Supporting Information for

Palladium/sulfoxide-phosphine-catalyzed highly enantioselective allylic etherification and amination

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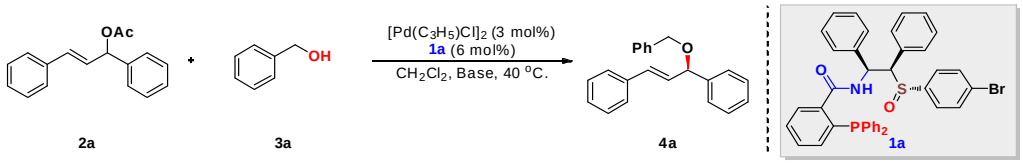
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts were reported on the delta (δ) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass spectra were measured on MS spectrometer (EI) or LC/MS/MS (ESI-MS). The high resolution mass spectra (HRMS) were measured on a Bruker UltraflexXtreme MALDI-TOF/TOF mass spectrometer by EI. Enantiomeric ratios were determined by chiral HPLC with chiral columns (chiralpak AS-H column, chiralpak AD-H column, chiralcel OJ-H column, chiralpak IC-H column or chiralcel OD-H column) with hexane and *i*-PrOH as solvents. Optical rotations were measured with a polarimeter.

2. Detailed Optimization of Reaction Conditions

2.1 Detailed optimization of enantioselective allylic etherification reaction

Table 1S. Screen of the bases for the enantioselective allylic etherification reaction[a]



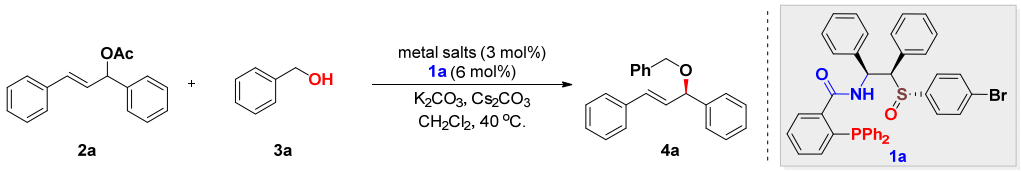
2a 3a 4a

Entry	Base	Temp. (^{o}C)	t (h)	Yield [b] (%)	ee [c] (%)
1	K_2CO_3 (3.0 eq.)	40 ^{o}C	10 h	17	98.0
2	Li_2CO_3 (3.0 eq.)	40 ^{o}C	10 h	17.8	6.7
3	Na_2CO_3 (3.0 eq.)	40 ^{o}C	10 h	20.3	66.6
4	Cs_2CO_3 (3.0 eq.)	40 ^{o}C	10 h	78.5	95.0
5	Cs_2CO_3 (1.5 eq.)+ K_2CO_3 (1.5 eq.)	40 ^{o}C	10 h	68	97.7
6	Cs_2CO_3 (1.0 eq.)+ K_2CO_3(2.0 eq.)	40 ^{o}C	10 h	30	97.6
7	Cs_2CO_3(0.5 eq.)+ K_2CO_3(2.5 eq.)	40 ^{o}C	10 h	32	91.9
8	***Cs_2CO_3 (1.5 eq.)+ K_2CO_3(1.5 eq.)***	***40 ^{o}C***	***24 h***	***99***	***97.5***

[a] Unless otherwise noted, reactions were carried out with **2a** (0.20 mmol), **3a** (0.60 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **1a** (0.012 mmol) in CH_2Cl_2 (2.0 mL). [b] Determined by GC using biphenyl as internal standard. [c] Determined by chiral HPLC, the absolute configuration was established as *R* by comparison with literature data.

As shown in Table 1S, among all the bases, the combination of Cs_2CO_3 (1.5 eq.) and K_2CO_3 (1.5 eq.) in CH_2Cl_2 at 40 ^{o}C gave the best result in terms of yield and enantioselectivity (entry 8), and was thus selected for further optimization studies.

Table 2S. Screening of the metal salts for the enantioselective allylic etherification reaction[a]

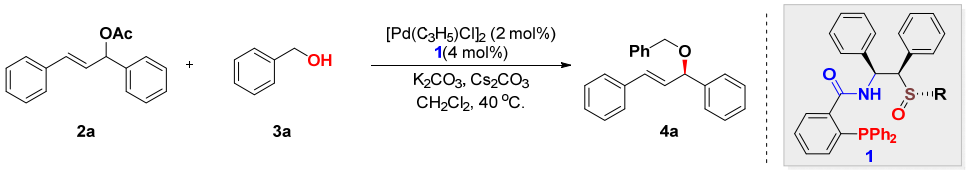


Entry	Metal salts	t (h)	Yield [b] (%)	ee[c] (%)
1	$Pd(PPh_3)_4$	24 h	97	34.5
2	***$[Pd(C_3H_5)Cl]_2$***	***24 h***	***99***	***97.6***
3	$Pd(OAc)_2$	24 h	42	98.0
4	$Pd_2dba_3CHCl_3$	24 h	58	36.3

[a] Unless otherwise noted, reactions were carried out with **2a** (0.20 mmol), **3a** (0.60 mmol), Metal salt (0.006 mmol), **1a** (0.012 mmol), K_2CO_3 (0.30 mmol), Cs_2CO_3 (0.30 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C. [b] Determined by GC using biphenyl as internal standard. [c] Determined by chiral HPLC.

As shown in Table 2S, among all the metal salts tested, the $[Pd(C_3H_5)Cl]_2$ gave the best results in terms of yield and enantioselectivity (entry 2), and was thus selected for further optimization studies.

Table 3S. Screen of ligands for the the enantioselective allylic etherification reaction[a]

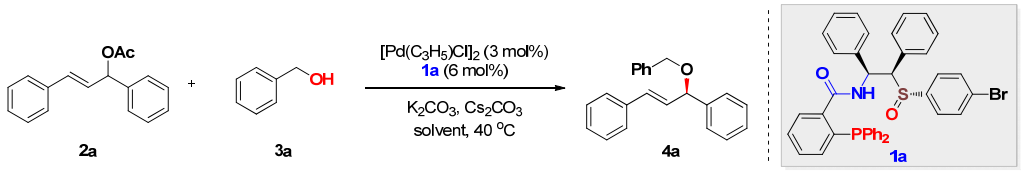


Entry	Ligand	R	Time (h)	yield [b] (%)	ee [c] (%)
1	***1a***	***4-BrPh***	***24 h***	***99***	***97.7***
2	**1b**	Ph	24 h	97	95.3
3	**1c**	4-MePh	24 h	99	93.7
4	**1d**	2-MePh	24 h	84	94.3
5	**1e**	1-Naphthyl	24 h	99	96.7
6	**1f**	3,5-$(Me)_2$Ph	24 h	99	96.3
7	**1g**	2,4,6-$(Me)_3$Ph	24 h	64	96.5

[a] Unless otherwise noted, reactions were carried out with **2a** (0.20 mmol), **3a** (0.60 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **1** (0.012 mmol), K_2CO_3 (0.30 mmol), Cs_2CO_3 (0.30 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C. [b] Determined by GC using biphenyl as internal standard. [c] Determined by chiral HPLC.

As shown in Table 3S, among the ligands tested, ligand **1a** gave the best results (entry 1), and was thus selected for further studies.

Table 4S. Screen the solvents for the enantioselective allylic etherification reaction[a]



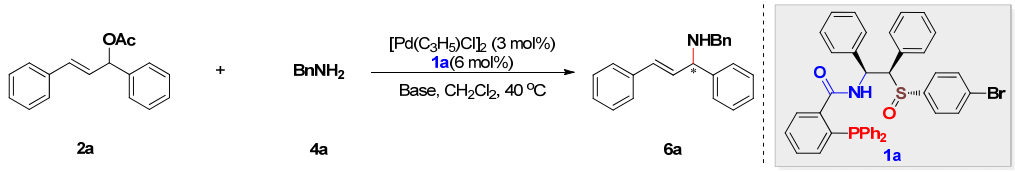
Entry	Solvent	t (h)	Yield [b] (%)	ee [c] (%)
1	CH_2Cl_2	24	99	97.7
2	DCE	24	87	97.7
3	CH_3CN	24	74	97.1
4	***Toluene***	***4***	***99***	***98.2***
5	THF	24	85	97.7
6	DMF	24	9	83.3

[a] Unless otherwise noted, reactions were carried out with **2a** (0.20 mmol), **3a** (0.60 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **1a** (0.012 mmol), K_2CO_3 (0.30 mmol), Cs_2CO_3 (0.30 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C. [b] Determined by GC using biphenyl as internal standard. [c] Determined by chiral HPLC.

As shown in Table 4S, among the solvents tested, Toluene gave the best result in terms of yieldand enantioselectivity (entry 4), and thus the optimized reaction condition was confirmed.

2.2 Detailed optimization of enantioselective allylic amination reaction

Table 5S. Screen of bases for the enantioselective allylic amination reaction[a]

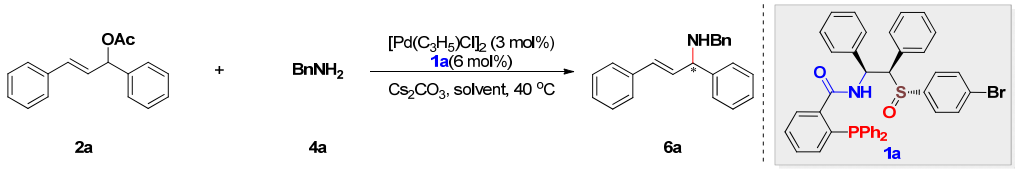


Entry	Base	Time (h)	Yield [b] (%)	ee [c] (%)
1	***Cs_2CO_3 (3.0 eq.)***	***4***	***89***	***97.1***
2	K_2CO_3 (3.0 eq.)	4	82	93.1
3	Na_2CO_3 (3.0 eq.)	16	71	74.3
4	Li_2CO_3 (3.0 eq.)	16	35	55.1
5	BSA (3.0 eq.) + LiOAc (0.1 eq.)	16	54	91.1
6	BSA (3.0 eq.) + NaOAc (0.1 eq.)	16	79	94.5
7	BSA (3.0 eq.) + KOAc (0.1 eq.)	16	53	96.0
8	Cs_2CO_3 (1.5 eq.) + K_2CO_3 (1.5 eq.)	16	85	96.8

[a] Unless otherwise noted, reactions were carried out with **2a** (0.20 mmol), **4a** (0.60 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **1a** (0.012 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C. [b] Determined by GC using biphenyl as internal standard. [c] Determined by chiral HPLC.

As shown in Table 5S, among all the bases tested, Cs_2CO_3 (3.0 eq.) gave the best results in terms of yield and enantioselectivity (entry 1), and was thus selected for further studies.

***Table 6S*. Screen of solvents for the enantioselective allylic amination reaction[a]**

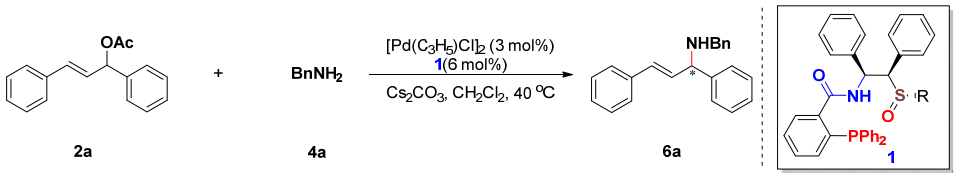


Entry[a]	Solvent	Time (h)	Yield[c] (%)	ee[d] (%)
1	***CH_2Cl_2***	***4***	***89***	***97.1***
2	Toluene	16	90	94.9
3	THF	16	80	95.5
4	CH_3CN	16	70	91.7
5	DCE	4	93	95.0

[a] Unless otherwise noted, reactions were carried out with **2a** (0.20 mmol), **4a** (0.60 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **1a** (0.012 mmol), Cs_2CO_3 (0.30 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C. [b] Determined by GC using biphenyl as internal standard. [c] Determined by chiral HPLC.

As shown in Table 6S, among all the solvents tested, CH_2Cl_2 gave the best results in terms of yield and enantioselectivity (entry 1), and was thus selected for further studies.

***Table 7S*. Screen of ligands for the enantioselective allylic amination reaction[a]**



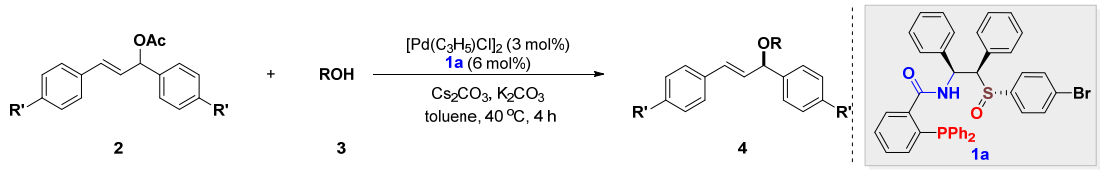
Entry	Ligand	R	Time (h)	yield[b] (%)	ee[c] (%)
1	***1a***	***4-BrPh***	***4 h***	***99***	***97.7***
2	**1b**	Ph	4 h	97	95.3
3	**1c**	4-MePh	4 h	99	93.7
4	**1d**	2-MePh	16 h	84	94.3
5	**1e**	1-Naphthyl	4 h	99	96.7
6	**1f**	$3,5\text{-}(Me)_2C_6H_3$	4 h	99	96.3
7	**1g**	$2,4,6\text{-}(Me)_3C_6H_2$	16 h	64	96.5
8	**1h**	Bn	5	17	12.0

[a] Unless otherwise noted, reactions were carried out with **2a** (0.20 mmol), **4a** (0.60 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **1** (0.012 mmol), Cs_2CO_3 (0.30 mmol) in CH_2Cl_2 (2 mL) at 40 °C. [b] Determined by GC using biphenyl as internal standard. [c] Determined by chiral HPLC.

As shown in Table 7S, among the ligands tested, **1a** gave the best results in terms of yield and enantioselectivity (entry 1), and thus the optimized reaction condition was confirmed.

3. General Procedure for Pd-Catalyzed Enantioselective Allylic Substitution Reactions and Spectral Data

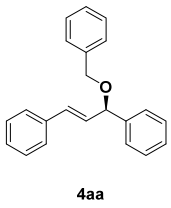
3.1 General Procedure for Pd-Catalyzed Enantioselective Allylic Etherification Reactions



Ligand **1a** (8.3 mg, 0.012 mmol, 6 mol%) and $[Pd(C_3H_5)Cl]_2$ (2.2 mg, 0.006 mmol, 3 mol%) were dissolved in Toluene (1.0 mL) in a Schlenk tube under Ar. After stirring at room temperature for 1 h, allylic acetate **2** (0.2 mmol) in toluene (1.0 mL) was added, followed by alcohol **3** (0.6 mmol), K_2CO_3 (41 mg, 0.3 mmol), and Cs_2CO_3 (98 mg, 0.3 mmol). The mixture was stirred at 40 °C for 5 h, and then was diluted with diethyl ether and washed with saturated NH_4Cl (aq). The organic layers were dried over Na_2SO_4 and filtered, and the solvents were evaporated in vacuo. The residue was purified by flash column chromatrography, eluting with petroleum ether and ethyl ether to afford the corresponding product **4**.

3.2 Spectral Data of Allylic EtherificationProducts

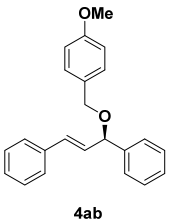
(*R*, E)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzene (4aa) [1]



4aa

Yield: 90%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 17.816 min (minor) for (*S*)-isomer, t_R = 20.357 min (major) for (*R*)-isomer. ee = 98.2%. $[\alpha]_D^{23}$ -15.53 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.41-7.33 (m, 8H), 7.21-7.28 (m, 4H), 7.24-7.20 (m, 1H), 6.63 (d, *J* = 16.2 Hz, 1H), 6.34 (dd, *J* = 16.7, 7.2 Hz, 1H), 5.01 (d, *J* = 7.2 Hz, 1H), 4.57 (dd, *J* = 15.6, 12.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.04, 138.32, 136.46, 131.47, 130.16, 128.49, 128.47, 128.33, 127.68, 127.66, 127.65, 127.48, 126.91, 126.54, 81.50, 70.01. HRMS (EI) m/z: calcd for $C_{22}H_{20}O$ $[M]^+$: 300.1514, found: 300.1520.

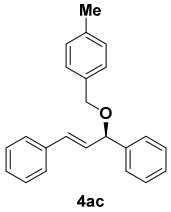
(*R*, E)-(3-((4-methoxybenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (4ab) [1]



4ab

Yield: 82%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 86:14 v/v, flow rate 0.75 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 27.981 min (minor) for (*S*)-isomer, t_R = 32.659 min (major) for (*R*)-isomer. ee = 98.1%. $[\alpha]_D^{23}$ -17.775 (c = 0.4, toluene). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 9.0 Hz, 4H), 7.30-7.28 (m, 5H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 7.0 Hz, 1H), 4.99 (d, *J* = 7.0 Hz, 1H), 4.50 (s, 2H), 3.81 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.09, 141.17, 136.55, 131.40, 130.39, 130.32, 129.30, 128.46, 127.62, 126.95, 126.54, 113.75, 81.19, 69.72, 55.19. HRMS (EI) m/z: anal. calcd for $C_{23}H_{22}O_2$ $[M]^+$: 330.1620, found: 330.1621.

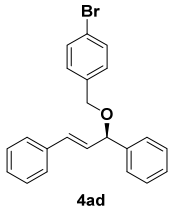
(*R*, E)-(3-((4-methylbenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (4ac) [1]



4ac

Yield: 84%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 21.720 min (minor) for (*S*)-isomer, t_R = 29.594 min (major) for (*R*)-isomer. ee = 97.2%. $[\alpha]_D^{23}$ -19.125 (c = 1.0, toluene). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 4H), 7.31-7.20 (m, 6H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 20.4 Hz, 1H), 6.33 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.00 (d, *J* = 6.9 Hz, 1H), 4.53 (s, 2H), 2.35 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.12, 137.18, 136.51, 135.22, 131.40, 130.26, 129.03, 128.47, 127.81, 127.65, 127.63, 126.93, 126.53, 81.25, 69.87, 21.16. HRMS (EI) m/z: anal. calcd for $C_{23}H_{22}O$ $[M]^+$: 314.1671, found: 314.1683.

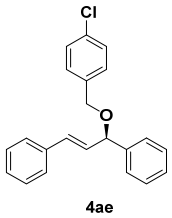
(*R*, E)-(3-((4-bromobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (4ad) [1]



4ad

Yield: 87%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 32.881 min (minor) for (*S*)-isomer, t_R = 39.912 min (major) for (*R*)-isomer. ee = 96.3%.$[\alpha]_D^{23}$ -18.75 (c = 0.4, toluene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.44-7.34 (m, 6H), 7.30 (t, *J* = 7.4 Hz, 3H), 7.25-7.21 (m, 3H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 24, 11.2 Hz, 1H), 4.98 (d, *J* = 7.2 Hz, 1H), 4.51 (dd, *J* = 16, *J* = 12 Hz, 2H). ^{13}C **NMR** (100 MHz, $CDCl_3$) δ 140.85, 137.42, 136.41, 131.70, 131.46, 129.95, 129.32, 128.58, 128.53, 127.81, 126.90, 126.58, 121.35, 81.79, 69.31. HRMS (EI) m/z: anal. calcd for $C_{22}H_{19}BrO$ $[M]^+$: 378.0619, found: 378.0621.

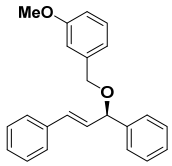
(*R*, E)-(3-((4-chlorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (4ae) [1]



4ae

Yield: 97%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 96:4 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 47.258 min (minor) for (*S*)-isomer, t_R = 54.604 min (major) for (*R*)-isomer. ee = 93.8%. $[\alpha]_D^{23}$ -2.94 (c = 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 4H), 7.33-7.28 (m, 7H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 15.9, 6.6 Hz, 1H), 4.98 (d, *J* = 7.1 Hz, 1H), 4.53 (dd, *J* = 20.4, *J* = 12.1 Hz , 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.87, 136.89, 136.42, 133.24, 131.69, 129.98, 128.99, 128.53, 127.81, 126.91, 126.59, 81.80, 69.32. HRMS (EI) m/z: anal. calcd for $C_{22}H_{19}OCl$ $[M]^+$: 334.1124, found: 334.1138.

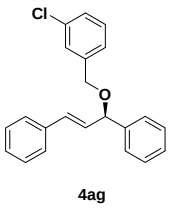
(*R*, E)-(3-((3-methoxybenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (4af) [1]



4af

Yield: 85%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 28.743 min (minor) for (*S*)-isomer, t_R = 34.532 min (major) for (*R*)-isomer. ee = 95.9%. $[\alpha]_D^{23}$ -33.6 (c = 1.0, toluene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.39-7.35 (m, 4H), 7.33-7.26 (m, 3H), 7.25-7.16 (m, 2H), 6.95 (d, *J* = 6.2 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.34 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.01 (d, *J* = 7.0 Hz, 1H), 4.56 (s, 2H), 3.80 (s, 3H).**^{13}C NMR**(100 MHz, $CDCl_3$) δ 159.65, 141.02, 139.98, 136.49, 131.52, 130.14, 129.34, 128.47, 127.67, 126.92, 126.54, 119.88, 113.08, 112.96, 81.50, 69.90, 55.14. HRMS (EI) m/z: anal. calcd for $C_{23}H_{22}O_2$ $[M]^+$: 330.1620, found: 330.1629.

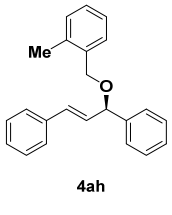
(*R*, E)-(3-((3-chlorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (4ag) [1]



4ag

Yield: 87%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 96:4 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 27.374 min (minor) for (*S*)-isomer, t_R = 34.416 min (major) for (*R*)-isomer. ee = 96.9%. $[\alpha]_D^{23}$ -13.98 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.39-7.38(m, 4H), 7.34 -7.28 (m, 3H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 16.2 Hz, 1H), 6.34 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.01 (d, *J* = 7.1 Hz, 1H), 4.62 (dd, *J* = 17.2, 8 Hz, 2H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.74, 140.45, 136.33, 134.22, 131.73, 129.84, 129.62, 128.57, 128.51, 127.81, 127.61, 126.87, 126.57, 125.57, 81.94, 69.29. HRMS (EI) m/z: anal. calcd for $C_{22}H_{19}OCl$ $[M]^+$: 334.1124, found: 334.1130.

(*R*, E)-(3-((2-methylbenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (4ah) [1]

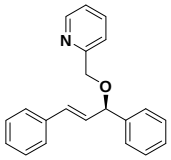


4ah

Yield: 83%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 6.191 min (major) for (*R*) isomer, t_R = 7.381 min (minor) for (*S*)-isomer. ee = 96.1%. $[\alpha]_D^{23}$ 1.63 (c = 1.0, toluene). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.30-7.27 (m, 5H), 7.21 (t, *J* = 7.4 Hz, 3H), 7.18-7.03 (m, 5H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.27 (dd, *J* = 16.2, 6.6, 1H), 4.93 (d, *J* = 6.9 Hz, 1H), 4.48 (dd, *J* = 26.5, 11.9 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (100MHz, CDCl3) δ 141.13, 136.71, 136.57, 136.22, 131.41, 130.34,

130.18, 128.61, 128.49, 128.47, 127.70, 127.67, 127.65, 126.94, 126.56, 125.73, 81.75, 68.66, 18.91. HRMS (EI) m/z: anal. calcd for $C_{23}H_{22}O$ $[M]^+$: 314.1671, found: 314.1685.

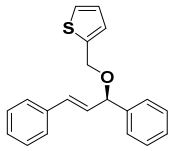
(*R*, E)-2-(((1,3-diphenylallyl)oxy)methyl)pyridine (4ai) [1]



4ai

Yield: 82%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 12.760 min (minor) for (*S*)-isomer, t_R = 13.942 min (major) for (*R*) isomer. ee = 96.1%. $[\alpha]_D^{23}$ -17.555 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.7 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.37 (dd, *J* = 16.1, 8.2 Hz, 4H), 7.33 – 7.27 (m, 3H), 7.23 (dd, *J* = 14.5, 7.2 Hz, 1H), 7.19 – 7.15 (m, 1H), 6.68 (d, *J* = 16.9 Hz, 1H), 6.36 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.08 (d, *J* = 7.2 Hz, 1H), 4.71 (dd, *J* = 41.4 Hz, 13.2 Hz 2H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.66, 148.89, 140.78, 136.56, 136.40, 131.80, 129.80, 128.50, 128.44, 127.74, 126.84, 126.56, 122.19, 121.31, 82.54, 71.10. MS (ESI) m/z: anal. calcd for $C_{22}H_{19}NO$ $[M+Na]^+$: 324.1, found: 324.2.

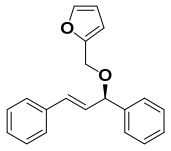
(*R*, E)-2-(((1,3-diphenylallyl)oxy)methyl)thiophene (4aj) [1]



4aj

Yield: 87%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 18.276 min (minor) for (*S*)-isomer, t_R = 20.647 min (major) for (*R*)-isomer. ee = 96.9%. $[\alpha]_D^{23}$ -27.09 (c = 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.38-7.26 (m, 4H), 7.31 (d, *J* = 7.2 Hz, 4H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 6.3 Hz, 2H), 6.62 (d, *J* = 16.2 Hz, 1H), 6.32 (dd, *J* = 16.2, 7.1 Hz, 1H), 5.05 (d, *J* = 7.0 Hz, 1H), 4.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.17, 140.75, 136.45, 132.35, 131.87, 129.84, 128.50, 128.48, 127.74, 126.99, 126.57, 126.26, 125.70, 82.54, 64.59. MS m/z: anal. calcd for $C_{20}H_{18}OS$ $[M]^+$: 306.42, found: 306.36.

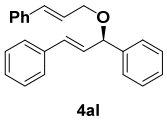
(*R*, E)-2-(((1,3-diphenylallyl)oxy)methyl)furan (4ak) [1]



4ak

Yield: 81%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 12.103 min (minor) for (*S*)-isomer, t_R = 13.070 min (major) for (*R*)-isomer. ee = 95.5%. $[\alpha]_D^{23}$ -6.07 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 3H), 7.37 (t, *J* = 7.8 Hz, 4H), 7.29 (t, *J* = 7.4 Hz, 3H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.32 (dd, *J* = 16.2, 7.6 Hz, 3H), 5.02 (d, *J* = 7.2 Hz, 1H), 4.50 (s, 2H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.67, 142.77, 140.65, 136.39, 131.81, 129.76, 128.50, 128.45, 127.73, 126.98, 126.55, 110.19, 109.35, 81.34, 62.04. HRMS (EI) m/z: anal. calcd for $C_{20}H_{18}O_2$ $[M]^+$: 290.1307, found: 290.1315.

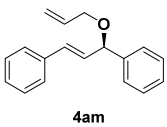
(*R*, E)-3-(cinnamyloxy)prop-1-ene-1,3-diyl)dibenzene (4al) [1]



4al

Yield: 74%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 4.984 min (minor) for (*S*)-isomer, t_R =5.946 min (major) for (*R*)-isomer. ee = 95.5%. $[\alpha]_D^{23}$ -12.100 (c = 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.48 -7.36 (m, 6H), 7.33-7.29 (m, 5H), 7.26-7.23 (m, 2H), 6.63 (t, *J* = 14.6 Hz, 2H), 6.38-6.30 (m, 2H), 5.05 (d, *J* = 7.2 Hz, 1H), 4.21 (dd, *J* = 9.7, 6.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.09, 141.06, 136.71, 136.51, 132.37, 131.50, 130.18, 128.53, 128.50, 127.71, 127.61, 126.92, 126.57, 126.45, 126.11, 81.75, 68.90. HRMS (EI) m/z: anal. calcd for $C_{24}H_{22}O$ $[M]^+$: 326.1671, found: 326.1675.

(*R*, E)-(3-(allyloxy)prop-1-ene-1,3-diyl)dibenzene (4am) [1]

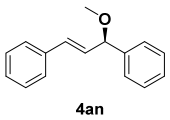


4am

Yield: 89%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 99:1 v/v, flow rate 0.5mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 12.630 min (minor) for (*S*)-isomer, t_R = 14.560 min (major) for (*R*)-isomer. ee = 95.1%. $[\alpha]_D^{23}$ 7.95 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 6H), 7.31-7.27 (m, 3H), 7.22-7.17 (m, 1H), 6.60 (d, *J* = 16 Hz, 1H), 6.30 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.97 (ddd, *J* = 22.7, 10.7, 5.5 Hz, 1H), 5.31 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dd, *J* = 10.4, 1.2 Hz,

1H), 4.98 (d, *J* = 7.0 Hz, 1H), 4.10-3.96 (m, 2H).**^{13}C NMR** (100MHz, $CDCl_3$) δ 141.04, 136.44, 134.72, 131.26, 130.17, 128.40, 127.60, 127.57, 126.78, 126.48, 116.78, 81.61, 69.11. HRMS (EI) m/z: anal. calcd for $C_{18}H_{18}O$ $[M]^+$: 250.1358, found: 250.1365.

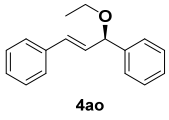
(*R*, E)-(3-methoxyprop-1-ene-1,3-diyl)dibenzene (4an) [1]



4an

Yield: 87%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 96:4 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). R The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 96:4 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). etension times: t_R = 26.882 min (minor) for (*S*)-isomer, t_R = 28.171 min (major) for (*R*)-isomer. ee = 97.5%. $[\alpha]_D^{23}$ -21.5 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38-7.35 (m, 6H), 7.30-7.28 (m, 3H), 7.20-7.23 (m, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.8, 7.0 Hz, 1H), 4.80 (d, *J* = 6.9 Hz, 1H), 3.38 (d, *J* = 1.5 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.97, 136.52, 131.43, 130.08, 128.48, 127.68, 126.89, 126.83, 126.80, 126.54, 84.26, 56.39. HRMS (EI) m/z: anal. calcd for C16H16O $[M]^+$: 224.1201, found: 224.1191.

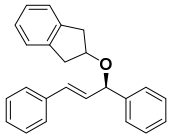
(*R*, E)-(3-ethoxyprop-1-ene-1,3-diyl)dibenzene (4ao) [1]



4ao

Yield: 84%.The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95:5 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 9.135 min (minor) for (*S*)-isomer, t_R= 9.905 min (major) for (*R*)-isomer. ee = 95.3%. $[\alpha]_D^{23}$ 18.48 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40-7.34 (m,6H), 7.30-7.28 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.9, 7.0 Hz, 1H), 4.92 (d, *J* = 7.1 Hz, 1H), 3.61-3.56 (m, 1H), 3.50-3.45 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.46, 136.59, 131.08, 130.60, 128.44, 127.59, 127.53, 126.78, 126.53, 82.47, 63.96, 15.31. HRMS (EI) m/z: anal. calcd for $C_{17}H_{18}O$ $[M]^+$: 238.1358, found: 238.1365.

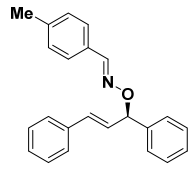
(*R*, E)-2-((1,3-diphenylallyl)oxy)-2,3-dihydro-1H-indene (4ap) [1]



4ap

Yield: 80%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 99:1 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 15.630 min (minor)for (*S*)-isomer, t_R = 16.950 min (major) for (*R*)-isomer. ee = 94.4%. $[\alpha]_D^{23}$ -0.85 (c = 1.0, toluene). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.7 Hz, 2H), 7.29-7.21 (m, 4H), 7.19-7.16 (m, 3H), 7.13-6.97 (m, 5H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 7.0 Hz, 1H), 4.99 (d, *J* = 7.0 Hz, 1H), 4.40 (t, *J* = 6 Hz 1H), 3.15-2.85 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.40, 140.82, 136.49, 131.15, 130.60, 128.45, 127.60, 126.88, 126.54, 126.42, 124.59, 80.93, 76.68, 39.49 . MS m/z: anal. calcd for $C_{24}H_{22}O$ $[M]^+$: 326.17, found: 248.30, 193.27, 115.12, 91.17.77.18.

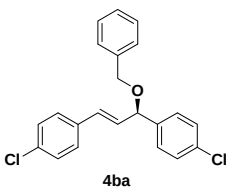
.**(*R*, E)-4-methylbenzaldehyde O-((E)-1,3-diphenylallyl) oxime (4aq)** [5]



4aq

Yield: 80%. The ee was determined by chiral HPLC (Chiralpak IC-H, hexane/isopropanol 95:5 v/v, flow rate 0.7 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 9.071 min (minor) for (*S*)-isomer, t_R = 11.907 min (major) for (*R*)-isomer. ee = 93.3%. $[\alpha]_D^{23}$ -58.07 (c = 1.0, toluene). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 4H), 7.41-7.36 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 3H), 7.20 (d, *J* = 9.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.50 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.86 (d, *J* = 6.4 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR**(100 MHz, $CDCl_3$) δ 149.23, 140.40, 139.95, 136.53, 132.29, 129.36, 129.28, 128.97, 128.46, 128.43, 127.80, 127.74, 127.30, 127.04, 126.62, 85.72, 21.43. MS m/z: anal. calcd for $C_{23}H_{21}NO$ $[M]^+$: 327.16, found: 193.25, 178.26, 115.24, 91.18, 77.14.

(*R*, E)-4,4'-(3-(benzyloxy)prop-1-ene-1,3-diyl)bis(chlorobenzene) (4ba) [1]

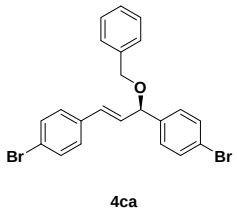


4ba

Yield: 81%.The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 98:2 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 25.142 min (major) for (*R*)-isomer, t_R = 31.485 min (minor) for (*S*)-isomer. ee = 96.9%. $[\alpha]_D^{23}$ -9.01 (c = 1.0, toluene)

^{1}H NMR (600 MHz, $CDCl_3$)δ 7.35-7.33 (m, 7H), 7.31-7.28 (m, 3H), 7.27-7.25 (m, 3H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.97 (d, *J* = 7.2 Hz, 1H), 4.54 (s, 2H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.37, 137.98, 134.81, 133.49, 133.46, 130.42, 128.71, 128.67, 128.41, 128.29, 127.77, 127.66, 80.63, 70.21. MS m/z: anal. calcd for $C_{22}H_{18}Cl_2O$ $[M]^+$: 368.07, found: 368.32.

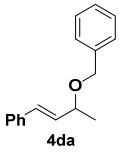
(*R*, E)-4,4'-(3-(benzyloxy)prop-1-ene-1,3-diyl)bis(bromobenzene) (4ca) [1]



4ca

Yield: 80%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 98:2 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 35.622 min (major) for (*R*)-isomer, t_R = 52.040 min (minor) for (*S*)-isomer. ee = 96.8%. $[\alpha]_D^{23}$ -0.96 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 14.2 Hz, 4H), 7.29 (d, *J* = 7.0 Hz, 3H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.26 (dd, *J* = 15.8, 6.8 Hz, 1H), 4.95 (d, *J* = 7.2 Hz, 1H), 4.54 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.81, 137.92, 135.21, 131.64, 131.60, 130.50, 130.46, 128.62, 128.40, 128.06, 127.65, 121.64, 121.62, 80.66, 70.21. HRMS (EI) m/z: anal. calcd for $C_{22}H_{18}Br_2O$ $[M]^+$: 455.9724, found: 455.9728.

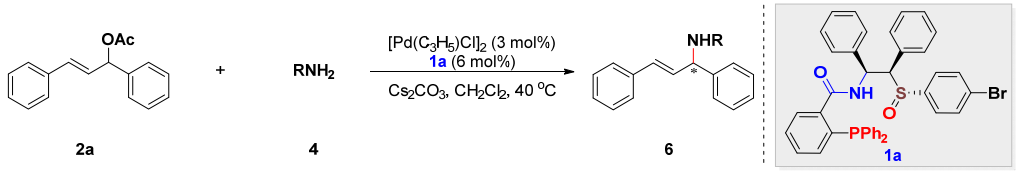
(E)-(3-(benzyloxy)but-1-en-1-yl)benzene(4da)[6]



4da

Yield: 64%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 97:3 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 10.845 min (major) for (*R*)-isomer, t_R = 13.672 min (minor) for (*S*)-isomer. ee = 52.1%. $[\alpha]_D^{26}$ -37.91 (c = 0.6, toluene). **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.45-7.49 (m, 2H), 7.38 – 7.31 (m, 6H), 7.29-7.23 (m, 6.0 Hz, 2H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 7.7 Hz, 1H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.21 – 4.03 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.74, 136.62, 131.66, 131.41, 128.58, 128.36, 127.67, 127.43, 126.46, 75.84, 70.03, 21.75. HRMS (EI) m/z: anal. calcd for $C_{17}H_{18}O$ $[M]^+$: 238.1358, found: 238.1364.

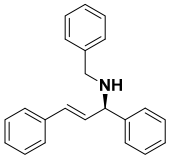
3.3 General Procedure for Pd-Catalyzed Enantioselective Allylic Amination Reactions



Ligand **1a** (8.3 mg, 0.012 mmol, 6 mol%) and $[Pd(C_3H_5)Cl]_2$ (2.2 mg, 0.006 mmol, 3 mol%) were dissolved in CH_2Cl_2 (1.0 mL) in a Schlenk tube under Ar. After stirring at room temperature for 1 h,allylic acetate **2**(0.2 mmol) dissolved inCH_2Cl_2 (1.0 mL) was added, followed by amine(0.6 mmol), and Cs_2CO_3 (196 mg, 0.6 mmol). The mixture wasstirred at 40 °C for 4 h and then was dilutedwith diethyl ether and washed with saturated NH_4Cl(aq). Theorganic layers were dried over Na_2SO_4 and filtered, and thesolvents were evaporated in vacuo. The residue was purified byflash columnchromatrography,eluting with petroleum ether and ethyl acetateto afford the corresponding product **6**.

3.3Spectral Data of Allylic AminationProducts

(*R*, E)-(3-(benzyloxy)but-1-en-1-yl)benzene (6a) [1]

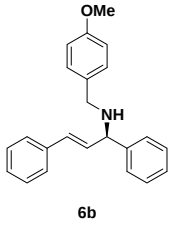


6a

Yield: 83%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 7.427 min (major) for (*R*)-isomer, t_R = 7.877 min (minor) for (*S*)-isomer. ee = 97.1%. $[\alpha]_D^{23}$ -18.47 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.39 (m, 2H), 7.36-7.32 (m, 7H), 7.30 (s, 1H), 7.29 – 7.12 (m, 5H). 6.58 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.40 (d, *J* = 7.5 Hz, 1H), 3.79 (dd, *J* = 17.6 Hz, *J* = 9.2 Hz,

2H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.76, 140.26, 136.85, 132.47, 130.34, 128.59, 128.47, 128.39, 128.15, 127.42, 127.33, 127.27, 126.92, 126.37, 64.53, 51.32. MS m/z: anal. calcd for $C_{22}H_{21}N$ $[M]^+$: 299.17, found: 299.22.

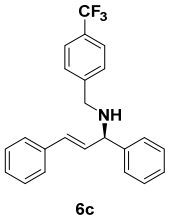
. **(R, E)-N-(4-methoxybenzyl)-1,3-diphenylprop-2-en-1-amine (6b)** [1]



6b

Yield: 97%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 22.175 min (minor) for (*S*)-isomer, t_R = 23.649 min (major) for (*R*)-isomer. ee = 98.5%. $[\alpha]_D^{23}$ -16.6 (c = 1.0, toluene). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 4H), 7.29 – 7.11 (m, 6H), 6.85 (d, *J* = 8.6 Hz, 2H). 6.56 (d, *J* = 10.5 Hz, 1H), 6.31 (dd, *J* = 10.5, 5 Hz, 1H), 4.37 (d, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.70 (dd, *J* = 9.8, 5.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.57, 142.90, 136.93, 132.64, 132.48, 130.24, 129.29, 128.55, 128.45, 127.33, 127.20, 126.36, 113.77, 64.43, 55.21, 50.74. HRMS (EI) m/z: anal. calcd for $C_{23}H_{23}NO$ $[M]^+$: 329.1780, found: 329.1783.

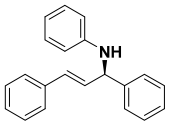
(*R*, E)-1,3-diphenyl-N-(4-(trifluoromethyl)benzyl)prop-2-en-1-amine (6c)



6c

Yield: 83%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 6.309 min (minor) for (*S*)-isomer, t_R = 7.577 min (major) for (*R*)-isomer. ee =97.0%. $[\alpha]_D^{23}$ -12.41(c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 9.4 Hz, 4H), 7.39 -7.32 (m, 4H), 7.27 (t, *J* = 7.2 Hz, 3H), 7.22 -7.18 (m, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.31 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.37 (d, *J* = 7.4 Hz, 1H), 3.84 (s, 2H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 144.60, 142.58, 136.76, 132.25, 130.52, 129.25, 128.93, 128.63, 128.48, 128.27, 127.51, 127.38, 127.26, 126.37, 125.63, 125.27, 125.24, 125.20, 125.16, 122.93, 64.61, 50.75. HRMS (EI) m/z: anal. calcd for $C_{23}H_{20}NF_3$ $[M]^+$: 367.1548, found: 367.1548.

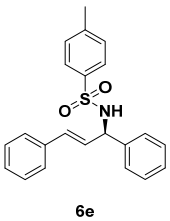
(*R*, E)-N-(1,3-diphenylallyl)aniline (6d) [1]



6d

Yield: 90%. The ee was determined by chiral HPLC (Chiralpak AS-H, hexane/isopropanol 99:1 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 18.353 min (minor) for (*S*)-isomer, t_R= 20.731 min (major) for (*R*)-isomer.ee = 97.3%. $[\alpha]_D^{23}$ -46.54 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, CDCl3) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.36 (dd, *J* = 7.3, 5.5 Hz, 4H), 7.29 (dd, *J* = 9.6, 5.5 Hz, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.65-6.60 (m, 3H), 6.40 (dd, *J* = 15.8, 6.2 Hz, 1H), 5.08 (d, *J* = 6.1 Hz, 1H), 4.11 (s, 1H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 147.17, 141.99, 136.56, 130.99, 130.63, 129.10, 128.78, 128.50, 127.62, 127.48, 127.17, 126.47, 117.64, 113.53, 60.60. HRMS (EI) m/z: anal. calcd for $C_{21}H_{19}N$ $[M]^+$: 285.1517, found: 285.1518.

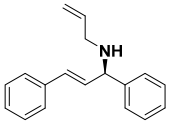
(*R*, E)-N-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (6e) [2]



6e

Yield: 87%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 90:10 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C): Retension times: t_R = 33.632 min (major) (*R*)-isomer, t_R= 47.897 min (minor) for (*S*)-isomer. ee = 93.6%. $[\alpha]_D^{23}$ -29.52 (c = 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.40-7.22 (m, 6H), 7.21-6.99 (m, 6H), 6.35 (d, *J* = 16.6 Hz, 1H), 6.07 (dd, *J* = 16.2, 6.7 Hz, 1H), 5.11 (t, *J* = 6.9 Hz, 1H), 4.95 (s, 1H), 2.33 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$)δ 143.14, 139.58, 137.60, 135.99, 131.90, 129.34, 128.59, 128.34, 128.08, 127.76, 127.68, 127.21, 126.97, 126.44, 59.70, 21.33. MS (EI) m/z: anal. calcd for $C_{22}H_{21}NO_2S$ $[M+Na]^+$: 386.11, found: 386.20.

