Supporting Information

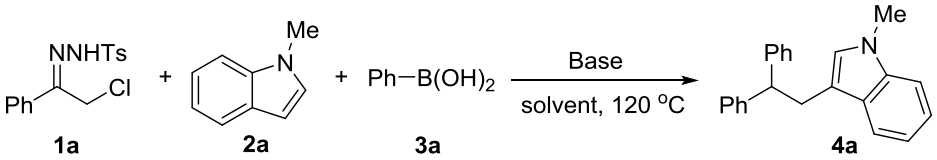
Contents

1. General experimental methods

All solvents and reagents were purchased from commercial suppliers and used without further purification. Column chromatograph was performed on 200-300 mesh silica gal. ^{1}H NMR spectra were recorded on Bruker ARX 400 (400 MHz) and are referenced relative to tetramethylsilane (TMS) at δ 0.00 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration, and assignment; ^{13}C NMR spectra were recorded on Bruker ARX 400 MHz (100 MHz) and are referenced relative to $CDCl_3$ at δ 77.0 ppm. The IR spectra were recorded with a Thermo Electron Corporation Nicolet AVATAR 300 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectral were obtained on Bruker Apex IV FTMS spectrometer. *α*-Halo-*N*-tosylhydrazones were prepared according to the literatures.[1]

2. Optimization experiments

Table S1 Optimization of the three-component reaction with *α*-halo-*N*-tosylhydrazone, indole and phenylboronic acid[a]



1a **2a** **3a** **4a**

Entry	Ratio (**1a** : **2a** : **3a**)	Base (x equiv)	Solvent	Yield (%)[b]
1	1 : 1 : 1	K_2CO_3 (2)	PhMe	44
2	1 : 1 : 1	K_2CO_3 (2)	DCE	41
3	1 : 1 : 1	K_2CO_3 (2)	PS[c]	<15
4	1 : 1 : 1	K_2CO_3 (2)	PhMe/H_2O=10 : 1	64
5	1 : 1 : 1	K_2CO_3 (2)	PhMe/H_2O=15 : 1	69
6	1 : 1 : 1	K_2CO_3 (2)	PhMe/H_2O=30 : 1	69
7	1 : 1 : 1	Cs_2CO_3 (2)	PhMe/H_2O=30 : 1	57
8	1 : 1 : 1	K_3PO_4 (2)	PhMe/H_2O=30 : 1	58
9	1 : 1 : 1	NEt_3 (2)	PhMe/H_2O=30 : 1	-
10	1 : 1 : 1	LiO^tBu (2)	PhMe/H_2O=30 : 1	-
11	1.25 : 1 : 1.25	K_2CO_3 (2)	PhMe/H_2O=30 : 1	73
12	1.5 : 1 : 1	K_2CO_3 (3)	PhMe/H_2O=30 : 1	54
13	1.5 : 1 : 1.5	K_2CO_3 (3)	PhMe/H_2O=30 : 1	52
14	1.25 : 1 : 1.25	K_2CO_3 (2)	PhMe/H_2O=30 : 1	81[d]

[a] Reaciton was carried out with **1a** (0.375 mmol), **2a** (0.3 mmol) and **3a** (0.375 mmol) in 1.5 mL solvent (0.2 M). [b] Isolated yield. [c] PS = MeCN, THF, dioxane, EtOAc. [d] Reaciton was carried out in 3 mL solvent (0.1 M).

To our delight, the expected product **4a** could be isolated in 44% isolated yield with K_2CO_3 as the base and toluene as the solvent (Table S1, entry 1). To further improve the reaction, a series of solvents were screened and the reaction was found sensitive to solvent effects (entries 2-4). The reaction with DCE as the solvent afforded the product **4a** in comparable yield (entry 2), while other polar solvents such as MeCN, THF, dioxane and EtOAc gave only trace amount of the product **4a** (entry 3). Interestingly, the yield could be improved with appropriate amount of water as additive (entries 4-6). This may be attributed to the slightly increased polarity of the reaction system that makes the conjugate addition more favourable. Subsequently, the effect of base was examined. The reaction with Cs_2CO_3 or K_3PO_4 as the base gave comparable results, while that with NEt_3 or Li*O*t*Bu failed to afford **4a** (entries 7-10). Finally, the ratio of the reaction substrates were adjusted and an optimized result with 81% isolated yield could be achieved (entries 11-14)

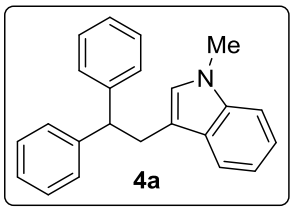
3. General procedure of transition-metal-free reactions

α-Halo-*N*-tosylhydrazones **1** (0.375 mmol), indoles **2** (0.3 mmol), aryl boronic acid **3** (0.375 mmol), and potassium carbonate (0.6 mmol) were added into a Schlenk tube, followed by 3 vacuum evacuation/nitrogen backfill cycles. Then toluene (3 mL), water (100 μL) were added into the mixture respectively. The mixture was stirred at 120 ^{o}C for 6 hours. After the mixture was cooled down to room temperature, the solvent was removed to leave a crude product, which was purified by column chromatography on silica gel to afford the product **4** and **5**.

4. Characterization data for 4a-l, 5a-h, 6a-i

3-(2,2-diphenylethyl)-1-methylindole (**4a**)

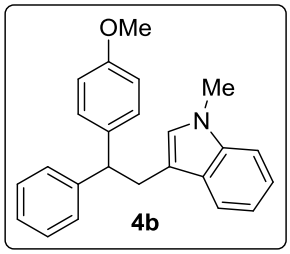
(*N*'-(2-chloro-1-phenyl-ethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), phenylboronic acid (46 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4a** as a white solid (76 mg, 81%). Using 1-methylindole (5 mmol, 0.655 g) did the gram scale experiment giving 1.21 g **4a** (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9 Hz, 1H), 7.27-7.14 (m, 12H), 7.08 (t, J = 7.9 Hz, 1H), 6.42 (s, 1H), 4.37 (t, J = 7.7 Hz, 1H), 3.59 (s, 3H), 3.49 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.7, 128.4, 128.1, 127.1, 126.1, 121.4, 118.8, 118.6, 113.0, 109.1, 51.7, 32.5, 31.6; IR (film) 2917, 911, 737, 700 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}N$ $[M+H]^+$ 312.1747, found 312.1747; mp 105-107 ^{o}C.



4a

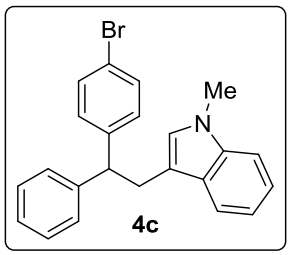
3-(2-(4-methoxyphenyl)-2-phenylethyl)-1-methylindole (**4b**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4b** as a pale yellow solid (76 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9 Hz, 1H), 7.25-7.16 (m, 9H), 7.07 (t, J = 7.9 Hz, 1H), 6.79 (d, J = 8.6 Hz, 2H), 6.42 (s, 1H), 4.32 (t, J = 7.6 Hz, 1H), 3.74 (s, 3H), 3.58 (s, 3H), 3.45 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 145.7, 137.4, 136.8, 129.0, 128.4, 128.1, 127.1, 126.1, 121.4, 118.8, 118.6, 113.8, 113.1, 109.1, 55.3, 50.9, 32.5, 31.9; IR (film) 2930, 1510, 1248, 738, 1034 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}NO$ $[M+H]^+$ 342.1852, found 342.1856. mp: 90-92 ^{o}C.



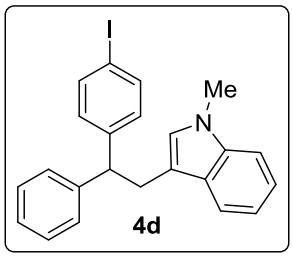
3-(2-(4-bromophenyl)-2-phenylethyl)-1-methylindole (**4c**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-bromophenyl)boronic acid (75 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4c** as a pale yellow solid (83 mg, 71%). Using 1-methylindole (5 mmol, 0.655 g) did the gram scale experiment giving 1.28 g **4c** (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 7.0 Hz, 2H), 7.32-7.16 (m, 7H), 7.11 (d, J = 8.4 Hz, 3H), 6.44 (s, 1H), 4.34 (t, J = 7.4 Hz, 1H), 3.62 (s, 3H), 3.52-3.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 144.1, 136.8, 131.4, 129.9, 128.5, 127.9, 127.1, 126.4, 121.5, 119.9, 118.7, 112.5, 109.2, 51.1, 32.6, 31.6; IR (film) 2968, 1485, 1073, 1010, 738 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{21}BrN$ $[M+H]^+$ 390.0852, found 390.0854; mp 101-103 ^{o}C.



3-(2-(4-iodophenyl)-2-phenylethyl)-1-methylindole (**4d**)

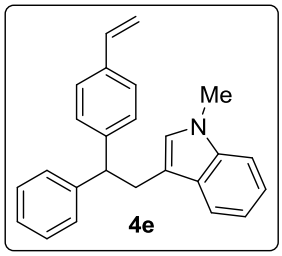
(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-iodophenyl)boronic acid (93 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4d** as a pale yellow solid (88 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.49 (m, 3H), 7.30-7.15 (m, 7H), 7.08 (m, 1H), 6.98 (d, J = 8.2 Hz, 2H), 6.43 (s, 1H), 4.32 (t, J = 7.7 Hz, 1H),



3.61 (s, 3H), 3.51-3.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.6, 137.4, 136.8, 130.2, 128.5, 127.9, 127.1, 126.4, 121.5, 118.7, 118.7, 112.5, 109.2, 91.4, 51.2, 32.6, 31.5; IR (film) 2930, 1483, 1005, 739, 699 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{21}IN$ $[M+H]^+$ 438.0713, found 438.0718; mp 130-132 ^{o}C.

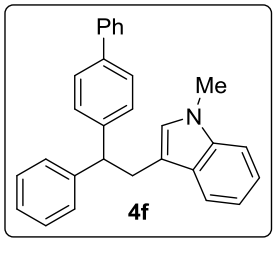
1-methyl-3-(2-phenyl-2-(4-viylphenyl)ethyl)-indole (**4e**)

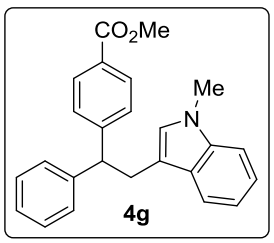
(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-vinylphenyl)boronic acid (55 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4** as a pale yellow oil (68 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9 Hz, 1H), 7.33-7.14 (m, 11H), 7.11-7.04 (m, 1H), 6.65 (dd, J = 17.6, 10.9 Hz, 1H), 6.42 (s, 1H), 5.67 (d, J = 17.6 Hz, 1H), 5.16 (d, J = 10.9 Hz, 1H), 4.36 (t, J = 7.6 Hz, 1H), 3.54 (s, 3H), 3.47 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 144.9, 136.8, 136.7,135.5, 128.5, 128.3, 128.1, 127.2, 126.3, 126.3, 121.5, 118.9, 118.7, 113.3, 112.9, 109.2, 51.5, 32.6, 31.6; IR (film) 2926, 1326, 739, 700 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{24}N$ $[M+H]^+$ 338.1903, found 338.1905.



3-(2-([1,1'-biphenyl]-4-yl)-2-phenylethyl)-1-methylindole (**4f**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), [1,1'-biphenyl]-4-ylboronic acid (74 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4f** as a pale yellow solid (102 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 3H), 7.50 (d, J = 8.2 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.35-7.28 (m, 7H), 7.25-7.18 (m, 3H), 7.09 (t, J = 7.3 Hz, 1H), 6.47 (s, 1H), 4.42 (t, J = 7.6 Hz, 1H), 3.62 (s, 3H), 3.53 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.3, 141.0, 138.9, 136.7, 128.7, 128.5, 128.4, 128.1,127.1, 127.1, 127.0, 126.2, 121.4, 118.8, 118.6, 112.9, 109.1, 51.4, 32.6, 31.7; IR (film) 2921, 2853, 1486, 737, 699 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{26}N$ $[M+H]^+$ 388.2060, found 388.2060; mp 135-137 ^{o}C.





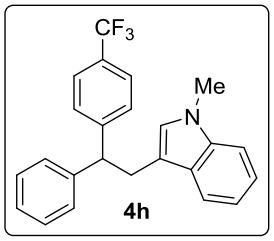
methyl 4-(2-(1-methylindol-3-yl)-1-phenylethyl)benzoate (**4g**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (67 mg, 0.375 mmol),

potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and MeCN (100 μL). After column chromatography giving **4g** as a pale yellow solid (64 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 7.9 Hz, 1H), 7.36-7.16 (m, 9H), 7.09 (t, J = 7.3 Hz, 1H), 6.42 (s, 1H), 4.43 (t, J = 7.7 Hz, 1H), 3.88 (s, 3H), 3.60 (s, 3H), 3.50 (d, J = 10.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 150.4, 144.4, 136.8, 129.7, 128.5, 128.2, 128.1, 128.0,127.9, 127.1, 126.4, 121.5, 118.7, 112.4, 109.2, 52.0, 51.8, 32.6, 31.5; IR (film) 2987, 1718, 1280, 1065, 740 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$ 370.1802, found 370.1805; mp 120-122 ^{o}C.

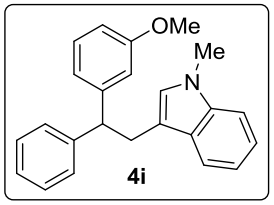
1-methyl-3-(2-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)-indole (**4h**)

(*N'*-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-(trifluoromethyl)phenyl)boronic acid (71 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4h** as a pale yellow solid (64 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.20-7.08 (m, 7H), 7.00 (t, J = 7.1 Hz, 1H), 6.34 (s, 1H), 4.34 (t, J = 7.6 Hz, 1H), 3.49 (s, 3H), 3.45-3.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 143.1, 135.8, 127.5, 127.4, 126.9, 126.0, 125.5, 124.2 (q, J = 3.7 Hz), 123.3 (q, J = 268.7 Hz), 120.5, 117.7, 117.6, 113.3, 108.1; IR (film) 2964, 1325, 1067, 799, 700 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}F_3N$ $[M+H]^+$ 380.1621, found 380.1625; mp 98-100 ^{o}C.



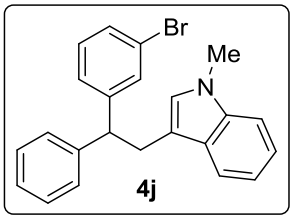
3-(2-(3-methoxyphenyl)-2-phenylethyl)-1-methylindole (**4i**)

(*N'*-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (3-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4i** as a pale yellow solid (76 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9 Hz, 1H), 7.28-7.13 (m, 8H), 7.07 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.81 (s, 1H), 6.70 (d, J = 8.1 Hz, 1H), 6.44 (s, 1H), 4.33 (t, J = 7.6 Hz, 1H), 3.71 (s, 3H), 3.57 (s, 3H), 3.48 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 146.9, 145.0, 136.8, 129.3, 128.4, 128.1, 128.1, 127.1, 126.2, 121.4, 120.6, 118.8, 118.6, 114.2, 113.0, 111.2, 109.1, 55.2, 21.8, 32.5, 31.6; IR (film) 2987, 1593, 1257, 1052, 739 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}NO$ $[M+H]^+$ 342.1852, found 342.1852; mp 79-80 ^{o}C.



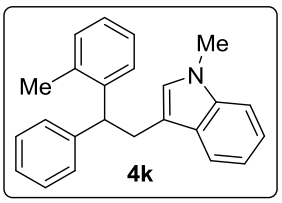
3-(2-(3-bromophenyl)-2-phenylethyl)-1-methylindole (**4j**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (3-bromophenyl)boronic acid (75 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4j** as a pale yellow oil (76 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.39 (s, 1H), 7.31-7.25 (m, 5H), 7.24-7.16 (m, 4H), 7.11 (t, J = 8.0 Hz, 2H), 6.43 (s, 1H), 4.32 (t, J = 7.7 Hz, 1H), 3.62 (s, 3H), 3.47-3.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 144.3, 136.8, 131.1, 129.9, 129.3, 128.5, 128.0, 127.9, 127.1, 126.8, 126.4, 122.5, 121.5, 118.7, 112.4, 109.2, 51.5, 32.6, 31.5; IR (film) 2923, 1473, 739, 701 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{21}BrN$ $[M+H]^+$ 390.0852, found 390.0854.



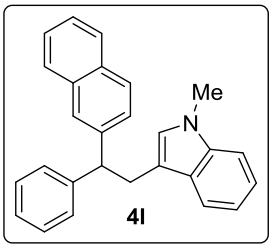
1-methyl-3-(2-phenyl-2-(*o*-tolyl)ethyl)-indole (**4k**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), *o*-tolylboronic acid (51 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4k** as a pale yellow oil (66 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.22-7.04 (m, 11H), 6.38 (s, 1H), 4.55 (t, J = 7.6 Hz, 1H), 3.56 (s, 3H), 3.51-3.36 (m, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.0, 136.8, 136.5, 130.5, 128.5, 128.2, 128.2, 127.1, 127.0, 126.1, 126.0, 126.0, 121.4, 118.8, 118.7, 113.1, 109.1, 47.4, 32.5, 32.0, 20.0; IR (film) 2966, 1066, 908, 734, 700 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}N$ $[M+H]^+$ 326.1903, found 326.1906.



1-methyl-3-(2-(naphthalen-2-yl)-2-phenylethyl)-indole (**4l**)

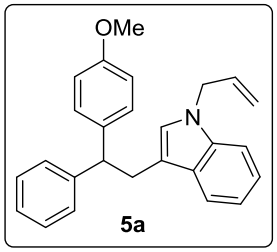
(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), naphthalen-1-ylboronic acid (64 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **4l** as a pale yellow solid (85 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 4H), 7.61 (d, J = 7.9 Hz, 1H), 7.43-7.38 (m, 3H), 7.33-7.15 (m, 7H), 7.11-7.07 (m, 1H), 6.44 (s, 1H), 4.55 (t, J = 7.6 Hz, 1H), 3.69-3.49 (m, 5H, overlap); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.5, 136.7, 133.5, 132.2, 128.4, 128.2, 128.1, 128.0, 127.8, 127.6, 127.1, 127.1, 126.2, 126.1, 125.9, 125.4, 121.4, 118.8,



118.6, 112.9, 109.1, 51.7, 32.6, 31.5; IR (film) 3055, 908, 737, 701 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}N$ $[M+H]^+$ 362.1903, found 362.1905; mp 126-129 ^oC.

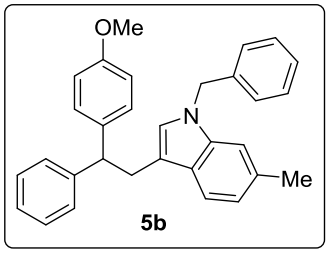
1-allyl-3-(2-(4-methoxyphenyl)-2-phenylethyl)-indole (**5a**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-allyl-indole (47 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^oC in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5a** as a colorless oil (61 mg, 55%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 1H), 7.26-7.20 (m, 5H), 7.18-7.12 (m, 4H), 7.11-7.04 (m, 1H), 6.78 (d, J = 8.7 Hz, 2H), 6.43 (s, 1H), 5.89-5.74 (m, 1H), 5.05 (dd, J = 10.3, 1.3 Hz, 1H), 4.83 (dd, J = 17.1, 1.3 Hz, 1H), 4.53-4.51 (m, 2H), 4.32 (t, J = 7.7 Hz, 1H), 3.74 (s, 3H), 3.45 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 133.6, 129.0, 128.3, 128.0, 126.4, 126.0, 121.4, 118.9, 118.8, 116.7, 113.7, 113.4, 109.5, 55.2, 50.8, 48.4, 31.9; IR (film) 2918, 1510, 1178, 1036, 739 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{26}NO$ $[M+H]^+$ 368.2009, found 368.2013.



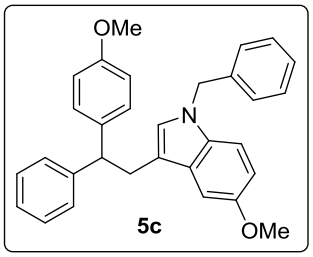
1-benzyl-3-(2-(4-methoxyphenyl)-2-phenylethyl)-6-methyl-indole (**5b**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-benzyl-6-methyl-indole (66 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^oC in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5b** as a pale yellow oil (80 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 1H), 7.22-7.12 (m, 10H), 6.98-6.89 (m, 2H), 6.88-6.79 (m, 2H), 6.76 (d, J = 8.6 Hz, 2H), 6.40 (s, 1H), 5.06 (s, 2H), 4.32 (t, J = 7.8 Hz, 1H), 3.72 (s, 3H), 3.44 (d, J = 7.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 145.6, 138.0, 137.3, 136.8, 131.4, 129.1, 128.6, 128.4, 128.1, 127.3, 126.5, 126.3, 126.2, 126.1, 120.8, 118.9, 113.7, 113.4, 109.6, 55.3, 50.8, 49.5, 32.1, 22.0; IR (film) 3029, 1510, 1248, 1031, 800 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{30}NO$ $[M+H]^+$ 432.2322, found 432.2325.



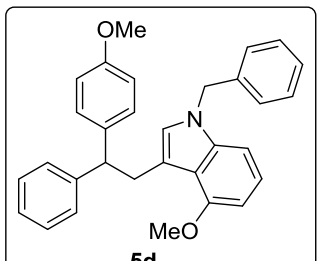
1-benzyl-5-methoxy-3-(2-(4-methoxyphenyl)-2-phenylethyl)-indole (**5c**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-benzyl-5-methoxy-indole (71 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5c** as a pale yellow oil (93 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 7H), 7.16（d, J = 8.4 Hz, 3H), 7.05 (d, J = 8.8 Hz, 1H), 6.97 (d, J = 2.2 Hz, 1H), 6.88-6.86 (m, 2H), 6.70-6.76 (m, 3H), 6.48 (s, 1H), 5.10 (s, 2H), 4.31 (t, J = 7.7 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.44 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.7, 145.5, 137.8, 137.2, 131.5, 129.0, 128.5, 128.5, 128.3, 128.0, 127.4, 127.3, 126.4, 126.0, 113.6, 113.0, 111.6, 110.3, 100.7, 55.9, 55.1, 50.7, 49.8 31.9; IR (film) 2914, 1487, 1248, 1038, 913 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{30}NO_2$ $[M+H]^+$ 448.2271, found 448.2274.



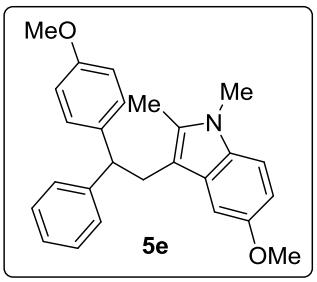
1-benzyl-4-methoxy-3-(2-(4-methoxyphenyl)-2-phenylethyl)-indole (**5d**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-benzyl-4-methoxy-indole (71 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5d** as a pale yellow oil (101 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.01 (m, 10H), 6.92 (t, J = 8.0 Hz, 1H), 6.72-6.62 (m, 5H), 6.38 (d, J = 7.7 Hz, 1H), 6.25 (s, 1H), 4.91 (s, 2H), 4.36 (t, J = 7.6 Hz, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 3.50-3.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 155.1, 145.8, 138.2, 137.9, 137.5, 129.3, 128.6, 128.4, 128.3, 127.3, 126.5, 125.9, 125.8, 118.0, 114.2, 113.6, 103.1, 99.2, 55.2, 51.8, 49.8, 34.0; IR (film) 2921, 1510, 1257, 909, 729 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{30}NO_2$ $[M+H]^+$ 448.2271: found 448.2273.



5-methoxy-3-(2-(4-methoxyphenyl)-2-phenylethyl)-1,2-dimethyl-indole (**5e**)

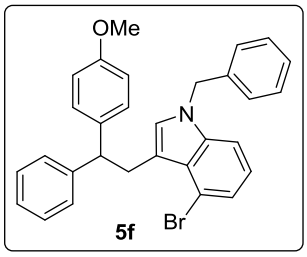
(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 5-methoxy-1,2-dimethyl-indole (53 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5e** as a pale yellow solid (74 mg, 64%). ^{1}H



NMR (400 MHz, $CDCl_3$) δ 7.24-7.15 (m, 5H), 7.11-7.08 (m, 3H), 6.82-6.76 (m, 4H), 4.16 (t, J = 7.6 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.51 (s, 3H), 3.34 (d, J = 7.5 Hz, 2H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 153.6, 145.6, 137.5, 134.8, 132.0, 129.2, 128.2, 128.1, 128.1, 126.0, 113.5, 109.8, 109.0, 108.7, 100.5, 56.1, 55.2, 50.1, 31.9, 29.6, 9.72; IR (film) 2930, 1487, 1248, 1034, 909 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{28}NO_2$ $[M+H]^+$ 386.2115, found 386.2118; mp 103-104 ^{o}C.

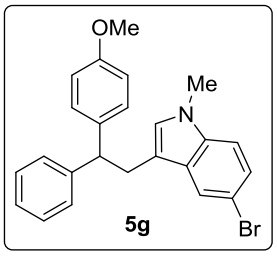
1-benzyl-4-bromo-3-(2-(4-methoxyphenyl)-2-phenylethyl)-indole (**5f**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-benzyl-4-bromo-indole (86 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5f** as a pale yellow oil (60 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.07 (m, 12H), 6.96-6.89 (m, 1H), 6.83-6.73 (m, 4H), 6.46 (s, 1H), 5.06 (s, 2H), 4.46 (t, J = 7.8 Hz, 1H), 3.74 (s, 3H), 3.70 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 145.2, 137.6, 137.0, 129.2, 129.2, 128.7, 128.2, 128.2, 127.5, 126.5, 125.9, 122.2, 114.5, 113.9, 113.6, 109.0, 55.2, 51.9, 49.8, 32.5; IR (film) 2923, 1510, 1248, 1024, 909 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{27}BrNO$ $[M+H]^+$ 496.1271, found 496.1273.



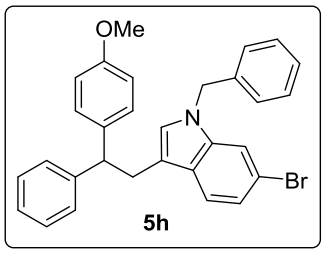
5-bromo-3-(2-(4-methoxyphenyl)-2-phenylethyl)-1-methylindole (**5g**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 4-bromo-1-methylindole (63 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5g** as a pale yellow oil (81 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.28-7.23 (m, 5H), 7.18-7.14 (m, 3H), 7.07 (d, J = 8.6 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 6.44 (s, 1H), 4.24 (t, J = 7.7 Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H), 3.39 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 145.4, 137.1, 129.0, 128.4, 128.3, 127.9, 126.2, 124.1, 121.5, 113.8, 112.8, 112.1, 110.6, 55.3, 51.0, 32.7, 31.7; IR (film) 2919, 1510, 1476, 1248, 1036 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}BrNO$ $[M+H]^+$ 420.0958, found 420.0960.



