Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Iron-Catalyzed Hydroarylation of 1,3-Dienes with Indoles

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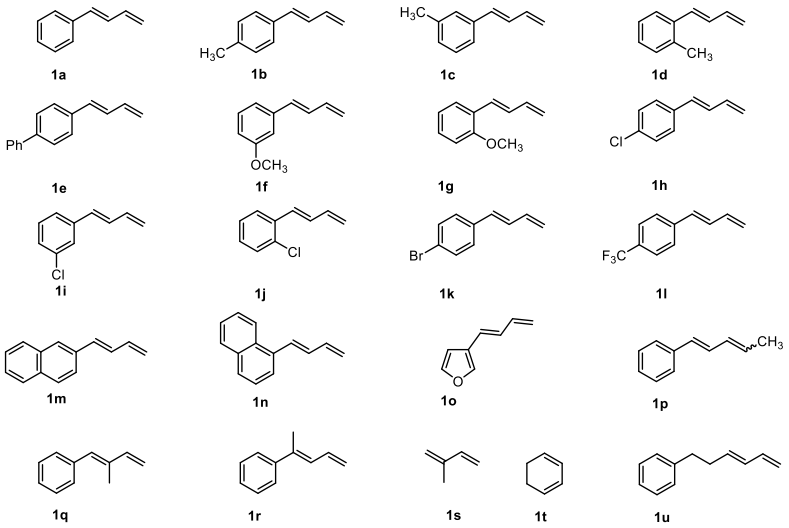
1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon, using over-dried or flame-dried glassware equipped with a magnetic stir bar. All chemicals were purchased from commercial suppliers and used without further purification. In addition to commercially available extra dry solvents, all solvents were purified by standard operating method. Toluene was distilled from sodium, Tetrahydrofuran (THF) was distilled from sodium and acetonitrile (MeCN) was purchased from commercial suppliers (*J&K Technology*) and used without further purification. PhCl was purchased from Energy Chemical. Thin-layer chromatography was performed with EMD silica gel 60 F_{254} plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid (PMA). **^{1}H NMR**, **^{13}C NMR** and **^{19}F NMR** spectra were obtained on Bruker AM-400 and Bruker AM-500. Chemical shifts (δ) were quoted in ppm relative to tetramethylsiane or deuterated solvent as internal standard (TMS: 0 ppm for **^{1}H NMR** $CDCl_3$: 77.16 ppm for **^{13}C NMR**), multiplicities are as indicated: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectral analysis **(HRMS)** data were measured on a Buker impact II (Q-TOF) mass spectrum by means of the ESI technique.

2. The preparation of substrates

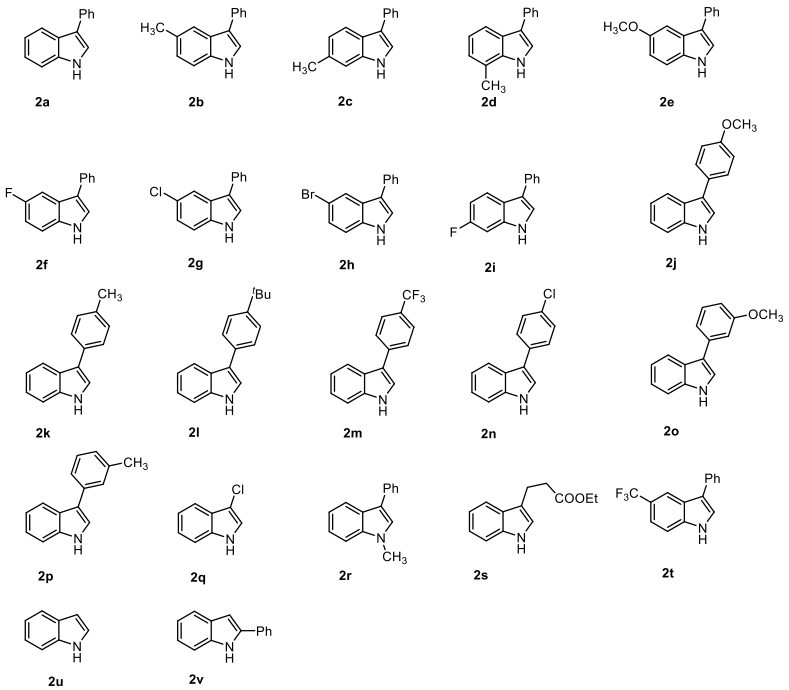
2.1 All of the used 1,3-dienes are known compounds. Compounds **1a-1r** and **1u** were prepared according to reported literature.[1] **1s** and **1t** were purchased from Heowns. (**Figure S1)**.

Figure S1 Substrate scope of 1,3-dienes

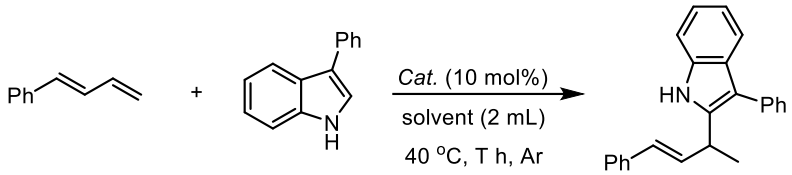


2.2 All of the used indoles are known compounds. Compounds **2a-2q**, **2t**[2a-2e],**2r**[2f] and **2s**[2h] were prepared according to reported literature. **2u** were purchased from Energy Chemical. **2v** was purchased from Bidepharm. (**Figure S2**).

Figure S2. Substrate scope of known indoles.



3. Screening of reaction conditions[a]

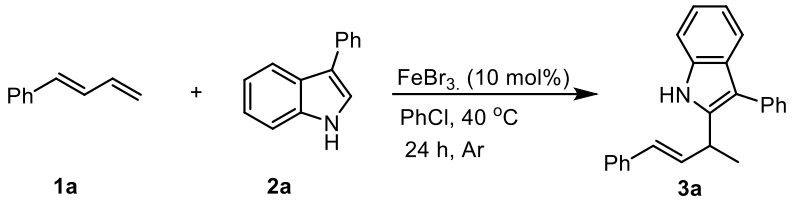


1a 2a 3a

Entry	Cat.	Solvent	T (h)	Yield (%)[b]
1	$FeBr_3$	$PhCH_3$	24	67
2	$FeCl_3$	$PhCH_3$	24	trace
3	$FeCl_2$	$PhCH_3$	24	no
4	$Fe(OAc)_2$	$PhCH_3$	24	no
5	$InBr_3$	$PhCH_3$	24	16
6	$GaCl_3$	$PhCH_3$	24	37
7	$ZnBr_2$	$PhCH_3$	24	no
8	$AlCl_3$	$PhCH_3$	24	trace
9	$Sc(OTf)_3$	$PhCH_3$	24	trace
10	$Cu(OTf)_2$	$PhCH_3$	24	trace
11	$Ni(OTf)_2$	$PhCH_3$	24	no
12	$CoCl_2$	$PhCH_3$	24	no
13	$FeBr_3$	$PhCF_3$	24	74
14	$FeBr_3$	PhCl	24	82
15	$FeBr_3$	EA	24	no
16	$FeBr_3$	CH_3CN	24	no
17	$FeBr_3$	1,4-dioxane	24	trace
18	$FeBr_3$	THF	24	no
19	$FeBr_3$	DCM	24	no
20[c]	$FeBr_3$	PhCl	24	48
21[d]	$FeBr_3$	PhCl	24	57
22	**$FeBr_3$**	**PhCl**	**3**	**80**
23	$FeBr_3$	PhCl	6	81

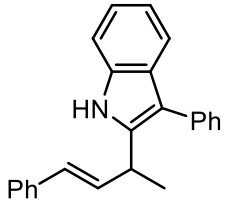
[a]Reactions conditions: unless stated otherwise, 1-phenyl-1,3-butadiene **1a** (19.6 mg, 0.075 mmol, 1.5 equiv), 3-phenylindole **2a** (19.4 mg, 0.05 mmol, 1.0 equiv) in PhCl (2 mL) at 40 °C under argon. [b]Isolated yield. [c]5 mol% $FeBr_3$ was used. [d]1.2 equiv **1a** was used.

4. General procedure for iron-catalyzed hydroarylation of 1,3-dienes with indoles



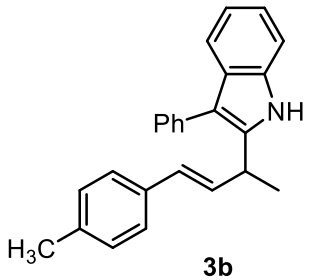
1a **2a** **3a**

In Ar-filled glove box, the $FeBr_3$ (3.0 mg, 0.01 mmol, 0.1 equiv) was added to the oven-dried reaction tube with a dried stir bar. The tube was capped, then it was transferred out of the glovebox. indole **2** (0.10 mmol, 1.0 equiv) was added to this oven-dried reaction tube, 1,3-diene **1** (0.15 mmol, 1.5 equiv) was added with PhCl (2 mL). (If 1,3-diene **1** is solid, adding it directly to the reaction tube). After all reagents were added, the reaction tube was replaced with argon three times, and then sealed. The reaction mixture was stirred in a 40 °C oil bath under argon for 3-28 h (monitored by TLC). After the reaction was completed, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether (PE)/ethyl acetate (EA) to give the desired product **3**.



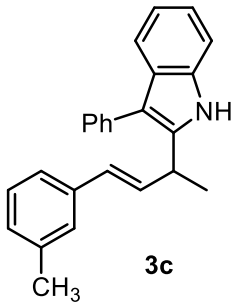
3a

The reaction of **1a** (19.6 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3a** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 80% yield (25.9 mg) as yellow solid, R_f = 0.55 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 7.89 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.21 (m, 6H), 7.21 – 7.13 (m, 2H), 7.13 – 7.05 (m, 1H), 6.47 – 6.32 (m, 2H), 4.23 – 4.01 (m, 1H), 1.45 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.8, 137.1, 135.4, 135.3, 132.9, 129.8, 129.7, 128.7, 128.7, 128.0, 127.6, 126.3, 126.3, 122.0, 120.1, 119.3, 114.5, 110.8, 33.5, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{21}NNa$: 346.1566. Found 346.1563.



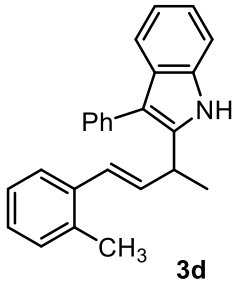
3b

The reaction of **1b** (21.6 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3b** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 64% yield (21.5 mg) as yellow oil, R_f = 0.54 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.02 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 3H), 6.51 – 6.34 (m, 2H), 4.22 – 4.04 (m, 1H), 2.32 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 138.0, 137.4, 135.5, 135.3, 134.3, 131.9, 129.9, 129.6, 129.4, 128.7, 128.0, 126.3, 126.3, 122.0, 120.1, 119.3, 114.5, 110.8, 33.5, 21.3, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1722.



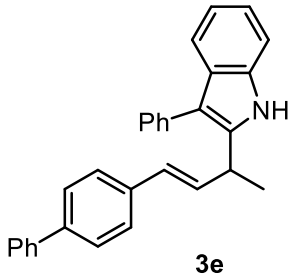
3c

The reaction of **1c** (21.6 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3c** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~50:1, v/v) in 84% yield (28.2 mg) as white solid, R_f = 0.56 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.01 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.37 – 7.29 (m, 2H), 7.25 – 7.09 (m, 5H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.56 – 6.30 (m, 2H), 4.21 – 4.04 (m, 1H), 2.31 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 138.3, 137.9, 137.1, 135.5, 135.3, 132.7, 129.9, 129.8, 128.7, 128.7, 128.4, 128.0, 127.1, 126.3, 123.5, 122.0, 120.1, 119.3, 114.5, 110.8, 33.5, 21.5, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1727.



3d

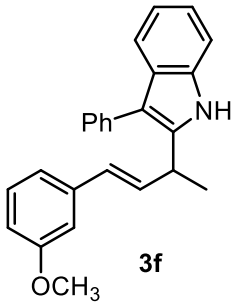
The reaction of **1d** (21.6 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3d** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 95% yield (32.1 mg) as yellow solid, R_f = 0.49 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.04 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.30 (m, 3H), 7.27 – 7.18 (m, 1H), 7.17 – 7.09 (m, 4H), 6.66 (dd, *J* = 15.6, 1.6 Hz, 1H), 6.32 (dd, *J* = 16.0, 5.6 Hz, 1H), 4.27 – 4.11 (m, 1H), 2.29 (s, 3H), 1.54 (d, *J* = 6.8,3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.9, 136.3, 135.4, 135.4, 135.3, 134.3, 130.4, 129.9, 128.7, 128.1, 127.7, 127.5, 126.3, 126.3, 125.7, 122.0, 120.1, 119.3, 114.5, 110.7, 34.0, 20.4, 20.0. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1724.



3e

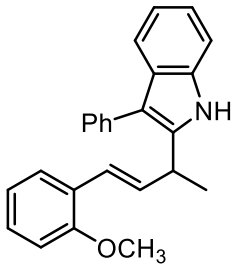
The reaction of **1e** (30.9 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3e** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 77% yield (30.7 mg) as yellow oil, R_f = 0.35 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.03 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.51 (m, 6H), 7.50 – 7.38 (m, 6H), 7.37 – 7.28 (m, 3H), 7.23 – 7.17 (m, 1H), 7.15 – 7.10 (m, 1H), 6.51 (dd, *J* = 16.4, 4.4 Hz, 1H), 6.44 (d, *J* = 16.4 Hz, 1H), 4.29 – 3.97 (m, 1H), 1.53 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 140.8, 140.4, 137.7, 136.1, 135.5, 135.3, 133.1, 129.9, 129.3, 128.9,

128.7, 128.0, 127.4, 127.4, 127.0, 126.8, 126.3, 122.0, 120.1, 119.3, 114.6, 110.8, 33.6, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}NNa$: 422.1879. Found 422.1877.



3f

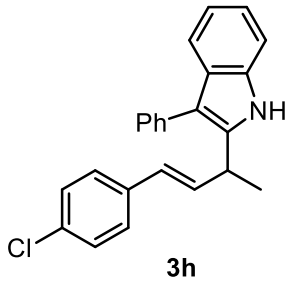
The reaction of **1f** (24.0 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 6 h. Compound **3f** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~50:1, v/v) in 79% yield (27.6 mg) as yellow solid, R_f = 0.44 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.05 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.16 (m, 2H), 7.15 – 7.08 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.47 (dd, *J* = 16.0, 4.8 Hz, 1H), 6.39 (d, *J* = 16.8 Hz, 1H), 4.21 – 4.06 (m, 1H), 3.78 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 160.0, 138.6, 137.7, 135.5, 135.2, 133.3, 129.8, 129.7, 129.7, 128.7, 128.0, 126.3, 122.0, 120.1, 119.3, 119.0, 114.6, 113.5, 111.5, 110.8, 55.4, 33.5, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NONa$: 376.1672. Found 376.1671.



3g

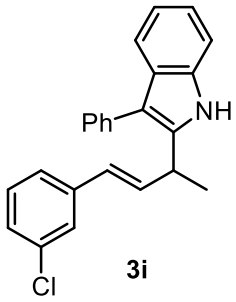
The reaction of **1g** (24.0 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3g** was isolated by flash column

chromatography (SiO_2, PE/EA = 80:1~40:1, v/v) in 69% yield (24.1 mg) as white solid, R_f = 0.30 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.08 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.24 – 7.15 (m, 2H), 7.14 – 7.08 (m, 1H), 6.90 (m, 1H), 6.88 – 6.80 (m, 2H), 6.47 (dd, *J* = 16.4, 5.6 Hz, 1H), 4.29 – 4.08 (m, 1H), 3.83 (s, 3H), 1.54 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 156.7, 138.3, 135.5, 135.4, 133.4, 129.9, 128.6, 128.6, 128.1, 126.8, 126.2, 124.5, 121.9, 120.8, 120.0, 119.3, 114.3, 111.0, 110.8, 55.6, 33.9, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NONa$: 376.1672. Found 376.1673.



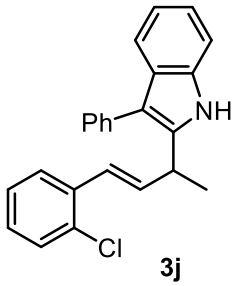
3h

The reaction of **1h** (24.7 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 3 h. Compound **3h** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 59% yield (20.9 mg) as yellow oil, R_f = 0.49 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.00 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.25 (s, 4H), 7.22 – 7.17 (m, 1H), 7.15 – 7.08 (m, 1H), 6.43 (dd, *J* = 16.0, 4.8 Hz, 1H), 6.34 (dd, *J* = 16.0, 1.6 Hz, 1H), 4.17 – 4.08 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.5, 135.7, 135.5, 135.2, 133.7, 133.2, 129.9, 128.9, 128.7, 128.6, 128.0, 127.6, 126.4, 122.1, 120.2, 119.4, 114.8, 110.8, 33.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}ClNNa$: 380.1176. Found 380.1179.



3i

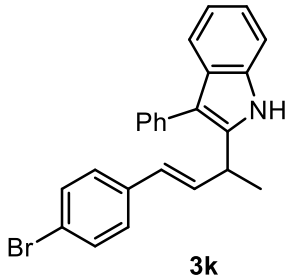
The reaction of **1i** (24.7 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 28 h. Compound **3i** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 63% yield (22.2 mg) as yellow oil, R_f = 0.44 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.00 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.50 – 7.43 (m, 2H), 7.38 – 7.30 (m, 3H), 7.26 – 7.16 (m, 4H), 7.15 – 7.07 (m, 1H), 6.48 (dd, *J* = 16.0, 4.8 Hz, 1H), 6.34 (dd, *J* = 16.0, 2.0 Hz, 1H), 4.22 – 4.06 (m, 1H), 1.53 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 139.0, 137.3, 135.5, 135.2, 134.7, 134.6, 129.9, 129.8, 128.7, 128.5, 128.0, 127.5, 126.4, 126.3, 124.6, 122.1, 120.2, 119.4, 114.8, 110.8, 33.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}ClNNa$: 380.1176. Found 380.1180.



3j

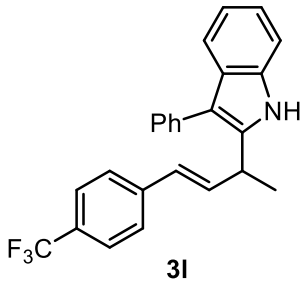
The reaction of **1j** (24.7 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 28 h. Compound **3j** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 42% yield (14.7 mg) as yellow oil, R_f = 0.42 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.04 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 3H), 7.39 – 7.31 (m, 3H), 7.23 – 7.15 (m, 3H), 7.15 – 7.07 (m, 1H), 6.89 (dd, *J* = 16.0, 2.0 Hz, 1H), 6.42 (dd, *J* = 16.0, 5.2 Hz, 1H), 4.24 – 4.12 (m, 1H), 1.57 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.5, 135.8, 135.5, 135.4, 135.2, 133.1, 129.9, 129.8,

128.7, 128.6, 128.1, 127.0, 126.9, 126.4, 126.1, 122.1, 120.2, 119.4, 114.6, 110.8, 33.9, 20.1. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}ClNNa$: 380.1176. Found 380.1175.



3k

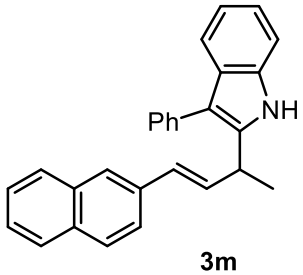
The reaction of **1k** (31.4 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^oC oil bath under argon for 6 h. Compound **3k** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 54% yield (21.5 mg) as yellow solid, R_f = 0.53 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.01 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.30 (m, 2H), 7.23 – 7.17 (m, 3H), 7.16 – 7.09 (m, 1H), 6.45 (dd, *J* = 16.0, 5.2 Hz, 1H), 6.33 (dd, *J* = 16.0, 1.6 Hz, 1H), 4.22 – 4.06 (m, 1H), 1.53 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.4, 136.1, 135.5, 135.2, 133.9, 131.8, 129.8, 128.7, 128.6, 128.0, 127.9, 126.4, 122.1, 121.3, 120.2, 119.4, 114.7, 110.8, 33.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}BrNNa$: 424.0671. Found 424.0672.



3l

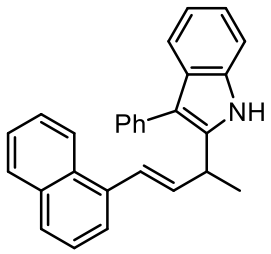
The reaction of **1l** (29.7 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^oC oil bath under argon for 24 h. Compound **3l** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~60:1, v/v) in 27% yield (10.3 mg) as yellow solid, R_f = 0.27 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.03

(s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.50 (m, 4H), 7.50 – 7.40 (m, 4H), 7.40 – 7.30 (m, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.09 (m, 1H), 6.56 (dd, *J* = 16.0, 5.2 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.29 – 4.10 (m, 1H), 1.56 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 140.6, 137.1, 135.8, 135.5, 135.1, 129.8, 129.4 (q, *J* = 32.5 Hz), 128.7, 128.6, 128.0, 126.5, 126.4, 125.7 (q, *J* = 3.9 Hz), 122.2, 120.3, 119.4, 114.9, 110.8, 33.7, 20.2. **^{19}F NMR** ($CDCl_3$, 376 MHz, ppm) δ -62.5. (s, 3F). **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{20}F_3NNa$: 414.1440. Found 414.1443.



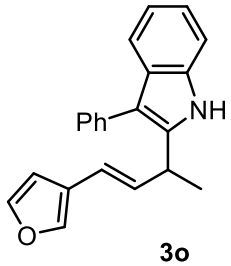
3m

The reaction of **1m** (27.0 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3m** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~60:1, v/v) in 88% yield (32.6 mg) as yellow solid, R_f = 0.34 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.04 (s, 1H), 7.81 – 7.72 (m, 1H), 7.69 – 7.62 (m, 2H), 7.56 (d, *J* = 7.6 Hz, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 (m, 2H), 7.37 – 7.30 (m, 2H), 7.22 – 7.16 (m, 1H), 7.16 – 7.10 (m, 1H), 6.66 – 6.50 (m, 2H), 4.30 – 4.12 (m, 1H), 1.56 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.8, 135.5, 135.3, 134.6, 133.7, 133.4, 133.0, 129.9 (d, *J* = 1.7 Hz), 128.7, 128.4, 128.0, 127.8, 126.4, 126.3, 126.3, 125.9, 123.5, 122.1, 120.2, 119.4, 114.6, 110.8, 33.7, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{23}NNa$: 396.1723. Found 396.1723.



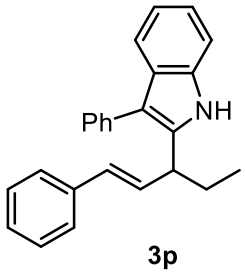
3n

The reaction of **1n** (27.0 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 3 h. Compound **3n** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~60:1, v/v) in 74% yield (27.5 mg) as yellow solid, R_f = 0.36 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.11 (s, 1H), 8.04 – 7.97 (m, 1H), 7.86 – 7.80 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.51 – 7.45 (m, 4H), 7.44 – 7.31 (m, 3H), 7.25 – 7.05 (m, 3H), 6.47 (dd, *J* = 15.6, 5.2 Hz, 1H), 4.33 – 4.17 (m, 1H), 1.62 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.8, 136.3, 135.5, 135.4, 134.9, 133.7, 131.2, 129.9, 128.7, 128.7, 128.1, 128.0, 127.1, 126.4, 126.2, 125.9, 125.7, 123.8, 122.1, 120.2, 119.4, 114.7, 110.8, 34.2, 20.5. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{23}NNa$: 396.1723. Found 396.1723.



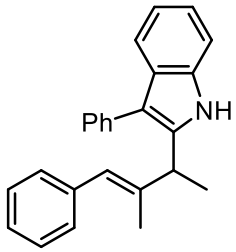
3o

The reaction of **1o** (18.0 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred at rt under argon for 24 h. Compound **3o** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~60:1, v/v) in 37% yield (11.5 mg) as yellow oil, R_f = 0.28 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.01 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.29 (m, 4H), 7.23 – 7.16 (m, 1H), 7.16 – 7.09 (m, 1H), 6.50 (s, 1H), 6.28 (d, *J* = 16.8 Hz, 1H), 6.18 (dd, *J* = 16.0, 4.4 Hz, 1H), 4.32 – 3.96 (m, 1H), 1.50 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 143.7, 140.4, 137.8, 135.3, 132.6, 129.8, 128.7, 128.0, 126.3, 124.1, 122.0, 120.1, 119.6, 119.3, 114.6, 110.8, 107.5, 33.4, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{19}NONa$: 336.1359. Found 336.1351.



3p

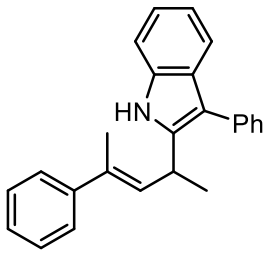
The reaction of **1p** (21.6 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 24 h. Compound **3p** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 72% yield (24.1 mg) as yellow solid, R_f = 0.40 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.02 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.39 – 7.25 (m, 6H), 7.24 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 6.53 – 6.22 (m, 2H), 3.85 (q, *J* = 6.8 Hz, 1H), 2.12 – 1.73 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.3, 136.5, 135.6, 135.3, 132.0, 130.5, 130.0, 128.7, 128.6, 128.1, 127.5, 126.3, 126.3, 122.0, 120.0, 119.3, 116.0, 110.8, 41.3, 28.2, 12.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1726.



3q

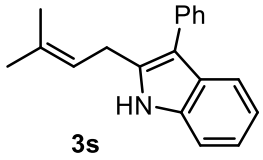
The reaction of **1q** (21.6 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 21 h. Compound **3q** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 93% yield (31.1 mg) as yellow oil, R_f = 0.43 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.03 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 2H), 7.38 – 7.31 (m, 4H), 7.29 – 7.24 (m, 2H), 7.24 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 6.49 (s, 1H), 3.96 (q, *J* = 7.0 Hz, 1H), 1.80 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 141.1, 138.0, 138.0, 135.4, 135.3, 129.9, 129.1, 128.6, 128.3, 128.3, 126.5, 126.3, 124.9, 121.9, 120.0, 119.3, 115.2, 110.8, 39.6, 19.5, 18.1. **HRMS** (ESI)

m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1725.



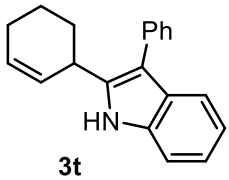
3r

The reaction of **1r** (21.6 mg, 0.15 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^oC oil bath under argon for 9 h. Compound **3r** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 76% yield (22.5 mg) as yellow solid, R_f = 0.40 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.08 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.50 – 7.43 (m, 2H), 7.40 – 7.27 (m, 6H), 7.26 – 7.21 (m, 1H), 7.20 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 5.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.51 – 4.16 (m, 1H), 1.89 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 143.4, 139.2, 136.5, 135.5, 135.3, 130.4, 130.0, 128.6, 128.4, 128.1, 127.2, 126.3, 125.9, 121.8, 120.1, 119.2, 114.0, 110.7, 31.0, 22.0, 16.2. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1719.



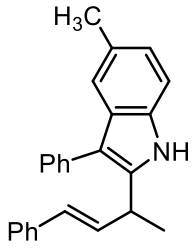
3s

The reaction of **1s** (21 μL, 2.0 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^oC oil bath under argon for 28 h. Compound **3s** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 41% yield (10.5 mg) as yellow oil, R_f = 0.41 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.01 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.27 (m, 2H), 7.20 – 7.07 (m, 2H), 5.49 – 5.30 (m, 1H), 3.60 (d, *J* = 7.2 Hz, 2H), 1.79 (s, 3H), 1.73 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 135.5, 135.3, 135.1, 134.8, 129.7, 128.6, 128.1, 126.0, 121.7, 120.6, 120.1, 119.1, 114.1, 110.6, 26.0, 25.7, 18.1. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NNa$: 284.1410. Found 284.1395.



3t

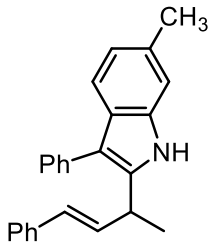
The reaction of **1t** (20 μL, 2.0 mmol) and **2a** (19.4 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 28 h. Compound **3t** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 37% yield (9.9 mg) as yellow oil, R_f = 0.43 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.10 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.42 – 7.32 (m, 2H), 7.24 – 7.18 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.12 – 5.94 (m, 1H), 5.88 – 5.67 (m, 1H), 4.19 – 3.82 (m, 1H), 2.27 – 2.04 (m, 3H), 1.92 – 1.64 (m, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 139.2, 135.4, 135.1, 130.1, 129.8, 128.6, 128.5, 128.2, 126.1, 121.8, 120.0, 119.2, 114.0, 110.7, 33.2, 30.9, 25.0, 21.5. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{19}NNa$: 296.1410. Found 296.1417.



3v

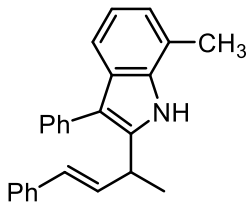
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2b** (20.7 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 10 h. Compound **3v** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 63% yield (21.0 mg) as yellow oil, R_f = 0.61 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 7.92 (s, 1H), 7.56 – 7.50 (m, 2H), 7.49 – 7.41 (m, 3H), 7.38 – 7.26 (m, 5H), 7.25 – 7.18 (m, 2H), 7.01 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.51 – 6.36 (m, 2H), 4.24 – 4.06 (m, 1H), 2.42 (s, 3H), 1.51 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.9, 137.2, 135.5, 133.8, 133.1, 129.9, 129.7, 129.4, 128.7, 128.7, 128.3, 127.6, 126.4, 126.2, 123.5, 119.0, 114.2, 110.5, 33.6, 21.6, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for

$C_{25}H_{23}NNa$: 360.1723. Found 360.1725.



3w

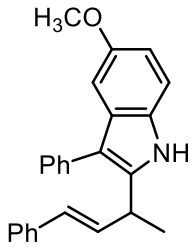
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2c** (20.7 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 5 h. Compound **3w** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 74% yield (24.9 mg) as yellow oil, R_f = 0.50 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 500 MHz, ppm) δ 7.88 (s, 1H), 7.57 – 7.49 (m, 3H), 7.48 – 7.42 (m, 2H), 7.37 – 7.25 (m, 5H), 7.24 – 7.18 (m, 1H), 7.13 (s, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.52 – 6.35 (m, 2H), 4.35 – 3.95 (m, 1H), 2.46 (s, 3H), 1.51 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.2, 137.0, 135.9, 135.5, 133.1, 131.8, 129.8, 129.6, 128.7, 128.6, 127.5, 126.3, 126.2, 125.8, 121.8, 119.0, 114.4, 110.8, 33.5, 21.8, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1728.



3x

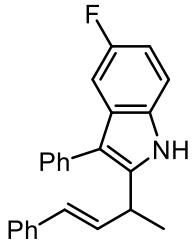
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2d** (20.7 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3x** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 60% yield (20.0 mg) as yellow oil, R_f = 0.51 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 500 MHz, ppm) δ 7.87 (s, 1H), 7.51 (dd, *J* = 13.5, 8.0 Hz, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.24 – 7.19 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.49 (dd, *J* = 16.0, 4.5 Hz, 1H), 6.43 (d, *J* = 16.5 Hz, 1H), 4.20 – 4.11 (m, 1H), 2.50 (s, 3H), 1.55 (d, *J* = 7.0

Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.5, 137.2, 135.4, 135.0, 133.1, 129.9, 129.8, 128.7, 128.7, 127.6, 126.4, 126.3, 122.7, 120.4, 120.0, 117.1, 115.2, 33.6, 20.4, 16.9. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1725.



