Enantioselective Functionalization of Allylic C-H Bonds Following a Strategy of Functionalization and Diversification

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Supporting Information

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General Experimental Details

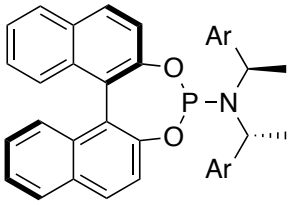
Equipment and methods

All air-sensitive manipulations were conducted in a nitrogen-filled glovebox or by standard Schlenk technique under nitrogen. All glassware was heated in an oven and cooled under an inert atmosphere prior to use.

NMR spectra were acquired on 400 MHz, 500 MHz, or 600 MHz Bruker instruments at the University of California. NMR spectra were processed with MestReNova 5.0 (Mestrelab Research SL). Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H and 77.36 ppm for ^{13}C). Coupling constants are reported in hertz. HPLC analyses were conducted on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector) with using chiral stationary columns (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High-resolution mass spectra were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. GC analyses were obtained on an Agilent 6890 GC equipped with an HP- 5 column (25 m x 0.20 mm ID x 0.33 m film) and an FID detector.

Solvents and reagents

Substrate alkenes, dodacane and *tert*-butyl perbenzoate were purchased from Sigma-Aldrich and used without further purification unless mentioned otherwise. 2-(But-3-en-1-yl)-2-methyl-1,3-dioxolane,[1] (but-3-en-1-yloxy)(*tert*-butyl)dimethylsilane,[2] but-3-en-1-yl benzoate, 2-(but-3-en-1-yl)isoindoline-1,3-dione,[3] 1-(hept-6-en-1-ylsulfonyl)-4-methylbenzene[4] and *N*,*N*-diethylundec-10-enamide[4] were prepared according to reported procedures. Enantioenriched alkenes were derived from commercially available glycidol (ee 98%) following reported procedures.[5] $Pd(OAc)_2$ and $Ir(COD)Cl]_2$ were obtained from Johnson-Matthey and used without further purification. Phosphoramidite ligands (**L9** and **L10**)[6] and iridium complexes ([Ir(COD)(κ2-**L9**)(ethylene)] (**1**) and [Ir(COD)(κ2-**L10**)(ethylene)] (**11**))[7] were prepared according to literature procedures. DCM, toluene and THF were degassed by purging with argon for 15 minutes and dried with a solvent purification system containing a one-meter column of activated alumina.



L9: Ar= C_6H_5
L10: Ar 2-OMe-C_6H_4

General procedure (I): Sequential C-H functionalization reactions

To a dry 4 ml vial containing a magnetic stirbar, $Pd(OAc)_2$ (3.3 mg, 5 mol%) and **L5** (3.0 mg, 5.5 mol%) were added, followed by 25.0 μL of DCM. The reaction mixture was stirred for 15 min at room temperature. The solvent was removed under vacuum, and dodecane (25.0 μL) and alkene (0.6 or 0.3 mmol) were added, followed by *tert*-butyl perbenzoate (58.27 mg, 0.3 mmol). The vial was sealed with a cap containing a PTFE septum and then heated at 65 or 80 ^oC (as mentioned in Chart 1, 2 and 3) for 6-8 h (monitored by ^1H-NMR for consumption of oxidant). The vial was kept at high vacuum for 3-4 h to remove volatile materials and brought into a glove box. The reaction mixture was dissolved in 0.5 ml of dry toluene. To the resulting solution K_3PO_4 (95.5 mg, 0.45 mmol) and the aniline (2.0 mmol) were added, followed by solution of iridium catalyst **1** (13.0 mg, 5 mol%) in 0.5 ml of dry toluene. The resulting reaction mixture was stirred at 25 ^oC until the linear benzoyl ester was fully consumed, as determined by GC or TLC. The crude reaction mixture was then treated with 5 ml of EtOAc and extracted with brine. The solvent was evaporated from the organic layer, and the product was purified by flash column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate.

General procedure II: Hydroboration and Vinylation of 3

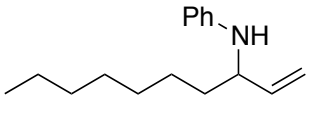
To a dry 4-mL vial equipped with a magnetic stirring bar in the glove box, alkene **3** (0.5 mmol), followed by a solution of 9-BBN (0.5 M solution in THF, 1.2 ml) were added. The mixture was stirred at room temperature (20 ^oC) for 10 h to give a solution of B-alkyl-9-BBN. To above solution, $K_3PO_4 \bullet H_2O$ (230.3 mg, 1.0 mmol) was added, and the heterogeneous mixture was stirred for 5 min. Vinyl bromide (1.0 M solution in THF, 1.5 ml), followed by $Pd(dppf)Cl_2$ (5 mol%, 0.025 mmol) in DMF (2.5 ml), were added. The reaction was sealed with a cap containing a PTFE septum and then heated at 50 ^oC for 6-8 h. The crude reaction mixture was then treated with 5 mL of EtOAc and extracted with water, followed by a saturated $CuSO_4$ solution (in water) to remove the remaining DMF. The solvent was evaporated from the organic layer, and the product was purified by flash column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate.

General procedure III: Hydroboration and Alkylation of 3

To a dry 4 mL vial equipped with a magnetic stirring bar in the glove box, an alkene **3** (0.5 mmol), followed by a solution of 9-BBN (0.5 M solution in THF, 1.2 ml), were added. The mixture was allowed to stir at room temperature (20 ^oC) for 10 h. To the above solution, $K_3PO_4 \bullet H_2O$ (230.3 mg, 1.0 mmol) was added and stirred for 5 min. In another dry 4 ml vial equipped with a magnetic stirring bar in the glove box, $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), PCy_3 (22.4 mg, 0.080 mmol) and 0.5 ml of THF were added. After 15 min of stirring, this solution was added to the above B-alkyl-9-BBN solution, followed by *n*-bromo-1-alkene (0.3 mmol). The resulting heterogeneous reaction mixture was sealed and stirred vigorously at room temperature for 24 h. The crude mixture was diluted with Et_2O, filtered through silica gel, concentrated, and then purified by flash column chromatography on silica gel eluting with a mixture of hexane and ethyl acetate.

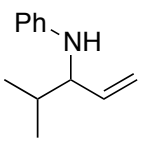
Procedures and spectral data for isolated products

N-(dec-1-en-3-yl)aniline (3a)



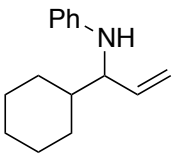
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 99:1) to give **3a** as an oil in 58% yield (40.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 20.18 min (major); t_R 23.78 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 89%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16–7.13 (m, 2H), 6.69 – 6.60 (m, 1H), 6.59 (d, *J* = 7.7 Hz, 2H), 5.73 (ddd, *J* = 16.8, 10.3, 6.6 Hz, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 10.3 Hz, 1H), 3.79 (m, 1H), 3.63 (b, 1H), 1.72–1.48 (m, 2H), 1.47–1.17 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 140.6, 129.4(2C), 117.4, 115.3, 113.6(2C), 56.3, 36.2, 32.2, 29.9, 29.6, 26.3, 23.0, 14.4. HRMS (ESI) Calcd. for $C_{16}H_{25}N$ ($[M+H]^+$): 232.2060. Found: 232.2058.

N-(4-methylpent-1-en-3-yl)aniline (3b)



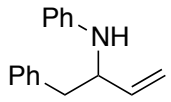
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 99:1) to give **3b** as an oil in 52% yield (27.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 19.24 min (major); t_R 20.79 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.2 (m, 2H), 6.65 (t, 1H, *J* = 7.3 Hz), 6.6 (d, 2H, *J* = 8.0 Hz), 5.72 (ddd, 1H, *J* = 17.2, 10.3, 6.3 Hz), 5.19 (d, 1H, *J* = 17.1 Hz), 5.16 (d, 1H, *J* = 10.2 Hz), 3.71 (br, 1H), 3.65 (t, 1H, *J* = 5.9 Hz), 1.87 (qqd, 1H, *J* = 6.8, 6.8, 5.7 Hz). 0.99 (d, 3H, *J* = 6.8 Hz), 0.96 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) 147.9, 137.9, 129.1, 117.1, 116.0, 113.4, 61.5, 32.5, 18.8, 18.5. The data match those reported previously.[8]

N-(1-cyclohexylallyl)aniline (3c)



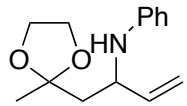
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 99:1) to give **3c** as an oil in 68% yield (40.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.14 min (minor); t_R 8.79 min (major) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.9:0.1, 1.0 mL/min] to be 92%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16–7.11 (m, 2H), 6.68–6.60 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 2H), 5.72 (ddd, *J* = 16.9, 10.2, 6.4 Hz, 1H), 5.28–5.05 (m, 2H), 3.69 (br, 1H), 3.68–3.6 (m, *J* = 5.7 Hz, 1H), 1.92–1.63 (m, 5H), 1.55–1.45 (m, 1H), 1.31–1.02 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 138.7, 129.4(2C), 117.3, 116.1, 113.6(2C), 61.3, 43.1, 29.8, 29.7, 26.9, 26.7, 26.6. The data match those reported previously.[8]

***N*-(1-phenylbut-3-en-2-yl)aniline (3d)**



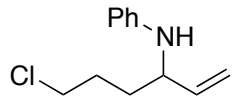
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 98:2) to give **3d** as an oil in 71% yield (47.5 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 21.94 min (major); t_R 22.95 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 96%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.27–7.20 (m, 3H), 7.18–7.13 (m, 2H), 6.71–6.66 (m, 1H), 6.61 (d, *J* = 7.7 Hz, 2H), 5.82 (ddd, *J* = 16.3, 10.4, 5.7 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 4.18–4.12 (m, 1H), 3.72 (br, 1H), 2.93 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 139.6, 138.0, 129.8(2C), 129.5(2C), 128.8(2C), 126.9, 117.8, 115.8, 113.9(2C), 56.9, 42.2. HRMS (ESI) Calcd. for $C_{16}H_{17}N$ ($[M+H]^+$): 224.1434 Found: 224.1432.

***N*-(1-(2-methyl-1,3-dioxolan-2-yl)but-3-en-2-yl)aniline (3e)**



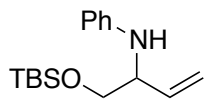
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3e** as an oil in 70% yield (49.0 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 37.61 min (minor); t_R 40.48 min (major) [(Chiralpak OJ-H) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 95%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20–7.07 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.66–6.57 (m, 2H), 5.81 (ddd, *J* = 17.1, 10.3, 5.4 Hz, 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.69 (br, 1H), 4.09–3.76 (m, 5H), 2.01–1.88 (m, 2H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 141.0, 129.3(2C), 117.4, 114.8, 113.7(2C), 109.9, 65.4, 64.7, 53.6, 44.2, 24.8. HRMS (ESI) Calcd. for $C_{14}H_{19}NO_2$ ($[M+H]^+$): 234.1489. Found: 234.1486.

***N*-(6-chlorohex-1-en-3-yl)aniline (3f)**



Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 99:1) to give **3f** as an oil in 65% yield (40.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.47 min (major); t_R 9.95 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 88%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 2H), 5.82 (ddd, *J* = 17.0, 10.2, 5.2 Hz, 1H), 5.27–4.90 (m, 2H), 4.27–4.13 (m, 1H), 3.58–3.41 (m, 1H), 3.28–3.22(m, 1H), 2.17–1.90 (m, 3H), 1.86–1.78 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 139.6, 129.3(2C), 115.9, 114.8, 112.4(2C), 61.2, 48.9, 32.9, 23.5. HRMS (ESI) Calcd. for $C_{12}H_{16}ClN$ ($[M+H]^+$): 167.1067. Found: 167.1072.

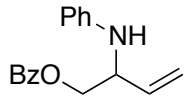
***N*-(1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-yl)aniline(3g)**



Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 99:1) to give **3g** as an oil in 69% yield (57.4 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 12.92 min (major); t_R 15.72 min (minor) [(Chiralpak OD-H)

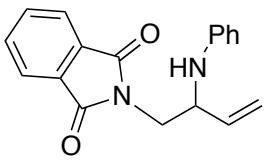
hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 97%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.66–6.63 (m, 2H), 5.92–5.72 (m, 1H), 5.32 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.20 (dd, *J* = 12.5, 1.4 Hz, 1H), 4.21 (br, 1H), 3.89 (br, 1H), 3.76 (dd, *J* = 9.9, 4.5 Hz, 1H), 3.65 (dd, *J* = 9.9, 6.0 Hz, 1H), 0.91 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 138.0, 129.4, 117.9(2C), 116.9, 114.2(2C), 66.0, 58.1, 26.2(3C), 18.6, -4.9, -5.0. HRMS (ESI) Calcd. for $C_{16}H_{27}NOSi$ ($[M+H]^+$): 278.1935. Found: 278.1934.

2-(phenylamino)but-3-en-1-yl benzoate (3h)



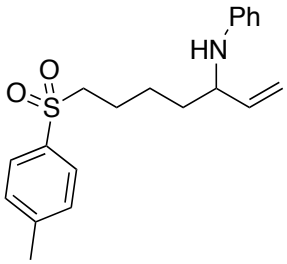
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3h** as an oil in 56% yield (44.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 13.8 min (major); t_R 14.6 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.6 mL/min] to be 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.64 – 7.52 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.18 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.80–6.61 (m, 3H), 5.91 (ddd, *J* = 17.2, 10.4, 5.5 Hz, 1H), 5.44 (dd, *J* = 9.9, 8.6 Hz, 1H), 5.30 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.50 (dd, *J* = 11.2, 6.6 Hz, 1H), 4.42 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.33 (br, 1H), 4.04 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 147.3, 136.2, 133.5, 130.1, 130.0(2C), 129.6(2C), 128.8(2C), 118.2, 117.9, 113.9(2C), 66.9, 55.5. HRMS (ESI) Calcd. for $C_{17}H_{17}NO_2$ ($[M+H]^+$): 268.1332. Found: 268.1332.

2-(2-(phenylamino)but-3-en-1-yl)isoindoline-1,3-dione (3i)



Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3i** as an oil in 59% yield (51.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 23.20 min (minor); t_R 26.91 min (major) [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min] to be 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.09 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.65–6.55 (m, 2H), 5.90–5.77 (m, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.26 (br, 2H), 3.92 – 3.81 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 147.2, 136.5, 134.4, 132.2, 129.4, 123.7, 117.9, 117.8, 113.6, 55.9, 42.3. HRMS (ESI) Calcd. for $C_{18}H_{16}N_2O_2$ ($[M+H]^+$): 293.1285. Found: 293.1284.

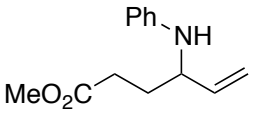
***N*-(7-tosylhept-1-en-3-yl)aniline (3j)**



Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 90:10) to give **3j** as an oil in 57% yield (58.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 26.14 min (minor); t_R 29.86 min (major) [(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 89%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 5.72 (ddd, *J* = 16.8, 10.3, 6.2 Hz, 1H),

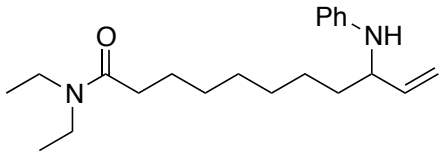
5.21 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 3.80 (q, *J* = 6.0 Hz, 1H), 3.62 (br, 1H), 3.18–2.99 (m, 2H), 2.49 (s, 3H), 1.90–1.65 (m, 2H), 1.69–1.44 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 145.0, 139.9, 136.5, 130.2(2C), 129.5(2C), 128.4(2C), 117.7, 115.8, 113.7(2C), 56.5, 55.8, 35.4, 24.9, 23.0, 22.0. HRMS (ESI) Calcd. for $C_{20}H_{25}NO_2S$ ($[M+H]^+$): 344.1679. Found: 344.1679.

Methyl 4-(phenylamino)hex-5-enoate (3k)



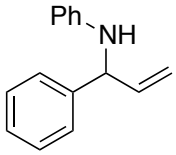
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3k** as an oil in 59% yield (38.8 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 13.57 min (major); t_R 21.36 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 88%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18–7.12 (m, 2H), 6.71–6.66 (m, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 5.73 (ddd, *J* = 16.7, 10.3, 6.1 Hz, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 3.91–3.84 (m, 1H), 3.72 (br, 1H), 3.67 (s, 3H), 2.47 (dd, *J* = 7.3, 6.3 Hz, 2H), 1.94 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 147.6, 139.5, 129.5(2C), 117.8, 116.2, 113.7(2C), 55.8, 52.0, 31.0, 30.7. HRMS (ESI) Calcd. for $C_{13}H_{17}NO_2$ ($[M+H]^+$): 220.1332. Found: 220.1331.

***N*,*N*-diethyl-9-(phenylamino)undec-10-enamide (3l)**



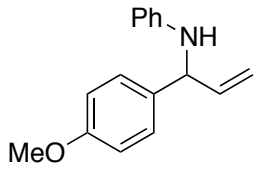
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3l** as an oil in 52% yield (51.5 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 25.87 min (major); t_R 39.04 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 87%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 2H), 5.76–5.66 (m, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 3.78 (br, 1H), 3.65 (br, 1H), 3.37 (q, *J* = 7.1 Hz, 2H), 3.29 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.69–1.52 (m, 4H), 1.45–1.26 (m, 8H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 148.0, 140.5, 129.4, 117.4, 115.3, 113.6, 56.3, 42.3, 40.4, 36.2, 33.5, 29.8, 29.7, 26.2, 25.8, 14.8, 13.5. HRMS (ESI) Calcd. for $C_{21}H_{34}N_2O$ ($[M+H]^+$): 331.2744. Found: 331.2744.

***N*-(1-phenylallyl)aniline (3m)**



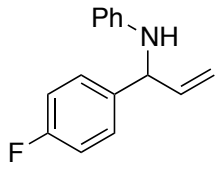
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3m** as an oil in 76% yield (47.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 22.3 min (minor); t_R 25.9 min (major) [(Chiralpak OD-H) hexane/*i*-PrOH, 99.75:0.25, 0.6 mL/min] to be 93%. The data match those reported previously.[8]

***N*-(1-(4-methoxyphenyl)allyl)aniline (3n)**



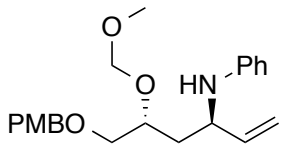
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3n** as an oil in 81% yield (58.1 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 14.84 min (major); t_R 16.50 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min] to be 90%. The data match those reported previously.[8]

***N*-(1-(4-fluorophenyl)allyl)aniline(3o)**



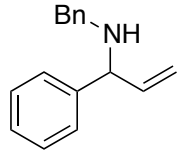
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3o** as an oil in 77% yield (52.5 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 14.45 min (major); t_R 15.17 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min] to be 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.36 (m, 2H), 7.24–7.14 (m, 2H), 7.12–7.04 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.67–6.55 (m, 2H), 6.07 (ddd, *J* = 17.0, 10.2, 5.9 Hz, 1H), 5.37–5.22 (m, 2H), 4.97 (d, *J* = 5.8 Hz, 1H), 4.06 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 139.3, 137.9, 129.5, 129.1, 129.0, 118.1, 116.7, 116.0, 115.8, 113.9, 60.5. HRMS (ESI) Calcd. for $C_{15}H_{14}FN$ ($[M+H]^+$): 228.1183 Found: 228.1182.

***N*-((3*R*,5*R*)-6-((4-methoxybenzyl)oxy)-5-(methoxymethoxy)hex-1-en-3-yl)aniline (3p)**



Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 80:20) to give **5c** as an oil in 57% yield (63.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 2H), 5.84 – 5.65 (m, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 4.76 (d, *J* = 6.8 Hz, 1H), 4.68 (d, *J* = 6.9 Hz, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.03 – 3.91 (m, 2H), 3.87 (dq, *J* = 9.6, 4.8 Hz, 1H), 3.81 (s, 3H), 3.50 (ddd, *J* = 20.5, 10.0, 4.9 Hz, 2H), 3.39 (s, 3H), 1.94 – 1.86 (m, 1H), 1.87 – 1.80 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 147.8, 140.1, 130.5, 129.7(2C), 129.4(2C), 117.5, 115.8, 114.2(2C), 113.7(2C), 96.8, 75.1, 73.3, 72.3, 56.1, 55.6, 53.8, 38.5. HRMS (ESI) Calcd. For $C_{22}H_{29}NO_4$ ($[M+H]^+$): 372.2169 Found: 372.2172.

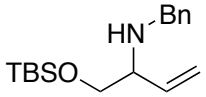
***N*-benzyl-1-phenylprop-2-en-1-amine (3q)**



Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3p** as an oil in 60% yield (40.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 31.1 min (major); t_R 35.9 min (minor) [(Chiralpak OJ-H) hexane/*i*-PrOH, 95:5, 0.5 mL/min] to be 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (m, 4H), 7.30-7.24 (m, 1H), 7.17-7.11 (m, 2H), 6.70 (t, 1H, *J* = 7.3 Hz), 6.60 (d, 2H,

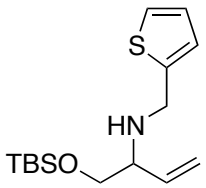
J = 7.9 Hz), 6.04 (ddd, 1H, *J* = 17.1, 10.2, 5.9 Hz), 5.28 (d, 1H, *J* = 17.1 Hz), 5.22 (d, 1H, *J* = 10.2 Hz), 4.93 (d, 1H, *J* = 5.8 Hz), 4.1 (br, 1H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 141.9, 139.1, 129.1, 128.7, 127.4, 127.1, 117.6, 116.0, 113.5, 60.8. The data match those reported previously.[9]

_N_-benzyl-1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-amine (3r)



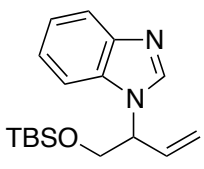
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 98:2) to give **3q** as an oil in 51% yield (43.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 28.5 min (major); t_R 29.0 min (minor) [(Chiralpak OJ-H) hexane/*i*-PrOH, 95:5, 0.5 mL/min] to be 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 3H), 7.30–7.25 (m, 2H), 5.69 (ddd, *J* = 17.8, 10.2, 7.9 Hz, 1H), 5.37–5.15 (m, 2H), 3.91 (d, *J* = 13.5 Hz, 1H), 3.70 (d, *J* = 13.5 Hz, 1H), 3.65 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.59–3.52 (m, 1H), 3.25 (td, *J* = 8.1, 4.3 Hz, 1H), 0.92 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 138.2, 128.7(2C), 128.4(2C), 127.1, 118.1, 66.5, 62.8, 51.4, 26.2(3C), 18.6, -5.0, -5.1. HRMS (ESI) Calcd. for $C_{17}H_{29}NOSi$ ([M+H]$^+$): 292.2091. Found: 292.2090.

1-((*tert*-butyldimethylsilyl)oxy)-_N_-(thiophen-2-ylmethyl)but-3-en-2-amine (3s)



Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 98:2) to give **3r** as an oil in 55% yield (47.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 25.3 min (major); t_R 26.2 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 95:5, 0.5 mL/min] to be 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.94 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.91 (d, *J* = 2.6 Hz, 1H), 5.64 (ddd, *J* = 18.0, 10.2, 8.0 Hz, 1H), 5.30–5.23 (m, 1H), 5.20 (dd, *J* = 10.3, 1.2 Hz, 1H), 4.03 (d, *J* = 14.3 Hz, 1H), 3.88 (d, *J* = 14.3 Hz, 1H), 3.61 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.51 (dd, *J* = 9.8, 8.3 Hz, 1H), 3.26 (td, *J* = 8.0, 4.2 Hz, 1H), 0.88 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 137.9, 126.9, 125.0, 124.4, 118.3, 66.5, 62.5, 45.9, 26.2(3C), 18.6, -5.0, -5.1. HRMS (ESI) Calcd. for $C_{15}H_{27}NOSSi$ ([M+H]$^+$): 298.1655. Found: 298.1653.

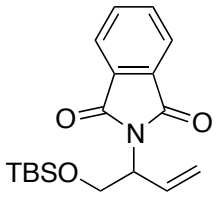
1-(1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-yl)-1*H*-benzo[*d*]imidazole (3t)



Prepared according to the modified general procedure (I) using benzimidazole as nucleophile and (*R, R, R*)-**1** as catalyst. The reaction mixture obtained after oxidation step was brought inside the glove box and dissolved in 0.5 ml of THF followed by filtered through a 30 x 6 mm plug of silica gel (in a 9 mm pipette) and collected in another 4 ml vial. The silica gel was washed with 1.0 mL THF. The resulting THF solution was used for the next step. The crude mixture obtained after completion of second step, was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3s** as an oil in 55% yield (47.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.3 min (major); t_R 9.2 min (minor) [(Chiralpak AD-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.85–7.74 (m,

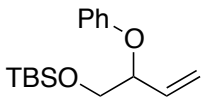
1H), 7.43–7.35 (m, 1H), 7.31–7.22 (m, 2H), 6.32–6.03 (m, 1H), 5.37 (d, *J* = 10.6 Hz, 1H), 5.28–5.17 (m, 1H), 4.98 (dd, *J* = 10.7, 5.6 Hz, 1H), 4.18–4.04 (m, 2H), 0.80 (s, 9H), -0.07 (s, 3H), -0.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 142.8, 133.9, 133.5, 122.9, 122.4, 120.8, 119.3, 110.7, 64.7, 60.2, 26.0(3C), 18.4, -5.3, -5.4. HRMS (ESI) Calcd. for $C_{17}H_{26}N_2OSi$ ([M+H]$^+$): 303.1887. Found: 303.1885.

2-(1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-yl)isoindoline-1,3-dione (3u)



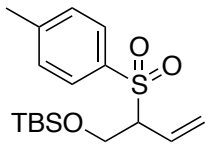
Prepared according to the general procedure (I) using potassium phthalimide as nucleophile and (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **3t** as an oil in 57% yield (47.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 27.3 min (major); t_R 28.9 min (minor) [(Chiralpak OJ-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.17 (ddd, *J* = 17.5, 10.4, 7.4 Hz, 1H), 5.30 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 4.95–4.86 (m, 1H), 0.74 (s, 9H), -0.00 (s, 3H), -0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6(2C), 134.2(2C), 132.7, 132.3, 123.5(2C), 119.3, 62.5, 56.2, 25.9(3C), 18.3, -5.1, -5.3. HRMS (ESI) Calcd. for $C_{18}H_{25}NO_3Si$ ([M-Me]$^+$): 316.1369 Found: 316.1369.

***tert*-butyldimethyl((2-phenoxybut-3-en-1-yl)oxy)silane (3w)**



Prepared according to the general procedure (I) using sodium phenoxide as nucleophile and (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 99:1) to give **3w** as an oil in 50% yield (45.9 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.6 min (major); t_R 10.7 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min] to be 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 2H), 6.94–6.90 (m, 3H), 5.89 (ddd, *J* = 17.2, 10.7, 5.7 Hz, 1H), 5.35 (d, *J* = 17.4 Hz, 1H), 5.27 (d, *J* = 10.7 Hz, 1H), 4.73–4.68 (m, 1H), 3.85 (dd, *J* = 10.7, 6.7 Hz, 1H), 3.76 (dd, *J* = 10.7, 4.9 Hz, 1H), 0.89 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 135.4, 129.6(2C), 121.1, 118.0, 116.4(2C), 80.1, 66.4, 26.2(3C), 18.7, -4.8, -4.9.

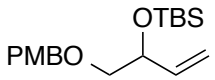
***tert*-butyldimethyl((2-tosylbut-3-en-1-yl)oxy)silane (3x)**



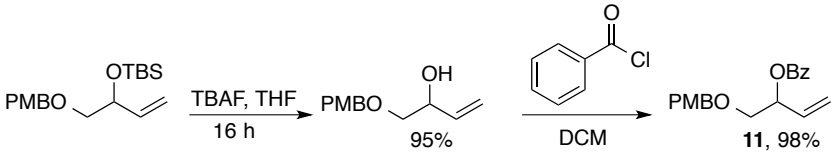
Prepared according to the modified general procedure (I) using sodium *p*-toluenesulfinate as nucleophile and (*R, R, R*)-**1** as catalyst. The reaction mixture obtained after oxidation step was brought into a glove box. The reaction mixture was dissolved in 0.5 ml of dry THF and filtered through a 30 x 6 mm plug of silica gel (in a 9 mm pipette) and collected in another 4 ml vial. The silica gel was washed with 1.0 mL THF. To the combined resulting solution of THF, K_3PO_4 (95.5 mg, 0.45 mmol) and the sodium *p*-toluenesulfinate (1.5 equiv) were added, followed by solution of iridium catalyst **1** (13.0 mg, 5 mol%) in 0.5 ml of dry THF and the reaction mixture was stirred at 50 ^{o}C until the linear benzoyl ester was fully consumed, as determined by GC or TLC. The crude mixture obtained after completion of second step, was purified by flash column

chromatography (hexanes:EtOAc, 97:3) to give **3x** as an oil in 55% yield (56.2 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.96 min (minor); t_R 10.72 min (major) [(Chiralpak OD-H) hexane/*i*-PrOH, 99:1, 1 mL/min] to be 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.75 (ddd, *J* = 17.1, 10.1, 9.3 Hz, 1H), 5.35 (d, *J* = 9.9 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 4.14 (dd, *J* = 10.5, 4.3 Hz, 1H), 4.00 (dd, *J* = 10.5, 7.1 Hz, 1H), 3.72–3.65 (m, 1H), 2.43 (s, 2H), 0.81 (s, 5H), 0.00 (s, 1H), -0.01 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 135.7, 129.8(2C), 129.5(2C), 129.0, 124.3, 71.9, 61.0, 26.0(3C), 21.9, 18.5, -5.1, -5.2. HRMS (ESI) Calcd. for $C_{17}H_{28}O_3SSi$ ([M+Na]$^+$): 363.1421. Found: 363.1421.

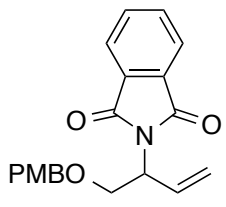
***tert*-butyl((1-((4-methoxybenzyl)oxy)but-3-en-2-yl)oxy)dimethylsilane (3aa)**



Prepared according to the modified general procedure (I) using (*R, R, R*)-**1** as catalyst. The reaction mixture obtained after oxidation step was brought into a glove box. The reaction mixture was dissolved in 0.5 ml of dry toluene, followed by filtered through a 30 x 6 mm plug of silica gel (in a 9 mm pipette) and collected in another 4 ml vial. To the resulting solution, K_3PO_4 (95.5 mg, 2 equiv.) and the *tert*-butyldimethylsilanol (2.0 equiv.) were added, followed by solution of iridium catalyst **1** (13.0 mg, 5.0 mol%) and 1-phenyl-propyne (10.0 mol%) in 1.5 ml of dry toluene. The reaction mixture was stirred at 25 ºC until the linear benzoyl ester was fully consumed, as determined by GC or TLC. The crude mixture obtained after completion of second step, was purified by flash column chromatography (hexanes:Et_2O, 99:1) to give an oil in 70% yield (67.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.6 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.92 – 5.82 (m, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 4.49 (s, 2H), 4.31 (d, *J* = 5.3 Hz, 1H), 3.81 (s, 3H), 3.39 (t, *J* = 4.8 Hz, 2H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 138.5, 135.5, 129.1, 127.5, 114.9, 113.6, 74.6, 72.9, 72.7, 55.2, 25.8, 18.3, -4.7, -4.8. The enantiomeric excess was determined by deprotecting TBS group with TBAF,[10] and protecting the corresponding alcohol with benzoyl chloride to give compound **11** in 98% yield. Data matches with the reported compound.[11] HPLC analysis (254 nm, 25 °C) t_R 22.2 min (minor); t_R 28.1 min (major) [(Chiralpak OJ-H) hexane/*i*-PrOH, 90:10, 1 mL/min] to be 87%.



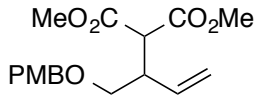
2-(1-((4-methoxybenzyl)oxy)but-3-en-2-yl)isoindoline-1,3-dione (3bb)



Prepared according to the general procedure (I) using (*S, S, S*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 90:10) to give an oil in 62% yield (62.7 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 13.7 min (minor); t_R 18.5 min (major) [(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 1.0 mL/min] to be 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.14 (ddd, *J* = 17.4, 10.4, 7.2 Hz,

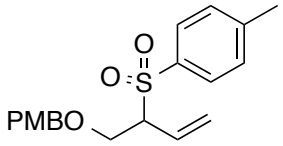
1H), 5.29 (d, *J* = 17.3 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.09 – 5.02 (m, 1H), 4.84 (s, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.08 (t, *J* = 9.9 Hz, 1H), 3.76 (s, 3H), 3.72 (dd, *J* = 10.1, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 159.5, 134.2, 132.6, 132.3, 130.3, 129.6, 123.5, 119.3, 114.0, 72.8, 68.9, 55.5, 53.5. HRMS (ESI) Calcd. for $C_{20}H_{19}NO_4Si$ ([M+Na]$^+$): 360.1204 Found: 360.1206.

Dimethyl 2-(1-((4-methoxybenzyl)oxy)but-3-en-2-yl)malonate (3cc)



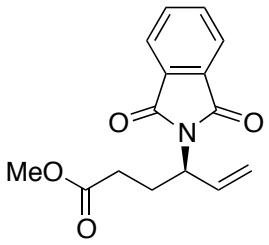
Prepared according to the general procedure (I) using sodium dimethyl malonate as nucleophile and (*R, R, R*)-**11** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 90:10) to give **3cc** as an oil in 50% yield (48.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 28.4 min (minor); t_R 31.6 min (major) [(Chiralpak OJ-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min] to be 88%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.87 – 5.79 (m, 1H), 5.16 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 4.40 (s, 2H), 3.80 (s, 3H), 3.75 (s, 1H), 3.68 (d, *J* = 8.3 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.51 (ddd, *J* = 16.3, 9.5, 6.0 Hz, 2H), 3.16 – 3.10 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 169.0, 159.5, 135.8, 130.5, 129.6, 118.4, 114.0, 73.1, 71.1, 55.6, 53.6, 52.7, 52.6, 44.3, 41.5. HRMS (ESI) Calcd. for $C_{17}H_{22}O_6$ ([M+Na]$^+$): 345.1309 Found: 345.1309.

1-methoxy-4-(((2-tosylbut-3-en-1-yl)oxy)methyl)benzene (3dd)



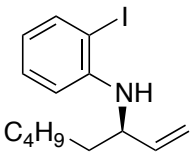
Prepared according to the modified general procedure (I) using (*S, S, S*)-**1** as catalyst. The reaction mixture obtained after oxidation step was brought into a glove box. The reaction mixture was dissolved in 0.5 ml of dry THF and filtered through a 30 x 6 mm plug of silica gel (in a 9 mm pipette) and collected in another 4 ml vial. The silica gel was washed with 1.0 mL THF. To the combined resulting solution of THF, K_3PO_4 (95.5 mg, 0.45 mmol) and the sodium *p*-toluenesulfinate (1.5 equiv) were added, followed by solution of iridium catalyst **1** (13.0 mg, 5 mol%) in 0.5 ml of dry THF and the reaction mixture was stirred at 50 °C until the linear benzoyl ester was fully consumed, as determined by GC or TLC. The crude mixture obtained after completion of second step, was purified by flash column chromatography (hexanes:EtOAc, 90:10) to give an oil in 53% yield (55.1 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 37.1 min (minor); t_R 38.2 min (major) [(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min] to be 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.84 – 5.70 (m, 1H), 5.37 (d, *J* = 10.2 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 4.40 (s, 2H), 3.95 (dd, *J* = 9.0, 3.6 Hz, 1H), 3.87 – 3.75 (m, 5H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 145.0, 135.4, 129.7, 129.7, 129.5, 128.7, 124.4, 114.1, 73.3, 69.7, 67.1, 55.6, 22.0. HRMS (ESI) Calcd. for $C_{19}H_{22}O_4S$ ([M+Na]$^+$): 369.1131. Found: 369.1131.

