

Supporting Information

Palladium/GF-Phos-Catalyzed Asymmetric Carbenylative Amination to Access Chiral Pyrrolidines and Piperidines

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Contents

1. General Information.....	S2
2. Optimization of Reaction Conditions	S3
3. General Procedure for the Synthesis of Substrates 1, 4.....	S6
4. General Procedure for the Synthesis of Products 3, 5	S12
5. Gram-scale Reaction and Synthetic Applications.....	S45
6. Nonlinear Effect Study	S48
7. References.....	S49
8. X-ray Single Crystal Data for Compound 3ac.....	S50
9. ¹ H, ¹³ C, ¹⁹ F NMR Spectra.....	S51

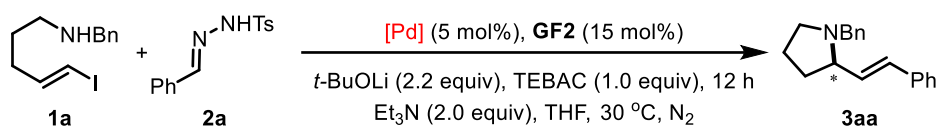
1. General Information

¹H NMR spectra, ¹³C NMR spectra and ¹⁹F NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl₃. All signals are reported in parts per million (ppm), and were referenced to CDCl₃ (δ 7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) as the internal standard. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet), coupling constant (Hz) and integration. HRMS analysis was performed on a Q-TOF mass analyzer using the ESI ionization method. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The *er* value was determined by HPLC with a chiral stationary phase using a Chiralpak AD-H, OD-H, OJ-H. All samples tested by chiral stationary phase HPLC were dissolved in *n*-hexane/isopropanol.

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in sealed tube with magnetic stirring. All commercial materials were used without further purification. 2-Methyltetrahydrofuran (anhydrous) was purchased from Energy Chemical. Visualization of the developed chromatogram was performed by UV light, staining with iodine (dispersed in silica gel), or by KMnO₄ stain. Flash column chromatography was performed over silica gel (300-400 mesh, purchased from Yantai, China). Substrates (*E*)-vinyl iodides **1**, **4**^[1-3], *N*-tosylhydrazones **2**^[4] were synthesized according to the literature method.

2. Optimization of Reaction Conditions

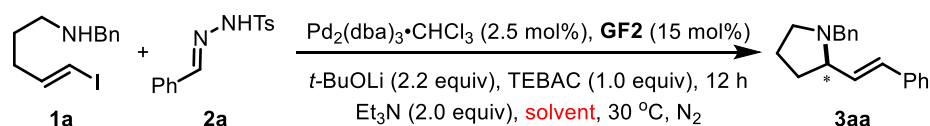
2.1 Table S1. Optimization of palladium catalyst.^a



entry	[Pd]	yield (%) ^b	<i>er</i> ^c
1	Pd ₂ (dba) ₃	77	91.5:8.5
2	Pd ₂ (dba) ₃ •CHCl ₃	75	92:8
3	Pd(dba) ₂	86	89.5:10.5
4	[Pd(C ₃ H ₅)Cl] ₂	80	91.5:8.5
5	Pd(OAc) ₂	82	85:15
6	PdBr ₂	78	88:12
7	PdI ₂	74	88.5:11.5
8	Pd(TFA) ₂	81	89:11
9	Pd(acac) ₂	89	86.5:13.5

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.16 mmol), [Pd] (5 mol%), **GF2** (15 mol%), *t*-BuOLi (2.2 equiv), TEAC (1.0 equiv), Et₃N (2.0 equiv) in 0.1 M THF at 30 °C for 12 h. ^bDetermined by GC analysis with *n*-tetradecane as an internal standard. ^cThe *er* value was determined by HPLC.

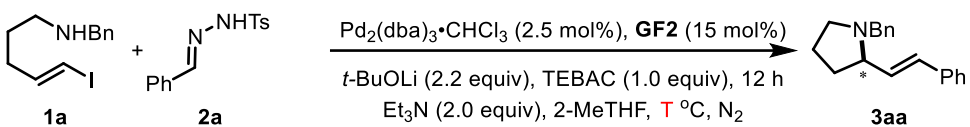
2.2 Table S2. Optimization of solvent.^a



entry	solvent	yield (%) ^b	<i>er</i> ^c
1	THF	75	92:8
2	2-MeTHF	89	93:7
3	1,4-Dioxane	38	88.5:11.5
4	MTBE	28	93:7
5	DMF	90	80:20
6	MeOH	23	86.5:13.5
7	DCE	38	79.5:20.5
8	Toluene	23	92.5:7.5
9	DMSO	71	66.5:33.5
10	CH ₃ CN	53	80:20
11	EtOAc	67	93:7

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.16 mmol), Pd₂(dba)₃•CHCl₃ (2.5 mol%), **GF2** (15 mol%), *t*-BuOLi (2.2 equiv), TEAC (1.0 equiv), Et₃N (2.0 equiv) in 0.1 M solvent at 30 °C for 12 h. ^bDetermined by GC analysis with *n*-tetradecane as an internal standard. ^cThe *er* value was determined by HPLC. THF = Tetrahydrofuran. MTBE = methyl *tert*-butyl ether. DMF = *N,N*-Dimethylformamide. DCE = 1,2-Dichloroethane. DMSO = Dimethyl sulfoxide.

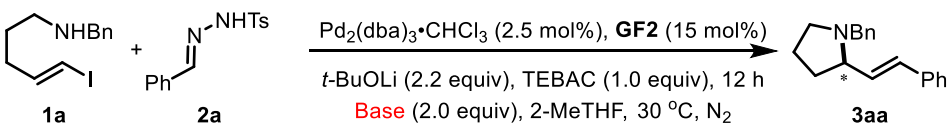
2.3 Table S3 Optimization of temperature.^a



entry	T (°C)	yield (%) ^b	er ^c
1	15	26	94.5:5.5
2	30	89	93:7
3	45	71	90:10
4	60	63	88:12

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.16 mmol), Pd₂(dba)₃·CHCl₃ (2.5 mol%), **GF2** (15 mol%), *t*-BuOLi (2.2 equiv), TEAC (1.0 equiv), Et₃N (2.0 equiv) in 0.1 M 2-MeTHF for 12 h. ^bDetermined by GC analysis with *n*-tetradecane as an internal standard. ^cThe *er* value was determined by HPLC.

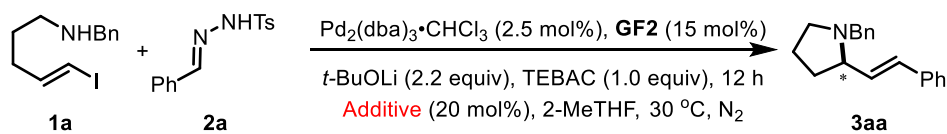
2.4 Table S4. Optimization of base.^a



entry	Base	yield (%) ^b	er ^c
1	None	83	93:7
2	Et ₃ N	89	93:7
3	DABCO	76	94:6
4	DIPEA	86	93:7
5	PhNHMe	91	92.5:7.5
6	PhNMe ₂	83	92.5:7.5
7	KOH	89	93:7
8	KHCO ₃	70	93.5:6.5
9	NaHCO ₃	83	93:7
10	Na ₂ CO ₃	83	92:8
11	Cs ₂ CO ₃	93	92.5:7.5
12	CsOAc	69	88:12
13 ^d	None	84	91:9

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.16 mmol), Pd₂(dba)₃·CHCl₃ (2.5 mol%), **GF2** (15 mol%), *t*-BuOLi (2.2 equiv), TEAC (1.0 equiv), Base (2.0 equiv) in 0.1 M 2-MeTHF at 30 °C for 12 h. ^bDetermined by GC analysis with *n*-tetradecane as an internal standard. ^cThe *er* value was determined by HPLC. ^dWithout TEAC. DABCO = Triethylenediamine. DIPEA = *N,N*-Diisopropylethylamine.

2.5 Table S5. Optimization of additive.^a

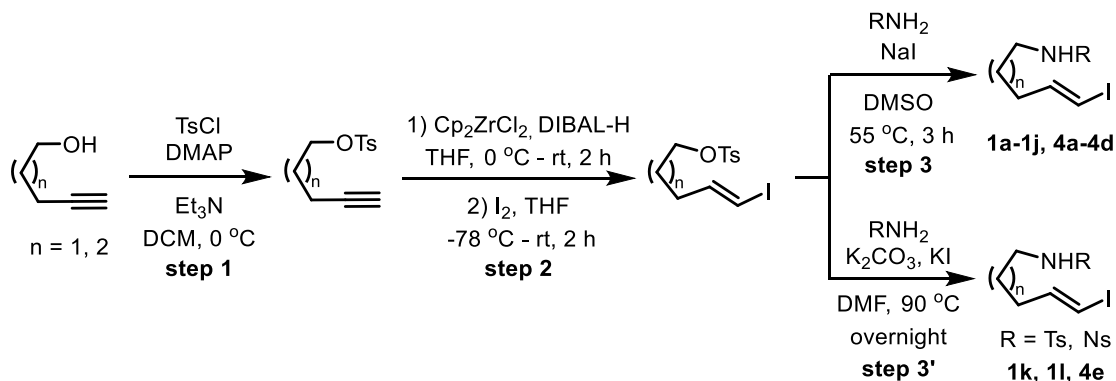


entry	Additive	yield (%) ^b	<i>er</i> ^c
1	None	83	93:7
2	AcOH	71	93:7
3	TsOH	64	93:7
4	Sc(OTf) ₃	57	92.5:7.5
5	Zn(OTf) ₂	56	92.5:7.5
6	AgOTf	87	93:7
7	AgClO ₄	76	92.5:7.5
8	AgPF ₆	78	93:7
9	AgBF ₄	75	93:7
10	AgF	77	94:6
11	Ag ₂ SO ₄	79	94:6
12	Ag ₂ CO ₃	81	94.5:5.5
13 ^d	Ag ₂ CO ₃	77	94.5:5.5
14 ^e	Ag ₂ CO ₃	67	92.5:7.5

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.16 mmol), Pd₂(dba)₃·CHCl₃ (2.5 mol%), **GF2** (15 mol%), *t*-BuOLi (2.2 equiv), TEBAC (1.0 equiv), additive (20 mol%) in 0.1 M 2-MeTHF at 30 °C for 12 h. ^bDetermined by GC analysis with *n*-tetradecane as an internal standard. ^cThe *er* value was determined by HPLC. ^d15 mol% Ag₂CO₃. ^e30 mol% Ag₂CO₃.

3. General Procedure for the Synthesis of Substrates 1, 4

The materials **1** and **4** were prepared according to the known synthetic route in literature.^[1-3]



Step 1: To a solution of alkynol (1.0 equiv), Et_3N (1.5 equiv), and 4-(dimethylamino) pyridine (5 mol%) in DCM (0.5 M) at $0\text{ }^\circ\text{C}$ was added *p*-toluenesulfonyl chloride (1.3 equiv) in three portions. The reaction mixture was stirred at room temperature until the starting material was no longer detectable by thin layer chromatography (2 h). The reaction mixture was added aqueous NaOH solution (1 M) and vigorously stirred for 30 min at room temperature, and then was extracted with DCM . The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel chromatography using $\text{PE/EA} = 20/1$ as the eluent to afford the desired product.

Step 2: A flame-dried flask equipped with a stir bar under N_2 was charged with Cp_2ZrCl_2 (1.2 equiv) in dry THF to give a 2.5 M suspension. The reaction mixture was kept in ice bath, DIBAL-H (1.22 equiv) was added dropwise and stirred for 1 h at room temperature. Then the reaction mixture was cooled to $0\text{ }^\circ\text{C}$ again and the alkyne obtained above in THF was added dropwise and stirred for 1 h at room temperature. After cooling to $-78\text{ }^\circ\text{C}$, iodine (1.4 equiv) in THF (1 M) was added dropwise and the reaction mixture was stirred for 3 h at room temperature. Upon completion, the reaction was quenched with water at $0\text{ }^\circ\text{C}$ and then added aqueous NaOH solution (3 M). The mixture was extracted with EtOAc and washed with $\text{Na}_2\text{S}_2\text{O}_3$. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel

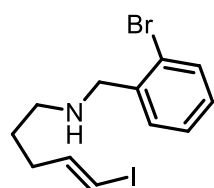
chromatography using PE/EA = 20/1 as the eluent to afford the desired vinyl iodide.

Step 3: To a solution of the above obtained vinyl iodide (1.0 equiv), NaI (0.055 equiv) in DMSO (0.3 M) was added corresponding primary amine (1.5 equiv). The mixture was heated to 55 °C until the starting material was no longer detectable by thin layer chromatography (3-6 h). The reaction mixture was cooled to room temperature and quenched with a saturated solution of NH₄Cl. Then the mixture was extracted with EtOAc and washed with water. The organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by silica gel chromatography using PE/EA/Et₃N as the eluent to afford the desired product **1a-1j**, **4a-4d**.

Step 3': To a solution of the above obtained vinyl iodide (1.0 equiv), K₂CO₃ (2 equiv), KI (0.1 equiv) in DMF (0.5 M) was added corresponding primary amine (1.5 equiv). The mixture was heated to 90 °C and stirred overnight. The reaction mixture was cooled to room temperature and quenched with a saturated solution of NH₄Cl. Then the mixture was extracted with EtOAc and washed with water. The organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by silica gel chromatography using PE/EA/DCM as the eluent to afford the desired product **1k**, **1l**, **4e**.

Characterization of structurally novel substrates **1b-1l**, **4c-4e**

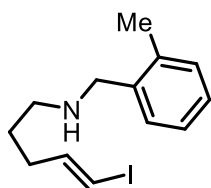
(E)-N-(2-bromobenzyl)-5-iodopent-4-en-1-amine (1b):



Orange oil.

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.11 (td, *J* = 7.7, 1.6 Hz, 1H), 6.49 (dt, *J* = 14.3, 7.2 Hz, 1H), 5.99 (d, *J* = 14.4 Hz, 1H), 3.83 (s, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 2.15 – 2.07 (m, 2H), 1.64 – 1.59 (m, 2H), 1.58 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.9, 139.1, 132.7, 130.2, 128.5, 127.3, 123.8, 74.9, 53.6, 48.0, 33.6, 28.5. HRMS (ESI) calculated for C₁₂H₁₆BrIN [(M+H)⁺]: 379.9505, found: 379.9505.

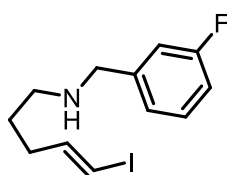
(E)-5-iodo-N-(2-methylbenzyl)pent-4-en-1-amine (1c):



Dark orange oil.

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.26 (m, 1H), 7.23 – 7.15 (m, 3H), 6.54 (dt, $J = 14.3, 7.1$ Hz, 1H), 6.01 (d, $J = 14.4$ Hz, 1H), 3.77 (s, 2H), 2.69 (t, $J = 7.1$ Hz, 2H), 2.37 (s, 3H), 2.20 – 2.09 (m, 2H), 1.68 – 1.58 (m, 2H), 1.38 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 138.2, 136.1, 130.2, 128.2, 126.9, 125.8, 74.7, 51.5, 48.7, 33.7, 28.6, 18.9. HRMS (ESI) calculated for $\text{C}_{13}\text{H}_{19}\text{IN}$ [(M+H) $^+$]: 316.0557, found: 316.0551.

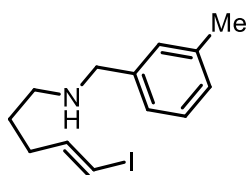
(E)-N-(3-fluorobenzyl)-5-iodopent-4-en-1-amine (1d):



Brown oil.

^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.23 (m, 1H), 7.07 (d, $J = 7.7$ Hz, 1H), 7.05 – 7.00 (m, 1H), 6.93 (td, $J = 8.4, 2.2$ Hz, 1H), 6.50 (dt, $J = 14.3, 7.1$ Hz, 1H), 6.00 (d, $J = 14.4$ Hz, 1H), 3.76 (s, 2H), 2.61 (t, $J = 7.1$ Hz, 2H), 2.14 – 2.08 (m, 2H), 1.64 – 1.54 (m, 2H), 1.46 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.9 (d, $J = 244.2$ Hz), 145.9, 143.1 (d, $J = 7.0$ Hz), 129.7 (d, $J = 8.1$ Hz), 123.5 (d, $J = 2.8$ Hz), 114.7 (d, $J = 21.0$ Hz), 113.7 (d, $J = 21.1$ Hz), 74.8, 53.3, 53.2, 48.3, 33.7, 28.6. ^{19}F NMR (377 MHz, CDCl_3) δ -113.5. HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{16}\text{FIN}$ [(M+H) $^+$]: 320.0306, found: 320.0300.

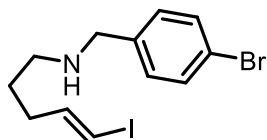
(E)-5-iodo-N-(3-methylbenzyl)pent-4-en-1-amine (1e):



Orange oil.

^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.20 (m, 1H), 7.16 – 7.07 (m, 2H), 7.07 (d, $J = 7.5$ Hz, 1H), 6.52 (dt, $J = 14.3, 7.2$ Hz, 1H), 6.00 (dt, $J = 14.3, 1.4$ Hz, 1H), 3.74 (s, 2H), 2.63 (t, $J = 7.1$ Hz, 2H), 2.35 (s, 3H), 2.15 – 2.09 (m, 2H), 1.64 – 1.58 (m, 2H), 1.34 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 140.2, 138.0, 128.8, 128.2, 127.6, 125.1, 74.8, 53.9, 48.4, 33.7, 28.6, 21.4. HRMS (ESI) calculated for $\text{C}_{13}\text{H}_{19}\text{IN}$ [(M+H) $^+$]: 316.0557, found: 316.0549.

(E)-N-(4-bromobenzyl)-5-iodopent-4-en-1-amine (1f):

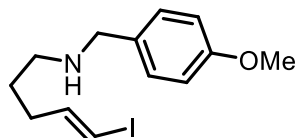


Orange oil.

^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.2$ Hz, 2H), 6.49 (dt, $J = 14.3, 7.1$ Hz, 1H), 5.99 (dt, $J =$

14.4, 1.4 Hz, 1H), 3.72 (s, 2H), 2.60 (t, $J = 7.1$ Hz, 2H), 2.14 – 2.07 (m, 2H), 1.64 – 1.54 (m, 2H), 1.51 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 139.3, 131.4, 129.7, 120.6, 74.8, 53.2, 48.3, 33.7, 28.6. HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{16}\text{BrIN}$ $[(\text{M}+\text{H})^+]$: 379.9505, found: 379.9503.

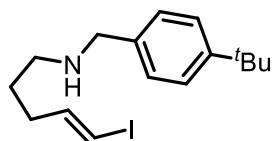
(E)-5-iodo-N-(4-methoxybenzyl)pent-4-en-1-amine (1g):



Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 7.3$ Hz, 2H), 6.86 (d, $J = 7.3$ Hz, 2H), 6.50 (dt, $J = 14.3, 7.1$ Hz, 1H), 5.99 (d, $J = 14.4$ Hz, 1H), 3.80 (s, 3H), 3.71 (s, 2H), 2.61 (t, $J = 7.1$ Hz, 2H), 2.15 – 2.07 (m, 2H), 1.63 – 1.55 (m, 2H), 1.43 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 146.0, 132.4, 129.1, 113.7, 74.7, 55.2, 53.2, 48.2, 33.7, 28.6. HRMS (ESI) calculated for $\text{C}_{13}\text{H}_{19}\text{INO}$ $[(\text{M}+\text{H})^+]$: 332.0506, found: 332.0506.

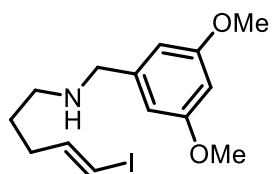
(E)-N-(4-(tert-butyl)benzyl)-5-iodopent-4-en-1-amine (1h):



Brown oil.

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 6.54 (dt, $J = 14.3, 7.2$ Hz, 1H), 6.02 (dt, $J = 14.3, 1.4$ Hz, 1H), 3.77 (s, 2H), 2.67 (t, $J = 7.1$ Hz, 2H), 2.17 – 2.11 (m, 2H), 1.67 – 1.61 (m, 2H), 1.58 (s, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.8, 146.0, 137.1, 127.8, 125.3, 74.8, 53.5, 48.4, 34.4, 33.7, 31.3, 28.6. HRMS (ESI) calculated for $\text{C}_{16}\text{H}_{25}\text{IN}$ $[(\text{M}+\text{H})^+]$: 358.1026, found: 358.1021.

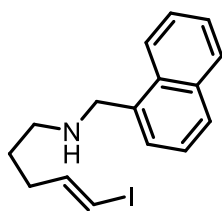
(E)-N-(3,5-dimethoxybenzyl)-5-iodopent-4-en-1-amine (1i):



Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 6.54 – 6.47 (m, 1H), 6.46 (s, 2H), 6.34 (s, 1H), 5.98 (d, $J = 14.3$ Hz, 1H), 3.77 (s, 6H), 3.69 (s, 2H), 2.60 (t, $J = 7.1$ Hz, 2H), 2.12 – 2.05 (m, 2H), 1.71 (s, 1H), 1.61 – 1.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 145.9, 142.7, 105.8, 98.8, 74.7, 55.2, 53.9, 48.2, 33.6, 28.5. HRMS (ESI) calculated for $\text{C}_{14}\text{H}_{21}\text{INO}_2$ $[(\text{M}+\text{H})^+]$: 362.0612, found: 362.0613.

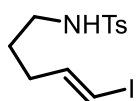
(E)-5-iodo-N-(naphthalen-1-ylmethyl)pent-4-en-1-amine (1j):



Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.3$ Hz, 1H), 7.88 (d, $J = 7.9$ Hz, 1H), 7.78 (d, $J = 7.7$ Hz, 1H), 7.56 – 7.42 (m, 4H), 6.52 (dddt, $J = 14.3, 8.7, 7.1, 1.5$ Hz, 1H), 5.98 (dq, $J = 14.4, 1.7$ Hz, 1H), 4.23 (s, 2H), 2.78 – 2.72 (m, 2H), 2.17 – 2.10 (m, 2H), 1.68 – 1.61 (m, 2H), 1.42 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 135.8, 133.7, 131.6, 128.6, 127.6, 125.9, 125.8, 125.5, 125.3, 123.5, 74.8, 51.5, 48.8, 33.6, 28.5. HRMS (ESI) calculated for $\text{C}_{16}\text{H}_{19}\text{IN}$ [(M+H) $^+$]: 352.0557, found: 352.0557.

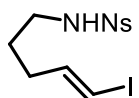
(E)-N-(5-iodopent-4-en-1-yl)-4-methylbenzenesulfonamide (1k):



Gray solid (m.p. 62-63 °C).

^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 6.37 (dt, $J = 14.4, 7.2$ Hz, 1H), 5.94 (d, $J = 14.4$ Hz, 1H), 4.76 (t, $J = 6.1$ Hz, 1H), 2.97 – 2.88 (m, 2H), 2.43 (s, 3H), 2.08 – 2.01 (m, 2H), 1.59 – 1.51 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 143.5, 136.7, 129.7, 127.0, 75.7, 42.1, 32.7, 28.1, 21.5. HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{16}\text{INNaO}_2\text{S}$ [(M+Na) $^+$]: 387.9839, found: 387.9839.

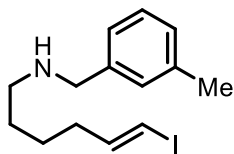
(E)-N-(5-iodopent-4-en-1-yl)-4-nitrobenzenesulfonamide (1l):



Yellow solid (m.p. 105-106 °C).

^1H NMR (400 MHz, CDCl_3) δ 8.41 – 8.33 (m, 2H), 8.09 – 8.01 (m, 2H), 6.39 (dt, $J = 14.4, 7.2$ Hz, 1H), 6.01 (dt, $J = 14.4, 1.4$ Hz, 1H), 5.04 (t, $J = 6.1$ Hz, 1H), 3.04 – 2.95 (m, 2H), 2.12 – 2.02 (m, 2H), 1.67 – 1.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 145.7, 144.3, 128.2, 124.5, 76.1, 42.3, 32.6, 28.2. HRMS (ESI) calculated for $\text{C}_{11}\text{H}_{13}\text{IN}_2\text{NaO}_4\text{S}$ [(M+Na) $^+$]: 418.9533, found: 418.9526.

(E)-N-(6-iodohex-5-en-1-yl)-3-methylaniline (4c):

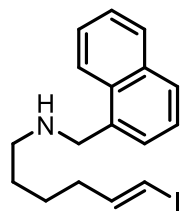


Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.19 (m, 1H), 7.14 (s, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.50 (dt, $J = 14.3, 7.1$ Hz, 1H), 5.98 (dt, $J = 14.4, 1.4$ Hz, 1H), 3.74 (s, 2H), 2.62 (t, $J = 7.0$ Hz, 2H), 2.35 (s, 3H), 2.11 – 2.02 (m, 2H), 1.56 – 1.49 (m, 2H), 1.49 – 1.41 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.3, 140.3, 138.0, 128.8, 128.2, 127.6, 125.1, 74.6, 54.0, 49.1, 35.8,

29.3, 26.0, 21.4. HRMS (ESI) calculated for C₁₄H₂₁IN [(M+H)⁺]: 330.0713, found: 330.0716.

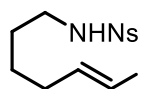
(E)-N-(6-iodohex-5-en-1-yl)naphthalen-1-amine (4d):



Yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.50 – 7.47 (m, 1H), 7.47 – 7.42 (m, 1H), 6.51 (dt, *J* = 14.3, 7.2 Hz, 1H), 5.99 (dt, *J* = 14.3, 1.4 Hz, 1H), 4.24 (s, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.61 – 1.51 (m, 2H), 1.51 – 1.43 (m, 2H), 1.41 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.3, 135.9, 133.8, 131.7, 128.6, 127.6, 126.0, 125.9, 125.5, 125.3, 123.5, 74.6, 51.6, 49.5, 35.8, 29.3, 26.0. HRMS (ESI) calculated for C₁₇H₂₁IN [(M+H)⁺]: 366.0713, found: 366.0709.

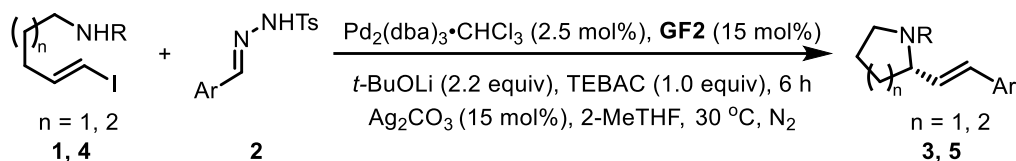
(E)-N-(6-iodohex-5-en-1-yl)-4-nitrobenzenesulfonamide (4e):



Yellow solid (m.p. 73-74 °C).

¹H NMR (400 MHz, CDCl₃) δ 8.35 – 8.30 (m, 2H), 8.07 – 8.01 (m, 2H), 6.35 (dt, *J* = 14.3, 7.1 Hz, 1H), 5.91 (dt, *J* = 14.4, 1.4 Hz, 1H), 5.39 (s, 1H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.03 – 1.94 (m, 2H), 1.50 – 1.41 (m, 2H), 1.40 – 1.31 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.7, 145.6, 145.4, 128.1, 124.3, 75.1, 42.8, 35.0, 28.5, 24.8. HRMS (ESI) calculated for C₁₂H₁₅IN₂NaO₄S [(M+Na)⁺]: 432.9689, found: 432.9694.

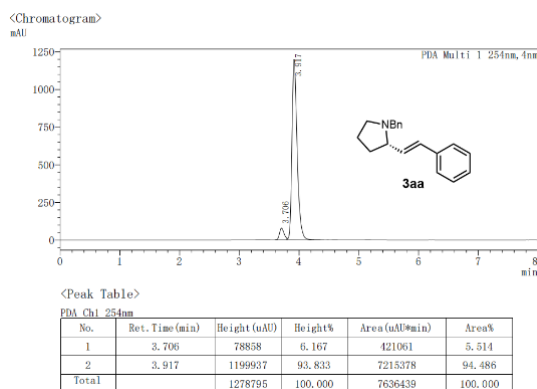
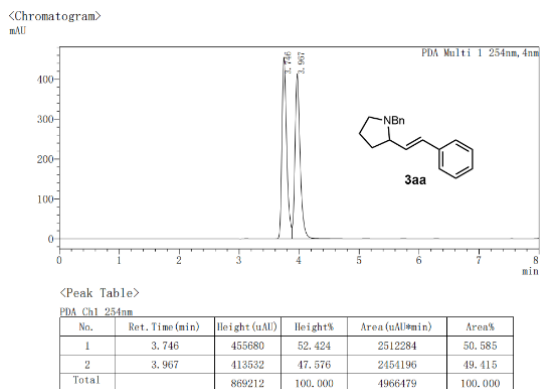
4. General Procedure for the Synthesis of Products 3, 5



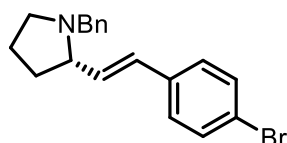
To a 10 mL sealed tube was added *N*-tosylhydrazones **2** (0.48 mmol, 1.6 equiv), Pd₂(dba)₃·CHCl₃ (0.0075 mmol, 2.5 mol%), **GF2** (0.045 mmol, 15 mol%), *t*-BuOLi (0.66 mmol, 2.2 equiv), Ag₂CO₃ (0.045 mmol, 15 mol%), and triethylbenzylammonium chloride (TEBAC, 0.3 mmol, 1.0 equiv) was added in the glove box. The reaction tube was evacuated and back-filled with N₂ three times and a solution of the vinyl iodide **1**, **4** (0.3 mmol, 1.0 equiv, 0.1 M in 2- MeTHF) was added under nitrogen atmosphere. Then the tube was stirred at 30 °C for 6 h. Upon completion, the reaction mixture was filtered through celite, evaporated *in vacuo* and purified by silica gel column chromatography (DCM to PE/Et₃N = 50/1) to give the desired product **3**, **5**.

(*S,E*)-1-benzyl-2-styrylpyrrolidine (**3aa**):

White solid (69 mg, 87% yield), 94.5:5.5 *er.* m.p. 61-62 °C; [α]_D²⁰ = -38.2 (*c* 0.56, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.27 (m, 6H), 7.27 – 7.17 (m, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.09 (d, *J* = 12.9 Hz, 1H), 3.16 (d, *J* = 12.9 Hz, 1H), 3.01 (t, *J* = 8.2 Hz, 2H), 2.25 – 2.13 (m, 1H), 2.10 – 1.97 (m, 1H), 1.92 – 1.71 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.5, 137.2, 132.7, 131.6, 129.0, 128.5, 128.1, 127.3, 126.7, 126.3, 67.9, 58.3, 53.4, 31.8, 22.2. HRMS (ESI) calculated for C₁₉H₂₂N [(M+H)⁺]: 264.1747, found: 264.1749. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (minor) = 3.7 min, t_R (major) = 3.9 min.



(S,E)-1-benzyl-2-(4-bromostyryl)pyrrolidine (3ab):



Yellow solid (90.2 mg, 88% yield), 93.5:6.5 *er.* m.p. 51-52 °C;

$[\alpha]_D^{20} = +8.2$ (*c* 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.40 (m, 2H), 7.35 – 7.28 (m, 4H), 7.27 – 7.26 (m, 1H),

7.26 – 7.20 (m, 2H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.04 (d,

J = 13.0 Hz, 1H), 3.18 (d, *J* = 13.0 Hz, 1H), 3.06 – 2.93 (m, 2H), 2.25 – 2.14 (m, 1H),

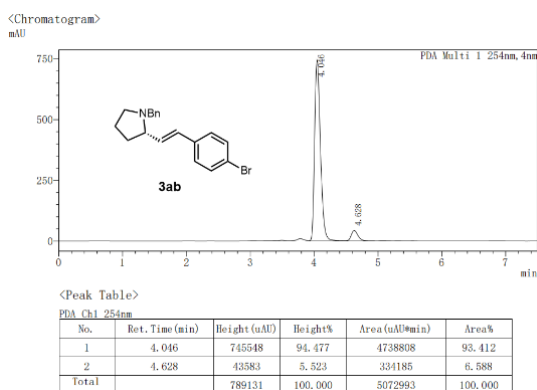
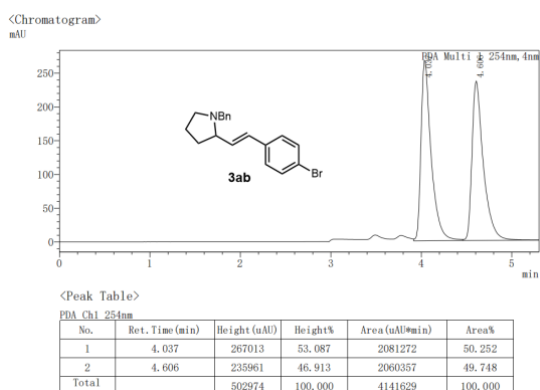
2.06 – 2.00 (m, 1H), 1.89 – 1.70 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.3, 136.1,

133.6, 131.6, 130.3, 128.9, 128.1, 127.8, 126.8, 121.0, 67.7, 58.4, 53.4, 31.8, 22.2.

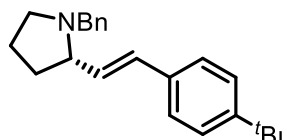
HRMS (ESI) calculated for C₁₉H₂₁BrN [(M+H)⁺]: 342.0852, found: 342.0851. HPLC

(Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min,

254 nm): *t*_R (major) = 4.0 min, *t*_R (minor) = 4.6 min.



(S,E)-1-benzyl-2-(4-(tert-butyl)styryl)pyrrolidine (3ac):

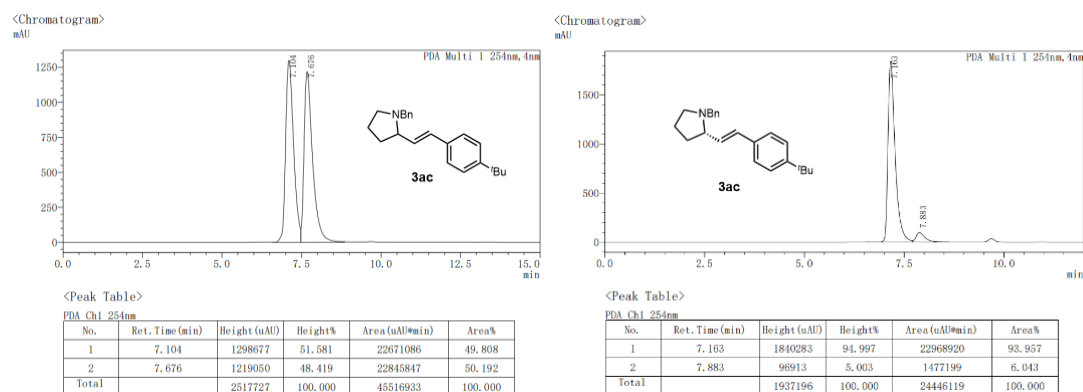


White solid (77.1 mg, 81% yield), 94:6 *er.* m.p. 77-78 °C;

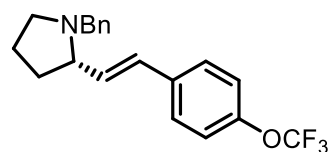
$[\alpha]_D^{20} = -17.9$ (*c* 0.62, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.37 (m, 4H), 7.36 – 7.28 (m, 4H), 7.28 – 7.22 (m, 1H),

6.59 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.11 (d, *J* = 12.9 Hz, 1H),

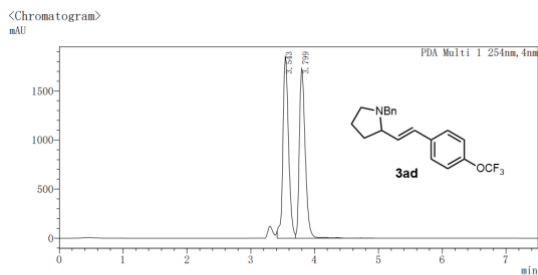
3.16 (d, $J = 12.9$ Hz, 1H), 3.07 – 2.94 (m, 2H), 2.26 – 2.15 (m, 1H), 2.09 – 2.02 (m, 1H), 1.92 – 1.69 (m, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 139.4, 134.3, 131.8, 131.5, 129.0, 128.1, 126.7, 126.0, 125.4, 67.9, 58.2, 53.3, 34.5, 31.8, 31.3, 22.1. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{30}\text{N}$ [(M+H) $^+$]: 320.2373, found: 320.2366. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 97/3, flow rate 0.5 mL/min, 254 nm): t_{R} (major) = 7.2 min, t_{R} (minor) = 7.9 min.



(*S,E*)-1-benzyl-2-(4-(trifluoromethoxy)styryl)pyrrolidine (3ad):

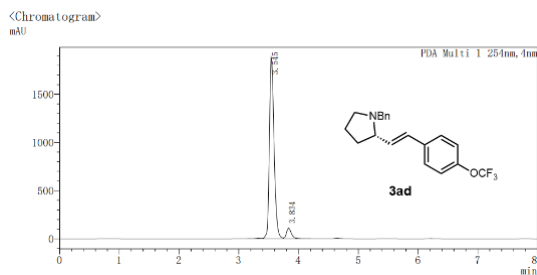


Yellow solid (89.5 mg, 86% yield), 94:6 *er*. m.p. 31-32 °C; $[\alpha]_{\text{D}}^{20} = -7.7$ (c 0.73, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.38 (m, 2H), 7.37 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 7.18 (d, $J = 8.2$ Hz, 2H), 6.55 (d, $J = 15.9$ Hz, 1H), 6.19 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.06 (d, $J = 13.0$ Hz, 1H), 3.19 (d, $J = 13.0$ Hz, 1H), 3.07 – 2.94 (m, 2H), 2.26 – 2.16 (m, 1H), 2.08 – 2.01 (m, 1H), 1.92 – 1.71 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.3, 139.4, 136.0, 133.9, 130.1, 129.0, 128.2, 127.5, 126.8, 121.1, 120.5 (d, $J = 255.2$ Hz), 67.7, 58.4, 53.5, 31.9, 22.3; ^{19}F NMR (377 MHz, CDCl_3) δ -57.8. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{21}\text{F}_3\text{NO}$ [(M+H) $^+$]: 348.1570, found: 348.1568. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 3.5 min, t_{R} (minor) = 3.8 min.



<Peak Table>

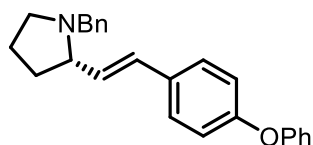
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	3.543	1846943	51.635	11401707	50.684
2	3.799	1729988	48.365	11094102	49.316
Total		3576931	100.000	22495809	100.000



<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	3.545	1881584	94.508	10224428	94.185
2	3.804	109339	5.492	631312	5.815
Total		1990923	100.000	10855740	100.000

(*S,E*)-1-benzyl-2-(4-phenoxystyryl)pyrrolidine (**3ae**):



Yellow solid (79.7 mg, 75% yield), 94:6 *er.* m.p. 64-65 °C;

$[\alpha]_D^{20} = +12.5$ (*c* 0.59, CHCl₃); ¹H NMR (400 MHz, CDCl₃)

δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.35 – 7.30

(m, 4H), 7.27 – 7.23 (m, 1H), 7.16 – 7.10 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J*

= 8.6 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.11 (d, *J* =

13.0 Hz, 1H), 3.17 (d, *J* = 13.0 Hz, 1H), 3.07 – 2.95 (m, 2H), 2.26 – 2.15 (m, 1H), 2.08

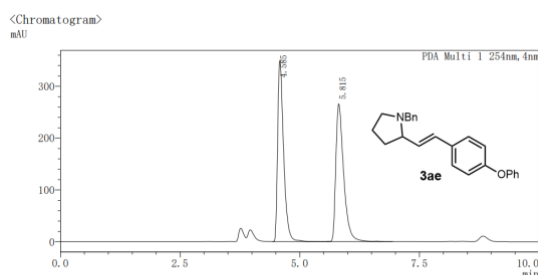
– 2.01 (m, 1H), 1.90 – 1.72 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 156.5, 139.4,

132.4, 131.7, 130.8, 129.7, 129.0, 128.1, 127.6, 126.7, 123.2, 119.0, 118.8, 67.9, 58.3,

53.3, 31.8, 22.1. HRMS (ESI) calculated for C₂₅H₂₆NO [(M+H)⁺]: 356.2009, found:

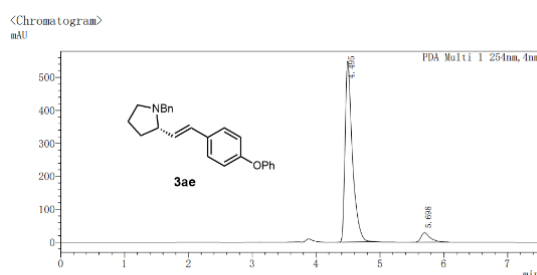
356.2007. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow

rate 1.0 mL/min, 254 nm): *t_R* (major) = 4.5 min, *t_R* (minor) = 5.7 min.



<Peak Table>

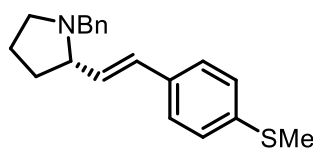
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.585	349557	56.780	3042456	49.938
2	5.815	266081	43.220	3049992	50.062
Total		615638	100.000	6092448	100.000



<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.495	547904	95.079	4382958	93.862
2	5.698	28356	4.921	286802	6.138
Total		576260	100.000	4669560	100.000

(*S,E*)-1-benzyl-2-(4-(methylthio)styryl)pyrrolidine (**3af**):

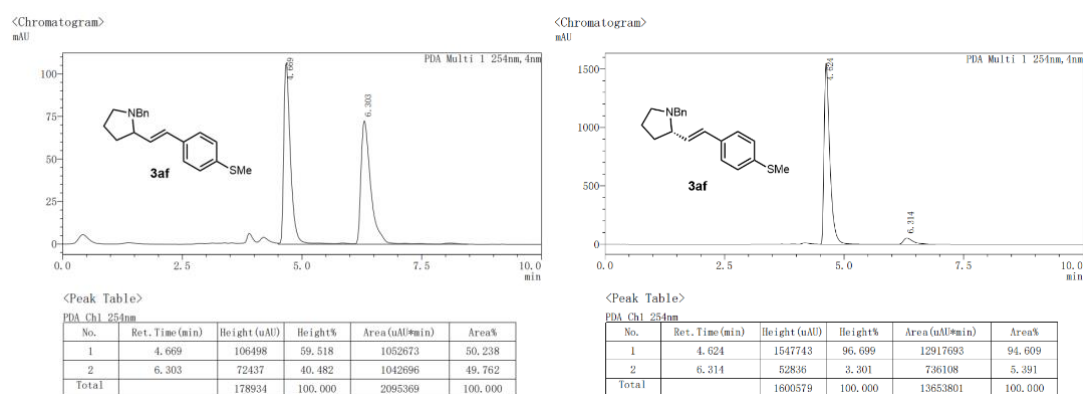


Yellow solid (65.1 mg, 70% yield), 94.5:5.5 *er.* m.p. 49-50

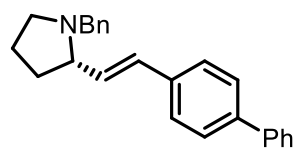
°C; $[\alpha]_D^{20} = -26.0$ (*c* 0.58, CHCl₃); ¹H NMR (400 MHz,

CDCl₃) δ 7.37 – 7.28 (m, 6H), 7.26 – 7.20 (m, 3H), 6.53 (d,

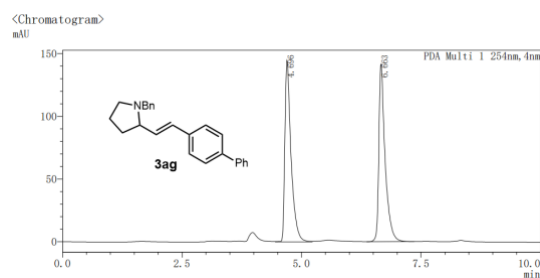
$J = 15.8$ Hz, 1H), 6.17 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.08 (d, $J = 13.0$ Hz, 1H), 3.16 (d, $J = 13.0$ Hz, 1H), 3.05 – 2.95 (m, 2H), 2.50 (s, 3H), 2.24 – 2.14 (m, 1H), 2.07 – 2.01 (m, 1H), 1.89 – 1.71 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 137.3, 134.2, 132.1, 130.9, 128.9, 128.1, 126.8, 126.7, 126.6, 67.8, 58.3, 53.3, 31.8, 22.1, 15.9. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{24}\text{NS}$ $[(\text{M}+\text{H})^+]$: 310.1624, found: 310.1619. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 4.6 min, t_{R} (minor) = 6.3 min.



(*S,E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-1-benzylpyrrolidine (3ag**):**

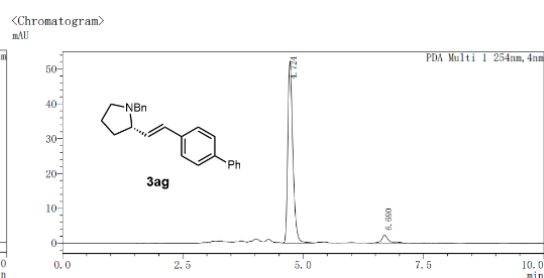


Yellow solid (68.5 mg, 67% yield), 94.5:5.5 *er.* m.p. 99-100 °C; $[\alpha]_{\text{D}}^{20} = -13.0$ (*c* 0.71, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.61 (m, 2H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.50 (d, $J = 8.3$ Hz, 2H), 7.48 – 7.43 (m, 2H), 7.39 – 7.30 (m, 5H), 7.28 – 7.22 (m, 1H), 6.63 (d, $J = 15.8$ Hz, 1H), 6.27 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.11 (d, $J = 13.0$ Hz, 1H), 3.19 (d, $J = 13.0$ Hz, 1H), 3.11 – 2.97 (m, 2H), 2.28 – 2.17 (m, 1H), 2.09 – 2.04 (m, 1H), 1.90 – 1.73 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 140.1, 139.4, 136.2, 132.8, 131.2, 129.0, 128.7, 128.1, 127.2, 126.9, 126.8, 126.7, 67.9, 58.3, 53.4, 31.8, 22.2. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{26}\text{N}$ $[(\text{M}+\text{H})^+]$: 340.2060, found: 340.2051. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 4.7 min, t_{R} (minor) = 6.7 min.



<Peak Table>

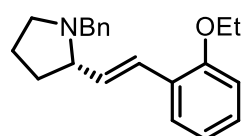
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.696	144720	50.534	1303977	50.194
2	6.663	141663	49.466	1293888	49.806
Total		286383	100.000	2597866	100.000



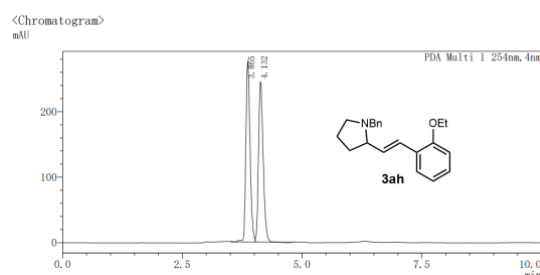
<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.724	52013	95.824	381646	94.440
2	6.690	2267	4.176	22470	5.560
Total		54280	100.000	404115	100.000

(*S,E*)-1-benzyl-2-(2-ethoxystyryl)pyrrolidine (**3ah**):

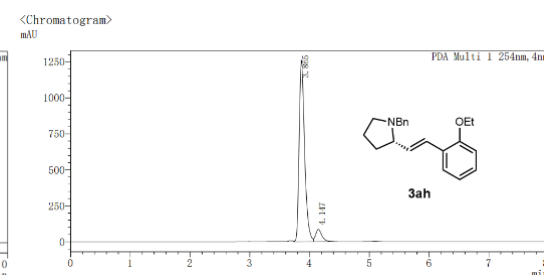


Yellow oil (81.5 mg, 88% yield), 93:7 *er*. $[\alpha]_D^{20} = +15.3$ (*c* 0.66, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 7.5$ Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.19 (m, 2H), 6.96 (dd, $J = 16.3, 9.3$ Hz, 2H), 6.88 (d, $J = 8.2$ Hz, 1H), 6.25 (dd, $J = 16.0, 8.3$ Hz, 1H), 4.14 (d, $J = 13.2$ Hz, 1H), 4.09 (dd, $J = 14.1, 7.1$ Hz, 2H), 3.20 (d, $J = 13.0$ Hz, 1H), 3.10 – 2.96 (m, 2H), 2.25 – 2.17 (m, 1H), 2.11 – 2.03 (m, 1H), 1.91 – 1.73 (m, 3H), 1.49 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 155.9, 139.5, 132.7, 129.1 (overlap), 128.2, 128.0, 126.6, 126.4, 126.2, 120.5, 112.0, 68.1, 63.8, 58.1, 53.2, 31.8, 22.1, 14.9. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}$ $[(\text{M}+\text{H})^+]$: 308.2009, found: 308.2006. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 3.9 min, t_R (minor) = 4.1 min.



<Peak Table>

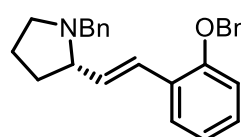
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	3.865	275630	52.970	1682792	50.564
2	4.132	244719	47.030	1645249	49.436
Total		520349	100.000	3328041	100.000



<Peak Table>

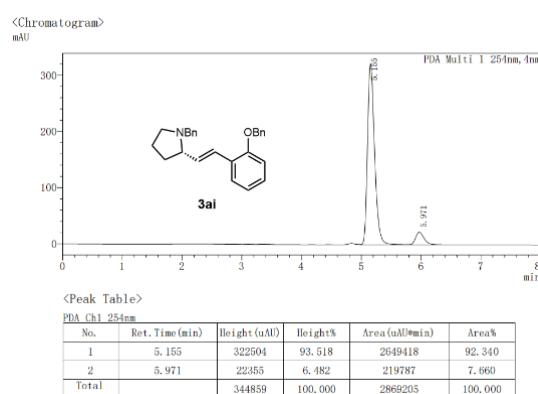
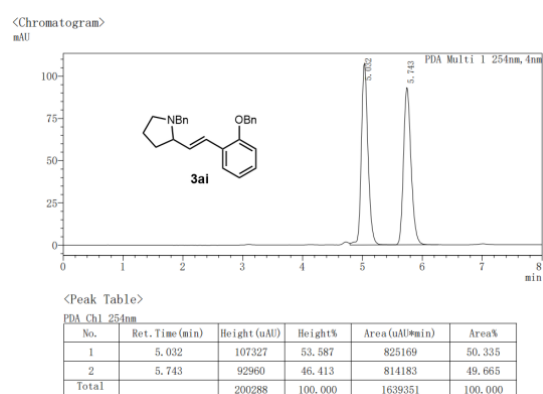
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	3.865	1257508	93.592	7973247	92.897
2	4.147	86099	6.408	609628	7.103
Total		1343608	100.000	8582875	100.000

(*S,E*)-1-benzyl-2-(2-(benzyloxy)styryl)pyrrolidine (**3ai**):

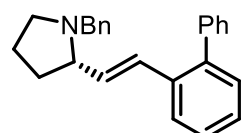


Yellow oil (72.8 mg, 66% yield), 92.5:7.5 *er*. $[\alpha]_D^{20} = +66.3$ (*c* 0.61, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.49 (d, $J = 7.3$ Hz, 2H), 7.44 – 7.39 (m, 2H), 7.39 – 7.33

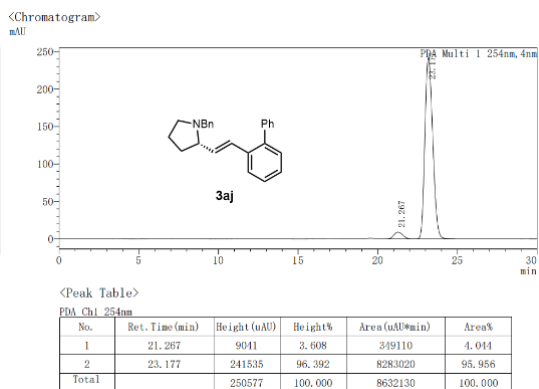
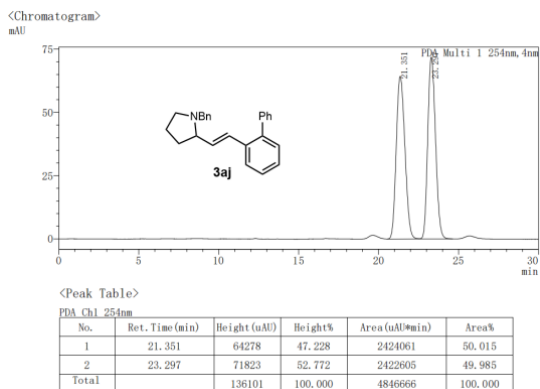
(m, 3H), 7.33 – 7.28 (m, 2H), 7.27 – 7.20 (m, 2H), 7.03 (d, $J = 16.1$ Hz, 1H), 7.01 – 6.93 (m, 2H), 6.25 (dd, $J = 16.0, 8.4$ Hz, 1H), 5.15 (s, 2H), 4.13 (d, $J = 13.0$ Hz, 1H), 3.20 (d, $J = 13.0$ Hz, 1H), 3.10 – 2.97 (m, 2H), 2.26 – 2.16 (m, 1H), 2.08 – 2.02 (m, 1H), 1.90 – 1.72 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 139.4, 137.2, 133.1, 129.1, 128.5, 128.3, 128.0, 127.8 (overlap), 127.2, 126.7, 126.6, 126.3, 121.0, 112.5, 70.3, 68.0, 58.1, 53.2, 31.8, 22.1. HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{28}\text{NO}$ [(M+H) $^+$]: 370.2165, found: 370.2164. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 5.2 min, t_{R} (minor) = 6.0 min.



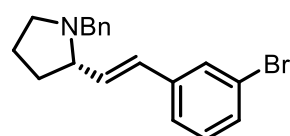
(*S,E*)-2-(2-([1,1'-biphenyl]-2-yl)vinyl)-1-benzylpyrrolidine (3aj):



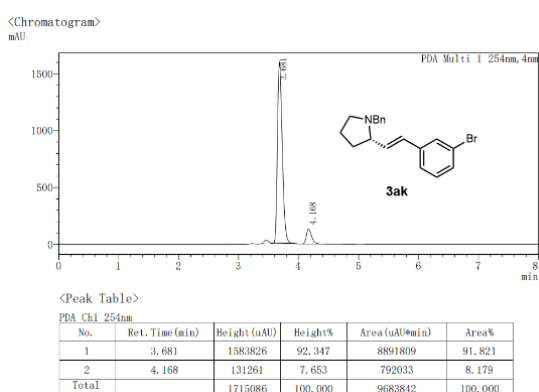
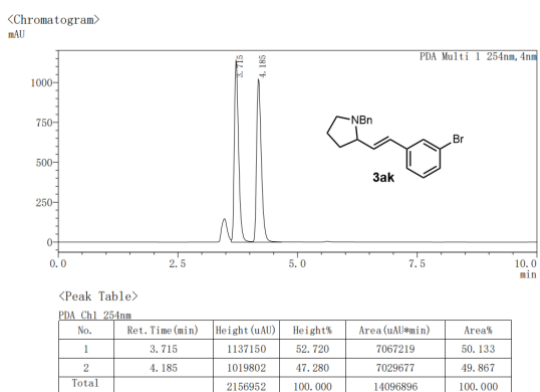
Yellow oil (82.7 mg, 81% yield), 96:4 *er*. $[\alpha]_{\text{D}}^{20} = +118.0$ (c 0.52, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.3$ Hz, 1H), 7.46 – 7.36 (m, 6H), 7.35 – 7.28 (m, 6H), 7.27 – 7.23 (m, 1H), 6.59 (d, $J = 15.8$ Hz, 1H), 6.16 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.05 (d, $J = 13.0$ Hz, 1H), 3.17 (d, $J = 13.0$ Hz, 1H), 2.98 (t, $J = 7.7$ Hz, 1H), 2.94 – 2.84 (m, 1H), 2.19 – 2.12 (m, 1H), 2.05 – 1.93 (m, 1H), 1.86 – 1.69 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 140.6, 139.2, 135.3, 133.5, 130.6, 130.1, 129.8, 129.0, 128.1, 128.0, 127.4, 127.2, 126.9, 126.7, 126.2, 67.6, 58.0, 53.1, 31.7, 22.1. HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{26}\text{N}$ [(M+H) $^+$]: 340.2060, found: 340.2064. HPLC (Daicel Chiralpak OD-H+OD-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): t_{R} (minor) = 21.3 min, t_{R} (major) = 23.2 min.



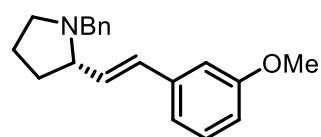
(*S,E*)-1-benzyl-2-(3-bromostyryl)pyrrolidine (3ak):



Yellow oil (76.6 mg, 75% yield), 92:8 *er*. $[\alpha]_D^{20} = +50.2$ (*c* 0.55, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 – 7.51 (m, 1H), 7.38 – 7.33 (m, 1H), 7.32 – 7.30 (m, 4H), 7.30 – 7.28 (m, 1H), 7.26 – 7.20 (m, 1H), 7.21 – 7.14 (m, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.20 (dd, $J = 15.8, 8.2$ Hz, 1H), 4.03 (d, $J = 13.0$ Hz, 1H), 3.18 (d, $J = 13.0$ Hz, 1H), 3.05 – 2.95 (m, 2H), 2.24 – 2.13 (m, 1H), 2.08 – 1.98 (m, 1H), 1.86 – 1.72 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.3, 139.2, 134.4, 130.1, 130.0, 129.9, 129.2, 128.9, 128.1, 126.8, 124.9, 122.7, 67.6, 58.3, 53.4, 31.8, 22.2. HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{21}\text{BrN}$ $[(\text{M}+\text{H})^+]$: 342.0852, found: 342.0844. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 3.7 min, t_R (minor) = 4.2 min.

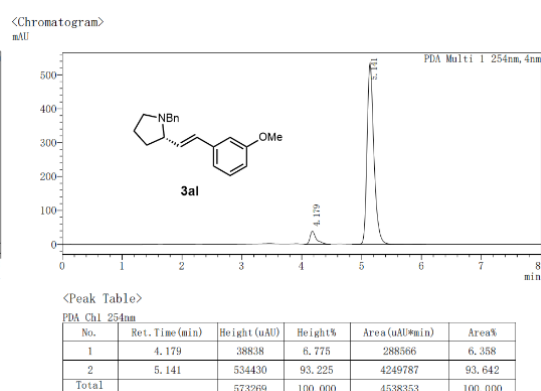
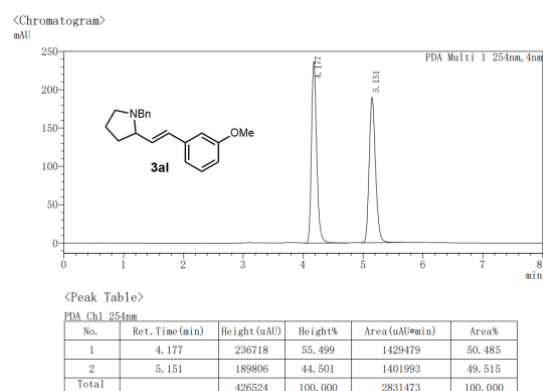


(*S,E*)-1-benzyl-2-(3-methoxystyryl)pyrrolidine (3al):

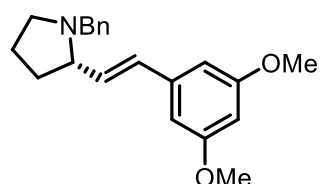


Yellow oil (78.6 mg, 89% yield), 93.5:6.5 *er*. $[\alpha]_D^{20} = -21.3$ (*c* 0.67, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.27 (m, 4H), 7.26 – 7.19 (m, 2H), 7.00 (d, $J = 7.7$ Hz, 1H), 6.97

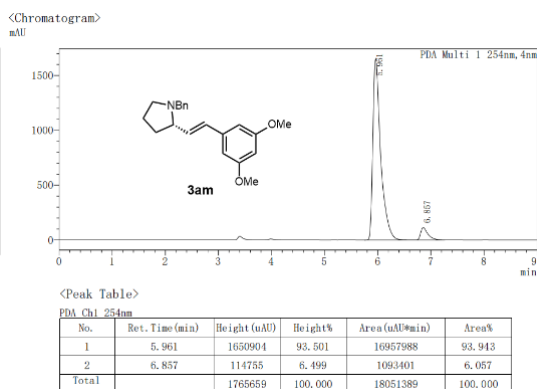
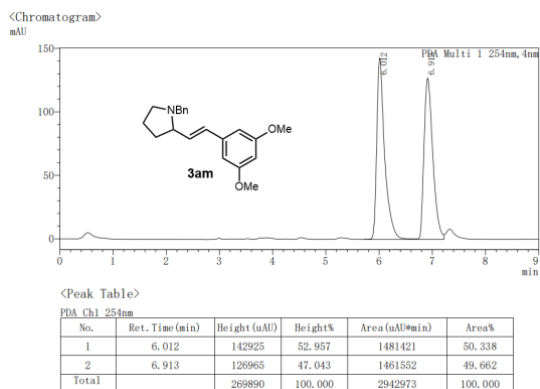
– 6.94 (m, 1H), 6.80 (dd, $J = 8.1, 2.3$ Hz, 1H), 6.54 (d, $J = 15.8$ Hz, 1H), 6.21 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.08 (d, $J = 13.0$ Hz, 1H), 3.82 (s, 3H), 3.16 (d, $J = 13.0$ Hz, 1H), 3.05 – 2.95 (m, 2H), 2.23 – 2.14 (m, 1H), 2.07 – 2.00 (m, 1H), 1.89 – 1.70 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 139.3, 138.6, 132.9, 131.5, 129.5, 129.0, 128.1, 126.7, 119.0, 113.1, 111.4, 67.8, 58.3, 55.2, 53.3, 31.8, 22.2. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{24}\text{NO}$ [(M+H) $^+$]: 294.1852, found: 294.1853. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (minor) = 4.2 min, t_{R} (major) = 5.1 min.