1-benzyl-6-bromo-3-(2-(4-methoxyphenyl)-2-phenylethyl)-indole (**5h**)

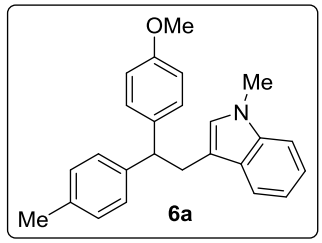
(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), 1-benzyl-6-bromo-indole (86 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **5h** as a pale yellow oil (60 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 1H), 7.31 (s, 1H), 7.25-7.09 (m, 11H), 6.84-6.81 (m, 2H), 6.77 (d, J = 8.6 Hz, 2H), 6.45 (s, 1H), 5.04 (s, 2H), 4.27 (t, J = 7.8 Hz, 1H), 3.73 (s, 3H), 3.42 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 129.0, 128.8, 128.4, 128.0, 127.6, 127.5, 126.5, 126.2, 122.2, 120.3, 113.9, 113.8, 112.6, 55.2, 50.8, 49.7, 31.8; IR (film) 2922, 1605, 1510, 1248, 1174 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{27}BrNO$ $[M+H]^+$ 496.1271, found 496.1273.



5h

3-(2-(4-methoxyphenyl)-2-(p-tolyl)ethyl)-1-methylindole (**6a**)

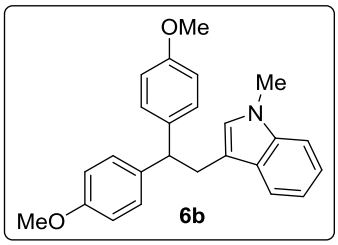
N'-(2-bromo-1-(p-tolyl)ethylidene)-4-methylbenzenesulfonohydrazide (142 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6a** as a pale yellow solid (73 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 1H), 7.23-7.14 (m, 6H), 7.09-7.05 (m, 3H), 6.78 (d, J = 8.6 Hz, 2H), 6.44 (s, 1H), 4.30 (t, J = 7.6 Hz, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 3.43 (d, J = 7.7 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 142.6, 137.6, 136.7, 135.5, 129.0, 128.9, 128.1, 127.8, 127.1, 121.3, 118.8, 118.5, 113.7, 113.2, 109.0, 55.2, 50.3, 32.6, 31.8, 21.0; IR (film) 2988, 1509, 1247, 1038, 740 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{26}NO$ $[M+H]^+$ 356.2009, found 356.2010; mp 100-103 ^{o}C.



6a

3-(2,2-bis(4-methoxyphenyl)ethyl)-1-methylindole (**6b**)

N'-(2-bromo-1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (149 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6b** as a pale yellow oil (67 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.8 Hz, 1H), 7.24-7.15 (m, 6H), 7.08 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 8.6 Hz, 4H), 6.43 (s, 1H), 4.28 (t, J = 7.6 Hz, 1H), 3.76 (s, 6H), 3.61 (s, 3H), 3.42 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 137.8, 136.7, 128.9, 128.1, 127.1, 121.4,

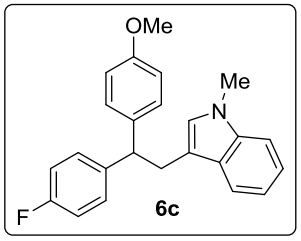


6b

118.8, 118.6, 113.7, 113.2, 109.1, 55.3, 50.0, 32.6, 32.0; IR (film) 2927, 1510, 1247, 1010, 738 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{26}NO_2$ $[M+H]^+$ 372.1958, found 372.1955.

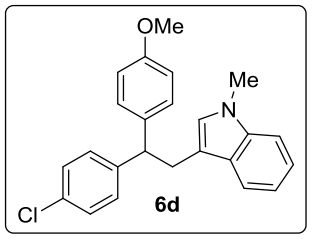
3-(2-(4-fluorophenyl)-2-(4-methoxyphenyl)ethyl)-1-methylindole (**6c**)

N'-(2-bromo-1-(4-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (144 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^oC in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6c** as a pale yellow oil (81 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.26-7.13 (m, 6H), 7.08 (t, J = 7.3 Hz, 1H), 6.92 (t, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 6.42 (s, 1H), 4.30 (t, J = 7.7 Hz, 1H), 3.76 (s, 3H), 3.60 (s, 3H), 3.49-3.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 141.3, 141.2, 137.2, 136.8, 129.4 (d, J = 7.6 Hz), 128.9, 128.0, 127.1, 121.4, 118.8, 118.7, 115.1 (d, J = 21.1 Hz), 113.8, 112.8, 109.2, 55.3, 50.1, 32.6, 32.0; IR (film) 2899, 1508, 1248, 826, 739 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}FNO$ $[M+H]^+$ 360.1758, found 360.1758.



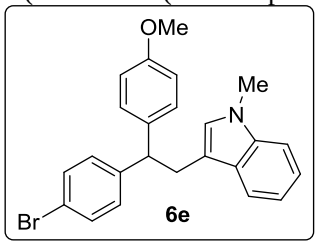
3-(2-(4-chlorophenyl)-2-(4-methoxyphenyl)ethyl)-1-methylindole (**6d**)

N'-(2-bromo-1-(4-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (150 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^oC in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6d** as a pale yellow solid (91 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.25-7.04 (m, 9H), 6.80 (d, J = 8.6 Hz, 2H), 6.42 (s, 1H), 4.29 (t, J = 7.7 Hz, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 3.46-3.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 144.1, 136.9, 136.8, 131.7, 129.4, 128.9, 128.4, 128.0, 127.1, 121.5, 118.8, 118.7, 113.9, 112.7, 109.2, 55.3, 50.2, 32.6, 31.8; IR (film) 2927, 1511, 1248, 909, 734 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}ClNO$ $[M+H]^+$ 376.1463, found 376.1457; mp 101-102 ^oC.



3-(2-(4-bromophenyl)-2-(4-methoxyphenyl)ethyl)-1-methylindole (**6e**)

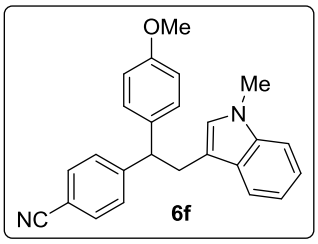
N'-(2-bromo-1-(4-bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (167 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^oC in the solvent



of toluene (3 mL) and water (100 μL). After column chromatography giving **6e** as a pale yellow solid (82 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.25-7.06 (m, 7H), 6.80 (d, J = 8.7 Hz, 2H), 6.43 (s, 1H), 4.28 (t, J = 7.7 Hz, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 3.46-3.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 144.6, 136.8, 131.4, 129.8, 128.9, 128.0, 127.1, 121.5, 119.8, 118.7, 118.7, 113.9, 112.6, 109.2, 55.3, 50.2, 32.6, 31.8; IR (film) 2927, 1510, 1248, 1010, 821 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}BrNO$ $[M+H]^+$ 420.0958, found 420.0953; mp 112-114 ^{o}C.

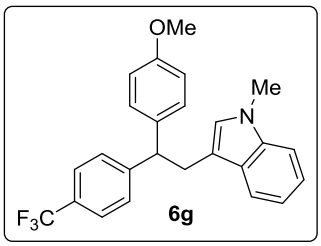
4-(1-(4-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)benzonitrile (**6f**)

N'-(2-bromo-1-(4-cyanophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (147 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6f** as a white solid (42 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.46 (m, 3H), 7.33-7.21 (m, 4H), 7.16 (d, J = 8.7 Hz, 2H), 7.09 (t, J = 7.9 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 6.43 (s, 1H), 4.38 (t, J = 7.7 Hz, 1H), 3.78 (s, 3H), 3.63 (s, 3H), 3.52-3.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 151.1, 136.8, 135.7, 132.2, 128.9, 128.8, 127.8, 127.1, 121.6, 119.1, 118.8, 118.6, 114.0, 112.1, 109.8, 109.2, 55.3, 51.0, 32.6, 31.6; IR (film) 2918, 2227, 1511, 1249, 909 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{23}N_2O$ $[M+H]^+$ 367.1805, found 367.1804; mp 154-156 ^{o}C.



3-(2-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)ethyl)-1-methylindole (**6g**)

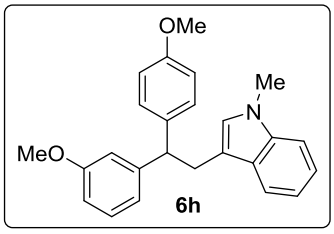
N'-(2-bromo-1-(4-(trifluoromethyl)phenyl)ethylidene)-4-methylbenzenesulfonohydrazide (162 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6g** as a pale yellow solid (44 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 7.23-7.15 (m, 4H), 7.10-7.07 (m, 1H), 6.82 (d, J = 8.1 Hz, 2H), 6.43 (s, 1H), 4.38 (t, J = 7.3 Hz, 1H), 3.75 (s, 3H), 3.59 (s, 3H), 3.47-3.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 149.7, 136.8, 136.3, 129.0, 128.3, 128.3 (q, J = 32.4 Hz), 127.9, 127.1, 125.3 (q, J =3.6 Hz), 124.4 (q, J =272.5 Hz), 121.5, 118.8, 118.7, 114.0, 112.4, 109.2, 55.3, 50.7, 32.6, 31.7; IR (film) 2909, 1505, 1325, 1249, 1068 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{23}F_3NO$ $[M+H]^+$ 410.1726, found



410.1724; mp 98-100 ^{o}C.

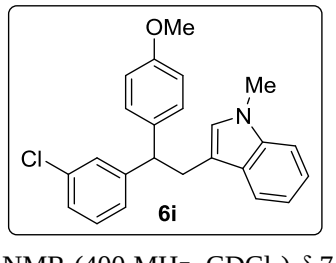
3-(2-(3-methoxyphenyl)-2-(4-methoxyphenyl)ethyl)-1-methylindole (**6h**)

N'-(2-bromo-1-(3-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (149 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6h** as a pale yellow oil (81 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.8 Hz, 1H), 7.26-7.12 (m, 5H), 7.07 (t, J = 7.1 Hz, 1H), 6.87-6.78 (m, 4H), 6.70 (d, J = 8.1 Hz, 1H), 6.44 (s, 1H), 4.29 (t, J = 7.6 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.57 (s, 3H), 3.44 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 157.9, 147.4, 137.2, 136.8, 129.3, 129.0, 128.1, 127.1, 121.4, 120.4, 118.8, 118.6, 114.1, 113.8, 113.0, 111.1, 109.1, 55.3, 55.2, 50.9, 32.6, 31.8; IR (film) 2924, 1510, 1248, 1037, 739 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{26}NO_2$ $[M+H]^+$ 372.1958, found 372.1952.



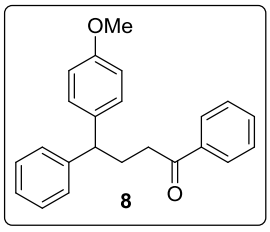
3-(2-(3-chlorophenyl)-2-(4-methoxyphenyl)ethyl)-1-methylindole (**6i**)

N'-(2-chloro-1-(3-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (134 mg, 0.375 mmol), 1-methylindole (39 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL). After column chromatography giving **6i** as a pale yellow oil (78 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.27-7.05 (m, 9H), 6.80 (d, J = 8.7 Hz, 2H), 6.43 (s, 1H), 4.28 (t, J = 7.7 Hz, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 3.42 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 147.7, 136.8, 136.5, 134.1, 129.6, 129.0, 128.1, 128.0, 127.1, 126.3, 126.2, 121.5, 118.8, 118.7, 113.9, 112.6, 109.2, 55.3, 50.7, 32.6, 31.7; IR (film) 2930, 1510, 1248, 908, 738 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}ClNO$ $[M+H]^+$ 376.1463, found 376.1460.



4-(4-methoxyphenyl)-1,4-diphenylbutan-1-one (**8**)

(*N*'-(2-chloro-1-phenylethylidene)-4-methylbenzenesulfonohydrazide (121 mg, 0.375 mmol), trimethyl((1-phenylvinyl)oxy)silane (58 mg, 0.3 mmol), (4-methoxyphenyl)boronic acid (57 mg, 0.375 mmol), potassium carbonate (83 mg, 0.6 mmol), zinc fluoride (6.2 mg, 0.06 mmol) were reacted at 120 ^{o}C in the solvent of toluene (3 mL) and water (100 μL).

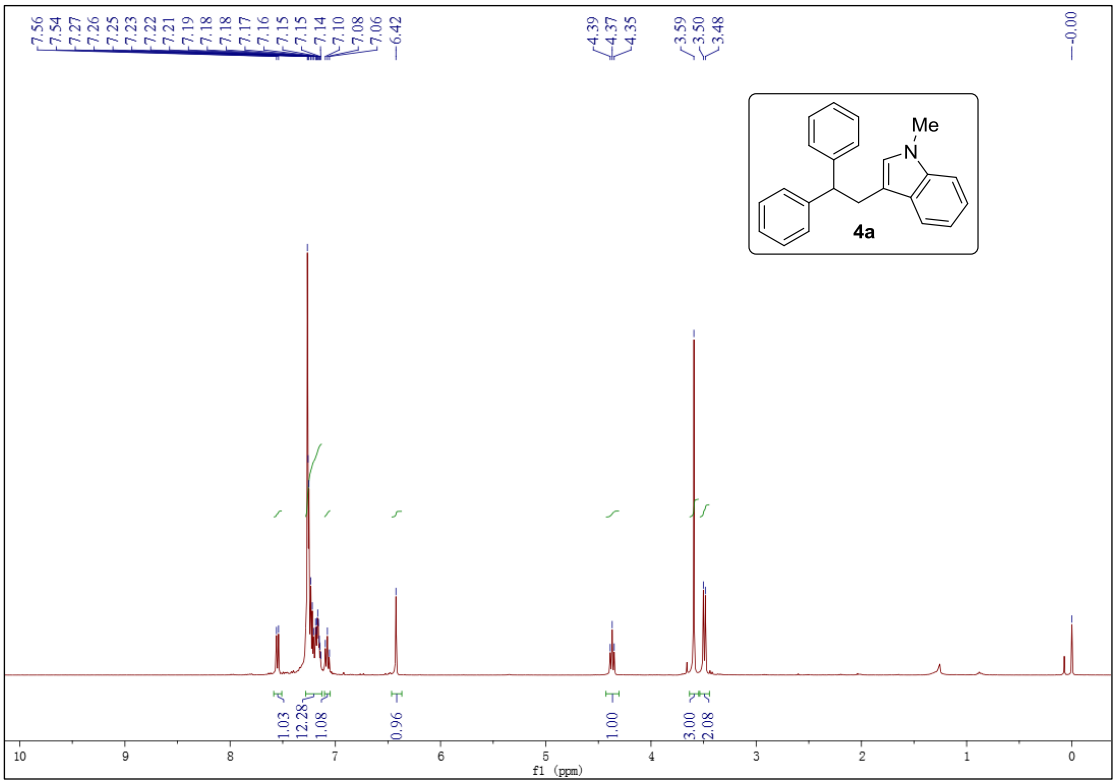


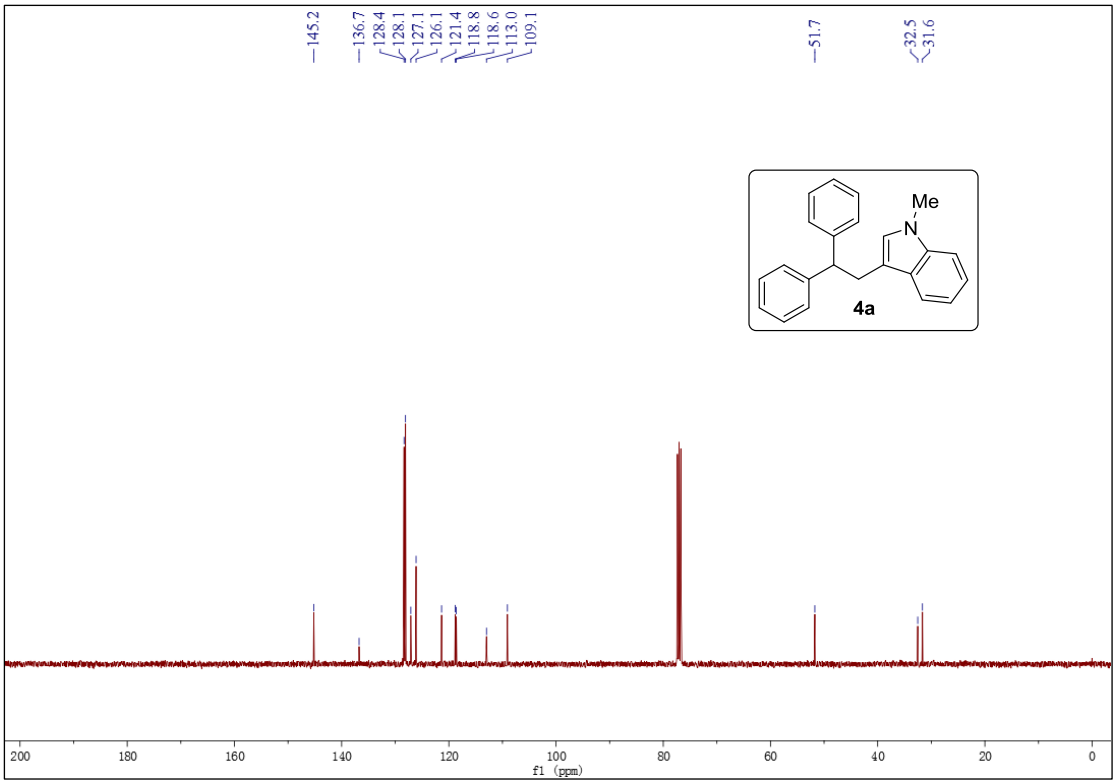
After column chromatography giving **8** as a colorless oil (45 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.5 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.31-7.23 (m, 4H), 7.18 (d, J = 8.5 Hz, 3H), 6.83 (d, J = 8.7 Hz, 2H), 3.97 (t, J = 7.9 Hz, 1H), 3.77 (s, 3H), 2.97-2.85 (m, 2H), 2.47 (q, J = 15.1, 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 158.0, 144.8, 136.9, 136.5, 133.0, 128.8, 128.5, 128.5, 128.0, 127.8, 126.3, 113.9, 55.2, 49.7, 37.0, 30.0; IR (film) 2919, 1683, 1511, 1249, 910 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}NaO_2$ $[M+Na]^+$ 353.1512, found 353.1512.