(*R*)-methyl 4-(1,3-dioxoisoindolin-2-yl)hex-5-enoate



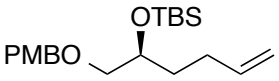
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 90:10) to give an oil in 55% yield (45.1 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 14.1 min (major); t_R 14.9 min (minor) [(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.4 mL/min] to be 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.20 (ddd, *J* = 17.6, 10.2, 7.7 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 4.77 – 4.71 (m, 1H), 3.61 (s, 3H), 2.45 – 2.21 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 168.2(2C), 135.2(2C), 134.3(2C), 132.1, 123.6(3C), 118.5, 53.7, 52.0, 31.3, 27.5. HRMS (ESI) Calcd. for $C_{15}H_{15}NO_4$ ([M+H$^+$): 273.1007 Found: 273.1001.

(*R*)-2-iodo-*N*-(oct-1-en-3-yl)aniline



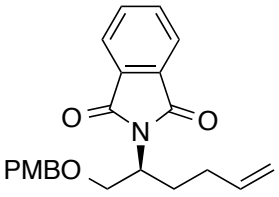
Prepared according to the general procedure (I) using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 96:4) to give **3y** as an oil in 57% yield (56.3 mg). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.1 min (minor); t_R 12.6 min (major) [(Chiralpak OD-H) hexane/*i*-PrOH, 99:1, 0.5 mL/min] to be 88%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.20 – 7.11 (m, 1H), 6.57 – 6.51 (m, 1H), 6.45 – 6.35 (m, 1H), 5.82 – 5.68 (m, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 4.22 (s, 1H), 3.91 – 3.76 (m, 1H), 1.71 – 1.63 (m, 2H), 1.53 – 1.39 (m, 2H), 1.39 – 1.29 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 139.9, 139.2, 129.5, 118.7, 115.5, 112.0, 86.0, 56.8, 36.1, 32.0, 25.9, 22.9, 14.4.

***tert*-butyl((1-((4-methoxybenzyl)oxy)hex-5-en-2-yl)oxy)dimethylsilane (6a)**



Prepared according to the general procedure II. The crude mixture was purified by flash column chromatography (hexanes:Et_2O, 98:2) in 85% yield (149 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J*= 8.8 Hz, 2H), 6.83 (d, *J*= 8.8 Hz, 2H), 5.81 (ddt, *J*= 16.8, 12.8, 6.4 Hz, 1H), 5.05 (dq, *J*= 17.2, 1.6 Hz, 1H), 4.90-4-86 (m, 1H), 4.45 (s, 2H), 3.81 (s, 4H), 3.38 (dd, *J*= 9.6, 5.6 Hz, 1H), 3.33 (dd, *J*= 9.6, 5.6 Hz, 1H), 2.1 (m, 2H), 1.62-1.58 (m, 1H), 1.56-1.52 (m, 1H), 0.87 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H). Data matches with reported molecule.[5a]

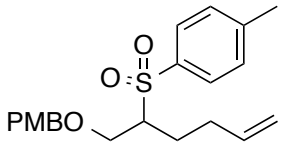
2-(1-((4-methoxybenzyl)oxy)hex-5-en-2-yl)isoindoline-1,3-dione (6b)



Prepared according to the general procedure II. The crude mixture was purified by flash column chromatography (hexanes:Et_2O, 95:5) in 81% yield (148 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J*= 5.0, 3.1 Hz, 2H), 7.65 (dd, *J*= 5.0, 3.1 Hz), 7.14 (d, *J*= 9.0 Hz, 2H), 6.76 (d, *J*= 9.0 Hz, 2H), 5.75 (ddd, *J*= 15.8, 10.0, 7.0 Hz, 1H), 4.96 (dd, *J*= 15.8, 1.5 Hz, 1H), 4.91 (dd, *J*= 10.0, 1.5 Hz, 1H), 4.52 (m, 1H), 4.46 (d, *J*= 12.0 Hz, 1H), 4.35 (d, *J*= 11.5 Hz, 1H),

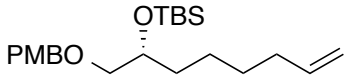
3.97 (m, 1H), 3.75 (s, 3H), 3.66 (dd, *J*= 10.0, 5.0 Hz, 1H), 2.18 (m, 1H), 2.05 (q, *J*= 6.5 Hz, 2H), 1.77 (m, 1H). Data matches with reported molecule.[5a]

1-methoxy-4-(((2-tosylhex-5-en-1-yl)oxy)methyl)benzene (6d)



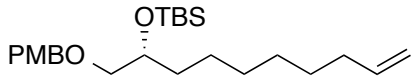
Prepared according to the modified general procedure II, reaction was conducted at room temperature using only THF as solvent for 24 h. The crude mixture was purified by flash column chromatography (hexanes:Et_2O, 95:5) in 85% yield (159.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 5.75 – 5.64 (m, 1H), 5.00 (d, *J* = 6.9 Hz, 1H), 4.98 (d, *J* = 10.2 Hz, 1H), 4.31 (q, *J* = 11.6 Hz, 2H), 3.80 (s, 3H), 3.72 (d, *J* = 4.6 Hz, 2H), 3.25 – 3.14 (m, 1H), 2.42 (s, 3H), 2.27 – 2.17 (m, 1H), 2.14 – 1.97 (m, 2H), 1.82 – 1.70 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 144.8, 137.3, 136.1, 129.9, 129.8, 129.6, 129.2, 116.4, 114.0, 73.2, 66.9, 64.6, 55.6, 31.1, 25.2, 21.9. HRMS (ESI) Calcd. for $C_{21}H_{26}O_4S$ ([M+Na]$^+$): 397.1441. Found: 397.1444.

***tert*-butyl((1-((4-methoxybenzyl)oxy)oct-7-en-2-yl)oxy)dimethylsilane (6e)**



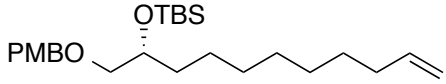
Prepared according to the general procedure III. The crude mixture was purified by flash column chromatography (hexanes:Et_2O, 98:2) in 68% yield (128.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.81 (ddq, *J* = 13.4, 10.2, 6.6 Hz, 1H), 4.99 (ddd, *J* = 17.1, 3.4, 1.5 Hz, 1H), 4.93 (dd, *J* = 5.5, 4.6 Hz, 1H), 3.81 (s, 3H), 3.82 – 3.76 (m, 2H), 3.39 – 3.30 (m, 2H), 2.09 – 1.98 (m, 2H), 1.57 – 1.23 (m, 6H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 139.4, 131.0, 129.5, 114.6, 114.1, 74.9, 73.3, 71.8, 55.6, 34.9, 34.1, 29.4, 26.3, 25.1, 18.5, -4.0, -4.4. HRMS (ESI) Calcd. for $C_{22}H_{38}O_3Si$ ([M+Na]$^+$): 401. 2486. Found: 401.2484.

***tert*-butyl((1-((4-methoxybenzyl)oxy)dec-9-en-2-yl)oxy)dimethylsilane (6f)**



Prepared according to the general procedure III. The crude mixture was purified by flash column chromatography (hexanes:Et_2O, 98:2) in 63% yield (128.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.4 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.86 – 5.76 (m, 1H), 4.99 (d, *J* = 17.1 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.45 (s, 2H), 3.81 (s, 3H), 3.82 – 3.75 (m, 1H), 3.38 – 3.29 (m, 2H), 2.04 (q, *J* = 6.8 Hz, 2H), 1.56 – 1.17 (m, 10H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 139.5, 131.0, 129.5, 114.5, 114.0, 74.9, 73.3, 71.9, 55.6, 35.1, 34.1, 30.0, 29.4, 29.2, 26.3, 25.5, 18.5, -4.0, -4.4. HRMS (ESI) Calcd. for $C_{24}H_{42}O_3Si$ ([M+Na]$^+$): 429.2795. Found: 429.2795.

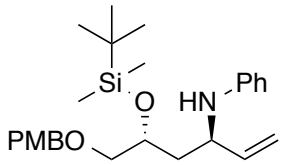
***tert*-butyl((1-((4-methoxybenzyl)oxy)undec-10-en-2-yl)oxy)dimethylsilane (6g)**



Prepared according to the general procedure III. The crude mixture was purified by flash column chromatography (hexanes:Et_2O, 98:2) in 65% yield

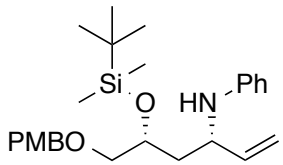
(132.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 5.81 (td, *J* = 16.7, 6.9 Hz, 1H), 4.99 (d, *J* = 17.1 Hz, 1H), 4.93 (d, *J* = 10.1 Hz, 1H), 4.45 (s, 2H), 3.81 (s, 3H), 3.40 – 3.28 (m, 2H), 2.02 (dt, *J* = 23.3, 10.1 Hz, 2H), 1.61 – 1.25 (m, 12H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 139.6, 131.0, 129.5, 114.4, 114.0, 74.9, 73.3, 71.9, 55.6, 35.1, 34.1, 30.0, 29.8, 29.4, 29.3, 26.3, 25.5, 18.5, -4.0, -4.4. HRMS (ESI) Calcd. for $C_{25}H_{44}O_3Si$ ($[M+Na]^+$): 443.2949. Found: 443.2952

_N_-((3_R_,5_R_)-5-((_tert_-butyldimethylsilyl)oxy)-6-((4-methoxybenzyl)oxy)hex-1-en-3-yl)aniline (7a)



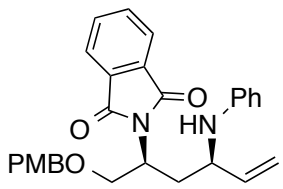
Prepared according to the general procedure I using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 93:7) to give an oil in 68% yield (90.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 9.6 Hz, 2H), 7.13 (t, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 2H), 5.76 (ddd, *J* = 16.8, 10.4, 6.1 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.45 (d, *J* = 4.0 Hz, 2H), 4.05 – 3.94 (m, 2H), 3.90 (b, 1H), 3.81 (s, 3H), 3.42 (dd, *J* = 9.5, 5.2 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.3 Hz, 1H), 1.82 (t, *J* = 6.2 Hz, 2H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 147.7, 140.1, 130.6, 129.6(2C), 129.4(2C), 117.4, 115.6, 114.1(2C), 113.7(2C), 74.4, 73.3, 69.5, 55.6, 52.9, 41.0, 26.3(3C), 18.5, -3.8, -4.3. HRMS (ESI) Calcd. for $C_{26}H_{39}NO_3Si$ ($[M+H]^+$): 442.2772 Found: 442.2774.

_N_-((3_S_,5_R_)-5-((_tert_-butyldimethylsilyl)oxy)-6-((4-methoxybenzyl)oxy)hex-1-en-3-yl)aniline (7b)



Prepared according to the general procedure using (*S, S, S*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 93:7) to give an oil in 65% yield (86.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 5.86 – 5.69 (m, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 4.53 – 4.39 (m, 2H), 4.22 (b, 1H), 4.08 – 4.00 (m, 1H), 3.95 (dt, *J* = 10.3, 5.2 Hz, 1H), 3.81 (s, 3H), 3.48 (q, *J* = 7.0 Hz, 2H), 3.44 (dd, *J* = 9.4, 6.7 Hz, 1H), 3.35 (dd, *J* = 9.4, 6.7 Hz, 1H), 1.84 – 1.77 (m, 2H), 0.89 (s, 9H), 0.02 (s, 3H), -0.01 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 148.1, 140.8, 130.6, 129.7(2C), 129.3(2C), 117.2, 115.0, 114.1(2C), 113.6(2C), 74.2, 73.4, 69.2, 66.2, 55.6, 53.1, 41.2, 26.3(3C), 18.4, -4.0, -4.5. HRMS (ESI) Calcd. for $C_{26}H_{39}NO_3Si$ ($[M+H]^+$): 442.2772 Found: 442.2773.

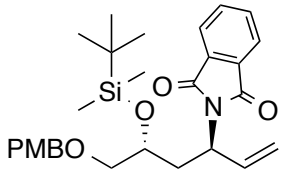
2-((2_S_,4_R_)-1-((4-methoxybenzyl)oxy)-4-(phenylamino)hex-5-en-2-yl)isoindoline-1,3-dione (7e)



Prepared according to the general procedure using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 70:30) to give an oil in 67% yield (91.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.12 (d, *J* = 8.5 Hz,

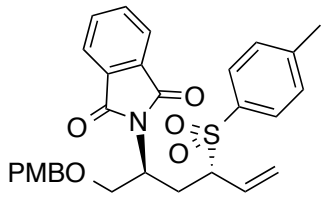
2H), 7.05 (t, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 2H), 5.71 (ddd, *J* = 16.4, 10.4, 5.7 Hz, 1H), 5.16 (d, *J* = 17.2 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 4.69 (tt, *J* = 9.9, 5.1 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 3.94 (dd, *J* = 18.6, 9.4 Hz, 2H), 3.76 (s, 3H), 3.66 (dd, *J* = 9.9, 5.8 Hz, 1H), 2.49 – 2.29 (m, 1H), 2.10 – 1.92 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1(2C), 159.5, 147.2, 139.1, 134.2(2C), 132.2, 130.24, 129.6(2C), 129.4(2C), 123.9(2C), 123.5, 117.8, 116.1, 114.0(2C), 113.8(2C), 72.7, 69.4, 55.6, 53.6, 48.3, 34.5. HRMS (ESI) Calcd. for $C_{28}H_{28}N_2O_4$ ([M+H]$^+$): 457.2122 Found: 457.2123.

2-((3*R*,5*R*)-5-((*tert*-butyldimethylsilyl)oxy)-6-((4-methoxybenzyl)oxy)hex-1-en-3-yl)isoindoline-1,3-dione (7c)



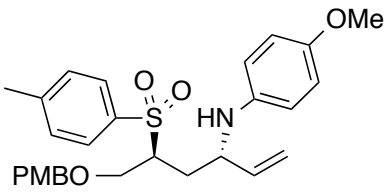
Prepared according to the general procedure using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 90:10) to give an oil in 54% yield (80.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.16 (ddd, *J* = 17.7, 10.2, 7.7 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.3 Hz, 1H), 5.01 (dd, *J* = 14.4, 7.9 Hz, 1H), 4.49 – 4.35 (m, 2H), 3.88 – 3.81 (m, 1H), 3.80 (s, 3H), 3.46 – 3.29 (m, 2H), 2.49 – 2.34 (m, 1H), 2.02 (ddd, *J* = 13.8, 8.0, 5.7 Hz, 1H), 0.91 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.25, 159.42, 135.83, 134.19, 132.36, 130.66, 129.57, 123.47, 118.36, 114.03, 74.51, 73.30, 69.31, 55.60, 50.48, 37.72, 26.26(3C), 18.49, -3.72, -4.44. HRMS (ESI) Calcd. for $C_{28}H_{37}NO_5Si$ ([M+Na]$^+$): 518.2333 Found: 518.2343.

2-((2*S*,4*S*)-1-((4-methoxybenzyl)oxy)-4-tosylhex-5-en-2-yl)isoindoline-1,3-dione (7f)



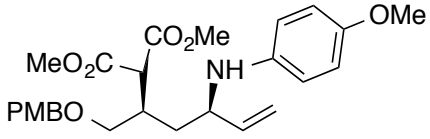
Prepared according to the modified general procedure (I) using (*S, S, S*)-**1** as catalyst. The reaction mixture obtained after oxidation step was brought inside the glove box and dissolved in 0.5 ml of THF followed by filtered through a 30 x 6 mm plug of silica gel (in a 9 mm pipette) and collected in another 4 ml vial. The silica gel was washed with 1.0 mL THF. The resulting THF solution was used for the next step. The crude mixture obtained after completion of second step, was purified by flash column chromatography (hexanes:EtOAc, 50:50) to give an oil in 53% yield (82.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 5.66 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.40 (d, *J* = 10.2 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 4.50 – 4.38 (m, 2H), 4.34 (d, *J* = 11.7 Hz, 1H), 3.86 (t, *J* = 9.3 Hz, 1H), 3.76 (s, 3H), 3.63 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.44 – 3.33 (m, 1H), 2.90 (ddd, *J* = 14.0, 11.4, 2.6 Hz, 1H), 2.41 (s, 3H), 1.95 (ddd, *J* = 14.4, 11.6, 3.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5(2C), 159.5, 145.0, 134.4, 132.0, 130.1, 129.8 (2C), 129.6(2C), 129.5(2C), 129.4(2C), 123.7, 114.1, 72.9, 69.3, 67.4, 55.6, 48.7, 27.4, 22.00. HRMS (ESI) Calcd. for $C_{29}H_{19}NO_6S$ ([M+Na]$^+$): 542.1608 Found: 542.1618.

4-methoxy-*N*-((3*S*,5*S*)-6-((4-methoxybenzyl)oxy)-5-tosylhex-1-en-3-yl)aniline (7g)



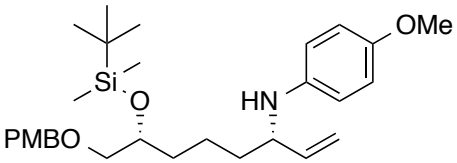
Prepared according to the general procedure I using (*S, S, S*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 70:30) to give an oil in 60% yield (89.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 8.8 Hz, 2H), 5.65 (ddd, *J* = 16.8, 10.4, 6.1 Hz, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 4.36 (d, *J* = 11.5 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.57 – 3.48 (m, 1H), 2.44 (s, 3H), 2.23 – 2.11 (m, 1H), 2.02 – 1.93 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 152.5, 144.9, 141.5, 139.4, 135.8, 130.0, 130.0, 129.9, 129.8, 129.6 129.3, 116.2, 115.2, 114.1, 73.2, 67.1, 62.1, 56.1, 55.6, 31.9, 30.0, 22.0. HRMS (ESI) Calcd. for $C_{28}H_{34}NO_5S$ ([M+H]$^+$): 496.2155 Found: 496.2152.

Dimethyl 2-((2*R*,4*R*)-1-((4-methoxybenzyl)oxy)-4-((4-methoxyphenyl)amino)hex-5-en-2-yl)malonate (7d)



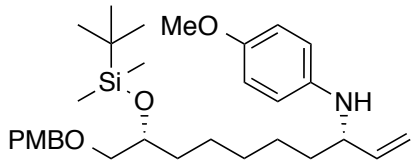
Prepared according to the general procedure using (*R, R, R*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 80:20) to give an oil in 57% yield (80.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 8.5 Hz, 2H), 5.68 (ddd, *J* = 16.4, 10.2, 5.9 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.41 (d, *J* = 11.5 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 3.69 (s, 1H), 3.66 (s, 3H), 3.45 (d, *J* = 6.0 Hz, 2H), 2.68 (s, 1H), 1.70 – 1.62 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 169.7, 159.6, 152.1, 140.8, 130.5, 129.8, 128.7, 128.2, 115.1, 114.6, 114.1, 73.1, 70.0, 56.2, 55.6, 55.2, 53.4, 52.8, 52.7, 36.1, 35.6, 30.0. HRMS (ESI) Calcd. for $C_{26}H_{34}NO_7$ ([M+H]$^+$): 472.2331 Found: 472.2330

***N*-((3*S*,7*R*)-7-((*tert*-butyldimethylsilyl)oxy)-8-((4-methoxybenzyl)oxy)oct-1-en-3-yl)-4-methoxyaniline (7h)**



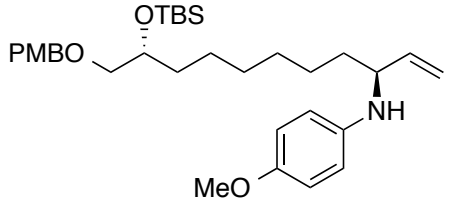
Prepared according to the general procedure using (*S, S, S*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **7h** as an oil in 65% yield (97.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.61 – 6.52 (m, 2H), 5.69 (ddd, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.44 (d, *J* = 1.3 Hz, 2H), 3.89 – 3.64 (m, 8H), 3.34 (qd, *J* = 9.6, 5.6 Hz, 2H), 1.58 – 1.30 (m, 6H), 0.87 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 152.2, 142.1, 140.8, 130.9, 129.6, 115.5, 115.1, 114.0, 74.7, 73.3, 71.6, 57.3, 56.1, 55.6, 36.3, 34.9, 26.2, 21.9, 18.5, -4.0, -4.4. HRMS (ESI) Calcd. for $C_{29}H_{46}NO_4Si$ ([M+H]$^+$): 500.3191 Found: 500.3195

***N*-((3*S*,9*R*)-9-((*tert*-butyldimethylsilyl)oxy)-10-((4-methoxybenzyl)oxy)dec-1-en-3-yl)-4-methoxyaniline (7i)**



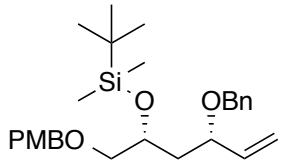
Prepared according to the general procedure using (*S, S, S*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **7i** as an oil in 63% yield (99.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 10.0 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 5.84 – 5.61 (m, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.17 (d, *J* = 10.3 Hz, 1H), 4.45 (s, 2H), 3.90 – 3.69 (m, 8H), 3.4 – 3.2 (m, 2H), 1.5 – 1.2 (m, 8H), 0.84 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 139.5, 131.0, 129.5, 114.5, 114.0, 74.9, 73.3, 71.9, 55.6, 35.1, 34.1, 30.0, 29.4, 29.2, 26.3, 25.5, 18.5, -4.0, -4.4. HRMS (ESI) Calcd. for $C_{31}H_{49}NO_4Si$ ($[M+Na]^+$): 528.3504 Found: 528.3501.

***N*-((3S,10*R*)-10-((*tert*-butyldimethylsilyl)oxy)-11-((4-methoxybenzyl)oxy)undec-1-en-3-yl)-4-methoxyaniline (7j)**



Prepared according to the general procedure using (*S, S, S*)-**1** as catalyst. The crude mixture was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **7j** as an oil in 65% yield (105.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 10.2 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 5.84 – 5.61 (m, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.45 (s, 2H), 3.90 – 3.66 (m, 8H), 3.43 – 3.26 (m, 2H), 1.55 – 1.23 (m, 10H), 0.88 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 141.0, 131.0, 129.5, 115.3, 115.2, 114.1, 74.9, 73.3, 71.9, 57.4, 56.2, 55.6, 36.2, 35.1, 30.0, 29.9, 26.3, 26.2, 25.5, 18.5, -4.0, -4.4. HRMS (ESI) Calcd. for $C_{32}H_{52}NO_4Si$ ($[M+H]^+$): 542.3660 Found: 542.3663

***(((2R,4S)*-4-(benzyloxy)-1-((4-methoxybenzyl)oxy)hex-5-en-2-yl)oxy)(tert-butyl) dimethylsilane (9)**

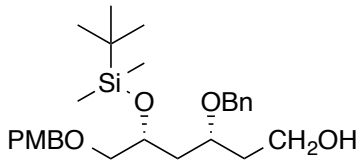


Prepared according to the modified general procedure (I) using (*S, S, S*)-**1** as catalyst.

The reaction mixture obtained after oxidation step was brought into a glove box. The reaction mixture was dissolved in 0.5 ml of dry toluene and filtered through a 30 x 6 mm plug of silica gel (in a 9 mm pipette) and collected in another 4 ml vial. The silica gel was washed with 1.0 mL toluene. To the resulting solution, K_3PO_4 (95.5 mg, 2 equiv.) and the benzyl alcohol (2.0 equiv.) were added, followed by solution of iridium catalyst **1** (13.0 mg, 5.0 mol%) and 1-phenyl-propyne (10.0 mol%) in 1.5 ml of dry toluene. The reaction mixture was stirred at 25 °C until the linear benzoyl ester was fully consumed, as determined by GC or TLC. The crude reaction mixture obtained after second step, was purified by flash column chromatography (hexanes:EtOAc, 95:5) to give **9** as an oil in 53% yield (72.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.79 – 5.63 (m, 1H), 5.27 – 5.15 (m, 2H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.41 (s, 2H), 4.31 (d, *J* = 11.9 Hz, 1H), 3.97 – 3.86 (m, 2H), 3.80 (s, 3H), 3.35 (d, *J* = 5.2

Hz, 2H), 1.86 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.79 – 1.67 (m, 1H), 0.84 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 139.1, 139.0, 130.9, 129.5, 128.6, 128.1, 127.7, 123.6, 122.9, 117.8, 114.0, 102.1, 73.2, 70.3, 69.2, 55.6, 41.1, 26.3, 18.5, -3.8, -4.4.

***(3R,5R)-3-(*benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-6-((4-methoxybenzyl)oxy) hexan-1-ol (10)**



To a dry 4 mL vial equipped with a magnetic stirring bar in the glove box, an alkene **3** (0.1 mmol), followed by a solution of 9-BBN (0.5 M solution in THF, 0.5 ml). The mixture was allowed to stir at room temperature (25 ^{o}C). After 10 h, 0.2 ml of water was slowly added. Evolution of gas was observed. After 10 min, Sodium perborate tetrahydrate (0.2 g) was added. The white suspension was stirred for 24 h. Reaction mixture was then filtered and washed with chloroform, solvent was removed and crude mixture was purified by flash column chromatography (hexanes:EtOAc, 85:15) to give **10** as an oil in 95% yield (46.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.23 (d, *J* = 8.6 Hz, 2H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.48 – 4.41 (m, 3H), 3.93 – 3.66 (m, 7H), 3.40 – 3.30 (m, 2H), 1.99 – 1.84 (m, 2H), 1.78 – 1.66 (m, 2H), 0.86 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 138.6, 130.7, 129.6, 128.8, 128.2, 128.1, 114.1, 73.3, 71.0, 69.2, 61.1, 55.6, 38.9, 36.2, 26.2, 18.9, 18.4, 11.5, -3.8, -4.5. HRMS (ESI) Calcd. for $C_{27}H_{42}O_5Si$ ($[M+Na]^+$): 497.2694 Found: 497.2691.

Reference

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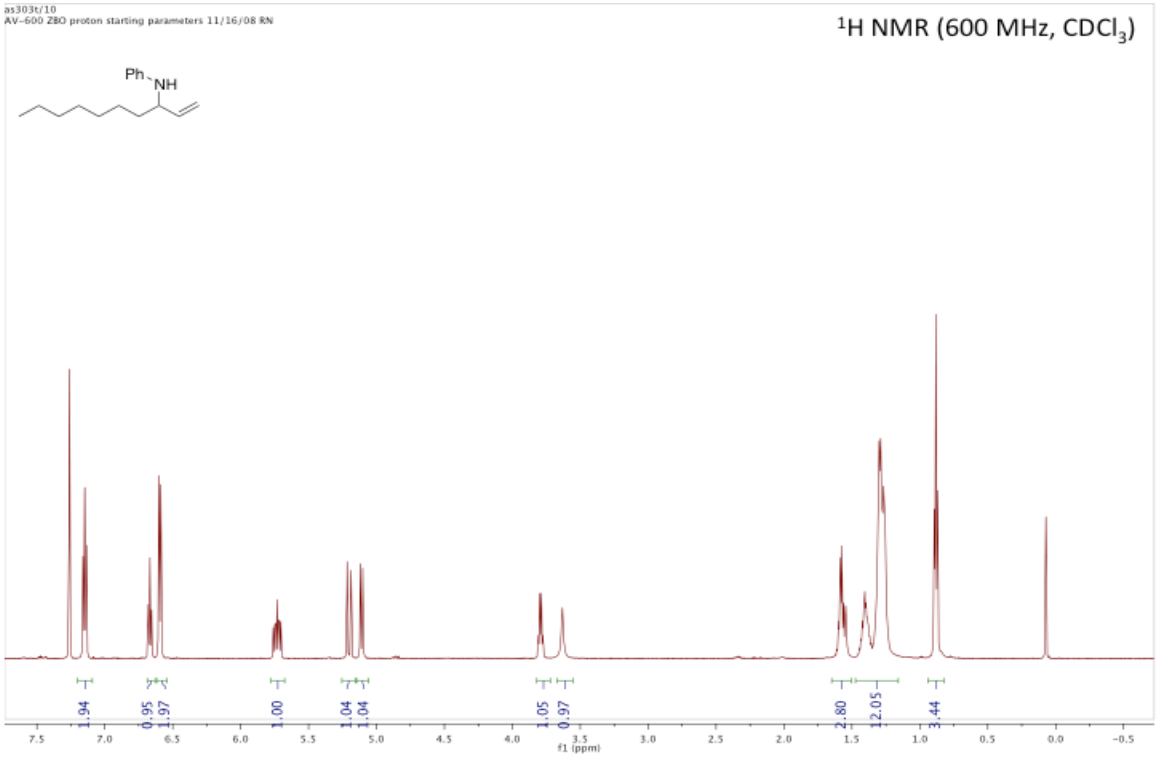
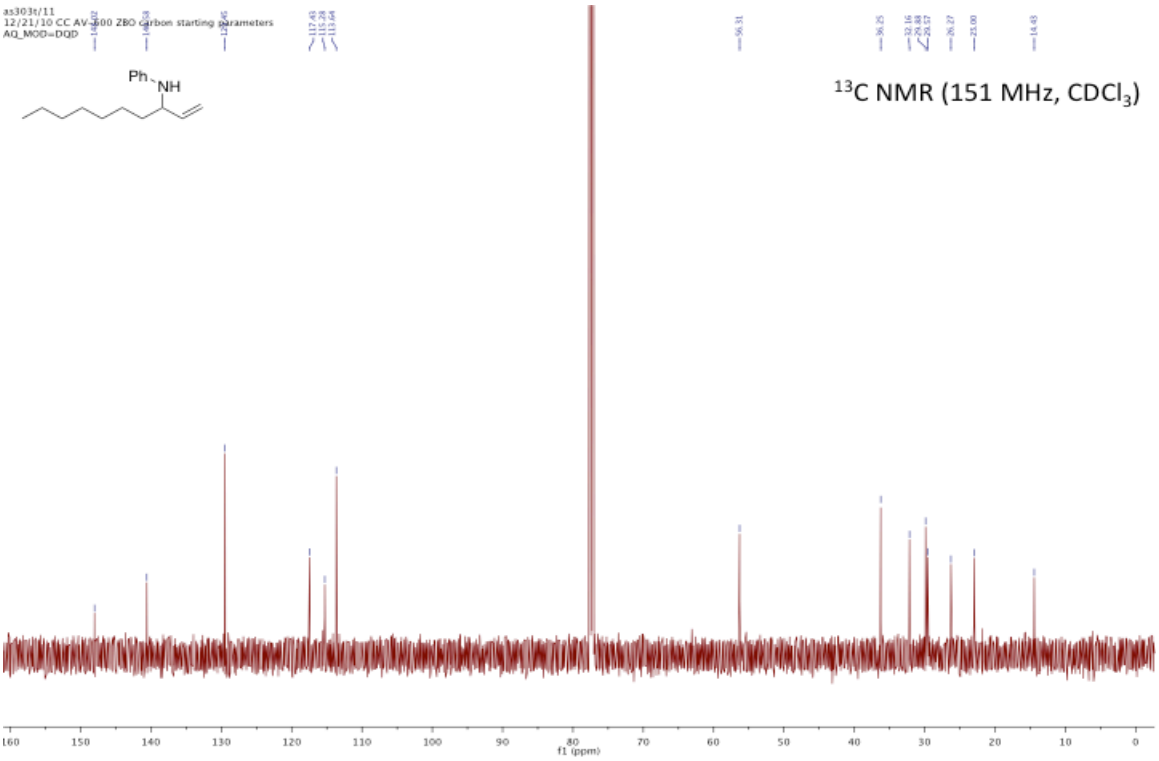
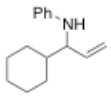
Spectral Data of Isolated Compounds

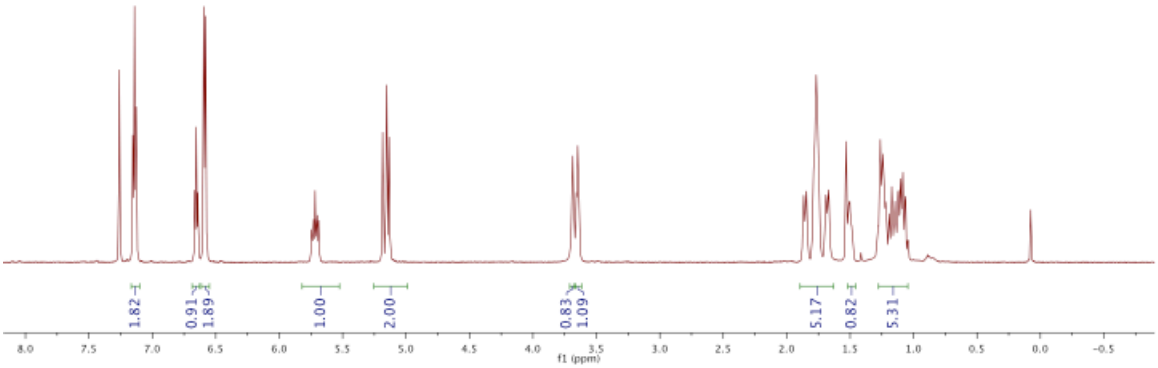




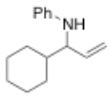
as306t/11
AV-600 ZBO proton starting parameters 11/16/08 RN

^{1}H NMR (600 MHz, $CDCl_3$)



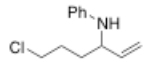


as306t/10
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

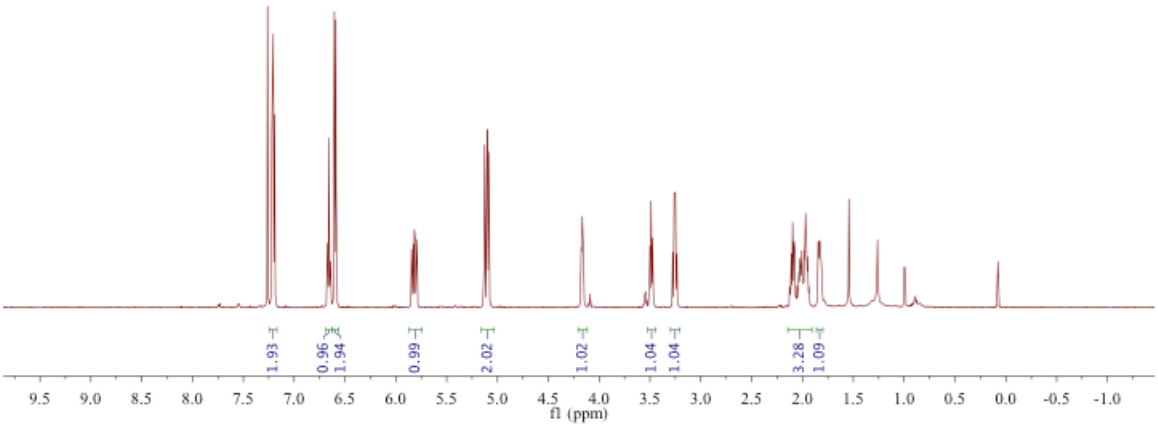


^{13}C NMR (151 MHz, $CDCl_3$)

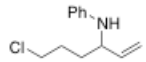
as321t/10
AV-600 ZBO proton starting parameters 11/16/08 RN



^{1}H NMR (600 MHz, $CDCl_3$)



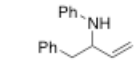
as321t/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