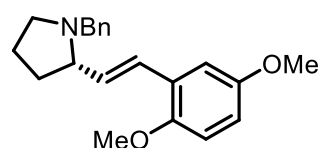
(*S,E*)-1-benzyl-2-(3,5-dimethoxystyryl)pyrrolidine (3am):



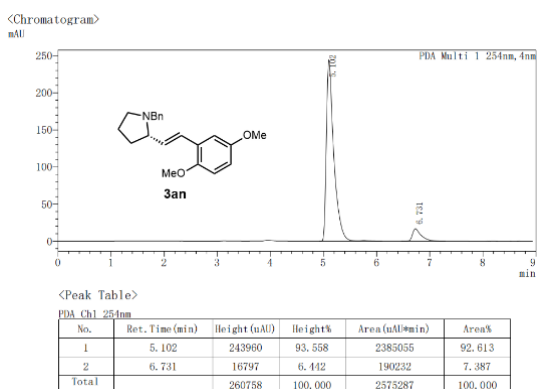
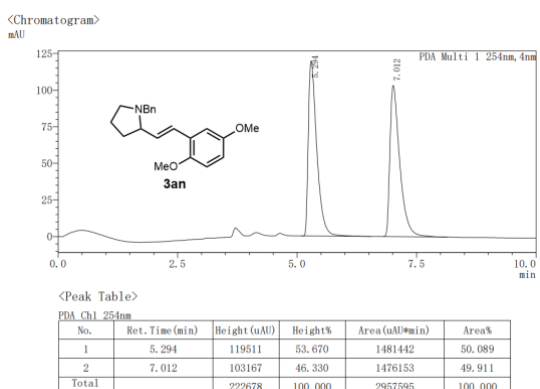
Yellow oil (77.1 mg, 80% yield), 94:6 *er*. $[\alpha]_{\text{D}}^{20} = -41.9$ (c 0.93, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 6.59 (s, 2H), 6.51 (d, $J = 15.8$ Hz, 1H), 6.39 (s, 1H), 6.21 (dd, $J = 15.7, 8.3$ Hz, 1H), 4.08 (d, $J = 13.0$ Hz, 1H), 3.82 (s, 6H), 3.18 (d, $J = 13.0$ Hz, 1H), 3.06 – 2.94 (m, 2H), 2.23 – 2.15 (m, 1H), 2.09 – 2.00 (m, 1H), 1.89 – 1.70 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 139.2, 139.1, 133.1, 131.6, 129.0, 128.1, 126.7, 104.3, 100.0, 67.7, 58.3, 55.6, 53.3, 31.8, 22.1. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}_2$ [(M+H) $^+$]: 324.1958, found: 324.1950. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 6.0 min, t_{R} (minor) = 6.9 min.



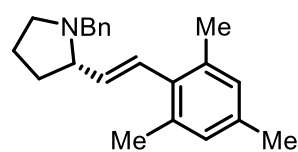
(*S,E*)-1-benzyl-2-(2,5-dimethoxystyryl)pyrrolidine (3an):



Yellow oil (73.2 mg, 75% yield), 92.5:7.5 *er*. $[\alpha]_D^{20} = +20.6$ (*c* 0.51, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 7.08 – 7.05 (m, 1H), 6.90 (d, $J = 16.0$ Hz, 1H), 6.84 – 6.75 (m, 2H), 6.20 (dd, $J = 16.0, 8.4$ Hz, 1H), 4.09 (d, $J = 13.0$ Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.16 (d, $J = 13.0$ Hz, 1H), 3.07 – 2.95 (m, 2H), 2.24 – 2.15 (m, 1H), 2.09 – 2.00 (m, 1H), 1.87 – 1.71 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 153.7, 151.0, 139.5, 133.3, 129.0, 128.1, 126.9, 126.7, 126.1, 113.6, 112.3, 111.8, 68.2, 58.3, 56.2, 55.7, 53.4, 31.8, 22.1. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}_2$ $[(\text{M}+\text{H})^+]$: 324.1958, found: 324.1954. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 5.1 min, t_R (minor) = 6.7 min.

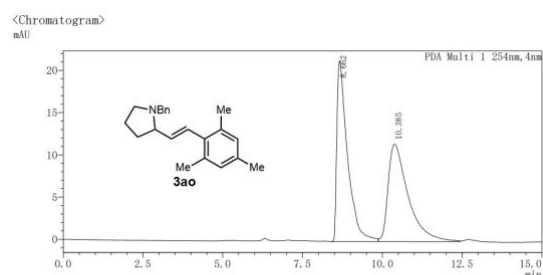


(*S,E*)-1-benzyl-2-(2,4,6-trimethylstyryl)pyrrolidine (3ao):



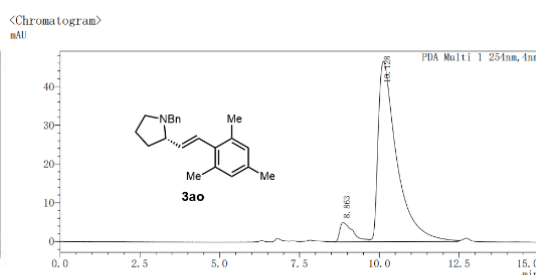
Yellow oil (52.6 mg, 57% yield, 7:1 *E/Z*), 93:7 *er*. $[\alpha]_D^{20} = +68.0$ (*c* 0.49, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) *E* isomer: δ 7.37 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 6.89 (s, 2H), 6.54

(d, $J = 16.2$ Hz, 1H), 5.69 (dd, $J = 16.2, 8.3$ Hz, 1H), 4.21 (d, $J = 12.8$ Hz, 1H), 3.18 (d, $J = 12.8$ Hz, 1H), 3.05 – 2.95 (m, 2H), 2.32 (s, 6H), 2.29 (s, 3H), 2.11 – 2.04 (m, 1H), 2.00 – 1.87 (m, 1H), 1.84 – 1.72 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 137.3, 136.0, 135.8, 134.0, 129.3, 129.1, 128.5, 128.2, 126.8, 68.4, 58.9, 53.2, 31.8, 22.1, 21.0, 20.9. HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{28}\text{N}$ [(M+H) $^+$]: 306.2216, found: 306.2210. HPLC (Daicel Chiralpak OJ-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): t_{R} (minor) = 8.9 min, t_{R} (major) = 10.1 min.



<Peak Table>

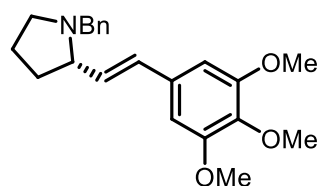
PDA Chl 254nm					
No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	8.862	21387	64.931	501547	49.762
2	10.385	11551	35.069	506352	50.238
Total		32939	100.000	1007898	100.000



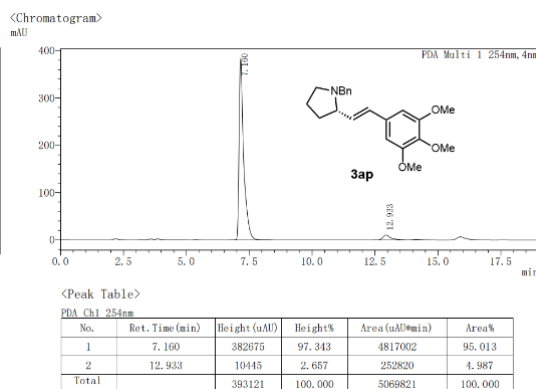
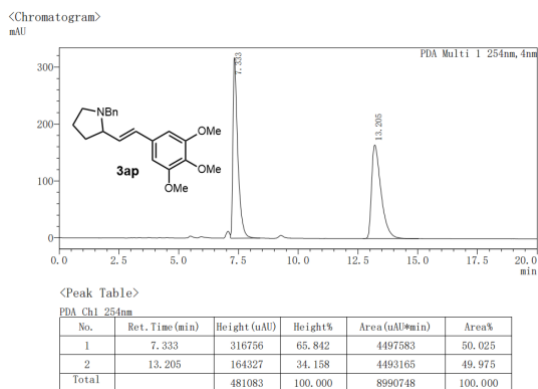
<Peak Table>

PDA Chl 254nm					
No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	8.863	4980	9.671	142506	6.989
2	10.128	46512	90.329	1896600	93.011
Total		51492	100.000	2039107	100.000

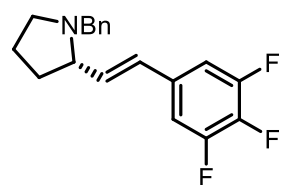
(*S,E*)-1-benzyl-2-(3,4,5-trimethoxystyryl)pyrrolidine (3ap):



Yellow oil (83.2 mg, 79% yield), 95:5 *er*. $[\alpha]_{\text{D}}^{20} = +4.1$ (c 0.55, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 6.63 (s, 2H), 6.49 (d, $J = 15.7$ Hz, 1H), 6.11 (dd, $J = 15.7, 8.3$ Hz, 1H), 4.07 (d, $J = 13.0$ Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 3.17 (d, $J = 13.0$ Hz, 1H), 3.05 – 2.94 (m, 2H), 2.22 – 2.14 (m, 1H), 2.08 – 2.00 (m, 1H), 1.86 – 1.70 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 139.2, 137.6, 132.8, 132.1, 131.4, 128.9, 128.1, 126.7, 103.3, 67.7, 60.8, 58.3, 56.0, 53.4, 31.8, 22.1. HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{28}\text{NO}_3$ [(M+H) $^+$]: 354.2064, found: 354.2061. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 7.2 min, t_{R} (minor) = 12.9 min.

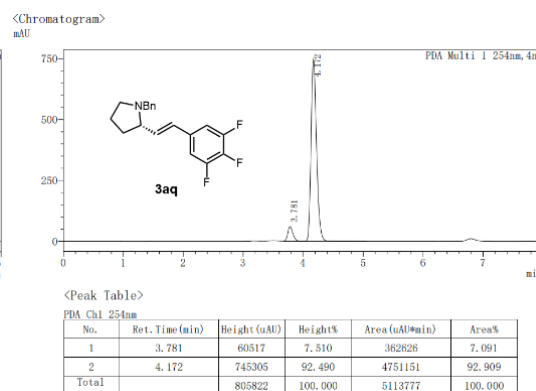
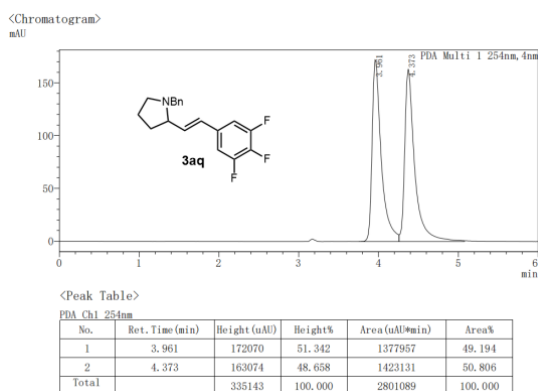


(*S,E*)-1-benzyl-2-(3,4,5-trifluorostyryl)pyrrolidine (3aq):

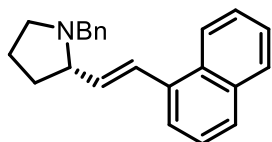


Yellow oil (81.1 mg, 85% yield), 93:7 *er*. $[\alpha]_D^{20} = +59.5$ (*c* 0.44, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (s, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.18 (m, 1H), 7.08 – 6.86 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.8, 8.1 Hz, 1H), 3.99 (d, *J* = 13.0

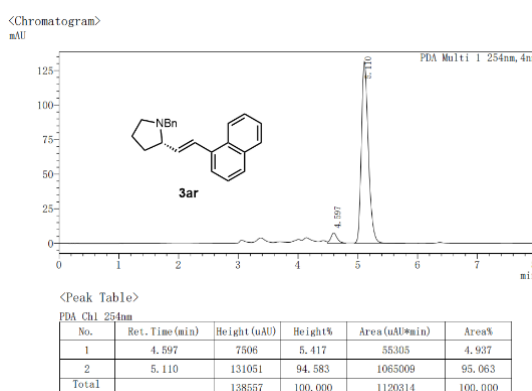
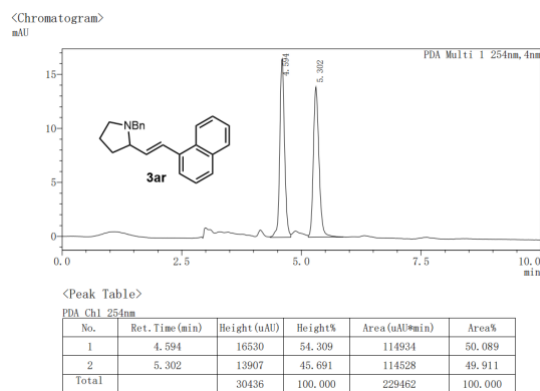
Hz, 1H), 3.22 (d, *J* = 13.0 Hz, 1H), 3.08 – 2.94 (m, 2H), 2.27 – 2.15 (m, 1H), 2.07 – 2.01 (m, 1H), 1.90 – 1.67 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.3 (ddd, *J* = 247.5, 10.0, 4.2 Hz), 139.3, 138.8 (dt, *J* = 249.5, 15.1 Hz), 135.5, 133.5 (td, *J* = 7.5, 4.4 Hz), 128.8, 128.5 (d, *J* = 2.1 Hz), 128.2, 126.8, 109.9 (dd, *J* = 15.8, 5.7 Hz), 67.3, 58.5, 53.5, 31.8, 22.3; ¹⁹F NMR (377 MHz, CDCl₃) δ -134.9, -162.2. HRMS (ESI) calculated for C₁₉H₁₉F₃N [(M+H)⁺]: 318.1464, found: 318.1457. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 95/5, flow rate 1.0 mL/min, 254 nm): *t_R* (minor) = 3.8 min, *t_R* (major) = 4.2 min.



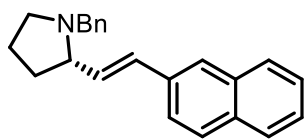
(*S,E*)-1-benzyl-2-(2-(naphthalen-1-yl)vinyl)pyrrolidine (3ar):



Yellow oil (81.7 mg, 87% yield), 95:5 *er.* $[\alpha]_D^{20} = +48.9$ (*c* 0.64, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 7.7$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.66 (d, $J = 7.1$ Hz, 1H), 7.58 – 7.47 (m, 3H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.39 – 7.33 (m, 3H), 7.29 (d, $J = 7.0$ Hz, 1H), 6.29 (dd, $J = 15.5, 8.3$ Hz, 1H), 4.21 (d, $J = 13.0$ Hz, 1H), 3.29 (d, $J = 13.0$ Hz, 1H), 3.23 – 3.13 (m, 1H), 3.08 (t, $J = 8.1$ Hz, 1H), 2.33 – 2.23 (m, 1H), 2.20 – 2.10 (m, 1H), 1.95 – 1.79 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.5, 135.9, 134.8, 133.6, 131.1, 129.0, 128.7, 128.5, 128.1, 127.7, 126.7, 125.9, 125.7, 125.6, 123.9, 123.8, 68.0, 58.4, 53.5, 31.9, 22.2. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{24}\text{N}$ $[(\text{M}+\text{H})^+]$: 314.1903, found: 314.1898. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (minor) = 4.6 min, t_R (major) = 5.1 min.

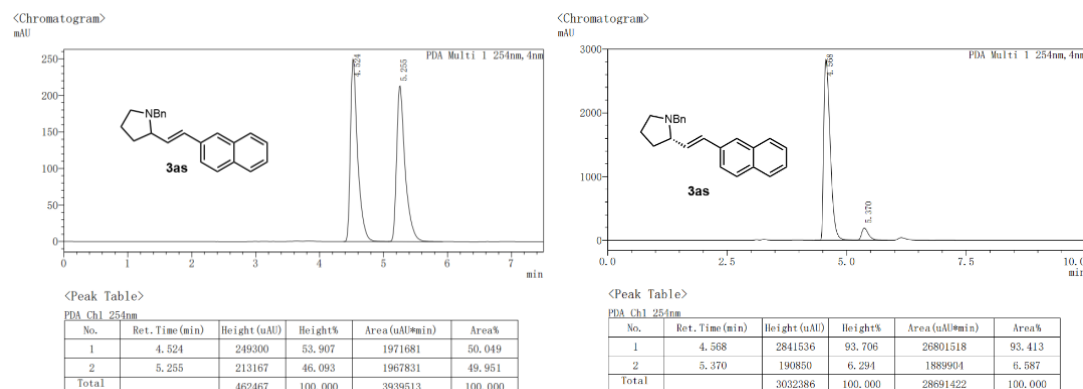


(*S,E*)-1-benzyl-2-(2-(naphthalen-2-yl)vinyl)pyrrolidine (**3as**):

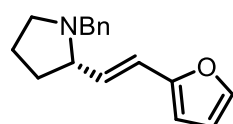


Yellow solid (70.8 mg, 75% yield), 93.5:6.5 *er.* m.p. 109-110 °C; $[\alpha]_D^{20} = +28.4$ (*c* 0.55, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.76 (m, 3H), 7.74 (s, 1H), 7.64 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.50 – 7.41 (m, 2H), 7.38 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 6.74 (d, $J = 15.8$ Hz, 1H), 6.33 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.12 (d, $J = 13.0$ Hz, 1H), 3.20 (d, $J = 13.0$ Hz, 1H), 3.11 – 2.98 (m, 2H), 2.28 – 2.16 (m, 1H), 2.11 – 2.03 (m, 1H), 1.87 – 1.77 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.4, 134.6, 133.6, 133.1, 132.9, 131.7, 129.0, 128.1, 127.9, 127.6, 126.8, 126.2, 126.0, 125.7, 123.7, 68.0, 58.4, 53.4, 31.9, 22.2. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{24}\text{N}$ $[(\text{M}+\text{H})^+]$: 314.1903, found: 314.1896.

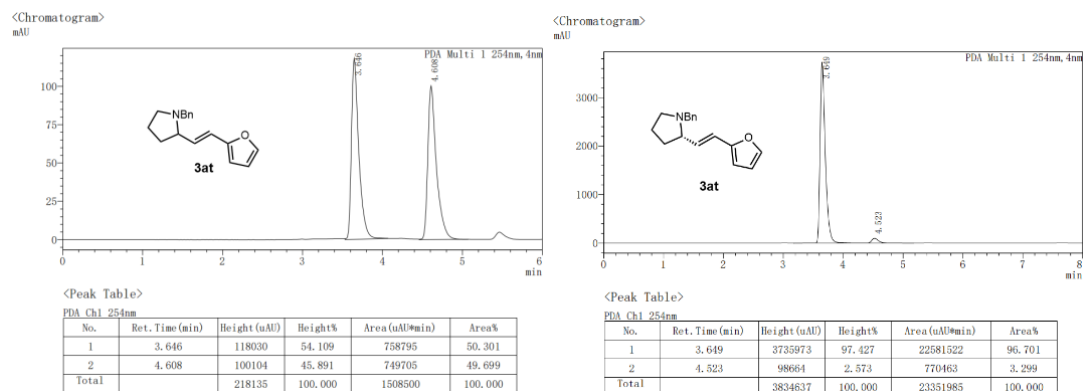
HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 4.6 min, t_R (minor) = 5.4 min.



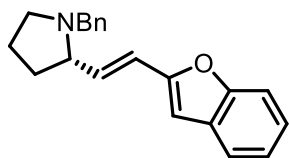
(*S,E*)-1-benzyl-2-(2-(furan-2-yl)vinyl)pyrrolidine (3at):



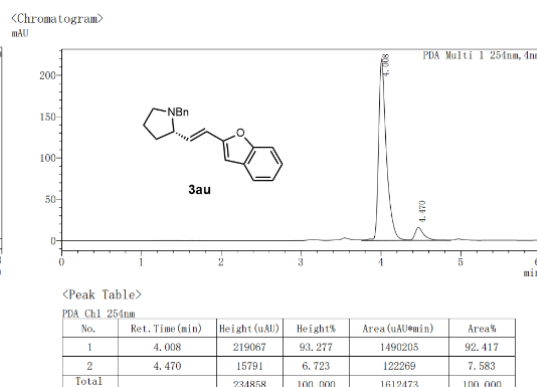
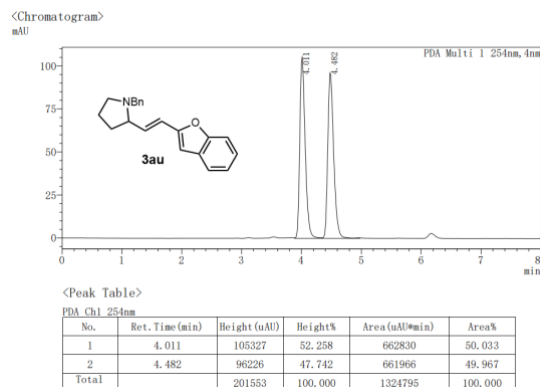
Yellow solid (34.0 mg, 45% yield), 96.5:3.5 *er.* m.p. 43-44 °C; $[\alpha]_D^{20} = -21.0$ (*c* 0.63, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.34 (m, 1H), 7.34 – 7.25 (m, 4H), 7.25 – 7.20 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.37 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 6.15 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.08 (d, *J* = 13.0 Hz, 1H), 3.14 (d, *J* = 13.0 Hz, 1H), 3.03 – 2.91 (m, 2H), 2.22 – 2.13 (m, 1H), 2.06 – 1.98 (m, 1H), 1.85 – 1.68 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 141.7, 139.5, 131.4, 128.9, 128.1, 126.7, 120.0, 111.2, 107.1, 67.5, 58.3, 53.3, 31.9, 22.2. HRMS (ESI) calculated for C₁₇H₂₀NO [(M+H)⁺]: 254.1539, found: 254.1537. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 3.6 min, t_R (minor) = 4.5 min.



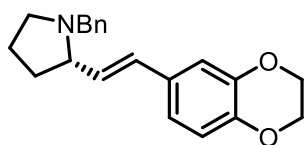
(*S,E*)-2-(2-(benzofuran-2-yl)vinyl)-1-benzylpyrrolidine (3au):



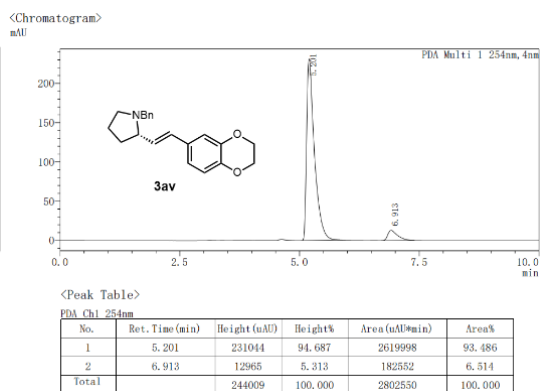
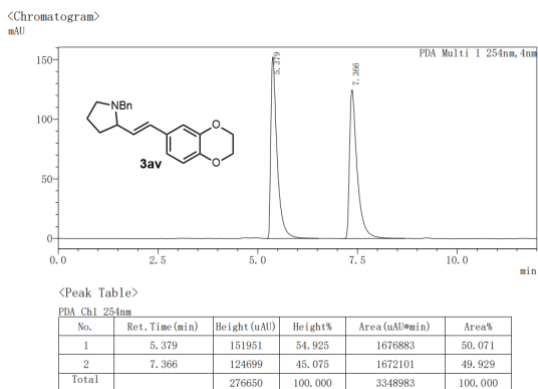
Yellow solid (62.9 mg, 69% yield) with 92.5:7.5 *er.* m.p. 78-79 °C; $[\alpha]_D^{20} = +89.7$ (*c* 0.27, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.30 – 7.20 (m, 3H), 6.58 (s, 1H), 6.57 (d, *J* = 15.7 Hz, 2H), 6.50 (dd, *J* = 15.8, 7.3 Hz, 1H), 4.12 (d, *J* = 13.0 Hz, 1H), 3.21 (d, *J* = 13.0 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.27 – 2.18 (m, 1H), 2.13 – 2.03 (m, 1H), 1.91 – 1.74 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.7, 154.6, 139.4, 135.1, 128.9, 128.8, 128.1, 126.7, 124.2, 122.7, 120.7, 119.8, 110.8, 103.7, 67.3, 58.4, 53.3, 31.9, 22.3. HRMS (ESI) calculated for C₂₁H₂₂NO [(M+H)⁺]: 304.1696, found: 304.1688. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 4.0 min, t_R (minor) = 4.5 min.



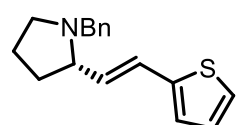
(*S,E*)-1-benzyl-2-(2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)vinyl)pyrrolidine (3av):



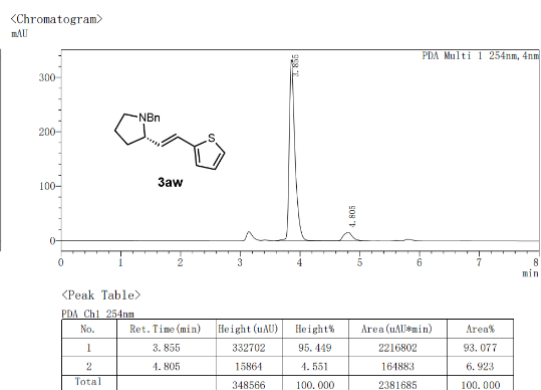
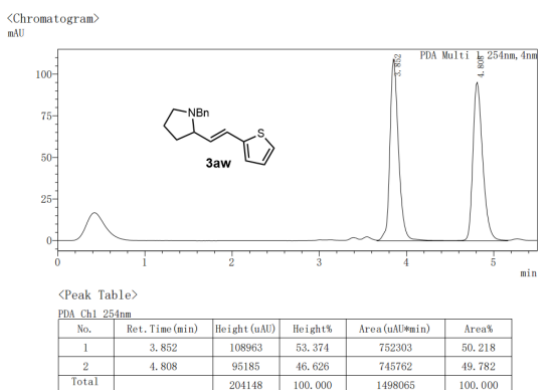
Yellow oil (58.1 mg, 60% yield), 93.5:6.5 *er.* $[\alpha]_D^{20} = -7.7$ (*c* 0.73, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 6.94 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.05 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.25 (s, 4H), 4.07 (d, *J* = 12.9 Hz, 1H), 3.13 (d, *J* = 12.9 Hz, 1H), 3.03 – 2.89 (m, 2H), 2.20 – 2.13 (m, 1H), 2.06 – 1.98 (m, 1H), 1.84 – 1.68 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 143.0, 139.3, 131.1, 131.0, 130.9, 129.0, 128.1, 126.7, 119.7, 117.2, 114.8, 67.8, 64.4, 64.3, 58.2, 53.3, 31.8, 22.1. HRMS (ESI) calculated for C₂₁H₂₄NO₂ [(M+H)⁺]: 322.1802, found: 322.1796. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 5.2 min, t_R (minor) = 6.9 min.



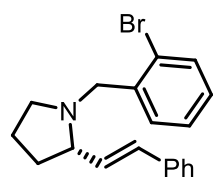
(*S,E*)-1-benzyl-2-(2-(thiophen-2-yl)vinyl)pyrrolidine (3aw):



Yellow solid (63.7 mg, 79% yield), 93:7 *er.* m.p. 47–48 °C; $[\alpha]_D^{20} = -110.1$ (*c* 0.98, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.28 (m, 4H), 7.26 – 7.19 (m, 1H), 7.15 (d, *J* = 4.3 Hz, 1H), 7.02 – 6.91 (m, 2H), 6.71 (d, *J* = 15.7 Hz, 1H), 6.06 (dd, *J* = 15.6, 8.2 Hz, 1H), 4.09 (d, *J* = 13.0 Hz, 1H), 3.16 (d, *J* = 13.0 Hz, 1H), 3.03 – 2.92 (m, 2H), 2.23 – 2.14 (m, 1H), 2.08 – 1.98 (m, 1H), 1.88 – 1.71 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 139.5, 132.5, 129.0, 128.2, 127.3, 126.8, 125.1, 124.7, 123.9, 67.6, 58.4, 53.4, 31.9, 22.2. HRMS (ESI) calculated for C₁₇H₂₀NS [(M+H)⁺]: 270.1311, found: 270.1310. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 3.9 min, *t*_R (minor) = 4.8 min.

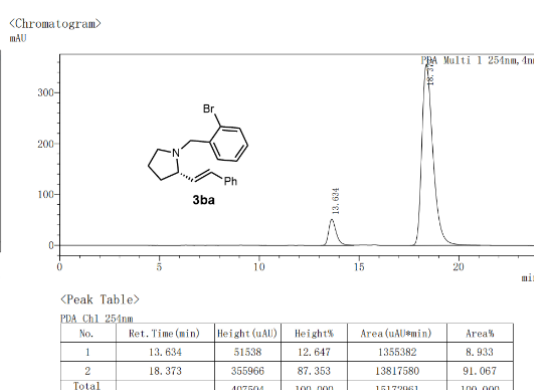
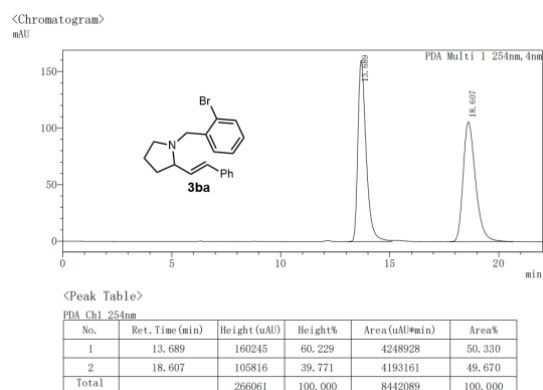


(*S,E*)-1-(2-bromobenzyl)-2-styrylpyrrolidine (3ba):

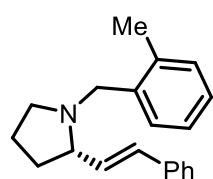


Yellow oil (86.7 mg, 85% yield), 91:9 *er.* $[\alpha]_D^{20} = +4.7$ (*c* 0.60, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.26 (m, 3H), 7.25 – 7.19 (m, 1H), 7.11 – 7.04 (m, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 15.8, 8.3 Hz,

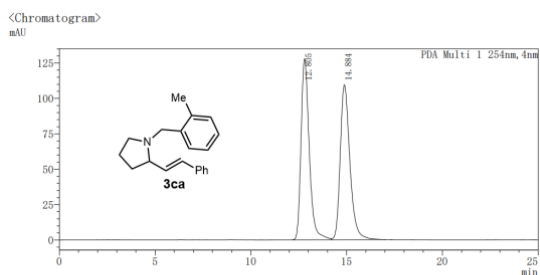
1H), 4.07 (d, $J = 14.1$ Hz, 1H), 3.42 (d, $J = 14.1$ Hz, 1H), 3.15 – 3.06 (m, 2H), 2.31 – 2.22 (m, 1H), 2.10 – 1.98 (m, 1H), 1.89 – 1.74 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.0, 137.1, 132.7, 132.6, 131.5, 130.8, 128.5, 128.1, 127.3, 127.1, 126.3, 124.2, 68.2, 57.5, 53.7, 31.9, 22.4. HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{21}\text{BrN}$ [(M+H) $^+$]: 342.0852, found: 342.0852. HPLC (Daicel Chiralpak OJ-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): t_{R} (minor) = 13.6 min, t_{R} (major) = 18.4 min.



(*S,E*)-1-(2-methylbenzyl)-2-styrylpyrrolidine (3ca):

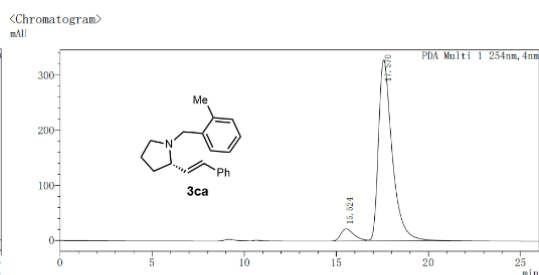


Orange oil (70.0 mg, 84% yield), 94:6 *er*. $[\alpha]_{\text{D}}^{20} = -3.3$ (c 0.68, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 7.7$ Hz, 2H), 7.40 – 7.33 (m, 3H), 7.29 (d, $J = 7.1$ Hz, 1H), 7.22 – 7.14 (m, 3H), 6.62 (d, $J = 15.8$ Hz, 1H), 6.25 (dd, $J = 15.8, 8.4$ Hz, 1H), 4.11 (d, $J = 13.1$ Hz, 1H), 3.14 (d, $J = 13.1$ Hz, 1H), 3.10 – 2.99 (m, 2H), 2.40 (s, 3H), 2.27 – 2.18 (m, 1H), 2.13 – 2.02 (m, 1H), 1.91 – 1.75 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 137.2, 136.8, 132.8, 131.5, 130.1, 129.4, 128.5, 127.2, 126.7, 126.3, 125.4, 68.5, 56.2, 53.8, 31.9, 22.3, 19.3. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{24}\text{N}$ [(M+H) $^+$]: 278.1903, found: 278.1901. HPLC (Daicel Chiralpak OJ-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): t_{R} (minor) = 15.5 min, t_{R} (major) = 17.6 min.



<Peak Table>

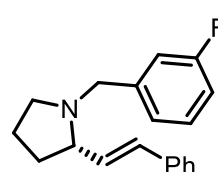
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	12.805	127858	53.885	3818599	49.884
2	14.884	109423	46.115	3836391	50.116
Total		237281	100.000	7654990	100.000



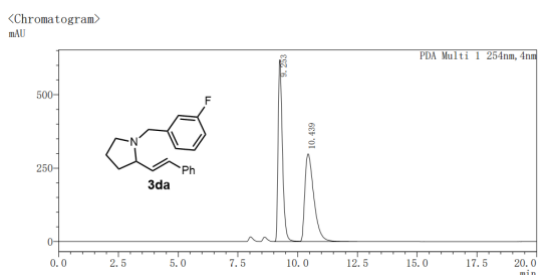
<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	15.524	22127	6.317	1112859	6.138
2	17.570	328130	93.683	17016528	93.862
Total		350258	100.000	18129387	100.000

(*S,E*)-1-(3-fluorobenzyl)-2-styrylpyrrolidine (**3da**):

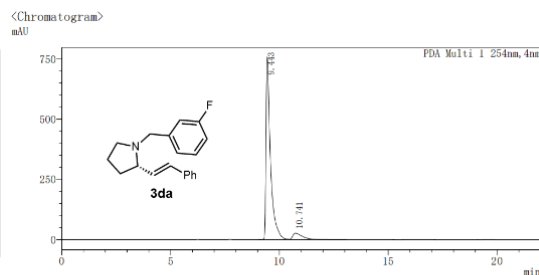


Yellow solid (78.1 mg, 93% yield), 93:7 *er.* m.p. 43-44 °C; $[\alpha]_D^{20} = -11.0$ (*c* 0.63, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.17 – 7.09 (m, 2H), 6.99 – 6.90 (m, 1H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.22 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.10 (d, *J* = 13.3 Hz, 1H), 3.19 (d, *J* = 13.3 Hz, 1H), 3.09 – 2.99 (m, 2H), 2.26 – 2.16 (m, 1H), 2.13 – 2.03 (m, 1H), 1.92 – 1.77 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.9 (d, *J* = 243.6 Hz), 142.4 (d, *J* = 7.0 Hz), 137.0, 132.4, 131.8, 129.5 (d, *J* = 8.3 Hz), 128.5, 127.4, 126.3, 124.3 (d, *J* = 2.5 Hz), 115.6 (d, *J* = 21.0 Hz), 113.5 (d, *J* = 21.1 Hz), 67.9, 57.8, 53.4, 31.8, 22.2; ¹⁹F NMR (377 MHz, CDCl₃) δ -113.9. HRMS (ESI) calculated for C₁₉H₂₁FN [(M+H)⁺]: 282.1653, found: 282.1650. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): *t*_R (major) = 9.4 min, *t*_R (minor) = 10.7 min.



<Peak Table>

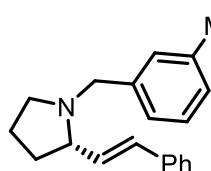
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	9.253	618366	67.445	7793995	49.928
2	10.439	298484	32.555	7816568	50.072
Total		916850	100.000	15610563	100.000



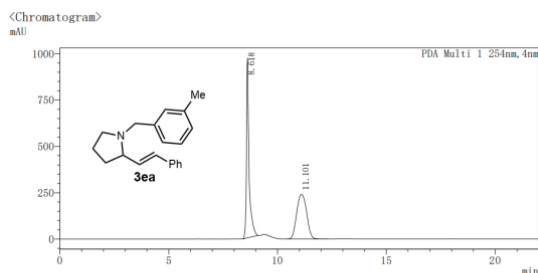
<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	9.443	75522	96.583	10896917	92.786
2	10.741	26729	3.417	847266	7.214
Total		782250	100.000	11744183	100.000

(*S,E*)-1-(3-methylbenzyl)-2-styrylpyrrolidine (**3ea**):

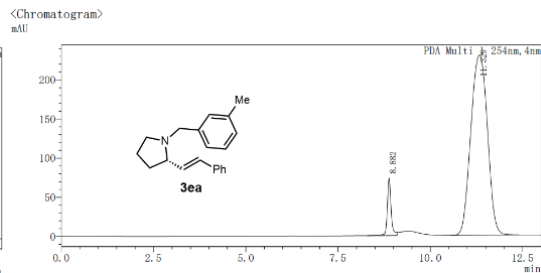


Orange oil (72.6 mg, 87% yield), 93:7 *er*. $[\alpha]_D^{20} = -39.5$ (*c* 0.83, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (d, $J = 7.7$ Hz, 2H), 7.40 – 7.33 (m, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.14 (m, 2H), 7.09 (d, $J = 7.4$ Hz, 1H), 6.61 (d, $J = 15.8$ Hz, 1H), 6.26 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.09 (d, $J = 12.9$ Hz, 1H), 3.16 (d, $J = 12.9$ Hz, 1H), 3.09 – 2.99 (m, 2H), 2.39 (s, 3H), 2.27 – 2.18 (m, 1H), 2.13 – 2.03 (m, 1H), 1.93 – 1.77 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.3, 137.7, 137.1, 132.6, 131.6, 129.7, 128.5, 128.0, 127.5, 127.3, 126.3, 126.1, 68.0, 58.4, 53.4, 31.8, 22.1, 21.4. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{24}\text{N}$ [(M+H) $^+$]: 278.1903, found: 278.1902. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): t_R (minor) = 8.9 min, t_R (major) = 11.3 min.



<Peak Table>

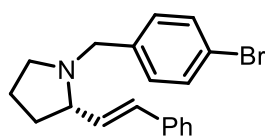
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	8.618	970741	80.121	7938264	50.862
2	11.101	240848	19.879	7669215	49.138
Total		1211589	100.000	15607479	100.000



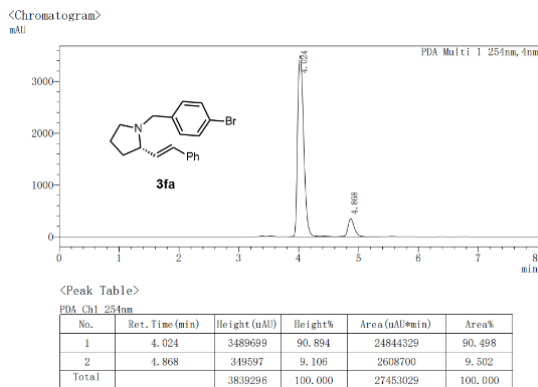
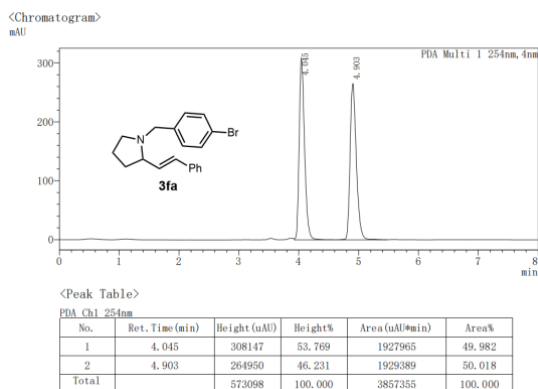
<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	8.882	73062	24.113	528550	6.827
2	11.329	229936	75.887	7213522	93.173
Total		302998	100.000	7742072	100.000

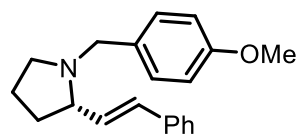
(S,E)-1-(4-bromobenzyl)-2-styrylpyrrolidine (3fa):



Orange oil (89.8 mg, 88% yield), 90.5:9.5 *er*. $[\alpha]_D^{20} = +42.9$ (*c* 0.58, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 – 7.37 (m, 4H), 7.36 – 7.30 (m, 2H), 7.27 – 7.18 (m, 3H), 6.56 (d, $J = 15.8$ Hz, 1H), 6.17 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.01 (d, $J = 13.2$ Hz, 1H), 3.12 (d, $J = 13.2$ Hz, 1H), 3.03 – 2.94 (m, 2H), 2.21 – 2.12 (m, 1H), 2.09 – 2.00 (m, 1H), 1.88 – 1.71 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 138.6, 137.0, 132.4, 131.8, 131.2, 130.6, 128.5, 127.4, 126.3, 120.5, 67.9, 57.6, 53.3, 31.8, 22.2. HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{21}\text{BrN}$ [(M+H) $^+$]: 342.0852, found: 342.0846. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 4.0 min, t_R (minor) = 4.9 min.



(*S,E*)-1-(4-methoxybenzyl)-2-styrylpyrrolidine (3ga):



Yellow solid (72.4 mg, 82% yield), 92:8 *er.* m.p. 46-47 °C;

$[\alpha]_D^{20} = +18.5$ (*c* 0.56, CHCl₃); ¹H NMR (400 MHz, CDCl₃)

δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.24 (d, *J* =

8.2 Hz, 3H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 8.3

Hz, 1H), 4.01 (d, *J* = 12.8 Hz, 1H), 3.79 (s, 3H), 3.13 (d, *J* = 12.8 Hz, 1H), 3.03 – 2.92

(m, 2H), 2.23 – 2.14 (m, 1H), 2.05 – 2.00 (m, 1H), 1.88 – 1.70 (m, 3H); ¹³C NMR (100

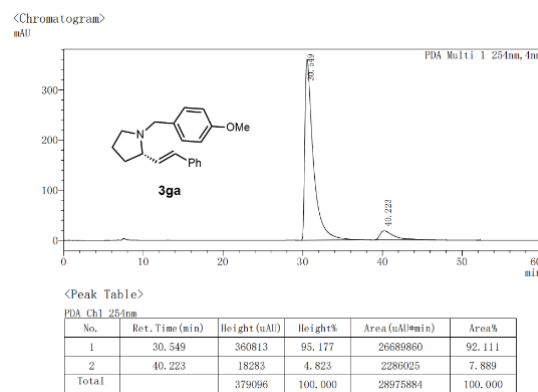
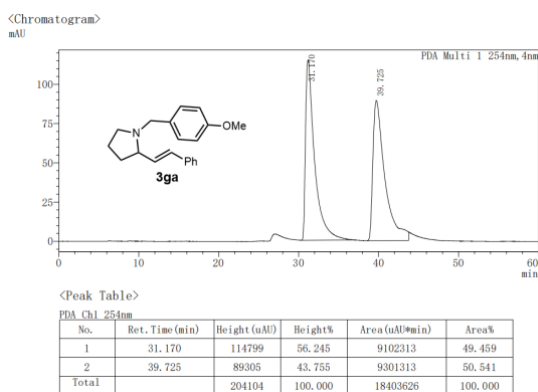
MHz, CDCl₃) δ 158.5, 137.1, 132.7, 131.5, 131.4, 130.1, 128.5, 127.3, 126.3, 113.5,

67.7, 57.6, 55.2, 53.2, 31.8, 22.1. HRMS (ESI) calculated for C₂₀H₂₄NO [(M+H)⁺]:

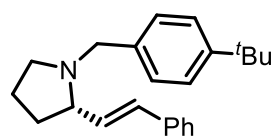
294.1852, found: 294.1851. HPLC (Daicel Chiralpak OJ-H column, *n*-

hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): *t*_R (major) = 30.5 min, *t*_R

(minor) = 40.2 min.



(*S,E*)-1-(4-(*tert*-butyl)benzyl)-2-styrylpyrrolidine (3ha):

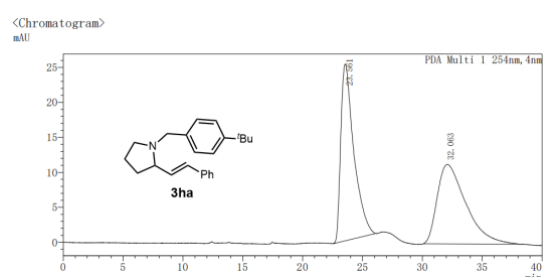


Yellow oil (84.3 mg, 88% yield), 95:5 *er.* $[\alpha]_D^{20} = +26.4$ (*c* 0.59,

CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 7.7 Hz, 2H),

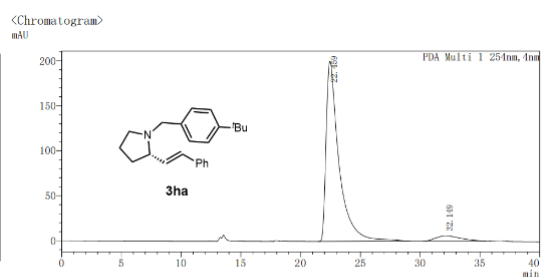
7.38 – 7.32 (m, 4H), 7.31 – 7.25 (m, 3H), 6.59 (d, *J* = 15.8 Hz,

1H), 6.22 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.05 (d, $J = 13.0$ Hz, 1H), 3.21 (d, $J = 13.0$ Hz, 1H), 3.11 – 2.98 (m, 2H), 2.28 – 2.19 (m, 1H), 2.08 – 2.02 (m, 1H), 1.91 – 1.74 (m, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.5, 137.2, 136.3, 132.8, 131.4, 128.7, 128.5, 127.3, 126.3, 125.0, 67.8, 57.9, 53.5, 34.4, 31.9, 31.4, 22.2. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{30}\text{N}$ [(M+H) $^+$]: 320.2373, found: 320.2367. HPLC (Daicel Chiralpak OJ-H+OJ-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): t_{R} (major) = 22.5 min, t_{R} (minor) = 32.1 min.



<Peak Table>

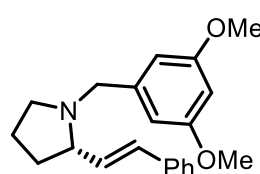
No.	Ret. Time (min)	Height (aAU)	Height%	Area (aAU*min)	Area%
1	23.561	25257	69.000	1919260	50.441
2	32.063	11348	31.000	1885670	49.559
Total		36605	100.000	3804930	100.000



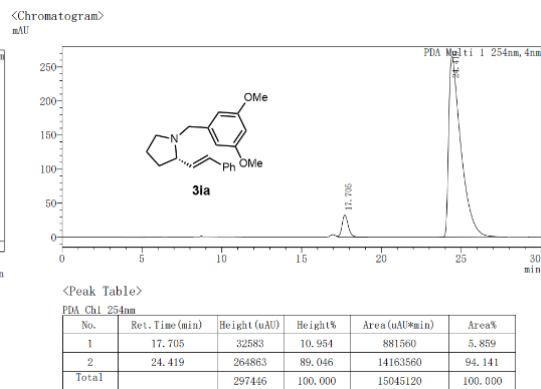
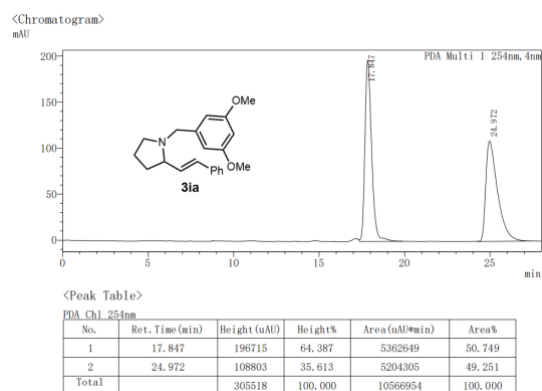
<Peak Table>

No.	Ret. Time (min)	Height (aAU)	Height%	Area (aAU*min)	Area%
1	22.459	200387	97.166	15042731	94.722
2	32.149	5845	2.834	838208	5.278
Total		206232	100.000	15880939	100.000

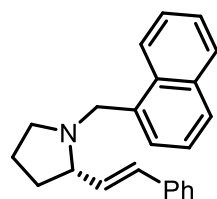
(*S,E*)-1-(3,5-dimethoxybenzyl)-2-styrylpyrrolidine (**3ia**):



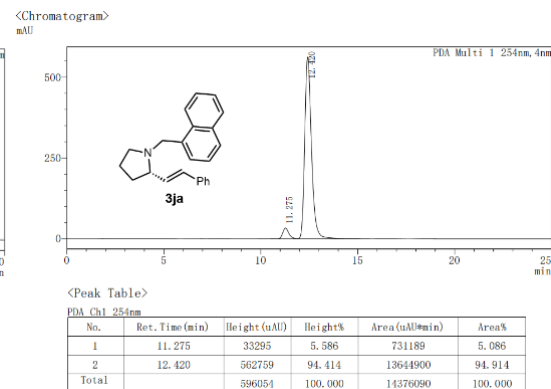
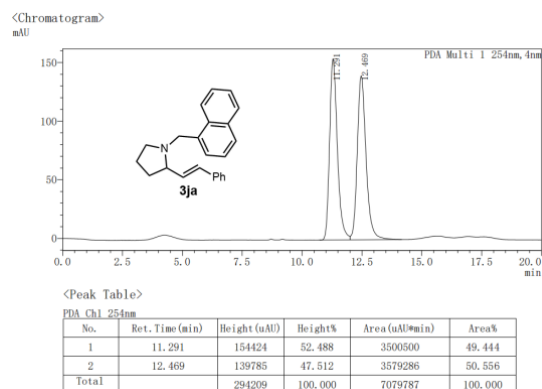
Yellow oil (80.5 mg, 83% yield), 94:6 *er*. $[\alpha]_{\text{D}}^{20} = +17.6$ (*c* 0.62, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.7$ Hz, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 6.57 (d, $J = 15.8$ Hz, 1H), 6.52 (s, 2H), 6.35 (s, 1H), 6.20 (dd, $J = 15.8, 8.3$ Hz, 1H), 4.02 (d, $J = 13.1$ Hz, 1H), 3.79 (s, 6H), 3.12 (d, $J = 13.1$ Hz, 1H), 3.09 – 2.94 (m, 2H), 2.24 – 2.16 (m, 1H), 2.07 – 2.00 (m, 1H), 1.89 – 1.69 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 141.9, 137.1, 132.6, 131.6, 128.5, 127.3, 126.3, 106.8, 98.8, 67.8, 58.4, 55.2, 53.4, 31.8, 22.2. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}_2$ [(M+H) $^+$]: 324.1958, found: 324.1956. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): t_{R} (minor) = 17.7 min, t_{R} (major) = 24.4 min.



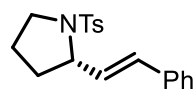
(S,E)-1-(naphthalen-1-ylmethyl)-2-styrylpyrrolidine (3ja):



Yellow solid (82.8 mg, 88% yield), 95:5 *er.* m.p. 59-60 °C; $[\alpha]_D^{20} = +36.8$ (*c* 0.58, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.25 (m, 1H), 7.88 – 7.82 (m, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.44 (m, 5H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.28 – 7.23 (m, 1H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.33 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.60 (d, *J* = 13.0 Hz, 1H), 3.49 (d, *J* = 13.1 Hz, 1H), 3.18 – 3.07 (m, 1H), 2.99 – 2.91 (m, 1H), 2.31 – 2.22 (m, 1H), 2.14 – 2.04 (m, 1H), 1.85 – 1.73 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.2, 135.7, 133.8, 132.8, 132.2, 131.8, 128.5, 128.4, 127.6, 127.3, 126.8, 126.3, 125.7, 125.4, 125.2, 124.6, 68.7, 56.4, 54.0, 32.0, 22.3. HRMS (ESI) calculated for C₂₃H₂₄N [(M+H)⁺]: 314.1903, found: 314.1896. HPLC (Daicel Chiralpak OJ-H+OJ-H column, *n*-hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 254 nm): *t*_R (minor) = 11.3 min, *t*_R (major) = 12.4 min.

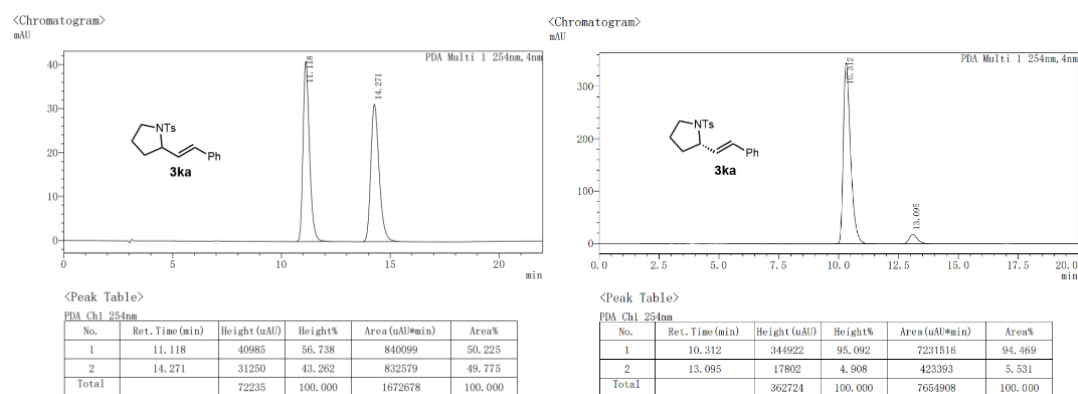


(S,E)-2-styryl-1-tosylpyrrolidine (3ka):

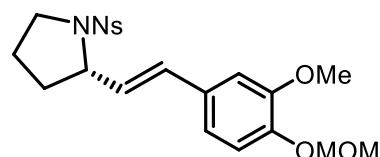


Purified by chromatography on silica gel, eluting with PE/EA = 10/1; yellow solid (87.0 mg, 89% yield), 94.5:5.5 *er.* m.p. 119-120 °C;

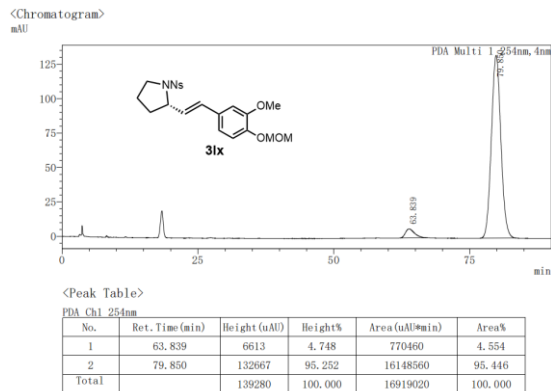
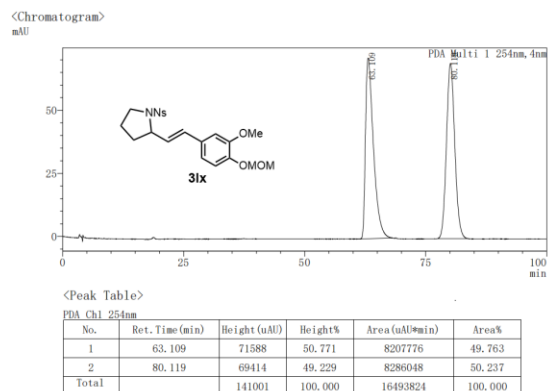
$[\alpha]_D^{20} = +5.3$ (*c* 0.54, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.26 – 7.19 (m, 2H), 6.55 (dd, *J* = 15.8, 1.3 Hz, 1H), 6.05 (dd, *J* = 15.8, 6.7 Hz, 1H), 4.42 – 4.29 (m, 1H), 3.54 – 3.44 (m, 1H), 3.41 – 3.28 (m, 1H), 2.40 (s, 3H), 1.94 – 1.81 (m, 2H), 1.78 – 1.65 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 136.6, 135.6, 130.6, 129.9, 129.5, 128.4, 127.6, 127.5, 126.5, 61.6, 48.6, 32.8, 23.9, 21.4. HRMS (ESI) calculated for C₁₉H₂₁NNaO₂S [(M+Na)⁺]: 350.1158, found: 350.1182. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 10.3 min, t_R (minor) = 13.1 min.



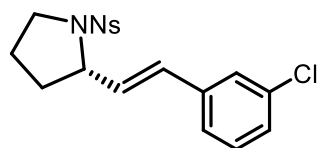
(*S,E*)-2-(3-methoxy-4-(methoxymethoxy)styryl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine (3lx):



Purified by chromatography on silica gel, eluting with PE/EA/DCM = 10/1/1; yellow solid (698.1 mg, 87% yield), 95.5:4.5 *er*. m.p. 119-120 °C; $[\alpha]_D^{20} = -95.7$ (*c* 0.62, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.90 – 6.74 (m, 2H), 6.49 (d, *J* = 15.6 Hz, 1H), 5.79 (dd, *J* = 15.7, 7.4 Hz, 1H), 5.23 (s, 2H), 4.55 – 4.35 (m, 1H), 3.87 (s, 3H), 3.62 – 3.43 (m, 5H), 2.05 – 1.91 (m, 2H), 1.90 – 1.73 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.83, 149.81, 146.5, 145.1, 131.5, 130.6, 128.6, 127.2, 124.1, 119.4, 116.3, 109.6, 95.5, 62.3, 56.2, 55.9, 48.7, 33.0, 24.1. HRMS (ESI) calculated for C₂₁H₂₄N₂NaO₇S [(M+Na)⁺]: 471.1196, found: 471.1207. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (minor) = 63.8 min, t_R (major) = 79.9 min.

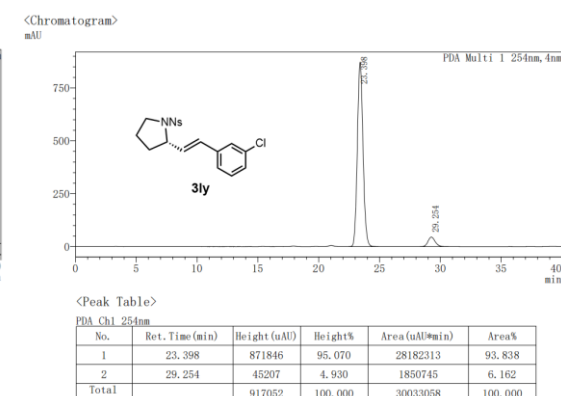
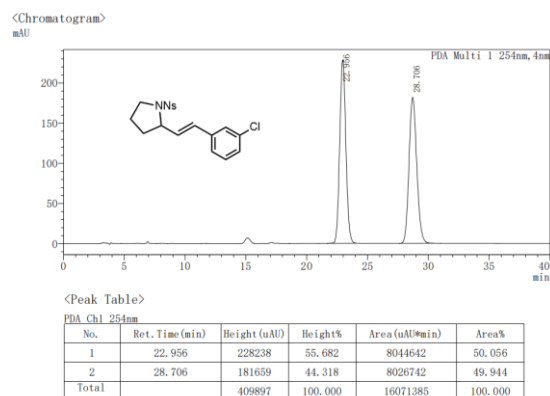


(S,E)-2-(3-chlorostyryl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine (3ly):

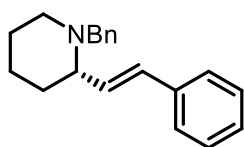


Purified by chromatography on silica gel, eluting with PE/EA/DCM = 20/1/1; yellow solid (708.0 mg, 90% yield), 94:6 *er.* m.p. 130-131 °C; $[\alpha]_D^{20} = -127.2$ (*c* 1.06, CHCl₃);

¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.18 (m, 3H), 7.13 (d, *J* = 6.6 Hz, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 5.95 (dd, *J* = 15.7, 7.2 Hz, 1H), 4.53 – 4.32 (m, 1H), 3.58 – 3.38 (m, 2H), 2.03 – 1.90 (m, 2H), 1.88 – 1.74 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 144.8, 137.9, 134.6, 130.4, 130.3, 129.8, 128.5, 127.9, 126.2, 124.7, 124.2, 61.9, 48.7, 32.9, 24.1. HRMS (ESI) calculated for C₁₈H₁₇ClN₂NaO₄S [(M+Na)⁺]: 415.0490, found: 415.0487. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 23.4 min, *t*_R (minor) = 29.2 min.

