Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Rhodaelectro-catalyzed Chemo-Divergent C–H Activations with Alkylidenecyclopropanes for Selective Cyclopropylations

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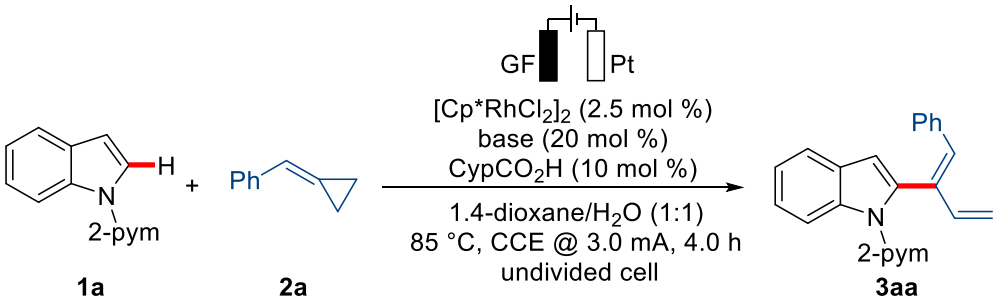
1. General Remarks

All organic solvents were distilled prior to their use. The following starting materials were synthesized according to previously described methods: **1**,[1] **2**[2] and **4**.[2] Other substrates were obtained from commercial sources and were used without further purification. Platinum (Pt) electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur, Karlsruhe, Germany) and graphite felt (GF) electrodes (thickness of 6 mm, SIGRACELL® GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using a Keysight E36104A or an AXIOMET AX-3003P potentiostat. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR spectroscopy. Chromatography was carried out on Merck silica gel 60 (40–63 µm). NMR spectra were recorded on a Varian Mercury VX 300, Inova 500 or Bruker Avance III 300, Avance III 400 and Avance III HD 500 in the solvent indicated; chemical shifts (δ) are given in ppm relative to the residual solvent peak. All IR spectra were recorded on a Bruker FT-IR Alpha-P device. EI-MS was recorded on Jeol AccuTOF at 70eV, ESI-MS on Bruker MicrOTOF and maXis. GC-MS was recorded on Agilent 7890B and Agilent 5977B. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industries (JAI) LC-92XX II NEXT system equipped with a JAIGEL 2.5HR or JAIGEL 2HH column. Chloroform was used as solvent. M.p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected.

2. Optimization of the Dienylation and Cyclopropylation

Table S-1: Screening of the bases.[a]

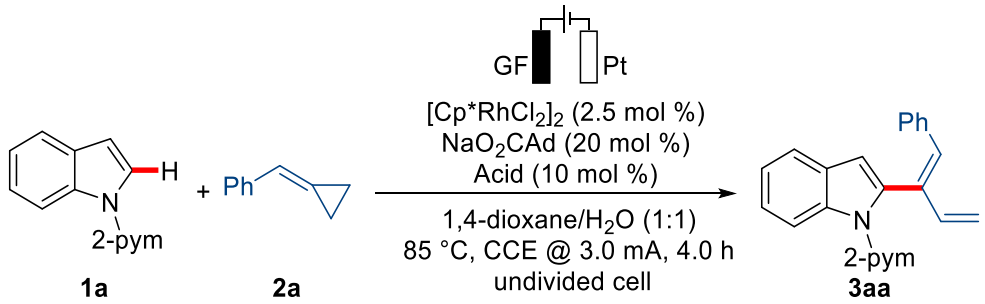


1a **2a** **3aa**

Entry	Base	Yield (%)	*Z/E*
1	NaOAc	72	3.9/1
2	NaOPiv	78	3.5/1
3	NaO_2CMes	60	4.0/1
4	NaO_2CPh	82	3.6/1
5	**NaO_2CAd**	**85**	**4.5/1**
6	NaO_2CCF_3	72	3.5/1
7	NaO_3SCF_3	trace	n.d.

[a] Undivided cell, graphite felt anode (GF), platinum plate cathode (Pt), **1a** (0.10 mmol) **2a** (0.16 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), base (20 mol %), $CypCO_2H$ (10 mol %), 1,4-dioxane/H_2O (1:1) 4.0 mL, 85 °C, CCE @ 3.0 mA, under air, 4.0 h, yield of isolated product, *Z/E* ratio determined by ^1H NMR spectroscopy, $CypCO_2H$ = cyclopentanecarboxylic acid.

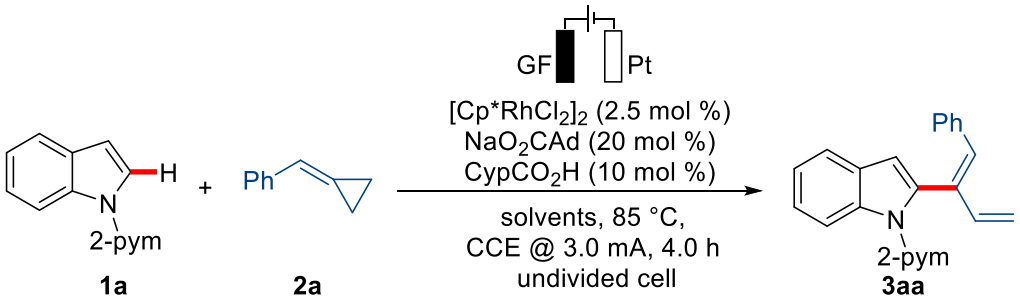
Table S-2: Screening of acids.[a]



Entry	Acid	Yield (%)	*Z/E*
1	$CpCO_2H$	85	4.5/1
2	AcOH	76	3.6/1
3	PivOH	82	3.3/1
4	$AdCO_2H$	82	4.0/1
5	$PhCO_2H$	79	3.7/1
6	$MesCO_2H$	78	3.8/1
7	--	72	2.0/1

[a] Undivided cell, graphite felt anode (GF), platinum plate cathode (Pt), **1a** (0.10 mmol) **2a** (0.16 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), NaO_2CAd (20 mol %), acid (10 mol %), 1,4-dioxane/H_2O (1:1) 4.0 mL, 85 °C, CCE @ 3.0 mA, under air, 4.0 h, yield of isolated product, *Z/E* ratio determined by ^1H NMR spectroscopy.

Table S-3: Optimization of solvents.[a]

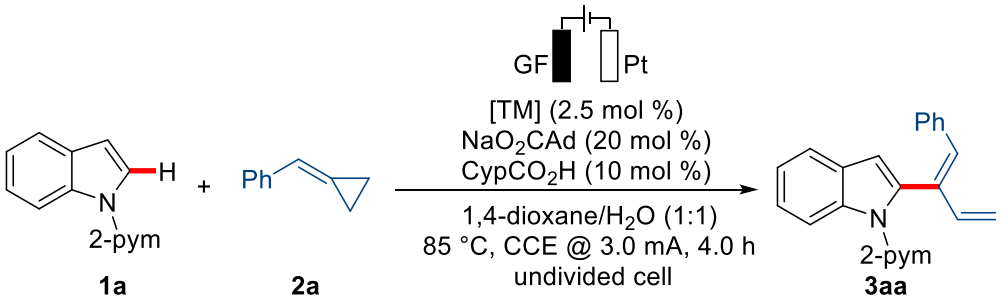


1a **2a** **3aa**

Entry	Solvents	Yield (%)	*Z/E*
1	1,4-dioxane/H_2O (1/1)	85	4.5/1
2	H_2O	trace	n.d.
3	1,4-dioxane/H_2O (2/1)	72	3.4/1
4	*t*AmOH/H_2O (3/1)	82	2.5/1
5	DMF	trace	n.d.
6	EtOH	74	3.7/1

[a] Undivided cell, graphite felt anode (GF), platinum plate cathode (Pt), **1a** (0.10 mmol) **2a** (0.16 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), NaO_2CAd (20 mol %), $CypCO_2H$ (10 mol %), solvent 4.0 mL, 85 °C, CCE @ 3.0 mA, under air, 4.0 h, yield of isolated product, *Z/E* ratio determined by ^1H NMR spectroscopy.

Table S-4: Control experiments.[a]

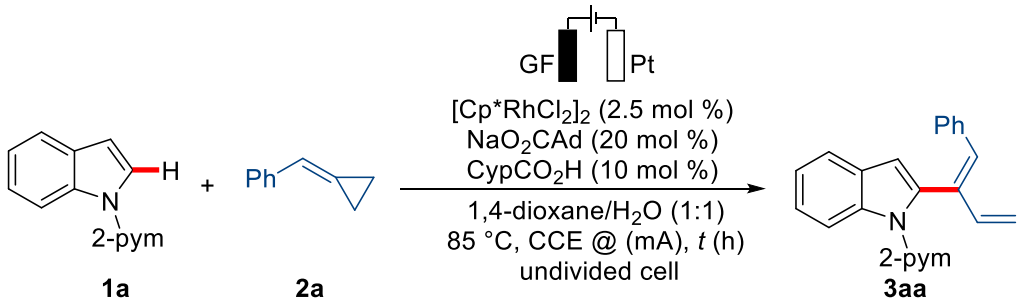


1a **2a** **3aa**

Entry	[TM]	Base	Acid	Yield (%)	*Z/E*
1	$[Cp^*RhCl_2]_2$	NaO_2CAd	$CypCO_2H$	85	4.5/1
2	--	NaO_2CAd	$CypCO_2H$	--	--
3	$[Cp^*RhCl_2]_2$	--	$CypCO_2H$	32	3.2/1
4	$[Cp^*RhCl_2]_2$	NaO_2CAd	--	72	3.6/1
5[b]	$[Cp^*RhCl_2]_2$	NaO_2CAd	$CypCO_2H$	24	2.4/1
6	$[RuCl_2(p\text{-cymene})]_2$	NaO_2CAd	$CypCO_2H$	--	--
7	$Pd(OAc)_2$	NaO_2CAd	$CypCO_2H$	--	--

[a] Undivided cell, graphite felt anode (GF), platinum plate cathode (Pt), **1a** (0.10 mmol) **2a** (0.16 mmol), [TM] (2.5 mol %), NaO_2CAd (20 mol %), $CypCO_2H$ (10 mol %), 1,4-dioxane/H_2O (1:1) 4.0 mL, 85 °C, CCE @ 3.0 mA, under air, 4.0 h, yield of isolated product, *Z/E* ratio determined by ^1H NMR spectroscopy. [b] Without electricity, 12 h.

Table S-5: Further optimization of dienylation.[a]

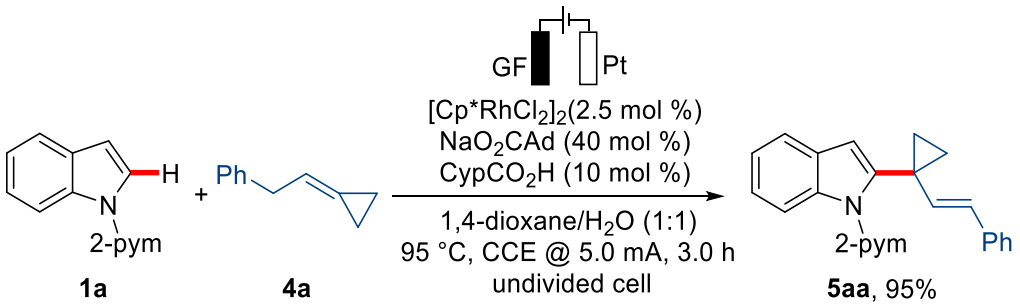


1a **2a** **3aa**

Entry	Current (mA)	*t* (h)	Yield (%)	*Z*/*E*
1	3.0	4.0	85	4.5/1
2	2.0	6.0	87	3.8/1
3	4.0	3.0	72	3.2/1
4[b]	3.0	4.0	82	6.0/1
5[b, c]	5.0	3.0	87	6.5/1
6[b, c, d]	5.0	3.0	89	7.0/1

[a] Undivided cell, graphite felt anode (GF), platinum plate cathode (Pt), **1a** (0.10 mmol) **2a** (0.16 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), NaO_2CAd (20 mol %), $CypCO_2H$ (10 mol %), 1,4-dioxane/H_2O (1:1) 4.0 mL, 85 °C, CCE @ 3.0 mA, under air, yields of isolated product, *Z*/*E* ratio determined by ^1H NMR spectroscopy. [b] NaO_2CAd (40 mol %). [c] 0.20 mmol scale, 1,4-dioxane/H_2O (1:1) 8.0 mL. [d] 95 °C.

Under the optimized reaction conditions, the transformation of ACP **4a** yielded the cyclopropylated compound **5aa** in 95% yield (Scheme S-1).

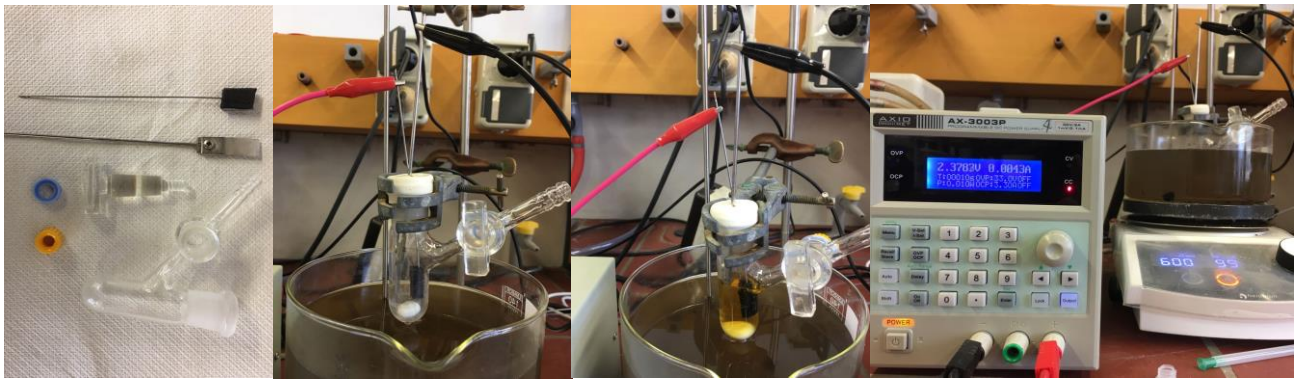


Scheme S-1. Cyclopropylation of indole **1a**

3. General Procedures

General Procedure A for the Rhodaelectro-Catalyzed Dienylation.

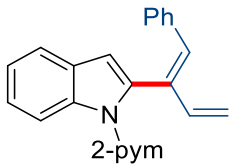
The electrolysis was carried out in an undivided cell with a GF anode (10 mm x 15 mm x 6 mm) and a Pt cathode (10 mm x 15 mm x 0.25 mm). $[Cp^*RhCl_2]_2$ (3.0 mg, 5.0 µmol, 2.5 mol %), NaO_2CAd (16.0 mg, 0.80 mmol, 40 mol %), cyclopentanecarboxylic acid (2.3 mg, 0.20 mmol, 10 mol %), ACP **2** (0.32 mmol, 1.6 equiv) and indole **1** (0.20 mmol, 1.0 equiv) were dissolved in 1,4-dioxane (4.0 mL) and then H_2O (4.0 mL) was added sequentially. At 95 °C, electrolysis was conducted with a constant current of 5.0 mA for 3.0 to 10 hours. Then the mixture was transferred to a flask and the electrodes were rinsed with EtOAc (3 x 5.0 mL). The combined solvent was extracted with EtOAc (3 x 10 mL), the organic layers combined and the solvent removed under reduced pressure. Column chromatography on silica gel (*n*-hexane/EtOAc) yielded the desired product **3**.



General Procedure B for the Rhodaelectro-Catalyzed Cyclopropylation.

The electrolysis was carried out in an undivided cell with a GF anode (10 mm x 15 mm x 6 mm) and a Pt cathode (10 mm x 15 mm x 0.25 mm). $[Cp^*RhCl_2]_2$ (3.0 mg, 5.0 µmol, 2.5 mol %), NaO_2CAd (16.0 mg, 0.8 mmol, 40 mol %), cyclopentanecarboxylic acid (2.3 mg, 0.2 mmol, 10 mol %), ACP **4** (0.32 mmol, 1.6 equiv) and indole **1** (0.20 mmol, 1.0 equiv) were dissolved in 1,4-dioxane (4.0 mL) and then water (4.0 mL) was added sequentially. At 95 °C, electrolysis was conducted with a constant current of 5.0 mA for 3.0 to 10 hours. Then the mixture was transferred to a flask and the electrodes were rinsed with EtOAc (3 x 5.0 mL). The combined solvent was extracted with EtOAc (3 x 10 mL), the organic layers combined and the solvent removed under reduced pressure. Column chromatography on silica gel (*n*-hexane/EtOAc) yielded the desired product **5.**

4. Characterization Data of Products



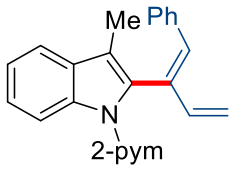
(*Z*)-2-(1-Phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3aa)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3aa** (57.6 mg, 89%, *Z*/*E* = 7.0/1 as determined by ^{1}H NMR spectroscopy) as a yellow solid. The isomeric mixture was separated by GPC ($CHCl_3$) and the *Z* (7.8 mg, 12%) and the *E* isomer (1.8 mg, 3%) were obtained as colorless oil or solid, respectively. **Mixture: M.p. =** 137–139 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 4.8 Hz, 0.25H, *E* isomer), 8.62 (d, *J* = 4.8 Hz, 1.75H, Z isomer), 8.33 (d, *J* = 8.3 Hz, 0.87H, Z isomer), 8.27 (d, *J* = 8.3 Hz, 0.13H, *E* isomer), 7.68 (d, *J* = 7.6 Hz, 0.13H, *E* isomer), 7.60 (d, *J* = 7.6, 0.87H, *Z* isomer), 7.66 – 7.46 (m, 0.53H, *E* isomer), 7.36 – 7.24 (m, 2.67H, *Z* isomer), 7.08 – 6.99 (m, 4.46H, *Z* isomer), 6.90 (s, 0.13H, *E* isomer), 6.83 (s, 0.13H, *E* isomer), 6.83 (dd, *J* = 17.4, 10.6 Hz, 0.13H, *E* isomer), 6.69 (dd, *J* = 17.4, 10.6 Hz, 0.87H, *Z* isomer), 6.68 (s, 0.87H, *Z* isomer), 6.57 (s, 0.87H, *Z* isomer), 5.06 (d, *J* = 10.6 Hz, 1H, *E* and *Z* isomer), 5.02 (d, *J* = 17.4 Hz, 1H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 157.9 (CH), 157.5 (C_q), 140.6 (CH), 136.7 (C_q), 136.7 (C_q), 135.4 (C_q), 134.0 (C_q), 133.0 (CH), 129.5 (C_q), 129.1 (CH), 128.1 (CH), 127.2 (CH), 123.4 (CH), 122.0 (CH), 120.8 (CH), 117.0 (CH_2), 115.7 (CH), 114.2 (CH), 108.7 (CH). *Minor isomer*: δ = 158.1 (CH), 140.5 (CH), 137.1 (C_q), 134.8 (C_q), 134.6 (C_q), 134.2 (C_q), 130.8 (CH), 129.8 (C_q), 129.0 (CH), 128.3 (CH), 127.4 (CH), 123.7 (CH), 122.9 (CH), 122.1 (CH), 120.7 (CH), 117.8 (CH_2), 117.2 (CH), 113.4 (CH), 109.4 (CH). One C_q is missing due to low signal to noise ratio. **IR** (ATR): 3000, 2201, 1564, 1437, 1419, 1360, 1256, 1075, 812, 769 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 324 (100) $[M+H]^+$, 346 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{18}N_3$ $[M+H]^+$ 324.1495, found 324.1484.

Isolated (*Z*)-3aa: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.00 (m, 6H), 6.69 (dd, *J* = 17.4, 10.6 Hz, 1H), 6.68 (s, 1H), 6.57 (s, 1H), 5.07 (d, *J* = 10.6 Hz, 1H), 5.05 (d, *J* = 17.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.9 (CH), 157.5 (C_q), 140.6 (CH), 136.7 (C_q), 136.7 (C_q), 135.4 (C_q), 134.0 (C_q), 133.0 (CH), 129.5 (C_q), 129.1 (CH), 128.1 (CH), 127.2 (CH), 123.4 (CH), 122.0 (CH), 120.8 (CH), 117.0 (CH_2), 115.7 (CH), 114.2 (CH), 108.7

(CH). **IR** (ATR): 3015, 2221, 1565, 1458, 1419, 1315, 1218, 984, 909, 810 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 324 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{18}N_3$ $[M+H]^+$ 324.1495, found 324.1495.

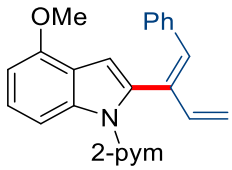
Isolated (*E*)-3aa: M.p. = 129-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 4.8 Hz, 2H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.36 (m, 4H), 7.36 – 7.25 (m, 2H), 7.27 – 7.21 (m, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.89 (s, 1H), 6.83 (dd, *J* = 17.4, 10.6 Hz, 1H), 6.82 (s, 1H), 5.08 (d, *J* = 17.4 Hz, 1H), 5.00 (d, *J* = 10.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (CH), 157.9 (C_q), 140.5 (CH), 137.3 (C_q), 134.8 (C_q), 134.2 (C_q), 134.2 (C_q), 130.9 (CH), 129.8 (C_q), 129.2 (CH), 129.1 (CH), 128.3 (CH), 128.1 (CH), 127.4 (CH), 123.7 (CH), 122.1 (CH), 120.7 (CH), 117.8 (CH_2), 117.4 (CH), 113.4 (CH), 109.4 (CH). **IR** (ATR): 3046, 2922, 1567, 1426, 1349, 1319, 915, 805, 746, 700 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 324 (100) $[M+H]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{18}N_3$ $[M+H]^+$ 324.1495, found 324.1497.



(*Z*)-3-Methyl-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ba)

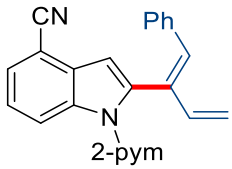
The general procedure **A** was followed using 3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (**1b**) (41.8 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ba** (46.5 mg, 69%, *Z/E* = 9.5/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 102–104 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.69 (d, *J* = 4.8 Hz, 0.19H, *E* isomer), 8.65 (d, *J* = 4.8 Hz, 1.81H, *Z* isomer), 8.44 (d, *J* = 8.3 Hz, 0.89H, *Z* isomer), 8.33 (d, *J* = 8.3 Hz, 0.11H, *E* isomer), 7.65 (d, *J* = 7.5 Hz, 0.14H, *E* isomer), 7.58 (d, *J* = 7.5 Hz, 0.86H, *Z* isomer), 7.51 – 7.28 (m, 3.13H, *E* and *Z* isomer), 7.28 – 7.21 (m, 1.26H, *E* and *Z* isomer), 7.19 – 7.07 (m, 4.07H, *Z* isomer), 7.01 (t, *J* = 4.8 Hz, 0.95H, *Z* isomer), 6.89 (dd, *J* = 17.2, 10.9 Hz, 0.19H, *E* isomer), 6.81 (s, 0.86H, *Z* isomer), 6.71 (s, 0.14H, *E* isomer), 6.65 (dd, *J* = 17.2, 10.9 Hz, 0.81H, *Z* isomer), 5.03 (d, *J* = 10.9 Hz, 0.16H, *E* isomer), 4.97 (d, *J* = 10.9 Hz, 0.84H, *Z* isomer), 4.81 (d, *J* = 17.2 Hz, 1H, *E* and *Z* isomer), 2.00 (s, 2.87H, *Z* isomer), 1.79 (s, 0.13H, *E* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 157.9 (CH), 157.8 (C_q), 140.3 (CH), 137.2 (C_q), 136.5 (C_q), 133.6 (C_q), 133.5 (CH), 132.0 (C_q), 130.7 (C_q), 128.8 (CH), 128.2 (CH), 127.2 (CH), 123.6 (CH), 121.6 (CH), 119.0 (CH), 116.6 (CH), 115.2 (CH_2), 114.9 (C_q), 114.4 (CH), 9.0 (CH_3). *Minor isomer*: δ = 158.1 (CH), 130.5 (CH), 129.8 (CH), 129.0 (CH), 128.3 (CH), 128.0 (CH), 126.1 (CH), 123.1 (CH), 121.8 (CH), 121.2 (C_q), 117.2 (CH), 113.0 (CH_2), 16.2 (CH_3). **IR** (ATR): 3048, 2920,

1565, 1425, 1354, 1223, 1017, 988, 801, 748 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (100) $[M+H]^+$, 360 (68) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}N_3$ $[M+H]^+$ 338.1657, found 338.1642.



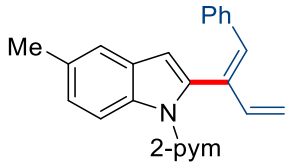
(*Z*)-4-Methoxy-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ca)

The general procedure **A** was followed using 4-methoyl-1-(pyrimidin-2-yl)-1*H*-indole (**1c**) (45.0 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 2.8 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ca** (67.2 mg, 95%, *Z/E* = 3.3/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 98–99 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 4.8 Hz, 0.46H, *E* isomer), 8.61 (d, *J* = 4.8 Hz, 1.54H, *Z* isomer), 7.90 (d, *J* = 8.5 Hz, 0.76H, *Z* isomer), 7.85 (d, *J* = 8.5 Hz, 0.24H, *E* isomer), 7.44 (d, *J* = 7.6 Hz, 0.70H, *Z* isomer), 7.39 (t, *J* = 7.6 Hz, 0.23H, *E* isomer), 7.31 (d, *J* = 7.6 Hz, 0.30H, *E* isomer), 7.25 (t, *J* = 7.6 Hz, 0.77H, *Z* isomer), 7.13 – 6.95 (m, 5H, *E* and *Z* isomer), 6.95 (d, *J* = 1.0 Hz, 0.25H, *E* isomer), 6.90 (s, 0.27H, *E* isomer), 6.81 (ddd, *J* = 17.5, 10.9, 1.0 Hz, 0.35H, *E* isomer), 6.73 – 6.64 (m, 3H, *E* and *Z* isomer), 5.09 (d, *J* = 10.6 Hz, 0.76H, *Z* isomer), 5.09 (d, *J* = 17.4 Hz, 1H, *E* and *Z* isomer), 4.99 (d, *J* = 10.9 Hz, 0.24H, *E* isomer), 4.02 (s, 0.75H, *E* isomer), 3.98 (s, 2.25H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.1 (C_q), 157.8 (CH), 153.1 (C_q), 140.6 (CH), 138.0 (C_q), 136.7 (C_q), 133.9 (C_q), 133.8 (C_q), 133.0 (CH), 129.1 (CH), 128.0 (CH), 127.1 (CH), 124.2 (CH), 120.0 (C_q), 117.1 (CH), 115.8 (CH_2), 107.4 (CH), 105.7 (CH), 102.1 (CH), 55.5 (CH_3). *Minor isomer*: δ = 158.1 (C_q), 157.5 (CH) 139.1 (C_q), 138.6 (C_q), 137.4 (C_q), 134.8 (CH), 134.1 (C_q), 130.8 (CH), 129.8 (CH), 128.3 (CH), 127.3 (CH), 124.5 (CH), 119.6 (C_q), 117.7 (CH), 117.4 (CH_2), 106.6 (CH), 106.4 (CH), 102.2 (CH), 55.6 (CH_3). One C_q is missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 3026, 1693, 1564, 1420, 1336, 1240, 1149, 910, 805, 740 cm^{-1}**. MS** (ESI) *m/z* (relative intensity): 354 (15) $[M+H]^+$, 376 (30) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}N_3O$ $[M+H]^+$ 354.1606, found 354.1601.



(*Z*)-2-(1-Phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole-4-carbonitrile (3da)

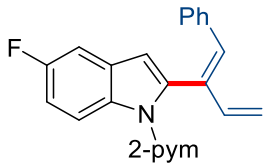
The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole-4-carbonitrile (**1d**) (44.0 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3da** (41.8 mg, 60%, *Z*/*E* = 2.0/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 4.8 Hz, 0.66H, *E* isomer), 8.63 (d, *J* = 4.8 Hz, 1.34H, *Z* isomer), 8.46 (d, *J* = 8.5 Hz, 0.64H, *Z* isomer), 8.42 (d, *J* = 8.5 Hz, 0.36H, *E* isomer), 7.57 (d, *J* = 7.5 Hz, 0.64H, *Z* isomer), 7.45 – 7.29 (m, 3H, *E* and *Z* isomer), 7.16 (t, *J* = 4.8 Hz, 0.36H, *E* isomer), 7.14 – 6.84 (m, 5H, *E* and *Z* isomer), 6.79 – 6.64 (m, 1H, *E* and *Z* isomer), 5.10 (d, *J* = 10.7 Hz, 0.64H, *Z* isomer), 5.04 (d, *J* = 17.6 Hz, 0.36H, *E* isomer), 5.04 (d, *J* = 10.7 Hz, 0.36H, *E* isomer), 4.97 (d, *J* = 17.6 Hz, 0.64H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 156.7 (C_q), 139.8 (CH), 138.4 (C_q), 136.7 (C_q), 136.1 (C_q), 133.9 (CH), 132.6 (C_q), 130.8 (C_q), 128.8 (CH), 128.1 (CH), 127.5 (CH), 126.8 (CH), 122.9 (CH), 118.7 (CH), 118.4 (C_q), 117.9 (CH), 115.9 (CH_2), 106.6 (CH), 103.1 (C_q). *Minor isomer*: δ = 158.3 (CH), 157.3 (C_q), 143.3 (C_q), 136.8 (C_q), 136.1 (C_q), 132.9 (C_q), 132.4 (CH), 130.7 (C_q), 129.7 (CH), 128.3 (CH), 127.7 (CH), 126.8 (CH), 123.1 (CH), 118.2 (CH_2), 118.0 (CH), 107.1 (CH), 102.9 (C_q). One C_q is missing due to low signal to nois ratio or signal overlap. **IR** (ATR): 3050, 1693, 1567, 1425, 1318, 1263, 1234, 1078, 913, 786 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 349 (100) $[M+H]^+$, 371 (40) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}N_4$ $[M+H]^+$ 349.1448, found 349.1449.



(*Z*)-5-Methyl-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ea)

The general procedure **A** was followed using 5-methyl-1-(pyrimidin-2-yl)-1*H*-indole (**1e**) (41.8 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ea** (50.6 mg, 75%, *Z*/*E* = 8.3/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (d, *J* = 4.8 Hz, 0.21H, *E* isomer), 8.61 (d, *J* = 4.8 Hz, 1.79H, *Z* isomer), 8.25 (d, *J* = 8.6 Hz, 0.89H, *Z* isomer), 8.17 (d, *J* = 8.6 Hz, 0.11H, *E* isomer), 7.50 – 7.28 (m, 2H, *E* and *Z*

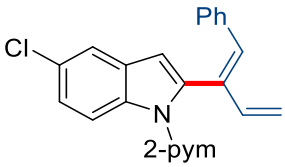
isomer), 7.15 (d, J = 8.2 Hz, 1.06H, *E* and *Z* isomer), 7.13 – 6.92 (m, 4.06H, *E* and *Z* isomer), 6.88 (s, 0.12H, *E* isomer), 6.87 (s, 0.11H, *E* isomer), 6.82 (dd, J = 17.4, 10.7 Hz, 0.13H, *E* isomer), 6.72 (dd, J = 17.4, 10.7 Hz, 0.87H, *Z* isomer), 6.68 (s, 0.89H, *Z* isomer), 6.50 (s, 0.88H, *Z* isomer), 5.06 (d, J = 10.7 Hz, 1.04H, *E* and *Z* isomer), 5.01 (d, J = 17.5 Hz, 1.04H, *E* and *Z* isomer), 2.50 (s, 3.01H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 157.8 (CH), 157.5 (C_q), 140.7 (CH), 136.8 (C_q), 135.4 (C_q), 135.0 (C_q), 134.3 (C_q), 132.8 (CH), 131.4 (C_q), 129.8 (C_q), 129.1 (CH), 128.1 (CH), 127.2 (CH), 124.9 (CH), 120.6 (CH), 116.8 (CH), 115.6 (CH_2), 114.1 (CH), 108.5 (CH), 21.5 (CH_3) *Minor isomer*: δ = 158.1 (CH), 140.5 (C_q), 137.4 (CH), 135.7 (C_q), 134.9 (CH), 134.4 (C_q), 131.4 (C_q) 130.6 (CH), 129.4 (C_q), 128.3 (CH_2), 127.3 (CH), 125.2 (CH), 120.5 (CH), 117.6 (CH), 117.1 (CH), 113.3 (CH), 109.3 (CH), 21.5 (CH_3). Two C_q are missing due to low signal to noise ration or signal overlap. **IR** (ATR): 2919, 2860, 1565, 1423, 1217, 1080, 987, 806, 751, 699 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (80) $[M+H]^+$, 360 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3Na$ $[M+Na]^+$ 360.1470, found 360.1471.



(*Z*)-5-Fluoro-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3fa)

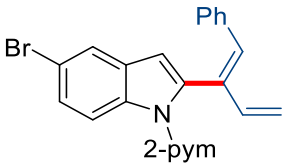
The general procedure **A** was followed using 5-fluoro-1-(pyrimidin-2-yl)-1*H*-indole (**1f**) (42.6 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3fa** (48.5 mg, 71%, *Z/E* = 5.1/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p.** = 104–106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.67 (d, J = 4.8 Hz, 0.33H, *E* isomer), 8.58 (d, J = 4.8 Hz, 1.67H, *Z* isomer), 8.25 (dd, J = 9.1, 4.7 Hz, 0.84H, *Z* isomer), 8.17 (dd, J = 9.1, 4.7 Hz, 0.16H, *E* isomer), 7.65 – 7.48 (m, 0.15H, *E* isomer), 7.45 – 7.31 (m, 0.85H, *Z* isomer), 7.20 (d, J = 9.0 Hz, 0.88H, *Z* isomer), 7.18 (d, J = 9.1 Hz, 0.12H, *E* isomer), 7.05 – 7.03 (m, 2H, *E* and *Z* isomer), 7.01 – 6.94 (m, 3H, *E* and *Z* isomer), 6.83 (s, 0.20H, *E* isomer), 6.78 (dd, J = 17.7, 10.5 Hz, 0.25H, *E* isomer), 6.78 (s, 0.15H, *E* isomer), 6.66 (dd, J = 17.7, 10.5 Hz, 0.80H, *Z* isomer), 6.65 (s, 0.85H, *Z* isomer), 6.48 (s, 0.80H, *Z* isomer), 5.03 (d, J = 10.5, 1H, *E* and *Z* isomer), 4.95 (d, J = 17.6 Hz, 1H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.8 (d, $^1J_{C\text{-}F}$ = 297.2 Hz, C_q), 157.9 (CH), 157.9 (d, $^4J_{C\text{-}F}$ = 2.7 Hz, C_q), 140.4 (CH), 137.1 (C_q), 136.6 (C_q), 133.9 (C_q), 133.1 (CH), 132.9 (CH), 130.2 (d, $^3J_{C\text{-}F}$ = 10.0 Hz, C_q), 129.1 (CH), 128.1 (CH), 127.3 (CH), 123.4 (CH), 122.0 (CH), 120.8 (CH), 117.2 (CH), 115.7 (CH_2), 115.3 (d, $^3J_{C\text{-}}$

$_F$ = 9.1 Hz, CH), 111.3 (d, $^2J_{C\text{-}F}$ = 25.3 Hz, CH), 108.4 (d, $^4J_{C\text{-}F}$ = 4.1 Hz, C_q), 105.8 (d, $^2J_{C\text{-}F}$ = 23.5 Hz, CH). *Minor isomer*: δ = 158.2 (CH), 142.0 (C_q), 140.6 (CH), 137.2 (C_q), 135.4 (C_q), 134.7 (C_q), 134.1 (C_q), 133.1 (CH), 133.0 (CH), 131.2 (C_q), 129.8 (CH), 128.4 (CH), 127.5 (CH), 117.7 (CH), 117.5 (CH), 117.1 (CH_2), 114.5 (d, $^3J_{C\text{-}F}$ = 9.1 Hz, CH), 114.2 (CH), 111.6 (CH) (d, $^2J_{C\text{-}F}$ = 25.3 Hz, CH), 109.1 (d, $^4J_{C\text{-}F}$ = 4.1 Hz, C_q), 108.7, (d, ^2J = 23.5 Hz, CH). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -118.5 (td, *J* = 9.1, 4.6 Hz, *E* isomer), -122.3 (td, *J* = 9.1, 4.6 Hz, *Z* isomer). **IR** (ATR): 3053, 2130, 1961, 1710, 1568, 1427, 1419, 1196, 804, 698 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$, 364 (95) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3F$ $[M+H]^+$ 342.1401, found 342.1403.



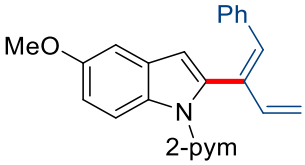
(*Z*)-5-chloro-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ga)

The general procedure **A** was followed using 5-chloro-1-(pyrimidin-2-yl)-1*H*-indole (**1g**) (45.9 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ga** (40.8 mg, 57%, *Z/E* = 3.6/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 4.8 Hz, 0.43H, *E* isomer), 8.63 (d, *J* = 4.8 Hz, 1.57H, *Z* isomer), 8.28 (d, *J* = 8.9 Hz, 0.79H, *Z* isomer), 8.20 (d, *J* = 8.9 Hz, 0.21H, *E* isomer), 7.63 (d, *J* = 2.1 Hz, 0.21H, *E* isomer), 7.58 (d, *J* = 2.1 Hz, 0.79H, *Z* isomer), 7.50 – 7.35 (m, 1H, *E* isomer), 7.33 (d, *J* = 6.8 Hz, 0.20H, *E* isomer), 7.28 (dd, *J* = 8.7, 2.3 Hz, 0.80H, *Z* isomer), 7.12 – 7.07 (m, 2.50H, *Z* isomer), 7.05 (t, *J* = 4.8 Hz, 0.78H, *Z* isomer), 7.02 – 6.97 (m, 1.50H, *E* isomer), 6.89 (s, 0.22H, *E* isomer), 6.83 (dd, *J* = 17.8, 10.9 Hz, 0.25H, *E* isomer), 6.76 (s, 0.21H, *E* isomer), 6.71 (s, 0.79H, *Z* isomer), 6.70 (dd, *J* = 17.8, 10.9 Hz, 0.85H, *Z* isomer), 6.52 (s, 0.78H, *Z* isomer), 5.09 (d, *J* = 10.9 Hz, 1H, *E* and *Z* isomer), 5.00 (d, *J* = 17.8 Hz, 1H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.2 (C_q), 141.8 (C_q), 140.3 (CH), 136.9 (C_q), 136.5 (C_q), 135.0 (C_q), 133.6 (C_q), 133.3 (CH), 130.6 (C_q), 129.0 (CH), 128.1 (CH), 127.3 (CH), 123.5 (CH), 120.1 (CH), 117.3 (CH), 115.7 (CH_2), 115.5 (CH), 108.0 (CH). *Minor isomer*: δ = 158.2 (CH), 157.7 (C_q), 137.1 (C_q), 135.6 (CH), 134.7 (CH), 133.8 (C_q), 131.4 (CH), 130.3 (C_q), 128.4 (CH), 127.5 (CH), 123.8 (CH), 120.0 (CH), 117.8 (CH), 117.6 (CH_2), 114.7 (CH), 108.6 (CH). Three C_q are missing due to low signal to noise ratio or signal overlap. **MS** (ESI) *m/z* (relative intensity): 358 (90) (^{35}Cl) $[M+H]^+$, 380 (40) (^{35}Cl) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3{}^{35}Cl$ $[M+H]^+$ 358.1106, found 358.1104.



(*Z*)-5-Bromo-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ha)

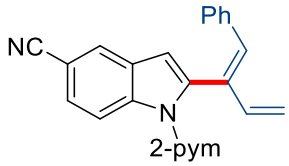
The general procedure **A** was followed using 5-bromo-1-(pyrimidin-2-yl)-1*H*-indole (**1h**) (54.8 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.9 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ha** (54.7 mg, 68%, *Z/E* = 6.9/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 4.8 Hz, 0.26H, *E* isomer), 8.63 (d, *J* = 4.7 Hz, 1.74H, *Z* isomer), 8.23 (d, *J* = 8.9 Hz, 0.84H, *Z* isomer), 8.15 (d, *J* = 8.9 Hz, 0.16H, *E* isomer), 7.79 (d, *J* = 2.0 Hz, 0.15H, *E* isomer), 7.73 (d, *J* = 2.0 Hz, 0.85H, *Z* isomer), 7.48 – 7.43 (m, 0.51H, *E* isomer), 7.40 (dd, *J* = 8.9, 2.0 Hz, 1.10H, *Z* isomer), 7.36 – 7.31 (m, 0.33H, *E* isomer), 7.09 (dd, *J* = 5.1, 2.1 Hz, 2.36H, *Z* isomer), 7.05 (t, *J* = 4.7 Hz, 1.02H, *Z* isomer), 6.99 (dd, *J* = 5.1, 2.1 Hz, 1.58H, *Z* isomer), 6.89 (s, 0.11H, *E* isomer), 6.82 (dd, *J* = 17.3, 10.6 Hz, 0.20H, *E* isomer), 6.76 (s, 0.16H, *E* isomer), 6.70 (s, 0.89H, *Z* isomer), 6.70 (dd, *J* = 17.3, 10.6 Hz, 0.80H, *Z* isomer), 6.51 (s, 0.76H, *Z* isomer), 5.08 (d, *J* = 10.6 Hz, 1H, *E* and *Z* isomer), 4.99 (d, *J* = 17.3 Hz, 1H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.2 (C_q), 140.3 (CH), 136.7 (C_q), 136.5 (C_q), 135.3 (C_q), 133.6 (C_q), 133.3 (CH), 131.2 (C_q), 129.0 (CH), 128.1 (CH), 127.4 (CH), 126.1 (CH), 123.2 (CH), 117.4 (CH), 115.9 (CH), 115.7 (CH_2), 115.2 (C_q), 107.8 (CH). *Minor isomer*: δ = 158.2 (CH), 157.1 (C_q), 141.7 (CH), 137.1 (C_q), 135.9 (C_q), 134.7 (CH), 133.7 (C_q), 131.4 (CH), 130.9 (C_q) 129.8 (CH), 128.4 (CH), 127.5 (CH), 126.4 (CH), 123.1 (CH), 117.8 (CH), 117.7 (CH_2), 115.1 (CH), 108.5 (CH). One C_q missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 3049, 1561, 1313, 1264, 1076, 912, 808 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 278 (47), 402 (54) (^{79}Br) $[M+H]^+$, 418 (100), 424 (20) (^{79}Br) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3{}^{79}Br$ $[M+H]^+$ 402.0600, found 402.0594.



(*Z*)-5-Methoxy-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ia)

The general procedure **A** was followed using 5-methoxyl-1-(pyrimidin-2-yl)-1*H*-indole (**1i**) (45.0 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.9 mg, 0.32 mmol) for 2.8 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ia** (59.4 mg, 84%, *Z/E*

= 5.7/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 111–112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (d, *J* = 4.8 Hz, 0.30H, *E* isomer), 8.62 (d, *J* = 4.8 Hz, 1.70H, *Z* isomer), 8.32 (d, *J* = 9.1 Hz, 0.84H, *Z* isomer), 8.23 (d, *J* = 9.1 Hz, 0.16H, *E* isomer), 7.50 – 7.29 (m, 1H, *E* and *Z* isomer), 7.14 – 7.02 (m, 5H, *E* and *Z* isomer), 7.03 – 6.94 (m, 2H, *E* and *Z* isomer), 6.89 (s, 0.16H, *E* isomer), 6.87 (dd, *J* = 17.4, 10.5 Hz, 0.15H, *E* isomer), 6.77 (s, 0.15H, *Z* isomer), 6.73 (dd, *J* = 17.4, 10.5 Hz, 0.85H, *Z* isomer), 6.70 (s, 0.84H, *Z* isomer), 6.51 (s, 0.85H, *Z* isomer), 5.08 (d, *J* = 10.5 Hz, 1H, *E* and *Z* isomer), 5.03 (d, *J* = 17.4 Hz, 1H, *E* and *Z* isomer), 3.92 (s, 0.55H, Z isomer), 3.91 (s, 2.55H, Z isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 157.8 (CH), 157.4 (C_q), 155.5 (C_q), 140.6 (CH), 136.8 (C_q), 136.0 (C_q), 134.3 (C_q), 132.8 (CH), 131.6 (C_q), 130.3 (C_q), 129.1 (CH), 128.1 (CH), 127.2 (CH), 116.8 (CH), 115.6 (CH_2), 115.4 (CH), 112.8 (CH), 108.6 (CH), 102.7 (CH), 55.8 (CH_3). *Minor isomer*: δ = 158.0 (CH), 157.9 (C_q), 155.6 (C_q), 141.0 (CH), 137.3 (C_q), 134.9 (C_q), 134.4 (C_q), 132.3 (C_q), 130.6 (CH), 129.9 (CH), 129.6 (C_q), 128.3 (CH), 127.3 (CH), 117.6 (CH_2), 117.1 (CH), 114.6 (CH), 113.0 (CH), 109.4 (CH), 102.7 (CH), 55.9 (CH_3). **IR** (ATR): 3044, 2950, 2249, 1717, 1565, 1421, 1280, 1202, 1106, 908, 804, 728 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 354 (100) $[M+H]^+$, 376 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}N_3O$ $[M+H]^+$ 354.1601, found 354.1597.



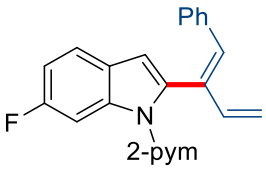
(*Z*)-2-(1-Phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole-5-carbonitrile (3ja)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole-5-carbonitrile (**1j**) (44.0 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.9 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 5:1) yielded **3ja** (46.0 mg, 66%, *Z/E* = 3.2/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. The isomeric mixture was separated by GPC ($CHCl_3$) and the *Z* (18.3 mg, 26%) and the *E* isomer (7.0 mg, 10%) were obtained as a yellow oil and colorless solid, respectively. **Mixture**: **M.p. =** 103–104 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 4.8 Hz, 0.48H, *E* isomer), 8.67 (d, *J* = 4.8 Hz, 1.52H, *Z* isomer), 8.34 (d, *J* = 8.7 Hz, 0.75H, *Z* isomer), δ 8.28 (d, *J* = 8.7 Hz, 0.25H, *E* isomer), 8.00 (d, *J* = 1.5 Hz, 0.23H, *E* isomer), 7.95 (d, *J* = 1.5 Hz, 0.77H, *Z* isomer), 7.55 (dd, *J* = 8.7, 1.7 Hz, 1H, *E* and *Z* isomer), 7.49 – 7.30 (m, 2H, *E* and *Z* isomer), 7.19 (t, *J* = 4.8 Hz, 0.29H, *E* isomer), 7.13 (t, *J* = 4.8 Hz, 0.71H, *Z* isomer), 7.11 – 7.06 (m, 2H, *E* and *Z* isomer), 6.99 – 6.93 (m, 1H, *E* and *Z* isomer), 6.90 (s, 0.22H, *E* isomer), 6.86 (s, 0.22H, *E* isomer), 6.80 (dd, *J* =

16.9, 10.0 Hz, 0.30H, *E* isomer). 6.73 (s, 0.78H, *Z* isomer), 6.69 (dd, *J* = 16.9, 10.0 Hz, 0.70H, *Z* isomer), 6.63 (s, 0.78H, *Z* isomer), 5.09 (d, *J* = 10.0 Hz, 0.78H, Z isomer), 5.00 (d, *J* = 10.0 Hz, 0.22H, *E* isomer), 5.00 (d, *J* = 16.9 Hz, 0.22H, *E* isomer), 4.97 (d, *J* = 16.9 Hz, 0.78H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.2 (CH), 156.8 (C_q), 140.0 (CH), 138.2 (C_q), 138.0 (C_q), 136.3 (C_q), 133.9 (CH), 132.9 (C_q), 129.2 (C_q), 129.0 (CH), 128.2 (CH), 127.6 (CH), 126.3 (CH), 125.9 (CH), 120.4 (C_q), 118.1 (CH), 115.9 (CH_2), 115.0 (CH), 108.3 (CH), 105.2 (C_q). *Minor isomer*: δ = 158.3 (CH), 157.2 (C_q), 142.9 (C_q), 138.9 (C_q), 136.7 (C_q), 134.3 (CH), 133.1 (C_q) 132.2 (CH), 129.8 (CH), 129.5 (C_q) 128.4 (CH), 127.6 (CH), 126.5 (CH), 125.7 (CH), 118.4 (CH), 118.0 (CH_2), 114.3 (CH), 108.7 (CH), 105.0 (C_q). One C_q is missing due to signal overlap. **IR** (ATR): 3050, 2921, 2221, 1608, 1565, 1415, 1316, 1217, 1030, 986, 886, 809, 735 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 349 (90) $[M+H]^+$, 371 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}N_4$ $[M+H]^+$ 349.1448, found 349.1440.

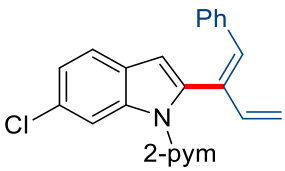
Isolated (*Z*)-3ja: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 4.9 Hz, 2H), 8.34 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 1.5 Hz, 1H), 7.55 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 7.11 – 7.06 (m, 3H), 6.97 (d, *J* = 2.2 Hz, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 6.73 (s, 1H), 6.69 (dd, *J* = 16.9, 10.0 Hz, 1H), 6.63 (s, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.97 (d, *J* = 16.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (CH), 156.8 (C_q), 140.0 (CH), 138.2 (C_q), 138.1 (C_q), 136.3 (C_q), 133.9 (CH), 132.9 (C_q), 129.2 (C_q), 129.0 (CH), 128.2 (CH), 127.6 (CH), 126.3 (CH), 125.9 (CH), 120.4 (C_q), 118.1 (CH), 115.9 (CH_2), 115.0 (CH), 108.3 (CH), 105.2 (C_q). **IR** (ATR): 3015, 2221, 1608, 1565, 1419, 1315, 1218, 909, 810, 730 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 349 (100) $[M+H]^+$, 371 (65) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}N_4$ $[M+H]^+$ 349.1448, found 349.1448.

Isolated (*E*)-3ja: M.p. = 133–134 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 1.5 Hz, 1H), 7.52 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.44 – 7.28 (m, 5H), 7.17 (t, *J* = 4.8 Hz, 1H), 6.88 (s, 1H), 6.84 (s, 1H), 6.77 (dd, *J* = 16.9, 10.0 Hz, 1H), 4.98 (d, *J* = 16.9 Hz, 1H), 4.98 (d, *J* = 10.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4 (CH), 157.4 (C_q), 142.9 (C_q), 138.9 (C_q), 136.8 (C_q), 134.4 (CH), 133.1 (C_q), 132.2 (CH), 129.8 (CH), 129.0 (C_q), 128.4 (CH), 127.8 (CH), 126.6 (CH), 125.7 (CH), 120.5 (C_q), 118.4 (CH), 118.0 (CH_2), 114.3 (CH), 108.7 (CH), 105.2 (C_q). **IR** (ATR): 3125, 2219, 1590, 1456, 1417, 1321, 1218, 914, 810, 701 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 349 (100) $[M+H]^+$, 371 (65) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}N_4$ $[M+H]^+$ 349.1448, found 349.1447.



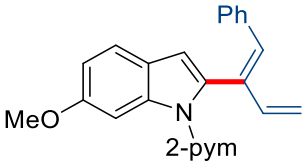
(*Z*)-6-Fluoro-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ka)

The general procedure **A** was followed using 6-fluoro-1-(pyrimidin-2-yl)-1*H*-indole (**1k**) (42.6 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ka** (42.3 mg, 62%, *Z/E* = 2.7/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 4.8 Hz, 0.55H, *E* isomer), 8.64 (d, *J* = 4.8 Hz, 1.45H, *Z* isomer), 8.12 (dd, *J* = 10.8, 2.4 Hz, 0.73H, *E* isomer), 8.04 (dd, *J* = 10.8, 2.4 Hz, 0.27H, *Z* isomer), 7.57 (dd, *J* = 8.6, 5.5 Hz, 0.27H, *Z* isomer), 7.51 (dd, *J* = 8.6, 5.5 Hz, 0.73H, *E* isomer), 7.47 – 7.38 (m, 1.39H, *Z* isomer), 7.32 (dd, *J* = 7.1, 2.4 Hz, 0.27H, *Z* isomer), 7.18 (t, *J* = 4.8 Hz, 0.27H, *Z* isomer), 7.12 – 7.07 (m, 2H, *Z* isomer), 7.05 – 6.99 (m, 3H, *Z* isomer), 6.73 (dd, *J* = 17.6, 10.8 Hz, 0.27H, *E* isomer), 6.88 (s, 0.27H, *E* isomer), 6.83 (dd, *J* = 17.3, 10.8 Hz, 0.27H, *E* isomer), 6.79 (s, 0.29H, *E* isomer), 6.71 (dd, *J* = 17.3, 10.8 Hz, 0.73H, *Z* isomer), 6.69 (s, 0.71H, *Z* isomer), 6.54 (s, 0.73H, *Z* isomer), 5.10 (d, *J* = 10.8 Hz, 1H, *E* and *Z* isomer), 5.05 (d, *J* = 17.5 Hz, 1H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 160.6 (d, $^1J_{C\text{-}F}$ = 238.2 Hz, C_q), 157.9 (CH), 157.3 (C_q), 140.5 (CH), 137.2 (C_q), 136.7 (C_q), 135.8 (d, $^4J_{C\text{-}F}$ = 4.2 Hz, C_q), 133.9 (C_q), 133.0 (CH), 129.1 (CH), 128.1 (CH), 127.2 (CH), 125.9 (C_q), 121.3 (d, $^3J_{C\text{-}F}$ = 10.0 Hz, CH), 117.2 (CH), 115.7 (CH_2), 110.5 (d, $^2J_{C\text{-}F}$ = 24.8 Hz, CH), 108.5 (CH), 101.6 (d, $^2J_{C\text{-}F}$ = 28.5 Hz, CH). *Minor isomer*: δ = 161.2 (d, $^1J_{C\text{-}F}$ = 238.2 Hz, C_q), 158.2 (CH), 157.8 (C_q), 140.9 (CH), 136.8 (C_q), 136.7 (C_q), 134.0 (C_q), 130.8 (CH), 129.8 (CH), 128.3 (CH), 127.4 (CH), 125.3 (C_q), 121.2 (CH), 121.1 (CH), 115.7 (CH_2), 109.2 (CH), 107.7 (d, $^2J_{C\text{-}F}$ = 24.8 Hz, CH), 108.8 (d, $^2J_{C\text{-}F}$ = 28.5 Hz, CH). One C_q is missing due to low signal to noise ratio or signal overlap. **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -118.5 – -118.6 (m, *E* isomer), -118.9 – -119.0 (m, *Z* isomer). **IR** (ATR): 3050, 1724, 1566, 1418, 1261, 1077, 986 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$, 364 (20) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3F$ $[M+H]^+$ 342.1401, found 342.1398.



(*Z*)-6-Chloro-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3la)

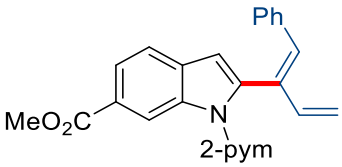
The general procedure **A** was followed using 6-chloro-1-(pyrimidin-2-yl)-1*H*-indole (**1l**) (45.9 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 4.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3la** (43.7 mg, 61%, *Z/E* = 2.2/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 4.8 Hz, 0.62H, *E* isomer), 8.65 (d, *J* = 4.8 Hz, 1.38H, *Z* isomer), 8.39 (d, *J* = 1.9 Hz, 0.69H, *Z* isomer), 8.31 (d, *J* = 1.9 Hz, 0.31H, *E* isomer), 7.57 (d, *J* = 8.3 Hz, 0.31H, *E* isomer), 7.50 (d, *J* = 8.3 Hz, 0.69H, *E* isomer), 7.47 – 7.38 (m, 2H, *E* and *Z* isomer), 7.34 – 7.31 (m, 0.32H, *E* isomer), 7.23 (dd, *J* = 8.4, 1.9 Hz, 0.32H, *E* isomer), 7.23 (dd, *J* = 8.4, 1.9 Hz, 0.68H, *Z* isomer), 7.13 (t, *J* = 4.8 Hz, 0.34H, *E* isomer), 7.12 – 7.07 (m, 2H, *E* and *Z* isomer), 7.06 (t, *J* = 4.8 Hz, 0.68H, *Z* isomer), 7.01 – 6.98 (m, 1H, *E* isomer), 6.89 (s, 0.32H, *E* isomer), 6.82 (dd, *J* = 17.1, 10.4 Hz, 0.33H, *E* isomer), 6.78 (s, 0.32H, *Z* isomer), 6.69 (s, 0.68H, *Z* isomer), 6.69 (dd, *J* = 17.1, 10.4 Hz, 0.67H, *Z* isomer), 6.53 (s, 0.68H, *Z* isomer), 5.07 (d, *J* = 10.4 Hz, 0.88H, *Z* isomer), 4.99 (d, *J* = 17.1 Hz, 1H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.2 (C_q), 140.4 (CH), 136.9 (C_q), 136.6 (C_q), 136.2 (C_q), 133.7 (C_q), 133.2 (CH), 129.3 (C_q), 129.1 (CH), 128.1 (CH), 128.0 (C_q), 127.3 (CH), 122.6 (CH), 121.5 (CH), 117.4 (CH), 115.7 (CH_2), 114.5 (CH), 108.4 (CH). *Minor isomer*: δ = 158.3 (CH), 157.7 (C_q), 141.2 (CH), 137.6 (C_q), 137.2 (C_q), 136.6 (C_q), 134.7 (CH), 131.2 (C_q), 129.8 (CH), 129.5 (C_q), 128.4 (CH), 127.7 (C_q), 127.5 (CH), 122.7 (CH), 121.4 (CH), 117.7 (CH_2), 117.7 (CH), 113.7 (CH), 109.1 (CH). **IR** (ATR): 3051, 1709, 1567, 1426, 1352, 1315, 1264, 1218, 908, 811 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 358 (80) (^{35}Cl) $[M+H]^+$, 380 (100) (^{35}Cl) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{16}N_3{}^{35}ClNa$ $[M+Na]^+$ 380.0925, found 380.0925.



(*Z*)-6-Methoxy-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3ma)

The general procedure **A** was followed using 6-methoxyl-1-(pyrimidin-2-yl)-1*H*-indole (**1m**) (45.0 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3ma** (43.1 mg, 61%, *Z/E* = 3.6/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 4.8 Hz, 0.42H, *E* isomer), 8.63 (d, *J* = 4.8 Hz, 1.58H, *Z* isomer), 7.96 (d, *J* = 2.3 Hz, 0.79H, *Z* isomer), 7.87 (d, *J* = 2.3 Hz, 0.21H, *E* isomer), 7.54 (d, *J* = 8.6 Hz, 0.21H, *E* isomer), 7.48 (d, *J* = 8.5 Hz, 0.79H, *Z* isomer), 7.44 – 7.36 (m, 0.89H, *Z* isomer), 7.33 – 7.29 (m, 0.21H, *E* isomer), 7.12 – 7.06 (m, 4H, *E* and *Z* isomer), 7.02 (t, *J* = 4.8 Hz, 0.80H, *Z* isomer),

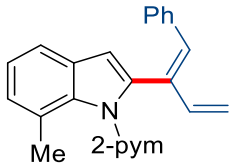
6.92 (dd, *J* = 8.5, 2.3 Hz, 1H, *E* and *Z* isomer), 6.87 (s, 0.23H, *E* isomer), 6.83 (dd, *J* = 17.3, 10.5 Hz, 0.23H, *E* isomer), 6.76 (s, 0.26H, *E* isomer), 6.71 (dd, *J* = 17.3, 10.5 Hz, 0.77H, *Z* isomer), 6.66 (s, 0.77H, *Z* isomer), 6.49 (s, 0.79H, *Z* isomer), 5.08 (d, *J* = 17.3 Hz, 0.21H, *E* isomer), 5.05 (d, *J* = 10.5 Hz, 0.79H, *Z* isomer), 5.02 (d, *J* = 17.3 Hz, 0.79H, *Z* isomer), 4.99 (d, *J* = 10.5 Hz, 0.21H, *E* isomer), 3.92 (s, 3H, *E* and *Z* isomer). **^{13}C NMR** (126 MHz, $CDCl_3$) *Major isomer*: δ = 157.9 (CH), 157.6 (C_q), 157.3 (C_q), 140.8 (CH), 137.6 (C_q), 136.9 (C_q), 134.3 (C_q), 134.2 (C_q), 132.6 (CH), 129.2 (CH), 128.1 (CH), 127.1 (CH), 123.7 (C_q), 121.2 (CH), 116.9 (CH), 115.6 (CH_2), 111.3 (CH), 108.6 (CH), 98.7 (CH), 55.9 (CH_3). *Minor isomer*: δ = 158.1 (CH), 157.8 (C_q), 157.6 (C_q), 139.5 (CH), 138.2 (C_q), 137.4 (C_q), 134.9 (C_q), 134.3 (C_q), 130.2 (CH), 129.8 (CH), 128.3 (CH), 127.3 (CH), 123.3 (C_q), 121.1 (CH), 117.6 (CH_2), 117.2 (CH), 111.3 (CH), 109.4 (CH), 97.8 (CH). One CH_3 is missing due to signal overlap. **IR** (ATR): 2924, 1948, 1612, 1565, 1484, 1418, 1265, 1159, 906, 728 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 354 (100) $[M+H]^+$, 376 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}N_3O$ $[M+H]^+$ 354.1606, found 354.1590.



Methyl (*Z*)-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole-6-carboxylate (3na)

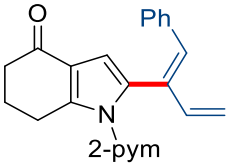
The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole-6-carboxylate (**1n**) (50.7 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.9 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 5:1) yielded **3na** (59.5 mg, 78%, *Z/E* = 3.8/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 9.00 (s, 0.79H, *Z* isomer), 8.92 (s, 0.21H, *E* isomer), 8.77 (d, *J* = 4.8 Hz, 0.42H, *E* isomer), 8.68 (d, *J* = 4.8 Hz, 1.58H, *Z* isomer), 7.96 (d, *J* = 8.3 Hz, 1H, *E* and *Z* isomer), 7.69 (d, *J* = 8.3 Hz, 0.21H, *E* isomer), 7.63 (d, *J* = 8.3 Hz, 0.79H, *Z* isomer), 7.40 (d, *J* = 7.6 Hz, 1H, *E* and *Z* isomer), 7.33 (d, *J* = 6.7 Hz, 0.22H, *E* isomer), 7.15 (t, *J* = 4.8 Hz, 0.25H, *E* isomer), 7.11 – 6.98 (m, 5H, *E* and *Z* isomer), 6.92 (s, 0.21H, *E* isomer), 6.86 (dd, *J* = 17.2, 10.5 Hz, 0.23H, *E* isomer), 6.86 (s, 0.19H, *E* isomer), 6.72 (s, 0.77H, *Z* isomer), 6.70 (dd, *J* = 17.2, 10.5 Hz, 0.81H, *Z* isomer), 6.61 (s, 0.79H, *Z* isomer), 5.08 (d, *J* = 10.5 Hz, 1H, *E* and *Z* isomer), 5.00 (d, *J* = 17.2 Hz, 1H, *E* and *Z* isomer), 3.97 (s, 3H, *E* and *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 168.2 (C_q), 158.1 (CH), 157.1 (C_q), 140.1 (CH), 138.8 (C_q), 136.4 (C_q), 136.0 (C_q), 133.6 (CH), 133.4 (C_q), 133.1 (C_q), 129.0 (CH), 128.2 (CH), 127.4 (CH), 125.1 (C_q), 123.1

(CH), 120.4 (CH), 117.6 (CH), 116.3 (CH), 115.8 (CH_2), 108.4 (CH), 52.1 (CH_3). *Minor isomer*: δ = 168.1 (C_q), 158.4 (CH), 158.0 (C_q), 143.7 (CH), 137.0 (C_q), 136.7 (C_q), 134.4 (CH), 132.8 (C_q), 131.8 (C_q), 129.8 (CH), 128.4 (CH), 127.6 (CH), 125.2 (C_q), 123.2 (CH), 120.3 (CH), 118.0 (CH_2), 117.9 (CH), 115.5 (CH), 109.0 (CH), 52.1 (CH_3). One C_q is missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 3052, 2950, 1709, 1566, 1421, 1361, 1276, 1217, 1092, 990, 804, 732 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 382 (100) $[M+H]^+$, 404 (75) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{20}N_3O_2$ $[M+H]^+$ 382.1550, found 382.1543.



(*Z*)-7-Methyl-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3oa)

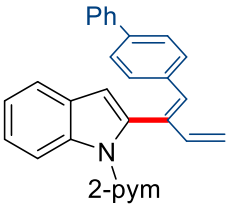
The general procedure **A** was followed using 7-methyl-1-(pyrimidin-2-yl)-1*H*-indole (**1o**) (41.8 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.9 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3na** (41.2 mg, 61%, *Z/E* = 3.6/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.78 (d, *J* = 4.8 Hz, 0.43H, *E* isomer), 8.64 (d, *J* = 4.8 Hz, 1.57H, *Z* isomer), 7.59 (d, *J* = 7.8 Hz, 0.22H, *E* isomer), 7.55 (d, *J* = 7.8 Hz, 0.78H, *Z* isomer), 7.42 – 7.29 (m, 1H, *E* and *Z* isomer), 7.22 – 7.18 (m, 1H, *E* and *Z* isomer), 7.15 – 7.11 (m, 5H, *E* and *Z* isomer), 7.10 (t, *J* = 4.8 Hz, 1H, *E* and *Z* isomer), 6.81 (s, 0.22H, *E* isomer), 6.79 (s, 0.22H, *E* isomer), 6.72 (dd, *J* = 17.0, 10.6, 0.78 Hz, 0.22H, *E* isomer), 6.69 (s, 0.78H, *Z* isomer), 6.59 (s, 0.78H, *Z* isomer), 6.58 (dd, *J* = 17.0, 10.6 Hz, 0.78H, *Z* isomer), 5.19 (d, *J* = 17.0 Hz, 0.22H, *E* isomer), 5.07 (d, *J* = 10.6 Hz, 1H, *E* and *Z* isomer), 5.00 (d, *J* = 17.0, 0.78H, *Z* isomer), 2.14 (s, 2.44H, *Z* isomer), 2.11 (s, 0.66H, *E* isomer). **^{13}C NMR** (75 MHz, $CDCl_3$) *Major isomer*: δ = 158.1 (C_q), 157.6 (CH), 140.2 (CH), 136.4 (C_q), 136.2 (C_q), 136.2 (C_q), 135.1 (CH), 132.7 (C_q), 129.9 (C_q), 129.3 (CH), 128.1 (CH), 127.5 (CH), 125.9 (CH), 122.7 (C_q), 121.5 (CH), 118.8 (CH), 118.5 (CH), 116.5 (CH_2), 106.6 (CH), 20.7 (CH_3). *Minor isomer*: δ = 159.0 (C_q), 158.0 (CH), 140.9 (CH), 136.9 (C_q), 133.5 (CH), 133.4 (C_q), 133.3 (C_q), 132.8 (C_q), 129.6 (CH), 129.5 (C_q), 128.3 (CH), 127.4 (CH), 126.0 (CH), 122.0 (C_q), 121.4 (CH), 119.3 (CH_2), 119.1 (CH), 118.7 (CH), 107.2 (CH), 20.5 (CH_3). **IR** (ATR): 3051, 1691, 1567, 1422, 1309, 1208, 1058, 913, 868, 733 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (80) $[M+H]^+$, 360 (25) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}N_3$ $[M+H]^+$ 338.1652, found 338.1647.



(*Z*)-2-(1-phenylbuta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1,5,6,7-tetrahydro-4*H*-indol-4-one (3pa)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1,5,6,7-tetrahydro-4*H*-indol-4-one (**1p**) (42.4 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.9 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 3:1) yielded (*Z*)-**3pa** (38.7 mg, 57%) as a yellow solid and (*E*)-**3pa** (19.2 mg, 28%) as a yellow solid. (*Z*)-**3pa: M.p.** = 148–150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.54 (d, *J* = 4.8 Hz, 2H), 7.13 – 7.05 (m, 4H), 6.88 – 6.82 (m, 2H), 6.64 (s, 1H), 6.60 (dd, *J* = 17.2, 10.5 Hz, 1H), 6.49 (s, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.14 (d, *J* = 10.5 Hz, 1H), 3.02 (t, *J* = 6.0 Hz, 2H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.18 (tt, *J* = 6.0, 6.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 195.2 (C_q), 157.9 (CH), 156.2 (C_q), 145.6 (C_q), 140.1 (CH), 136.4 (C_q), 133.4 (CH), 132.3 (C_q), 130.1 (C_q), 128.8 (CH), 128.1 (CH), 127.3 (CH), 122.3 (C_q), 118.7 (CH), 116.1 (CH_2), 109.4 (CH), 38.1 (CH_2), 24.3 (CH_2), 24.0 (CH_2). **IR** (ATR): 3051, 2945, 1657, 1562, 1413, 1261, 1179, 996, 903, 821, 730, 695 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$, 364(20) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{20}N_3O$ $[M+H]^+$ 342.1601, found 342.1601.

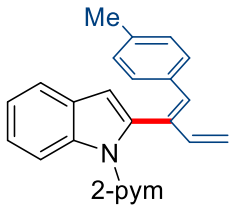
(*E*)-**3pa: M.p.** = 129–131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 4.8 Hz, 2H), 7.35 (d, *J* = 4.4 Hz, 3H), 7.32–7.25 (m, 2H), 7.22 (t, *J* = 4.9 Hz, 1H), 6.79 (s, 1H), 6.73 (s, 1H), 6.64 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.05 (d, *J* = 17.5 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 3.02 (t, *J* = 6.1 Hz, 2H), 2.58 (t, *J* = 6.4 Hz, 2H), 2.19 (tt, *J* = 6.1, 6.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 158.5 (CH), 157.1 (C_q), 145.8 (C_q), 137.1 (C_q), 135.8 (C_q), 134.2 (CH), 132.5 (C_q), 131.4 (CH), 129.7 (CH), 128.3 (CH), 127.4 (CH), 121.9 (C_q), 119.2 (CH), 118.0 (CH_2), 109.3 (CH), 38.1 (CH_2), 24.1 (CH_2), 23.9 (CH_2). **IR** (ATR): 3051, 2926, 1727, 1658, 1564, 1418, 1265, 1182, 1000, 910, 733, 700 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$, 364 (70) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{20}N_3O$ $[M+H]^+$ 342.1601, found 342.1606.



(*Z*)-2-{1-[(1,1'-Biphenyl)-4-yl]buta-1,3-dien-2-yl}-1-(pyrimidin-2-yl)-1*H*-indole (3ab)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20

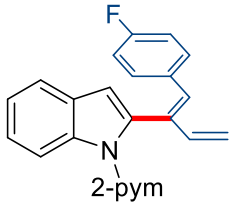
mmol) and 4-(cyclopropylidenemethyl)-1,1'-biphenyl (**2b**) (66.0 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ab** (64.7 mg, 81%, *Z/E* = 3.4/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p.** = 127–128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.8 Hz, 0.46H, *Z* isomer), 8.65 (d, *J* = 4.8 Hz, 1.54H, *E* isomer), 8.40 (d, *J* = 8.3 Hz, 0.77H, *E* isomer), 8.28 (d, J = 8.3 Hz, 0.23H, *Z* isomer), 7.71 – 7.63 (m, 2H, *E* and *Z* isomer), 7.55 – 7.47 (m, 3H, *E* and *Z* isomer), 7.39 – 7.32 (m, 5H, *E* and *Z* isomer), 7.15 (d, *J* = 8.0 Hz, 1H, *E* and *Z* isomer), 7.10 (t, *J* = 4.8 Hz, 0.34H, *Z* isomer), 7.04 (t, *J* = 4.8 Hz, 0.66H, *Z* isomer), 6.94 (s, 0.26H, *Z* isomer), 6.90 (dd, J = 17.3, 10.6 Hz, 0.37H, *Z* isomer), 6.86 (s, 0.20H, *Z* isomer), 6.75 (s, 0.80H, *E* isomer), 6.72 (dd, *J* = 17.3, 10.6 Hz, 0.65H), 6.61 (s, 0.82H, *E* isomer), 5.12 (d, *J* = 17.3 Hz, 0.22H, *Z* isomer), 5.07 (d, *J* = 10.6 Hz, 1H, *E* and *Z* isomer), 5.00 (d, *J* = 17.3 Hz, 0.78H, *E* isomer). **^{13}C NMR** (126 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.6 (C_q), 140.7 (CH), 140.6 (C_q), 139.7 (C_q), 136.7 (C_q), 135.8 (C_q), 135.5 (C_q), 134.2 (C_q), 132.7 (CH), 129.6 (CH), 129.6 (C_q), 128.8 (CH), 127.3 (CH), 126.9 (CH), 126.7 (CH), 123.4 (CH), 122.0 (CH), 120.8 (CH), 117.1 (CH), 115.7 (CH_2), 114.4 (CH), 108.6 (CH). *Minor isomer*: δ = 158.2 (CH), 158.0 (C_q), 140.8 (CH), 140.1 (C_q), 137.4 (C_q), 136.4 (C_q), 134.9 (C_q), 134.3 (C_q), 134.2 (CH), 130.4 (CH), 130.3 (C_q), 129.0 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 123.7 (CH), 122.1 (CH), 120.7 (CH), 117.9 (CH_2), 117.4 (CH), 113.4 (CH), 109.5 (CH). One C_q is missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 3032, 1716, 1688, 1564, 1420, 1347, 1305, 1212, 904, 804 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 400 (100) $[M+H]^+$, 422 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{28}H_{22}N_3$ $[M+H]^+$ 400.1808, found 400.1806.



(*Z*)-1-(Pyrimidin-2-yl)-2-[1-(p-tolyl)buta-1,3-dien-2-yl]-1*H*-indole (3ac)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-4-methylbenzene (**2c**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ac** (58.0 mg, 86%, *Z/E* = 4.7/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 4.8 Hz, 0.35H, *E* isomer), 8.65 (d, *J* = 4.8 Hz, 1.65H, *Z* isomer), 8.39 (d, *J* = 8.4 Hz, 0.82H, *Z* isomer), 8.27 (d, *J* = 8.4 Hz, 0.18H, *E* isomer), 7.69 (d, *J* = 7.8 Hz, 0.18H, *E* isomer), 7.63 (d, *J* = 7.8 Hz, 0.82H, *Z* isomer), 7.39 – 7.21 (m, 3H, *E* and *Z* isomer), 7.08 (t, *J*

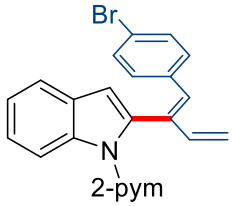
= 4.8 Hz, 0.23H, *E* isomer), 7.02 (t, *J* = 4.8 Hz, 0.77H, *Z* isomer), 6.99 – 6.91 (m, 3H, *E* and *Z* isomer), 6.89 (s, 0.21H, *E* isomer), 6.85 (dd, *J* = 17.2, 10.6 Hz, 0.18H, *E* isomer), 6.84 (s, 0.18H, *E* isomer), 6.70 (dd, *J* = 17.2, 10.6 Hz, 0.82H, *Z* isomer), 6.70 (s, 0.82H, *Z* isomer), 6.59 (s, 0.79H, *Z* isomer), 5.06 (d, *J* = 17.2 Hz, 0.13H, *E* isomer), 5.04 (d, *J* = 10.6 Hz, 0.87H, *Z* isomer), 5.01 (d, *J* = 17.2 Hz, 0.13H, *E* isomer), 4.98 (d, *J* = 17.2 Hz, 0.87H, *Z* isomer), 2.42 (s, 0.54H, *E* isomer) 2.26 (s, 2.46H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 157.9 (CH), 157.5 (C_q), 140.8 (CH), 137.1 (C_q), 136.6 (C_q), 135.7 (C_q), 133.9 (C_q), 133.2 (C_q), 133.2 (CH), 129.6 (CH), 129.1 (C_q), 128.9 (CH), 123.3 (CH), 122.0 (CH), 120.8 (CH), 117.0 (CH), 115.1 (CH_2), 114.2 (CH), 108.4 (CH), 21.3 (CH_3). *Minor isomer*: δ = 158.1 (CH), 158.0 (C_q), 140.7 (CH), 137.3 (C_q), 137.3 (C_q), 134.9 (C_q), 134.5 (C_q), 133.5 (C_q), 131.0 (CH), 129.7 (C_q), 129.2 (CH), 129.0 (CH), 123.6 (CH), 122.0 (CH), 120.6 (CH), 117.4 (CH_2), 117.3 (CH), 113.4 (CH), 109.3 (CH), 21.4 (CH_3). **IR** (ATR): 3043, 1710, 1590, 1421, 1351, 1307, 1179, 985, 899, 744 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (80) $[M+H]^+$, 360 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}N_3$ $[M+H]^+$ 338.1652, found 338.1650.



(*Z*)-2-[1-(4-fluorophenyl)buta-1,3-dien-2-yl]-1-(pyrimidin-2-yl)-1*H*-indole (3ad)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-4-fluorobenzene (**2d**) (47.4 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ad** (51.9 mg, 76%, *Z/E* = 5.1/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 4.8 Hz, 0.33H, *E* isomer), 8.66 (d, *J* = 4.8 Hz, 1.67H, *Z* isomer), 8.36 (d, *J* = 8.2, 0.83H, Z isomer), 8.30 (d, *J* = 8.2 Hz, 0.17H, *E* isomer), 7.69 (d, *J* = 7.2 Hz, 0.17H, *E* isomer), 7.64 (d, *J* = 7.2, 0.83H, *Z* isomer), 7.42 –6.98 (m, 6H, *E* and *Z* isomer), 6.88 (s, 0.20H, *E* isomer), 6.83 – 6.72 (m, 2H, *E* and *Z* isomer), 6.69 (dd, *J* = 17.0, 10.6 Hz, 0.83H, *Z* isomer), 6.66 (s, 0.83H, *Z* isomer), 6.58 (s, 0.83H, *Z* isomer), 5.13 (d, *J* = 17.0 Hz, 0.17H, *E* isomer), 5.08 (d, *J* = 10.6 Hz, 0.83H, *Z* isomer), 5.06 (d, *J* = 10.6 Hz, 0.17H, *E* isomer), 5.03 (d, *J* = 17.0 Hz, 0.83H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 161.9 (d, $^1J_{C\text{-}F}$ = 247.7 Hz, C_q), 157.9 (CH), 157.4 (C_q), 140.3 (CH), 136.7 (C_q), 135.2 (C_q), 133.85 (d, $^4J_{C\text{-}F}$ = 2.0 Hz, C_q), 132.9 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, C_q), 131.7 (CH), 130.7 (d, $^3J_{C\text{-}F}$ = 7.9 Hz, CH), 129.4 (C_q), 123.5 (CH), 122.1 (CH), 120.8 (CH), 117.1 (CH), 115.8 (CH_2), 115.1 (d, $^2J_{C\text{-}F}$ = 21.3 Hz, CH), 114.2 (CH),

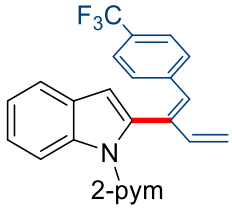
108.7 (CH). *Minor isomer*: δ = 163.0 (d, $^{1}J_{C\text{-}F}$ = 247.7 Hz, C_q), 158.1 (CH), 157.6 (C_q), 140.1 (CH), 137.3 (C_q), 134.1 (C_q), 134.1 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz, C_q), 133.4 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz, C_q), 130.9 (CH), 129.6 (CH), 129.2 (C_q), 123.8 (CH), 122.1 (CH), 120.7 (CH), 118.0 (CH), 117.3 (CH_2), 115.4 (CH), 113.5 (CH), 109.5 (CH). **^{19}F NMR** (282 MHz, $CDCl_3$) δ = (-114.1) – (-114.2) (m, *E* and *Z* isomer). **IR** (ATR): 3044, 2245, 1717, 1690, 1565, 1503, 1420, 1347, 1307, 1220, 1153, 985,906, 805, 729 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$, 364 (70) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3F$ $[M+H]^+$ 342.1401, found 342.1397.



(*Z*)-2-[1-(4-Bromophenyl)buta-1,3-dien-2-yl]-1-(pyrimidin-2-yl)-1*H*-indole (3ae)

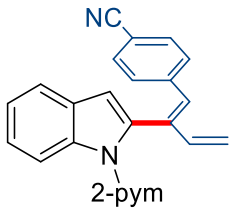
The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-4-bromobenzene (**2e**) (66.9 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ae** (48.3 mg, 60%, *Z/E* = 1.8/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 100–102 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 4.8 Hz, 0.71H, *E* isomer), 8.66 (d, *J* = 4.8 Hz, 1.30H, *Z* isomer), 8.36 (d, *J* = 8.2 Hz, 0.64H, *Z* isomer), 8.28 (d, *J* = 8.2 Hz, 0.36H, *E* isomer), 7.67 (d, *J* = 7.7 Hz, 0.36H, *E* isomer), 7.62 (d, *J* = 7.7 Hz, 0.64H, *Z* isomer), 7.52 (d, *J* = 8.2 Hz, 0.64H, *Z* isomer), 7.39 – 7.18 (m, 5H, *E* and *Z* isomer), 7.10 (t, *J* = 4.8 Hz, 0.40H, *E* isomer), 7.05 (t, *J* = 4.8 Hz, 0.60H, *Z* isomer), 6.93 (d, *J* = 8.5 Hz, 0.83H, *Z* isomer), 6.82 (s, 0.36H, *E* isomer), 6.80 (s, 0.36H, *E* isomer), 6.75 (dd, *J* = 17.2, 10.6 Hz, 0.36H, *E* isomer), 6.66 (dd, *J* = 17.2, 10.6 Hz, 0.64H, *Z* isomer), 6.62 (s, 0.64H, *Z* isomer), 6.54 (s, 0.64H, *Z* isomer), 5.08 (d, *J* = 17.2 Hz, 0.35H, *E* isomer), 5.08 (d, *J* = 10.6 Hz, 0.65H, *Z* isomer), 5.03 (d, *J* = 10.6 Hz, 0.35H, *E* isomer), 5.01 (d, *J* = 17.2 Hz, 0.65H, *Z* isomer). **^{13}C NMR** (126 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.4 (C_q), 140.3 (CH), 140.2 (C_q), 136.7 (C_q), 135.7 (C_q), 134.9 (C_q), 131.6 (CH), 131.2 (CH), 130.6 (CH), 129.4 (C_q), 123.6 (CH), 122.1 (CH), 121.1 (CH), 120.8 (C_q), 117.2 (CH), 116.3 (CH_2), 114.3 (CH), 108.7 (CH). *Minor isomer*: δ = 158.1 (CH), 157.9 (C_q), 137.4 (CH), 136.2 (C_q), 135.0 (C_q), 134.5 (C_q), 131.5 (CH), 131.3 (CH), 129.4 (CH), 129.1 (C_q), 123.8 (CH), 122.2 (CH), 121.3 (CH), 120.7 (C_q), 118.4 (CH_2), 117.4 (CH), 113.5 (CH), 109.6 (CH). One C_q is missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 3044, 1711, 1561, 1487, 1421, 1346, 1302, 1008, 906, 727 cm^{-1}. **MS** (ESI) *m/z* (relative intensity):

342 (75), (^{79}Br) $[M+H]^+$, 364 (100) (^{79}Br) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3{}^{79}Br$ $[M+H]^+$ 402.0606, found 402.0604.



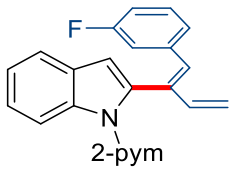
(*Z*)-1-(Pyrimidin-2-yl)-2-{1-[4-(trifluoromethyl)phenyl]buta-1,3-dien-2-yl}-1*H*-indole (3af)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-4-trifluoromethylbenzene (**2f**) (63.4 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3af** (40.7 mg, 52%, *Z/E* = 3.6/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 4.8 Hz, 0.43H, *E* isomer), 8.66 (d, *J* = 4.8 Hz, 1.57H, *Z* isomer), 8.42 (d, *J* = 8.2 Hz, 0.79H, *Z* isomer), 8.34 (d, *J* = 8.2 Hz, 0.21H, *E* isomer), 7.74 – 7.53 (m, 2H, *E* and *Z* isomer), 7.42 – 7.26 (m, 4H, *E* and *Z* isomer), 7.20 (d, *J* = 8.2 Hz, 1H, *E* and *Z* isomer), 7.10 (t, *J* = 4.9 Hz, 0.29H, *E* isomer), 7.05 (t, *J* = 4.8 Hz, 0.82H, *Z* isomer), 6.91 (s, 0.18H, *E* isomer), 6.88 (s, 0.19H, *E* isomer), 6.82 (dd, *J* = 17.3, 10.7 Hz, 0.21H, *E* isomer), 6.73 (s, 0.80H, *Z* isomer), 6.71 (dd, *J* = 17.3, 10.7 Hz, 0.88H, *Z* isomer), 6.58 (s, 0.76H, *Z* isomer), 5.17 (d, *J* = 17.3 Hz, 0.18H, *E* isomer), 5.14 (d, *J* = 10.7 Hz, 0.78H, *Z* isomer), 5.09 (d, *J* = 10.7 Hz, 0.22H, *E* isomer), 5.04 (d, *J* = 17.3 Hz, 0.82H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.5 (C_q), 140.4 (q, $^3J_{C\text{-}F}$ = 1.4 Hz, C_q), 140.1 (CH), 136.7 (C_q), 136.4 (C_q), 134.8 (C_q), 131.1 (CH), 129.4 (C_q), 129.2 (CH), 128.7 (q, $^2J_{C\text{-}F}$ = 32.3 Hz, C_q), 125.0 (q, *J* = 3.9 Hz, CH), 124.3 (q, $^1J_{C\text{-}F}$ = 271.9 Hz, C_q), 123.7 (CH), 122.2 (CH), 120.9 (CH), 117.2 (CH), 117.1 (CH_2), 114.4 (CH), 109.0 (CH). *Minor isomer*: δ = 158.1 (CH), 157.1 (C_q), 140.8 (q, $^3J_{C\text{-}F}$ = 1.4 Hz, C_q), 139.9 (CH), 137.4 (C_q), 136.2 (C_q), 134.3 (C_q), 129.9 (CH), 129.0 (CH), 129.0 (q, $^2J_{C\text{-}F}$ = 32.3 Hz, C_q), 128.6 (C_q), 128.1 (q, $^1J_{C\text{-}F}$ = 271.9 Hz, C_q), 125.2 (q, *J* = 3.9 Hz, CH), 124.0 (CH), 123.0 (CH), 120.8 (CH), 119.0 (CH_2), 117.4 (CH), 113.6 (CH), 109.8 (CH). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -62.4 (*E* isomer), -62.5 (*Z* isomer). **IR** (ATR): 3048, 1573, 1562, 1453, 1423, 1352, 1322, 1124, 1067, 827 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 392 (90) $[M+H]^+$, 414 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}N_3F_3$ $[M+H]^+$ 392.1368, found 392.1362.



(*Z*)-4-{2-[1-(Pyrimidin-2-yl)-1*H*-indol-2-yl]buta-1,3-dien-1-yl}benzonitrile (3ag)

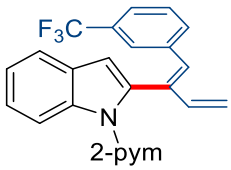
The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 4-(cyclopropylidenemethyl)benzonitrile (**2g**) (49.7 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ag** (62.7 mg, 90%, *Z/E* = 1.4/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 140–141 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 4.8 Hz, 0.84H, *E* isomer), 8.65 (d, *J* = 4.8 Hz, 1.16H, *Z* isomer), 8.37 (d, *J* = 8.4 Hz, 0.58H, *Z* isomer), 8.31 (d, *J* = 8.4 Hz, 0.42H, *E* isomer), 7.67 (d, *J* = 8.2 Hz, 1H, *E* and *Z* isomer), 7.61 (d, *J* = 7.6 Hz, 0.58H, *Z* isomer), 7.53 (d, *J* = 8.3 Hz, 0.59H, *Z* isomer), 7.38 – 7.26 (m, 2H, *E* and *Z* isomer), 7.30 – 7.26 (m, 1H, *E* and *Z* isomer), 7.16 – 7.04 (m, 2H, *E* and *Z* isomer), 7.06 (t, *J* = 4.8 Hz, 0.63H, *Z* isomer), 6.85 (s, 0.42H, *E* isomer), 6.84 (s, 0.42H, *E* isomer), 6.75 (dd, *J* = 17.3, 10.8 Hz, 0.42H, *E* isomer), 6.68 (dd, *J* = 17.3, 10.8 Hz, 0.58H, *Z* isomer), 6.67 (s, 0.58H, *Z* isomer), 6.54 (s, 0.58H, *Z* isomer), 5.16 (d, *J* = 17.3 Hz, 0.42H, *E* isomer), 5.15 (d, *J* = 10.8 Hz, 0.58H, *Z* isomer), 5.10 (d, *J* = 10.8 Hz, 0.42H, *E* isomer), 5.08 (d, *J* = 17.3 Hz, 0.58H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.4 (C_q), 141.6 (C_q), 139.8 (CH), 137.4 (C_q), 136.7 (C_q), 134.4 (C_q), 131.8 (CH), 130.2 (CH), 129.5 (CH), 129.3 (C_q), 123.9 (CH), 122.3 (CH), 120.9 (CH), 119.2 (C_q), 117.9 (CH_2), 117.2 (CH), 114.3 (CH), 110.1 (CH), 109.2 (C_q). *Minor isomer*: δ = 158.1 (CH), 157.8 (C_q), 141.9 (C_q), 139.7 (CH), 137.5 (C_q), 137.1 (C_q), 134.1 (C_q), 132.1 (CH), 130.5 (CH), 129.0 (CH), 128.3 (C_q), 124.1 (CH), 120.8 (CH), 120.8 (CH), 119.7 (CH_2), 119.1 (C_q), 117.4 (CH), 113.7 (CH), 110.5 (CH), 110.1 (C_q). **IR** (ATR): 2221, 2135, 2023, 1701, 1563, 1420, 1346, 1307, 905, 800 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 349 (100) $[M+H]^+$, 371 (40) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}N_4$ $[M+H]^+$ 349.1448, found 349.1446.



(*Z*)-2-[1-(3-Fluorophenyl)buta-1,3-dien-2-yl]-1-(pyrimidin-2-yl)-1*H*-indole (3ah)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-3-fluorobenzene (**2h**) (47.4 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ah** (53.9 mg, 79%, *Z/E*

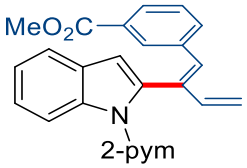
= 4.4/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.73 (d, J = 4.8 Hz, 0.37H, *E* isomer), 8.66 (d, J = 4.8 Hz, 1.63H, *Z* isomer), 8.36 (d, J = 8.3, 0.82H, Z isomer), 8.30 (d, J = 8.3 Hz, 0.18H, *E* isomer), 7.69 (d, J = 7.4 Hz, 0.18H, *E* isomer), 7.64 (d, J = 7.4 Hz, 0.82H, *Z* isomer), 7.42 – 7.12 (m, 3H, *E* and *Z* isomer), 7.14 – 6.98 (m, 2H, *E* and *Z* isomer), 6.88 – 6.72 (m, 2H, *E* and *Z* isomer), 6.69 (dd, J = 17.0, 10.6 Hz, 0.83H, *Z* isomer), 6.66 (s, 0.84H, *Z* isomer), 6.58 (s, 0.84H, *Z* isomer), 5.13 (d, J = 17.0 Hz, 0.17H, *E* isomer), 5.08 (d, J = 10.6 Hz, 0.82H, *Z* isomer), 5.06 (d, J = 10.6 Hz, 0.17H, *E* isomer), 5.03 (d, J = 17.0 Hz, 0.82H, *Z* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 162.5 (d, $^1J_{C\text{-}F}$ = 244.5 Hz, C_q), 157.9 (CH), 157.4 (C_q), 140.2 (CH), 139.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, C_q), 136.7 (C_q), 135.4 (CH), 134.8 (C_q), 134.4 (C_q), 131.4 (CH), 129.4 (CH), 129.1 (C_q), 124.8 (d, $^4J_{C\text{-}F}$ = 2.8 Hz, CH), 123.6 (CH), 122.1 (CH), 120.8 (CH), 117.1 (CH), 116.6 (CH_2), 115.7 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, CH), 114.3 (CH), 114.0 (d, $^2J_{C\text{-}F}$ = 21.4 Hz, CH), 109.0 (CH). *Minor isomer*: δ = 163.0 (d, $^1J_{C\text{-}F}$ = 247.7 Hz, C_q), 158.1 (CH), 157.6 (C_q), 140.1 (CH), 139.5 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, C_q), 137.3 (C_q), 135.3 (C_q), 131.4 (CH), 129.7 (C_q), 129.8 (CH), 129.5 (CH), 129.3 (CH), 129.1 (CH), 125.6 (d, $^4J_{C\text{-}F}$ = 2.8 Hz, CH), 123.9 (CH), 122.2 (CH), 120.7 (CH), 118.6 (CH), 117.4 (CH_2), 116.3 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, CH), 109.6 (CH). Two C_q are missing due to low signal to noise ratio or signal overlap. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -113.5 (ddd, J = 9.5, 6.4 Hz, *E* isomer), -113.8 (ddd, J = 9.5, 6.4 Hz, *Z* isomer). **IR** (ATR): 3045, 1998, 1718, 1566, 1420, 1347, 1307, 1244, 1143, 905, 803, 729 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) $[M+H]^+$, 364 (50) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3F$ $[M+H]^+$ 342.1712, found 342.1400.