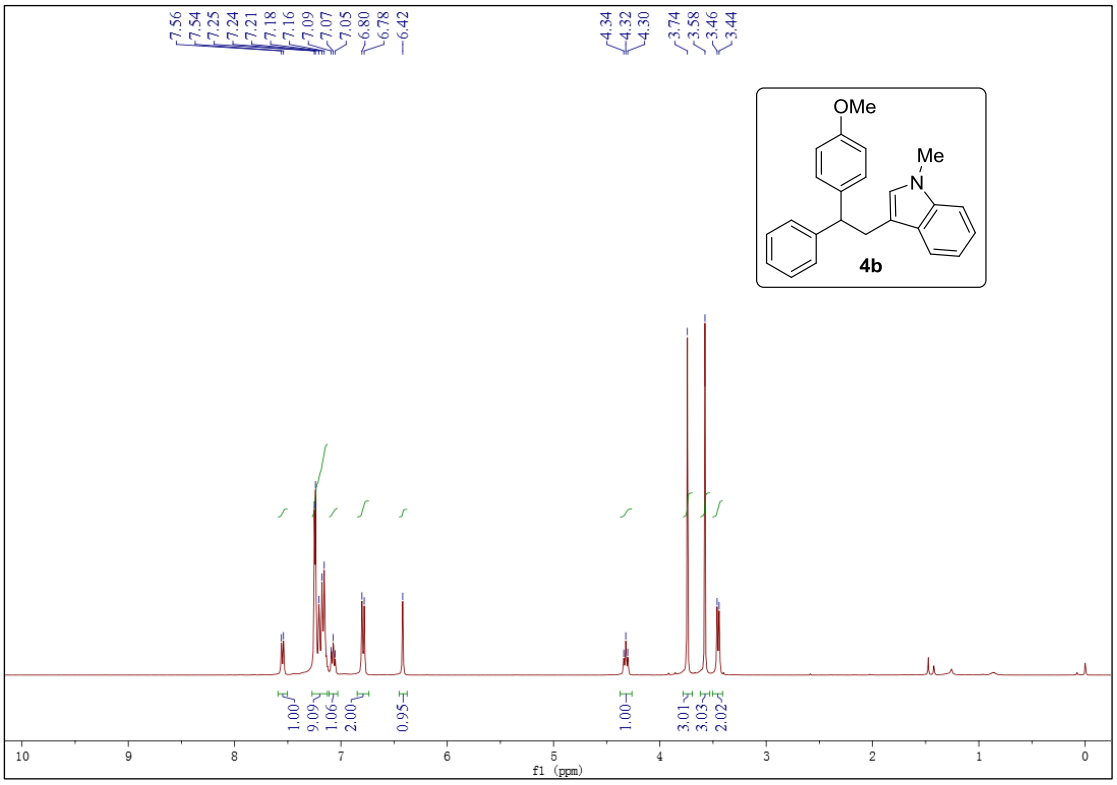
5. Reference

1 J. M. Hatcher, D. M. Coltart, *J. Am. Chem. Soc*. **2010**, *132*, 4546.

6. ^{1}H and ^{13}C spectra



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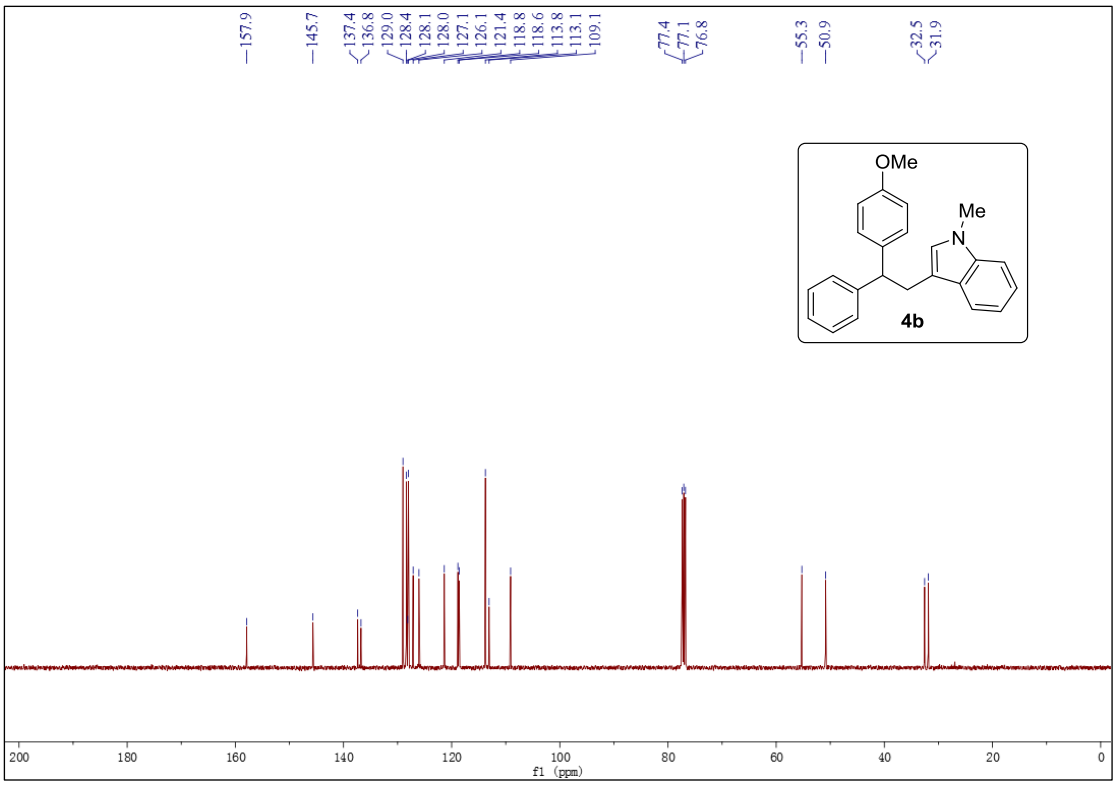
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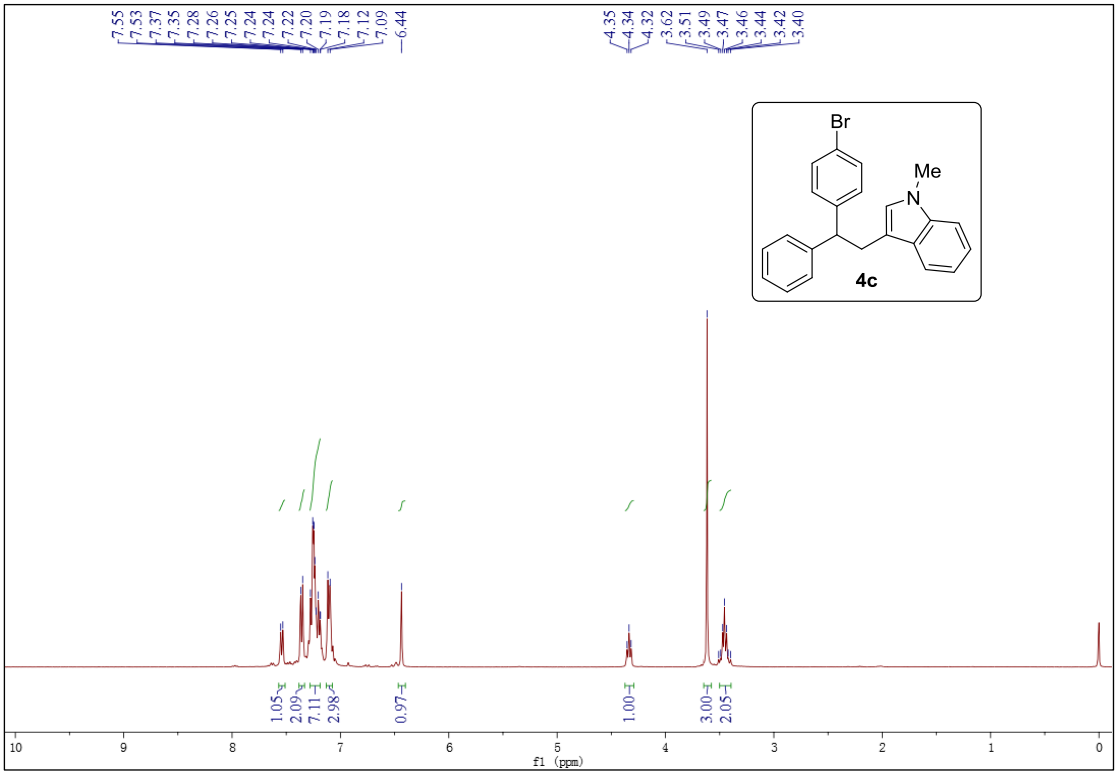
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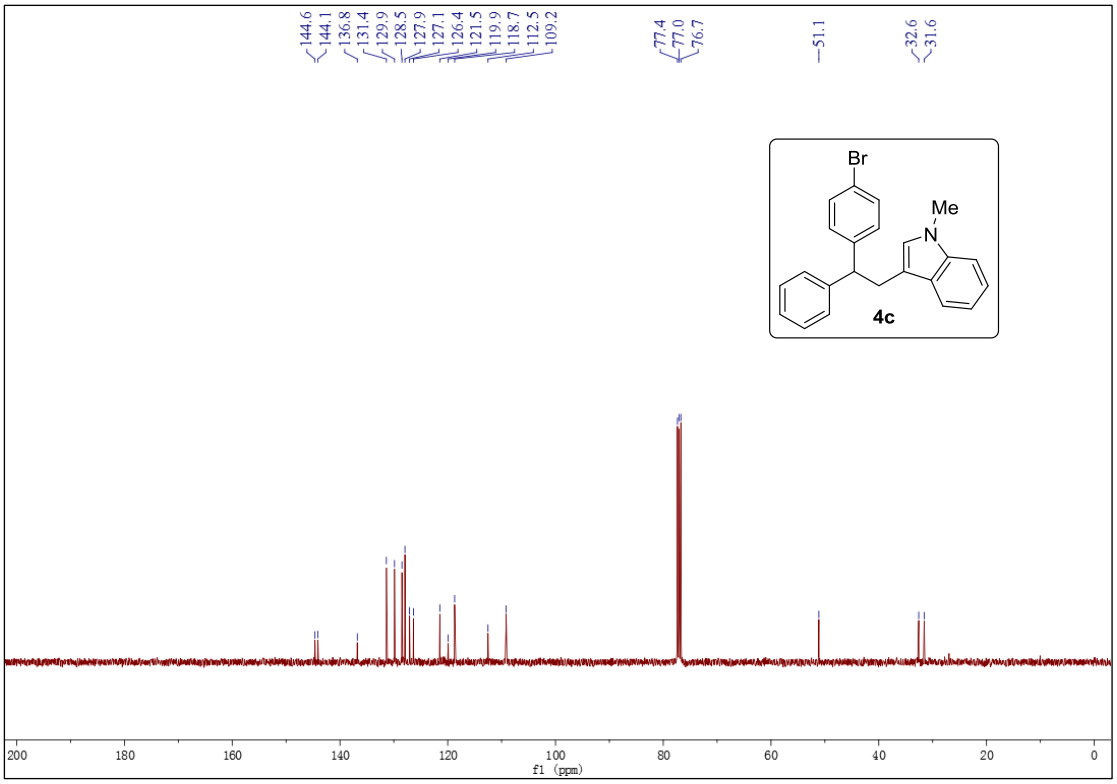
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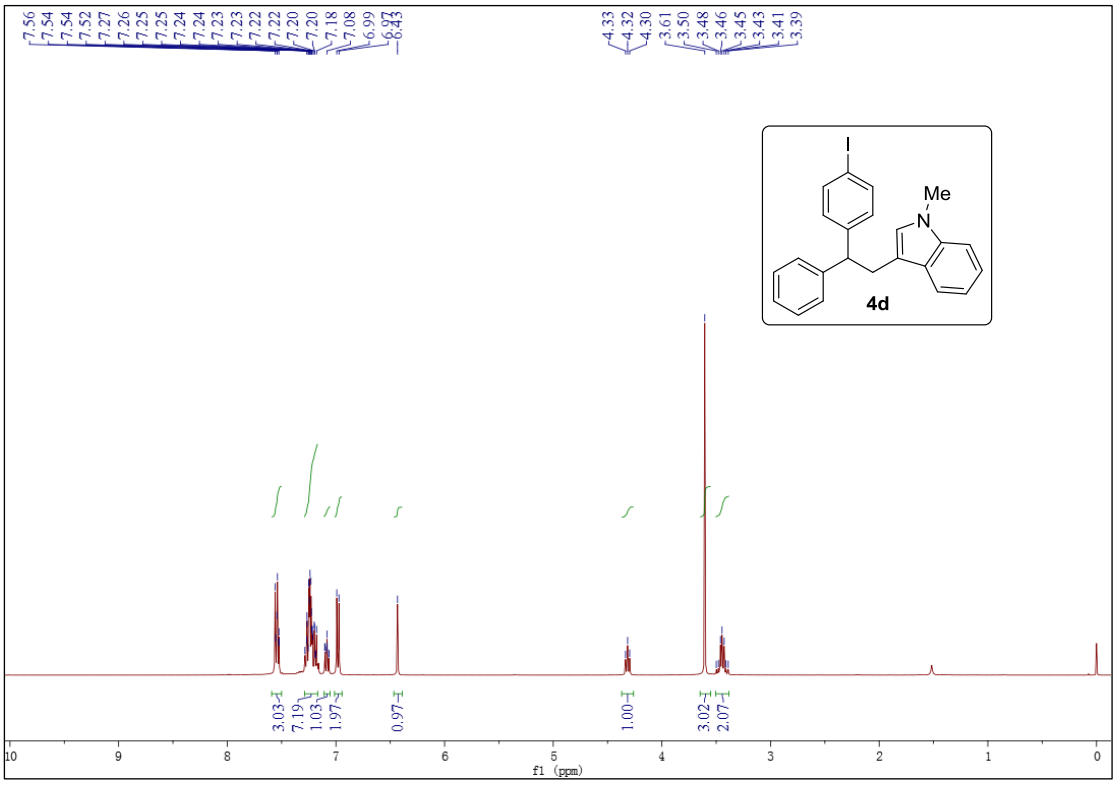
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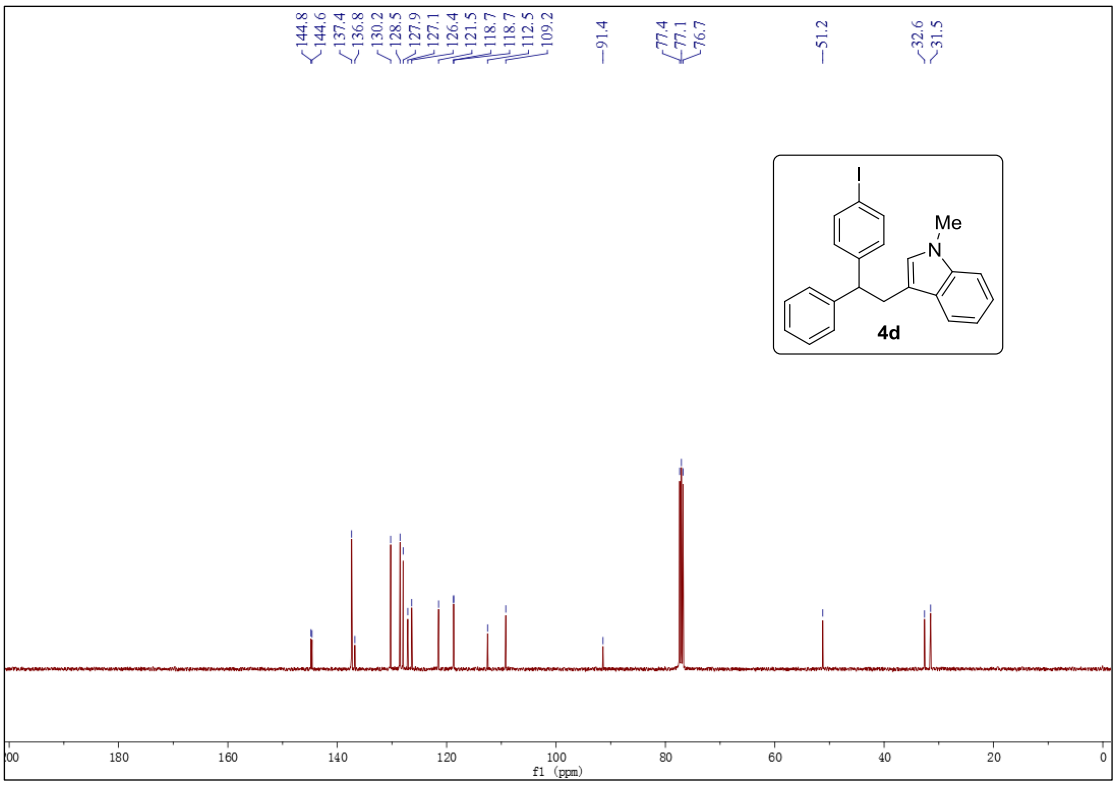
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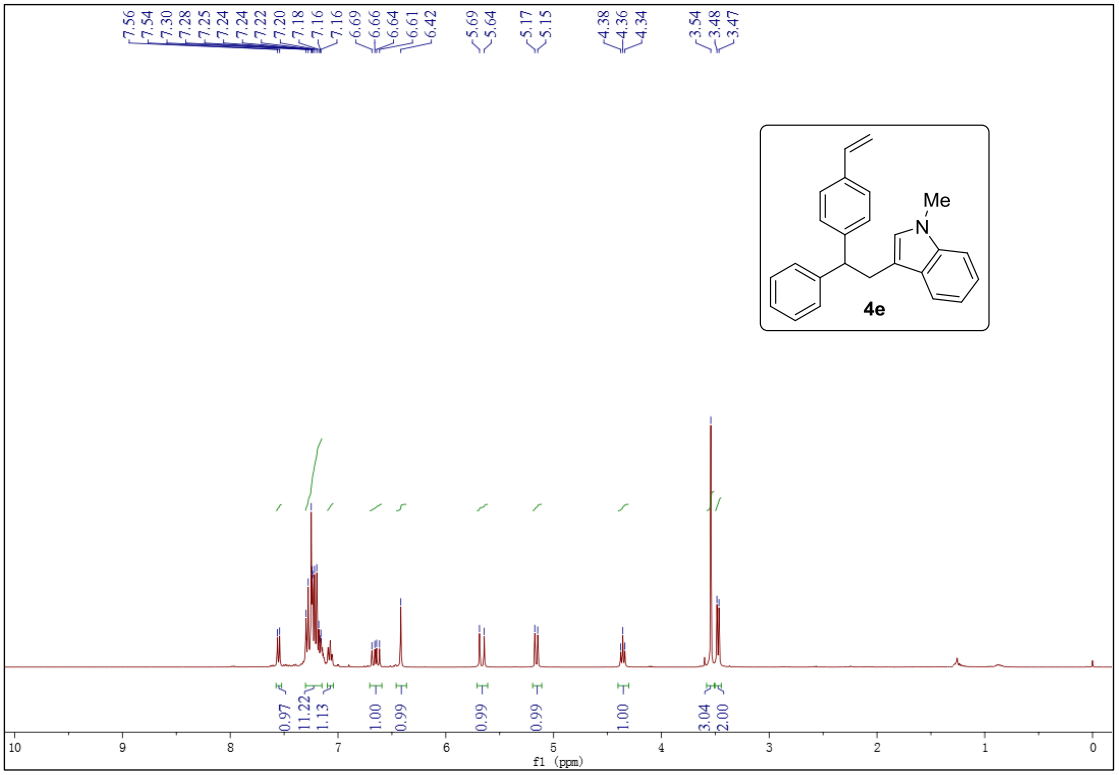
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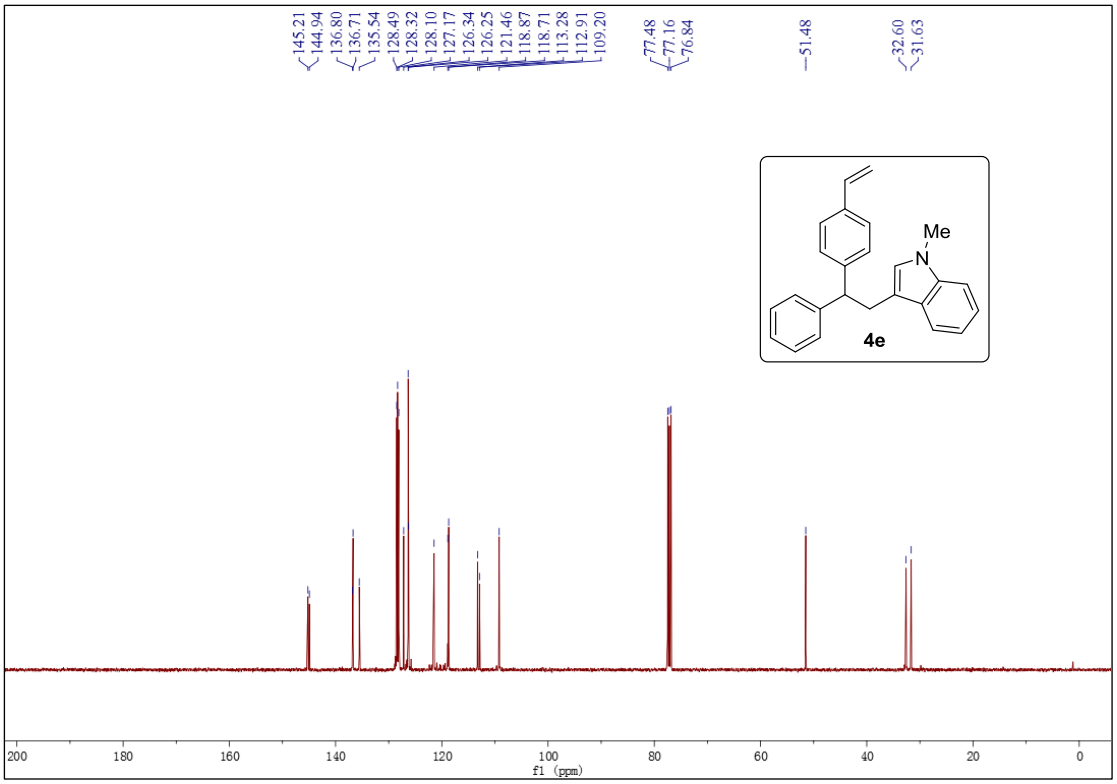
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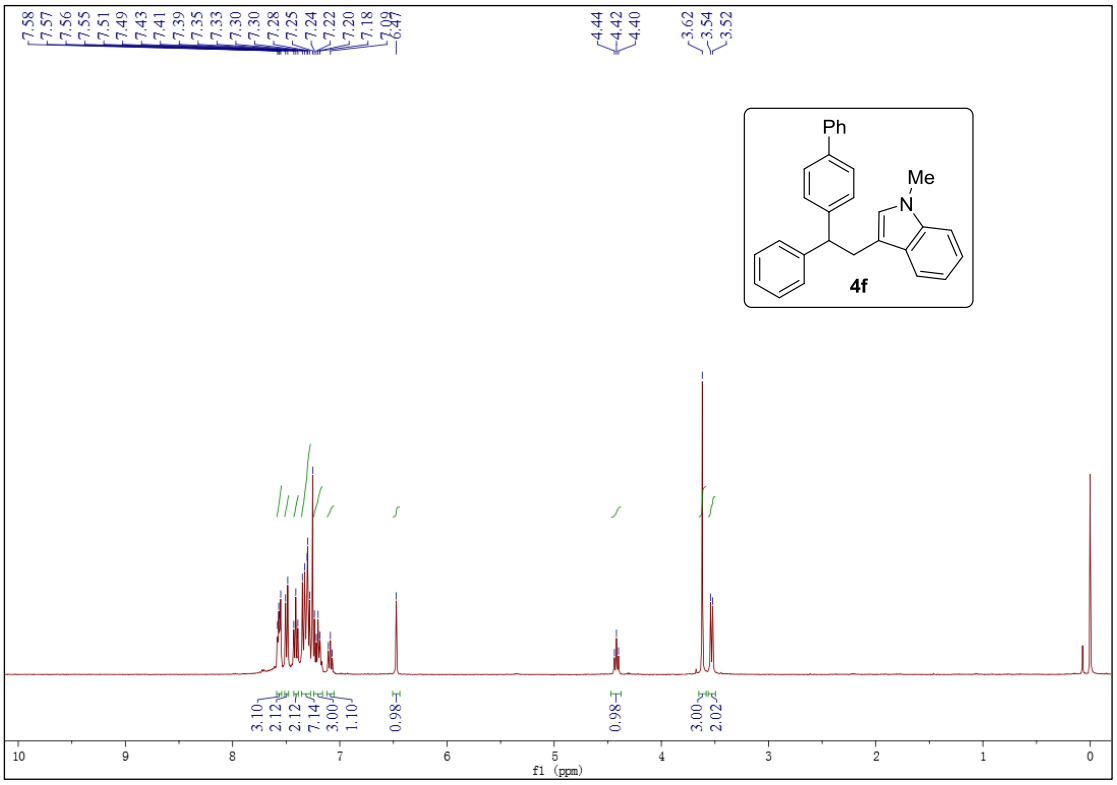
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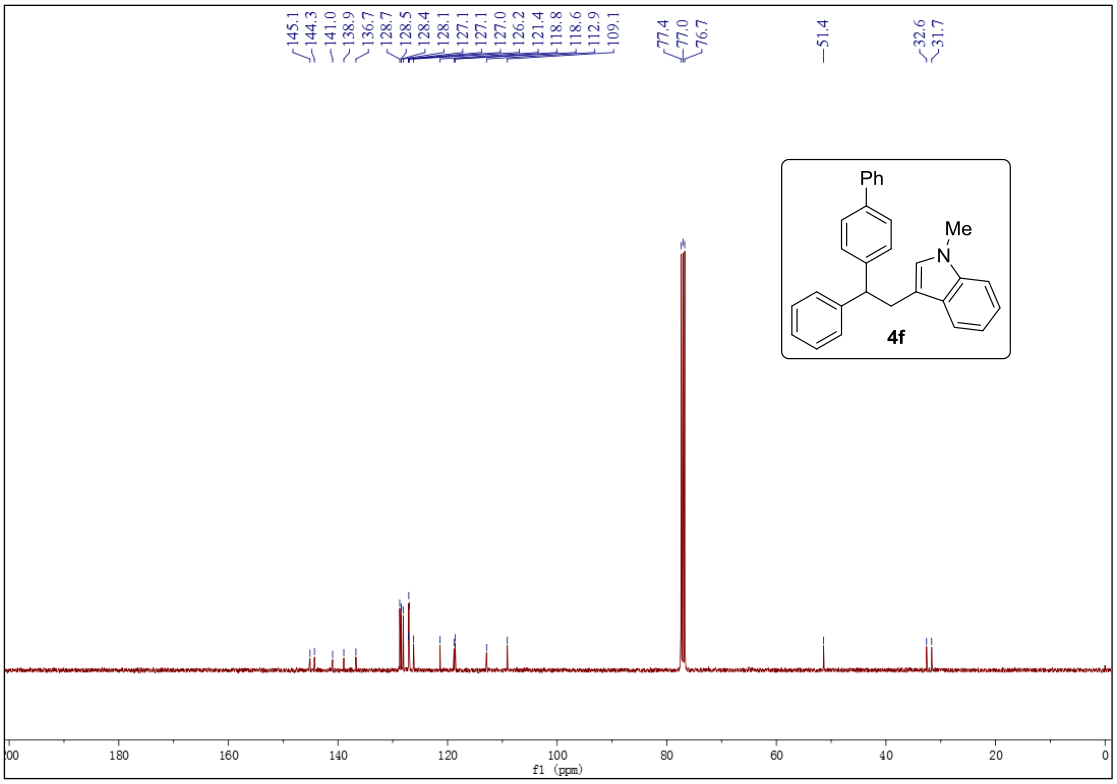
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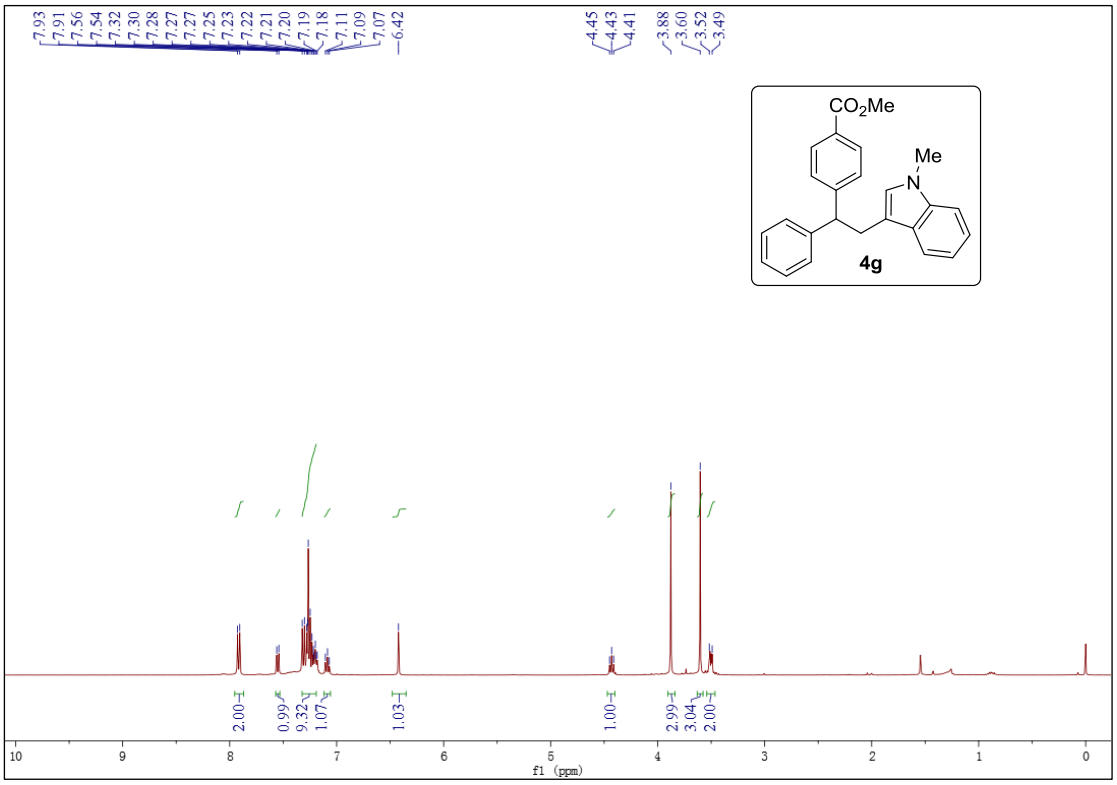
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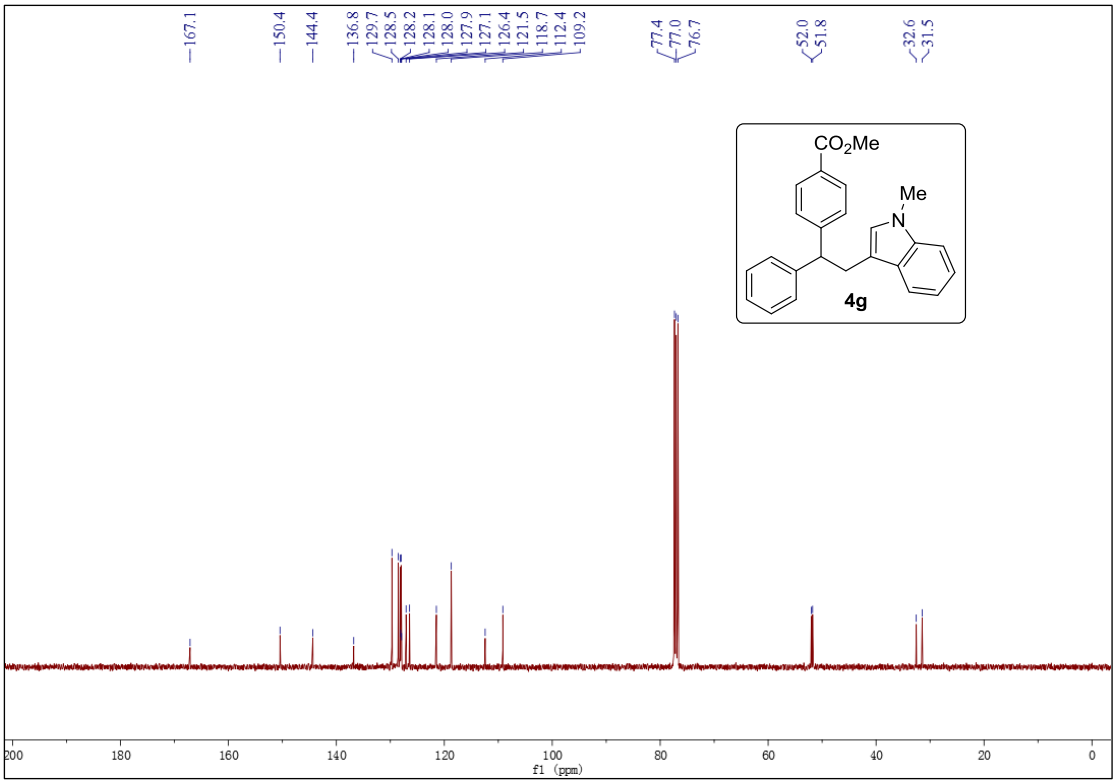
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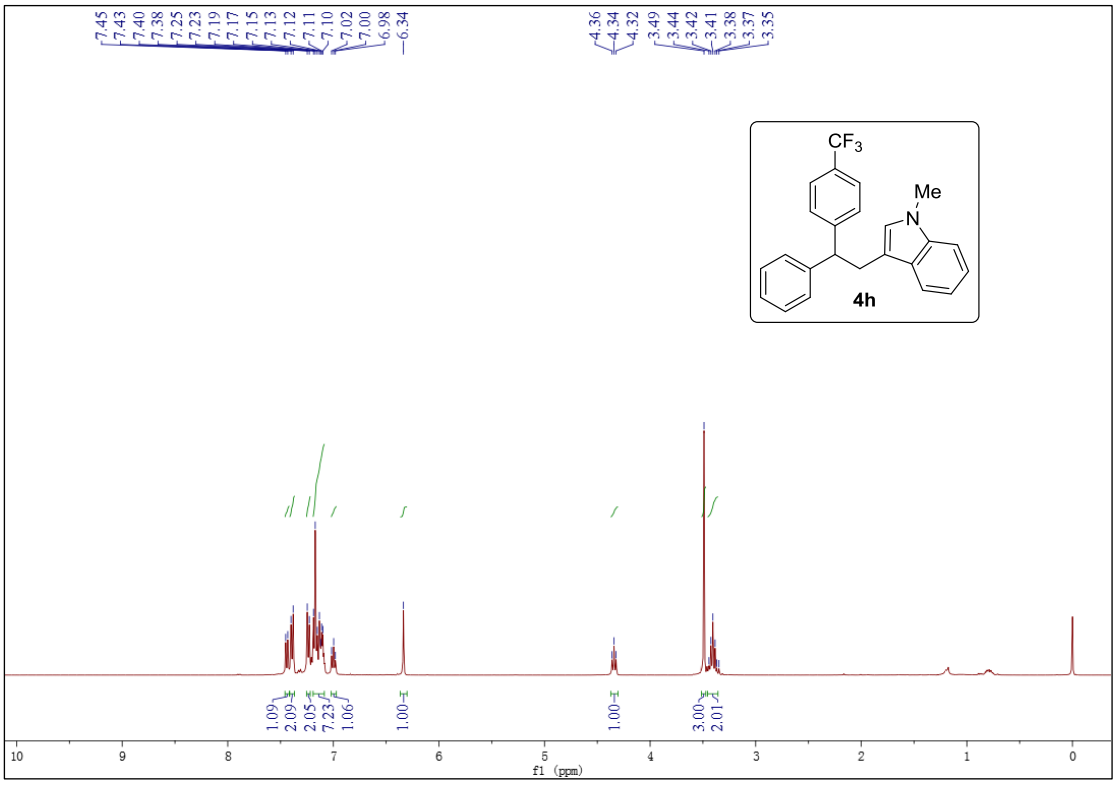
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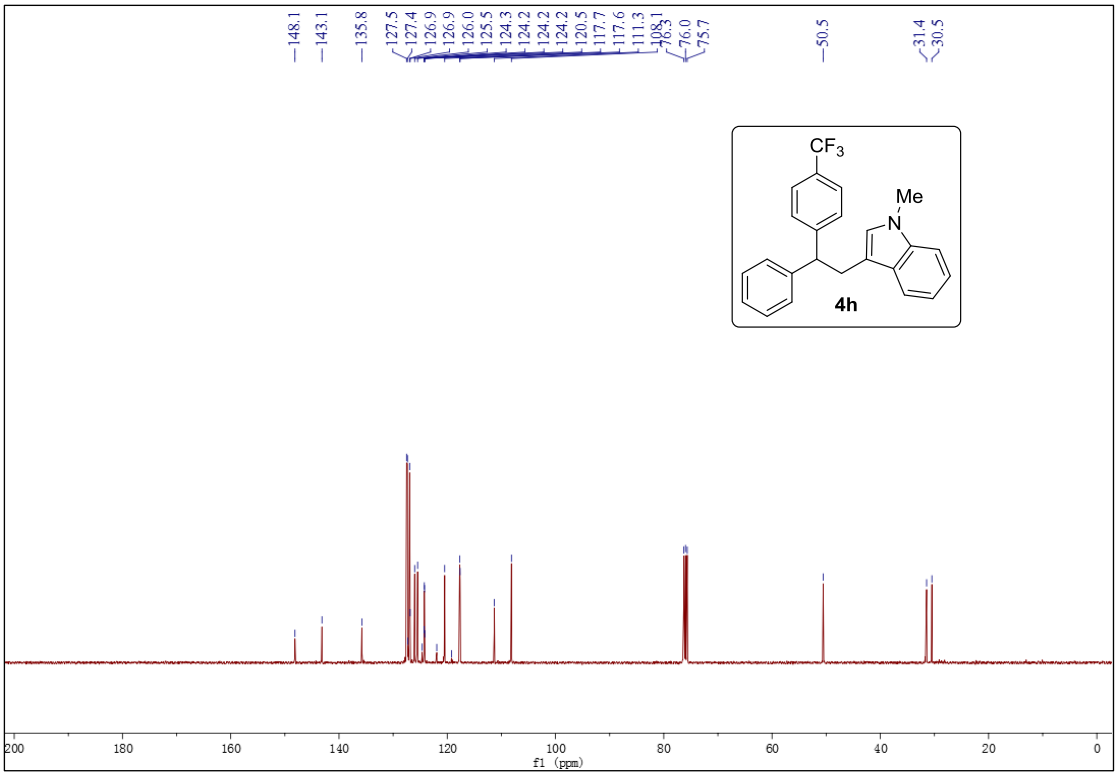
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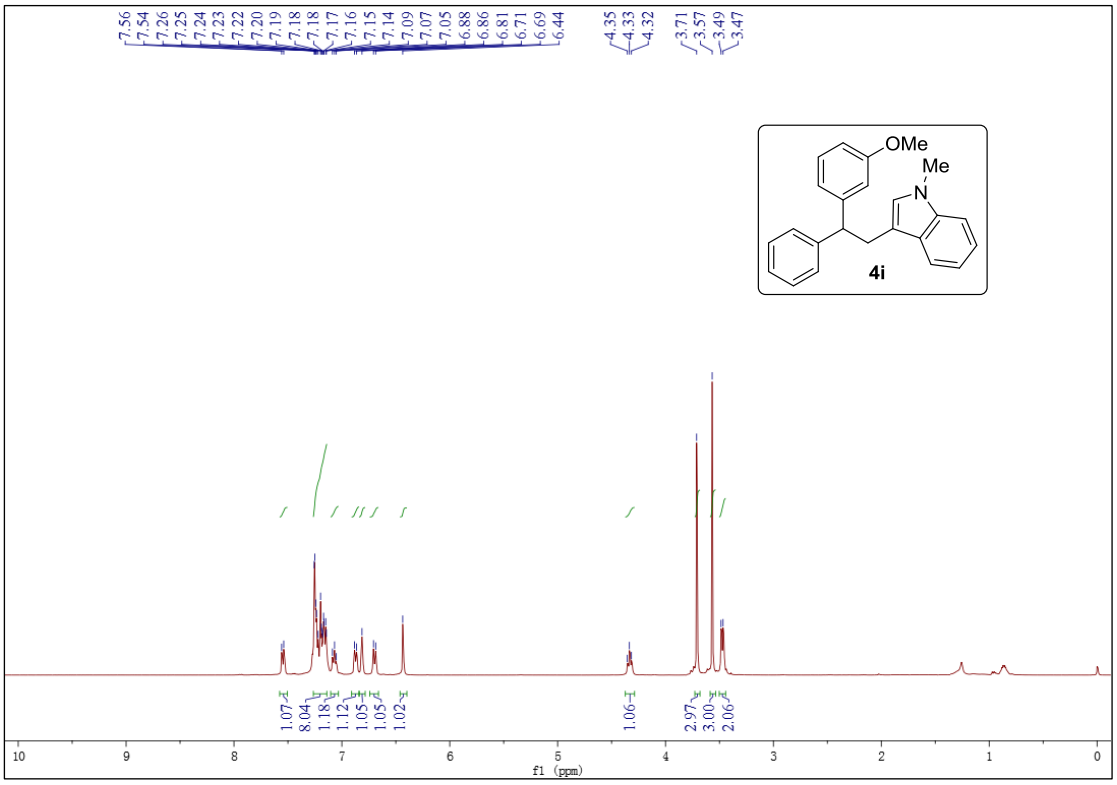
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4.32
3.71
3.57
3.49
3.47
OMe
Me
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4i
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1.18
1.12
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1.02
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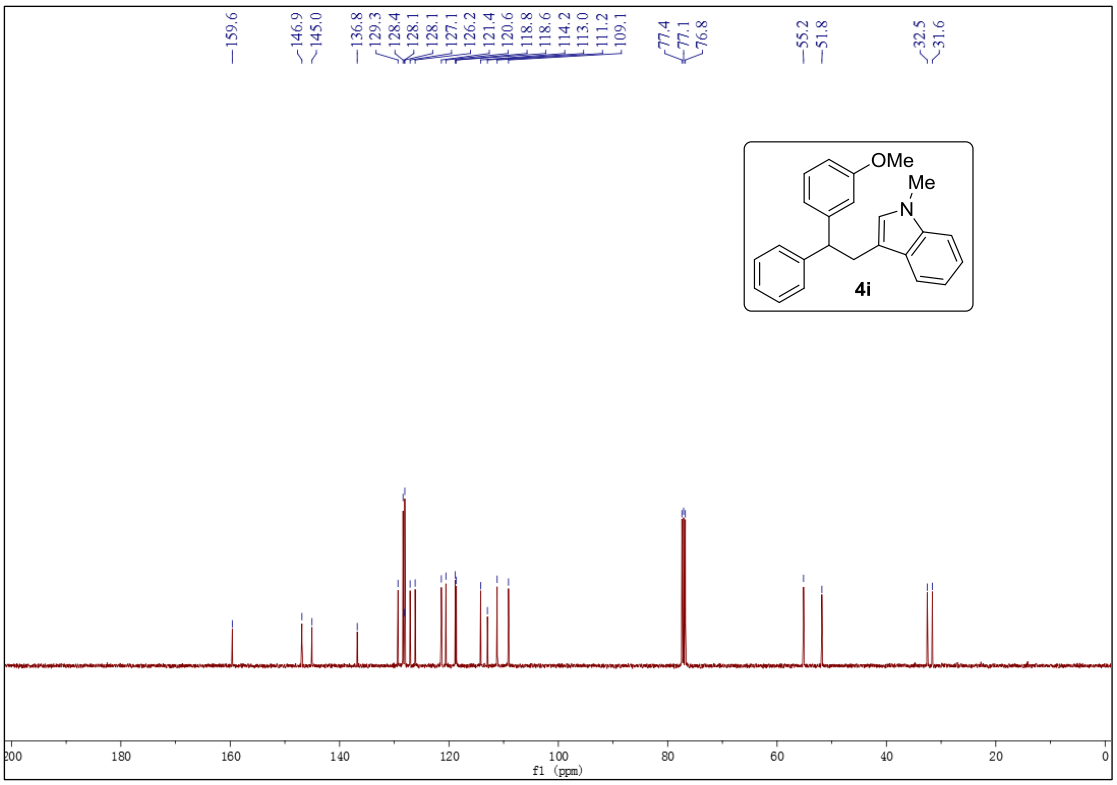