(*R*, E)-N-allyl-1,3-diphenylprop-2-en-1-amine (6f) [2]

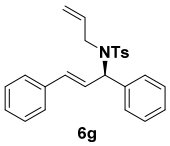


6f

Yield: 72%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 5.296 min (minor) for (*S*)-isomer, t_R = 5.581 min (major) for (*R*)-isomer, ee = 97.9%. $[\alpha]_D^{23}$ -1.22 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.36 (dd, *J* = 7.4, 2.5 Hz, 3H), 7.33-7.23 (m, 4H), 7.23-7.16 (m, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.8, 7.5 Hz, 1H), 6.04 -5.84 (m, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H), 4.40 (d, *J* = 7.4 Hz, 1H), 3.32-3.14 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.76, 136.82, 136.69, 132.46, 130.19, 128.50, 128.40, 127.34, 127.22, 127.17, 126.31, 115.85, 64.60, 49.88. HRMS (EI) m/z: anal. calcd for $C_{18}H_{19}N$ $[M]^+$: 249.1517, found: 249.1522.

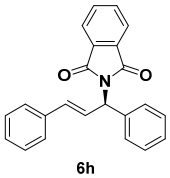
(*R*, E)-N-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (6g)



6g

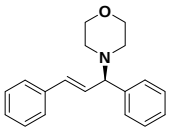
Yield: 81%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 70:30 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 7.893 min (major) for (*R*)-isomer, t_R = 8.979 min (minor) for (*S*)-isomer. ee = 89.9%. $[\alpha]_D^{23}$ -2.56 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.38-7.26 (m, 7H), 7.24-7.22 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.32 – 6.31 (m, 2H), 5.80 (s, 1H), 5.61-5.51(m, 1H), 4.95-4.90 (m, 2H), 3.89 (dd, *J* = 16.2, 6.0 Hz, 1H), 3.78 (dd, *J* = 16.3, 6.3 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) 1δ 143.00, 138.74, 137.78, 136.08, 135.09, 133.90, 129.30, 128.44, 128.31, 128.05, 127.84, 127.66, 127.38, 126.34, 125.50, 117.14, 77.29, 76.97, 76.66, 62.93, 47.92, 21.31. 75.02, 64.64, 49.88. HRMS (EI) m/z: anal. calcd for $C_{25}H_{25}NO_2S$ $[M+Na]^+$: 426.1504, found: 426.1500.

(*R*, E)-2-(1,3-diphenylallyl)isoindoline-1,3-dione (6h) [2]


6h

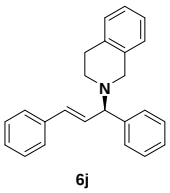
Yield: 80%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 98:2 v/v, flow rate 0.5 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 32.969 min (minor) for (*S*)-isomer, t_R= 41.587 min (major) for (*R*)-isomer. ee = 98.3%. $[\alpha]_D^{23}$ -15.99 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.77 (m, 2H), 7.75-7.62 (m, 2H), 7.46 (dd, *J* = 18.0, 7.5 Hz, 4H), 7.31-7.22 (m, 6H), 7.07 (dd, *J* = 15.9, 8.6 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.13 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.76, 138.86, 136.21, 134.37, 134.02, 131.95, 128.58, 128.07, 127.75, 127.39, 126.72, 125.26, 123.35, 56.46. MS m/z: anal. calcd for $C_{23}H_{17}NO_2$ $[M]^+$: 339.13, found: 339.31.

(*R*, E)-4-(1,3-diphenylallyl)morpholine (6i) [2]


6i

Yield: 80%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 6.918 min (minor) for (*S*)-isomer, t_R= 13.509 min (major) for (*R*)-isomer, ee = 95.3%. $[\alpha]_D^{23}$ -4.28 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.38-7.30 (m, 4H), 7.28 (t, *J* = 15 Hz, 2H), 7.25-7.13 (m, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.28 (dd, *J* = 15.8, 9 Hz, 1H), 3.78 (d, *J* = 8.9 Hz, 1H), 3.71 (t, *J* = 4.6 Hz, 4H), 2.65-2.33 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.45, 136.64, 131.51, 131.30, 128.63, 128.47, 127.97, 127.53, 127.28, 126.33, 74.82, 67.10, 52.16. MS m/z: anal. calcd for $C_{19}H_{21}NO$ $[M]^+$: 279.16, found: 279.31.

(*R*,E)-2-(1,3-diphenylallyl)-1,2,3,4-tetrahydroisoquinoline (6j)


6j

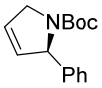
Yield: 84%. The ee was determined by chiral HPLC (Chiralcel AD-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 5.647 min (minor) for (*S*)-isomer, t_R= 6.670 min (major) for (*R*)-isomer, ee = 85.1%. $[\alpha]_D^{26}$ -31.88 (c = 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.22 – 7.18 (m, 1H), 7.13-7.07 (m, 3H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.40 (dd, *J* = 15.8, 8.9 Hz, 1H), 4.01 (d, *J* = 8.9 Hz, 1H), 3.80 (d, *J* = 15.1 Hz, 1H), 3.60 (d, *J* = 15.0 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.77 (t, *J* = 5.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.05, 136.79, 134.98, 134.56, 131.71, 131.14, 128.65, 128.60, 128.50, 127.87, 127.50, 127.23, 126.78, 126.39, 126.05, 125.53, 73.74, 54.66, 48.47, 29.12. HRMS (EI) m/z: anal. calcd for C24H23N $[M+H]^+$: 325.1830, found: 326.1900.

(R)-2-phenyl-2,5-dihydrofuran (7) [3]

7

A solution of Grubbs II catalyst (8.5 mg, 0.01 mmol) and **4m** (78 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 12 h. The solution was directly purified by flash column chromatrography, eluting with petroleum ether and ethyl acetate to afford the corresponding product **7**. Yield: 56%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, λ = 210 nm, 25 °C). Retension times: t_R = 5.772 min (major) for (*R*)-isomer, t_R = 6.288 min (minor) for (*S*)-isomer. ee = 96.8%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 1H), 7.31 (dd, *J* = 5.4, 1.2 Hz, 2H), 7.29-7.21 (m, 2H),, 6.00-6.00 (m, 1H), 5.88 (ddd, *J* = 4.4, 3.2, 1.6 Hz, 1H), 5.79 (ddd, *J* = 6, 3.2, 2.0 Hz, 1H), 4.89-4.84 (m, 1H), 4.79-4.73 (m, 1H).**^{13}C NMR** (100MHz, $CDCl_3$) δ 141.97, 129.89, 128.42, 127.73, 126.55, 126.31, 87.82, 75.73. HRMS (EI) m/z: anal. calcd for $C_{10}H_{10}O$ $[M]^+$: 146.0732, found: 146.0726.

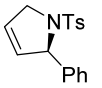
tert-butyl (R)-2-phenyl-2,5-dihydro-1H-pyrrole-1-carboxylate (8) [4]



8

To a stirred solution of 6d (50 mg, 0.2 mmol) in ethanol (2 ml) was added $(Boc)_2O$ (52 mg, 0.24 mmol), stirred overnight, then put to flash chratgraphy directly to afford the Boc protected product, dried over oil pump to get the desired product in 90% yield. A solution of Grubbs II catalyst (8.5 mg, 0.01 mmol) and **the above product** (70 mg, 0.20 mmol) in benzene (4 mL) was stirred at 40 °C for 1 h. The solution was directly purified by flash column chromatrography, eluting with petroleum ether and ethyl acetate to afford the corresponding product **8**. Yield in two steps: 72%. The ee was determined by chiral HPLC (Chiralpak IC-H hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 210 nm, 25 °C). Retension times: t_R = 10.389 min (major) for (*R*)-isomer, t_R =11.107 min (minor) for (*S*)-isomer. ee = 98.3%. $[\alpha]_D^{23}$ 238.6 (c = 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz,$CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 (dd, *J* = 14.1, 4.9 Hz, 2H), 7.17 (t, *J* = 27.6 Hz, 1H), 5.87 (d, *J* = 23, 1H), 5.73 (dd, *J* = 13.0, 11.2 Hz, 1H), 5.45 (d, *J* = 91.8 Hz, 1H), 4.46-4.20 (m, 2H), 1.32 (d, *J* = 135.8 Hz, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.01, 142.38, 131.10, 128.35, 128.06, 127.12, 126.57, 126.44, 124.49, 79.41, 68.06, 67.74, 54.00, 53.61, 28.40, 28.06. MS m/z: anal. calcd for $C_{15}H_{19}NO_2$ $[M]^+$: 254.14, found: 254.48.

(R)-2-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (9) [4]



9

A solution of Grubbs II catalyst (1.7 mg, 0.002 mmol) and **6e** (40 mg, 0.10 mmol) in benzene (2 mL) was stirred at 60°C for 1 h.The solution was directly purified by flash column chromatrography, eluting with petroleum ether and ethyl acetate to afford the corresponding product **9**. Yield: 70%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 85:15 v/v, flow rate 1.0 mL/min, λ = 210 nm, 25 °C). Retension times: t_R = 11.174 min (major) for (*R*)-isomer, t_R = 12.895 min (minor) for (*S*)-isomer. ee = 89.7%. $[\alpha]_D^{23}$ 231.94 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.27 (dt, *J* = 15.2, 4.9 Hz, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.78 (dd, *J* = 6 Hz, 2 Hz, 1H), 5.65 (dd, *J* = 6.1, 2.2 Hz, 1H), 5.56-5.46 (m, 1H), 4.35(dd, *J* = 14.6, 1.8 Hz, 1H), 4.25 (dd, *J* = 13.2, 5.6 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.09, 140.38, 135.36, 130.50, 129.39, 128.38, 127.73, 127.20, 127.16, 124.44, 70.15, 55.34, 21.43.HRMS (EI) m/z: anal. calcd for $C_{17}H_{17}NO_2S$ $[M+H]^+$: 300.1058, found: 300.1056.

Reference:

[1] (a) Lam, F. L.; Au-Yeung, T. T. L.; Kwong, F. Y.; Zhou, Z.; Wong, K. Y.; Chan, A. S. C. *Angew. Chem., Int. Ed*. **2008**, *47*, 1280; (b) Haight, A. R.; Stoner, E. J.; Peterson M. J.; Grover, V. K. *J. Org. Chem*. **2003**, *68*, 8092; (c) Kato, M.; Nakamura, T.; Ogata, K.; Fukuzawa, S. *Eur. J. Org. Chem*. **2009**, 5232; (d) Liu, Z.; Du, H. *Org. Lett*. **2010**, *12*, 3054; (e)Sasaki,; Higashi, M.; Masu, H.; Yamaguchi, K.; Takeda K. *Org. Lett*. **2005**, *7*, 5913; (f) Caldentey, X.; Pericàs, M. A. *J. Org. Chem*. **2010**, *75*, 2628; Wang, Y.; Vaismaa, M. J. P.; Hämäläinen, A. M.; Tois, J. E.; Franzén, R. *Tetrahedron:Asymmetry* **2011**, *22*, 524; (f) Dai, L.; Li, X.; Yuan, H.; Li, X.; Li, Z.; Xu, D.; Fei, F.; Liu, Y.; Zhang, J.; Zhou, Z. *Tetrahedron: Asymmetry* **2011**, *22*, 1379; (g) Gavrilov, K. N.; Zheglov, S. V.;

Shiryaev, A. A.; Groshkin, N. N.; Rastorguev, E. A.; Benetskiy, E. B.; Davankov, V. A. *Tetrahedron Lett*. **2011**, *52*, 964; (*h*) Du, L.; Cao, P.; Liao, J. *Acta Chim. Sinica.*, **2013**, *71*, 1239.

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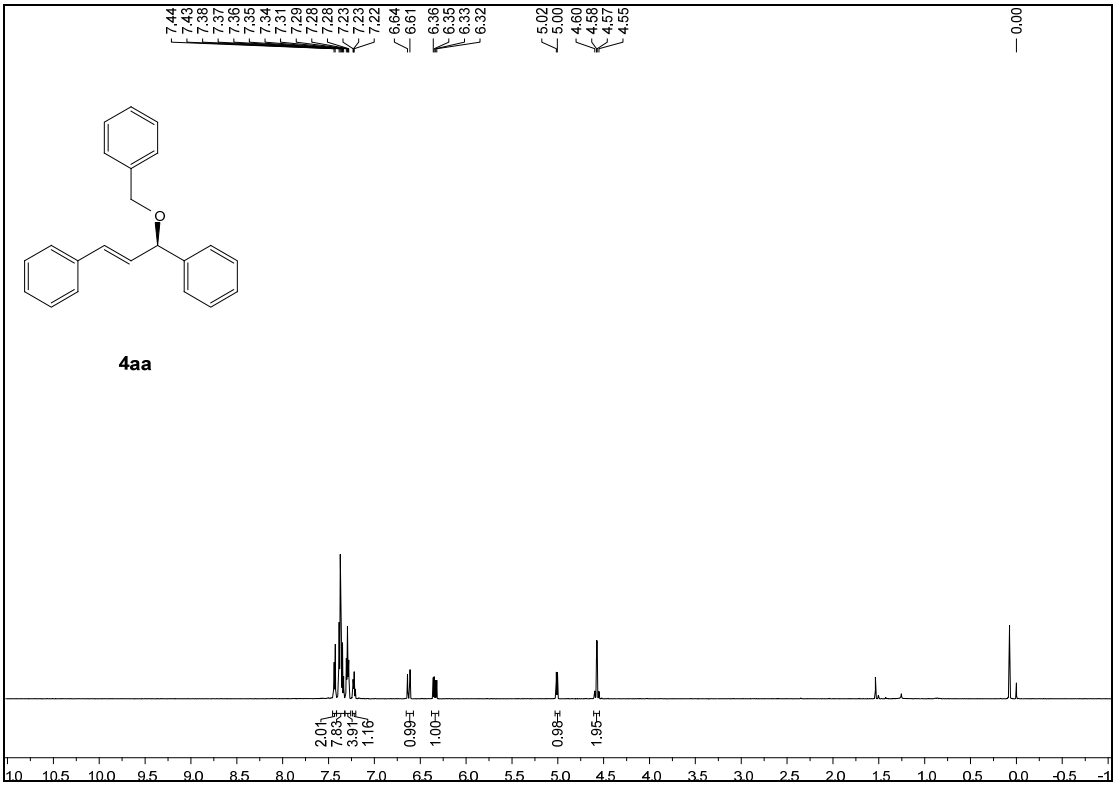
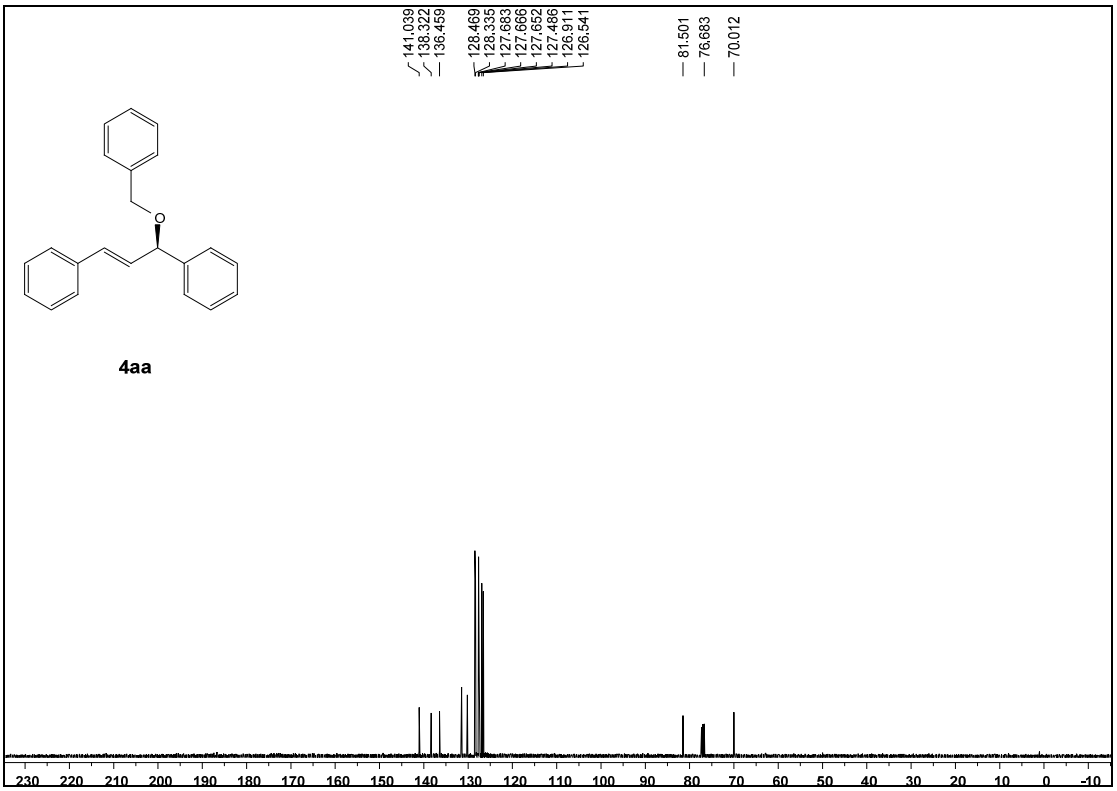
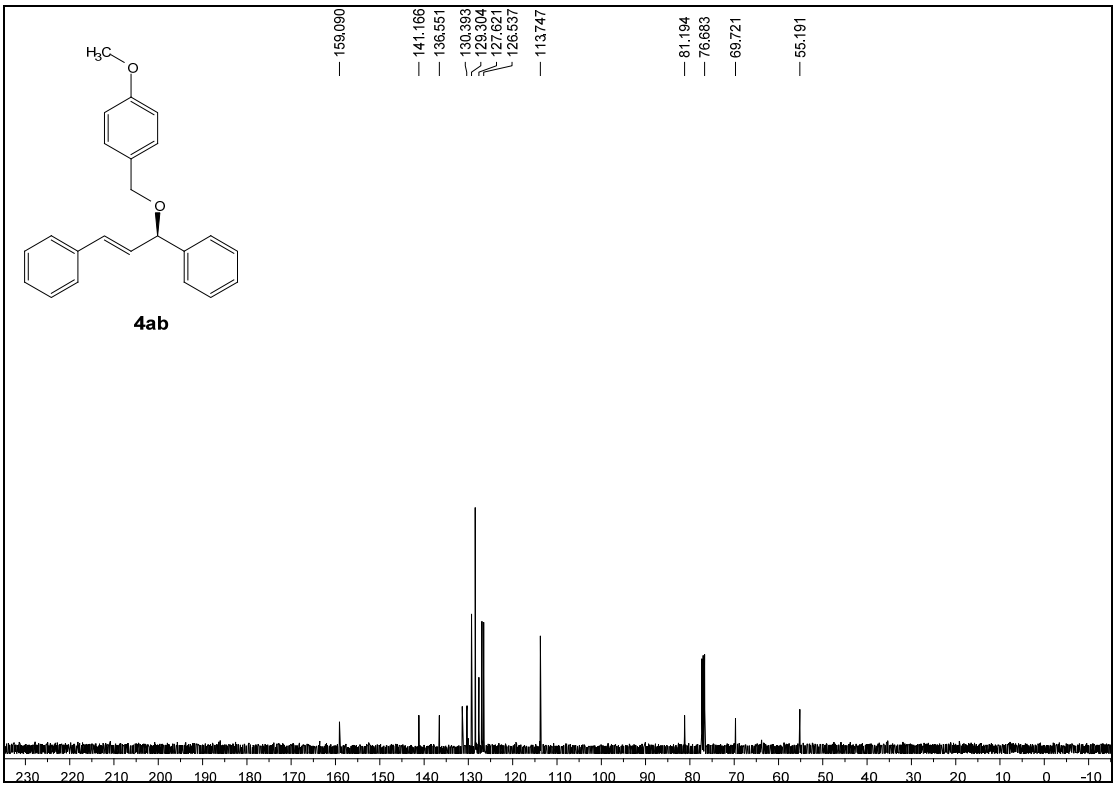
4. Copies of ^{1}H NMR and ^{13}C NMR Spectra

^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4aa

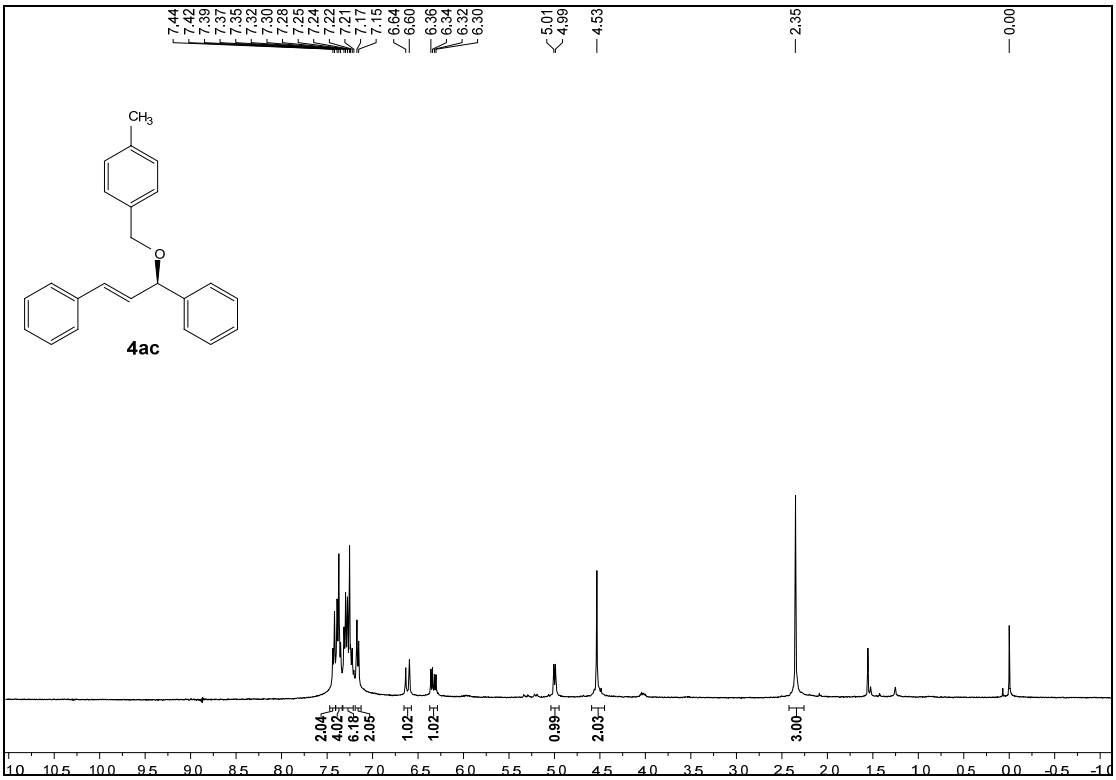


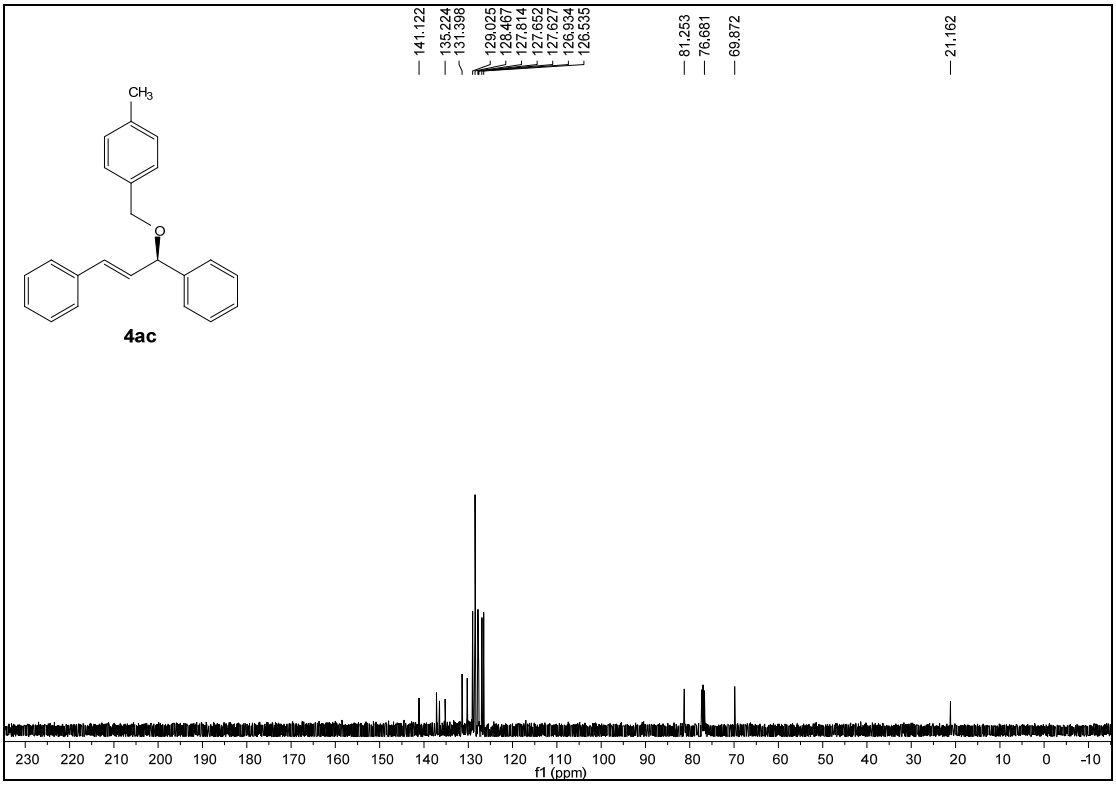


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ab

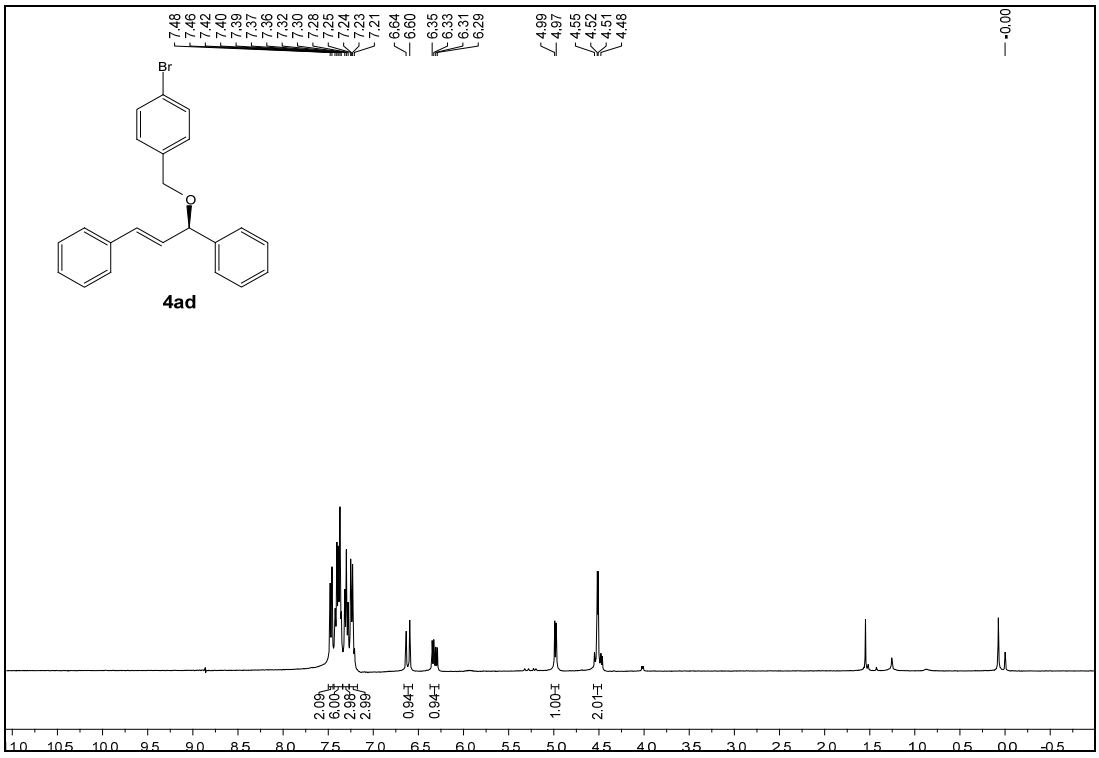


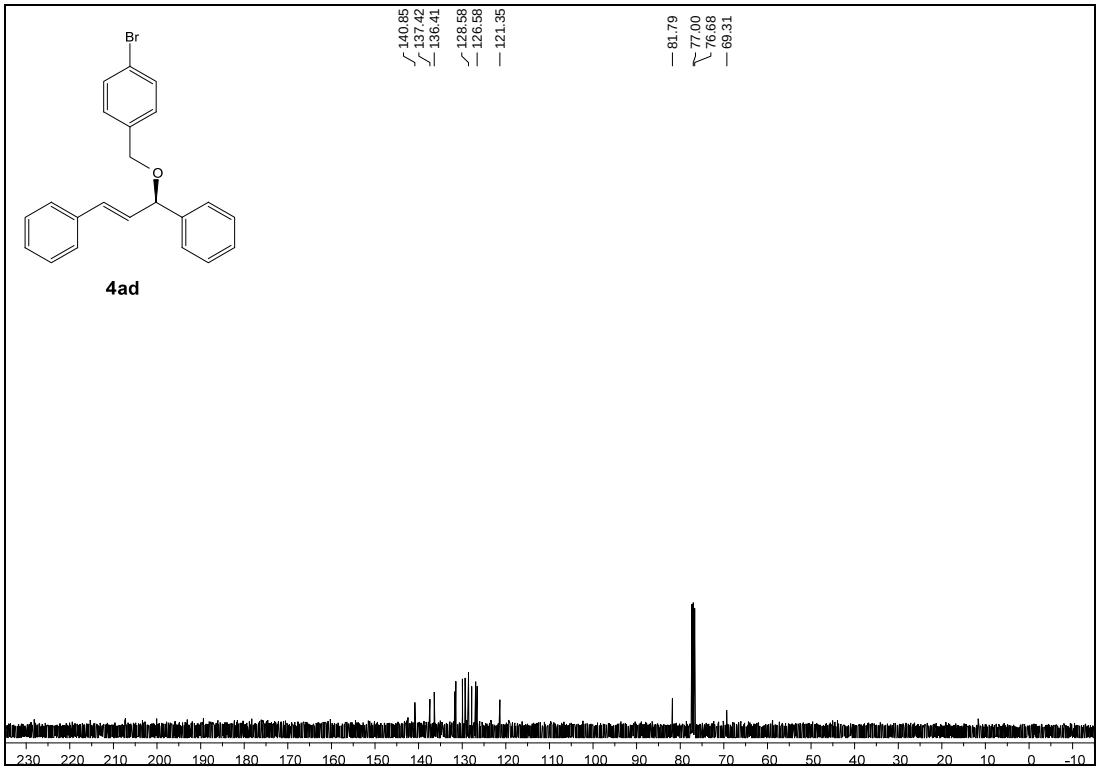
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ac



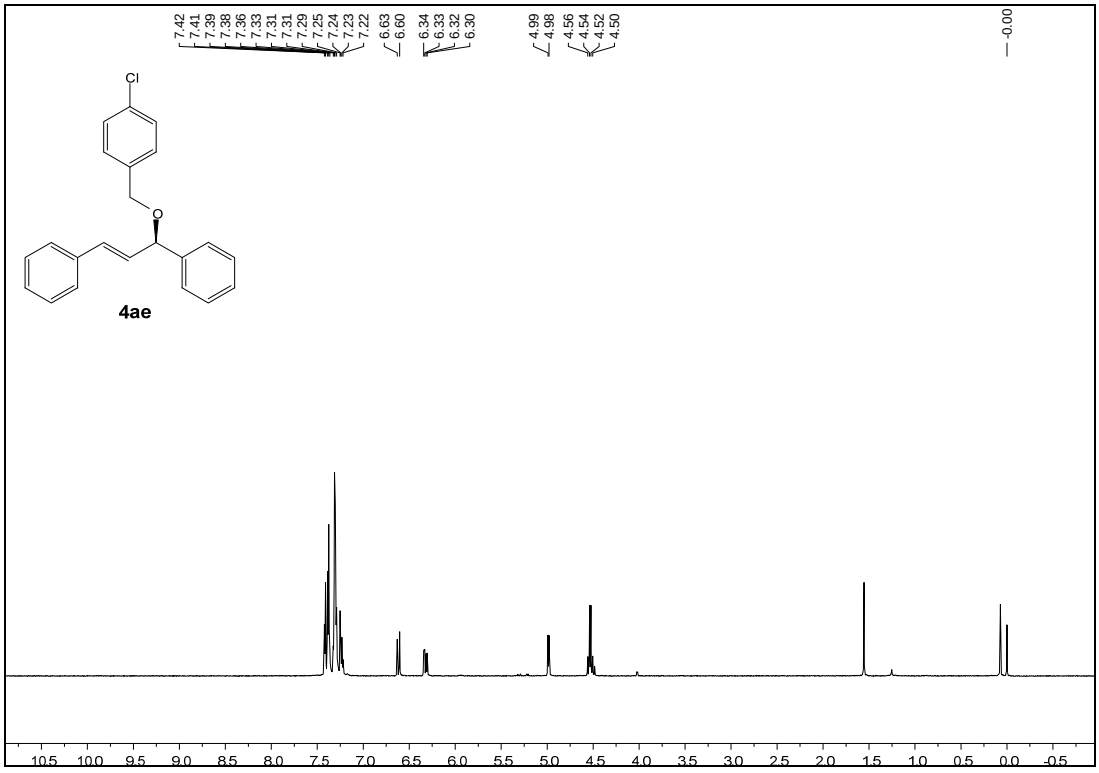


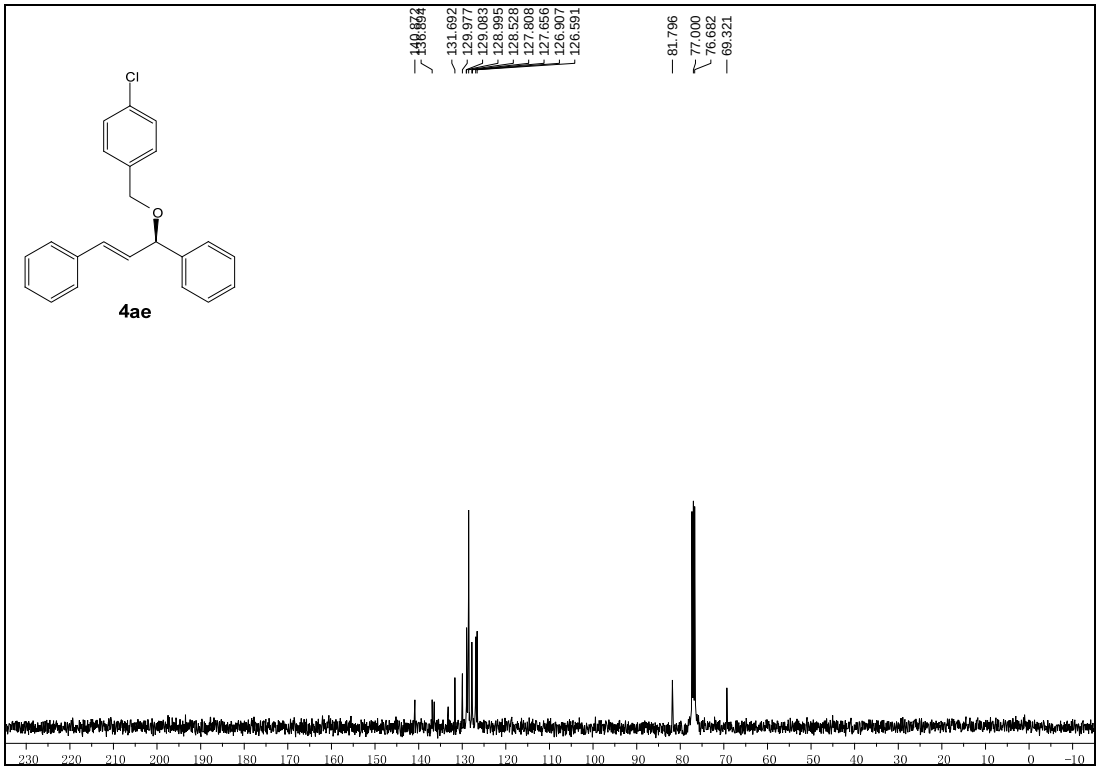
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ad





^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ae





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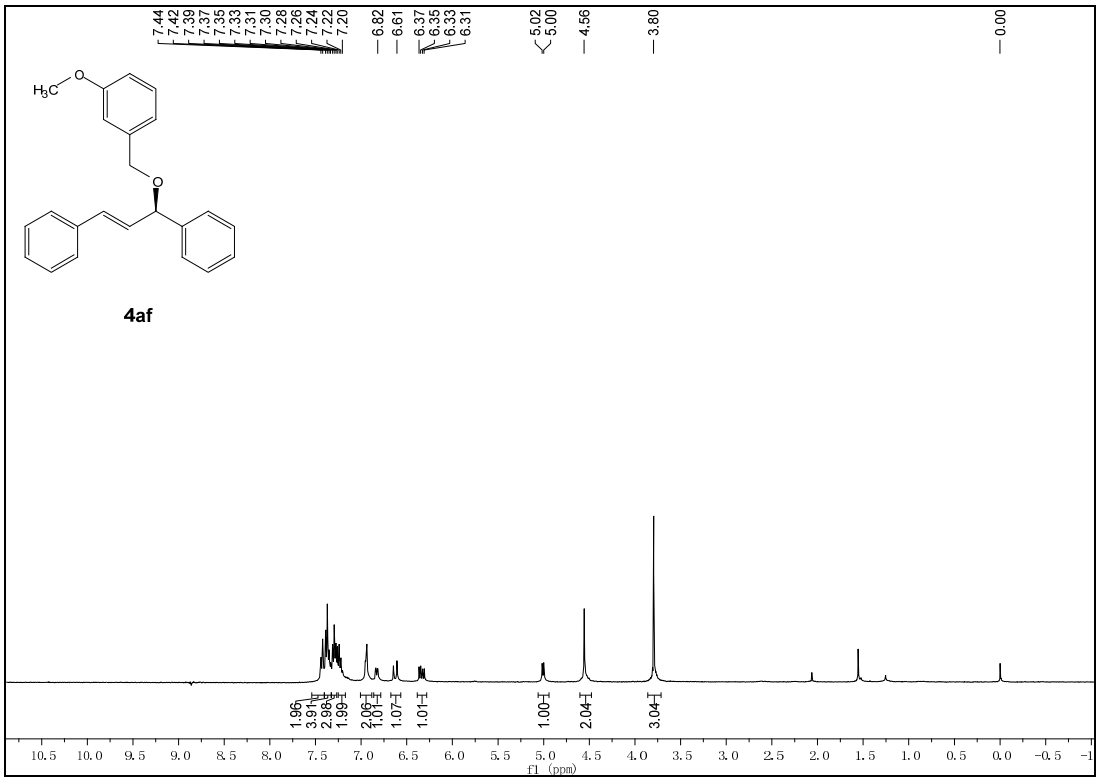

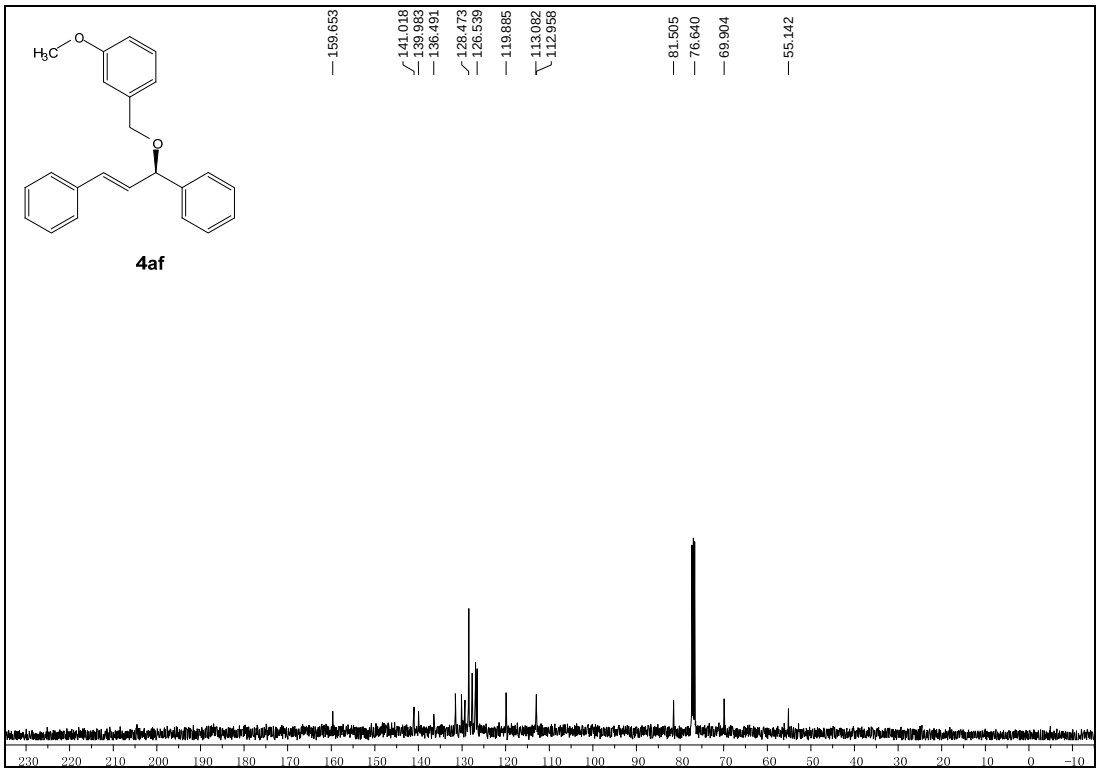

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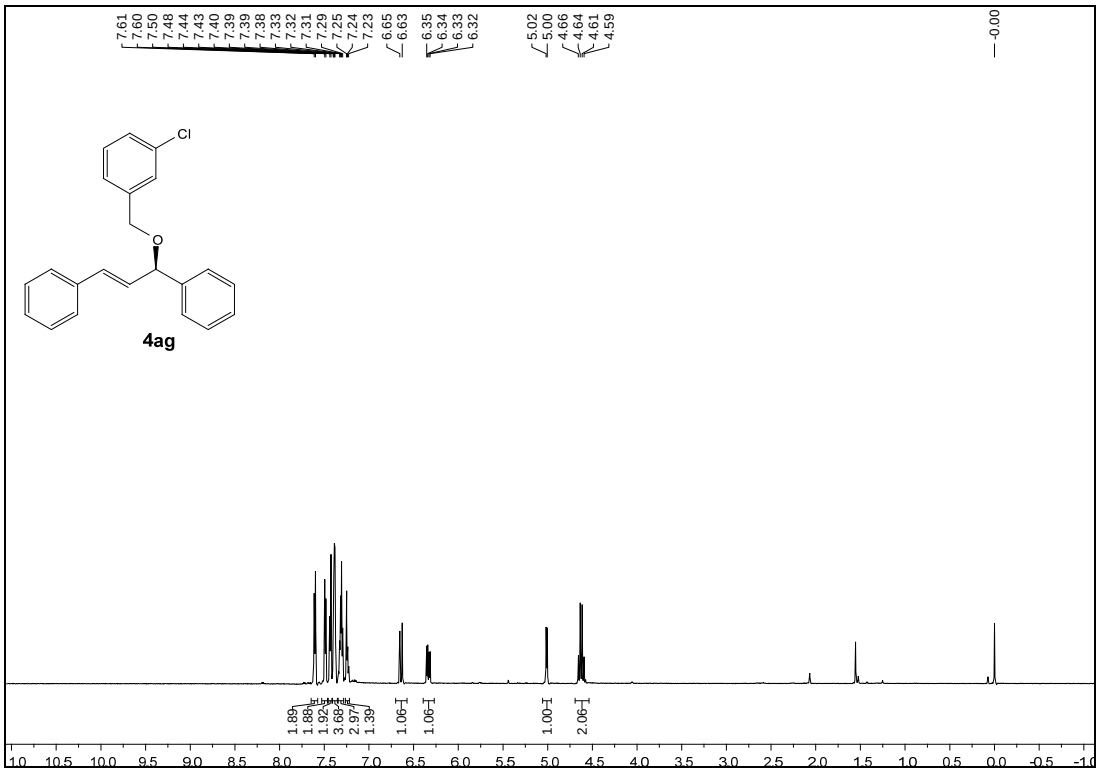

