

**Dual Palladium/Photoredox-Catalyzed Enantioselective and Regioselective
Decarboxylative Hydroaminoalkylation of Allenes**

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General methods and materials

Reactions were monitored by TLC analysis which was performed on aluminum plates pre-coated with silica gel (MERCK, 60 F-254), and visualized by UV fluorescence ($\lambda_{\text{max}} = 254 \text{ nm}$) and/or by staining with 1% w/v KMnO_4 in 0.5 M aqueous K_2CO_3 . Chromatographic purification was accomplished by flash chromatography on MACHEREY-NAGEL silica gel 60® (230-400 mesh).

NMR (Nuclear Magnetic Resonance) spectra were acquired on a Varian Mercury (300 MHz) or on a Bruker Avance 400 spectrometer or on a Bruker 500 DRX NMR spectrometer. Chemical shifts for ^1H NMR spectra are reported in ppm and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Chemical shifts for ^{13}C NMR spectra are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , 77.16 ppm) and with complete proton decoupling.

HRMS (High Resolution Mass Spectra) was measured on a THERMO SCIENTIFIC Advantage and a THERMO SCIENTIFIC Exactive instrument equipped with an APCI source in the positive-ion mode.

PerkinElmer LS55 Fluorescence Spectrometer was used for Stern-Volmer quenching experiment.

The optical rotation for chiral compounds was determined on a Perkin-Elmer *PE 241* apparatus as well as on a A. Krüss Optronic *P8000-T* apparatus and recalculated for a given temperature according to the following formula (α : measured value for optical rotation; c: mass concentration in g/100 mL; d: cuvette length in dm; T: temperature in $^{\circ}\text{C}$): $[\alpha]_D^T = \frac{\alpha \cdot 100}{c \cdot d}$

Melting points for solids were measured on a BÜCHI Dr. Tottoli melting point apparatus and are given uncorrected.

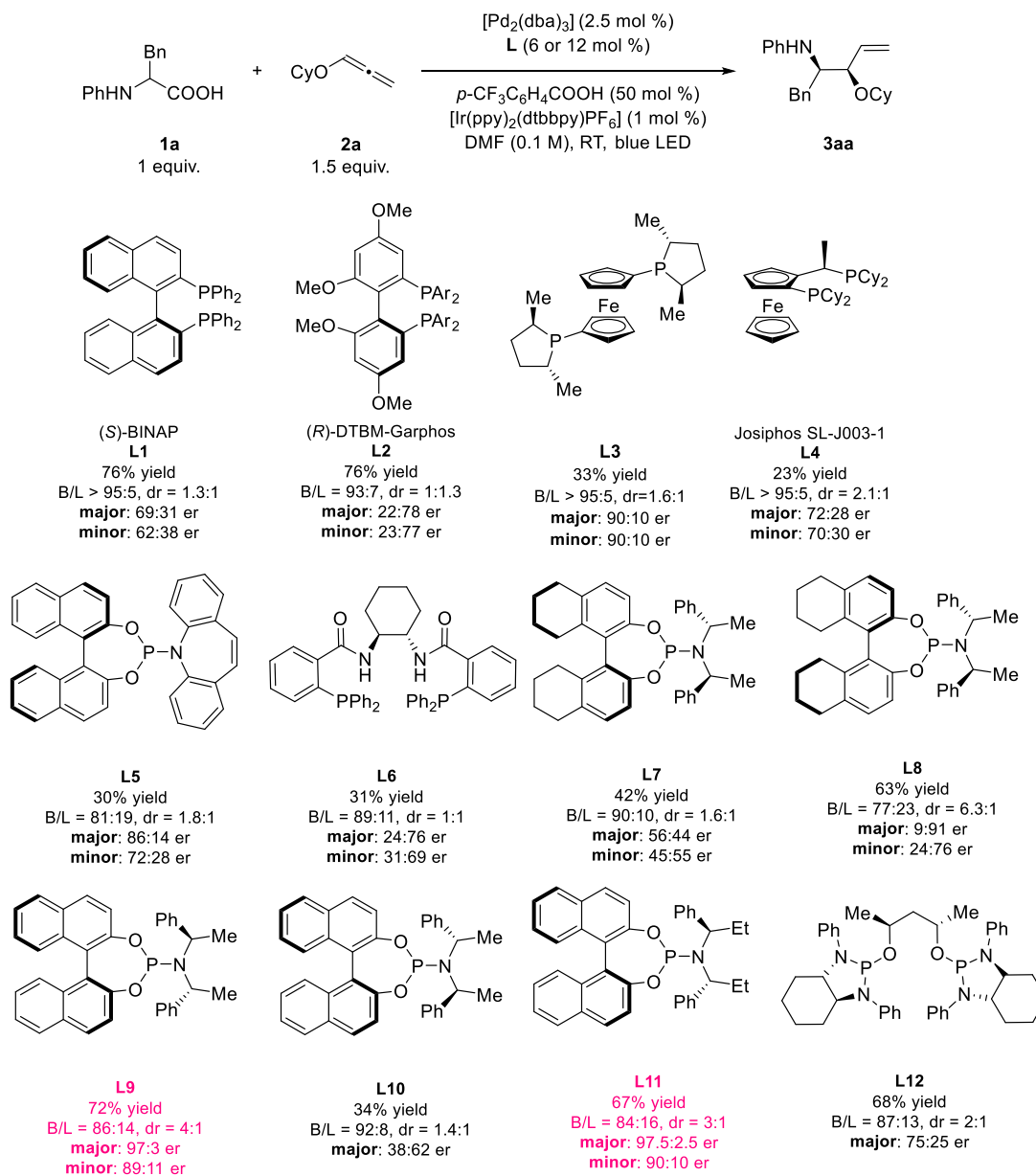
Solvents: Toluene was freshly distilled over sodium/benzophenone. THF was freshly distilled over Na and collected under Argon. Unless otherwise noted, all commercially available reagents were

used without further purification. Solvents employed for work-up and column chromatography were purified prior to use by evaporation on a rotary evaporator.

Allenenes were synthesized according to the reported procedures.¹⁻³ **L12**⁴ was synthesized according to the reported procedures. All other reagents were purchased from various commercial sources and used as received.

Optimization studies

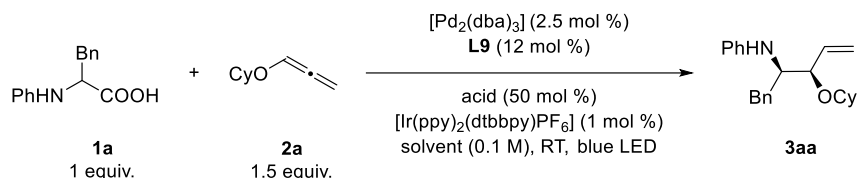
Table S1. Screening of ligands of asymmetric decarboxylative addition of aminoacids to alkoxyallenes towards chiral 1,2-amino ethers.



^aReaction conditions (unless otherwise specified): **1a** (0.1 mmol), **2a** (0.15 mmol), $[\text{Pd}_2(\text{dba})_3]$ (2.5 mol%), bidentate ligands (6 mol%) or monodentate ligands (12 mol%), $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (1 mol%), $p\text{-CF}_3\text{C}_6\text{H}_4\text{COOH}$ (50 mol%), DMF (1 mL), 16 h, rt, blue LED strips. NMR yield was determined by ^1H -NMR spectroscopy using isoquinoline as an internal standard.

Diastereoselective ratio was determined by ¹H-NMR spectroscopy of the crude mixture. Ee was determined by chiral HPLC analysis.

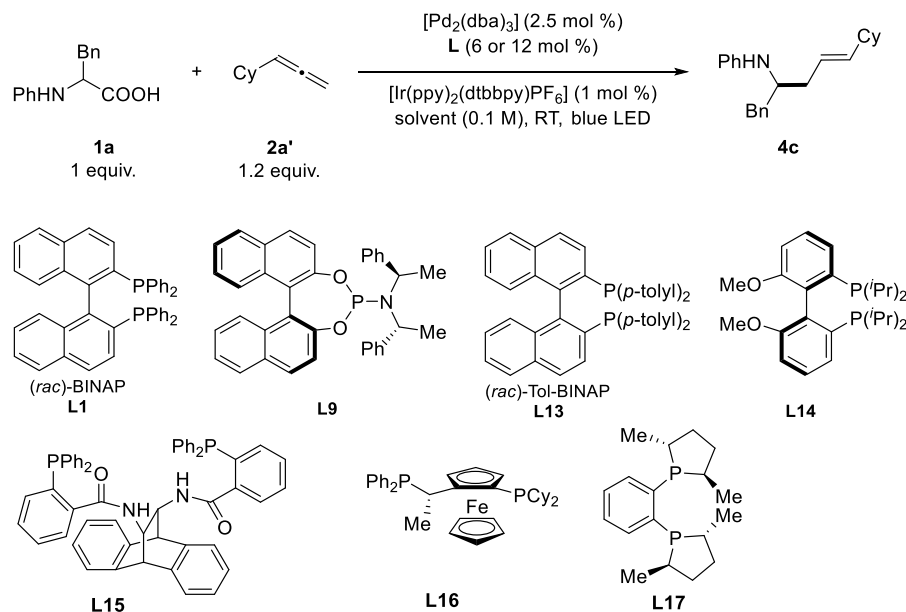
Table S2. Screening of solvents and other conditions of asymmetric decarboxylative addition of aminoacids to alkoxyallenes towards chiral 1,2-amino ethers



entry ^a	acid	solvent	yield/%	dr	B/L	major isomer	minor isomer
1	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	DMF	72	4:1	86:14	97:3 er	89:11 er
2	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	DMA	31	2.3:1	91:9	96:4 er	89:11 er
3	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	MeCN	29	3.5:1	82:18	93:7 er	75:25 er
4	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	DCM	trace	--	--	--	--
5	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	THF	25	1.6:1	77:23	96:4 er	98:2 er
6	PhCOOH	DMF	63	4.7:1	87:13	96:4 er	87:13 er
7	<i>p</i> -MeO-C ₆ H ₄ CO ₂ H	DMF	67	3.8:1	86:14	95:5 er	87:13 er
8	--	DMF	58	3.8:1	83:17	96:4 er	--
9 ^b	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	DMF	70	4:1	82:18	96:4 er	89:11 er
10 ^c	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	DMF	62	4.1:1	83:17	95:5 er	82:18 er
11 ^d	<i>p</i> -CF ₃ -C ₆ H ₄ CO ₂ H	DMF	33	2.4:1	85:15	96:4 er	89:11 er

^aReaction conditions (unless otherwise specified): **1a** (0.1 mmol), **2a** (0.15 mmol), [Pd₂(dba)₃] (2.5 mol%), **L9** (12 mol%), [Ir(ppy)₂(dtbbpy)]PF₆ (1 mol%), acid (50 mol%), solvent (1 mL), 16 h, rt, blue LED strips. NMR yields are reported by using isoquinoline as internal standard. Ratio was determined by ¹H-NMR spectroscopy of the crude mixture. ^b20 mol% acid was used. ^c[Pd₂(dba)₃] (1.2 mol%), ligands (6 mol%) were used. ^d[Pd] (10 mol%), ligands (24 mol%) were used.

Table S3. Screening of ligands and solvents of decarboxylative addition of aminoacids to terminal allenes towards achiral linear homoallylic amines.

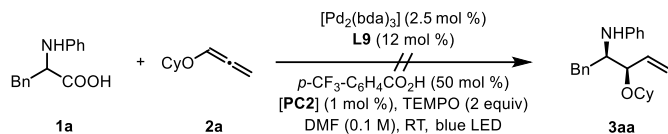


entry ^a	L	solvent	yield/%	E/Z	L/B
1 ^b	L9	DMF	nr	--	--
2	L9	DMF	nr	--	--
3	L1	DMF	64	>95:5	>95:5
4	L1	MeCN	77(67)	>95:5	>95:5
5	L1	THF	54	>95:5	>95:5
6	L1	Toluene	62	>95:5	>95:5
7	L1	DCM	40	>95:5	>95:5
8	L13	MeCN	69	>95:5	>95:5
9	L14	MeCN	38	>95:5	>95:5
10	L15	MeCN	trace	--	--
11	L16	MeCN	45	>95:5	>95:5
12	L17	MeCN	trace	--	--

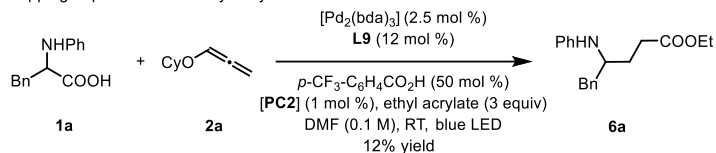
^aReaction conditions (unless otherwise specified): **1a** (0.2 mmol), **2a'** (1.2 equiv.), $[\text{Pd}_2(\text{dba})_3]$ (2.5 mol%), bidentate ligands (6 mol%) or monodentate ligands (12 mol%), $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (1 mol%), solvent (2 mL), 16 h, rt, blue led strips. NMR yields are reported by using isoquinoline as internal standard. Isolated yields are reported in parentheses. Ratio was determined by ¹H-NMR spectroscopy of the crude mixture. ^b50 mol% *p*-CF₃C₆H₄COOH was used.

Mechanistic studies

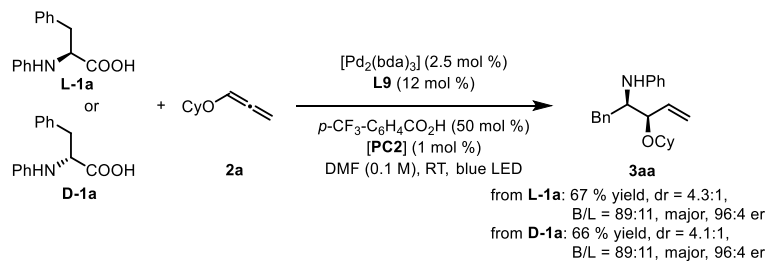
a. Reaction in the presence of TEMPO



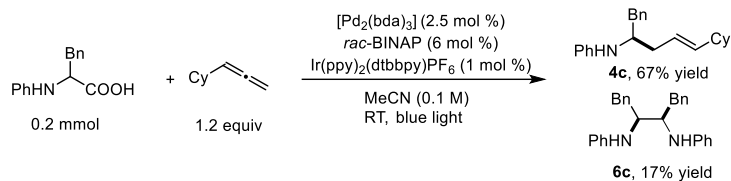
b. Trapping experiment with ethyl acrylate



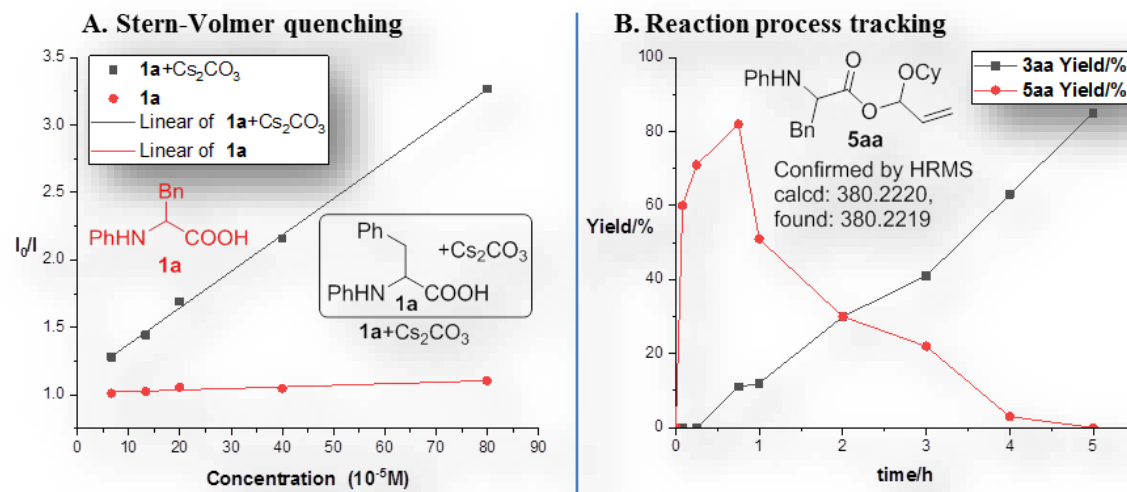
c. Control experiment with chiral amino acid **L-1a** and **D-1a**



d. Analysis of linear selective reaction



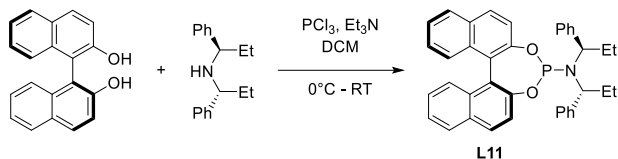
Scheme S1. Preliminary mechanistic studies.



Scheme S2. A. Stern-Volmer quenching study. B. Reaction process tracking experiment.

Experimental details and characterization data

Synthesis of L11



According to a modified procedure from Trost and coworkers,⁵ triethylamine (0.7 μ L, 5 mmol, 5.0 eq.) was added dropwise to a stirred ice-cooled solution of PCl_3 (100 μ L, 1.0 mmol, 1.0 eq.) in CH_2Cl_2 (7 mL / mmol amine). The ice bath was removed and the solution left to warm to room temperature before (*R*)-bis((*R*)-1-phenylpropyl)amine (253.4 mg, 1 mmol, 1.0 eq.) was added to the stirring solution. After 5 additional hours of stirring, (*S*)-binaphthol (343.5 mg, 1.2 mmol, 1.2 eq.) was added to the suspension and the subsequent mixture was left to stir for an additional 18 h. The solution was then filtered on a small pad of neutral alumina and rinsed with CH_2Cl_2 (ca 20 mL). The resulting solution was concentrated under reduced pressure to afford a yellow residue. After flash column chromatography with toluene, the ligand was obtained as a crystalline solid (376.8 mg, 66% yield) (m.p. = 109-110 $^\circ\text{C}$).

^1H NMR (400 MHz, CDCl_3) δ 8.05 – 7.86 (m, 4H), 7.59 (dd, J = 8.8, 0.8 Hz, 1H), 7.49 (dd, J = 8.8, 0.8 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.34 – 7.28 (m, 1H), 7.25 – 7.20 (m, 1H), 7.07 – 6.94 (m, 10H), 4.17 (td, J = 10.4, 5.2 Hz, 2H), 2.36 – 2.22 (m, 2H), 2.21 – 2.05 (m, 2H), 0.78 (d, J = 8.8 Hz, 6H).

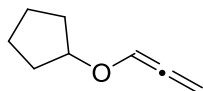
^{13}C NMR (101 MHz, CDCl_3) δ 150.1 (d, J = 8.4 Hz), 149.8, 141.0, 132.9, 131.52, 130.47, 130.41, 129.74, 129.13, 128.47, 128.42, 128.32, 128.16, 127.66, 127.3 (d, J = 6.4 Hz), 126.43, 126.09, 126.06, 125.40, 124.83, 124.54, 124.2 (d, J = 5.3 Hz), 122.5 (d, J = 2.3 Hz), 122.20, 121.9 (d, J = 2.6 Hz), 59.94, 59.84, 11.70.

^{31}P NMR (162 MHz, CDCl_3) δ 143.0.

HRMS ($\text{C}_{38}\text{H}_{35}\text{O}_2\text{NP}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 568.2400, found: 568.2388.

$[\alpha]_D^{25} = +495.0$ (CH_2Cl_2 , c = 0.2).

General procedure A for synthesis of allenes



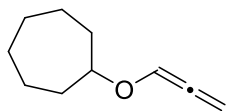
(Propa-1,2-dienyloxy)cyclopentane (2b)

At room temperature, 112 mg (1 mmol, 0.2 equiv.) of *t*-BuOK was added into a solution of (620 mg, 5 mmol) of cyclopentyl-propargyl ether in 5 ml of THF. The suspension was stirred at room temperature for 3 h, then filtered through a celite pad and washed with 20 ml of Et₂O. The combined solution was concentrated *in vacuo* and purified by silica gel chromatography (1% Et₂O in pentanes) to afford the **2b** as a light yellowish, oily liquid (309 mg, 50%).

¹H NMR (400 MHz, C₆D₆) δ 6.62 (td, *J* = 6.0, 0.4 Hz, 1H), 5.21 (dd, *J* = 6.0, 0.4 Hz, 2H), 1.17 – 1.12 (m, 1H), 1.82 – 1.74 (m, 2H), 1.67 – 1.59 (m, 2H), 1.57 – 1.48 (m, 2H), 1.38 – 1.28 (m, 2H).

¹³C NMR (101 MHz, C₆D₆) δ 202.8, 120.7, 89.2, 80.5, 33.0, 24.2.

HRMS (C₈ H₁₂O; [M+H]⁺, APCI): calcd: 125.0961, found: 125.0962.



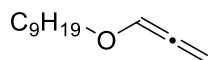
(Propa-1,2-dien-1-yloxy)cycloheptane (2c)

Allene **2c** was prepared according to the general procedure A for allene preparation starting from (prop-2-ynyloxy)cycloheptane (800 mg, 5.2 mmol). Yield 650 mg (81%).

¹H NMR (400 MHz, C₆D₆) δ 6.64 (td, *J* = 6.0, 0.4 Hz, 1H), 5.21 (d, *J* = 6.0 Hz, 2H), 3.82 (tt, *J* = 8.0, 4.4 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.76 – 1.67 (m, 2H), 1.61 – 1.51 (m, 2H), 1.44 – 1.34 (m, 4H), 1.30 – 1.21 (m, 2H).

¹³C NMR (101 MHz, C₆D₆) δ 202.8, 120.7, 89.2, 78.8, 33.9, 28.7, 23.2.

HRMS (C₁₀ H₁₇O; [M+H]⁺, pESI): calcd: 153.1274, found: 153.1273.



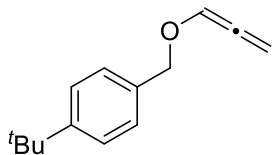
1-(Propa-1,2-dien-1-yloxy)nonane (2e)

Allene **2e** was prepared according to the general procedure A for allene preparation starting from 1-(prop-2-yn-1-yloxy)nonane (800 mg, 4.4 mmol). Yield 572 mg (72%).

¹H NMR (400 MHz, C₆D₆) δ 6.78 (t, *J* = 6.0 Hz, 1H), 5.26 (d, *J* = 6.0 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.33 – 1.20 (m, 12H), 0.94 – 0.85 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, C₆D₆) δ 202.2, 122.3, 90.1, 69.0, 32.2, 29.9, 29.7, 29.6, 29.57, 26.4, 23.0, 14.3.

HRMS (C₉H₂₃O; [M+H]⁺, pAPCI): calcd: 183.1743, found: 183.1742.



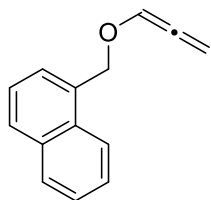
1-(Tert-butyl)-4-((propa-1,2-dien-1-yloxy)methyl)benzene (2h)

Allene **2h** was prepared according to the general procedure A for allene preparation starting from 1-(tert-butyl)-4-((prop-2-yn-1-yloxy)methyl)benzene (800 mg, 4.0 mmol). Yield 510 mg (64%).

¹H NMR (400 MHz, C₆D₆) δ 7.25 (s, 4H), 6.82 (td, *J* = 6.0, 0.4 Hz, 1H), 5.23 (dt, *J* = 6.0, 0.4 Hz, 2H), 4.56 (d, *J* = 0.4 Hz, 2H), 1.19 (s, 9H).

¹³C NMR (101 MHz, C₆D₆) δ 202.1, 150.7, 135.0, 125.5, 122.2, 90.7, 70.8, 34.5, 31.4.

HRMS (C₁₄H₁₉O; [M+H]⁺, pAPCI): calcd: 203.1430, found: 203.1429.



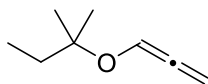
1-((Propa-1,2-dien-1-yloxy)methyl)naphthalene (2i)

Allene **2i** was prepared according to the general procedure A for allene preparation starting from 1-((prop-2-yn-1-yloxy)methyl)naphthalene (800 mg, 4.1 mmol). Yield 630 mg (79%).

¹H NMR (400 MHz, C₆D₆) δ 8.00 (ddt, *J* = 8.4, 1.6, 0.8 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.59 – 7.55 (m, 1H), 7.37 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.32 – 7.22 (m, 2H), 7.19 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.81 (t, *J* = 6.0 Hz, 1H), 5.26 (d, *J* = 6.0 Hz, 2H), 4.94 (s, 2H).

¹³C NMR (101 MHz, C₆D₆) δ 201.9, 134.2, 133.4, 132.3, 129.0, 128.8, 126.8, 126.4, 126.0, 125.4, 124.3, 122.1, 91.0, 69.3.

HRMS (C₁₄H₁₃O; [M+H]⁺, pAPCI): calcd: 197.0961, found: 197.0963.



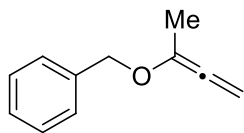
2-Methyl-2-((propa-1,2-dienyloxy)butane (2j)

Allene **2j** was prepared according to the general procedure A for allene preparation starting from (prop-2-ynyloxy)cycloheptane (824 mg, 6.5 mmol). Yield 250 mg (30%).

¹H NMR (400 MHz, CDCl₃) δ 6.46 (t, *J* = 6.0 Hz, 1H), 5.12 (d, *J* = 6.0 Hz, 2H), 1.42 (q, *J* = 7.6 Hz, 2H), 1.07 (s, 6H), 0.82 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 204.6, 115.02, 86.2, 78.4, 33.5, 25.3, 8.2.

HRMS (C₈H₁₅O; [M+H]⁺, pAPCI): calcd: 127.1117, found: 127.1118.



((buta-2,3-dien-2-yloxy)methyl)benzene (2m)

Allene **2m** was prepared according to the general procedure A for allene preparation starting from ((but-3-yn-2-yloxy)methyl)benzene (800 mg, 5 mmol). Yield 470 mg (59%).

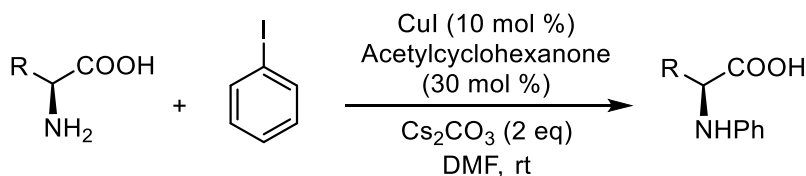
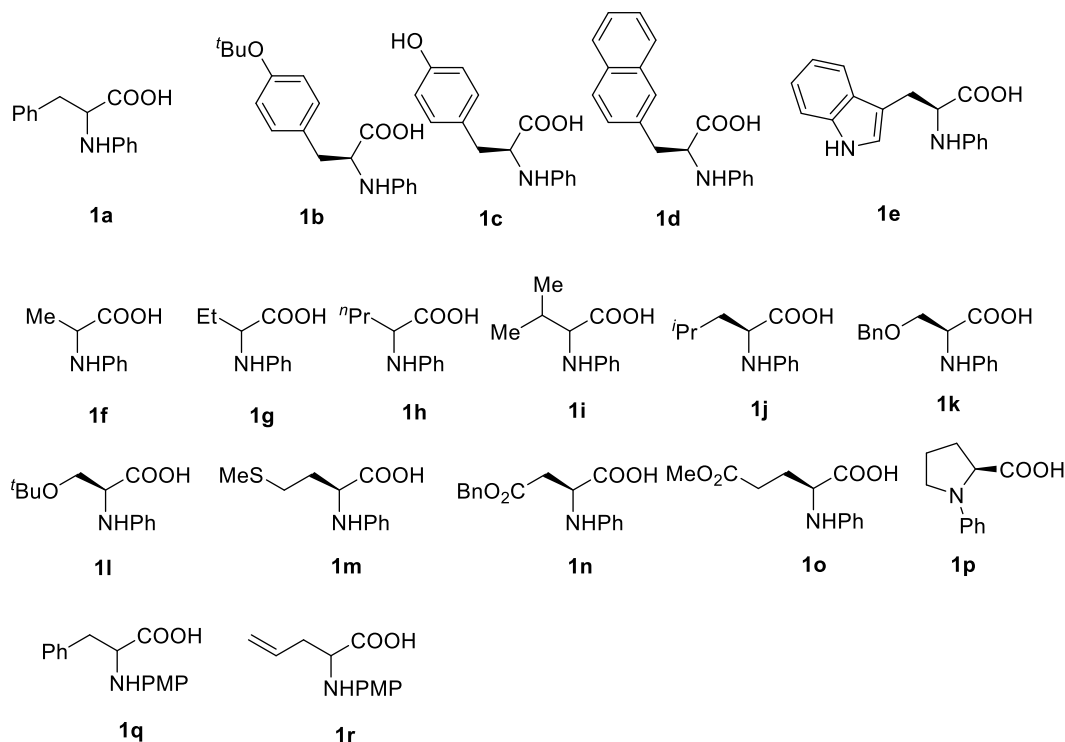
¹H NMR (300 MHz, CDCl₃) δ 7.45 – 7.28 (m, 5H), 5.38 (q, *J* = 2.7 Hz, 2H), 4.62 (s, 2H), 1.98 (t, *J* = 2.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.2, 137.3, 133.3, 128.5, 127.8, 127.3, 114.6, 87.9, 69.3.

HRMS (C₁₁H₁₂O; [M+H]⁺, pAPCI): calcd: 161.0961, found: 161.0961.

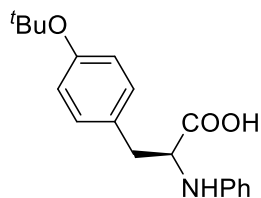
General procedure B for preparation of substrates *N*-phenyl α -amino acids

1a,^[6] **1e-1g**,^[6] **1i-j**,^[6] **1l**,^[7] **1k**,^[6] and **1p**^[6] were prepared according to the literature reports. **1b-d**, **1h**, **1k** and **1n-o** were synthesized with Ullmann coupling reaction of amino acid with phenyl iodine. **1q** and **1r** was prepared by saponification of related esters.



In a pre-dried round bottom flask (25 mL) was added phenyl iodide (10 mmol, 1.0 equiv.), amino acid (1.2 equiv.), copper iodide (5 mol%), 2-acetylcyclohexan-1-one (30 mol%), Cs₂CO₃ (2.0 equiv.) and DMF (15 mL). After that the round bottom flask was sealed and allowed to stir at room temperature. For amino acids, after the completion of reaction, the crude was worked up using cold water and ethyl acetate for 2 times, the combined organic phase was then washed with aqueous 1N NaOH. The combined aqueous phase were acidified to pH 3-4 by using aqueous HCl and then extracted with ethyl acetate. The organic phase was dried over Na₂SO₄, concentrated

under reduced pressure and purified using flash chromatography to afford the *N*-arylated amino acids.



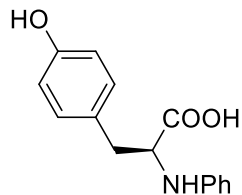
***(S)*-3-(4-(*Tert*-butoxy)phenyl)-2-(phenylamino)propanoic acid (**1b**)**

Follow the **general procedure B**, starting from the *L*-O-*tert*-butyl-tyrosine, **1b** was obtained as a white solid in 64% yield (m.p. = 128-130 °C).

¹H-NMR (400 MHz, CDCl₃) δ 7.21 – 7.14 (m, 2H), 7.12 – 7.05 (m, 2H), 6.96 – 6.89 (m, 2H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.58 (t, *J* = 5.4 Hz, 2H), 4.28 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.22 (dd, *J*_{AB} = 14.0, 5.4 Hz, 1H), 3.06 (dd, *J*_{BA} = 14.0, 7.2 Hz, 1H), 1.33 (s, 9H).

¹³C-NMR (101 MHz, CDCl₃) δ 177.0, 154.7, 146.2, 130.7, 130.1, 129.8, 129.5, 124.4, 119.4, 114.1, 78.7, 58.3, 37.8, 28.9.

HR-MS (C₁₉H₂₂O₃N; [M-H]⁻, pos. ESI): calcd: 312.1605, found: 312.1608.



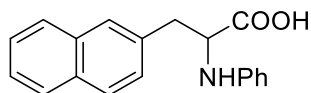
***Phenyl-L*-tyrosine (**1c**)**

Follow the **general procedure B**, starting from the *L*-tyrosine, **1c** was obtained as a white solid in 25% yield (m.p. = 155-156 °C).

¹H-NMR (500 MHz, DMSO-*d*₆) δ 12.50 (brs, 1H), 9.17 (brs, 1H), 7.21 – 6.99 (m, 4H), 6.77 – 6.61 (m, 2H), 6.53 (dd, *J* = 16.0, 8.0 Hz, 3H), 5.78 (brs, 1H), 4.00 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.93 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.84 (dd, *J* = 13.5, 8.0 Hz, 1H).

¹³C NMR (126 MHz, DMSO-*d*₆) δ 174.7, 155.8, 147.7, 130.0, 128.8, 127.8, 116.2, 114.9, 112.4, 57.7, 37.0.

HR-MS (C₁₅H₁₄O₃N; [M-H]⁻, -pAPCI): calcd: 256.0979, found: 256.0978.



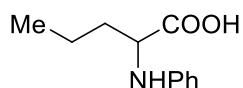
3-(Naphthalen-2-yl)-2-(phenylamino)propanoic acid (**1d**)

Follow the **general procedure B**, starting from the 3-(naphthalen-2-yl)-2-aminopropanoic acid, **1d** was obtained as a white solid in 41% yield (m.p. = 186-188 °C).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.88 – 7.75 (m, 8H), 7.52 – 7.40 (m, 6H), 7.09 – 6.97 (m, 4H), 6.64 – 6.56 (m, 4H), 6.53 (tt, *J* = 7.2, 1.2 Hz, 2H), 4.23 (dd, *J* = 8.0, 6.0 Hz, 2H), 3.23 (dd, *J* = 13.6, 6.0 Hz, 2H), 3.14 (dd, *J* = 13.6, 8.0 Hz, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 174.5, 147.6, 135.5, 132.9, 131.8, 128.8, 127.7, 127.44, 127.4, 127.37, 127.3, 125.9, 125.4, 116.3, 112.5, 57.4, 37.9.

HR-MS (C₁₉H₁₇O₂N; [M-H]⁻, -ESI): calcd: 290.1187, found: 290.1189.



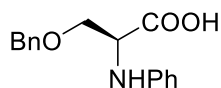
2-(Phenylamino)pentanoic acid (**1h**)

Follow the **general procedure B**, starting from the DL-norvaline (824 mg, 6.5 mmol), **1h** was obtained as a white solid in 30% yield (m.p. = 140-142 °C).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.11 – 6.93 (m, 2H), 6.54 (dd, *J* = 14.0, 7.6 Hz, 3H), 3.91 – 3.73 (m, 1H), 1.82 – 1.59 (m, 2H), 1.53 – 1.28 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 175.4, 148.0, 128.8, 116.1, 112.3, 55.4, 34.1, 18.7, 13.6.

HRMS (C₁₁H₁₄O₂N; [M+H]⁺, pESI): calcd: 192.1030, found: 192.1031.



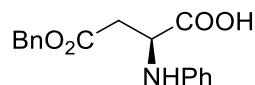
O-Benzyl-N-phenyl-L-serine (**1k**)

Follow the **general procedure B**, starting from the *O*-benzyl -*L*-serine, **1k** was obtained as a white solid in 81% yield (m.p. = 94-96 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 5H), 7.24 – 7.17 (m, 2H), 6.82 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.68 – 6.62 (m, 2H), 4.58 (s, 2H), 4.21 (t, *J* = 4.2 Hz, 1H), 3.95 (dd, *J* = 9.2, 4.2 Hz, 1H), 3.83 (dd, *J* = 9.2, 4.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 176.0, 146.2, 137.3, 129.5, 128.6, 128.1, 127.8, 119.4, 114.1, 73.6, 69.7, 57.5.

HR-MS ($\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}$; $[\text{M}-\text{H}]^-$, -ESI): calcd: 270.1136, found: 270.1135.



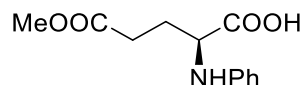
4-(Benzyloxy)-4-oxo-2-(phenylamino)butanoic acid (1n)

Follow the **general procedure B**, starting from the 3-(naphthalen-2-yl)-2-aminopropanoic acid (824 mg, 6.5 mmol), **1n** was obtained as a white solid in 30% yield (m.p. = 81-83 °C).

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.29 (m, 5H), 7.25 – 7.15 (m, 2H), 6.82 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 5.15 (s, 2H), 4.47 (t, J = 5.6 Hz, 1H), 3.06 – 2.92 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 176.0, 170.7, 145.8, 135.4, 129.6, 128.7, 128.6, 128.4, 119.7, 114.4, 67.2, 53.9, 36.9.

HRMS ($\text{C}_{17}\text{H}_{16}\text{O}_4\text{N}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 298.1085, found: 298.1084.



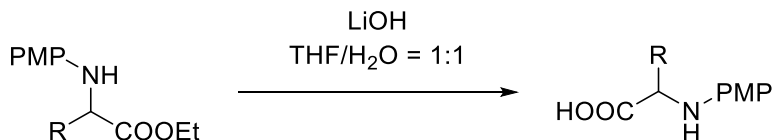
(S)-5-Methoxy-5-oxo-2-(phenylamino)pentanoic acid (1o)

Follow the **general procedure B**, starting from the (S)-5-methoxy-5-oxo-2-(amino)pentanoic acid (10 mmol), **1o** was obtained as a white solid in 34% yield (m.p. = 97-99 °C).

^1H NMR (300 MHz, CDCl_3) δ 7.16 – 7.08 (m, 2H), 6.76 – 6.68 (m, 1H), 6.62 – 6.53 (m, 2H), 4.04 (dd, J = 8.0, 5.4 Hz, 1H), 3.60 (s, 3H), 2.47 (td, J = 7.2, 4.8 Hz, 2H), 2.28 – 1.98 (m, 2H).

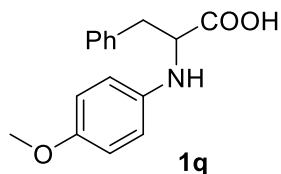
^{13}C NMR (101 MHz, CDCl_3) δ 176.6, 173.6, 146.4, 129.6, 119.4, 114.0, 56.7, 52.0, 30.5, 27.7.

HRMS ($\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}$; $[\text{M}-\text{H}]^-$, -pESI): calcd: 236.0928, found: 236.0928.



A solution of amino acid ester (20 mmol) in THF (15 ml) and H_2O (15 ml) was treated with LiOH (2.4 g, 100 mmol), and the mixture was stirred at rt overnight. After consuming the amino acid ester, the reaction mixture poured into water and extracted with Et_2O . The organic phase was extracted twice with 1 M aq. sodium hydroxide solution. The aqueous phases were combined,

acidified to pH 3-4 by addition of 37% aq. HCl solution, and extracted with EtOAc. The organic layer was dried (MgSO₄), filtered, and evaporated to produce the title compound. After washing with Et₂O, the solid was dried under high vacuum.



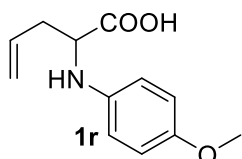
(4-Methoxyphenyl)phenylalanine (1q)

White solid in 88% yield (m.p. = 183-185 °C).

¹H-NMR (400 MHz, DMSO-*d*₆): δ 7.31 – 7.23 (m, 4H), 7.22 – 7.15 (m, 1H), 6.73 – 6.65 (m, 2H), 6.58 – 6.50 (m, 2H), 4.05 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.61 (s, 3H), 3.02 (dd, *J*_{AB} = 13.6, 6.0 Hz, 1H), 2.94 (dd, *J*_{BA} = 13.6, 8.0 Hz, 1H).

¹³C-NMR (101 MHz, DMSO-*d*₆): δ 174.7, 151.1, 141.6, 137.9, 129.1, 128.0, 126.3, 114.5, 113.8, 58.2, 55.3, 37.9.

HR-MS (C₁₆H₁₈O₃N; [M+H]⁺, pos. APCI): calcd: 272.1281, found: 272.1279.



2-((4-Methoxyphenyl)amino)pent-4-enoic acid (1r)

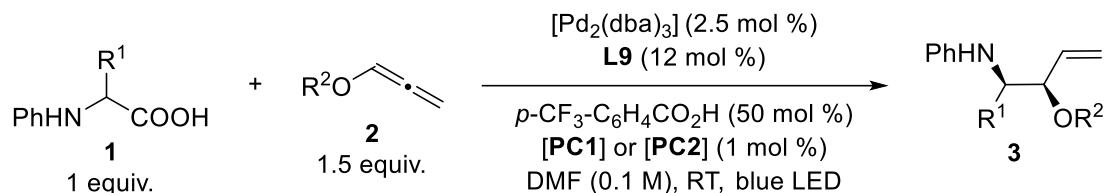
white solid in 28% yield (m.p. = 147-149 °C).

¹H-NMR (400 MHz, DMSO-*d*₆): δ 6.78 – 6.62 (m, 2H), 6.60 – 6.47 (m, 2H), 5.83 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.15 – 4.97 (m, 2H), 3.81 (dd, *J* = 6.8, 6.0 Hz, 1H), 3.61 (s, 3H), 2.48 – 2.38 (m, 2H).

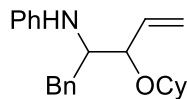
¹³C-NMR (101 MHz, DMSO-*d*₆): δ 175.0, 151.0, 142.0, 134.8, 117.1, 114.5, 113.7, 56.9, 55.3, 36.5.

HR-MS (C₁₂H₁₆O₃N; [M+H]⁺, pos. ESI): calcd: 222.1125, found: 222.1124.

General procedure C for photoredox palladium catalyzed enantioselective decarboxylative hydroaminoalkylation of alkoxyallenes



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $[\text{Pd}_2(\text{dba})_3]$ (2.3 mg, 0.0025 mmol, 2.5 mol%), **L9** (6.5 mg, 0.012 mmol, 12 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards DMF (1 mL) was added by syringe under a flow of argon and the solution was stirred for 30 min. **[PC1]** (0.9 mg, 0.001 mmol, 1 mol%) or **[PC2]** (1.1 mg, 0.001 mmol, 1 mol%), **1** (0.1 mmol, 1.0 equiv), $p\text{-CF}_3\text{-C}_6\text{H}_4\text{CO}_2\text{H}$ (9.5 mg, 0.05 mmol, 0.5 equiv.) were added sequentially and **2** (0.15 mmol, 1.5 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 1 inch from blue led strips and irradiated and stirred for 16-24 hrs. at room temperature. After filtration through celite and evaporation of the solvents under reduced pressure, the dr was determined by ^1H NMR measurement of the crude reaction mixture. The residue was purified with column chromatography on silica gel afford the corresponding product after drying in vacuo.



***N*-(3-(Cyclohexyloxy)-1-phenylpent-4-en-2-yl)aniline (**3aa**)**

Prepared according to the general procedure C. Flash column chromatography (SiO_2 , Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 23.5 mg, 70%) as colorless oils (4.5:1 ratio as determined by ^1H NMR).

HRMS ($\text{C}_{23}\text{H}_{30}\text{ON}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 336.2322, found: 336.2321.

Major diastereomer (*R,R*)-**3aa**: ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 7.18 – 7.12 (m, 2H), 6.66 (t, $J = 7.5$ Hz, 1H), 6.61 (d, $J = 8.0$ Hz, 2H), 5.94 – 5.82 (m, 1H), 5.19 – 5.06 (m, 2H), 4.25 (brs, 1H), 3.93 (dd, $J = 7.5, 2.0$ Hz, 1H), 3.70 – 3.60 (m, 1H), 3.38

– 3.29 (m, 1H), 2.96 (dd, $J = 13.9, 7.8$ Hz, 1H), 2.86 (dd, $J = 14.0, 6.0$ Hz, 1H), 1.94 – 1.68 (m, 4H), 1.55 (dq, $J = 8.0, 4.1$ Hz, 1H), 1.45 – 1.27 (m, 5H).

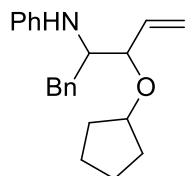
^{13}C NMR (126 MHz, CDCl_3) δ 147.5, 139.5, 138.0, 129.3, 129.2, 128.4, 126.1, 117.2, 116.9, 113.2, 77.0, 74.94, 58.97, 37.10, 33.62, 31.81, 25.84, 24.24, 24.11.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/ethanol = 100:0, 0.5 mL/min), t (*syn*, major) = 16.24 min, t (*syn*, minor) = 18.56 min, 96:4 er; $[\alpha]_D^{25} = +23.4$ (CH_2Cl_2 , $c = 0.512$).

Minor diastereomer: ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.22 (m, 4H), 7.20 – 7.13 (m, 1H), 7.13 – 7.07 (m, 2H), 6.65 (tt, $J = 7.4, 1.1$ Hz, 1H), 6.58 – 6.49 (m, 2H), 5.85 (ddd, $J = 17.2, 10.4, 6.4$ Hz, 1H), 5.33 – 5.22 (m, 2H), 4.04 (ddt, $J = 6.4, 3.6, 1.2$ Hz, 1H), 3.68 (ddd, $J = 8.8, 4.4, 3.6$ Hz, 1H), 3.30 – 3.18 (m, 1H), 3.00 (dd, $J = 14.4, 4.4$ Hz, 1H), 2.78 (dd, $J = 14.4, 8.8$ Hz, 1H), 1.86 – 1.64 (m, 4H), 1.56 – 1.45 (m, 1H), 1.26 – 1.14 (m, 5H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.7, 139.7, 137.9, 129.4, 129.3, 128.3, 126.1, 117.4, 117.2, 113.9, 78.8, 75.8, 58.9, 35.6, 33.6, 32.0, 25.9, 24.3, 24.2.

HPLC (CHIRALPAK[®] IA, $\text{H}_2\text{O}/\text{MeCN} = 75:25$, 1 mL/min), t (*anti*, major) = 33.93 min, t (*anti*, minor) = 36.08 min, 88:12 er; $[\alpha]_D^{25} = -23.4$ (CH_2Cl_2 , $c = 0.312$).



N-(3-(Cyclopentyloxy)-1-phenylpent-4-en-2-yl)aniline (**3ab**)

Prepared according to the general procedure C. Flash column chromatography (SiO_2 , Pentanes/Dichloromethane – 4:1) furnished two separable diastereoisomers of the title compound (Combined yield: 25.0 mg, 78%) as colorless oils (4.3:1 ratio as determined by ^1H NMR). **HRMS** ($\text{C}_{22}\text{H}_{27}\text{ON}$; $[\text{M}+\text{H}]^+$, APCI): calcd: 322.2165, found: 322.2170.

Major diastereomer (*R,R*)-**3ab**: ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.24 (m, 4H), 7.24 – 7.18 (m, 1H), 7.18 – 7.11 (m, 2H), 6.65 (t, $J = 7.2$ Hz, 1H), 6.63 – 6.57 (m, 2H), 5.94 – 5.81 (m, 1H), 5.20 – 5.08 (m, 2H), 4.11 (brs, 1H), 4.04 – 3.96 (m, 1H), 3.82 (dd, $J = 7.6, 2.4$ Hz, 1H), 3.69 – 3.59 (m, 1H), 2.89 (qd, $J = 14.0, 6.8$ Hz, 2H), 1.79 – 1.53 (m, 8H).

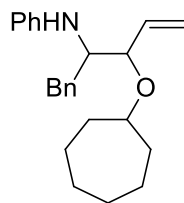
^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 139.6, 137.8, 129.4, 129.3, 128.5, 126.2, 117.6, 117.0, 113.2, 79.1, 78.1, 58.8, 37.3, 33.4, 31.9, 23.64, 23.6.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/ethanol = 100:0, 0.5 mL/min), *t* (*syn*, major) = 15.45 min, *t* (*syn*, minor) = 17.71 min, 95:5 er; $[\alpha]_D^{25} = +19.8$ (CH₂Cl₂, *c* = 0.262).

Minor diastereomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.28 – 7.20 (m, 4H), 7.19 – 7.14 (m, 1H), 7.14 – 7.09 (m, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.58 – 6.49 (m, 2H), 5.84 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.28 (ddt, *J* = 10.8, 7.6, 1.6 Hz, 2H), 3.98 – 3.89 (m, 2H), 3.83 (brs, 1H), 3.69 (dt, *J* = 8.4, 4.4 Hz, 1H), 2.98 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.77 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.81 – 1.61 (m, 4H), 1.58 – 1.46 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 139.7, 137.5, 130.1, 129.4, 129.3, 128.3, 126.1, 117.5, 117.4, 113.9, 79.7, 79.5, 58.7, 35.7, 33.3, 32.0, 23.6, 23.5.

HPLC (CHIRALPAK[®] OD-R, H₂O/MeCN = 25:75, 1 mL/min), *t* (*anti*, major) = 6.9 min, *t* (*anti*, minor) = 8.08 min, 85:15 er; $[\alpha]_D^{25} = -8.0$ (CH₂Cl₂, *c* = 0.088).



***N*-(3-(Cycloheptyloxy)-1-phenylpent-4-en-2-yl)aniline (3ac)**

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 4:1) furnished two separable diastereoisomers of the title compound (Combined yield: 24.7 mg, 71%) as colorless oils (5.6:1 ratio as determined by ¹H NMR). **HRMS** (C₂₄H₃₂ON; [M+H]⁺, pESI): calcd: 350.2478, found: 350.2483.

Major diastereomer (*R,R*)-**3ac**: **¹H NMR** (400 MHz, CDCl₃) δ 7.33 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 7.18 – 7.12 (m, 2H), 6.65 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.63 – 6.56 (m, 2H), 5.88 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.18 – 5.07 (m, 2H), 4.14 (brs, 1H), 3.88 (ddt, *J* = 7.6, 2.4, 0.8 Hz, 1H), 3.67 (ddd, *J* = 7.6, 6.0, 2.4 Hz, 1H), 3.55 (tt, *J* = 7.6, 4.4 Hz, 1H), 2.95 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.85 (dd, *J* = 14.0, 6.2 Hz, 1H), 1.91 – 1.76 (m, 2H), 1.73 – 1.52 (m, 8H), 1.46 – 1.33 (m, 2H).

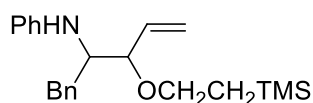
¹³C NMR (101 MHz, CDCl₃) δ 147.8, 139.7, 138.0, 129.4, 129.3, 128.5, 126.2, 117.4, 117.0, 113.2, 77.5, 77.3, 59.0, 37.3, 35.5, 33.3, 28.7, 28.6, 23.1, 23.0.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-propanol = 100:0, 0.5 mL/min), *t* (*syn*, major) = 18.37 min, *t* (*syn*, minor) = 21.37 min, 97:3 er; $[\alpha]_D^{25} = +19.7$ (CH₂Cl₂, *c* = 0.294).

Minor diastereomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.27 – 7.21 (m, 4H), 7.19 – 7.14 (m, 1H), 7.14 – 7.08 (m, 2H), 6.64 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.56 – 6.51 (m, 2H), 5.84 (ddd, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.36 – 5.22 (m, 2H), 4.00 (ddt, *J* = 6.4, 3.6, 1.2 Hz, 1H), 3.88 (brs, 1H), 3.68 (dt, *J* = 8.4, 4.0 Hz, 1H), 3.44 (dddd, *J* = 8.4, 7.6, 4.4, 4.0 Hz, 1H), 3.00 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.78 (dd, *J* = 14.4, 8.8 Hz, 1H), 1.91 – 1.80 (m, 1H), 1.68 – 1.48 (m, 9H), 1.40 – 1.30 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 139.8, 137.8, 129.4, 129.3, 128.3, 126.1, 117.3, 117.2, 113.9, 79.0, 78.0, 59.0, 35.8, 35.3, 33.3, 28.7, 28.6, 23.1, 22.9.

HPLC (CHIRALPAK® OJ-3R, H₂O/MeCN = 35:65, 1 mL/min), *t* (*anti*, major) = 9.39 min, *t* (*anti*, minor) = 10.97 min, 87:13 er; [α]_D²⁵ = +46.4 (CH₂Cl₂, *c* = 0.056).



***N*-(1-Phenyl-3-(2-(trimethylsilyl)ethoxy)pent-4-en-2-yl)aniline (3ad)**

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 5:1) furnished two separable diastereoisomers of the title compound (Combined yield: 26.6 mg, 75%) as colorless oils (3.4:1 ratio as determined by ¹H NMR). **HRMS** (C₂₂H₃₂ONSi; [M+H]⁺, pAPCI): calcd: 354.2248, found: 354.2245.

Major diastereomer (*R,R*)-**3ad**: **¹H NMR** (400 MHz, CDCl₃) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.12 (m, 5H), 6.66 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.63 – 6.57 (m, 2H), 5.86 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.21 – 5.07 (m, 2H), 4.10 (brs, 1H), 3.71 (ddt, *J* = 7.6, 2.0, 0.8 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.42 – 3.34 (m, 1H), 3.00 – 2.85 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 2H), 0.07 (s, 9H).

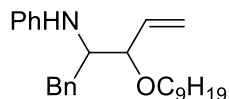
¹³C NMR (101 MHz, CDCl₃) δ 147.7, 139.5, 137.1, 129.4, 129.4, 128.5, 126.2, 117.9, 117.1, 113.3, 79.8, 66.2, 58.8, 37.4, 18.5, -1.1.

HPLC (CHIRALPAK® LC-4, *n*-heptane/2-propanol = 100:0, 0.5 mL/min), *t* (*syn*, major) = 13.69 min, *t* (*syn*, minor) = 17.43 min, 90:10 er; [α]_D²⁵ = +27.0 (CH₂Cl₂, *c* = 0.2).

Minor diastereomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.29 – 7.08 (m, 7H), 6.66 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.60 – 6.53 (m, 2H), 5.88 – 5.76 (m, 1H), 5.33 – 5.23 (m, 2H), 3.80 – 3.69 (m, 2H), 3.66 – 3.57 (m, 1H), 3.32 (td, *J* = 9.2, 6.8 Hz, 1H), 2.99 (dd, *J* = 14.0, 4.4 Hz, 1H), 2.87 (dd, *J* = 14.0, 7.6 Hz, 1H), 0.94 (ddd, *J* = 9.2, 6.8, 2.0 Hz, 2H), 0.03 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 139.3, 137.0, 129.5, 129.3, 128.3, 126.2, 118.1, 117.4, 113.9, 81.3, 66.4, 58.5, 35.8, 18.5, -1.2.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-propanol = 100:0, 0.5 mL/min), t (*anti*, major) = 28.55 min, t (*anti*, minor) = 36.43 min, 74:26 er; $[\alpha]_D^{25} = +76.7$ (CH₂Cl₂, c = 0.03).



***N*-(3-(Nonyloxy)-1-phenylpent-4-en-2-yl)aniline (3ae)**

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 4:1) furnished two separable diastereoisomers of the title compound (Combined yield: 27.7 mg, 73%) as colorless oils (2.7:1 ratio as determined by ¹H NMR). **HRMS** (C₂₆H₃₈ON; [M+H]⁺, pESI): calcd: 380.2948, found: 380.2947.

Major diastereomer (*R,R*)-**3ae**: **¹H NMR** (400 MHz, CDCl₃) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 7.18 – 7.12 (m, 2H), 6.66 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.64 – 6.59 (m, 2H), 5.85 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.20 – 5.07 (m, 2H), 4.09 (brs, 1H), 3.73 – 3.69 (m, 1H), 3.68 – 3.60 (m, 1H), 3.53 (dt, *J* = 9.2, 6.4 Hz, 1H), 3.26 (dt, *J* = 9.2, 6.4 Hz, 1H), 2.99 – 2.84 (m, 2H), 1.67 – 1.59 (m, 2H), 1.36 – 1.26 (m, 12H), 0.95 – 0.85 (m, 3H).

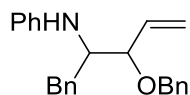
¹³C NMR (101 MHz, CDCl₃) δ 147.7, 139.5, 137.1, 129.38, 129.36, 128.5, 126.2, 117.9, 117.1, 113.3, 80.0, 69.1, 58.8, 37.4, 32.0, 30.0, 29.7, 29.6, 29.4, 26.5, 22.8, 14.2.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-propanol = 100:0, 0.5 mL/min), t (*syn*, major) = 17.73 min, t (*syn*, minor) = 22.11 min, 89:11 er; $[\alpha]_D^{25} = +18.0$ (CH₂Cl₂, c = 0.3).

Minor diastereomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.28 – 7.23 (m, 2H), 7.23 – 7.16 (m, 3H), 7.16 – 7.10 (m, 2H), 6.66 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.61 – 6.53 (m, 2H), 5.87 – 5.75 (m, 1H), 5.32 – 5.24 (m, 2H), 3.82 – 3.68 (m, 3H), 3.51 (dt, *J* = 9.2, 6.8 Hz, 1H), 3.23 (dt, *J* = 9.2, 6.8 Hz, 1H), 3.04 – 2.94 (m, 1H), 2.87 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.63 – 1.52 (m, 2H), 1.32 – 1.20 (m, 12H), 0.93 – 0.86 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 139.2, 136.9, 129.6, 129.3, 128.3, 126.2, 118.1, 117.4, 113.9, 81.6, 69.4, 58.4, 35.7, 32.0, 30.0, 29.7, 29.6, 29.4, 26.4, 22.8, 14.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-propanol = 100:0, 0.5 mL/min), t (*syn*, major) = 33.94 min, t (*syn*, minor) = 45.19 min, 73:27 er; $[\alpha]_D^{25} = +3.7$ (CH₂Cl₂, c = 0.082).



***N*-(3-(Benzyloxy)-1-phenylpent-4-en-2-yl)aniline (3af)**

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 27.7 mg, 81%) as light brown oils (3.9:1 ratio as determined by ¹H NMR).

HRMS (C₂₄H₂₆ON; [M+H]⁺, ESI): calcd: 344.2009, found: 344.2009.

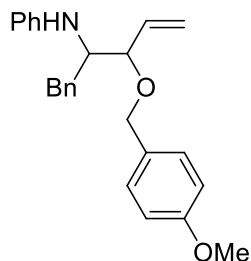
HPLC (CHIRALPAK[®] OD-3, *n*-heptane/2-propanol = 99.7:0.3, 0.3 mL/min), t (*syn*, minor) = 23.80 min, t (*syn*, major) = 24.73 min, 91:9 er; t (*anti*, major) = 26.42 min, t (*anti*, minor) = 29.78 min, 72:28 er.

Major diastereomer (*R,R*)-**3af**: ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.33 (m, 4H), 7.30 – 7.09 (m, 8H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 2H), 6.04 – 5.86 (m, 1H), 5.32 – 5.15 (m, 2H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.13 (brs, 1H), 3.87 (dd, *J* = 7.6, 2.4 Hz, 1H), 3.69 (ddd, *J* = 8.0, 6.0, 2.4 Hz, 1H), 2.97 (dd, *J*_{AB} = 13.6, 8.0 Hz, 1H), 2.89 (dd, *J*_{BA} = 13.6, 8.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 139.3, 138.5, 136.6, 129.4, 129.3, 128.6, 128.5, 128.2, 127.8, 126.2, 118.8, 117.1, 113.2, 79.4, 70.5, 58.9, 37.4.

Minor diastereomer: ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 4H), 7.27 – 7.21 (m, 3H), 7.21 – 7.06 (m, 5H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.56 – 6.46 (m, 2H), 5.94 – 5.81 (m, 1H), 5.40 – 5.29 (m, 2H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 3.94 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.84 – 3.66 (m, 2H), 3.03 (dd, *J*_{AB} = 14.4, 4.4 Hz, 1H), 2.90 (dd, *J*_{BA} = 14.4, 7.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 139.1, 138.6, 136.4, 129.5, 129.3, 128.5, 128.3, 127.8, 127.6, 126.2, 118.9, 117.5, 113.9, 81.2, 70.9, 58.5, 35.8.



***N*-(3-(4-Methoxybenzyloxy)-1-phenylpent-4-en-2-yl)aniline (3ag)**

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 1:1) furnished two separable diastereoisomers of the title compound

(Combined yield: 30.1 mg, 81%) as light brown oils (3.8:1 ratio as determined by ^1H NMR).

HRMS ($\text{C}_{25}\text{H}_{28}\text{O}_2\text{N}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 374.2115, found: 374.2112.

Major diastereomer (*R,R*)-**3ag**: ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 2H), 7.25 – 7.08 (m, 7H), 6.97 – 6.92 (m, 2H), 6.66 (tt, $J = 7.2, 1.2$ Hz, 1H), 6.60 – 6.55 (m, 2H), 5.93 (ddd, $J = 17.2, 10.4, 7.6$ Hz, 1H), 5.25 (ddd, $J = 10.4, 1.6, 0.8$ Hz, 1H), 5.18 (ddd, $J = 17.2, 1.6, 0.8$ Hz, 1H), 4.60 (d, $J = 11.2$ Hz, 1H), 4.29 (d, $J = 11.2$ Hz, 1H), 4.12 (brs, 1H), 3.85 (s, 3H), 3.84 (dt, $J = 2.4, 0.8$ Hz, 1H), 3.66 (ddd, $J = 8.4, 6.0, 2.4$ Hz, 1H), 3.00 – 2.82 (m, 2H).

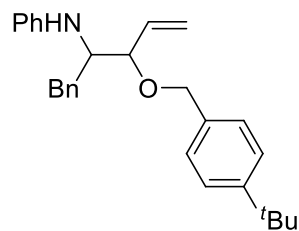
^{13}C NMR (101 MHz, CDCl_3) δ 159.5, 147.6, 139.3, 136.7, 130.6, 129.8, 129.4, 129.3, 128.5, 126.2, 118.6, 117.1, 114.0, 113.2, 78.9, 70.1, 58.9, 55.4, 37.4.

HPLC (CHIRALPAK[®] AD-3, *n*-heptane/ethanol = 97:3, 0.5 mL/min), t (*syn*, minor) = 5.52 min, t (*syn*, major) = 6.32 min, 92:8 er; $[\alpha]_D^{25} = -5.8$ (CH_2Cl_2 , $c = 0.4$).

Minor diastereomer: ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.20 (m, 4H), 7.20 – 7.14 (m, 3H), 7.13 – 7.07 (m, 2H), 6.90 – 6.84 (m, 2H), 6.65 (tt, $J = 7.2, 1.2$ Hz, 1H), 6.53 – 6.47 (m, 2H), 5.87 (ddd, $J = 16.8, 11.2, 7.2$ Hz, 1H), 5.39 – 5.29 (m, 2H), 4.56 (d, $J = 11.2$ Hz, 1H), 4.25 (d, $J = 11.2$ Hz, 1H), 3.91 (ddd, $J = 7.2, 4.4, 1.2$ Hz, 1H), 3.82 (s, 3H), 3.76 (dt, $J = 7.2, 4.4$ Hz, 2H), 3.00 (dd, $J = 14.2, 4.4$ Hz, 1H), 2.87 (dd, $J = 14.2, 7.6$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.3, 147.6, 139.1, 136.5, 130.6, 129.5, 129.4, 129.3, 128.3, 126.2, 118.7, 117.4, 113.9, 113.9, 80.8, 70.6, 58.4, 55.4, 35.8.

HPLC (CHIRALPAK[®] AD-3, *n*-heptane/ethanol = 97:3, 0.5 mL/min), t (*anti*, minor) = 5.89 min, t (*anti*, major) = 6.27 min, 75:25 er; $[\alpha]_D^{25} = -11.0$ (CH_2Cl_2 , $c = 0.1$).



***N*-(3-(4-*Tert*-butylbenzyloxy)-1-phenylpent-4-en-2-yl)aniline (3ah)**

Prepared according to the general procedure C. Flash column chromatography (SiO_2 , Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 32.2 mg, 81%) as light brown oils (4.5:1 ratio as determined by ^1H NMR).

HRMS ($\text{C}_{28}\text{H}_{28}\text{ON}$; $[\text{M}+\text{H}]^+$, pAPCI): calcd: 394.2165, found: 394.2167.

Major diastereomer (*R,R*)-**3ah**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 – 7.42 (m, 2H), 7.40 – 7.32 (m, 2H), 7.27 – 7.22 (m, 2H), 7.22 – 7.08 (m, 5H), 6.67 (t, $J = 7.2$ Hz, 1H), 6.60 (d, $J = 7.6$ Hz, 2H), 6.00 – 5.87 (m, 1H), 5.30 – 5.15 (m, 2H), 4.65 (d, $J = 11.6$ Hz, 1H), 4.33 (d, $J = 11.6$ Hz, 1H), 4.16 (brs, 1H), 3.86 (dd, $J = 7.6, 2.0$ Hz, 1H), 3.74 – 3.57 (m, 1H), 2.96 (dd, $J = 13.6, 8.0$ Hz, 1H), 2.89 (dd, $J = 13.6, 5.6$ Hz, 1H), 1.38 (s, 9H).

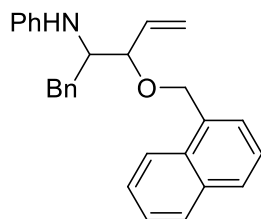
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.9, 147.6, 139.4, 136.7, 135.5, 129.4, 129.3, 128.5, 128.1, 126.2, 125.5, 118.6, 117.1, 113.2, 79.0, 70.3, 58.9, 37.4, 34.7, 31.5.

HPLC (CHIRALPAK[®] OD-3, *n*-heptane/2-isopropanol = 99.5:0.5, 0.5 mL/min), t (*syn*, minor) = 8.13 min, t (*syn*, major) = 9.47 min, 90:10 er; $[\alpha]_D^{25} = +8.2$ (CH_2Cl_2 , $c = 0.45$).

Minor diastereomer: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 – 7.35 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 7.21 – 7.16 (m, 3H), 7.13 – 7.06 (m, 2H), 6.65 (t, $J = 7.6$ Hz, 1H), 6.49 (d, $J = 7.6$ Hz, 2H), 5.95 – 5.82 (m, 1H), 5.41 – 5.31 (m, 2H), 4.62 (d, $J = 11.6$ Hz, 1H), 4.29 (d, $J = 11.6$ Hz, 1H), 3.93 (dd, $J = 7.2, 4.4$ Hz, 1H), 3.77 (dt, $J = 8.8, 4.4$ Hz, 2H), 3.02 (dd, $J = 14.0, 4.4$ Hz, 1H), 2.90 (dd, $J = 14.0, 7.6$ Hz, 1H), 1.34 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.7, 147.6, 139.1, 136.5, 135.5, 129.6, 129.3, 128.3, 127.7, 126.2, 125.4, 118.8, 117.5, 113.9, 81.0, 70.7, 58.6, 35.7, 34.6, 31.5.

HPLC (CHIRALPAK[®] AD-3, *n*-heptane/2-isopropanol = 99.7:0.3, 0.5 mL/min), t (*anti*, major) = 8.85 min, t (*anti*, minor) = 9.81 min, 69:31 er; $[\alpha]_D^{25} = -2.0$ (CH_2Cl_2 , $c = 0.1$).



***N*-(3-(Naphthalen-1-ylmethoxy)-1-phenylpent-4-en-2-yl)aniline (3ai)**

Prepared according to the general procedure C. Flash column chromatography (SiO_2 , Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 30.1 mg, 77%) as light brown oils (4.7:1 ratio as determined by $^1\text{H NMR}$).

HRMS ($\text{C}_{28}\text{H}_{28}\text{ON}$; $[\text{M}+\text{H}]^+$, pAPCI): calcd: 394.2165, found: 394.2167.

Major diastereomer (*R,R*)-**3ai**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.4$ Hz, 1H), 7.98 – 7.91 (m, 1H), 7.89 (dd, $J = 7.2, 2.4$ Hz, 1H), 7.64 – 7.52 (m, 2H), 7.52 – 7.42 (m, 2H), 7.20 – 7.07 (m,

5H), 6.86 (dd, $J = 7.4, 2.0$ Hz, 2H), 6.65 (t, $J = 7.4$ Hz, 1H), 6.54 (d, $J = 7.6$ Hz, 2H), 6.02 (ddd, $J = 17.6, 10.4, 8.0$ Hz, 1H), 5.32 (dd, $J = 10.4, 1.6$ Hz, 1H), 5.25 (d, $J = 17.6$ Hz, 1H), 5.23 (d, $J = 12.0$, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.14 (brs, 1H), 3.90 (dd, $J = 8.0, 2.4$ Hz, 1H), 3.64 (td, $J = 7.2, 2.4$ Hz, 1H), 2.81 (d, $J = 7.2$ Hz, 2H).

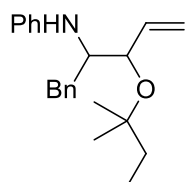
^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 139.2, 136.6, 134.0, 133.9, 132.2, 129.4, 129.2, 128.8, 128.7, 128.4, 127.1, 126.4, 126.1, 126.0, 125.3, 124.5, 119.0, 117.1, 113.2, 78.9, 68.7, 58.9, 37.3.

HPLC (CHIRALPAK[®] AD-3, *n*-heptane/2-isopropanol = 99.5:0.5, 0.5 mL/min), t (*syn*, major) = 13.18 min, t (*syn*, minor) = 14.22 min, 92:8 er; $[\alpha]_D^{25} = -9.8$ (CH_2Cl_2 , $c = 0.36$).

Minor diastereomer: **^1H NMR** (400 MHz, CDCl_3) δ 8.17 – 8.11 (m, 1H), 7.90 (dd, $J = 7.4, 2.0$ Hz, 1H), 7.81 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.62 – 7.50 (m, 2H), 7.46 – 7.36 (m, 2H), 7.24 – 7.10 (m, 5H), 7.07 – 7.00 (m, 2H), 6.61 (t, $J = 7.6$ Hz, 1H), 6.34 – 6.22 (m, 2H), 6.04 – 5.86 (m, 1H), 5.45 – 5.34 (m, 2H), 5.14 (d, $J = 12.0$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.04 (dd, $J = 7.2, 4.0$ Hz, 1H), 3.75 (dt, $J = 8.4, 4.4$ Hz, 1H), 3.69 (brs, 1H), 3.00 (dd, $J = 14.4, 4.4$ Hz, 1H), 2.83 (dd, $J = 14.4, 8.0$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.4, 139.2, 136.4, 134.0, 133.9, 132.0, 129.5, 129.2, 128.8, 128.7, 128.3, 126.8, 126.3, 126.1, 125.9, 125.3, 124.2, 118.9, 117.3, 113.8, 81.0, 69.3, 58.5, 35.7.

HPLC (CHIRALPAK[®] AD-3, *n*-heptane/2-isopropanol = 99.5:0.5, 0.5 mL/min), t (*anti*, major) = 6.97 min, t (*anti*, minor) = 8.22 min, 76:24 er; $[\alpha]_D^{25} = -12.2$ (CH_2Cl_2 , $c = 0.07$).



***N*-(3-(*Tert*-pentyloxy)-1-phenylpent-4-en-2-yl)aniline (3aj)**

Prepared according to the general procedure C. Flash column chromatography (SiO_2 , Pentanes/Dichloromethane – 4:1) furnished two separable diastereoisomers of the title compound (Combined yield: 17.0 mg, 53%) as colorless oils (4.5:1 ratio as determined by ^1H NMR). **HRMS** ($\text{C}_{22}\text{H}_{30}\text{ON}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 324.2322, found: 324.2318.

Major diastereomer (*R,R*)-**3aj**: **^1H NMR** (400 MHz, CDCl_3) δ 7.29 – 7.26 (m, 1H), 7.26 – 7.24 (m, 3H), 7.22 – 7.15 (m, 1H), 7.15 – 7.09 (m, 2H), 6.63 (tt, $J = 7.6, 1.2$ Hz, 1H), 6.59 – 6.51 (m, 2H), 6.03 – 5.91 (m, 1H), 5.10 (dddd, $J = 14.0, 4.0, 2.0, 1.2$ Hz, 2H), 4.13 (ddt, $J = 7.2, 3.2, 1.1$ Hz,

1H), 3.95 (brs, 1H), 3.68 (ddd, $J = 8.4, 5.2, 3.2$ Hz, 1H), 3.08 (dd, $J = 14.0, 5.2$ Hz, 1H), 2.60 (dd, $J = 14.0, 8.0$ Hz, 1H), 1.63 – 1.45 (m, 3H), 1.18 (s, 3H), 1.14 (s, 3H), 0.95 (t, $J = 7.2$ Hz, 3H).

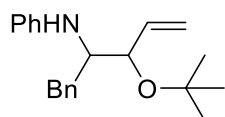
^{13}C NMR (101 MHz, CDCl_3) δ 147.7, 140.1, 140.0, 129.4, 129.1, 128.4, 126.1, 117.0, 115.7, 113.4, 72.7, 59.8, 36.8, 35.1, 26.3, 25.7, 8.7.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-propanol = 100:0, 0.5 mL/min), *t* (*syn*, major) = 20.05 min, *t* (*syn*, minor) = 23.84 min, 96:4 er; $[\alpha]_D^{25} = +36.0$ (CH_2Cl_2 , *c* = 0.2).

Minor diastereomer: **^1H NMR** (400 MHz, CDCl_3) δ 7.25 – 7.21 (m, 4H), 7.21 – 7.14 (m, 1H), 7.14 – 7.08 (m, 2H), 6.63 (tt, $J = 7.6, 1.2$ Hz, 1H), 6.56 – 6.49 (m, 2H), 5.98 (ddd, $J = 17.2, 10.4, 6.0$ Hz, 1H), 5.35 – 5.25 (m, 1H), 5.20 (ddd, $J = 10.4, 1.2$ Hz, 1H), 4.20 (ddd, $J = 6.0, 2.8, 1.2$ Hz, 1H), 3.86 (s, 1H), 3.64 (ddd, $J = 8.8, 4.8, 2.8$ Hz, 1H), 2.94 (dd, $J = 14.4, 4.8$ Hz, 1H), 2.77 (dd, $J = 14.4, 8.8$ Hz, 1H), 1.44 (qd, $J = 7.6, 5.4$ Hz, 2H), 1.02 (s, 3H), 0.99 (s, 3H), 0.88 (t, $J = 7.6$, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.7, 140.5, 140.0, 129.3, 129.2, 128.3, 126.1, 117.1, 115.6, 113.6, 73.1, 60.1, 35.9, 35.1, 25.9, 25.5, 8.8.

HPLC (CHIRALPAK[®] OJ-3R, $\text{H}_2\text{O}/\text{MeCN} = 35:65$, 1 mL/min), *t* (*anti*, major) = 6.00 min, *t* (*anti*, minor) = 6.97 min, 90:10 er; $[\alpha]_D^{25} = +26.8$ (CH_2Cl_2 , *c* = 0.056).



N-(3-(*Tert*-butoxy)-1-phenylpent-4-en-2-yl)aniline (**3ak**)

Prepared according to the general procedure C. Flash column chromatography (SiO_2 , Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 17.6 mg, 57%) as light brown oils (5.7:1 ratio as determined by ^1H NMR).

HRMS ($\text{C}_{21}\text{H}_{28}\text{ON}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 310.2165, found: 310.2162.

Major diastereomer (*R,R*)-**3ak**: **^1H NMR** (400 MHz, CDCl_3) δ 7.31 – 7.23 (m, 5H), 7.22 – 7.15 (m, 1H), 7.15 – 7.09 (m, 2H), 6.63 (tt, $J = 7.2, 1.2$ Hz, 1H), 6.61 – 6.52 (m, 2H), 6.04 – 5.90 (m, 1H), 5.17 – 5.07 (m, 2H), 4.12 (ddt, $J = 7.2, 3.2, 1.2$ Hz, 1H), 3.96 (brs, 1H), 3.68 (ddd, $J = 8.4, 5.6, 3.2$ Hz, 1H), 3.04 (dd, $J = 14.0, 5.6$ Hz, 1H), 2.64 (dd, $J = 14.0, 8.0$ Hz, 1H), 1.23 (s, 9H).

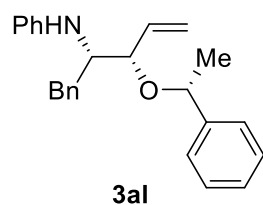
^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 140.3, 140.0, 129.3, 129.1, 128.4, 126.1, 117.0, 115.7, 113.4, 74.6, 73.1, 59.7, 36.8, 29.0.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-isopropanol = 100:0, 0.5 mL/min), *t* (*syn*, major) = 22.07 min, *t* (*syn*, minor) = 27.77 min, 96:4 er; $[\alpha]_D^{25} = +28.1$ (CH_2Cl_2 , *c* = 0.26).

Minor diastereomer: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 – 7.22 (m, 4H), 7.20 – 7.14 (m, 1H), 7.14 – 7.08 (m, 2H), 6.63 (tt, $J = 7.6, 1.2$ Hz, 1H), 6.57 – 6.49 (m, 2H), 5.98 (ddd, $J = 17.2, 10.4, 6.0$ Hz, 1H), 5.31 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.22 (dt, $J = 10.4, 1.6$ Hz, 1H), 4.20 (ddt, $J = 6.0, 2.8, 1.2$ Hz, 1H), 3.87 (brs, 1H), 3.64 (ddd, $J = 9.2, 4.8, 2.8$ Hz, 1H), 2.93 (dd, $J = 14.4, 4.8$ Hz, 1H), 2.76 (dd, $J = 14.4, 8.8$ Hz, 1H), 1.10 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.7, 140.4, 140.0, 129.3, 129.2, 128.3, 126.1, 117.1, 115.7, 113.6, 74.6, 73.4, 59.8, 35.8, 28.8.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 100:0, 0.5 mL/min), *t* (*syn*, major) = 22.43 min, *t* (*syn*, minor) = 27.18 min, 93:7 er; $[\alpha]_D^{25} = -7.8$ (CH_2Cl_2 , *c* = 0.09).



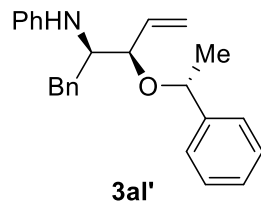
N-((2S,3S)-1-Phenyl-3-((R)-1-phenylethoxy)pent-4-en-2-yl)aniline (3al)

Prepared according to the general procedure C, using *ent-L* as the ligand. Flash column chromatography (SiO_2 , Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 29.7 mg, 83%) as light brown oils (7.3:1 ratio as determined by $^1\text{H NMR}$). (for the major isomer the diastereoselectivity is >20:1 ratio and for the minor isomer the diastereoselectivity is 12:1 ratio as determined by $^1\text{H NMR}$).

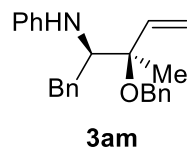
HRMS ($\text{C}_{28}\text{H}_{28}\text{ON}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 358.2165, found: 358.2161.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 – 7.32 (m, 5H), 7.18 – 7.03 (m, 5H), 6.93 – 6.85 (m, 2H), 6.62 (t, $J = 7.2$ Hz, 1H), 6.45 (d, $J = 7.6$ Hz, 2H), 5.90 (ddd, $J = 17.6, 10.4, 7.6$ Hz, 1H), 5.23 (dd, $J = 10.4, 1.2$ Hz, 1H), 5.11 (d, $J = 17.6$ Hz, 1H), 4.50 (q, $J = 6.4$ Hz, 1H), 4.10 (brs, 1H), 3.74 (dd, $J = 7.6, 2.0$ Hz, 1H), 3.53 (td, $J = 6.8, 2.4$ Hz, 1H), 2.87 (dd, $J = 14.0, 7.2$ Hz, 1H), 2.72 (dd, $J = 14.0, 6.4$ Hz, 1H), 1.52 (d, $J = 6.4$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.6, 143.6, 139.4, 136.8, 129.3, 129.2, 128.6, 128.3, 127.9, 127.2, 126.0, 118.2, 116.9, 113.1, 75.1, 58.8, 37.1, 30.4, 24.1.



When **L** was used as the ligand, the **3al'** (Combined yield: 21.5 mg, 60%) as light brown oils (7.1:1 ratio as determined by ¹H NMR). (for the major isomer the diastereoselectivity is 2.2:1 ratio and for the minor isomer the diastereoselectivity is 2:1 ratio as determined by ¹H NMR).



N-(2-(benzyloxy)-2-methylbut-3-en-1-yl)aniline (**3am**)

Prepared according to the general procedure C, using [**PC1**] as photocatalyst. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 2:1) furnished the title compound (Combined yield: 13.3 mg, 37%) as colorless oils.

HRMS (C₂₅H₂₈ON; [M+H]⁺, pESI): calcd: 358.2165, found: 358.2163.

Major diastereomer (*R,R*)-**3am**: **¹H NMR** (400 MHz, CDCl₃) δ 7.42 – 7.28 (m, 5H), 7.25 – 7.17 (m, 4H), 7.16 – 7.07 (m, 1H), 7.04 – 6.96 (m, 2H), 6.55 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 2H), 6.15 – 6.00 (m, 1H), 5.41 – 5.27 (m, 2H), 4.59 – 4.44 (m, 2H), 4.00 (brs, 1H), 3.66 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.27 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.78 (dd, *J* = 14.0, 9.6 Hz, 1H), 1.46 (s, 3H).

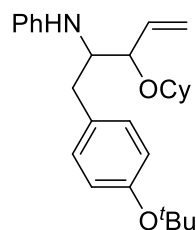
¹³C NMR (101 MHz, CDCl₃) δ 149.1, 141.6, 140.3, 139.7, 129.5, 129.0, 128.4, 128.2, 127.2, 127.0, 125.9, 116.7, 116.6, 113.0, 81.9, 64.8, 64.2, 37.7, 20.1.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/isopropanol = 330:1, 0.5 mL/min), *t* (minor) = 20.26 min, *t* (major) = 29.64 min, 95:5 er; [α]_D²⁵ = +50.0 (CH₂Cl₂, *c* = 0.09).

Minor diastereomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.39 – 7.26 (m, 5H), 7.23 – 7.14 (m, 4H), 7.13 – 7.06 (m, 1H), 7.04 – 6.92 (m, 2H), 6.53 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 2H), 6.05 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.35 (ddd, *J* = 18.8, 14.4, 1.2 Hz, 2H), 4.56 – 4.40 (m, 2H), 3.73 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.72 (brs, 1H), 3.40 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.57 (dd, *J* = 14.0, 9.6 Hz, 1H), 1.44 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.8, 140.5, 140.2, 139.7, 129.5, 129.1, 128.4, 128.2, 127.2, 127.1, 125.9, 117.9, 116.7, 113.1, 81.6, 65.0, 63.4, 37.9, 20.0.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/isopropanol = 330:1, 0.5 mL/min), *t* (major) = 19.79 min, *t* (minor) = 25.25 min, 89:11 er; [α]_D²⁵ = -7.0 (CH₂Cl₂, c = 0.09).



***N*-(1-(4-(*Tert*-butoxy)phenyl)-3-(cyclohexyloxy)pent-4-en-2-yl)aniline (3ba)**

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Et₂O – 30:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 28.7 mg, 70%) as colorless oils (3.8:1 ratio as determined by ¹H NMR). **HRMS** (C₂₇H₃₈O₂N; [M+H]⁺, pAPCI): calcd: 408.2897, found: 408.2899.

Major diastereomer (*R,R*)-**3ba**: **¹H NMR** (400 MHz, CDCl₃) δ 7.14 – 7.10 (m, 4H), 6.94 – 6.82 (m, 2H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 2H), 5.95 – 5.80 (m, 1H), 5.20 – 4.96 (m, 2H), 4.12 (brs, 1H), 3.91 (dd, *J* = 7.6, 2.4 Hz, 1H), 3.64 – 3.55 (m, 1H), 3.41 – 3.21 (m, 1H), 2.90 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.81 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.90 – 1.66 (m, 4H), 1.55 – 1.53 (m, 1H), 1.43 – 1.35 (m, 1H), 1.33 (s, 9H), 1.31 – 1.18 (m, 4H).

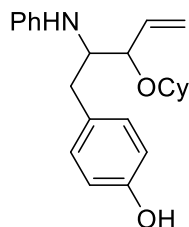
¹³C NMR (101 MHz, CDCl₃) δ 153.7, 147.9, 141.7, 138.2, 134.5, 129.7, 129.3, 124.2, 117.2, 116.9, 113.2, 78.3, 77.45, 75.0, 59.2, 36.9, 33.7, 31.9, 28.9, 26.0, 24.3, 24.2.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-isopropanol = 99.7:0.3, 0.5 mL/min), *t* (*syn*, major) = 7.14 min, *t* (*syn*, minor) = 7.77 min, 96:4 er; [α]_D²⁵ = +16.8 (CH₂Cl₂, c = 0.31).

Minor diastereomer : **¹H NMR** (400 MHz, CDCl₃) δ 7.14 – 7.04 (m, 4H), 6.89 – 6.81 (m, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.54 – 6.47 (m, 2H), 5.83 (ddd, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.25 (ddt, *J* = 19.2, 10.4, 1.6 Hz, 2H), 4.06 – 3.98 (m, 1H), 3.85 (brs, 1H), 3.64 (dt, *J* = 8.4, 4.0 Hz, 1H), 3.23 (td, *J* = 8.8, 4.4 Hz, 1H), 2.94 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.74 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.87 – 1.61 (m, 4H), 1.49 (d, *J* = 5.3 Hz, 1H), 1.39 – 1.32 (m, 1H), 1.30 (s, 9H), 1.27 – 1.13 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 153.6, 147.9, 137.9, 134.6, 129.7, 129.2, 124.1, 117.2, 117.1, 113.9, 79.1, 78.2, 75.7, 59.2, 35.4, 33.6, 31.9, 28.9, 25.9, 24.3, 24.2.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-isopropanol = 99.7:0.3, 0.5 mL/min), *t* (*syn*, minor) = 8.49 min, *t* (*syn*, major) = 9.19 min, 89:11 er; [α]_D²⁵ = -20.7 (CH₂Cl₂, c = 0.092).



4-(3-(Cyclohexyloxy)-2-(phenylamino)pent-4-enyl)phenol (3ca)

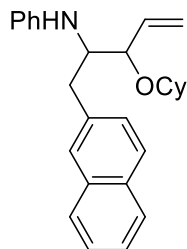
Prepared according to the general procedure C, using [PC1] as photocatalyst and run in 0.2 mmol scale. Flash column chromatography (SiO₂, Pentanes/Et₂O – 5:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 44.3 mg, 63%) as colorless oils (5:1 ratio as determined by ¹H NMR).

HRMS (C₁₇H₂₆ON; [M+H]⁺, pAPCI): calcd: 352.2271, found: 352.2270.

HPLC (CHIRALPAK[®] LA-2, *n*-heptane/2-propanol = 99.8:0.2, 0.3 mL/min), *t* (*syn*, minor) = 92.28 min, *t* (*syn*, major) = 100.29 min, 96:4 er; *t* (*anti*, major) = 118.13 min, *t* (*anti*, minor) = 122.29 min, 90:10 er; [α]_D²⁵ = -2.0 (CH₂Cl₂, c = 1.8).

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.07 (m, 4H), 6.79 – 6.68 (m, 2H), 6.67 – 6.63 (m, 1H), 6.59 – 6.52 (m, 2H), 5.94 – 5.78 (m, 1H), 5.26 (minor, ddt, *J* = 15.6, 10.4, 1.6 Hz, 0.37H), 5.18 – 5.07 (major, m, 1.71H), 4.44 (brs, 2H), 4.05 – 4.00 (minor, m, 0.2H), 3.93 (major, dd, *J* = 7.6, 2.4 Hz, 0.87H), 3.69 – 3.51 (m, 1H), 3.39 – 3.29 (major, m, 0.86H), 3.23 (minor, m, 0.19H), 2.96 – 2.66 (m, 2H), 1.79 (m, 4H), 1.55 (m, 1H), 1.39 – 1.22 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 153.9, 153.87, 147.84, 147.81, 138.1, 137.9, 131.8, 131.78, 131.77, 130.5, 130.4, 130.1, 129.4, 129.3, 117.3, 117.27, 117.2, 116.9, 115.4, 115.2, 113.9, 113.2, 78.9, 75.8, 75.1, 59.2, 59.1, 36.4, 34.8, 33.7, 33.6, 32.0, 31.9, 30.4, 25.9, 25.9, 24.3, 24.3, 24.21, 24.18.



***N*-(3-(Cyclohexyloxy)-1-(naphthalen-2-yl)pent-4-en-2-yl)aniline (3da)**

Prepared according to the general procedure C, using [PC1] as photocatalyst and run in 0.2 mmol scale. Flash column chromatography (SiO₂, Pentanes/DCM – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 56.8 mg, 74%) as colorless oils (4.2:1 ratio as determined by ¹H NMR).

HRMS (C₂₇H₃₁ON; [M+H]⁺, pESI): calcd: 386.2478, found: 386.2482.

Major diastereomer (*R,R*)-**3da**: **¹H NMR** (400 MHz, CDCl₃) δ 7.87 – 7.76 (m, 3H), 7.70 (s, 1H), 7.51 – 7.38 (m, 3H), 7.20 – 7.14 (m, 2H), 6.72 – 6.63 (m, 3H), 5.92 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.18 – 5.04 (m, 2H), 3.96 (ddt, *J* = 7.6, 2.4, 0.8 Hz, 1H), 3.78 (ddd, *J* = 8.0, 6.0, 2.4 Hz, 1H), 3.36 (tt, *J* = 9.2, 3.6 Hz, 1H), 3.13 (dd, *J* = 14.0, 8.0 Hz, 1H), 3.09 – 2.99 (m, 1H), 1.94 – 1.74 (m, 4H), 1.59 – 1.52 (m, 1H), 1.48 – 1.34 (m, 2H), 1.33 – 1.24 (m, 3H).

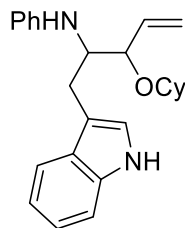
¹³C NMR (101 MHz, CDCl₃) δ 147.7, 138.1, 137.2, 133.7, 132.3, 129.4, 128.1, 127.8, 127.72, 127.70, 127.6, 126.0, 125.4, 117.4, 117.1, 113.3, 77.2, 75.0, 59.0, 37.4, 33.7, 32.0, 26.0, 24.3, 24.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99:1, 0.15 mL/min), *t* (*syn*, minor) = 23.08 min, *t* (*syn*, major) = 24.39 min, 96:4 er; [α]_D²⁵ = +38.9 (CH₂Cl₂, c = 0.75).

Minor diastereomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.71 (m, 3H), 7.67 (s, 1H), 7.47 – 7.37 (m, 3H), 7.14 – 7.07 (m, 2H), 6.64 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.60 – 6.53 (m, 2H), 5.89 (ddd, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.31 (ddd, *J* = 17.2, 1.6, 1.2 Hz, 1H), 5.26 (ddd, *J* = 10.4, 1.6, 1.2 Hz, 1H), 4.07 (ddt, *J* = 6.4, 3.6, 1.2 Hz, 1H), 3.93 (brs, 1H), 3.80 (dt, *J* = 8.4, 4.0 Hz, 1H), 3.30 – 3.21 (m, 1H), 3.21 – 3.12 (m, 1H), 2.97 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.86 – 1.66 (m, 4H), 1.56 – 1.49 (m, 1H), 1.43 – 1.35 (m, 1H), 1.27 – 1.18 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 138.0, 137.3, 133.6, 132.2, 129.3, 128.0, 127.8, 127.7, 127.6, 125.9, 125.2, 117.4, 117.3, 114.0, 78.9, 75.8, 58.9, 35.8, 33.7, 32.0, 25.9, 24.3, 24.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99:1, 0.15 mL/min), *t* (*syn*, minor) = 25.69 min, *t* (*syn*, major) = 28.21 min, 87:14 er; [α]_D²⁵ = +6.5 (CH₂Cl₂, c = 0.15).



***N*-(3-(Cyclohexyloxy)-1-(1*H*-indol-3-yl)pent-4-en-2-yl)aniline (3ea)**

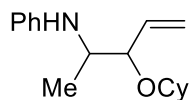
Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Et₂O – 5:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 22.1 mg, 59%) as colorless oils (3.6:1 ratio as determined by ¹H NMR).

HRMS (C₂₅H₃₁ON₂; [M+H]⁺, pESI): calcd: 375.2431, found: 375.2431.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-propanol = 99:1, 0.5 mL/min), *t* (*syn*, major) = 60.17 min, *t* (*syn*, minor) = 81.46 min, 96:4 er; *t* (*anti*, major) = 78.47 min, *t* (*anti*, minor) = 74.75 min, 92:8 er.

¹H NMR (400 MHz, CDCl₃) δ 7.92 (major, brs, 0.69H), 7.88 (minor, brs, 0.24H), 7.69 (major, d, *J* = 7.6 Hz, 0.79H), 7.62 (minor, d, *J* = 7.6 Hz, 0.23H), 7.37 – 7.32 (m, 1H), 7.23 – 7.07 (m, 4H), 7.03 – 6.99 (m, 1H), 6.68 – 6.49 (m, 3H), 6.00 – 5.84 (m, 1H), 5.38 – 5.24 (minor, m, 0.46H), 5.17 – 5.08 (major, m, 1.62H), 4.22 – 4.00 (m, 2H), 3.92 – 3.75 (m, 1H), 3.41 – 3.31 (major, m, 0.82H), 3.27 (minor, td, *J* = 9.0, 4.3 Hz, 0.24H), 3.21 – 3.10 (m, 1H), 2.97 – 2.89 (m, 1H), 1.93 – 1.69 (m, 4H), 1.54 – 1.52 (m, 1H), 1.38 – 1.21 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 148.1, 148.05, 138.1, 136.4, 136.2, 129.4, 129.3, 128.0, 122.3, 122.26, 122.1, 121.9, 119.4, 119.3, 119.0, 118.9, 117.2, 117.1, 117.0, 116.8, 113.7, 113.7, 113.3, 111.2, 111.1, 79.2, 77.8, 75.2, 58.0, 57.6, 33.7, 33.66, 32.02, 31.99, 30.5, 30.4, 27.0, 26.0, 25.95, 25.4, 24.3, 24.2.



***N*-(3-(Cyclohexyloxy)pent-4-en-2-yl)aniline (3fa)**

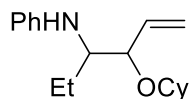
Prepared according to the general procedure C, using [PC1] as photocatalyst and run in 0.2 mmol scale. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 22.5 mg, 41%) as colorless oils (3.1:1 ratio as determined by ¹H NMR).

HRMS (C₁₇H₂₆ON; [M+H]⁺, pESI): calcd: 260.2009, found: 260.2007.

HPLC (CHIRALPAK[®] LA-2, *n*-heptane/2-propanol = 99.8:0.2, 0.3 mL/min), *t* (*syn*, major) = 11.13 min, *t* (*syn*, minor) = 13.1 min, 94:6 er; *t* (*anti*, major) = 13.92 min, *t* (*anti*, minor) = 15.63 min, 86:14 er; [α]_D²⁵ = -2.0 (CH₂Cl₂, c = 1.8).

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.09 (m, 2H), 6.73 – 6.55 (m, 3H), 5.87 – 5.76 (m, 1H), 5.31 – 5.16 (m, 2H), 3.99 (minor, dd, *J* = 6.4, 3.6 Hz, 0.27H), 3.89 (major, dd, *J* = 7.6, 3.6 Hz, 1.71H), 3.60 – 3.50 (m, 1H), 3.37 – 3.29 (major, m, 0.81H), 3.26 – 3.21 (minor, m, 0.24H), 1.97 – 1.63 (m, 5H), 1.39 – 1.26 (m, 5H), 1.19 (major, d, *J* = 6.4 Hz, 2.61H), 1.15 (minor, d, *J* = 6.4 Hz, 0.67H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 147.5, 138.2, 137.5, 129.4, 129.3, 125.6, 117.7, 117.3, 117.1, 116.8, 113.9, 113.5, 80.2, 79.7, 75.2, 52.5, 52.1, 33.64, 33.60, 31.9, 31.8, 30.4, 26.0, 24.3, 24.2, 24.1, 16.9, 14.8.



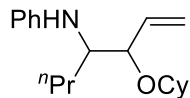
***N*-(4-(Cyclohexyloxy)hex-5-en-3-yl)aniline (3ga)**

Prepared according to the general procedure C, using [PC1] as photocatalyst. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 14.0 mg, 51%) as colorless oils (3.6:1 ratio as determined by ¹H NMR). Ee was determined after derivation, see in Transformation part.

HRMS (C₁₈H₂₈ON; [M+H]⁺, pESI): calcd: 274.2165, found: 274.2163.

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.09 (m, 2H), 6.70 – 6.53 (m, 3H), 5.92 – 5.72 (m, 1H), 5.32 – 5.11 (m, 2H), 3.97 (dd, *J* = 7.4, 3.2 Hz, 1H), 3.85 (brs, 1H), 3.37 – 3.26 (major, m, 1.72H), 3.26 – 3.16 (minor, m, 0.32H), 1.92 – 1.69 (m, 5H), 1.53 – 1.44 (m, 2H), 1.37 – 1.17 (m, 6H), 0.98 (major, t, *J* = 7.6 Hz, 2H), 0.97 (minor, t, *J* = 7.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 148.5, 148.4, 138.3, 138.0, 129.3, 117.1, 117.0, 116.7, 116.6, 113.7, 113.1, 79.5, 78.5, 75.6, 75.1, 58.9, 58.7, 33.6, 31.9, 31.8, 26.0, 25.9, 24.4, 24.3, 24.3, 24.13, 24.11, 22.8, 11.2, 11.1.



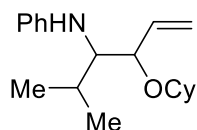
***N*-(3-(Cyclohexyloxy)hept-1-en-4-yl)aniline (3ha)**

Prepared according to the general procedure C, using [PC1] as photocatalyst in 0.2 mmol scale. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 3:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 28.2 mg, 49%) as colorless oils (4:1 ratio as determined by ¹H NMR). Ee was determined after derivation, see in Transformation part.

HRMS (C₁₉H₃₀ON; [M+H]⁺, pESI): calcd: 288.2322, found: 288.2321.

¹H NMR (400 MHz, CDCl₃) δ 7.18 – 7.10 (m, 2H), 6.69 – 6.55 (m, 3H), 5.89 – 5.77 (m, 1H), 5.30 – 5.13 (m, 2H), 4.00 – 3.94 (m, 1H), 3.82 (brs, 1H), 3.46 – 3.35 (m, 1H), 3.35 – 3.28 (major, m, 0.85H), 3.27 – 3.16 (minor, m, 0.22H), 1.89 – 1.61 (m, 6H), 1.56 – 1.45 (m, 2H), 1.43 – 1.32 (m, 3H), 1.26 – 1.18 (m, 3H), 0.96 – 0.89 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.41, 148.35, 138.3, 138.0, 129.3, 125.6, 117.1, 117.0, 116.6, 116.5, 113.7, 113.1, 79.5, 78.8, 75.8, 75.1, 57.2, 56.8, 33.8, 33.63, 33.61, 32.4, 31.99, 31.95, 31.8, 26.0, 25.9, 24.5, 24.3, 24.2, 24.1, 19.8, 14.29, 14.26.



N-((3R,4R)-4-(Cyclohexyloxy)-2-methylhex-5-en-3-yl)aniline (3ia)

Prepared according to the general procedure C, using [PC1] as photocatalyst. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 12.8 mg, 45%) as colorless oils (4:1 ratio as determined by ¹H NMR).

HRMS (C₁₉H₃₀ON; [M+H]⁺, pESI): calcd: 288.2322, found: 288.2320.

Major diastereomer (*R,R*)-**3ia**: **¹H NMR** (400 MHz, CDCl₃) δ 7.14 – 7.06 (m, 2H), 6.62 – 6.52 (m, 3H), 5.88 – 5.75 (m, 1H), 5.17 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.09 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.13 (brs, 1H), 4.06 (dd, *J* = 7.6, 2.4 Hz, 1H), 3.40 – 3.24 (m, 1H), 3.08 (dd, *J* = 7.6, 2.4 Hz, 1H), 1.97 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.90 – 1.64 (m, 4H), 1.53 – 1.48 (m, 1H), 1.33 – 1.21 (m, 5H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H).

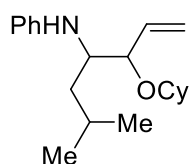
¹³C NMR (101 MHz, CDCl₃) δ 149.5, 139.0, 129.2, 116.7, 116.1, 112.8, 78.2, 74.5, 63.1, 33.7, 31.6, 31.1, 26.0, 24.3, 24.1, 20.3, 19.9.

HPLC (CHIRALPAK[®] LC-3, *n*-heptane/2-isopropanol = 100:0, 0.1 mL/min), *t* (*syn*, minor) = 33.9 min, *t* (*syn*, major) = 38.75 min, 95:5 er; [α]_D²⁵ = +12.5 (CH₂Cl₂, c = 0.2).

Minor diastereomer : **¹H NMR** (400 MHz, CDCl₃) δ 7.17 – 7.07 (m, 2H), 6.67 – 6.58 (m, 3H), 5.79 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.26 – 5.19 (m, 1H), 5.19 – 5.13 (m, 1H), 3.90 (t, *J* = 6.4 Hz, 1H), 3.69 (brs, 1H), 3.30 (dd, *J* = 6.0, 3.6 Hz, 1H), 3.25 (td, *J* = 8.8, 4.2 Hz, 1H), 2.19 – 2.11 (m, 1H), 1.77 – 1.67 (m, 4H), 1.51 – 1.47 (m, 1H), 1.33 – 1.20 (m, 5H), 0.98 (d, *J* = 3.6 Hz, 3H), 0.96 (d, *J* = 3.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.2, 138.5, 129.2, 117.0, 116.8, 113.6, 79.7, 75.2, 61.8, 33.6, 31.7, 28.8, 26.0, 24.2, 24.1, 21.4, 17.1.

HPLC (CHIRALPAK[®] LC-3, *n*-heptane/2-isopropanol = 100:0, 0.1 mL/min), *t* (*syn*, major) = 36.28 min, *t* (*syn*, minor) = 41.21 min, 74:26 er; [α]_D²⁵ = +19.4 (CH₂Cl₂, *c* = 0.062).



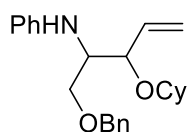
N-(3-(Cyclohexyloxy)-6-methylhept-1-en-4-yl)aniline (**3ja**)

Prepared according to the general procedure C, using [**PC1**] as photocatalyst. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 16.7 mg, 55%) as colorless oils (4.3:1 ratio as determined by ¹H NMR). *Ee* was determined after derivation, see in Transformation part.

HRMS (C₂₀H₃₂ON; [M+H]⁺, pESI): calcd: 302.2478, found: 302.2478.

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.10 (m, 2H), 6.70 – 6.54 (m, 3H), 5.88 – 5.75 (m, 1H), 5.29 – 5.12 (m, 2H), 4.02 – 3.99 (minor, m, 0.2H), 3.97 – 3.93 (m, 2H), 3.75 (brs, 1H), 3.52 (major, ddd, *J* = 8.4, 5.6, 2.8 Hz, 0.84H), 3.44 (minor, dt, *J* = 10.0, 3.6 Hz, 0.2H), 3.35 – 3.28 (major, m, 0.83H), 3.20 – 3.13 (minor, m, 0.2 H), 1.87 – 1.66 (m, 5H), 1.59 – 1.48 (m, 2H), 1.38 – 1.21 (m, 6H), 0.96 (major, d, *J* = 6.8 Hz, 2.6H), 0.94 (minor, d, *J* = 6.4 Hz, 0.8H), 0.91 (major, d, *J* = 6.8 Hz, 2.6H), 0.87 (minor, d, *J* = 6.4 Hz, 0.8H).

¹³C NMR (101 MHz, CDCl₃) δ 148.3, 138.4, 138.0, 129.39, 129.36, 117.04, 116.97, 116.6, 116.2, 113.7, 113.0, 79.4, 78.7, 76.0, 75.1, 55.6, 54.8, 40.5, 38.6, 33.6, 33.6, 32.0, 31.8, 30.4, 26.0, 25.9, 25.0, 24.8, 24.3, 24.21, 24.18, 24.1, 23.9, 23.2, 22.7, 21.9.



***N*-(1-(Benzyloxy)-3-(cyclohexyloxy)pent-4-en-2-yl)aniline (3ka)**

Prepared according to the general procedure C, using [PC1] as photocatalyst in 0.2 mmol scale. Flash column chromatography (SiO₂, Pentanes/DCM – 1:1) furnished two separable diastereoisomers of the title compound (Combined yield: 39.7 mg, 54%) as colorless oils (3.2:1 ratio as determined by ¹H NMR).

Major diastereomer (*R,R*)-3ka: ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.27 (m, 5H), 7.16 – 7.09 (m, 2H), 6.64 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.62 – 6.56 (m, 2H), 5.86 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.26 (ddd, *J* = 17.2, 2.0, 1.2 Hz, 1H), 5.14 (ddd, *J* = 10.4, 2.0, 1.2 Hz, 1H), 4.53 (dd, *J* = 3.6, 0.4 Hz, 2H), 4.28 – 4.22 (m, 1H), 4.12 (brs, 1H), 3.66 – 3.51 (m, 3H), 3.34 – 3.28 (m, 1H), 1.88 – 1.78 (m, 2H), 1.79 – 1.70 (m, 2H), 1.54 – 1.50 (m, 1H), 1.33 – 1.18 (m, 5H).

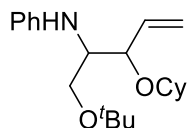
¹³C NMR (101 MHz, CDCl₃) δ 147.8, 138.4, 137.9, 129.3, 128.5, 127.9, 127.8, 117.0, 116.8, 113.0, 76.1, 75.5, 73.4, 69.0, 56.6, 33.6, 31.7, 25.9, 24.3, 24.1.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99.7:0.3, 0.5 mL/min), *t* (*syn*, minor) = 16.2 min, *t* (*syn*, major) = 19.25 min, 94:6 er; [α]_D²⁵ = -27.0 (CH₂Cl₂, *c* = 0.5).

Minor diastereomer: ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.28 (m, 5H), 7.18 – 7.10 (m, 2H), 6.67 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.65 – 6.60 (m, 2H), 5.86 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.28 (ddd, *J* = 17.2, 2.0, 1.2 Hz, 1H), 5.19 (ddd, *J* = 10.4, 2.0, 1.2 Hz, 1H), 4.56 – 4.48 (m, 2H), 4.09 (ddt, *J* = 7.2, 6.0, 1.2 Hz, 1H), 4.02 (brs, 1H), 3.72 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.64 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.59 (dt, *J* = 6.0, 4.4 Hz, 1H), 3.32 – 3.26 (m, 1H), 1.85 – 1.76 (m, 2H), 1.74 – 1.66 (m, 2H), 1.54 – 1.49 (m, 1H), 1.34 – 1.19 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 138.5, 137.7, 129.3, 128.4, 127.8, 127.7, 117.4, 117.1, 113.9, 77.78, 75.7, 73.4, 69.1, 57.3, 33.6, 31.8, 25.9, 24.3, 24.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99.7:0.3, 0.5 mL/min), *t* (*syn*, minor) = 15.21 min, *t* (*syn*, major) = 26.37 min, 81:19 er; [α]_D²⁵ = +14.9 (CH₂Cl₂, *c* = 0.19).



***N*-(1-(Tert-butoxy)-3-(cyclohexyloxy)pent-4-en-2-yl)aniline (3la)**

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Et₂O – 30:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 21.0 mg, 63%) as colorless oils (4.5:1 ratio as determined by ¹H NMR).

HRMS (C₂₁H₃₄O₂N; [M+H]⁺, pESI): calcd: 332.2584, found: 332.2580.

Major diastereomer (*R,R*)-**3la**: **¹H NMR** (400 MHz, CDCl₃) δ 7.17 – 7.09 (m, 2H), 6.66 – 6.57 (m, 3H), 5.88 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.25 (ddd, *J* = 17.4, 2.0, 1.2 Hz, 1H), 5.13 (ddd, *J* = 10.4, 2.0, 1.2 Hz, 1H), 4.23 (ddt, *J* = 7.2, 2.4, 1.2 Hz, 1H), 4.16 (s, 1H), 3.50 – 3.30 (m, 4H), 1.95 – 1.68 (m, 4H), 1.51 (d, *J* = 4.4 Hz, 1H), 1.37 – 1.22 (m, 5H), 1.19 (s, 9H).

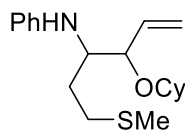
¹³C NMR (101 MHz, CDCl₃) δ 148.0, 138.3, 129.3, 116.7, 116.6, 112.9, 76.1, 75.5, 72.9, 60.1, 57.2, 33.7, 31.9, 27.7, 26.0, 24.4, 24.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99.9:0.1, 0.5 mL/min), *t* (*syn*, minor) = 6.83 min, *t* (*syn*, major) = 7.63 min, 95:5 er; [α]_D²⁵ = -28.4 (CH₂Cl₂, c = 0.25).

Minor diastereomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.18 – 7.09 (m, 2H), 6.72 – 6.56 (m, 3H), 5.91 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.29 (ddd, *J* = 17.2, 2.0, 1.2 Hz, 1H), 5.18 (ddd, *J* = 10.4, 2.0, 1.2 Hz, 1H), 4.06 (tt, *J* = 6.4, 1.2 Hz, 2H), 3.59 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.54 – 3.46 (m, 1H), 3.43 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.38 – 3.27 (m, 1H), 1.89 – 1.68 (m, 4H), 1.52 – 1.47 (m, 1H), 1.34 – 1.21 (m, 5H), 1.17 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 148.1, 138.1, 129.2, 117.2, 116.8, 114.0, 75.6, 72.9, 60.2, 57.7, 33.6, 32.0, 27.7, 26.0, 24.4, 24.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99.9:0.1, 0.5 mL/min), *t* (*anti*, major) = 8.57 min, *t* (*anti*, minor) = 10.33 min, 81:19 er; [α]_D²⁵ = -3.1 (CH₂Cl₂, c = 0.064).