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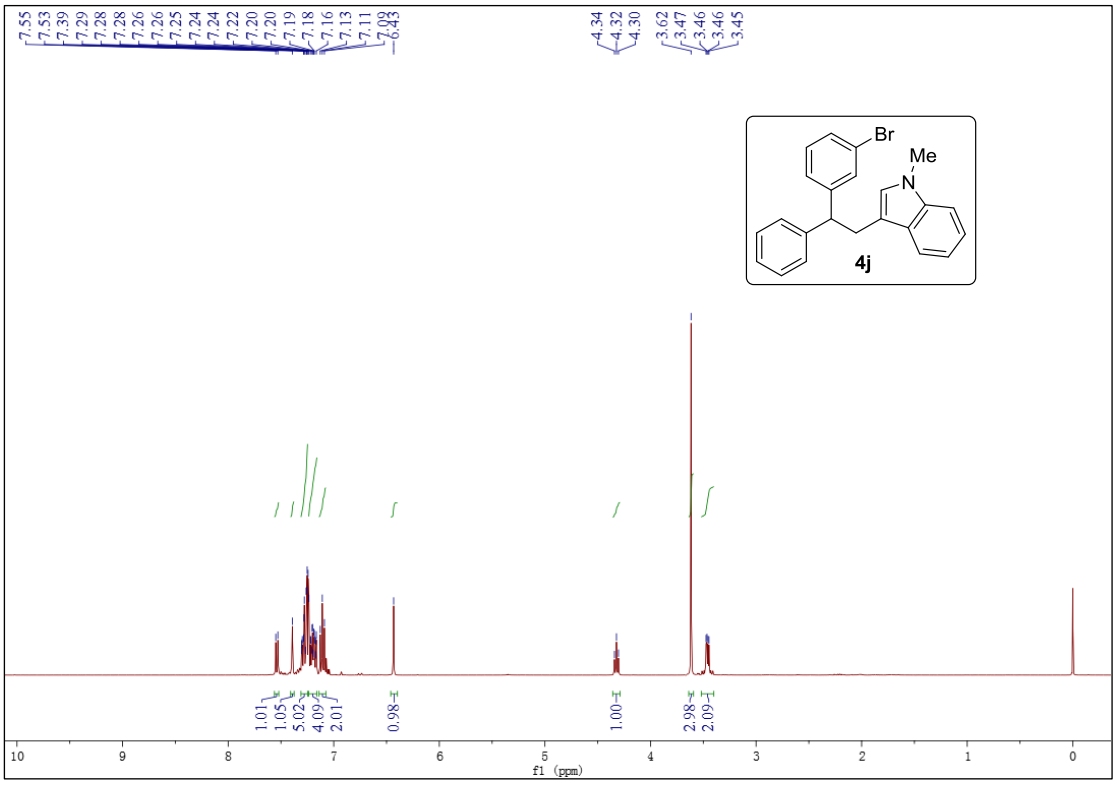
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3.47
3.46
3.46
3.45
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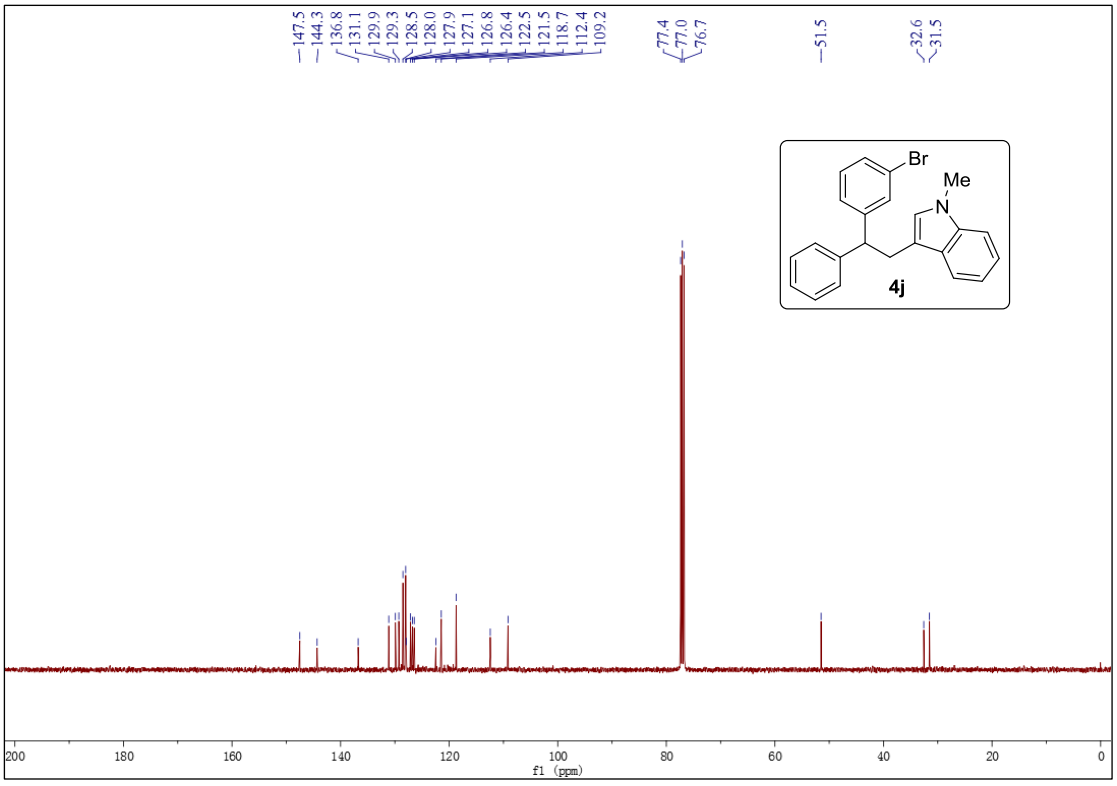
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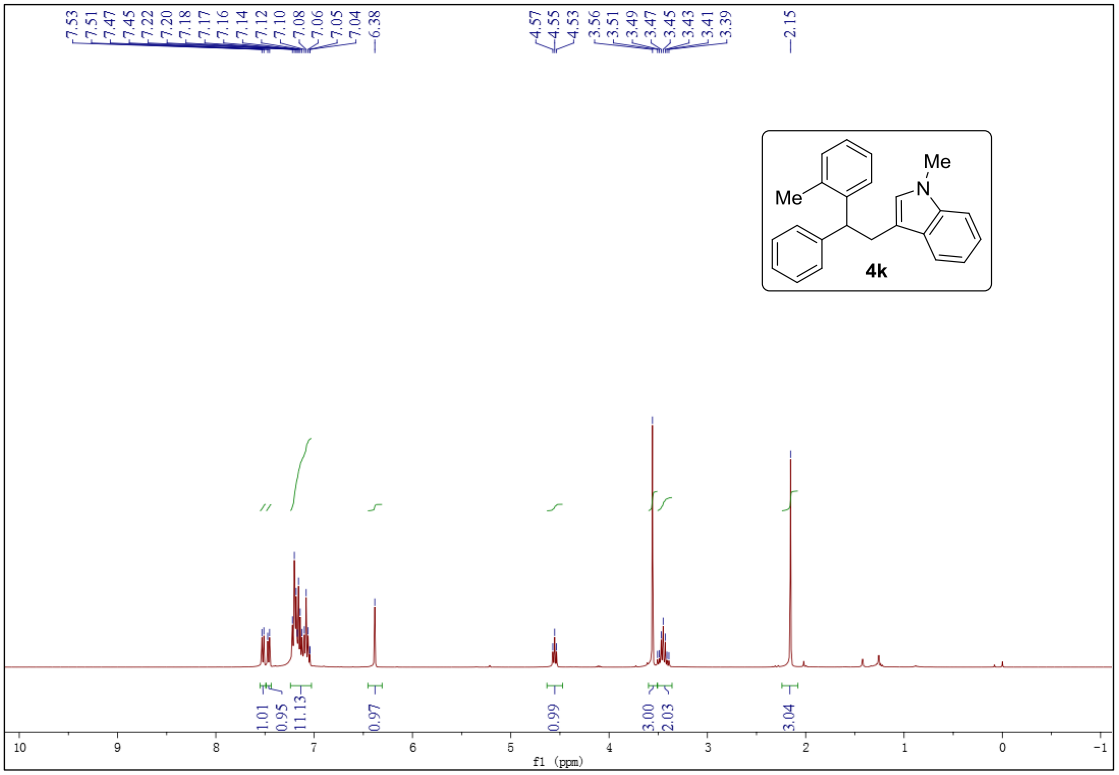
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7.05
7.04
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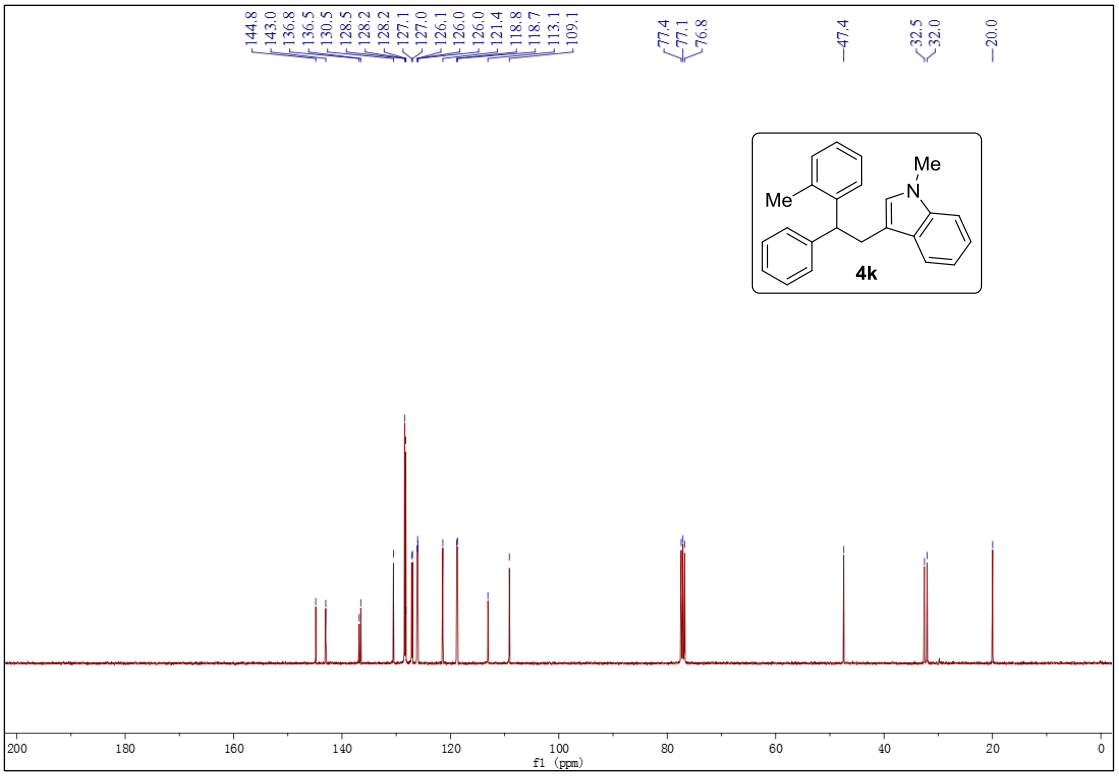
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118.7
113.1
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Me
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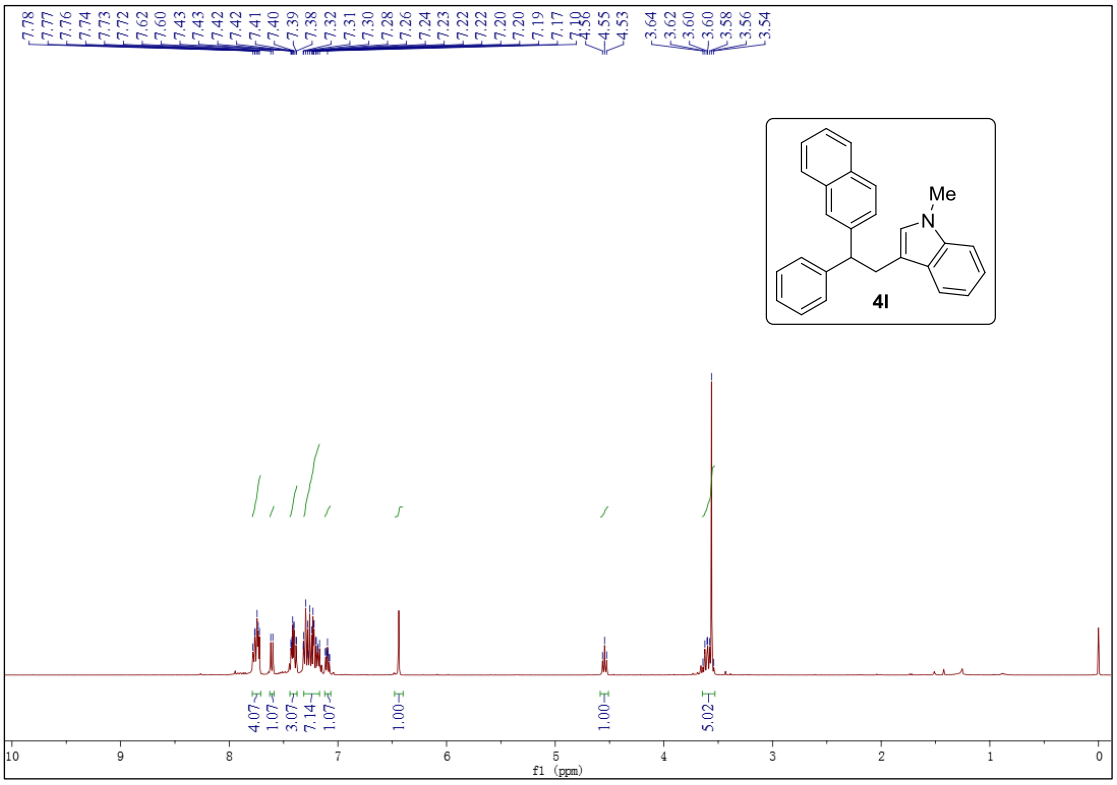
4k
f1 (ppm)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3.60
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3.56
3.54
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1.07
3.07
7.14
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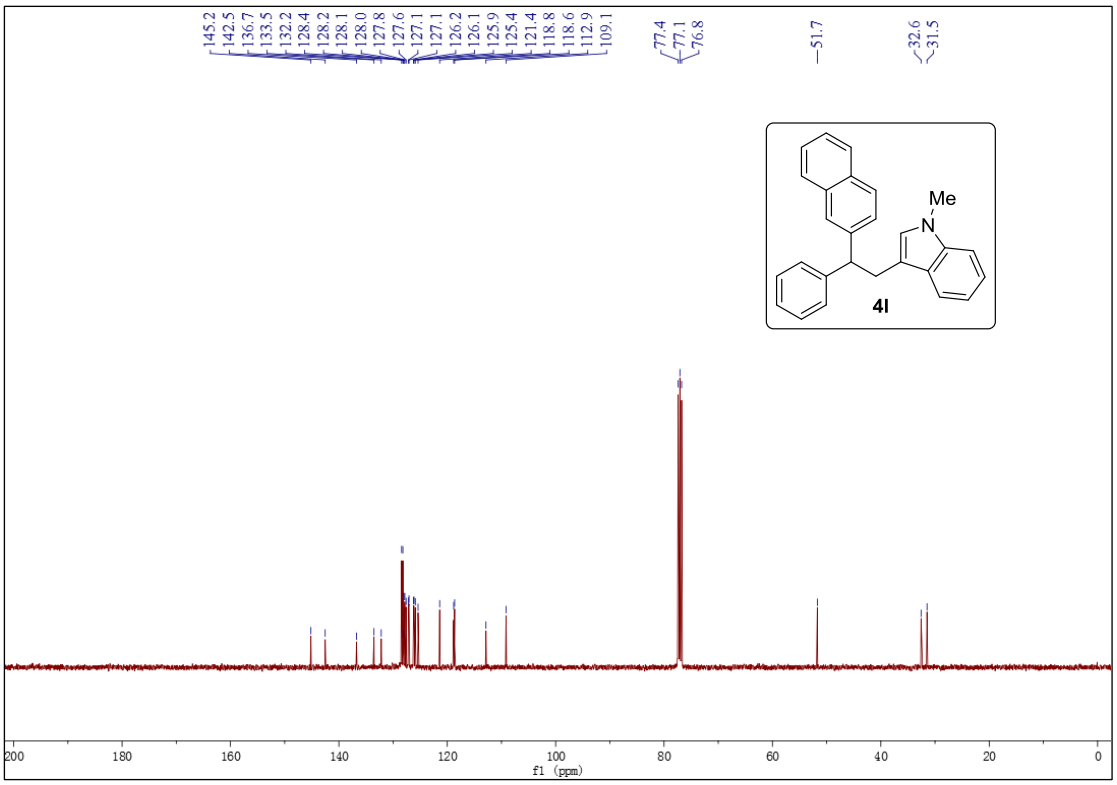
f1 (ppm)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121.4
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77.4
77.1
76.8
51.7
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4l
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100
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20
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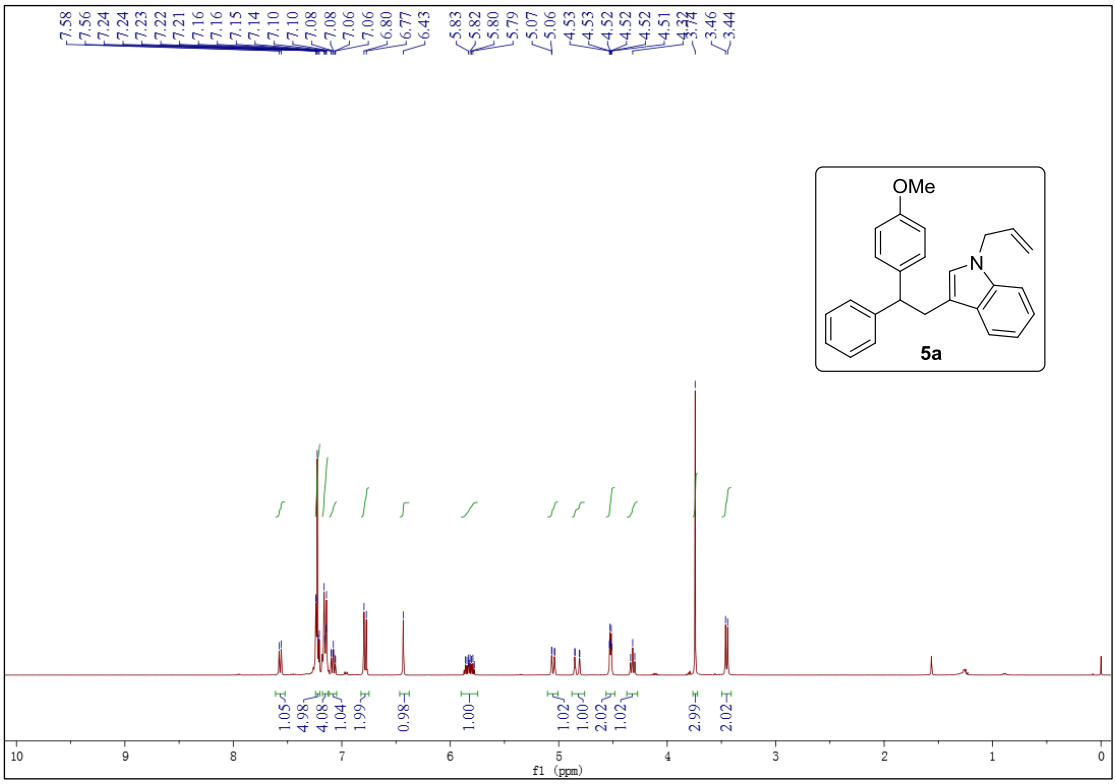
f1 (ppm)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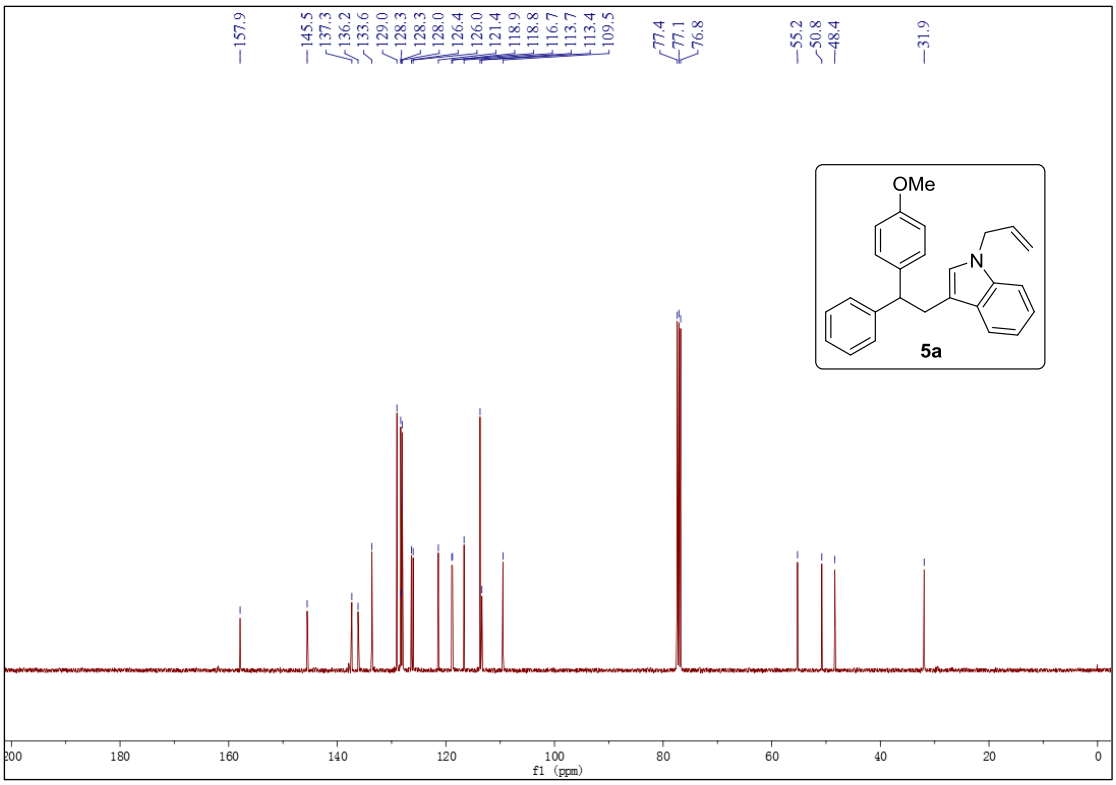
f1 (ppm)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76.8
55.2
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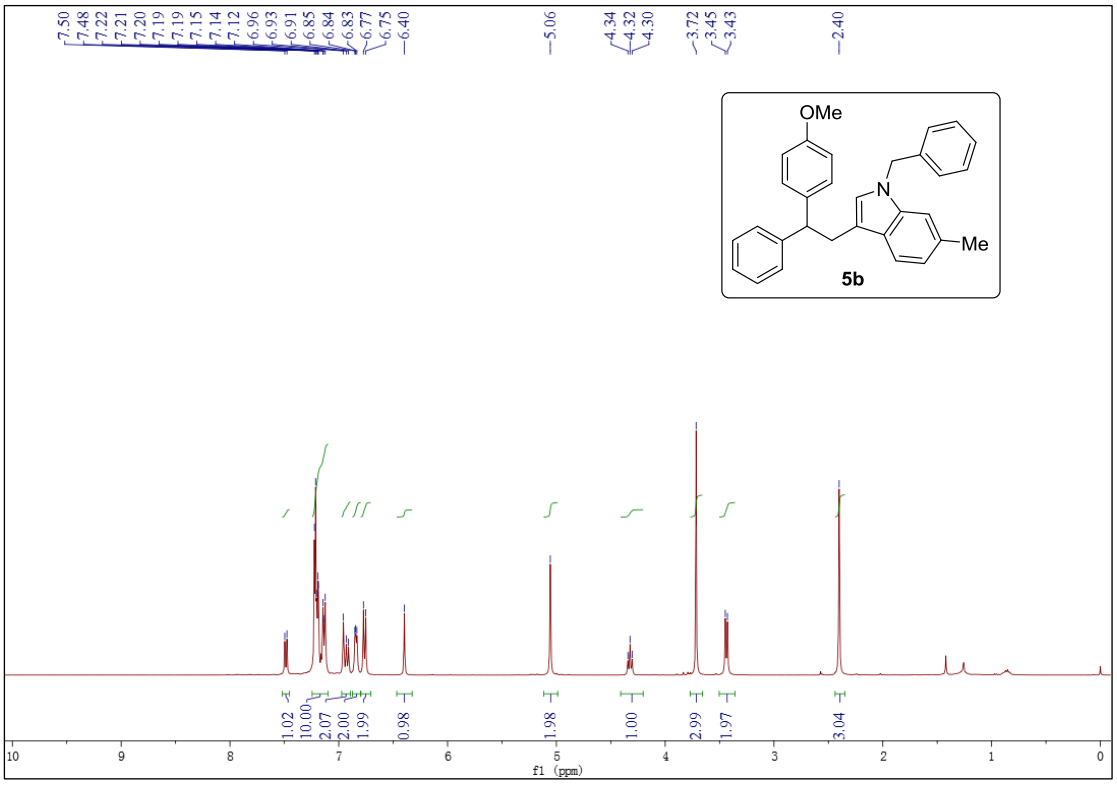
f1 (ppm)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Me