(*Z*)-1-(Pyrimidin-2-yl)-2-{1-[3-(trifluoromethyl)phenyl]buta-1,3-dien-2-yl}-1*H*-indole (3ai)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-3-trifluoromethylbenzene (**2i**) (63.1 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ai** (64.2 mg, 82%, *Z/E* = 5.7/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.74 (d, J = 4.8 Hz, 0.30H, *E* isomer), 8.63 (d, J = 4.8 Hz, 1.70H, *Z* isomer), 8.32 (d, J = 8.2 Hz, 1H, *E* and *Z* isomer), 7.74 – 7.67 (m, 0.30H, *E* isomer), 7.64 (d, J = 7.8 Hz, 1H, *E* and *Z* isomer), 7.60 – 7.48 (m, 0.45H, *E* isomer), 7.41 – 7.27 (m, 2.65H, *Z* isomer), 7.41 – 7.27 (m, 3H, *E* and *Z* isomer), 7.16 – 7.12 (m, 1.70H, *Z* isomer), 7.10 (t, J = 4.8 Hz, 0.21H, *E* isomer), 7.04 (t, J = 4.8 Hz, 0.79H, *Z* isomer), 6.90 (s, 0.15H, *E* isomer), 6.86 (s, 0.15H, *E*

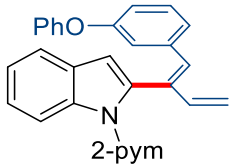
isomer), 6.79 (dd, J = 17.4, 10.4 Hz, 0.15H, *E* isomer), 6.75 (dd, J = 17.4, 10.4 Hz, 0.85H, *Z* isomer), 6.69 (s, 0.85H, *Z* isomer), 5.18 (d, J = 10.4 Hz, 0.85H, *Z* isomer), 5.15 (d, J = 17.4 Hz, 0.85H, *Z* isomer), 5.14 (d, J = 17.4 Hz, 0.15H, *E* isomer), 5.08 (d, J = 10.4 Hz, 0.15H, *E* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 157.9 (CH), 157.3 (C_q), 139.9 (CH), 137.6 (C_q), 136.7 (C_q), 135.9 (C_q), 134.5 (C_q), 131.7 (CH), 130.9 (C_q), 130.3 (q, $^2J_{C\text{-}F}$ = 32.1 Hz, C_q), 128.5 (CH), 125.9 (CH), 125.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, CH), 124.1 (q, $^1J_{C\text{-}F}$ = 273.7 Hz, C_q), 123.7 (CH), 123.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, CH), 122.1 (CH), 120.8 (CH), 117.1 (CH), 117.1 (CH_2), 114.2 (CH), 109.1 (CH). *Minor isomer*: δ = 158.1 (CH), 138.0 (CH), 137.9 (C_q), 134.1 (C_q), 132.9 (C_q), 130.6 (C_q), 129.3 (CH), 129.1 (C_q), 128.8 (CH), 126.3 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, CH), 124.0 (q, $^1J_{C\text{-}F}$ = 273.7 Hz, C_q), 123.9 (CH), 123.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, CH), 122.2 (CH), 120.8 (CH), 119.0 (CH), 117.4 (CH_2), 113.6 (CH), 109.8 (CH). Two Cq and one CH are missing due to low signal to noise ratio and signal overlap. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -62.6 (E isomer), -62.9 (*Z* isomer). **IR** (ATR): 3045, 1720, 1594, 1420, 1347, 1224, 1090, 908, 800, 731 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 392 (100) $[M+H]^+$, 414 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}N_3F_3$ $[M+H]^+$ 392.1369, found 392.1365.



Methyl (*Z*)-3-{2-[1-(pyrimidin-2-yl)-1*H*-indol-2-yl]buta-1,3-dien-1-yl}benzoate (3aj)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and methyl-3-(cyclopropylidenemethyl)benzoate (**2j**) (59.9 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 8:1) yielded **3aj** (58.7 mg, 77%, *Z/E* = 4.5/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.73 (d, J = 4.8 Hz, 0.36H, *E* isomer), 8.62 (d, J = 4.8 Hz, 1.64H, *Z* isomer), 8.34 (d, J = 8.4 Hz, 0.82H, *Z* isomer), 8.30 (d, J = 8.4 Hz, 0.18H, *E* isomer), 8.14 (s, 0.18H, *E* isomer), 7.98 (d, J = 7.8 Hz, 0.18H, *E* isomer), 7.75 (d, J = 7.6 Hz, 0.82H, *Z* isomer), 7.68 (d, J = 7.7 Hz, 0.18H, *E* isomer), 7.65 (s, 0.82H, *Z* isomer), 7.64 – 7.57 (m, 0.82H, *Z* isomer), 7.47 (t, J = 7.8 Hz, 0.19H, *E* isomer), 7.37 – 7.31 (m, 1H, *E* and *Z* isomer), 7.30 – 7.24 (m, 1H, *E* and *Z* isomer), 7.18 – 7.16 (m, 0.82H, *Z* isomer), 7.10 – 7.12 (m, 1H, *E* and *Z* isomer), 7.01 (t, J = 4.8 Hz, 0.81H, *Z* isomer), 6.89 (s, 0.18H, *E* isomer), 6.84 (s, 0.18H, *E* isomer), 6.78 (dd, J = 17.2, 10.4 Hz, 0.17H, *E* isomer), 6.73 (dd, J = 17.2, 10.4 Hz, 0.83H, *Z* isomer), 6.71(s, 0.82H, *Z* isomer), 6.59 (s, 0.82H, *Z* isomer), 5.14 (d, J = 10.4 Hz, 0.82H, *Z* isomer) , 5.12 (d, J = 17.2 Hz, 1H, *E* and *Z* isomer), 5.05 (d, J = 10.4 Hz, 0.18H, *E* isomer), 3.96 (s, 0.54H, *E* isomer), 3.75 (s, 2.56H,

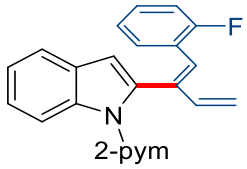
Z isomer). **^{13}C NMR** (126 MHz, $CDCl_3$) *Major isomer*: δ = 167.0 (C_q), 157.9 (CH), 157.3 (C_q), 140.2 (CH), 137.0 (C_q), 136.7 (C_q), 135.2 (C_q), 134.9 (C_q), 133.0 (CH), 131.6 (CH), 130.5 (CH), 129.9 (C_q), 129.4 (C_q), 128.2 (CH), 128.1 (CH), 123.5 (CH), 122.0 (CH), 120.8 (CH), 117.1 (CH), 116.6 (CH_2), 114.3 (CH), 108.9 (CH), 52.1 (CH_3). *Minor isomer*: δ = 167.1 (C_q), 158.1 (CH), 157.8 (C_q), 140.1 (CH), 137.5 (C_q), 137.3 (C_q), 135.3 (C_q), 134.3 (C_q), 134.0 (CH), 130.8 (CH), 130.3 (CH), 129.6 (C_q), 129.1 (C_q), 128.4 (CH), 128.3 (CH), 123.8 (CH), 122.1 (CH), 120.7 (CH), 118.6 (CH_2), 117.3 (CH), 113.5 (CH), 109.6 (CH), 52.3 (CH_3). **IR** (ATR): 3045, 1720, 1594, 1420, 1347, 1224, 1090, 908, 800, 731 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 382 (100) $[M+H]^+$, 414 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{20}N_3O_2$ $[M+H]^+$ 382.1556, found 382.1559.



(*Z*)-2-[1-(3-Phenoxyphenyl)buta-1,3-dien-2-yl]-1-(pyrimidin-2-yl)-1*H*-indole (3ak)

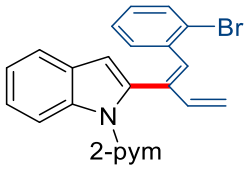
The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-3-phenoxybenzene (**2k**) (70.8 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ak** (70.6 mg, 85%, *Z*/*E* = 6.7/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 86–88 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.72 (d, *J* = 4.8 Hz, 0.26H, *E* isomer), 8.63 (d, *J* = 4.8 Hz, 1.74H, *Z* isomer), 8.34 (d, *J* = 8.2 Hz, 0.87H, *Z* isomer), 8.29 (d, *J* = 8.2 Hz, 0.13H, *E* isomer), 7.68 (d, *J* = 7.6 Hz, 0.87H, *Z* isomer), 7.44 – 6.74 (m, 12.4H, *E* and *Z* isomer), 6.66 (s, 0.87H, *Z* isomer), 6.65 (dd, *J* = 17.3, 10.8 Hz, 0.87H, *Z* isomer), 6.54 (s, 0.87H, *Z* isomer), 5.07 (d, *J* = 17.3 Hz, 0.13H, *E* isomer), 5.06 (d, *J* = 10.8 Hz, 0.87H, *Z* isomer), 5.00 (d, *J* = 17.3 Hz, 0.87H, *Z* isomer), 5.00 (d, *J* = 10.8 Hz, 0.13H, *E* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 157.8 (CH), 157.4 (C_q), 157.2 (C_q), 156.5 (C_q), 140.2 (CH), 138.6 (C_q), 136.7 (C_q), 135.1 (C_q), 134.9 (C_q), 132.1 (CH), 129.5 (CH), 129.4 (C_q), 129.3 (CH), 123.6 (CH), 123.4 (CH), 123.2 (CH), 122.0 (CH), 120.8 (CH), 119.2 (CH), 118.8 (CH), 117.7 (CH), 117.0 (CH), 116.1 (CH_2), 114.3 (CH), 108.9 (CH). *Minor isomer*: δ = 158.1 (CH), 157.9 (C_q), 157.1 (C_q), 139.0 (C_q), 137.3 (C_q), 134.8 (C_q), 134.6 (C_q), 130.1 (C_q), 129.9 (CH), 129.6 (CH), 129.1 (CH), 124.7 (CH), 123.7 (CH), 123.5 (CH), 122.1 (CH), 120.7 (CH), 119.8 (CH), 118.1 (CH_2), 117.6 (CH), 117.3 (CH), 113.5 (CH), 109.5 (CH). One C_q and two CH are missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 3047, 1692, 1568, 1423, 1244, 1154, 1079, 900, 800, 732

cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 416 (70) [M+H]$^+$, 438 (100) [M+Na]. **HR-MS** (ESI) *m/z* calcd for $C_{28}H_{22}N_3O$ [M+H] 416.1757, found 416.1744.



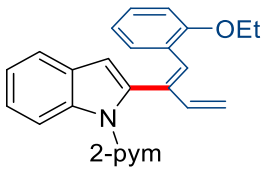
(*Z*)-2-(1-(2-Fluorophenyl)buta-1,3-dien-2-yl)-1-(pyrimidin-2-yl)-1*H*-indole (3al)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-2-fluorobenzene (**2l**) (47.1 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3al** (51.2 mg, 75%, *Z/E* = 4.8/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 4.8 Hz, 0.35H, *E* isomer), 8.65 (d, *J* = 4.8 Hz, 1.65H, *Z* isomer), 8.32 (dd, *J* = 8.2, 1.2 Hz, 1H, *E* and *Z* isomer), 7.62 (d, *J* = 7.8 Hz, 0.17H, *E* isomer), 7.62 (d, *J* = 7.8 Hz, 0.83H, *Z* isomer), 7.49 (td, *J* = 8.4, 1.5 Hz, 0.17H, *E* isomer), 7.34 (td, *J* = 8.4, 1.5 Hz, 0.84H, *Z* isomer), 7.30 – 7.12 (m, 2H, *E* and *Z* isomer), 7.21 – 7.00 (m, 2H, *E* and *Z* isomer), 7.00 – 6.82 (m, 3.H, *E* and *Z* isomer), 6.74 (dd, *J* = 18.0, 9.6 Hz, 0.87H, *Z* isomer), 6.61 (s, 0.83H, *Z* isomer), 5.16 (dd, J = 17.4 Hz, 0.13H, *E* isomer), 5.10 (d, J = 10.9 Hz, 0.87H, *Z* isomer), 5.12 (d, *J* = 17.4 Hz, 0.87H, *Z* isomer), 5.06 (d, *J* = 10.9 Hz, 0.13H, *E* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 160.6 (d, $^1J_{C\text{-}F}$ = 248.3 Hz, C_q), 157.9 (CH), 157.4 (CH), 140.2 (C_q), 136.7 (C_q), 135.5 (d, $J_{C\text{-}F}$ = 1.6 Hz, C_q), 135.1 (C_q), 130.1 (d, $^4J_{C\text{-}F}$ = 2.8 Hz, CH), 129.4 (C_q), 128.7 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, CH), 124.4 (d, $^3J_{C\text{-}F}$ = 5.1 Hz, C_q), 123.8 (CH), 123.8 (CH), 123.6 (CH), 122.0 (CH), 120.8 (CH), 117.1 (CH), 116.5 (CH_2), 114.8 (d, $^2J_{C\text{-}F}$ = 21.9 Hz, CH), 114.1 (CH), 109.0 (CH). *Minor isomer*: δ = 158.1 (CH), 157.8 (CH), 139.8 (C_q), 137.3 (C_q), 135.8 (C_q), 134.5 (C_q), 131.3 (d, $^4J_{C\text{-}F}$ = 2.8 Hz, CH), 129.2 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, CH), 129.1 (C_q), 124.6 (d, $^3J_{C\text{-}F}$ = 5.1 Hz, C_q), 123.7 (CH), 123.7 (CH), 123.6 (CH), 122.1 (CH), 120.7 (CH), 118.3 (CH_2), 117.3 (CH), 115.6 (d, $^2J_{C\text{-}F}$ = 21.9 Hz, CH), 113.6 (CH), 109.5 (CH). One C_q is missing due to low signal to noise ratio or signal overlap. **^{19}F NMR** (282 MHz, $CDCl_3$) δ = (-113.9) – (-114.0) (m, *E* isomer), (-116.9) – (-117.0) (m, *Z* isomer). **IR** (ATR): 3044, 1565, 1437, 1421, 1347, 1347, 1071, 906, 803, 727 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 342 (100) [M+H]$^+$, 364 (25) [M+Na]$^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3F$ [M+H]$^+$ 342.1407, found 342.1401.



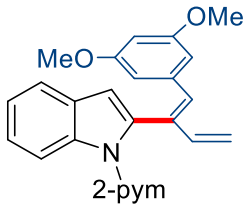
(*Z*)-2-[1-(2-Bromophenyl)buta-1,3-dien-2-yl]-1-(pyrimidin-2-yl)-1*H*-indole (3am)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-2-bromobenzene (**2m**) (66.6 mg, 0.32 mmol) for 4.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3am** (49.1 mg, 61%, *Z/E* = 1.3/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 143–145 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.75 (d, *J* = 4.8 Hz, 0.86H, *E* isomer), 8.65 (d, *J* = 4.8 Hz, 1.10H, *Z* isomer), 8.31 (d, *J* = 8.4 Hz, 0.50H, *E* isomer), 8.22 (d, *J* = 8.3 Hz, 0.51H, *Z* isomer), 7.68 (d, *J* = 7.7 Hz, 0.50H, *E* isomer), 7.63 (dd, *J* = 8.0, 1.5 Hz, 0.50H, *E* isomer). 7.59 (d, *J* = 7.8 Hz, 0.56H, *Z* isomer), 7.47 (d, *J* = 7.6 Hz, 0.52H, *Z* isomer), 7.40 – 7.30 (m, 2H, *Z* and *E* isomer), 7.26 – 7.13 (m, 1H, *Z* and *E* isomer), 7.13 – 7.08 (m, 0.62H, *E* isomer). 7.05 (t, *J* = 4.8 Hz, 0.70H, *Z* isomer), 7.03 – 6.98 (m, 0.65H, *E* isomer), 6.91 (t, *J* = 7.4, 1H, *Z* and *E* isomer), 6.85 (s, 0.48H, *E* isomer), 6.80 (s, 1.13H, *Z* isomer), 6.76 (d, *J* = 6.7 Hz, 0.30H, *E* isomer), 6.68 (dd, *J* = 17.6, 10.6 Hz, 0.61H, *Z* isomer), 6.59 (s, 0.58H, *E* isomer), 5.22 (d, *J* = 17.3 Hz, 0.54H, *Z* isomer), 5.18 (d, *J* = 10.6 Hz, 0.67H, *Z* isomer), 5.15 (d, *J* = 11.1 Hz, 0.51H, *E* isomer), 5.05 (ddd, *J* = 10.6, 1.7, 1.7 Hz, 0.52H, *E* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.2 (C_q), 139.8 (CH), 139.4 (C_q), 137.3 (C_q), 136.8 (C_q), 135.3 (C_q), 132.0 (CH), 131.1 (CH), 130.8 (CH), 129.2 (C_q), 128.5 (CH), 127.1 (CH), 124.3 (C_q), 123.6 (CH), 122.0 (CH), 120.8 (CH), 117.2 (CH), 116.9 (CH_2), 113.9 (CH), 109.6 (CH). *Minor isomer*: δ = 158.2 (C_q), 158.1 (CH), 137.3 (C_q), 136.7 (C_q), 135.4 (C_q), 134.7 (C_q), 134.3 (CH), 132.8 (CH), 131.7 (CH), 130.7 (CH), 129.2 (C_q), 128.9 (CH), 127.0 (CH), 124.6 (C_q), 123.8 (CH), 122.2 (CH), 120.7 (CH), 118.4 (CH_2), 117.3 (CH), 113.7 (CH), 109.5 (CH). **IR** (ATR): 3049, 1695, 1565, 1423, 1349, 1262, 1213, 1013, 987, 805 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 381 (45), 402 (100) (^{79}Br) $[M+H]^+$, 424 (70) (^{79}Br) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{17}N_3{}^{79}Br$ $[M+H]^+$ 402.0606, found 402.0594.



(*Z*)-2-[1-(2-Ethoxyphenyl)buta-1,3-dien-2-yl]-1-(pyrimidin-2-yl)-1*H*-indole (3an)

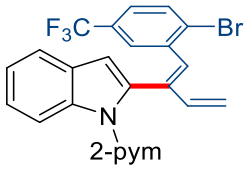
The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-2-ethoxybenzene (**2n**) (66.6 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3an** (57.3 mg, 78%, *Z/E* = 3.0/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 86–89 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 4.8 Hz, 0.50H, *E* isomer), 8.64 (d, *J* = 4.8 Hz, 1.51H, *Z* isomer), 8.29 (d, *J* = 8.1 Hz, 1H, *Z* and *E* isomer), 7.69 (d, *J* = 7.5 Hz, 0.28H, *E* isomer), 7.61 (d, *J* = 7.6 Hz, 0.72H, *Z* isomer), 7.47 (d, *J* = 7.5 Hz, 0.28H, *E* isomer), 7.32 (t, *J* = 7.2 Hz, 0.88H, *Z* isomer), 7.25 (t, *J* = 7.6 Hz, 1H, *Z* and *E* isomer), 7.09 – 6.86 (m, 4H, *Z* and *E* isomer), 6.83 (d, *J* = 4.6 Hz, 0.39H, *E* isomer), 6.78 (dd, *J* = 16.4, 11.2 Hz, 0.65H, *Z* isomer), 6.72 (d, *J* = 8.2 Hz, 0.68H, *E* isomer), 6.61 (s, 0.70H, *Z* isomer), 6.58 (t, *J* = 7.5 Hz, 0.75H, *Z* isomer), 5.17 (d, *J* = 16.4 Hz, 0.33H, *E* isomer), 5.10 (d, *J* = 11.2 Hz, 0.77H, *Z* isomer), 5.06 (d, *J* = 16.4 Hz, 0.77H, *Z* isomer), 5.07 (d, *J* = 11.2 Hz, 0.33H, *E* isomer), 4.09 (q, *J* = 7.0 Hz, 0.61H, *E* isomer). 3.99 (q, *J* = 7.2 Hz, 1.39H, *Z* isomer), 1.46 (t, *J* = 7.2 Hz, 2.11H, *Z* isomer), 1.41 (t, *J* = 7.0 Hz, 0.91H, *E* isomer). **^{13}C NMR** (75 MHz, $CDCl_3$) *Major isomer:* δ = 157.8 (CH), 157.4 (C_q), 156.7 (C_q), 140.8 (CH), 136.7 (C_q), 135.9 (C_q), 133.2 (C_q), 129.9 (CH), 129.5 (C_q), 128.4 (CH), 128.1 (CH), 125.7 (C_q), 123.2 (CH), 121.8 (CH), 120.7 (CH), 120.3 (CH), 116.8 (CH), 114.9 (CH_2), 113.9 (CH), 111.0 (CH), 108.7 (CH), 63.7 (CH_2), 15.1 (CH_3). *Minor isomer:* δ = 158.0 (CH), 157.1 (C_q), 140.6 (CH), 137.2 (C_q), 135.2 (C_q), 133.3 (C_q), 131.1 (CH), 129.3 (C_q), 128.8 (CH), 127.4 (CH), 126.5 (C_q), 123.5 (CH), 122.0 (CH), 120.6 (CH), 120.1 (CH), 117.3 (CH_2), 117.1 (CH), 113.4 (CH), 112.0 (CH), 109.1 (CH), 64.2 (CH_2), 15.0 (CH_3). One C_q is missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 2978, 2508, 2162, 2088, 2011, 1957, 1563, 1422, 1239, 1039, 742 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 368 (50) $[M+H]^+$, 390 (60) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{21}N_3ONa$ $[M+Na]^+$ 390.1577, found 390.1574.



(*Z*)-2-[1-(3,5-Dimethoxyphenyl)buta-1,3-dien-2-yl]-1-(pyrimidin-2-yl)-1*H*-indole (3ao)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-3,5-dimethoxybenzene (**2o**) (60.6 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3ao** (69.8 mg, 91%, *Z/E* = 3.8/1 determined by ^{1}H NMR spectroscopy) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$)

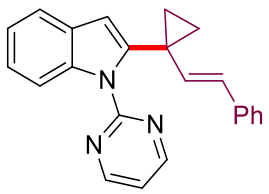
δ = 8.73 (d, *J* = 4.8 Hz, 0.42H, *E* isomer), 8.63 (dd, *J* = 4.8 Hz, 1.58H, *Z* isomer), 8.33 (d, *J* = 7.8 Hz, 0.78H, *Z* isomer), 8.28 (d, *J* = 8.5 Hz, 0.22H, *E* isomer), 7.68 (d, *J* = 7.8 Hz, 0.22H, *E* isomer), 7.64 (dd, *J* = 7.8 Hz, 0.78H, *Z* isomer), 7.32 (t, *J* = 7.2 Hz, 1H, *Z* and *E* isomer), 7.25 (t, *J* = 7.2 Hz, 1H, *Z* and *E* isomer), 7.09 (t, *J* = 4.8 Hz, 0.24H, *E* isomer), 7.01 (t, *J* = 4.8 Hz, 0.76H, *Z* isomer), 6.86 – 6.83 (m, 0.45H, *E* isomer), 6.78 (dd, *J* = 17.2, 10.5 Hz, 0.80H, *Z* isomer), 6.66 (s, 0.73H, *Z* isomer), 6.64 (d, *J* = 2.3 Hz, 0.40H, *E* isomer), 6.59 (s, 0.72H, *Z* isomer), 6.46 (t, *J* = 2.3 Hz, 0.23H, *E* isomer), 6.22 (t, *J* = 2.1 Hz, 0.83H, *Z* isomer), 6.07 (d, *J* = 2.1 Hz, 1.31H, *Z* isomer), 5.25 (d, *J* = 17.2 Hz, 0.77H, *Z* isomer), 5.21 (d, *J* = 10.5 Hz, 0.78H, *Z* isomer), 5.08 (d, *J* = 17.5 Hz, 0.23H, *E* isomer), 5.01 (d, *J* = 10.8 Hz, 0.22H, *E* isomer), 3.84 (s, 1.26H, *E* isomer), 3.38 (s, 4.74H, *Z* isomer). **^{13}C NMR** (75 MHz, $CDCl_3$) *Major isomer*: δ = 160.2 (C_q), 157.8 (CH), 157.2 (C_q), 140.4 (CH), 138.3 (C_q), 136.6 (C_q), 135.0 (C_q), 134.5 (C_q), 132.8 (CH), 129.4 (C_q), 123.4 (CH), 122.0 (CH), 120.6 (CH), 117.0 (CH), 116.3 (CH_2), 114.3 (CH), 108.7 (CH), 106.5 (CH), 100.6 (CH), 55.0 (CH_3). *Minor isomer*: δ = 160.6 (C_q), 158.1 (CH), 140.3 (CH), 139.1 (C_q), 137.3 (C_q), 134.9 (C_q), 134.6 (C_q), 130.7 (CH), 129.1 (C_q), 123.7 (CH), 122.1 (CH), 120.7 (CH), 117.8 (CH), 117.3 (CH_2), 113.4 (CH), 109.4 (CH), 107.8 (CH), 99.7 (CH), 55.5 (CH_3). One C_q is missing due to low signal to noise ratio or signal overlap. **IR** (ATR): 3047, 2937, 2835, 1730, 1590, 1423, 1344, 1303, 1263, 1201, 1152, 1061, 985, 904, 805, 735 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 384 (70) $[M+H]^+$, 406 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_3O_2$ $[M+H]^+$ 384.1707, found 384.1705.



(*Z*)-2-{1-[2-Bromo-5-(trifluoromethyl)phenyl]buta-1,3-dien-2-yl}-1-(pyrimidin-2-yl)-1*H*-indole (3ap)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and 1-(cyclopropylidenemethyl)-2-bromo-5-trifluoromethylbenzene (**2p**) (88.3 mg, 0.32 mmol) for 6.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3ap** (48.0 mg, 51%, *Z*/*E* = 10.5/1 determined by ^{1}H NMR spectroscopy) as a yellow solid. **M.p. =** 71–72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (d, *J* = 4.8 Hz, 0.17H, *E* isomer), 8.60 (d, *J* = 4.8 Hz, 1.81H, *Z* isomer), 8.32 (dq, *J* = 8.4, 0.8 Hz, 0.09H, *Z* isomer), 8.18 (dq, *J* = 8.4, 0.8 Hz, 0.96H, *Z* isomer), 7.71 (d, *J* = 7.9 Hz, 0.10H, *E* isomer), 7.69 (d, *J* = 2.4 Hz, 0.10H, *E* isomer), 7.65 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 0.10H, *E* isomer), 7.54 (dd, *J* = 7.7, 1.4 Hz, 0.90H, *Z* isomer), 7.45 (d, *J* = 8.4 Hz, 0.90H, *Z* isomer), 7.38 (ddt, *J* = 8.4, 2.2, 0.6, 0.0 Hz, 0.15H, *E* isomer), 7.32

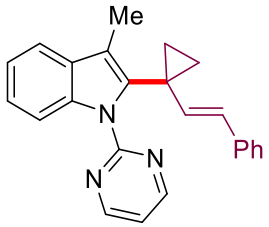
(ddd, J = 8.4, 7.1, 1.4 Hz, 0.17H, *E* isomer), 7.28 – 7.23 (m, 1H, *E* and *Z* isomer), 7.22 – 7.21 (m, 1H, *E* and *Z* isomer), 7.19 (dd, J = 7.7, 2.4 Hz, 1H, *E* and *Z* isomer), 7.11 (dd, J = 8.4, 2.3 Hz, 0.92H, *Z* isomer), 7.07 (t, J = 4.8 Hz, 0.16H, *E* isomer) , 7.02 (t, J = 4.8 Hz, 0.84H, *Z* isomer), 6.83 (d, J = 0.8 Hz, 0.08H, *E* isomer), 6.72 (dd, J = 17.5, 10.7, 0.8 Hz, 0.92H, *Z* isomer), 6.71 (s, 0.92H, *Z* isomer), 6.60 (ddd, J = 17.4, 10.7, 0.9 Hz, 0.07H, *E* isomer), 6.60 (s, 0.07H, *E* isomer), 6.56 (d, J = 0.8 Hz, 0.93H, *Z* isomer), 5.27 (dt, J = 17.5, 0.8 Hz, 0.93H, *Z* isomer), 5.21 (dt, J = 10.7, 0.8 Hz, 093H, *Z* isomer), 5.20 (dt, J = 17.5, 0.8 Hz, 0.07H, *E* isomer), 5.09 (dt, J = 10.7, 0.8 Hz, 0.07H, *E* isomer). **^{13}C NMR** (101 MHz, $CDCl_3$) *Major isomer*: δ = 158.0 (CH), 157.2 (C_q), 139.1 (CH), 137.9 (C_q), 137.3 (C_q), 136.8 (C_q), 133.8 (C_q), 132.4 (CH), 129.5 (q, $^2J_{C\text{-}F}$ = 33.5 Hz, C_q), 129.3 (CH), 129.0 (C_q), 127.9 (q, $^3J_{C\text{-}F}$ = 3.9 Hz, CH), 127.5 (C_q), 124.6 (q, $^3J_{C\text{-}F}$ = 3.6 Hz, CH), 123.9 (CH), 123.5 (q, $^1J_{C\text{-}F}$ = 272.5 Hz, C_q), 122.2 (CH), 120.8 (CH), 118.1 (CH_2), 117.2 (CH), 113.9 (CH), 110.0 (CH). *Minor isomer*: δ = 158.1 (CH), 157.9 (C_q), 138.9 (CH), 138.2 (C_q), 136.2 (C_q), 133.5 (C_q), 133.4 (CH) 132.4 (CH), 130.0 (CH), 129.0 (C_q), 128.8 (C_q), 124.0 (CH), 122.1 (CH), 120.8 (CH), 119.8 (CH), 119.4 (CH_2), 117.4 (CH), 109.8 (CH). Three C_q and one CH are missing due to low signal to noise ratio or signal overlap. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.61 (*E* isomer), -63.32 (*Z* isomer). **IR** (ATR): 3048, 2922, 1701, 1566, 1423, 1324, 1263, 1166, 1123, 1079, 1025, 912, 811, 741 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 470 (13) (^{79}Br) $[M+H]^+$, 492 (50) (^{79}Br) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{16}{}^{79}BrF_3N_3$ $[M+H]^+$ 470.0474, found 470.0459.



(*E*)-1-(Pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5aa)

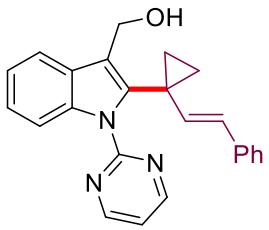
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (39.0 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5aa** (64.1 mg, 95%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.77 (d, J = 4.7 Hz, 2H), 8.17 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.14 (m, 5H), 7.09 (t, J = 4.8 Hz, 1H), 6.69 (s, 1H), 6.09 (d, J = 16.0 Hz, 1H), 6.00 (d, J = 16.0 Hz, 1H), 1.50 (dd, J = 4.6, 4.0 Hz, 2H), 1.25 (dd, J = 4.6, 4.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.3 (C_q), 158.1 (CH), 142.7 (C_q), 137.8 (C_q), 137.2 (C_q), 136.8 (CH), 128.8 (C_q), 128.4 (CH), 127.1 (CH), 126.6 (CH), 125.7 (CH), 123.1 (CH), 121.7 (CH), 120.3 (CH), 117.6 (CH), 113.4 (CH), 107.4 (CH),

22.7 (C_q), 18.4 (CH_2). **IR** (ATR): 3026, 1643, 1562, 1452, 1417, 1351, 1298, 1151, 955, 740 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (85) $[M+H]^+$, 360 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{20}N_3$ $[M+H]^+$ 338.1652, found 338.1652.



(*E*)-3-Methyl-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5ba)

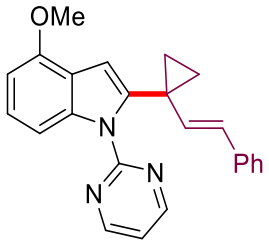
The general procedure **B** was followed using 3-methyl-1-(pyrimidin-2-yl)-1*H*-indole (41.6 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ba** (51.3 mg, 73%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 4.8 Hz, 2H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 1.7 Hz, 1H), 7.40 – 7.30 (m, 6H), 7.24 – 7.19 (m, 1H), 7.13 (td, *J* = 4.8, 1.6 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 2.44 (s, 3H), 1.18 (s, 2H), 1.04 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1 (C_q), 158.0 (CH), 138.2 (C_q), 137.2 (C_q), 136.5 (CH), 135.8 (C_q), 130.1 (C_q), 128.5 (CH), 127.2 (CH), 126.5 (CH), 125.9 (CH), 123.3 (CH), 121.5 (CH), 118.3 (CH), 117.0 (CH), 116.4 (C_q), 113.3 (CH), 21.3 (C_q), 18.1 (CH_2), 9.5 (CH_3). **IR** (ATR): 3029, 2916, 1645, 1563, 1453, 1420, 1347, 1298, 1178, 956, 736 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 352 (100) $[M+H]^+$, 374 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_3$ $[M+H]^+$, 352.1808, found 352.1808.



(*E*)-(1-(Pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indol-3-yl)methanol (5ca)

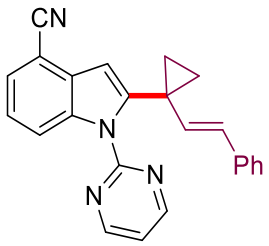
The general procedure **B** was followed using (1-(pyrimidin-2-yl)-1H-indol-3-yl)methanol (44.8 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 4.5 h. Isolation by column chromatography (*n*-hexane/EtOAc 5:1) yielded **5ca** (33.1 mg, 45%) as a colorless solid. **M.p. =** 145–146 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 4.6 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.26 (m, 6H), 7.21 – 7.17 (m, 2H), 6.31 (s, 2H), 5.06 (d, *J* = 5.0 Hz, 2H), 1.56 (t, *J* = 5.0 Hz, 1H), 1.23 – 1.15 (m, 2H), 1.15 – 1.06

(m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.3 (CH), 158.0 (C_q), 139.4 (C_q), 137.8 (C_q), 137.0 (CH), 136.1 (C_q), 128.6 (CH), 128.3 (C_q), 127.7 (CH), 126.8 (CH), 126.0 (CH), 123.8 (CH), 122.0 (CH), 119.2 (C_q), 118.8 (CH), 117.8 (CH), 113.3 (CH), 56.4 (CH_2), 21.0 (C_q), 17.8 (CH_2). **IR** (ATR): 3492, 3023, 2858, 1562, 1455, 1423, 1358, 1298, 1100, 953, 746 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 368 (20) $[M+H]^+$, 381 (40) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_3O$ $[M+H]^+$ 368.1755, found 368.1757.



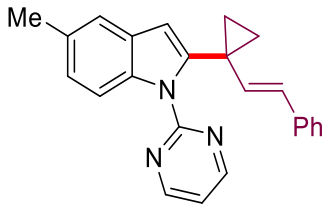
(*E*)-4-Methoxy-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5da)

The general procedure **B** was followed using 4-methoxy-1-(pyrimidin-2-yl)-1H-indole (44.8 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5da** (55.1 mg, 75%) as a colorless solid. **M.p. =** 115–116 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 4.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.17 – 7.12 (m,, 3H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.82 (s, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 4.03 (s, 3H), 1.53 – 1.48 (m, 2H), 1.25 – 1.20 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 158.3 (C_q), 158.1 (CH), 152.7 (C_q), 141.2 (C_q), 138.5 (C_q), 137.8 (C_q), 136.8 (CH), 128.3 (CH), 127.1 (CH), 126.5 (CH), 125.7 (CH), 123.9 (CH), 119.1 (C_q), 117.7 (CH), 106.7 (CH), 104.2 (CH), 101.8 (CH), 55.5 (CH_3), 22.6 (C_q), 18.3 (CH_2). **IR** (ATR): 3000, 2201, 1564, 1437, 1419, 1360, 1256, 1075, 812, 769 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 368 (100) $[M+H]^+$, 390 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_3O$ $[M+H]^+$ 368.1755, found 368.1757.



(*E*)-1-(Pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole-4-carbonitrile (5ea)

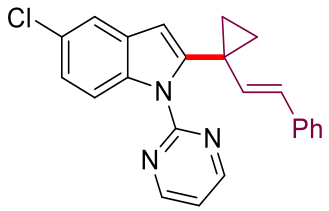
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1H-indole-4-carbonitrile (43.8 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 4.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 4:1) yielded **5ea** (39.9 mg, 55%) as a white solid. **M.p. =** 153–155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.80 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 8.2 Hz, 1H), 7.57 (dd, J = 7.4, 1.1 Hz, 1H), 7.31 (td, J = 8.1, 7.5, 1.4 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.15 – 7.09 (m, 3H), 6.88 (s, 1H), 6.01 (d, J = 16.0 Hz, 1H), 5.95 (d, J = 16.0 Hz, 1H), 1.53 – 1.49 (m, 2H), 1.29 – 1.25 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4 (CH), 157.7 (C_q), 145.9 (C_q), 137.4 (C_q), 137.0 (C_q), 135.6 (CH), 130.5 (C_q), 128.4 (CH), 127.7 (CH), 126.8 (CH), 126.5 (CH), 125.8 (CH), 122.8 (CH), 118.7 (C_q), 118.5 (CH), 118.0 (CH), 105.4 (CH), 102.7 (C_q), 22.6 (C_q), 18.4 (CH_2). **IR** (ATR): 3037, 2213, 1646, 1561, 1411, 1361, 1302, 1202, 928, 814, 775, 742 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 363 (55) $[M+H]^+$, 385 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{19}N_4$ $[M+H]^+$ 363.1604, found 363.1603.



(*E*)-5-Methyl-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5fa)

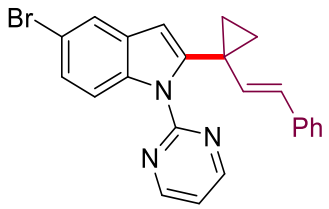
The general procedure **B** was followed using 4-methoxy-1-(pyrimidin-2-yl)-1H-indole (41.6 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5fa** (56.9 mg, 81%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.72 (d, J = 4.8 Hz, 2H), 8.07 (d, J = 8.5 Hz, 1H), 7.41 (s, 2H), 7.22 – 7.09 (m, 6H), 7.03 (t, J = 4.8 Hz, 1H), 6.59 (s, 1H), 6.04 (d, J = 16.0 Hz, 1H), 5.98 (d, J = 16.0 Hz, 1H), 2.49 (s, 3H), 1.48 – 1.36 (m, 2H), 1.23 – 1.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.3 (C_q), 158.0 (CH), 142.7 (C_q), 137.9 (C_q), 137.0 (CH), 135.5 (C_q), 131.1 (C_q), 129.1 (C_q), 128.4 (CH), 127.0 (CH), 126.5 (CH), 125.7 (CH), 124.6 (CH), 120.1 (CH), 117.3 (CH), 113.4 (CH), 107.3 (CH), 22.9 (C_q), 21.5 (CH_3), 18.4 (CH_2). **IR** (ATR): 3023, 1644, 1564, 1418, 1336, 1215, 1151, 952, 907, 802, 731, 688 cm^{-1}. **MS** (ESI)

m/z (relative intensity): 352 (100) $[M+H]^+$, 374 (95) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_3$ $[M+H]^+$ 352.1814, found 352.1808.



(*E*)-5-Chloro-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5ga)

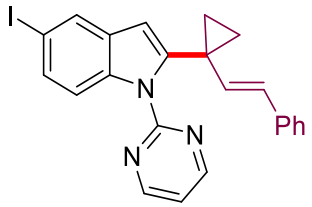
The general procedure **B** was followed using 5-chloro-1-(pyrimidin-2-yl)-1*H*-indole (45.7 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ga** (54.3 mg, 73%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 4.8 Hz, 2H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.14 – 7.10 (m, 4H), 6.60 (s, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 5.96 (d, *J* = 16.0 Hz, 1H), 1.47 – 1.44 (m, 2H), 1.24 – 1.21 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (CH), 158.0 (C_q), 144.1 (C_q), 137.7 (C_q), 136.4 (CH), 135.6 (C_q), 130.0 (C_q), 130.0 (C_q), 128.4 (CH), 127.2 (CH), 126.7 (CH), 125.8 (CH), 123.2 (CH), 119.7 (CH), 117.9 (CH), 114.7 (CH), 106.8 (CH), 22.8 (C_q), 18.4 (CH_2). **IR** (ATR): 3025, 1644, 1564, 1416, 1335, 1186, 1067, 950, 866, 800, 742, 687 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 372 (100) (^{35}Cl) $[M+H]^+$, 394 (50) (^{35}Cl) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3{}^{35}Cl$ $[M+H]^+$ 372.1268, found 372.1262



(*E*)-5-Bromo-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5ha)

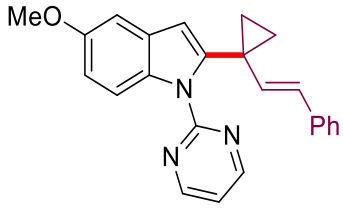
The general procedure **B** was followed using 5-bromo-1-(pyrimidin-2-yl)-1*H*-indole (54.6 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ha** (69.1 mg, 83%) as a yellow solid. **M.p. =** 153–155 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 4.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.09 (m, 4H), 6.60 (s, 1H), 6.03(d, *J* = 16.2 Hz, 1H), 5.97 (d, *J* = 16.2 Hz, 1H), 1.49 – 1.44 (m, 2H), 1.26 – 1.21 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (C_q), 158.0 (CH), 144.0 (C_q), 137.6 (C_q), 136.4 (CH), 135.9 (C_q), 130.5 (C_q), 128.4 (CH), 127.2 (CH), 126.7

(CH), 125.8 (CH), 125.7 (CH), 122.8 (CH), 117.9 (CH), 115.1 (CH), 114.9 (C_q), 106.7 (CH), 22.7 (C_q), 18.4 (CH_2). **IR** (ATR): 3022, 1644, 1563, 1415, 1334, 1185, 949, 907, 866, 799, 740, 688 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 381 (60), 416 (100) (^{79}Br) $[M+H]^+$, 438 (60) (^{79}Br) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3{}^{79}Br$ $[M+H]^+$ 416.0762, found 416.0757.



(*E*)-5-Iodo-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5ia)

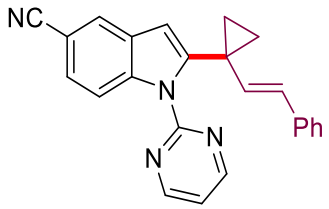
The general procedure **B** was followed using 5-iodo-1-(pyrimidin-2-yl)-1H-indole (64.0 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 4.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ia** (50.0 mg, 54%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.75 (d, *J* = 4.8 Hz, 2H), 7.95 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.15 – 7.08 (m, 4H), 6.57 (s, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 5.95 (d, *J* = 16.0 Hz, 1H), 1.49 – 1.42 (m, 2H), 1.24 – 1.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (CH), 143.6 (C_q), 137.6 (C_q), 136.5 (C_q), 136.4 (C_q), 131.4 (CH), 131.3 (C_q), 129.1 (CH), 128.4 (CH), 127.2 (CH), 126.7 (CH), 125.8 (CH), 117.9 (CH), 115.6 (CH), 106.4 (CH), 85.4 (C_q), 22.6 (C_q), 18.4 (CH_2). **IR** (ATR): 3025, 2921, 2849, 1732, 1643, 1563, 1415, 1330, 1183, 1023, 947, 799, 738, 689 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (40), 464 (100) $[M+H]^+$, 486 (60) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3I$ $[M+H]^+$ 464.0624, found 464.0618.



(*E*)-5-Methoxyl-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5ja)

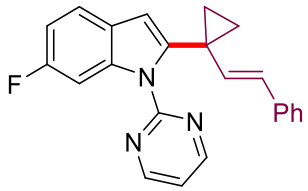
The general procedure **B** was followed using 5-methoxyl-1-(pyrimidin-2-yl)-1*H*-indole (44.8 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ja** (61.7 mg, 84%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 9.0 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.14 (m, 3H), 7.12 (d, *J* = 2.5 Hz, 1H), 7.05 (t, *J* = 4.8 Hz, 1H), 6.98 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.63 (s, 1H), 6.09 (d, *J* = 16.0 Hz, 1H), 6.03 (d, *J* = 16.0 Hz, 1H),

3.93 (s, 3H), 1.49 – 1.46 (m, 2H), 1.26 – 1.23 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (C_q), 158.0 (CH), 155.4 (C_q), 143.2 (C_q), 137.8 (C_q), 137.0 (CH), 132.1 (C_q), 129.5 (C_q), 128.4 (CH), 126.9 (CH), 126.5 (CH), 125.7 (CH), 117.2 (CH), 114.7 (CH), 112.4 (CH), 107.6 (CH), 102.5 (CH), 55.9 (CH_3), 23.0 (C_q), 18.4 (CH_2). **IR** (ATR): 3002, 1614, 1564, 1418, 1341, 1214, 1154, 1030, 951, 801, 737, 688 cm^{-1}. MS (ESI) m/z (relative intensity) 368 (100) $[M+H]^+$, 390 (25) $[M+Na]^+$. HR-MS (ESI) *m/z* calcd for $C_{24}H_{22}N_3O$ $[M+H]^+$ 368.1757 found 368.1759.



(*E*)-1-(Pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole-5-carbonitrile (5ka)

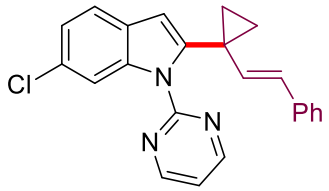
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole-5-carbonitrile (43.8 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 5:1) yielded **5ka** (60.2 mg, 83%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.80 (d, J = 4.9 Hz, 2H), 8.09 (d, J = 8.7 Hz, 1H), 7.95 (s, 1H), 7.51 (dd, J = 8.6, 1.5 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.18 – 7.07 (m, 3H), 6.69 (s, 1H), 5.99 (d, J = 16.0 Hz, 1H), 5.92 (d, J = 16.0 Hz, 1H), 1.49 – 1.46 (m, 2H), 1.26 – 1.23 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4 (CH), 157.6 (C_q), 145.3 (C_q), 138.9 (C_q), 137.3 (C_q), 135.6 (CH), 128.5 (C_q), 128.4 (CH), 127.6 (CH), 126.8 (CH), 126.0 (CH), 125.7 (CH), 125.4 (CH), 120.6 (C_q), 118.6 (CH), 114.0 (CH), 106.8 (CH), 104.7 (C_q), 22.4 (C_q), 18.3 (CH_2). **IR** (ATR): 3025, 2221, 1733, 1564, 1463, 1418, 1375, 1309, 1239, 1040, 952, 808, 743, 690 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 363 (65) $[M+H]^+$, 385 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{19}N_4$ $[M+H]^+$ 363.1604, found 363.1603.



(*E*)-6-Fluoro-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5la)

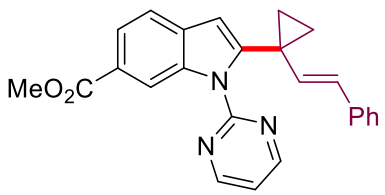
The general procedure **B** was followed using 6-fluoro-1-(pyrimidin-2-yl)-1*H*-indole (42.4 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5la** (64.0 mg, 90%) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.76 (d, J = 4.8 Hz, 2H), 7.96 (dd, J = 10.9, 2.4 Hz,

1H), 7.54 (dd, J = 8.6, 5.5 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.15 – 7.13 (m, 3H), 7.03 (td, J = 8.9, 2.3 Hz, 1H), 6.65 (d, J = 0.8 Hz, 1H), 6.07 (d, J = 16.0 Hz, 1H), 6.00 (d, J = 16.0 Hz, 1H), 1.51 – 1.46 (m, 2H), 1.28 – 1.22 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 160.6 (d, $^1J_{C\text{-}F}$ = 237.4 Hz, C_q), 158.1 (CH), 158.1 (C_q), 143.2 (d, $^4J_{C\text{-}F}$ = 3.9 Hz, C_q), 137.7 (C_q), 137.3 (d, $^3J_{C\text{-}F}$ = 12.6 Hz, C_q), 136.7 (CH), 128.4 (CH), 127.1 (CH), 126.6 (CH), 125.7 (CH), 125.1 (d, $^5J_{C\text{-}F}$ = 1.4 Hz, C_q), 120.8 (d, $^3J_{C\text{-}F}$ = 10.0 Hz, CH), 117.7 (CH), 110.1 (d, $^2J_{C\text{-}F}$ = 24.2 Hz, CH), 107.3 (CH), 100.8 (d, $^2J_{C\text{-}F}$ = 28.3 Hz, CH), 22.8 (C_q), 18.4 (CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$) δ = -119.5 (td, J = 10.1, 5.5 Hz). **IR** (ATR): 3025, 1734, 1565, 1417, 1357, 1261, 1192, 1150, 936, 813, 739, 689 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 356 (100) $[M+H]^+$, 378 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3F$ $[M+H]^+$ 356.1563, found 356.1558.



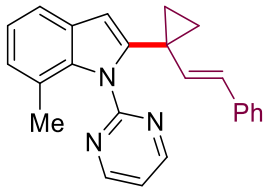
(*E*)-6-Chloro-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5ma)

The general procedure **B** was followed using 6-chloro-1-(pyrimidin-2-yl)-1*H*-indole (45.7 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ma** (58.8 mg, 79%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.77 (d, J = 4.8 Hz, 2H), 8.19 (d, J = 1.9 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.16 – 7.10 (m, 4H), 6.63 (s, 2H), 6.04 (d, J = 16.0 Hz, 1H), 5.96 (d, J = 16.0 Hz, 1H), 1.50 – 1.45 (m, 2H), 1.26 – 1.21 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (CH), 157.9 (C_q), 143.5 (C_q), 137.6 (C_q), 137.5 (C_q), 136.5 (CH), 129.0 (C_q), 128.4 (CH), 127.3 (C_q), 127.2 (CH), 126.7 (CH), 125.7 (CH), 122.3 (CH), 121.0 (CH), 117.9 (CH), 113.7 (CH), 107.2 (CH), 22.7 (C_q), 18.4 (CH_2). **IR** (ATR): 3025, 2221, 1562, 1417, 1350, 1298, 958, 911, 811, 739, 688 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 372 (100) (^{35}Cl) $[M+H]^+$, 394 (30) (^{35}Cl) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3{}^{35}Cl$ $[M+H]^+$ 372.1262, found 372.1264.



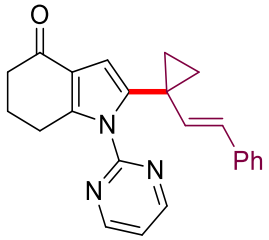
Methyl (*E*)-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole-6-carboxylate (5na)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole-6-carboxylate (50.5 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 5:1) yielded **5na** (62.5 mg, 79%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.80 (d, J = 4.8 Hz, 2H), 8.78 (s, 1H), 7.96 (dd, J = 8.3, 1.5 Hz, 1H), 7.65 (dd, J = 8.3, 0.6 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.16 – 7.10 (m, 4H), 6.70 (s, 1H), 6.04 (d, J = 16.2 Hz, 1H), 5.95 (d, J = 16.2 Hz, 1H), 3.96 (s, 3H), 1.52 – 1.46 (m, 2H), 1.27 – 1.22 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 168.2 (C_q), 158.4 (CH), 157.8 (C_q), 146.0 (C_q), 137.5 (C_q), 136.6 (C_q), 135.9 (CH), 132.5 (C_q), 128.4 (CH), 127.4 (CH), 126.7 (CH), 125.7 (CH), 124.7 (C_q), 122.8 (CH), 119.9 (CH), 118.2 (CH), 115.3 (CH), 107.0 (CH), 52.0 (CH_3), 22.6 (C_q), 18.3 (CH_2). **IR** (ATR): 3023, 2949, 1708, 1563, 1418, 1360, 1279, 1221, 1127, 1093, 956, 910, 811, 735, 688 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 396 (100) $[M+H]^+$, 418 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{22}N_3O_3$ $[M+H]^+$ 396.1712, found 396.1707.



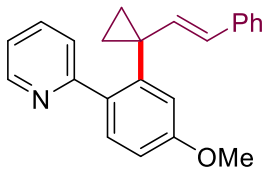
(*E*)-7-Methyl-1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indole (5oa)

The general procedure **B** was followed using 7-methyl-1-(pyrimidin-2-yl)-1*H*-indole (41.6 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5oa** (52.7 mg, 75%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.78 (d, J = 4.9 Hz, 2H), 7.54 (d, J = 7.4 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.20 – 7.12 (m, 5H), 7.04 (d, J = 7.2 Hz, 1H), 6.63 (s, 1H), 6.01 (d, J = 16.0 Hz, 1H), 5.83 (d, J = 16.0 Hz, 1H), 2.00 (s, 3H), 1.45 – 1.39 (m, 2H), 1.08 – 1.01 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.5 (C_q), 157.9 (CH), 143.2 (C_q), 137.4 (C_q), 136.9 (C_q), 134.9 (CH), 128.9 (C_q), 128.3 (CH), 127.7 (CH), 126.6 (CH), 125.8 (CH), 125.4 (CH), 121.7 (C_q), 121.2 (CH), 119.4 (CH), 118.4 (CH), 105.3 (CH), 21.5 (C_q), 19.7 (CH_3), 16.8 (CH_2). **IR** (ATR): 3029, 1644, 1593, 1560, 1415, 1355, 1229, 955, 807, 739, 689 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 352 (100) $[M+H]^+$, 374 (95) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_3$ $[M+H]^+$ 352.1808, found 352.1809.



(*E*)-1-(Pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1,5,6,7-tetrahydro-4*H*-indol-4-one (5pa)

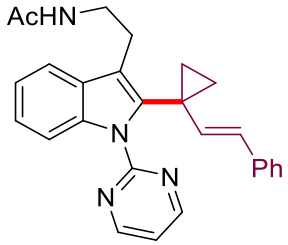
The general procedure **B** was followed using 1-(Pyrimidin-2-yl)-1,5,6,7-tetrahydro-4*H*-indol-4-one (42.5 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 2:1) yielded **5pa** (54.0 mg, 76%) as a white solid. **M.p. =** 157–159 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.75 (d, *J* = 4.8 Hz, 2H), 7.22 – 7.17 (m, 3H), 7.14 – 7.08 (m, 3H), 6.58 (s, 1H), 5.95 (d, *J* = 15.9 Hz, 1H), 5.75 (d, *J* = 15.9 Hz, 1H), 2.92 (t, *J* = 6.2 Hz, 2H), 2.55 (dd, *J* = 7.2, 5.6 Hz, 2H), 2.19 – 2.13 (m, 2H), 1.32 (dd, *J* = 3.5, 4.5 Hz, 2H), 1.03 (dd, *J* = 3.5, 4.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 158.4 (CH), 157.3 (C_q), 145.5 (C_q), 137.8 (C_q), 137.5 (C_q), 135.7 (CH), 128.4 (CH), 127.4 (CH), 126.7 (CH), 125.7 (CH), 121.0 (C_q), 119.5 (CH), 106.9 (CH), 38.0 (CH_2), 23.9 (CH_2), 23.8 (CH_2), 21.2 (C_q), 17.5 (CH_2). **IR** (ATR): 2942, 1649, 1566, 1415, 1303, 1226, 974, 940, 805, 750, 692 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 733 (100), 356 (60) $[M+H]^+$, 378 (60) $[M+Na]^+$,. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{22}N_3O$ $[M+H]^+$ 356.1763, found 356.1768.



(*E*)-2-[4-Methoxy-2-(1-styrylcyclopropyl)phenyl]pyridine (5qa)

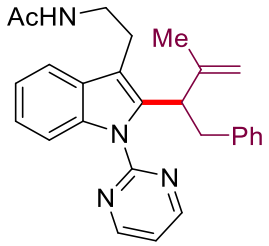
The general procedure **B** was followed using 2-(4-methoxylphenyl)pyridine (36.8 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 10:1) yielded **5qa** (26.8 mg, 41%) as a colorless solid. **M.p. =** 103–106 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.71 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.9 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.17 (m, 6H), 7.14 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.96 (dd, *J* = 8.3, 1.0 Hz, 1H), 5.95 (d, *J* = 15.9 Hz, 1H), 5.86 (d, *J* = 15.9 Hz, 1H), 3.77 (s, 3H), 1.02 – 0.97 (m, 2H), 0.76 – 0.70 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 157.3 (C_q), 156.8 (C_q), 148.7 (CH), 142.0 (C_q), 139.2 (CH), 137.7 (C_q), 135.5 (CH), 131.8 (C_q), 129.1 (CH), 128.4 (CH), 127.5 (CH), 126.6 (CH), 125.7 (CH), 125.6 (CH), 124.4 (CH), 121.7 (CH), 109.8 (CH), 55.9 (CH_3), 27.7 (C_q), 16.3 (CH_2). **IR** (ATR): 3004, 2937, 2837, 1640, 1574, 1459, 1426, 1352, 1254, 1056, 961, 784, 736, 694

cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 328 (100) $[M+H]^+$, 350 (30) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{22}NO$ $[M+H]^+$ 328.1701, found 328.1698.



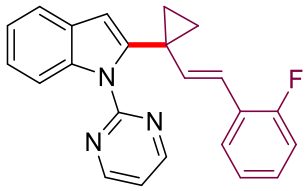
(*E*)-*N*-{2-[1-(pyrimidin-2-yl)-2-(1-styrylcyclopropyl)-1*H*-indol-3-yl]ethyl}acetamide (5ra)

The general procedure **B** was followed using *N*-(2-(1-(pyrimidin-2-yl)-1*H*-indol-3-yl)ethyl)acetamide (55.9 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (CH_2Cl_2/EtOAc 20:1) yielded **5ra** (15.2 mg, 18%) as a colorless solid and **5ra'** (28.9 mg, 34%) as a colorless solid. **5ra**: **M.p. =** 83–84 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.82 (d, *J* = 4.8 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.35 – 7.25 (m, 6H), 7.19 (t, *J* = 4.9 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 5.62 (t, *J* = 6.6 Hz, 1H), 3.68 (dt, *J* = 6.6, 6.9 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 1.74 (s, 3H), 1.22 – 1.09 (m, 2H), 1.04 – 1.09 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 170.3 (C_q), 158.3 (CH), 158.0 (C_q), 138.4 (C_q), 137.7 (C_q), 137.0 (CH), 136.1 (C_q), 129.1 (C_q), 128.7 (CH), 127.7 (CH), 127.0 (CH), 126.0 (CH), 123.6 (CH), 121.8 (CH), 118.9 (CH), 117.7 (CH), 117.0 (C_q), 113.2 (CH), 39.5 (CH_2), 25.1 (CH_2), 23.3 (CH_3), 21.0 (C_q), 18.0 (CH_2). **IR** (ATR): 3293, 3051, 2923, 1648, 1562, 1455, 1424, 1356, 1296, 1204, 963, 744, 696 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 423 (100) $[M+H]^+$, 445 (50) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{27}N_4O$ $[M+H]^+$ 423.2185, found 423.2179.



***N*-{2-[2-(3-Methyl-1-phenylbut-3-en-2-yl)-1-(pyrimidin-2-yl)-1H-indol-3-yl]ethyl}acetamide (5ra')**

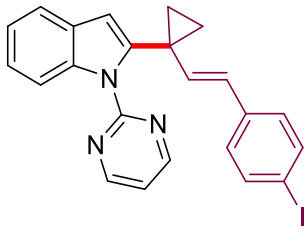
The general procedure **B** was followed using *N*-(2-(1-(pyrimidin-2-yl)-1*H*-indol-3-yl)ethyl)acetamide (55.9 mg, 0.20 mmol) and (2-cyclopropylideneethyl)benzene (**4a**) (46.1 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (CH_2Cl_2/EtOAc 20:1) yielded **5ra** (15.2 mg, 18%) as a yellow oil and **5ra'** (28.9 mg, 34%) as a yellow solid. **5ra'**: **M.p. =** 74–75 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.77 (d, J = 4.8 Hz, 2H), 7.79 – 7.73 (m, 1H), 7.61 (dd, J = 6.3, 2.8 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.12 – 7.05 (m, 3H), 7.01 – 6.96 (m, 2H), 5.46 (brs, 1H), 4.88 (d, J = 8.5 Hz, 2H), 4.57 (t, J = 7.7 Hz, 1H), 3.53 – 3.27 (m, 4H), 3.03 – 2.84 (m, 2H), 1.93 (s, 3H), 1.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 169.9 (C_q), 158.1 (CH), 158.0 (C_q), 145.8 (C_q), 140.5 (C_q), 137.0 (C_q), 136.5 (C_q), 129.4 (C_q), 128.7 (CH), 128.0 (CH), 125.9 (CH), 123.0 (CH), 121.3 (CH), 118.4 (CH), 117.8 (CH), 114.9 (C_q), 112.5 (CH), 110.7 (CH_2), 44.6 (CH), 39.5 (CH_2), 38.7 (CH_2), 24.4 (CH_2), 23.4 (CH_3), 23.1 (CH_3). **IR** (ATR): 3294, 3055, 2927, 1647, 1561, 1454, 1420, 1365, 1263, 1020, 803, 741, 698 cm−1**. MS** (ESI) *m/z* (relative intensity): 425 (65) $[M+H]^+$, 447 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{29}N_4O$ $[M+H]^+$425.2336, found 425.2340.



(*E*)-2-[1-(2-Fluorostyryl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5ab)

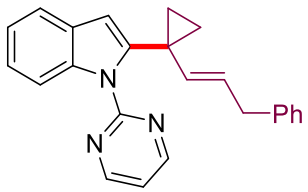
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and 1-(2-cyclopropylideneethyl)-2-fluorobenzene (**4b**) (51.9 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ab** (57.6 mg, 81%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.77 (d, J = 4.8 Hz, 2H), 8.15 (dd, J = 8.3, 1.0 Hz, 1H), 7.62 (d, J = 7.4 Hz, 1H), 7.33 – 7.15 (m, 3H), 7.13 – 7.05 (m, 2H), 7.01 – 6.89 (m, 2H), 6.67 (s, 1H), 6.16 (s, 2H), 1.49 – 1.43 (m, 2H), 1.27 – 1.22 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.84 (d, $^1J_{C\text{-}F}$ = 249 Hz, C_q), 158.3 (C_q), 158.1 (CH), 142.6 (C_q), 139.7 (d, $^4J_{C\text{-}F}$ =

5.5 Hz, CH), 137.2 (C_q), 128.1 (C_q), 127.7 (d, $^4J_{C\text{-}F}$ = 8.0 Hz, CH), 127.4 (d, $^4J_{C\text{-}F}$ = 4.2 Hz, CH), 125.6 (d, $^3J_{C\text{-}F}$ = 12 Hz, C_q), 123.9 (d, $^4J_{C\text{-}F}$ = 3.5 Hz, CH), 123.2 (CH), 121.8 (CH), 120.3 (CH), 119.8 (d, $^4J_{C\text{-}F}$ = 2.8 Hz, CH), 117.6 (CH), 115.6 (d, $^2J_{C\text{-}F}$ = 22 Hz, CH), 113.5 (CH), 107.6 (CH), 23.1 (C_q), 18.5 (CH_2). **^{19}F NMR** (377 MHz, $CDCl_3$) δ = (-117.8) – (-117.9) (m). **IR** (ATR): 3044, 1644, 1563, 1418, 1352, 1222, 1192, 958, 803, 743, 676, 629 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 356.2 (100) $[M+H]^+$, 378.2 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3F$ $[M+H]^+$ 356.1563, found 356.1559.



(*E*)-2-[1-(4-Iodostyryl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5ac)

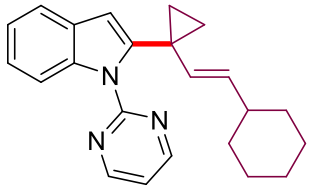
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and 1-(2-cyclopropylideneethyl)-4-iodobenzene (**4c**) (84.4 mg, 0.32 mmol) for 4.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded a mixture of **5ac** and **5aa** (51.8 mg, 45% yield for **5ac**, 15% yield for **5aa**) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.75 (d, *J* = 4.7 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.66 (s, 0.25H, **5aa**), 6.65 (s, 0.75H, **5ac**), 5.95 (s, 2H), 1.49 – 1.43 (m, 2H), 1.27 – 1.22 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.3 (C_q), 158.1 (CH), 142.3 (C_q), 137.9 (CH), 137.41 (CH), 128.8 (C_q), 128.4 (C_q), 127.6 (CH), 126.1 (C_q), 125.8 (CH), 123.2 (CH), 121.8 (CH), 120.4 (CH), 117.6 (CH), 113.5 (CH), 107.6 (CH), 91.4 (C_q), 22.8 (C_q), 18.5 (CH_2). **IR** (ATR): 3044, 2924, 1710, 1564, 1453, 1424, 1354, 1301, 1218, 1004, 959, 804, 745, 697 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 381 (100), 464 (60) $[M+H]^+$, 486 (45) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{19}N_3I$ $[M+H]^+$ 464.0617, found 464.0618.



(*E*)-2-[1-(3-phenylprop-1-en-1-yl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5ad)

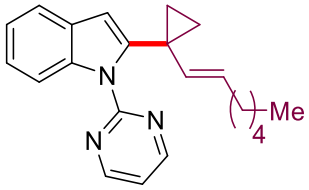
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and (3-cyclopropylidenepropyl)benzene (**4d**) (50.6 mg, 0.32 mmol) for 3.5 h. Isolation

by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ad** (52.0 mg, 74%) as a colorless solid. **M.p. =** 81–82 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.69 (d, *J* = 4.8 Hz, 2H), 8.04 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.57 (d, *J* = 6.6 Hz, 1H), 7.26 – 7.13 (m, 5H), 7.05 (t, *J* = 4.8 Hz, 1H), 6.91 (d, *J* = 6.4 Hz, 2H), 6.58 (s, 1H), 5.31 (d, *J* = 15.5 Hz, 1H), 5.22 (dt, *J* = 15.5, 5.9 Hz, 1H), 3.11 (d, *J* = 5.9 Hz, 2H), 1.39 – 1.35 (m, 2H), 1.10 – 1.06 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.2 (C_q), 157.9 (CH), 143.2 (C_q), 140.9 (C_q), 137.3 (C_q), 137.2 (CH), 128.7 (C_q), 128.5 (CH), 128.3 (CH), 126.5 (CH), 125.8 (CH), 123.0 (CH), 121.6 (CH), 120.2 (CH), 117.5 (CH), 113.2 (CH), 106.8 (CH), 38.8 (C_q), 22.0 (CH_2), 17.6 (CH_2). **IR** (ATR): 3026, 1728, 1562, 1418, 1352, 1302, 1198, 1024, 964, 802, 740, 693, 630 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 352 (75) $[M+H]^+$, 374 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}N_3$ $[M+H]^+$ 352.1814, found 352.1823.



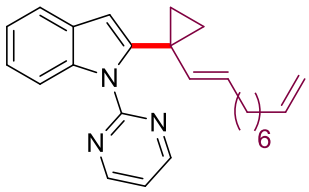
(*E*)-2-[1-(2-Cyclohexylvinyl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5ae)

The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and (2-cyclopropylideneethyl)cyclohexane (**4e**) (48.1 mg, 0.32 mmol) for 3.0 h. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **5ae** (52.9 mg, 77%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 4.8 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.27 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.16 (t, *J* = 4.8 Hz, 1H), 6.56 (s, 1H), 5.07 (d, *J* = 15.6 Hz, 1H), 4.95 (dd, *J* = 15.6, 7.0 Hz, 1H), 1.67 – 1.54 (m, 4H), 1.44 – 1.39 (m, 2H), 1.35 – 1.29 (m, 2H), 1.18 – 1.00 (m, 5H), 0.73 (ddd, *J* = 12.2, 12.2, 3.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4 (C_q), 158.1 (CH), 143.5 (C_q), 137.4 (C_q), 134.1 (CH), 133.0 (CH), 128.7 (C_q), 122.9 (CH), 121.5 (CH), 120.2 (CH), 117.5 (CH), 112.9 (CH), 106.2 (CH), 40.7 (CH), 33.2 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 21.7 (C_q), 17.7 (CH_2). **IR** (ATR): 2925, 1561, 1421, 1351, 1324, 1206, 815, 747 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 344 (40) $[M+H]^+$, 366 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{26}N_3$ $[M+H]^+$ 344.2127, found 344.2129.



(*E*)-2-[1-(Hept-1-en-1-yl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5af)

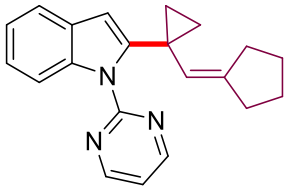
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and heptylidenecyclopropane (**4f**) (44.2 mg, 0.32 mmol) for 4.0 h. Isolation by column chromatography (*n*-hexane/CH_2Cl_2 8:1) yielded **5ag** (41.8 mg, 63%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 4.8 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.14 (m, 3H), 6.56 (s, 1H), 5.14 (d, *J* = 15.5 Hz, 1H), 5.02 (dt, *J* = 15.5, 6.5 Hz, 1H), 1.72 (dt, *J* = 6.5, 6.5 Hz, 2H), 1.39 – 1.34 (m, 2H), 1.23 – 1.16 (m, 2H), 1.10 – 0.95 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.3 (C_q), 158.0 (CH), 143.4 (C_q), 137.2 (C_q), 135.3 (CH), 128.7 (C_q), 128.2 (CH), 122.8 (CH), 121.5 (CH), 120.1 (CH), 117.4 (CH), 112.9 (CH), 106.4 (CH), 32.3 (CH_2), 31.2 (CH_2), 29.3 (CH_2), 22.5 (CH_2), 21.7 (C_q), 17.4 (CH_2), 14.0 (CH_3). **IR** (ATR): 2923, 2853, 1564, 1454, 1424, 1354, 1301, 1200, 967, 802, 743, 679 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 332 (100) $[M+H]^+$, 354 (90) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{26}N_3$ $[M+H]^+$ 332.2127, found 332.2133.



(*E*)-2-[1-(Deca-1,9-dien-1-yl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5ag)

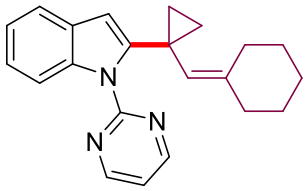
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and dec-9-en-1-ylidenecyclopropane (**4g**) (57.1 mg, 0.32 mmol) for 4.0 h. Isolation by column chromatography (*n*-hexane/CH_2Cl_2 8:1) yielded **5ag** (58.7 mg, 79%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 4.7 Hz, 2H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.20 (td, *J* = 7.4, 1.1 Hz, 1H), 7.15 (t, *J* = 4.8 Hz, 1H), 6.57 (s, 1H), 5.83 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.15 (d, *J* = 15.5 Hz, 1H), 5.09 – 4.94 (m, 3H), 2.03 (dt, *J* = 7.2, 7.2 Hz, 1H), 1.74 (dt, *J* = 7.2, 7.2 Hz, 1H), 1.39 – 1.29 (m, 4H), 1.20 (tt, *J* = 9.9, 6.6 Hz, 2H), 1.13 – 0.99 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4 (C_q), 158.1 (CH), 143.5 (C_q), 139.3 (CH), 137.3 (C_q), 135.4 (CH), 128.8 (C_q), 128.2 (CH), 122.9 (CH), 121.6 (CH), 120.2 (CH), 117.5 (CH), 114.3 (CH_2), 113.1 (CH), 106.5 (CH), 33.9 (CH_2), 32.4 (CH_2), 29.7 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 21.8 (C_q), 17.6 (CH_2). **IR** (ATR): 2923,

2851, 1564, 1453, 1421, 1353, 1198, 965, 908, 802, 742, 679 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 372 (100) $[M+H]^+$, 394 (18) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{30}N_3$ $[M+H]^+$ 372.2434, found 372.2433.



2-[1-(Cyclopentylidenemethyl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5ah)

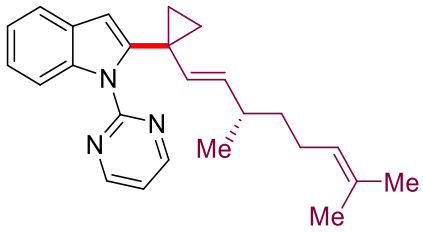
The general procedure **B** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and (cyclopropylidenemethyl)cyclopentane (**4h**) (39.1 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (*n*-hexane/CH_2Cl_2 8:1) yielded **5ah** (29.0 mg, 46%) as a white solid. **M.p. =** 113–115 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.84 (d, *J* = 4.8 Hz, 2H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.54 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.25 – 7.14 (m, 3H), 6.49 (s, 1H), 5.18 (d, *J* = 2.5 Hz, 1H), 2.04 – 1.93 (m, 4H), 1.55 – 1.45 (m, 2H), 1.45 – 1.37 (m, 2H), 1.33 – 1.27 (m, 2H), 1.00 – 0.93 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.5 (C_q), 158.2 (CH), 146.7 (C_q), 145.4 (C_q), 137.0 (C_q), 128.9 (C_q), 124.1 (CH), 122.6 (CH), 121.5 (CH), 120.0 (CH), 117.5 (CH), 112.9 (CH), 105.0 (CH), 34.4 (CH_2), 28.6 (CH_2), 26.8 (CH_2), 26.0 (CH_2), 19.9 (C_q), 17.9 (CH_2). **IR** (ATR): 2921, 2855, 1563, 1455, 1422, 1349, 1318, 1283, 1195, 1022, 803, 744, 680 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 316 (100) $[M+H]^+$, 338 (30) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{22}N_3$ $[M+H]^+$ 316.1814, found 316.1802.



2-[1-(Cyclohexylidenemethyl)cyclopropyl]-1-(pyrimidin-2-yl)-1*H*-indole (5ai)

The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and (cyclopropylidenemethyl)cyclohexane (**4i**) (43.6 mg, 0.32 mmol) for 5.0 h. Isolation by column chromatography (*n*-hexane/CH_2Cl_2 8:1) yielded **5ai** (34.3 mg, 52%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.85 (d, *J* = 4.8 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.25 – 7.13 (m, 3H), 6.49 (d, *J* = 0.8 Hz, 1H), 5.08 (s, 1H), 2.23 – 2.10 (m, 2H), 1.83 – 1.72 (m, 2H), 1.37 – 1.25 (m, 8H), 1.02 – 0.92 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.6 (C_q), 158.2 (CH), 146.5 (C_q), 144.1 (C_q), 137.0 (C_q), 129.0 (C_q),

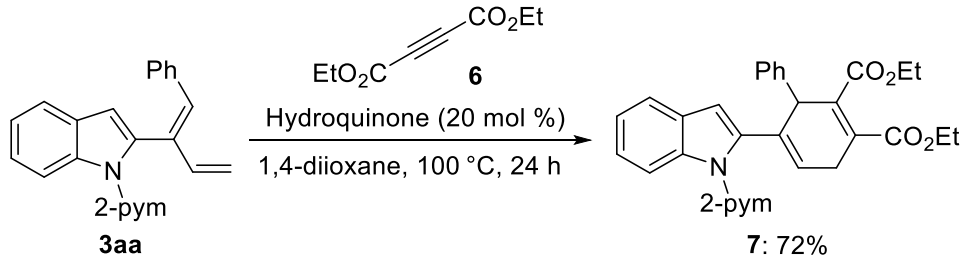
125.5 (CH), 122.6 (CH), 121.5 (CH), 120.0 (CH), 117.5 (CH), 112.7 (CH), 104.0 (CH), 36.8 (CH_2), 29.4 (CH_2), 28.6 (CH_2), 27.0 (CH_2), 26.6 (C_q), 18.2 (CH_2). **IR** (ATR): 2921, 2849, 1559, 1454, 1420, 1352, 1262, 1196, 1024, 967, 801, 737, 681 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 330 (25) $[M+H]^+$, 352 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{24}N_3$ $[M+H]^+$ 330.1970, found 330.1965.



(*S*,*E*)-2-(1-(3,7-Dimethylocta-1,6-dien-1-yl)cyclopropyl)-1-(pyrimidin-2-yl)-1*H*-indole (5aj)

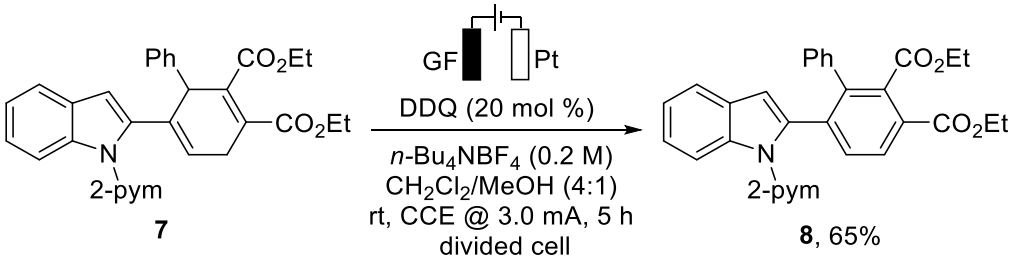
The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**2a**) (41.6 mg, 0.20 mmol) and (*S*)-(3,7-dimethyloct-6-en-1-ylidene)cyclopropane (**4j**) (57.1 mg, 0.32 mmol) for 7.0 h. Isolation by column chromatography (*n*-hexane/CH_2Cl_2 8:1) yielded **5aj** (45.3 mg, 61%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.78 (d, *J* = 4.8 Hz, 2H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.13 (m, 3H), 6.56 (s, 1H), 5.08 (d, *J* = 15.5 Hz, 1H), 4.97 (t, *J* = 7.1 Hz, 1H), 4.87 (dd, *J* = 15.5, 8.1 Hz, 1H), 1.87 – 1.78 (m, 2H), 1.72 – 1.67 (m, 1H), 1.67 (s, 3H), 1.54 (s, 3H), 1.38 – 1.34 (m, 2H), 1.08 – 0.94 (m, 4H), 0.66 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4 (C_q), 158.1 (CH), 143.6 (C_q), 137.4 (C_q), 134.1 (CH), 133.8 (CH), 131.1 (C_q), 128.8 (C_q), 125.0 (CH), 122.9 (CH), 121.6 (CH), 120.2 (CH), 117.5 (CH), 113.1 (CH), 106.5 (CH), 37.1 (CH_2), 36.2 (CH), 25.8 (CH_2), 21.8 (C_q), 21.0 (CH_3), 18.0 (CH_3), 17.8 (CH_3), 17.5 (CH_2). **IR** (ATR): 2915, 2855, 1564, 1453, 1423, 1353, 1199, 965, 803, 743, 679 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 372 (100) $[M+H]^+$, 394 (80) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{30}N_3$ $[M+H]^+$ 372.2440, found 372.2434.

5. Derivatization of 3aa



Diethyl-6-[1-(pyrimidin-2-yl)-1*H*-indol-2-yl]-1,4-dihydro-[1,1'-biphenyl]-2,3-dicarboxylate (7)

Product **7** was prepared *via* a variation of the reported method.[3] To a 25 mL schlenk tube was added **3aa** (135 mg, 0.40 mmol, 1.0 equiv), diethyl acetylenedicarboxylate **6** (204 mg, 1.2 mmol, 3.0 equiv), hydroquinone (8.8 mg, 0.080 mmol, 20 mol %) and 1,4-dioxane (2.0 mL). Then, the mixture was stirred at 100 °C for 24 h. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5:1), affording **7** (140 mg, 72%) as a yellow solid. **M.p. =** 149–150 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.83 (d, *J* = 4.8 Hz, 2H), 8.29 (dd, J = 8.3, 1.0 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.21 – 7.12 (m, 5H), 7.06 (dd, J = 7.8, 1.8 Hz, 2H), 6.20 (s, 1H), 6.00 (dd, *J* = 4.7, 2.7 Hz, 1H), 4.61 (t, *J* = 5.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.01 (dddd, *J* = 17.9, 10.8, 7.1, 3.7 Hz, 2H), 3.44 (ddd, *J* = 23.4, 6.5, 2.8 Hz, 1H), 3.23 (dt, *J* = 23.5, 5.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 167.8 (C_q), 167.5 (C_q), 158.4 (CH), 158.1 (C_q), 140.2 (C_q), 139.1 (C_q), 138.3 (C_q), 137.1 (C_q), 133.6 (C_q), 129.8 (C_q), 129.2 (C_q), 128.8 (CH), 128.4 (CH), 127.2 (CH), 123.5 (CH), 122.8 (CH), 122.1 (CH), 120.5 (CH), 117.3 (CH), 113.9 (CH), 109.3 (CH), 61.4 (CH_2), 60.9 (CH_2), 48.2 (CH), 28.8 (CH_2), 14.2 (CH_3), 13.9 (CH_3). **IR** (ATR): 2983, 1715, 1567, 1423, 1344, 1248, 1147, 1068, 810, 744, 705 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 494 (90) $[M+H]^+$, 516 (100) $[M+Na]^+$. **HR-MS** (ESI) *m/z* calcd for $C_{30}H_{28}N_3O_4$ $[M+H]^+$ 494.2074, found 494.2072.



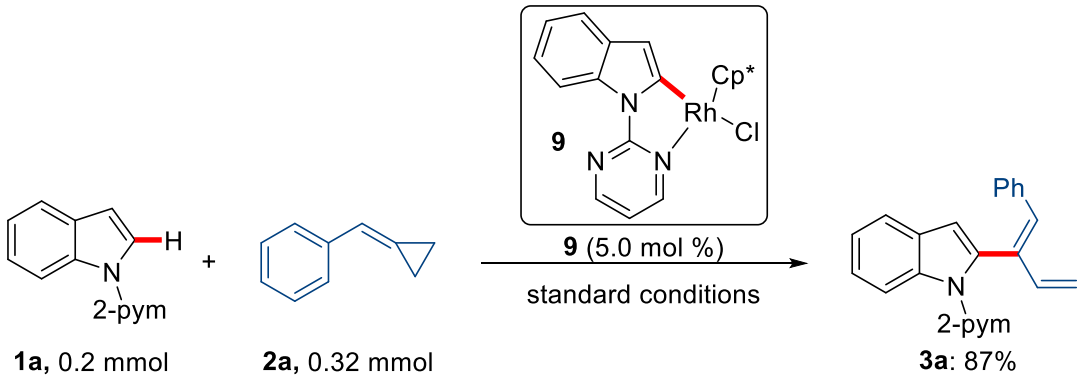
Diethyl 6-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-[1,1'-biphenyl]-2,3-dicarboxylate (8)

The dehydrogenative aromatization by electricity was conducted according to the related report.[4] The electrochemical dehydrogenative aromatization of **7** was carried out in a divided

cell (P4 glass frit as separator) with a GF anode (10 mm × 15 mm × 6 mm) and a Pt cathode (10 mm × 15 mm × 0.25 mm). The anodic cell was charged with **7** (49.3 mg, 0.1 mmol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (5.5 mg, 0.020 mmol, 20 mol %,), *n*-Bu_4NBF_4 (32.9 mg, 1.0 mmol), CH_2Cl_2 (4.0 mL) and MeOH (1.0 mL). The cathodic cell was charged with *n*-Bu_4NBF_4 (32.9 mg, 1.0 mmol), CH_2Cl_2 (4.0 mL) and MeOH (1.0 mL). Electrolysis was performed at 25 °C with a constant current of 5.0 mA maintained for 5.0 h. The anodic solution was transferred to a separating funnel charged with H_2O (50 mL) and CH_2Cl_2 (50 mL) and the GF anode was rinsed with CH_2Cl_2 (4 × 10 mL). The organic phase was collected and dried over anhydrous sodium sulfate. The evaporation of the solvent and subsequent column chromatography on silica gel (*n*-hexane/EtOAc 5:1) afforded **8** (32.1 mg, 65%) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.50 (d, *J* = 4.8 Hz, 2H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.06 – 6.98 (m, 3H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.60 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 168.7 (C_q), 165.9 (C_q), 157.9 (CH), 157.2 (C_q), 139.5 (C_q), 138.5 (C_q), 137.8 (C_q), 137.2 (C_q), 137.0 (C_q), 136.3 (C_q), 130.7 (CH), 129.2 (CH), 129.1 (CH), 129.0 (C_q), 127.5 (CH), 127.5 (CH), 127.3 (C_q), 124.0 (CH), 122.2 (CH), 120.7 (CH), 117.1 (CH), 114.0 (CH), 111.3 (CH), 61.7 (CH_2), 61.3 (CH_2), 14.3 (CH_3), 13.7 (CH_3). **IR** (ATR): 2982, 2259, 1719, 1565, 1422, 1263, 1183, 1147, 1067, 1019, 911, 803, 733, 700 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 1005 (70), 514 (100) $[M+Na]^+$, 492 (35) $[M+H]^+$, 446 (35). **HR-MS** (ESI) *m/z* calcd for $C_{30}H_{26}N_3O_4$ $[M+H]^+$ 492.1918, found 492.1912.

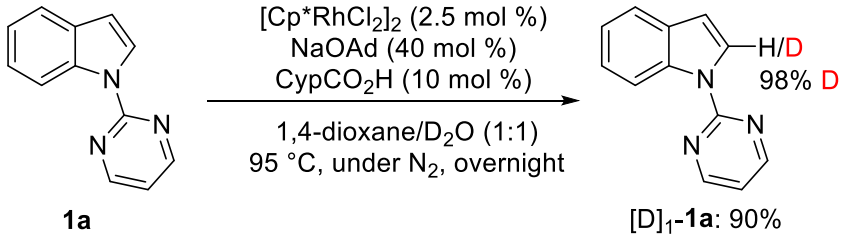
6. Mechanistic Studies

Catalytic reaction of 9



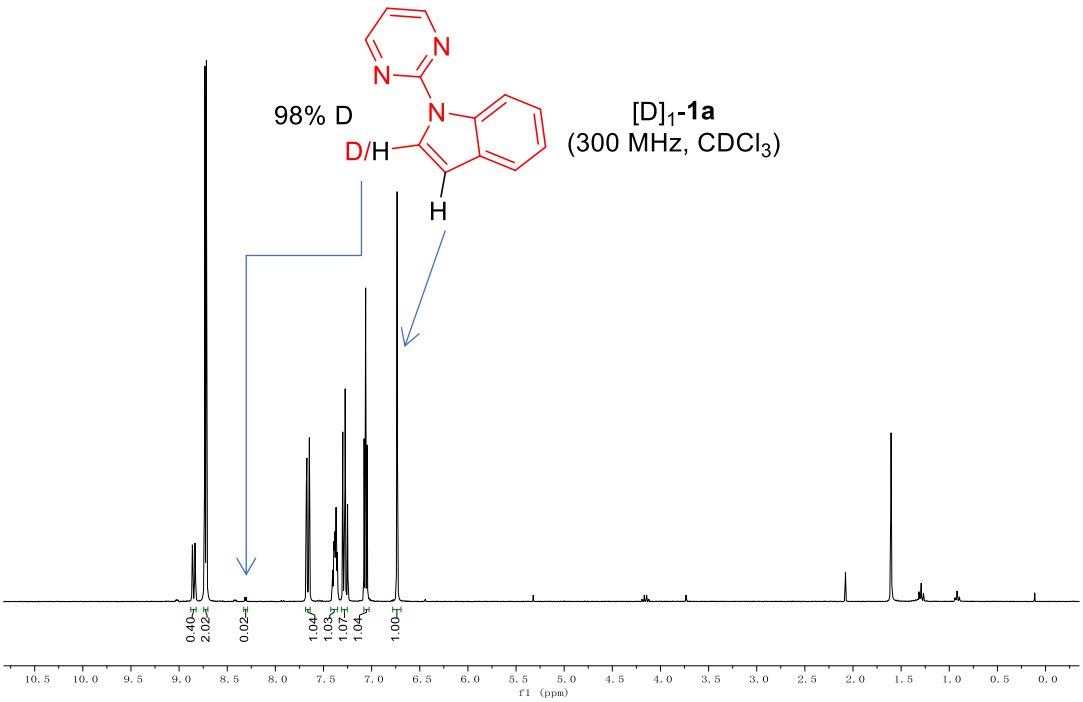
Complex **9** was synthesized according to the corresponding literature.[5] The general procedure **A** was followed using 1-(pyrimidin-2-yl)-1*H*-indole (**1a**) (39.0 mg, 0.20 mmol) and (cyclopropylidenemethyl)benzene (**2a**) (41.6 mg, 0.32 mmol) for 3.0 h with complex **9** (4.7 mg, 10 µmol, 5.0 mol %) replacing $[Cp^*RhCl_2]_2$. Isolation by column chromatography (*n*-hexane/EtOAc 15:1) yielded **3aa** (56.3 mg, 87%).

H/D Exchange

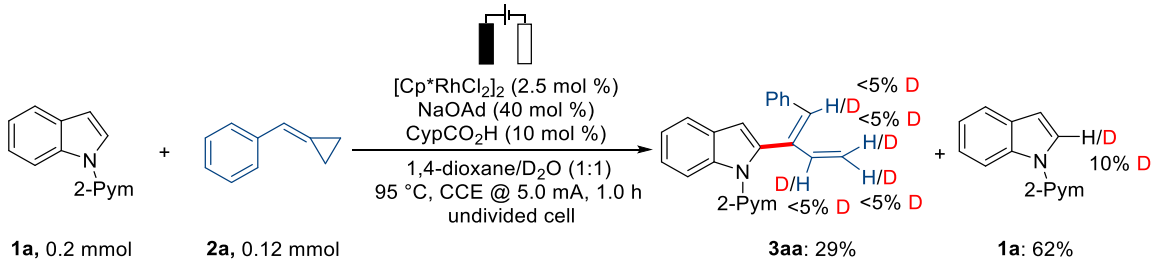


Scheme S-2. Deuteration of indole **1a** in the presence of D_2O.

The electrolysis was carried out in an undivided cell with a GF anode (10 mm x 15 mm x 6 mm) and a Pt cathode (10 mm x 15 mm x 0.25 mm). $[Cp^*RhCl_2]_2$ (3.0 mg, 5.0 µmol, 2.5 mol %), NaO_2CAd (16.0 mg, 0.8 mmol, 40 mol %), cyclopentanecarboxylic acid (2.3 mg, 0.2 mmol, 10 mol %), and indole **1a** (0.2 mmol) were dissolved in 1,4-dioxane (4.0 mL) and then water (4.0 mL) was added. Stirred overnight at 95 °C. The reaction mixture was extracted with EtOAc (3 x 10 mL), the organic layers combined and the solvent removed under reduced pressure. Subsequent column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded the desired product $[D]_1$-**1a** (35.2 mg, 90%, 98% D).

