Modular and Stereoselective Synthesis of Tetra-substituted Helical Alkenes via a Palladium-Catalyzed Domino Reaction

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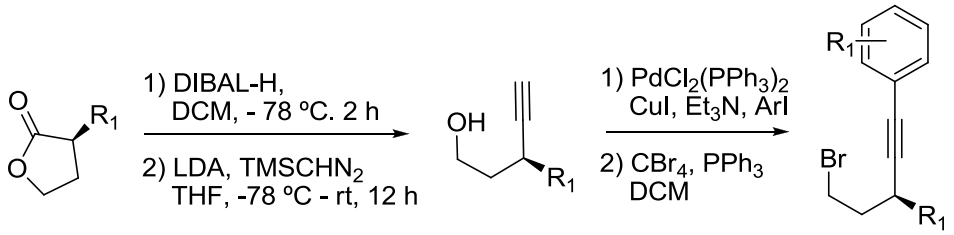
General Experimental Procedures. Unless otherwise noted, reactions were carried out under argon atmosphere, in sealed tubes (5.0 mL glass tubes with sealable cap and Teflon septa provided by Biotage) with magnetic stirring. Air- or water-sensitive liquids and solutions were transferred via syringe or stainless steel canula. Organic solutions were concentrated by rotary evaporation at 23–40 °C under 40 Torr (house vacuum). Analytical thin layer chromatography (TLC) was carried out on precoated SIL G/UV$_{254}$ (0.2 mm) plates from EM Separations. Visualization was done under a 254 nm UV light source and generally by immersion in acidic aqueous-ethanolic vanillin solution, anisol aldehyde or in potassium permanganate(KMnO4), followed by heating using a heat gun. Purification of reaction products wasgenerally done by flash chromatography with Silicycle™ Ultra-Pure 230–400 mesh silica gel..

Materials. Acetonitrile was distilled under nitrogen from CaH_2 immediately prior to use. All reagents and metal catalysts were purchased from Sigma-Aldrich, Lancaster, Alfa Aesar or Strem-Chemical Company and used without further purification unless otherwise noted.

Instrumentalization. Melting points were recorded using a Fisher–Johns melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at room temperature

using a Varian Gemini-300, Unity-400 or Mercury 400 machine. ^{1}H spectra were referenced to tetramethylsilane (TMS, 0 ppm) and ^{13}C spectra were referenced to solvent carbons (77.23 ppm for $CDCl_3$. No special notation is used for equivalent carbons. IR spectra were obtained using a Nicolet DX FT IR spectrometer in $CHCl_3$ as thin films on NaCl plates. Highresolution mass spectra were obtained using a VG 70-250S (double focusing) mass spectrometer at 70 eV unless otherwise noted.

Synthesis of optically pure bromoalkyl aryl alkynes



General procedure for homologative akynylation reaction

Step 1: The chiral lactone (1 mmol) was dissolved in CH_2Cl_2 (2 mL), cooled to -78°C under argon, and treated dropwise with a solution of diisobutylaluminium hybride in hexanes (1.3 equiv). The reaction mixture was stirred at -78°C for 1 h, quenched cautiously with a saturated solution of Rochelle's salt (~ 1 mL), and stirred for 5 h while slowly being warmed to room temperature. The separated aqueous layer was extracted with ether and the combined organic phases were washed with a small amount of brine, dried and concentrated to give the lactol product, which was used for next step without further purification.

Step 2: *n*BuLi (2.6 mmol, 2.6 equiv related to the lactol starting material) was slowly added to a solution of $(i\text{Pr})_2\text{NH}$ (2.6 mmol, 2.6 equiv) in THF (6 mL) at -78°C and the resulting mixture was stirred for 10 min, and then for 30 min at room temperature. The newly prepared LDA solution was cooled to -78°C and a solution of $TMSCHN_2$ (1.2 mmol, 1.2 equiv) was introduced. After stirring for another 1 h at -78°C, a solution of the lactol (1.0 mmol) in THF (4 mL) was added. The resulting mixture was allowed to warm to ambient temperature and stirred overnight (the release of nitrogen was observed upon warming, so care should be taken to have adequate ventilation). The reaction was then quenched with sat. aq. NH_4Cl solution. A standard work up with ether followed by flash chromatography (Hexanes/EtOAc, 6/1 to 4/1) of the crude product affords the desired alkyne and the corresponding *C*-silyated alkyne.

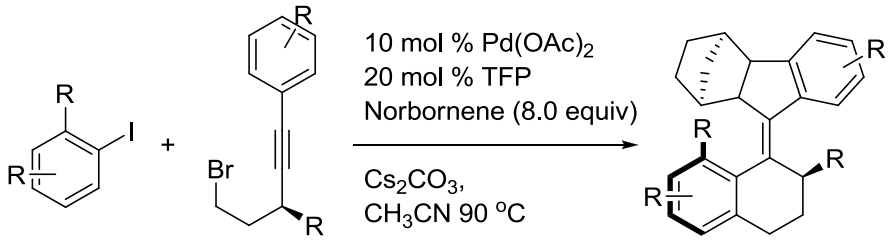
To convert the side product to the desired product, TBAF (1.3 equiv) was added to a THF solution of the silylated alkyne. After stirring 10 min at room temperature, the reaction mixture was diluted in ether, and washed with sat.NH_4Cl. Repeated extraction of the aqueous phase with ether, drying of the combined organic layers (Na_2SO_4), evaporation of the solvent and flash chromatography as described above afforded a second crop of the desired alkyne.

General procedure for Sonogashira coupling

To the corresponding aryl iodides (1.0 equiv) in Et_3N (5 mL/mmol) were added subsequently $PdCl_2(PPh_3)_2$ (5 mol %), CuI (1.2–5 mol %) and appropriate alkyne (1.2 equiv) at 25 °C. Stirring was continued for 16 h at 25 °C. The reaction mixture was treated with satd NH_4Cl solution and the resulting mixture was extracted with DCM. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography and concentration of the appropriate fractions *in vacuo* afforded the desired compounds.

General procedure for synthesis of bromides via Appel reaction

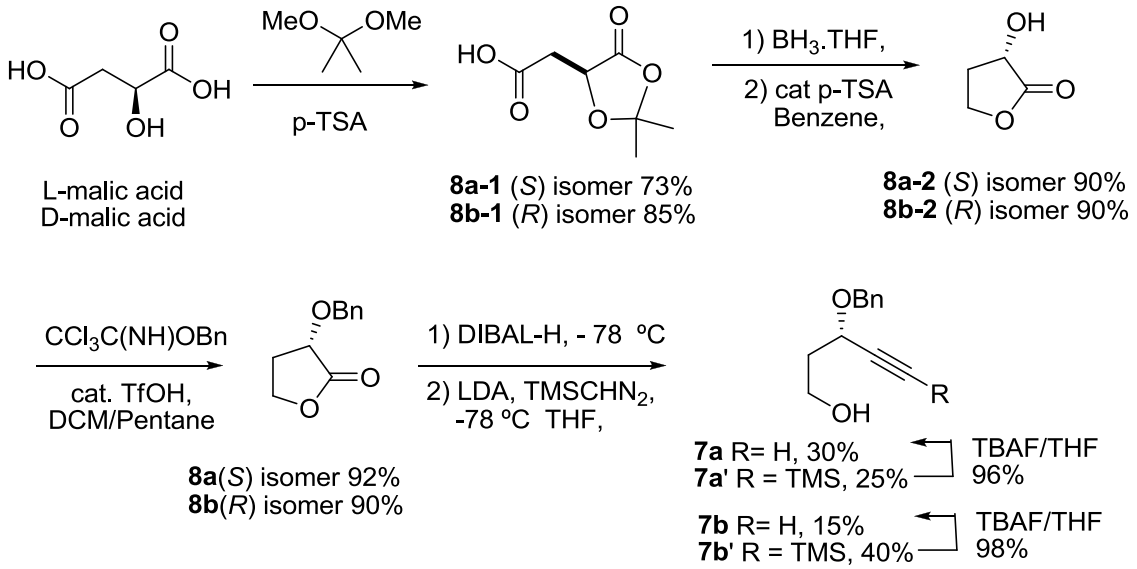
To the corresponding alcohols (1.0 equiv) and CBr_4 (1.2 equiv) in CH_2Cl_2 (3–5 mL/mmol) was added PPh_3 (1.2 equiv) in small portions. The reaction mixture was allowed to warm up to 25 °C and stirring was continued until reaction is completed as indicated by TLC. The solvent was then removed in *vacuo*, and the crude product was purified by silica gel flash chromatography, and concentration of the appropriate fractions *in vacuo* afforded the desired compounds.



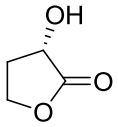
General procedure for synthesis of helical tetra-substituted alkenes

To a 10 mL microwave vessel with a magnetic stir bar were added $Pd(OAc)_2$ (4.50 mg, 10 mol%, 0.02 mmol), TFP (20 mol%, 0.04 mmol), Cs_2CO_3 (0.6 equiv, 195.5mg, 0.6 mmol), bromide precursor (0.2 mmol), aryl iodide (0.4 mmol), norbornene (8.0 equiv). The solvent (CH_3CN, 2 mL) was then added. The tube was flushed with argon for 5 min and sealed. The

reaction was stirred at 90 °C for 16 h and then cooled to r.t., diluted with CH_2Cl_2 (4 mL) and filter through a pad of Celite. The filtrate was concentrated to yield the crude product. Purification by flash silica chromatography gave the pure product.



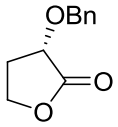
(S)-3-hydroxydihydrofuran-2(3H)-one **(8a-2)**



The known compound was prepared in three steps from L-malic acid according to the literature procedure[1]. The crude compound was purified by flash column (EtOAC/Hexanes 1/1 to 7/3) to afford desired product as a colorless oil (8.22g, 66% over 3 steps); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ4.51 (ddd, *J* = 10.1, 8.3, 4.0 Hz, 1H), 4.45 (ddd, *J* = 9.0, 2.0 Hz, 1H), 4.24 (ddd, *J* = 10.5, 9.3, 6.0, 1H), 3.12 (br, s, 1H, HO) 2.59 (dddd, *J* = 14.5, 8.0, 6.0, 2.0 Hz, 1H), 2.27 (dddd, *J* = 12.7, 10.5, 10.3, 8.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 178.0, 67.7, 65.3, 31.1; The data is consistent with that reported in the literature.

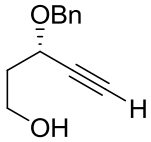
(S)-3-(benzyloxy)dihydrofuran-2(3H)-one **(8a)**

[1] Denmark, S.E. ; Yang, S.-M. *J. Am. Chem. Soc.* **2004**, *126*, 12432-12440.



The known compound was prepared according to the literature procedure[2]. The crude compound was purified by flash column on silica (EtOAC/Hexanes 1/6 to 1/3) to afford desired product as a colorless oil (14.17g, 92%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.50 – 7.31 (m, 5H), 4.91 (d, *J* = 12 Hz, 1H), 4.74 (d, *J* = 12 Hz, 1H), 4.41 (ddd, *J* = 9.1, 8.1, 4.2 Hz, 1H), 4.21 (ddd, *J* = 9.1, 8.1, 4.2 Hz, 1H), 4.17 (t, *J* = 7.9 Hz), 2.45 (dddd, *J* = 13.0, 7.9, 4.2, 4.5 Hz, 1H), 2.28 (qd, *J* = 13.0, 7.9 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ175.4, 137.1, 128.8, 128.5, 128.2, 72.7, 72.4, 65.8, 30.1; The data is consistent with that reported in the literature.

(S)-3-(benzyloxy)pent-4-yn-1-ol **(7a)**



The titled compound was prepared according to the general procedure for homologative akynylation reaction. The crude compound was purified by a flash column (EtOAc: Hexane 1:4) to afford the chiral alkye **7a** as a light yellow oil (3.0g, 30 %) and the *C*-silylated alkyne **7a'** as orange oil (4.5g, 25%). To convert the isolated side product to the desired product, TBAF (1.3 equiv, 20.5 mmol) was added to a THF solution of the silylated alkyne. After stirring 20 min at room temperature, the reaction mixture was diluted in ether, and washed with sat.NH_4Cl. Repeated extraction of the aqueous phase with ether, drying of the combined organic layers (Na_2SO_4), evaporation of the solvent and flash chromatography as described above afforded a second crop of the desired alkyne **7a**.

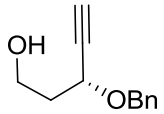
Alkyne **7a: $[\alpha]_D^{25}$** -95° (*c* 0.26, $CHCl_3$); **IR** ($CHCl_3$, cast): 3590, 3566, 3545, 3483, 3439, 3417, 3404, 3396, 3391, 2343, 2088, 1646, 1634, 1251, 1053, 734, 697, 626, 603, 570 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ:7.30-7.15 (m, 5H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.24 (td, *J* = 5.5, 2.1 Hz, 1H), 3.79 (dd, *J* = 11.1, 5.5 Hz, 1H), 3.69 (dd, *J* = 11.1, 5.5 Hz, 1H), 2.7 (br, 1H), 2.43 (d, *J* = 2.1 Hz, 1H), 1.94 (dt, *J* = 11.1, 5.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ137.6, 128.7, 128.3, 128.2, 82.2, 74.9, 71.1, 67.6, 59.9 38.1; **HRMS** (ESI): calcd for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072; found: 191.1063.

[2] Bandur, N.G. ; Bruckner D. ; Hoffmann, R.W. ; Koert, U. *Org. Lett.* **2006**, *8*, 3829-3831

Alkyne 7a': $[\alpha]_D^{25}$ -90° (c 0.3, CH_2Cl_2); **IR** ($CHCl_3$, cast): 3590, 3566, 3545, 3483, 3439, 3417, 3404, 3396, 3391, 2343, 2088, 1646, 1634, 1251, 1053, 734, 697, 626, 603, 570 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ:7.35-7.16 (m, 5H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.31 (d, *J* = 11.7 Hz, 1H), 4.15 (t, *J* = 6.0, 1H), 3.70 (dt, *J* = 11.2, 5.5 Hz, 1H), 3.58 (dt, *J* = 11.2, 5.5 Hz, 1H), 2.5 (br, 1H), 1.82 (dt, *J* = 11.2, 5.5 Hz, 2H), 0.1-0.0 (m, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 137.6, 128.6 (2C), 128.2, 127.9 (2C), 104.8, 103.6, 70.9, 68.2, 60.3, 38.0, 4.2 (3C); **HRMS** (ESI): $C_{15}H_{22}O_2Si$ [M+]: 263.1467; found: 263.1469

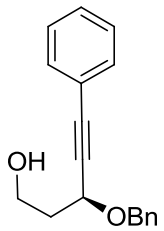
The enantiomer of alkyne was prepared using the same synthetic routes starting from D-malic acid.