N-(4-(Cyclohexyloxy)-1-(methylthio)hex-5-en-3-yl)aniline (**3ma**)

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Et₂O – 20:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 15.7 mg, 49%) as colorless oils (3.5:1 ratio as determined by ¹H NMR).

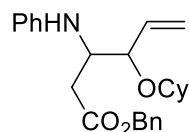
HRMS (C₁₉H₃₀ONS; [M+H]⁺, pESI): calcd: 320.2043, found: 320.2043.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-propanol = 99.9:0.1, 0.5 mL/min), *t* (*syn*, major) = 20.23 min, *t* (*syn*, minor) = 21.49 min, 96:4 er; *t* (*anti*, minor) = 19.32 min, *t* (*anti*, major) = 22.10 min, 87:13 er.

¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.11 (m, 2H), 6.72 – 6.60 (m, 3H), 5.87 – 5.75 (m, 1H), 5.31 – 5.15 (m, 2H), 4.02 – 4.01 (minor, m, 0.18H), 3.97 (major, ddt, *J* = 7.6, 3.2, 1.2 Hz, 0.83H), 3.83

(brs, 1H), 3.69 – 3.60 (major, m, 0.83H), 3.57 – 3.55 (minor, m, 0.18H), 3.32 (major, tt, $J = 8.8$, 3.6 Hz, 0.81H), 3.32 – 3.17 (minor, m, 0.18H), 2.77 – 2.52 (m, 2H), 2.10 (major, s, 2.46H), 2.07 (minor, s, 0.56H), 2.05 – 1.95 (m, 1H), 1.88 – 1.68 (m, 5H), 1.53 – 1.47 (m, 1H), 1.34 – 1.17 (m, 5H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.2, 148.0, 138.0, 137.4, 129.42, 129.40, 117.6, 117.5, 117.1, 116.8, 114.0, 113.3, 79.1, 78.7, 75.8, 75.1, 56.4, 55.8, 33.6, 33.5, 31.9, 31.7, 31.5, 31.4, 31.1, 25.9, 25.9, 24.2, 24.1, 24.0, 15.6, 15.5.



Benzyl 4-(cyclohexyloxy)-3-(phenylamino)hex-5-enoate (3na)

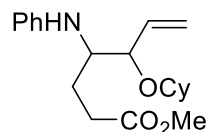
Prepared according to the general procedure C, using [PC1] as photocatalyst in 0.2 mmol scale. Flash column chromatography (SiO_2 , Pentanes/ Et_2O – 15:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 45.5 mg, 58%) as colorless oils (5.3:1 ratio as determined by ^1H NMR).

HRMS ($\text{C}_{25}\text{H}_{32}\text{O}_3\text{N}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 394.2377, found: 394.2382.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-propanol = 99.5:0.5, 0.5 mL/min), t (*syn*, minor) = 16.55 min, t (*syn*, major) = 19.63 min, 95:5 er; t (*anti*, major) = 21.14 min, t (*anti*, minor) = 26.58 min, 84:16 er.

^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.30 (m, 5H), 7.20 – 7.12 (m, 2H), 6.76 – 6.59 (m, 3H), 5.89 – 5.70 (m, 1H), 5.35 – 5.17 (m, 2H), 5.16 – 5.07 (m, 2H), 4.12 – 3.92 (m, 3H), 3.35 – 3.26 (major, m, 0.88H), 3.25 – 3.20 (minor, m, 0.14H), 2.78 – 2.57 (m, 2H), 1.84 – 1.64 (m, 4H), 1.53 – 1.45 (m, 1H), 1.34 – 1.19 (m, 5H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.4, 172.1, 147.13, 147.08, 137.2, 137.0, 136.0, 135.97, 129.4, 129.2, 128.6, 128.56, 128.4, 128.34, 128.29, 128.2, 118.0, 117.95, 117.5, 117.4, 114.3, 113.5, 78.3, 78.1, 75.6, 75.2, 66.4, 54.8, 54.3, 36.4, 34.8, 33.5, 33.49, 31.7, 31.5, 30.4, 25.8, 25.8, 24.2, 24.1, 24.0.



Methyl (5-(cyclohexyloxy)-4-(phenylamino)hept-6-enoate (3oa)

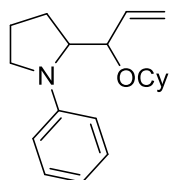
Prepared according to the general procedure C, using [PC1] as photocatalyst in 0.2 mmol scale. Flash column chromatography (SiO₂, Pentanes/Et₂O – 10:1) furnished two inseparable diastereoisomers of the title compound (Combined yield: 35.4 mg, 53%) as colorless oils (3.8:1 ratio as determined by ¹H NMR).

HRMS (C₂₀H₃₀O₃N; [M+H]⁺, pAPCI): calcd: 332.2220, found: 332.2219.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-propanol = 99.9:0.1, 0.2 mL/min), t (*anti*, major) = 179.50 min, t (*anti*, minor) = 187.44 min, 85:15 er; t (*syn*, minor) = 197.03 min, t (*syn*, major) = 214.50 min, 96:4 er.

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.10 (m, 2H), 6.72 – 6.54 (m, 3H), 5.88 – 5.73 (m, 1H), 5.30 – 5.15 (m, 2H), 4.01 – 3.95 (m, 1H), 3.82 (brs, 1H), 3.64 (major, s, 2.48H), 3.63 (minor, s, 0.61H), 3.51 (major, ddd, *J* = 8.4, 4.8, 3.2 Hz, 0.8H), 3.45 – 3.40 (minor, m, 0.2H), 3.31 (major, tt, *J* = 9.2, 3.6 Hz, 0.8H), 3.23 – 3.16 (minor, m, 0.2H), 2.58 – 2.36 (m, 2H), 2.10 – 1.96 (m, 1H), 1.88 – 1.66 (m, 5H), 1.54 – 1.47 (m, 1H), 1.37 – 1.18 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 174.6, 174.4, 148.1, 147.9, 137.9, 137.2, 129.4, 129.37, 117.7, 117.5, 117.1, 116.8, 113.9, 113.2, 79.1, 78.8, 75.7, 75.1, 56.9, 56.4, 51.6, 51.5, 33.6, 33.55, 31.8, 31.7, 31.21, 31.18, 26.9, 25.92, 25.89, 24.7, 24.23, 24.20, 24.08, 24.05.



2-(1-(Cyclohexyloxy)allyl)-1-phenylpyrrolidine (3pa)

Prepared according to the general procedure C. Flash column chromatography (SiO₂, Pentanes/Dichloromethane – 3:1) furnished two separable diastereoisomers of the title compound (Combined yield: 16.7 mg, 55%) as colorless oils (4.3:1 ratio as determined by ¹H NMR).

HRMS (C₁₉H₂₈ON; [M+H]⁺, pAPCI): calcd: 286.2165, found: 286.2164.

Major diastereomer (*R,R*)-**3pa**: **¹H NMR** (500 MHz, CDCl₃) δ 7.26 – 7.21 (m, 2H), 6.72 – 6.65 (m, 3H), 5.77 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.22 – 5.19 (m, 1H), 5.17 – 5.13 (m, 1H), 4.20 (dd, *J* = 6.0, 4.8 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.47 – 3.39 (m, 1H), 3.31 (ddd, *J* = 12.8, 9.2, 3.6 Hz, 1H), 3.14 (dd, *J* = 16.4, 9.2 Hz, 1H), 2.15 – 2.05 (m, 1H), 2.05 – 1.96 (m, 1H), 1.93 – 1.86 (m, 3H), 1.85 – 1.80 (m, 1H), 1.77 – 1.70 (m, 2H), 1.54 – 1.49 (m, 1H), 1.38 – 1.20 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 147.8, 136.8, 129.2, 117.1, 115.7, 112.4, 76.9, 75.6, 62.3, 49.1, 33.5, 32.2, 26.5, 26.0, 24.4, 24.2, 24.1.

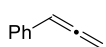
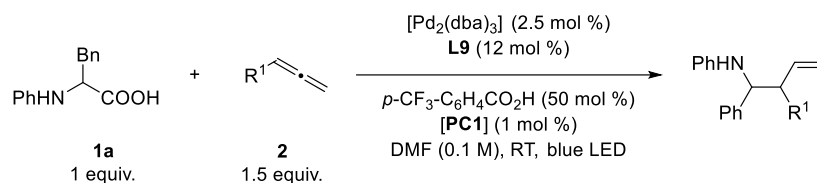
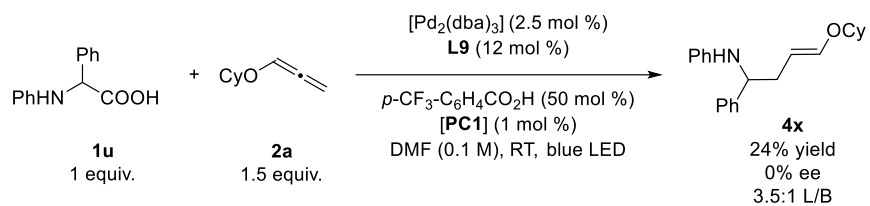
HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 100:0, 0.5 mL/min), *t* (*syn*, minor) = 10.66 min, *t* (*syn*, major) = 11.14 min, 93:7 er; [α]_D²⁵ = +39.7 (CH₂Cl₂, c = 0.23).

Minor diastereomer : **¹H NMR** (400 MHz, CDCl₃) δ 7.25 – 7.17 (m, 2H), 6.69 – 6.58 (m, 3H), 5.92 – 5.77 (m, 1H), 5.32 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.18 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.21 – 4.15 (m, 1H), 3.81 – 3.72 (m, 1H), 3.49 (td, *J* = 8.8, 2.8 Hz, 1H), 3.18 (dt, *J* = 10.4, 5.2 Hz, 1H), 3.15 – 3.08 (m, 1H), 2.34 – 2.21 (m, 1H), 2.19 – 2.10 (m, 1H), 1.94 – 1.85 (m, 1H), 1.85 – 1.61 (m, 3H), 1.60 – 1.54 (m, 2H), 1.45 – 1.41 (m, 1H), 1.31 – 1.06 (m, 5H).

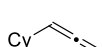
¹³C NMR (101 MHz, CDCl₃) δ 147.4, 138.5, 129.2, 115.7, 115.4, 112.2, 77.9, 76.2, 62.3, 49.1, 33.5, 31.9, 26.3, 26.0, 24.3, 24.1, 23.8.

HPLC (CHIRALPAK[®] LC-3, *n*-heptane/2-isopropanol = 100:0, 0.5 mL/min), *t* (*syn*, minor) = 6.12 min, *t* (*syn*, major) = 12.85 min, 85:15 er; [α]_D²⁵ = -19.6 (CH₂Cl₂, c = 0.05).

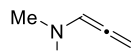
Unsuccessful substrates with branched-selective reaction conditions:



No reaction

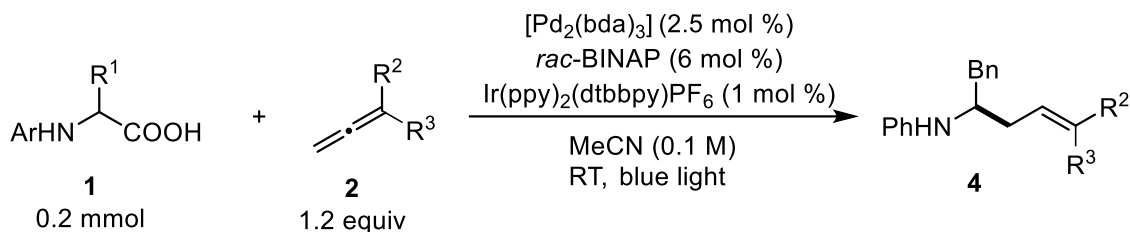


No reaction

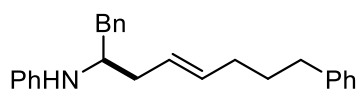


No reaction

General procedure D for photoredox palladium catalyzed linear- and stereoselective decarboxylative hydroaminoalkylation of allenes



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with [Pd₂(dba)₃] (4.6 mg, 0.005 mmol, 2.5 mol%), *rac*-BINAP (7.6 mg, 0.012 mmol, 6 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards MeCN (2 mL) was added by syringe under a flow of argon and the solution was stirred for 30 min. [PC1] (1.8 mg, 0.002 mmol, 1 mol%) and **1** (0.2 mmol, 1.0 equiv) were added sequentially and **2** (0.24 mmol, 1.2 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 1 inch from blue led strips and irradiated and stirred for 16 hrs at room temperature. After filtration through celite and evaporation of the solvents under reduced pressure, the regio and stereoselectivity were determined by ¹H NMR measurement of the crude reaction mixture. The residue was purified with column chromatography on silica gel afford the corresponding product after drying in vacuo.



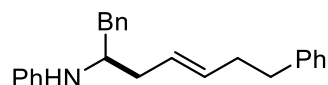
(E)-N-(1,8-diphenyloct-4-en-2-yl)aniline (4a)

Follow the general procedure D, **4a** (57.1 mg, 80%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.31 (tdt, *J* = 7.6, 6.4, 1.0 Hz, 4H), 7.25 – 7.18 (m, 8H), 6.72 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.67 – 6.62 (m, 2H), 5.61 – 5.46 (m, 2H), 3.71 (ddd, *J* = 11.2, 6.8, 5.6 Hz, 1H), 2.92 (dd, *J*_{AB} = 13.6, 5.2 Hz, 1H), 2.83 (dd, *J*_{BA} = 13.6, 7.2 Hz, 1H), 2.69 – 2.60 (m, 2H), 2.35 – 2.14 (m, 2H), 2.14 – 2.06 (m, 2H), 1.77 – 1.68 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.0, 142.5, 138.7, 133.7, 129.6, 129.4, 128.5, 128.4, 128.36, 126.6, 126.3, 125.8, 117.2, 113.5, 53.8, 39.8, 36.6, 35.5, 32.3, 31.2.

HRMS (C₂₅H₂₈N; [M+H]⁺, pos. ESI): calcd: 356.2373, found: 356.2370.



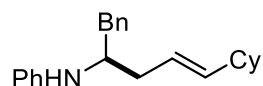
(E)-N-(1,7-diphenylhept-4-en-2-yl)aniline (4b)

Follow the general procedure D, **4b** (52.5 mg, 77%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 4H), 7.26 – 7.16 (m, 8H), 6.71 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.64 – 6.57 (m, 2H), 5.60 – 5.43 (m, 2H), 3.67 (p, *J* = 6.0 Hz, 1H), 3.56 (s, 1H), 2.84 (dd, *J*_{AB} = 13.6, 5.2 Hz, 1H), 2.75 (dd, *J*_{BA} = 13.6, 6.8 Hz, 1H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.43 – 2.33 (m, 2H), 2.31 – 2.09 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.5, 141.9, 138.8, 133.1, 129.6, 129.4, 128.6, 128.41, 128.40, 126.9, 126.3, 125.9, 117.2, 113.5, 53.7, 39.7, 36.4, 35.9, 34.4.

HR MS (C₂₅H₂₈N; [M+H]⁺, pos. ESI): calcd: 342.2216, found: 342.2217.



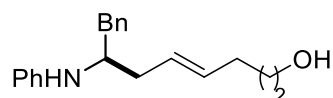
(E)-N-(5-cyclohexyl-1-phenylpent-4-en-2-yl)aniline (4c)

Follow the general procedure D, **4c** (46.6 mg, 67%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.16 (m, 5H), 6.70 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.66 – 6.61 (m, 2H), 5.52 – 5.37 (m, 2H), 3.68 (dq, *J* = 7.6, 6.0 Hz, 2H), 2.91 (dd, *J*_{AB} = 13.6, 5.2 Hz, 1H), 2.81 (dd, *J*_{BA} = 13.6, 7.2 Hz, 1H), 2.31 – 2.11 (m, 2H), 2.01 – 1.90 (m, 1H), 1.78 – 1.62 (m, 5H), 1.37 – 1.02 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 140.4, 138.8, 129.6, 129.4, 128.4, 126.3, 123.3, 117.2, 113.5, 53.8, 41.0, 39.8, 36.6, 33.3, 33.26, 26.3, 26.1.

HR-MS (C₂₃H₃₀N; [M+H]⁺, pos. ESI): calcd: 320.2373, found: 320.2376.



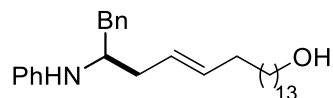
(E)-8-phenyl-7-(phenylamino)oct-4-en-1-ol (4d)

Follow the general procedure D, **4d** (52.6 mg, 89%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.31 (ddt, *J* = 7.2, 6.8, 1.2 Hz, 2H), 7.25 – 7.16 (m, 5H), 6.70 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.65 – 6.61 (m, 2H), 5.58 – 5.46 (m, 2H), 3.69 (tt, *J* = 6.8, 5.4 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.90 (dd, *J*_{AB} = 13.6, 5.2 Hz, 1H), 2.81 (dd, *J*_{BA} = 13.6, 7.2 Hz, 1H), 2.33 – 2.24 (m, 1H), 2.21 – 2.08 (m, 3H), 1.69 – 1.59 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.5, 138.7, 133.3, 129.6, 129.4, 128.4, 126.8, 126.3, 117.3, 113.5, 62.5, 53.8, 39.9, 36.6, 32.4, 29.1.

HR MS ($\text{C}_{20}\text{H}_{26}\text{ON}$; $[\text{M}+\text{H}]^+$, pos. ESI): calcd: 296.2009, found: 296.2007.



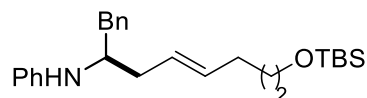
(E)-19-phenyl-18-(phenylamino)nonadec-15-en-1-ol (4e)

Follow the general procedure D, **4e** (80.5 mg, 90%) was obtained as a pale-yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.15 (m, 5H), 6.69 (tt, $J = 7.2$, 1.2 Hz, 1H), 6.64 – 6.60 (m, 2H), 5.56 – 5.40 (m, 2H), 3.71 – 3.62 (m, 1H), 3.64 (t, $J = 6.4$ Hz, 2H), 2.89 (dd, $J_{AB} = 13.6$, 5.2 Hz, 1H), 2.80 (dd, $J_{BA} = 13.6$, 7.2 Hz, 1H), 2.33 – 2.10 (m, 2H), 2.05 – 1.98 (m, 2H), 1.61 – 1.52 (m, 2H), 1.41 – 1.25 (m, 22H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 138.9, 134.5, 129.6, 129.5, 128.5, 126.4, 126.0, 117.3, 113.6, 63.3, 53.9, 39.8, 36.6, 33.0, 32.9, 29.82, 29.80, 29.8, 29.7, 29.6, 29.3, 25.9.

HRMS ($\text{C}_{31}\text{H}_{48}\text{ON}$; $[\text{M}+\text{H}]^+$, pos. ESI): calcd: 450.3730, found: 450.3730.



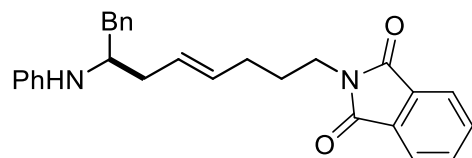
(E)-N-(8-((tert-butyldimethylsilyl)oxy)-1-phenyloct-4-en-2-yl)aniline (4f)

Follow the general procedure D, **4f** (39.9 mg, 49%) was obtained as a pale-yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.15 (m, 5H), 6.69 (tt, $J = 7.2$, 1.2 Hz, 1H), 6.64 – 6.60 (m, 2H), 5.57 – 5.43 (m, 2H), 3.67 (p, $J = 6.0$ Hz, 1H), 3.62 (t, $J = 6.4$ Hz, 2H), 2.89 (dd, $J_{AB} = 13.6$, 5.2 Hz, 1H), 2.81 (dd, $J_{BA} = 13.6$, 6.8 Hz, 1H), 2.31 – 2.12 (m, 2H), 2.12 – 2.05 (m, 2H), 1.63 – 1.55 (m, 2H), 0.91 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.5, 138.8, 133.7, 129.6, 129.4, 128.4, 126.34, 126.32, 117.3, 113.5, 62.7, 53.8, 39.8, 36.6, 32.7, 29.1, 26.1, 18.4, -5.2.

HRMS ($\text{C}_{26}\text{H}_{40}\text{ONSi}$; $[\text{M}+\text{H}]^+$, pos. ESI): calcd: 410.2874, found: 410.2875.



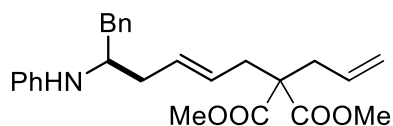
(E)-2-(8-phenyl-7-(phenylamino)oct-4-en-1-yl)isoindoline-1,3-dione (4g)

Follow the general procedure D, **4g** (76.5 mg, 90%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.82 (m, 2H), 7.73 – 7.68 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.14 (m, 5H), 6.69 – 6.60 (m, 3H), 5.57 – 5.45 (m, 2H), 3.74 – 3.65 (m, 4H), 2.89 (dd, J_{AB} = 13.6, 5.2 Hz, 1H), 2.80 (dd, J_{BA} = 13.6, 6.8 Hz, 1H), 2.30 – 2.21 (m, 1H), 2.17 – 2.05 (m, 3H), 1.86 – 1.72 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 168.5, 147.5, 138.8, 133.9, 132.4, 132.3, 129.6, 129.4, 128.4, 127.2, 126.3, 123.3, 117.2, 113.5, 53.7, 39.8, 37.6, 36.4, 29.9, 28.2.

HRMS (C₂₈H₂₉O₂N₂; [M+H]⁺, pos. ESI): calcd: 425.2224, found: 425.2224.



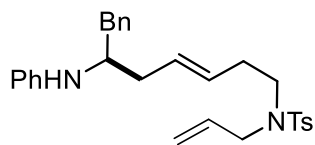
dimethyl (E)-2-allyl-2-(6-phenyl-5-(phenylamino)hex-2-en-1-yl)malonate (4h)

Follow the general procedure D, **4h** (56.3 mg, 67%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.30 (ddt, J = 7.2, 6.4, 1.2 Hz, 2H), 7.24 – 7.15 (m, 5H), 6.71 – 6.63 (m, 3H), 5.70 – 5.51 (m, 2H), 5.37 (dtt, J = 15.2, 7.6, 1.2 Hz, 1H), 5.10 (q, J = 1.2 Hz, 1H), 5.09 – 5.05 (m, 1H), 3.72 – 3.66 (m, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 2.89 (dd, J_{AB} = 13.6, 5.2 Hz, 1H), 2.74 (dd, J_{BA} = 13.6, 7.2 Hz, 1H), 2.65 (dt, J = 7.2, 1.2 Hz, 2H), 2.61 (dd, J = 7.6, 1.2 Hz, 2H), 2.34 – 2.22 (m, 1H), 2.13 (dt, J = 13.6, 6.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 171.4, 171.3, 147.3, 138.7, 132.4, 131.1, 129.5, 129.4, 128.5, 127.4, 126.4, 119.3, 117.3, 113.5, 58.1, 53.5, 52.5, 52.4, 39.7, 37.1, 36.2, 36.0.

HRMS (C₂₆H₃₂O₄N; [M+H]⁺, pos. ESI): calcd: 423.2326, found: 425.2328.



(E)-N-allyl-4-methyl-N-(7-phenyl-6-(phenylamino)hept-3-en-1-yl)benzenesulfonamide (4i)

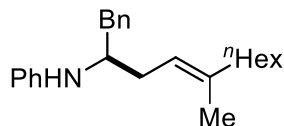
Follow the general procedure D, **4i** (84.9 mg, 89%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.68 (m, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.15 (m, 5H), 6.69 (tt, J = 7.2, 1.2 Hz, 1H), 6.65 – 6.61 (m, 2H), 5.63 (ddt, J = 17.2, 10.0, 6.4 Hz, 1H), 5.54 – 5.36 (m, 2H), 5.15 (dq, J = 27.0, 1.2 Hz, 1H), 5.14 (q, J = 1.2 Hz, 1H), 3.80 (dt, J = 6.4, 1.2 Hz, 2H),

3.68 (tt, $J = 6.8, 5.2$ Hz, 1H), 3.15 (td, $J = 7.2, 1.6$ Hz, 2H), 2.90 (dd, $J_{AB} = 13.6, 5.2$ Hz, 1H), 2.78 (dd, $J_{BA} = 13.6, 7.2$ Hz, 1H), 2.42 (s, 3H), 2.32 – 2.20 (m, 3H), 2.16 – 2.07 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.5, 143.2, 138.7, 137.4, 133.4, 129.7, 129.6, 129.5, 129.4, 129.0, 128.4, 127.2, 126.4, 118.8, 117.2, 113.5, 53.7, 50.7, 47.2, 39.9, 36.6, 31.8, 21.5.

HRMS ($\text{C}_{29}\text{H}_{35}\text{O}_2\text{N}_2\text{S}$; $[\text{M}+\text{H}]^+$, pos. ESI): calcd: 475.2414, found: 475.2414.



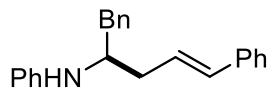
(E)-N-(5-methyl-1-phenylundec-4-en-2-yl)aniline (4j)

Follow the general procedure D, **4j** (52.5 mg, 56%) was obtained as a pale-yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.20 (dtdd, $J = 13.6, 7.6, 2.0, 1.2$ Hz, 5H), 6.69 (tq, $J = 7.6, 0.8$ Hz, 1H), 6.64 – 6.60 (m, 2H), 5.23 (tdd, $J = 7.6, 2.8, 1.2$ Hz, 1H), 3.73 – 3.62 (m, 1H), 2.94 – 2.78 (m, 2H), 2.31 – 2.11 (m, 2H), 2.06 – 1.89 (m, 2H), 1.75 – 1.54 (m, 3H), 1.37 – 1.21 (m, 8H), 0.90 (d, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 147.6, 138.9, 138.7, 138.5, 129.6, 129.5, 129.4, 128.4, 126.3, 120.7, 120.1, 117.2, 113.5, 113.4, 54.4, 54.3, 40.0, 39.9, 39.86, 32.2, 32.1, 31.9, 29.4, 29.1, 28.1, 28.05, 23.7, 22.75, 22.73, 16.4, 14.2.

HRMS ($\text{C}_{24}\text{H}_{34}\text{N}$; $[\text{M}+\text{H}]^+$, pos. ESI): calcd: 336.2686, found: 336.2683.



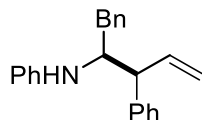
(E)-N-(1,5-diphenylpent-4-en-2-yl)aniline (4k)

Follow the general procedure D, **4k** (35.5 mg, 57%) was obtained as a pale-yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.29 (m, 6H), 7.28 – 7.25 (m, 2H), 7.25 – 7.19 (m, 4H), 6.73 (tt, $J = 7.2, 1.2$ Hz, 1H), 6.69 – 6.65 (m, 2H), 6.50 – 6.44 (m, 1H), 6.27 (dt, $J = 15.8, 7.2$ Hz, 1H), 3.84 (ddd, $J = 12.0, 6.8, 5.6$ Hz, 1H), 3.67 (s, 1H), 2.96 (dd, $J_{AB} = 13.6, 5.2$ Hz, 1H), 2.57 (dd, $J_{BA} = 13.6, 6.8$ Hz, 1H), 2.61 – 2.33 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.4, 138.5, 137.5, 133.0, 129.6, 129.5, 128.6, 128.5, 127.3, 126.6, 126.5, 126.2, 117.4, 113.6, 53.9, 40.0, 37.1.

HRMS ($\text{C}_{23}\text{H}_{24}\text{N}$; $[\text{M}+\text{H}]^+$, pos. ESI): calcd: 314.1903, found: 314.1905.



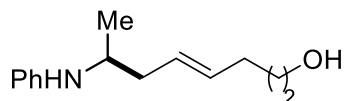
***N*-(1,3-diphenylpent-4-en-2-yl)aniline (**4'**)**

Follow the general procedure D, **4k'** (12.1 mg, 19%, dr = 1:1) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.26 (m, 4H), 7.25 – 7.21 (m, 3H), 7.20 – 7.11 (m, 5H), 6.28 – 6.14 (m, 1H), 5.26 – 5.10 (m, 2H), 4.05 (qd, *J* = 5.6, 3.2 Hz, 1H), 3.70 – 3.50 (m, 1H), 3.02 – 2.49 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.5, 141.5, 141.2, 139.1, 138.8, 138.7, 137.9, 129.6, 129.4, 129.37, 128.73, 128.68, 128.6, 128.5, 128.4, 128.3, 126.77, 126.76, 126.31, 126.27, 125.6, 117.8, 117.44, 117.37, 117.3, 113.8, 113.6, 58.7, 58.2, 52.6, 52.4, 37.8, 37.4.

HRMS (C₂₃H₂₄N; [M+H]⁺, pos. ESI): calcd: 314.1903, found: 314.1904.



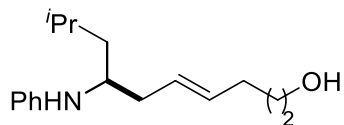
***(E)*-7-(phenylamino)oct-4-en-1-ol (**4l**)**

Follow the general procedure D, **4l** (22.8 mg, 52%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.14 (m, 2H), 6.68 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.61 – 6.57 (m, 2H), 5.57 – 5.43 (m, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.55 – 3.47 (m, 1H), 2.33 – 2.08 (m, 4H), 1.64 (tt, *J* = 7.2, 6.4 Hz, 2H), 1.19 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 133.0, 129.3, 126.9, 117.1, 113.7, 113.3, 62.5, 62.4, 48.6, 48.4, 39.8, 32.4, 29.1, 20.5.

HRMS (C₁₄H₂₂ON; [M+H]⁺, pos. ESI): calcd: 220.1696, found: 220.1696.



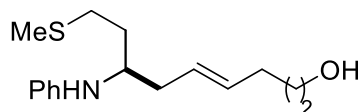
***(E)*-9-methyl-7-(phenylamino)dec-4-en-1-ol (**4m**)**

Follow the general procedure, **4m** (39.1 mg, 79%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.10 (m, 2H), 6.65 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.60 – 6.55 (m, 2H), 5.54 – 5.40 (m, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.47 (dp, *J* = 7.6, 6.0 Hz, 1H), 2.31 – 2.15 (m, 2H), 2.15 – 2.06 (m, 2H), 1.77 (dh, *J* = 7.6, 6.8 Hz, 1H), 1.67 – 1.58 (m, 2H), 1.36 (ddd, *J* = 7.6, 6.8, 3.2 Hz, 2H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.0, 133.0, 129.4, 126.8, 116.9, 113.2, 62.5, 50.8, 44.2, 37.7, 32.5, 29.1, 25.0, 23.1, 22.7.

HRMS (C₁₇H₂₈ON; [M+H]⁺, pos. ESI): calcd: 262.2165, found: 262.2165.



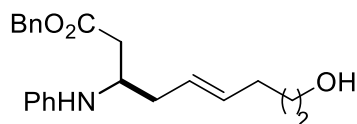
(E)-9-(methylthio)-7-(phenylamino)non-4-en-1-ol (4n)

Follow the general procedure D, **4n** (37.6 mg, 67%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.11 (m, 2H), 6.67 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.65 – 6.56 (m, 2H), 5.57 – 5.38 (m, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 3.56 (dq, *J* = 7.6, 5.6 Hz, 1H), 2.68 – 2.51 (m, 2H), 2.34 – 2.15 (m, 2H), 2.09 (s, 3H), 2.14 – 2.06 (m, 2H), 1.92 – 1.68 (m, 2H), 1.62 (tt, *J* = 7.2, 6.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 133.4, 129.4, 126.4, 117.3, 113.3, 62.4, 52.0, 37.6, 34.1, 32.4, 31.1, 29.1, 15.8.

HRMS (C₁₆H₂₆ONS; [M+H]⁺, pos. ESI): calcd: 280.1730, found: 280.1730.



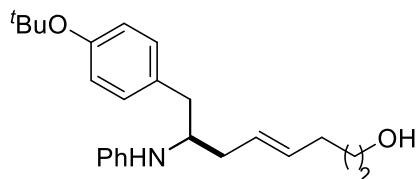
Benzyl (E)-9-hydroxy-3-(phenylamino)non-5-enoate (4o)

Follow the general procedure D, **4o** (56.5 mg, 80%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 5H), 7.20 – 7.14 (m, 2H), 6.71 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.65 – 6.58 (m, 2H), 5.55 – 5.39 (m, 2H), 5.12 (s, 2H), 3.90 (p, *J* = 6.0 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.61 (dd, *J*_{AB} = 15.2, 6.0 Hz, 1H), 2.57 (dd, *J*_{BA} = 15.2, 6.4 Hz, 1H), 2.44 – 2.21 (m, 2H), 2.09 (dt, *J* = 8.0, 6.4 Hz, 2H), 1.66 – 1.56 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 171.8, 147.0, 135.9, 133.9, 129.4, 128.6, 128.3, 128.3, 126.0, 117.8, 113.8, 113.7, 66.5, 62.4, 50.4, 38.9, 37.6, 32.3, 29.0.

HRMS (C₂₂H₂₈O₃N; [M+H]⁺, pos. ESI): calcd: 354.2064, found: 354.2060.



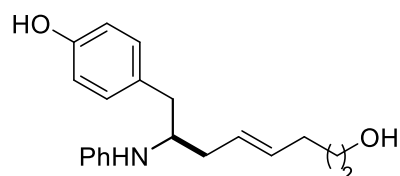
(E)-8-(4-(tert-butoxy)phenyl)-7-(phenylamino)oct-4-en-1-ol (4p)

Follow the general procedure D, **4p** (48.8 mg, 66%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.11 (m, 2H), 7.12 – 7.04 (m, 2H), 6.95 – 6.87 (m, 2H), 6.68 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.63 – 6.55 (m, 2H), 5.58 – 5.42 (m, 2H), 3.64 (ddd, *J* = 12.0, 6.8, 5.2 Hz, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.83 (dd, *J*_{AB} = 13.6, 5.2 Hz, 1H), 2.75 (dd, *J*_{BA} = 13.6, 6.8 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.19 – 2.07 (m, 3H), 1.63 (tt, *J* = 7.2, 6.4 Hz, 2H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 153.9, 147.6, 133.5, 133.2, 129.9, 129.4, 126.9, 124.1, 117.2, 113.5, 78.3, 62.5, 54.0, 39.4, 36.8, 32.4, 29.1, 29.0.

HRMS (C₂₄H₃₄O₂N; [M+H]⁺, pos. ESI): calcd: 368.2584, found: 368.2585.



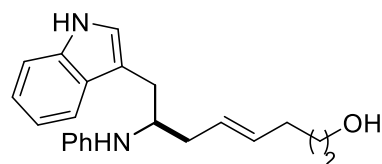
(E)-4-(8-hydroxy-2-(phenylamino)oct-4-en-1-yl)phenol (4q)

Follow the general procedure D, **4q** (41.7 mg, 67%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.12 (m, 2H), 7.09 – 7.00 (m, 2H), 6.79 – 6.71 (m, 2H), 6.69 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.65 – 6.57 (m, 2H), 5.56 – 5.41 (m, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.68 – 3.56 (m, 1H), 2.80 (dd, *J*_{AB} = 13.6, 5.2 Hz, 1H), 2.72 (dd, *J*_{BA} = 13.6, 6.8 Hz, 1H), 2.31 – 2.06 (m, 4H), 1.63 (tt, *J* = 7.2, 6.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 154.3, 147.5, 133.1, 130.7, 130.6, 129.4, 127.0, 117.3, 115.4, 113.6, 62.6, 54.0, 39.0, 36.6, 32.3, 29.1.

HRMS (C₂₀H₂₆O₂N; [M+H]⁺, pos. ESI): calcd: 312.1958, found: 312.1958.



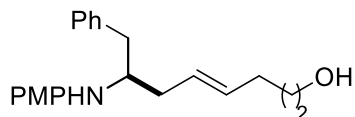
(E)-8-(1H-indol-3-yl)-7-(phenylamino)oct-4-en-1-ol (4r)

Follow the general procedure D, **4r** (63.7 mg, 95%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.02 (s, 1H), 7.61 (ddt, *J* = 8.0, 1.2, 0.8 Hz, 1H), 7.36 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.24 – 7.11 (m, 4H), 7.02 – 6.99 (m, 1H), 6.69 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.67 – 6.59 (m, 2H), 5.59 – 5.47 (m, 2H), 3.78 (p, *J* = 6.0 Hz, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.04 – 2.98 (m, 2H), 2.39 – 2.17 (m, 2H), 2.17 – 2.03 (m, 2H), 1.72 – 1.54 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 136.3, 132.9, 129.4, 128.2, 127.2, 122.7, 122.1, 119.5, 119.1, 117.1, 113.5, 112.7, 111.2, 62.5, 53.2, 37.3, 32.4, 30.4, 29.6, 29.1.

HRMS (C₂₂H₂₇ON₂; [M+H]⁺, pos. ESI): calcd: 335.2118, found: 335.2116.



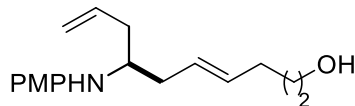
(E)-7-((4-methoxyphenyl)amino)-8-phenyloct-4-en-1-ol (4s)

Follow the general procedure D, **4s** (58.5 mg, 90%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.30 (ddt, *J* = 7.4, 6.8, 1.2 Hz, 2H), 7.25 – 7.18 (m, 3H), 6.83 – 6.77 (m, 2H), 6.63 – 6.57 (m, 2H), 5.57 – 5.45 (m, 2H), 3.76 (s, 3H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.62 – 3.55 (m, 1H), 2.88 (dd, *J*_{AB} = 13.6, 5.2 Hz, 1H), 2.77 (dd, *J*_{BA} = 13.6, 7.2 Hz, 1H), 2.35 – 2.21 (m, 1H), 2.18 – 2.08 (m, 3H), 1.64 (ddt, *J* = 8.0, 7.2, 6.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 152.1, 141.7, 138.8, 133.2, 129.5, 128.4, 126.9, 126.3, 115.1, 115.07, 62.5, 55.9, 54.9, 39.9, 36.6, 32.4, 29.2.

HRMS (C₂₁H₂₈O₂N; [M+H]⁺, pos. ESI): calcd: 326.2115, found: 326.2112.



(E)-7-((4-methoxyphenyl)amino)deca-4,9-dien-1-ol (4t)

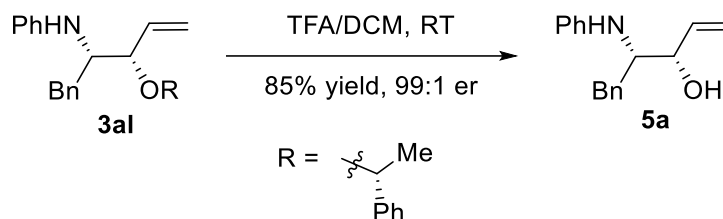
Follow the general procedure D, **4t** (35.2 mg, 64%) was obtained as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 6.80 – 6.75 (m, 2H), 6.59 – 6.54 (m, 2H), 5.89 – 5.76 (m, 1H), 5.56 – 5.42 (m, 2H), 5.13 – 5.05 (m, 2H), 3.74 (s, 3H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.36 (p, *J* = 6.0 Hz, 1H), 2.34 – 2.19 (m, 4H), 2.11 (dtd, *J* = 8.4, 6.0, 1.2 Hz, 2H), 1.69 – 1.58 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 152.2, 141.8, 135.1, 133.1, 126.9, 117.6, 115.1, 115.09, 62.5, 55.9, 53.5, 38.3, 37.0, 32.5, 29.2.

HR-MS (C₁₇H₂₆O₂N; [M+H]⁺, pos. ESI): calcd: 276.1958, found: 276.1956.

Transformations



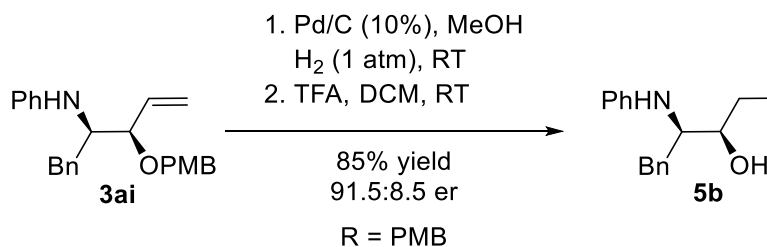
To a solution of **3al** (18.8 mg, 50 μmol) in dichloromethane (2 ml), trifluoroacetic acid (0.2 mL) was added and stirred for 2h. Solid potassium carbonate was added and was stirred overnight. The suspension was filtered and concentrated. The crude mixture was purified by column chromatography (SiO_2 , Et_2O /pentane, 1/2) to provide 10.8 mg (85%, 42.7 μmol) of as a colorless oil.

HRMS ($\text{C}_{17}\text{H}_{20}\text{ON}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 254.1539, found: 254.1538.

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.12 (m, 5H), 6.71 (tt, $J = 7.6, 1.2$ Hz, 1H), 6.68 – 6.61 (m, 2H), 5.99 (ddd, $J = 17.2, 10.4, 6.4$ Hz, 1H), 5.32 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.23 (ddd, $J = 10.4, 1.2$ Hz, 1H), 4.15 (ddt, $J = 6.4, 4.4, 1.2$ Hz, 1H), 3.84 (brs, 1H), 3.66 (ddd, $J = 7.2, 6.0, 4.4$ Hz, 1H), 3.00 (dd, $J = 13.8, 7.2$ Hz, 1H), 2.88 (dd, $J = 13.8, 6.0$ Hz, 1H), 2.14 (brs, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 138.4, 138.3, 129.5, 129.4, 128.6, 126.5, 118.0, 117.3, 114.0, 73.1, 59.2, 37.2.

HPLC (CHIRALPAK[®] LC-1, n -heptane/2-isopropanol = 99:1, 0.15 mL/min), t (*syn*, major) = 8.27 min, t (*syn*, minor) = 8.95 min, >99:1 er; $[\alpha]_D^{25} = -20.1$ (CH_2Cl_2 , $c = 0.19$).



To a solution of **3ai** (18.6 mg, 50 μmol) in methanol (1 ml), 5% Pd/C (10 mol%) was added, and the mixture was stirred under 1 atm H_2 atmosphere overnight. The suspension was filtered and concentrated. The crude mixture was dissolved in dichloromethane (1 ml) and 10% TFA in dichloromethane (1 ml) was added. After 2 h, solid potassium carbonate was added and was stirred

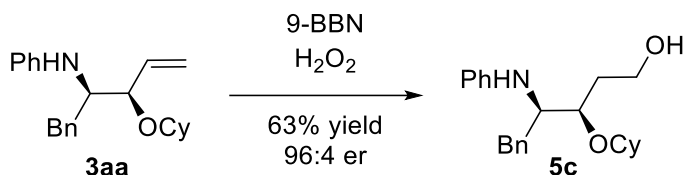
overnight. The suspension was filtered and concentrated. The crude mixture was purified by column chromatography (SiO₂, Et₂O/pentane, 1/2) to provide 10.1 mg (80%, 40 μmol) of **3aa** as a colorless oil.

HRMS (C₁₇H₂₂ON; [M+H]⁺, pESI): calcd: 256.1696, found: 256.1694.

¹H NMR (500 MHz, CDCl₃) δ 7.29 (ddt, *J* = 7.6, 6.4, 0.8 Hz, 2H), 7.24 – 7.14 (m, 5H), 6.70 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.67 – 6.61 (m, 2H), 3.93 (brs, 1H), 3.62 – 3.51 (m, 2H), 2.97 – 2.87 (m, 2H), 1.88 (brs, 1H), 1.70 – 1.57 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 147.8, 138.5, 129.5, 129.4, 128.7, 126.5, 117.6, 113.7, 73.1, 57.9, 37.7, 27.3, 10.3.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 98:2, 0.5 mL/min), *t* (*syn*, minor) = 29.10 min, *t* (*syn*, major) = 31.1 min, 91.5:8.5 er; [α]_D²⁵ = +18.5 (CH₂Cl₂, *c* = 0.13).



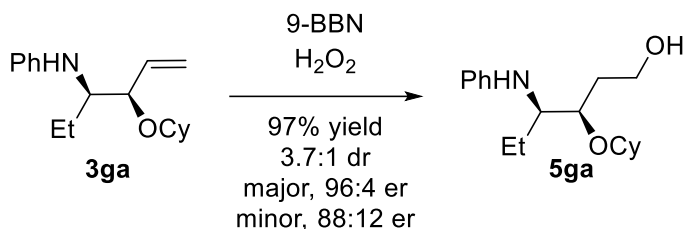
3aa (55 mg, 0.16 mmol) was dissolved in dry degassed THF (1.6 mL) and cooled to -78 °C. Then 9-BBN (0.32 mmol, 0.64 mL, 2.0 equiv., 0.5 M solution in hexane) was slowly added. The reaction was stirred for 15 min at 0 °C and then slowly warmed up to room temperature, at which it was stirred for overnight. The reaction mixture was cooled to -10 °C, then EtOH (0.5 mL), 2 M NaOH (0.5 mL) and 30 % H₂O₂ (0.5 mL) were added slowly in the given order. The reaction was allowed to warm up to room temperature and stirred for 3 h. The reaction mixture was diluted with CH₂Cl₂ and transferred into a separation funnel. The aqueous phase was extracted with CH₂Cl₂ (3 x 5 mL) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated by rotary evaporation. The crude product was purified by flash column silica gel chromatography (SiO₂, Et₂O/pentane, 1/2) to give **5c** (36.7 mg, 63% yield) as a colorless oil.

HRMS (C₂₃H₃₁O₂N; [M+H]⁺, pESI): calcd: 354.2428, found: 354.2433.

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 7.19 – 7.13 (m, 2H), 6.70 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.66 – 6.61 (m, 2H), 3.78 (td, *J* = 6.0, 2.0 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.63 (ddd, *J* = 11.2, 6.0, 4.8 Hz, 1H), 3.44 (tt, *J* = 9.2, 3.6 Hz, 1H), 3.34 (brs, 1H), 2.96 – 2.82 (m, 2H), 2.00 – 1.70 (m, 7H), 1.58 (tdd, *J* = 6.0, 4.4, 3.2 Hz, 1H), 1.41 – 1.21 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 147.2, 139.6, 129.5, 129.1, 128.6, 126.3, 117.9, 113.8, 74.5, 59.9, 57.6, 37.1, 34.4, 33.4, 33.2, 25.8, 24.5, 24.4.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 95:5, 0.5 mL/min), *t* (*syn*, minor) = 12.89 min, *t* (*syn*, major) = 13.81 min, 96:4 er; [α]_D²⁵ = +20.6 (CH₂Cl₂, *c* = 0.39).



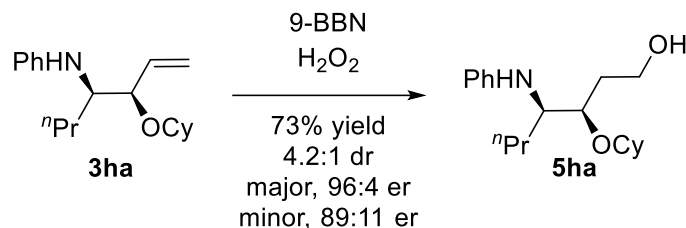
3ga (19.4 mg, 71 μmol) was dissolved in dry degassed THF (1 mL) and cooled to -78 °C. Then 9-BBN (0.21 mmol, 0.42 mL, 3.0 equiv., 0.5 M solution in hexane) was slowly added. The reaction was stirred for 15 min at 0 °C and then slowly warmed up to room temperature, at which it was stirred for overnight. The reaction mixture was cooled to -10 °C, then EtOH (0.5 mL), 2 M NaOH (0.5 mL) and 30 % H₂O₂ (0.5 mL) were added slowly in the given order. The reaction was allowed to warm up to room temperature and stirred for 3 h. The reaction mixture was diluted with CH₂Cl₂ and transferred into a separation funnel. The aqueous phase was extracted with CH₂Cl₂ (3 x 5 mL) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated by rotary evaporation. The crude product was purified by flash column silica gel chromatography (SiO₂, Et₂O/pentane, 1/2) to give **5ga** (20.0 mg, 97% yield) as a colorless oil.

HRMS (C₁₈H₃₀O₂N; [M+H]⁺, pESI): calcd: 292.2271, found: 292.2270.

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.10 (m, 2H), 6.67 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.64 – 6.56 (m, 2H), 3.87 – 3.62 (m, 3H), 3.47 – 3.27 (m, 2H), 3.15 (brs, 1H), 1.98 – 1.86 (m, 2H), 1.83 – 1.65 (m, 5H), 1.60 – 1.49 (m, 2H), 1.37 – 1.22 (m, 5H), 0.98 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.4, 148.1, 129.43, 129.39, 125.6, 117.2, 113.4, 113.3, 77.0, 76.96, 75.7, 60.8, 60.5, 57.6, 57.5, 34.0, 33.7, 33.3, 33.23, 33.19, 32.9, 30.4, 29.8, 25.8, 25.7, 24.44, 24.38, 24.32, 24.27, 23.9, 11.5, 11.0.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99:1, 0.5 mL/min), *t* (*syn*, major) = 42.16 min, *t* (*syn*, minor) = 55.21 min, , 96:4 er; *t* (*anti*, minor) = 45.84 min, *t* (*anti*, major) = 73.61 min, 88:12 er.



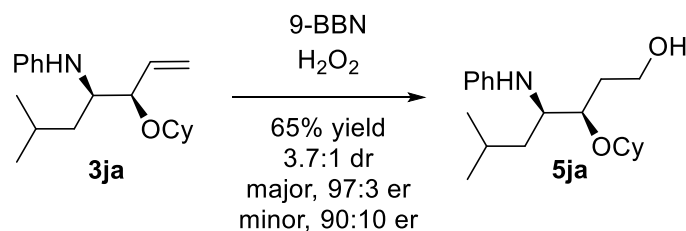
3ha (24.3 mg, 85 μ mol) was dissolved in dry degassed THF (1 mL) and cooled to -78 $^{\circ}\text{C}$. Then 9-BBN (0.26 mmol, 0.51 mL, 3.0 equiv., 0.5 M solution in hexane) was slowly added. The reaction was stirred for 15 min at 0 $^{\circ}\text{C}$ and then slowly warmed up to room temperature, at which it was stirred for overnight. The reaction mixture was cooled to -10 $^{\circ}\text{C}$, then EtOH (0.5 mL), 2 M NaOH (0.5 mL) and 30 % H_2O_2 (0.5 mL) were added slowly in the given order. The reaction was allowed to warm up to room temperature and stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were dried over Na_2SO_4 , filtered and concentrated by rotary evaporation. The crude product was purified by flash column silica gel chromatography (SiO_2 , Et_2O /pentane, 1/2) to give **5ha** (19.0 mg, 73% yield) as a colorless oil.

HRMS ($\text{C}_{19}\text{H}_{32}\text{O}_2\text{N}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 306.2428, found: 306.2426.

^1H NMR (400 MHz, CDCl_3) δ 7.19 – 7.10 (m, 2H), 6.66 (tq, $J = 7.2, 1.2$ Hz, 1H), 6.63 – 6.55 (m, 2H), 3.83 – 3.65 (m, 3H), 3.51 – 3.37 (major, m, 1.85H), 3.35 – 3.29 (minor, m, 0.35H), 3.14 (brs, 1H), 2.00 – 1.86 (m, 2H), 1.84 – 1.50 (m, 8H), 1.43 – 1.38 (m, 1H), 1.32 – 1.21 (m, 5H), 0.92 (td, $J = 7.2, 2.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.4, 148.0, 129.5, 129.4, 117.2, 117.1, 113.3, 113.2, 77.00, 76.1, 60.8, 60.6, 55.9, 55.3, 33.82, 33.79, 33.5, 33.34, 33.30, 33.28, 33.2, 32.9, 30.4, 25.77, 25.75, 24.49, 24.47, 24.4, 24.34, 20.1, 19.8, 14.3, 14.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99:1, 0.5 mL/min), t (*syn*, major) = 39.53 min, t (*syn*, minor) = 43.06 min, , 96:4 er; t (*anti*, minor) = 37.97 min, t (*anti*, major) = 62.46 min, 89:11 er.



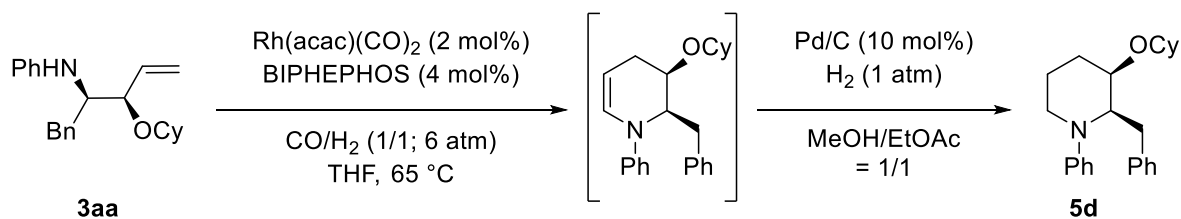
3ja (28.3 mg, 98 μ mol) was dissolved in dry degassed THF (1 mL) and cooled to -78 $^{\circ}$ C. Then 9-BBN (0.29 mmol, 0.59 mL, 3.0 equiv., 0.5 M solution in hexane) was slowly added. The reaction was stirred for 15 min at 0 $^{\circ}$ C and then slowly warmed up to room temperature, at which it was stirred for overnight. The reaction mixture was cooled to -10 $^{\circ}$ C, then EtOH (0.5 mL), 2 M NaOH (0.5 mL) and 30 % H₂O₂ (0.5 mL) were added slowly in the given order. The reaction was allowed to warm up to room temperature and stirred for 3 h. The reaction mixture was diluted with CH₂Cl₂ and transferred into a separation funnel. The aqueous phase was extracted with CH₂Cl₂ (3 x 5 mL) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated by rotary evaporation. The crude product was purified by flash column silica gel chromatography (SiO₂, Et₂O/pentane, 1/2) to give **5ja** (20.2 mg, 65% yield) as a colorless oil.

HRMS (C₂₀H₃₄O₂N; [M+H]⁺, pESI): calcd: 320.2584, found: 320.2585.

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.12 (m, 2H), 6.66 (tdt, *J* = 7.4, 4.0, 1.2 Hz, 1H), 6.62 – 6.54 (m, 2H), 3.82 – 3.65 (m, 3H), 3.55 (major, ddd, *J* = 8.0, 5.4, 2.8 Hz, 0.81H), 3.52 – 3.49 (minor, m, 0.22H), 3.42 (tt, *J* = 9.2, 4.4 Hz, 0.83H), 3.34 – 3.33 (minor, m, 0.30H), 3.08 (brs, 1H), 2.00 – 1.86 (m, 2H), 1.84 – 1.65 (m, 6H), 1.59 – 1.52 (m, 2H), 1.35 – 1.23 (m, 5H), 0.97 – 0.95 (m, 3H), 0.91 – 0.88 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.2, 147.8, 129.5, 129.4, 117.2, 117.0, 113.1, 113.0, 76.95, 76.91, 75.9, 60.8, 60.7, 54.2, 53.1, 40.02, 39.99, 34.9, 34.1, 33.44, 33.38, 33.36, 33.0, 32.97, 25.77, 25.75, 25.2, 24.9, 24.52, 24.47, 24.35, 23.8, 23.2, 22.8, 22.7, 22.2.

HPLC (CHIRALPAK[®] LC-1, *n*-heptane/2-isopropanol = 99:1, 0.5 mL/min), *t* (*syn*, minor) = 29.83 min, *t* (*syn*, major) = 30.90 min, , 97:3 er; *t* (*anti*, minor) = 34.05 min, *t* (*anti*, major) = 38.63 min, 90:10 er.



In a 25 mL vial containing [Rh(acac)(CO)₂] (1.3 mg, 5.2 μ mol, 2 mol%) and BIPHEPHOS (9.8 mg, 10.4 μ mol, 4 mol%), the air was replaced by argon and 2 mL THF was added. A solution of **3aa** (86.5 mg, 0.258 mmol) in 2 mL THF was added into the vial which was placed into a 300 mL stainless steel autoclave. The air was replaced by a mixture gas of CO/H₂ (1:1, 6 atm). The reaction

mixture was allowed to stir at 65 °C overnight. The autoclave was subsequently cooled at rt and the pressure of syngas was released. After removing the solvent, the reaction mixture was measured by ^1H NMR.

The crude product was dissolved in MeOH/EtOAc (1:1, 6.0 mL) again, into which 5% Pd/C (52 mg, 10 mol%) was added, and the mixture was stirred under a hydrogen atmosphere until complete by TLC at room temperature. The mixture is then filtered through celite, washing with EtOAc, and concentrated in vacuum. The product is purified by silica gel column chromatography (Pentanes:DCM = 1:1) to give **5d** (54.4 mg, 60% over two steps) as a colorless oil.

HRMS ($\text{C}_{24}\text{H}_{32}\text{ON}$; $[\text{M}+\text{H}]^+$, pESI): calcd: 350.2478, found: 350.2475.

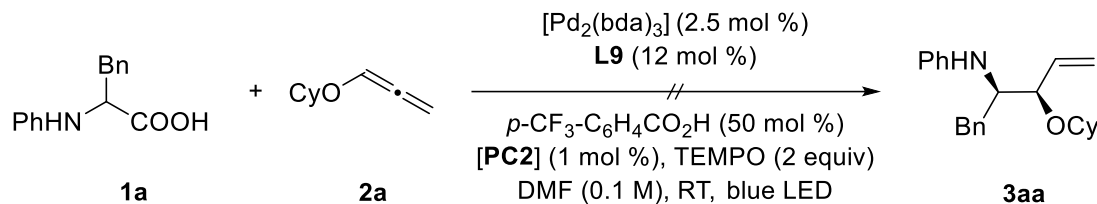
^1H NMR (400 MHz, CDCl_3) δ 7.22 – 7.05 (m, 7H), 6.71 – 6.62 (m, 3H), 4.24 (dt, J = 9.2, 4.8 Hz, 1H), 3.68 (ddt, J = 11.2, 6.0, 2.8 Hz, 1H), 3.47 (dddt, J = 13.8, 3.6, 2.4, 1.2 Hz, 1H), 3.35 (tt, J = 9.2, 3.6 Hz, 1H), 3.23 (tdd, J = 10.8, 3.6, 2.4 Hz, 1H), 3.04 (dd, J = 14.0, 4.4 Hz, 1H), 2.93 (dd, J = 14.0, 8.8 Hz, 1H), 1.93 – 1.83 (m, 2H), 1.82 – 1.69 (m, 6H), 1.55 – 1.49 (m, 1H), 1.35 – 1.18 (m, 5H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.9, 141.3, 129.4, 129.0, 128.1, 125.6, 117.9, 116.0, 75.8, 73.8, 62.8, 41.2, 33.3, 33.0, 30.1, 27.2, 25.9, 24.4, 24.2, 24.0.

HPLC (CHIRALPAK[®] LC-4, *n*-heptane/2-isopropanol = 100:0, 0.5 mL/min), t (*syn*, minor) = 33.47 min, t (*syn*, major) = 39.68 min, 96:4 er; $[\alpha]_D^{25}$ = -57.7 (CH_2Cl_2 , c = 1.0).

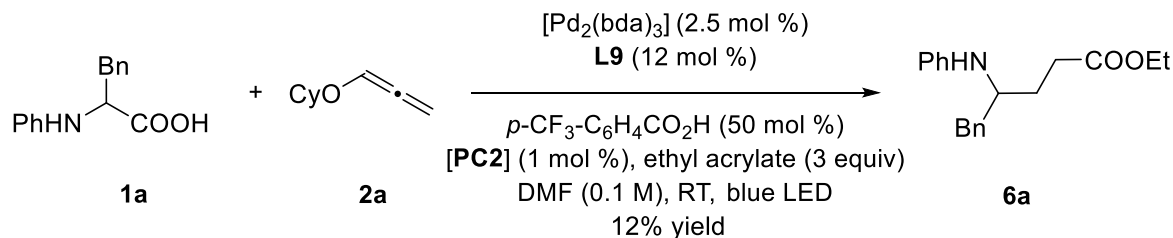
Experimental details for mechanistic studies

Control experiment in the presence of TEMPO



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $[\text{Pd}_2(\text{dba})_3]$ (2.3 mg, 0.0025 mmol, 2.5 mol%), **L9** (6.5 mg, 0.012 mmol, 12 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards DMF (1 mL) was added by syringe under a flow of argon and the solution was stirred for 30 min. **[PC2]** (1.1 mg, 0.001 mmol, 1 mol%), **1a** (0.1 mmol, 1.0 equiv), *p*-CF₃-C₆H₄CO₂H (9.5 mg, 0.05 mmol, 0.5 equiv.) and TEMPO (31.3 mg, 0.2 mmol, 2 equiv.) were added sequentially and **2a** (0.15 mmol, 1.5 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 1 inch from blue led strips and irradiated and stirred for 16 hrs. at room temperature. After filtration through celite and evaporation of the solvents under reduced pressure, the crude reaction mixture was measured by ¹H NMR. No product **3aa** and TEMPO adducts could be detected.

Trapping experiment with ethyl acrylate



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $[\text{Pd}_2(\text{dba})_3]$ (2.3 mg, 0.0025 mmol, 2.5 mol%), **L9** (6.5 mg, 0.012 mmol, 12 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards DMF (1 mL) was added

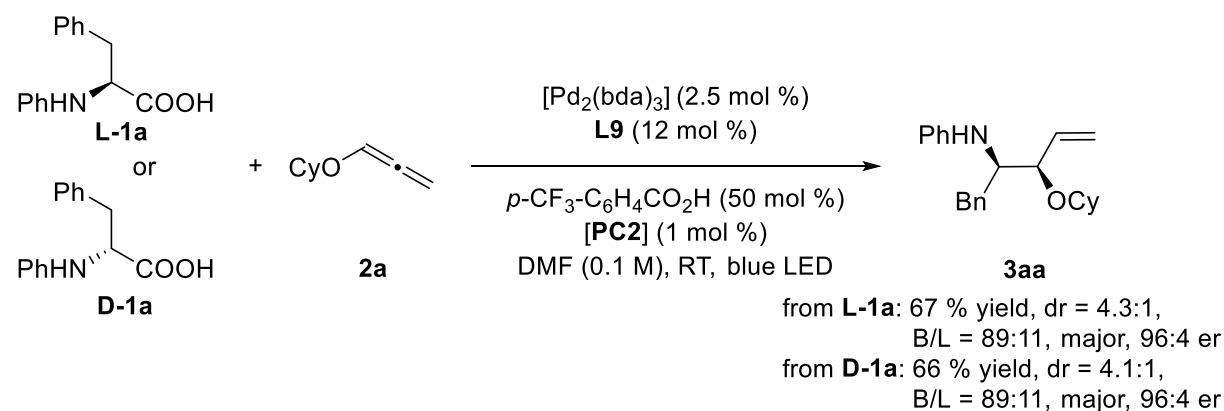
by syringe under a flow of argon and the solution was stirred for 30 min. [**PC2**] (1.1 mg, 0.001 mmol, 1 mol%), **1a** (0.1 mmol, 1.0 equiv), *p*-CF₃-C₆H₄CO₂H (9.5 mg, 0.05 mmol, 0.5 equiv.) and ethyl acrylate (33 μ L, 0.3 mmol, 3 equiv.) were added sequentially and **2a** (0.15 mmol, 1.5 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 1 inch from blue led strips and irradiated and stirred for 16 hrs. at room temperature. After filtration through celite and evaporation of the solvents under reduced pressure, the crude reaction mixture was measured by ¹H NMR. After evaporation of the solvents under reduced pressure, the crude reaction mixture was purified with column chromatography on silica gel (Pentanes/Et₂O = 5:1) afford the corresponding product **6a** (3.7 mg, 12% yield) as a colorless oil after drying in vacuum.

¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 5H), 6.70 (tt, *J* = 7.6, 1.2 Hz, 1H), 6.65 – 6.57 (m, 2H), 4.09 (qd, *J* = 7.2, 0.8 Hz, 2H), 3.74 – 3.65 (m, 1H), 3.55 (brs, 1H), 2.92 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.78 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.50 – 2.32 (m, 2H), 1.99 – 1.91 (m, 1H), 1.73 – 1.63 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 173.9, 147.5, 138.1, 129.6, 129.5, 128.5, 126.5, 117.4, 113.4, 60.5, 53.6, 40.7, 31.4, 29.3, 14.2.

HR-MS (C₁₉H₂₄O₂N; [M+H]⁺, pos. ESI): calcd: 298.1802, found: 298.1801.

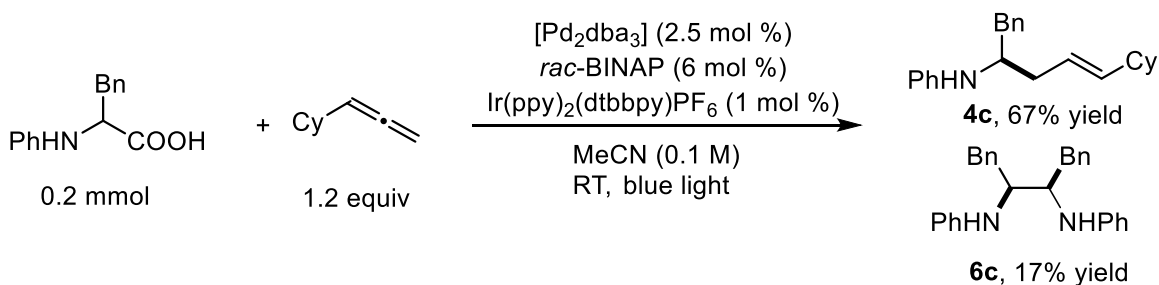
Reactions with enantiomerically pure substrates **L-1a** or **D-1a**



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with [Pd₂(dba)₃] (2.3 mg, 0.0025 mmol, 2.5 mol%), **L9** (6.5 mg, 0.012 mmol, 12 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards DMF (1 mL) was added

by syringe under a flow of argon and the solution was stirred for 30 min. [**PC2**] (1.1 mg, 0.001 mmol, 1 mol%), **L-1a** or **D-1a** (0.1 mmol, 1.0 equiv), *p*-CF₃-C₆H₄CO₂H (9.5 mg, 0.05 mmol, 0.5 equiv.) were added sequentially and **2a** (0.15 mmol, 1.5 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 1 inch from blue led strips and irradiated and stirred for 16 hrs. at room temperature. After filtration through celite and evaporation of the solvents under reduced pressure, the crude reaction mixture was measured by ¹H NMR. After evaporation of the solvents under reduced pressure, the crude reaction mixture was purified with column chromatography on silica gel (Pentanes/DCM = 4:1) afford the corresponding product **3aa** (22.5 mg, 67% yield, 96:4 er from **L-1a**; 22.2 mg, 66% yield, 96:4 er from **D-1a**).

Analysis of linear selective reaction



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with [Pd₂(dba)₃] (4.6 mg, 0.005 mmol, 2.5 mol%), *rac*-BINAP (7.6 mg, 0.012 mmol, 6 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards MeCN (2 mL) was added by syringe under a flow of argon and the solution was stirred for 30 min. [**PC1**] (1.8 mg, 0.002 mmol, 1 mol%) and **1a** (0.2 mmol, 1.0 equiv) were added sequentially and cyclohexyl allene (0.24 mmol, 1.2 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 1 inch from blue led strips and irradiated and stirred for 16 hrs at room temperature. After filtration through celite and evaporation of the solvents under reduced pressure, the internal standard isoquinoline (14.4 mg, 0.111 mmol) was added inside. Yield of **6c** (17% yield) was determined by ¹H NMR measurement of the crude reaction mixture. The residue was purified with column chromatography on silica gel afford the corresponding product after drying in vacuo.

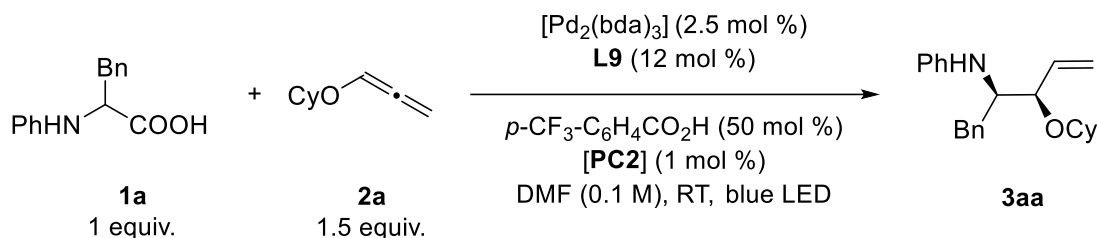
Dimer (**6c**) as a colorless oil with 1.5:1 dr.

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.10 (m, 12H), 7.08 – 7.01 (m, 2H), 6.75 – 6.67 (m, 2H), 6.61 – 6.55 (major, m, 2.22H), 6.48 – 6.43 (minor, m, 1.47H), 3.80 – 3.76 (m, 2H), 3.62 (brs, 2H), 2.99 – 2.94 (minor, m, 1.47H), 2.90 (major, d, *J* = 6.8 Hz, 2.26H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 147.3, 138.6, 138.2, 129.3, 129.5, 129.3, 128.6, 128.5, 126.6, 126.4, 118.1, 117.7, 114.1, 113.9, 55.8, 55.7, 38.7, 36.4.

HR-MS (C₁₉H₂₄O₂N; [M-H]⁻, -p ESI): calcd: 391.2180, found: 391.2182.

On/Off studies



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with [Pd₂(dba)₃] (4.6 mg, 0.005 mmol, 2.5 mol%), **L9** (13.0 mg, 0.024 mmol, 12 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards DMF (2 mL) was added by syringe under a flow of argon and the solution was stirred for 30 min. **[PC2]** (2.2 mg, 0.002 mmol, 1 mol%), **1a** (48.4 mg, 0.2 mmol, 1.0 equiv), *p*-CF₃-C₆H₄CO₂H (19.0 mg, 0.1 mmol, 0.5 equiv.) and 1,3,5-trimethoxybenzene (11.2 mg, 66.6 μmol) were added sequentially and **2a** (45 μL, 0.3 mmol, 1.5 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 1 inch from blue led strips, irradiated and stirred at room temperature. For each indicated time 0.3 mL reaction mixture was taken from the Schlenk tube under a flow of argon. After dried in vacuo, the yield of product (**3aa**) was monitored by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

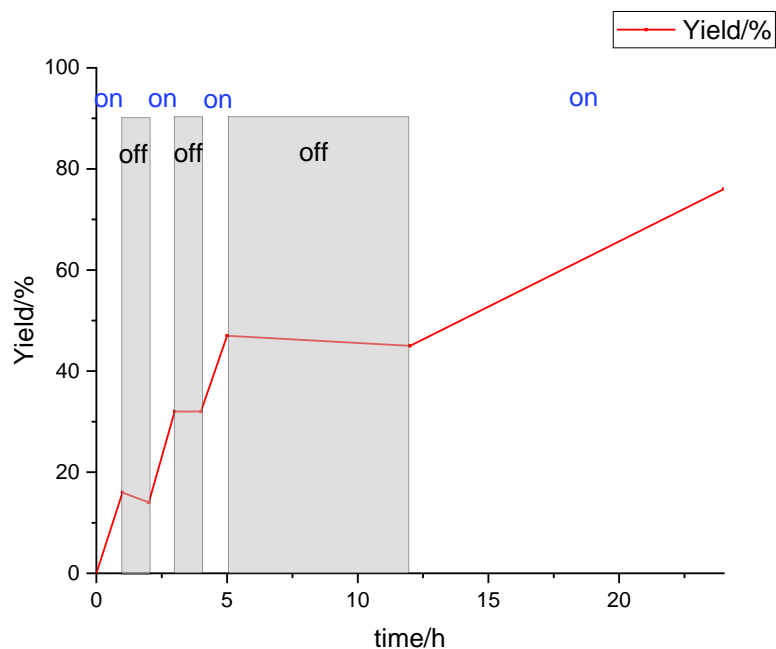
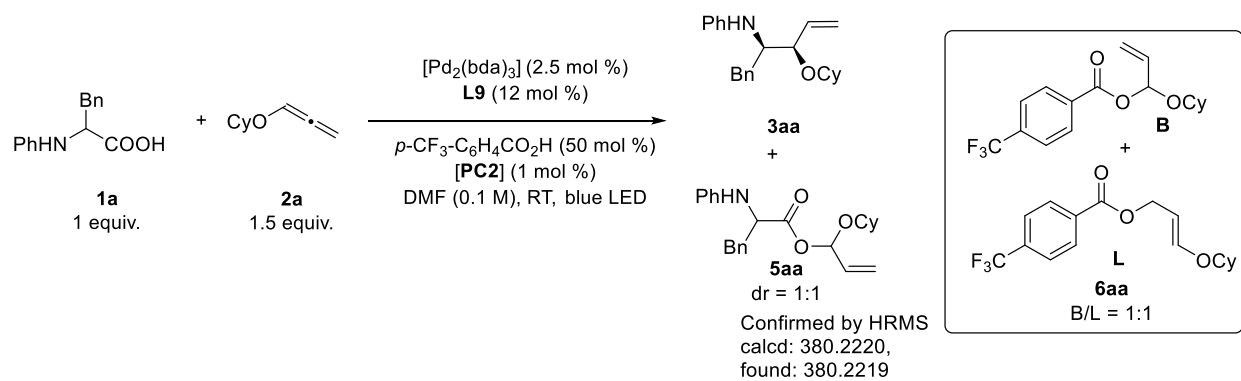


Figure S1. Monitor the formation of **3aa** with light on/off.

To make a comparison, under the same conditions a continuous irradiation was carried out.



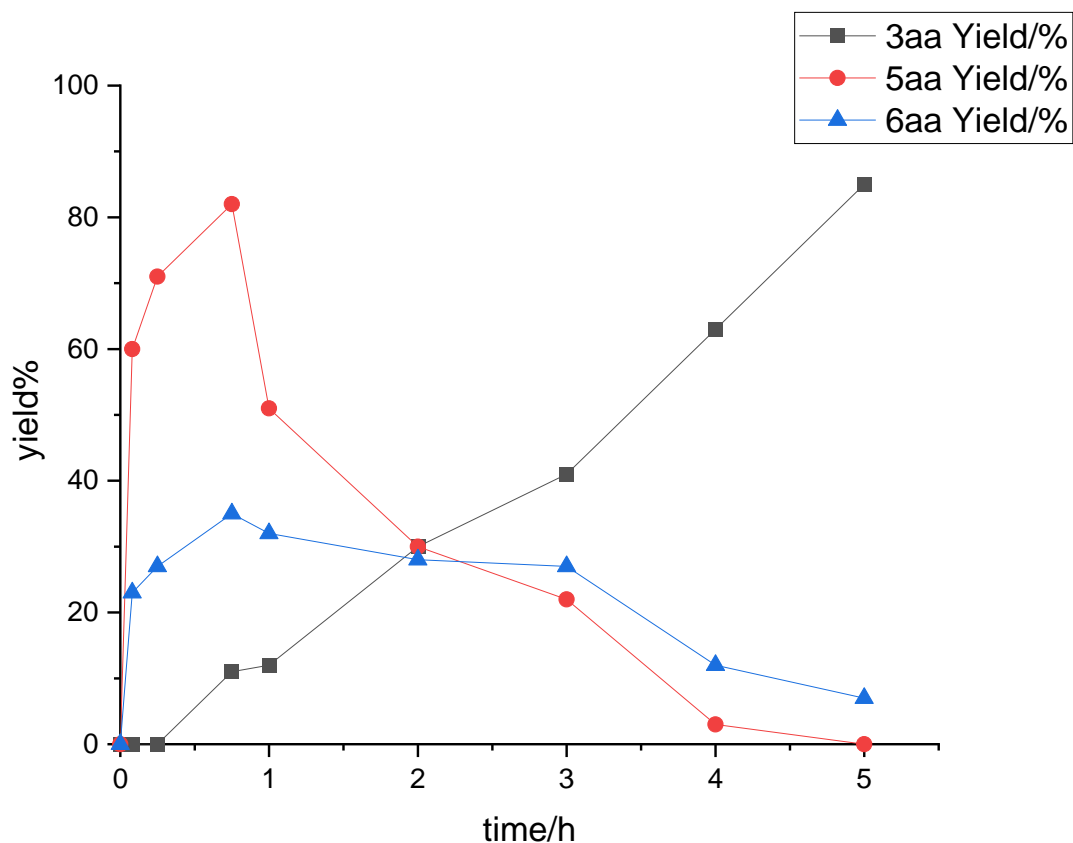
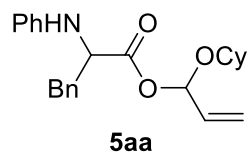


Figure S2. Reaction profile under continuous irradiation.

Since purification of **5aa** on silica gel is not successful, the relative pure **5aa** could be obtained following the general procedure C without adding *p*-CF₃-C₆H₄CO₂H, and evaporating the solvent after 1 h. For other 2D NMR spectra see in NMR spectra section.

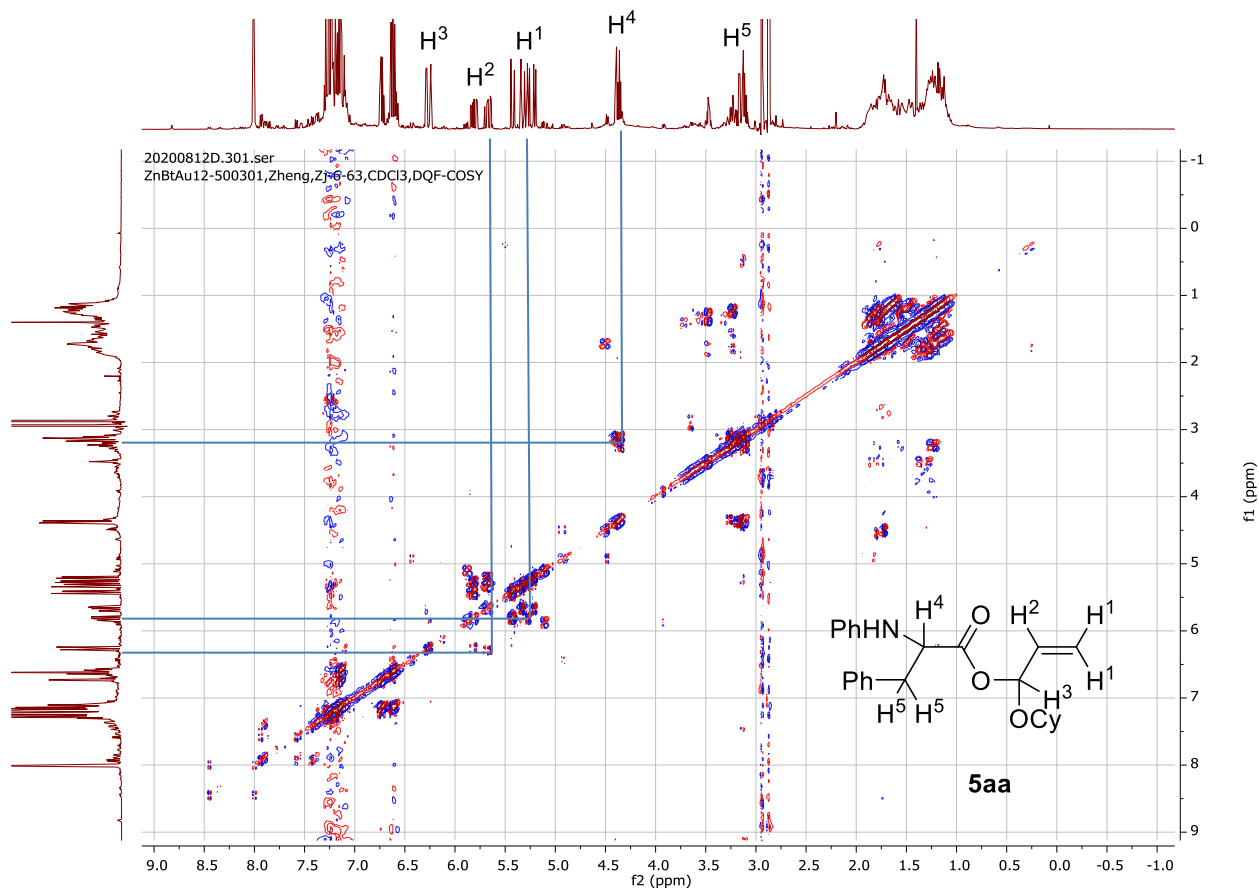


HRMS (C₂₄H₃₀O₃N; [M+H]⁺, pESI): calcd: 380.2220, found: 380.2219.

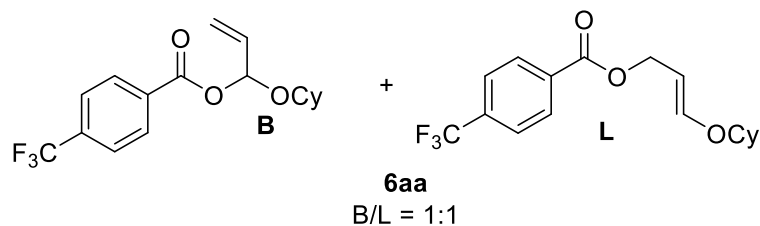
¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.08 (m, 7H), 6.78 – 6.69 (m, 1H), 6.66 – 6.56 (m, 2H), 6.29 (dd, *J* = 5.0, 1.0 Hz, 0.46H), 6.25 (dd, *J* = 5.0, 1.0 Hz, 0.47H), 5.81 (ddd, *J* = 17.5, 10.5, 5.0 Hz, 0.46H), 5.67 (ddd, *J* = 17.5, 10.5, 5.0 Hz, 0.47H), 5.43 (dd, *J* = 17.5, 1.0 Hz, 0.5H), 5.33 (dd, *J* =

17.5, 1.0 Hz, 0.5H), 5.27 (dd, $J = 10.5, 1.0$ Hz, 0.5H), 5.21 (dd, $J = 10.5, 1.0$ Hz, 0.5H), 4.40 – 4.35 (m, 1H), 3.33 – 3.20 (m, 1H), 3.18 – 3.08 (m, 2H), 1.90 – 1.12 (m, 10H).

Identified ^{13}C NMR (126 MHz, CDCl_3) δ 173.0, 172.9, 133.7, 133.6, 118.8, 118.7, 118.6, 118.58, 113.8, 113.7, 113.6, 113.1, 96.4, 96.1, 58.3, 58.0, 38.6, 38.5, 38.3.



Since purification of **6aa** on silica gel is not successful, the relative pure **6aa** (B/L = 1:1) could be obtained following the general procedure C without adding aminoacid **1a**, and evaporating the solvent after 1 h. For other 2D NMR spectra see in NMR spectra section.



¹H NMR (500 MHz, CDCl₃) δ 8.20 – 8.13 (m, 2H), 7.72 – 7.68 (m, 2H), 6.60 – 6.56 (m, 1H), 5.99 (**B**, ddd, *J* = 17.0, 10.5, 5.0 Hz, 0.43H), 5.56 (**B**, d, *J* = 17.5 Hz, 0.46H), 5.35 (**B**, d, *J* = 10.5 Hz, 0.49H), 5.14 (**L**, dt, *J* = 12.4, 8.0 Hz, 0.39H), 4.76 (**L**, d, *J* = 8.0 Hz, 0.82H), 3.82 – 3.65 (m, 1H), 1.98 – 1.82 (m, 2H), 1.78 – 1.68 (m, 2H), 1.56 – 1.49 (m, 1H), 1.47 – 1.37 (m, 2H), 1.32 – 1.20 (m, 3H).

¹⁹F NMR (471 MHz, CDCl₃) δ -63.09, -63.15.

¹³C NMR (126 MHz, CDCl₃) δ 152.1 (**B**), 133.9 (**B**), 130.3, 130.0, 125.5 (q, 3.8 Hz), 125.4 (q, 3.8 Hz), 119.0 (**B**), 98.7 (**L**), 97.2 (**L**), 79.0, 77.6, 64.1, 33.4, 33.2, 32.1, 32.0, 25.6, 25.5, 23.9, 23.7.

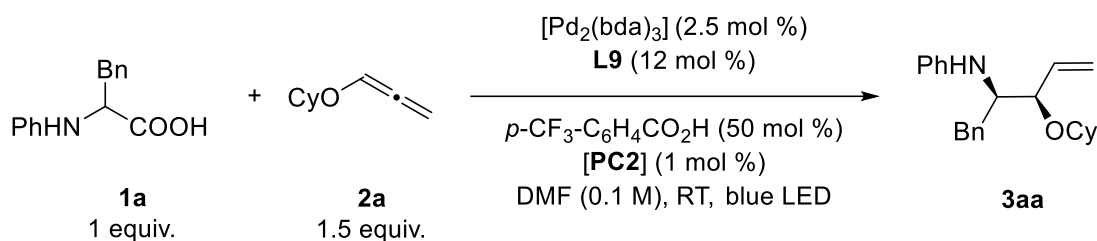
Quantum yield measurements

Determination of the light intensity of the blue LED

The photon flux of blue LED was determined by standard ferrioxalate actinometry.^[8]

$$\text{photo flux (Einstein} \cdot \text{s}^{-1}) = 1.03 \times 10^{-6}$$

Measurement of quantum yield:



A 10 ml Schlenk tube was flame-dried under vacuum, backfilled with argon and cooled to room temperature using a standard Schlenk line apparatus. The Schlenk tube was charged with $[\text{Pd}_2(\text{dba})_3]$ (2.3 mg, 0.0025 mmol, 2.5 mol%), **L9** (6.5 mg, 0.012 mmol, 12 mol%). The Schlenk tube was put on vacuum and backfilled with argon three times. Afterwards DMF (1 mL) was added by syringe under a flow of argon and the solution was stirred for 30 min. **[PC2]** (1.1 mg, 0.001 mmol, 1 mol%), **1a** (24.2 mg, 0.1 mmol, 1.0 equiv), $p\text{-CF}_3\text{-C}_6\text{H}_4\text{CO}_2\text{H}$ (9.5 mg, 0.05 mmol, 0.5 equiv.) and 1,3,5-trimethoxybenzene (5.8 mg, 34.5 μmol) were added sequentially and **2a** (22 μL , 0.15 mmol, 1.5 equiv) was added by syringe under a flow of argon. The Schlenk tube was sealed by a screw cap and the resulting mixture was placed approximately 2.5 cm away from one 34 W blue LED and irradiated and stirred for 5 min at room temperature. The solvents were removed under reduced pressure. The moles of product (**3aa**) formed (29 μmol) were measured by $^1\text{H NMR}$ using 1,3,5-trimethoxybenzene as internal standard. The quantum yield calculation is then as following:

$$\Phi = \frac{\text{moles of product}}{\text{moles of absorbed photons}} = \frac{\text{moles of product}}{\text{flux} \cdot t \cdot f}$$

Where flux is the photon flux determined by ferrioxalate actinometry (1.03×10^{-6} Einstein/s), t is the time (300 s), and f is the fraction of light absorbed by $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbpy})]\text{PF}_6$ **[PC2]** at 450 nm. A 1×10^{-3} M solution of **[PC2]** in DMF was prepared, and the absorbance of the solution at

450 nm was 0.476. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-0.476} = 0.67$.

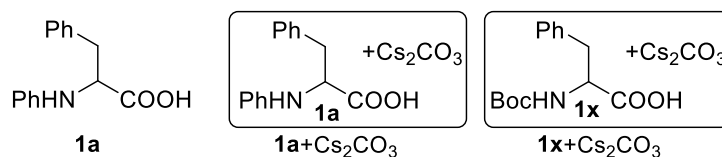
$$\Phi = \frac{\text{moles of product}}{\text{moles of absorbed photons}} = \frac{\text{moles of product}}{\text{flux} \cdot t \cdot f} = \frac{2.9 \times 10^{-5}}{1.03 \times 10^{-6} \cdot 300 \cdot 0.67} = 0.14$$

Stern-Volmer fluorescence quenching study

The rate of quenching (k_q) was determined using Stern-Volmer relationship:

$$\frac{I_0}{I} = K_q \times \tau_0 \times [\text{quencher}] + 1$$

Where I_0 is the fluorescence intensity without the quencher, I is the fluorescence intensity with the quencher, and τ_0 is the lifetime of the photoexcited state of the photocatalyst. The excited state lifetime of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2][\text{PF}_6]$ in MeCN is 557 ns^[9]. In this study the compounds below are tested.



Evaluation of **1a** as potential quencher for photoexcited $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2][\text{PF}_6]$.

$[\text{Ir}(\text{dtbbpy})(\text{ppy})_2][\text{PF}_6]$ (5.83 mg, 6.38×10^{-3} mmol) was dissolved in 5.0 mL DMF to prepare a 1.28×10^{-3} M solution. 50 μL of this solution was added to each of a set of 6 volumetric flasks (10 mL). Subsequently, the solution of quencher **1a** in DMF (10.0 mL, 6.66×10^{-3} M) was added in increasing amounts (0, 100 μL , 200 μL , 300 μL , 600 μL , 1200 μL) to the volumetric flasks and the volume of volumetric flasks were adjusted to 10 mL by adding DMF. 2 mL solution was added into the cuvette, and the solution was degassed with argon for 1 minute before the measure. All solutions were excited at 375 nm and the fluorescence emission was detected at 542 nm. The ratio of the maximum fluorescence emission intensities maximum between samples without and with quencher were plotted against the quencher concentration to generate the Stern-Volmer plots below.

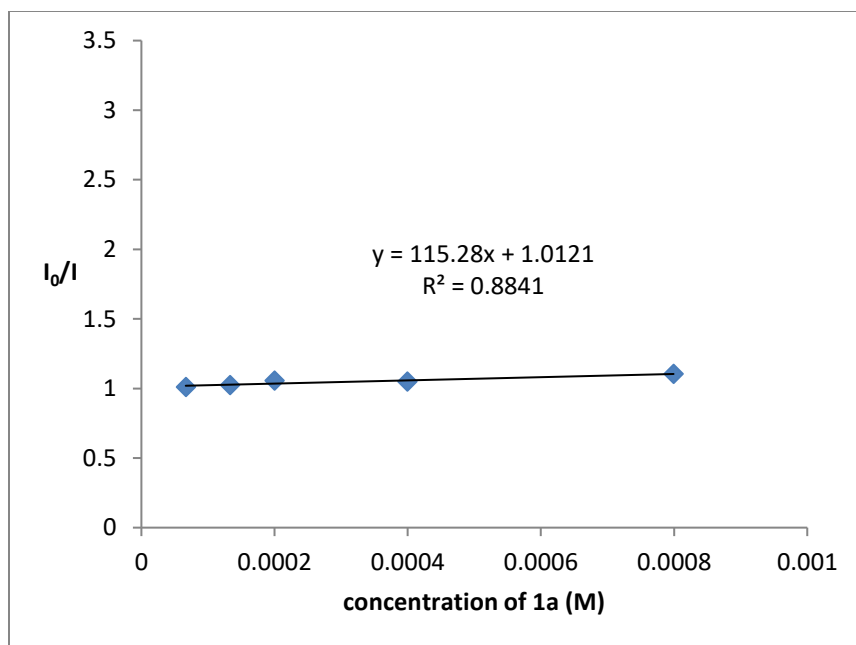


Figure S3. Stern-Volmer quenching experiment of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2][\text{PF}_6]$ and **1a**. No quenching observed.

Evaluation of **1a**+ Cs_2CO_3 as potential quencher for photoexcited $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2][\text{PF}_6]$.

To the solution of **1a** in DMF (10.0 mL, 6.66×10^{-3} M) was added Cs_2CO_3 (43.4 mg, 1.33×10^{-2} M), and the mixture was stirred for 2 h. $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2][\text{PF}_6]$ (5.83 mg, 6.38×10^{-3} mmol) was dissolved in 5.0 mL DMF to prepare a 1.28×10^{-3} M solution. 50 μL of this solution was added to each of a set of 6 volumetric flasks (10 mL). Subsequently, the mixture of quencher **1a**+ Cs_2CO_3 in DMF was added in increasing amounts (0, 100 μL , 200 μL , 300 μL , 600 μL , 1200 μL) to the volumetric flasks and the volume of volumetric flasks were adjusted to 10 mL by adding DMF. 2 mL solution was added into the cuvette, and the solution was degassed with argon for 1 minute before the measure. All solutions were excited at 375 nm and the fluorescence emission was detected at 542 nm. The ratio of the maximum fluorescence emission intensities maximum between samples without and with quencher were plotted against the quencher concentration to generate the Stern-Volmer plots below.

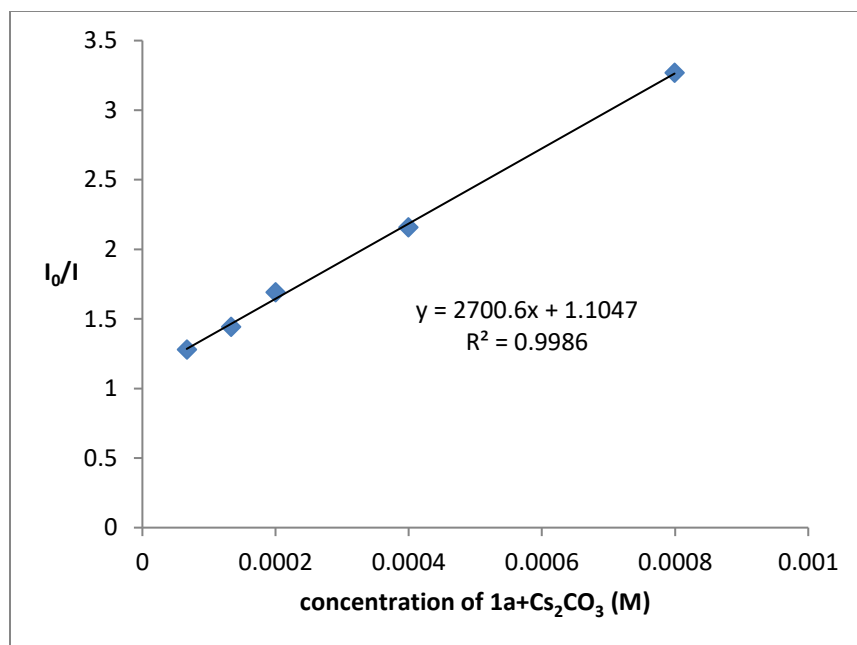


Figure S4. Stern-Volmer quenching experiment of $[Ir(dtbbpy)(ppy)_2][PF_6]$ and $1a+Cs_2CO_3$. k_q is $4.8 \times 10^9 M^{-1}s^{-1}$.

Evaluation of $1x+Cs_2CO_3$ as potential quencher for photoexcited $[Ir(dtbbpy)(ppy)_2][PF_6]$.

To the solution of **1x** in DMF (10.0 mL, 6.66×10^{-3} M) was added Cs_2CO_3 (43.4 mg, 1.33×10^{-2} M), and the mixture was stirred for 2 h. $[Ir(dtbbpy)(ppy)_2][PF_6]$ (5.83 mg, 6.38×10^{-3} mmol) was dissolved in 5.0 mL DMF to prepare a 1.28×10^{-3} M solution. 50 μ L of this solution was added to each of a set of 6 volumetric flasks (10 mL). Subsequently, the mixture of quencher **1x**+ Cs_2CO_3 in DMF was added in increasing amounts (0, 100 μ L, 200 μ L, 300 μ L, 600 μ L, 1200 μ L) to the volumetric flasks and the volume of volumetric flasks were adjusted to 10 mL by adding DMF. 2 mL solution was added into the cuvette, and the solution was degassed with argon for 1 minute before the measure. All solutions were excited at 375 nm and the fluorescence emission was detected at 542 nm. The ratio of the maximum fluorescence emission intensities maximum between samples without and with quencher were plotted against the quencher concentration to generate the Stern-Volmer plots below.

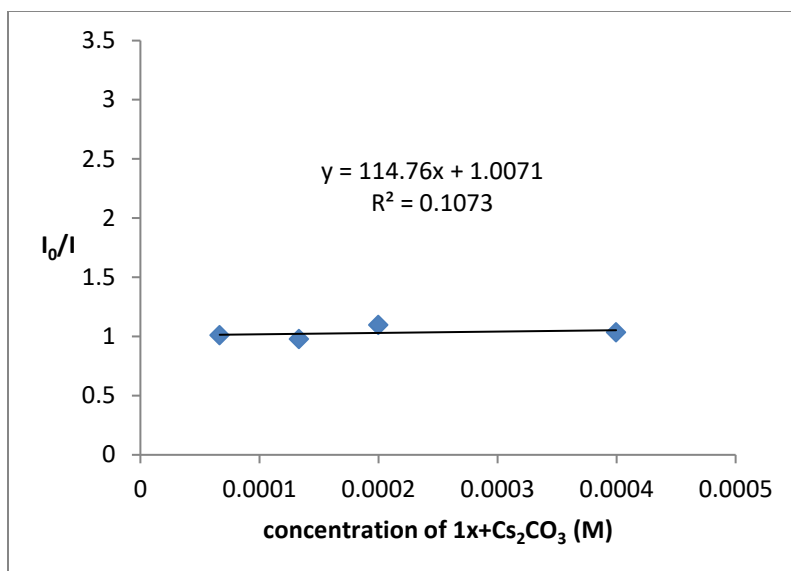


Figure S5. Stern-Volmer quenching experiment of $[Ir(dtbbpy)(ppy)_2][PF_6]$ and $1x+Cs_2CO_3$. No quenching observed.

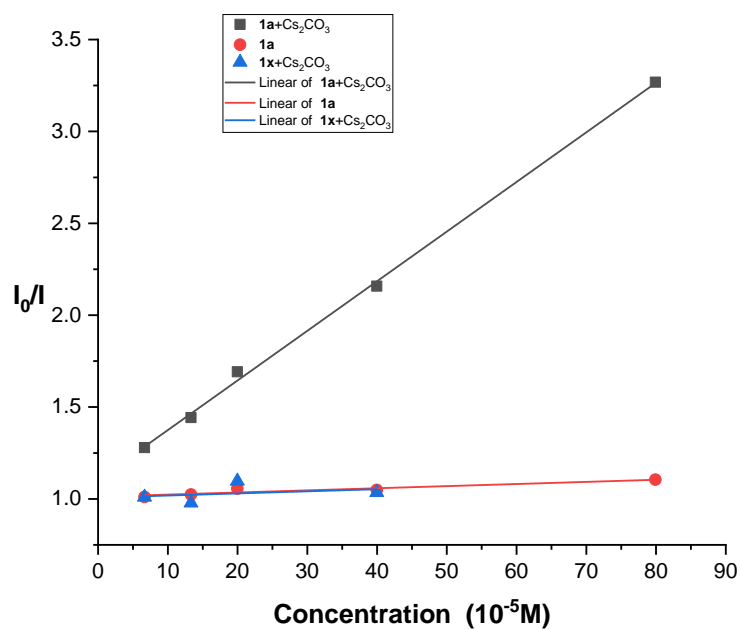
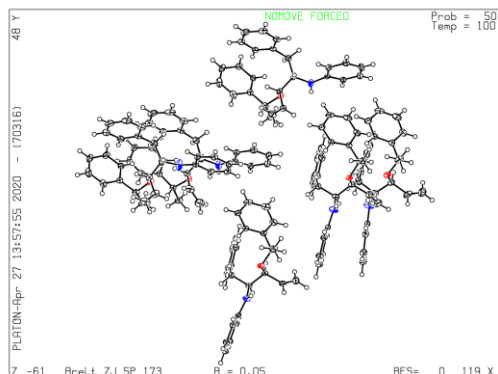


Figure S6. The overlap of all the Stern-Volmer quenching experiments.

X-Ray crystal structure of 3al



The following text is only a suggestion: The compound was crystallized from DCM/pentane by solvent layering. The data for Breit_ZJ_5_1473 were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used CuK α radiation ($\lambda = 1.54184$ Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied. The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3 using ShelXle.^[3-5] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1999447 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.