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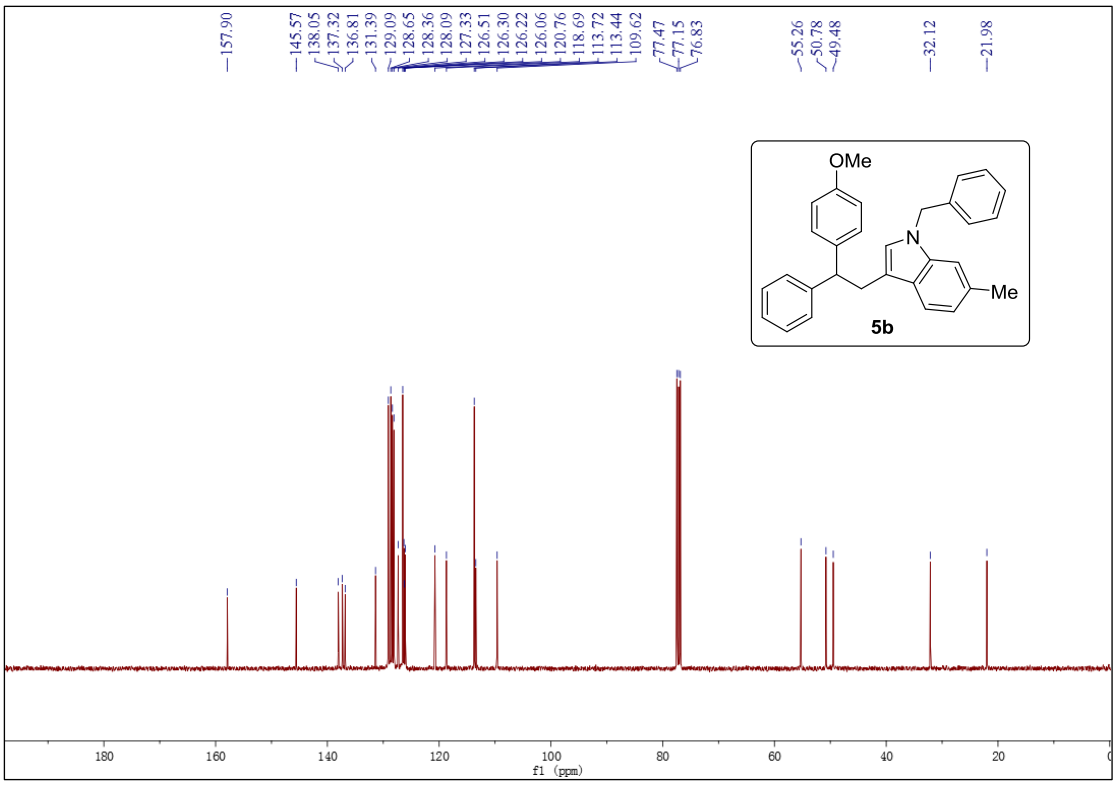
f1 (ppm)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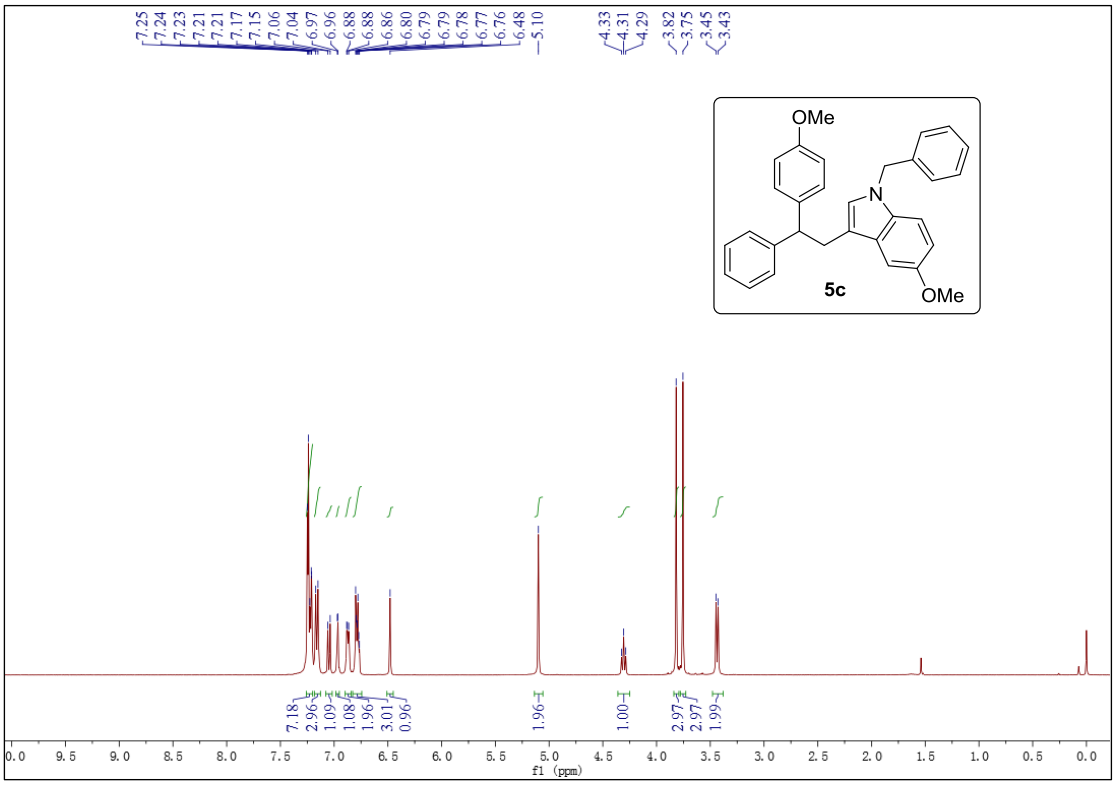
5b
f1 (ppm)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6.76
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4.29
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3.75
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3.43
OMe
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5c
OMe
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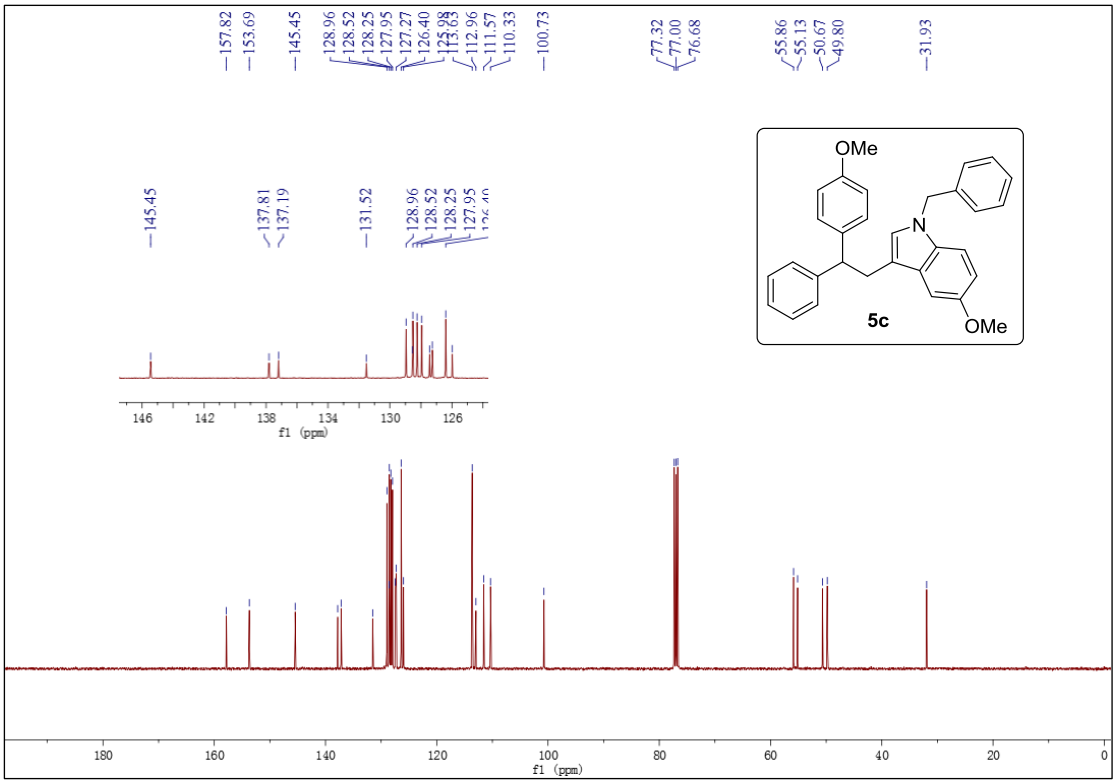
f1 (ppm)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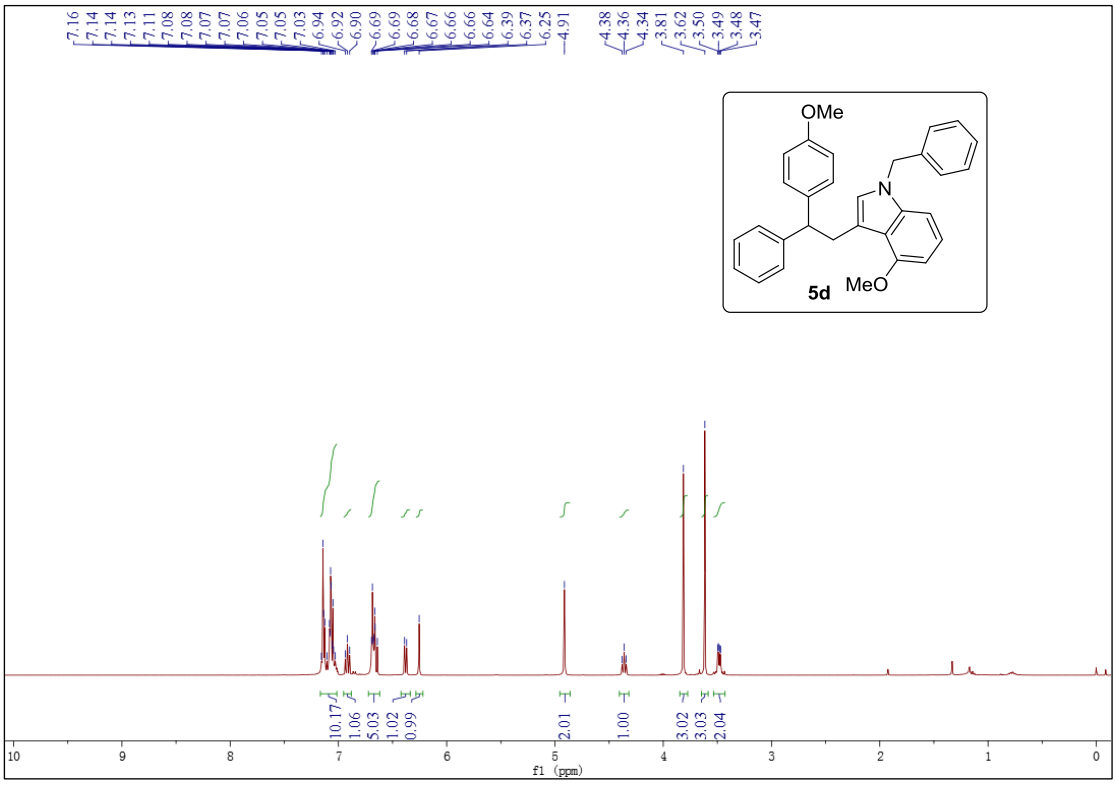
f1 (ppm)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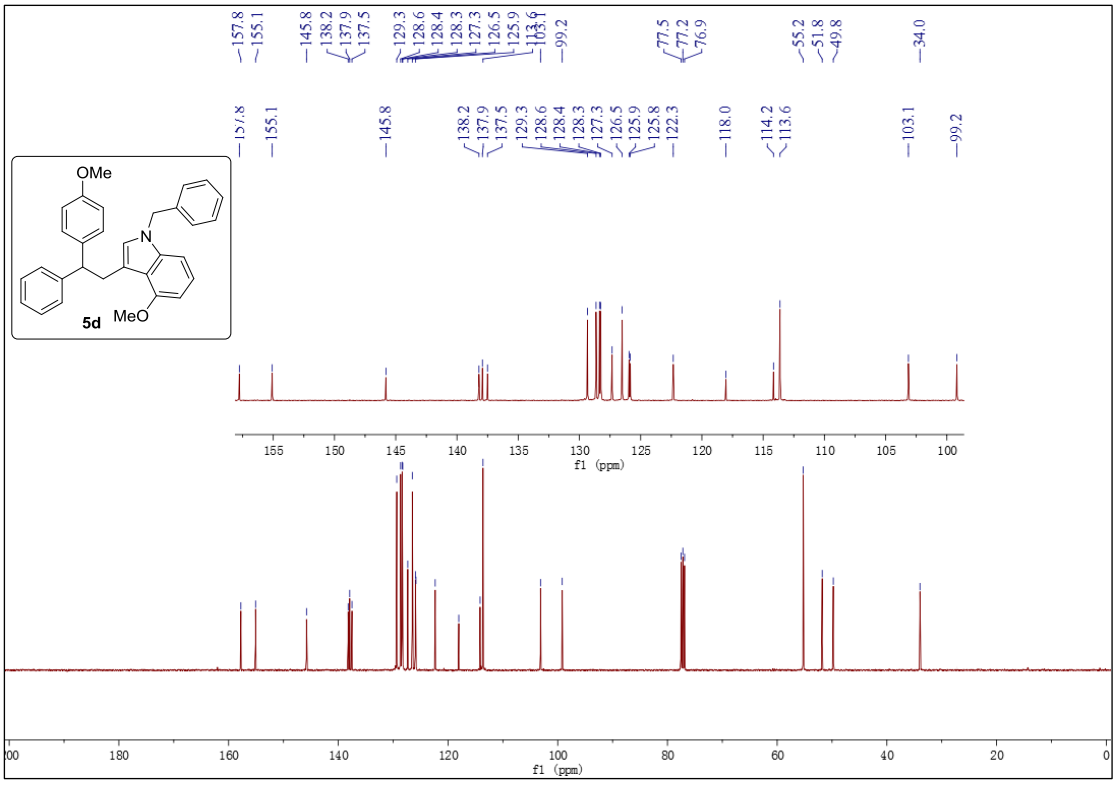
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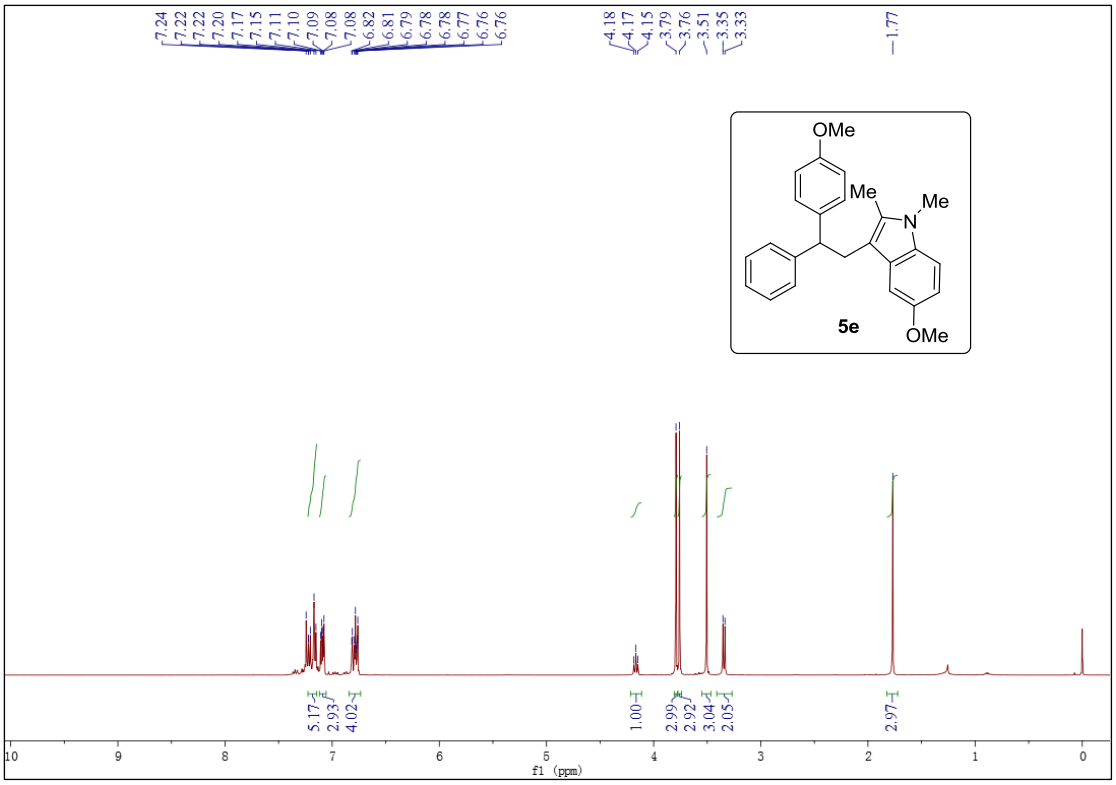
f1 (ppm)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Me
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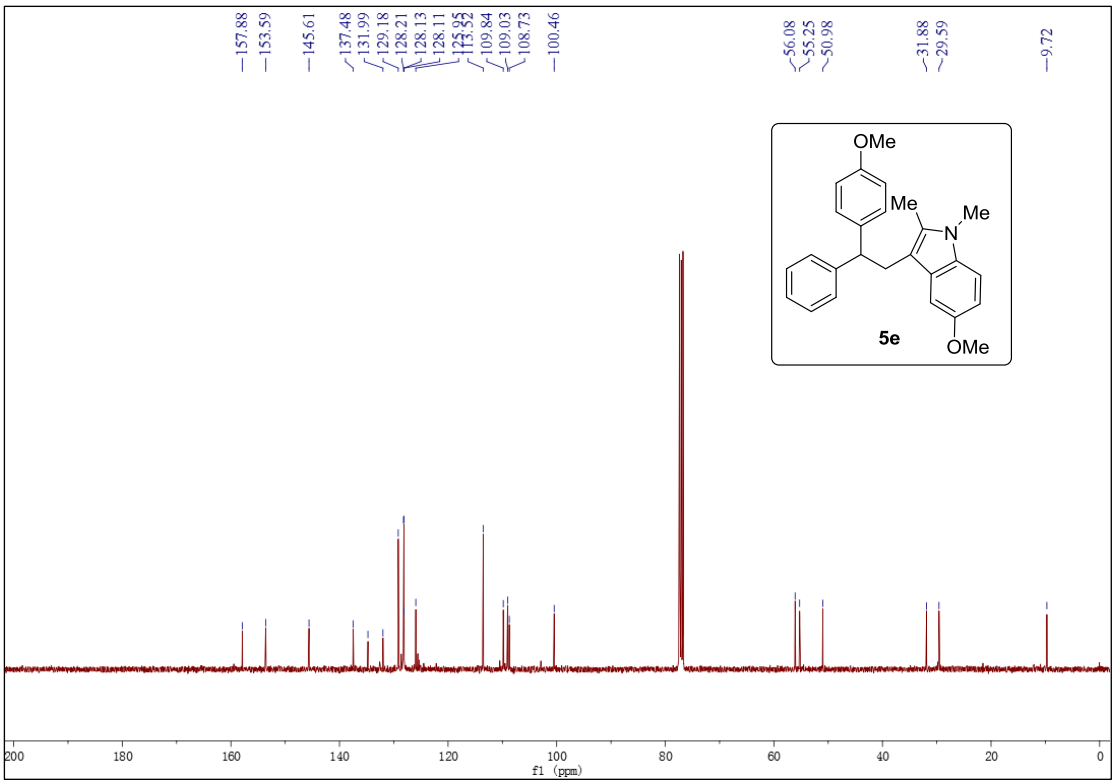
2.97
f1 (ppm)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Me
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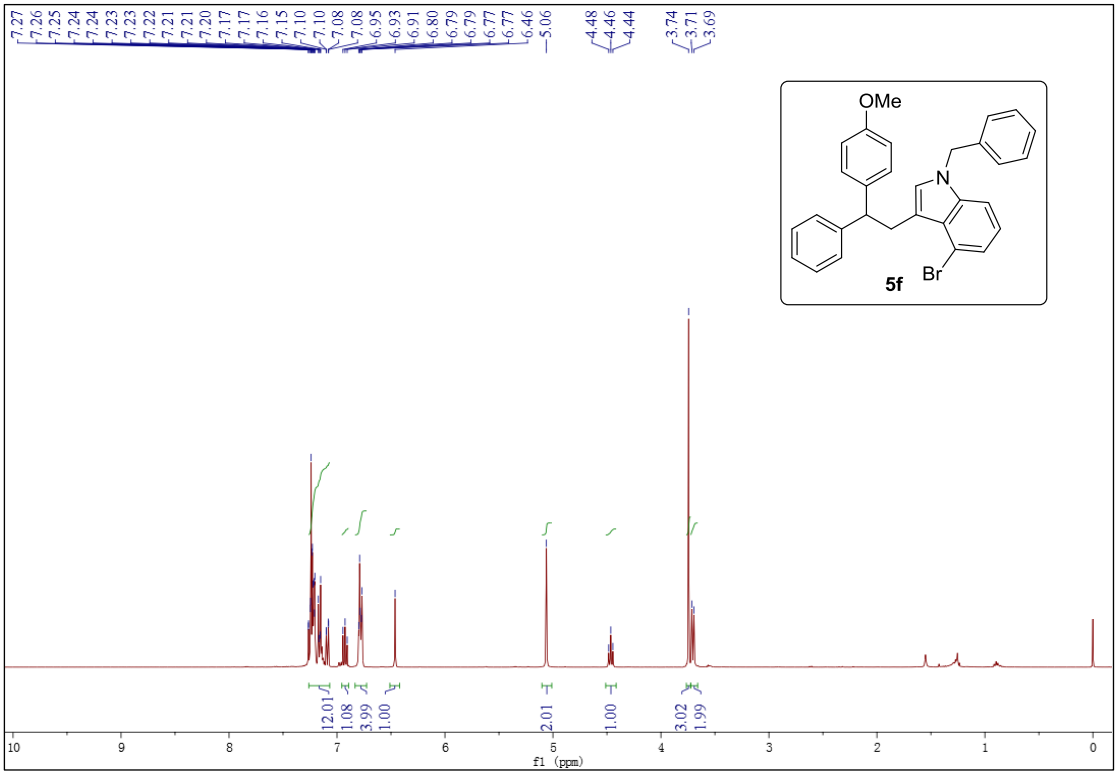
OMe
f1 (ppm)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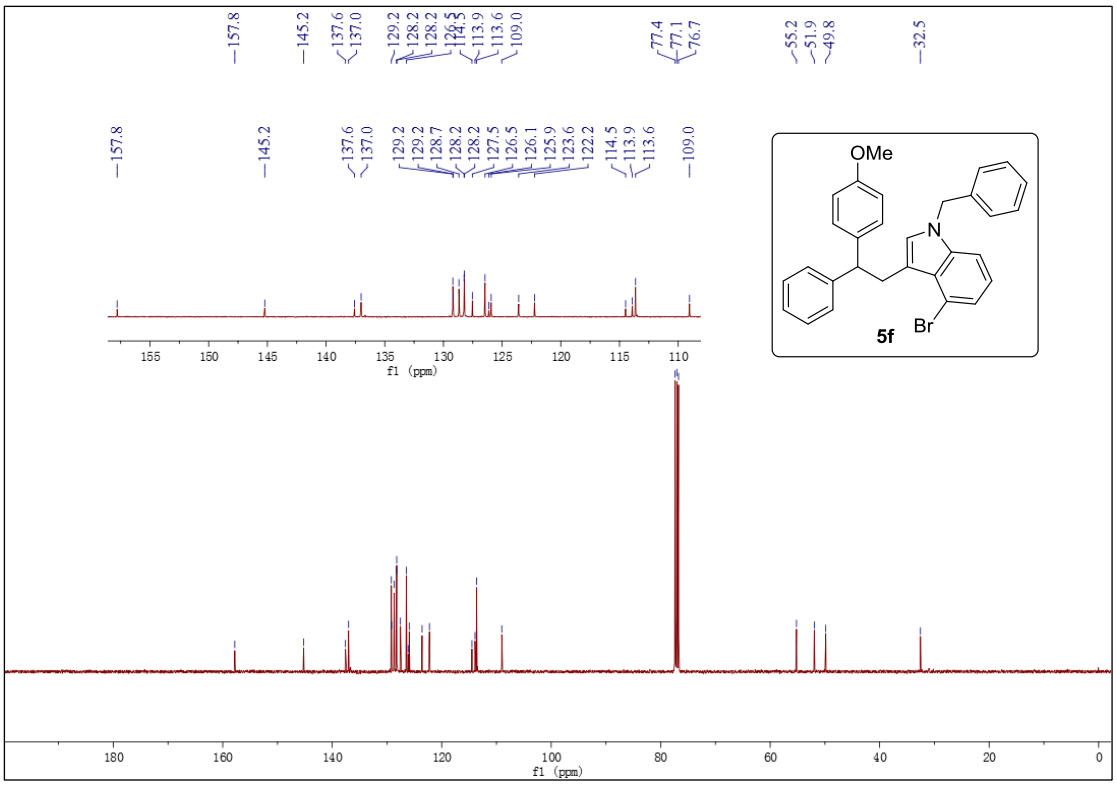
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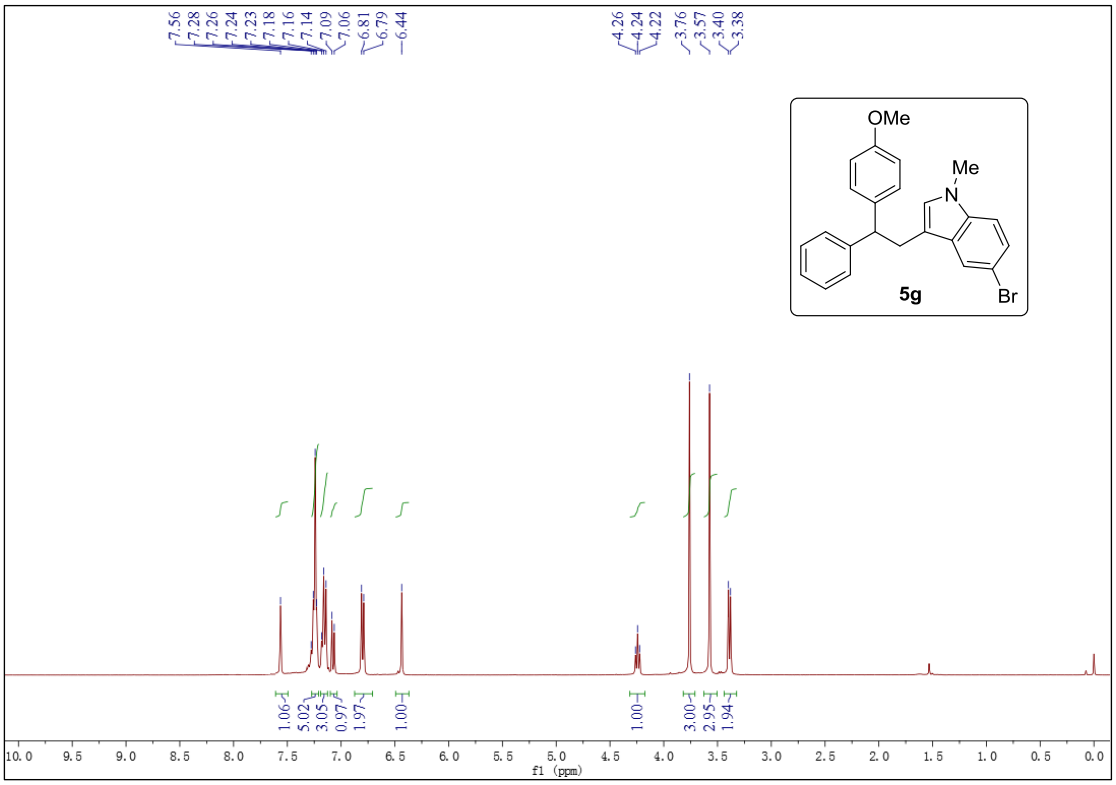
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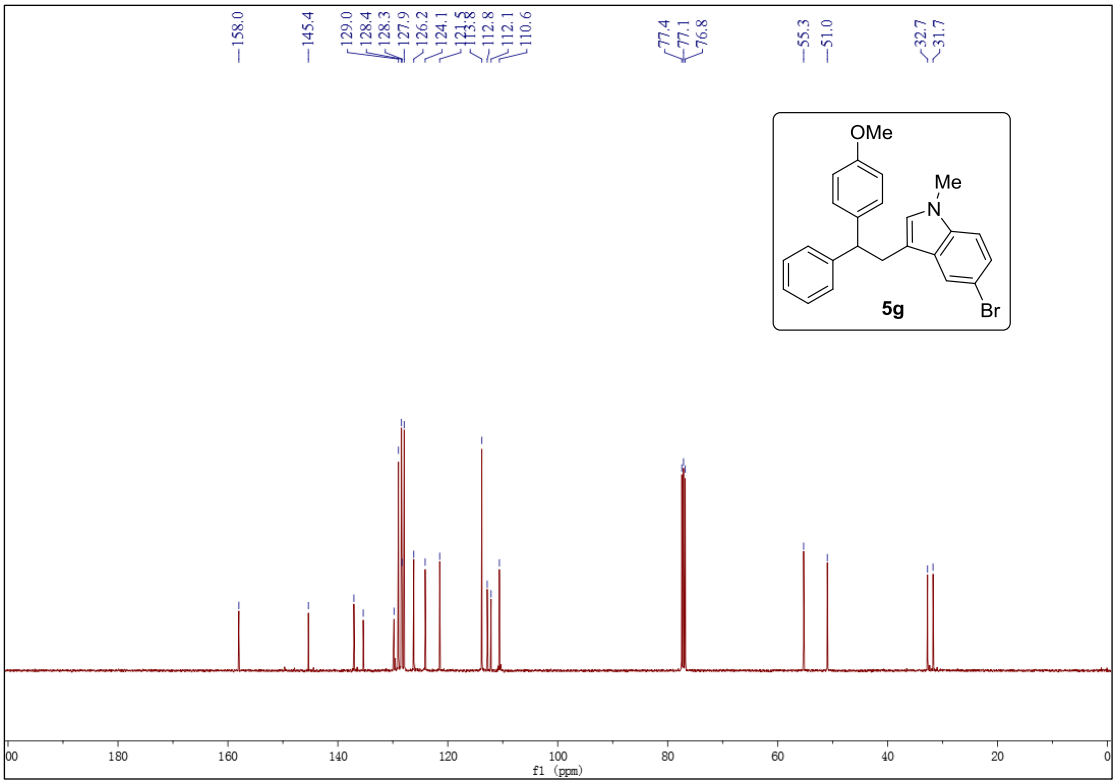
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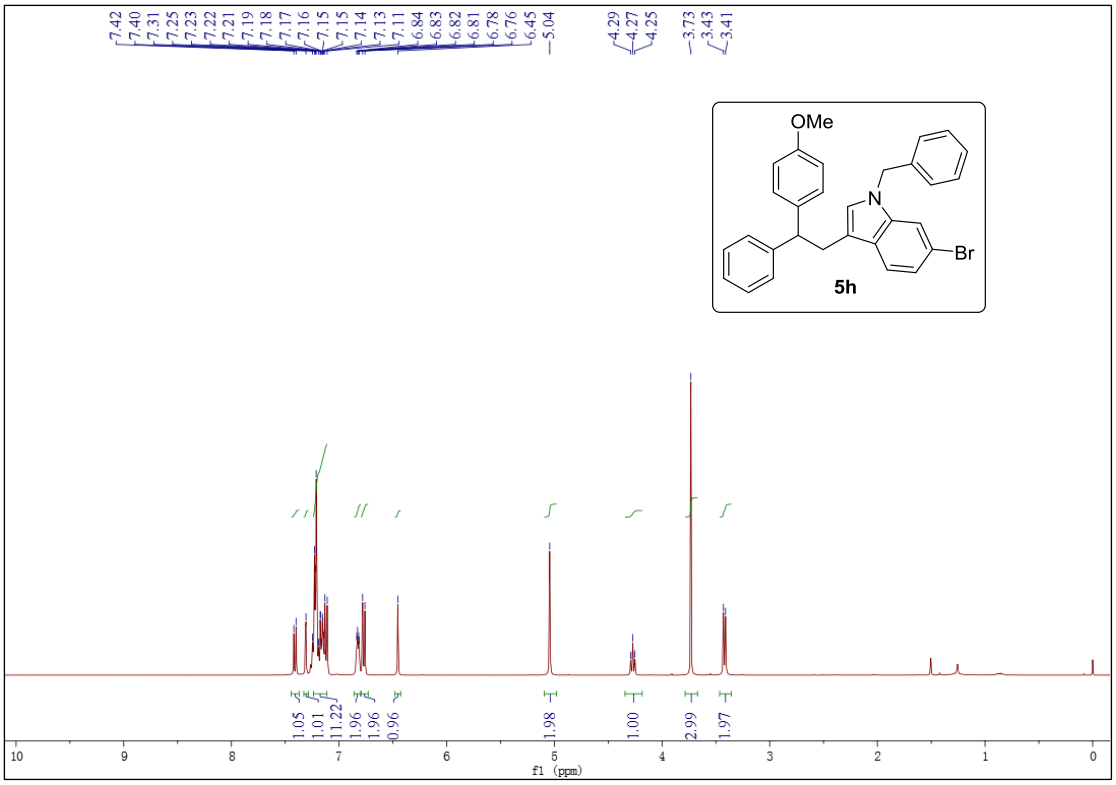
Br
f1 (ppm)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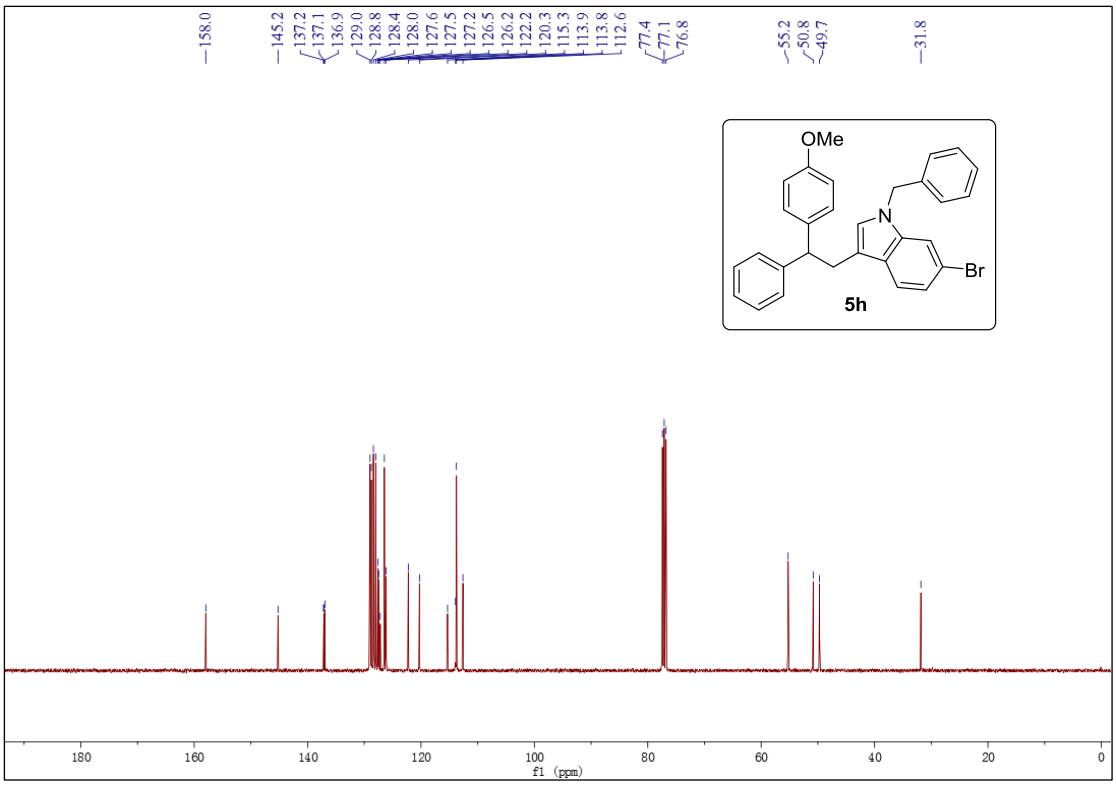
1.97
f1 (ppm)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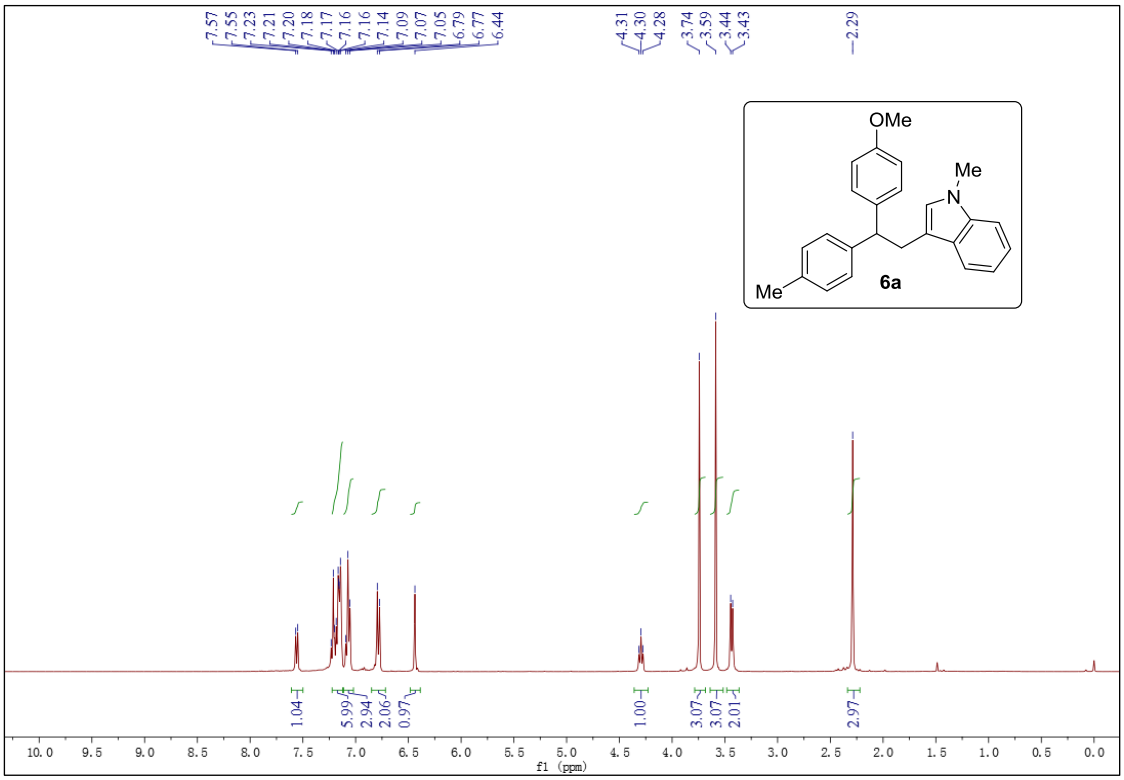
5h
f1 (ppm)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4.30