(R)-3-(benzyloxy)pent-4-yn-1-ol (**7b**)



The titled compound was prepared from D-malic acid in the same manor to **7a**. The desired product was obtained as a light yellow oil (1.5g, 55% yield). **$[\alpha]_D^{25}$** + 97° (*c* 0.3, CH_2Cl_2); **IR** ($CHCl_3$, cast): 3590, 3566, 3545, 3483, 3439, 3417, 3404, 3396, 3391, 2343, 2088, 1646, 1634, 1251, 1053, 734, 697, 626, 603, 570 cm^{-1} **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.37-7.17 (m, 5H), 4.82 (d, 1H, *J* = 11.4 Hz), 4.5 (d, 1H, *J* = 11.4 Hz), 4.32 (td, 1H, *J* = 6.2, 2.1 Hz), 3.89-3.71(m, 2H), 2.76 (br, 1H), 2.52 (d, 1H, *J* = 2.1 Hz), 2.04-1.79 (m, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ137.6, 128.7, 128.3, 128.1, 82.2, 74.9, 71.0, 67.3, 59.9, 38.1; ^{1}H-NMR and C^{13}-NMR data are consistent with the corresponding enantiomer **7a**

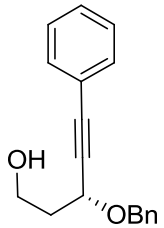
(S)-3-(benzyloxy)-5-phenylpent-4-yn-1-ol (**6a**)



The titled compound was prepared according to the general procedure for Sonogashira coupling. The crude compound was purified by a flash column (EtOAc: Hexane 1:3) to afford a light yellow oil (110 mg, 80 %). **$[\alpha]_D^{25}$** -96° (*c* 0.3, $CHCl_3$); **IR** ($CHCl_3$, cast): 3569,

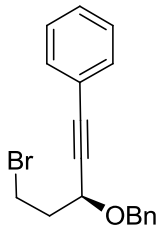
3525, 3517, 3417, 3355, 3332, 3272, 3245, 2364, 2337, 2319, 2101, 1635, 658, 460 cm^{-1} ; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ7.51–7.15 (m, 10H), 4.87 (d, *J* = 11.7 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.15 (t, *J* = 5.5, 1H), 3.92 (dd, *J* = 11.2, 5.5 Hz, 1H), 3.81 (dd, *J* = 11.2, 5.5 Hz, 1H), 2.5 (br, 1H), 2,09 (dt, *J* = 11,2, 5,5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ137.8, 129.3, 129.1, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.3, 128.1, 122.7, 87.4, 87.0, 71.2, 68.5, 60.5, 38.3; **HRMS** (ESI) calcd for $C_{18}H_{18}O_2$ [M^+]: 284.1651; found: 284.1657.

(R)-3-(benzyloxy)-5-phenylpent-4-yn-1-ol **(6b)**



The titled compound was prepared according to the general procedure for Sonogashira coupling. The crude compound was purified by a flash column (EtOAc: Hexane 1:3) to afford a light yellow oil (120 mg, 83 %), **$[\alpha]_D^{25}$** + 92° (*c* 0.3, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48-7.43 (m, 2H), 7.40-7.28 (m, 8H), 4.90 (d, 1H, *J* = 11.7 Hz), 4.60-4.55 (m, 2H), 3.96 (dt, 1H, *J* = 11.1, 5.7 Hz), 3.83 (dt, 1H, *J* = 11.2, 5.4 Hz), 2.33 (br, 1H), 2.16-2.09 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ137.8, 132.0, 128.78, 128.73, 128.57, 128.54, 128.3, 128.1, 122.6, 87.4, 86.9, 71.1, 68.4, 60.4, 38.3; ^{1}H-NMR and C^{13}-NMR data are consistent with the corresponding enantiomer (**6a**).

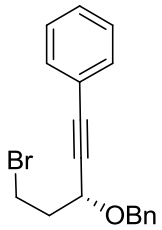
(S)-(3-(benzyloxy)-5-bromopent-1-ynyl)benzene **(6aa)**



The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane/EtOAc 9:1) to yield the desired product as a yellow oil (100 mg, 89%). $[\alpha]_D^{25}$ -57.8° (*c* 0.045, $CHCl_3$); **IR** ($CHCl_3$, cast): 2960, 2922, 2853, 2363, 2356, 1718, 1662, 1599, 1555, 1539, 1490, 1261 cm^{-1} **; ^{1}H NMR** ($CDCl_3$, 400 MHz): δ7.40–7.13 (m, 10H), 4.80 (d, *J* = 11.6

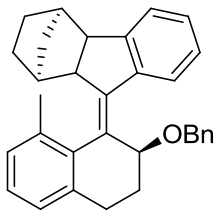
Hz, 1H), 4.51 (d, *J* = 11.6 Hz, 1H), 4.48 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.53 (m, 2H), 2.30 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 137.9, 132.3, 128.9, 128.7, 128.6, 128.3, 128.0, 122.6, 87.1, 86.9, 71.2, 67.6, 39.0, 29.4; **HRMS** (ESI) calcd for $C_{18}H_{17}BrO$ [M^+]: 346.0807; found: 346.0815; **HPLC analysis:** (Chiralcel ADH, 0.5% iPrOH/Hexane, 1.00 mL/min, 254 nm); >99 % *ee*, t_R = 11.75 min.

(R)-(3-(benzyloxy)-5-bromopent-1-ynyl)benzene **(6ba)**



The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane/EtOAc 9:1) to yield the desired product as a yellow oil (272 mg, 86%). **$[\alpha]_D^{25}$** +60° (*c* 0.10, DCM); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ7.46–7.13 (m, 10H), 4.87 (d, *J* = 11.7 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.54 (dd, *J* = 7.5, 5.4 Hz, 1H), 3,65-3.52 (m, 2H), 2.36-2.27 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 137.9, 132.0, 128.8, 128.7, 128.5, 128.3, 128.0, 122.6, 87.0, 86.9, 71.2, 67.6, 39.0, 29.3; ^{1}H-NMR and C^{13}-NMR data are consistent with the corresponding enantiomer (**6aa**); **HPLC analysis** (Chiralcel ADH, 0.5% iPrOH/Hexane, 1.00 mL/min, 254 nm); >99 % *ee*, t_R = 13.39 min.

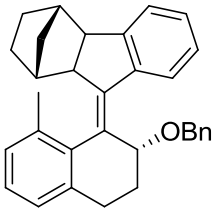
Tetra-substituted alkene **4a**



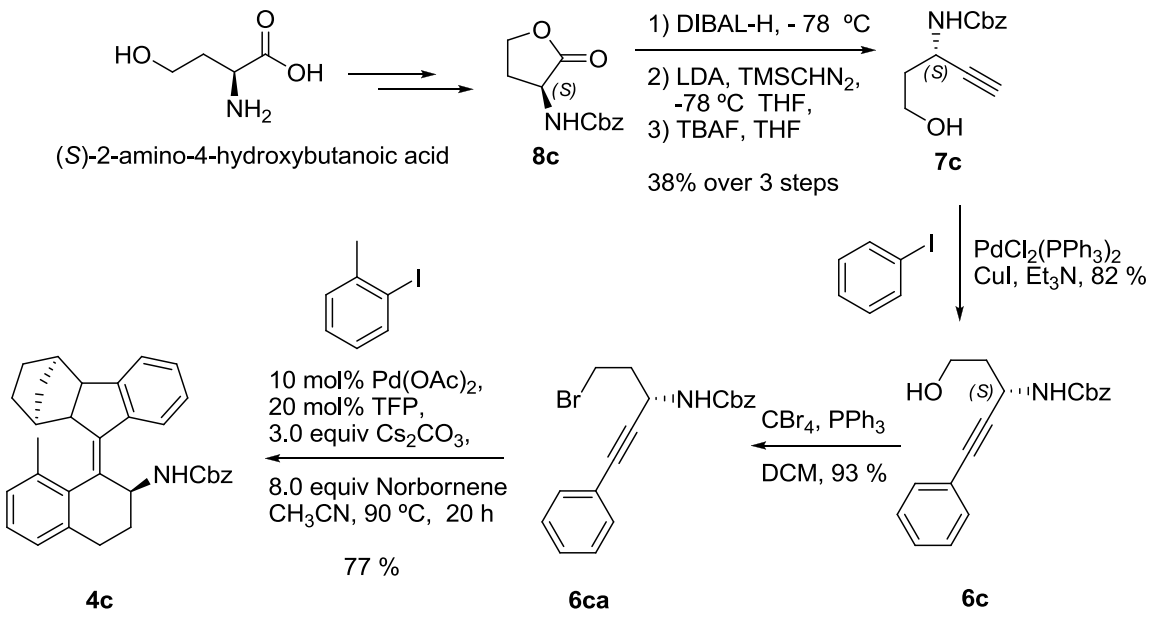
The title compound was prepared according to the general procedure for tetra-substituted alkene synthesis (0.4 mmol scale). The crude compound was purified with a flash column chromatography on silica gel (Hexane) to yield the desired product as a sticky light yellow mass (122 mg, 71%). **$[\alpha]_D^{25}$** +127° (*c* 0.15, DCM); d.r. = 6.6:1; **IR** ($CHCl_3$, cast): 3030, 2949, 2870, 1734, 1653, 1539, 1471, 1452, 1296, 1087, 1066, 908, 734, 696 cm^{-1}; **^{1}H-NMR** (400

MHz, CDCl3): δ 7.93 (d, J = 8.0 Hz, 1H), 7.40–7.06 (m, 11H), 5.6 (dd, J = 8, 5.5 Hz, 2H), 4.58 (dd, J = 11.6, 14.8 Hz, 2H), 3.11-3.01 (m, 2H), 2.68 (ddd, J = 14, 4.9, 2.7 Hz, 1H), 2.54–2.46 (m, 4H), 2.38–2.33 (m, 2H), 1.80-1.71(m, 1H), 1.57-1.49 (m, 1H), 1.43–1.39 (m, 2H), 1.28-1.20 (m,1H), 1.01 (d, J = 9.9 Hz, 1H), 0.95-0.89 (m, 1H), 0.80-0.74 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 100 MHz): δ 151.2, 148.6, 142.4, 141.4, 139.4, 138.4, 134.6, 130.6, 129.0, 128.6, 128.5, 127.9, 127.5, 126.9, 126.8, 125.6, 125.3, 123.6, 75.4, 67.9, 52.9, 52.3, 43.7, 40.8, 32.7, 30.6, 29.3, 28.8, 28.3, 20.0; **HRMS** (ESI): calcd for $C_{32}H_{32}O$ [M^+]: 432.2453; found: 432.2435; **HPLC analysis** (Chiracel ODH, 1% iPrOH/Hexane, 1.00 mL/min, 210 nm); 98.7% *ee*, t_R = 6.257 min.

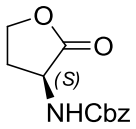
Tetra-substituted alkene **4b**



The title compound was prepared according to the general procedure for tetrasubstituted alkene synthesis (0.2 mmol scale). The crude compound was purified with a flash column chromatography on silica gel (Hexane) to yield the desired product as a light yellow oil (62 mg, 72%). **$[\alpha]_D^{25}$** -110° (c 0.1, DCM); d.r. = 6.3:1, ^{1}H-NMR and C^{13}-NMR data are consistent with the corresponding enantiomer (**4a**); HPLC analysis (Chiracel ODH, 1% iPrOH/Hexane, 1.00 mL/min, 210 nm); 97.2% *ee*, t_R = 7.96 min

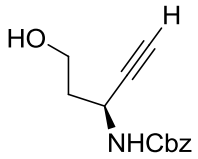


(S)-benzyl 2-oxotetrahydrofuran-3-ylcarbamate **(8c)**



This known compound was prepared according to literature procedure as a white crystalline solid (89 % yield) **mp** 121 °C, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (m, 5H), 5.35 (br s, 1H), 5.13 (s, 2H), 4.43 (m, 2H), 4.25 (m, 1H), 2.79 (m, 1H), 2.21 (dddd, *J* = 12.0, 11.7, 11.7, 9.0 Hz, 1H). **m/z** (ESI) Calculated $C_{12}H_{13}NO_4$ [M+Na]: 258.0736, Found: 258.0736. Characterization is in agreement with literature values [*Org. Lett.*, **1999**, *1*, 803-806]

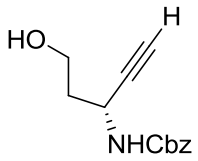
(S)-benzyl 5-hydroxypent-1-yn-3-ylcarbamate **(7c)**



This compound was obtained according to the general procedure for alkyne synthesis. The crude product was purified by flash chromatography on silica gel to afford the desire product as a white gummy oil (38 % yield). **IR** ($CHCl_3$, cast): 3392, 3291, 2958, 2889, 1679, 1532, 1454, 1256, 1056, 739 cm^{-1}; **^{1}H NMR** ($CDCl_3$ 400 MHz): δ 7.32 (m, 5H), 5.83 (br d, *J* =

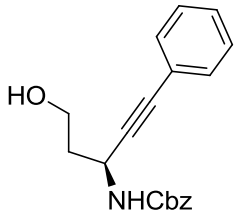
8.1 Hz, 1H), 5.09 (s, 2H), 4.67 (m, 1H), 3.77 (m, 2H), 2.32 (d, *J* = 2.3 Hz, 1H), 2.13 (s, 1H), 1.95 (m, 1H), 1.82 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 136.0, 128.4, 128.1, 128.0, 82.5, 71.7, 67.0, 58.6, 40.8, 38.0; **HRMS** (ESI) Calculated $C_{13}H_{15}NO_3$ $[M+Na]^+$: 256.0944, Found: 256.0947

(R)-benzyl 5-hydroxypent-1-yn-3-ylcarbamate **(7d)**



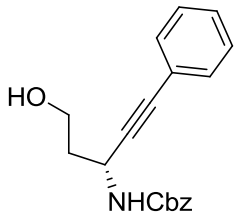
This compound was obtained from D-homoserine in the same manner to **7c**. The homologative akynylation gave the desired product as white gummy oil (41%). NMR data is consistent with the corresponding enantiomer (**7c**).