Table S4. Crystal data and structure refinement for Breit_ZJ_5_1473

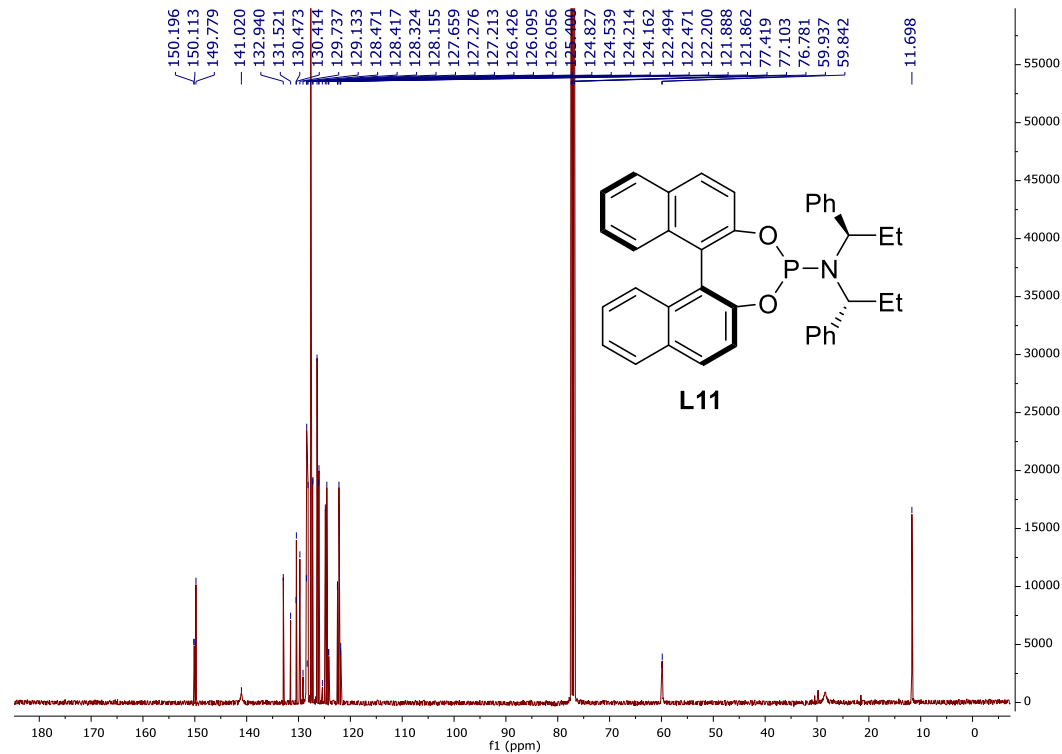
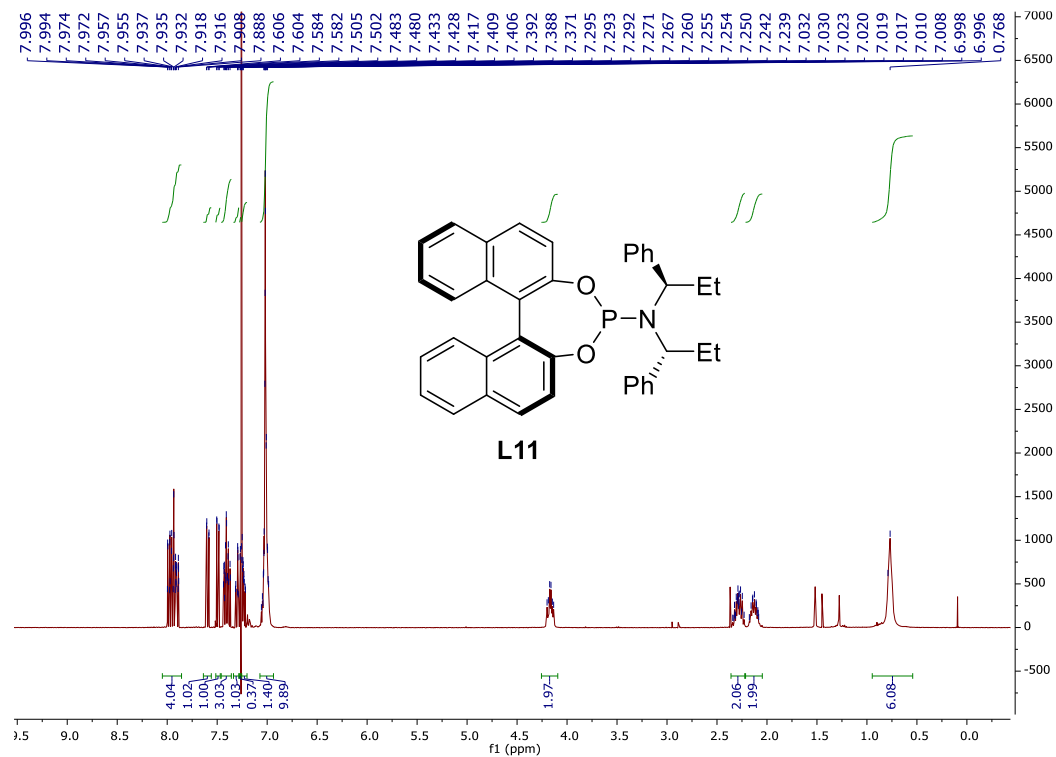
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Empirical formula	C ₂₅ H ₂₇ NO

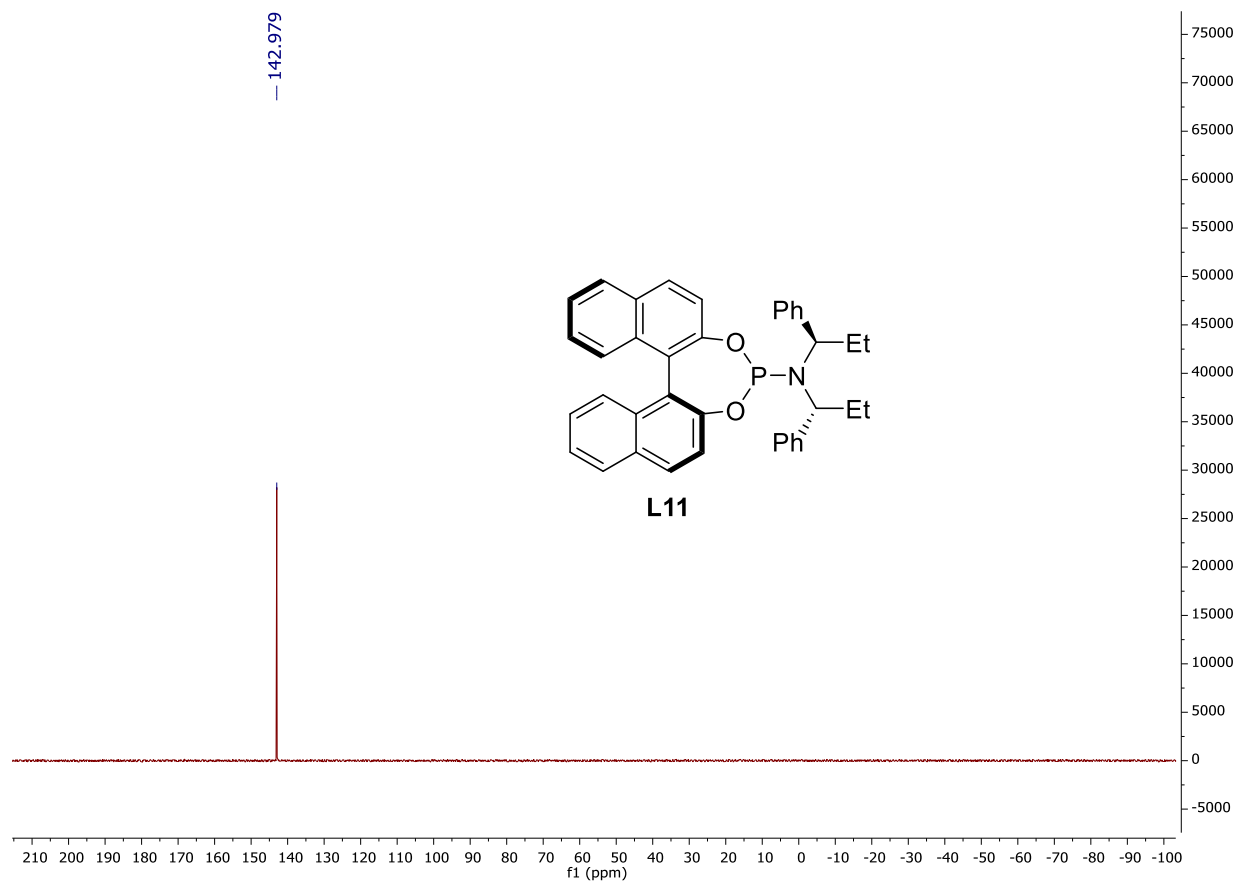
Formula weight	357.47
Temperature [K]	100(2)
Crystal system	triclinic
Space group (number)	<i>P</i> 1 (1)
<i>a</i> [Å]	10.065(6)
<i>b</i> [Å]	16.479(5)
<i>c</i> [Å]	18.705(6)
α [°]	89.89(2)
β [°]	89.96(3)
γ [°]	79.81(3)
Volume [Å ³]	3054(2)
<i>Z</i>	6
ρ_{calc} [g/cm ³]	1.166
μ [mm ⁻¹]	0.539
<i>F</i> (000)	1152
Crystal size [mm ³]	0.120×0.060×0.040
Crystal colour	colourless
Crystal shape	needle
Radiation	CuK α (λ =1.54184 Å)
2 θ range [°]	4.72 to 149.92 (0.80 Å)
Index ranges	-12 ≤ <i>h</i> ≤ 12 -20 ≤ <i>k</i> ≤ 20 -23 ≤ <i>l</i> ≤ 23
Reflections collected	107574
Independent reflections	24209 <i>R</i> _{int} = 0.0499 <i>R</i> _{sigma} = 0.0407
Completeness to $\theta = 67.684^\circ$	99.3 %
Data / Restraints / Parameters	24209/3/1465
Goodness-of-fit on <i>F</i> ²	1.051
Final <i>R</i> indexes	<i>R</i> ₁ = 0.0459
[<i>I</i> ≥ 2σ(<i>I</i>)]	w <i>R</i> ₂ = 0.1227
Final <i>R</i> indexes	<i>R</i> ₁ = 0.0477
[all data]	w <i>R</i> ₂ = 0.1245
Largest peak/hole [eÅ ³]	0.57/-0.28
Flack X parameter	-0.01(4)

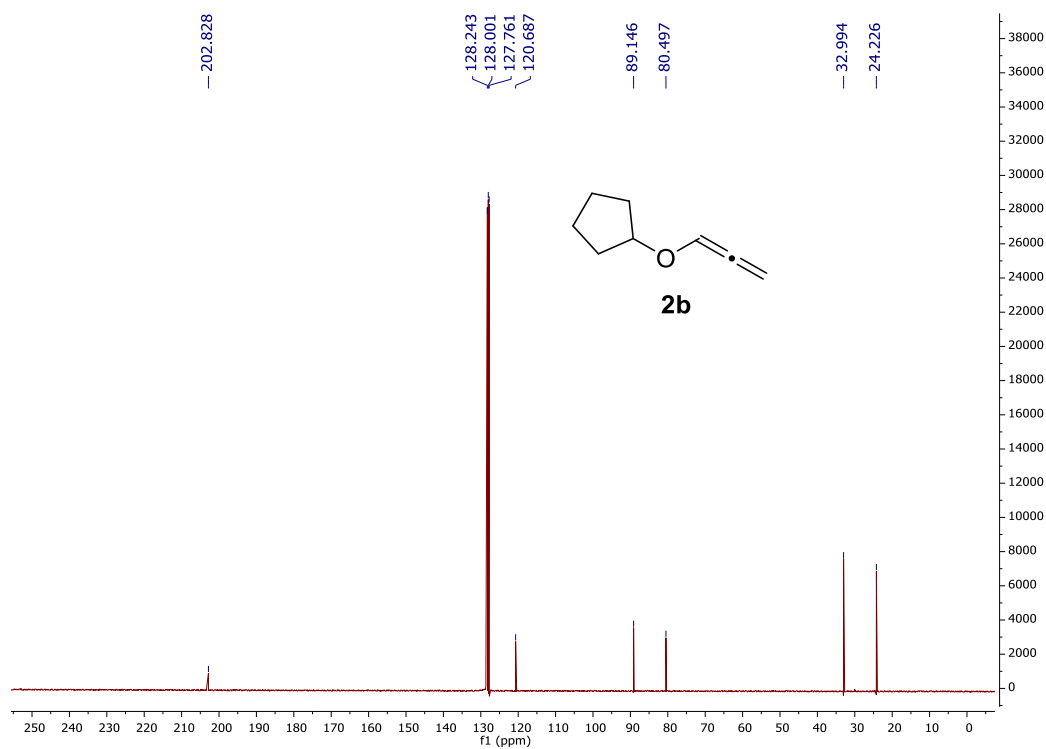
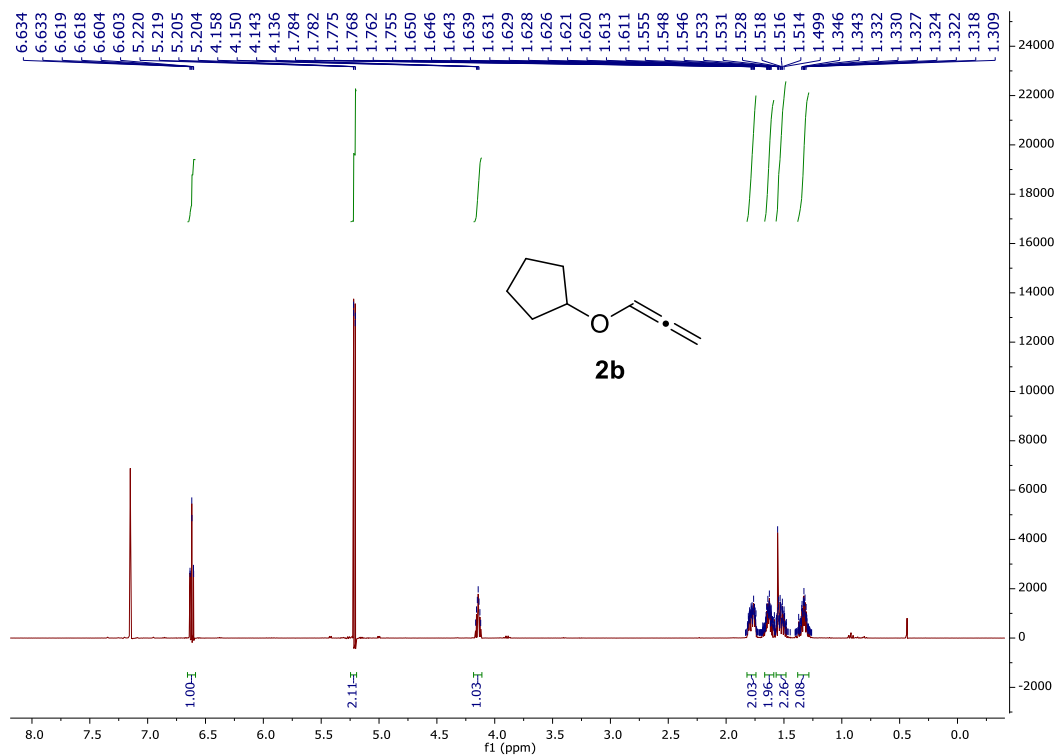
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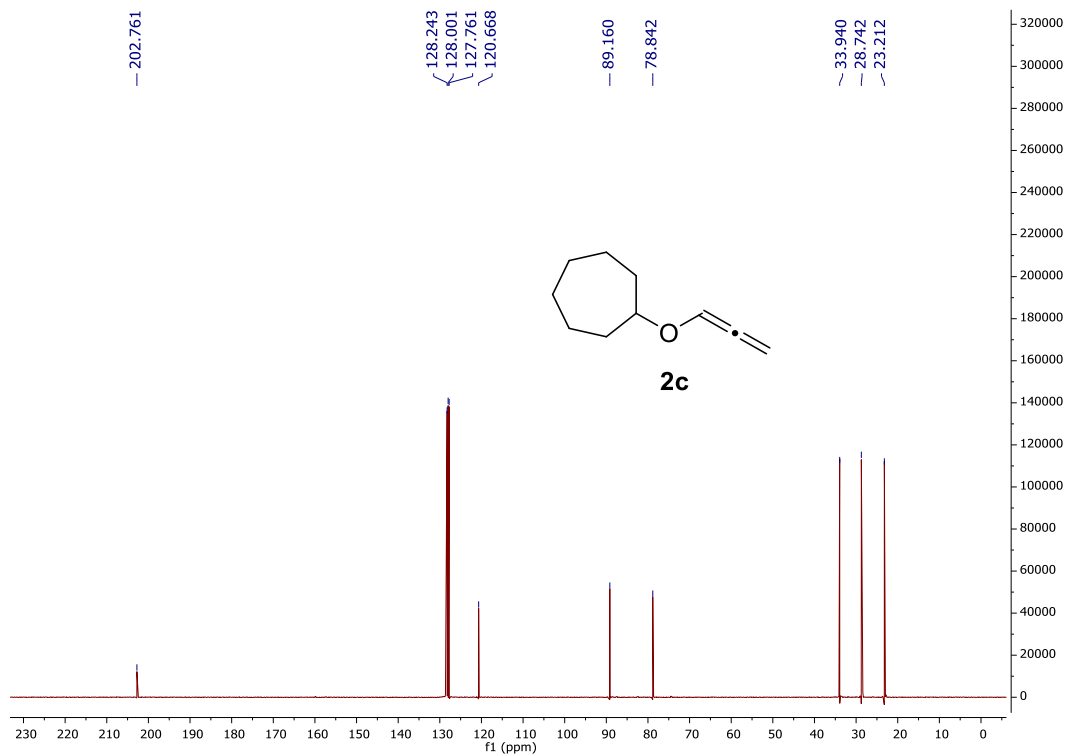
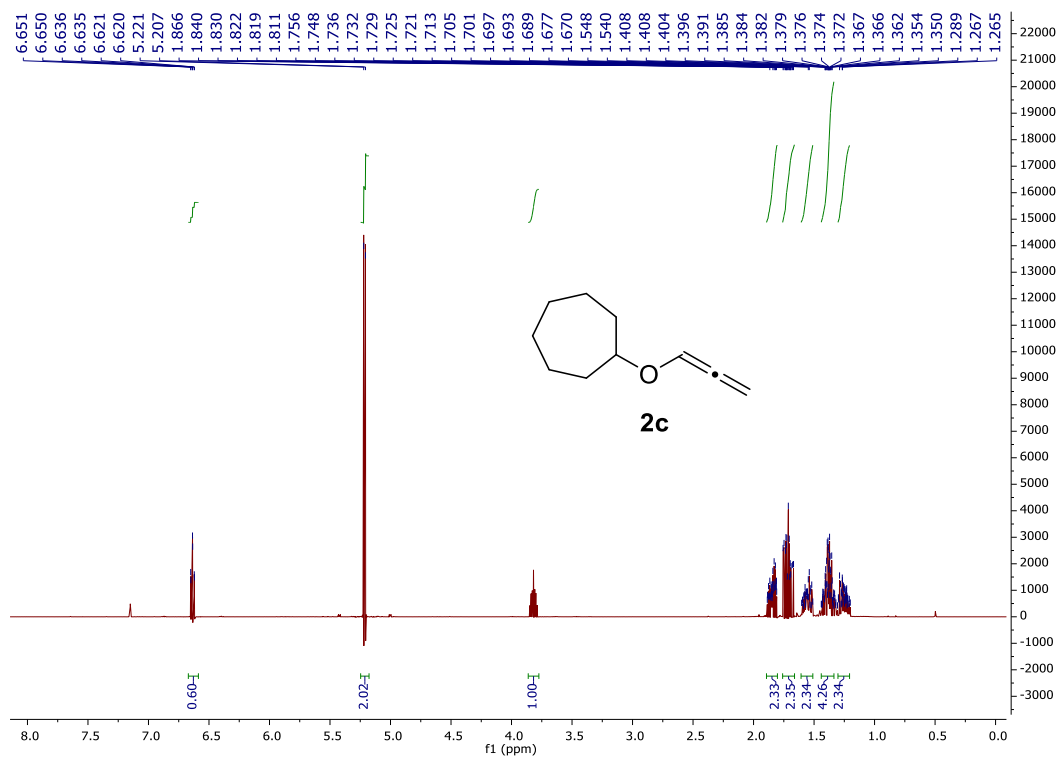
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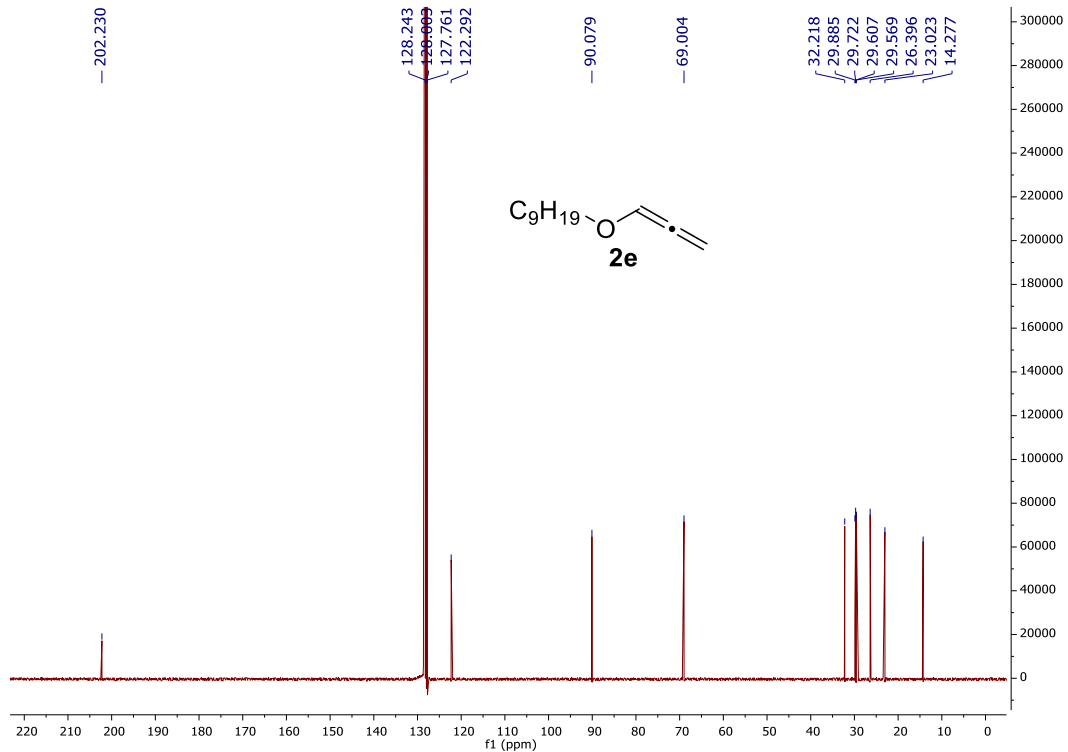
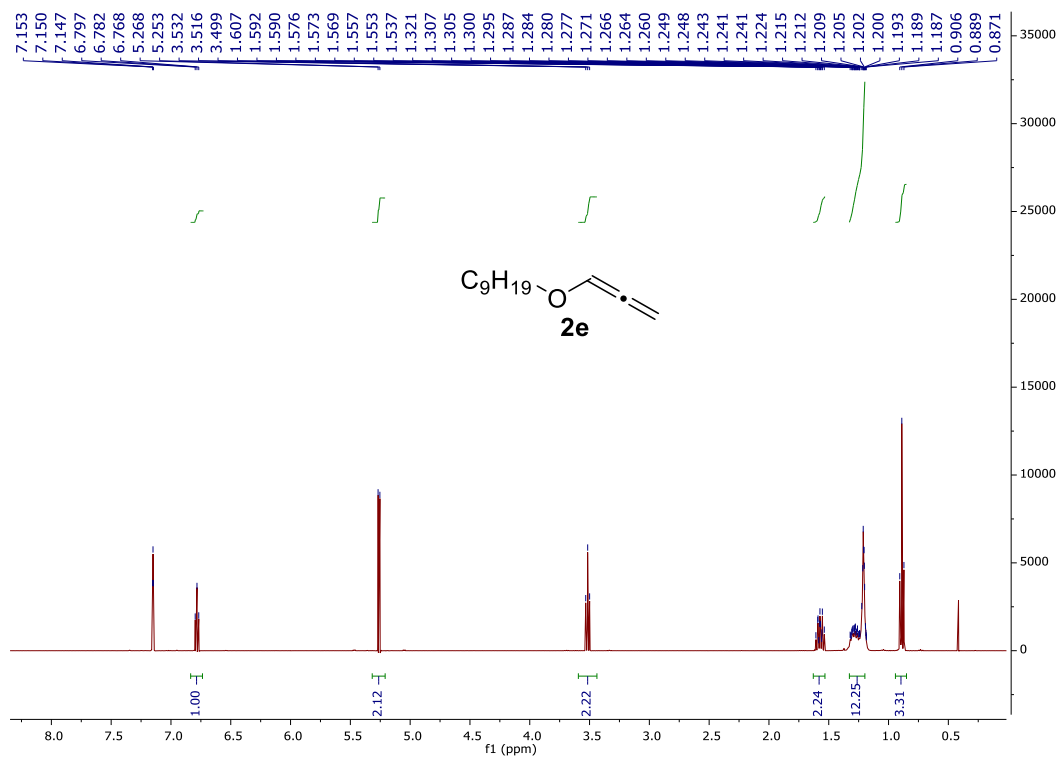
Copies of NMR spectra and HPLC chromatographs

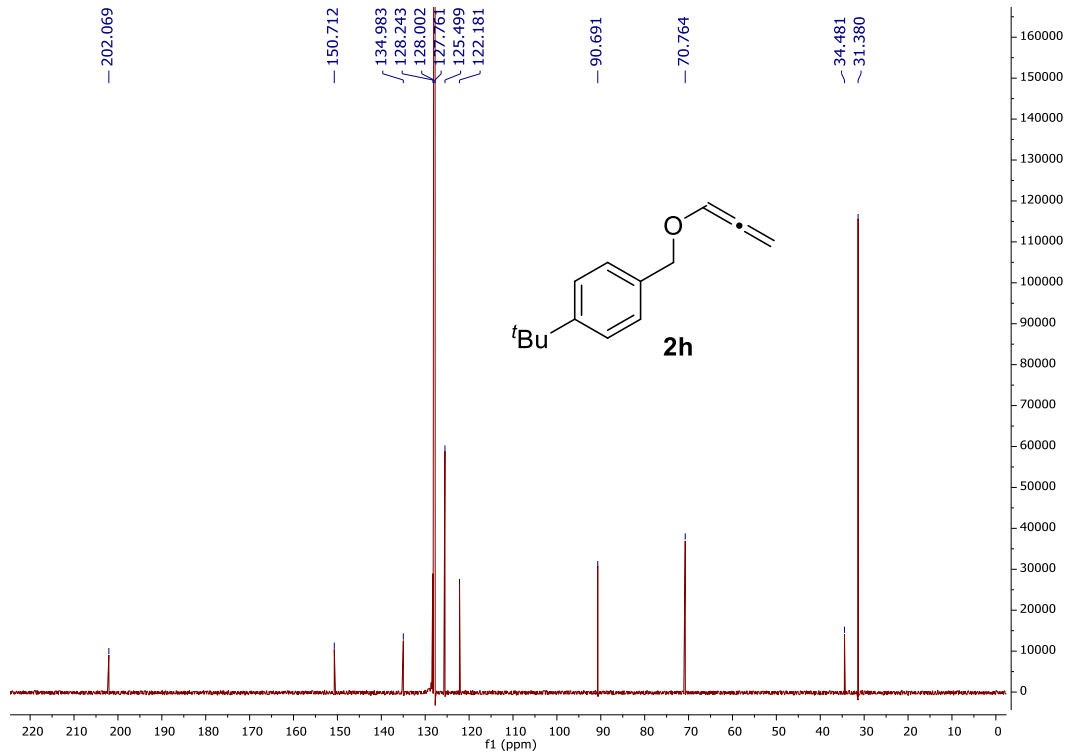
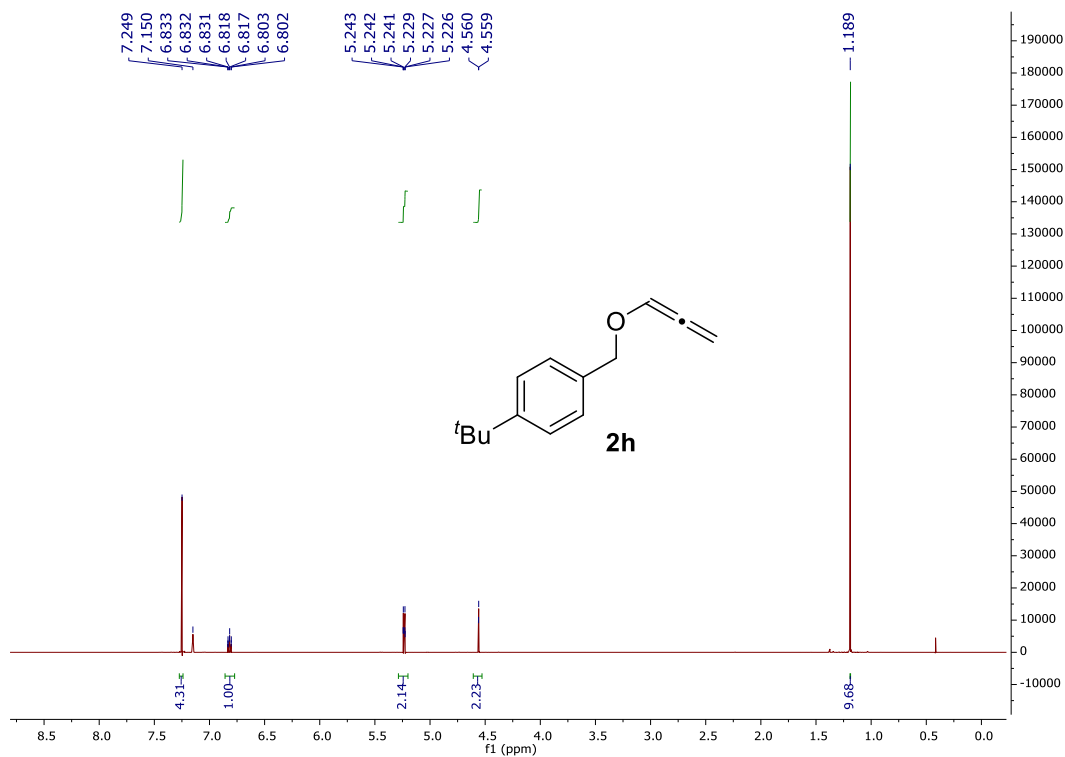


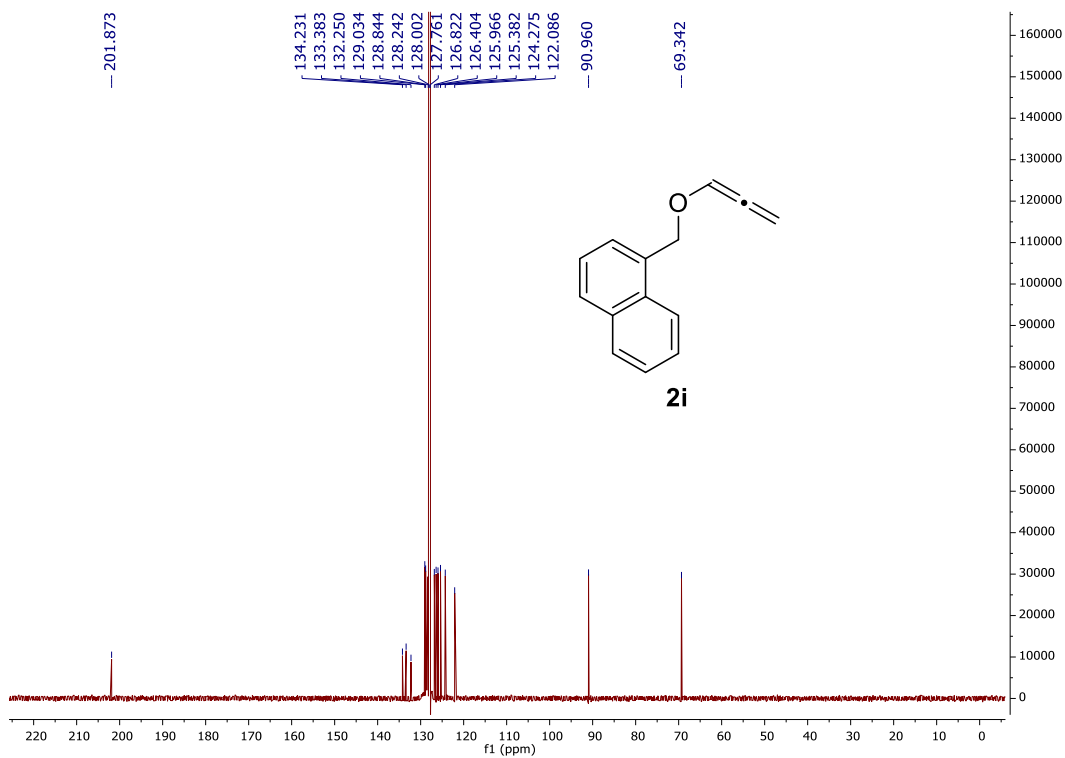
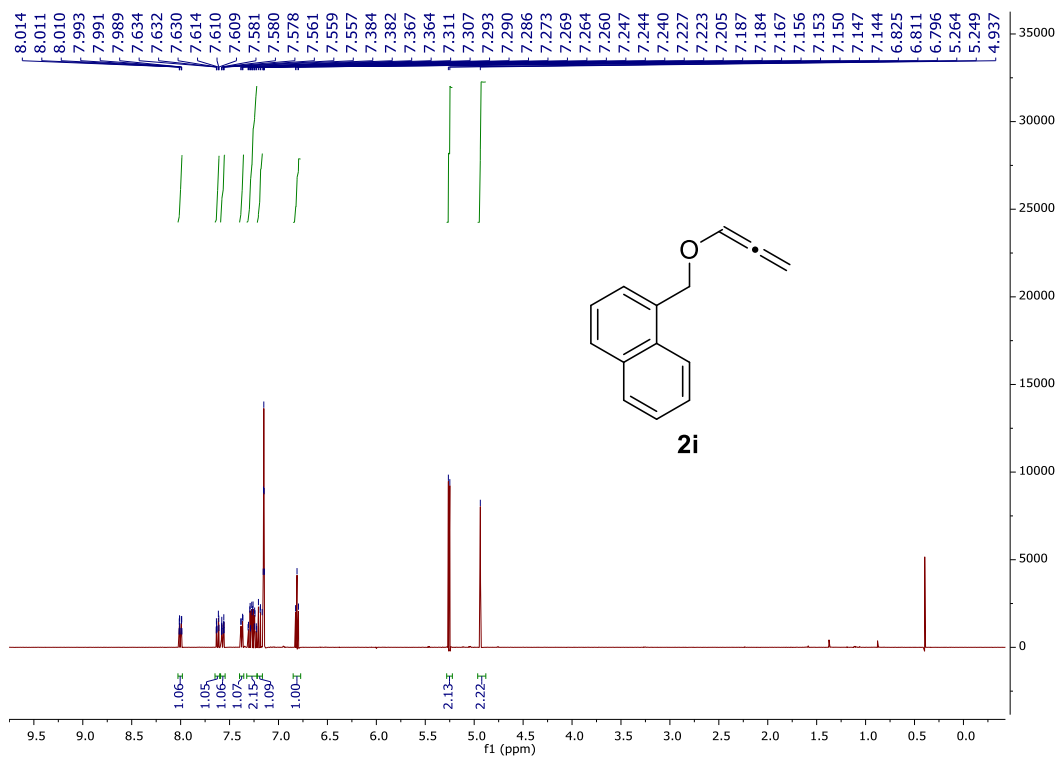


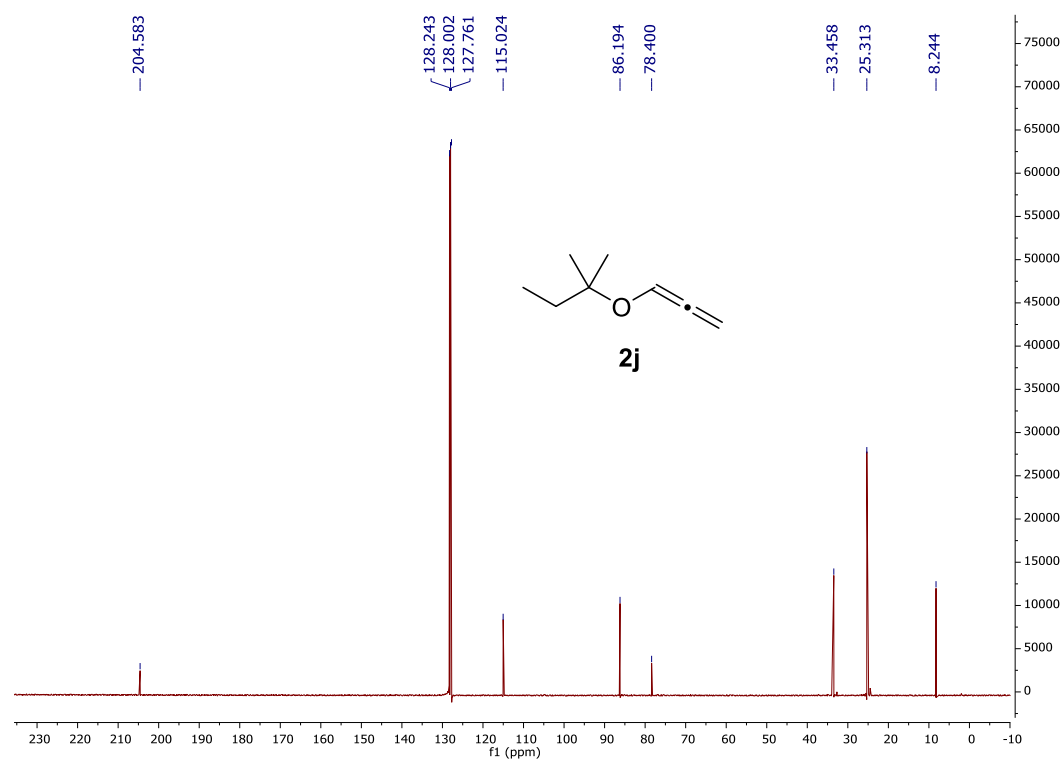
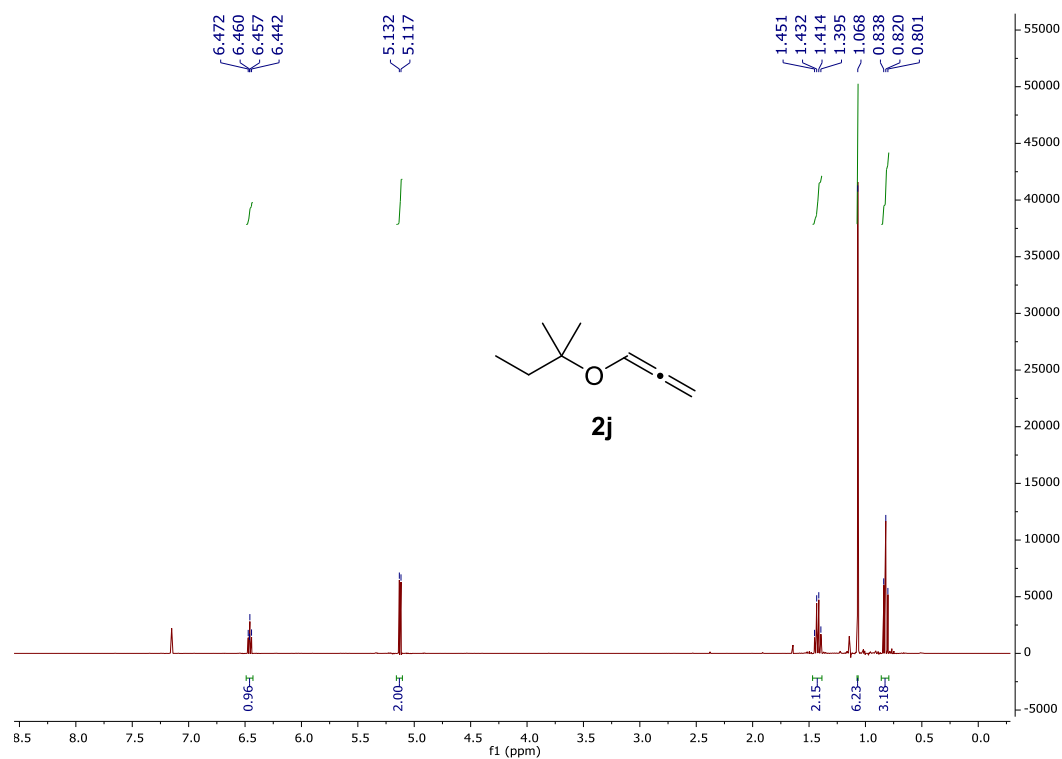


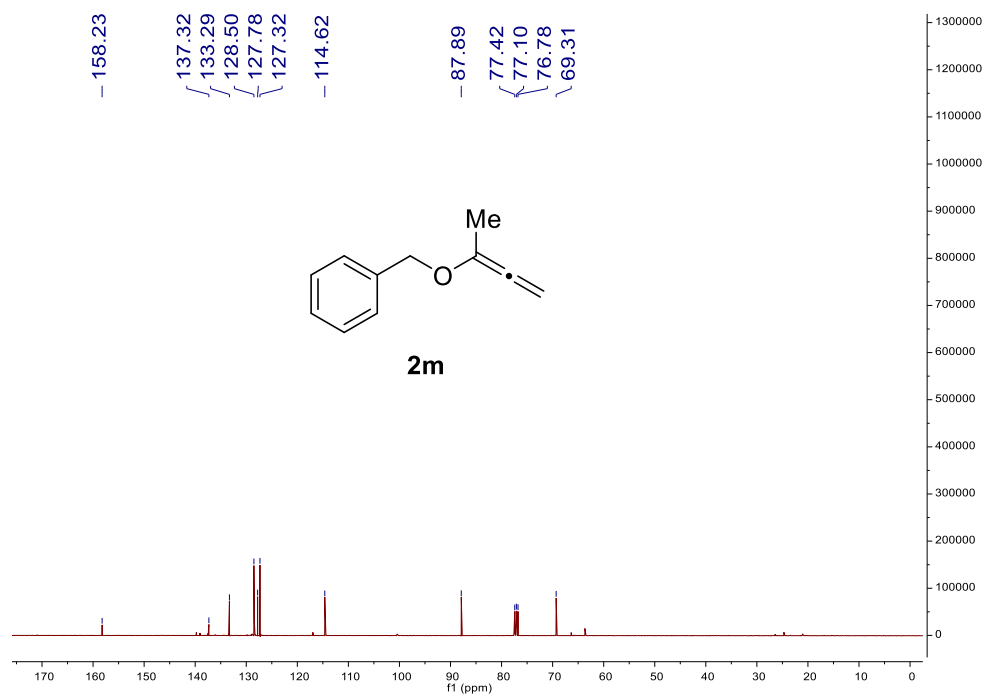
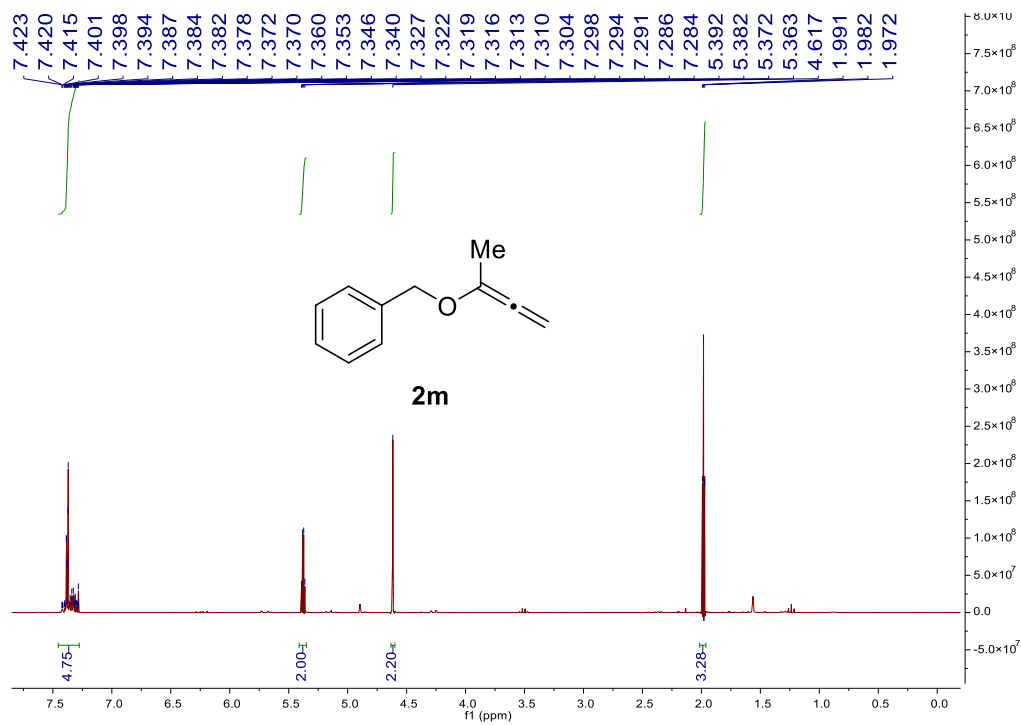


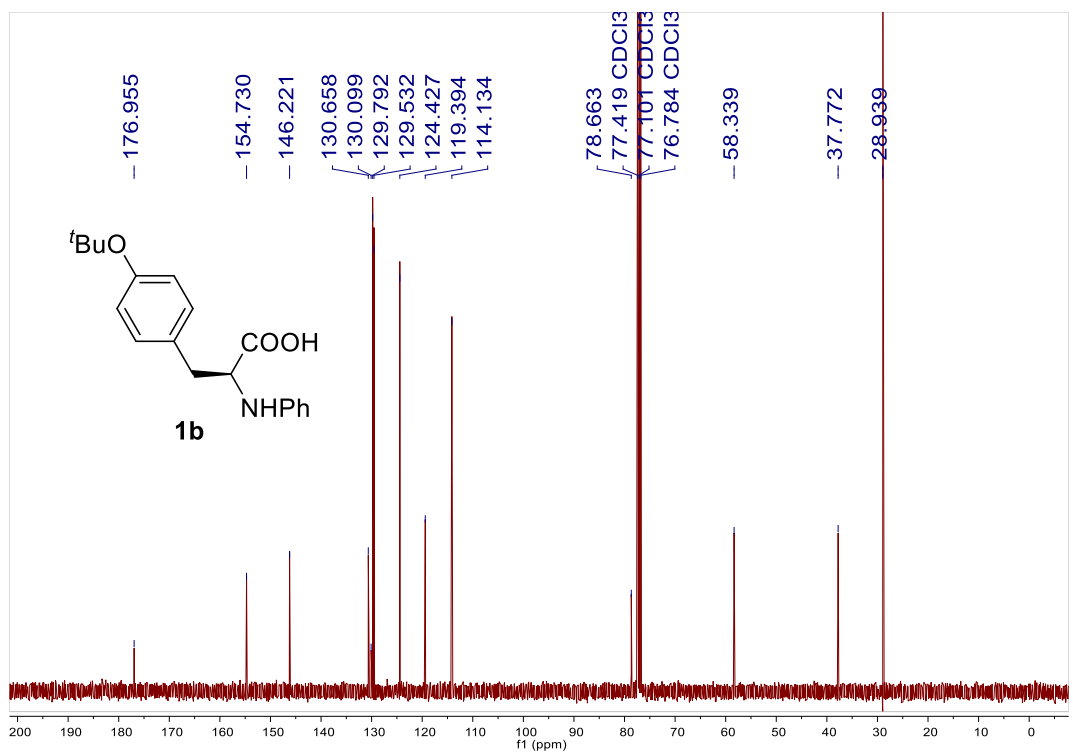
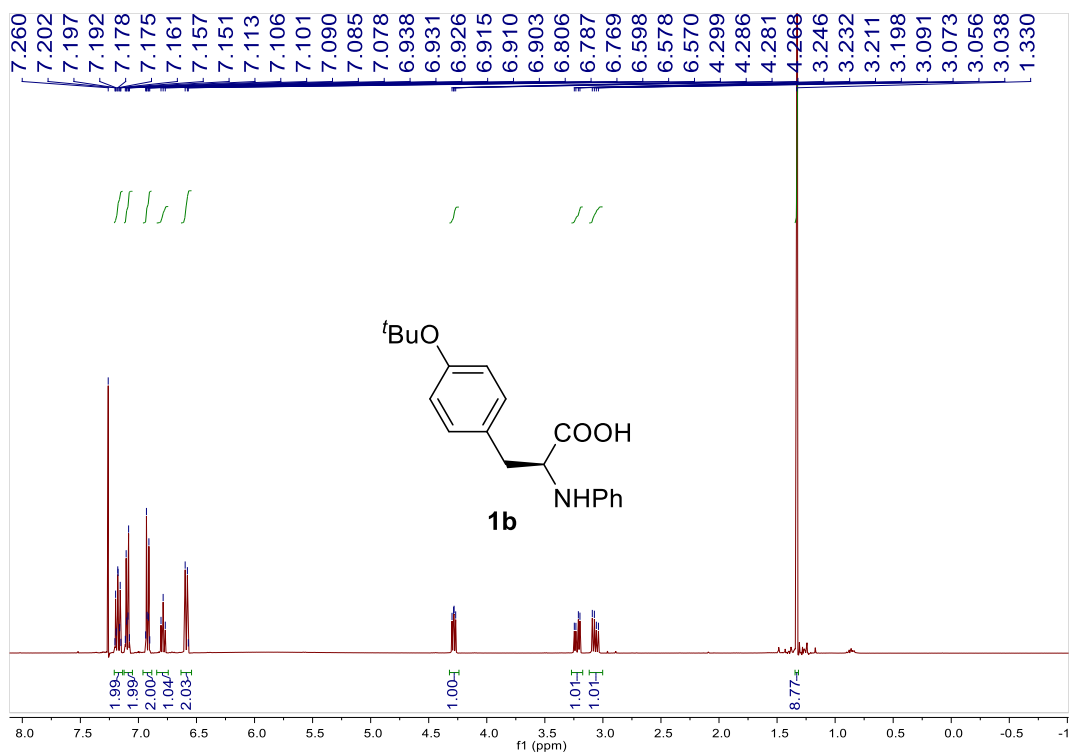


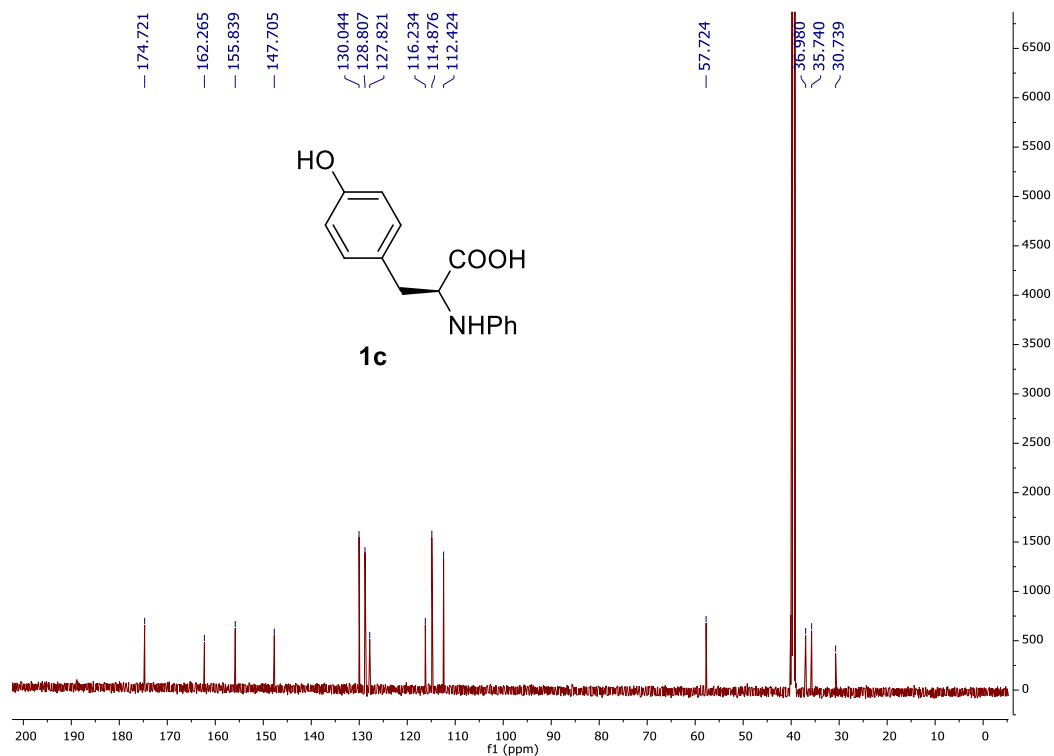
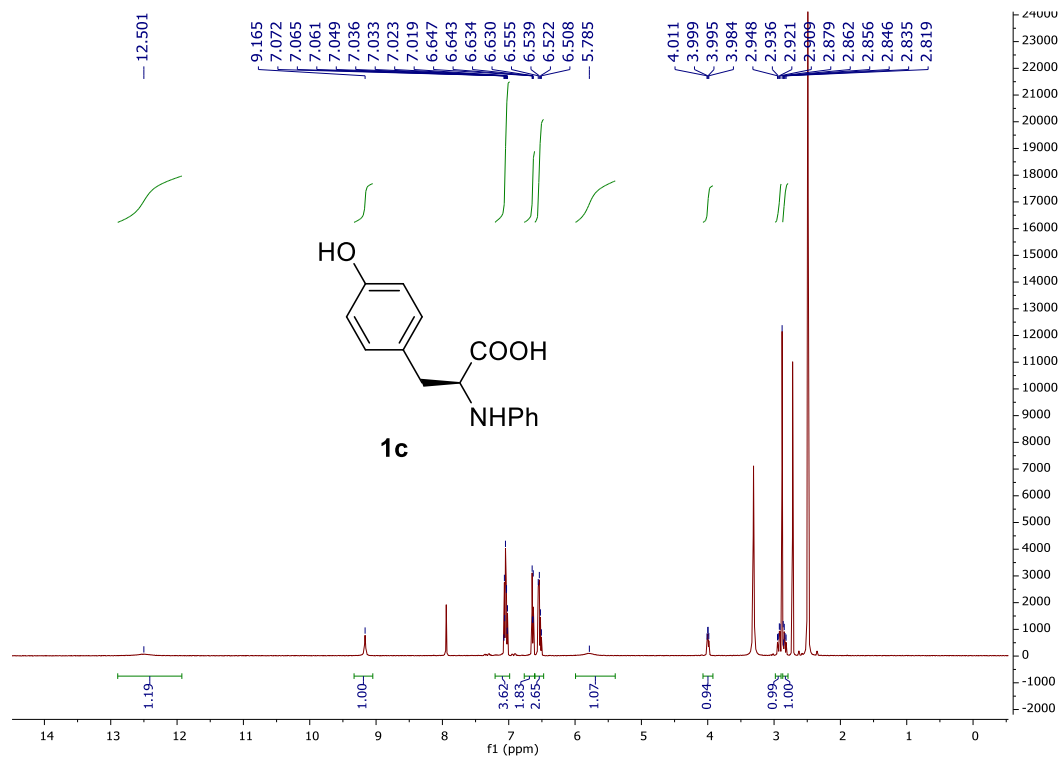


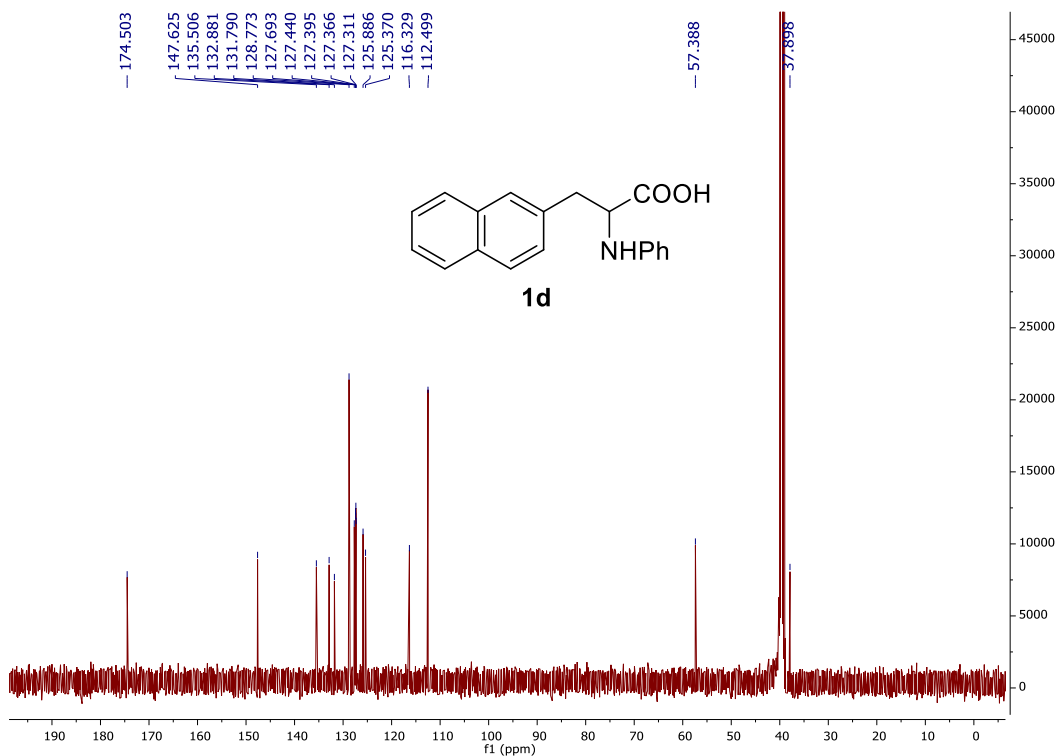
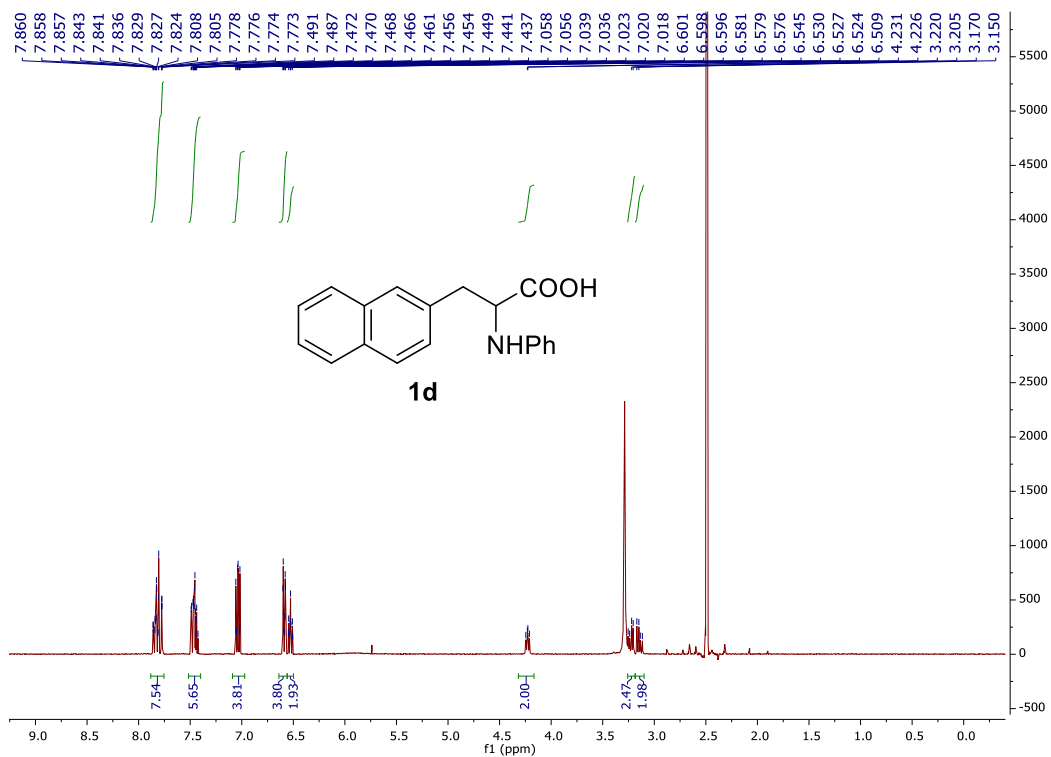


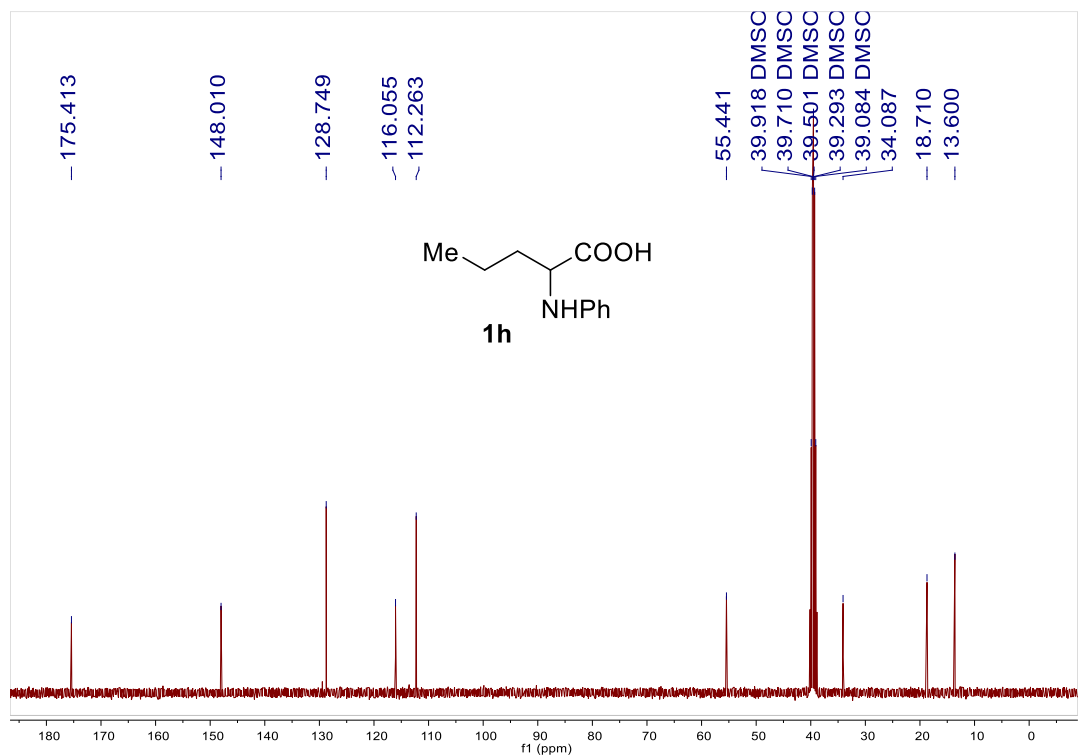
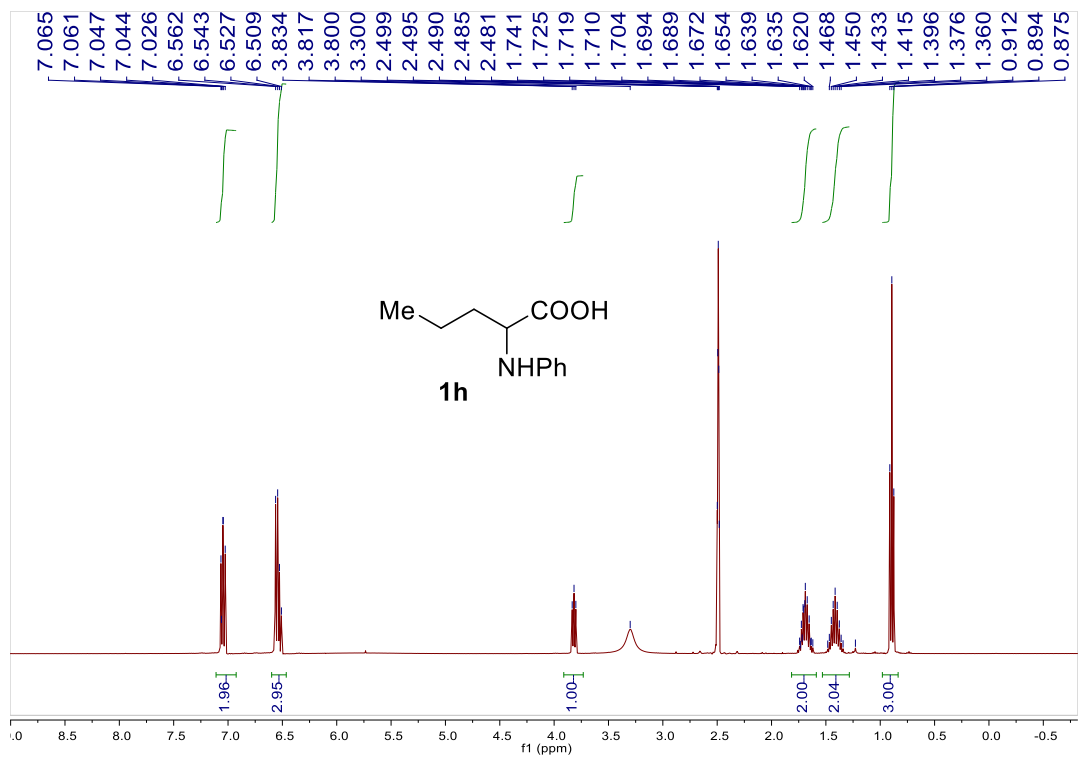


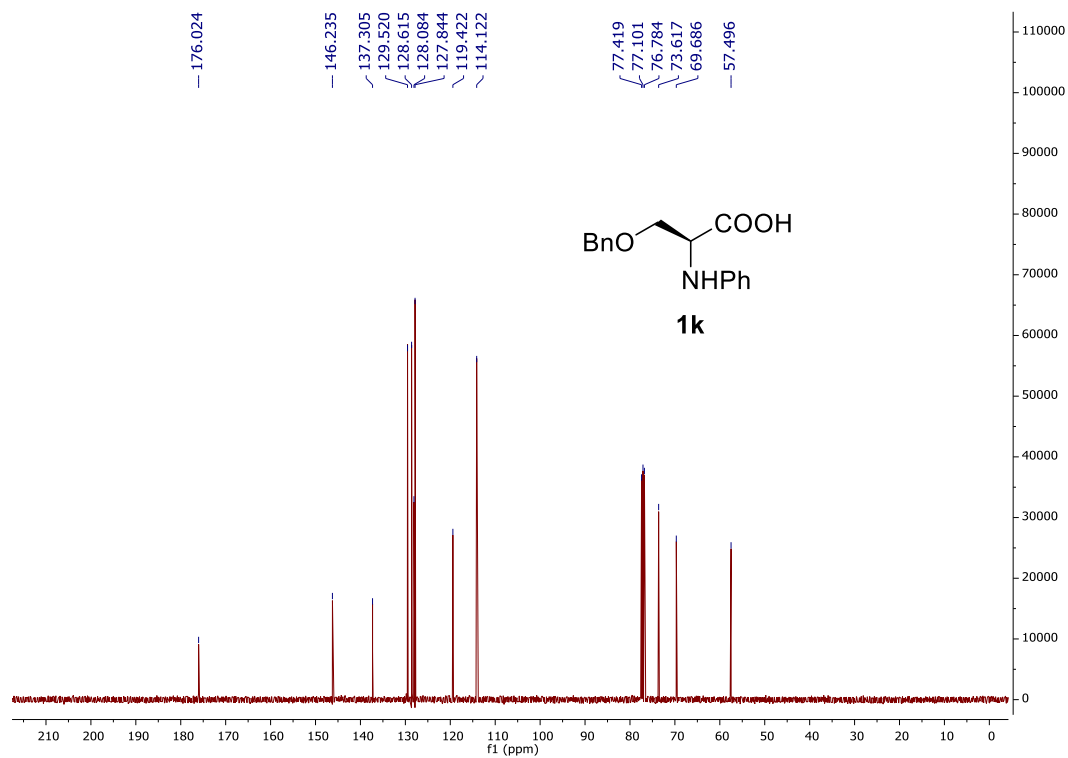
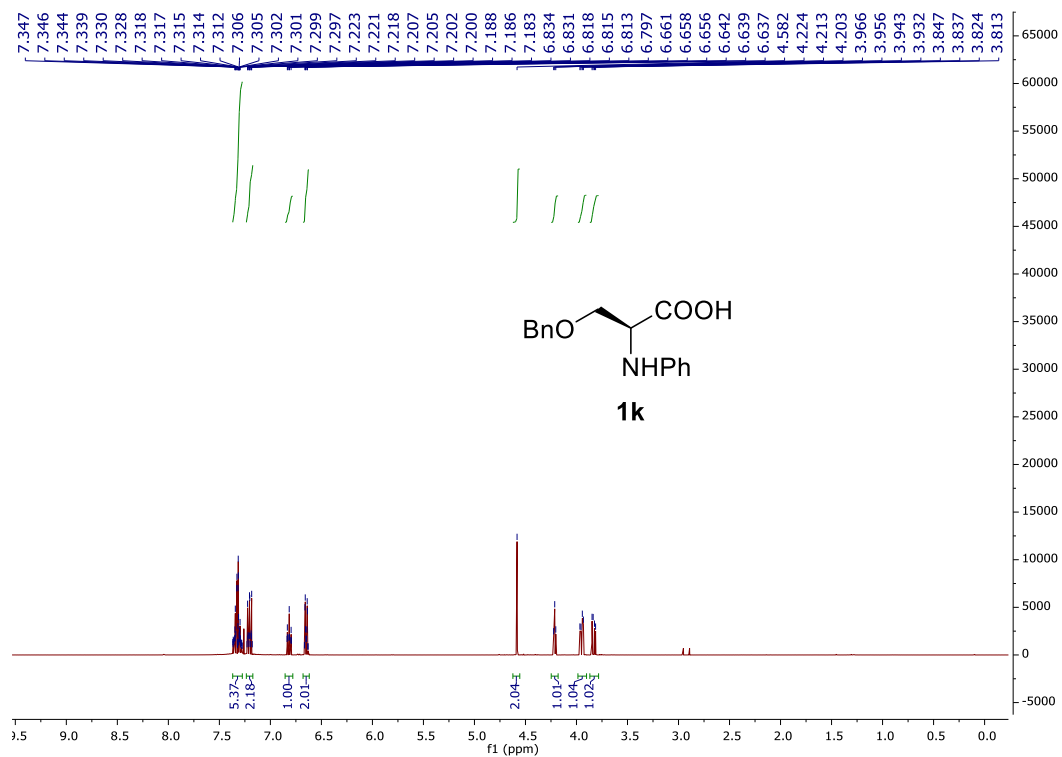


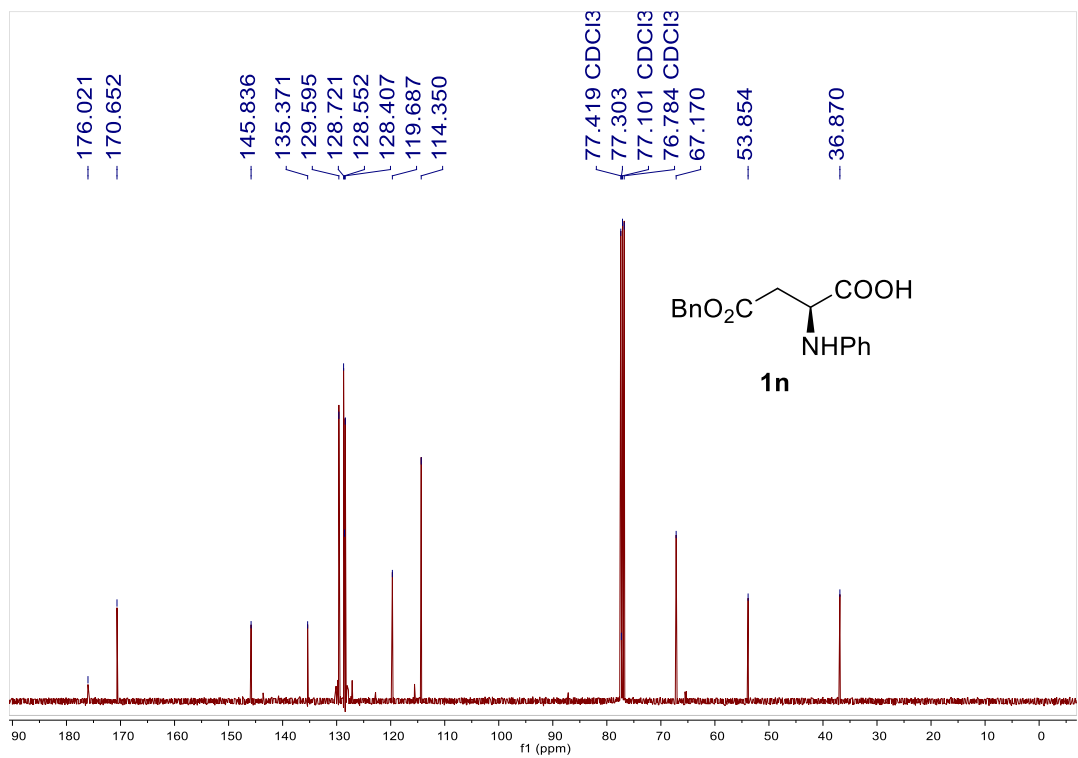
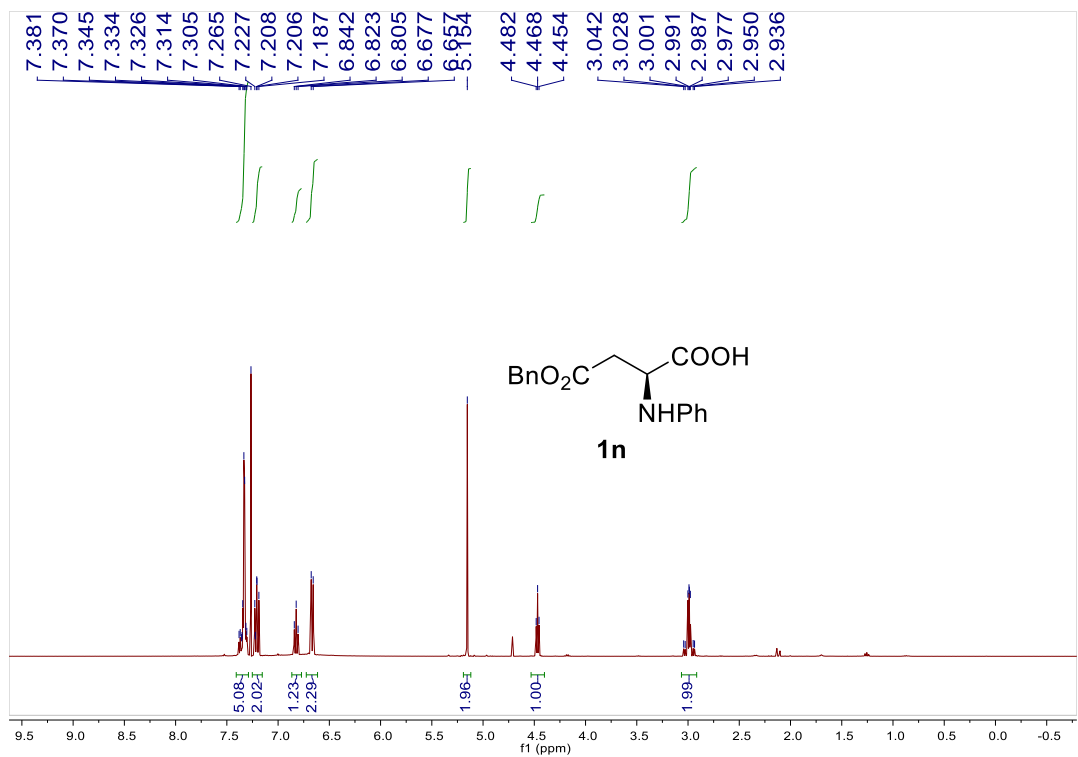


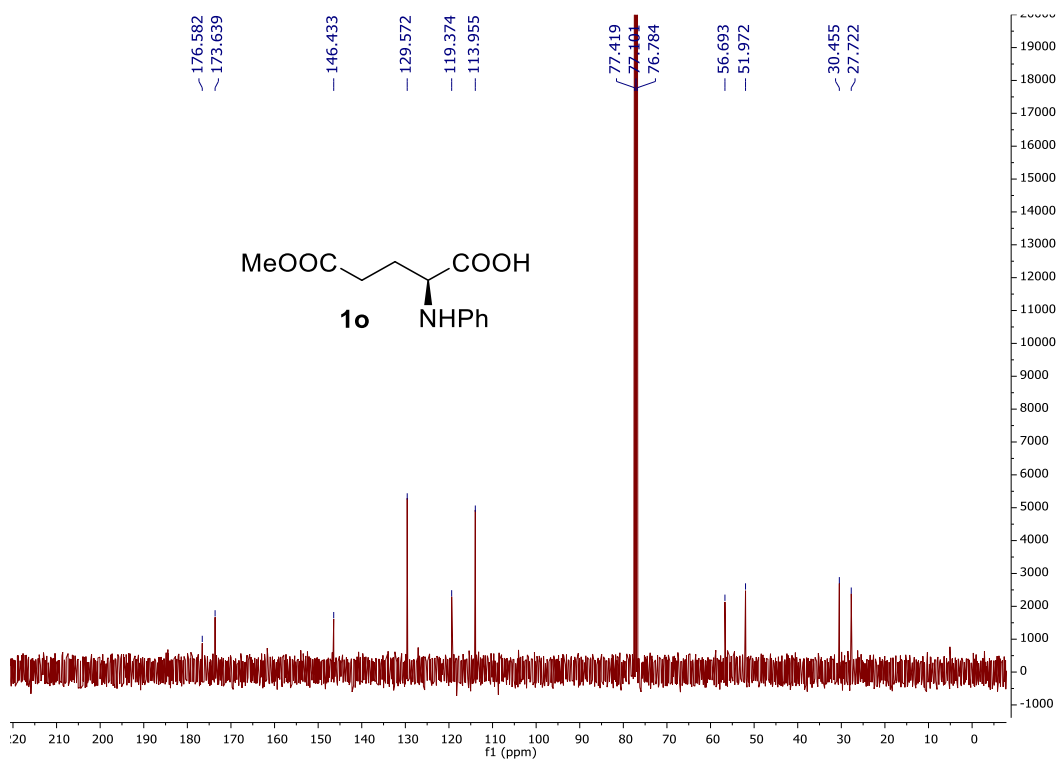
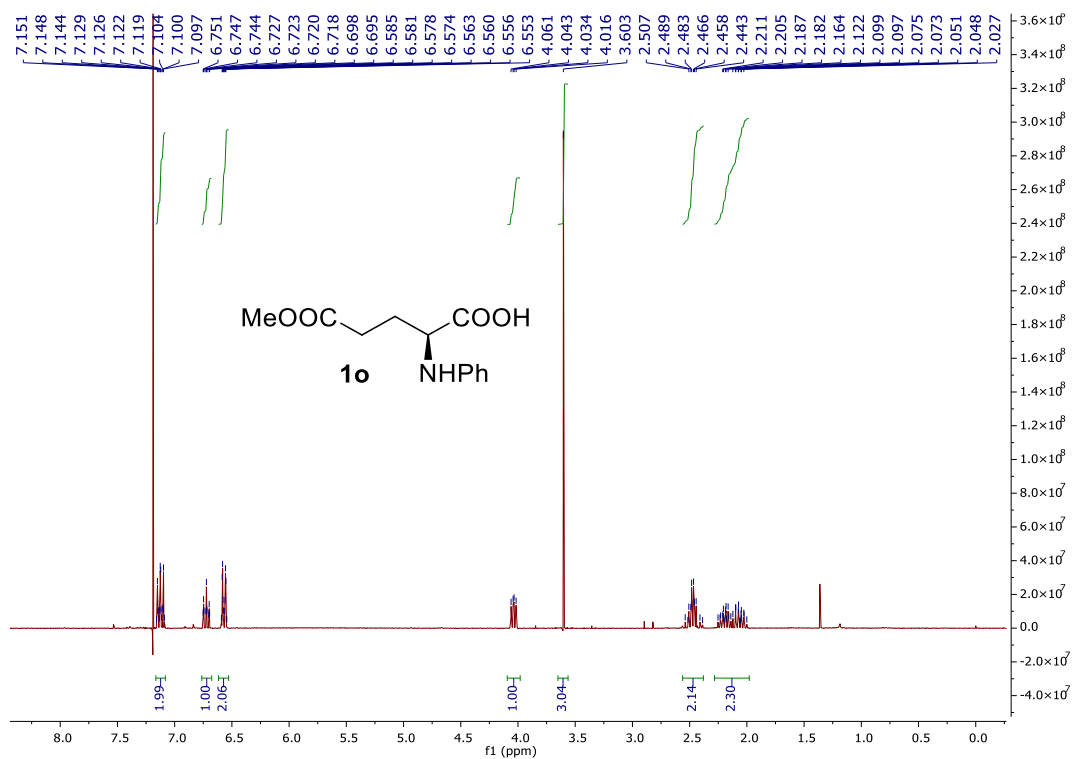


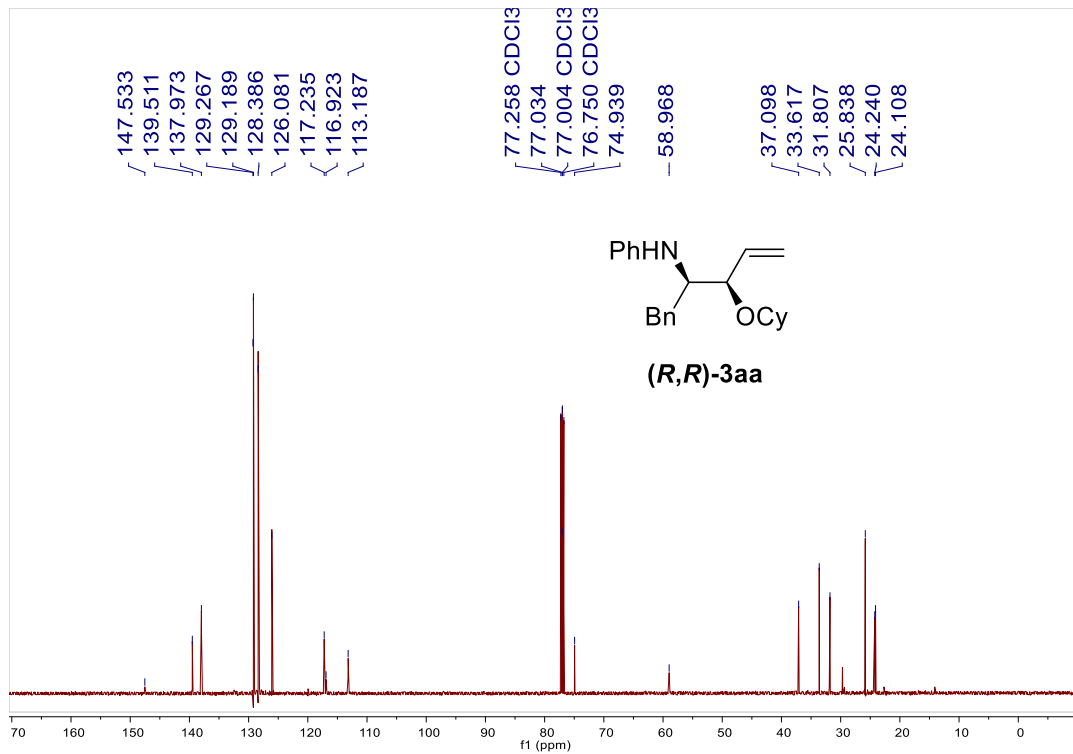
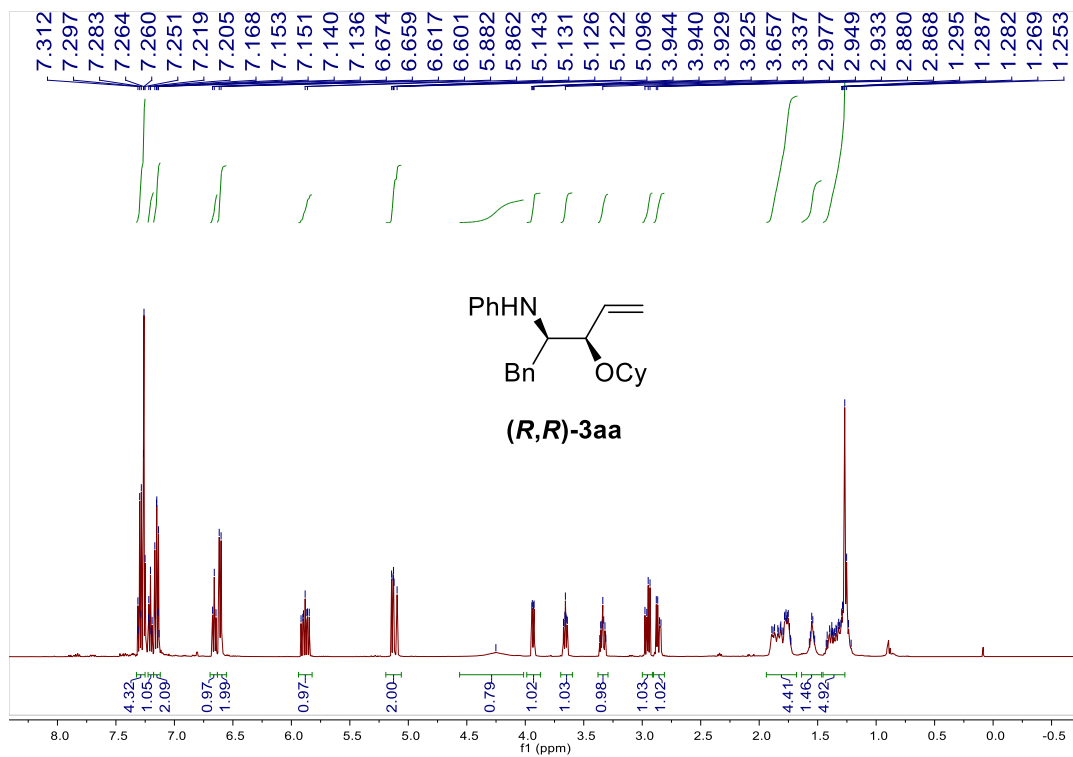


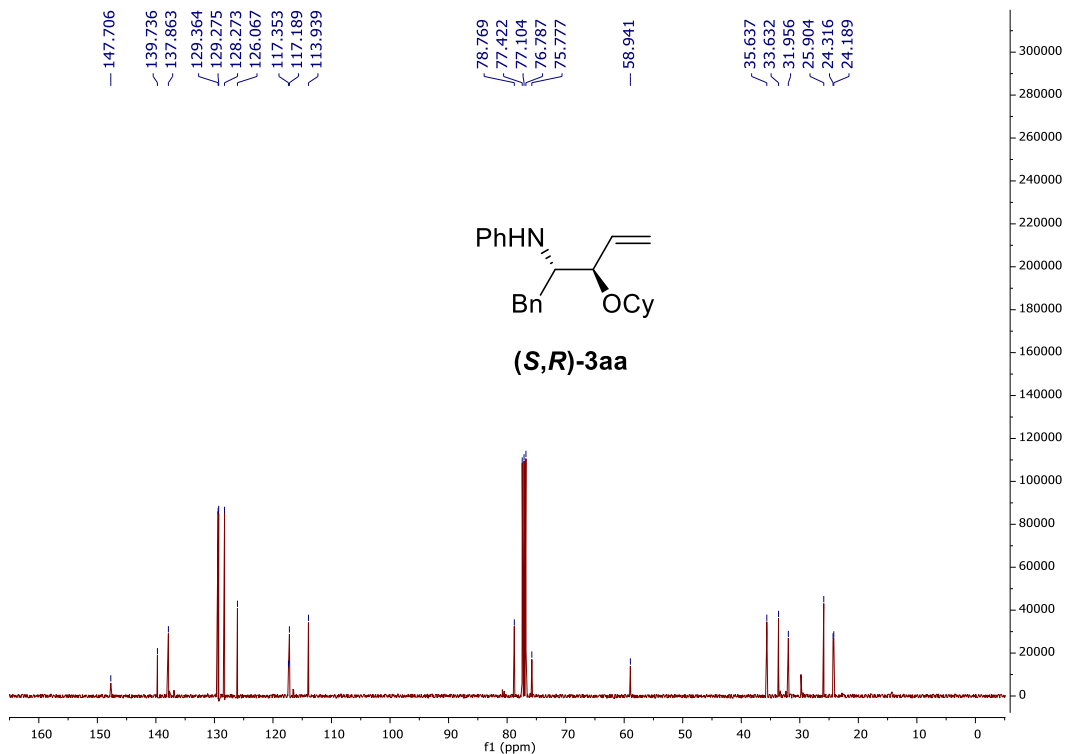
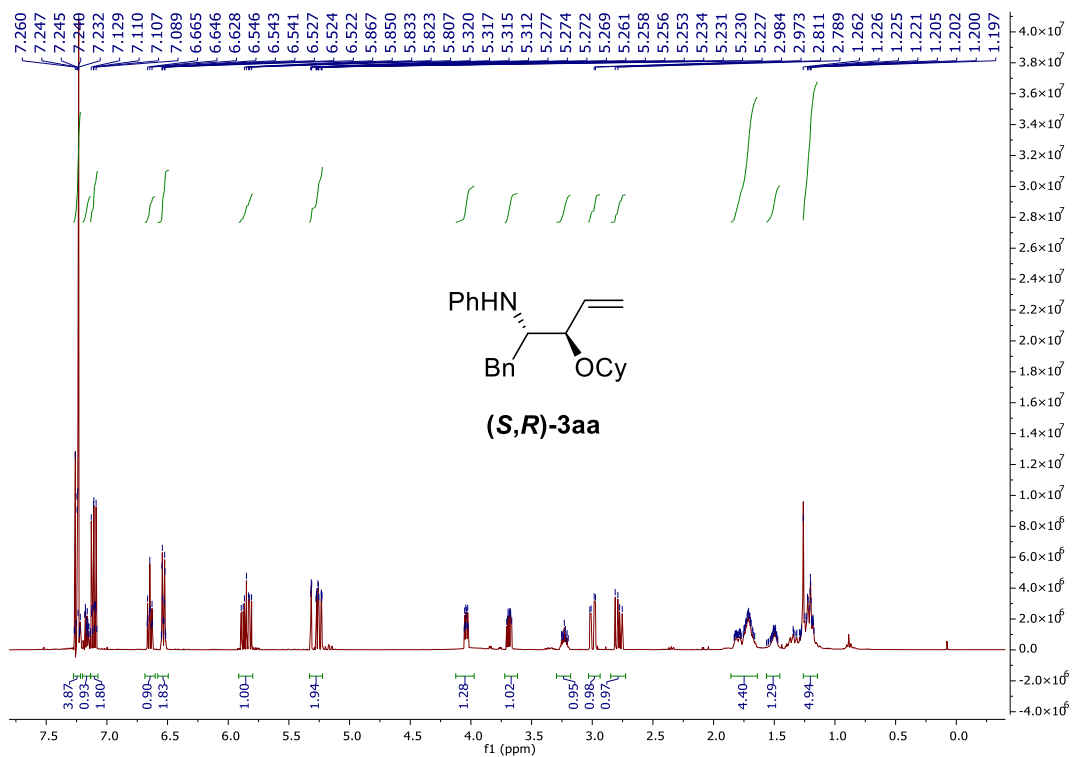


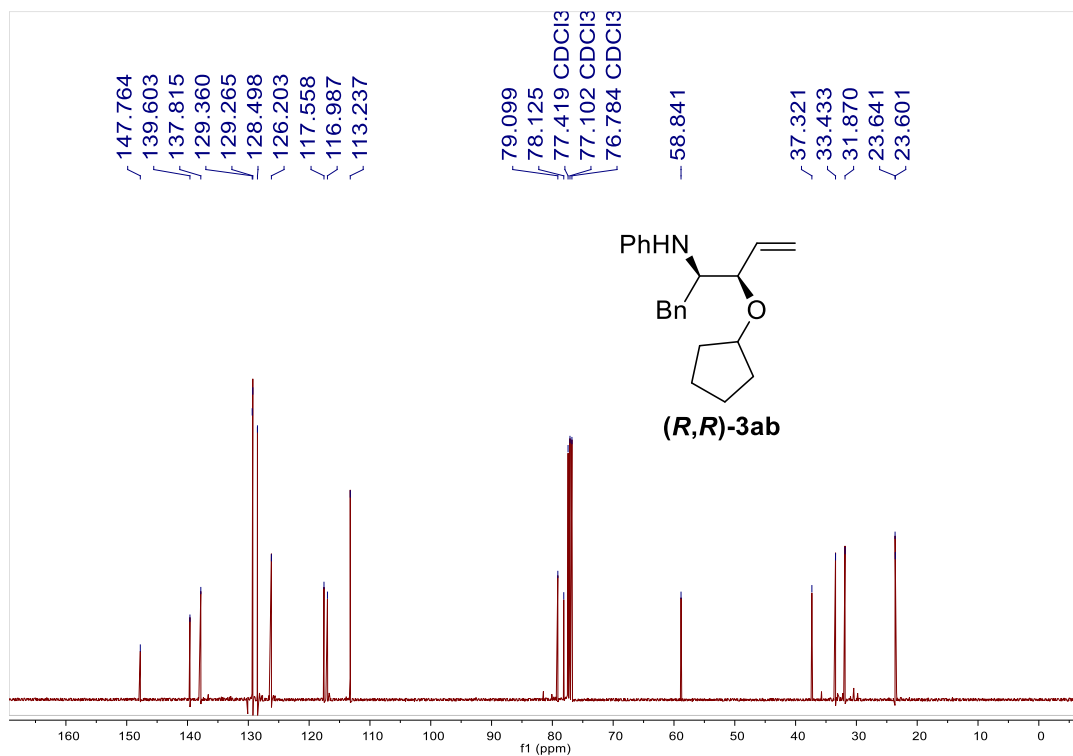
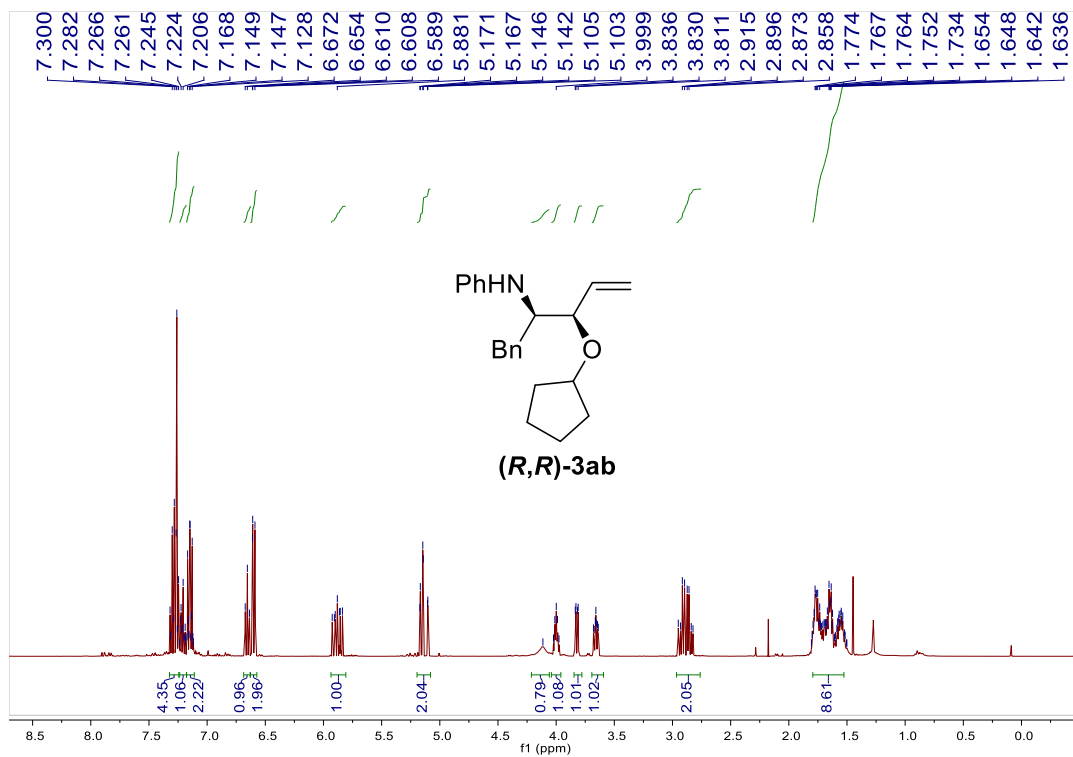


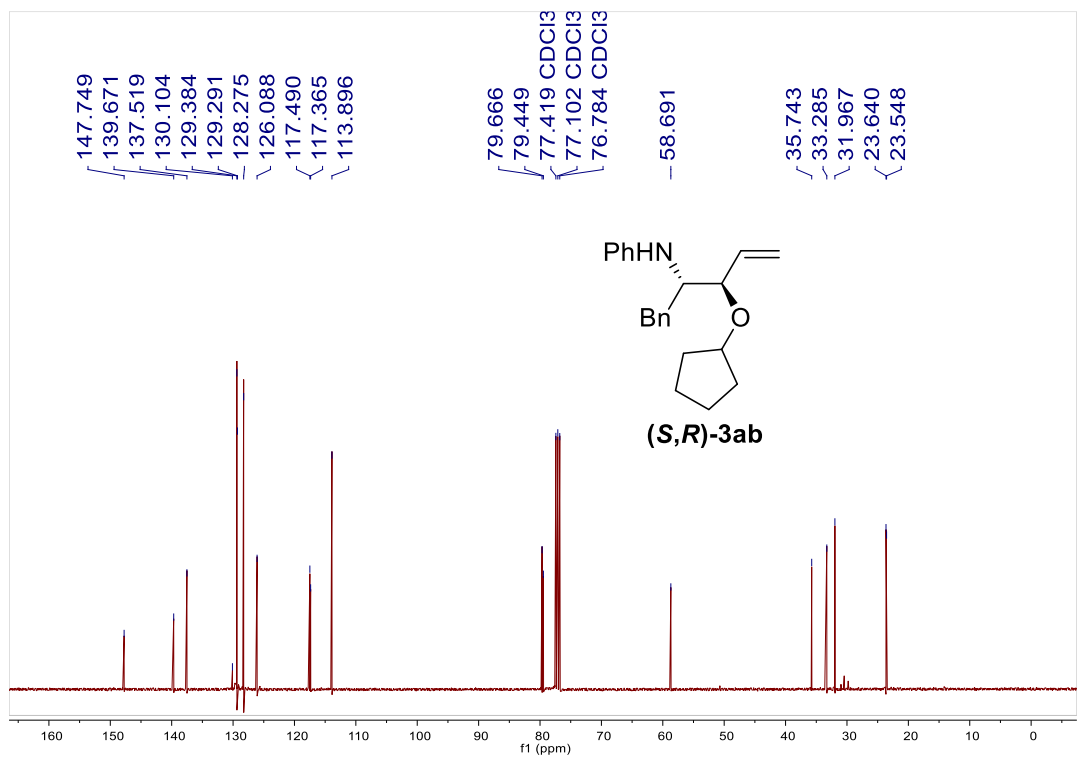
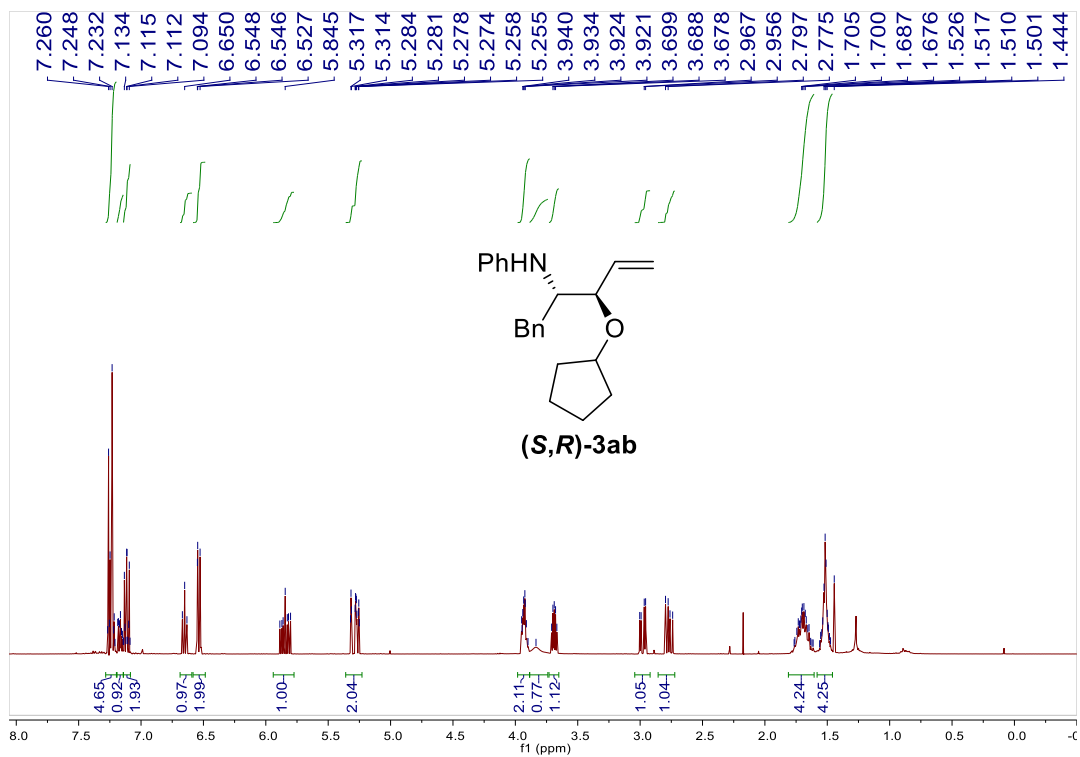


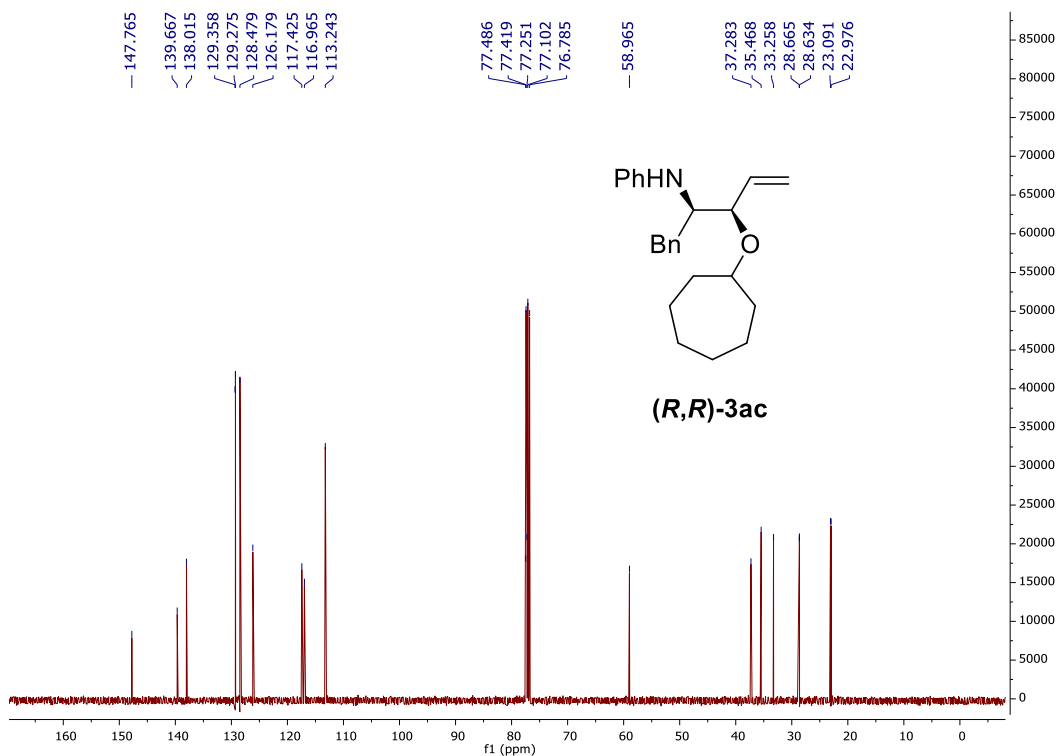
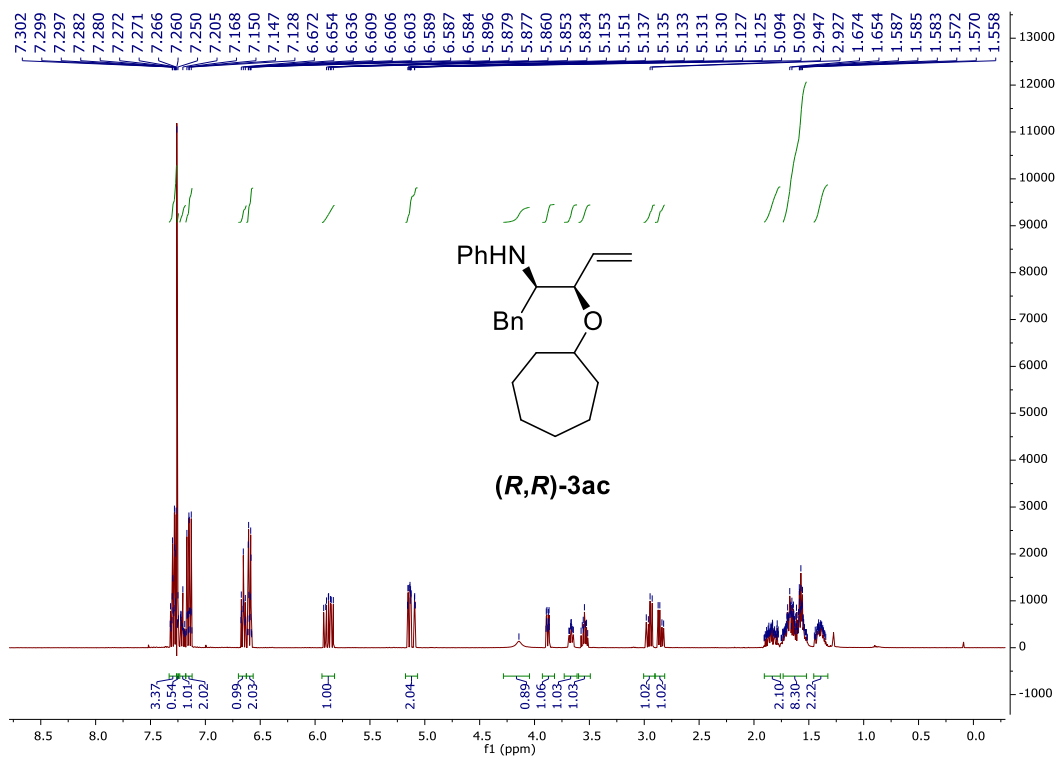


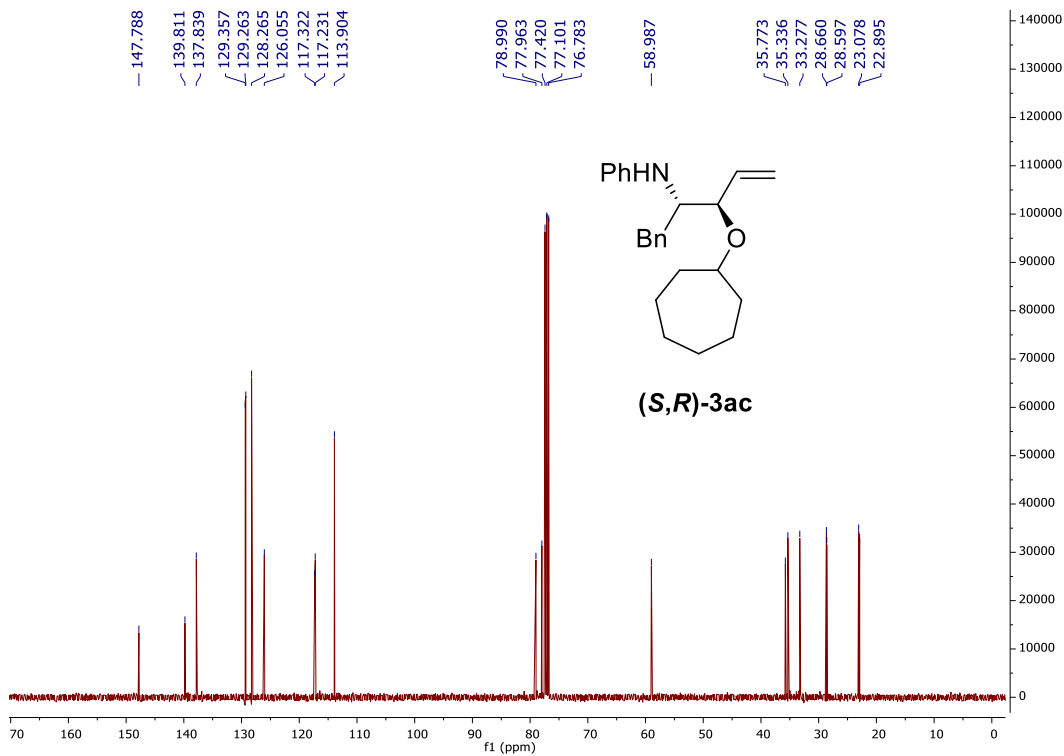
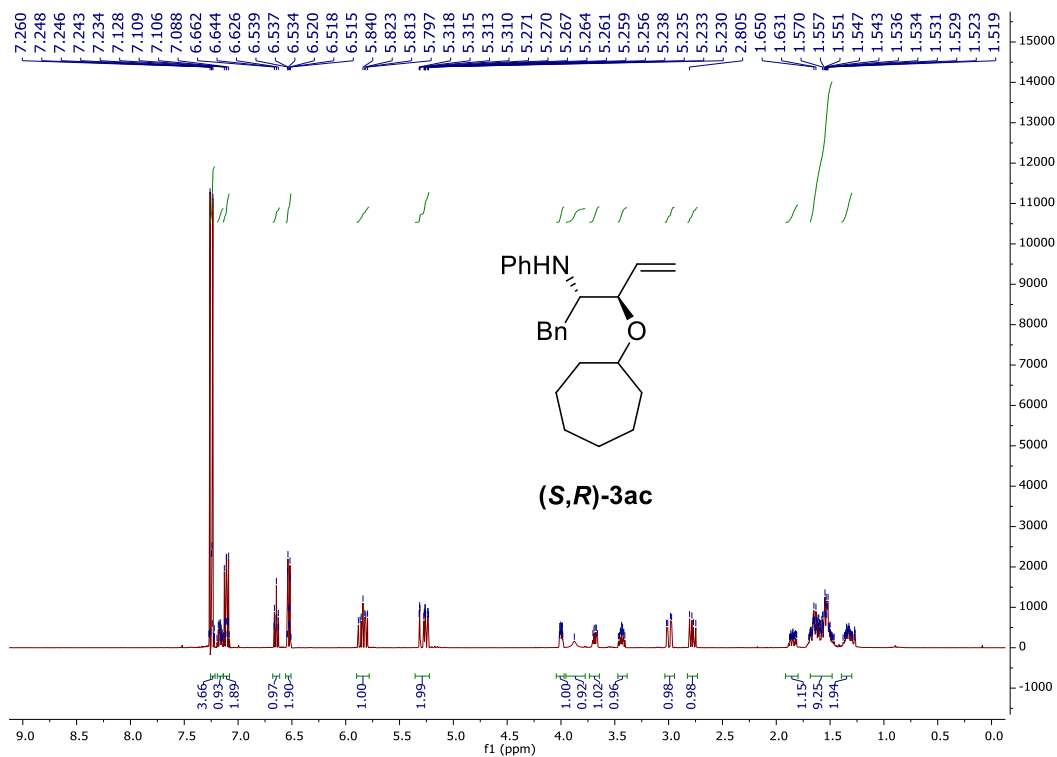


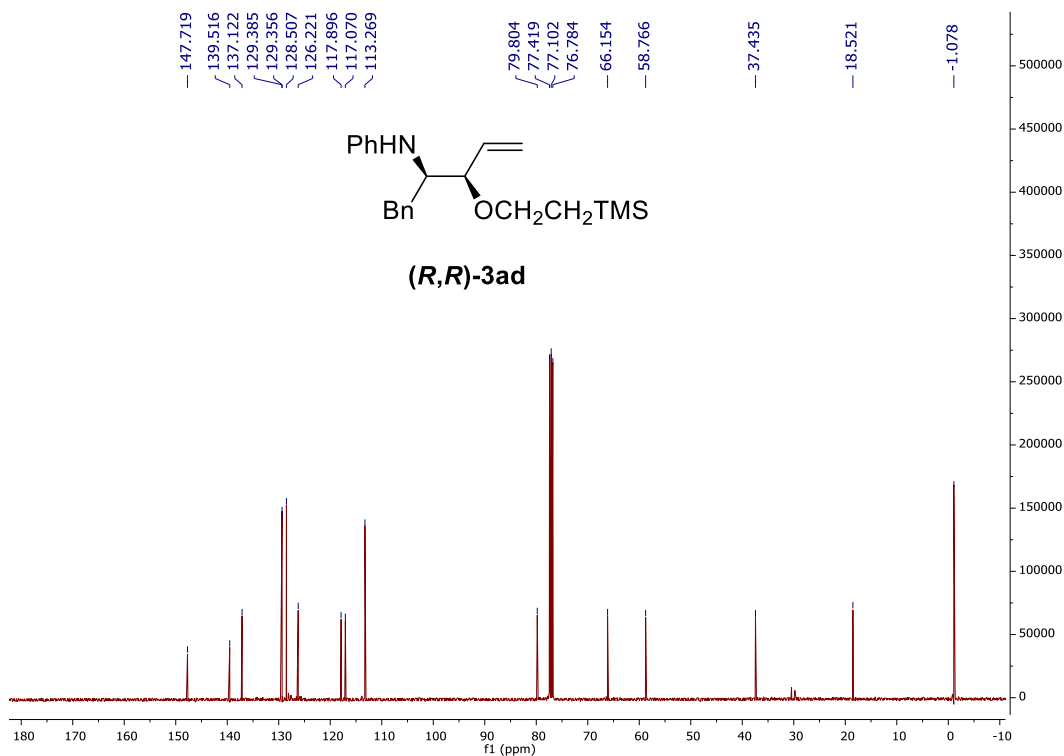
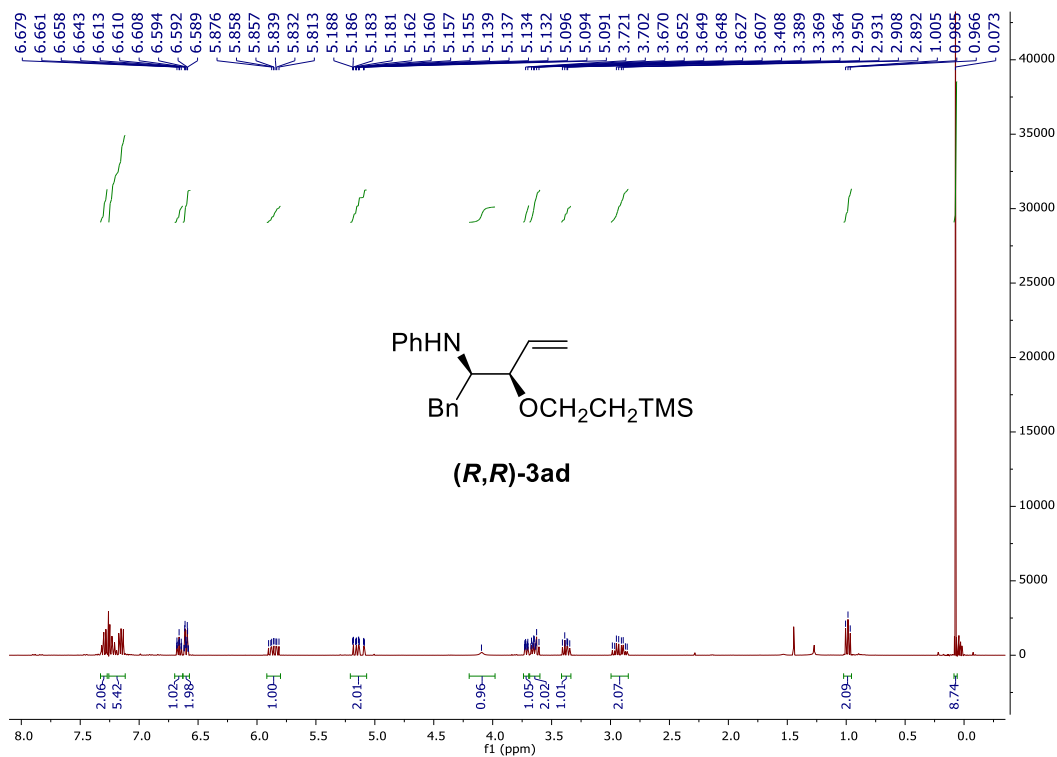