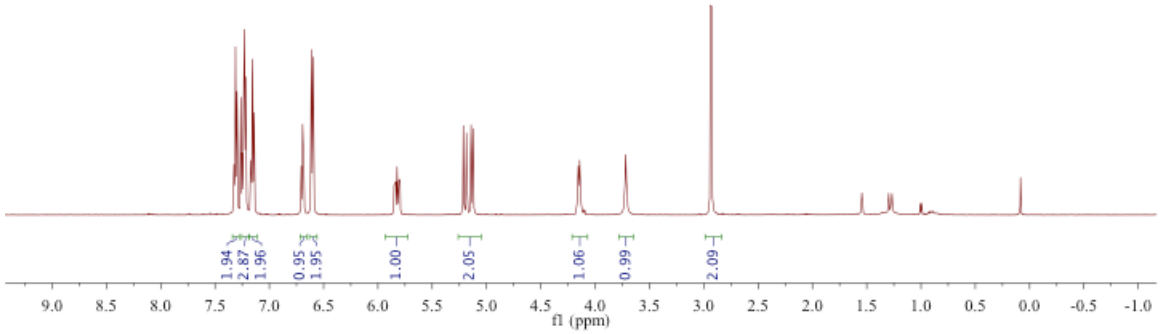


^{13}C NMR (151 MHz, $CDCl_3$)

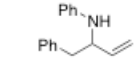
as305t/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

^{1}H NMR (600 MHz, $CDCl_3$)





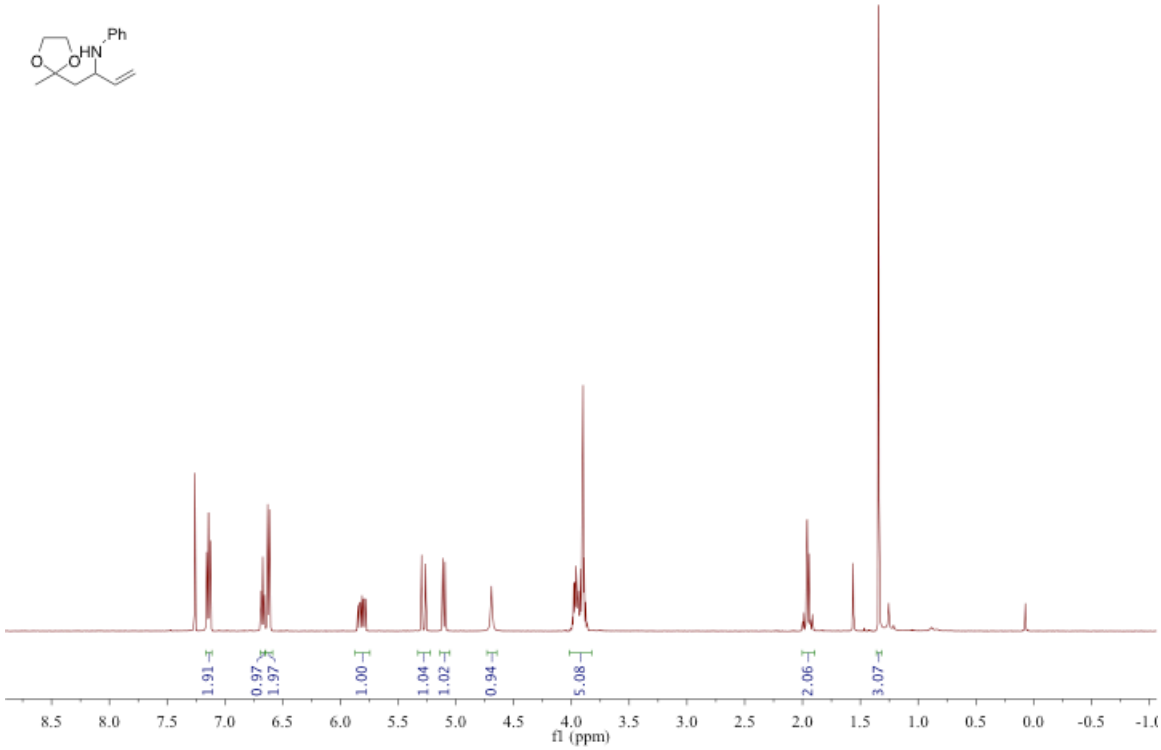
as305t/10
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD



^{13}C NMR (151 MHz, $CDCl_3$)

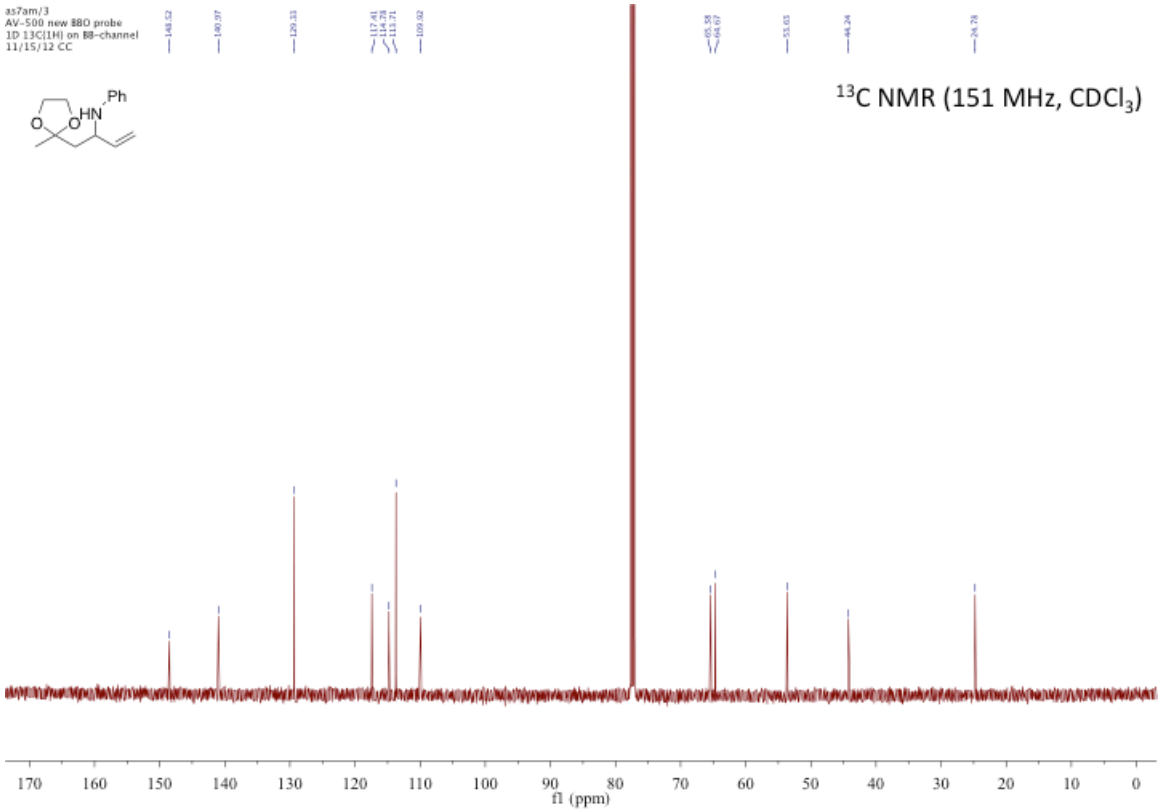
as7am/2
AV-500 new 880 probe
CC:111512

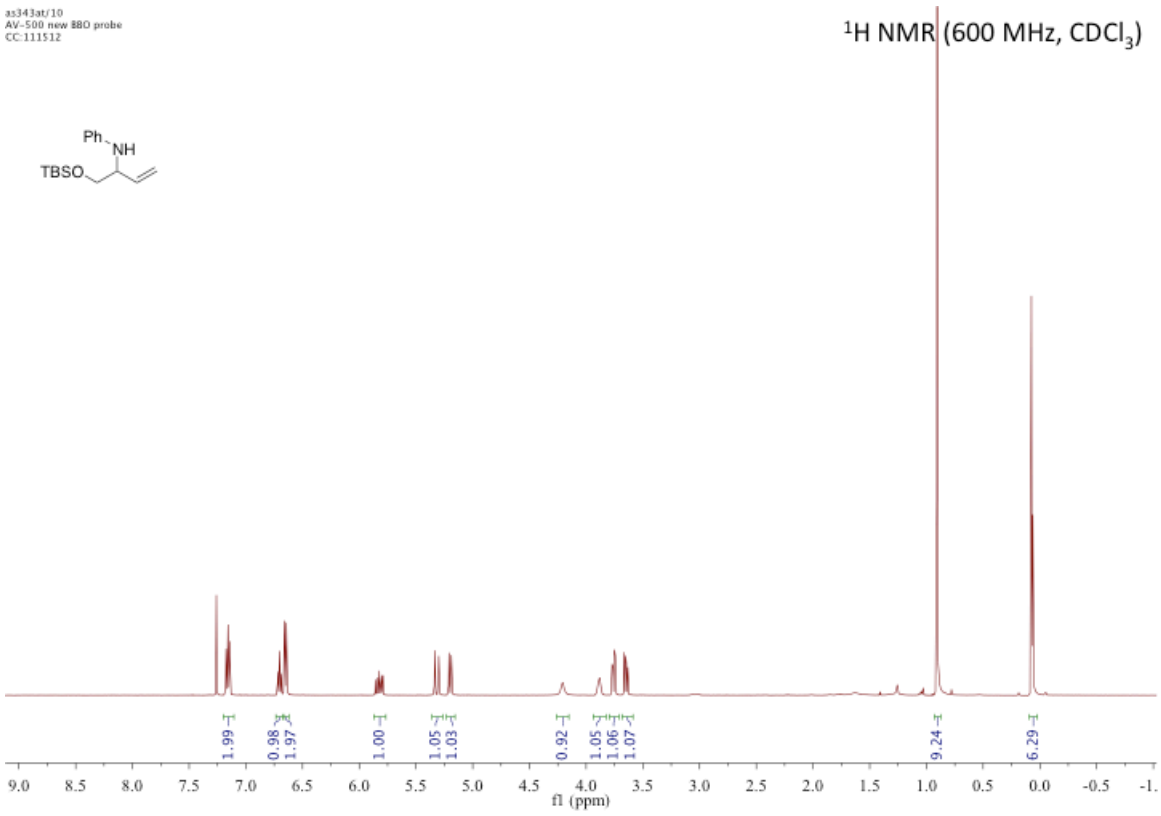
^{1}H NMR (600 MHz, $CDCl_3$)

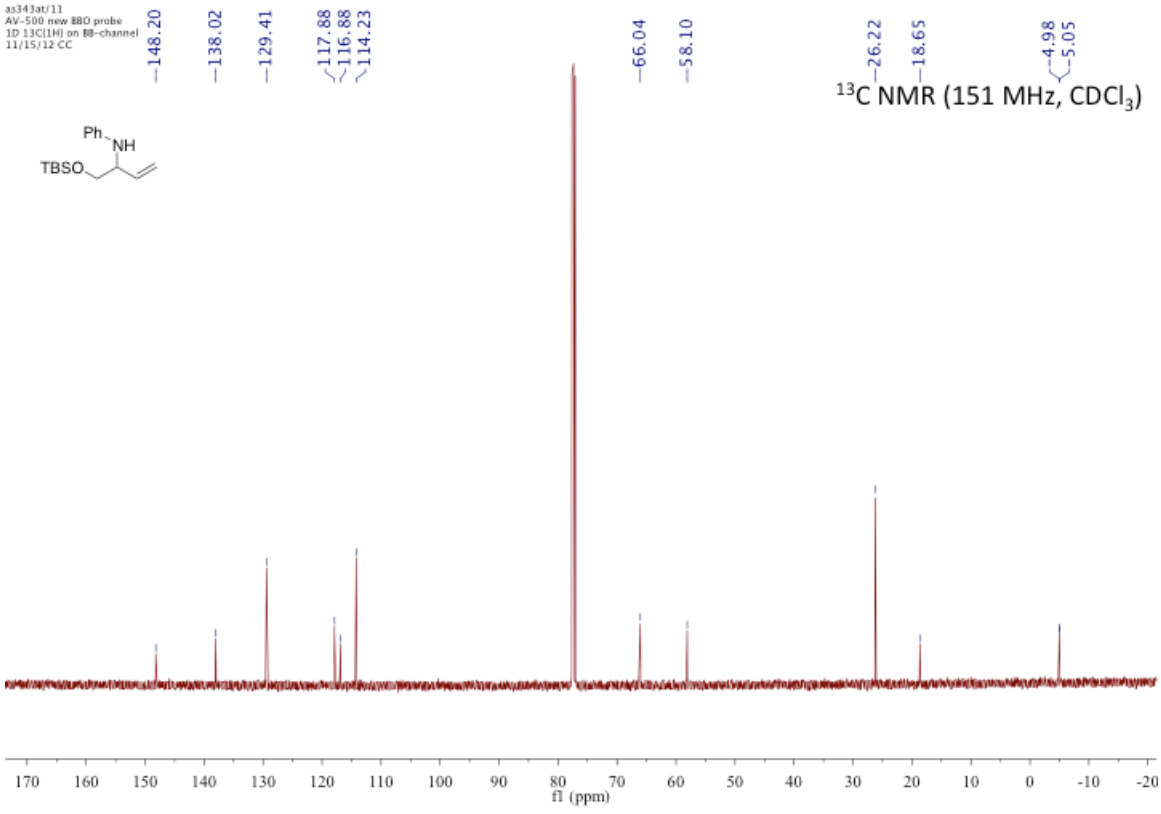


as7am/3
AV-500 new 880 probe
1D 13C{1H} on B8-channel
11/15/12 CC

^{13}C NMR (151 MHz, $CDCl_3$)

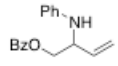


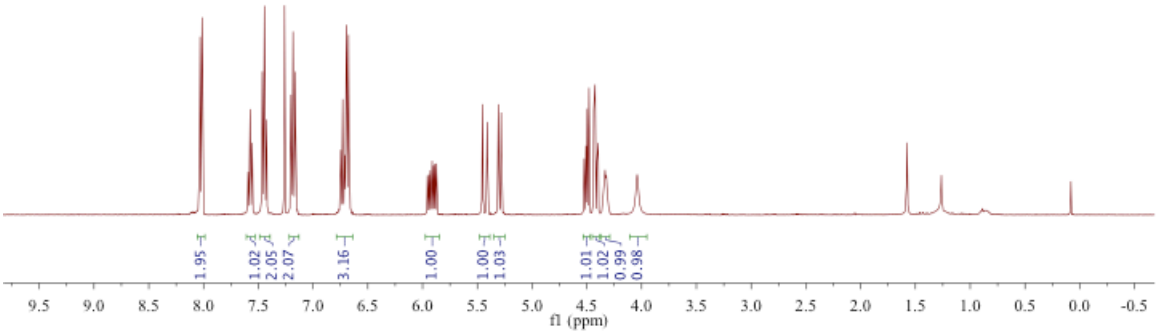

as343at/10
AV-500 new BBO probe
CC:111512
^{1}H NMR (600 MHz, $CDCl_3$)
Ph
NH
TBSO
1.99
0.98
1.97
1.00
1.05
1.03
0.92
1.05
1.06
1.07
9.24
6.29
f1 (ppm)


as343at/11
AV-500 new BBO probe
1D 13C{1H} on BB-channel
11/15/12 CC
148.20
138.02
129.41
117.88
116.88
114.23
66.04
58.10
26.22
18.65
4.98
5.05
^{13}C NMR (151 MHz, $CDCl_3$)
Ph
NH
TBSO
f1 (ppm)

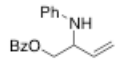
as370bm/10
AVB-400 ZBO Proton starting parameters. 6/11/03 RN

^{1}H NMR (600 MHz, $CDCl_3$)

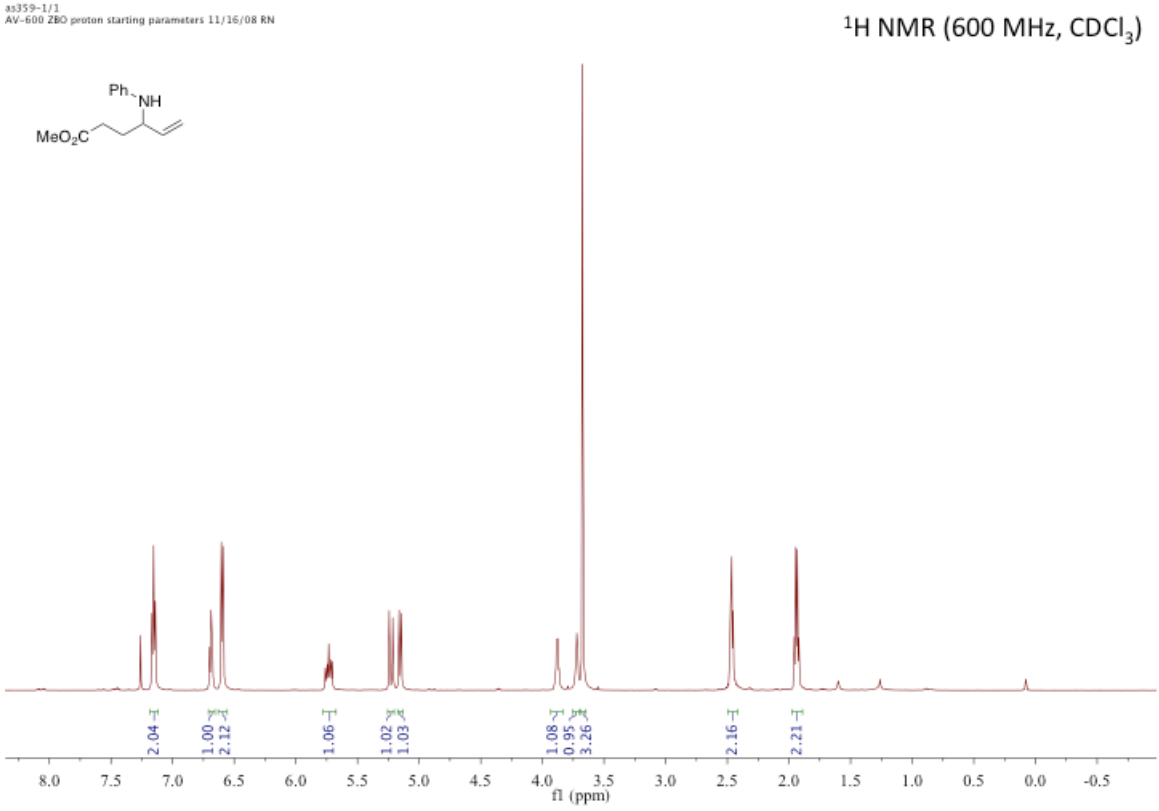




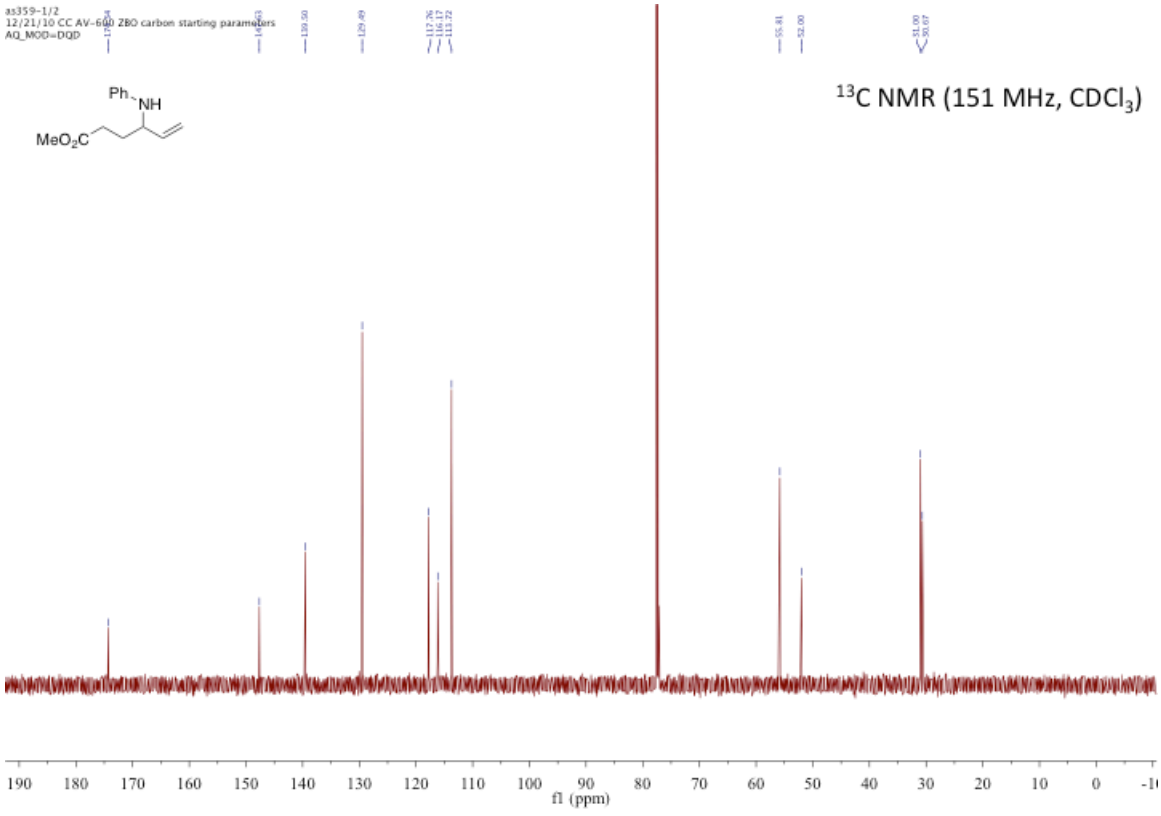
as370bm/11
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN



^{13}C NMR (151 MHz, $CDCl_3$)



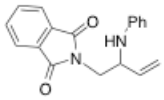
^{1}H NMR (600 MHz, $CDCl_3$)

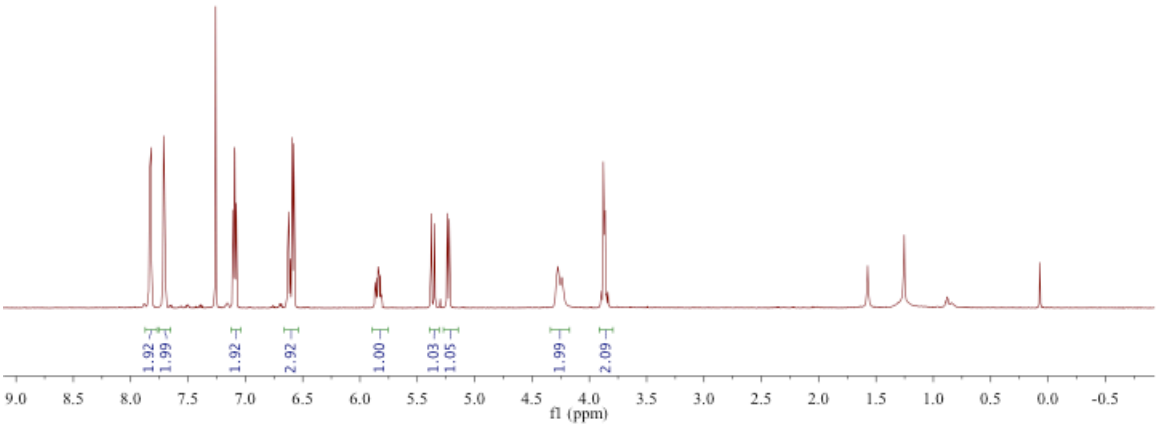


^{13}C NMR (151 MHz, $CDCl_3$)

as358a/30
AV-600 ZBO proton starting parameters 11/16/08 RN

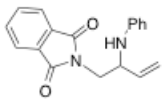
^{1}H NMR (600 MHz, $CDCl_3$)





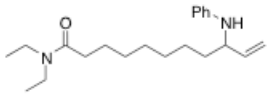
as358a/31
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

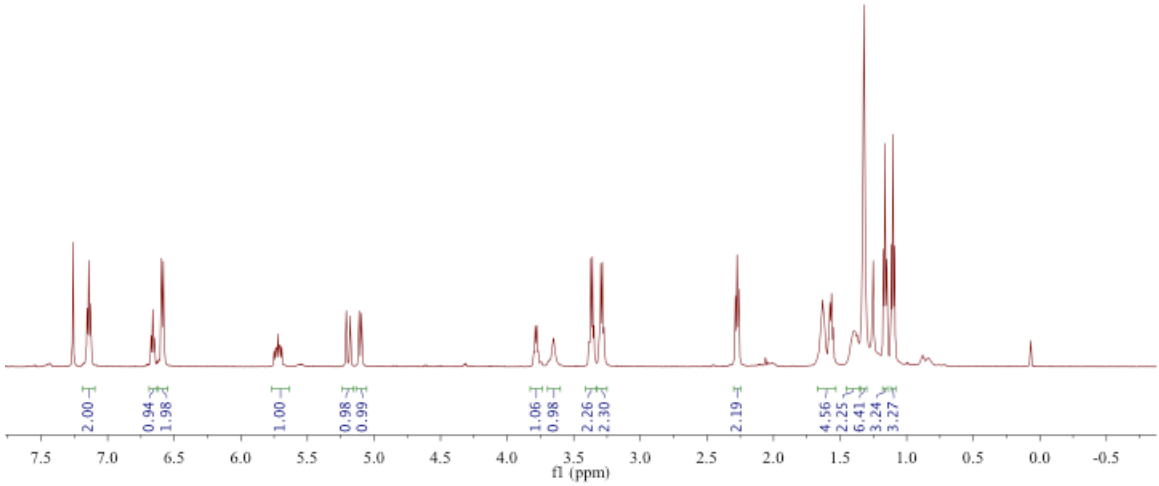
^{13}C NMR (151 MHz, $CDCl_3$)



as345bm/1
AV-600 ZBO proton starting parameters 11/16/08 RN

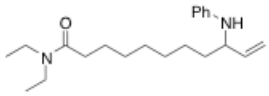
^{1}H NMR (600 MHz, $CDCl_3$)





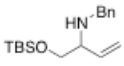
as345bm/2
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

^{13}C NMR (151 MHz, $CDCl_3$)



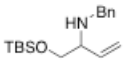
as386c/10
AVB-400 ZBO Proton starting parameters. 6/11/03 RN

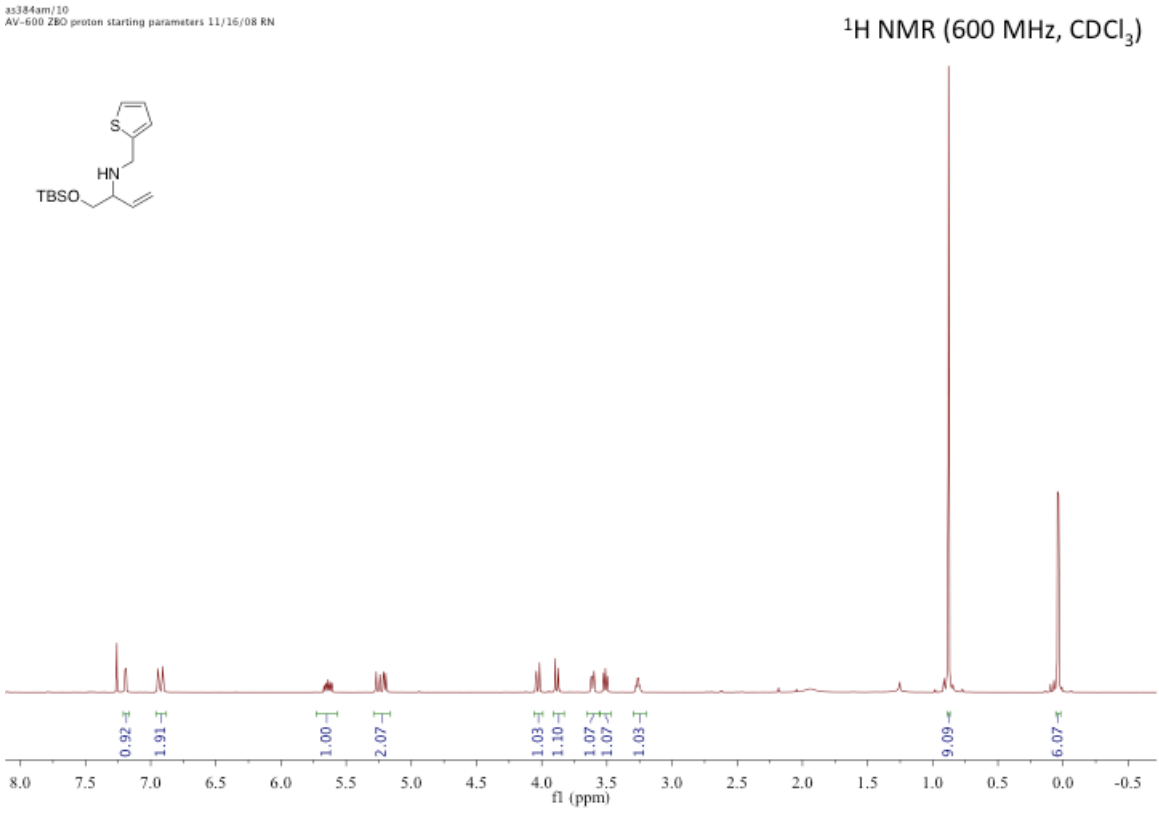
^{1}H NMR (600 MHz, $CDCl_3$)

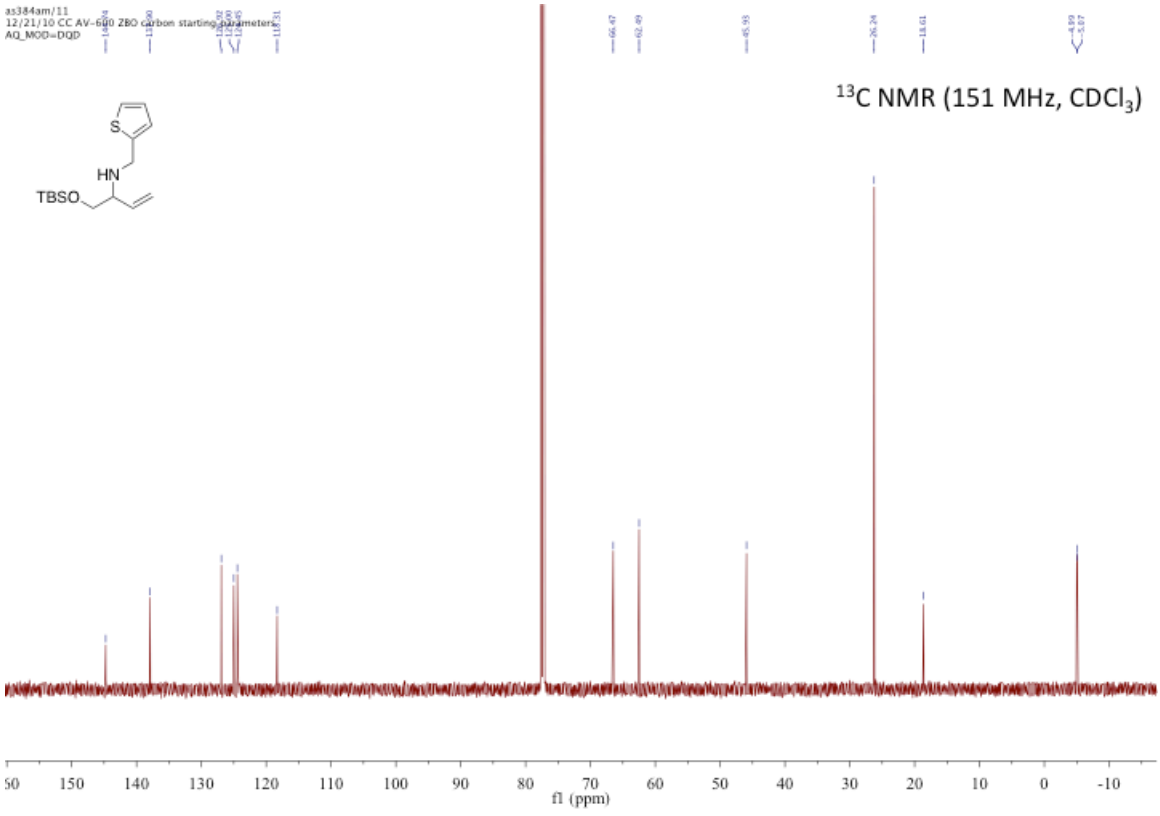


as386c/11
AVB-400 ZBO Carbon Starting parameters 6/11/03 RN

^{13}C NMR (151 MHz, $CDCl_3$)

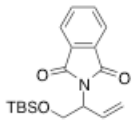


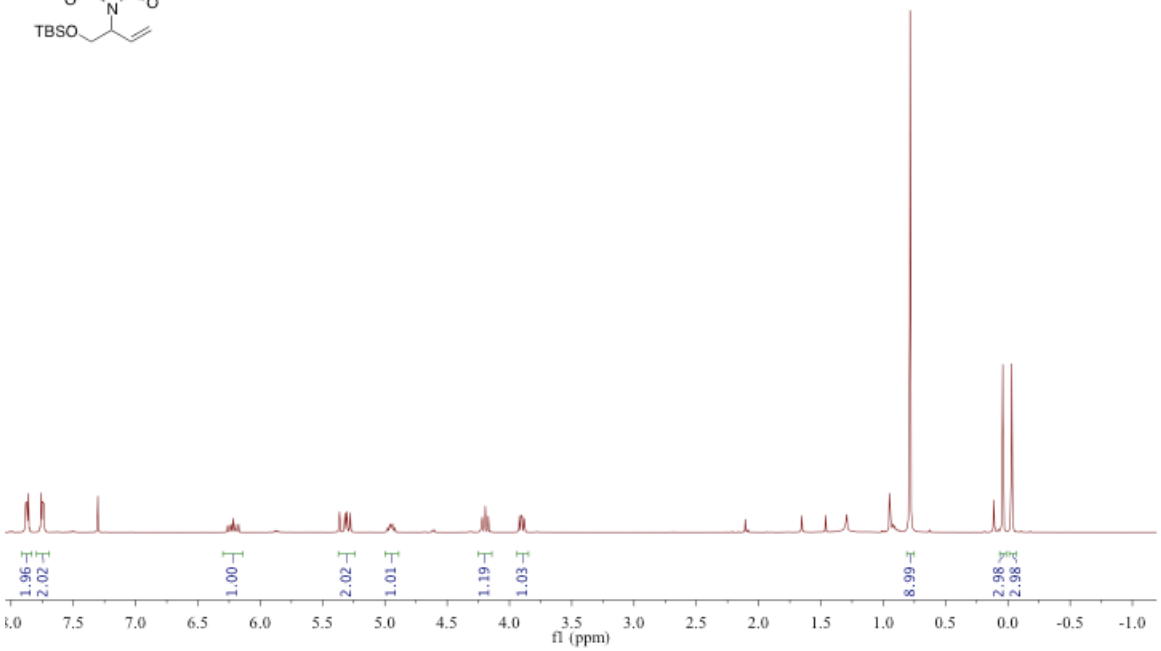

as384am/10
AV-600 ZBO proton starting parameters 11/16/08 RN
^{1}H NMR (600 MHz, $CDCl_3$)
S
HN
TBSO
0.92
1.91
1.00
2.07
1.03
1.10
1.07
1.07
1.03
9.09
6.07
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


as384am/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
S
HN
TBSO
66.47
62.49
45.93
26.24
18.61
-4.89
-5.07
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

as387bm/10
AVB-400 ZBO Proton starting parameters. 6/11/03 RN

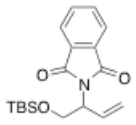
^{1}H NMR (600 MHz, $CDCl_3$)