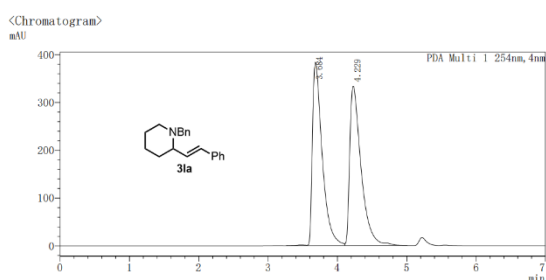


(S,E)-1-benzyl-2-styrylpiperidine (5aa):



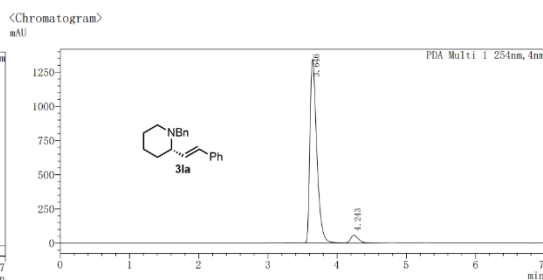
White solid (63.9 mg, 77% yield), 95:5 *er.* m.p. 63-64 °C; $[\alpha]_D^{20} = -152.9$ (*c* 0.64, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.27 (m, 6H), 7.27 – 7.19 (m, 2H), 6.58 (d,

$J = 16.0$ Hz, 1H), 6.32 (dd, $J = 15.9$, 8.6 Hz, 1H), 4.13 (d, $J = 13.6$ Hz, 1H), 3.15 (d, $J = 13.6$ Hz, 1H), 2.88 (t, $J = 10.5$ Hz, 2H), 1.98 (td, $J = 11.2$, 2.0 Hz, 1H), 1.84 – 1.71 (m, 2H), 1.66 – 1.49 (m, 3H), 1.43 – 1.31 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 137.2, 134.1, 130.7, 129.0, 128.5, 128.0, 127.3, 126.6, 126.2, 66.0, 60.2, 52.3, 33.8, 25.8, 24.0. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{24}\text{N}$ [(M+H) $^+$]: 278.1903, found: 278.1908. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 3.6 min, t_{R} (minor) = 4.2 min.



<Peak Table>

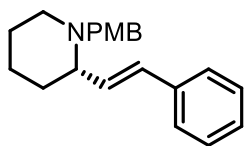
PDA Chl 254nm					
No.	Ret. Time (min)	Height (aAU)	Height%	Area (aAU*min)	Area%
1	3.684	383481	53.492	3776571	49.954
2	4.229	333418	46.508	3783499	50.046
Total		716899	100.000	7560073	100.000



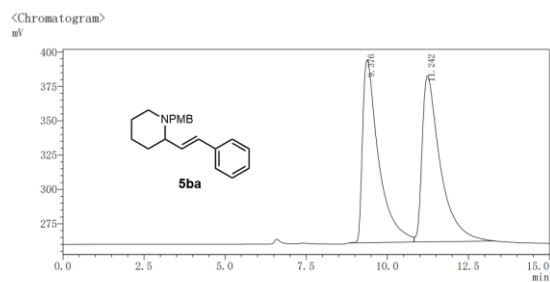
<Peak Table>

PDA Chl 254nm					
No.	Ret. Time (min)	Height (aAU)	Height%	Area (aAU*min)	Area%
1	3.646	1342032	95.927	9255088	95.138
2	4.243	56976	4.073	472937	4.862
Total		1399008	100.000	9728025	100.000

(*S,E*)-1-(4-methoxybenzyl)-2-styrylpiperidine (**5ba**):

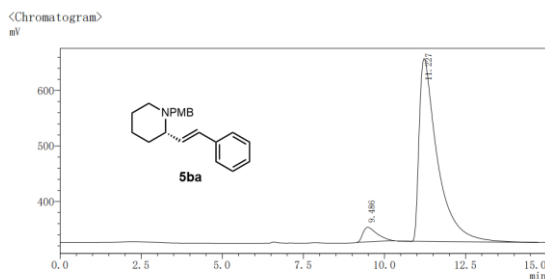


White solid (77.6 mg, 84% yield), 94:6 *er*. m.p. 85-86 °C; $[\alpha]_{\text{D}}^{20} = -109.4$ (c 1.08, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.6$ Hz, 2H), 7.38 – 7.29 (m, 2H), 7.29 – 7.19 (m, 3H), 6.90 – 6.81 (m, 2H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.32 (dd, $J = 16.1$, 8.8 Hz, 1H), 4.04 (d, $J = 13.4$ Hz, 1H), 3.81 (s, 3H), 3.12 (d, $J = 13.4$ Hz, 1H), 2.94 – 2.80 (m, 2H), 2.02 – 1.89 (m, 1H), 1.82 – 1.68 (m, 2H), 1.66 – 1.47 (m, 3H), 1.42 – 1.30 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 137.2, 134.1, 131.1, 130.7, 130.2, 128.5, 127.2, 126.2, 113.4, 65.9, 59.5, 55.2, 52.1, 33.7, 25.8, 23.9. HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{26}\text{NO}$ [(M+H) $^+$]: 308.2009, found: 308.2011. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 95/5, flow rate 0.5 mL/min, 254 nm): t_{R} (minor) = 9.5 min, t_{R} (major) = 11.2 min.



<Peak Table>

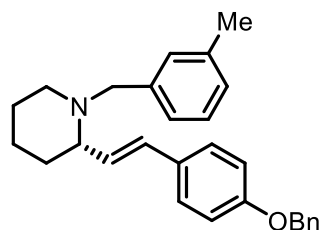
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	9.376	133133	52.415	4590413	49.236
2	11.242	120867	47.585	4732897	50.764
Total		254000	100.000	9323310	100.000



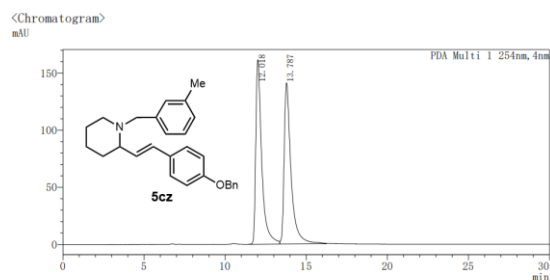
<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	9.486	26285	7.396	802017	5.829
2	11.227	329127	92.604	12957058	94.171
Total		355412	100.000	13759075	100.000

(*S,E*)-2-(4-(benzyloxy)styryl)-1-(3-methylbenzyl)piperidine (**5cz**):

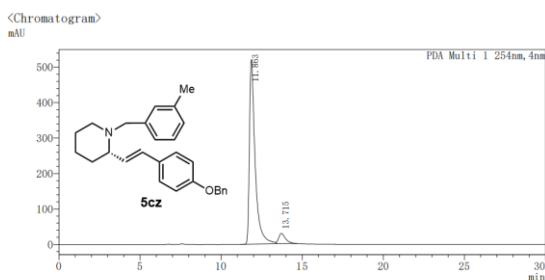


Yellow solid (101.6 mg, 85% yield), 93.5:6.5 *er.* m.p. 73-74 °C; $[\alpha]_D^{20} = -81.7$ (*c* 0.72, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.28 (m, 3H), 7.22 – 7.15 (m, 1H), 7.13 (s, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.9, 8.6 Hz, 1H), 5.08 (s, 2H), 4.07 (d, *J* = 13.5 Hz, 1H), 3.06 (d, *J* = 13.5 Hz, 1H), 2.92 – 2.84 (m, 1H), 2.85 – 2.74 (m, 1H), 2.34 (s, 3H), 1.98 – 1.88 (m, 1H), 1.79 – 1.69 (m, 3H), 1.63 – 1.49 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 139.3, 138.1, 137.6, 137.0, 132.1, 130.4, 130.2, 129.9, 128.6, 128.0, 127.9, 127.4, 127.4, 126.3, 115.0, 70.1, 66.3, 60.3, 52.5, 33.9, 25.9, 24.1, 21.4. HRMS (ESI) calculated for C₂₈H₃₂NO [(M+H)⁺]: 398.2478, found: 398.2486. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 95/5, flow rate 0.5 mL/min, 254 nm): *t*_R (major) = 11.9 min, *t*_R (minor) = 13.7 min.



<Peak Table>

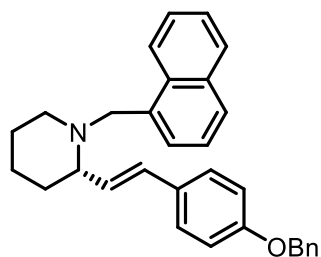
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	12.018	161419	53.369	4157987	49.860
2	13.787	141038	46.631	4181257	50.140
Total		302457	100.000	8339244	100.000



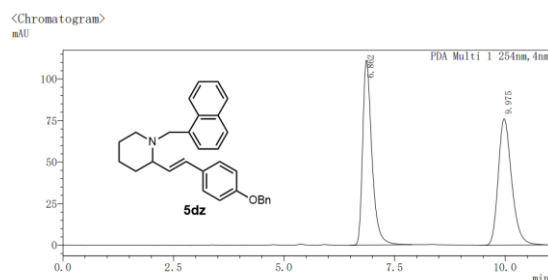
<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	11.863	520106	94.655	12757287	93.663
2	13.715	29370	5.345	863151	6.337
Total		549476	100.000	13620437	100.000

(*S,E*)-2-(4-(benzyloxy)styryl)-1-(naphthalen-1-ylmethyl)piperidine (**5dz**):

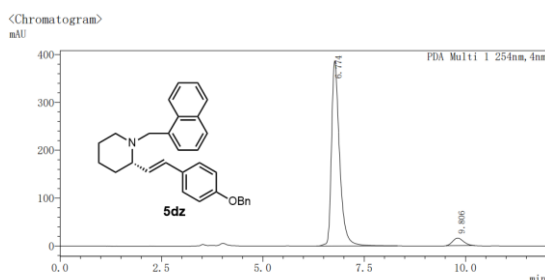


Yellow oil (100.7 mg, 77% yield), 95:5 *er.* $[\alpha]_D^{20} = -84.7$ (*c* 1.09, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 6.9 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.47 (m, 3H), 7.50 – 7.30 (m, 8H), 7.01 – 6.92 (m, 2H), 6.61 (dd, *J* = 15.9, 3.4 Hz, 1H), 6.35 (ddt, *J* = 15.8, 8.7, 2.5 Hz, 1H), 5.10 (s, 2H), 4.63 (dd, *J* = 13.8, 3.8 Hz, 1H), 3.47 (dd, *J* = 13.7, 3.2 Hz, 1H), 3.05 – 2.91 (m, 1H), 2.92 – 2.83 (m, 1H), 2.08 – 1.93 (m, 1H), 1.90 – 1.73 (m, 2H), 1.74 – 1.63 (m, 1H), 1.62 – 1.34 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 137.1, 135.6, 133.9, 132.6, 131.7, 130.5, 130.4, 128.6, 128.5, 128.0, 127.5, 127.4, 127.2, 125.6, 125.5, 125.3, 124.8, 115.1, 70.1, 67.2, 58.5, 52.6, 33.9, 26.0, 24.1. HRMS (ESI) calculated for C₃₁H₃₂NO [(M+H)⁺]: 434.2478, found: 434.2492. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 6.8 min, *t*_R (minor) = 9.8 min.



<Peak Table>

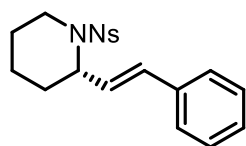
No.	Ret. Time (min)	Height (aU)	Height%	Area (aU*min)	Area%
1	6.862	111064	59.351	1616499	50.032
2	9.975	76066	40.649	1614437	49.968
Total		187130	100.000	3230936	100.000



<Peak Table>

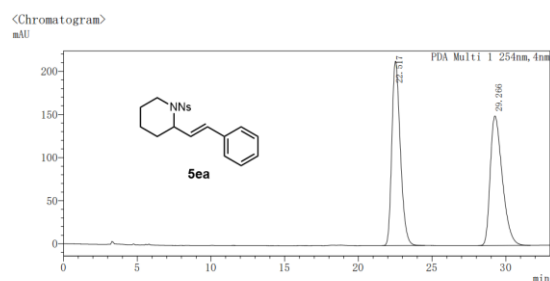
No.	Ret. Time (min)	Height (aU)	Height%	Area (aU*min)	Area%
1	6.774	386654	96.129	5366940	94.910
2	9.806	15571	3.871	287843	5.090
Total		402225	100.000	5654783	100.000

(*S,E*)-1-((4-nitrophenyl)sulfonyl)-2-styrylpiperidine (**5ea**):



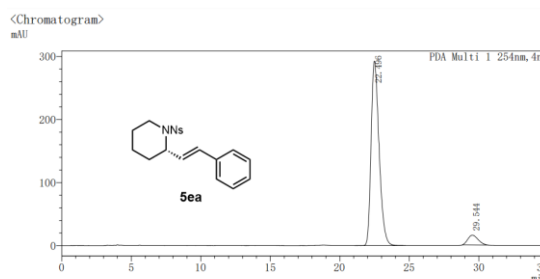
Purified by chromatography on silica gel, eluting with PE/EA/DCM = 20/1/1; yellow solid (90.3 mg, 81% yield), 93.5:6.5 *er.* m.p. 123-124 °C; $[\alpha]_D^{20} = -76.7$ (*c* 1.07, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.15 (m, 2H), 7.98 – 7.90 (m, 2H), 7.30 – 7.25 (m, 1H), 7.25 – 7.19 (m, 2H), 7.17 – 7.12 (m, 2H), 6.41 (d, *J* = 16.3 Hz, 1H), 5.98 (dd, *J* = 16.0, 6.9 Hz, 1H), 4.90 – 4.70 (m, 1H), 3.89 – 3.72 (m, 1H), 3.17 – 2.95 (m, 1H), 1.88 – 1.76 (m, 2H), 1.74 – 1.66 (m, 1H), 1.66 – 1.59 (m, 1H), 1.59 – 1.47 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 146.1, 135.8, 132.9, 128.6, 128.5, 128.0, 126.1, 124.9, 124.0, 55.7, 42.2, 30.7, 25.1, 18.9. HRMS (ESI) calculated for C₁₉H₂₀N₂NaO₄S

[(M+Na)⁺]: 395.1036, found: 395.1034. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 22.5 min, *t*_R (minor) = 29.5 min.



<Peak Table>
PDA Ch1 254nm

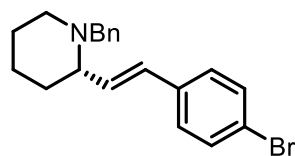
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	22.517	213866	58.727	8588411	50.082
2	29.266	150303	41.273	8560156	49.918
Total		364169	100.000	17148568	100.000



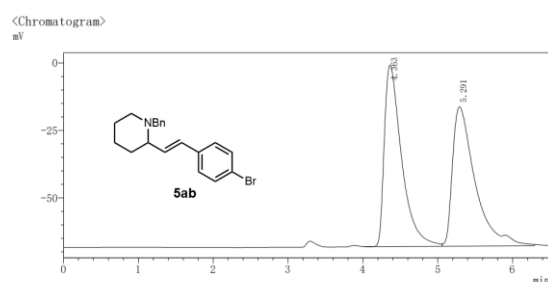
<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	22.496	292475	94.949	11710632	93.632
2	29.544	15559	5.051	796417	6.368
Total		308034	100.000	12507049	100.000

(*S,E*)-1-benzyl-2-(4-bromostyryl)piperidine (5ab):

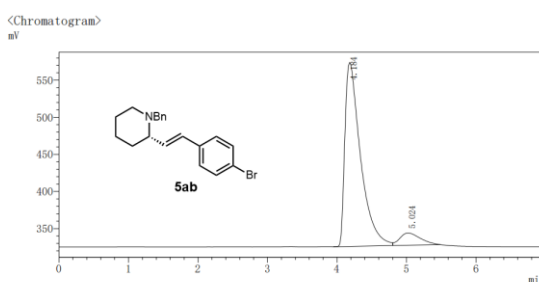


Yellow oil (95.2 mg, 89% yield), 92:8 *er*. [α]_D²⁰ = -89.7 (*c* 1.22, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.44 (m, 1H), 7.43 – 7.41 (m, 1H), 7.36 – 7.29 (m, 4H), 7.27 – 7.20 (m, 3H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 16.0, 8.5 Hz, 1H), 4.07 (d, *J* = 13.6 Hz, 1H), 3.13 (d, *J* = 13.6 Hz, 1H), 2.93 – 2.79 (m, 2H), 1.96 (td, *J* = 11.3, 3.2 Hz, 1H), 1.82 – 1.67 (m, 2H), 1.65 – 1.50 (m, 3H), 1.43 – 1.32 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 136.2, 135.0, 131.6, 129.5, 128.9, 128.0, 127.7, 126.6, 120.9, 66.0, 60.3, 52.4, 33.7, 25.8, 23.9. HRMS (ESI) calculated for C₂₀H₂₃BrN [(M+H)⁺]: 356.1008, found: 356.1010. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 4.2 min, *t*_R (minor) = 5.0 min.



<Peak Table>
检测器A Ch2 254nm

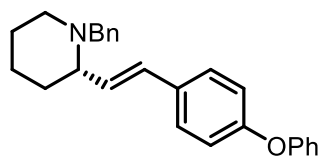
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.363	67208	56.536	1079564	49.817
2	5.291	51669	43.464	1087490	50.183
Total		118877	100.000	2167055	100.000



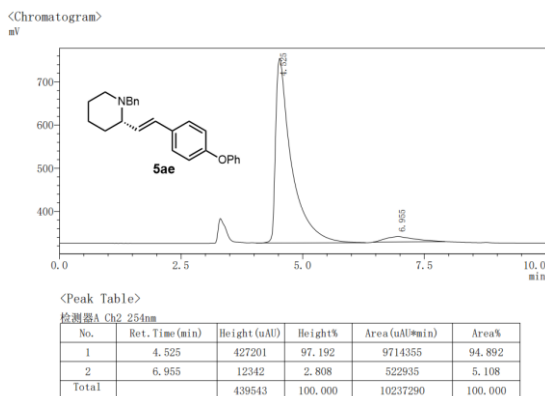
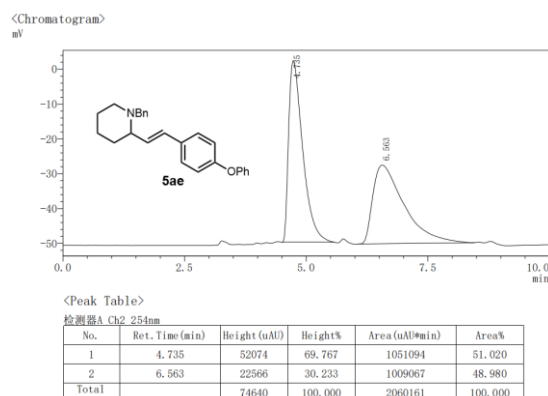
<Peak Table>
检测器A Ch2 254nm

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.184	247864	93.750	3866902	91.937
2	5.024	16523	6.250	339145	8.063
Total		264387	100.000	4206048	100.000

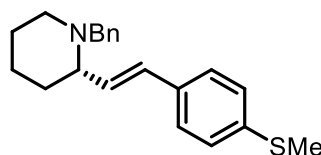
(*S,E*)-1-benzyl-2-(4-phenoxytyryl)piperidine (5ae):



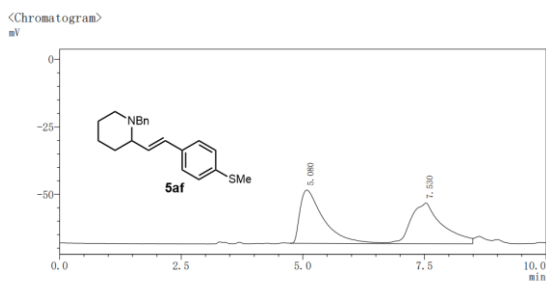
Yellow solid (99.8 mg, 90% yield), 95:5 *er.* m.p. 78-79 °C; $[\alpha]_D^{20} = -98.9$ (*c* 1.20, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.29 (m, 8H), 7.29 – 7.21 (m, 1H), 7.16 – 7.09 (m, 1H), 7.06 – 7.02 (m, 2H), 7.02 – 6.96 (m, 2H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 16.0, 8.6 Hz, 1H), 4.14 (d, *J* = 13.6 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 2.98 – 2.80 (m, 2H), 1.98 (td, *J* = 11.2, 3.3 Hz, 1H), 1.84 – 1.71 (m, 2H), 1.68 – 1.51 (m, 3H), 1.46 – 1.32 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 156.4, 139.4, 133.2, 132.5, 129.9, 129.7, 129.0, 128.0, 127.5, 126.6, 123.1, 119.0, 118.7, 66.1, 60.2, 52.3, 33.8, 25.8, 24.0. HRMS (ESI) calculated for C₂₆H₂₈NO [(M+H)⁺]: 370.2165, found: 370.2173. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 4.5 min, *t*_R (minor) = 7.0 min.



(*S,E*)-1-benzyl-2-(4-(methylthio)styryl)pyperidine (**5af**):

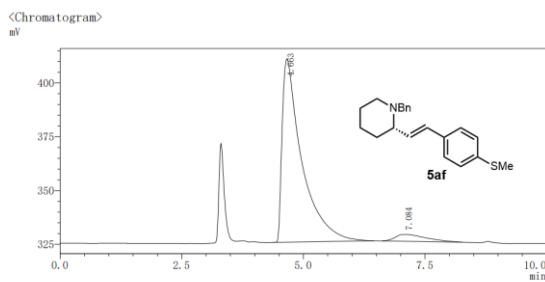


Yellow solid (76.8 mg, 79% yield), 94.5:5.5 *er.* m.p. 84-85 °C; $[\alpha]_D^{20} = -105.0$ (*c* 0.94, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 6H), 7.25 – 7.18 (m, 3H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 15.9, 8.6 Hz, 1H), 4.09 (d, *J* = 13.6 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 2.97 – 2.78 (m, 2H), 2.48 (s, 3H), 1.95 (td, *J* = 11.3, 3.2 Hz, 1H), 1.81 – 1.67 (m, 2H), 1.65 – 1.45 (m, 3H), 1.42 – 1.29 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 137.3, 134.3, 133.7, 130.1, 129.0, 128.0, 126.8, 126.6 (overlap), 66.1, 60.2, 52.4, 33.8, 25.8, 24.0, 16.0. HRMS (ESI) calculated for C₂₁H₂₆NS [(M+H)⁺]: 324.1780, found: 324.1780. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 4.7 min, *t*_R (minor) = 7.1 min.



<Peak Table>

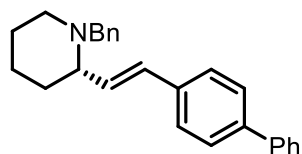
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	5.080	19754	56.779	662778	49.558
2	7.530	15037	43.221	674609	50.442
Total		34791	100.000	1337387	100.000



<Peak Table>

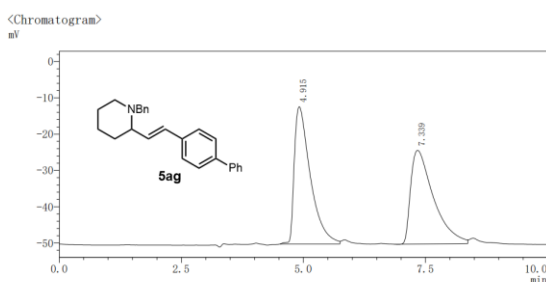
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.663	85214	96.441	2393485	94.436
2	7.084	3144	3.559	141022	5.564
Total		88359	100.000	2534507	100.000

(S,E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-1-benzylpiperidine (5ag):



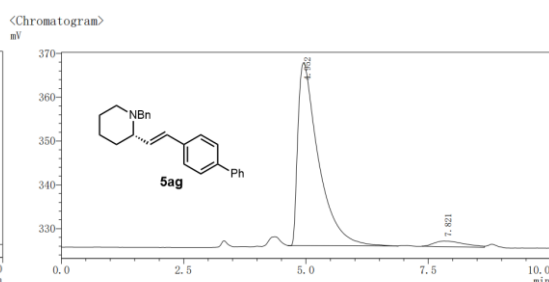
Yellow solid (63.2 mg, 60% yield), 95.5:4.5 *er.* m.p. 110-111 °C; $[\alpha]_D^{20} = -116.7$ (*c* 0.59, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.58 (m, 2H), 7.58 – 7.54 (m, 2H), 7.50 –

7.41 (m, 4H), 7.38 – 7.28 (m, 5H), 7.26 – 7.20 (m, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.35 (dd, *J* = 16.0, 8.6 Hz, 1H), 4.12 (d, *J* = 13.6 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 3.00 – 2.79 (m, 2H), 1.97 (td, *J* = 11.2, 3.3 Hz, 1H), 1.83 – 1.68 (m, 2H), 1.68 – 1.47 (m, 3H), 1.43 – 1.31 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.8, 140.1, 139.4, 136.3, 134.3, 130.3, 129.1, 128.8, 128.0, 127.2, 126.9, 126.6 (overlap), 66.1, 60.3, 52.4, 33.8 25.8, 24.0. HRMS (ESI) calculated for C₂₆H₂₈N [(M+H)⁺]: 354.2216, found: 354.2216. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): *t*_R (major) = 5.0 min, *t*_R (minor) = 7.8 min.



<Peak Table>

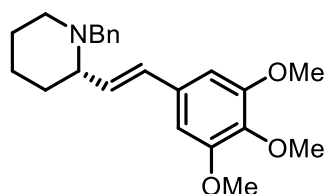
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.915	37823	59.418	868813	50.847
2	7.339	25832	40.582	839872	49.153
Total		63655	100.000	1708685	100.000



<Peak Table>

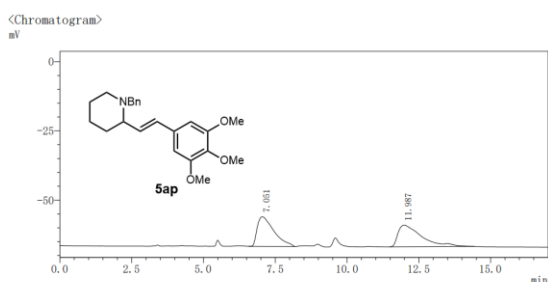
No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.952	41766	97.047	1226783	95.689
2	7.821	1271	2.953	55271	4.311
Total		43037	100.000	1282054	100.000

(S,E)-1-benzyl-2-(3,4,5-trimethoxystyryl)piperidine (5ap):



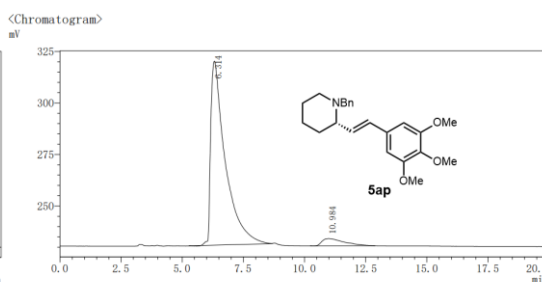
Yellow solid (93.3 mg, 85% yield), 94.5:5.5 *er.* m.p. 54-55 °C; $[\alpha]_D^{20} = -92.3$ (*c* 1.18, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 6.61 (s,

2H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.19 (dd, $J = 15.8, 8.6$ Hz, 1H), 4.10 (d, $J = 13.7$ Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H), 3.14 (d, $J = 13.7$ Hz, 1H), 2.94 – 2.77 (m, 2H), 1.95 (td, $J = 11.3, 3.1$ Hz, 1H), 1.83 – 1.68 (m, 2H), 1.67 – 1.49 (m, 3H), 1.41 – 1.29 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 139.3, 137.6, 133.6, 132.9, 130.5, 128.9, 127.9, 126.5, 103.2, 66.1, 60.8, 60.2, 56.0, 52.4, 33.8, 25.8, 23.9. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{30}\text{NO}_3$ $[(\text{M}+\text{H})^+]$: 368.2220, found: 368.2223. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (major) = 6.3 min, t_{R} (minor) = 11.0 min.



<Peak Table>

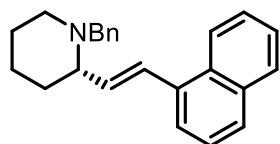
检测器A Ch2 254nm					
No.	Ret. Time (min)	Height (a.u.)	Height%	Area (a.u.*min)	Area%
1	7.051	10763	57.968	436464	49.256
2	11.987	7805	42.032	449658	50.744
Total		18568	100.000	886122	100.000



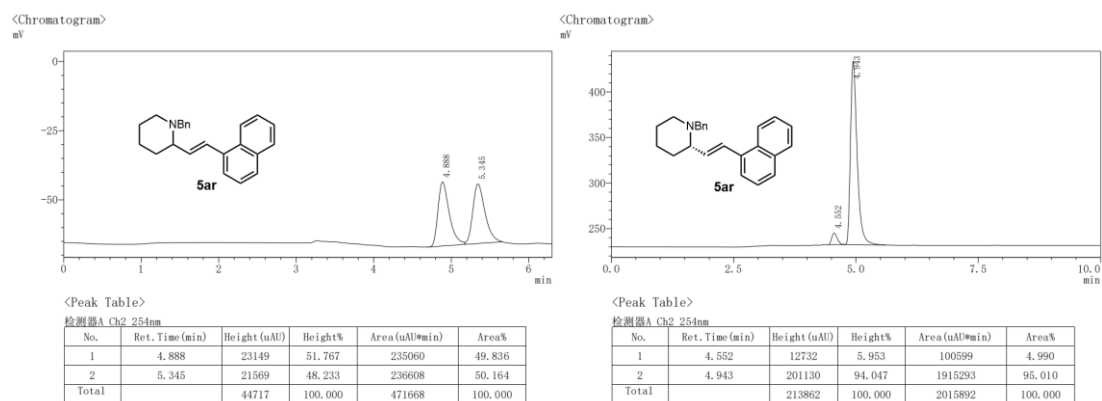
<Peak Table>

检测器A Ch2 254nm					
No.	Ret. Time (min)	Height (a.u.)	Height%	Area (a.u.*min)	Area%
1	6.314	89323	96.190	3720770	94.427
2	10.984	3538	3.810	219593	5.573
Total		92861	100.000	3940363	100.000

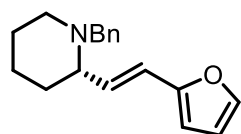
(*S,E*)-1-benzyl-2-(2-(naphthalen-1-yl)vinyl)piperidine (5ar):



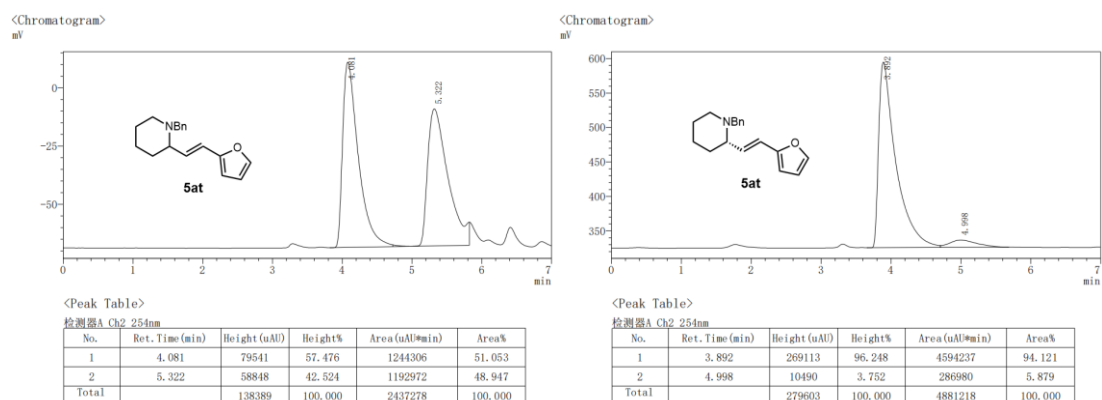
Yellow oil (49.6 mg, 51% yield), 95:5 *er*. $[\alpha]_{\text{D}}^{20} = -58.5$ (c 1.22, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 7.9$ Hz, 1H), 7.88 (d, $J = 8.6$ Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.62 (d, $J = 7.1$ Hz, 1H), 7.58 – 7.44 (m, 3H), 7.43 – 7.38 (m, 2H), 7.38 – 7.31 (m, 3H), 7.31 – 7.26 (m, 1H), 6.38 (ddd, $J = 15.8, 8.7, 1.5$ Hz, 1H), 4.23 (d, $J = 13.5$ Hz, 1H), 3.26 (d, $J = 13.6$ Hz, 1H), 3.12 – 3.00 (m, 1H), 2.98 – 2.88 (m, 1H), 2.06 (td, $J = 11.1, 3.3$ Hz, 1H), 1.90 – 1.79 (m, 2H), 1.76 – 1.54 (m, 3H), 1.51 – 1.38 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 137.3, 135.0, 133.6, 131.1, 129.1, 128.5, 128.1, 127.9, 127.6, 126.6, 125.9, 125.7, 125.6, 123.8 (overlap), 66.2, 60.3, 52.4, 33.9, 25.9, 24.0. HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{26}\text{N}$ $[(\text{M}+\text{H})^+]$: 328.2060, found: 328.2055. HPLC (Daicel Chiralpak OD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_{R} (minor) = 4.6 min, t_{R} (major) = 4.9 min.



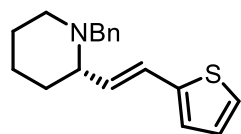
(*S,E*)-1-benzyl-2-(2-(furan-2-yl)vinyl)piperidine (**5at**):



Yellow oil (60.1 mg, 75% yield), 94:6 *er.* $[\alpha]_D^{20} = -112.6$ (*c* 1.17, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 – 7.27 (m, 5H), 7.26 – 7.20 (m, 1H), 6.43 – 6.35 (m, 2H), 6.26 (dd, $J = 16.0, 8.5$ Hz, 1H), 6.21 (d, $J = 3.3$ Hz, 1H), 4.10 (d, $J = 13.5$ Hz, 1H), 3.11 (d, $J = 13.6$ Hz, 1H), 2.93 – 2.77 (m, 2H), 1.95 (td, $J = 11.1, 3.4$ Hz, 1H), 1.81 – 1.68 (m, 2H), 1.66 – 1.49 (m, 3H), 1.43 – 1.31 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 152.8, 141.6, 139.4, 132.8, 129.0, 128.0, 126.6, 119.4, 111.1, 107.0, 65.7, 60.2, 52.1, 33.7, 25.8, 23.9. HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{22}\text{NO}$ $[(\text{M}+\text{H})^+]$: 268.1696, found: 268.1701. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (major) = 3.9 min, t_R (minor) = 5.0 min.

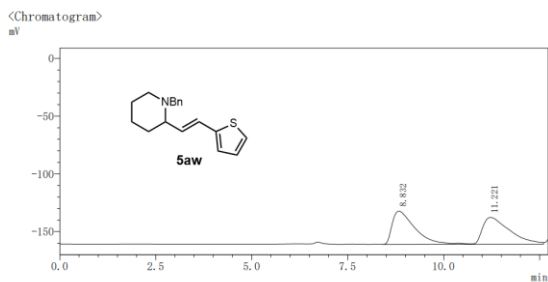


(*S,E*)-1-benzyl-2-(2-(thiophen-2-yl)vinyl)piperidine (**5aw**):



Yellow oil (55.8 mg, 66% yield), 95.5:4.5 *er.* $[\alpha]_D^{20} = -122.7$ (*c* 0.64, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 7.16 – 7.12 (m, 1H), 7.00 – 6.87 (m, 2H), 6.69 (d, $J = 15.8$ Hz, 1H), 6.15 (dd, $J = 15.8, 8.6$ Hz, 1H), 4.11 (d, $J = 13.6$ Hz, 1H), 3.12 (d,

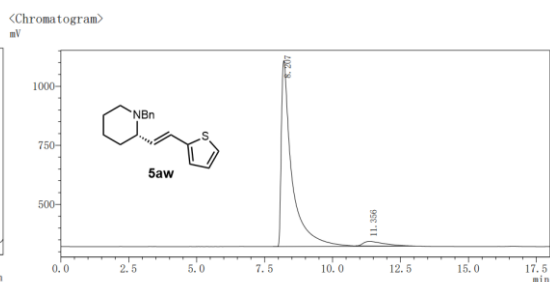
$J = 13.6$ Hz, 1H), 2.93 – 2.71 (m, 2H), 1.95 (td, $J = 11.3, 3.3$ Hz, 1H), 1.81 – 1.68 (m, 2H), 1.65 – 1.49 (m, 3H), 1.42 – 1.31 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 139.4, 133.8, 129.0, 128.0, 127.2, 126.6, 124.9, 124.0, 123.8, 65.8, 60.2, 52.2, 33.7, 25.8, 23.9. HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{22}\text{NS}$ [(M+H) $^+$]: 284.1467, found: 284.1473. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 95/5, flow rate 0.5 mL/min, 254 nm): t_{R} (major) = 8.2 min, t_{R} (minor) = 11.4 min.



<Peak Table>

检测器A Ch2 254nm

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	8.832	28774	55.261	1186213	50.853
2	11.221	23295	44.739	1146439	49.147
Total		52069	100.000	2332651	100.000

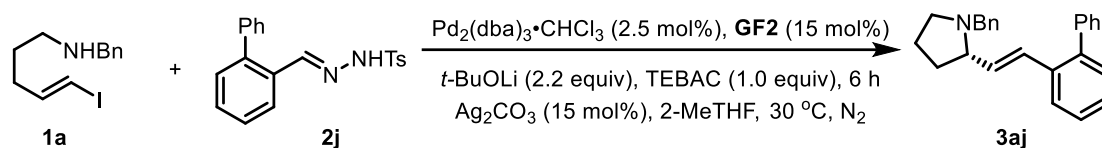


<Peak Table>

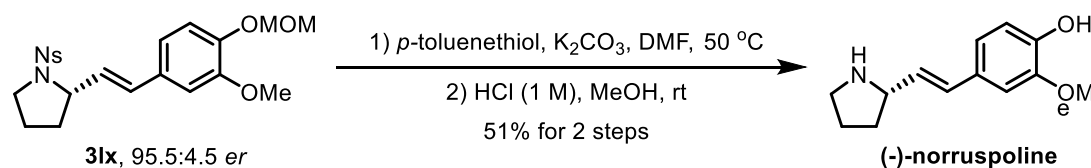
检测器A Ch2 254nm

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	8.207	786044	97.648	21400680	95.475
2	11.356	18934	2.352	1014299	4.525
Total		804978	100.000	22414979	100.000

5. Gram-scale Reaction and Synthetic Applications



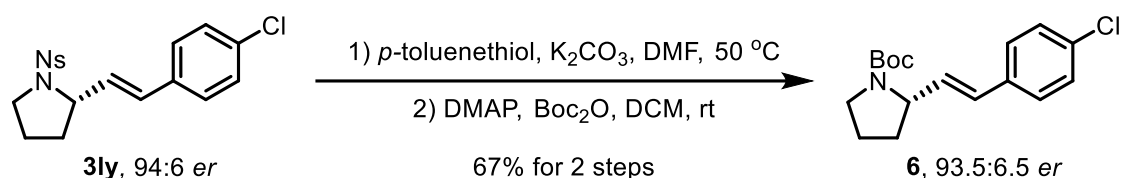
To a 100 mL flame-dried flask was added *N*-tosylhydrazones **2j** (9.6 mmol, 3.36 g), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.15 mmol, 155.3 mg), **GF2** (0.9 mmol, 681.3 mg), *t*-BuOLi (13.2 mmol, 1.06 g), Ag_2CO_3 (0.9 mmol, 248.2 mg), and triethylbenzylammonium chloride (TEBAC, 6 mmol, 1.37 g) was added in the glove box. The reaction was evacuated and back-filled with N_2 three times and a solution of the vinyl iodide **1a** (6 mmol, 1.81 g) in 60 mL 2- MeTHF was added under nitrogen atmosphere. Then the reaction was stirred at 30 °C for 6 h. Upon completion, the reaction mixture was filtered through celite, evaporated *in vacuo* and purified by silica gel column chromatography (DCM to PE/ Et_3N = 50:1) to give the product **3aj** (1.74 g, 85% yield, 95.5:4.5 *er*).



According to published literature,^[5, 6] to a round-bottom flask was added **3lx** (0.2 mmol, 89.6 mg), *p*-toluenethiol (0.3 mmol, 37.3 mg) and K_2CO_3 (0.6 mmol, 82.9 mg) in DMF (2 mL). The reaction mixture was stirred at 50 °C overnight, then cooled to room temperature, diluted with water and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was used in the next step without any further purification.

To a solution of the residue in MeOH (2 mL) at room temperature was added 1 M aqueous HCl (4 mL). The reaction mixture was stirred for 8 h, then added the saturated aqueous NaHCO_3 to basify the mixture to $\text{pH} \geq 7$ and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by thin-layer chromatography (DCM/MeOH = 3/1) gave (-)-norruspoline (22.2 mg, 51% yield) as an orange solid. m.p. 69-70 °C; $[\alpha]_{\text{D}}^{20} = -29.1$ (*c* 0.76, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 6.87 (s, 1H), 6.82 (s, 2H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.03 (dd, *J* = 15.7, 7.3

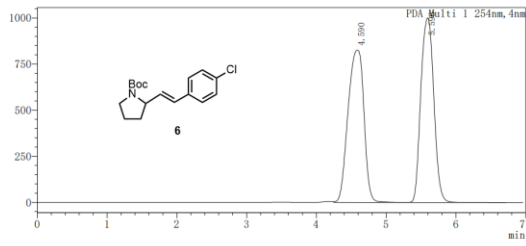
Hz, 1H), 3.86 (s, 3H), 3.68 (q, $J = 7.4$ Hz, 1H), 3.16 – 3.05 (m, 1H), 2.99 – 2.89 (m, 1H), 2.09 – 1.93 (m, 1H), 1.92 – 1.76 (m, 2H), 1.64 – 1.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 145.7, 130.2, 129.4, 129.3, 120.0, 114.8, 108.3, 61.0, 55.8, 46.2, 32.3, 25.2. HRMS (ESI) calculated for $\text{C}_{13}\text{H}_{18}\text{NO}_2$ $[(\text{M}+\text{H})^+]$: 220.1332, found: 220.1336.



According to published literature,^[5, 7] to a round-bottom flask was added **3ly** (0.15 mmol, 58.8 mg), *p*-toluenethiol (0.23 mmol, 27.9 mg) and K_2CO_3 (0.45 mmol, 62.2 mg) in DMF (2 mL). The following steps are the same as above to obtain the deprotected crude product.

To a solution of the crude product, 4-(dimethylamino) pyridine (0.015 mmol, 1.8 mg) in DCM (2 mL) at room temperature was added Boc_2O (0.17 mmol, 38 μL). The reaction mixture was stirred for 2 h. Upon completion, the mixture was concentrated *in vacuo* and purified by flash chromatography (PE/EA = 10/1) gave **6** (31.1 mg, 67% yield, 93.5:6.5 *er*) as colorless oil. $[\alpha]_D^{20} = -88.1$ (c 1.03, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (s, 1H), 7.25 – 7.12 (m, 3H), 6.33 (d, $J = 15.4$ Hz, 1H), 6.20 – 6.02 (m, 1H), 4.73 – 4.26 (m, 2H), 3.45 (s, 2H), 2.09 (s, 1H), 1.99 – 1.68 (m, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 138.8, 134.3, 132.2, 129.6, 128.0, 127.0, 126.0, 124.4, 79.1, 58.7, 46.2, 32.4, 28.4, 22.9. All spectroscopic data is in agreement with those previously reported.^[8] HRMS (ESI) calculated for $\text{C}_{17}\text{H}_{22}\text{ClNNaO}_2$ $[(\text{M}+\text{Na})^+]$: 330.1231, found: 330.1231. HPLC (Daicel Chiralpak AD-H column, *n*-hexane/isopropanol = 90/10, flow rate 1.0 mL/min, 254 nm): t_R (minor) = 4.6 min, t_R (major) = 5.6 min.

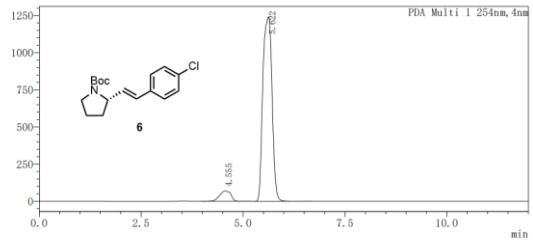
<Chromatogram>
mAU



<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.590	826404	45.232	13051970	50.124
2	5.596	1000619	54.768	12987415	49.876
Total		1827023	100.000	26039384	100.000

<Chromatogram>
mAU

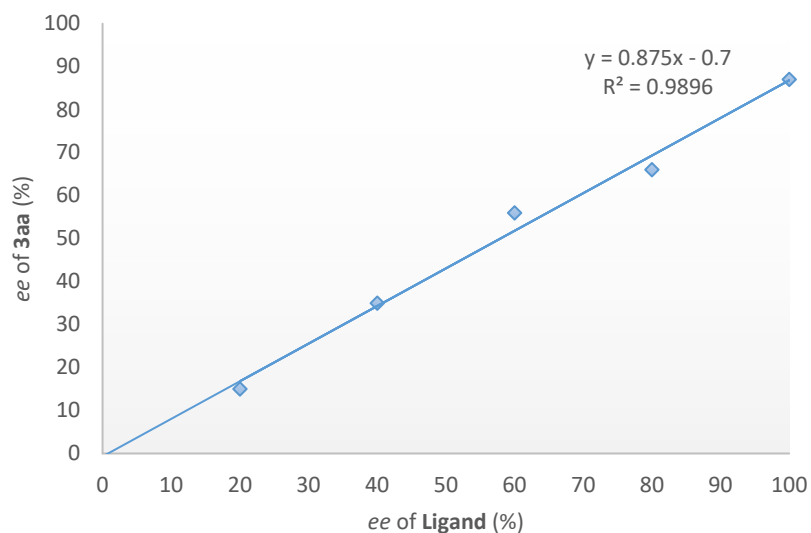


<Peak Table>

No.	Ret. Time (min)	Height (uAU)	Height%	Area (uAU*min)	Area%
1	4.555	69659	5.310	1328620	6.398
2	5.622	1242207	94.690	19436732	93.602
Total		1311866	100.000	20765352	100.000

6. Nonlinear Effect Study

In general, nonlinear effect study began with standard conditions (0.1 mmol), but the ratio of chiral ligands **GF2** and *ent*-**GF2** is various. They were weighed accurately on the analytical balance and the reaction was carried out according to general procedure. The results are listed below.

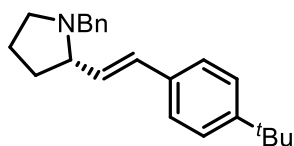


entry	1	2	3	4	5
GF2/ent-GF2 (ratio)	0.6/0.4	0.7/0.3	0.8/0.2	0.9/0.1	1
ee of Ligand (%)	20	40	60	80	100
ee of 3aa (%)	15	35	56	66	87

7. References

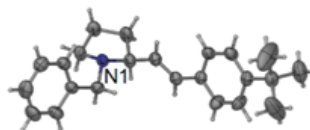
1. C.-L. Ma, X.-L. Yu, X.-L. Zhu, Y.-Z. Hu, X.-W. Dong, B. Tan, X.-Y. Liu, *Adv. Synth. Catal.* **2015**, *357*, 569-575.
2. H. Lu, C. Li, H. Jiang, C. L. Lizardi, X. P. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 7028-7032.
3. A. Khanna, C. Maung, K. R. Johnson, T. T. Luong, Van Vranken, D. L. *Org. Lett.* **2012**, *14*, 3233-3235.
4. A.-J. Xia, T.-R. Kang, L. He, L.-M. Chen, W.-T. Li, J.-L. Yang, Q.-Z. Liu, *Angew. Chem. Int. Ed.* **2016**, *55*, 1441-1444.
5. A. Becker, C. P. Grugel, B. Breit, *Org. Lett.* **2021**, *23*, 3788-3792.
6. C. E. Sear, P. Pieper, M. Amaral, M. M. Romanelli, T. A. Costa-Silva, M. M. Haugland, J. A. Tate, J. H. G. Lago, A. G. Tempone, E. A. Anderson, *ACS Infect. Dis.* **2020**, *6*, 2872-2878.
7. N. J. Taylor, E. Emer, S. Preshlock, M. Schedler, M. Tredwell, S. Verhoog, J. Mercier, C. Genicot, V. Gouverneur, *J. Am. Chem. Soc.* **2017**, *139*, 8267-8276.
8. H. Zhang, C. Huang, X.-A. Yuan, S. Yu, *J. Am. Chem. Soc.* **2022**, *144*, 10958-10967.

8. X-ray Single Crystal Data for Compound 3ac



(S)-3ac

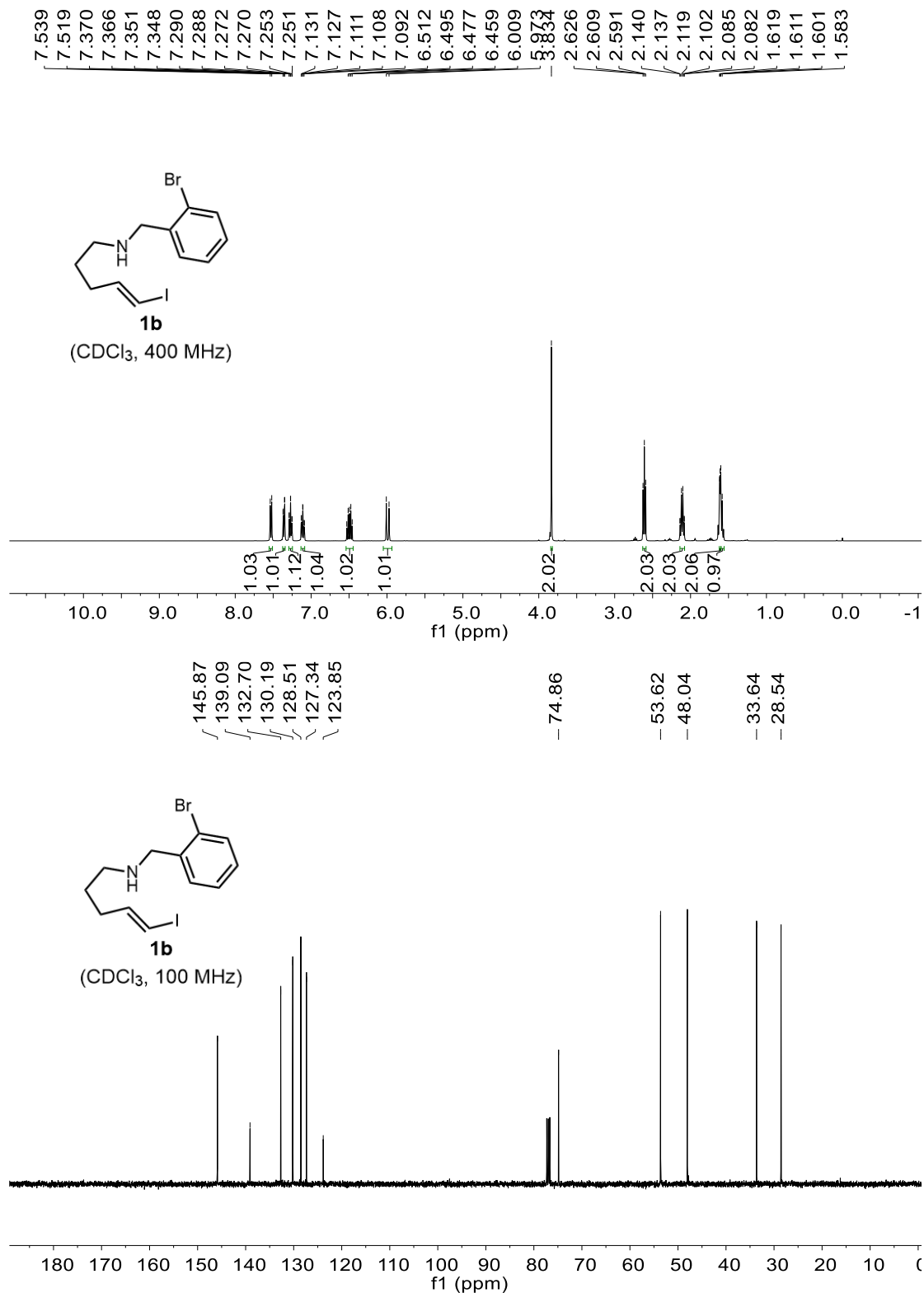
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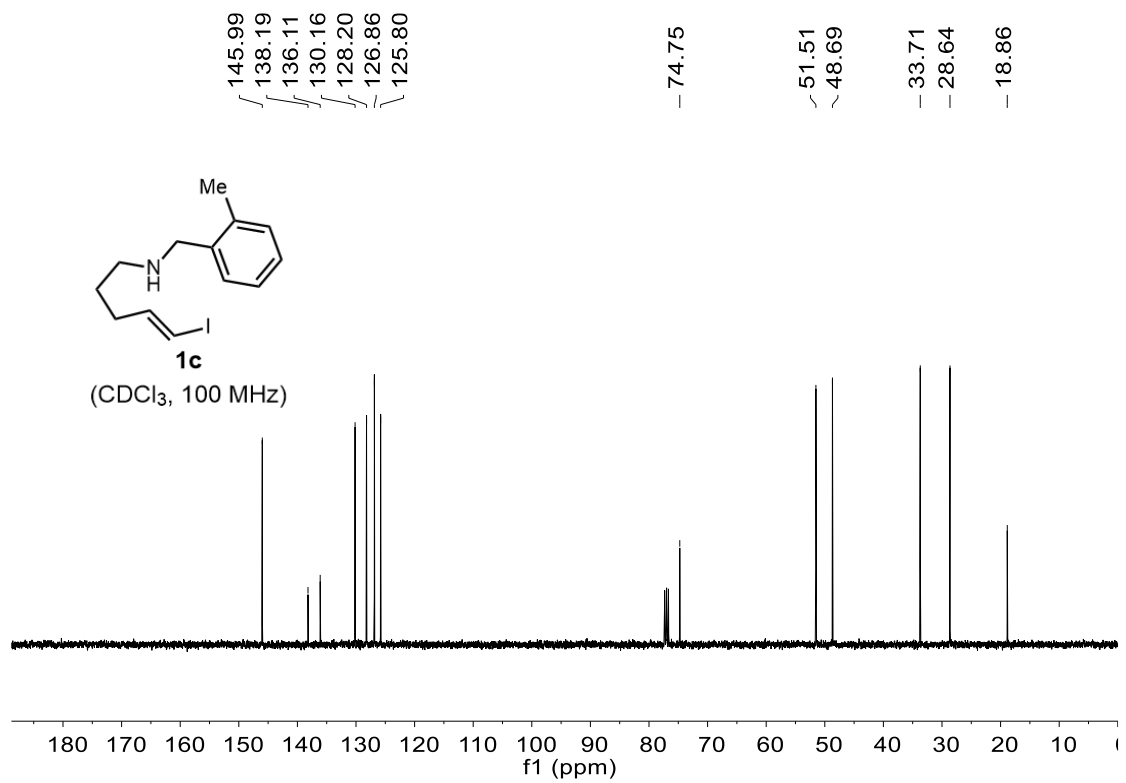
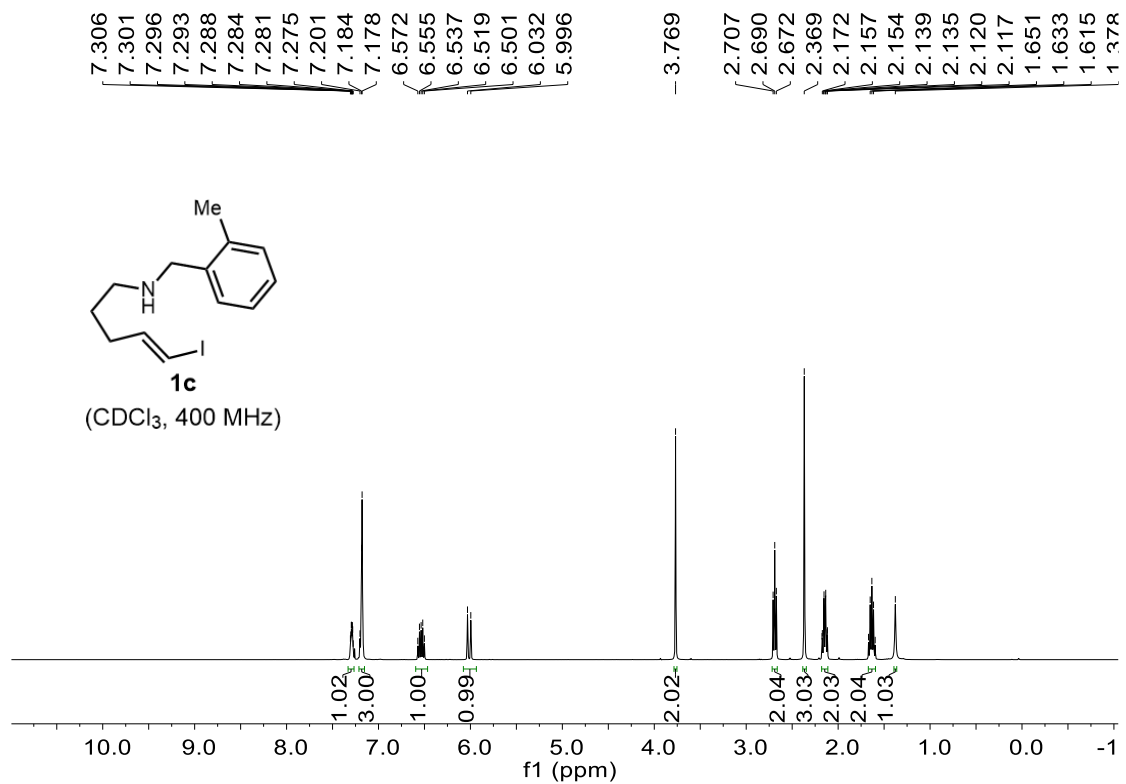


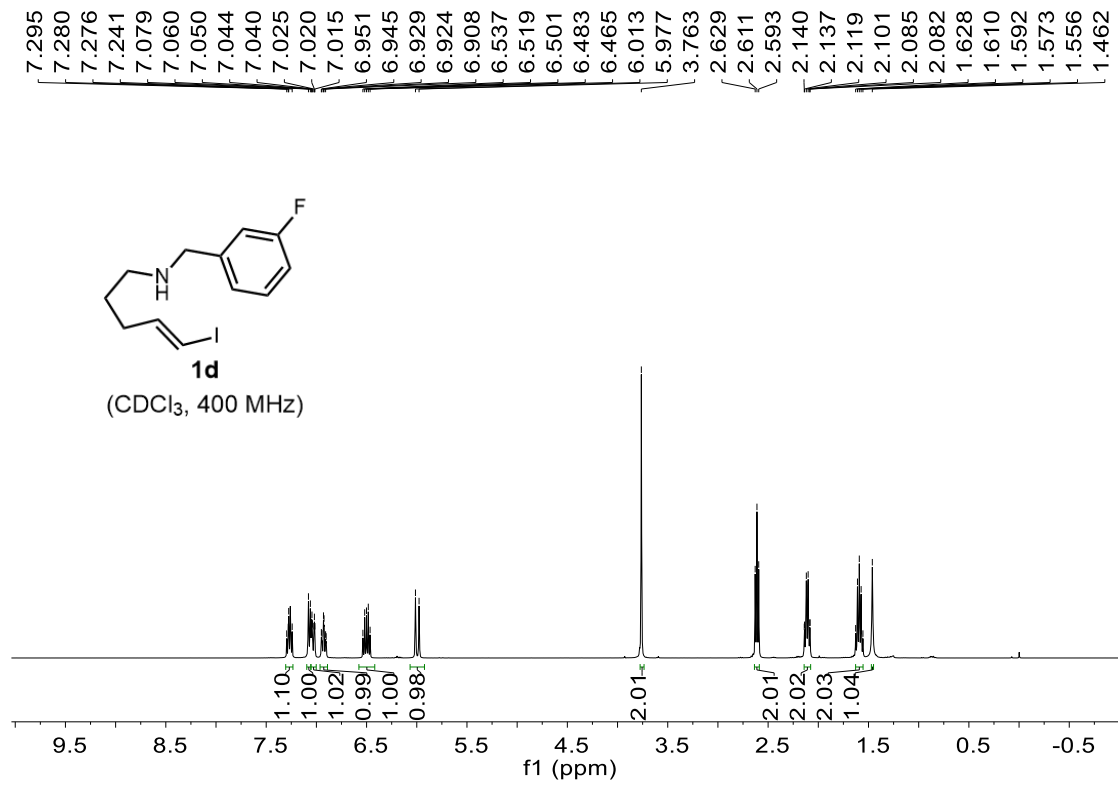
CCDC 2129469

Identification code	exp_2405
Empirical formula	C ₂₃ H ₂₉ N
Formula weight	319.47
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	10.9102(3)
b/Å	6.1038(2)
c/Å	14.7452(4)
α/°	90
β/°	99.500(3)
γ/°	90
Volume/Å ³	968.47(5)
Z	2
ρ _{calc} /cm ³	1.096
μ/mm ⁻¹	0.467
F(000)	348.0
Crystal size/mm ³	0.38 × 0.24 × 0.12
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.216 to 134.116
Index ranges	-13 ≤ h ≤ 13, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17
Reflections collected	19273
Independent reflections	3408 [R _{int} = 0.0629, R _{sigma} = 0.0387]
Data/restraints/parameters	3408/1/220
Goodness-of-fit on F ²	1.039
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0465, wR ₂ = 0.1281
Final R indexes [all data]	R ₁ = 0.0491, wR ₂ = 0.1301
Largest diff. peak/hole / e Å ⁻³	0.37/-0.17
Flack parameter	-0.1(4)