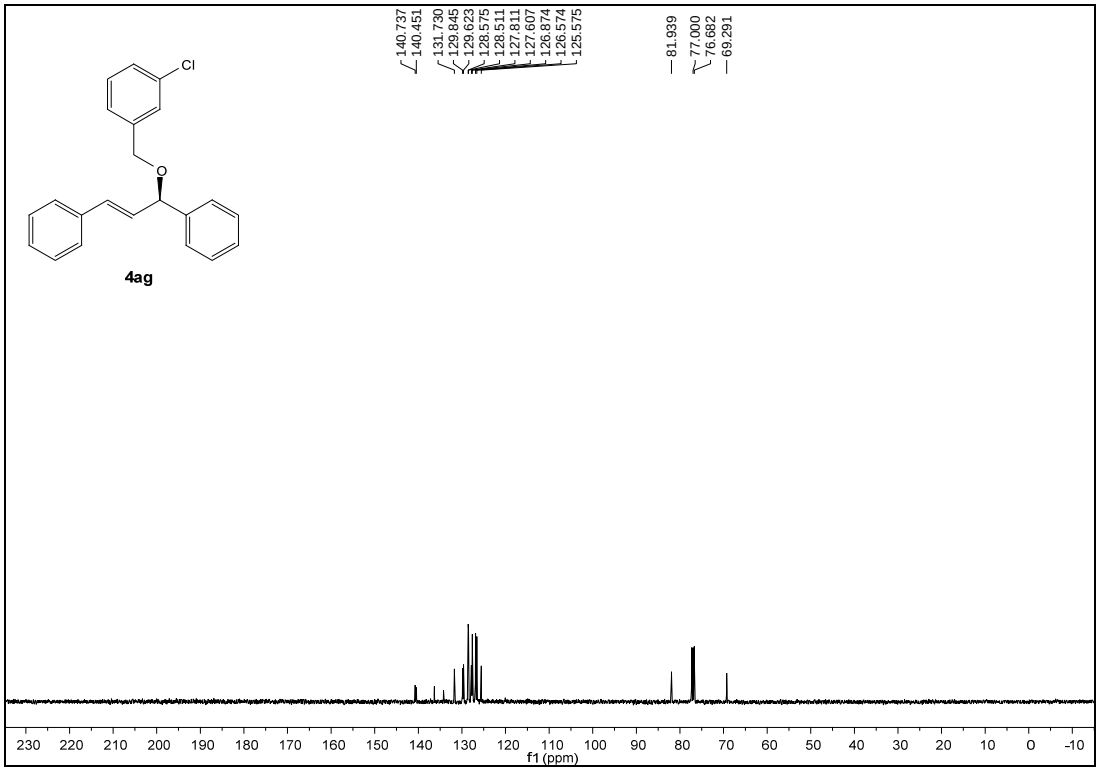

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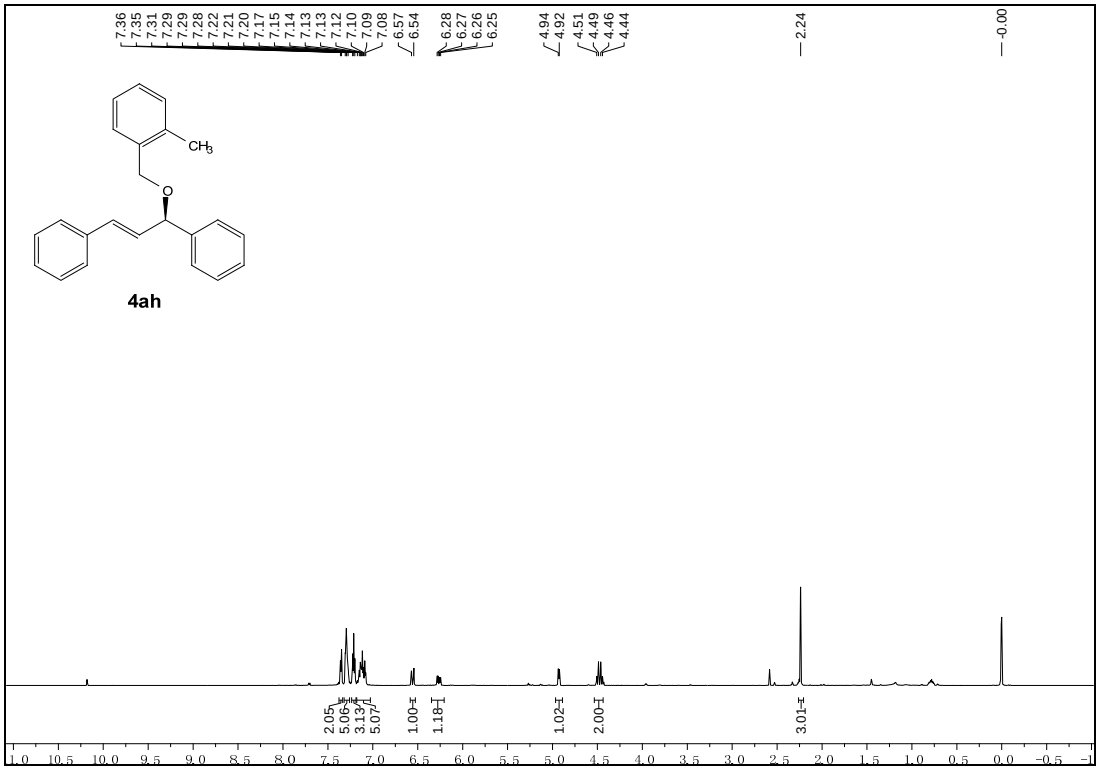

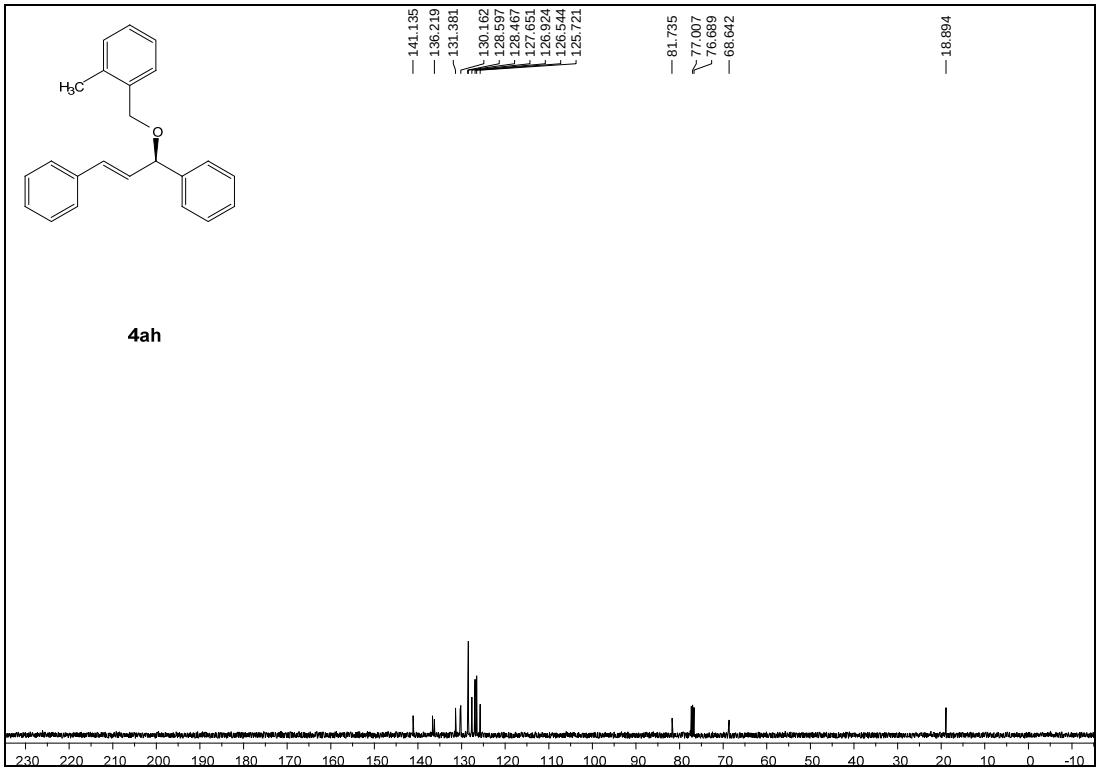

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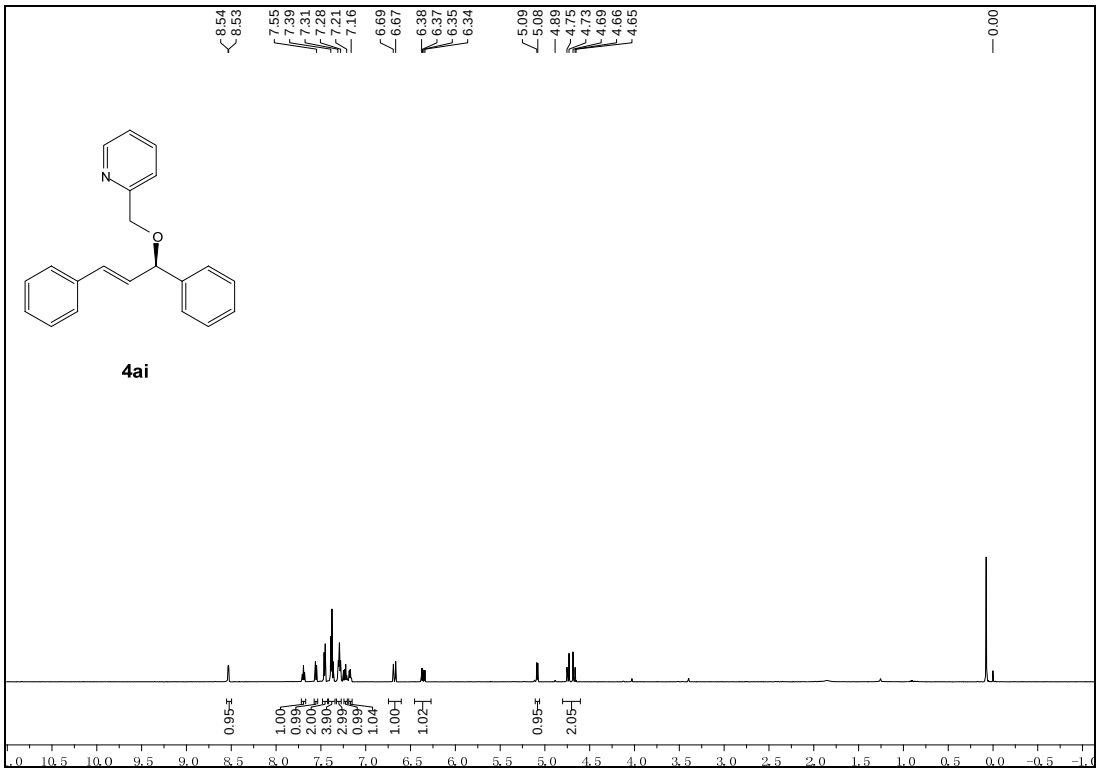

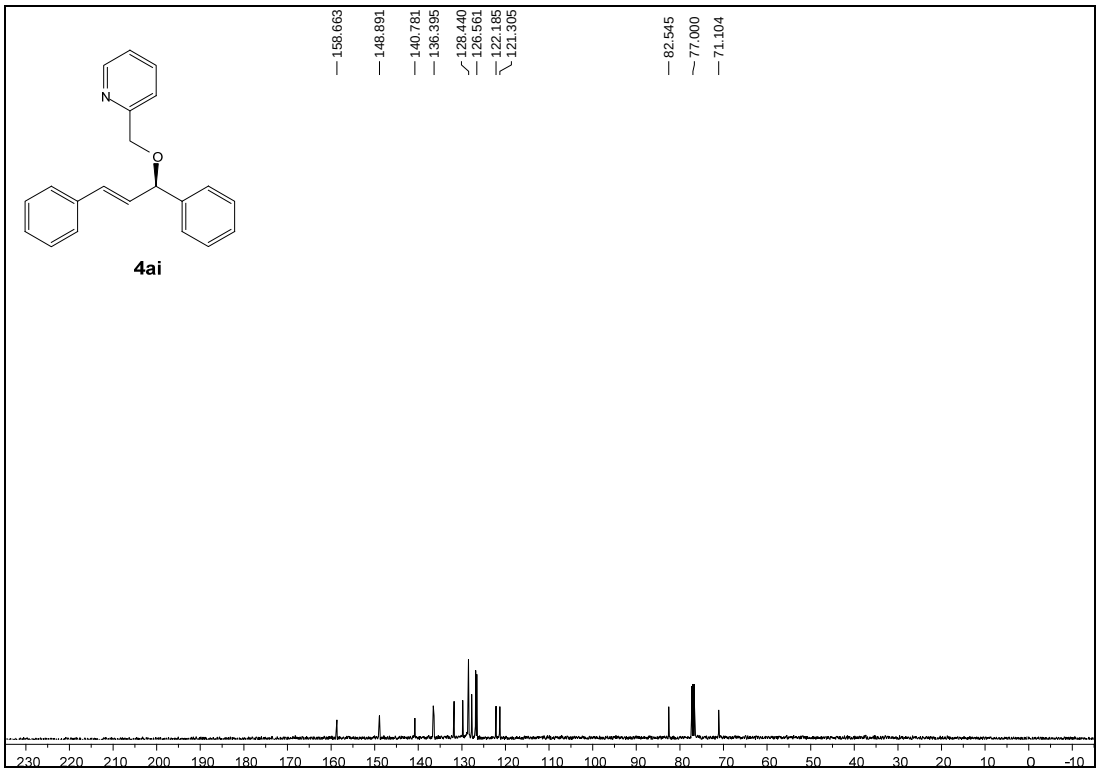

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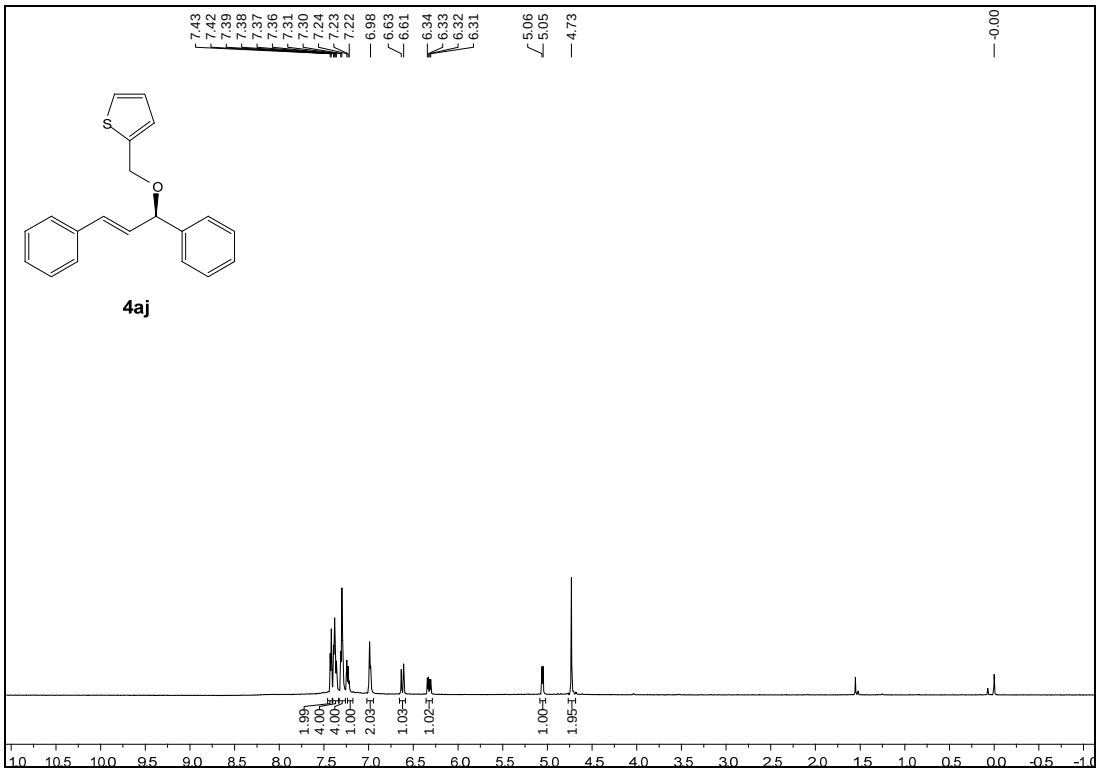

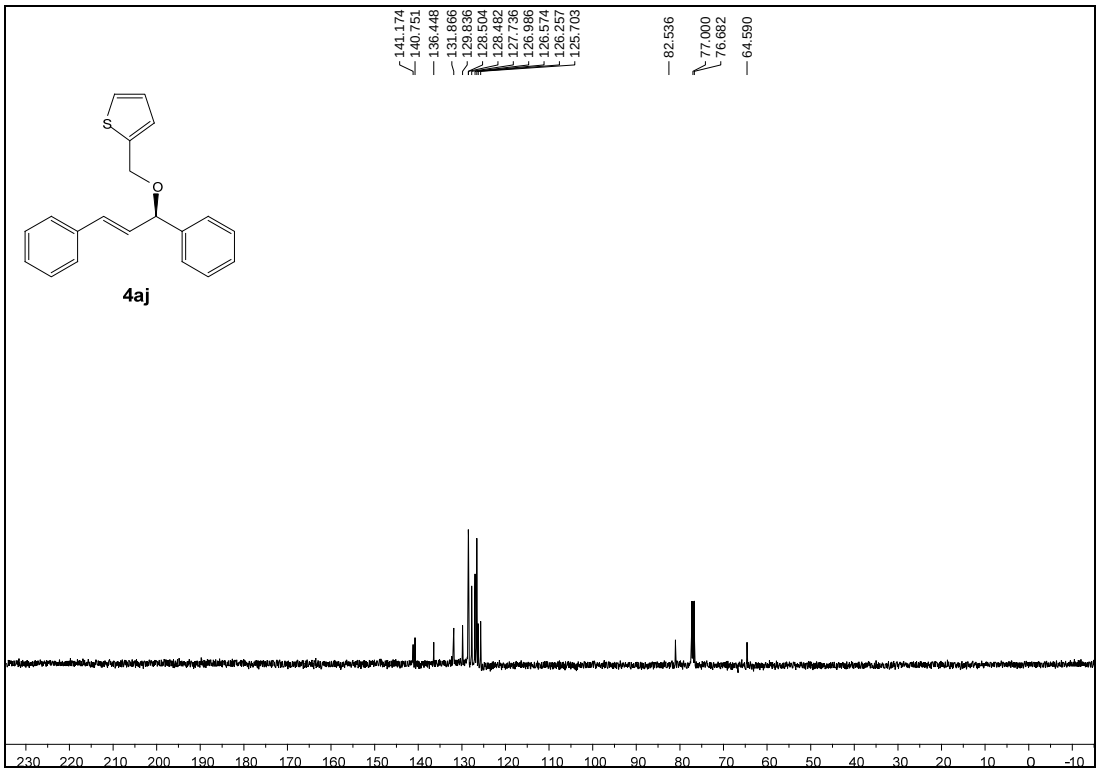

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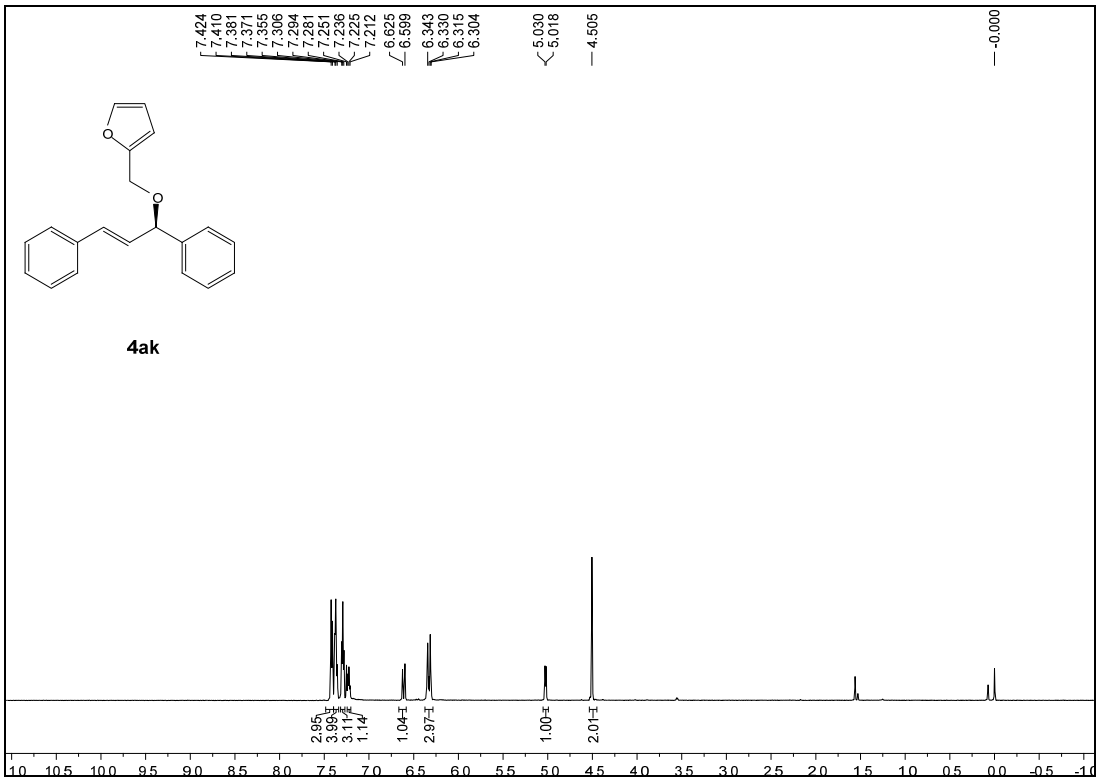
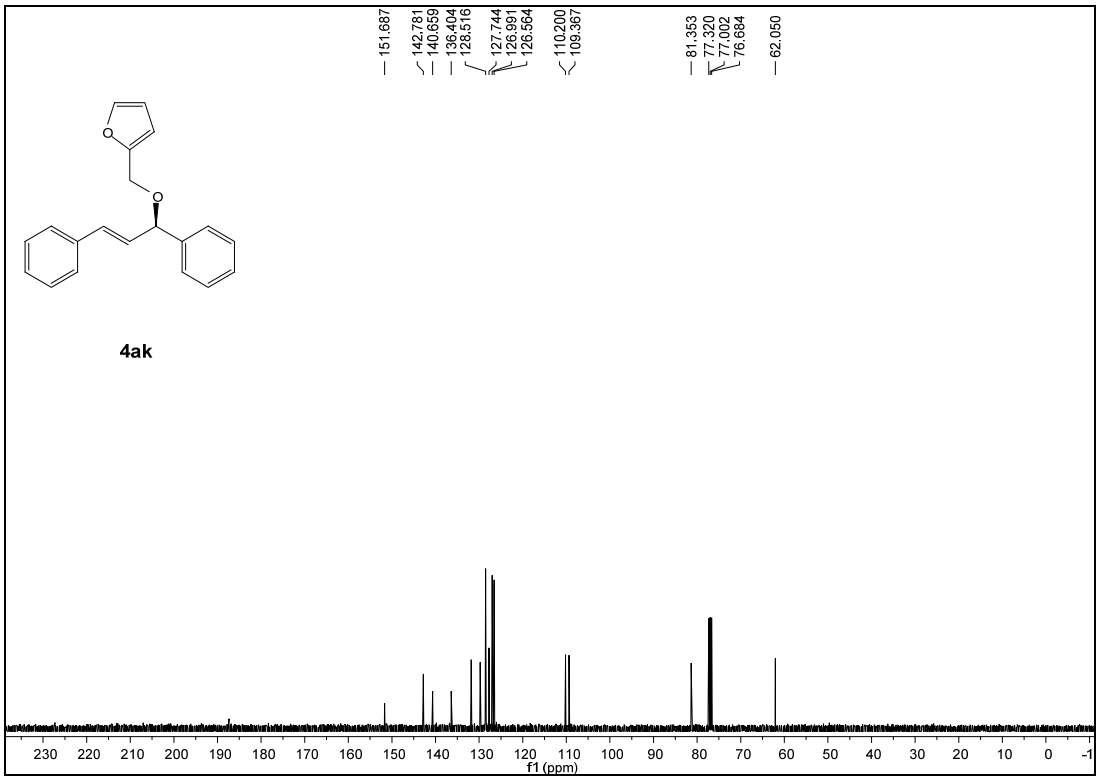
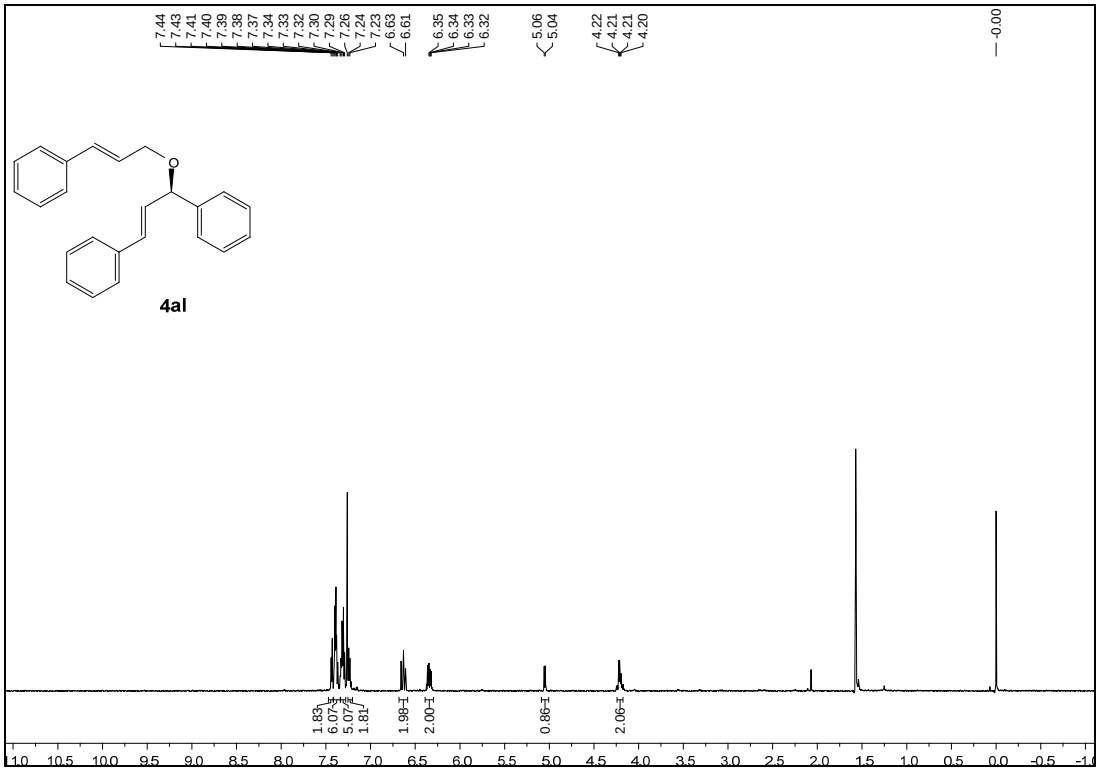
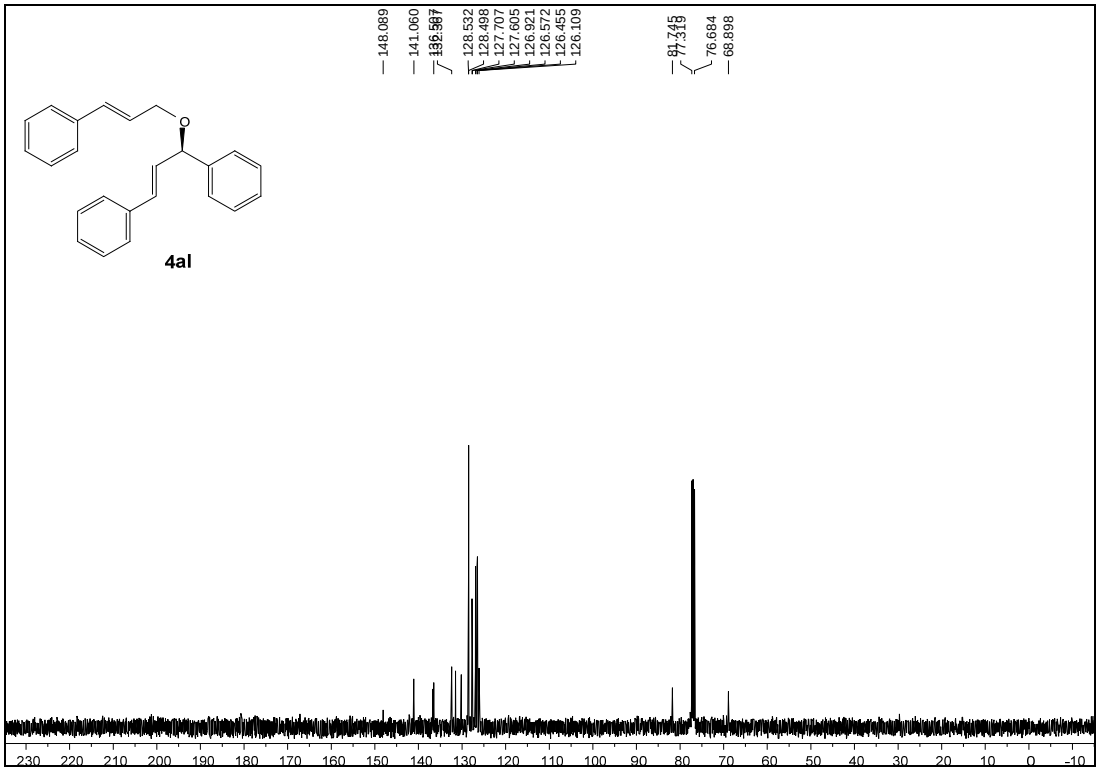


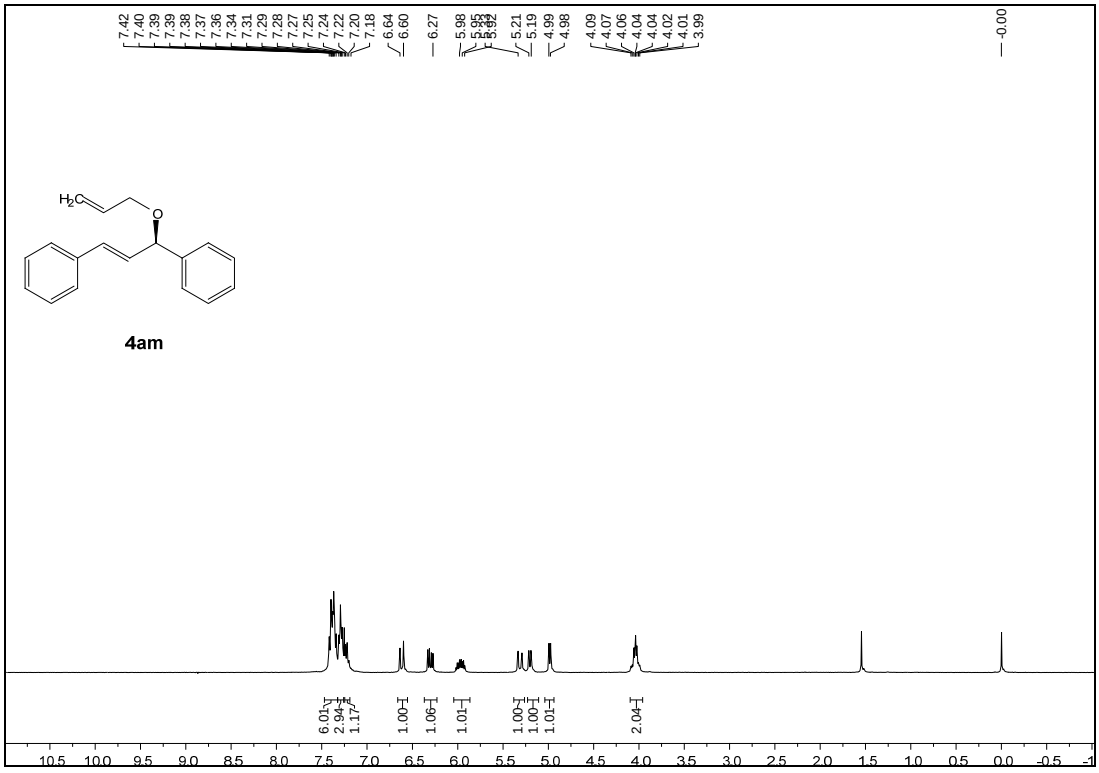


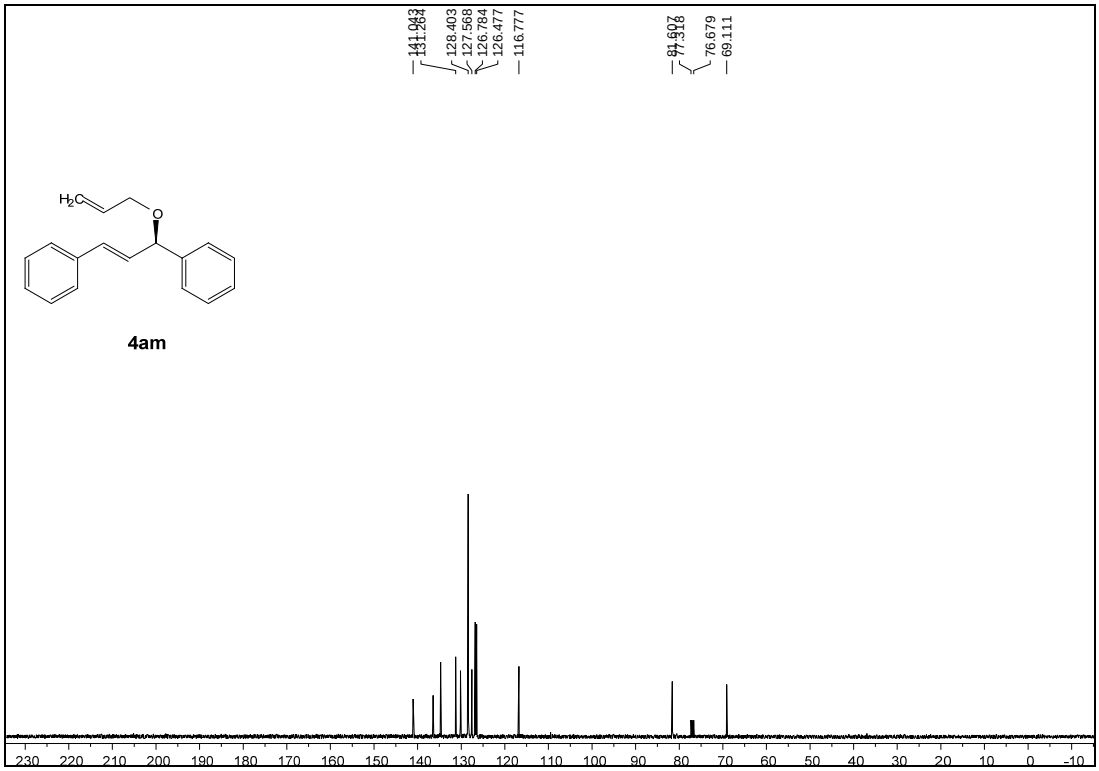
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4al





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4am





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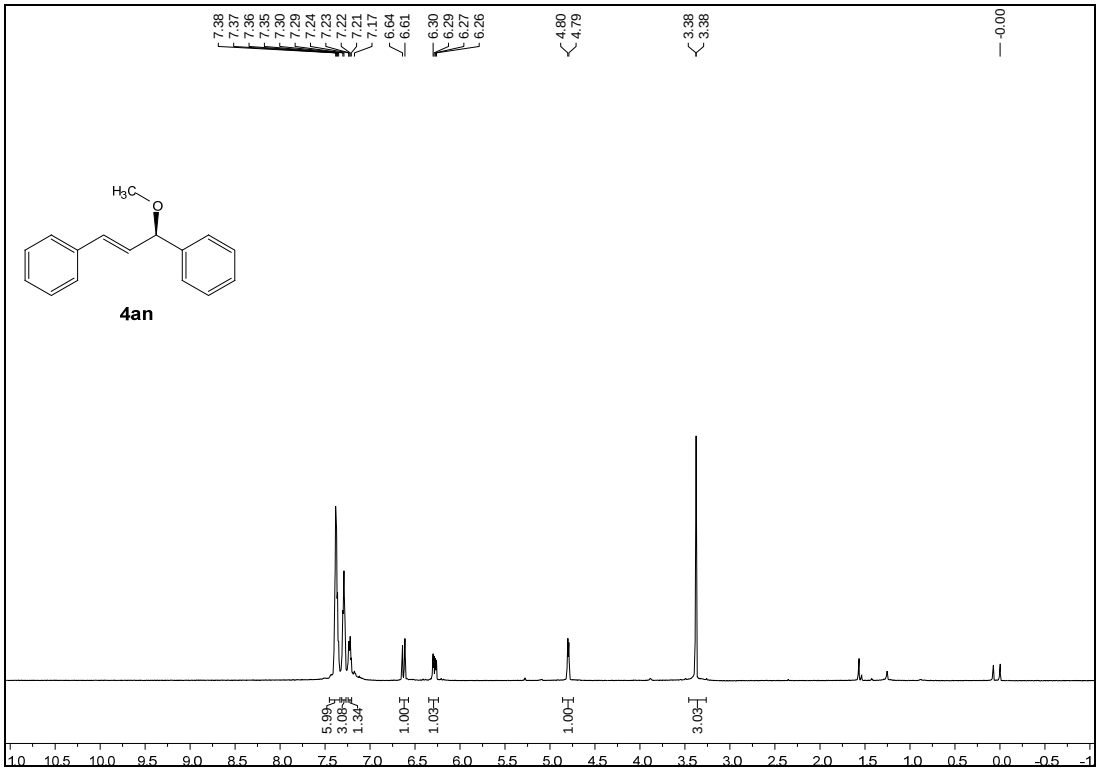
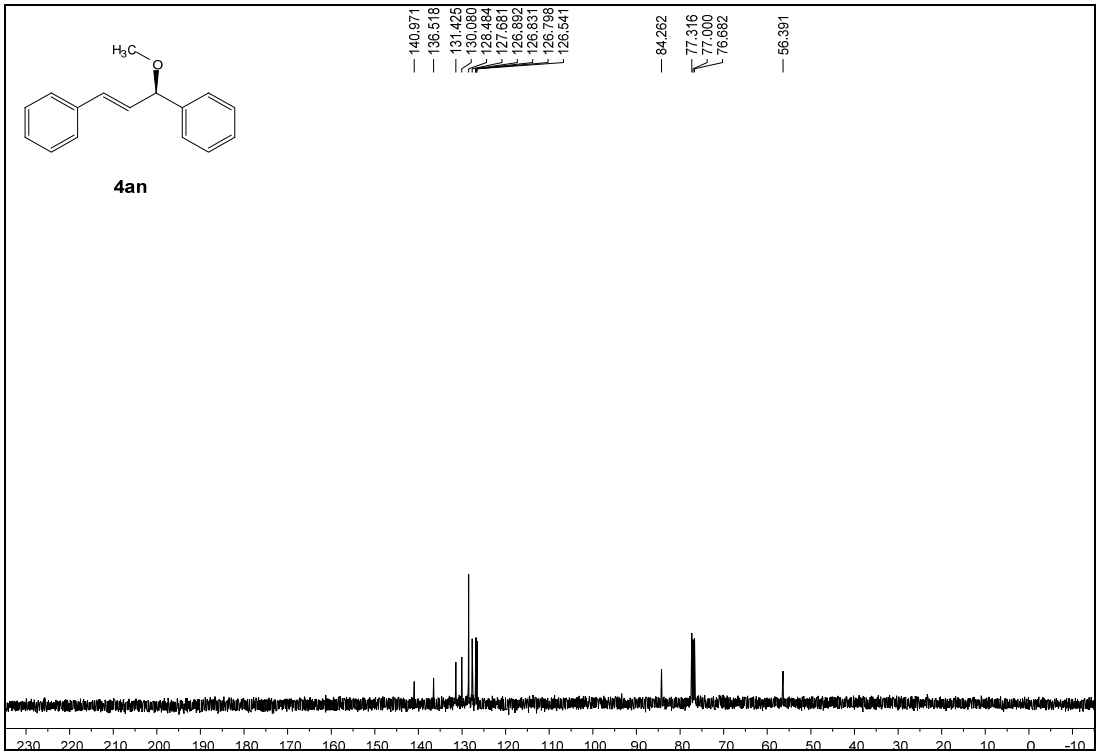
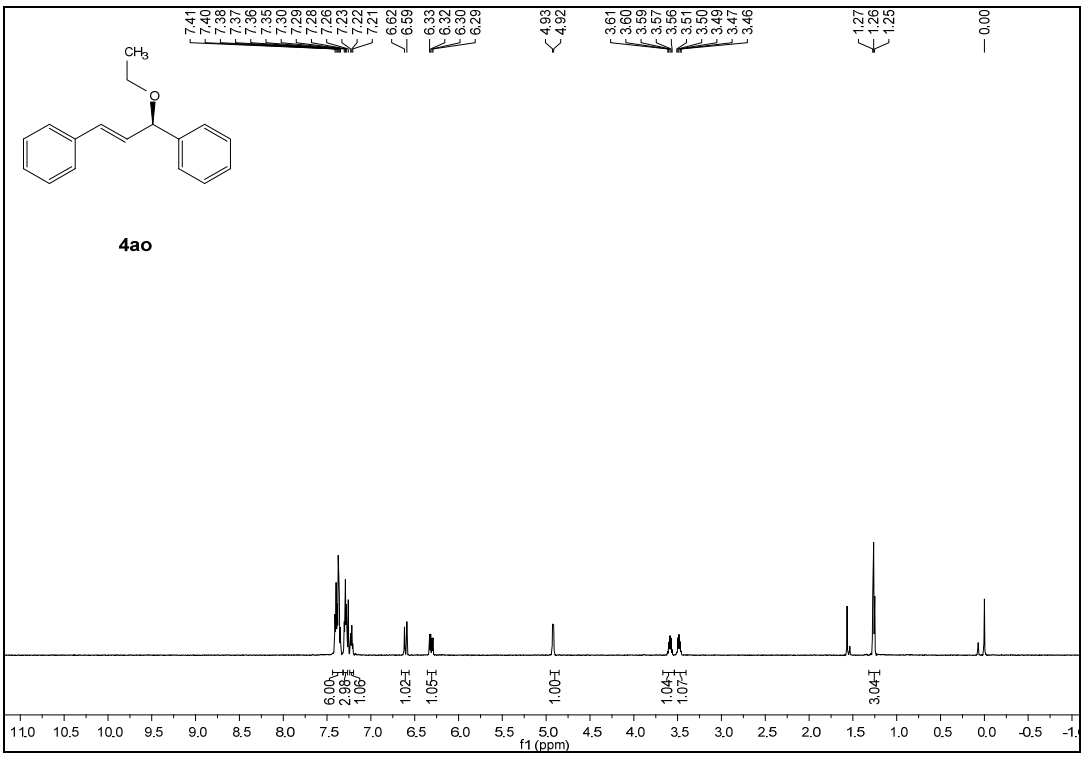
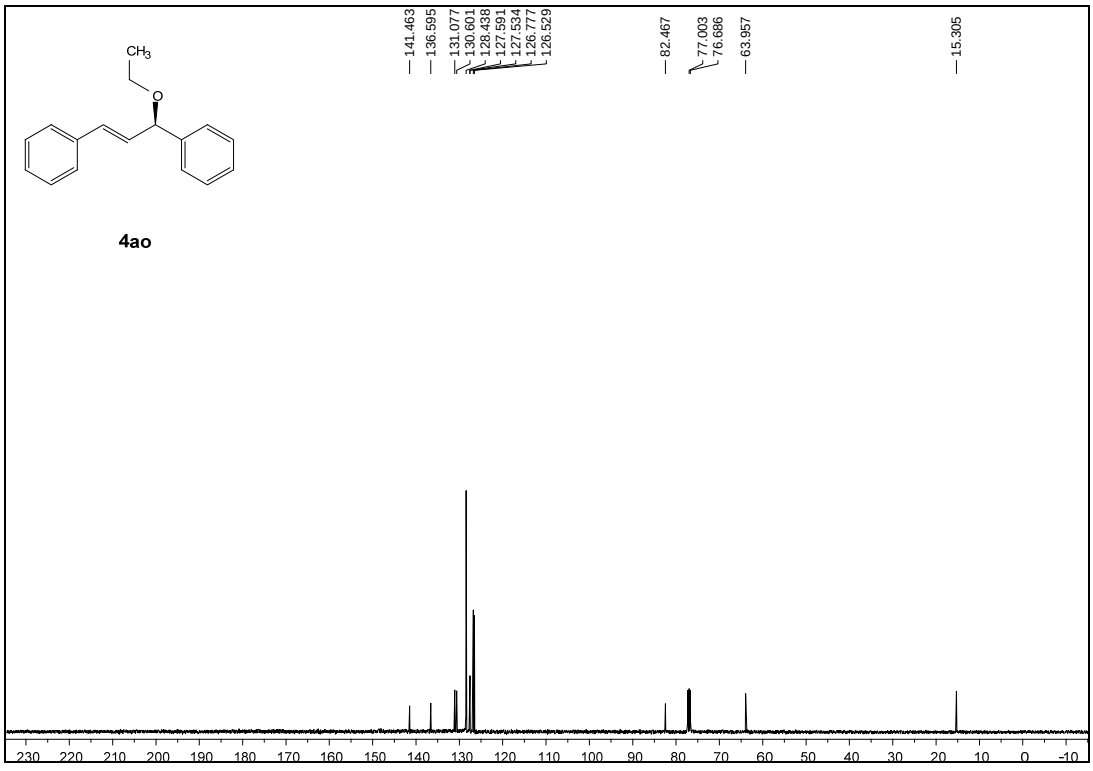