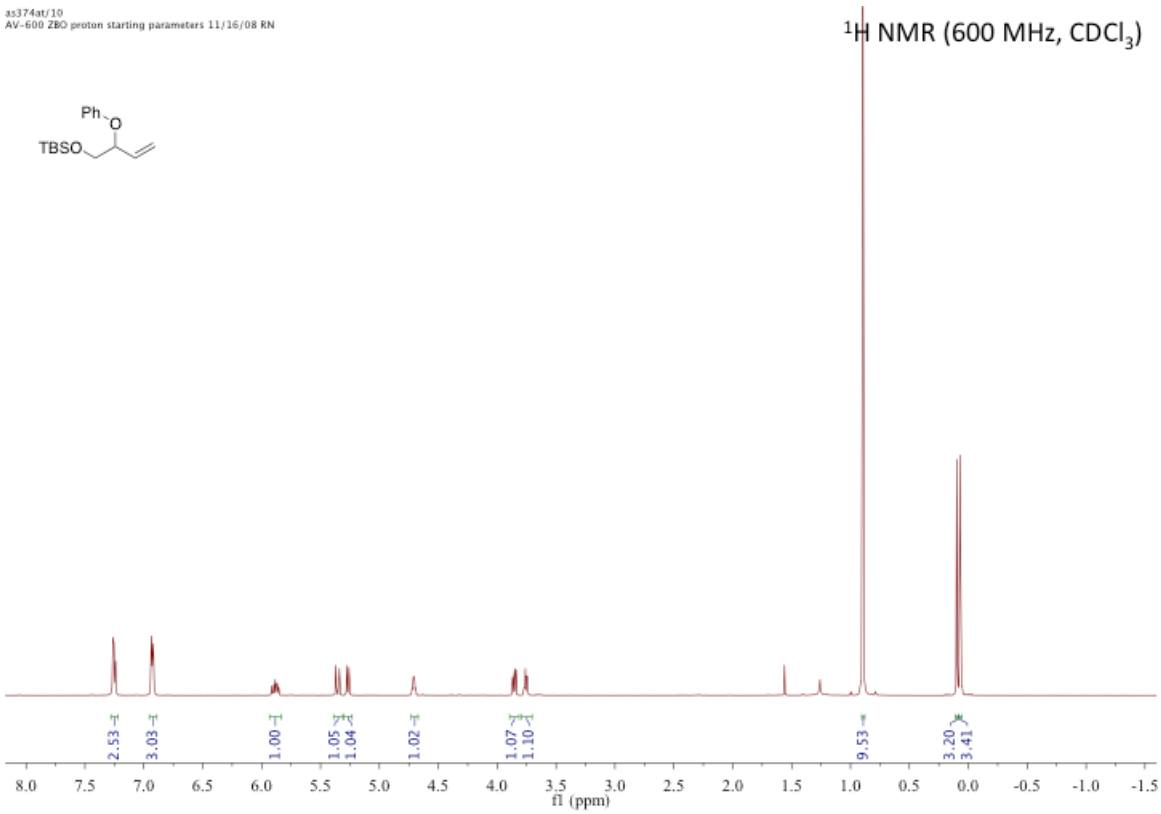


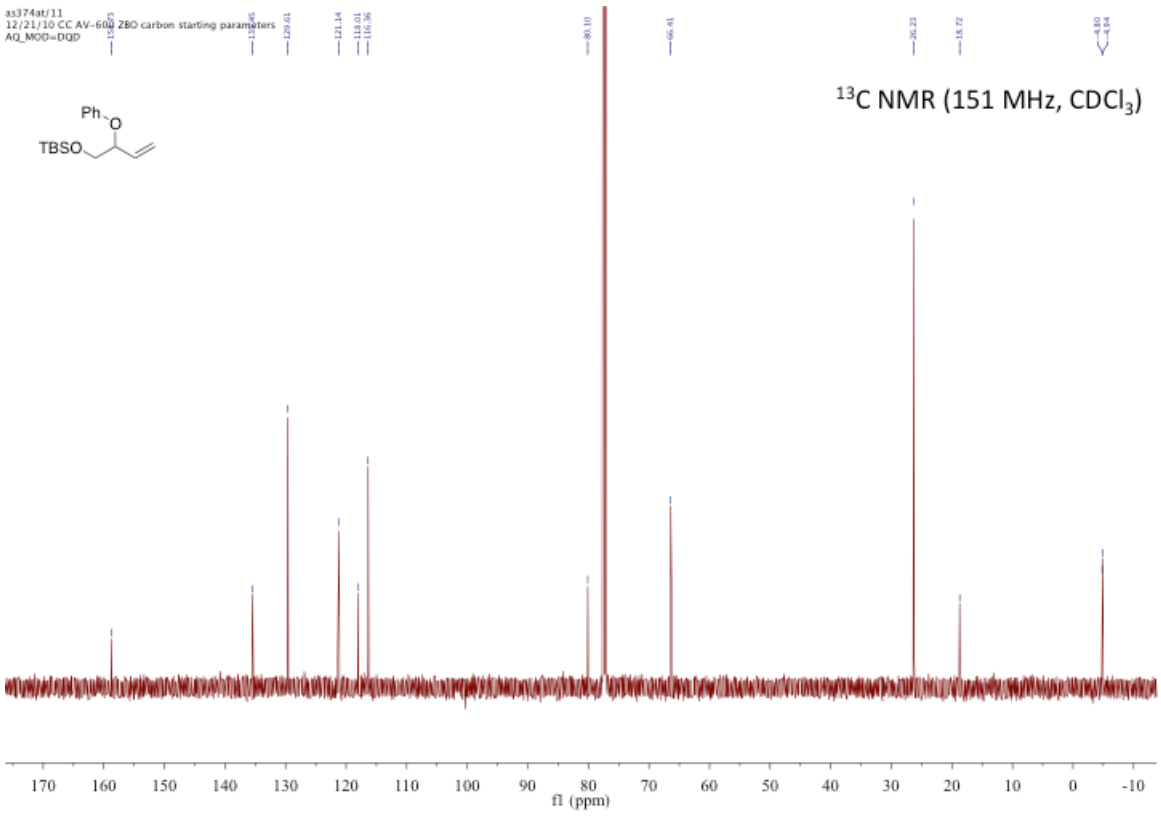


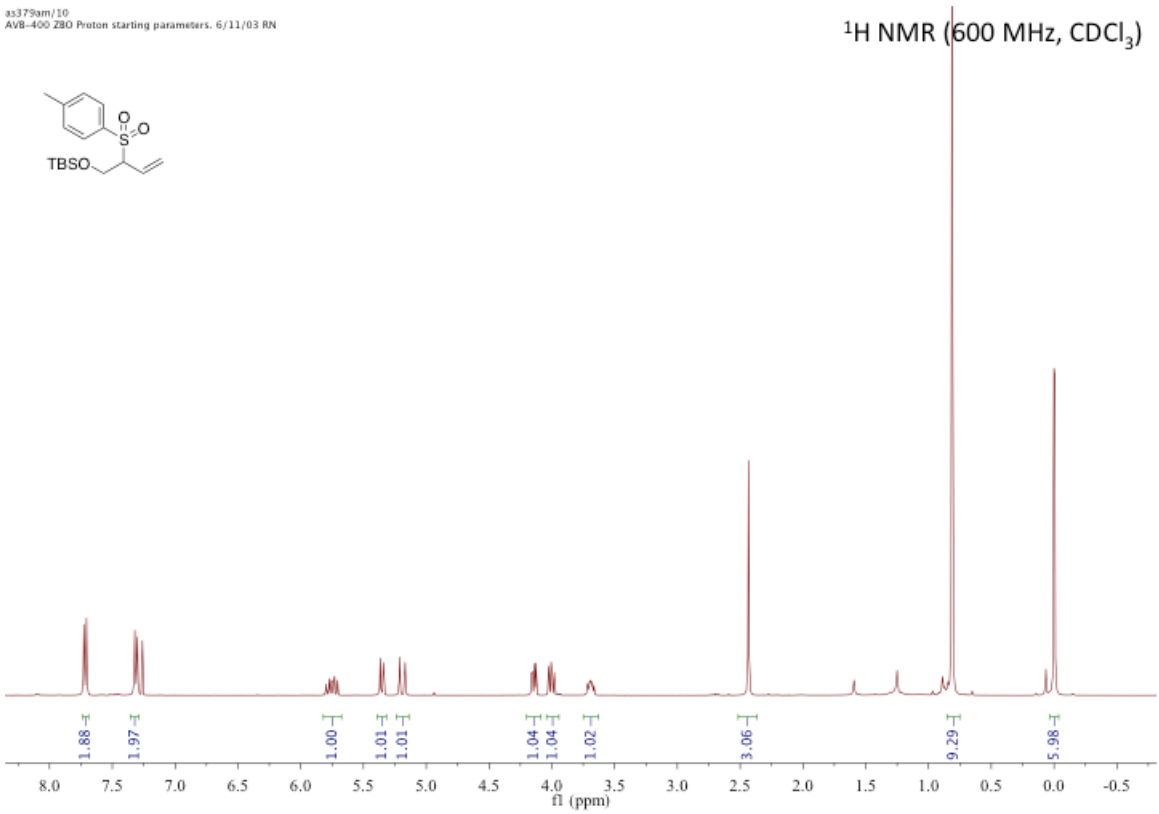
as387bm/12
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN

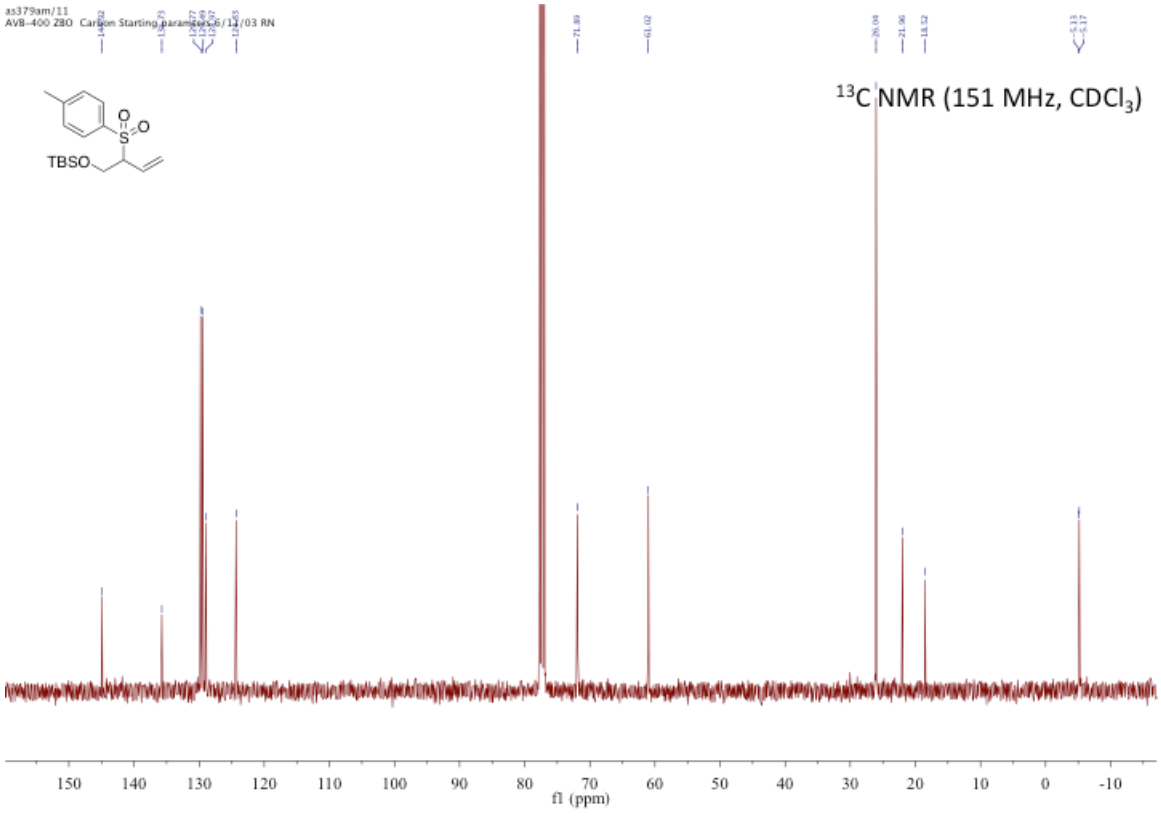
^{13}C NMR (151 MHz, $CDCl_3$)

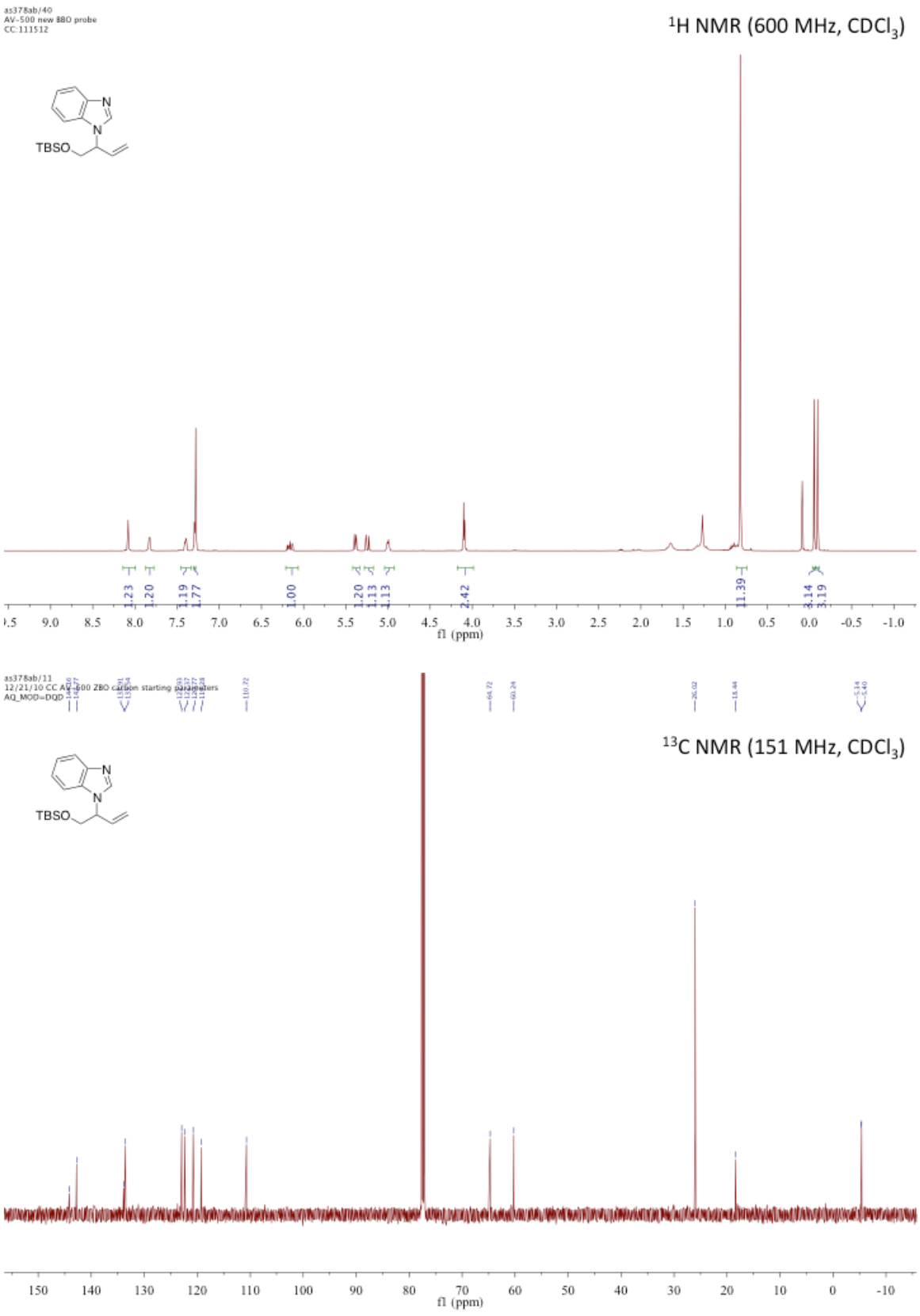


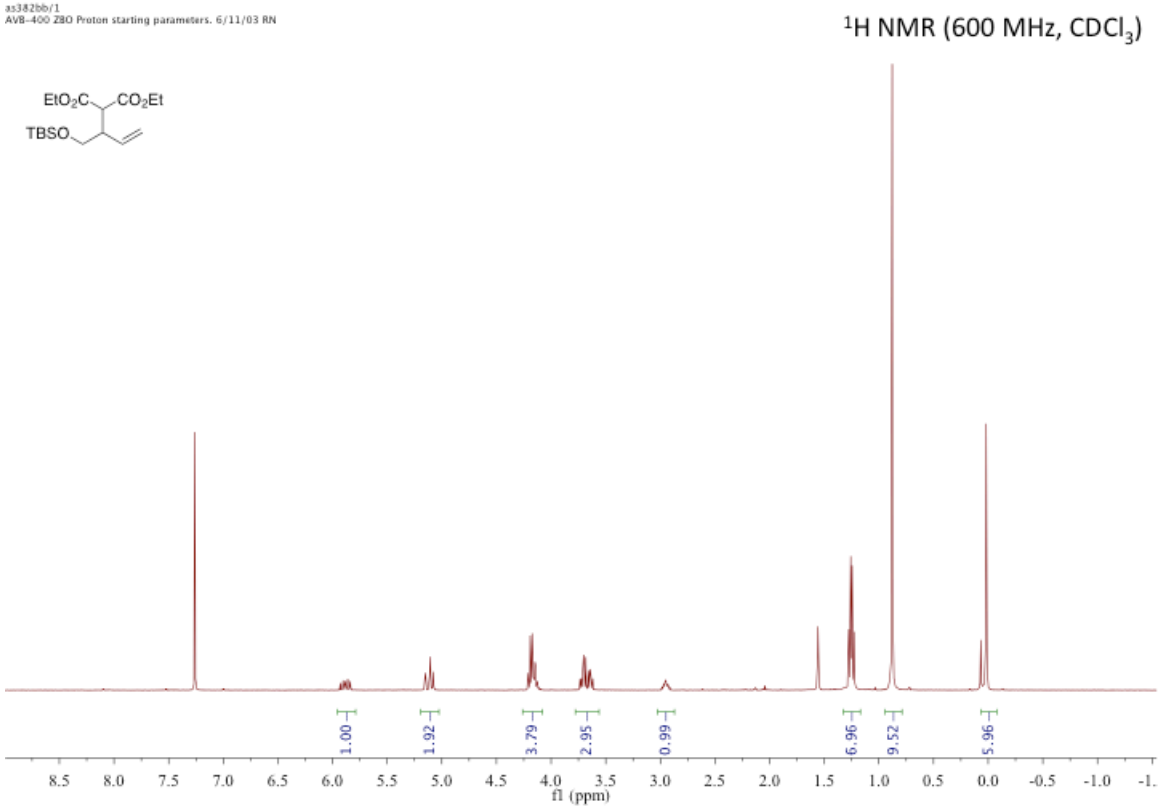

as374at/10
AV-600 ZBO proton starting parameters 11/16/08 RN
^{1}H NMR (600 MHz, $CDCl_3$)
Ph
O
TBSO
2.53
3.03
1.00
1.05
1.04
1.02
1.07
1.10
9.53
3.20
3.41
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

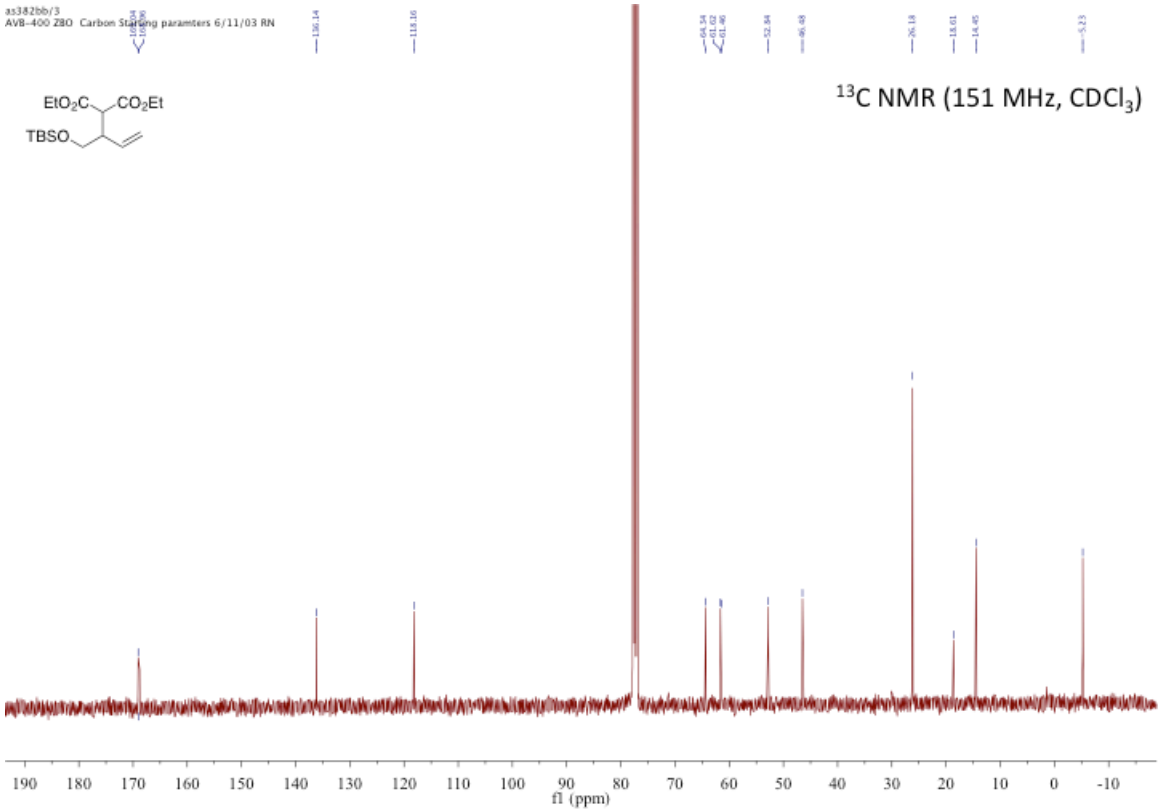

as374at/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
Ph
O
TBSO
80.10
66.41
26.23
18.72
-4.80
-4.84
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


as379am/10
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
^{1}H NMR (600 MHz, $CDCl_3$)
TBSO
1.88
1.97
1.00
1.01
1.01
1.04
1.04
1.02
3.06
9.29
5.98
f1 (ppm)


as379am/11
AVB-400 ZBO Carbon Starting parameters 6/11/03 RN
^{13}C NMR (151 MHz, $CDCl_3$)
TBSO
f1 (ppm)

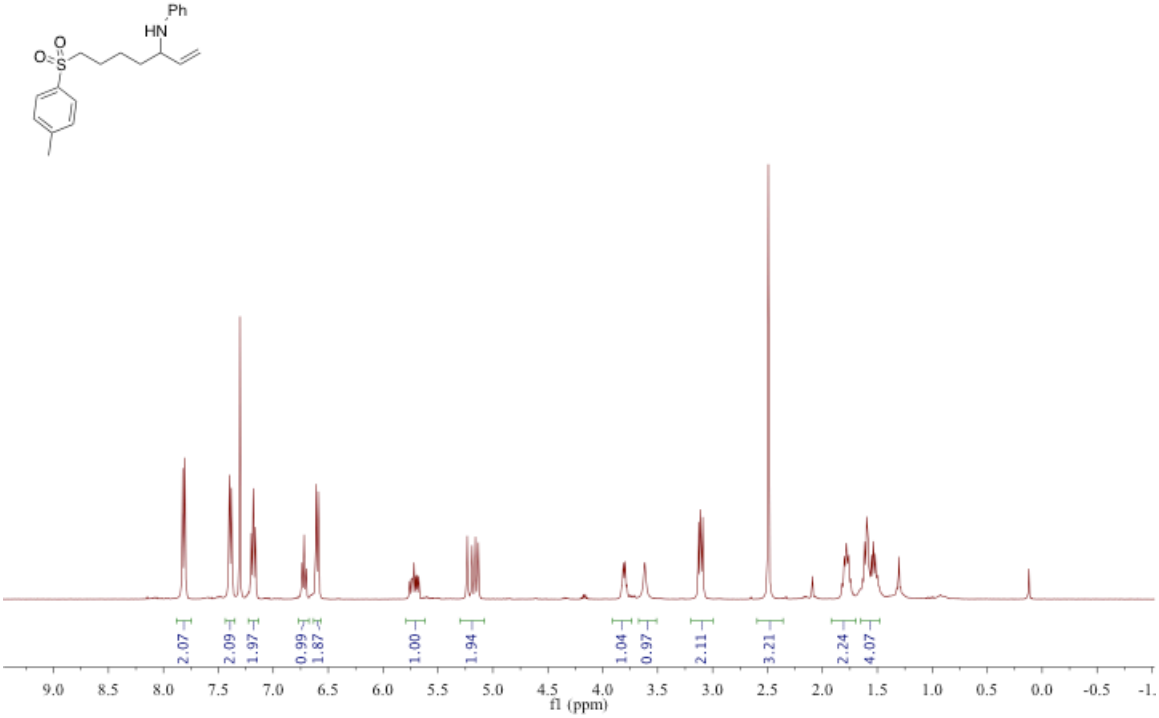

as378ab/40
AV-500 new BBO probe
CC:111512
^{1}H NMR (600 MHz, $CDCl_3$)
N
N
TBSO
1.23
1.20
1.19
1.77
1.00
1.20
1.13
1.13
2.42
11.39
3.14
3.19
f1 (ppm)
as378ab/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
N
N
TBSO
f1 (ppm)


as382bb/1
AVB-400 ZBO Proton starting parameters. 6/11/03 RN
^{1}H NMR (600 MHz, $CDCl_3$)
EtO_2C
CO_2Et
TBSO
1.00
1.92
3.79
2.95
0.99
6.96
9.52
5.96
f1 (ppm)


as382bb/3
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN
^{13}C NMR (151 MHz, $CDCl_3$)
EtO_2C
CO_2Et
TBSO
f1 (ppm)

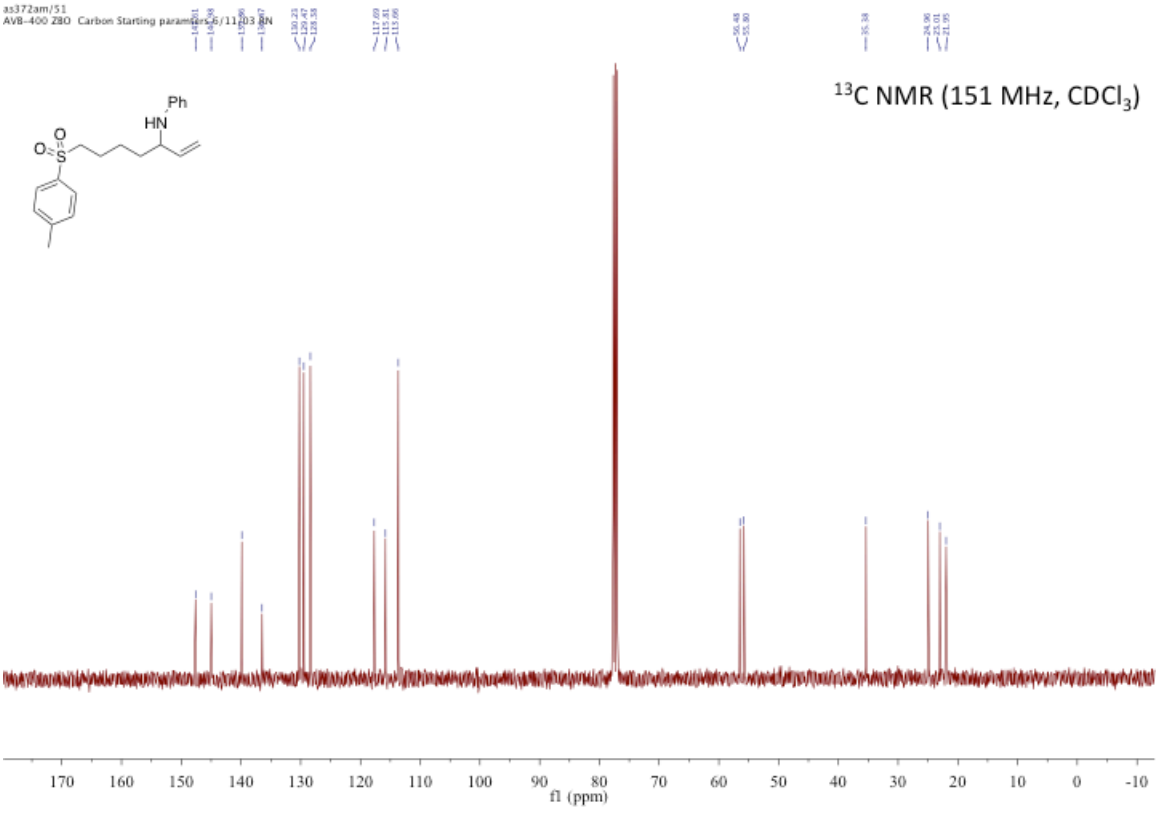
as372am/50
AVB-400 ZBO Proton starting parameters. 6/11/03 RN

^{1}H NMR (600 MHz, $CDCl_3$)



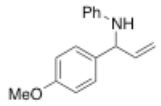
as372am/51
AVB-400 ZBO Carbon Starting parameters 6/11/03 RN

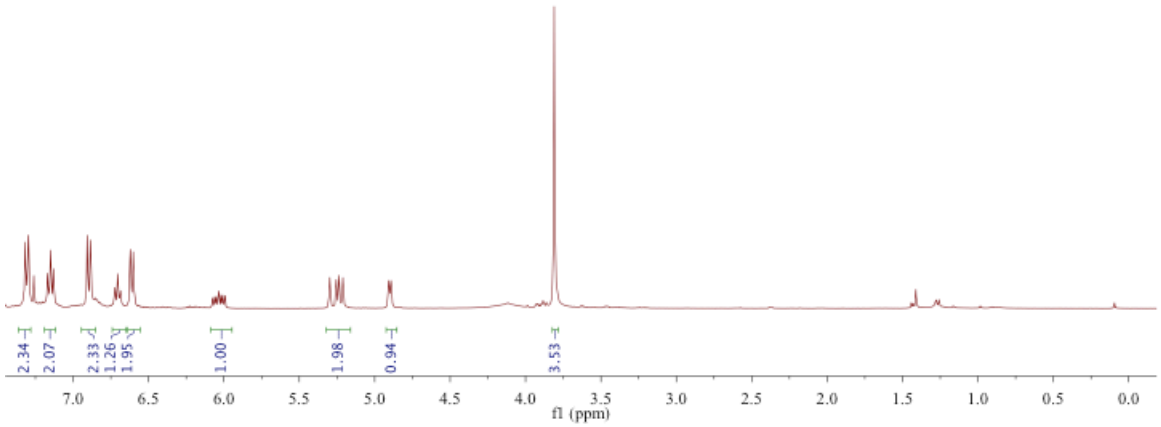
^{13}C NMR (151 MHz, $CDCl_3$)



as-22a/60
AVB-400 ZBO Proton starting parameters. 6/11/03 RN

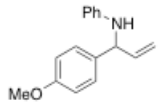
^{1}H NMR (400 MHz, $CDCl_3$)

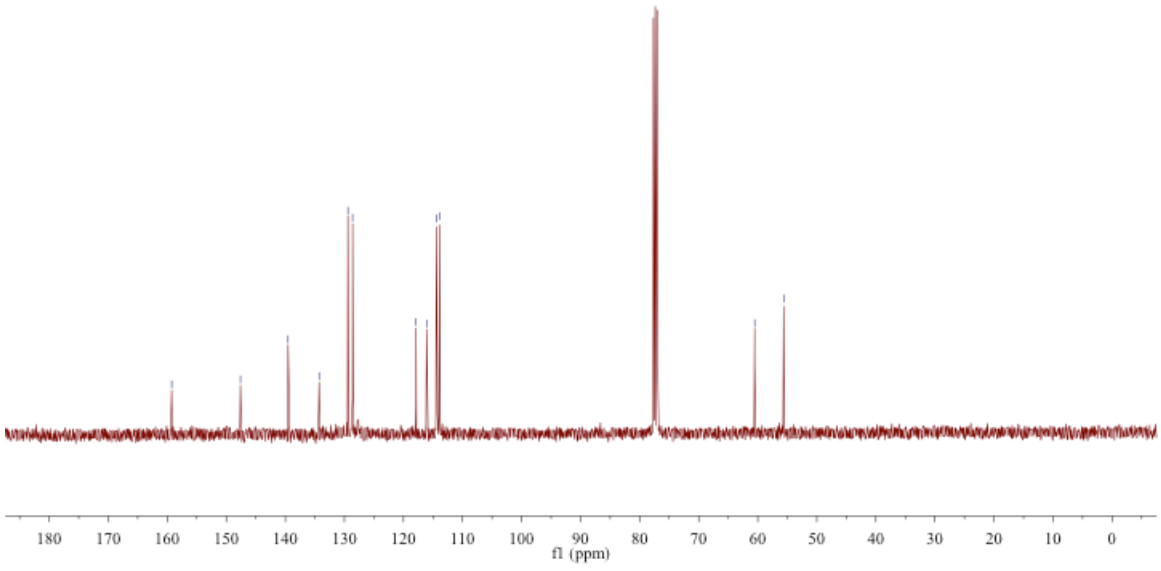




as-22a/61
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN

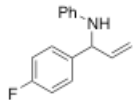
^{13}C NMR (101 MHz, $CDCl_3$)

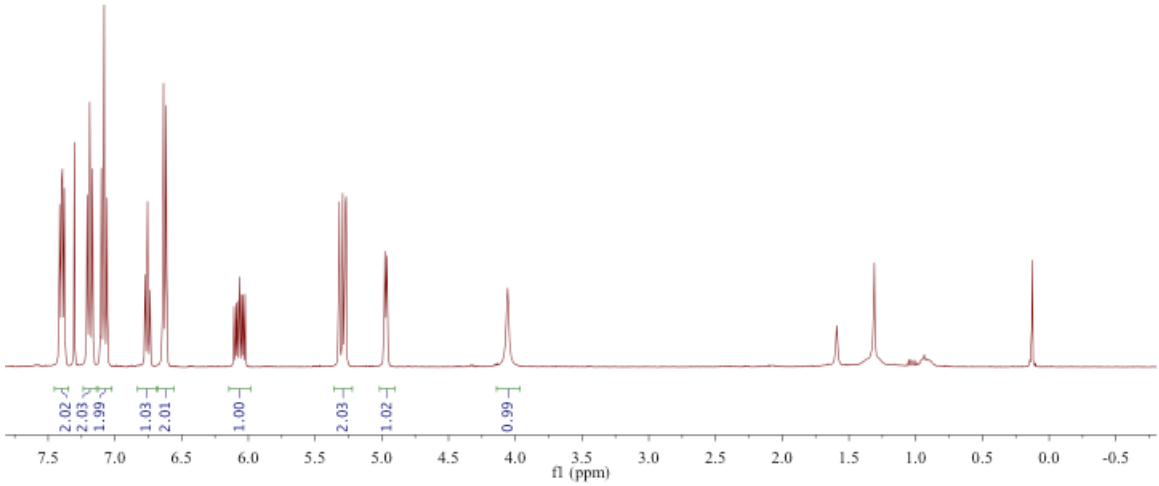




as23a/20
AVB-400 ZBO Proton starting parameters. 6/11/03 RN

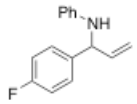
^{1}H NMR (600 MHz, $CDCl_3$)