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3.44
3.43
2.29
OMe
Me
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Me
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3.07
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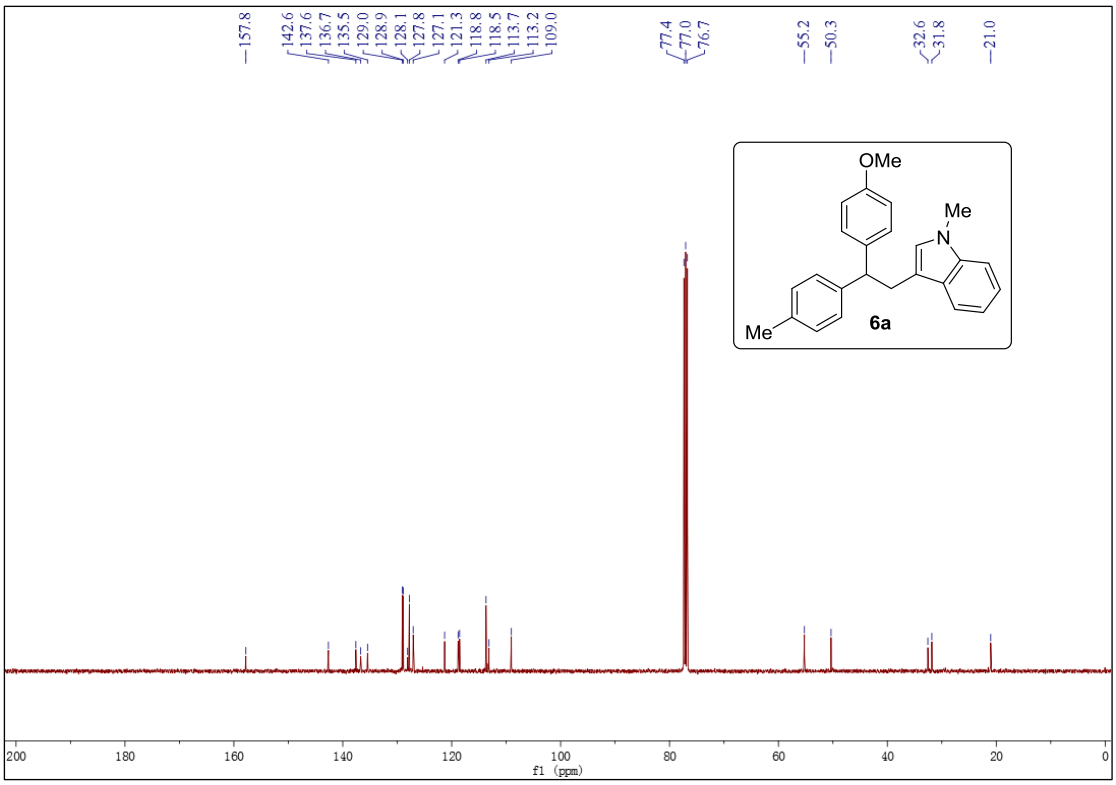
2.97
f1 (ppm)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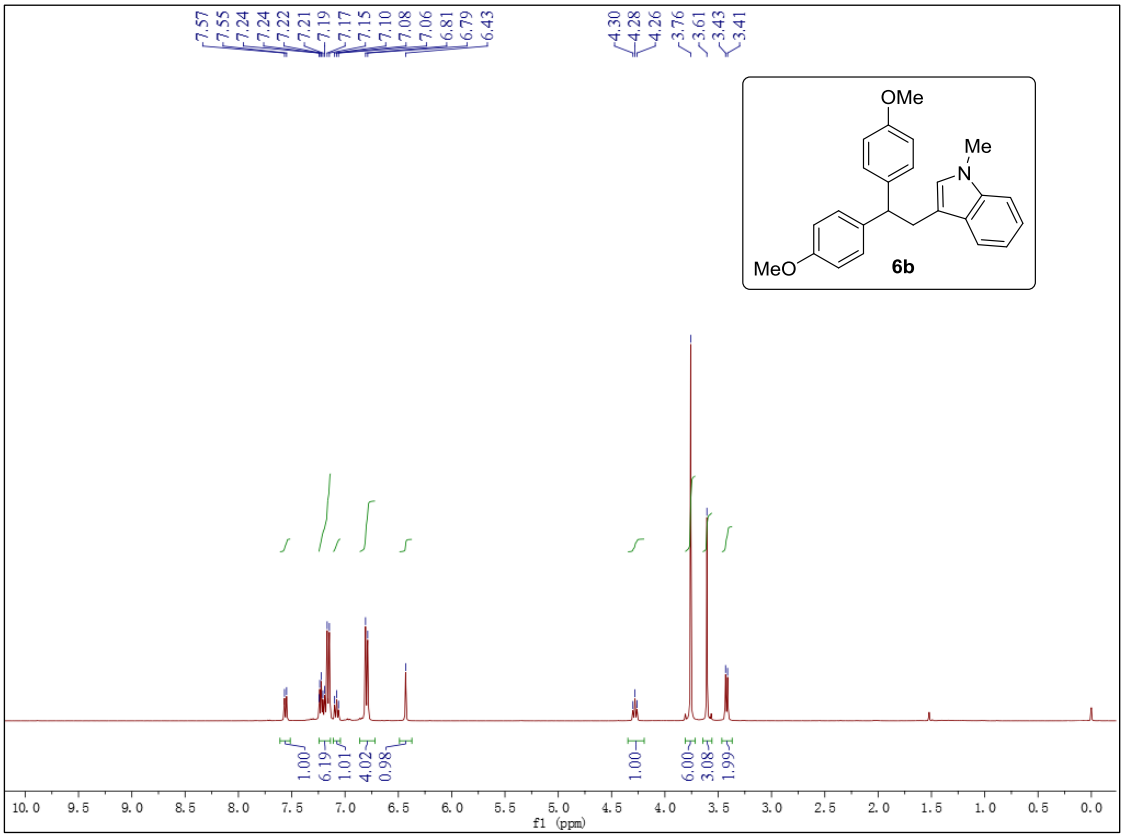
113.2
109.0
77.4
77.0
76.7
55.2
50.3
32.6
31.8
21.0
OMe
Me
N
Me
6a
f1 (ppm)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7.24
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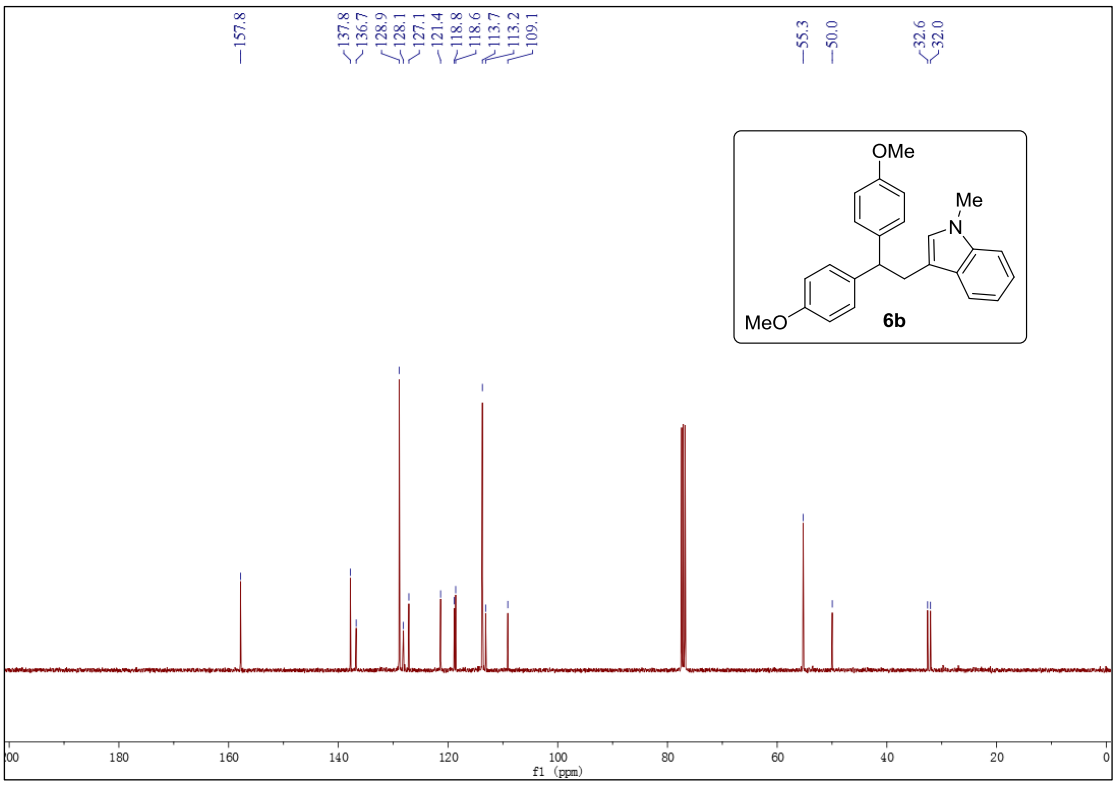
7.21
7.19
7.17
7.15
7.10
7.08
7.06
6.81
6.79
6.43
4.30
4.28
4.26
3.76
3.61
3.43
3.41
OMe
Me
N
MeO
6b
1.00
6.19
1.01
4.02
0.98
1.00
6.00
3.08
1.99
f1 (ppm)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127.1
121.4
118.8
118.6
113.7
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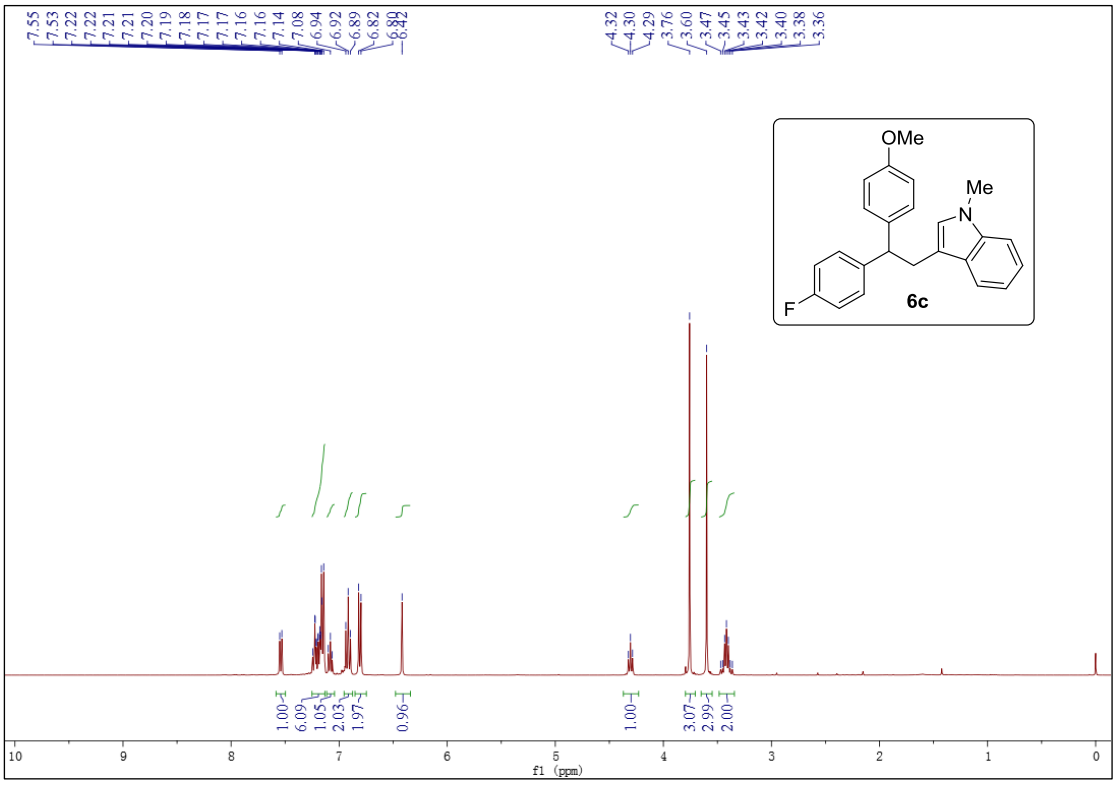
109.1
55.3
50.0
32.6
32.0
OMe
Me
N
MeO
6b
f1 (ppm)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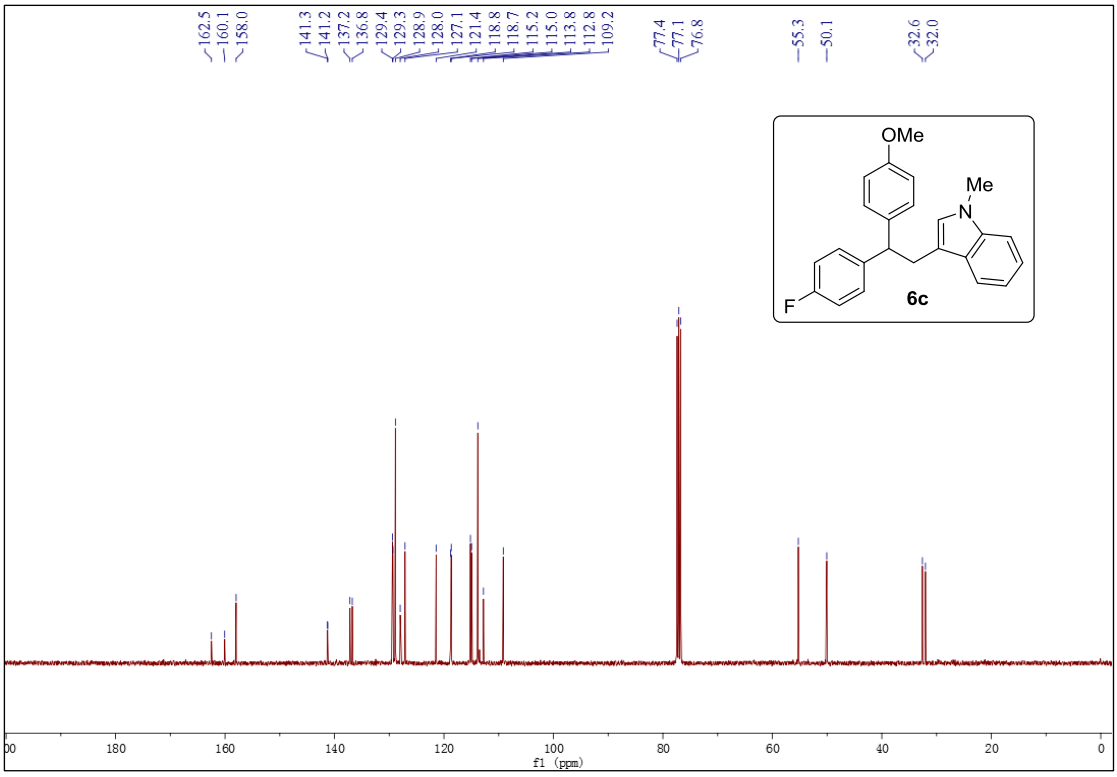
7.17
7.17
7.16
7.16
7.14
7.08
6.94
6.92
6.89
6.82
6.82
6.81
4.32
4.30
4.29
3.76
3.60
3.47
3.45
3.43
3.42
3.40
3.38
3.36
OMe
Me
N
F
6c
1.00
6.09
1.05
2.03
1.97
0.96
1.00
3.07
2.99
2.00
f1 (ppm)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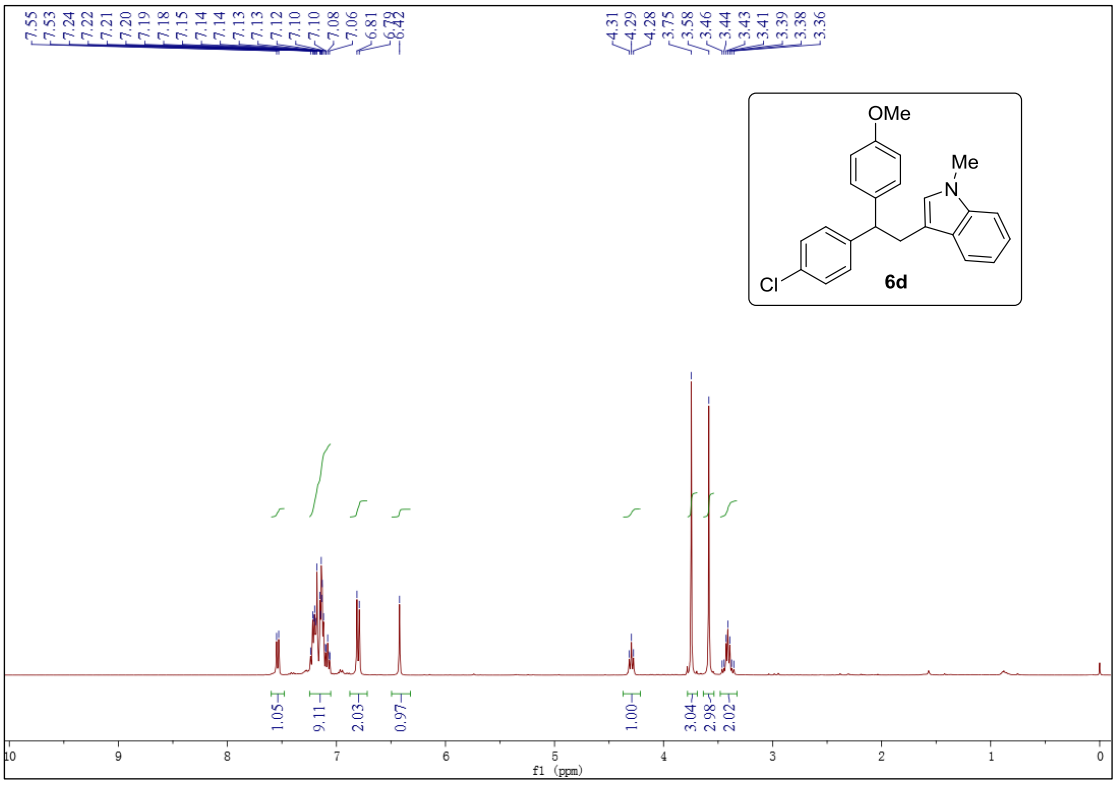
128.9
128.0
127.1
121.4
118.8
118.7
115.2
115.0
113.8
112.8
109.2
77.4
77.1
76.8
55.3
50.1
32.6
32.0
OMe
Me
N
F
6c
f1 (ppm)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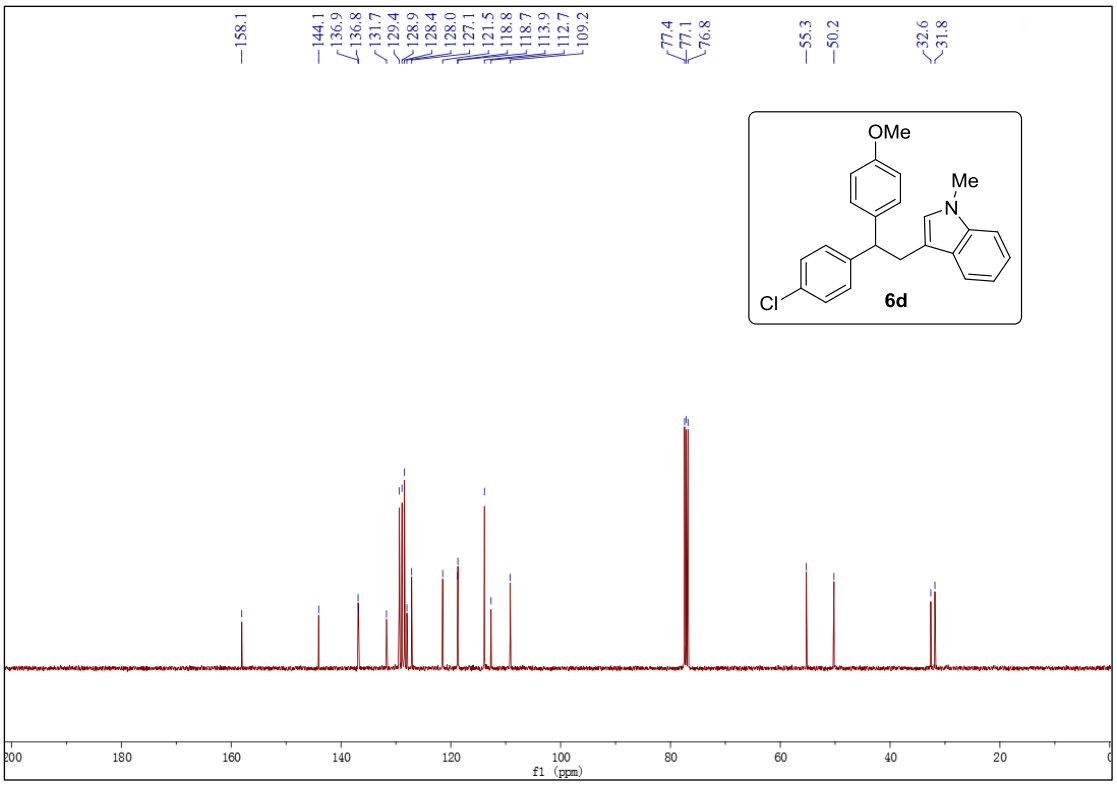
7.18
7.15
7.14
7.14
7.13
7.13
7.12
7.10
7.10
7.08
7.06
6.81
6.79
6.42
4.31
4.29
4.28
3.75
3.58
3.46
3.44
3.43
3.41
3.39
3.38
3.36
OMe
Me
N
Cl
6d
1.05
9.11
2.03
0.97
1.00
3.04
2.98
2.02