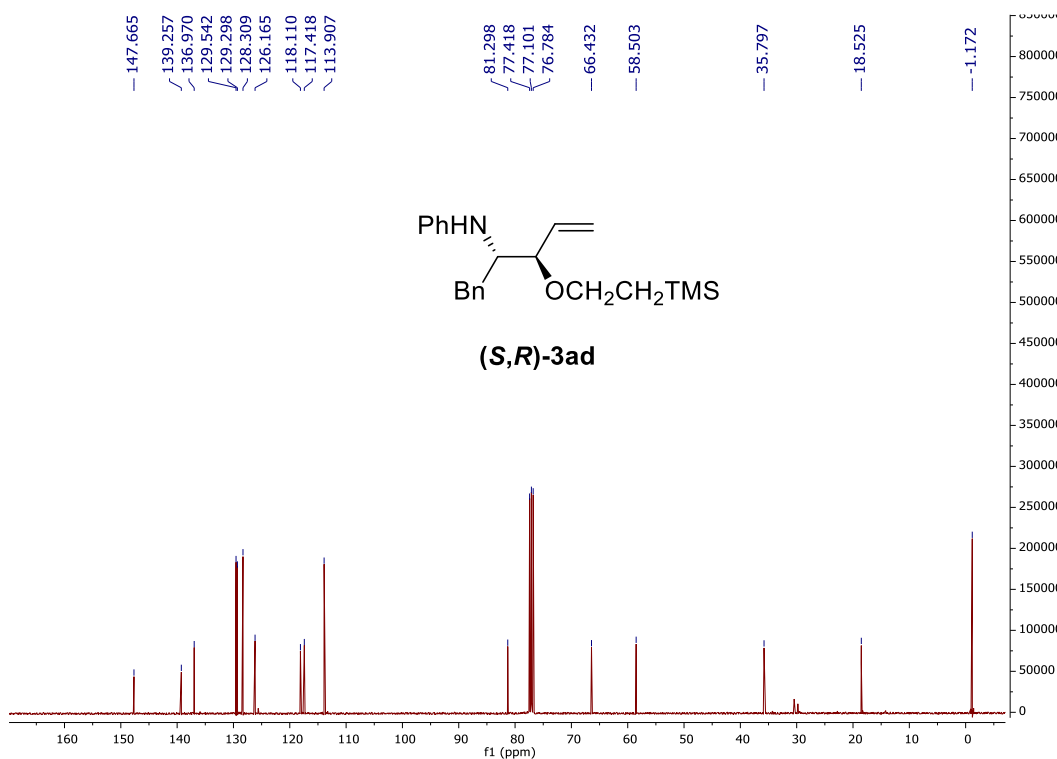
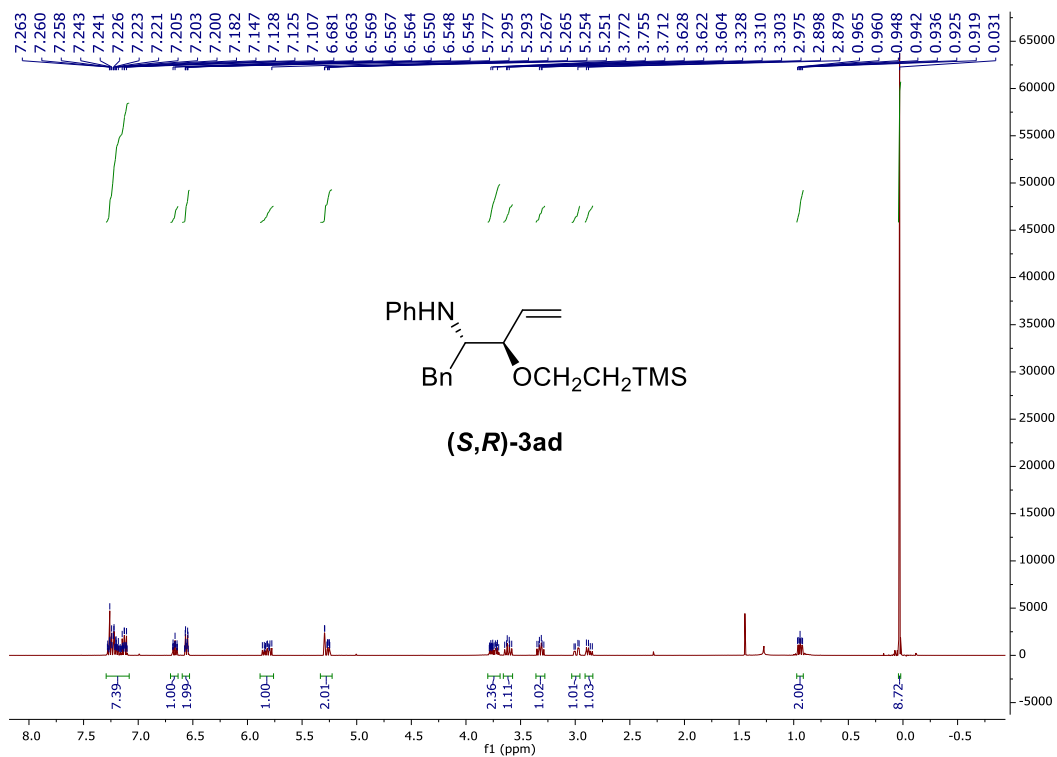


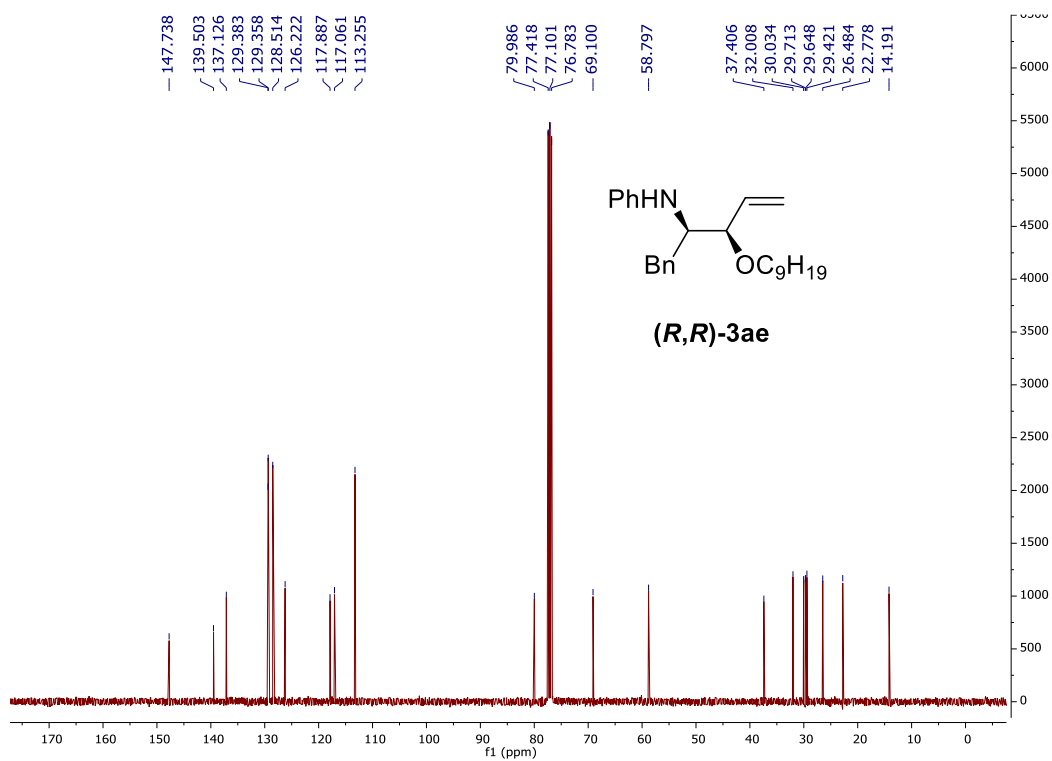
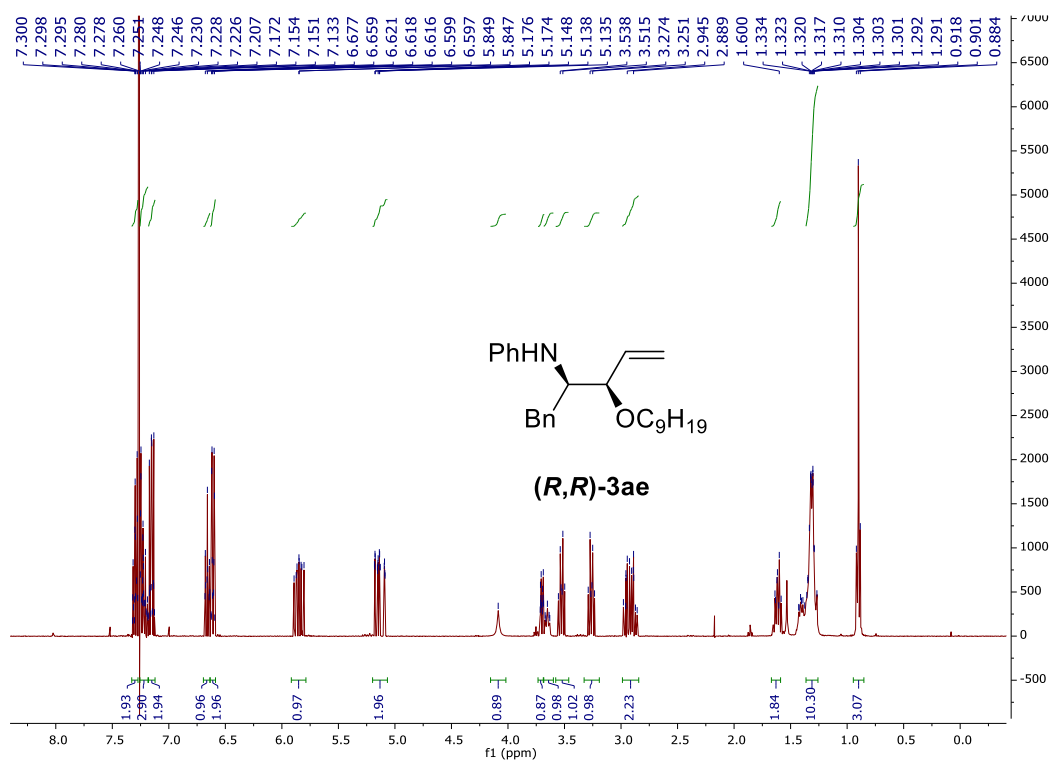


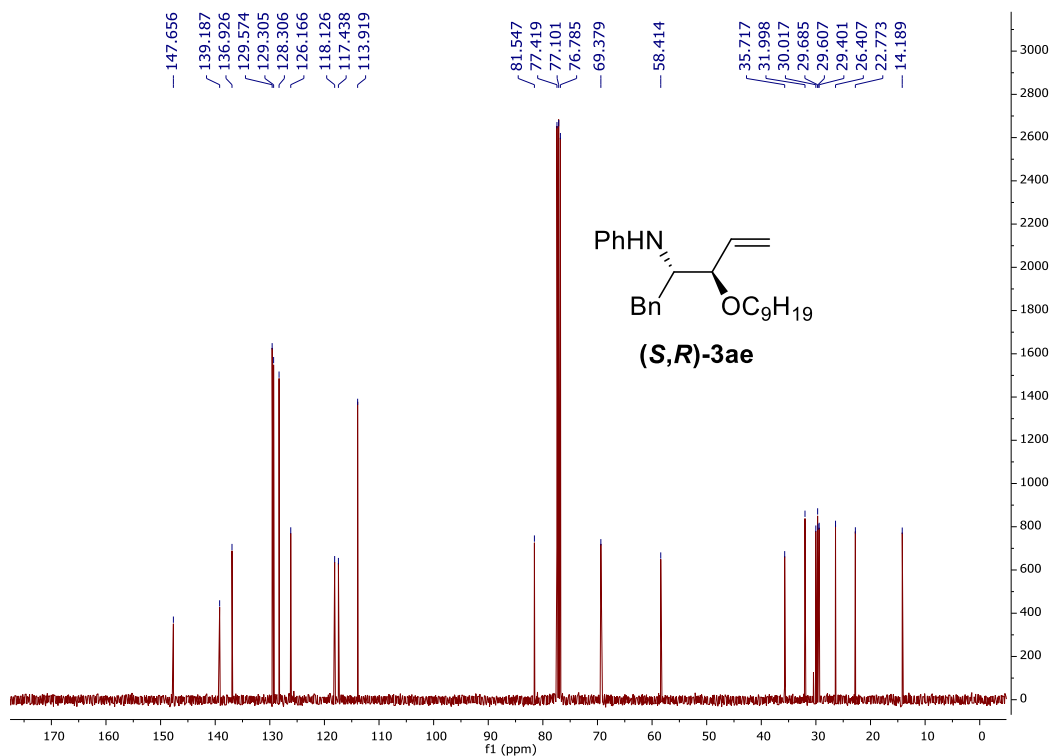
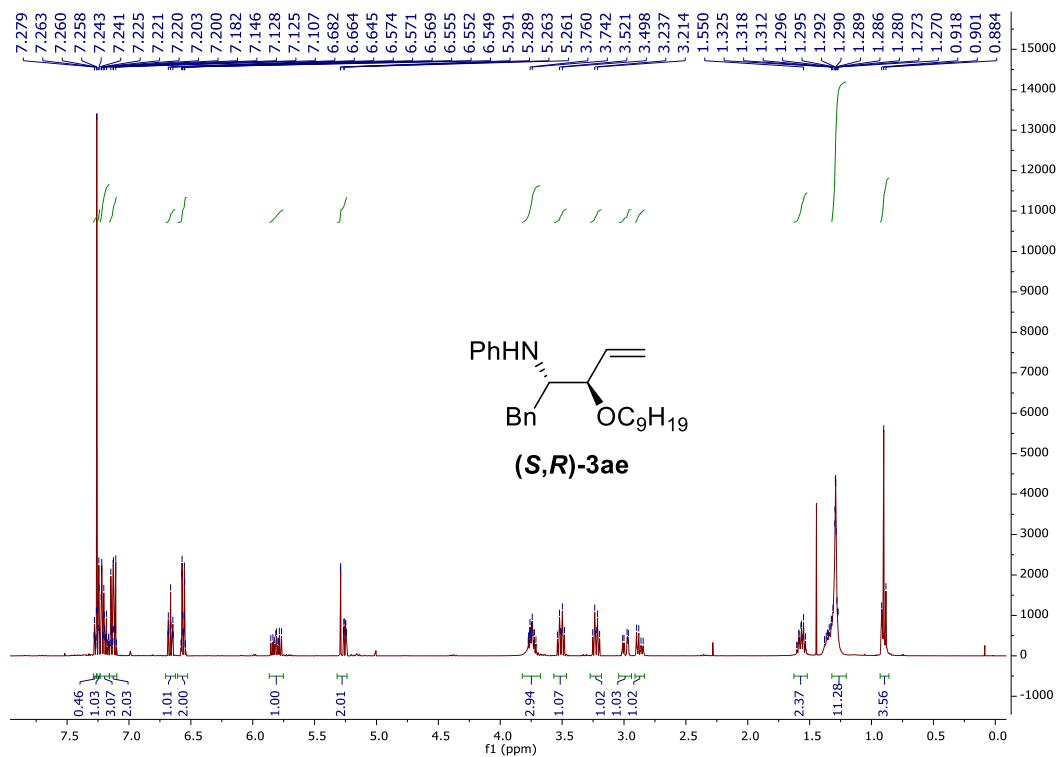


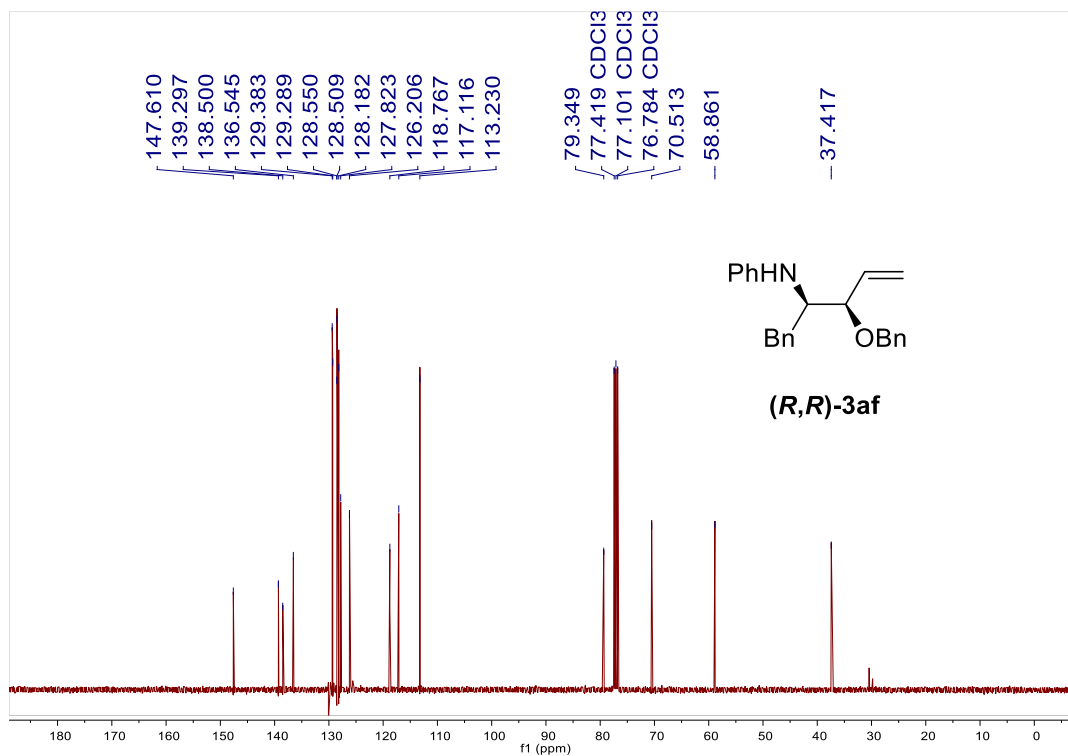
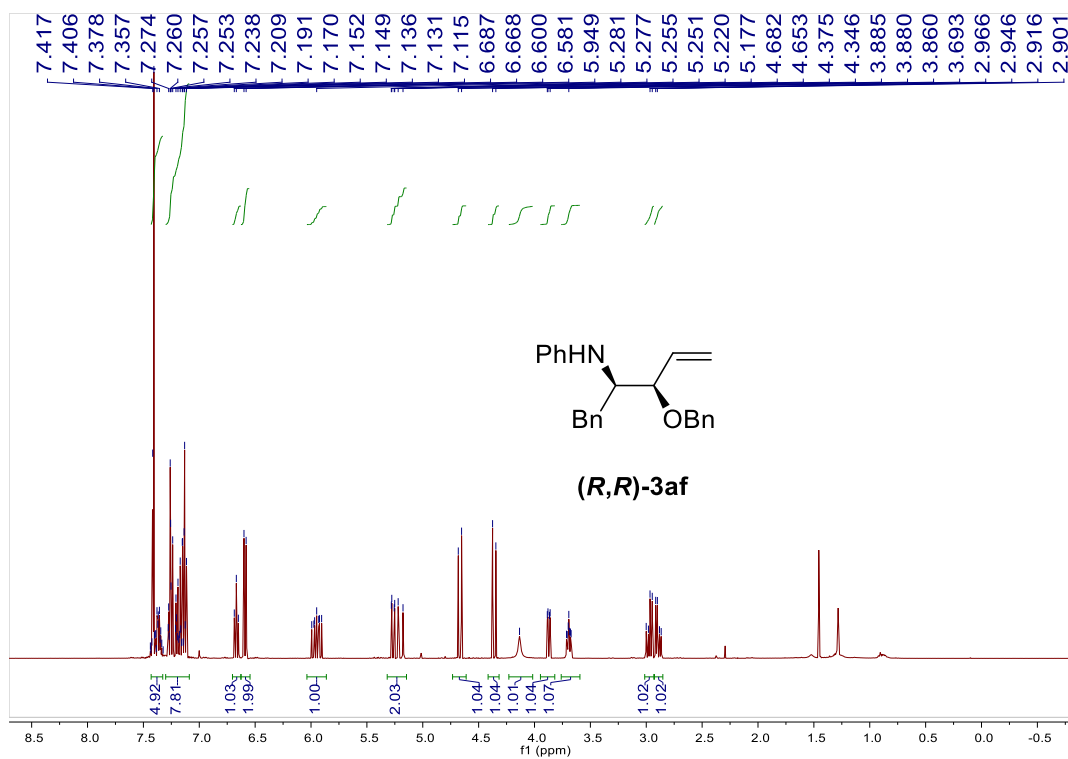


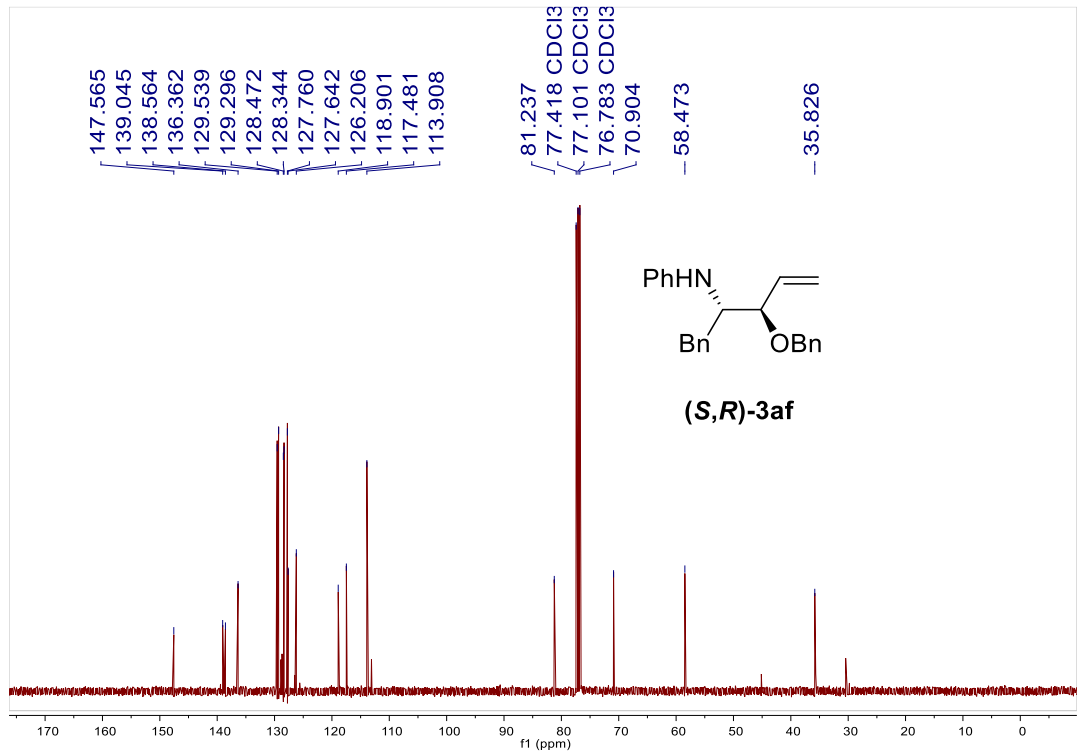
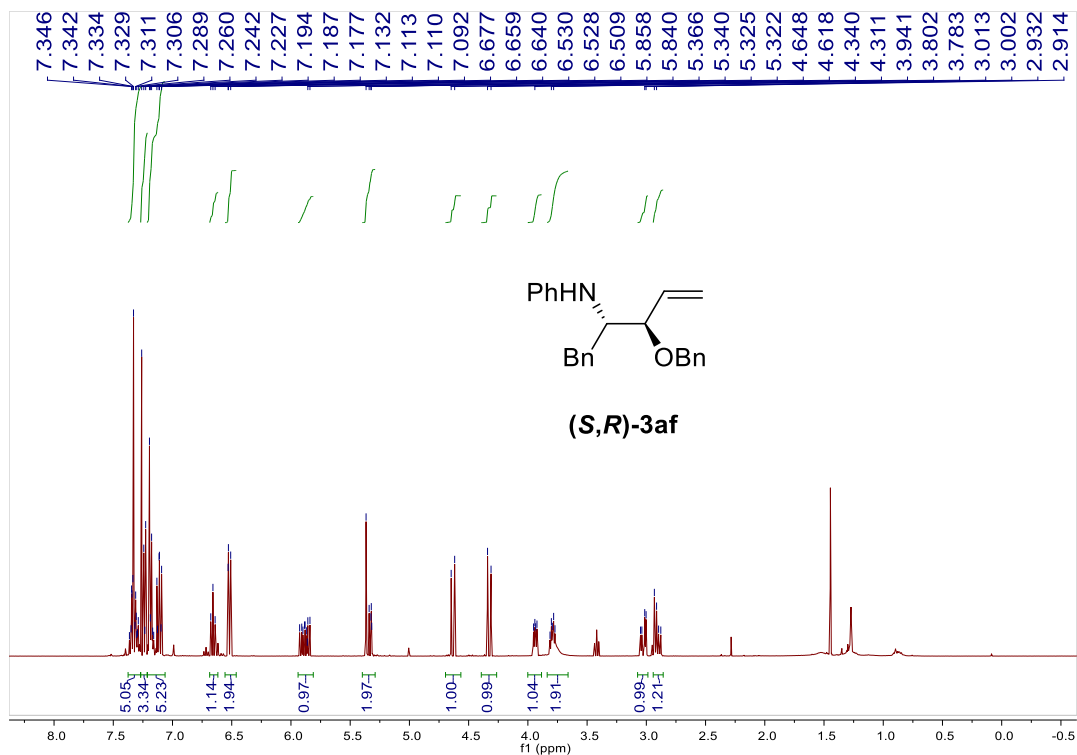


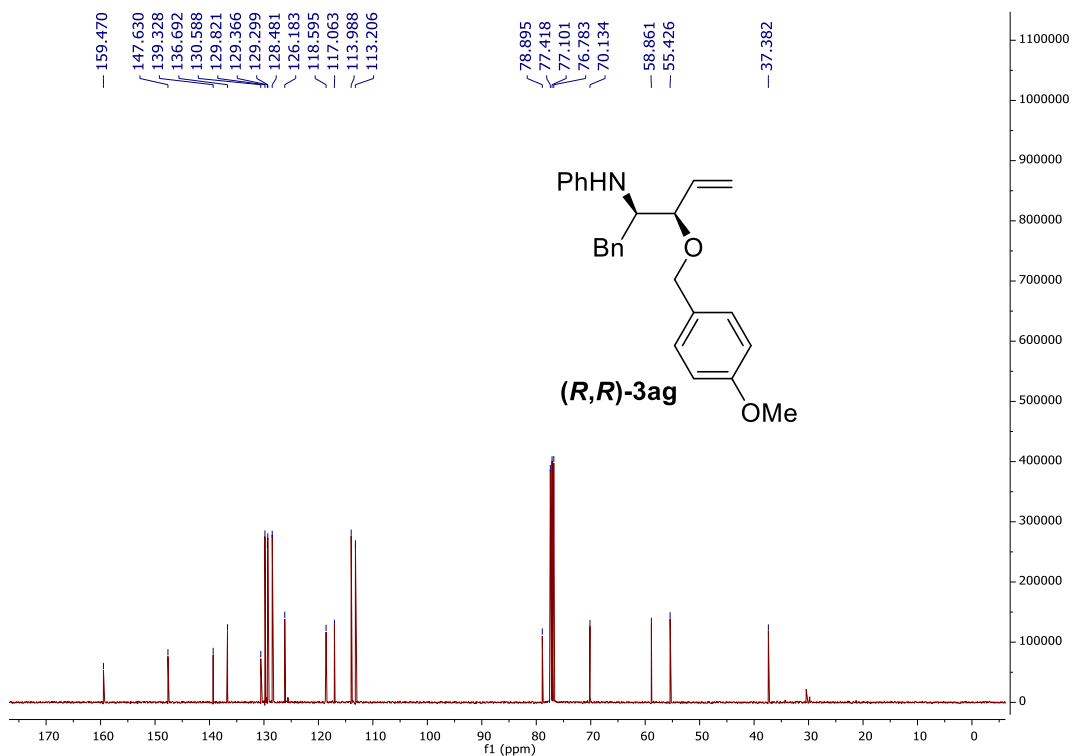
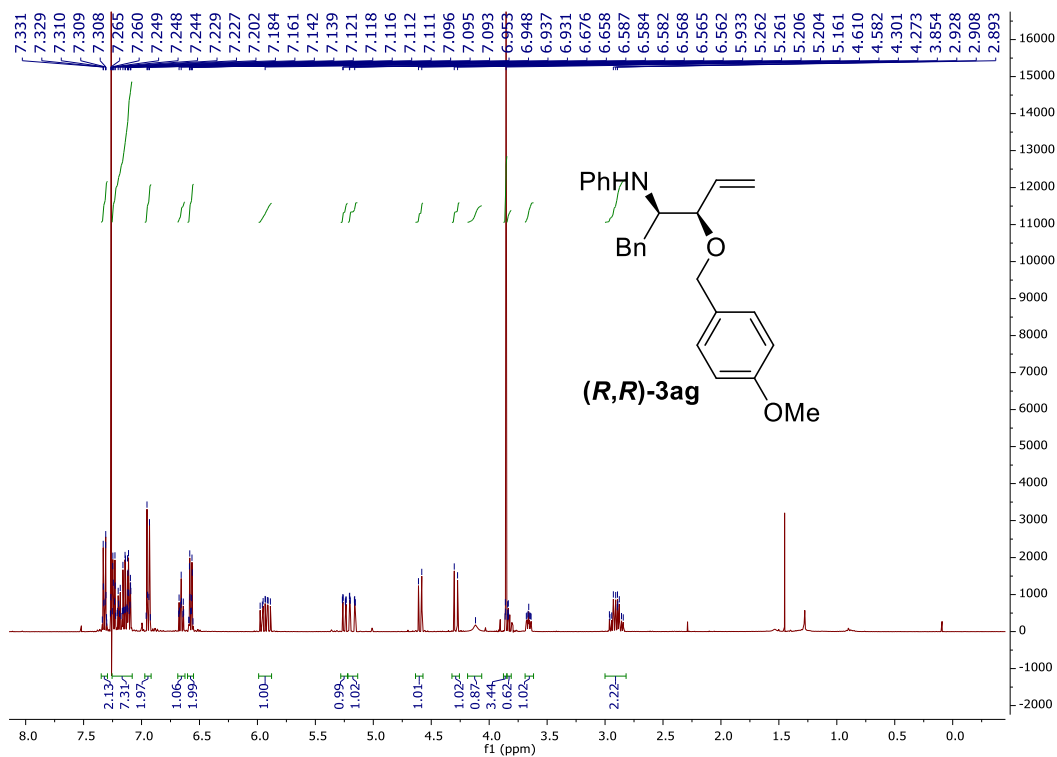


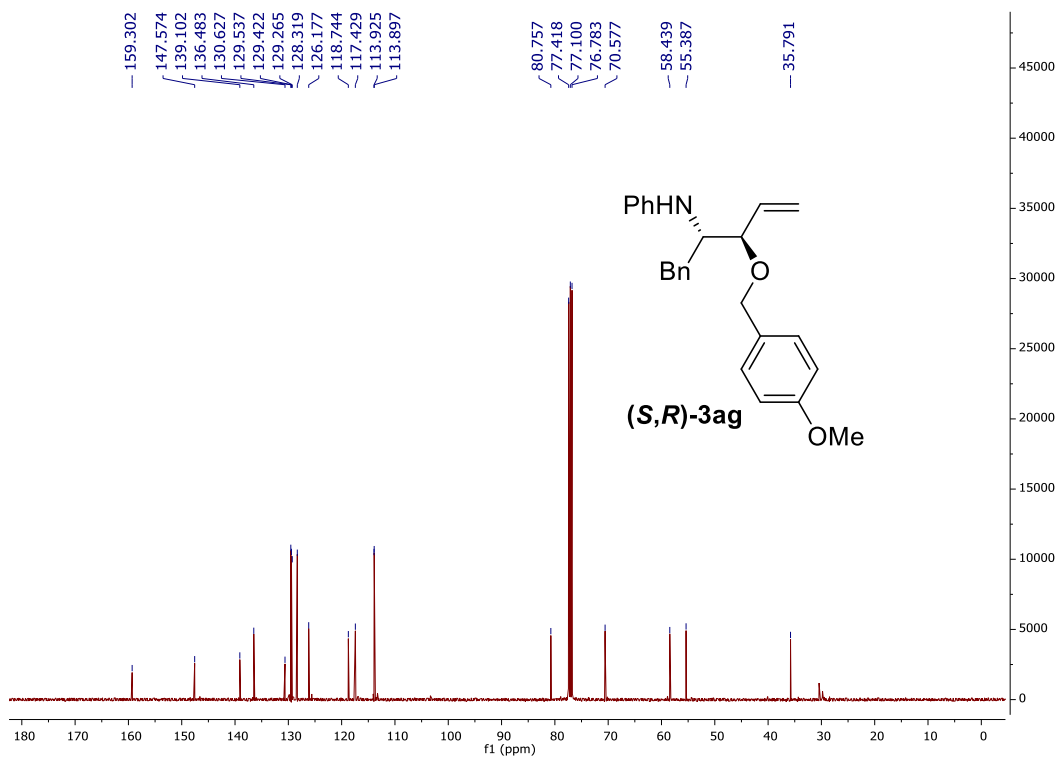
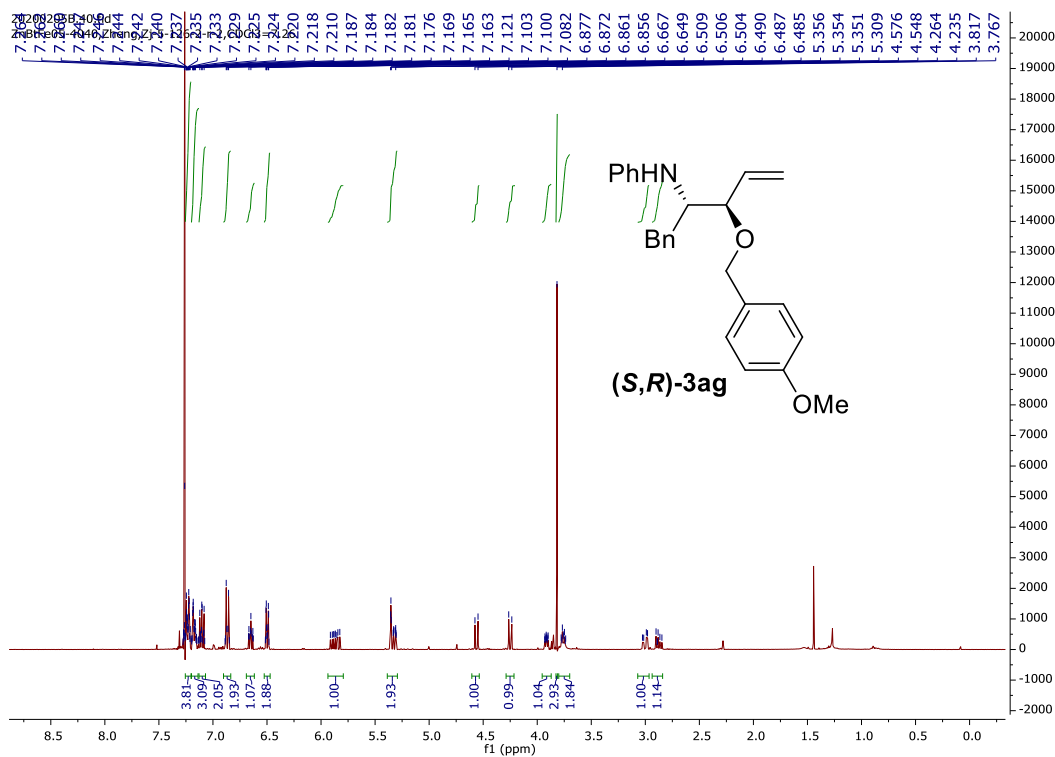


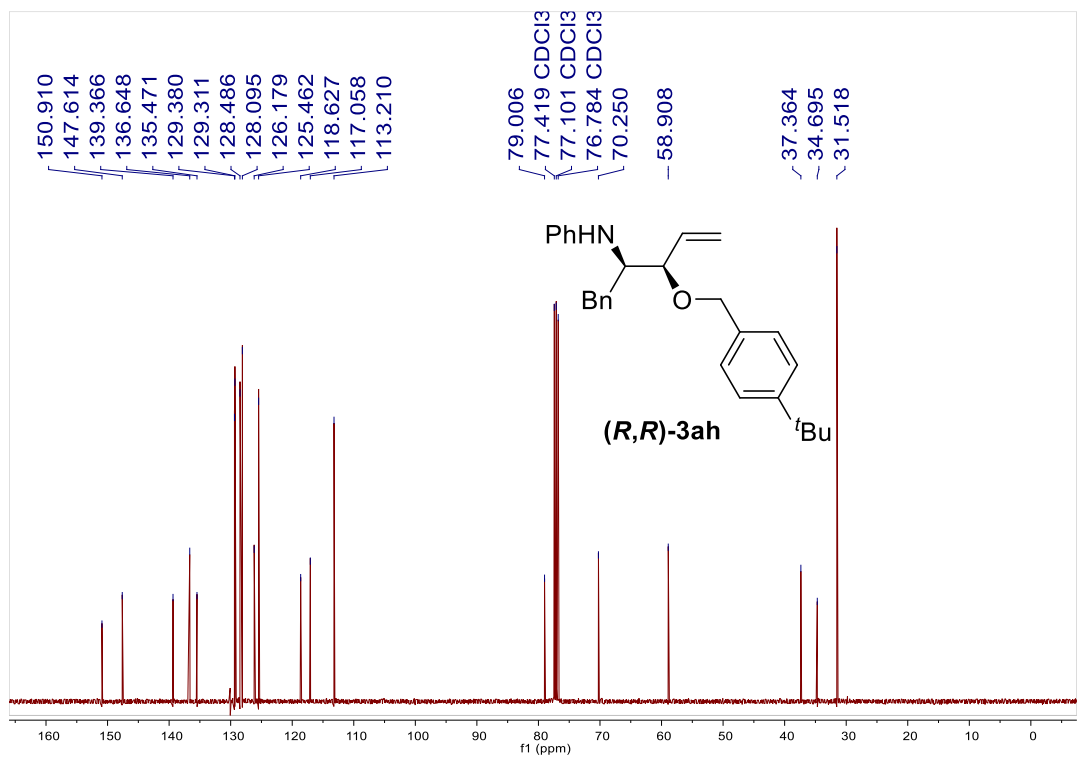
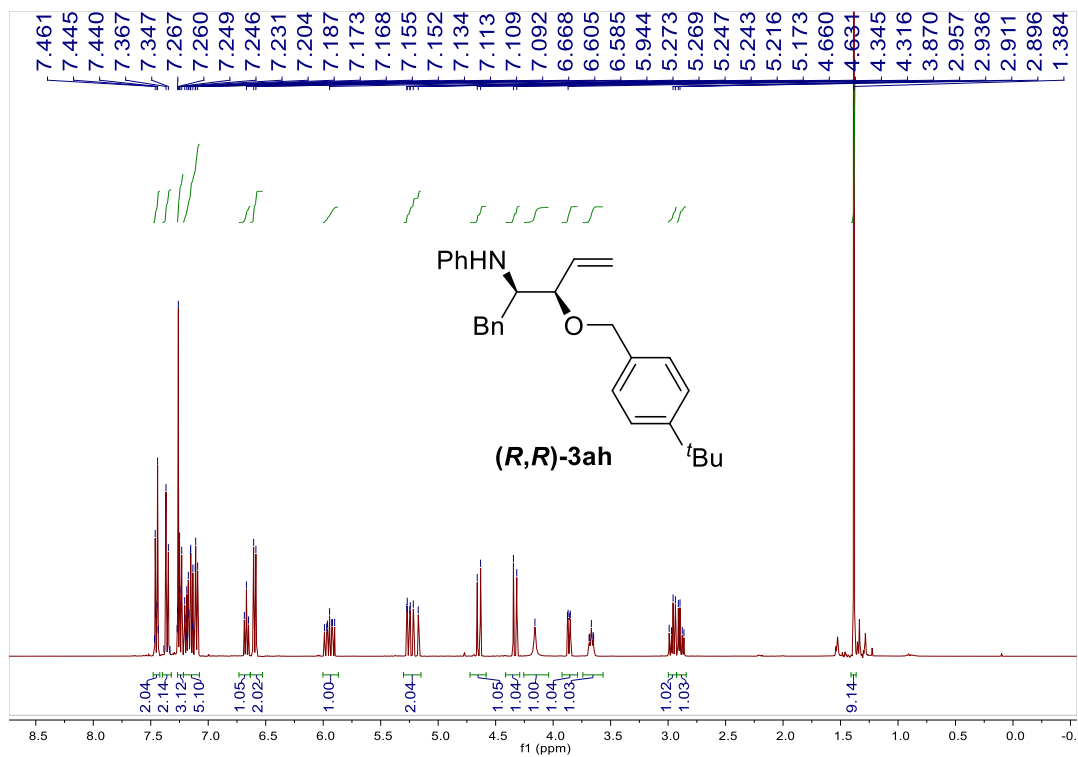


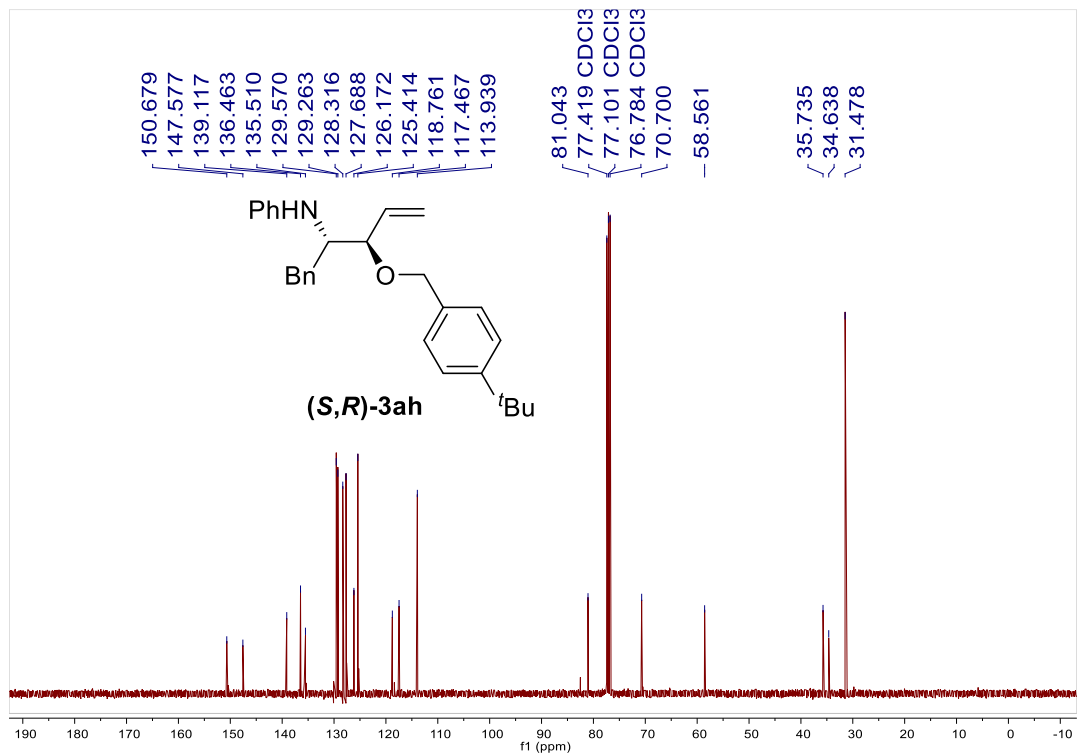
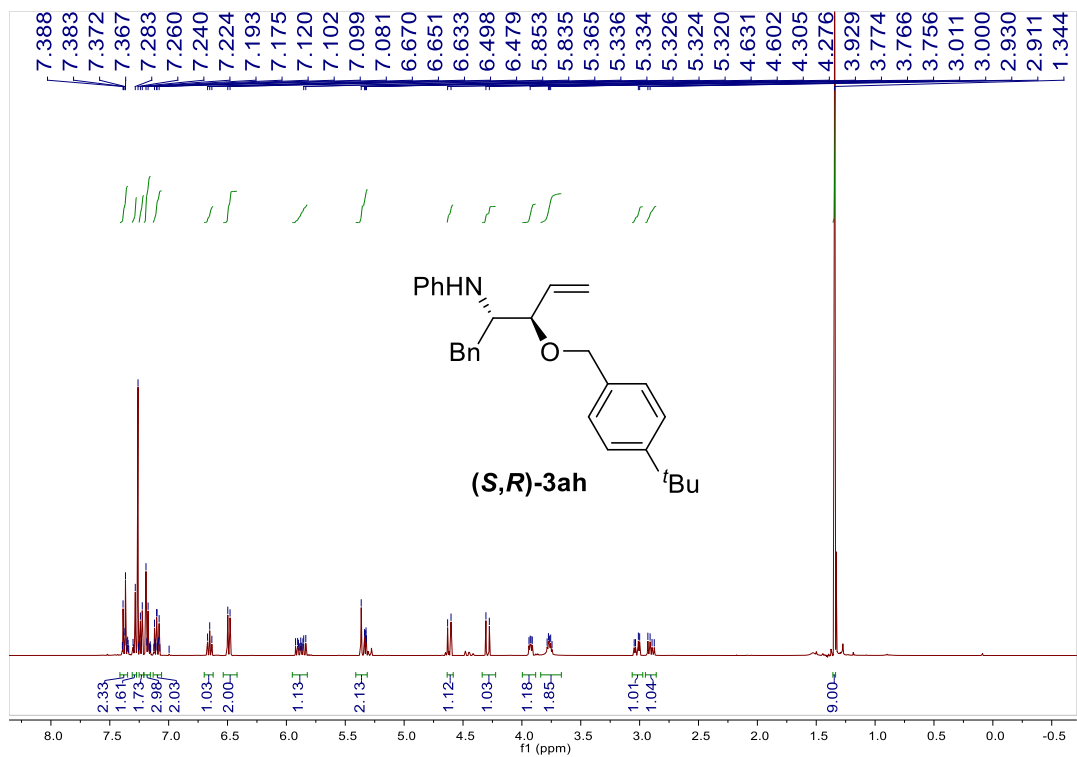


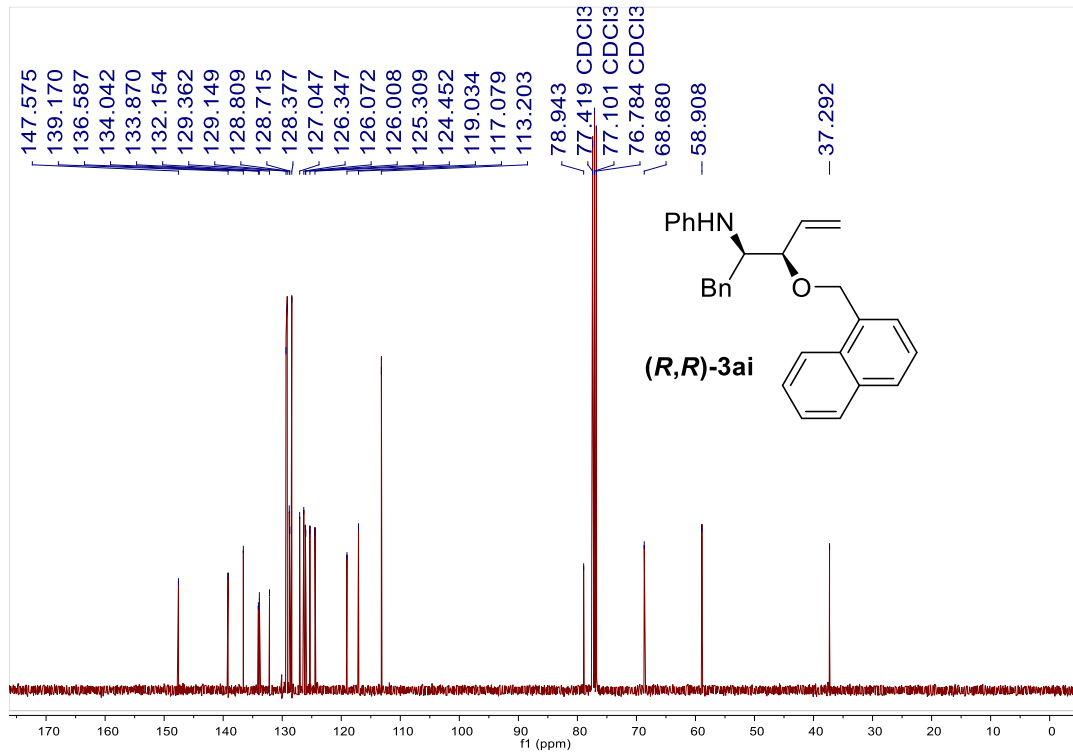
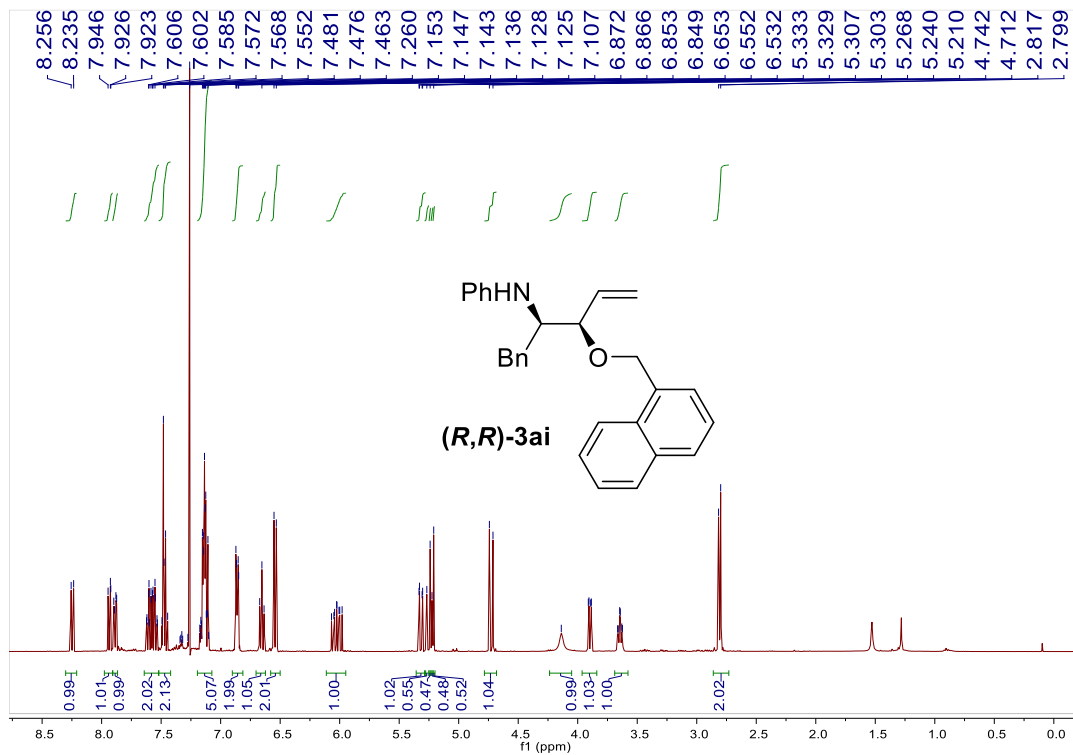


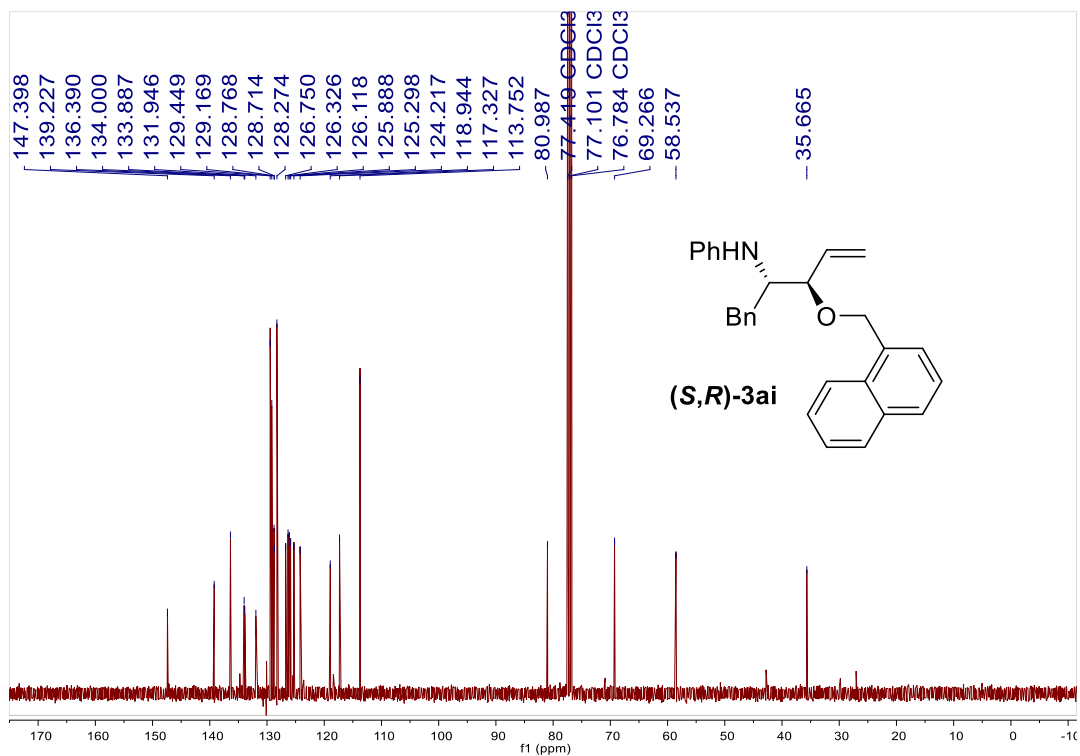
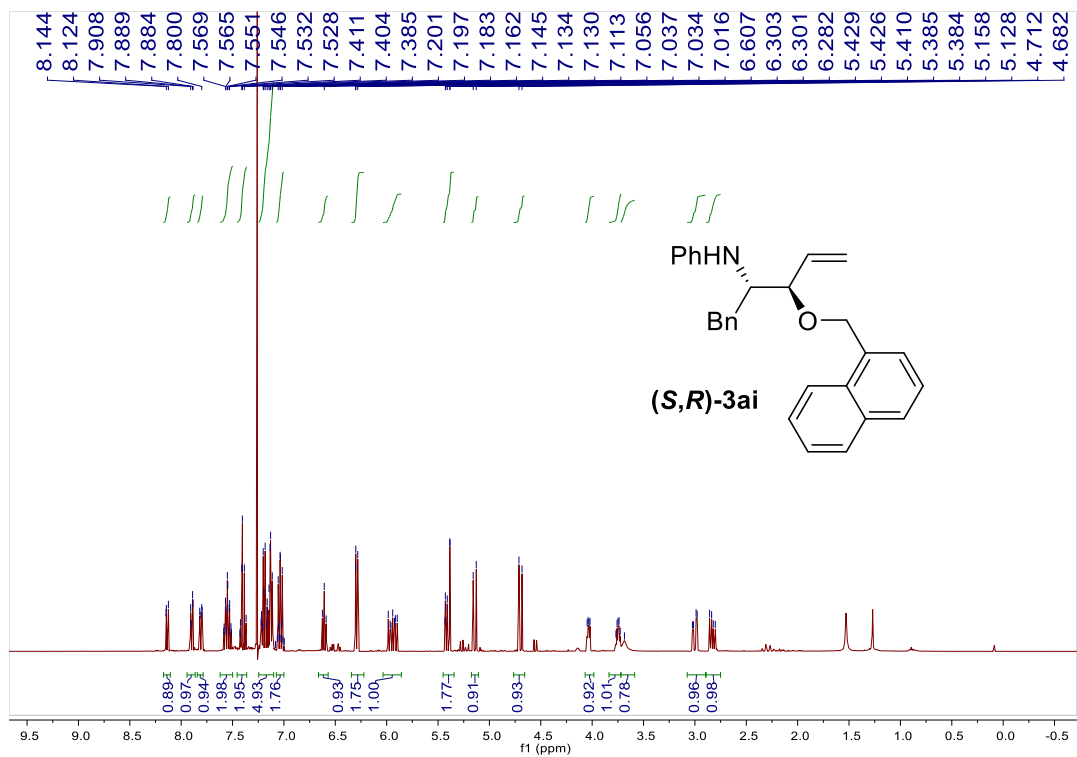


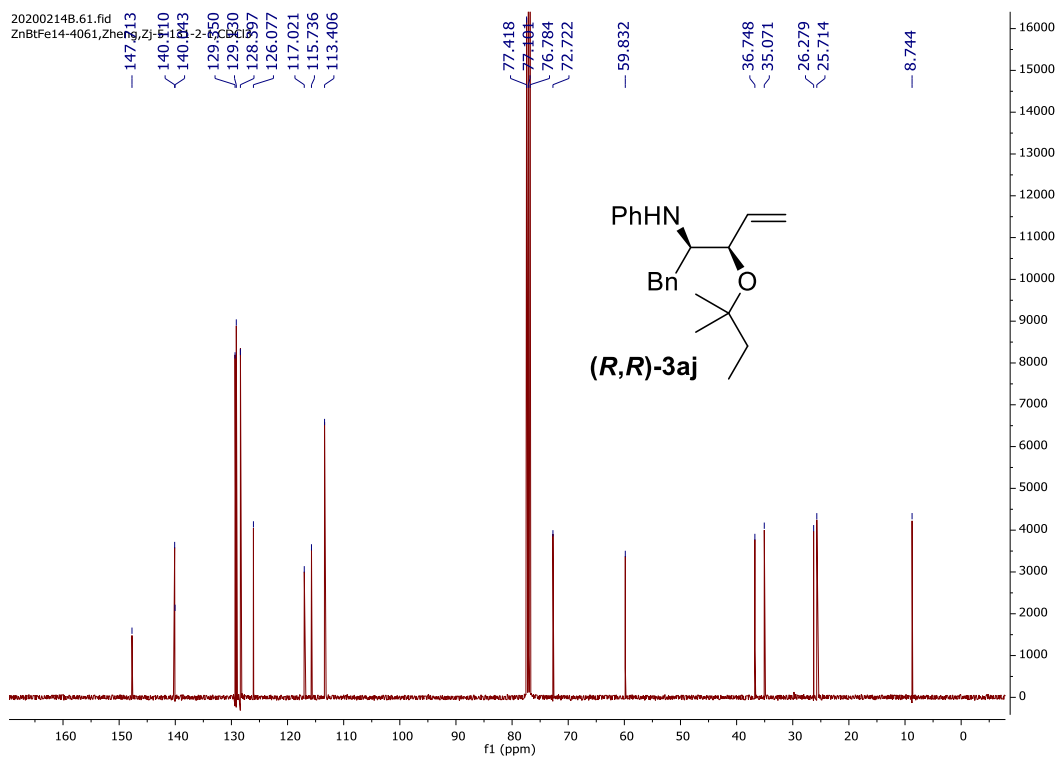
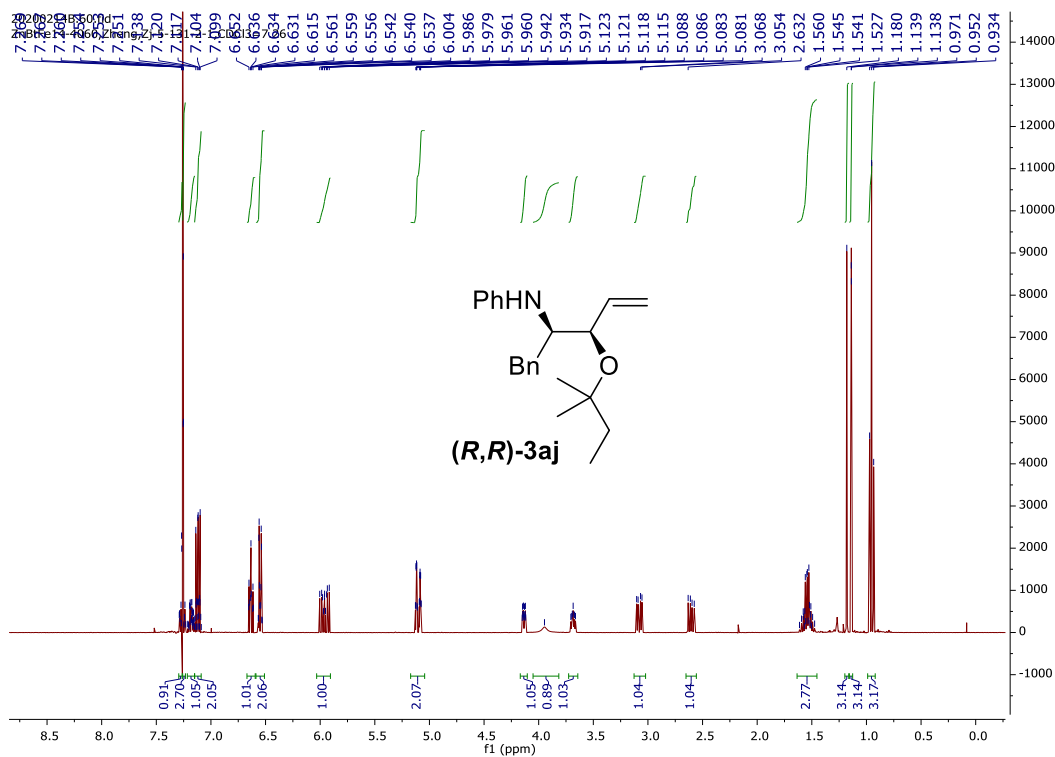


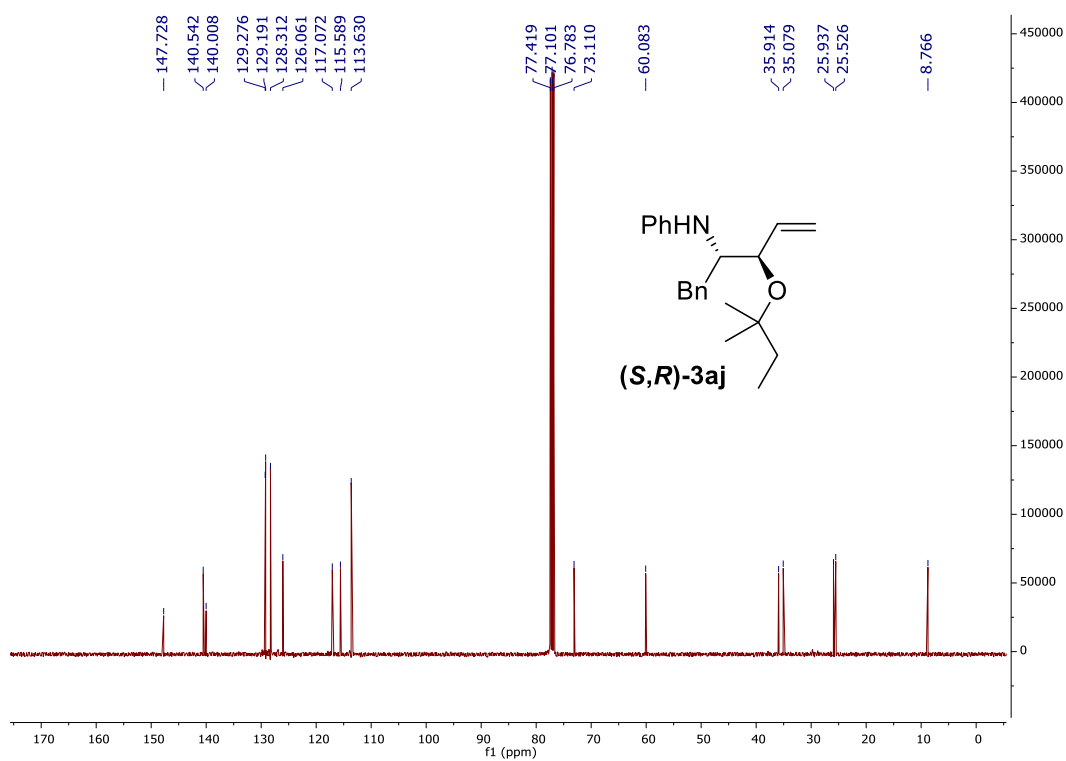
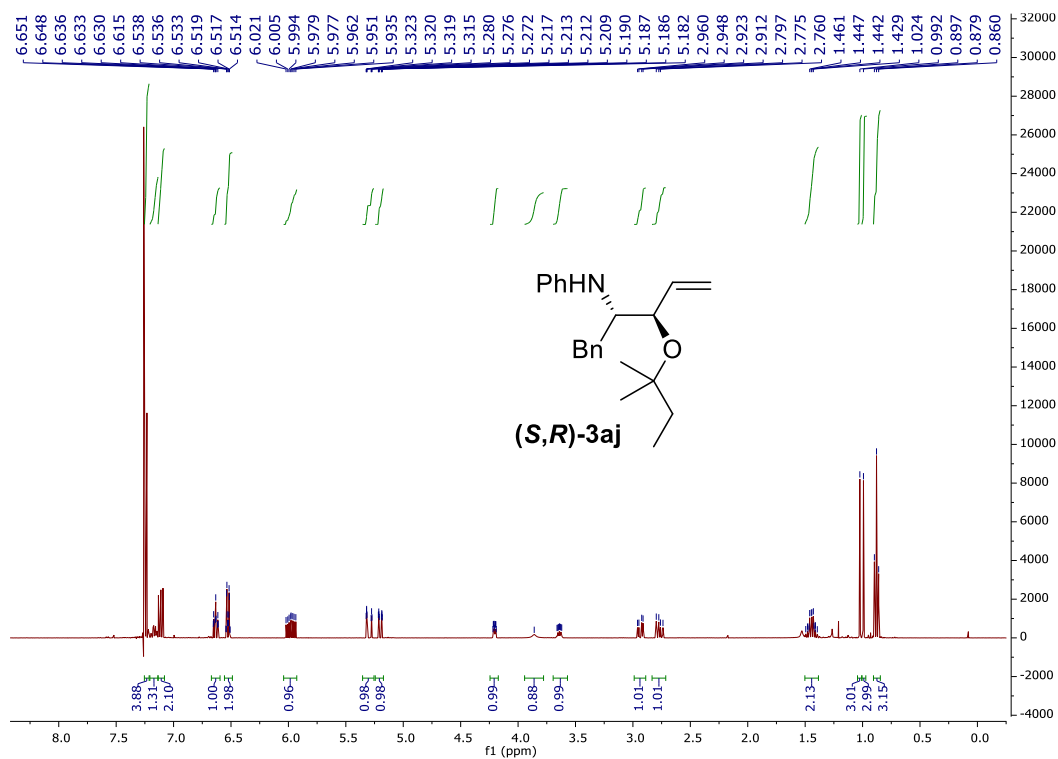


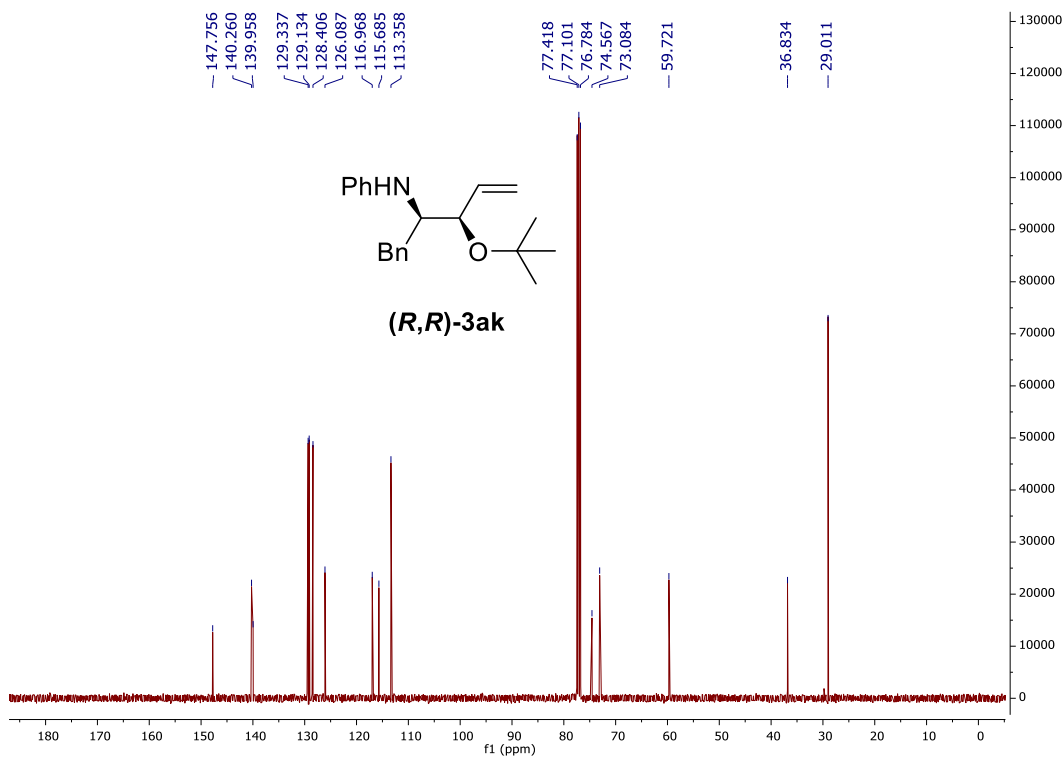
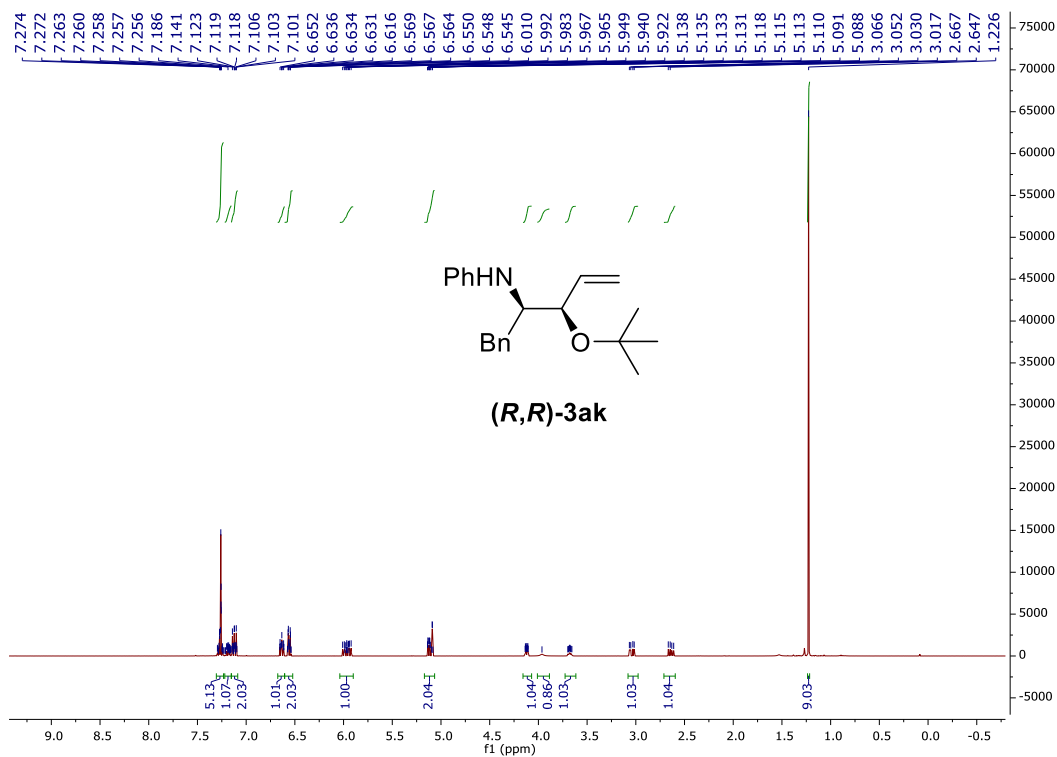


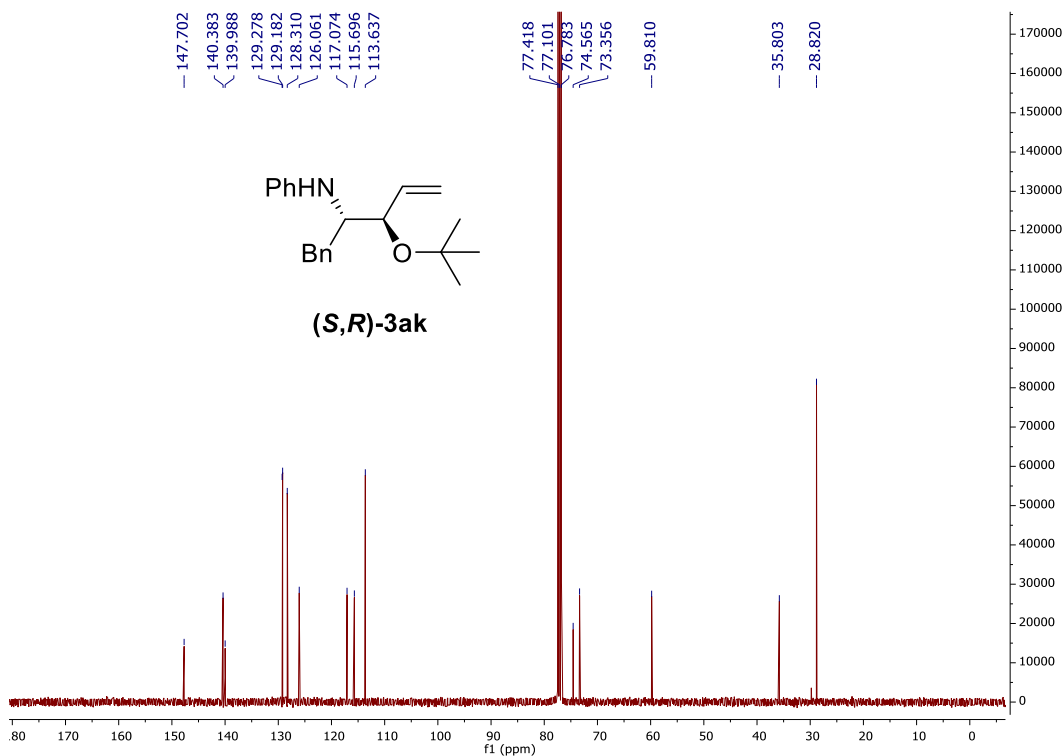
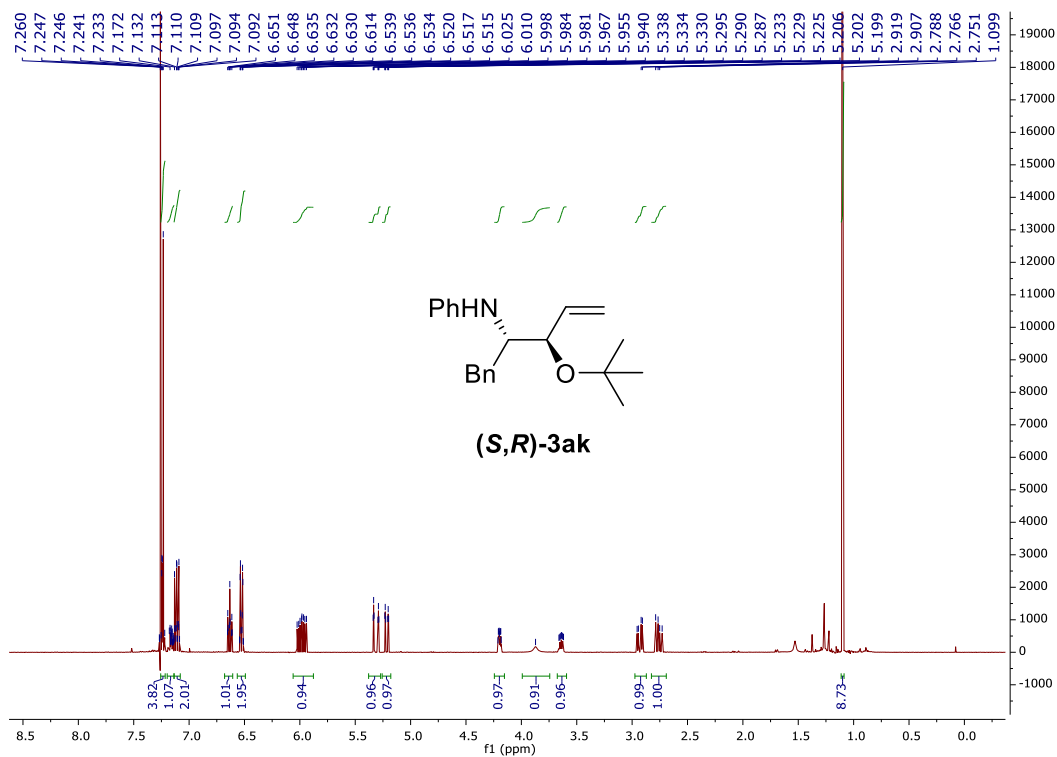


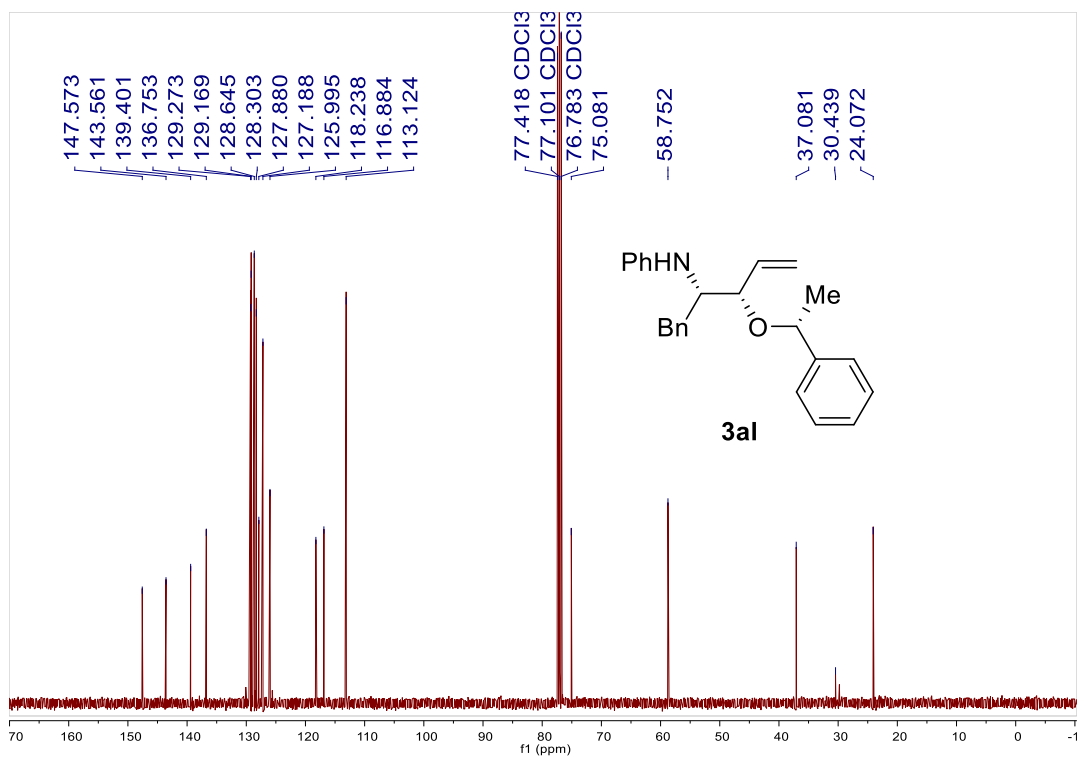
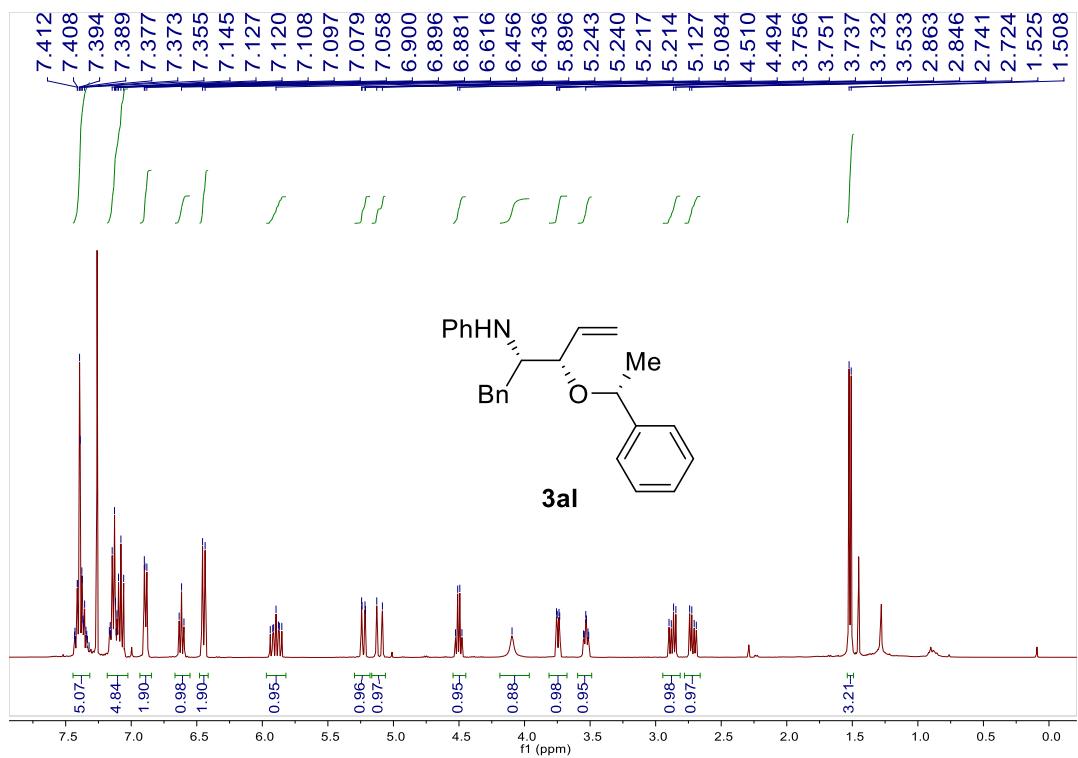


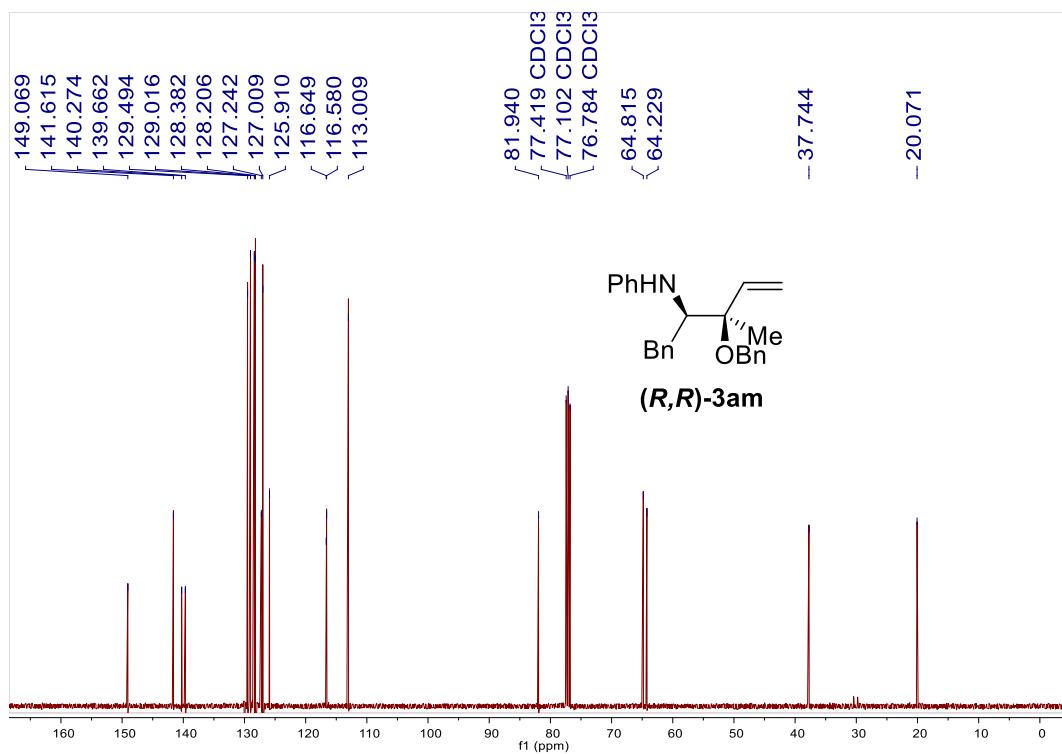
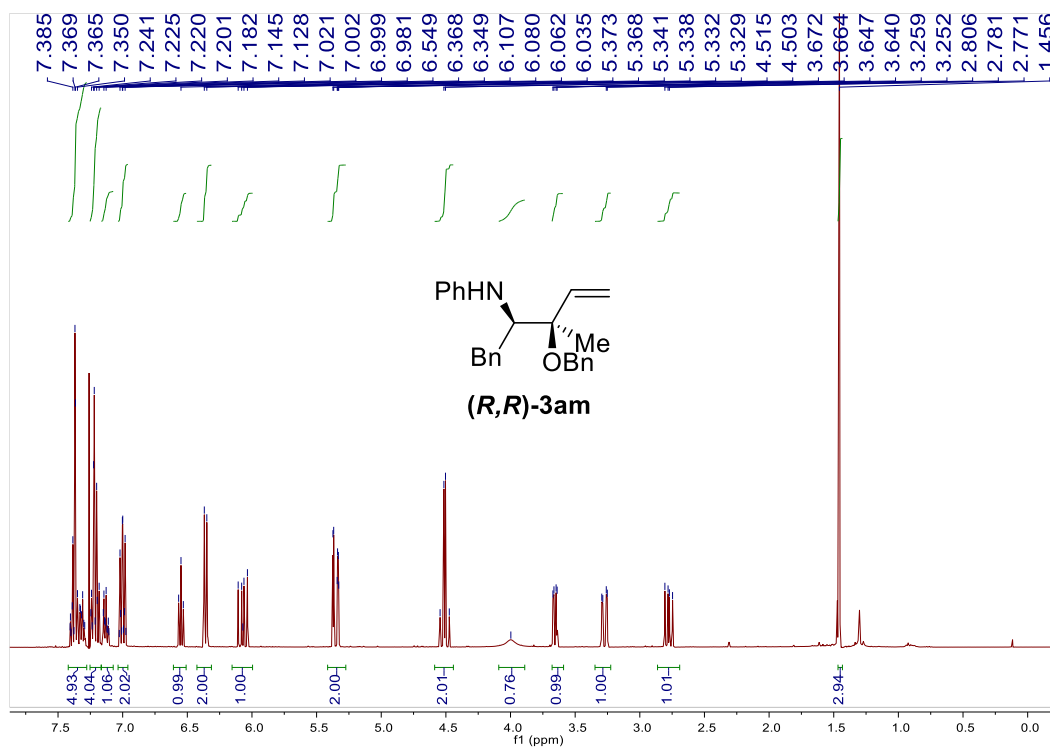


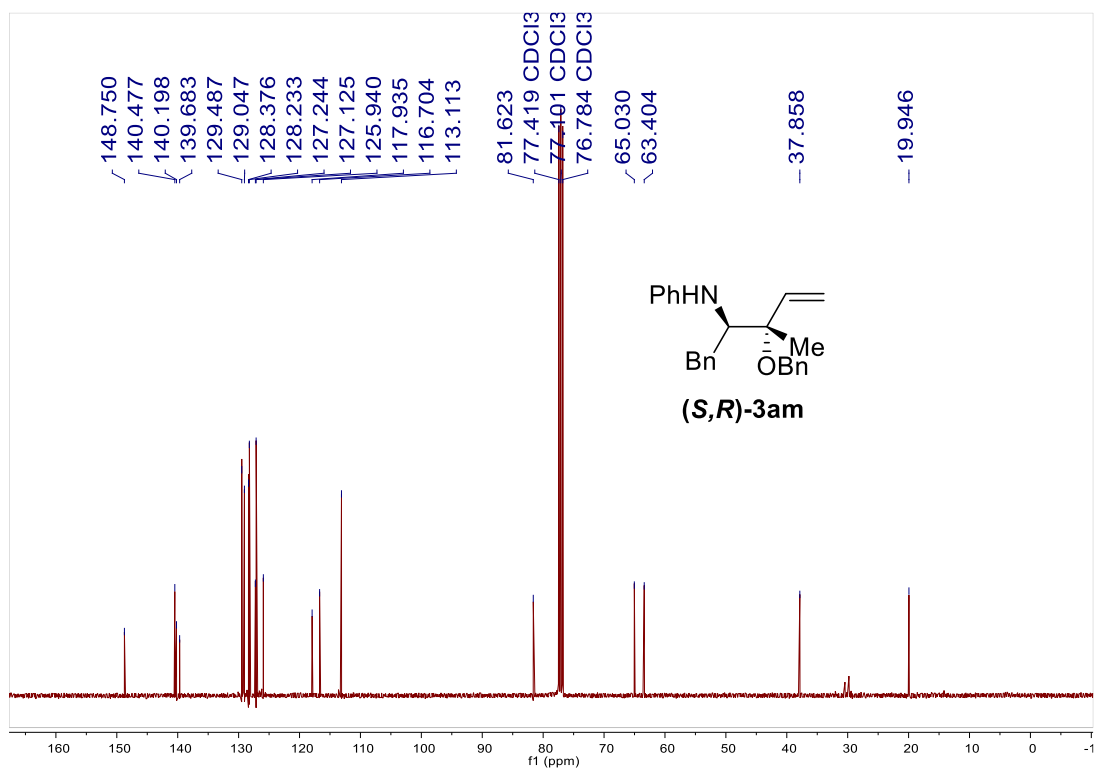
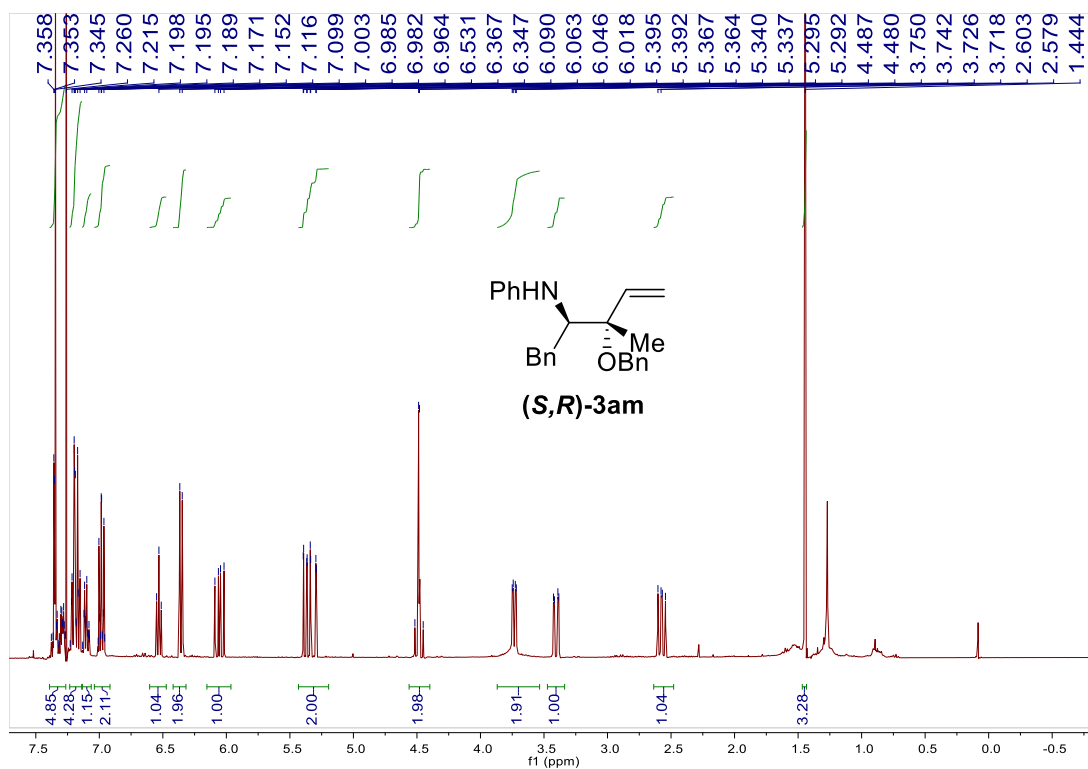


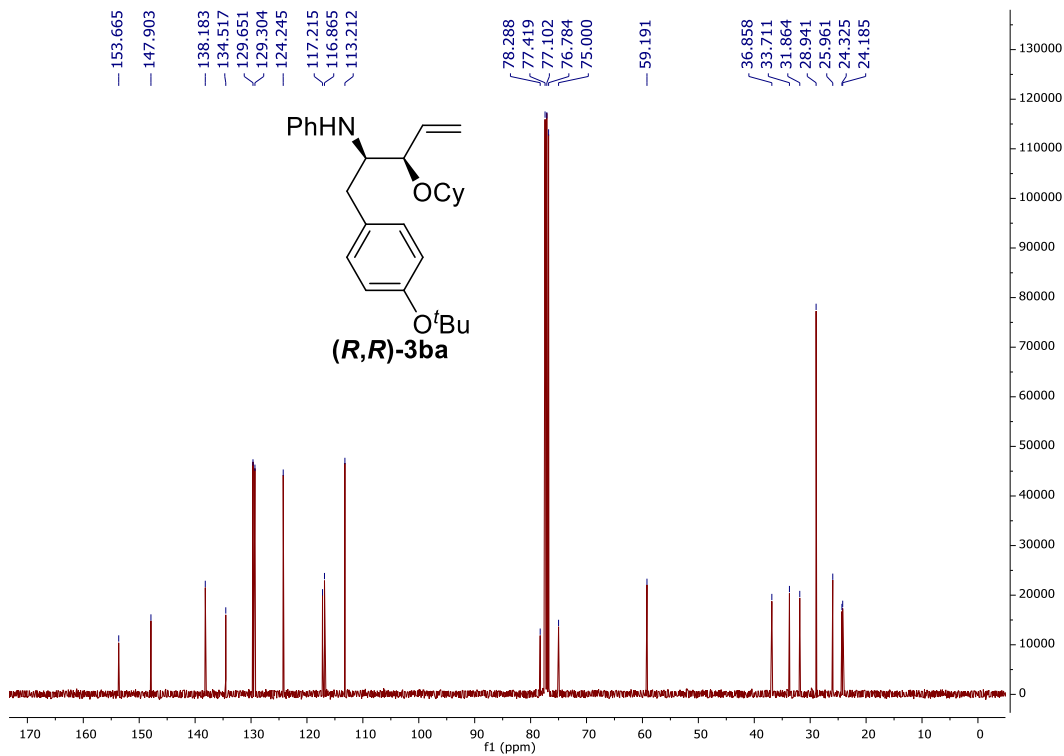
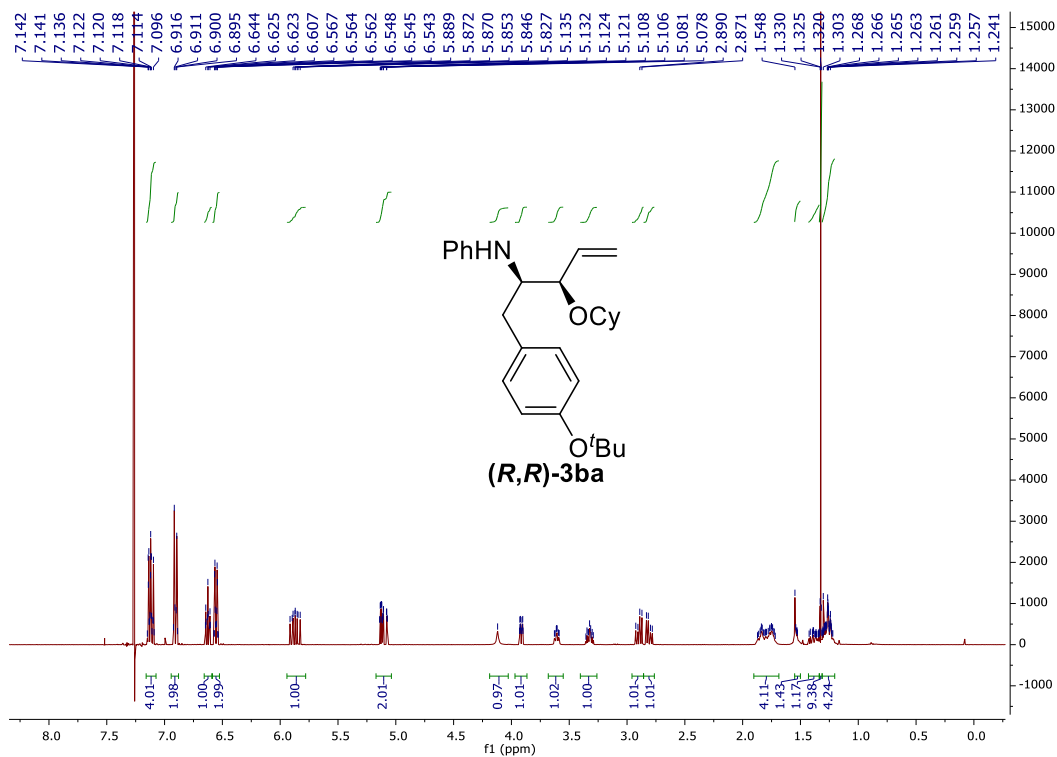


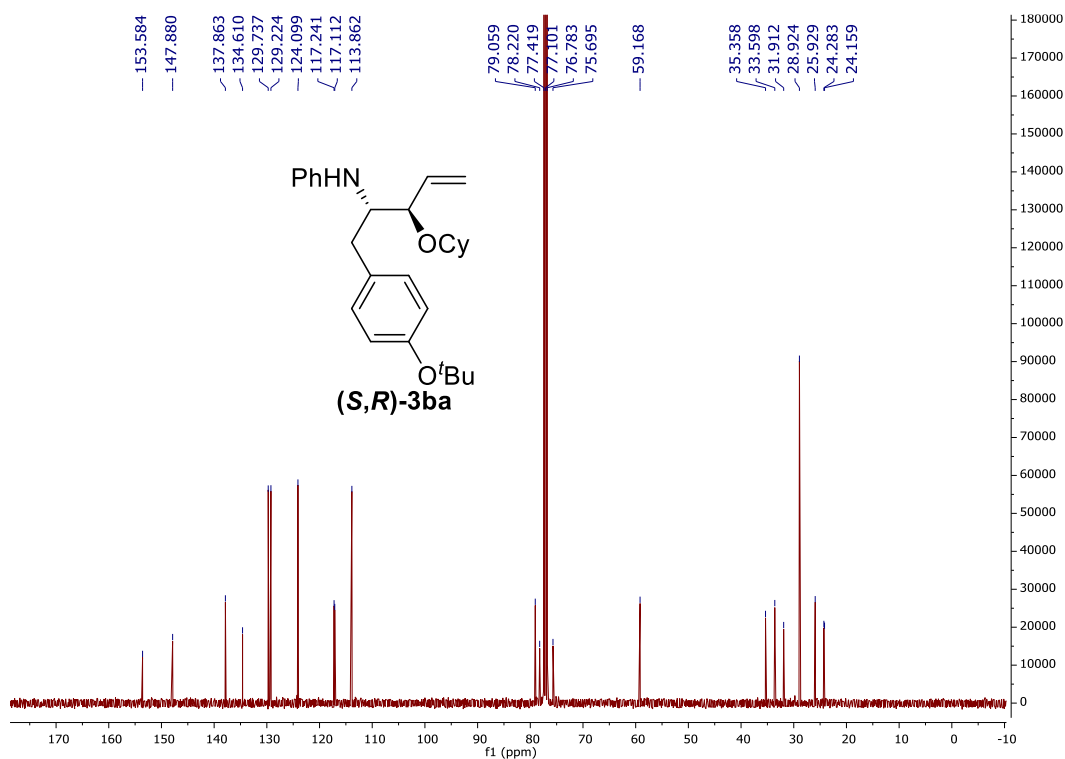
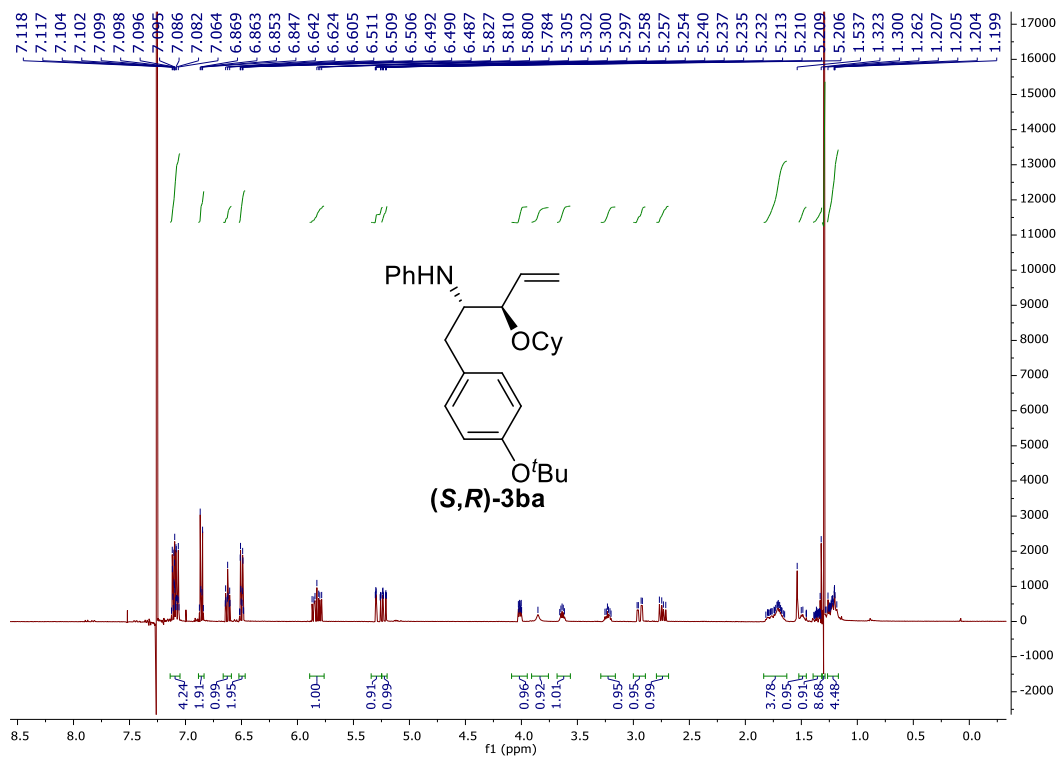


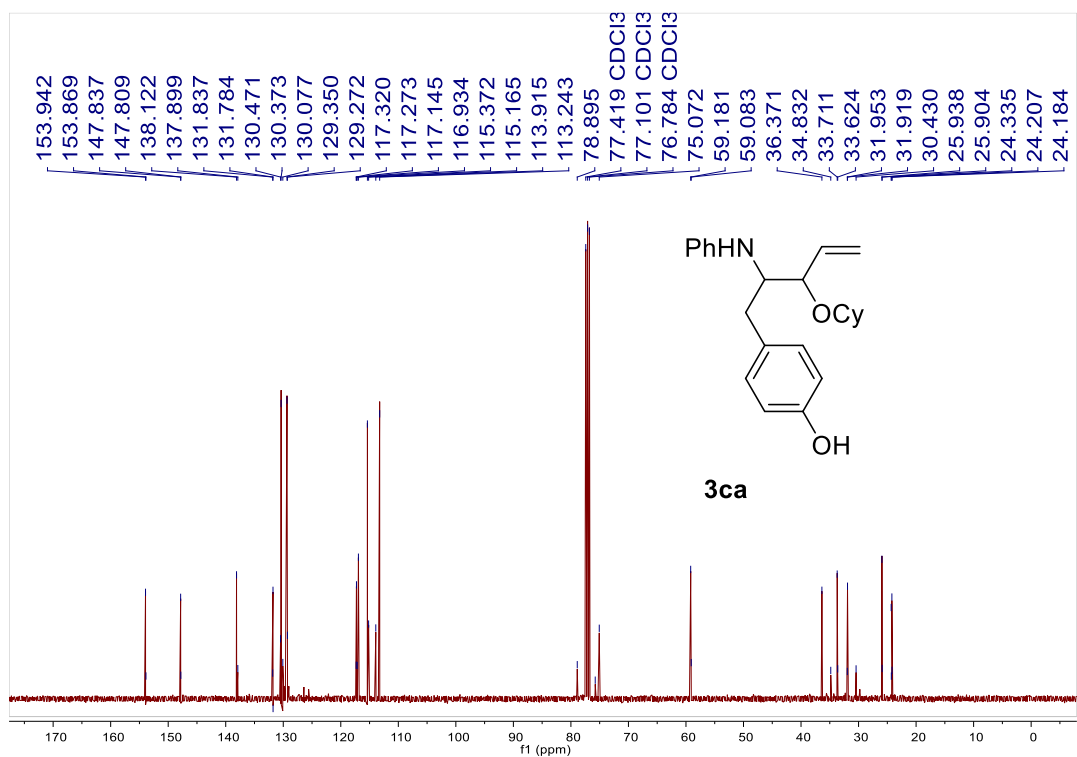
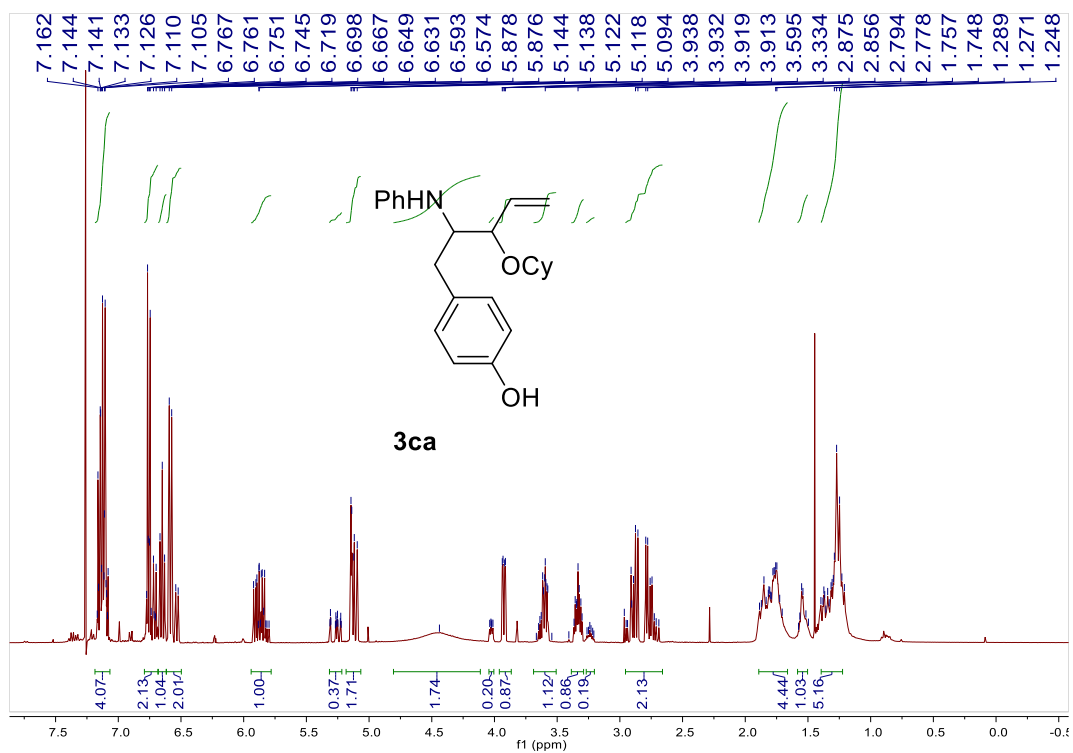


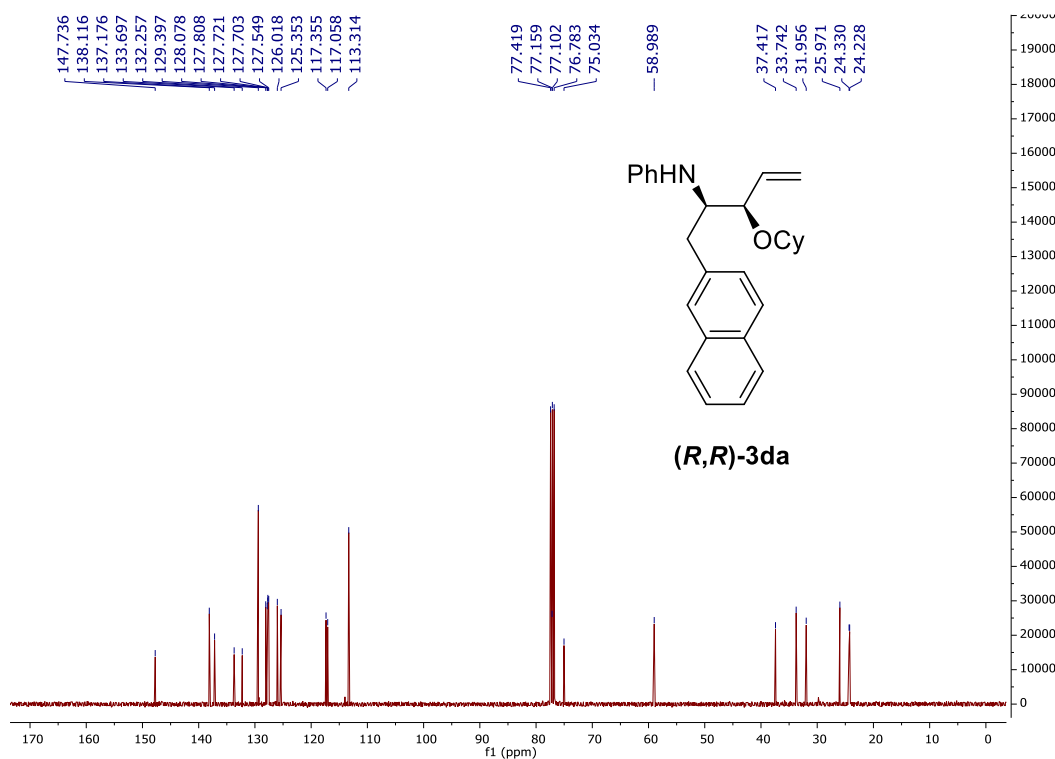
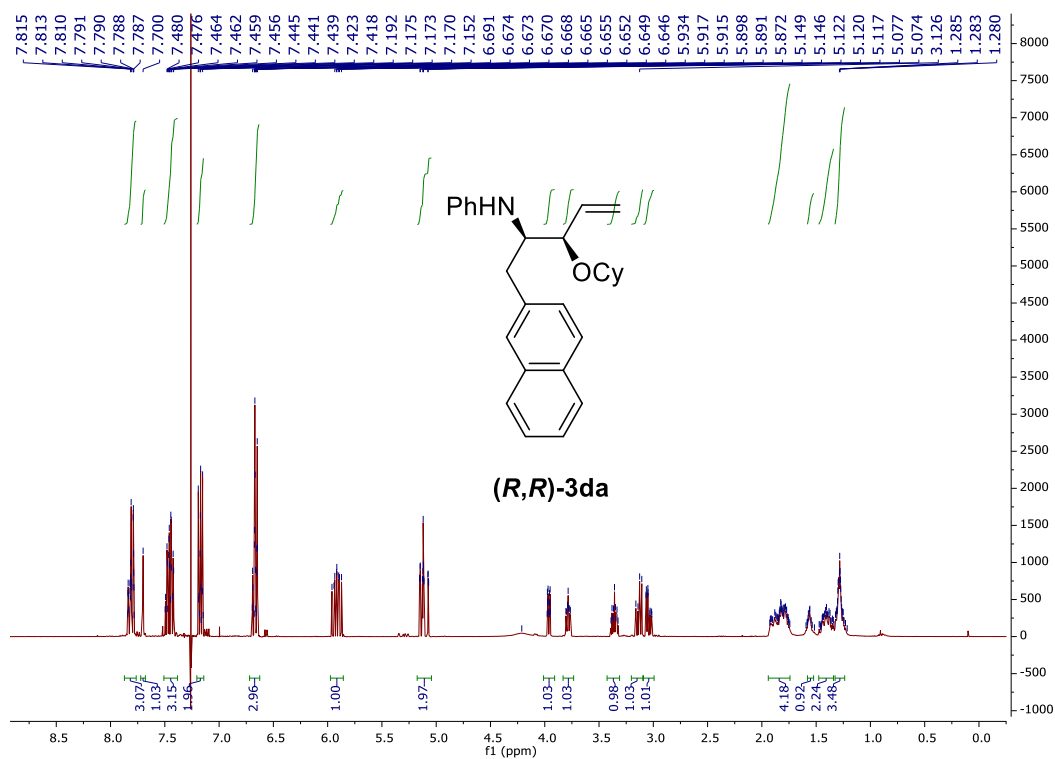