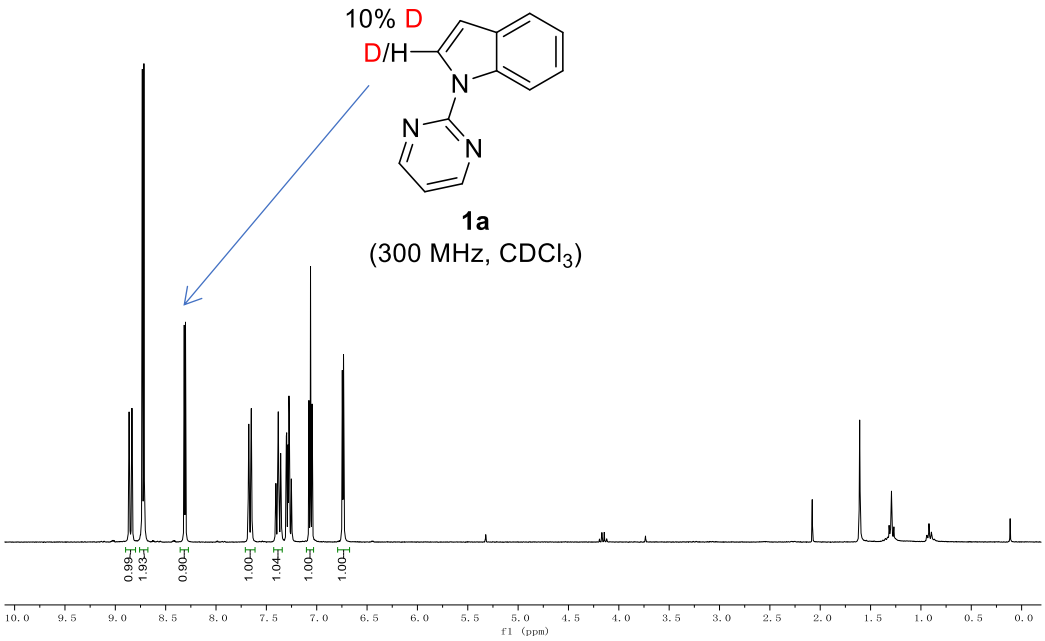


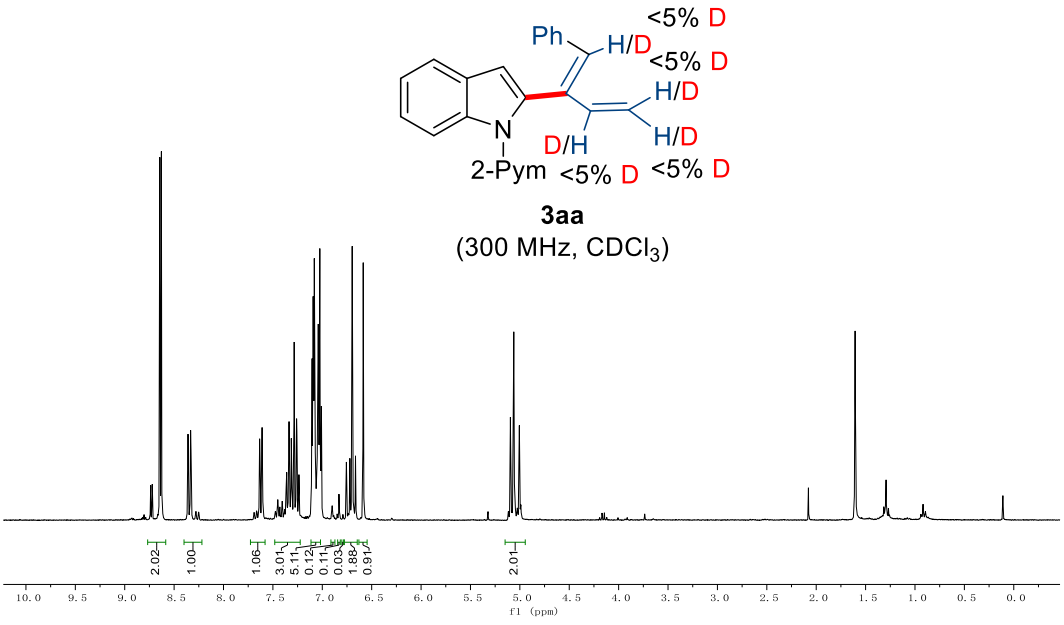
Dienylation in the presence of D_2O



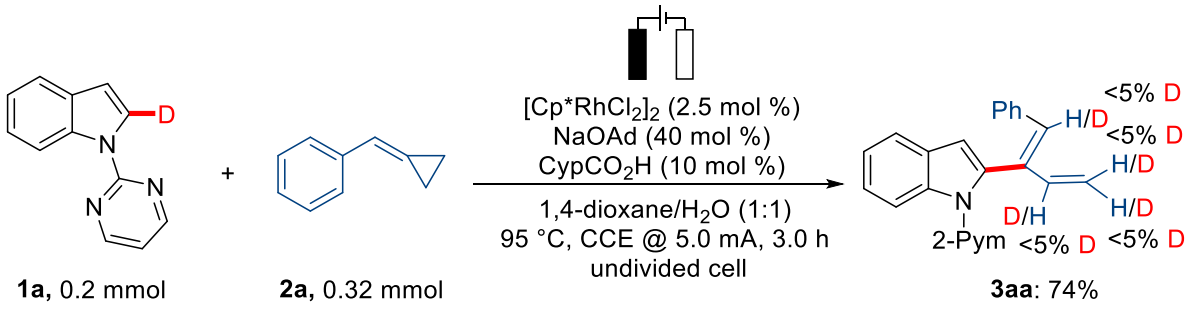
Scheme S-3. Reaction in the presence of D_2O.

The electrolysis was carried out in an undivided cell with a GF anode (10mm x 15 mm x 6 mm) and a Pt cathode (10mm x 15 mm x 0.25 mm). $[Cp^*RhCl_2]_2$ (3.0 mg, 5.0 μmol, 2.5 mol %), NaO_2CAd (16.0 mg, 0.8 mmol, 40 mol %), cyclopentanecarboxylic acid (2.3 mg, 0.2 mmol, 10 mol %), cyclopropane **2** (0.32 mmol, 1.6 equiv) and indole **1** (0.2 mmol) were dissolved in 1,4-dioxane (4.0 mL) and then D_2O (4.0 mL) was added sequentially. At 95 °C, electrolysis was conducted with a constant current of 5.0 mA for 1.0 h. Then the mixture was transferred to a flask and the electrodes were rinsed with EtOAc (3 x 5.0 mL). The combined solvent was extracted with EtOAc (3 x 10 mL), the organic layer combined and the solvent removed under reduced pressure. Column chromatography on silica gel (*n*-hexane/EtOAc 20:1) yielded the desired product **3aa** (19.1 mg, 29%) and **1a** (22.0 mg, 62%, 10% D).


10% D
D/H
N
N
N
1a
(300 MHz, CDCl3)
0.99
1.93
0.90
1.00
1.04
1.00
1.00
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)

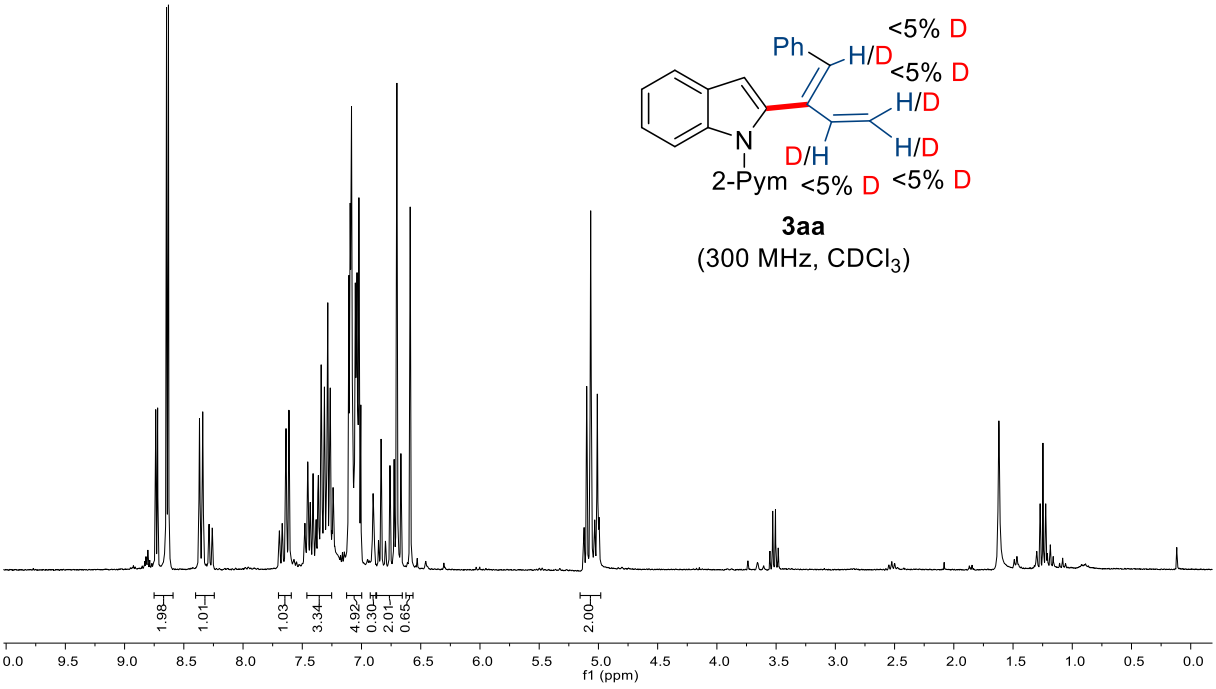

Ph
H/D
<5% D
<5% D
H/D
H/D
D/H
N
2-Pym
<5% D
<5% D
3aa
(300 MHz, CDCl3)
2.02
1.00
1.06
3.01
5.11
0.12
0.11
0.03
1.88
0.91
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Reaction with isotopically-labelled substrate

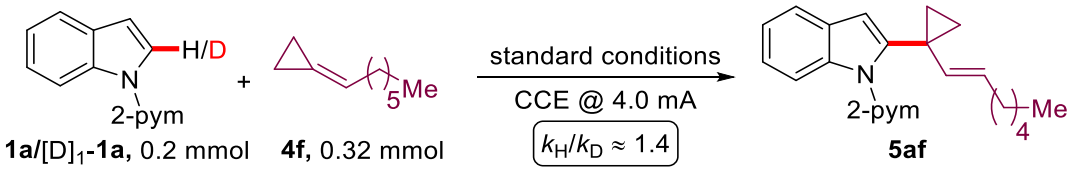


1a, 0.2 mmol **2a,** 0.32 mmol **3aa**: 74%

The electrolysis was carried out in an undivided cell with a GF anode (10mm x 15 mm x 6 mm) and a Pt cathode (10mm x 15 mm x 0.25 mm). $[Cp^*RhCl_2]_2$ (3.0 mg, 5.0 μmol, 2.5 mol %), NaO_2CAd (16.0 mg, 0.80 mmol, 40 mol %), cyclopentanecarboxylic acid (2.3 mg, 0.2 mmol, 10 mol %), cyclopropane **2a** (0.32 mmol, 1.6 equiv) and indole [D]-**1a** (0.2 mmol) were dissolved in 1,4-dioxane (4.0 mL) and then water (4.0 mL) was added sequentially. At 95 °C, electrolysis was conducted with a constant current of 5.0 mA for 3.0 hour. Then the mixture was transferred to a flask and the electrodes were rinsed with EtOAc (3 x 5.0 mL). The combined solvent was extracted with EtOAc (3 x 10 mL), the organic layers combined, and the solvent removed under reduced pressure. Column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded the desired product **3aa** (47.9 mg, 74%).



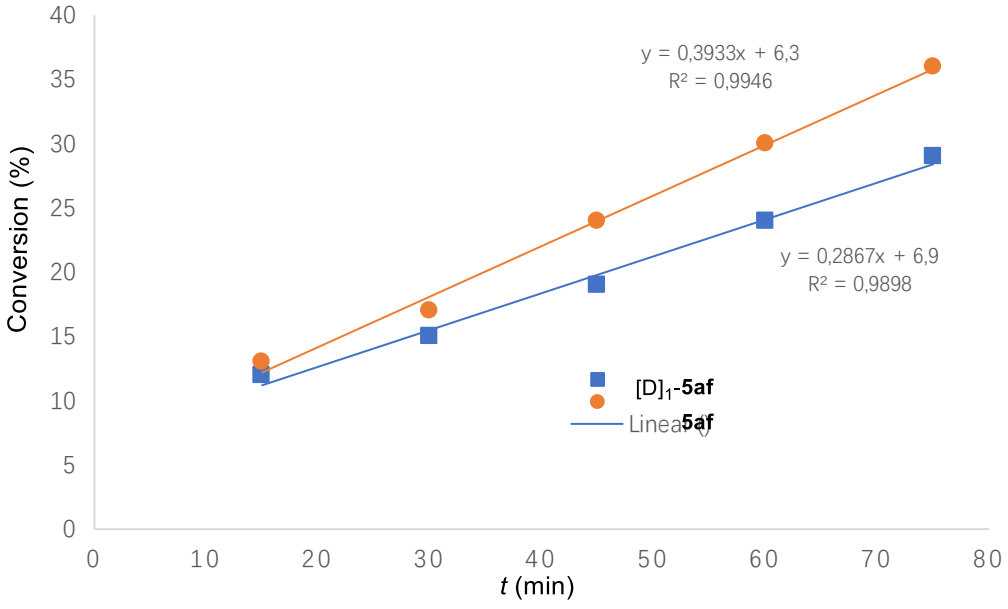
KIE Studies



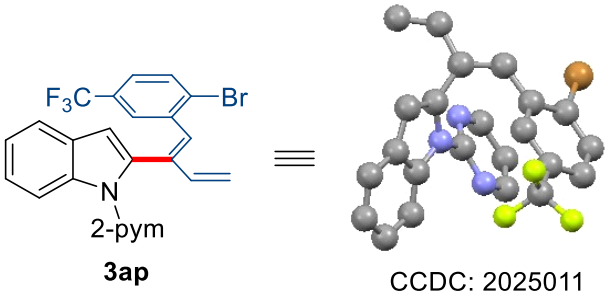
Ten parallel reactions of **1a** and [D]$_1$-**1a** with **4f** were performed to determine the KIE by comparison of the initial reaction rates through ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. A suspension of [Cp*RhCl$_2$]$_2$ (3.0 mg, 5.0 µmol, 2.5 mol %), NaO$_2$CAd (16.0 mg, 0.8 mmol, 40 mol %), cyclopentanecarboxylic acid (2.3 mg, 0.2 mmol, 10 mol %), **1a** (39.4 mg, 0.20 mmol, 1.0 equiv) or [D]$_1$-**1a** (39.5 mg, 0.20 mmol, 1.0 equiv), **4f** (44.2 mg, 0.32 mmol, 1.6 equiv) were dissolved in 1,4-dioxane (4.0 mL) and then water (4.0 mL) was added. Reactions were stopped after 15 min, 30 min, 45 min, 60 min, 75 min respectively and conversions were determined by ^{1}H NMR.

Table S-6: Conversions over time.

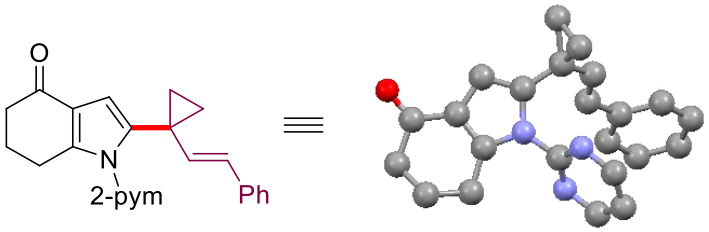
***t* (min)**	15	30	45	60	75
5af (%)	13	17	24	30	36
[D]$_1$-**5af** (%)	12	15	19	24	29



7. X-Ray Crystallographic Analysis



Identification code	mo_1115_CG_0m
Empirical formula	$C_{23}H_{15}BrF_3N_3$
Formula weight	470.29
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.9177(10)
b/Å	10.1630(7)
c/Å	11.8694(12)
α/°	65.772(3)
β/°	67.588(3)
γ/°	69.728(3)
Volume/Å^3	982.62(16)
Z	2
ρ_{calc}g/cm^3	1.589
μ/mm^{-1}	2.135
F(000)	472.0
Crystal size/mm^3	0.534 × 0.292 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.92 to 61.07
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	37997
Independent reflections	5982 [R_{int} = 0.0290, R_{sigma} = 0.0202]
Data/restraints/parameters	5982/0/279
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0263, wR_2 = 0.0711
Final R indexes [all data]	R_1 = 0.0286, wR_2 = 0.0725
Largest diff. peak/hole / e Å^{-3}	0.61/-0.46



5pa CCDC: 2025012

Identification code	mo_1112_CG_0m
Empirical formula	$C_{23}H_{21}N_3O$
Formula weight	355.43
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.0527(11)
b/Å	20.486(3)
c/Å	10.8176(12)
α/°	90
β/°	112.106(4)
γ/°	90
Volume/Å^3	1858.7(4)
Z	4
ρ_{calc}g/cm^3	1.270
μ/mm^{-1}	0.079
F(000)	752.0
Crystal size/mm^3	0.53 × 0.417 × 0.288
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.524 to 68.048
Index ranges	$-14 \le h \le 13$, $-31 \le k \le 29$, $-16 \le l \le 14$
Reflections collected	40729
Independent reflections	6592 [R_{int} = 0.0208, R_{sigma} = 0.0169]
Data/restraints/parameters	6592/2/314
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1129
Largest diff. peak/hole / e Å^{-3}	0.44/-0.24

8. Computational Data

All calculations were done by using DFT with the Gaussian 16, Revision A.03 package.[6] Geometry optimizations of all stationary points were carried out at the TPSS[7] level of theory in combination with D3 dispersion corrections with the Becke-Johnson damping scheme (D3BJ).[8] All atoms were described with a def2-SVP[9] basis set in combination with a Stuttgart-Dresden effective core potential for rhodium.[10] Analytical frequency calculations were carried out at the same level of theory in order to identify all intermediates (no imaginary frequencies) and transition states (only one imaginary frequency) and to provide thermal and non-thermal corrections to the free energy in gas-phase at 298.15 K and 1 atm.

The electronic energies were then refined through single-point calculations on the optimized structures at the PBE0[11] and PW6B95[12] level of theory including dispersion corrections (D3BJ). All atoms were described with a def2-TZVP[9] basis set in combination with a Stuttgart-Dresden effective core potential for rhodium. [10] Solvent effects were taken into consideration in the single-point calculations through the use of the SMD[13] model with a dielectric constant of ε = 2.2099, which corresponds to 1,4-dioxane. Unless otherwise stated, all reported energies are Gibbs free energies in kcal mol^{-1}, which were calculated by adding the gas-phase thermal and non-thermal corrections at 298.15 K to the single-point energies.

3D structures of optimized geometries were constructed with the CYLview software.[14]

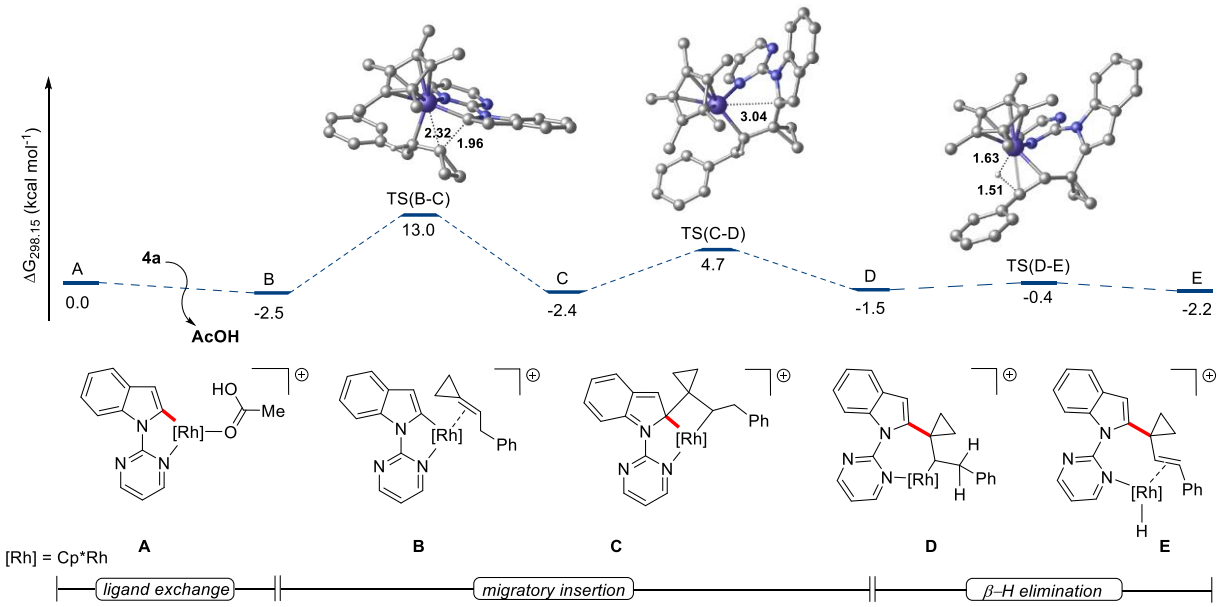


Figure S-1. Gibbs free energy profile in kcal mol^{-1} for the migratory insertion and β–H elimination pathway for the C–H cyclopropylation of indole **1a** with benzyl cyclopropane **4a** at the PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogen atoms in the transition state structures were omitted for clarity. Bond distances are given in Å.

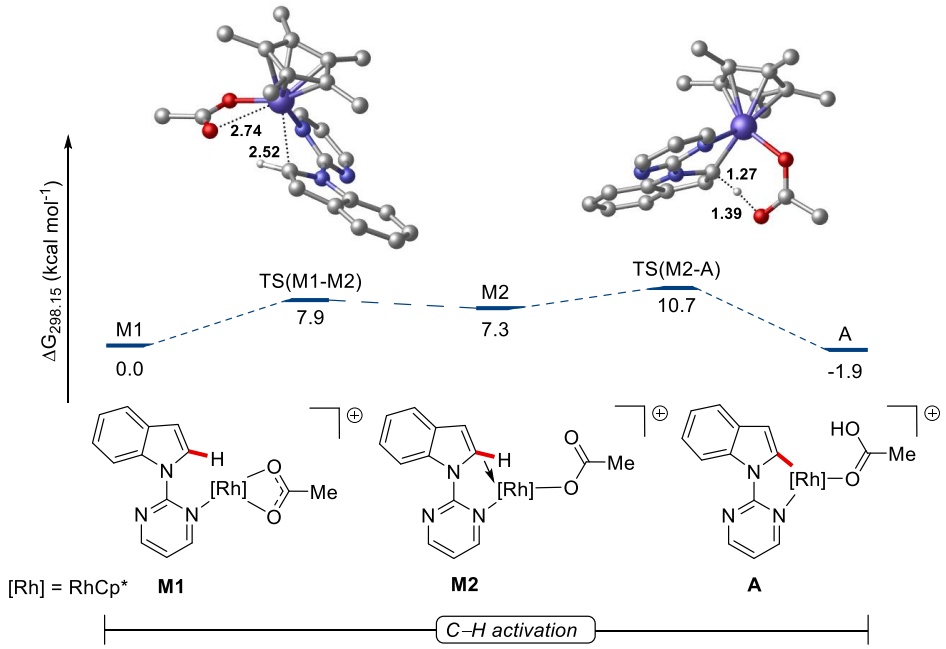


Figure S-2. Gibbs free energy profile in kcal mol^{-1} for the initial C–H activation of indole **1a** (with the model acetate ligand) at the PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-Dioxane)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogen atoms were omitted in the transition state structures for the clarity. Bond distances are given in Å.

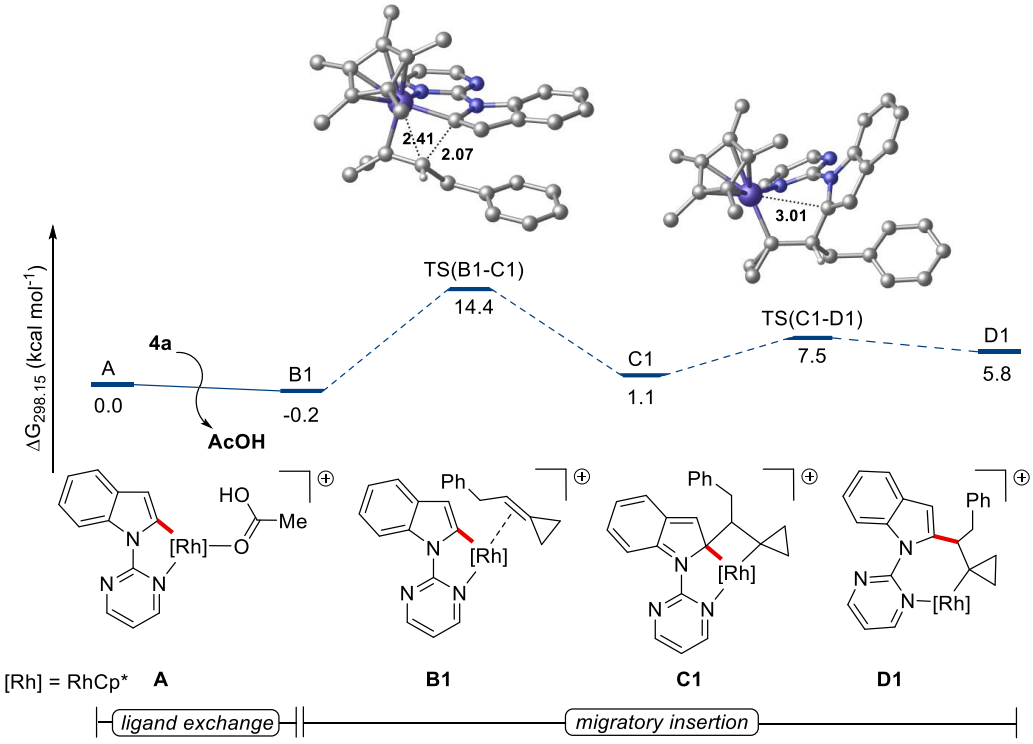


Figure S-3. Gibbs free energy profile in kcal mol^{-1} for the other possible migratory insertion at the PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogen atoms were omitted in the transition state structures for the clarity. Bond distances are given in Å.

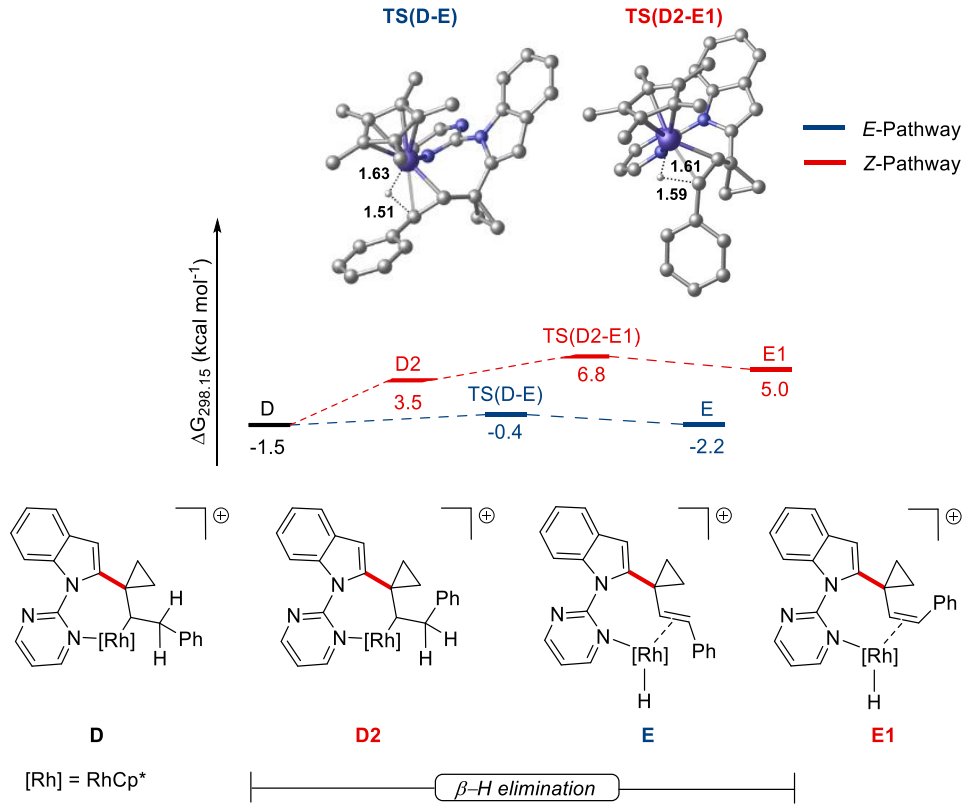


Figure S-4. Gibbs free energy profile in kcal mol^{-1} for the regioselective β–H elimination from the intermediate **D** at the PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogen atoms were omitted in the transition state structures for the clarity. Bond distances are given in Å.

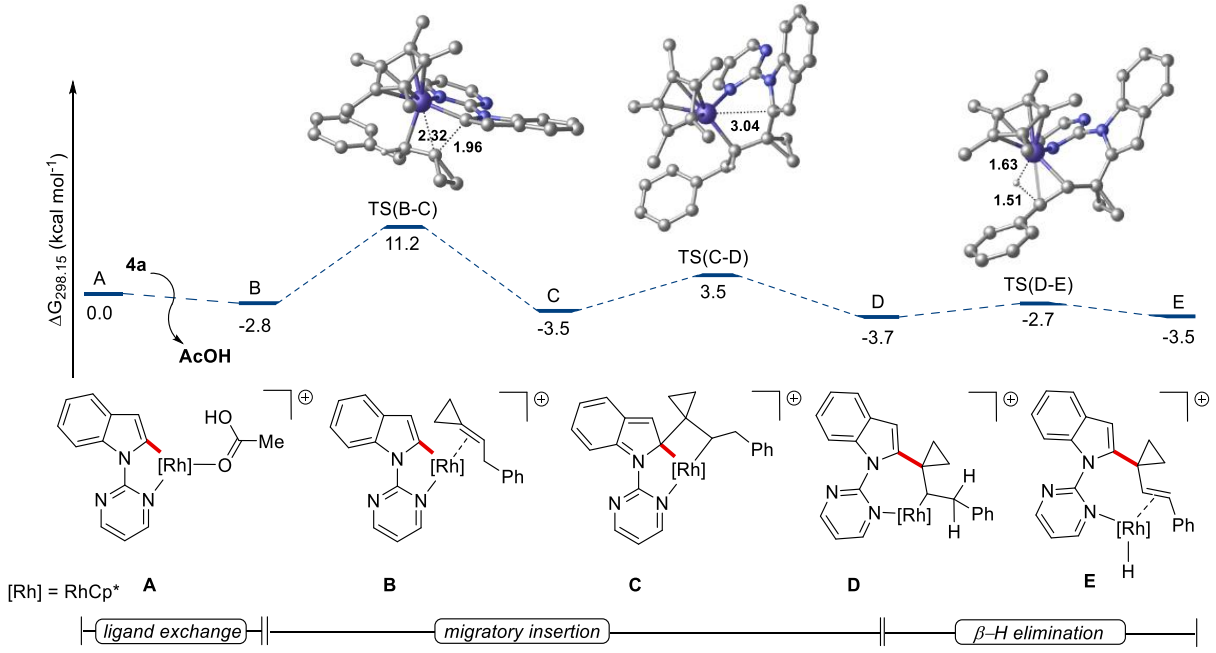


Figure S-5. Gibbs free energy profile in kcal mol^{-1} for the migratory insertion and β–H elimination for the C–H cyclopropylation pathway of indole with benzyl cyclopropane **4a** at the PBE0-D3(BJ)/def2-TZVP+ SMD(1,4-Dioxane)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogen atoms were omitted in the transition state structures for the clarity. Bond distances are given in Å.

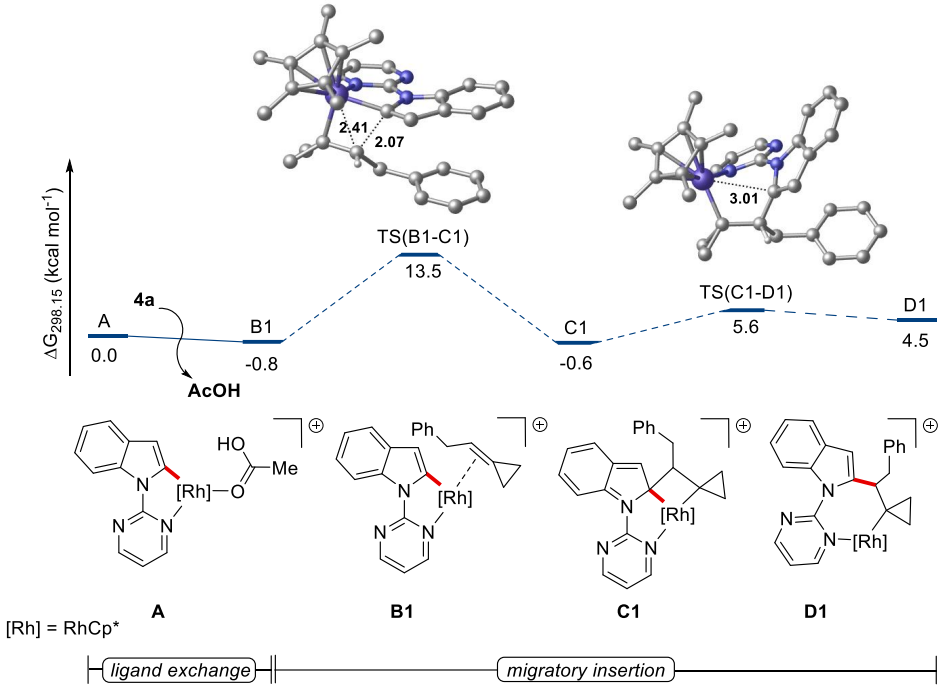


Figure S-6. Gibbs free energy profile in kcal mol^{-1} for the other possible migratory insertion at the PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogen atoms were omitted in the transition state structures for the clarity. Bond distances are given in Å.

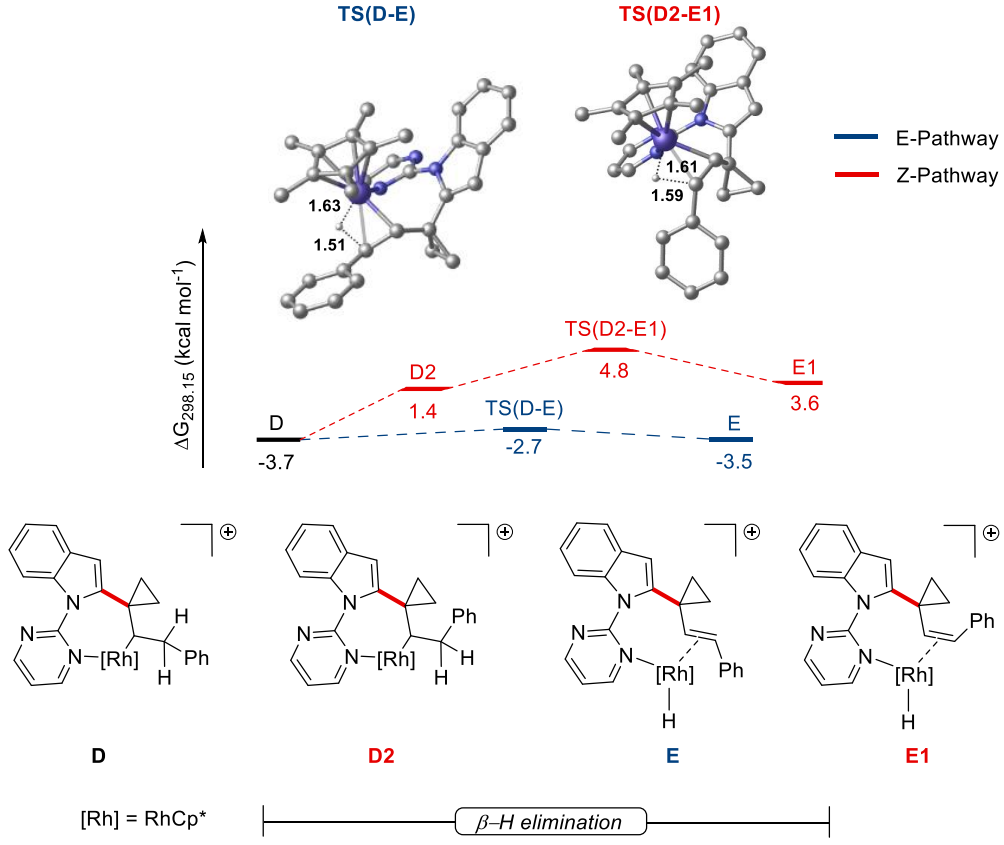


Figure S-7. Gibbs free energy profile in kcal mol^{-1} for the regioselective β–H elimination from the intermediate **D** at the PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)//TPSS-D3(BJ)/def2-SVP level of theory. Non-relevant hydrogen atoms were omitted in the transition state structures for the clarity. Bond distances are given in Å.

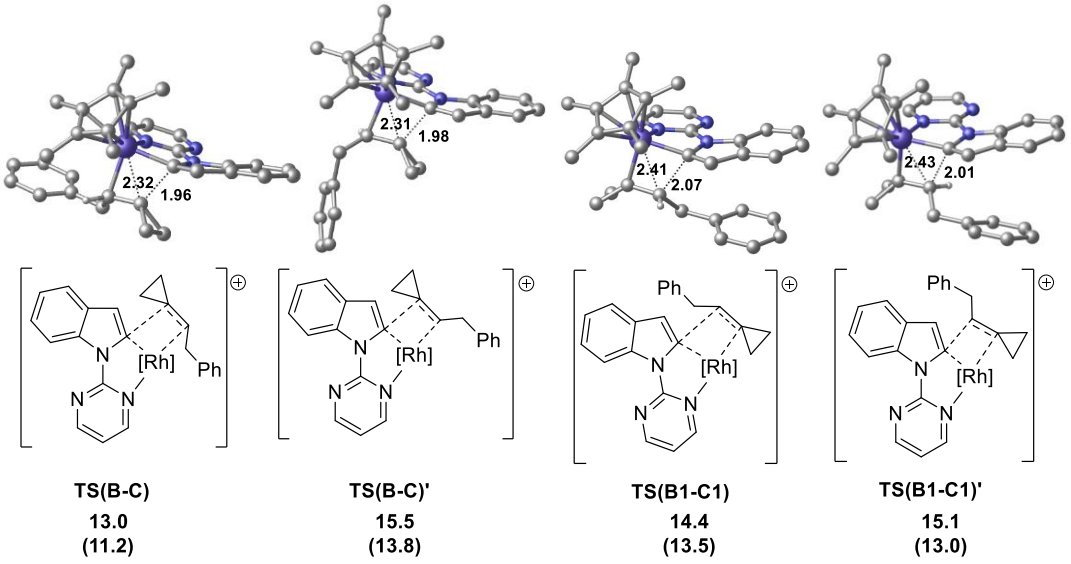


Figure S-8. Comparison of the Gibbs free energies in kcal mol^{-1} for the four possible regioselective migratory insertion transition states at the PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-Dioxane)//TPSS-D3(BJ)/def2-SVP level of theory (values in parenthesis are at the PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)//TPSS-D3(BJ)/ def2-SVP level of theory). Non-relevant hydrogen atoms were omitted in the transition state structures for the clarity. Bond distances are given in Å.

Cartesian Coordinates and Energies of all the optimized Geometries

Acetic Acid

Lowest frequency = 59.83 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -228.939159 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -229.455149 E_h

G_{corr} (298.15) = 0.033336 E_h

Charge = 0, Multiplicity = 1

C	-1.93863449	1.66002054	-0.00061440
O	-0.72668240	1.59345975	0.00000275
O	-2.60512368	2.84863765	0.00010900
H	-1.90870955	3.53925843	0.00040018
C	-2.89694716	0.49173177	-0.00000979
H	-3.54984800	0.54184601	0.88802736
H	-3.55004945	0.54115900	-0.88793380
H	-2.32835475	-0.44760277	0.00029729

4a

Lowest frequency = 19.82 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -425.987606 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -427.059458 E_h

G_{corr} (298.15) = 0.154829 E_h

Charge = 0, Multiplicity = 1

C	-0.99990285	-0.93966131	-2.43134331
C	-0.37308294	-2.08049280	-2.13945739
C	-0.89273504	0.47241160	-2.83454677
H	-0.53788000	1.21046206	-2.10117769
H	-0.62225203	0.71181190	-3.87267978
C	-2.25789851	-0.19533059	-2.58197720
H	-2.89688144	-0.40098557	-3.45228659
H	-2.81410719	0.09674522	-1.68008686
H	-0.96610247	-2.95951852	-1.84964262
C	1.12836521	-2.24640843	-2.14329659
H	1.41559048	-3.05049924	-2.84692340
H	1.59020821	-1.31266741	-2.51465472
C	1.68851765	-2.58321004	-0.76743702
C	2.50986380	-3.70755180	-0.56986670
C	1.39248157	-1.76482950	0.34039113
C	3.03106029	-4.00504966	0.69835098
H	2.74504696	-4.35695639	-1.42157427
C	1.91237359	-2.05685160	1.60765344
H	0.74157507	-0.89398618	0.20149897
C	2.73460213	-3.17954480	1.79152208
H	3.66887137	-4.88574677	0.83183508
H	1.67345117	-1.40764683	2.45727179
H	3.13938335	-3.41024637	2.78277806

Intermediate **M1**

Lowest frequency = 20.95 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1355.111479 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1358.193110 E_h

G_{corr} (298.15) = 0.396368 E_h

Charge = 1, Multiplicity = 1

C	2.84915351	-1.51558518	-0.32492980
C	2.93572806	-0.45165561	-1.31423008
C	1.50367187	-2.06386723	-0.39551812
C	1.64575372	-0.32076179	-1.95704044
C	0.76168113	-1.33779676	-1.39845049
C	4.14326788	0.39122582	-1.57317195
H	4.69717336	0.59073911	-0.64277571
H	4.81972352	-0.14261961	-2.26646584
H	3.87410775	1.35355847	-2.03383713
C	1.28615359	0.64032357	-3.04878927
H	1.88557800	1.56211772	-2.99038160
H	1.47172543	0.17752777	-4.03554649
H	0.22034264	0.91479119	-3.00384311
C	-0.61873234	-1.65581443	-1.87793505
H	-1.24062421	-2.09241314	-1.08275956

H	-1.13391817	-0.76876060	-2.27495924
H	-0.54902847	-2.39390815	-2.69909893
C	0.97382514	-3.17866289	0.44727929
H	-0.11722158	-3.10171467	0.56607219
H	1.20485075	-4.14502099	-0.03898098
H	1.43854585	-3.18083206	1.44527426
C	3.96222331	-2.00389418	0.55120257
H	4.52507378	-2.80588547	0.03863208
H	4.66827579	-1.19305314	0.78828942
H	3.57381089	-2.41311967	1.49652874
Rh	1.45773839	0.02269870	0.14450860
C	-2.39669088	-1.58957508	1.45384632
C	-3.44833891	-1.47158368	0.46671572
H	-2.31403317	-2.35331933	2.22763502
C	-3.20153125	-0.28390385	-0.28099228
C	-1.53961231	-0.53600648	1.28828324
N	-1.99878544	0.27813168	0.22923377
C	-1.36861392	1.42440191	-0.21216881
N	-0.03311292	1.58801077	0.04671547
C	0.48862417	2.81752104	-0.20006602
C	-1.56100391	3.49625659	-1.18655182
H	1.53912383	2.94293503	0.07909029
H	-2.18764474	4.19327043	-1.75705041
N	-2.11019435	2.32156440	-0.87660866
C	-0.25438769	3.83195386	-0.79571893
H	0.18146121	4.81450216	-0.98939246
C	-4.56230744	-2.27308816	0.15305192
C	-5.39747556	-1.87972819	-0.89670770
H	-4.76631659	-3.18483042	0.72287723
H	-6.27059796	-2.48761730	-1.15300934
C	-5.13284379	-0.70340387	-1.62887508
C	-4.03494079	0.11680981	-1.33416603
H	-5.80670212	-0.41266927	-2.44083900
H	-3.84907222	1.03893774	-1.88403049
O	2.59175467	1.43518041	1.31442861
C	2.12006236	0.97213038	2.41669383
O	1.31878168	-0.02090956	2.32268962
C	2.51561467	1.54751954	3.74259974
H	3.39165296	0.99063776	4.12112347
H	2.79883612	2.60501710	3.63455153
H	1.69657145	1.43102740	4.46803750
H	-0.67050638	-0.23582713	1.87137203

Transition State **TS(M1-M2)**

Lowest frequency = -84.19 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1355.097635 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1358.178657 E_h

G_{corr} (298.15) = 0.394532 E_h

Charge = 1, Multiplicity = 1

C	2.42816592	-1.42670812	-0.98944802
C	2.27957043	-0.19108685	-1.75505611
C	1.14544826	-2.07091098	-0.94098655
C	0.89310115	-0.12045872	-2.21296292
C	0.18586750	-1.26605849	-1.70333396
C	3.37786775	0.77392477	-2.07056340
H	4.04738431	0.90245141	-1.20545920
H	3.98049574	0.39497493	-2.91708545
H	2.98001753	1.75997088	-2.35637918
C	0.30941974	0.95888005	-3.07048337
H	0.82055038	1.92224352	-2.91741959
H	0.42385040	0.68462323	-4.13541782
H	-0.76525262	1.09364737	-2.87205467
C	-1.23578290	-1.62718627	-2.00550419
H	-1.66142167	-2.27978065	-1.23034728
H	-1.87518557	-0.73369706	-2.08230150
H	-1.28722934	-2.16297421	-2.97158104
C	0.85864714	-3.35333061	-0.22451552
H	-0.22182784	-3.54224106	-0.15468934
H	1.32220706	-4.19317075	-0.77412640
H	1.28140510	-3.33015484	0.79266520
C	3.68989983	-1.91804644	-0.35211957
H	4.24794072	-2.54892750	-1.06859459
H	4.33890170	-1.07847186	-0.05978074
H	3.47033153	-2.51763594	0.54341506
Rh	1.01395283	-0.09831715	-0.07295229
C	-1.81238634	-1.57583522	1.46952440
C	-3.12047933	-1.28419729	0.95162665
H	-1.48110601	-2.50117780	1.94067502
C	-3.12437971	0.08505960	0.53648156
C	-1.03965774	-0.43702909	1.34828229
N	-1.83886176	0.59318003	0.78822531
C	-1.28967082	1.80019781	0.39842761
N	0.05789741	1.77764073	0.19550809
C	0.68153933	2.95736544	-0.00275257
C	-1.44733734	4.03247963	-0.03204539
H	1.77136840	2.91396688	-0.08863085
H	-2.09544951	4.90442066	-0.18179319
N	-2.06350289	2.87534613	0.24393441
C	-0.04862381	4.14138224	-0.11055995
H	0.44789117	5.09952969	-0.27973724
C	-4.29072210	-2.05866786	0.79116558
C	-5.41274791	-1.45953088	0.21876191
H	-4.31174073	-3.10466792	1.11166532
H	-6.33106480	-2.03994640	0.08856690
C	-5.38820646	-0.10486370	-0.19115601
C	-4.24793942	0.69289537	-0.03996773
H	-6.28999762	0.33703539	-0.62633647
H	-4.23459874	1.74457859	-0.32993593

O	2.39269787	0.70289538	1.29819584
C	2.47839123	-0.14304792	2.29164358
O	1.75259994	-1.15564187	2.34760966
C	3.52913783	0.16292004	3.33759732
H	3.73070260	1.24262476	3.40181573
H	3.20962374	-0.23414623	4.31256944
H	4.46668322	-0.34694252	3.05128071
H	-0.13140179	-0.21181433	1.92528745

Intermediate **M2**
Lowest frequency = 20.78 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1355.099837 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1358.180560 E_h

G_{corr} (298.15) = 0.395433 E_h

Charge = 1, Multiplicity = 1

C	2.41815719	-1.24170071	-1.01083482
C	2.24618150	0.01556864	-1.72687104
C	1.16262871	-1.94007674	-1.01977724
C	0.87019539	0.05183326	-2.22038850
C	0.19742275	-1.13599933	-1.77971813
C	3.32222814	1.01769709	-2.00642410
H	4.00696026	1.11536087	-1.14927118
H	3.91923643	0.69837193	-2.88151427
H	2.90289570	2.00987562	-2.23656632
C	0.27197870	1.14201319	-3.05577449
H	0.72346097	2.12166899	-2.83252891
H	0.45226654	0.92949734	-4.12565351
H	-0.81673394	1.21436018	-2.90685763
C	-1.20219489	-1.53615679	-2.13261307
H	-1.61733672	-2.24617120	-1.40346568
H	-1.87646895	-0.66624694	-2.18162287
H	-1.21000684	-2.02399204	-3.12512179
C	0.92233638	-3.28460127	-0.40710151
H	-0.14992366	-3.52848715	-0.38097073
H	1.43567536	-4.06095638	-1.00371956
H	1.31914991	-3.30683932	0.62010699
C	3.68702675	-1.72074807	-0.37935279
H	4.27743137	-2.28236264	-1.12728837
H	4.30048804	-0.87716423	-0.02734929
H	3.47624485	-2.38141709	0.47351279
Rh	0.91452813	-0.01067990	-0.06431920
C	-1.54371494	-1.56358294	1.44647524
C	-2.85266627	-1.38396395	0.90747033
H	-1.11835077	-2.46695220	1.88340076
C	-2.99330536	0.00231618	0.56113652
C	-0.87789454	-0.33945111	1.39372571
N	-1.78937764	0.63088885	0.87797031
C	-1.31627780	1.87517502	0.48660030

N	0.02236015	1.89618313	0.23043074
C	0.59366915	3.09679235	0.01252401
C	-1.57307094	4.09850727	0.08660530
H	1.67827746	3.09803338	-0.13044975
H	-2.25631861	4.94877113	-0.02506685
N	-2.13740544	2.91577784	0.37869706
C	-0.18486695	4.25489507	-0.05364765
H	0.26912919	5.23123237	-0.23831235
C	-3.93012537	-2.27152922	0.66708455
C	-5.08954552	-1.76527712	0.08726700
H	-3.84686123	-3.32884478	0.93586232
H	-5.93779692	-2.42939346	-0.10310996
C	-5.19766815	-0.39232971	-0.25620663
C	-4.15826307	0.51443556	-0.02940737
H	-6.12983872	-0.02898062	-0.70021382
H	-4.24964712	1.57539585	-0.26899803
O	2.07096766	0.48833385	1.58460285
C	2.31639228	-0.52416035	2.39598065
O	1.80128668	-1.64189758	2.26901060
C	3.31551588	-0.20554075	3.49417585
H	3.27244215	0.85484616	3.78523091
H	3.13316862	-0.85795818	4.36089388
H	4.33147877	-0.41411454	3.11278310
H	-0.10534270	-0.01173482	2.09607562

Transition State **TS(M2-A)**

Lowest frequency = -220.96 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1355.098918 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1358.172383 E_h

G_{corr} (298.15) = 0.392729 E_h

Charge = 1, Multiplicity = 1

C	2.67343593	-1.55750620	-0.23284123
C	2.82982634	-0.43581244	-1.15018924
C	1.43669743	-2.22779072	-0.53307610
C	1.67250918	-0.42940574	-2.01869479
C	0.78825467	-1.50797236	-1.62830055
C	4.01692250	0.47675568	-1.20966205
H	4.37952969	0.71876264	-0.19791090
H	4.84616881	-0.00573186	-1.75999178
H	3.77855916	1.41883342	-1.72838026
C	1.42094908	0.53528166	-3.13625175
H	1.92178429	1.50063998	-2.96409691
H	1.82104373	0.11529146	-4.07747855
H	0.34465352	0.71635996	-3.28194222
C	-0.48791971	-1.89945162	-2.31197030
H	-1.19555357	-2.35797660	-1.60441930
H	-0.98226699	-1.02683773	-2.76693072
H	-0.28308541	-2.62958119	-3.11648637

C	0.95509549	-3.50216781	0.09259388
H	-0.11688406	-3.66098157	-0.09143872
H	1.50502187	-4.35434332	-0.34803628
H	1.13183327	-3.51609610	1.17968903
C	3.65139363	-1.92468377	0.83939157
H	4.55254764	-2.37533407	0.38478713
H	3.96315518	-1.03057695	1.40343449
H	3.22294429	-2.65133068	1.54549454
Rh	1.02296558	-0.17257599	0.04031735
C	-1.74572325	-1.59791958	1.10115729
C	-3.07785689	-1.36227488	0.63134449
H	-1.41145390	-2.47465973	1.65711077
C	-3.10724870	-0.05117460	0.05637166
C	-0.95134621	-0.47892938	0.83704877
N	-1.81475511	0.46686784	0.17631855
C	-1.28519929	1.65787468	-0.25181868
N	0.08367692	1.68314056	-0.24954816
C	0.69009680	2.85395118	-0.52411516
C	-1.44852569	3.81939384	-0.95459050
H	1.78261859	2.85776627	-0.46459637
H	-2.09682969	4.64259425	-1.27852194
N	-2.06299634	2.67426918	-0.63050541
C	-0.05448877	3.97949666	-0.88017987
H	0.43140841	4.93012603	-1.11066575
C	-4.25958860	-2.13845073	0.64973279
C	-5.41769188	-1.59894440	0.09218785
H	-4.25948352	-3.13910909	1.09235171
H	-6.34391060	-2.18143370	0.09384835
C	-5.41999661	-0.29995780	-0.47234041
C	-4.27150501	0.49955241	-0.49768543
H	-6.34955453	0.09522866	-0.89399860
H	-4.27488721	1.50778072	-0.91377772
O	1.92308419	0.68363079	1.73031031
C	1.28408898	0.92608006	2.82156914
O	0.05503955	0.69148831	2.98989288
C	2.08897296	1.49429087	3.96976166
H	2.43604339	0.65450426	4.59806968
H	2.96794996	2.04015874	3.59752615
H	1.45280978	2.14249025	4.59035196
H	-0.40586127	0.02668924	1.86567601

Intermediate **A**

Lowest frequency = 13.70 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1355.121477 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1358.195574 E_h

G_{corr} (298.15) = 0.395849 E_h

Charge = 1, Multiplicity = 1

C	0.43887170	2.30011310	-1.95540058

C	-0.37598799	3.38354718	-1.37857268
C	-0.44887128	1.30105127	-2.48247705
C	-1.73918449	3.00948490	-1.48949356
C	-1.80248330	1.67416749	-2.10411982
C	0.18716486	4.63313353	-0.77452522
H	0.98357071	4.39353408	-0.05000405
H	0.62820169	5.27384665	-1.55970439
H	-0.58682735	5.21683825	-0.25348939
C	-2.93605204	3.81478062	-1.08528593
H	-2.68105661	4.59123798	-0.34711358
H	-3.35164662	4.32475546	-1.97414969
H	-3.73625363	3.17920433	-0.67320371
C	-3.05543486	0.94360721	-2.48500530
H	-2.87891216	-0.14150440	-2.54288988
H	-3.86075470	1.12189717	-1.75500030
H	-3.41438211	1.28587390	-3.47363366
C	-0.07124499	0.12336926	-3.32589206
H	-0.72358003	-0.74166353	-3.13717778
H	-0.17295195	0.40476801	-4.39061772
H	0.97336709	-0.17990642	-3.16001296
C	1.93196562	2.33378585	-2.08649835
H	2.22273087	2.93415992	-2.96869456
H	2.39790670	2.79597810	-1.20175728
H	2.34932171	1.32282494	-2.21240247
Rh	-0.67572361	1.42090953	-0.32514464
C	0.18020918	-1.67519339	-0.51451856
C	-0.32241224	-2.88031571	0.12011172
H	0.98749219	-1.63956019	-1.24649198
C	-1.36921681	-2.49551678	1.00576476
C	-0.52443454	-0.58468096	-0.03868092
N	-1.47601997	-1.09161055	0.90048045
C	-2.25821706	-0.20515948	1.58568008
N	-2.05711893	1.10397131	1.22483870
C	-2.72946148	2.04768217	1.91167252
C	-3.80355465	0.33487433	3.17484267
H	-2.52664114	3.08558048	1.63458121
H	-4.51156962	-0.01495477	3.93623509
N	-3.11941894	-0.61228246	2.52428033
C	-3.63294489	1.70600918	2.91812548
H	-4.18005782	2.47232136	3.47148030
C	0.02192499	-4.24037839	0.01146135
C	-0.68327438	-5.17229989	0.78148205
H	0.82338803	-4.56028825	-0.66156785
H	-0.43031647	-6.23463697	0.70940035
C	-1.71630727	-4.76596601	1.65204911
C	-2.07968517	-3.41762300	1.78266991
H	-2.24887507	-5.51878387	2.24150563
H	-2.87485317	-3.09401068	2.45514092
O	0.71334384	1.95415039	1.25608689
C	1.58257043	1.27094578	1.84042452
O	1.76262400	-0.01203843	1.63638099

C	2.50897472	1.88532583	2.84978613
H	3.55356064	1.67102375	2.56813600
H	2.33998749	2.96793639	2.91490329
H	2.33450796	1.41411866	3.83249979
H	1.08863602	-0.35537776	0.96239124

Intermediate **B**

Lowest frequency = 12.05 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.180671 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.810047 E_h

G_{corr} (298.15) = 0.523600 E_h

Charge = 1, Multiplicity = 1

C	-0.86261491	-2.82723780	-0.04265985
C	-1.77890500	-2.00823529	0.74207213
C	0.40681296	-2.86940249	0.63632249
C	-1.05934808	-1.54620058	1.89569604
C	0.29898793	-2.03984327	1.82758695
C	-1.11942666	-0.28587629	-1.83000589
C	-3.24154620	-1.81533363	0.46792631
H	-3.45839467	-1.82722270	-0.61193158
H	-3.82839556	-2.62940878	0.93208445
H	-3.61256735	-0.86339930	0.88035612
C	-1.61405272	-0.71772529	3.01396240
H	-2.53765386	-0.19481080	2.72215883
H	-1.86373458	-1.37534861	3.86701760
H	-0.88353000	0.02418940	3.37399196
C	1.36048177	-1.85855732	2.87115834
H	2.36205553	-1.83294316	2.41411088
H	1.21707456	-0.92087797	3.43033372
H	1.32906041	-2.69320774	3.59555704
C	1.55342184	-3.76236160	0.27365978
H	2.48205738	-3.45035085	0.77178978
H	1.32545750	-4.79513511	0.59692537
H	1.72386477	-3.78594672	-0.81432199
C	-1.21047719	-3.63384127	-1.25734125
H	-1.44398210	-4.67061073	-0.95192306
H	-2.09389207	-3.23780219	-1.78135860
H	-0.37132816	-3.67346079	-1.96877375
Rh	0.00475115	-0.79492757	0.02557565
C	0.24373586	-0.48825758	-2.10703786
C	1.05335231	-1.30186853	-3.04534293
C	1.26194086	0.21254306	-2.92759002
H	0.55536276	-1.70669632	-3.93524306
H	1.86497488	-1.91968480	-2.64431028
H	2.20636892	0.53647225	-2.47761645
H	0.88880733	0.85255605	-3.73574372
C	3.18916931	-0.88342768	-0.34654708
C	4.22663340	0.13113428	-0.24138638

H	3.35873314	-1.92018717	-0.63083100
C	3.60085907	1.35781040	0.11798117
C	1.97880440	-0.30438416	-0.05654751
N	2.21958346	1.07069896	0.22647079
C	1.16986267	1.87119555	0.55273443
N	-0.04167191	1.22168771	0.55501684
C	-1.12298397	1.92647824	0.94377057
C	0.25138758	3.85371604	1.21705424
H	-2.07401696	1.38936964	0.95021170
H	0.40575039	4.91365266	1.45401147
N	1.33629860	3.16535145	0.85266134
C	-1.02524166	3.26982348	1.30082007
H	-1.90489967	3.83649784	1.61307344
C	5.62110960	0.10360805	-0.42201110
C	6.34460435	1.28960457	-0.24236937
H	6.12912437	-0.82542763	-0.69893808
H	7.43017691	1.28524363	-0.38205663
C	5.69992343	2.49115742	0.11577328
C	4.31070824	2.54824830	0.30531015
H	6.29271066	3.40135902	0.24930900
H	3.80119079	3.47165746	0.58303410
C	-1.81683324	1.05129432	-1.98122736
H	-2.61986330	1.15769975	-1.23038252
H	-1.10242917	1.87757781	-1.84575652
C	-2.42577769	1.10750208	-3.37580942
C	-3.59659202	0.38166793	-3.67022329
C	-1.80860454	1.84551976	-4.40279917
C	-4.13830783	0.39225234	-4.96189898
H	-4.09758824	-0.18718737	-2.87708561
C	-2.35033518	1.85878515	-5.69595342
H	-0.90804148	2.43031711	-4.18405071
C	-3.51345947	1.12907257	-5.97942792
H	-5.05368045	-0.16960910	-5.17421219
H	-1.86493620	2.44553624	-6.48250326
H	-3.93695613	1.14022371	-6.98867818
H	-1.78747171	-1.14583871	-1.95928747

Transition State **TS(B-C)**

Lowest frequency = -293.24 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.160947 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.788050 E_h

G_{corr} (298.15) = 0.526159 E_h

Charge = 1, Multiplicity = 1

C	-1.81916643	-2.34297319	0.37400538
C	-1.85551766	-1.49316645	1.52971916
C	-0.49213521	-2.91848698	0.27628577
C	-0.55385545	-1.61535045	2.20213987
C	0.26481331	-2.51641130	1.45565267

C	-1.11724865	0.03524323	-1.62756923
C	-3.06260714	-0.77364131	2.05964128
H	-3.63708796	-0.29261117	1.25197834
H	-3.73166945	-1.48415320	2.57993482
H	-2.78352246	-0.00182256	2.79421986
C	-0.18945519	-0.95105245	3.49540913
H	-0.65150938	0.04495547	3.58686751
H	-0.55253510	-1.55943587	4.34421705
H	0.90043685	-0.83763294	3.60034320
C	1.64257149	-2.98463576	1.80866345
H	2.08861030	-2.36493760	2.60113667
H	1.60650349	-4.02839532	2.17011198
H	2.31509887	-2.95069738	0.93566707
C	-0.05002295	-3.91714943	-0.75211768
H	1.04745452	-3.96447219	-0.81847595
H	-0.41186108	-4.92676207	-0.48200697
H	-0.44839654	-3.67437333	-1.75018754
C	-2.97264588	-2.66236411	-0.52627097
H	-3.43277496	-3.61403034	-0.20111357
H	-3.74428088	-1.88009054	-0.48643127
H	-2.65506235	-2.79669610	-1.57351045
Rh	-0.28409724	-0.74634462	0.17374578
C	0.24254573	-0.25576500	-2.02709294
C	0.63343000	-1.02673583	-3.24243808
C	1.02245688	0.44509812	-3.09860274
H	-0.17902632	-1.29301292	-3.92923422
H	1.45036805	-1.75079606	-3.20142292
H	2.08661524	0.65710997	-2.94777539
H	0.48266743	1.19964997	-3.68319488
C	2.66915681	-1.23718212	-1.02857900
C	3.88260455	-0.46704344	-0.93437216
H	2.59272611	-2.24974473	-1.42318054
C	3.53853921	0.83074378	-0.44846257
C	1.60031469	-0.44727220	-0.62614937
N	2.14289985	0.81956315	-0.23980128
C	1.36384090	1.69497373	0.46638261
N	0.12048220	1.20841080	0.78382753
C	-0.68127246	1.99610338	1.52748630
C	1.02165982	3.66531063	1.56681657
H	-1.67234086	1.59872849	1.75406719
H	1.41875053	4.64603503	1.85588869
N	1.82530831	2.89771933	0.82062380
C	-0.26002911	3.25345071	1.96300096
H	-0.91091195	3.88476083	2.57186404
C	5.23188326	-0.75730861	-1.22441683
C	6.18936917	0.24068423	-1.02155170
H	5.51969215	-1.74424662	-1.59948075
H	7.24073756	0.03479737	-1.24479935
C	5.82346495	1.51430358	-0.53372890
C	4.49039331	1.83359126	-0.23560842
H	6.59626050	2.27554748	-0.38877420

H	4.19876246	2.81568011	0.13762696
C	-1.68154902	1.44376113	-1.73974380
H	-0.95706385	2.19139406	-1.37822309
H	-1.80616995	1.65054148	-2.82494791
C	-3.02465520	1.63490848	-1.05998002
C	-3.24944249	2.71529699	-0.18693721
C	-4.09340223	0.75122092	-1.31111776
C	-4.48498503	2.88176687	0.45766358
H	-2.45098395	3.44730625	-0.02387902
C	-5.33100419	0.91432287	-0.67347949
H	-3.96681681	-0.06417686	-2.03143577
C	-5.52689063	1.97335110	0.22658035
H	-4.63745057	3.73152614	1.13145438
H	-6.14956382	0.21929682	-0.88828983
H	-6.49287496	2.10223426	0.72480829
H	-1.84141113	-0.73964895	-1.91241947

Intermediate **C**

Lowest frequency = 21.43 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.182713 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.810949 E_h

G_{corr} (298.15) = 0.52463 E_h

Charge = 1, Multiplicity = 1

C	-1.54865874	1.83124687	-0.41464605
C	-1.37632841	1.02354975	-1.60532703
C	-0.28836288	2.47123185	-0.14606793
C	-0.02587646	1.29036089	-2.13953441
C	0.63552888	2.17299960	-1.25678811
C	-0.94718526	-0.58418620	1.54720605
C	-2.45964374	0.26862444	-2.31531667
H	-3.14892933	-0.21690808	-1.60583774
H	-3.05644166	0.95919547	-2.94111499
H	-2.04749233	-0.50146873	-2.98680983
C	0.51685878	0.70074568	-3.40594631
H	0.23760103	-0.36168702	-3.51144548
H	0.10757362	1.23286952	-4.28448612
H	1.61465845	0.77206451	-3.44672754
C	2.01549014	2.73713642	-1.40276024
H	2.54555500	2.77022037	-0.43779750
H	2.62477594	2.14070876	-2.09941366
H	1.96796966	3.77121361	-1.79252302
C	-0.02015572	3.45846519	0.95174927
H	1.05463671	3.52270812	1.18088771
H	-0.35589449	4.46558131	0.64048276
H	-0.56055357	3.19723031	1.87548563
C	-2.81951677	2.00669590	0.36015276
H	-3.41761295	2.82431492	-0.08298614
H	-3.43764963	1.09514693	0.34383996

H	-2.62115452	2.27075142	1.41076439
Rh	-0.02550819	0.31866726	-0.09771073
C	0.35189451	-1.10579886	2.14010421
C	0.48122847	-1.53842308	3.59367058
C	0.58895935	-2.56195783	2.49546750
H	-0.44173182	-1.52136914	4.18317955
H	1.39208839	-1.26083378	4.13554598
H	1.57810182	-2.98539993	2.28786526
H	-0.24303054	-3.25835512	2.36215993
C	2.12605219	0.82590698	1.93538746
C	3.41657689	0.92073645	1.32558406
H	1.70755027	1.49447505	2.68820617
C	3.59223689	-0.24569969	0.51545807
C	1.50728385	-0.35318979	1.50771680
N	2.43163910	-1.01862406	0.63512967
C	1.92162689	-1.88853037	-0.32895067
N	0.63819667	-1.59875063	-0.69707444
C	0.04632585	-2.45352566	-1.55876106
C	2.09586336	-3.66954415	-1.73298653
H	-0.99492581	-2.24171665	-1.81583491
H	2.72882111	-4.45696606	-2.15853014
N	2.67420135	-2.85966210	-0.82865178
C	0.75140463	-3.52895770	-2.10502675
H	0.27383657	-4.21403121	-2.80956960
C	4.44615804	1.88980641	1.37877546
C	5.59458033	1.68102720	0.61731933
H	4.33963267	2.77946963	2.00712576
H	6.40769972	2.41233291	0.64772814
C	5.73245316	0.52862465	-0.19606279
C	4.73717954	-0.45250030	-0.26486614
H	6.65095461	0.39412369	-0.77599516
H	4.85098168	-1.35347153	-0.87147416
C	-2.07372284	-1.56912369	1.24523490
H	-2.82256862	-1.05895802	0.60936278
H	-1.68971223	-2.42038397	0.65694400
C	-2.77368778	-2.10578166	2.48906116
C	-3.33452772	-1.22619493	3.43628582
C	-2.87527298	-3.49010739	2.71953784
C	-3.96907111	-1.71718090	4.58490711
H	-3.28022276	-0.14356795	3.27274317
C	-3.50783854	-3.98623237	3.86872401
H	-2.45935473	-4.19096618	1.98525219
C	-4.05325188	-3.10006406	4.80755248
H	-4.40221404	-1.01849200	5.30834439
H	-3.57568300	-5.06722035	4.02908117
H	-4.54634258	-3.48402015	5.70622351
H	-1.32593186	0.26176710	2.14799440

Transition State **TS(C-D)**

Lowest frequency = -88.48 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.174457 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.802544 E_h

G_{corr} (298.15) = 0.527509 E_h

Charge = 1, Multiplicity = 1

C	-1.75979669	0.87314301	-2.00376748
C	-1.49877589	-0.51956929	-2.42797641
C	-0.49826411	1.52378312	-1.89419648
C	-0.09878399	-0.69291075	-2.65956596
C	0.53934941	0.53363033	-2.25426727
C	-0.96477651	0.81223339	1.31860845
C	-2.56712203	-1.54007578	-2.64878885
H	-3.39918022	-1.40266009	-1.94142507
H	-2.97524576	-1.42314050	-3.67128325
H	-2.17802624	-2.56660925	-2.56013067
C	0.59618434	-1.93864531	-3.12348188
H	0.00648668	-2.83964614	-2.88973432
H	0.75224717	-1.91778307	-4.21764321
H	1.58600939	-2.04531691	-2.64992756
C	1.99656244	0.83365955	-2.34050253
H	2.31347246	1.55562989	-1.57364235
H	2.61610092	-0.07047444	-2.24954216
H	2.20339780	1.28539801	-3.33038700
C	-0.23529393	2.95708422	-1.55424001
H	0.66754589	3.05516711	-0.93041508
H	-0.07609325	3.54036147	-2.48032264
H	-1.08427507	3.40236821	-1.01365513
C	-3.11238272	1.49348424	-1.86390209
H	-3.46286296	1.83125630	-2.85787622
H	-3.85065484	0.78073678	-1.46824311
H	-3.08860734	2.36713243	-1.19653347
Rh	-0.53969231	-0.10271158	-0.50757151
C	0.33867064	0.85162548	2.13179118
C	0.33080077	1.55382829	3.48473120
C	0.49497433	0.06072801	3.42978724
H	-0.63388744	1.94952713	3.82239612
H	1.19555180	2.16574352	3.75977222
H	1.48766213	-0.34938572	3.64772792
H	-0.33350916	-0.56878292	3.76671404
C	2.42463271	2.07360319	1.16659573
C	3.66971202	1.63339644	0.58420716
H	2.18180163	3.08696933	1.48760363
C	3.59556255	0.21624204	0.44786758
C	1.60628775	0.98245176	1.34995404
N	2.31195570	-0.17333556	0.88761723
C	1.80629420	-1.46502243	0.87302171
N	0.48642212	-1.62095223	0.55477260
C	-0.03617302	-2.86319154	0.68498044
C	2.12672596	-3.70998398	1.19676154
H	-1.10391383	-2.96382352	0.46699806

H	2.83450129	-4.52408215	1.39556621
N	2.63860341	-2.47607256	1.13976051
C	0.75421170	-3.95702309	1.02926699
H	0.32644821	-4.95756184	1.12454637
C	4.83001578	2.30859550	0.15511059
C	5.87569564	1.56263882	-0.39550518
H	4.90662116	3.39593370	0.25293262
H	6.78686829	2.06933306	-0.72801851
C	5.77931444	0.15903204	-0.52232497
C	4.63891017	-0.53881359	-0.10400568
H	6.61989423	-0.40096810	-0.94385555
H	4.57794221	-1.62596003	-0.17524250
C	-2.10576400	0.05639904	2.02573676
H	-1.82837627	-1.00487985	2.15957024
H	-2.21861977	0.46620144	3.05172650
C	-3.45437185	0.13287066	1.34389565
C	-4.00014136	-0.99025441	0.69518367
C	-4.21253414	1.31940174	1.37794085
C	-5.26591490	-0.93382375	0.09042103
H	-3.43856533	-1.93270375	0.68984378
C	-5.47645574	1.38268737	0.77611945
H	-3.81429808	2.19903499	1.89696966
C	-6.00688994	0.25650454	0.12679902
H	-5.68119633	-1.82397707	-0.39412627
H	-6.05565367	2.31069660	0.82186138
H	-6.99869029	0.30232285	-0.33390682
H	-1.28209834	1.84698058	1.09310285

Intermediate **D**

Lowest frequency = 13.62 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.184129 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.810504 E_h

G_{corr} (298.15) = 0.525620 E_h

Charge = 1, Multiplicity = 1

C	-1.52064069	-1.79061939	1.43724440
C	-2.67609492	-1.36830571	0.63125432
C	-0.92473565	-0.61054324	2.02150246
C	-2.74279005	0.04793589	0.65108526
C	-1.62573206	0.52870535	1.48090883
C	1.22855534	-1.16417626	-0.41956531
C	-3.61677667	-2.30997661	-0.05813851
H	-3.08444994	-3.18725704	-0.45895636
H	-4.36656622	-2.68228127	0.66461434
H	-4.15781710	-1.81763507	-0.88119895
C	-3.76930167	0.92716481	0.00068290
H	-4.27638147	0.41130619	-0.83011568
H	-4.54262734	1.22766831	0.73197789
H	-3.31668657	1.85201232	-0.39373415

C	-1.41077751	1.95843033	1.86906326
H	-0.39718040	2.13332915	2.25594282
H	-1.58500644	2.64624747	1.02635021
H	-2.13099944	2.22905569	2.66406379
C	0.19526969	-0.56826492	3.01646926
H	0.82360986	0.32530728	2.87676355
H	-0.21445961	-0.54509502	4.04331980
H	0.83975789	-1.45756066	2.93501180
C	-1.16517822	-3.21203009	1.75692270
H	-1.75998451	-3.56085136	2.62185343
H	-1.37099926	-3.88436335	0.90992376
H	-0.10042317	-3.31323961	2.01751173
Rh	-0.73540612	-0.55839402	-0.16034100
C	2.22054697	-0.08356786	-0.77879354
C	3.59470513	-0.49219495	-1.29781328
C	2.62903091	0.20537150	-2.21549574
H	3.75727683	-1.56470090	-1.45245830
H	4.46962636	0.06010138	-0.94023807
H	2.83147209	1.25116122	-2.47247349
H	2.16889277	-0.36963671	-3.02623703
C	2.94350254	1.39448960	1.22689607
C	2.56756863	2.70428634	1.70585904
H	3.74673311	0.76655750	1.61295711
C	1.54878010	3.19562757	0.84126388
C	2.16252912	1.08278114	0.14281272
N	1.26923291	2.16779616	-0.09615031
C	0.31962955	2.23680758	-1.10241678
N	-0.37170391	1.10698591	-1.45152412
C	-1.15777807	1.19431003	-2.55366571
C	-0.72397414	3.52263665	-2.69729889
H	-1.66960530	0.27278788	-2.84688852
H	-0.88880870	4.52473908	-3.11270845
N	0.11375620	3.43675923	-1.66328590
C	-1.35178944	2.38904987	-3.23952162
H	-1.99509741	2.43984426	-4.12078178
C	3.00535932	3.49777715	2.78431702
C	2.42189659	4.75362266	2.97458137
H	3.78817651	3.13405025	3.45708765
H	2.75241457	5.38576208	3.80449054
C	1.41545964	5.22347814	2.10382531
C	0.96359985	4.45579114	1.02225659
H	0.98425952	6.21628594	2.26592067
H	0.20559736	4.83471424	0.33581910
C	0.53909906	-1.96977916	-1.46597385
H	-0.61460385	-1.57428281	-1.61032636
H	0.86260004	-1.70466511	-2.48965854
C	0.39442544	-3.46373721	-1.28258371
C	-0.71544621	-4.13658496	-1.83022746
C	1.36399214	-4.20699647	-0.58660456
C	-0.86429076	-5.51971407	-1.67046138
H	-1.47235674	-3.56884470	-2.38519948

C	1.21661079	-5.59273860	-0.42635084
H	2.24321217	-3.70441194	-0.17110567
C	0.10081716	-6.25125632	-0.96056052
H	-1.73338838	-6.02818799	-2.10001682
H	1.97954198	-6.15913780	0.11714357
H	-0.01411541	-7.33196874	-0.83163138
H	1.53348717	-1.72300240	0.47669194

Transition State **TS(D-E)**

Lowest frequency = -616.27 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.179995 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.806341 E_h

G_{corr} (298.15) = 0.523113 E_h

Charge = 1, Multiplicity = 1

C	1.36690875	0.45730283	-2.15056956
C	1.92995991	1.66038511	-1.55016641
C	-0.07525264	0.57677169	-2.14243239
C	0.84601239	2.51565190	-1.14482818
C	-0.38705960	1.82698982	-1.49261834
C	0.83868851	-1.46647929	0.48538445
C	3.39373651	1.96861143	-1.45986793
H	3.98779495	1.05963702	-1.27853573
H	3.73748262	2.41272971	-2.41250693
H	3.60774344	2.68755765	-0.65399187
C	0.94802165	3.90041828	-0.57395191
H	1.90342898	4.04800773	-0.04601358
H	0.88699261	4.65908574	-1.37656231
H	0.12974482	4.10665506	0.13548323
C	-1.76124887	2.38901413	-1.29099513
H	-2.53232981	1.60486386	-1.30806214
H	-1.83988051	2.94717180	-0.34404691
H	-1.98596792	3.09879070	-2.10854348
C	-1.04961238	-0.36973935	-2.77623851
H	-2.04927499	-0.28669957	-2.32395208
H	-1.14635340	-0.14818659	-3.85566927
H	-0.72210332	-1.41599441	-2.67452488
C	2.15248291	-0.63021300	-2.81837304
H	2.32917641	-0.36201753	-3.87675827
H	3.13229710	-0.77870791	-2.33982502
H	1.60880919	-1.58834653	-2.80741627
Rh	0.73514687	0.57540564	-0.06002455
C	-0.36355629	-1.99214906	1.22533277
C	-0.22083946	-3.30740870	1.98513416
C	-0.42109200	-2.02561180	2.74491497
H	0.77848467	-3.75560331	1.99773294
H	-1.04868432	-4.02204248	1.93772137
H	-1.39910698	-1.85212045	3.20733506
H	0.42068684	-1.61959043	3.31556536

C	-2.36803255	-2.61101932	-0.29557958
C	-3.58141158	-1.94084421	-0.69797824
H	-2.07703037	-3.63259670	-0.54091374
C	-3.58014550	-0.65693539	-0.08245162
C	-1.64067194	-1.76284738	0.50008225
N	-2.35923251	-0.53749647	0.62904827
C	-1.99897309	0.53797662	1.42641169
N	-0.68201016	0.90642175	1.49902614
C	-0.36627323	1.85024159	2.42111705
C	-2.66820976	2.15781124	2.91360484
H	0.69480334	2.10273412	2.49611115
H	-3.50409040	2.67726316	3.39872546
N	-2.98631526	1.17634326	2.06832601
C	-1.33284712	2.49941874	3.18302211
H	-1.05880750	3.26265442	3.91480355
C	-4.65560180	-2.31070438	-1.53016016
C	-5.69669437	-1.39928626	-1.72913436
H	-4.67002018	-3.29361578	-2.01110293
H	-6.54111900	-1.67101652	-2.36994252
C	-5.67869283	-0.13261737	-1.10727960
C	-4.62430740	0.25935884	-0.27138312
H	-6.51262585	0.55777504	-1.26760953
H	-4.63324303	1.22593805	0.23373293
C	1.97014312	-0.85682552	1.15093888
H	1.87173690	0.65084276	1.10633691
H	1.86729337	-0.76161024	2.24314985
C	3.38912360	-1.07785096	0.71473347
C	4.40097765	-0.20304049	1.16162028
C	3.74913878	-2.17209499	-0.09446057
C	5.73562225	-0.40373860	0.79414383
H	4.13365979	0.65106996	1.79566681
C	5.08675422	-2.37242880	-0.46614164
H	2.98551307	-2.88350888	-0.42243047
C	6.08192987	-1.48827629	-0.02785117
H	6.50848834	0.28552716	1.14875483
H	5.35174504	-3.23074741	-1.09169886
H	7.12551035	-1.64795138	-0.31636759
H	1.04361908	-2.01652804	-0.44201124

Intermediate **E**

Lowest frequency = 14.26 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.183199 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.811109 E_h

G_{corr} (298.15) = 0.525118 E_h

Charge = 1, Multiplicity = 1

C	1.38267970	0.40461976	-2.09401711
C	1.95290518	1.60788211	-1.52293496
C	-0.06273182	0.52240847	-2.08769482

C	0.84829435	2.47133631	-1.13701123
C	-0.37998622	1.79467488	-1.50147761
C	0.84769749	-1.51138304	0.48104404
C	3.41327309	1.94396970	-1.48445721
H	4.02596162	1.05101628	-1.28713183
H	3.72380138	2.36394068	-2.45919960
H	3.63537144	2.68841708	-0.70491778
C	0.94766304	3.87698638	-0.61813229
H	1.90472727	4.04772499	-0.10202222
H	0.87831522	4.59779388	-1.45397053
H	0.13139637	4.10656120	0.08570084
C	-1.75104128	2.37232859	-1.33289660
H	-2.53048146	1.59816114	-1.37943977
H	-1.84834223	2.92050243	-0.38169699
H	-1.94479548	3.09570854	-2.14654119
C	-1.02221323	-0.43643721	-2.72475042
H	-2.03856547	-0.32670549	-2.31829761
H	-1.07135262	-0.25285608	-3.81456007
H	-0.71168184	-1.48191498	-2.57465917
C	2.15720554	-0.69079507	-2.75692660
H	2.27243984	-0.44674421	-3.82982138
H	3.16203713	-0.80197200	-2.32470949
H	1.63550796	-1.65922523	-2.69636089
Rh	0.80893366	0.62055201	0.03748357
C	-0.37493967	-2.00826376	1.19750845
C	-0.24437815	-3.33732003	1.93922906
C	-0.43154807	-2.06517565	2.71653965
H	0.75024735	-3.79535054	1.94444375
H	-1.08044783	-4.04093970	1.87592215
H	-1.40799799	-1.88952397	3.18128216
H	0.41664597	-1.67427150	3.28690495
C	-2.39031541	-2.60300373	-0.31650153
C	-3.59166561	-1.91399631	-0.72208959
H	-2.11739844	-3.63089792	-0.55622394
C	-3.56468878	-0.62486187	-0.11836905
C	-1.64567294	-1.76140467	0.46986584
N	-2.33906552	-0.52032970	0.58805335
C	-1.98598832	0.52430140	1.43010619
N	-0.66638128	0.87114766	1.56341387
C	-0.37513668	1.73671005	2.57027098
C	-2.68855603	2.06495799	2.98696724
H	0.68514434	1.96021530	2.70611015
H	-3.53480446	2.57642903	3.46235481
N	-2.98543897	1.14654310	2.06717690
C	-1.35966428	2.34605418	3.34100339
H	-1.09898252	3.04352334	4.14023538
C	-4.67444224	-2.27235356	-1.54831672
C	-5.70027653	-1.34500069	-1.75152151
H	-4.70748561	-3.25912834	-2.02029200
H	-6.55146139	-1.60734022	-2.38724870
C	-5.65858280	-0.07395144	-1.13954760

C	-4.59473285	0.30691293	-0.31083987
H	-6.48142432	0.62906379	-1.30224935
H	-4.58635983	1.27761178	0.18617854
C	1.96142929	-0.92261636	1.12445240
H	1.77047649	1.31966681	1.07567870
H	1.84165338	-0.67580693	2.18600404
C	3.37514944	-1.06292579	0.69079524
C	4.35265992	-0.17682320	1.19425704
C	3.78891778	-2.10088666	-0.16986855
C	5.69538093	-0.30412172	0.82557523
H	4.04532657	0.62921309	1.87034747
C	5.13436435	-2.22640147	-0.54393504
H	3.05831275	-2.83115633	-0.53132695
C	6.09053119	-1.32593923	-0.05368627
H	6.43853482	0.39399491	1.22403926
H	5.43831331	-3.04157919	-1.20851435
H	7.14132706	-1.42765919	-0.34240675
H	1.00843799	-1.99856380	-0.48906249

Intermediate **B1**

Lowest frequency = 12.32 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.176885 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.805962 E_h

G_{corr} (298.15) = 0.523048 E_h

Charge = 1, Multiplicity = 1

C	-2.97910725	-1.49766338	0.45316801
C	-3.43828776	-0.17051233	0.69961959
C	-1.84182736	-1.76175686	1.33670330
C	-2.59221302	0.40036629	1.74962376
C	-1.66348885	-0.60518930	2.18509787
C	-1.20890787	-0.55942365	-2.08103429
C	-4.66192991	0.47109156	0.11377211
H	-4.79989026	0.20370574	-0.94630513
H	-5.56282406	0.13206954	0.65802455
H	-4.62909778	1.56843405	0.19982931
C	-2.75402188	1.75980822	2.36056417
H	-3.12659363	2.49424910	1.62901155
H	-3.48439804	1.71556676	3.18958364
H	-1.80144542	2.13005163	2.77005515
C	-0.72957969	-0.49134423	3.34953345
H	0.11228567	-1.19292816	3.26704128
H	-0.31765752	0.52449334	3.44602475
H	-1.28266951	-0.72909032	4.27737822
C	-1.15629556	-3.08493952	1.50838556
H	-0.10337981	-2.95896939	1.80473190
H	-1.66218253	-3.67021688	2.29841551
H	-1.18634120	-3.68333460	0.58454125
C	-3.60085353	-2.49426251	-0.47635915

H	-4.22159337	-3.20070807	0.10500103
H	-4.24684658	-2.00780011	-1.22150246
H	-2.84353850	-3.08910661	-1.01217268
Rh	-1.27186135	-0.08645541	0.02328428
C	-0.37864921	-1.51189276	-1.46877546
C	1.72644125	-0.23050555	1.09881931
C	2.81118313	0.73608196	1.15390677
H	1.77801347	-1.25540516	1.46650178
C	2.35149632	1.94039741	0.54941048
C	0.64768568	0.35390670	0.48526379
N	1.01828621	1.68886898	0.14707078
C	0.09188833	2.49988394	-0.42749096
N	-1.12834442	1.89594024	-0.61883729
C	-2.10485999	2.63029719	-1.18668823
C	-0.61280057	4.48514405	-1.31079854
H	-3.05961853	2.12363792	-1.34866683
H	-0.36735302	5.52106281	-1.57569510
N	0.36951546	3.76729417	-0.76147336
C	-1.89584678	3.95966608	-1.55051370
H	-2.69154010	4.55245392	-2.00661433
C	4.12387246	0.68385256	1.65601762
C	4.93207002	1.82262588	1.54297325
H	4.50557334	-0.22885903	2.12413788
H	5.95642304	1.79671347	1.92777535
C	4.45095528	3.00318595	0.94132112
C	3.14607657	3.08479013	0.43112504
H	5.10673722	3.87620310	0.86743962
H	2.76314255	3.99218085	-0.03754416
C	-1.09783313	0.28312444	-3.29492233
H	-1.20600924	1.37206052	-3.23674650
H	-0.40186749	-0.05748420	-4.07064600
C	-2.35575802	-0.55164943	-3.02511897
H	-2.53845599	-1.45328113	-3.62330440
H	-3.26251994	0.01262263	-2.77314284
H	-0.84167750	-2.46307983	-1.17781248
C	1.10959395	-1.60712610	-1.73243135
H	1.53448228	-0.60945240	-1.91939714
H	1.62838434	-2.03139300	-0.85812906
C	1.30210480	-2.50698714	-2.94590414
C	1.69310828	-1.97030543	-4.18710395
C	1.05993391	-3.89220951	-2.85409595
C	1.83804412	-2.79717340	-5.31039895
H	1.90966593	-0.89890750	-4.26773914
C	1.20109830	-4.71967534	-3.97552075
H	0.77299552	-4.33099773	-1.89052903
C	1.58720870	-4.17279933	-5.20864792
H	2.15485131	-2.36611312	-6.26571084
H	1.01792803	-5.79546829	-3.88598693
H	1.70161237	-4.81899251	-6.08473408

Transition State **TS(B1-C1)**

Lowest frequency = -234.82 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.156825 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.785397 E_h

G_{corr} (298.15) = 0.525793 E_h

Charge = 1, Multiplicity = 1

C	-3.27702566	-1.43515539	0.65318147
C	-3.66254653	-0.05192749	0.55864041
C	-2.22130695	-1.54404488	1.63675992
C	-2.88097726	0.68239780	1.55857568
C	-2.01934314	-0.23329742	2.23924206
C	-1.27691694	-0.96949724	-1.88295974
C	-4.78474289	0.50492344	-0.26909498
H	-4.86551768	-0.01064661	-1.23971988
H	-5.75185586	0.38891356	0.25499815
H	-4.64884988	1.58115313	-0.46301118
C	-3.01040342	2.14869731	1.84147751
H	-3.25457424	2.72029506	0.93172618
H	-3.82987159	2.31689810	2.56435833
H	-2.08713575	2.56257204	2.27563902
C	-1.07824413	0.07399766	3.36412979
H	-0.10995144	-0.43426324	3.22179307
H	-0.88481852	1.15474415	3.44339292
H	-1.50440216	-0.26671025	4.32528102
C	-1.60390613	-2.83069886	2.09980741
H	-0.66836149	-2.65246906	2.64972739
H	-2.29982344	-3.35666345	2.77996975
H	-1.39248447	-3.50678309	1.25544674
C	-3.92779594	-2.59944781	-0.02768873
H	-4.58015224	-3.11922611	0.69838699
H	-4.55908899	-2.28501294	-0.87165633
H	-3.18925771	-3.33029625	-0.39340290
Rh	-1.52449158	-0.21036270	0.04549899
C	0.05664760	-1.28951365	-1.42562895
C	1.39880367	-1.10328968	1.10421852
C	2.52748940	-0.29014197	1.48848076
H	1.27265251	-2.16159882	1.32954540
C	2.34352772	1.00553839	0.92232739
C	0.52669611	-0.33442134	0.34960922
N	1.11952056	0.96019491	0.22006611
C	0.43137275	1.94856242	-0.42787624
N	-0.86214792	1.61377561	-0.74154490
C	-1.58684497	2.51612473	-1.43006831
C	0.26417768	4.01801448	-1.37542250
H	-2.60757949	2.22054956	-1.68740422
H	0.74651856	4.97797036	-1.59654073
N	1.00708438	3.12031850	-0.71685747
C	-1.05734962	3.76021154	-1.77568549
H	-1.64984909	4.49402558	-2.32630714

C	3.68805550	-0.55171367	2.24121425
C	4.61533249	0.48000257	2.42221070
H	3.85850109	-1.54279506	2.67182802
H	5.52309453	0.29518911	3.00484299
C	4.40244517	1.75725312	1.86209215
C	3.26123205	2.04469678	1.09739943
H	5.14643080	2.54411939	2.02121166
H	3.09784909	3.02381083	0.64570318
C	-1.69276810	-0.40934316	-3.20007304
H	-2.44063146	0.39239816	-3.22935326
H	-0.96041112	-0.35833249	-4.01628188
C	-2.19270550	-1.77758079	-2.74217601
H	-1.78183122	-2.67242851	-3.22824498
H	-3.25552613	-1.85601675	-2.49487198
H	0.17790943	-2.29747484	-1.00844703
C	1.23512744	-0.80624933	-2.26390045
H	1.08787201	-1.33610156	-3.23049702
H	1.11855336	0.26477688	-2.49950028
C	2.62413194	-1.09900222	-1.74962567
C	2.98953745	-2.39967368	-1.35072916
C	3.58174660	-0.07358177	-1.66856911
C	4.27268659	-2.65985684	-0.85385762
H	2.26838844	-3.22170704	-1.43308456
C	4.86913911	-0.33144356	-1.17899124
H	3.31248167	0.94192314	-1.97972719
C	5.21420594	-1.62361927	-0.76151332
H	4.54222439	-3.67528665	-0.54552339
H	5.59861428	0.48141684	-1.11341179
H	6.21696035	-1.82586569	-0.37212191

Intermediate **C1**

Lowest frequency = 12.37 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.179195 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.806424 E_h

G_{corr} (298.15) = 0.525664 E_h

Charge = 1, Multiplicity = 1

C	-3.34134649	-1.28434342	0.66302786
C	-3.59323275	0.13894603	0.68892965
C	-2.26658713	-1.55186244	1.58362704
C	-2.74459888	0.72715799	1.74085503
C	-1.94035419	-0.30134139	2.28945089
C	-1.12390652	-1.00298230	-1.78184087
C	-4.68865782	0.84934236	-0.04893184
H	-4.83067196	0.43458293	-1.06014087
H	-5.64721533	0.74289116	0.49378093
H	-4.48665825	1.92897311	-0.13699674
C	-2.75124338	2.17358434	2.13560613
H	-2.85512062	2.83339836	1.25755330