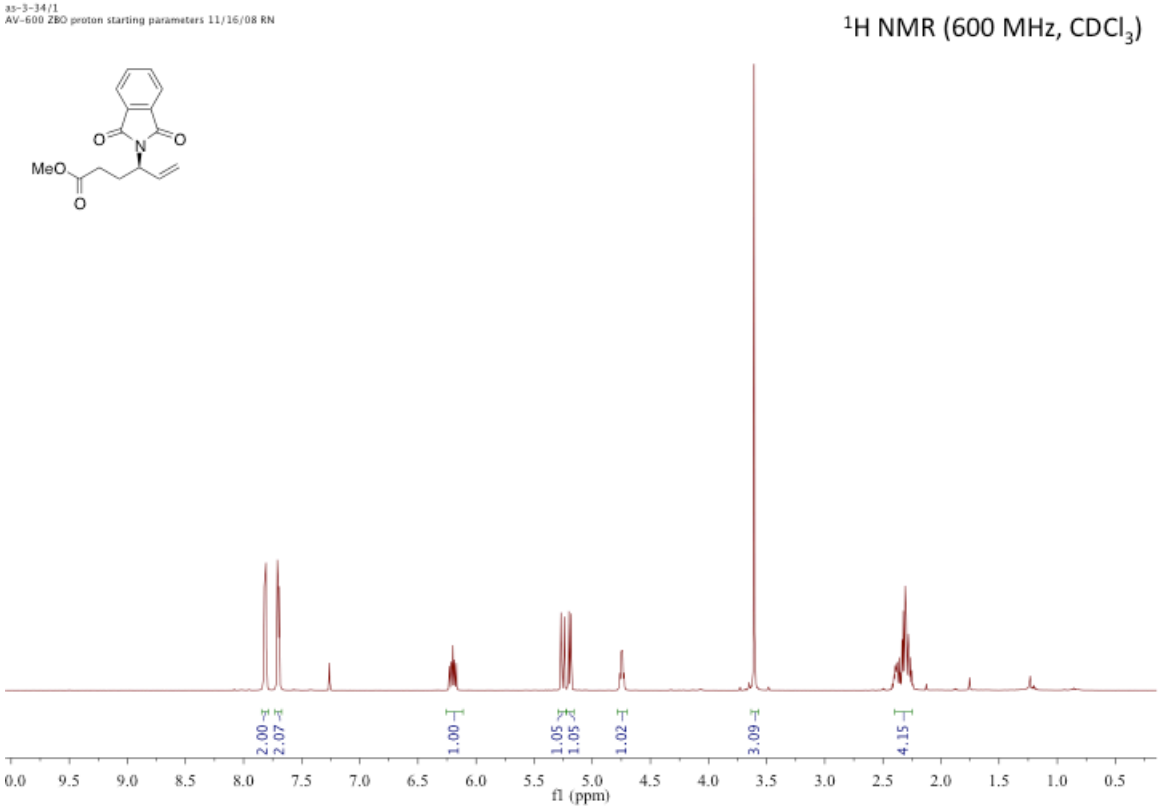


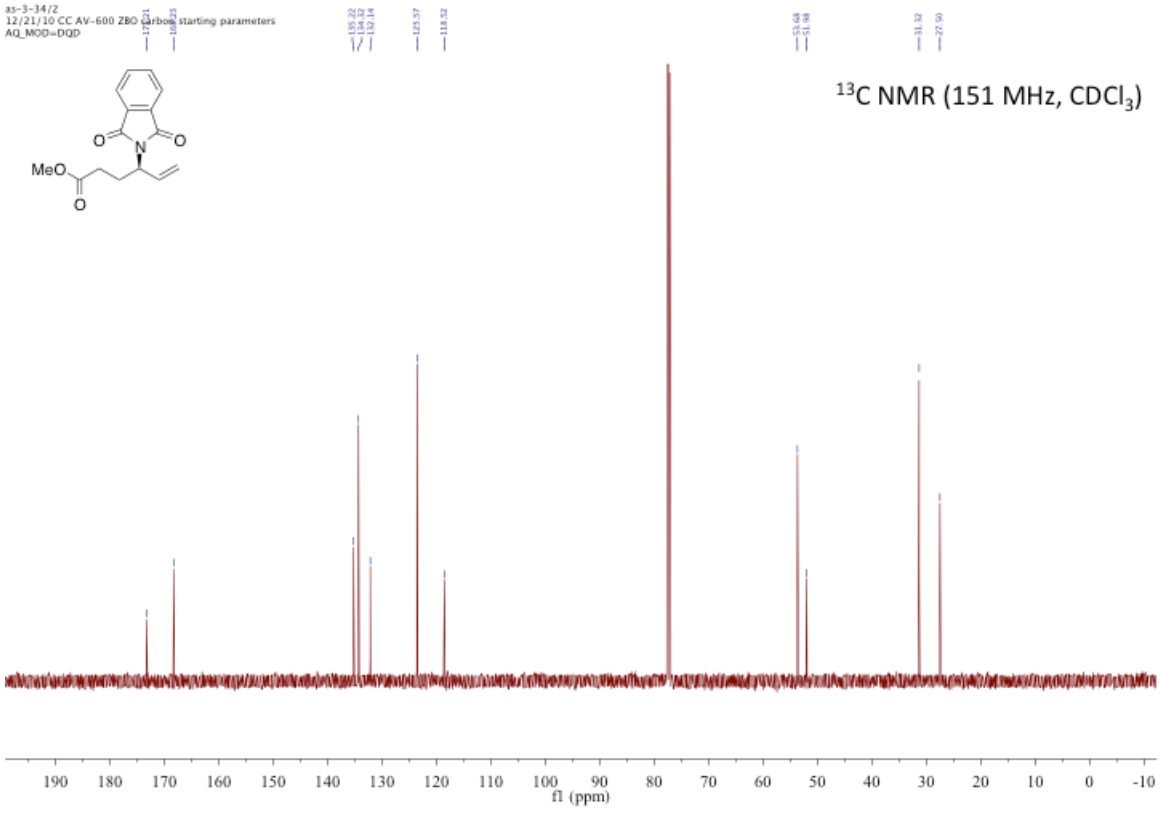


as23a/21
AVB-400 ZBO Carbon starting parameters 6/11/03 RN

^{13}C NMR (151 MHz, $CDCl_3$)

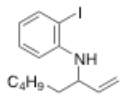


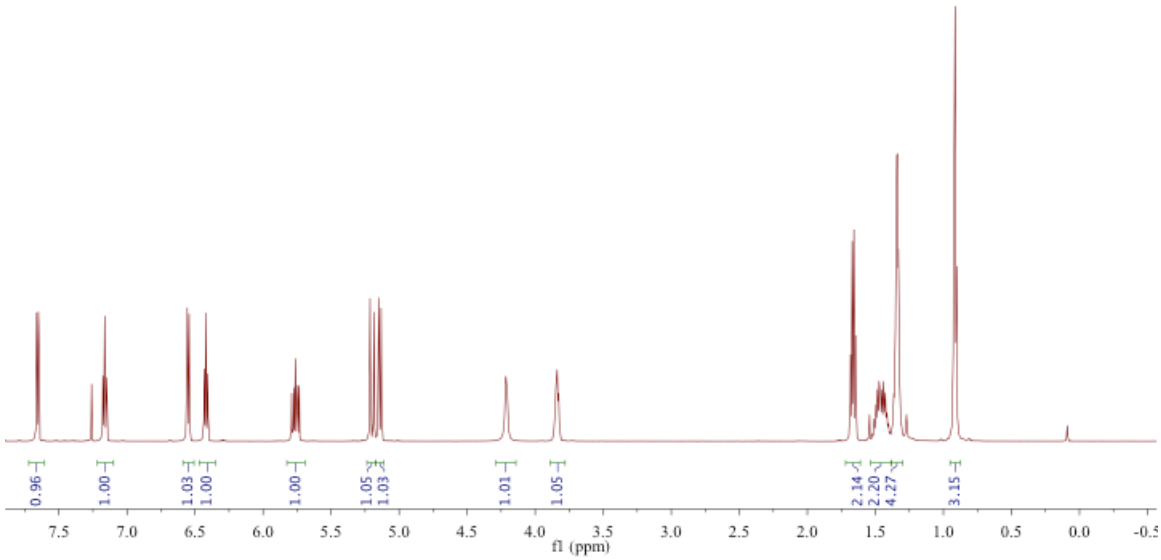

as-3-34/1
AV-600 ZBO proton starting parameters 11/16/08 RN
^{1}H NMR (600 MHz, $CDCl_3$)
MeO
O
N
O
O
2.00
2.07
1.00
1.05
1.05
1.02
3.09
4.15
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


as-3-34/2
12/21/10 CC AV-600 ZBO Carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
MeO
O
N
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

as-3-35/1
AV-600 ZBO proton starting parameters 11/16/08 RN

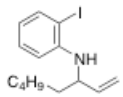
^{1}H NMR (600 MHz, $CDCl_3$)

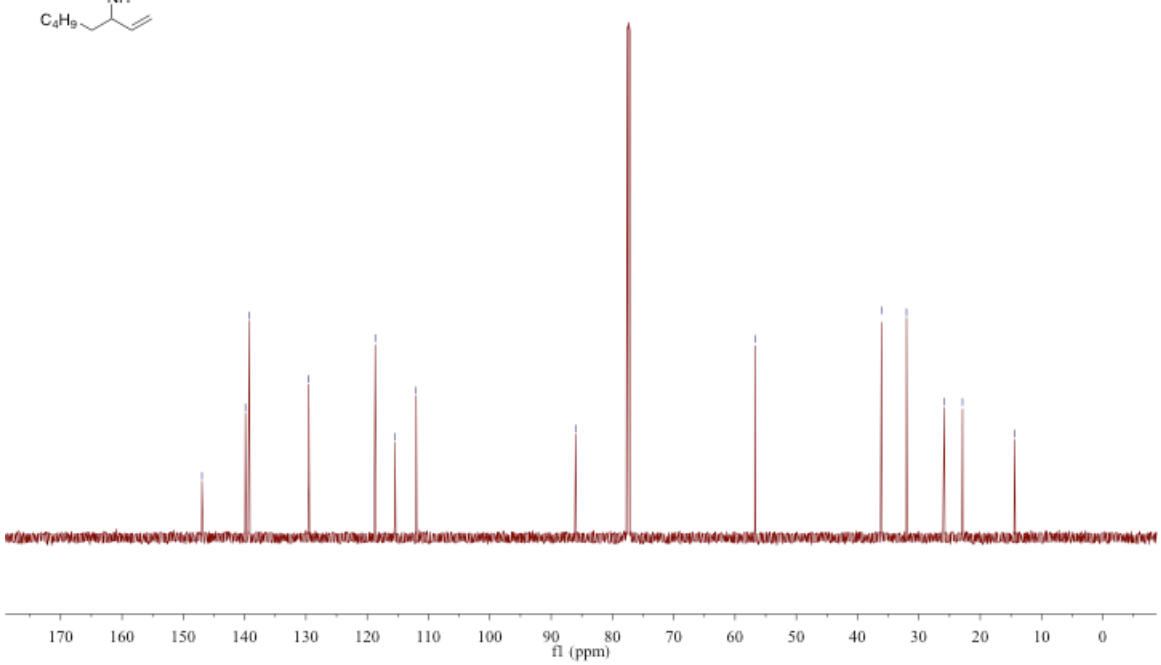




as-3-35/2
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

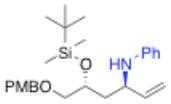
^{13}C NMR (151 MHz, $CDCl_3$)

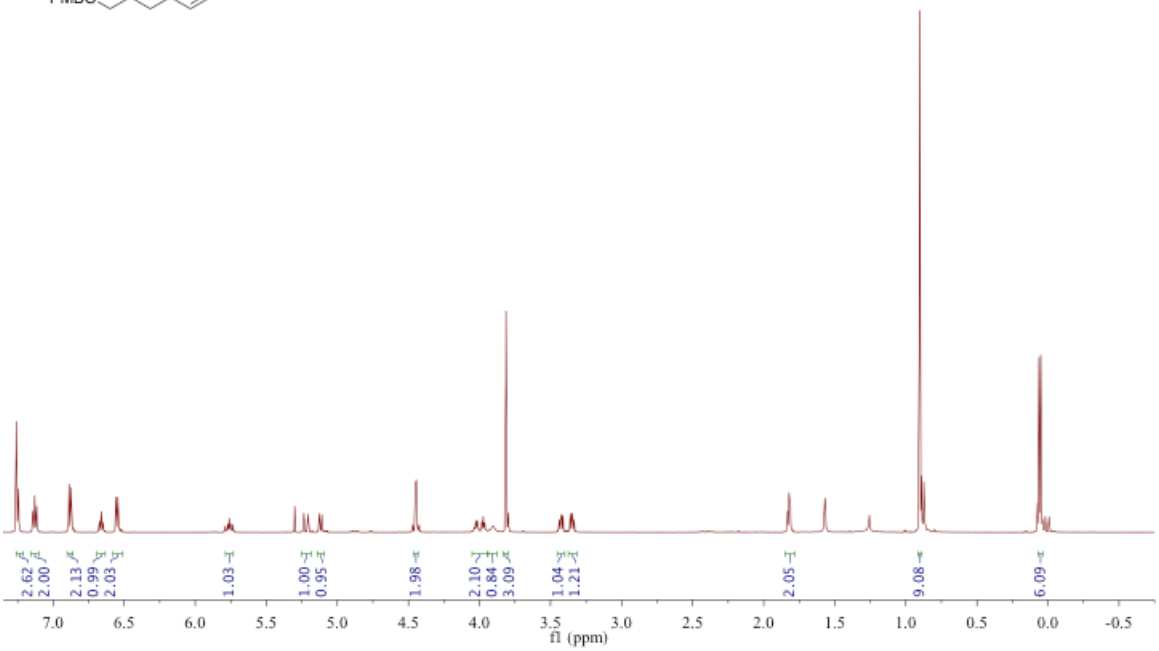




as-3-21at1/40
AV-600 ZBO proton starting parameters 11/16/08 RN

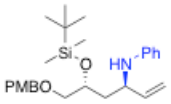
^{1}H NMR (600 MHz, $CDCl_3$)

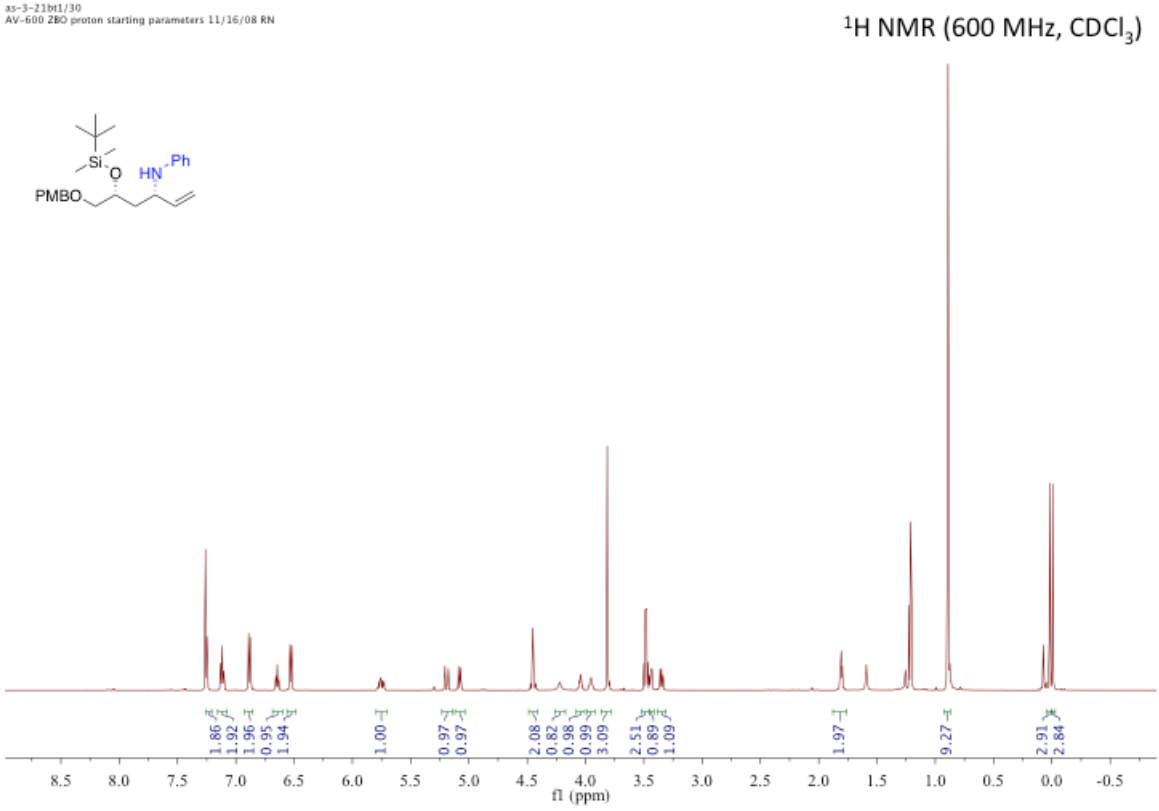


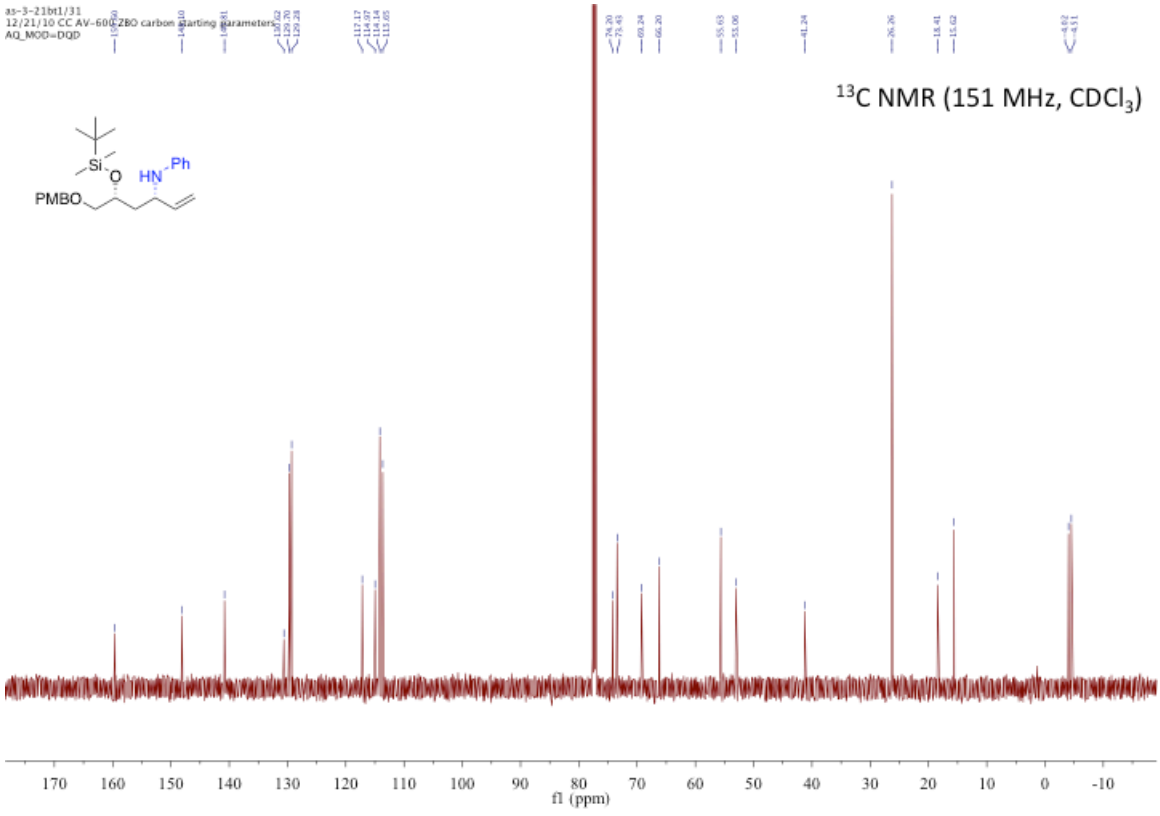


as-3-21at1/41
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

^{13}C NMR (151 MHz, $CDCl_3$)

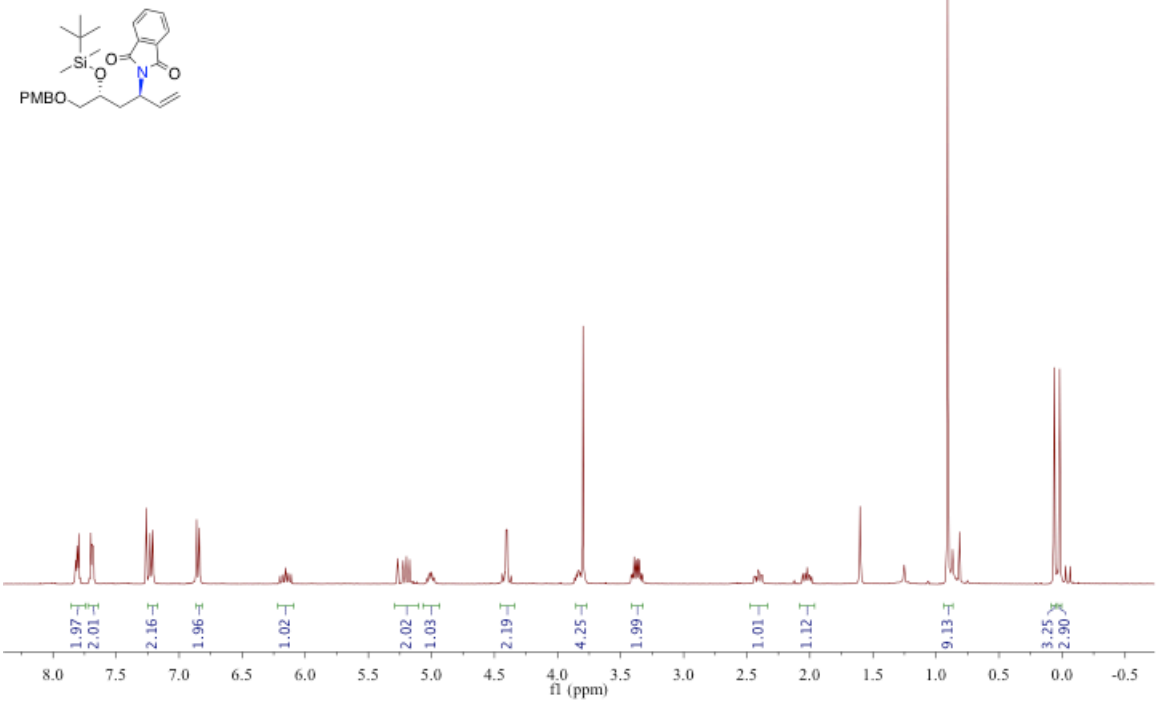



as-3-21bt1/30
AV-600 ZBO proton starting parameters 11/16/08 RN
^{1}H NMR (600 MHz, $CDCl_3$)
Si
O
HN
Ph
PMBO
1.86
1.92
1.96
0.95
1.94
1.00
0.97
0.97
2.08
0.82
0.98
0.99
3.09
2.51
0.89
1.09
1.97
9.27
2.91
2.84
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


as-3-21bt1/31
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
Si
O
HN
Ph
PMBO
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

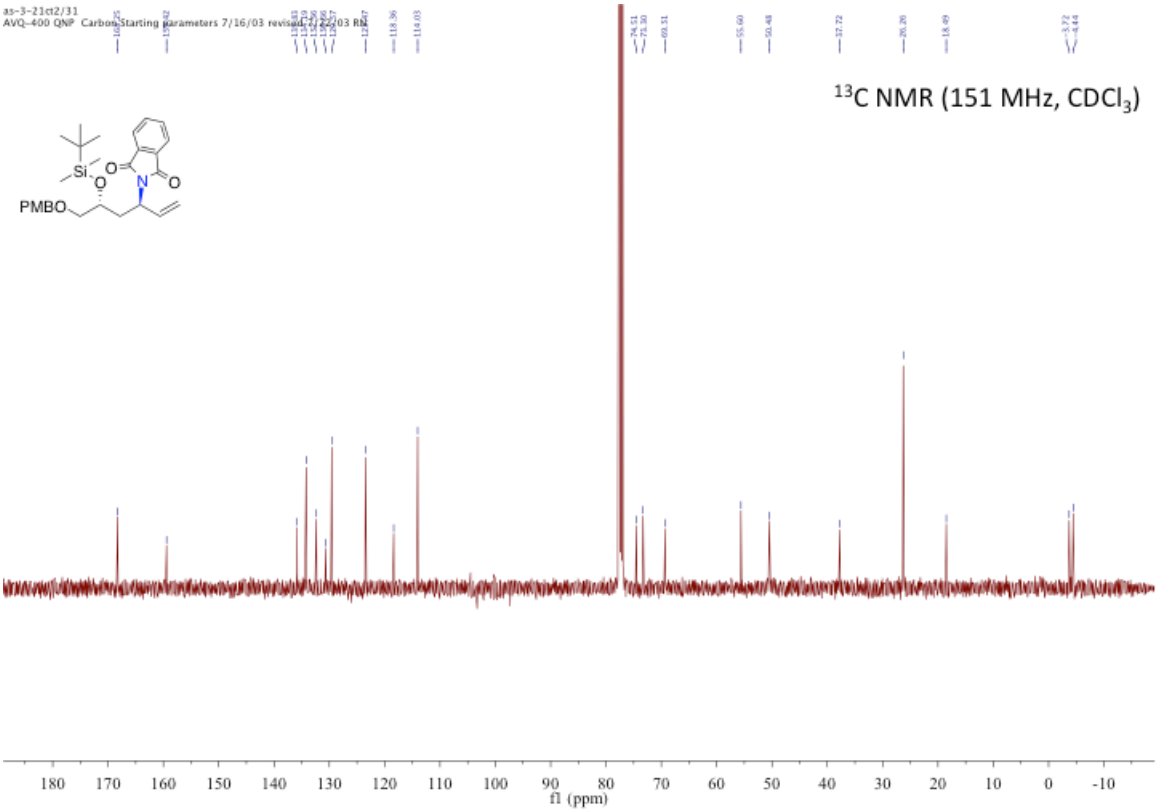
as-3-21ct2/30
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

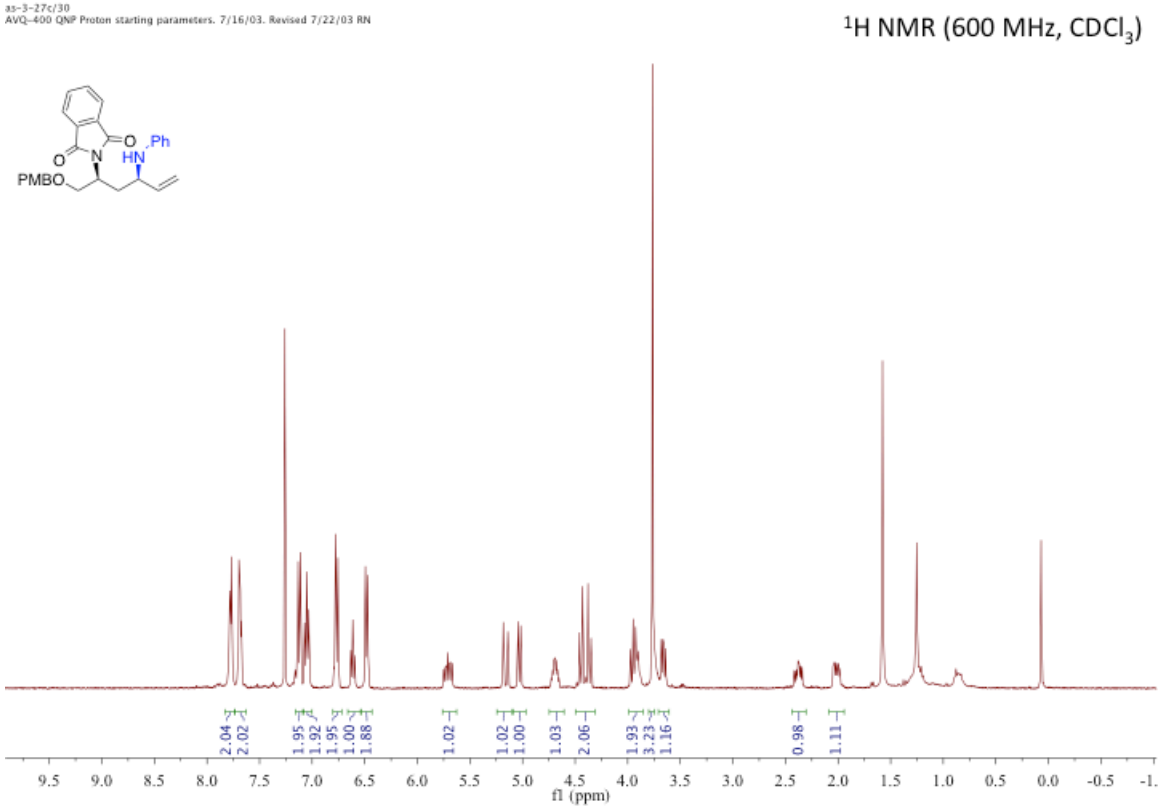
^{1}H NMR (600 MHz, $CDCl_3$)

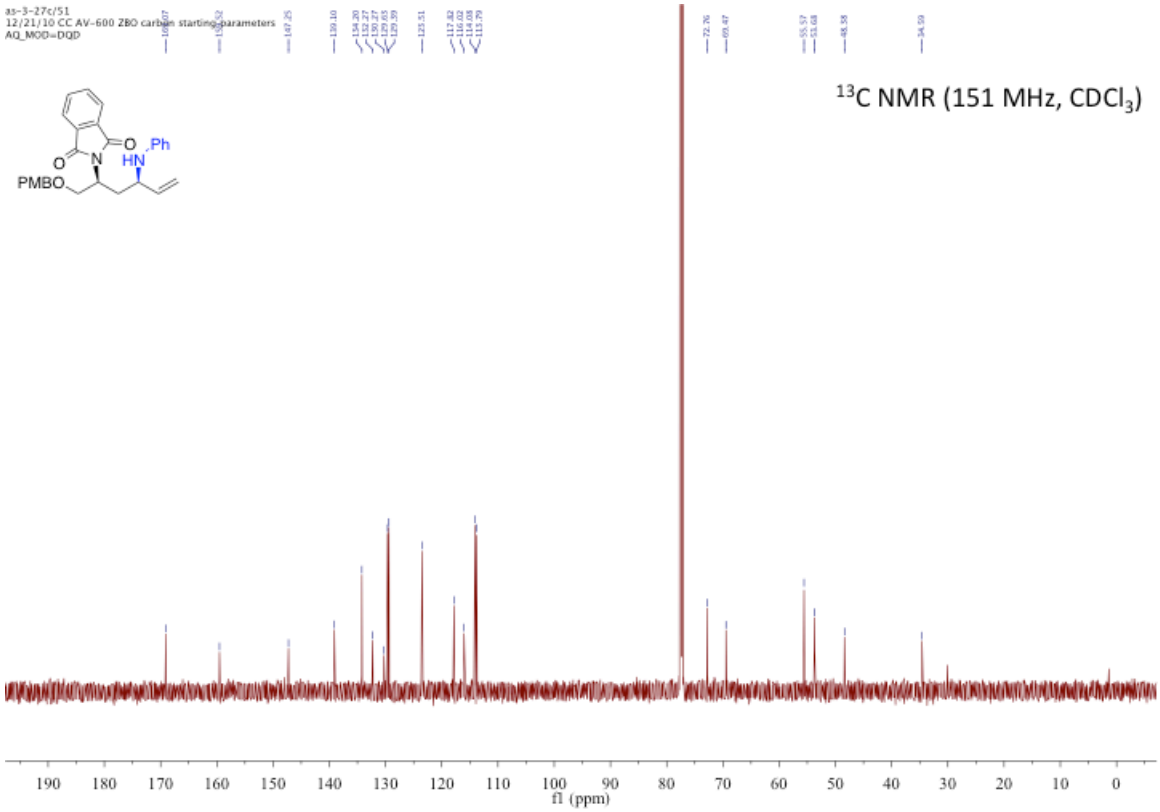


as-3-21ct2/31
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN

^{13}C NMR (151 MHz, $CDCl_3$)

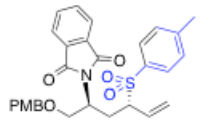



as-3-27c/30
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
^{1}H NMR (600 MHz, $CDCl_3$)
PMBO
Ph
HN
2.04
2.02
1.95
1.92
1.95
1.00
1.88
1.02
1.02
1.00
1.03
2.06
1.93
3.23
1.16
0.98
1.11
f1 (ppm)


as-3-27c/51
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
PMBO
Ph
HN
f1 (ppm)

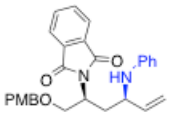
as-3-27bbt/40
AV-600 ZBO proton starting parameters 11/16/08 RN

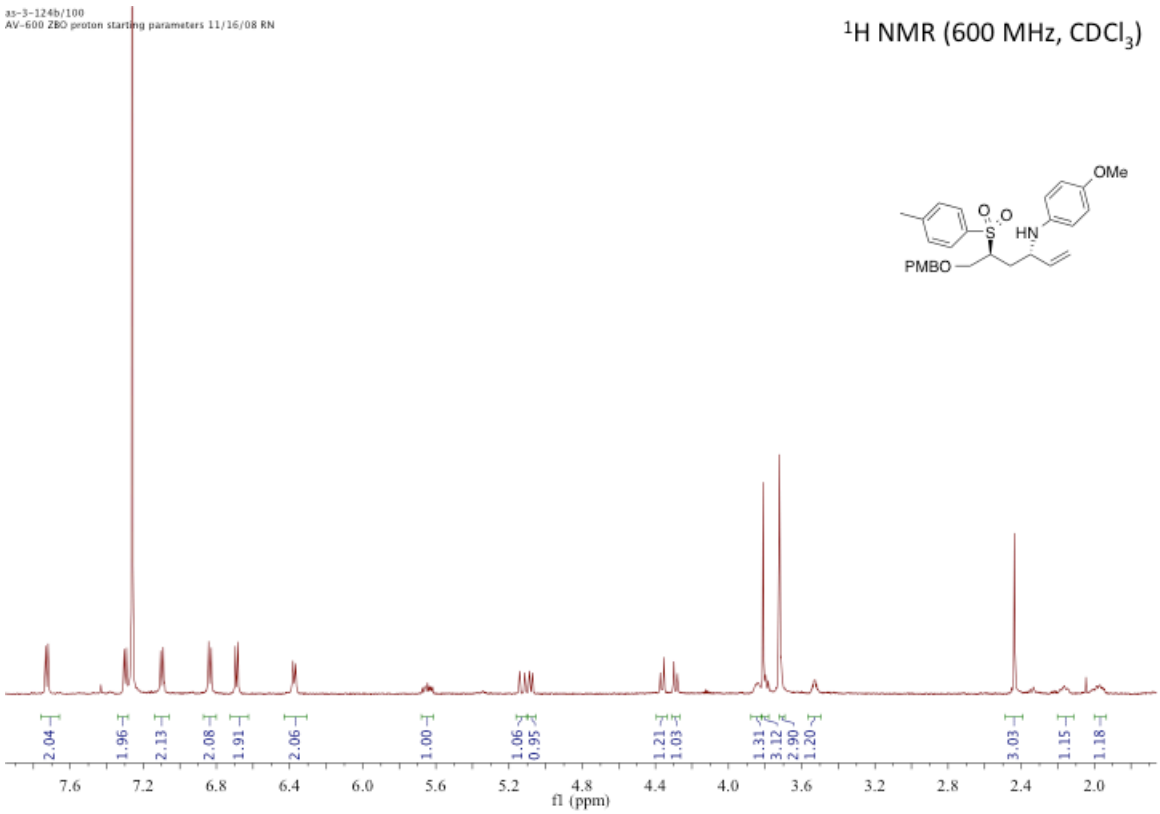
^{1}H NMR (600 MHz, $CDCl_3$)