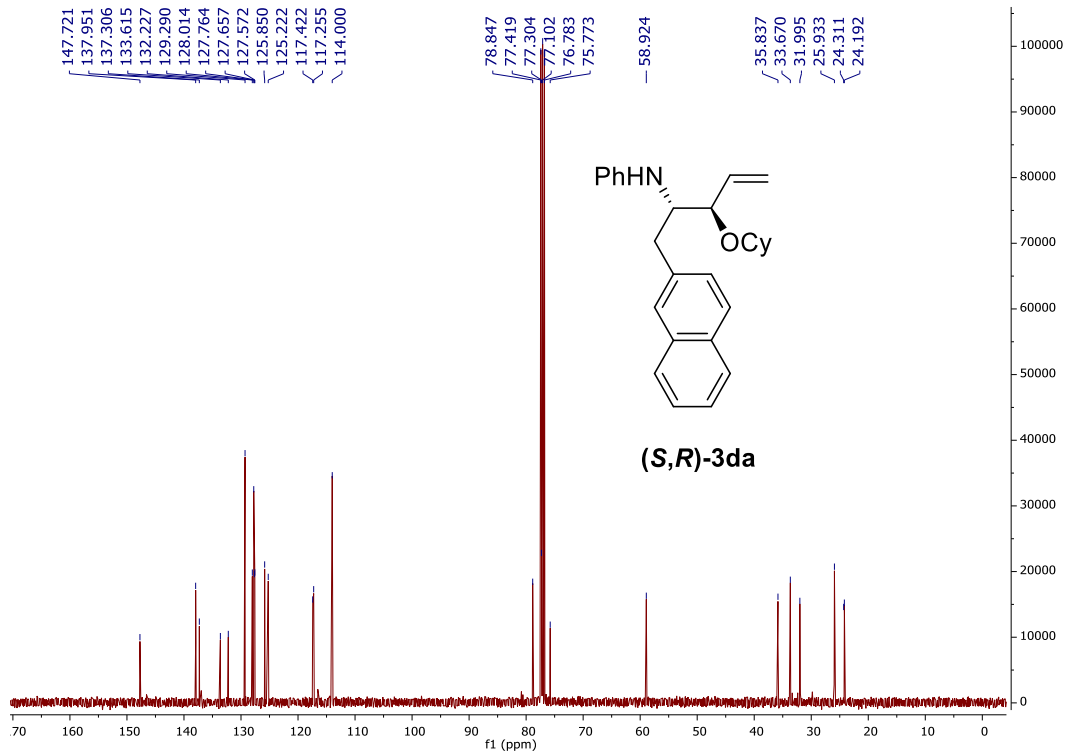
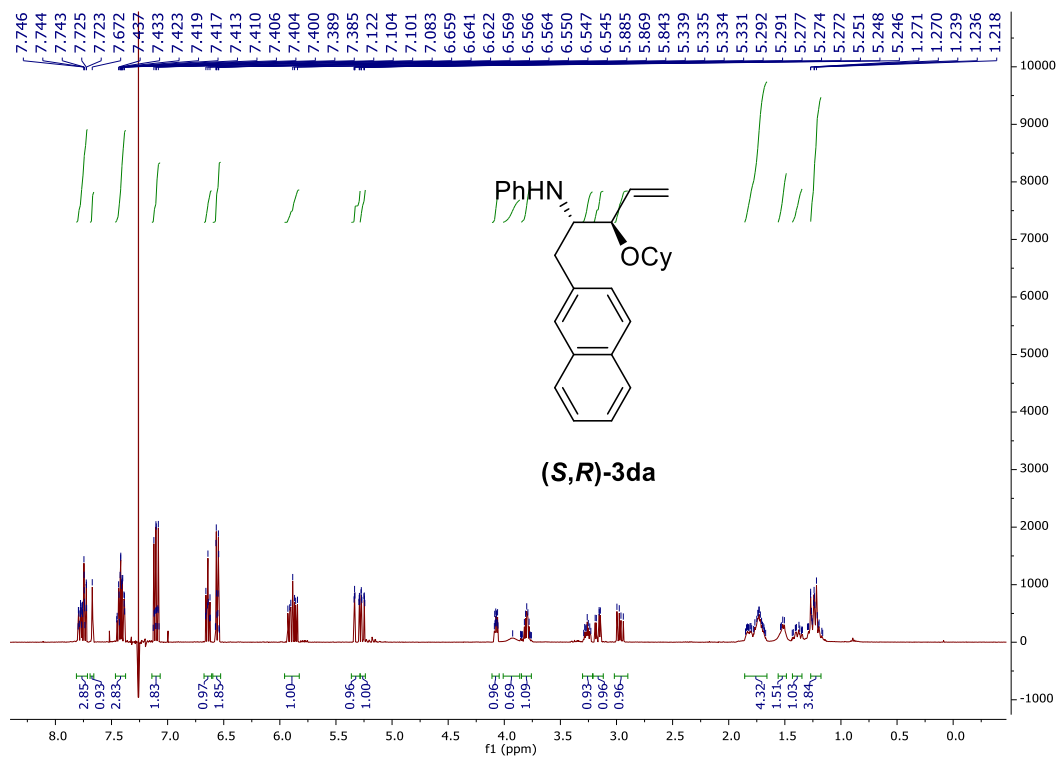


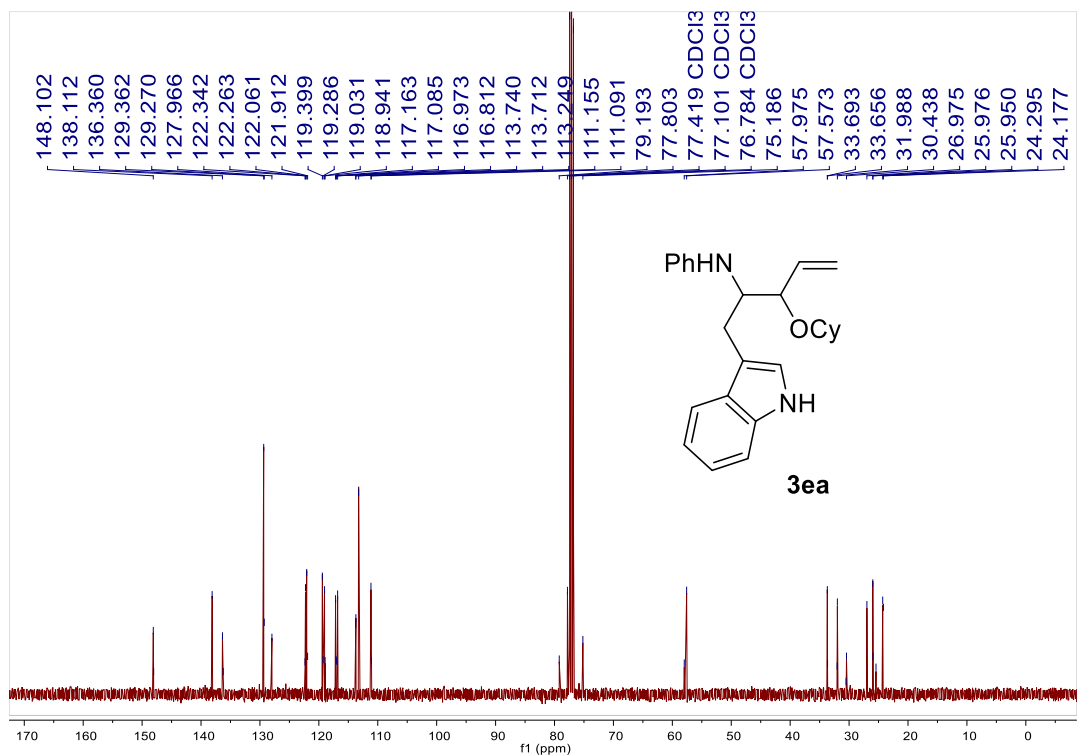
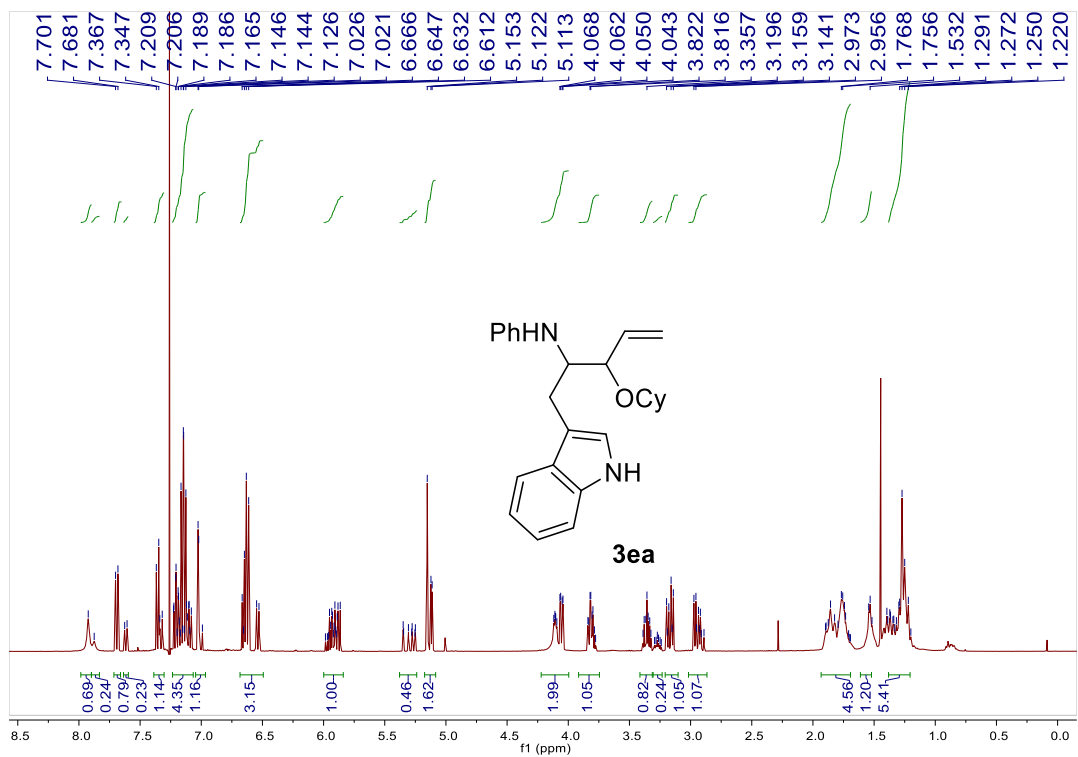


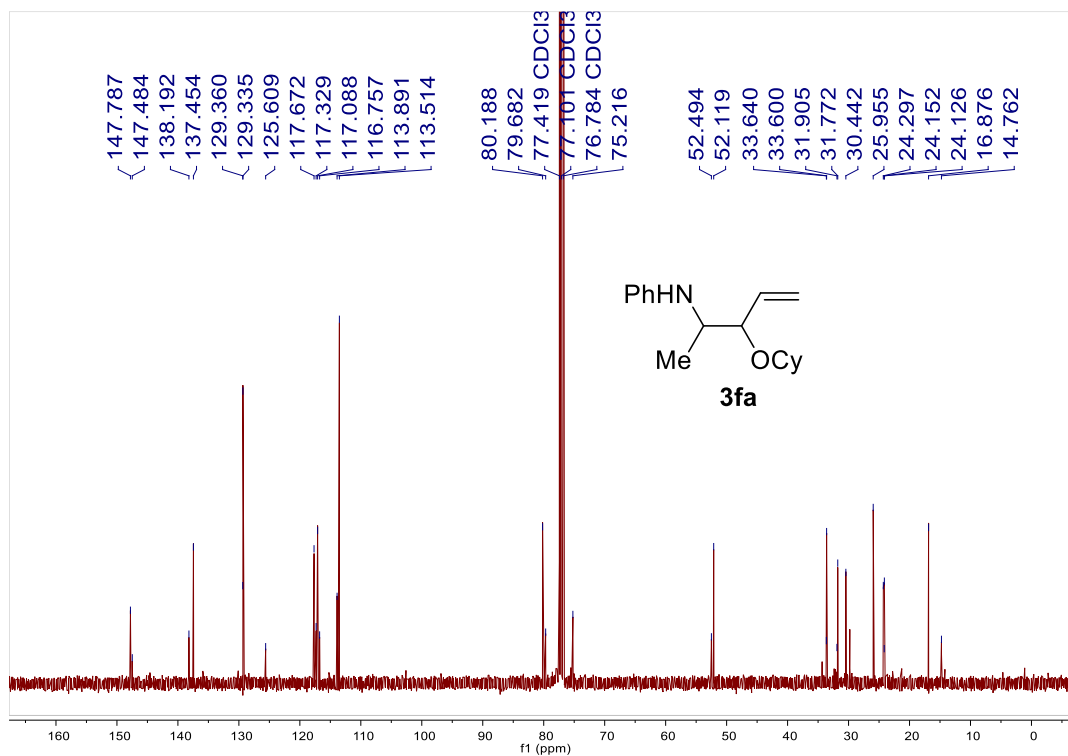
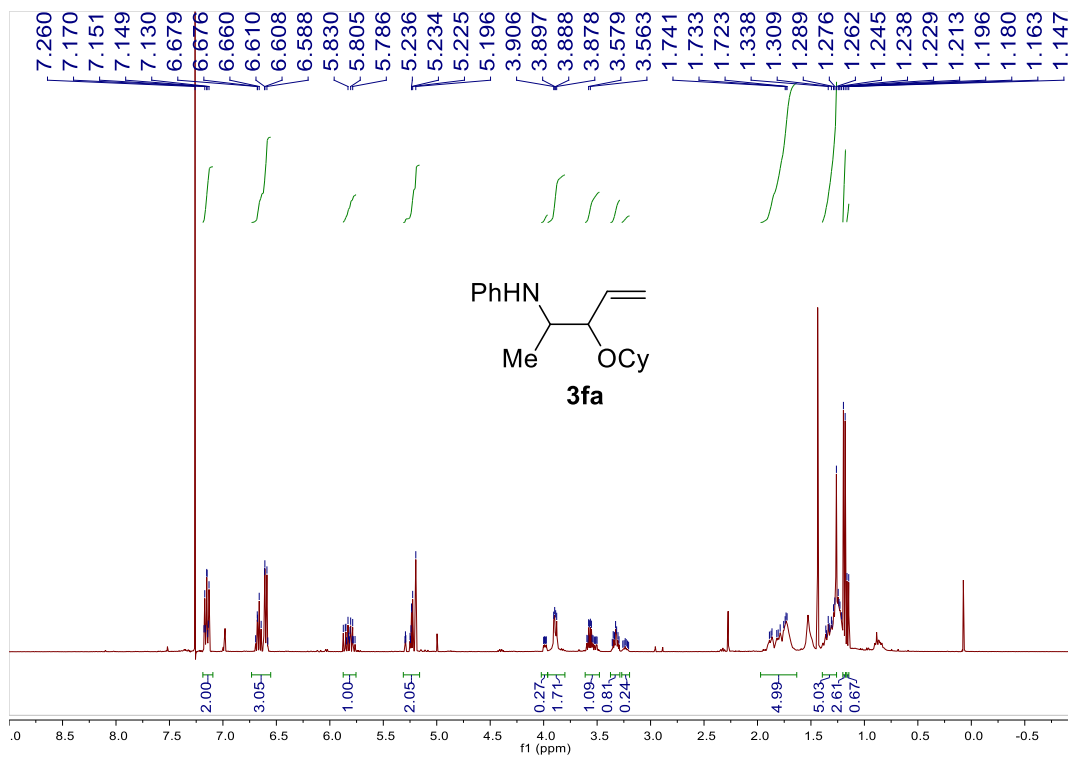


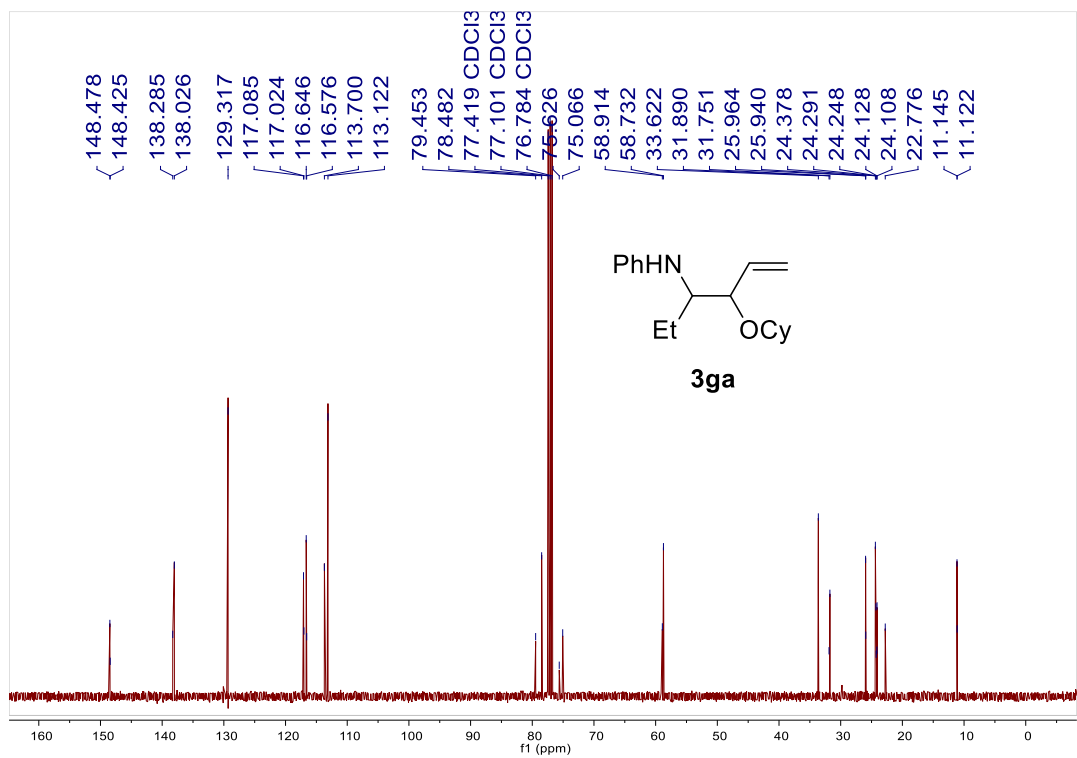
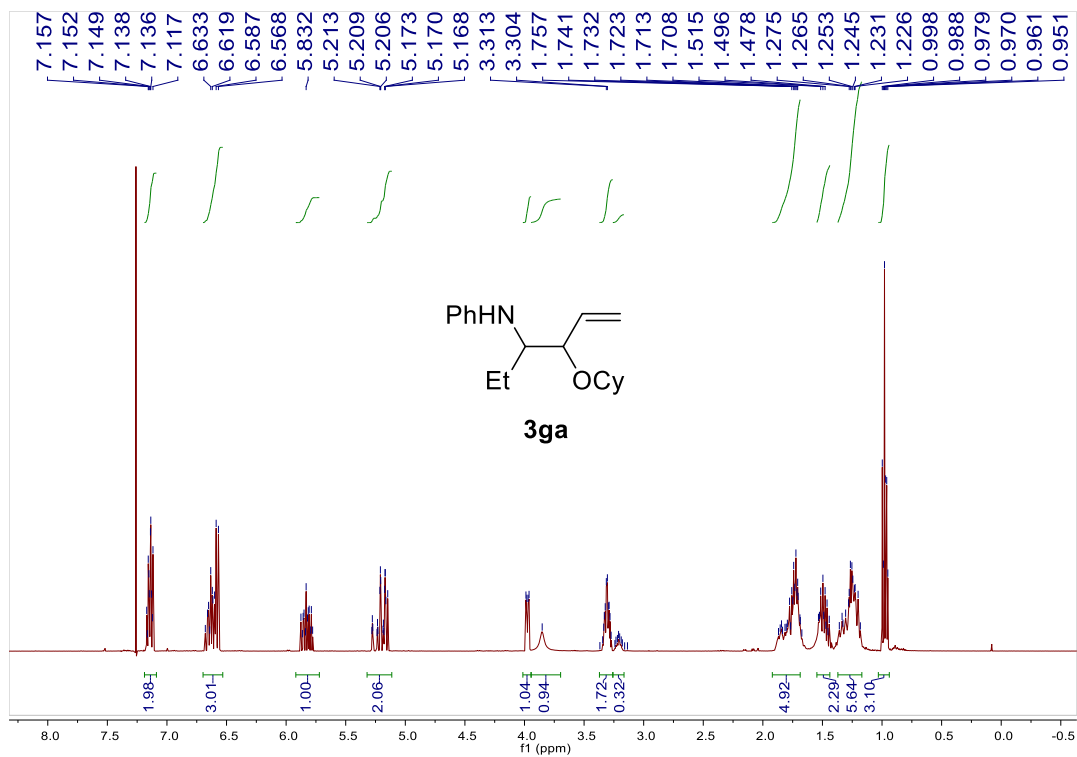


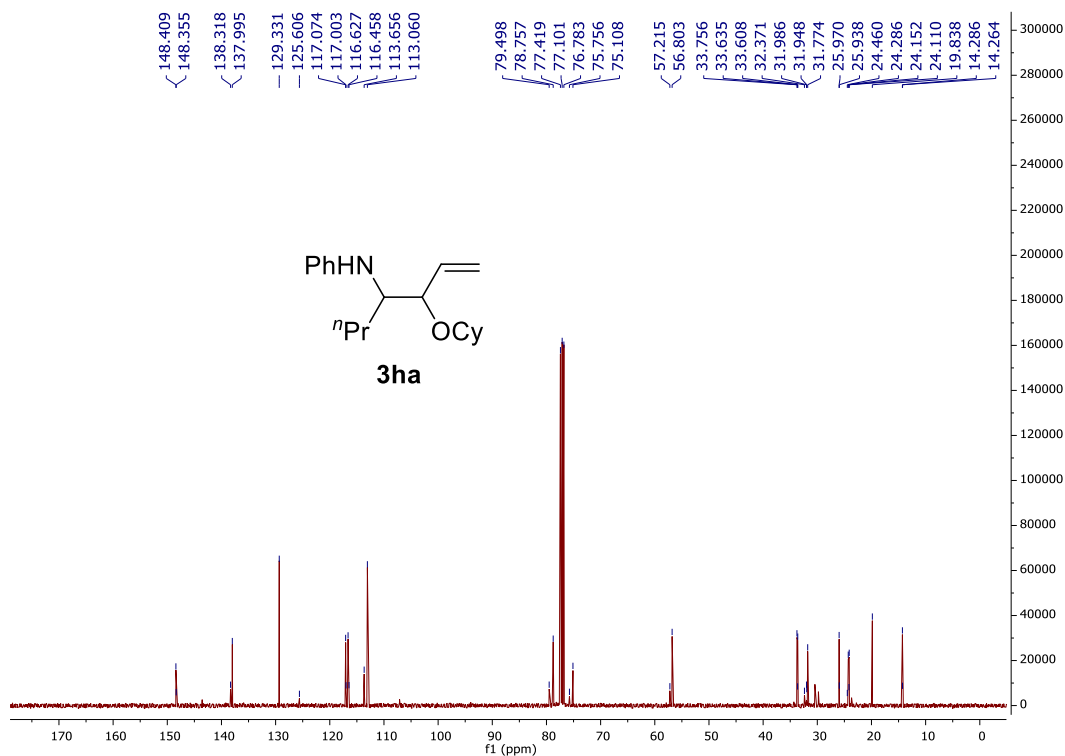
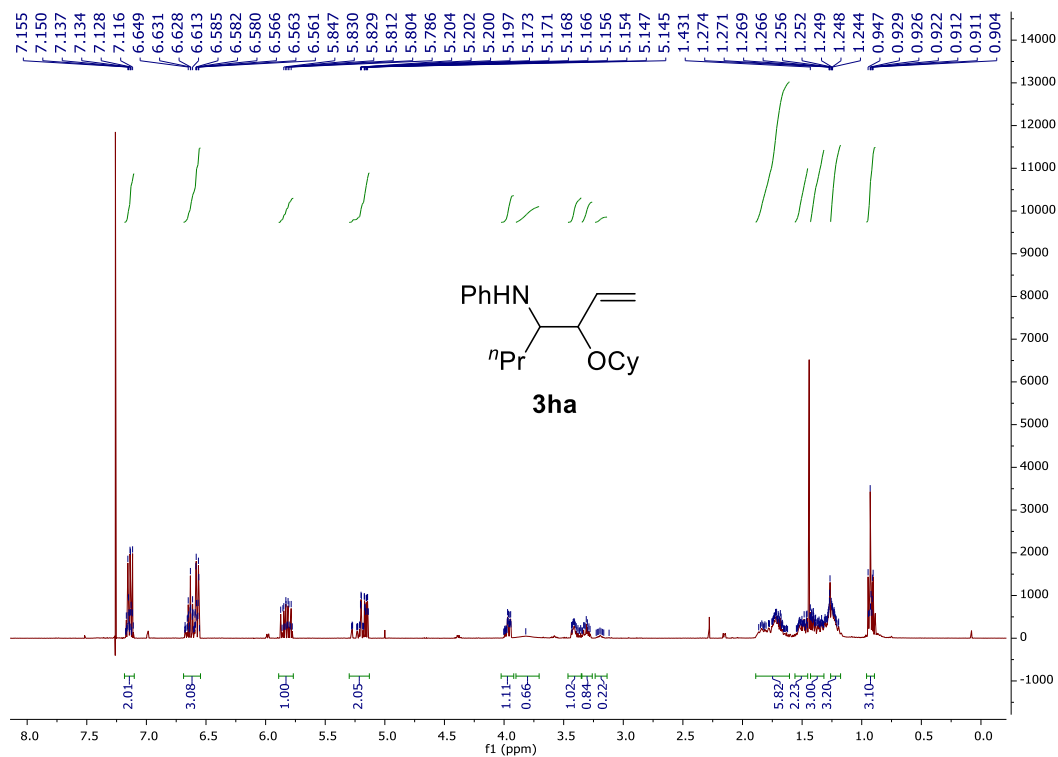


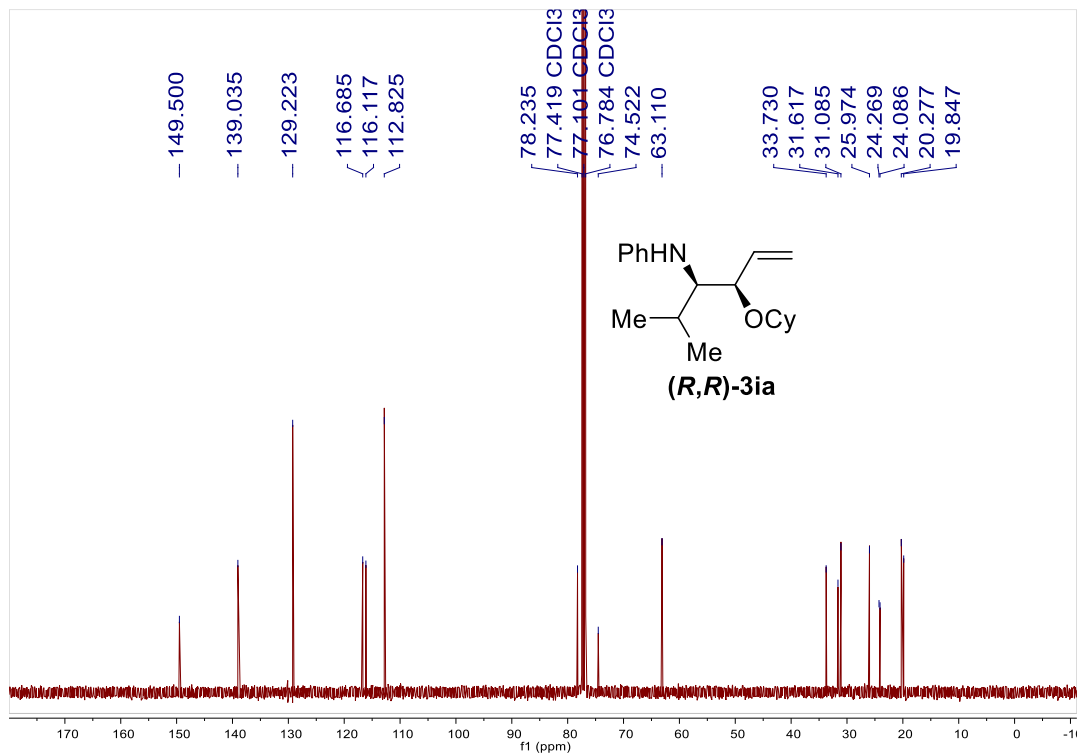
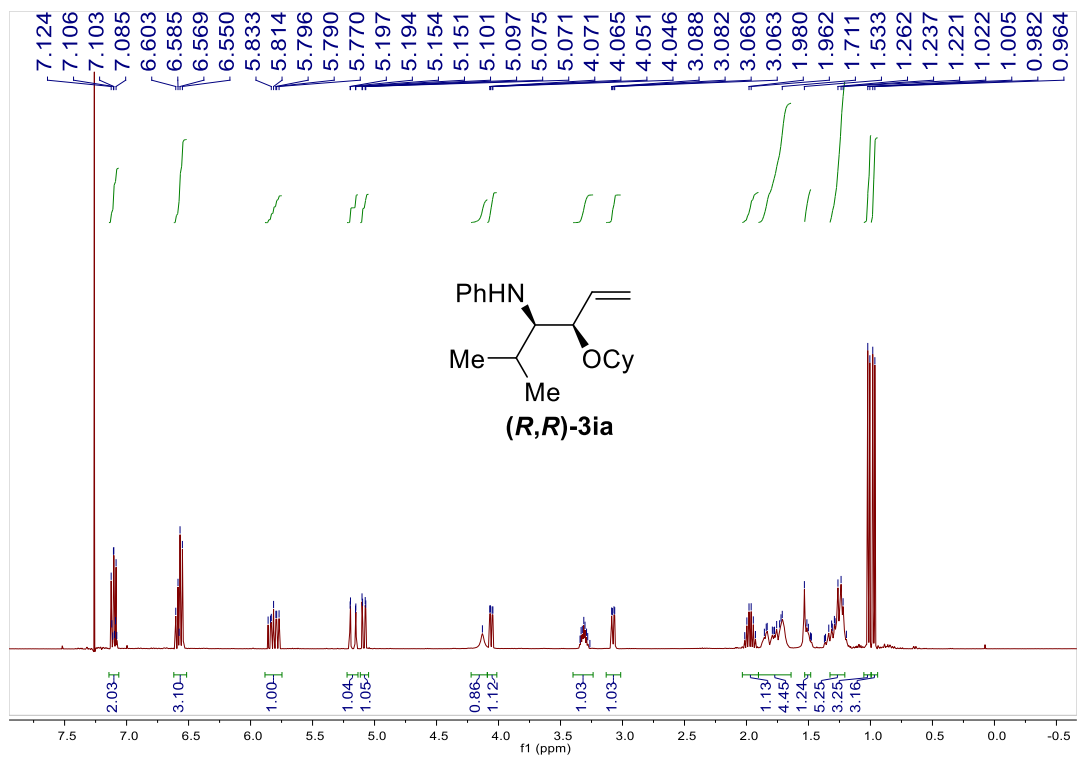


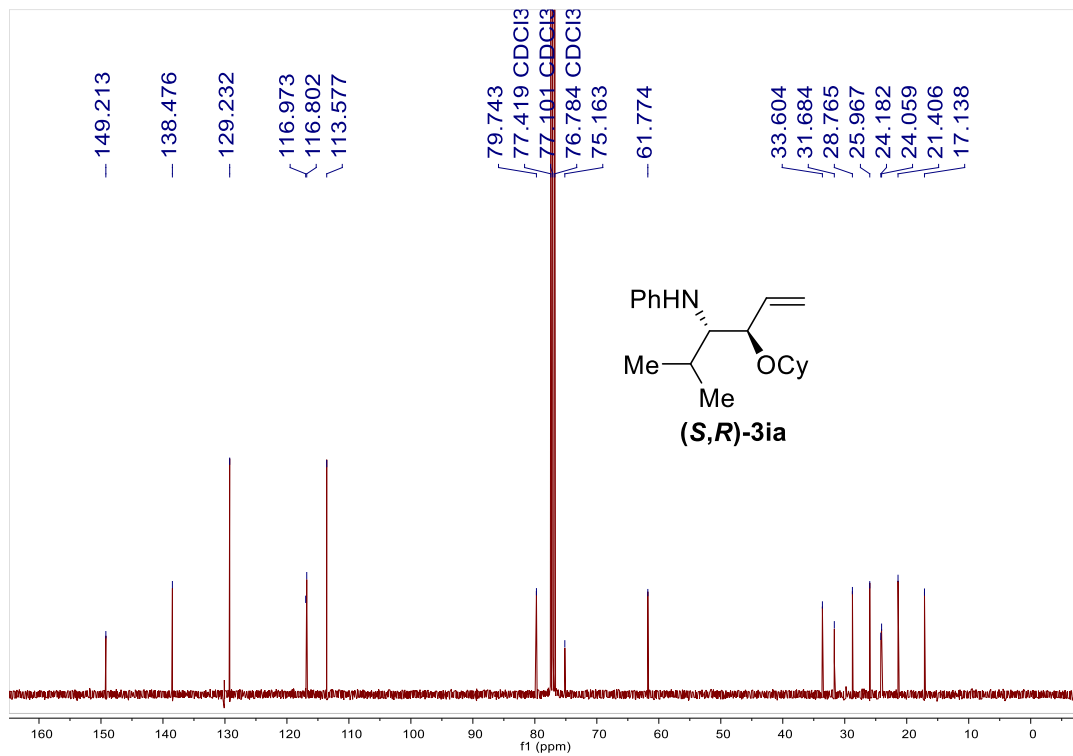
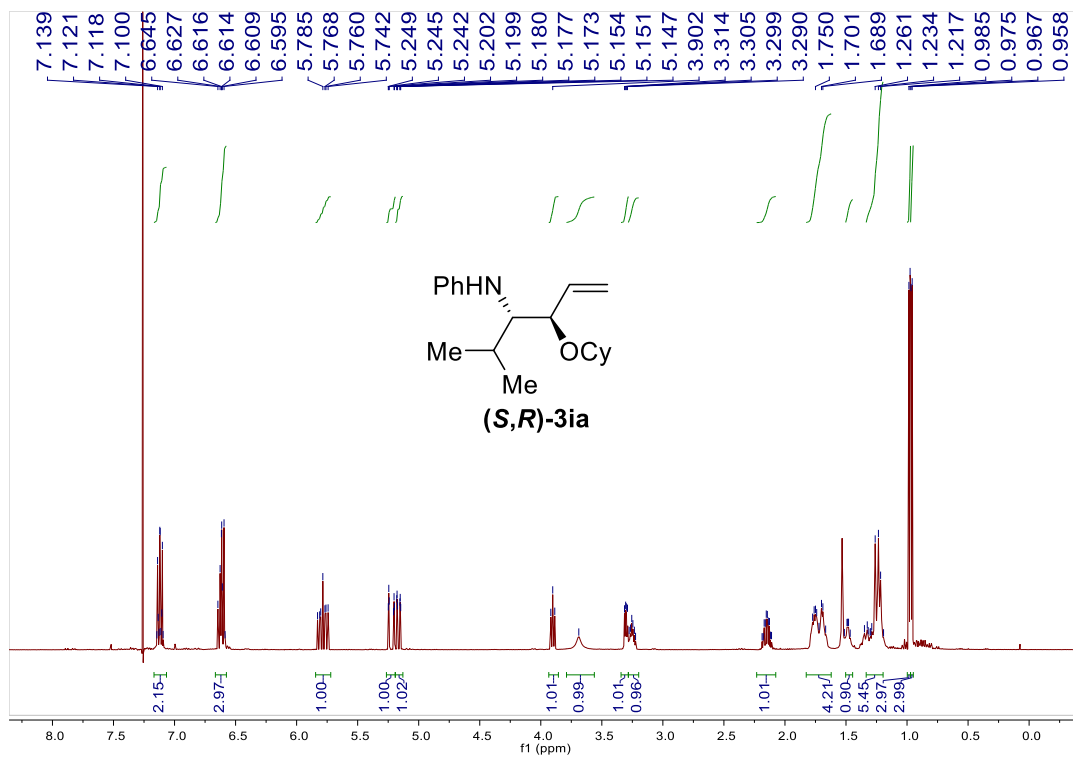


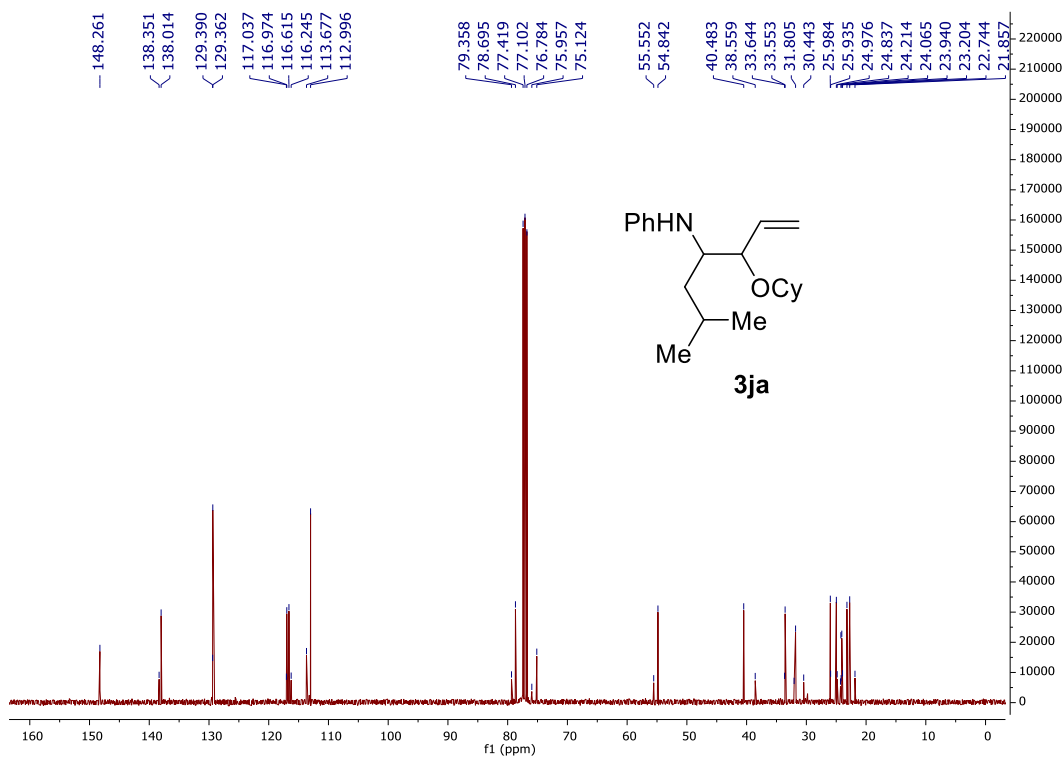
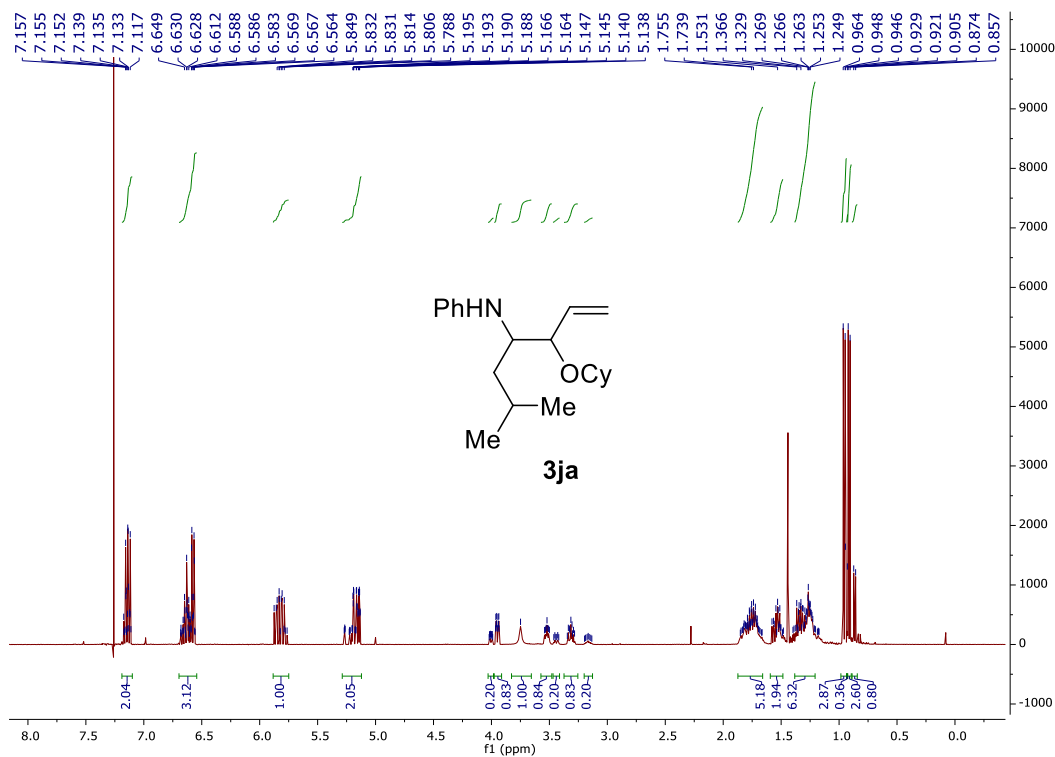


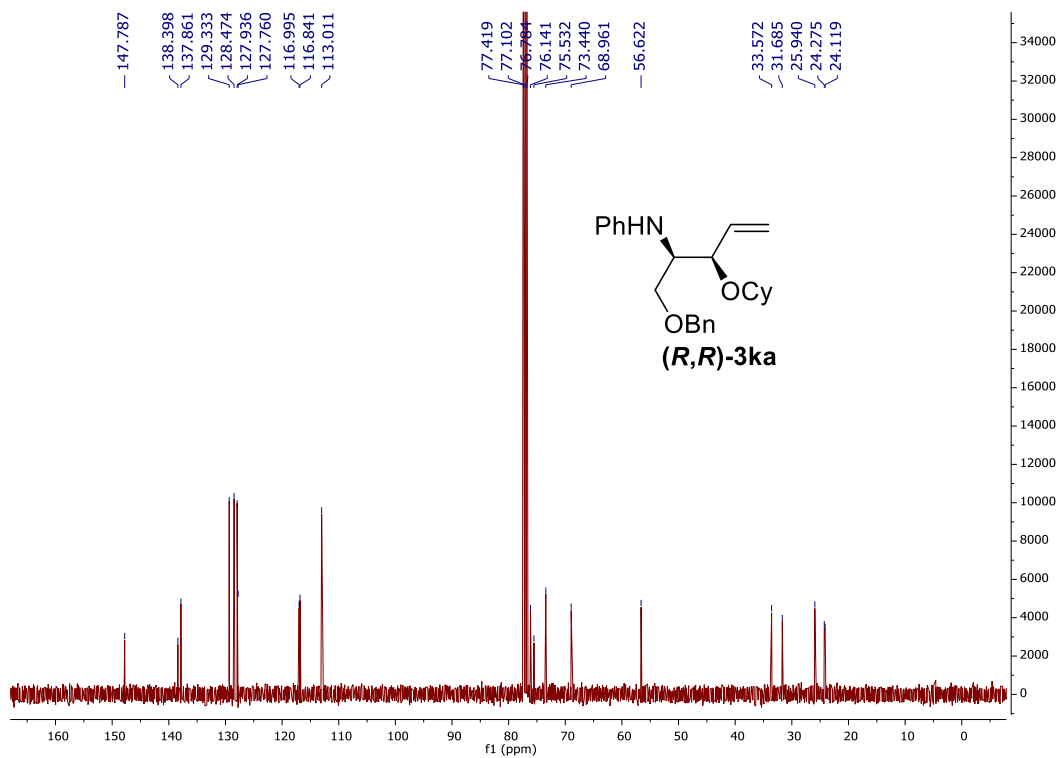
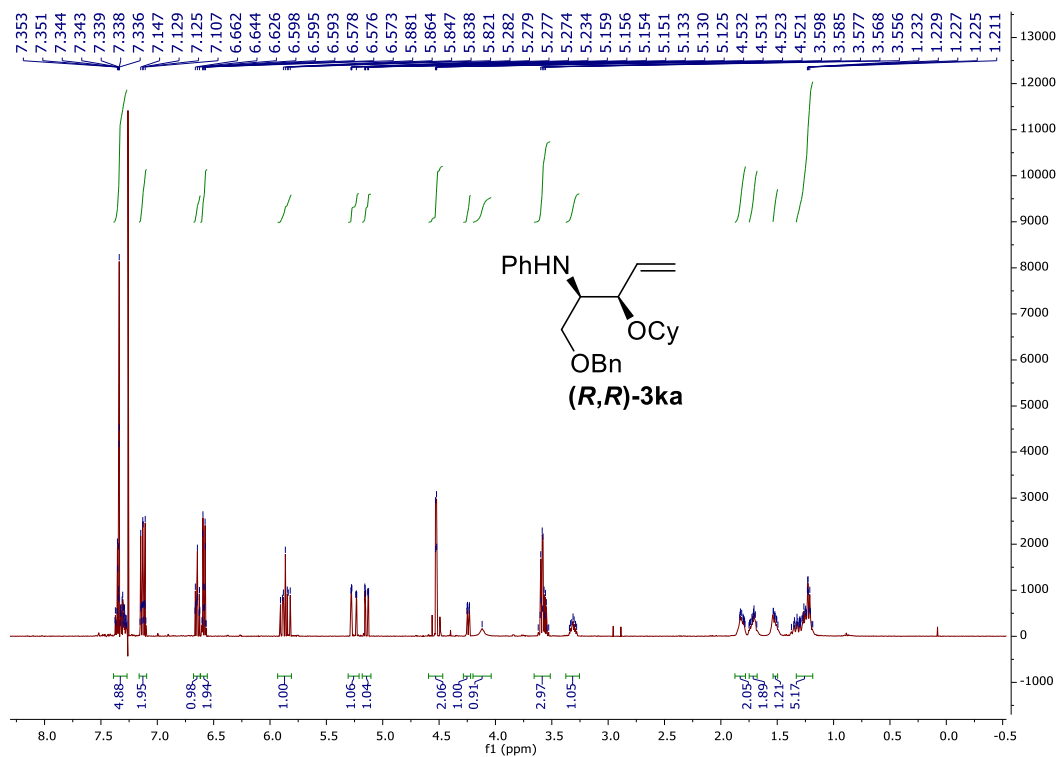


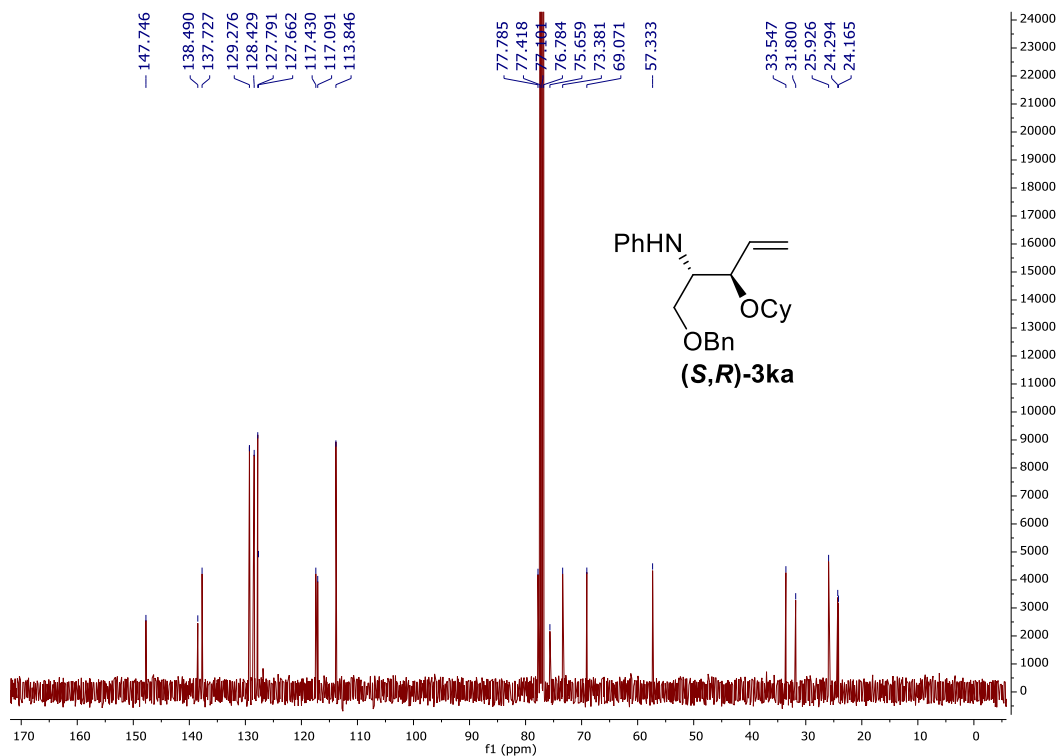
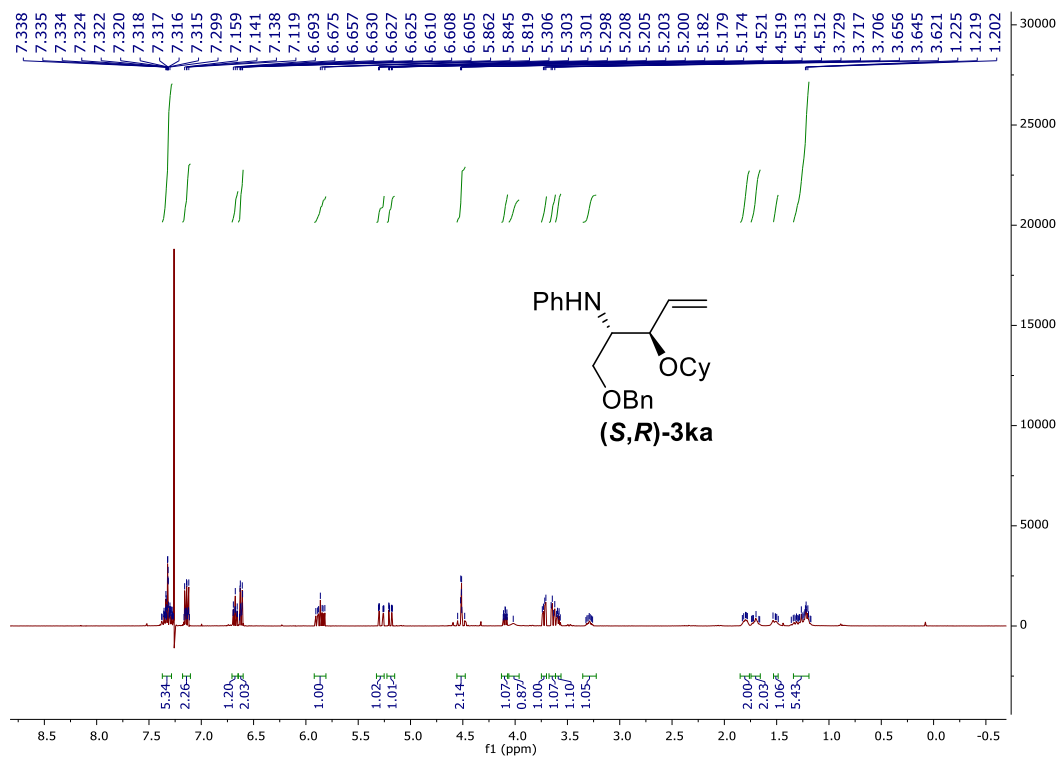


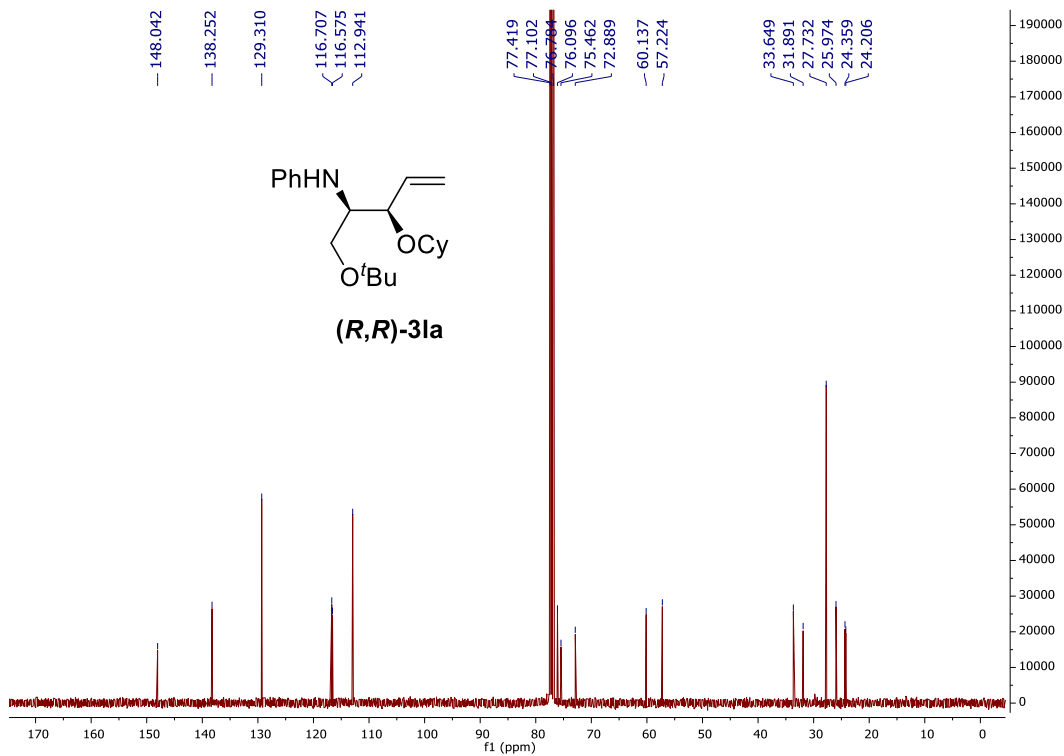
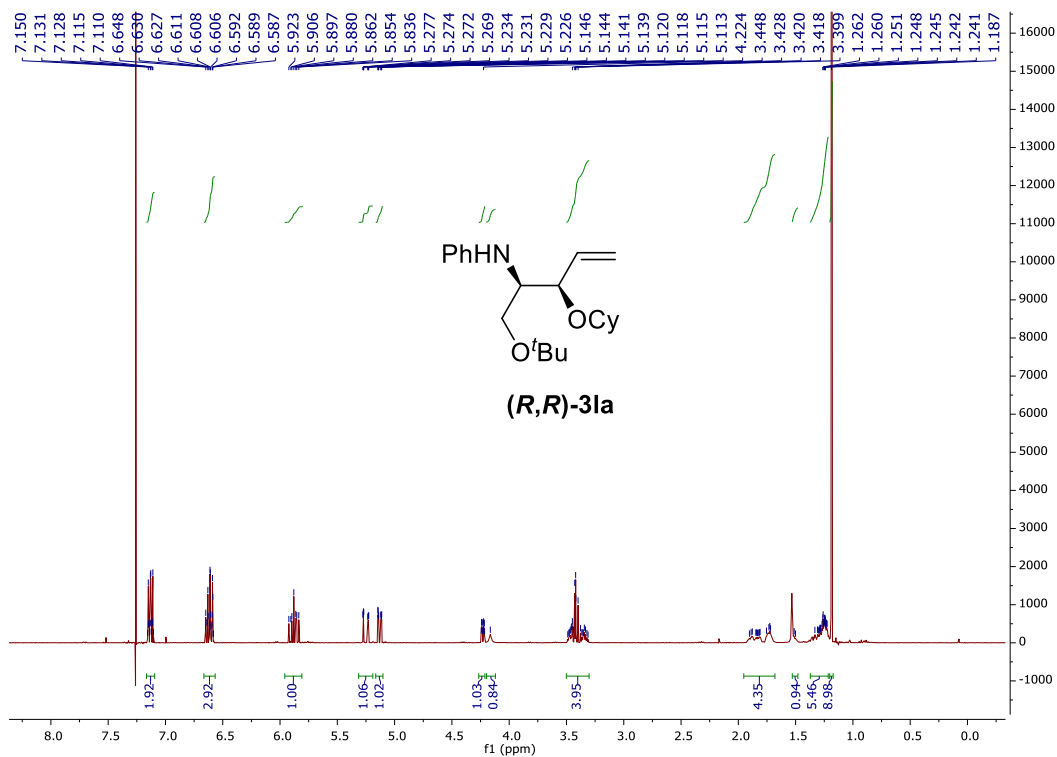


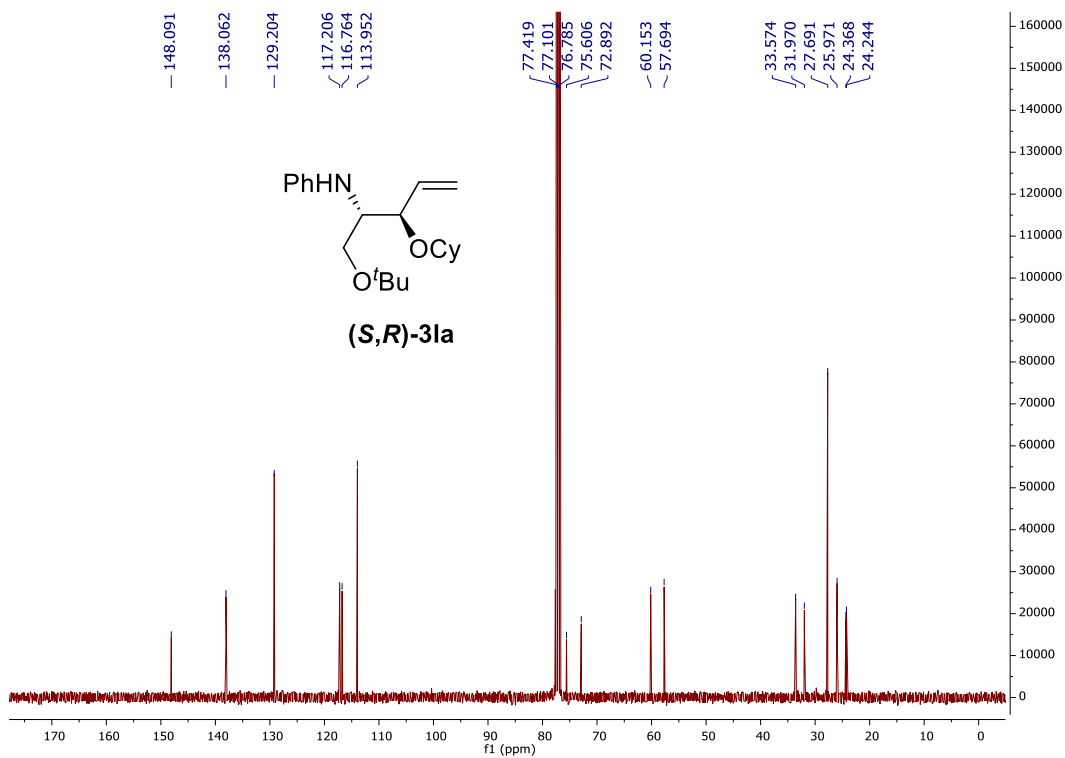
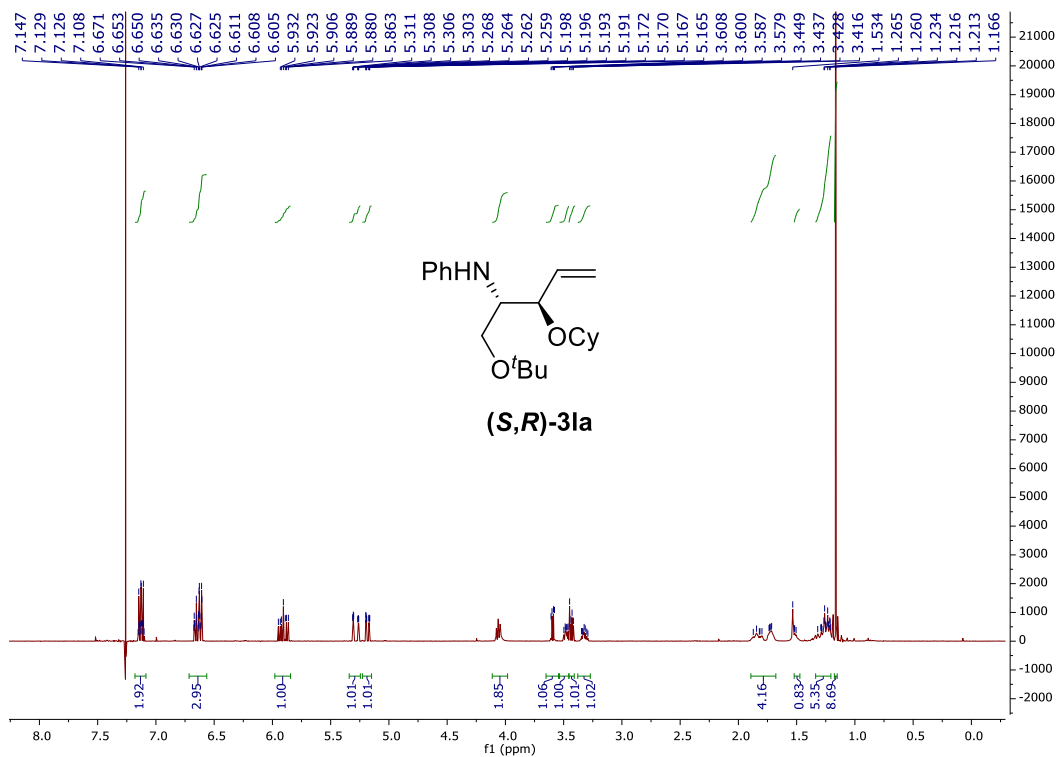


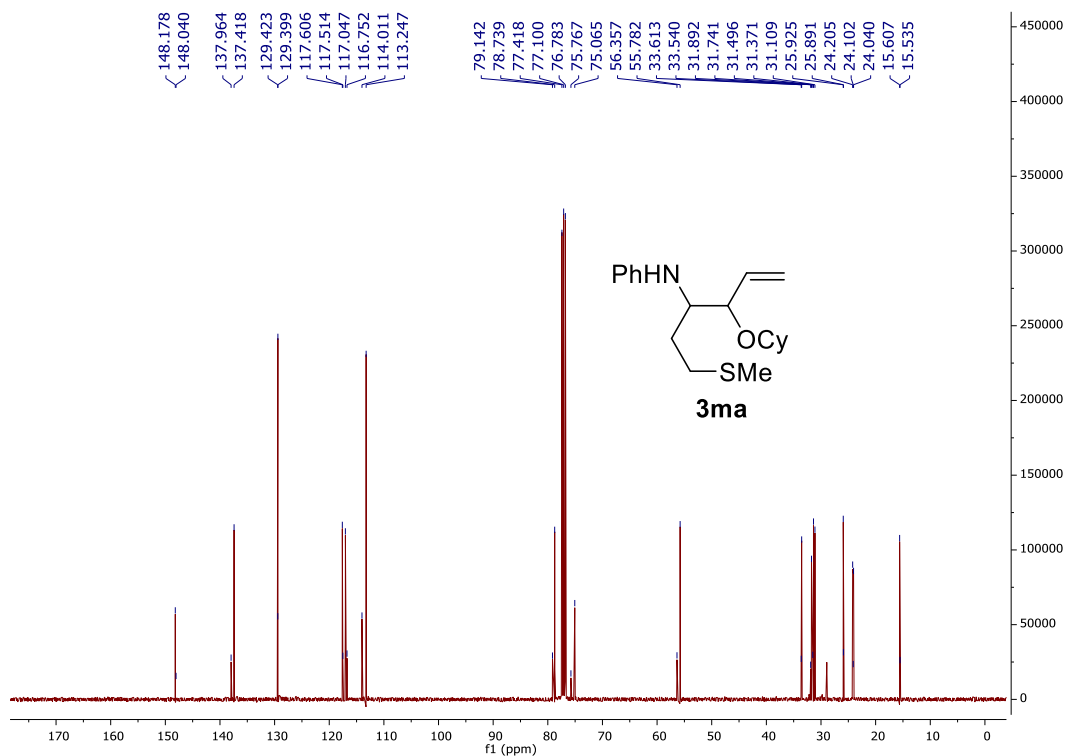
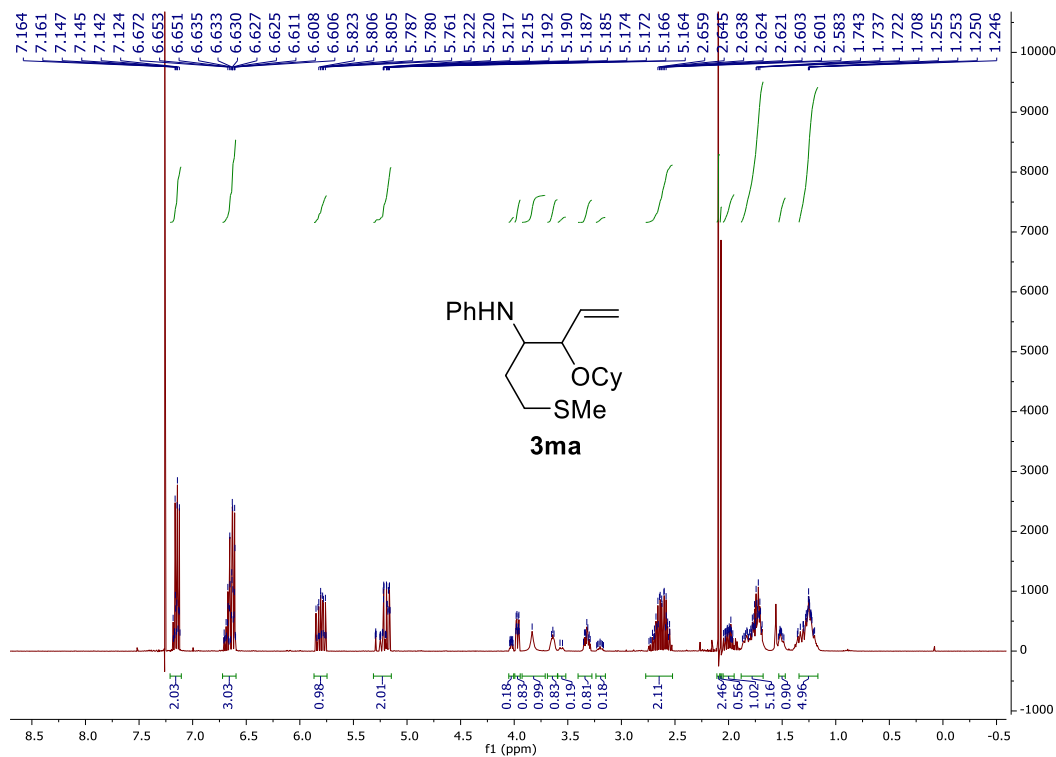


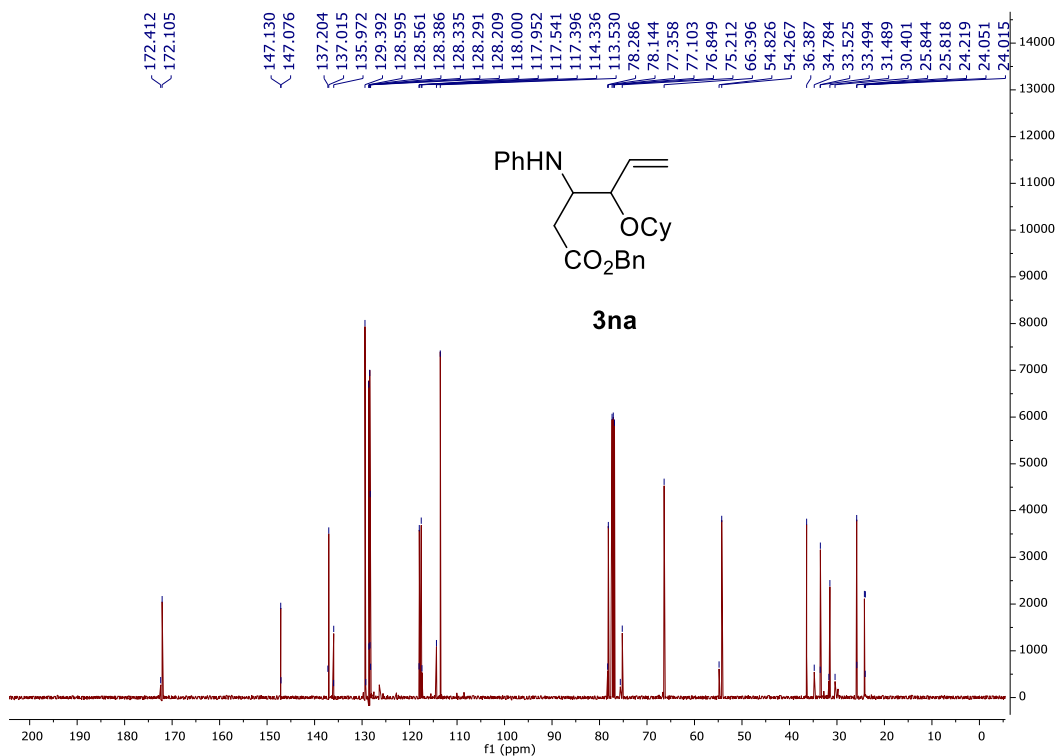
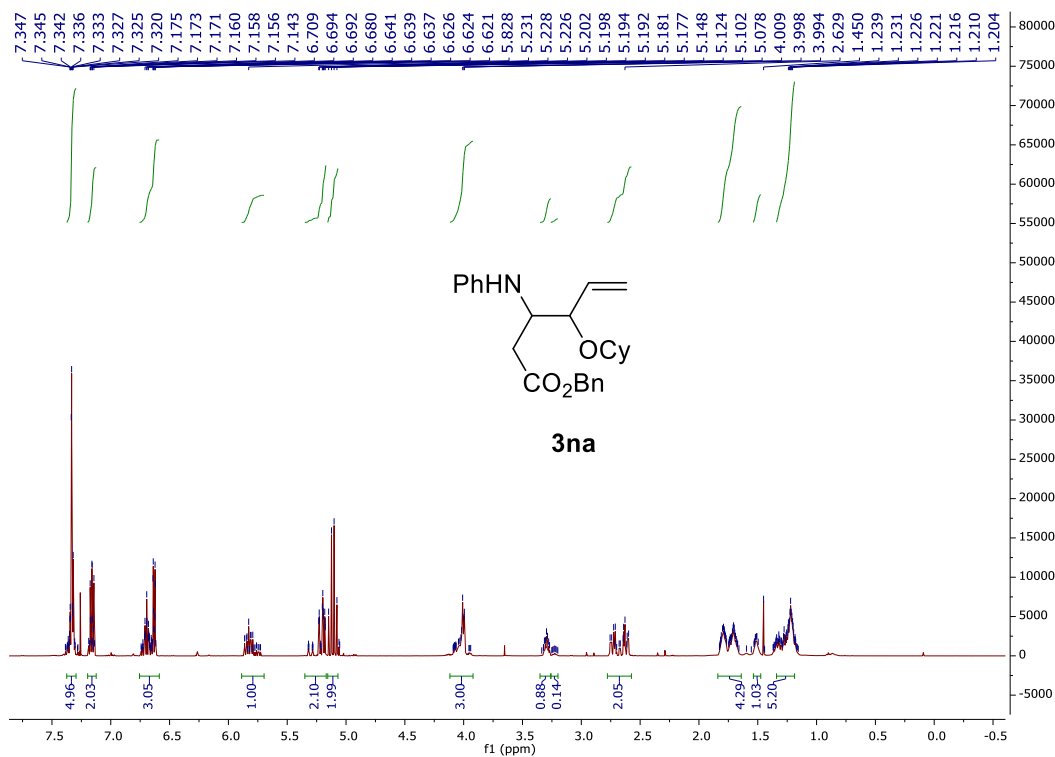


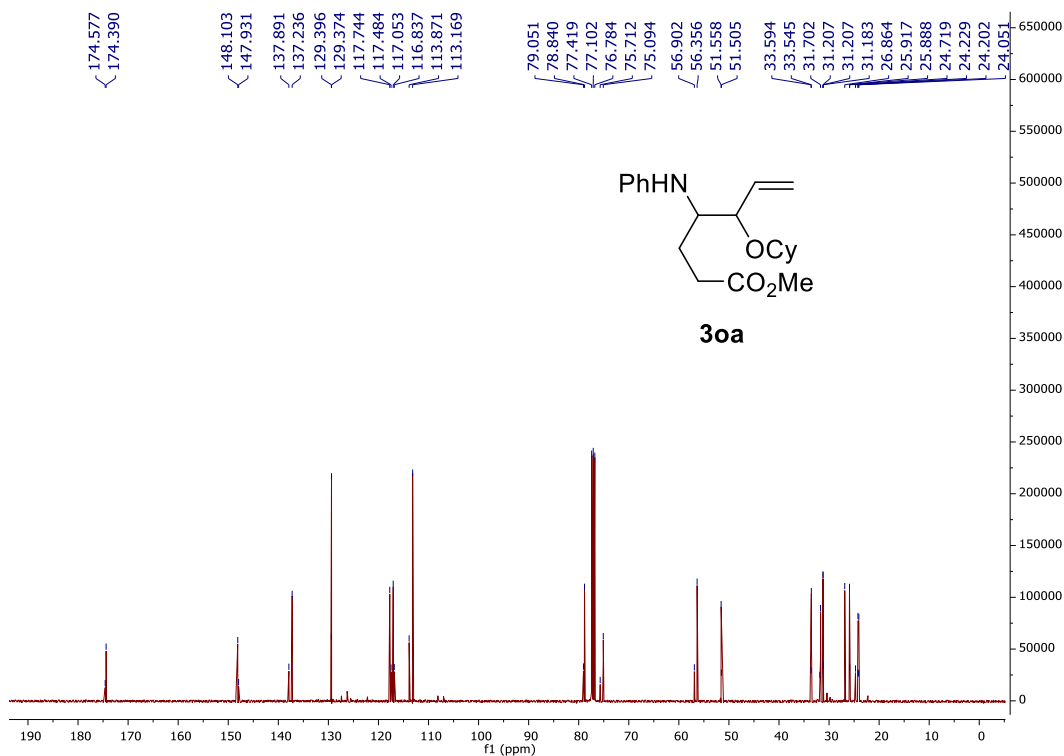
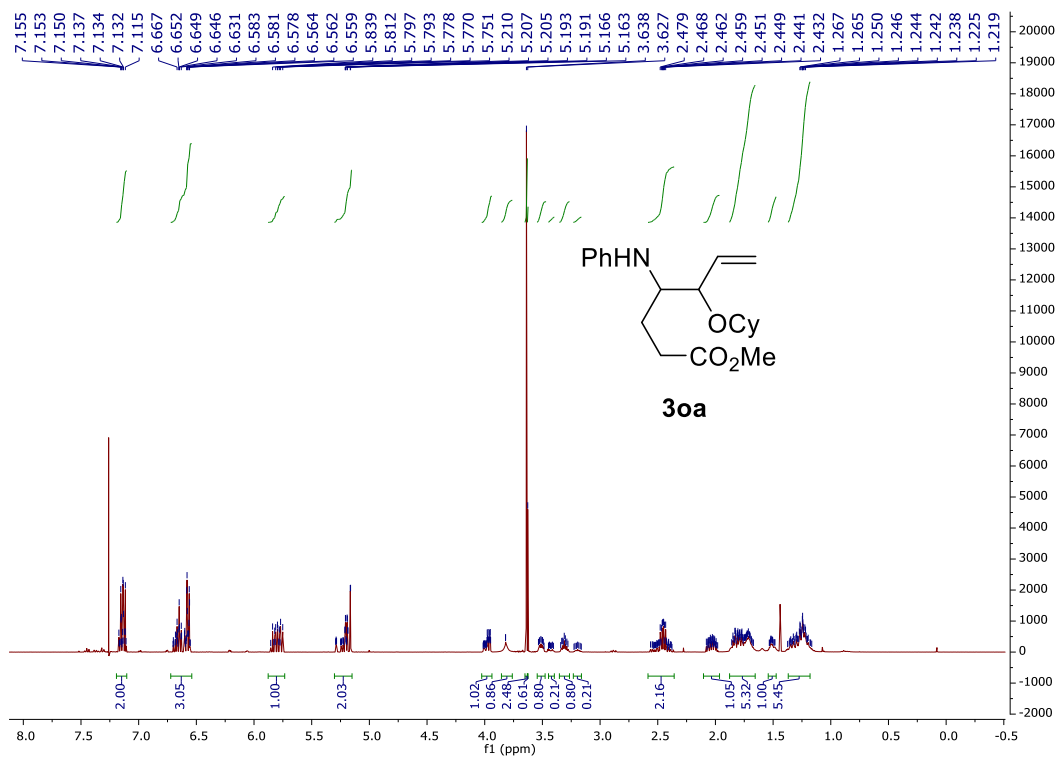


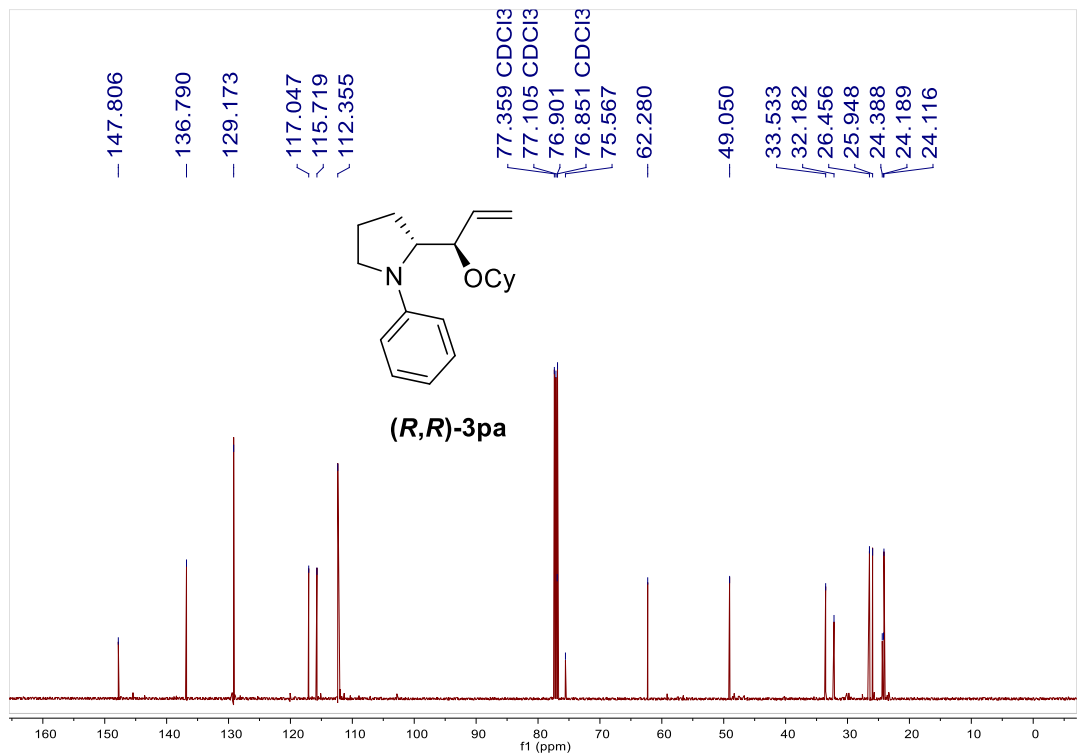
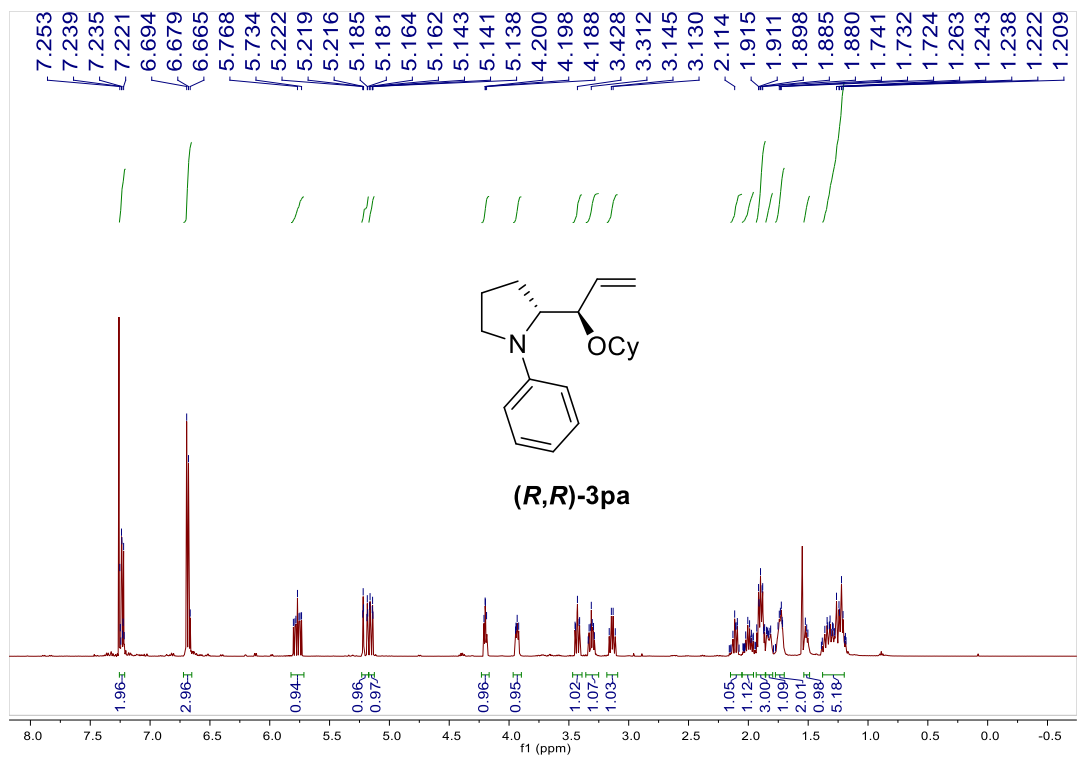


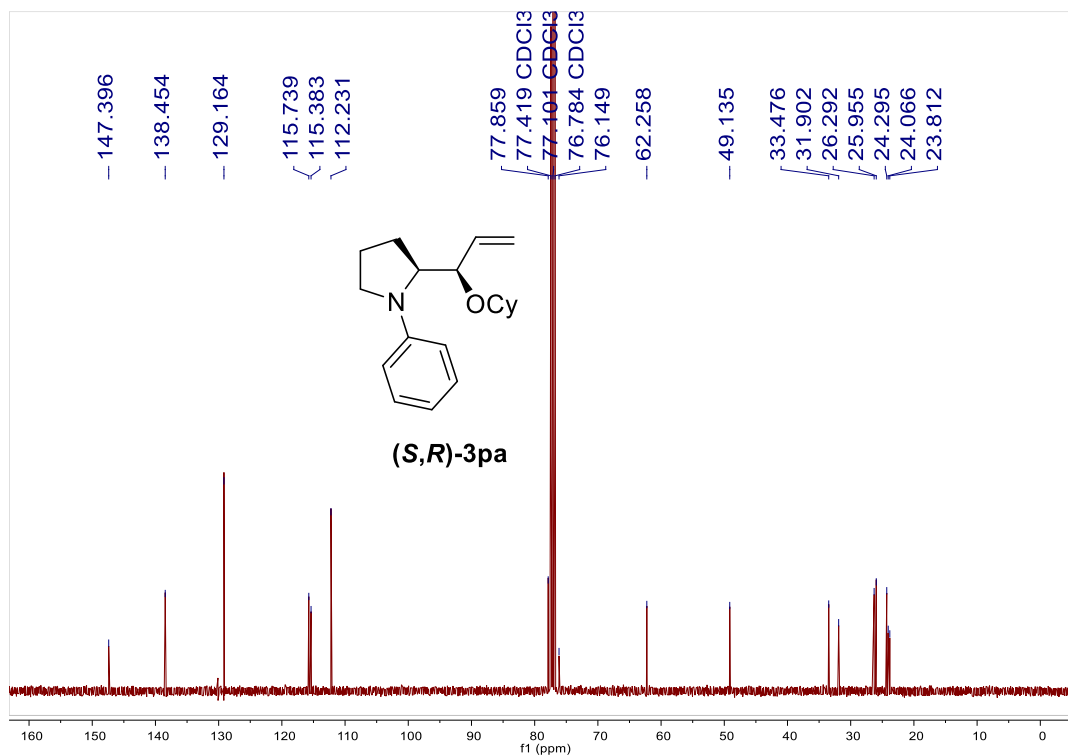
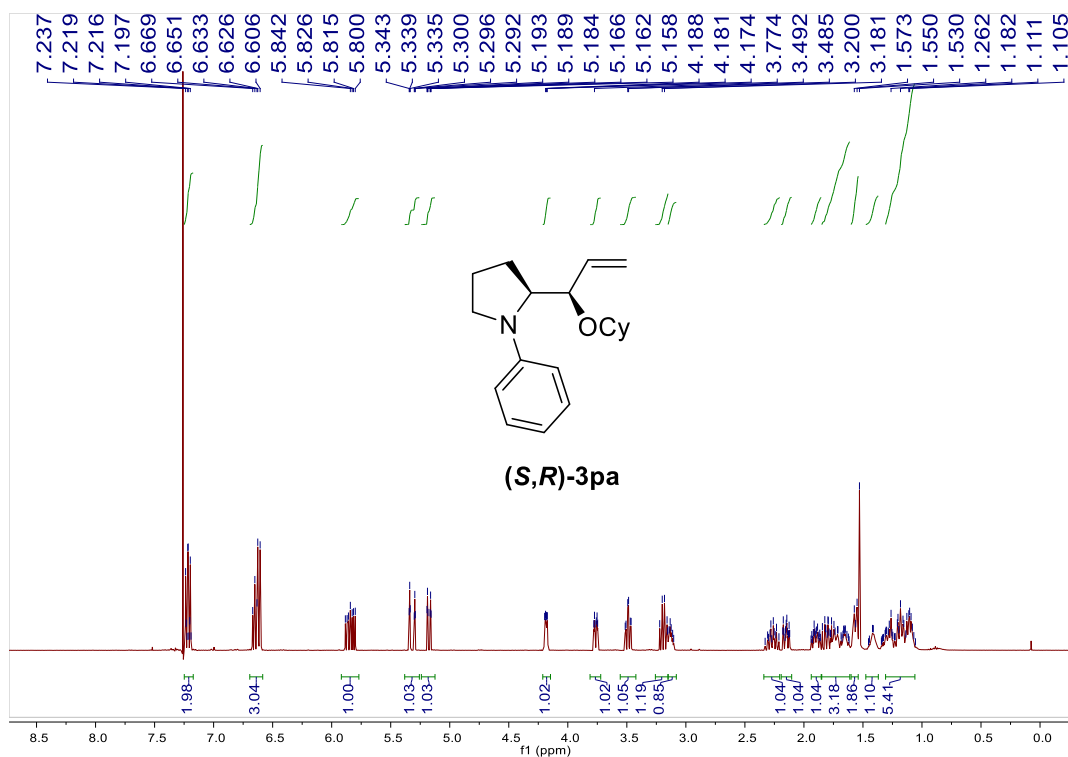


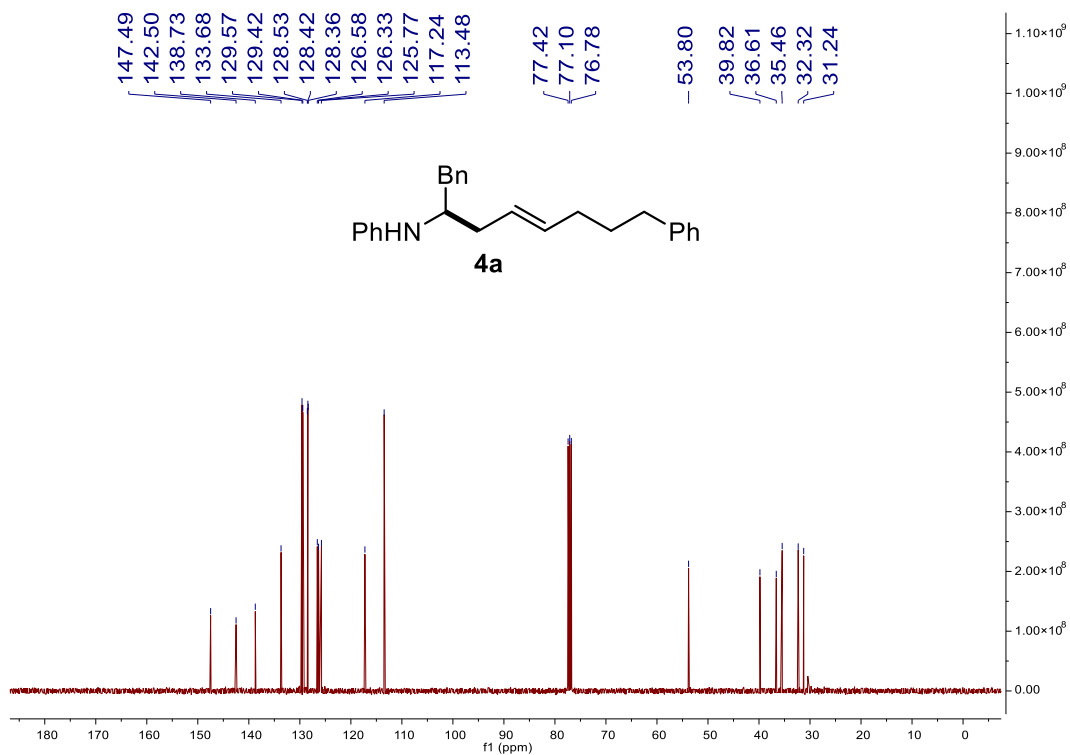
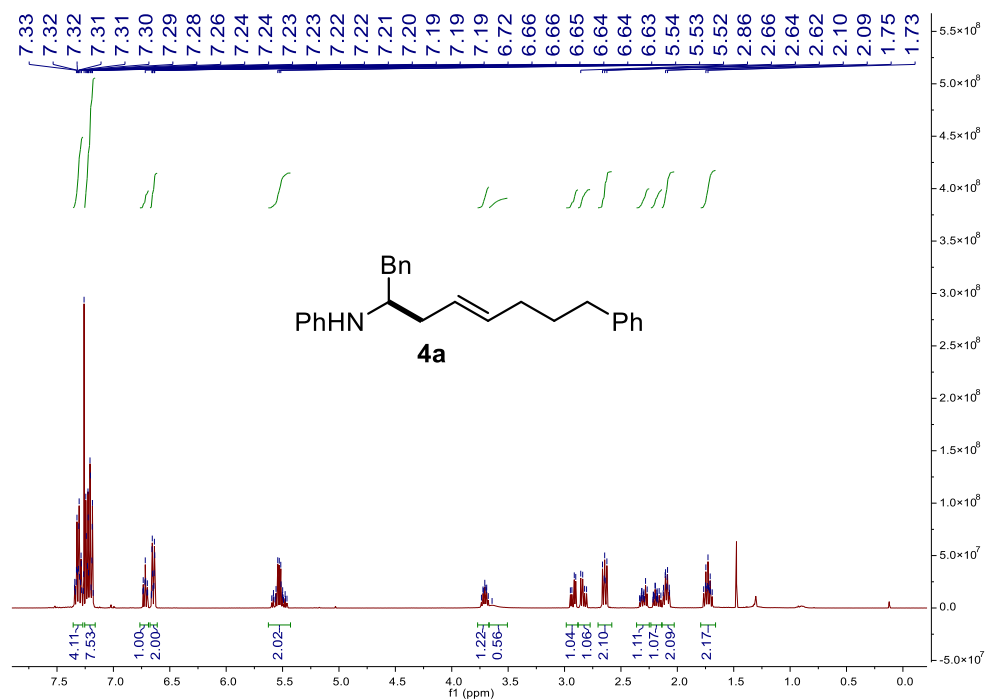


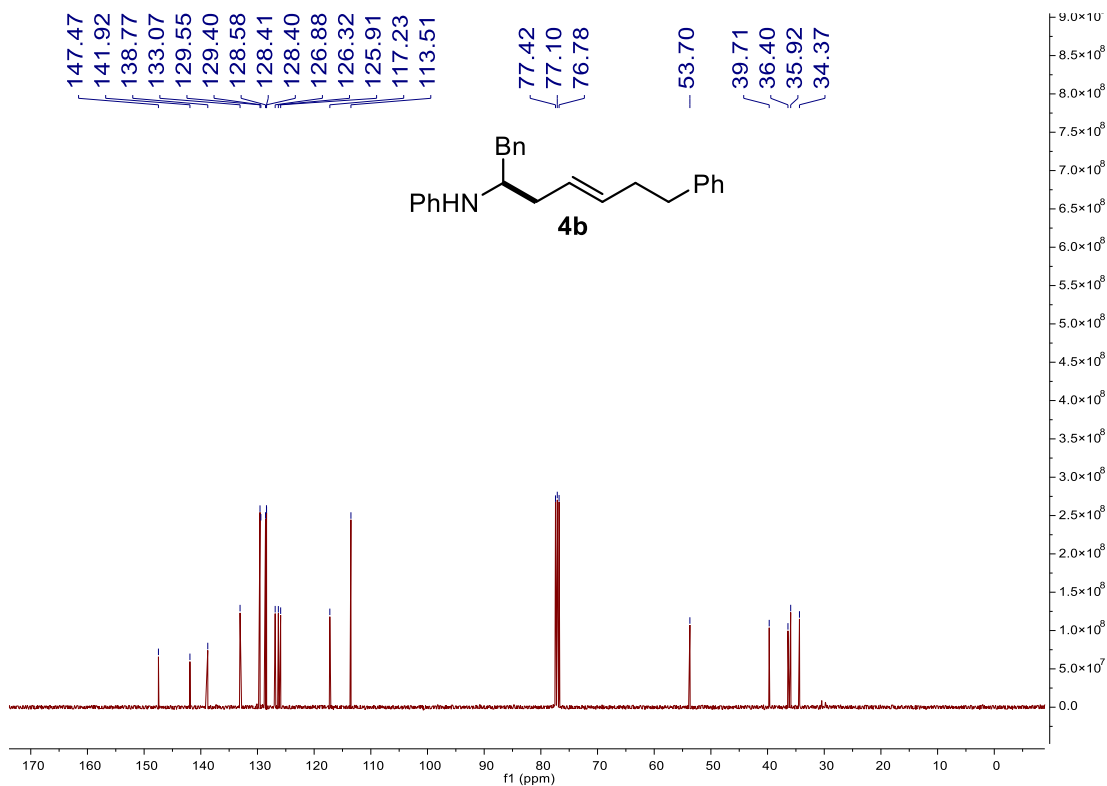
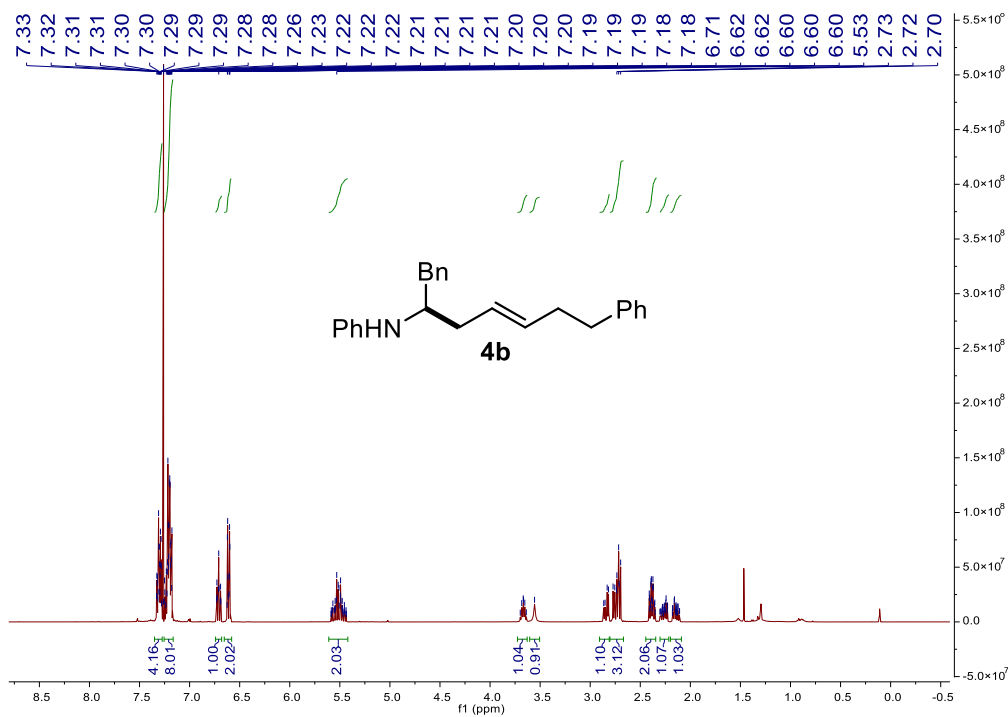


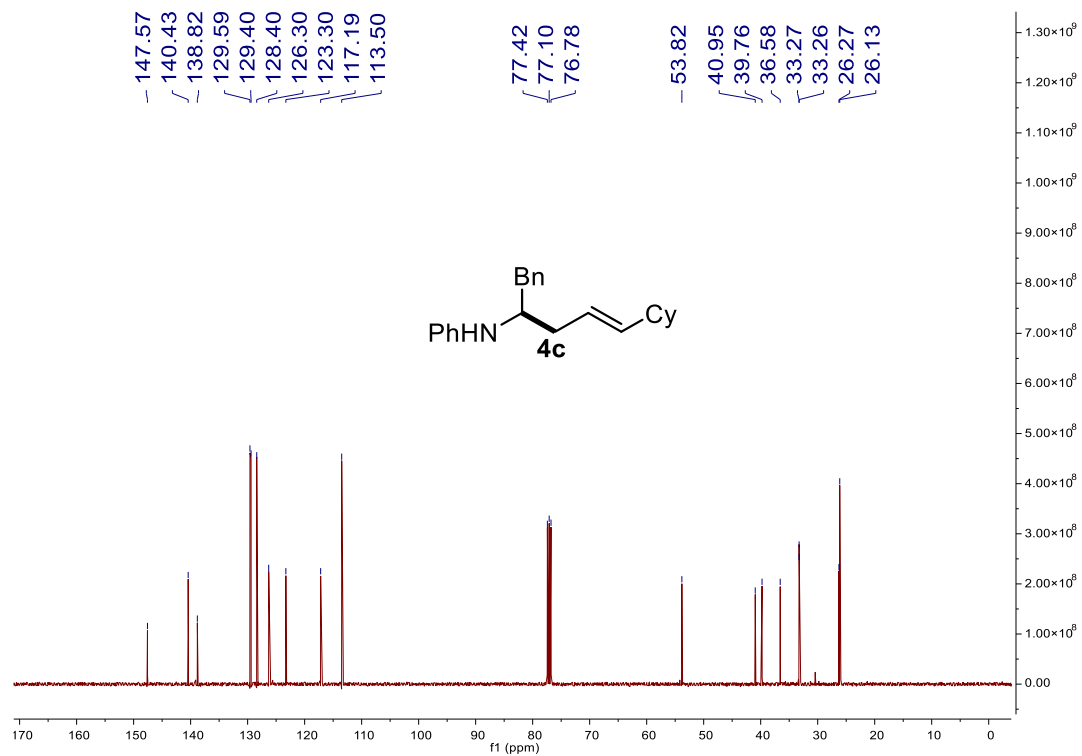
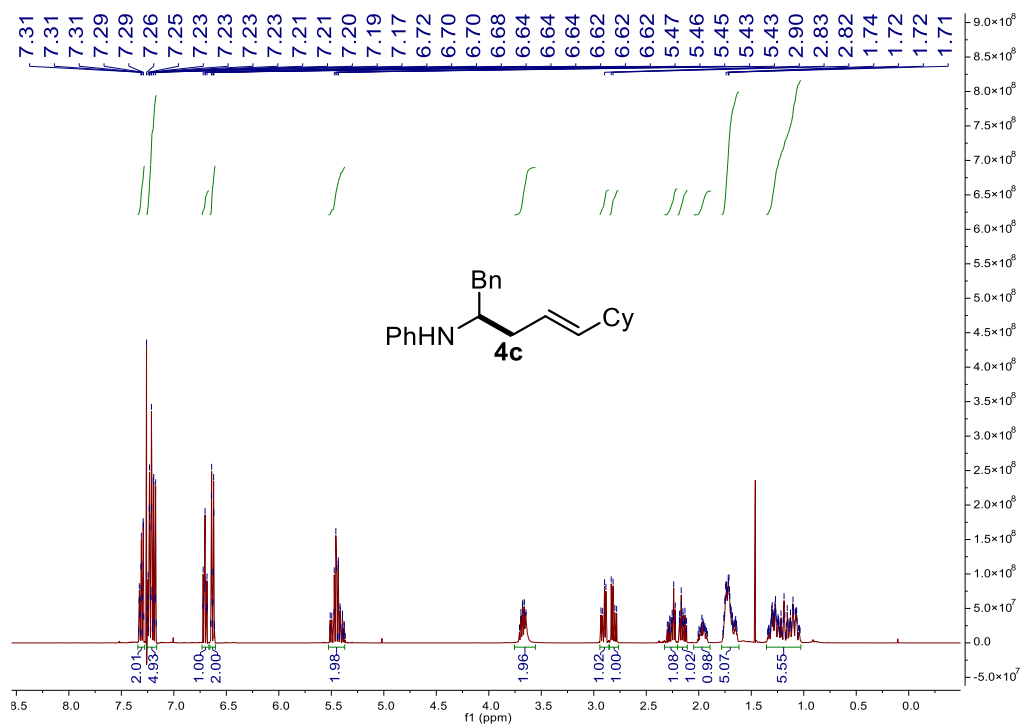


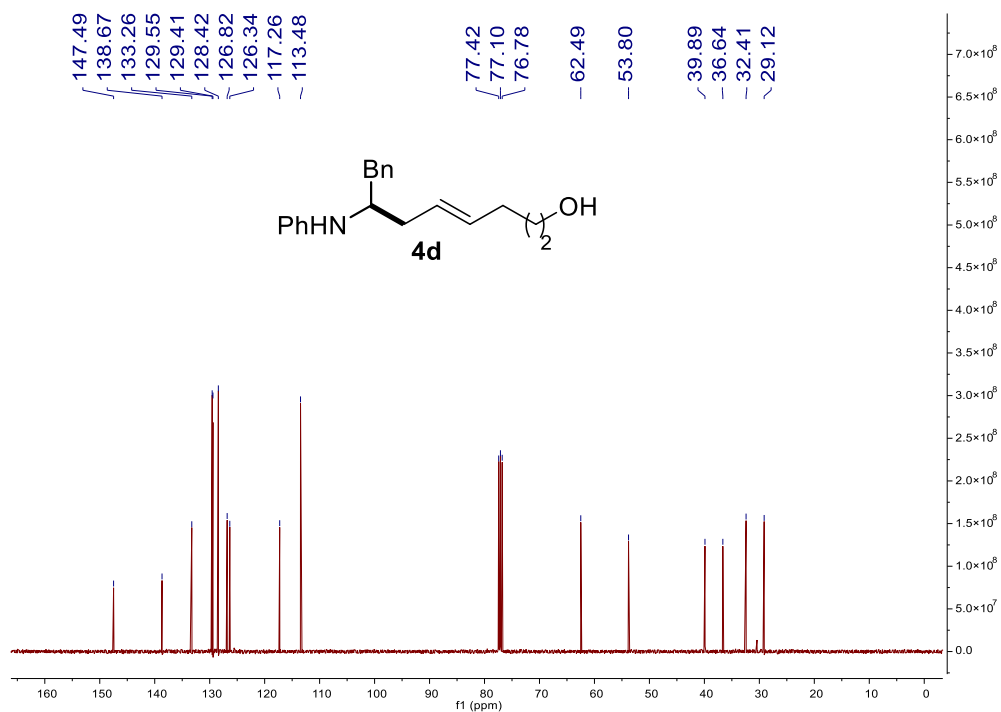
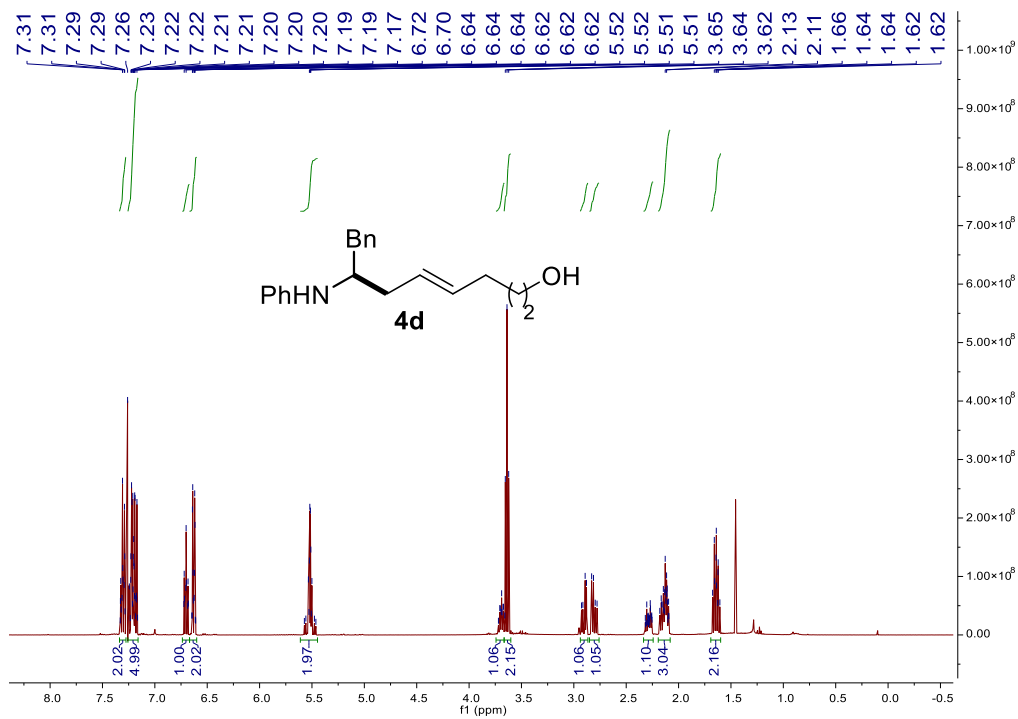