(S)-benzyl 5-hydroxy-1-phenylpent-1-yn-3-ylcarbamate (**6c**)



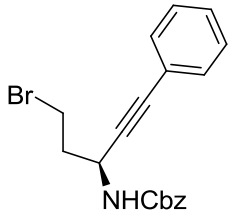
This compound was obtained according to the general procedure for sonogashira coupling. The crude product was purified to give the desire product as a light yellow solid; 82 % yield. **mp** 67 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (m, 10H), 5.63 (d, *J* = 8.5 Hz, 1H), 5.11 (s, 2H), 4.91 (m, 1H), 3.79 (m, 2H), 2.97 (br s, 1H), 2.04 (m, 1H), 1.88 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1, 136.1, 131.2, 128.4, 128.3, 128.2, 128.1, 128.0, 122.3, 87.7, 83.5, 67.0, 58.8, 41.4, 38.6; **IR ν_{max}** 3316, 3063, 2956, 1695, 1532, 1338, 1253, 1054, 757; **HRMS** (ESI) Calculated $C_{19}H_{19}NO_3$ [M+Na]: 310.1437, Found: 310.1443

(R)-benzyl 5-hydroxy-1-phenylpent-1-yn-3-ylcarbamate **(6d)**



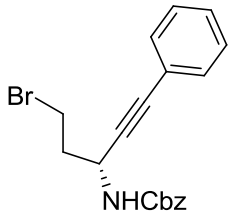
This compound was obtained from **7e** according to the general procedure for sonogashira coupling (82% yield)**.** NMR data is consistent with the corresponding enantiomer (**6c**).

(S)-benzyl 5-bromo-1-phenylpent-1-yn-3-ylcarbamate (**6ca**)



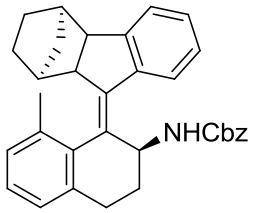
The title compound was prepared according to the general procedure for Appel reaction as a light yellow solid (93 % yield). **mp** 72 ^{o}C. $\mathbf{[\alpha]_D^{28}}$ +18.3^{o} (*c* 1.15, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (m, 10H), 5.13 (m, 3H), 4.91 (br q, *J* = 14.0, 6.8 Hz, 1H), 3.52 (t, *J* = 7.0 Hz, 2H), 2.31 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 136.0, 131.6, 128.5, 128.4, 128.2, 128.1, 128.1, 122.0, 86.5, 84.2, 67.0, 43.1, 38.8, 28.4; **IR $\mathbf{v_{max}}$** 3406, 3314, 3033, 2963, 1695, 1530, 1299, 1260, 1243, 1040, 756; **HRMS** (ESI) Calculated $C_{19}H_{18}BrNO_2$ [M+Na]: 372.0593, Found: 372.0600 (Chiracel ADH, 2.5% iPrOH/Hexane, 1.00 mL/min, 280 nm); 98.5% *ee*, t_R = 27.6 min.

(R)-benzyl 5-bromo-1-phenylpent-1-yn-3-ylcarbamate **(6da)**



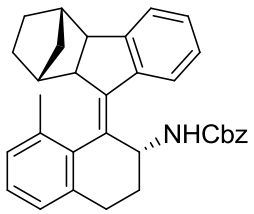
The title compound was prepared according to the general procedure for Appel reaction as a light yellow solid (92 % yield). $\mathbf{[\alpha]_D^{28}}$ -16.5^{o} (*c* 1.15, CHCl3); ^{1}H-NMR and C^{13}-NMR data are consistent with the corresponding enantiomer (**6da**). (Chiracel ADH, 2.5% iPrOH/Hexane, 1.00 mL/min, 280 nm); 98.5% *ee*, t_R = 33.3 min

Tetra-substituted alkene **4c**

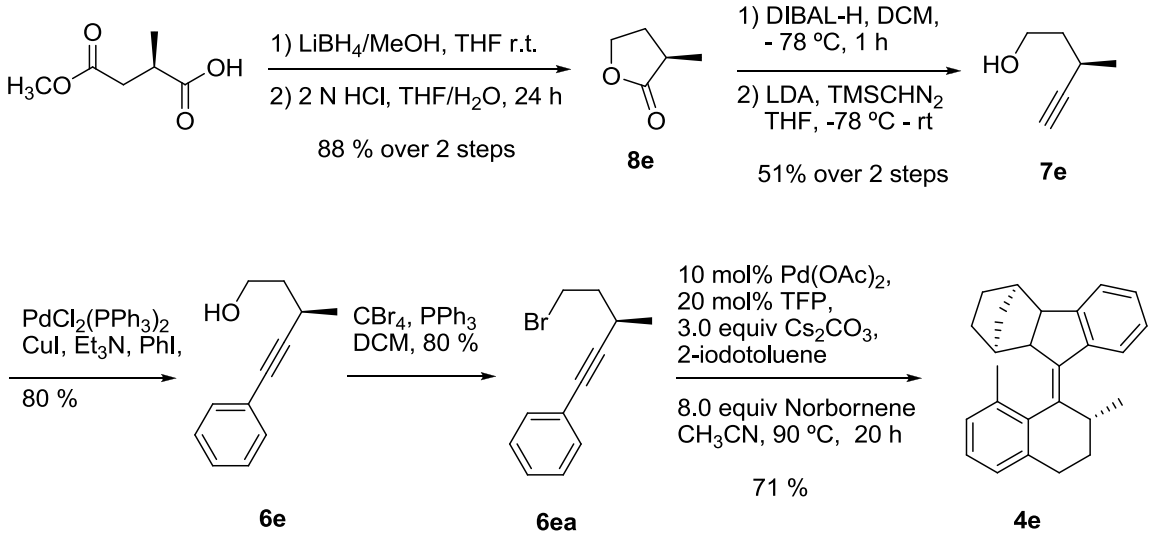


This compound was prepared according to the general procedure for tetra-substituted alkene synthesis (0.2 mmol scale) as a tan solid in 77 % yield. **mp** 107 ^{o}C; d.r. = 5.3:1, $\mathbf{[\alpha]_D^{28}}$ -98.2^{o} (*c* 0.34, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.32 (m, 8H), 7.13 (m, 2H), 7.00 (m, 1H), 5.66 (m, 1H), 5.10 (s, 2H), 4.69 (m, 1H), 2.98 (d, *J* = 7.5 Hz, 1H), 2.84 (d, *J* = 7.5 Hz, 1H), 2.75 (br s, 1H), 2.53 (m, 1H), 2.42 (m, 1H), 2.36 (s, 3H), 2.27 (m, 1H), 1.46 (m, 1H), 1.32 (m, 3H), 1.16 (m, 1H), 0.96 (m, 1H), 0.82 (m, 1H), 0.72 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.7, 150.8, 146.3, 141.5, 138.9, 136.5, 134.7, 128.7, 128.5, 128.5, 128.1, 127.5, 127.0, 125.3, 124.8, 123.6, 66.6, 52.5, 52.0, 51.4, 50.0, 43.3, 40.6, 36.6, 33.1, 32.4, 29.0, 28.4, 28.1, 26.2, 25.1, 20.5, 19.5 **IR $\mathbf{v_{max}}$** 3435, 3345, 2948, 2869, 1695, 1496, 1471, 1326, 1246, 1050, 909, 774, 736, 697; **HRMS**(ESI) Calculated $C_{33}H_{34}NO_2$: 476.2584, Found: 476.2568 **HPLC analysis** (Chiracel ODH, 1% iPrOH/Hexane, 1.00 mL/min, 210 nm); > 94.3% *ee*, t_R = 5.08 min

Tetra-substituted alkene **4d**

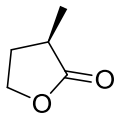


This compound **4d** was obtained as a tan solid in 77 % yield. dr = 5:1, $\mathbf{[\alpha]_D^{28}}$ +92.8^{o} (c 0.25, $CHCl_3$). ^{1}H-NMR and C^{13}-NMR data are consistent with the corresponding enantiomer (**4c**) **HPLC analysis** (Chiracel ODH, 1% iPrOH/Hexane, 1.00 mL/min, 210 nm); > 95.5% *ee*, t_R = 6.73 min.



The racemic product was prepared using the same synthetic routes starting from achiral lactone.

(R)-3-methyldihydrofuran-2(3H)-one **(8e)**

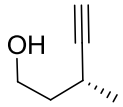


The compound was prepared according to the literature procedure[3]. To a solution of ester (1.0 g, 6.82 mmol) in THF (80 mL) was added $LiBH_4$ (2 M solution, 6.84 mL, 13.68 mmol, 2.0 equiv) dropwise at room temperature followed by MeOH (0.578 mL, 2.0 equiv). The resulting mixture was stirred at room temperature overnight. The reaction mixture was then cooled to 0 ^{o}C and 2 N HCl solution (20 mL) was added. The resulting solution was then stirred for overnight at room temperature. The volatile solvent was removed under vaccum (50 ^{o}C). The left aqueous layer was extracted with EtOAc (3 X 30 mL) and the combined organic layer was dried (Na_2SO4) and concentrated. The crude product was purified by flash column (Hexanes: EtOAc 6: 1) to afford the desired product as a colorless oil (600 mg 88%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.27 (td, 1H, *J* = 8.7, 2.6 Hz), 4.15-4.09 (m, 1H), 2.57-2.49 (m, 1H), 2.38 (dddd, 1H, *J* = 12.5, 8.8, 6.4, 2.7 Hz), 1.91-1.80 (m, 1H), 1.21 (d, 3H, *J* = 7.0

[3] Sibi, M. P.; Liu, P.; Ji, J.; Hajra, S.; Chen, J.; *J. Org. Chem.* **2002**, 67, 1738-1745

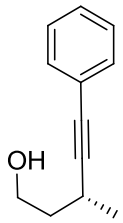
Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ180.4, 66.4, 34.3, 30.8, 15.3; The characterization data matched those reported in literature. [Midland, M. M. *et al*, *Tetrahedron*, **1984,** *40*, 1371 - 1380]

(R)-3-methylpent-4-yn-1-ol **(7e)**



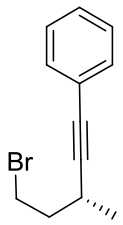
The titled compound was prepared according to the general procedure for chiral alkyne synthesis. The crude compound was purified by a flash column (EtOAc: Hexcane 1:4) to afford a light yellow oil (200 mg, 51 %).**$[\alpha]_D^{25}$** -10° (*c* 0.1, DCM); **IR** ($CHCl_3$, cast): 3300(br), 2970, 2935, 2875, 1653, 1548,1249, 1051,846, 632 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 3.78-3.74 (m, 2H), 2.63-2.58 (m, 1H), 2.34 (br, 1H), 2.06 (d, 1H, *J* = 2.5 Hz), 1.72-1.61 (m, 2H), 1.2 (d, 3H, *J* = 6.8 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 88.6, 69.0, 60.8, 39.4, 22.6, 21.1; **HRMS** (ESI): calcd for $C_6H_{11}O$ [M+H]+, 99.0809; found: 99.0808.

(R)-3-methyl-5-phenylpent-4-yn-1-ol **(6e)**



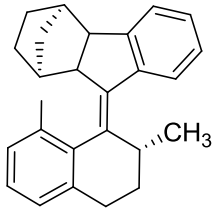
The titled compound was prepared according to the general procedure for Sonogashira coupling. The crude compound was purified by a flash column (EtOAc: Hexane 1:3) to afford a light yellow oil (119 mg, 80 %) **$[\alpha]_D^{25}$** -13.2° (*c* 0.55, DCM); **IR** ($CHCl_3$, cast): 3346(br), 2968, 2931, 2874, 1599, 1489, 1442, 1375, 1332, 1070, 1049, 756, 692 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.37-7.33 (m, 2H), 7.25-7.21 (m, 3H), 3.83-3.77 (m, 2H), 2.87-2.75 (m, 1H), 2.12 (br, 2H), 1.80-1.65 (m, 2H), 1.26 (d, 3H, *J* = 7.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ131.7, 128.4, 127.9, 123.8, 93.9, 81.5, 61.2, 39.8, 23.6, 21.4; **HRMS** (ESI): calcd for $C_{12}H_{15}O$ $[M+H]^+$: 175.1122; found: 175.1127.

(R)-(5-bromo-3-methylpent-1-ynyl)benzene **(6ea)**



The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane) to yield the desired product as a yellow oil (128mg, 80%).**$[\alpha]_D^{25}$** -146° (*c* 0.06, DCM); **IR** ($CHCl_3$, cast): 3055, 2968, 2931, 2872, 1599, 1489, 1442, 1334, 1257, 1070, 756, 692 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.43-7.39 (m, 2H), 7.32-7.27 (m, 3H), 3.62 (dd, 2H, *J* = 8.4, 9.6 Hz), 2.97-2.90 (m, 1H), 2.12-2.01 (m, 2H), 1.31 (d, 3H, *J* = 9.2 Hz); **^{13}C-NMR** ($CDCl_3$, 100 MHz): δ131.8, 128.4, 128.0, 123.7, 92.6, 82.1, 39.9, 31.7, 25.7, 20.9; **HRMS** (ESI)**:** calcd for $C_{12}H_{14}Br_1$ $[M+H]^+$: 237.0278; found:237.0269.; **HPLC analysis** (Chiralcel ADH, 0.5% iPrOH/Hexane, 1.00 mL/min, 235 nm); 99 % *ee*, t_R = 6.20 min.