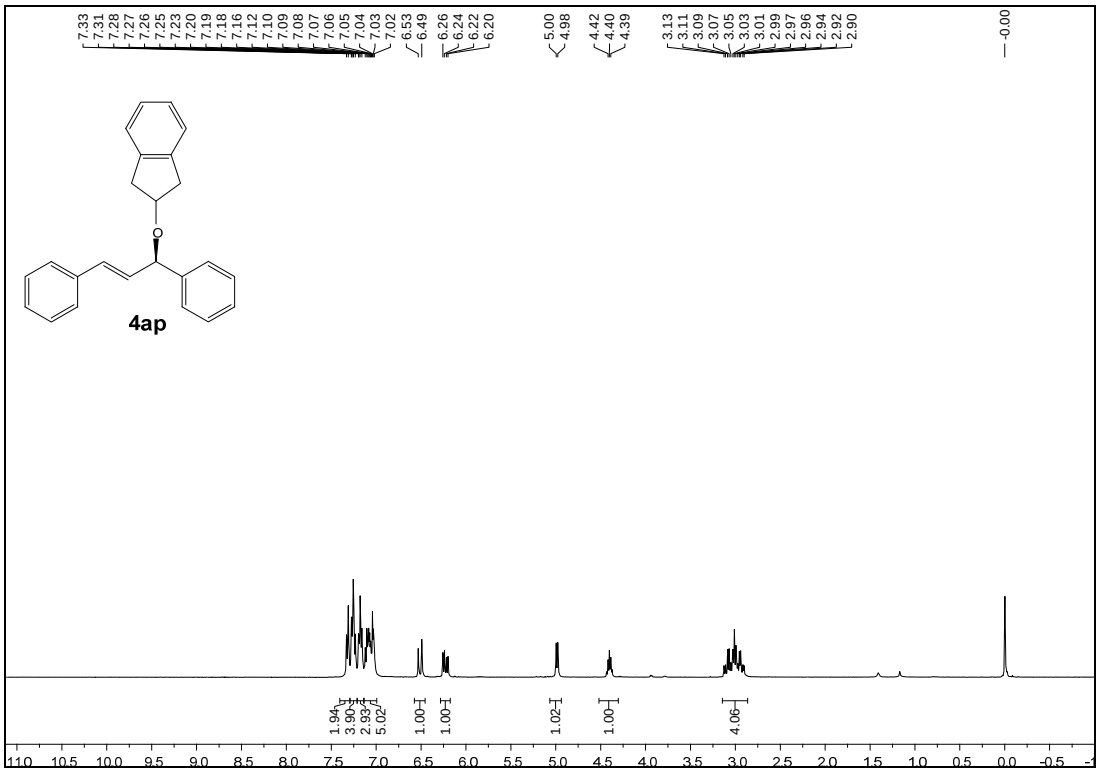


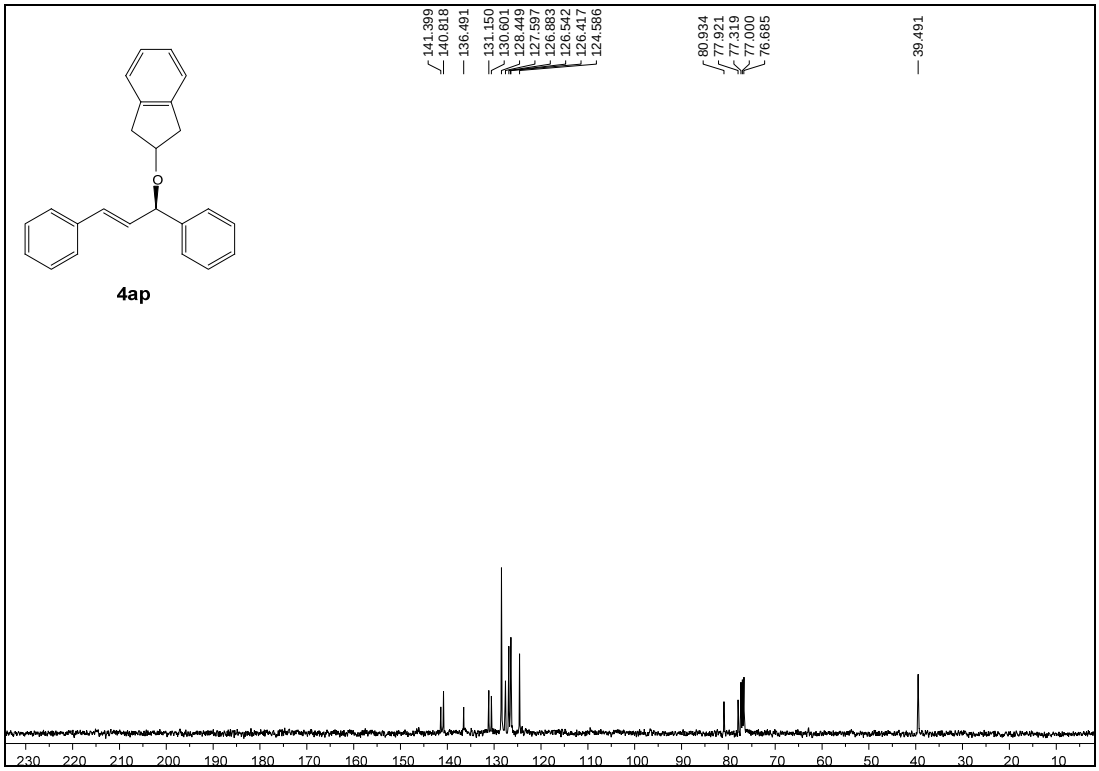
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ao





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ap





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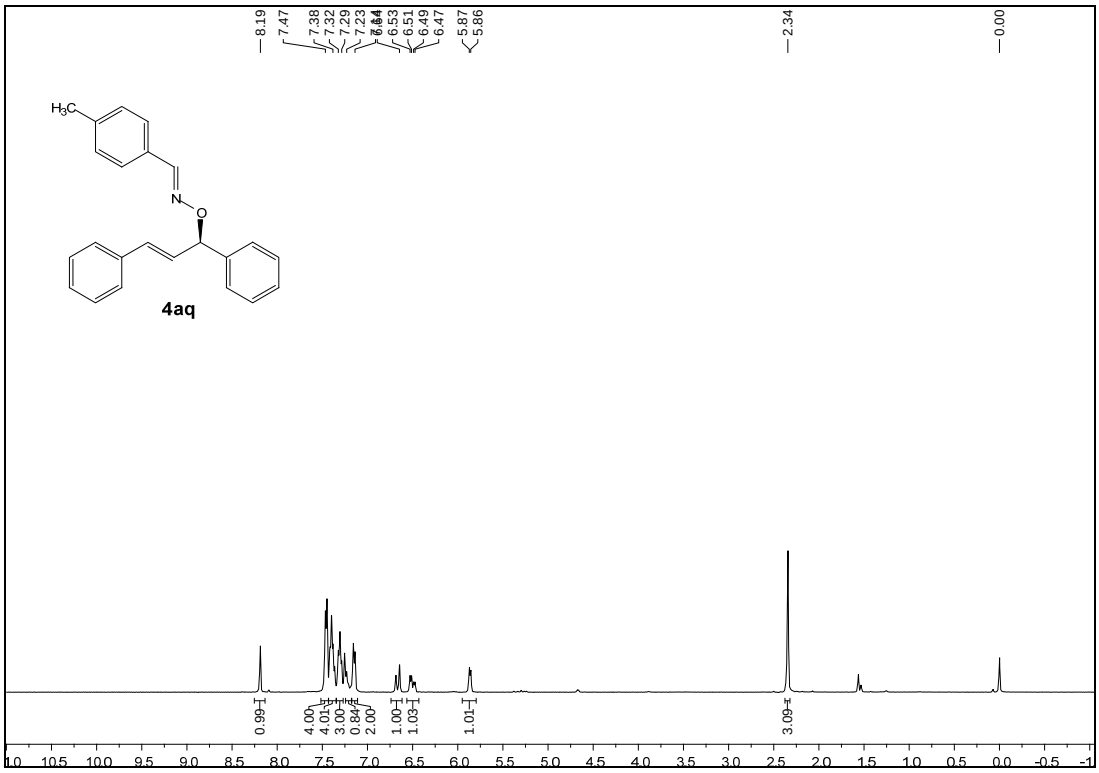
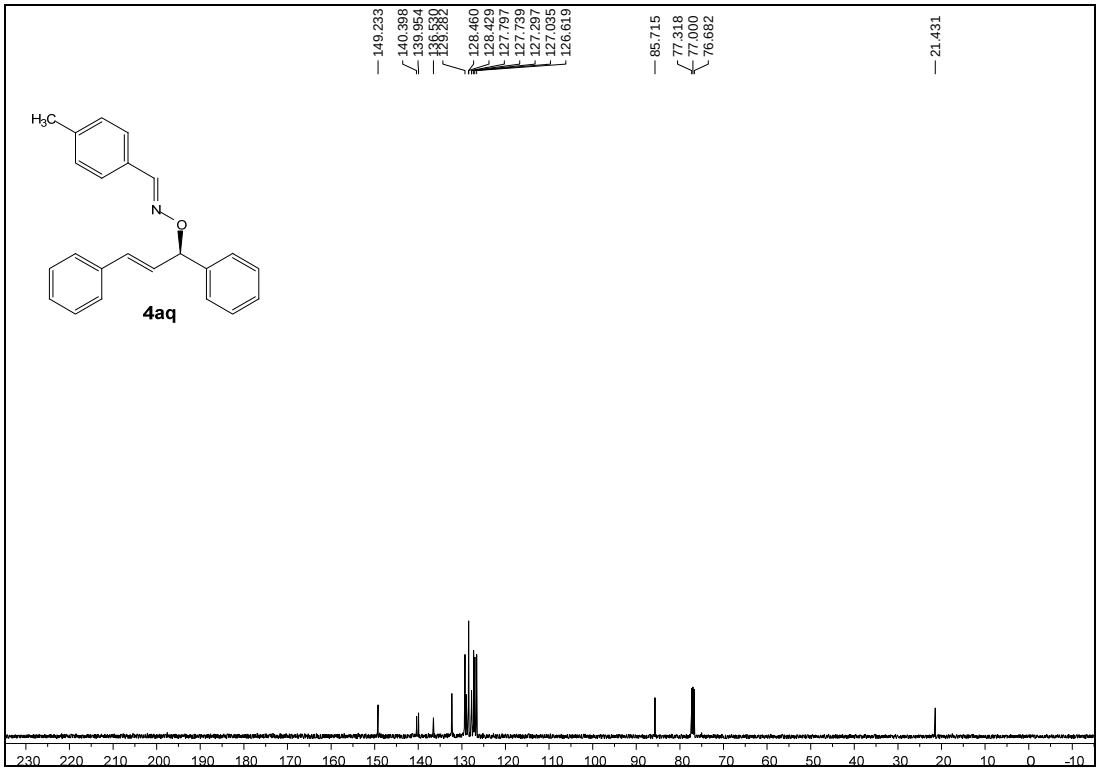
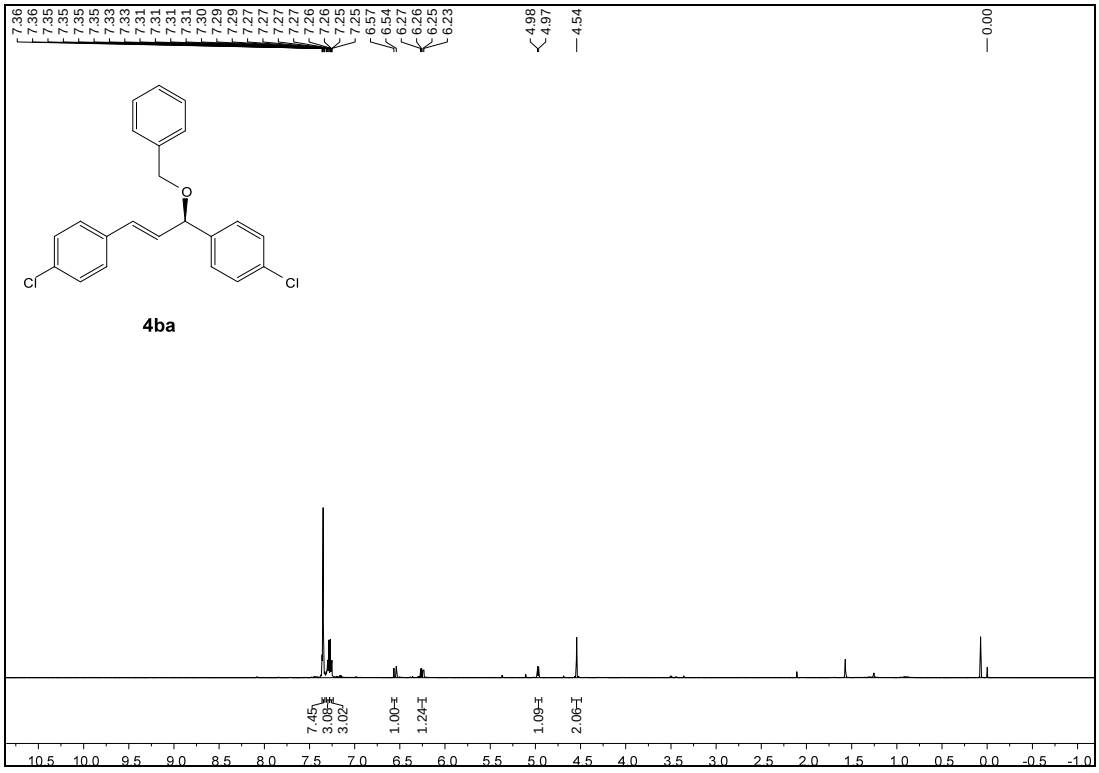
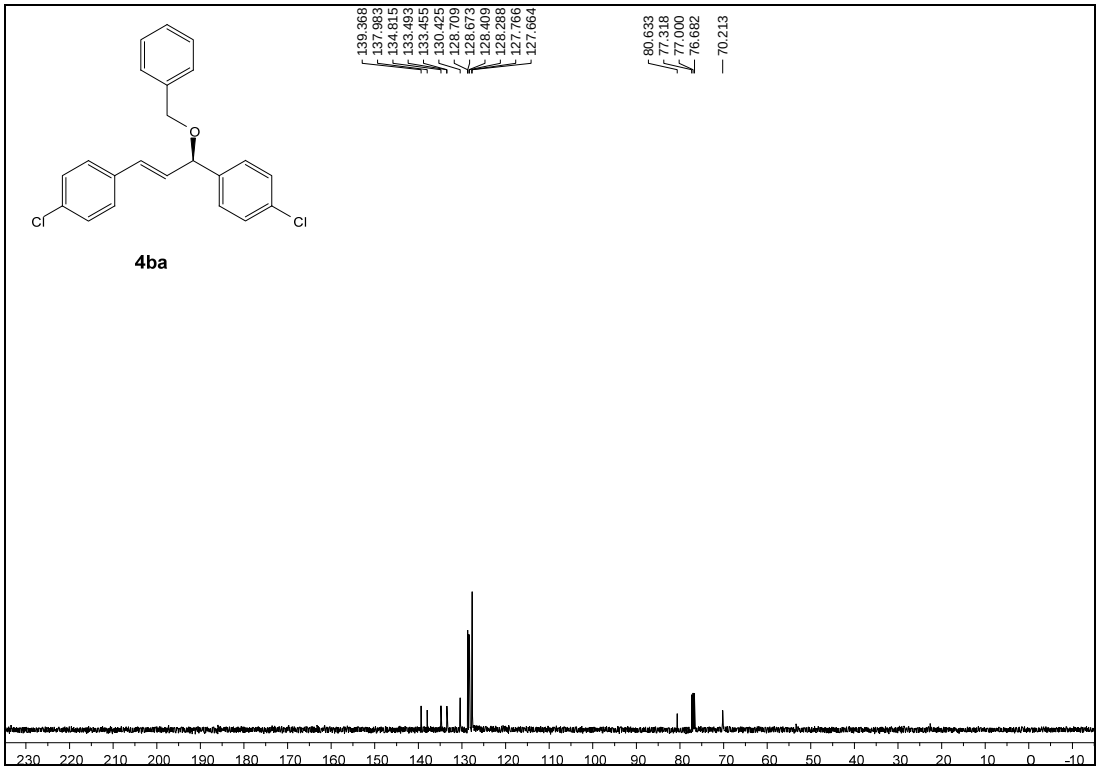


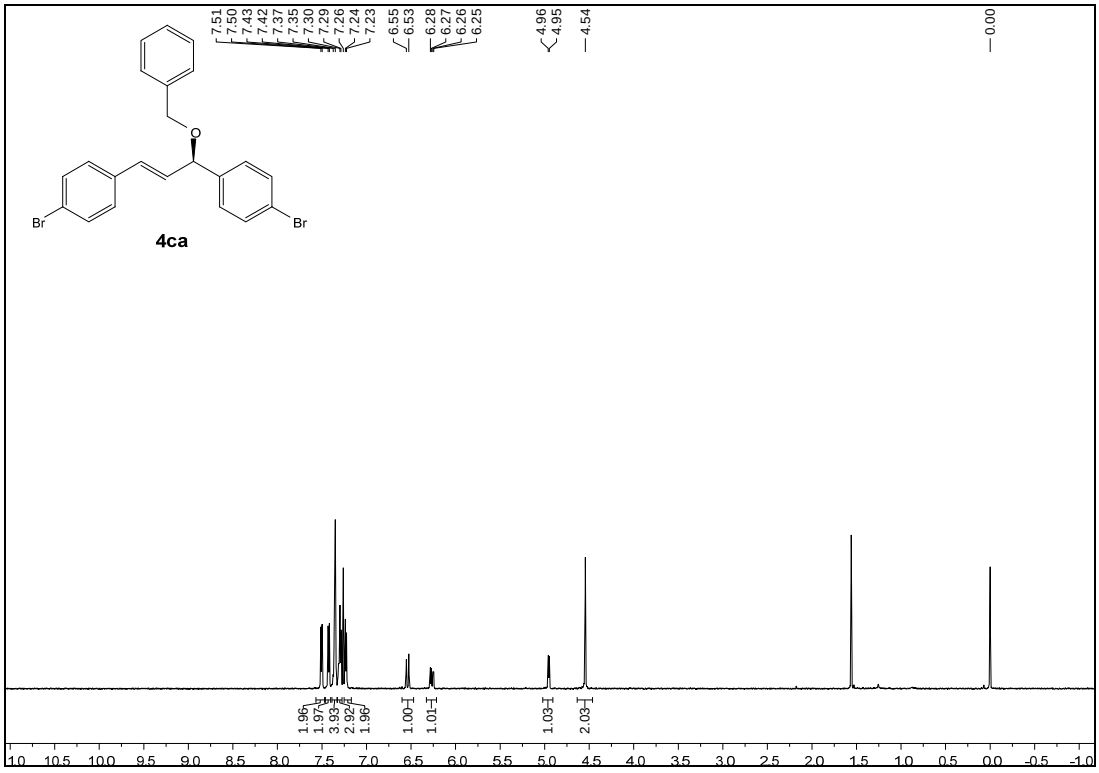


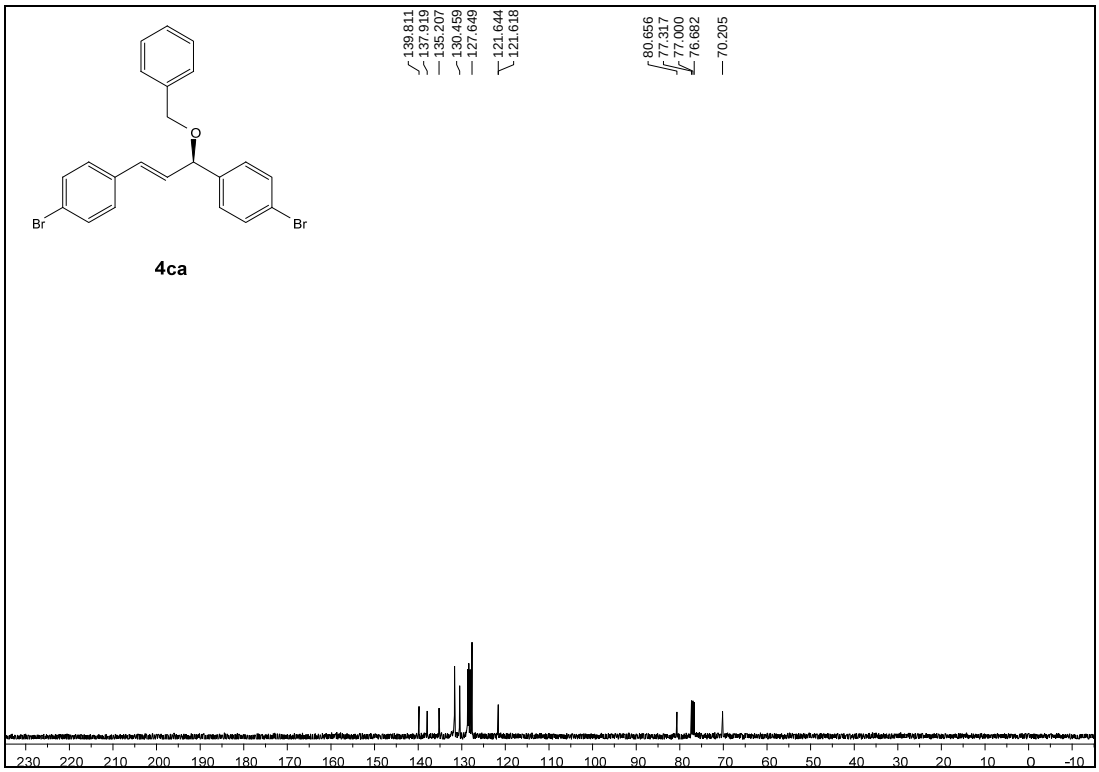
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ba





H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4ca





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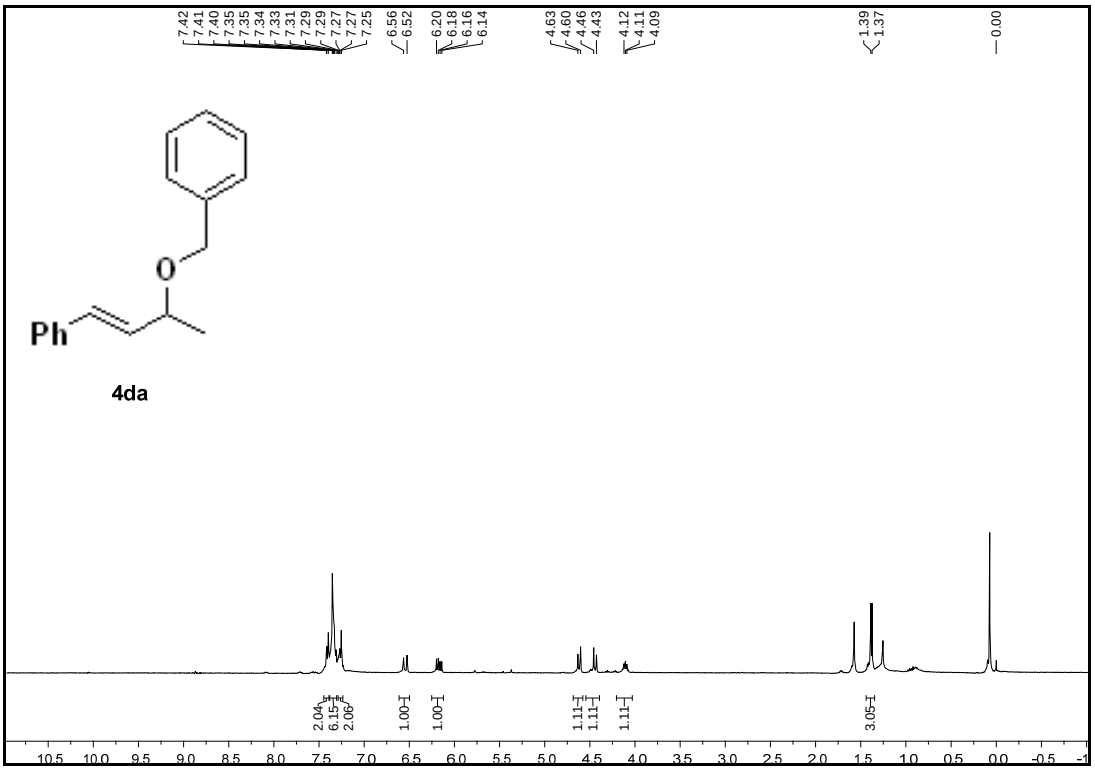
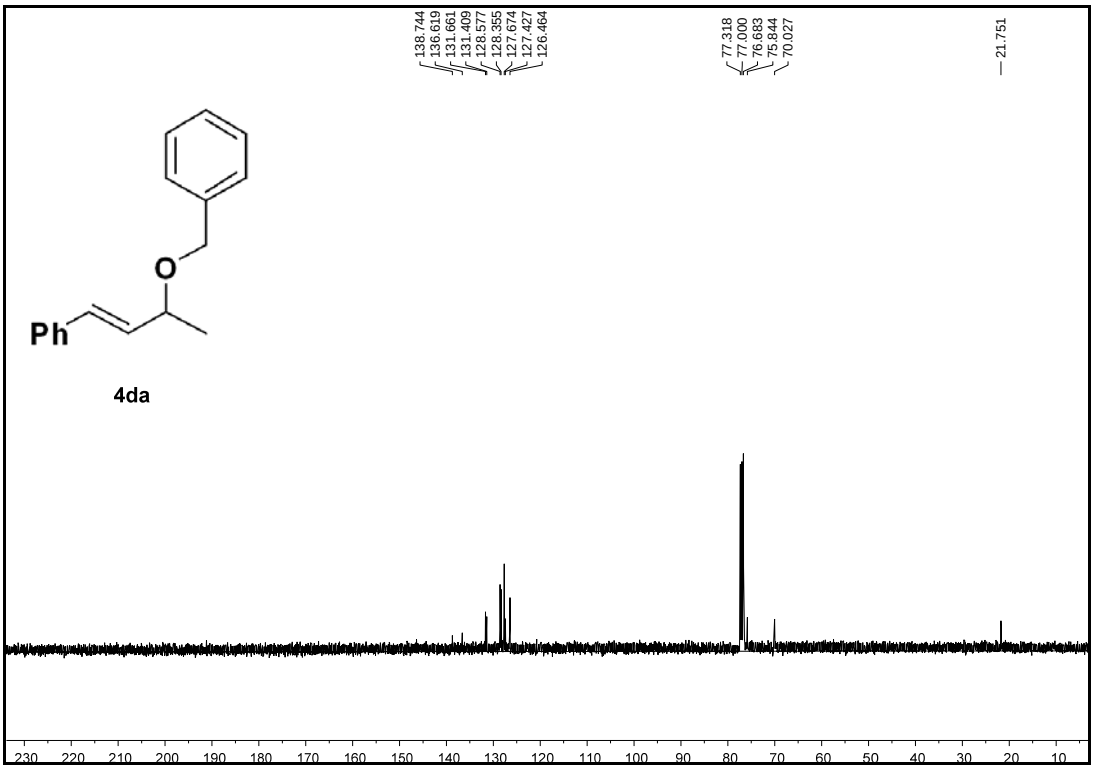
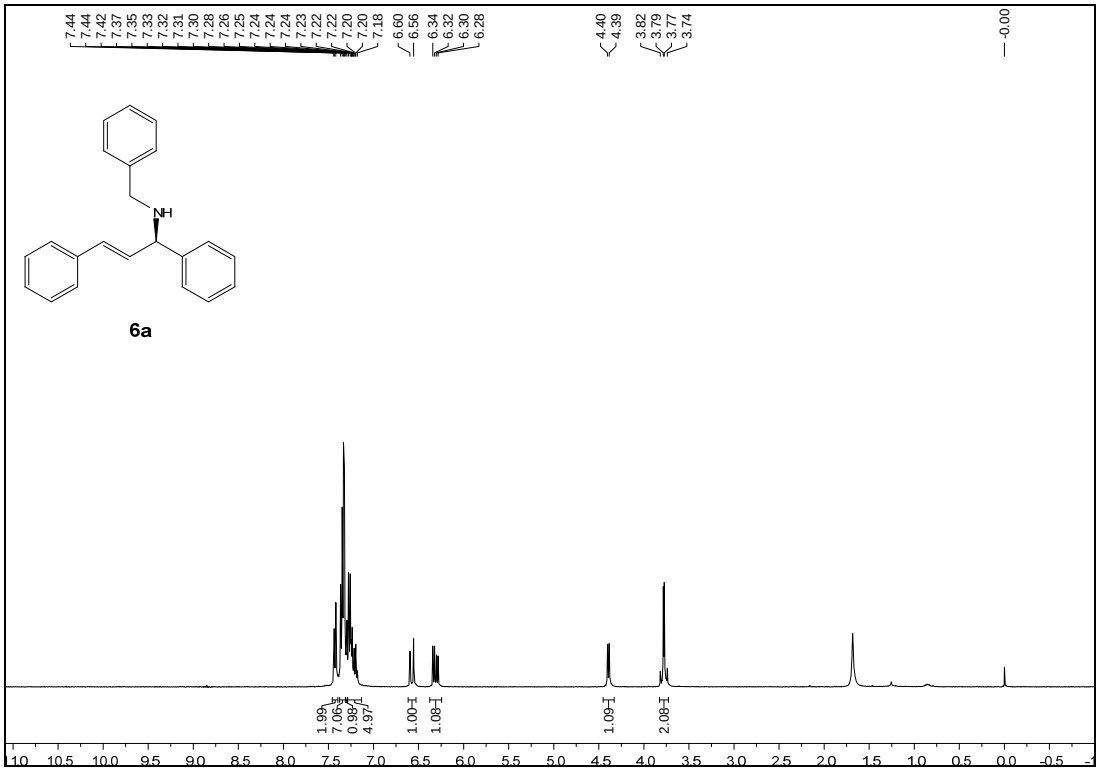
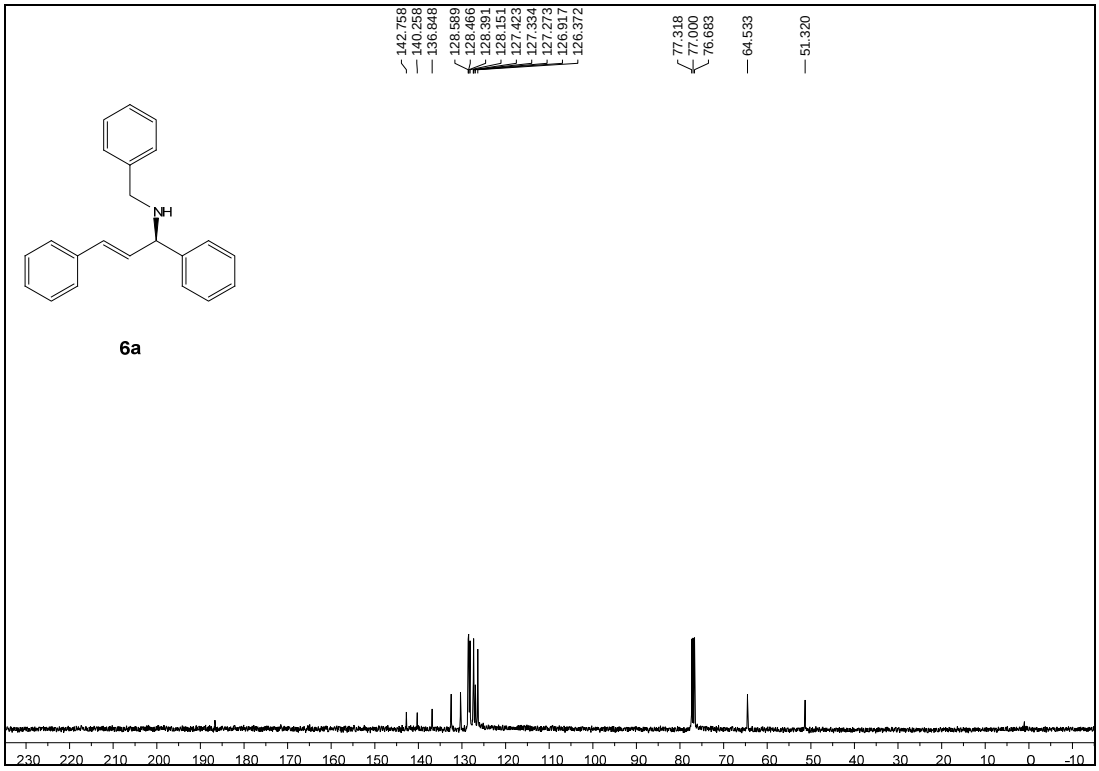


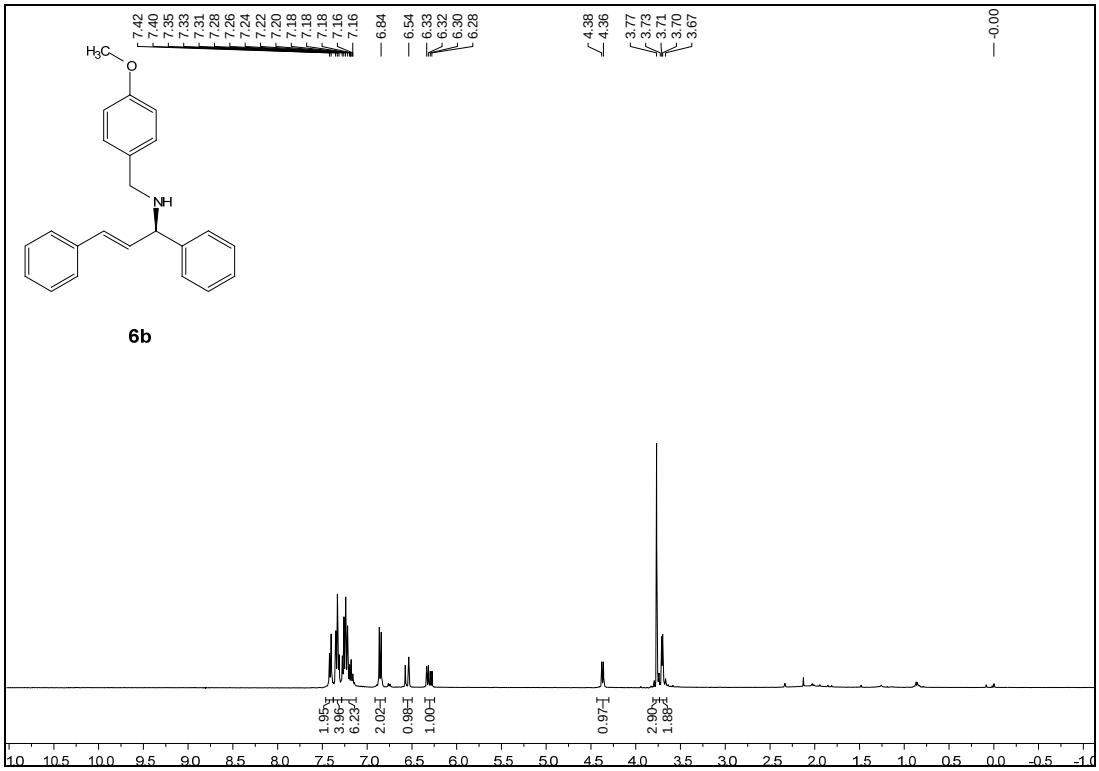


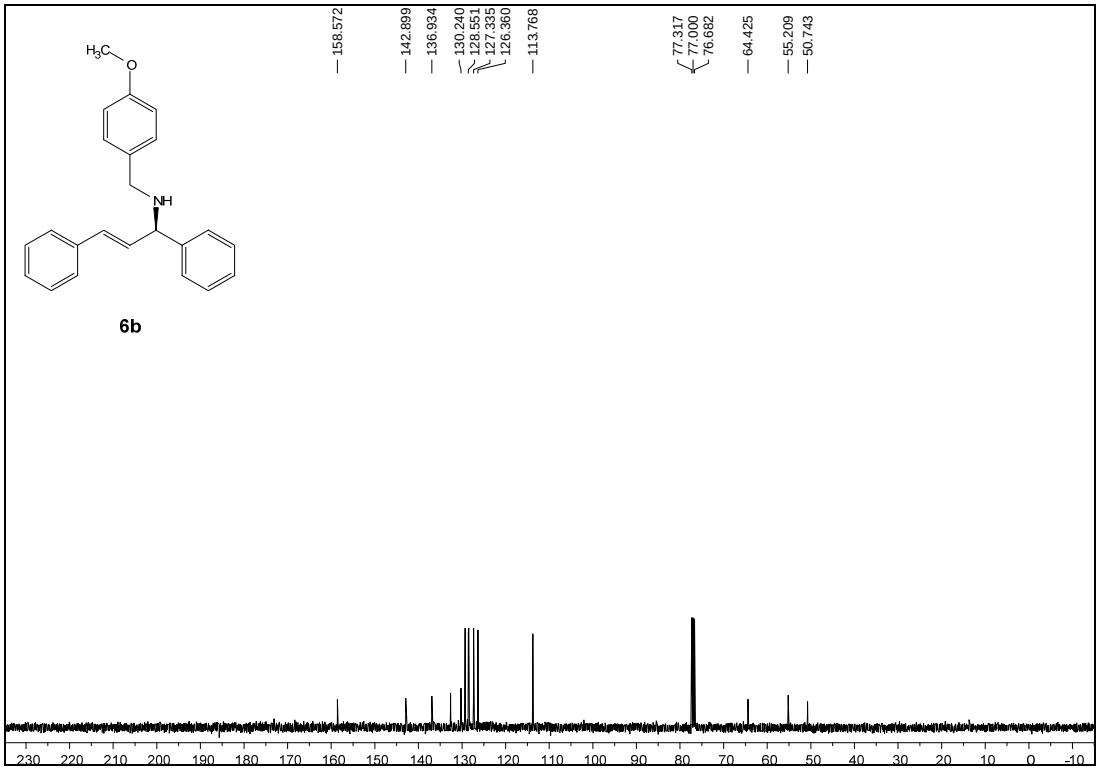
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6a