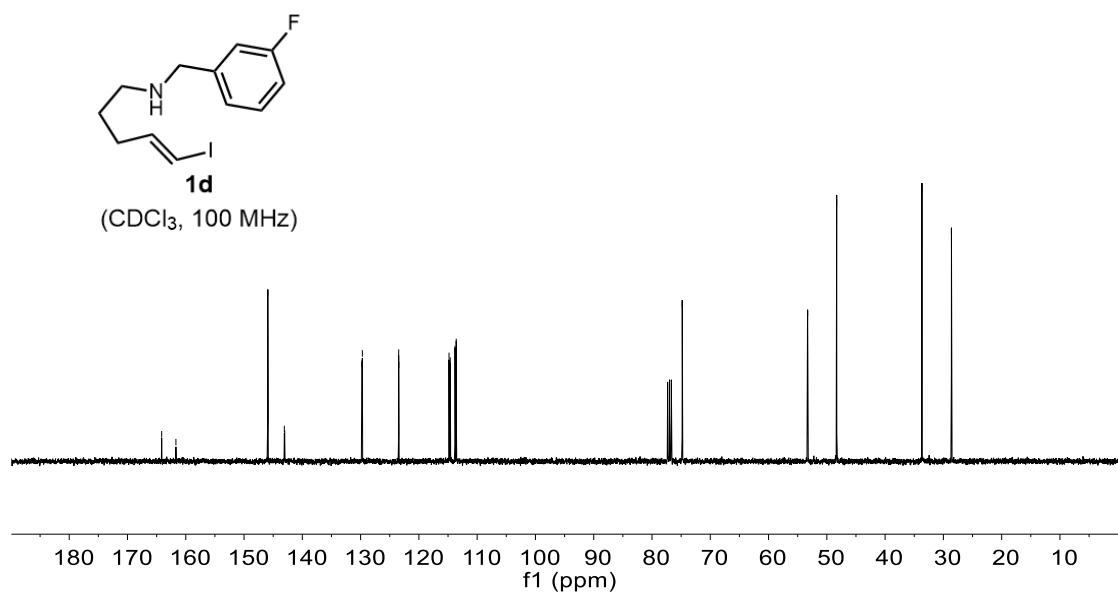
9. ¹H, ¹³C, ¹⁹F NMR Spectra

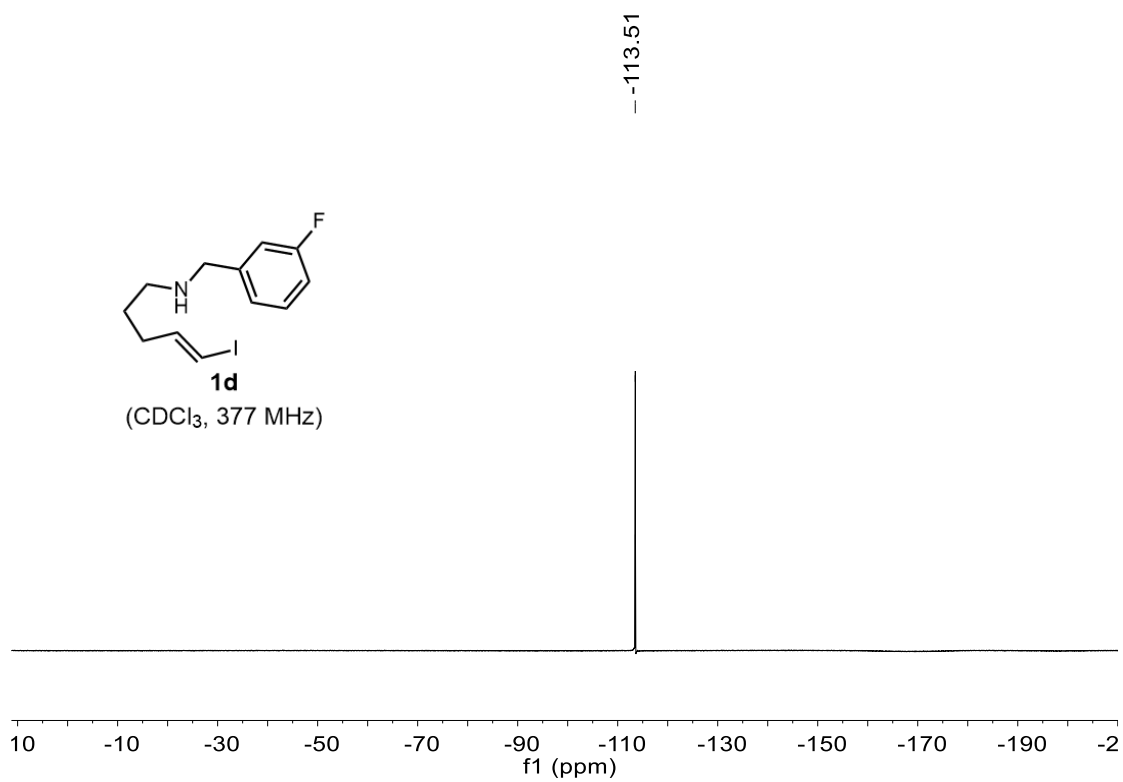
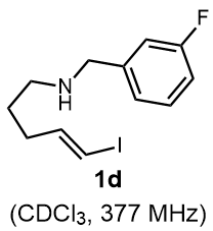


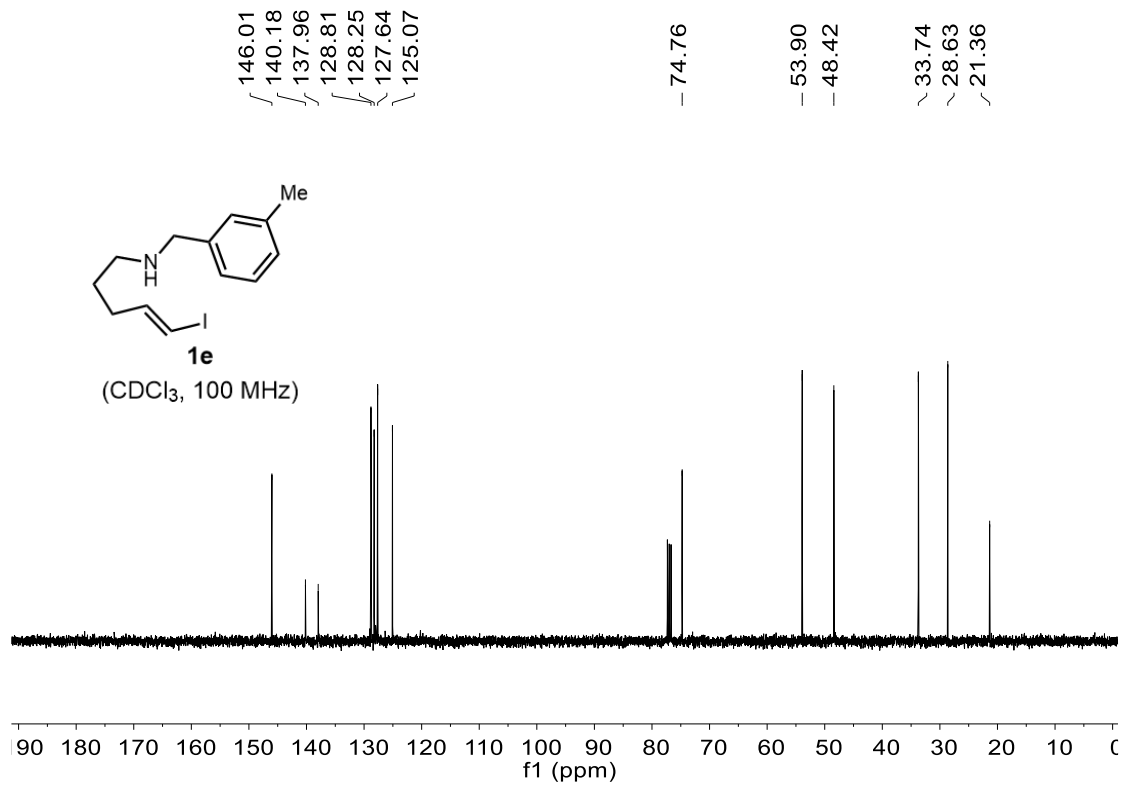
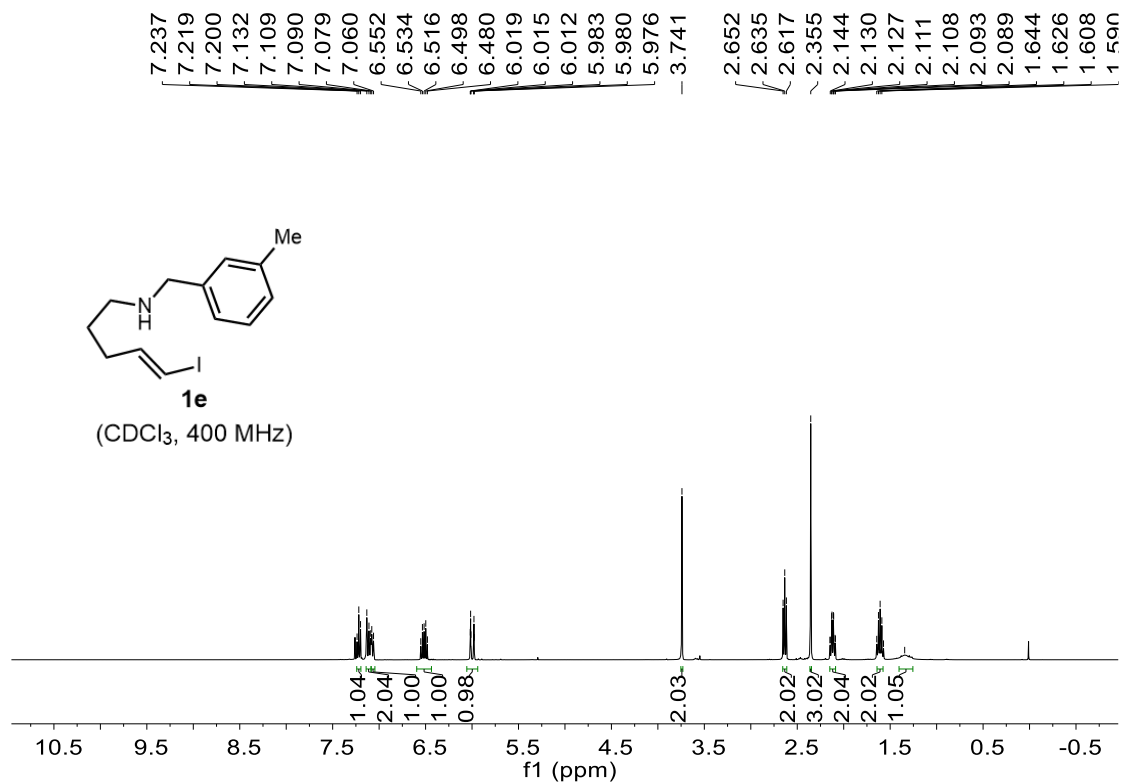


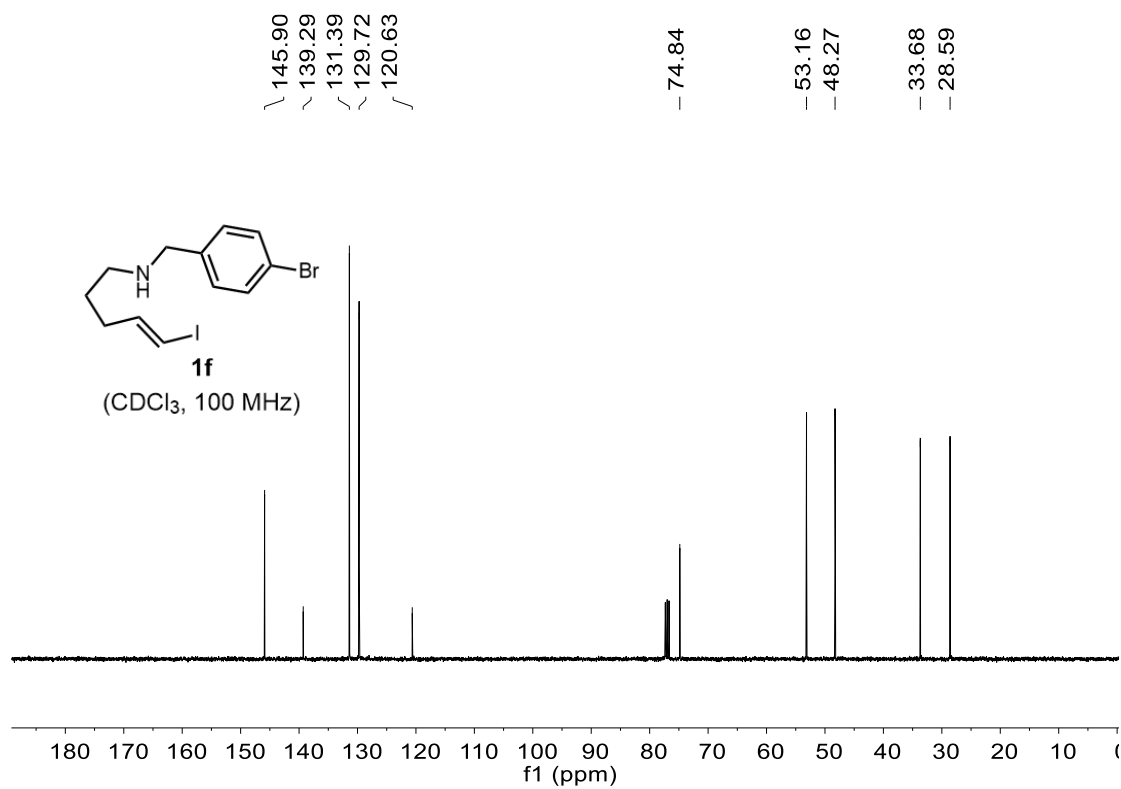
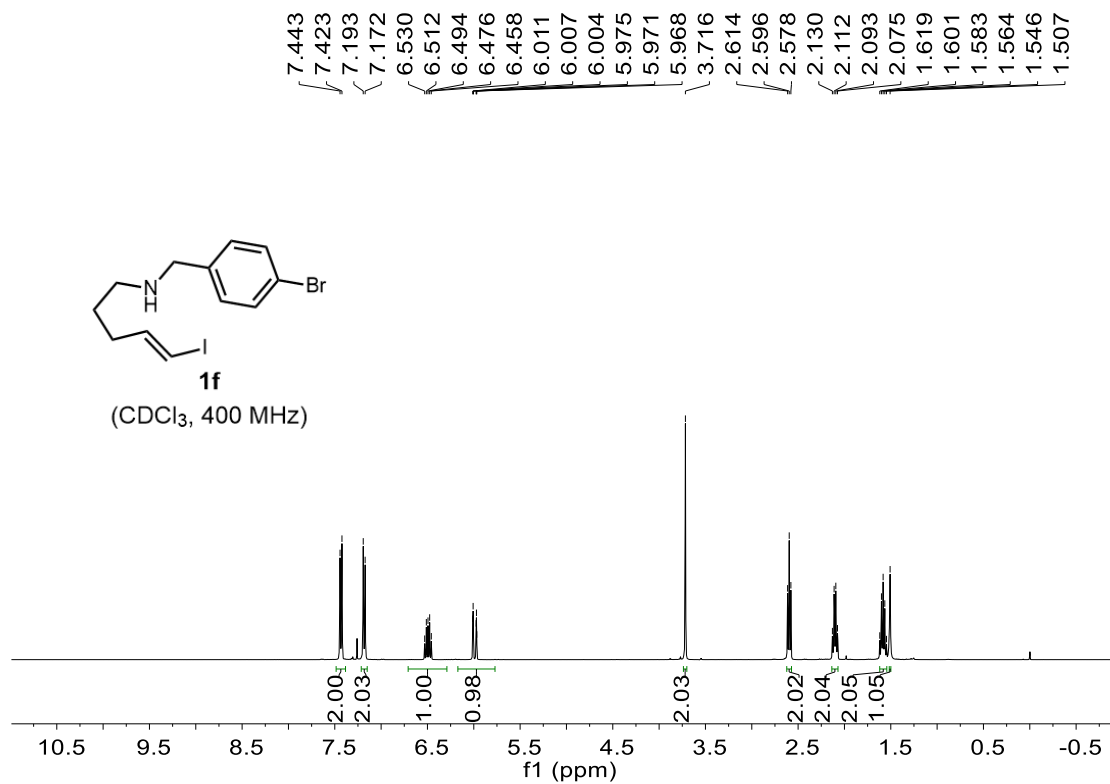


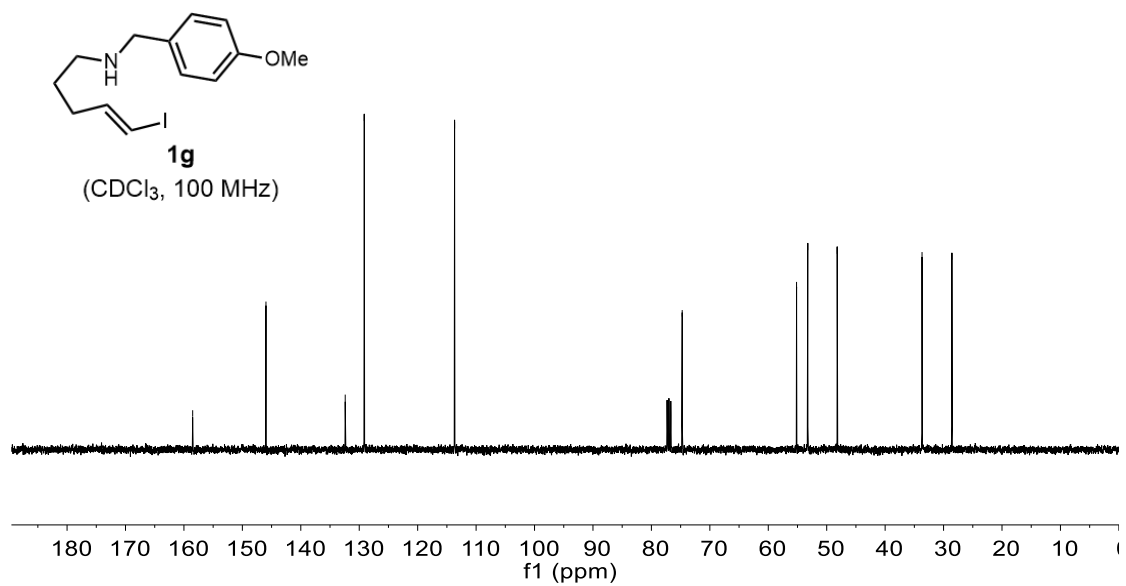
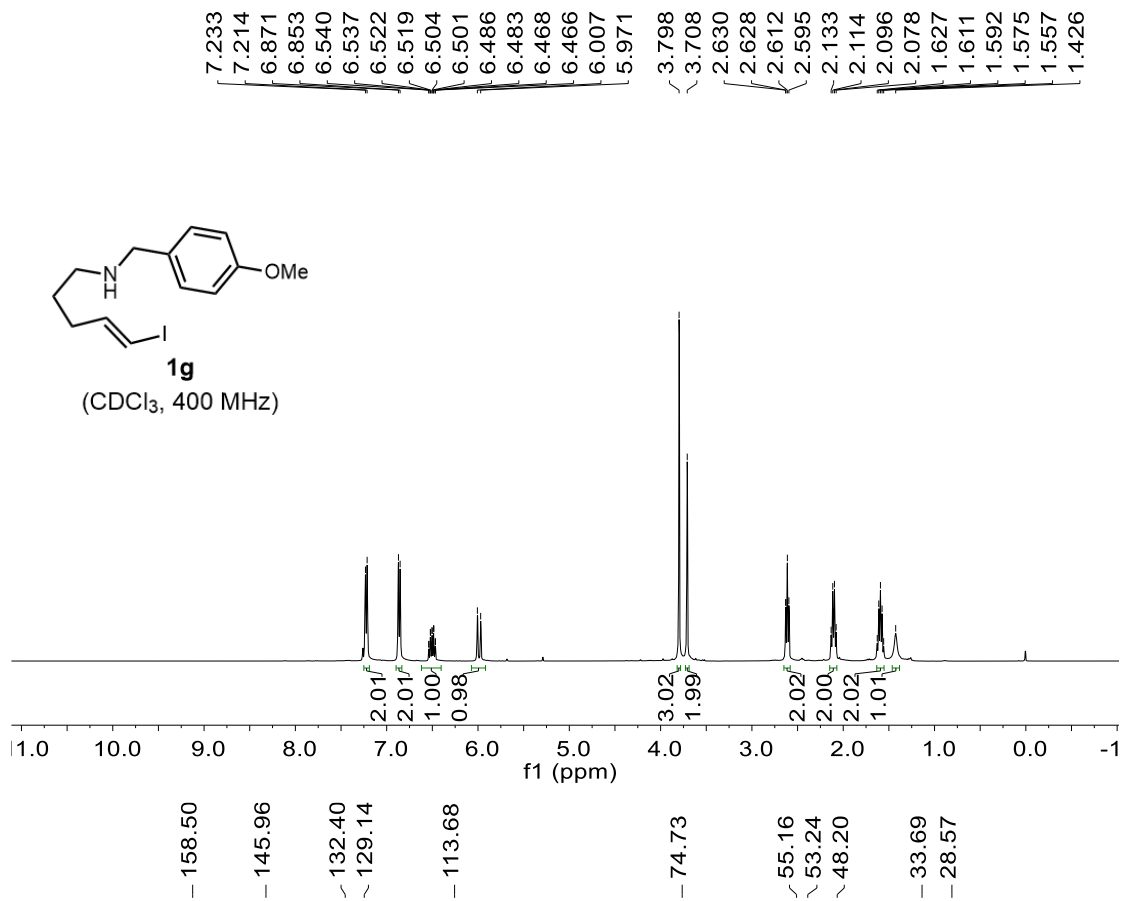
- 164.13
- 161.69
- 145.92
- 143.09
- 143.02
- 129.78
- 129.70
- 123.47
- 123.44
- 114.83
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- 113.80
- 113.59
- 74.81
- 53.31
- 53.29
- 48.31
- 33.68
- 28.62

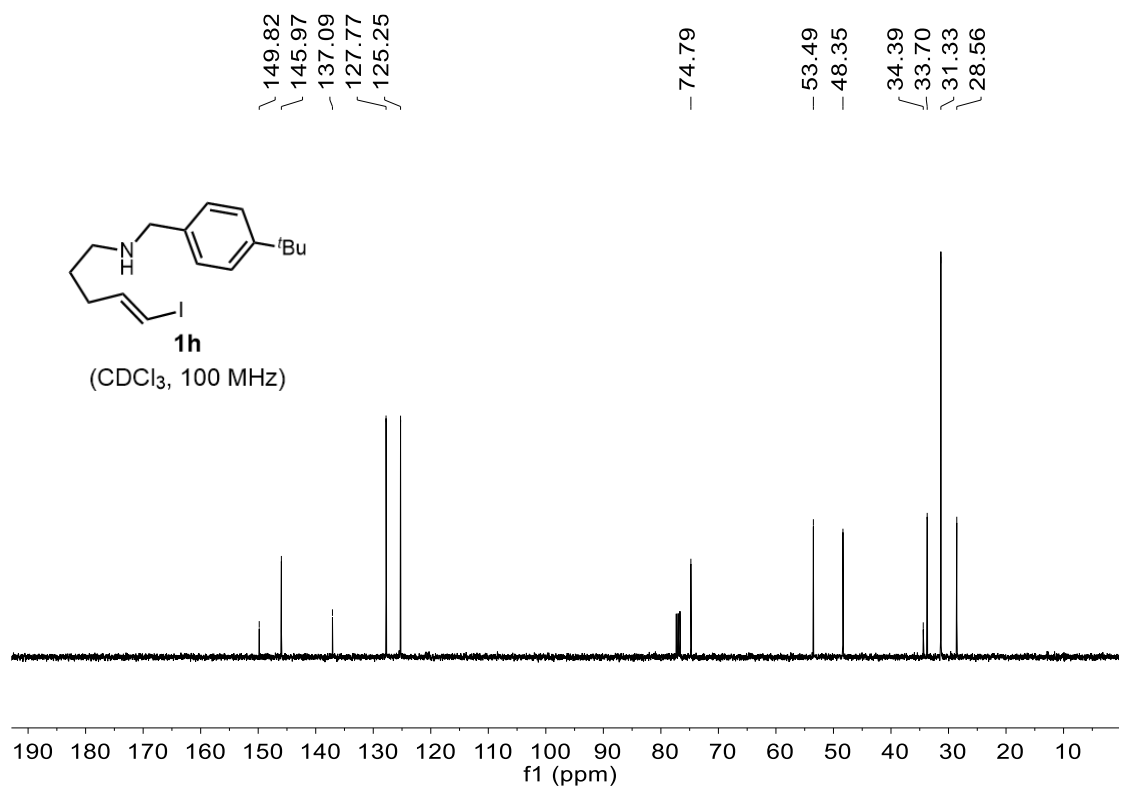
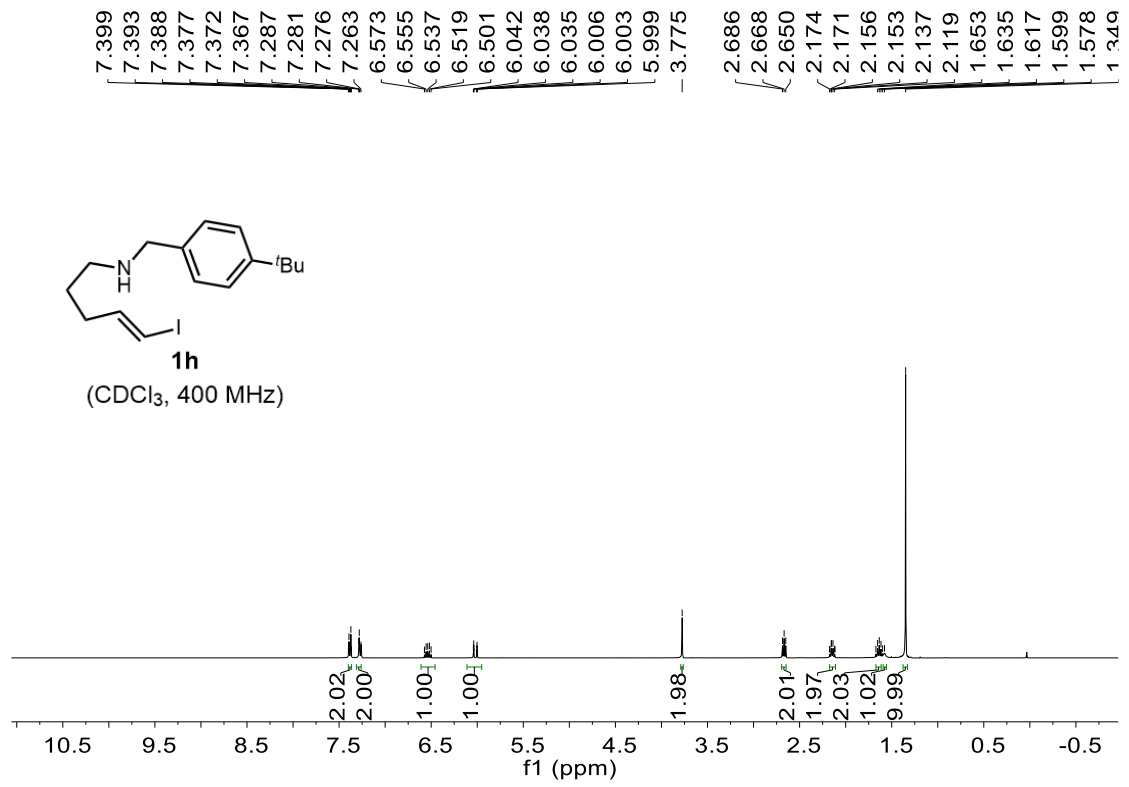


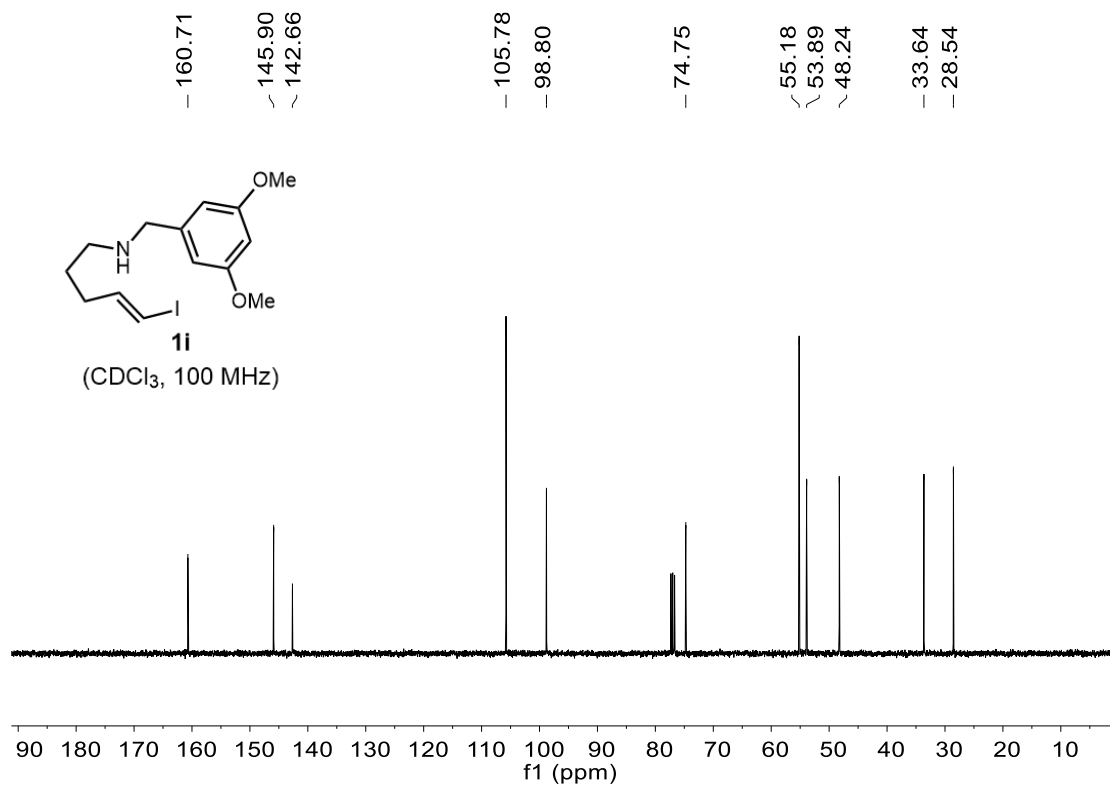
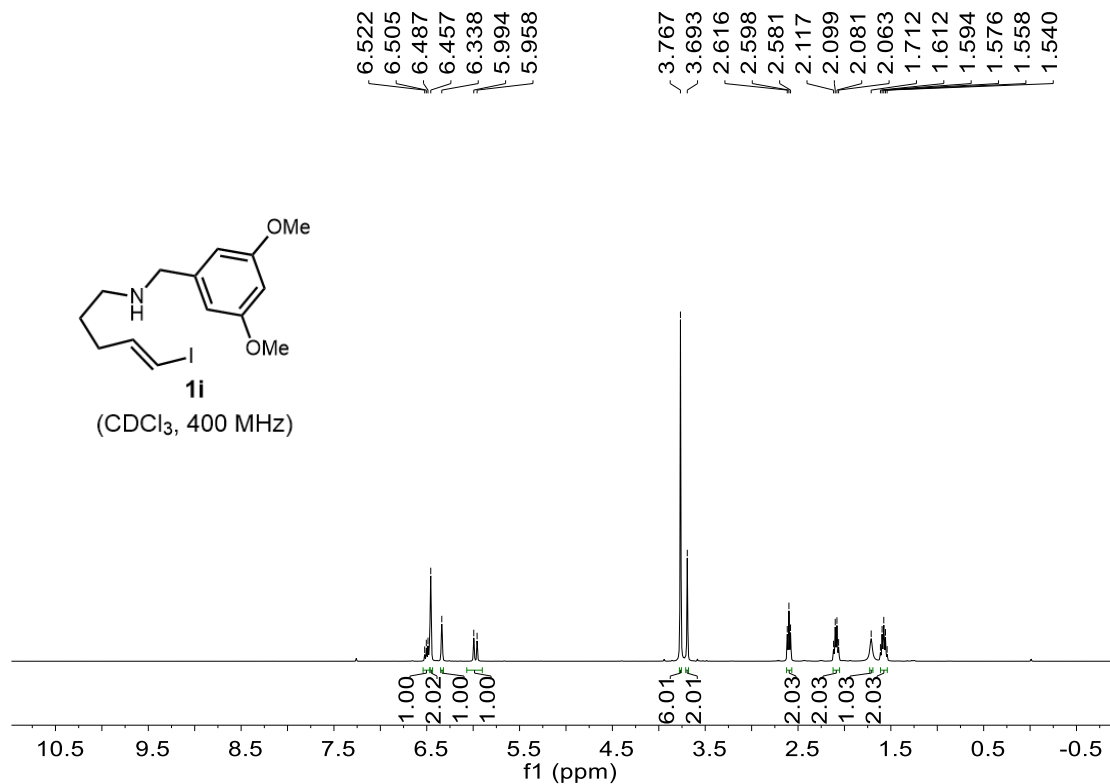


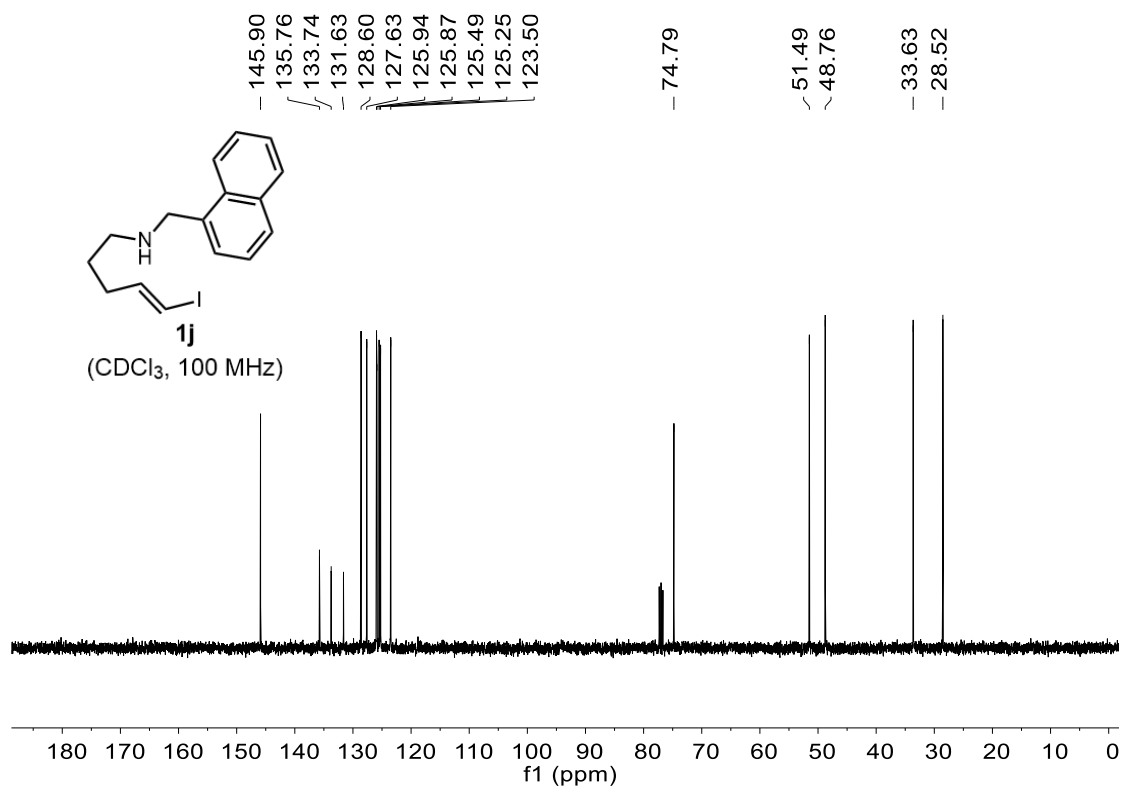
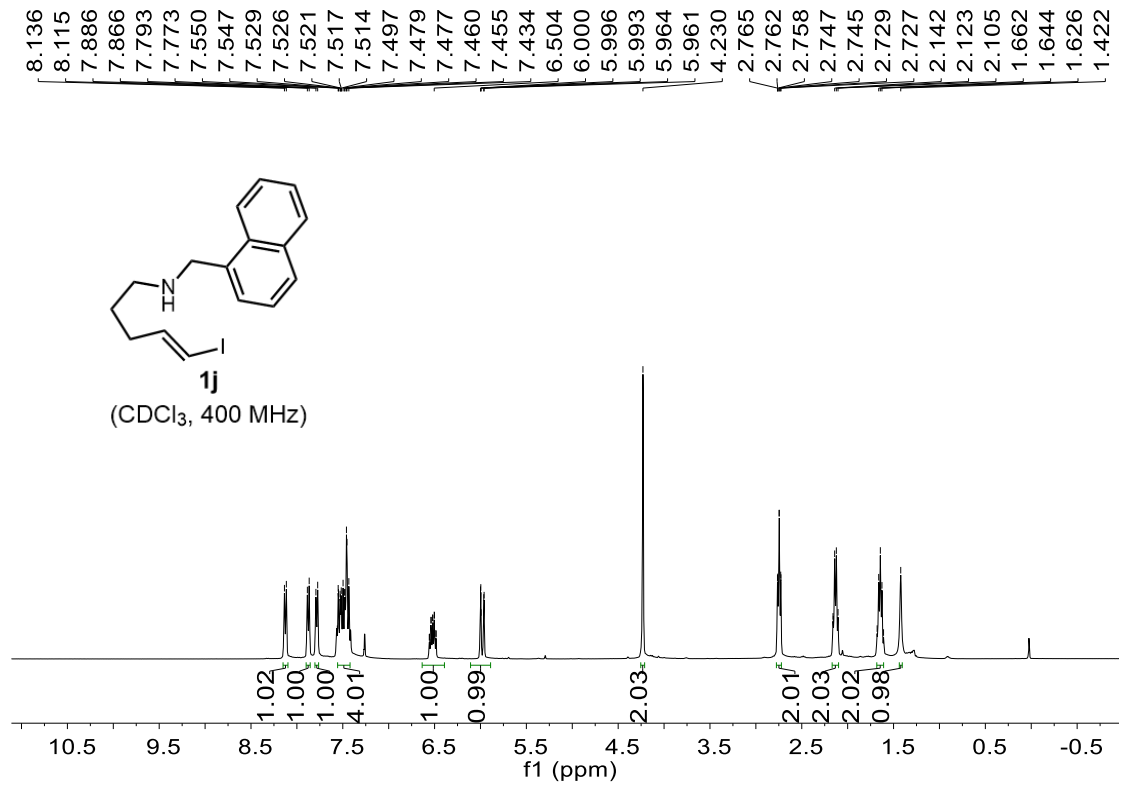


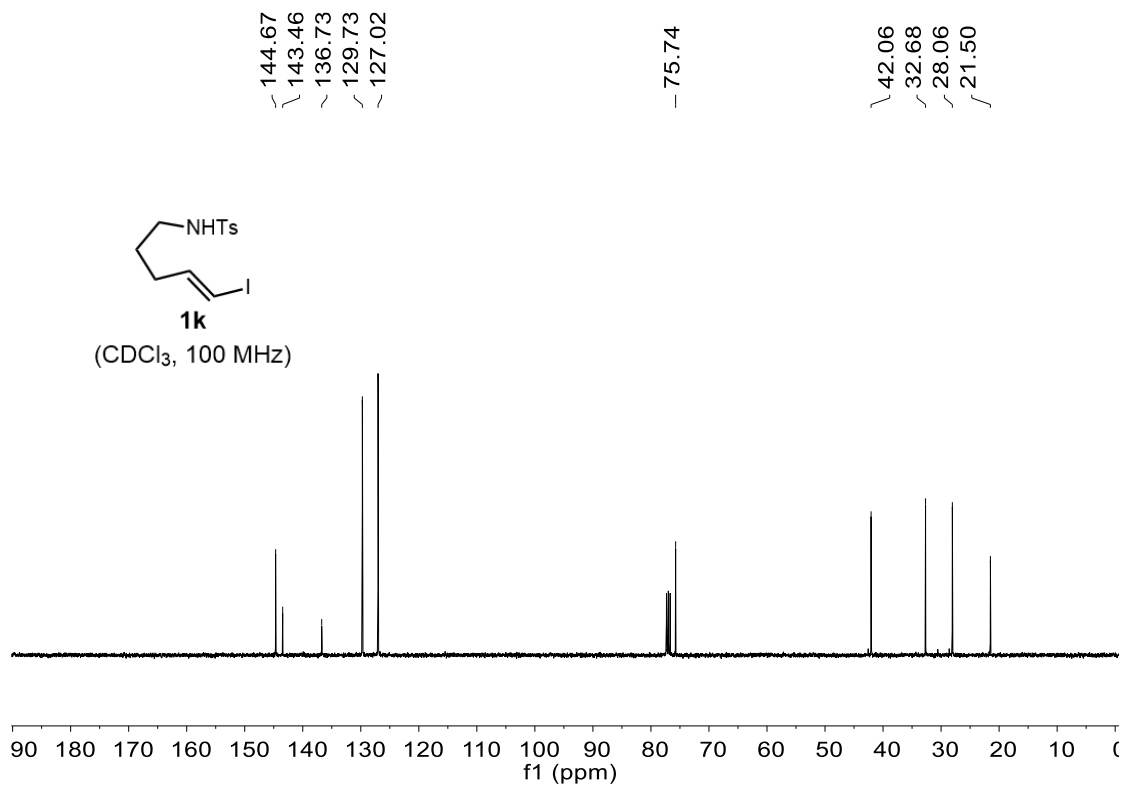
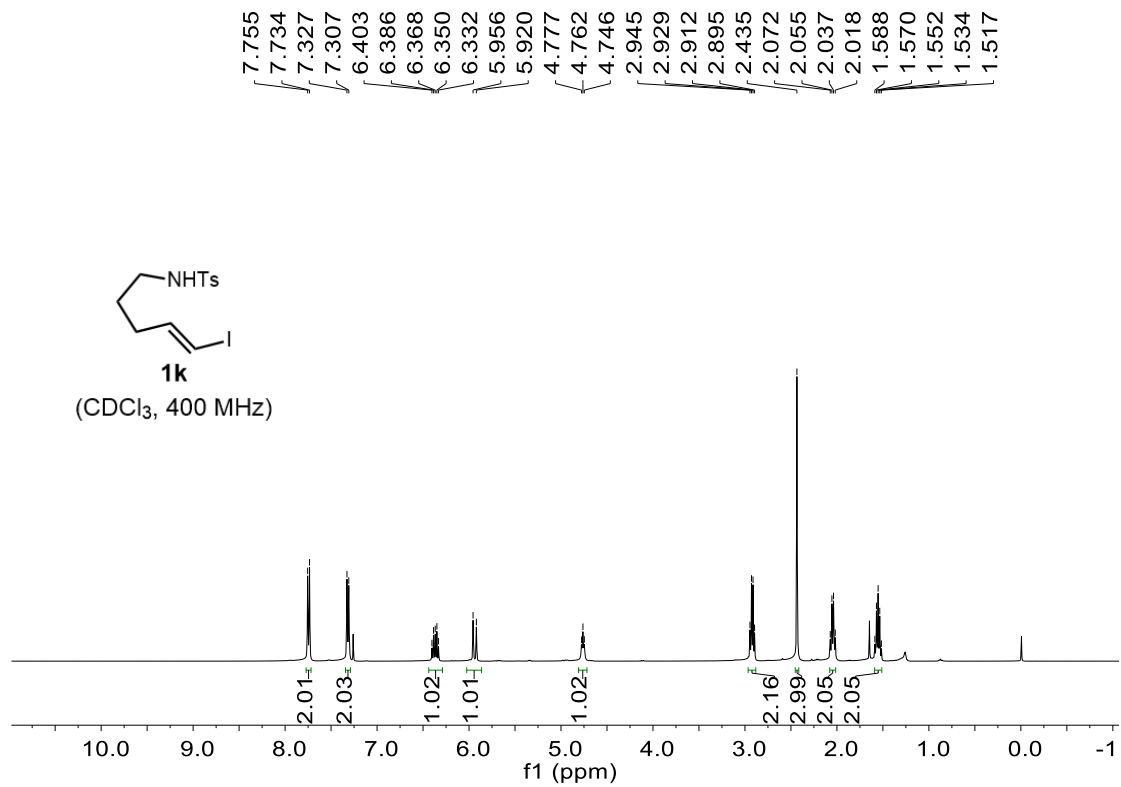


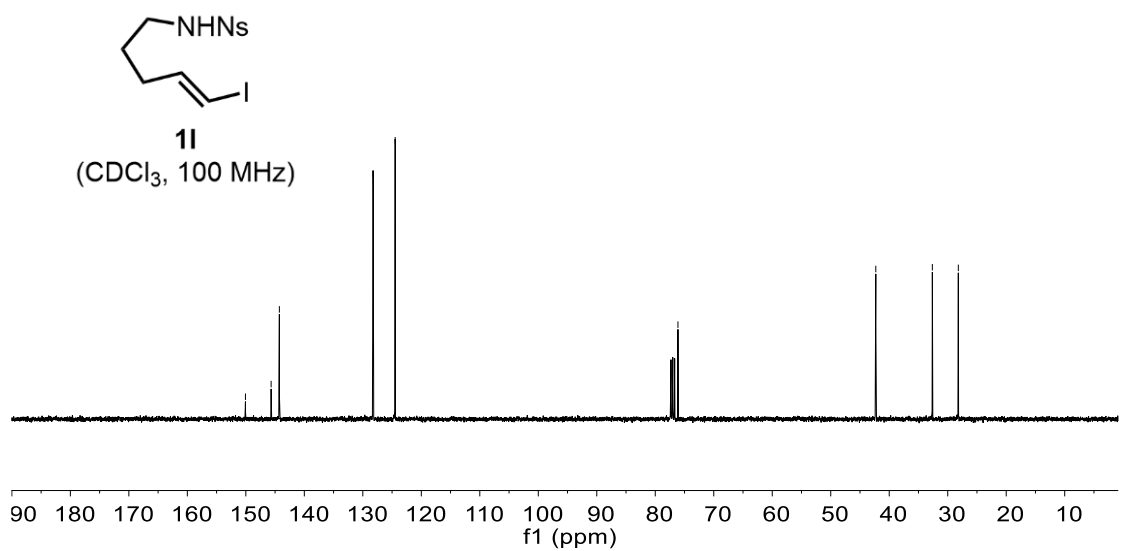
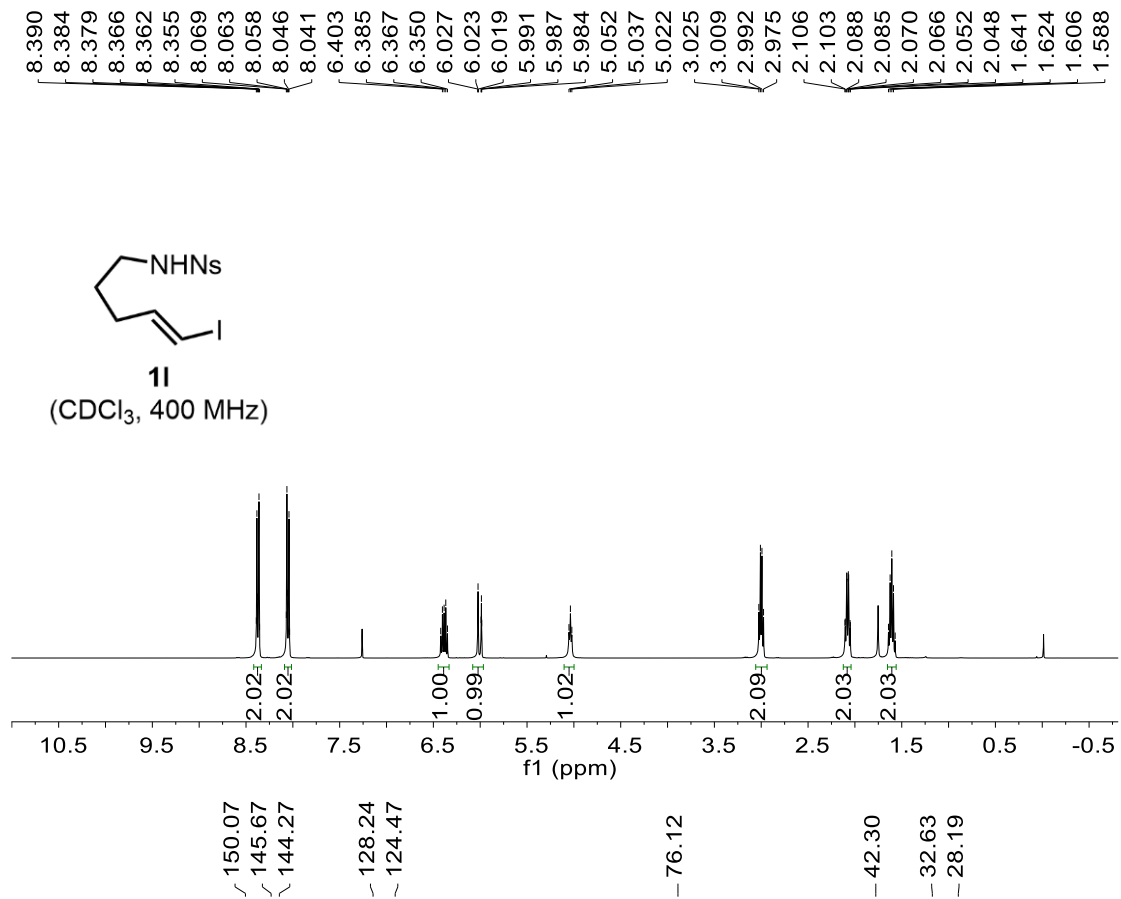




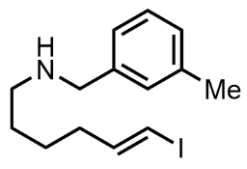




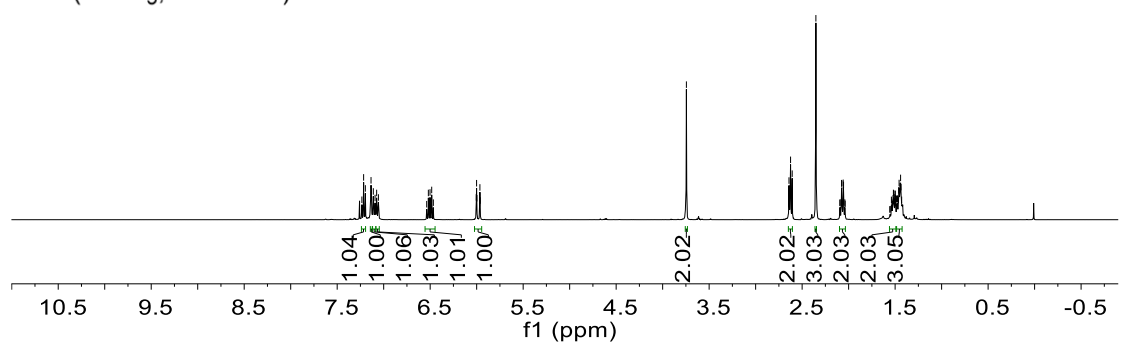




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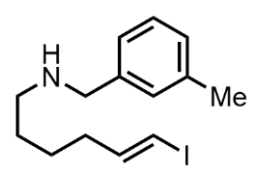


4c
(CDCl₃, 400 MHz)

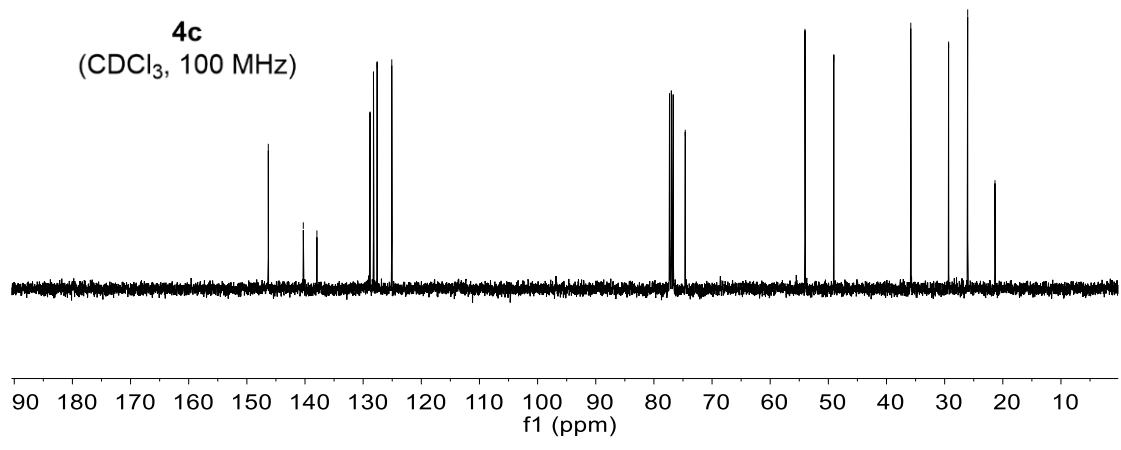


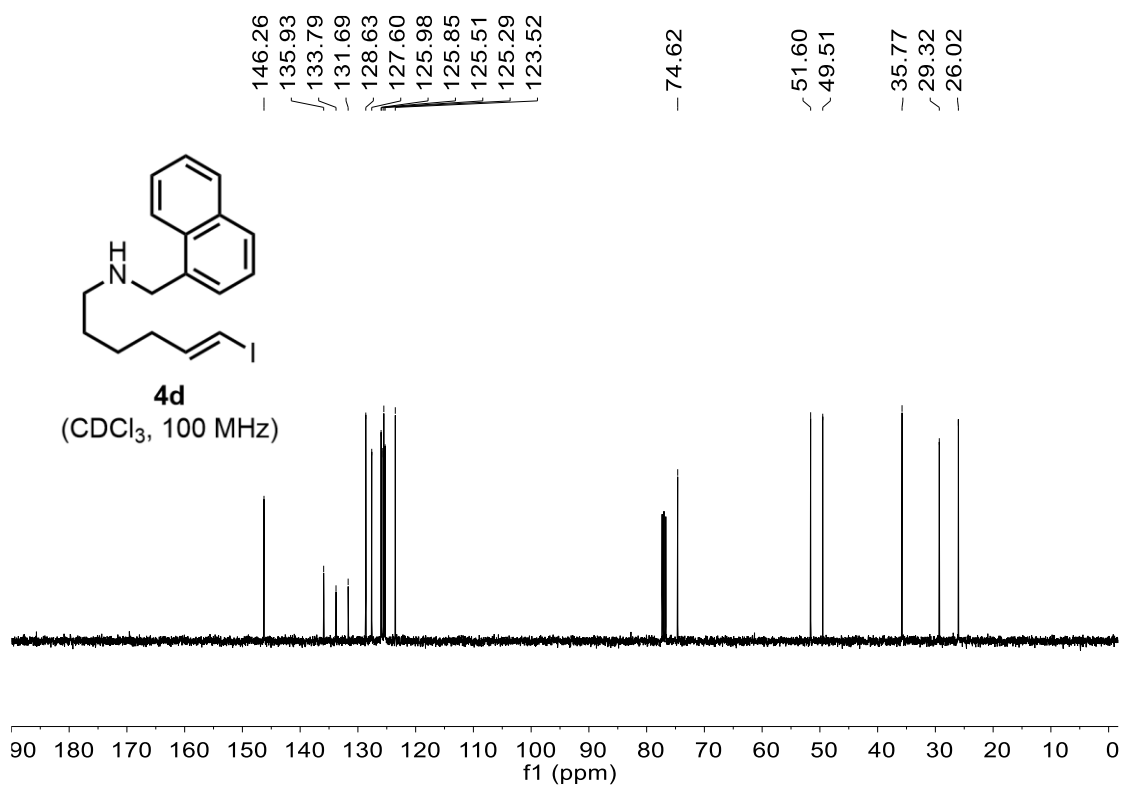
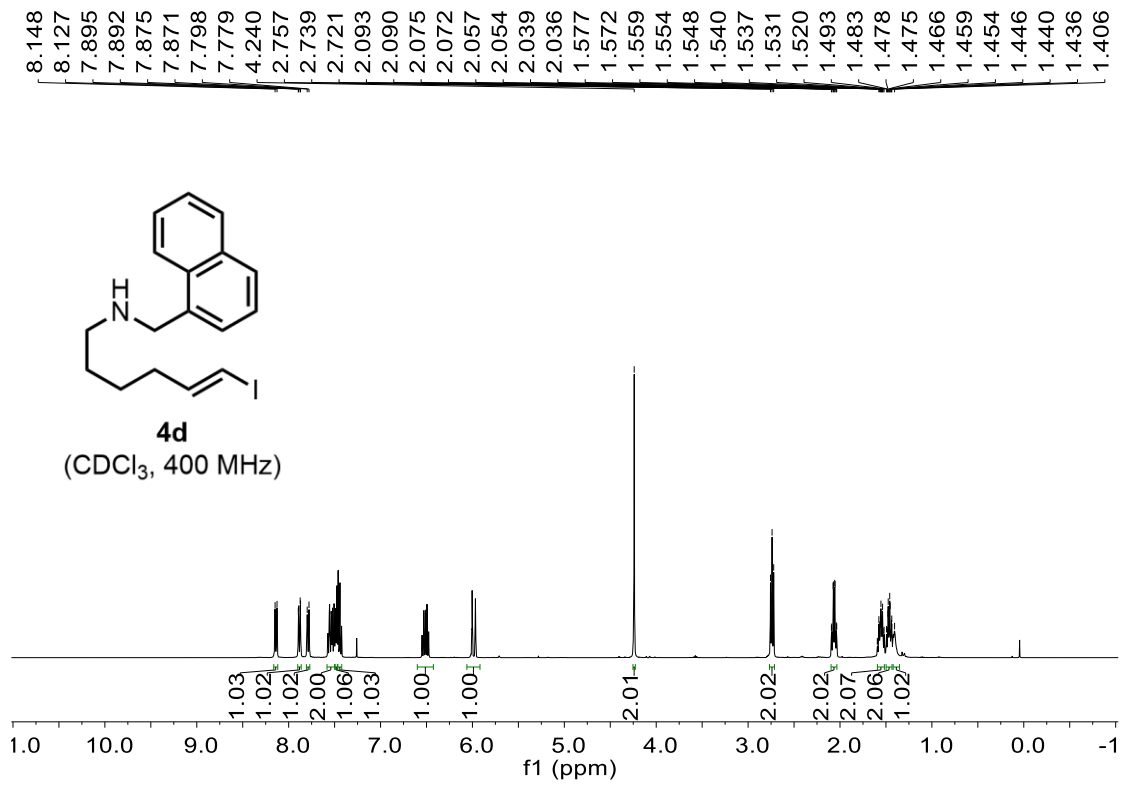
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137.95
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128.23
127.60
125.08

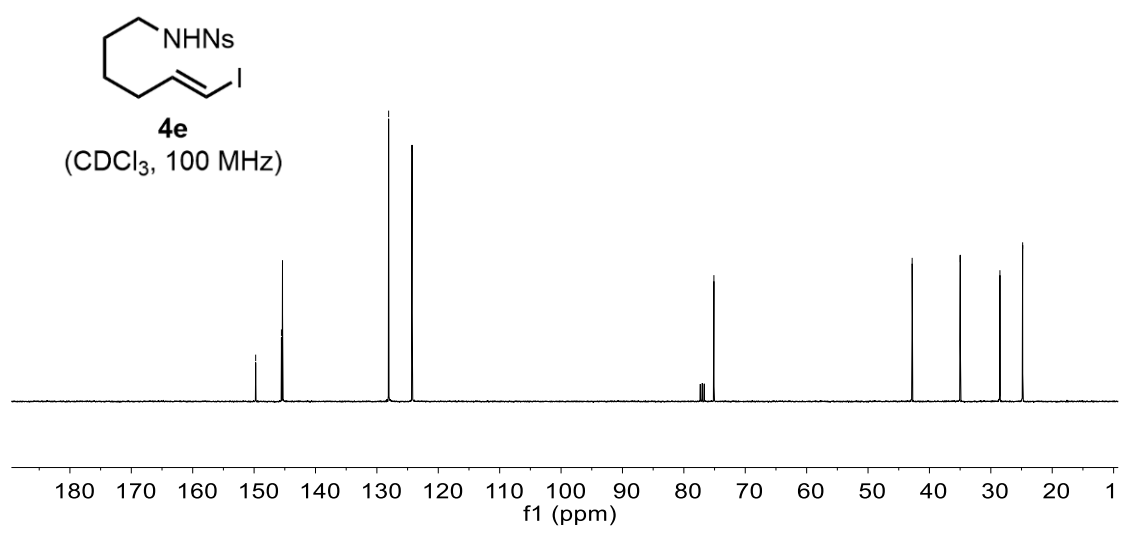
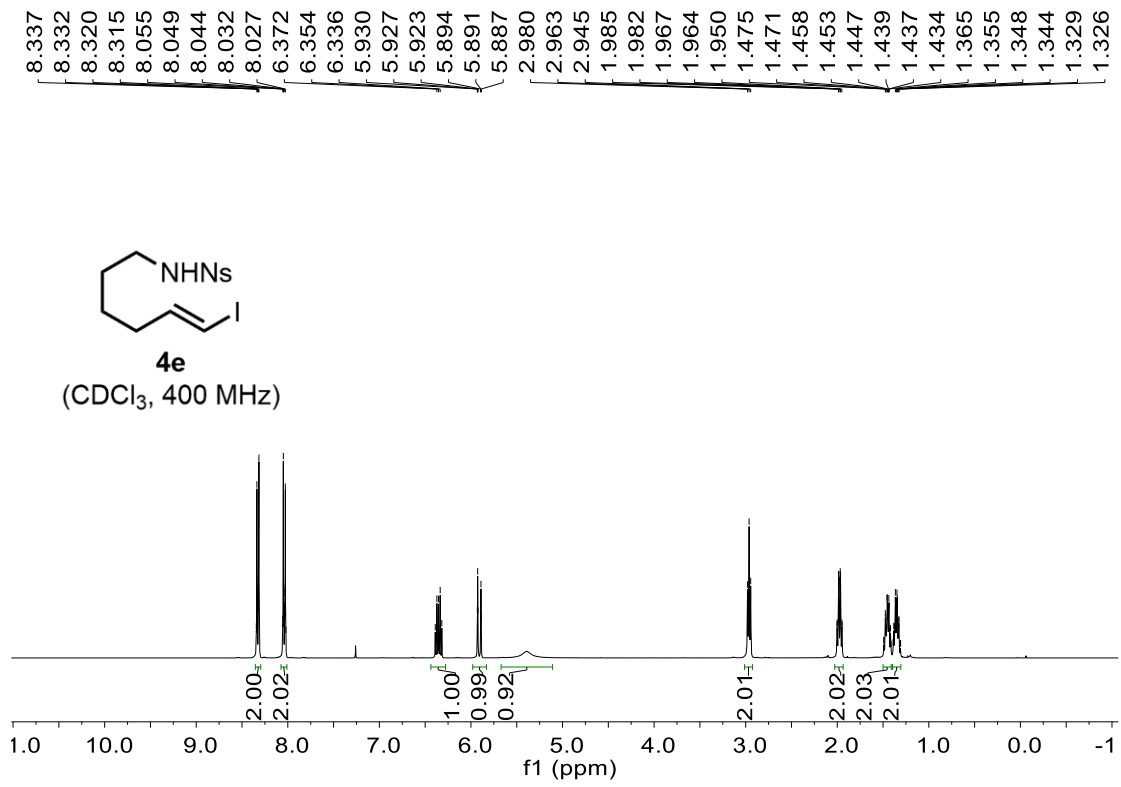
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-21.35