3y

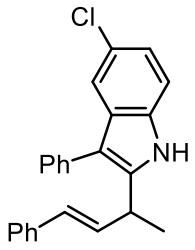
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2e** (22.3 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 21 h. Compound **3y** was isolated by flash column chromatography (SiO_2, PE/EA = 50:1, v/v) in 58% yield (20.3 mg) as yellow solid, R_f = 0.28 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 77.93 (s, 1H), 7.55 – 7.50 (m, 2H), 7.50 – 7.43 (m, 2H), 7.40 – 7.27 (m, 5H), 7.27 – 7.19 (m, 2H), 7.11 (d, *J* = 2.4 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.53 – 6.35 (m, 2H), 4.19 – 4.06 (m, 1H), 3.81 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 154.7, 138.7, 137.1, 135.4, 132.9, 130.6, 129.8, 129.7, 128.8, 128.4, 127.6, 126.4, 126.3, 114.5, 112.1, 111.5, 101.4, 56.2, 33.6, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NONa$: 376.1672. Found 376.1672.



3z

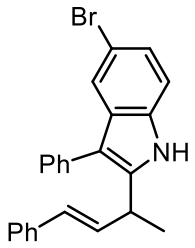
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2f** (21.1 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 10 h. Compound **3z** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 59% yield (20.0 mg) as yellow solid, R_f

= 0.49 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.01 (s, 1H), 7.55 – 7.43 (m, 4H), 7.37 – 7.27 (m, 6H), 7.25 – 7.19 (m, 2H), 6.99 – 6.88 (m, 1H), 6.52 – 6.37 (m, 2H), 4.19 – 4.07 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 158.5 (d, *J* = 235.2 Hz), 139.7, 137.0, 134.8, 132.6, 131.9, 129.9, 129.7, 128.8 (d, *J* = 4.4 Hz), 128.5 (d, *J* = 9.7 Hz), 127.7, 126.5, 126.4, 114.8 (d, *J* = 4.6 Hz), 111.3 (d, *J* = 9.6 Hz), 110.2 (d, *J* = 26.4 Hz), 104.4 (d, *J* = 24.0 Hz), 33.6, 20.3. **^{19}F NMR** ($CDCl_3$, 376 MHz, ppm) δ -124.2. (s, 1F). **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}FNNa$: 364.1472. Found 364.1470.



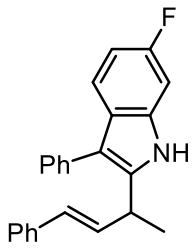
3aa

The reaction of **1a** (19.6 mg, 0.15 mmol) and **2g** (22.8 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 9 h. Compound **3aa** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 83% yield (29.6 mg) as yellow oil, R_f = 0.44 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.05 (s, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.38 – 7.29 (m, 5H), 7.27 – 7.20 (m, 2H), 7.13 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.54 – 6.36 (m, 2H), 4.36 – 4.04 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 139.3, 137.0, 134.6, 133.8, 132.5, 130.0, 129.8, 129.2, 128.8, 128.8, 127.7, 126.7, 126.4, 125.9, 122.2, 118.8, 114.4, 111.8, 33.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}ClNNa$: 380.1176. Found 380.1183.



3ab

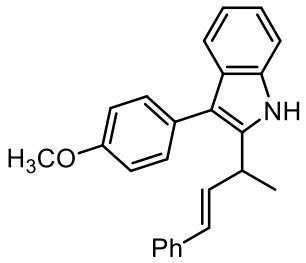
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2h** (27.2 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 21 h. Compound **3ab** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 58% yield (23.0 mg) as yellow solid, R_f = 0.46 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.07 (s, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.39 – 7.27 (m, 5H), 7.27 – 7.18 (m, 3H), 6.51 – 6.37 (m, 2H), 4.21 – 4.02 (m, 1H), 1.53 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 139.1, 137.0, 134.5, 134.1, 132.5, 130.0, 129.9, 129.8, 128.8, 128.8, 127.7, 126.7, 126.4, 124.8, 121.9, 114.3, 113.4, 112.2, 33.5, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}BrNNa$: 424.0671. Found 424.0673.



3ac

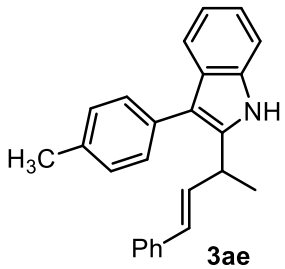
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2i** (21.1 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3ac** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 82% yield (27.7 mg) as yellow solid, R_f = 0.41 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.01 (s, 1H), 7.55 – 7.43 (m, 5H), 7.37 – 7.27 (m, 5H), 7.25 – 7.19 (m, 1H), 7.03 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.91 – 6.83 (m, 1H), 6.55 – 6.35 (m, 2H), 4.16 – 4.05 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 160.0 (d, *J* = 238.4 Hz), 138.0 (d, *J* = 3.6 Hz), 137.0, 135.4 (d, *J* = 12.4 Hz), 134.9, 132.7, 129.9, 129.8, 128.8, 127.7, 126.5, 126.4, 124.6, 120.1 (d, *J* = 10.0 Hz), 114.5, 108.6 (d, *J* = 24.2 Hz), 97.2 (d, *J* =

26.2 Hz), 33.6, 20.3. **^{19}F NMR** ($CDCl_3$, 376 MHz, ppm) δ -121.3. (s, 1F). **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}FNNa$: 364.1472. Found 364.1469.



3ad

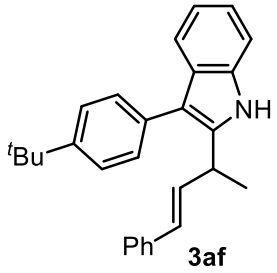
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2j** (22.3 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 5 h. Compound **3ad** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~50:1, v/v) in 79% yield (27.6 mg) as yellow oil, R_f = 0.36 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 7.99 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.39 – 7.26 (m, 5H), 7.25 – 7.15 (m, 2H), 7.14 – 7.08 (m, 1H), 7.05 – 6.99 (m, 2H), 6.53 – 6.37 (m, 2H), 4.17 – 4.05 (m, 1H), 3.86 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 158.3, 137.5, 137.2, 135.4, 133.1, 130.9, 129.7, 128.7, 128.3, 127.6, 127.6, 126.4, 121.9, 120.0, 119.3, 114.2, 114.1, 110.7, 55.5, 33.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NONa$: 376.1672. Found 376.1673.



3ae

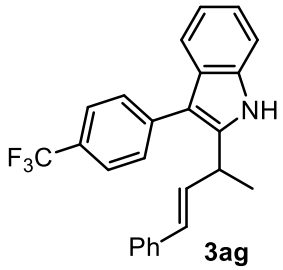
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2k** (22.3 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3ae** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 76% yield (25.4 mg) as yellow oil, R_f = 0.44 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.01 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.31 – 7.25 (m, 4H), 7.24 – 7.15 (m, 2H), 7.14 – 7.06 (m, 1H), 6.54 – 6.33 (m, 2H), 4.17 – 4.07 (m,

1H), 2.42 (s, 3H), 1.51 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.6, 137.2, 135.9, 135.5, 133.0, 132.2, 129.7, 129.7, 129.4, 128.7, 128.1, 127.6, 126.4, 121.9, 120.0, 119.4, 114.4, 110.8, 33.6, 21.4, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1723.



3af

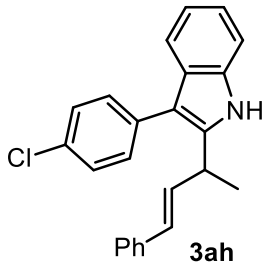
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2l** (24.9 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 21 h. Compound **3af** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~50:1, v/v) in 74% yield (28.0 mg) as yellow oil, R_f = 0.41 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 7.99 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.48 (s, 4H), 7.37 – 7.25 (m, 5H), 7.24 – 7.15 (m, 2H), 7.14 – 7.08 (m, 1H), 6.57 – 6.31 (m, 2H), 4.22 – 4.11 (m, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.38 (s, 9H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 149.0, 137.6, 137.2, 135.5, 133.1, 132.2, 129.7, 129.4, 128.7, 128.1, 127.6, 126.4, 125.6, 121.9, 120.0, 119.5, 114.4, 110.7, 34.7, 33.5, 31.6, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{29}NNa$: 402.2192. Found 402.2195.



3ag

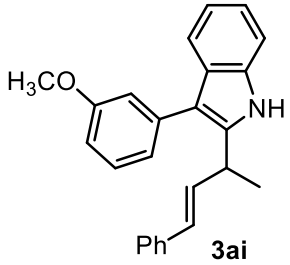
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2m** (26.1 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 21 h. Compound **3ag** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 77% yield (30.1 mg) as yellow solid, R_f = 0.46 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.11 (s, 1H),

7.71 (d, *J* = 8.0 Hz, 2H), 7.66 – 7.61 (m, 3H), 7.42 – 7.27 (m, 5H), 7.26 – 7.18 (m, 2H), 7.18 – 7.12 (m, 1H), 6.54 – 6.35 (m, 2H), 4.17 – 4.05 (m, 1H), 1.54 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 139.2, 138.5, 136.9, 135.5, 132.5, 130.1, 129.9, 128.8, 128.4 (q, *J* = 32.5 Hz), 127.8, 127.6, 126.4, 125.6 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 272.8 Hz), 122.4, 120.6, 119.0, 113.3, 111.0, 33.6, 20.4. **^{19}F NMR** ($CDCl_3$, 376 MHz, ppm) δ -62.2. (s, 3F). **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{20}F_3NNa$: 414.1440. Found 414.1443.



3ah

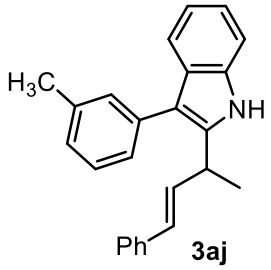
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2n** (22.8 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3ah** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 80% yield (28.5 mg) as yellow oil, R_f = 0.36 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.04 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.38 – 7.27 (m, 5H), 7.25 – 7.17 (m, 2H), 7.15 – 7.08 (m, 1H), 6.55 – 6.34 (m, 2H), 4.13 – 4.02 (m, 1H), 1.52 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 138.0, 137.0, 135.4, 133.8, 132.7, 132.1, 131.1, 130.0, 128.9, 128.8, 127.8, 127.7, 126.4, 122.2, 120.3, 119.0, 113.4, 110.9, 33.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}ClNNa$: 380.1176. Found 380.1181.



3ai

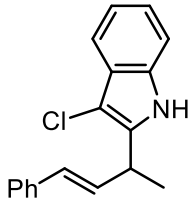
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2o** (22.3 mg, 0.10 mmol) was stirred in

a 40 °C oil bath under argon for 8 h. Compound **3ai** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1~50:1, v/v) in 77% yield (27.2 mg) as yellow oil, R_f = 0.33 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.04 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 2H), 7.15 – 7.07 (m, 3H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.57 – 6.37 (m, 2H), 4.23 – 4.08 (m, 1H), 3.83 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 159.9, 137.9, 137.1, 136.7, 135.5, 132.9, 129.8, 129.6, 128.7, 127.9, 127.6, 126.3, 122.3, 122.0, 120.2, 119.4, 115.3, 114.4, 111.9, 110.8, 55.4, 33.6, 20.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NONa$: 376.1672. Found 376.1674.



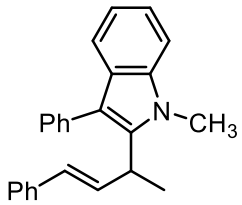
3aj

The reaction of **1a** (19.6 mg, 0.15 mmol) and **2p** (20.7 mg, 0.10 mmol) was stirred in a 40 °C oil bath under argon for 3 h. Compound **3aj** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 60% yield (20.2 mg) as yellow oil, R_f = 0.53 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 8.00 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.27 (m, 8H), 7.24 – 7.17 (m, 2H), 7.17 – 7.08 (m, 2H), 6.56 – 6.35 (m, 2H), 4.20 – 4.08 (m, 1H), 2.42 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 138.2, 137.7, 137.2, 135.5, 135.2, 133.0, 130.6, 129.7, 128.7, 128.6, 128.1, 127.6, 127.1, 126.9, 126.4, 122.0, 120.1, 119.4, 114.6, 110.8, 33.6, 21.8, 20.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1726.



3ak

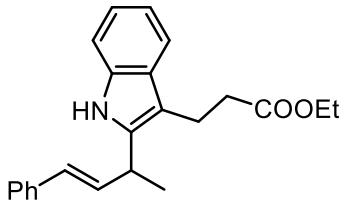
The reaction of **1a** (19.6 mg, 0.15 mmol) and **2q** (15.2 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 4 h. Compound **3ak** was isolated by flash column chromatography (SiO_2, PE/EA = 80:1, v/v) in 52% yield (14.4 mg) as yellow oil, R_f = 0.36 (silica gel, PE/EA = 15:1). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 7.93 (s, 1H), 7.66 – 7.52 (m, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.27 – 7.22 (m, 1H), 7.21 – 7.13 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.42 (dd, *J* = 16.0, 5.2 Hz, 1H), 4.20 – 4.10 (m, 1H), 1.56 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 137.0, 136.7, 134.2, 131.0, 130.5, 128.8, 127.8, 126.4, 122.6, 120.5, 117.9, 111.1, 33.6, 19.0. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}ClNNa$: 304.0863. Found 304.0878.



3al

The reaction of **1a** (19.6 mg, 0.15 mmol) and **2r** (20.7 mg, 0.10 mmol) was stirred in a 40 ^{o}C oil bath under argon for 22 h. Compound **3al** was isolated by flash column chromatography (SiO_2, PE/EA = 120:1~100:1, v/v) in 31% yield (10.6 mg) as yellow oil, R_f = 0.57 (silica gel, PE/EA = 15:1). When HFIP (10.7 μL, 0.10 mmol) was used as the additive, the compound **3al** was isolated in 47% yield (15.7 mg).**^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.38 – 7.26 (m, 6H), 7.25 – 7.18 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.49 (dd, *J* = 16.4, 4.4 Hz, 1H), 6.36 (dd, *J* = 16.0, 2.0 Hz, 1H), 4.39 – 4.21 (m, 1H), 3.78 (s, 3H), 1.57 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 138.8, 137.3, 137.3, 135.8, 133.0, 130.4,

129.7, 128.7, 128.5, 127.5, 127.4, 126.3, 126.3, 121.7, 119.8, 119.3, 115.2, 108.9, 33.4, 31.4, 19.4. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{23}NNa$: 360.1723. Found 360.1727.

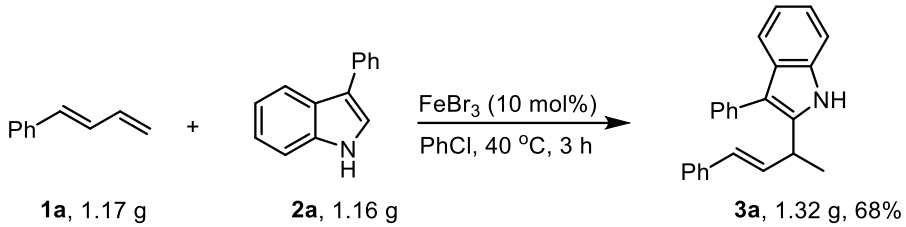


3am

The reaction of **1a** (19.6 mg, 0.15 mmol) and **2s** (21.7 mg, 0.10 mmol) was stirred in a 40 ^oC oil bath under argon for 22 h. Compound **3am** was isolated by flash column chromatography (SiO_2, PE/EA = 50:1~35:1, v/v) in 20% yield (7.0 mg) as yellow oil, R_f = 0.24 (silica gel, PE/EA = 15:1). When HFIP (10.7 μL, 0.10 mmol) was used as the additive, the compound **3am** was isolated in 32% yield (11.1 mg). **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) δ 7.85 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.25 – 7.18 (m, 1H), 7.16 – 7.06 (m, 2H), 6.51 – 6.36 (m, 2H), 4.22 – 3.98 (m, 3H), 3.10 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz, ppm) δ 173.6, 137.6, 137.1, 135.5, 132.6, 129.6, 128.7, 128.3, 127.5, 126.3, 121.5, 119.4, 118.4, 110.7, 110.0, 60.5, 35.7, 33.5, 20.0, 19.8, 14.3. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{25}NNaO_2$: 370.1777. Found 370.1777.

5. Gram-scale reaction and mechanistic study

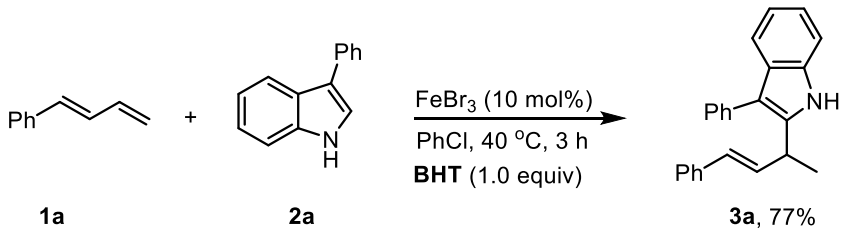
5.1 Gram scale experiment



1a, 1.17 g **2a**, 1.16 g **3a**, 1.32 g, 68%

In Ar-filled glove box, the $FeBr_3$ (177.3 mg, 0.6 mmol, 0.1 equiv) was added to the oven-dried reaction tube with a dried stir bar. The tube was capped, then it was transferred out of the glovebox. 3-phenylindole **2a** (1.16 g, 6 mmol, 1.0 equiv) was added to this oven-dried reaction tube, 1-phenyl-1,3-butadiene **1a** (1.17 g, 9 mmol, 1.5 equiv) was added with PhCl (120 mL). After all reagents were added, the reaction tube was replaced with argon three times, and then sealed. The reaction mixture was stirred in a 40 °C oil bath under argon for 3 h (monitored by TLC). After the reaction was completed, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel with a gradient eluent of PE/EA = 80:1 to give the desired product **3a** in 68% yield (1.32 g) as yellow solid.

5.2 Control experiment

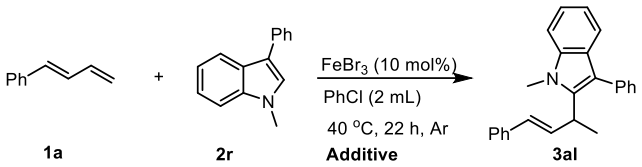


1a **2a** **3a**, 77%

In Ar-filled glove box, the $FeBr_3$ (3.0 mg, 0.01 mmol, 0.1 equiv) was added to the oven-dried reaction tube with a dried stir bar. The tube was capped, then it was transferred out of the glovebox. 3-phenylindole **2a** (19.4 mg, 0.10 mmol, 1.0 equiv) and BHT (22.0 mg, 0.10 mmol, 1.0 equiv) were added to this oven-dried reaction tube, 1-phenyl-1,3-butadiene **1a** (19.6 mg, 0.15 mmol, 1.5 equiv) was added with PhCl (2 mL). After all reagents were added, the reaction tube was replaced with argon three times, and then sealed. The reaction mixture was stirred in a 40 °C oil bath under argon for 3 h (monitored by TLC). After the reaction was completed, the solvent was

removed under vacuum, and the residue was purified by column chromatography on silica gel with a gradient eluent of PE/EA = 80:1 to give the desired product **3a** in 77% yield (24.7 mg) as yellow solid.

5.3 The investigation of some alcohols

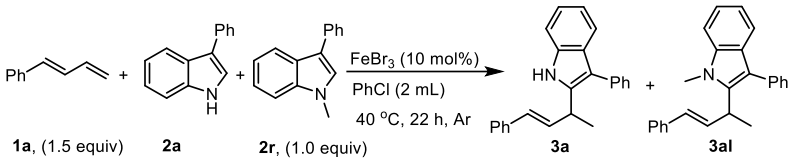


1a 2r 3al

entry	additive	yield (%)
1	no	31
2	(*R*)-1,1'-bi-2-naphthol (0.1 equiv)	31
3	(*R*)-1,1'-bi-2-naphthol (0.5 equiv)	20
4	(*R*)-1,1'-bi-2-naphthol (1.0 equiv)	19
5	(*R*)-1,1'-bi-2-naphthol (2.0 equiv)	20
6	2,6-dimethylphenol (0.1 equiv)	12
7	2,6-dimethylphenol (1.0 equiv)	28
8	Phenol (1.0 equiv)	24
9	^{t}BuOH (0.1 equiv)	6
10	^{t}BuOH (1.0 equiv)	6
11	^{t}BuOH (2.0 equiv)	13
12	^{t}BuOH (5.0 equiv)	9
13	*L*-menthol (1.0 equiv)	32
14	*L*-menthol (2.0 equiv)	23
15	*L*-menthol (5.0 equiv)	19
16	^{i}PrOH (1.0 equiv)	17
17	^{i}PrOH (2.0 equiv)	31
18	^{i}PrOH (5.0 equiv)	trace

In Ar-filled glove box, the $FeBr_3$ (3.0 mg, 0.01 mmol, 0.1 equiv) was added to the oven-dried reaction tube with a dried stir bar. The tube was capped, then it was transferred out of the glovebox. N-Me-3-phenylindole **2r** (20.7 mg, 0.10 mmol, 1.0 equiv) and **additive** were added to this oven-dried reaction tube, 1-phenyl-1,3-butadiene **1a** (19.6 mg, 0.15 mmol, 1.5 equiv) was added with PhCl (2 mL). After all reagents were added, the reaction tube was replaced with argon three times, and then sealed. The reaction mixture was stirred in a 40 ^{o}C oil bath under argon for 22 h. The solvent was removed under vacuum, and the residue was purified by analytic TLC purification (SiO_2, PE/EA = 15:1, v/v) to afford **3al**.

5.4 The cross-over experiments



entry	**2a** (equiv)	yield (**3a**)	yield (**3al**)
1	1.0	83%	15%
2	0.1	12%	31%

In Ar-filled glove box, the $FeBr_3$ (3.0 mg, 0.01 mmol, 0.1 equiv) was added to the oven-dried reaction tube with a dried stir bar. The tube was capped, then it was transferred out of the glovebox. N-Me-3-phenylindole **2r** (20.7 mg, 0.10 mmol, 1.0 equiv) and 3-phenylindole **2a** (1.0 equiv or 0.1 equiv) were added to this oven-dried reaction tube, 1-phenyl-1,3-butadiene **1a** (19.6 mg, 0.15 mmol, 1.5 equiv) was added with PhCl (2 mL). After all reagents were added, the reaction tube was replaced with argon three times, and then sealed. The reaction mixture was stirred in a 40 ^{o}C oil bath under argon for 22 h. The solvent was removed under vacuum, and the residue was purified by analytic TLC purification (SiO_2, PE/EA = 15:1, v/v) to afford **3a and 3al**.

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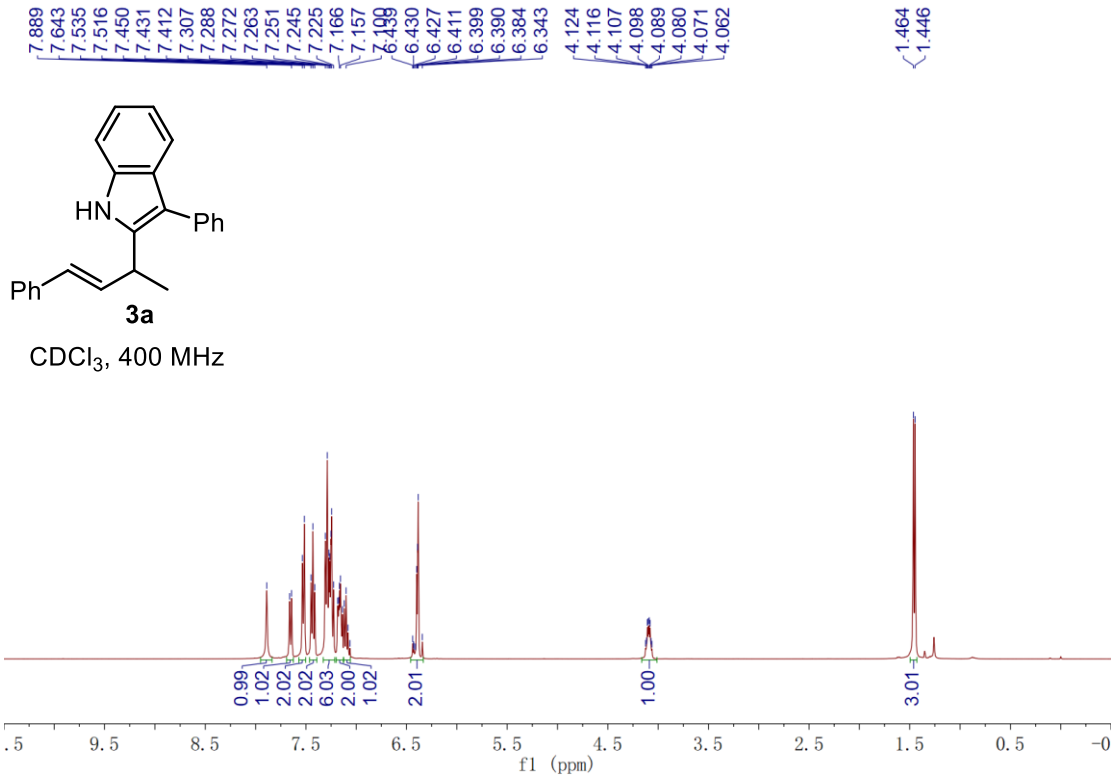
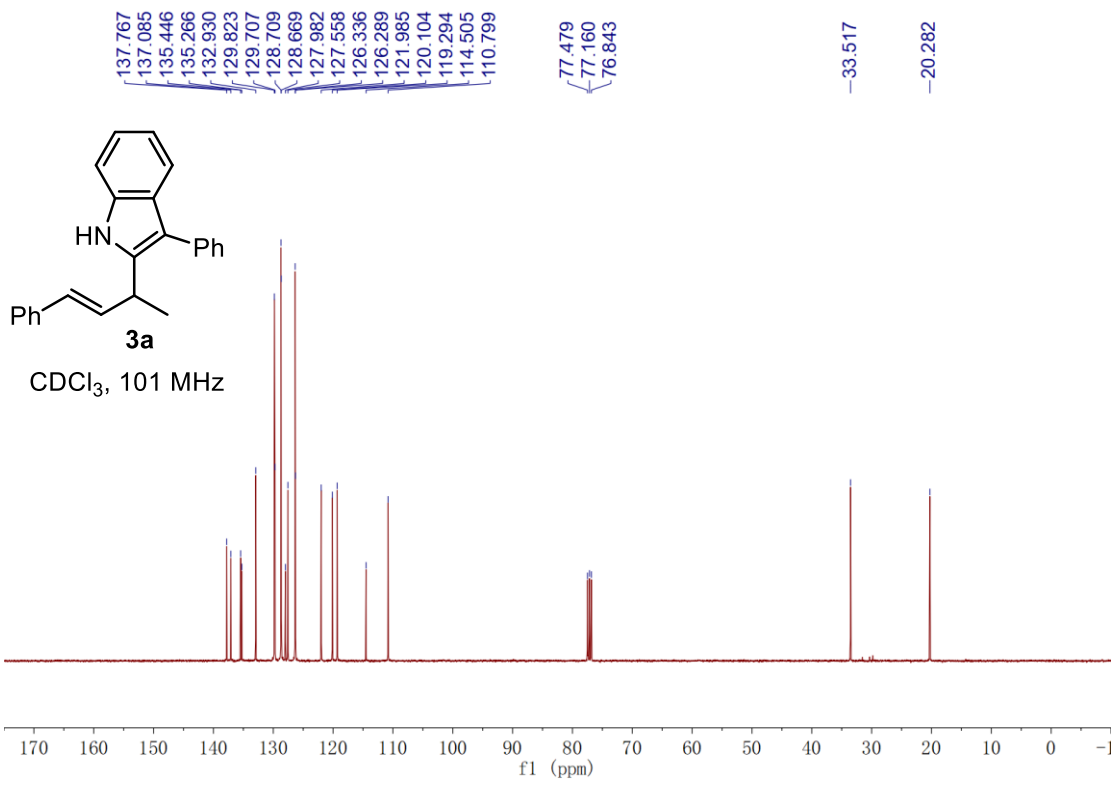
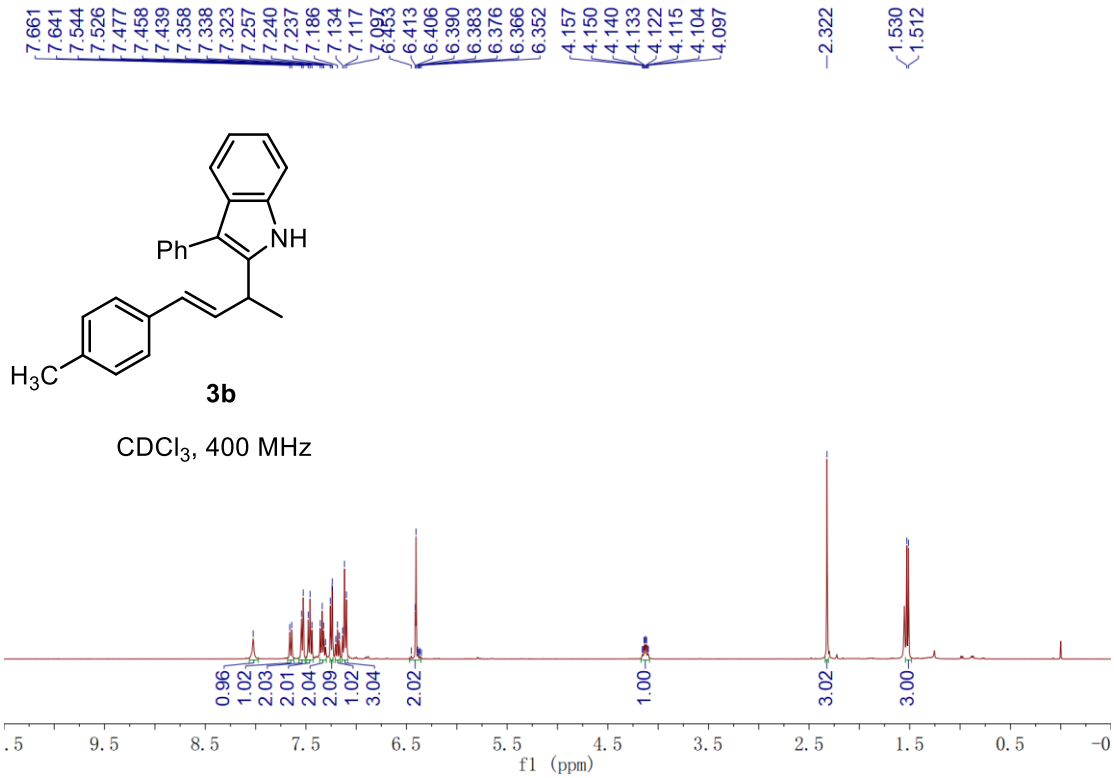
(2) (a) L. Bering, F. M. Paulussen and A. P. Antonchick, *Org. Lett.* 2018, **20**, 1978−1981. (b) F. Jiang, K.-W. Chen, P. Wu, Y.-C. Zhang, Y. Jiao and F. Shi, *Angew. Chem. Int. Ed.* 2019, **58**, 15104-15110. (c) Y. Chen, S. Guo, K. Li, J. Qu, H. Yuan, Q. Hua and B. Chen, *Adv. Synth. Catal.* 2013, **355**, 711-715. (d) H. Yuan, L. Guo, F. Liu, Z. Miao, L. Feng and H. Gao, *ACS Catal.* 2019, **9**, 3906−3912. (e) C. A. Kuttruff, H. Zipse and D. Trauner, *Angew. Chem. Int. Ed.* 2011, **50**, 1402-1405. (f) R. B. Bedford, N. Fey, M. F. Haddow and R. F. Sankey, *Chem. Commun.*, *2011*, **47**, 3649-3651. (g) S. Rapolu, M. Alla, V. R. Bommena, R. Murthy, J N. ain, V. R. Bommareddy and M. R. Bommineni, *Eur. J. Med. Chem*. 2013, **66**, 91–100. (h) S. Rapolu, M. Alla, V. R. Bommena, R. Murthy, N. Jain, V. R. Bommareddy and M. R. Bommineni, *Eur. J. Med. Chem*. 2013, **66**, 91–100.