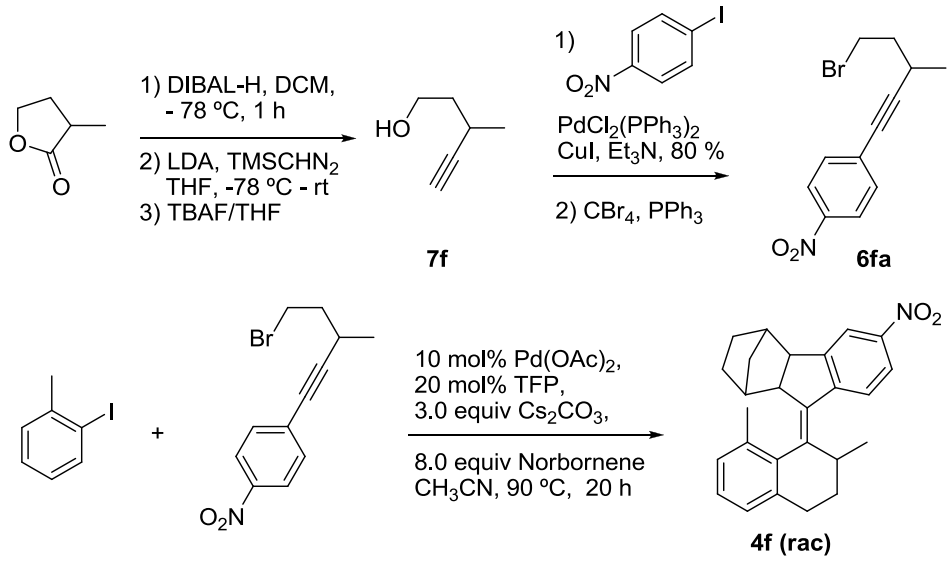
Tetra-substituted alkene **4e**



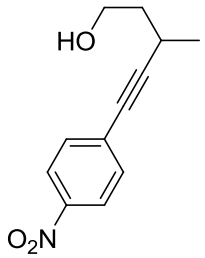
The title compound was prepared according to the general procedure for tetra-substituted alkene synthesis (0.2 mmol scale). The crude compound was purified with a flash column chromatography on silica gel (Hexane) to yield the desired product as a colorless oil (48 mg, 71%). d.r = 5:1; **$[\alpha]_D^{25}$** -143.8° (*c* 0.5, DCM); **IR** ($CHCl_3$, cast): 3061, 3014, 2949, 2866, 1471, 1456, 1375, 1296, 744 cm^{-1}; **^{1}H-NMR** *δ* (400 MHz, CDCl3) 7.71–7.69 (m, 1 H), 7.28–7.19 (m, 3 H),7.11–7.09 (m, 2 H), 6.97–6.94 (m, 1 H), 3.71 (dq, *J* = 14.8, 7.3 Hz, 1 H), 2.97 (d, *J* = 7.6 Hz, 1 H), 2.84(d, *J* = 7.8 Hz, 1 H), 2.48–2.44 (m, 1 H), 2.37 (s, 3 H), 2.30–2.22 (m, 3 H), 1.49–1.37 (m, 2H), 1.30–1.23 (m, 2 H), 1.11(d, *J* = 6.8 Hz, 3 H), 0.99-0.95 (m, 1H), 0.94-0.85 (m, 1H),0.83-0.77 (m, 1H), 0.71 (dt, *J* = 9.8, 1.4 Hz, 1 H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 150.7, 143.1, 142.9, 141.6, 138.9, 135.9, 134.8, 128.4, 127.5, 126.6, 126.4, 125.5, 124.4, 122.9, 52.5, 52.2, 43.7, 41.0, 33.2, 32.9, 32.6, 30.4, 29.3, 28.7, 20.9, 19.7; **HRMS**

(ESI): calcd for $C_{26}H_{29}$ $[M+H]^+$: 341.2269; found: 341.2272.; **HPLC analysis** (Chiralcel ADH, Hexane, 0.5 mL/min, 269 nm); 99 % *ee*, t_R = 9.98 min.

<u>Study of the stereochemical outcome of domino reaction using racemic starting materials</u>

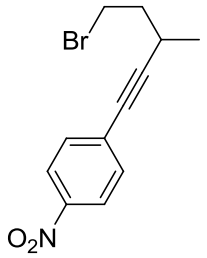


3-methyl-5-(4-nitrophenyl)pent-4-yn-1-ol **(6f)**



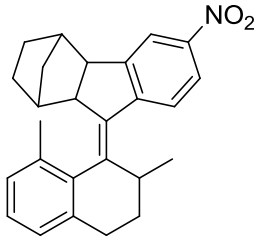
The titled compound was prepared according to the general procedure for Sonogashira coupling. **IR** ($CHCl_3$, cast): 3342(br), 3105, 2970, 2933, 2875, 2227, 1593, 1518, 1491, 1456, 1377, 1307, 1109, 1074, 1049, 854 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.1 (d, 2H, *J* = 9.0 Hz), 7.47 (d, 2H, *J* = 9.0 Hz), 3.82-3.79 (m, 2H), 2.88 (dt, 1H, *J* = 8.3, 6.8 Hz), 2.11 (br, 2H), 1.79-1.72 (m, 2H), 1.27 (d, 3H, *J* = 6.6 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ146.5, 132.2, 130.8, 123.4, 99.9, 79.7, 60.6, 39.2, 23.3, 20.7; **HRMS** (ESI): calcd for $C_{12}H_{14}NO_3$ $[M+H]^+$: 220.0973; found: 220.0973

1-(5-bromo-3-methylpent-1-ynyl)-4-nitrobenzene **(6fa)**



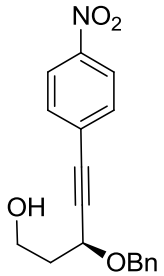
The title compound was prepared according to the general procedure for Appel reaction. **IR** ($CHCl_3$, cast): 3105, 2972, 1933, 1872, 2227, 1593, 1492, 1344, 1257, 1107, 852, 750, 688 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, 2H, *J* = 9 Hz), 7.43 (d, 2H, *J* = 9 Hz), 3.51-3.48 (m, 2H), 2.93-2.85 (m, 1H), 2.05-1.91 (m, 2H), 1.23 (d, 3H, *J* = 7.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.7, 132.3, 130.5, 123.4, 98.4, 80.2, 39.2, 31.2, 25.5, 20.2 ; **HRMS** (ESI): calcd for $C_{12}H_{13}Br_1N_1O_2$ $[M+H]^+$:282.0129; found:282.0124.;

Tetra-substituted alkene **(4f)**



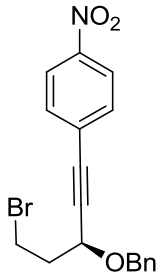
The title compound was prepared according to the general procedure for tetra-substituted alkene synthesis (0.3 mmol scale). The crude compound was purified with a flash column chromatography on silica gel (Hexane/DCM 2:1) to yield the desired product as a colorless oil (73 mg, 72%). d.r = 5:1; **IR** ($CHCl_3$, cast): 2953, 2926, 2868, 1683, 1653, 1581, 1516, 1506, 1471, 1338, 1298, 1078, 908, 775, 732 cm^{-1}; **^{1}H-NMR** *δ* (400 MHz, CDCl3) 8.03–8.00 (m, 2H), 7.68 (d, 1H), 7.10–7.04 (m, 3H), 6.92–6.90 (m, 1H), 3.61-3.56 (m, 1 H), 2.96 (d, *J* = 7.8 Hz, 1 H), 2.86(d, *J* = 7.8 Hz, 1 H), 2.48–2.41 (m, 1 H), 2.29 (s, 3 H), 2.27–2.18 (m, 3H), 1.48–1.36 (m, 2H), 1.24–1.17 (m, 2 H), 1.06(d, *J* = 7 Hz, 3 H), 0.95-0.84 (m, 2H), 0.81-0.69 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ149.2, 146.7, 141.6, 139.9, 139.5, 137.7, 134.3, 128.4, 127.0, 124.0, 123.0, 122.2, 122.0, 120.3, 52.7, 51.5, 43.6, 40.9, 33.4, 32.4, 32.1, 29.9, 28.9, 28.3, 20.5, 19.4 ; **HRMS** (ESI): calcd for $C_{26}H_{29}$ $[M+H]^+$: 341.2269; found: 341.2272.;

(S)-3-(benzyloxy)-5-(4-nitrophenyl)pent-4-yn-1-ol **(6h)**



The titled compound was prepared according to the general procedure for Sonogashira coupling. The crude compound was purified by a flash column (EtOAc: Hexane 1:3) to afford a light yellow oil (300 mg, 81 %), $[\alpha]_D^{25}$ - 241° (c 0.145, $CHCl_3$); **IR** ($CHCl_3$, cast): 3405(br), 2956, 2926, 2339, 1696, 1593, 1518, 1344, 1053 cm^{-1} **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.09 (d, 2H, *J* = 9.0 Hz), 7.48 (d, 2H, *J* = 9.0 Hz), 7.30-7.19 (m, 5H), 4.78 (d, 1H, *J* = 11.9 Hz) , 4.52-4.48 (m, 2H), 3.87-3.81 (m, 1H), 3.75-3.70 (m, 1H), 2.23(br, 1H), 2.06-2.00 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ147.4, 137.5, 132.7, 129.5, 128.7, 128.28, 128.24, 123.8, 93.1, 84.8, 71.5, 68.0, 60.0, 38.2; **HRMS** calcd for $C_{18}H_{21}N_2O_4$ [$M+NH_4^+$]: 329.1501; found: 329.1493.

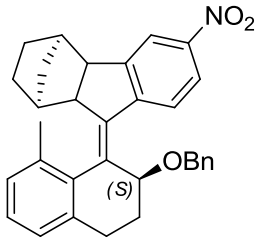
(S)-1-(3-(benzyloxy)-5-bromopent-1-ynyl)-4-nitrobenzene **(6ha)**



The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane) to yield the desired product as a yellow oil (70mg, 89%). $[\alpha]_D^{25}$ -60° (*c* 0.04, DCM); IR ($CHCl_3$, cast): 2956, 2924, 2853, 2360, 2330, 1688, 1653, 1594, 1517, 1457, 1343, 1260, 1092 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.13 (d, 2H, *J* = 9.0 Hz), 7.51 (d, 2H, *J* = 9.0 Hz), 7.31-7.22 (m, 5H), 4.79 (d, 1H, *J* = 11.5 Hz), 4.54-4.51 (m, 2H), 3.58-3.47 (m, 2H), 2.42-2.33 (m, 1H), 2.28-2.23(m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ147.5, 137.5, 132.7, 129.4, 128.7, 128.2,

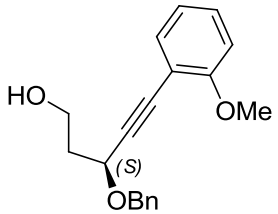
123.8, 123.7, 92.6, 84.9, 71.6, 67.4, 38.7, 29.0; **HRMS** calcd for $C_{18}H_{20}Br_1N_2O_3$ [M+NH_4^+]: 391.06573; found: 391.06666.

Tetra-substituted alkene **4h**



The title compound was prepared according to the general procedure for tetrasubstituted alkene synthesis (0.2 mmol scale). The crude compound was purified with a flash column chromatography on silica gel (Hexane) to yield the desired product as a colorless oil (57 mg, 60%). dr = 5.5 :1**, $[\alpha]_D^{25}$** +309° (*c* 0.06, DCM); **IR** ($CHCl_3$, cast): 3030, 2949, 2870, 1737, 1585, 1519, 1464, 1340, 1240, 1074, 844, 744 cm^{-1}; **^{1}H-NMR** δ (400 MHz, $CDCl_3$) 8.0 (d, *J* = 2.3 Hz, 1 H), 7.86-7.84 (m, 1 H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.29–7.17 (m, 5 H), 7.11–7.07 (m, 2H), 6.97–6.95 (m, 1 H), 5.30 (dd, *J* = 7.7, 6.1 Hz, 1H), 4.4 (dd, *J* = 11.6, 16.8 Hz, 2 H), 3.0-2.95 (m, 2H), 2.61-2.55 (m, 1H), 2.42-2.34 (m, 4H), 2.25-2.17 (m, 2H), 1.64 (tt, *J* = 12.8, 5.4 Hz, 1H), 1.29-1.10 (m, 2H), 1.14-1.08 (m, 1H), 0.82-0.75 (m, 2H), 0.71 (d, *J* = 9.8 Hz, 1 H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.2, 148.5, 147.6, 146.7, 141.4, 138.7, 137.4, 135.7, 134.5, 129.1, 128.6, 127.9, 127.8, 127.5, 125.5, 123.8, 122.5, 120.5, 75.1, 67.8, 53.3, 51.9, 43.7, 40.9, 32.7, 30.0, 29.1, 28.5, 28.0, 20.0**; HRMS** (ESI): calcd for $C_{32}H_{35}N_2O_3$ [M+NH_4^+]: 495.2647; found: 495.26646.