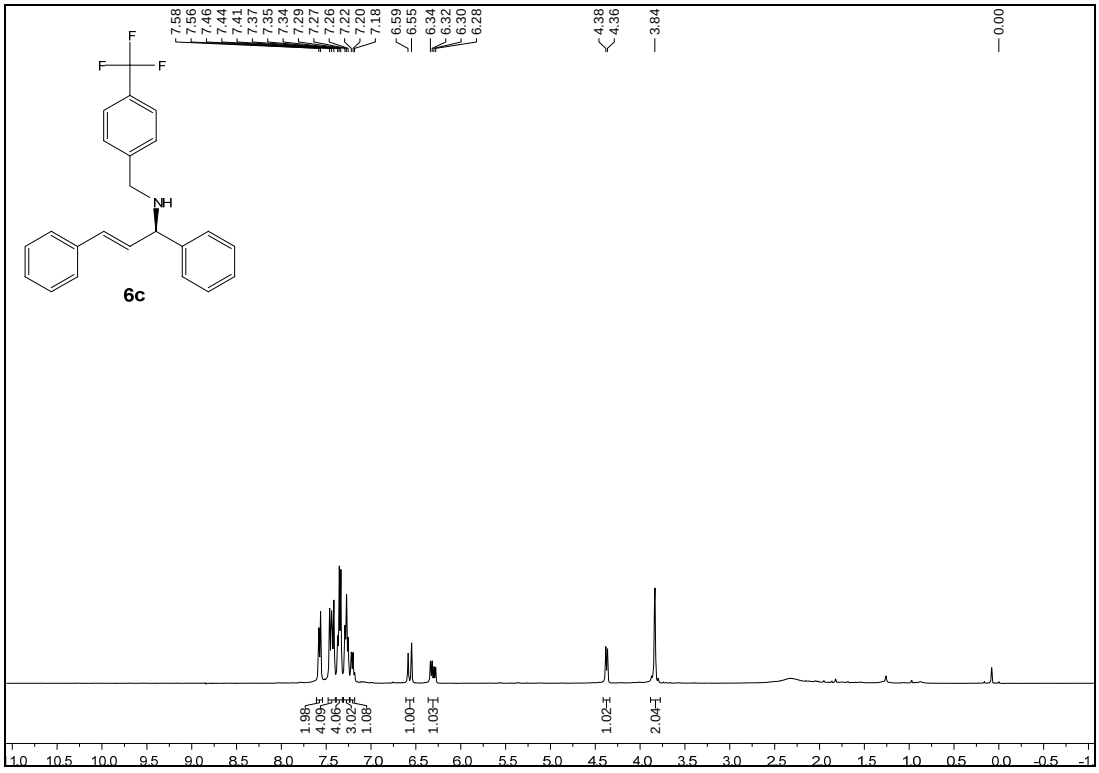


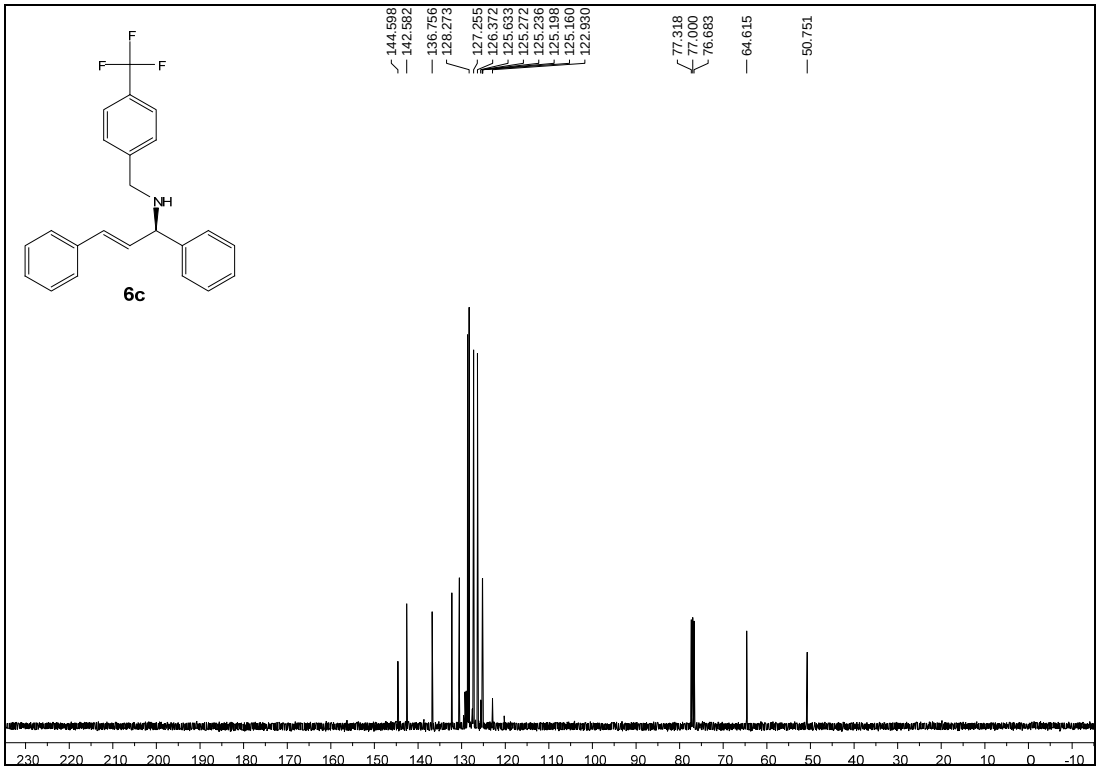
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6b



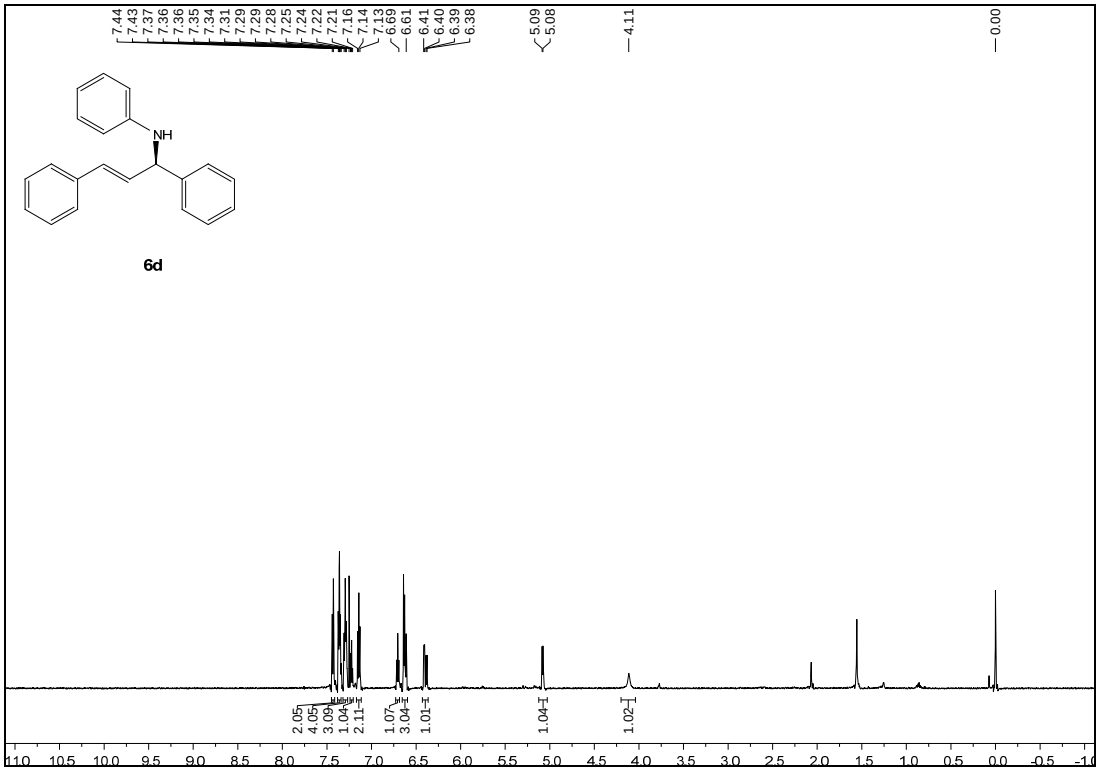


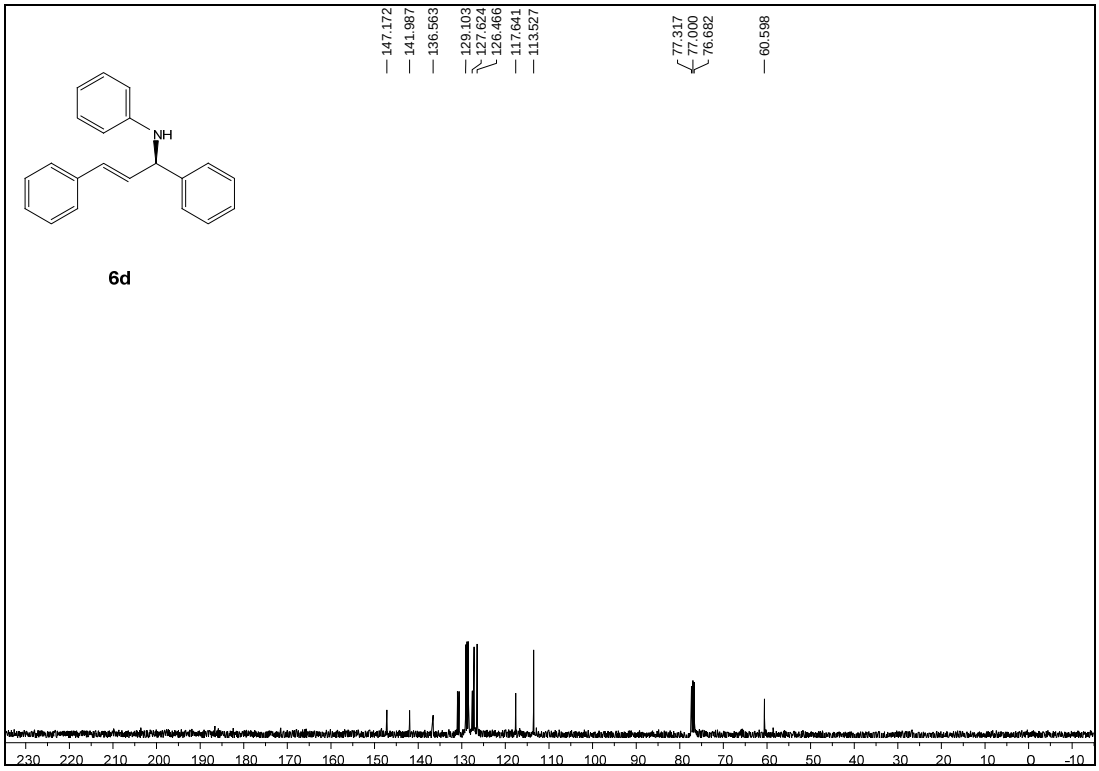
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6c



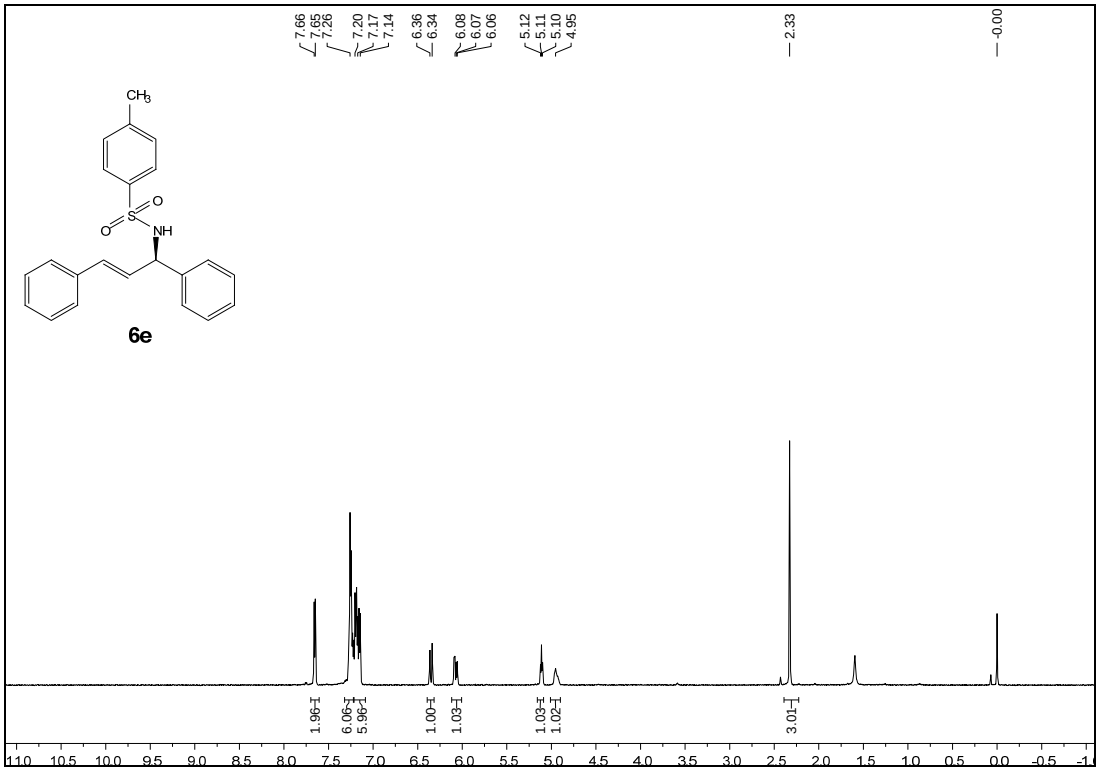


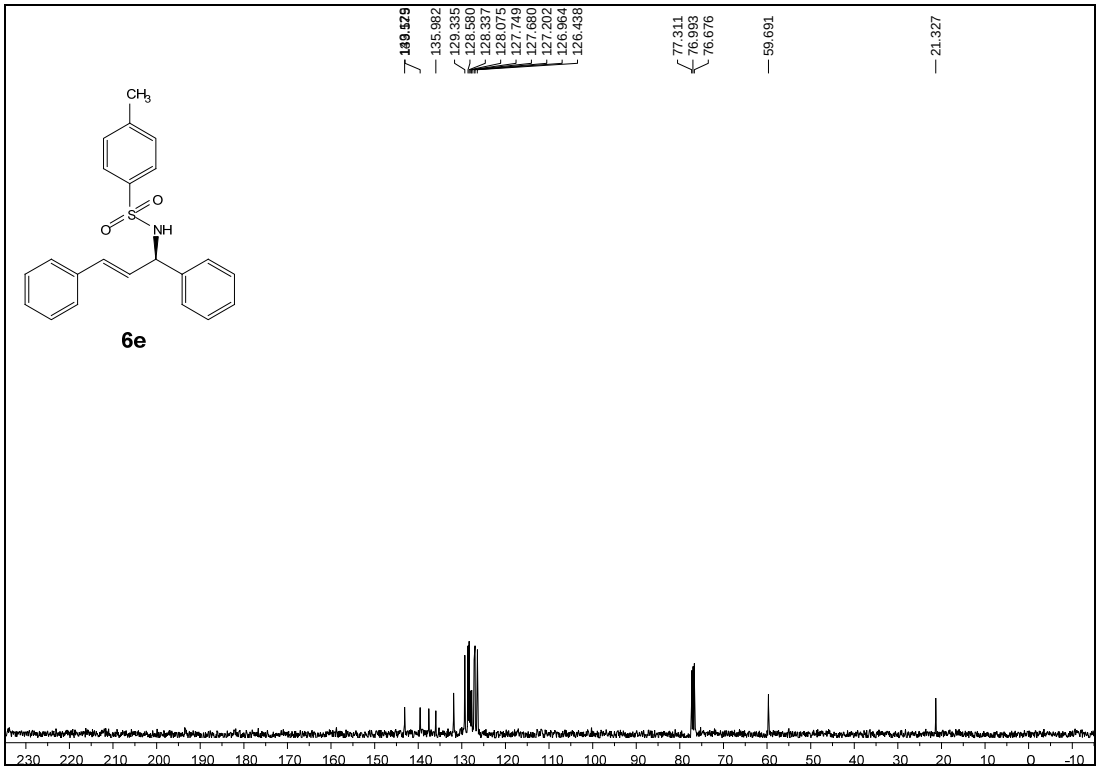
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6d



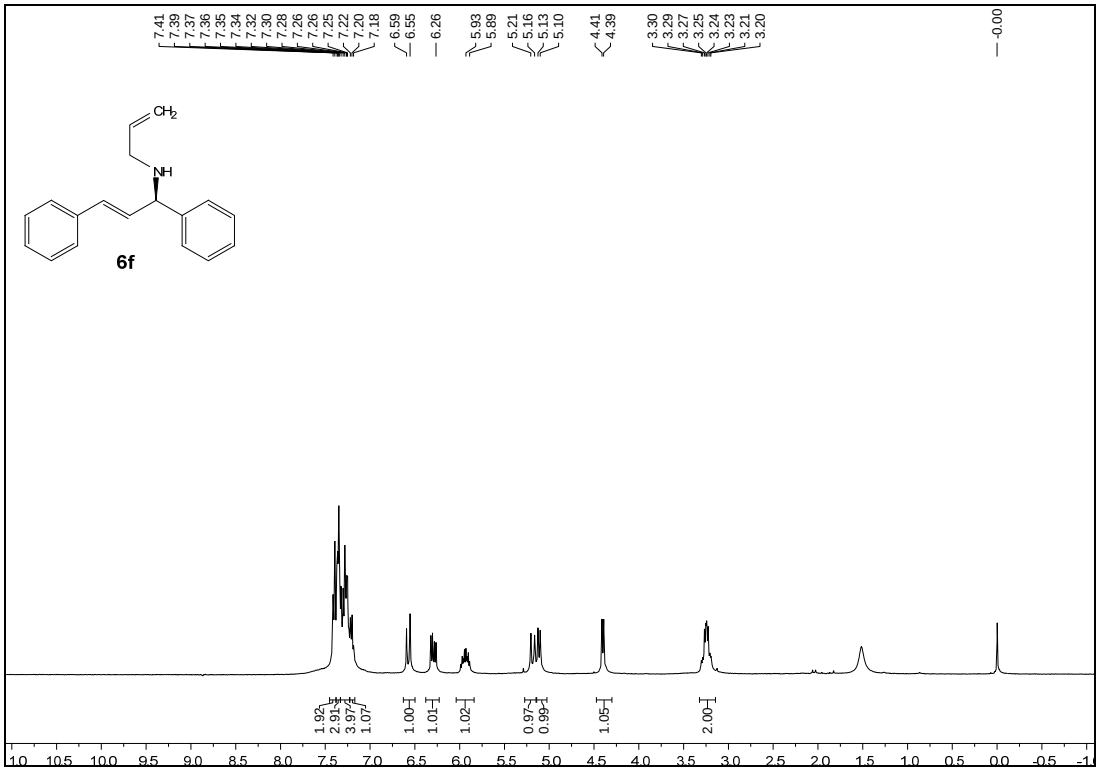


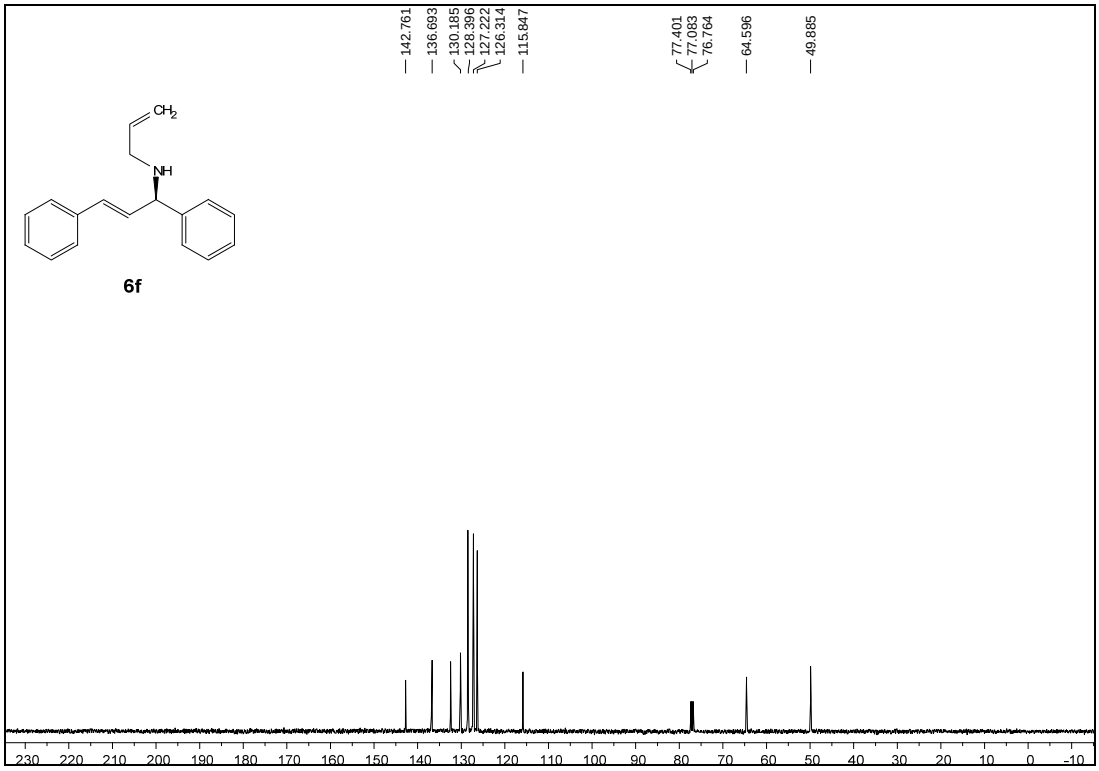
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6e



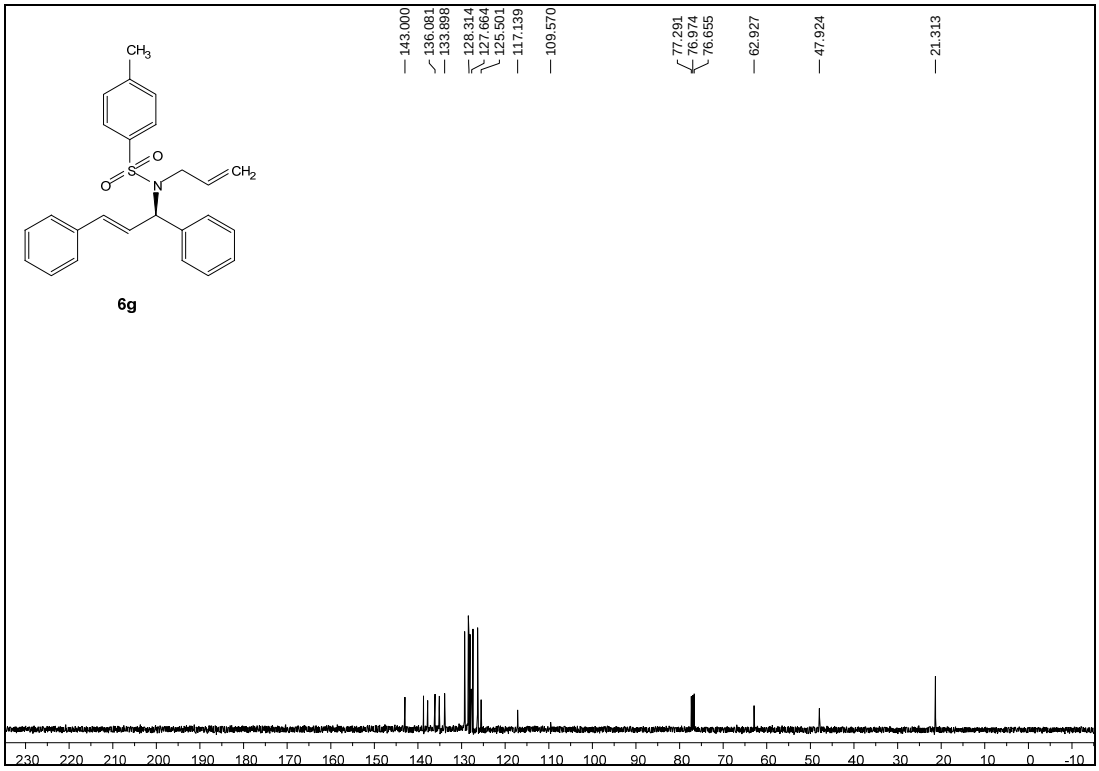


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6f

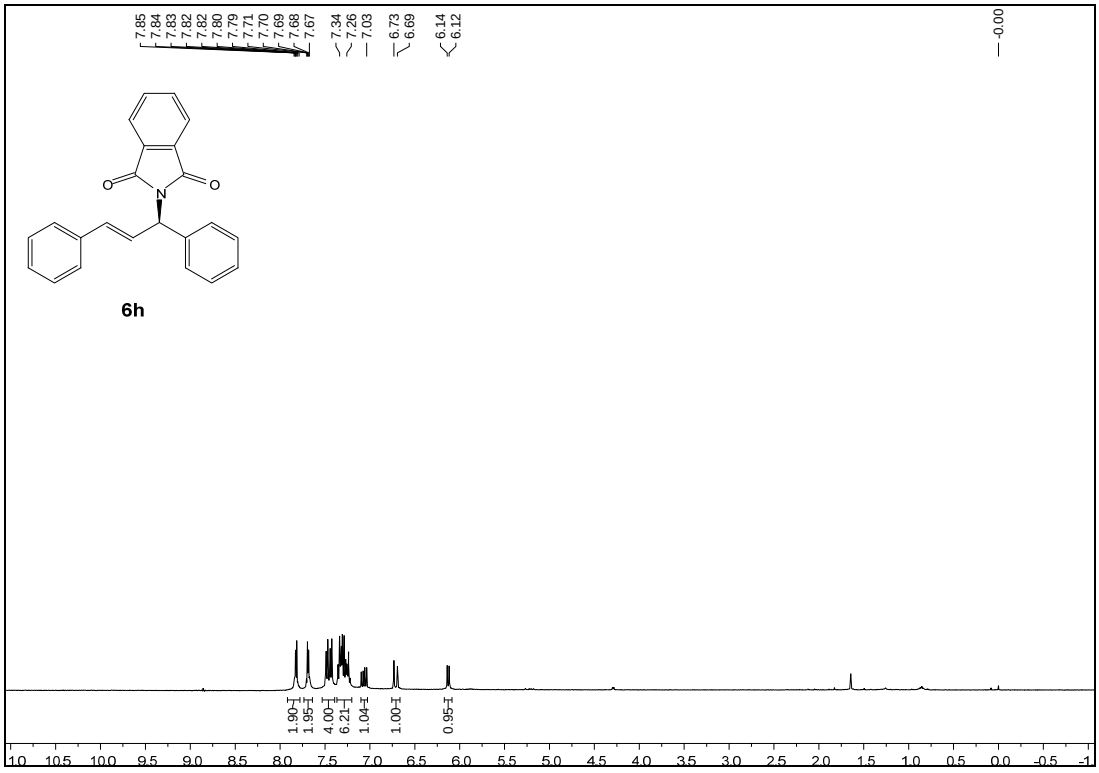


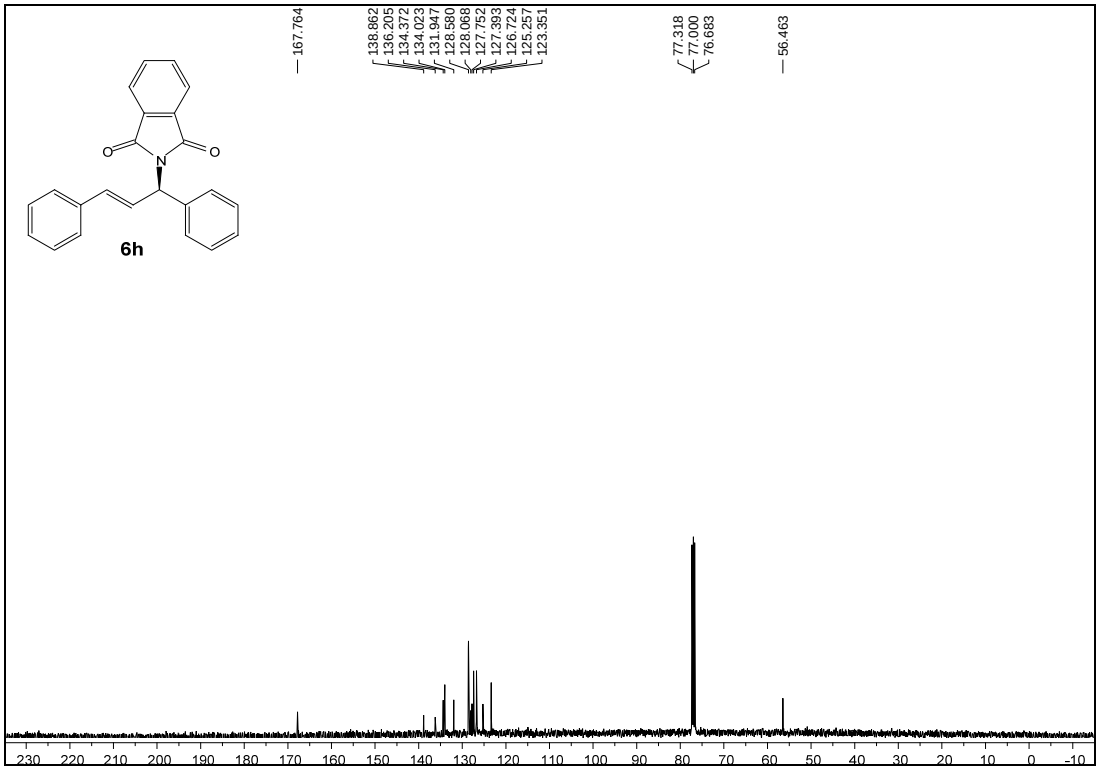


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6g

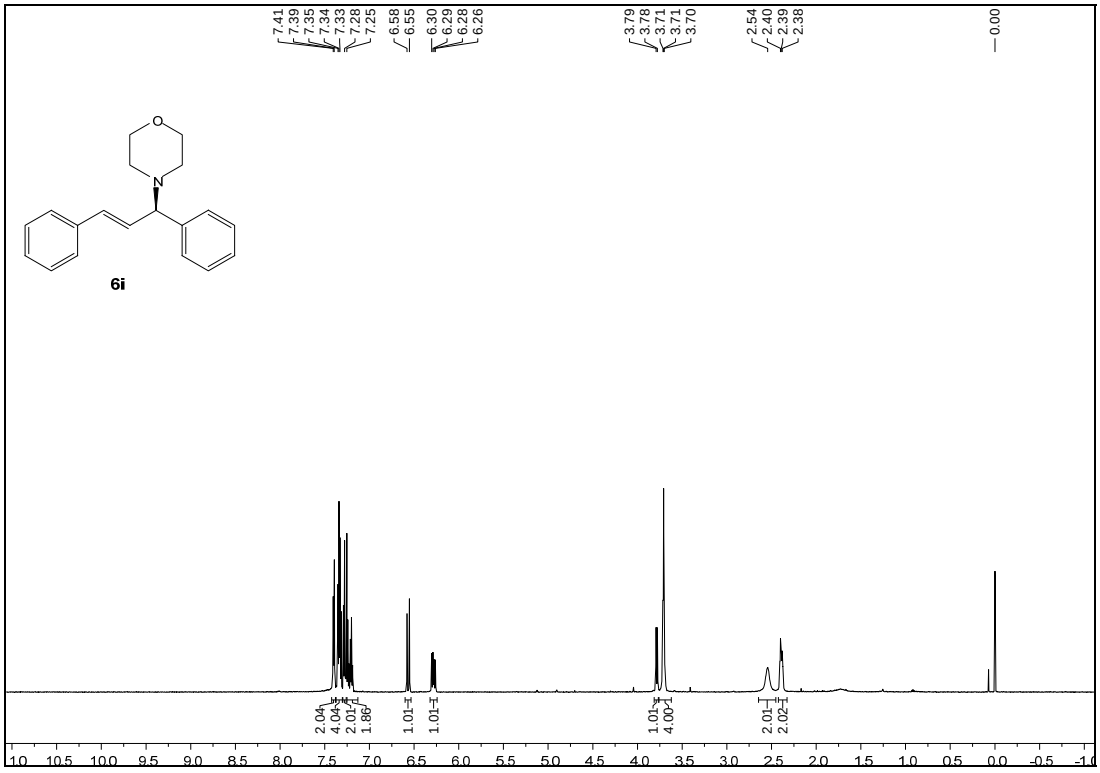


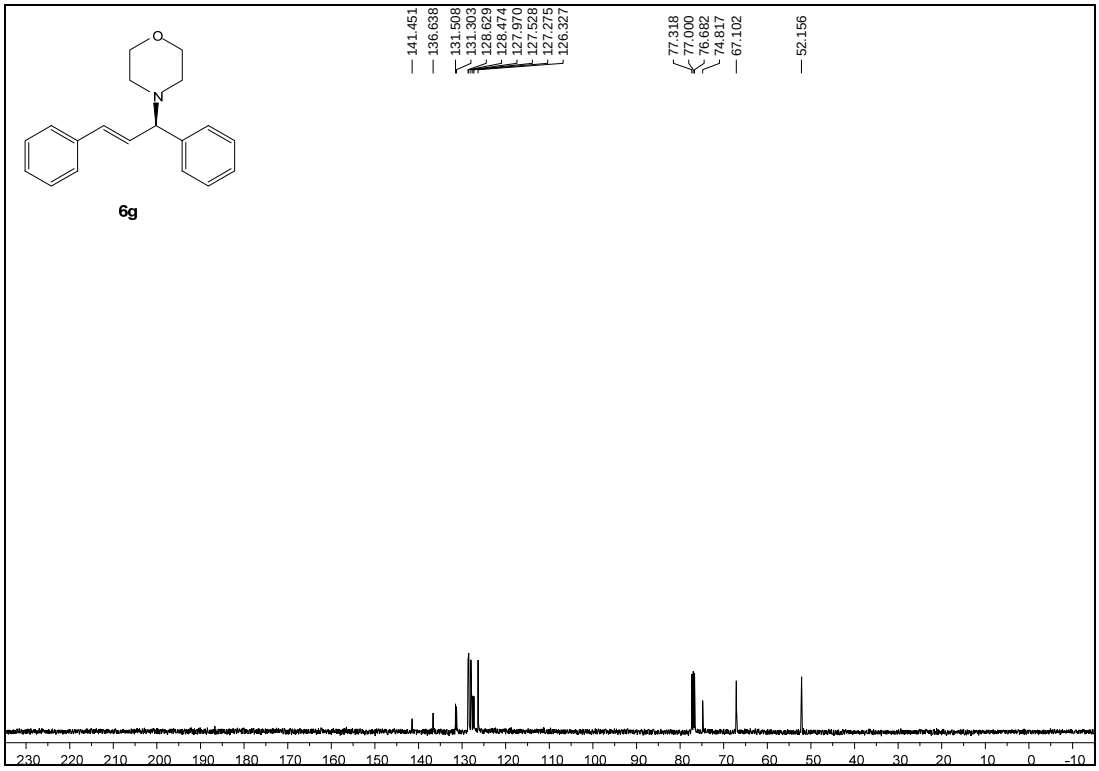
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6h



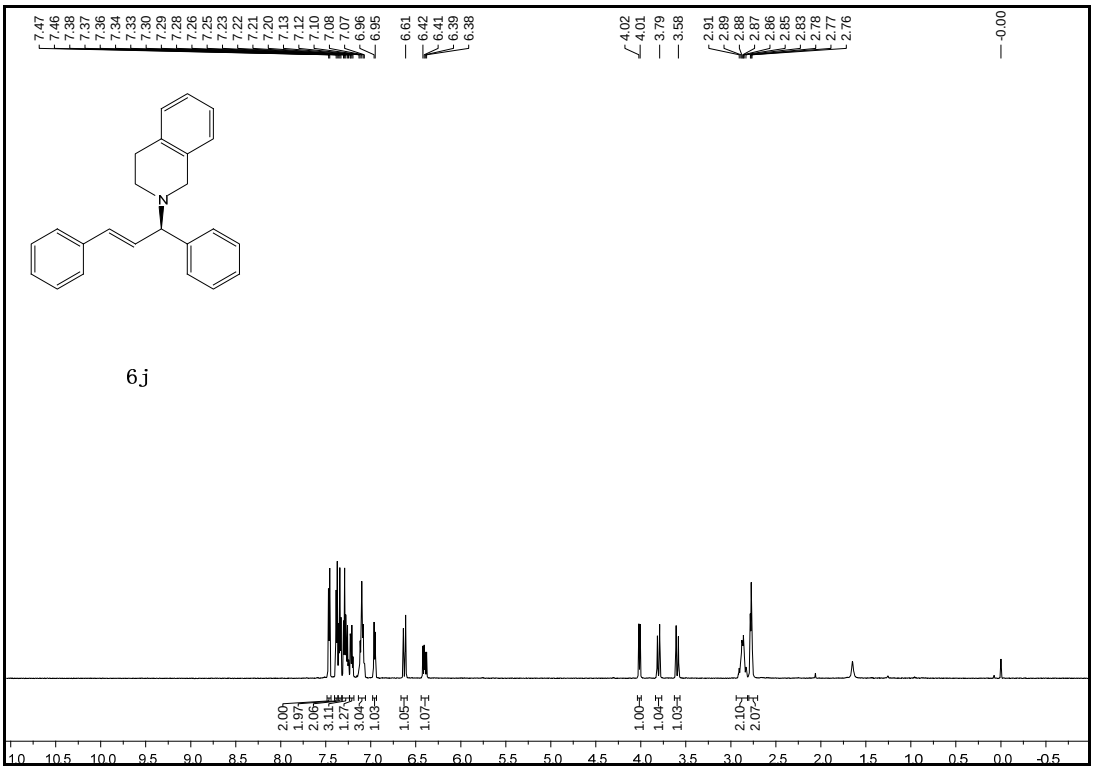


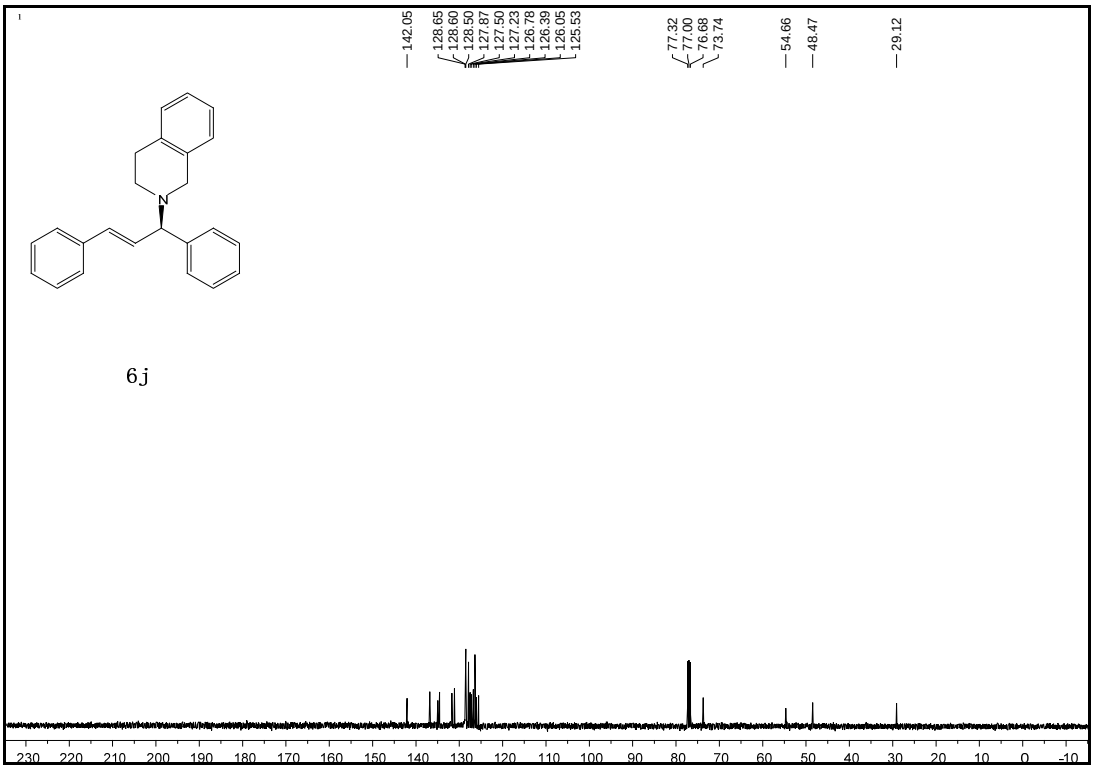
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 6i



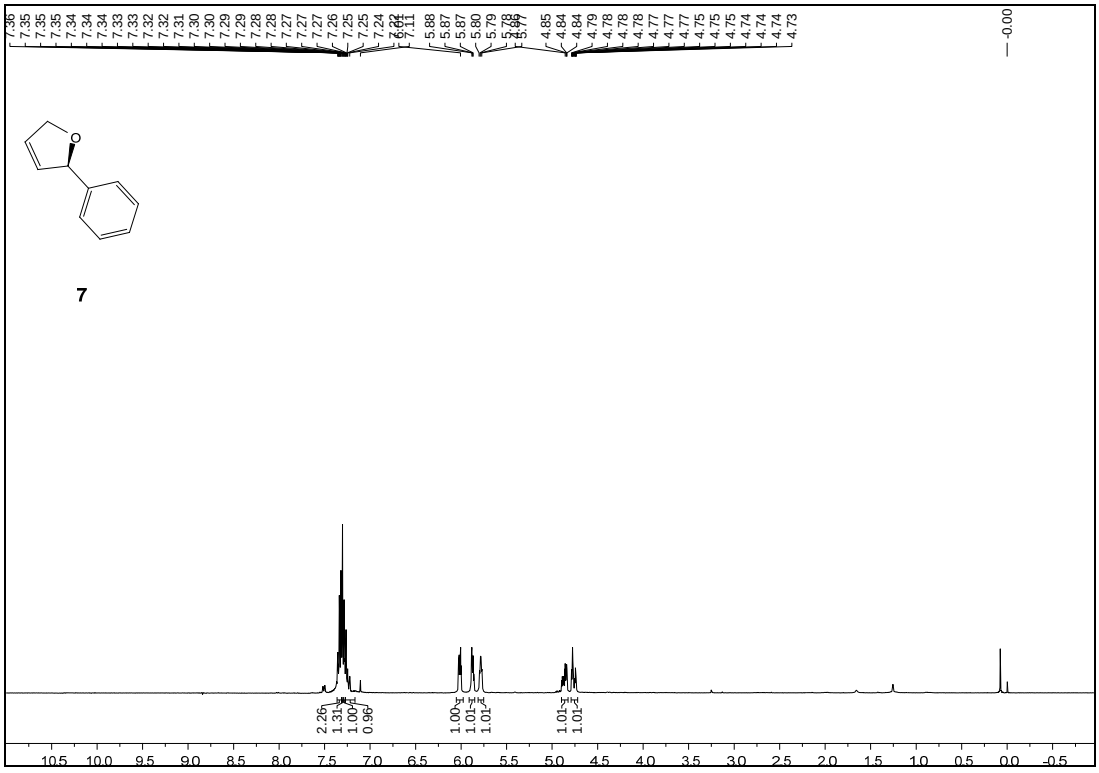


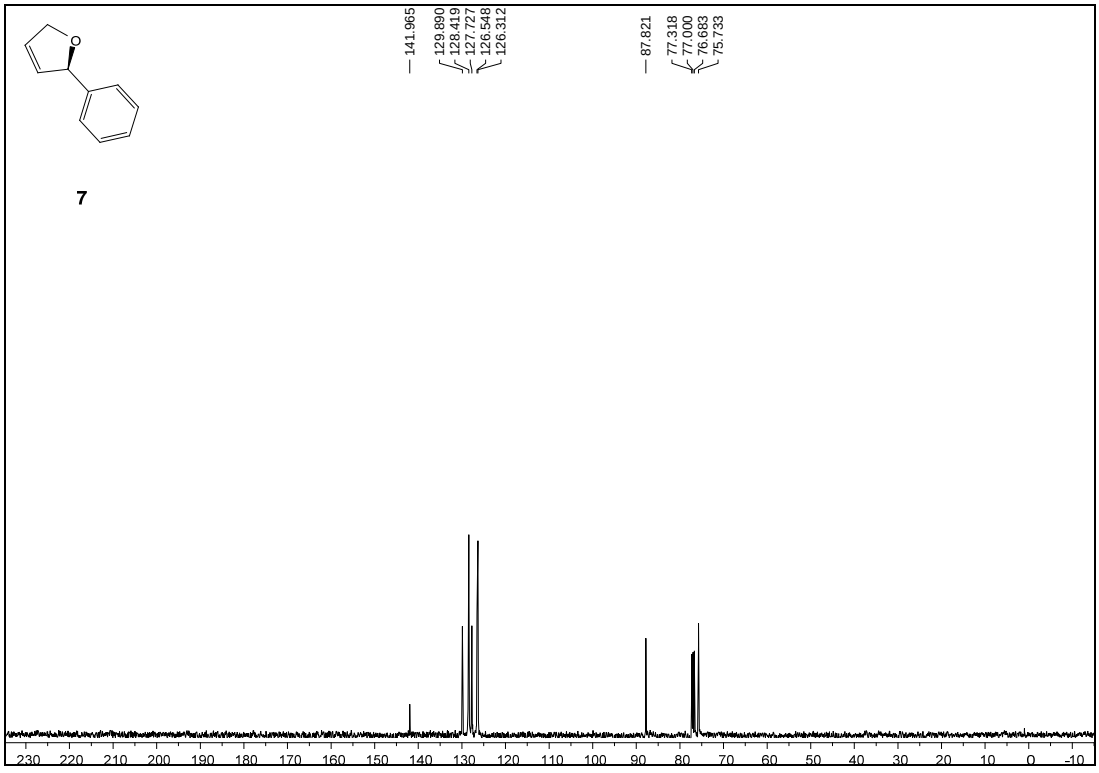
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product (6j)