H	-3.60438029	2.38536942	2.80641309
H	-1.82713905	2.45086614	2.66613783
C	-0.94590134	-0.16659450	3.40406413
H	-0.10974496	-0.87288806	3.28707933
H	-0.52375888	0.84973474	3.45111435
H	-1.43055194	-0.37752382	4.37554730
C	-1.72391118	-2.91158692	1.91434470
H	-0.72438138	-2.84695997	2.37053694
H	-2.38821830	-3.42173566	2.63697513
H	-1.65638407	-3.54564714	1.01572482
C	-4.12030999	-2.30800414	-0.10193230
H	-4.93407647	-2.69993305	0.53650059
H	-4.58414778	-1.87962938	-1.00398589
H	-3.49103878	-3.15969686	-0.40301832
Rh	-1.54700601	-0.18179307	0.07308607
C	0.31245732	-1.28982030	-1.39118169
C	1.44477189	-1.15897697	0.91050599
C	2.35468373	-0.23578787	1.49237711
H	1.38885489	-2.22702214	1.12111148
C	2.17704783	1.01583209	0.82125569
C	0.67802979	-0.51725192	-0.07930290
N	1.17177869	0.83906462	-0.13223350
C	0.44358700	1.83623780	-0.76106515
N	-0.88910122	1.56995930	-0.87228619
C	-1.64100729	2.46980977	-1.53865094
C	0.28110725	3.86241500	-1.79070729
H	-2.69984303	2.22495698	-1.65465452
H	0.78395541	4.78096801	-2.11551152
N	1.04825105	2.94741106	-1.17712985
C	-1.08663304	3.65677734	-2.02238736
H	-1.70006911	4.39232129	-2.54784169
C	3.33777405	-0.35453736	2.50342510
C	4.08998121	0.76992011	2.83088131
H	3.49880593	-1.31144954	3.00836070
H	4.86022363	0.70492192	3.60508376
C	3.87794190	2.00554070	2.16863481
C	2.92251178	2.15412601	1.15751769
H	4.49221035	2.86823759	2.44575853
H	2.78367224	3.09688430	0.62619267
C	-1.55493717	-0.50163657	-3.13106548
H	-2.38394460	0.21577589	-3.18756817
H	-0.80844463	-0.36885041	-3.92475856
C	-1.89871401	-1.91174754	-2.68600955
H	-1.35937848	-2.74643935	-3.15571523
H	-2.94962760	-2.13433764	-2.47567489
H	0.36521728	-2.34592032	-1.07389965
C	1.42279811	-1.05730180	-2.46108853
H	1.23504699	-1.77157531	-3.28394974
H	1.32468671	-0.04140569	-2.87928516
C	2.79857205	-1.24827443	-1.87100116
C	3.19904818	-2.50805797	-1.37648823

C	3.66492562	-0.15265853	-1.69828207
C	4.41964093	-2.66011315	-0.70496186
H	2.54976663	-3.37976223	-1.52293518
C	4.88412786	-0.30049726	-1.02445388
H	3.37009583	0.83156525	-2.07902974
C	5.25987308	-1.55284736	-0.51620015
H	4.71761839	-3.64540862	-0.33156967
H	5.54074731	0.56520662	-0.89188523
H	6.21133198	-1.66844284	0.01260161

Transition State **TS(C1-D1)**

Lowest frequency = -104.40 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.167312 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.794211 E_h

G_{corr} (298.15) = 0.523647 E_h

Charge = 1, Multiplicity = 1

C	3.74730131	-0.38574794	-0.95281140
C	3.81510511	0.42158166	0.29242327
C	2.81684785	0.23933251	-1.84139630
C	2.94247701	1.52737269	0.16409675
C	2.24945785	1.38021759	-1.11328267
C	0.67467250	-2.00160221	-0.68479714
C	4.69762813	0.09319098	1.45593759
H	4.71976028	-0.99184568	1.65123287
H	5.73661663	0.40589225	1.23988394
H	4.37398538	0.61100525	2.37190206
C	2.66055542	2.60118240	1.17206495
H	3.00692233	2.31384826	2.17708051
H	3.17366159	3.53988525	0.89393931
H	1.58121612	2.82259778	1.22859210
C	1.24780156	2.34588605	-1.65228487
H	0.63256050	1.89810394	-2.44485770
H	0.57721189	2.72444573	-0.86466976
H	1.78607891	3.21544907	-2.07747645
C	2.48878600	-0.14384518	-3.25180719
H	1.42150208	0.02259027	-3.46667092
H	3.08099946	0.46438855	-3.95986294
H	2.71279002	-1.20401527	-3.44310848
C	4.61537114	-1.57140328	-1.23615873
H	5.64562836	-1.23357014	-1.45594736
H	4.66949224	-2.25220484	-0.37062263
H	4.25452679	-2.14015278	-2.10594167
Rh	1.79167848	-0.41259117	-0.08383966
C	-0.83391593	-1.66657430	-0.74121153
C	-1.75988288	0.52424738	-1.73821588
C	-2.15400843	1.81573518	-1.23588972
H	-1.97738996	0.12000155	-2.72720362
C	-1.78419771	1.86172989	0.13832084

C	-1.13863682	-0.18271346	-0.73501268
N	-1.13999004	0.63909437	0.43540625
C	-0.59922568	0.30174083	1.66404286
N	0.56561180	-0.40413795	1.65365278
C	1.01237571	-0.88442393	2.83654089
C	-0.73942713	0.28019567	3.94866967
H	1.91857067	-1.49688800	2.80034118
H	-1.26151227	0.63042340	4.84745191
N	-1.23199477	0.69323613	2.77590661
C	0.37165743	-0.57559839	4.03451550
H	0.73965774	-0.95656005	4.98975809
C	-2.77275512	2.93743972	-1.82212917
C	-2.99943236	4.06796933	-1.03214808
H	-3.06902586	2.91944189	-2.87543190
H	-3.48529123	4.94610805	-1.46852034
C	-2.61592551	4.09426119	0.32699883
C	-2.00081422	2.99266721	0.93670152
H	-2.81578655	4.98907613	0.92466597
H	-1.73452343	3.00327798	1.99486387
C	1.19516461	-3.28049683	-0.02498752
H	2.16633694	-3.26299945	0.48906385
H	0.47580799	-3.97022484	0.43299399
C	1.20547087	-3.11905951	-1.53175870
H	0.47550370	-3.70900821	-2.10293124
H	2.17851852	-3.02601591	-2.02715503
H	-1.18000070	-1.97738737	-1.74278861
C	-1.74685240	-2.42018240	0.27733345
H	-1.61799356	-3.50383848	0.11343437
H	-1.41831367	-2.21384583	1.31079841
C	-3.19912740	-2.03566756	0.08961429
C	-3.93139655	-2.55880539	-0.99388674
C	-3.81912699	-1.09110463	0.92852015
C	-5.24596575	-2.14192641	-1.23928938
H	-3.46788678	-3.30502507	-1.65091029
C	-5.13298907	-0.66857398	0.68289392
H	-3.27299174	-0.67459286	1.78211719
C	-5.84886503	-1.18969907	-0.40367371
H	-5.80335267	-2.56397020	-2.08205180
H	-5.59800560	0.06944767	1.34459658
H	-6.87566312	-0.86170719	-0.59489652

Intermediate **D1**

Lowest frequency = 23.48 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.170694 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.798521 E_h

G_{corr} (298.15) = 0.525280 E_h

Charge = 1, Multiplicity = 1

C	0.72559930	2.45273074	-2.03987259

C	-0.49260916	3.23196431	-1.73091794
C	0.34204334	1.09717149	-2.31684966
C	-1.59416722	2.35114894	-1.75541234
C	-1.08755289	0.99887585	-2.05485782
C	1.18747945	0.38855562	0.75359918
C	-0.51061675	4.70885424	-1.47492511
H	0.35232282	5.02818251	-0.86804986
H	-0.45613218	5.25843412	-2.43350098
H	-1.43324894	5.02228774	-0.96224577
C	-3.03294602	2.67690146	-1.48908243
H	-3.14131887	3.63212511	-0.95207116
H	-3.59082115	2.75725081	-2.44005371
H	-3.51883775	1.88679567	-0.89236897
C	-1.93376740	-0.21154719	-2.29202078
H	-1.39331401	-1.13892708	-2.04850557
H	-2.86069996	-0.18855852	-1.70017144
H	-2.22077387	-0.25436552	-3.36021576
C	1.22033407	-0.02291554	-2.78563284
H	0.87465274	-0.98759536	-2.38220970
H	1.19881503	-0.08273570	-3.88939034
H	2.26571877	0.12551185	-2.47389929
C	2.08823029	3.05527930	-2.21410209
H	2.11714006	3.64537311	-3.14900459
H	2.34492869	3.73944880	-1.38814807
H	2.86890743	2.28297220	-2.28439809
Rh	-0.11306953	1.53671573	-0.26054913
C	0.76383527	-0.90725769	1.44854734
C	-0.36265482	-2.79876408	0.11592032
C	-1.71574989	-3.20685664	-0.17644747
H	0.54209463	-3.38187852	-0.05771647
C	-2.57841052	-2.20144141	0.33982811
C	-0.38933741	-1.58286827	0.75199115
N	-1.75053065	-1.18062394	0.87995056
C	-2.21954500	-0.01325341	1.45114935
N	-1.50703034	1.13933386	1.28155356
C	-1.90555463	2.22078473	1.99703006
C	-3.79549312	1.01357715	2.77320954
H	-1.29123054	3.11969700	1.88528397
H	-4.75233490	0.93016075	3.30344265
N	-3.37256274	-0.07809681	2.13468270
C	-3.04969116	2.20496498	2.78728794
H	-3.36230771	3.08522573	3.35318676
C	-2.26621415	-4.32566881	-0.83017049
C	-3.65577707	-4.41242714	-0.95752776
H	-1.61499936	-5.10936148	-1.22931855
H	-4.10241390	-5.27773713	-1.45688790
C	-4.49371534	-3.39961964	-0.44513574
C	-3.97102857	-2.27710365	0.21214150
H	-5.57910209	-3.49546849	-0.54831551
H	-4.62559708	-1.51290611	0.63263968
C	1.66509624	1.65620186	1.46647234

H	1.45717092	2.64929736	1.00883211
H	1.68483657	1.69308452	2.56185818
C	2.61987327	0.77398179	0.65792453
H	3.34245914	0.16917962	1.22329065
H	3.02754655	1.21742241	-0.25700271
H	1.59489305	-1.61991013	1.30802796
C	0.54425964	-0.81597468	2.99300180
H	1.48321848	-0.45257730	3.44684217
H	-0.23285493	-0.06880834	3.22664147
C	0.17552334	-2.16676129	3.56809016
C	1.17065549	-3.14048682	3.77828904
C	-1.16603515	-2.50661799	3.82279564
C	0.83372030	-4.42449519	4.22575981
H	2.22250675	-2.88938263	3.59405420
C	-1.50663803	-3.79166877	4.26697296
H	-1.95792616	-1.76493676	3.67079691
C	-0.50825314	-4.75500053	4.46670739
H	1.62033599	-5.16807454	4.39077630
H	-2.55587072	-4.03934059	4.45777994
H	-0.77326484	-5.75836174	4.81514946

Intermediate **D2**

Lowest frequency = 11.36 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.176052 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.802637 E_h

G_{corr} (298.15) = 0.525707 E_h

Charge = 1, Multiplicity = 1

C	-1.44395534	-1.82001895	1.21449558
C	-2.59750647	-1.28418145	0.47004589
C	-0.82489524	-0.73375460	1.93797878
C	-2.62476468	0.11780107	0.65568164
C	-1.49313904	0.47835273	1.53249506
C	1.38504416	-0.90762404	-0.47281907
C	-3.56752989	-2.11241707	-0.31942232
H	-3.06590842	-2.94526071	-0.83782802
H	-4.32265206	-2.55346919	0.35769409
H	-4.10152224	-1.50803032	-1.06904659
C	-3.62264733	1.09425077	0.10926890
H	-4.13694990	0.69614162	-0.77964601
H	-4.39240114	1.32342948	0.86946983
H	-3.14352352	2.04803495	-0.16653442
C	-1.25720989	1.84164311	2.10293778
H	-0.22886327	1.96042059	2.47280077
H	-1.45434662	2.63795217	1.36876216
H	-1.94666673	2.00277256	2.95334759
C	0.29692838	-0.82922791	2.92706194
H	0.97690432	0.03385401	2.84344398
H	-0.10878605	-0.84956193	3.95533869

H	0.88586189	-1.74879646	2.78373455
C	-1.10435158	-3.27581495	1.34462274
H	-1.69066280	-3.73150850	2.16408434
H	-1.33985199	-3.83211029	0.42301326
H	-0.03769296	-3.42373996	1.57806977
Rh	-0.62358681	-0.43434411	-0.21922433
C	2.27730506	0.26290781	-0.80987270
C	3.68338036	0.03854075	-1.36220560
C	2.64938625	0.71716096	-2.21507213
H	3.95075480	-0.99110211	-1.61836140
H	4.49762231	0.63824948	-0.94308201
H	2.74769139	1.79878794	-2.36359123
H	2.24301709	0.17488504	-3.07082808
C	2.88825969	1.63542541	1.31108990
C	2.45141020	2.90133631	1.85304777
H	3.71778214	1.02609292	1.67070521
C	1.42717280	3.39830562	0.99780300
C	2.13883172	1.35319699	0.19633378
N	1.20446985	2.41063165	0.00355236
C	0.24861678	2.47898911	-0.99566599
N	-0.38213688	1.33223966	-1.40168412
C	-1.21054505	1.44441408	-2.46917795
C	-0.89072474	3.79458210	-2.49954610
H	-1.69330679	0.51865118	-2.79373923
H	-1.10795027	4.80768479	-2.86067885
N	-0.02814470	3.69529972	-1.48760370
C	-1.48424549	2.66302136	-3.08159057
H	-2.15911148	2.72881165	-3.93787402
C	2.83998187	3.65203673	2.97975911
C	2.20233977	4.87108178	3.22762713
H	3.62697701	3.28407238	3.64534990
H	2.49445795	5.47006940	4.09566736
C	1.19005689	5.34614764	2.36678243
C	0.78655502	4.62083812	1.23758919
H	0.71570247	6.31035767	2.57460625
H	0.02395208	5.00542747	0.55954670
C	0.73515684	-1.84217766	-1.45940108
H	-0.40651697	-1.49152225	-1.65960229
H	1.73981738	-1.41385365	0.43736947
H	0.61195872	-2.83578913	-1.00032113
C	1.22576831	-2.00281027	-2.88876584
C	2.42609251	-2.70481465	-3.11124182
C	0.50996491	-1.51020255	-3.99199569
C	2.91585615	-2.87350975	-4.41242642
H	2.97720482	-3.12391819	-2.26217305
C	0.99867573	-1.67872983	-5.29518665
H	-0.43858680	-0.98710895	-3.83058957
C	2.20845577	-2.35380894	-5.50721920
H	3.85236689	-3.41713225	-4.57254314
H	0.43185203	-1.28567230	-6.14513651
H	2.59402846	-2.48541808	-6.52287748

Transition State **TS(D2-E1)**

Lowest frequency = -607.79 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.168688 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.795435 E_h

G_{corr} (298.15) = 0.523714 E_h

Charge = 1, Multiplicity = 1

C	0.30690230	2.67641897	-1.52367019
C	0.97707439	3.21421436	-0.34392685
C	-1.00813849	2.20721493	-1.12880608
C	0.11225262	3.02727239	0.78655590
C	-1.10537288	2.38868893	0.29290299
C	0.95971891	-0.55609489	-1.46003470
C	2.30842064	3.90636810	-0.34315018
H	2.99336051	3.47357452	-1.08915985
H	2.17192134	4.97397706	-0.59637929
H	2.79240494	3.85161445	0.64400751
C	0.33893789	3.50313407	2.19197278
H	1.41317875	3.59574870	2.41722302
H	-0.12424534	4.49547501	2.34737322
H	-0.10748562	2.81439212	2.92793098
C	-2.30238592	2.08734016	1.14116824
H	-2.96894687	1.35211681	0.66816943
H	-2.01442499	1.71664668	2.13830141
H	-2.87962462	3.01794965	1.29462740
C	-2.07742588	1.68970776	-2.04296359
H	-2.80255182	1.06209786	-1.50337228
H	-2.62848097	2.53304813	-2.49946213
H	-1.65455209	1.08427522	-2.86023176
C	0.81627586	2.76002480	-2.93232401
H	0.47805145	3.70468018	-3.39708207
H	1.91705444	2.74960786	-2.97221402
H	0.43462655	1.93369276	-3.55321459
Rh	0.63313945	1.06036721	-0.10655945
C	0.29238404	-1.84349323	-1.06368859
C	0.78576940	-3.17235136	-1.63470771
C	0.91091066	-2.90324435	-0.16265439
H	1.69985612	-3.13816854	-2.23489794
H	0.03123956	-3.88726772	-1.97788072
H	0.22111004	-3.42908620	0.50739933
H	1.90491230	-2.72397554	0.25246013
C	-2.16468245	-1.91981293	-1.89075558
C	-3.44708626	-1.66531077	-1.27947336
H	-1.98684466	-2.28866529	-2.90112434
C	-3.20422283	-1.28379357	0.07084912
C	-1.18163633	-1.66996803	-0.96726386
N	-1.79707618	-1.24847615	0.24662470
C	-1.14834298	-0.98223376	1.44401927

N	0.03907841	-0.29743031	1.43337631
C	0.67349724	-0.17250419	2.62511842
C	-1.15069248	-1.20977056	3.73332177
H	1.62695776	0.35915472	2.59962814
H	-1.69521879	-1.53892327	4.62722614
N	-1.76155568	-1.39328778	2.56201283
C	0.12699939	-0.63566266	3.81799540
H	0.65609445	-0.51675147	4.76617358
C	-4.77050612	-1.72124280	-1.75830603
C	-5.81505603	-1.39929633	-0.88712240
H	-4.97208510	-2.01176498	-2.79398512
H	-6.84976122	-1.44110017	-1.24093289
C	-5.55437139	-1.02868169	0.44942325
C	-4.24779753	-0.96813940	0.95241012
H	-6.39028999	-0.79590947	1.11640697
H	-4.05573813	-0.71347673	1.99532099
C	2.27407806	-0.08054024	-1.08144714
H	2.18519128	0.79227258	0.24581137
H	0.58393777	-0.17889099	-2.42049646
H	2.68412852	0.64936115	-1.79511883
C	3.37056466	-0.94659158	-0.50512373
C	4.03251196	-1.81357071	-1.39992683
C	3.79727805	-0.90554173	0.83159770
C	5.06770236	-2.64299244	-0.95197739
H	3.73530336	-1.83475009	-2.45408288
C	4.83380733	-1.73478631	1.28301558
H	3.31238789	-0.21184169	1.52633769
C	5.46625662	-2.61279489	0.39310963
H	5.56749715	-3.31389844	-1.65783056
H	5.14880409	-1.69109030	2.33041087
H	6.27366014	-3.26368359	0.74239361

Intermediate **E1**

Lowest frequency = 24.58 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.171650 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.799347 E_h

G_{corr} (298.15) = 0.524820 E_h

Charge = 1, Multiplicity = 1

C	-1.19520654	-1.58749371	1.28571399
C	-2.33932125	-1.47667981	0.39951780
C	-0.88221588	-0.26740675	1.81209993
C	-2.69582112	-0.07306811	0.32579902
C	-1.80276663	0.65190053	1.21630755
C	1.42607518	-0.94092773	-0.49161160
C	-3.08409135	-2.62268664	-0.22043795
H	-2.40457229	-3.43981945	-0.50809536
H	-3.81285821	-3.02869965	0.50523838
H	-3.63663365	-2.30553588	-1.11762474

C	-3.87929901	0.51769199	-0.38495619
H	-4.19054829	-0.10828362	-1.23537991
H	-4.73891201	0.60516829	0.30517280
H	-3.65704078	1.52791600	-0.76541140
C	-1.89999312	2.11879357	1.49670088
H	-0.97817175	2.51594676	1.94460150
H	-2.12954261	2.69438100	0.58532746
H	-2.72739940	2.29700712	2.20849993
C	0.14469253	0.03849154	2.85988215
H	0.43534102	1.09967896	2.84595690
H	-0.25617080	-0.19369256	3.86425121
H	1.05852707	-0.56124884	2.72126924
C	-0.55370640	-2.86793458	1.72952136
H	-0.98005151	-3.17171983	2.70349581
H	-0.73586442	-3.68707496	1.01734365
H	0.53387874	-2.75778181	1.87135549
Rh	-0.68025902	-0.39289541	-0.47682122
C	2.34819209	0.19576022	-0.81463147
C	3.72792467	-0.09875482	-1.40630559
C	2.70889643	0.63889771	-2.22474744
H	3.93496278	-1.13945929	-1.67170716
H	4.57823267	0.45594726	-0.99711293
H	2.85974715	1.71476491	-2.36931107
H	2.24246907	0.12100774	-3.06595973
C	3.07558935	1.44418968	1.33671476
C	2.63083140	2.63704518	2.01618285
H	3.91874023	0.81185480	1.61567985
C	1.55335790	3.17856938	1.25909560
C	2.28299070	1.24624638	0.23499793
N	1.31353700	2.28908497	0.17996834
C	0.42364229	2.51693572	-0.86106375
N	-0.22463230	1.46129053	-1.45079573
C	-0.93253231	1.75069833	-2.57334613
C	-0.52323412	4.06860030	-2.27354645
H	-1.40844848	0.90045986	-3.06322853
H	-0.67107151	5.12920439	-2.51241050
N	0.24004105	3.79510707	-1.21527053
C	-1.09276965	3.04783944	-3.04891575
H	-1.67269029	3.24852309	-3.95255342
C	3.04595567	3.28412792	3.19652289
C	2.38485693	4.45023391	3.59191090
H	3.87148760	2.87779330	3.78898549
H	2.69610229	4.96844598	4.50410885
C	1.32439525	4.97660661	2.82354866
C	0.89368867	4.35455139	1.64423007
H	0.83306798	5.90006542	3.14545672
H	0.09577114	4.78557553	1.03860293
C	0.73137009	-1.81797400	-1.36804611
H	-1.26645094	-0.83132347	-1.86617099
H	1.58101325	-1.30291237	0.53331486
H	0.42933973	-2.76840546	-0.90515299

C	0.99592920	-1.97175977	-2.84090216
C	2.15181192	-2.70629671	-3.19118977
C	0.17241353	-1.50327181	-3.87770313
C	2.48880538	-2.92276604	-4.53271454
H	2.78998025	-3.11503954	-2.40007085
C	0.50527540	-1.71836549	-5.22282125
H	-0.74919553	-0.97067832	-3.62241235
C	1.67064611	-2.42088470	-5.55561571
H	3.39291334	-3.48863536	-4.77917465
H	-0.15204059	-1.33866242	-6.01168745
H	1.93450808	-2.58676062	-6.60470283

Transition State **TS(B-C)'**

Lowest frequency = -283.03 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.154752 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.782018 E_h

G_{corr} (298.15) = 0.524198 E_h

Charge = 1, Multiplicity = 1

C	1.02415636	2.83874374	-0.93836464
C	0.44945177	3.18713434	0.32884533
C	-0.04205003	2.37642080	-1.80298270
C	-1.00672670	3.03853373	0.20539317
C	-1.30948377	2.58267358	-1.11271926
C	1.60611256	-0.27159125	0.27688909
C	1.17537646	3.81031399	1.48587770
H	2.18766494	3.39103194	1.60266516
H	1.27989236	4.90080508	1.33166753
H	0.62957462	3.67097204	2.43285046
C	-1.99832545	3.37637091	1.27786065
H	-1.60064182	3.16062714	2.28254811
H	-2.23451069	4.45587922	1.24257790
H	-2.93958515	2.81963322	1.15082979
C	-2.66984404	2.36212339	-1.69759971
H	-3.44474492	2.33311883	-0.91663309
H	-2.91803757	3.18235052	-2.39542232
H	-2.71834969	1.41277446	-2.25592325
C	0.12021278	1.96921967	-3.23803381
H	-0.76517360	1.42660945	-3.60146597
H	0.24984710	2.86322219	-3.87603603
H	1.00363969	1.32550968	-3.37727147
C	2.43749442	3.08940659	-1.36356965
H	2.50215228	4.12250817	-1.75495481
H	3.14997955	3.00685006	-0.52980288
H	2.75608528	2.41332445	-2.17093636
Rh	-0.03151454	1.06167178	-0.04295117
C	0.75312652	-1.04156005	-0.60178871
C	1.15793866	-1.74395740	-1.84973080
C	0.63027652	-2.53804379	-0.65507580

H	2.23006217	-1.78460190	-2.06916719
H	0.51068891	-1.70723001	-2.72907169
H	-0.35241337	-3.00945912	-0.76615185
H	1.35097985	-3.08880641	-0.03867200
C	-1.79126656	-0.94319246	-1.84105974
C	-2.90577899	-1.79544901	-1.50580419
H	-1.45530689	-0.70824081	-2.85038807
C	-2.95574132	-1.91063216	-0.08386858
C	-1.16400398	-0.54428133	-0.67081620
N	-1.89841105	-1.11962661	0.41394601
C	-1.60687292	-0.74208152	1.69367933
N	-0.68151272	0.26679263	1.78222119
C	-0.30283510	0.65641594	3.01611438
C	-1.84477005	-0.89828938	3.95843050
H	0.46719839	1.43168054	3.06165918
H	-2.34910551	-1.37706838	4.80675389
N	-2.20049746	-1.32372771	2.74206100
C	-0.87238548	0.09690950	4.15929516
H	-0.57259361	0.42183739	5.15796565
C	-3.86408416	-2.47702909	-2.28302098
C	-4.83472231	-3.24275307	-1.62930765
H	-3.84613505	-2.40666654	-3.37494090
H	-5.58405283	-3.78159499	-2.21736758
C	-4.86490414	-3.33557371	-0.22108123
C	-3.92542338	-2.66914540	0.57997655
H	-5.63520073	-3.94581339	0.26047605
H	-3.93713012	-2.73969979	1.66811771
C	2.99952468	0.14825852	-0.15751184
H	2.99022332	0.48685481	-1.20433677
H	3.33811857	0.99658339	0.46492286
C	3.98620149	-1.00653113	-0.01779606
C	4.70751962	-1.46980360	-1.13408950
C	4.19137864	-1.63788616	1.22506376
C	5.60739359	-2.53900089	-1.01610885
H	4.57292436	-0.97906870	-2.10557822
C	5.08888972	-2.70691481	1.34605493
H	3.65385431	-1.28466340	2.11287692
C	5.79713318	-3.16340911	0.22419963
H	6.16266889	-2.88204210	-1.89511469
H	5.24044652	-3.18257287	2.32058692
H	6.49835478	-3.99852514	0.31869482
H	1.57311581	-0.58427448	1.33007586

Transition State **TS(B1-C1)'**

Lowest frequency = -266.02 cm^{-1}

E(PBE0-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1552.155590 E_h

E(PW6B95-D3(BJ)/def2-TZVP+SMD(1,4-dioxane)) = -1555.782260 E_h

G_{corr} (298.15) = 0.523794 E_h

Charge = 1, Multiplicity = 1

C	2.83233885	-1.88768607	-0.68890144
C	3.53214275	-0.63132896	-0.66178483
C	1.74107727	-1.77679812	-1.63243994
C	2.90095051	0.23598715	-1.66232118
C	1.82342164	-0.47327343	-2.27731166
C	1.08553565	-0.89150485	1.89277842
C	4.78892125	-0.32958581	0.10251998
H	4.78775909	-0.81470210	1.09205013
H	5.67724737	-0.69124790	-0.44842495
H	4.92187496	0.75415476	0.25214724
C	3.35752899	1.62135484	-2.00712376
H	3.75966341	2.14988847	-1.12798826
H	4.16816871	1.57031397	-2.75725753
H	2.54077554	2.22514821	-2.43167847
C	0.93233697	0.00750966	-3.38161634
H	-0.12796740	-0.19763891	-3.15434882
H	1.03994038	1.09088172	-3.54347765
H	1.18247856	-0.50479330	-4.32828009
C	0.83170208	-2.89881878	-2.03773460
H	-0.07672452	-2.52404331	-2.53185240
H	1.35267196	-3.56200510	-2.75371976
H	0.53451842	-3.51574003	-1.17446263
C	3.22026048	-3.14839172	0.02027763
H	3.71228145	-3.82887084	-0.69924103
H	3.93320782	-2.96017088	0.83651460
H	2.34520071	-3.67555228	0.43236989
Rh	1.43818091	-0.27082376	-0.06825912
C	-0.31497788	-0.83543410	1.51452548
C	-1.63809636	-0.43196327	-1.00046245
C	-2.63209874	0.59268699	-1.19405900
H	-1.72299169	-1.46291924	-1.33447348
C	-2.17499226	1.77474655	-0.53817491
C	-0.59551754	0.08665441	-0.24529837
N	-0.91502068	1.46069716	0.01266858
C	0.03641833	2.26448028	0.57611641
N	1.26148120	1.66110415	0.72487684
C	2.23635821	2.37896743	1.31610529
C	0.74730579	4.23283038	1.48710589
H	3.19541313	1.87150746	1.45048523
H	0.50701735	5.26689108	1.76305489
N	-0.24185623	3.52320879	0.93287981
C	2.02565434	3.69784301	1.71861013
H	2.82186395	4.28011827	2.18733544
C	-3.88534722	0.60110646	-1.83689702
C	-4.63853011	1.77904933	-1.81540082
H	-4.25981894	-0.29960700	-2.33146027
H	-5.61666825	1.80525268	-2.30554881
C	-4.16023550	2.93831258	-1.16711481
C	-2.91782598	2.95894398	-0.51436480

H	-4.77437795	3.84427414	-1.16623719
H	-2.54535137	3.84754592	-0.00327067
C	1.70977574	-0.40714618	3.15794256
H	2.65015646	0.15635665	3.11672064
H	1.05259164	-0.11556629	3.98844130
C	1.78259512	-1.88090488	2.76168358
H	1.17279730	-2.60476303	3.31920636
H	2.76781703	-2.26448933	2.48038533
H	-0.85611509	0.01113212	1.95930781
C	-1.12643003	-2.12023426	1.49232414
H	-0.66939610	-2.85108881	0.80440073
H	-0.99213393	-2.54841375	2.50817301
C	-2.60981511	-1.97670709	1.21955144
C	-3.26599195	-2.89073484	0.37370437
C	-3.36564562	-0.94410985	1.80701308
C	-4.63319793	-2.76013706	0.09529616
H	-2.69486281	-3.70907084	-0.08123340
C	-4.72948389	-0.80366613	1.52308700
H	-2.89042731	-0.23050458	2.48965586
C	-5.36737188	-1.70873537	0.66234011
H	-5.12512795	-3.47992992	-0.56707125
H	-5.29676640	0.01499036	1.97690317
H	-6.43368767	-1.59905498	0.44116713

9. Proposed Mechanism

Based on our studies, we propose a plausible catalytic cycle for the electro-C–H-cyclopropylation, which is initiated by the formation of a catalytically competent mononuclear cationic Cp*Rh(III) species. As shown in figure 4, coordination of the N-atom of indole **1a** to Cp*Rh(III) and the subsequent cyclorhodation at the 2-position affords rhodacycle **A**. Then, the insertion of alkene **4a** occurs to furnish intermediate **D,** which undergoes β-H elimination to generate the cyclopropylated product **5aa** along with a rhodium(I) complex. Finally, the Cp*Rh(III) species is regenerated by reoxidation of rhodium(I) at the anode, while generating molecular hydrogen as the byproduct at the cathode and completing the catalytic cycle.

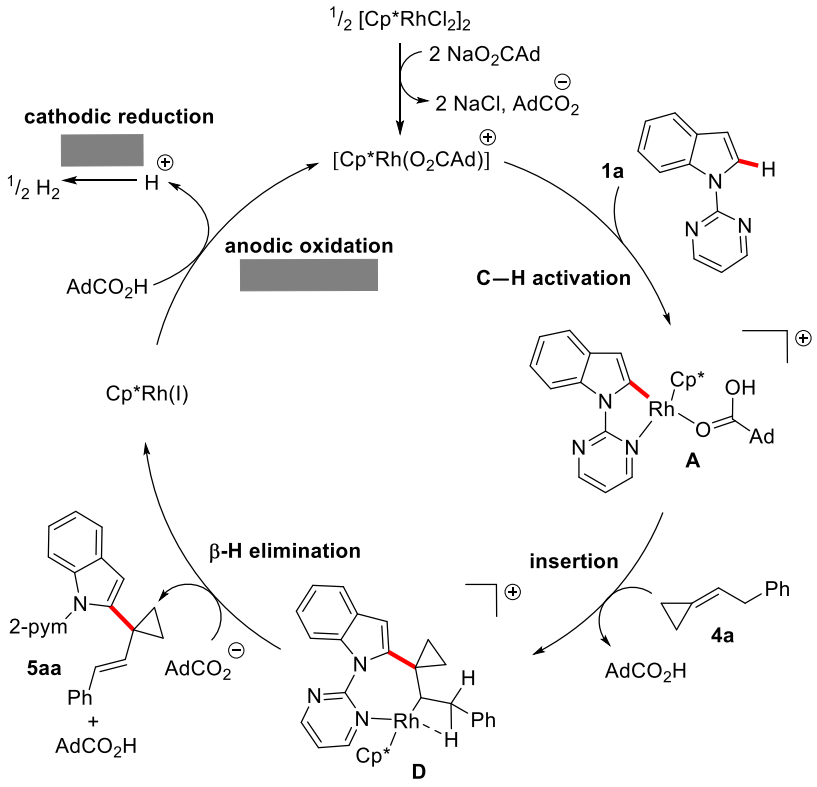


Figure S-9. Proposed mechanism for electro-C–H cyclopropylation with ACPs **4**.

In terms of dienylation, after the insertion of alkene **2a** the formed intermediate **D** preferentially undergoes β-C elimination to form intermediate **D** as there are no β-hydrogen atoms present (Figure S-9). The resulting intermediate **G** undergoes β-H elimination, delivering the dienylated indole **3aa**.

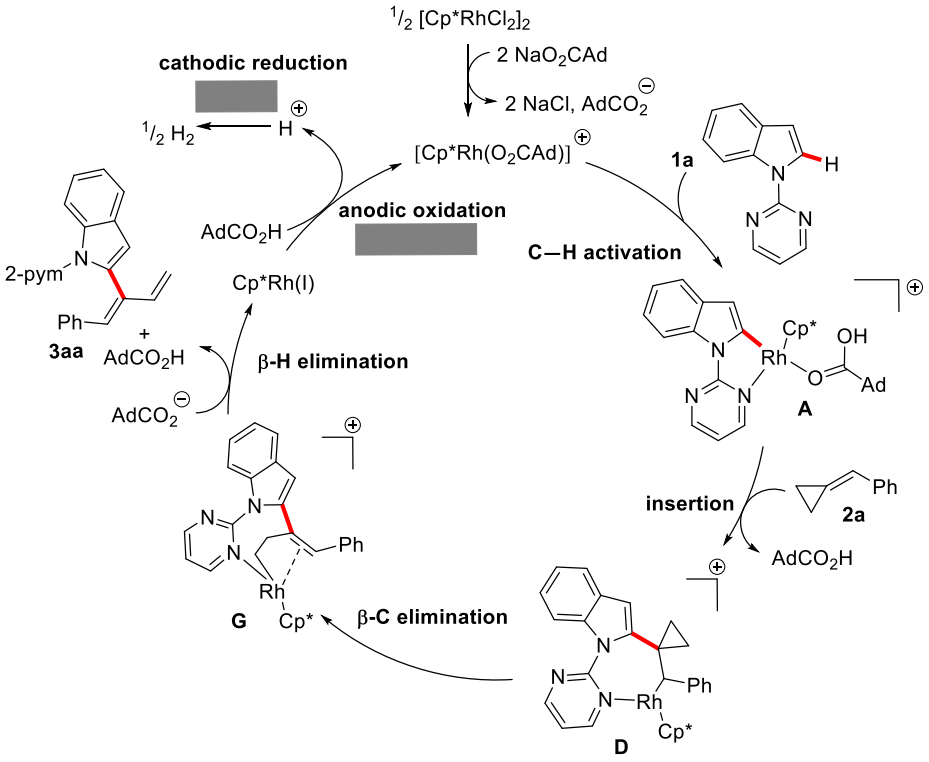


Figure S-10. Proposed mechanism for electrocatalytic C–H dienylation.

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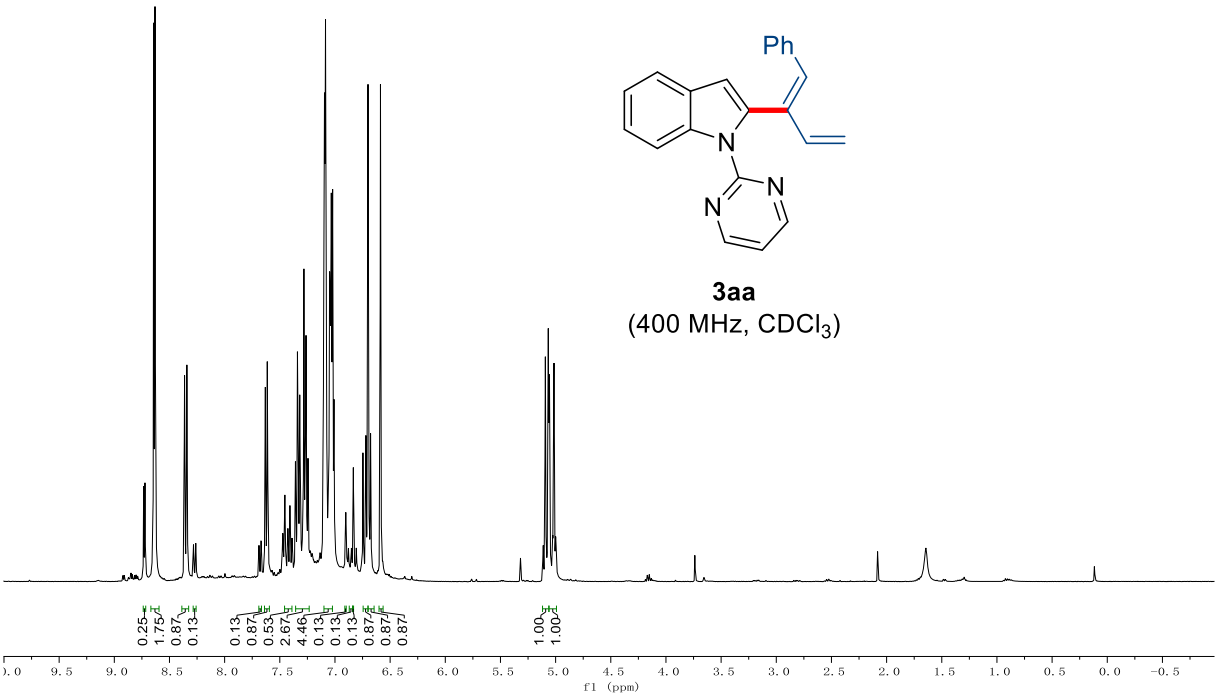
11. NMR Spectra



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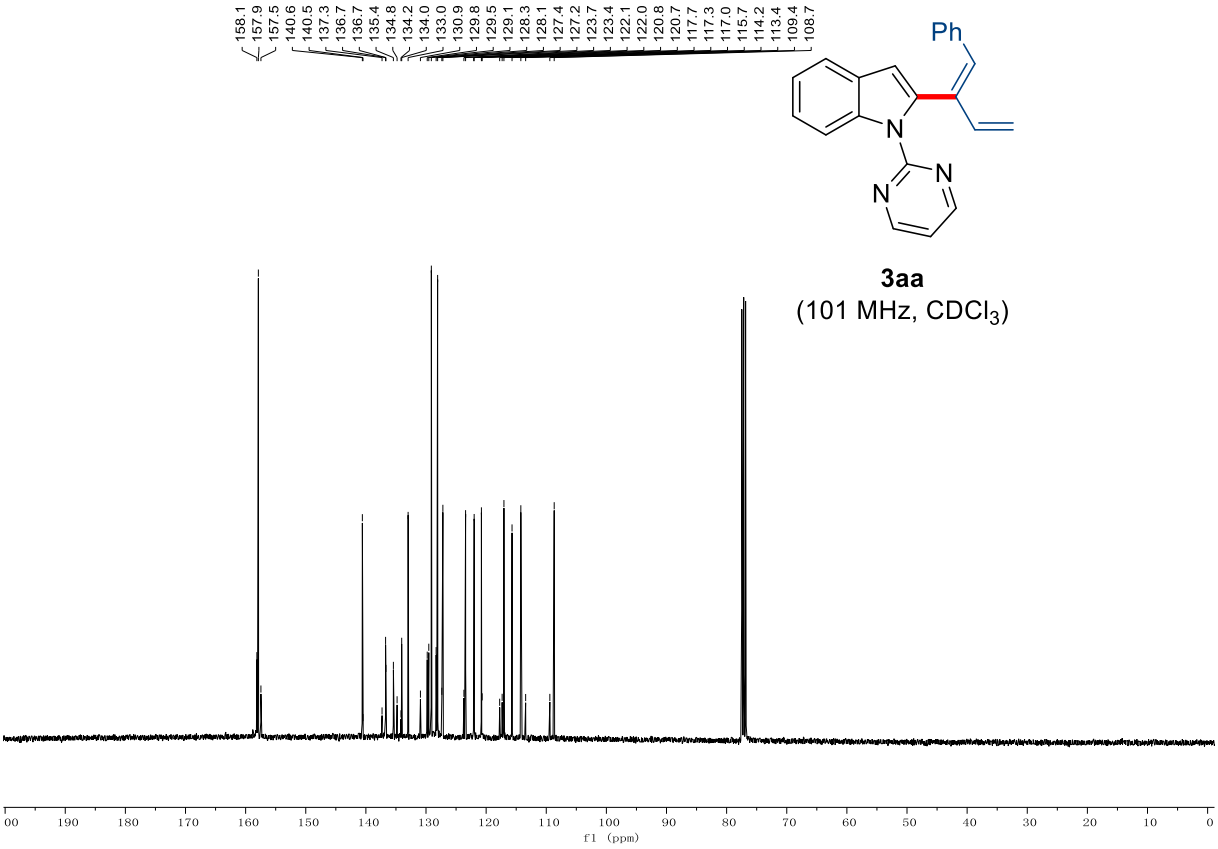

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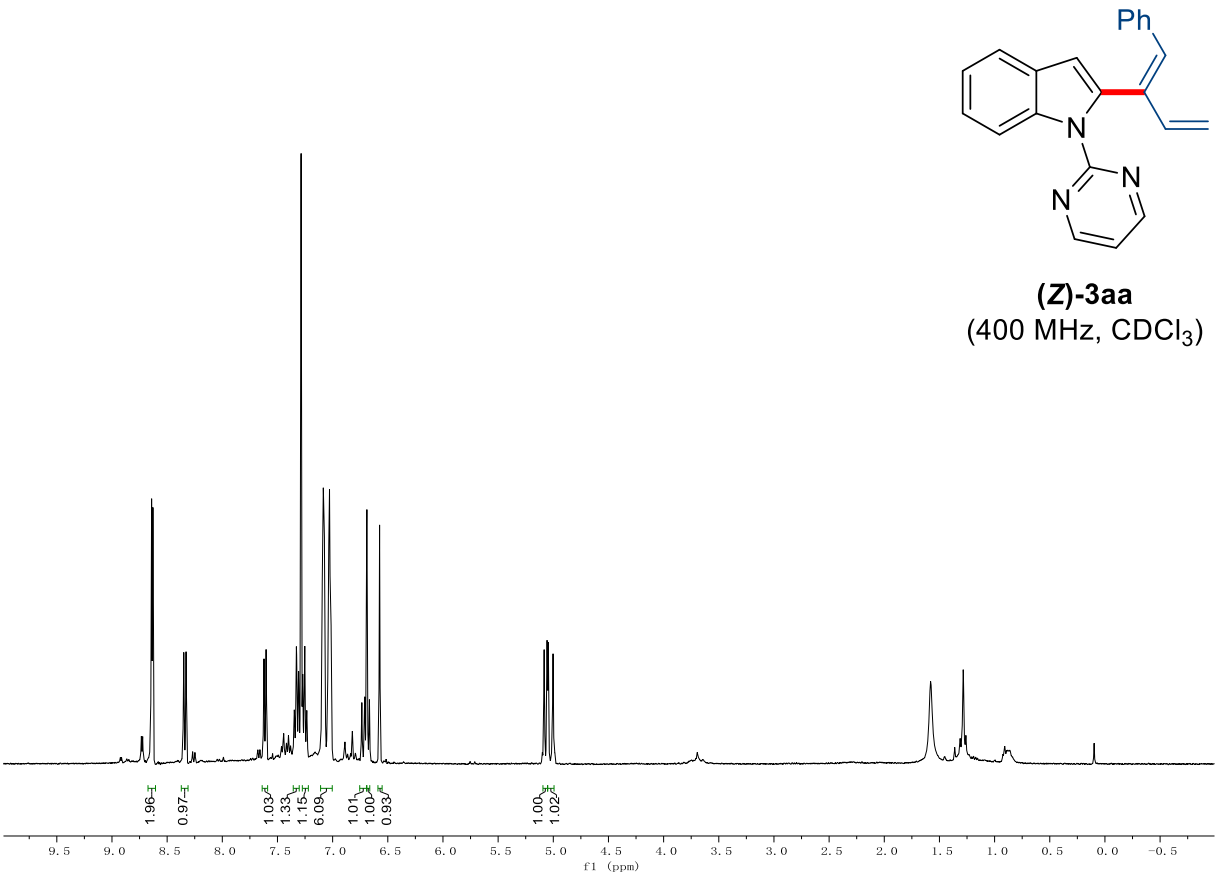

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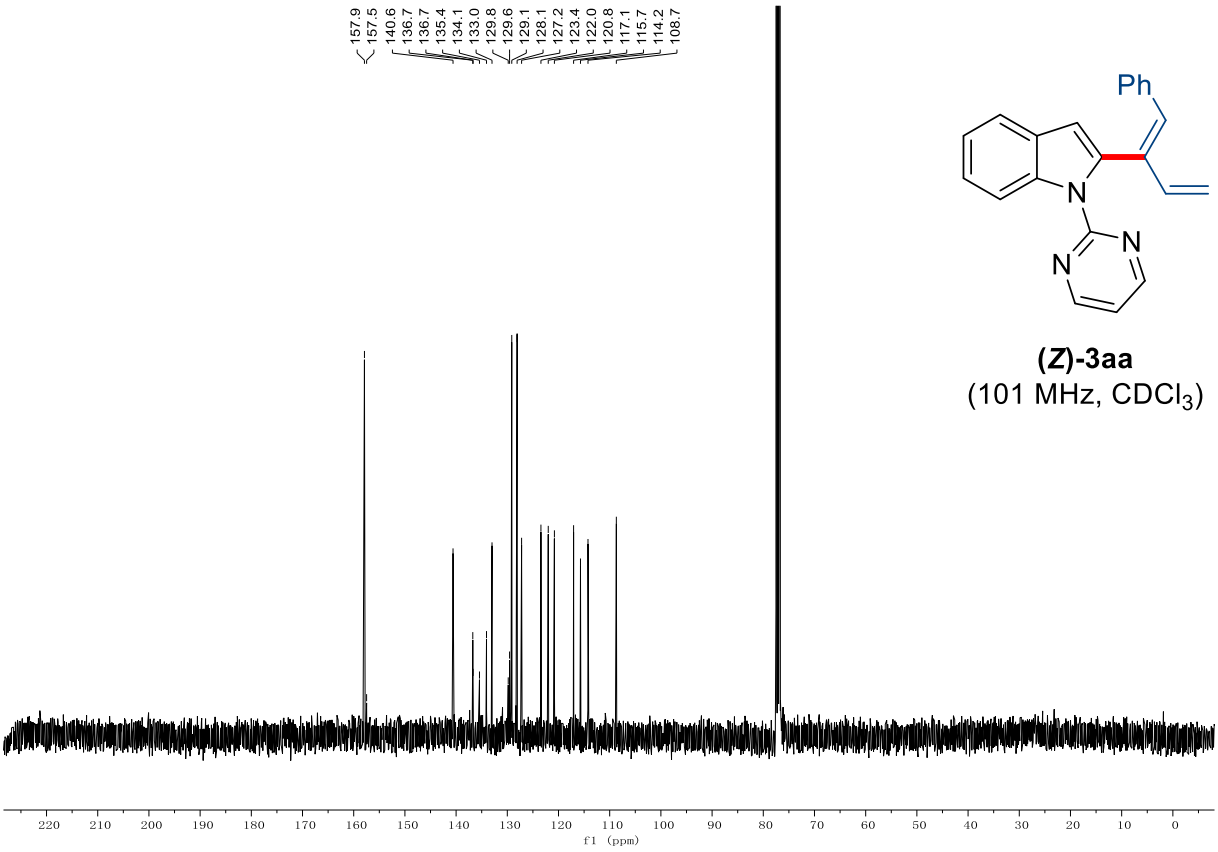

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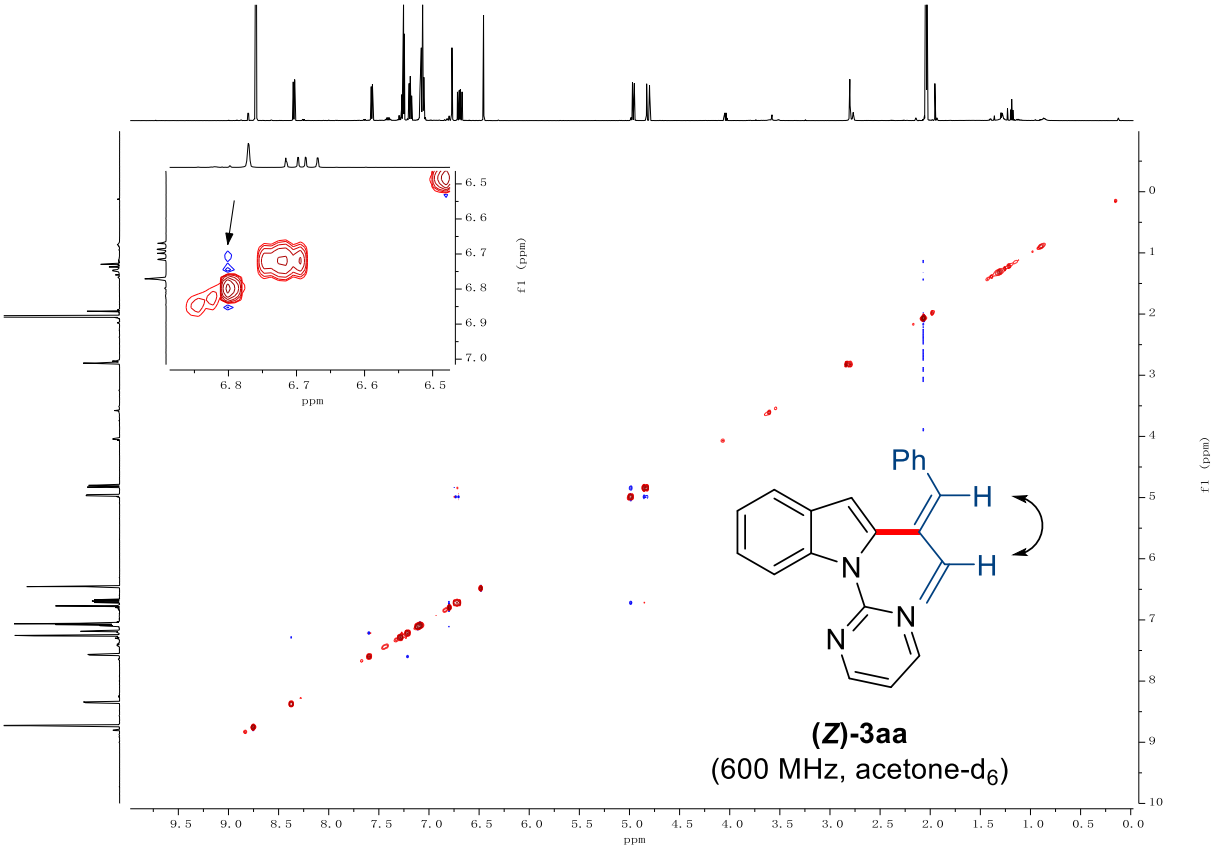

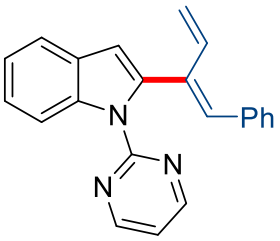

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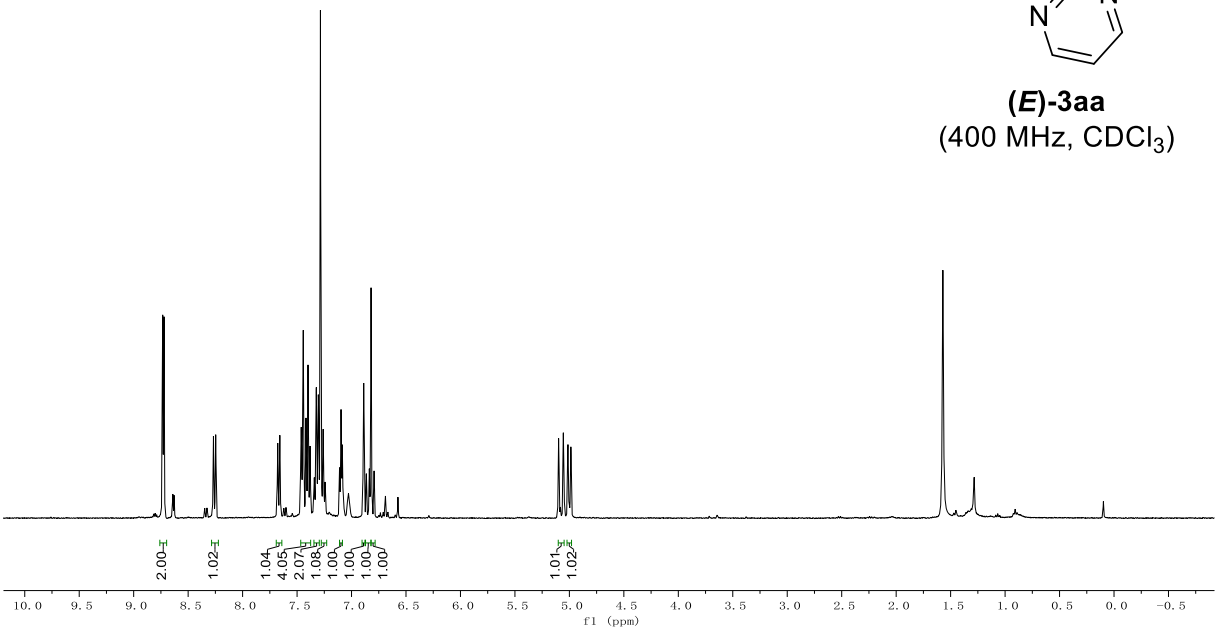

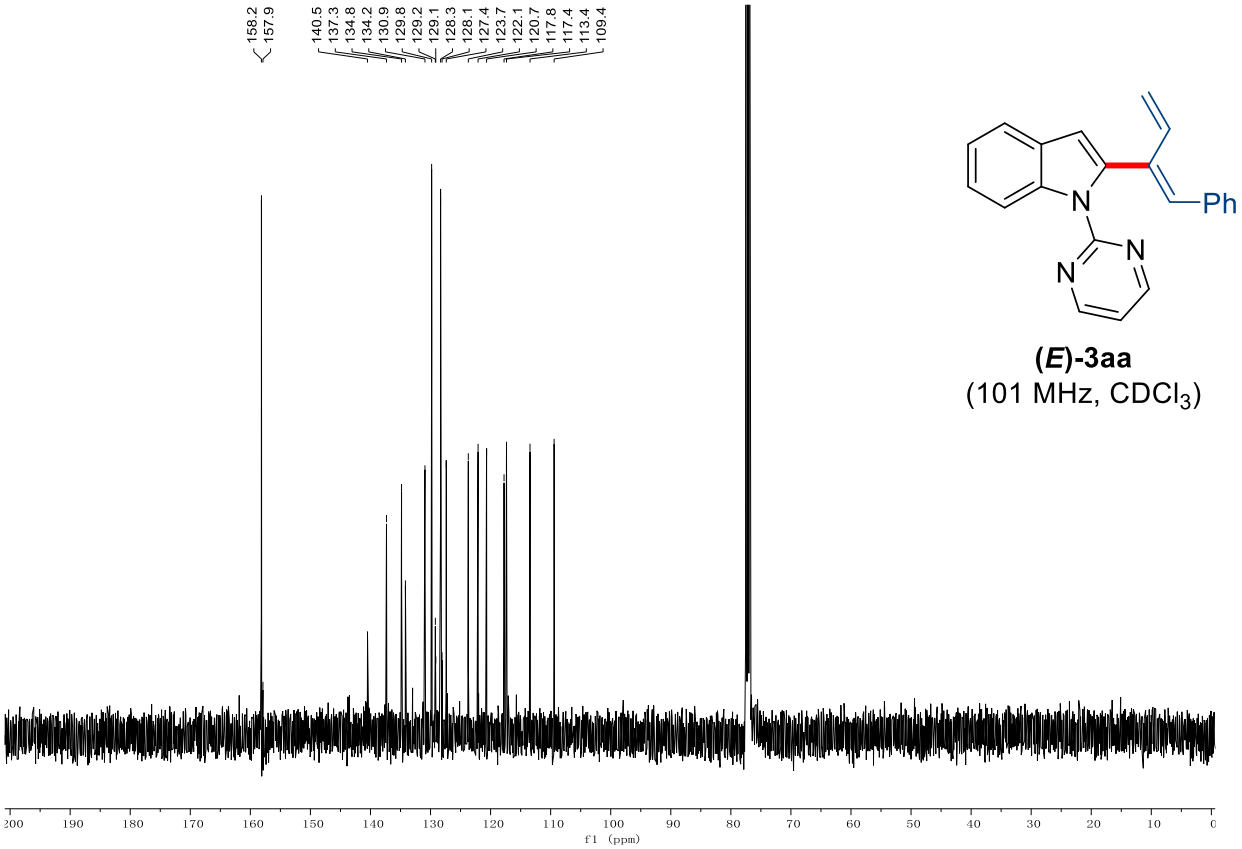

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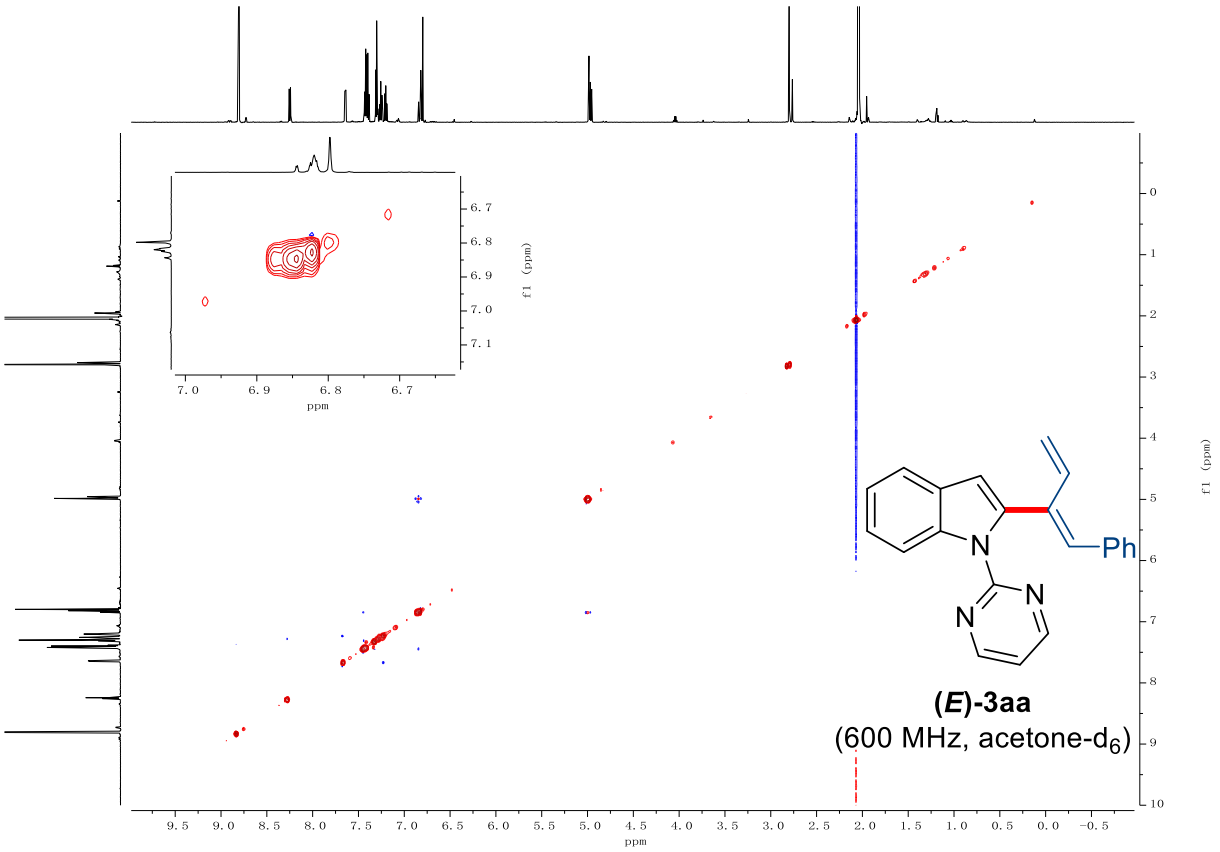

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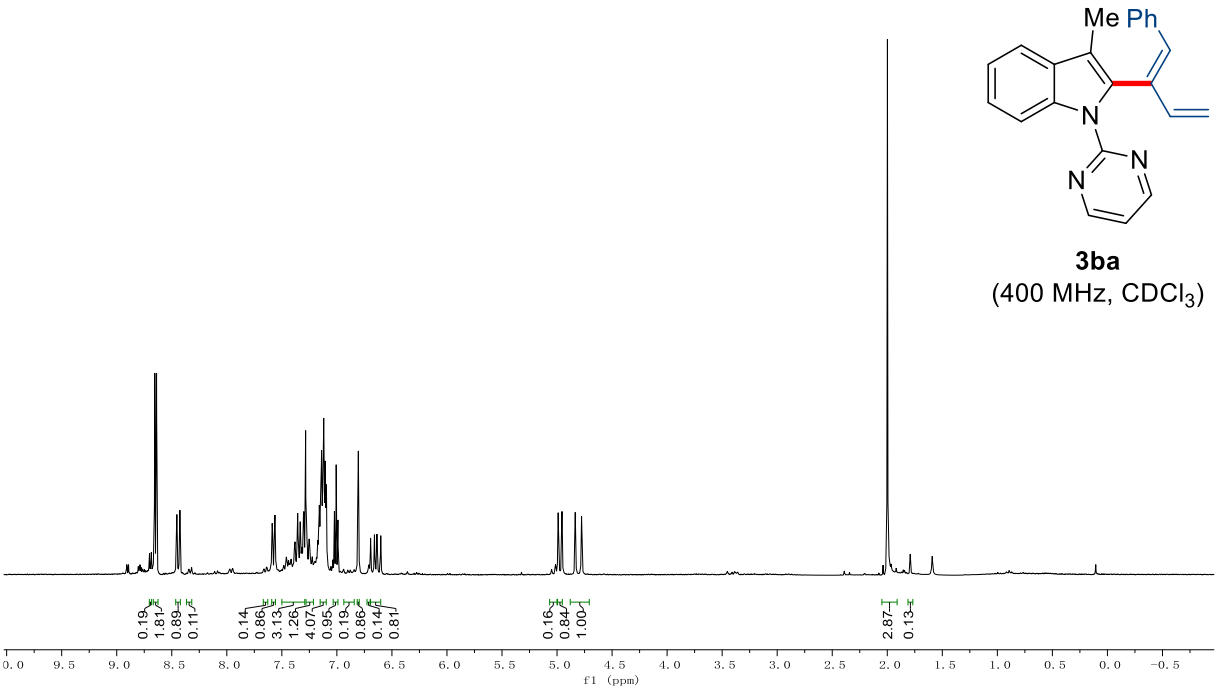

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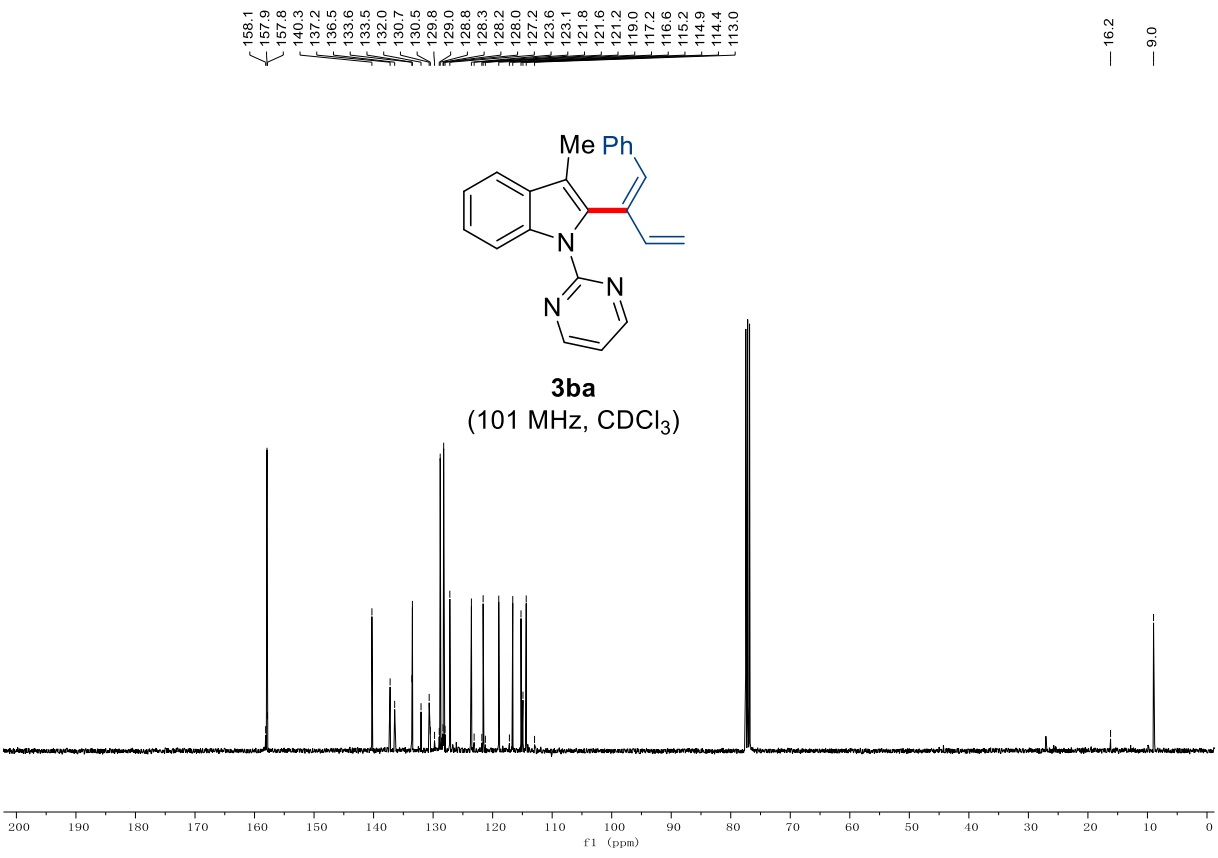

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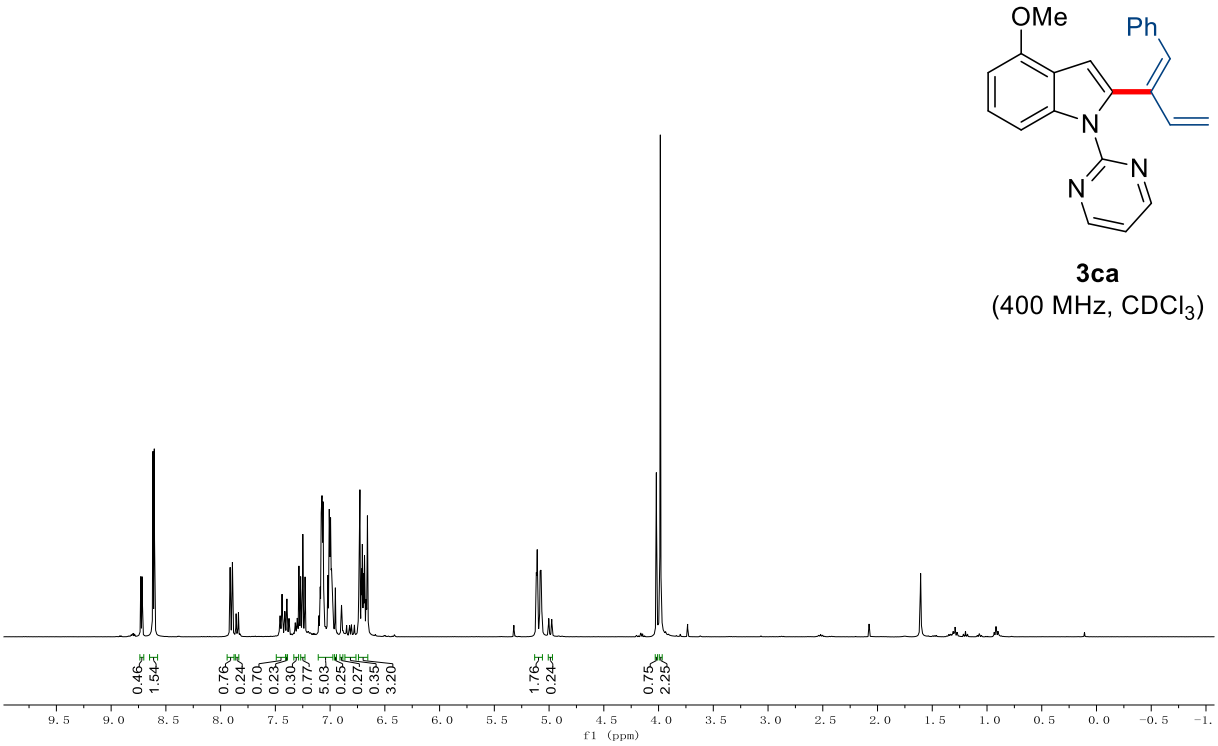

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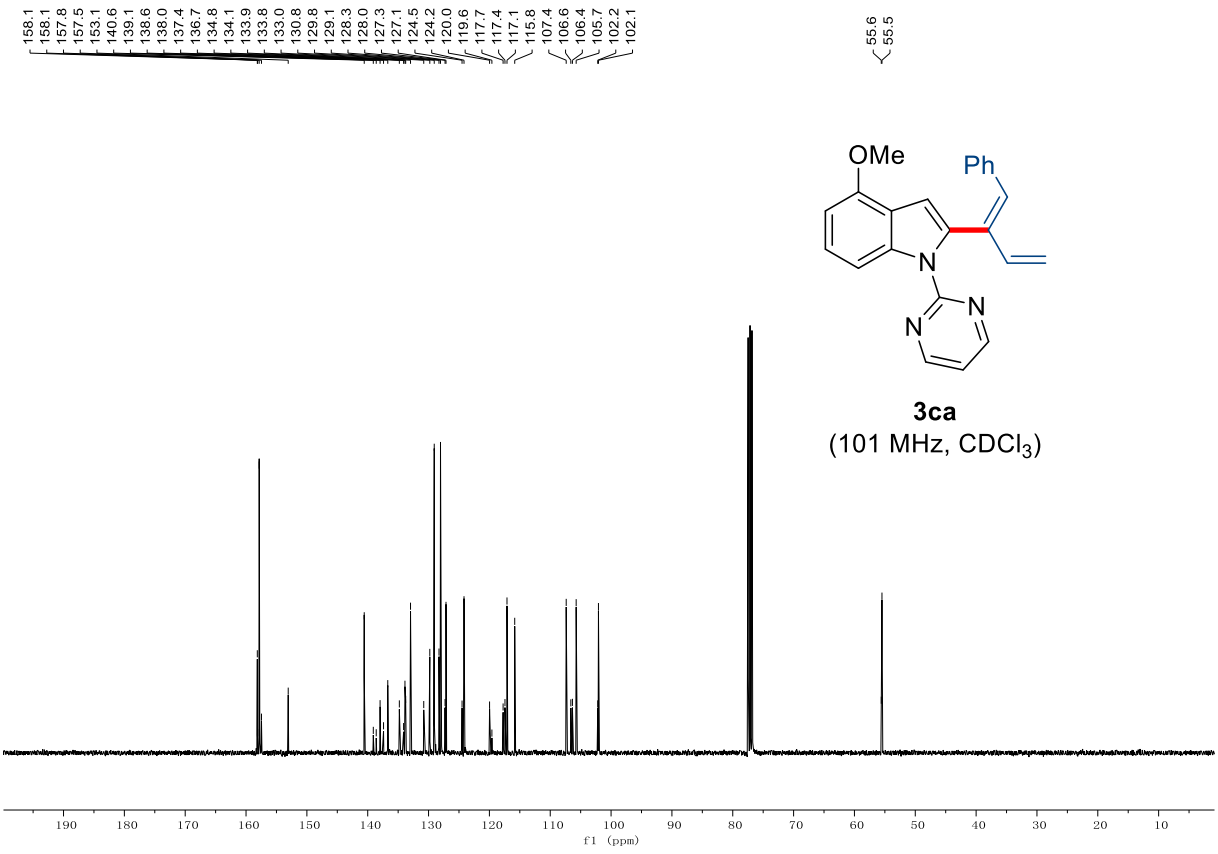

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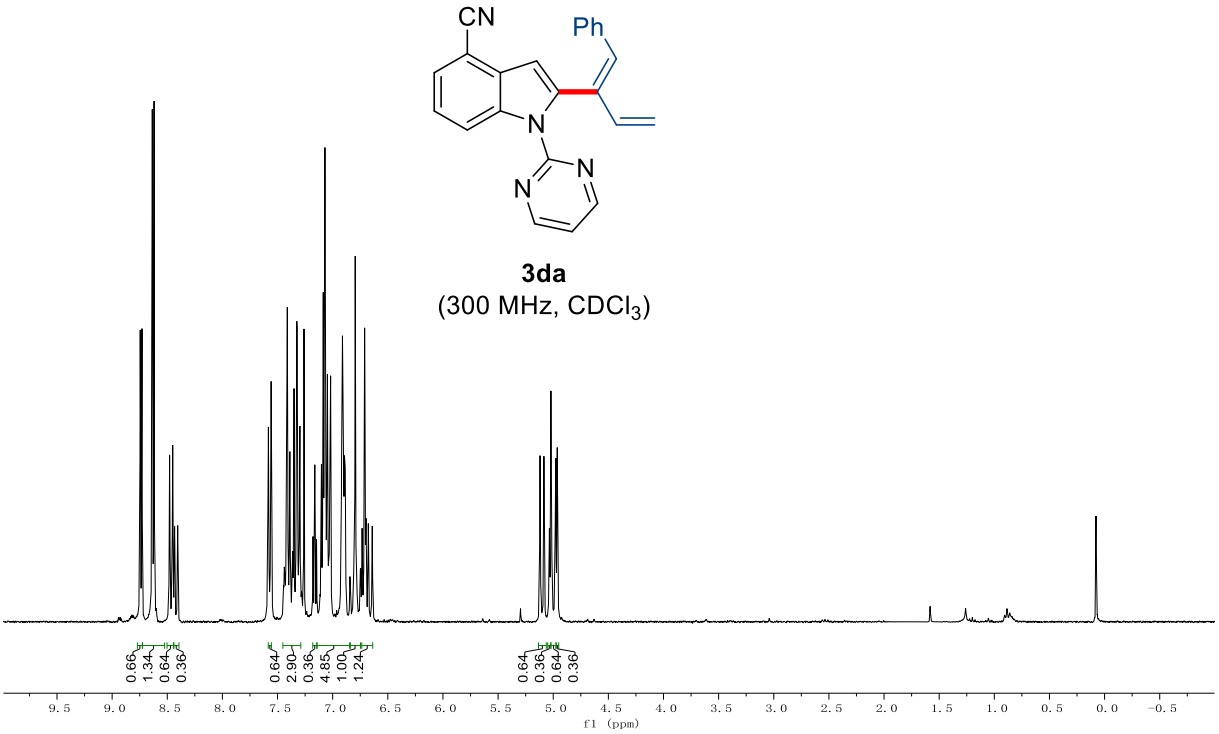

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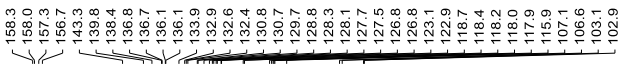

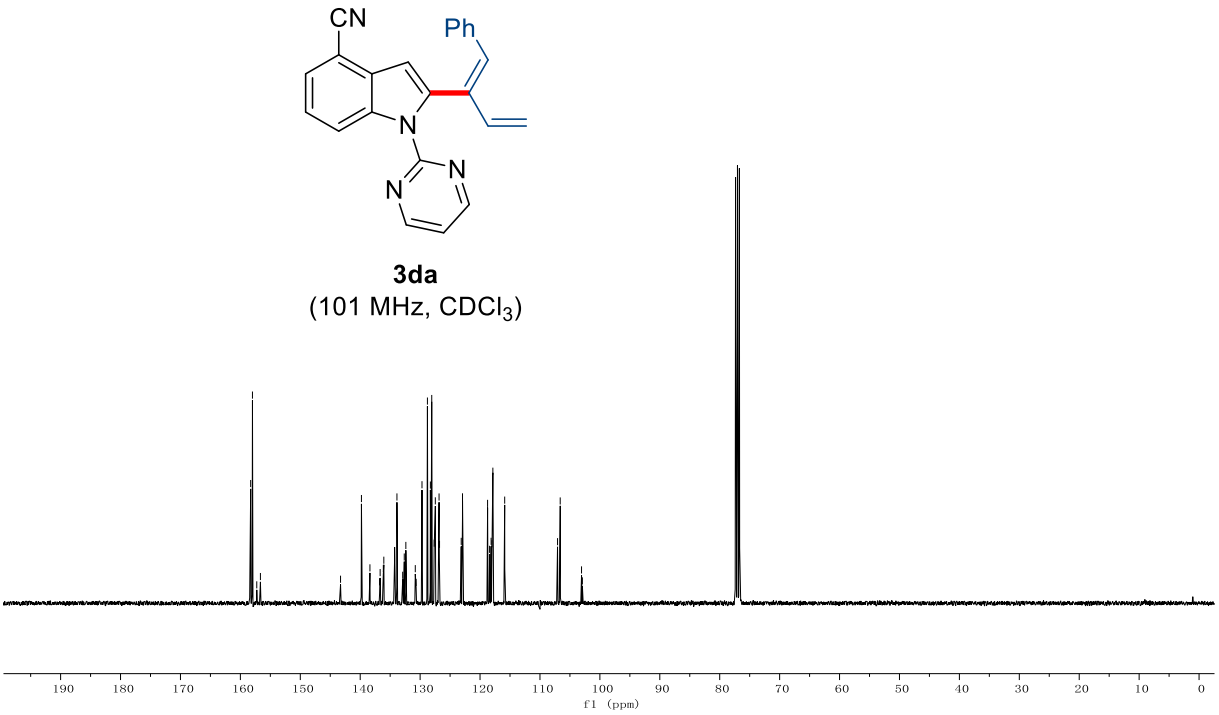

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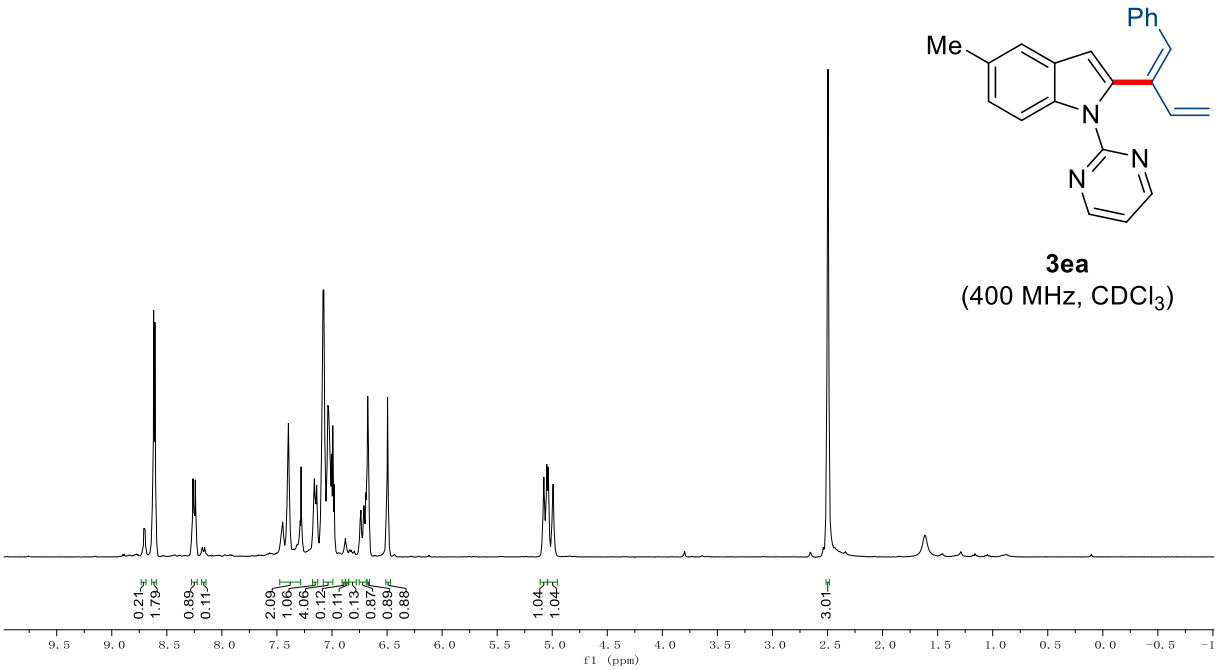

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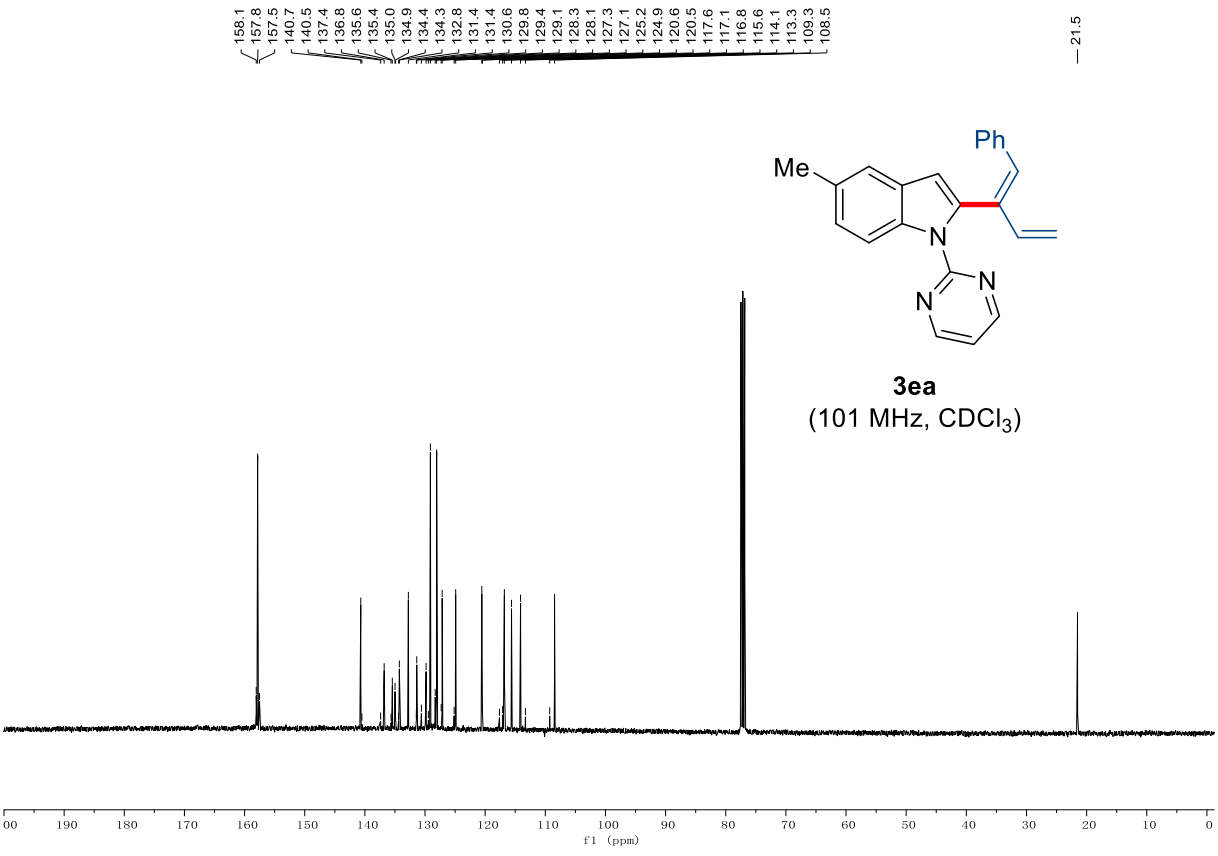

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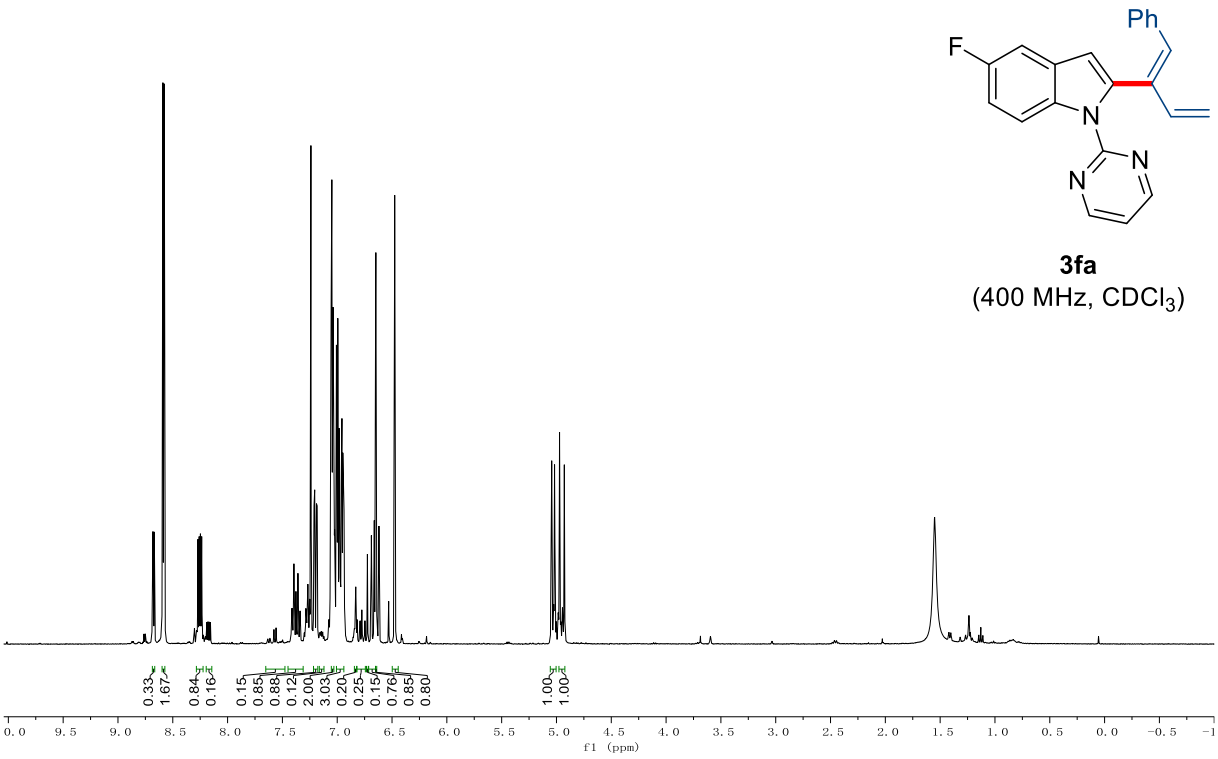

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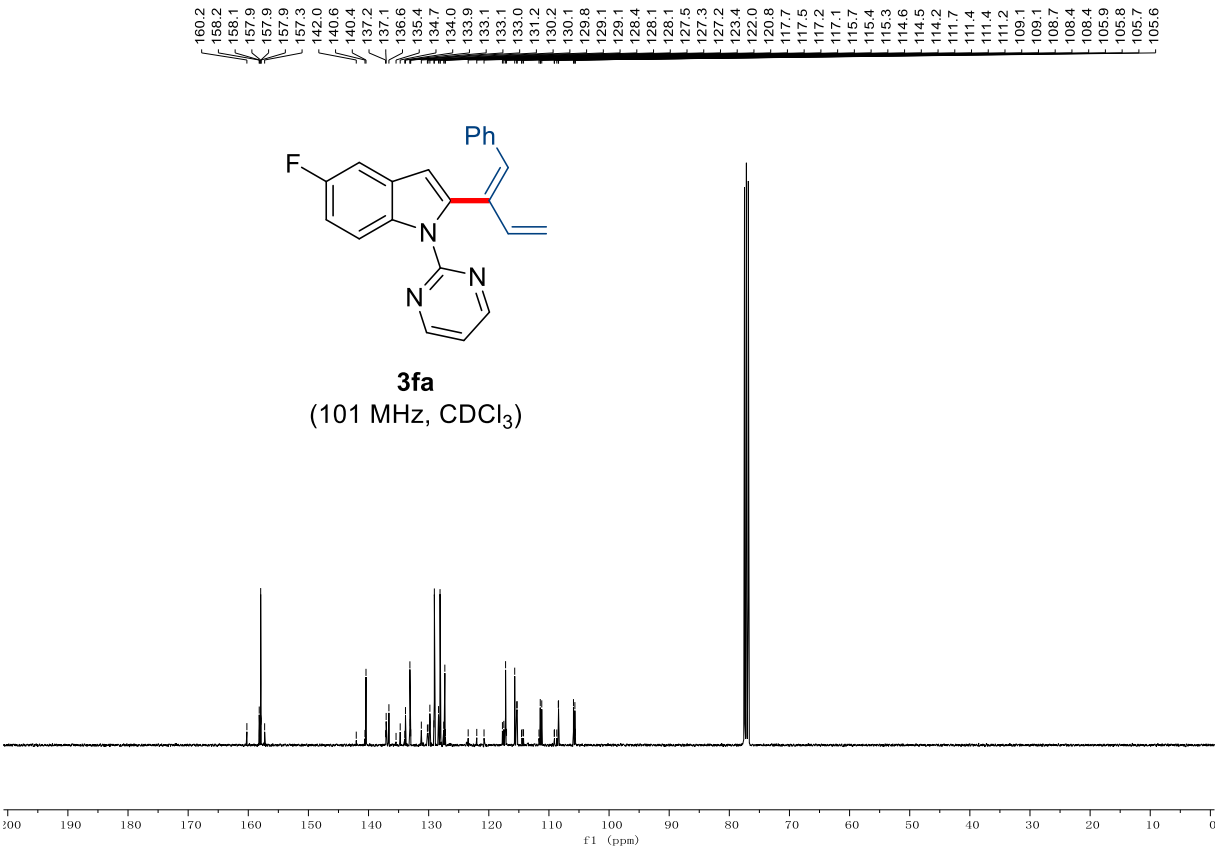