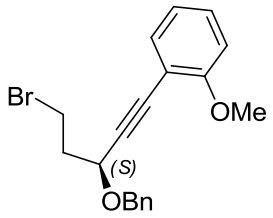
(S)-3-(benzyloxy)-5-(2-methoxyphenyl)pent-4-yn-1-ol **(6i)**



The titled compound was prepared according to the general procedure for Sonogashira coupling. The crude compound was purified by a flash column (EtOAc: Hexane 1:3) to afford a tan oil in 83 % yield. **IR**($CHCl_3$, cast): 3417, 2956, 2873, 1596, 1489, 1454, 1292, 1026, 751, 699 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.40 (m, 3H), 7.34 (t, *J* = 7.3 Hz, 2H),

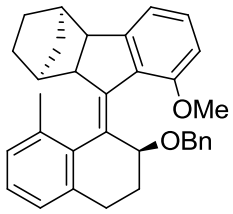
7.29 (m, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.4, 1H), 4.92 (d, *J* = 11.7 Hz, 1H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.58 (t, *J* = 6.0 Hz, 1H), 3.89 (m, 2H), 3.86 (s, 3H), 2.79 (br, 1H), 2.12 (q, *J* = 11.2, 5.7 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 160.1, 137.7, 133.4, 129.9, 128.3, 128.1, 127.7, 120.3, 111.5, 110.5, 91.4, 83.2, 70.6, 68.1, 59.9, 55.6, 38.0; **HRMS (ESI)** Calculated $C_{19}H_{20}O_3$ [M+NH_4]: 314.17562, Found: 314.17616

(S)-1-(3-(benzyloxy)-5-bromopent-1-ynyl)-2-methoxybenzene (**6ia**)



The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a tan oil in 99% yield. **$[\alpha]_D^{25}$** -66° (*c* 0.25, DCM); **IR** (CHCl3, cast): 3029, 2963, 2861, 1596, 1493, 1454, 1261, 1093, 1025, 798, 752, 697 cm^{-1} ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.4 Hz, 3H), 7.26 (t, J = 7.2 Hz, 2H), 7.21 (m, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.82 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.48 (m, 1H), 3.78 (s, 3H), 3.54 (t, *J* = 6.8 Hz, 2H), 2.34 (m, 1H), 2.27 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2, 137.8, 133.4, 129.9, 128.3, 128.1, 127.7, 120.3, 111.6, 110.6, 90.8, 83.2, 70.7, 67.5, 55.7, 38.7, 29.1; **HRMS** (ESI) Calculated C19H19BrO2 [M+NH4]: 376.09122, Found: 376.09126

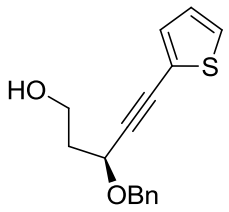
Tetra-substituted alkene **4i**



The title compound was prepared according to the general procedure for tetra-substituted alkene synthesis in 0.2 mmol scale. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a light tan

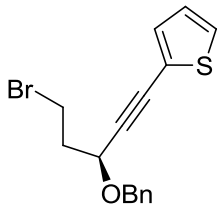
gummy oil (70mg, 76%). d.r = 5.3:1; $[\alpha]_D^{28}$ +126.8° (c 1.20, $CHCl_3$) **IR** ($CHCl_3$, cast): 3027, 2946, 1576, 1496, 1464, 1448, 1264, 1176, 1095, 1071, 909, 732, 697, 648 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (m, 1H), 7.14 (t, *J* = 7.2 Hz, 4H), 7.06 (m, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 3H), 6.75 (d, J = 8.1 Hz, 1H), 5.84 (dd, *J* = 5.2, 2.6 Hz, 1H), 4.47 (q, *J* = 22.4, 12.2 Hz, 2H), 3.77 (s, 3H), 2.95 (q, *J* = 14.6, 7.9 Hz, 2H), 2.81 (m, 1H), 2.62 (q, *J* = 16.1, 8.1 Hz, 1H), 2.39 (s, 3H), 2.29 (m, 1H), 2.04 (m, 2H), 1.59 (d, *J* = 4.1 Hz, 1H), 1.46 (m, 1H), 1.26 (m, 1H), 1.19 (m, 1H), 1.04 (d, *J* = 9.9 Hz, 1H), 0.79 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.4, 153.3, 142.9, 140.1, 140.1, 138.9, 134.1, 133.9, 130.3, 129.6, 128.2, 128.0, 127.9, 127.0, 126.7, 126.6, 126.4, 124.5, 117.8, 109.1, 75.5, 68.9, 54.6, 53.5, 52.0, 43.6, 40.9, 32.5, 30.6, 29.2, 28.3, 26.4, 19.5; **HRMS** (ESI) Calculated $C_{33}H_{34}O_2$ [M+Na]: 485.2451, Found: 485.2443

(S)-3-(benzyloxy)-5-(thiophen-2-yl)pent-4-yn-1-ol (**6j**)



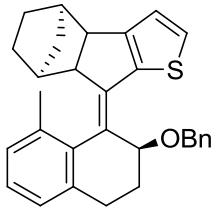
The titled compound was prepared according to the general procedure for Sonogashira coupling. The crude compound was purified by a flash column (EtOAc: Hexane 1:3) to afford a tan oil in 84 % yield, $[\alpha]_D^{25}$ + 90° (*c* 0.3, $CHCl_3$); **IR**($CHCl_3$, cast): 3420, 2929, 2869, 1639, 1498, 1456, 1332, 1189, 1064, 850, 734, 695 cm^{-1} ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.27 (m, 1H), 7.22 (m, 2H), 6.94 (t, *J* = 4.0 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.54 (m, 2H), 3.88 (m, 1H), 3.77 (m, 1H) 2.56 (s, 1H), 2.07 (m, 2H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.4, 132.3, 128.3, 127.9, 127.8, 127.3, 126.8, 122.2, 91.2, 79.7, 70.8, 67.9, 59.7, 37.9**;** **HRMS (ESI)** Calculated $C_{16}H_{16}O_2S$ [M+Na]: 295.0763, Found: 295.0772

(S)-2-(3-(benzyloxy)-5-bromopent-1-ynyl)thiophene (**6ja**)



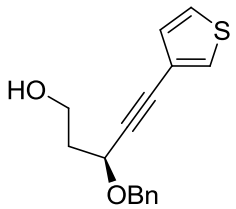
The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a light brown oil in 99% yield. $[\alpha]_D^{27}$ -82.2° (c 1.15 in $CHCl_3$); **IR** ($CHCl_3$, cast): 3105, 3071, 3029, 2911, 2862, 2218, 1496, 1454, 1330, 1258, 1190, 1095, 1071, 1028, 851, 736, 697, 667 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.27 (m, 1H), 7.22 (m, 2H), 7.15 (m, 1H), 6.94 (t, *J* = 4.1 Hz, 1H), 4.83 (d, *J* = 11.5 Hz, 1H), 4.54 (m, 1H), 4.52 (t, *J* = 2.5 Hz, 1H), 3.54 (m, 2H), 2.38 (m, 1H), 2.30 (m, 1H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.5, 132.4, 128.3, 128.0, 127.8, 127.4, 126.9, 122.1, 90.8, 79.8, 71.0, 67.4, 38.5, 29.0; **HRMS** (ESI) Calculated $C_{16}H_{15}BrOS$ [M+NH_4]: 352.03707, Found: 352.03791

Tetra-substituted alkene **4j**



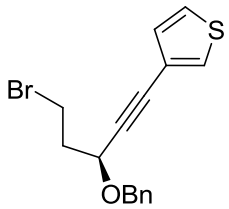
The title compound was prepared according to the general procedure for for tetrasubstituted alkene synthesis in 0.2 mmol scale. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a tan gummy oil (80mg, 91%). d.r.= 6.7:1, $[\alpha]_D^{29}$ +1.3° (*c* 1.50, $CHCl_3$); **IR** ($CHCl_3$, cast): 3029, 2948, 2869, 1471, 134, 1296, 1181, 1067, 909, 732 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 5.0 Hz, 1H), 7.22 (m, 3H), 7.17 (m, 2H), 7.11 (m, 2H), 7.00 (t, *J* = 3.7 Hz, 1H), 6.84 (d, *J* = 5.0 Hz, 1H), 5.22 (dd, *J* = 8.1, 3.2 Hz, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 3.27 (d, *J* = 6.5 Hz, 1H), 2.97 (d, *J* = 6.6 Hz, 1H), 2.60 (ddd, *J* = 14.2, 5.7, 1.6 Hz, 1H), 2.50 (m, 1H), 2.43 (s, 3H), 2.32 (m, 1H), 2.18 (m, 1H), 1.69 (m, 1H), 1.47 (m, 1H), 1.37 (m, 1H), 1.22 (m, 2H), 1.06 (d, *J* = 9.9 Hz, 1H), 0.87 (m, 1H), 0.79 (d, *J* = 9.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 142.9, 141.7, 140.7, 139.1, 138.9, 136.8, 134.1, 130.4, 129.7, 128.4, 128.1, 127.5, 127.1, 126.4, 125.7, 123.7, 122.2, 77.4, 69.4, 57.8, 48.8, 41.5, 40.1, 32.2, 30.9, 28.7, 28.5, 28.0, 19.9 **HRMS** (ESI) Calculated $C_{30}H_{30}OS$ [M+Na]: 461.1909, Found: 461.1920

(S)-3-(benzyloxy)-5-(thiophen-3-yl)pent-4-yn-1-ol **(6k)**



The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a tan oil in 94% yield. $\mathbf{[\alpha]_D^{27}}$ -82.2^o (*c* 1.15, $CHCl_3$) **; IR** ($CHCl_3$, cast): 3406, 3106, 2955, 2881, 1495, 1458, 1364, 1334, 1205, 1055, 783, 736, 697 cm^{-1} ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.9 Hz, 1H), 7.34 (m, 4H), 7.26 (m 1H), 7.21 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.10 (d, *J* = 4.9 Hz, 1H), 4.84 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.51 (t, *J* = 6.2 Hz, 1H), 3.88 (m, 1H), 3.77 (m, 1H), 2.68 (br, 1H), 2.06 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.5, 129.8, 129.0, 128.3, 127.9, 127.7, 125.3, 121.3, 86.8, 81.6, 70.7, 67.8, 59.7, 38.0 **; HRMS** (ESI) Calculated $C_{16}H_{16}O_2S$ [M+Na]: 295.0763, Found: 295.0763

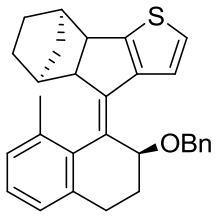
(S)-3-(3-(benzyloxy)-5-bromopent-1-ynyl)thiophene **(6ka)**



The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a light brown oil in 99% yield. $\mathbf{[\alpha]_D^{27}}$ -77.8^o (*c* 1.15, $CHCl_3$)**; IR** (CHCl3, cast): 3106, 3029, 2861, 2224, 1496, 1454, 1358, 1332, 1258, 1207, 1181, 1152, 1095, 1063, 783, 735, 697, 667, 624cm^{-1};**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.9 Hz, 1H), 7.35 (m, 4H), 7.27 (m, 1H), 7.22 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.10 (d, *J* = 4.9 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 4.50 (dd, *J* = 7.4, 5.5 Hz, 1H), 3.56 (q, *J* = 13.4, 6.9 Hz, 2H), 2.38 (m, 1H), 2.30 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.6, 129.8, 129.2, 128.3, 127.9, 127.7, 125.4,

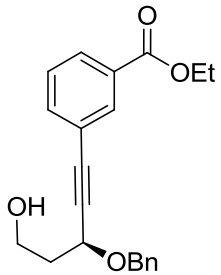
121.3, 86.4, 81.7, 70.9, 67.3, 38.6, 29.1; **HRMS** (ESI) Calculated $C_{16}H_{15}BrOS$ [M+NH_4]: 352.03707, Found: 352.03675

Tetra-substituted alkene **4k**



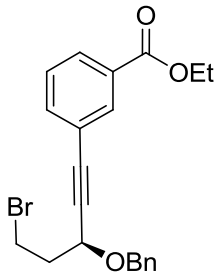
The title compound was prepared according to the general procedure for for tetrasubstituted alkene synthesis in 0.2 mmol scale. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a tan gummy oil (64mg, 73%). d.r.= 5:1, $\mathbf{[\alpha]_D^{29}}$ +6.9^o (*c*1.50, $CHCl_3$); **IR** ($CHCl_3$, cast): 2948, 2869, 1495, 1454, 1328, 1264, 1175, 1089, 734, 652 cm-1; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.24 (m, 3H), 7.19 (m, 3H), 7.12 (d, *J* = 4.5 Hz, 2H), 7.06 (d, *J* = 5.2 Hz, 1H), 7.00 (t, *J* = 4.2 Hz, 1H), 5.34 (dd, *J* = 8.3, 3.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.30 (d, *J* = 6.6 Hz, 1H), 3.09 (d, *J* = 6.6 Hz, 1H), 2.60 (ddd, *J* = 14.1, 5.6, 2.0 Hz, 1H), 2.44 (s, 3H), 2.31 (m, 2H), 2.20 (d, J = 3.7 Hz, 1H), 1.66 (tt, *J* = 12.3, 4.8 Hz, 1H), 1.46 (tt, *J* = 11.9, 4.3 Hz, 1H), 1.35 (m, 1H), 1.26 (m, 2H), 1.17 (m, 1H), 1.10 (d, *J* = 10.0 Hz, 1H), 0.80 (d, *J* = 10.1 Hz, 1H) ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 154.2, 146.5, 142.1, 140.9, 139.2, 138.9, 137.2, 134.1, 128.6, 128.4, 128.2, 128.1, 127.4, 127.1, 126.4, 125.4, 123.6, 122.2, 75.3, 68.5, 58.9, 49.0, 42.8, 40.1, 32.3, 30.8, 28.5, 28.3, 28.1, 19.8 **; HRMS** (ESI) Calculated $C_{30}H_{30}OS$ [M+Na]: 461.1909, Found: 461.1906

(S)-ethyl 3-(3-(benzyloxy)-5-hydroxypent-1-ynyl)benzoate **(6l)**



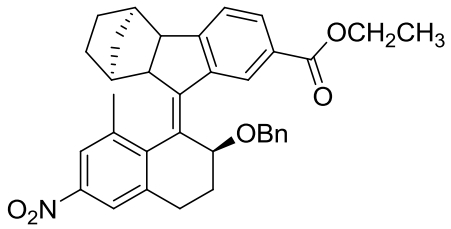
The titled compound was prepared according to the general procedure for Sonogashira coupling. The crude compound was purified by a flash column (EtOAc: Hexane 1:3) to afford a light yellow oil (425 mg, 80 %), $[\alpha]_D^{25}$ -75° (*c* 0.3, $CHCl_3$); **IR** ($CHCl_3$, cast): 3405(br), 2956, 2926, 2339, 1696, 1593, 1518, 1344, 1053, 754 cm^{-1} **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.03 (s, 1H), 7.91-7.89 (m, 1H), 7.52-7.50 (m, 1H), 7.31-7.15 (m, 6H), 4.49 (d, 1H, *J* = 11.7 Hz), 4.51-4.46 (m, 2H), 4.28 (q, 2H, *J* = 7.2 Hz) 3.87-3.81 (m, 1H), 3.73 (dt, 1H, *J* = 11.1, 5.6 Hz), 2.76(br, 1H), 2.04-1.99 (m, 2H), 1.3 (t, 3H, *J* = 7.1 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ166.0, 137.7, 136.0, 133.0, 131.0, 129.7, 128.7, 128.2, 128.1, 123.1, 88.5, 85.8, 71.3, 68.1, 61.5, 60.138.3, 14.5; **HRMS** (ESI): Calcd for $C_{21}H_{22}Br_1O_3$ [M+H]: 401.0752, found 401.0741.