Copies of NMR Spectra



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7.186
7.134
7.117
7.097
6.413
6.406
6.390
6.383
6.376
6.366
6.352
4.157
4.150
4.140
4.133
4.122
4.115
4.104
4.097
2.322
1.530
1.512
Ph
NH
H3C
3b
CDCl3, 400 MHz
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2.04
2.09
1.02
3.04
2.02
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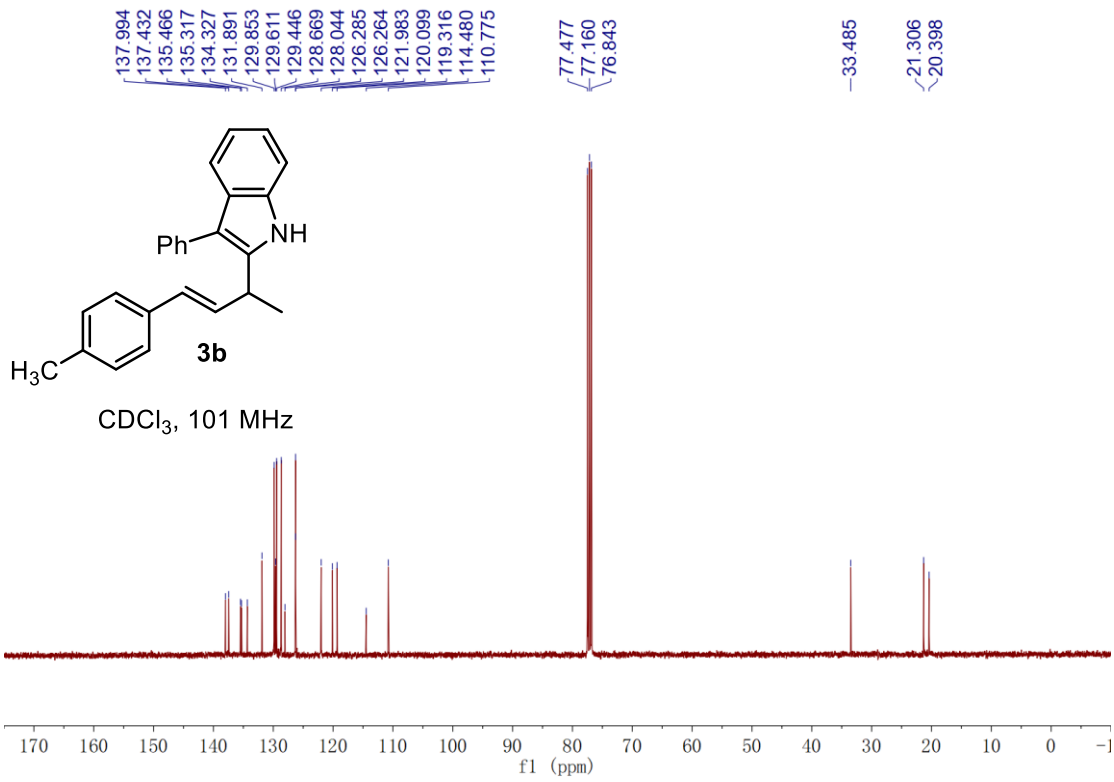
3.02
3.00
f1 (ppm)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126.264
121.983
120.099
119.316
114.480
110.775
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21.306
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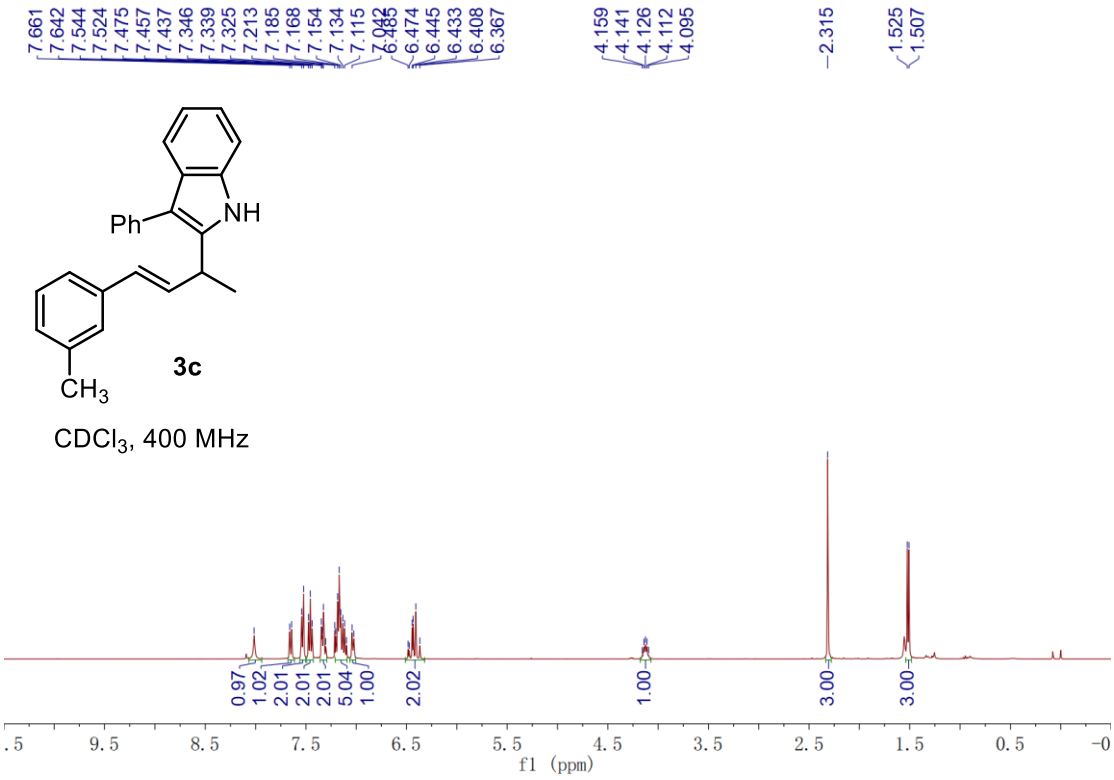
H3C
3b
CDCl3, 101 MHz
f1 (ppm)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7.168
7.154
7.134
7.115
6.474
6.445
6.433
6.408
6.367
4.159
4.141
4.126
4.112
4.095
2.315
1.525
1.507
Ph
NH
CH3
3c
CDCl3, 400 MHz
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2.01
2.01
5.04
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1.00
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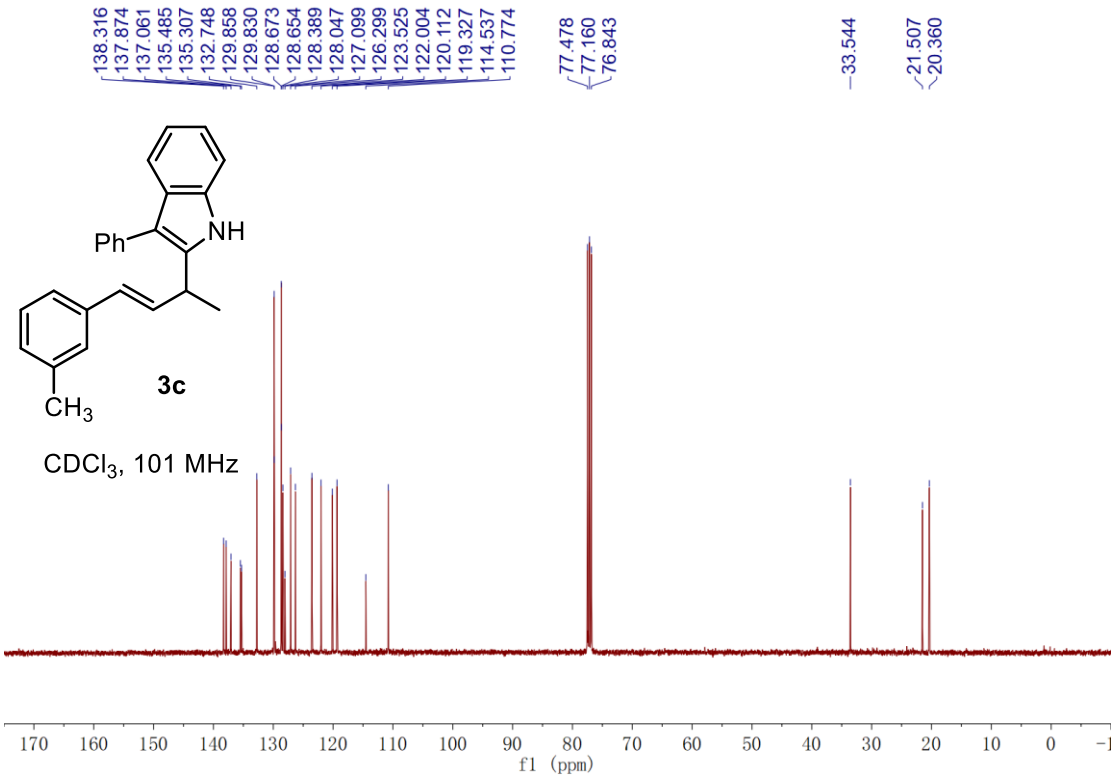
3.00
f1 (ppm)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126.299
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114.537
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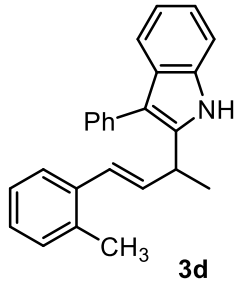
CH3
3c
CDCl3, 101 MHz
f1 (ppm)



3d

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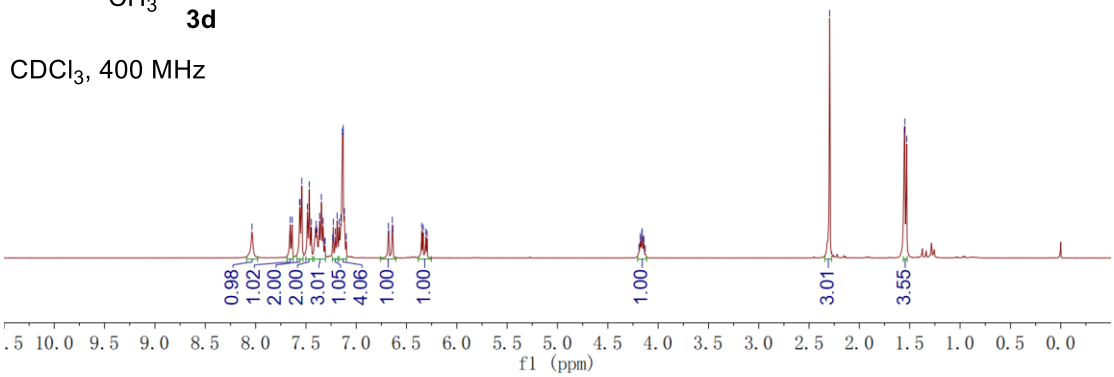
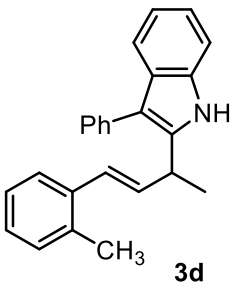
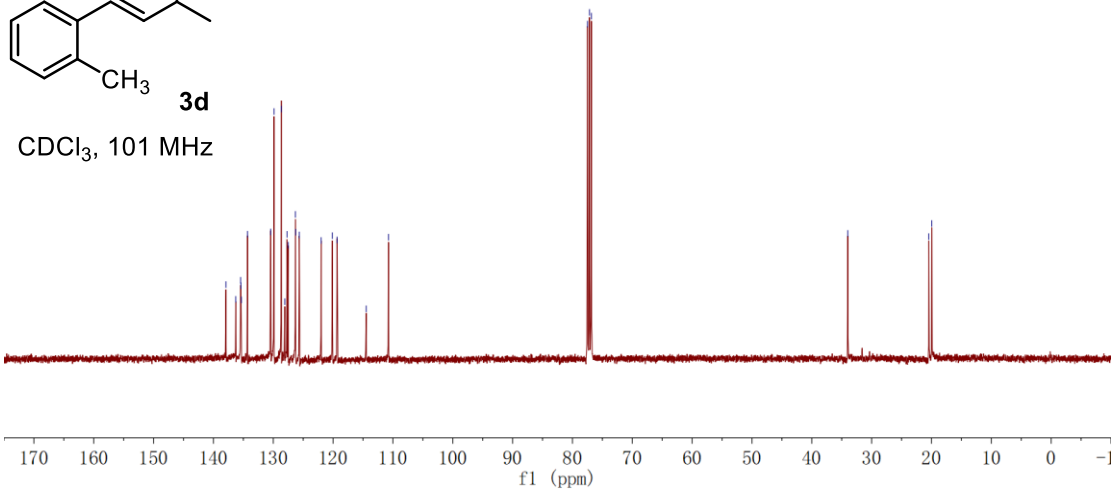
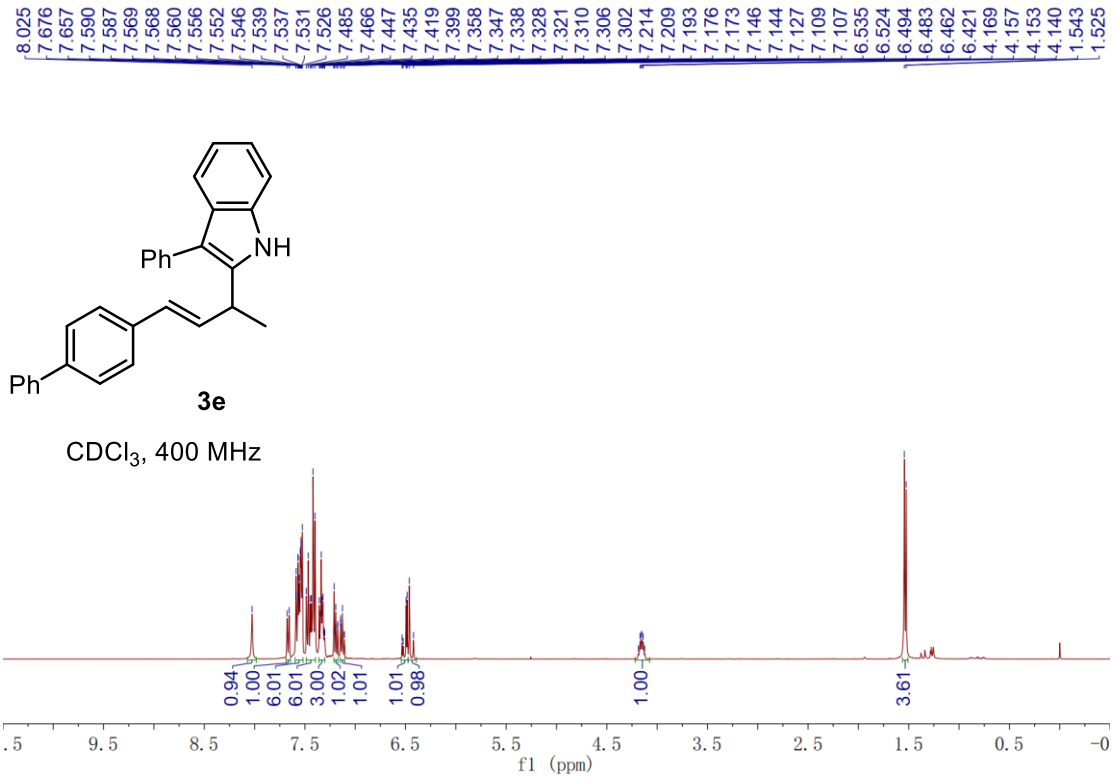




3d

$CDCl_3$, 101 MHz

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7.526
7.485
7.466
7.447
7.435
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7.347
7.338
7.328
7.321
7.310
7.306
7.302
7.214
7.209
7.193
7.176
7.173
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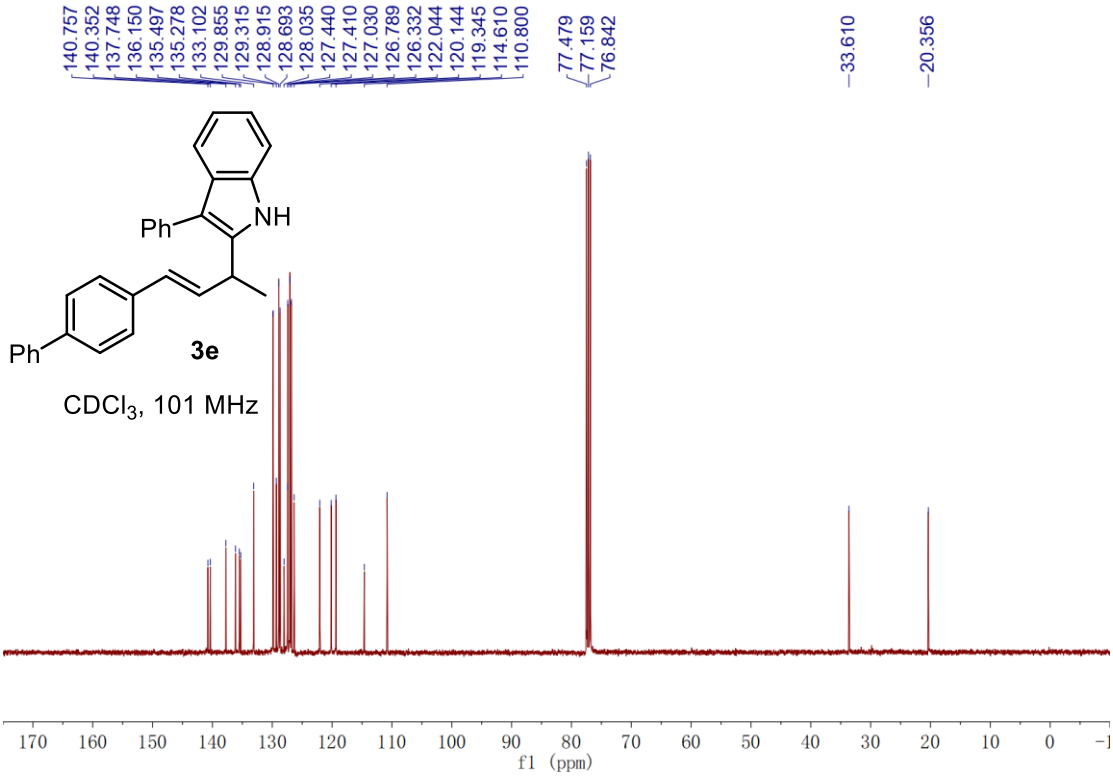
7.144
7.127
7.109
7.107
6.535
6.524
6.494
6.483
6.462
6.421
4.169
4.157
4.153
4.140
1.543
1.525
Ph
NH
Ph
3e
CDCl3, 400 MHz
0.94
1.00
6.01
6.01
3.00
1.02
1.01
1.01
0.98
1.00
3.61
.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0
f1 (ppm)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120.144
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110.800
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77.159
76.842
33.610
20.356
Ph
NH
Ph
3e
CDCl3, 101 MHz
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150
140
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120
110
100
90
80
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60
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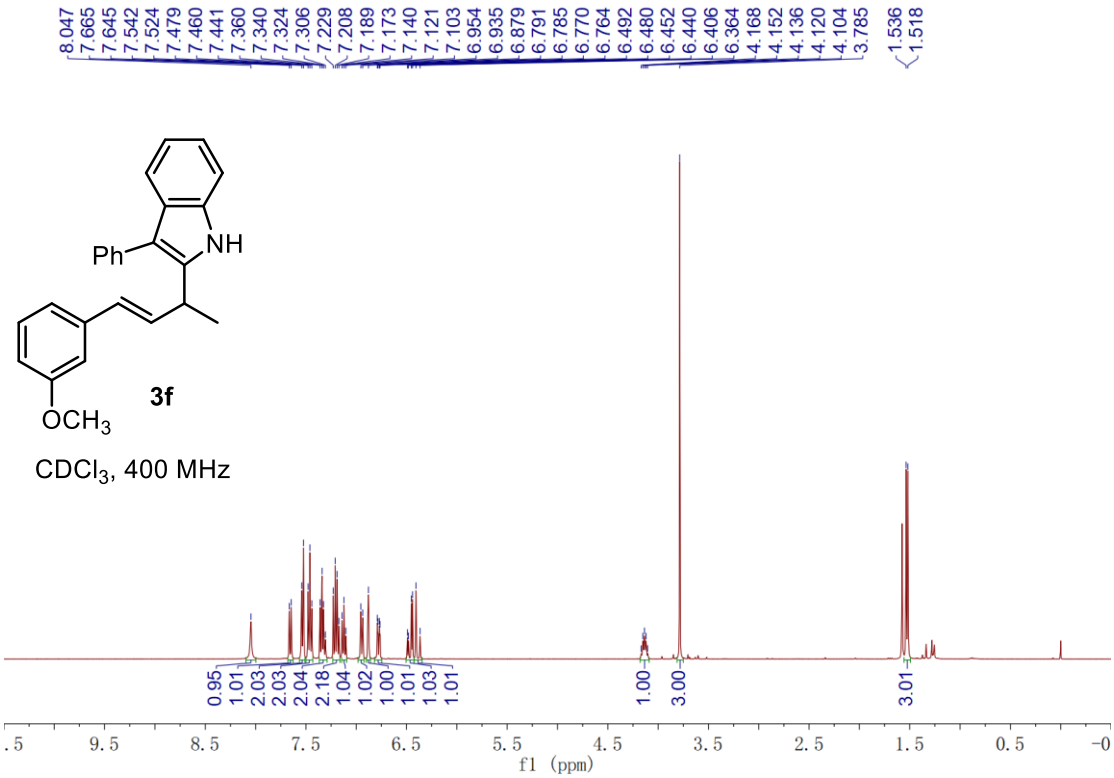
40
30
20
10
0
−1
f1 (ppm)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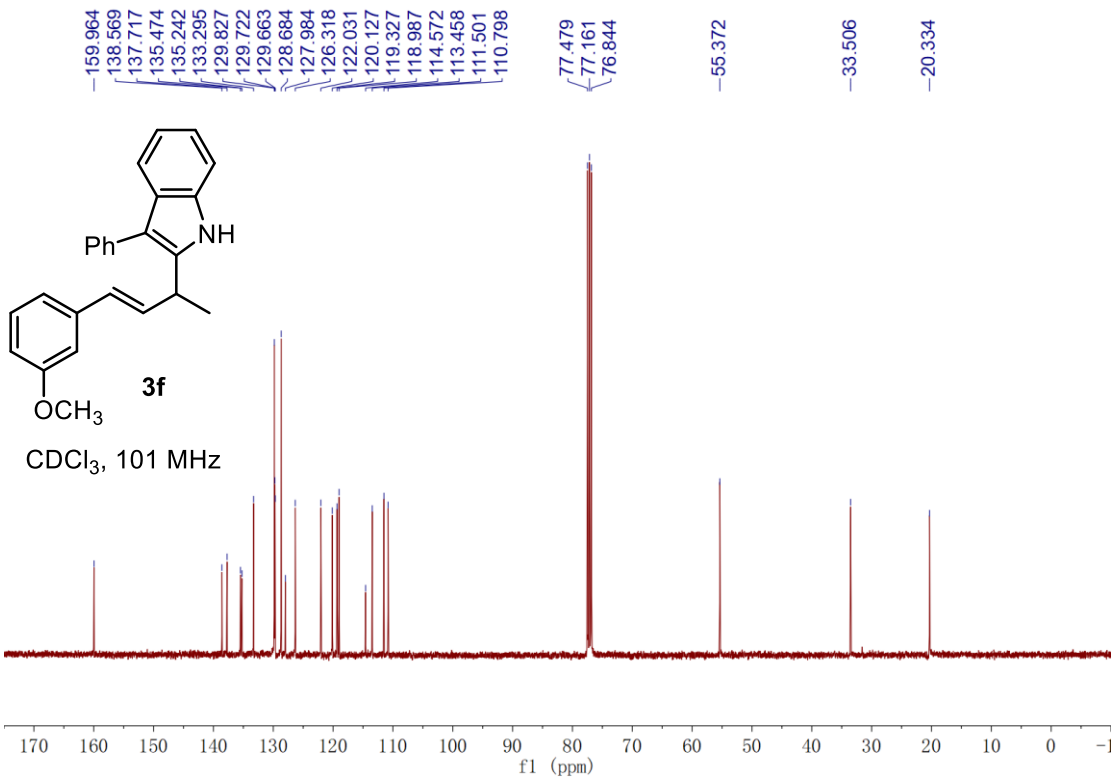
f1 (ppm)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3f
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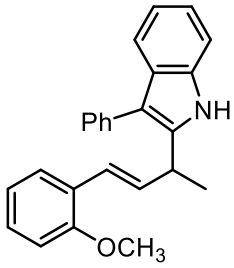
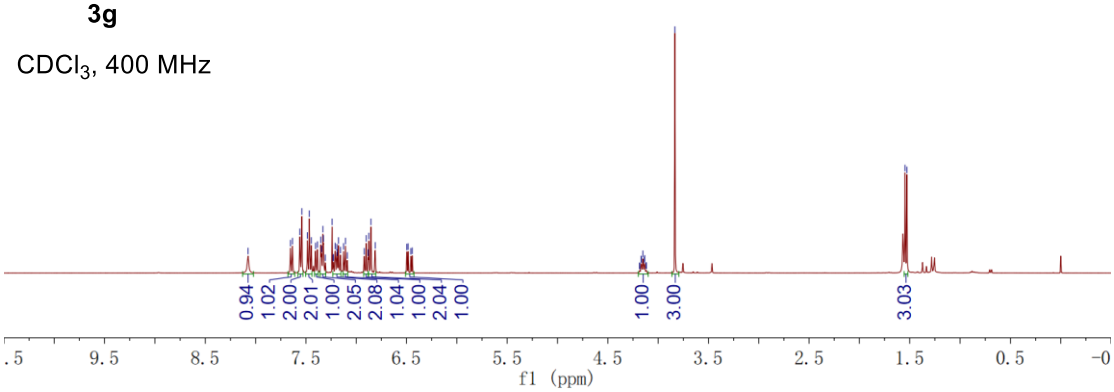
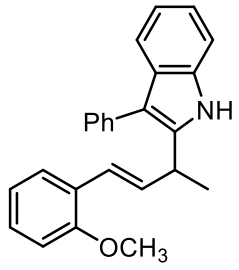
f1 (ppm)