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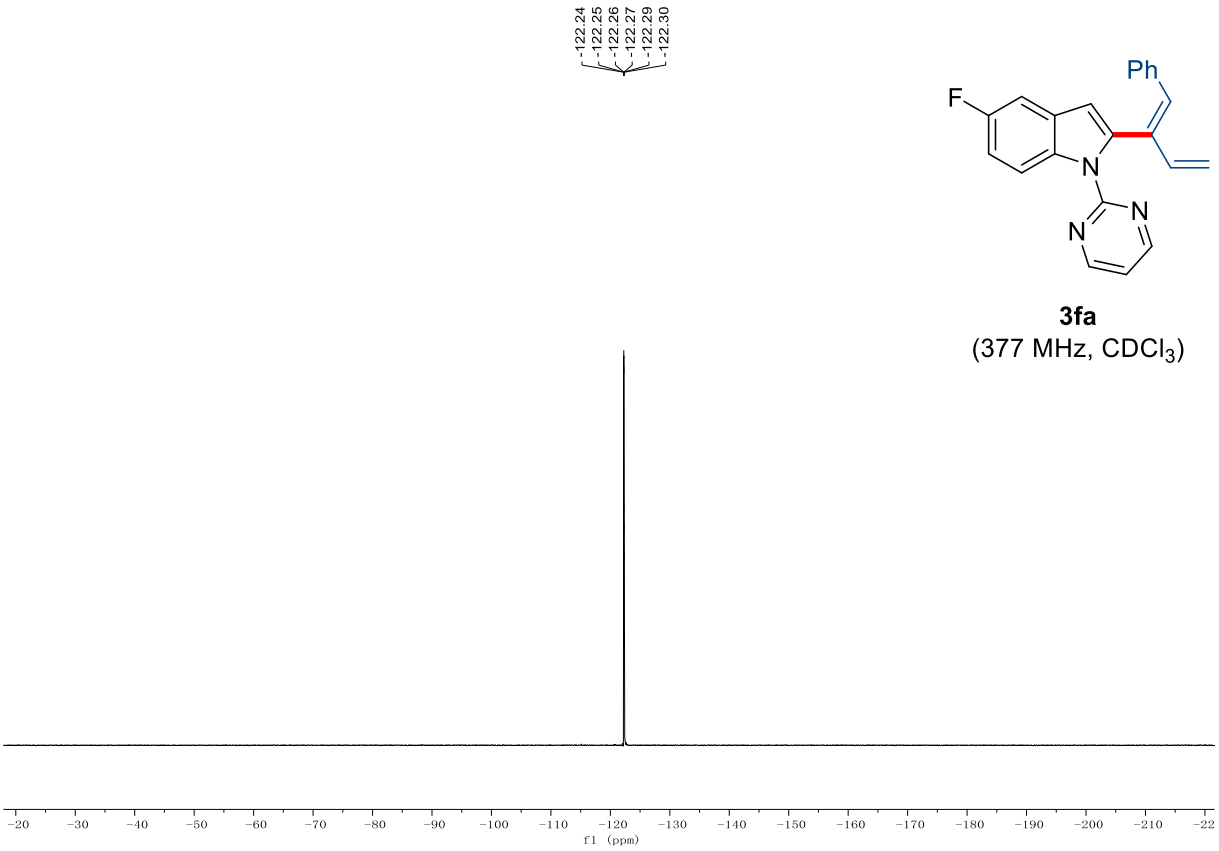

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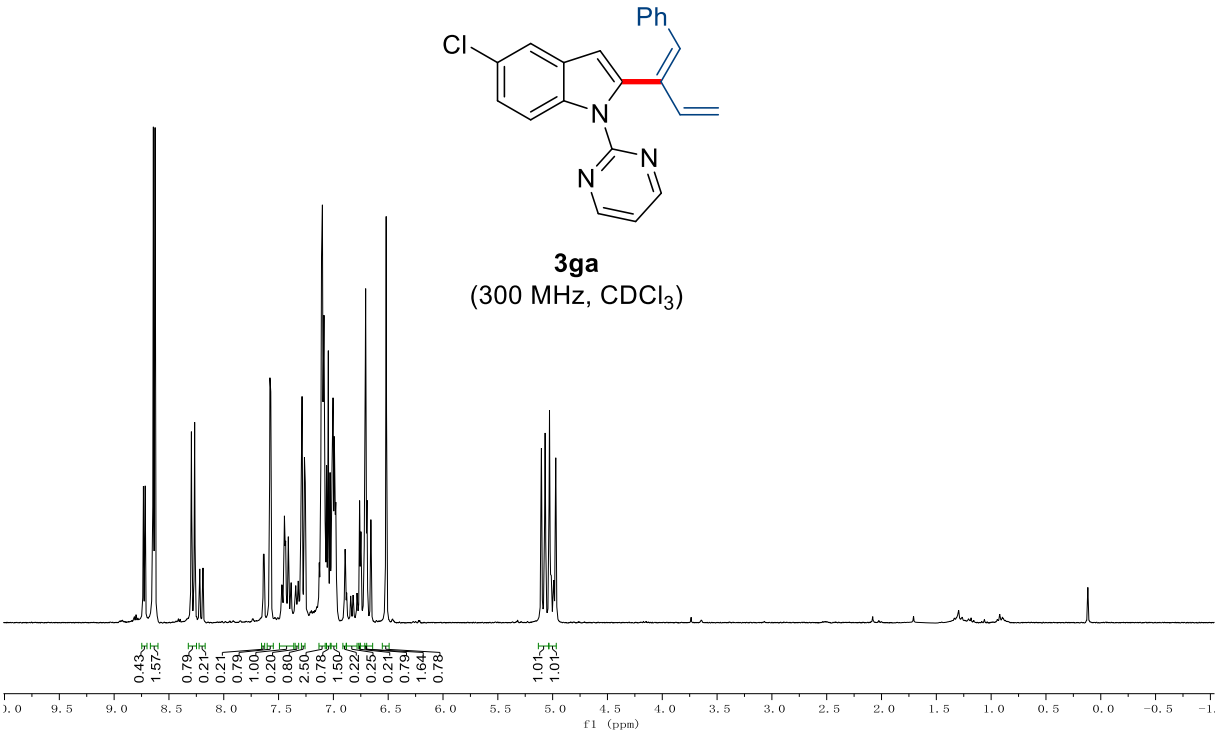

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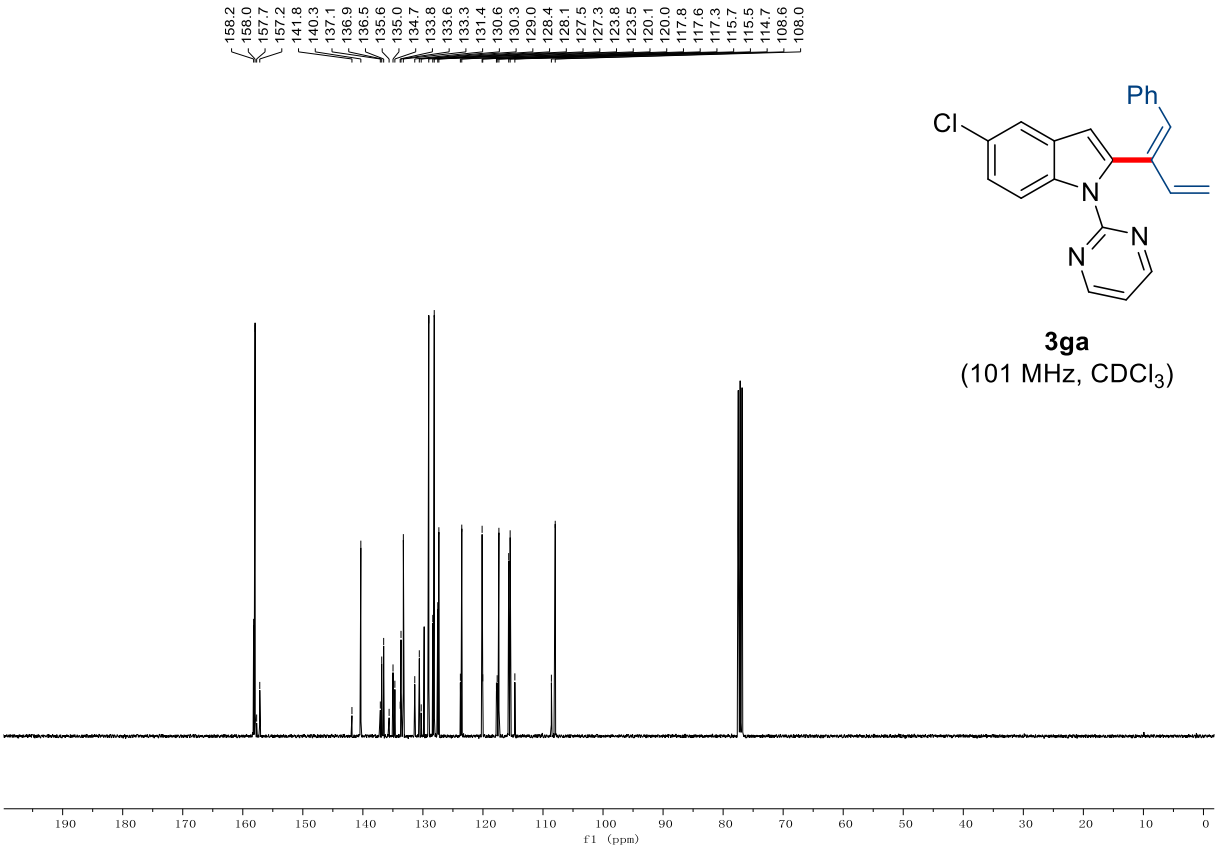

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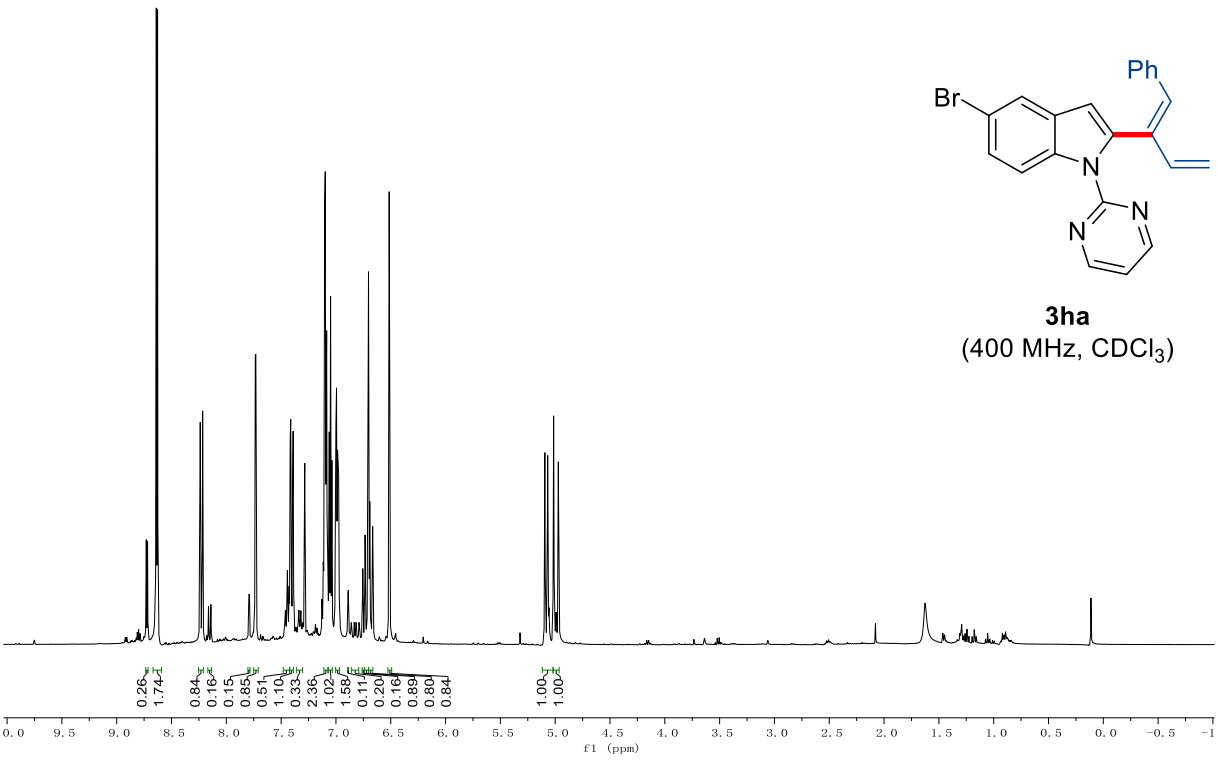

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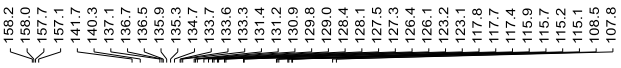
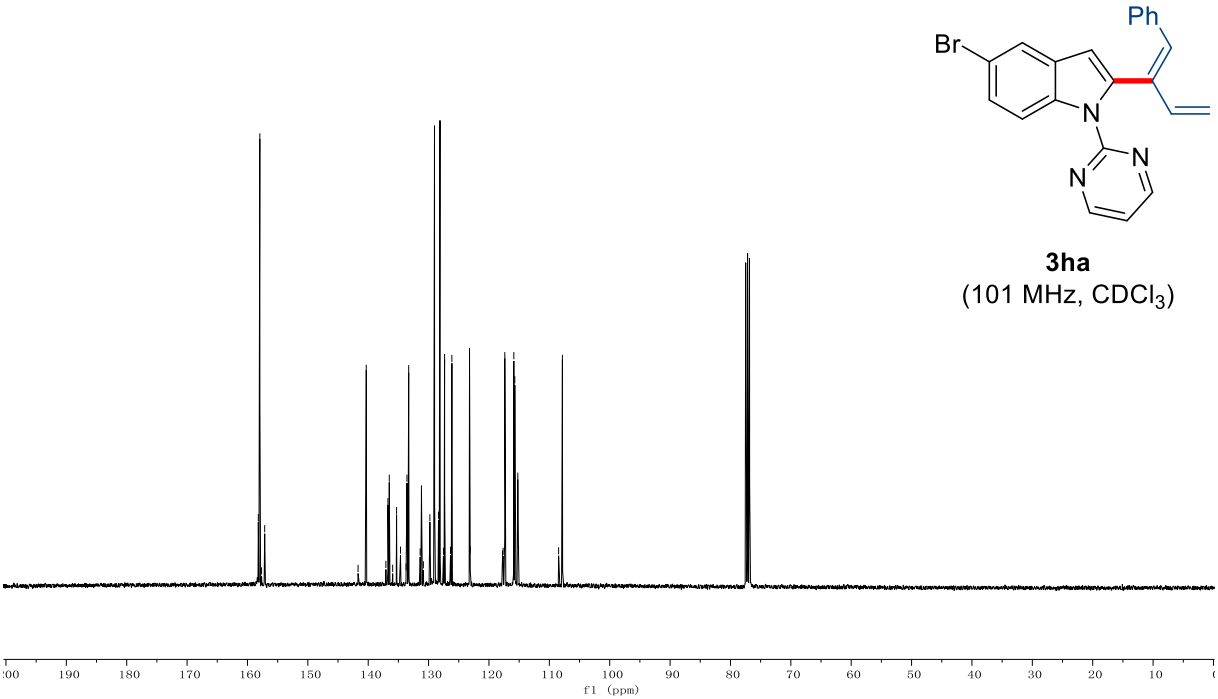
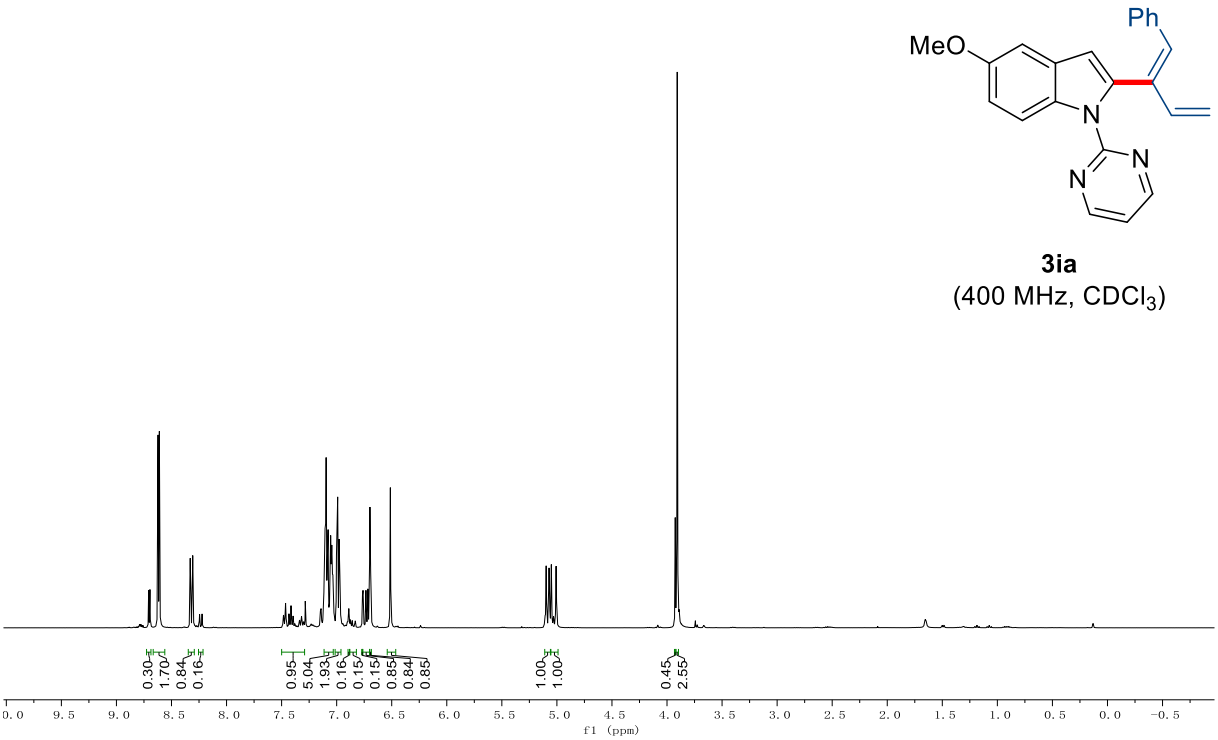
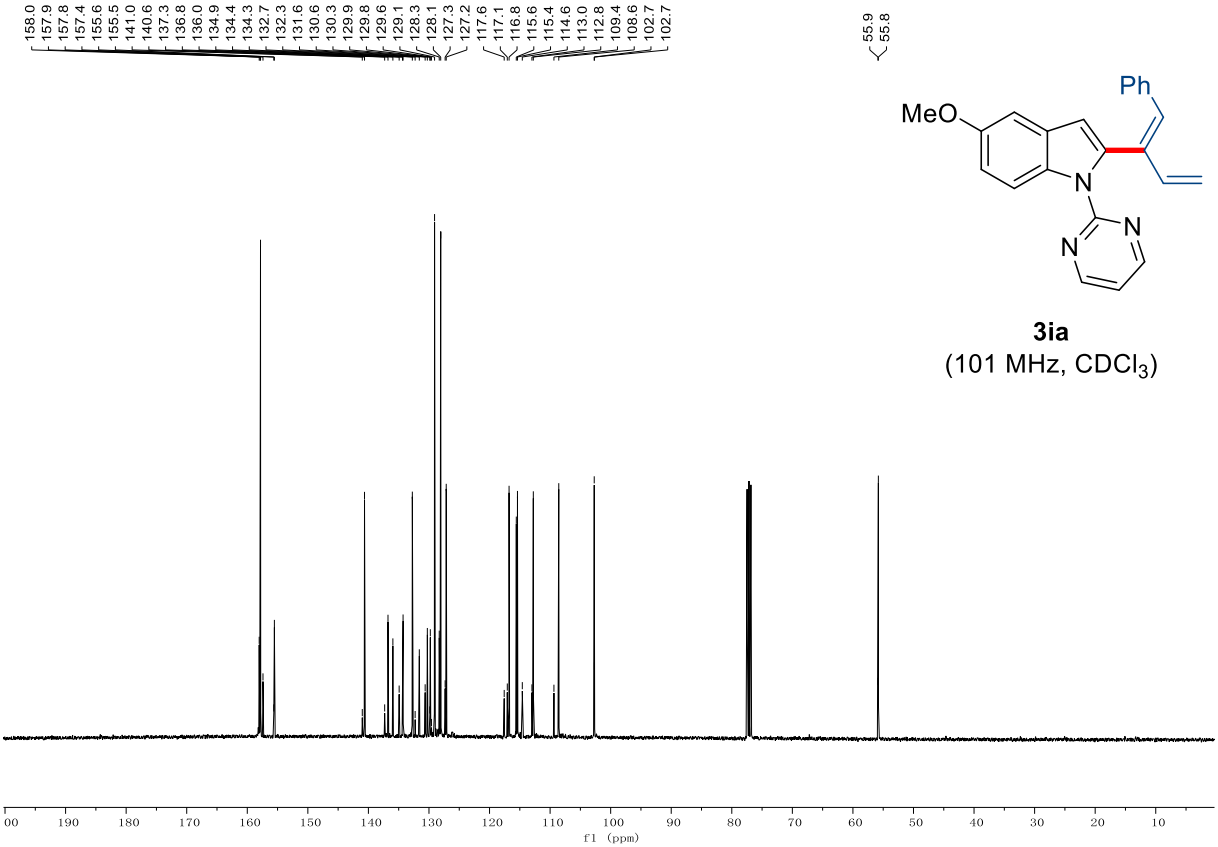




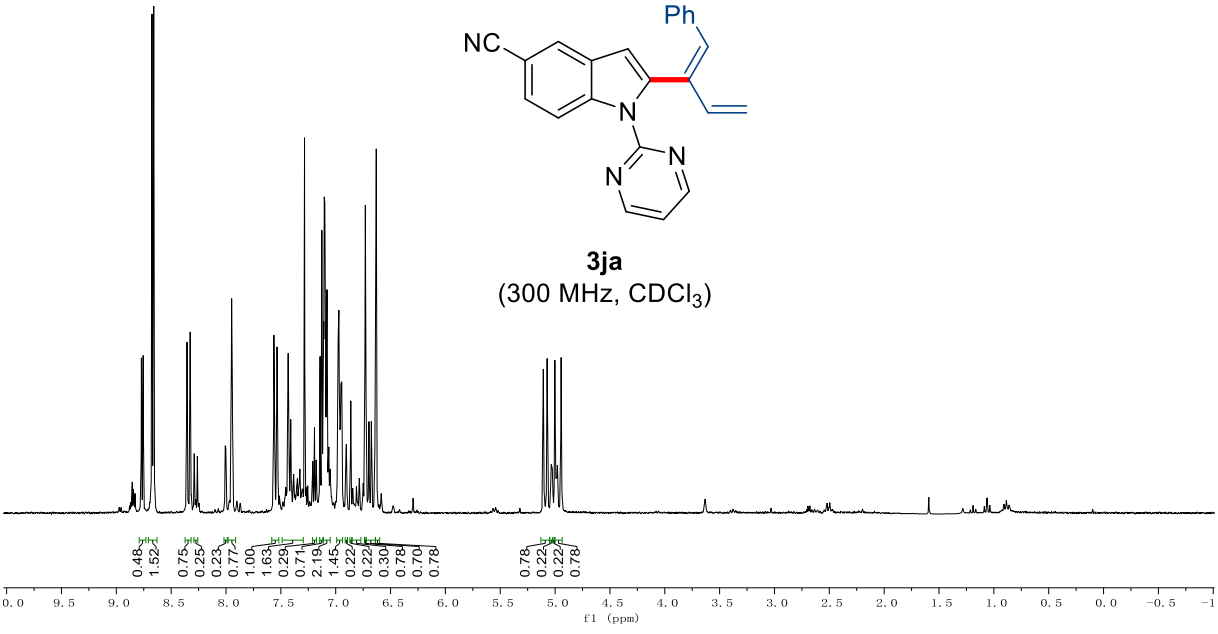
3ha
(101 MHz, $CDCl_3$)



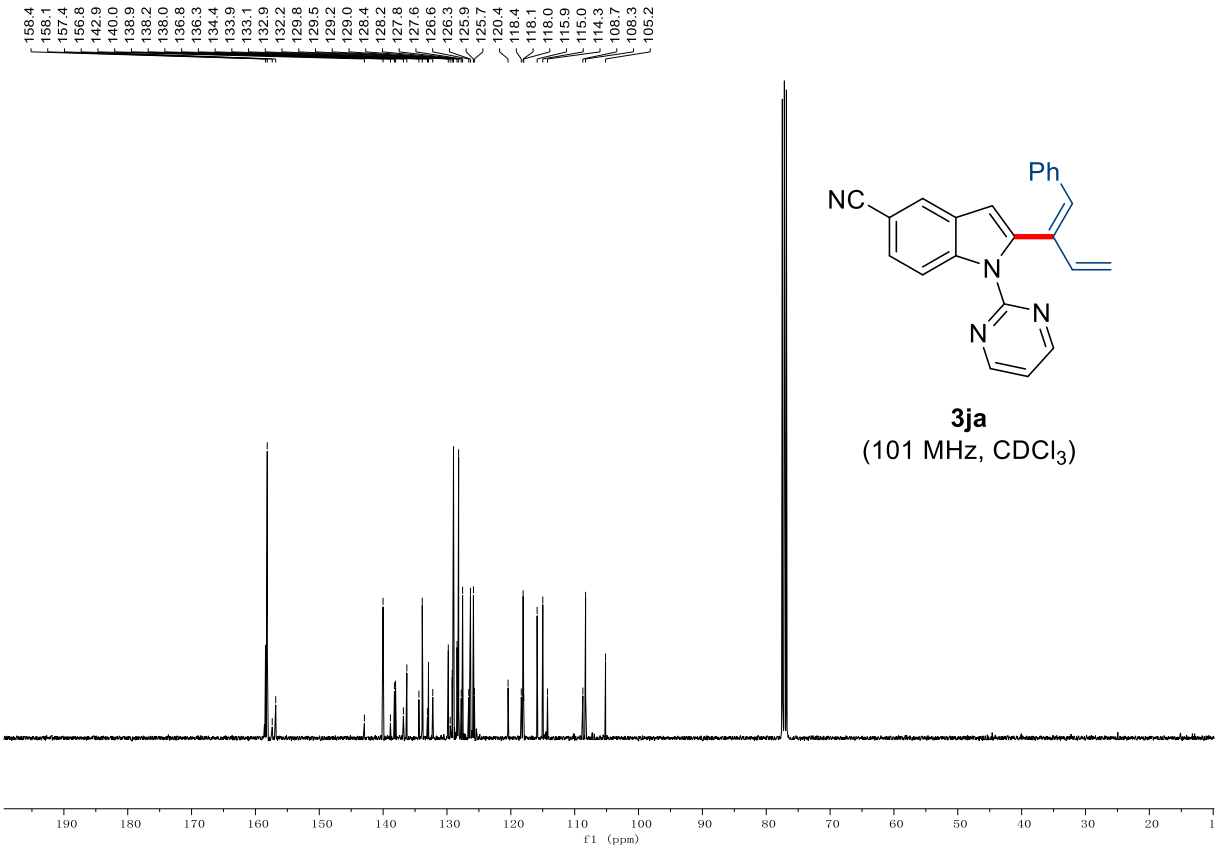
3ia
(400 MHz, $CDCl_3$)



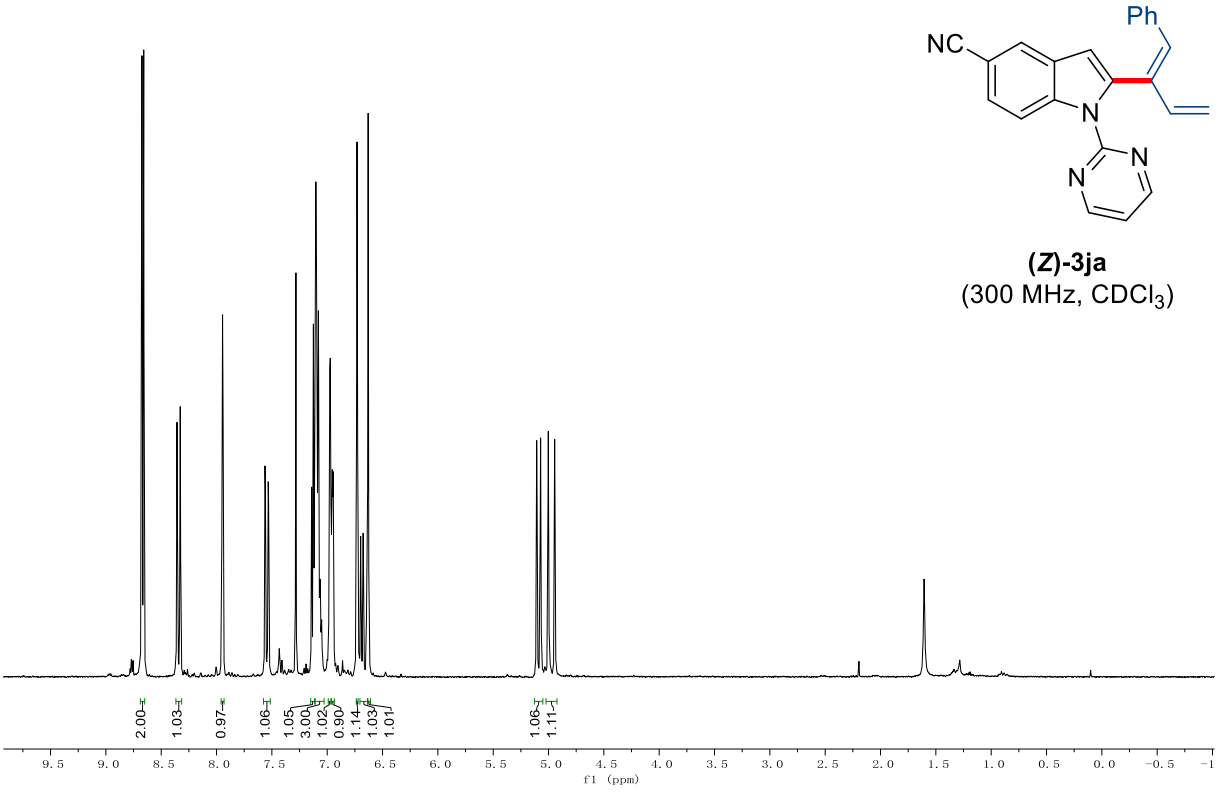
3ia
(101 MHz, $CDCl_3$)



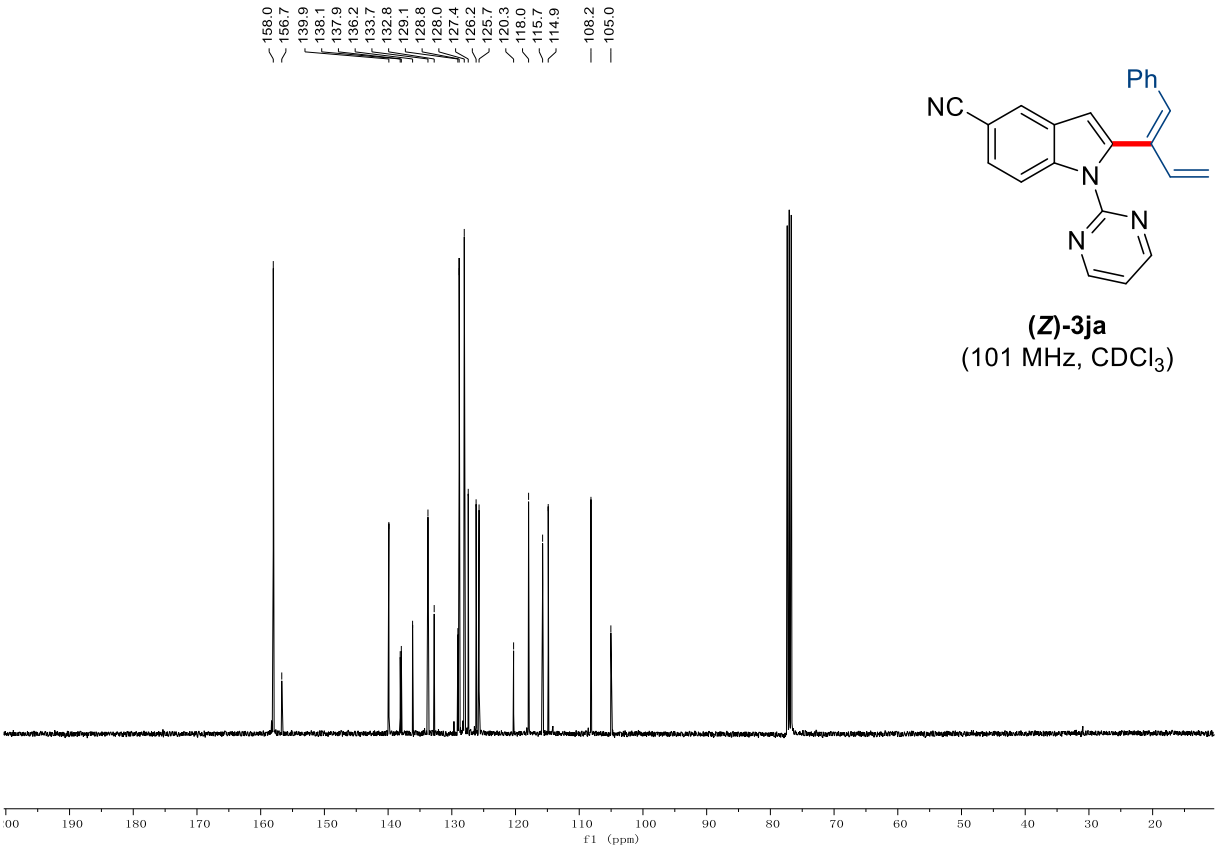
3ja
(300 MHz, $CDCl_3$)



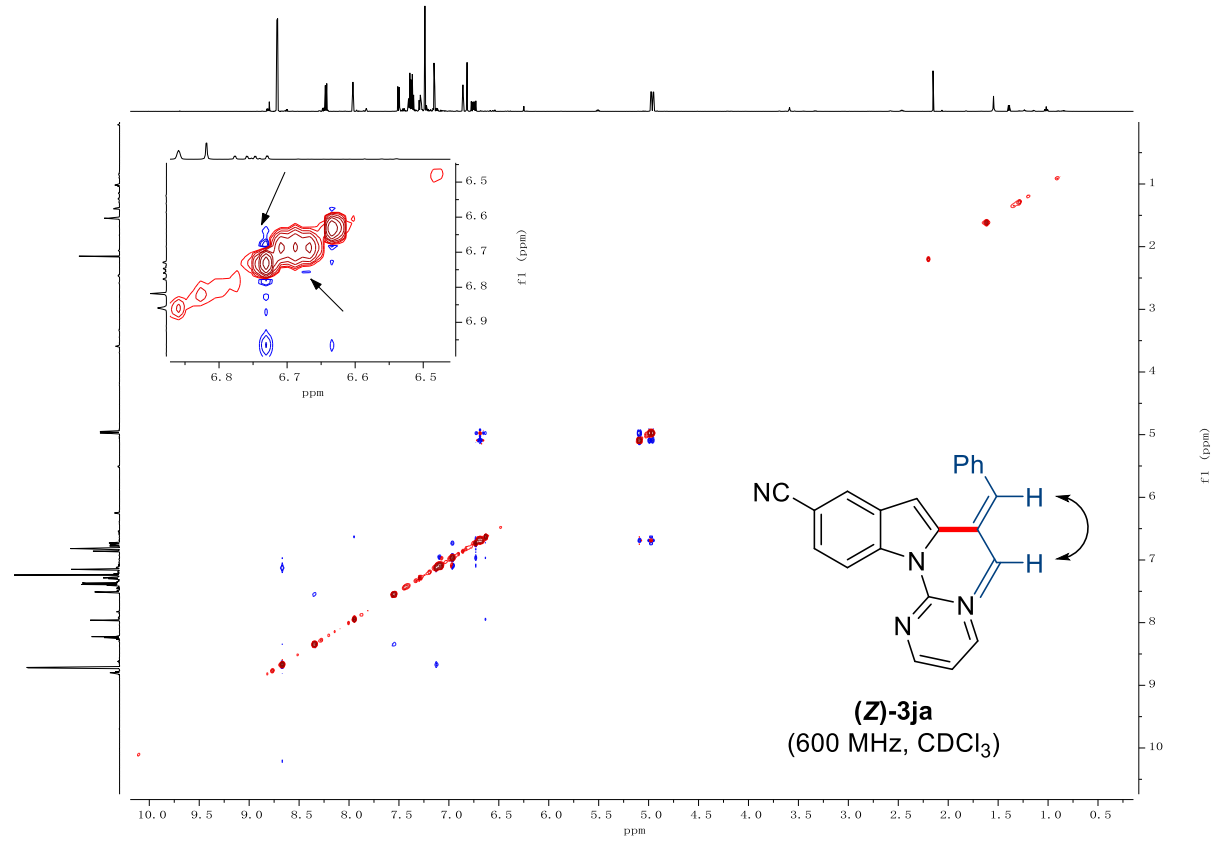
3ja
(101 MHz, $CDCl_3$)



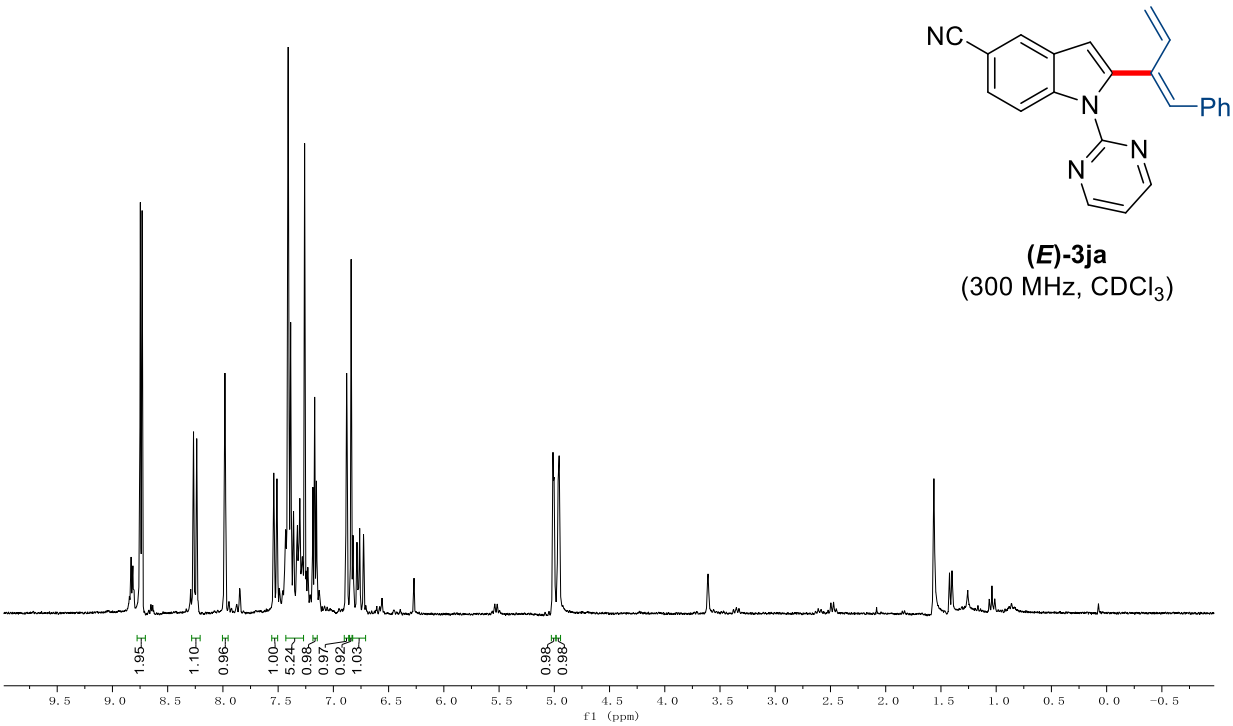
(*Z*)-3ja
(300 MHz, $CDCl_3$)



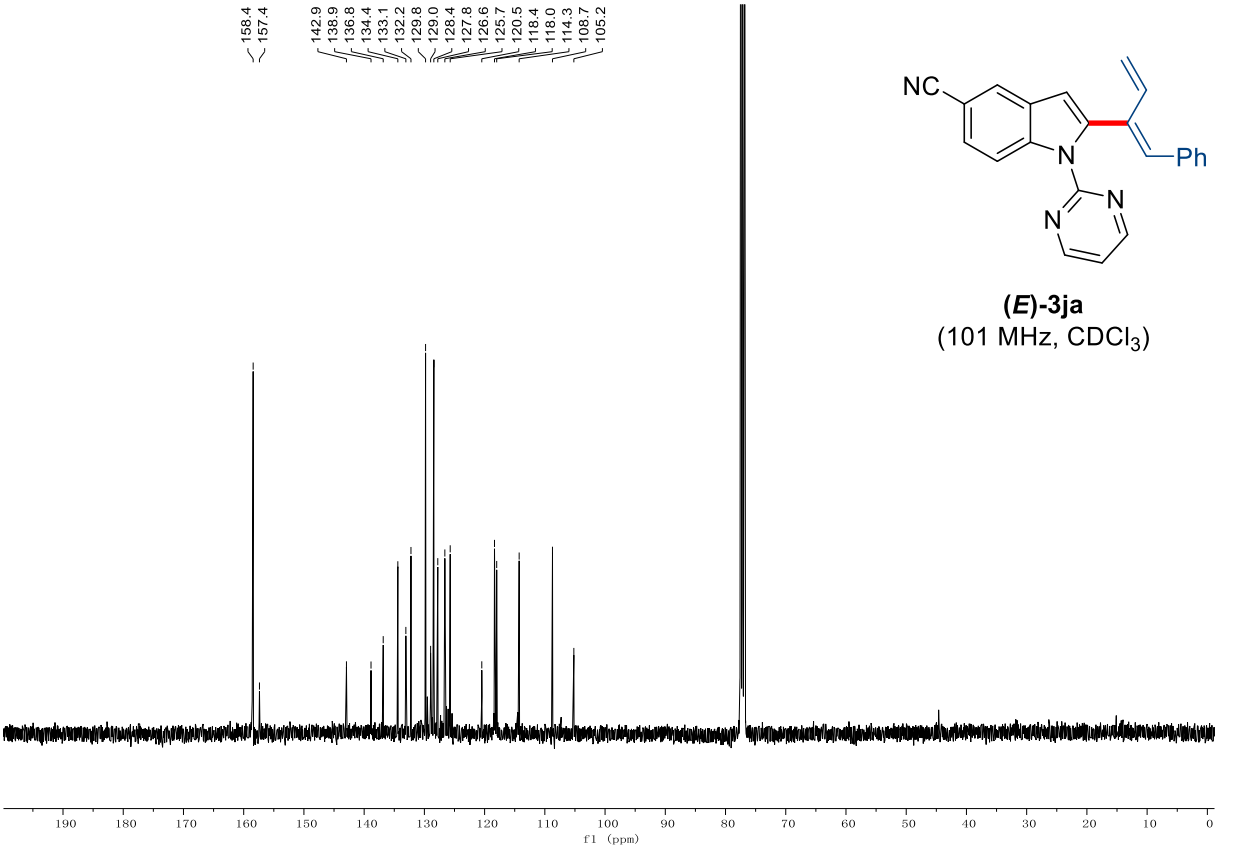
(*Z*)-3ja
(101 MHz, $CDCl_3$)



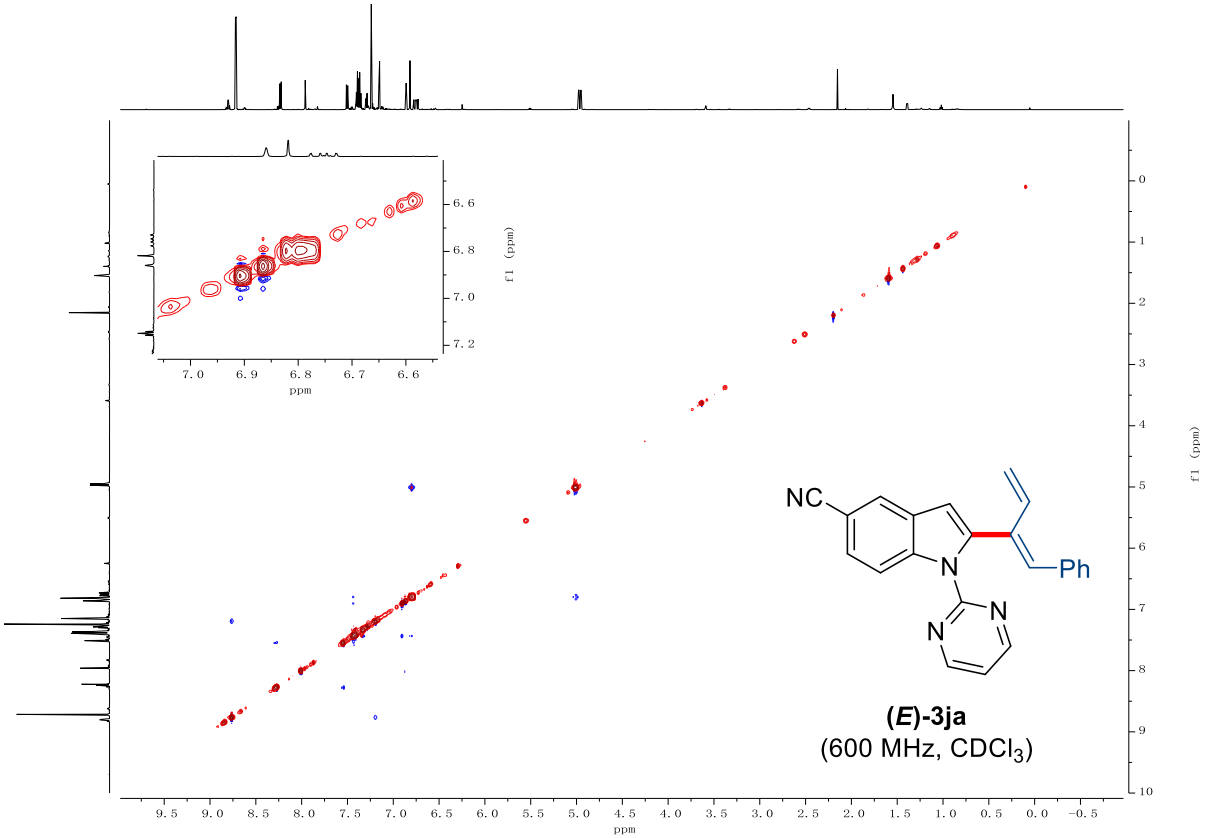
(*Z*)-3ja
(600 MHz, $CDCl_3$)

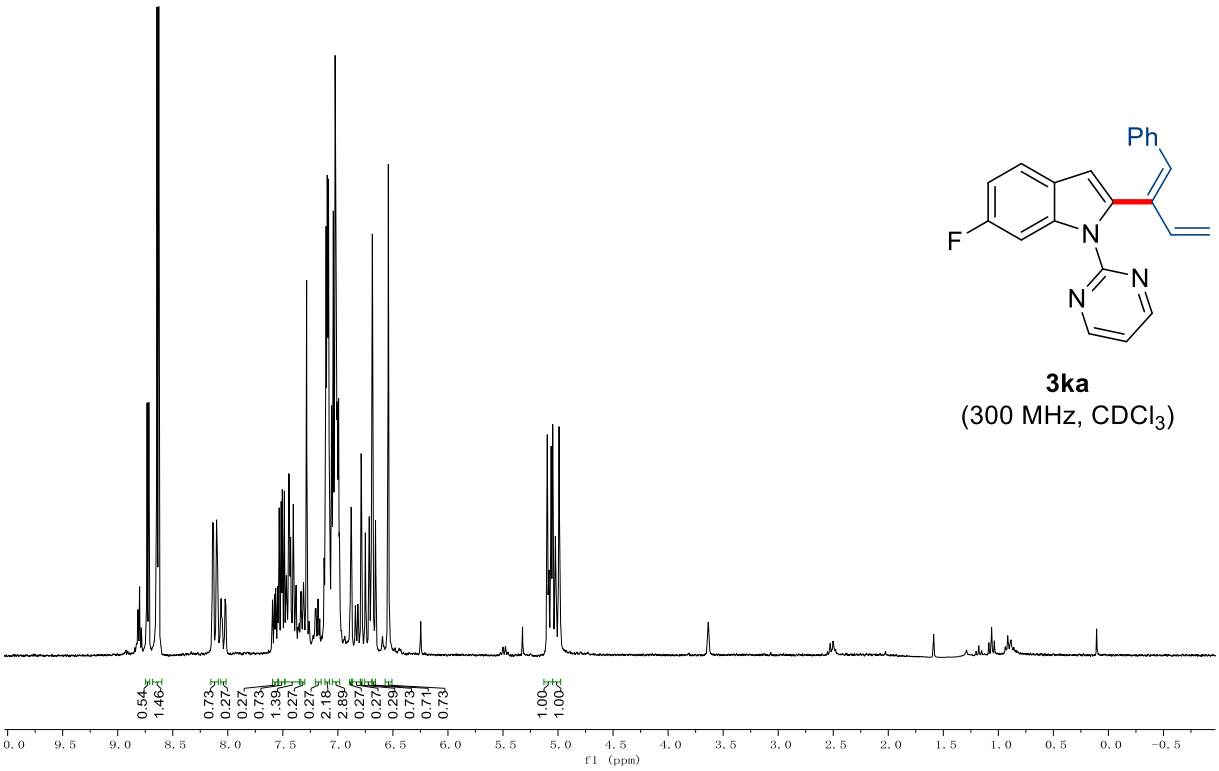


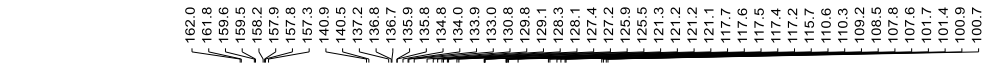
(*E*)-3ja
(300 MHz, $CDCl_3$)

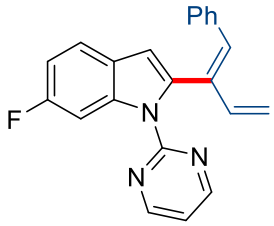


(*E*)-3ja
(101 MHz, $CDCl_3$)

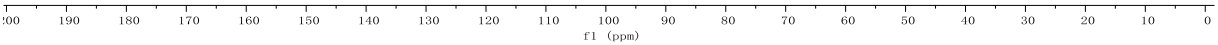

NC
N
N
N
Ph
(E)-3ja
(600 MHz, CDCl3)

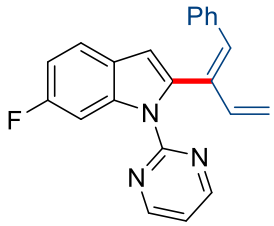

F
N
N
N
Ph
3ka
(300 MHz, CDCl3)



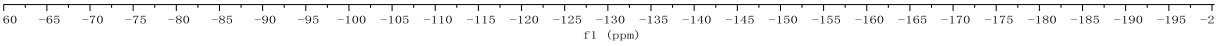


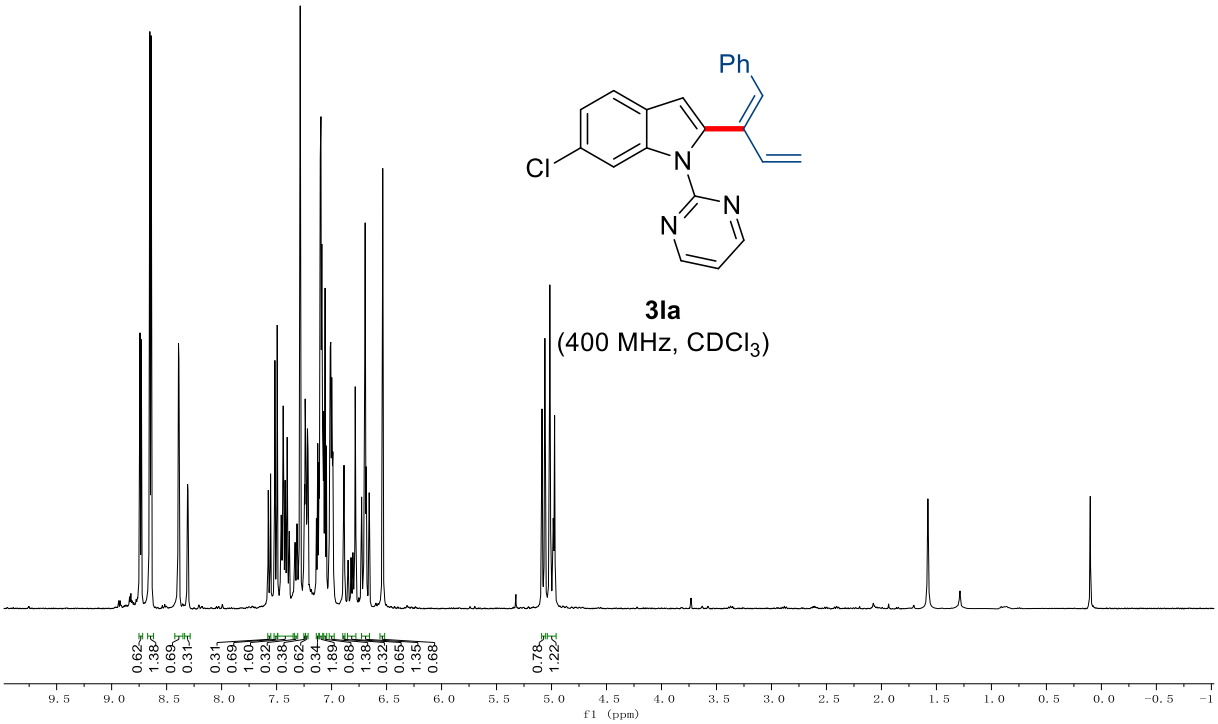
3ka
(101 MHz, $CDCl_3$)



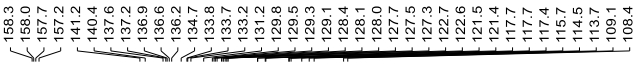


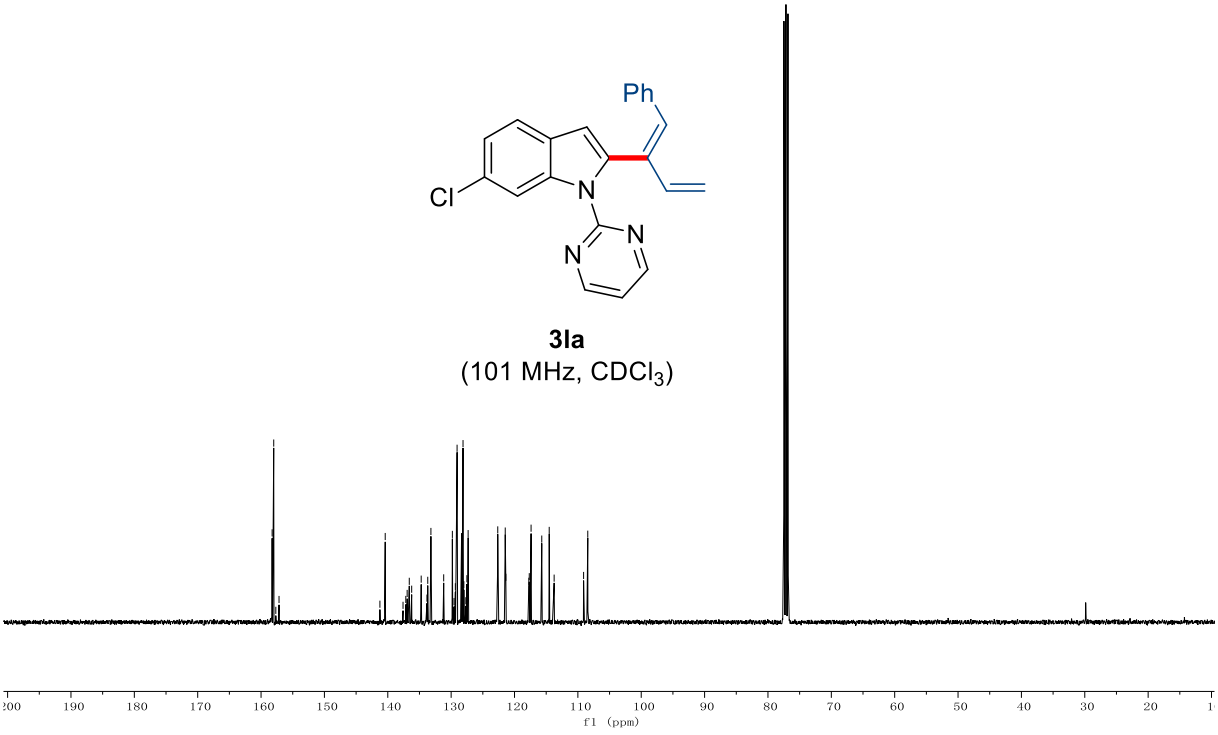
3ka
(377 MHz, $CDCl_3$)



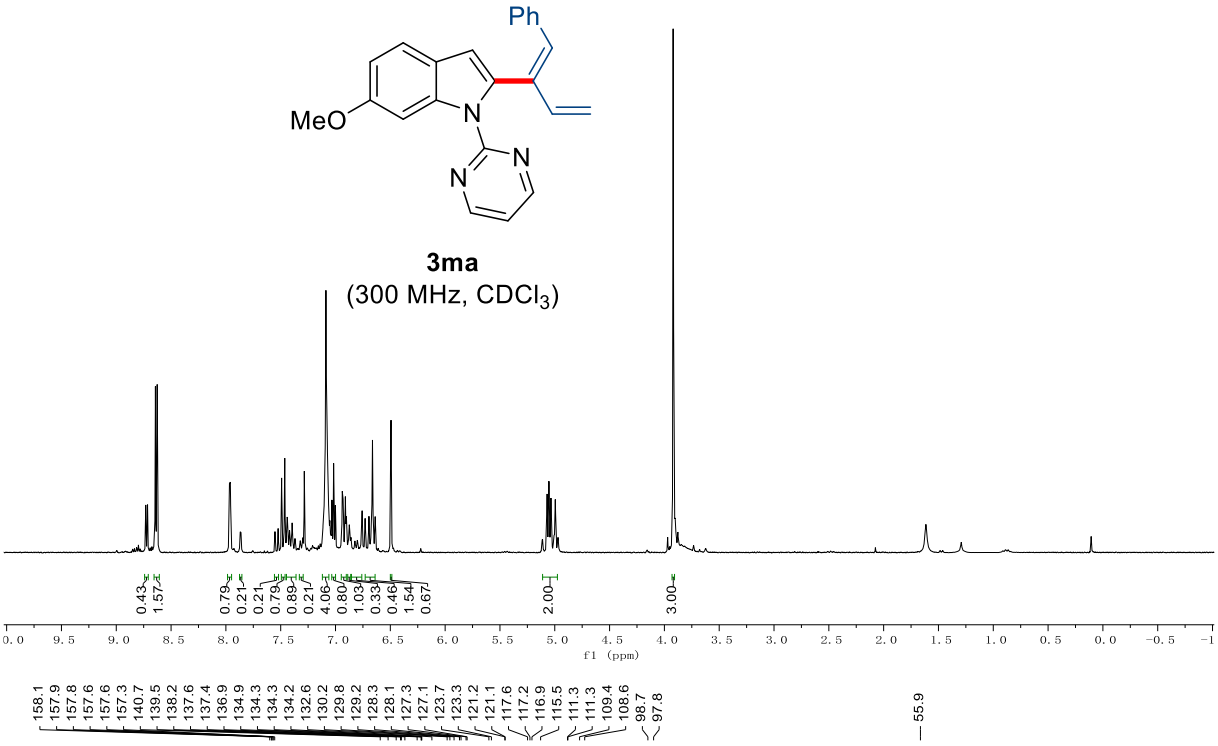


3la
(400 MHz, $CDCl_3$)

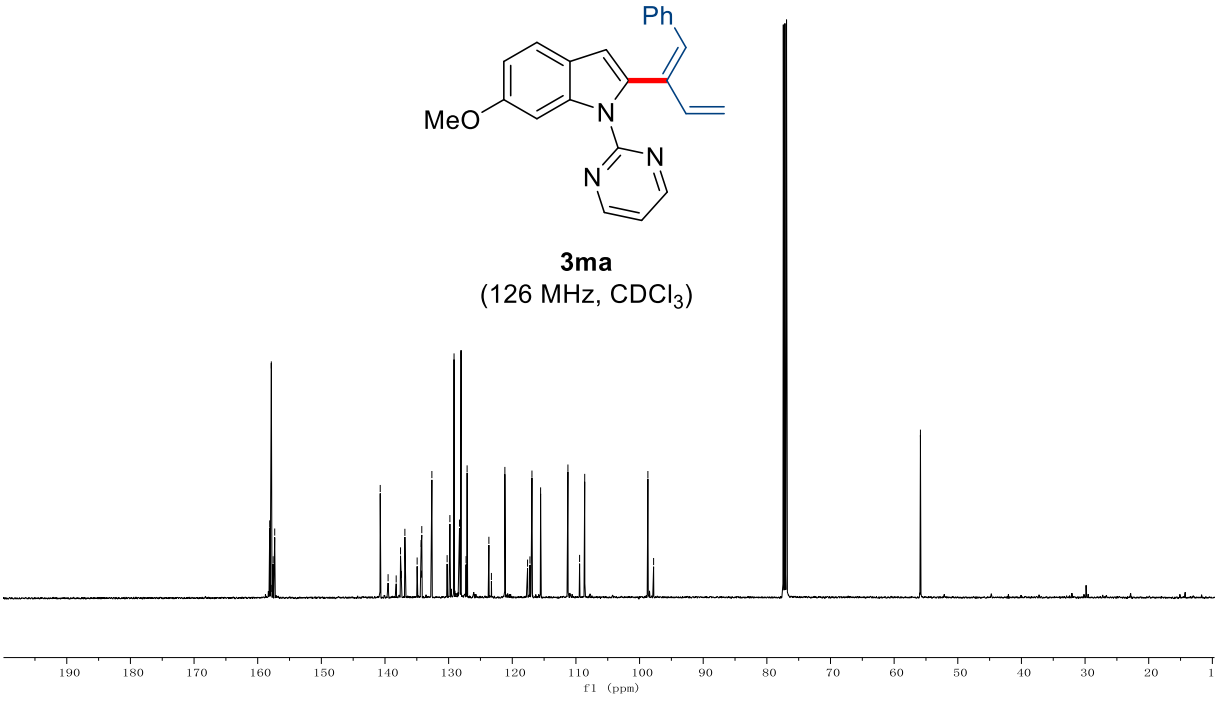




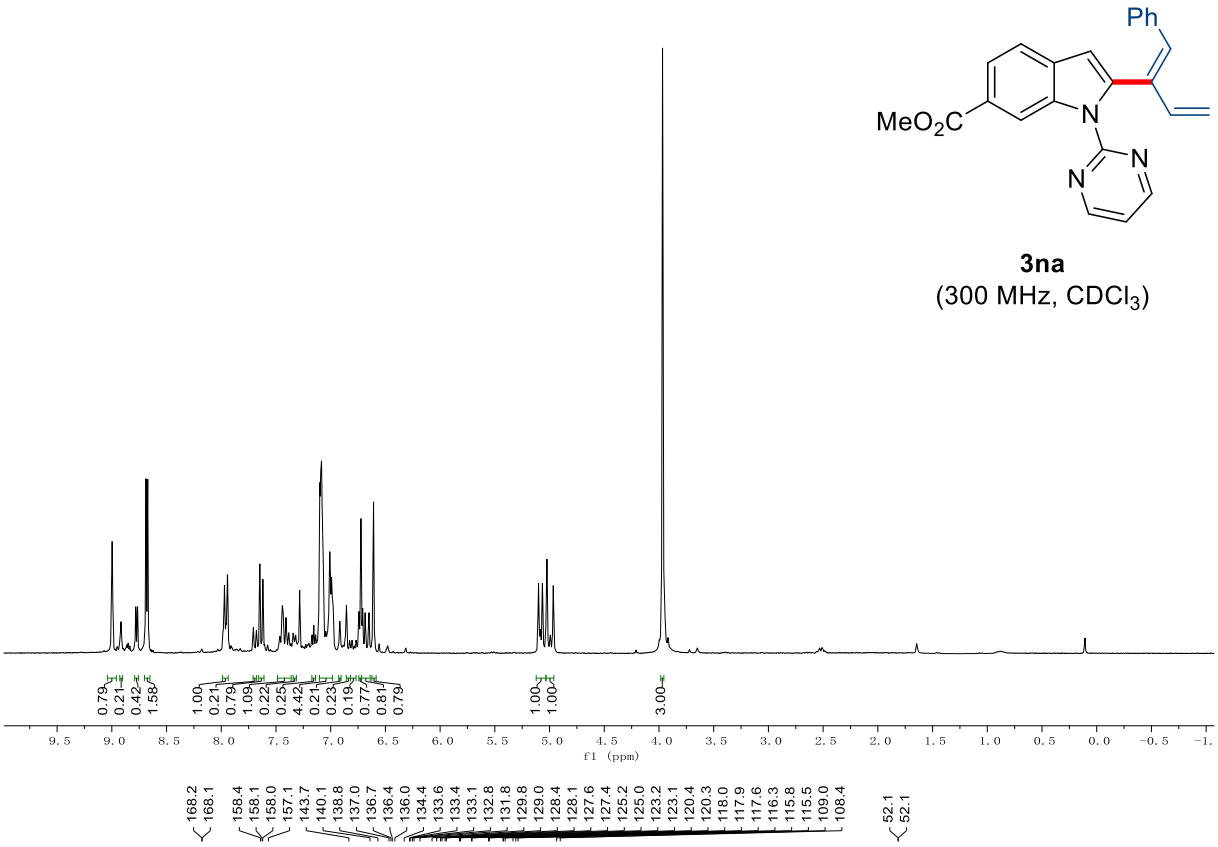
3la
(101 MHz, $CDCl_3$)

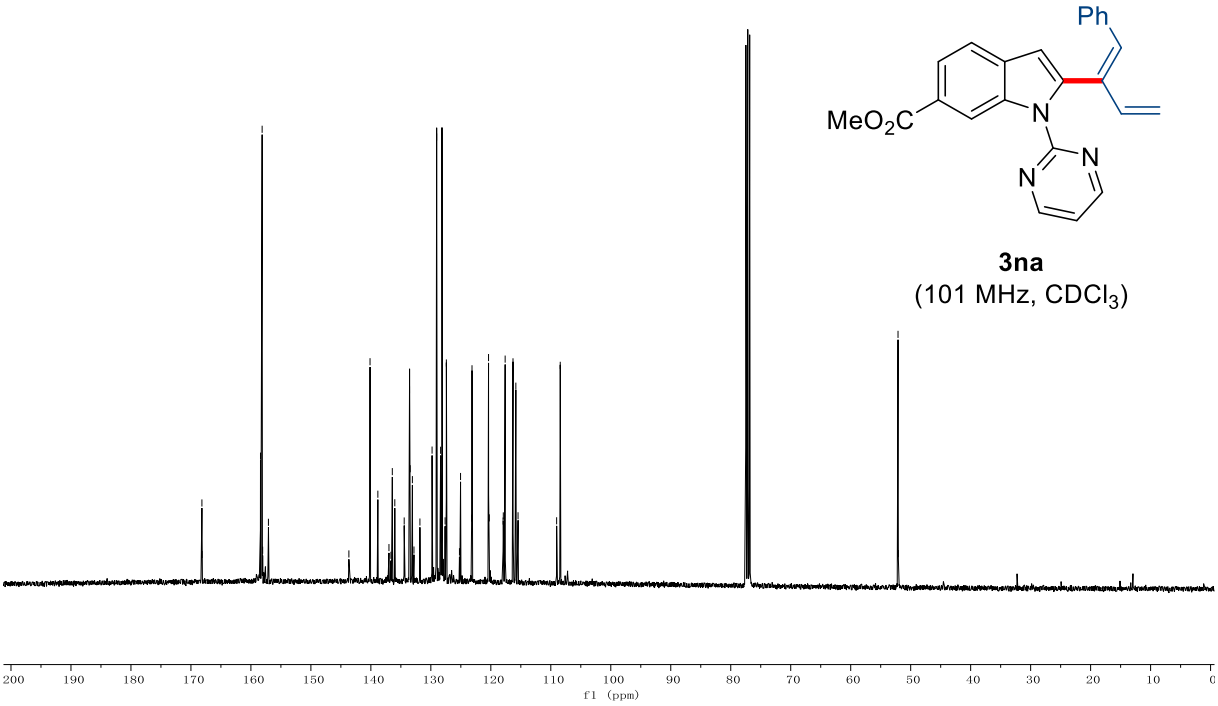


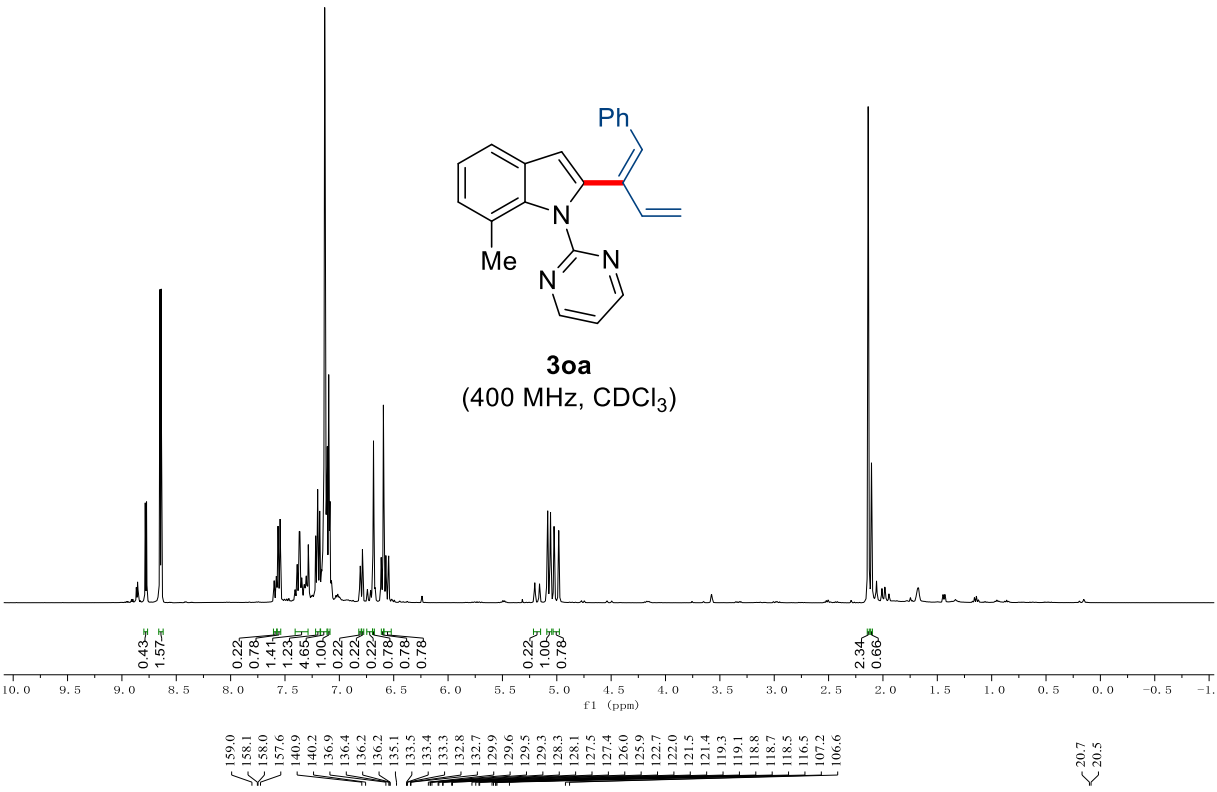
3ma
(300 MHz, $CDCl_3$)



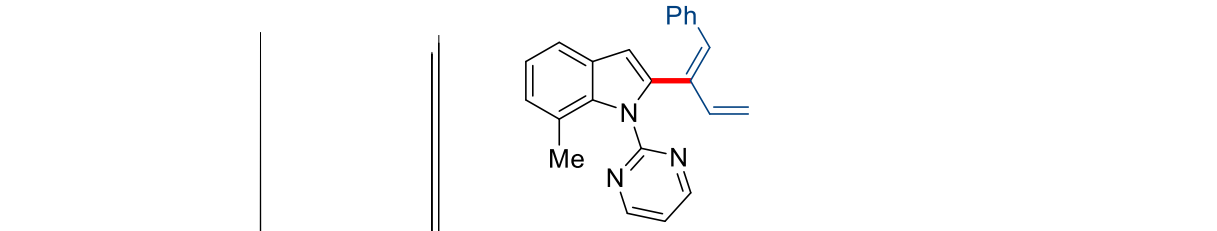
3ma
(126 MHz, $CDCl_3$)


Ph
MeO2C
N
N
N
3na
(300 MHz, CDCl3)
0.79
0.21
0.42
1.58
1.00
0.21
0.79
1.09
0.22
0.25
4.42
0.21
0.23
0.19
0.77
0.81
0.79
1.00
1.00
3.00
f1 (ppm)
168.2
168.1
158.4
158.1
158.0
157.1
143.7
140.1
138.8
137.0
136.7
136.4
136.0
134.4
133.6
133.4
133.1
132.8
131.8
129.8
129.0
128.4
128.1
127.6
127.4
125.2
125.0
123.2
123.1
120.4
120.3
118.0
117.9
117.6
116.3
115.8
115.5
109.0
108.4
52.1
52.1

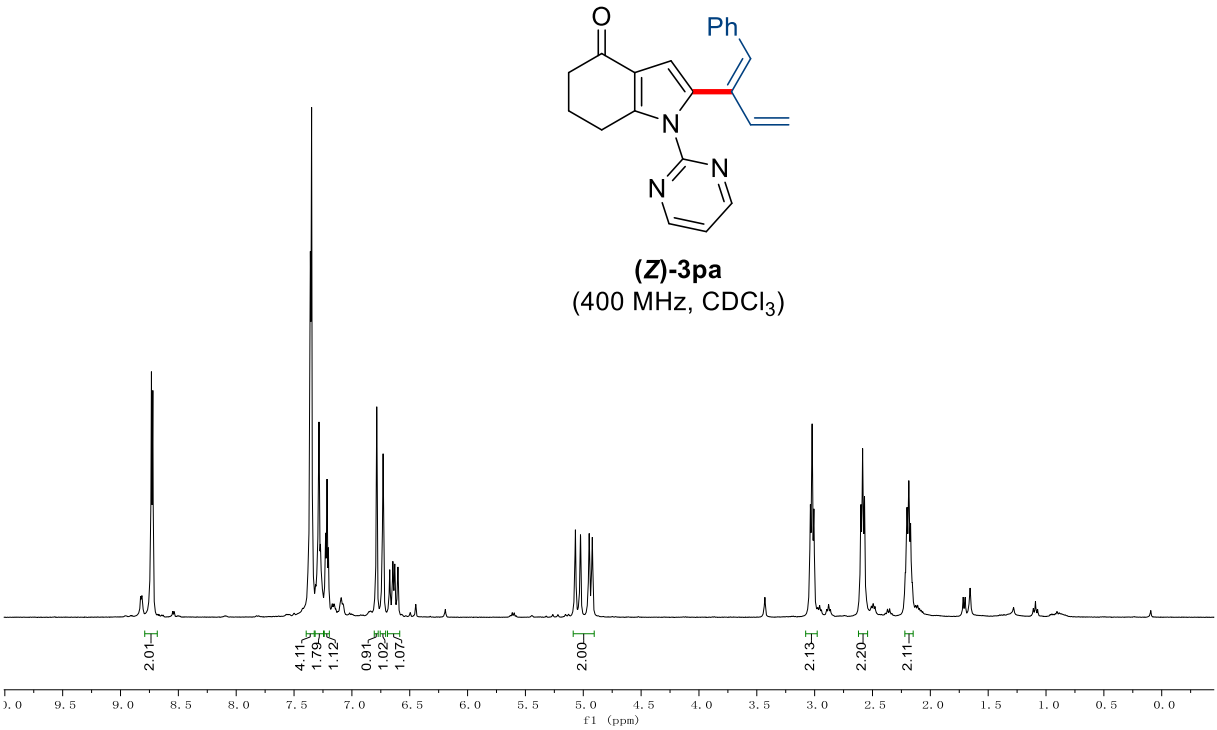

Ph
MeO2C
N
N
N
3na
(101 MHz, CDCl3)
f1 (ppm)

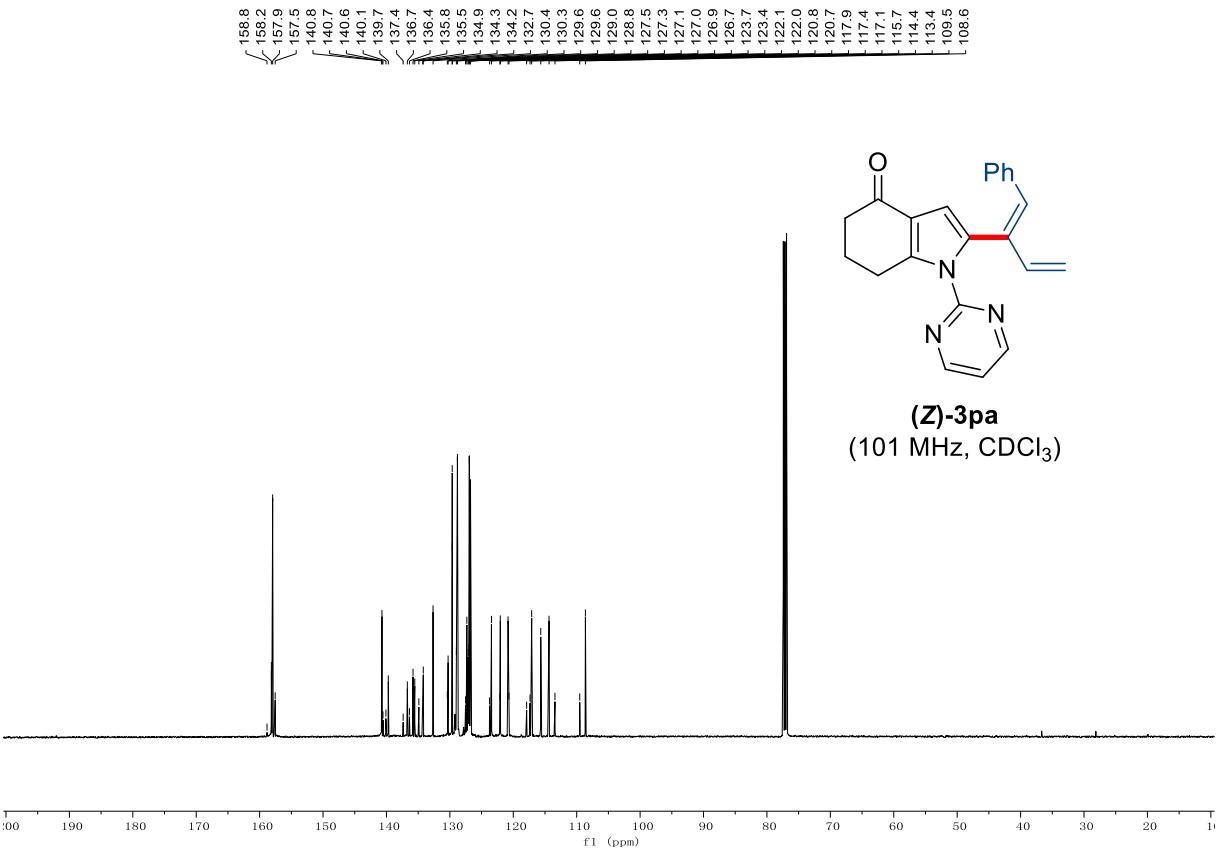


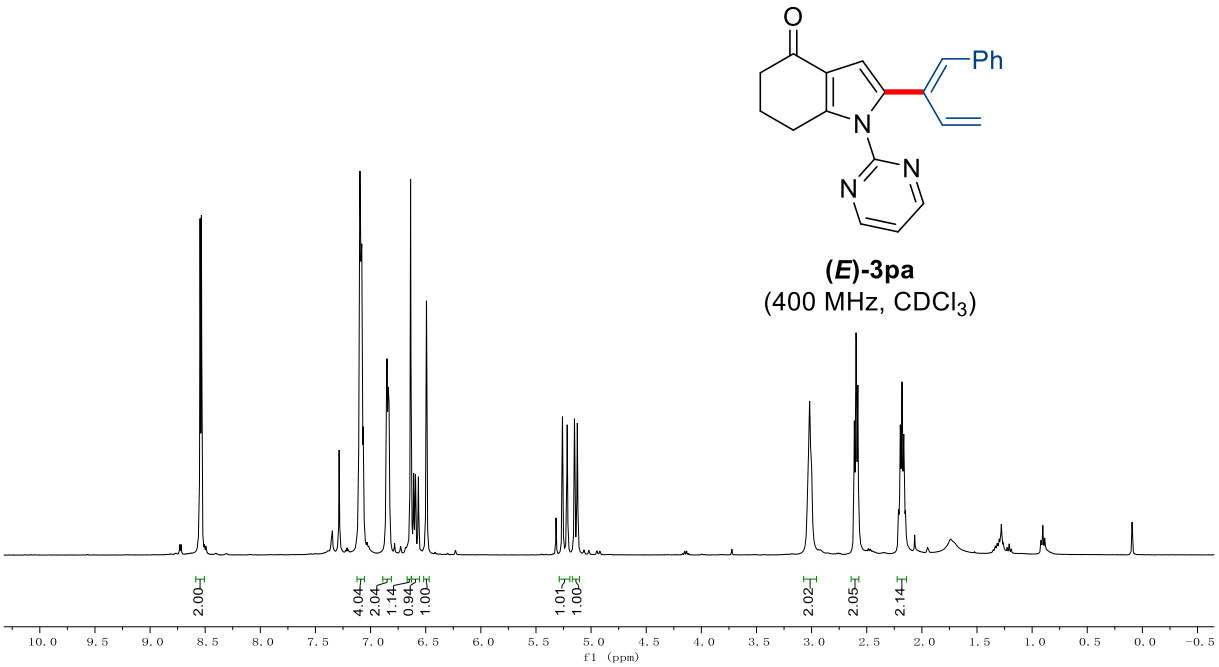
3oa
(400 MHz, $CDCl_3$)

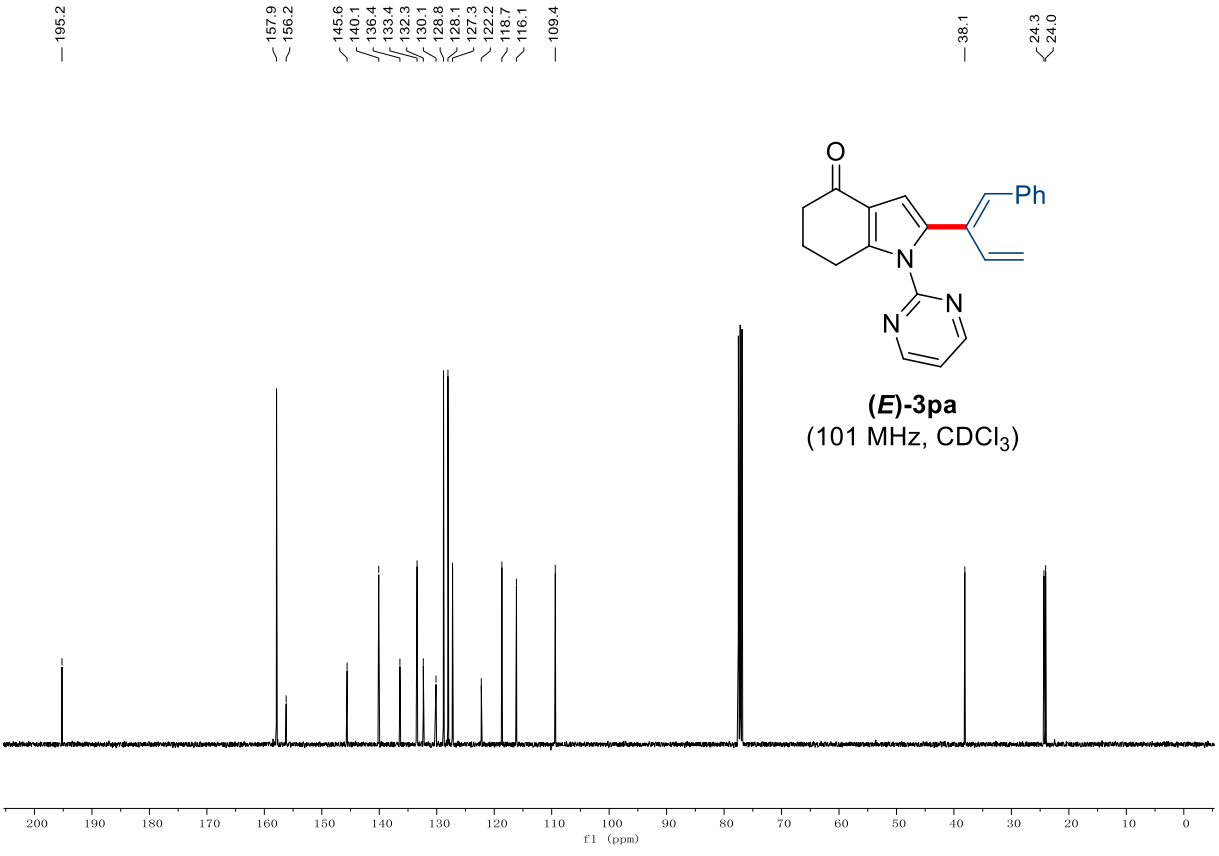


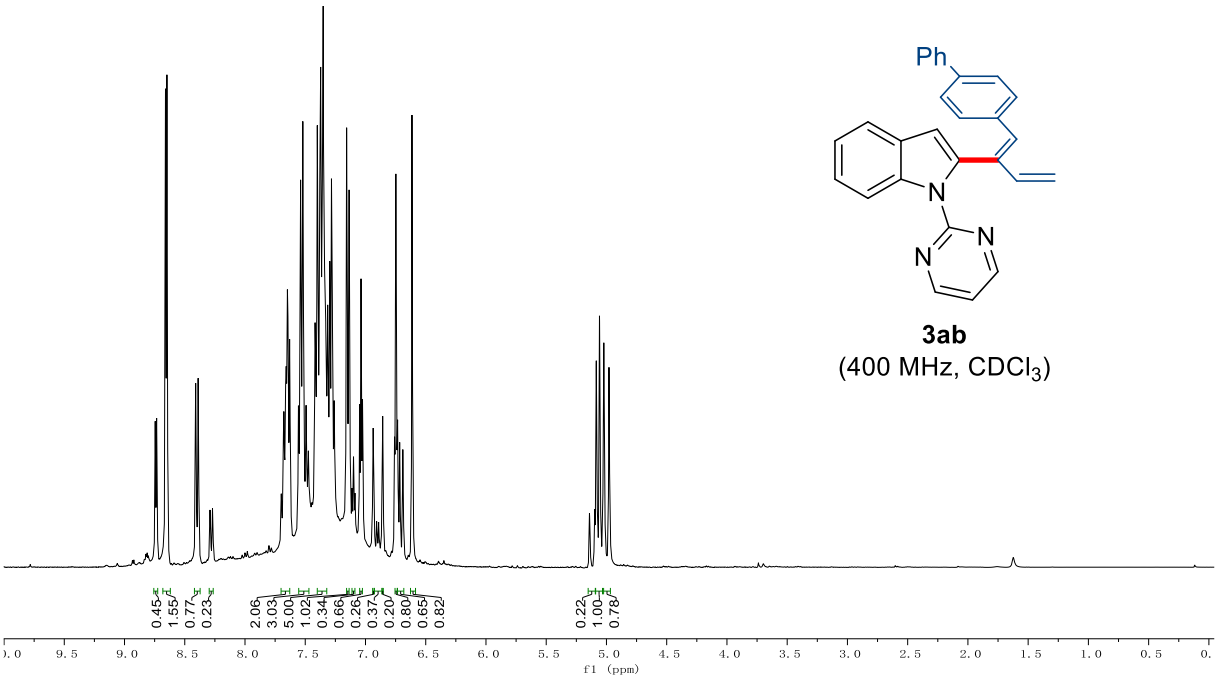
3oa
(75 MHz, $CDCl_3$)


O
Ph
N
N
N
(Z)-3pa
(400 MHz, CDCl3)
2.01
4.11
1.79
1.12
0.91
1.02
1.07
2.00
2.13
2.20
2.11
f1 (ppm)

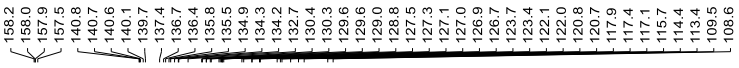

O
Ph
N
N
N
(Z)-3pa
(101 MHz, CDCl3)
f1 (ppm)

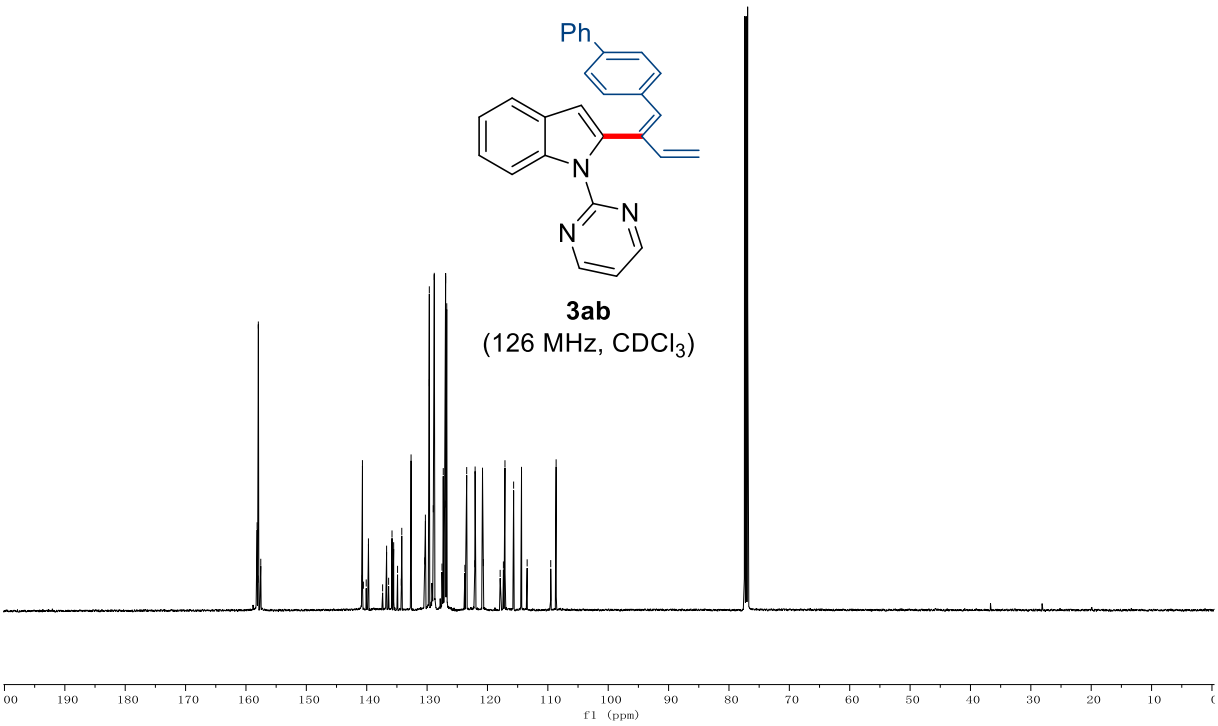

O
Ph
N
N
N
(E)-3pa
(400 MHz, CDCl3)
2.00
4.04
2.04
1.14
0.94
1.00
1.01
1.00
2.02
2.05
2.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


195.2
157.9
156.2
145.6
140.1
136.4
133.4
132.3
130.1
128.8
128.1
127.3
122.2
118.7
116.1
109.4
38.1
24.3
24.0
O
Ph
N
N
N
(E)-3pa
(101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

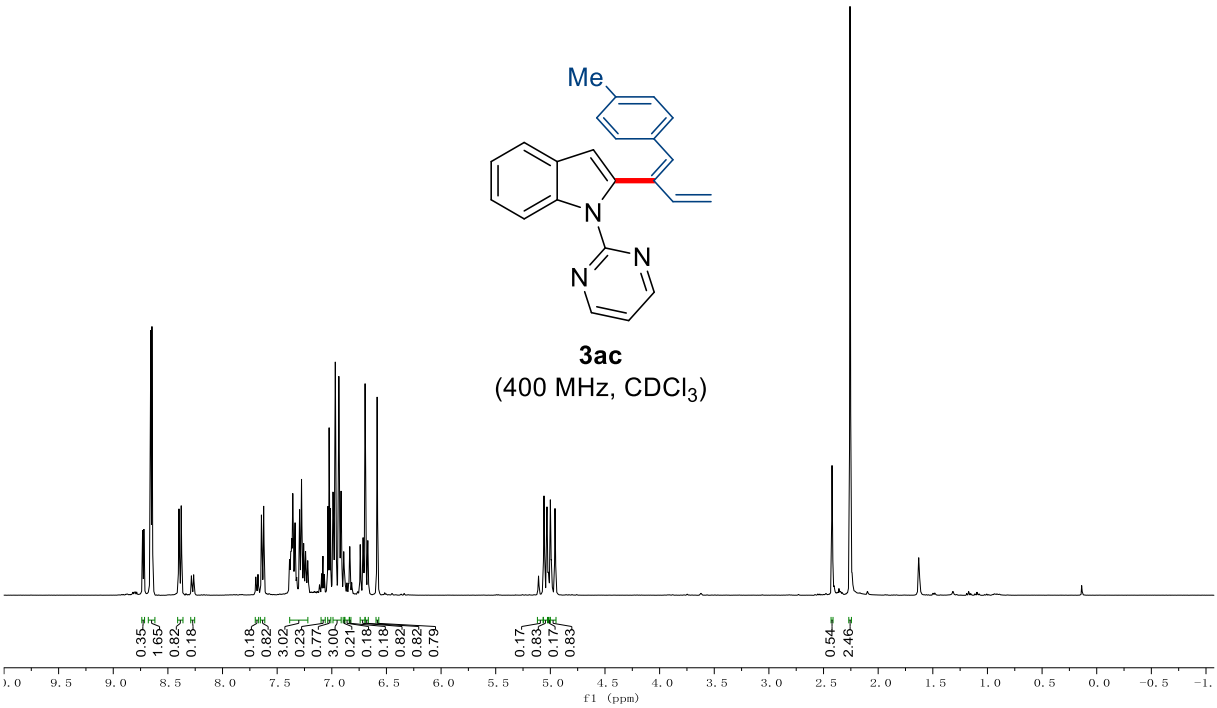


3ab
(400 MHz, $CDCl_3$)