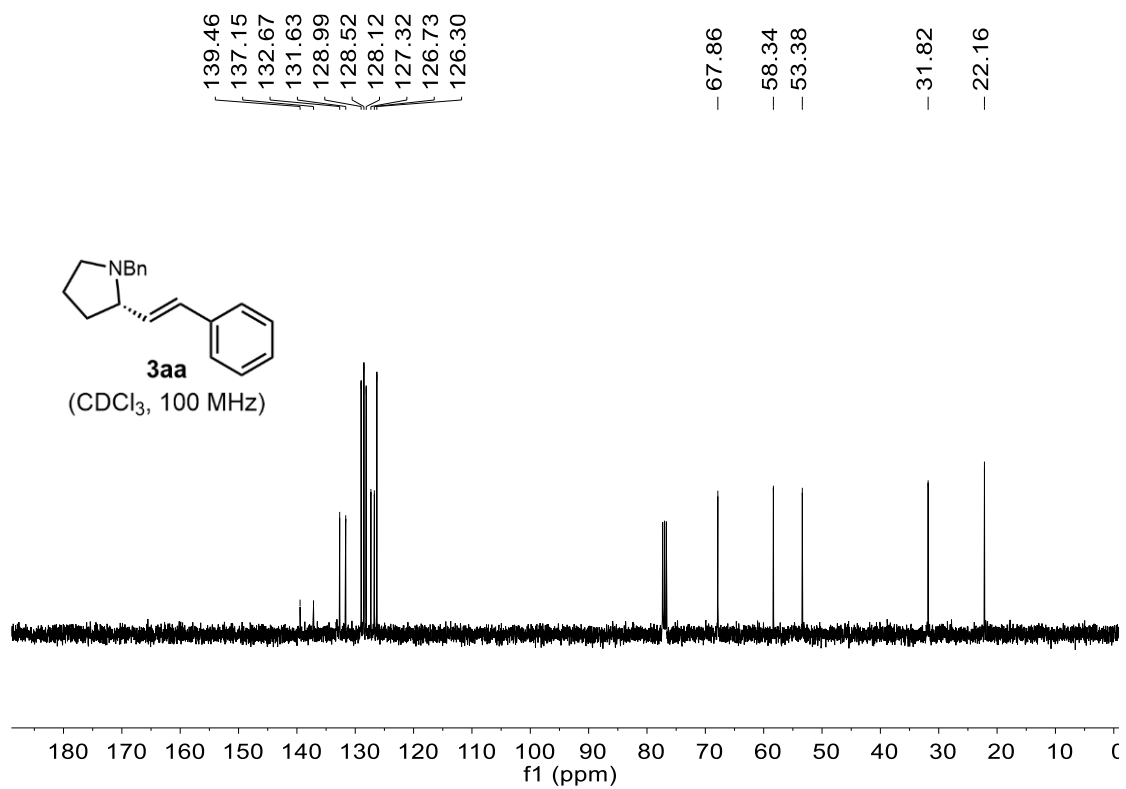
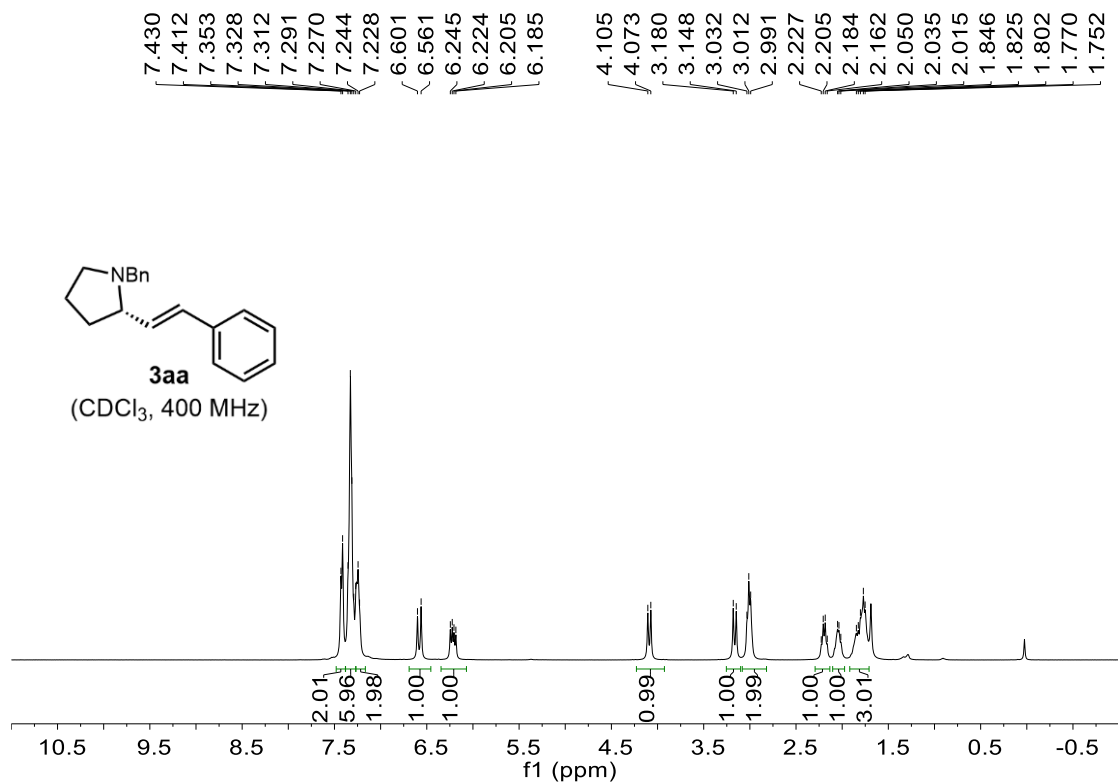


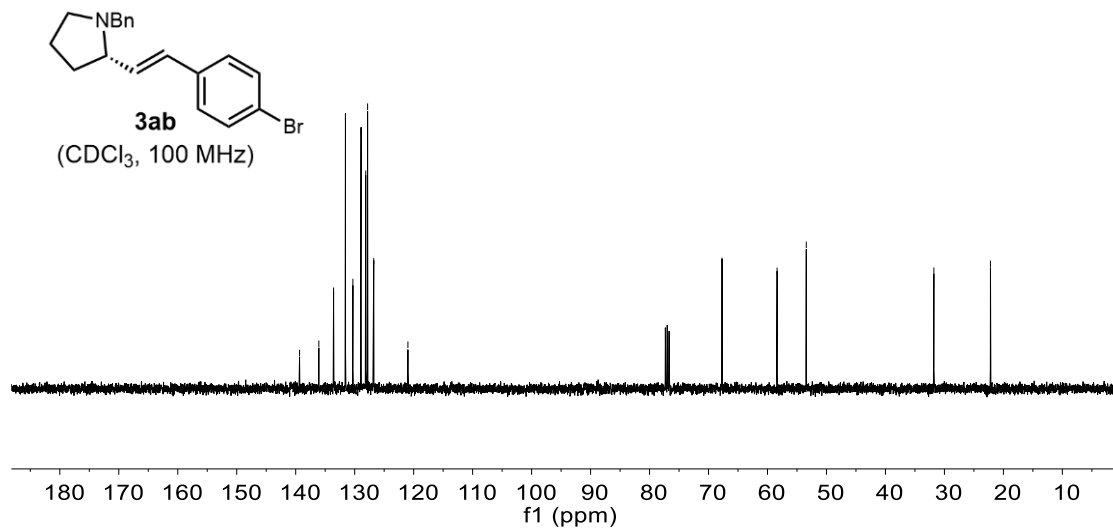
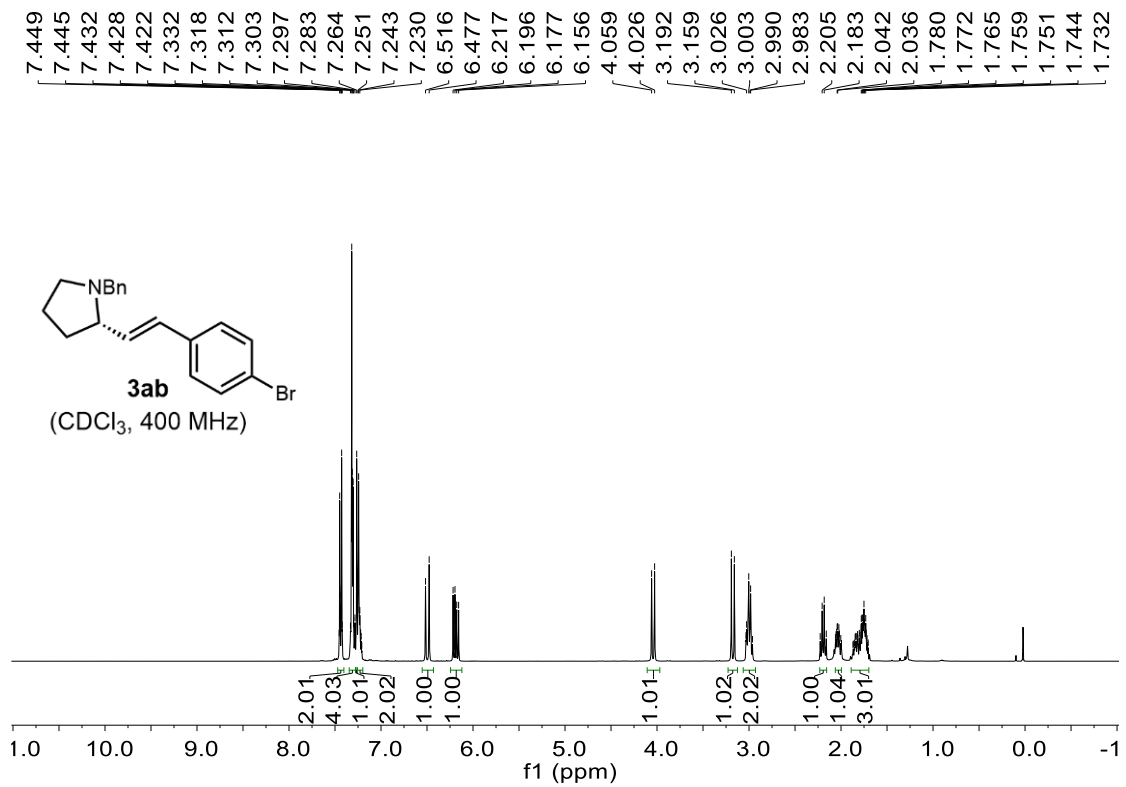
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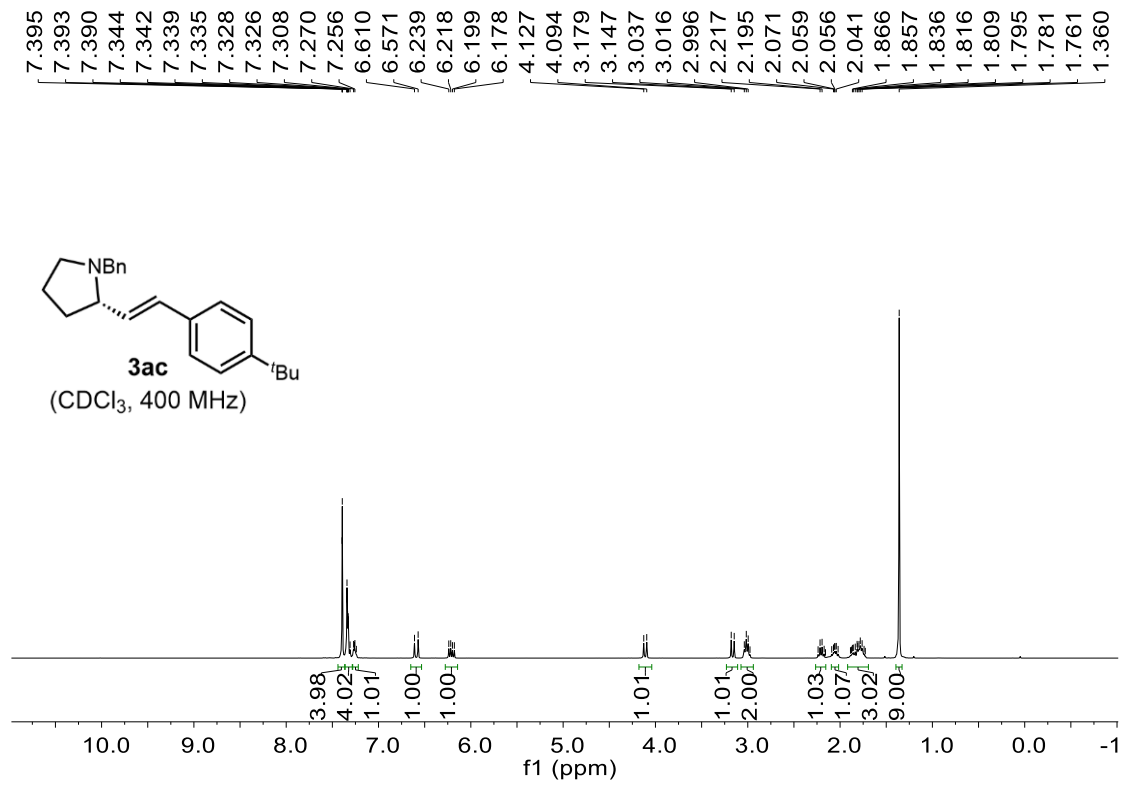






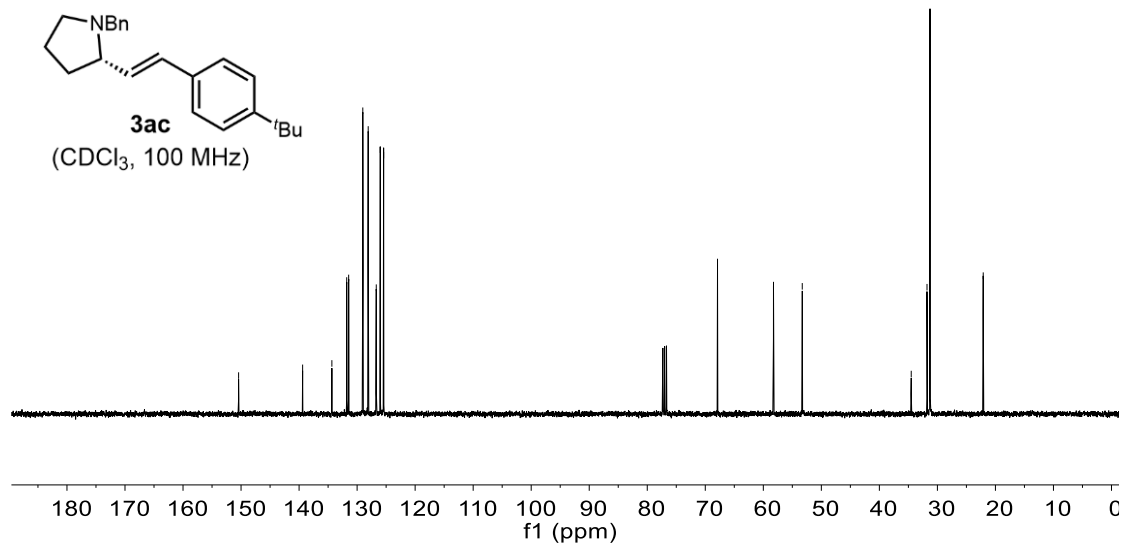


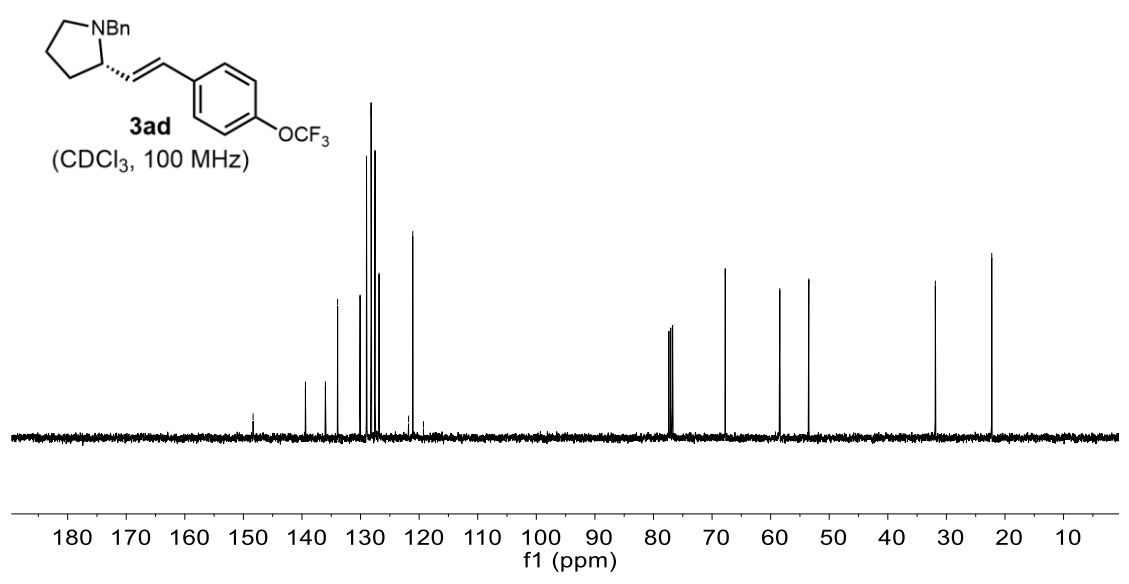
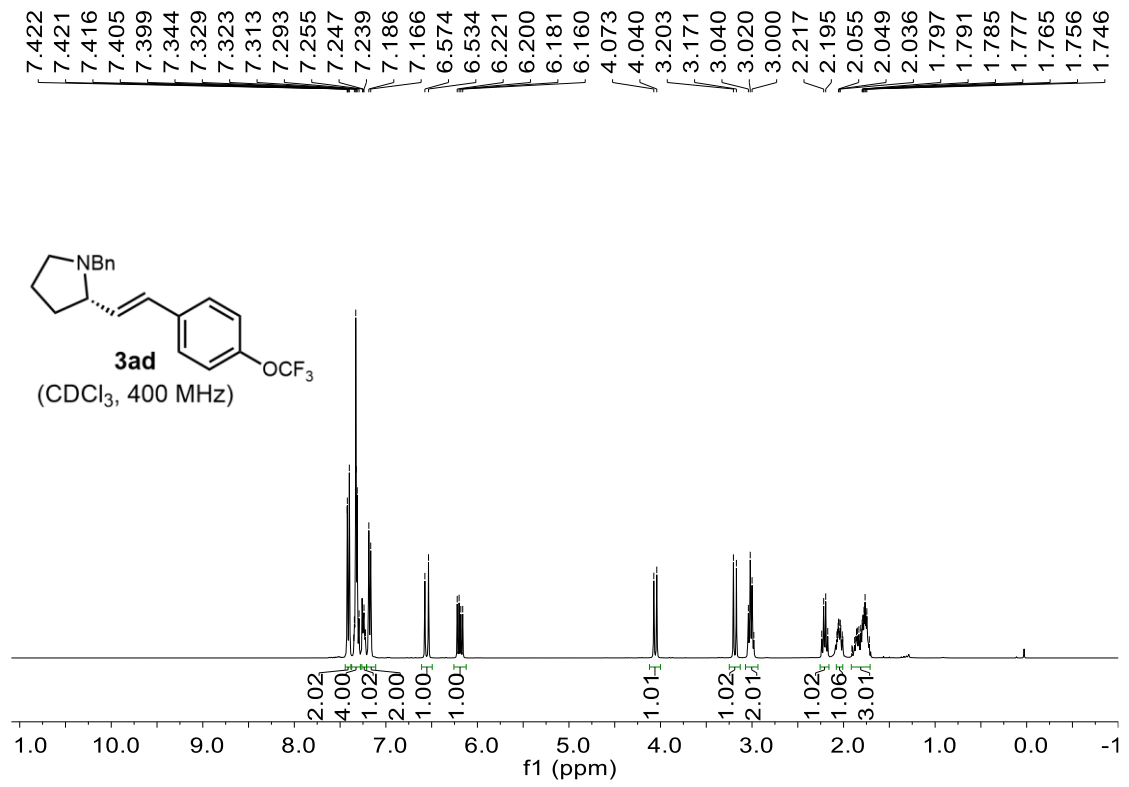


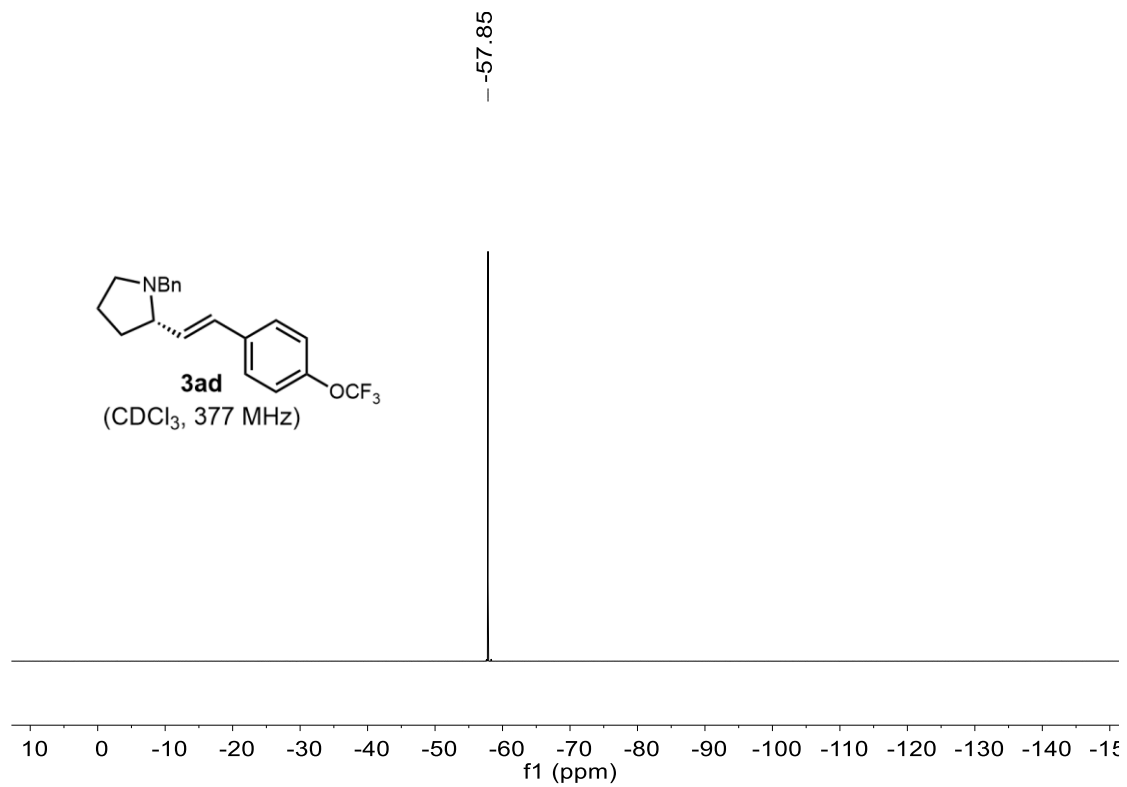


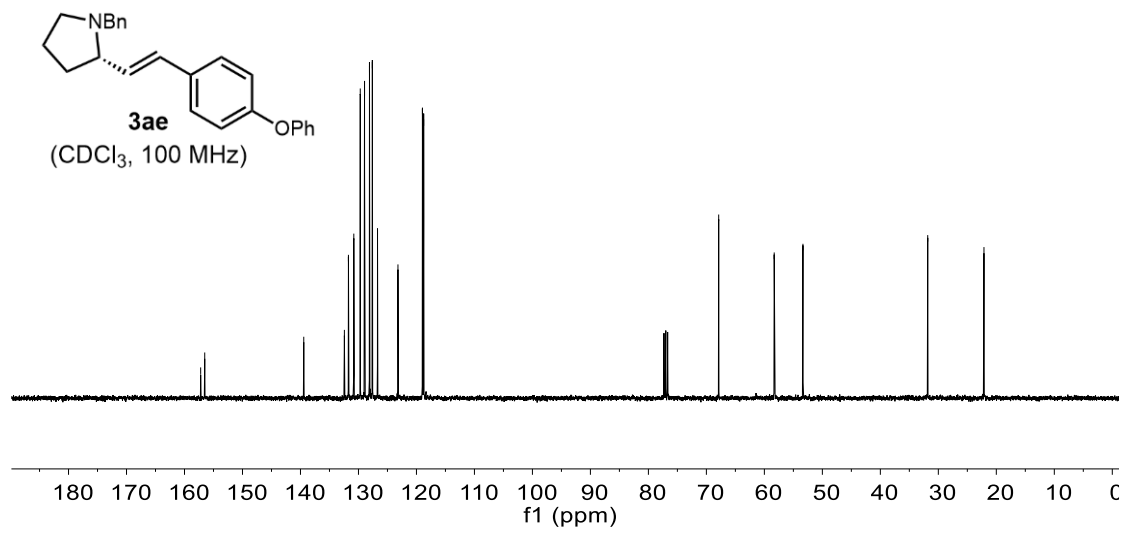
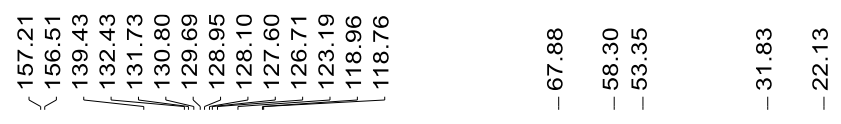
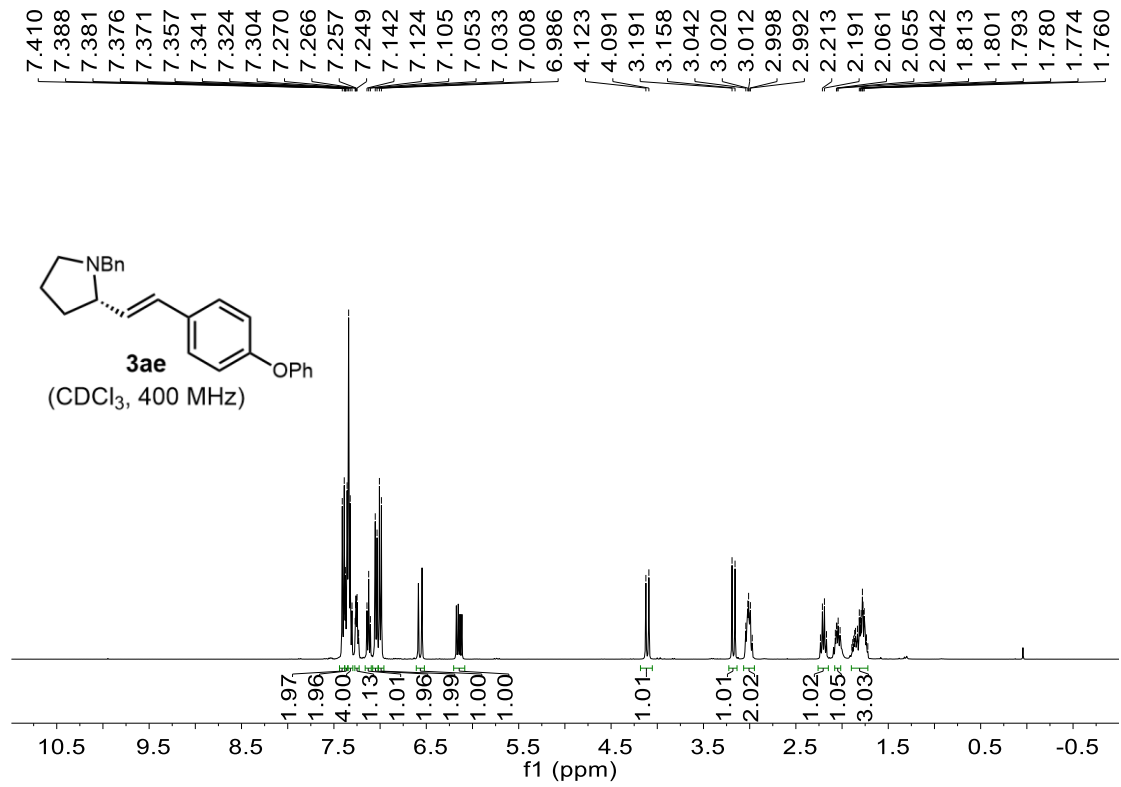
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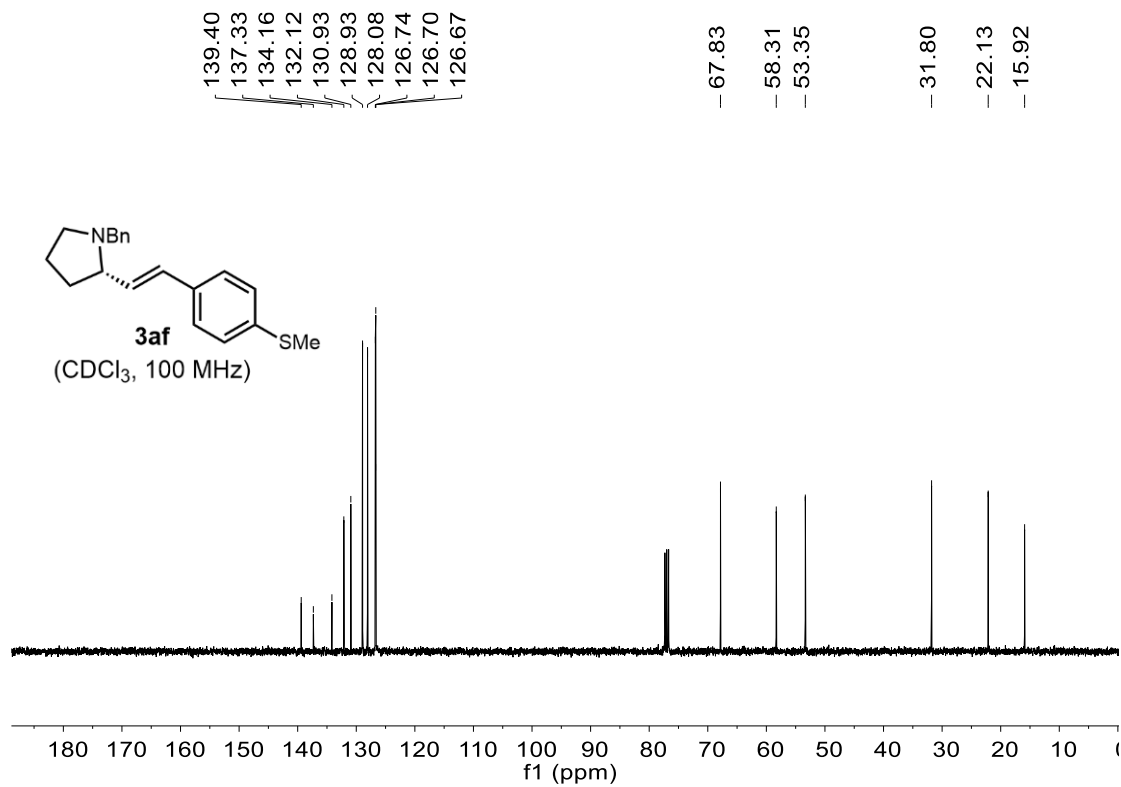
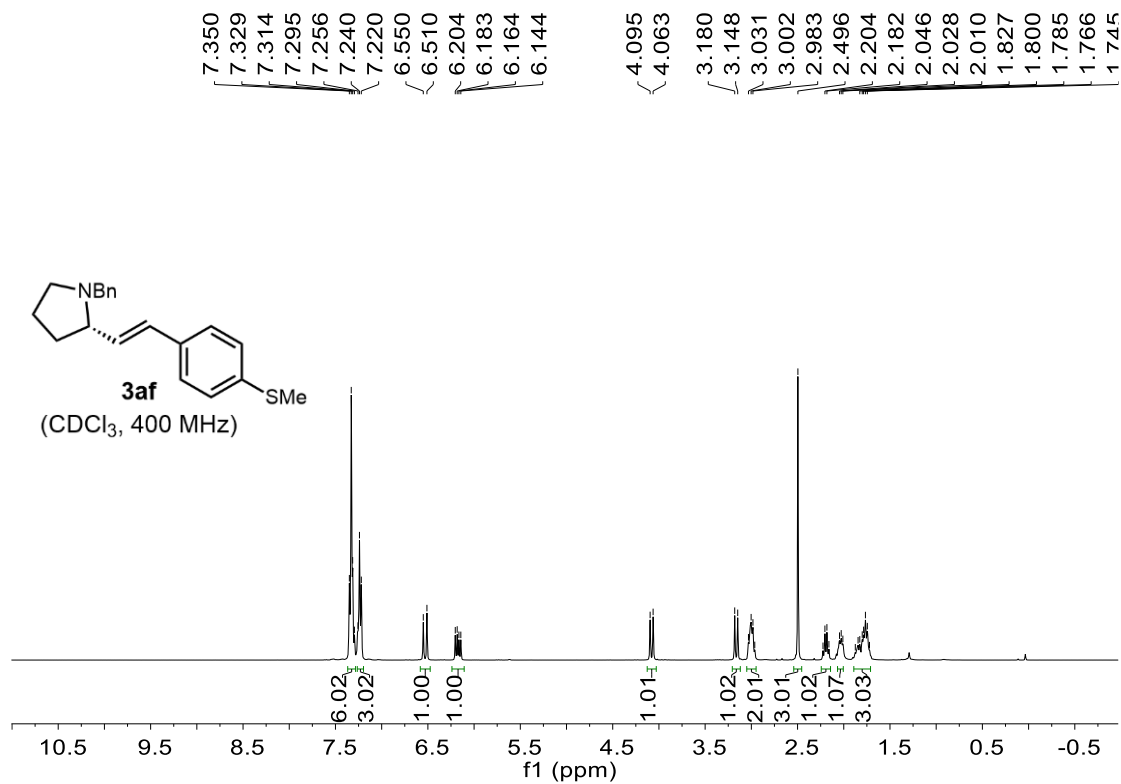
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 -22.10

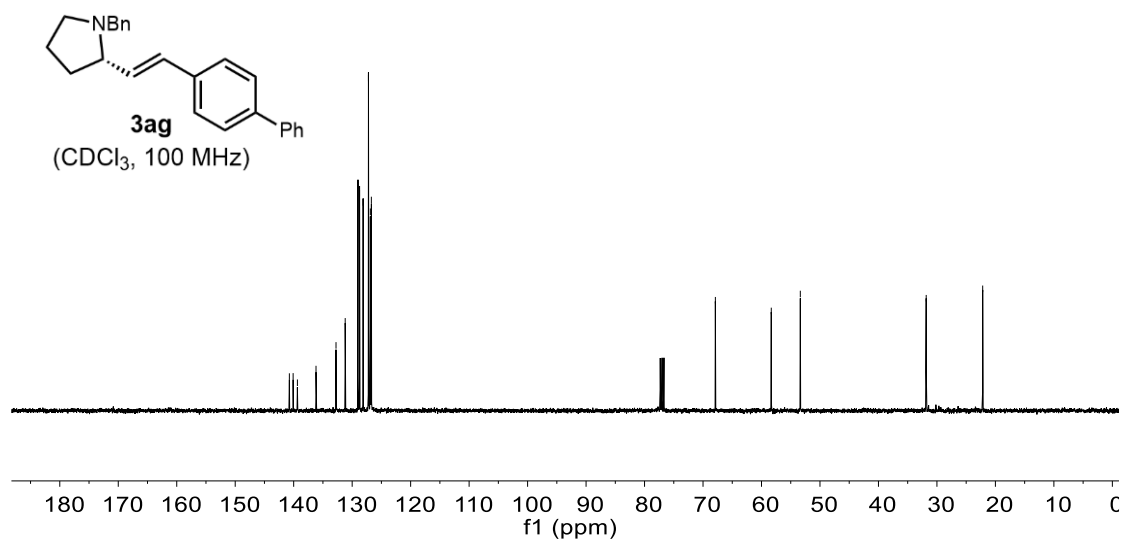
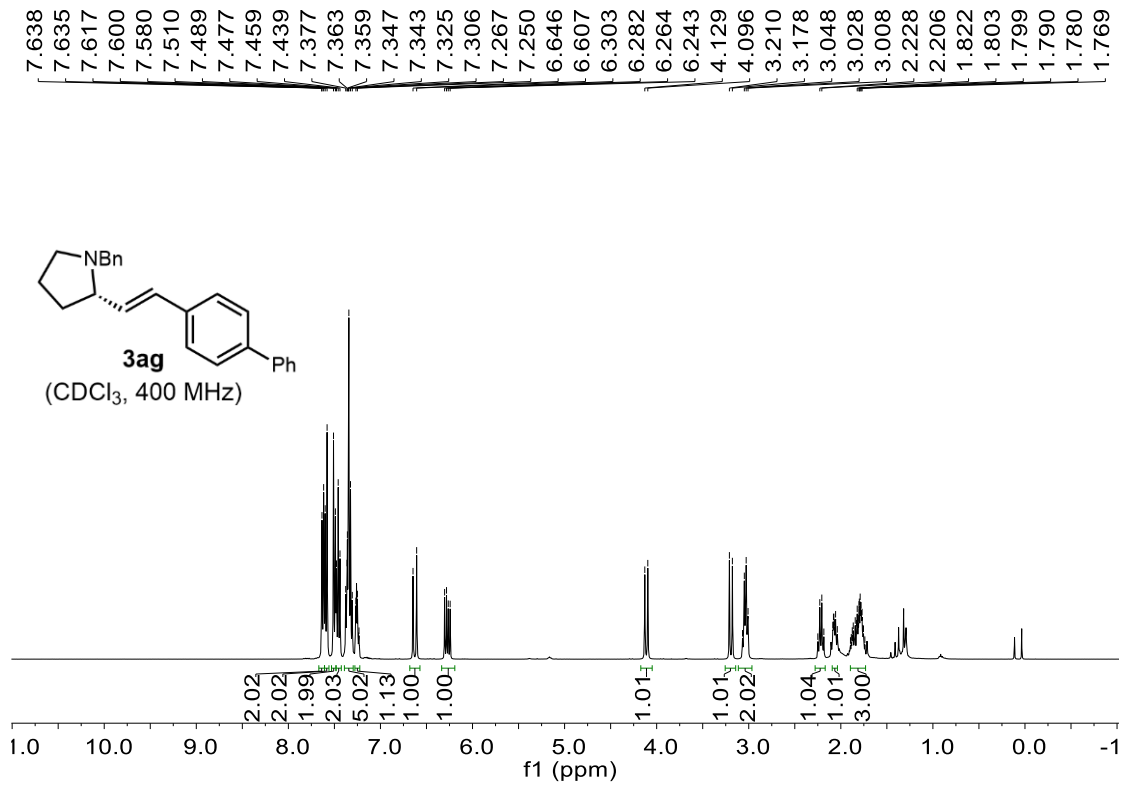




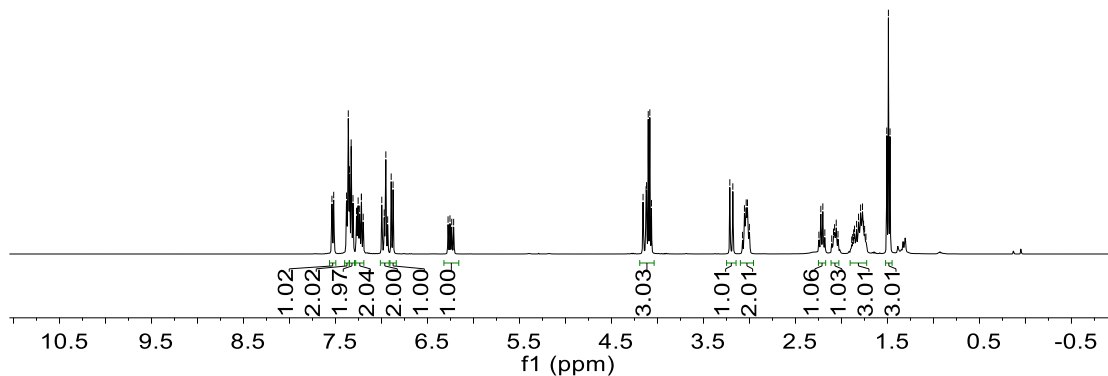
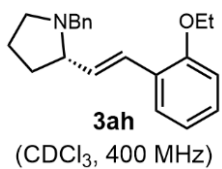




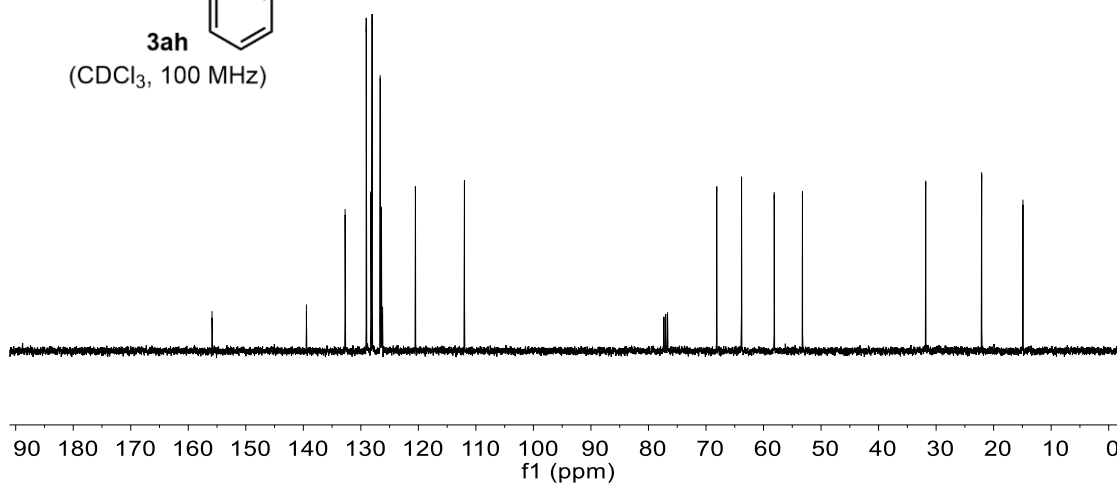
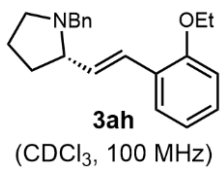


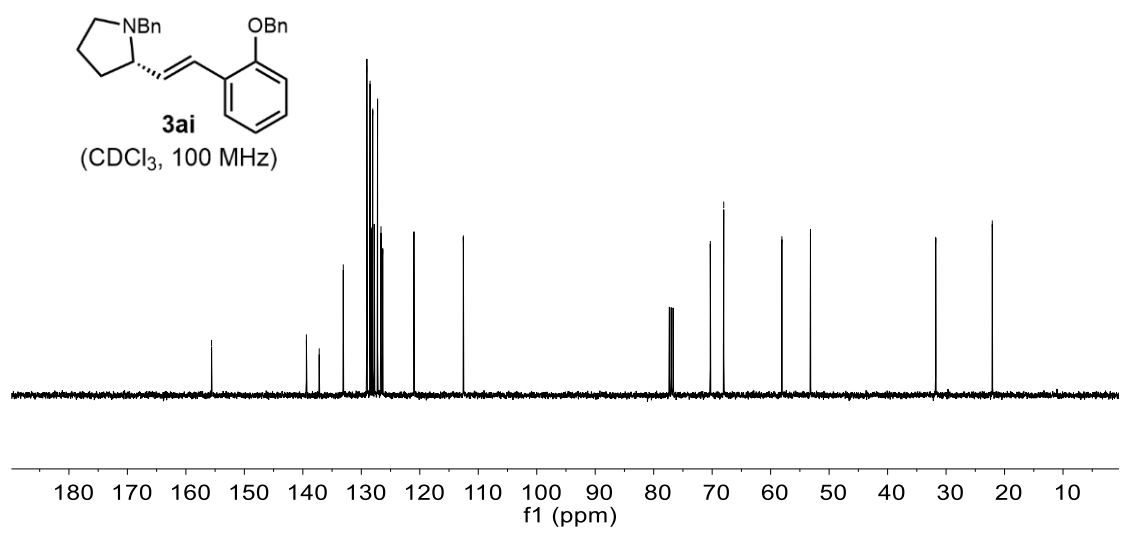
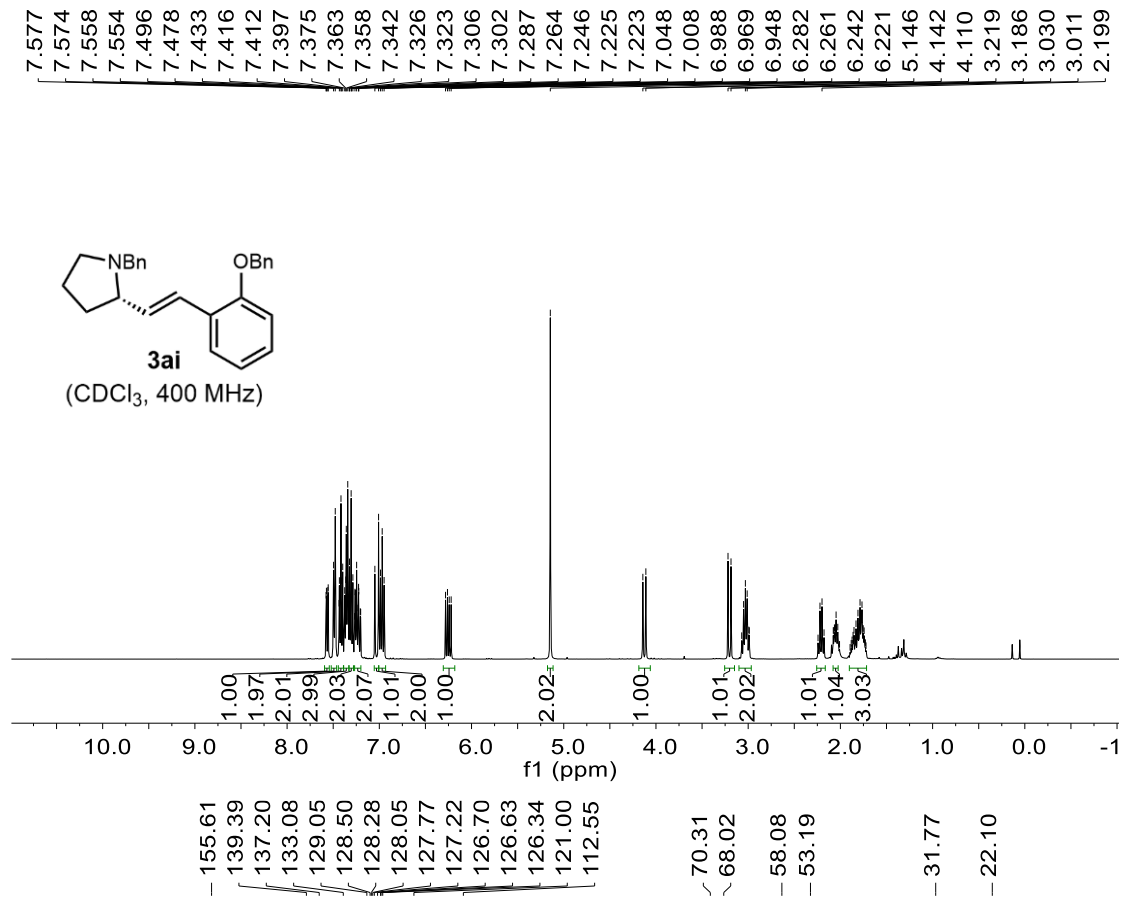


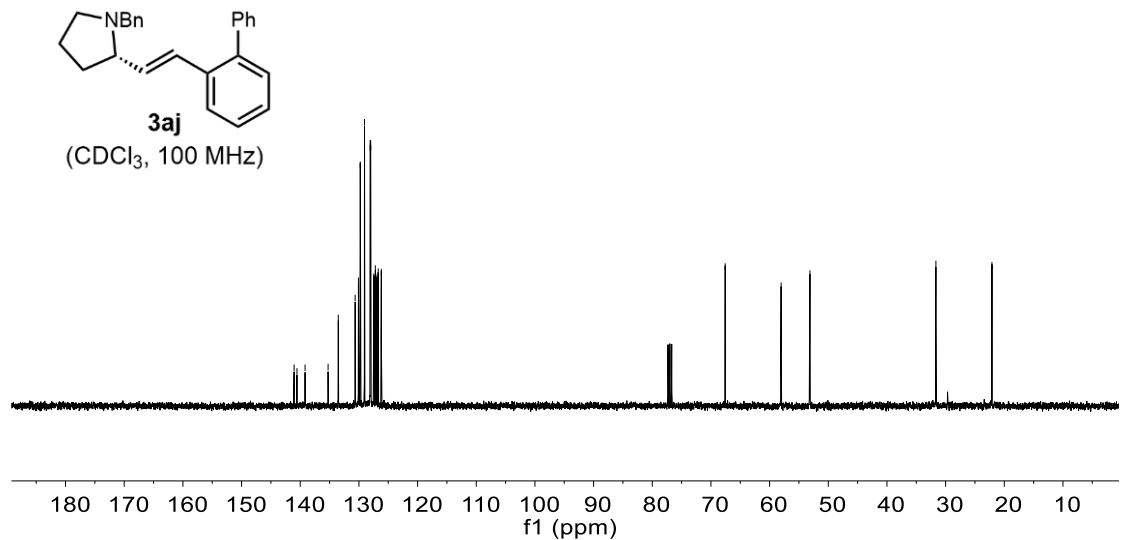
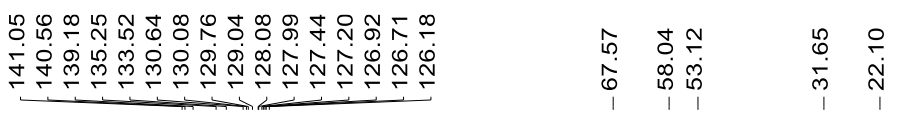
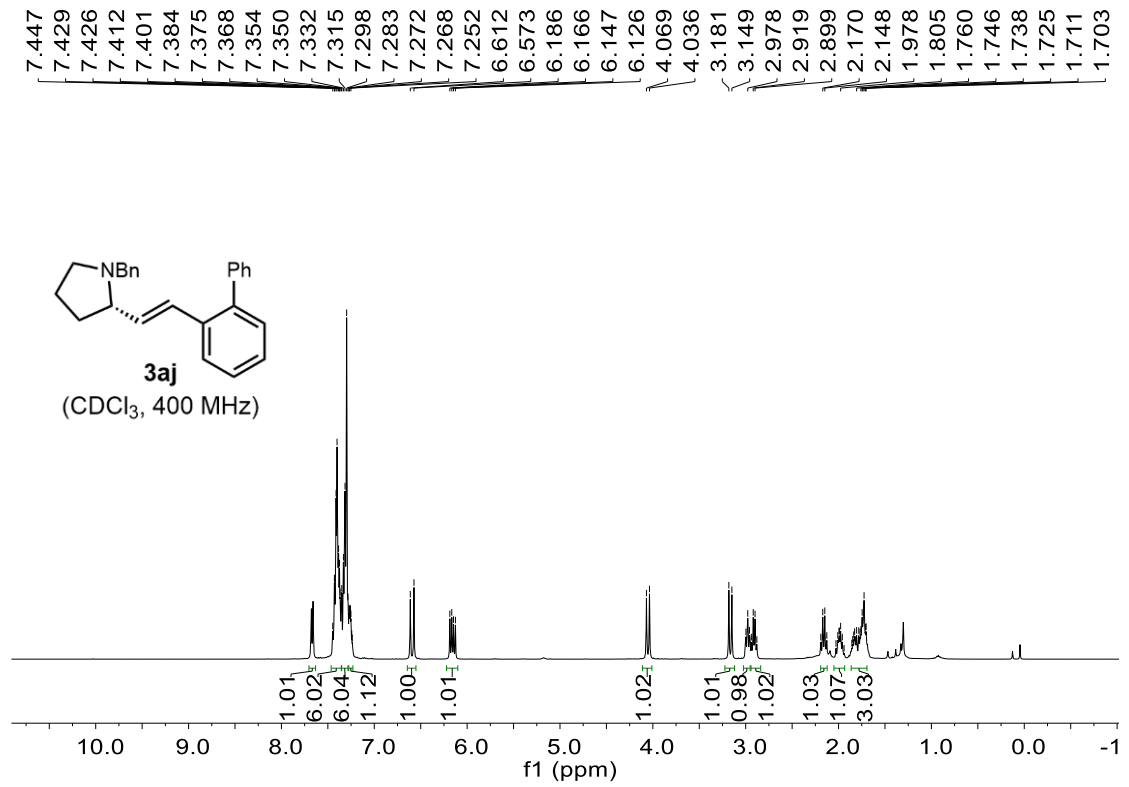
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6.970
6.953
6.895
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6.256
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4.101
4.083
4.066
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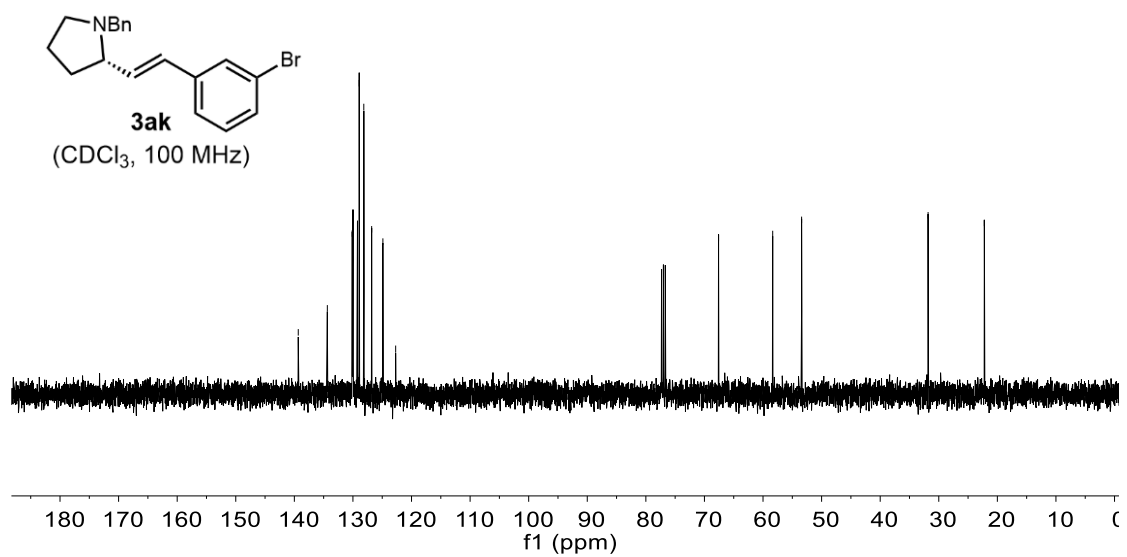
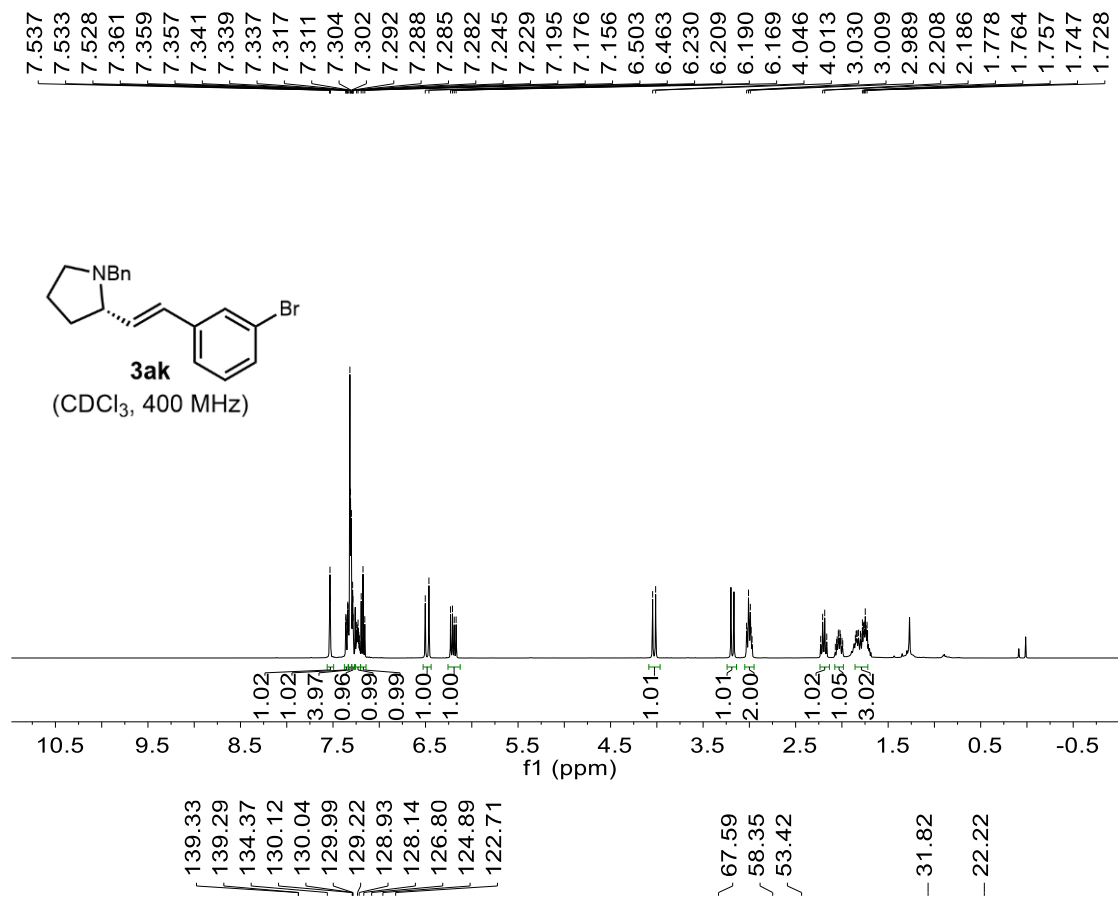


- 155.87
 139.46
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 129.06
 128.25
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 126.63
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 - 63.82
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 - 53.23
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 - 22.08
 - 14.90

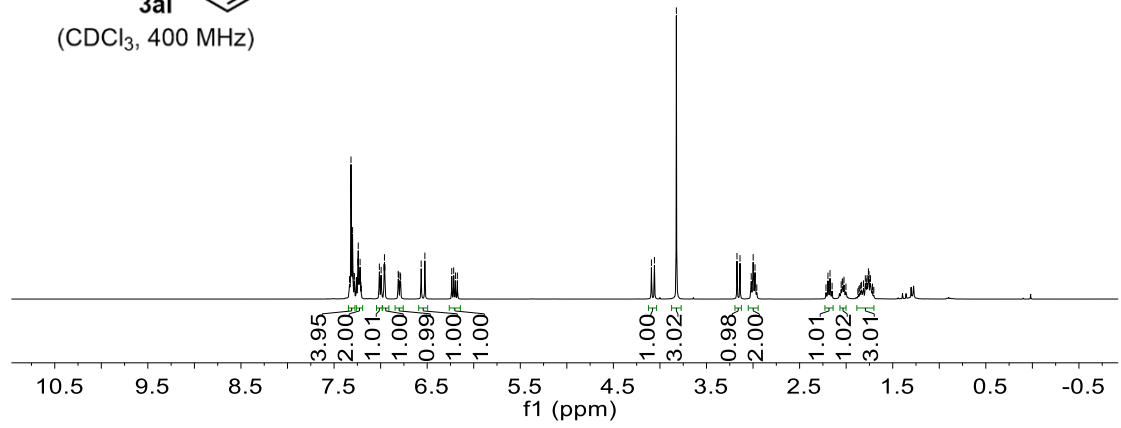
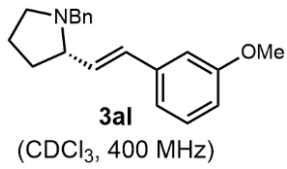