3g

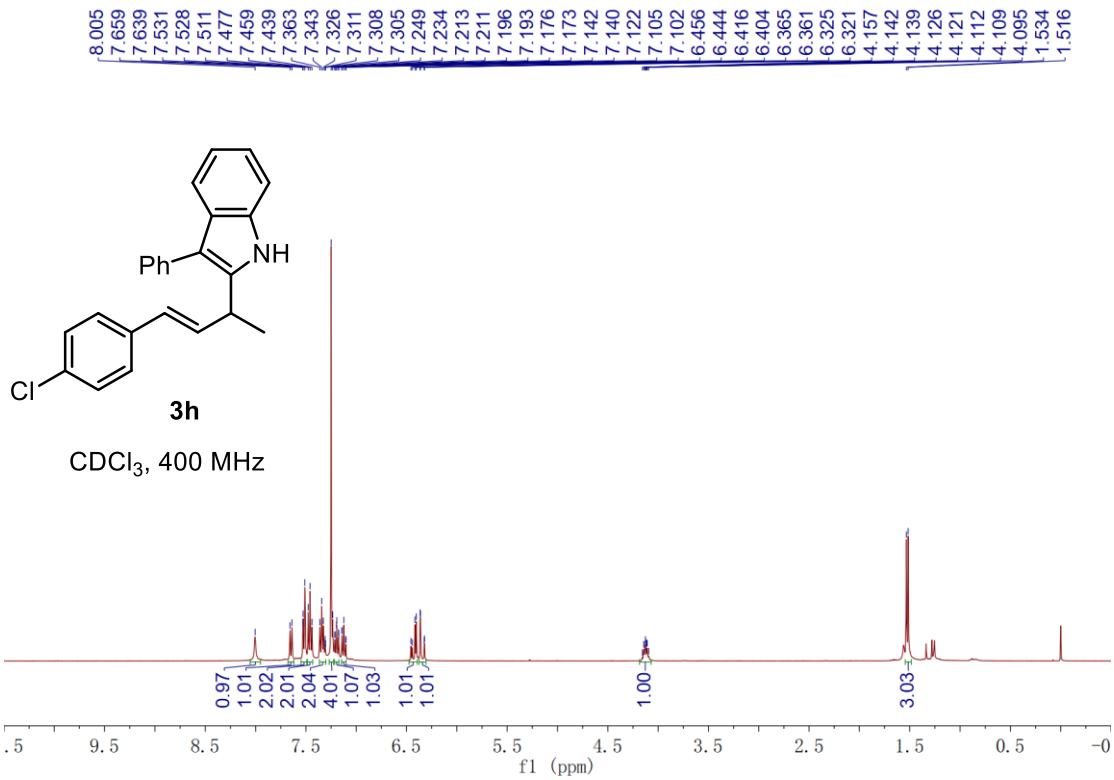
$CDCl_3$, 400 MHz





3g

$CDCl_3$, 101 MHz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4.139
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4.109
4.095
1.534
1.516
Ph
NH
Cl
3h
CDCl3, 400 MHz
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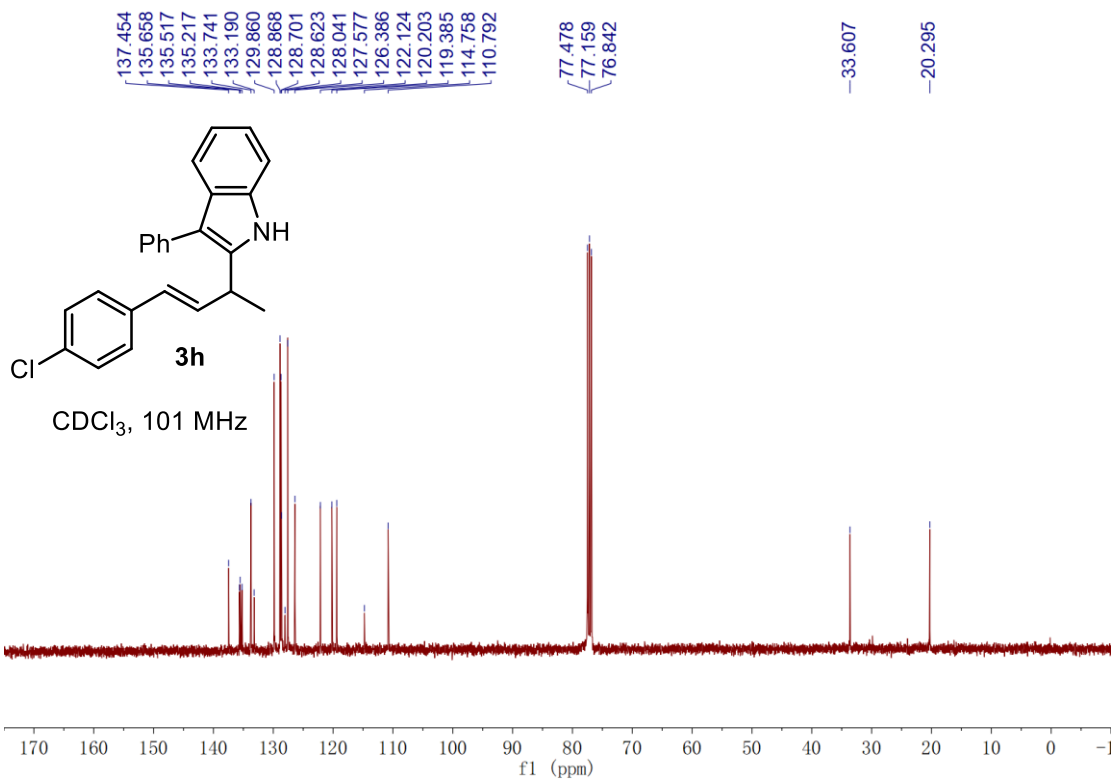
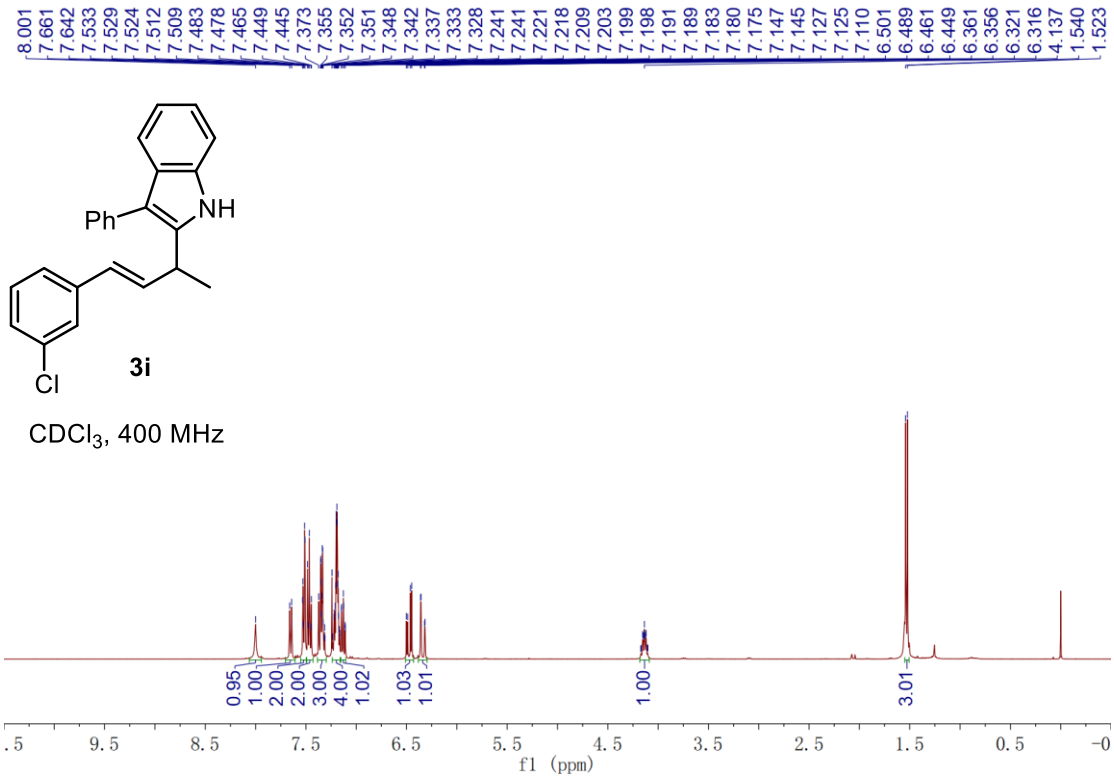
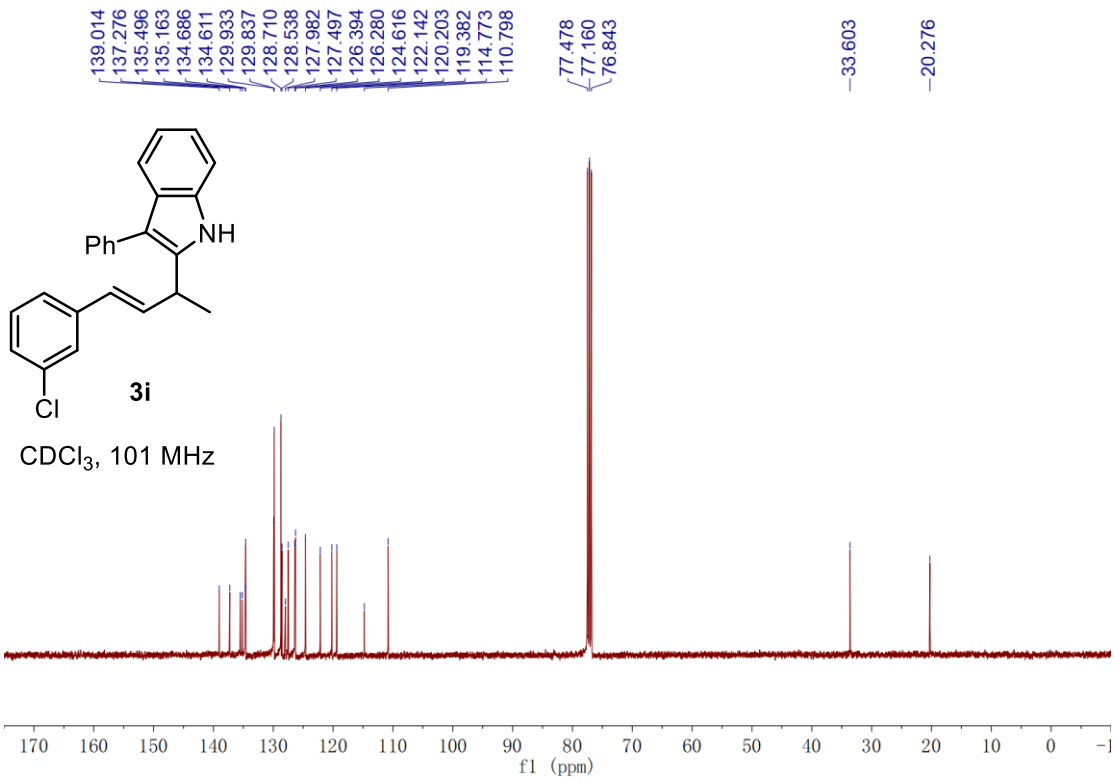
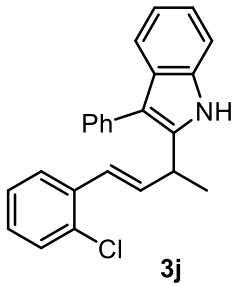
1.01
1.00
3.03
f1 (ppm)


137.454
135.658
135.517
135.217
133.741
133.190
129.860
128.868
128.701
128.623
128.041
127.577
126.386
122.124
120.203
119.385
114.758
110.792
77.478
77.159
76.842
33.607
20.295
Ph
NH
Cl
3h
CDCl3, 101 MHz
f1 (ppm)

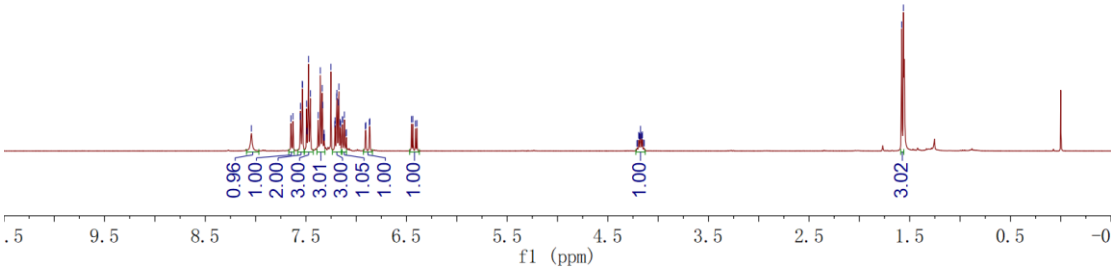

8.001
7.661
7.642
7.533
7.529
7.524
7.512
7.509
7.483
7.478
7.465
7.449
7.445
7.373
7.355
7.352
7.351
7.348
7.342
7.337
7.333
7.328
7.241
7.241
7.221
7.218
7.209
7.203
7.199
7.198
7.191
7.189
7.183
7.180
7.175
7.147
7.145
7.127
7.125
7.110
6.501
6.489
6.461
6.449
6.361
6.356
6.321
6.316
4.137
1.540
1.523
Ph
NH
Cl
3i
CDCl3, 400 MHz
0.95
1.00
2.00
2.00
3.00
4.00
1.02
1.03
1.01
1.00
3.01
f1 (ppm)

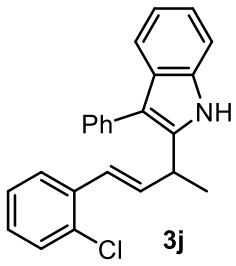

139.014
137.276
135.496
135.163
134.686
134.611
129.933
129.837
128.710
128.538
127.982
127.497
126.394
126.280
124.616
122.142
120.203
119.382
114.773
110.798
77.478
77.160
76.843
33.603
20.276
Ph
NH
Cl
3i
CDCl3, 101 MHz
f1 (ppm)



3j

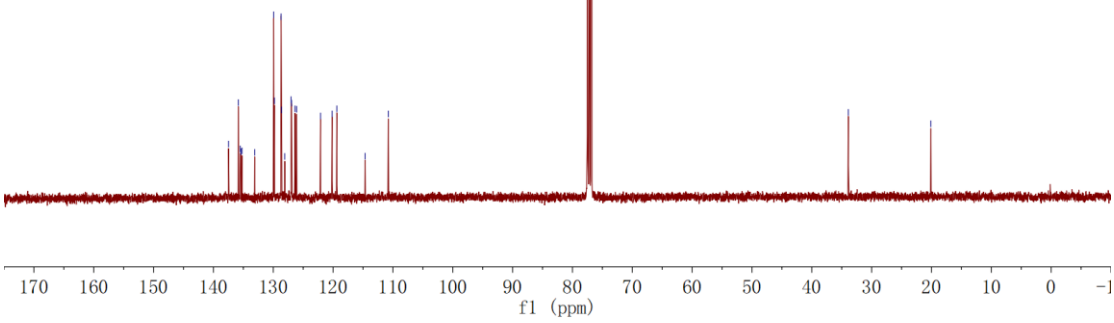
$CDCl_3$, 400 MHz

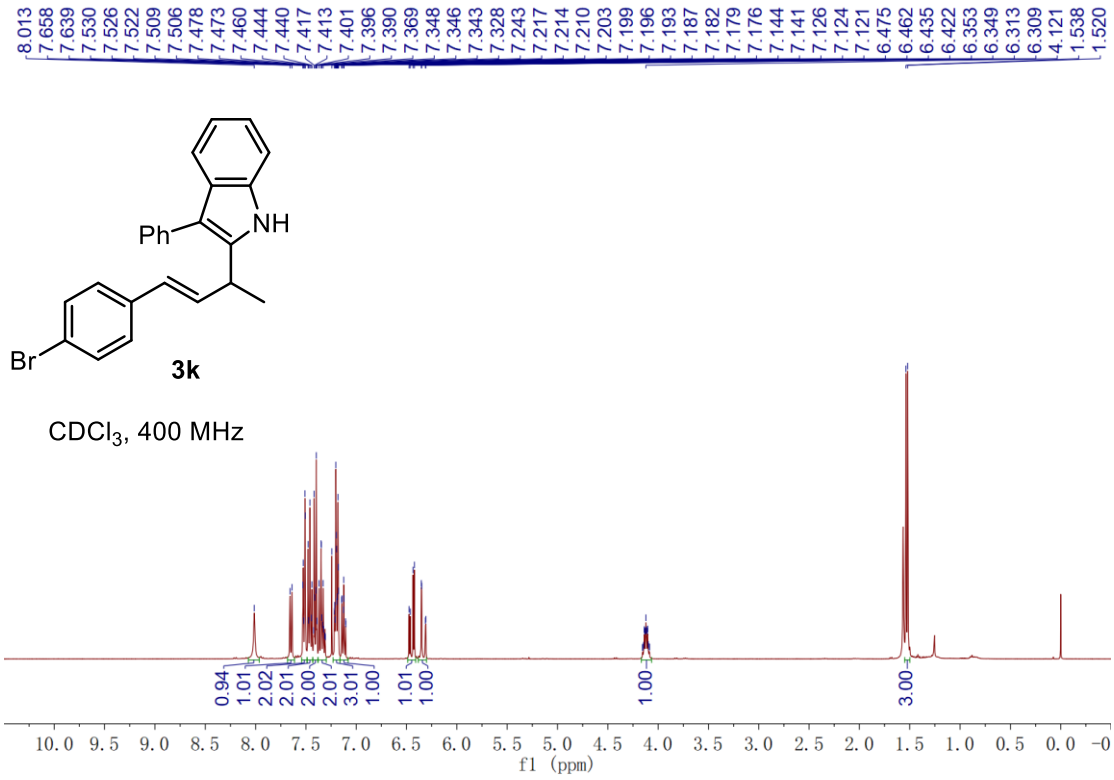


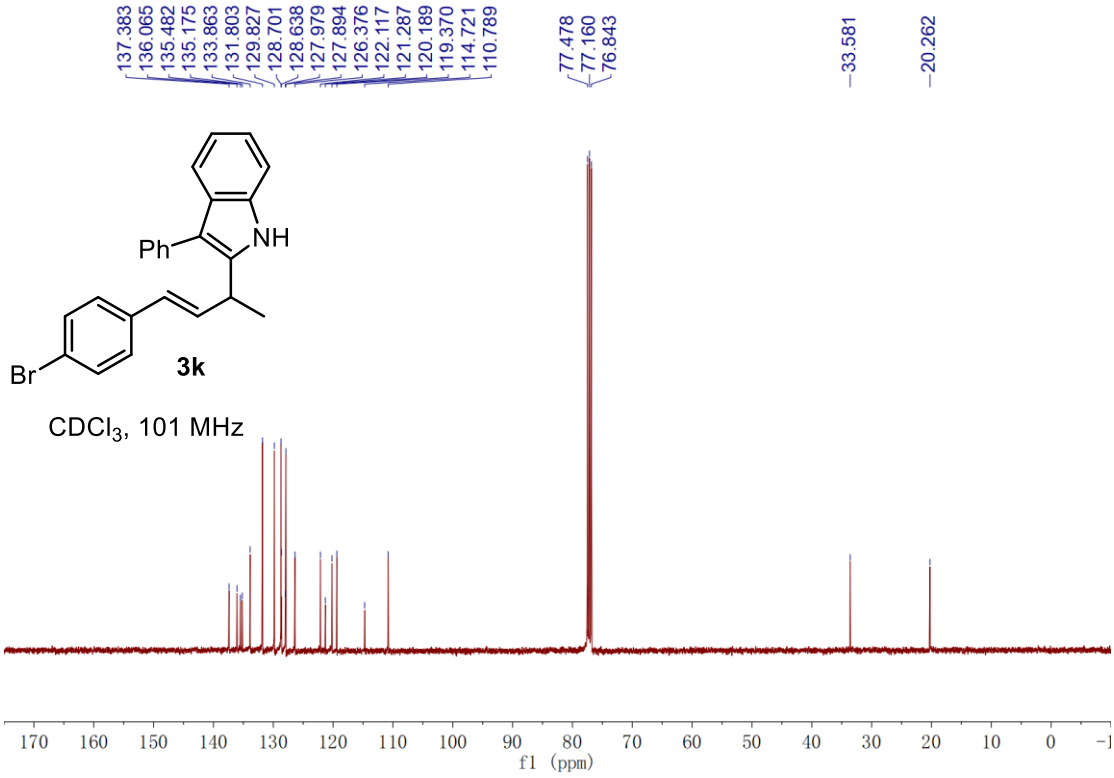


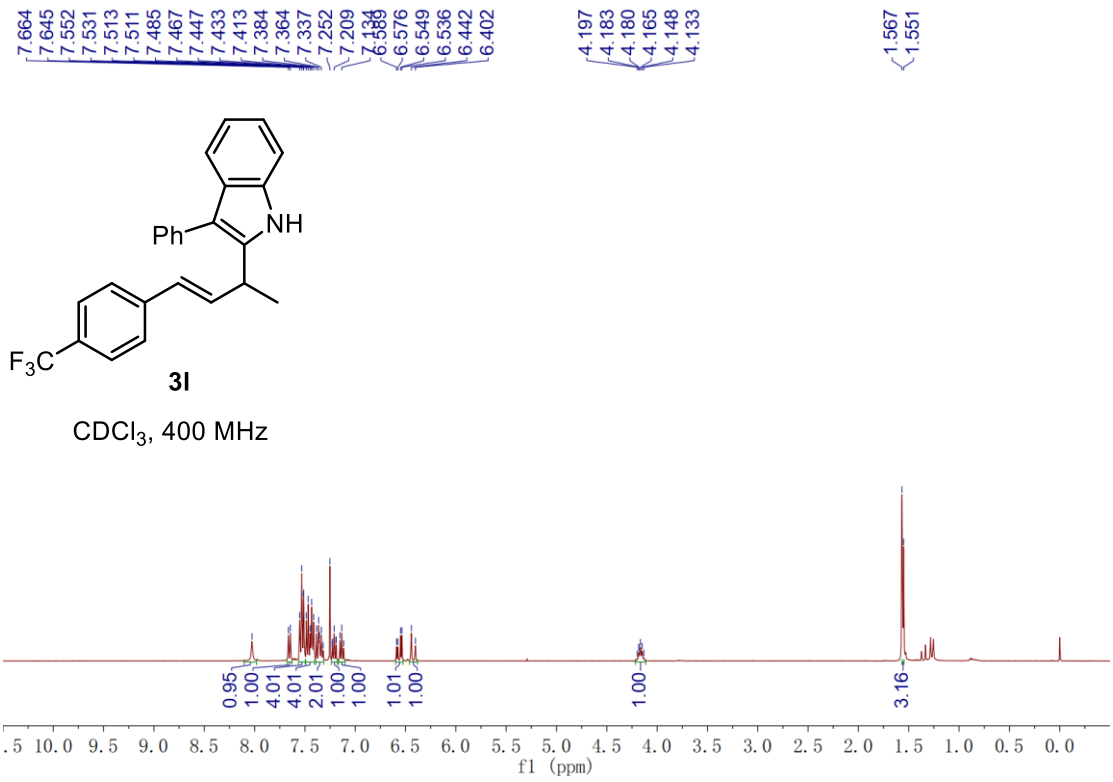
3j

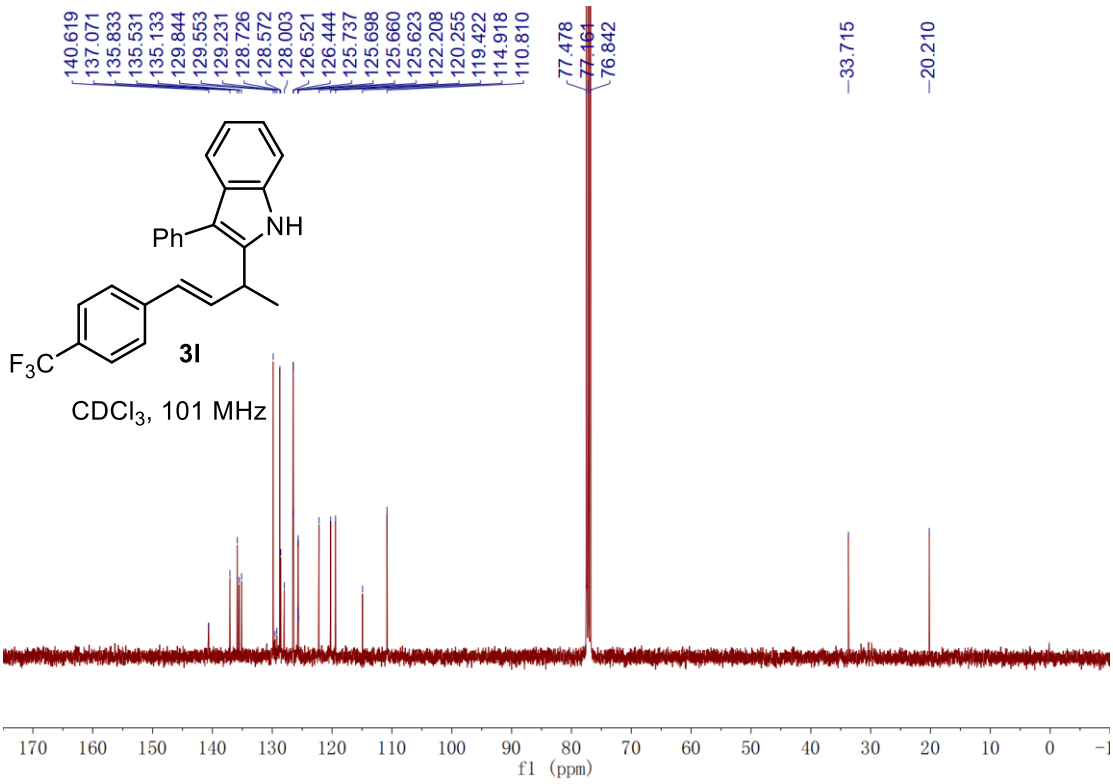
$CDCl_3$, 101 MHz

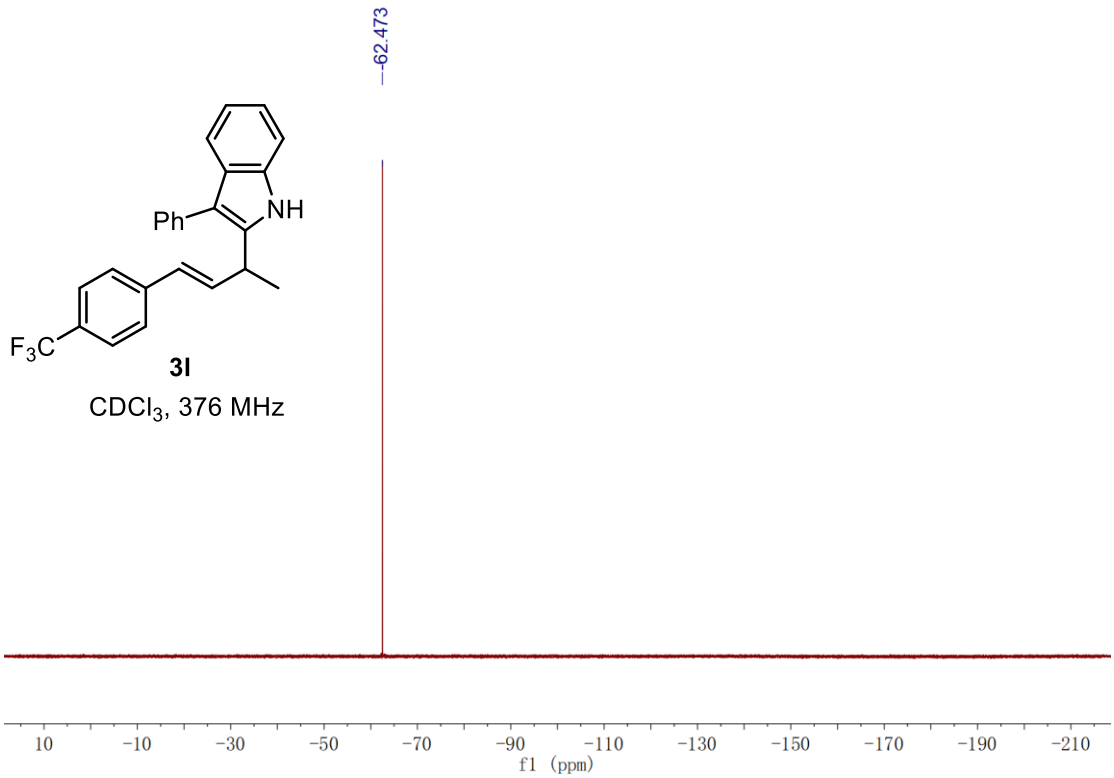



8.013
7.658
7.639
7.530
7.526
7.522
7.509
7.506
7.478
7.473
7.460
7.444
7.440
7.417
7.413
7.401
7.396
7.390
7.369
7.348
7.346
7.343
7.328
7.243
7.217
7.214
7.210
7.203
7.199
7.196
7.193
7.187
7.182
7.179
7.176
7.144
7.141
7.126
7.124
7.121
6.475
6.462
6.435
6.422
6.353
6.349
6.313
6.309
4.121
1.538
1.520
Ph
NH
Br
3k
CDCl3, 400 MHz
0.94
1.01
2.02
2.01
2.00
2.01
3.01
1.00
1.01
1.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


137.383
136.065
135.482
135.175
133.863
131.803
129.827
128.701
128.638
127.979
127.894
126.376
122.117
121.287
120.189
119.370
114.721
110.789
77.478
77.160
76.843
33.581
20.262
Ph
NH
Br
3k
CDCl3, 101 MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

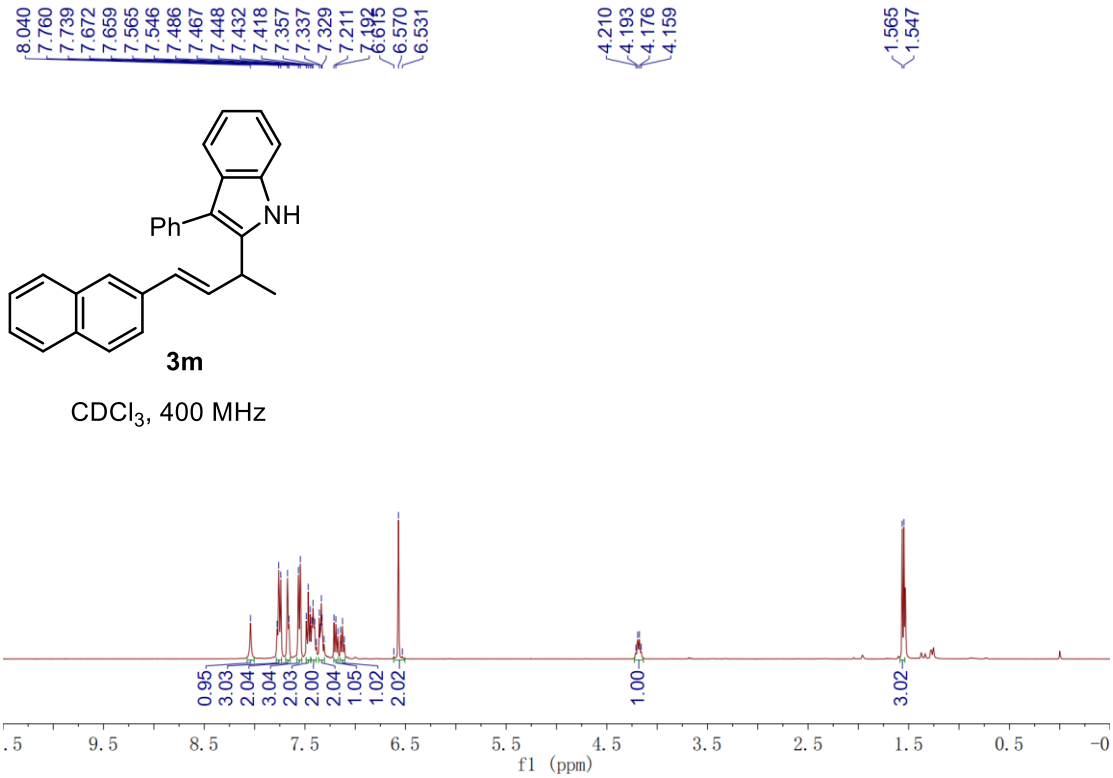

7.664
7.645
7.552
7.531
7.513
7.511
7.485
7.467
7.447
7.433
7.413
7.384
7.364
7.337
7.252
7.209
6.576
6.549
6.536
6.442
6.402
4.197
4.183
4.180
4.165
4.148
4.133
1.567
1.551
Ph
NH
F3C
3l
CDCl3, 400 MHz
0.95
1.00
4.01
4.01
2.01
1.00
1.00
1.01
1.00
1.00
3.16
f1 (ppm)

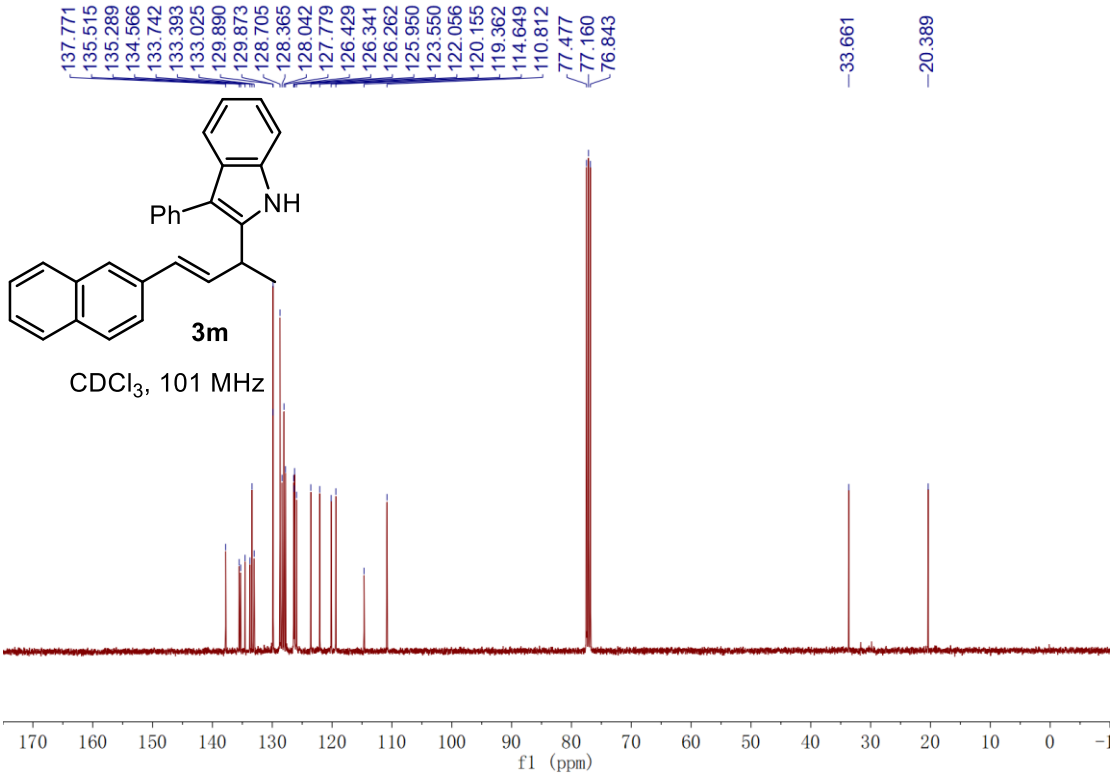

140.619
137.071
135.833
135.531
135.133
129.844
129.553
129.231
128.726
128.572
128.003
126.521
126.444
125.737
125.698
125.660
125.623
122.208
120.255
119.422
114.918
110.810
77.478
77.161
76.842
33.715
20.210
Ph
NH
F3C
3l
CDCl3, 101 MHz
f1 (ppm)

