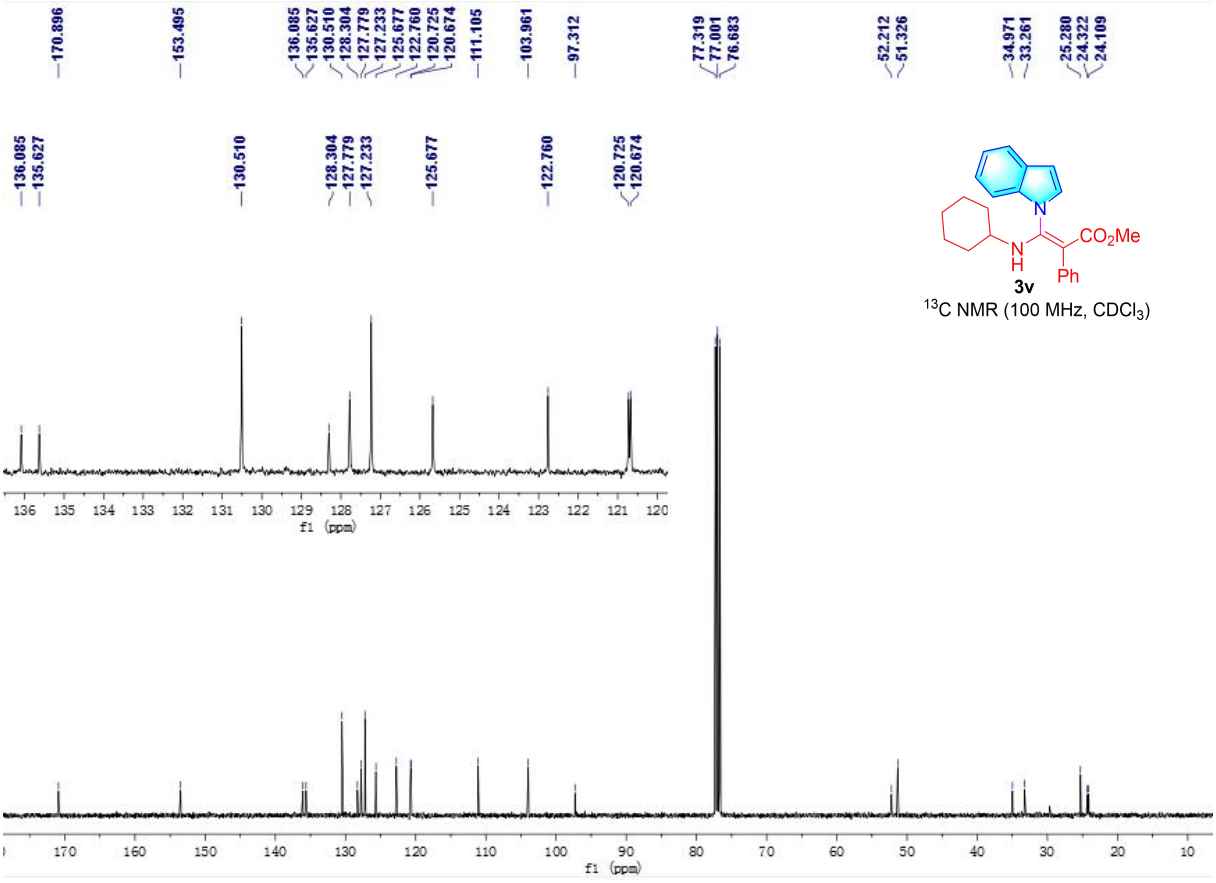
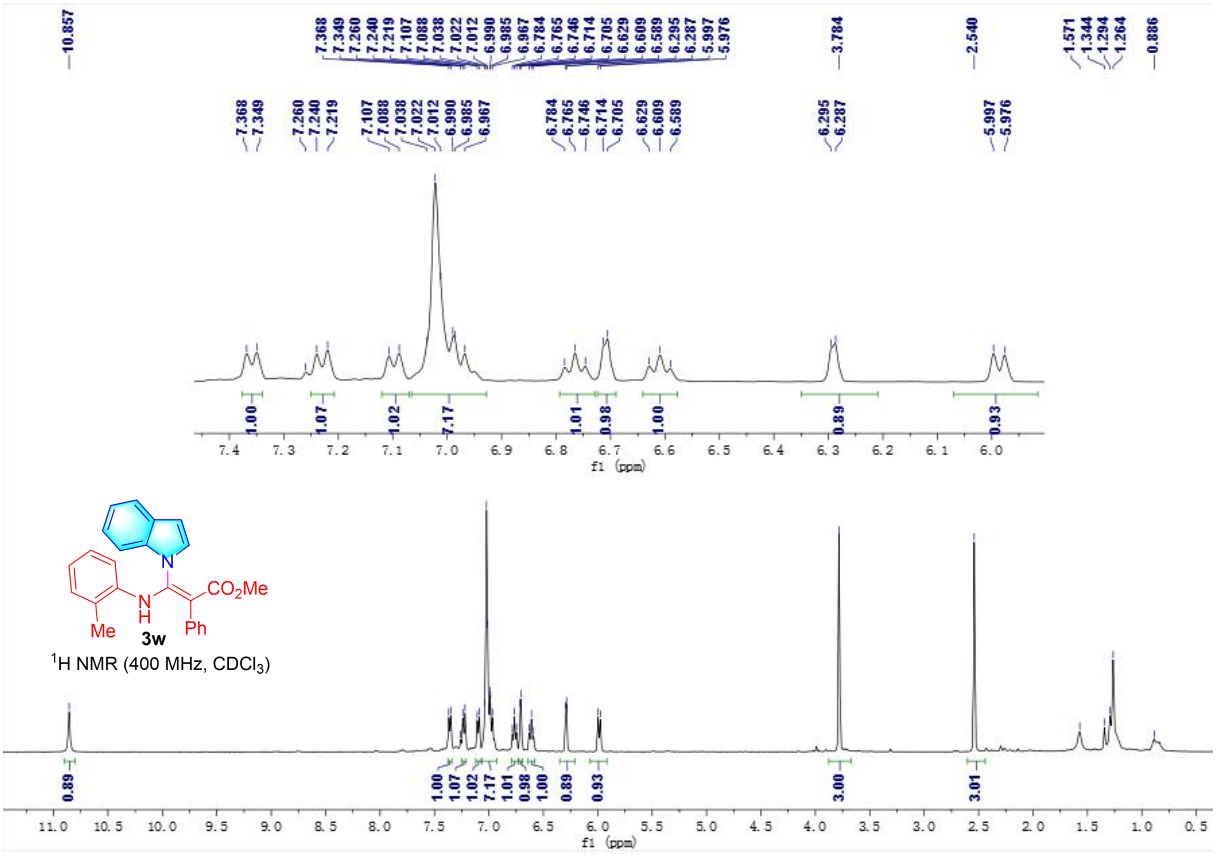
9.175
9.160
7.483
7.463
7.358
7.338
7.260
7.232
7.212
7.187
7.130
7.111
7.093
6.960
6.950
6.941
6.834
6.825
6.365
6.356
6.230
6.222
3.723
3.167
3.151
3.134
3.119
3.105
3.011
2.993
2.976
2.959
2.941
2.925
2.744
2.727
2.709
1.585
1.264
0.882
f1 (ppm)
Cl
N
N
H
CO2Me
Ph
3u
1H NMR (400 MHz, CDCl3)

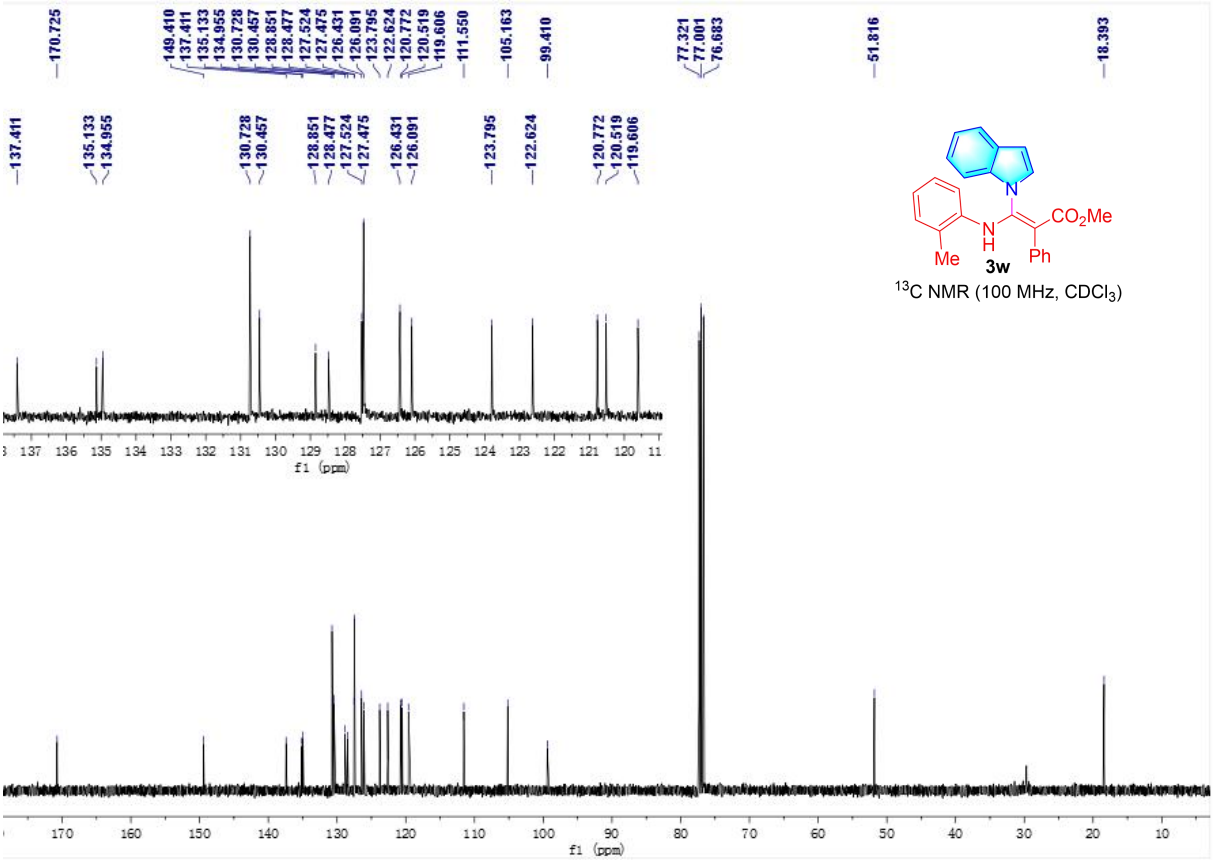

170.753
153.883
136.758
135.786
135.351
132.376
130.454
130.249
128.562
128.307
127.589
127.350
125.840
122.889
120.844
111.122
104.002
97.417
77.317
77.000
76.682
51.432
45.003
36.767
f1 (ppm)
Cl
N
N
H
CO2Me
Ph
3u
13C NMR (100 MHz, CDCl3)


3v
1H NMR (400 MHz, CDCl3)

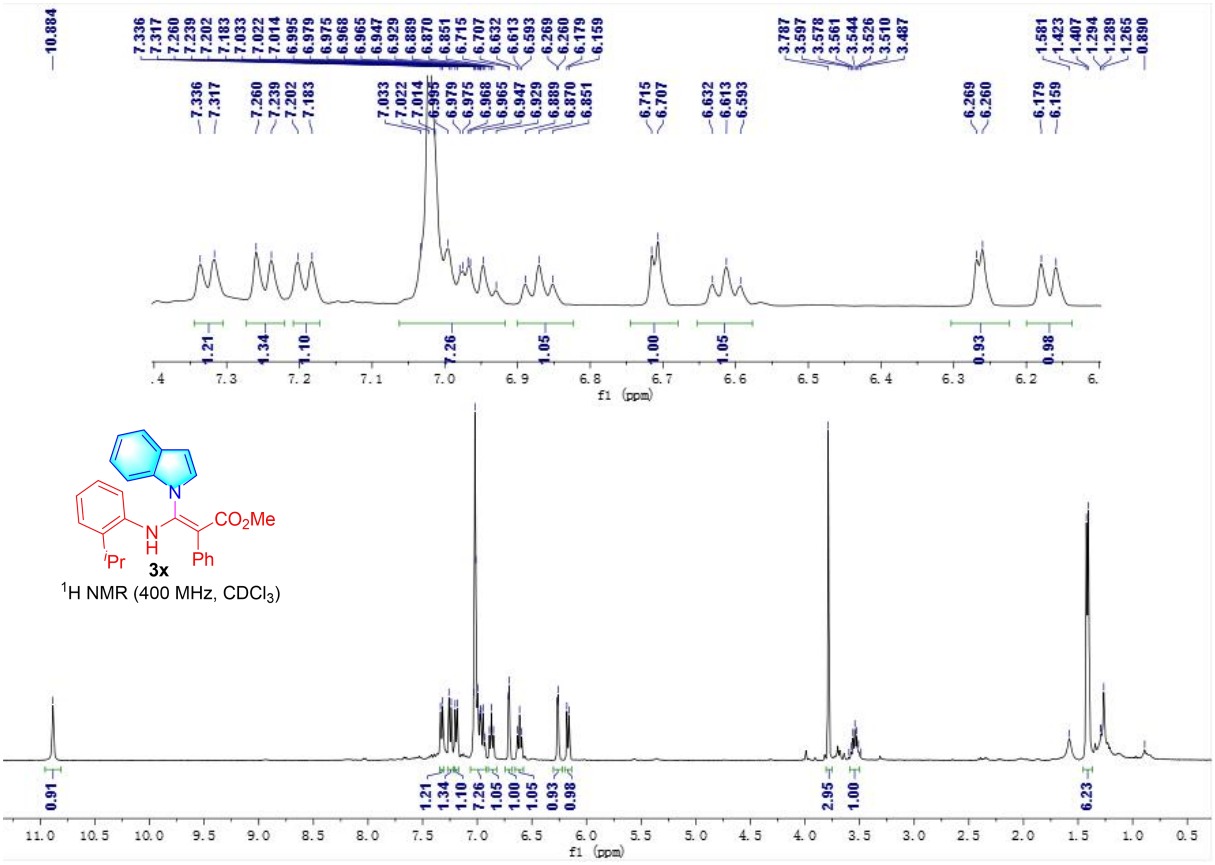

3v
13C NMR (100 MHz, CDCl3)