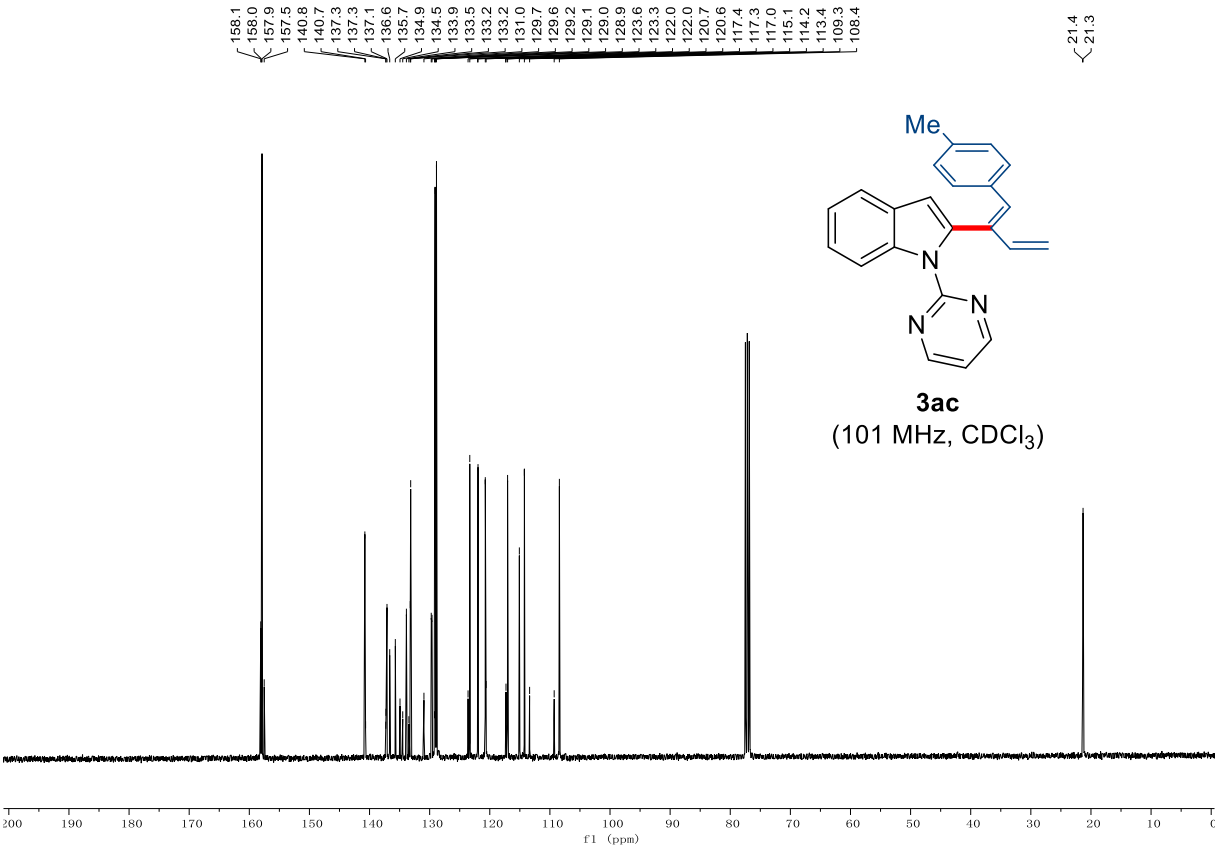




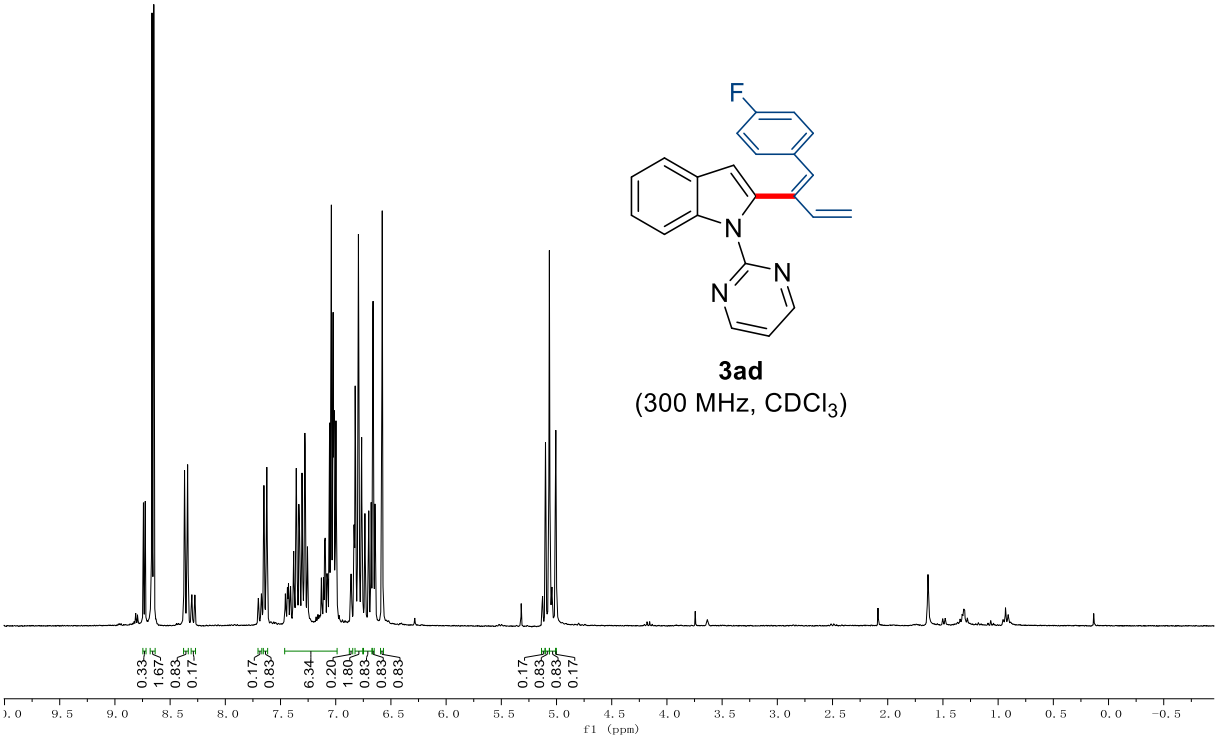
3ab
(126 MHz, $CDCl_3$)



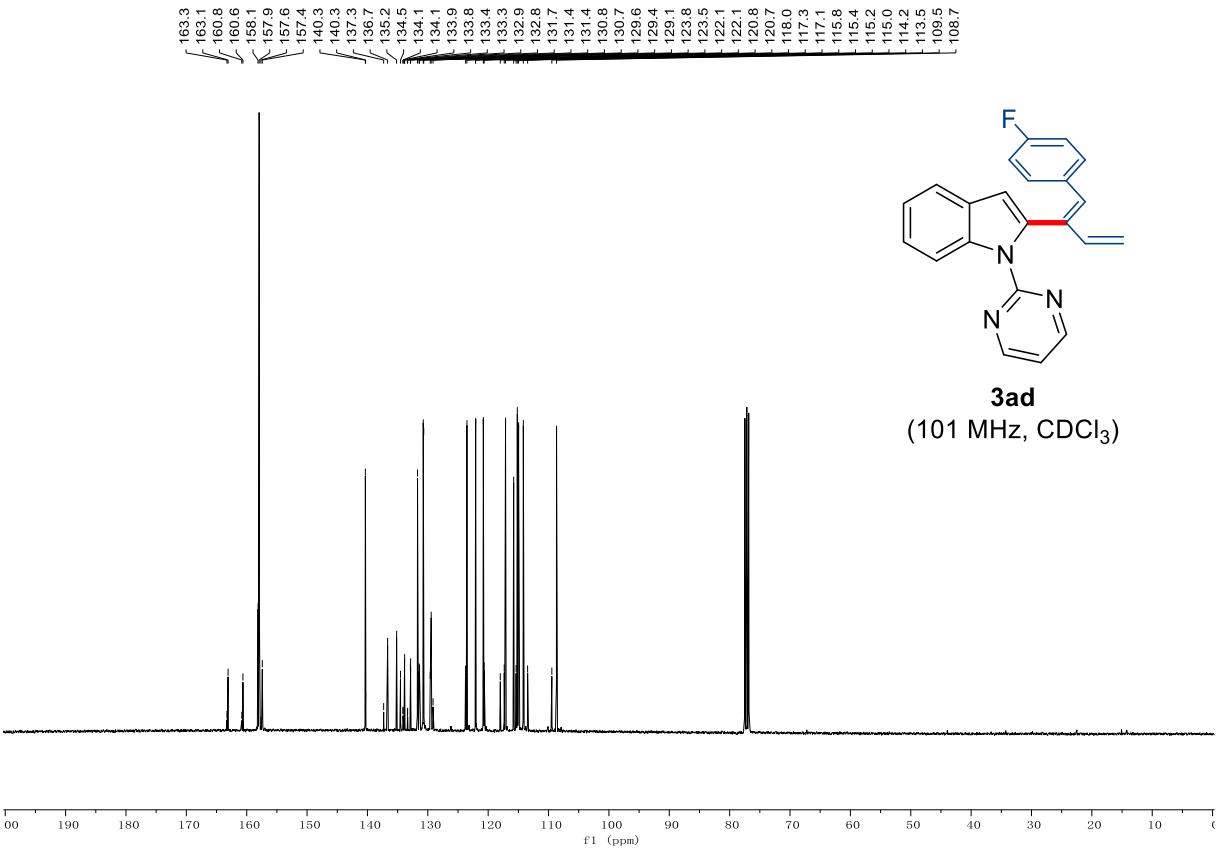
3ac
(400 MHz, $CDCl_3$)



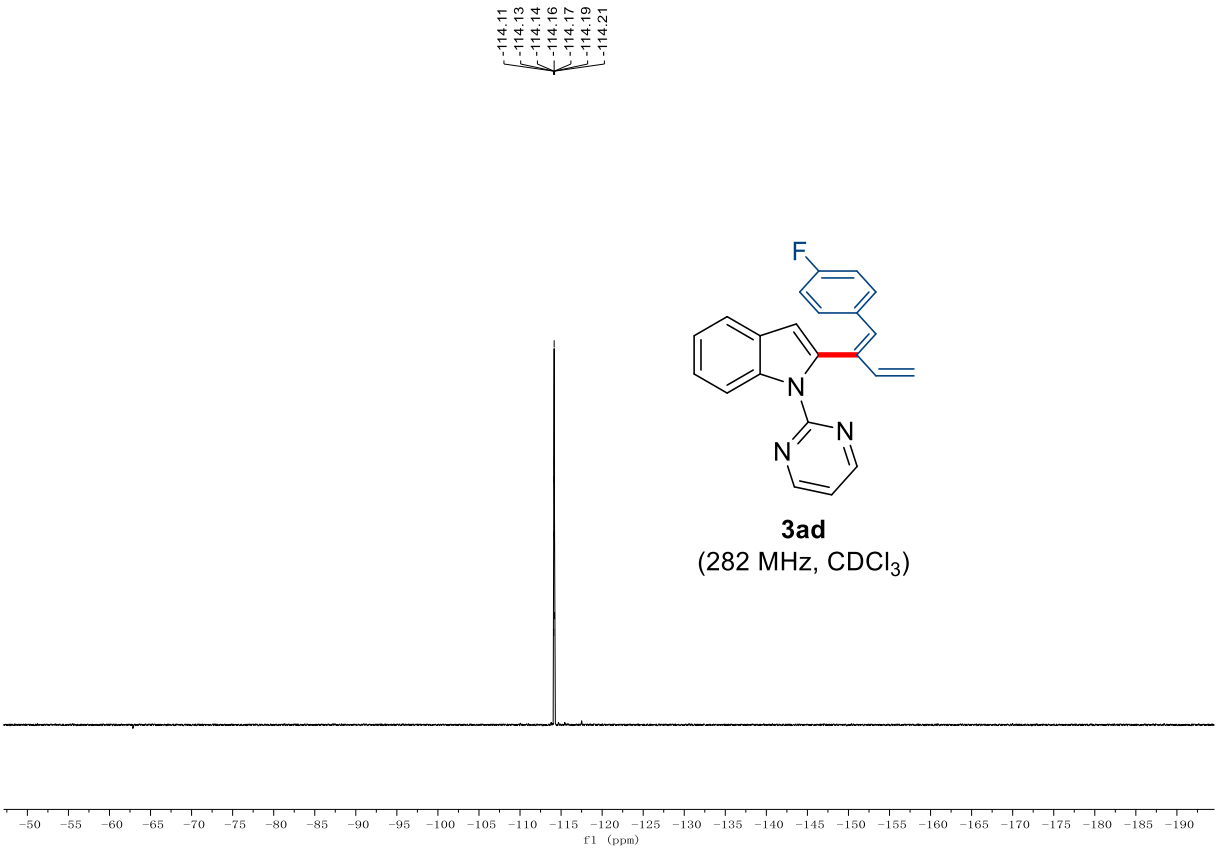
3ac
(101 MHz, $CDCl_3$)

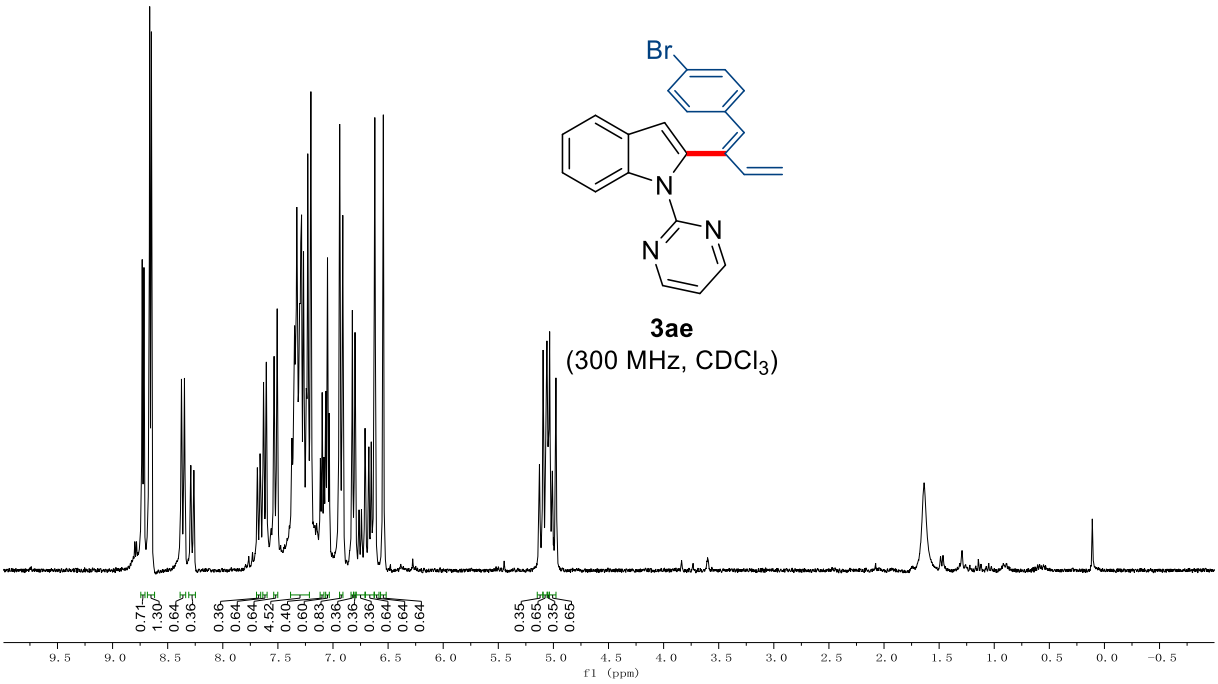


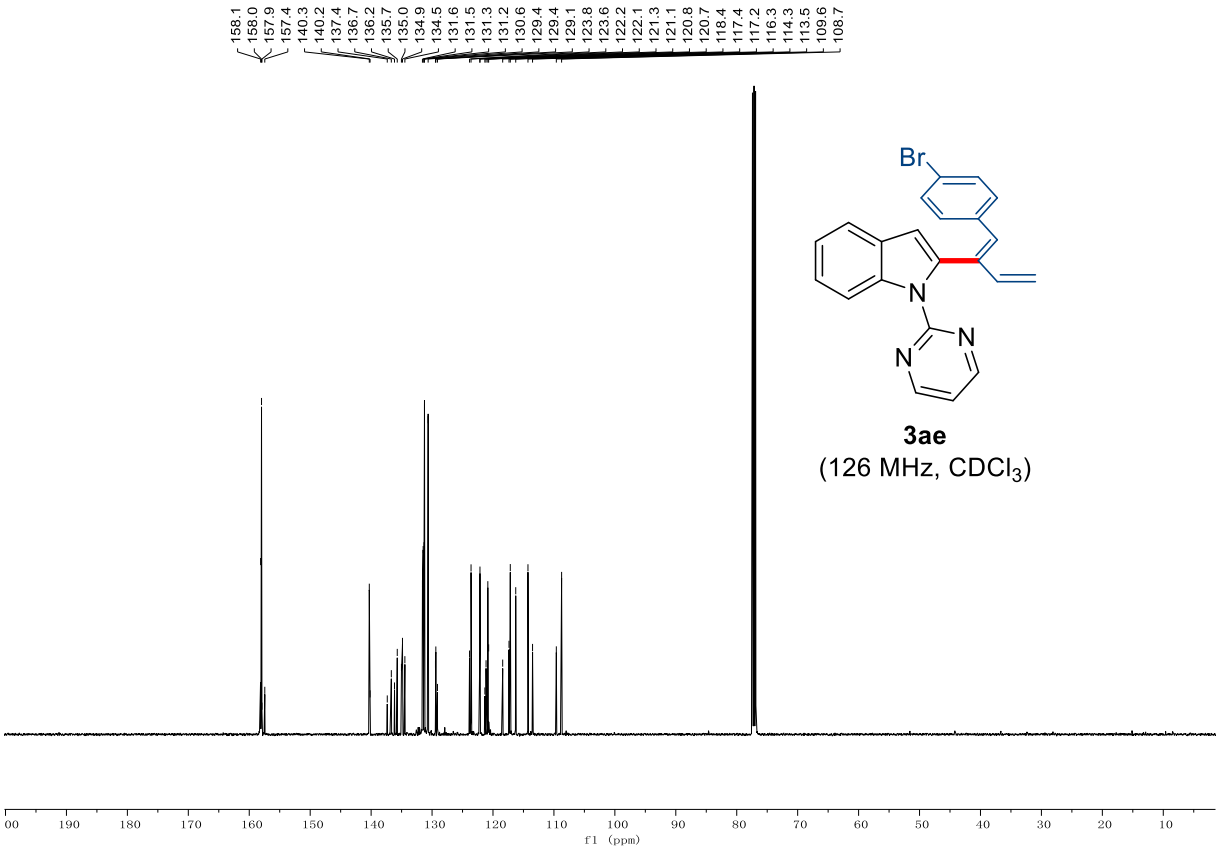
3ad
(300 MHz, $CDCl_3$)



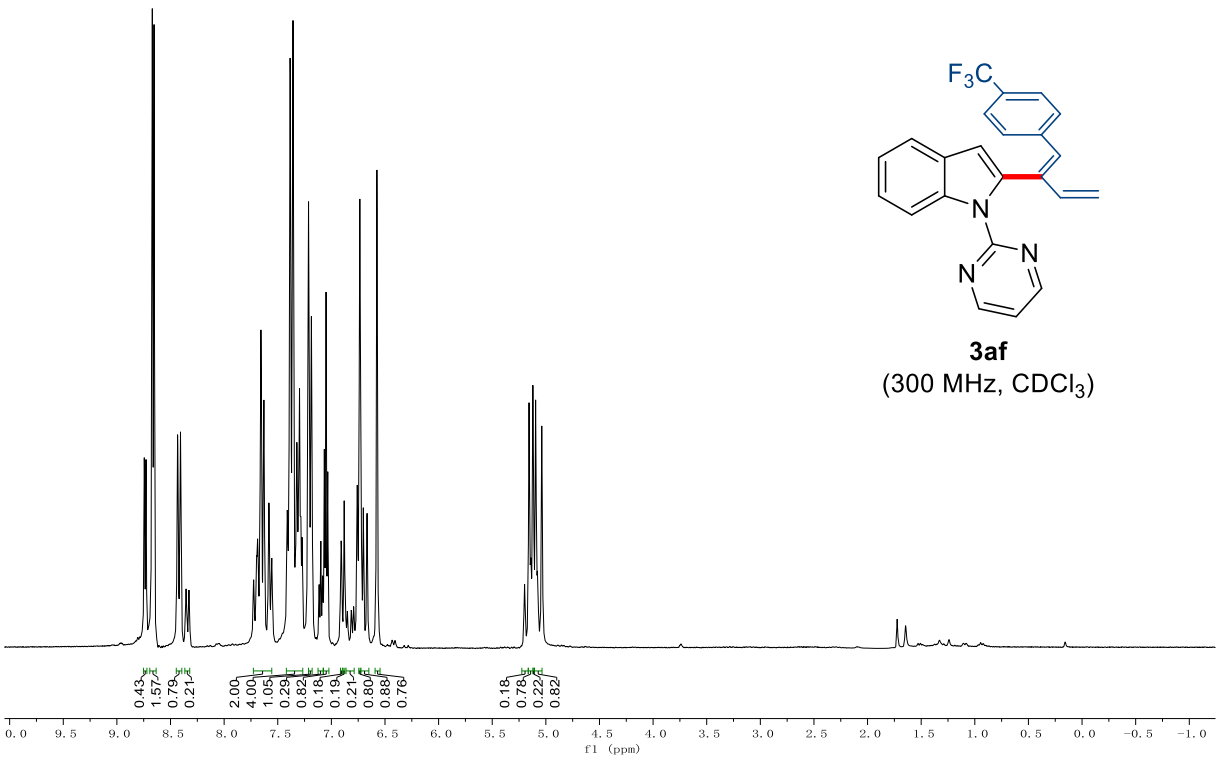
3ad
(101 MHz, $CDCl_3$)


-114.11
-114.13
-114.14
-114.16
-114.17
-114.19
-114.21
F
N
N
N
3ad
(282 MHz, CDCl3)
f1 (ppm)

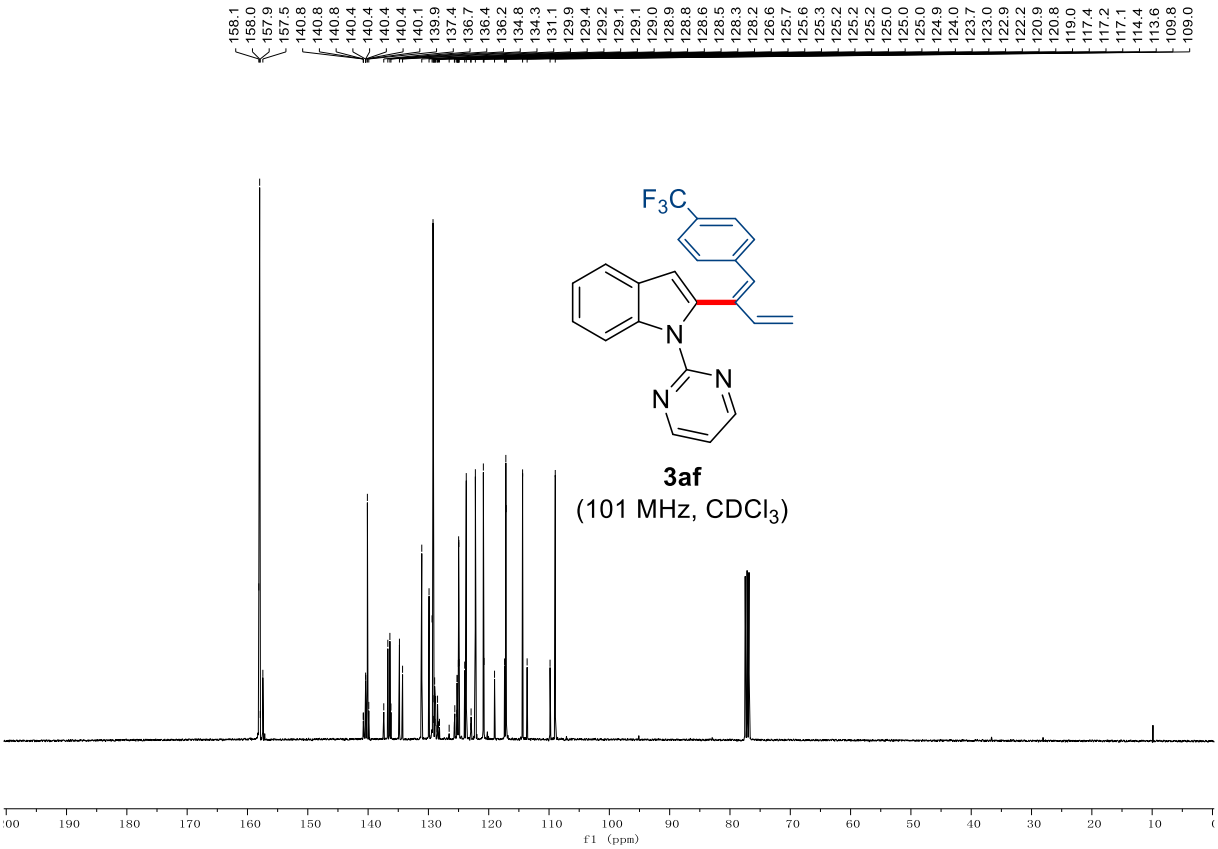

Br
N
N
N
3ae
(300 MHz, CDCl3)
0.71
1.30
0.64
0.36
0.36
0.64
0.64
4.52
0.40
0.60
0.83
0.36
0.36
0.36
0.64
0.64
0.64
0.35
0.65
0.35
0.65
f1 (ppm)

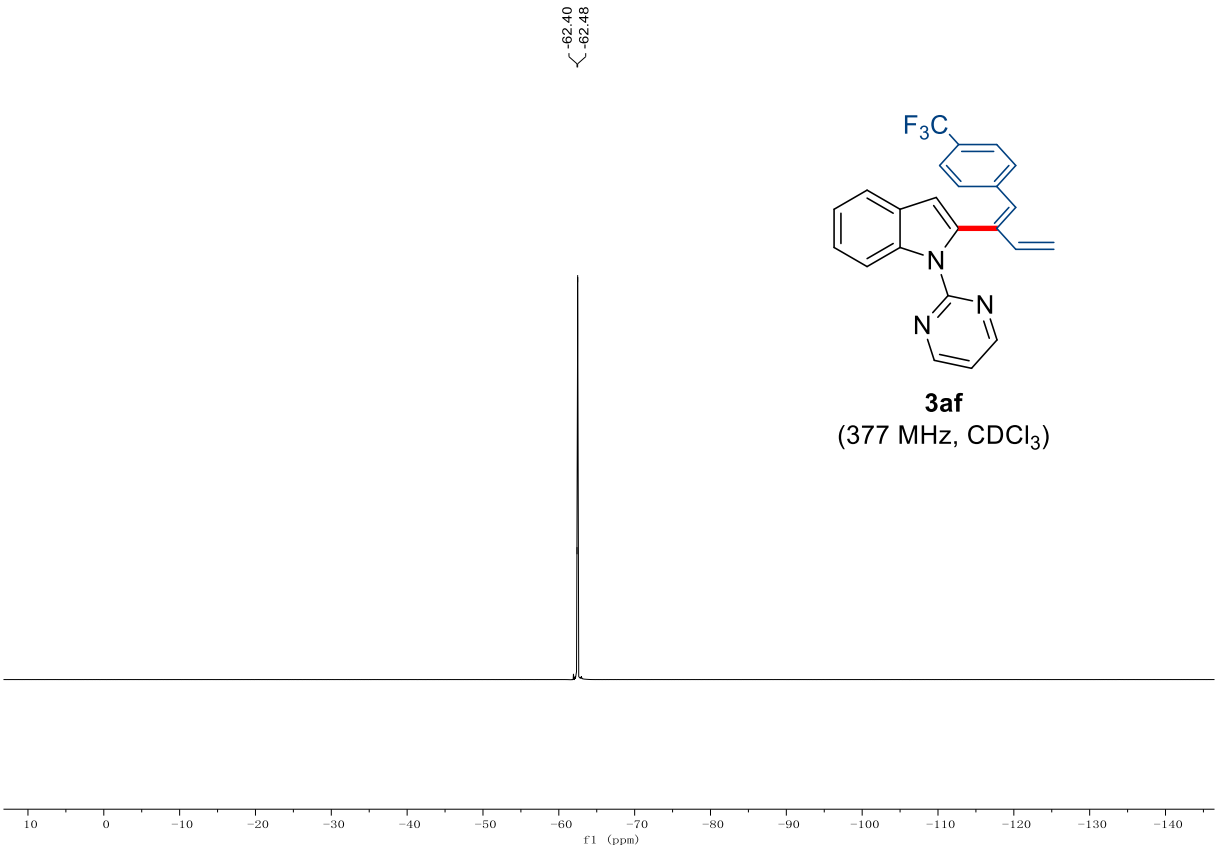


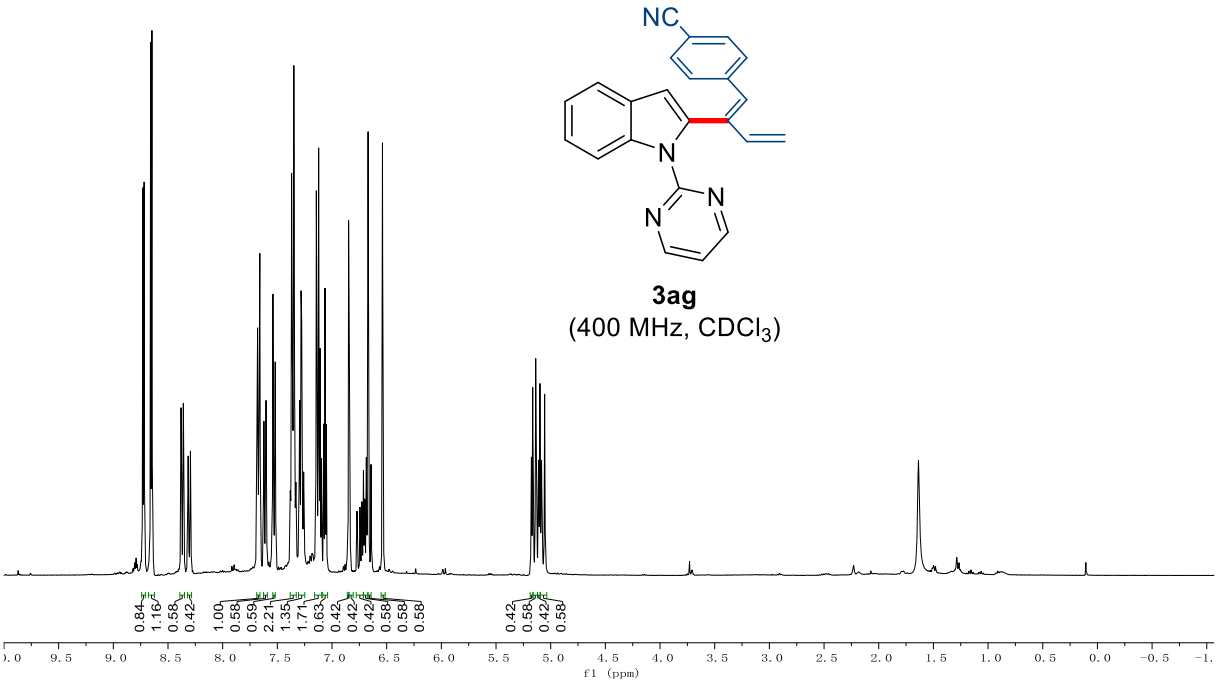
3ae
(126 MHz, $CDCl_3$)



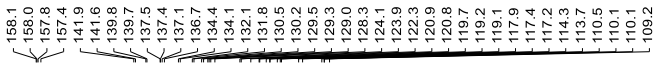
3af
(300 MHz, $CDCl_3$)

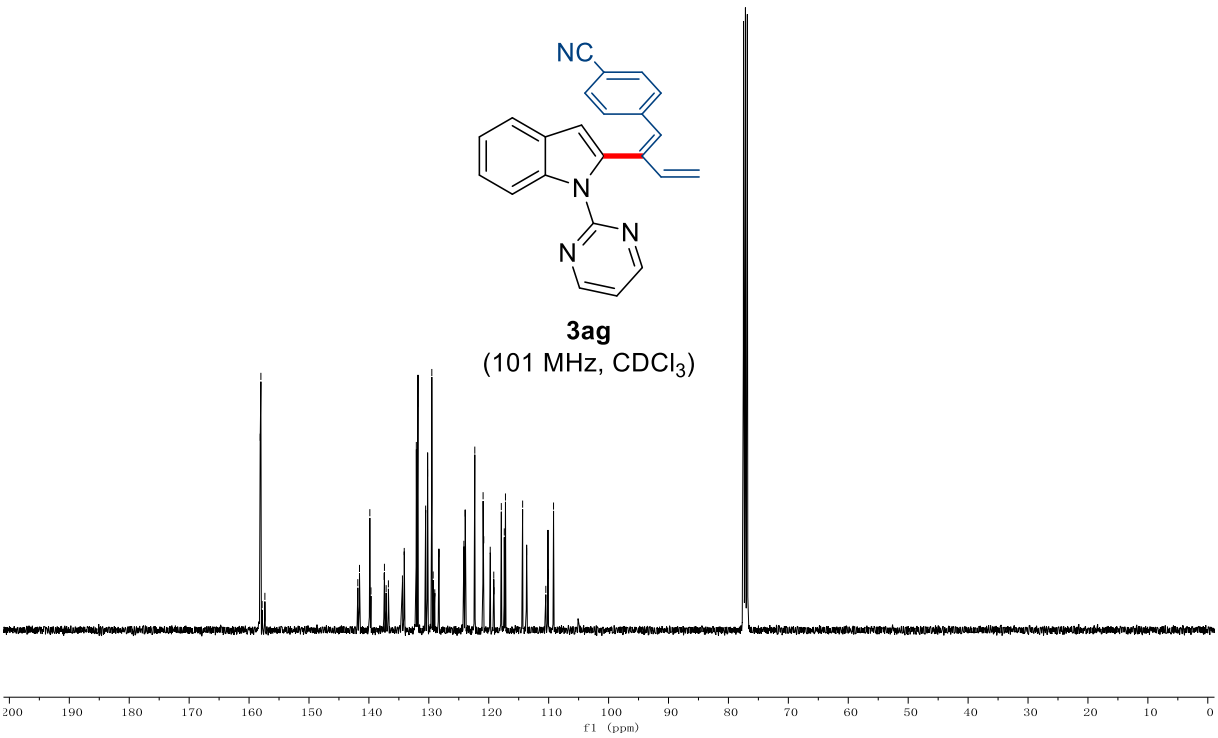

158.1
158.0
157.9
157.5
140.8
140.8
140.8
140.4
140.4
140.4
140.4
140.4
140.1
139.9
137.4
136.7
136.4
136.2
134.8
134.3
131.1
129.9
129.4
129.2
129.1
129.1
129.0
128.9
128.8
128.6
128.5
128.3
128.2
126.6
125.7
125.6
125.3
125.2
125.2
125.2
125.0
125.0
125.0
125.0
124.9
124.0
123.7
123.0
122.9
122.2
120.9
120.8
119.0
117.4
117.2
117.1
114.4
113.6
109.8
109.0
F3C
N
N
N
3af
(101 MHz, CDCl3)
f1 (ppm)


-62.40
-62.48
F3C
N
N
N
3af
(377 MHz, CDCl3)
f1 (ppm)

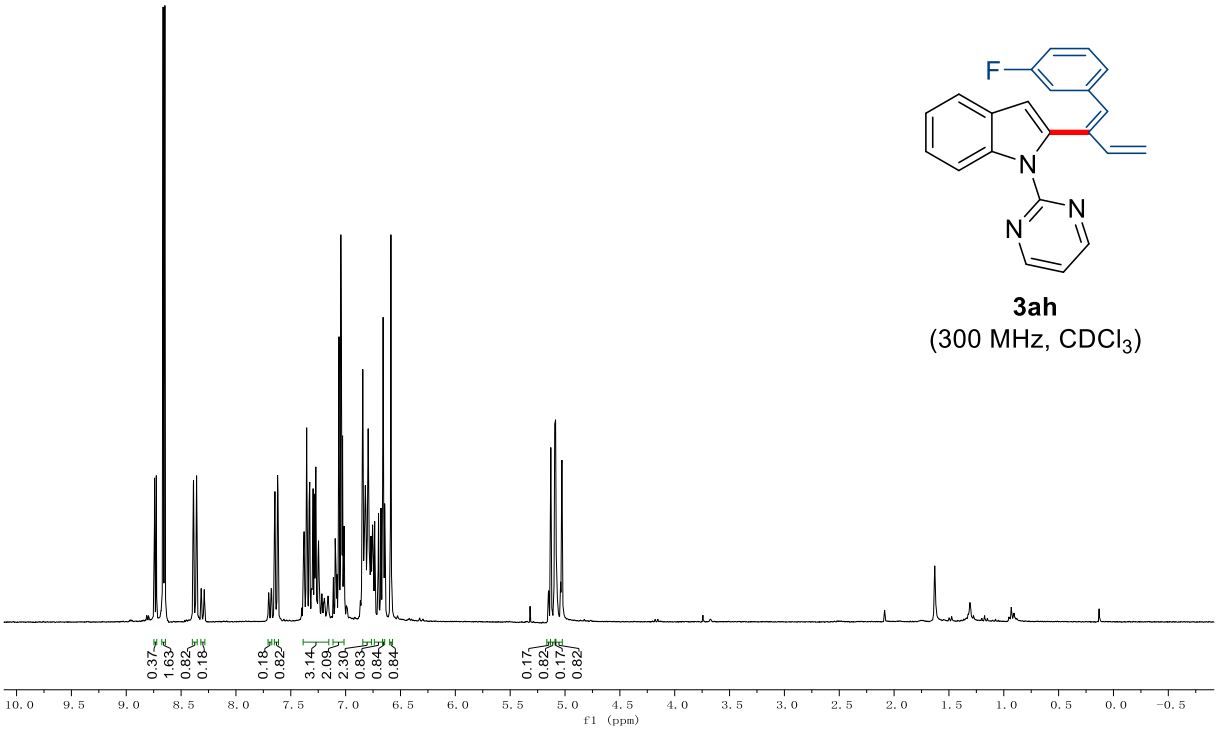


3ag
(400 MHz, $CDCl_3$)

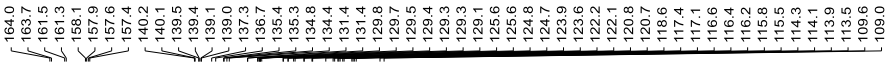


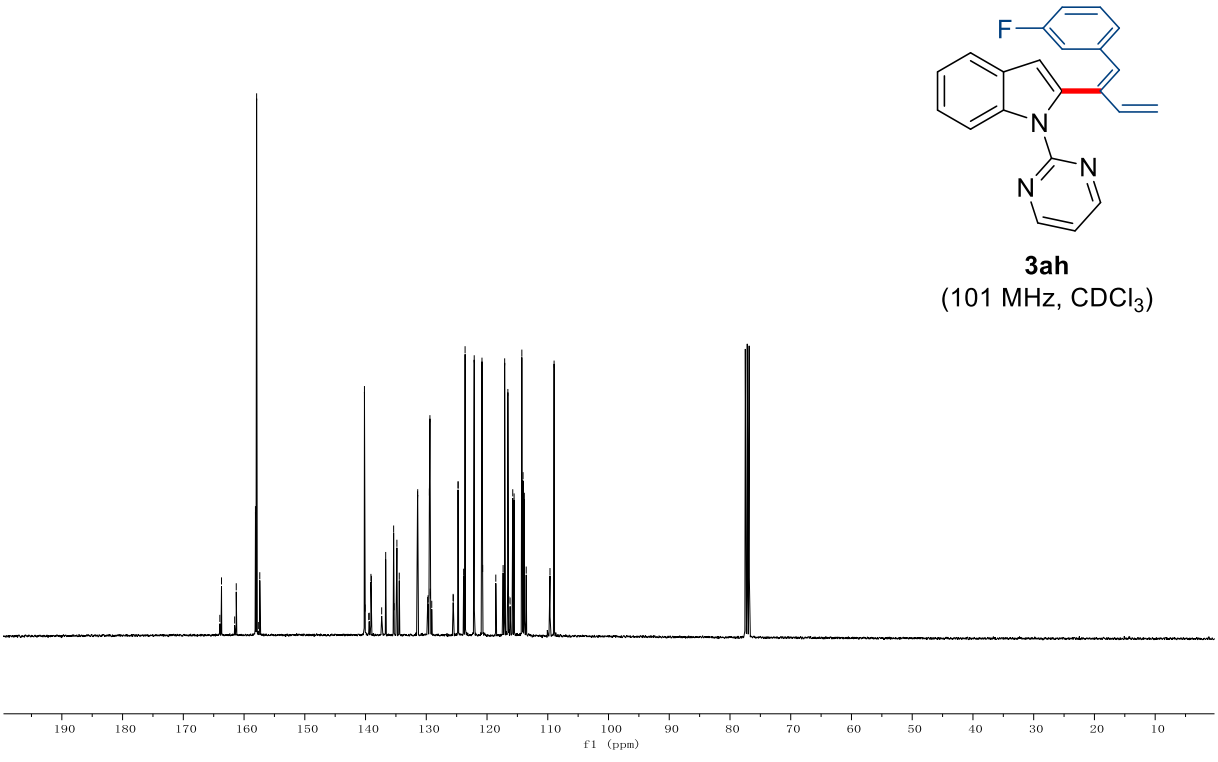


3ag
(101 MHz, $CDCl_3$)

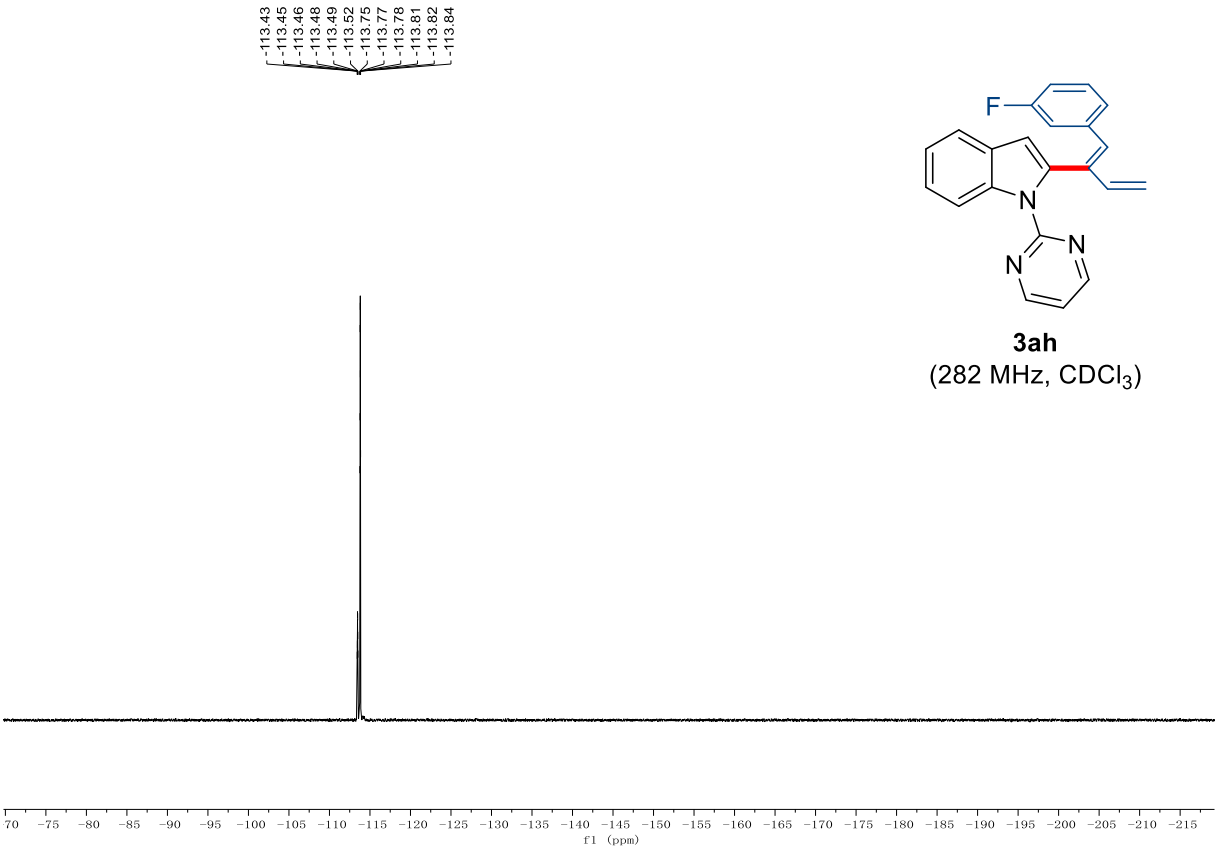


3ah
(300 MHz, $CDCl_3$)

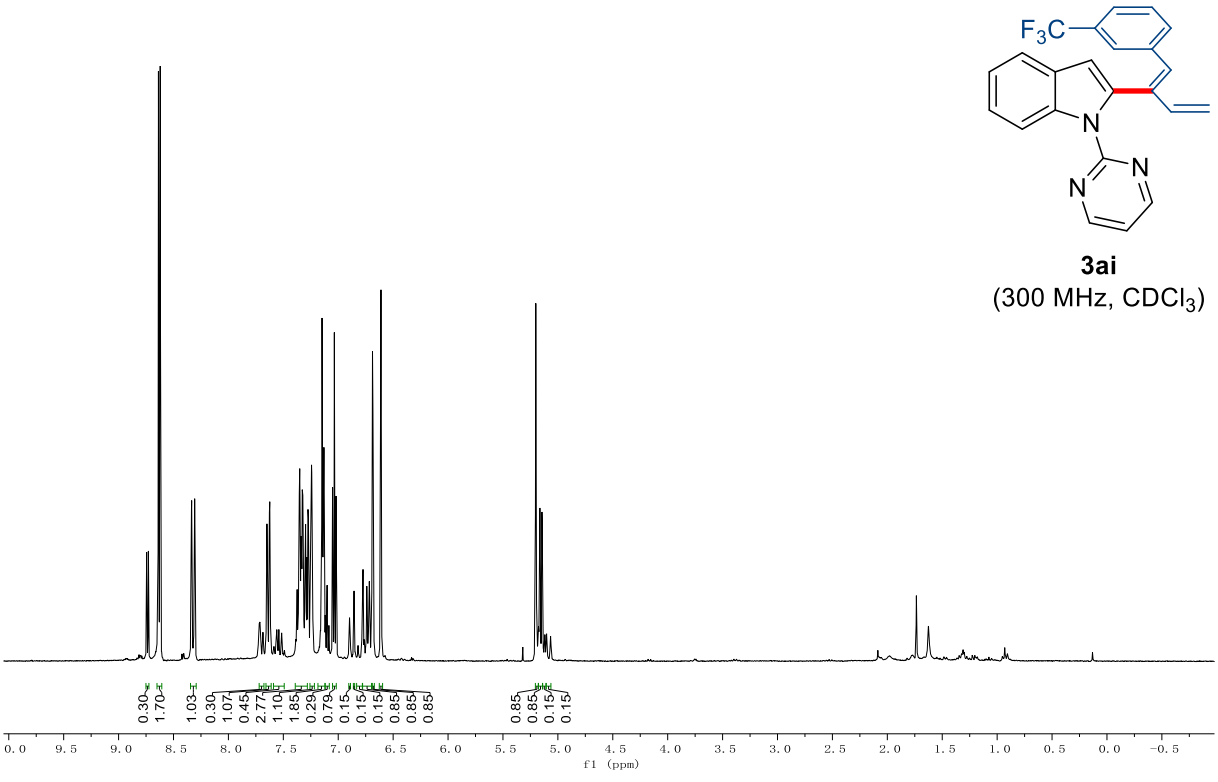




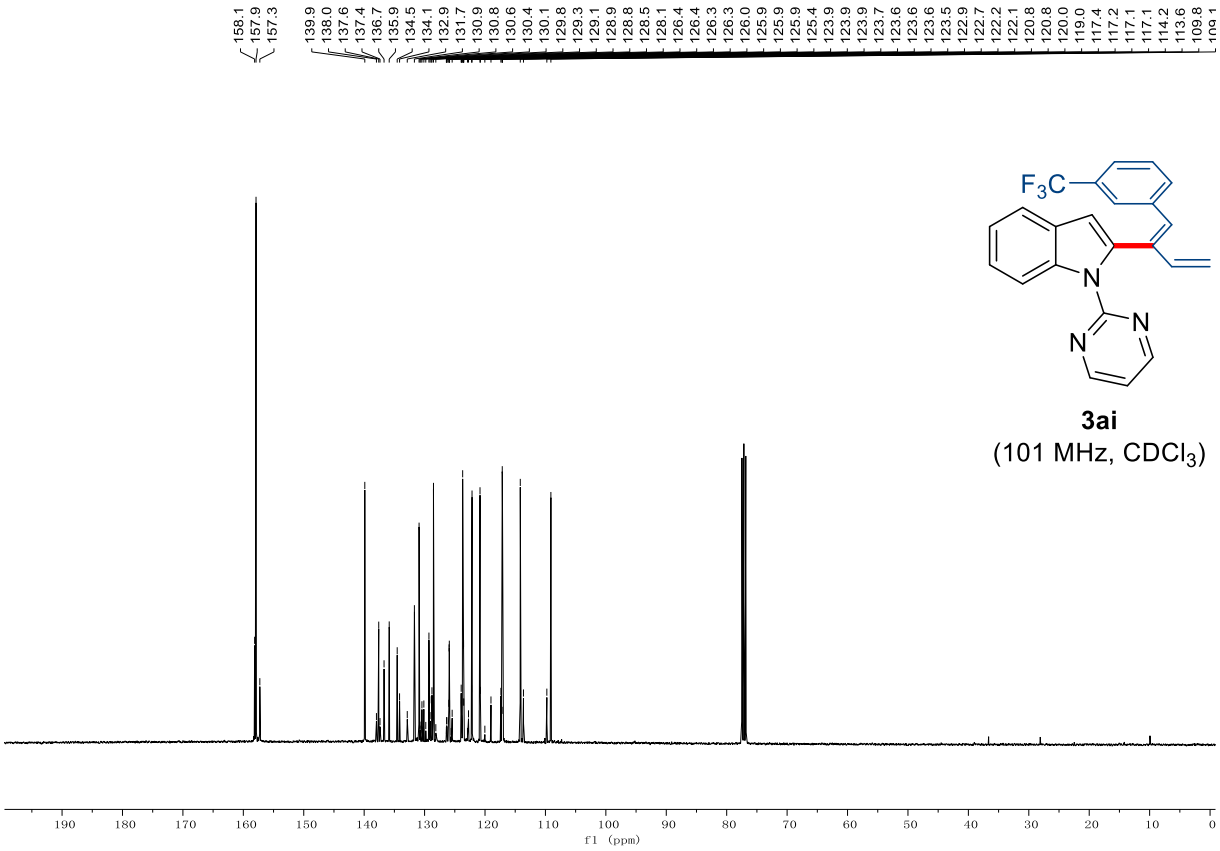
3ah
(101 MHz, $CDCl_3$)



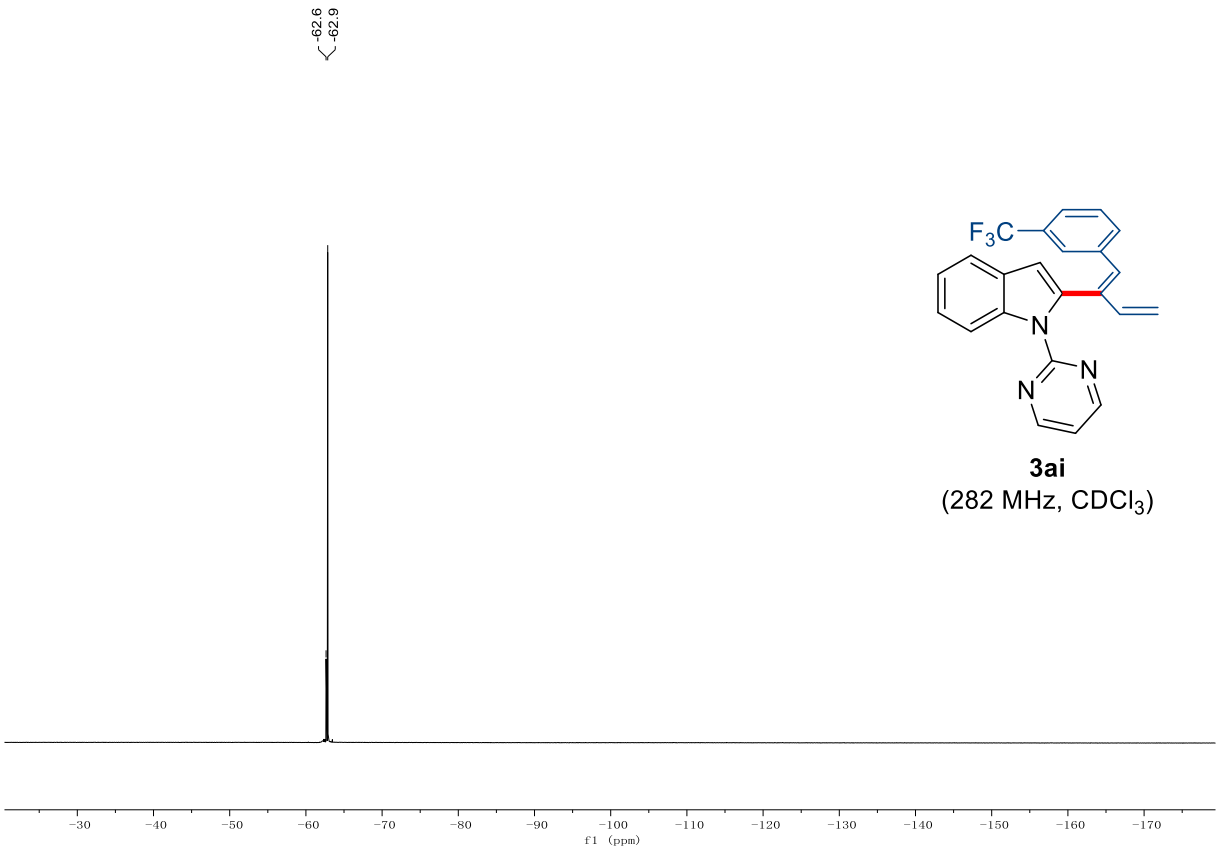
3ah
(282 MHz, $CDCl_3$)



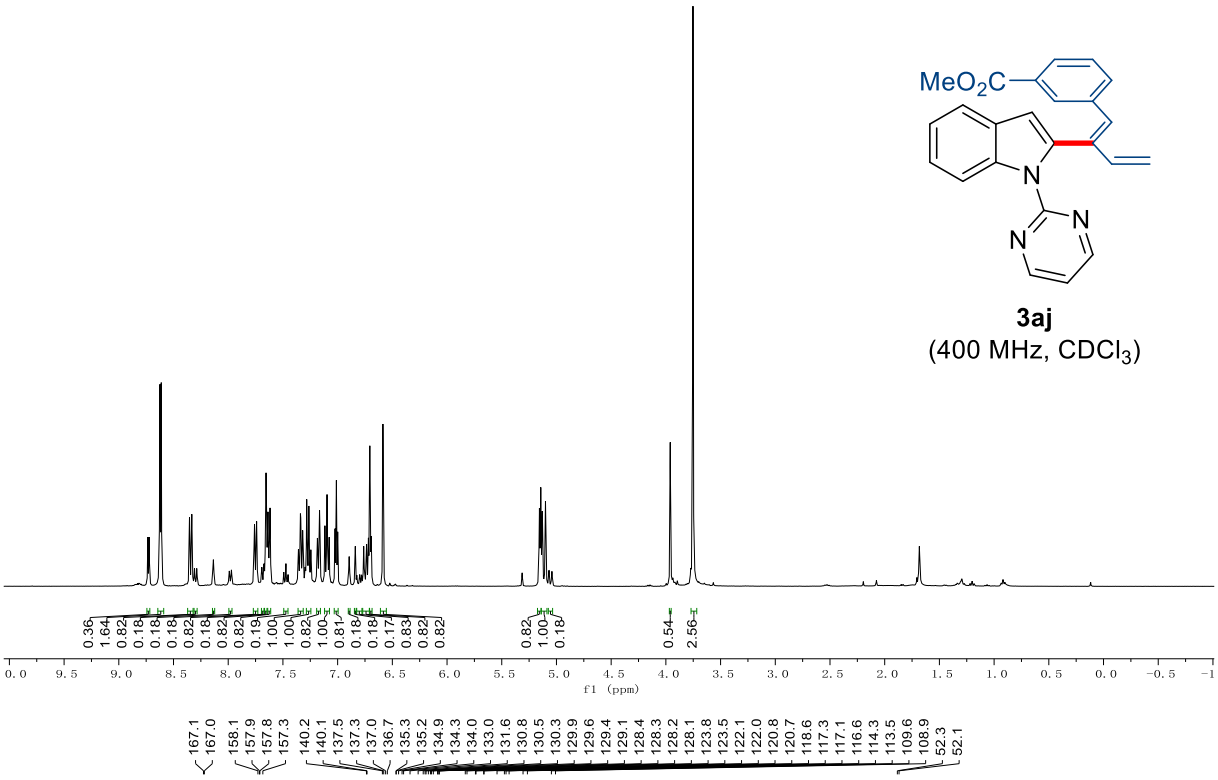
3ai
(300 MHz, $CDCl_3$)



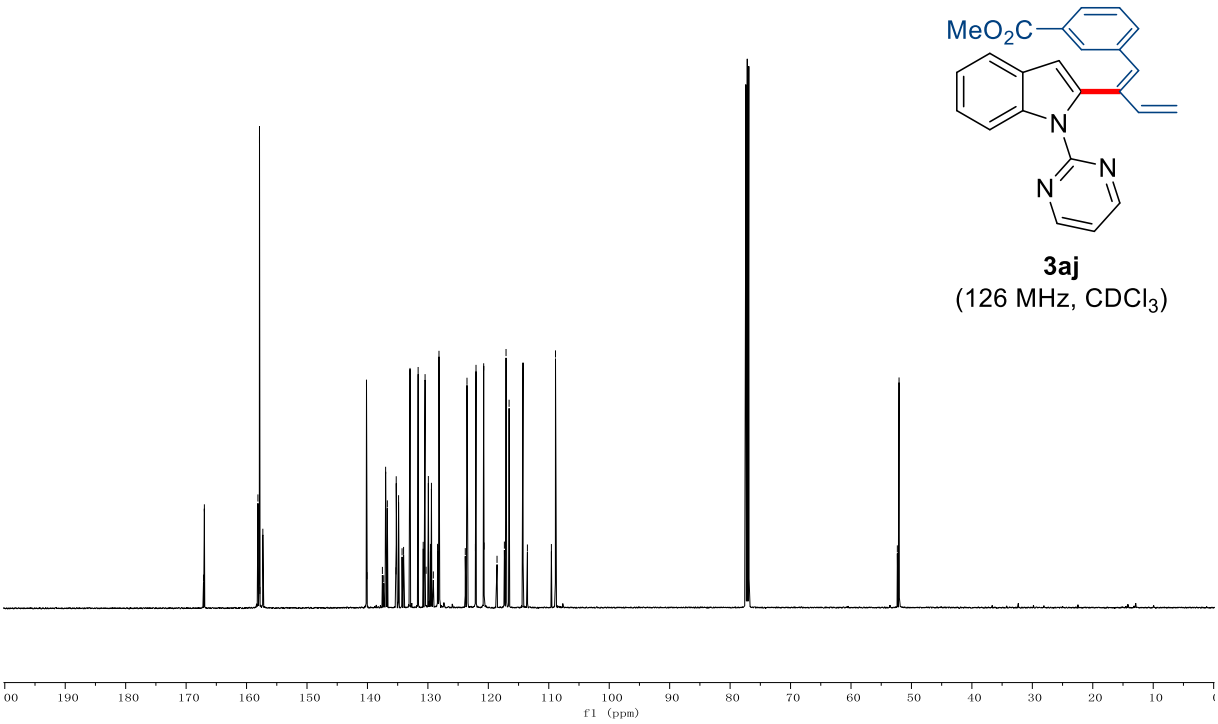
3ai
(101 MHz, $CDCl_3$)



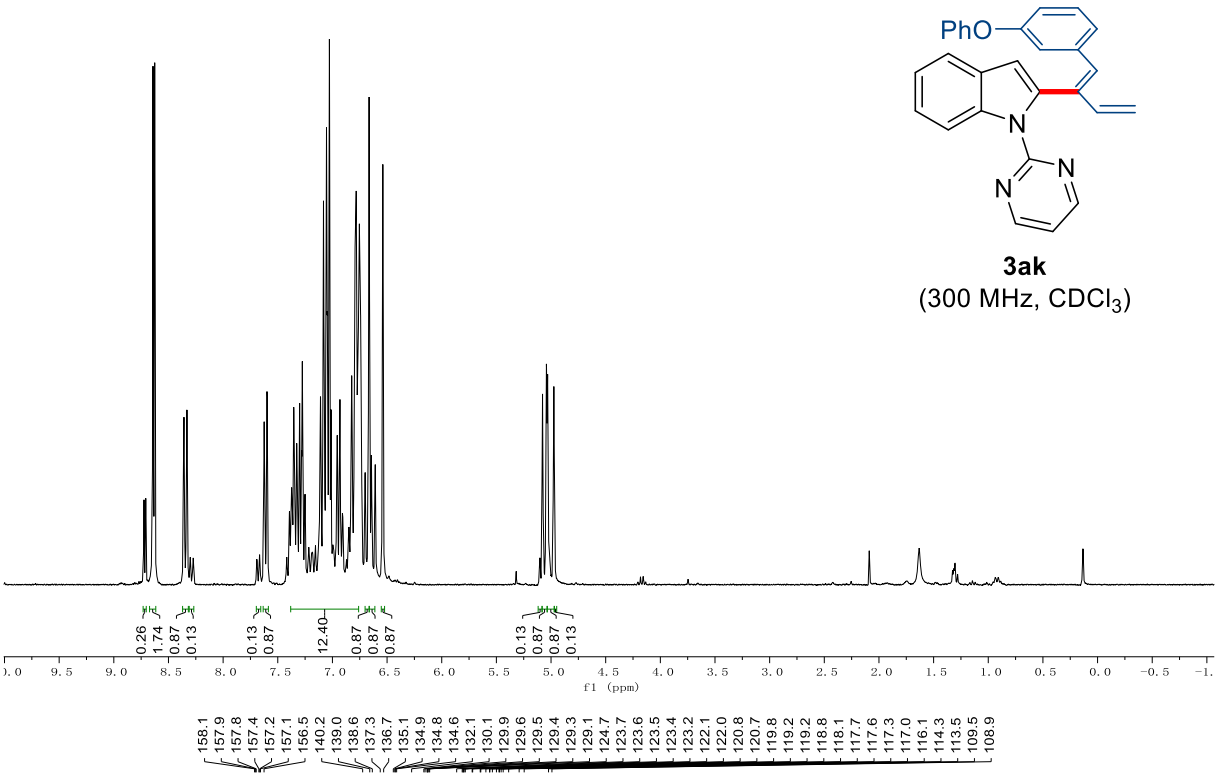
3ai
(282 MHz, $CDCl_3$)



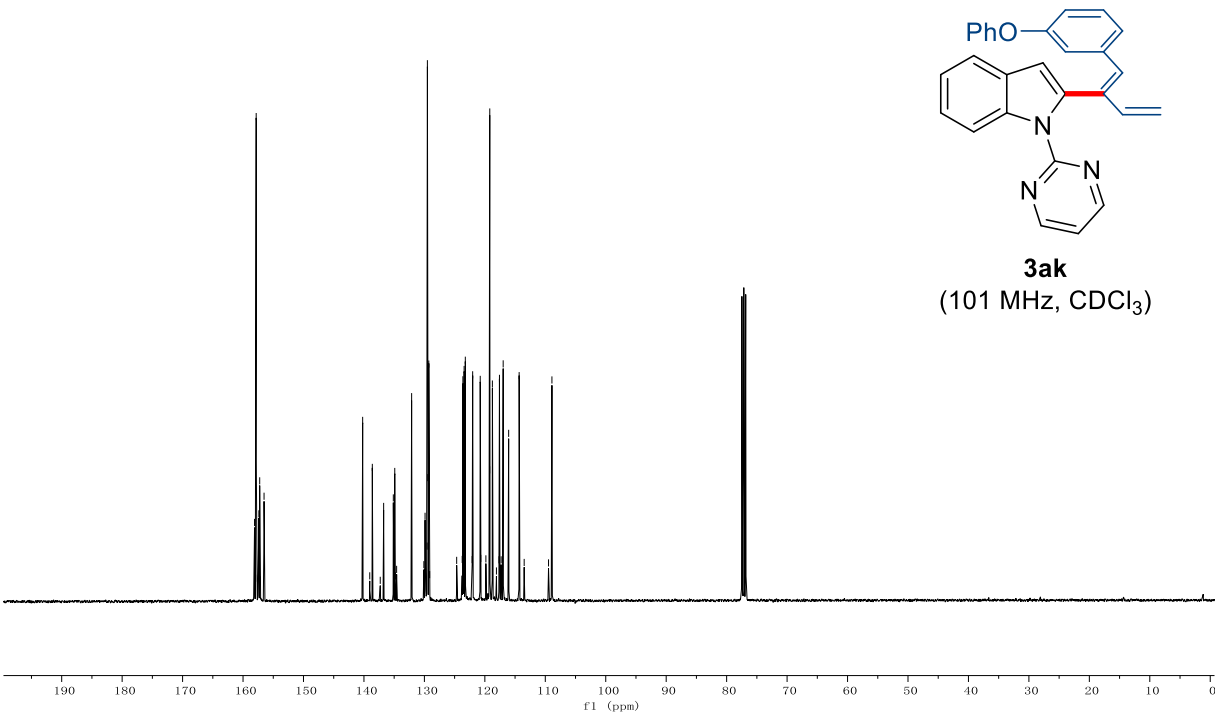
3aj
(400 MHz, $CDCl_3$)



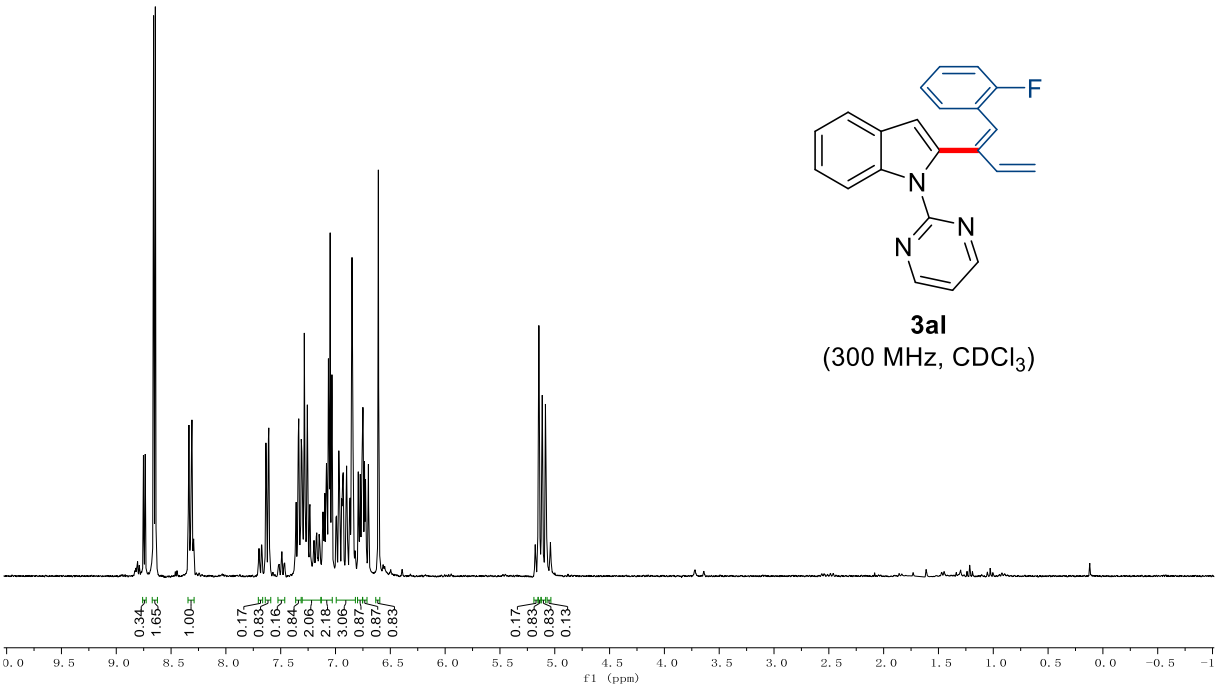
3aj
(126 MHz, $CDCl_3$)



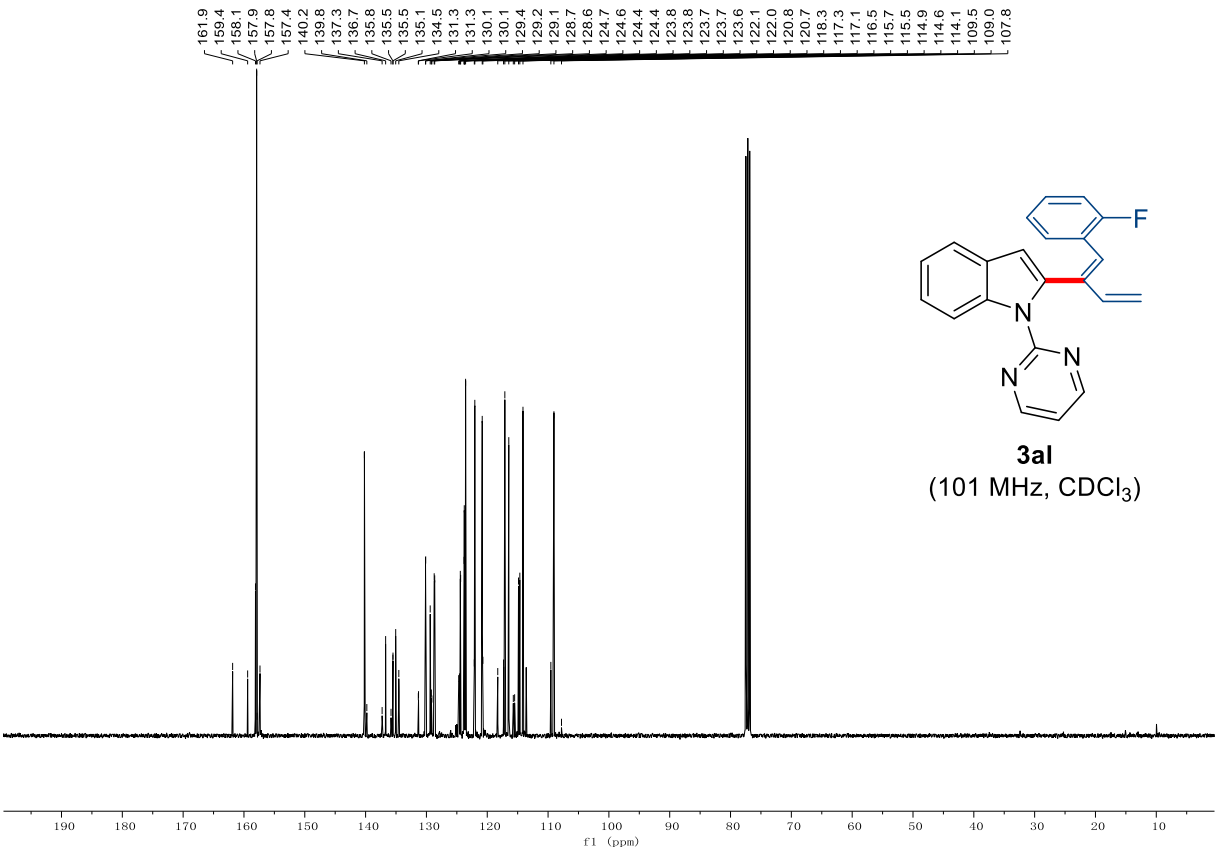
3ak
(300 MHz, $CDCl_3$)



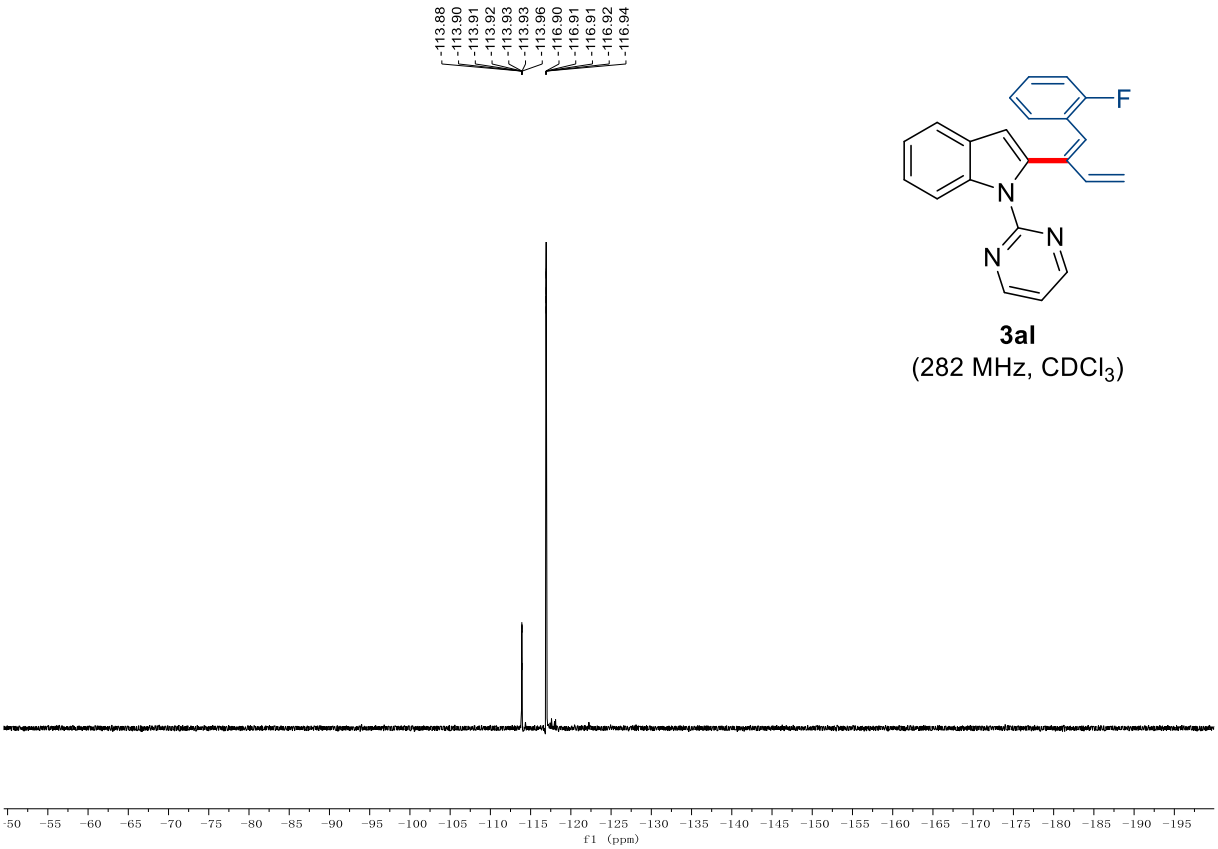
3ak
(101 MHz, $CDCl_3$)



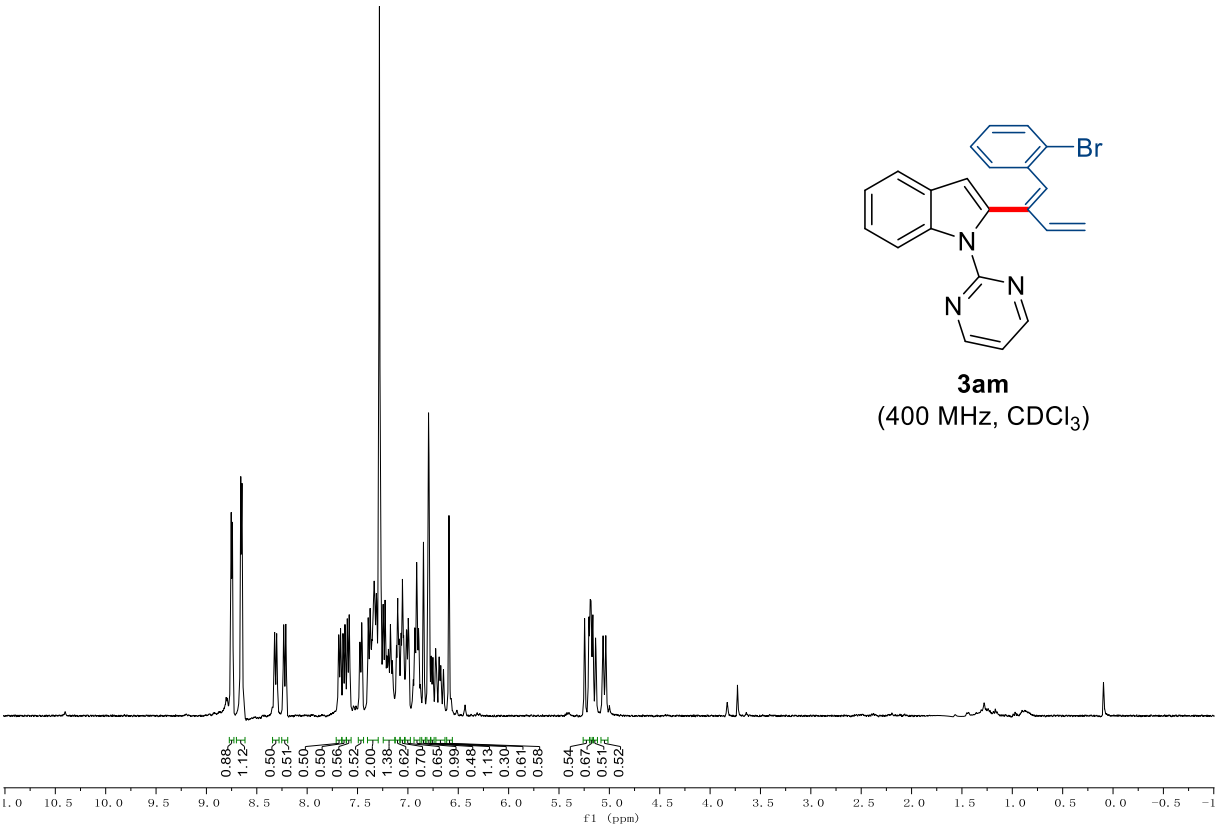
3al
(300 MHz, $CDCl_3$)



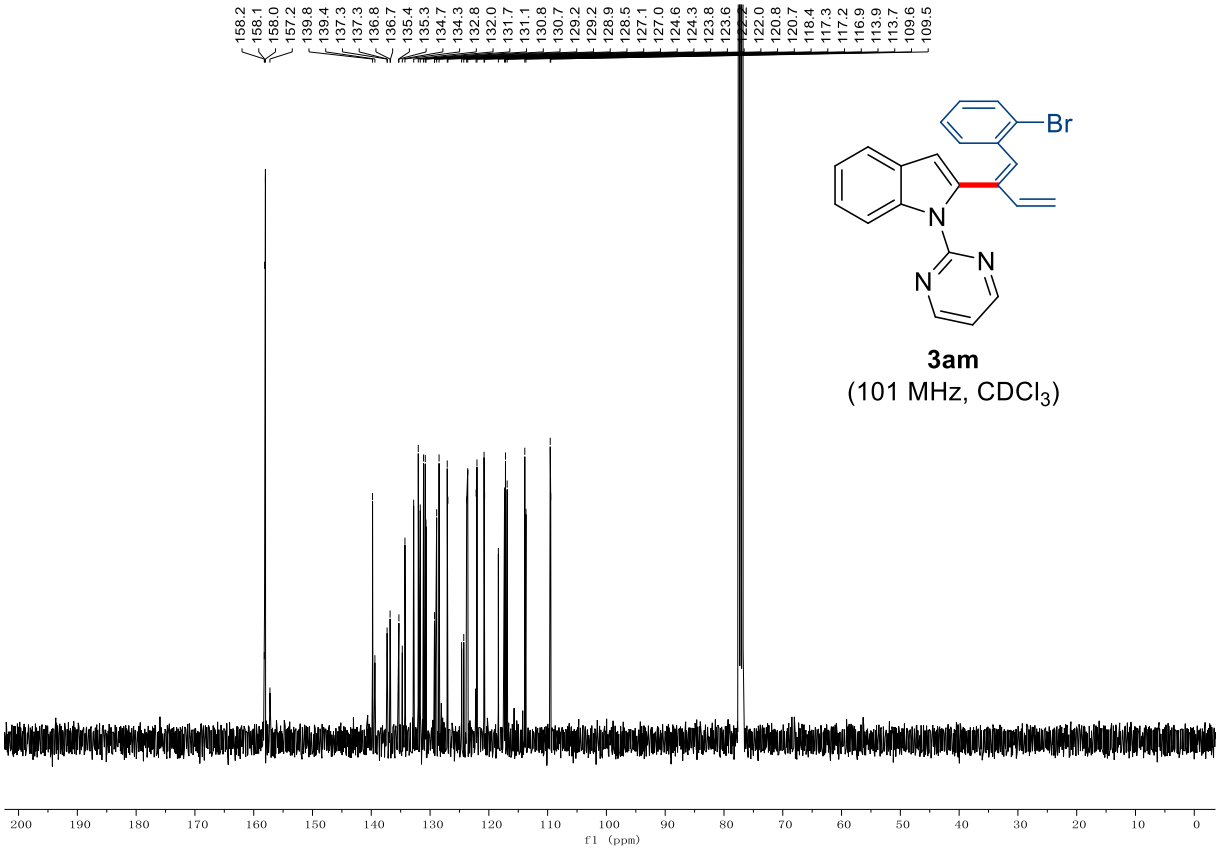
3al
(101 MHz, $CDCl_3$)



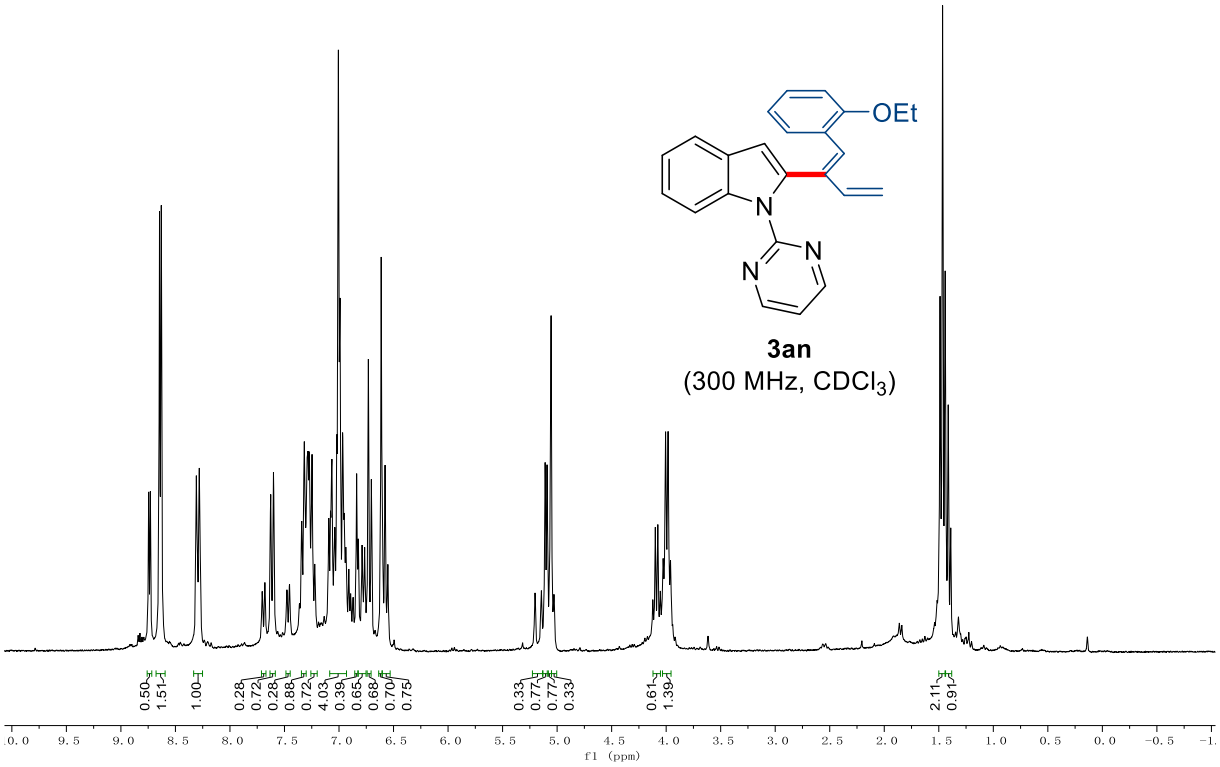
3al
(282 MHz, $CDCl_3$)



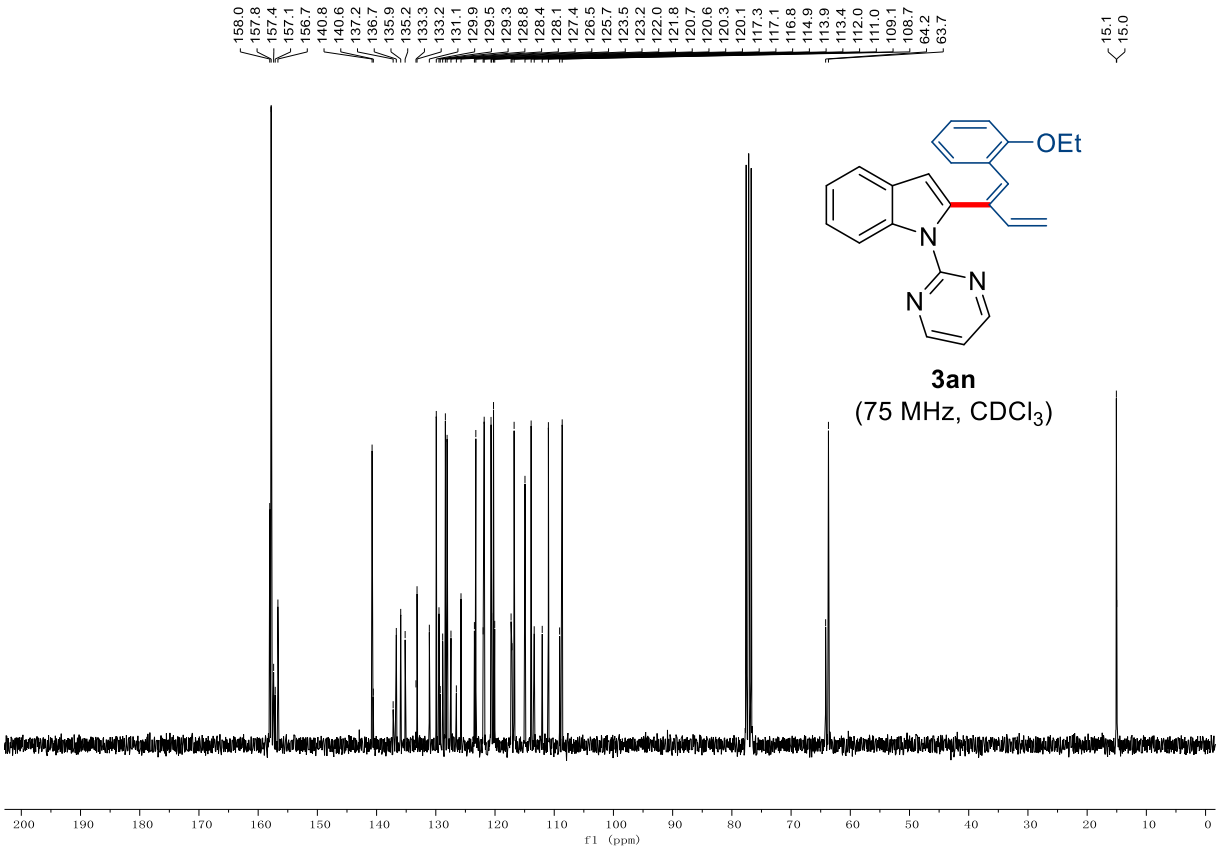
3am
(400 MHz, $CDCl_3$)