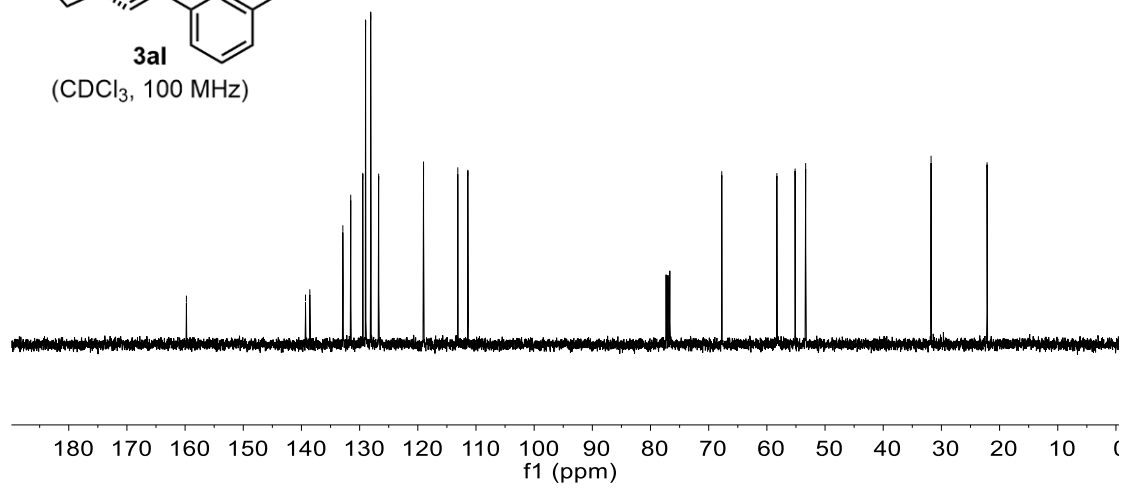
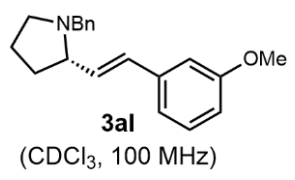


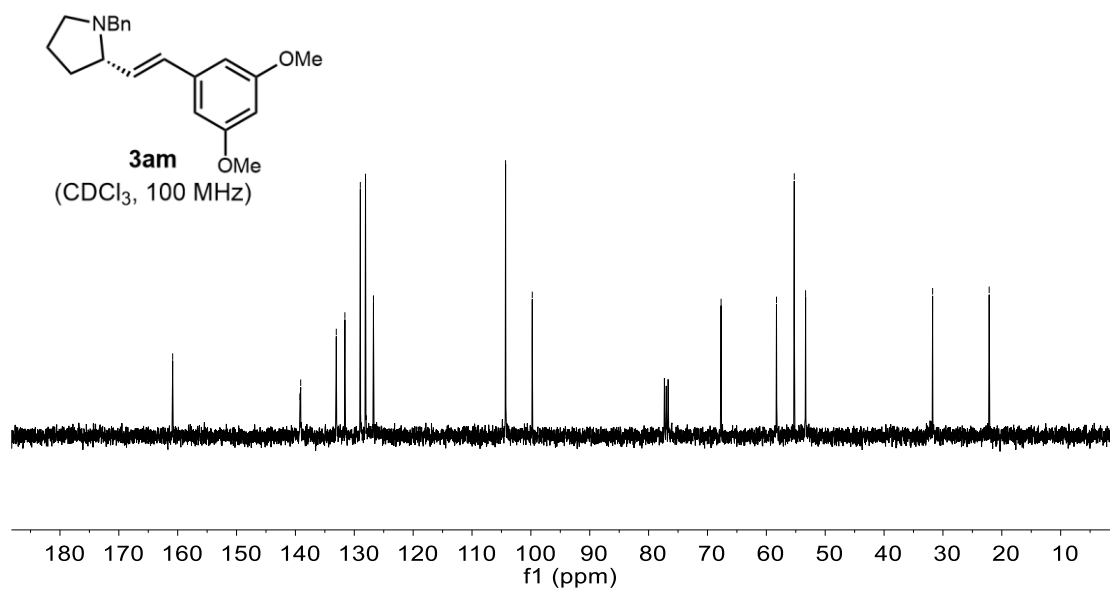
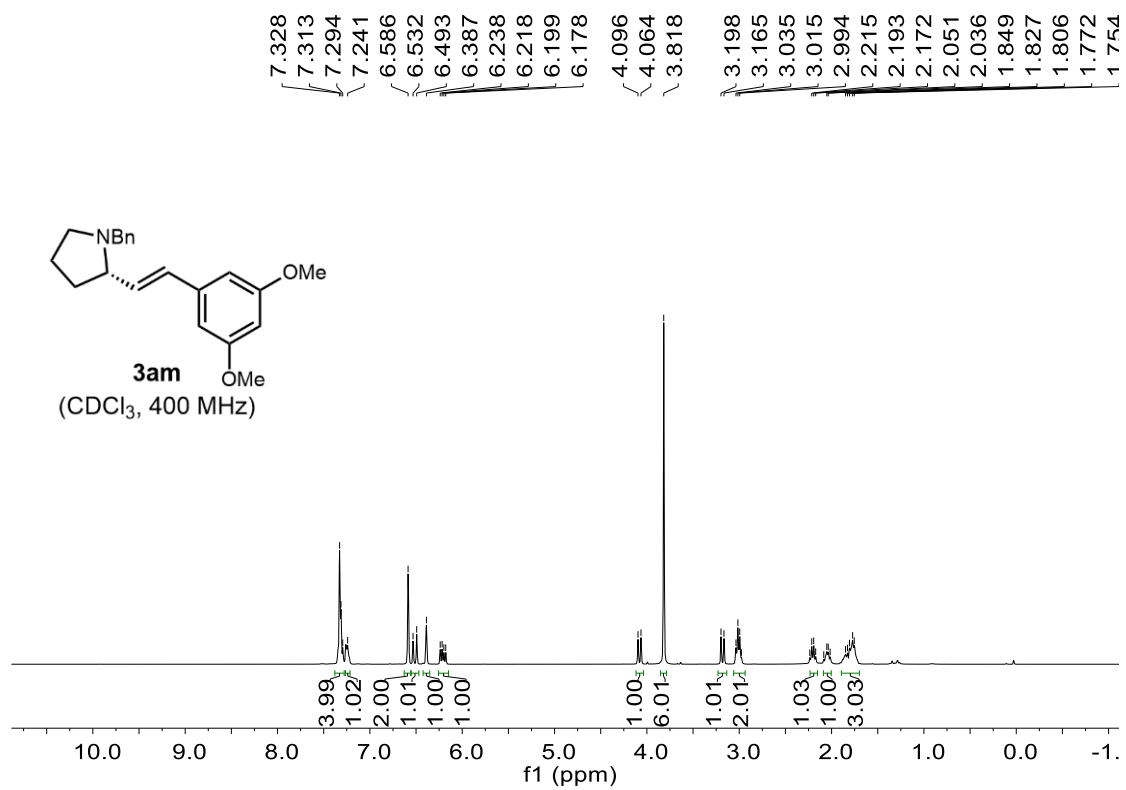


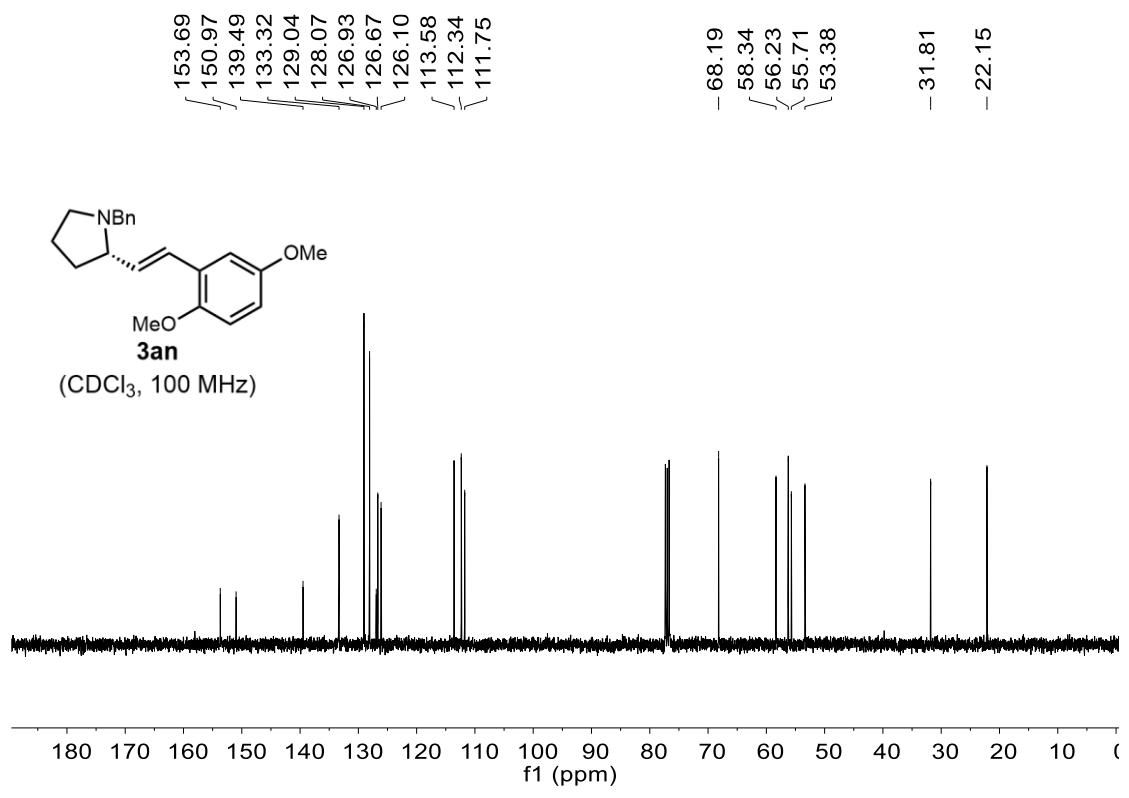
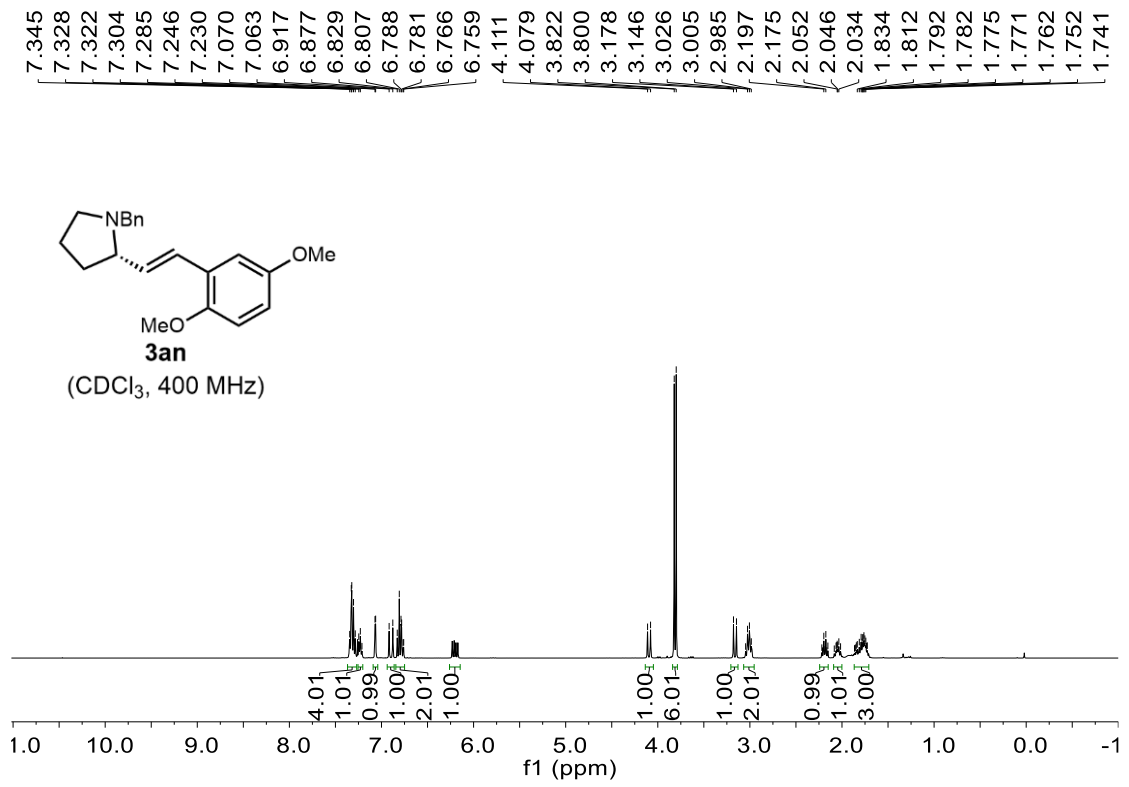
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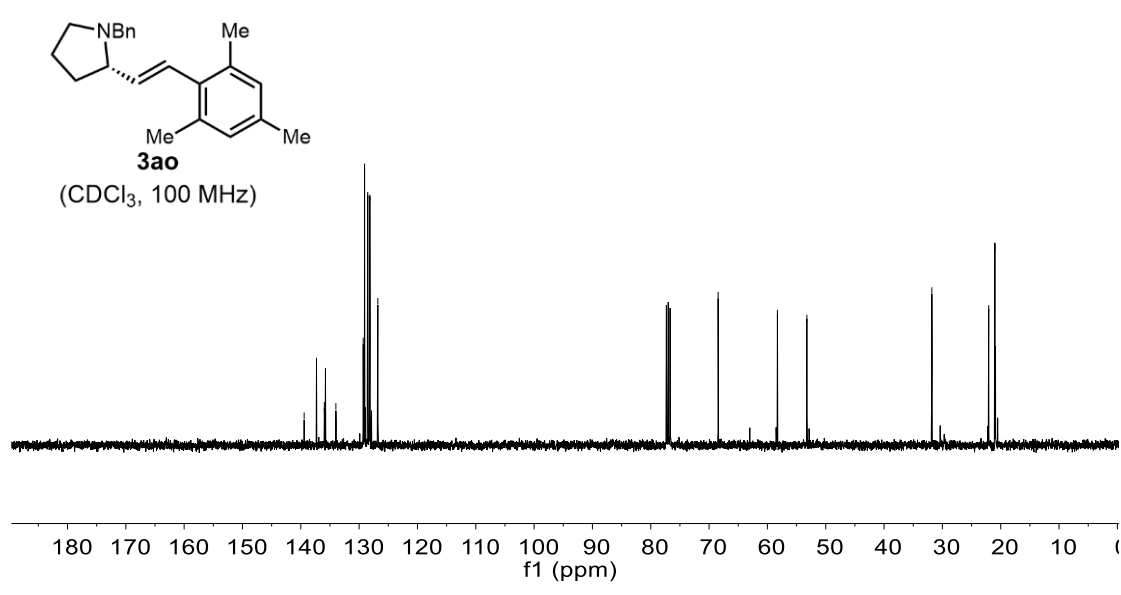
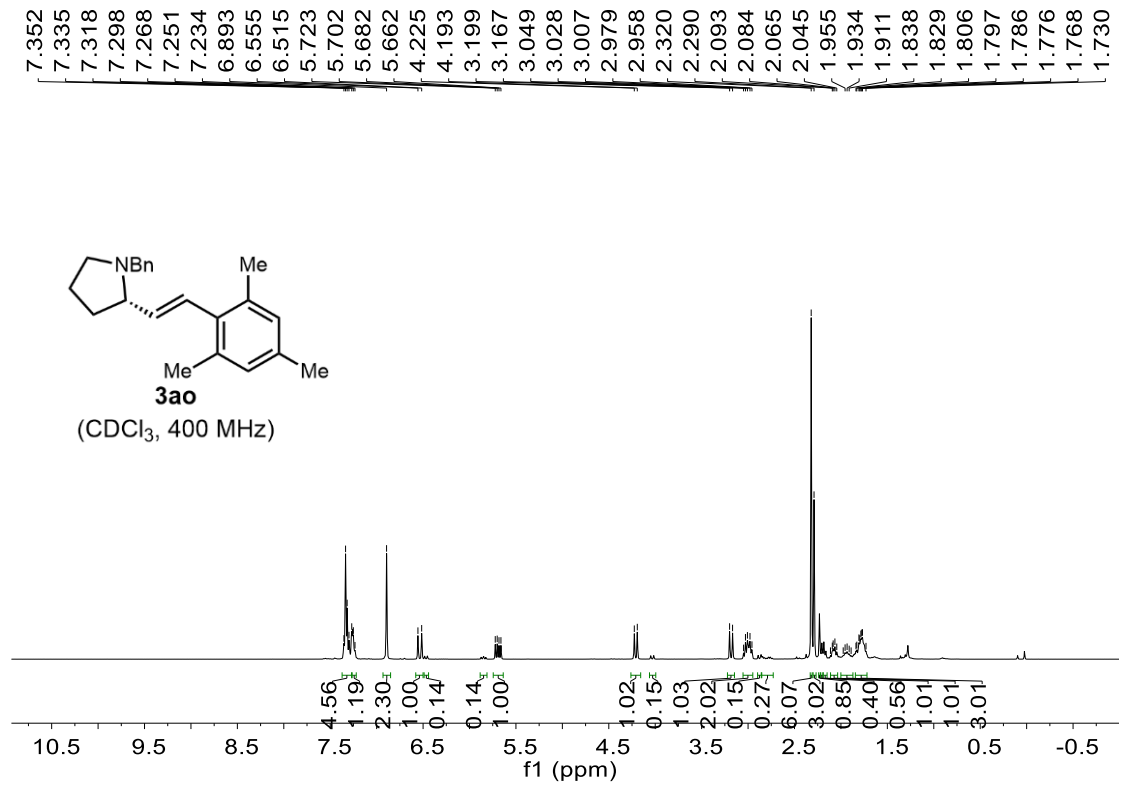


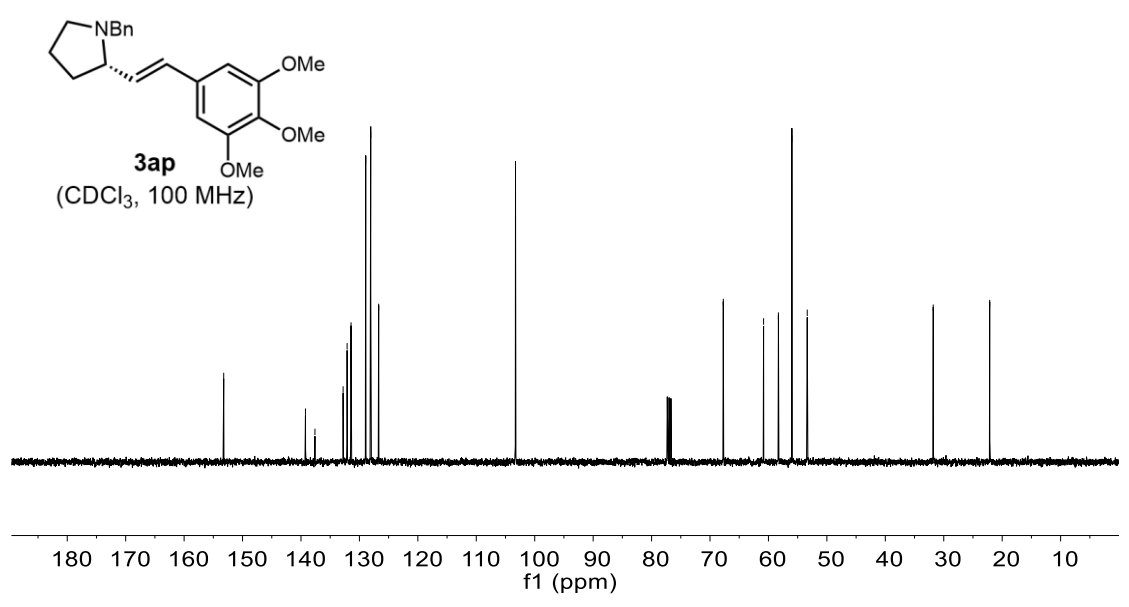
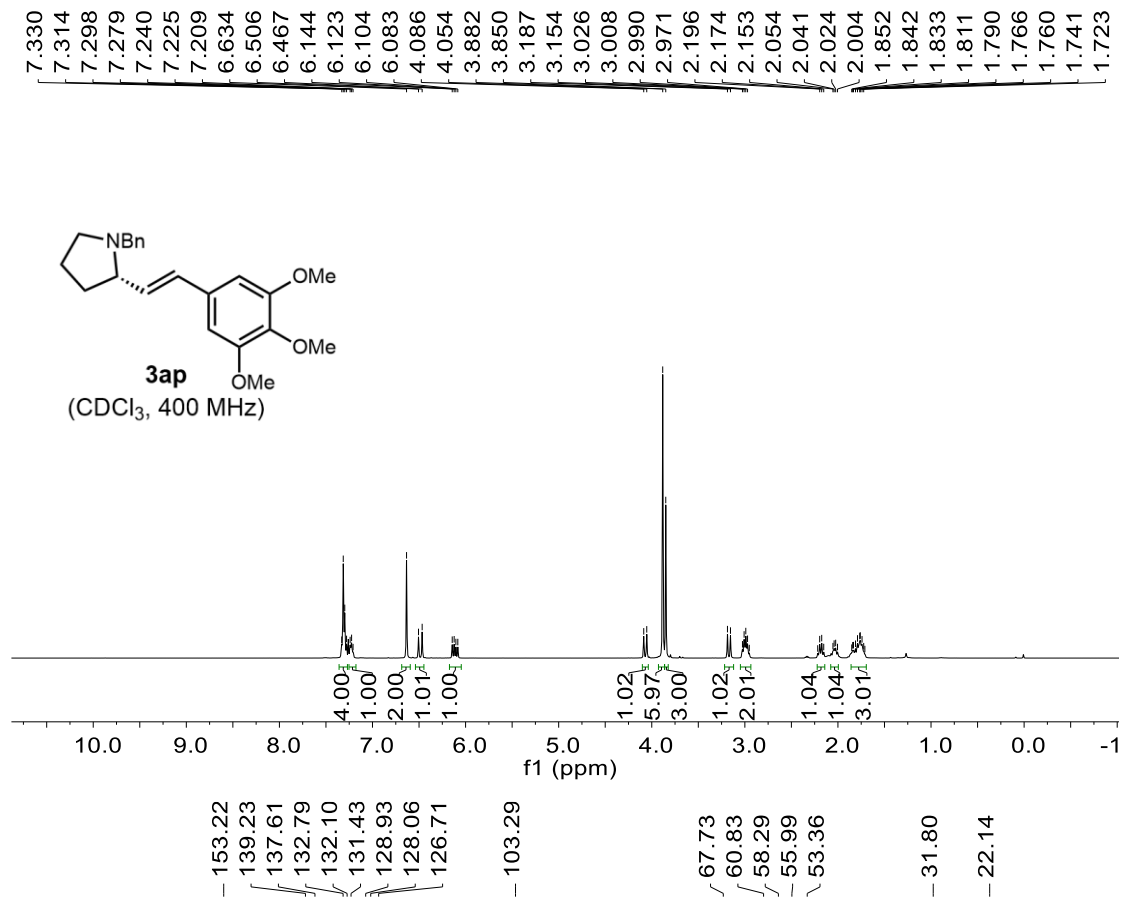
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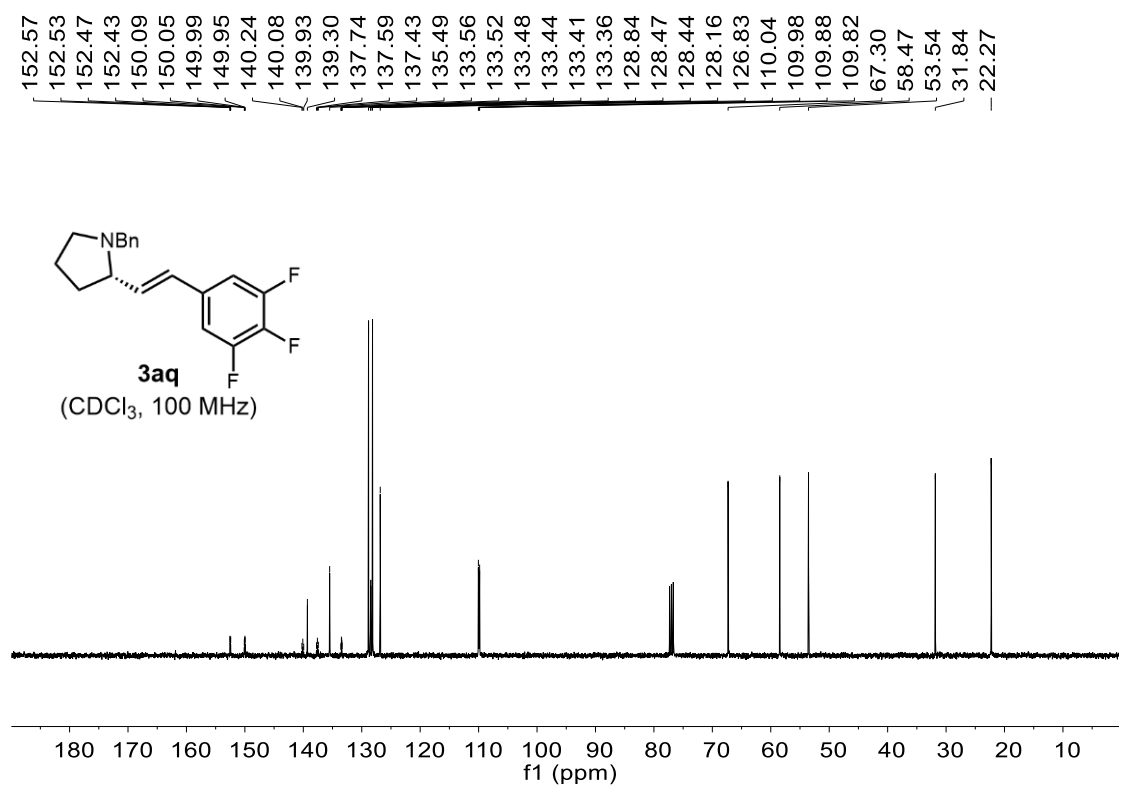
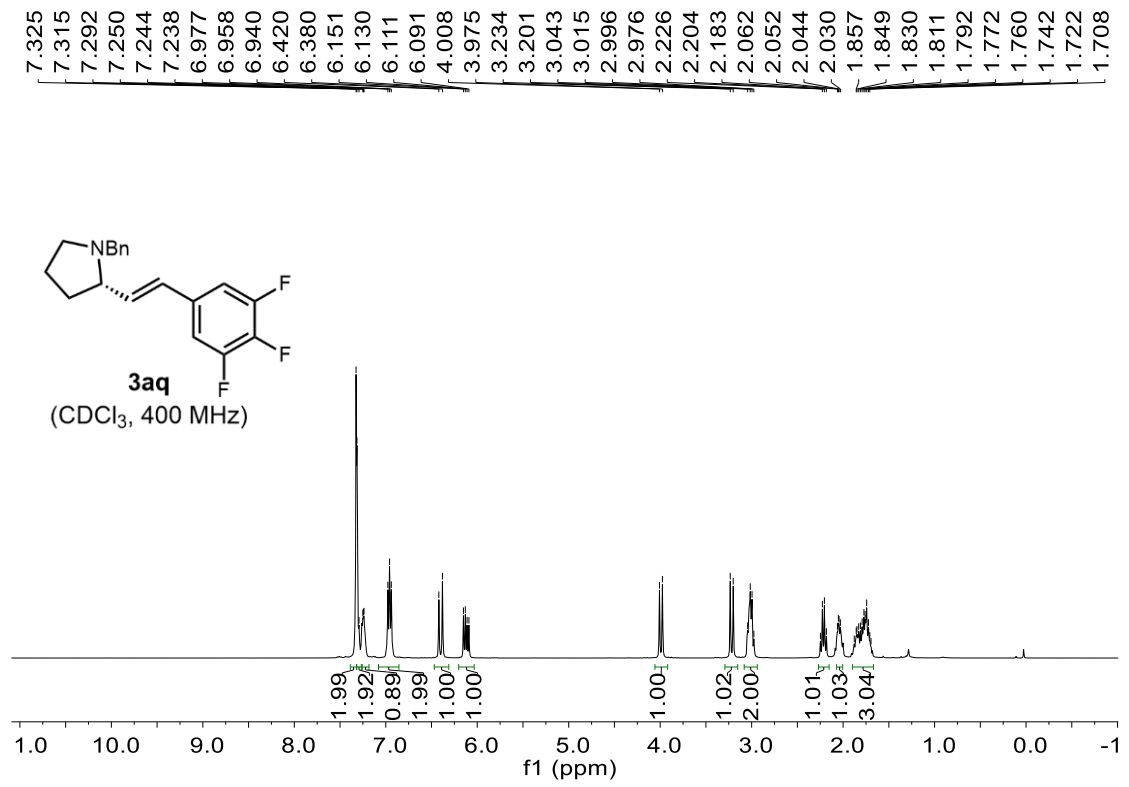


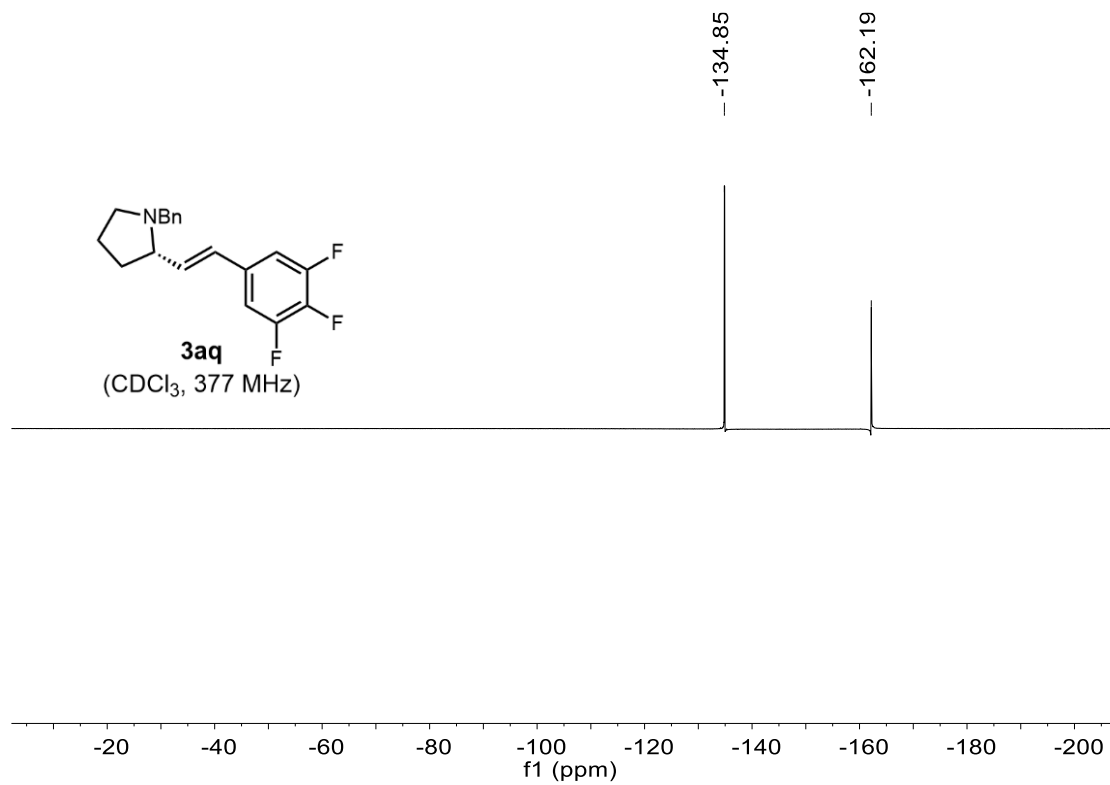


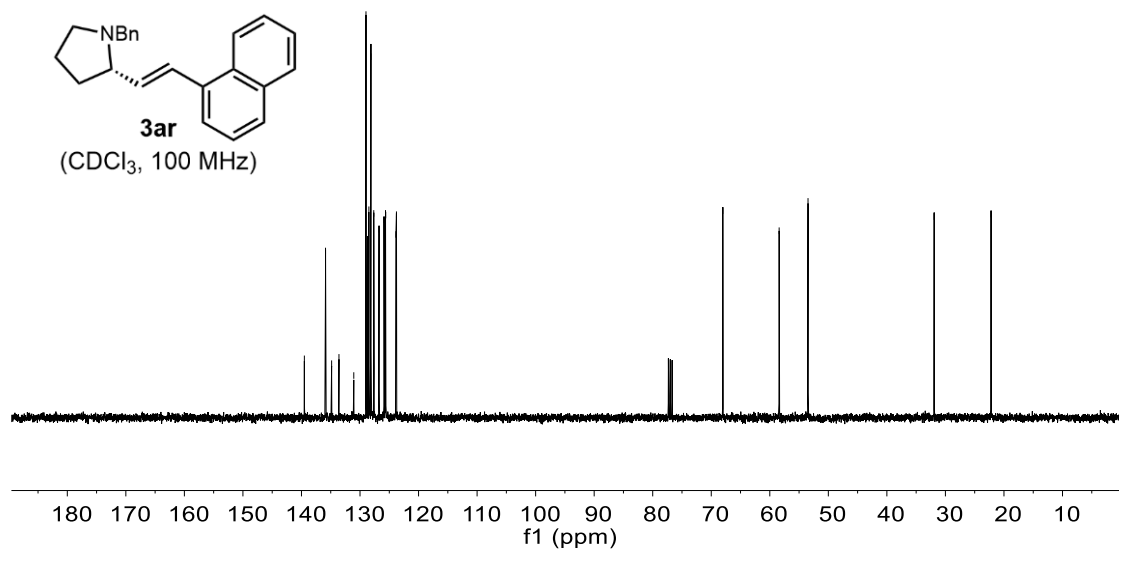
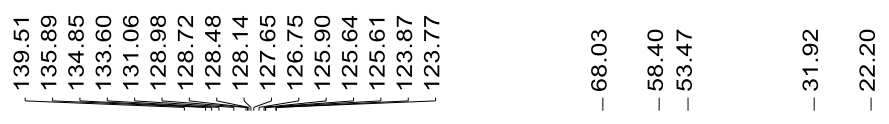
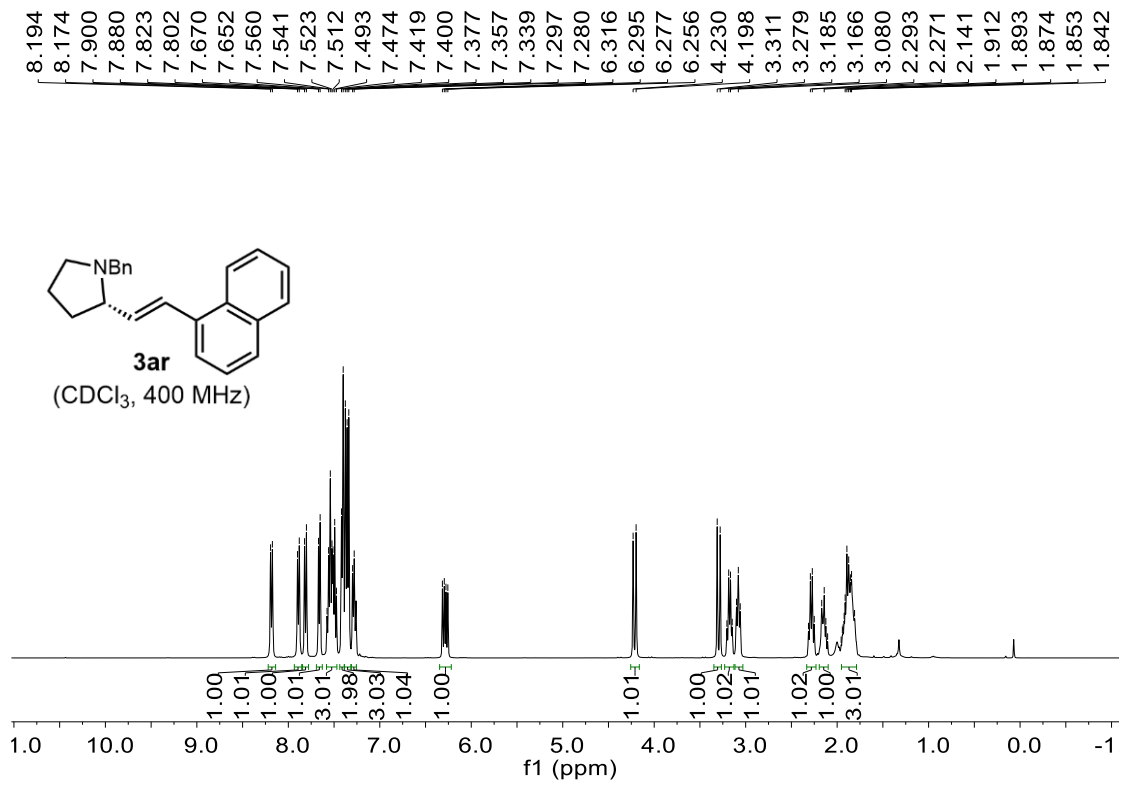




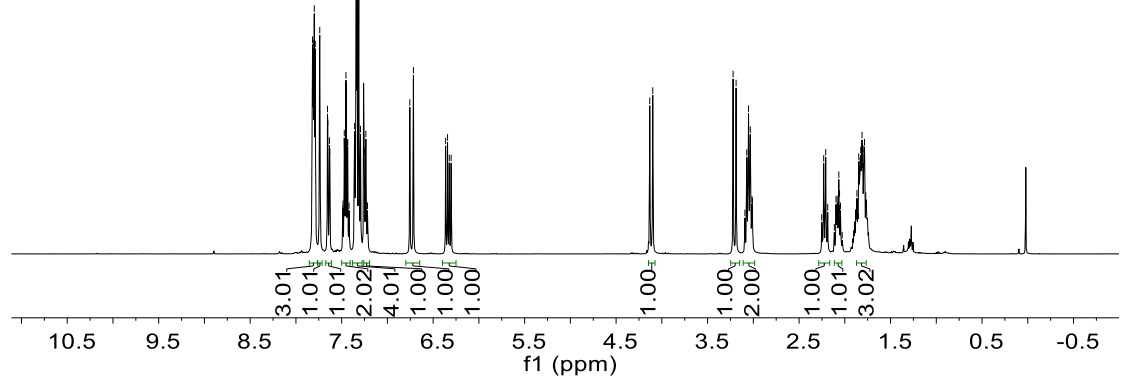
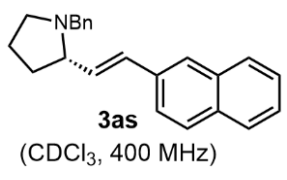




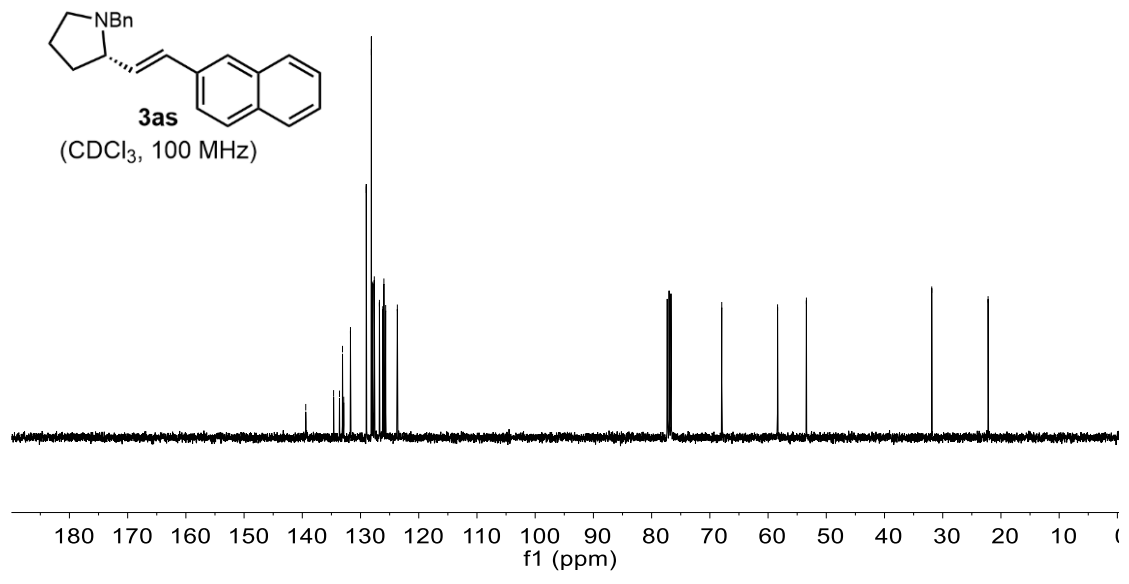
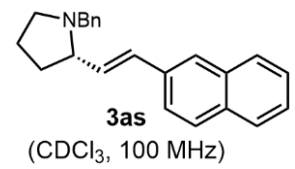


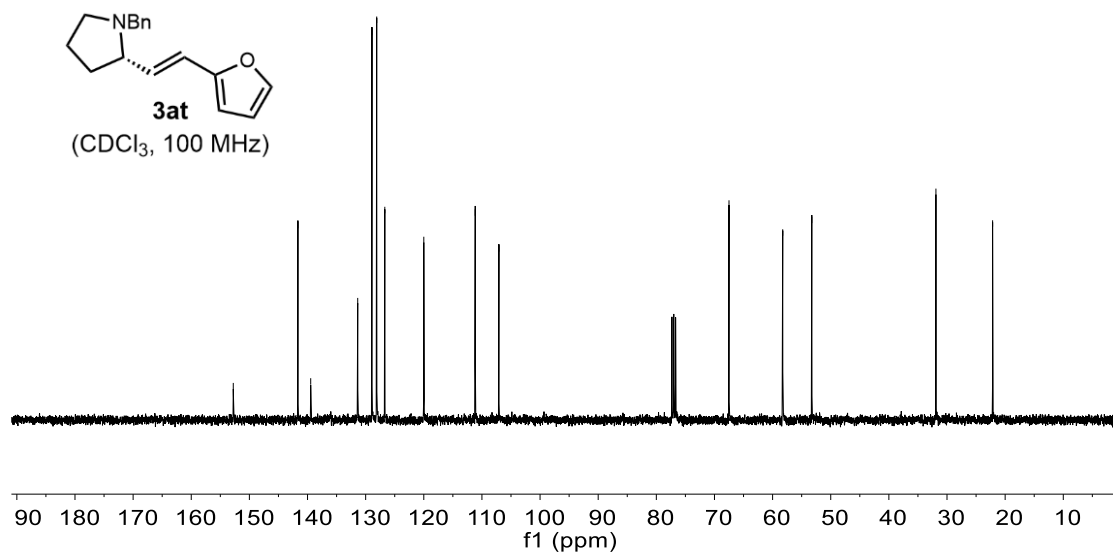
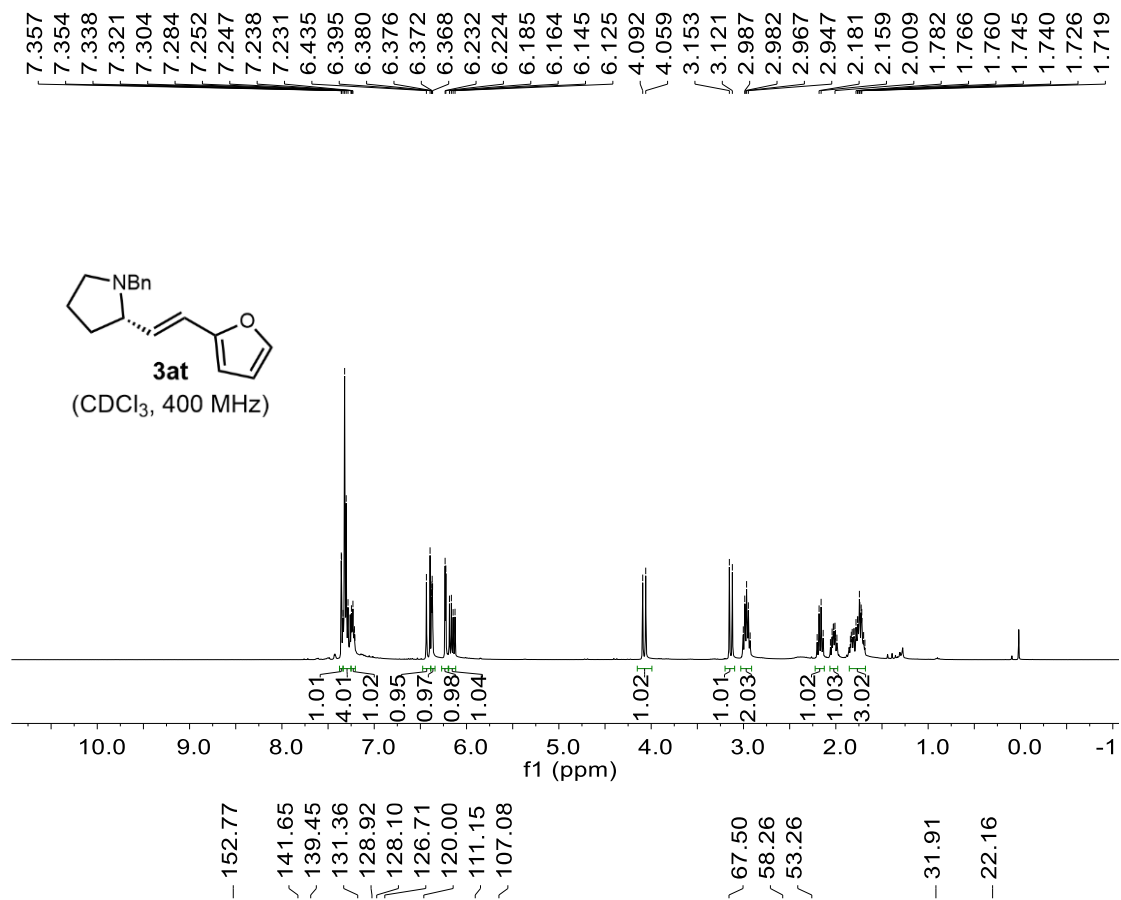


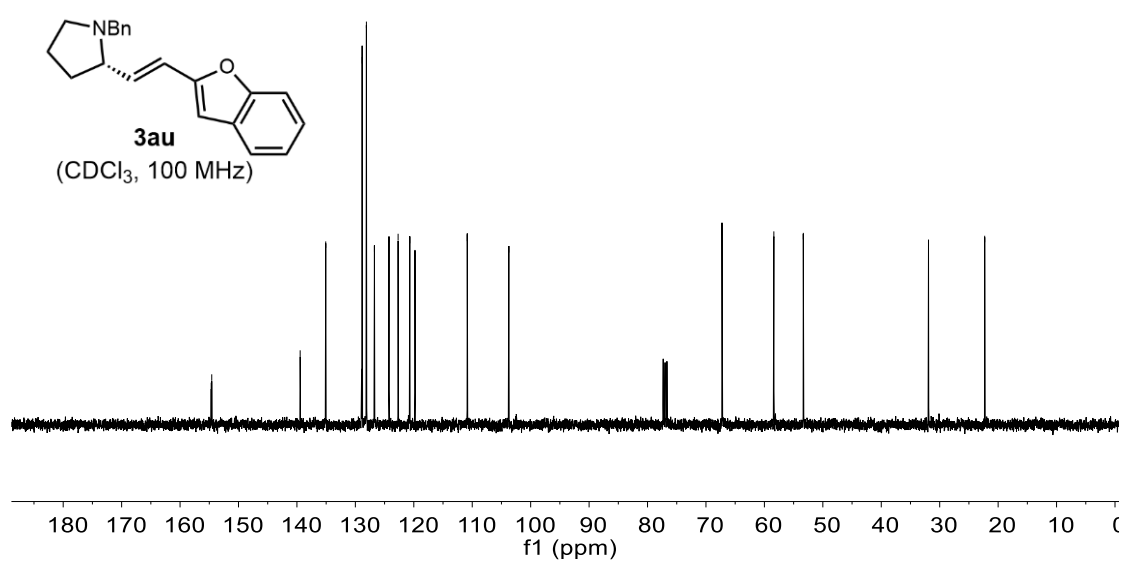
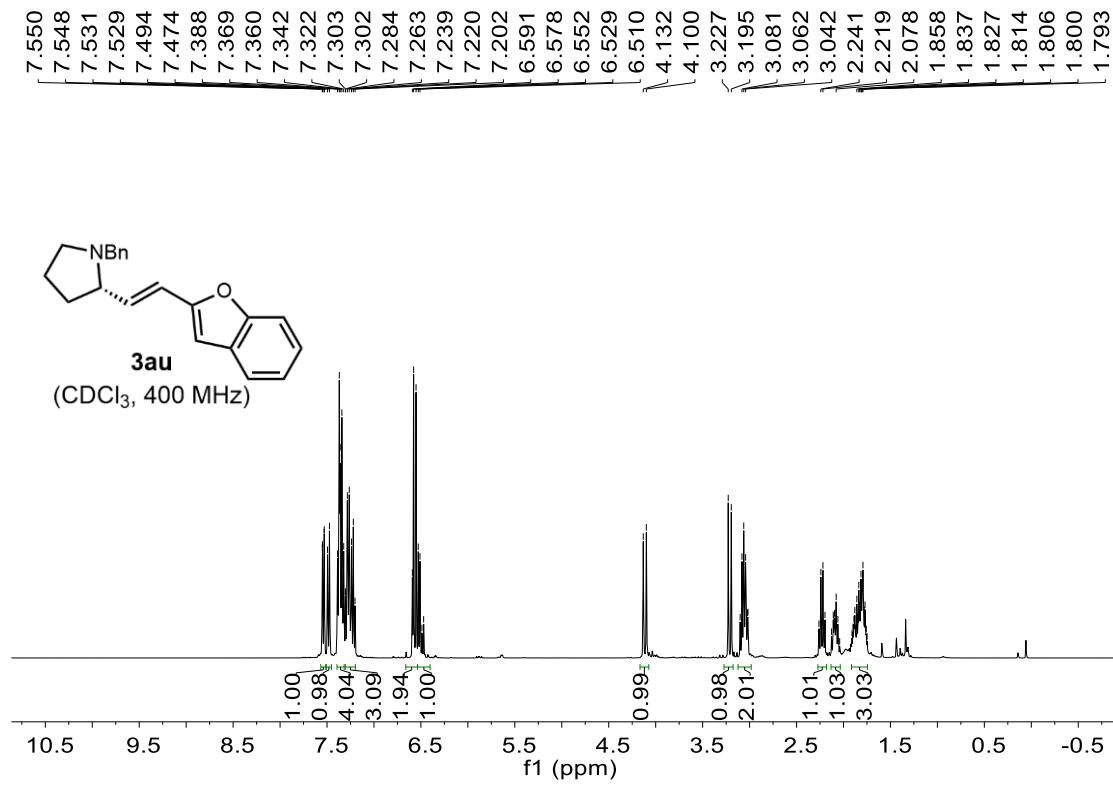
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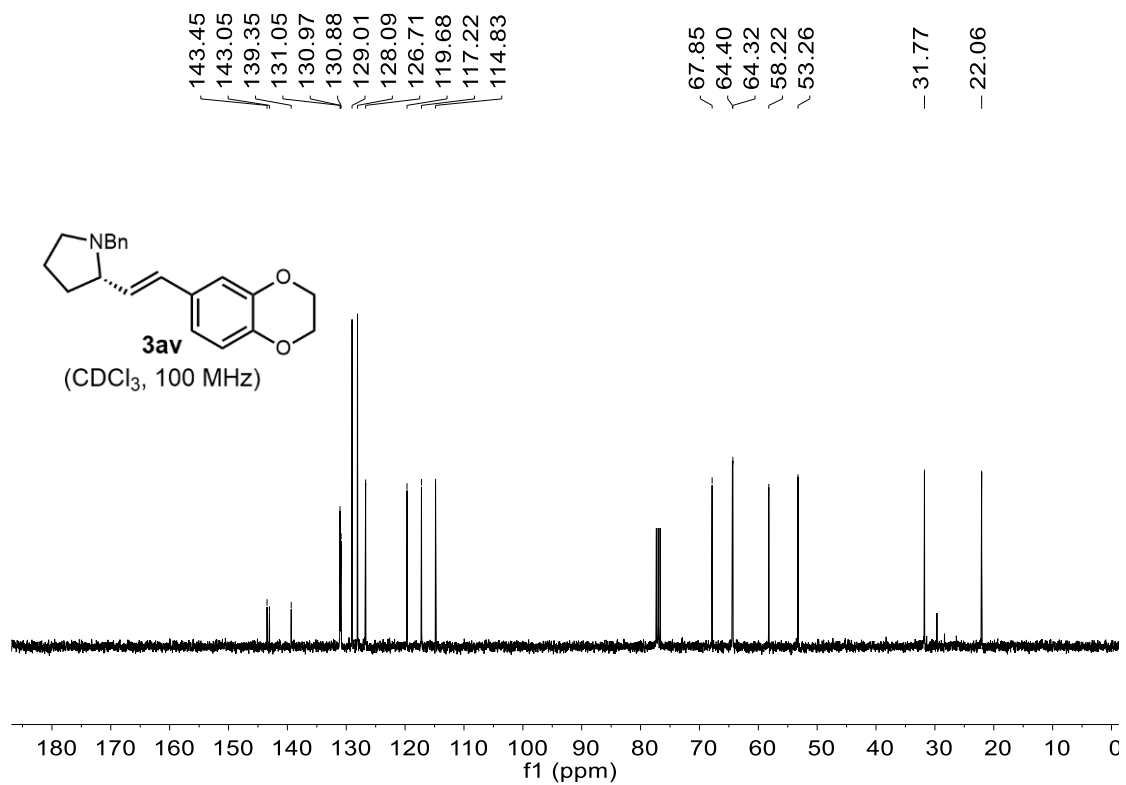
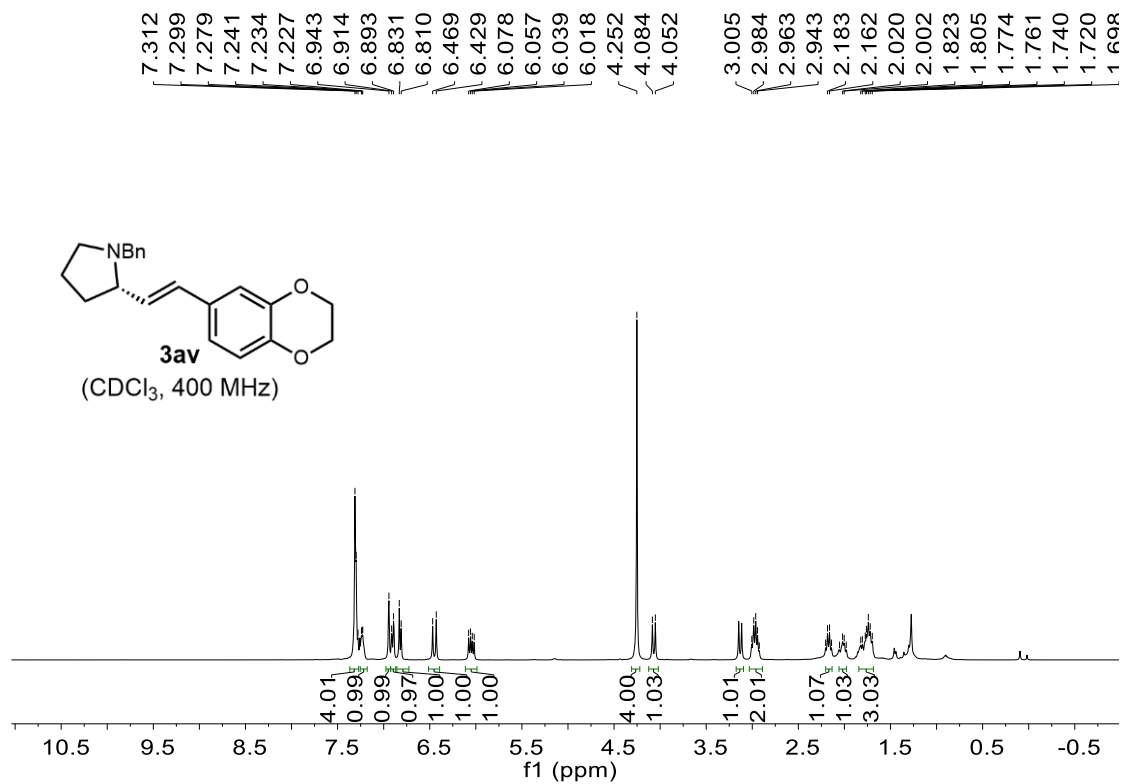


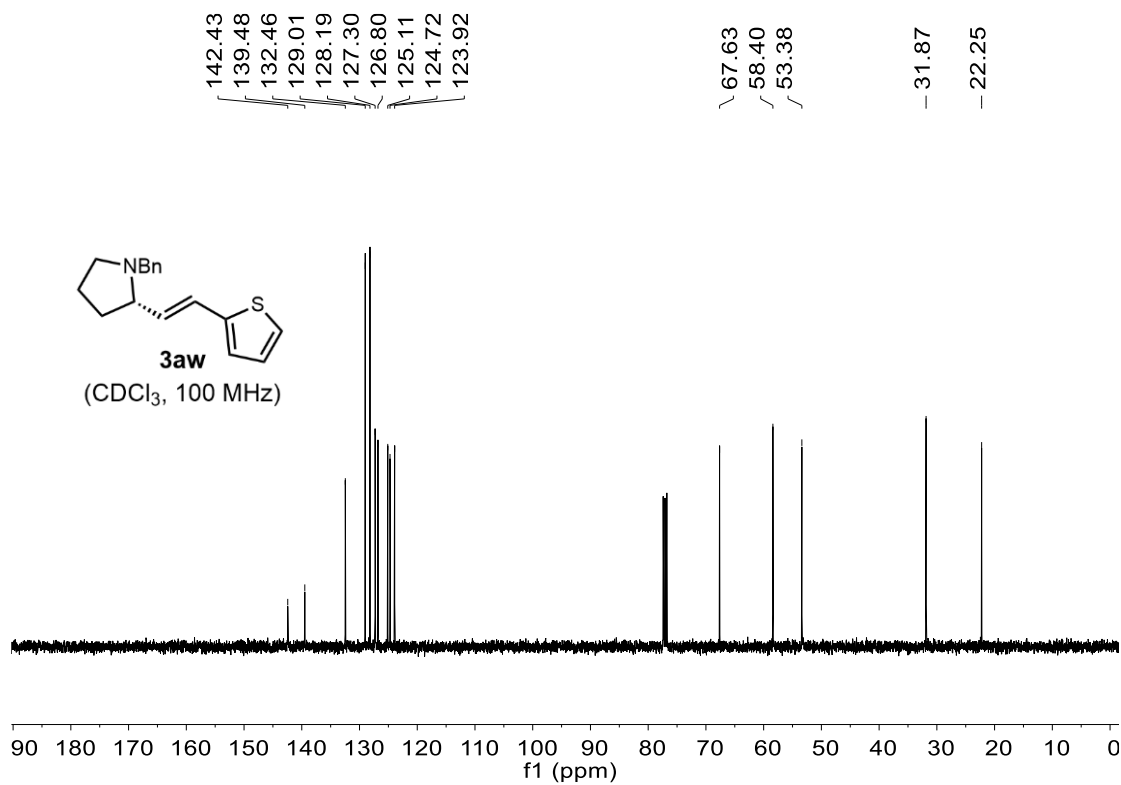
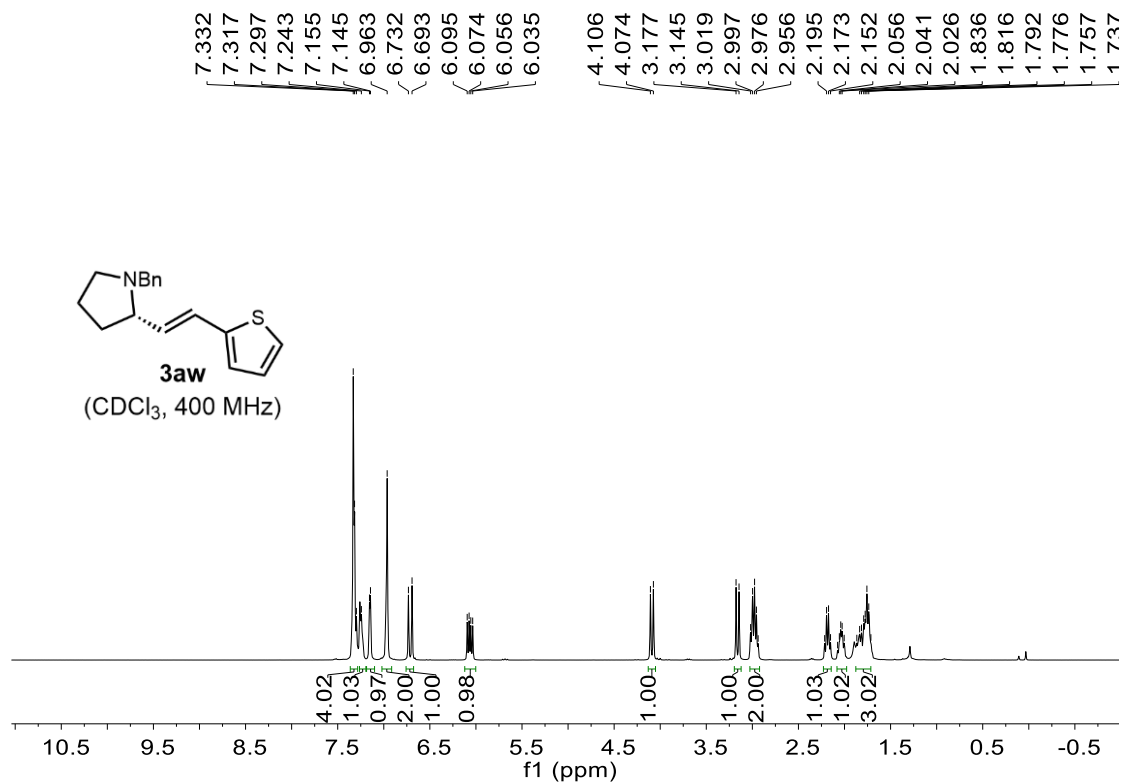
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 - 67.96
 - 58.37
 - 53.41
 - 31.89
 - 22.21