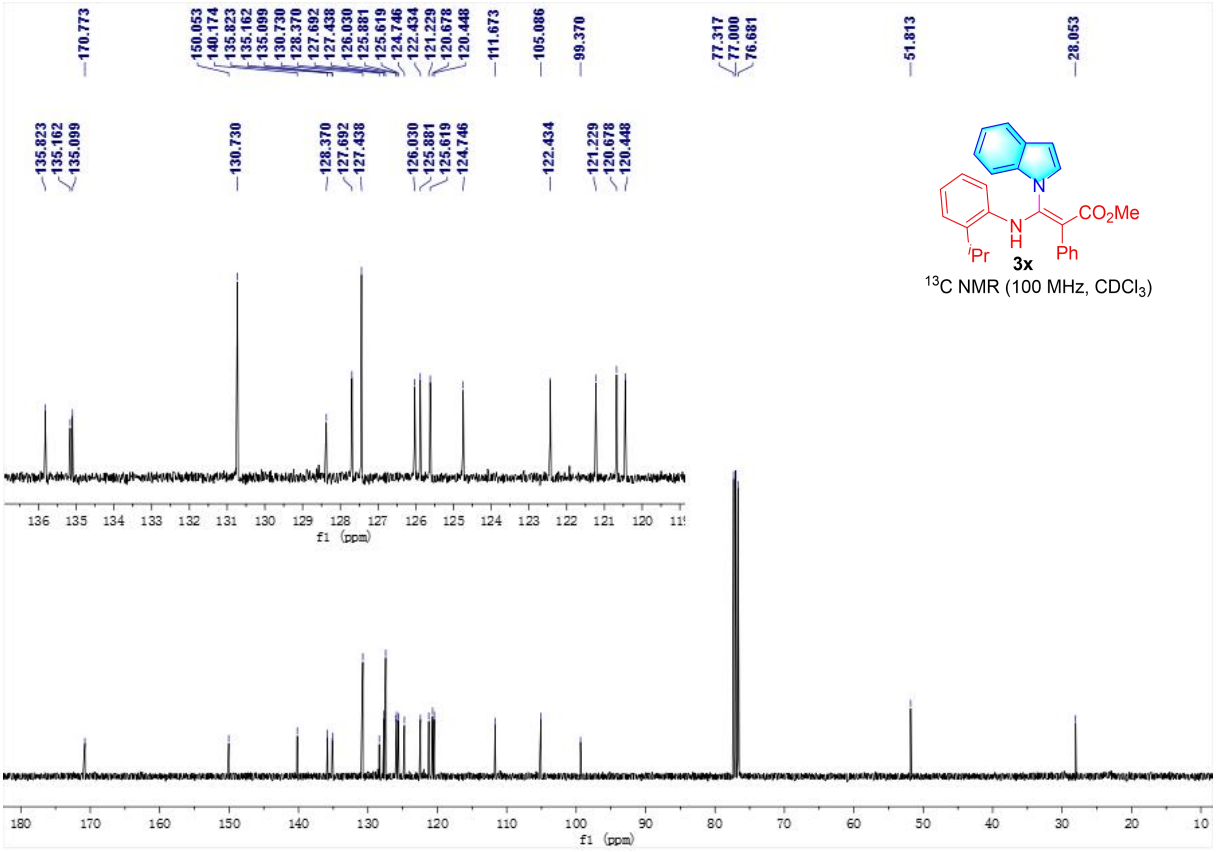


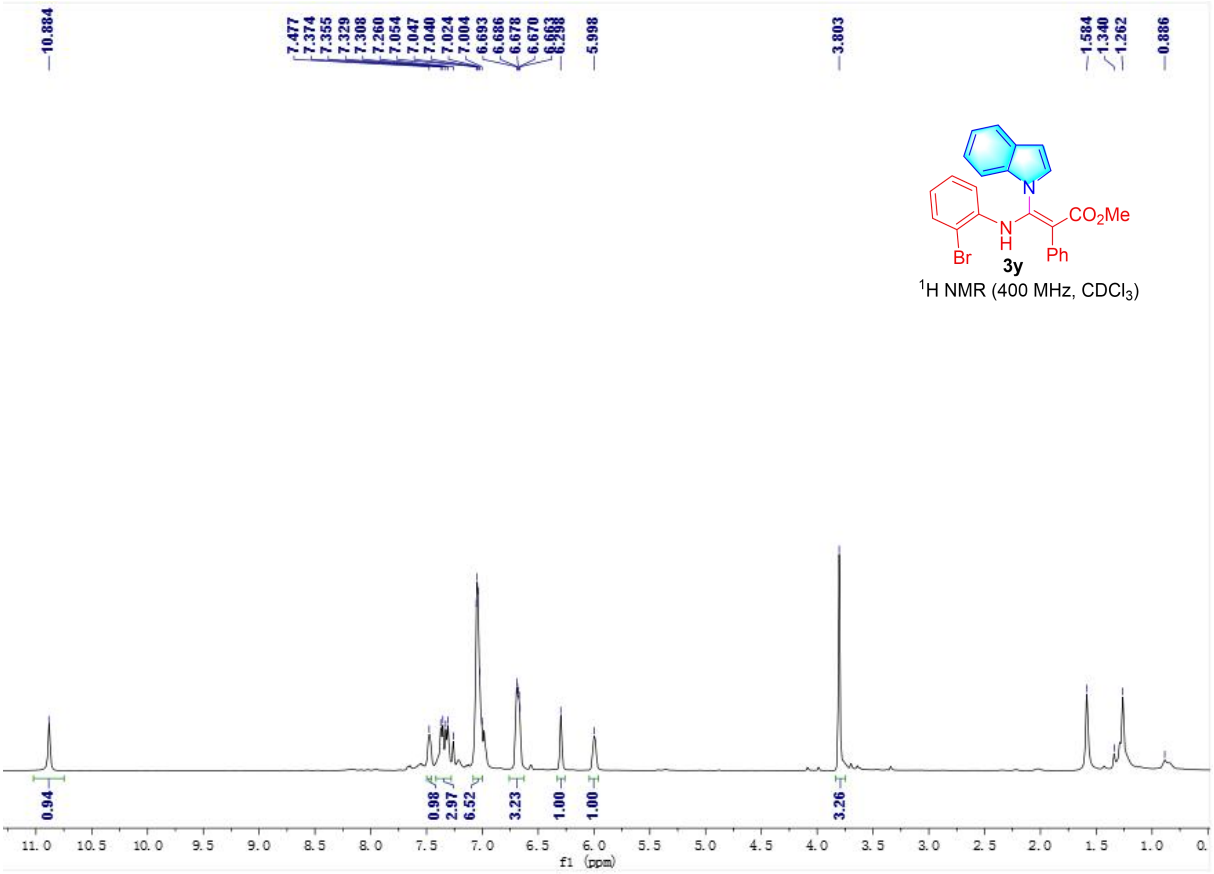
^{1}H NMR (400 MHz, $CDCl_3$)

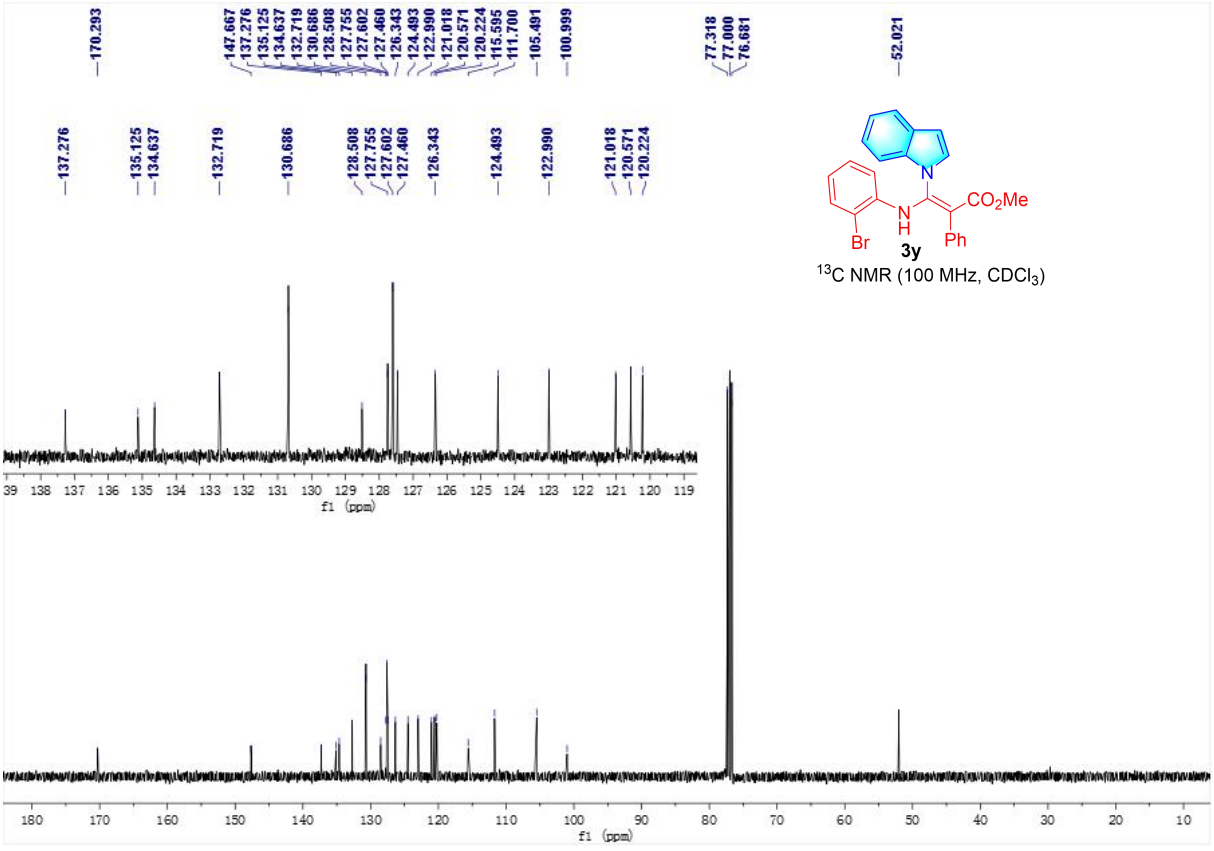


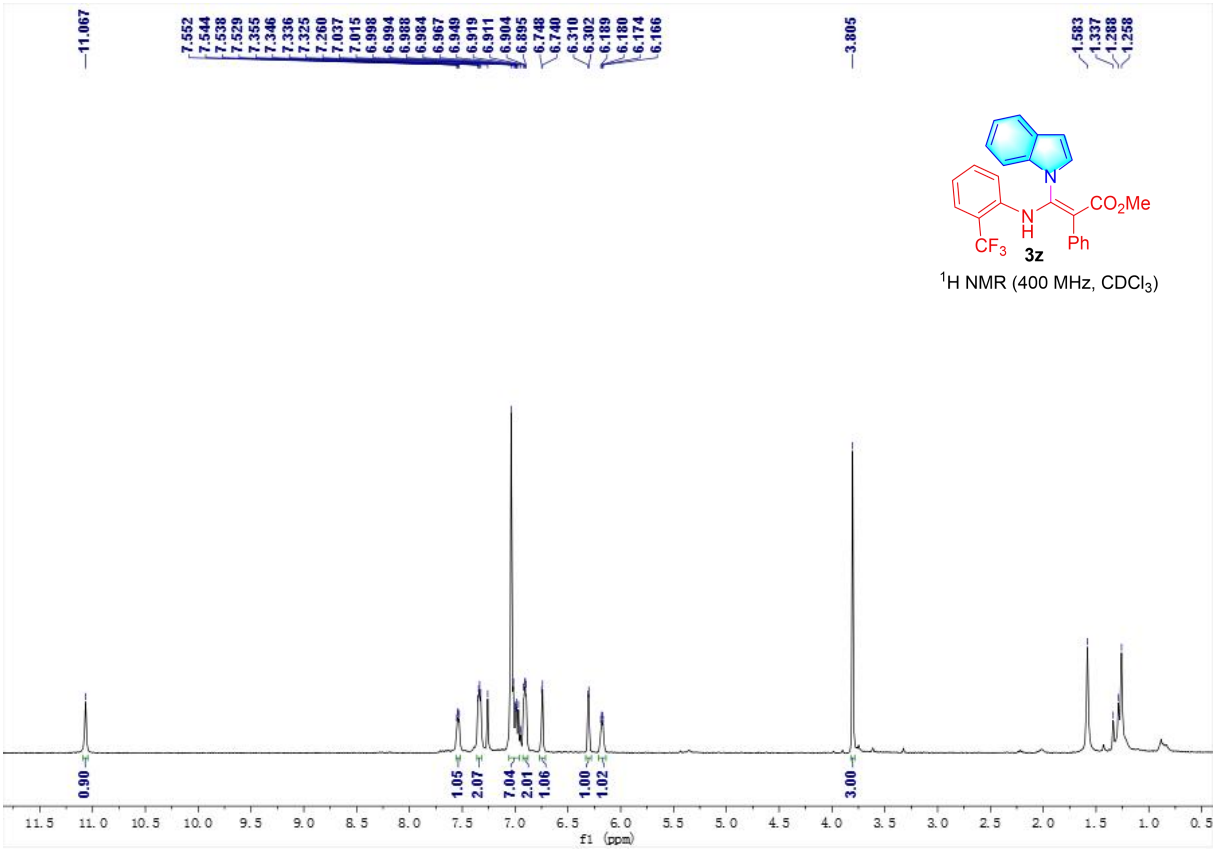
^{13}C NMR (100 MHz, $CDCl_3$)