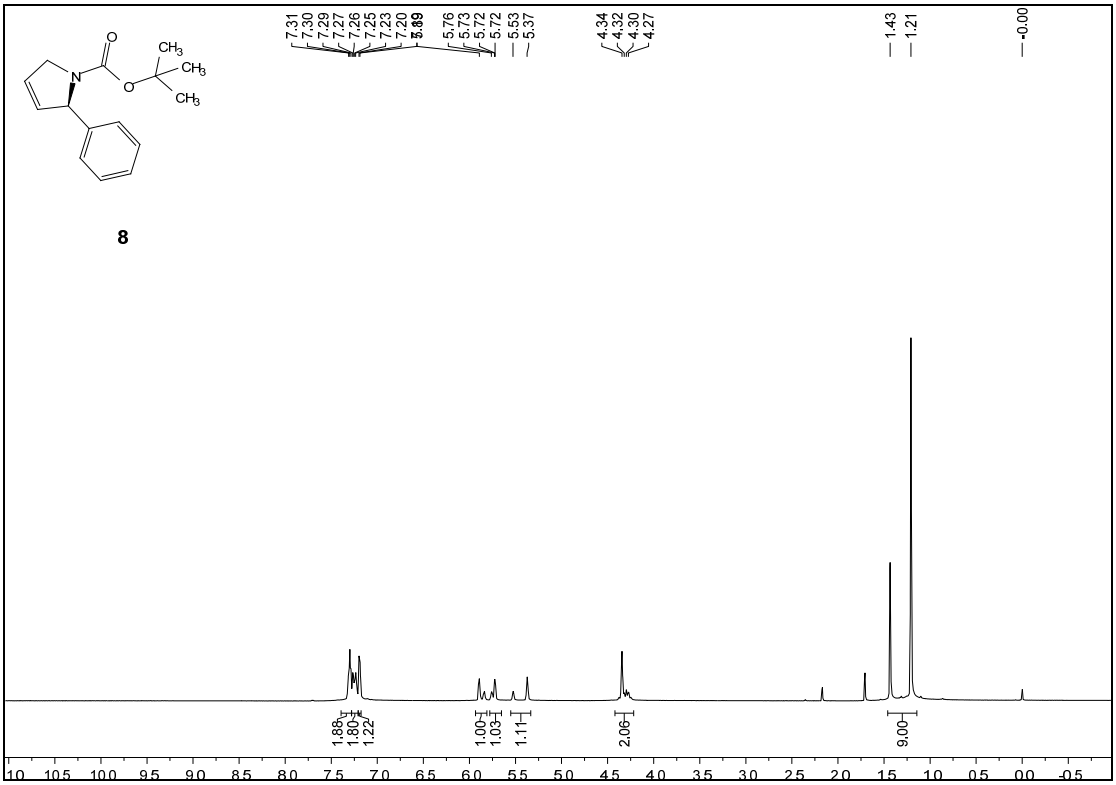


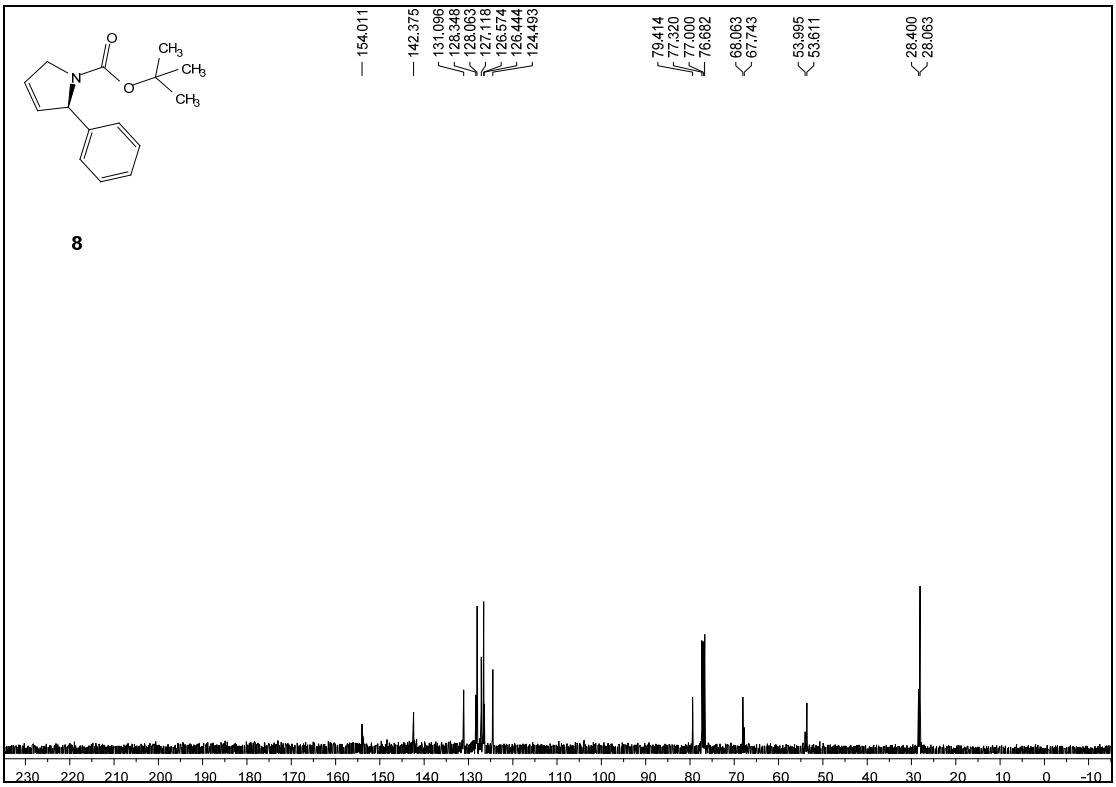
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 7



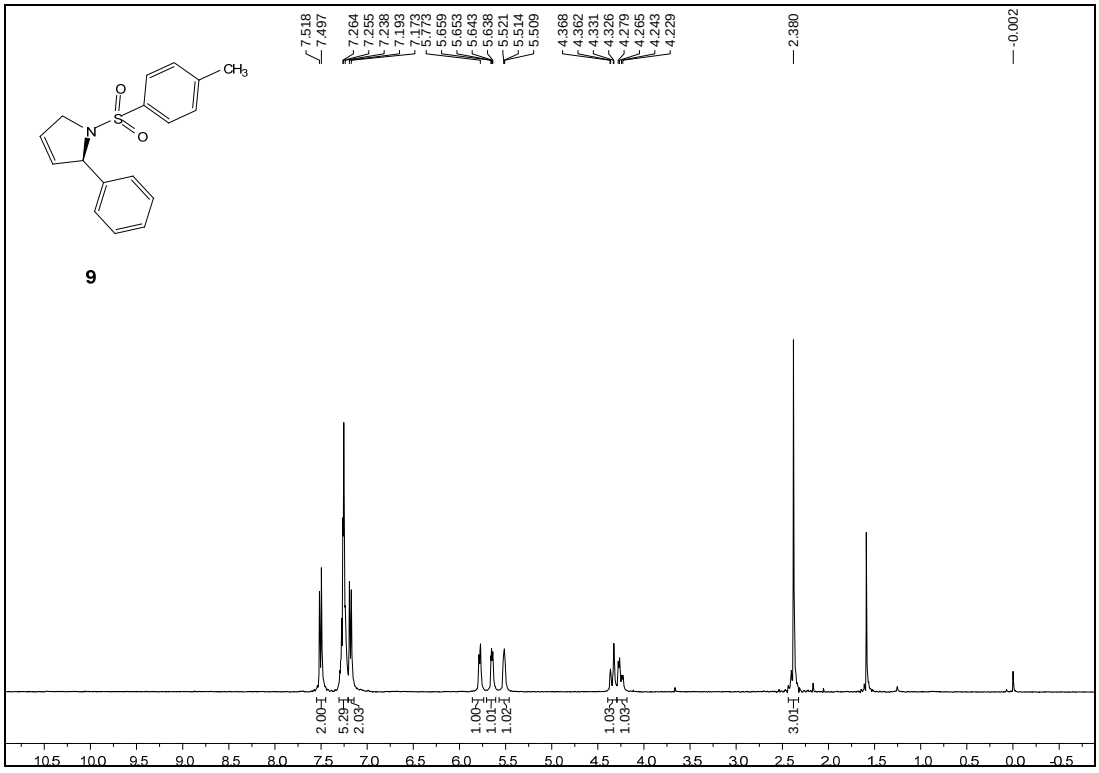


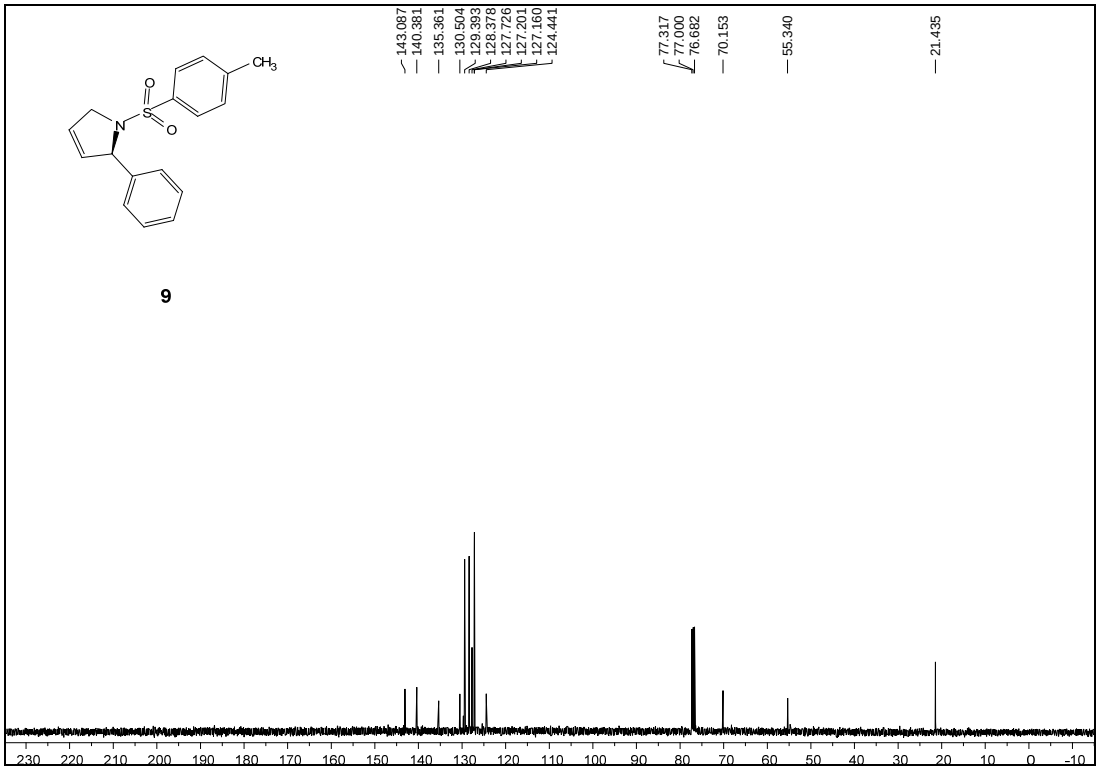
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 8



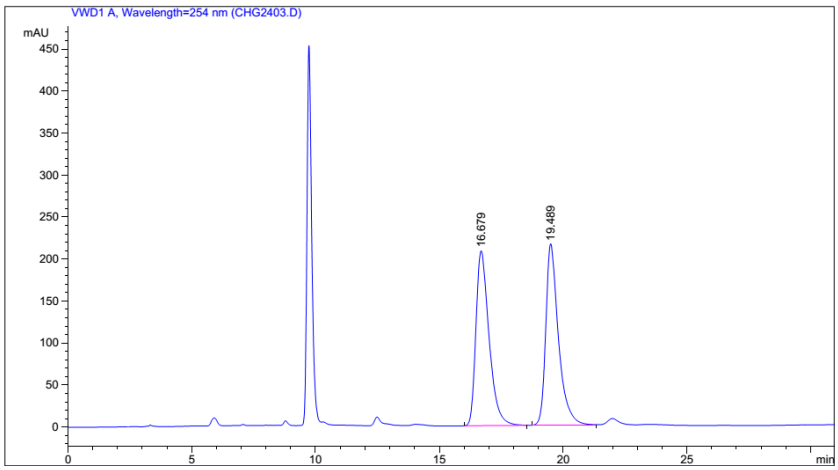


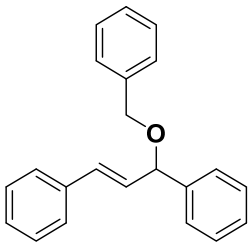
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 9





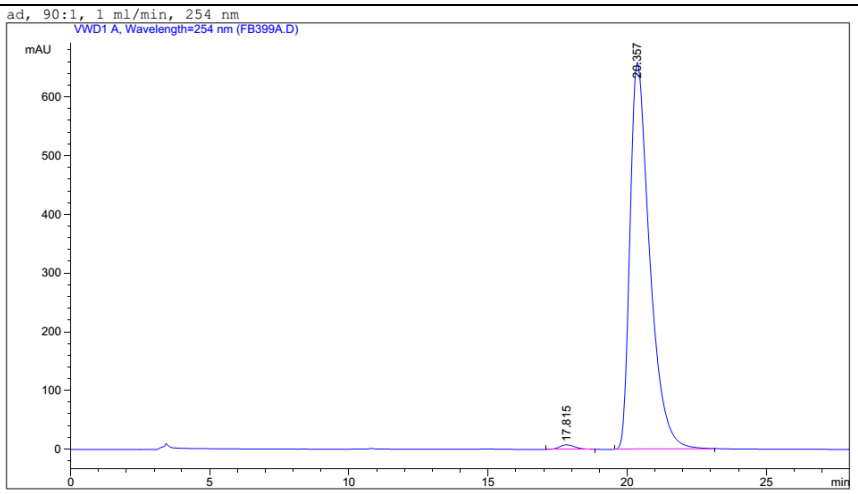
5. HPLC Chromatograms

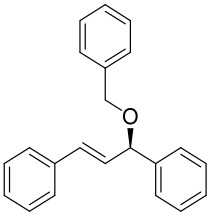




rac-4aa

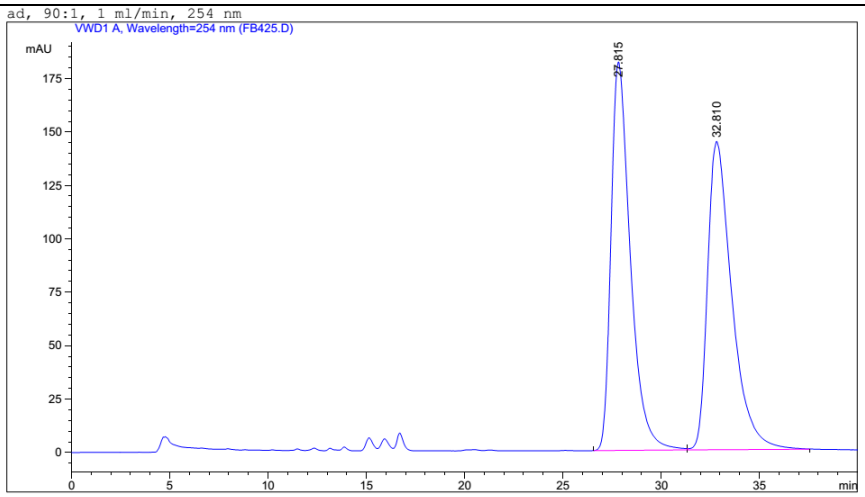
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.679	VV	0.5645	7746.83789	208.51996	49.8268
2	19.489	VV	0.5334	7800.69922	216.77052	50.1732

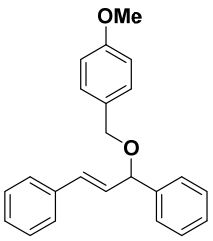




4aa

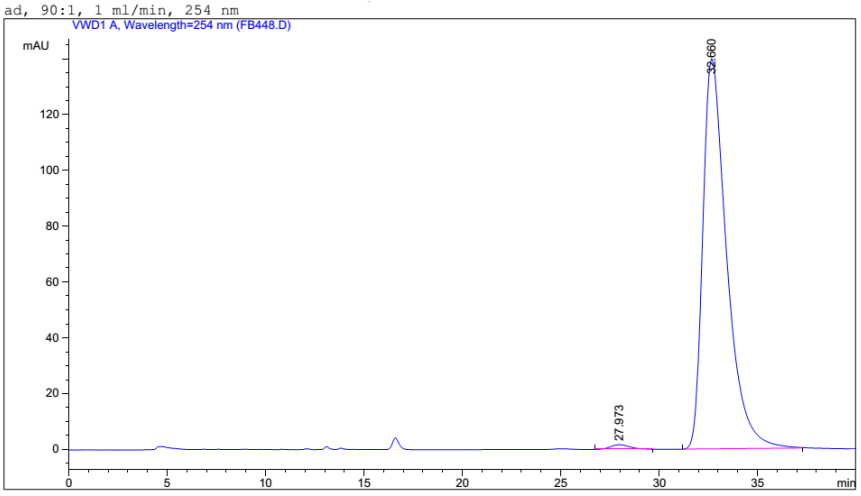
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.816	BB	0.5696	301.14816	7.75419	0.9244
2	20.357	BB	0.7377	3.22776e4	658.63110	99.0756

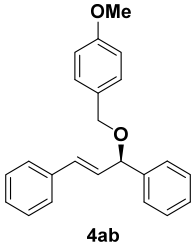




***rac*-4ab**

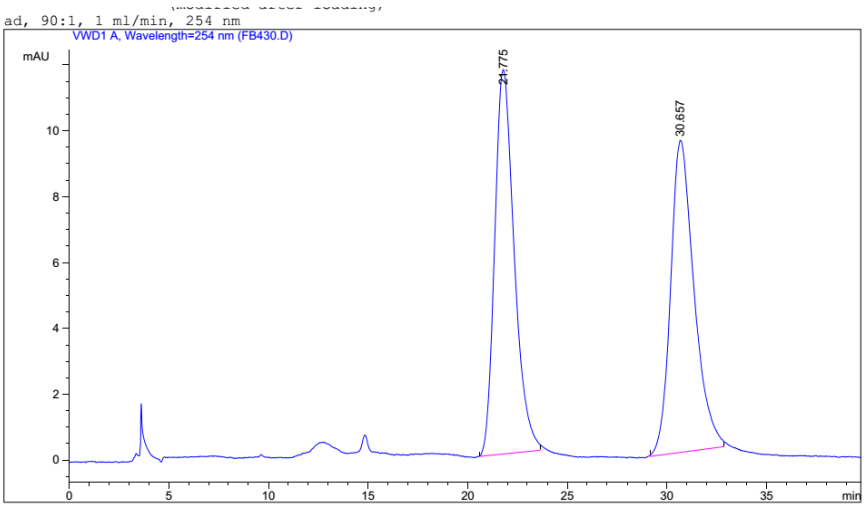
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.815	PB	1.0133	1.22814e4	181.58467	50.3257
2	32.810	BB	1.2567	1.21224e4	143.66986	49.6743

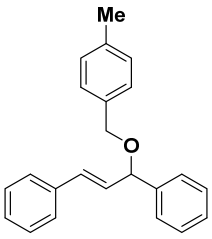




4ab

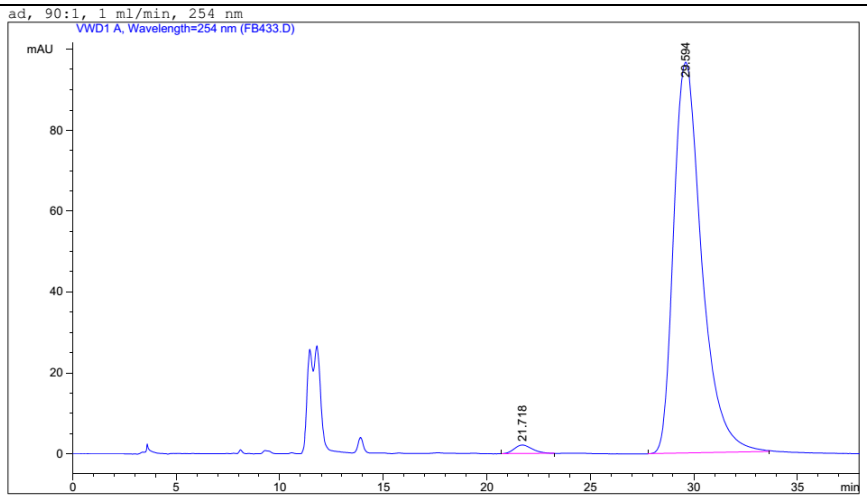
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.981	BB	0.8013	111.75985	1.65425	0.9458
2	32.659	BB	1.2611	1.17041e4	139.73511	99.0542

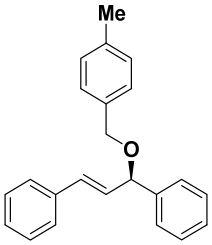




***rac*-4ac**

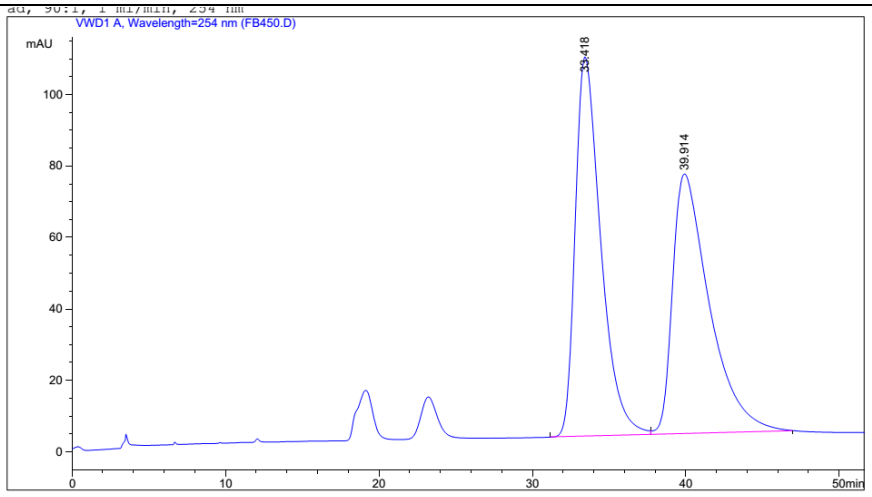
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.777	BB	0.9479	780.53461	11.62479	50.7741
2	30.656	BB	1.0302	756.73505	9.42231	49.2259

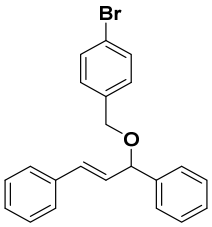




4ac

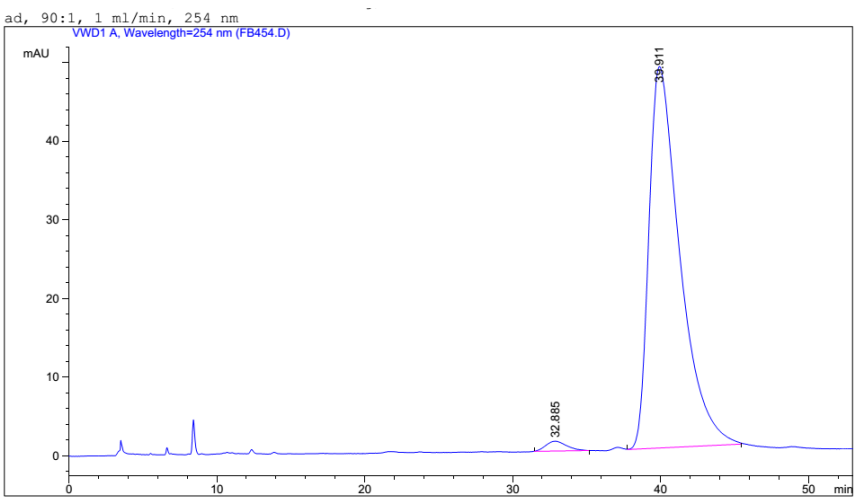
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.720	BB	0.7390	128.41718	2.11062	1.4020
2	29.594	PB	1.4180	9031.45605	96.50478	98.5980

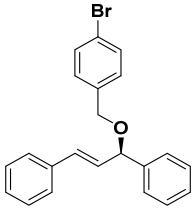




***rac*-4ad**

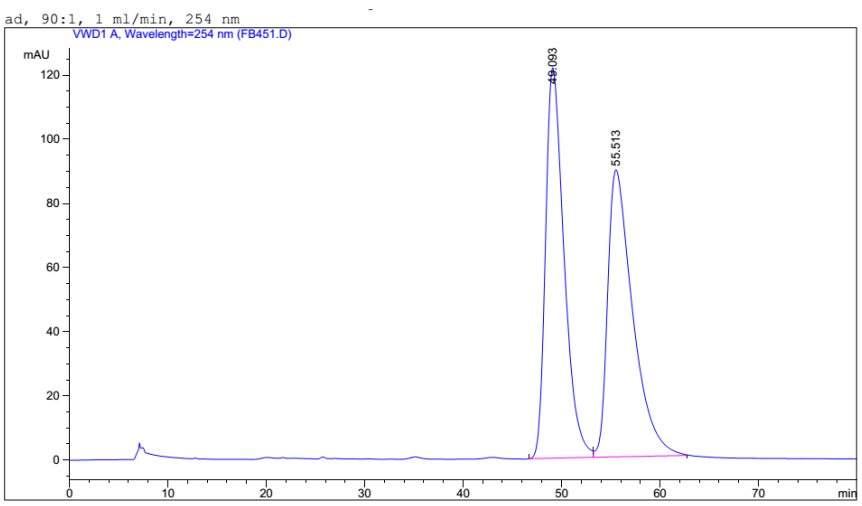
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.418	BB	1.6877	1.20819e4	105.78925	50.8114
2	39.912	PB	2.2280	1.16961e4	71.74796	49.1886

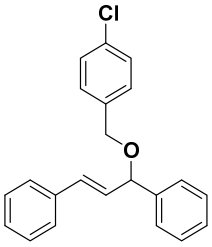




4ad

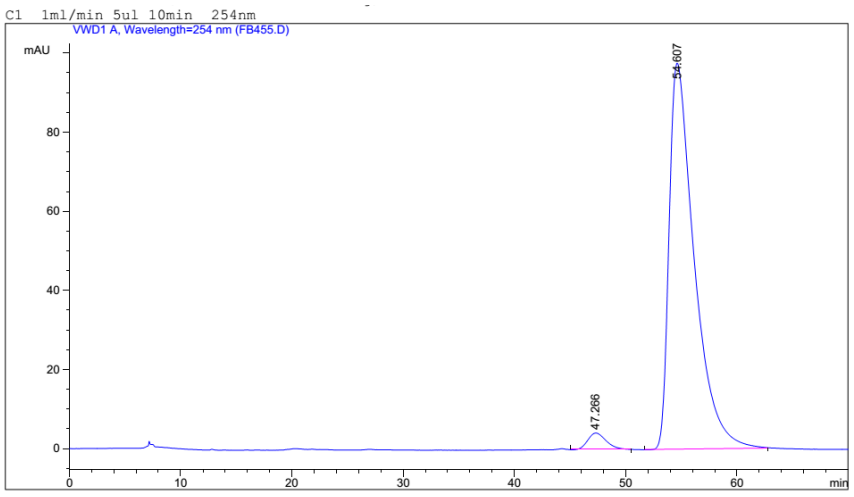
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.881	BB	1.1949	131.43045	1.29905	1.8556
2	39.912	BB	1.9388	6951.41162	48.36799	98.1444

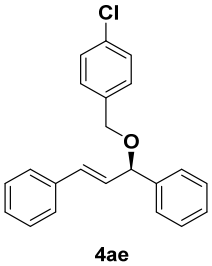




***rac*-4ae**

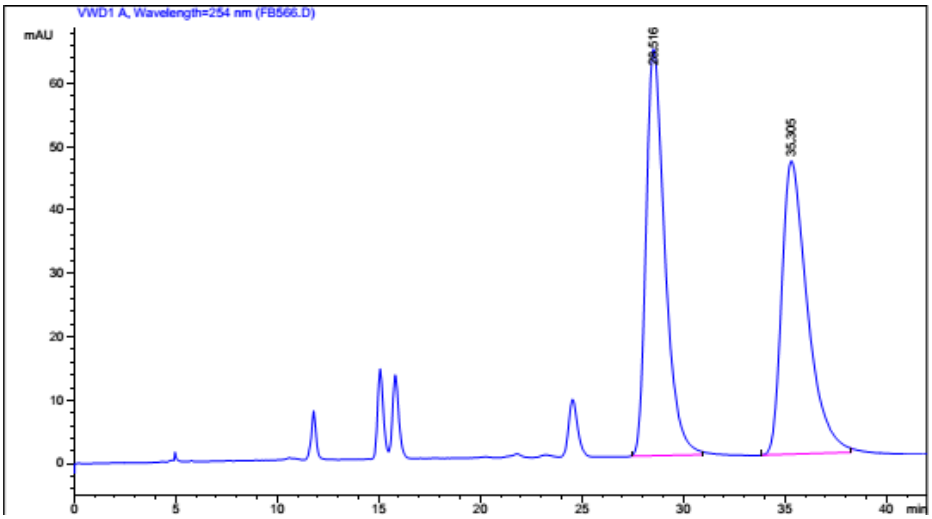
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.094	BB	1.5576	1.58605e4	121.63645	50.4293
2	55.513	BB	2.0551	1.55905e4	89.20287	49.5707

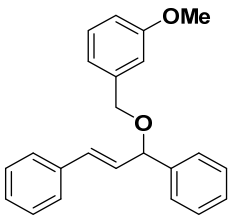




4ae

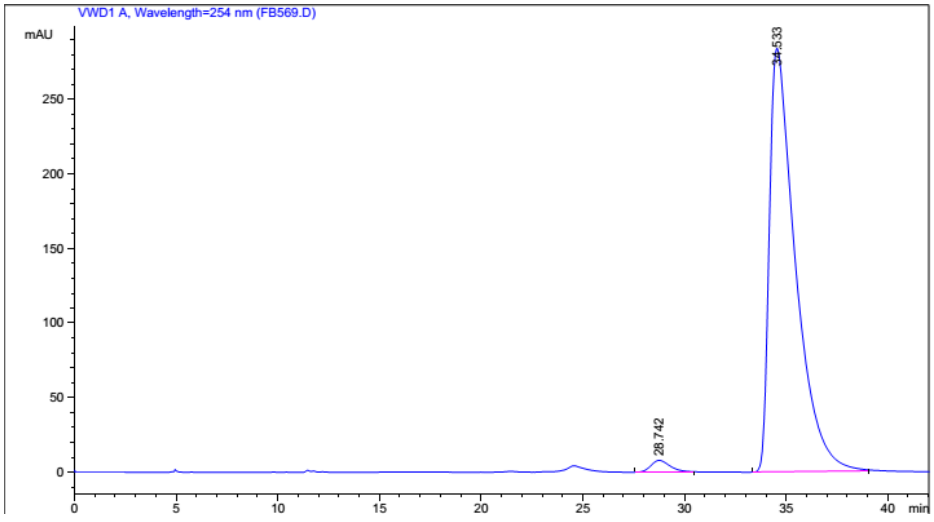
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.258	BB	1.3544	480.24924	4.18636	3.1090
2	54.604	BB	2.0144	1.49670e4	97.38019	96.8910

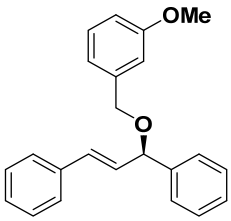




***rac*-4af**

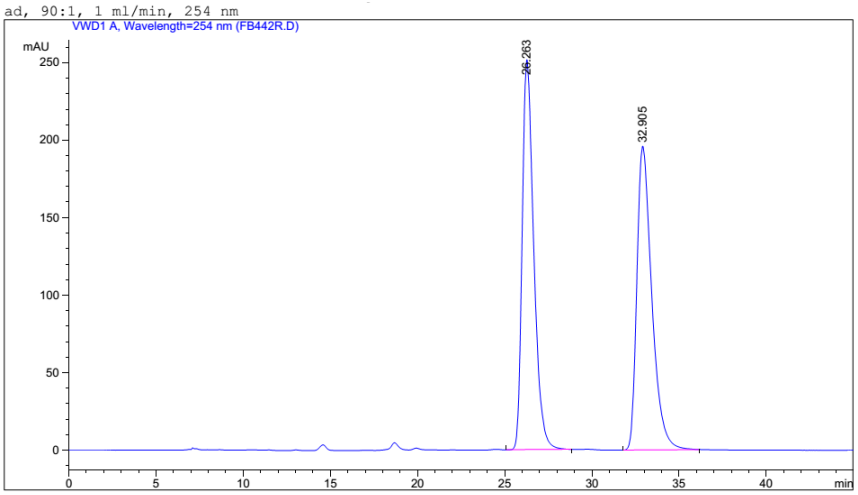
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.515	BB	0.9790	4103.18555	64.16971	50.5666
2	35.304	PB	1.2922	4011.23901	46.21552	49.4334

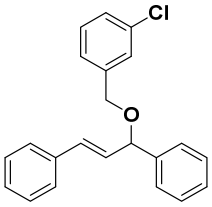




4af

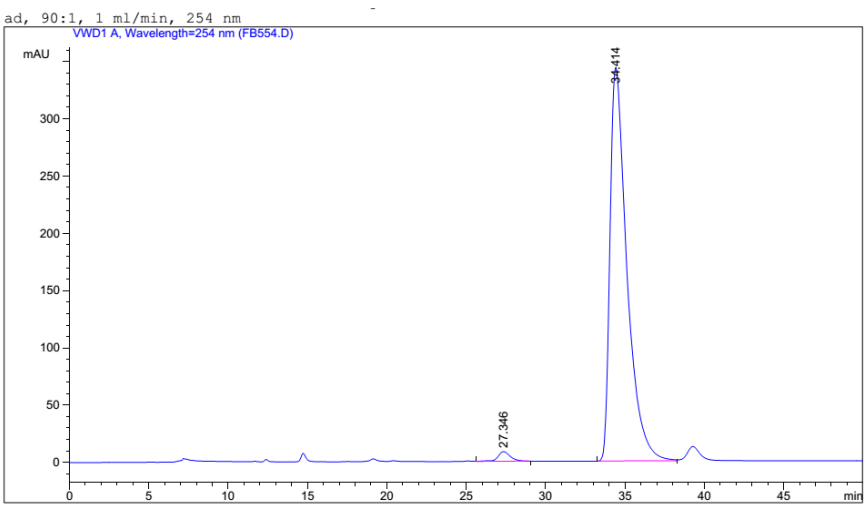
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.743	BB	0.9946	516.60199	7.85336	2.0102
2	34.532	PB	1.3028	2.51826e4	283.87927	97.9898

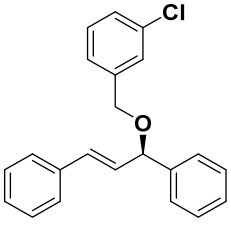




***rac*-4ag**

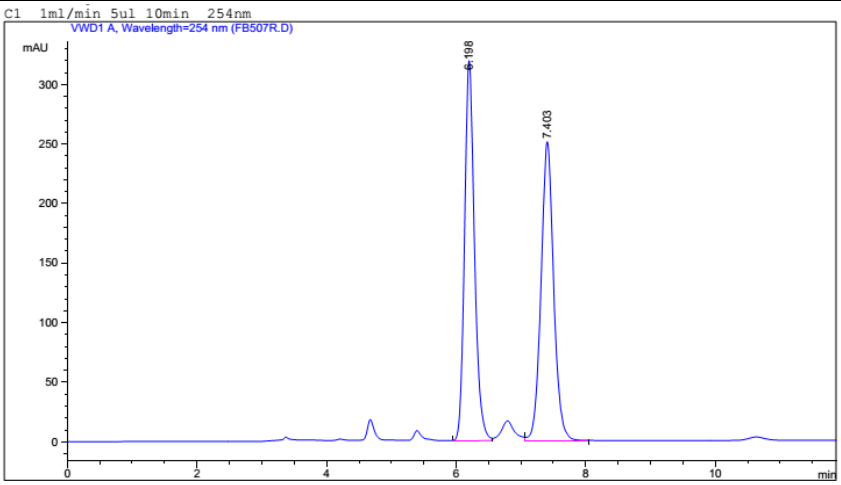
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.347	BB	0.6724	399.70044	8.13195	1.5574
2	34.416	BB	1.0252	2.52655e4	343.63156	98.4426

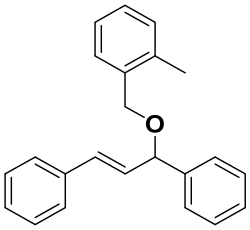




4ag

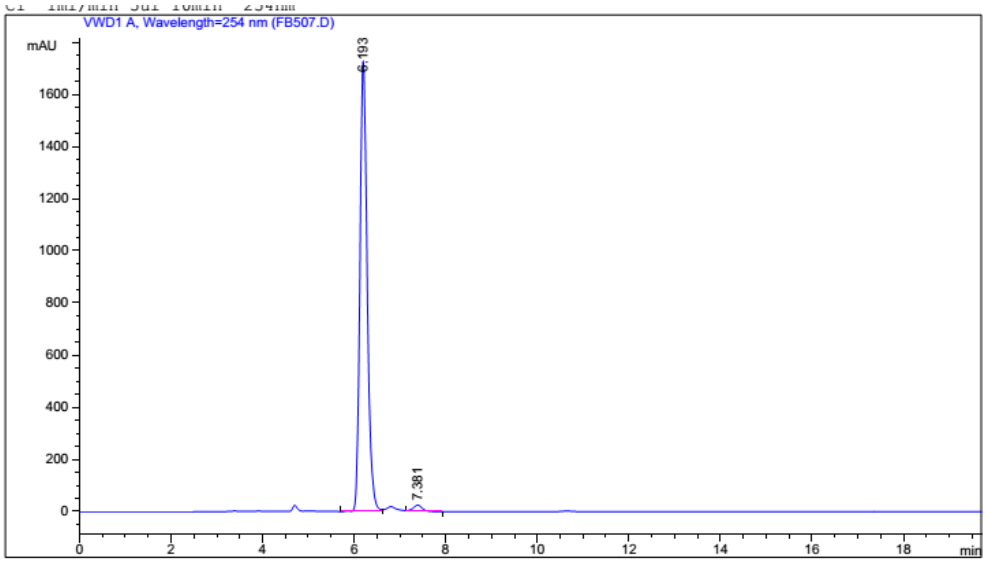
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.347	BB	0.6724	399.70044	8.13195	1.5574
2	34.416	BB	1.0252	2.52655e4	343.63156	98.4426

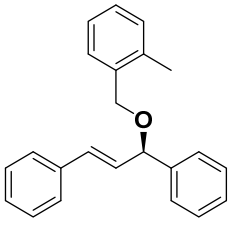




***rac*-4ah**

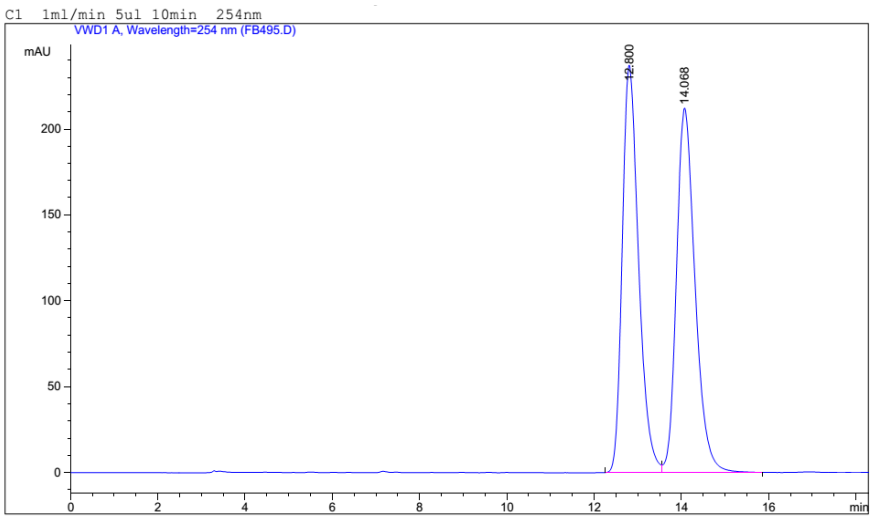
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.192	VV	0.1634	7067.63770	656.96606	50.0513
2	7.398	VB	0.2063	7053.16162	515.15479	49.9487

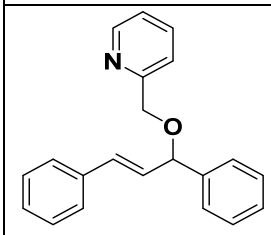




4ah

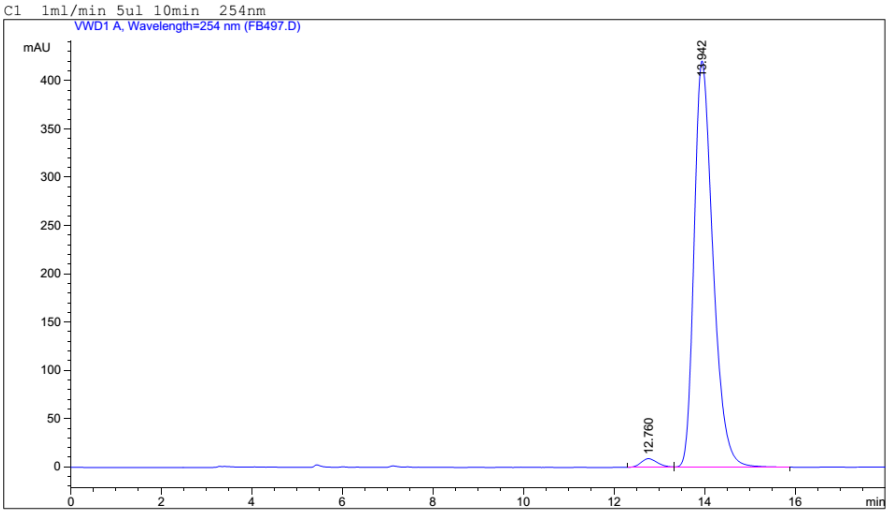
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.191	VV	0.1692	1.90519e4	1730.09937	98.0712
2	7.381	VB	0.2176	374.69171	25.35118	1.9288

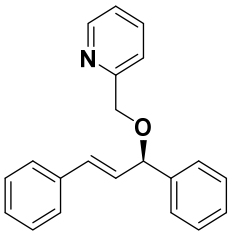




***rac*-4ai**

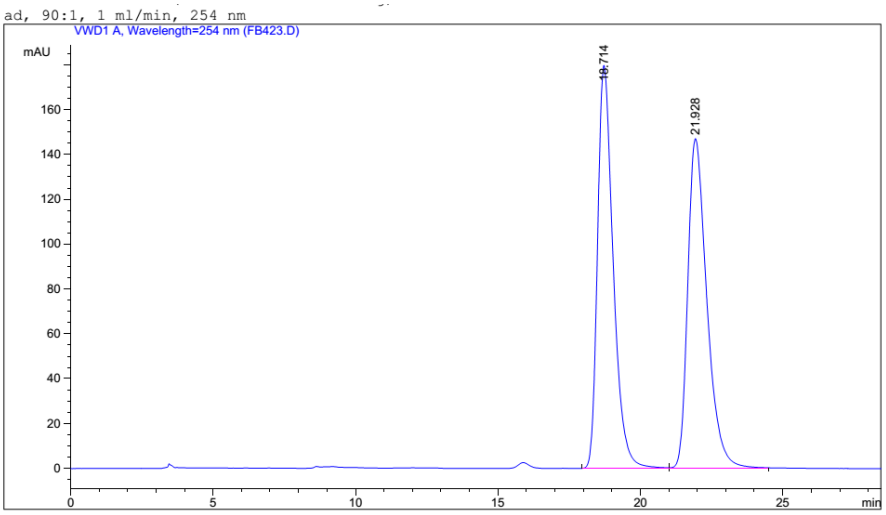
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.800	VV	0.4029	6178.76563	237.22247	49.5008
2	14.068	VB	0.4513	6303.39355	212.25533	50.4992