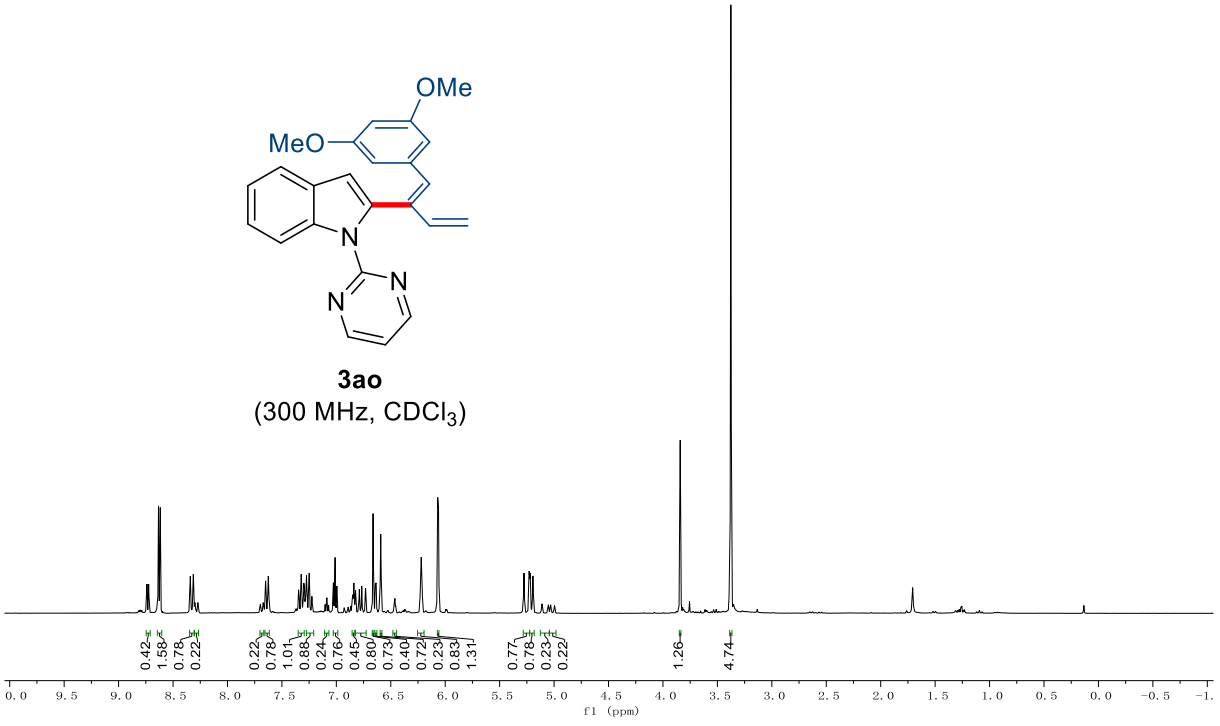


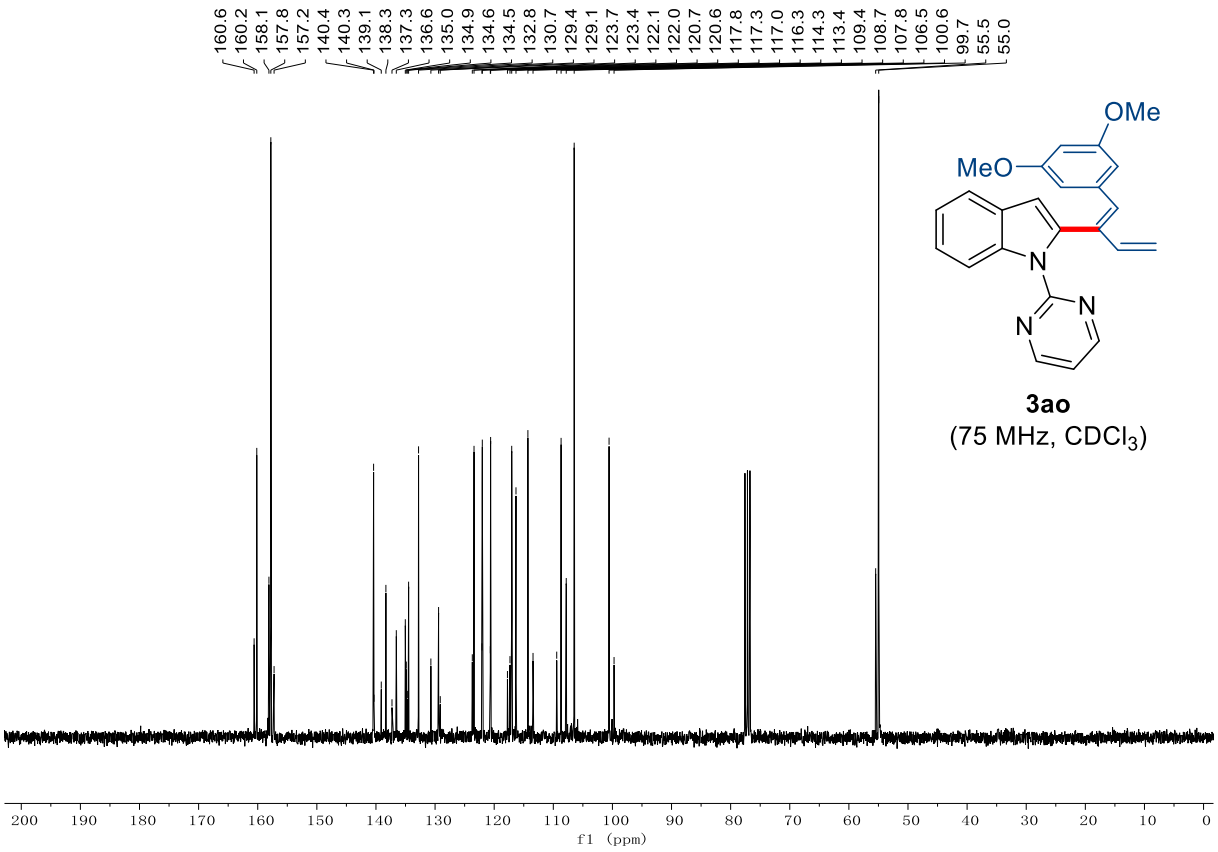
3am
(101 MHz, $CDCl_3$)



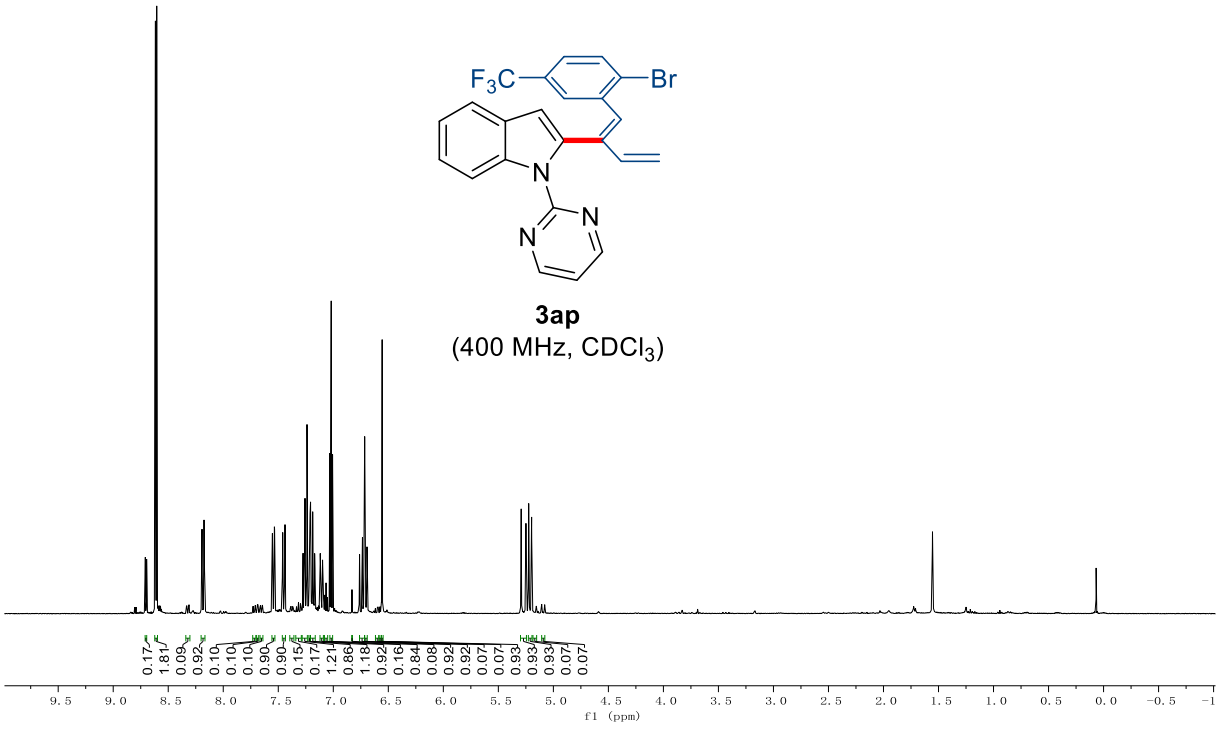
3an
(300 MHz, $CDCl_3$)


158.0
157.8
157.4
157.1
156.7
140.8
140.6
137.2
136.7
135.9
135.2
133.3
133.2
131.1
129.9
129.5
129.3
128.8
128.4
128.1
127.4
126.5
125.7
123.5
123.2
122.0
121.8
120.7
120.6
120.3
120.1
117.3
117.1
116.8
114.9
113.9
113.4
112.0
111.0
109.1
108.7
64.2
63.7
15.1
15.0
OEt
N
N
N
3an
(75 MHz, CDCl3)
f1 (ppm)

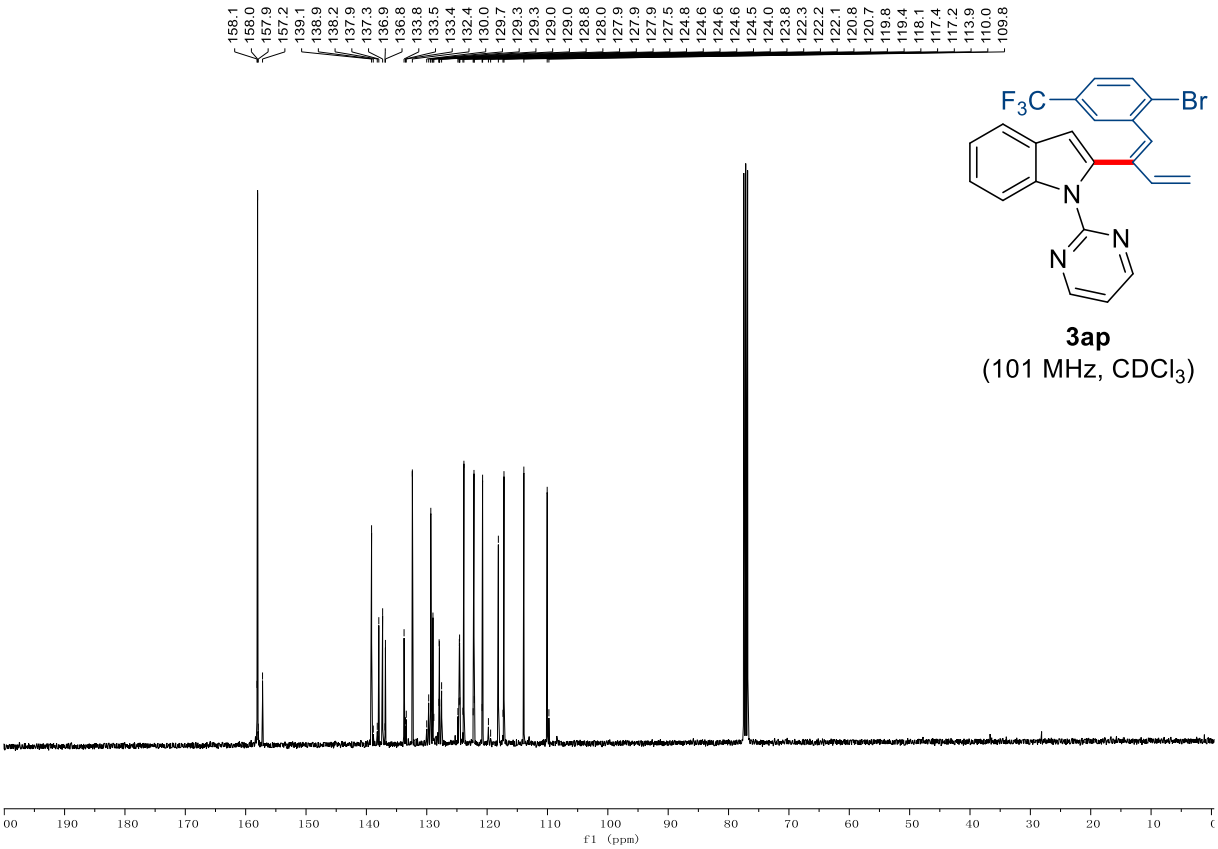

OMe
MeO
N
N
N
3ao
(300 MHz, CDCl3)
0.42
1.58
0.78
0.22
0.22
0.78
1.01
0.88
0.24
0.76
0.45
0.80
0.73
0.40
0.72
0.23
0.83
1.31
0.77
0.78
0.23
0.22
1.26
4.74
f1 (ppm)



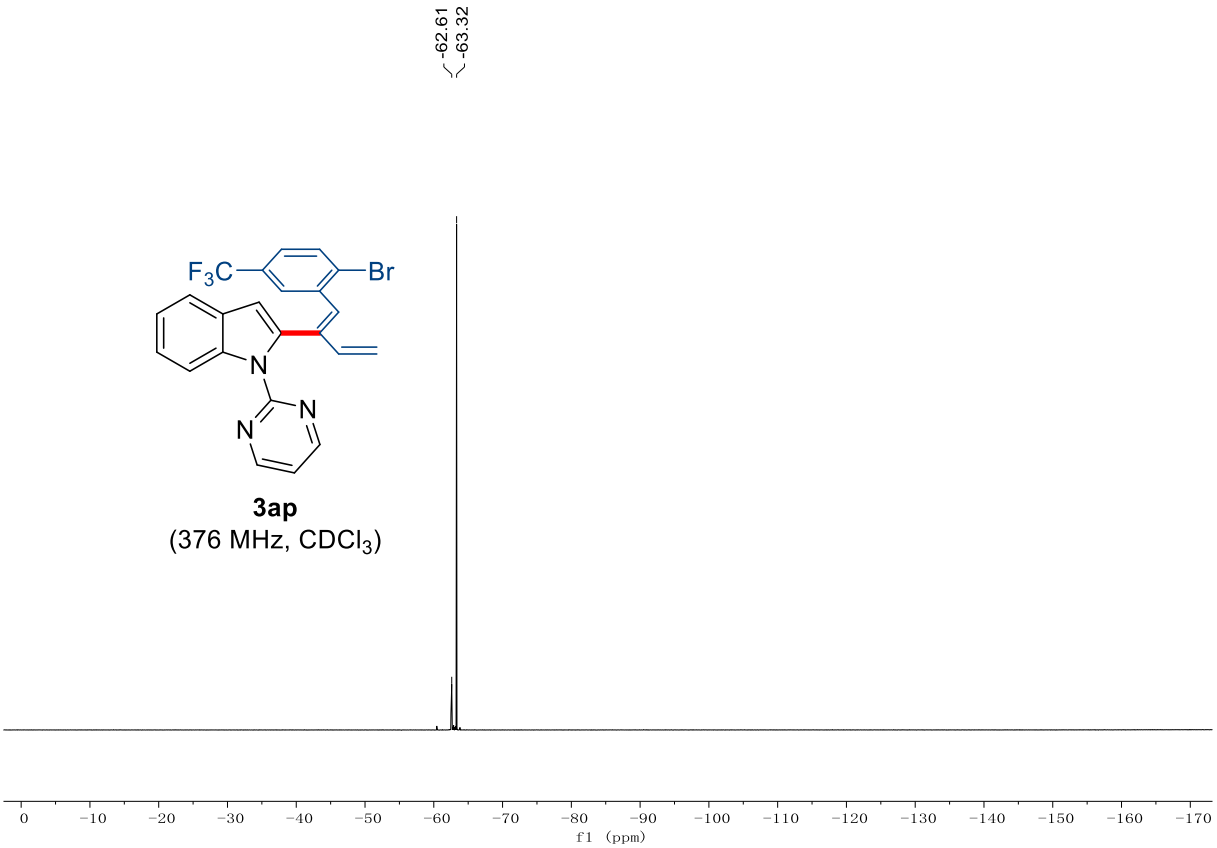
3ao
(75 MHz, $CDCl_3$)



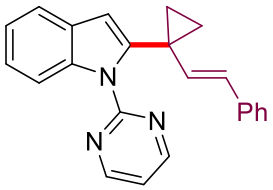
3ap
(400 MHz, $CDCl_3$)



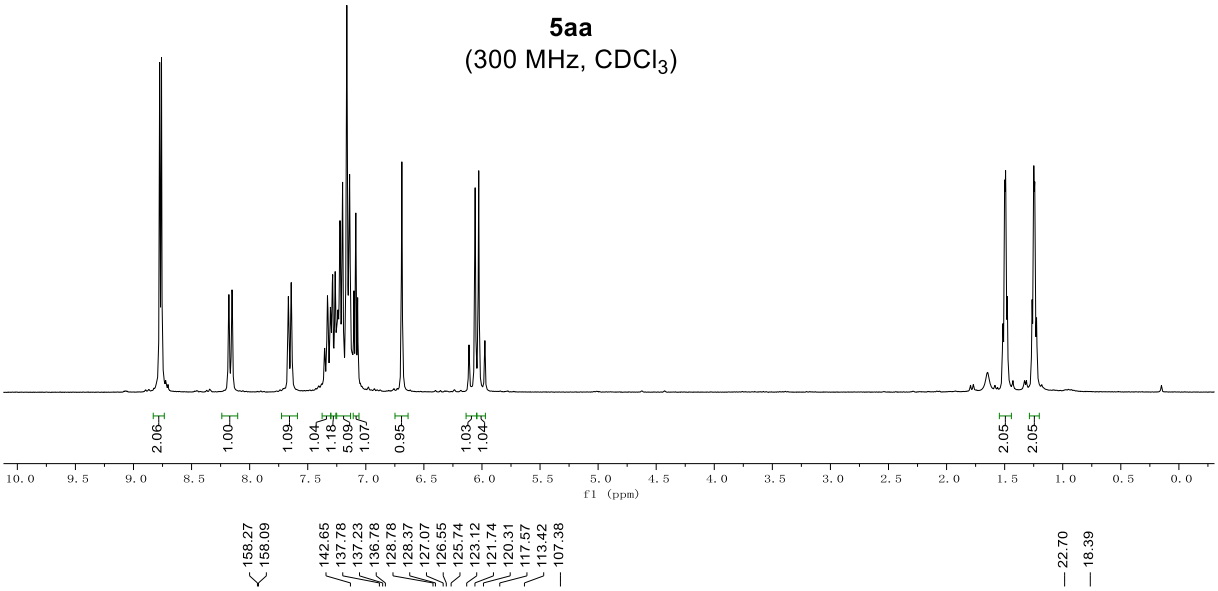
3ap
(101 MHz, $CDCl_3$)



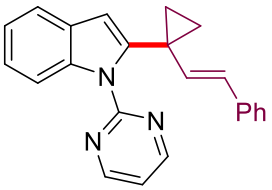
3ap
(376 MHz, $CDCl_3$)



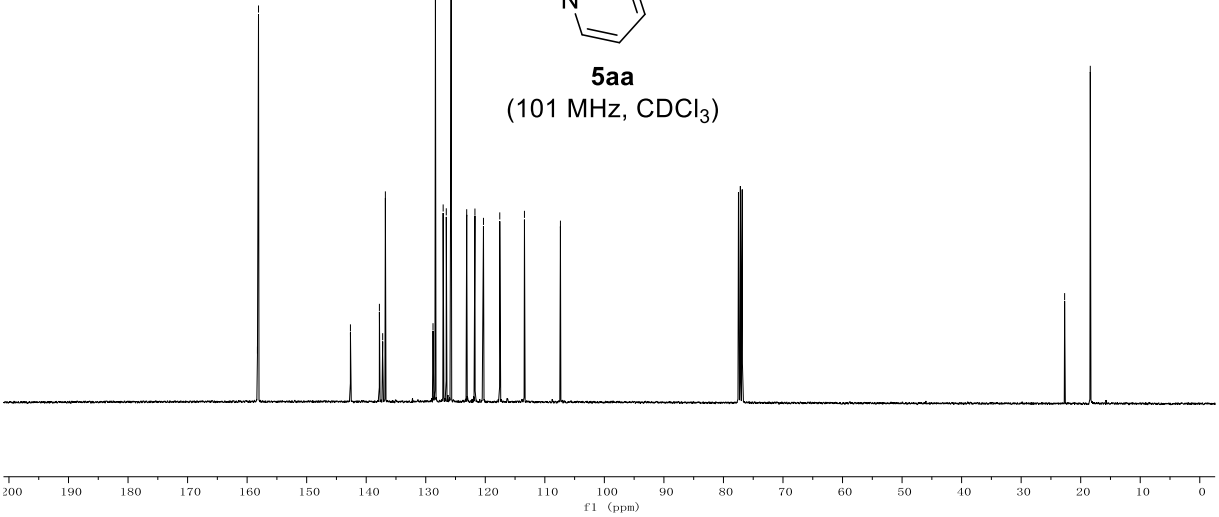
5aa
(300 MHz, $CDCl_3$)

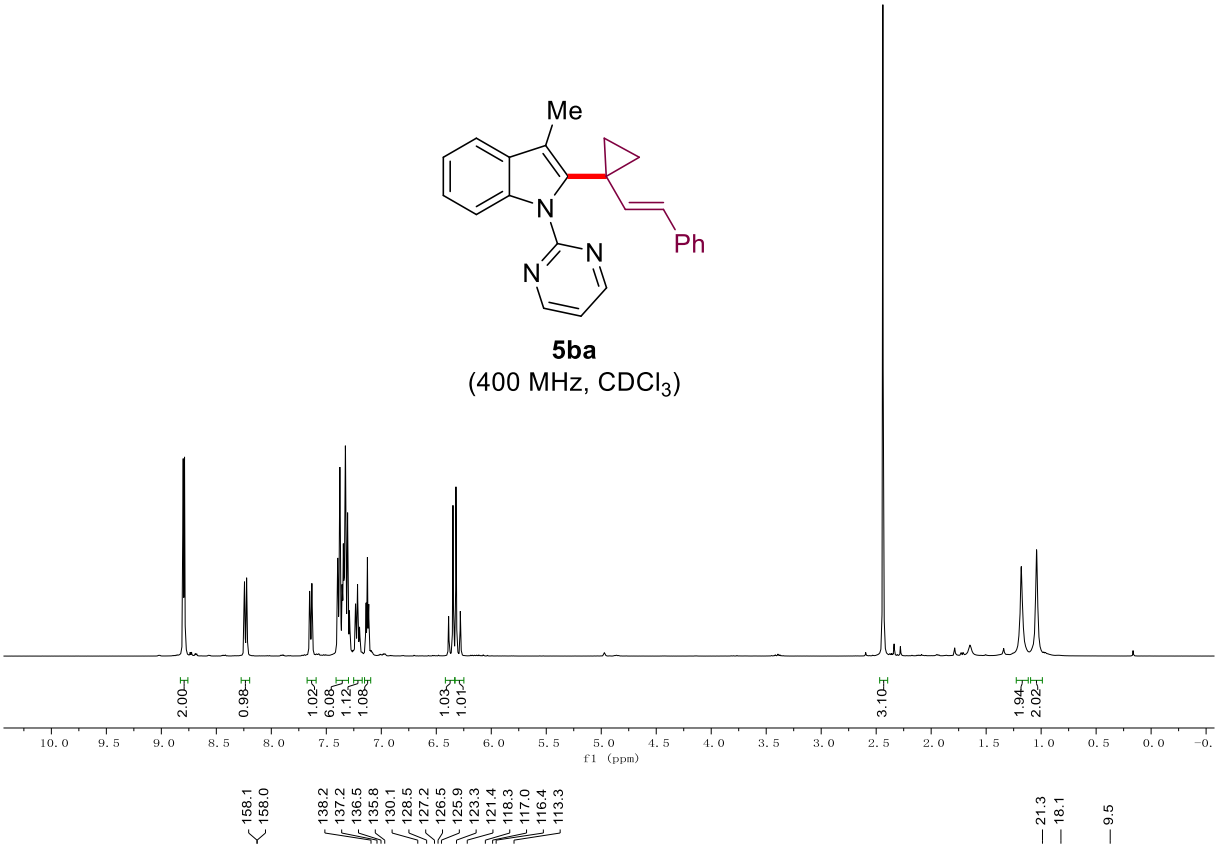


158.27
158.09
142.65
137.78
137.23
136.78
128.78
128.37
127.07
126.55
125.74
123.12
121.74
120.31
117.57
113.42
107.38
22.70
18.39

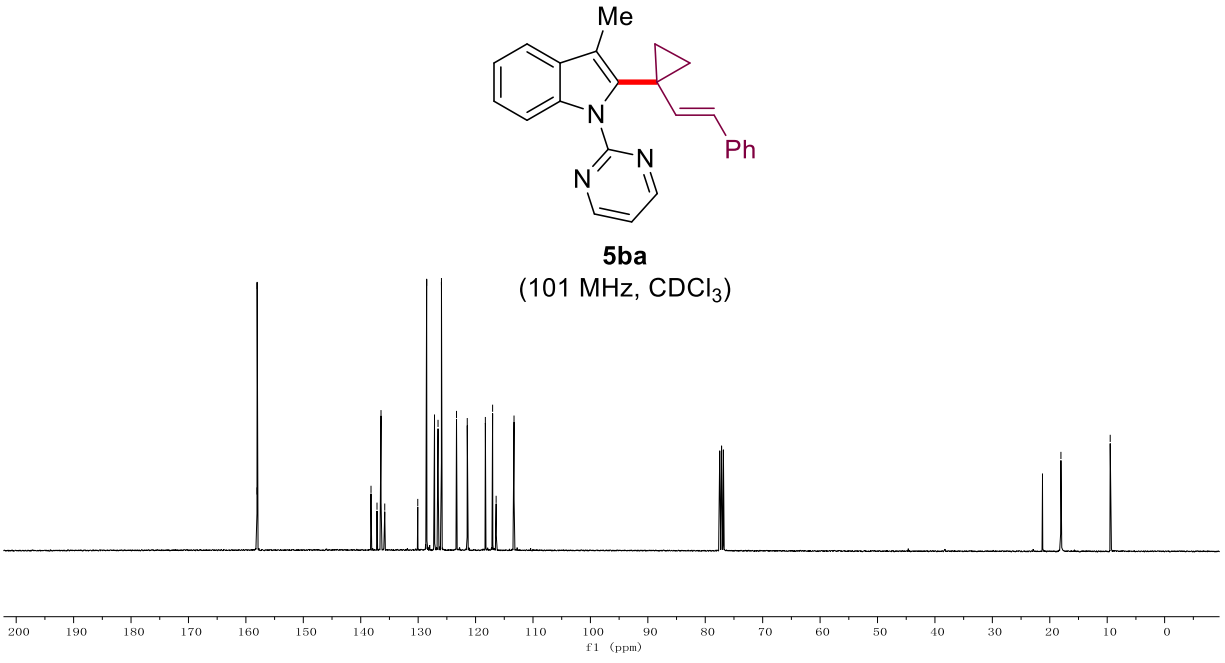


5aa
(101 MHz, $CDCl_3$)

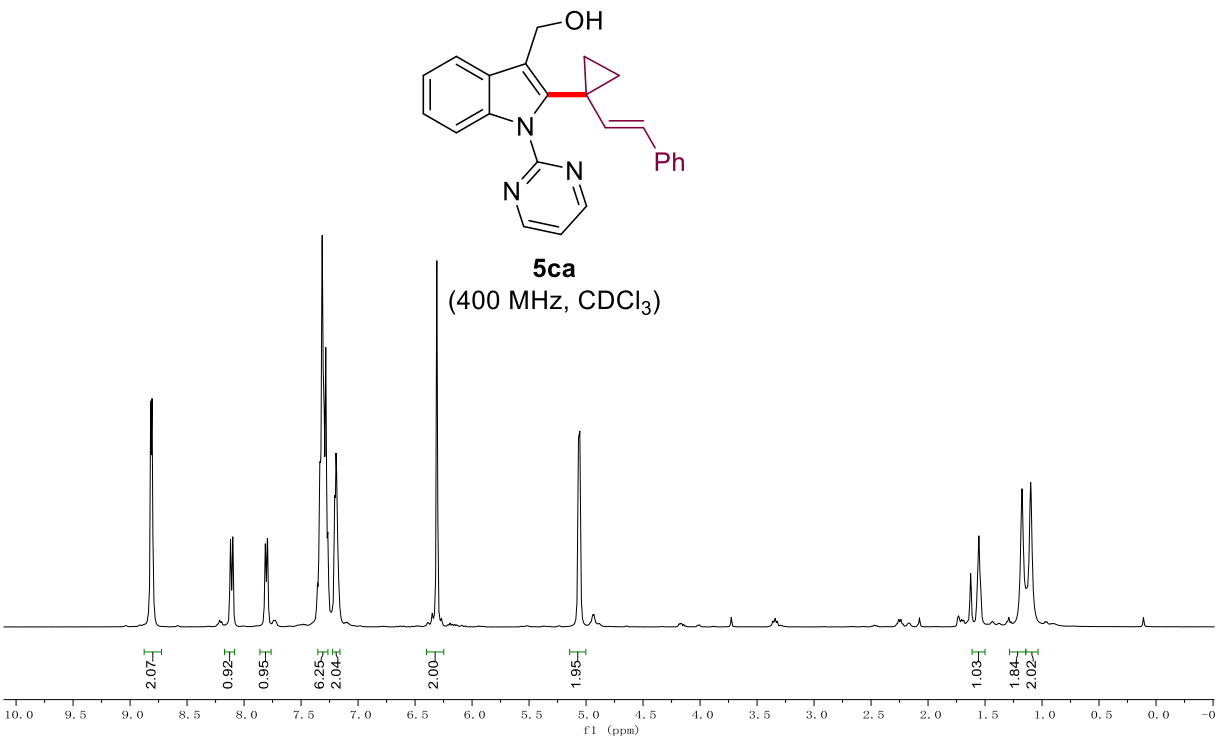




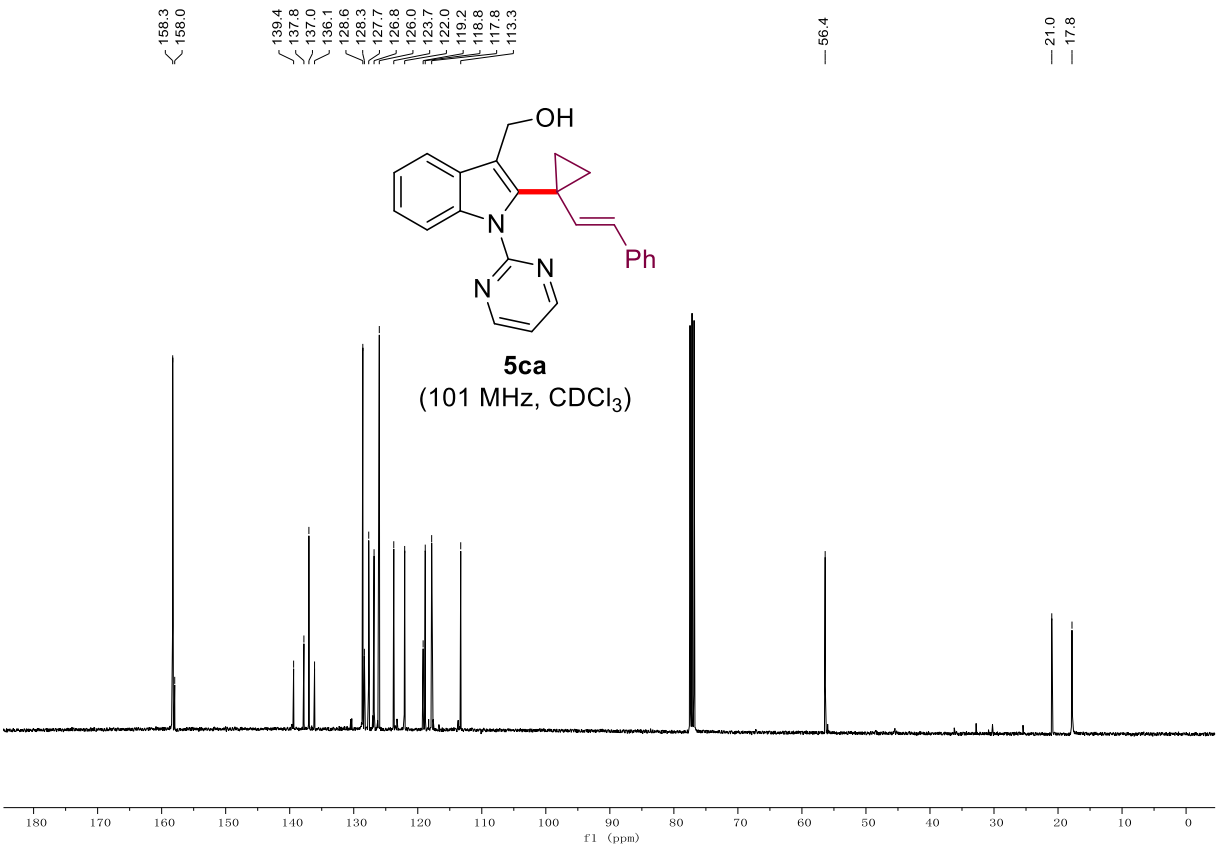
5ba
(400 MHz, $CDCl_3$)



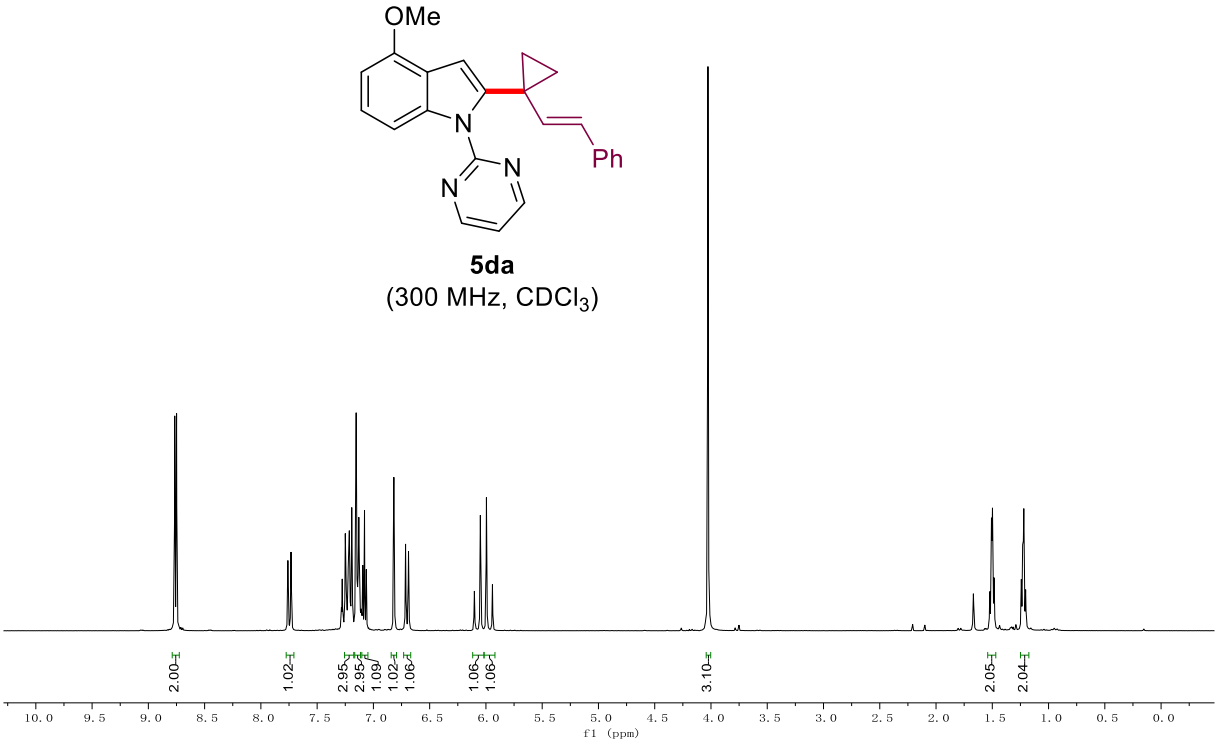
5ba
(101 MHz, $CDCl_3$)

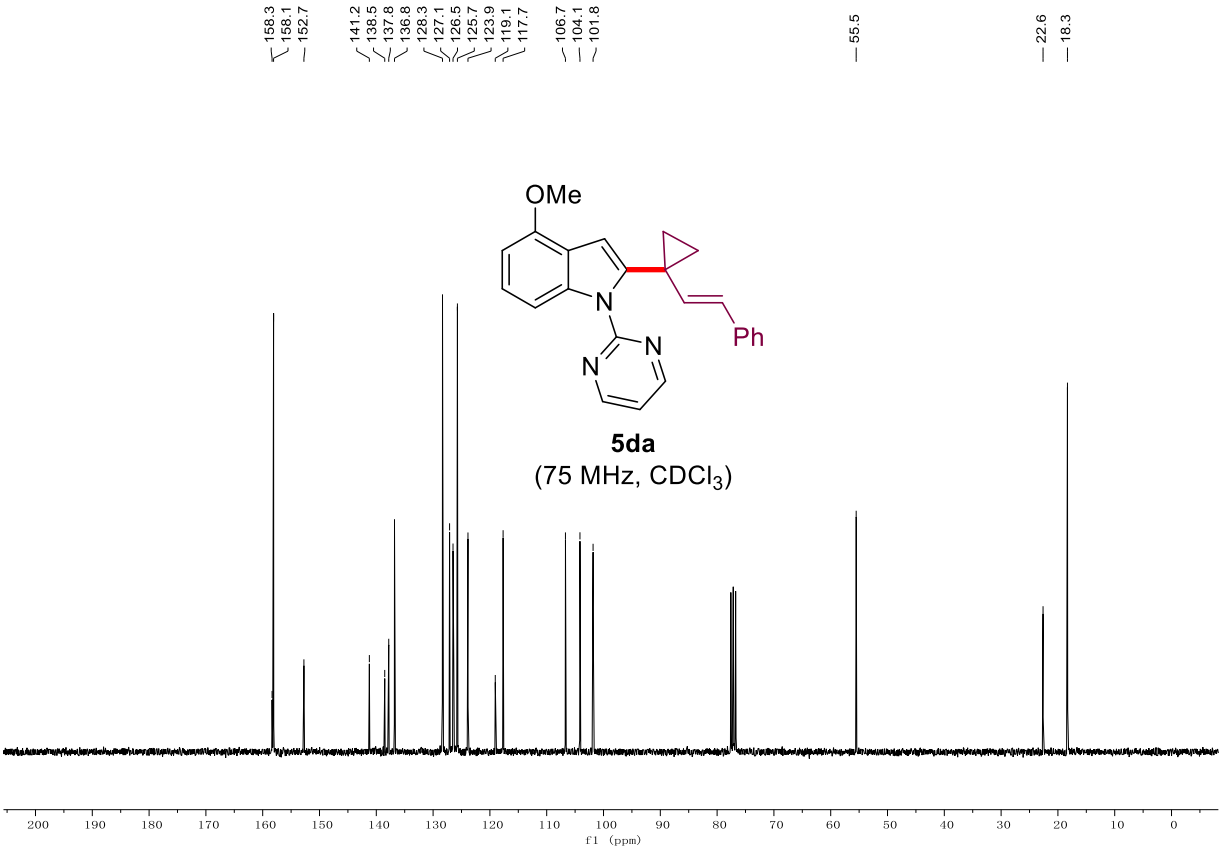


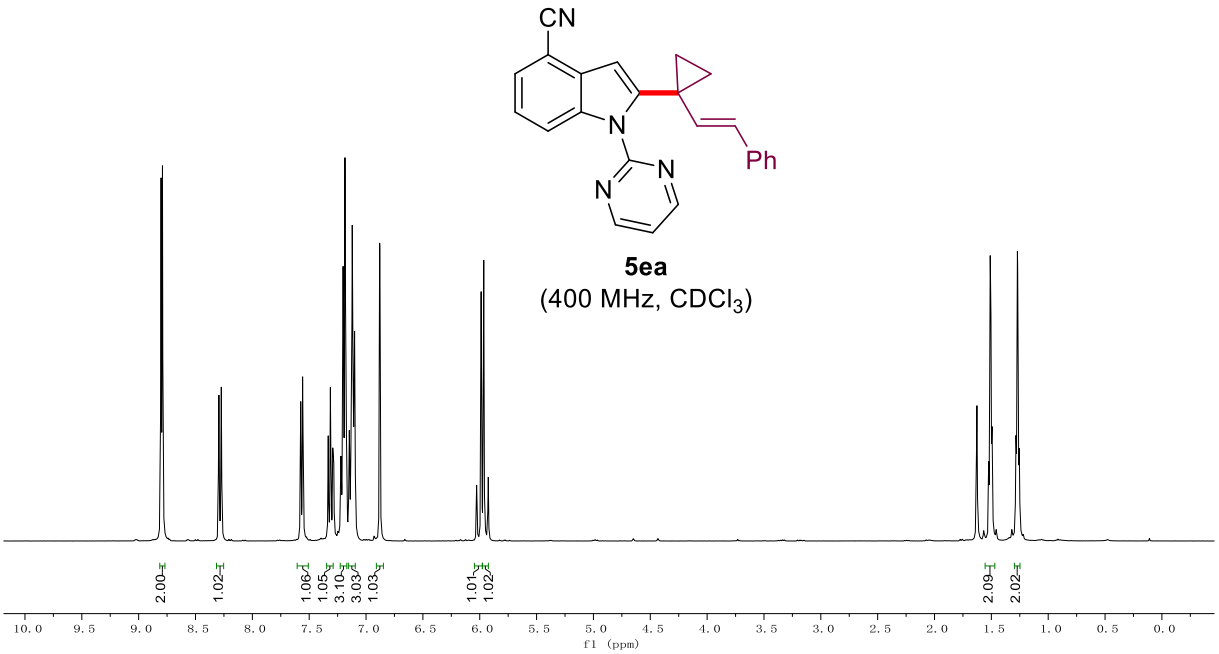
5ca
(400 MHz, $CDCl_3$)



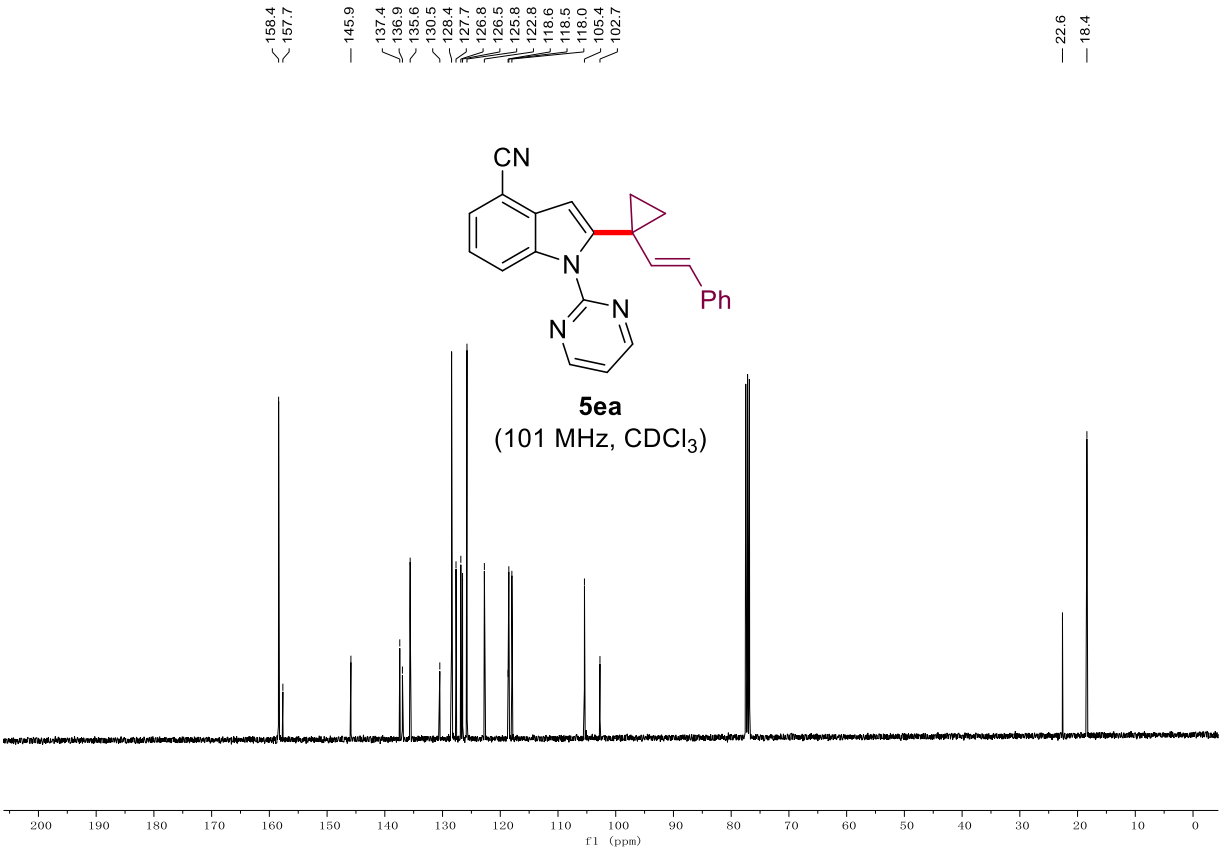
5ca
(101 MHz, $CDCl_3$)


OMe
N
N
N
Ph
5da
(300 MHz, CDCl3)
2.00
1.02
2.95
2.95
1.09
1.02
1.06
1.06
1.06
3.10
2.05
2.04
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)

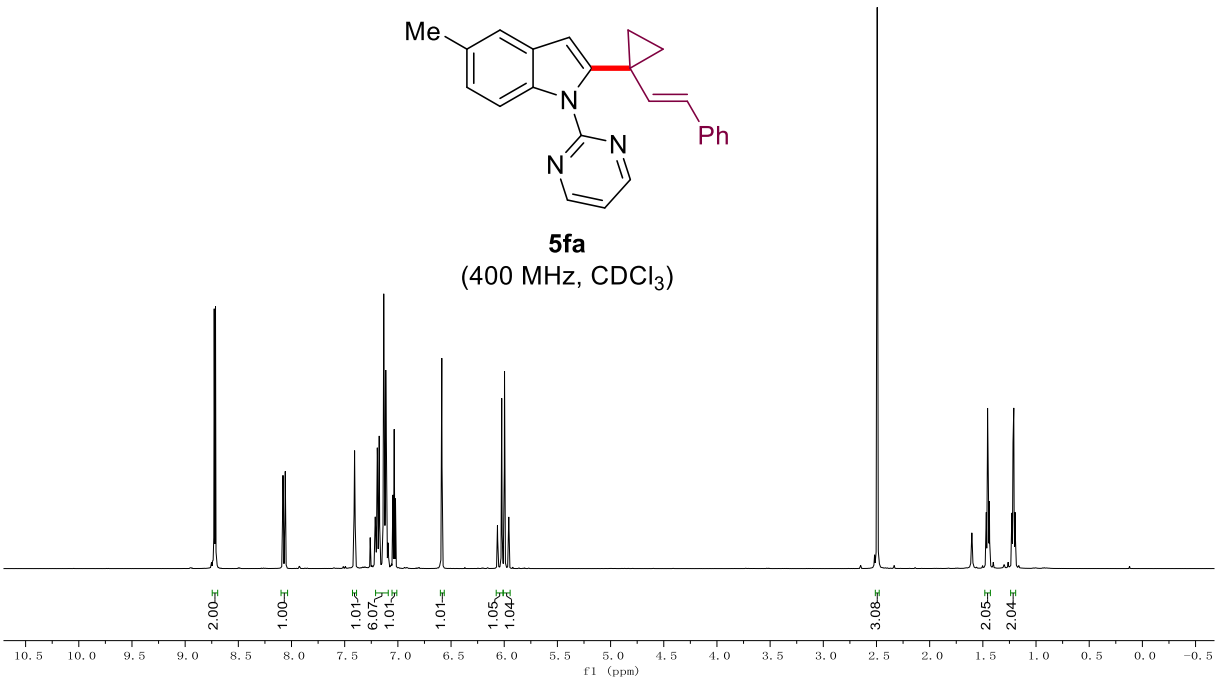

158.3
158.1
152.7
141.2
138.5
137.8
136.8
128.3
127.1
126.5
125.7
123.9
119.1
117.7
106.7
104.1
101.8
55.5
22.6
18.3
OMe
N
N
N
Ph
5da
(75 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



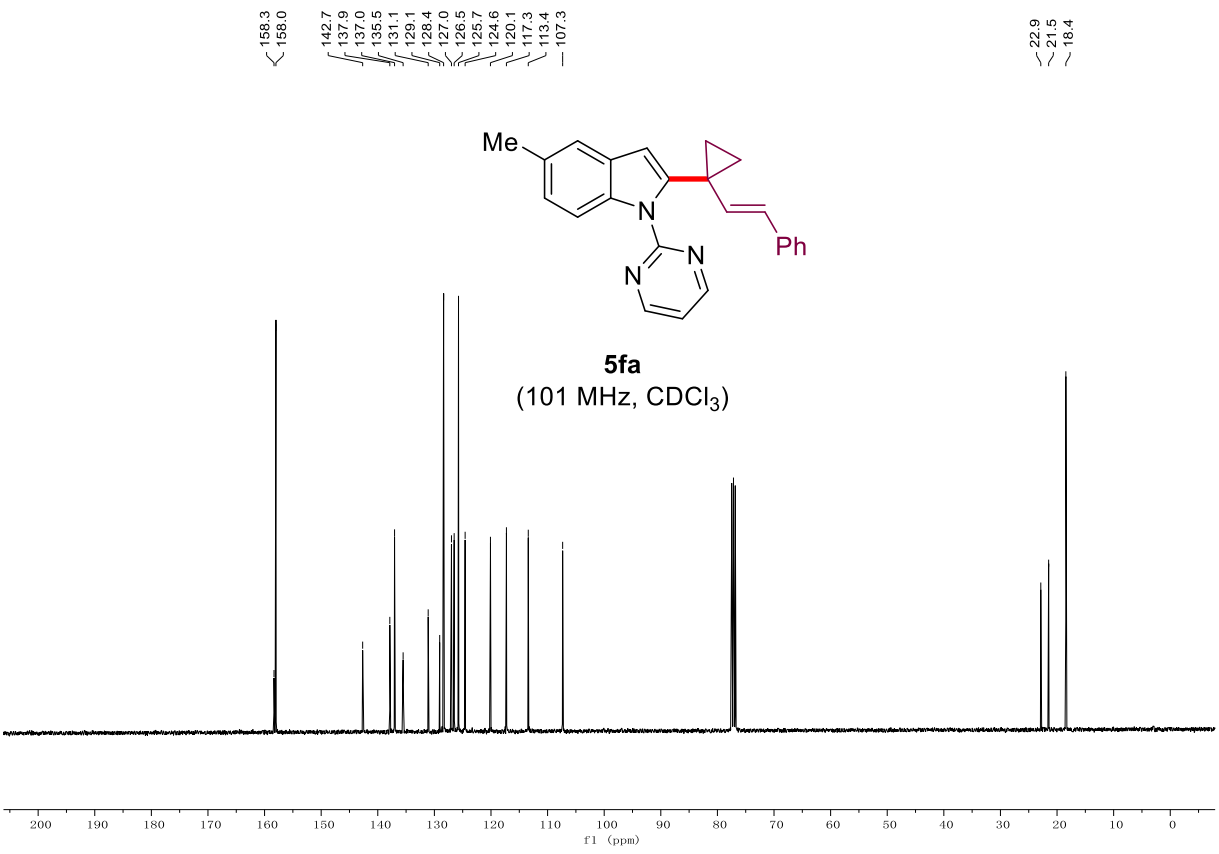
5ea
(400 MHz, $CDCl_3$)



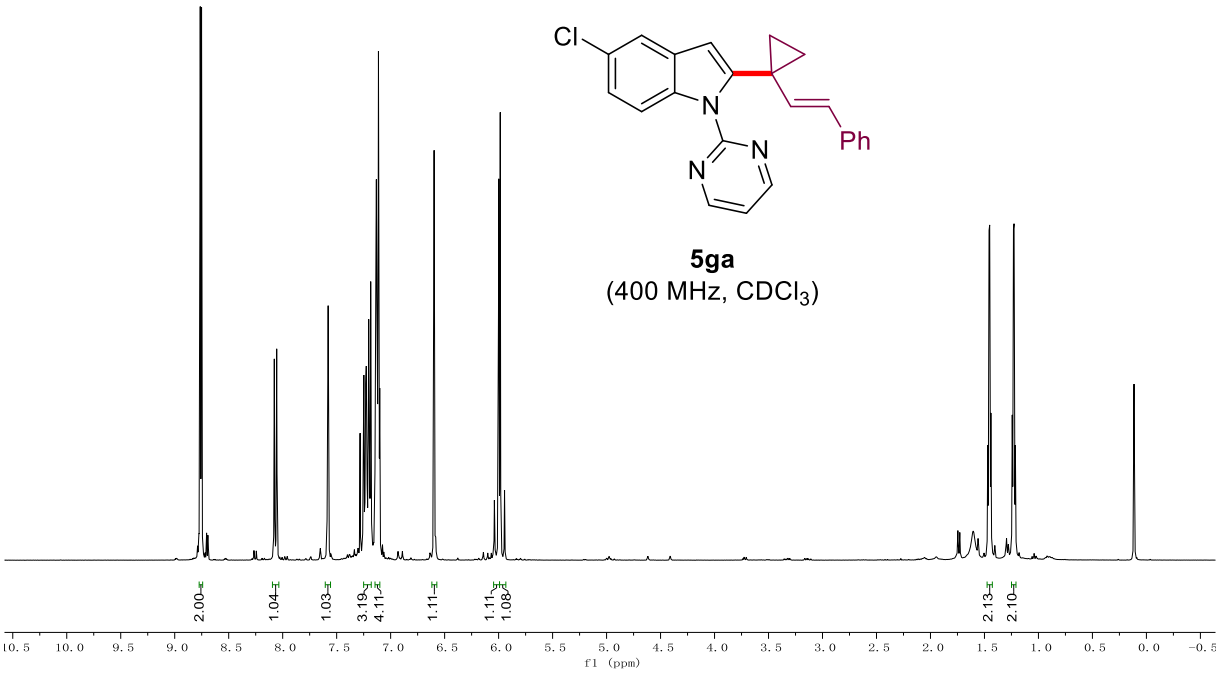
5ea
(101 MHz, $CDCl_3$)

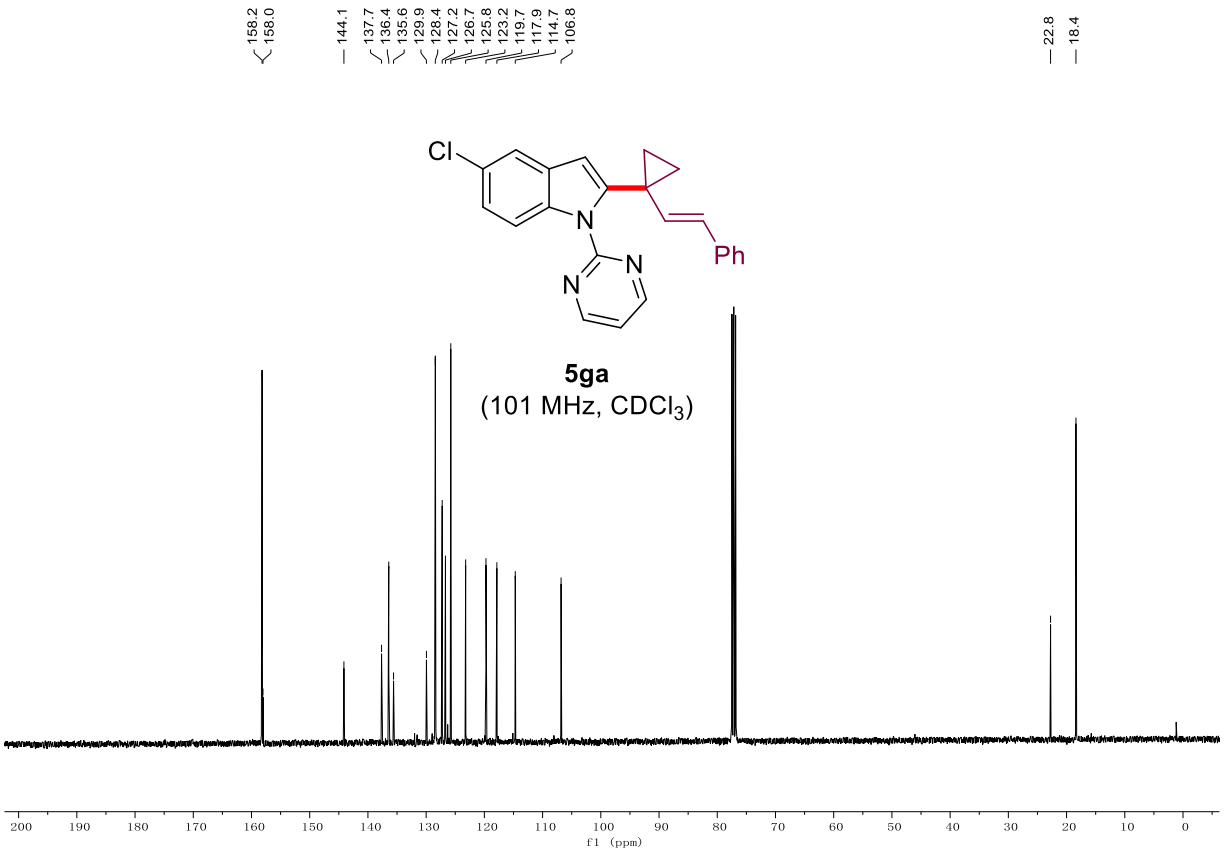


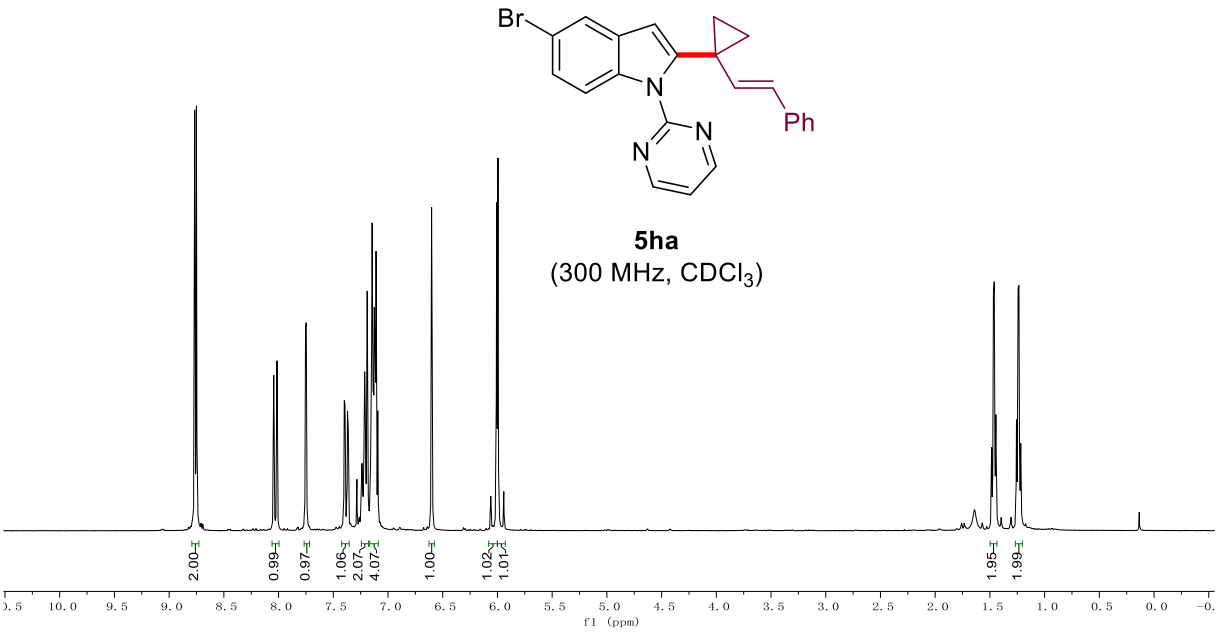
5fa
(400 MHz, $CDCl_3$)



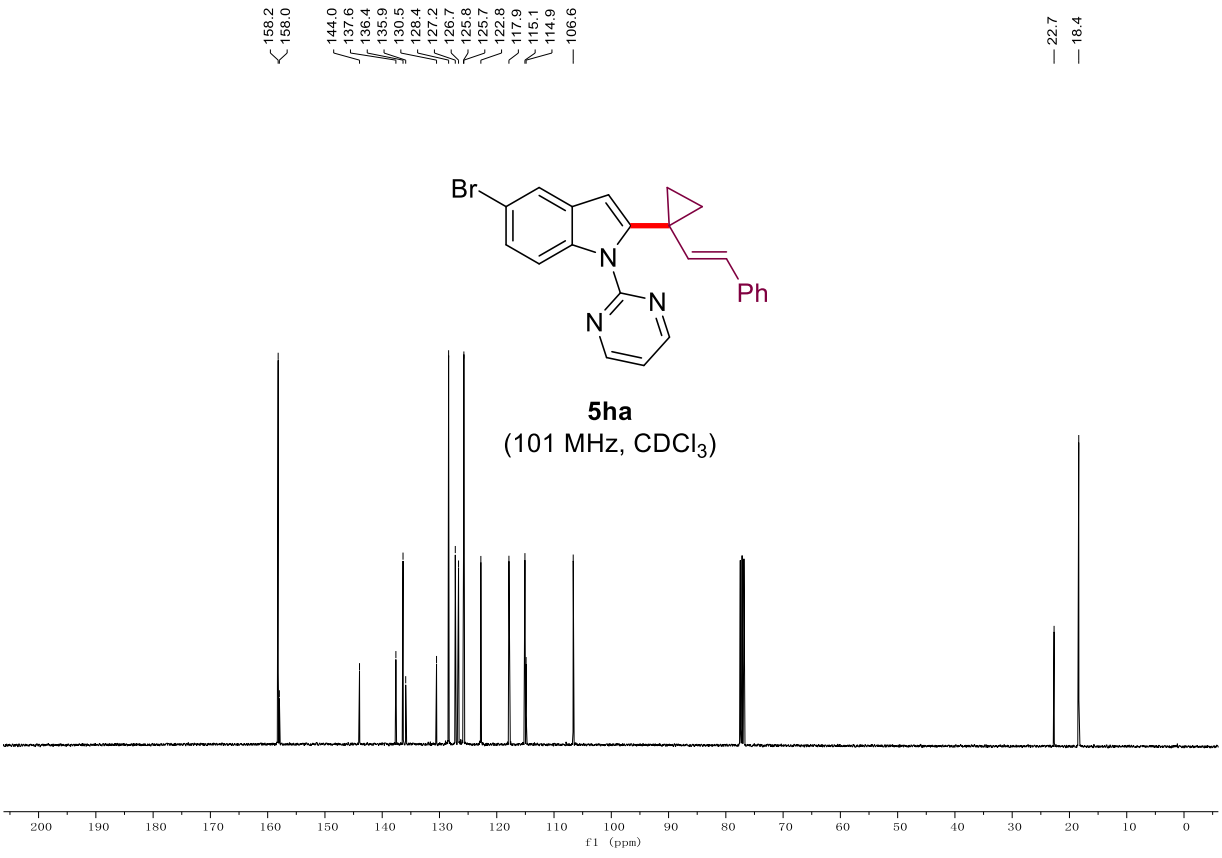
5fa
(101 MHz, $CDCl_3$)


Cl
N
N
N
Ph
5ga
(400 MHz, CDCl3)
2.00
1.04
1.03
3.19
4.11
1.11
1.11
1.08
2.13
2.10
f1 (ppm)

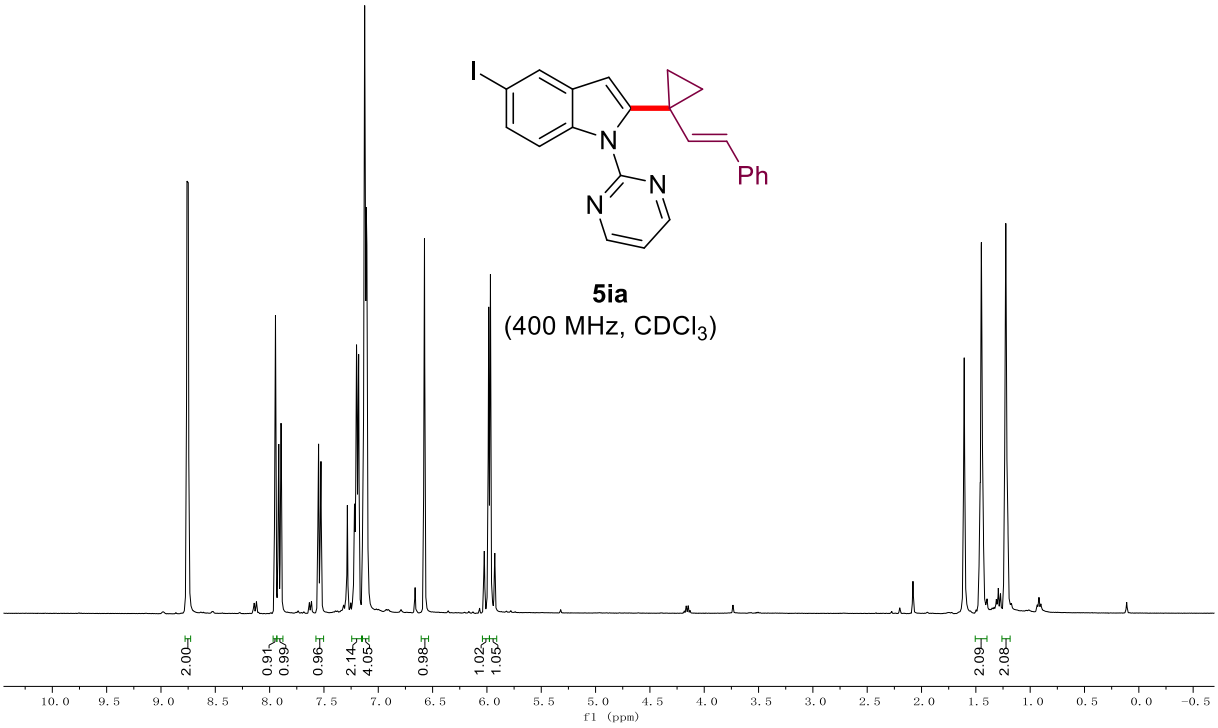

158.2
158.0
144.1
137.7
136.4
135.6
129.9
128.4
127.2
126.7
125.8
123.2
119.7
117.9
114.7
106.8
22.8
18.4
Cl
N
N
N
Ph
5ga
(101 MHz, CDCl3)
f1 (ppm)



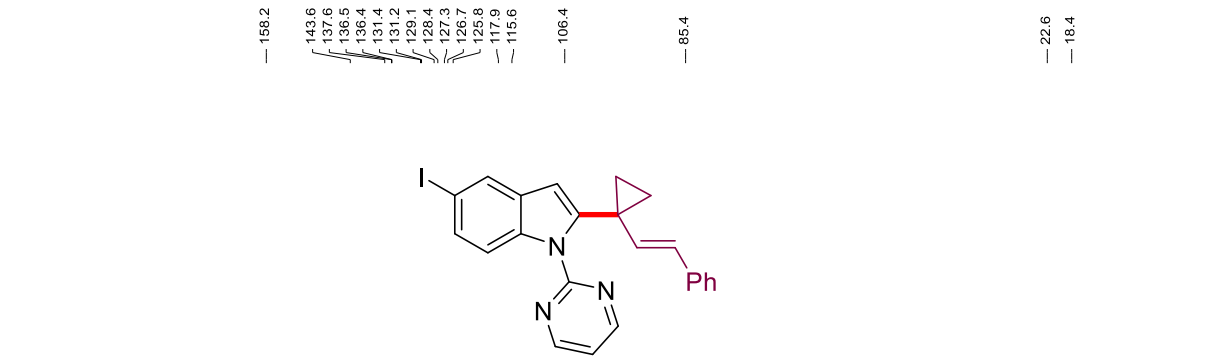
5ha
(300 MHz, $CDCl_3$)



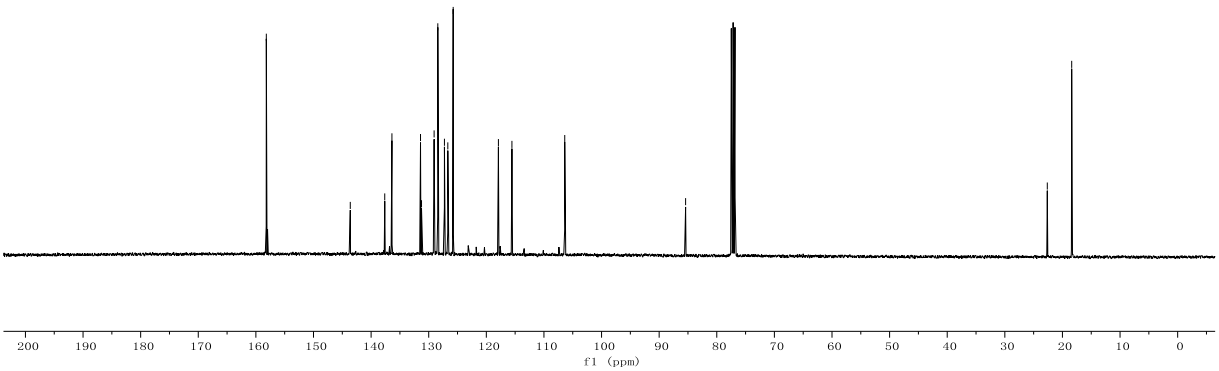
5ha
(101 MHz, $CDCl_3$)

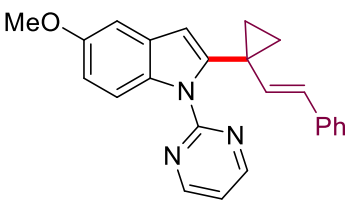


5ia
(400 MHz, $CDCl_3$)



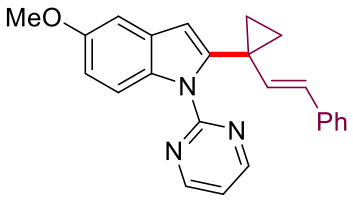
5ia
(101 MHz, $CDCl_3$)



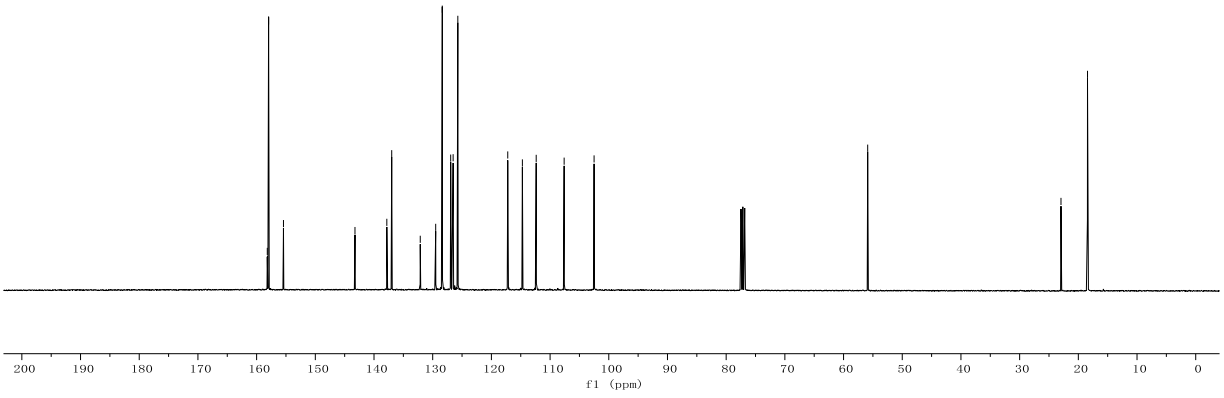


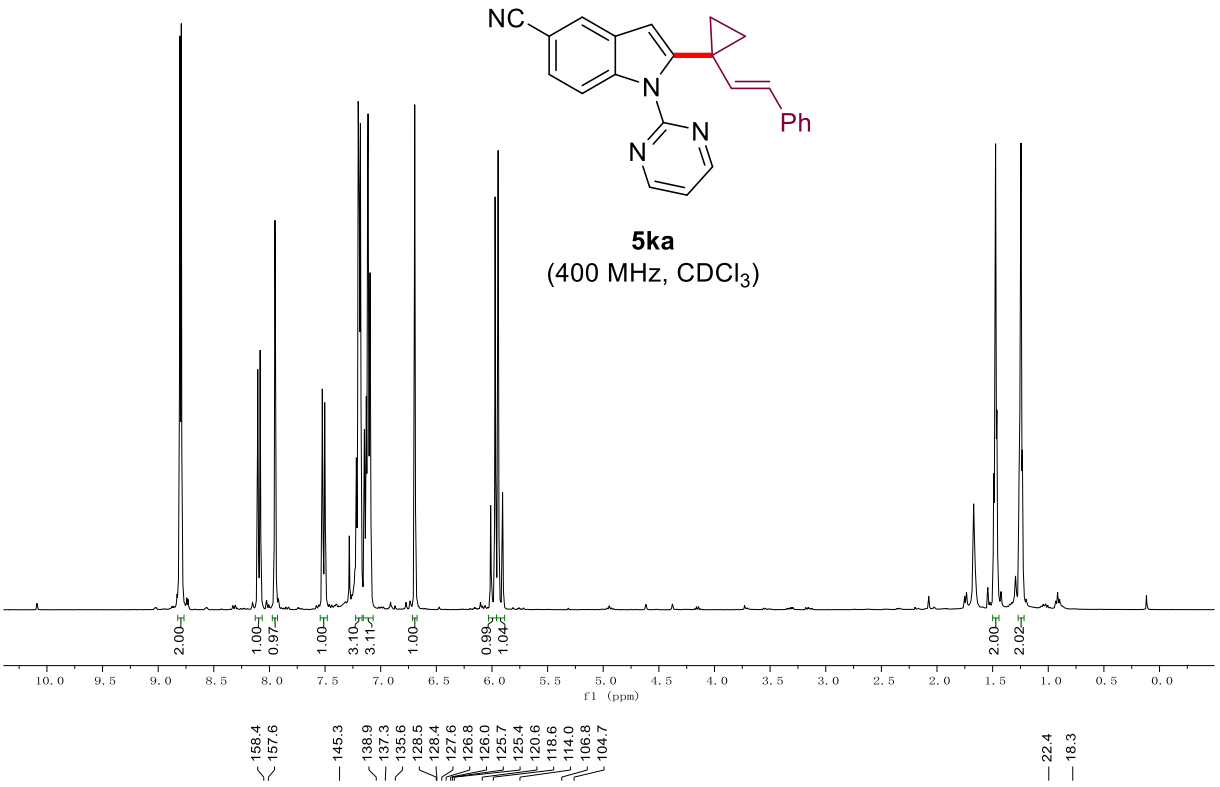
5ja
(400 MHz, $CDCl_3$)

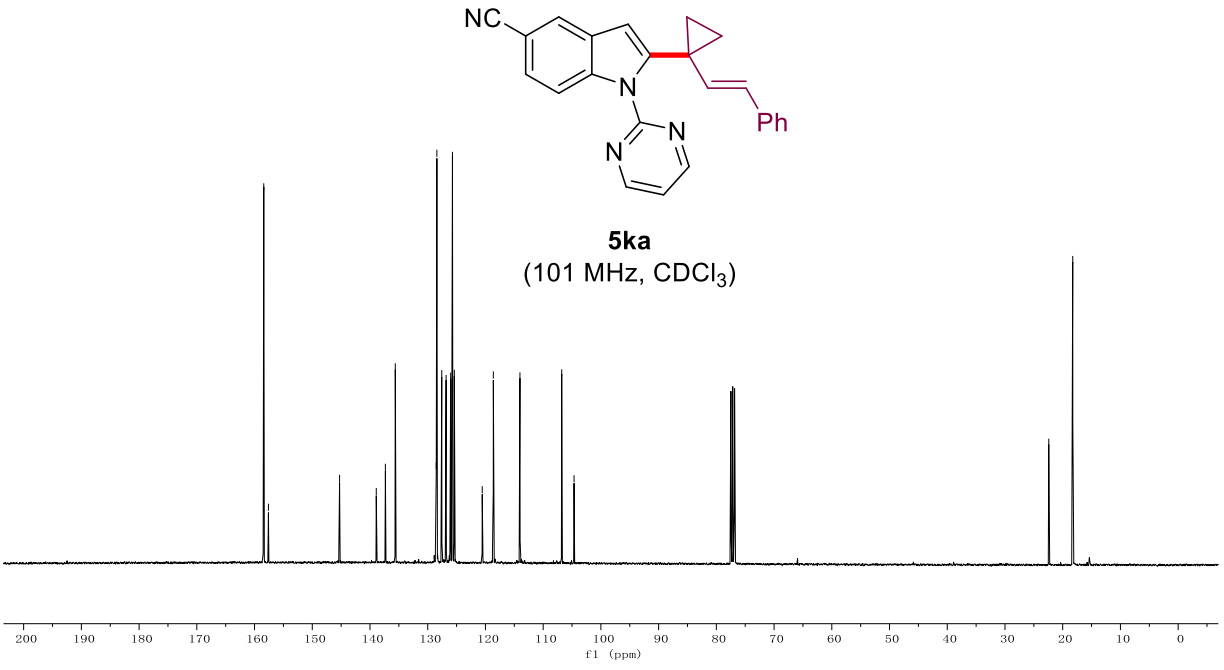
158.2
158.0
155.4
143.2
137.8
137.0
132.1
129.5
128.4
126.9
126.5
125.7
117.2
114.7
112.4
107.6
102.5
55.9
23.0
18.4

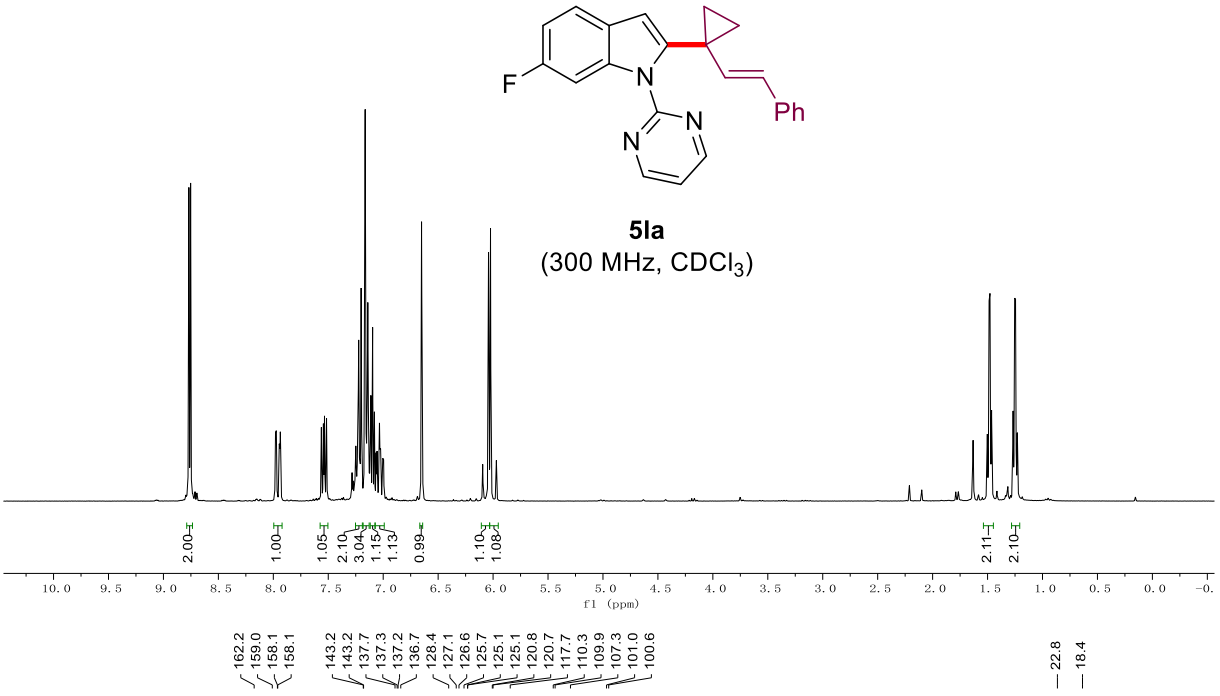


5ja
(101 MHz, $CDCl_3$)

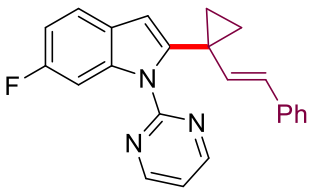



NC
N
N
N
Ph
5ka
(400 MHz, CDCl3)
2.00
1.00
0.97
1.00
3.10
3.11
1.00
0.99
1.04
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
158.4
157.6
145.3
138.9
137.3
135.6
128.5
128.4
127.6
126.8
126.0
125.7
125.4
120.6
118.6
114.0
106.8
104.7
22.4
18.3

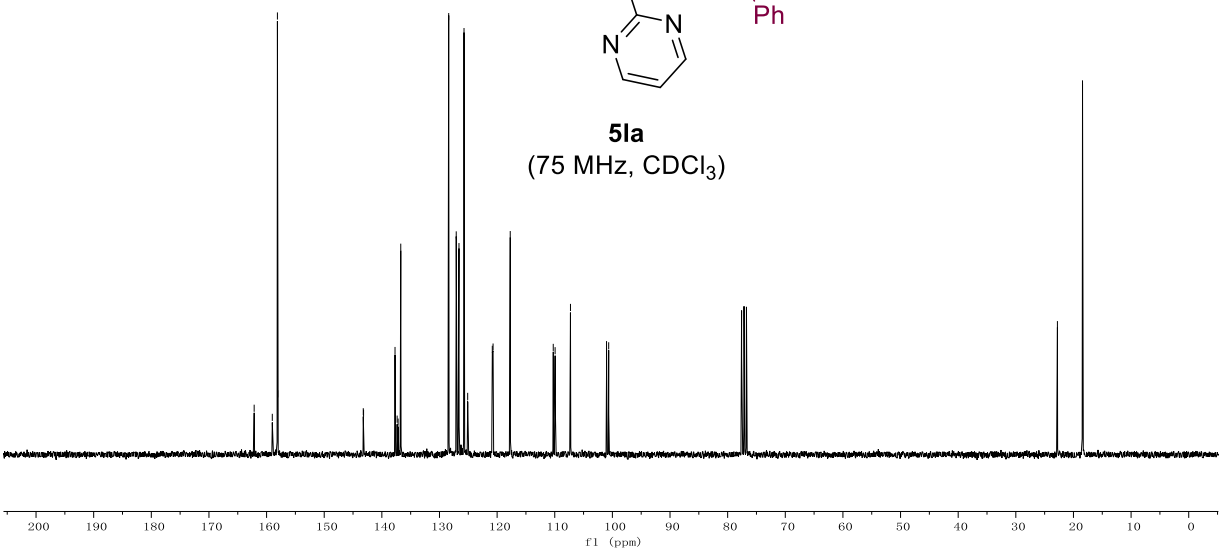

NC
N
N
N
Ph
5ka
(101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

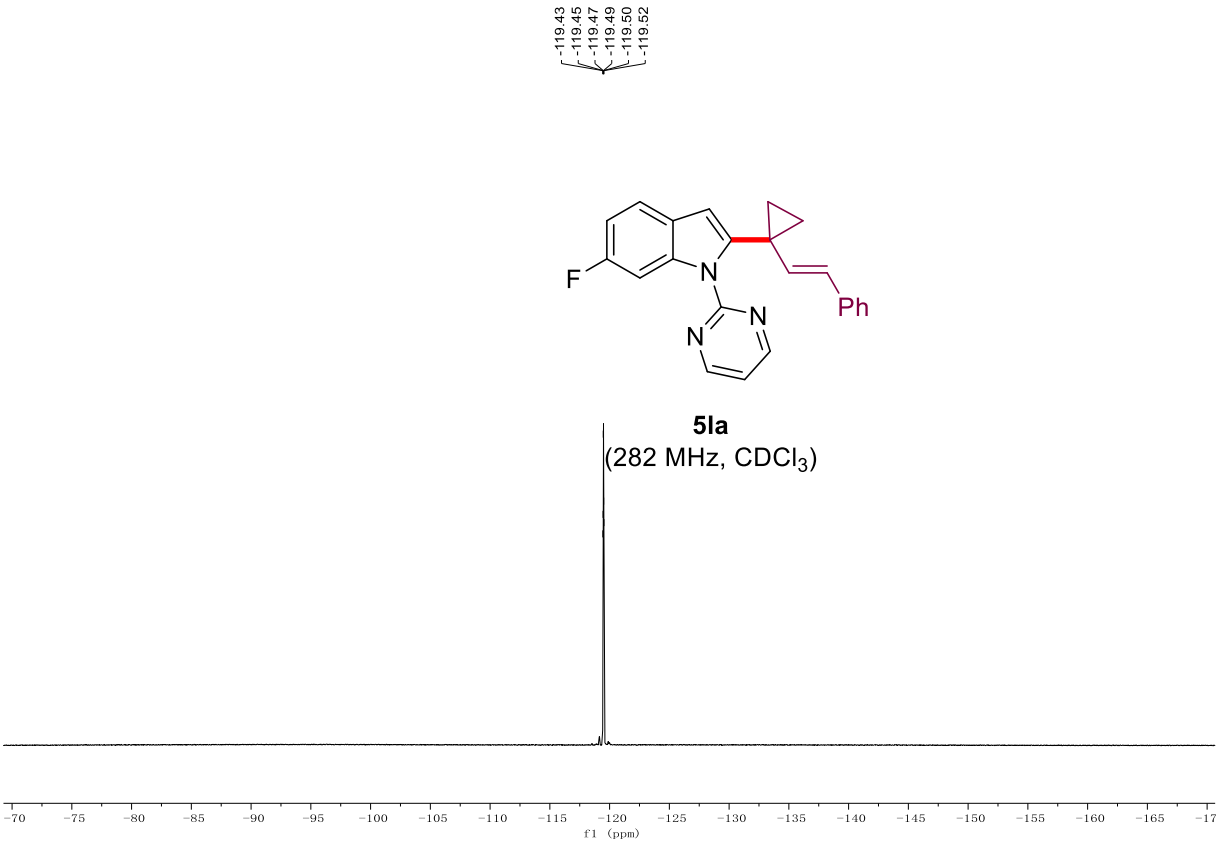


5la
(300 MHz, $CDCl_3$)

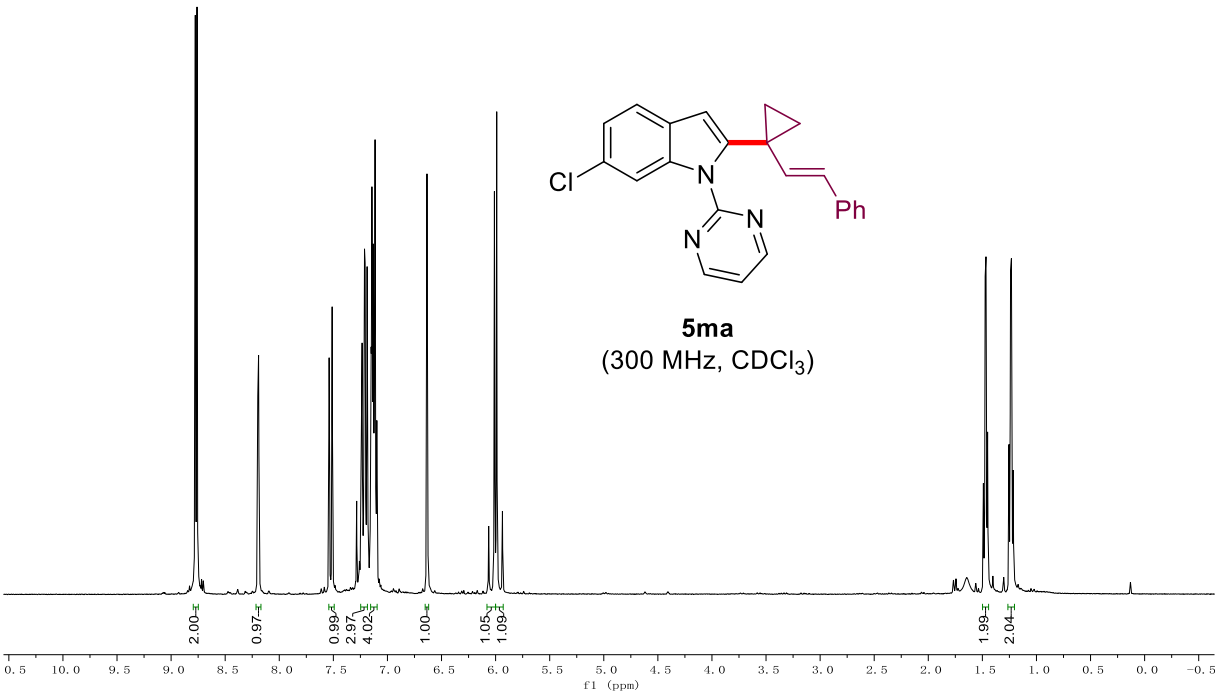


5la
(75 MHz, $CDCl_3$)

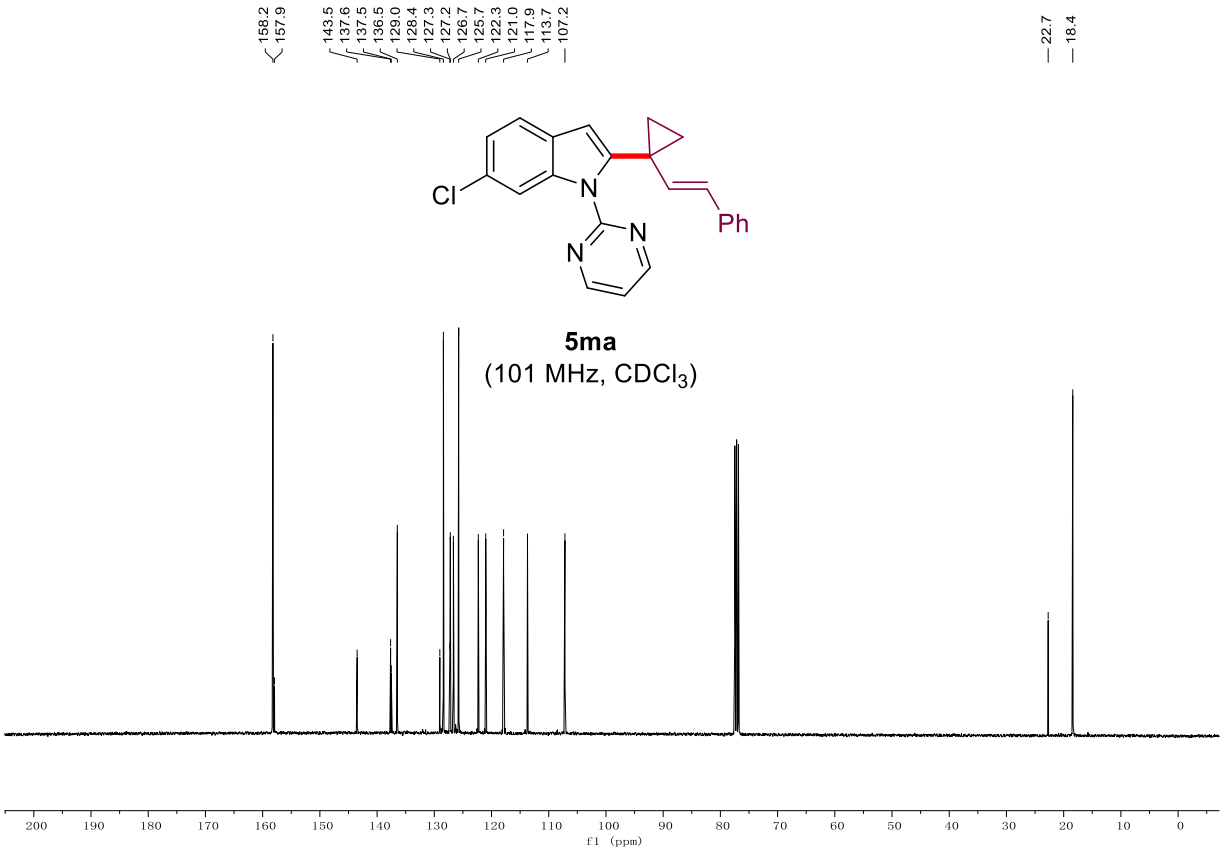


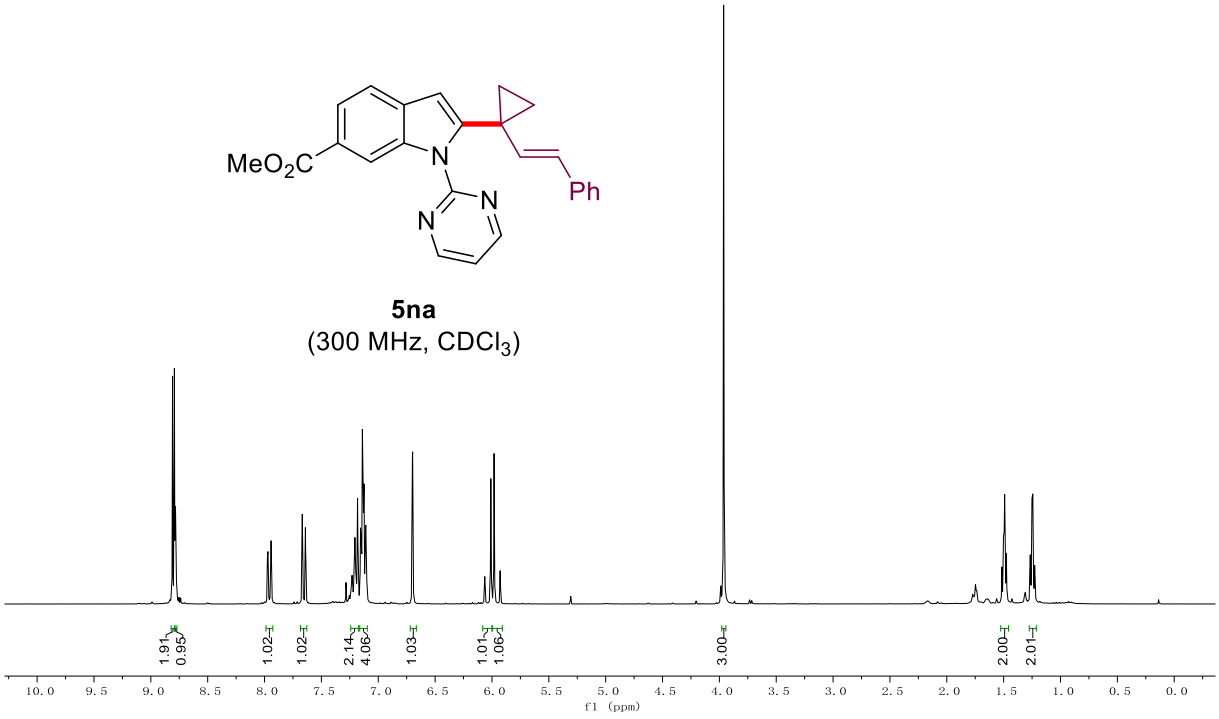


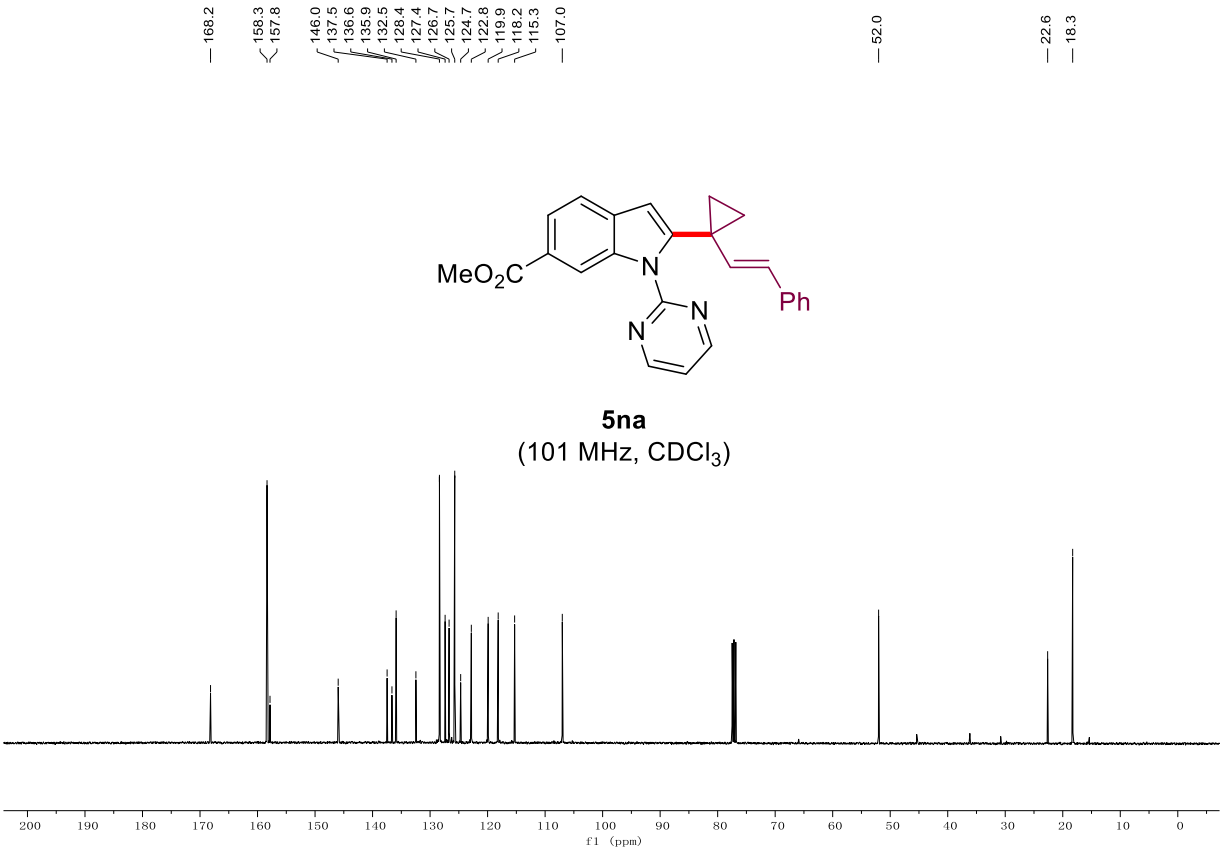
5la
(282 MHz, $CDCl_3$)