3x
^{1}H NMR (400 MHz, CDCl$_3$)


3x
^{13}C NMR (100 MHz, CDCl$_3$)

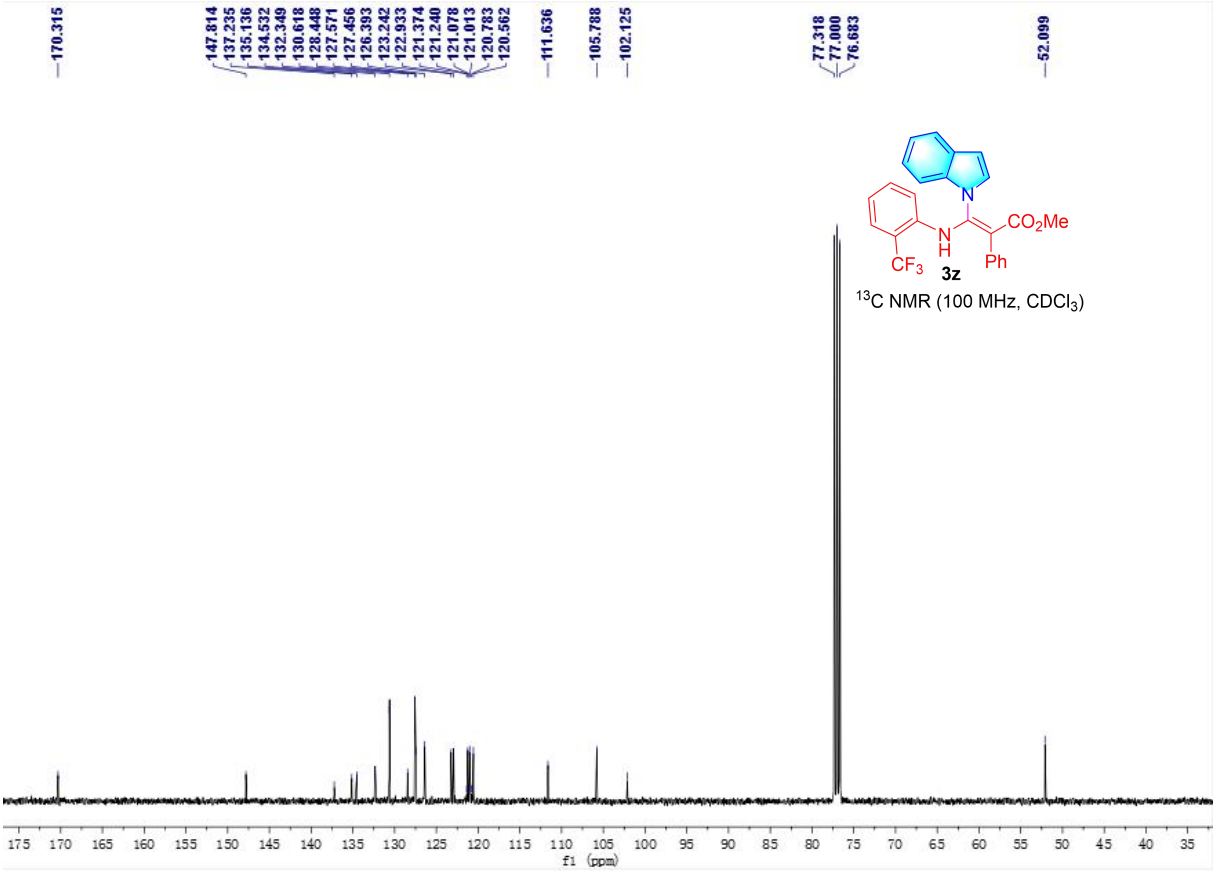

10.884
7.477
7.374
7.355
7.329
7.308
7.260
7.054
7.047
7.040
7.024
7.004
6.693
6.686
6.678
6.670
5.998
3.803
1.584
1.340
1.262
0.886
N
N
H
CO2Me
Br
Ph
3y
1H NMR (400 MHz, CDCl3)
0.94
0.98
2.97
6.52
3.23
1.00
1.00
3.26
f1 (ppm)


170.293
147.667
137.276
135.125
134.637
132.719
130.686
128.508
127.755
127.602
127.460
126.343
124.493
122.990
121.018
120.571
120.224
115.595
111.700
105.491
100.999
77.318
77.000
76.681
52.021
N
N
H
CO2Me
Br
Ph
3y
13C NMR (100 MHz, CDCl3)
f1 (ppm)



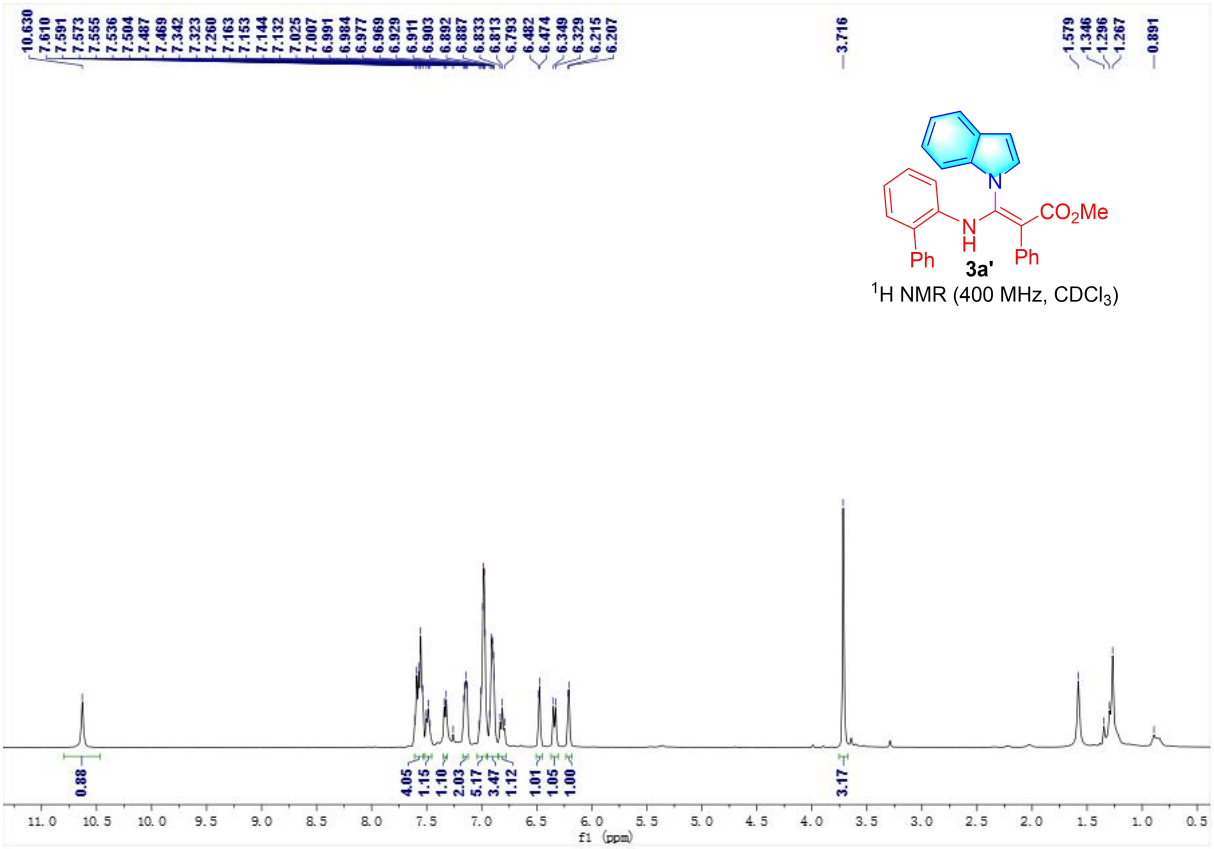
3z

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



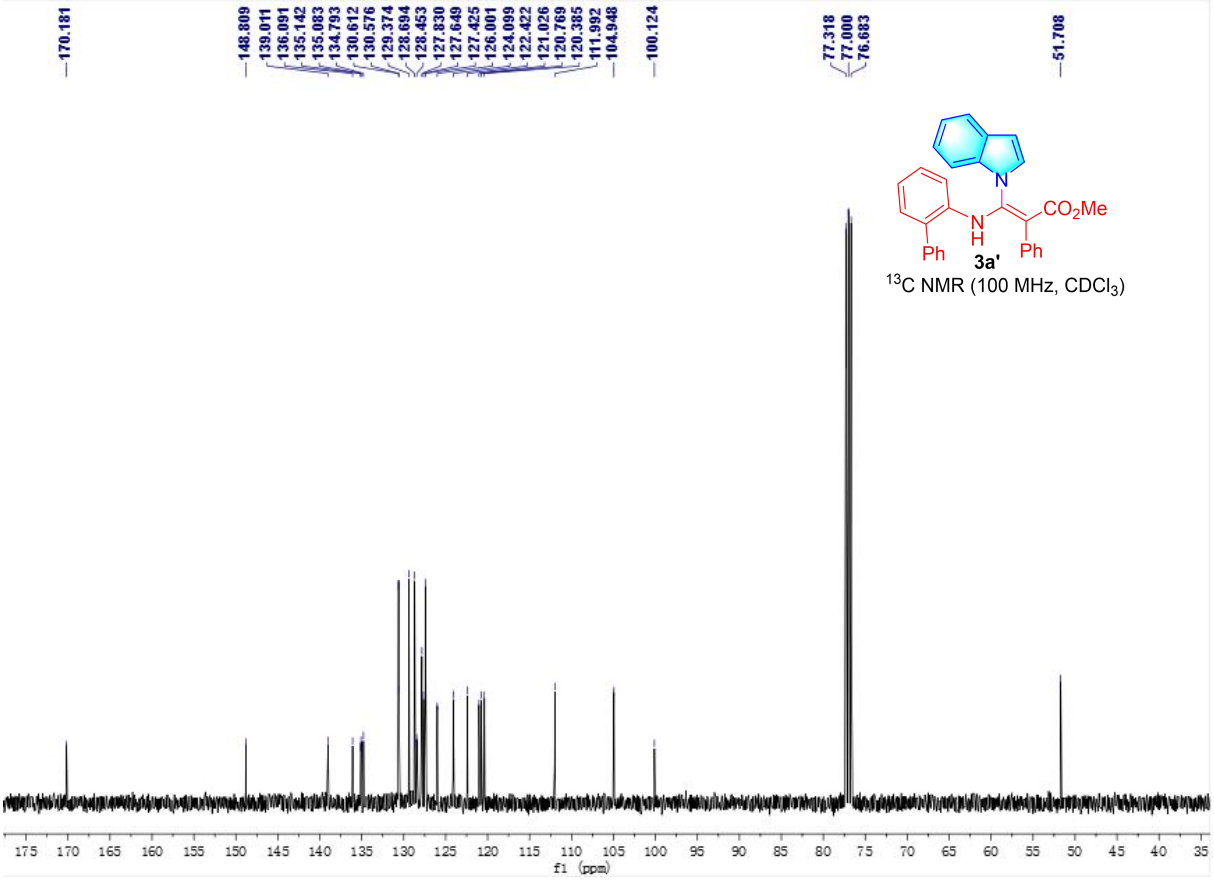
3z

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



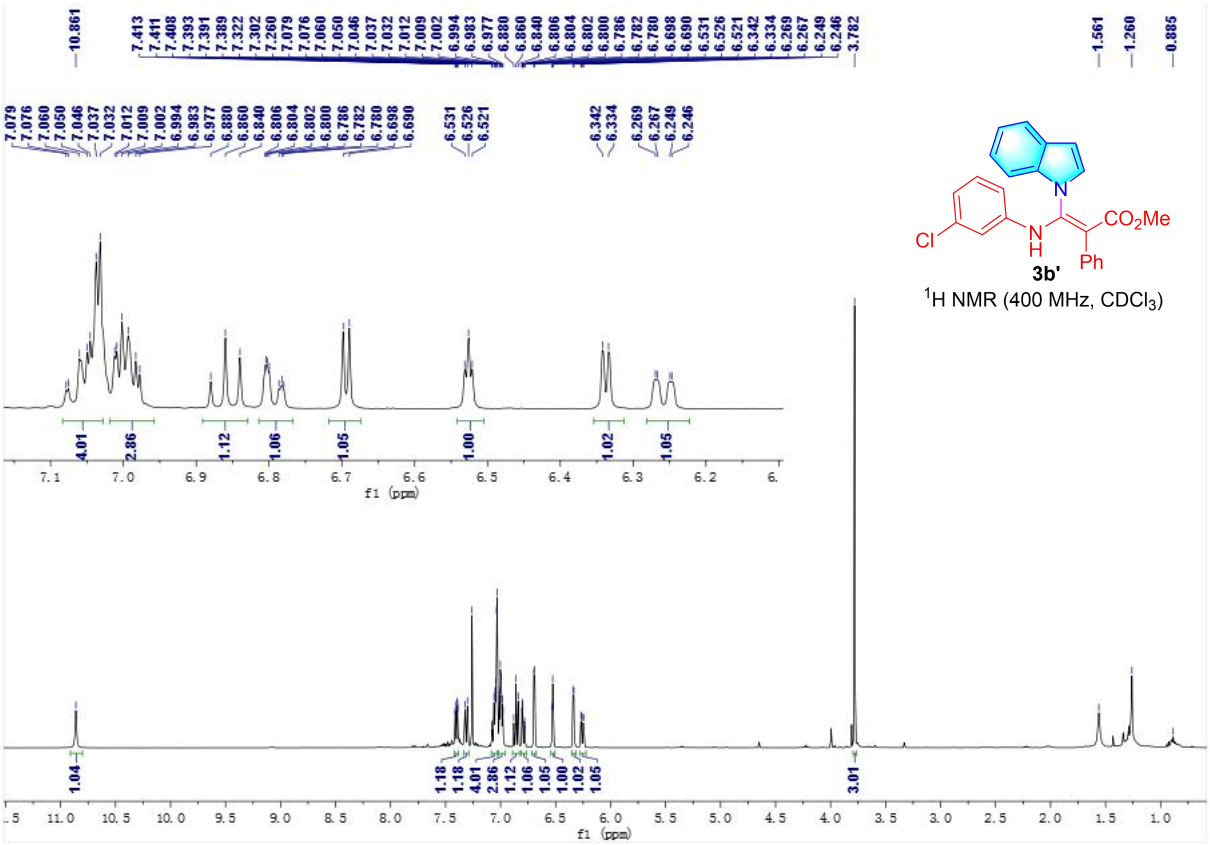
3a'