f1 (ppm)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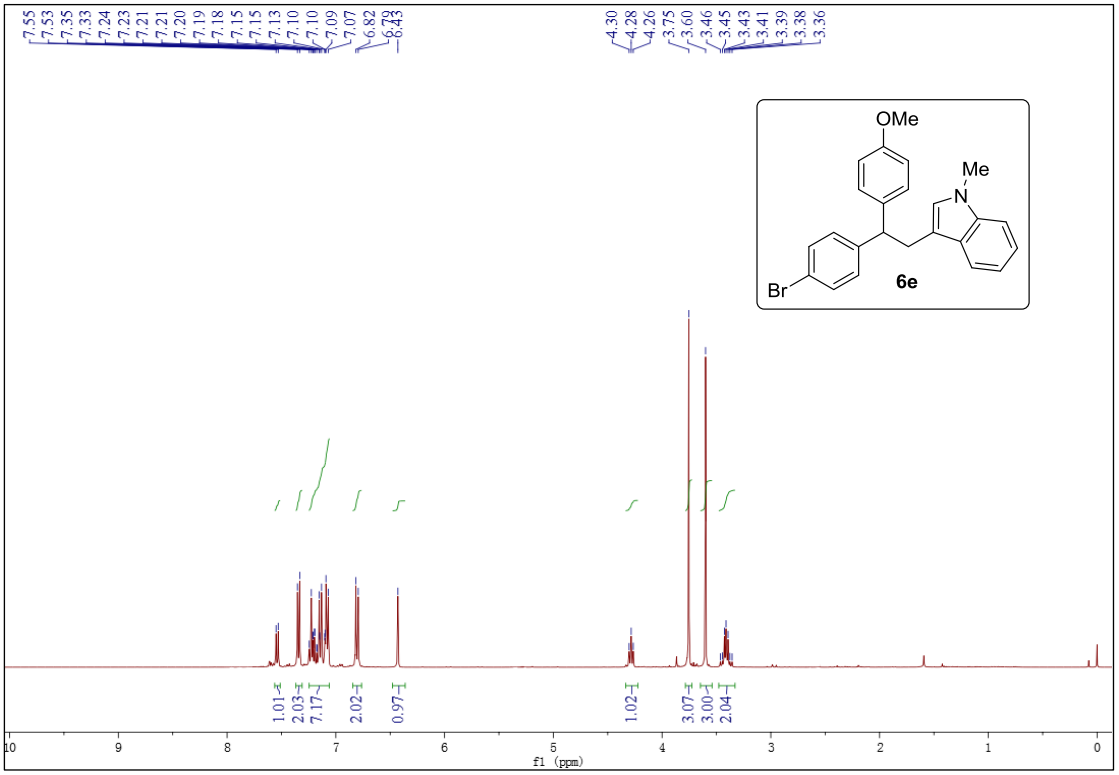
128.9
128.4
128.0
127.1
121.5
118.8
118.7
113.9
112.7
109.2
77.4
77.1
76.8
55.3
50.2
32.6
31.8
OMe
Me
N
Cl
6d
f1 (ppm)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7.19
7.18
7.15
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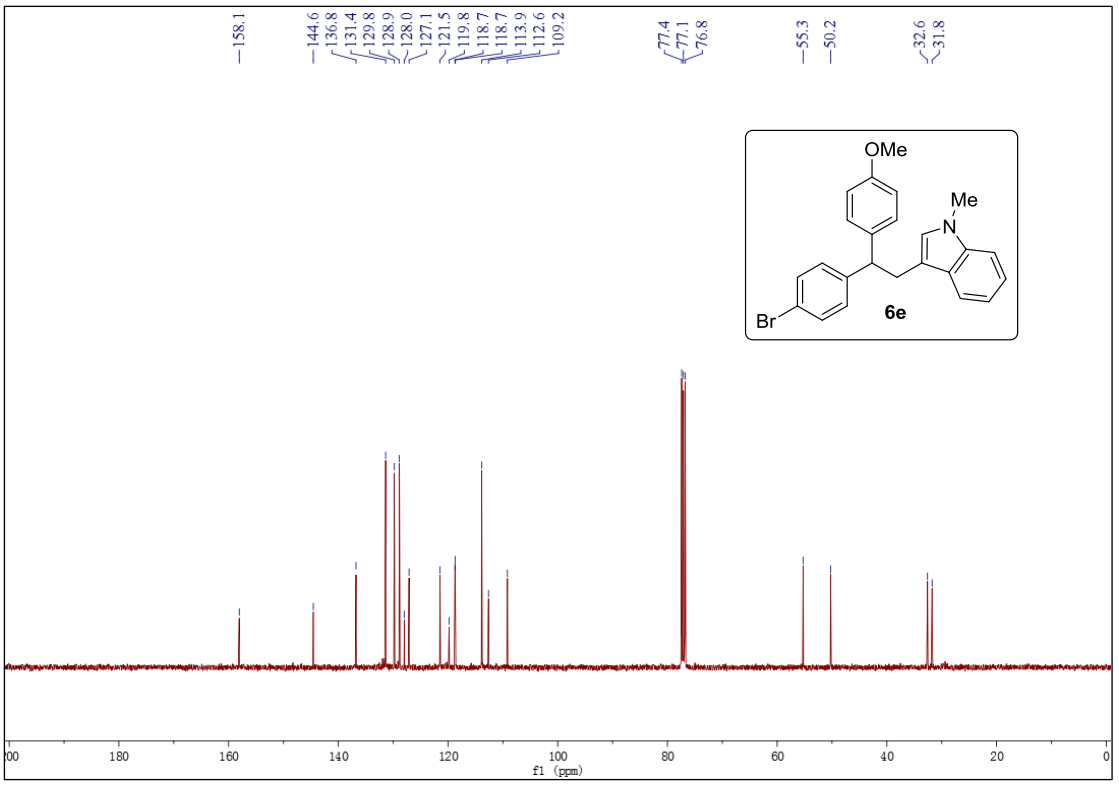
7.13
7.10
7.10
7.09
7.07
6.82
6.79
6.43
4.30
4.28
4.26
3.75
3.60
3.46
3.45
3.43
3.41
3.39
3.38
3.36
OMe
Me
N
Br
6e
1.01
2.03
7.17
2.02
0.97
1.02
3.07
3.00
2.04
f1 (ppm)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128.9
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118.7
118.7
113.9
112.6
109.2
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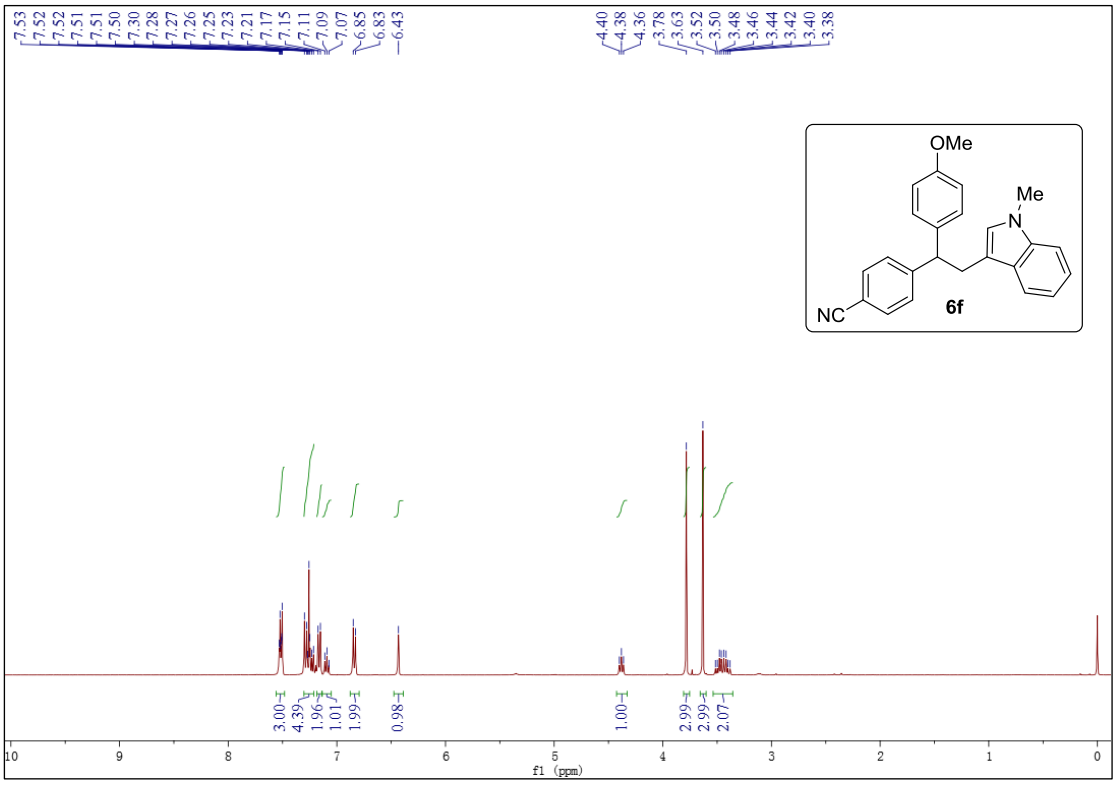
77.1
76.8
55.3
50.2
32.6
31.8
OMe
Me
N
Br
6e
f1 (ppm)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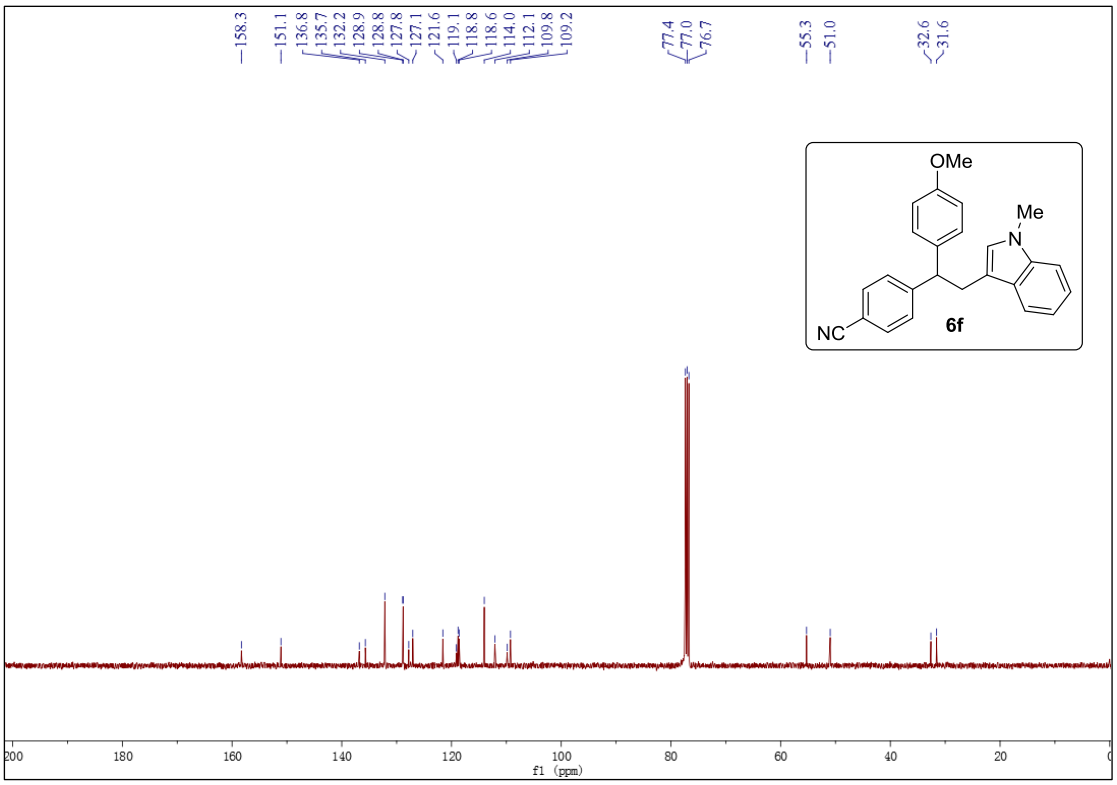
7.50
7.30
7.28
7.27
7.26
7.25
7.23
7.21
7.17
7.15
7.11
7.09
7.07
6.85
6.83
6.43
4.40
4.38
4.36
3.78
3.63
3.52
3.50
3.48
3.46
3.44
3.42
3.40
3.38
OMe
Me
N
NC
6f
3.00
4.39
1.96
1.01
1.99
0.98
1.00
2.99
2.99
2.07
f1 (ppm)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136.8
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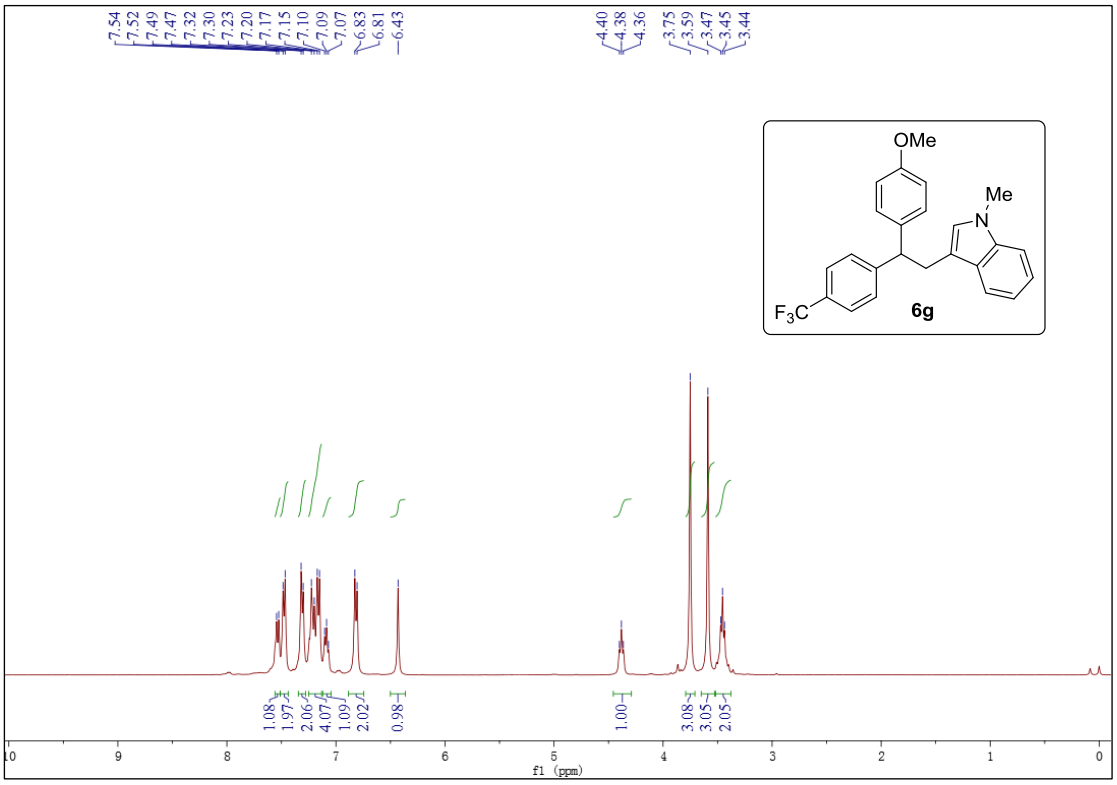
121.6
119.1
118.8
118.6
114.0
112.1
109.8
109.2
77.4
77.0
76.7
55.3
51.0
32.6
31.6
OMe
Me
N
NC
6f
f1 (ppm)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7.17
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7.10
7.09
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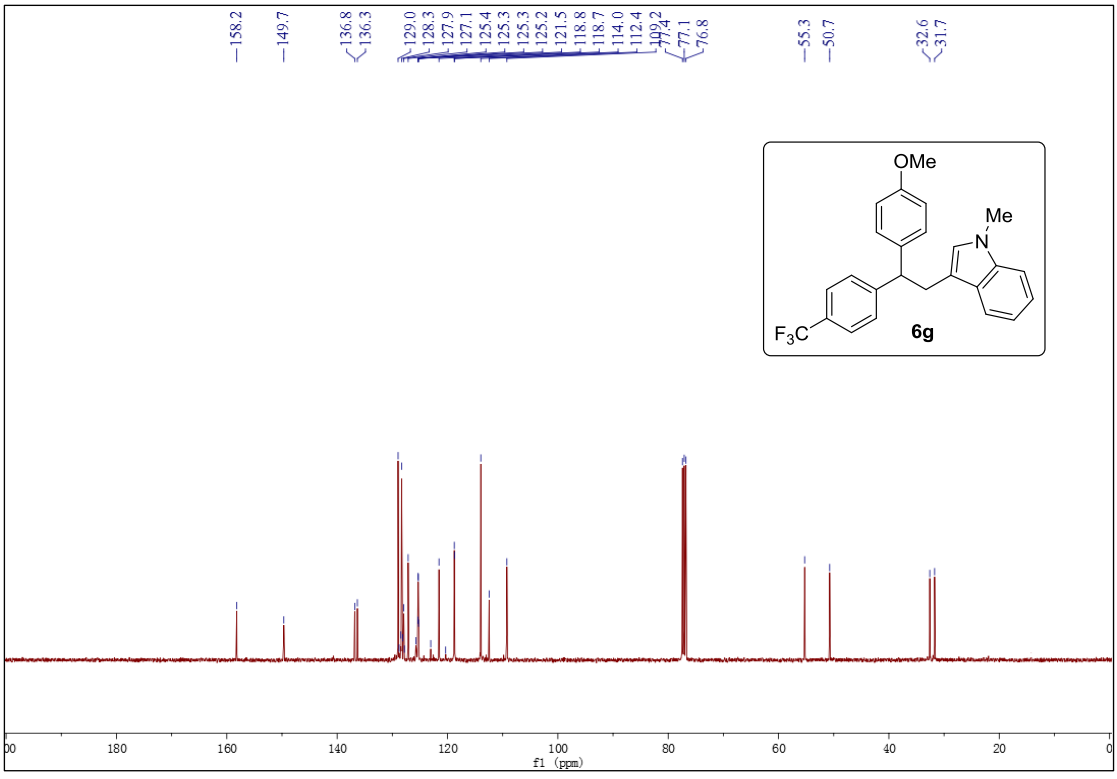
6.83
6.81
6.43
4.40
4.38
4.36
3.75
3.59
3.47
3.45
3.44
OMe
Me
N
F3C
6g
1.08
1.97
2.06
4.07
1.09
2.02
0.98
1.00
3.08
3.05
2.05
f1 (ppm)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125.3
125.2