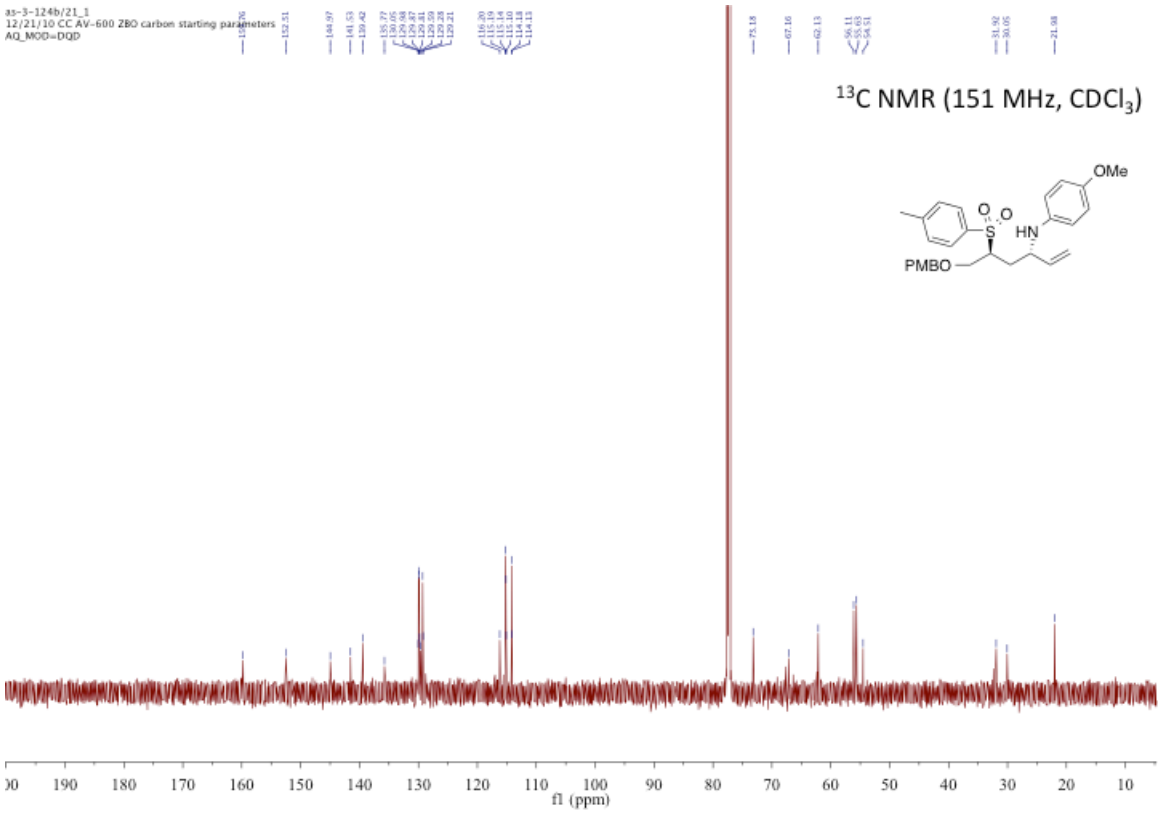


as-3-27c/51
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

^{13}C NMR (151 MHz, $CDCl_3$)

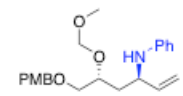


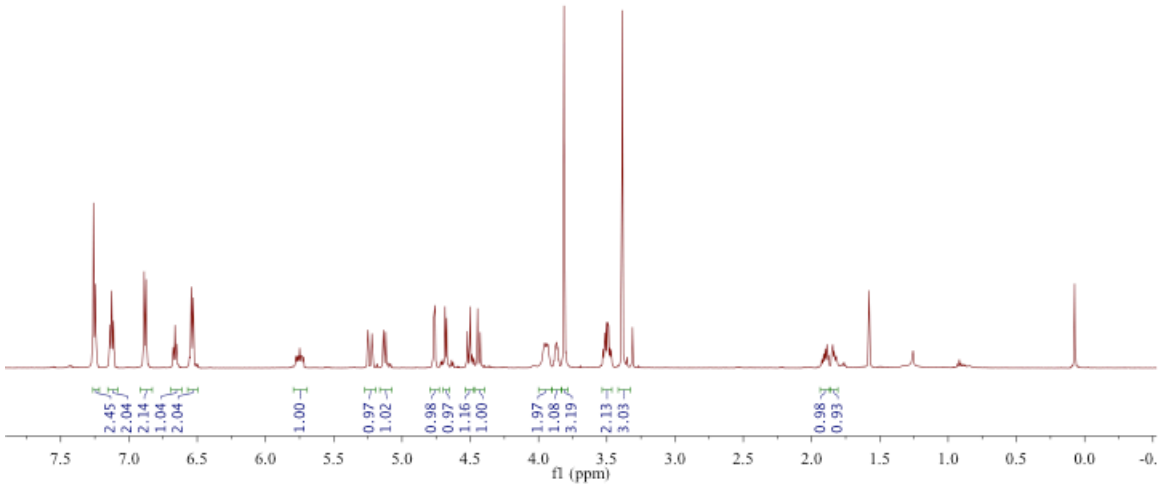

as-3-124b/100
AV-600 ZBO proton starting parameters 11/16/08 RN
^{1}H NMR (600 MHz, $CDCl_3$)
OMe
HN
PMBO
2.04
1.96
2.13
2.08
1.91
2.06
1.00
1.06
0.95
1.21
1.03
1.31
3.12
2.90
1.20
3.03
1.15
1.18
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
f1 (ppm)


as-3-124b/21_1
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
OMe
HN
PMBO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

as-3-mo/31
AV-600 ZBO proton starting parameters 11/16/08 RN

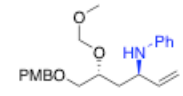
^{1}H NMR (600 MHz, $CDCl_3$)





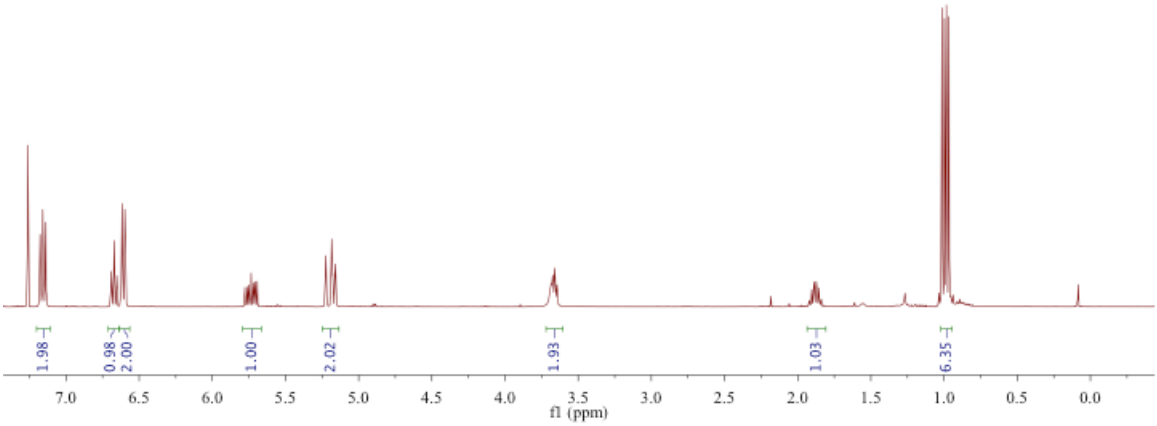
as-3-mo/32
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

^{13}C NMR (151 MHz, $CDCl_3$)



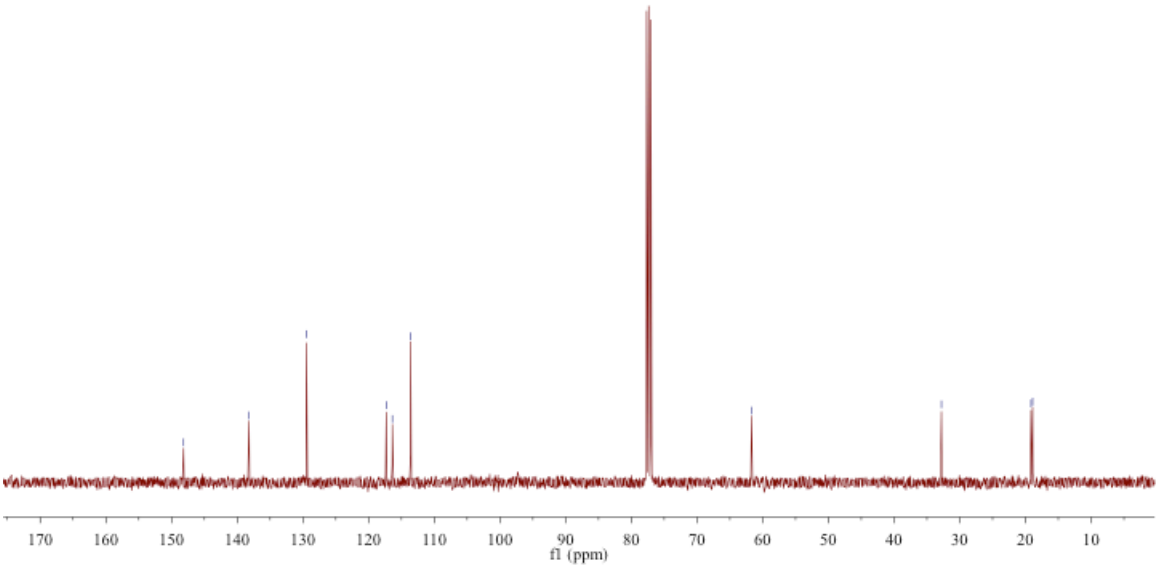
as-5b/80
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

^{1}H NMR (400 MHz, $CDCl_3$)



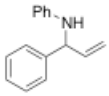
as-5b/81
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN

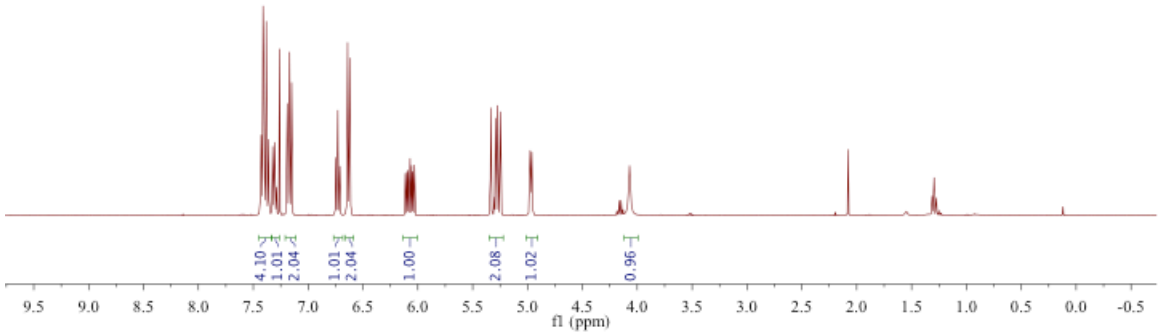
^{13}C NMR (101 MHz, $CDCl_3$)



as-phnh2/2
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

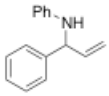
^{1}H NMR (400 MHz, $CDCl_3$)

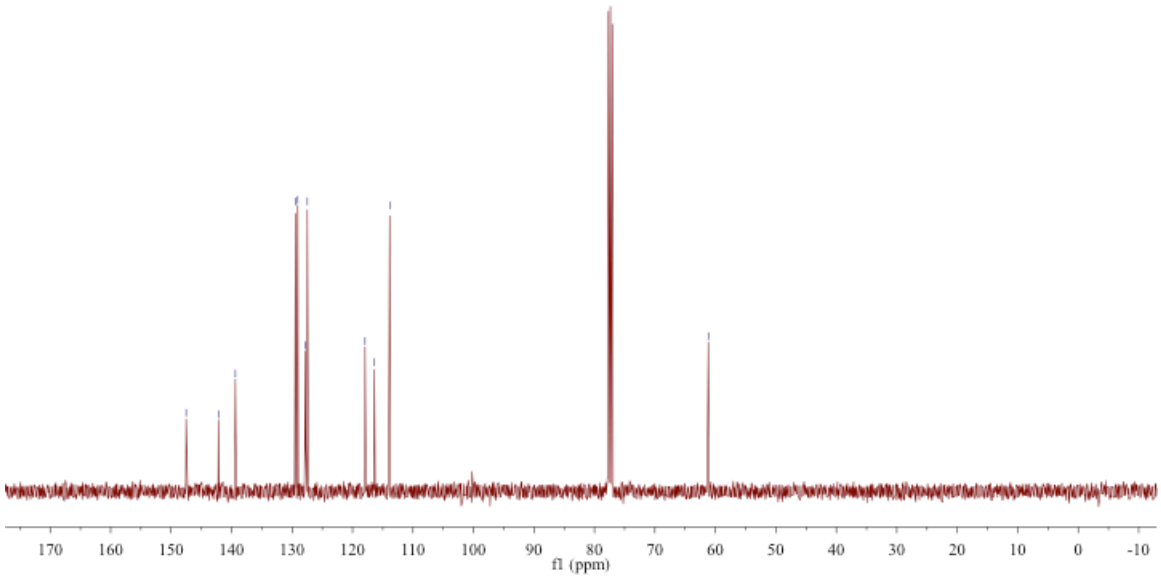




as-phnh2/3
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN

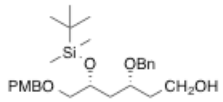
^{13}C NMR (101 MHz, $CDCl_3$)

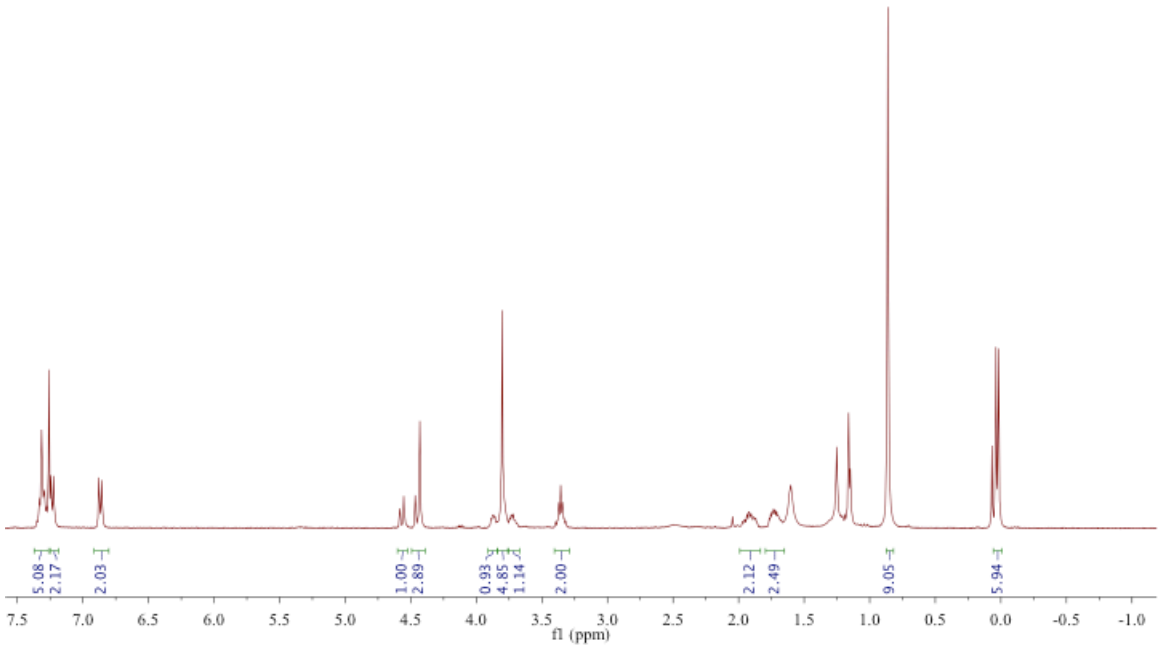




as-3-156/510
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

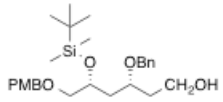
^{1}H NMR (400 MHz, $CDCl_3$)

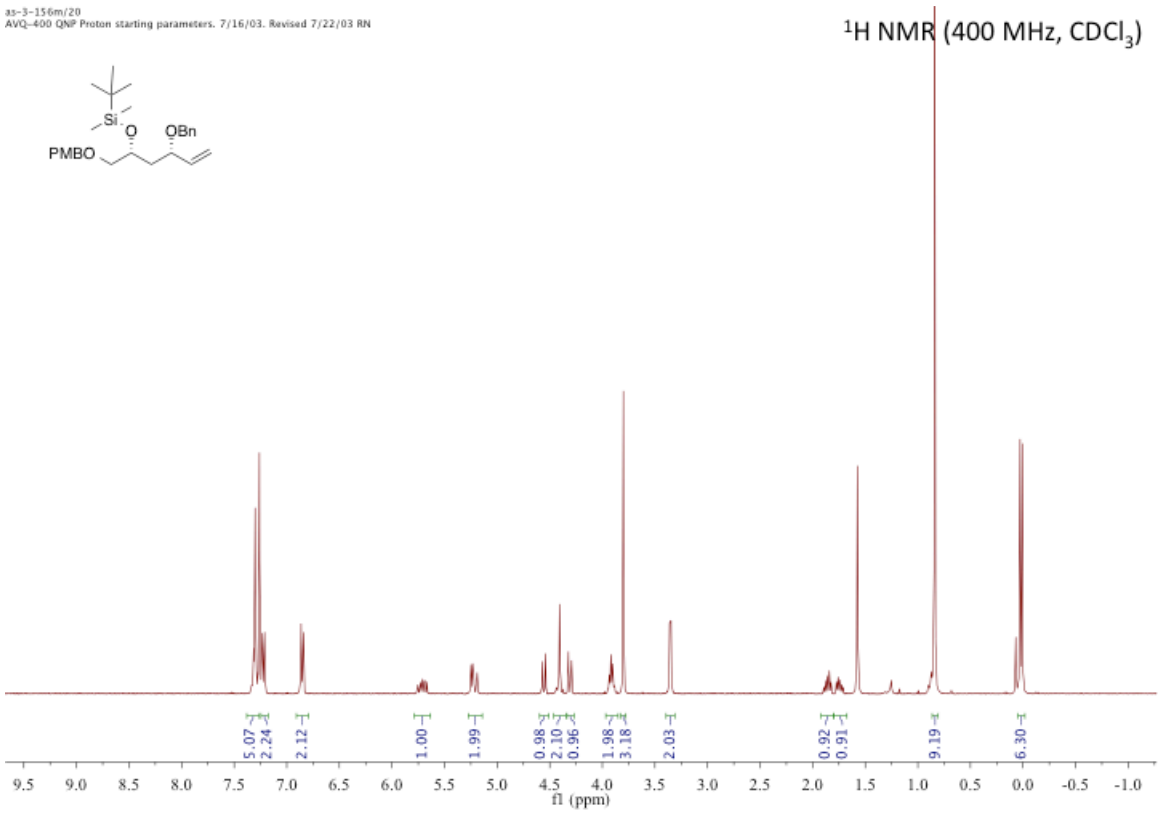


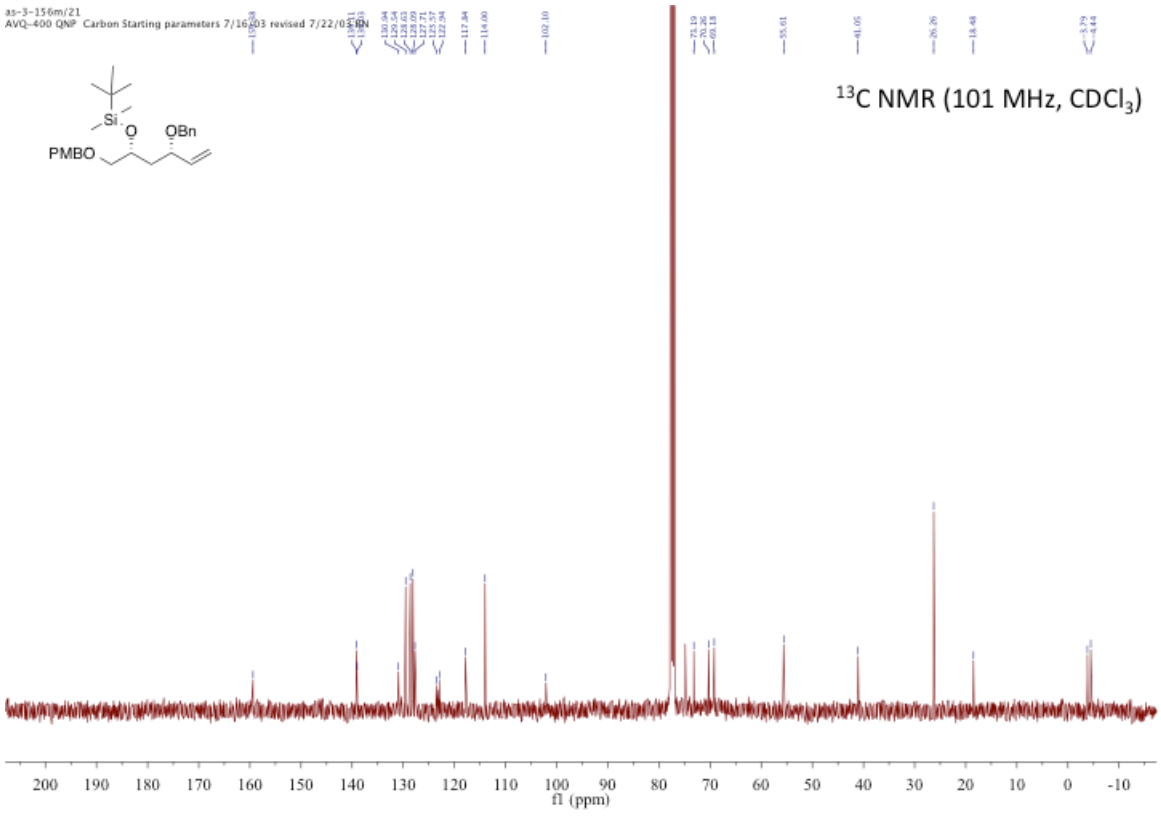


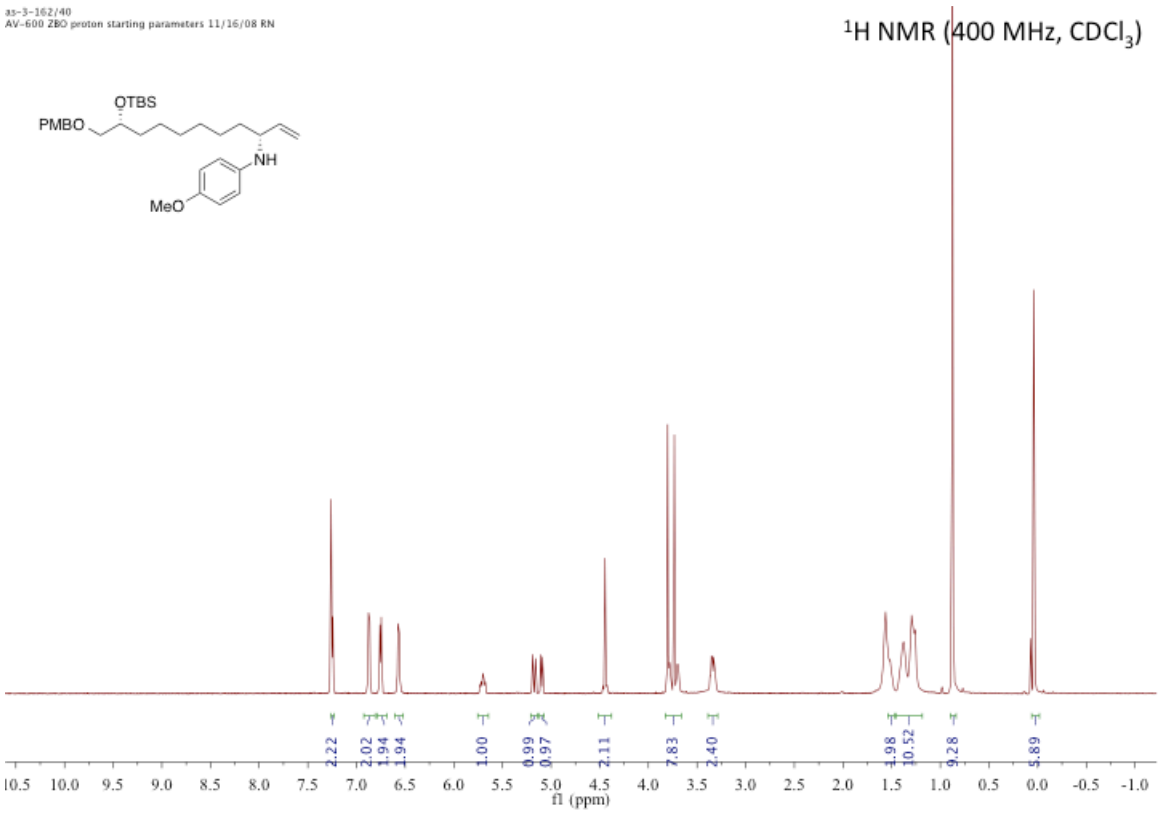
as-3-156/511
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN

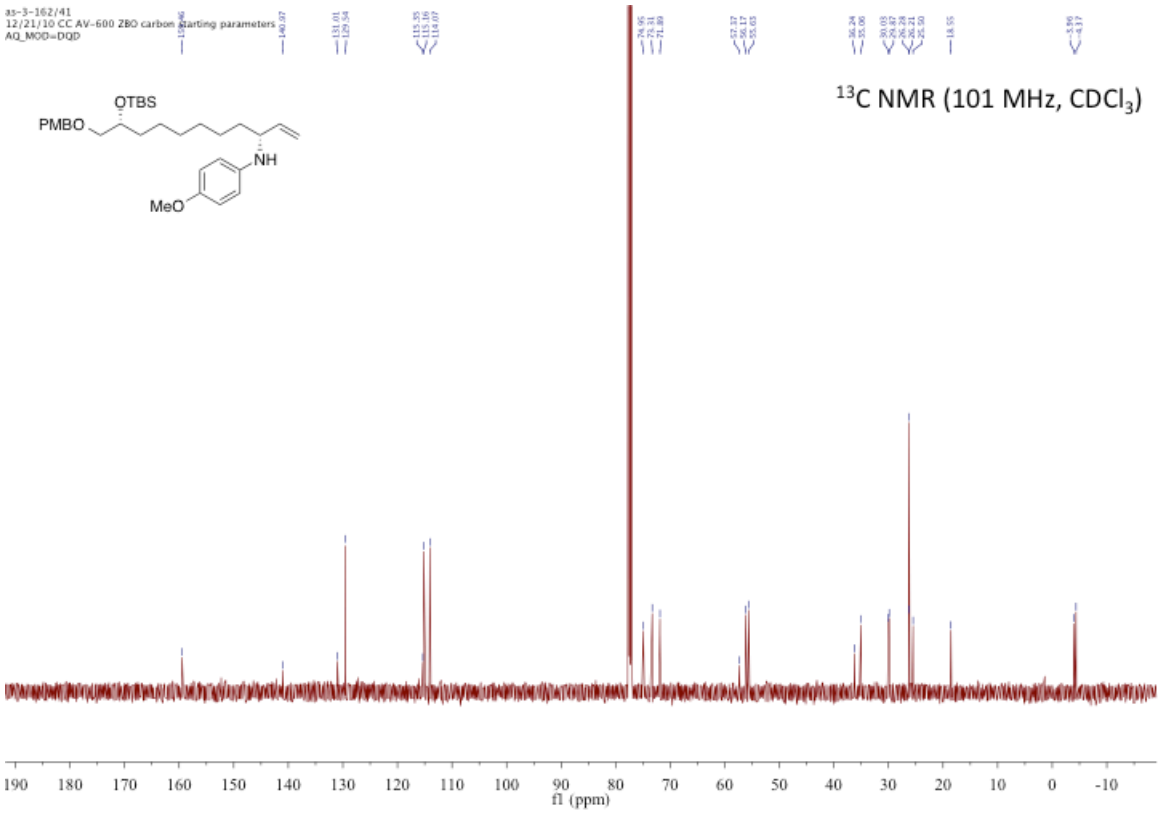
^{13}C NMR (101 MHz, $CDCl_3$)

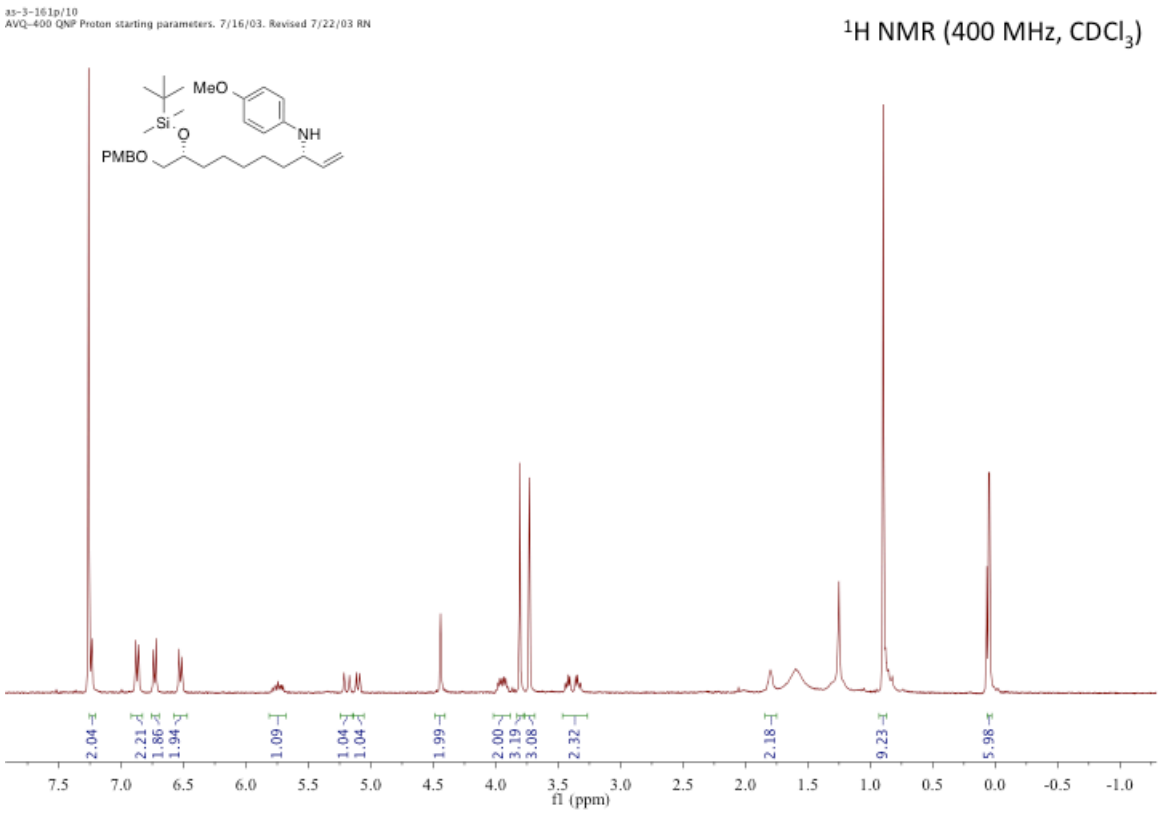


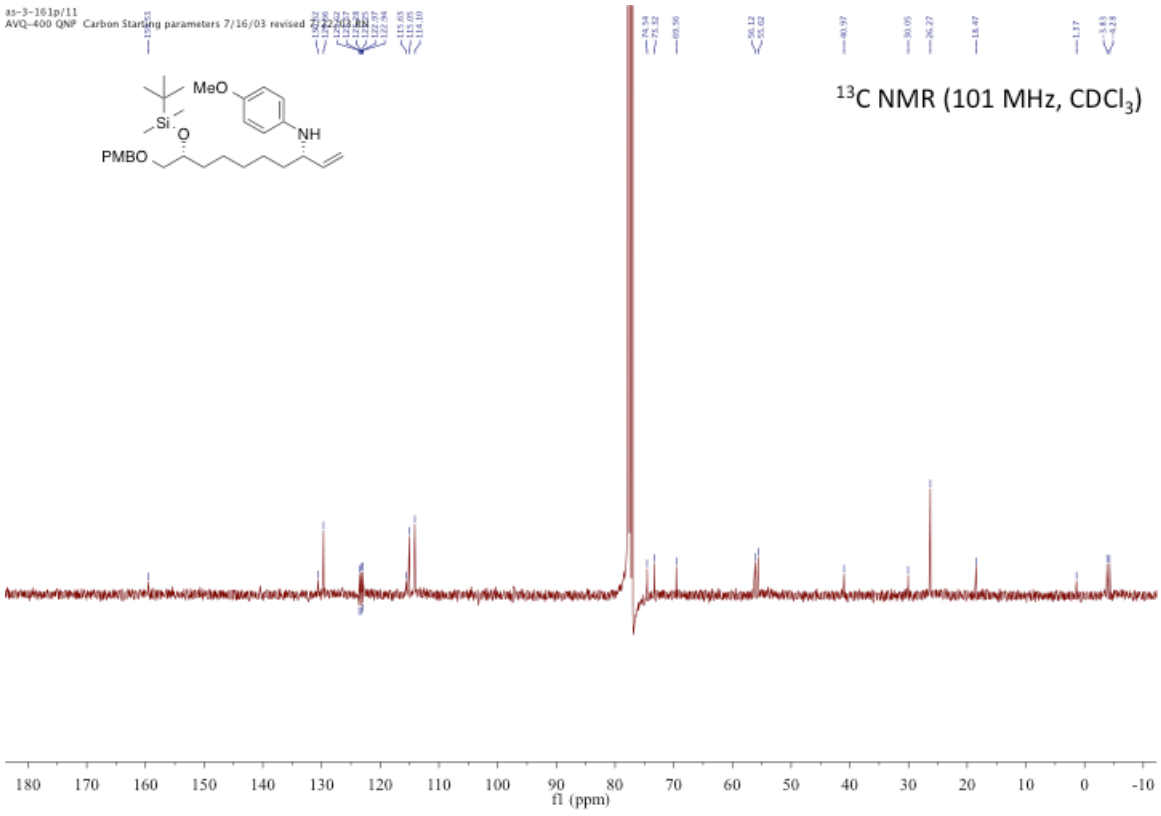

as-3-156m/20
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
^{1}H NMR (400 MHz, $CDCl_3$)
Si
O
OBn
PMBO
5.07
2.24
2.12
1.00
1.99
0.98
2.10
0.96
1.98
3.18
2.03
0.92
0.91
9.19
6.30
f1 (ppm)