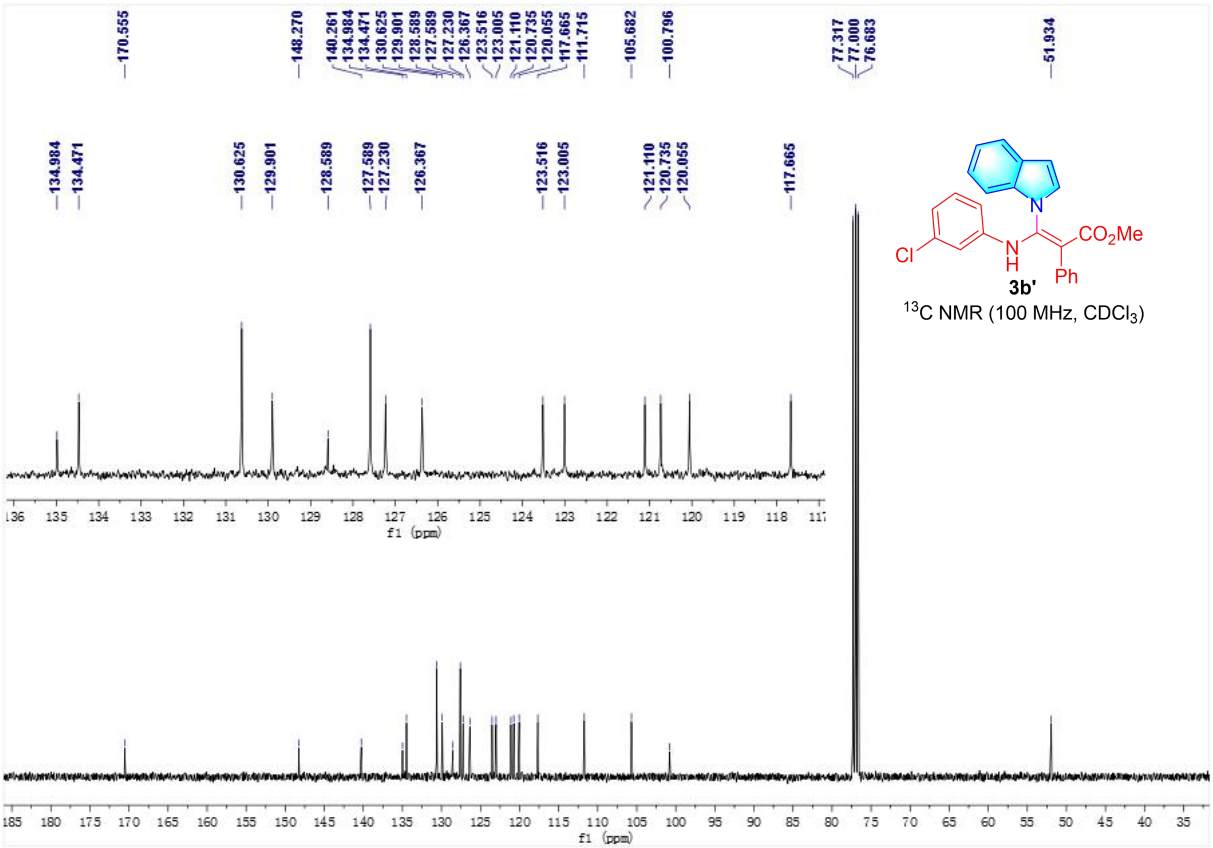
^{1}H NMR (400 MHz, $CDCl_3$)

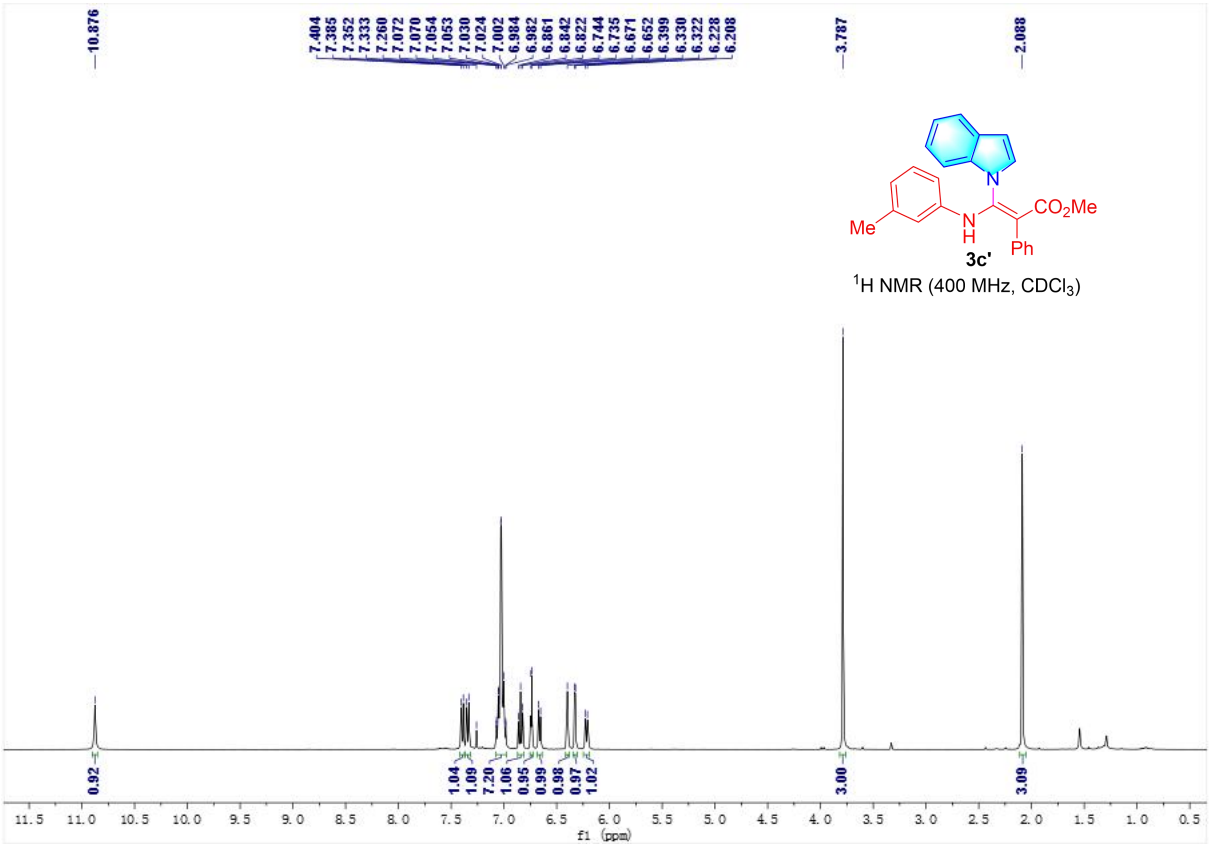


3a'

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

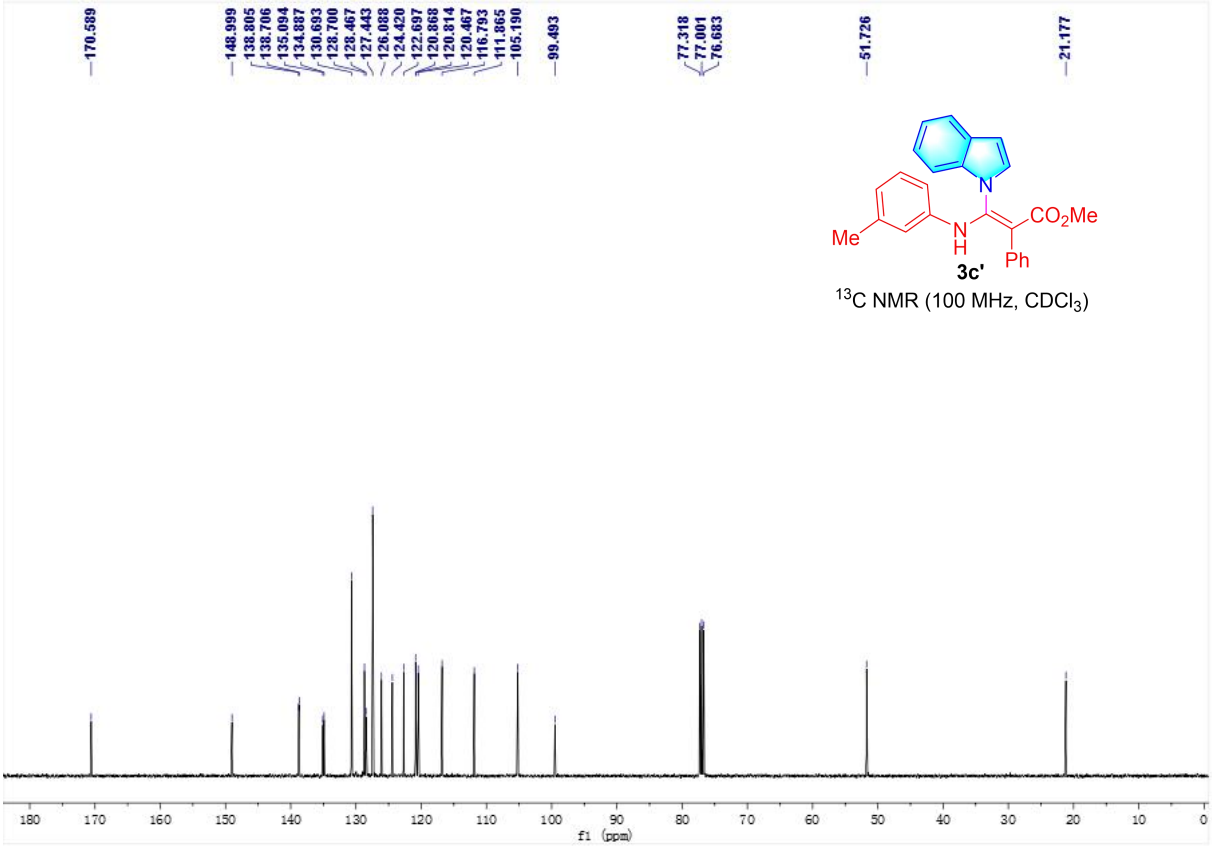

3b'
^{1}H NMR (400 MHz, $CDCl_3$)


3b'
^{13}C NMR (100 MHz, $CDCl_3$)



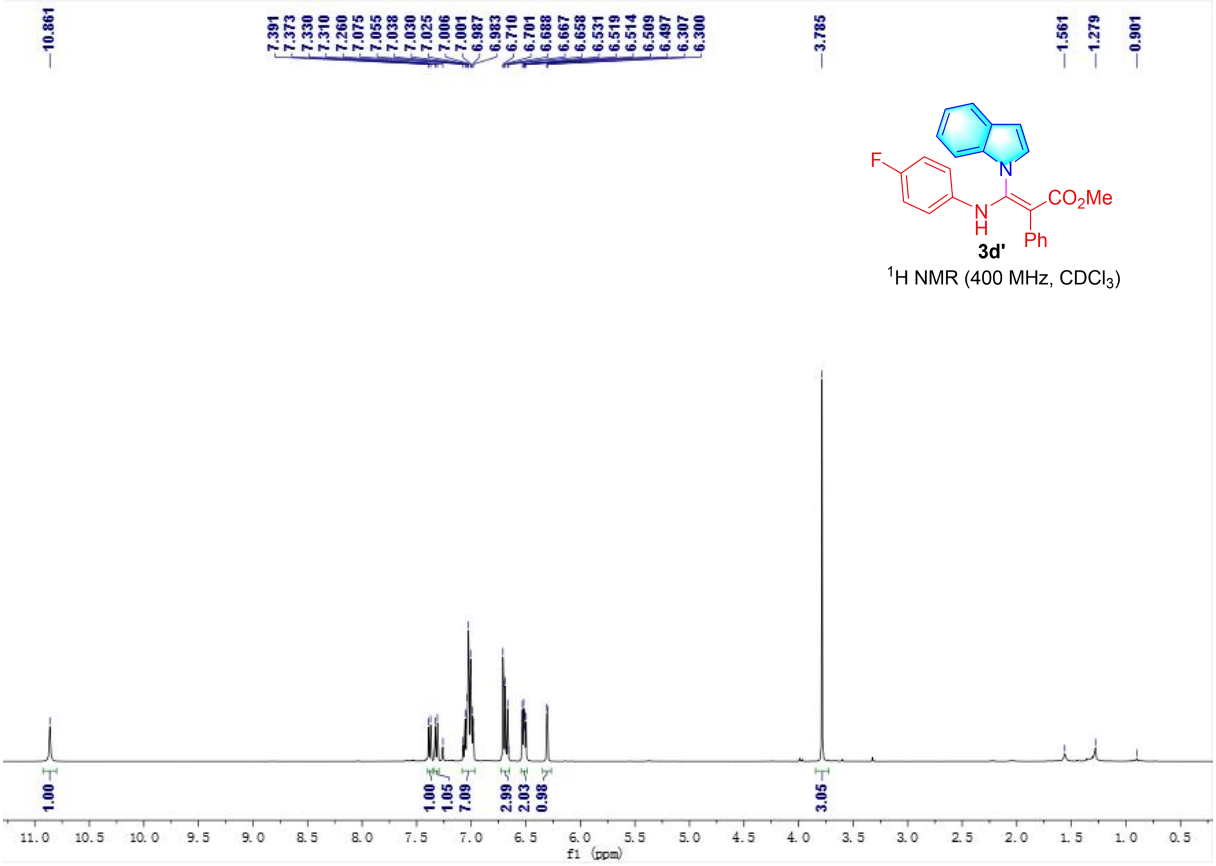
3c'