121.5
118.8
118.7
114.0
112.4
109.2
77.4
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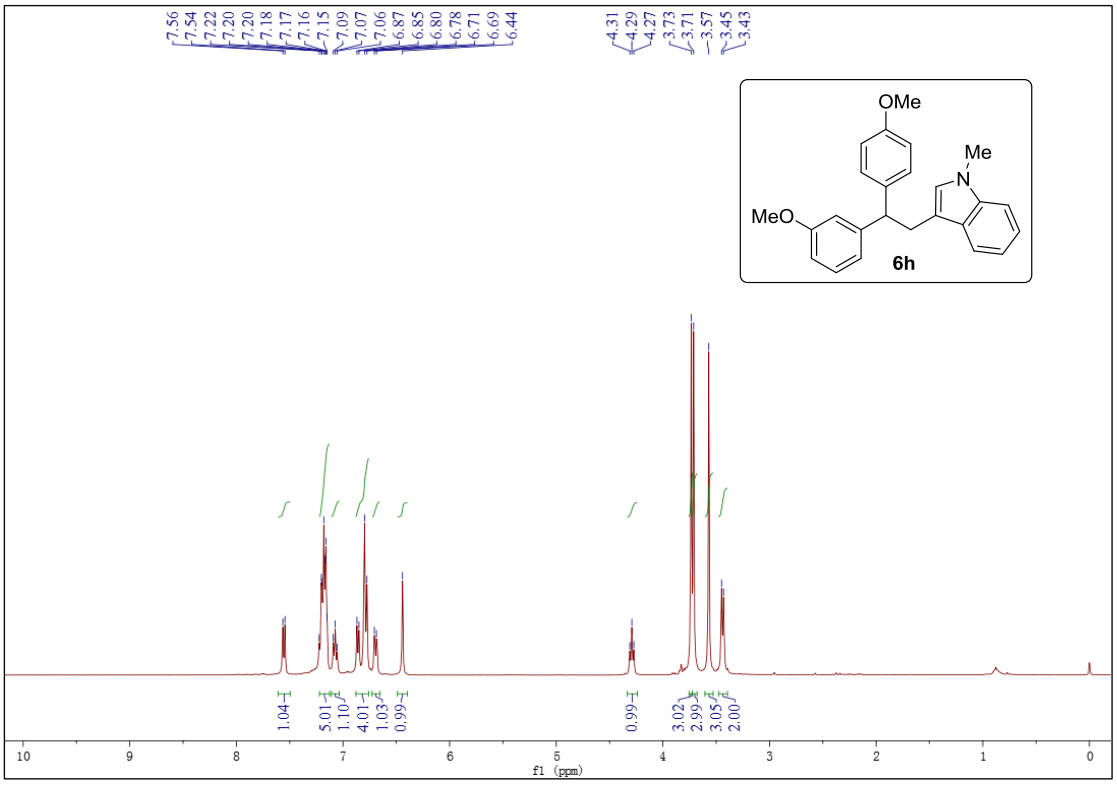
76.8
55.3
50.7
32.6
31.7
OMe
Me
N
F3C
6g
f1 (ppm)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7.09
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7.06
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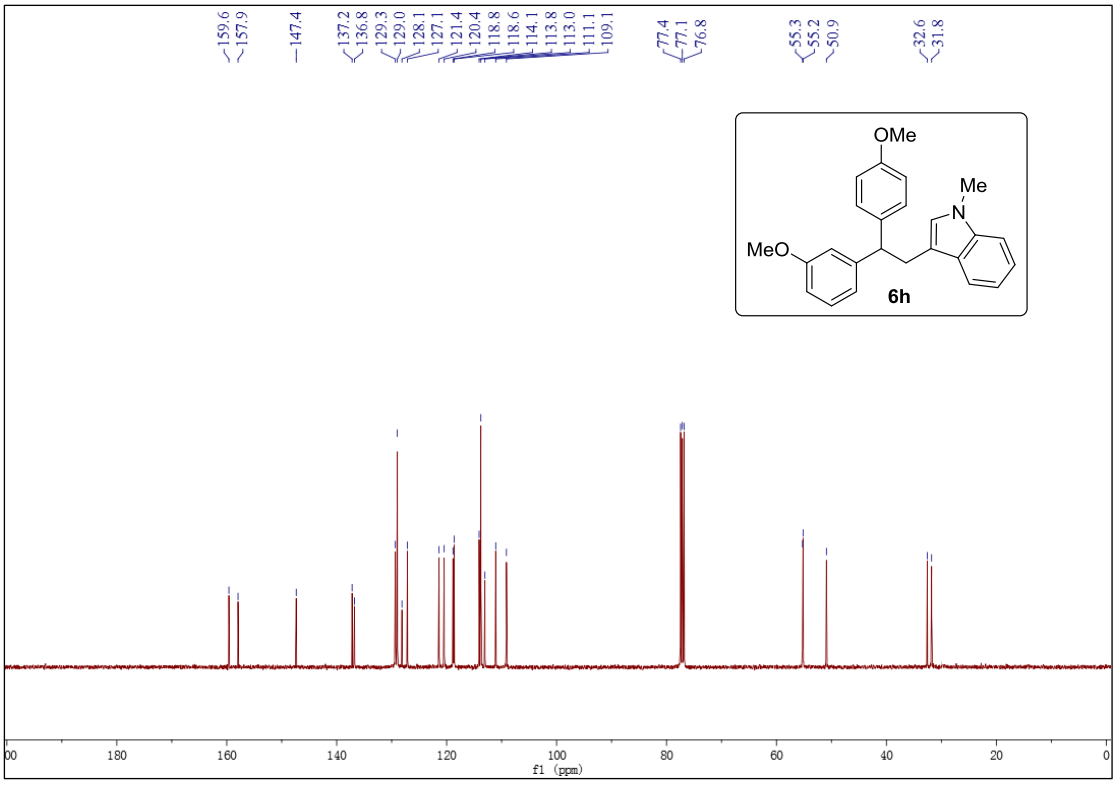
6.80
6.78
6.71
6.69
6.44
4.31
4.29
4.27
3.73
3.71
3.57
3.45
3.43
OMe
Me
N
MeO
6h
1.04
5.01
1.10
4.01
1.03
0.99
0.99
3.02
2.99
3.05
2.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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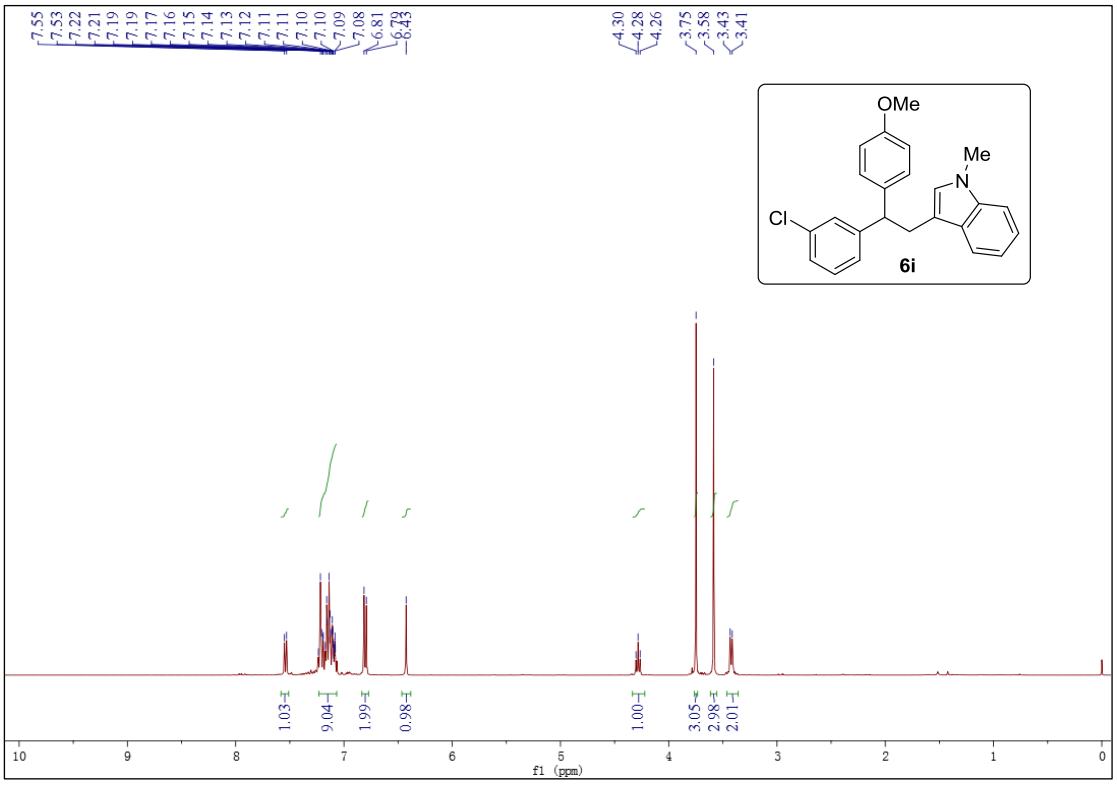
118.8
118.6
114.1
113.8
113.0
111.1
109.1
77.4
77.1
76.8
55.3
55.2
50.9
32.6
31.8
OMe
Me
N
MeO
6h
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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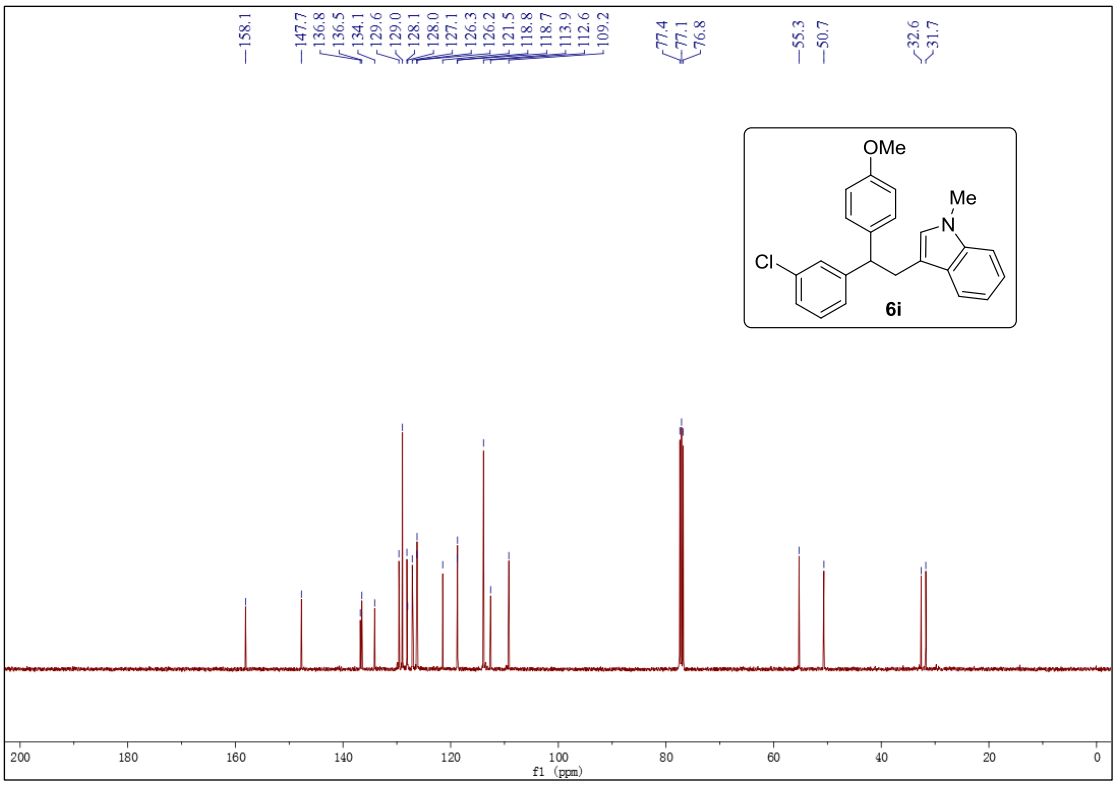
7.11
7.11
7.10
7.10
7.09
7.08
6.81
6.79
6.43
4.30
4.28
4.26
3.75
3.58
3.43
3.41
OMe
Me
N
Cl
6i
1.03
9.04
1.99
0.98
1.00
3.05
2.98
2.01
f1 (ppm)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136.8
136.5
134.1
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126.3
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121.5
118.8
118.7
113.9
112.6
109.2
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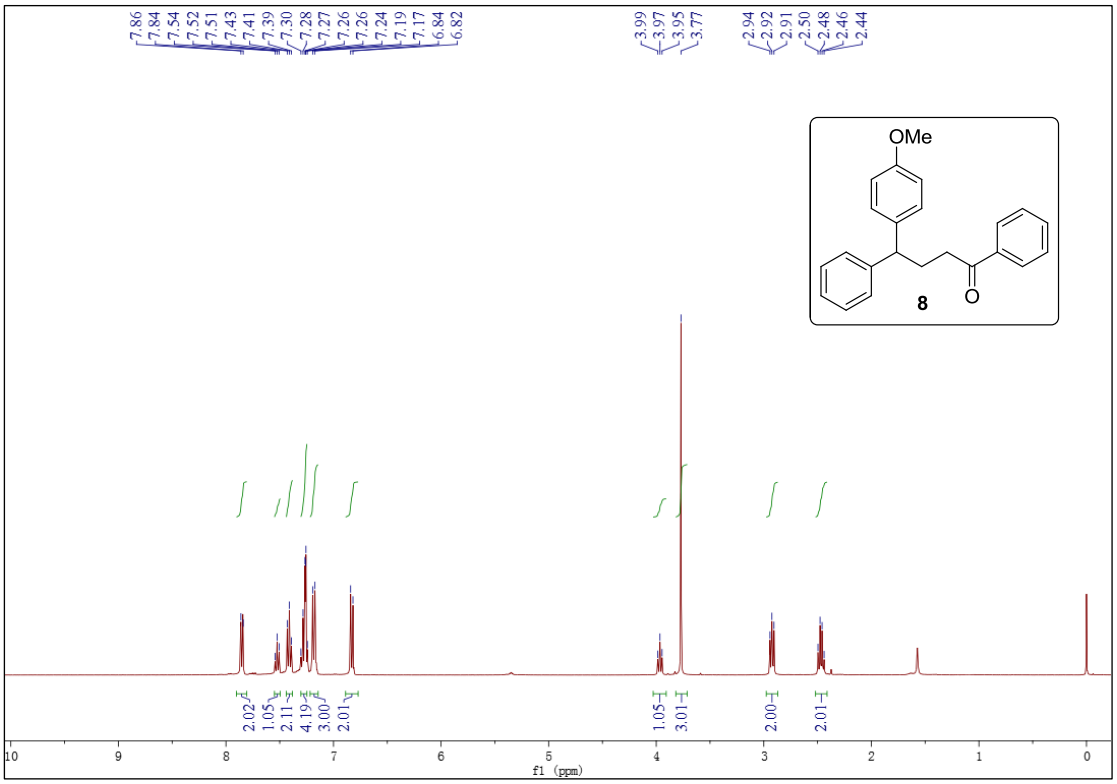
76.8
55.3
50.7
32.6
31.7
OMe
Me
N
Cl
6i
f1 (ppm)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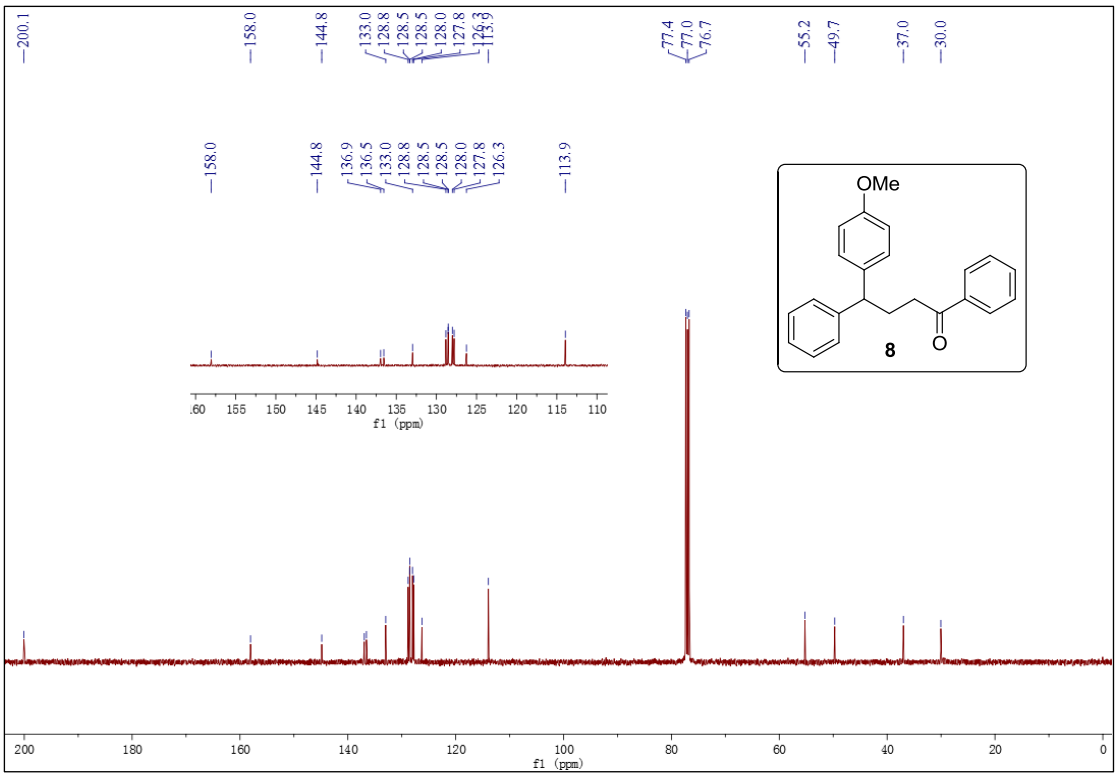
7.26
7.24
7.19
7.17
6.84
6.82
3.99
3.97
3.95
3.77
2.94
2.92
2.91
2.50
2.48
2.46
2.44
OMe
8
O
2.02
1.05
2.11
4.19
3.00
2.01
1.05
3.01
2.00
2.01
f1 (ppm)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128.8
128.5
128.5
128.0
127.8
126.3
113.9
77.4
77.0
76.7
55.2
49.7
37.0
30.0
OMe
8
O
f1 (ppm)