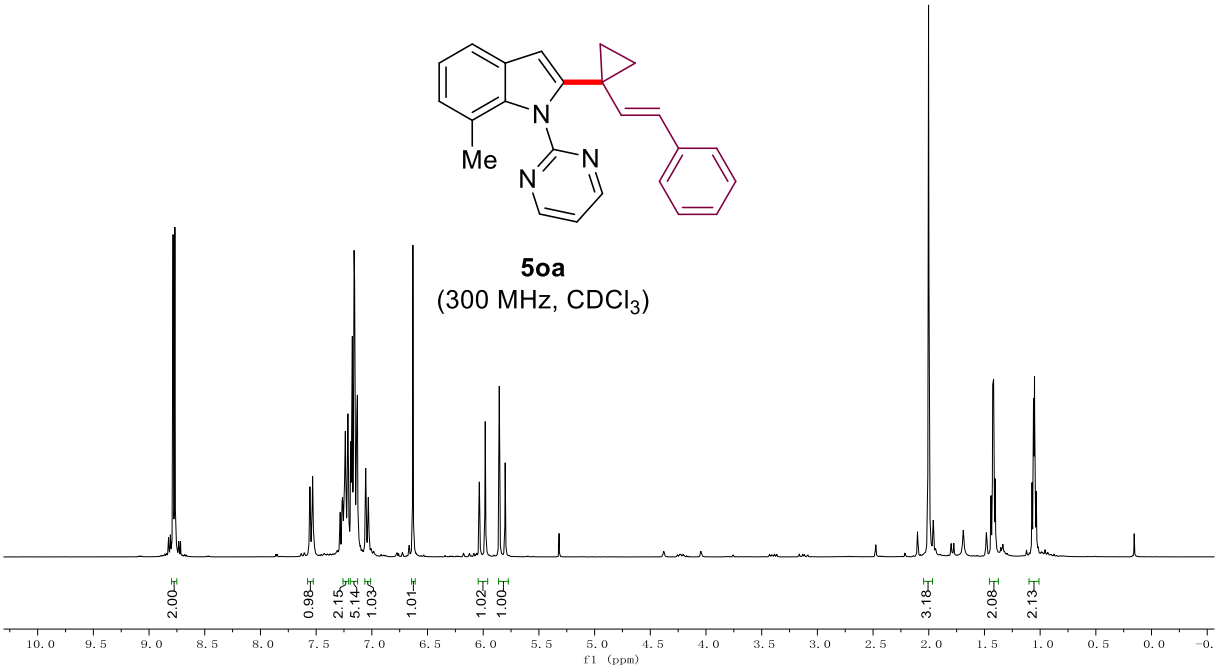


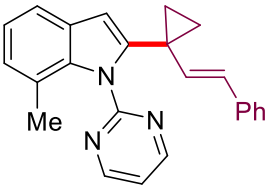
5ma
(300 MHz, $CDCl_3$)


158.2
157.9
143.5
137.6
137.5
136.5
129.0
128.4
127.3
127.2
126.7
125.7
122.3
121.0
117.9
113.7
107.2
22.7
18.4
Cl
N
N
N
Ph
5ma
(101 MHz, CDCl3)
f1 (ppm)


MeO2C
N
N
N
Ph
5na
(300 MHz, CDCl3)
1.91
0.95
1.02
1.02
2.14
4.06
1.03
1.01
1.06
3.00
2.00
2.01
f1 (ppm)

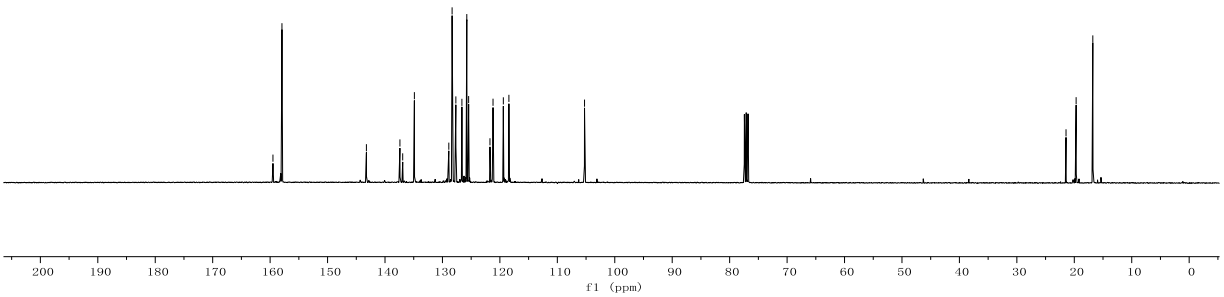

168.2
158.3
157.8
146.0
137.5
136.6
135.9
132.5
128.4
127.4
126.7
125.7
124.7
122.8
119.9
118.2
115.3
107.0
52.0
22.6
18.3
MeO2C
N
N
N
Ph
5na
(101 MHz, CDCl3)
f1 (ppm)

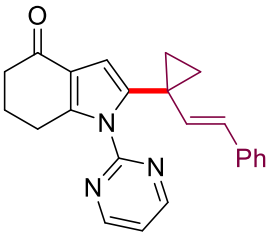

Me
N
N
N
5oa
(300 MHz, CDCl3)
2.00
0.98
2.15
5.14
1.03
1.01
1.02
1.00
3.18
2.08
2.13
f1 (ppm)



5oa

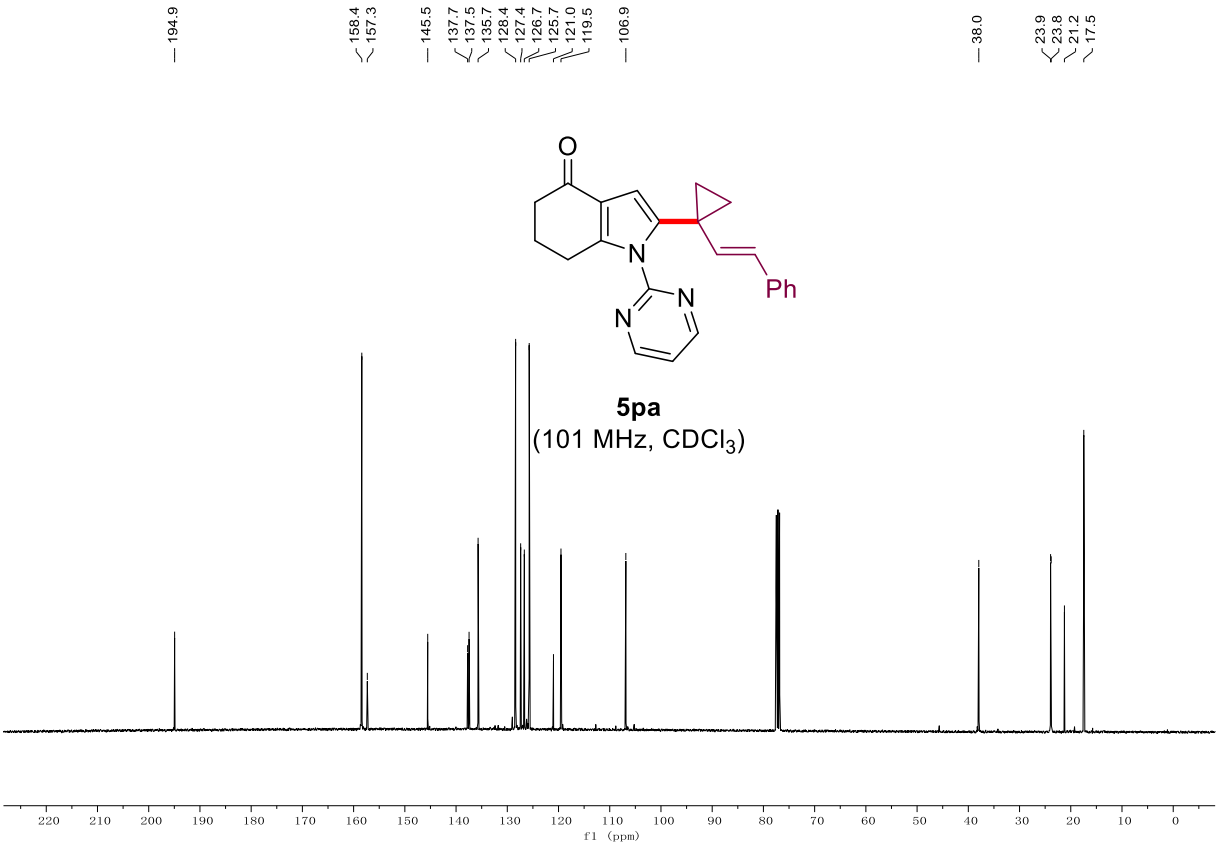
(101 MHz, $CDCl_3$)

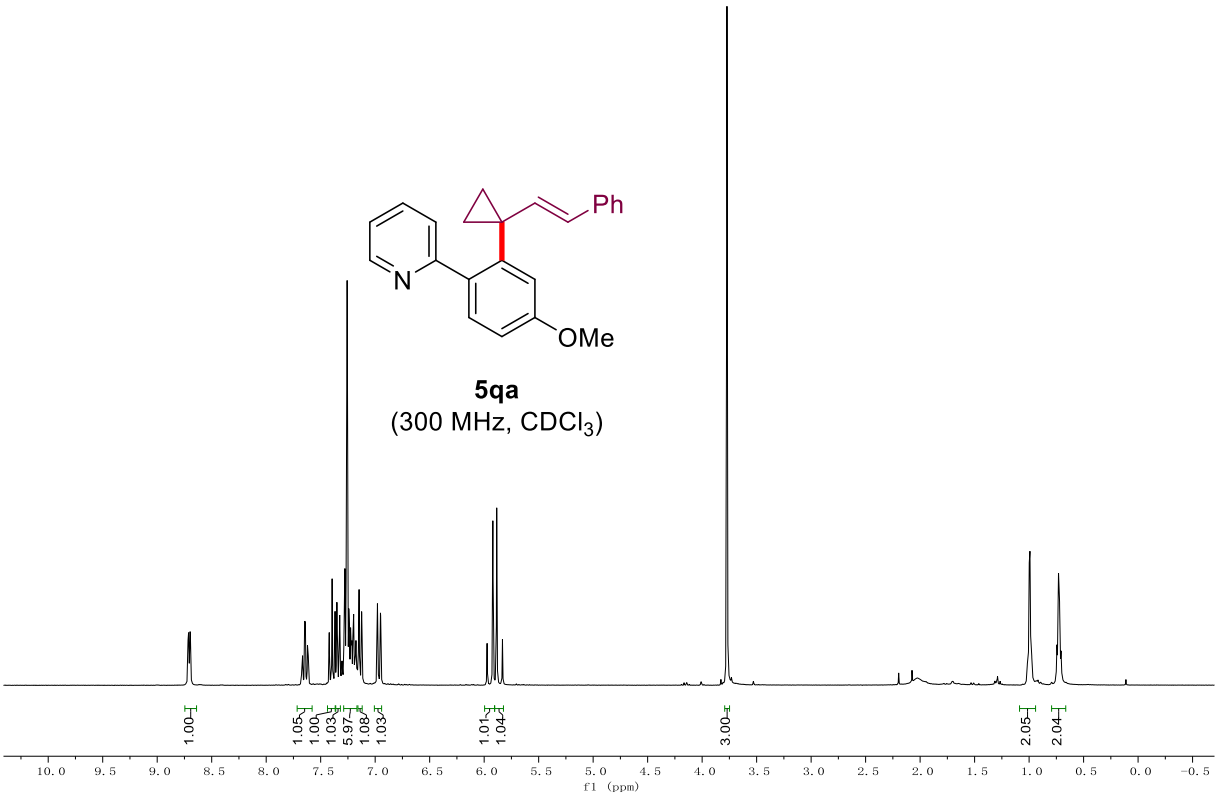


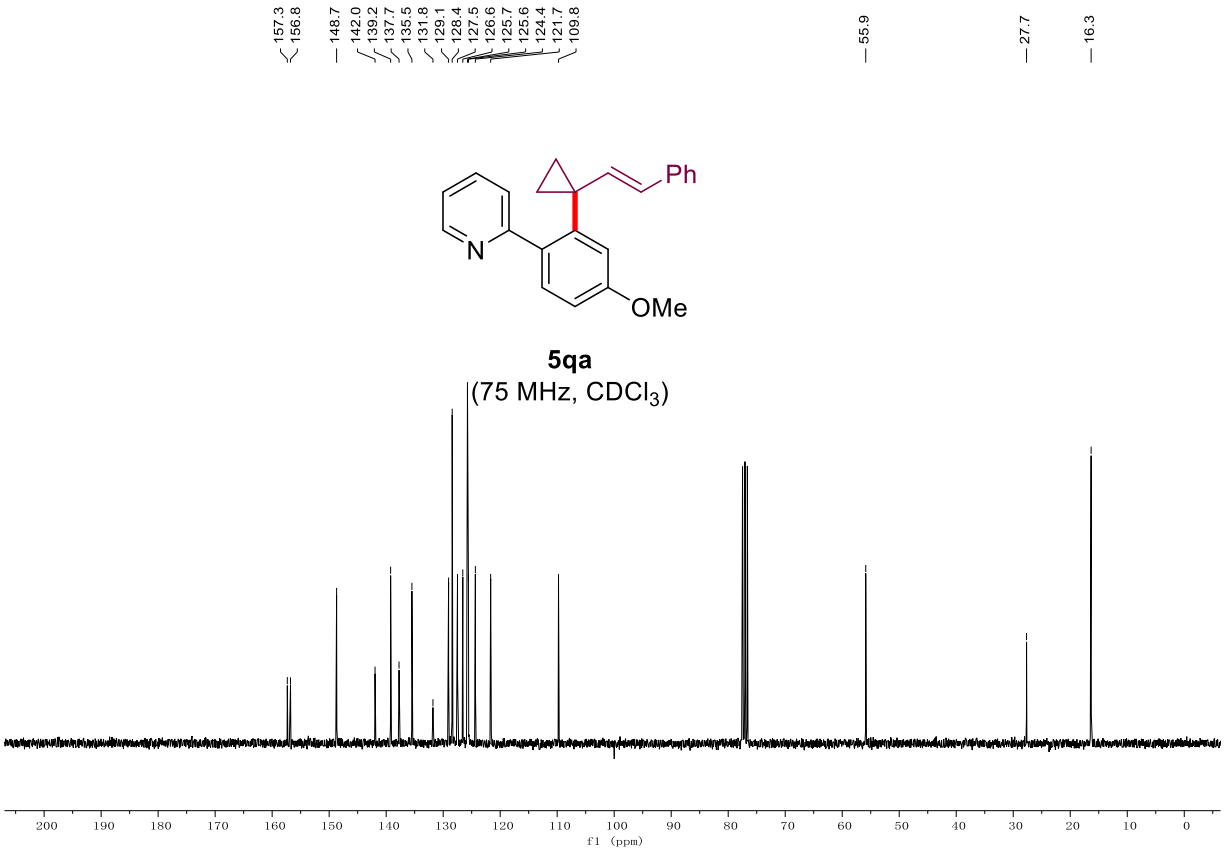


5pa

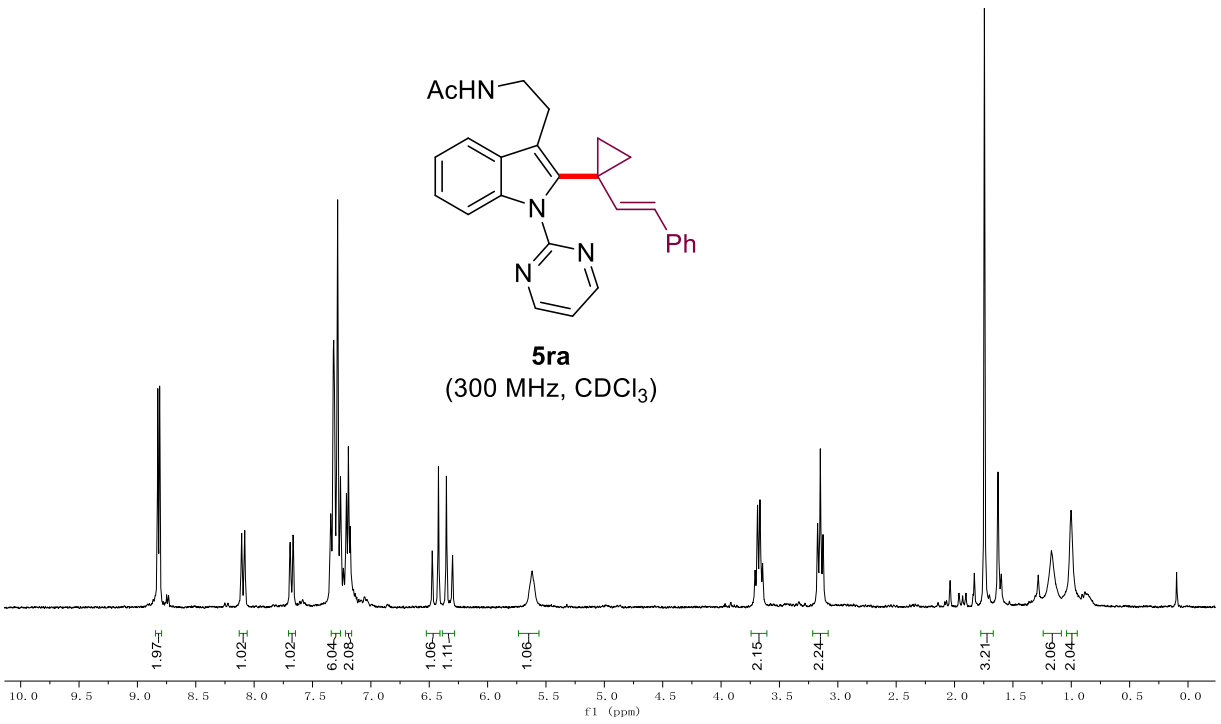
(400 MHz, $CDCl_3$)


194.9
158.4
157.3
145.5
137.7
137.5
135.7
128.4
127.4
126.7
125.7
121.0
119.5
106.9
38.0
23.9
23.8
21.2
17.5
O
N
N
N
Ph
5pa
(101 MHz, CDCl3)
f1 (ppm)

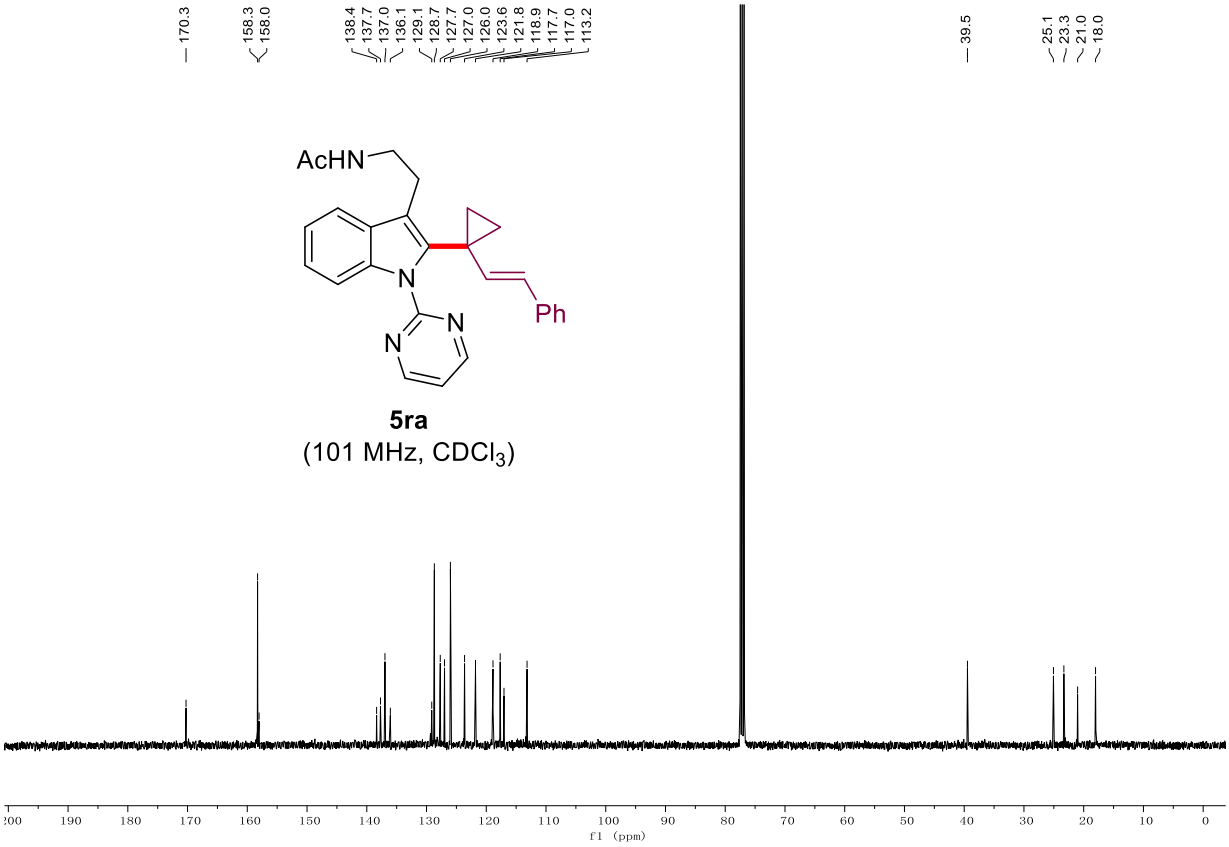

Ph
N
OMe
5qa
(300 MHz, CDCl3)
1.00
1.05
1.00
1.03
5.97
1.08
1.03
1.01
1.04
3.00
2.05
2.04
f1 (ppm)



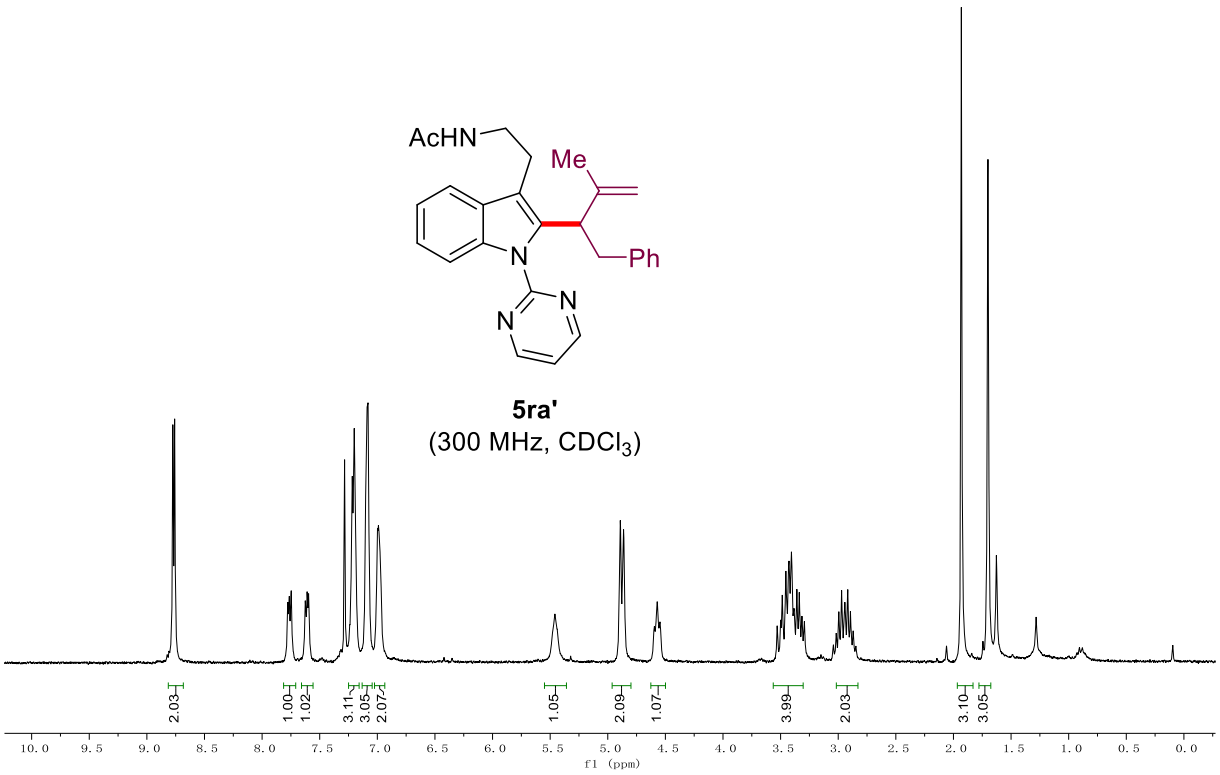
5qa
(75 MHz, $CDCl_3$)



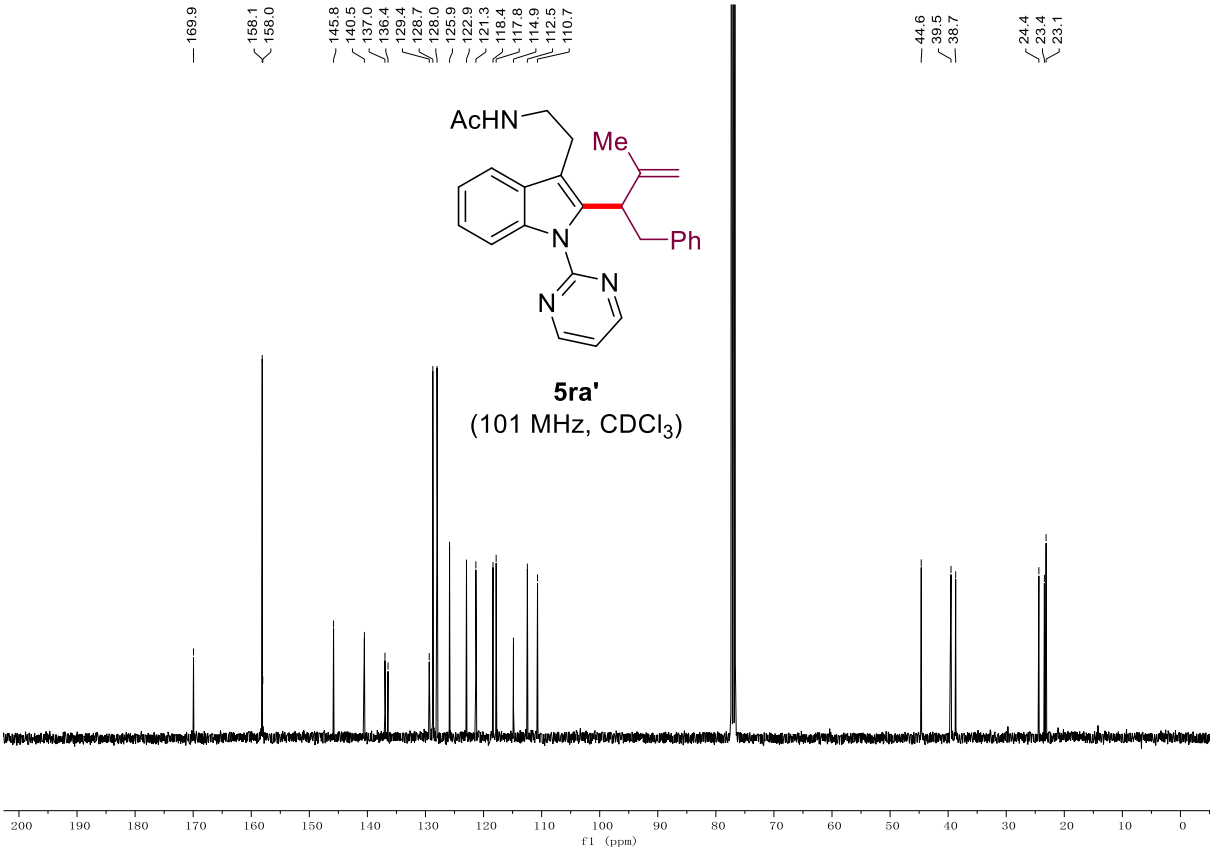
5ra
(300 MHz, $CDCl_3$)

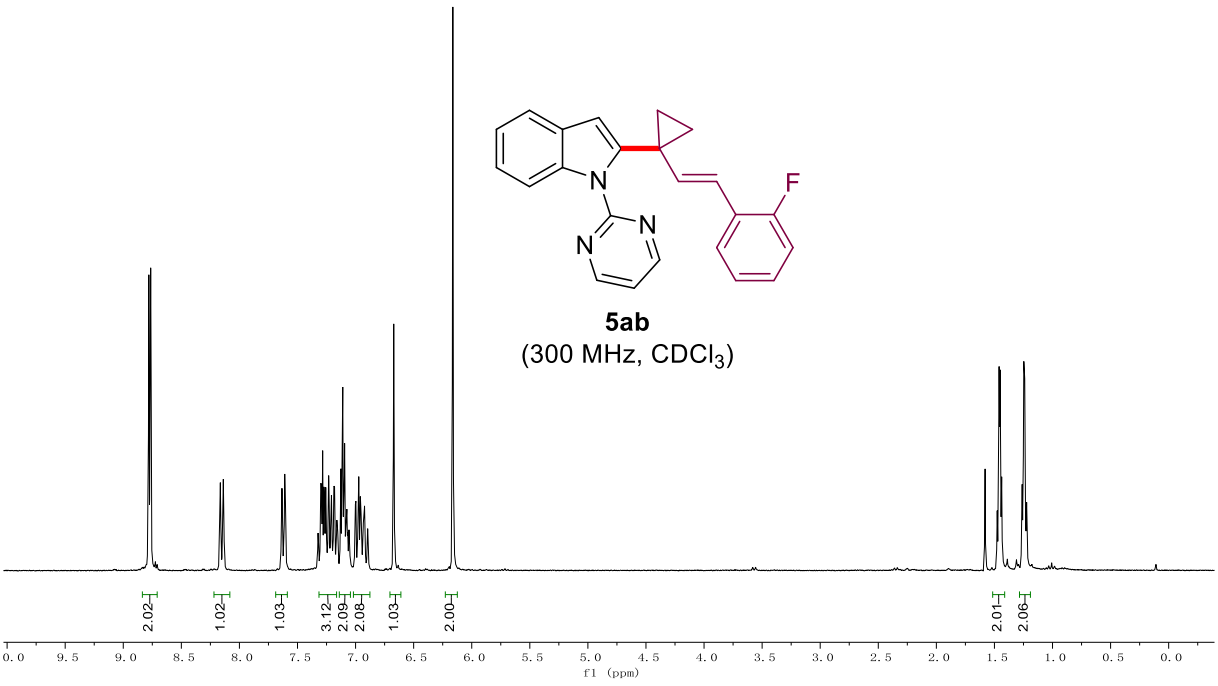


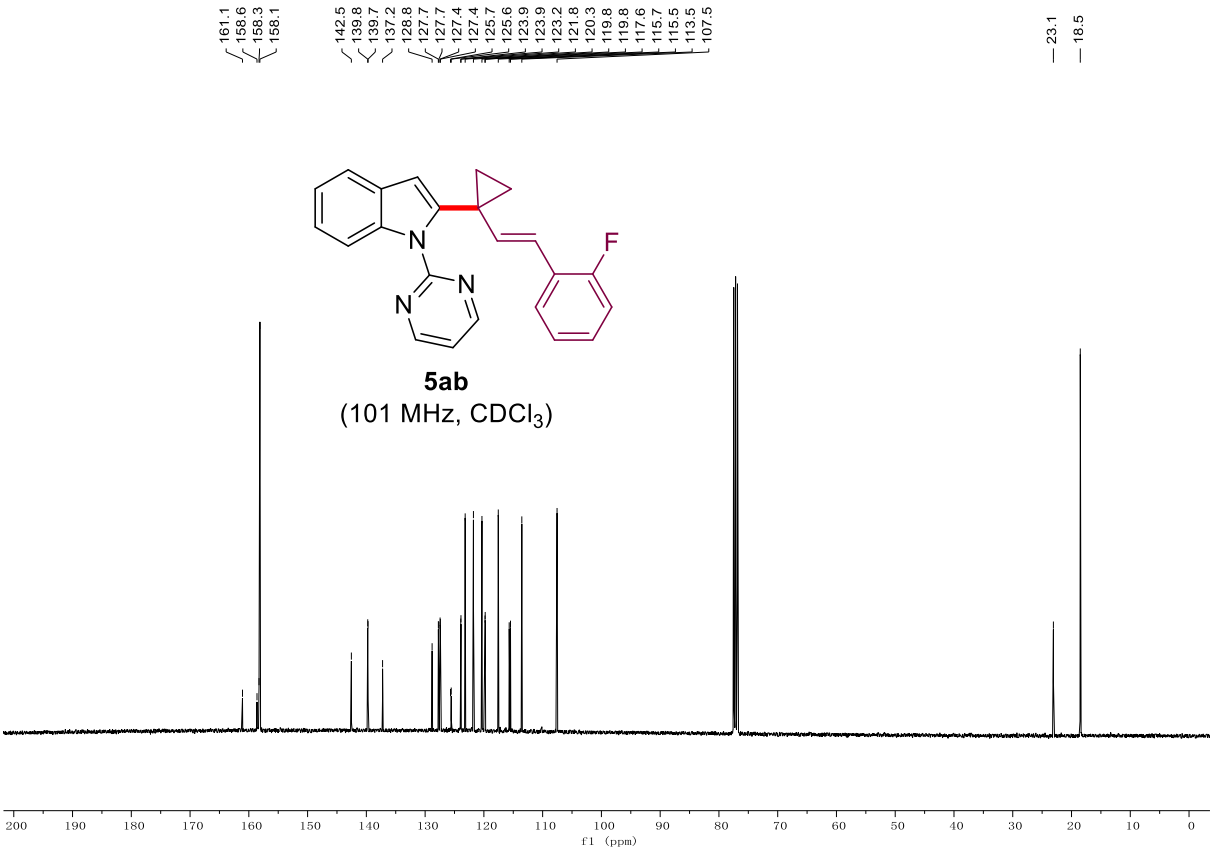
5ra
(101 MHz, $CDCl_3$)

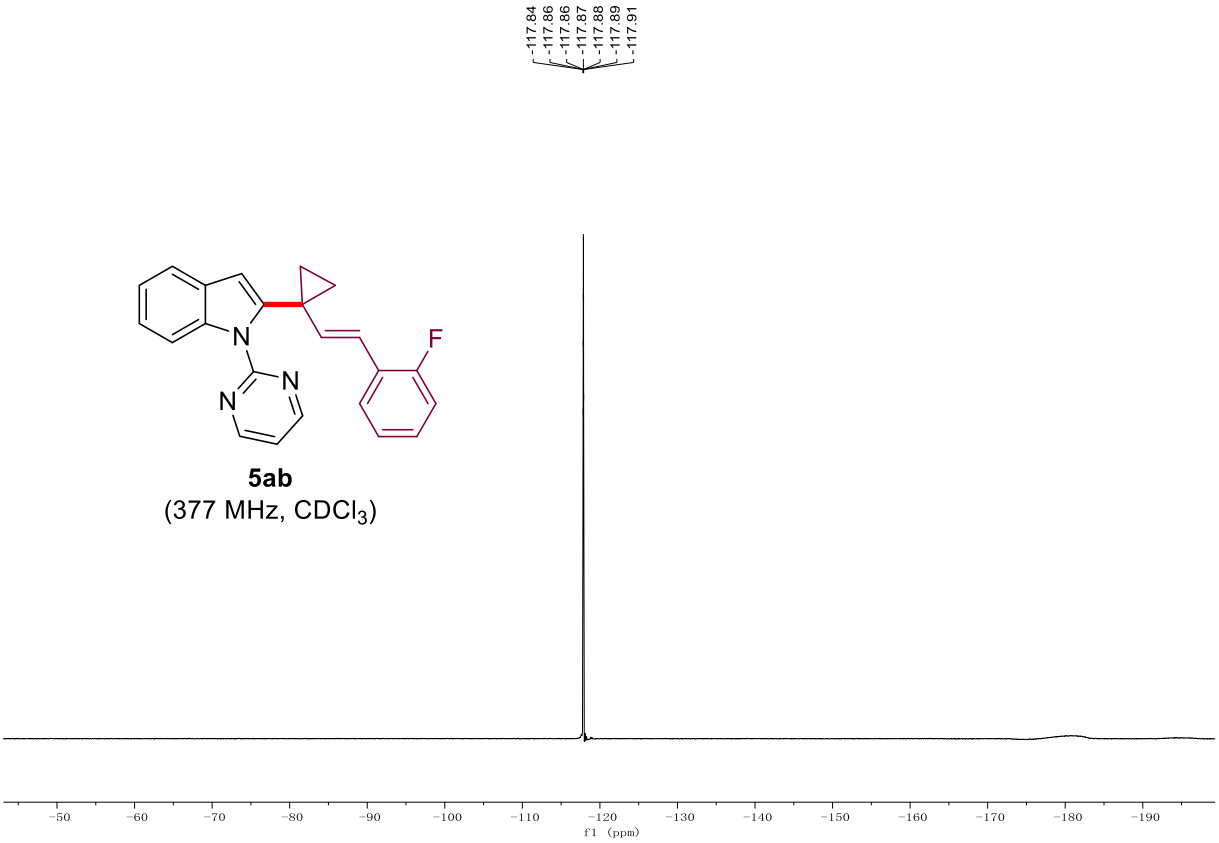


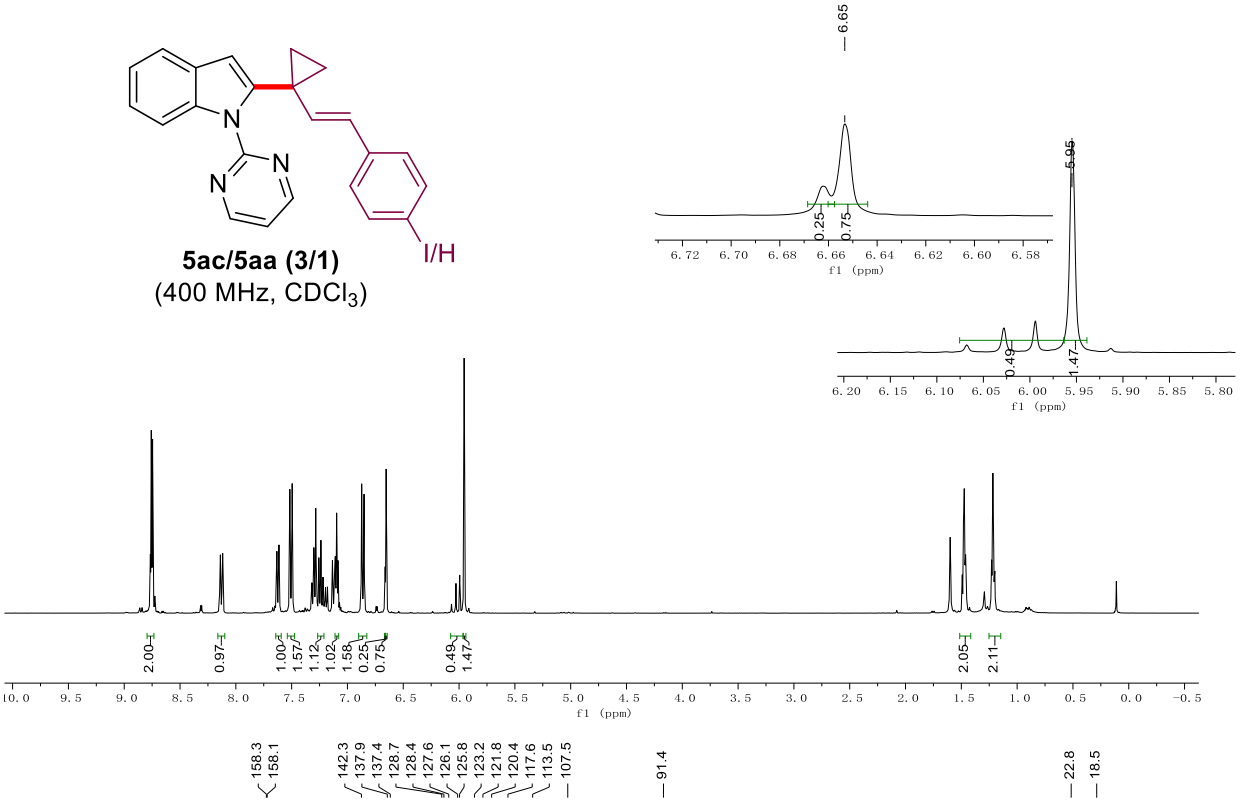
5ra'
(300 MHz, $CDCl_3$)

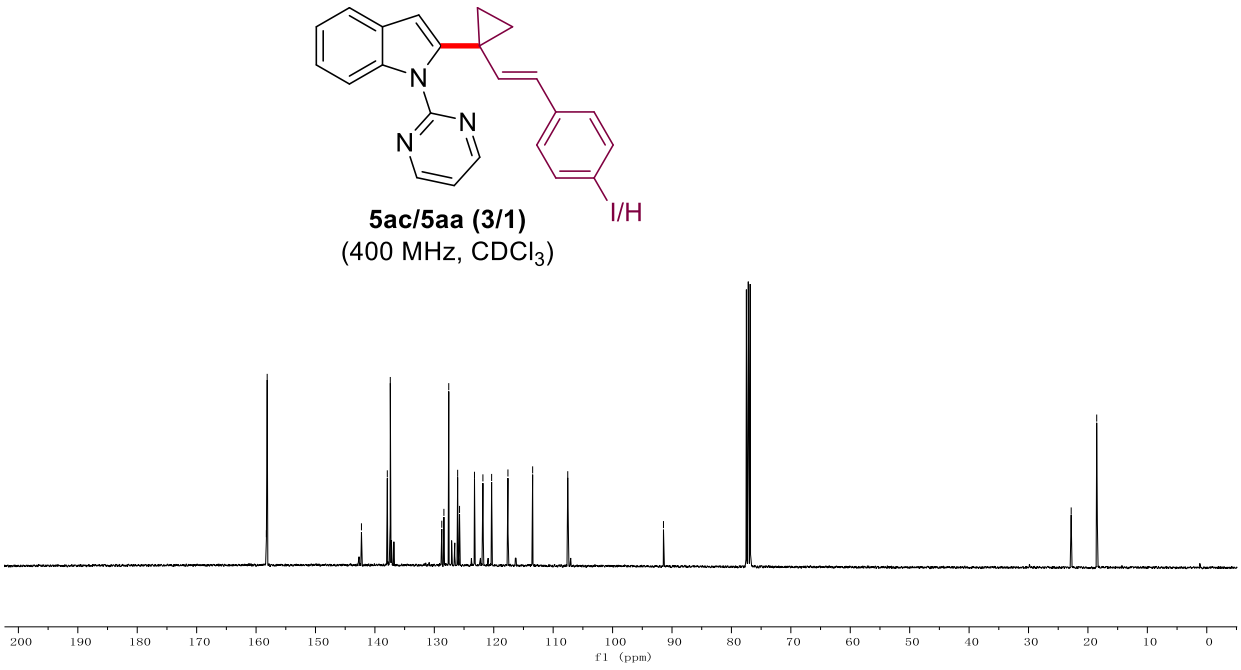

169.9
158.1
158.0
145.8
140.5
137.0
136.4
129.4
128.7
128.0
125.9
122.9
121.3
118.4
117.8
114.9
112.5
110.7
44.6
39.5
38.7
24.4
23.4
23.1
AcHN
Me
Ph
N
N
N
5ra'
(101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

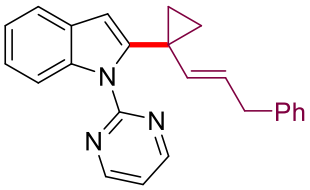

F
N
N
N
5ab
(300 MHz, CDCl3)
2.02
1.02
1.03
3.12
2.09
2.08
1.03
2.00
2.01
2.06
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.1
158.6
158.3
158.1
142.5
139.8
139.7
137.2
128.8
127.7
127.7
127.4
127.4
125.7
125.6
123.9
123.9
123.2
121.8
120.3
119.8
119.8
117.6
115.7
115.5
113.5
107.5
23.1
18.5
F
N
N
N
5ab
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

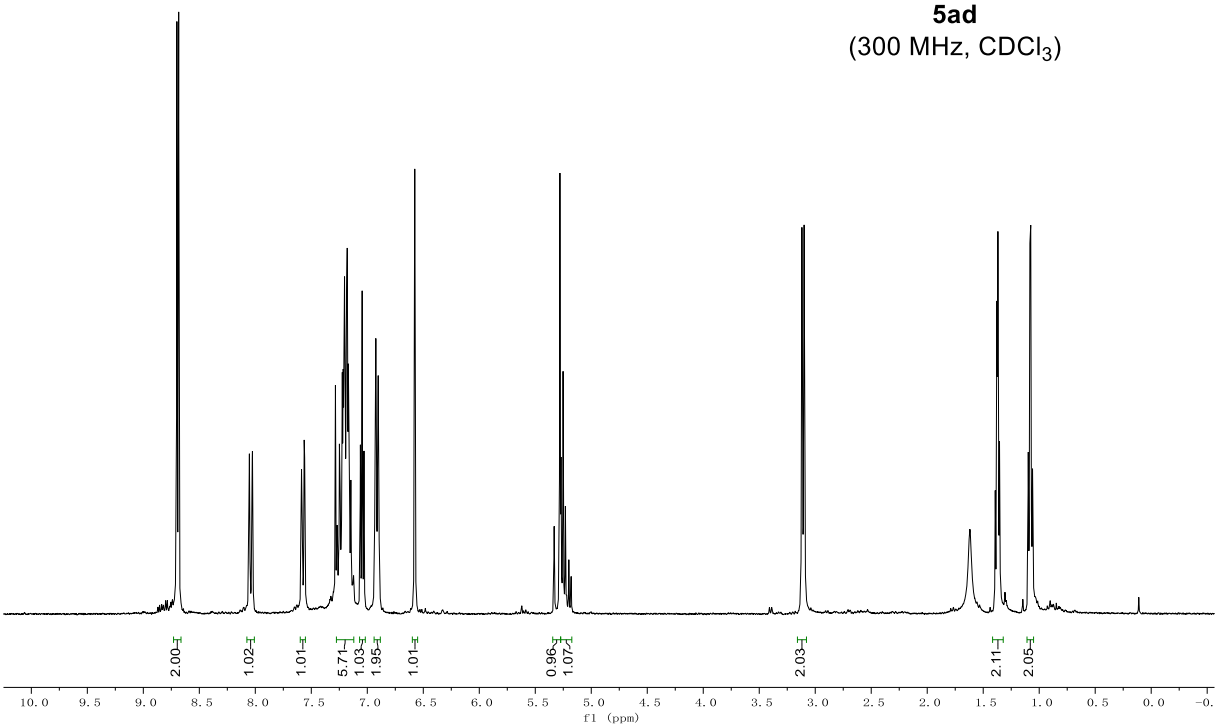

-117.84
-117.86
-117.86
-117.87
-117.88
-117.89
-117.91
F
N
N
N
5ab
(377 MHz, CDCl3)
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

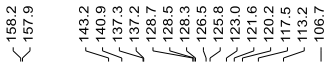

I/H
5ac/5aa (3/1)
(400 MHz, CDCl3)
6.65
5.95
0.25
0.75
0.49
1.47
2.00
0.97
1.00
1.57
1.12
1.02
1.58
0.25
0.75
0.49
1.47
2.05
2.11
f1 (ppm)
158.3
158.1
142.3
137.9
137.4
128.7
128.4
127.6
126.1
125.8
123.2
121.8
120.4
117.6
113.5
107.5
91.4
22.8
18.5

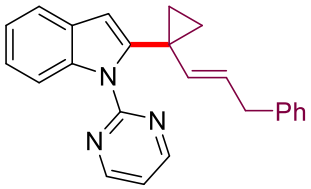

I/H
5ac/5aa (3/1)
(400 MHz, CDCl3)
f1 (ppm)



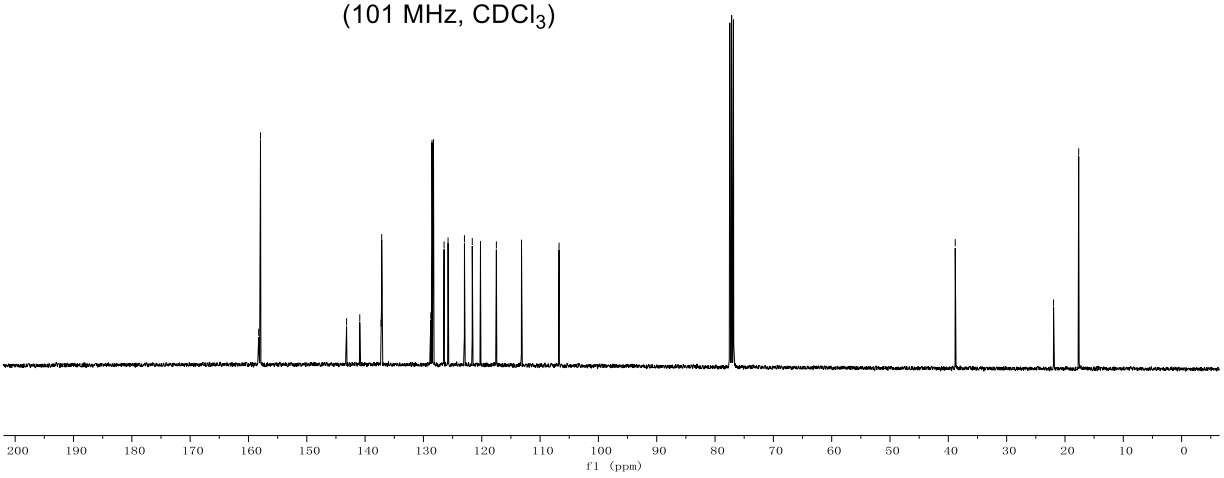
5ad
(300 MHz, $CDCl_3$)

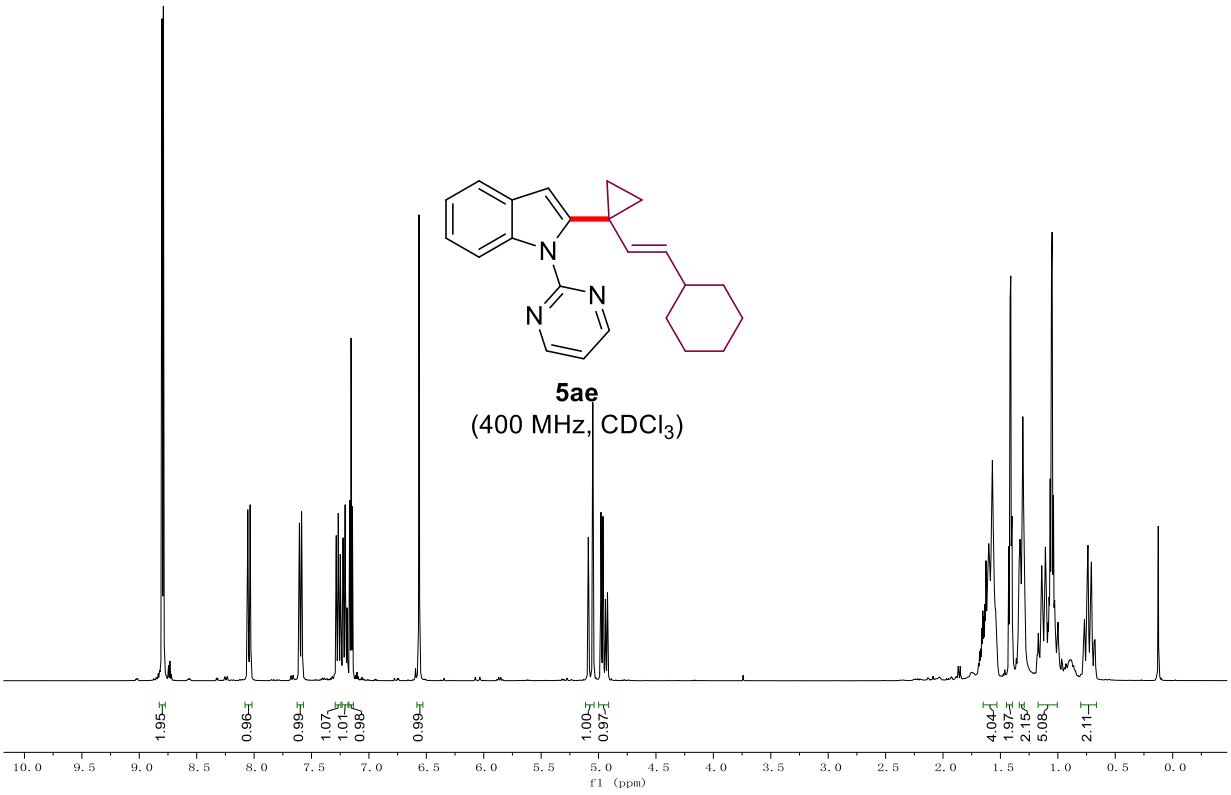


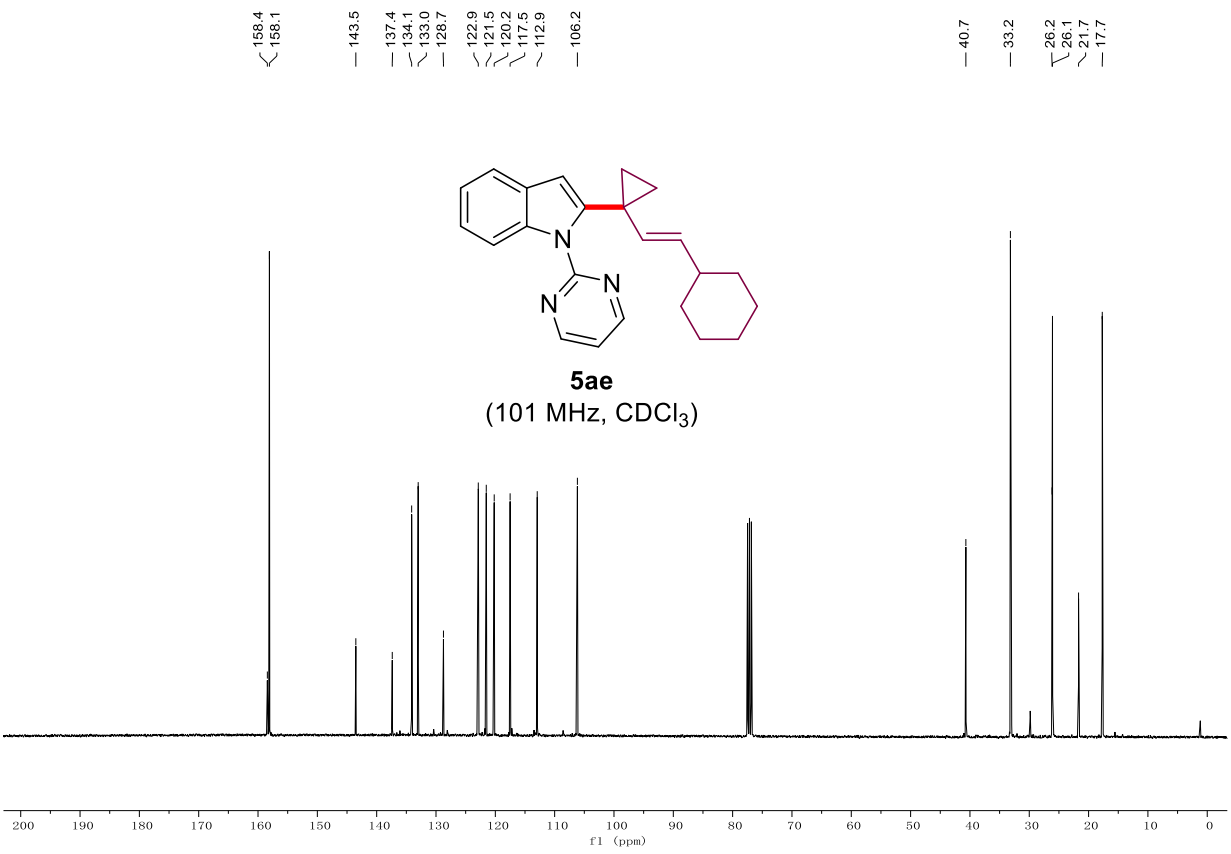


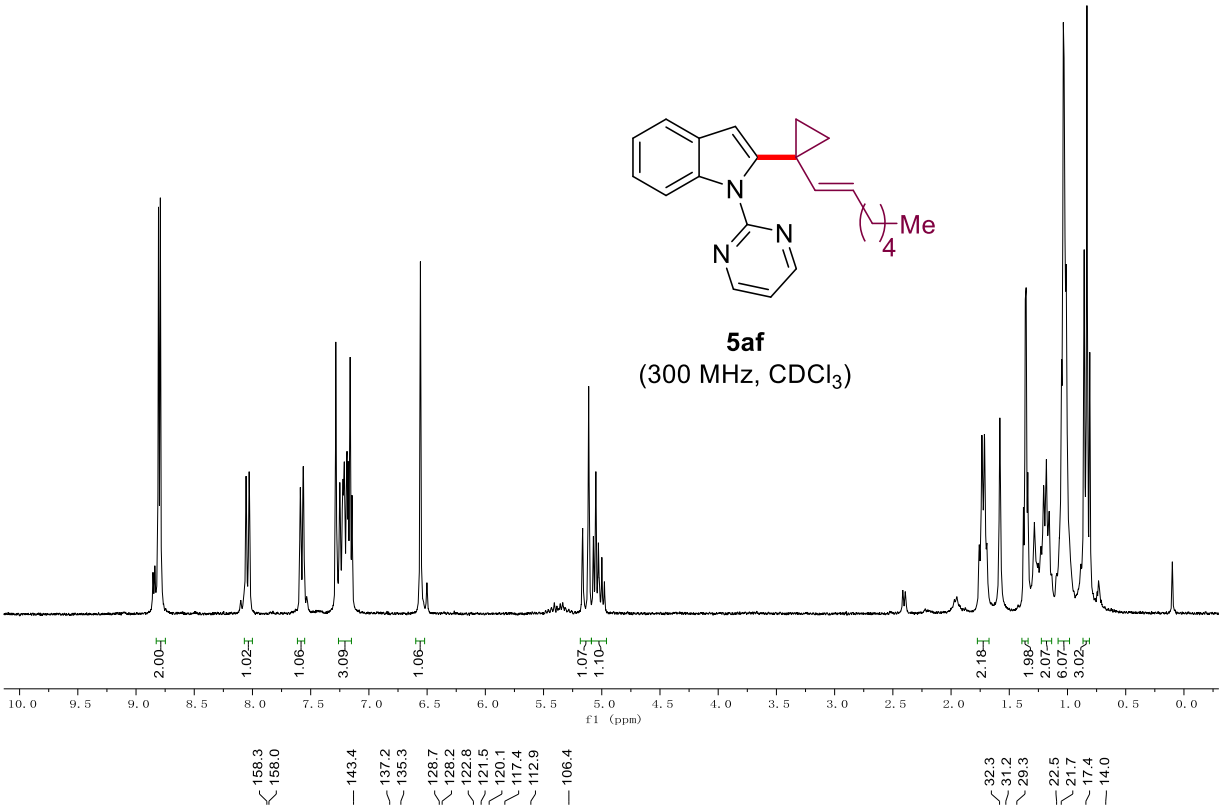


5ad
(101 MHz, $CDCl_3$)

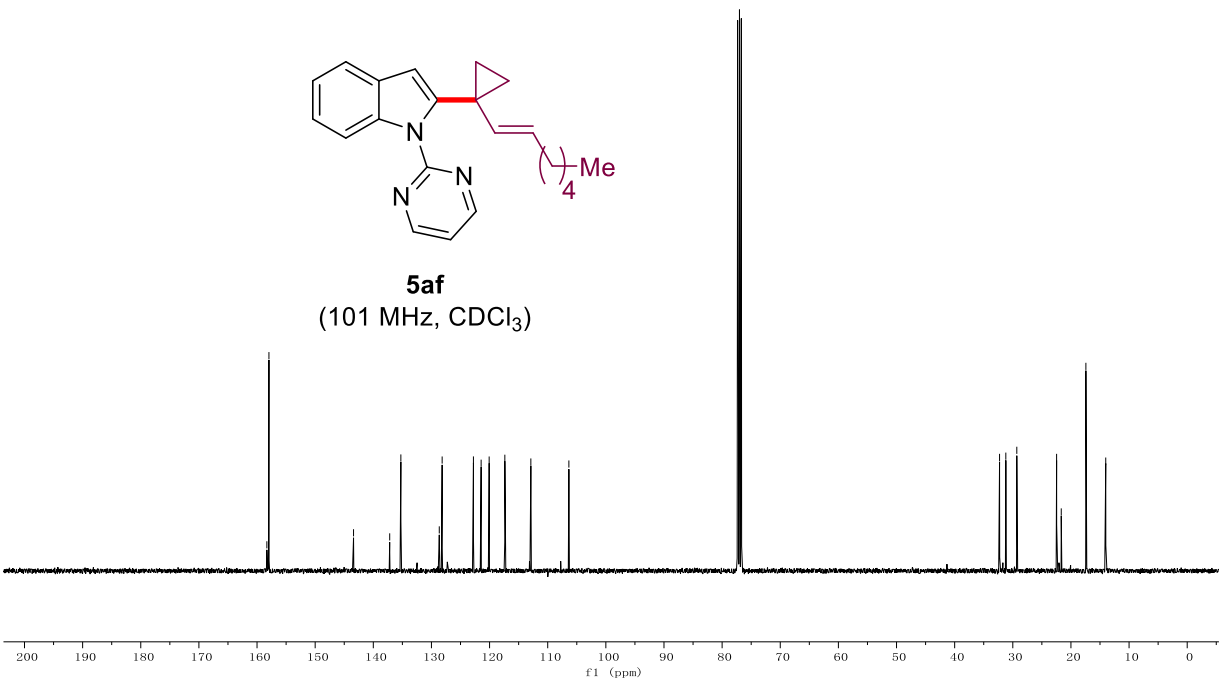



5ae
(400 MHz, CDCl3)
1.95
0.96
0.99
1.07
1.01
0.98
0.99
1.00
0.97
4.04
1.97
2.15
5.08
2.11
f1 (ppm)

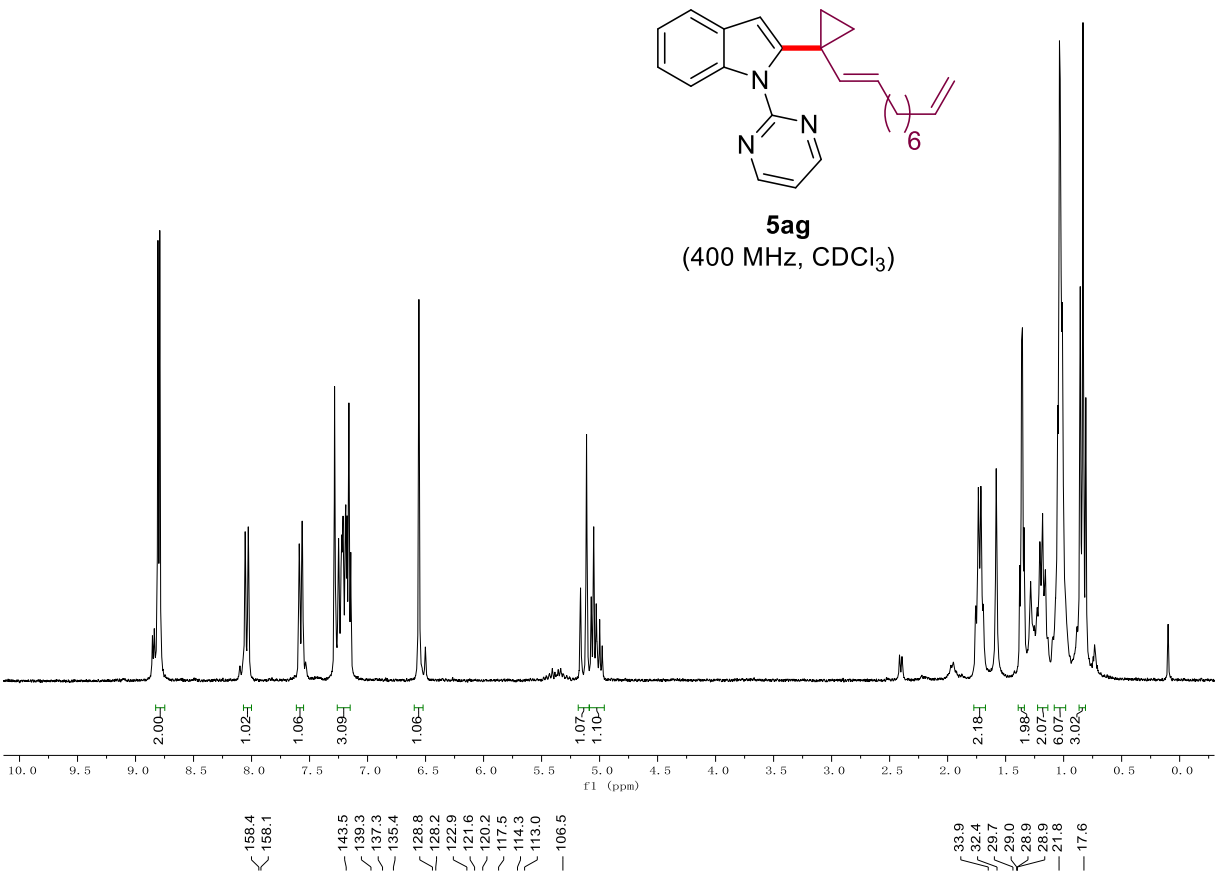

5ae
(101 MHz, CDCl3)
158.4
158.1
143.5
137.4
134.1
133.0
128.7
122.9
121.5
120.2
117.5
112.9
106.2
40.7
33.2
26.2
26.1
21.7
17.7
f1 (ppm)



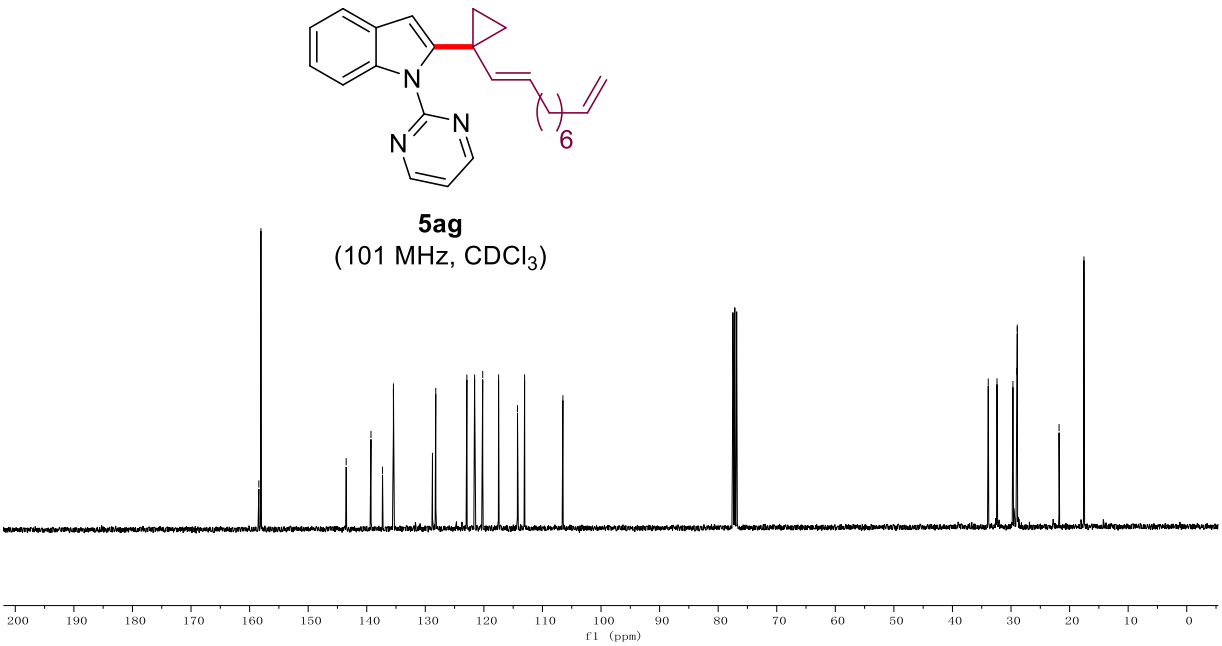
5af
(300 MHz, $CDCl_3$)



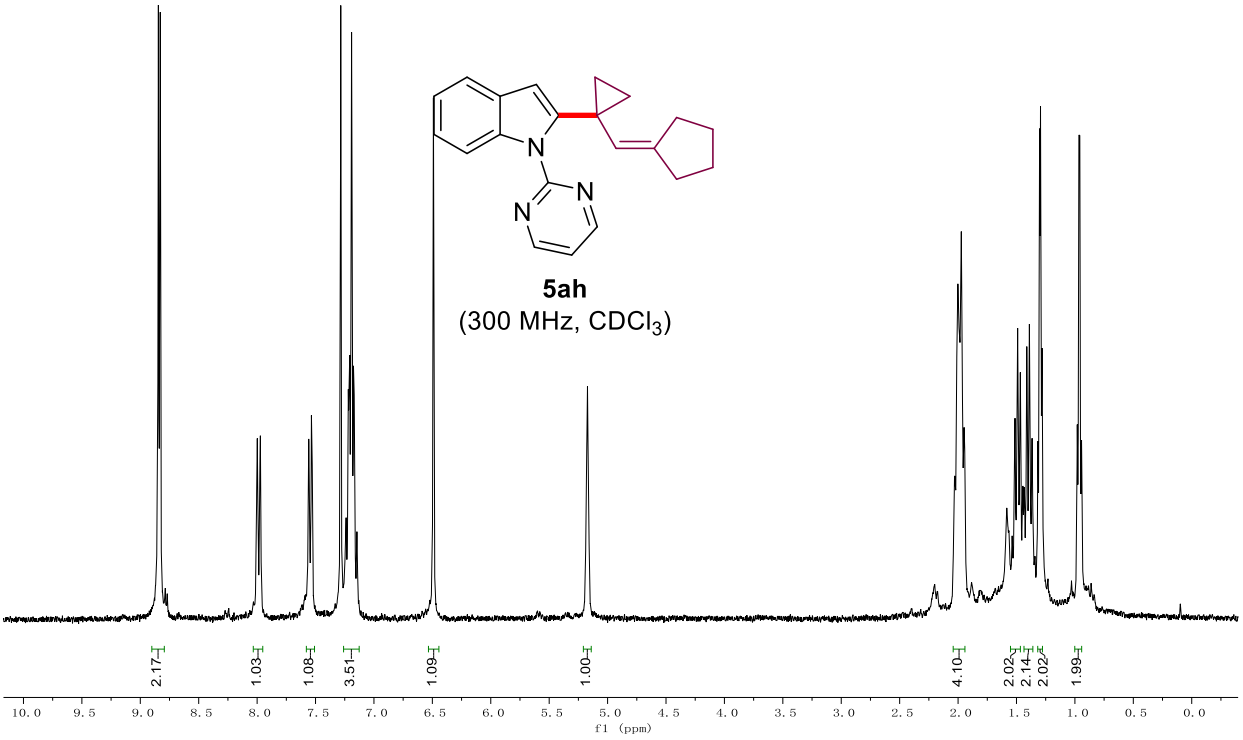
5af
(101 MHz, $CDCl_3$)

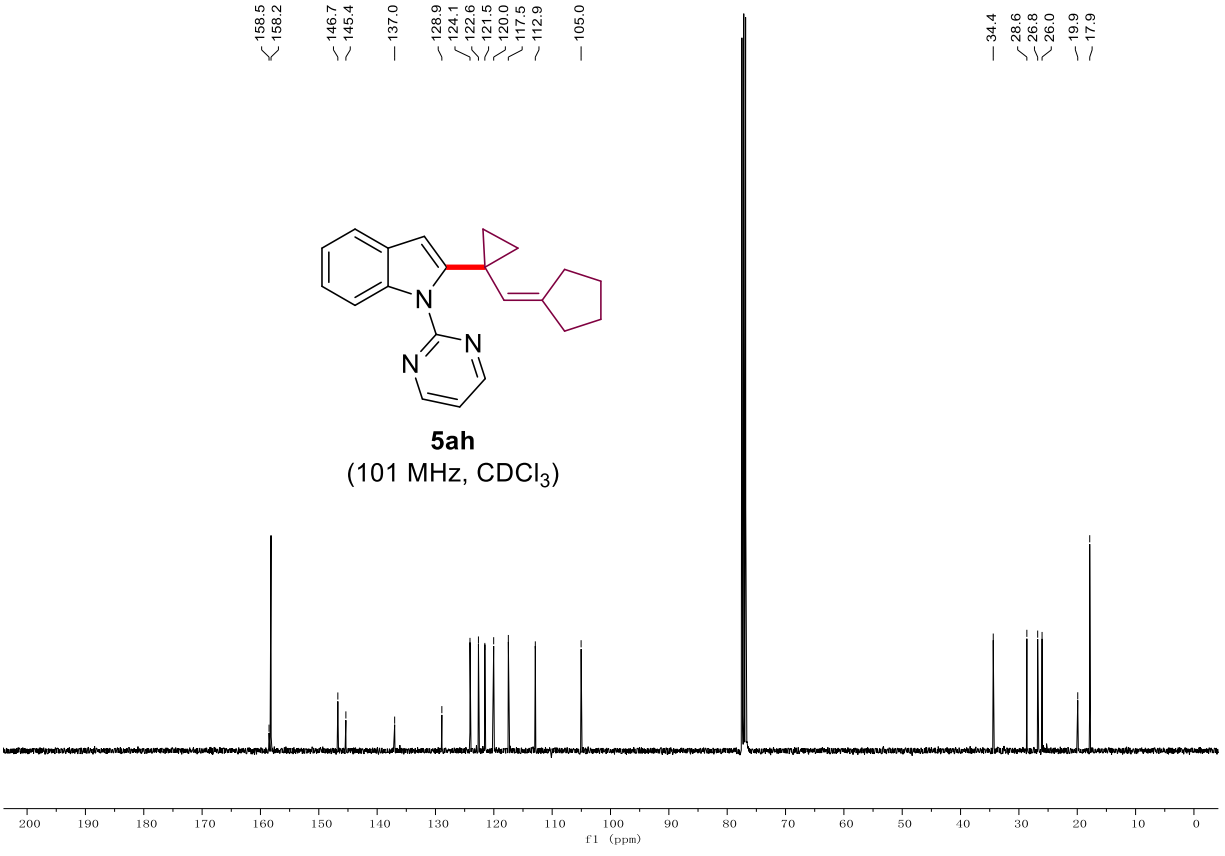


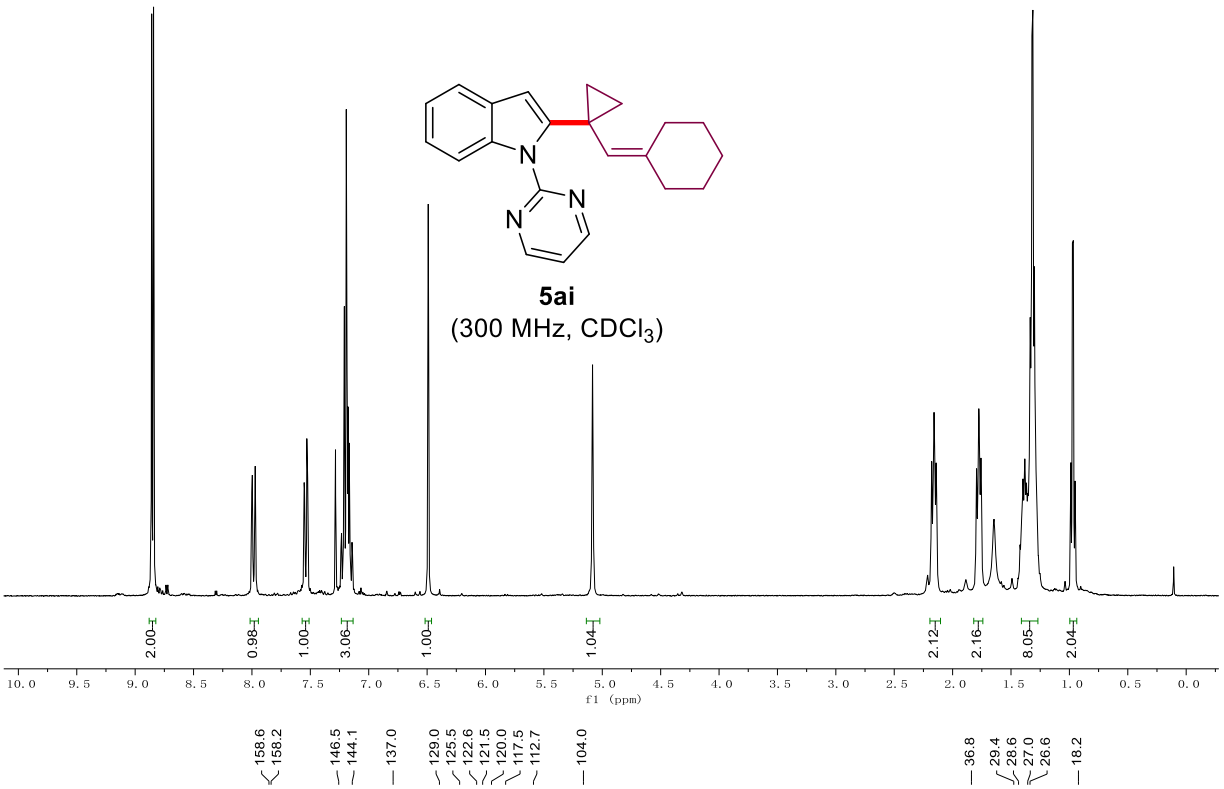
5ag
(400 MHz, $CDCl_3$)



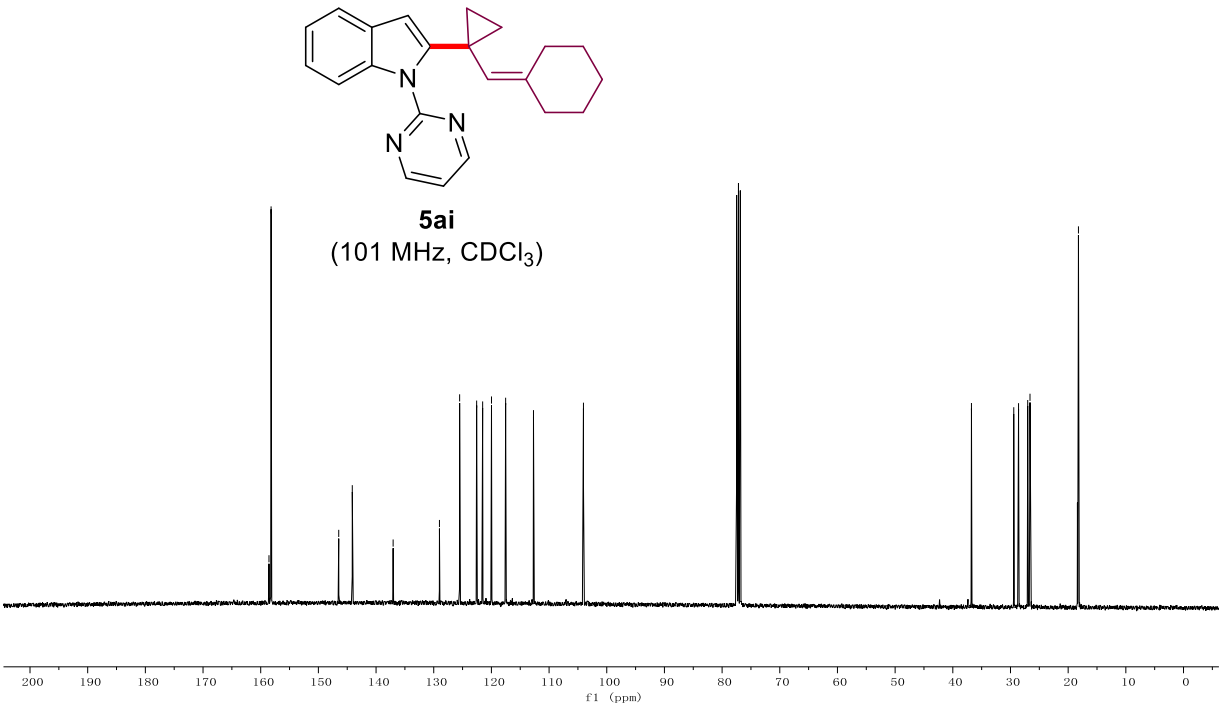
5ag
(101 MHz, $CDCl_3$)


5ah
(300 MHz, CDCl3)
2.17
1.03
1.08
3.51
1.09
1.00
4.10
2.02
2.14
2.02
1.99
f1 (ppm)

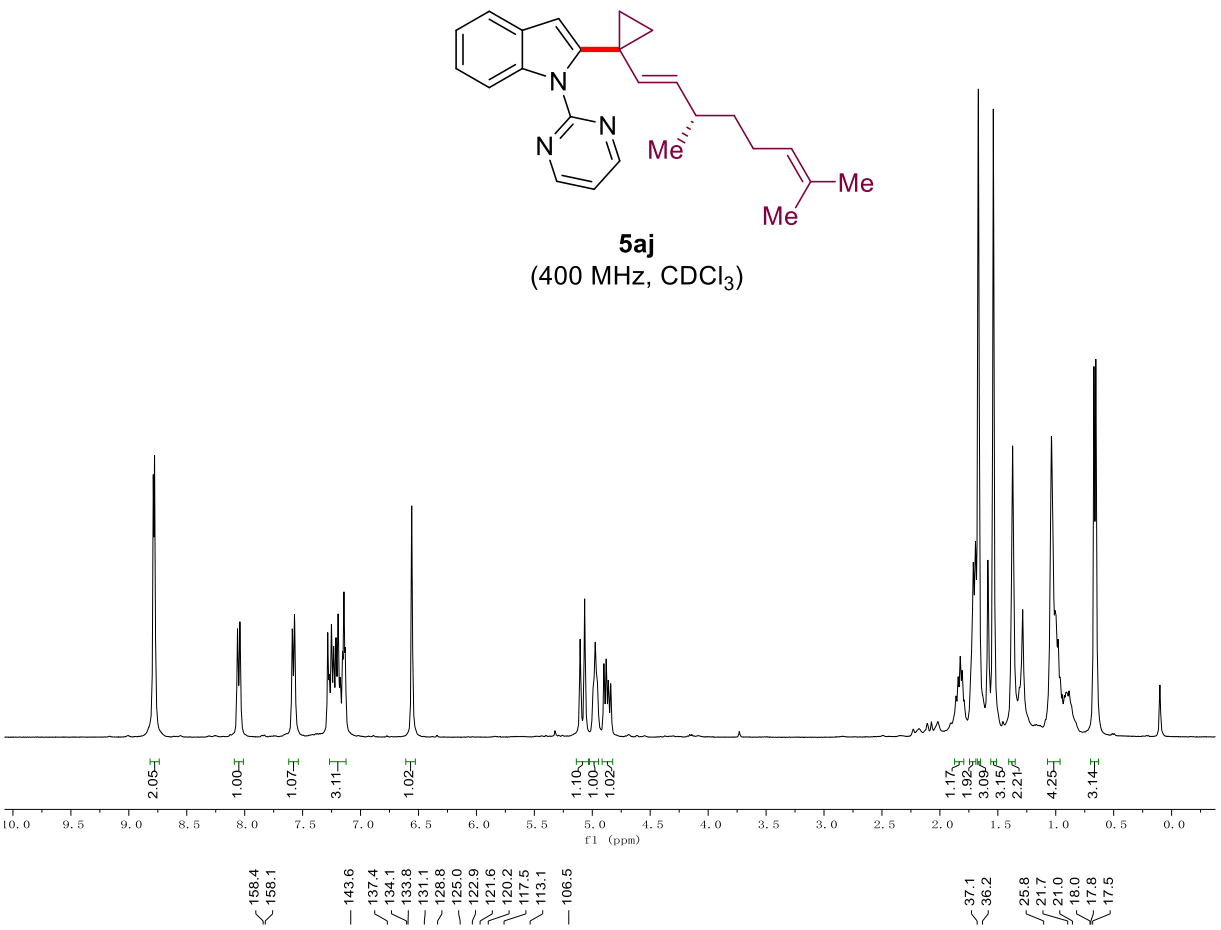

158.5
158.2
146.7
145.4
137.0
128.9
124.1
122.6
121.5
120.0
117.5
112.9
105.0
34.4
28.6
26.8
26.0
19.9
17.9
5ah
(101 MHz, CDCl3)
f1 (ppm)



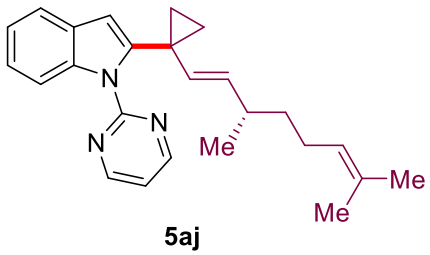
5ai
(300 MHz, $CDCl_3$)



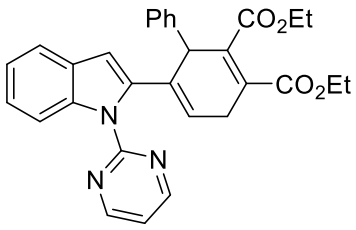
5ai
(101 MHz, $CDCl_3$)



5aj
(400 MHz, $CDCl_3$)

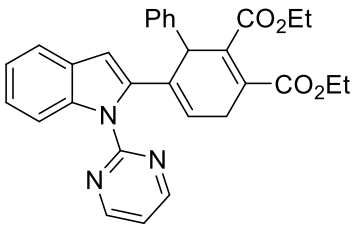


5aj
(400 MHz, $CDCl_3$)



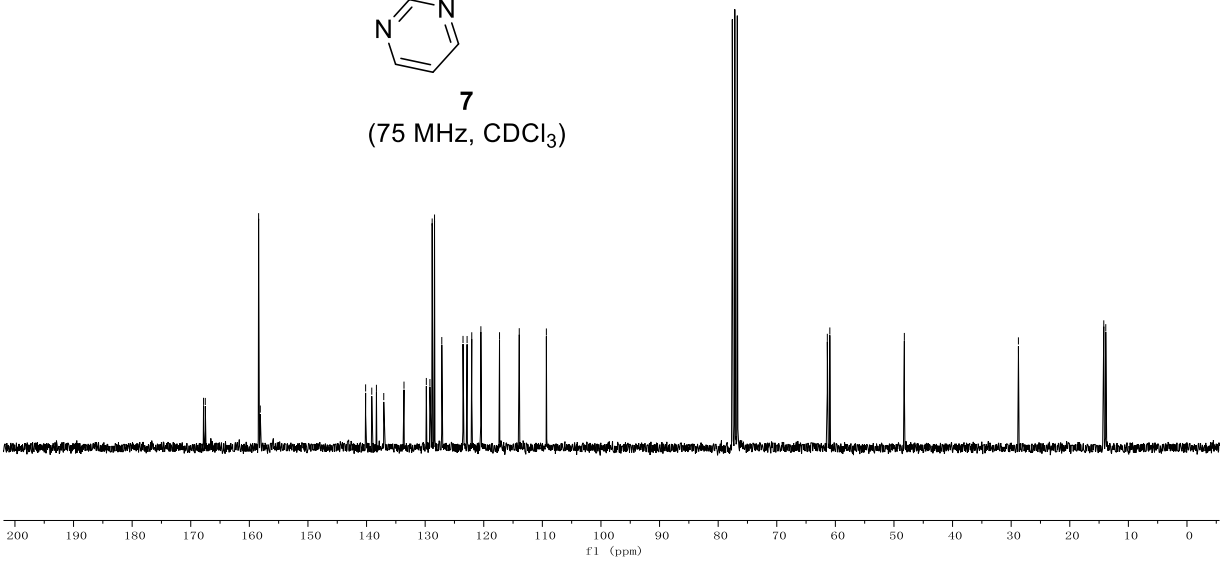
7

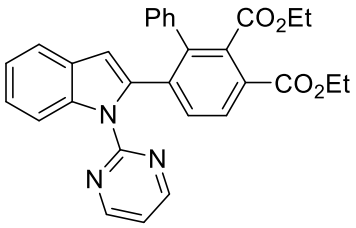
(300 MHz, $CDCl_3$)



7

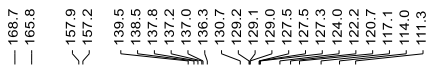
(75 MHz, $CDCl_3$)

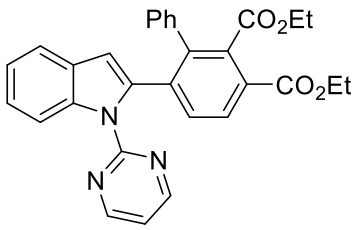




8

(300 MHz, $CDCl_3$)





8

(101 MHz, $CDCl_3$)