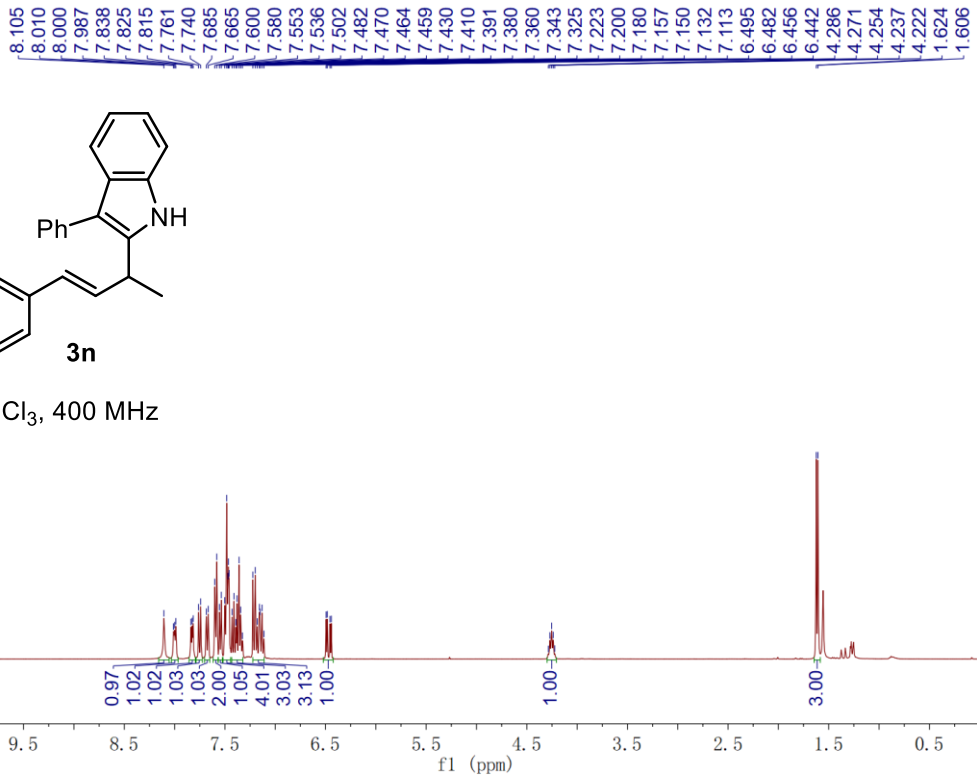


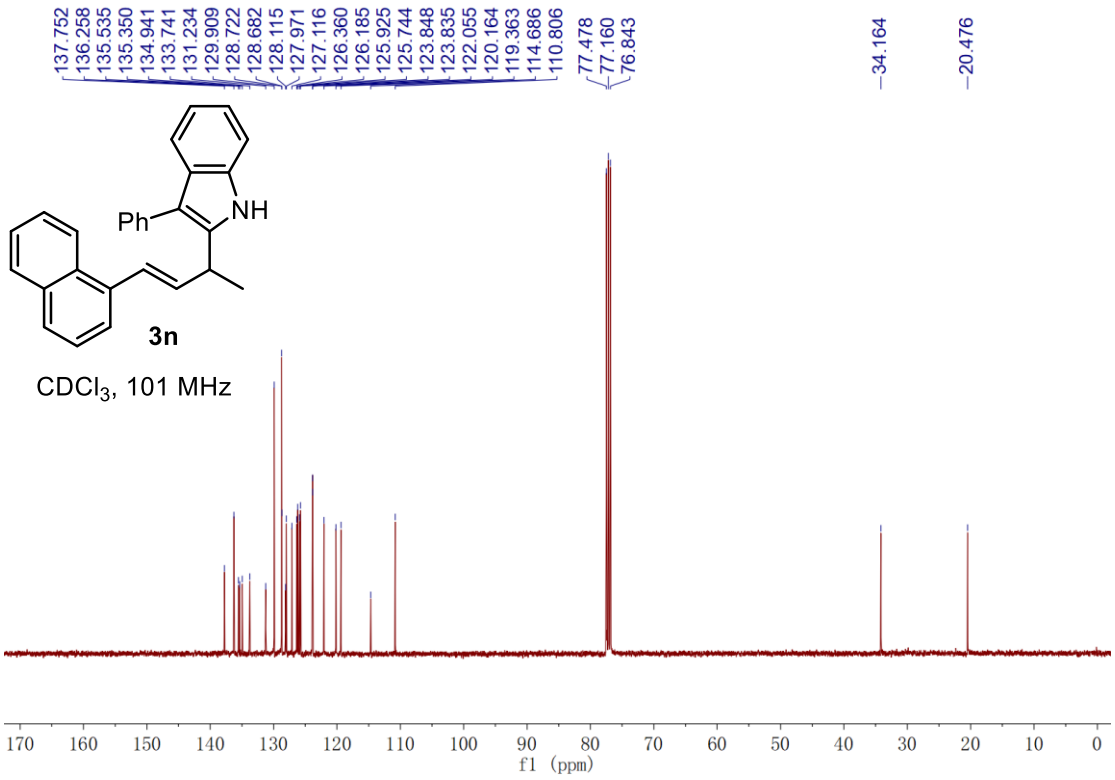
3l

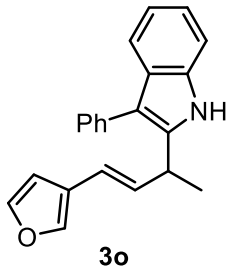
$CDCl_3$, 376 MHz


8.040
7.760
7.739
7.672
7.659
7.565
7.546
7.486
7.467
7.448
7.432
7.418
7.357
7.337
7.329
7.211
6.615
6.570
6.531
4.210
4.193
4.176
4.159
1.565
1.547
Ph
NH
3m
CDCl3, 400 MHz
0.95
3.03
2.04
3.04
2.03
2.00
2.04
1.05
1.02
2.02
1.00
3.02
f1 (ppm)


137.771
135.515
135.289
134.566
133.742
133.393
133.025
129.890
129.873
128.705
128.365
128.042
127.779
126.429
126.341
126.262
125.950
123.550
122.056
120.155
119.362
114.649
110.812
77.477
77.160
76.843
33.661
20.389
Ph
NH
3m
CDCl3, 101 MHz
f1 (ppm)

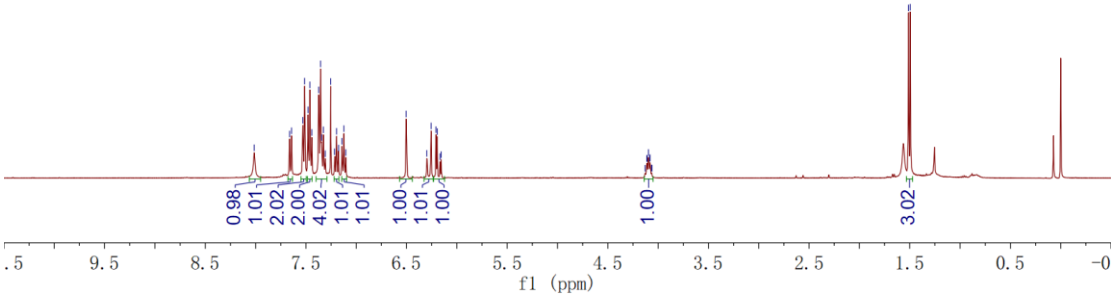

8.105
8.010
8.000
7.987
7.838
7.825
7.815
7.761
7.740
7.685
7.665
7.600
7.580
7.553
7.536
7.502
7.482
7.470
7.464
7.459
7.430
7.410
7.391
7.380
7.360
7.343
7.325
7.223
7.200
7.180
7.157
7.150
7.132
7.113
6.495
6.482
6.456
6.442
4.286
4.271
4.254
4.237
4.222
1.624
1.606
Ph
NH
3n
CDCl3, 400 MHz
0.97
1.02
1.02
1.03
1.03
2.00
1.05
4.01
3.03
3.13
1.00
1.00
3.00
f1 (ppm)

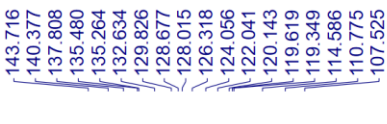

137.752
136.258
135.535
135.350
134.941
133.741
131.234
129.909
128.722
128.682
128.115
127.971
127.116
126.360
126.185
125.925
125.744
123.848
123.835
122.055
120.164
119.363
114.686
110.806
77.478
77.160
76.843
34.164
20.476
Ph
NH
3n
CDCl3, 101 MHz
f1 (ppm)

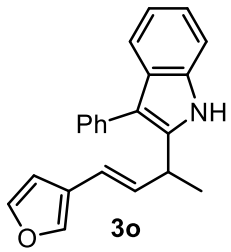


3o

$CDCl_3$, 400 MHz

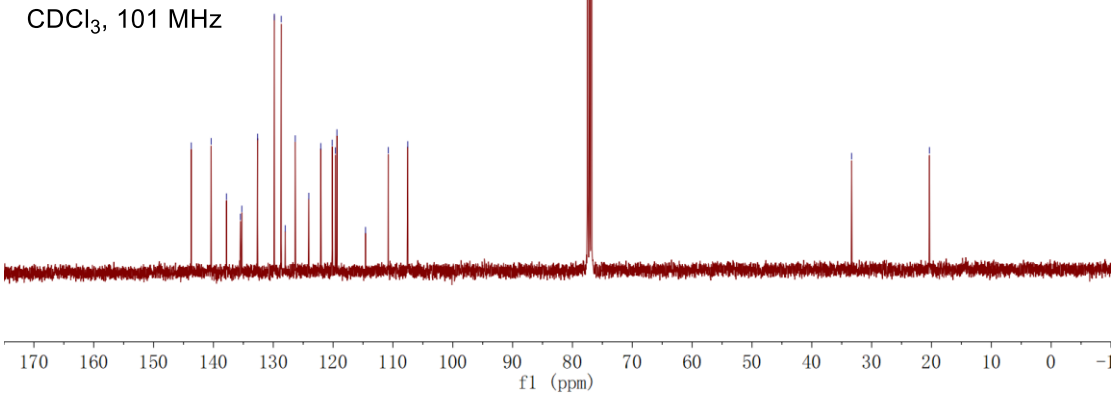


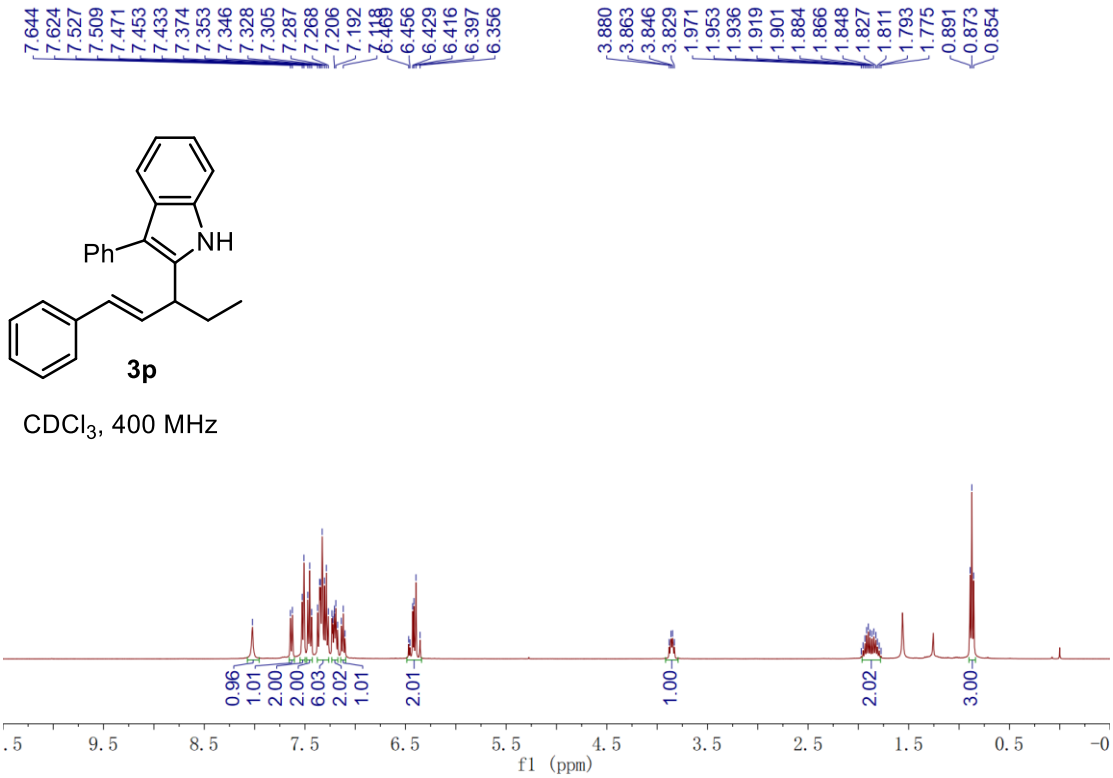


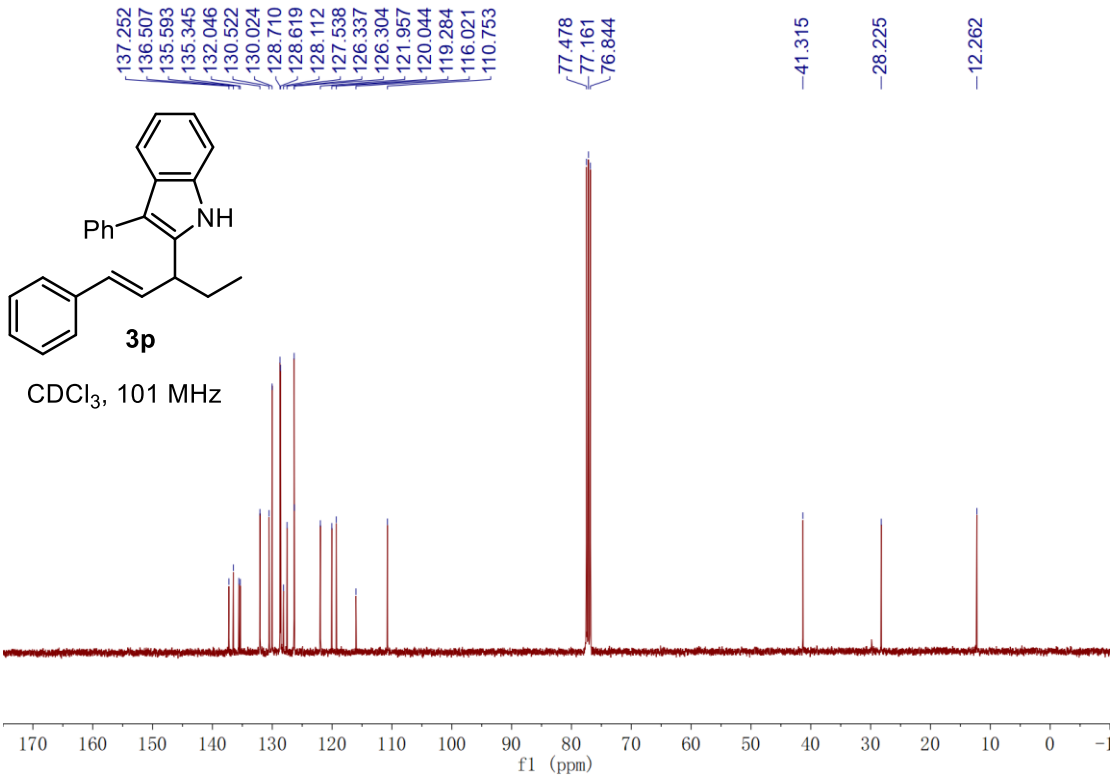


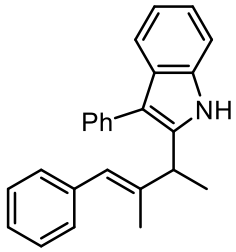
3o

$CDCl_3$, 101 MHz



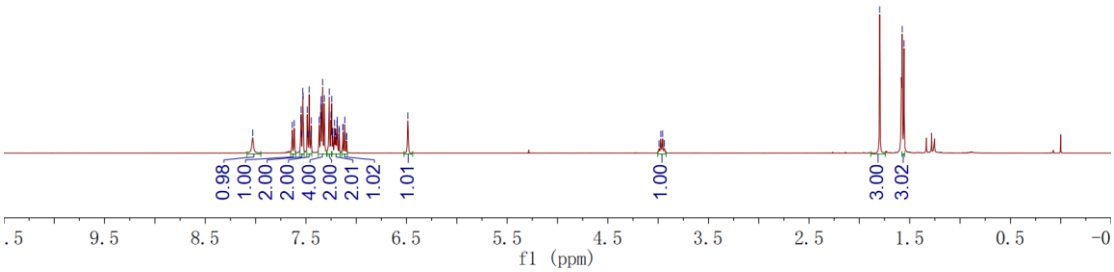

7.644
7.624
7.527
7.509
7.471
7.453
7.433
7.374
7.353
7.346
7.328
7.305
7.287
7.268
7.206
7.192
6.456
6.429
6.416
6.397
6.356
3.880
3.863
3.846
3.829
1.971
1.953
1.936
1.919
1.901
1.884
1.866
1.848
1.827
1.811
1.793
1.775
0.891
0.873
0.854
Ph
NH
3p
CDCl3, 400 MHz
0.96
1.01
2.00
2.00
6.03
2.02
1.01
2.01
1.00
2.02
3.00
f1 (ppm)

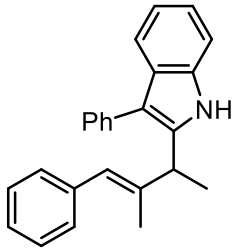

137.252
136.507
135.593
135.345
132.046
130.522
130.024
128.710
128.619
128.112
127.538
126.337
126.304
121.957
120.044
119.284
116.021
110.753
77.478
77.161
76.844
41.315
28.225
12.262
Ph
NH
3p
CDCl3, 101 MHz
f1 (ppm)