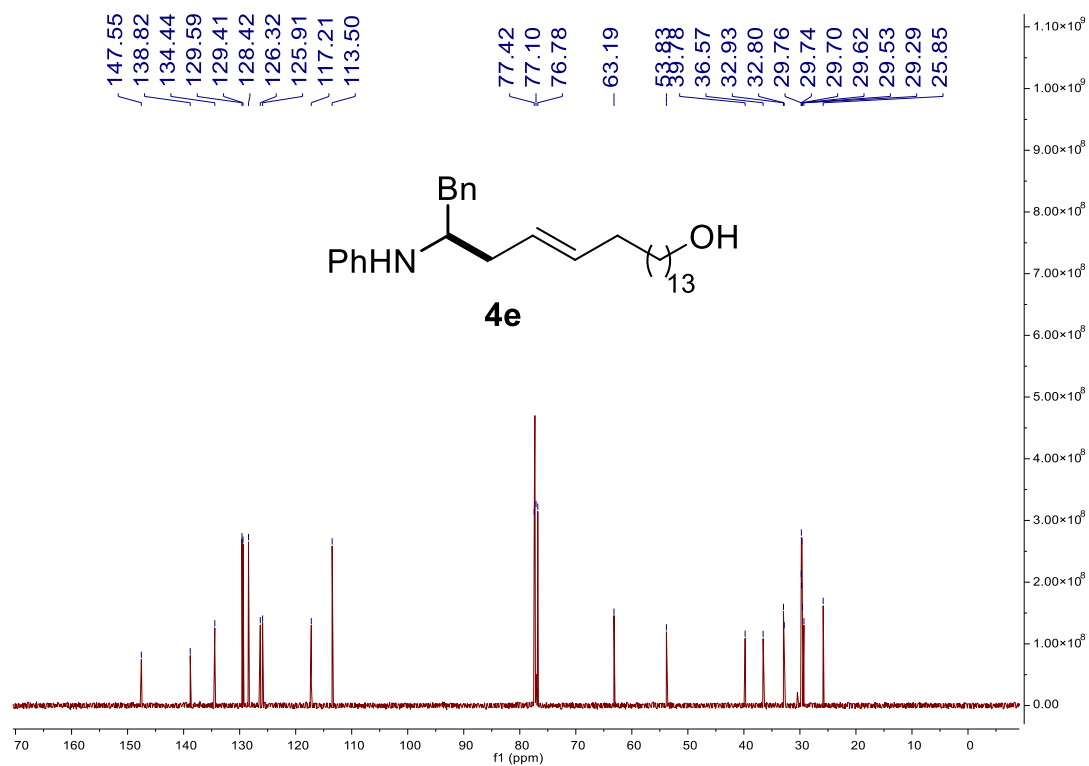
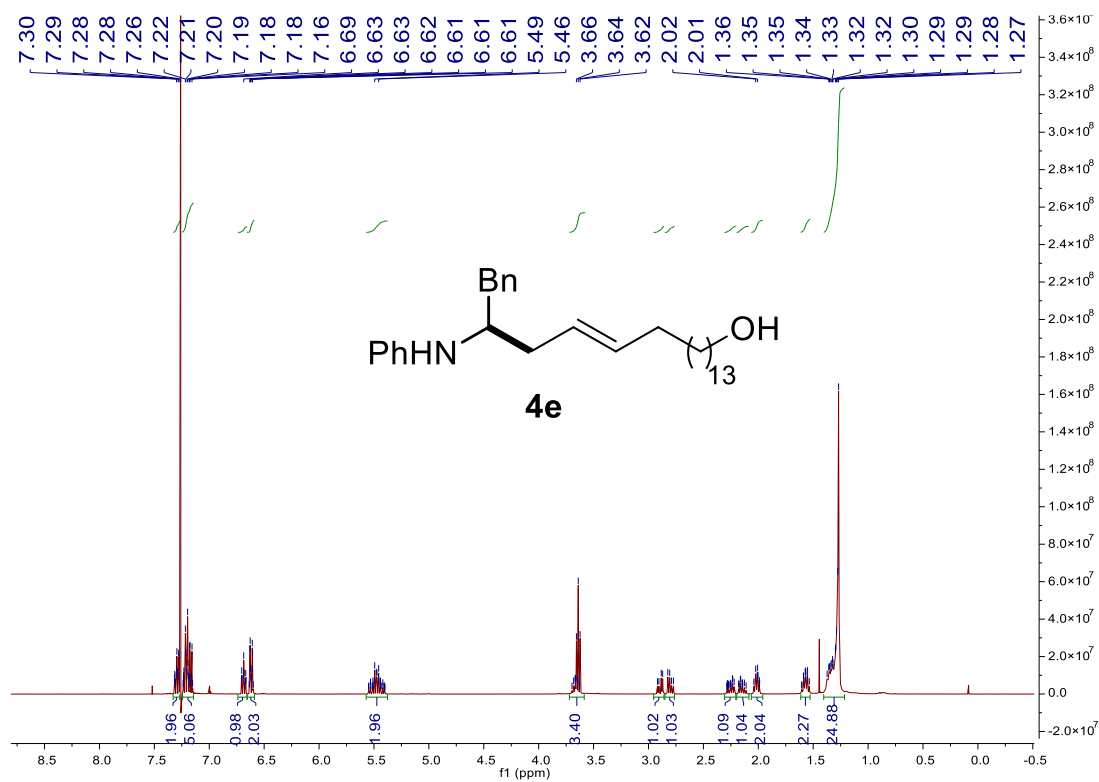


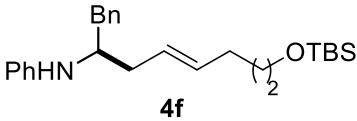
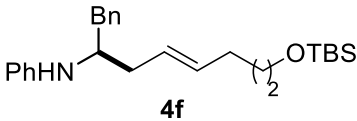


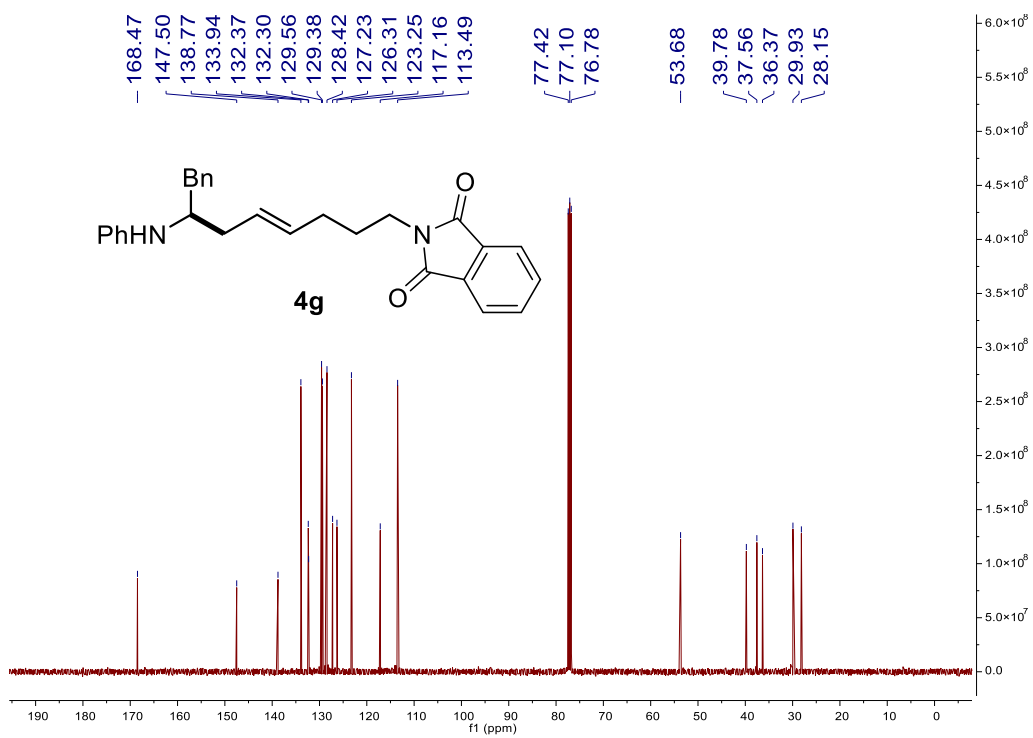
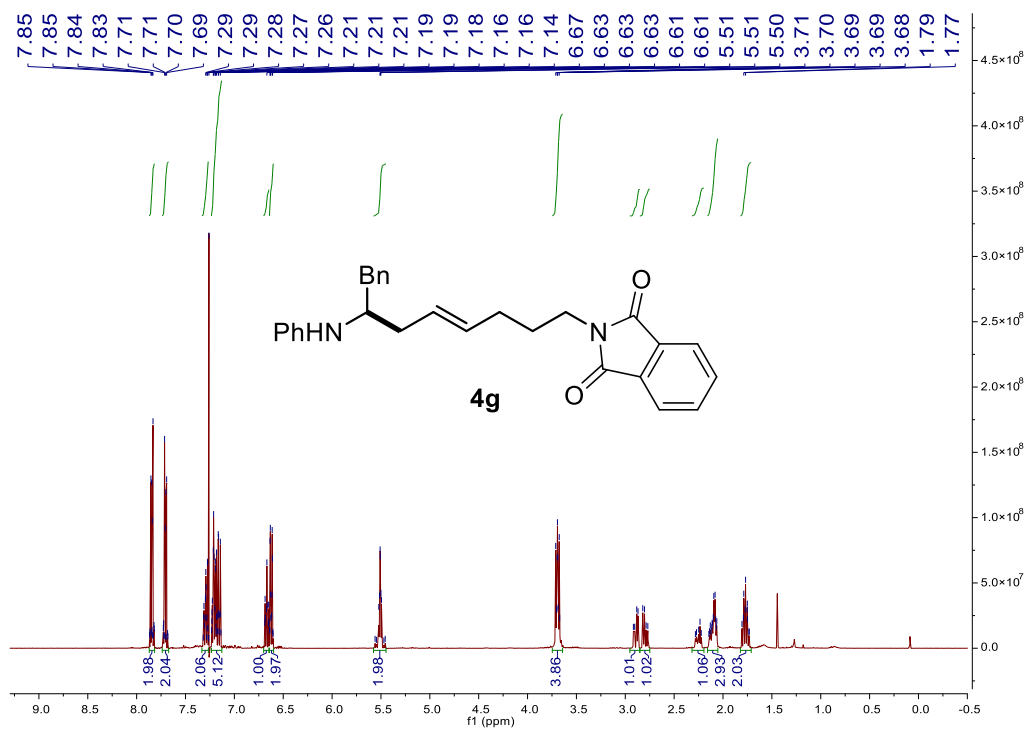


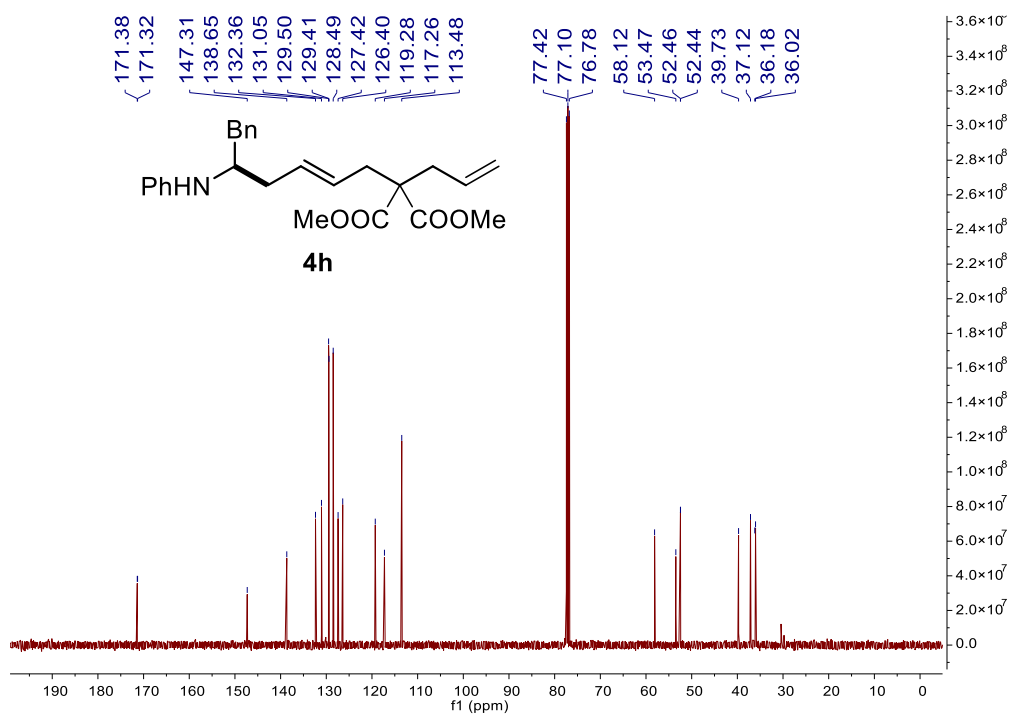
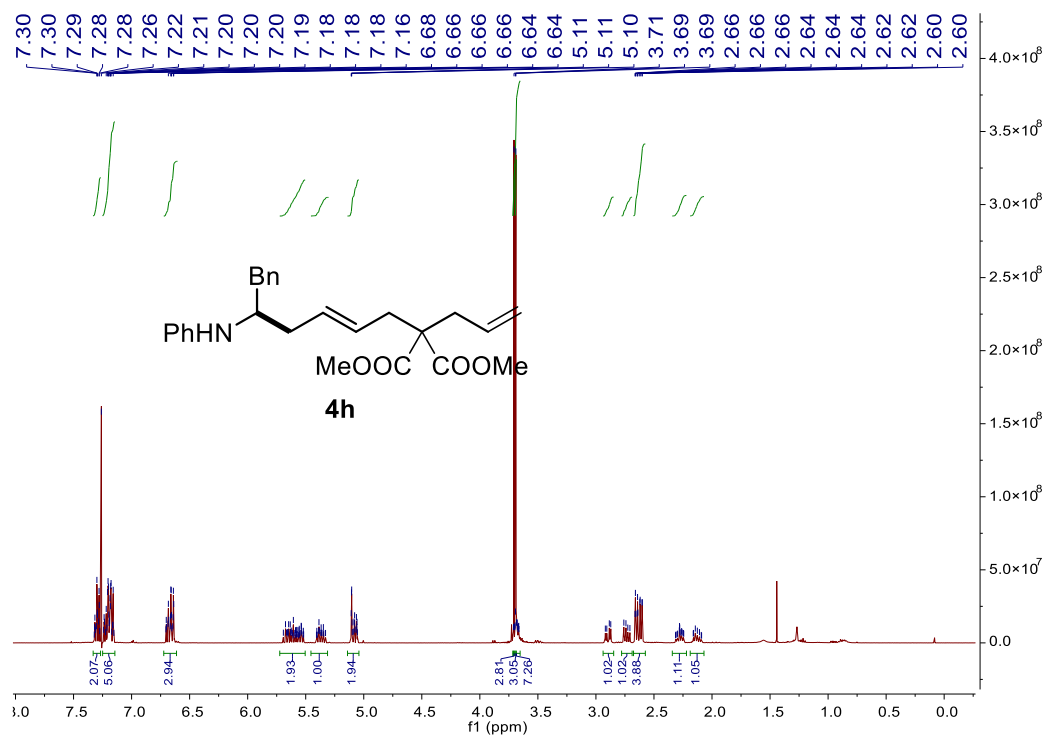


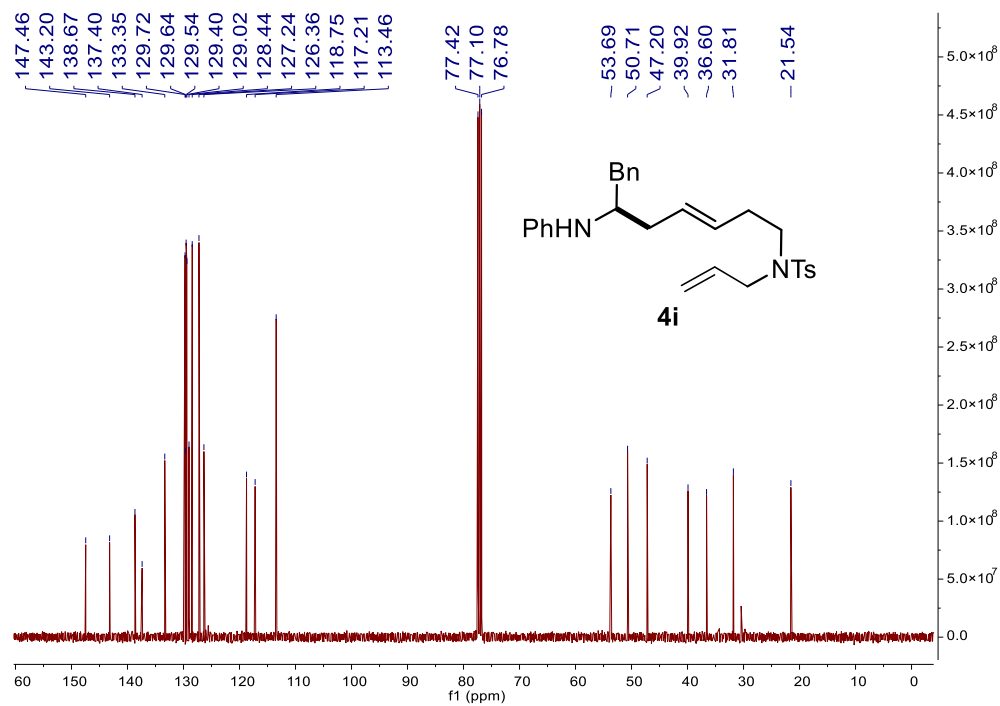
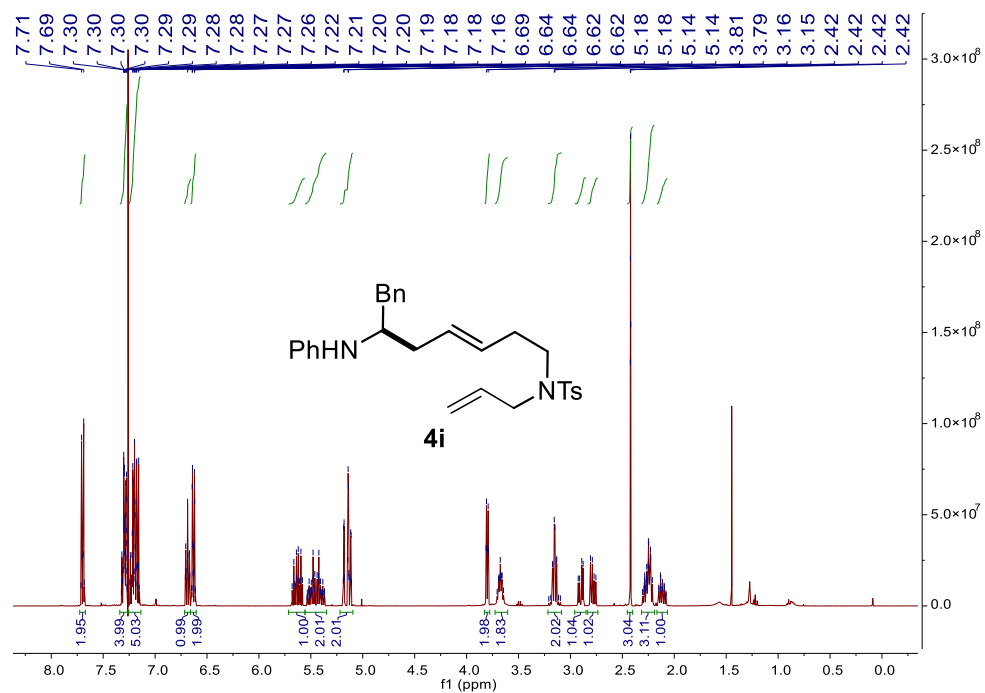


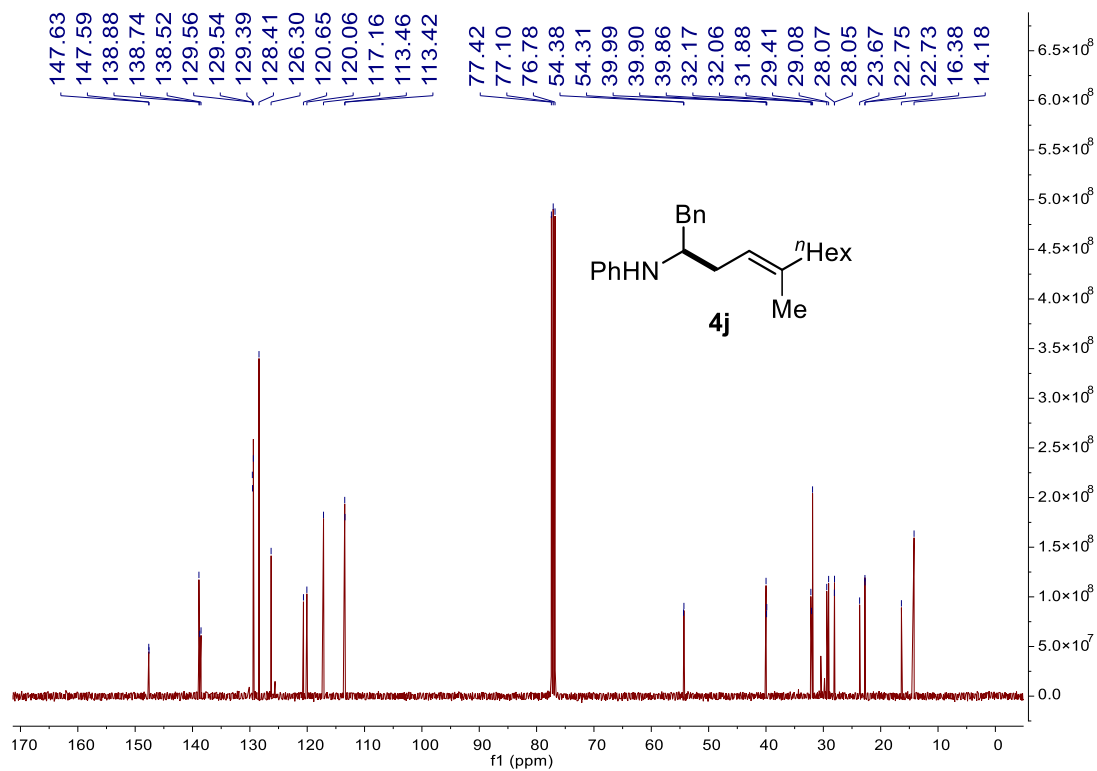
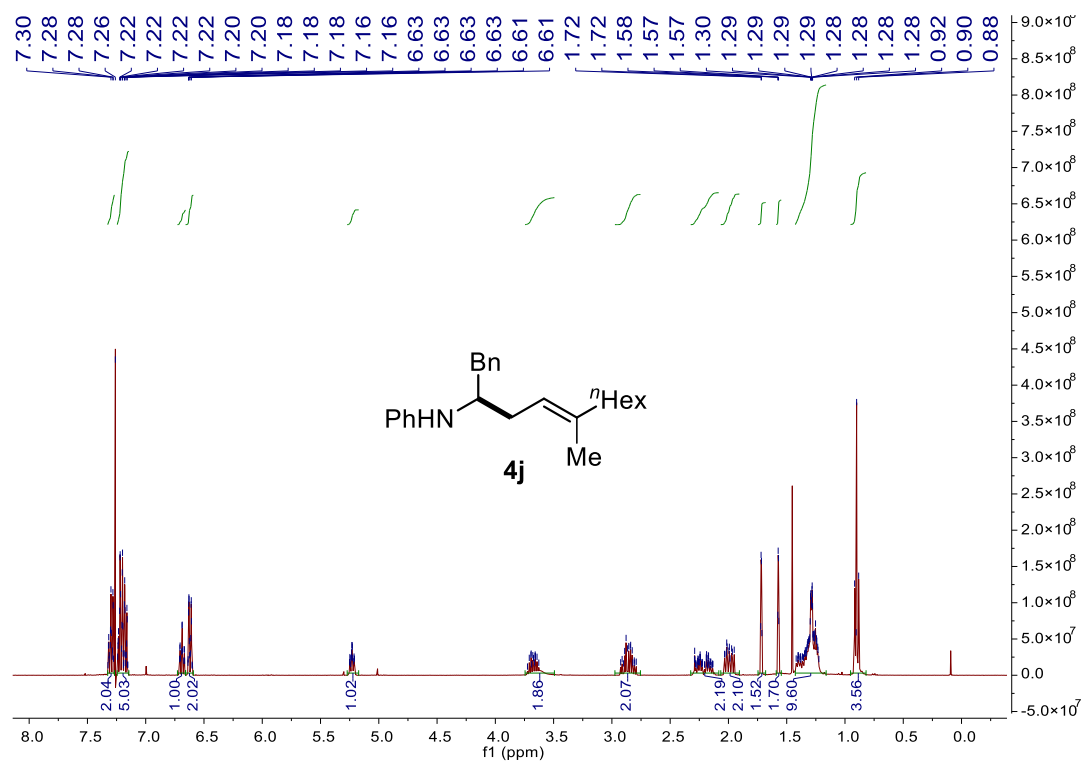


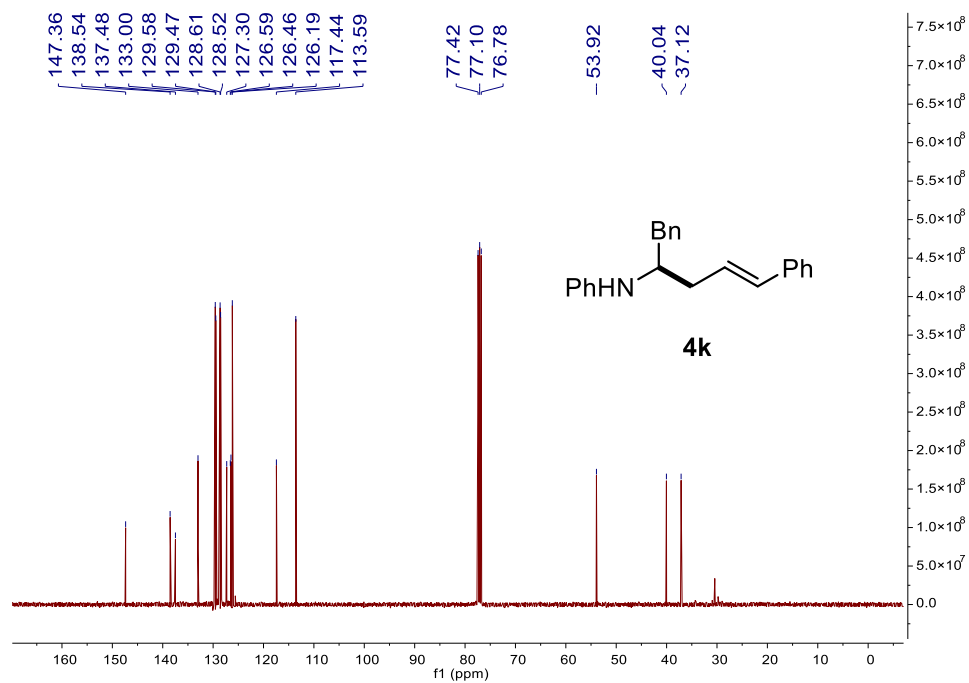
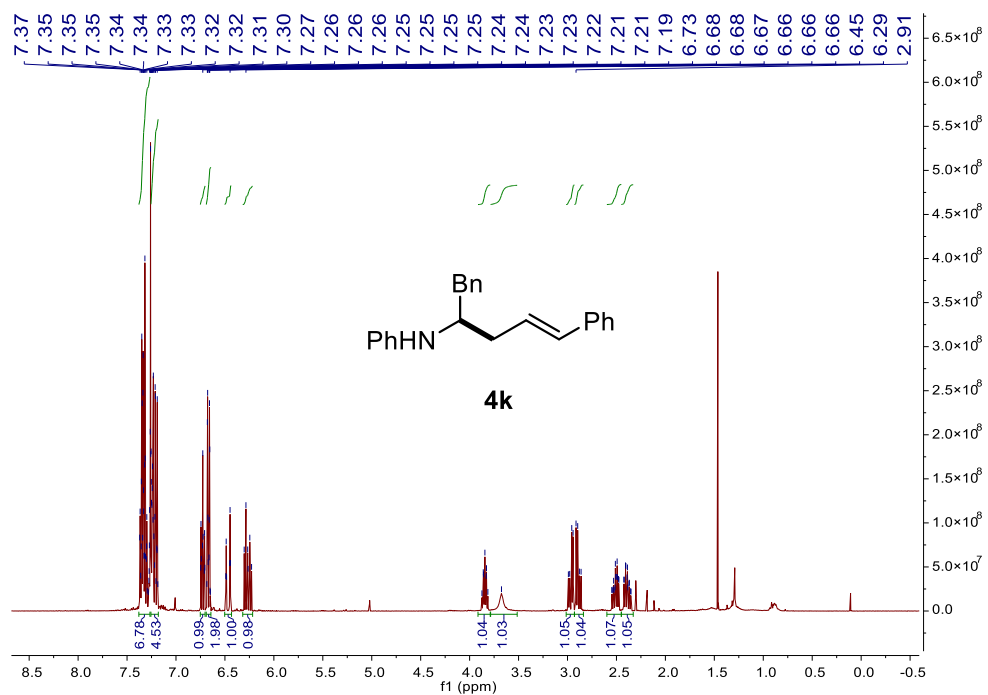


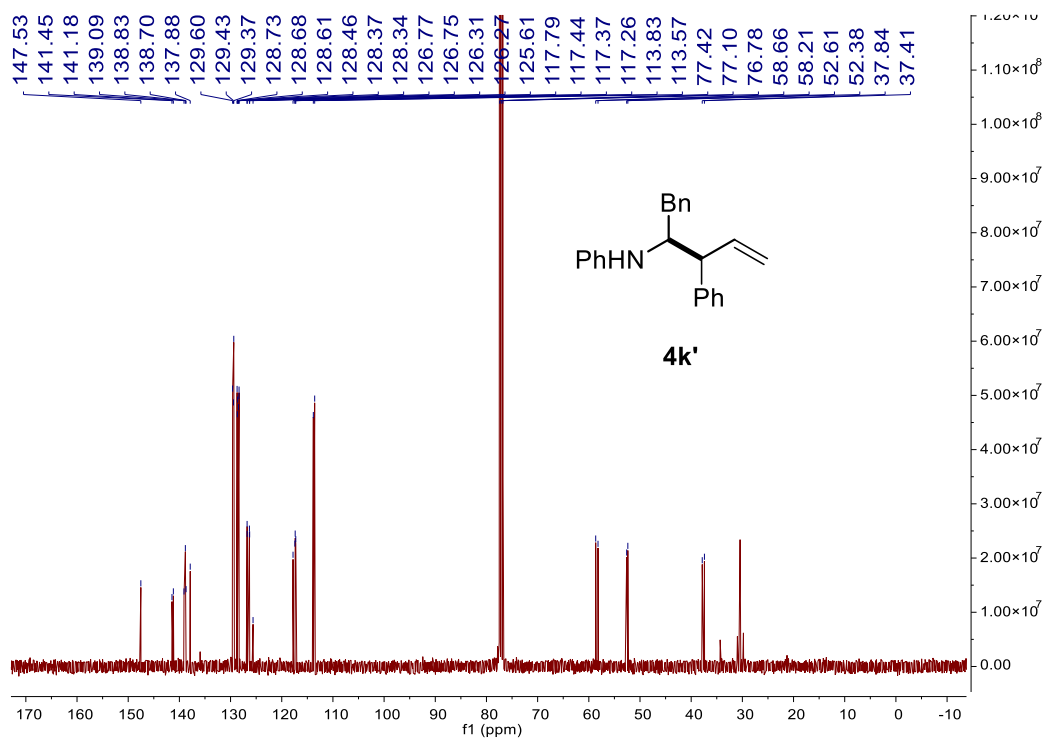
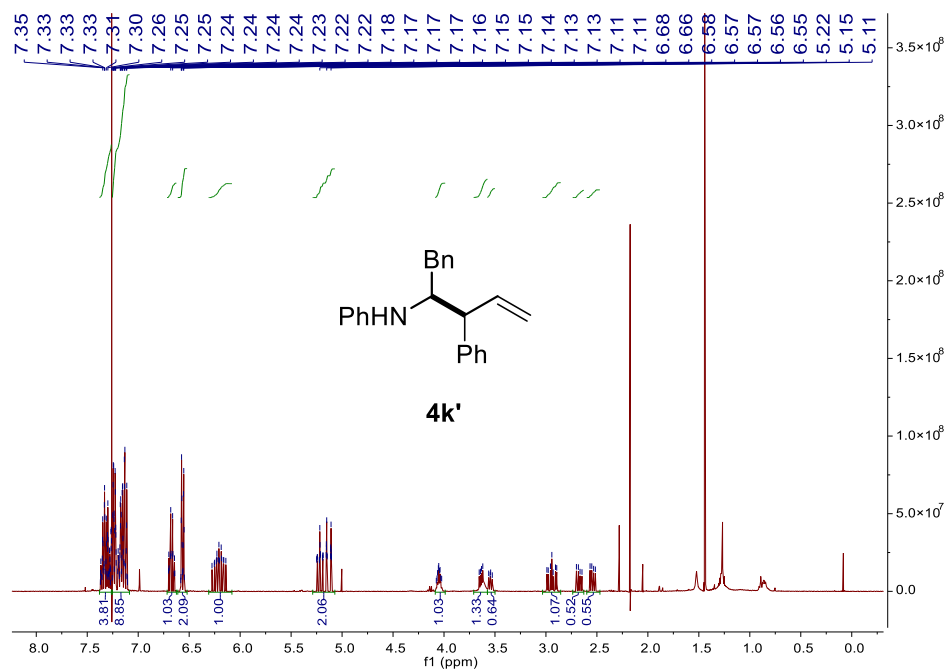


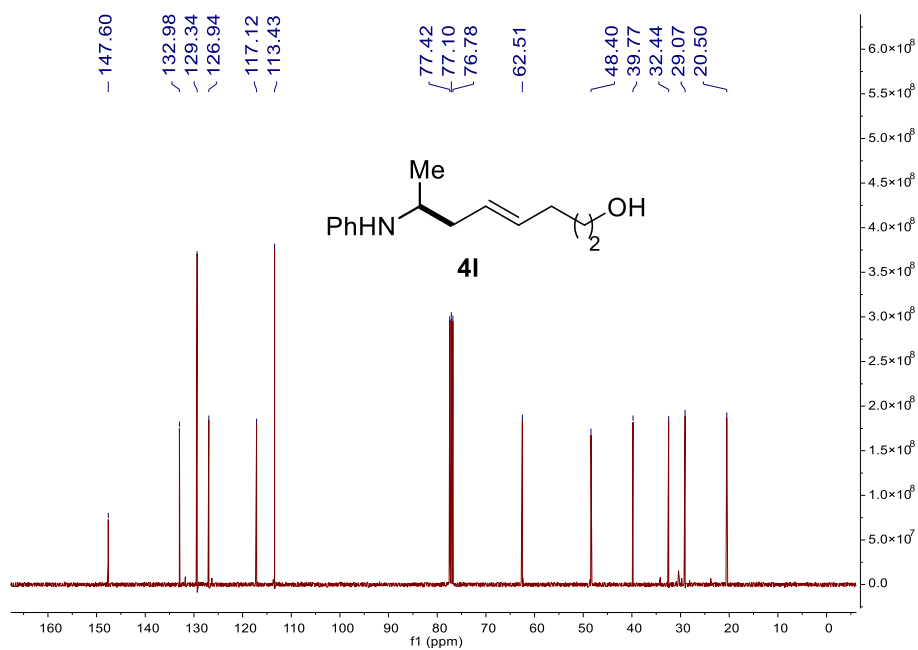
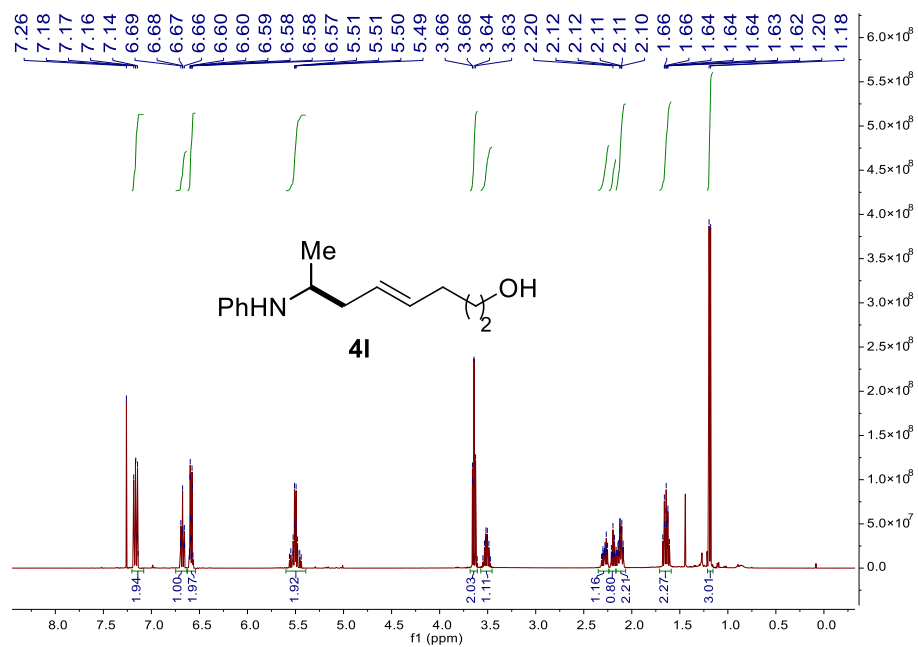


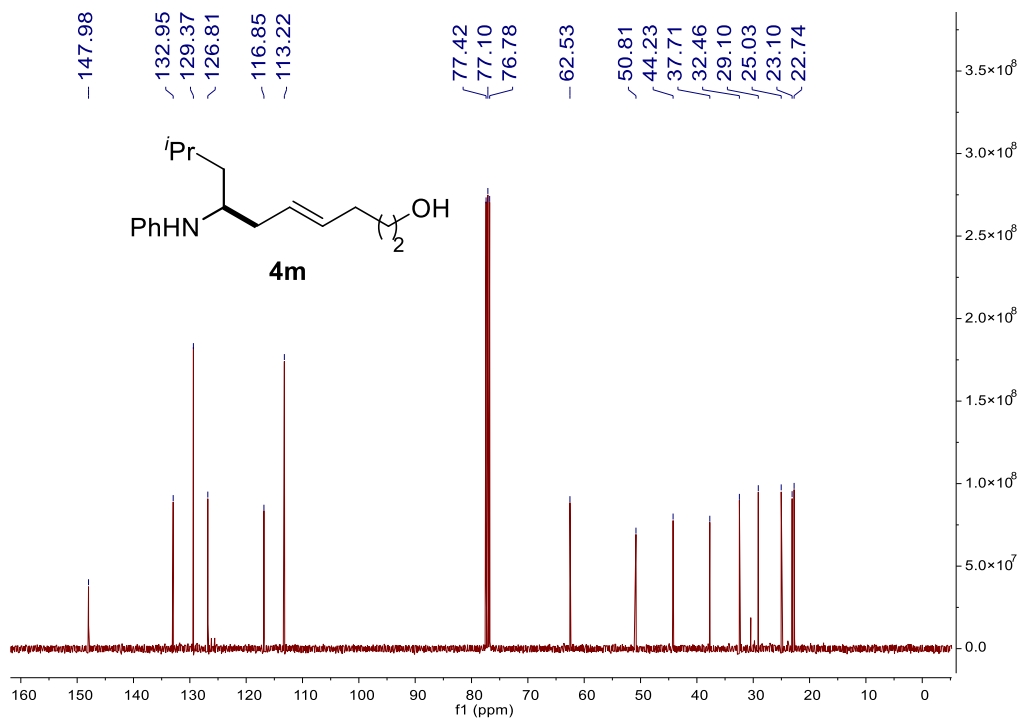
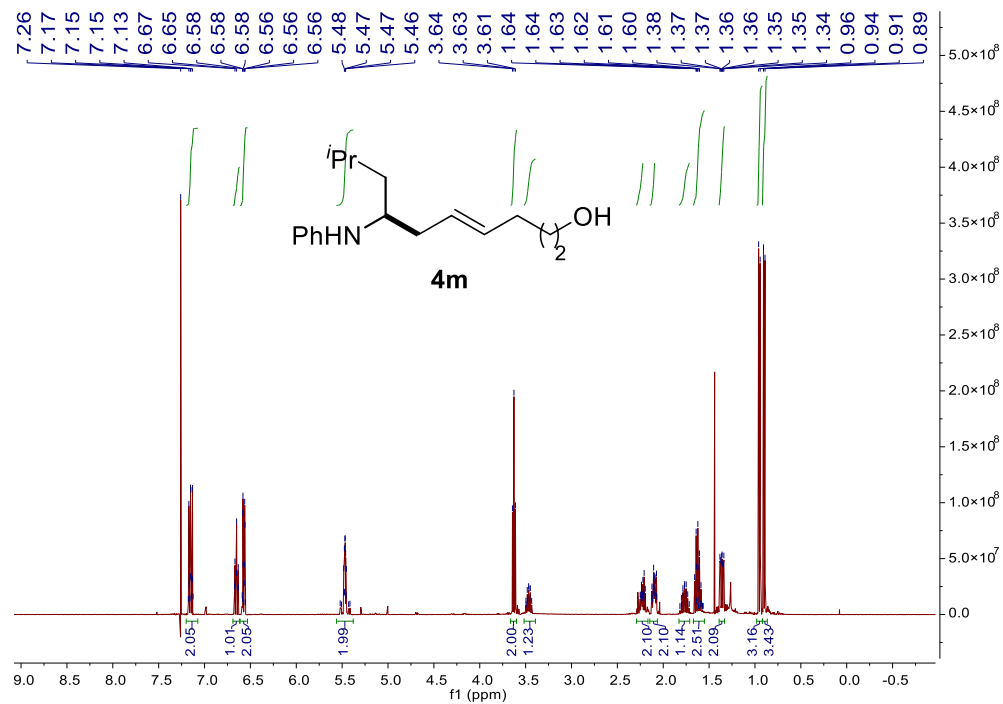


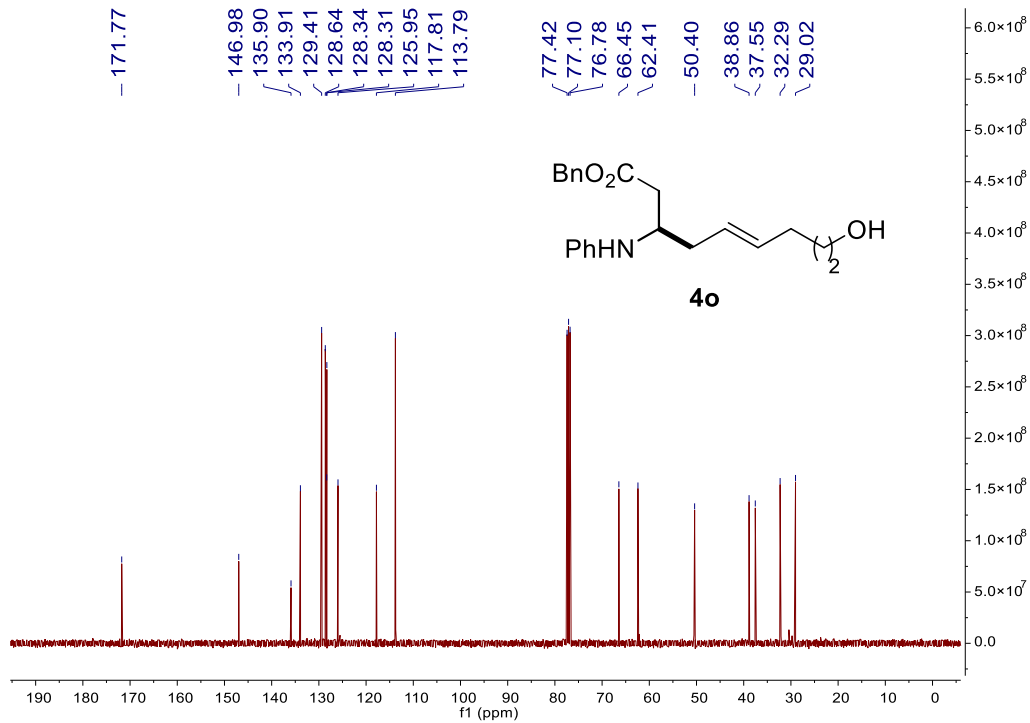
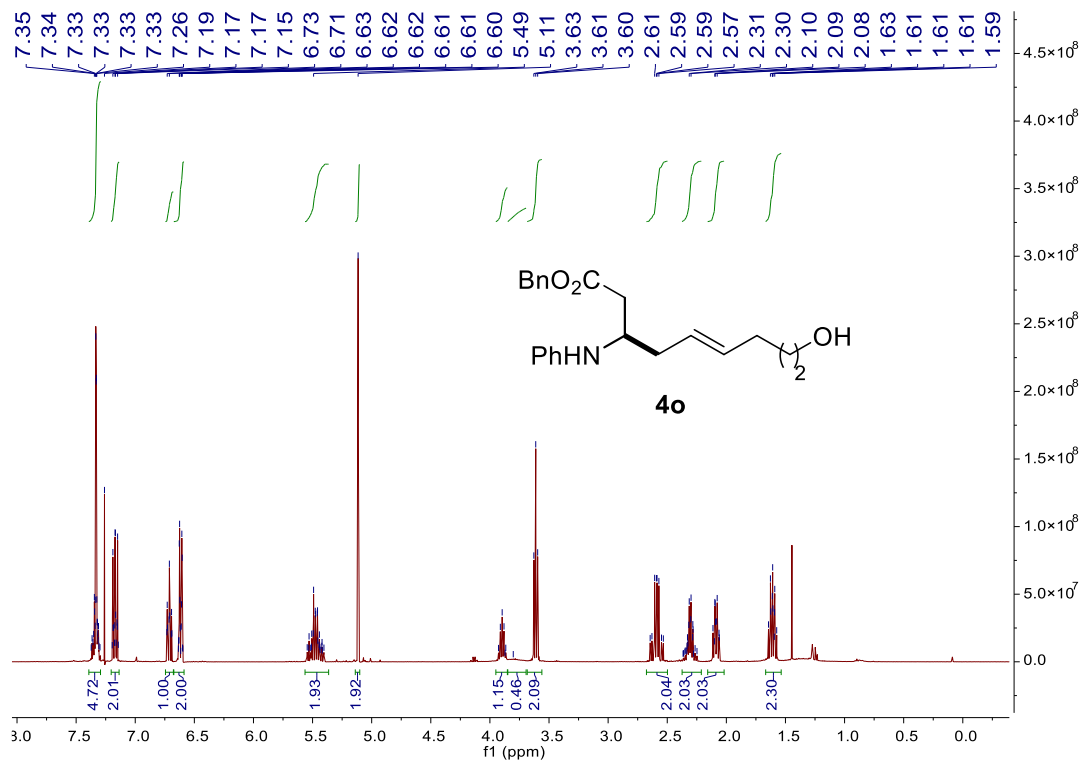


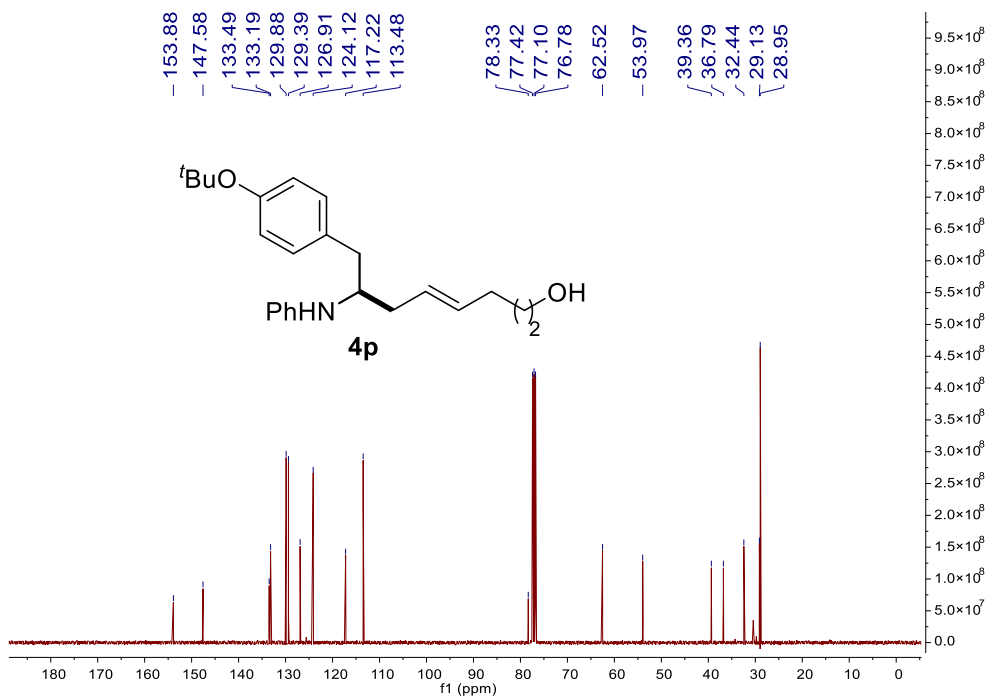
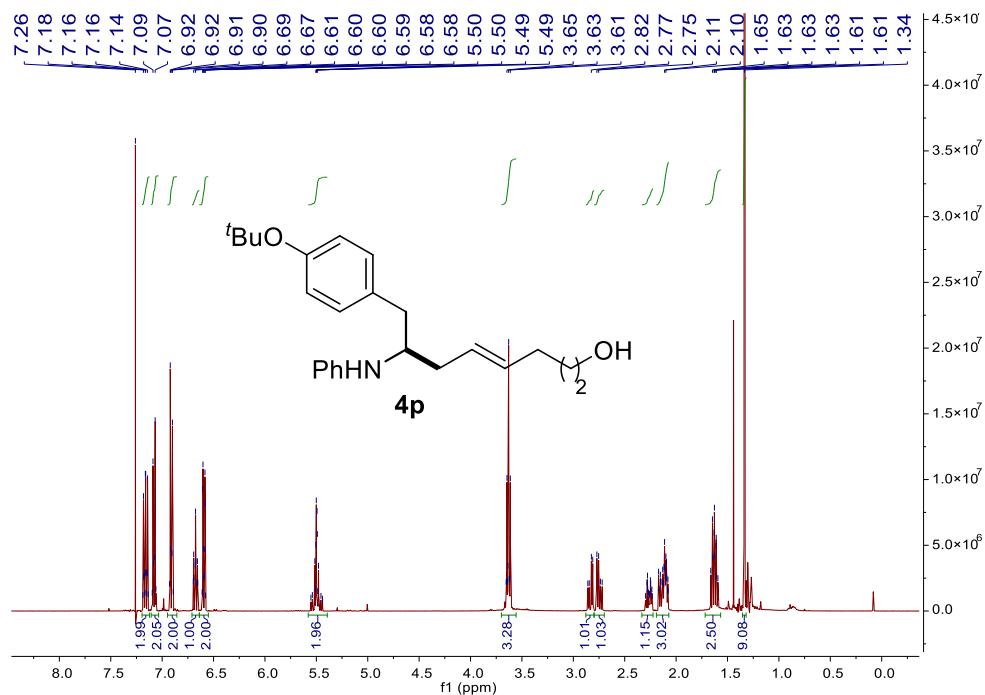


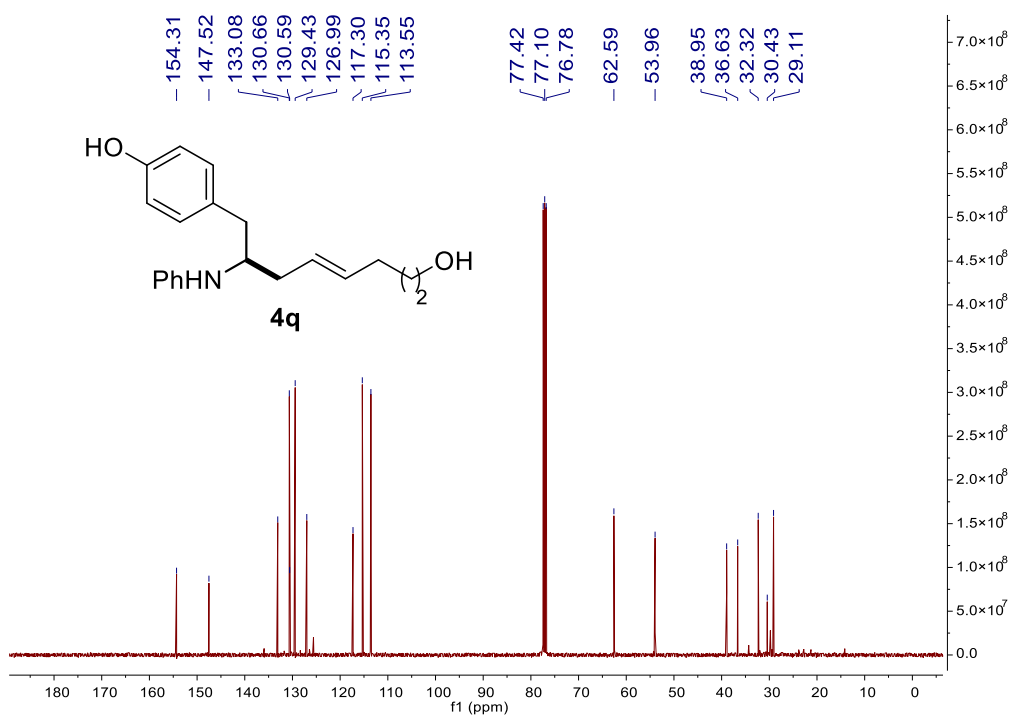
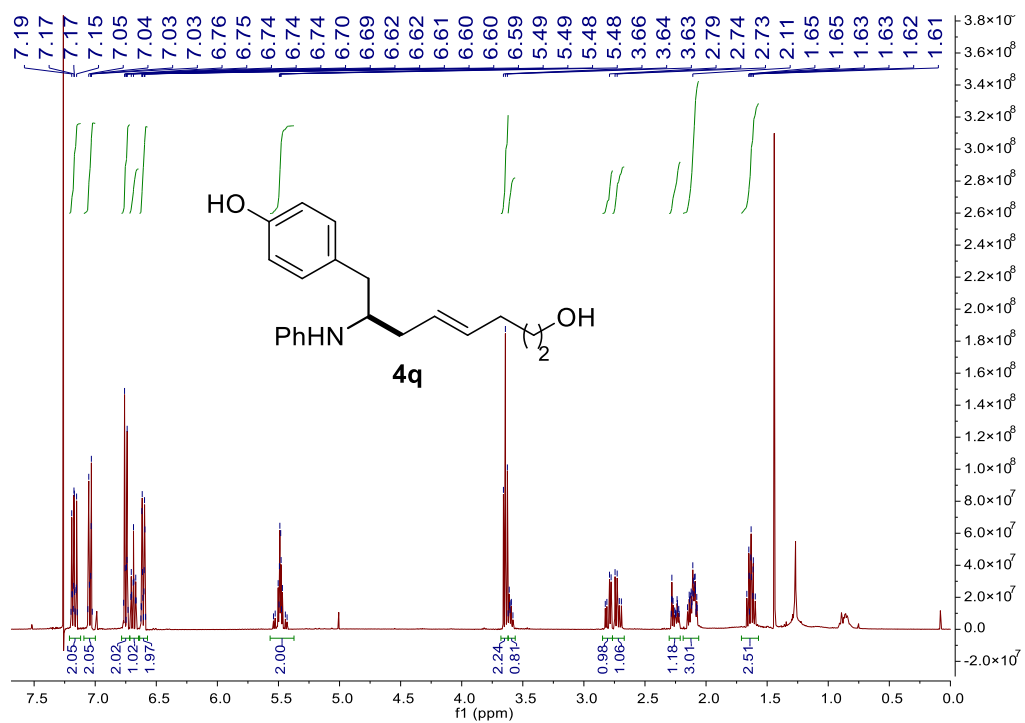


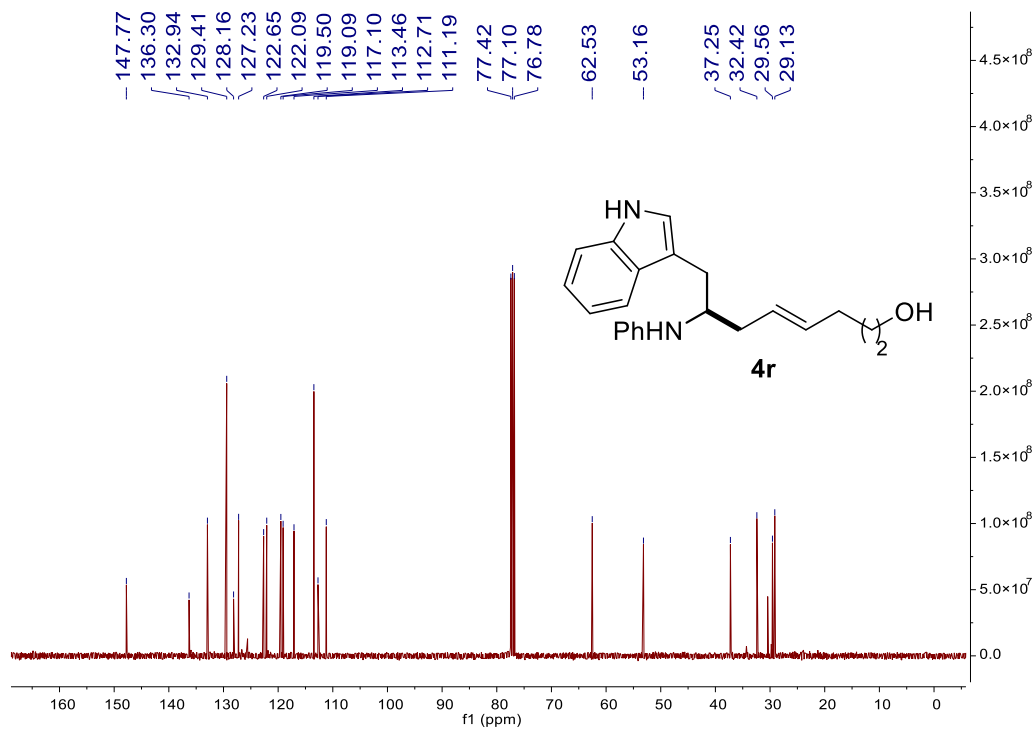
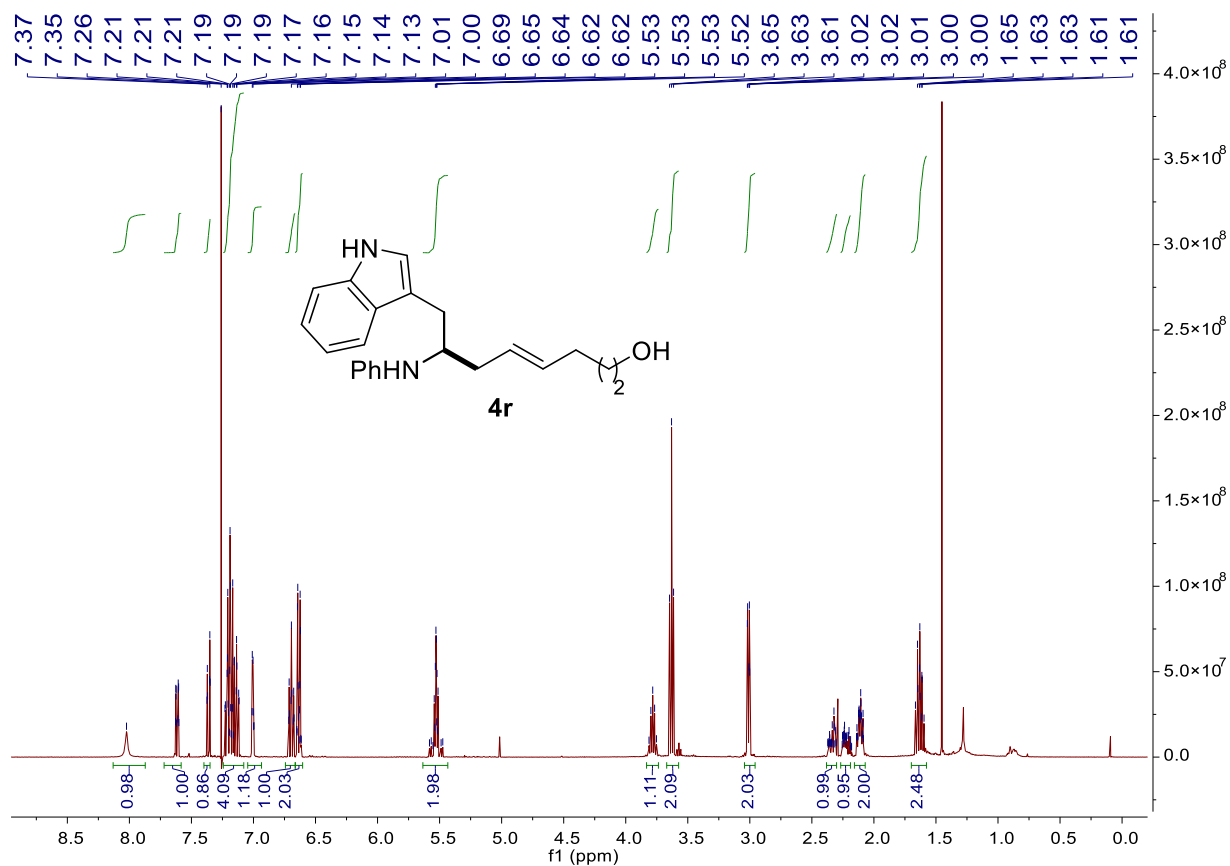


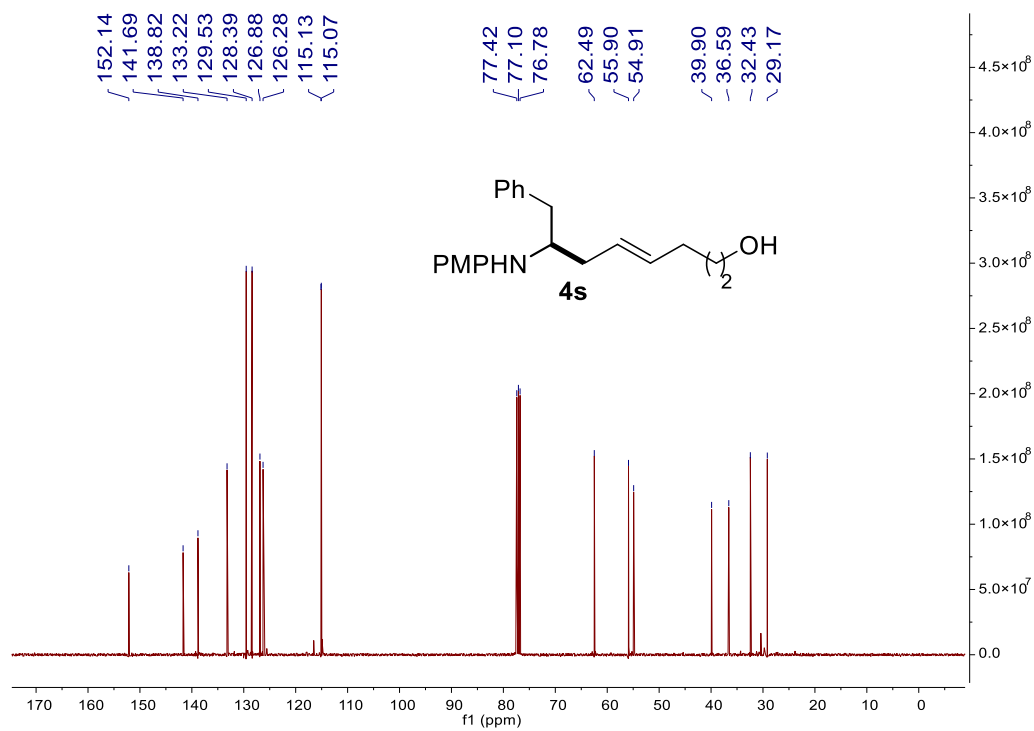
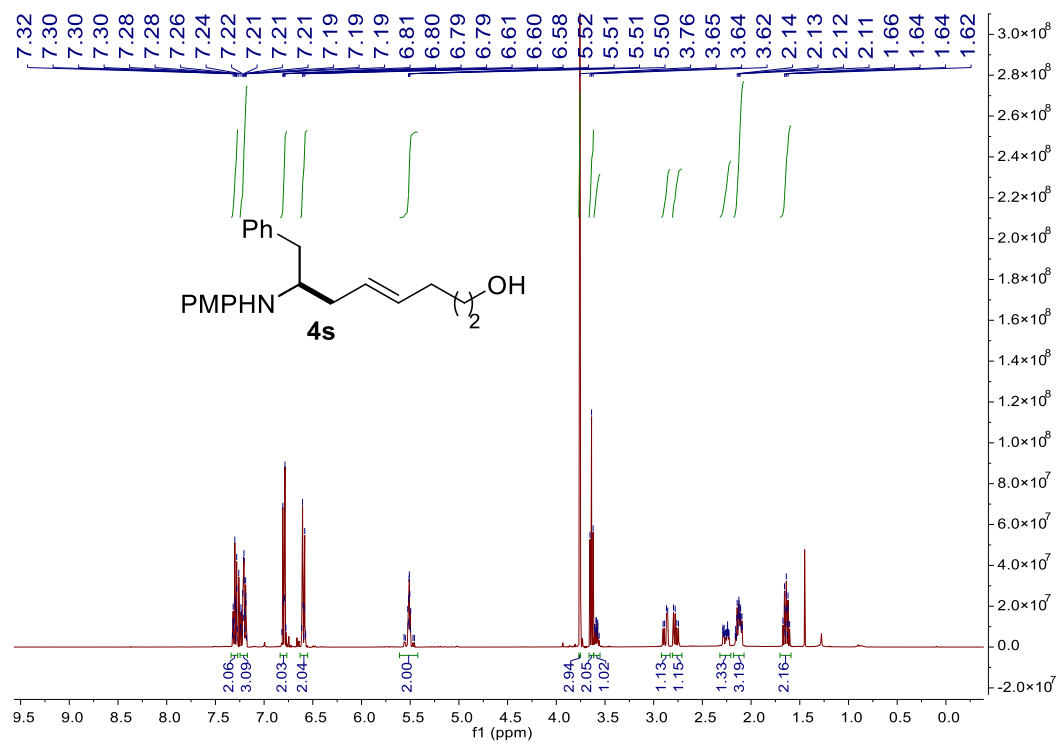


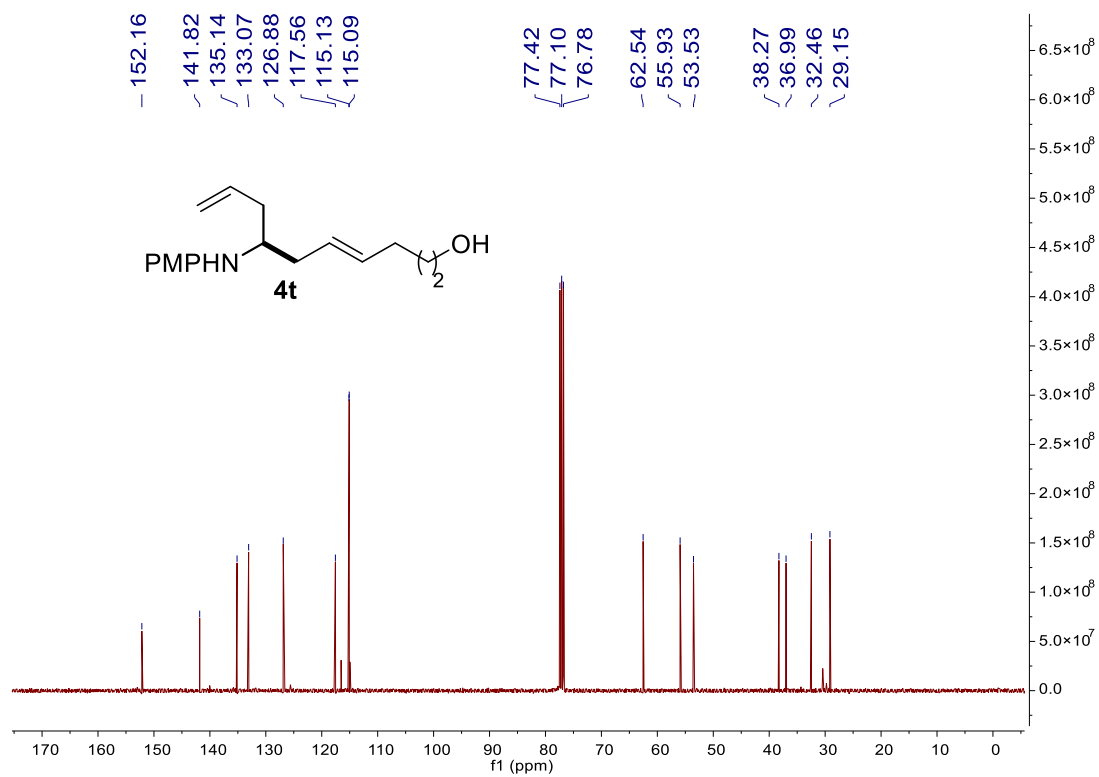
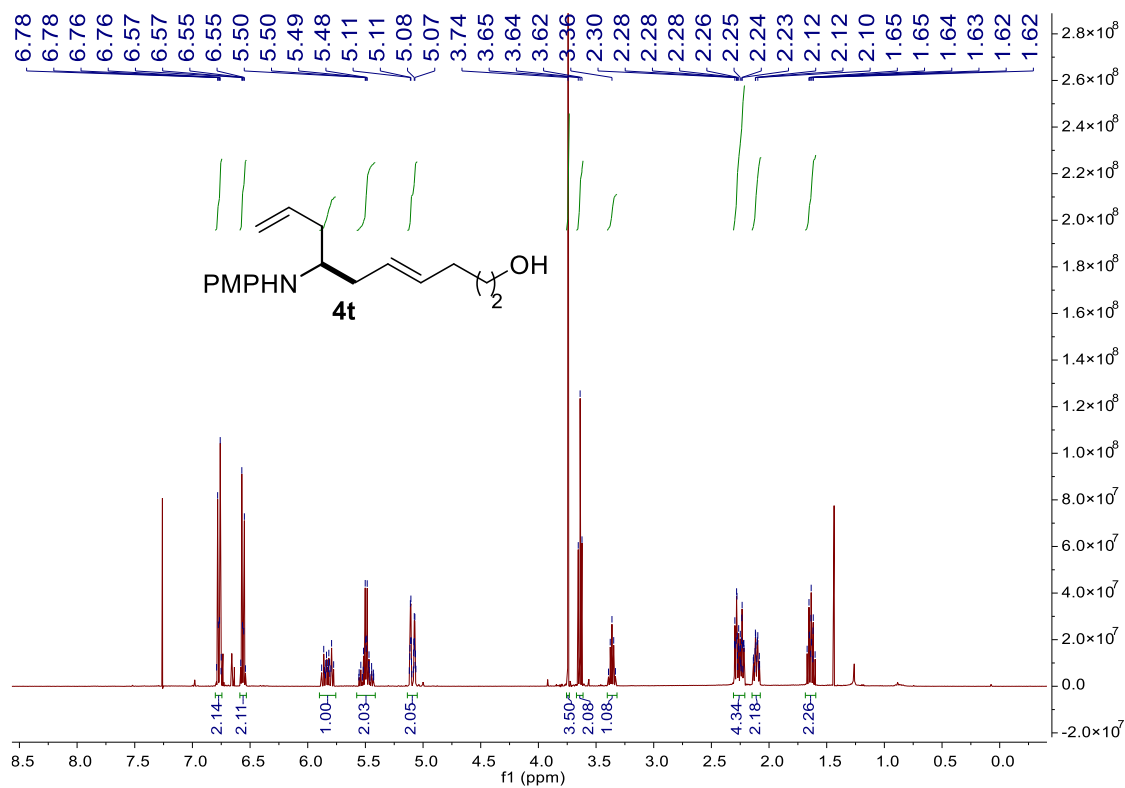


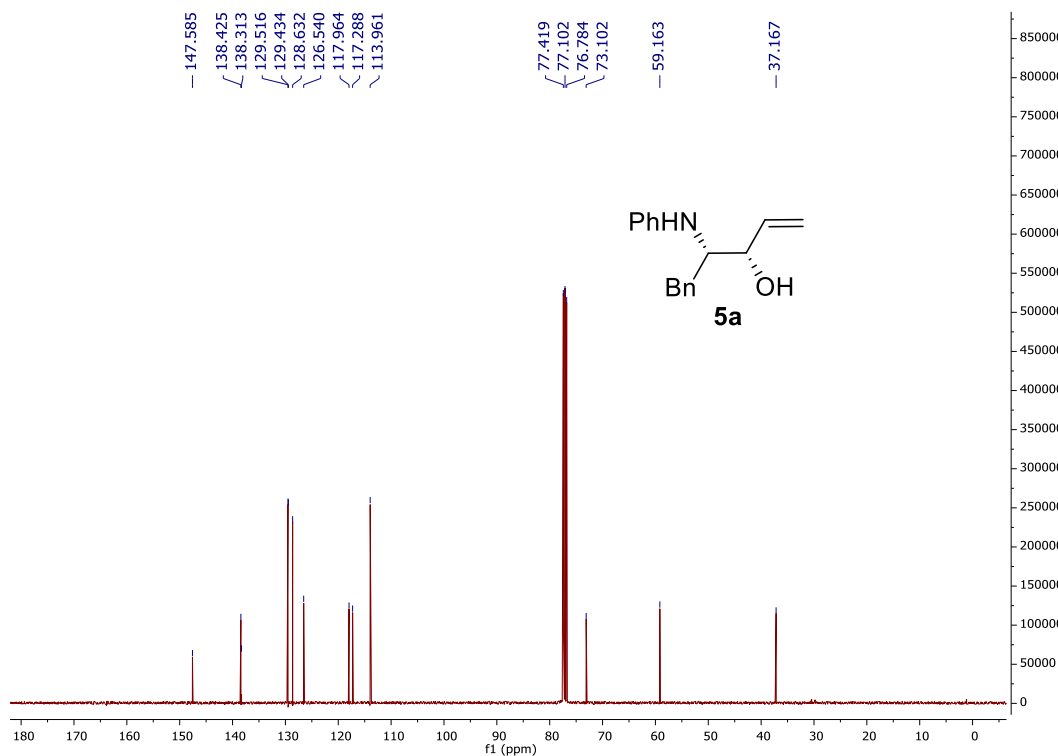
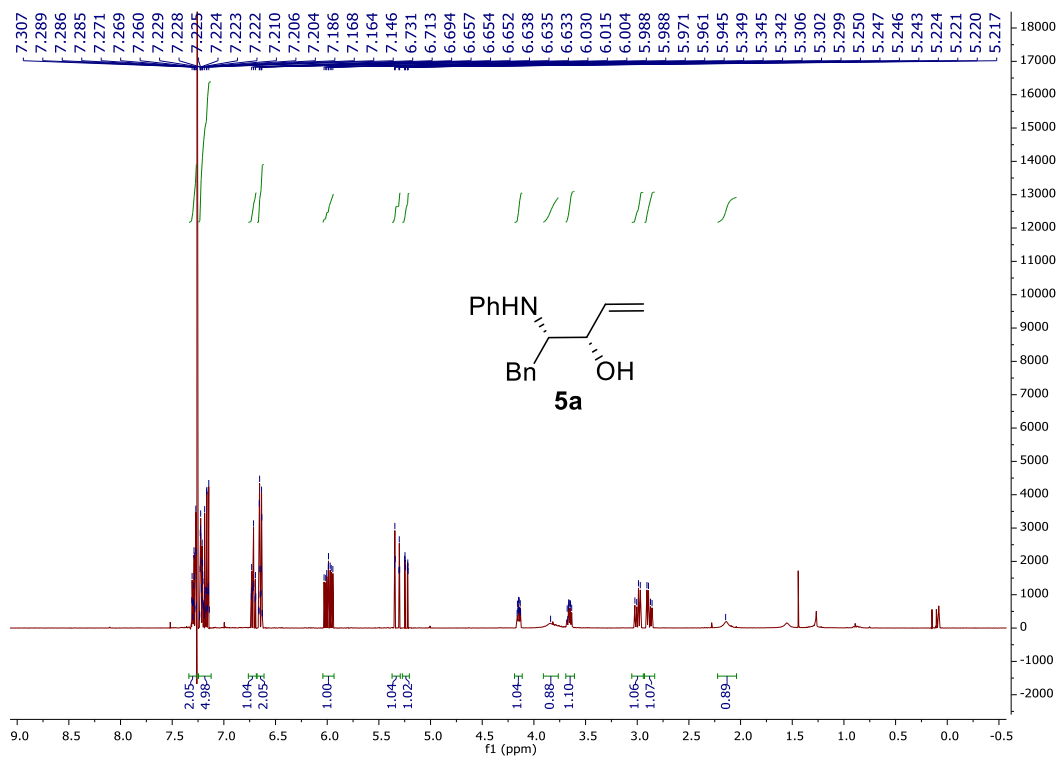


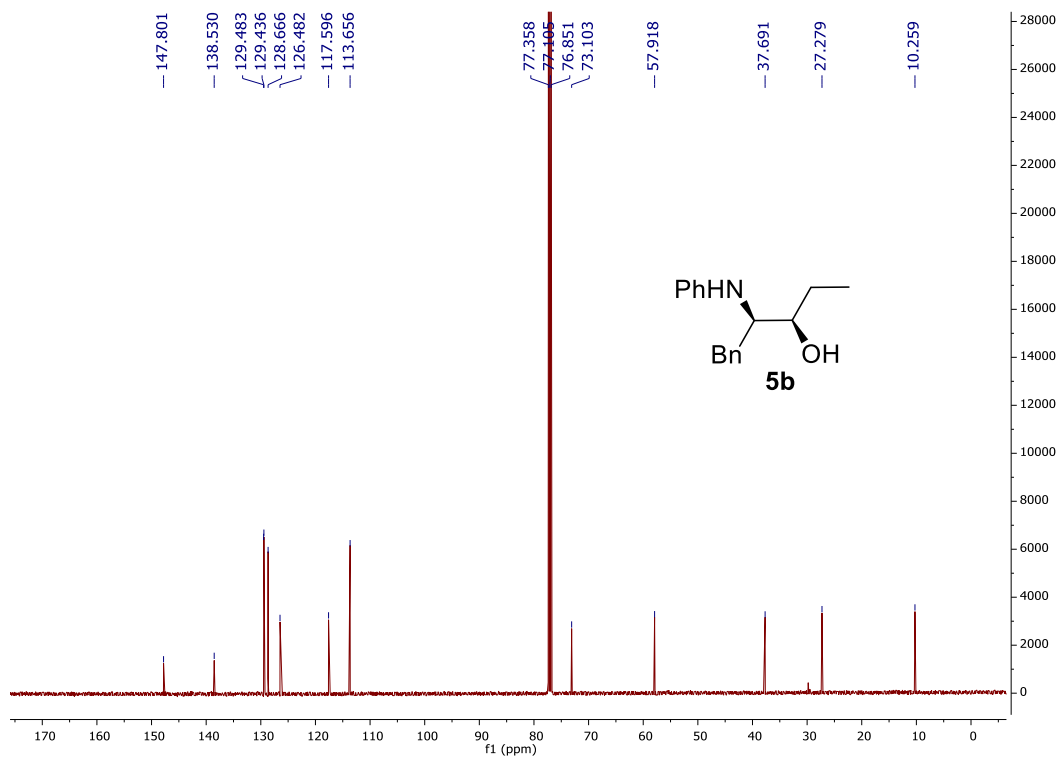
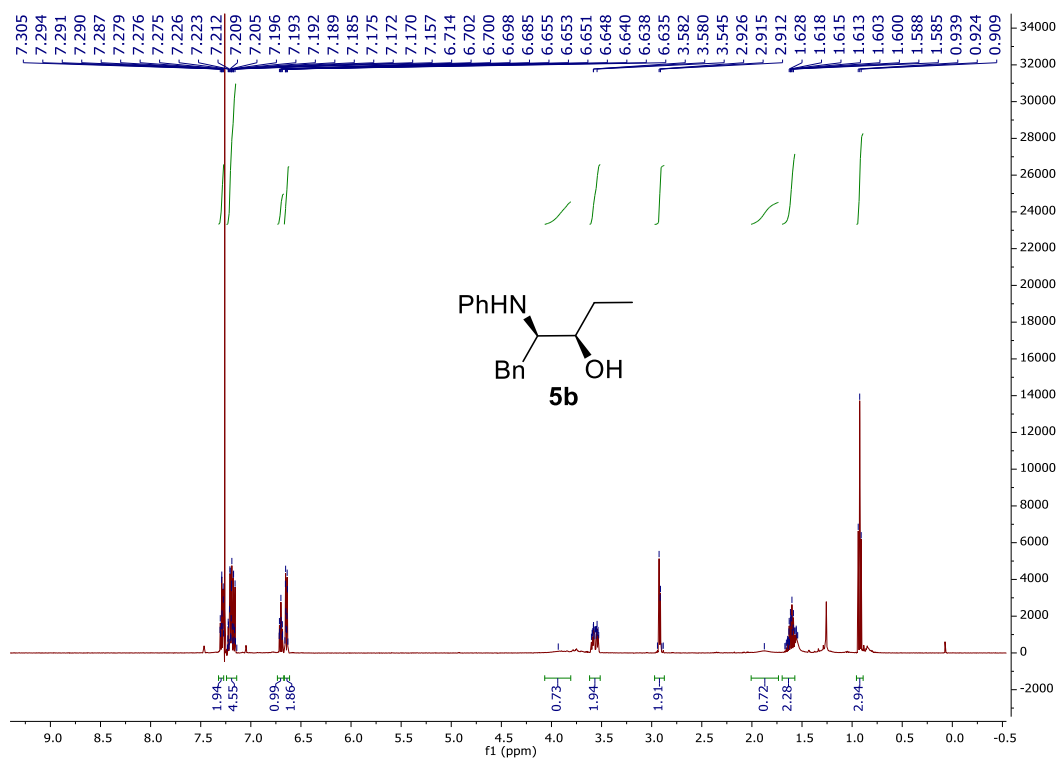


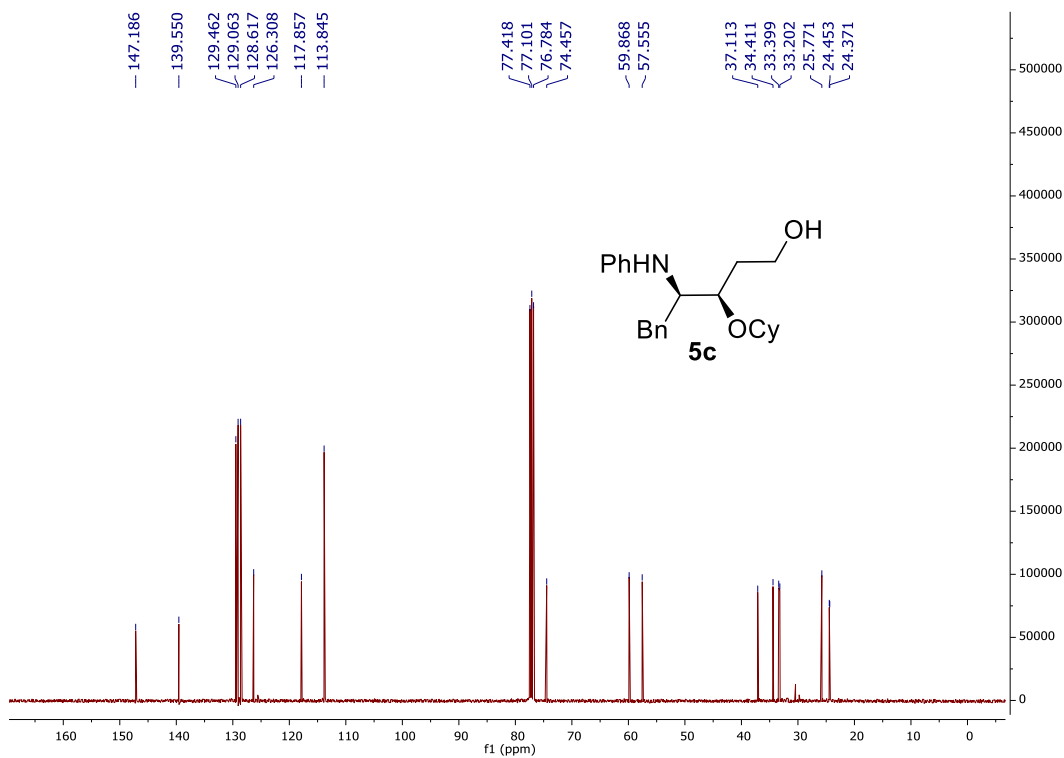
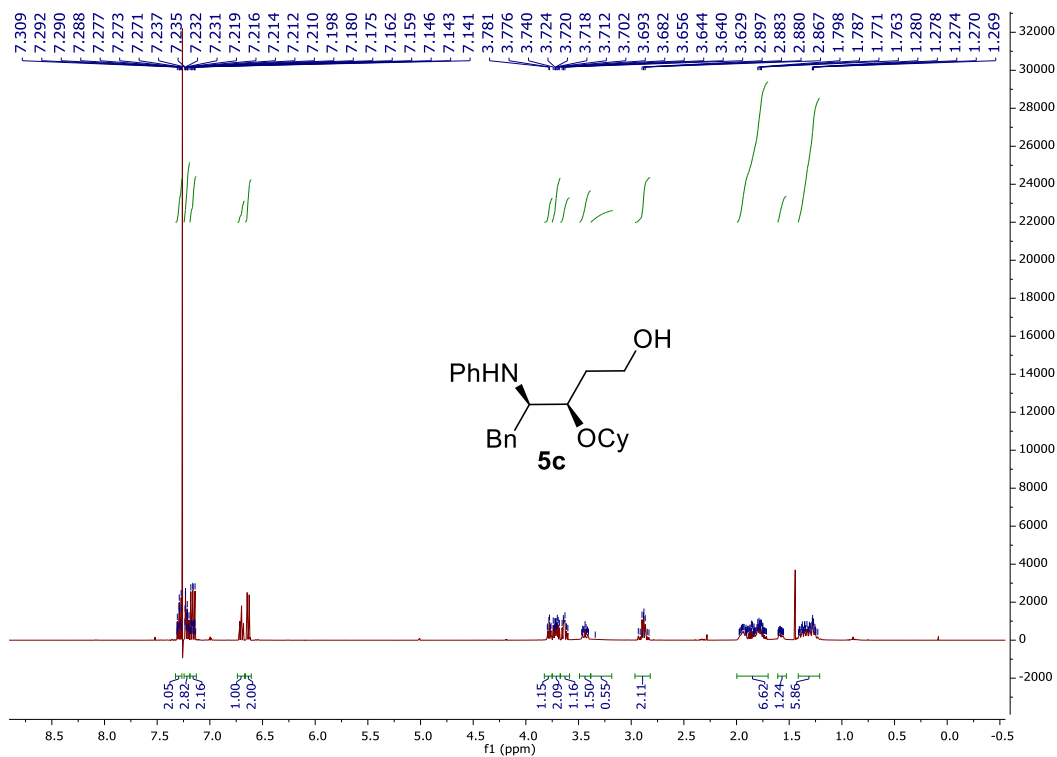


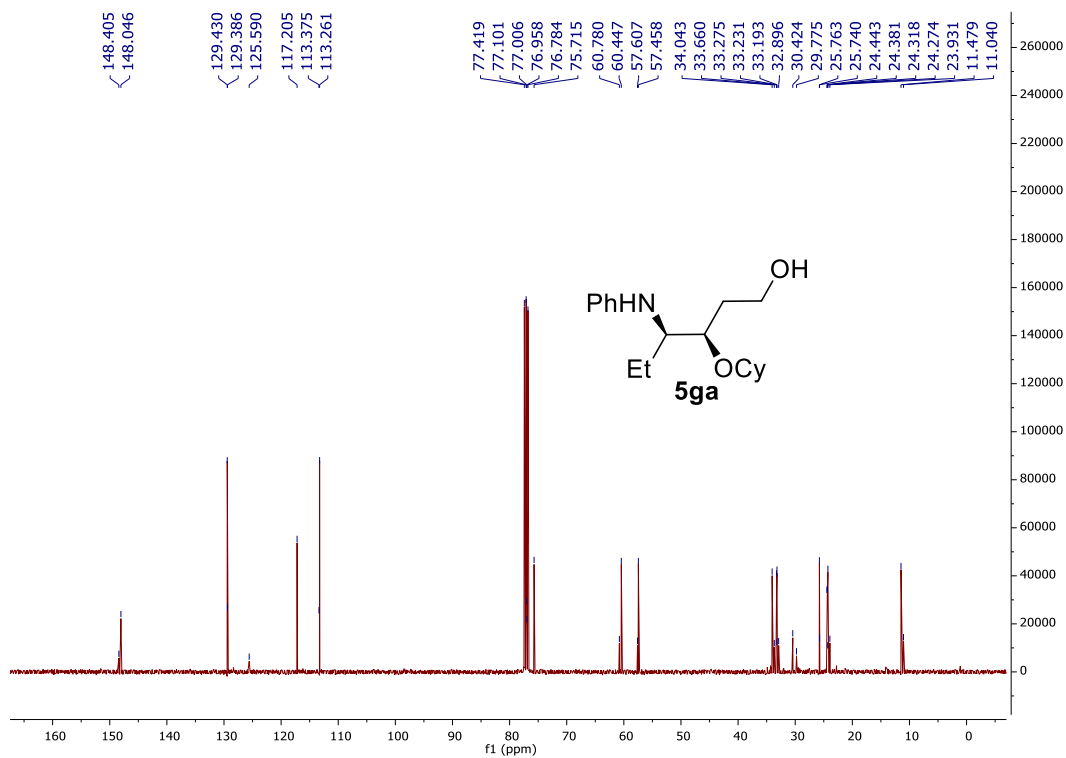
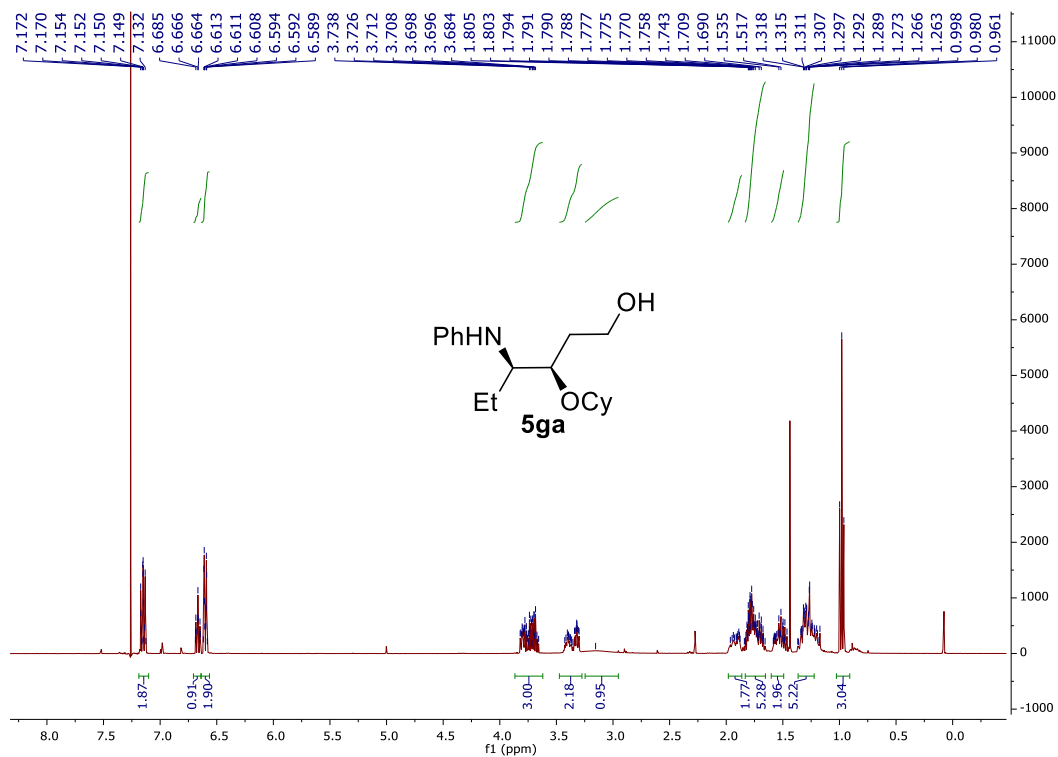


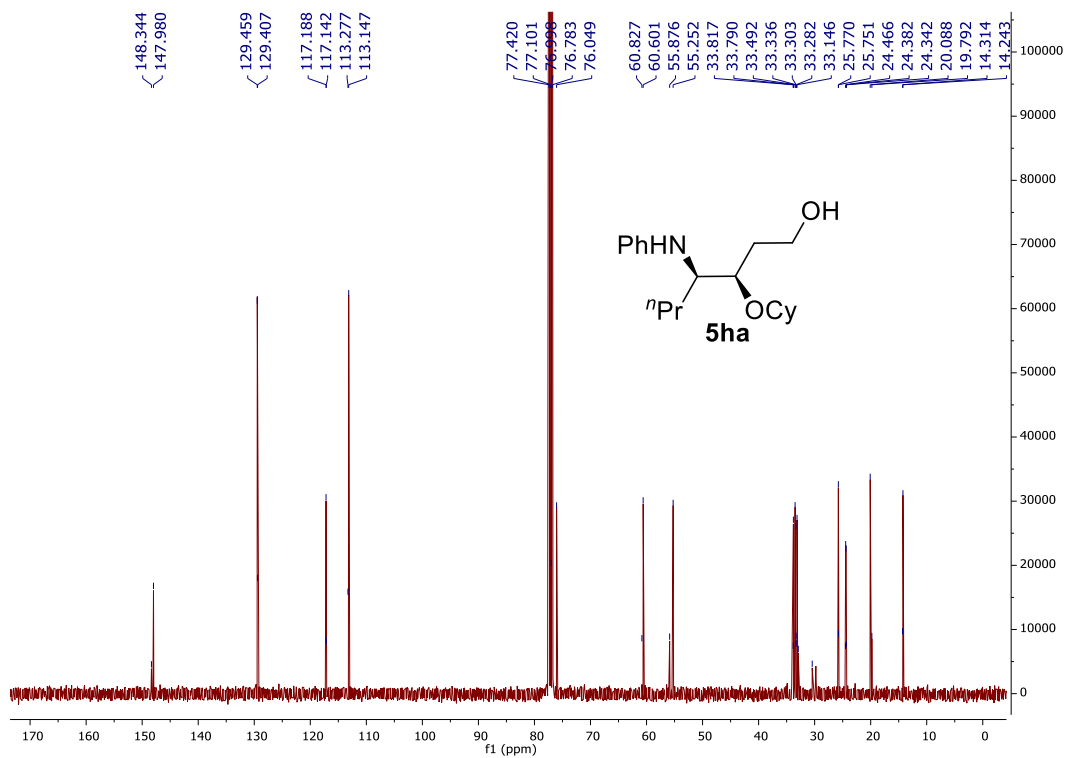
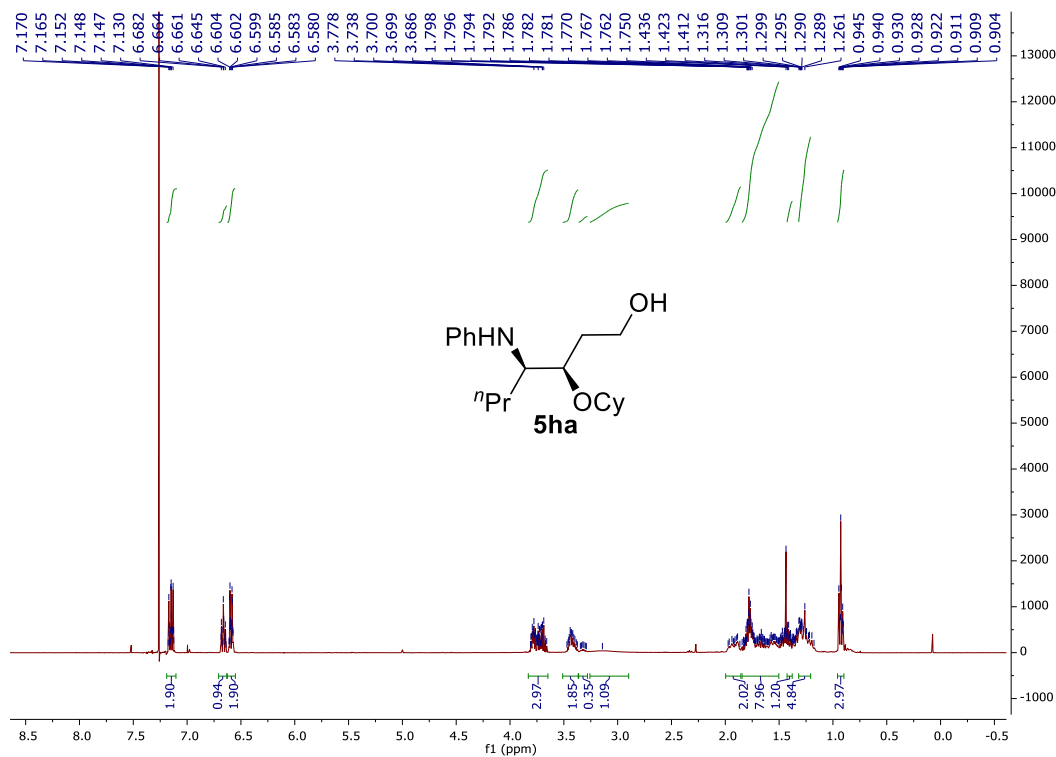


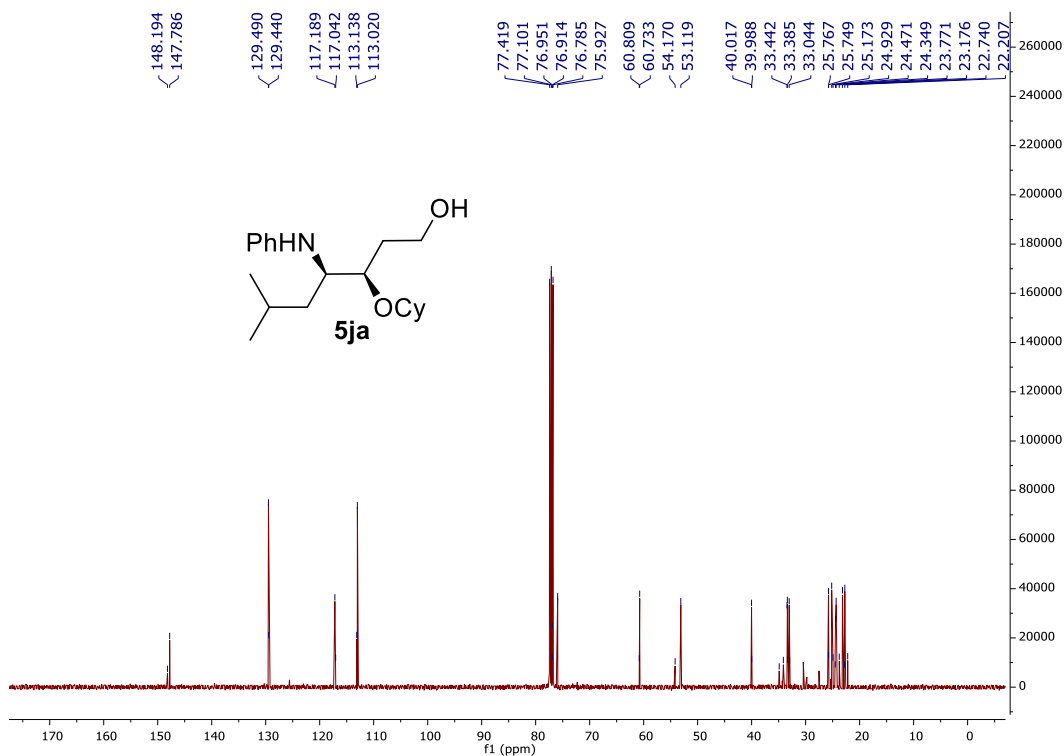
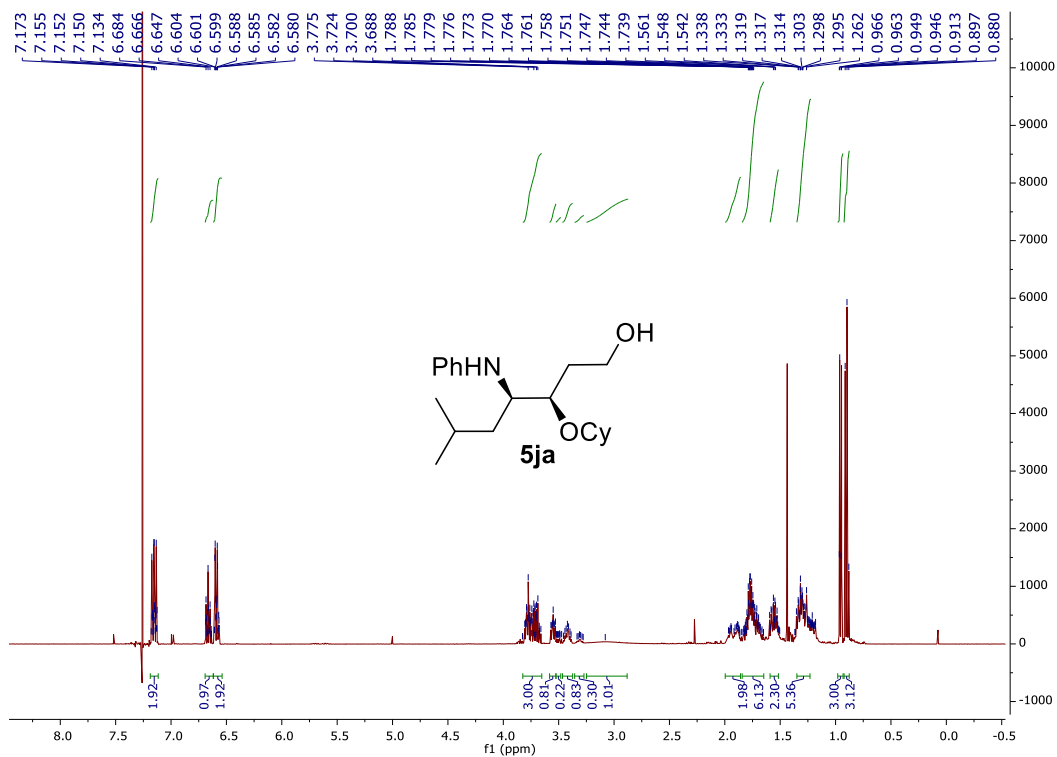


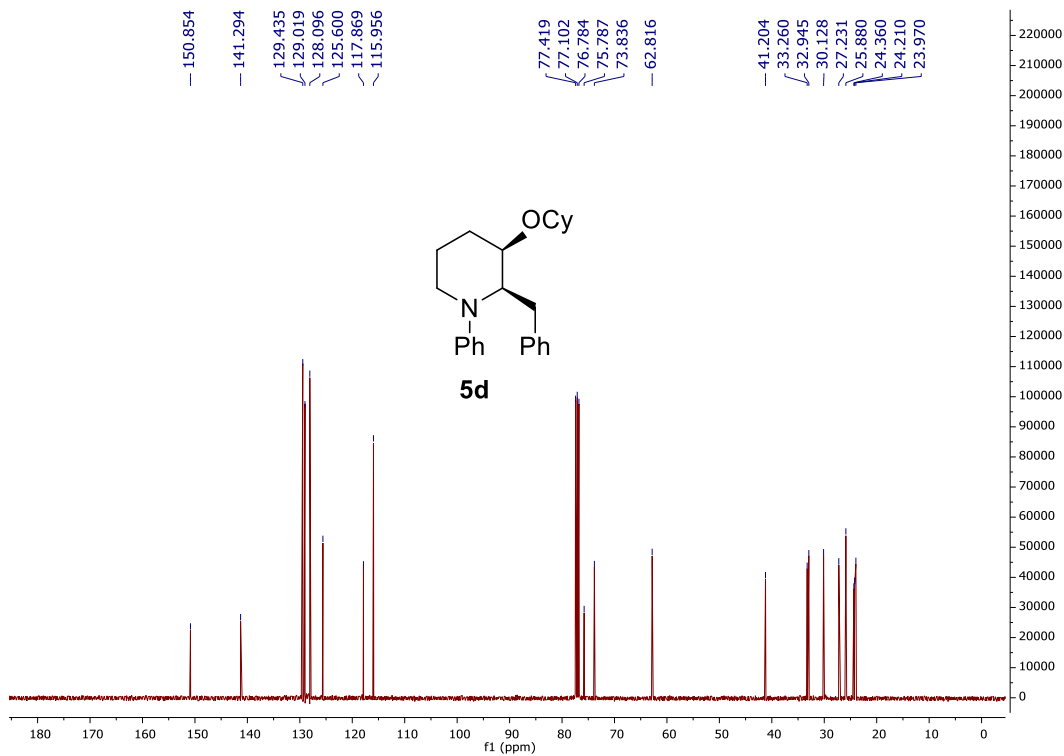
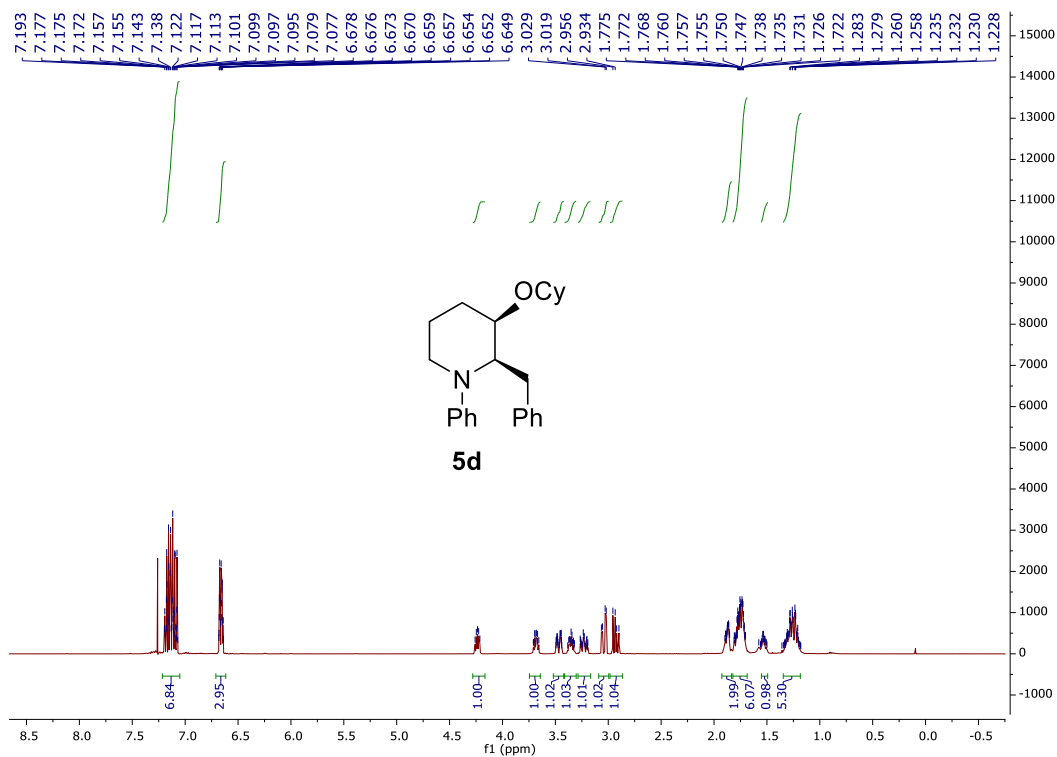