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

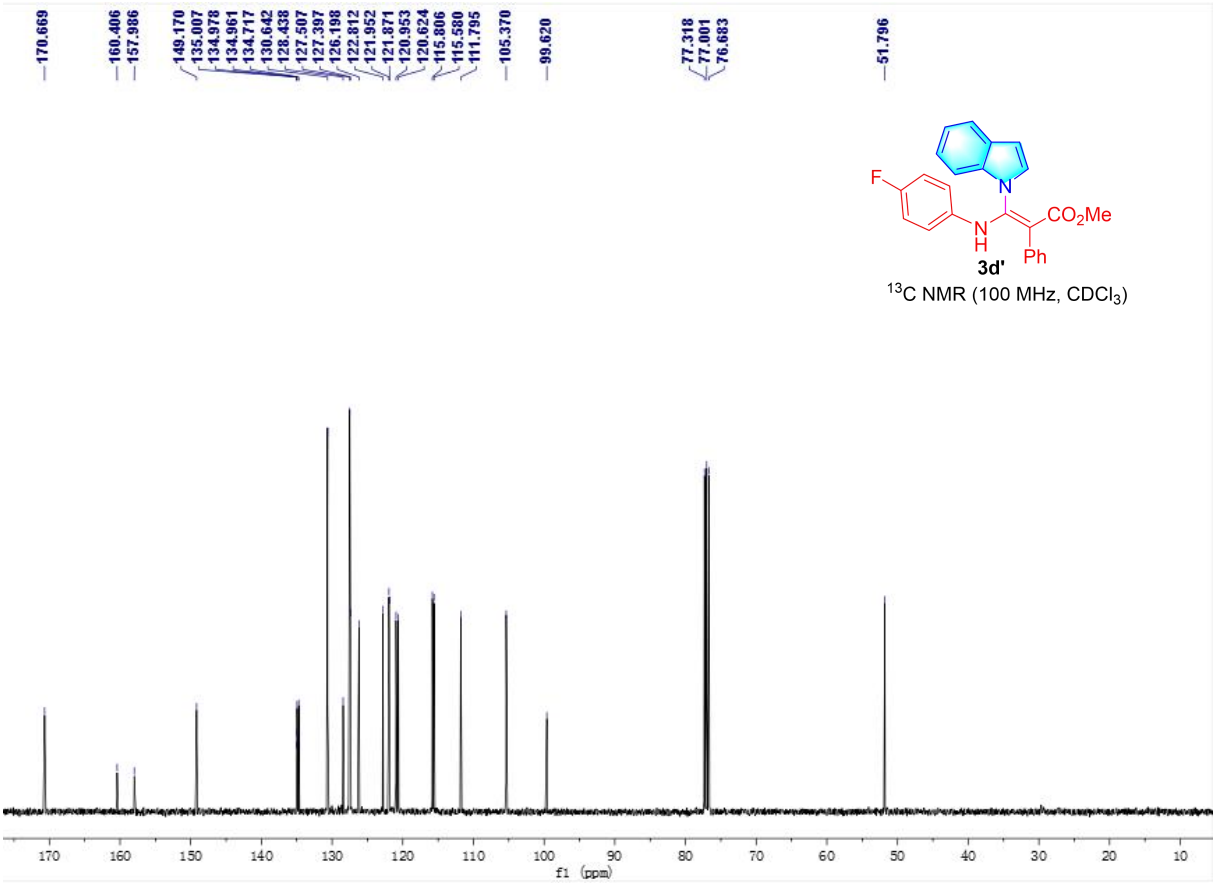


3c'

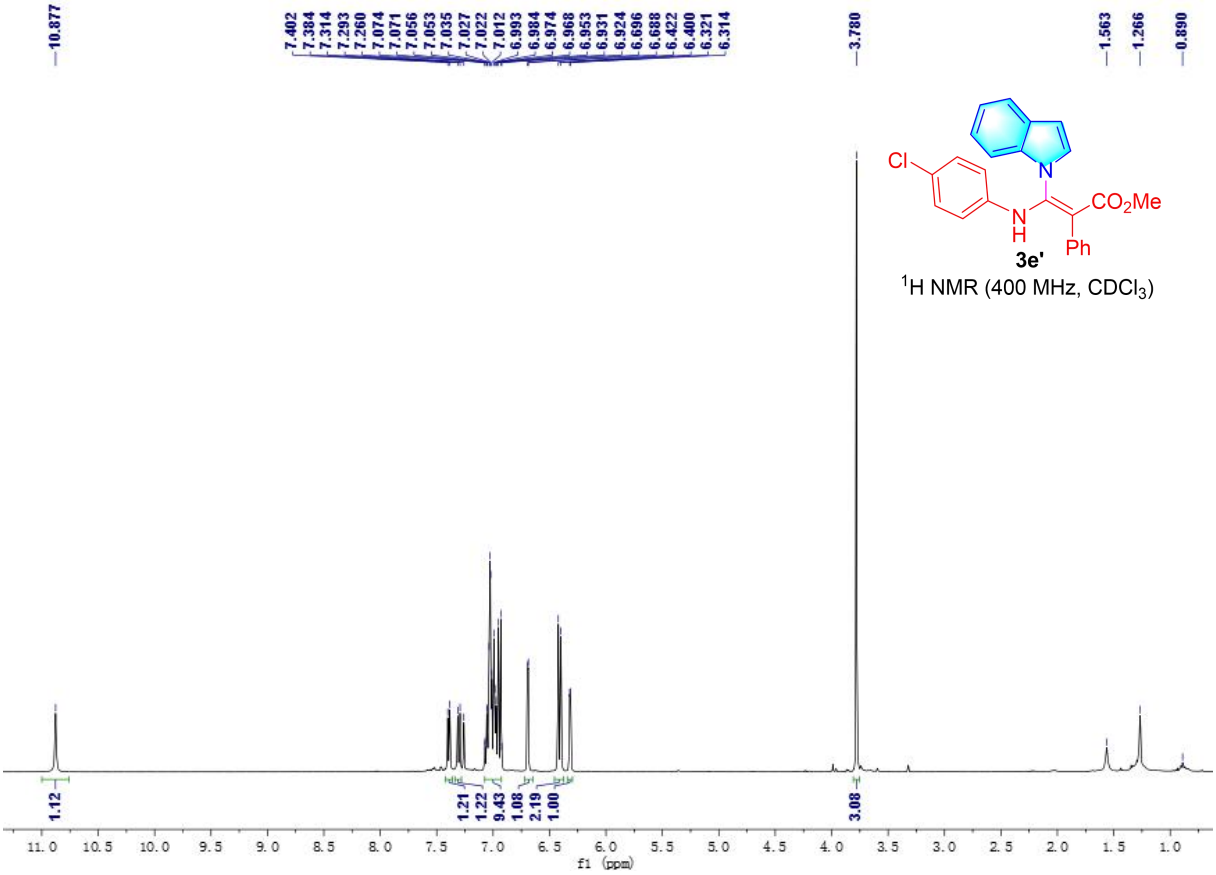
^{13}C NMR (100 MHz, $CDCl_3$)



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

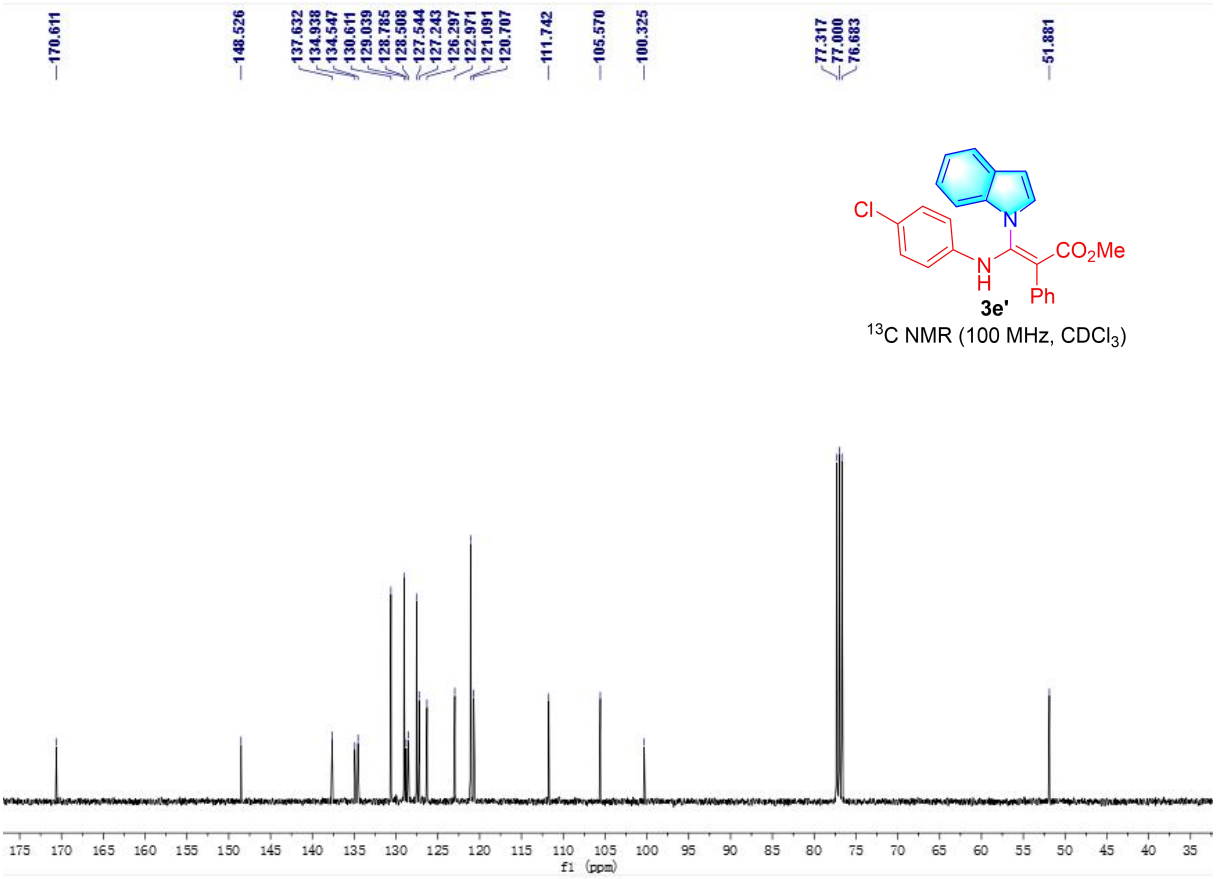


^{13}C NMR (100 MHz, $CDCl_3$)



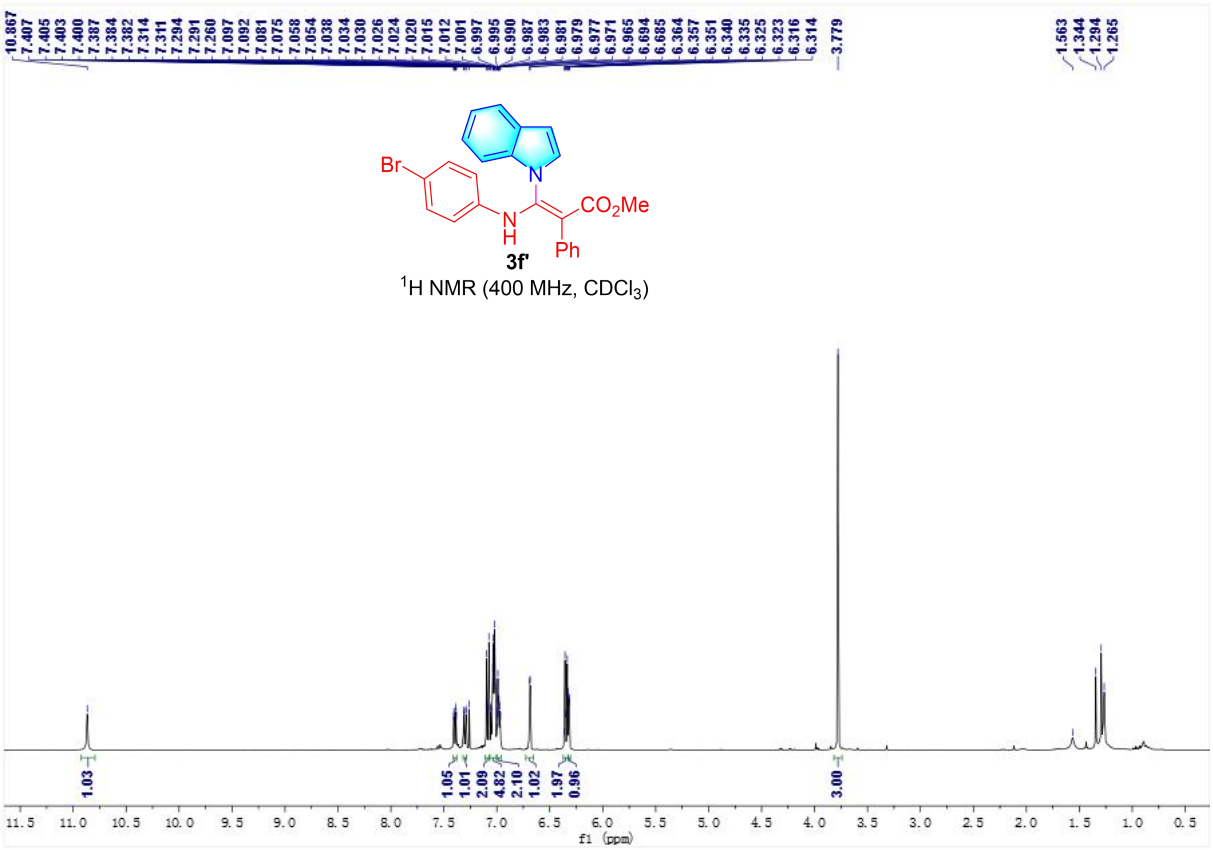
3e'