3q

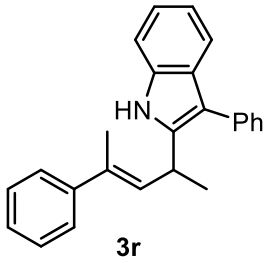
$CDCl_3$, 400 MHz





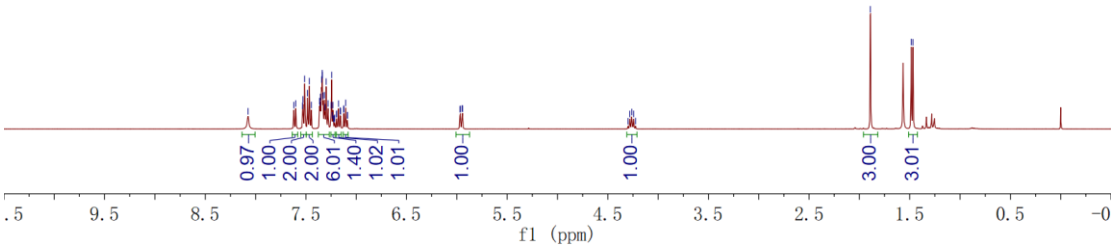
3q

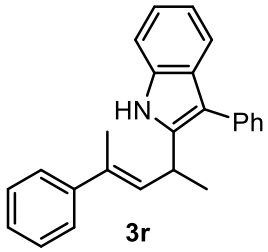
$CDCl_3$, 101 MHz



3r

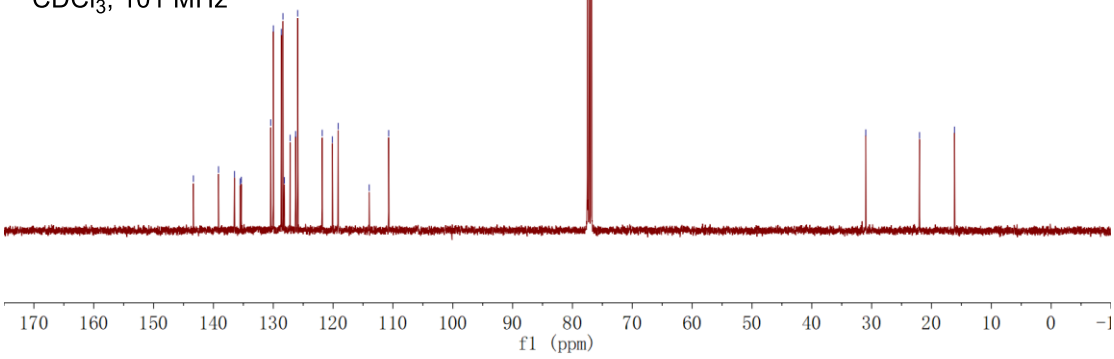
$CDCl_3$, 400 MHz

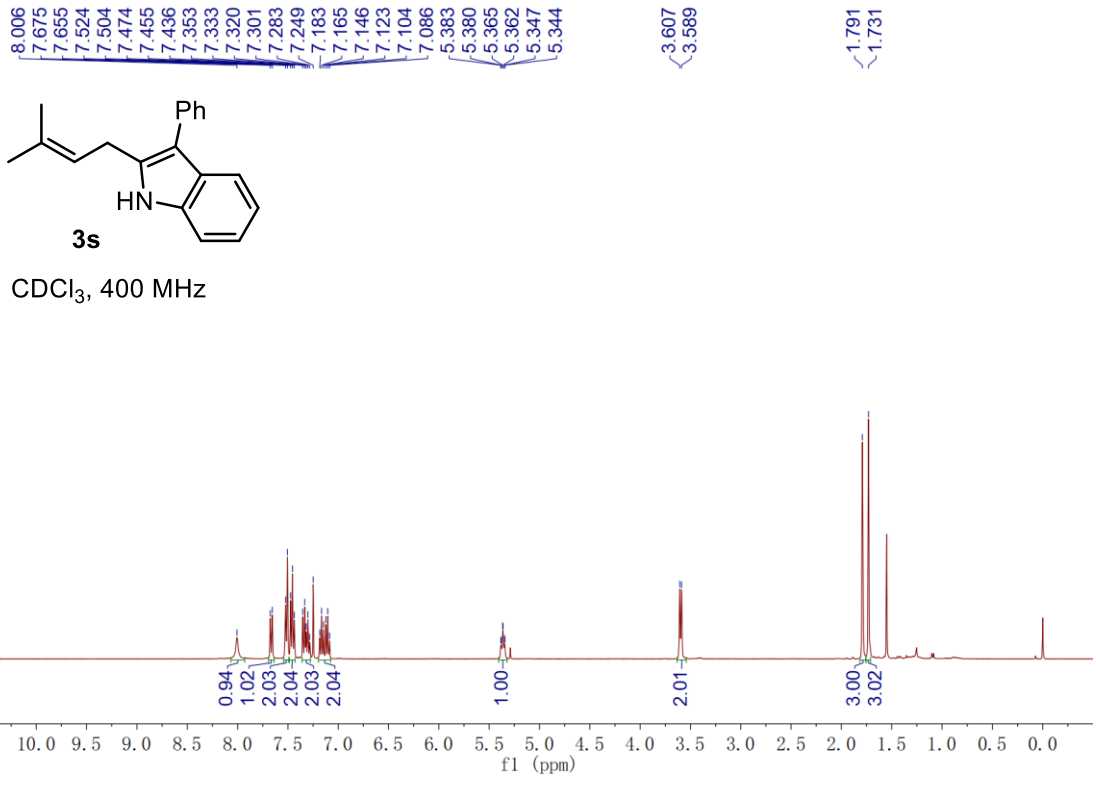




3r

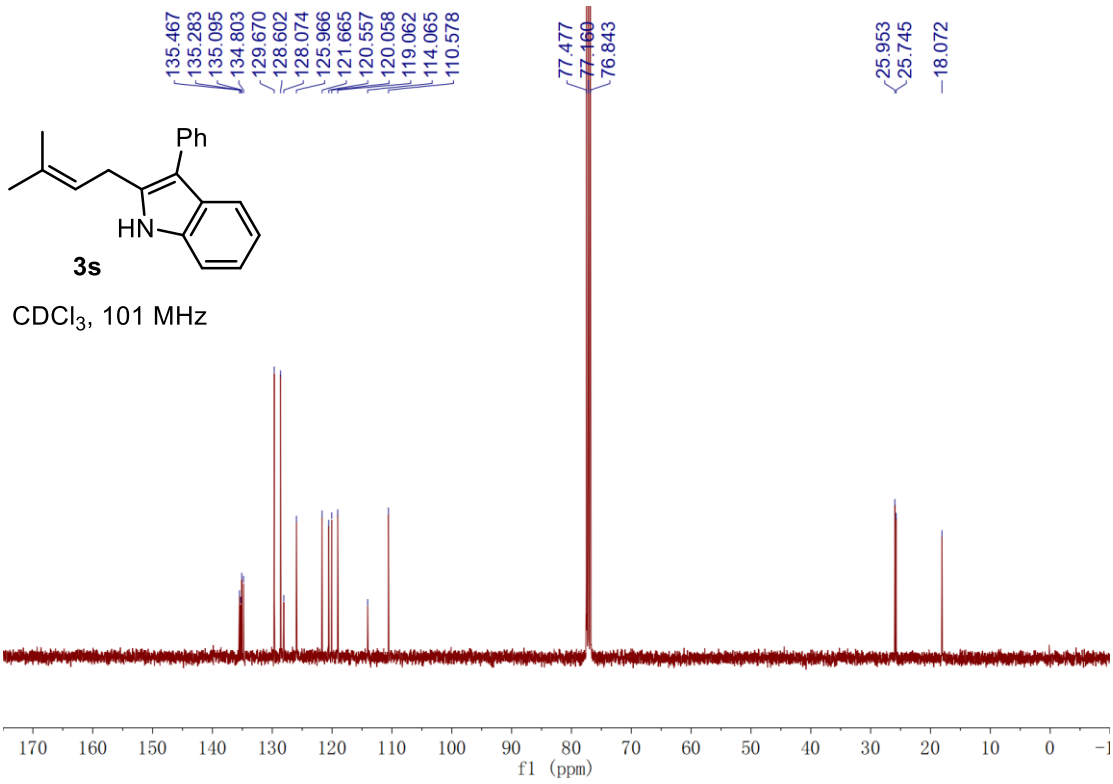
$CDCl_3$, 101 MHz





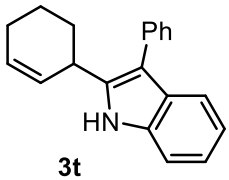
3s

$CDCl_3$, 400 MHz



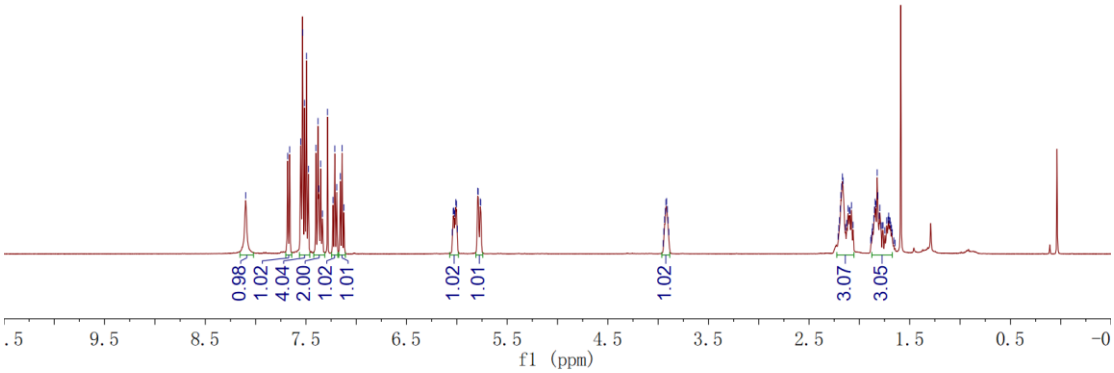
3s

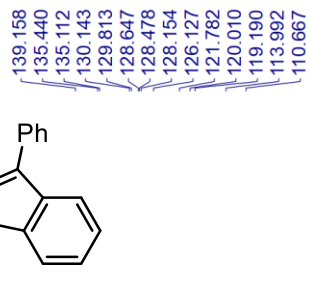
$CDCl_3$, 101 MHz

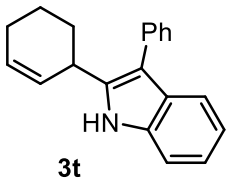


3t

$CDCl_3$, 400 MHz

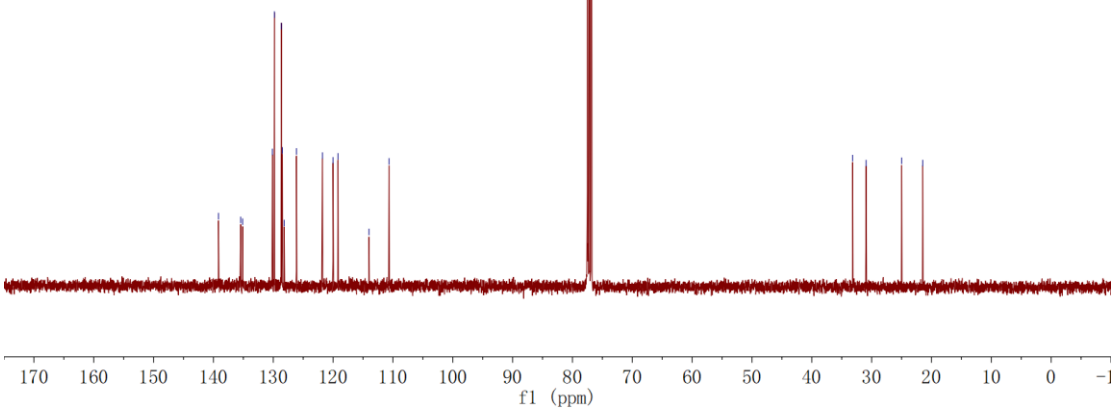


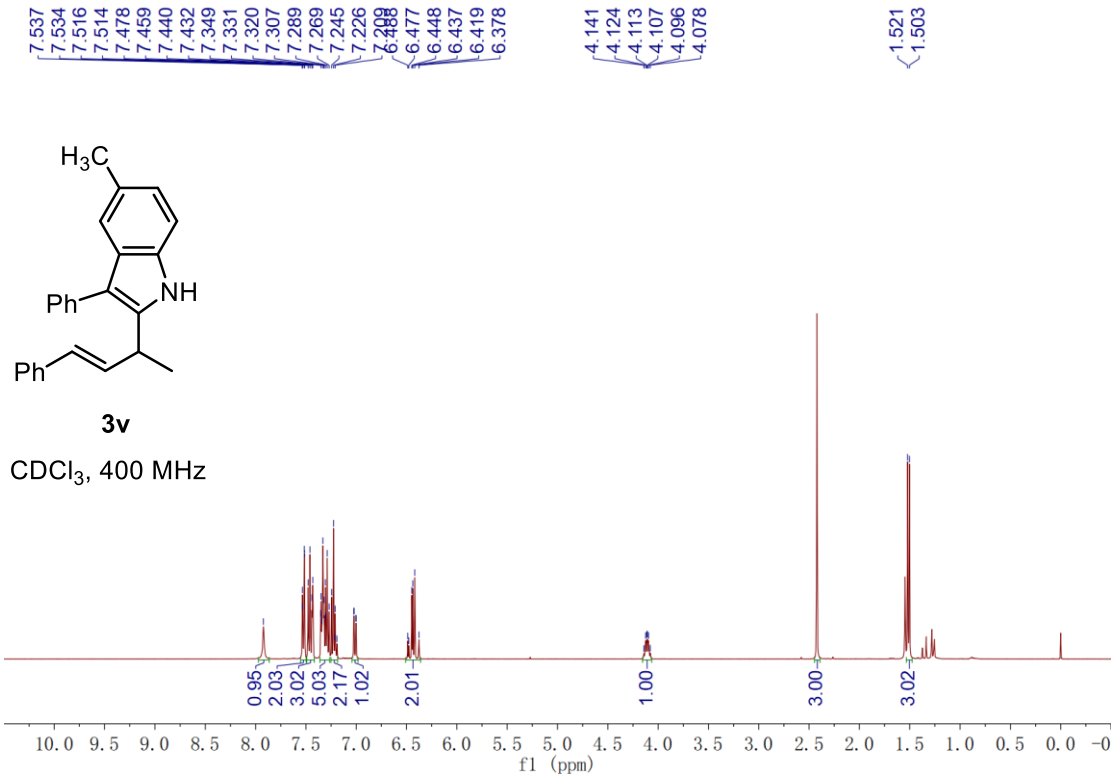




3t

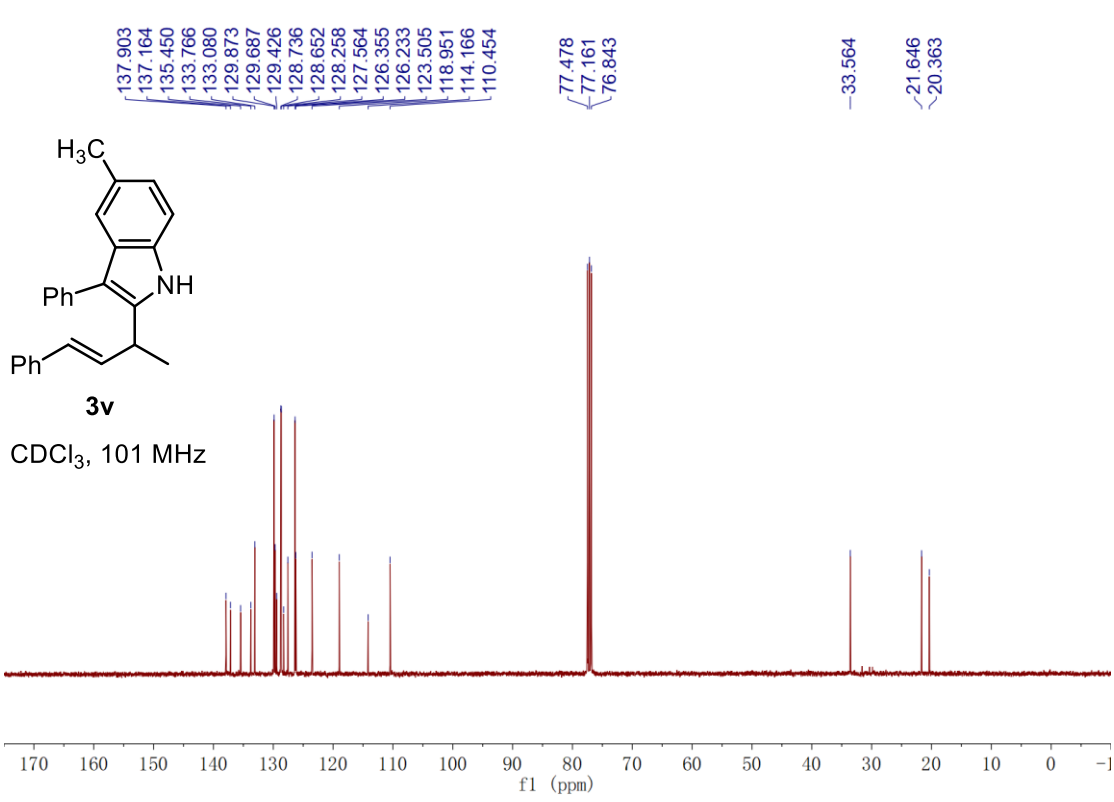
$CDCl_3$, 101 MHz





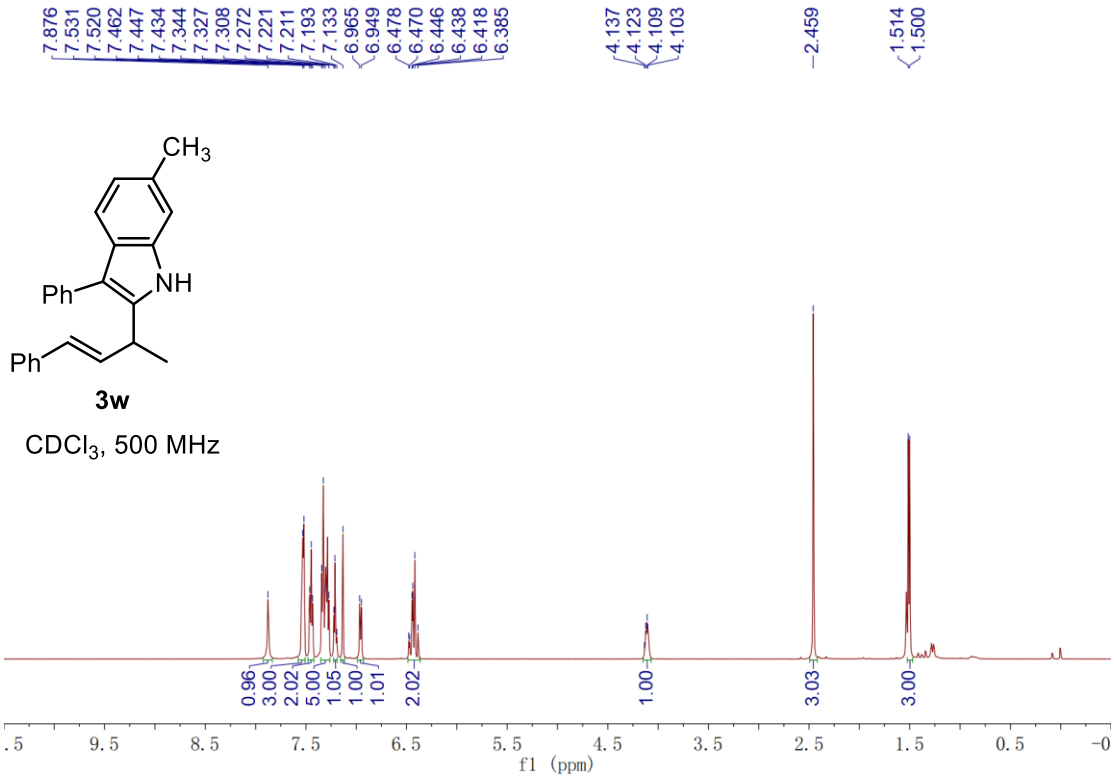
3v

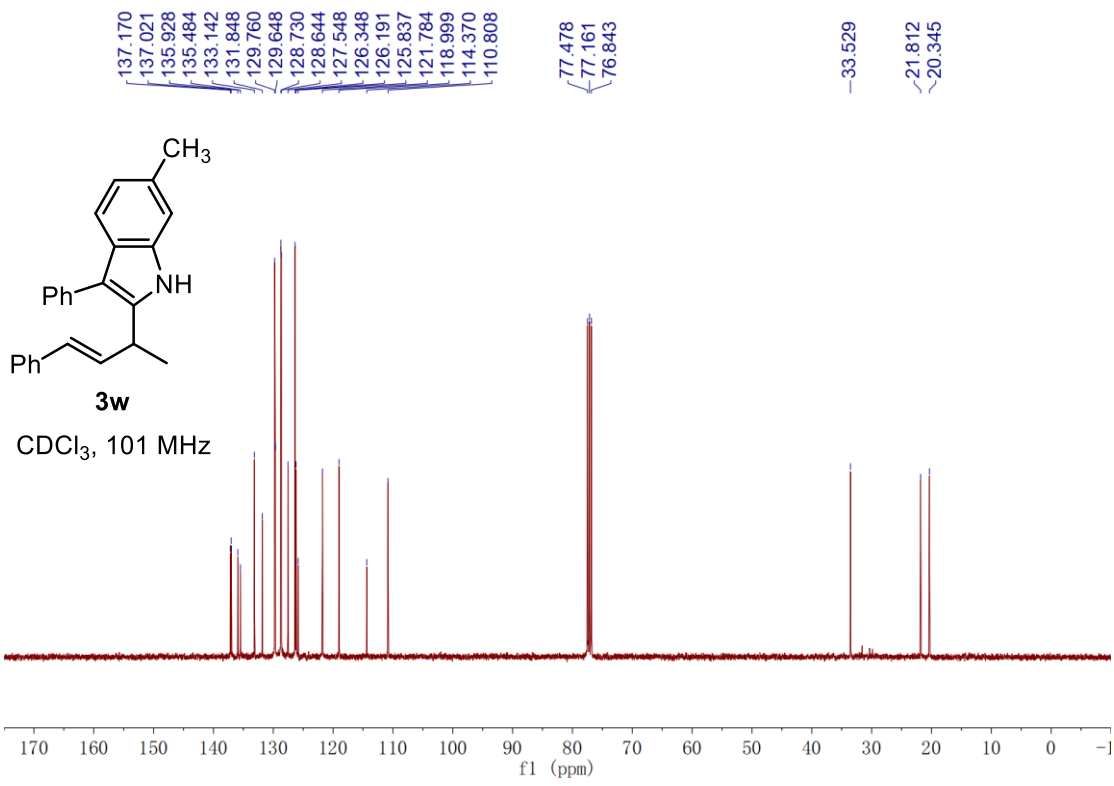
$CDCl_3$, 400 MHz

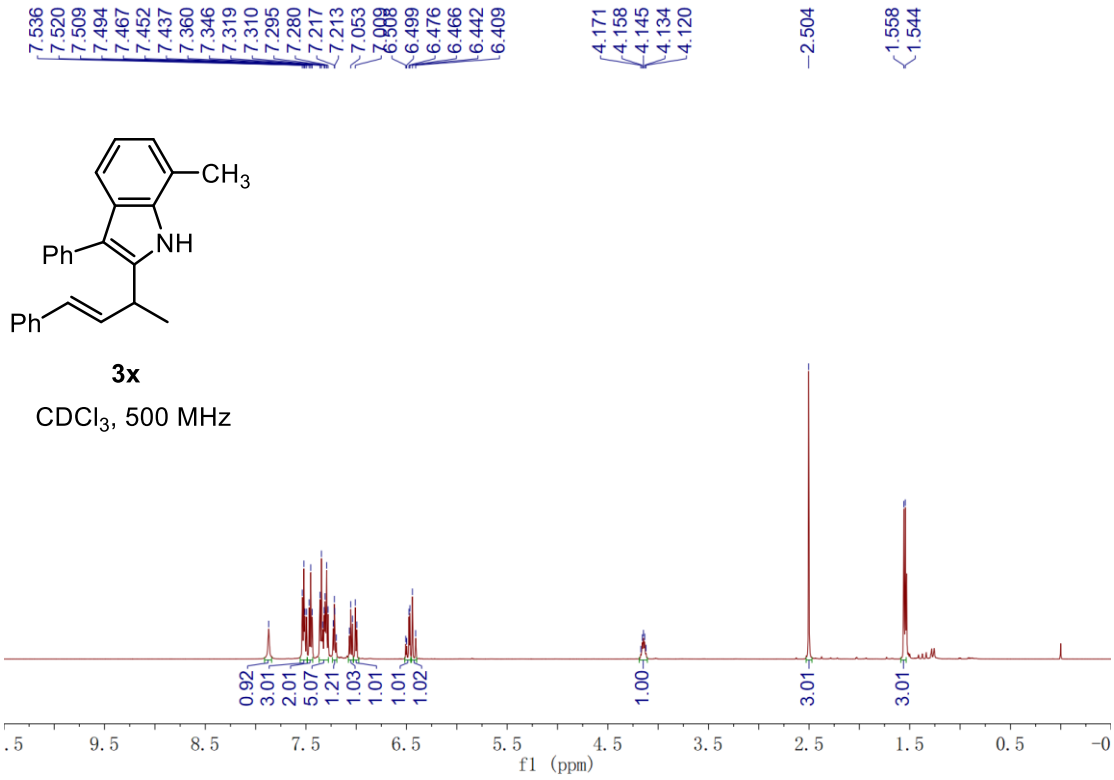


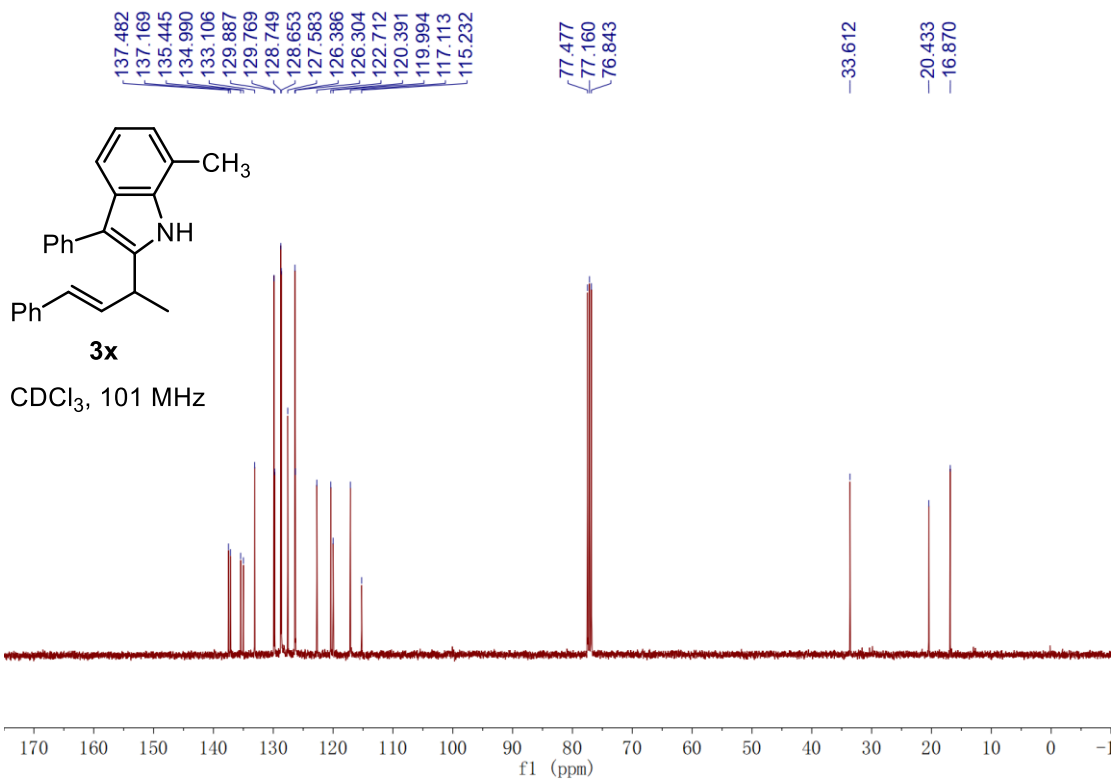
3v

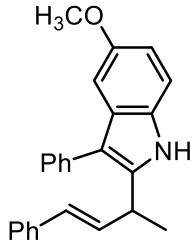
$CDCl_3$, 101 MHz


7.876
7.531
7.520
7.462
7.447
7.434
7.344
7.327
7.308
7.272
7.221
7.211
7.193
7.133
6.965
6.949
6.478
6.470
6.446
6.438
6.418
6.385
4.137
4.123
4.109
4.103
2.459
1.514
1.500
CH3
NH
Ph
Ph
3w
CDCl3, 500 MHz
0.96
3.00
2.02
5.00
1.05
1.00
1.01
2.02
1.00
3.03
3.00
f1 (ppm)


137.170
137.021
135.928
135.484
133.142
131.848
129.760
129.648
128.730
128.644
127.548
126.348
126.191
125.837
121.784
118.999
114.370
110.808
77.478
77.161
76.843
33.529
21.812
20.345
CH3
NH
Ph
Ph
3w
CDCl3, 101 MHz
f1 (ppm)

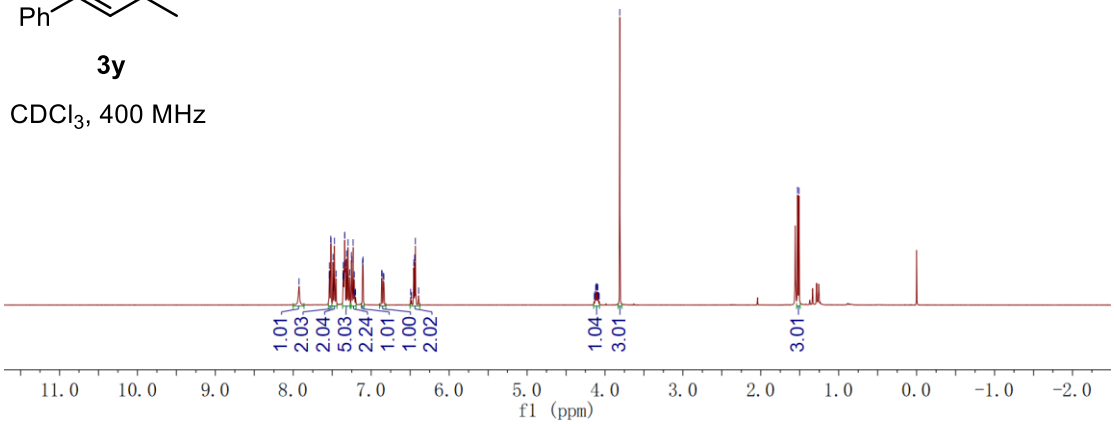

7.536
7.520
7.509
7.494
7.467
7.452
7.437
7.360
7.346
7.319
7.310
7.295
7.280
7.217
7.213
7.053
6.499
6.476
6.466
6.442
6.409
4.171
4.158
4.145
4.134
4.120
2.504
1.558
1.544
CH3
NH
Ph
Ph
3x
CDCl3, 500 MHz
0.92
3.01
2.01
5.07
1.21
1.03
1.01
1.01
1.02
1.00
3.01
3.01
f1 (ppm)

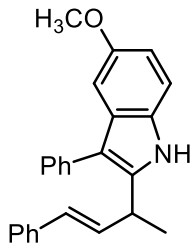

137.482
137.169
135.445
134.990
133.106
129.887
129.769
128.749
128.653
127.583
126.386
126.304
122.712
120.391
119.994
117.113
115.232
77.477
77.160
76.843
33.612
20.433
16.870
CH3
NH
Ph
Ph
3x
CDCl3, 101 MHz
f1 (ppm)



3y

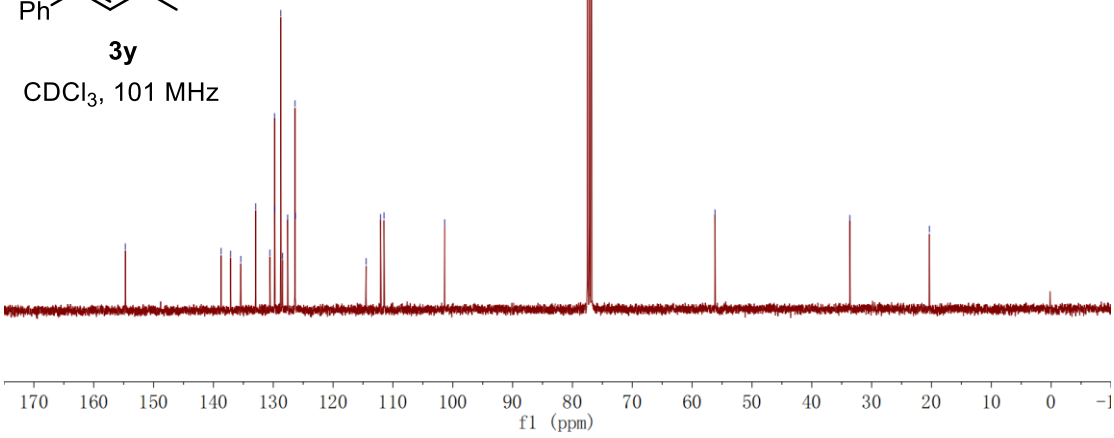
$CDCl_3$, 400 MHz

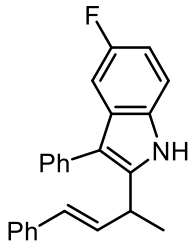




3y

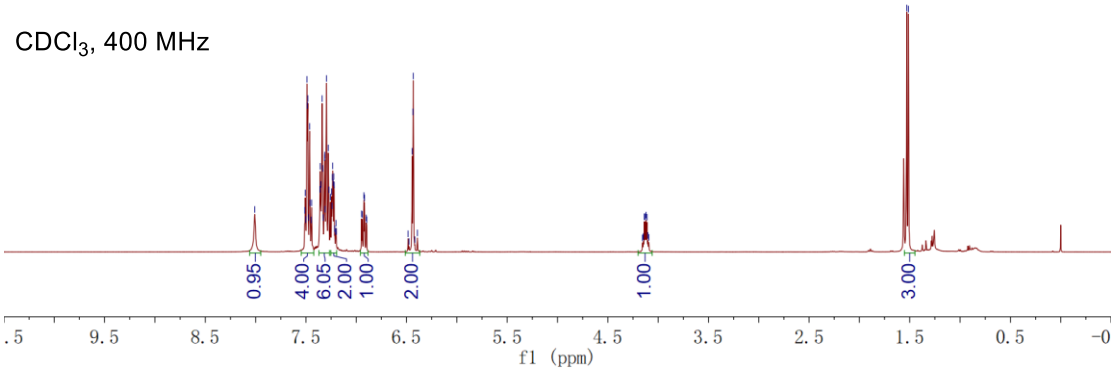
$CDCl_3$, 101 MHz

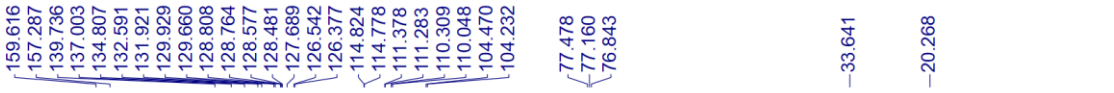


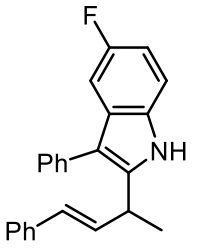


3z

$CDCl_3$, 400 MHz

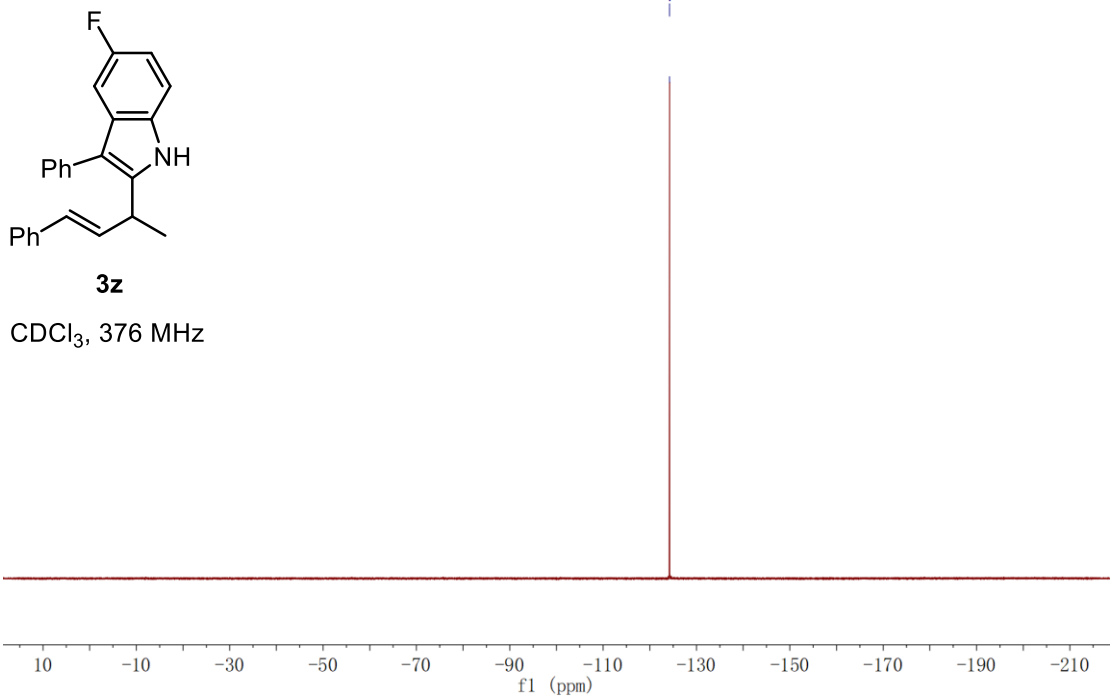






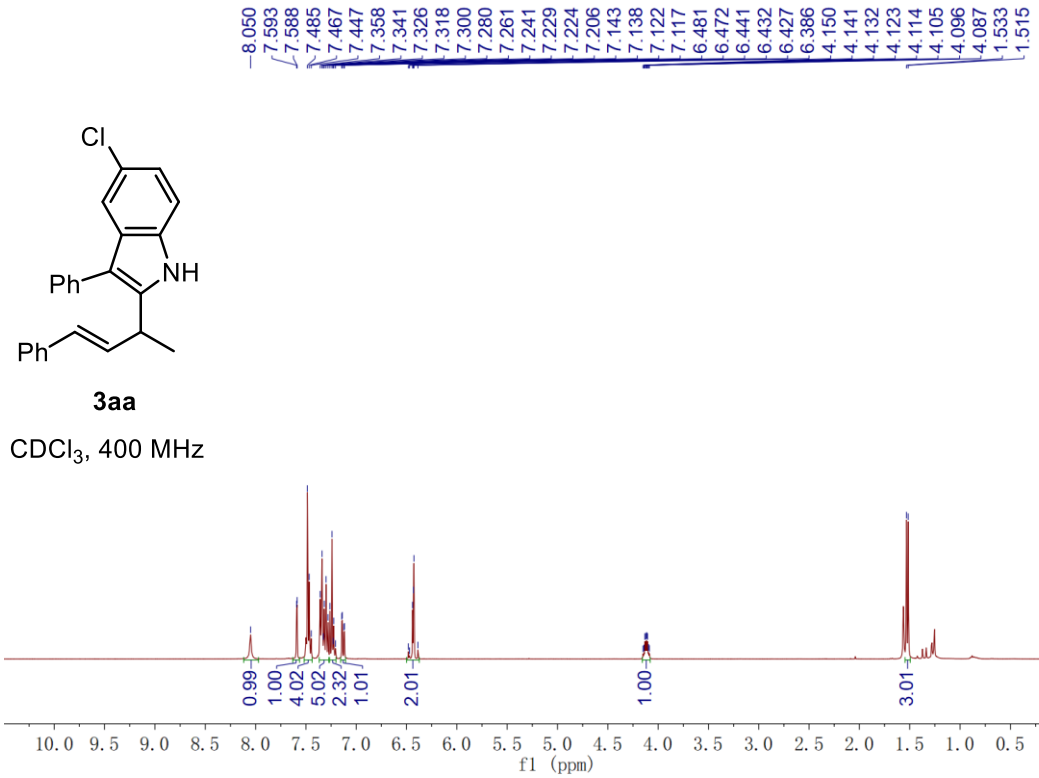
3z

$CDCl_3$, 101 MHz



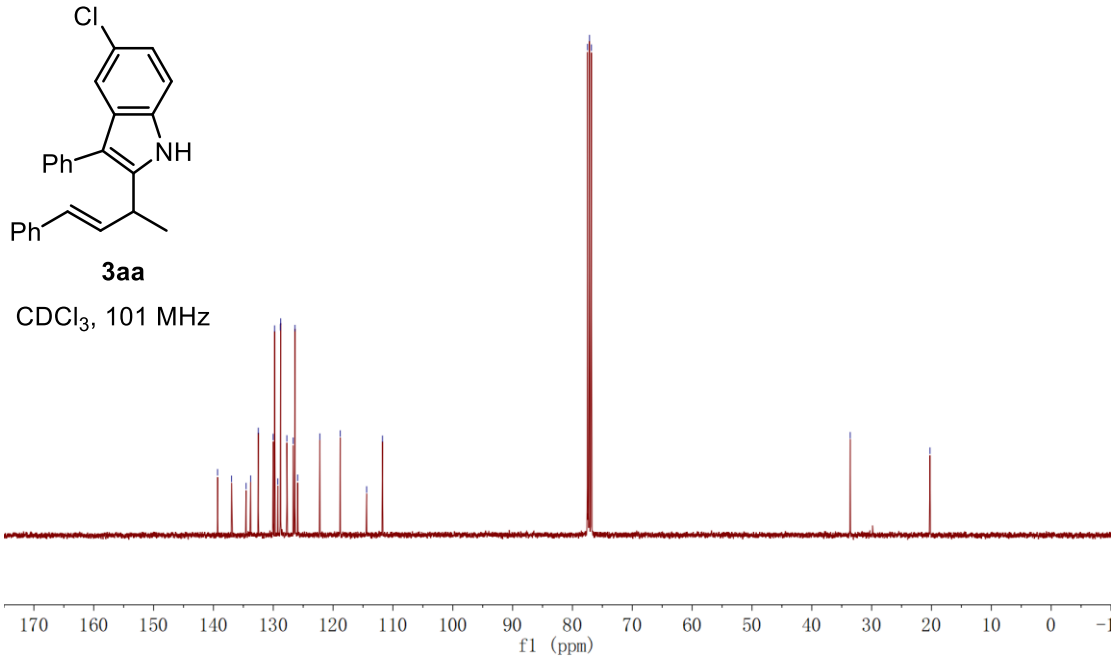
3z

$CDCl_3$, 376 MHz



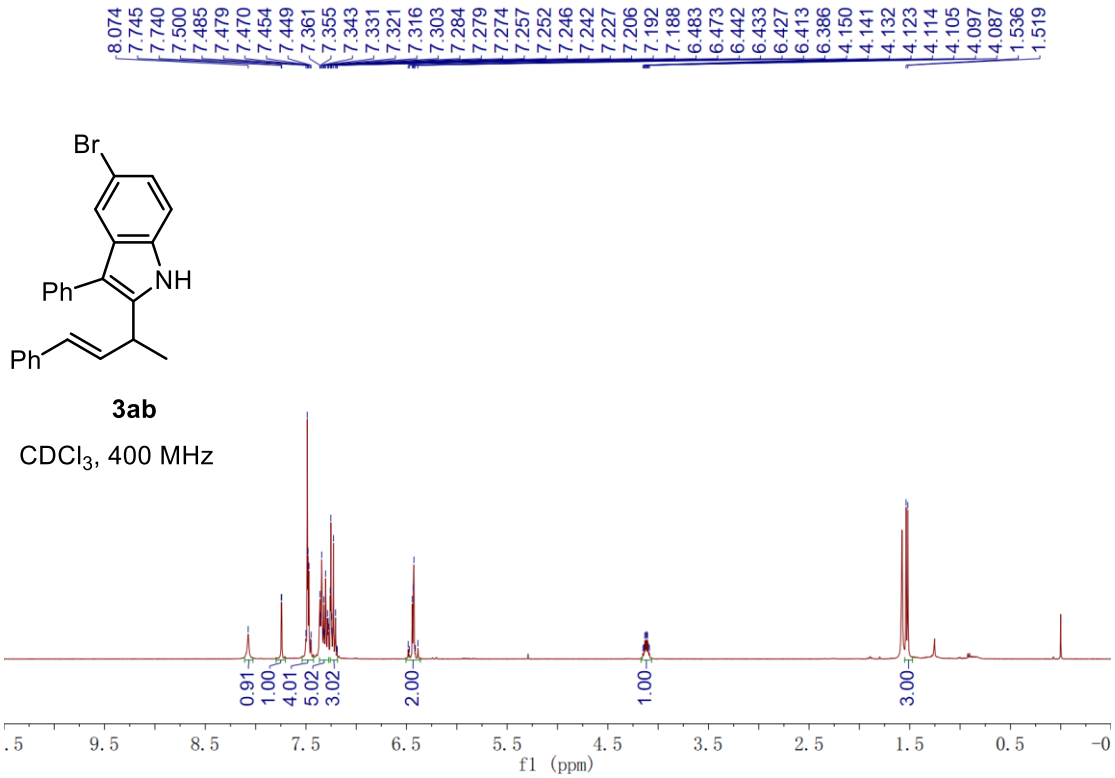
3aa

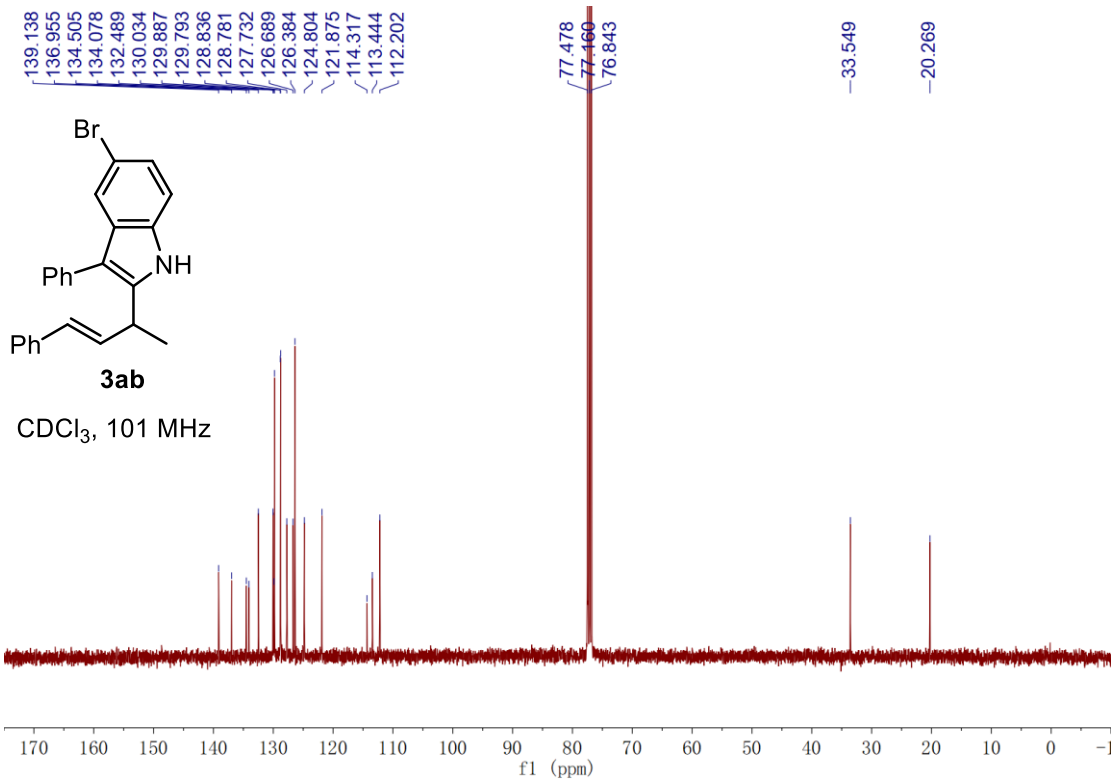
$CDCl_3$, 400 MHz

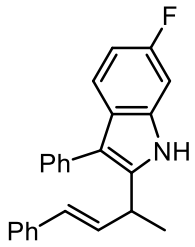


3aa

$CDCl_3$, 101 MHz

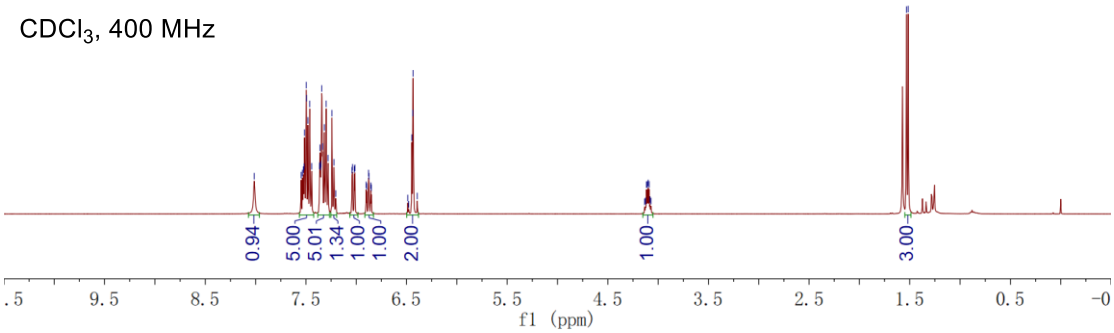

8.074
7.745
7.740
7.500
7.485
7.479
7.470
7.454
7.449
7.361
7.355
7.343
7.331
7.321
7.316
7.303
7.284
7.279
7.274
7.257
7.252
7.246
7.242
7.227
7.206
7.192
7.188
6.483
6.473
6.442
6.433
6.427
6.413
6.386
4.150
4.141
4.132
4.123
4.114
4.105
4.097
4.087
1.536
1.519
Br
NH
Ph
Ph
3ab
CDCl3, 400 MHz
0.91
1.00
4.01
5.02
3.02
2.00
1.00
3.00
f1 (ppm)