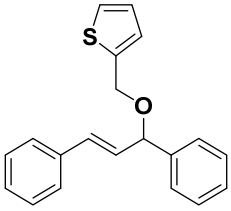




4ai

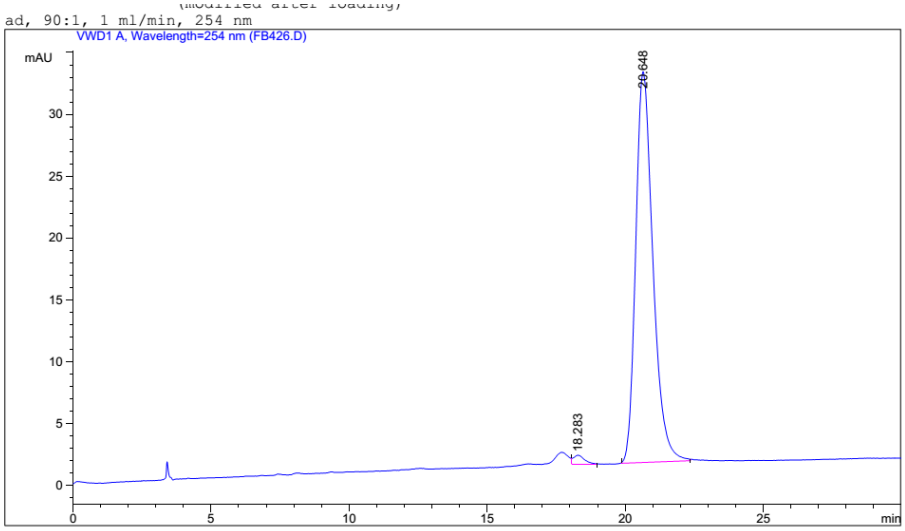
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.760	VV	0.4073	241.23447	9.13046	1.9355
2	13.942	VB	0.4497	1.22223e4	420.54813	98.0645

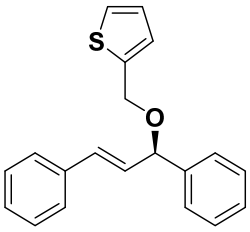




***rac*-4aj**

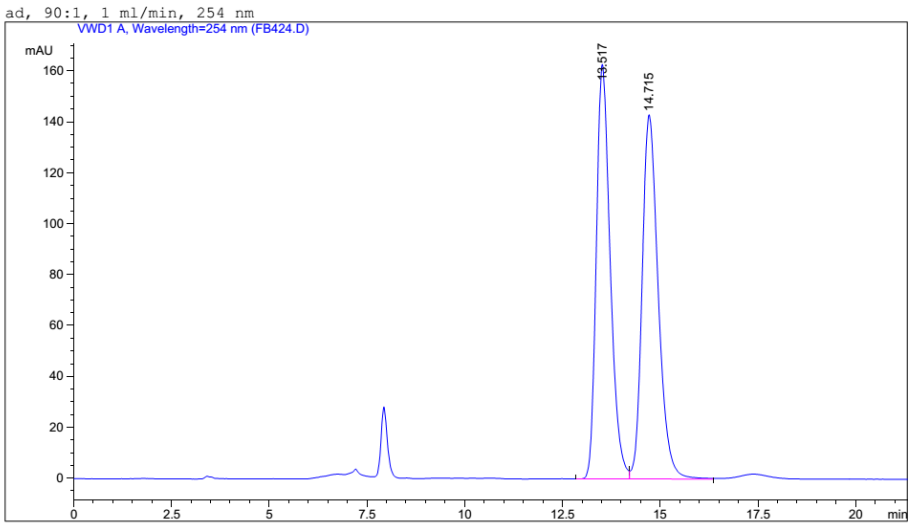
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.714	PB	0.5776	6807.91650	179.60841	50.1005
2	21.927	PB	0.7065	6780.61426	146.74788	49.8995

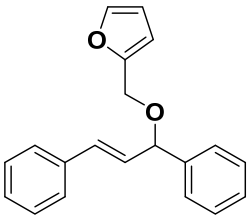




4aj

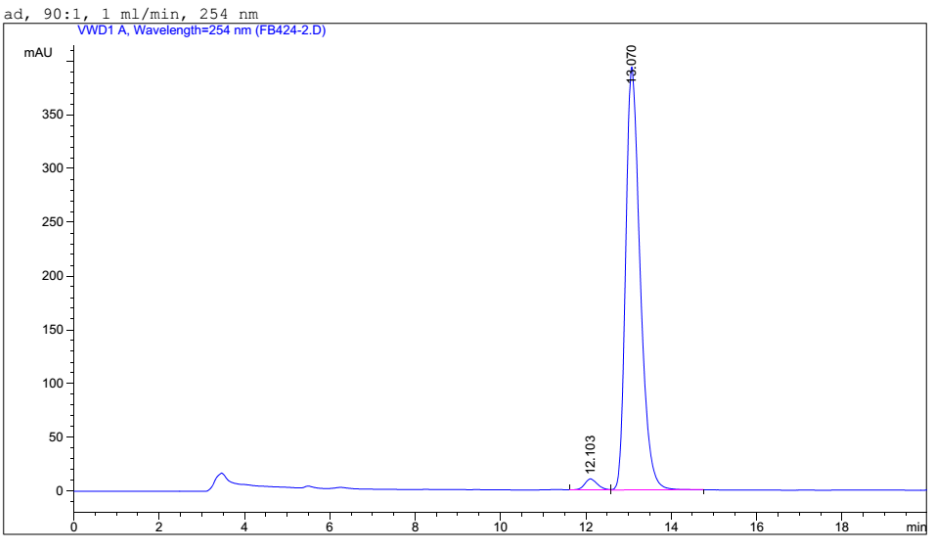
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.276	VB	0.3460	21.95608	7.72751e-1	1.5707
2	20.647	PB	0.6616	1375.90198	31.64633	98.4293

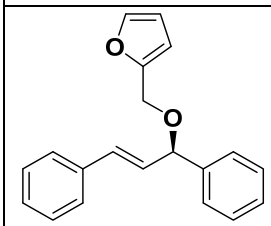




***rac*-4ak**

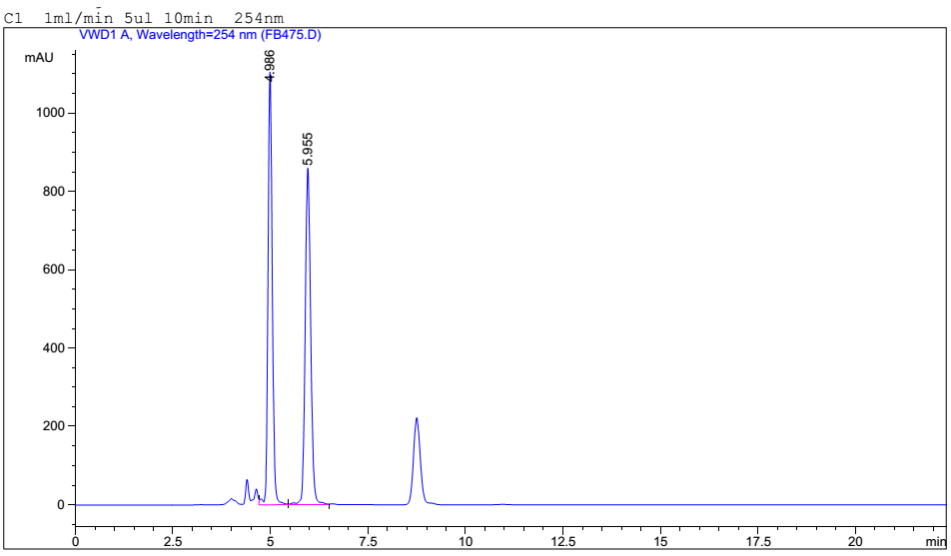
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.517	BV	0.3779	4012.15649	162.76120	49.6982
2	14.715	VB	0.4348	4060.88550	142.93089	50.3018

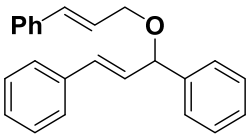




4ak

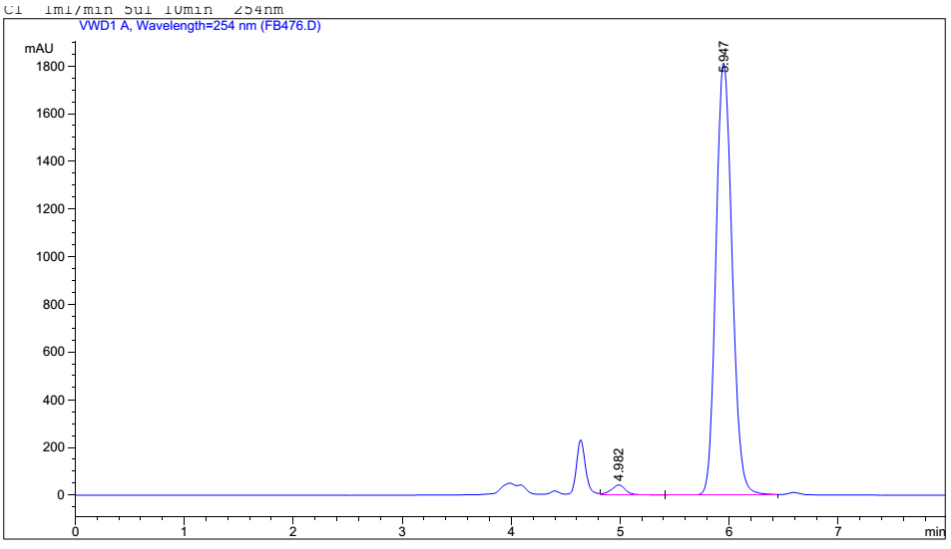
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.103	VV	0.3228	214.80096	10.26340	2.2640
2	13.070	VB	0.3594	9272.69922	393.48621	97.7360

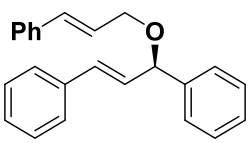




rac-4al

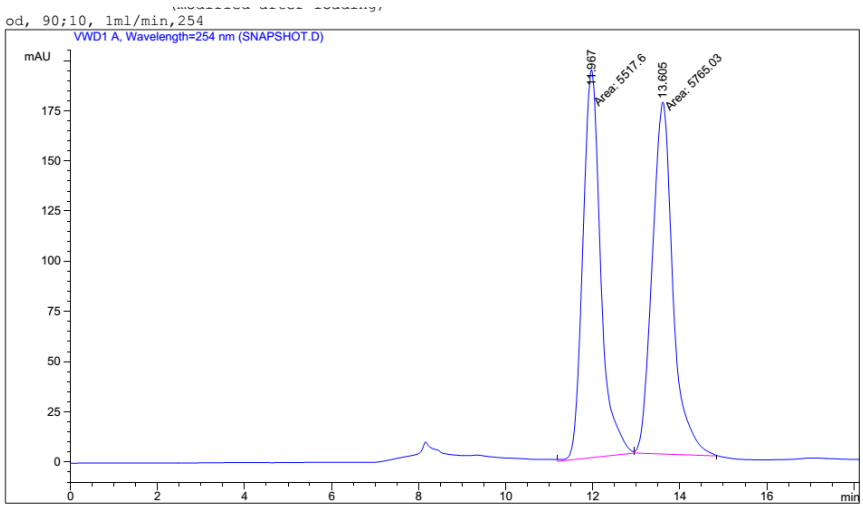
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.985	VV	0.1170	8268.02441	1097.11060	49.5687
2	5.954	VV	0.1495	8411.89844	856.88470	50.4313

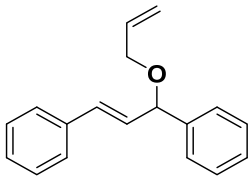




4al

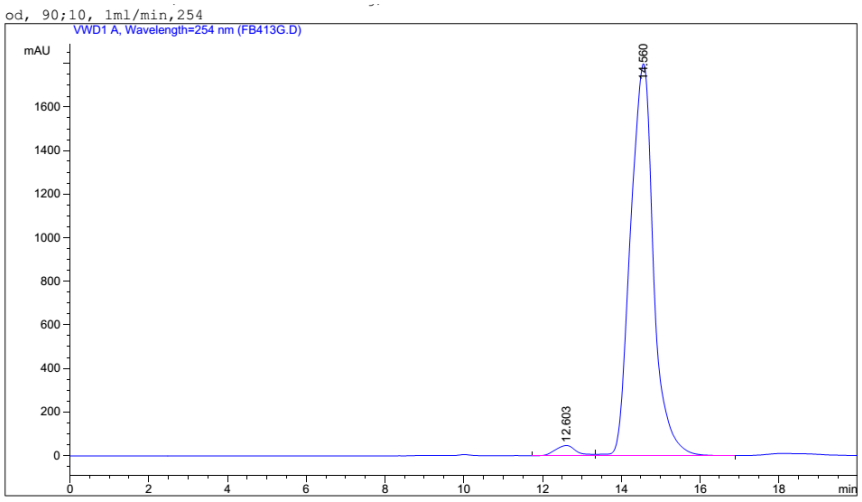
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.984	VV	0.1521	439.37335	43.75460	2.2779
2	5.946	VV	0.1623	1.88493e4	1809.04602	97.7221

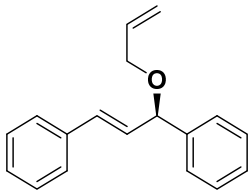




***rac*-4am**

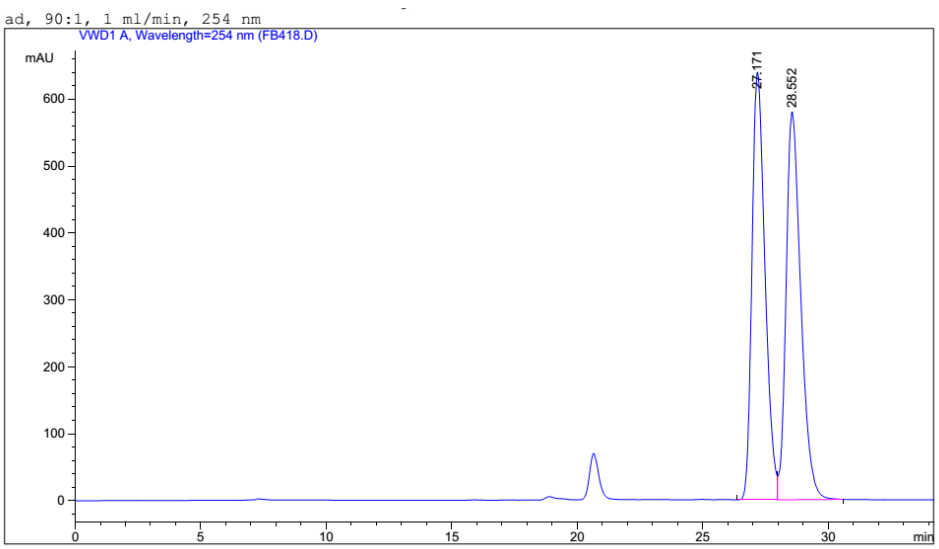
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.967	MM	0.4754	5517.60352	193.44177	48.9035
2	13.605	MM	0.5476	5765.02979	175.47192	51.0965

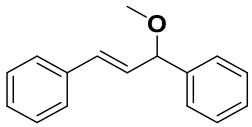




4am

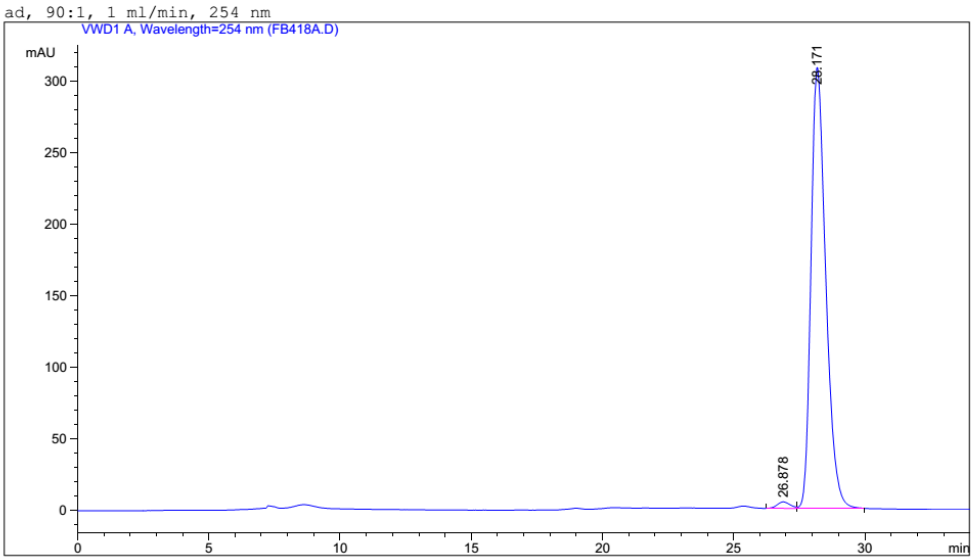
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.603	VV	0.6012	1843.35962	48.12568	2.4590
2	14.560	VV	0.6544	7.31218e4	1800.32703	97.5410

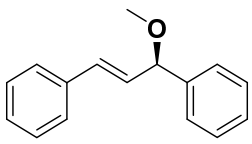




***rac*-4an**

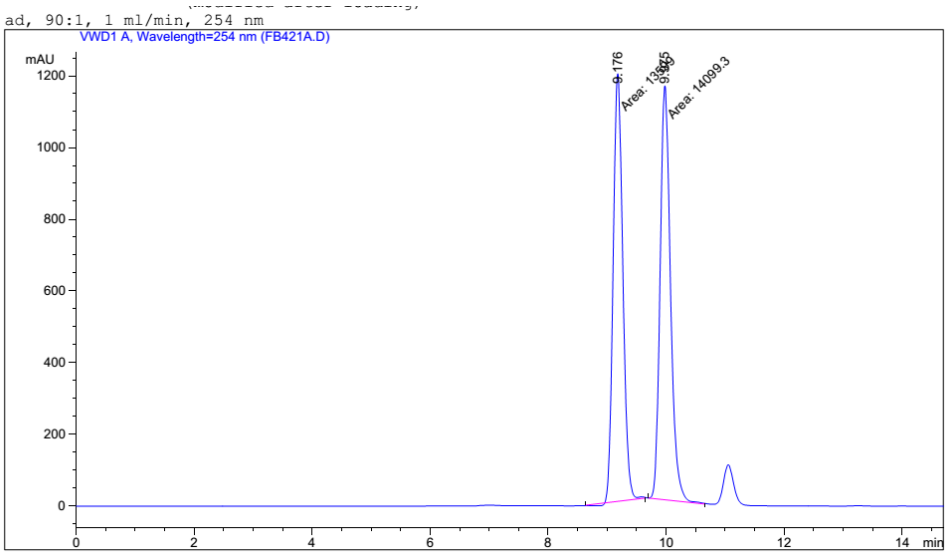
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.171	VV	0.5445	2.30571e4	639.31732	49.3953
2	28.550	VB	0.6166	2.36217e4	579.76691	50.6047

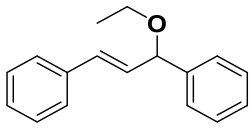




4an

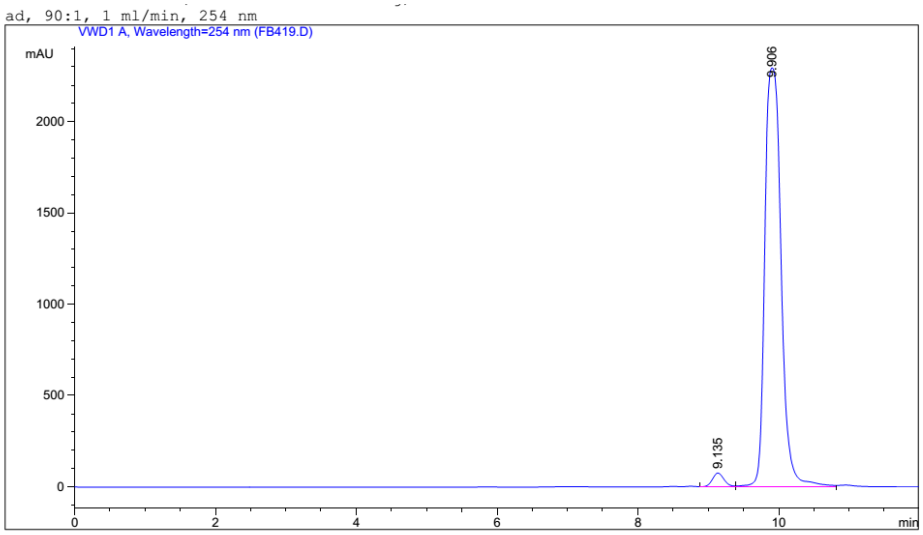
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.882	VV	0.4810	157.82146	4.57631	1.2894
2	28.171	VB	0.5954	1.20825e4	308.40244	98.7106

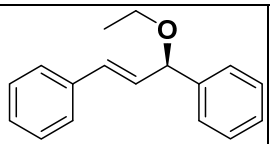




***rac*-4ao**

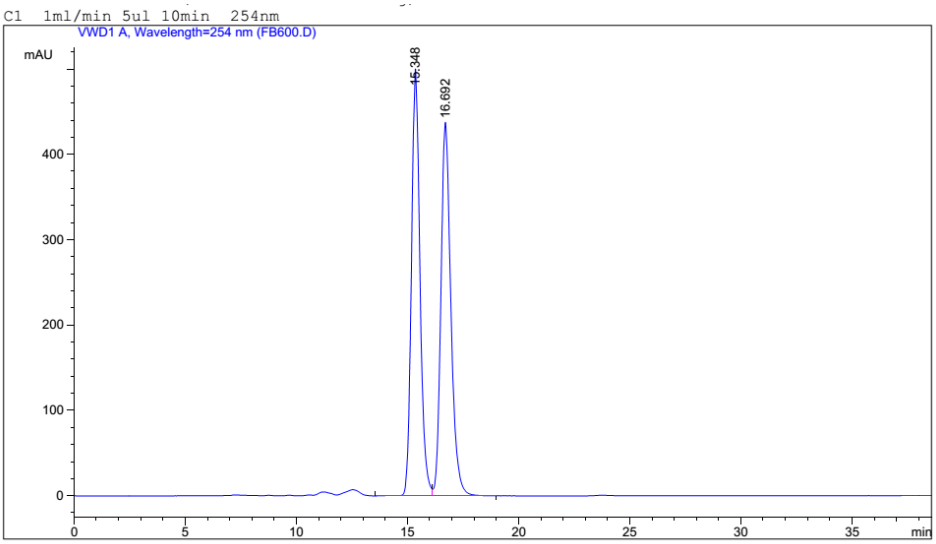
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.176	MM	0.1888	1.35239e4	1194.04822	49.6130
2	9.975	MM	0.1997	1.37349e4	1146.11682	50.3870

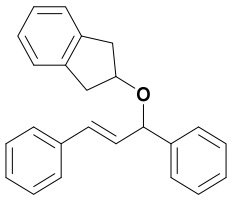




4ao

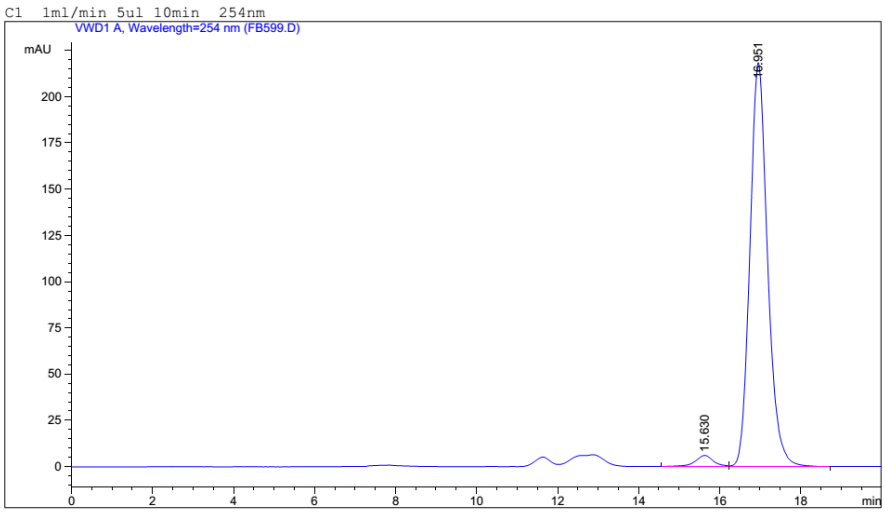
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.135	VV	0.1806	885.36407	76.25362	2.3431
2	9.905	VV	0.2531	3.69013e4	2295.23682	97.6569

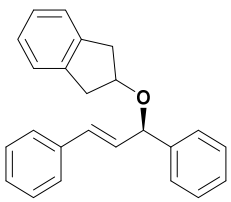




rac-4ap

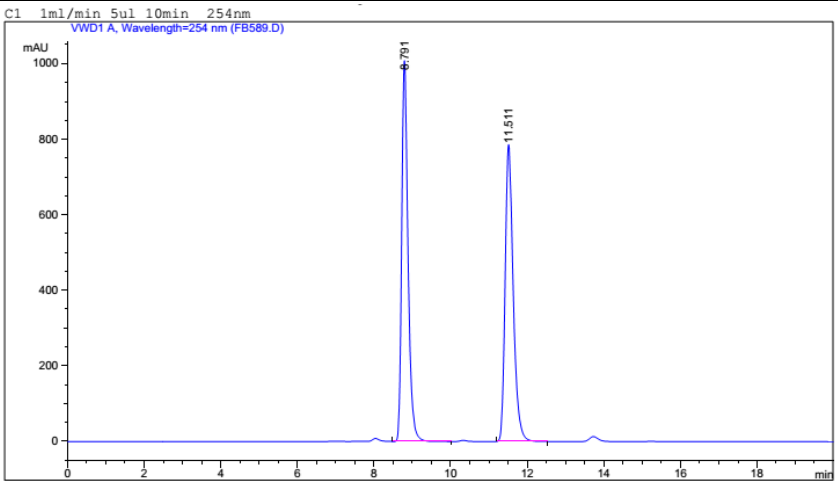
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.347	MM	0.4459	1.33825e4	500.23981	49.8963
2	16.692	MM	0.5124	1.34382e4	437.07175	50.1037

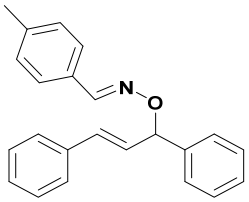




4ap

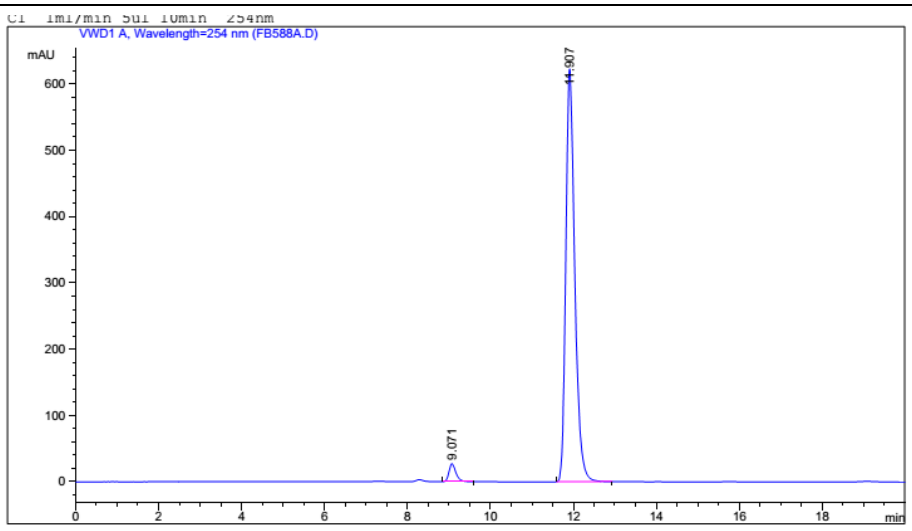
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.630	BV	0.4735	190.29846	6.02256	2.8110
2	16.950	VB	0.4566	6579.43213	218.22859	97.1890

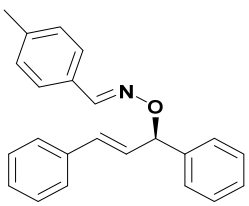




rac-4aq

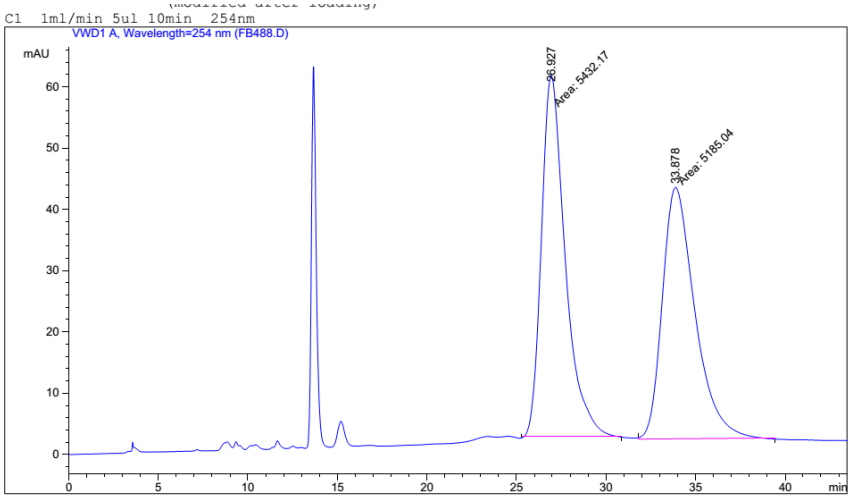
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.789	VV	0.1711	1.15185e4	1008.44739	49.8822
2	11.509	VV	0.2241	1.15729e4	786.35510	50.1178

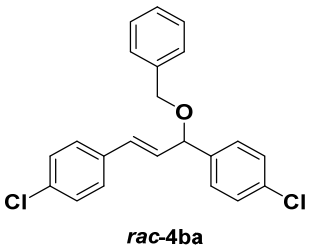




4aq

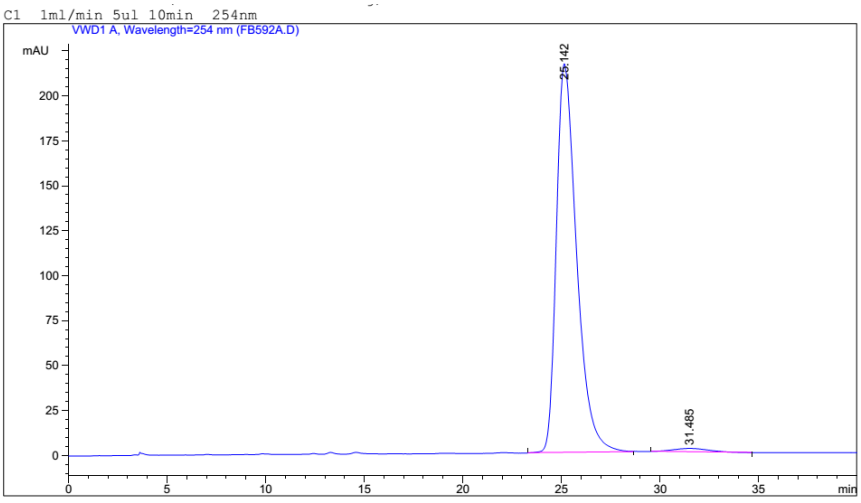
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.071	BB	0.1849	323.43115	27.28738	3.3556
2	11.907	BB	0.2271	9315.12402	622.27045	96.6444

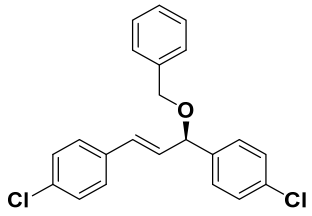




***rac*-4ba**

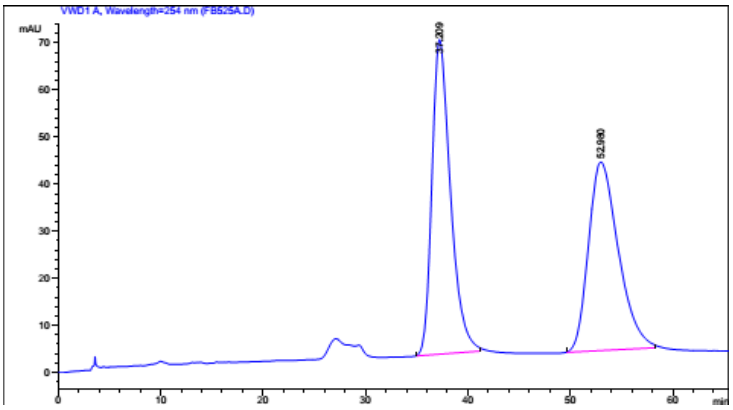
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.929	MM	1.5134	5327.39795	58.66871	50.8035
2	33.875	MM	2.1021	5158.88428	40.90199	49.1965

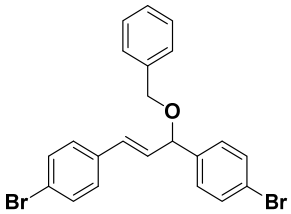




4ba

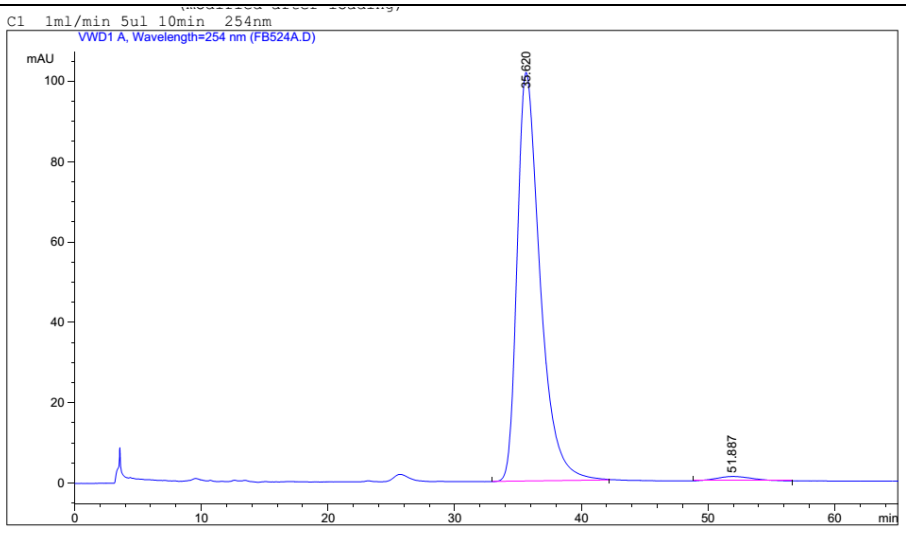
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.142	VB	1.0948	1.54343e4	216.24791	98.4092
2	31.485	BP	1.5152	249.50052	1.95114	1.5908

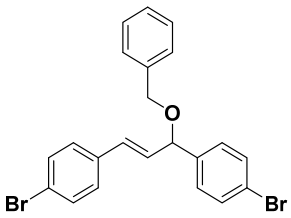




rac-4ca

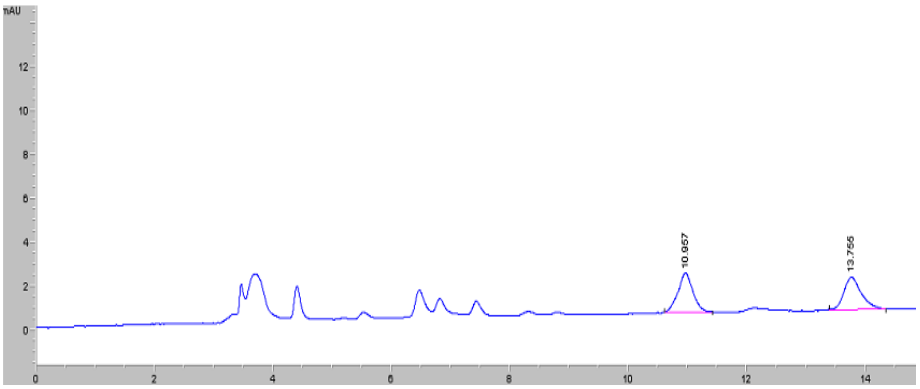
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.210	BB	1.8797	8438.49219	66.81258	50.7626
2	52.977	BB	2.4571	8184.94727	40.12417	49.2374

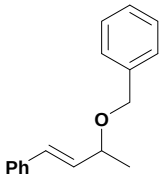




rac-4ca

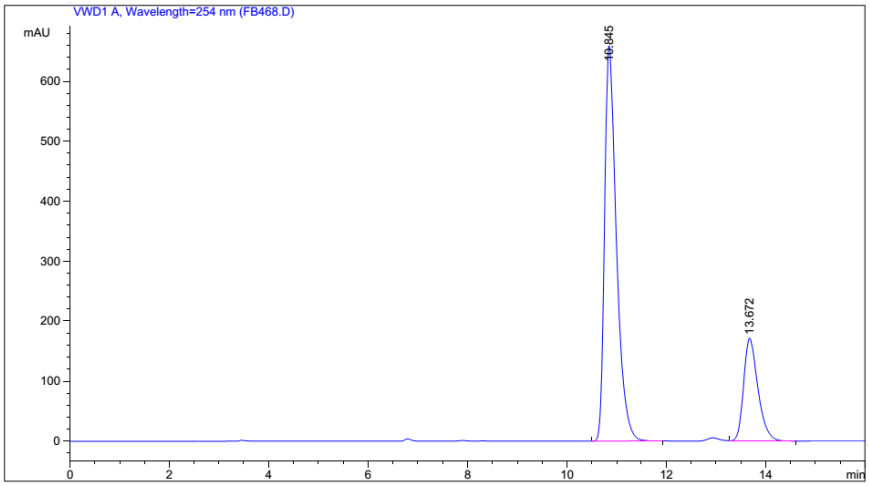
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.622	BB	1.8541	1.26098e4	101.50709	98.4167
2	52.040	BB	2.2472	202.86235	1.05867	1.5833

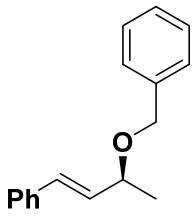




rac-4da

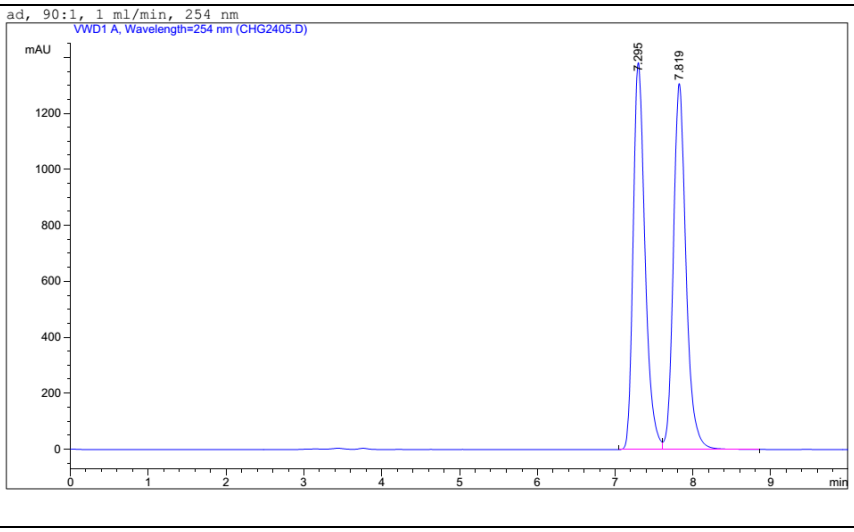
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.957	BB	0.2690	32.56630	1.80309	51.3262
2	13.755	BB	0.3122	30.88336	1.48672	48.6738

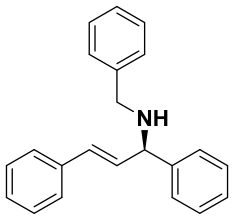




4da

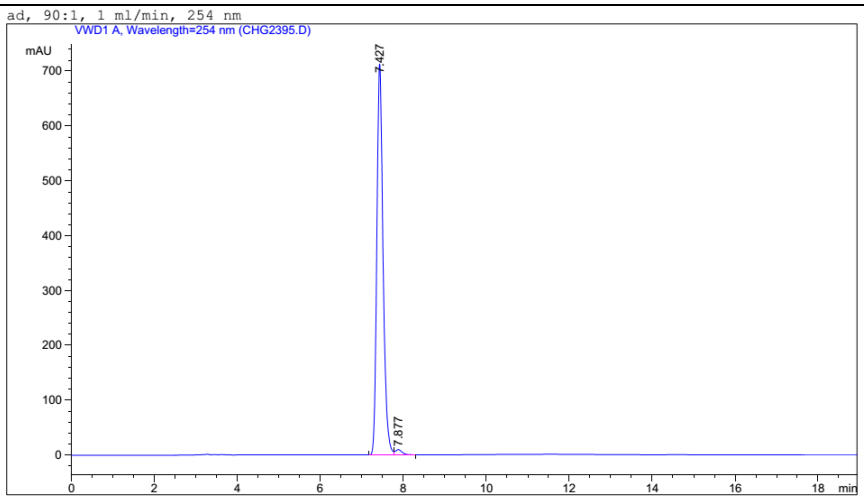
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.845	BB	0.2520	1.09498e4	659.18890	76.0895
2	13.672	VB	0.3036	3440.90039	171.76422	23.9105

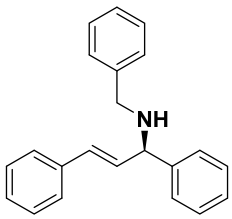




6a

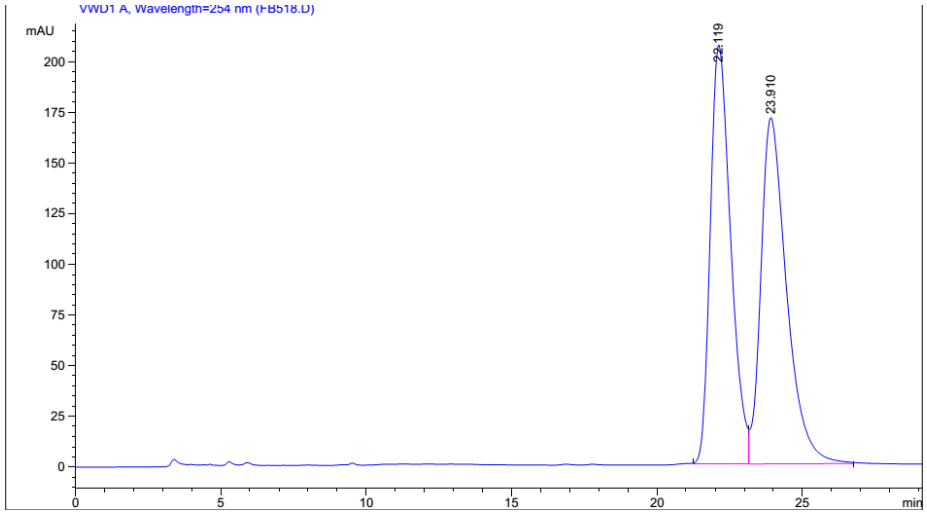
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.295	VV	0.1640	1.45794e4	1379.82568	49.5004
2	7.819	VB	0.1738	1.48738e4	1304.13123	50.4996