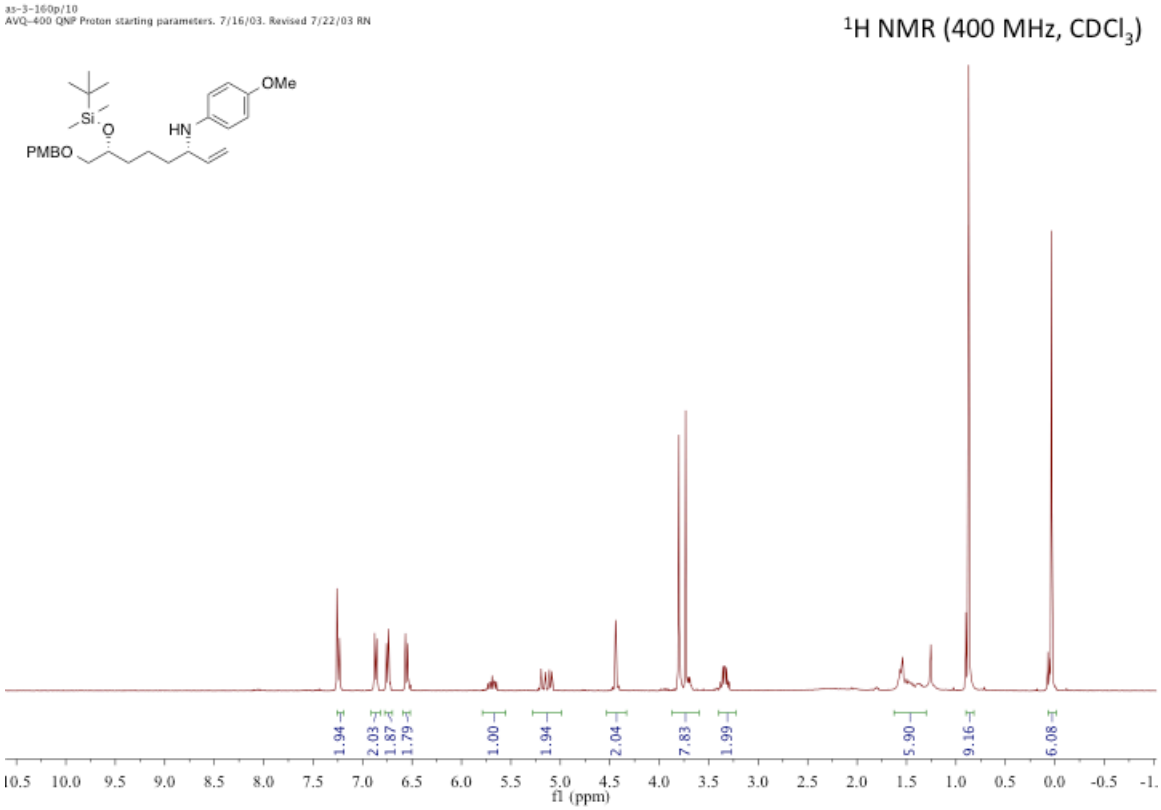

as-3-156m/21
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
^{13}C NMR (101 MHz, $CDCl_3$)
Si
O
OBn
PMBO
f1 (ppm)

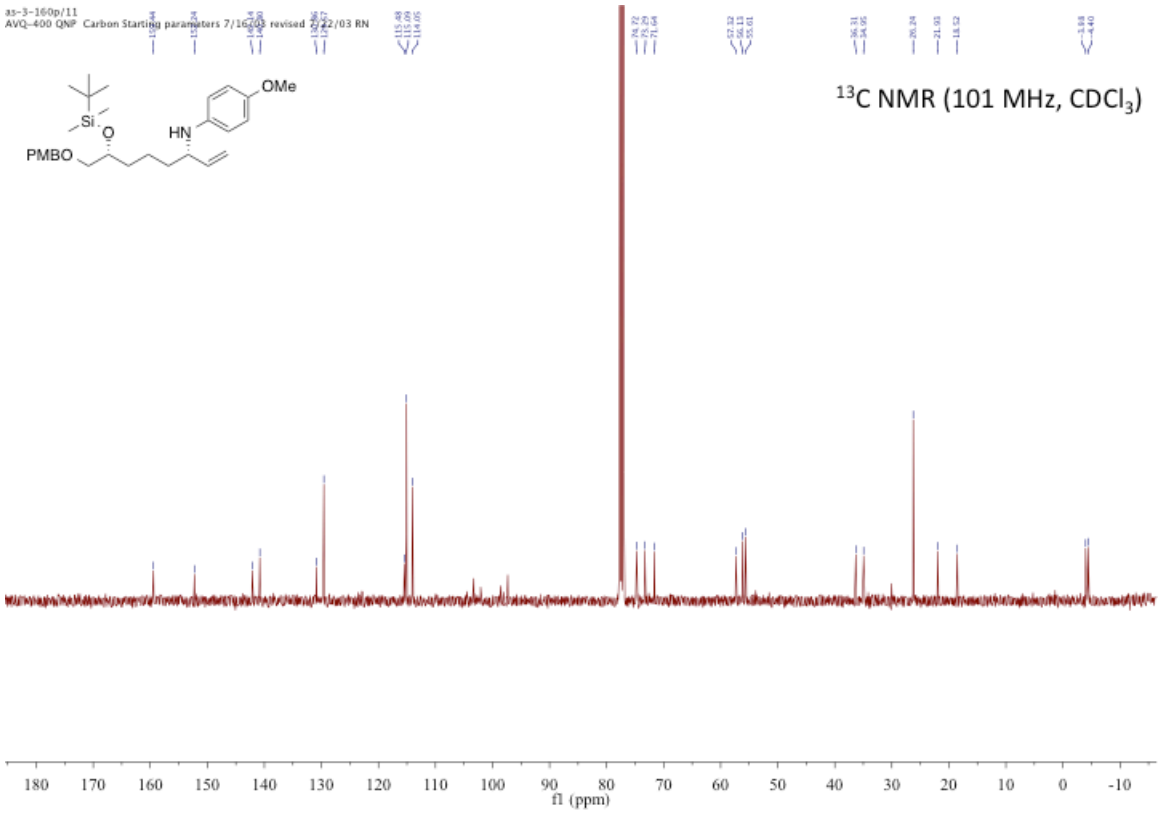

as-3-162/40
AV-600 ZBO proton starting parameters 11/16/08 RN
^{1}H NMR (400 MHz, $CDCl_3$)
OTBS
PMBO
NH
MeO
2.22
2.02
1.94
1.94
1.00
0.99
0.97
2.11
2.83
2.40
1.98
10.52
9.28
5.89
f1 (ppm)


as-3-162/41
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (101 MHz, $CDCl_3$)
OTBS
PMBO
NH
MeO
f1 (ppm)


as-3-161p/10
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
Si
O
NH
PMBO
2.04
2.21
1.86
1.94
1.09
1.04
1.04
1.99
2.00
3.19
3.08
2.32
2.18
9.23
5.98
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

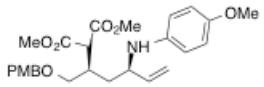

as-3-161p/11
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised
^{13}C NMR (101 MHz, $CDCl_3$)
MeO
Si
O
NH
PMBO
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

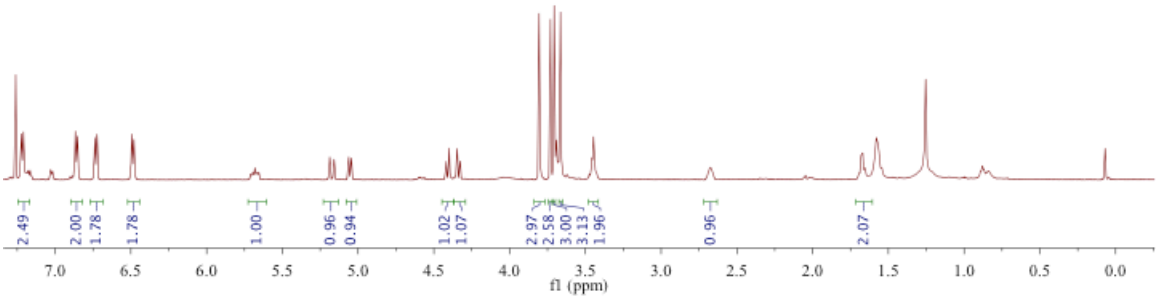

as-3-160p/10
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
^{1}H NMR (400 MHz, $CDCl_3$)
OMe
Si
O
HN
PMBO
1.94
2.03
1.87
1.79
1.00
1.94
2.04
7.83
1.99
5.90
9.16
6.08
f1 (ppm)


as-3-160p/11
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN
^{13}C NMR (101 MHz, $CDCl_3$)
OMe
Si
O
HN
PMBO
f1 (ppm)

as-3-139f/40
AV-600 ZBO proton starting parameters 11/16/08 RN

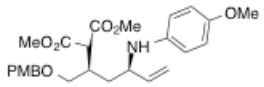
^{1}H NMR (600 MHz, $CDCl_3$)





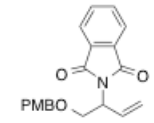
as-3-139f/42
12/21/10 CCAV-600 ZBO carbon starting parameters
AQ_MOD=PROB

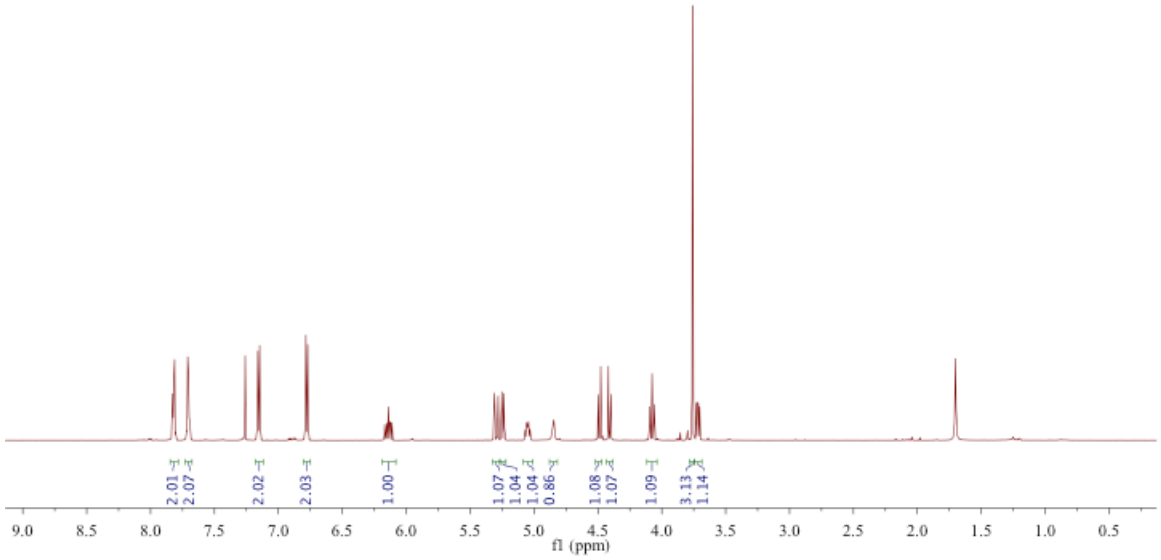
^{13}C NMR (151 MHz, $CDCl_3$)



as-3-131b/10
AV-600 ZBO proton starting parameters 11/16/08 RN

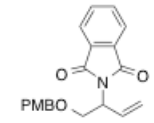
^{1}H NMR (600 MHz, $CDCl_3$)

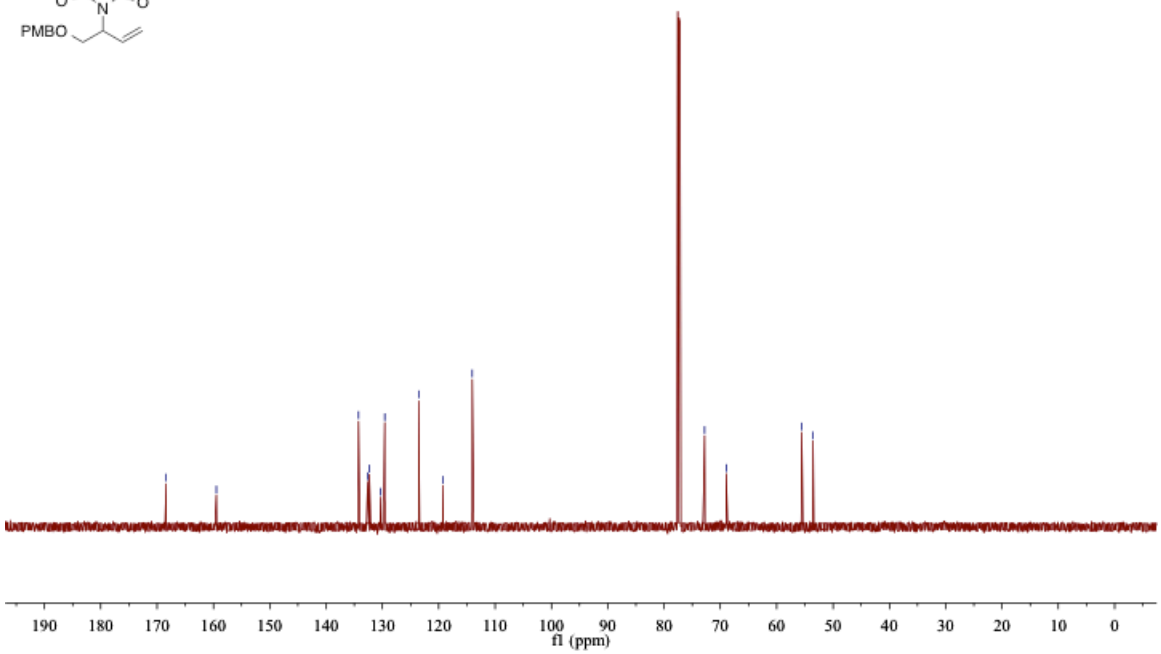




as-3-131b/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

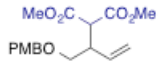
^{13}C NMR (151 MHz, $CDCl_3$)

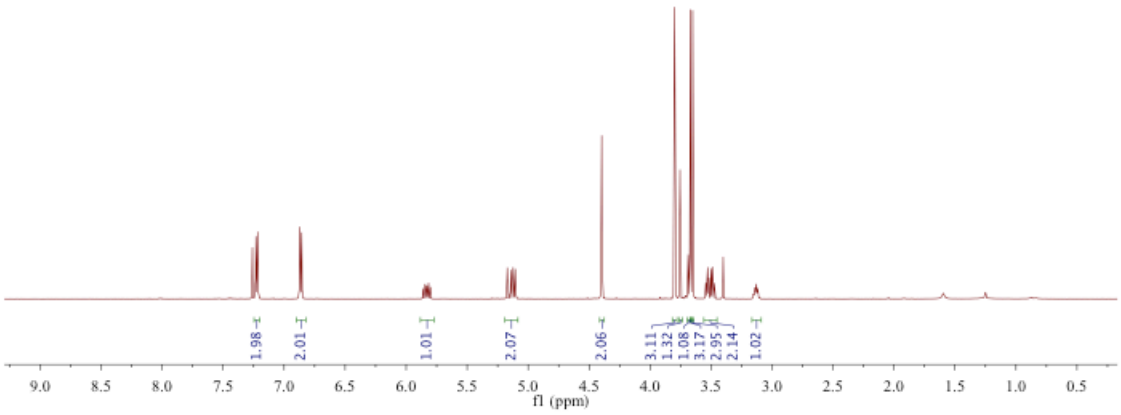




as-3-131c/10
AV-600 ZBO proton starting parameters 11/16/08 RN

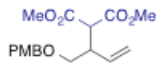
^{1}H NMR (600 MHz, $CDCl_3$)





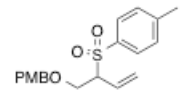
as-3-131c/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

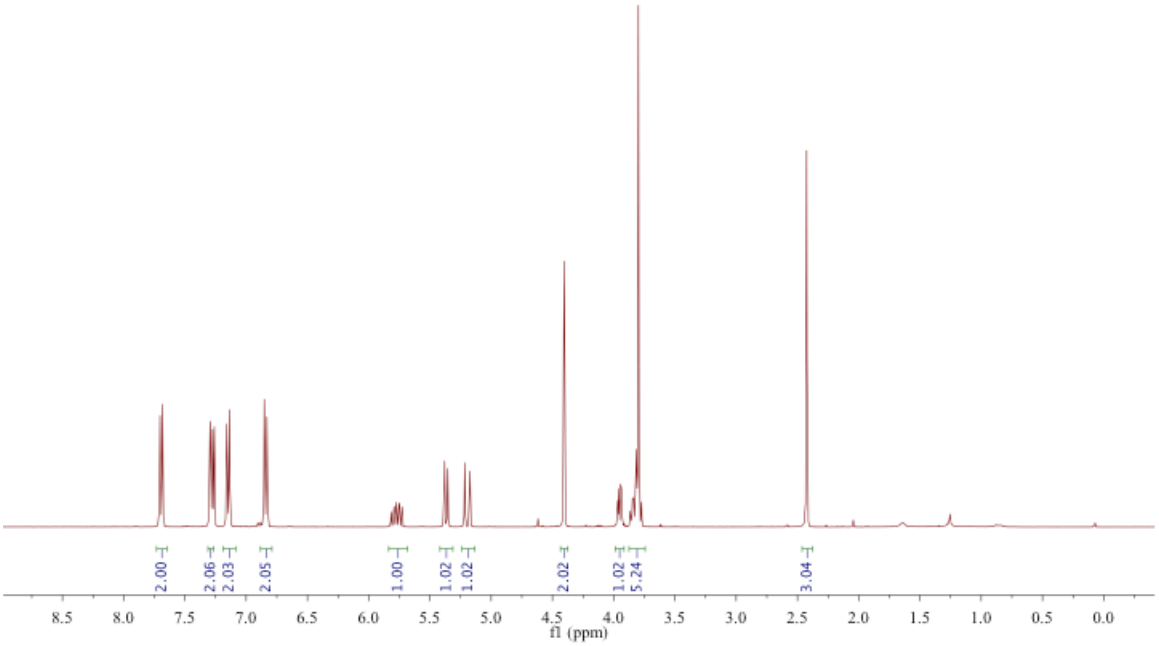
^{13}C NMR (151 MHz, $CDCl_3$)



as-3-137b/10
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

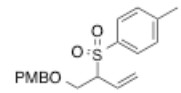
^{1}H NMR (400 MHz, $CDCl_3$)

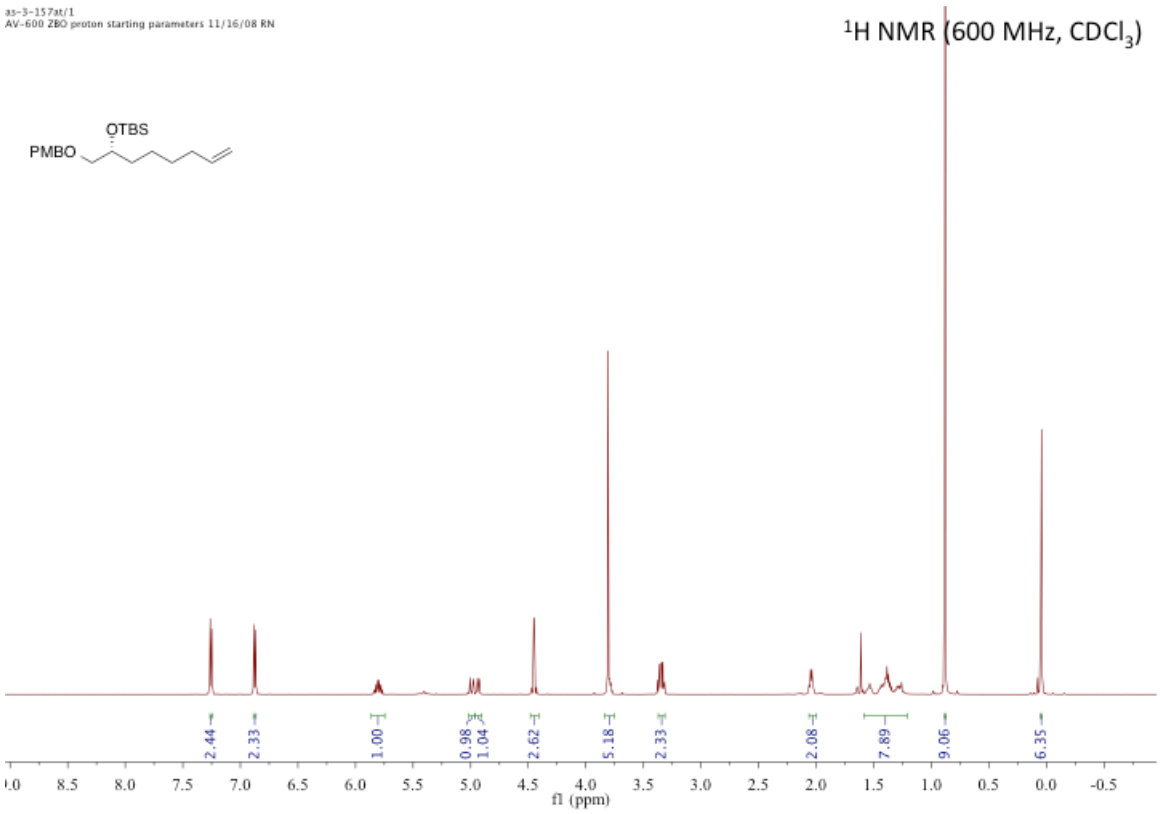


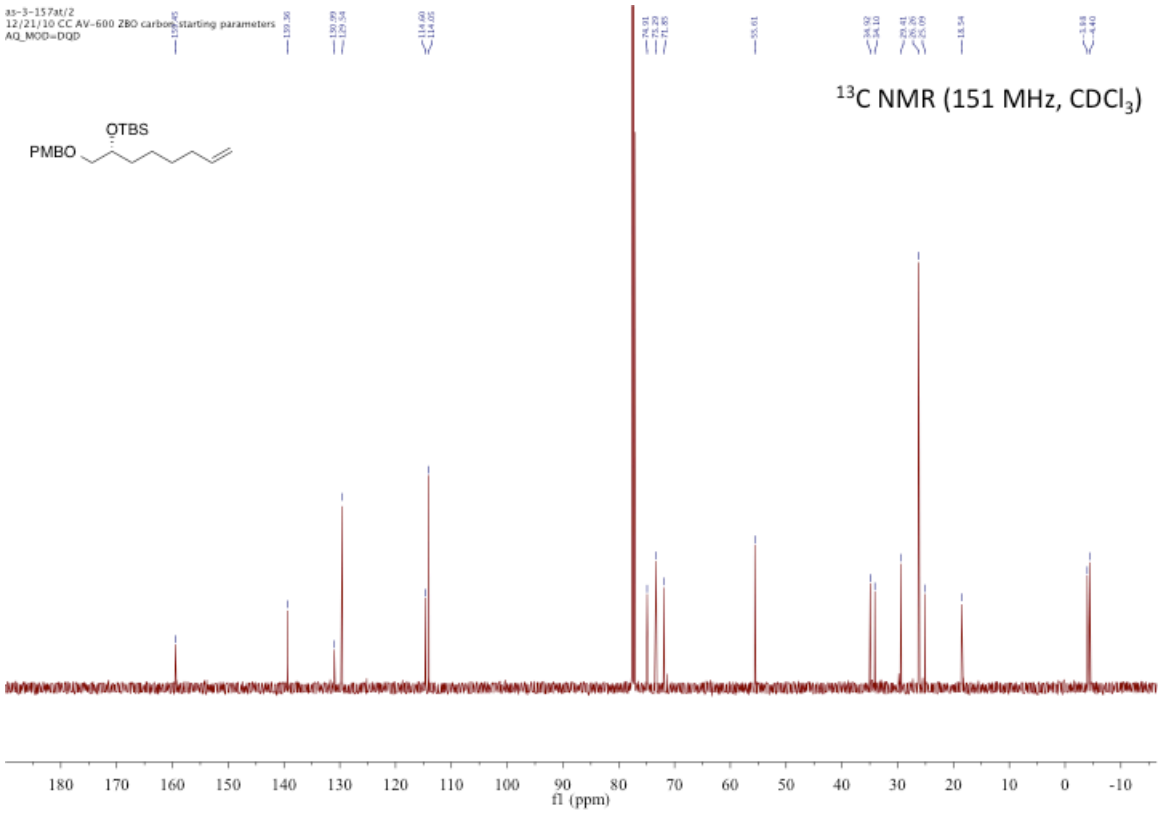


as-3-137b/11
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN

^{13}C NMR (101 MHz, $CDCl_3$)

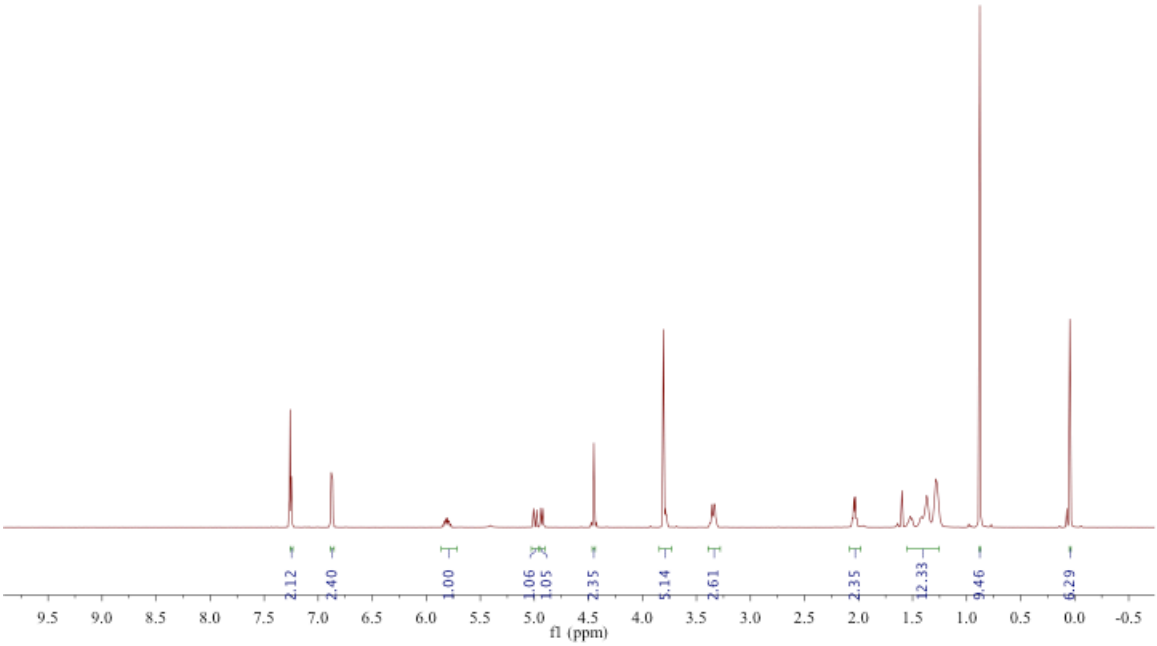



as-3-157at/1
AV-600 ZBO proton starting parameters 11/16/08 RN
^{1}H NMR (600 MHz, $CDCl_3$)
OTBS
PMBO
2.44
2.33
1.00
0.98
1.04
2.62
5.18
2.33
2.08
7.89
9.06
6.35
f1 (ppm)


as-3-157at/2
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
^{13}C NMR (151 MHz, $CDCl_3$)
OTBS
PMBO
f1 (ppm)

as-3-161s/1
AV-600 ZBO proton starting parameters 11/16/08 RN

^{1}H NMR (600 MHz, $CDCl_3$)

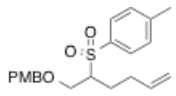


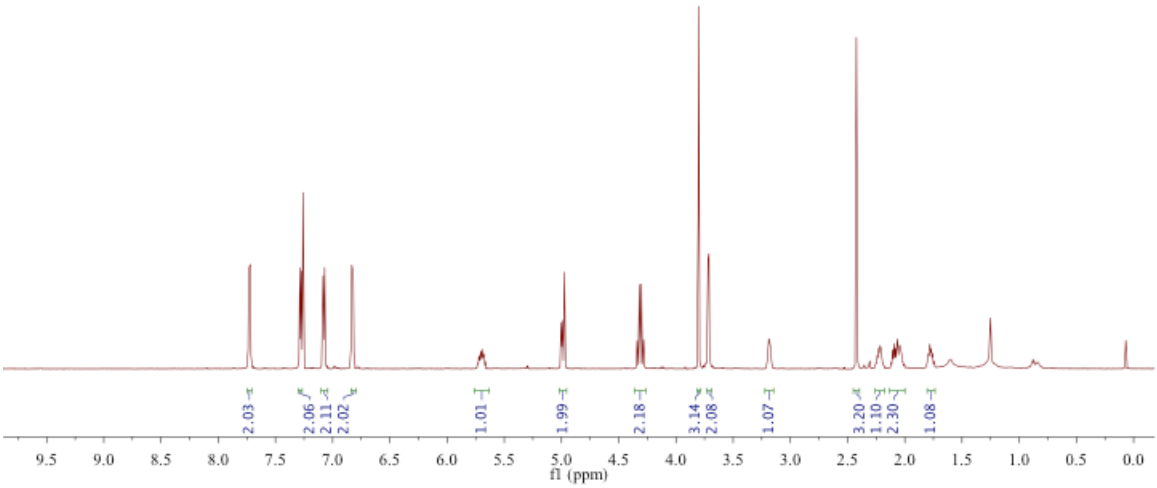
as-3-161s/2
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

^{13}C NMR (151 MHz, $CDCl_3$)

as-3-138b/10
AV-600 ZBO proton starting parameters 11/16/08 RN

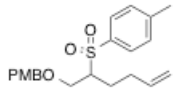
^{1}H NMR (600 MHz, $CDCl_3$)



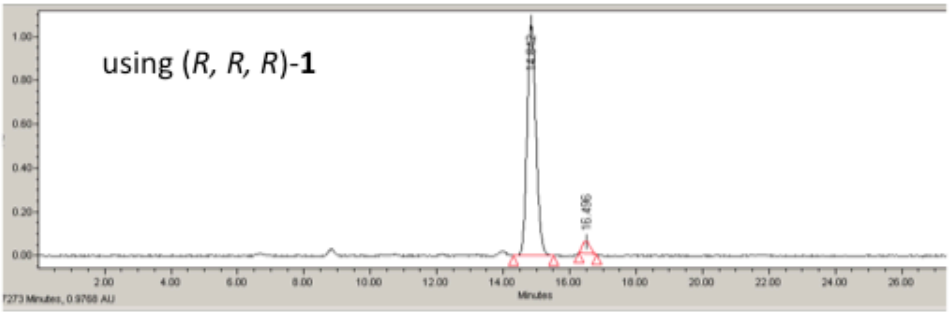


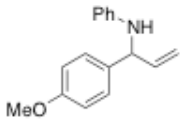
as-3-138b/11
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD

^{13}C NMR (151 MHz, $CDCl_3$)

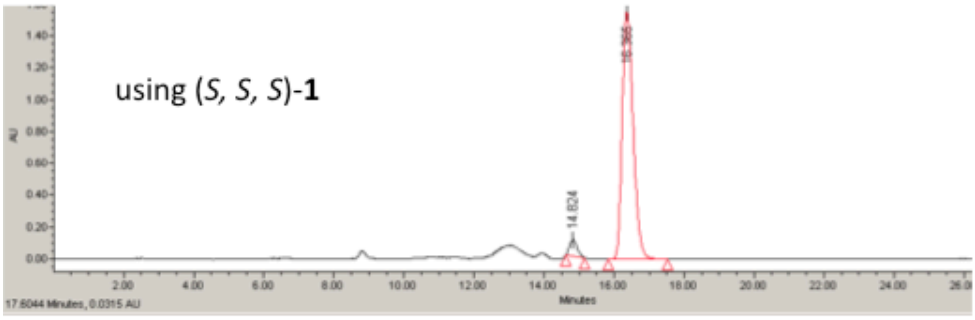


HPLC DATA:

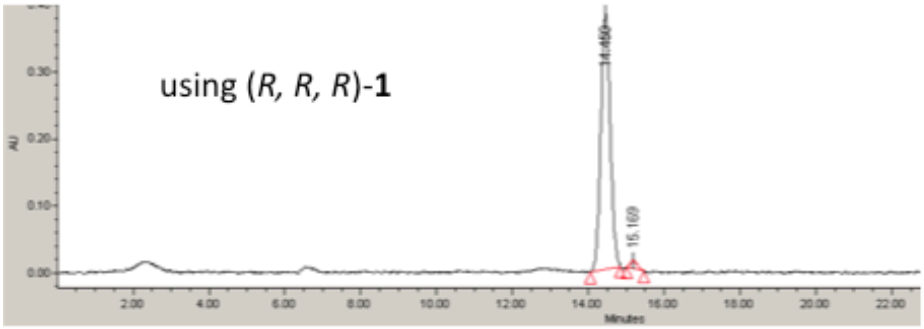


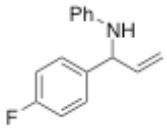


	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height
1		14.842	Unknown	19661784	95.77	1062492	95.14
2		16.496	Unknown	869427	4.23	54222	4.86

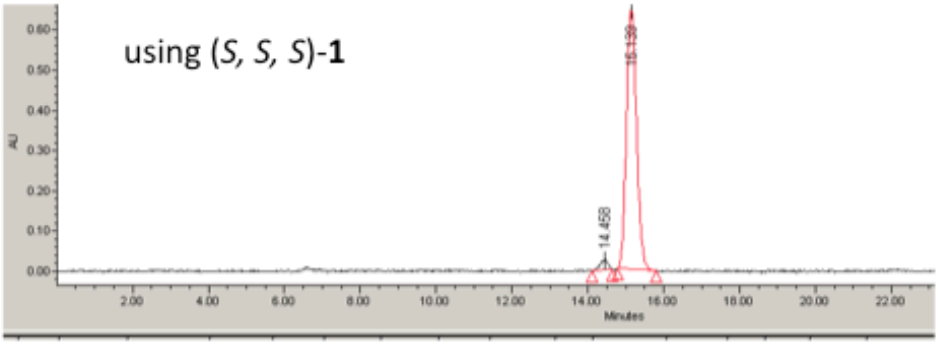


[(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]



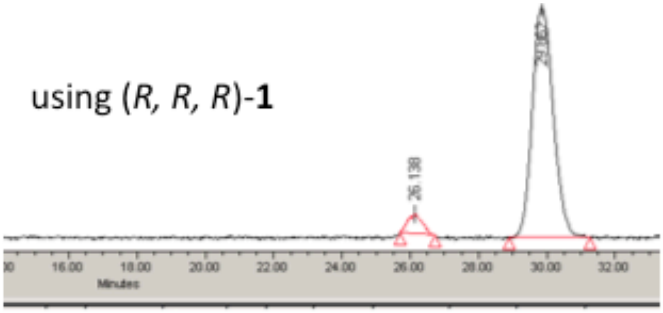


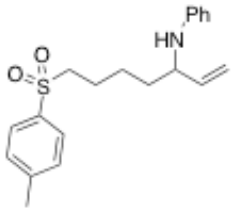
	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height
1		14.450	Unknown	6619686	97.60	384315	96.90
2		15.169	Unknown	162876	2.40	12291	3.10



[(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]