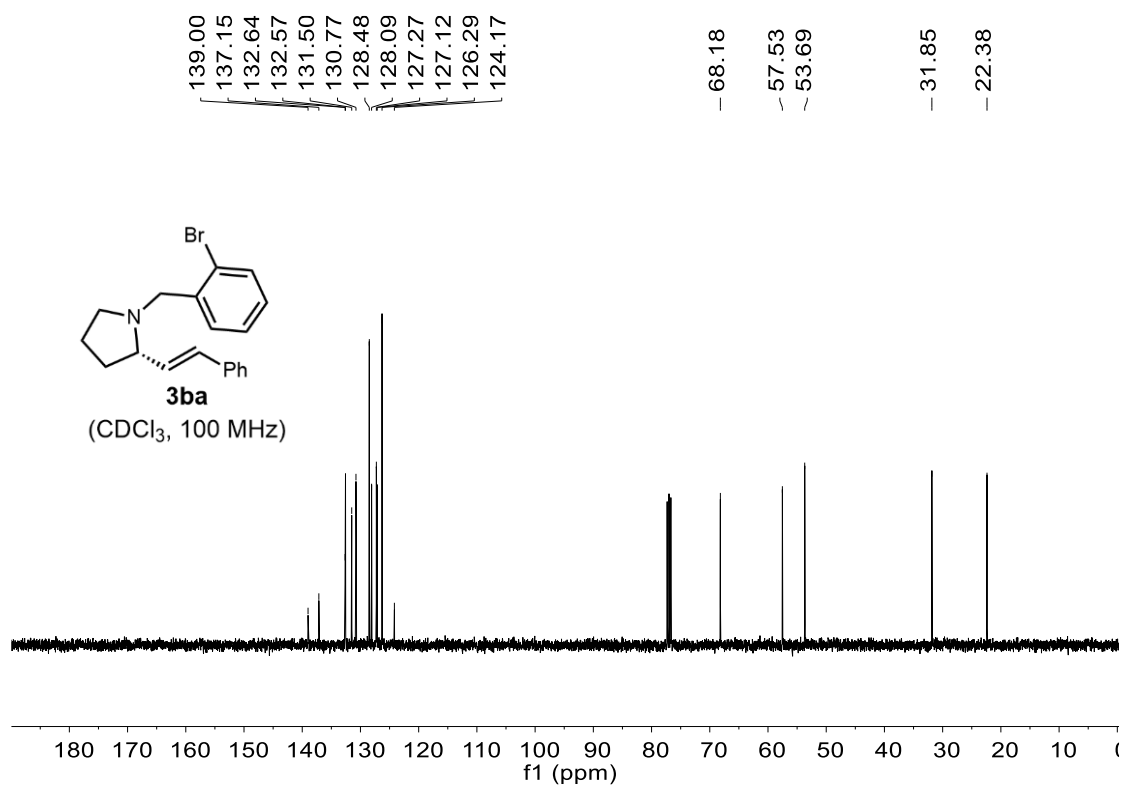
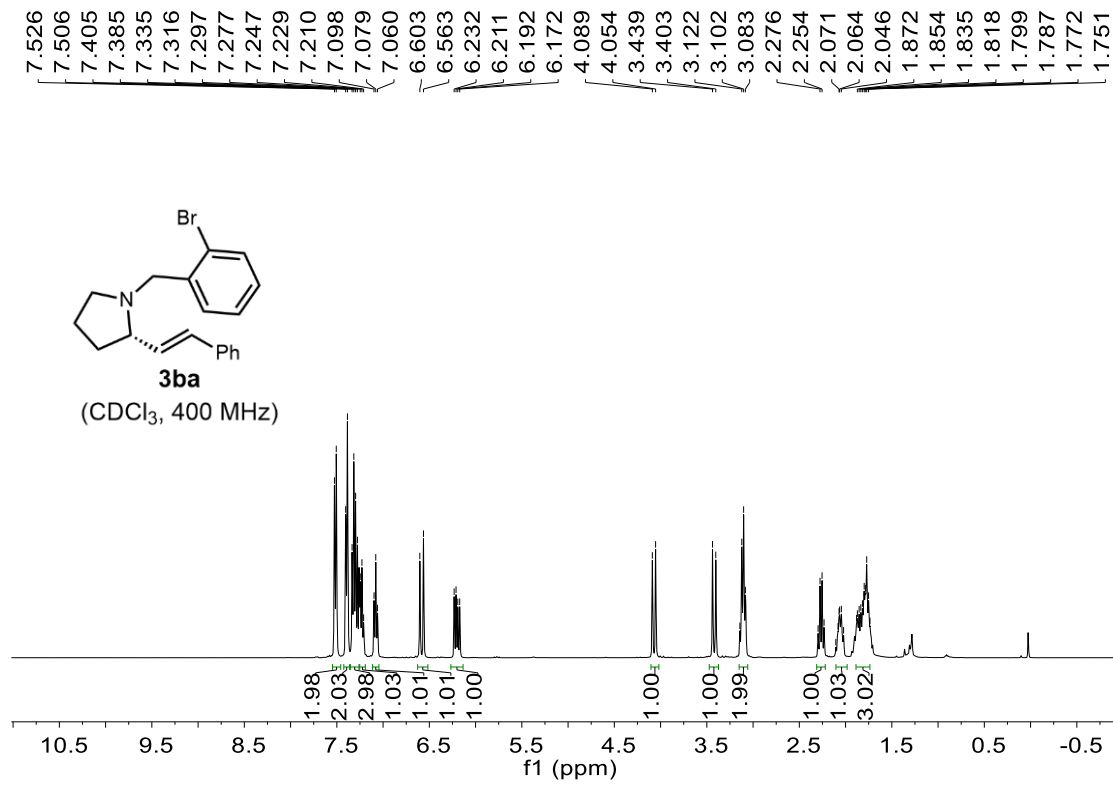


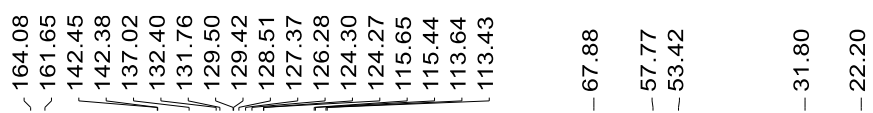
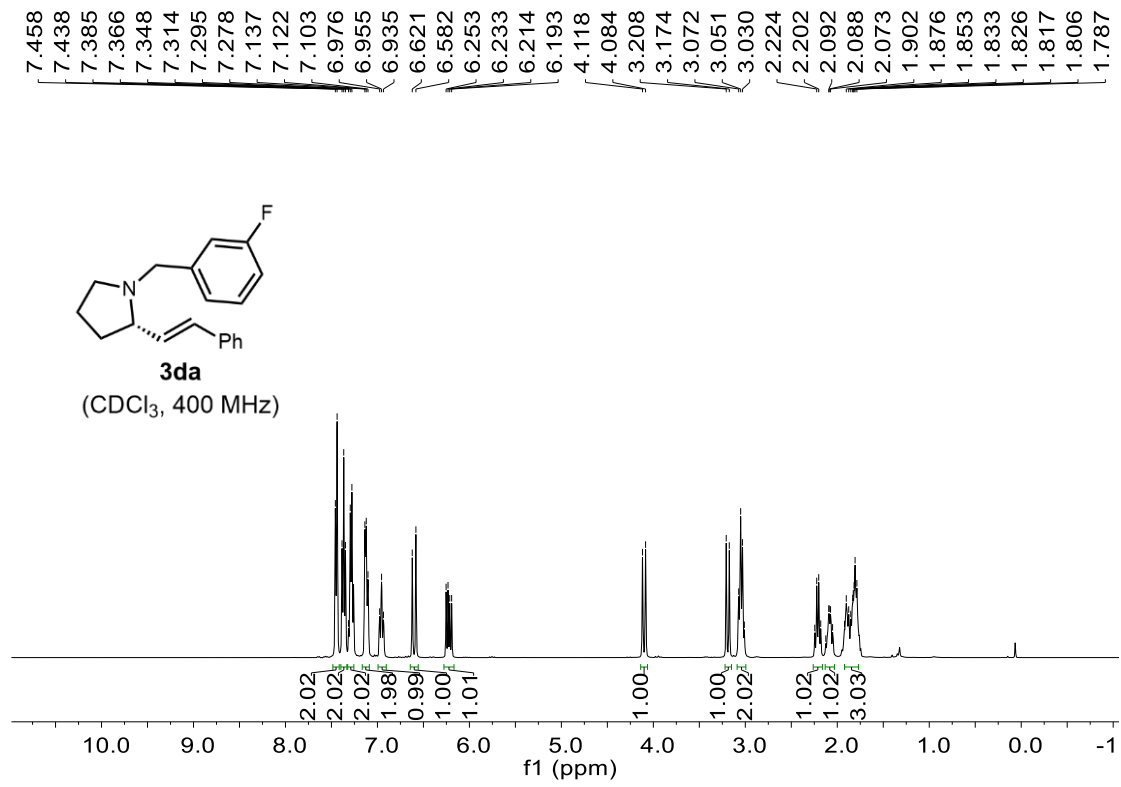


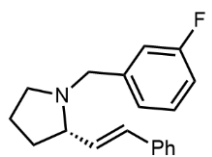




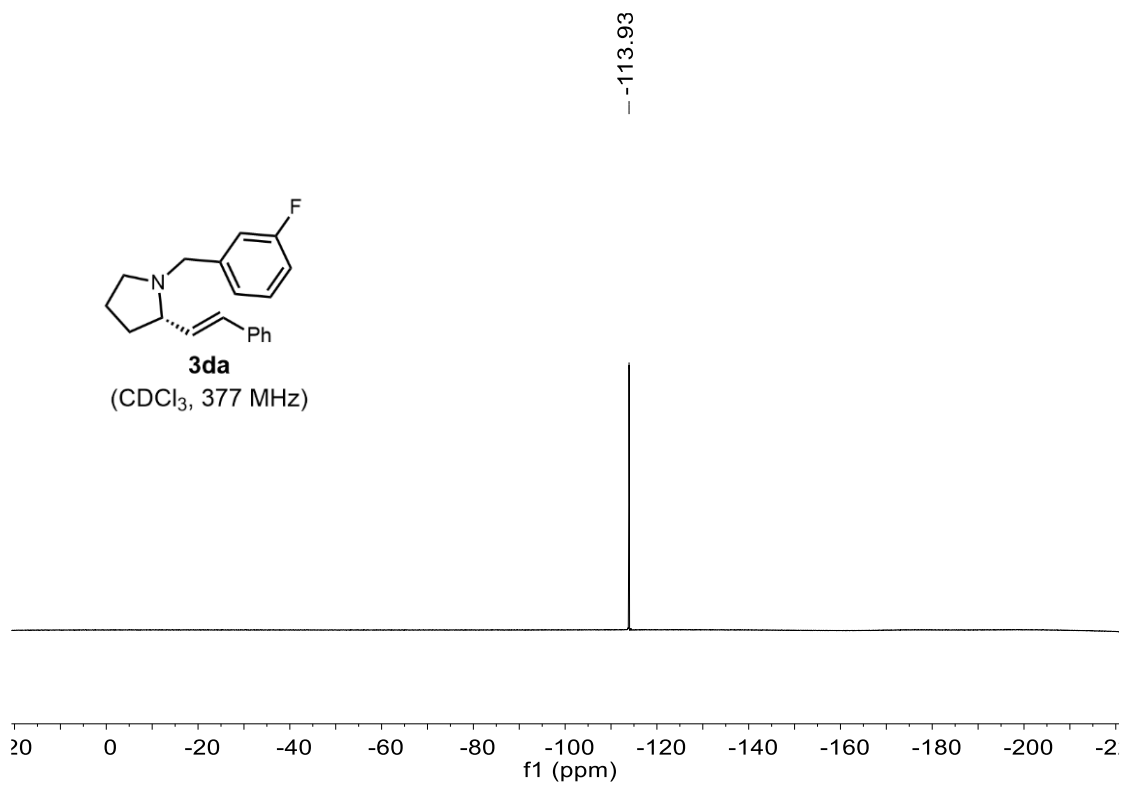


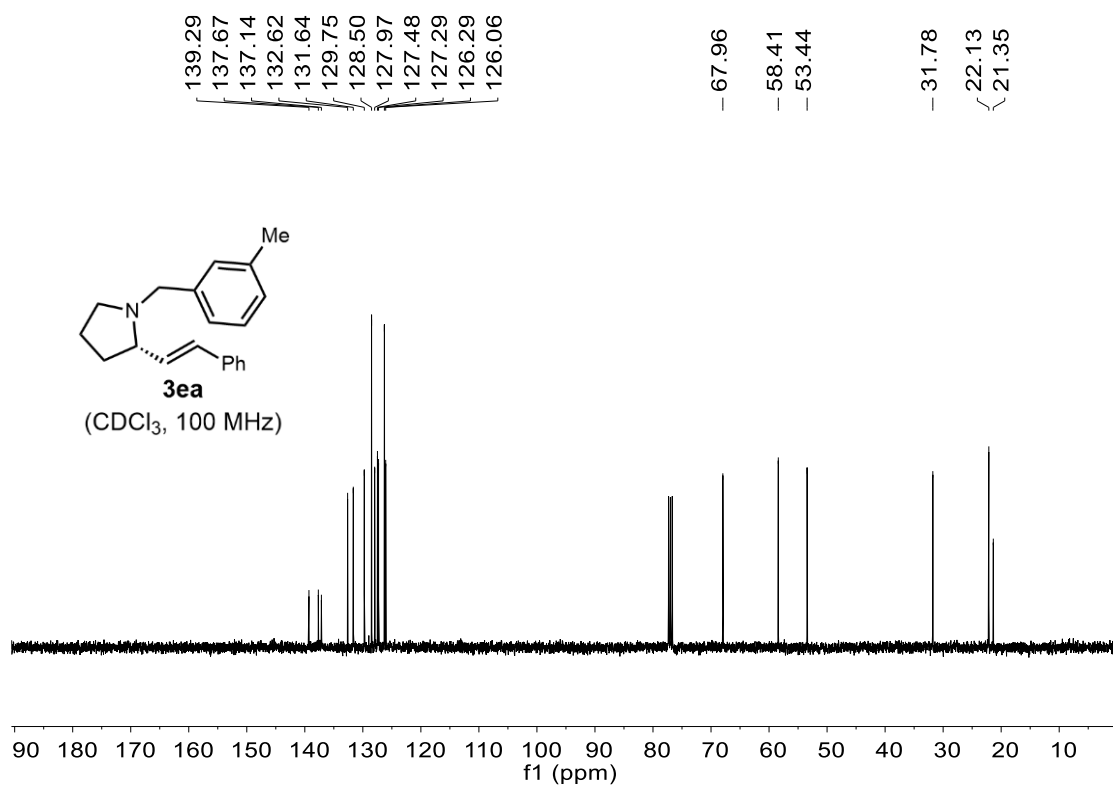
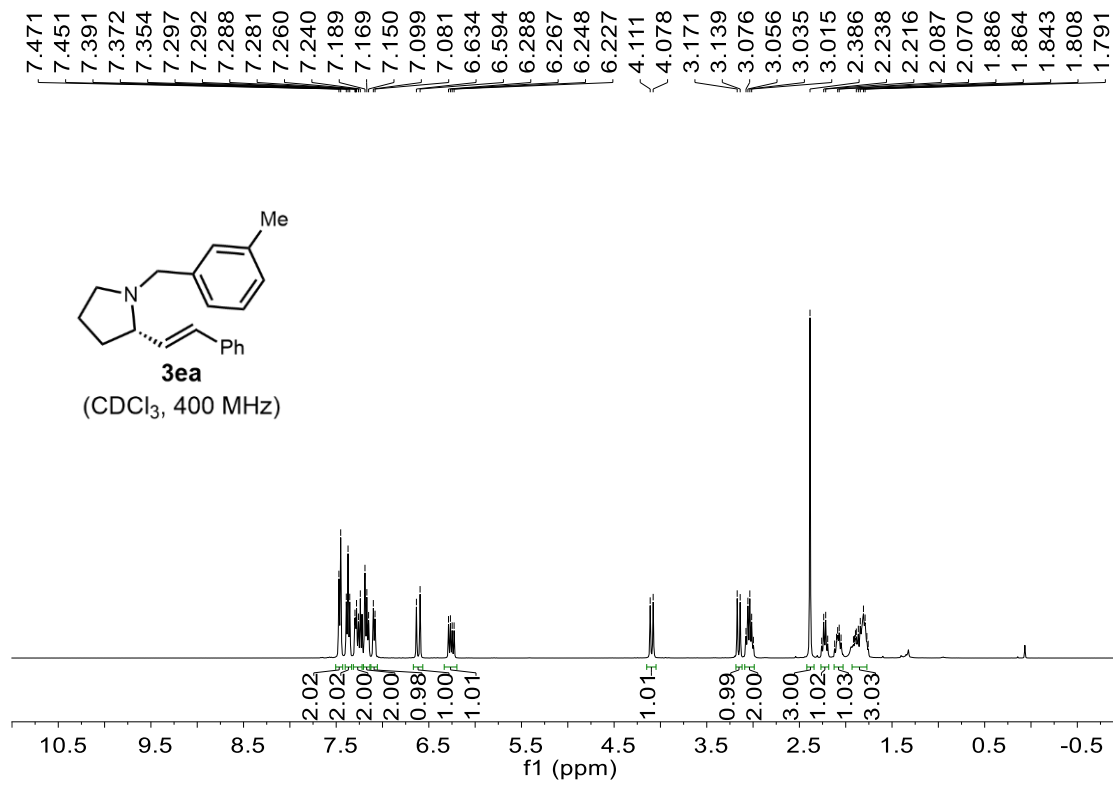


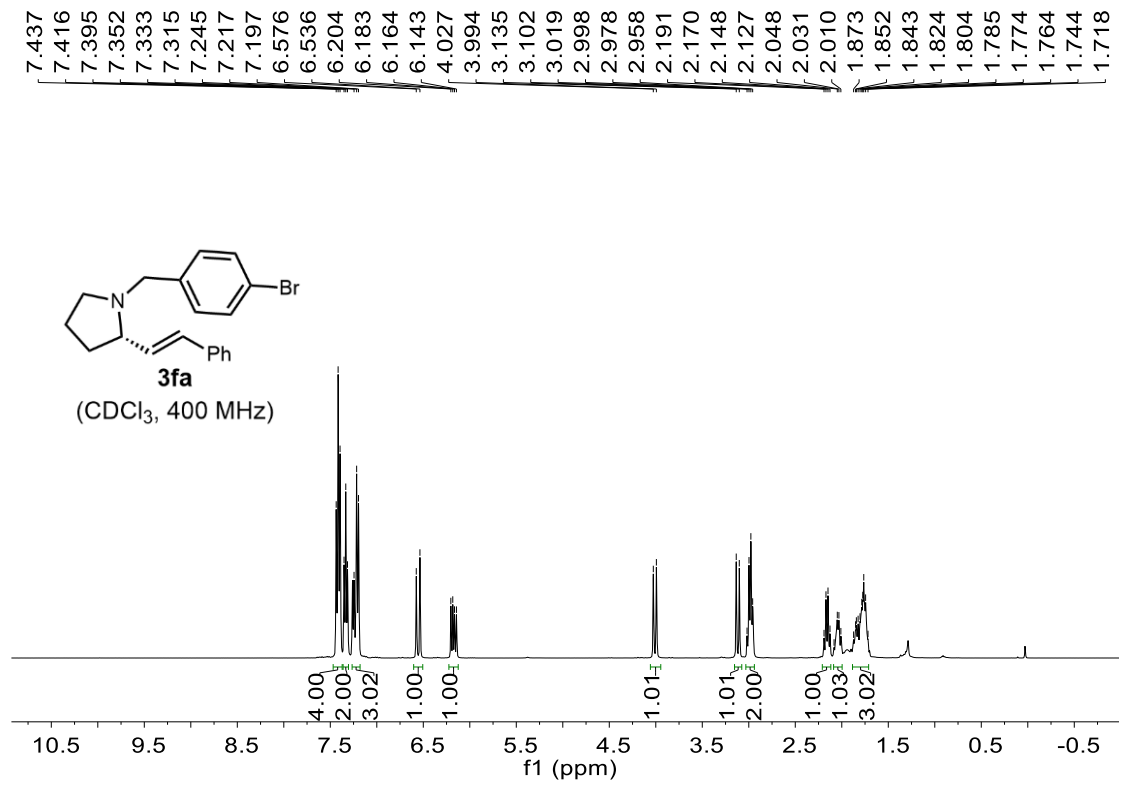




3da
(CDCl₃, 377 MHz)

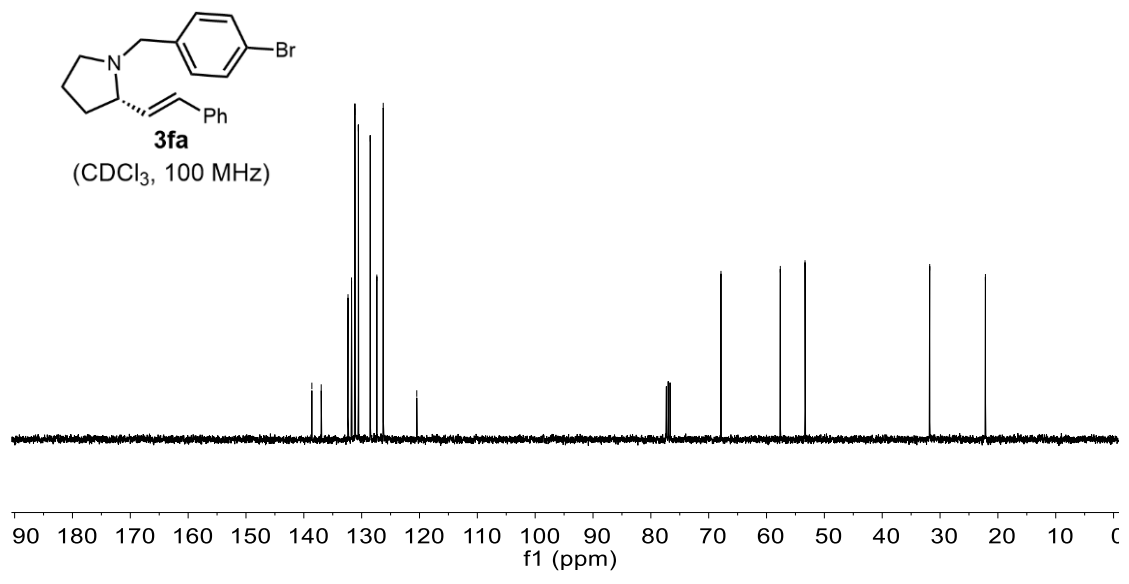


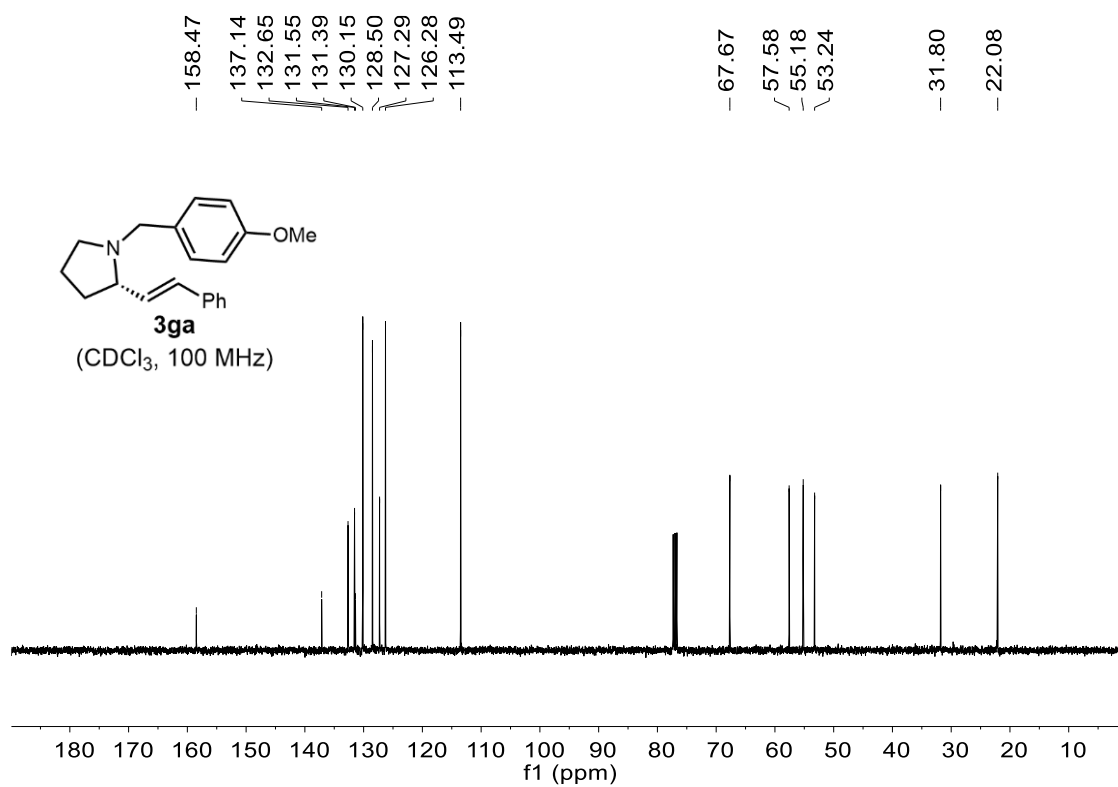
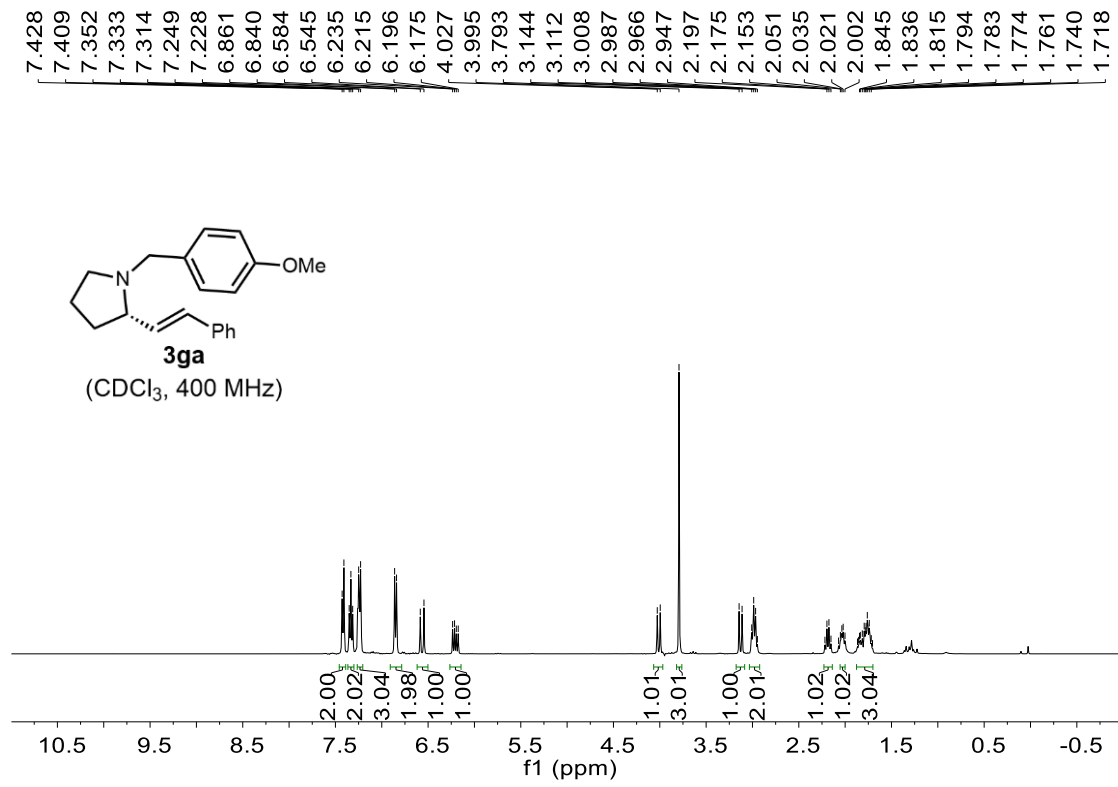


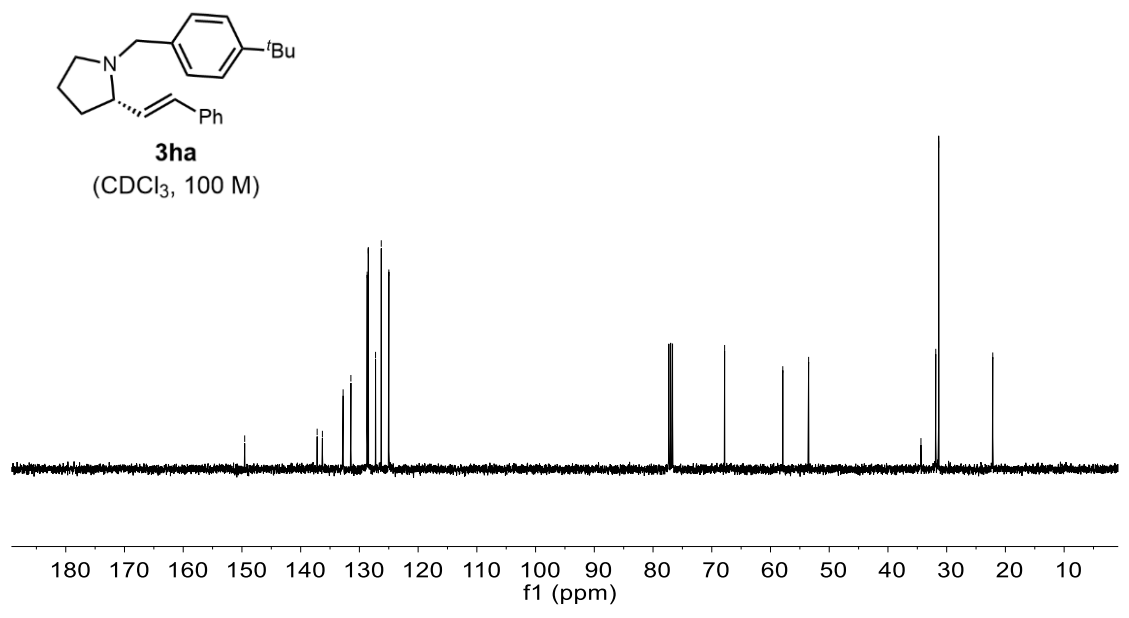
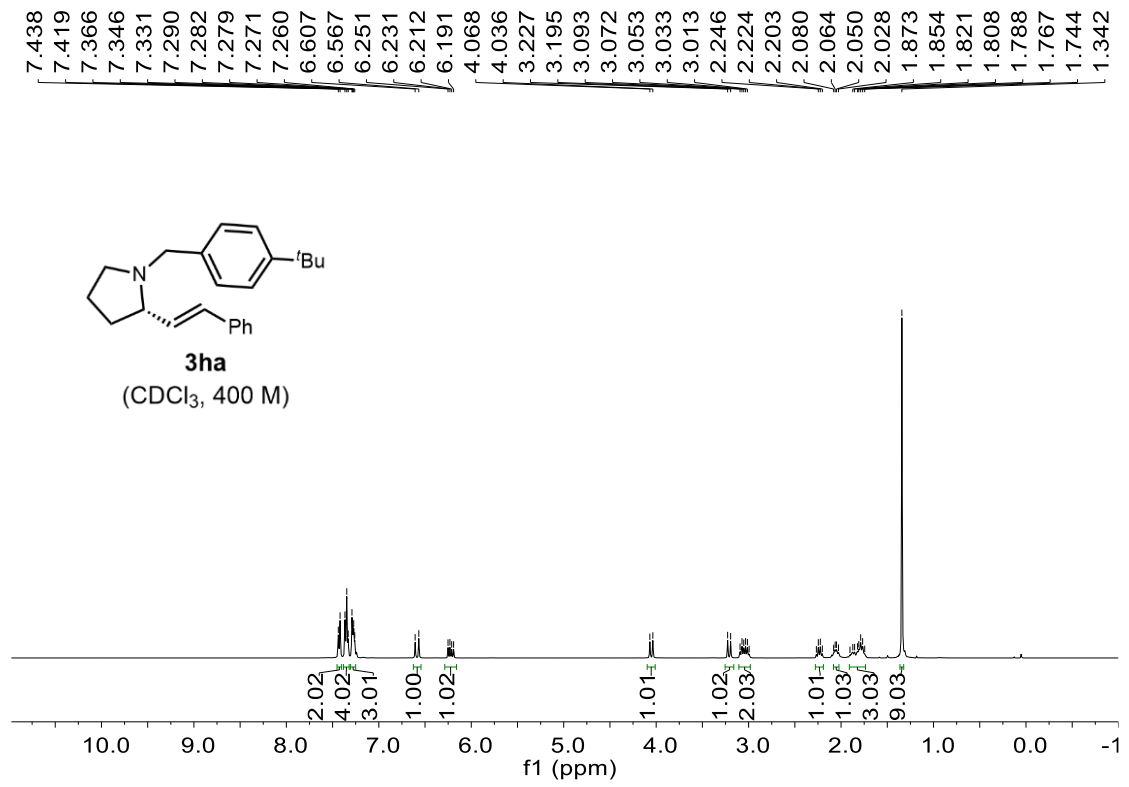


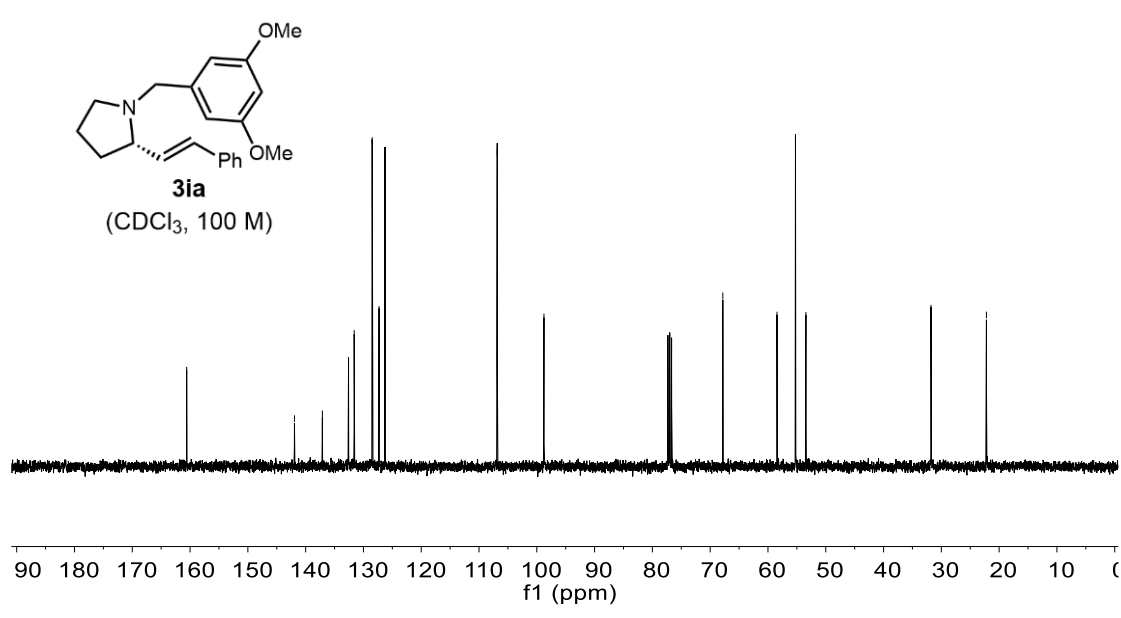
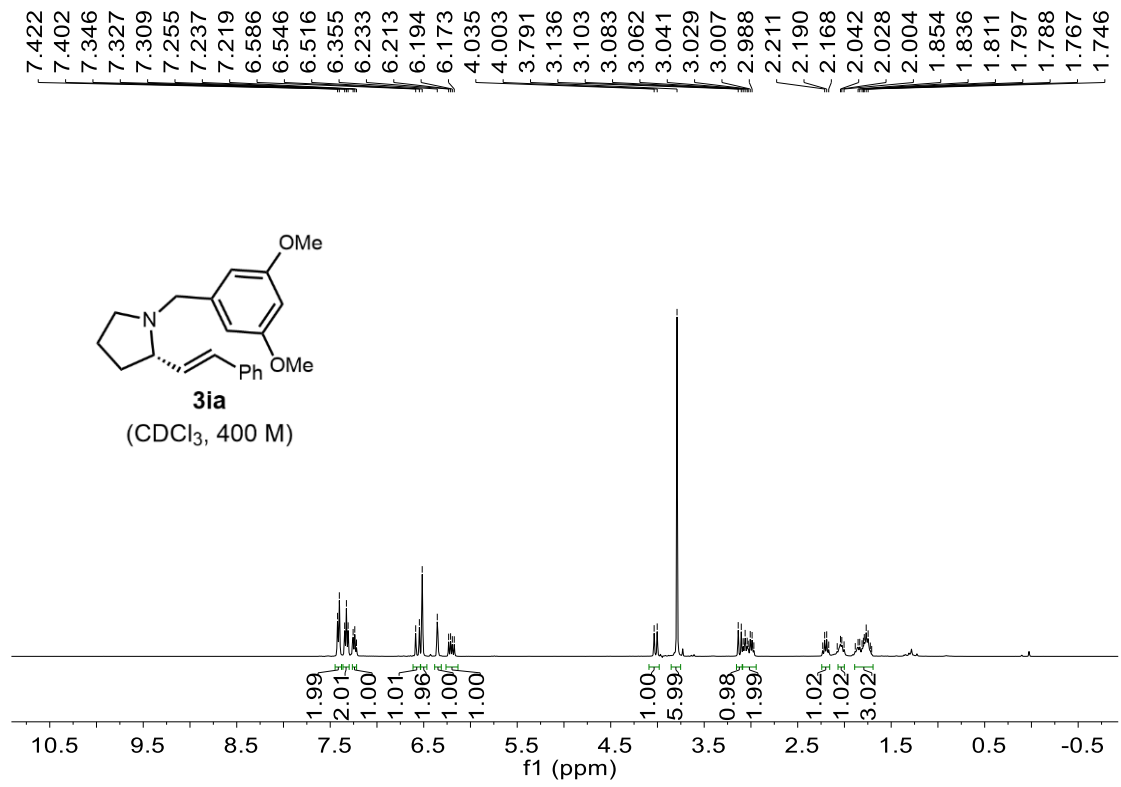
138.61
136.99
132.36
131.75
131.17
130.57
128.52
127.38
126.27
120.47

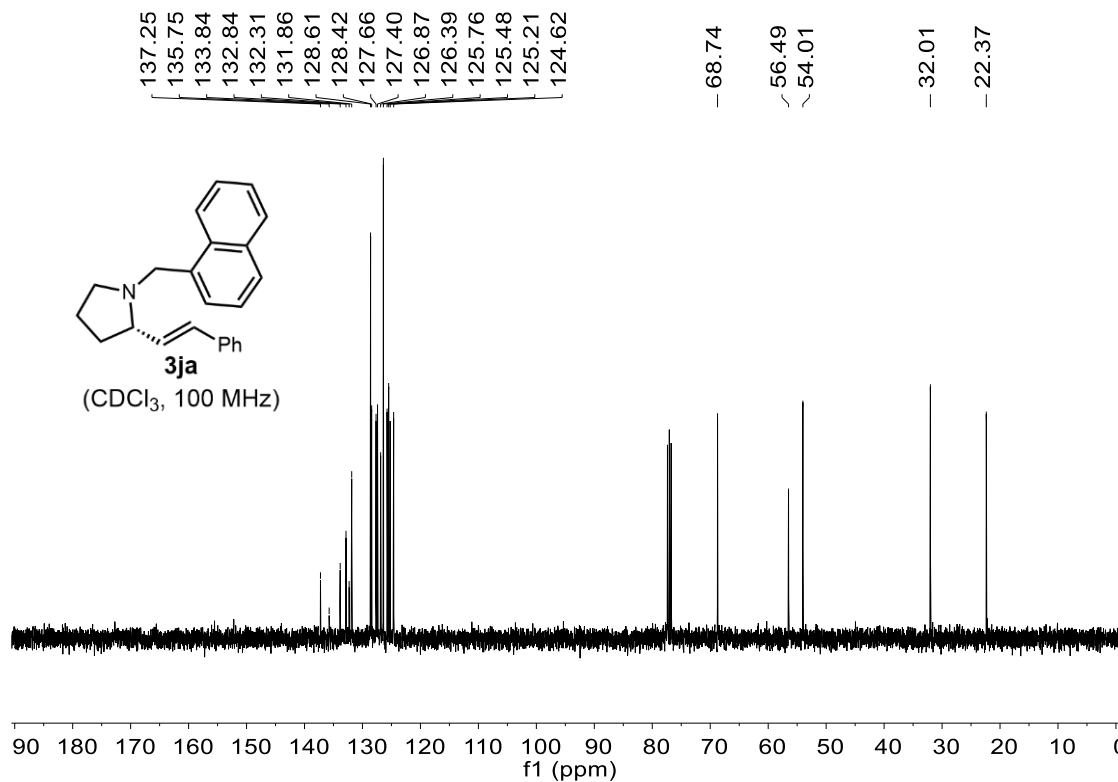
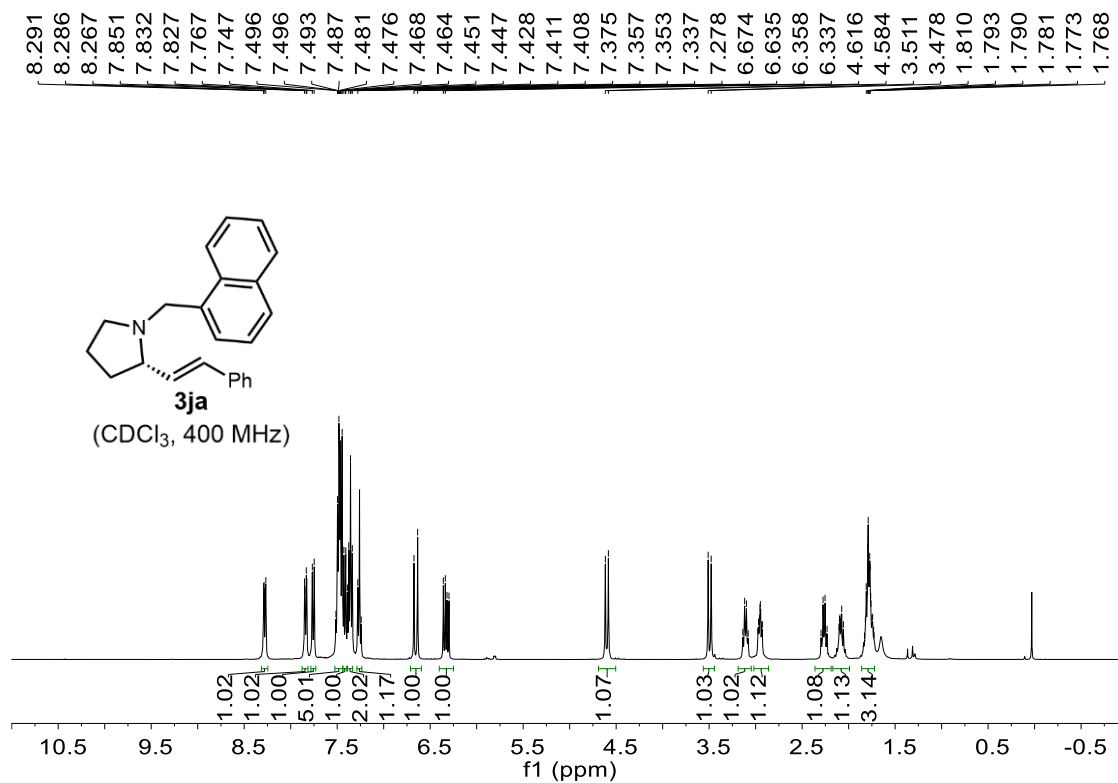
-67.88
-57.62
-53.34
-31.79
-22.15

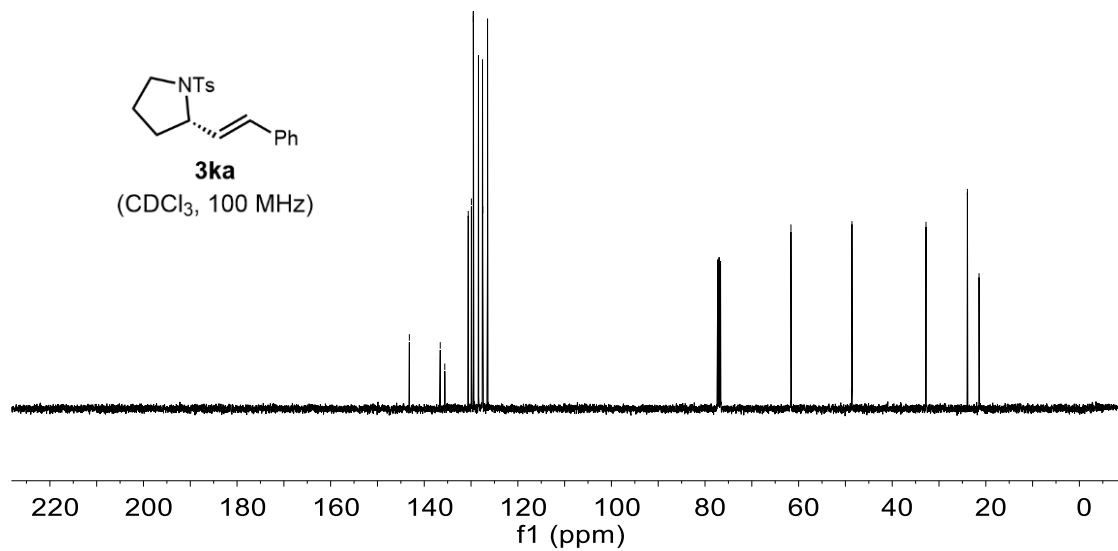
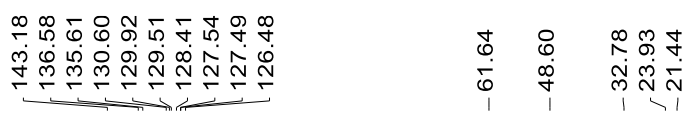
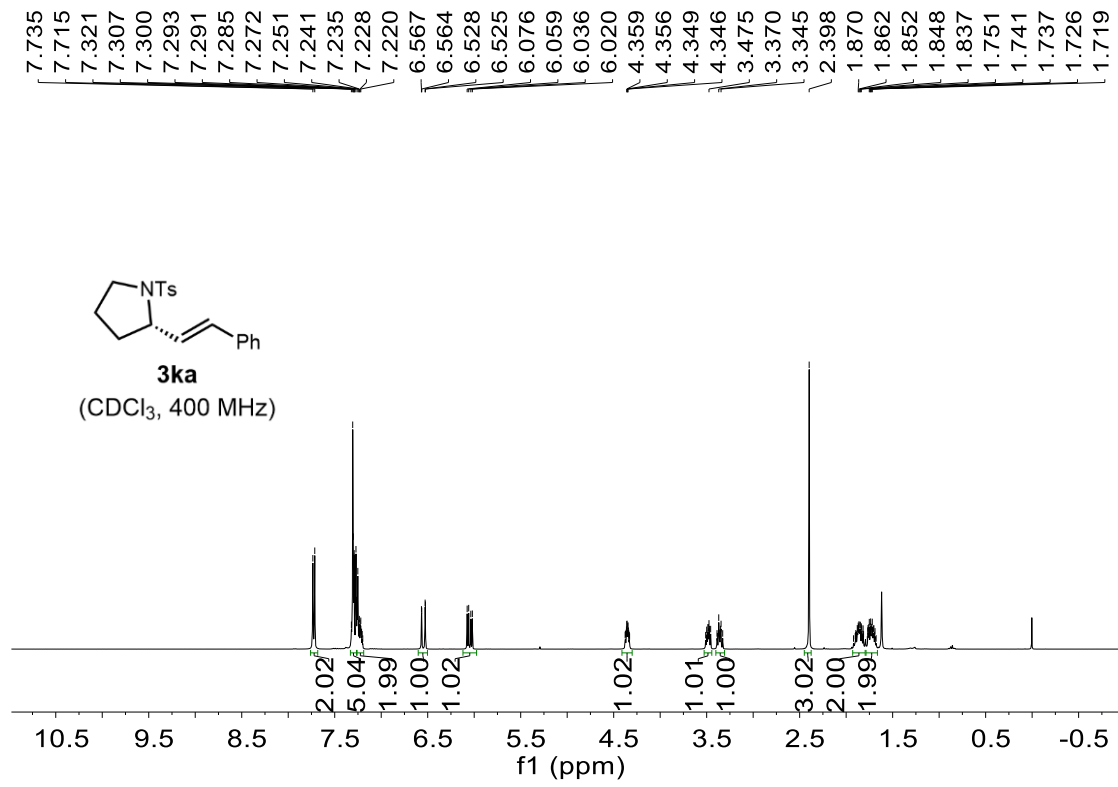


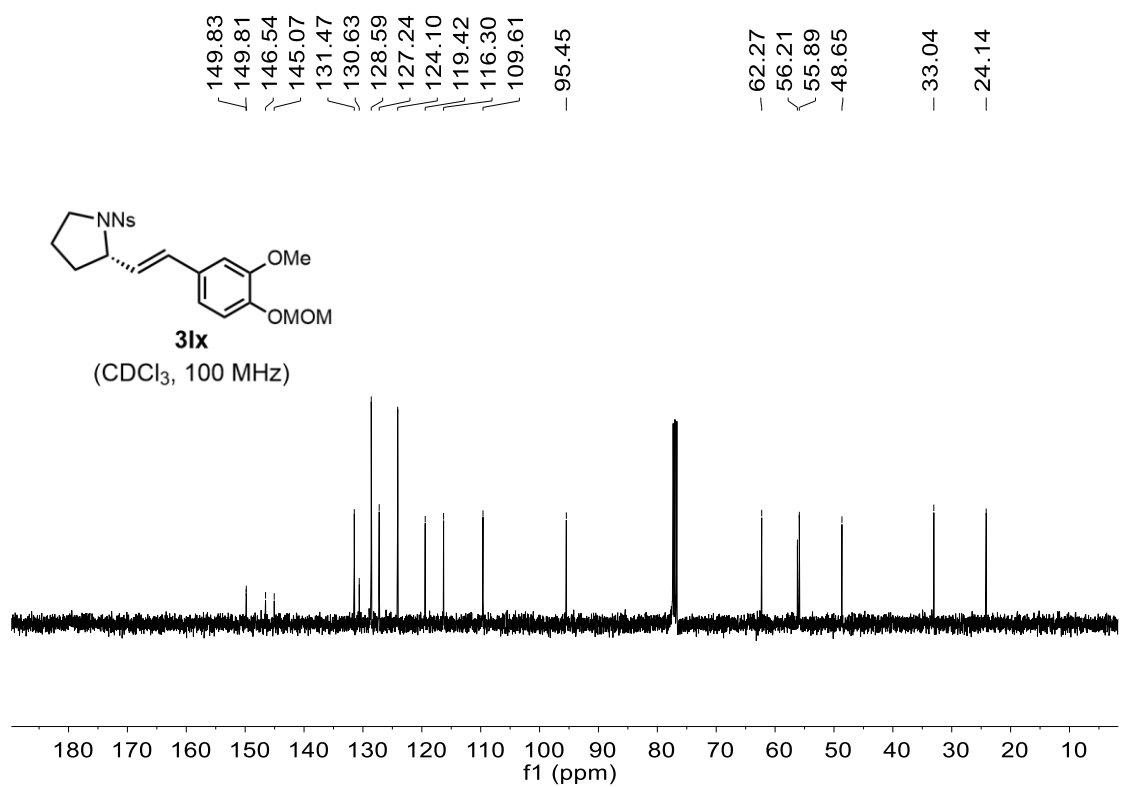
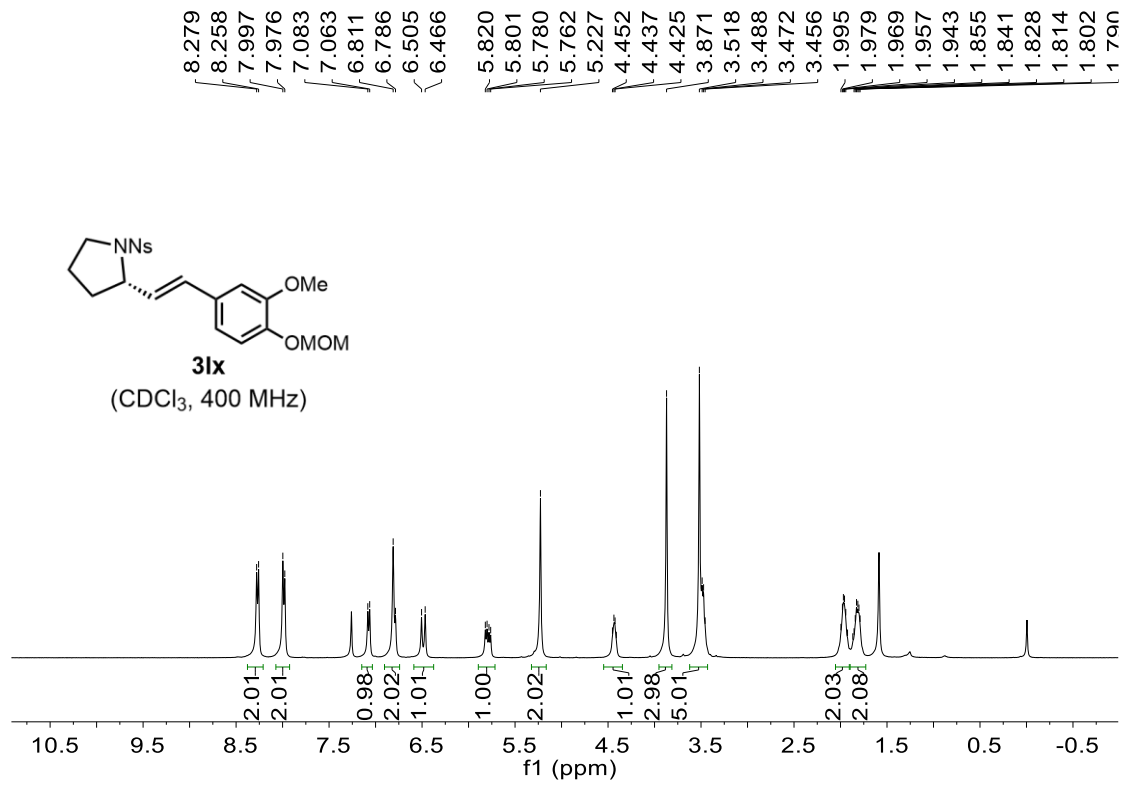


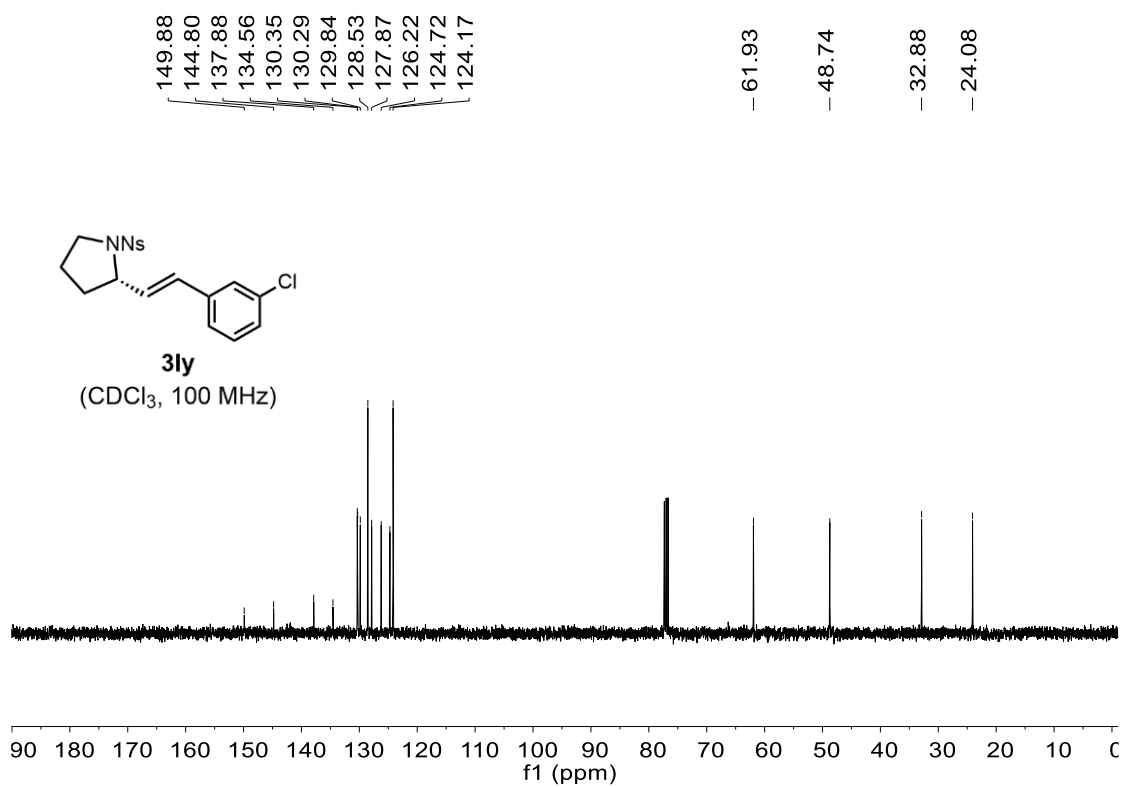
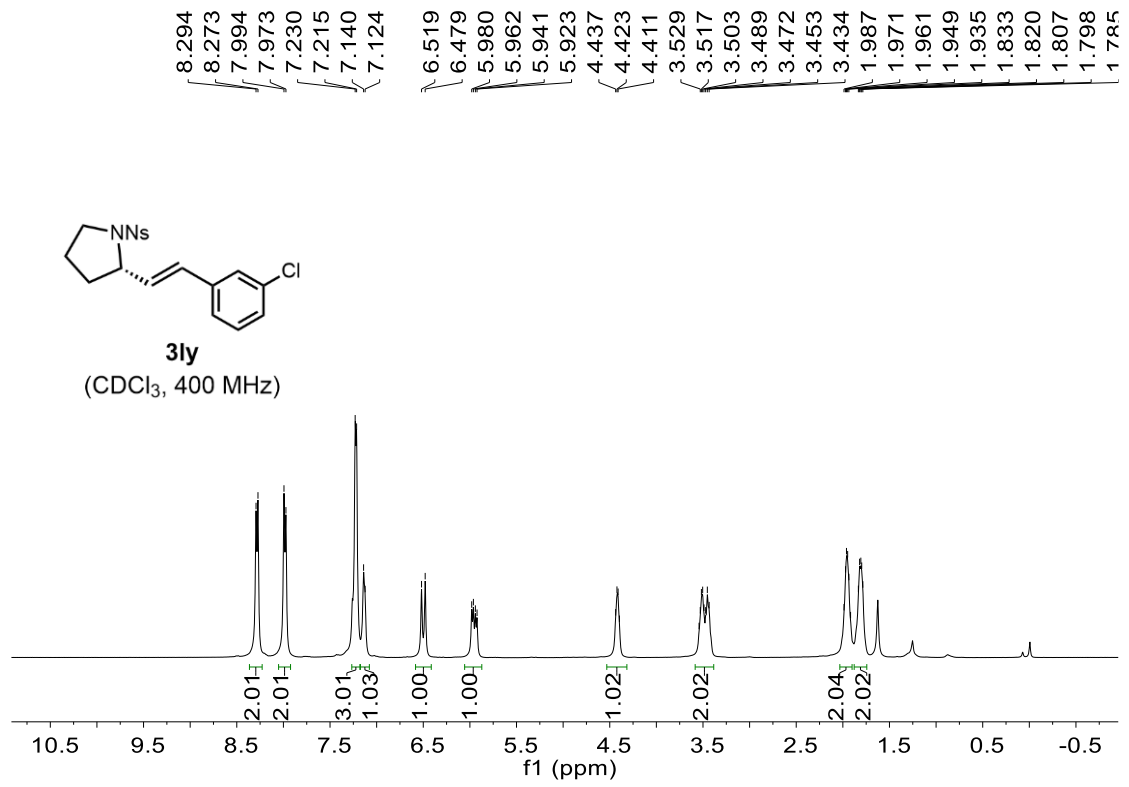