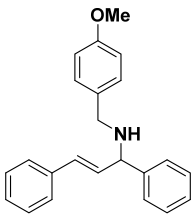




6a

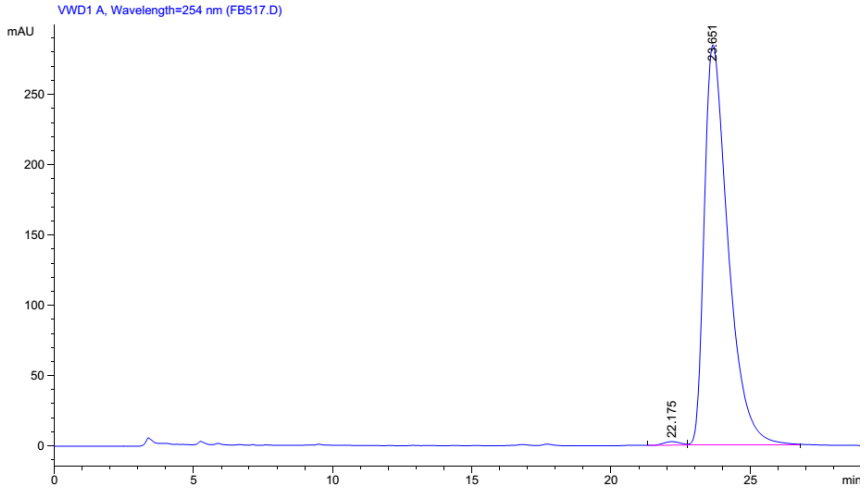
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.427	PV	0.1593	7417.94580	712.72455	98.5247
2	7.877	VB	0.1733	111.07510	9.56878	1.4753

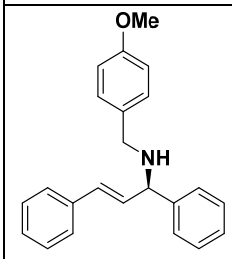




rac-6b

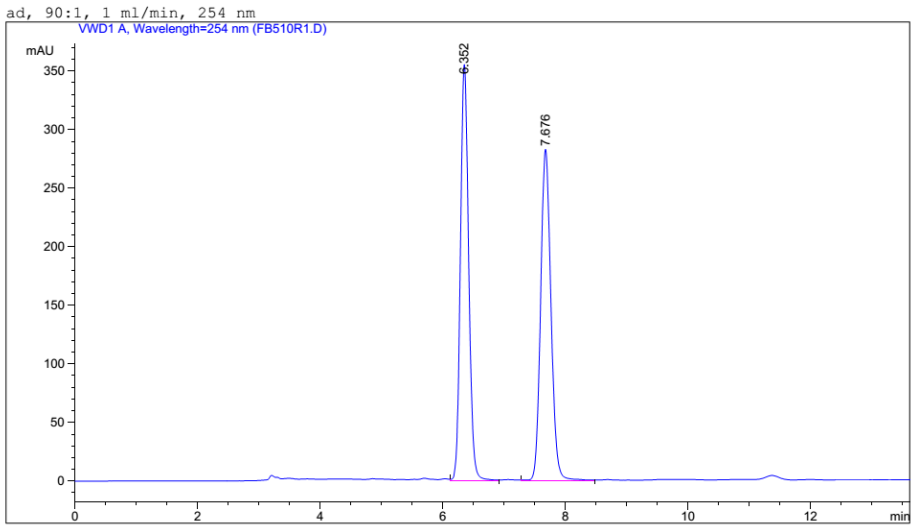
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.119	BV	0.7496	1.00847e4	206.76395	48.9798
2	23.910	VB	0.9329	1.05048e4	170.83842	51.0202

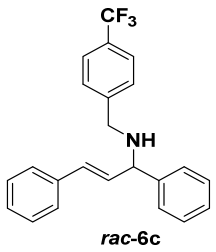




6b

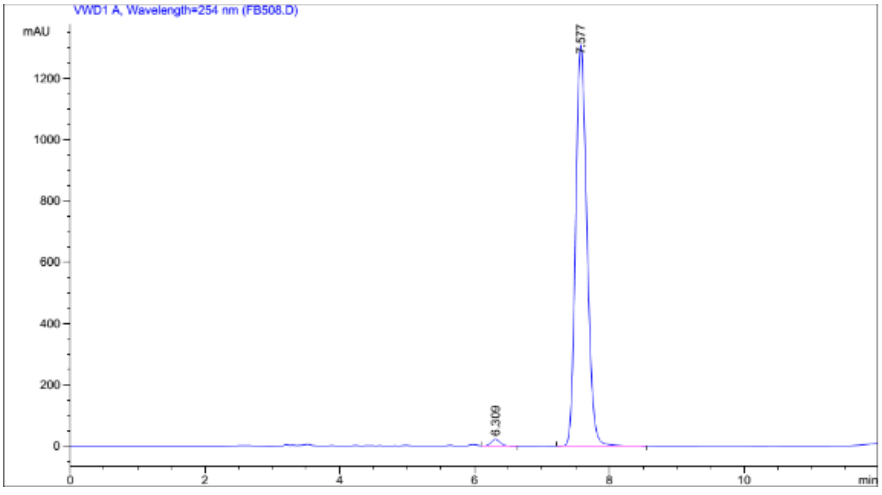
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.175	BV	0.6381	135.93066	2.77671	0.7928
2	23.649	VB	0.9037	1.70090e4	284.74225	99.2072

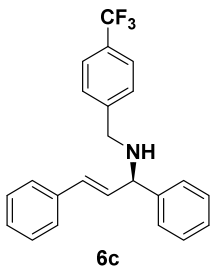




rac-6c

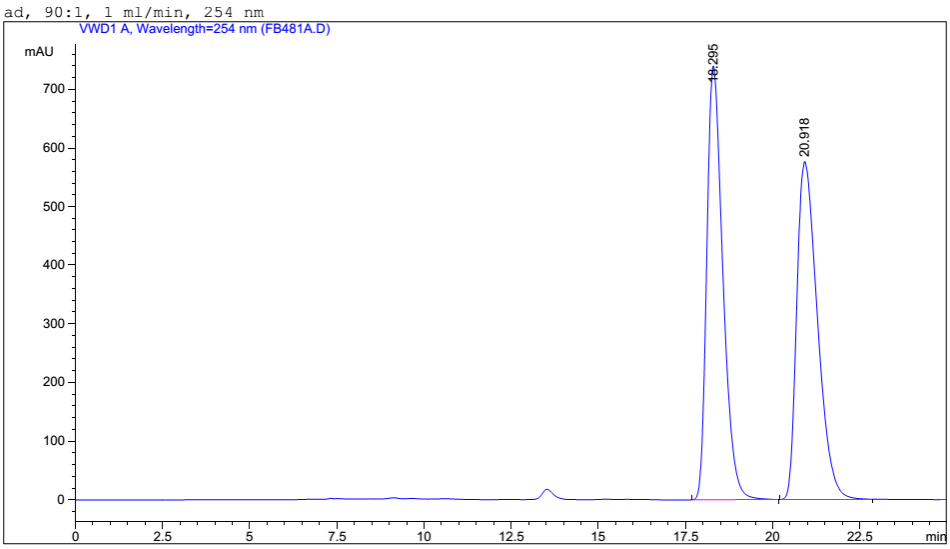
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.352	VV	0.1456	3327.39746	355.50116	49.9727
2	7.676	VB	0.1824	3331.02710	283.05582	50.0273

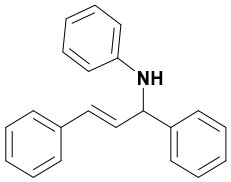




6c

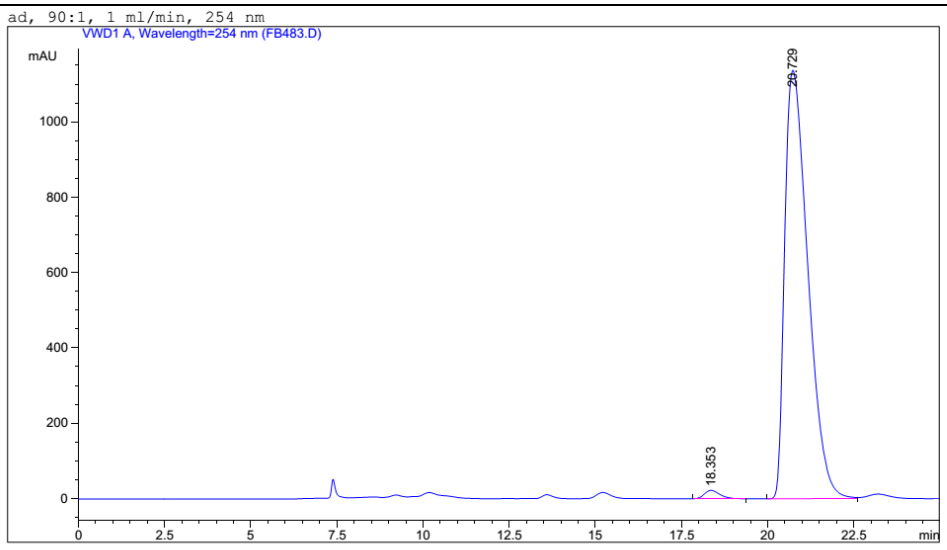
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.309	VB	0.1593	228.86871	22.52330	1.4723
2	7.577	VB	0.1892	1.53161e4	1306.02295	98.5277

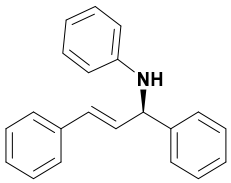




***rac*-6d**

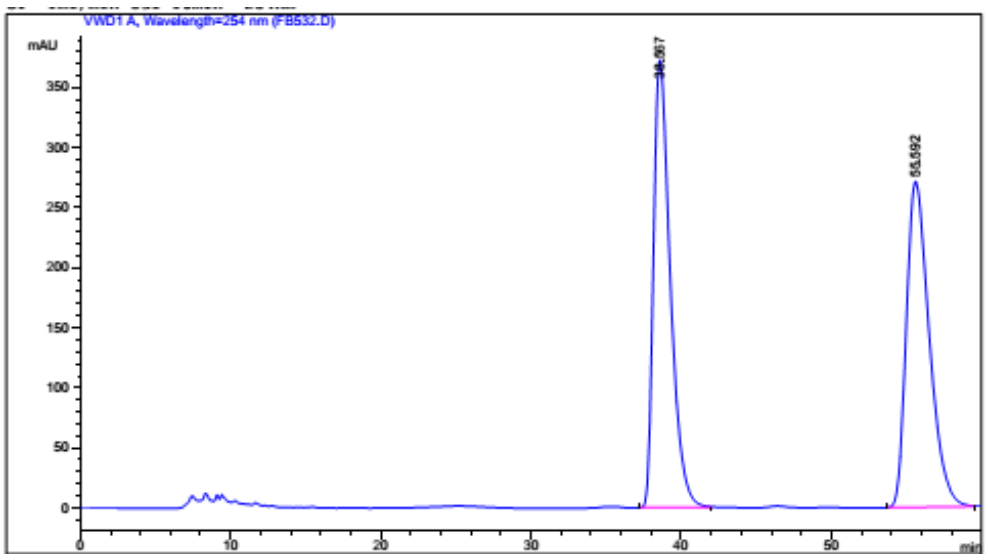
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.295	PV	0.4906	2.37143e4	739.54315	49.8469
2	20.918	VB	0.6458	2.38600e4	576.65918	50.1531

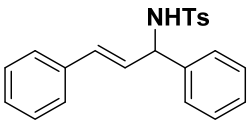




6d

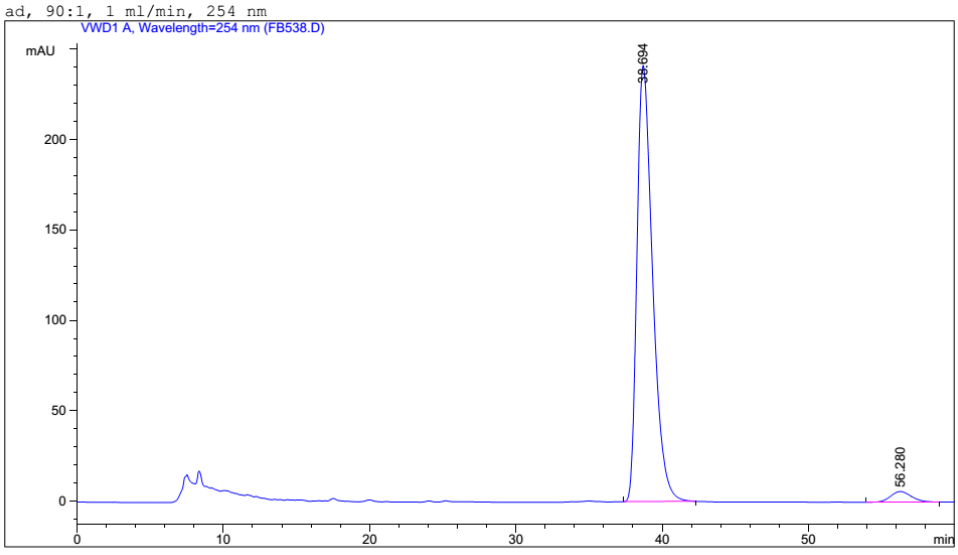
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.353	BB	0.4971	742.18494	22.74900	1.3786
2	20.731	BV	0.7308	5.30943e4	1137.76465	98.6214

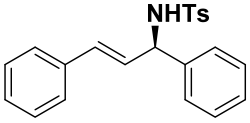




***rac*-6e**

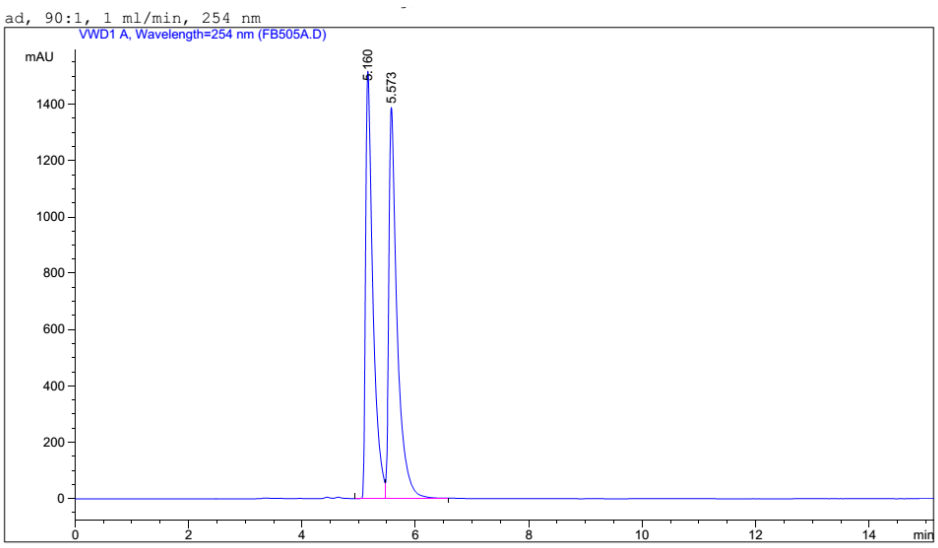
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.675	VB	0.9419	1.88954e4	294.59903	50.0481
2	51.307	BB	1.2815	1.88590e4	209.83209	49.9519

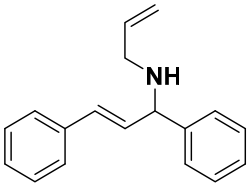




6e

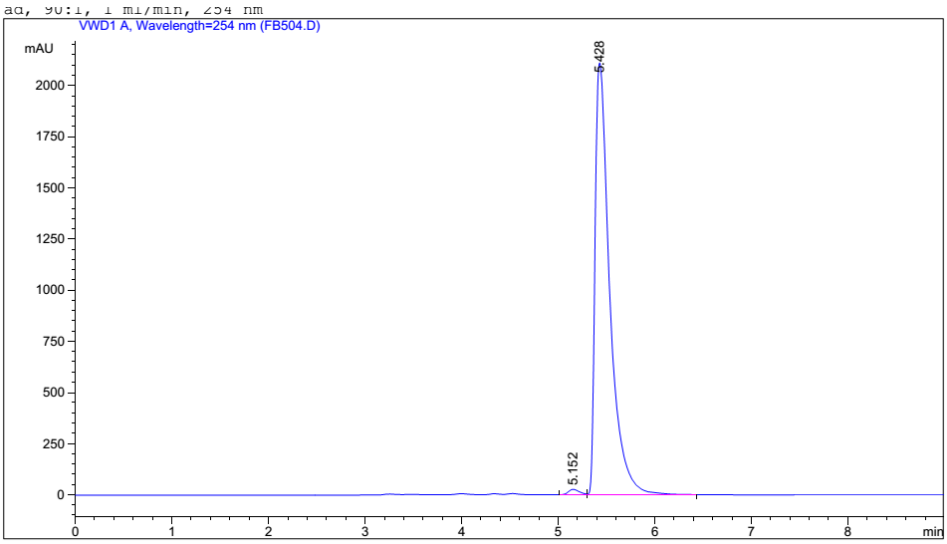
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.632	VB	0.8408	1.25895e4	221.97250	96.9346
2	47.897	BB	0.9319	398.12772	5.07132	3.0654

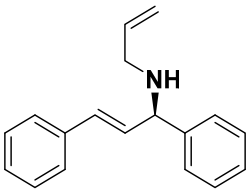




***rac*-6f**

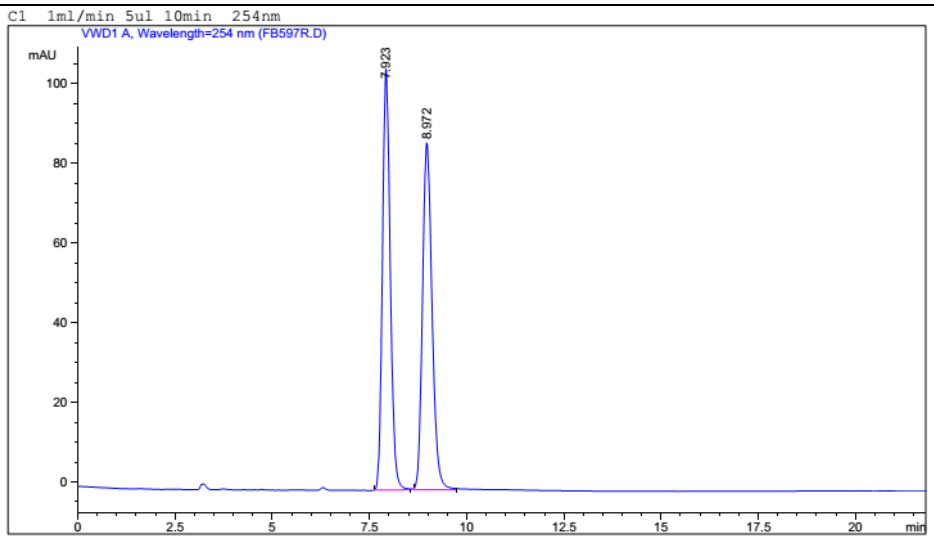
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.159	MM	0.1508	1.37917e4	1524.55872	49.0237
2	5.572	MM	0.1707	1.43410e4	1400.16260	50.9763

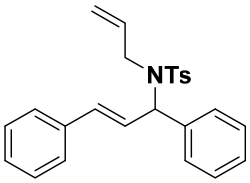




6f

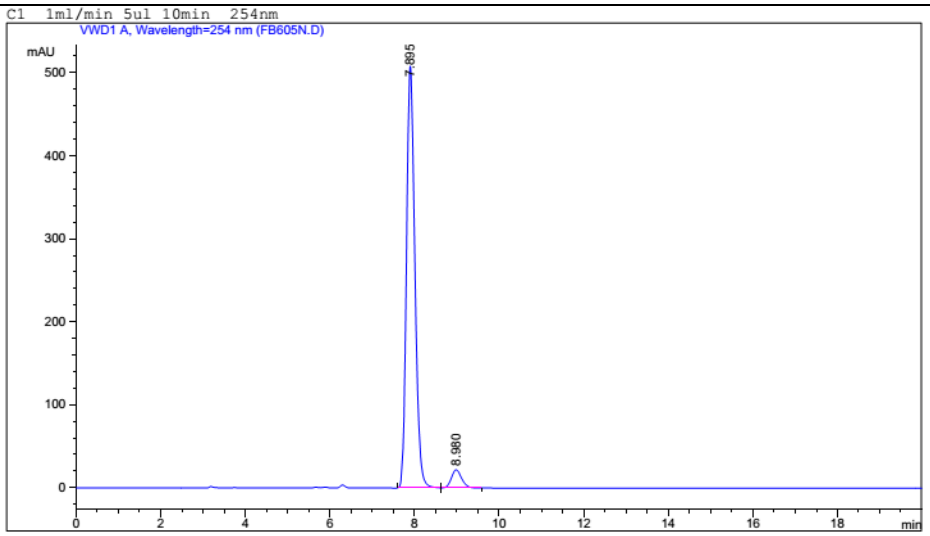
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.296	BV	0.1262	159.68785	19.47421	0.6845
2	5.581	VB	0.1654	2.31697e4	2095.69995	99.3155

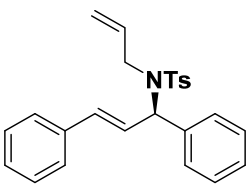




***rac*-6g**

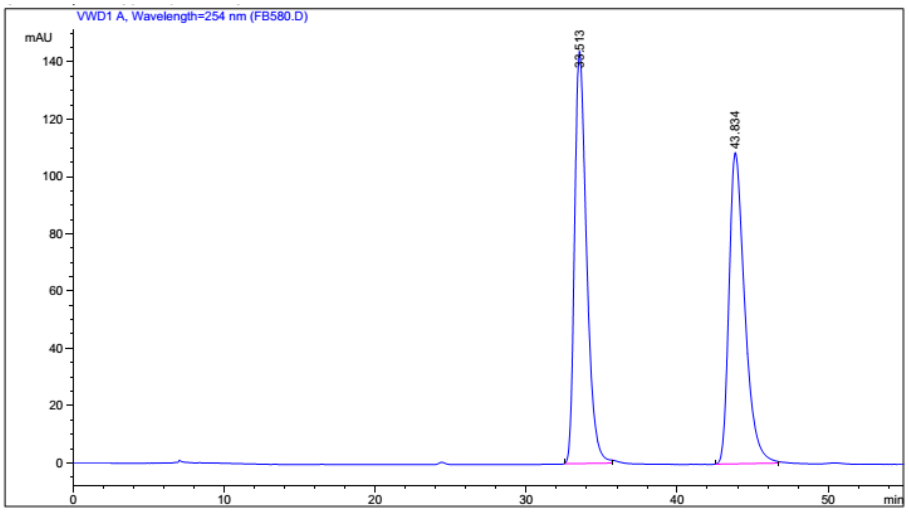
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.921	BV	0.2155	1477.09155	105.68945	49.7988
2	8.971	VB	0.2665	1489.02869	87.07211	50.2012

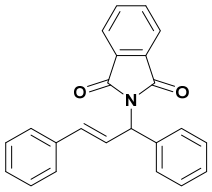




6g

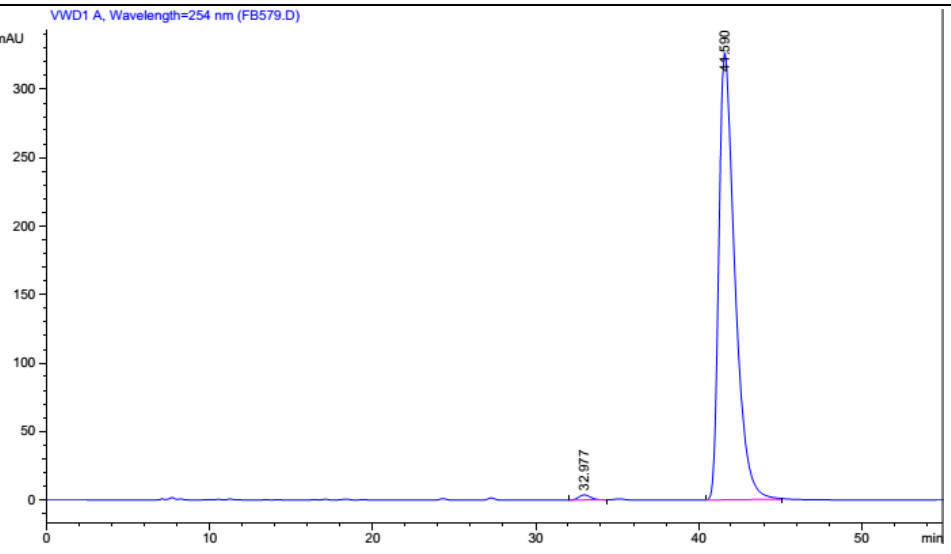
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.893	VV	0.2135	7020.03613	508.57196	94.8528
2	8.979	VB	0.2653	380.94415	22.08656	5.1472

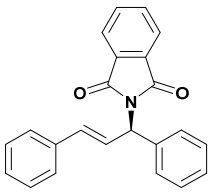




***rac*-6h**

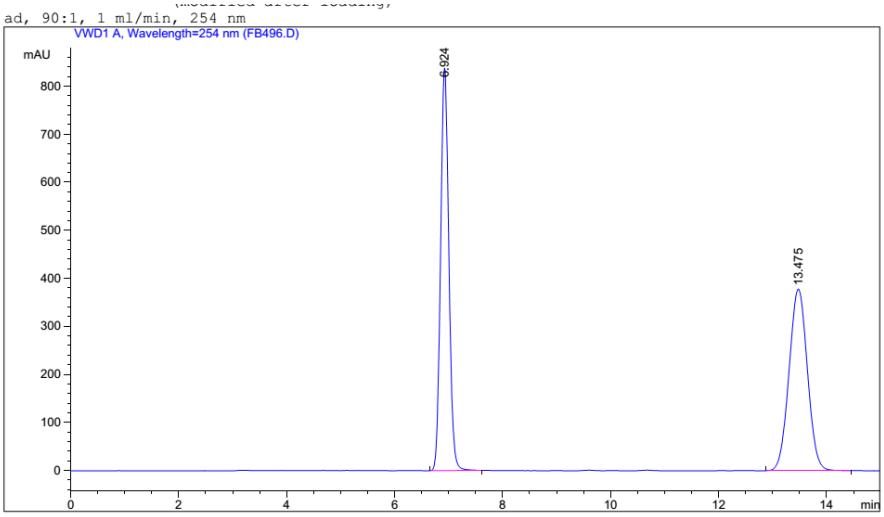
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.512	BB	0.7961	7790.00488	143.56857	50.1546
2	43.831	BB	1.0361	7741.98975	108.33613	49.8454

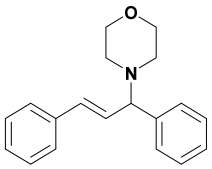




6h

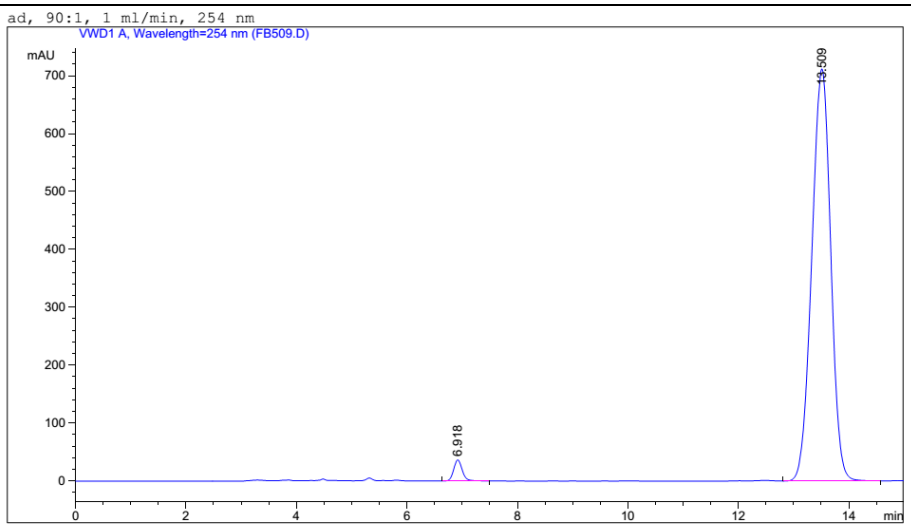
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.969	BP	0.6115	184.50880	3.62360	0.8281
2	41.587	BB	0.9840	2.20971e4	326.17310	99.1719

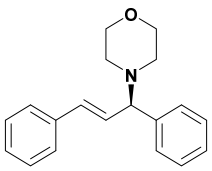




***rac*-6i**

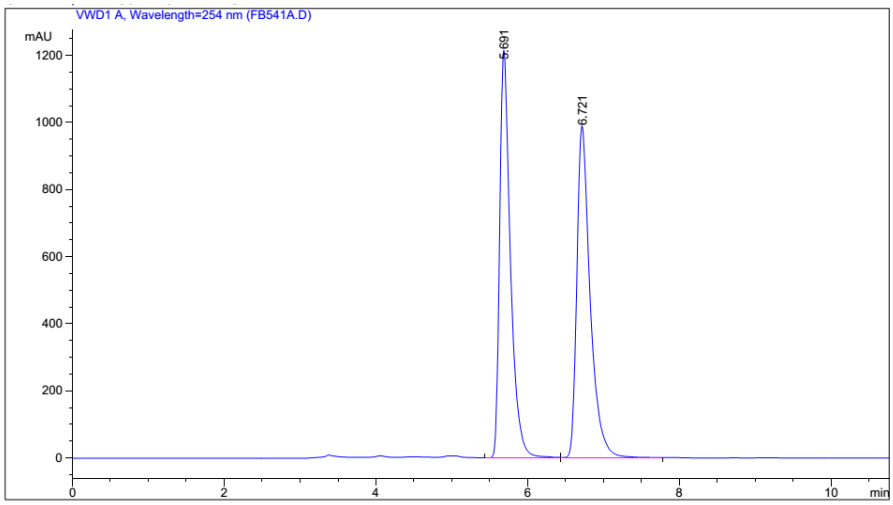
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.924	VV	0.1648	8883.54199	835.62073	49.8507
2	13.475	VB	0.3690	8936.76855	377.96429	50.1493

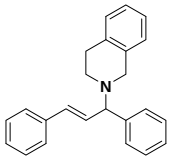




6i

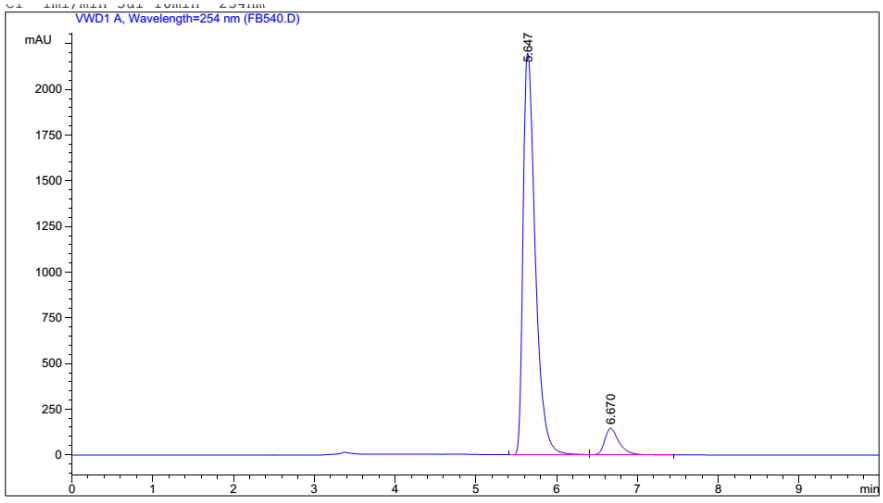
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.918	BB	0.1675	395.35849	36.39388	2.2833
2	13.509	VB	0.3764	1.69195e4	711.55206	97.7167

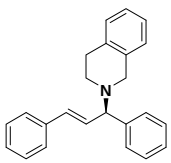




***rac*-6j**

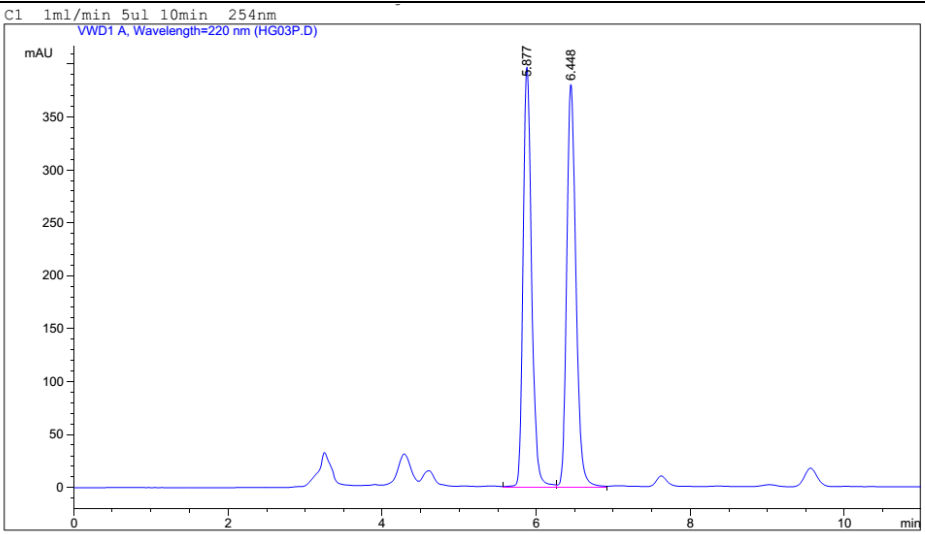
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	5.691	VV	0.1586	1.20294e4	1190.68152	49.7504	
2	6.721	VV	0.1913	1.21500e4	979.49359	50.2496	

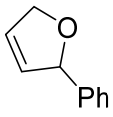




6j

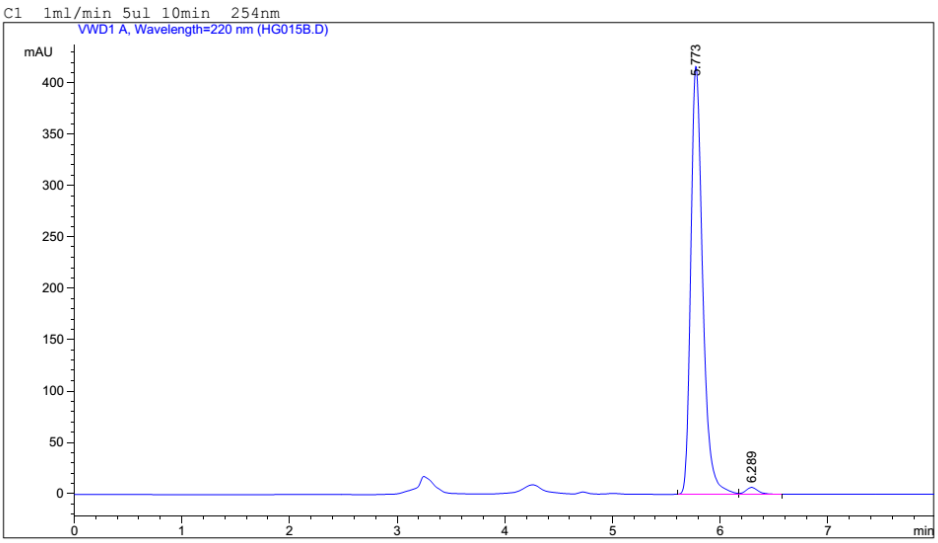
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	5.647	VV	0.1695	2.32882e4	2210.63916	92.5711	
2	6.670	VB	0.1953	1868.88989	146.61852	7.4289	

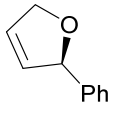




rac-7

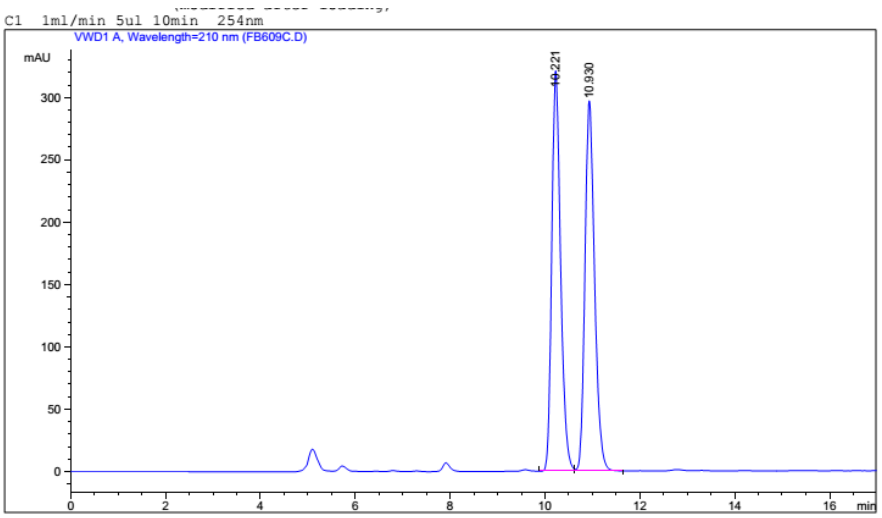
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.876	VV	0.1182	3025.23706	396.30328	49.0748
2	6.447	VB	0.1284	3139.30249	379.91611	50.9252

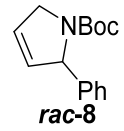




7

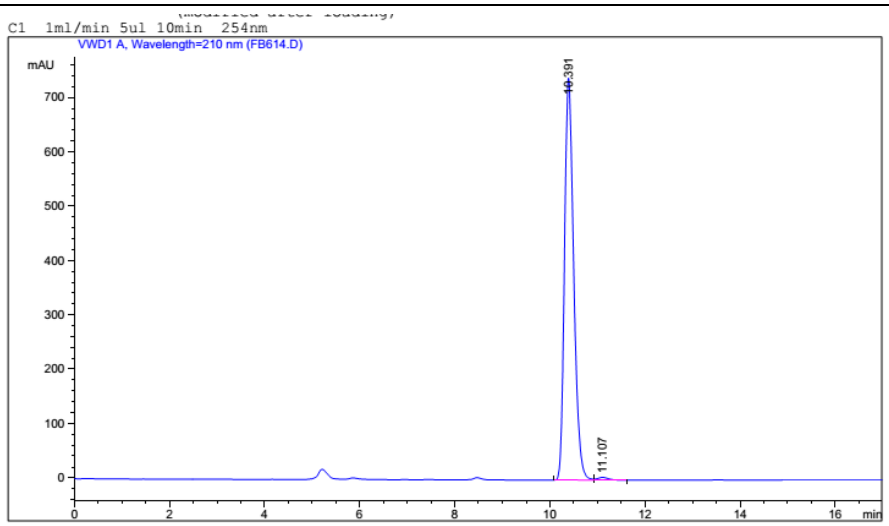
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.772	BV	0.1167	3180.98340	416.89914	98.3831
2	6.288	VB	0.1167	52.27726	6.73706	1.6169

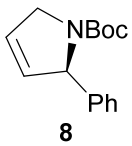




***rac*-8**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.219	VV	0.1976	4161.42578	321.45007	49.8641
2	10.928	VB	0.2153	4184.11572	297.04453	50.1359





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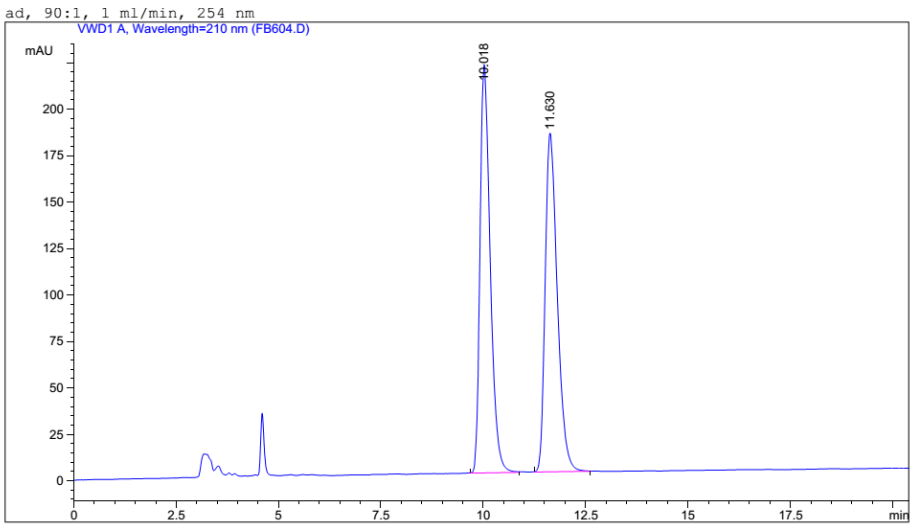
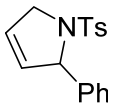
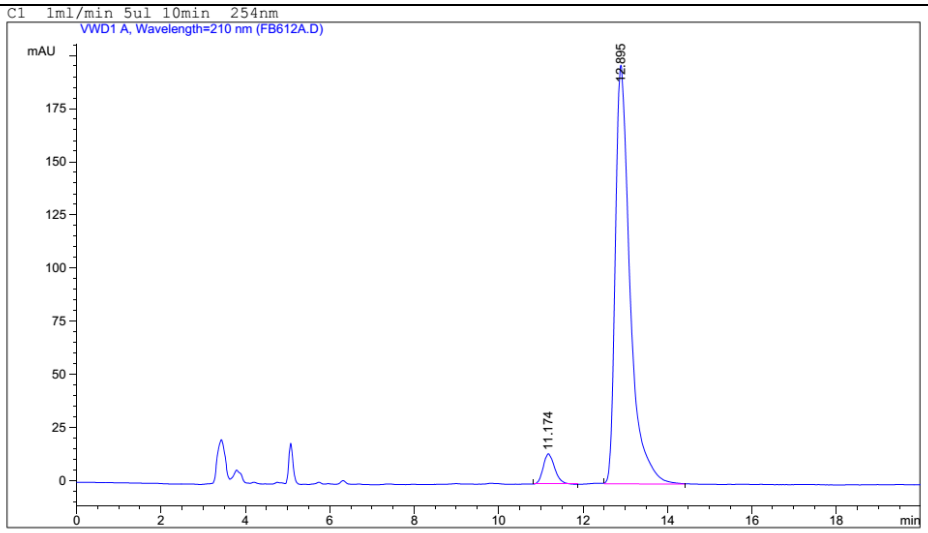
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.389	BV	0.2063	9941.74219	739.59564	99.1491
2	11.107	VB	0.2431	85.32208	5.21912	0.8509

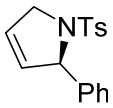




***rac*-9**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.018	VB	0.2690	3861.94629	219.86812	50.5835
2	11.630	BB	0.3170	3772.85376	182.45332	49.4165





9

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.174	BV	0.3076	283.49362	14.44225	5.5945
2	12.895	VB	0.3644	4783.91260	197.29671	94.4055