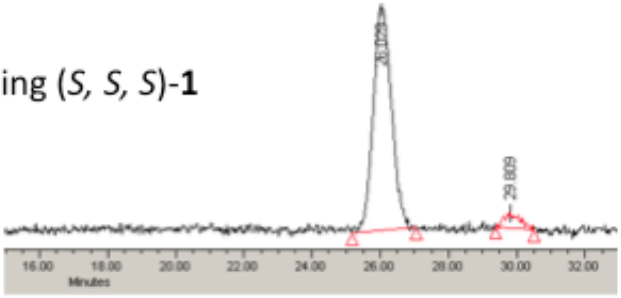
using (*R, R, R*)-**1**



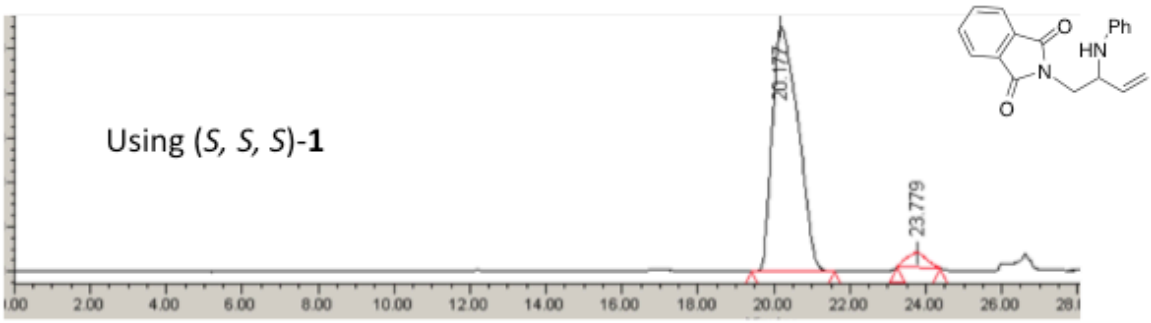


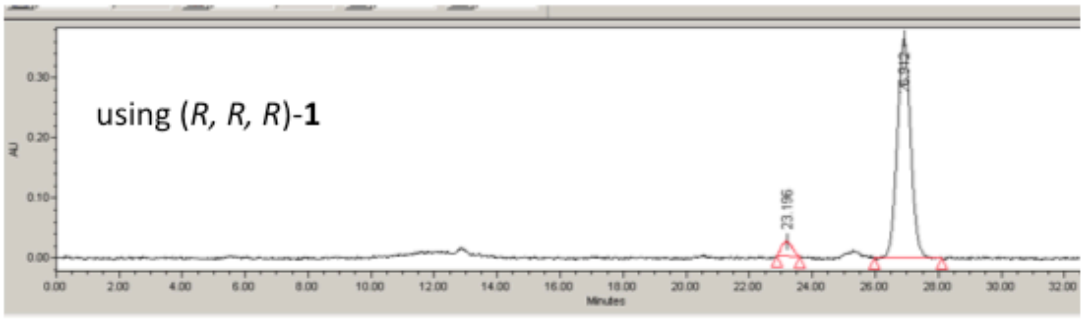
	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Amo
1		26.029	Unknown	3674094	94.63	99228	93.98	
2		29.809	Unknown	208525	5.37	6352	6.02	

using (*S, S, S*)-**1**



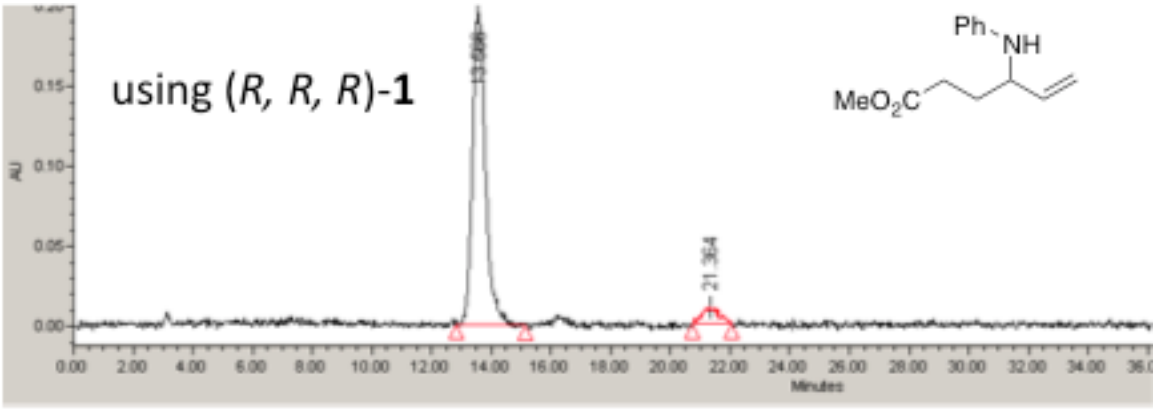
[(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 1.0 mL/min]



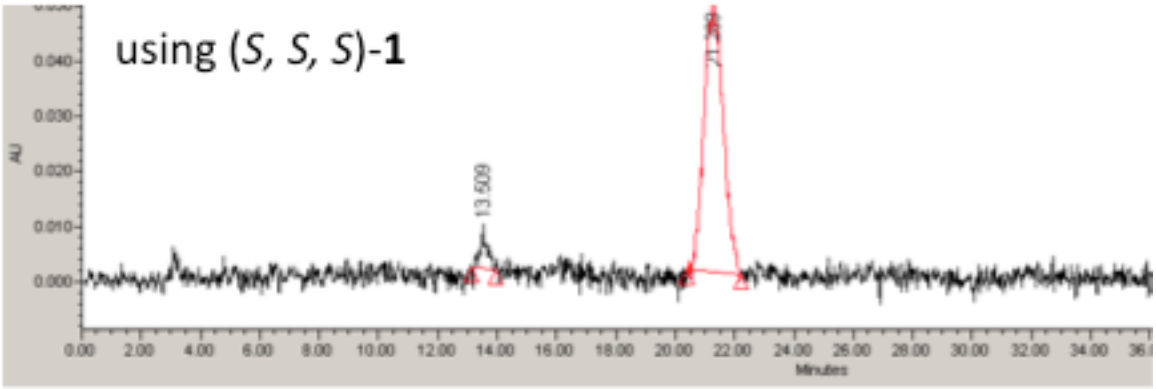


	Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height	Ar
1		23.196	Unknown	590913	5.13	25603	6.55	
2		26.912	Unknown	10917706	94.87	365298	93.45	

[(Chiralpak AD-H) hexane/*i*-PrOH, 90:10, 0.5 mL/min]

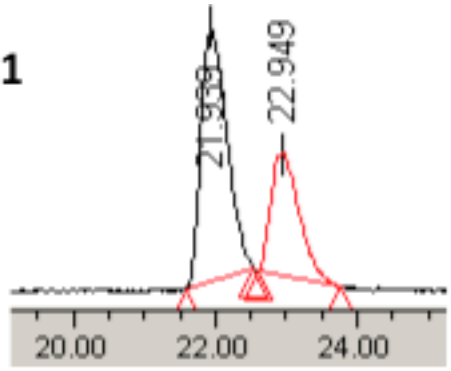


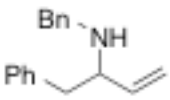
	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Ar
1		13.566	Unknown	5889876	93.85	194929	94.96	
2		21.364	Unknown	386279	6.15	10342	5.04	



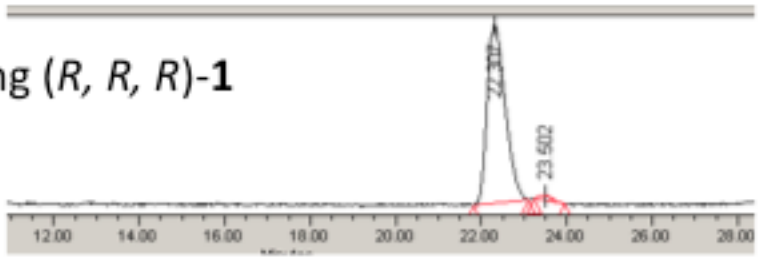
[(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 1.0 mL/min]

Using *rac*-**1**



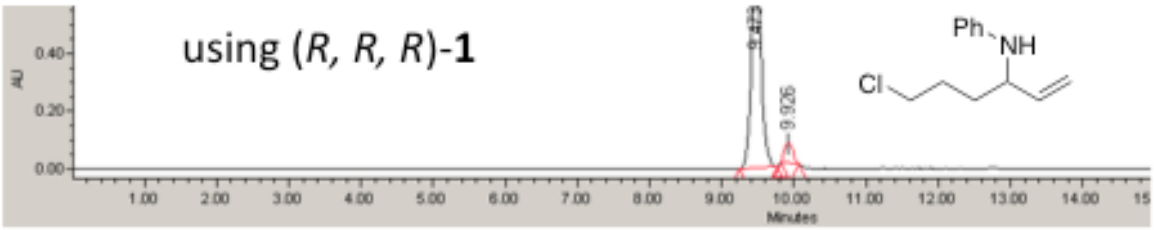


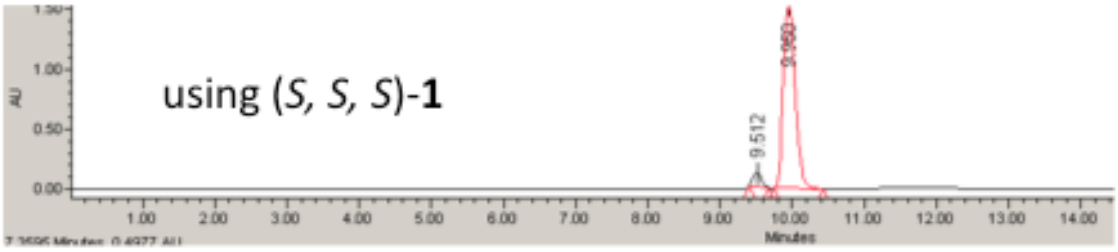
using (*R, R, R*)-**1**



	Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height	A
1		22.307	Unknown	8217120	98.37	285782	97.55	
2		23.502	Unknown	136375	1.63	7175	2.45	

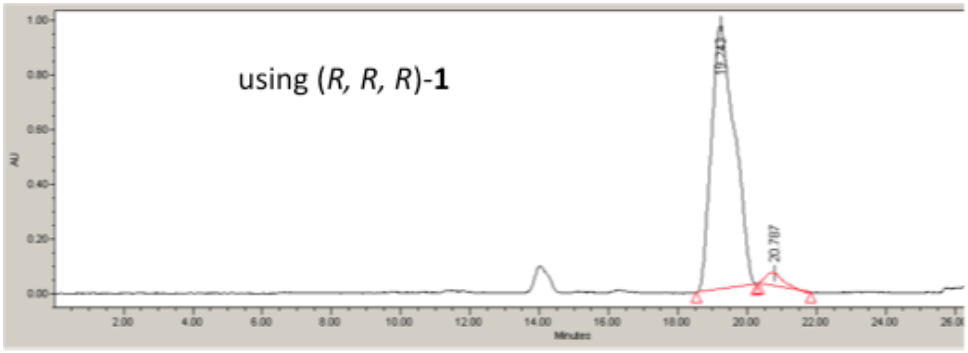
[(Chiralpak AD-H) hexane/*i*-PrOH, 99:1, 0.5 mL/min]

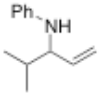




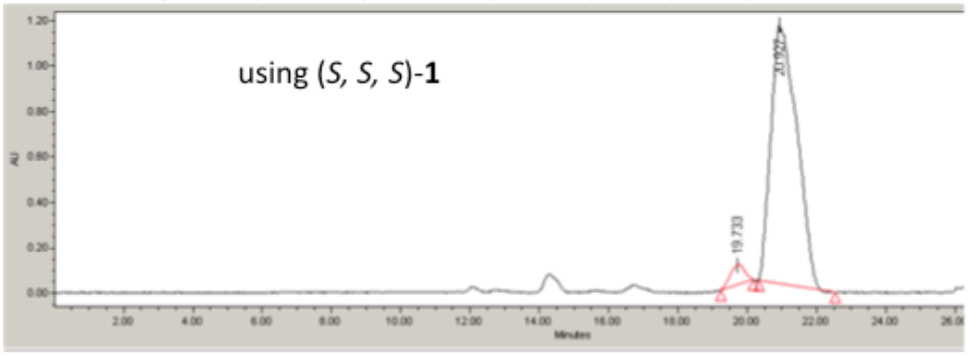
	Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height	Ar
1		9.512	Unknown	949099	5.19	115572	7.06	
2		9.950	Unknown	17346713	94.81	1520952	92.94	

[(Chiralpak AD-H) hexane/*i*-PrOH, 99.1:0.1, 0.5 mL/min]

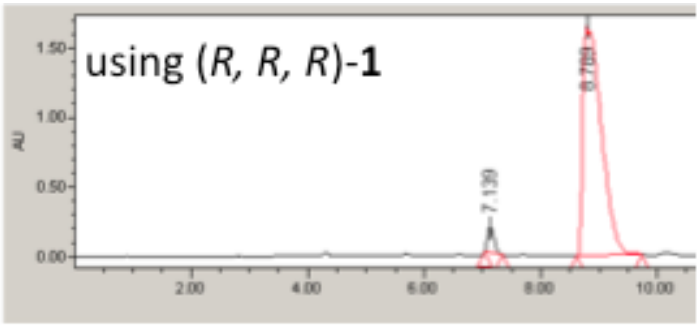


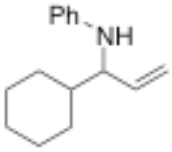


	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height
1		19.243	Unknown	44949844	96.36	971006	95.28
2		20.787	Unknown	1697140	3.64	48052	4.72

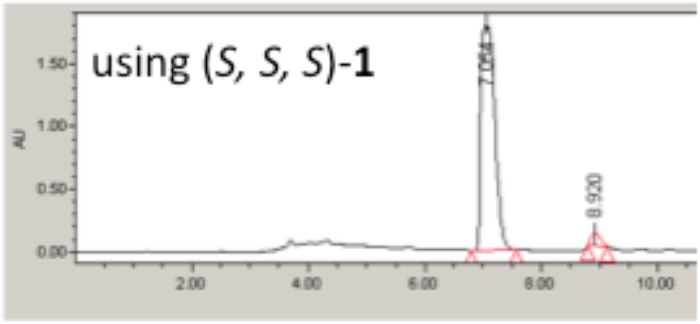


[(Chiralpak OD-H) hexane/*i*-PrOH, 99.1:0.1, 0.5 mL/min]

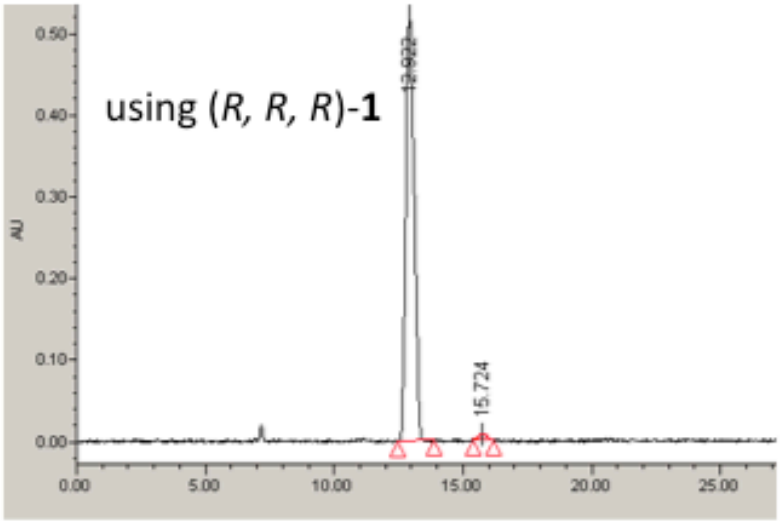


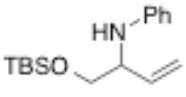


	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	A
1		7.139	Unknown	1493791	3.99	185042	10.12	
2		8.789	Unknown	35983298	96.01	1643554	89.88	

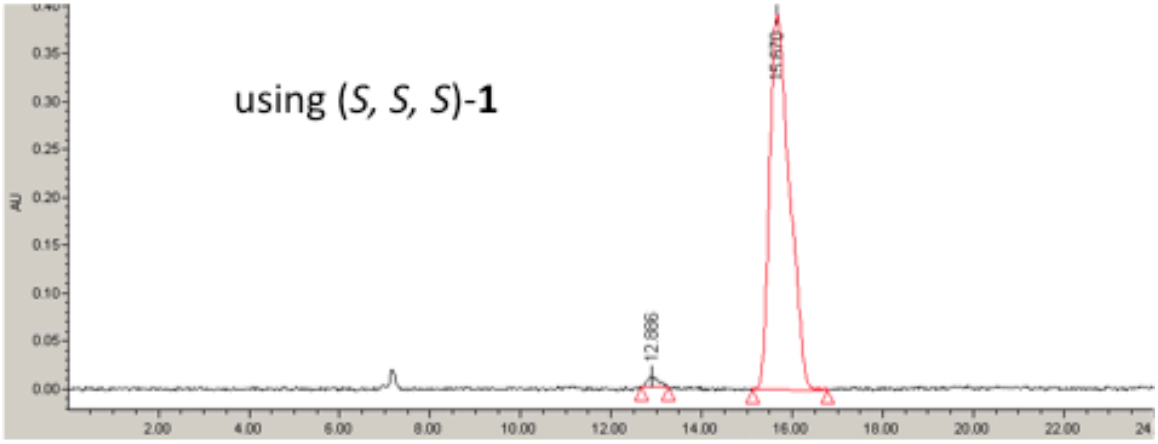


[(Chiralpak AD-H) hexane/*i*-PrOH, 99.1:0.1, 1.0 mL/min]

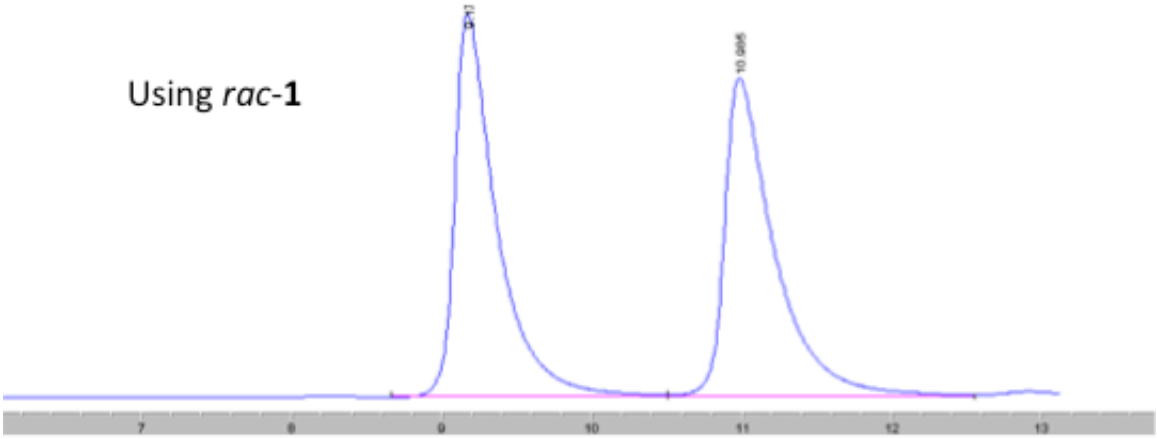


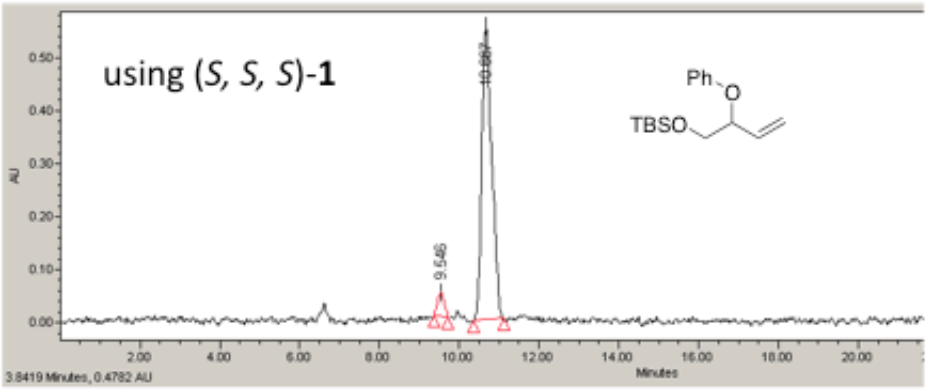


	Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height	Am
1		12.922	Unknown	11649743	98.77	519537	98.61	
2		15.724	Unknown	145535	1.23	7306	1.39	



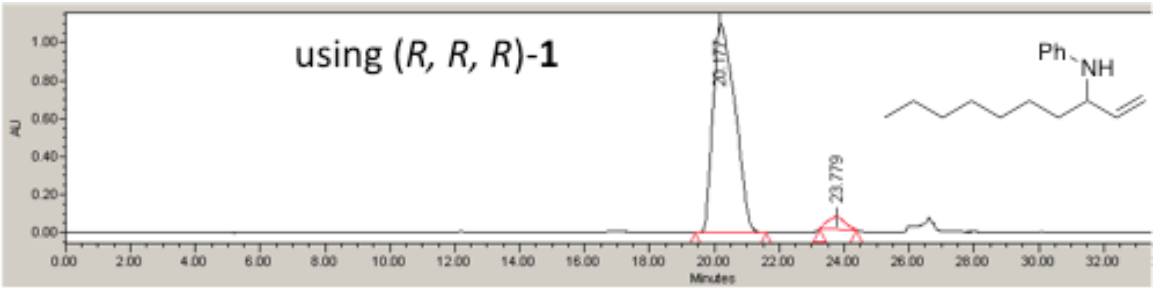
[(Chiralpak OD-H) hexane/*i*-PrOH, 99.:0.1, 0.5 mL/min]



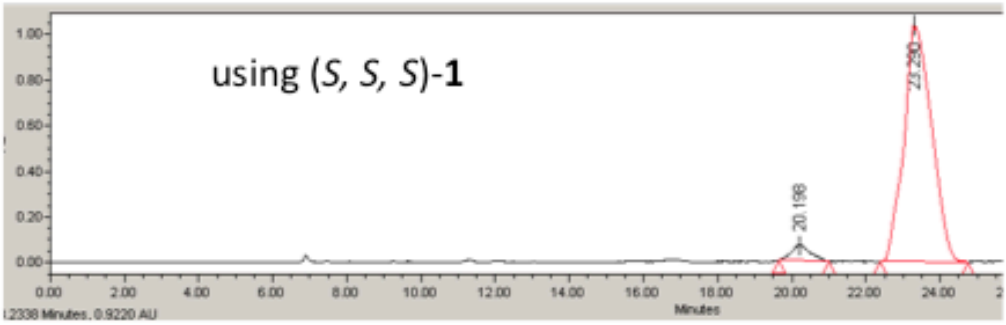


	Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height	A
1		9.546	Unknown	517250	5.09	44942	7.55	
2		10.667	Unknown	9639331	94.91	550198	92.45	

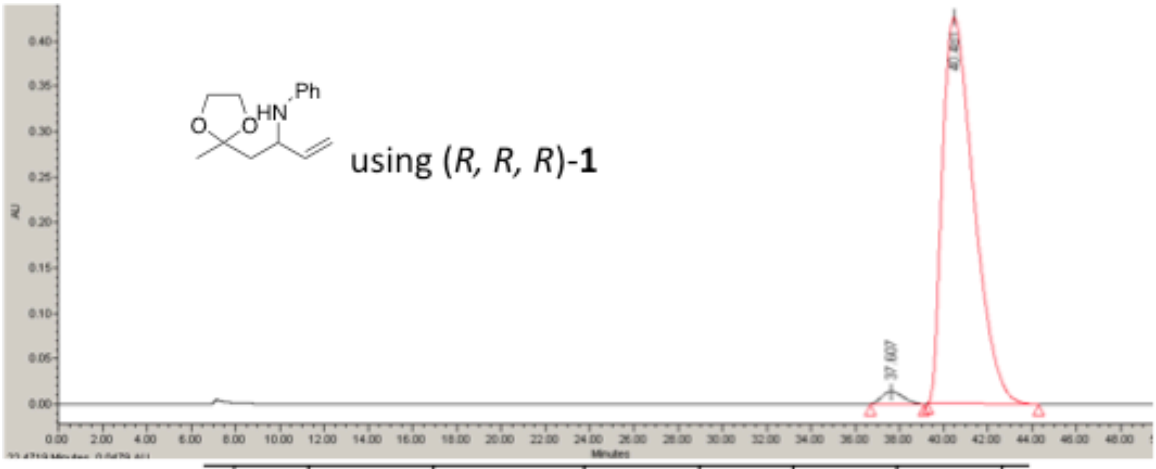
[(Chiralpak OD-H) hexane/*i*-PrOH, 99.9:0.1, 0.5 mL/min]



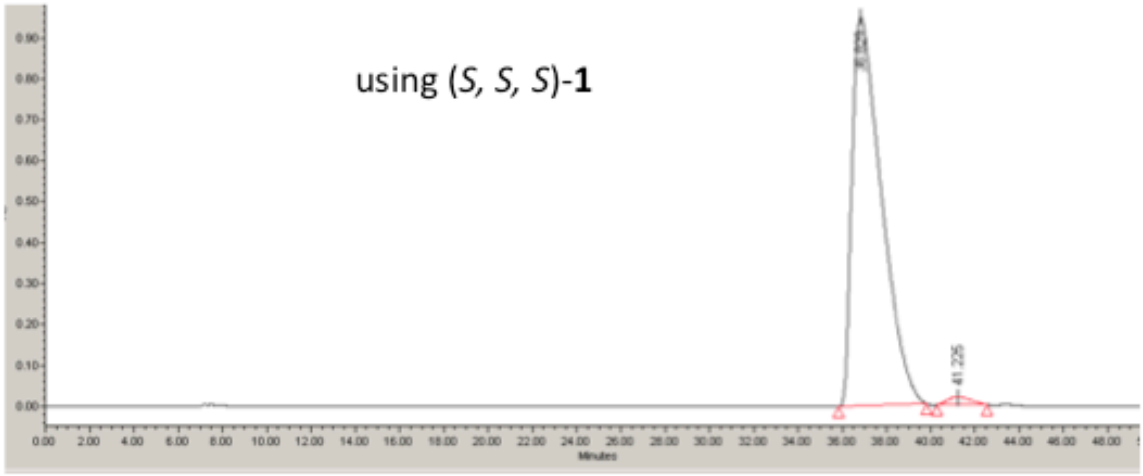
	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	A
1		20.177	Unknown	51663355	95.67	1100429	94.40	
2		23.779	Unknown	2336530	4.33	65267	5.60	



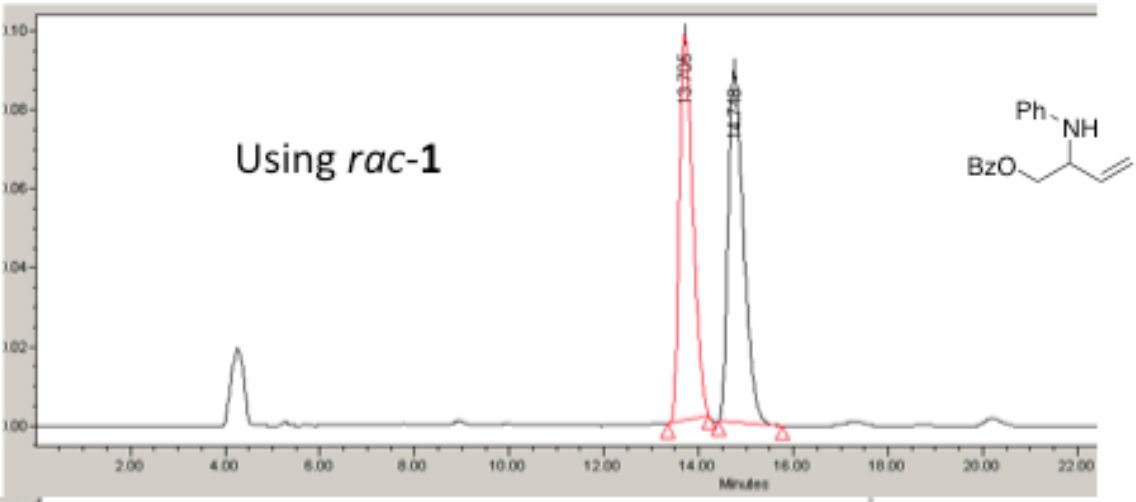
[(Chiralpak OD-H) hexane/*i*-PrOH, 99.1:0.1, 0.5 mL/min]

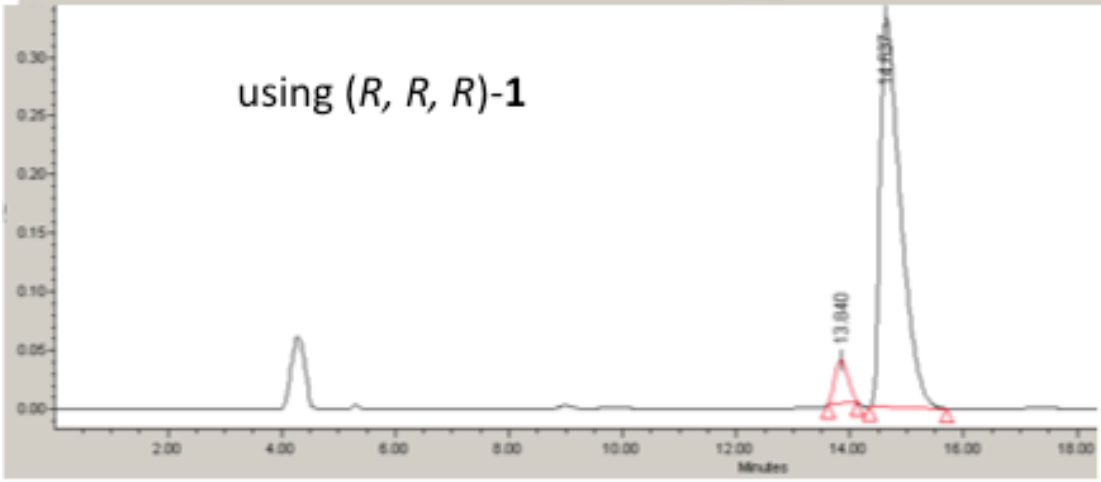


	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	A
1		37.607	Unknown	916207	2.14	13817	3.15	
2		40.481	Unknown	41864380	97.86	425358	96.85	



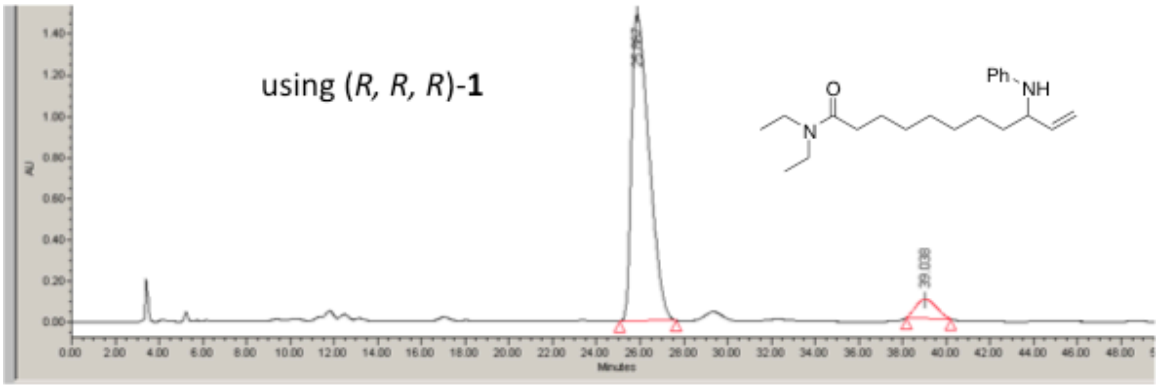
[(Chiralpak OJ-H) hexane/*i*-PrOH, 99.1:0.9, 0.5 mL/min]



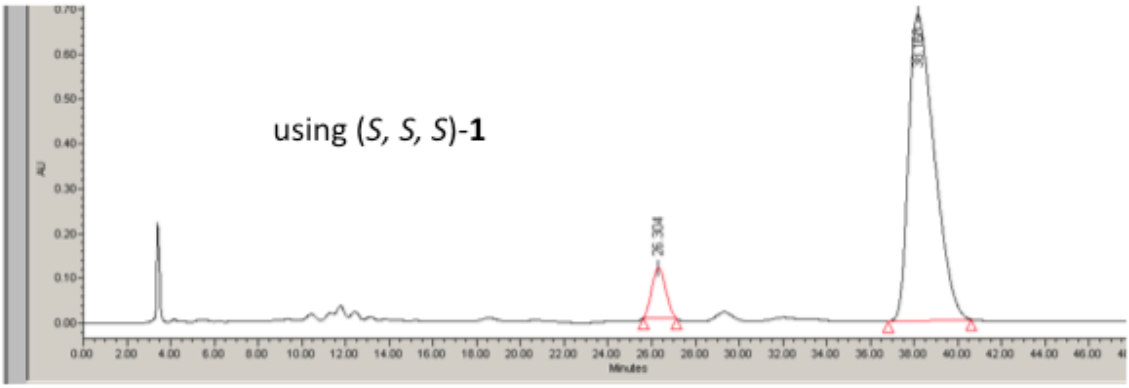


	Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height	Ar
1		13.840	Unknown	588757	6.61	36733	9.92	
2		14.637	Unknown	8320765	93.39	333450	90.08	

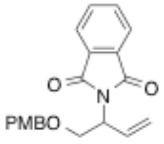
[(Chiralpak OD-H) hexane/*i*-PrOH, 90:10, 0.6 mL/min]

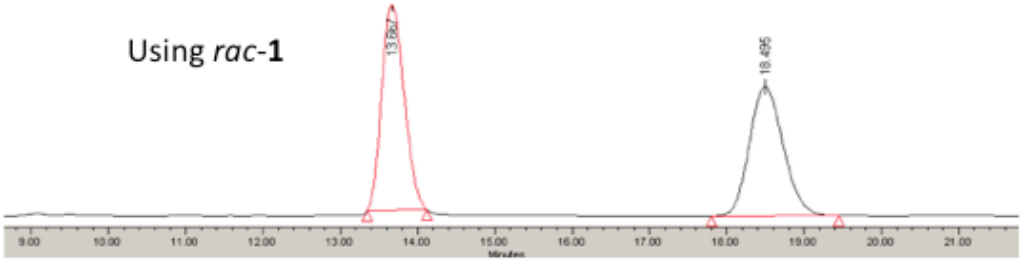


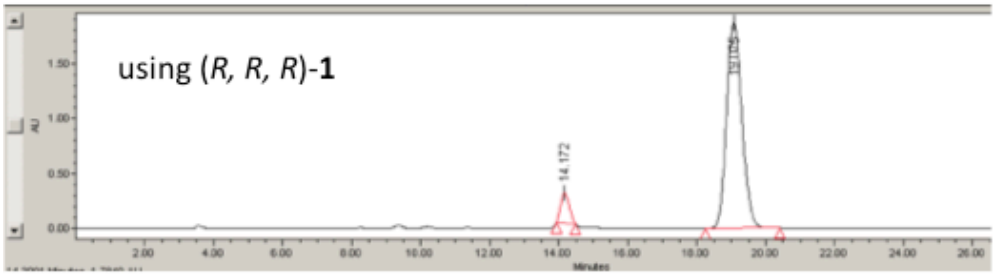
	Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height	Amount
1		25.867	Unknown	83190747	93.28	1489834	94.16	
2		39.038	Unknown	5994527	6.72	92467	5.84	



[(Chiralpak OD-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min]

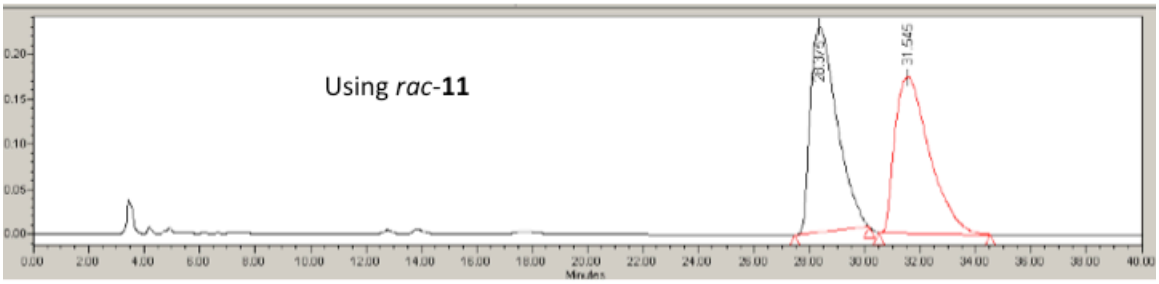




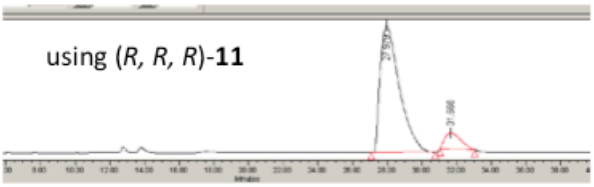


Name	Retention Time (min)	Peak Type	Area (µV*sec)	% Area	Height (µV)	% Height
	14.172	Unknown	4780593	7.63	276687	12.95
	19.075	Unknown	57876648	92.37	1859507	87.05

[(Chiralpak OJ-H) hexane/*i*-PrOH, 90:10, 1.0 mL/min]



	Name	Retention Time (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height
1		28.375	Unknown	15246557	50.41	228090	56.76
2		31.545	Unknown	15000817	49.59	173754	43.24



[(Chiralpak OJ-H) hexane/*i*-PrOH, 95:5, 1.0 mL/min]