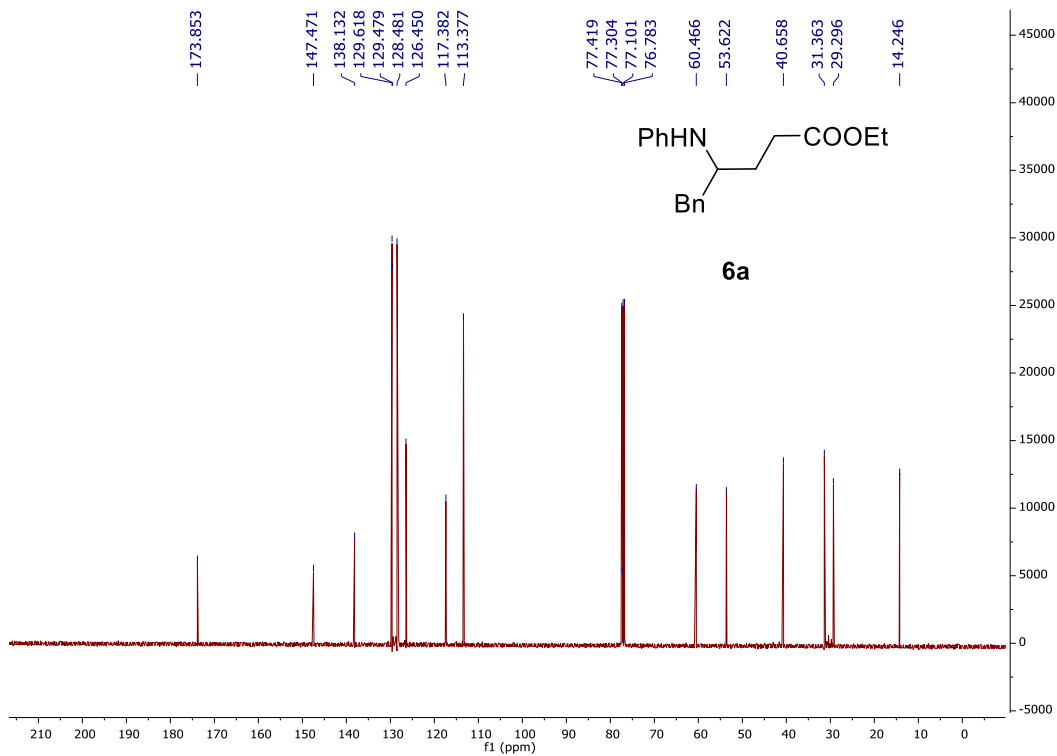
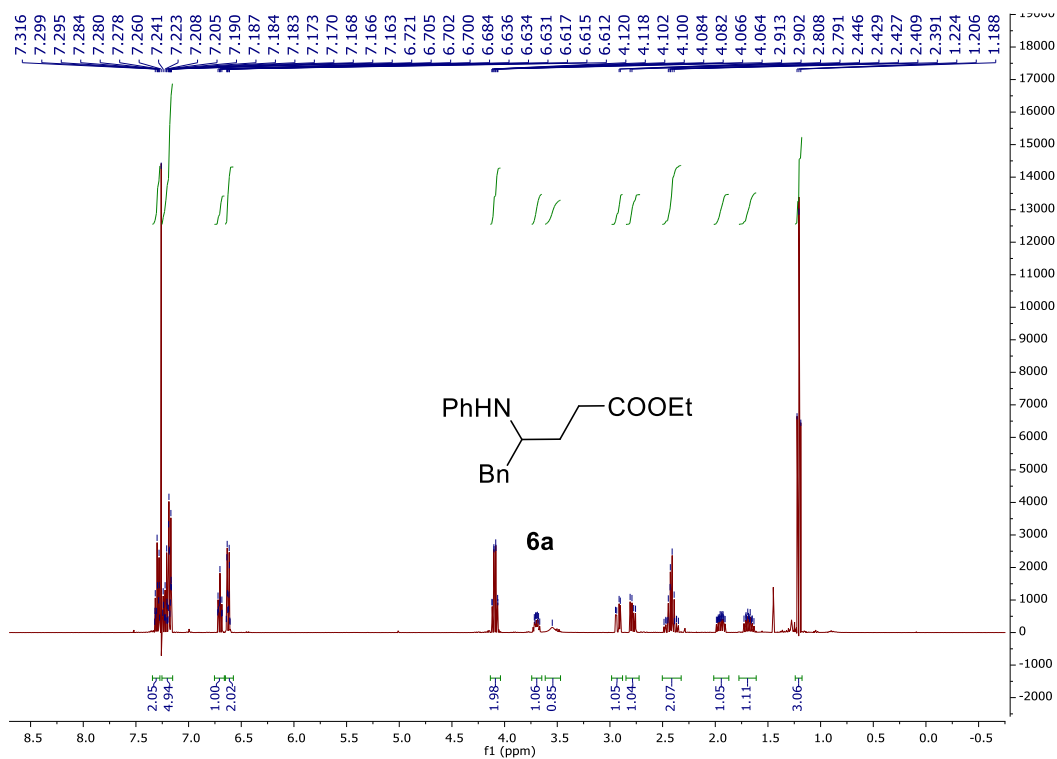


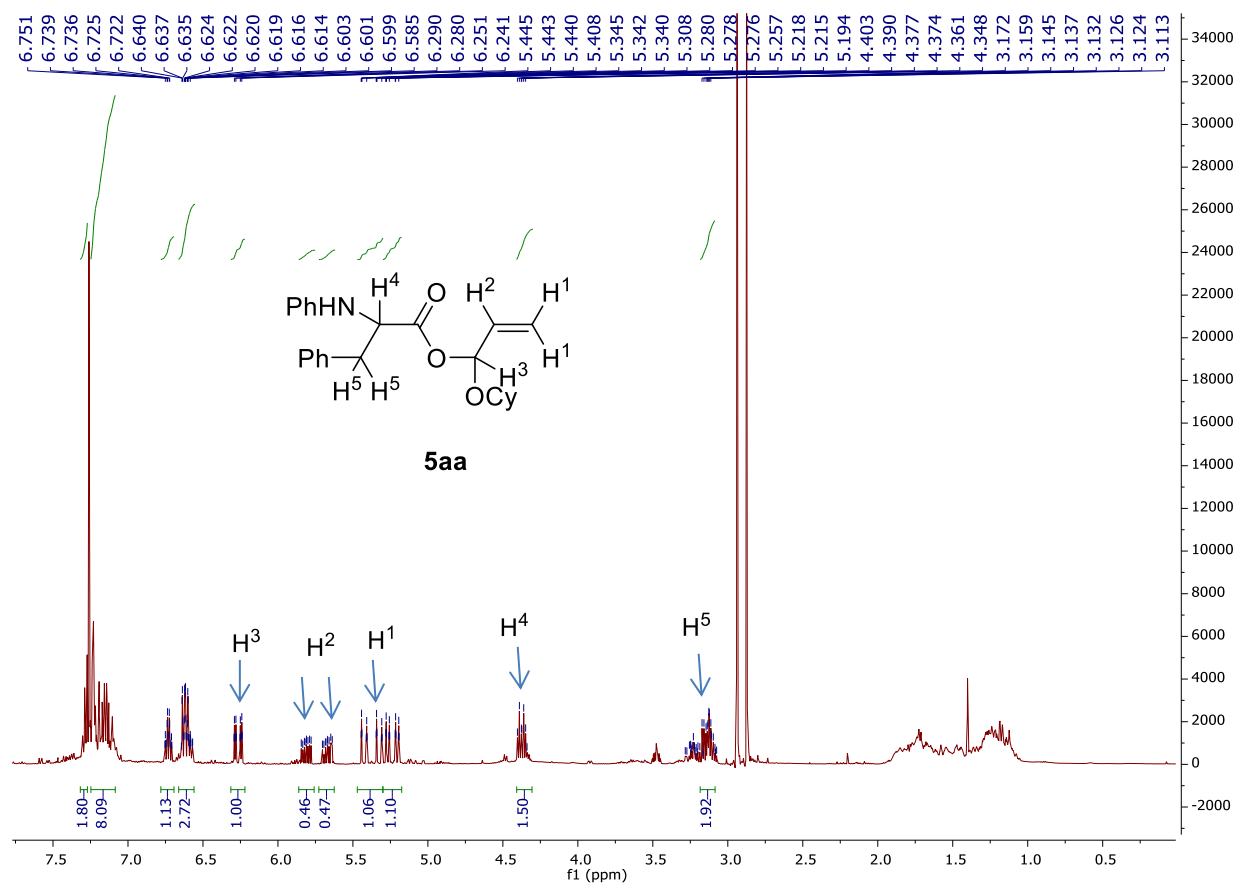


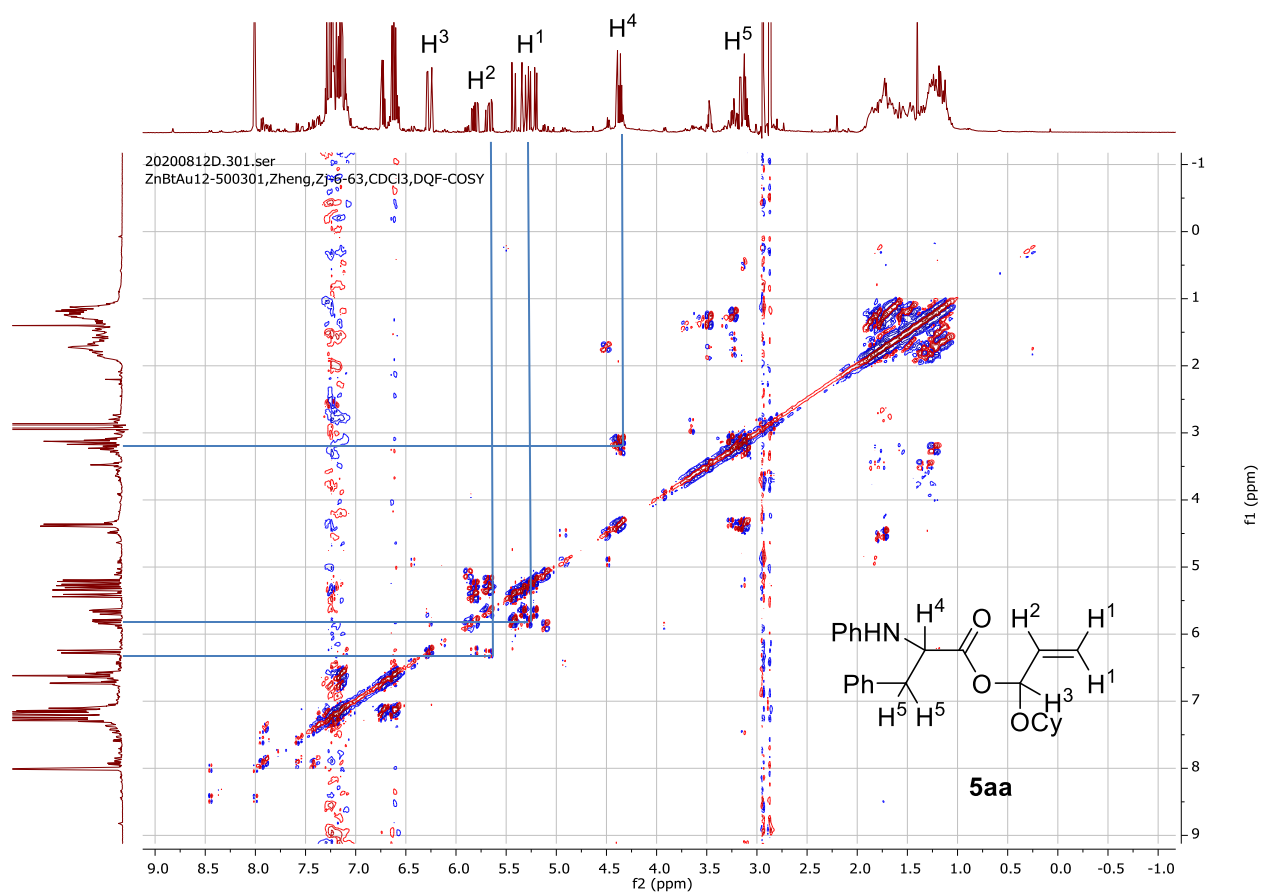


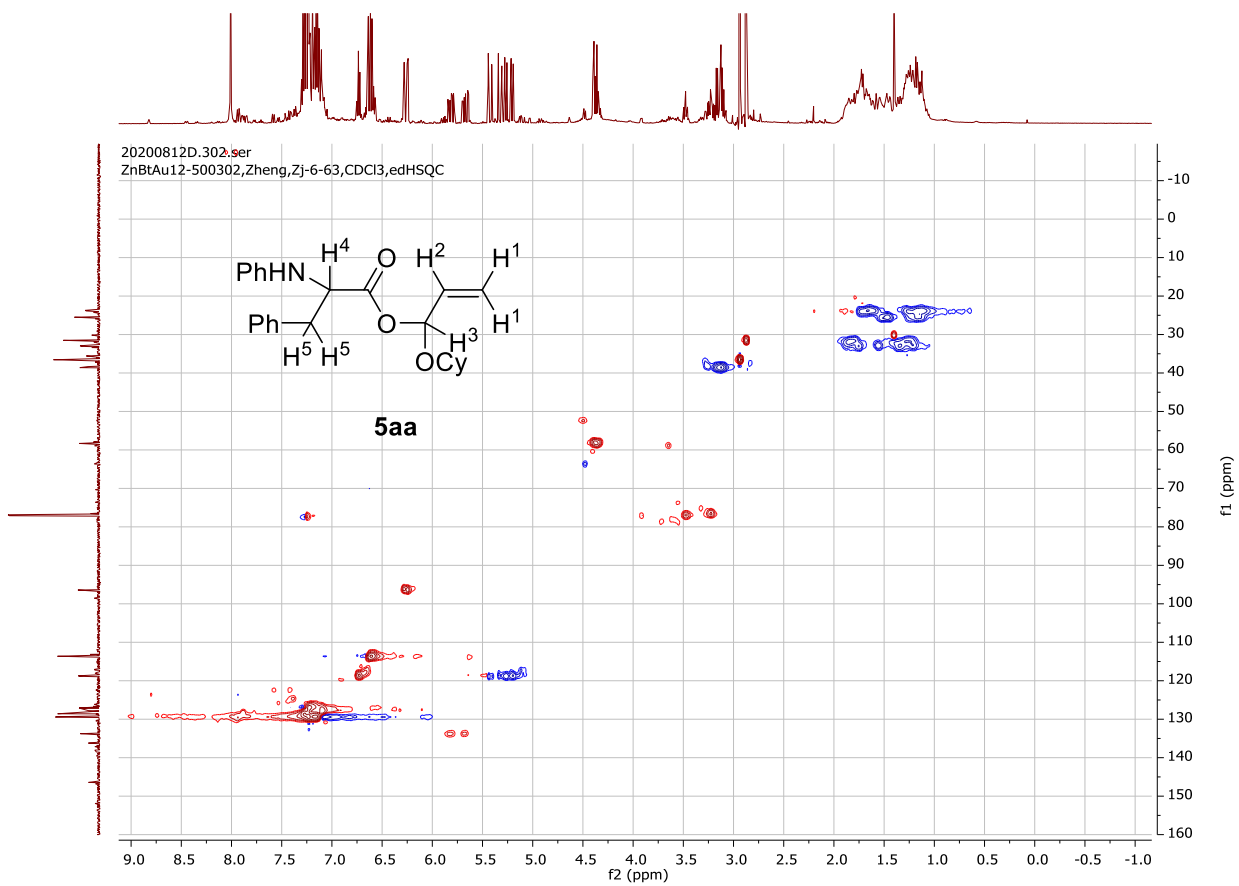


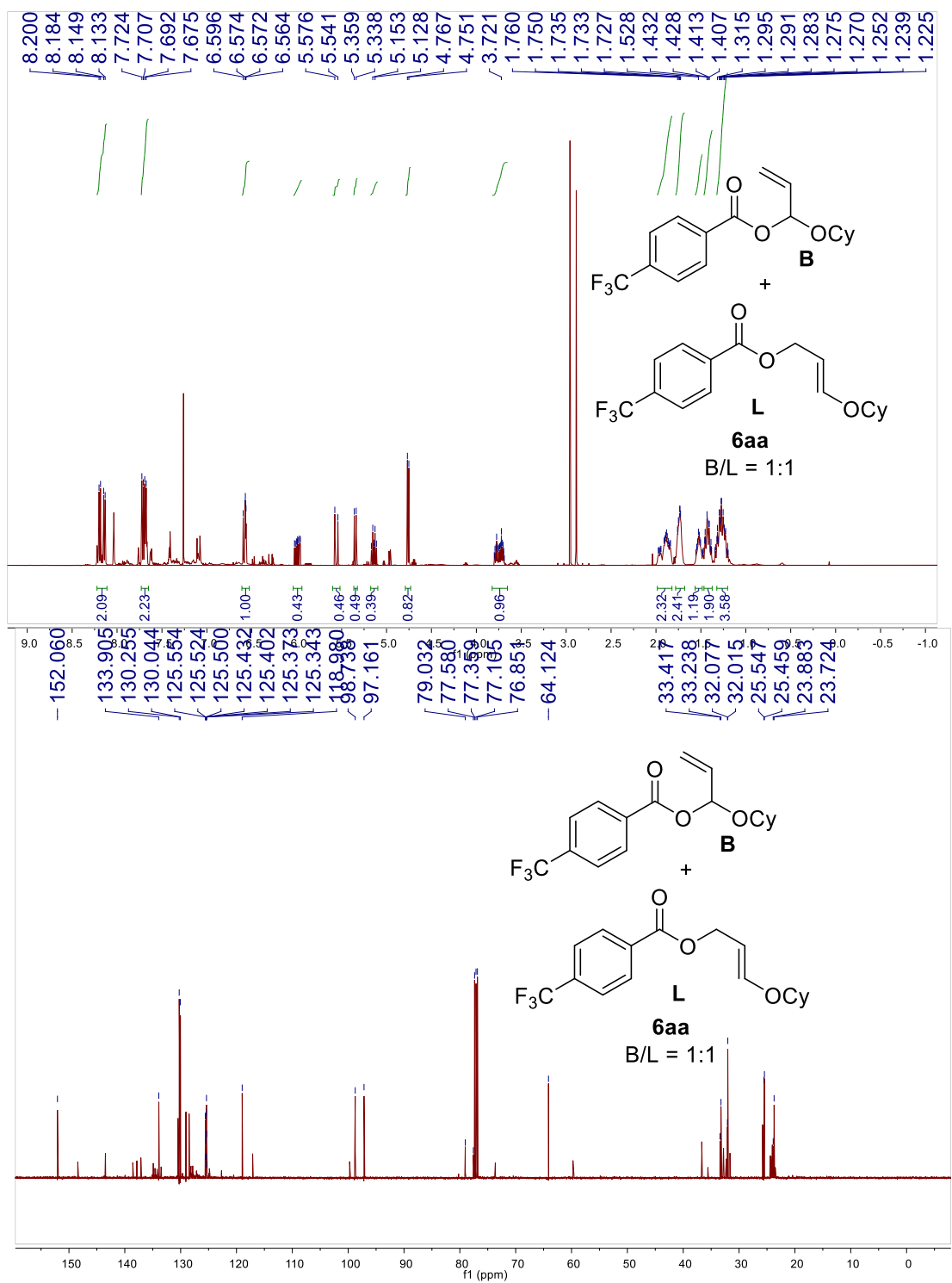


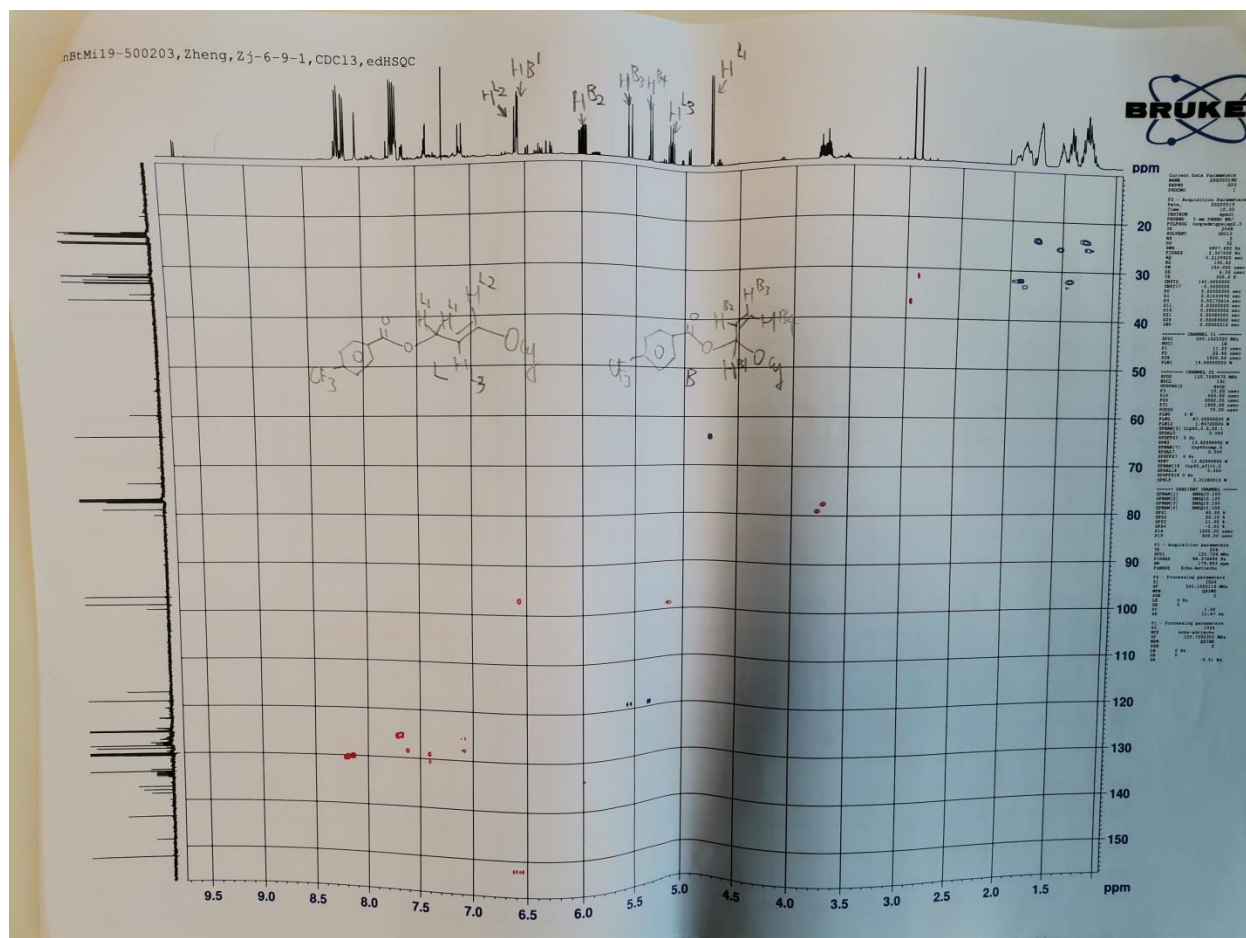
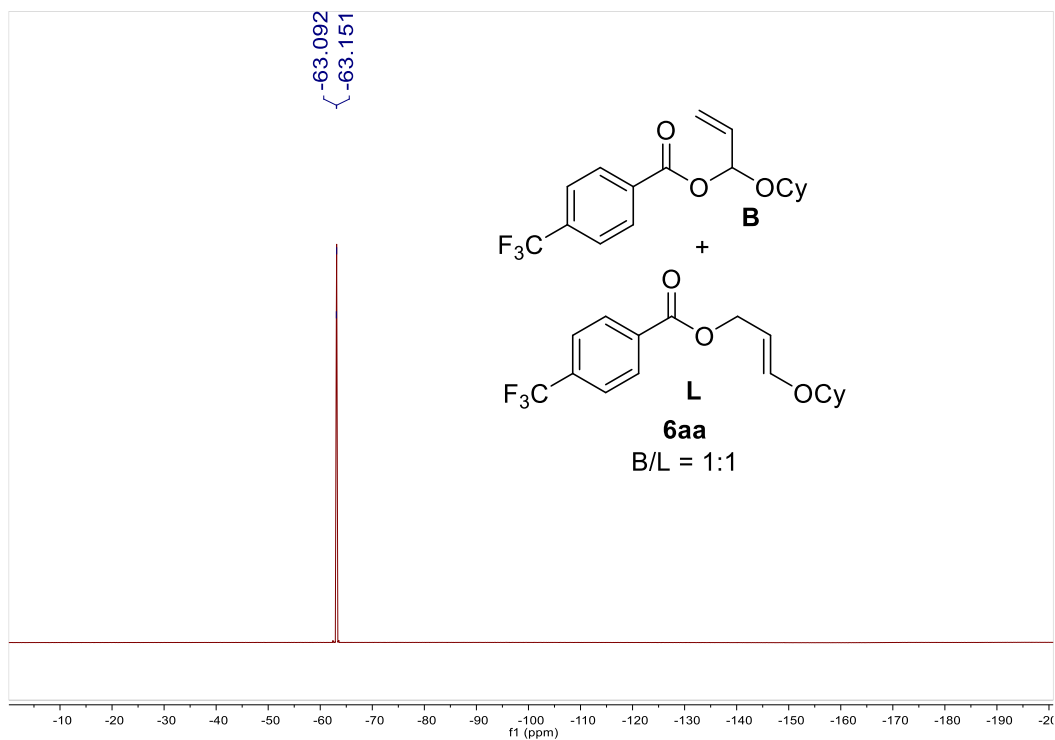


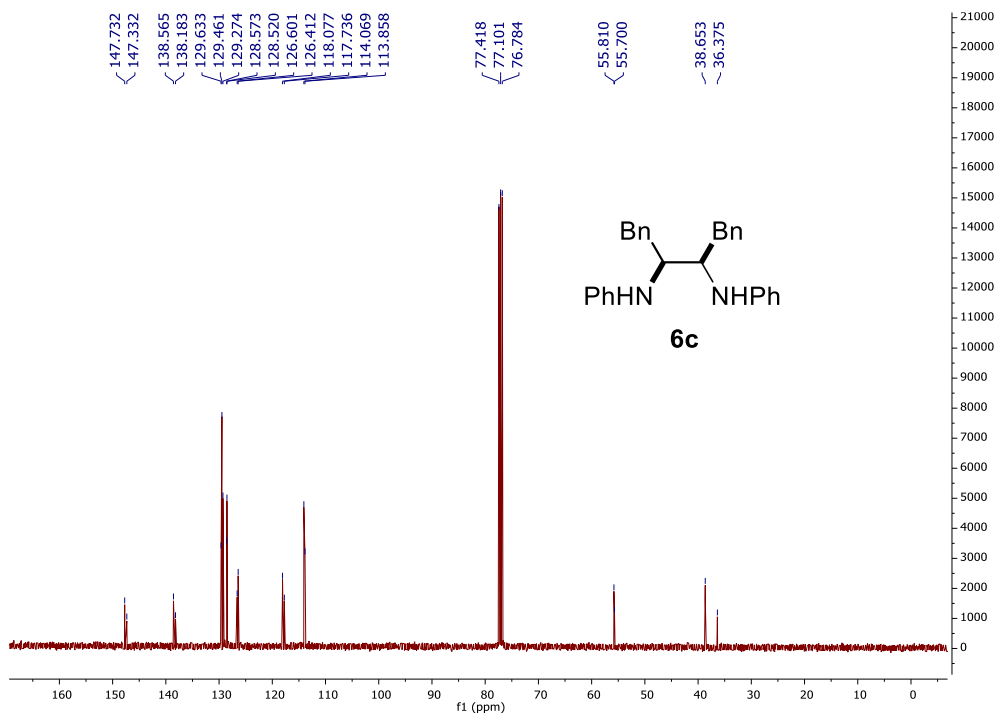
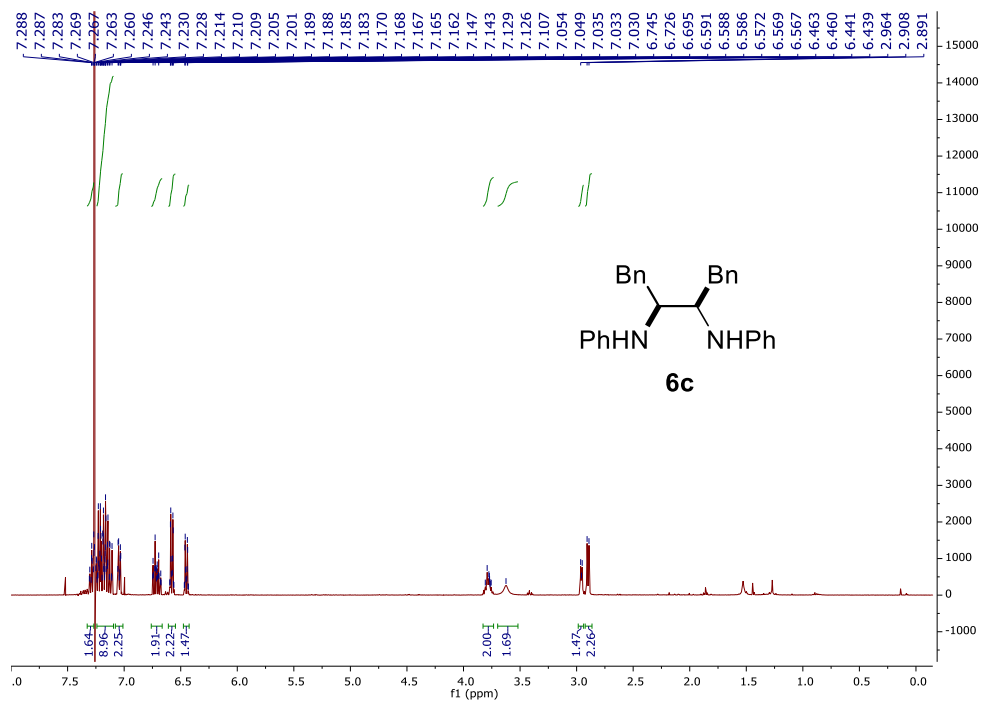


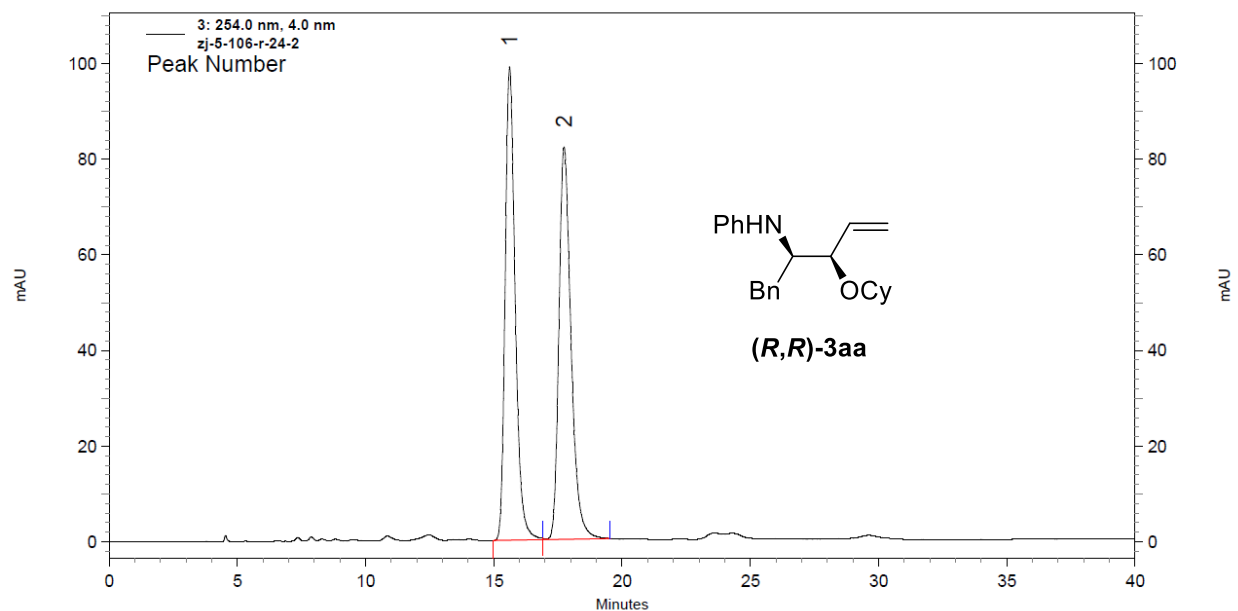






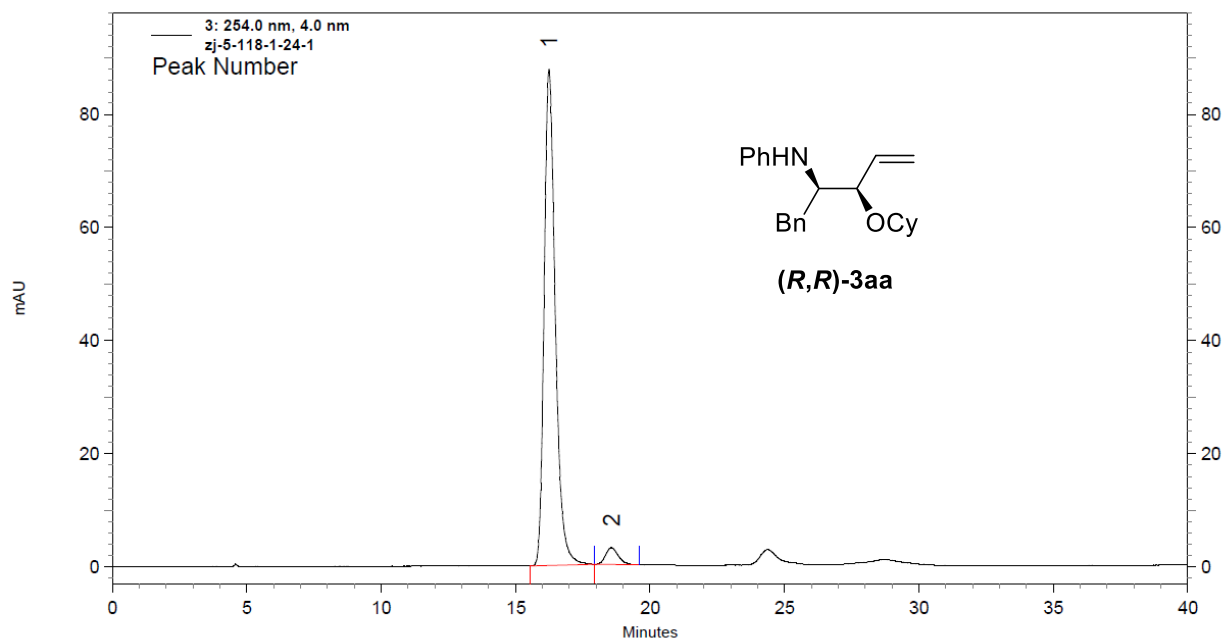






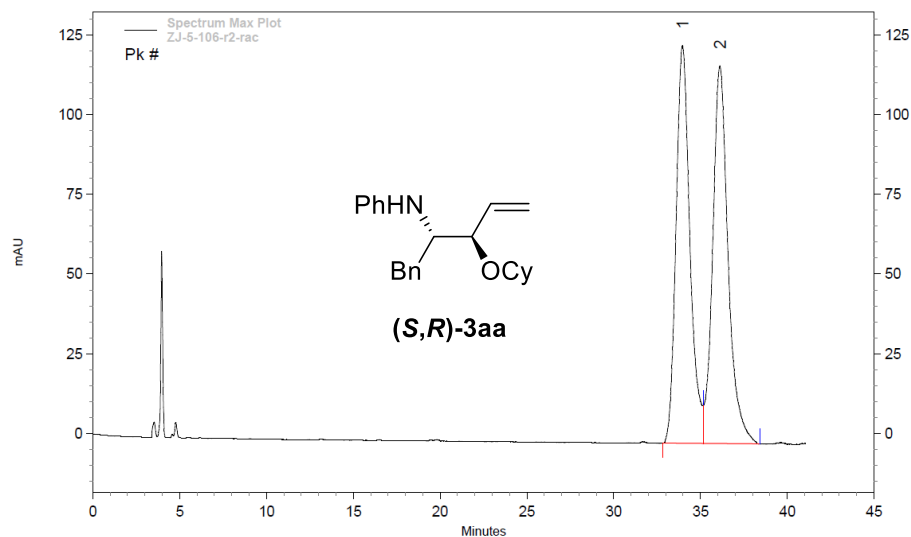
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	15.613	50.058	249.000
2	17.740	49.942	202.000

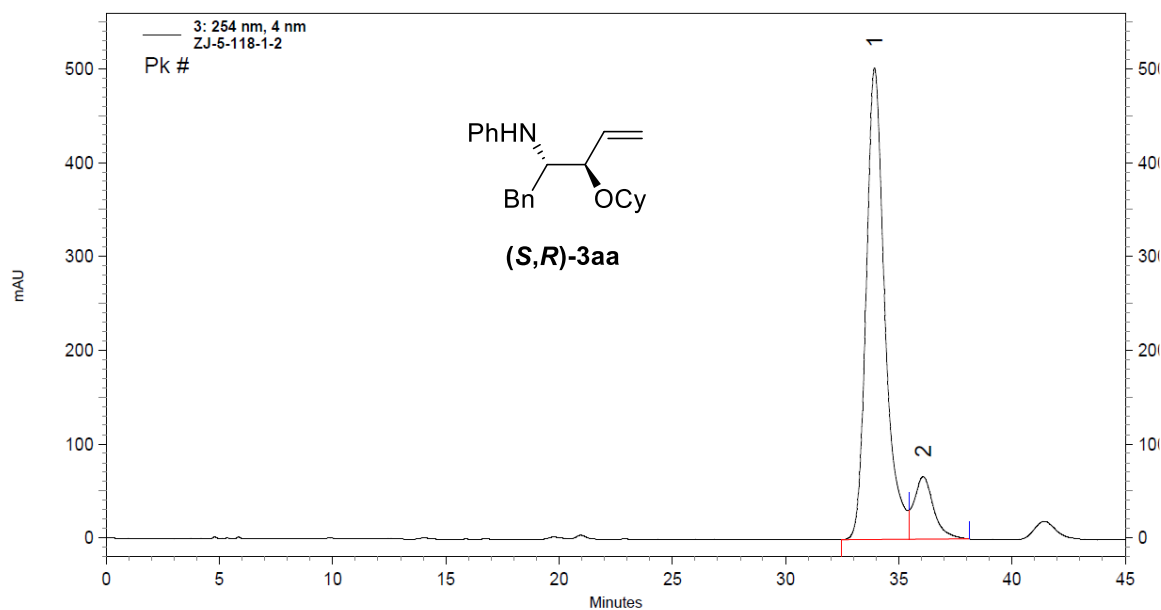


3: 254.0 nm,
4.0 nm Results

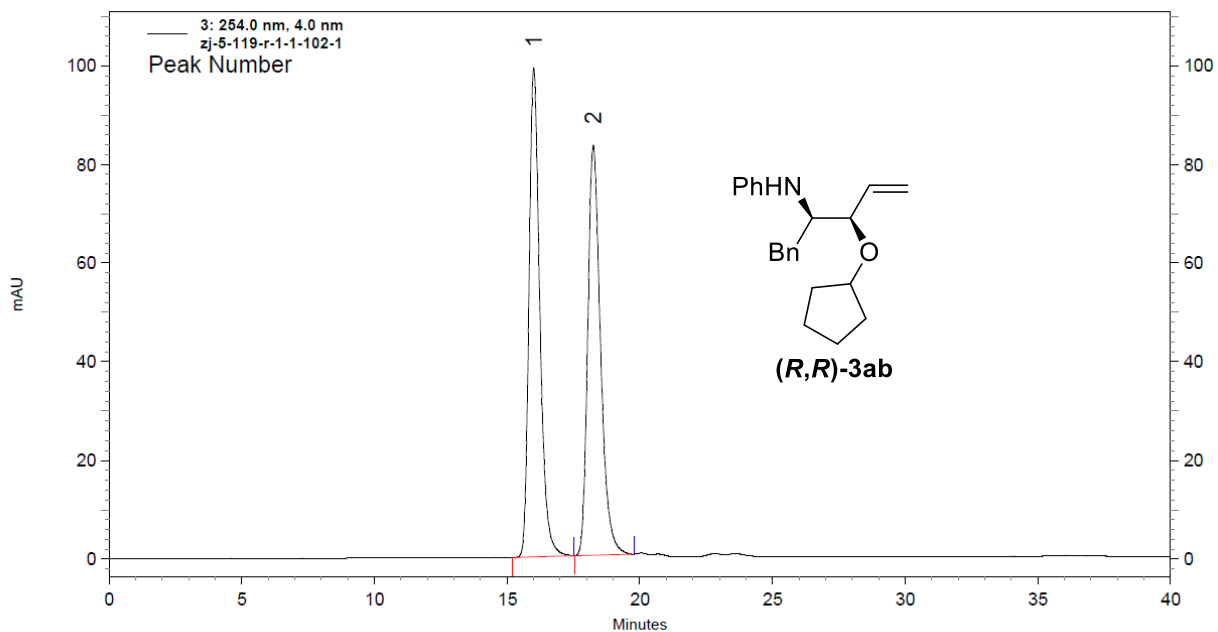
Pk #	Retention Time	Area Percent	Lambda Max
1	16.240	96.314	249.000
2	18.560	3.686	202.000



Spectrum Max Plot Results			
Pk #	Retention Time	Area Percent	Lambda Max
1	33,967	48,707	190
2	36,113	51,293	190

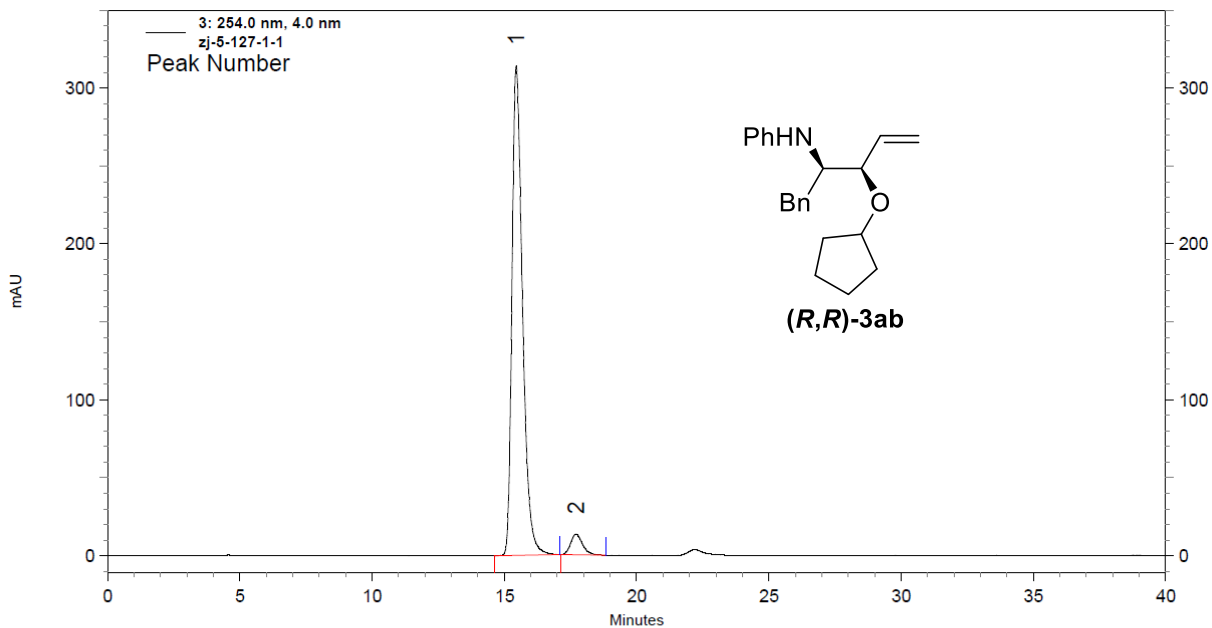


3: 254 nm, 4 nm Results			
Pk #	Retention Time	Area Percent	Lambda Max
1	33,933	87,738	194
2	36,080	12,262	190



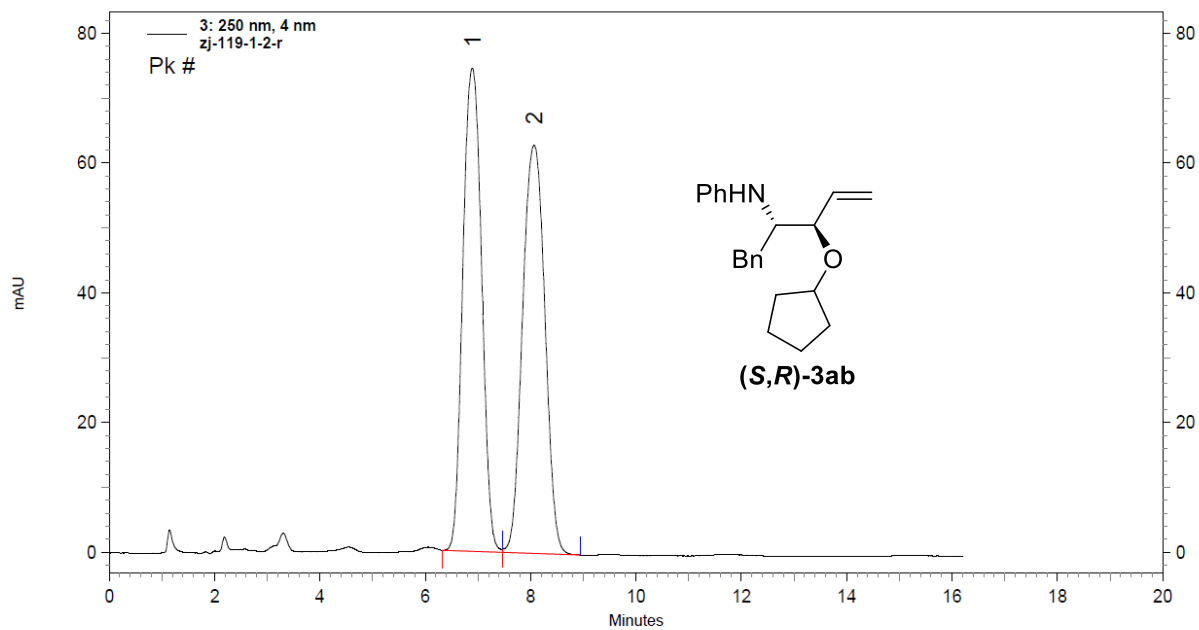
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	16.000	50.344	249.000
2	18.247	49.656	249.000



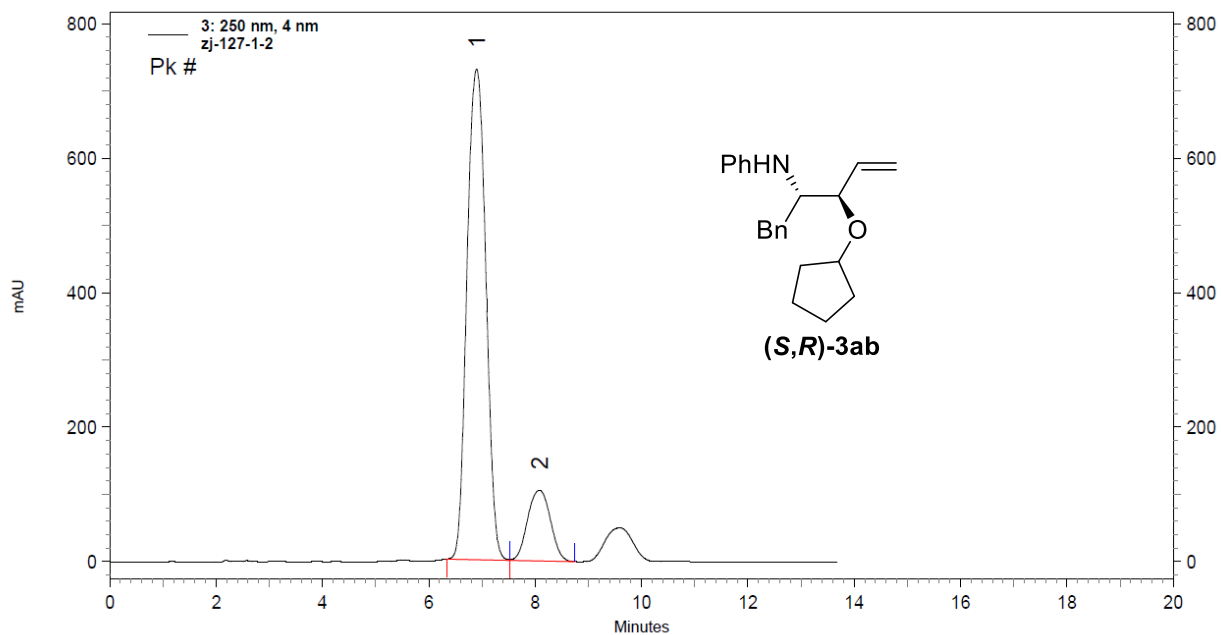
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	15.447	95.466	249.000
2	17.707	4.534	205.000



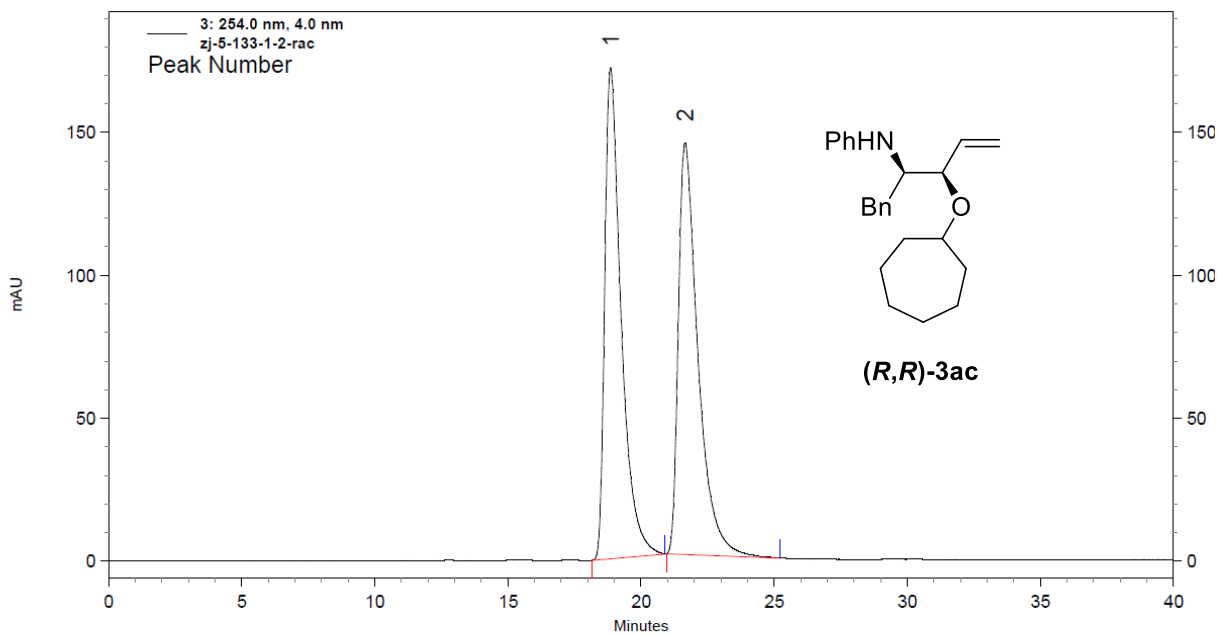
3: 250 nm, 4
nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6,893	49,790	252
2	8,067	50,210	252



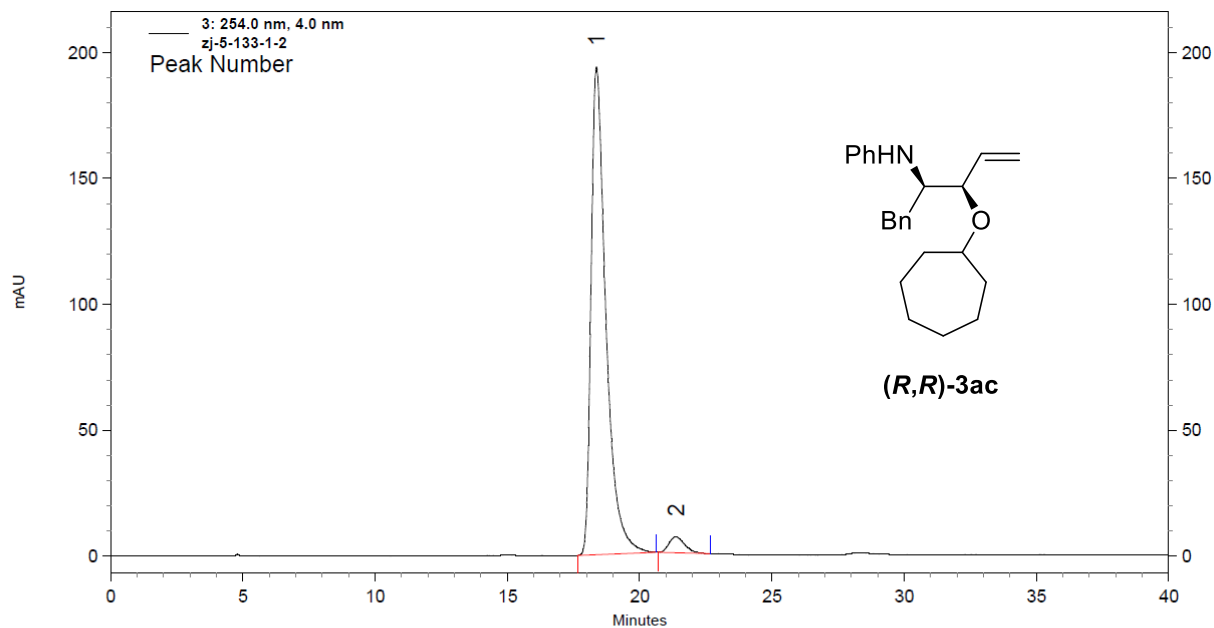
3: 250 nm, 4
nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6,900	85,168	252
2	8,080	14,832	252



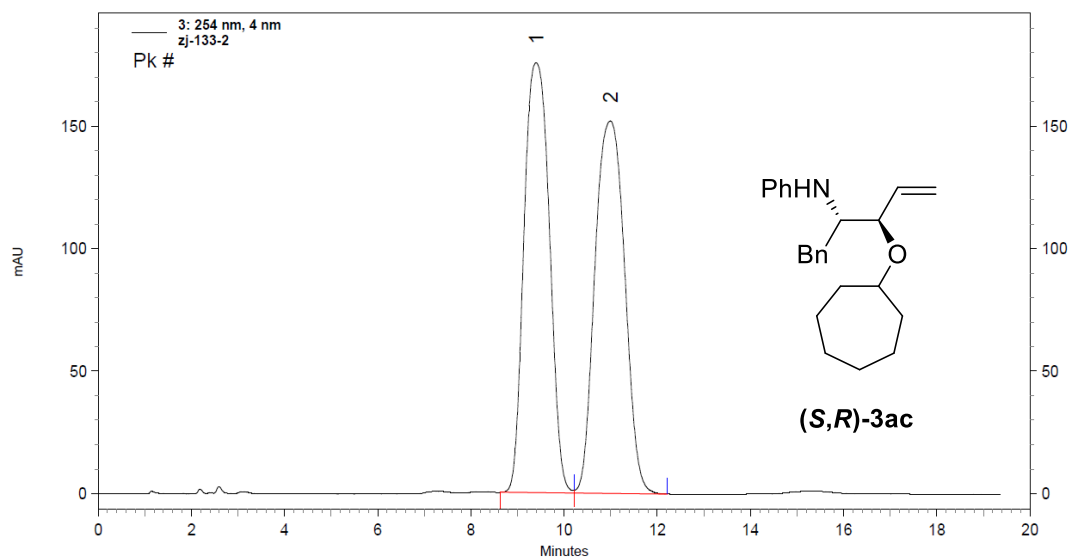
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18.853	49.921	249.000
2	21.653	50.079	249.000



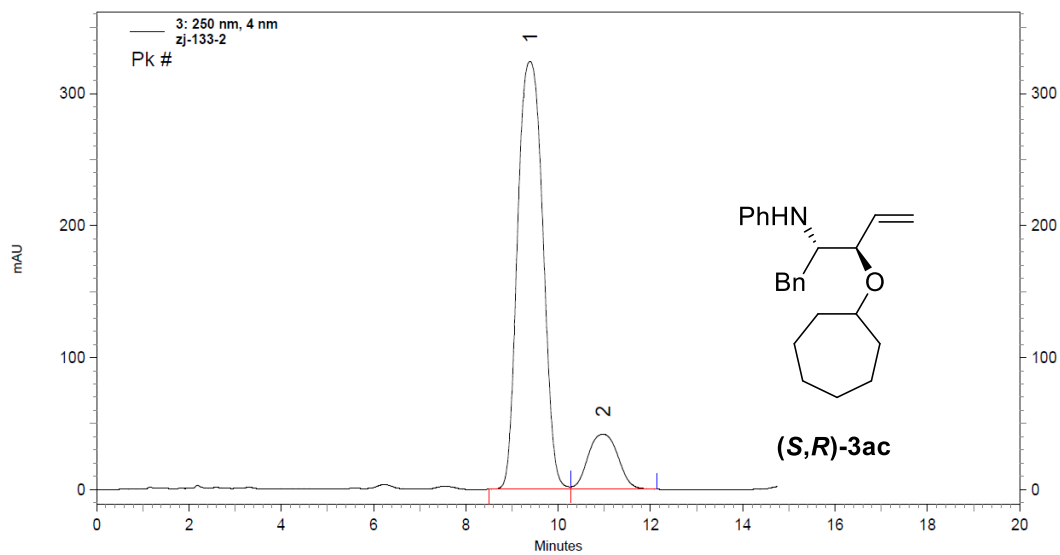
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18.367	96.624	249.000
2	21.367	3.376	202.000



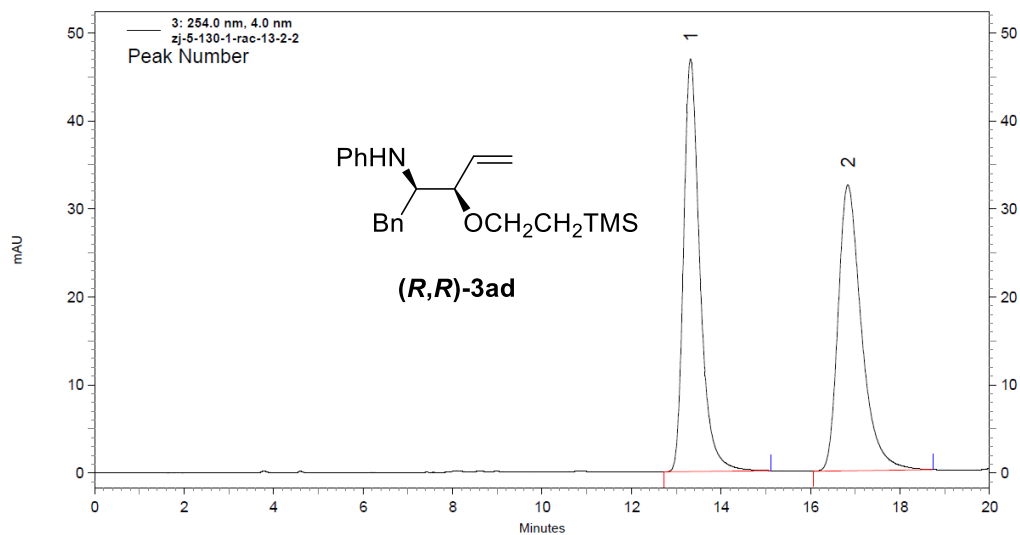
3: 254 nm, 4
nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9,400	49,646	252
2	10,993	50,354	252



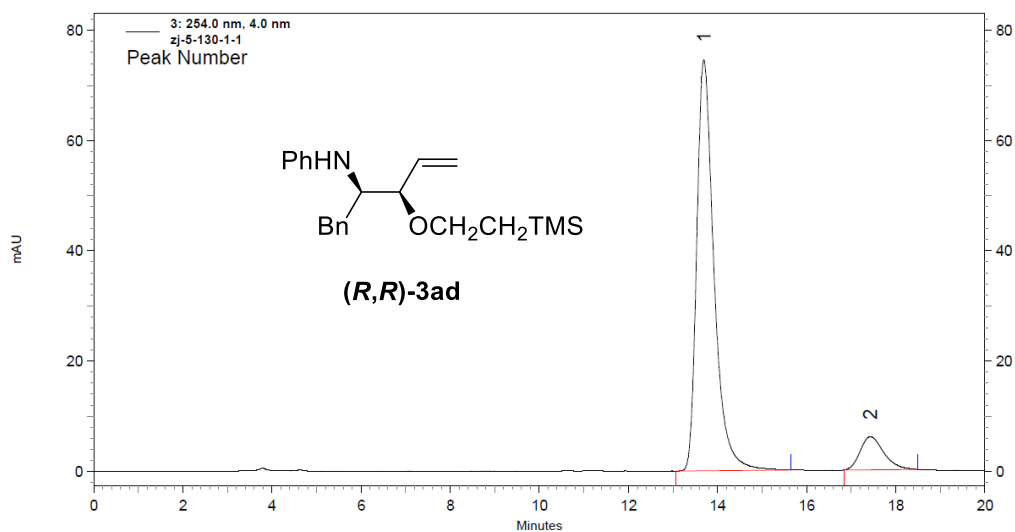
3: 250 nm, 4
nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9,387	86,721	252
2	10,973	13,279	252



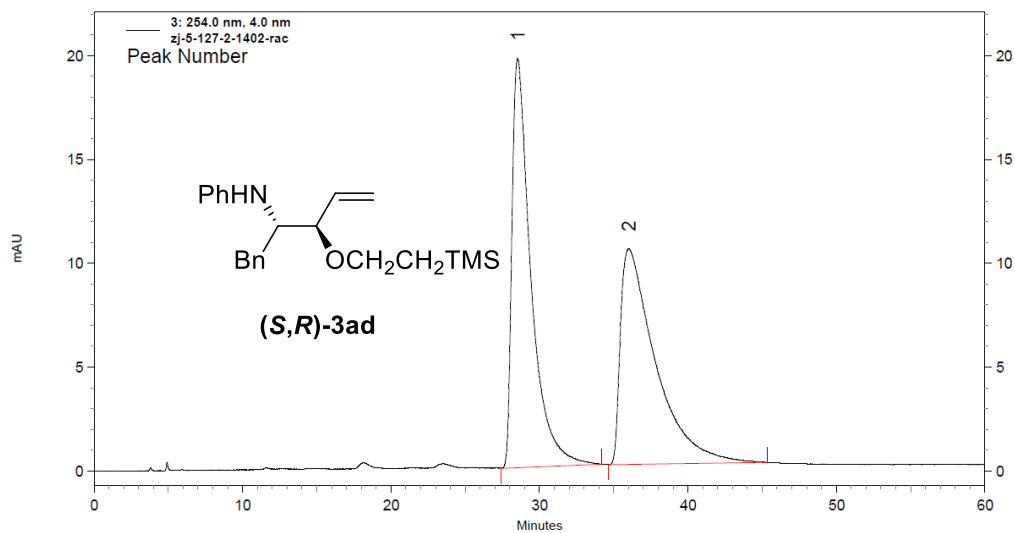
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	13.320	50.218	249.000
2	16.833	49.782	202.000



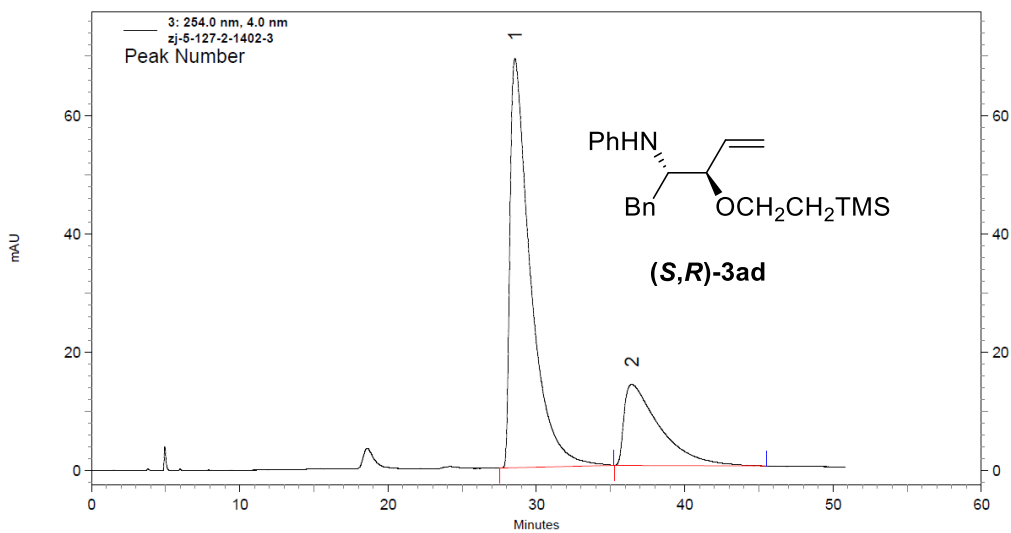
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	13.693	90.052	249.000
2	17.427	9.948	204.000



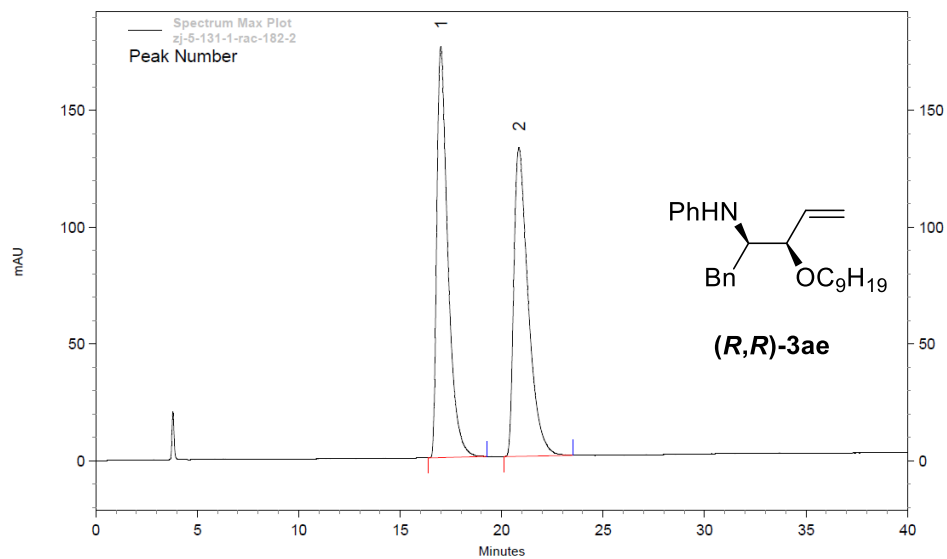
3: 254.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	28.520	50.682	249.000
2	36.000	49.318	248.000



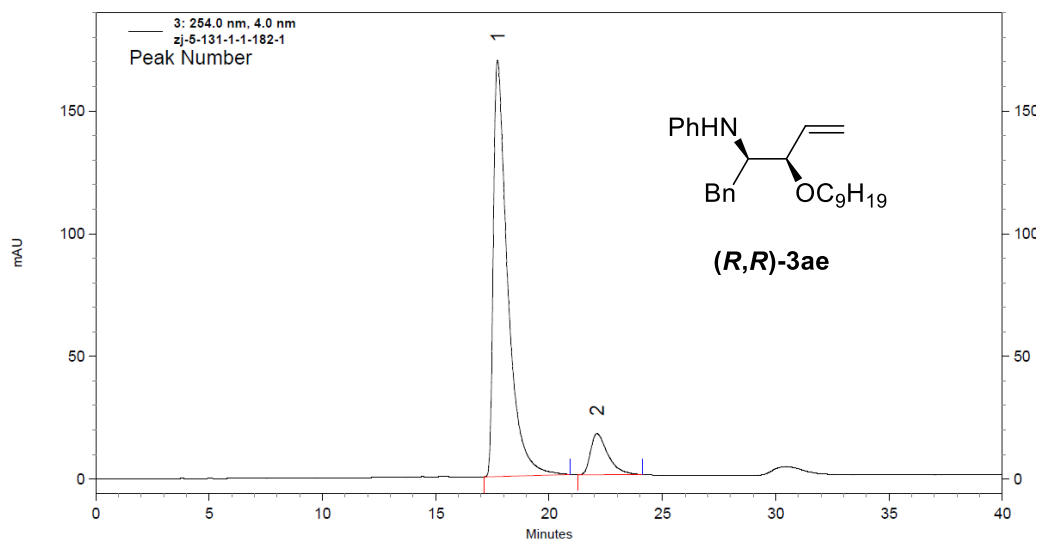
3: 254.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	28.553	74.339	249.000
2	36.427	25.661	248.000



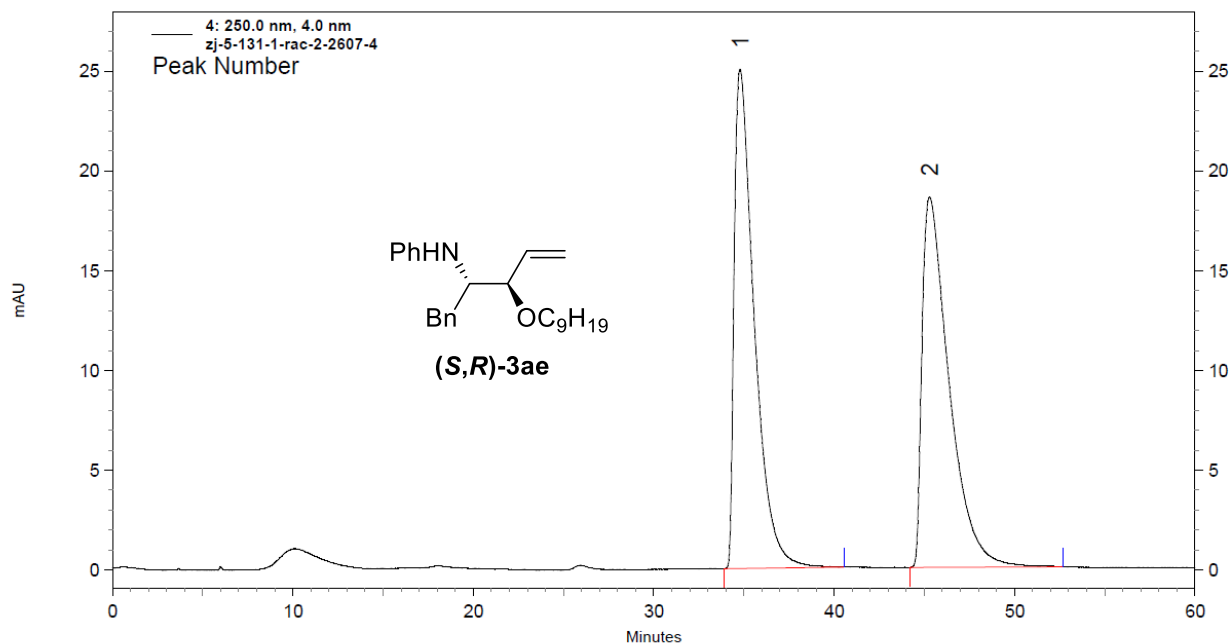
Spectrum Max
Plot Results

Pk #	Retention Time	Area Percent	Lambda Max
1	17.000	50.610	249.000
2	20.853	49.390	249.000



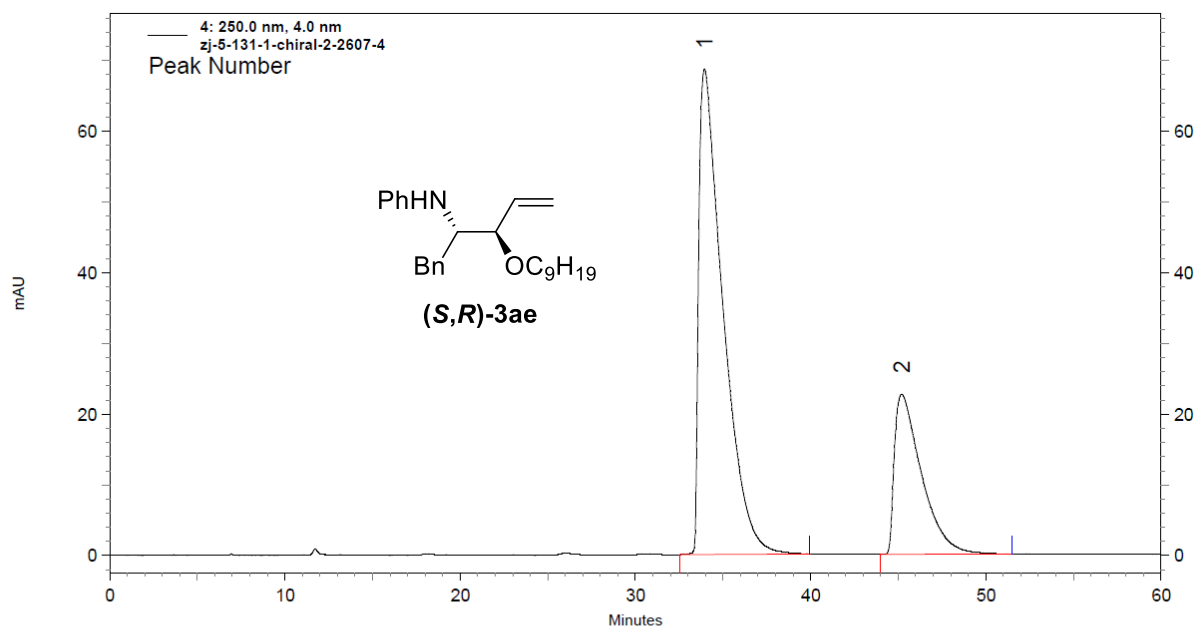
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	17.727	89.328	249.000
2	22.113	10.672	249.000



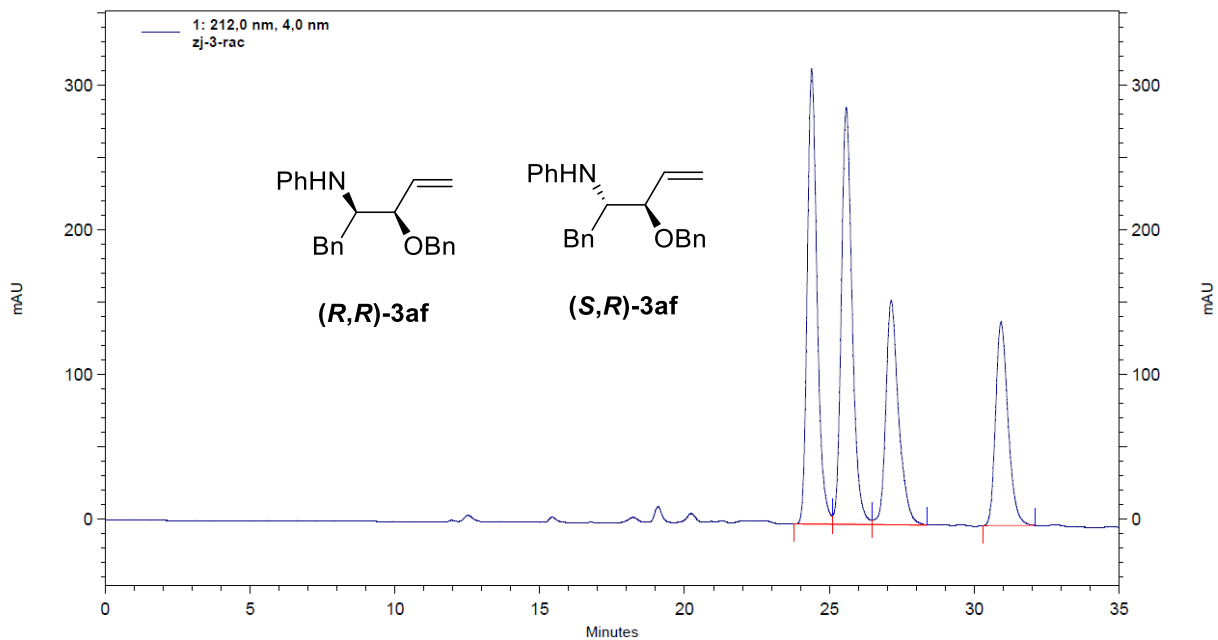
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	34.787	50.002	248.000
2	45.287	49.998	248.000



4: 250.0 nm,
4.0 nm Results

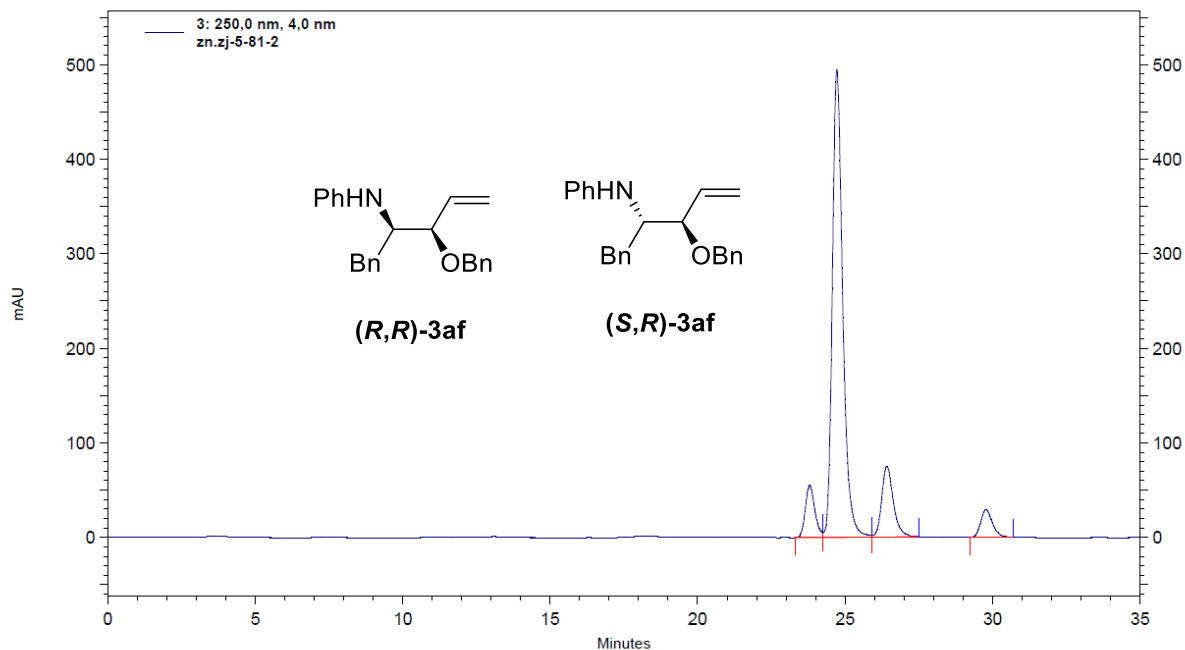
Pk #	Retention Time	Area Percent	Lambda Max
1	33.940	73.040	248.000
2	45.193	26.960	248.000



1: 212,0 nm, 4,0 nm

Results

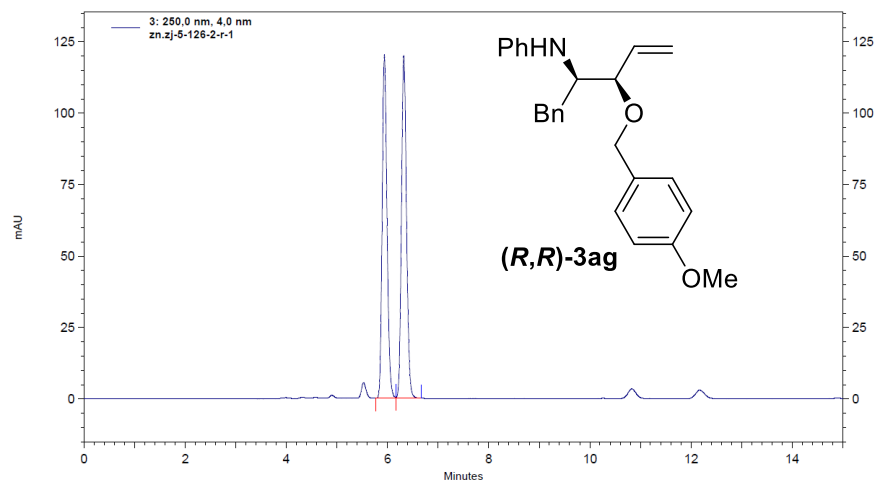
Peak Number	Retention Time	Area Percent	Area
1	24,392	30,976	991476172
2	25,586	31,366	1003967754
3	27,136	19,996	640038975
4	30,927	17,661	565287933
Totals		100,000	3200770834



3: 250,0 nm, 4,0 nm

Results

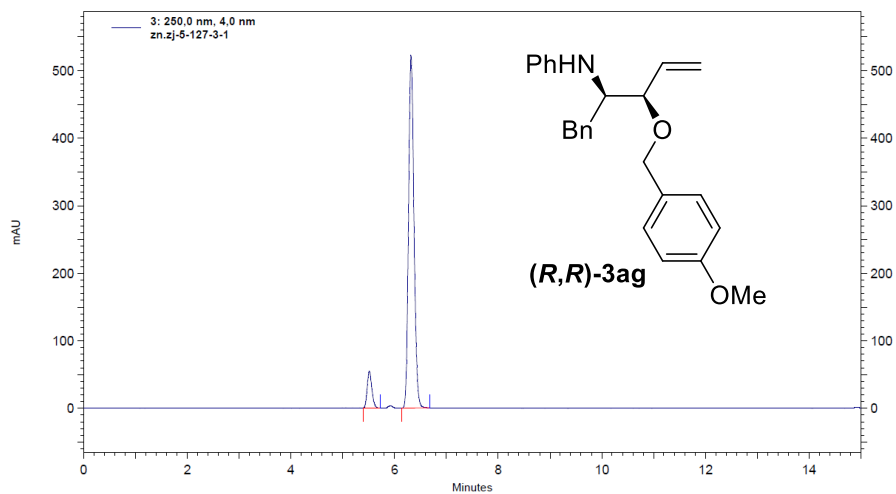
Peak Number	Retention Time	Area Percent	Area
1	23,804	7,662	167004612
2	24,727	74,693	1627968002
3	26,420	12,640	275496552
4	29,779	5,005	109075510
Totals		100,000	2179544676



3: 250,0 nm, 4,0 nm

Results

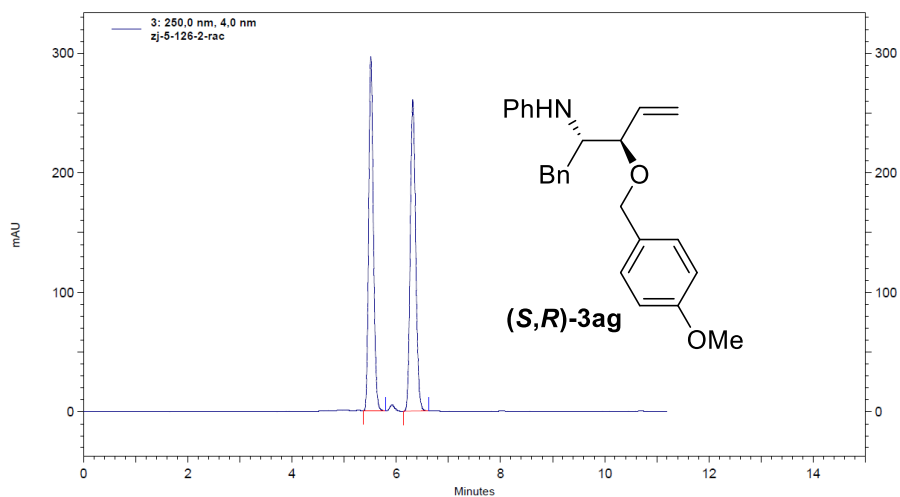
Peak Number	Retention Time	Area Percent	Area
1	5,940	48,850	106547867
2	6,323	51,150	111566431
Totals		100,000	218114298



3: 250,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	5,515	8,134	45170027
2	6,320	91,866	510141643
Totals		100,000	555311670

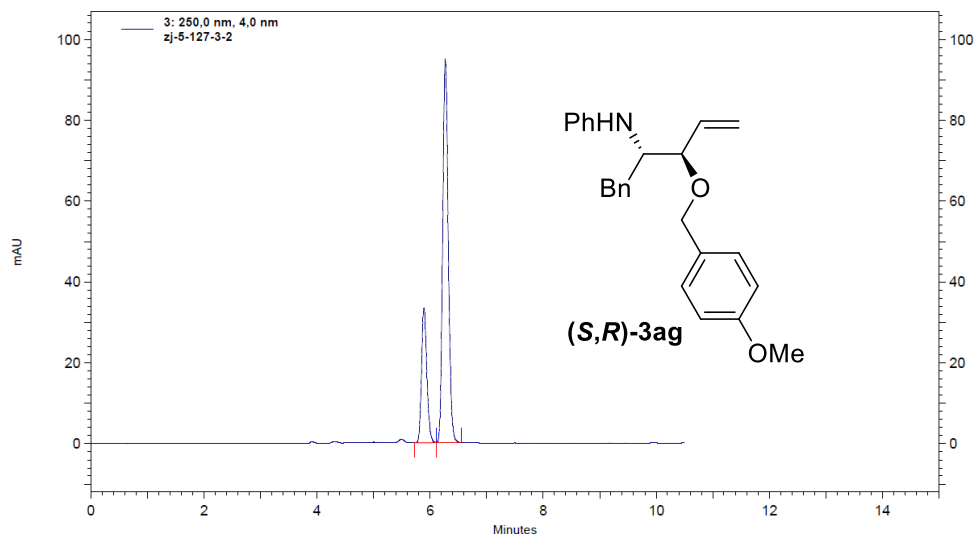


3: 250,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	5,513	49,511	248182832
2	6,318	50,489	253081495

Totals		100,000	501264327
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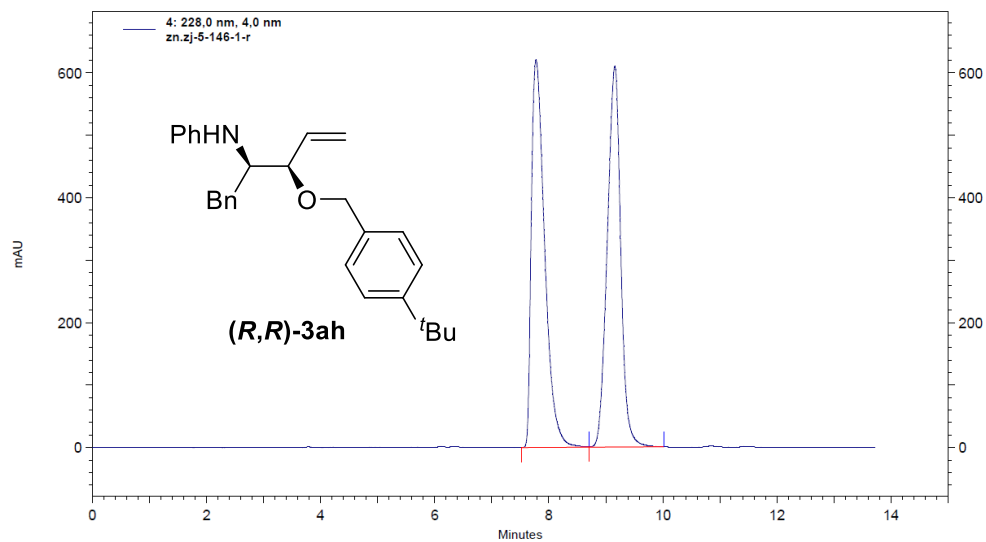


3: 250,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	5,893	24,916	28878672
2	6,270	75,084	87026744

Totals		100,000	115905416
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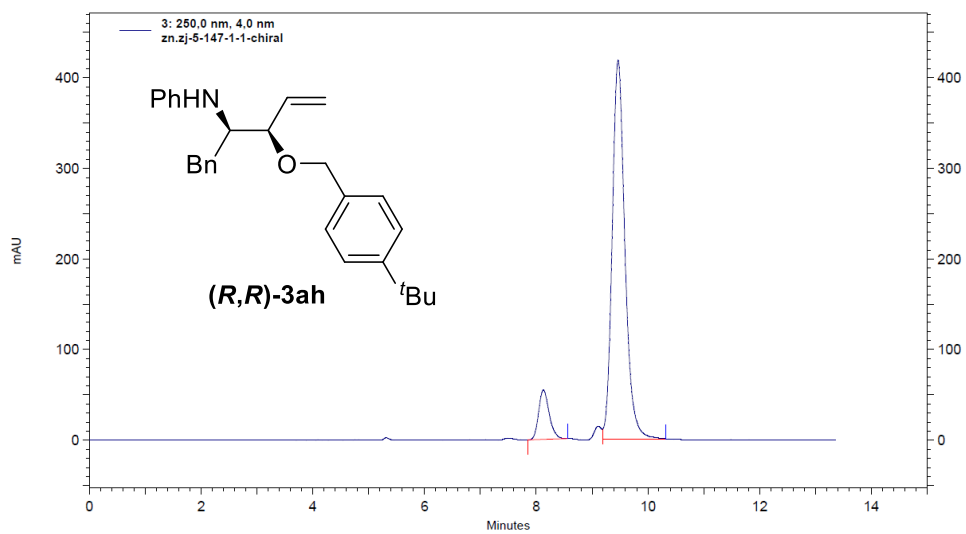


4: 228,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	7,778	50,219	1352967153
2	9,159	49,781	1341184968

Totals		100,000	2694152121
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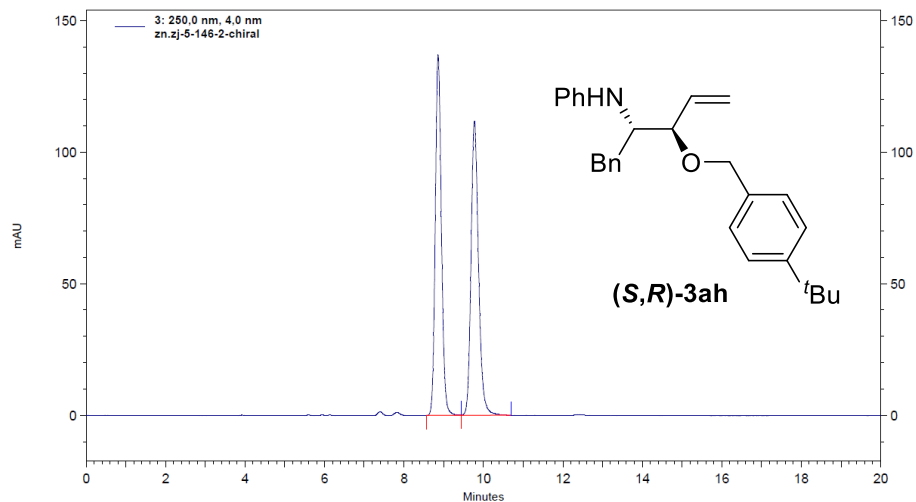


3: 250,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	8,129	9,770	96012571
2	9,467	90,230	886710094

Totals		100,000	982722665
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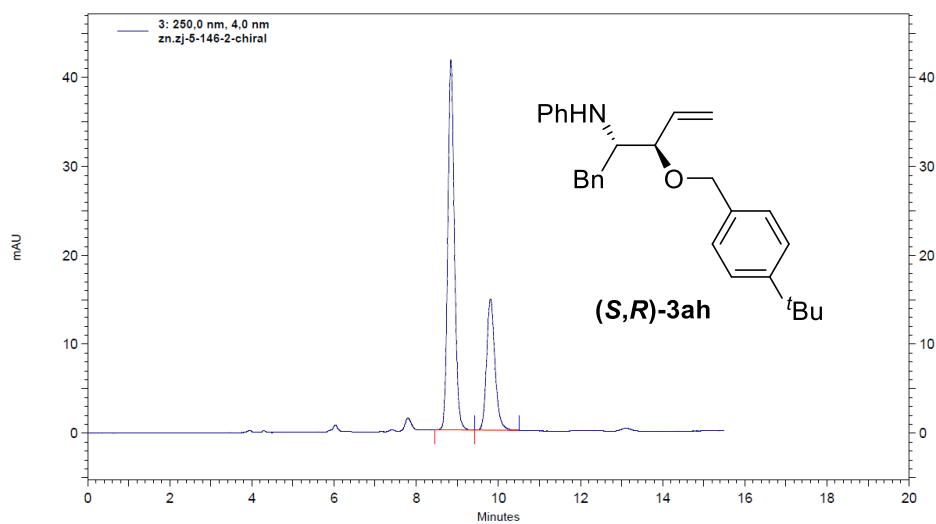


3: 250,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	8,860	50,011	196841353
2	9,773	49,989	196753103

Totals		100,000	393594456
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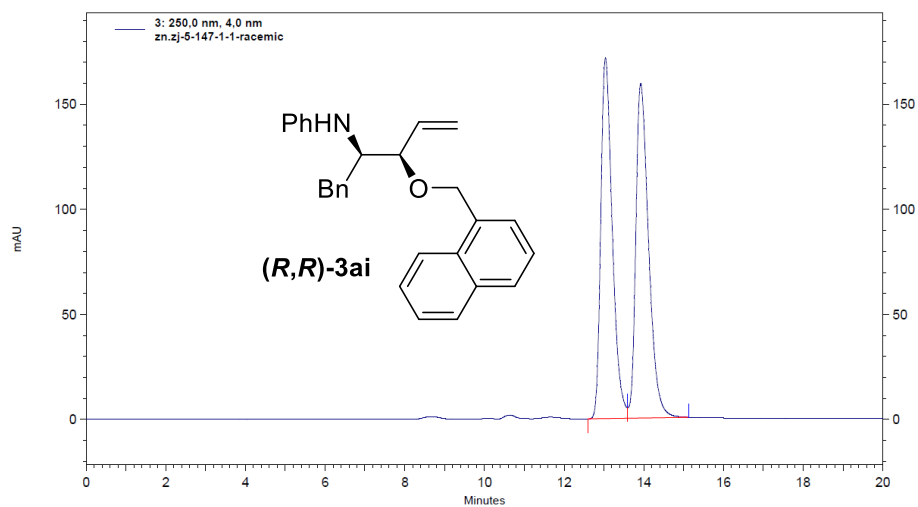


3: 250,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	8,845	69,073	62344630
2	9,807	30,927	27914022

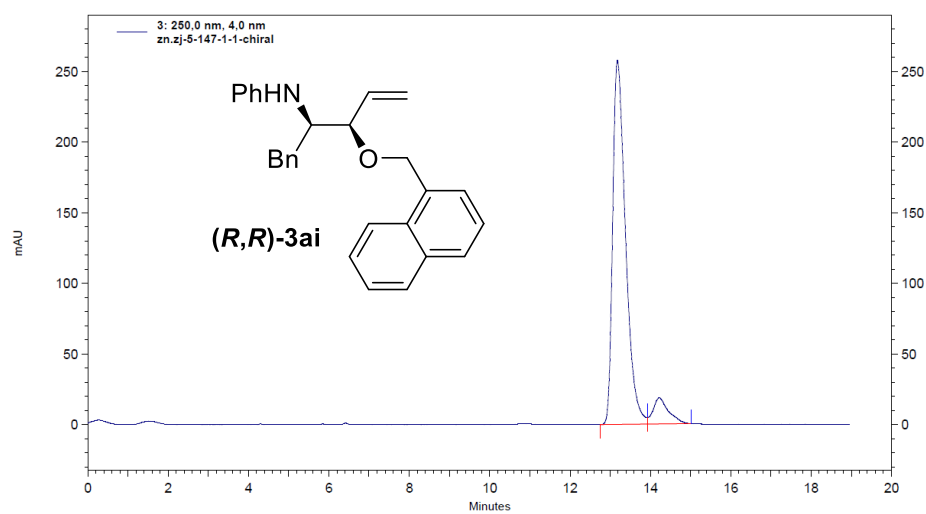
Totals		100,000	90258652
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3: 250,0 nm, 4,0 nm

Results

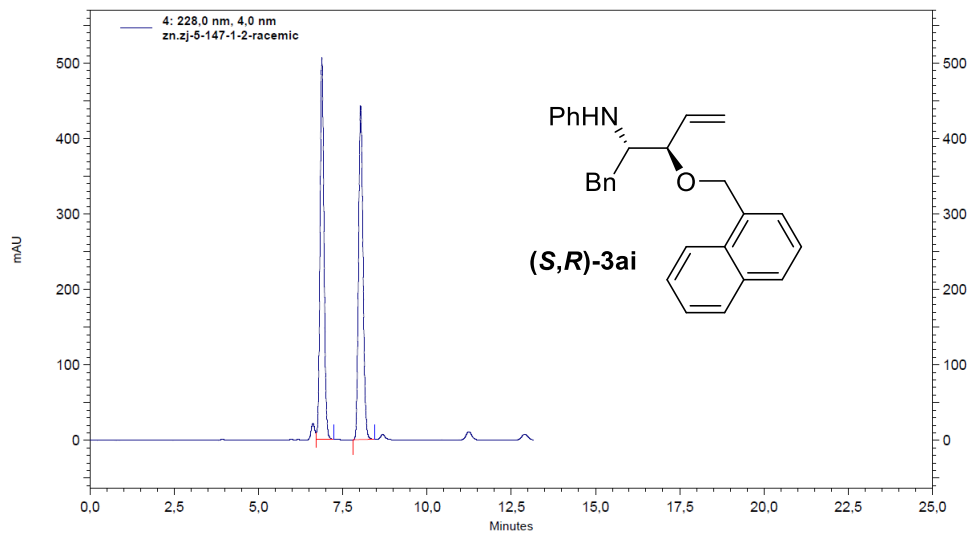
Peak Number	Retention Time	Area Percent	Area
1	13,038	49,198	462086029
2	13,923	50,802	477142820
Totals		100,000	939228849



3: 250,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	13,182	92,073	768827548
2	14,223	7,927	66188999
Totals		100,000	835016547

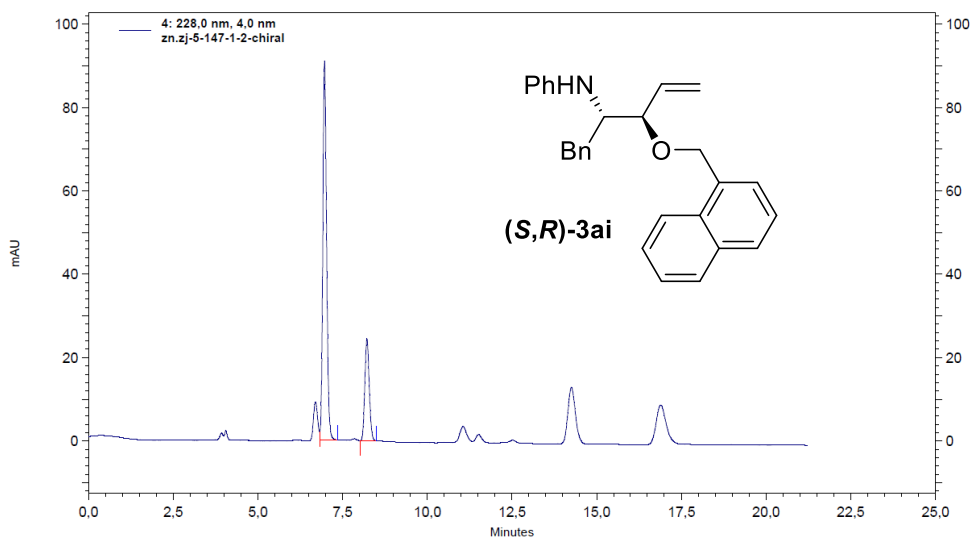


4: 228,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	6,883	50,173	551757491
2	8,033	49,827	547959416

Totals		100,000	1099716907
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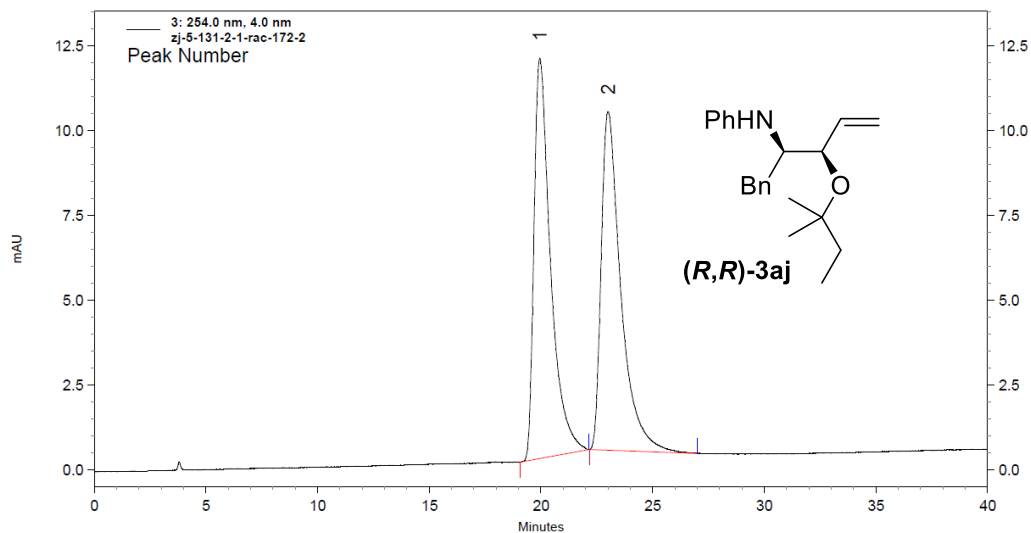


4: 228,0 nm, 4,0 nm

Results

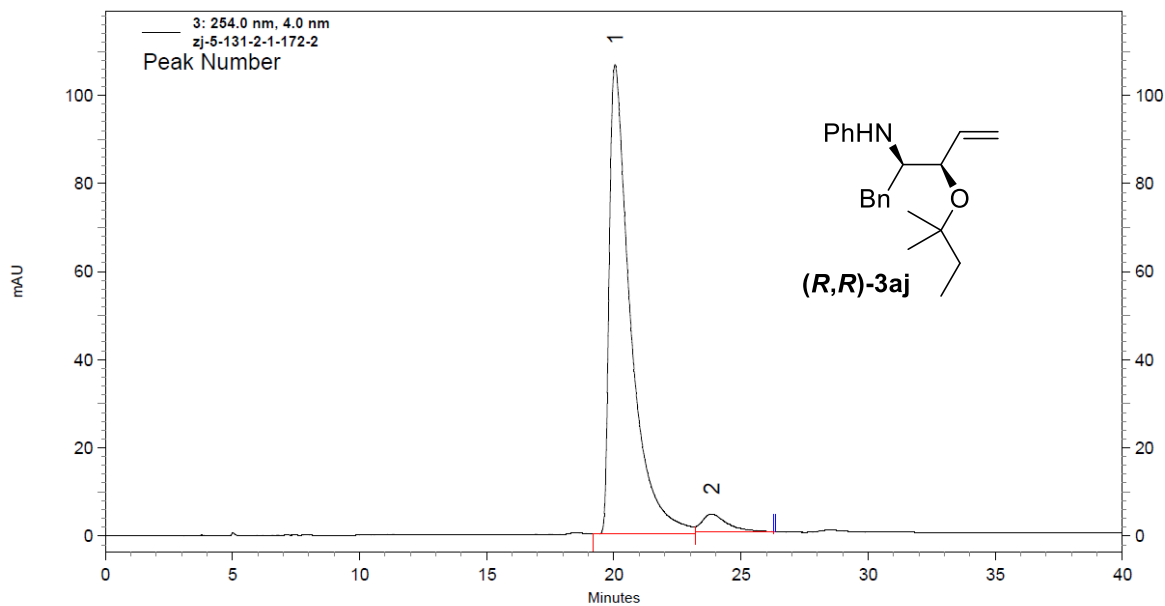
Peak Number	Retention Time	Area Percent	Area
1	6,970	76,132	94840474
2	8,220	23,868	29732828

Totals		100,000	124573302
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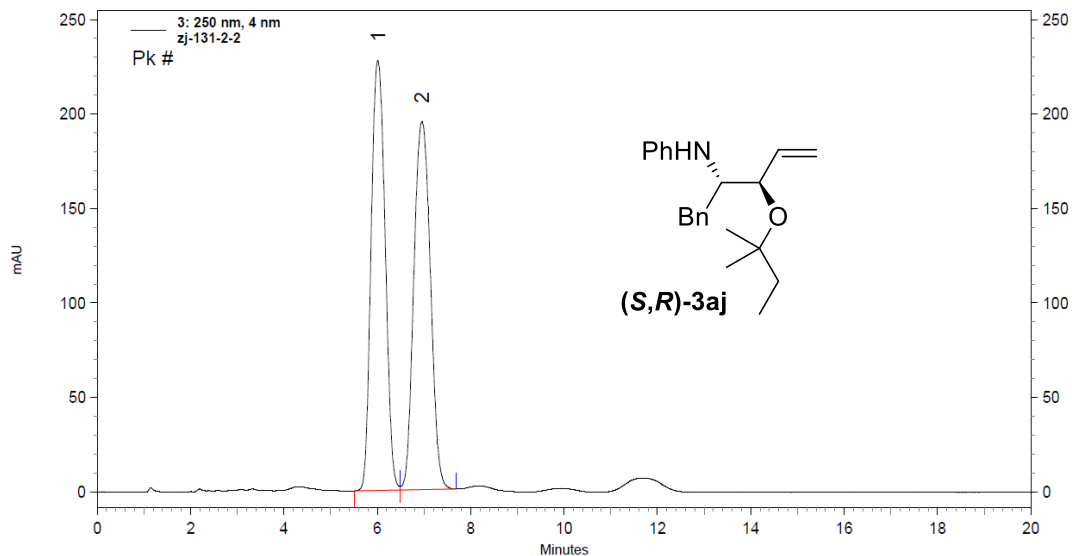
3: 254.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.947	49.857	203.000
2	23.007	50.143	203.000



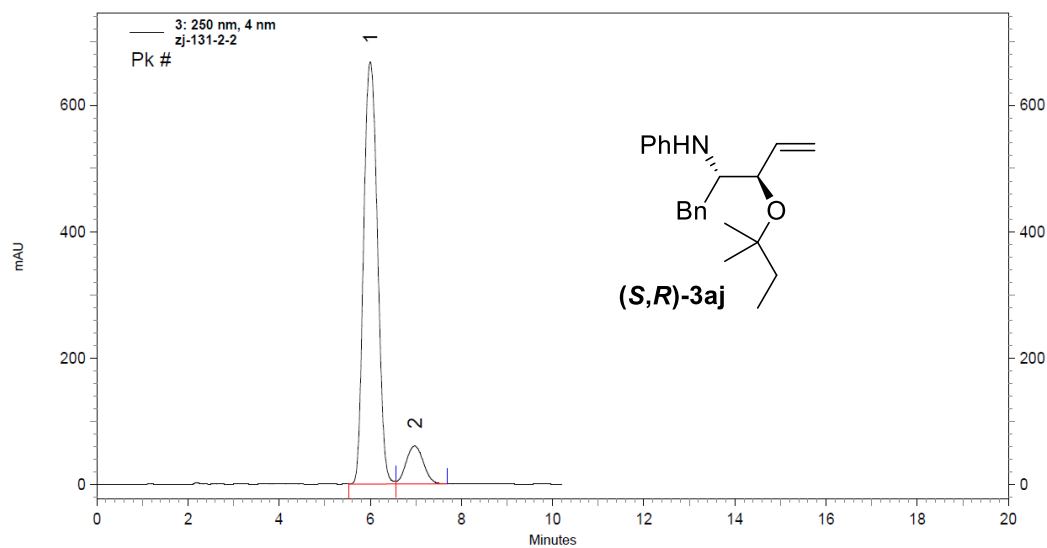
3: 254.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	20.047	95.774	249.000
2	23.840	4.226	249.000



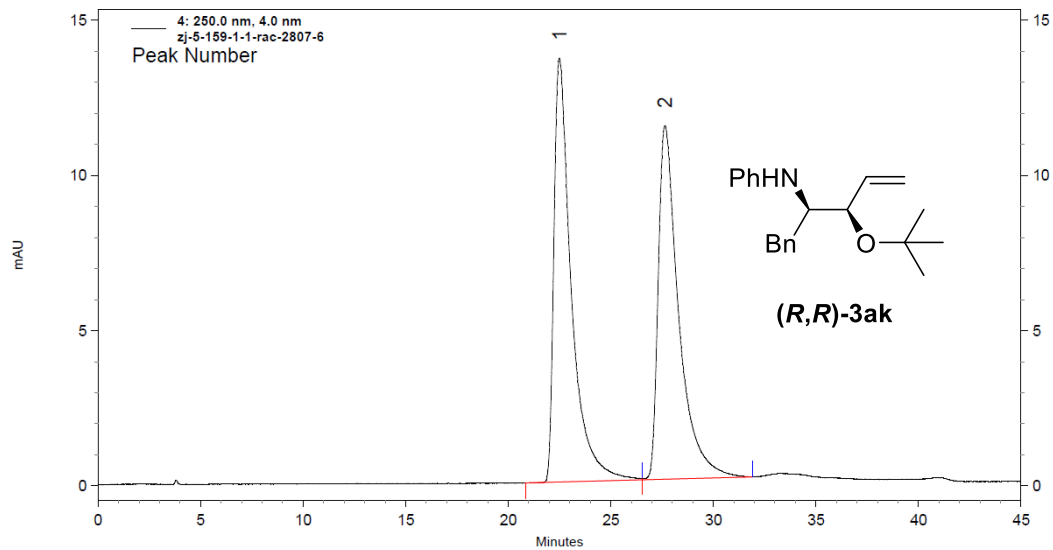
3: 250 nm, 4
nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6,013	49,658	253
2	6,953	50,342	253



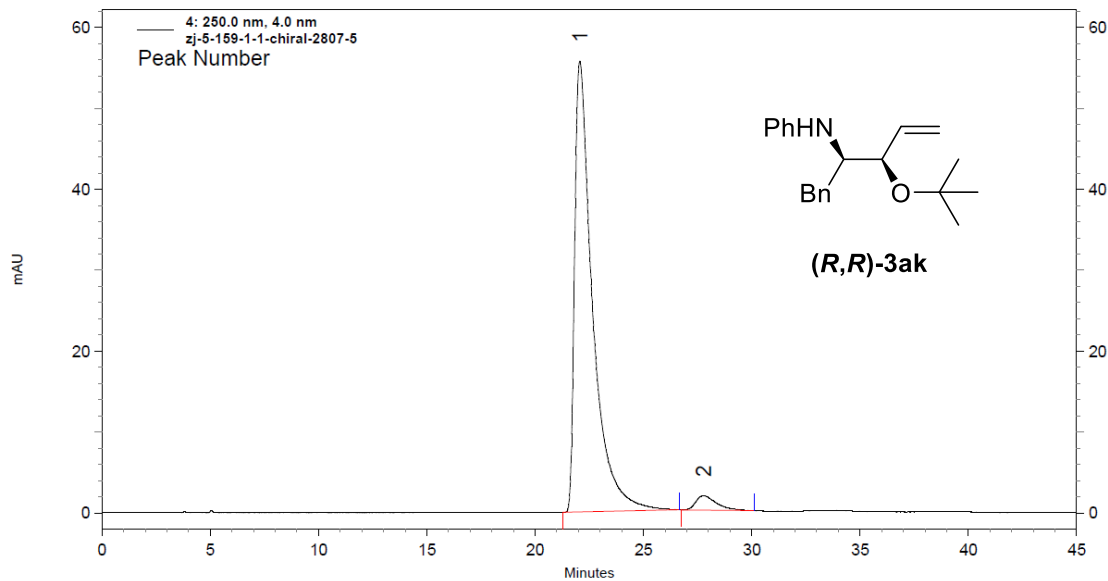
3: 250 nm, 4
nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6,000	89,892	253
2	6,973	10,108	253