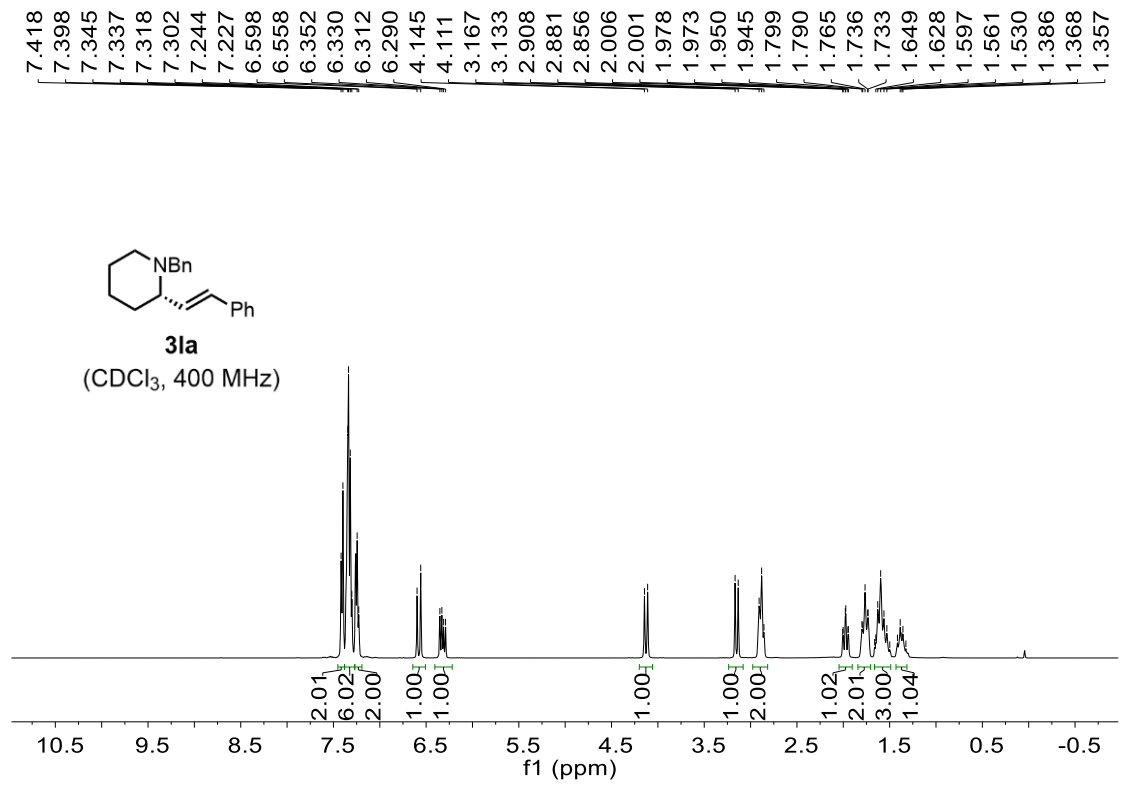








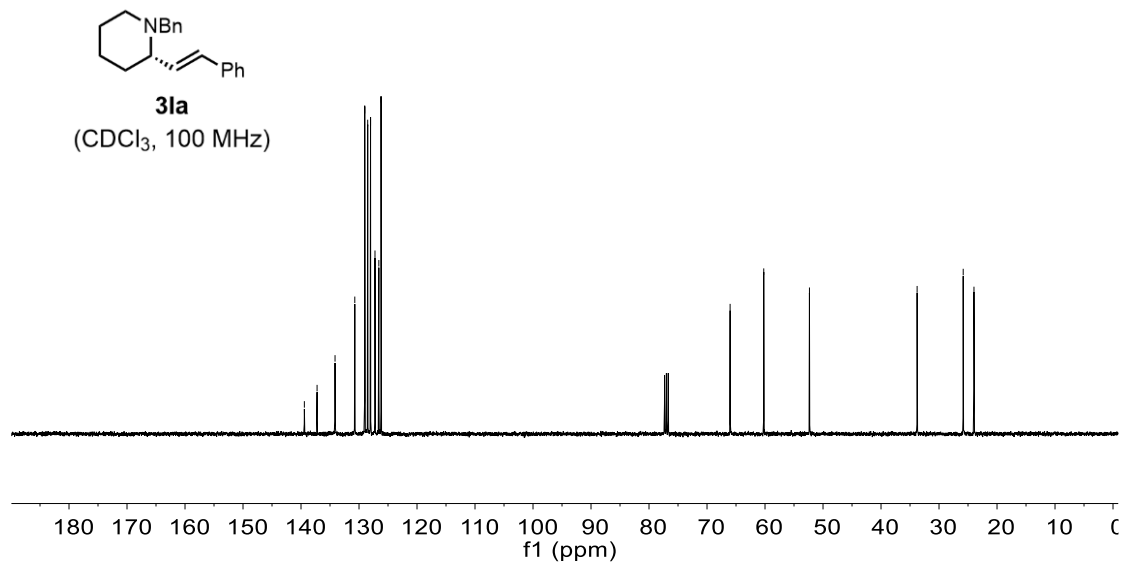


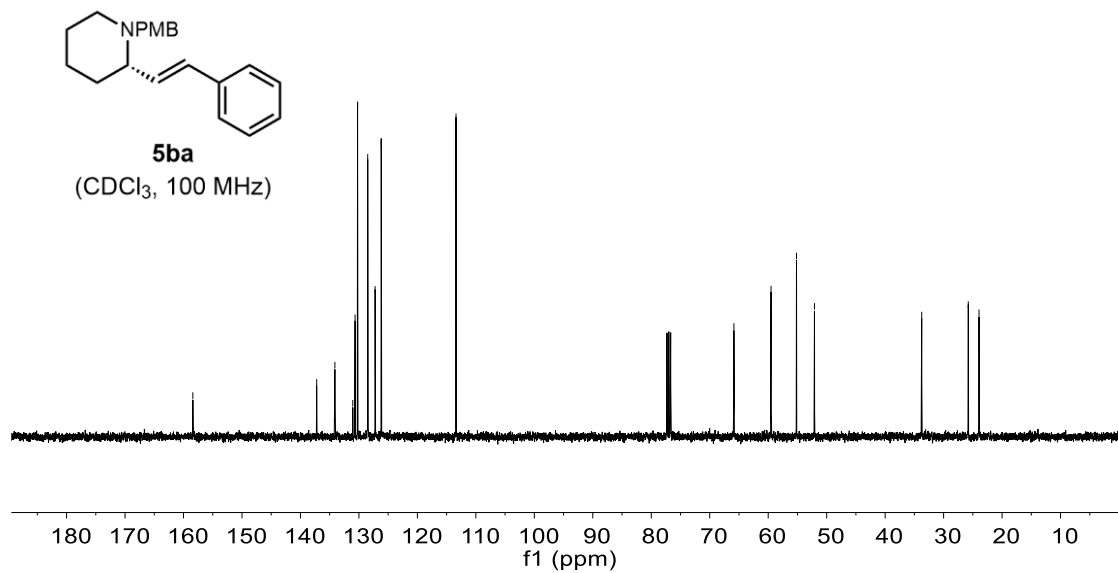
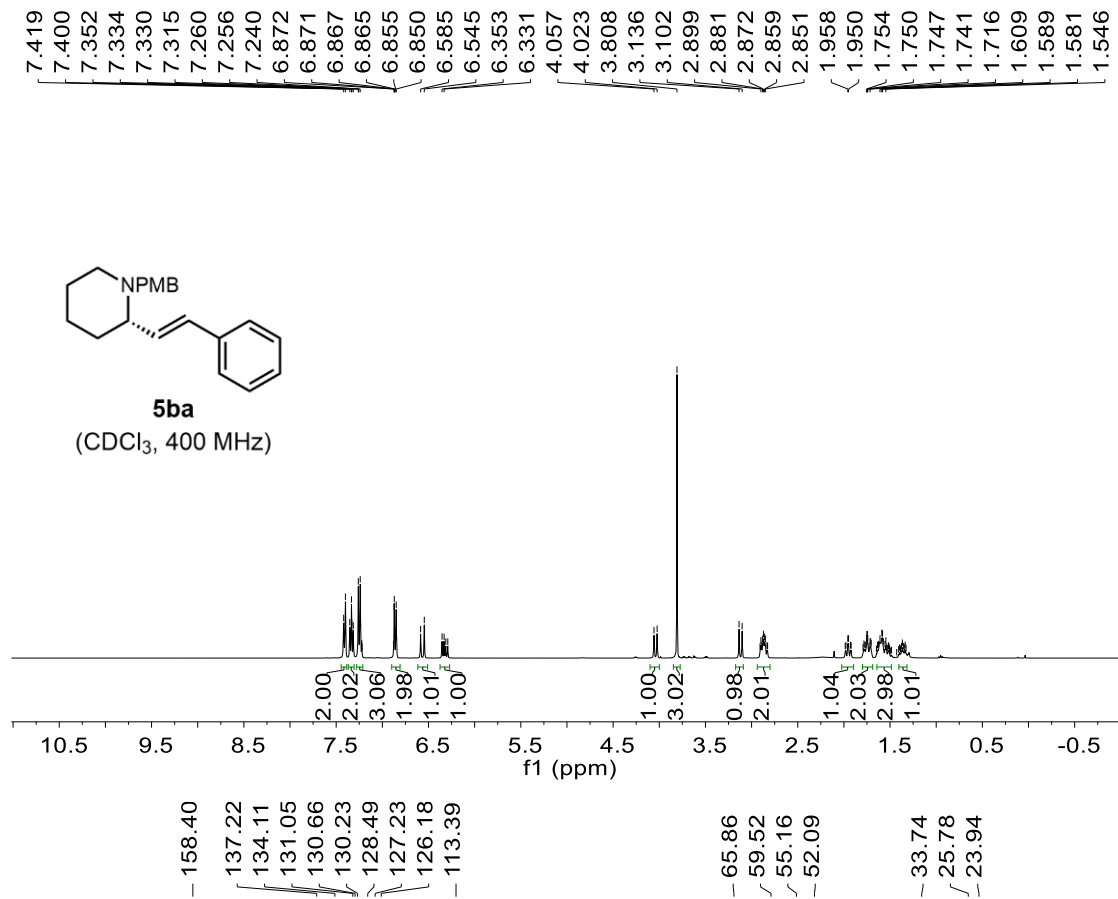


139.42
137.23
134.13
130.73
129.01
128.50
128.01
127.25
126.58
126.20

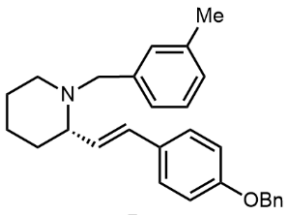
66.02
60.22
52.34

33.78
25.83
23.97

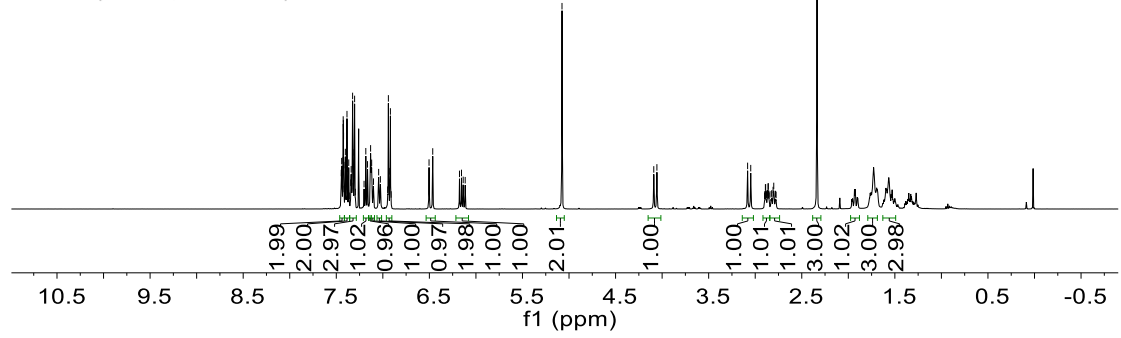




7.447
7.442
7.429
7.426
7.424
7.422
7.406
7.403
7.390
7.387
7.385
7.381
7.370
7.366
7.340
7.325
7.321
7.308
7.303
7.183
7.164
7.131
7.120
7.045
7.026
6.940
6.935
6.924
6.919
6.504
6.464
6.177
6.155
6.137
5.075
4.090
4.056
3.082
3.048
2.336



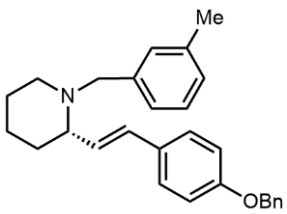
5cz
(CDCl₃, 400 MHz)



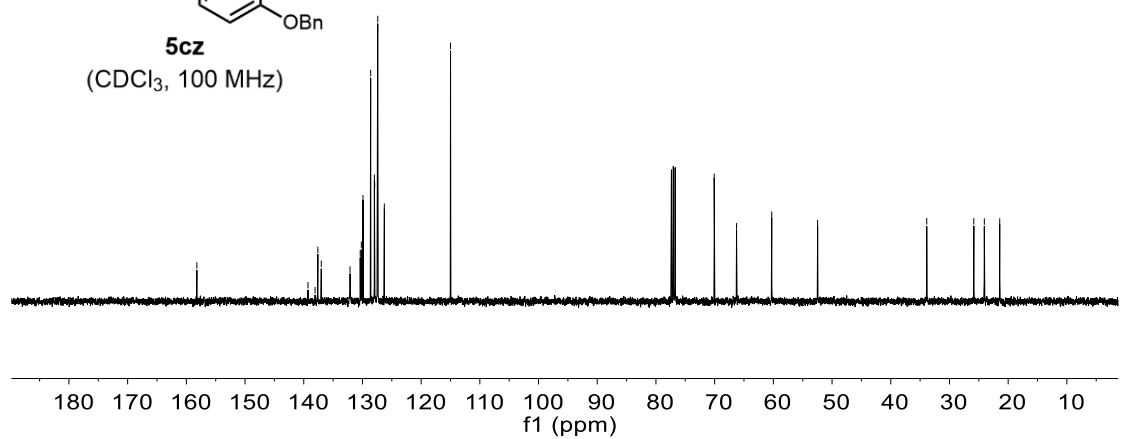
158.21
139.28
138.07
137.59
137.01
132.12
130.38
130.19
129.91
128.60
127.97
127.92
127.44
127.39
126.27
- 115.00

70.07
66.27
60.28
52.46

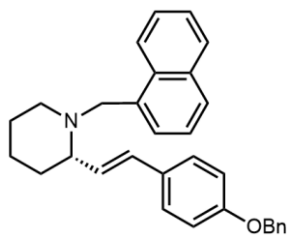
33.87
25.85
24.06
21.43



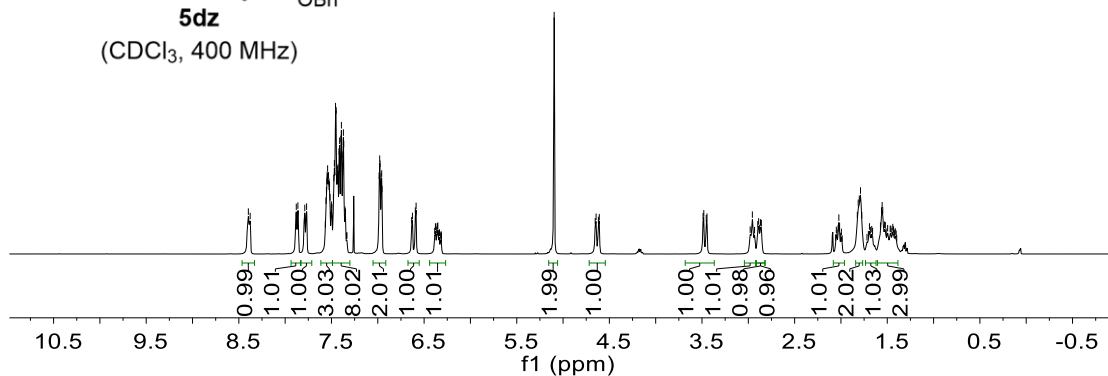
5cz
(CDCl₃, 100 MHz)



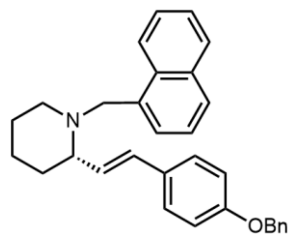
7.880
7.863
7.768
7.559
7.554
7.551
7.547
7.542
7.532
7.527
7.521
7.516
7.499
7.479
7.474
7.469
7.456
7.449
7.437
7.429
7.418
7.412
7.399
7.393
7.389
7.377
7.371
7.367
6.985
6.980
6.976
6.964
6.958
6.954
6.586
5.096
1.814
1.802
1.789
1.555



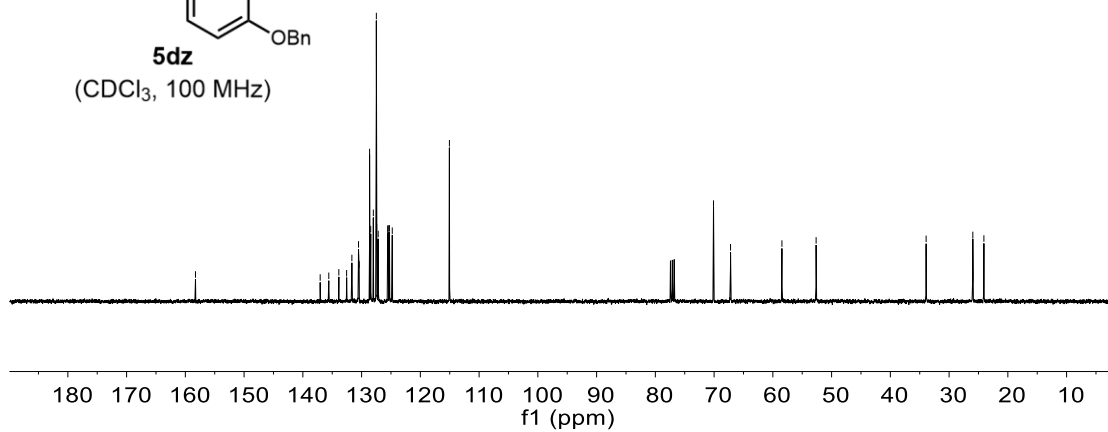
5dz
(CDCl₃, 400 MHz)



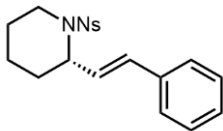
158.28
137.05
135.58
133.88
132.55
131.66
130.52
130.41
128.64
128.45
128.00
127.49
127.43
127.18
125.57
125.46
125.26
124.78
115.05
70.10
67.20
58.46
52.64
33.91
25.96
24.08



5dz
(CDCl₃, 100 MHz)

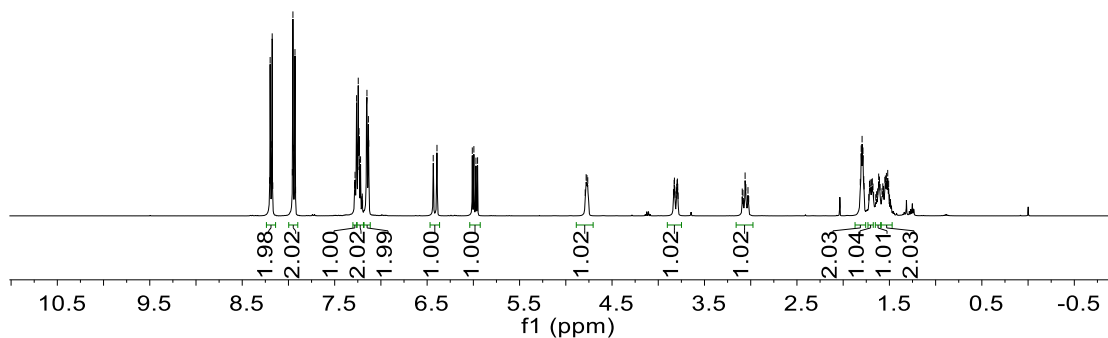


8.198
8.193
8.181
8.176
7.958
7.952
7.946
7.934
7.929
7.280
7.263
7.249
7.245
7.237
7.233
7.220
7.156
7.151
7.145
7.140
7.135
7.132
6.434
6.393
6.012
5.994
5.972
5.954
4.780
4.771
3.061
1.805
1.795
1.786
1.777
1.616
1.607
1.543
1.532
1.518



5ea

(CDCl₃, 400 MHz)



149.54
146.09
135.80
132.92
128.54
128.49
128.02
126.11
124.87
123.95

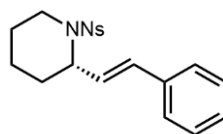
55.68

42.22

30.68

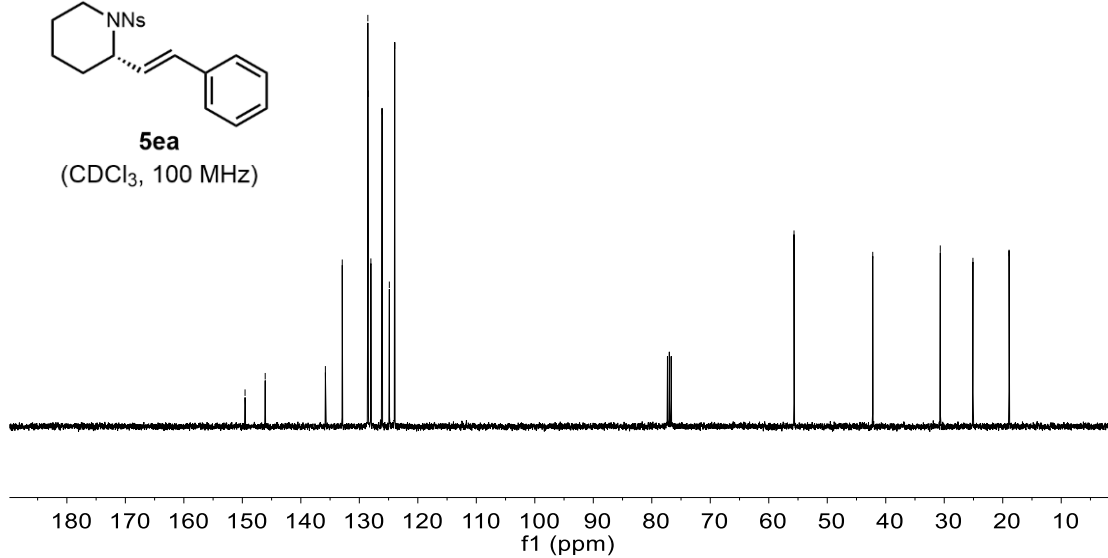
25.09

18.92

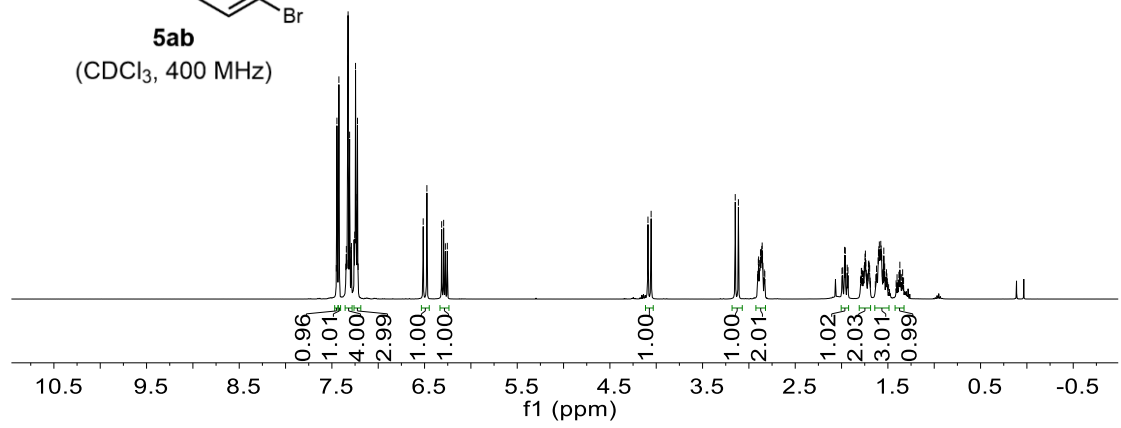
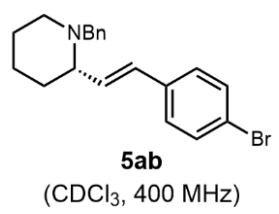


5ea

(CDCl₃, 100 MHz)

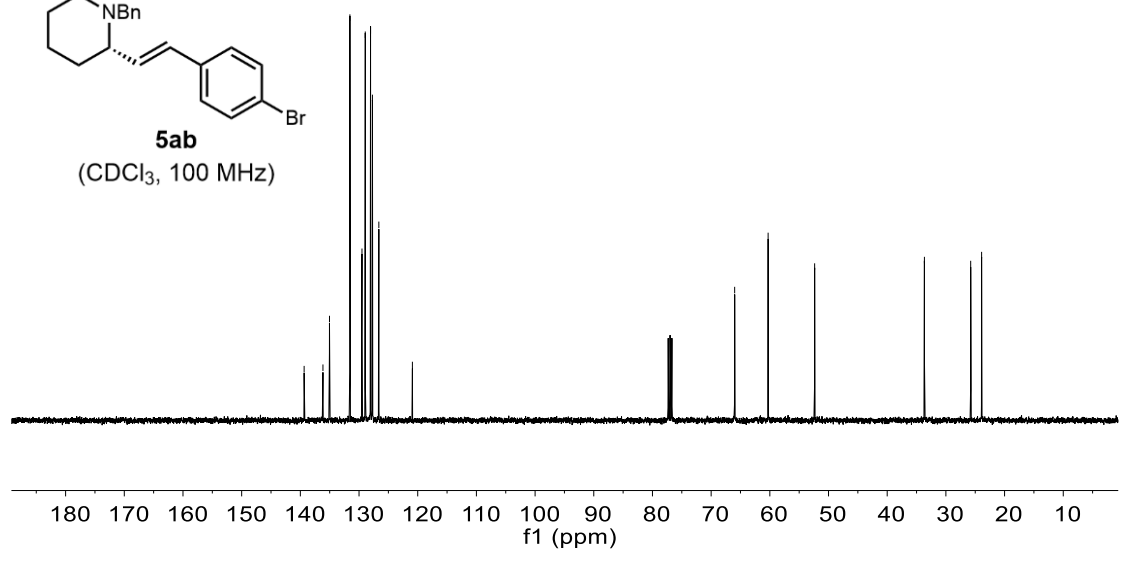
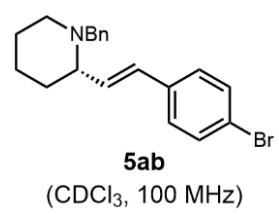


7.446
7.441
7.441
7.429
7.425
7.344
7.329
7.325
7.311
7.309
7.304
7.291
7.289
7.253
7.245
7.240
7.236
7.229
7.224
6.515
6.475
6.316
6.294
6.276
6.254
4.089
4.055
3.147
3.113
2.866
2.861
2.857
1.968
1.959
1.597
1.592
1.582
1.577
1.573
1.544

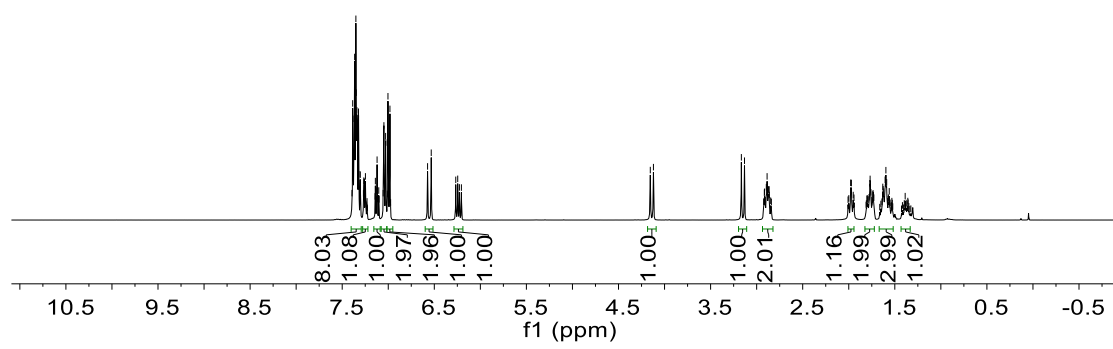
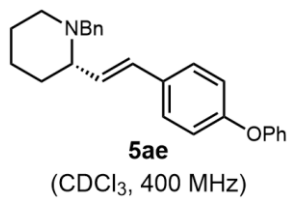


139.36
136.15
135.03
131.56
129.50
128.94
128.04
127.72
126.62
120.91

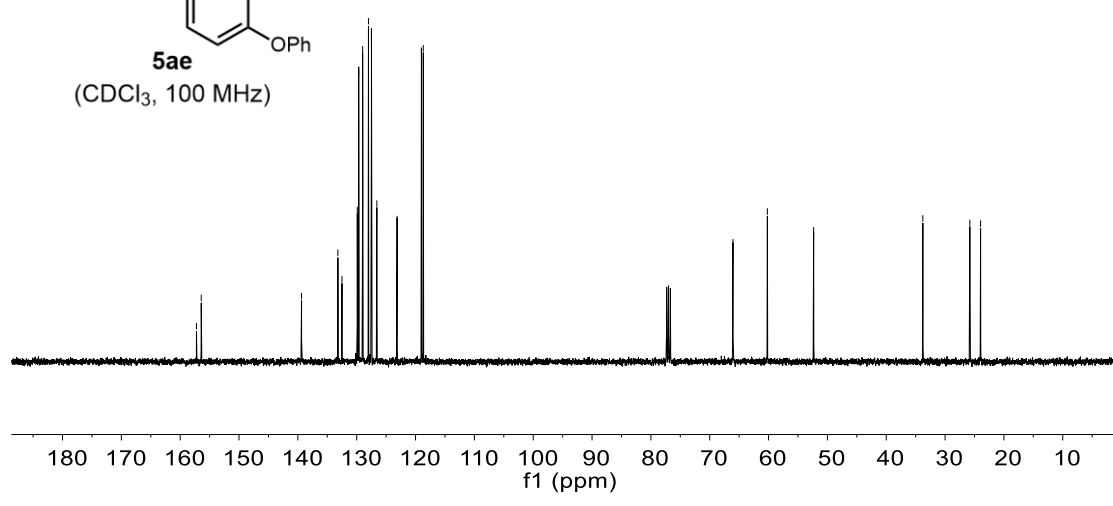
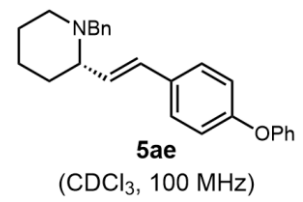
65.99
60.29
52.36
33.66
25.77
23.91

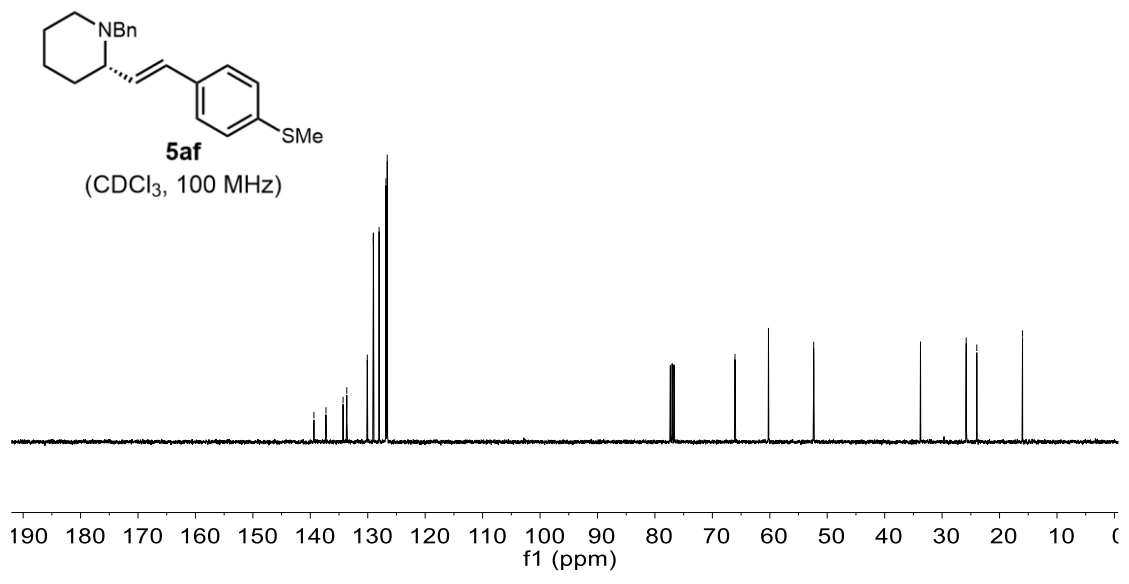
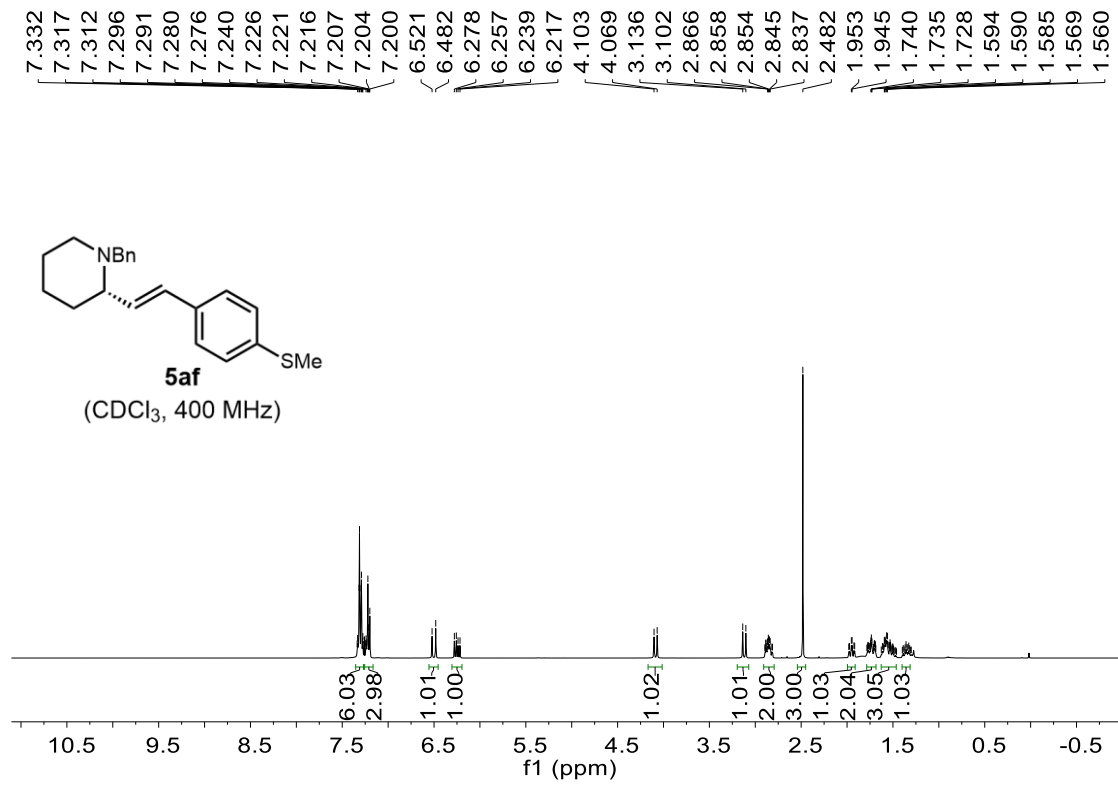


7.386
7.381
7.372
7.365
7.355
7.351
7.347
7.340
7.333
7.323
7.318
7.303
7.265
7.248
7.140
7.121
7.051
7.047
7.032
7.029
7.026
7.003
6.998
6.987
6.982
6.573
6.533
6.267
6.246
4.155
4.121
3.166
3.132
2.887
1.980
1.971
1.768
1.605
1.597
1.588

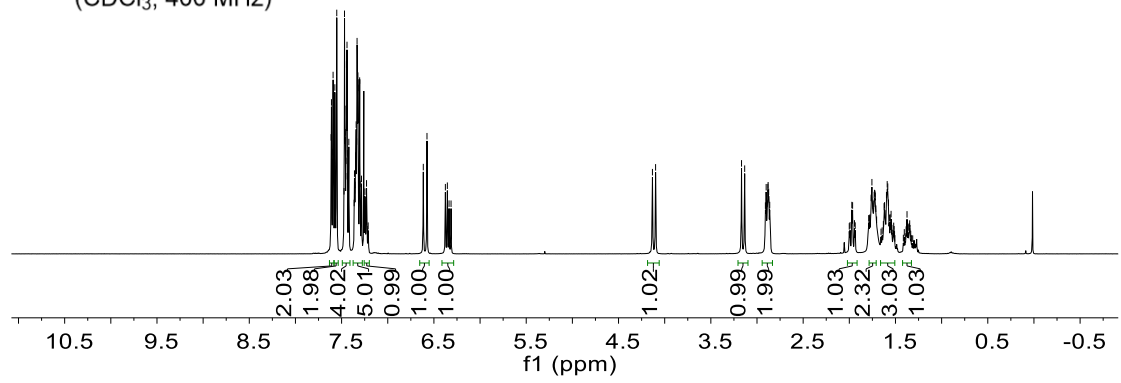
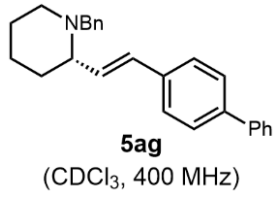


157.23
156.42
139.38
133.20
132.50
129.90
129.66
128.99
128.00
127.49
126.58
123.13
119.00
118.68
66.05
60.20
52.34
33.78
25.79
23.96

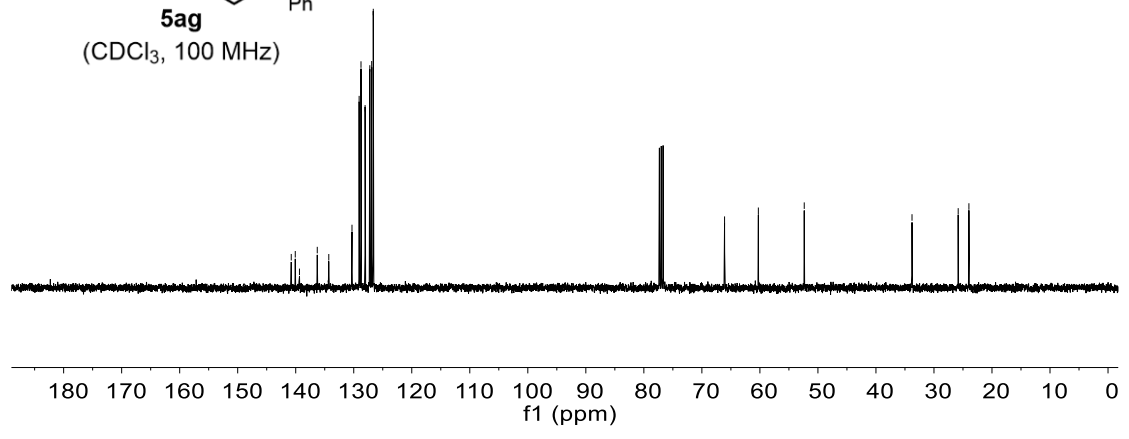
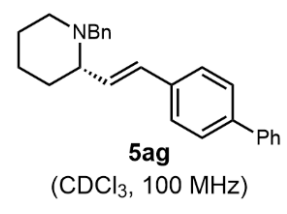


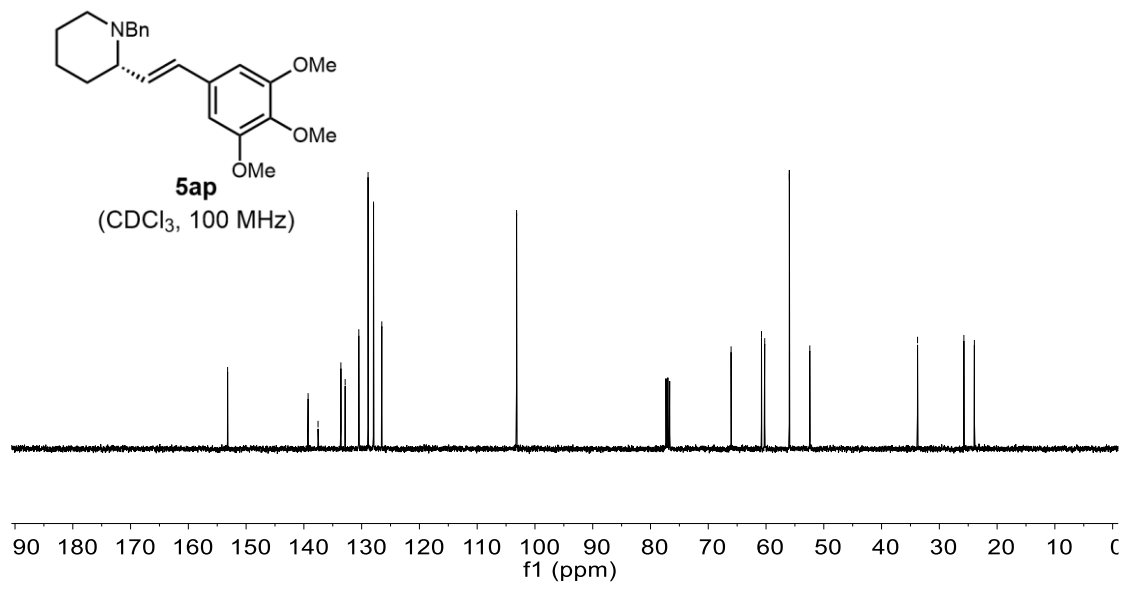
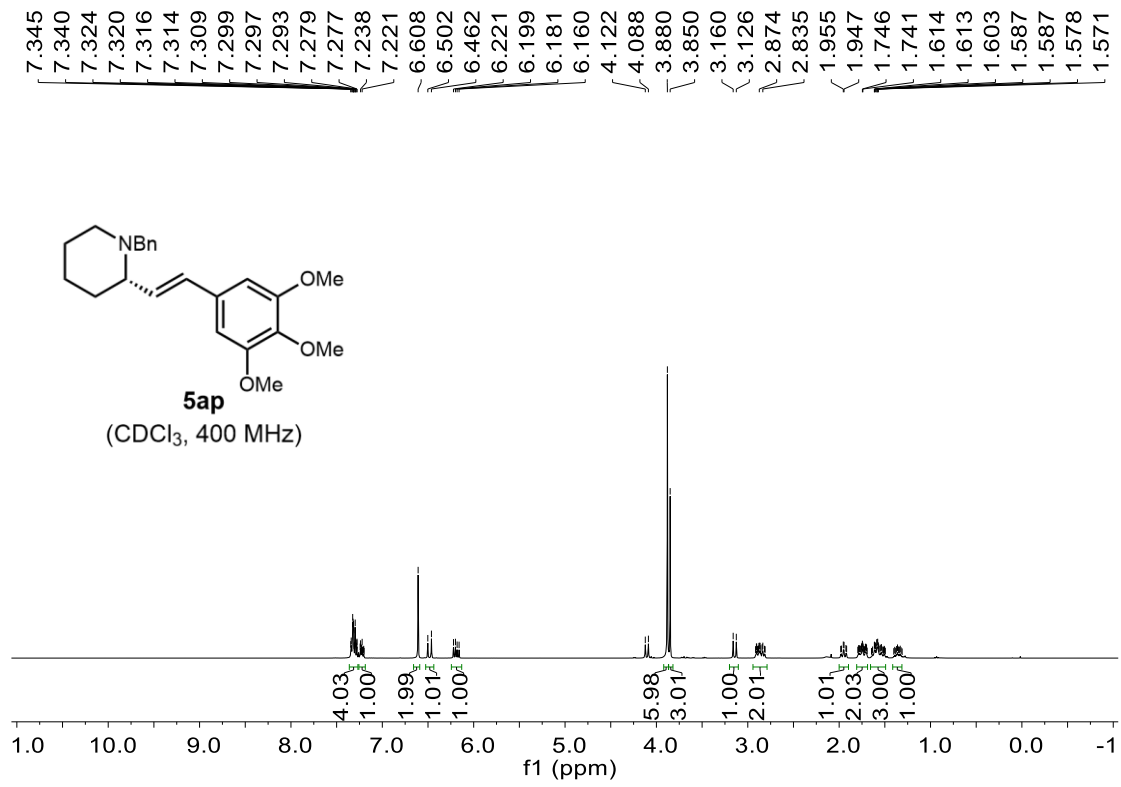


7.614
7.610
7.596
7.592
7.590
7.573
7.569
7.557
7.552
7.469
7.463
7.460
7.455
7.452
7.448
7.441
7.437
7.422
7.361
7.353
7.348
7.342
7.337
7.332
7.328
7.323
7.321
7.304
7.299
7.285
7.230
6.615
6.575
4.133
4.099
3.168
3.134
2.880
1.755
1.590

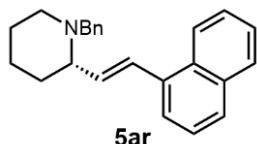


140.77
140.08
139.36
136.29
134.30
130.30
129.07
128.75
128.04
127.23
126.91
126.63
66.09
60.27
52.36
33.78
25.83
23.98

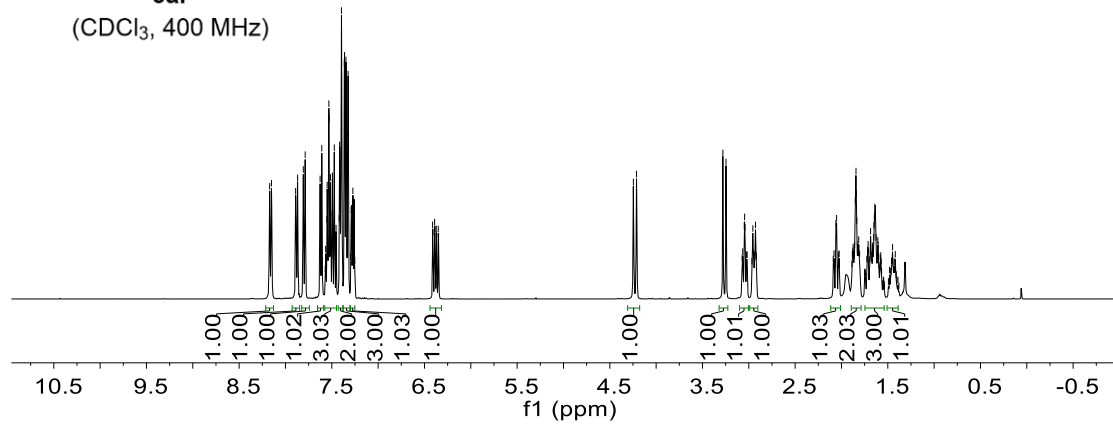




8.171
8.151
7.890
7.869
7.808
7.787
7.626
7.608
7.550
7.546
7.535
7.532
7.529
7.526
7.517
7.514
7.493
7.473
7.416
7.412
7.396
7.365
7.361
7.348
7.344
7.341
7.328
7.324
7.287
7.273
4.246
4.212
3.280
3.246
1.851
1.848
1.843
1.839
1.641
1.634



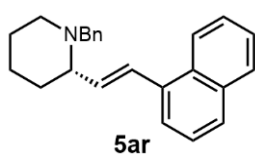
(CDCl₃, 400 MHz)



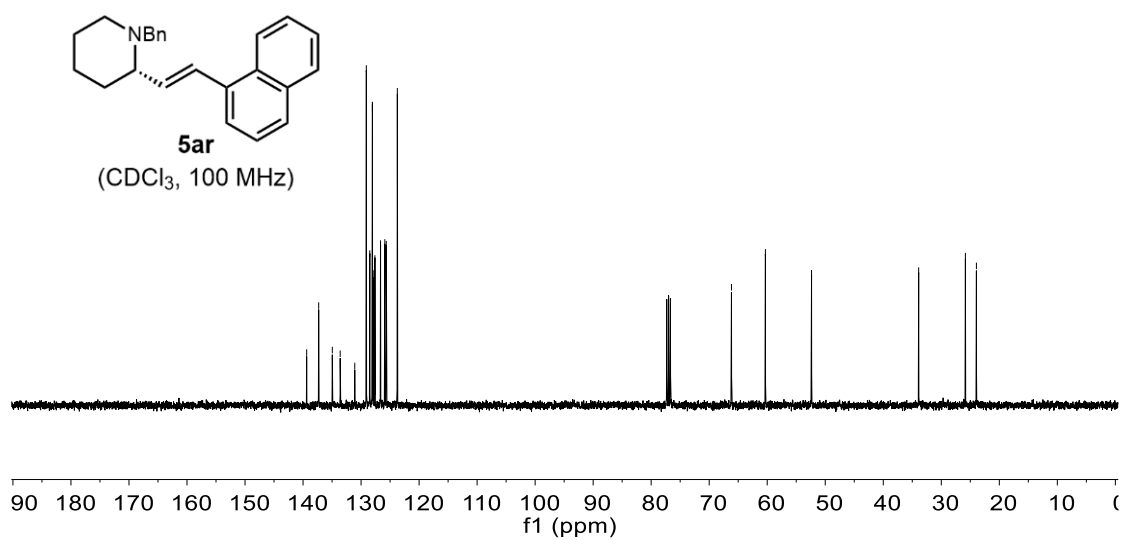
139.37
137.30
134.96
133.60
131.08
129.09
128.49
128.05
127.91
127.61
126.64
125.90
125.65
125.61
123.75

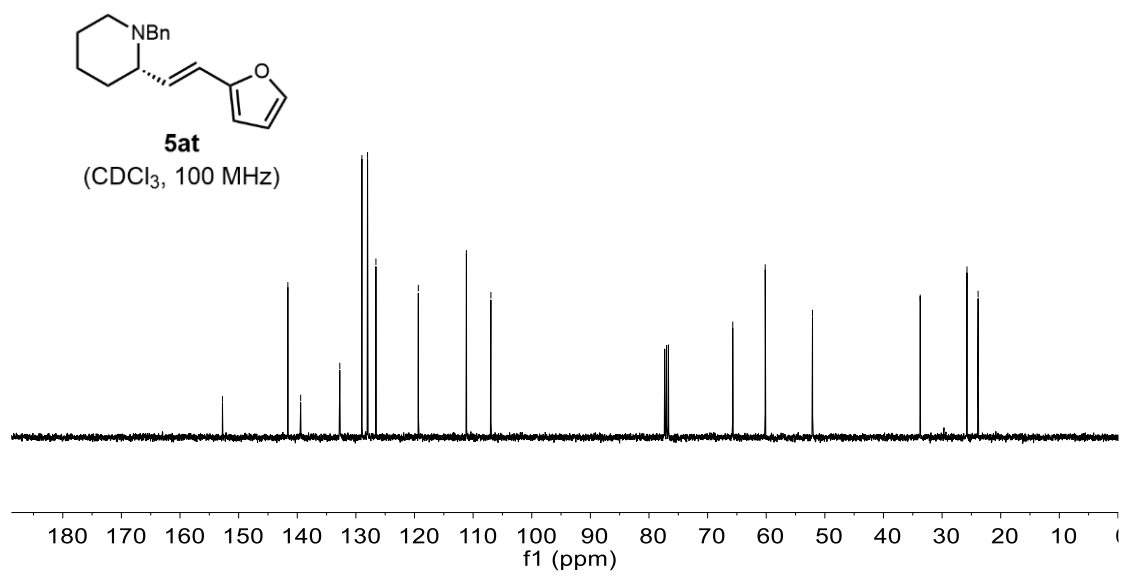
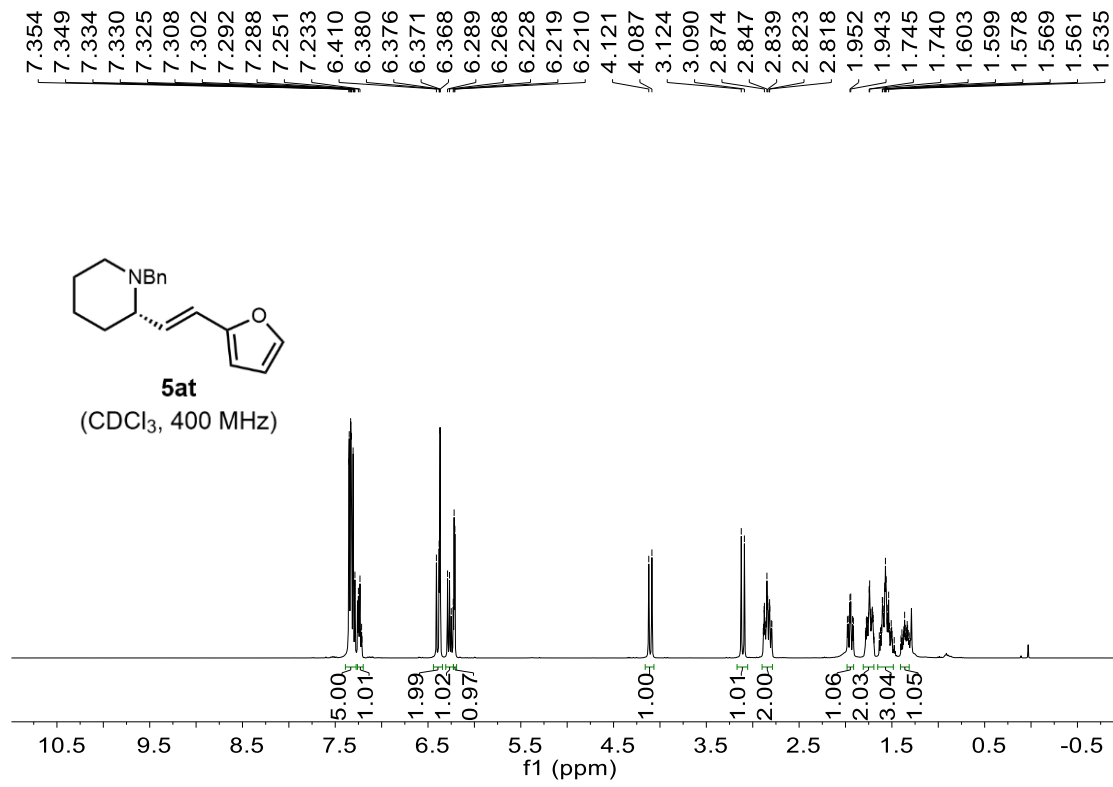
66.16
60.31
52.36

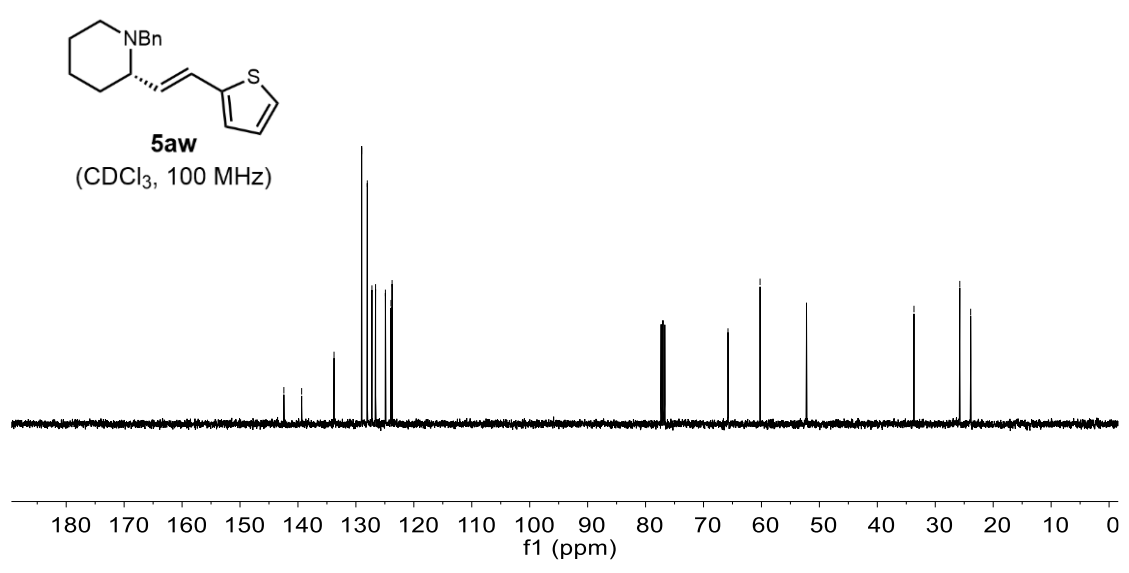
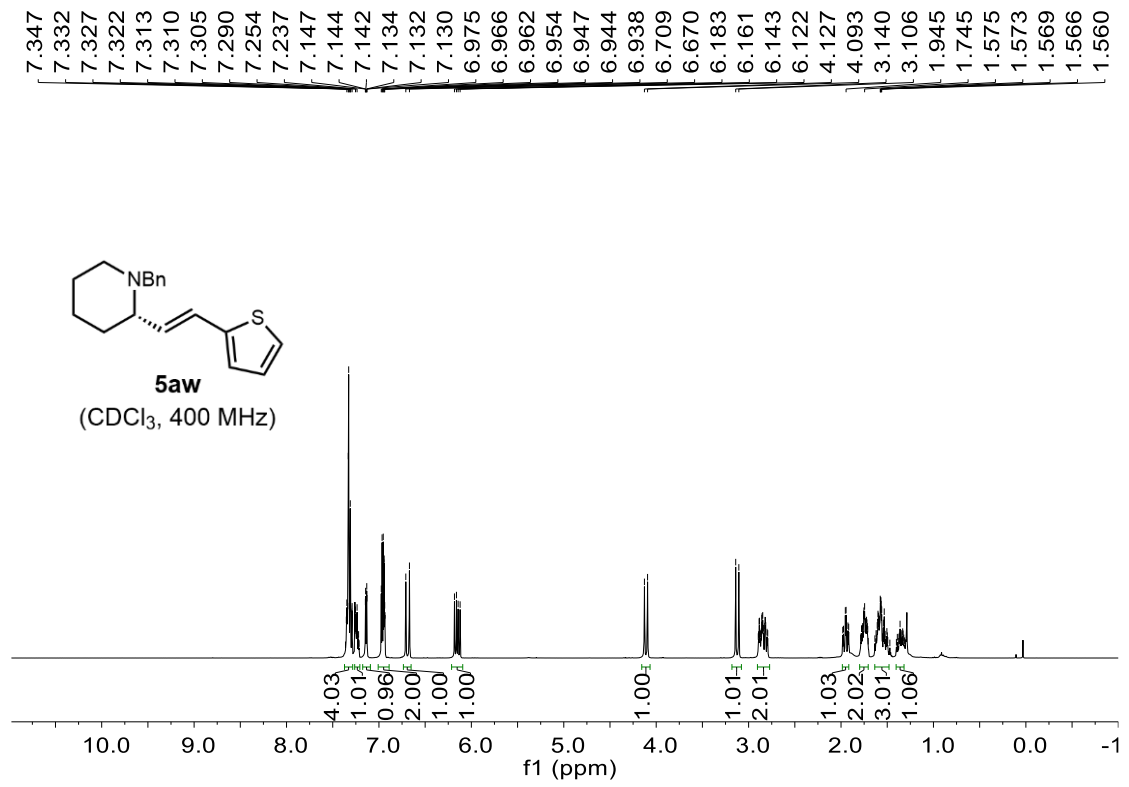
33.90
25.85
23.95



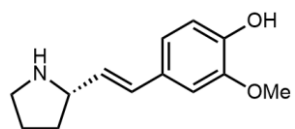
(CDCl₃, 100 MHz)



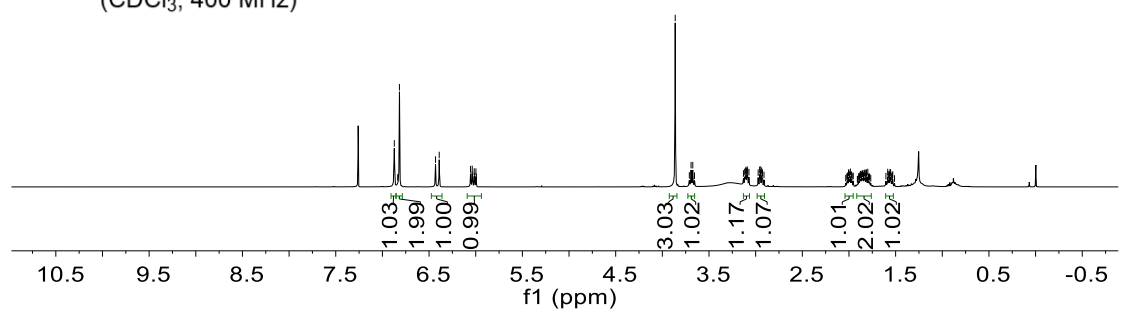




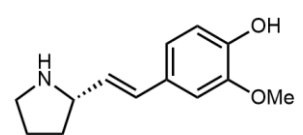
6.873
6.818
6.431
6.391
6.056
6.037
6.016
5.998
3.862
3.692
3.674
3.131
3.117
3.111
3.105
3.098
3.091
3.086
3.072
2.973
2.957
2.952
2.947
2.936
2.931
2.927
2.005
2.002
1.985
1.856
1.851
1.837
1.831
1.819
1.817
1.812
1.798
1.585
1.561
1.554



(-)-norruspoline
(CDCl₃, 400 MHz)



146.99
145.74
130.16
129.37
129.28
120.03
114.78
108.25
61.03
55.75
46.17
32.31
25.19



(-)-norruspoline
(CDCl₃, 100 MHz)