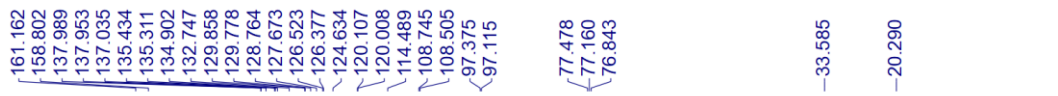

139.138
136.955
134.505
134.078
132.489
130.034
129.887
129.793
128.836
128.781
127.732
126.689
126.384
124.804
121.875
114.317
113.444
112.202
77.478
77.160
76.843
33.549
20.269
Br
NH
Ph
Ph
3ab
CDCl3, 101 MHz
f1 (ppm)

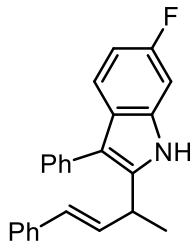


3ac

$CDCl_3$, 400 MHz

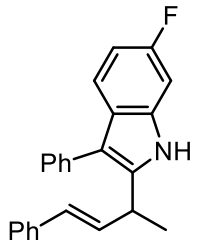






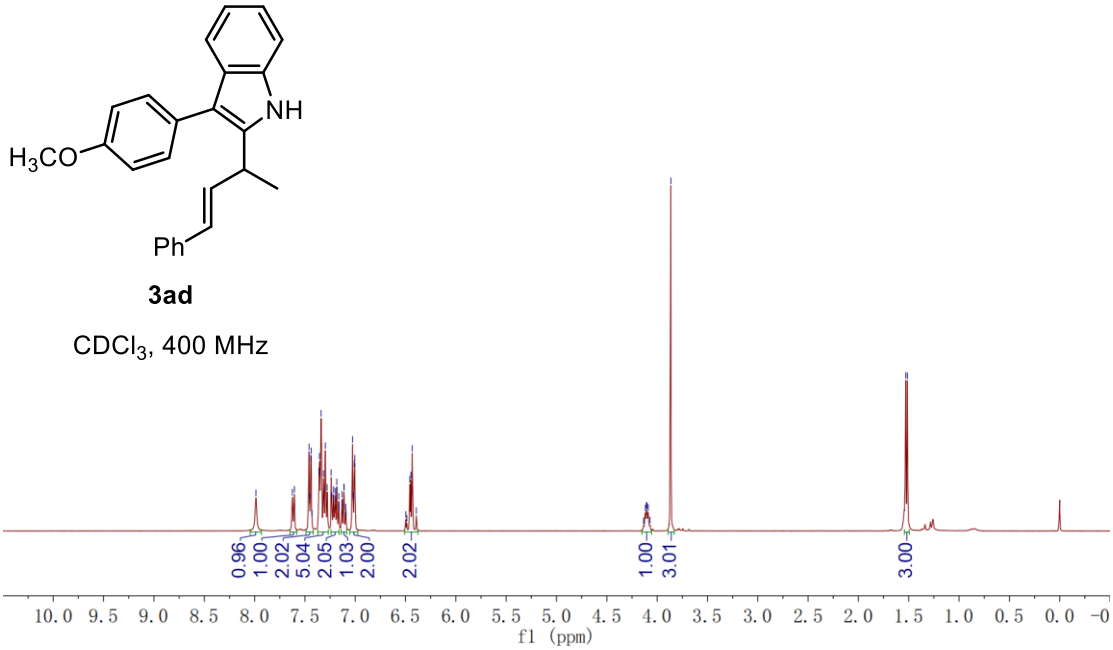
3ac

$CDCl_3$, 101 MHz



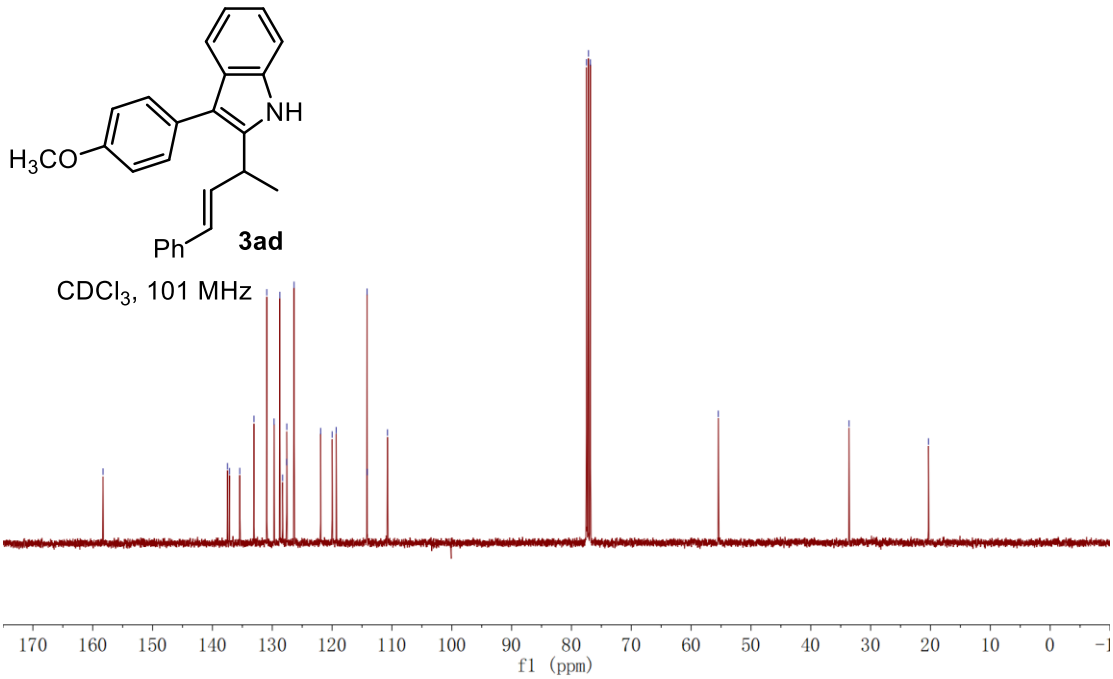
3ac

$CDCl_3$, 376 MHz

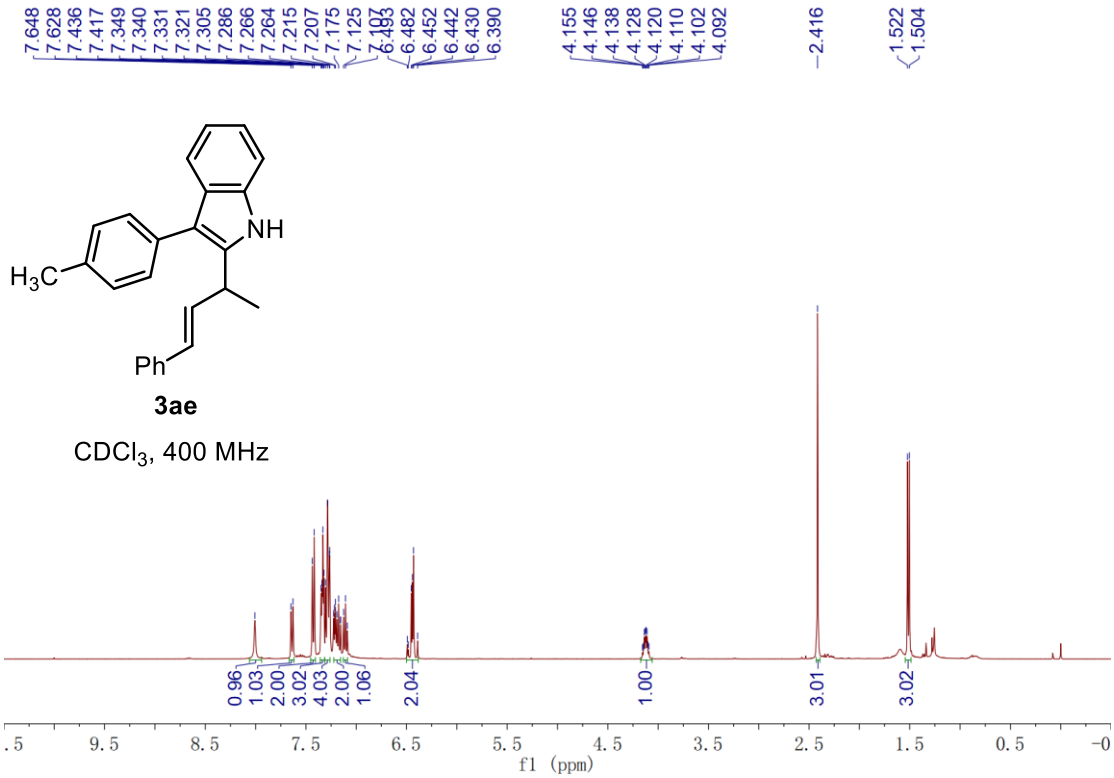


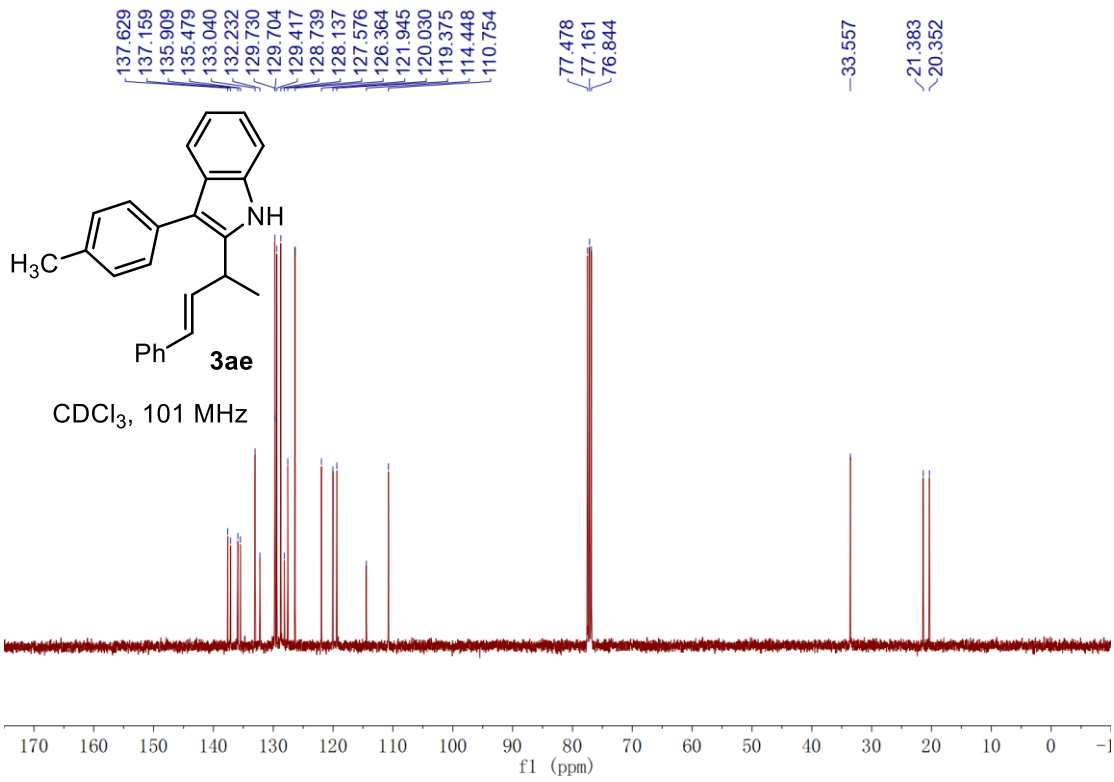
3ad

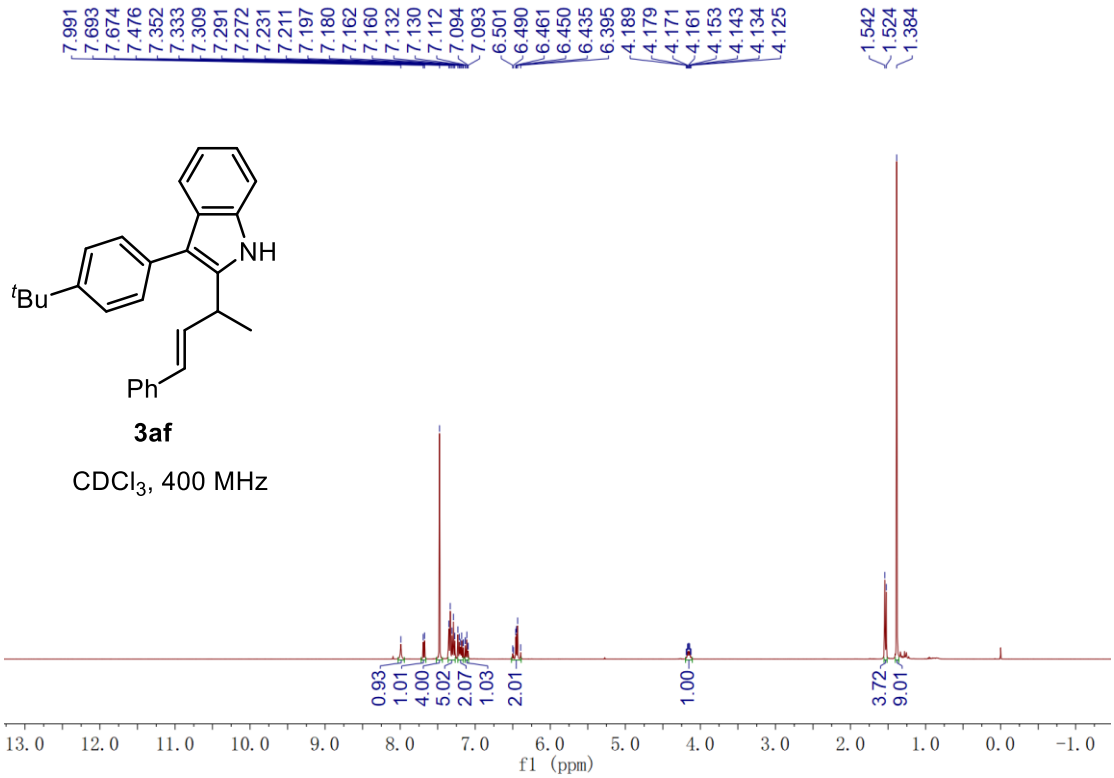
$CDCl_3$, 400 MHz

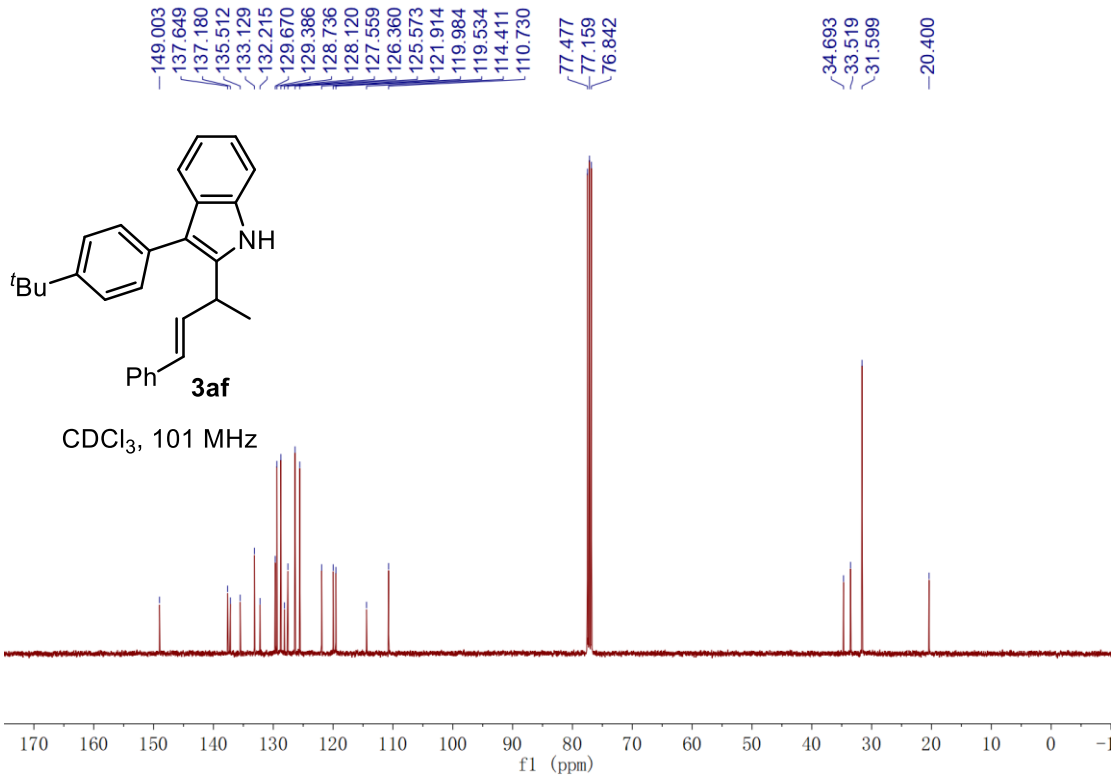


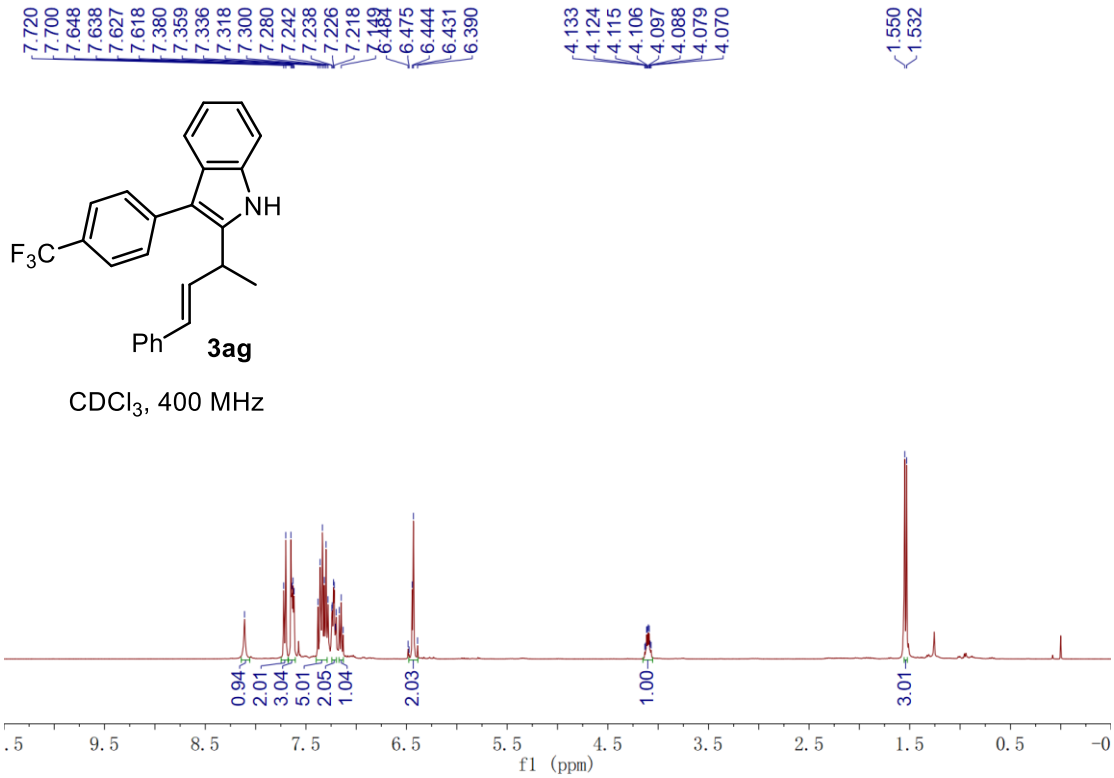
$CDCl_3$, 101 MHz

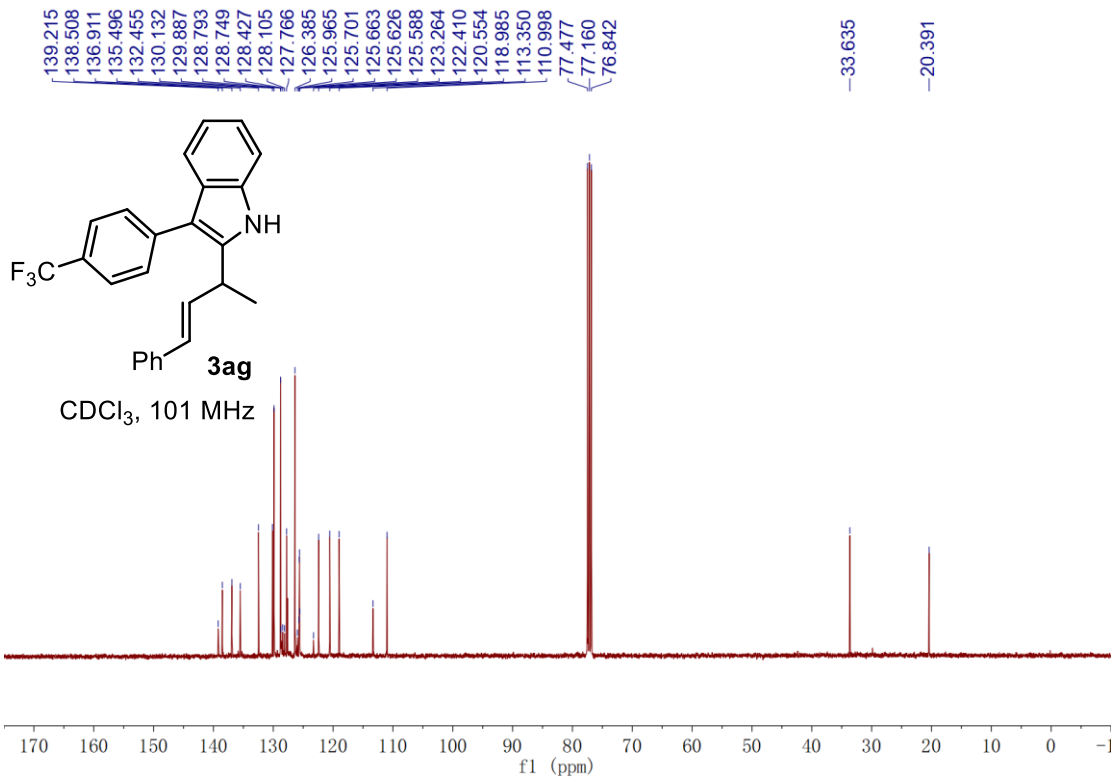

7.648
7.628
7.436
7.417
7.349
7.340
7.331
7.321
7.305
7.286
7.266
7.264
7.215
7.207
7.175
7.125
6.483
6.482
6.452
6.442
6.430
6.390
4.155
4.146
4.138
4.128
4.120
4.110
4.102
4.092
2.416
1.522
1.504
NH
H3C
Ph
3ae
CDCl3, 400 MHz
0.96
1.03
2.00
3.02
4.03
2.00
1.06
2.04
1.00
3.01
3.02
f1 (ppm)

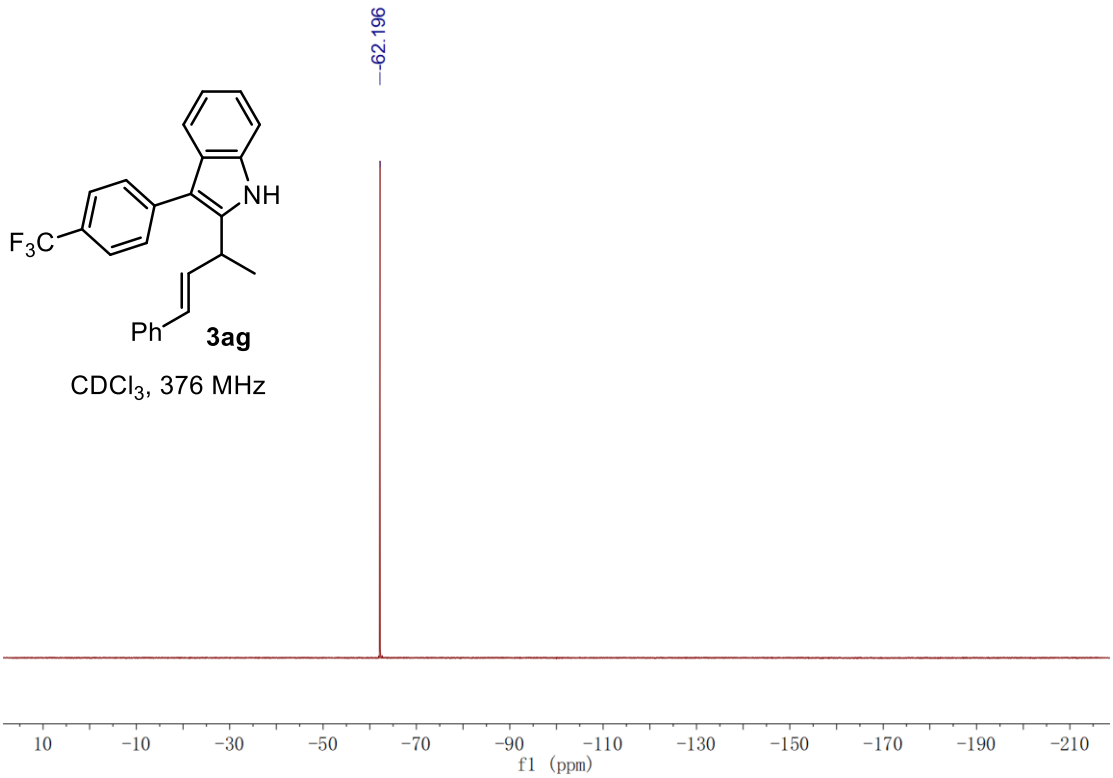

137.629
137.159
135.909
135.479
133.040
132.232
129.730
129.704
129.417
128.739
128.137
127.576
126.364
121.945
120.030
119.375
114.448
110.754
77.478
77.161
76.844
33.557
21.383
20.352
NH
H3C
Ph
3ae
CDCl3, 101 MHz
f1 (ppm)

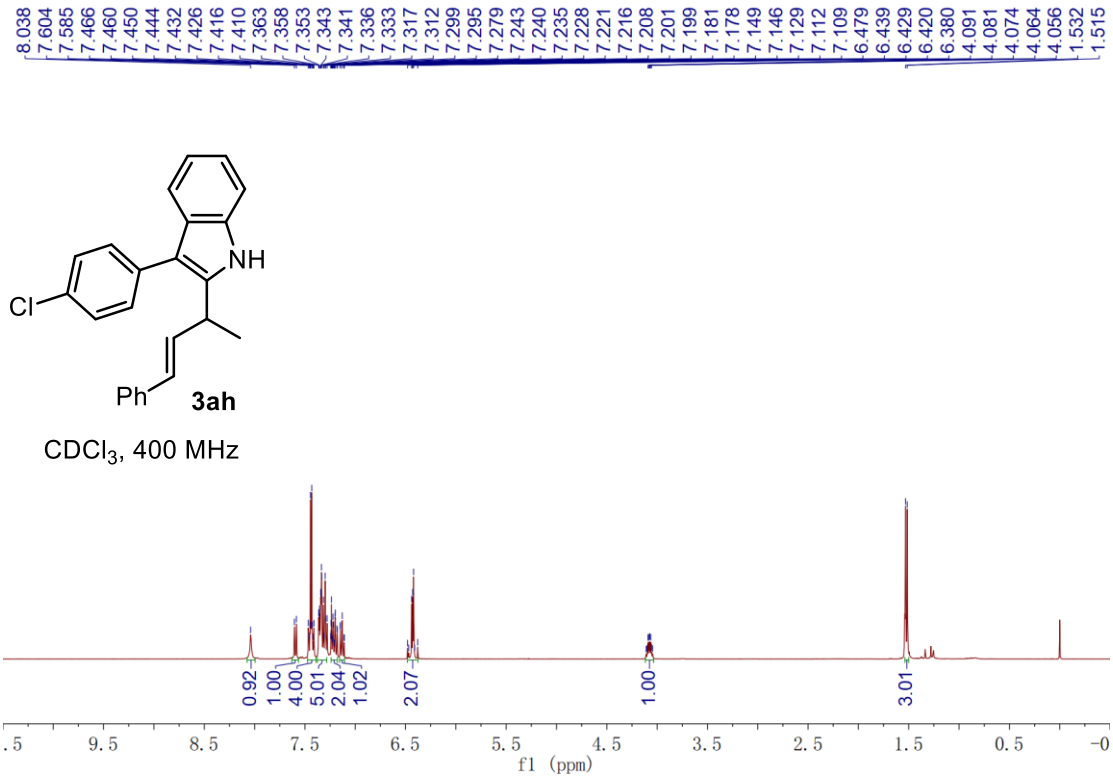

7.991
7.693
7.674
7.476
7.352
7.333
7.309
7.291
7.272
7.231
7.211
7.197
7.180
7.162
7.160
7.132
7.130
7.112
7.094
7.093
6.501
6.490
6.461
6.450
6.435
6.395
4.189
4.179
4.171
4.161
4.153
4.143
4.134
4.125
1.542
1.524
1.384
NH
tBu
Ph
3af
CDCl3, 400 MHz
0.93
1.01
4.00
5.02
2.07
1.03
2.01
1.00
3.72
9.01
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