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



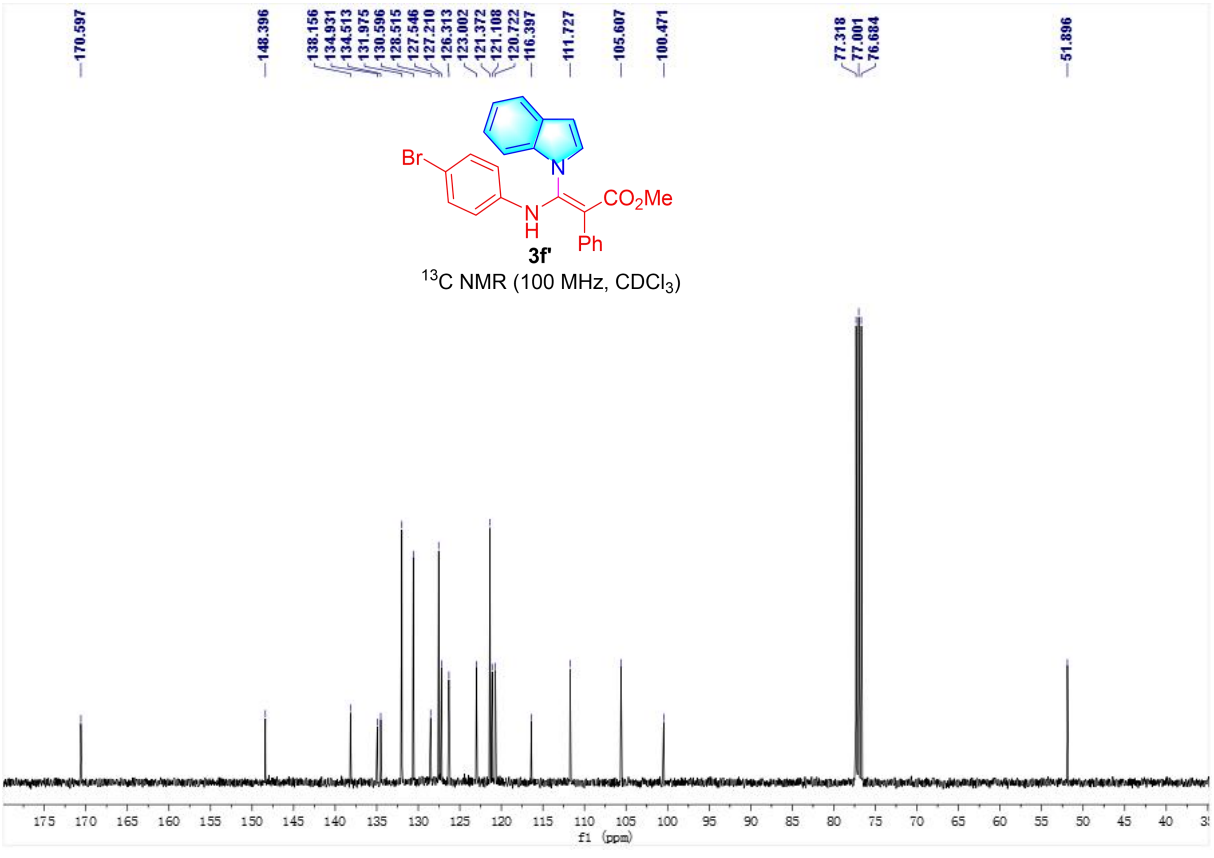
3e'

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



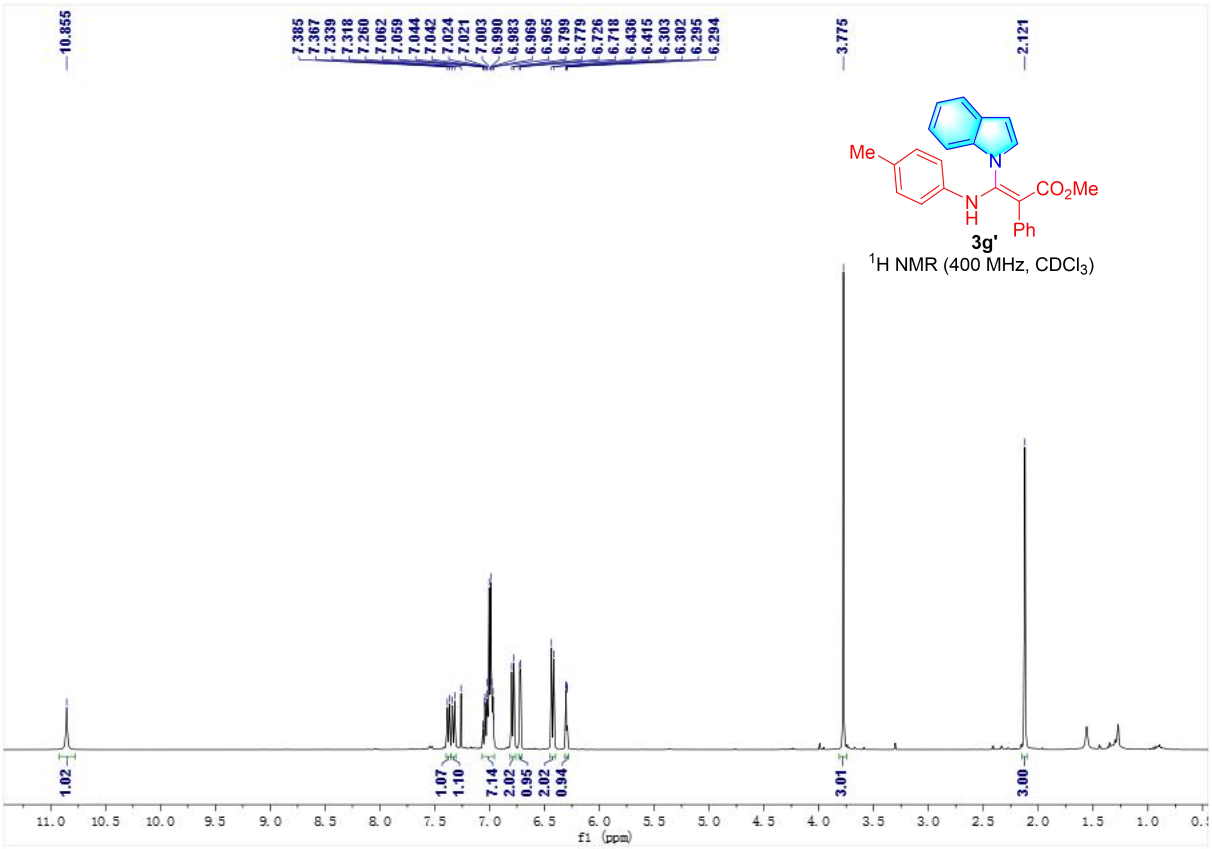
3f'

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



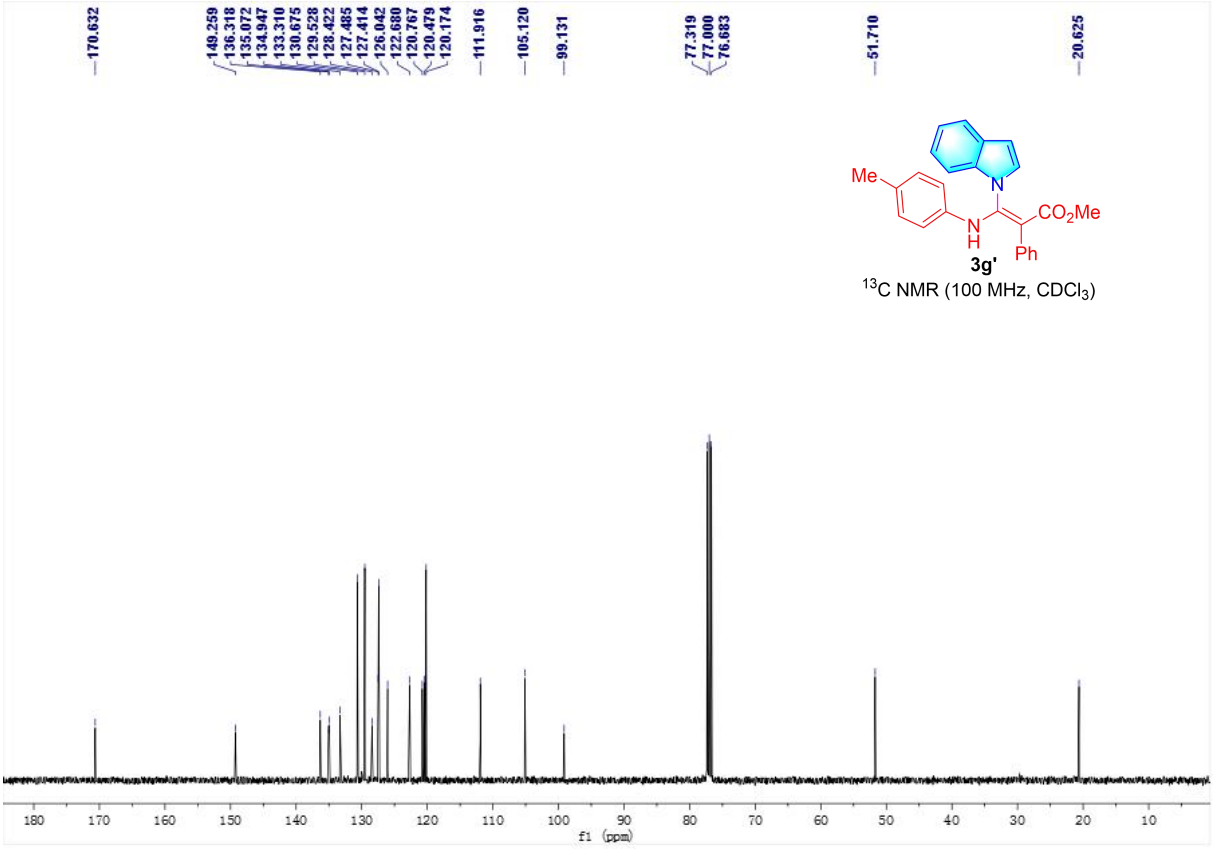
3f'

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



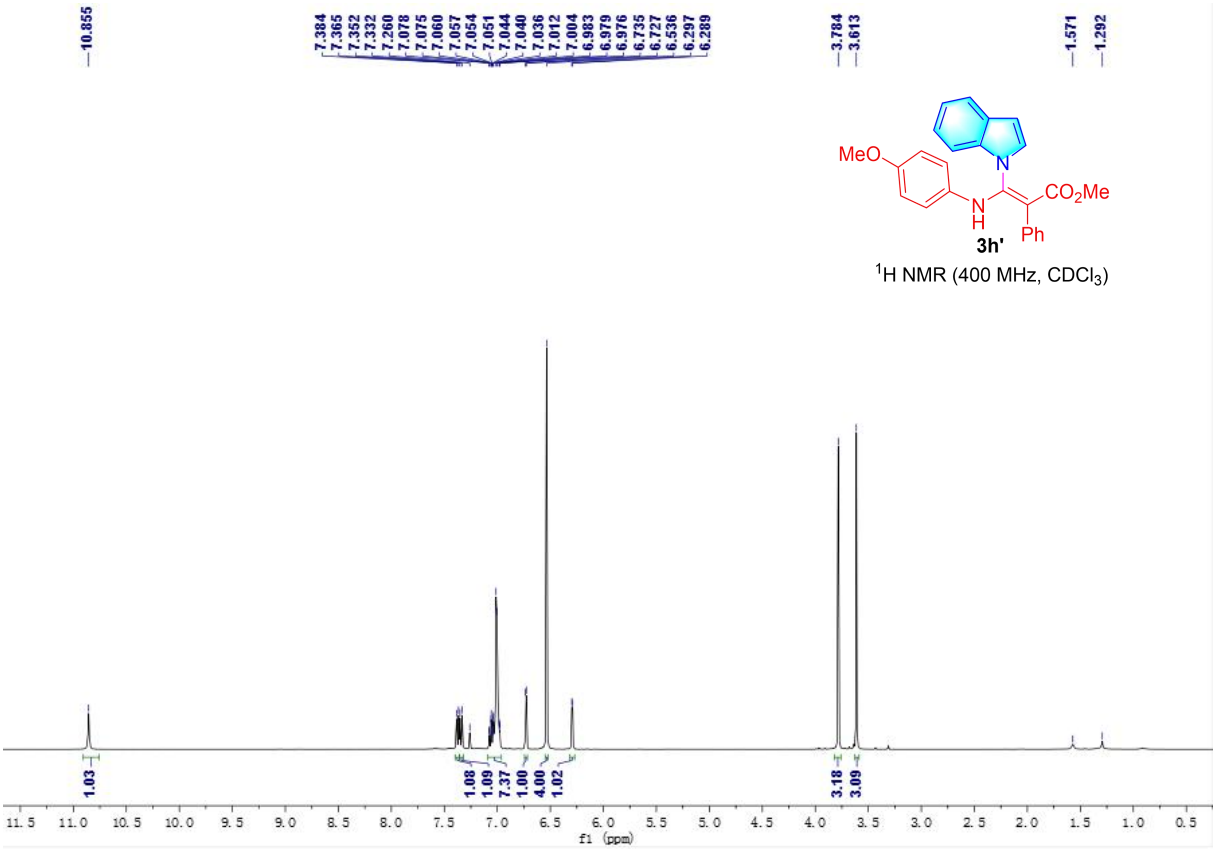
3g'