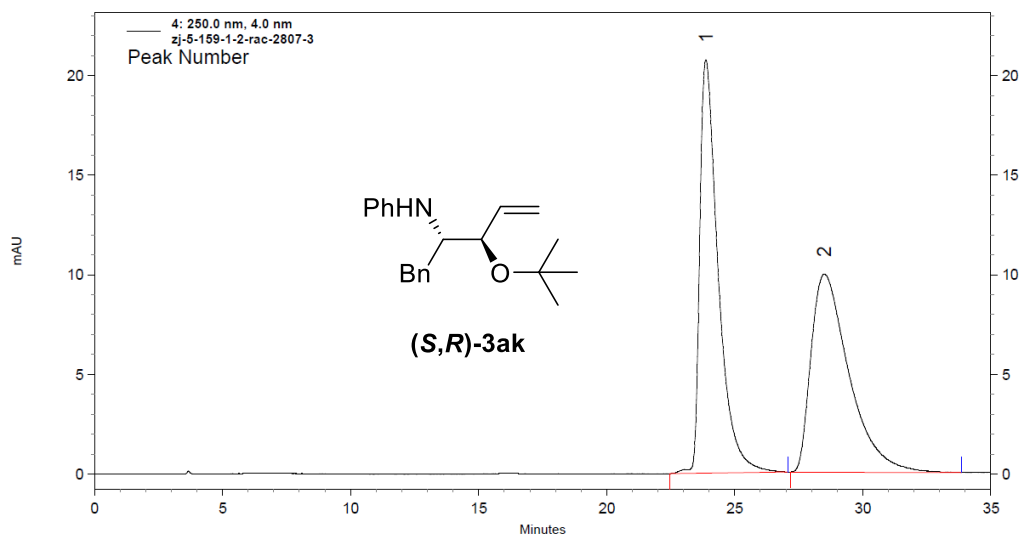
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	22.493	50.414	249.000
2	27.647	49.586	249.000



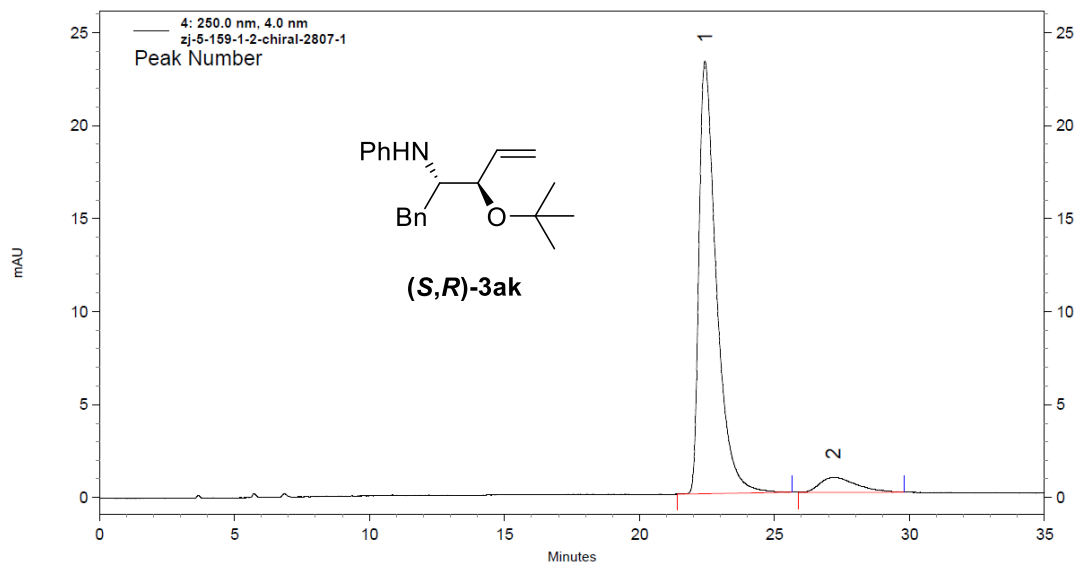
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	22.067	96.384	249.000
2	27.773	3.616	249.000



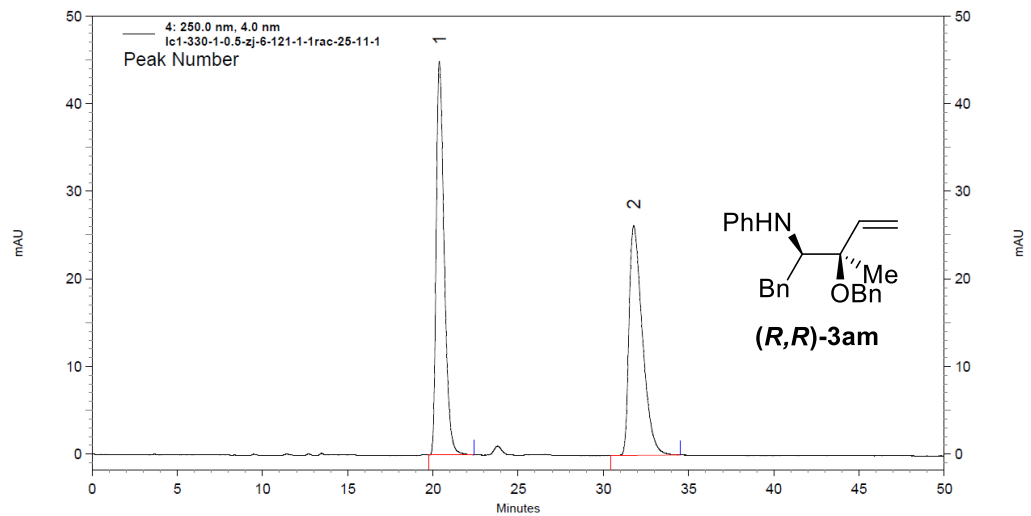
4: 250.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	23.873	50.324	250.000
2	28.500	49.676	203.000



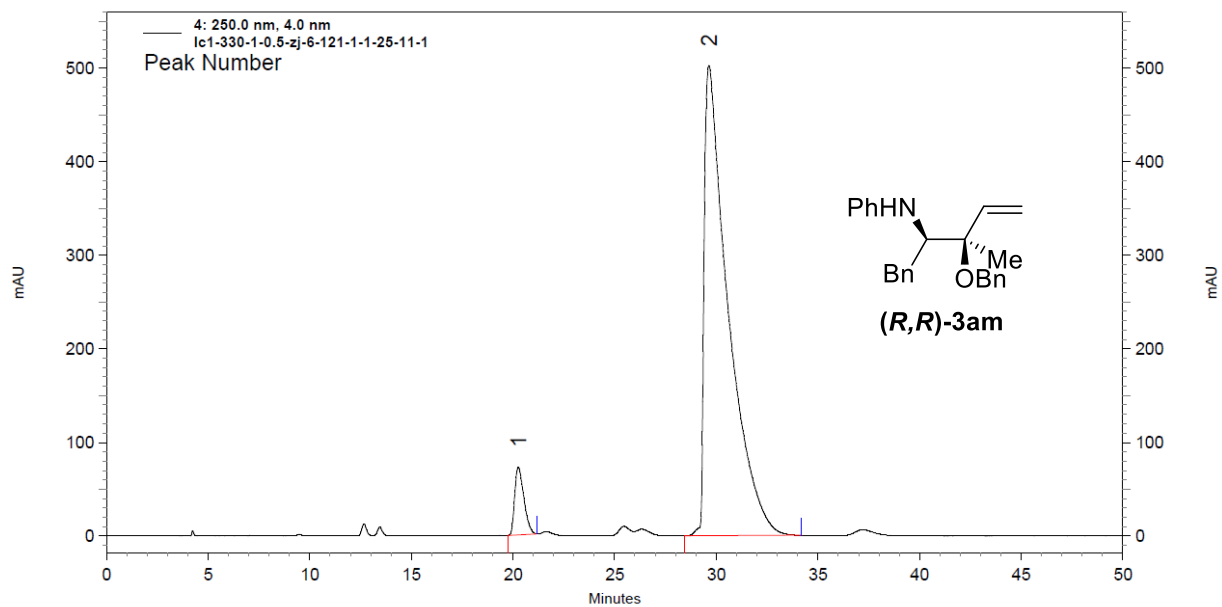
4: 250.0 nm, 4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	22.427	93.271	202.000
2	27.180	6.729	214.000



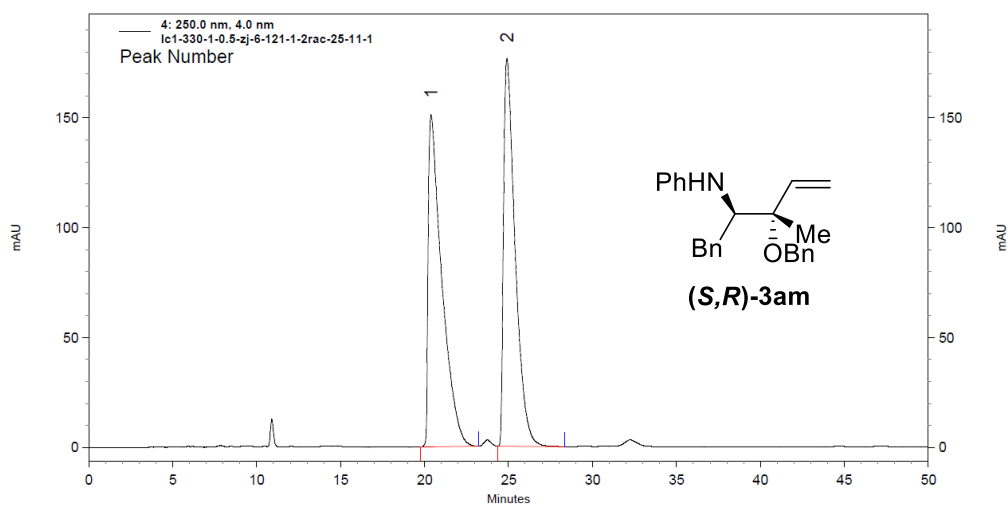
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	20.380	50.387	202.000
2	31.780	49.613	249.000



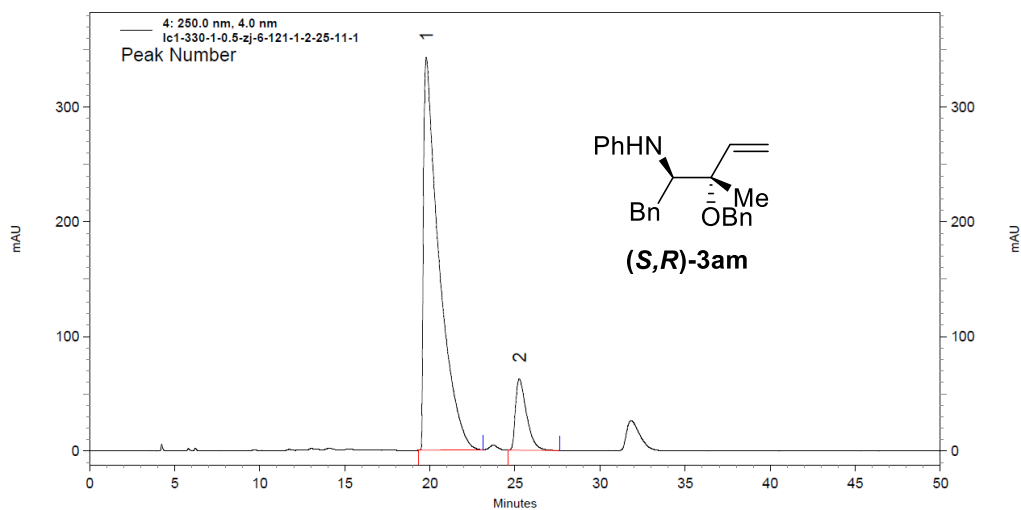
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	20.260	5.258	202.000
2	29.640	94.742	204.000



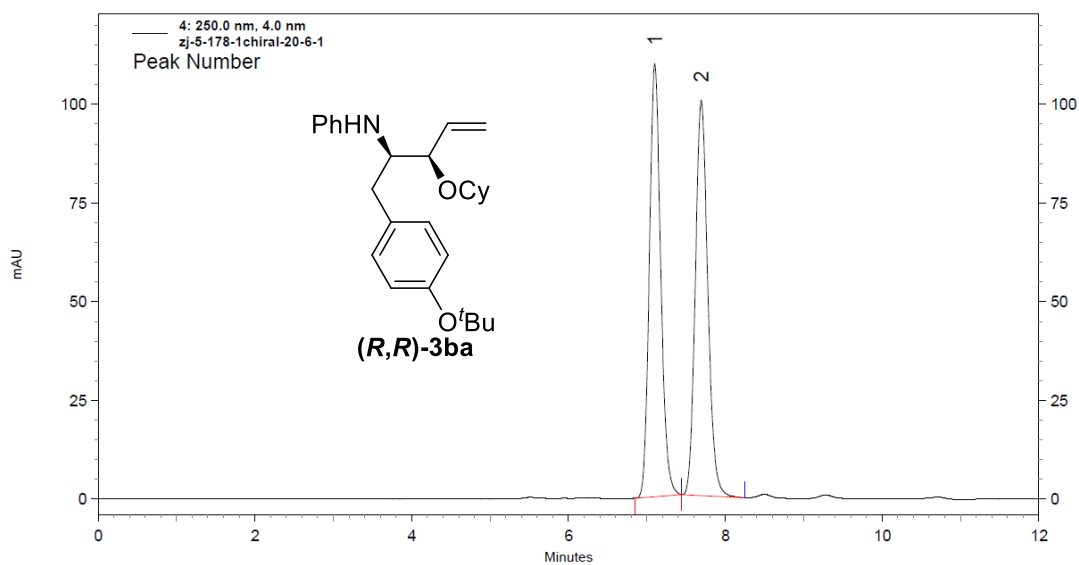
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	20.387	50.123	202.000
2	24.907	49.877	202.000



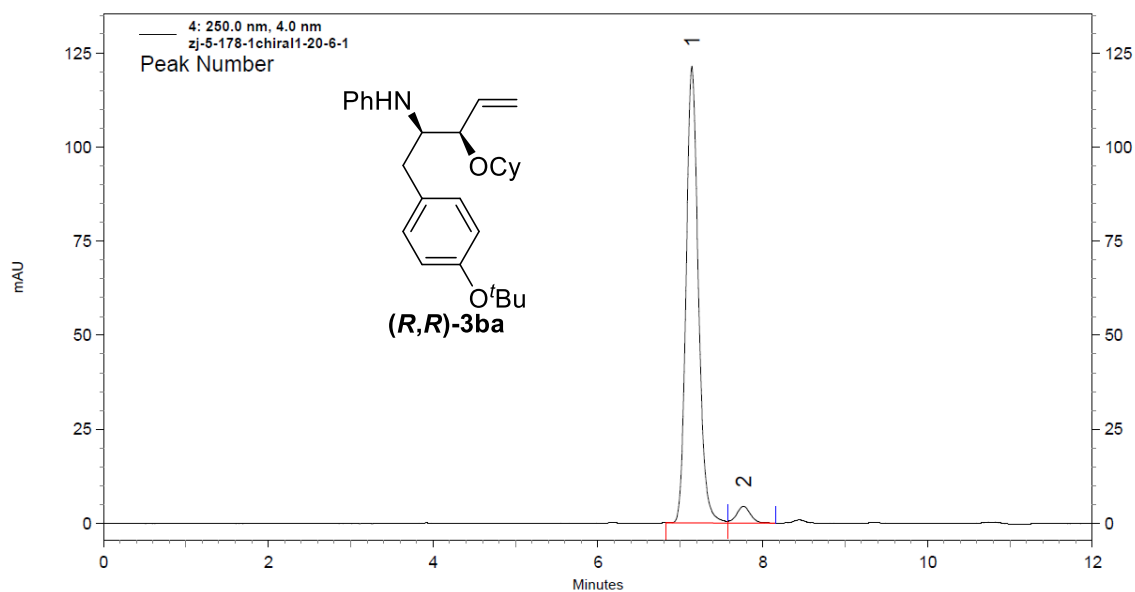
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.787	88.544	203.000
2	25.253	11.456	202.000



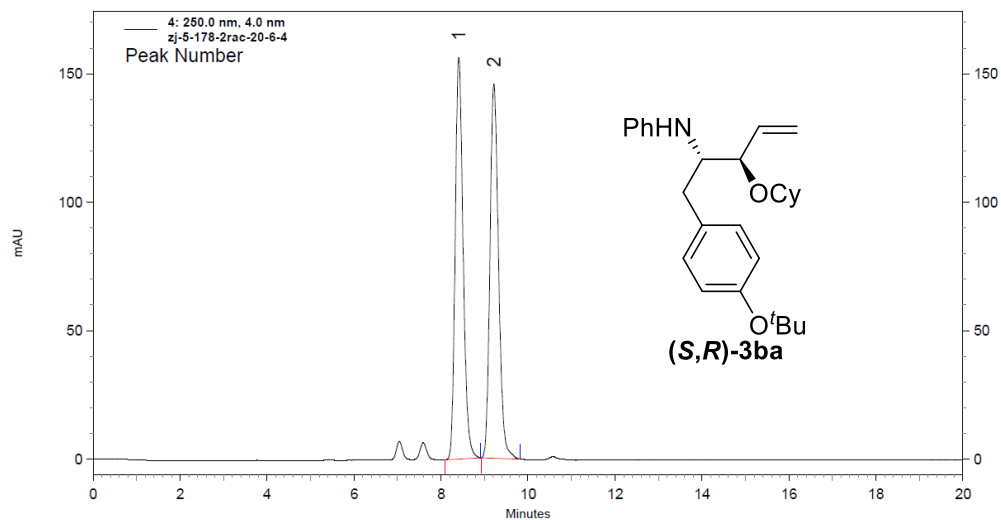
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.100	49.927	249.000
2	7.693	50.073	249.000



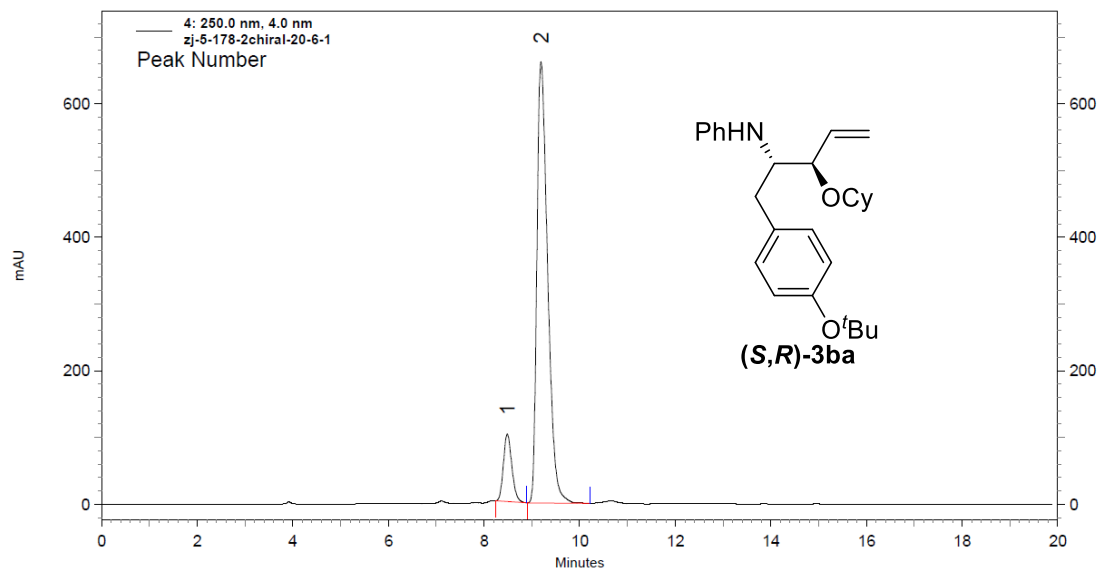
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.140	96.021	249.000
2	7.767	3.979	249.000



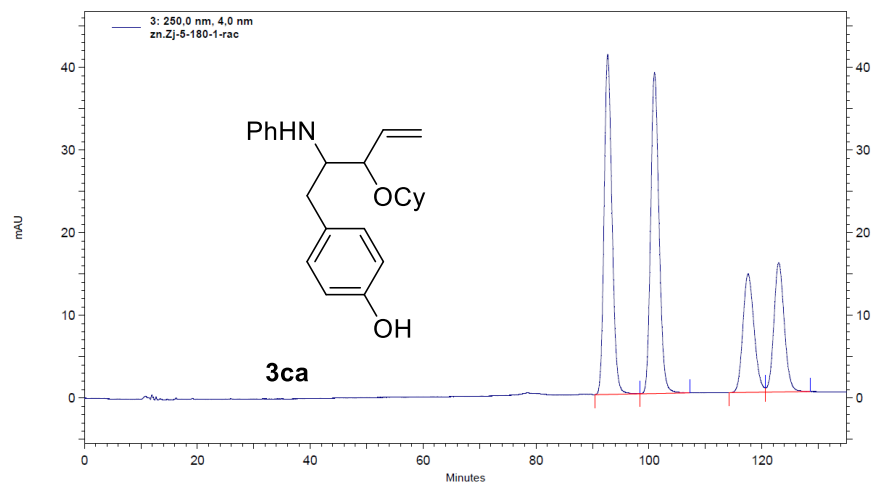
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.407	49.836	249.000
2	9.213	50.164	249.000



4: 250.0 nm,
4.0 nm Results

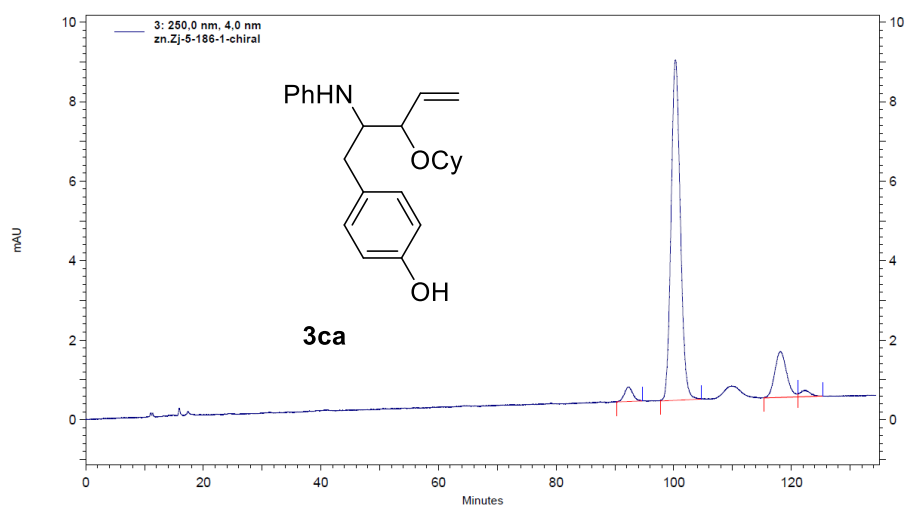
Pk #	Retention Time	Area Percent	Lambda Max
1	8.487	10.710	249.000
2	9.193	89.290	202.000



3: 250,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	92,703	33,325	534951495
2	100,983	33,450	536957433
3	117,575	16,494	264764226
4	122,993	16,731	268567728

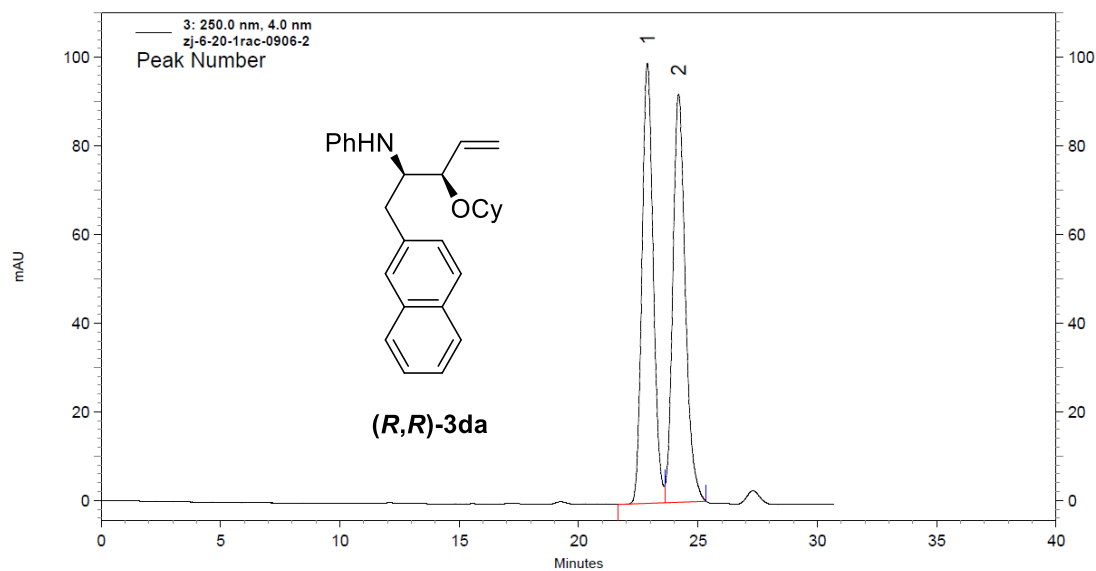
Totals		100,000	1605240882
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3: 250,0 nm, 4,0 nm
Results

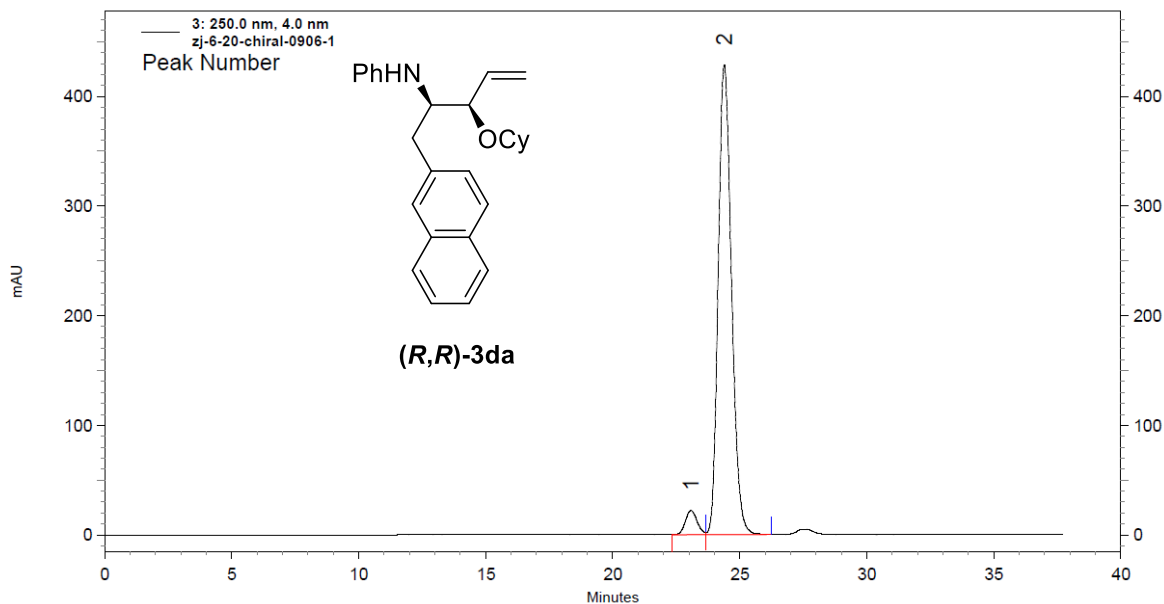
Peak Number	Retention Time	Area Percent	Area
1	92,280	3,195	4941581
2	100,292	81,097	125448451
3	118,130	14,071	21766694
4	122,288	1,637	2531845

Totals		100,000	154688571
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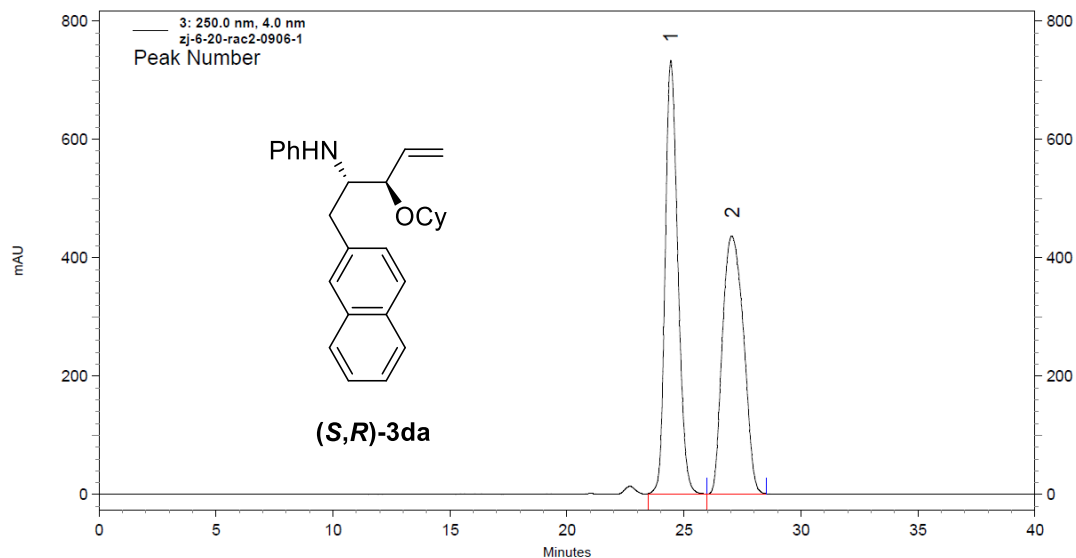
3: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	22.873	49.124	223.000
2	24.187	50.876	223.000



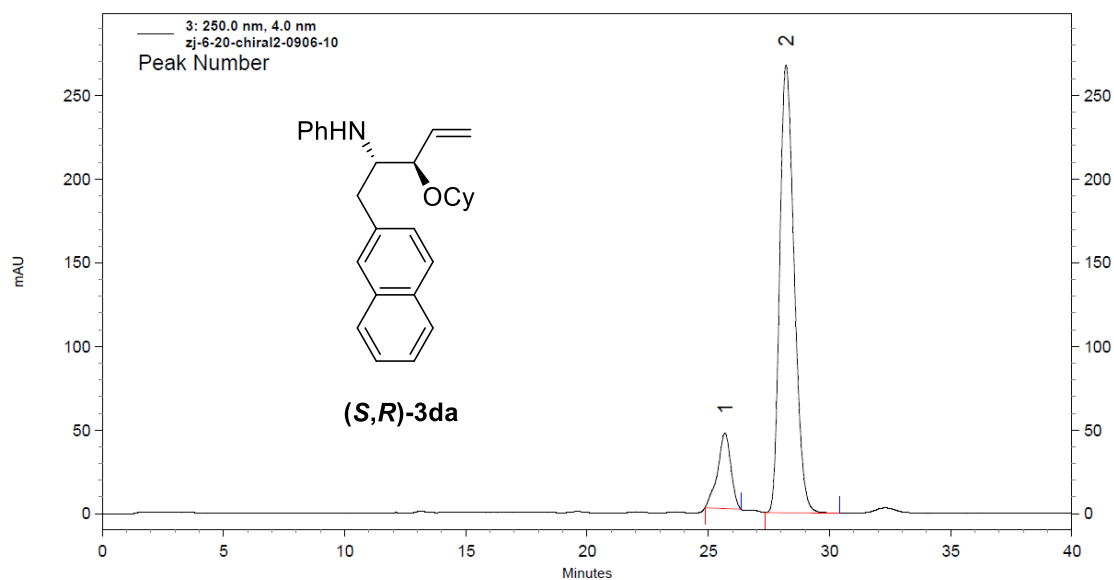
3: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	23.080	4.372	223.000
2	24.387	95.628	223.000



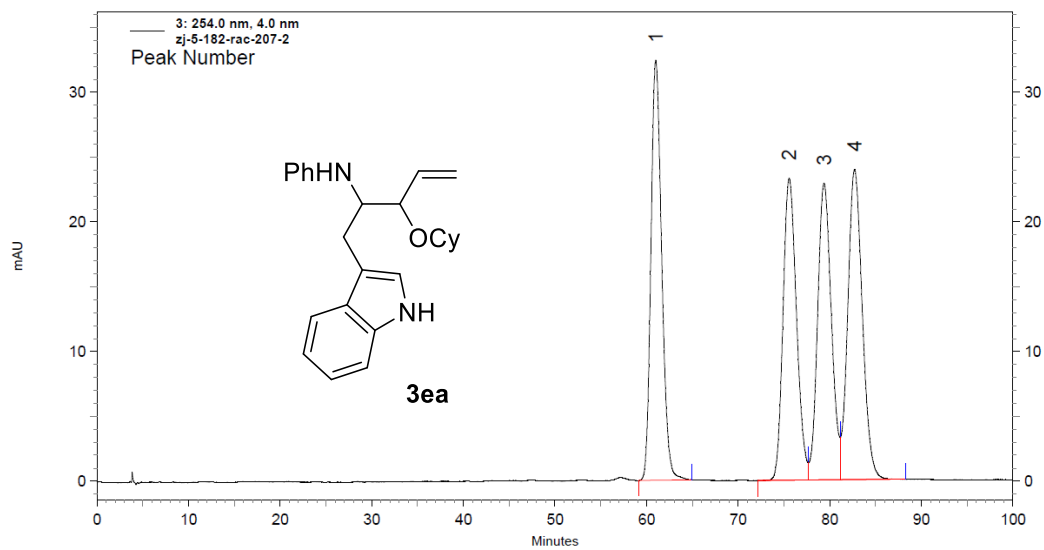
3: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24.433	50.204	223.000
2	27.047	49.796	224.000



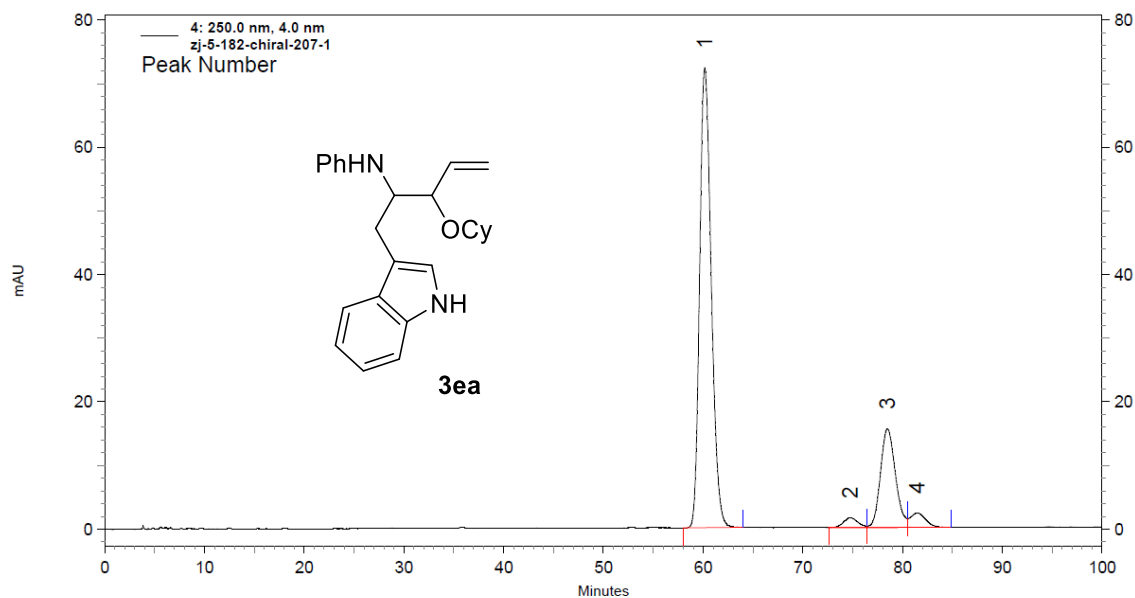
3: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	25.687	13.395	224.000
2	28.207	86.605	224.000



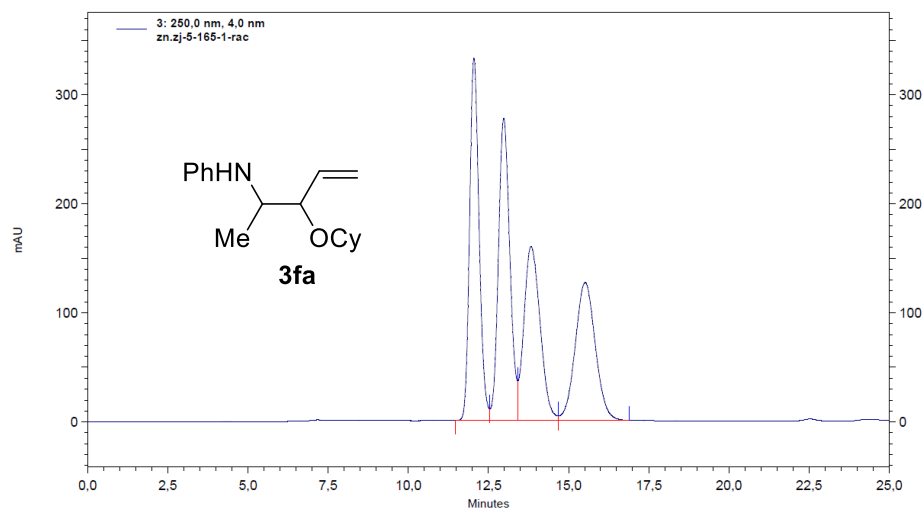
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	61.007	26.252	203.000
2	75.573	23.651	204.000
3	79.380	23.703	203.000
4	82.707	26.394	203.000



4: 250.0 nm,
4.0 nm Results

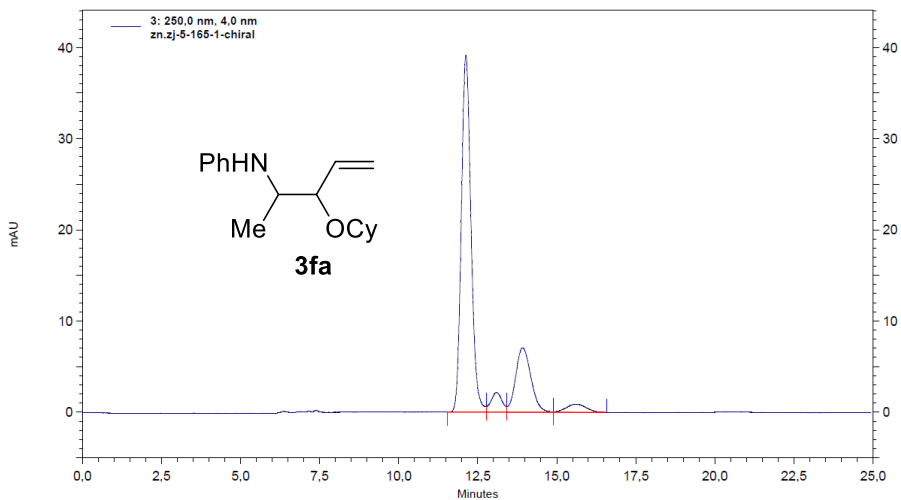
Pk #	Retention Time	Area Percent	Lambda Max
1	60.167	74.493	203.000
2	74.747	1.918	223.000
3	78.473	20.568	203.000
4	81.460	3.021	205.000



3: 250,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	12,052	27,500	916942840
2	12,978	27,660	922298627
3	13,832	22,651	755281364
4	15,517	22,189	739856422

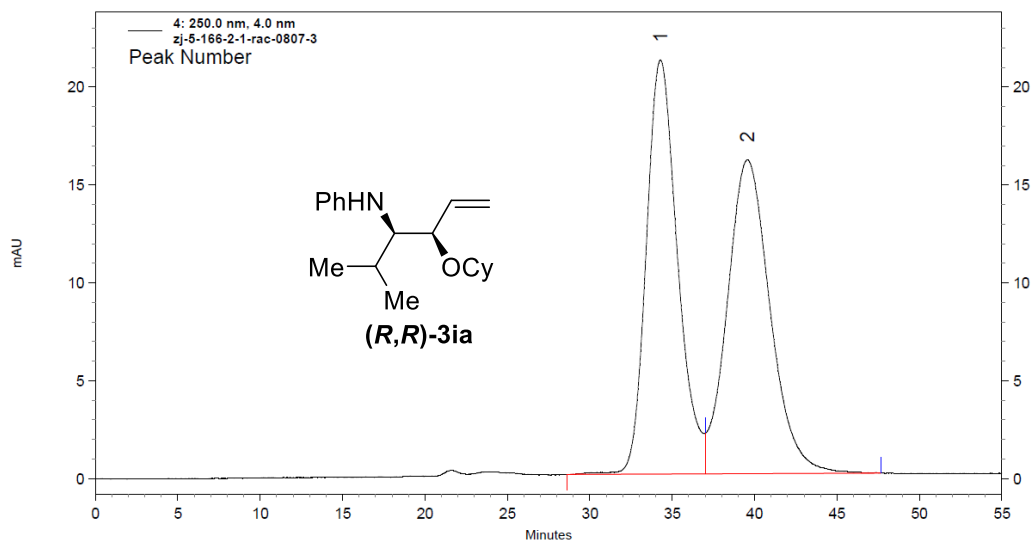
Totals		100,000	3334379253
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3: 250,0 nm, 4,0 nm
Results

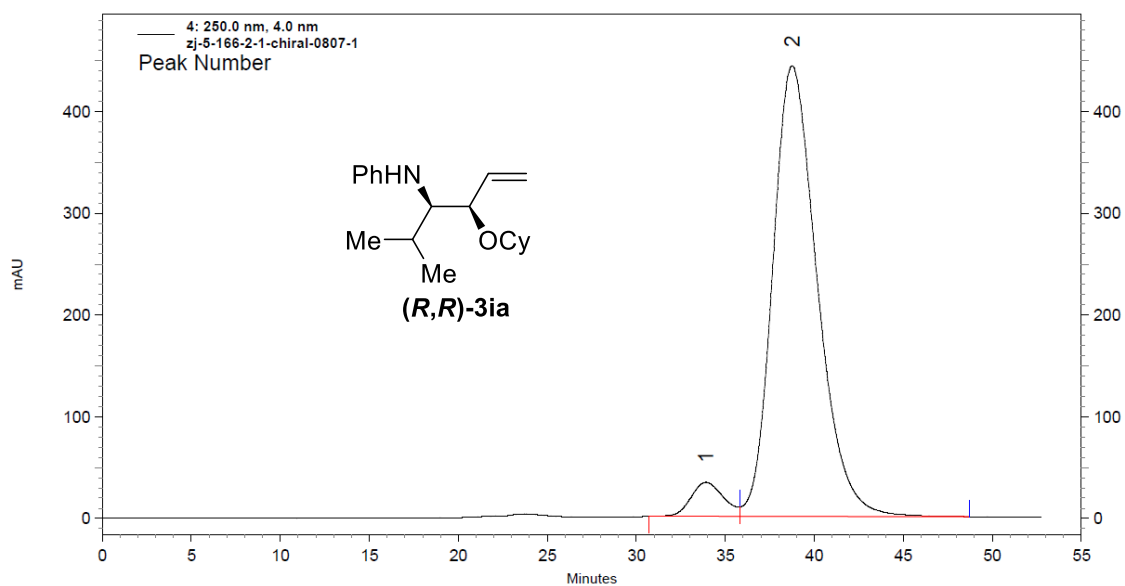
Peak Number	Retention Time	Area Percent	Area
1	12,128	71,504	111510362
2	13,097	4,573	7132299
3	13,918	20,457	31902180
4	15,628	3,466	5405515

Totals		100,000	155950356
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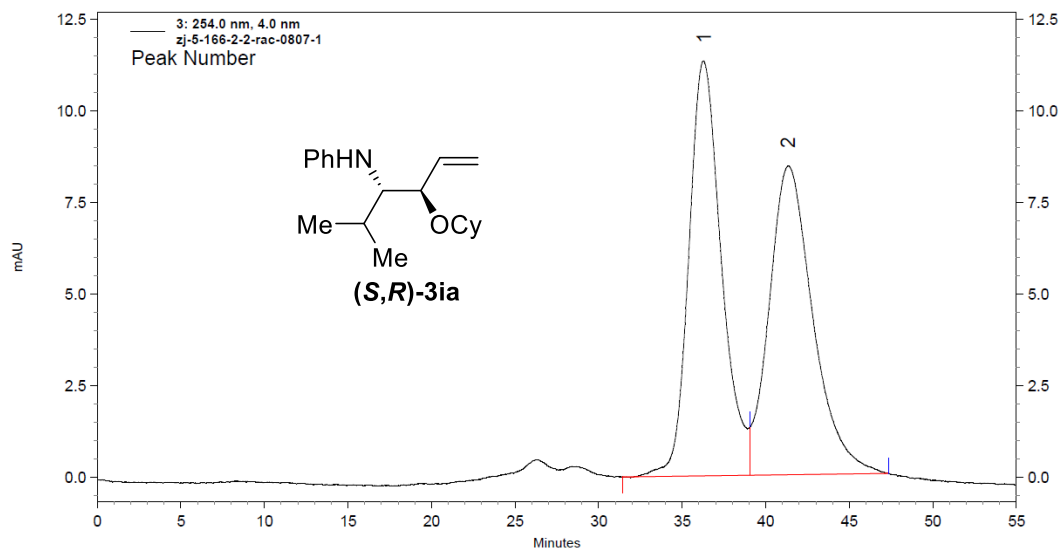
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	34.280	49.123	249.000
2	39.560	50.877	249.000



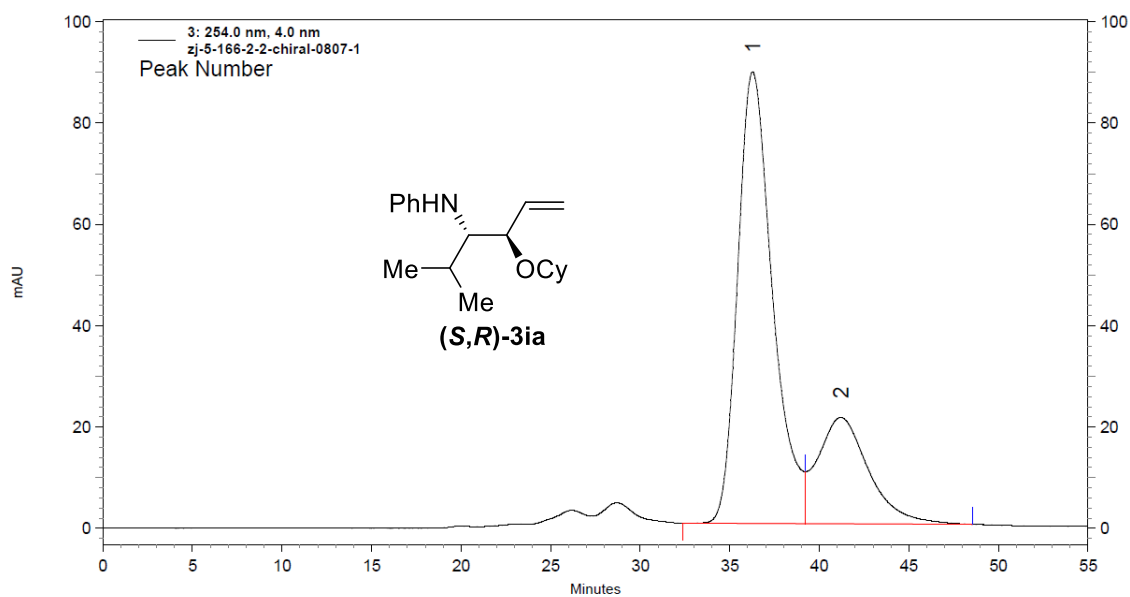
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	33.900	5.253	249.000
2	38.753	94.747	249.000



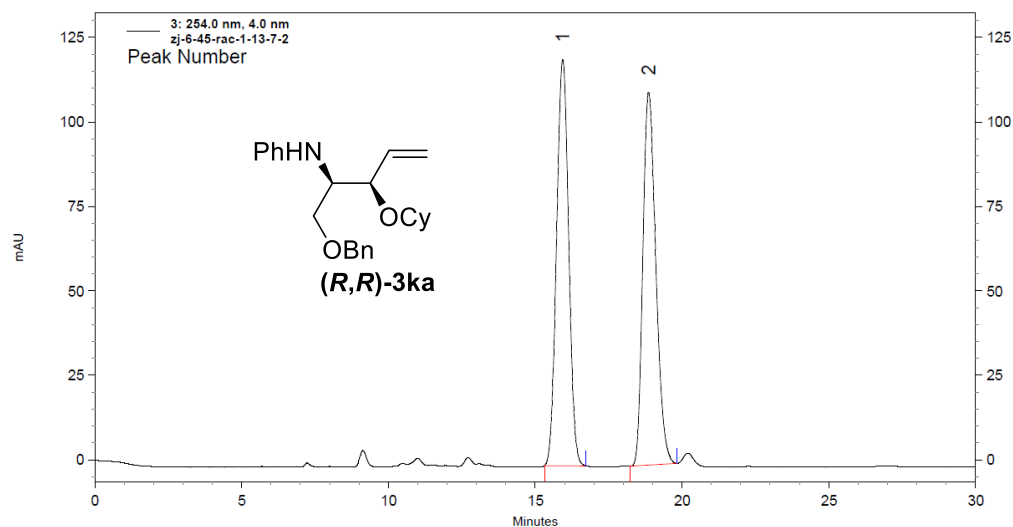
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	36.300	50.047	248.000
2	41.327	49.953	248.000



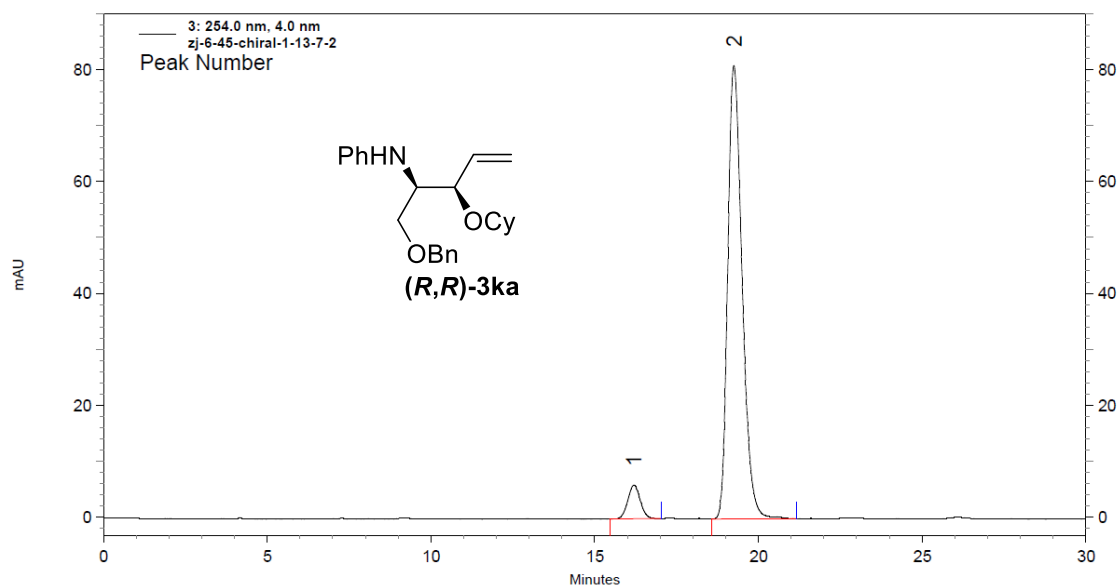
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	36.280	74.407	248.000
2	41.213	25.593	249.000



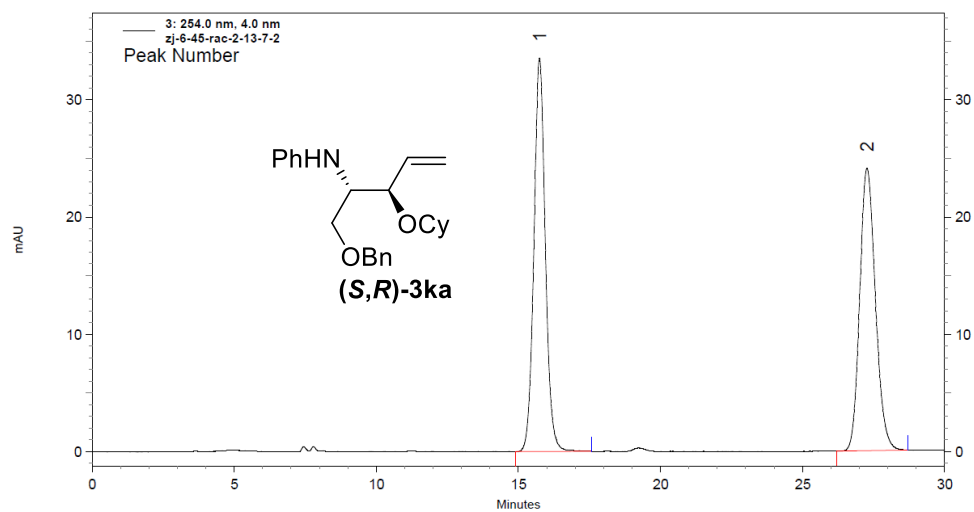
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	15.933	50.285	204.000
2	18.860	49.715	204.000



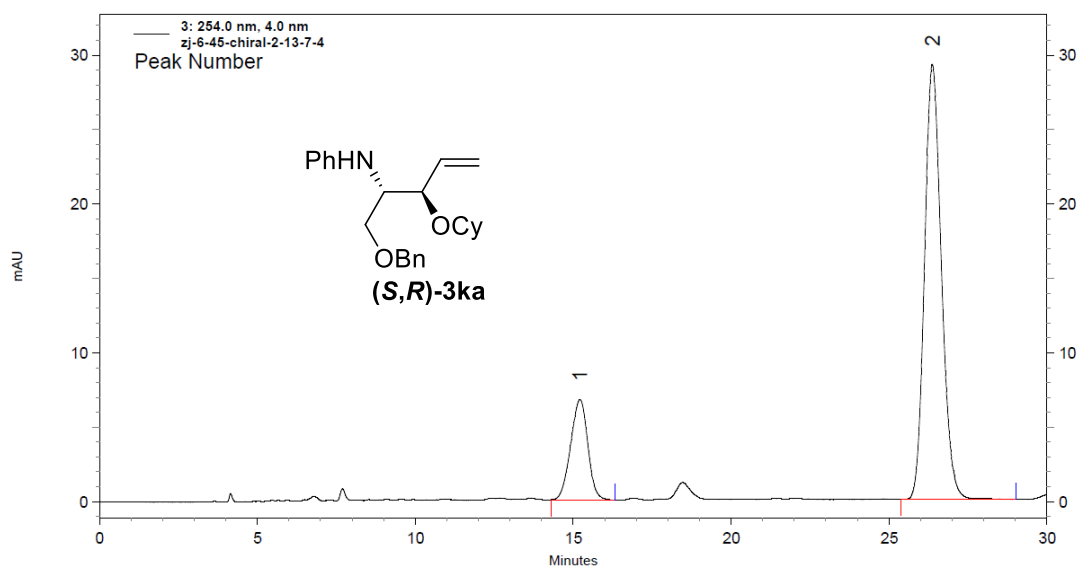
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	16.200	6.088	247.000
2	19.253	93.912	202.000



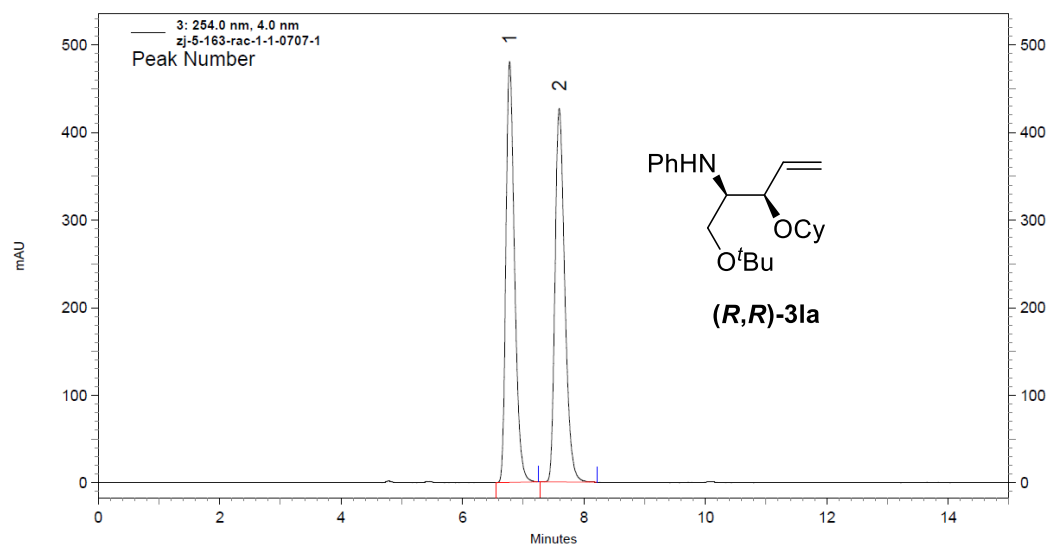
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	15.747	50.427	202.000
2	27.267	49.573	202.000



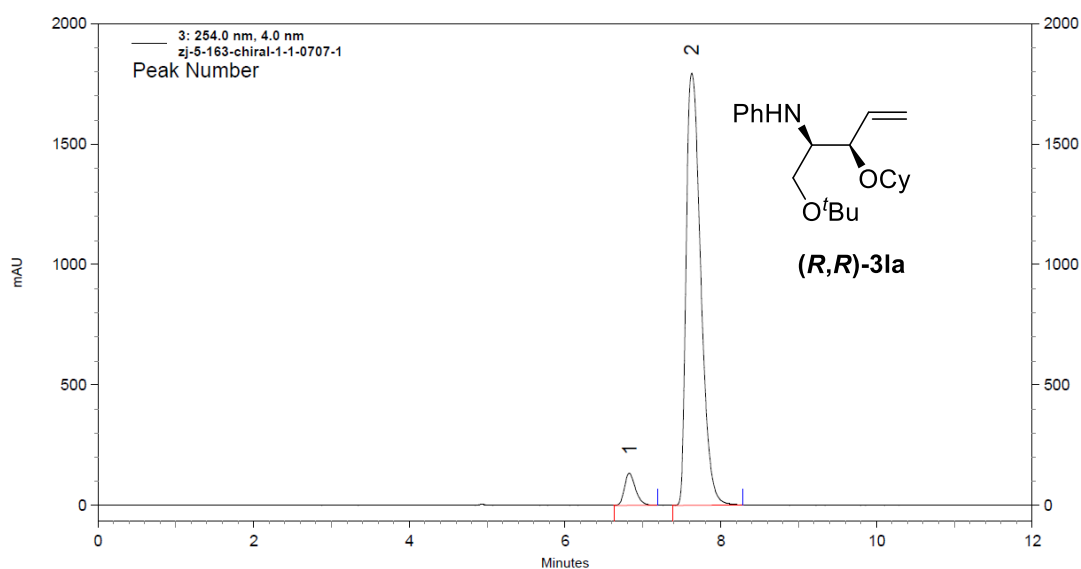
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	15.213	18.919	202.000
2	26.373	81.081	202.000



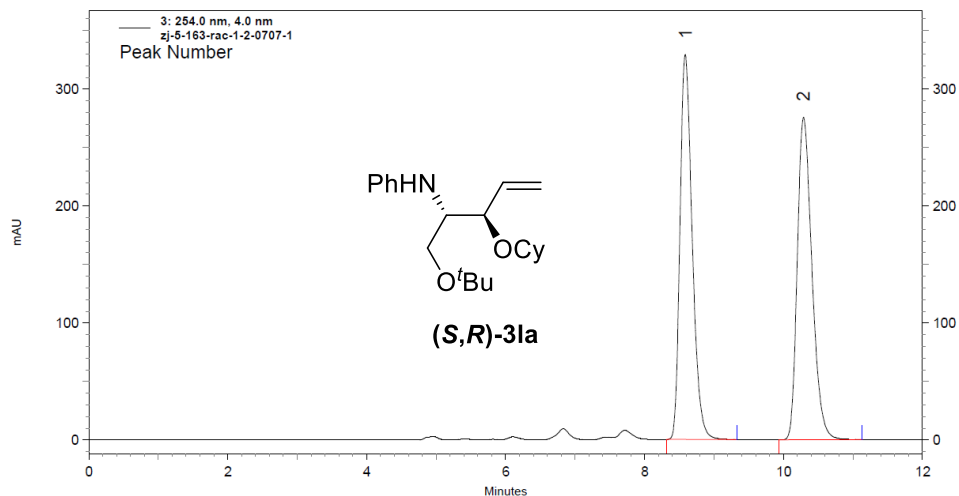
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6.773	49.923	248.000
2	7.593	50.077	248.000



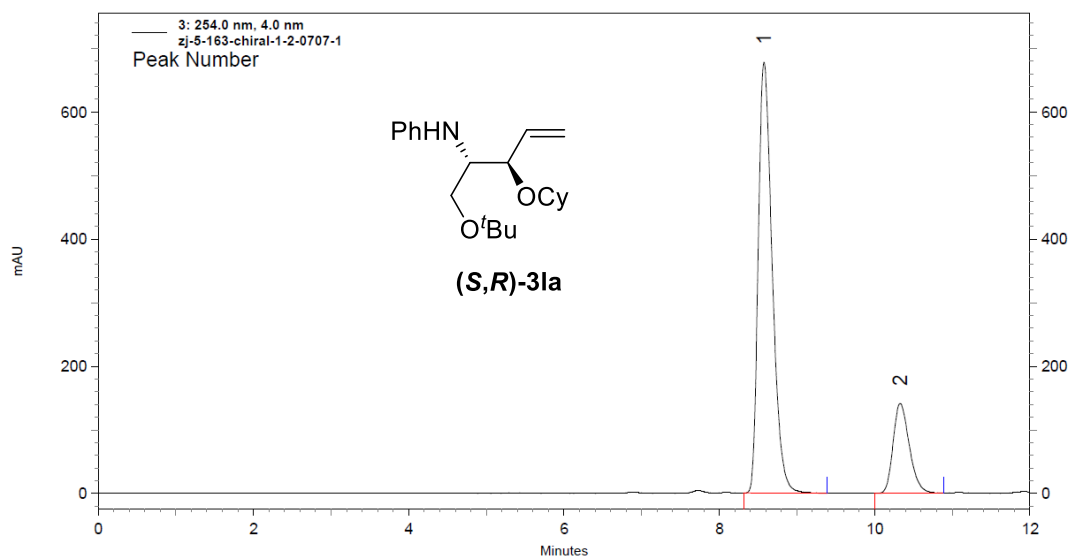
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6.827	5.307	248.000
2	7.627	94.693	249.000



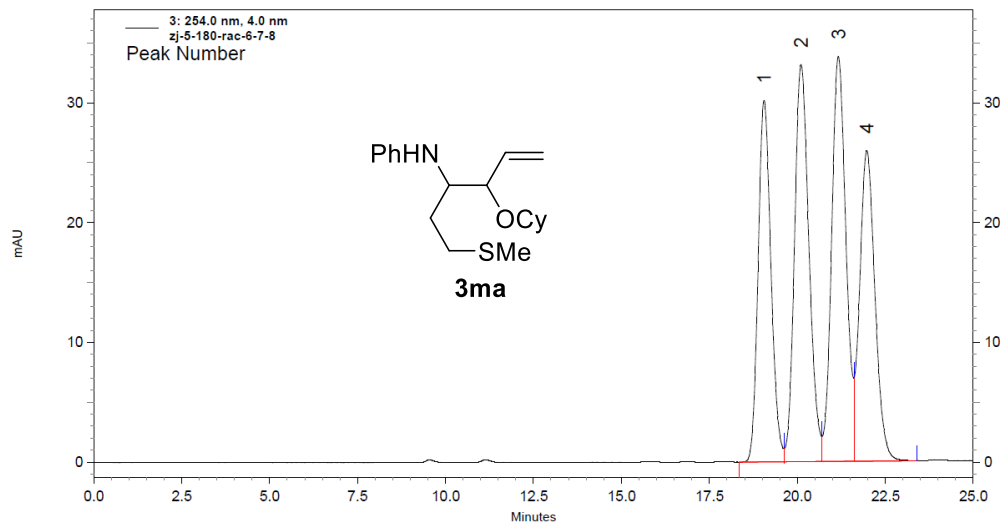
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.587	49.828	247.000
2	10.287	50.172	247.000



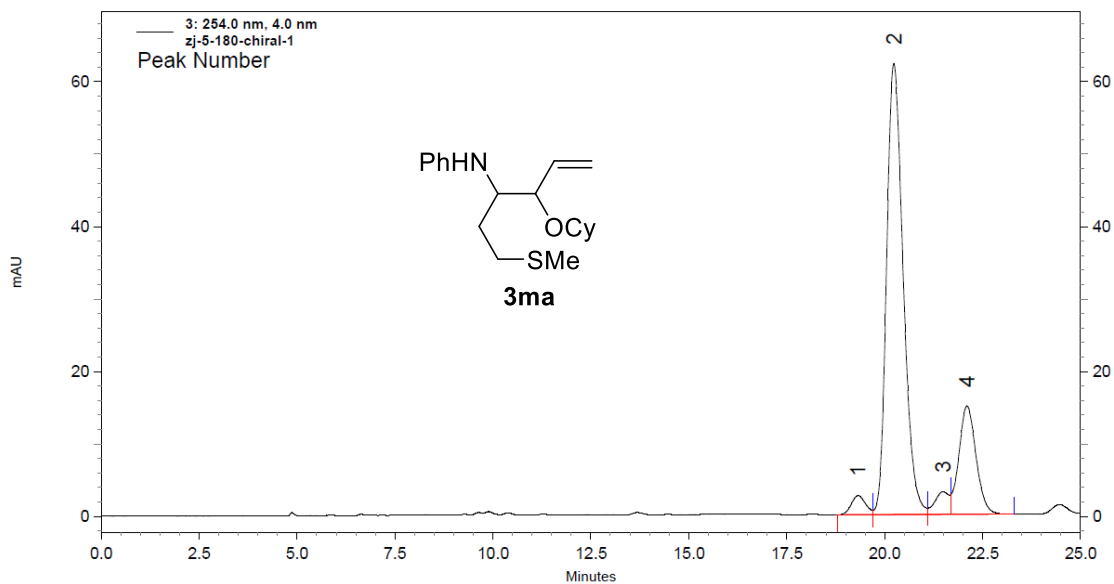
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.573	80.536	202.000
2	10.327	19.464	247.000



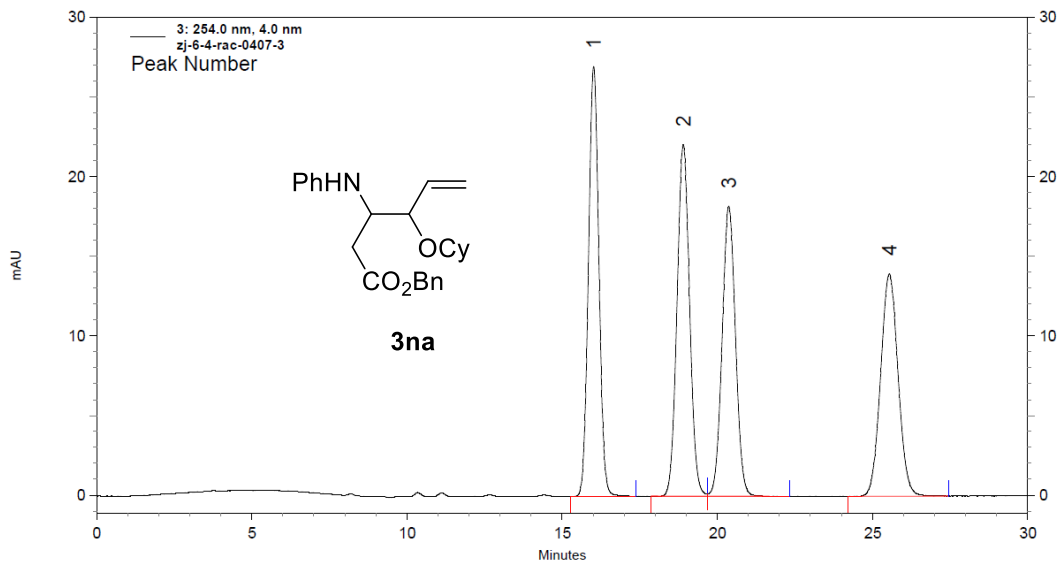
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.053	22.141	248.000
2	20.107	27.499	205.000
3	21.167	27.640	205.000
4	21.973	22.720	248.000



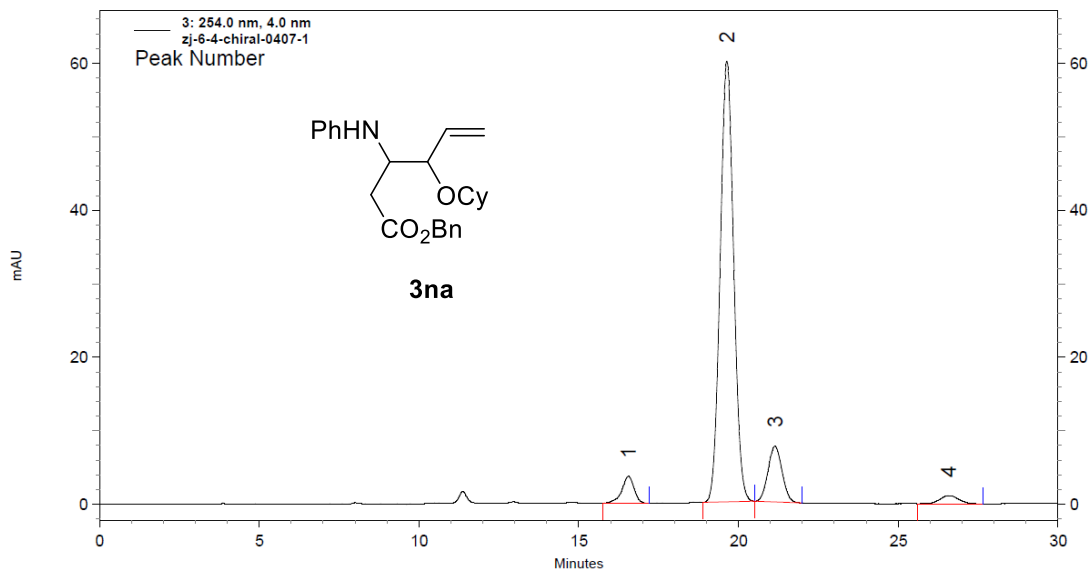
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.320	2.738	248.000
2	20.233	75.204	247.000
3	21.493	3.283	247.000
4	22.100	18.776	248.000



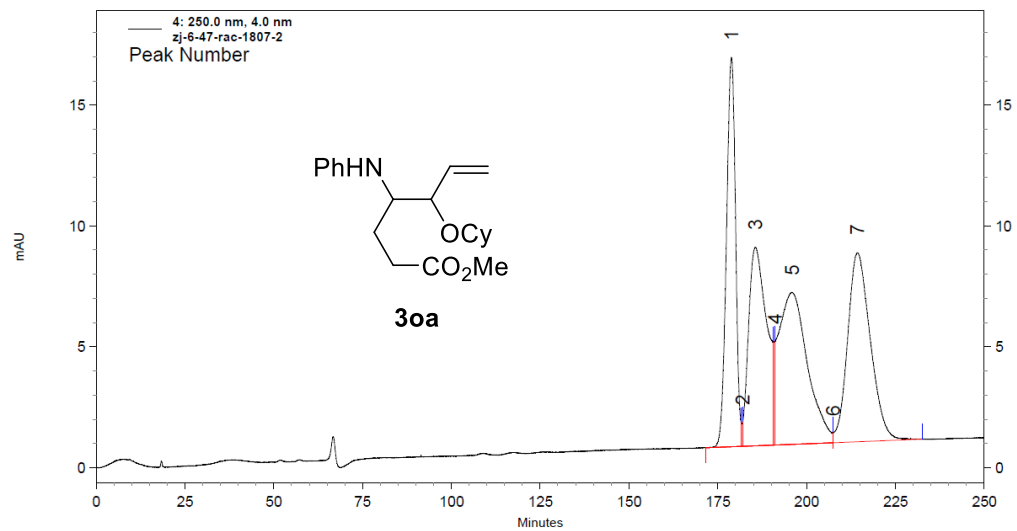
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	16.013	26.692	202.000
2	18.900	26.615	202.000
3	20.367	23.378	202.000
4	25.540	23.315	202.000



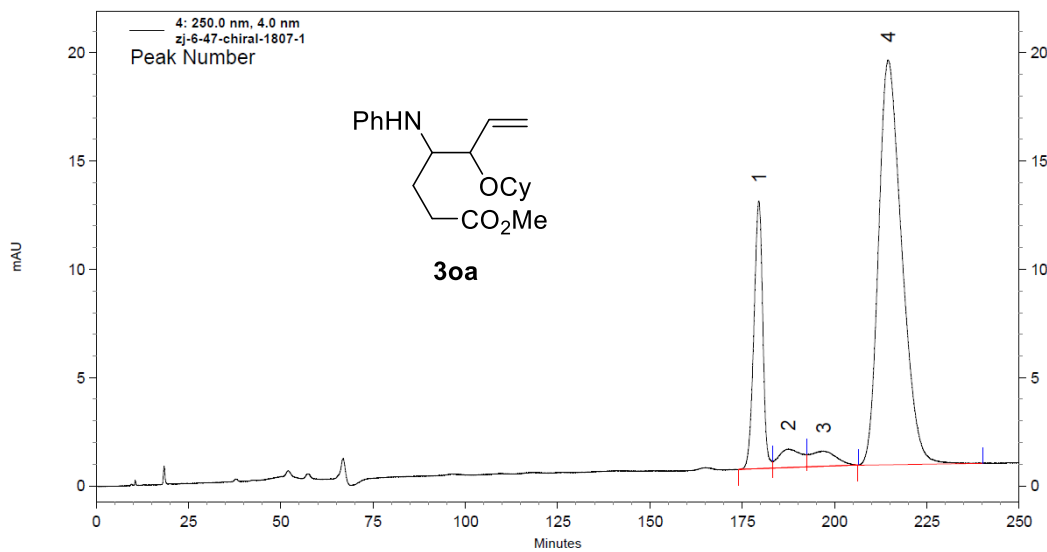
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	16.553	4.524	202.000
2	19.633	82.518	202.000
3	21.140	10.865	202.000
4	26.580	2.093	247.000



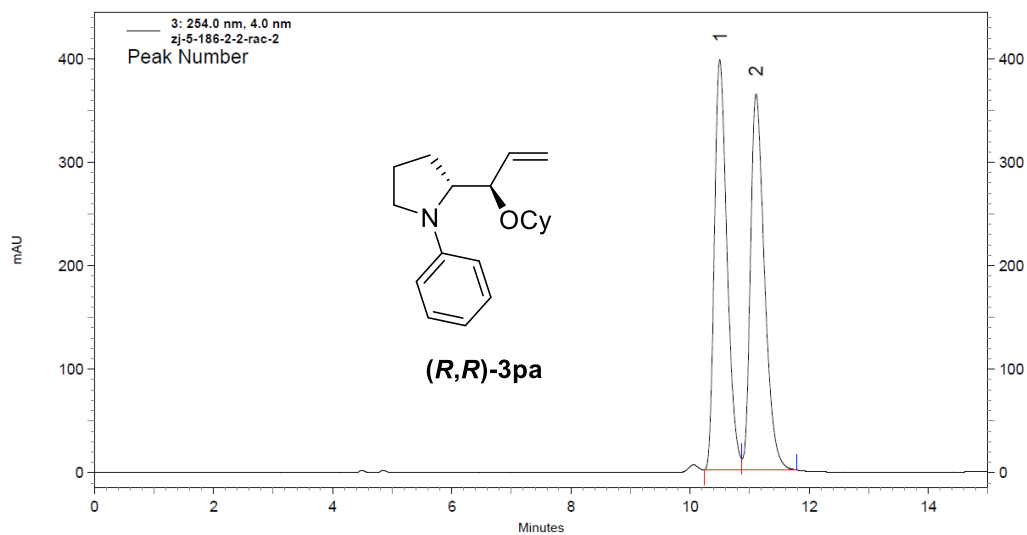
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	178.847	22.343	248.000
2	181.980	0.163	247.000
3	185.567	22.350	248.000
4	191.100	1.088	248.000
5	195.867	27.085	248.000
6	207.467	0.000	205.000
7	214.287	26.972	248.000



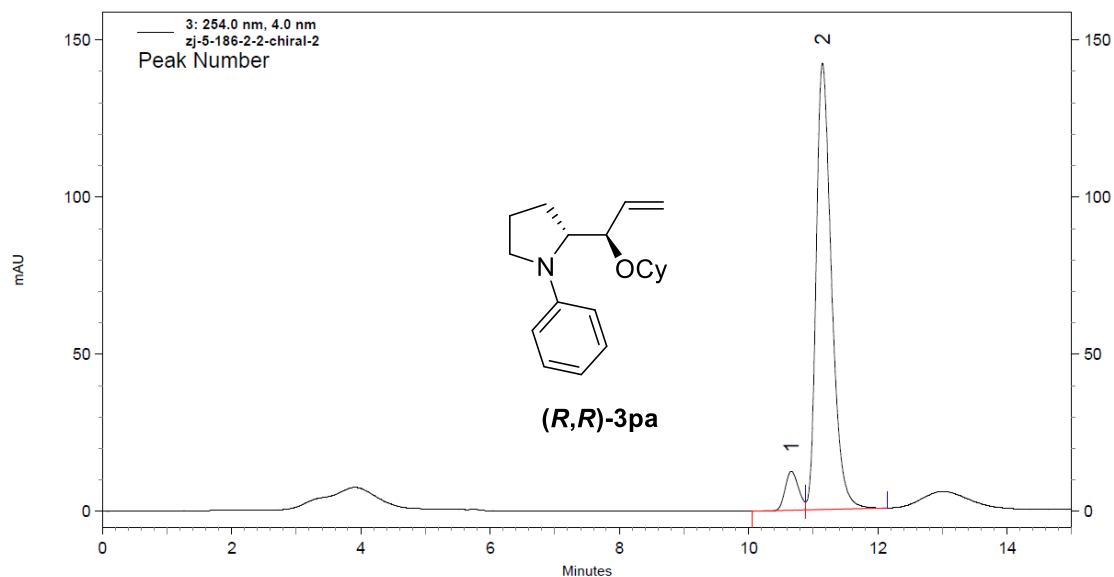
4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	179.500	18.849	248.000
2	187.440	3.308	245.000
3	197.027	3.135	246.000
4	214.500	74.708	247.000



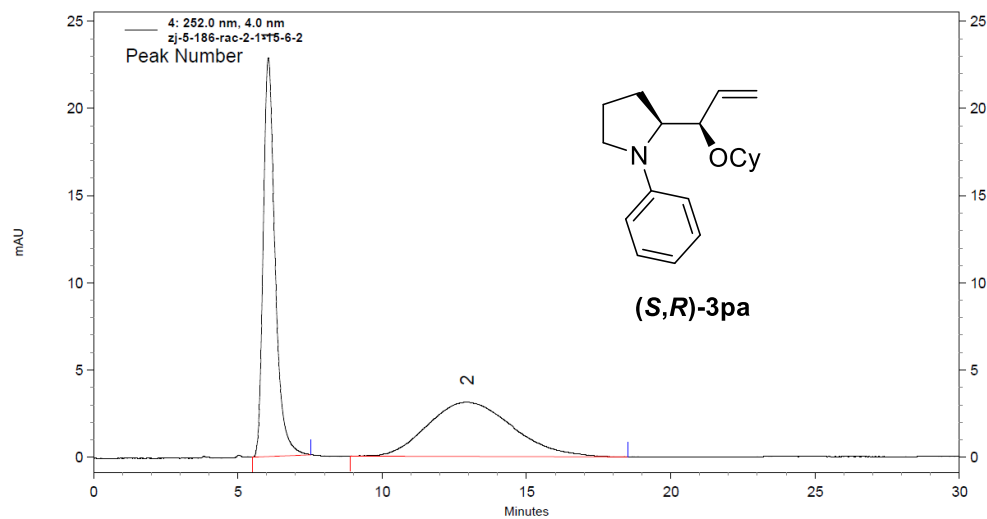
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10.500	49.529	254.000
2	11.107	50.471	254.000



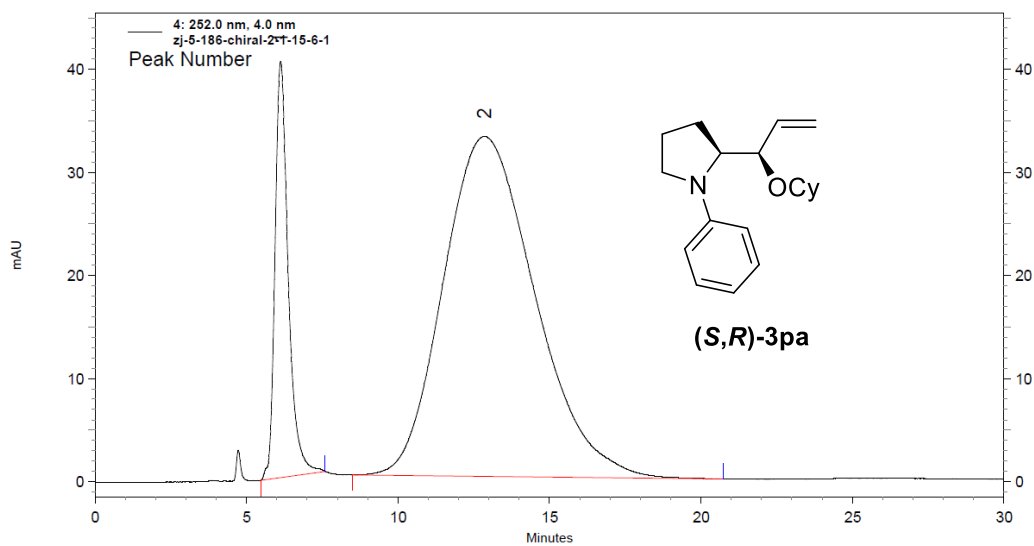
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10.660	6.949	254.000
2	11.140	93.051	254.000



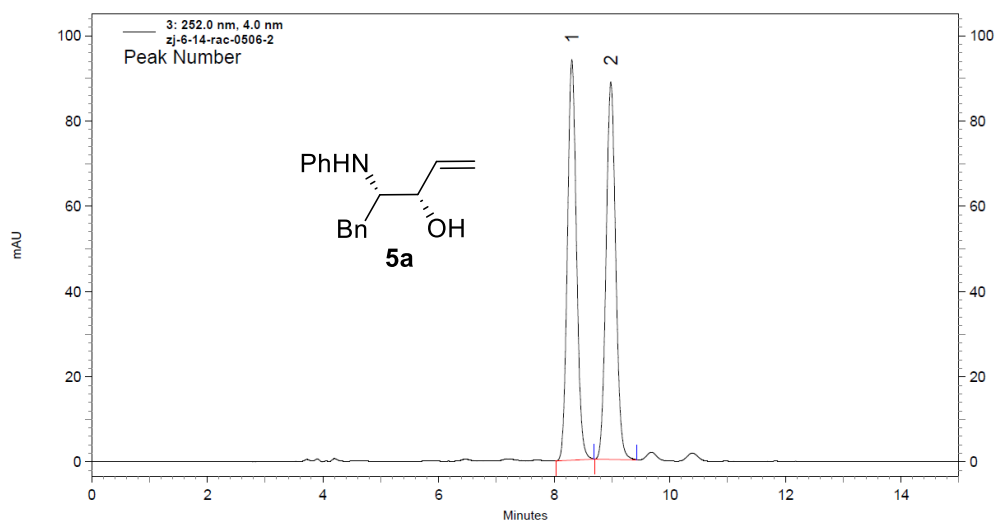
4: 252.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6.053	50.585	203.000
2	12.947	49.415	259.000



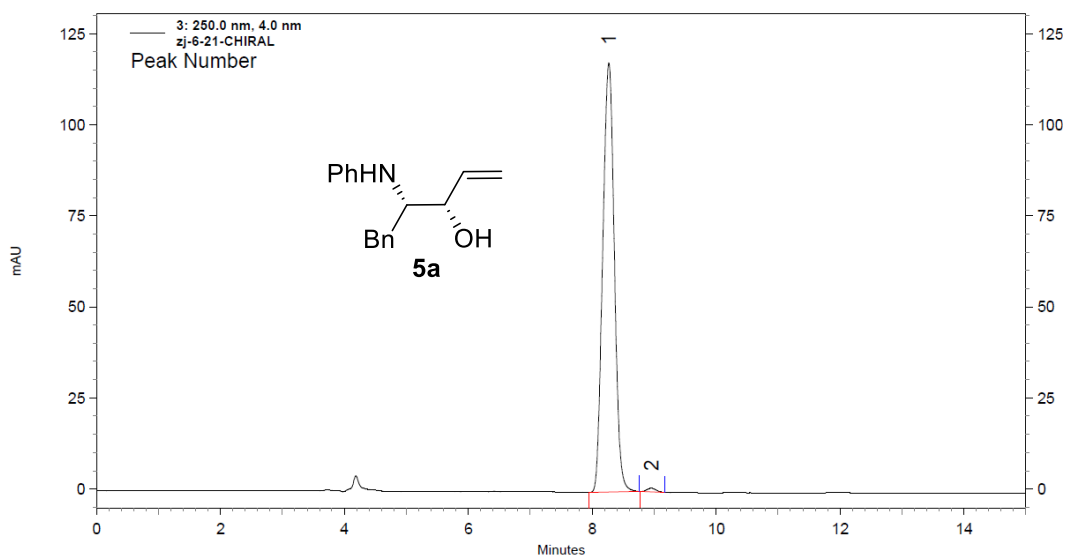
4: 252.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	6.120	15.030	257.000
2	12.847	84.970	257.000



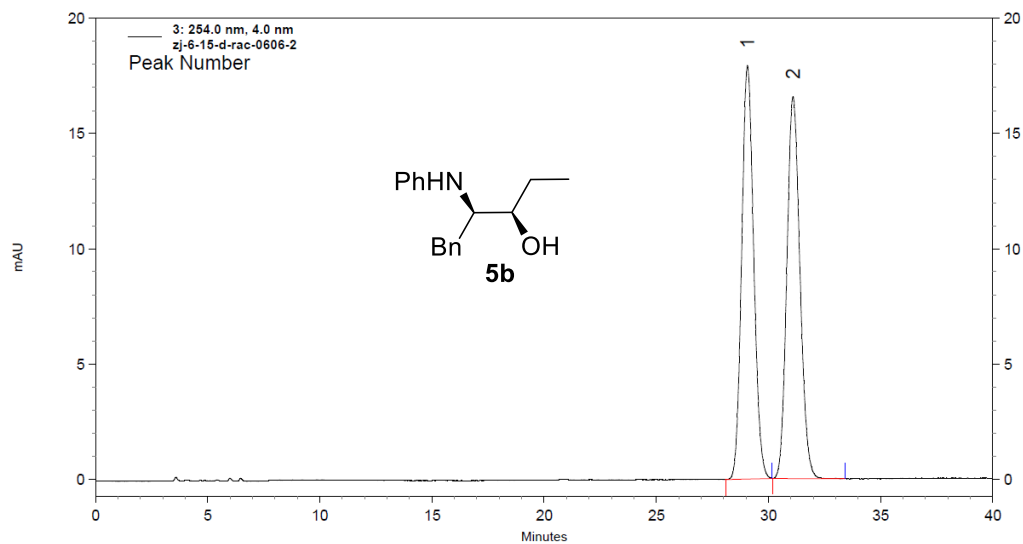
3: 252.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.307	49.999	204.000
2	8.980	50.001	204.000



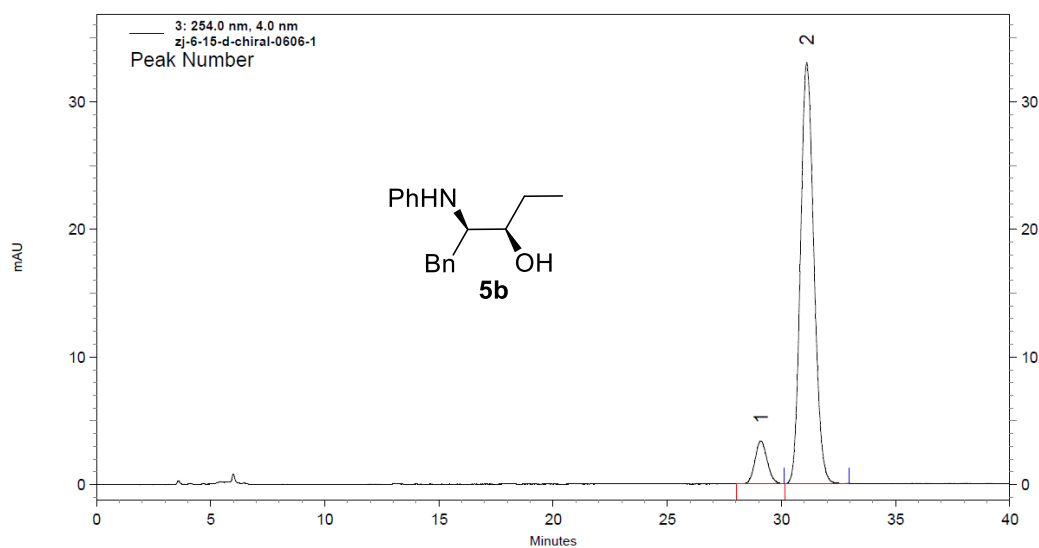
3: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.267	99.340	203.000
2	8.953	0.660	249.000



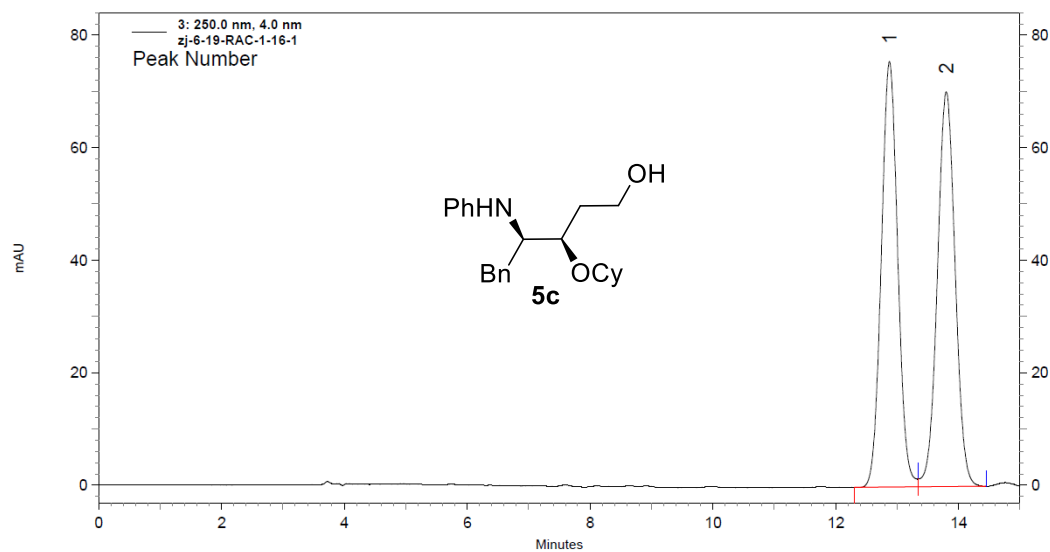
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	29.060	49.840	202.000
2	31.093	50.160	202.000



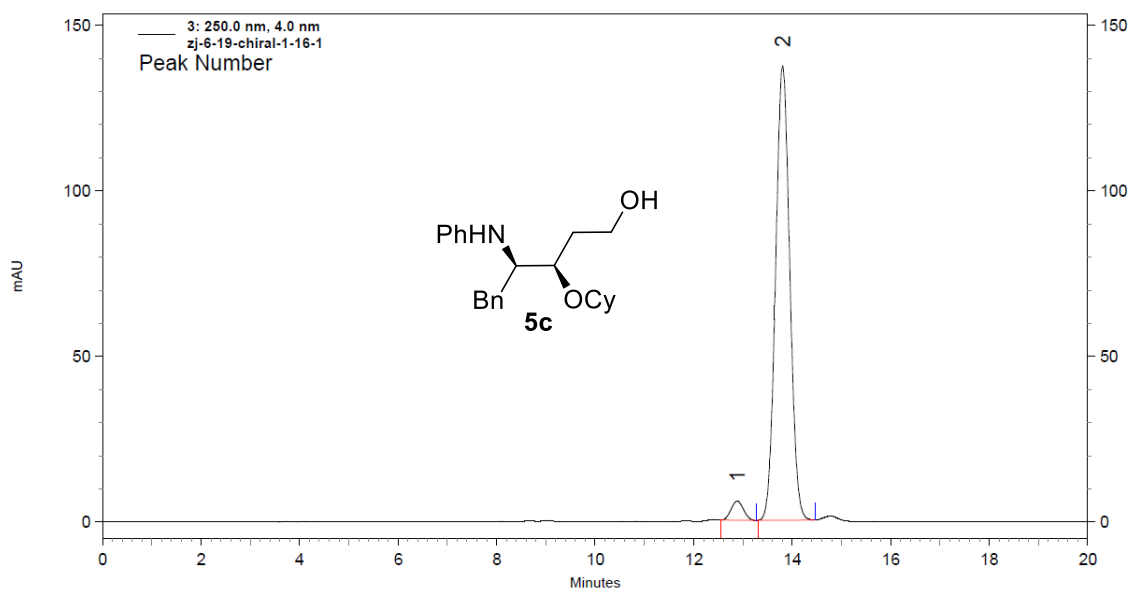
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	29.100	8.504	202.000
2	31.107	91.496	203.000



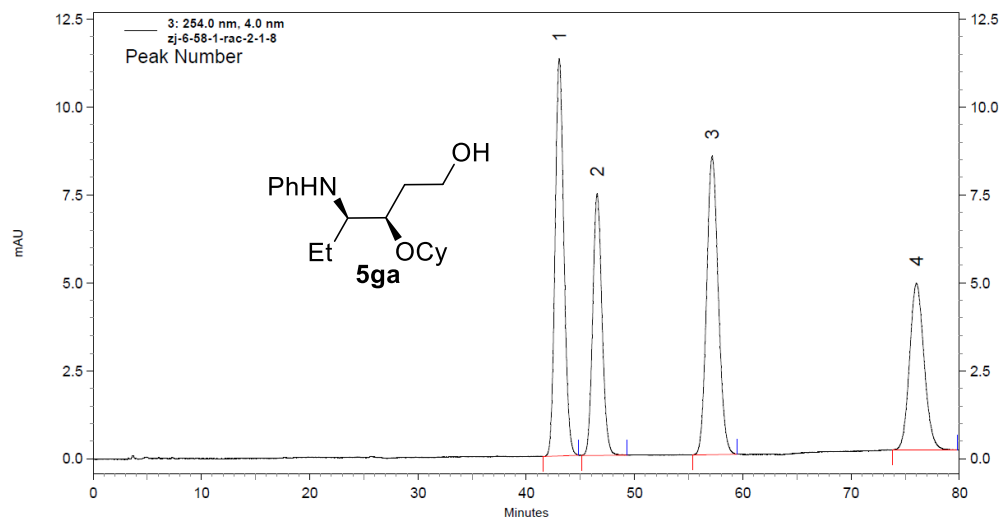
3: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	12.873	49.910	204.000
2	13.800	50.090	204.000



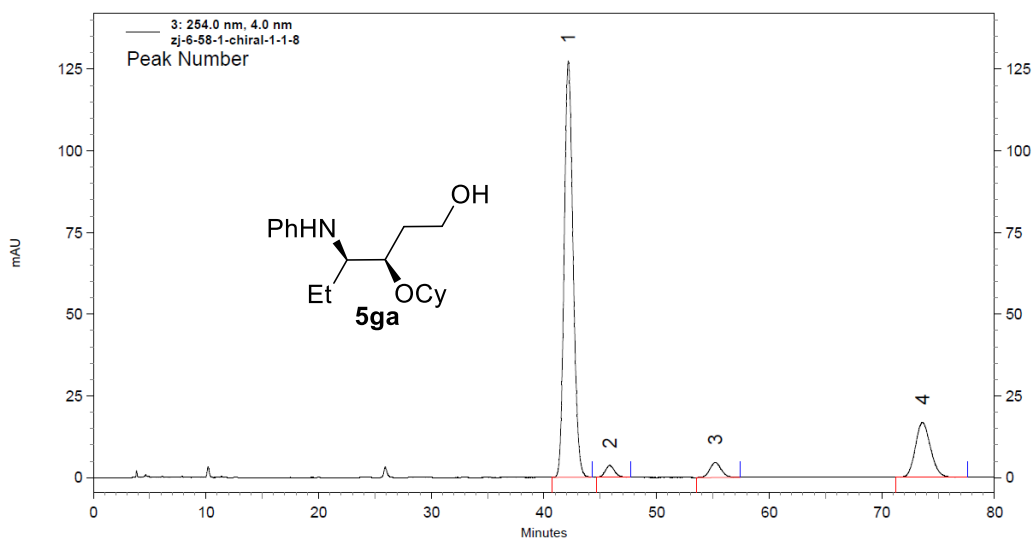
3: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	12.887	3.575	203.000
2	13.807	96.425	204.000



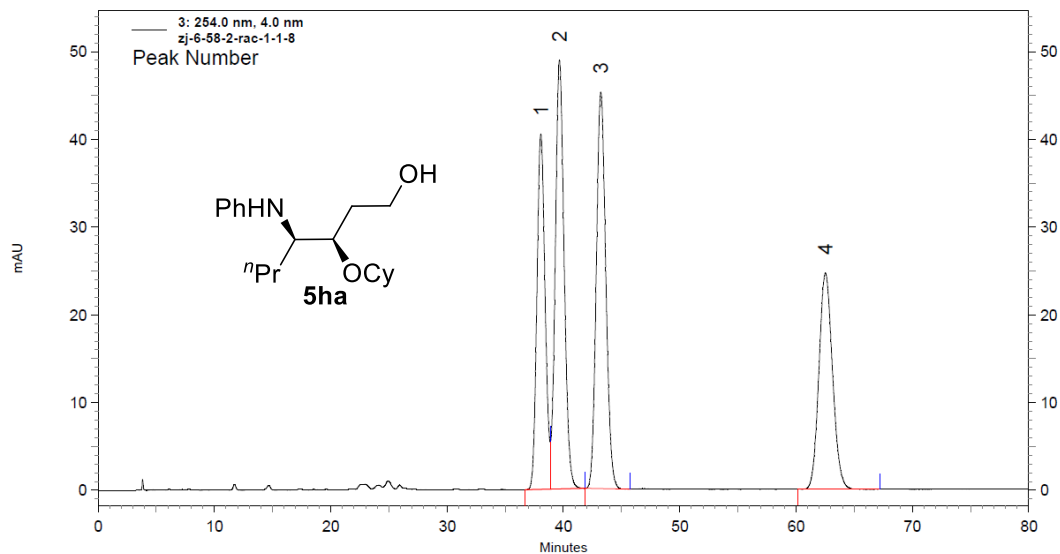
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	43.040	29.495	203.000
2	46.547	20.492	202.000
3	57.160	29.539	203.000
4	76.027	20.475	247.000



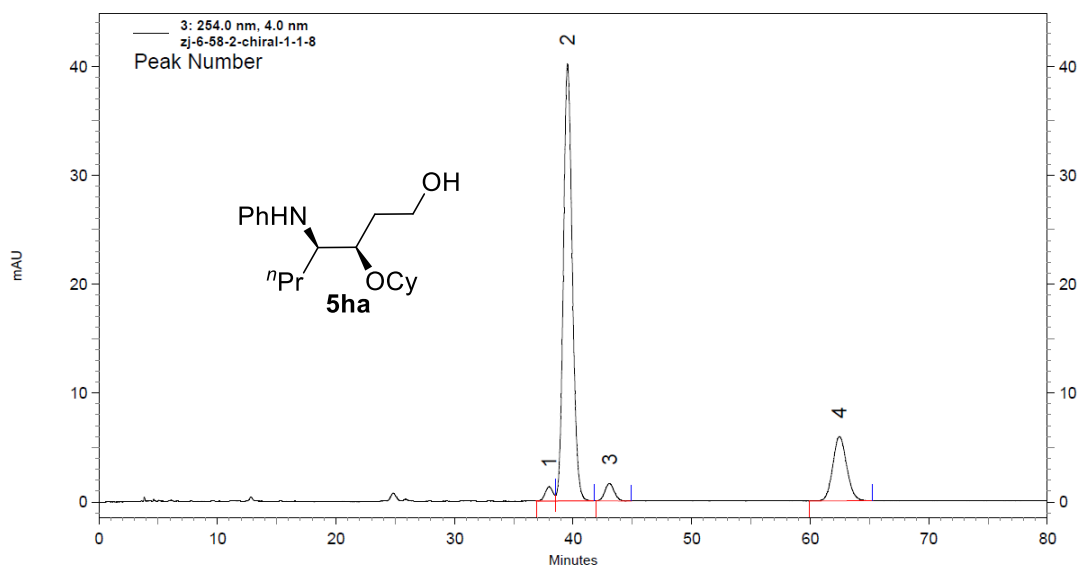
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	42.160	76.743	203.000
2	45.840	2.321	204.000
3	55.213	3.562	205.000
4	73.607	17.374	203.000



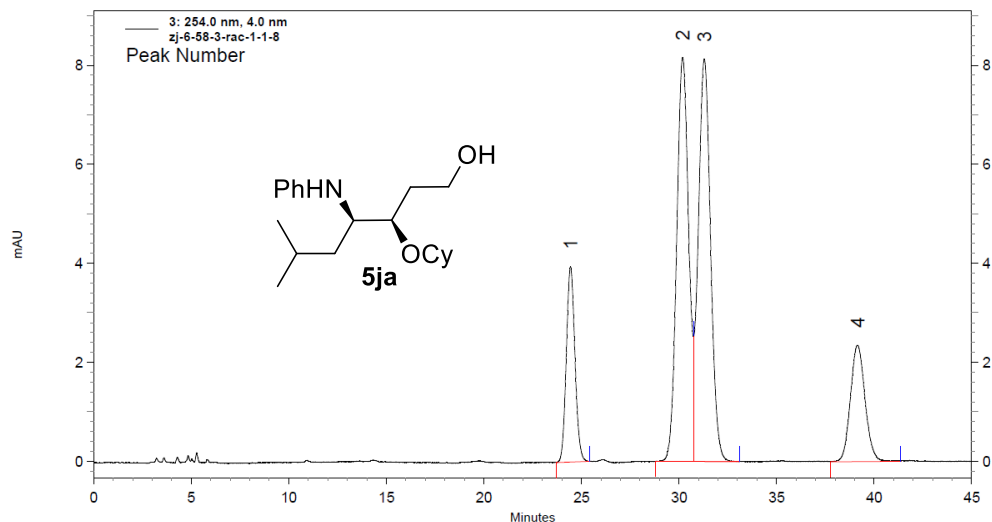
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	38.053	21.643	203.000
2	39.653	28.316	203.000
3	43.213	28.092	203.000
4	62.520	21.949	203.000



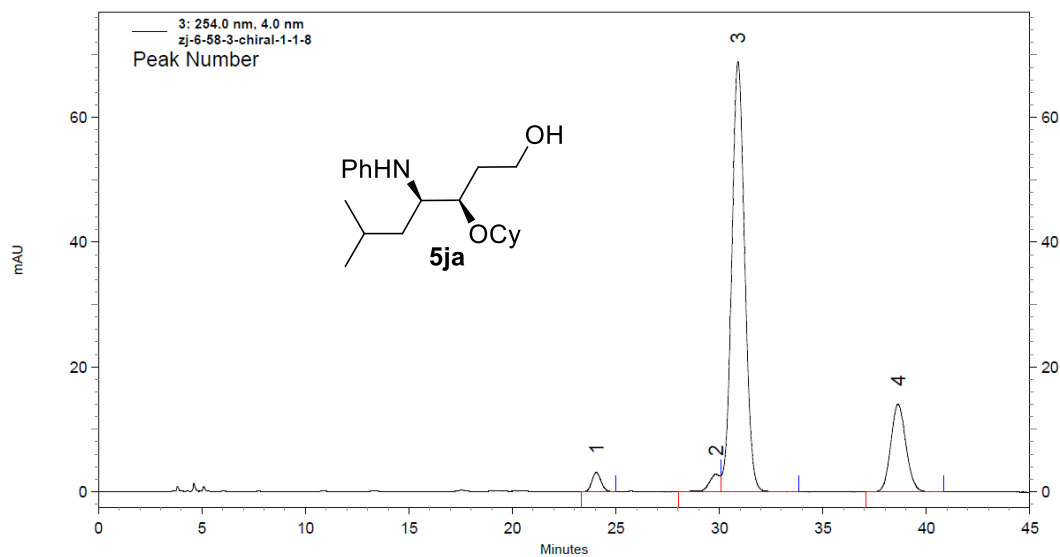
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	37.973	2.181	248.000
2	39.527	76.950	203.000
3	43.060	3.237	248.000
4	62.460	17.632	202.000



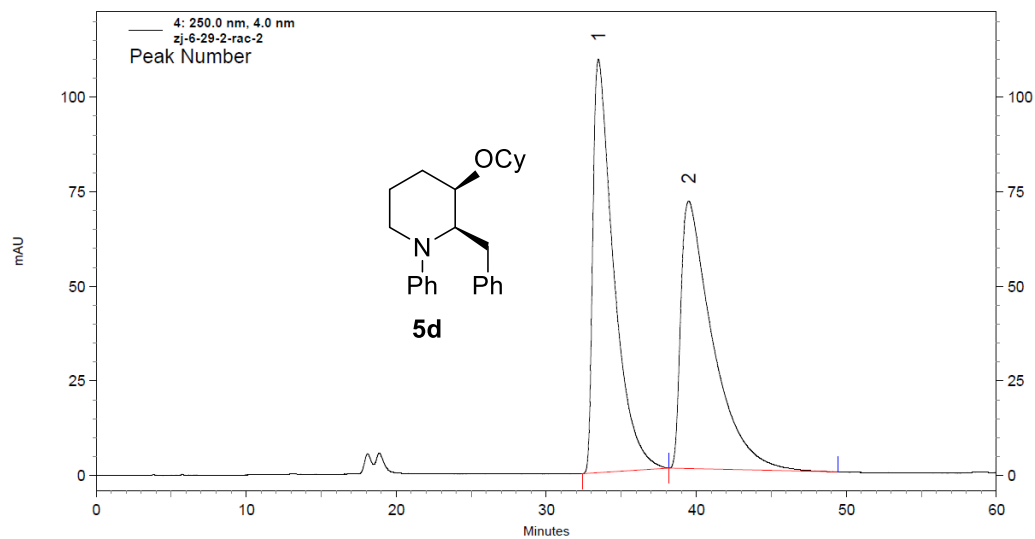
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24.440	12.769	205.000
2	30.193	36.588	203.000
3	31.300	37.680	203.000
4	39.160	12.963	248.000



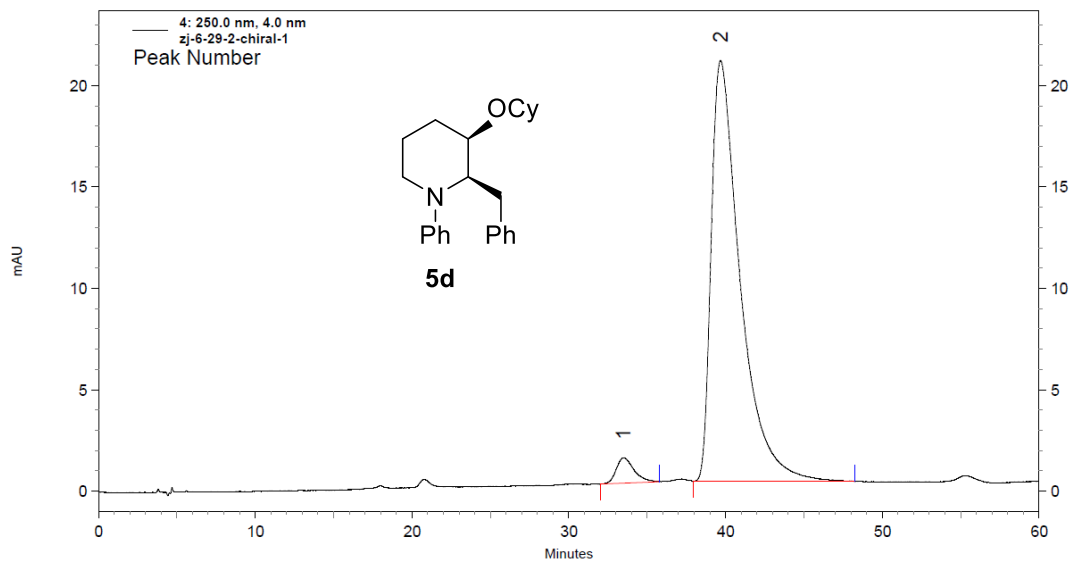
3: 254.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24.053	2.409	204.000
2	29.833	2.660	205.000
3	30.900	76.659	203.000
4	38.633	18.272	203.000



4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	33.467	50.229	260.000
2	39.487	49.771	260.000



4: 250.0 nm,
4.0 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	33.473	3.558	214.000
2	39.680	96.442	206.000