(S)-ethyl 3-(3-(benzyloxy)-5-bromopent-1-ynyl)benzoate **(6la)**

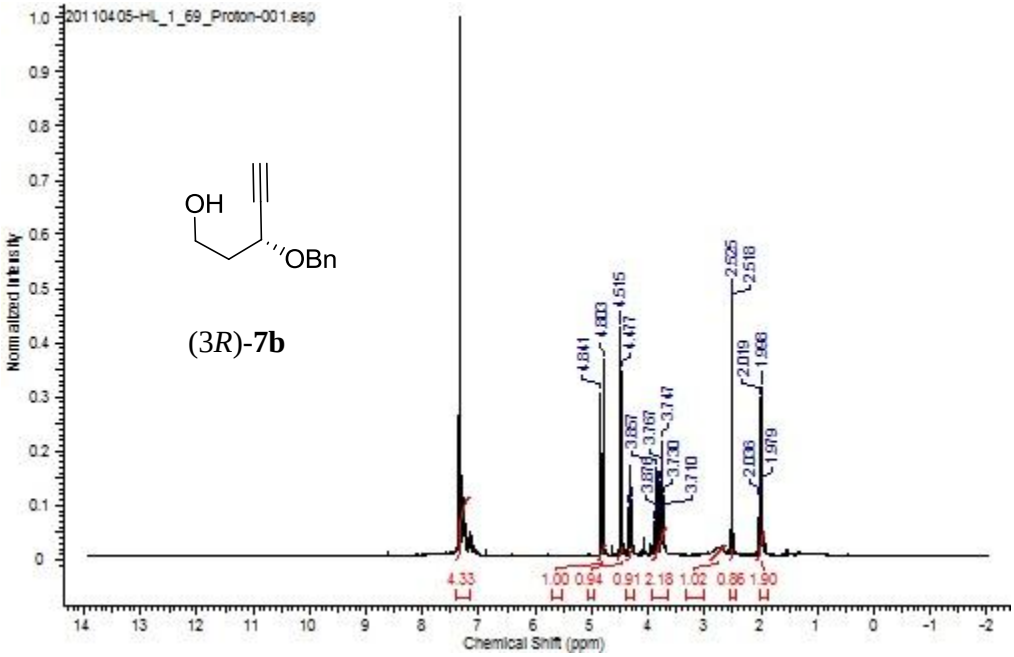


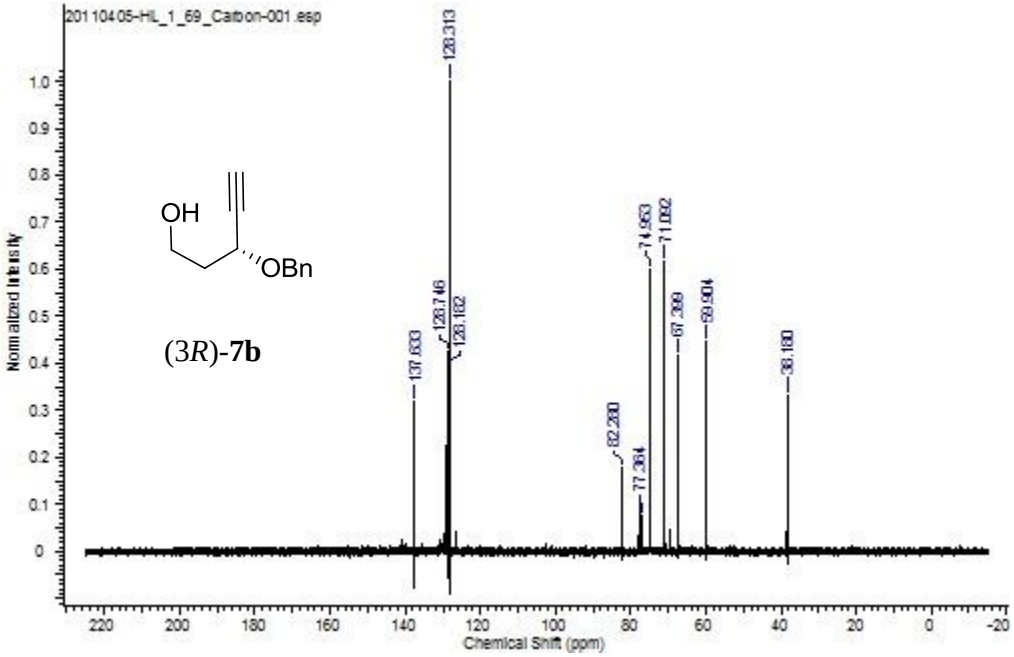
The title compound was prepared according to the general procedure for Appel reaction. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a yellow oil (310mg, 91%). $[\alpha]_D^{25}$ -66° (*c* 0.25, DCM); **IR** ($CHCl_3$, cast): 3030.2, 2980.1, 2904.8, 2866.3, 1720.5, 1454.3, 1431.2, 1390.7, 1367.5, 1290.4, 1226.7, 1105.2, 1028.0, 754.1 cm^{-1} ; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.16 (t, 1H, *J* = 1.6 Hz), 8.04 (td, 1H, *J* = 7.9, 1.4 Hz), 7.64 (dt, 1H, *J* = 7.7, 1.4 Hz), 7.44-7.30 (m, 5H), 4.49 (d, 1H, *J* = 11.7 Hz), 4.62-4.56 (m, 2H), 4.41 (q, 2H, *J* = 7.1 Hz), 3.67-3.56 (m, 2H), 2.50-2.31 (m, 2H), 1.42 (t, 3H, *J* = 7.1 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ166.0, 137.8, 136.0, 133.1, 131.0, 129.8, 128.7, 128.6, 128.3, 128.1, 123.0, 88.0, 85.9, 71.3, 67.5, 61.4, 38.9, 29.2, 14.5; **HRMS** (ESI): Calcd for $C_{21}H_{22}Br_1O_3$ 401.0752, found 401.0741.

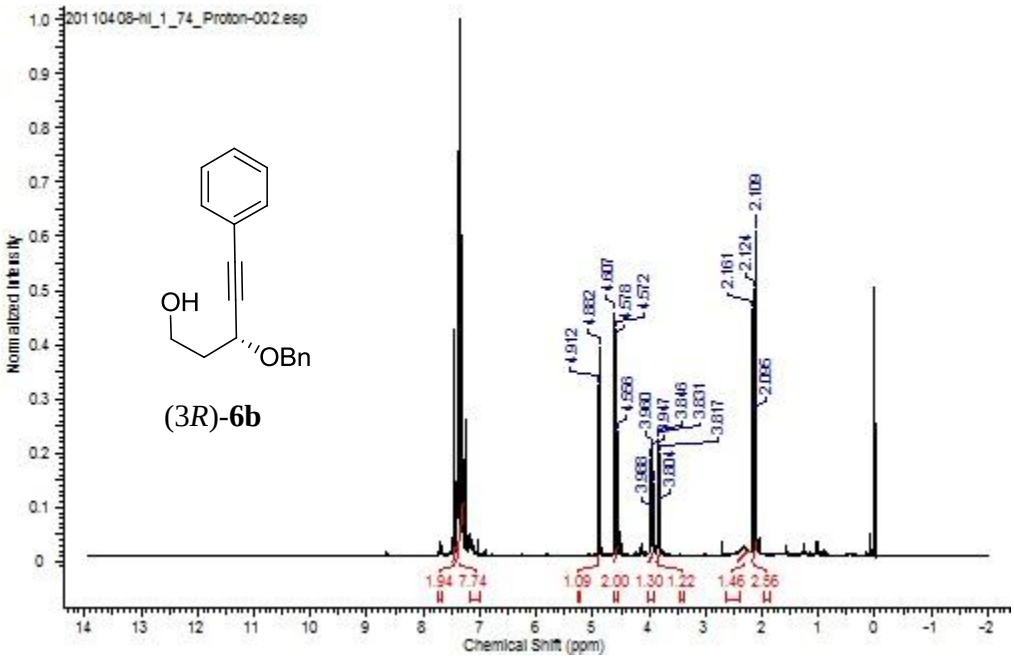
Tetra-substituted alkene **4l**

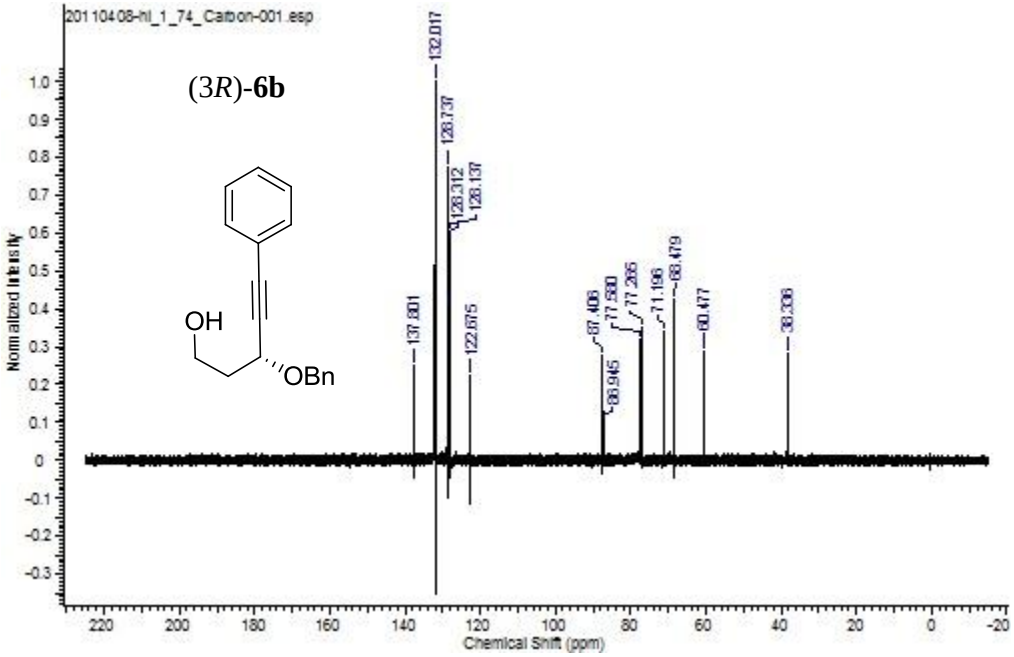


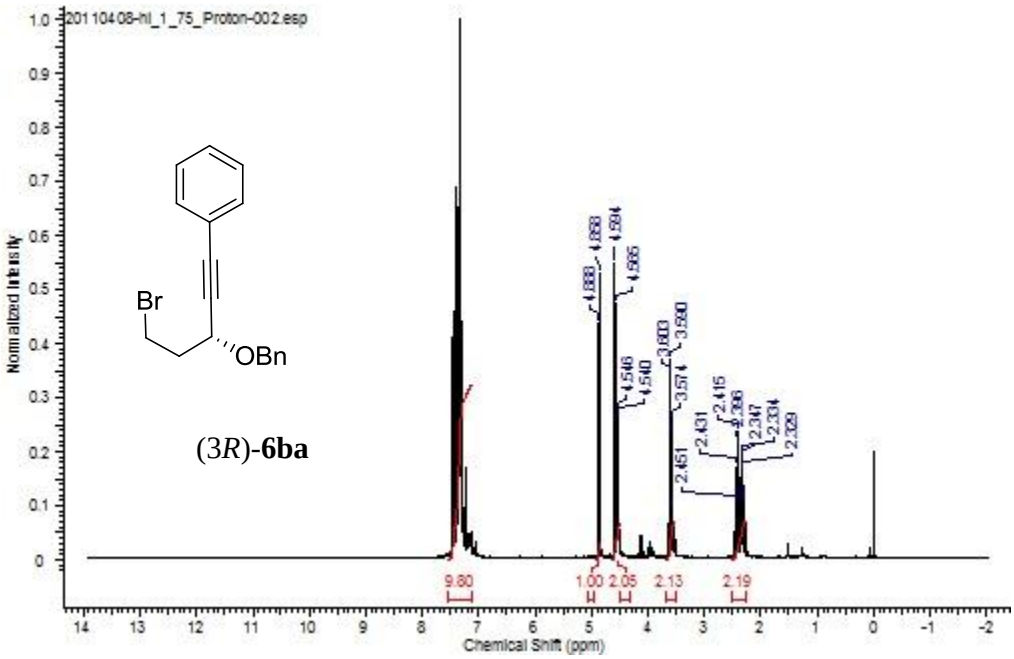
The title compound was prepared according to the general procedure for for tetrasubstituted alkene synthesis in 1.0 mmol scale. The crude compound was purified with a flash column chromatography on silica gel (Hexane/ EtOAc 10:1) to yield the desired product as a yellow sticky mass (400 mg, 73%). dr = 6:1; $[\alpha]_D^{25}$ +110 ° (*c* 0.01, DCM); **IR** ($CHCl_3$, cast): 2951, 2926, 2870, 1716, 1600, 1514, 1452, 1342, 1093, 1049, 881, 696 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.63 (s, 1H), 8.05-8.01 (m, 2H), 7.91 (d, 1H, *J* = 2.1 Hz), 7.39(d, 1H, *J* = 8.1 Hz), 7.33-7.29 (m, 1H), 7.28-7.18 (m, 5H), 5.56 (dd, 1H, *J* = 8.0, 5.3 Hz), 4.69-4.57 (m, 2H), 4.36-4.26 (q, 2H, *J* = 11.2 Hz), 4.31(dd, 2H, *J* = 9.1, 7.1 Hz), 3.10-2.95 (m, 2H), 2.79-2.74 (m, 1H), 2.62-2.56 (m, 1H), 2.53(s, 3H), 2.42-2.33(m, 3H), 1.71-1.62(m, 1H), 1.57-1.46(m, 2H), 1.28(t, 3H, *J* = 6.8 Hz), 0.92-0.79(m, 4H) ; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ166.7, 156.3, 149.2, 146.5, 145.4, 143.0, 141.7, 138.6, 136.6, 130.7, 130.3, 129.6, 128.4, 127.6, 127.5, 126.4, 125.6, 123.9, 118.7, 75.5, 68.9, 61.2, 53.1, 52.4, 43.4, 41.4, 32.7, 30.7, 29.2, 28.7, 28.3, 20.2, 14.5; **HRMS** (ESI): Calcd for $C_{35}H_{39}N_2O_5$ 567.2859, found 567.2840.