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

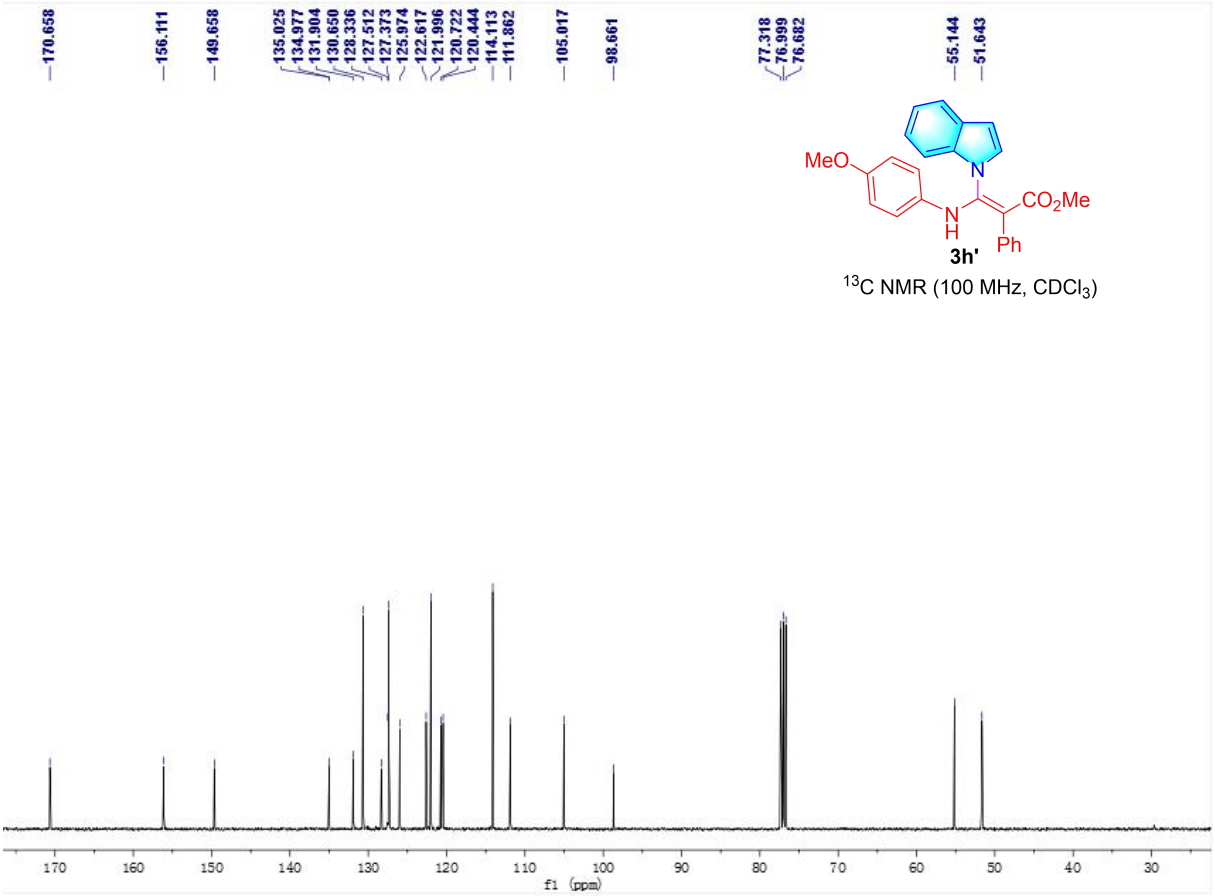


3g'

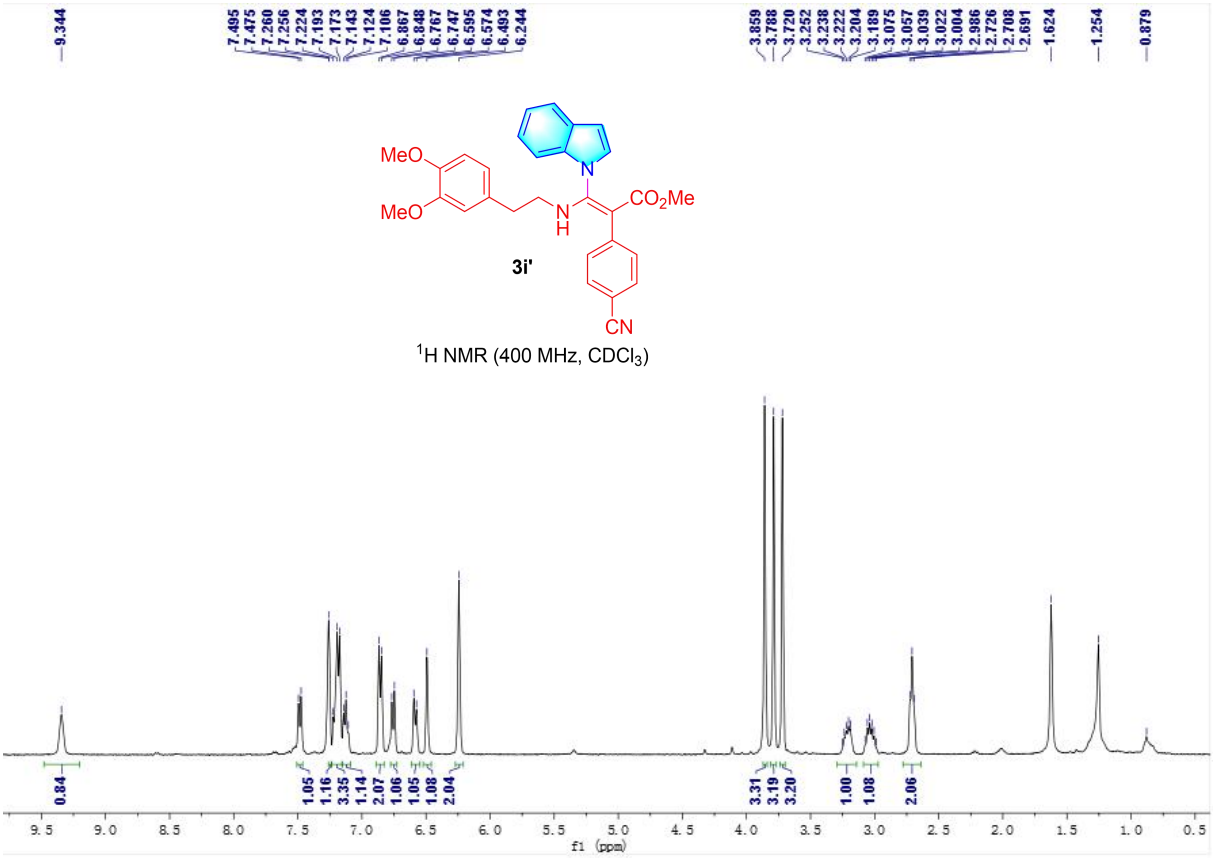
^{13}C NMR (100 MHz, $CDCl_3$)



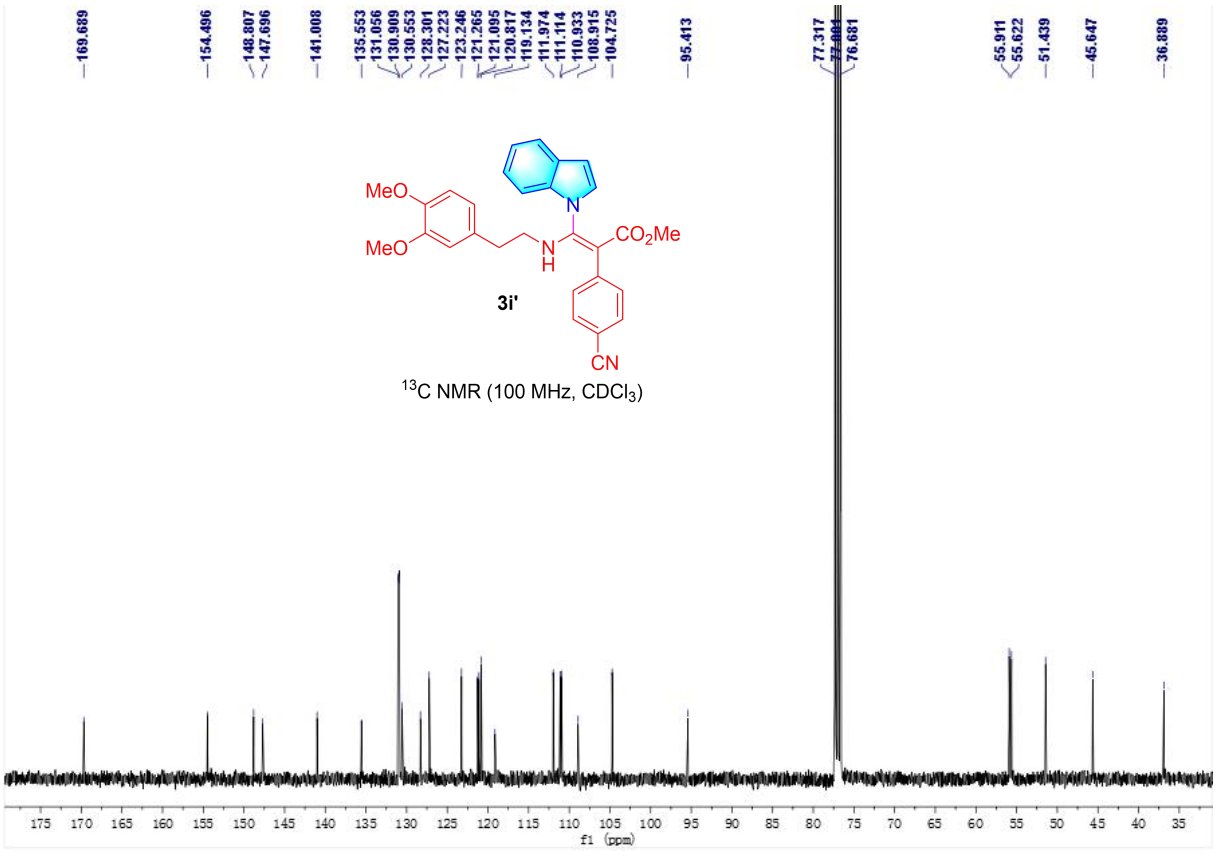
^{1}H NMR (400 MHz, $CDCl_3$)



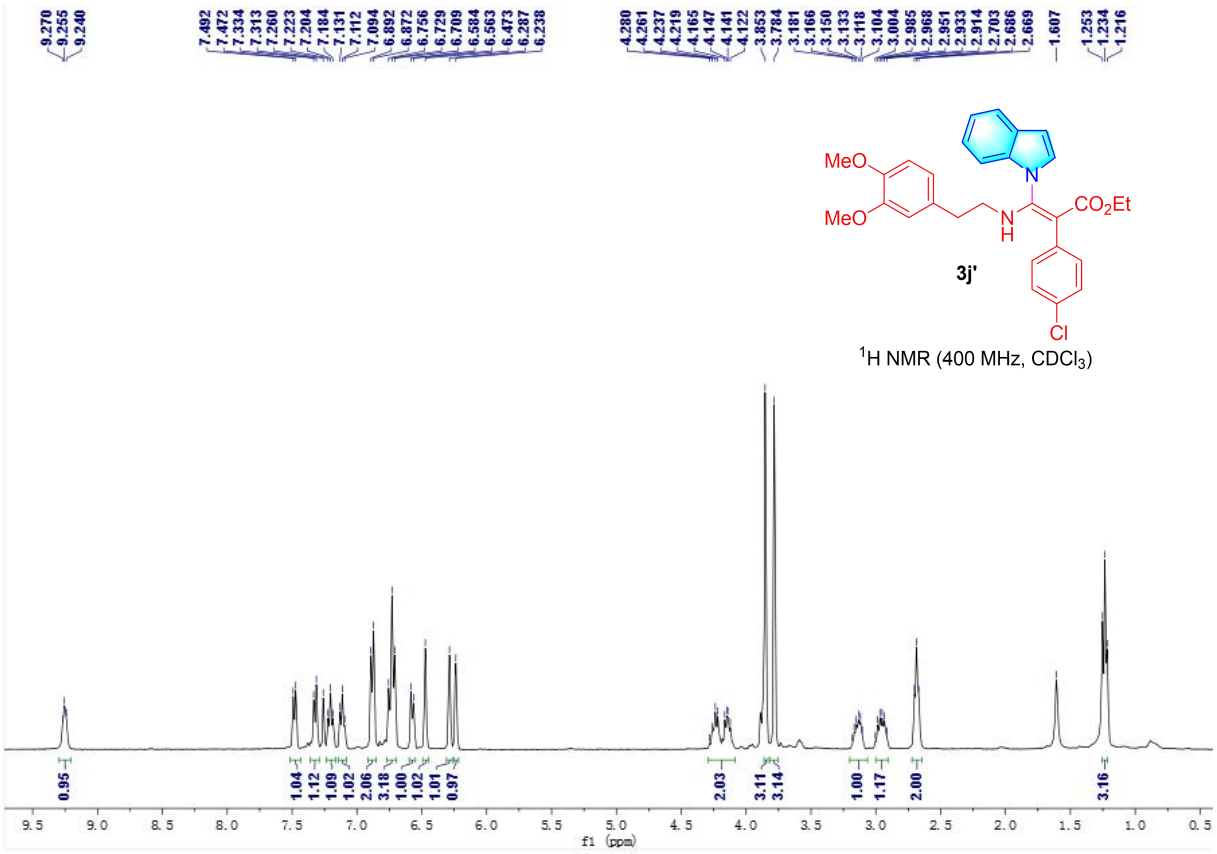
^{13}C NMR (100 MHz, $CDCl_3$)