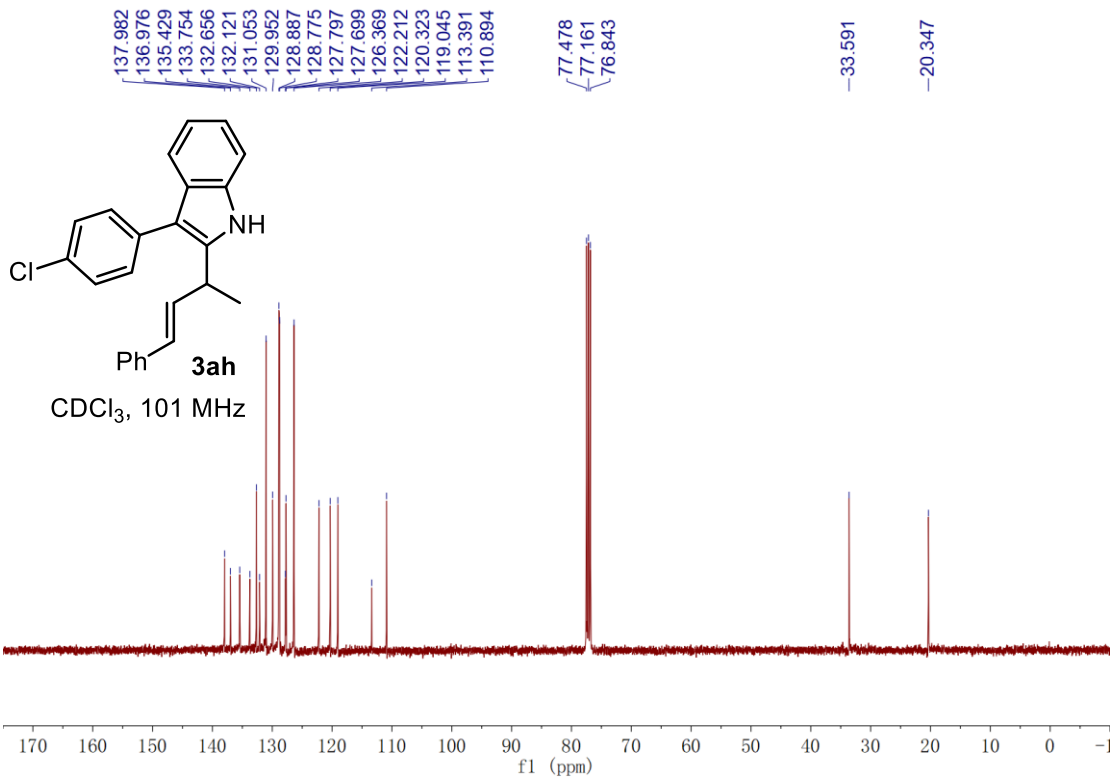

149.003
137.649
137.180
135.512
133.129
132.215
129.670
129.386
128.736
128.120
127.559
126.360
125.573
121.914
119.984
119.534
114.411
110.730
77.477
77.159
76.842
34.693
33.519
31.599
20.400
NH
tBu
Ph
3af
CDCl3, 101 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

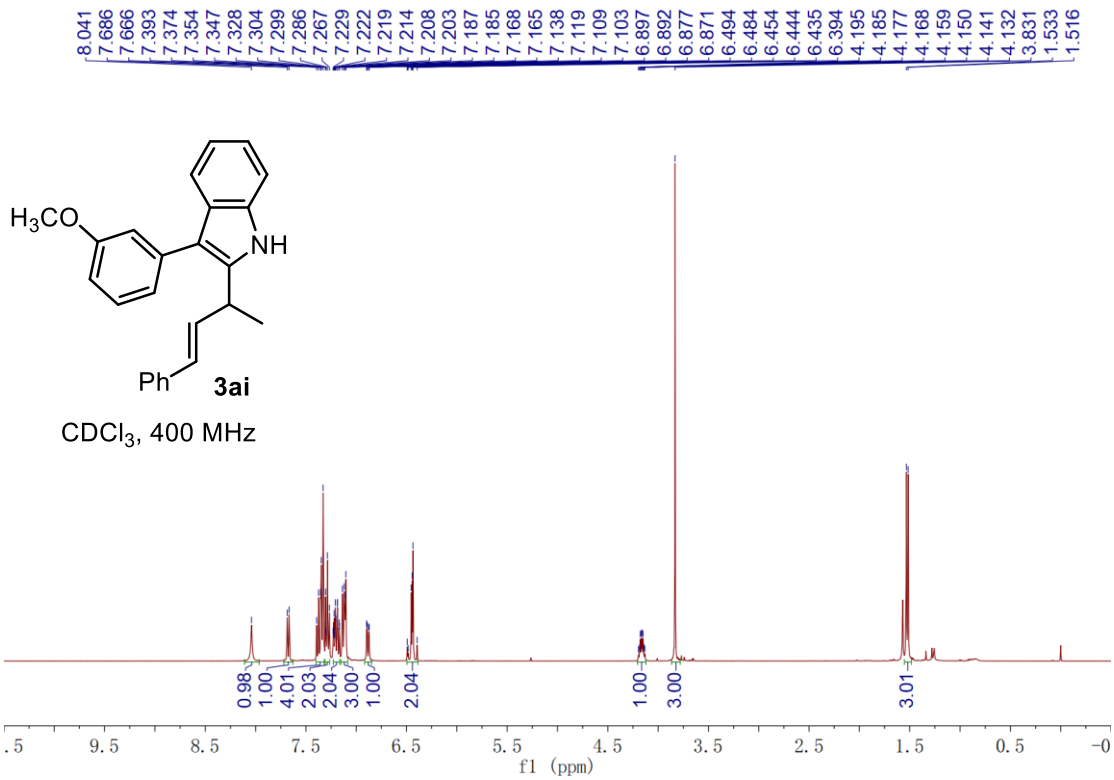

7.720
7.700
7.648
7.638
7.627
7.618
7.380
7.359
7.336
7.318
7.300
7.280
7.242
7.238
7.226
7.218
6.475
6.444
6.431
6.390
4.133
4.124
4.115
4.106
4.097
4.088
4.079
4.070
1.550
1.532
NH
F3C
Ph
3ag
CDCl3, 400 MHz
0.94
2.01
3.04
5.01
2.05
1.04
2.03
1.00
3.01
f1 (ppm)

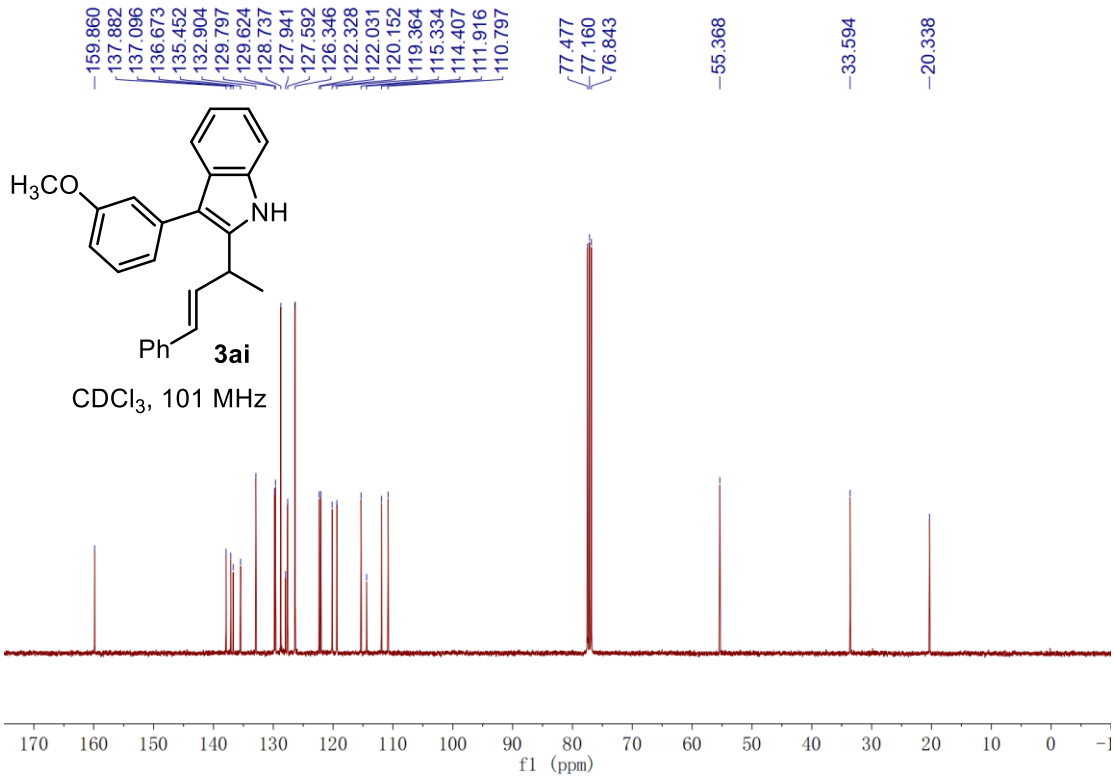

139.215
138.508
136.911
135.496
132.455
130.132
129.887
128.793
128.749
128.427
128.105
127.766
126.385
125.965
125.701
125.663
125.626
125.588
123.264
122.410
120.554
118.985
113.350
110.998
77.477
77.160
76.842
33.635
20.391
NH
F3C
Ph
3ag
CDCl3, 101 MHz
f1 (ppm)

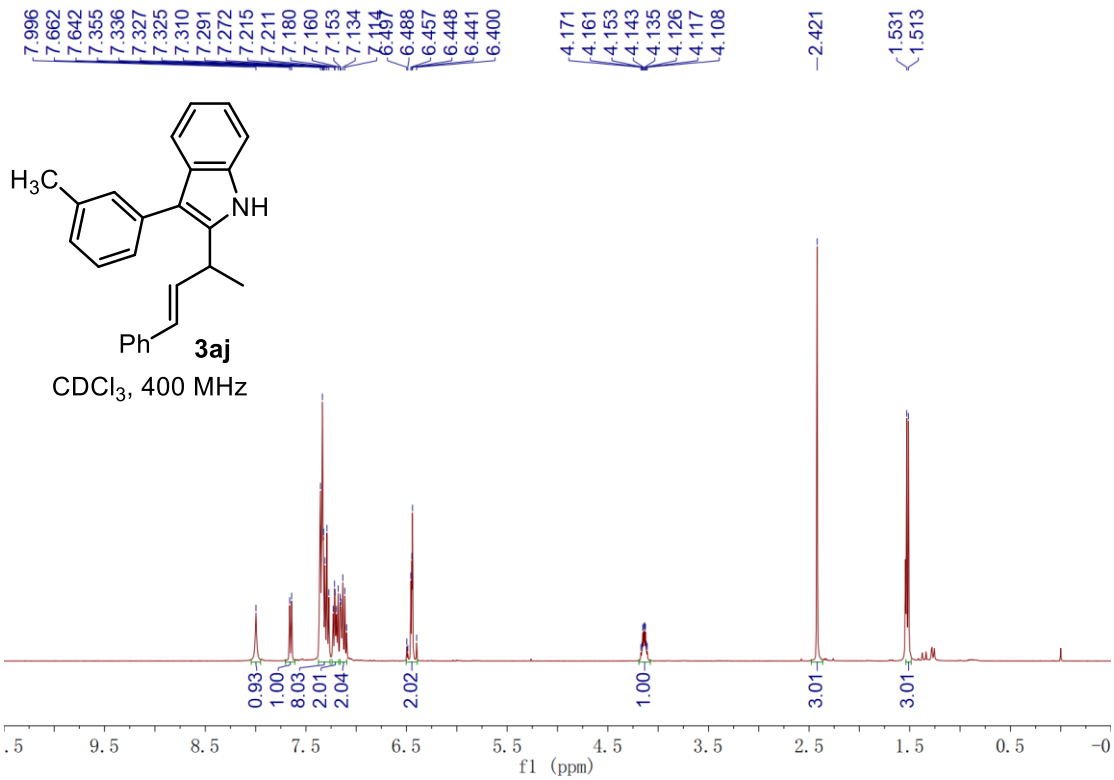

-62.196
NH
F3C
Ph
3ag
CDCl3, 376 MHz
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

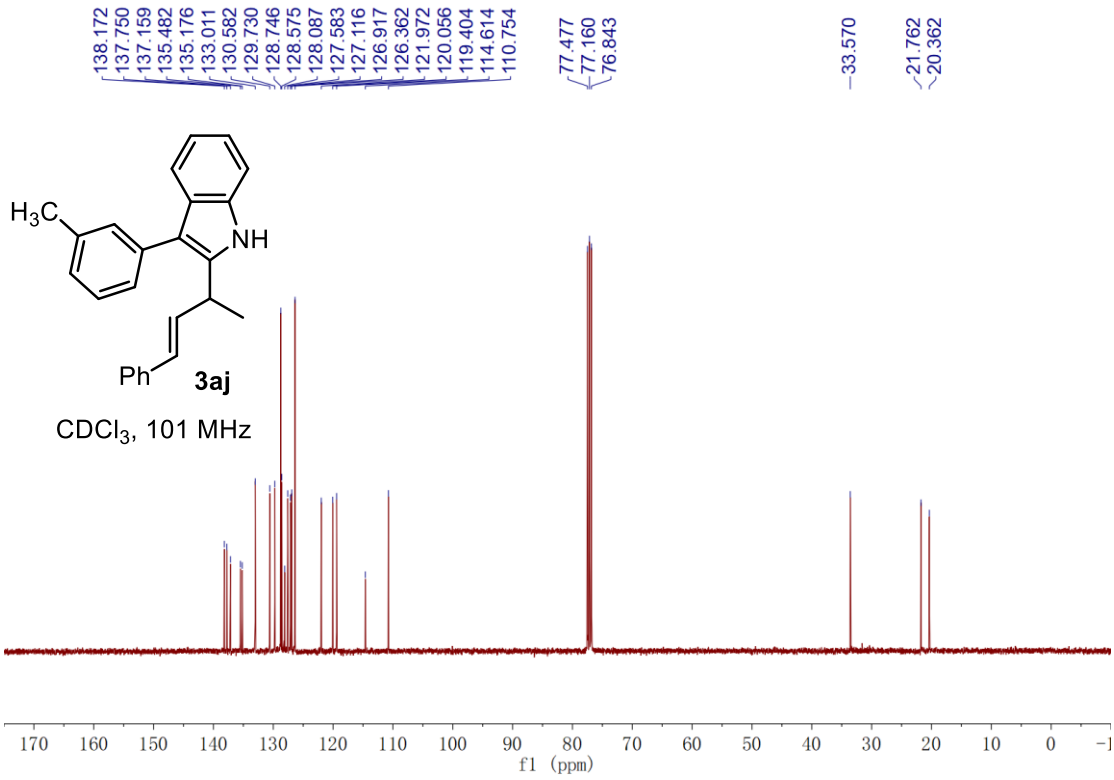

8.038
7.604
7.585
7.466
7.460
7.450
7.444
7.432
7.426
7.416
7.410
7.363
7.358
7.353
7.343
7.341
7.336
7.333
7.317
7.312
7.299
7.295
7.279
7.243
7.240
7.235
7.228
7.221
7.216
7.208
7.201
7.199
7.181
7.178
7.149
7.146
7.129
7.112
7.109
6.479
6.439
6.429
6.420
6.380
4.091
4.081
4.074
4.064
4.056
1.532
1.515
NH
Cl
Ph
3ah
CDCl3, 400 MHz
0.92
1.00
4.00
5.01
2.04
1.02
2.07
1.00
3.01
f1 (ppm)

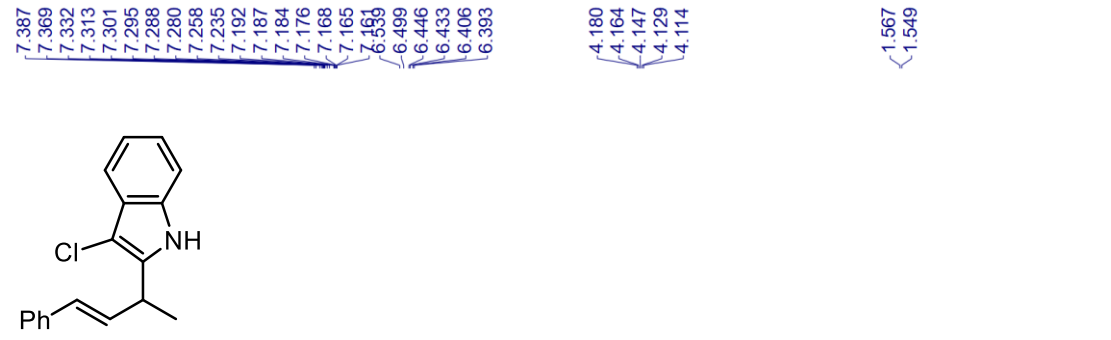

137.982
136.976
135.429
133.754
132.656
132.121
131.053
129.952
128.887
128.775
127.797
127.699
126.369
122.212
120.323
119.045
113.391
110.894
77.478
77.161
76.843
33.591
20.347
NH
Cl
Ph
3ah
CDCl3, 101 MHz
f1 (ppm)


8.041
7.686
7.666
7.393
7.374
7.354
7.347
7.328
7.304
7.299
7.286
7.267
7.229
7.222
7.219
7.214
7.208
7.203
7.187
7.185
7.168
7.165
7.138
7.119
7.109
7.103
6.897
6.892
6.877
6.871
6.494
6.484
6.454
6.444
6.435
6.394
4.195
4.185
4.177
4.168
4.159
4.150
4.141
4.132
3.831
1.533
1.516
H3CO
NH
Ph
3ai
CDCl3, 400 MHz
0.98
1.00
4.01
2.03
2.04
3.00
1.00
2.04
1.00
3.00
3.01
f1 (ppm)


159.860
137.882
137.096
136.673
135.452
132.904
129.797
129.624
128.737
127.941
127.592
126.346
122.328
122.031
120.152
119.364
115.334
114.407
111.916
110.797
77.477
77.160
76.843
55.368
33.594
20.338
H3CO
NH
Ph
3ai
CDCl3, 101 MHz
f1 (ppm)

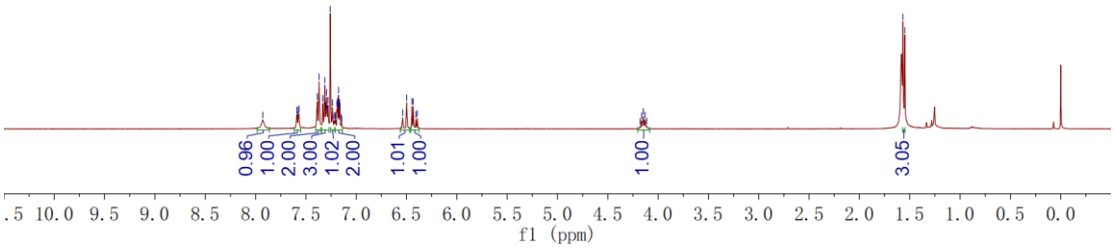

7.996
7.662
7.642
7.355
7.336
7.327
7.325
7.310
7.291
7.272
7.215
7.211
7.180
7.160
7.153
7.134
6.488
6.457
6.448
6.441
6.400
4.171
4.161
4.153
4.143
4.135
4.126
4.117
4.108
2.421
1.531
1.513
H3C
NH
Ph
3aj
CDCl3, 400 MHz
0.93
1.00
8.03
2.01
2.04
2.02
1.00
3.01
3.01
f1 (ppm)

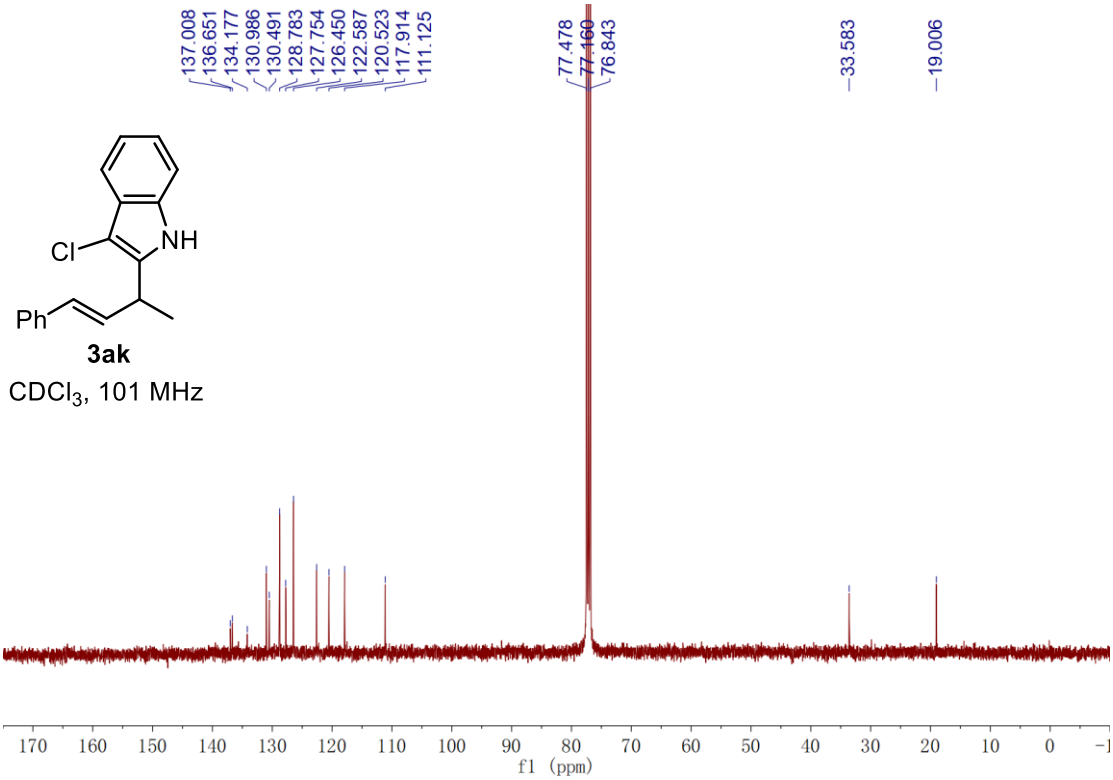

138.172
137.750
137.159
135.482
135.176
133.011
130.582
129.730
128.746
128.575
128.087
127.583
127.116
126.917
126.362
121.972
120.056
119.404
114.614
110.754
77.477
77.160
76.843
33.570
21.762
20.362
H3C
NH
Ph
3aj
CDCl3, 101 MHz
f1 (ppm)



3ak

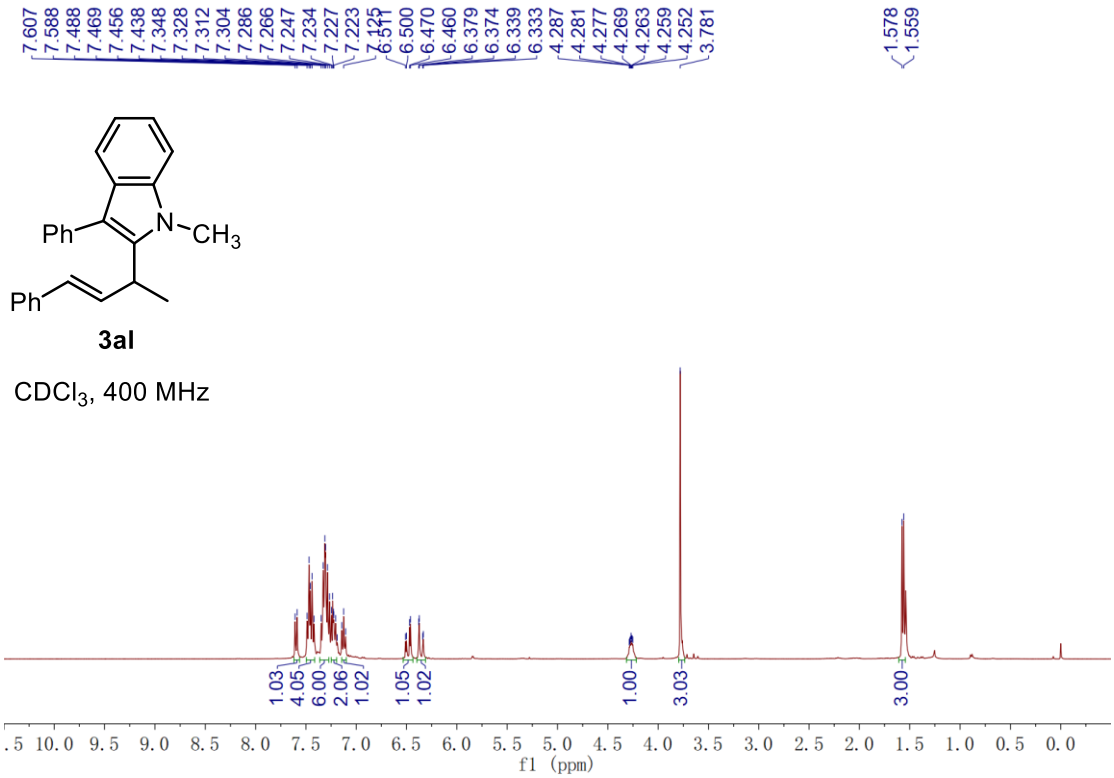
$CDCl_3$, 400 MHz





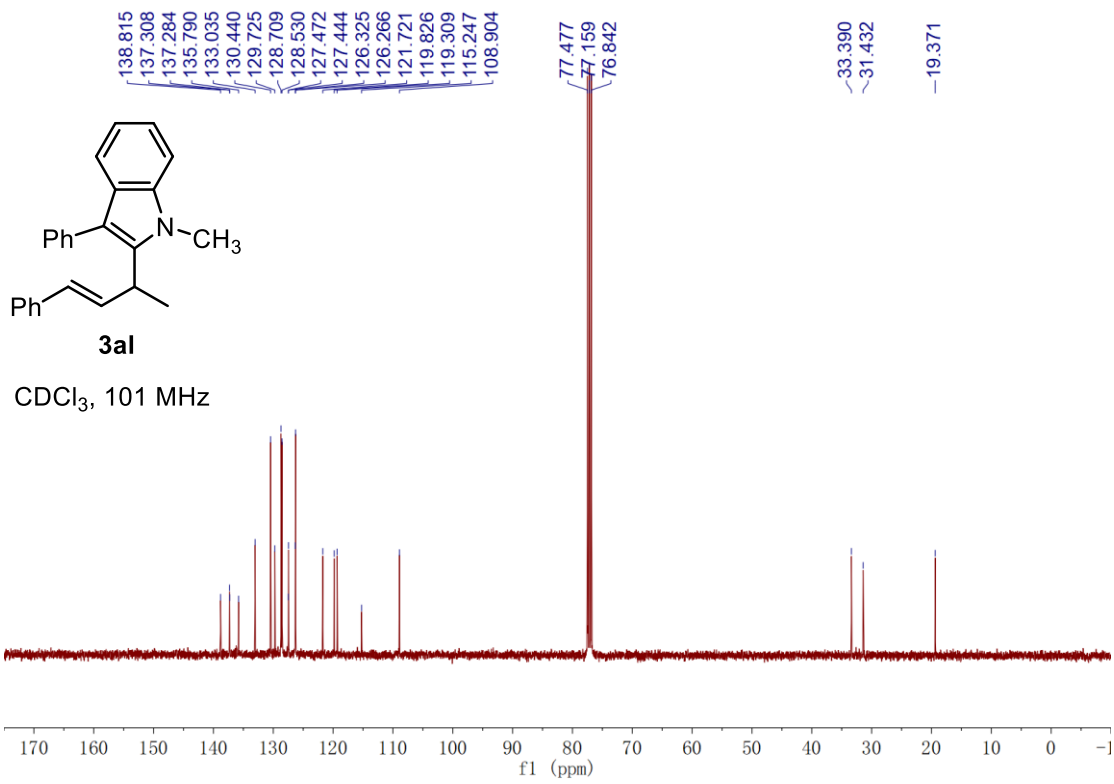
3ak

$CDCl_3$, 101 MHz



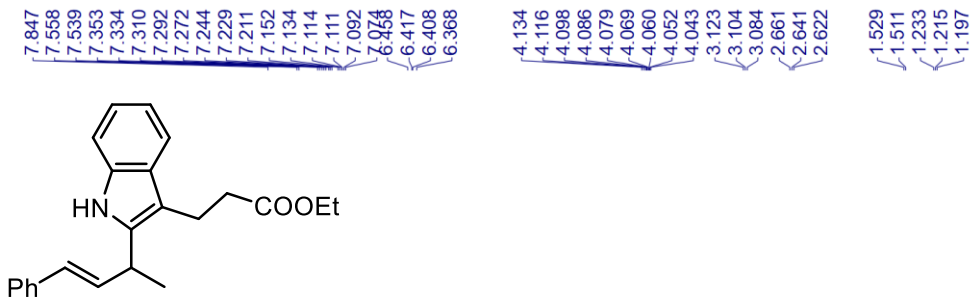
3al

$CDCl_3$, 400 MHz



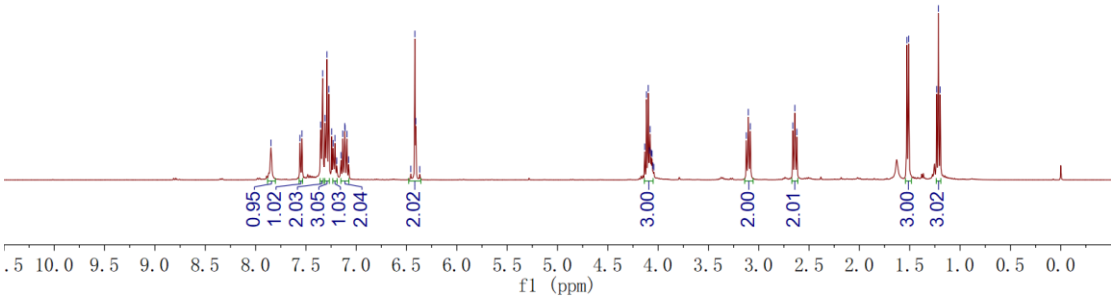
3al

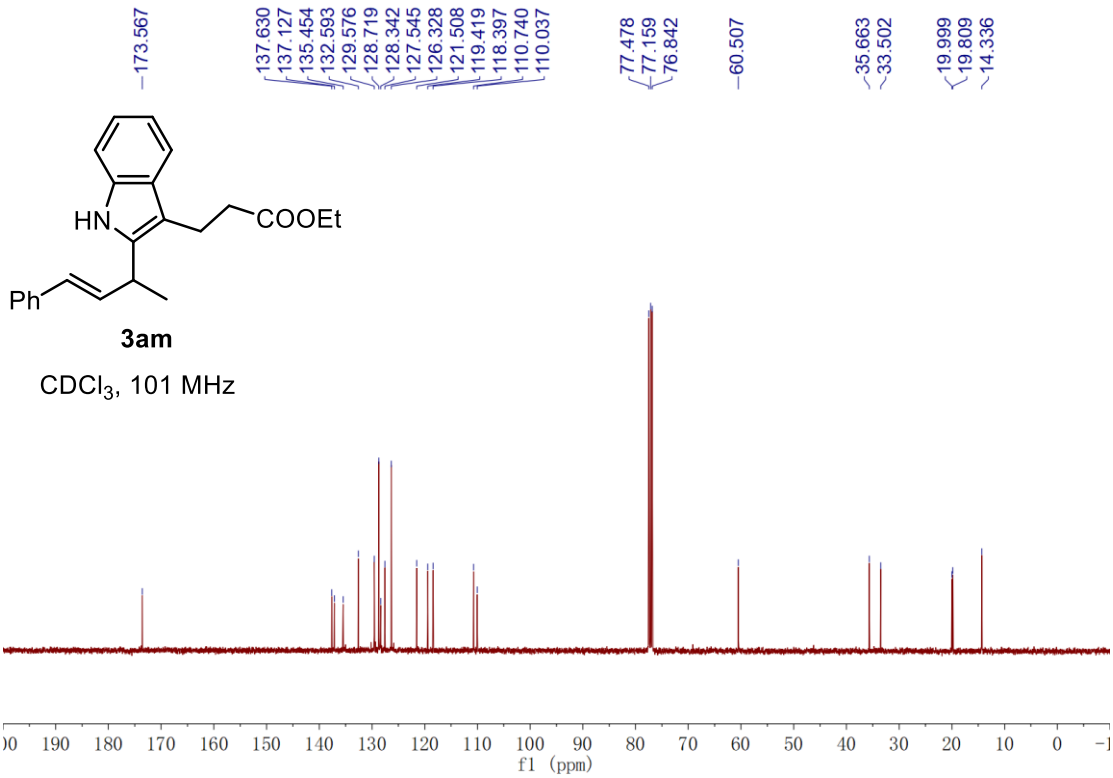
$CDCl_3$, 101 MHz



3am

$CDCl_3$, 400 MHz





3am

$CDCl_3$, 101 MHz