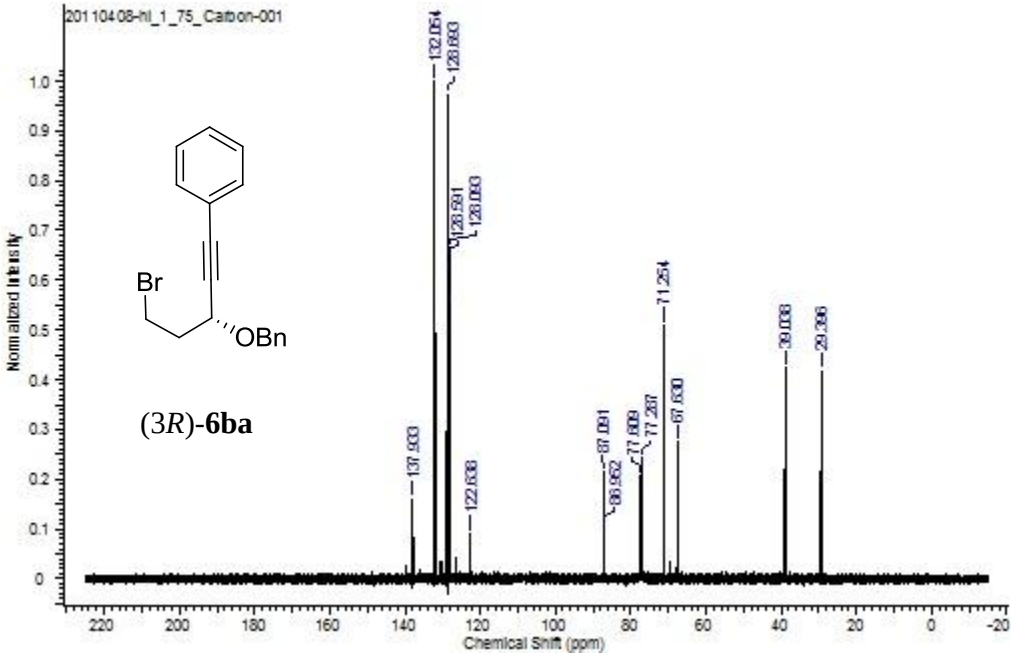

20110405-HL_1_69_Proton-001.esp
OH
OBn
(3R)-7b
Normalized Intensity
Chemical Shift (ppm)
4.841
4.803
4.515
4.477
3.767
3.747
3.730
3.710
2.525
2.518
2.019
1.966
2.006
1.979
4.33
1.00
0.94
0.91
2.18
1.02
0.86
1.90


20110405-HL_1_69_Carbon-001.esp
OH
OBn
(3R)-7b
Normalized Intensity
Chemical Shift (ppm)
128.313
137.633
128.746
128.162
82.330
77.364
74.963
71.062
67.399
59.904
38.180

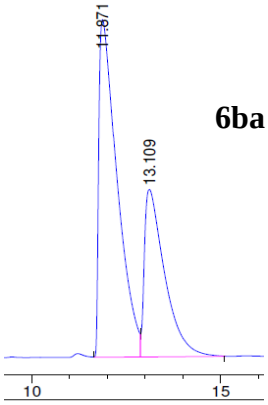

20110408-hl_1_74_Proton-002.esp
OH
OBn
(3R)-6b
Normalized Intensity
Chemical Shift (ppm)


20110408-hl_1_74_Carbon-001.esp
(3R)-6b
OH
OBn
Normalized Intensity
Chemical Shift (ppm)


20110408-hl_1_75_Proton-002.esp
Br
OBn
(3*R*)-**6ba**
Normalized Intensity
Chemical Shift (ppm)
9.80
1.00
2.05
2.13
2.19

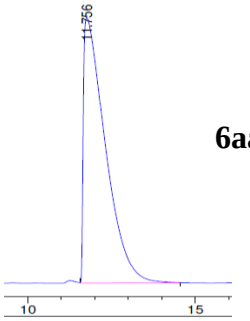

20110408-hl_1_75_Carbon-001
Br
OBn
(3*R*)-**6ba**
Normalized Intensity
Chemical Shift (ppm)

HPLC trace of **6aa** and **6ba**



6ba & **6aa**

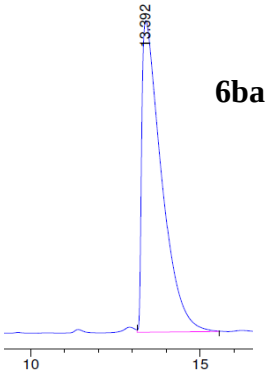
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.871	VV	0.4955	2.56954e4	761.86115	64.5914
2	13.109	VB	0.5448	1.40861e4	377.99646	35.4086



6aa

Signal 1: DAD1 D, Sig=254,16 Ref=360,100

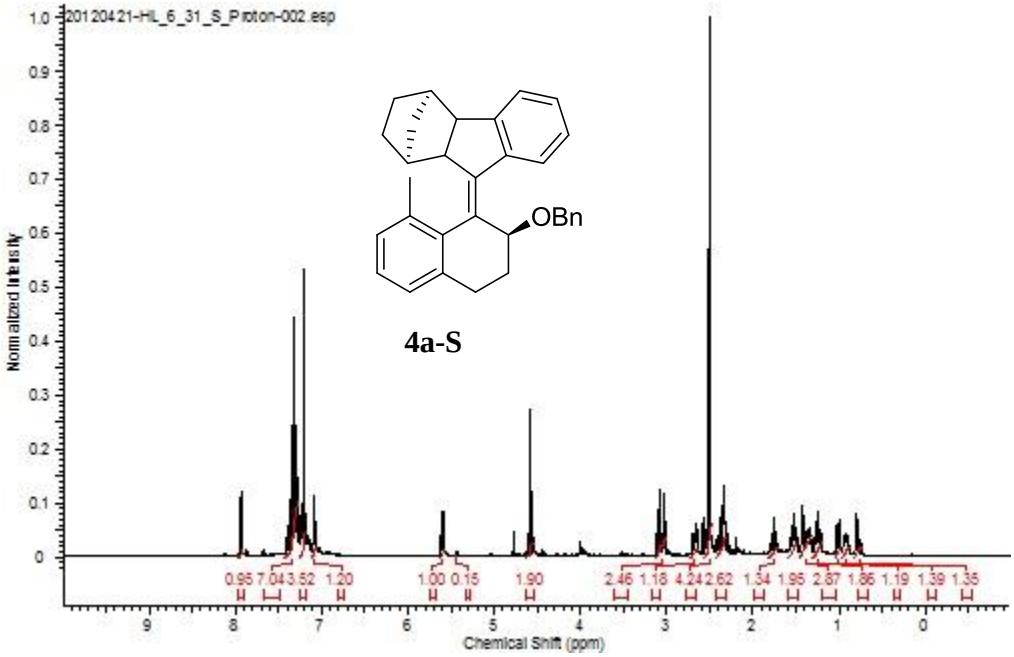
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.756	VB	0.6822	6.12563e4	1347.85083	100.0000

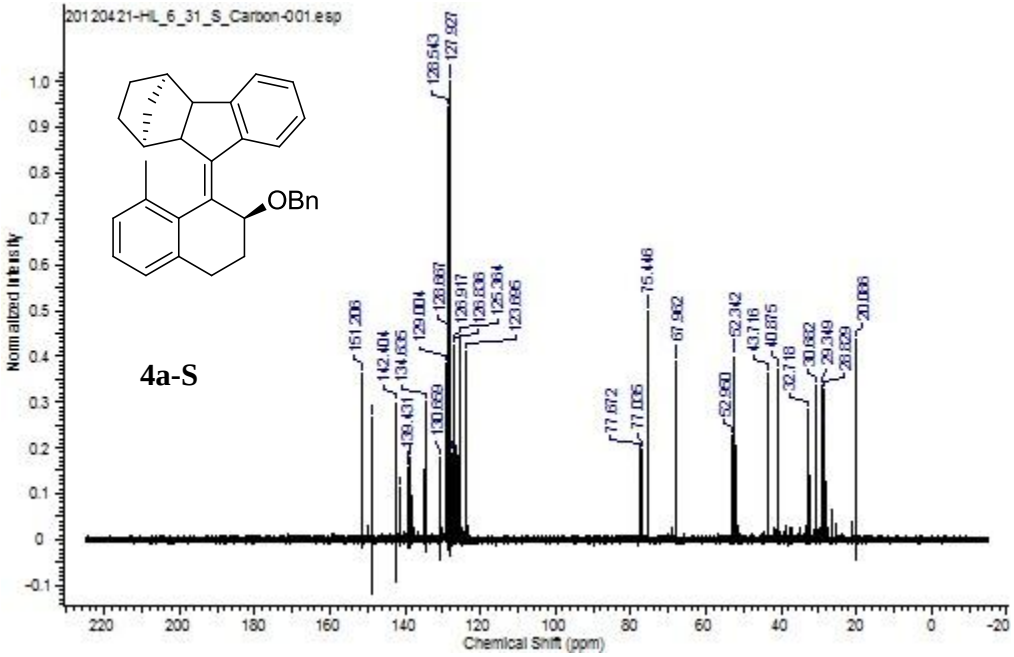


6ba

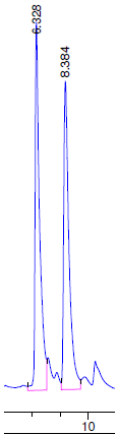
Signal 1: DAD1 D, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.392	VB	0.5954	2.63234e4	648.69214	100.0000


20120421-HIL_6_31_S_Proton-002.esp
OBn
4a-S
Normalized Intensity
Chemical Shift (ppm)
0.95 7.04 3.52 1.20 1.00 0.15 1.90 2.46 1.18 4.24 2.62 1.34 1.95 2.87 1.86 1.19 1.39 1.35


20120421-HIL_6_31_S_Carbon-001.esp
OBn
4a-S
Normalized Intensity
Chemical Shift (ppm)
151.206
142.404
134.635
139.431
129.004
128.867
130.669
128.543
127.927
126.917
126.836
125.364
123.686
77.672
77.035
75.446
67.962
52.342
52.060
43.716
40.675
32.718
30.682
29.349
28.829
20.066

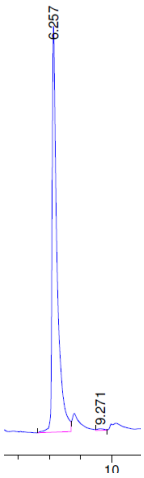
HPLC traces of 4a-S and 4b-R



Mixture of 4a-S & 4b-R

Signal 1: DAD1 A, Sig=210,6 Ref=360,40

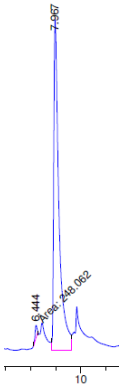
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.328	VV	0.3137	2.40733e4	1073.12439	50.5609
2	8.384	VV	0.3793	2.35391e4	899.43524	49.4391



4a-S

Signal 1: DAD1 A, Sig=210,6 Ref=360,40

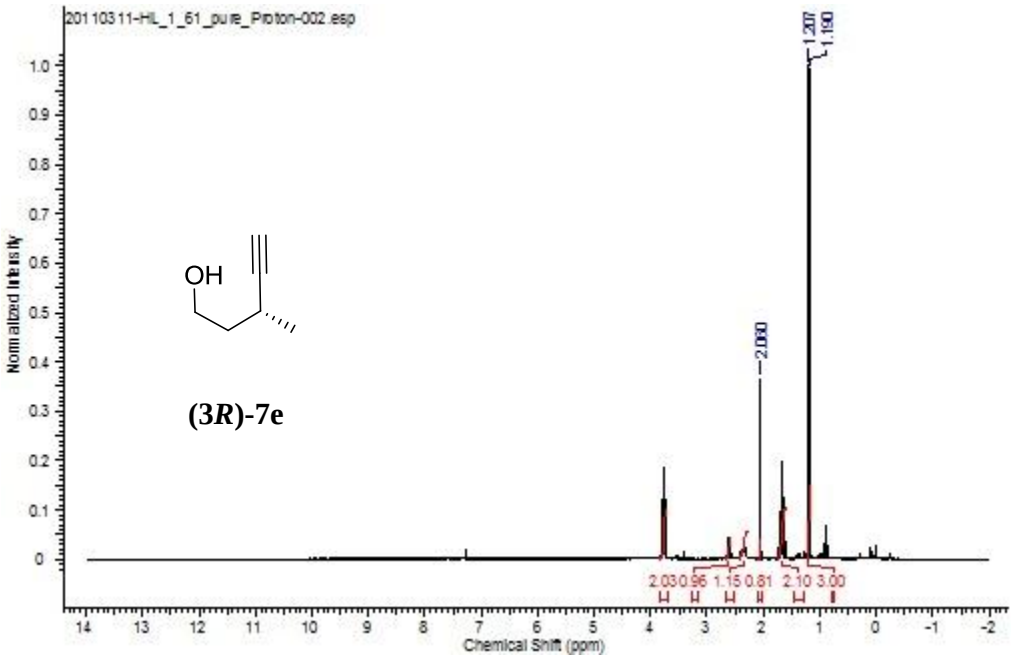
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.257	BV	0.3055	2.04257e4	925.56494	99.3666
2	9.271	BV	0.3680	130.20546	4.19635	0.6334