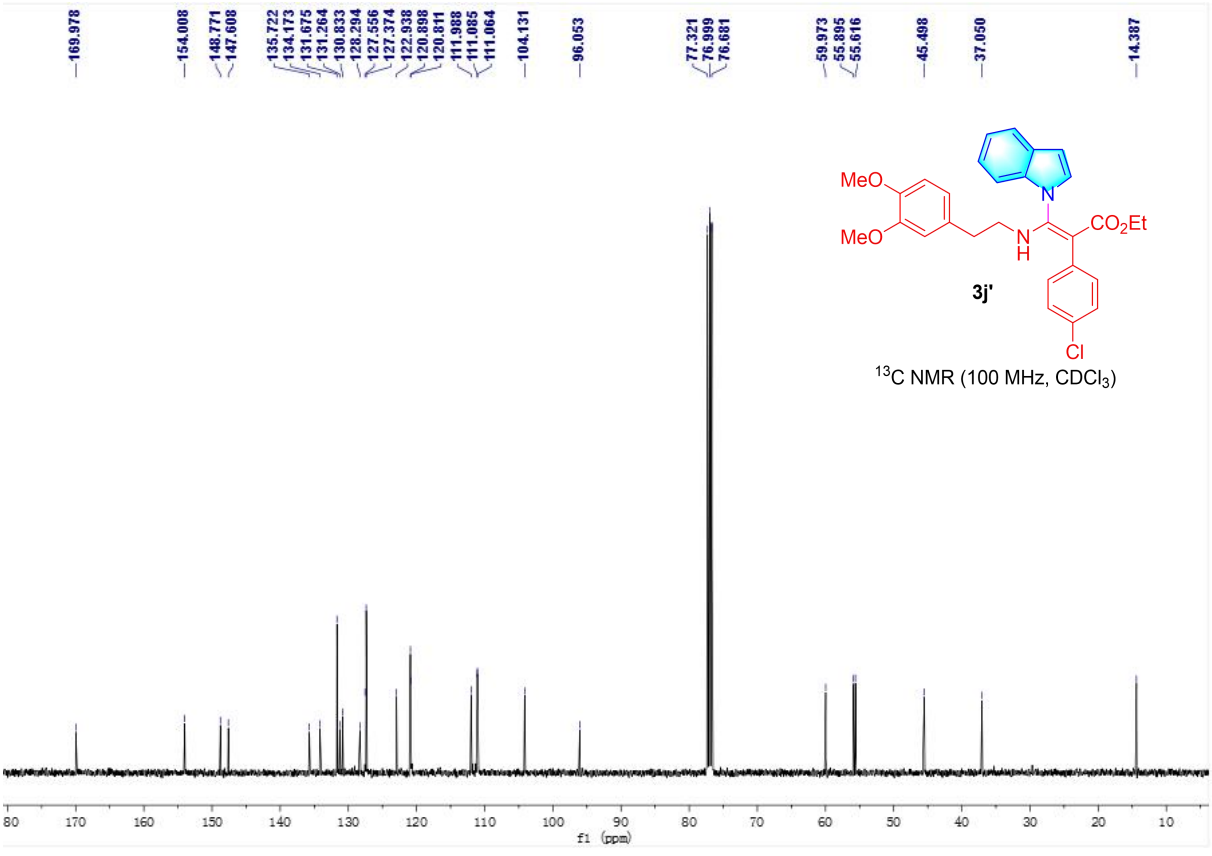
^{1}H NMR (400 MHz, $CDCl_3$)



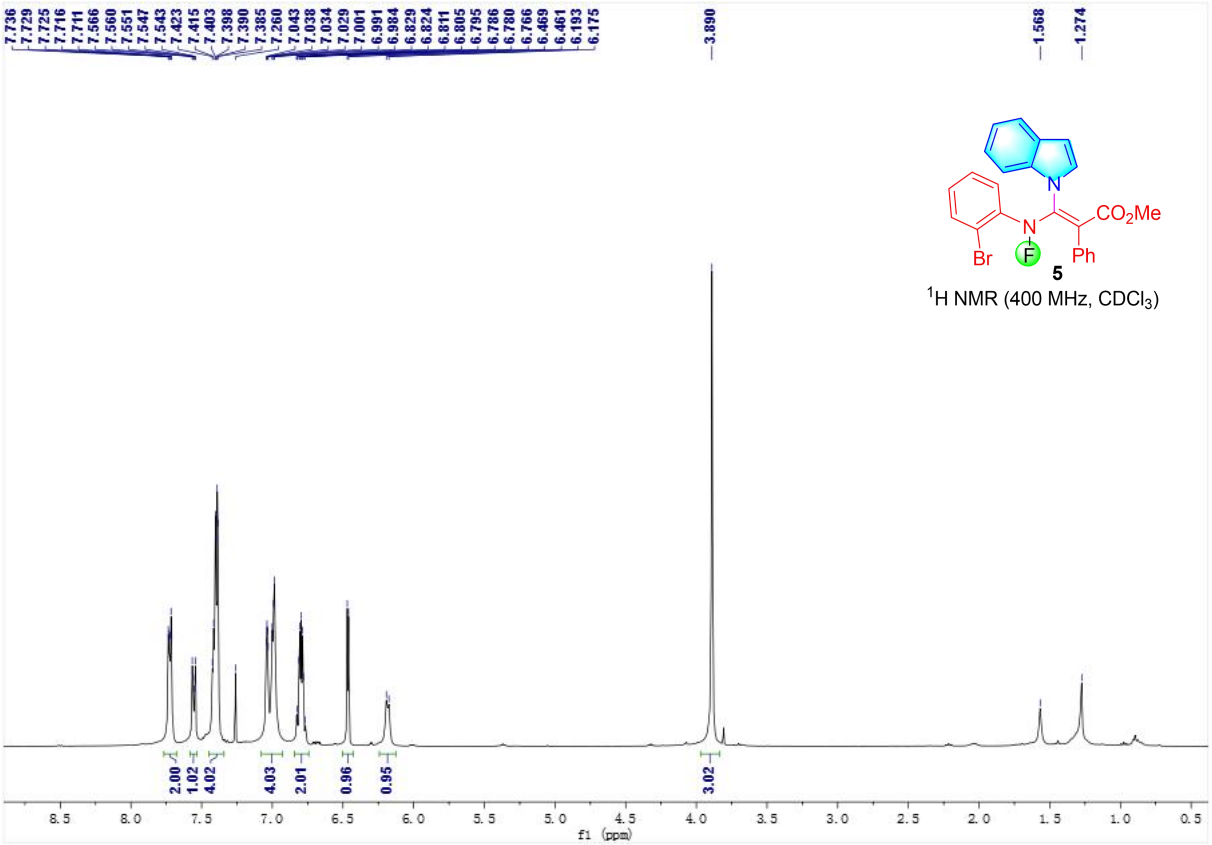
^{13}C NMR (100 MHz, $CDCl_3$)



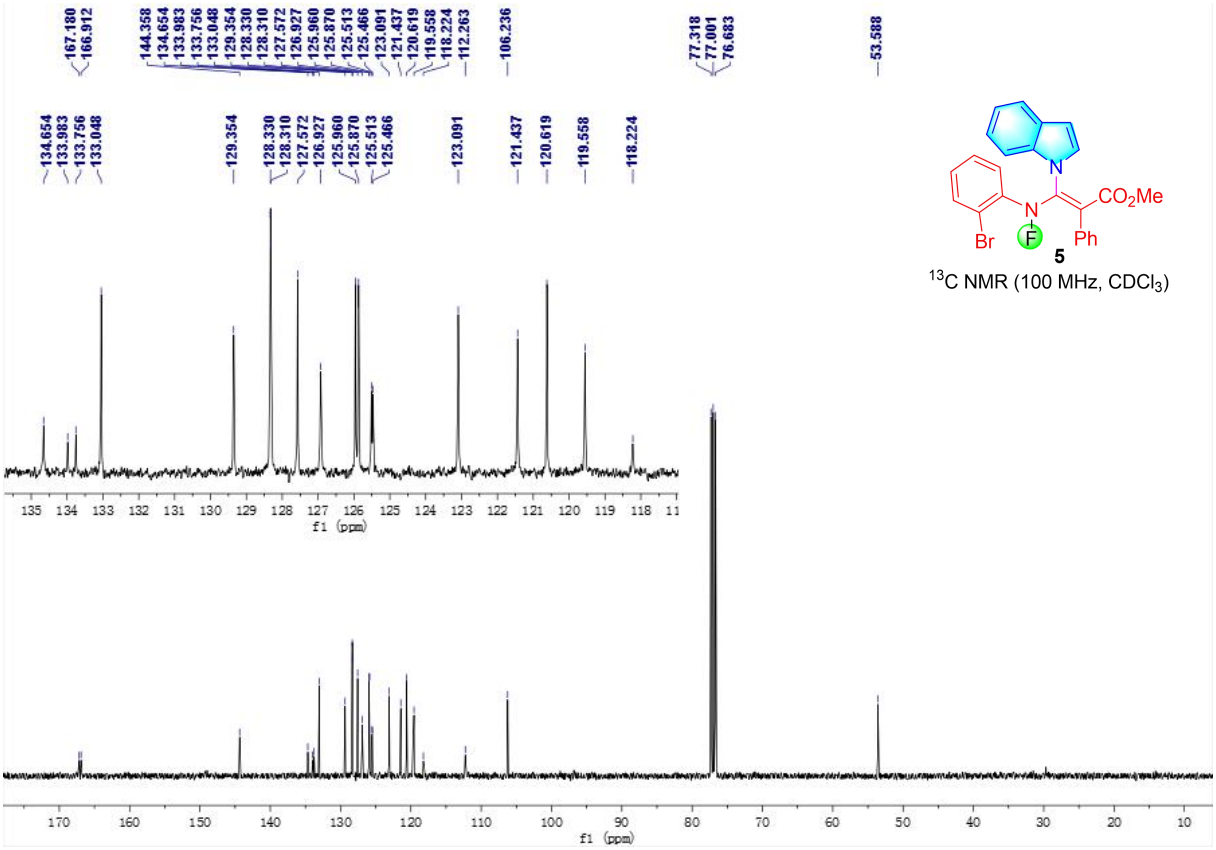
^{1}H NMR (400 MHz, $CDCl_3$)



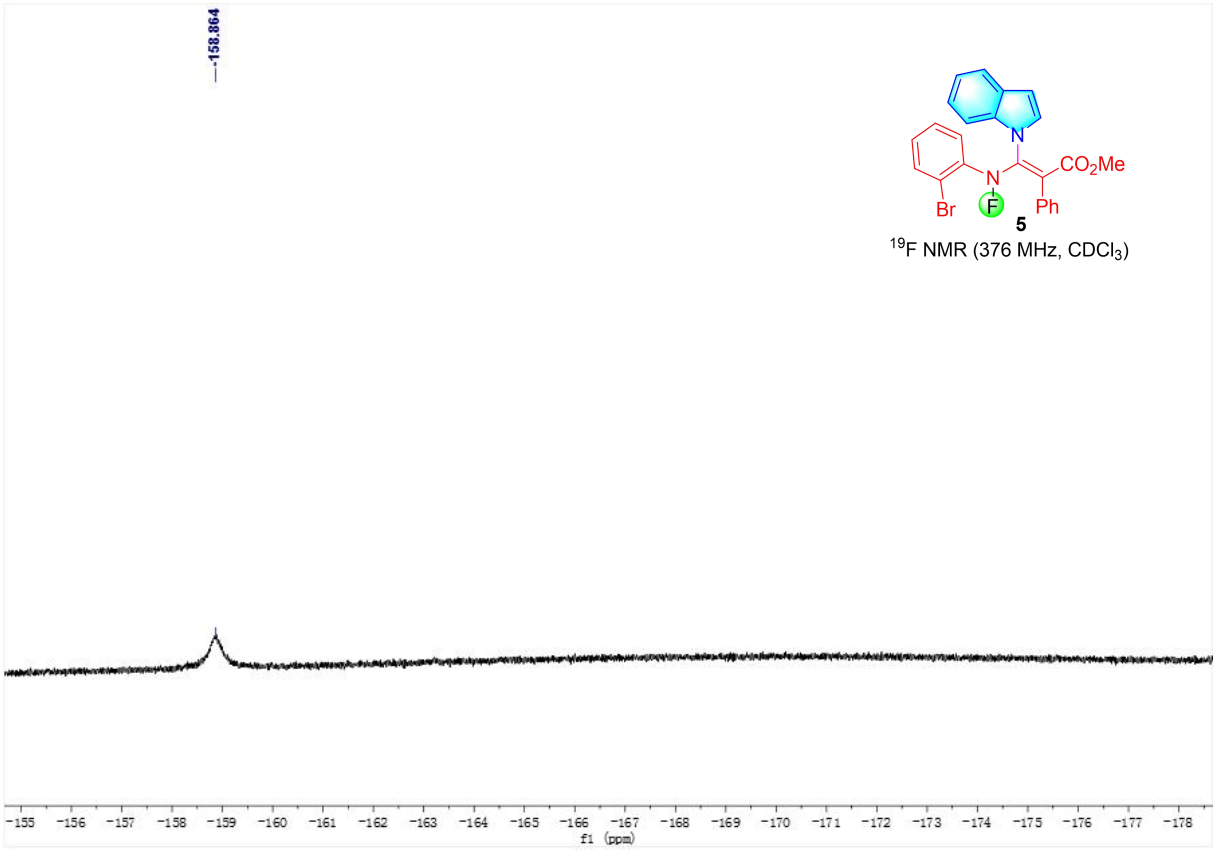
^{13}C NMR (100 MHz, $CDCl_3$)



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



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



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