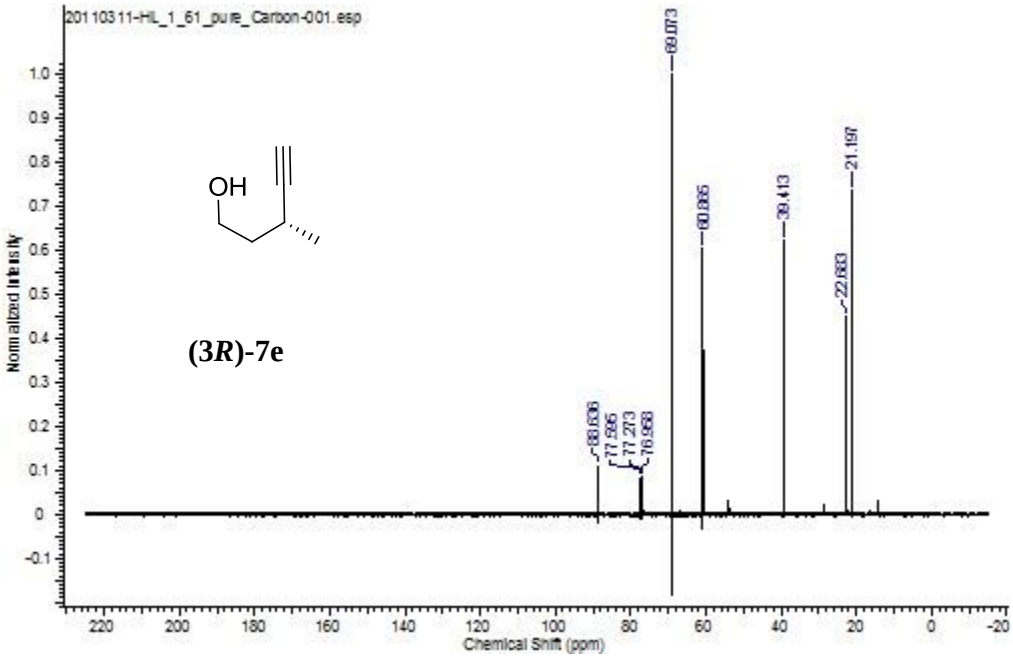


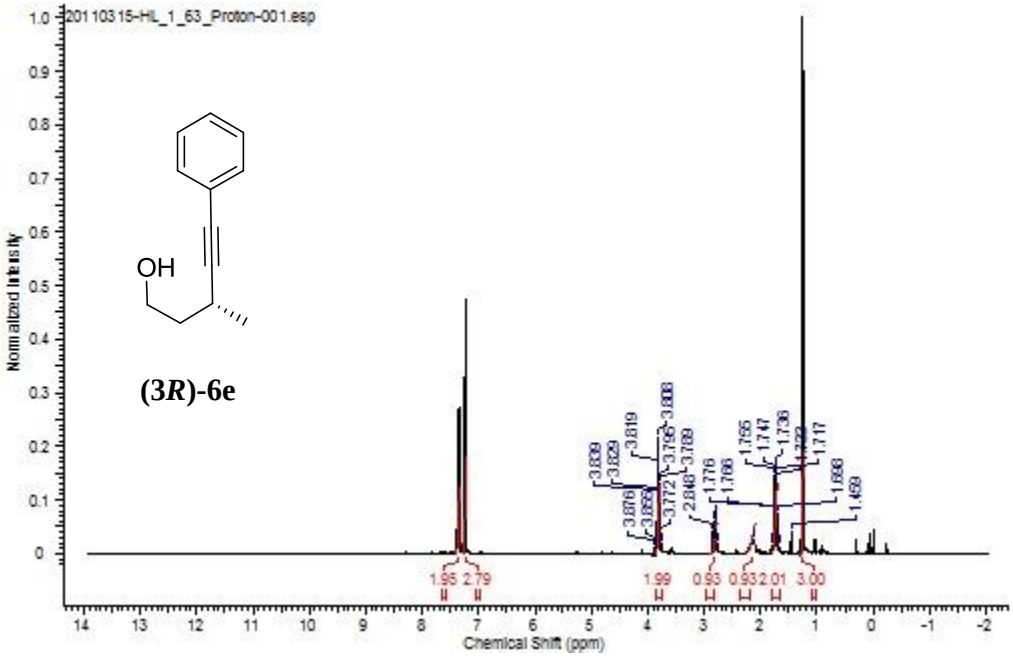
4b-R

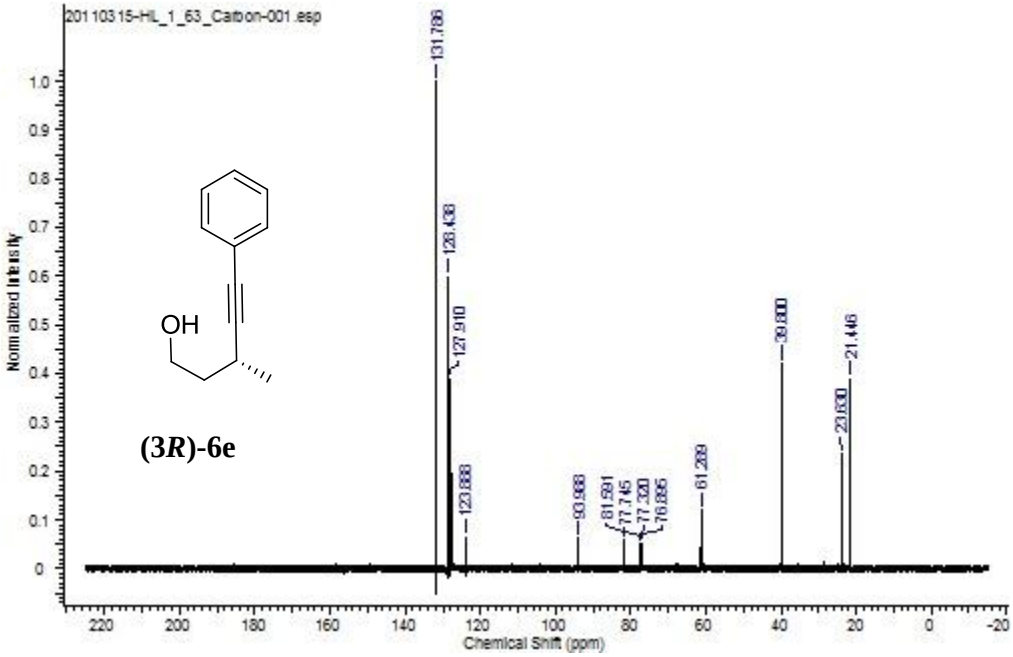
Signal 1: DAD1 A, Sig=210,6 Ref=360,40

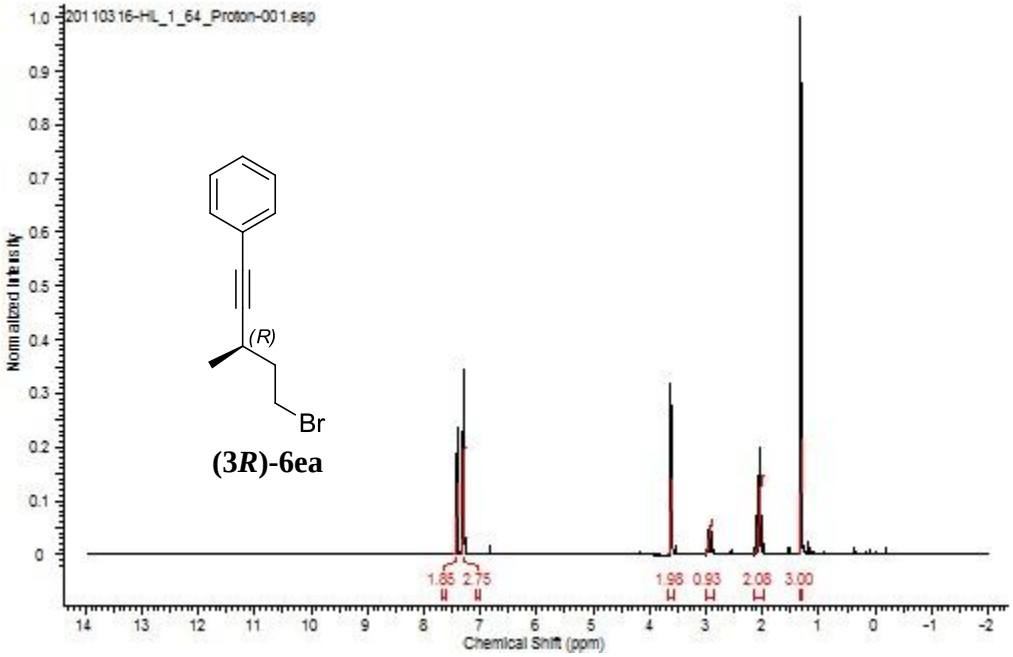
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.444	MM	0.1761	248.06198	23.47106	1.3767
2	7.967	VV	0.4136	1.77709e4	615.91846	98.6233

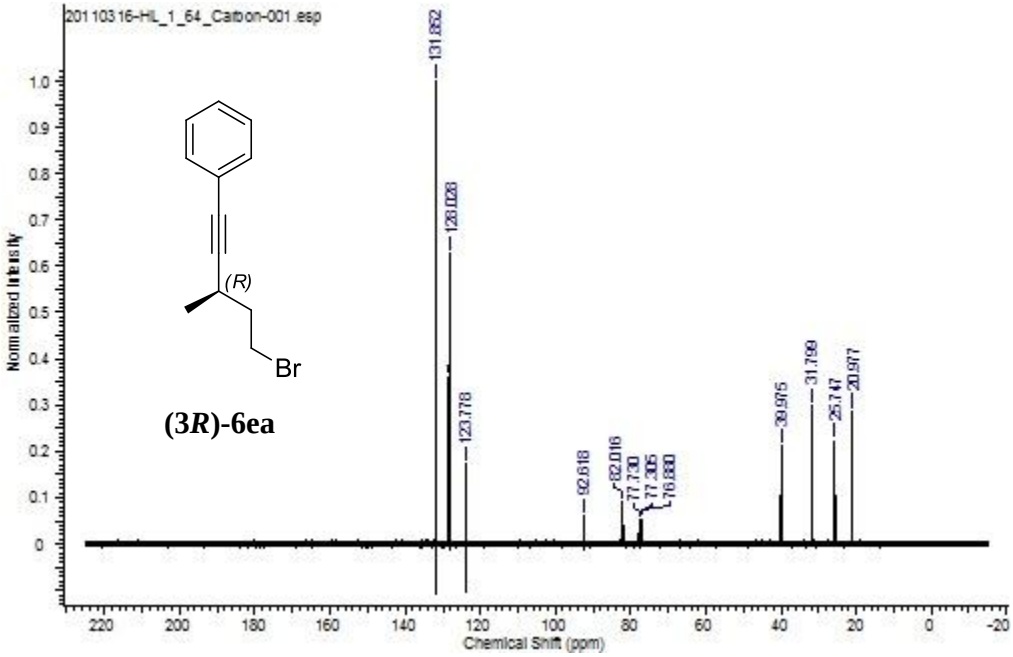

20110311-HIL_1_61_pure_Proton-002.esp
OH
(3R)-7e
1.207
1.190
2.000
2.03 0.96 1.15 0.81 2.10 3.00
Normalized Intensity
Chemical Shift (ppm)


20110311-HIL_1_61_pure_Carbon-001.esp
OH
(3R)-7e
69.073
60.835
39.413
21.197
22.683
88.606
77.595
77.273
76.958
Normalized Intensity
Chemical Shift (ppm)


20110315-HIL_1_63_Proton-001.esp
OH
(3R)-6e
Normalized Intensity
Chemical Shift (ppm)
1.95 2.79 1.99 0.93 0.93 2.01 3.00


20110315-HIL_1_63_Carbon-001.esp
OH
(3R)-6e
Normalized Intensity
Chemical Shift (ppm)
131.786
128.438
127.910
123.888
90.988
81.591
77.745
77.320
76.895
61.209
39.800
23.930
21.446


201103 16-HL_1_64_Proton-001.esp
(R)
Br
(3R)-6ea
1.85 2.75
1.96 0.93 2.08 3.00
Normalized Intensity
Chemical Shift (ppm)


201103 16-HL_1_64_Carbon-001.esp
(R)
Br
(3R)-6ea
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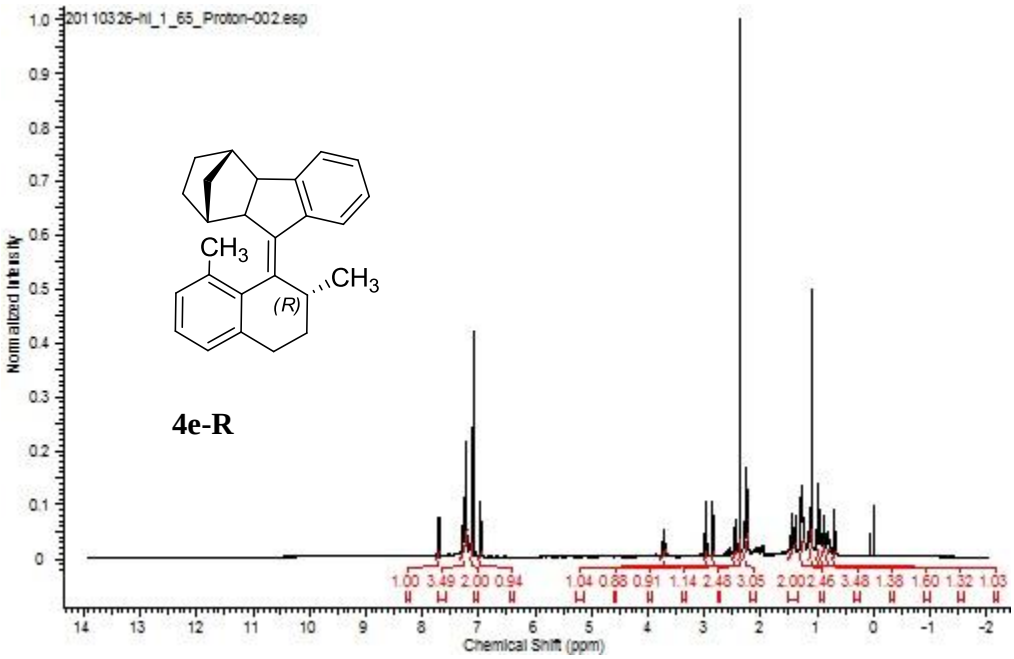
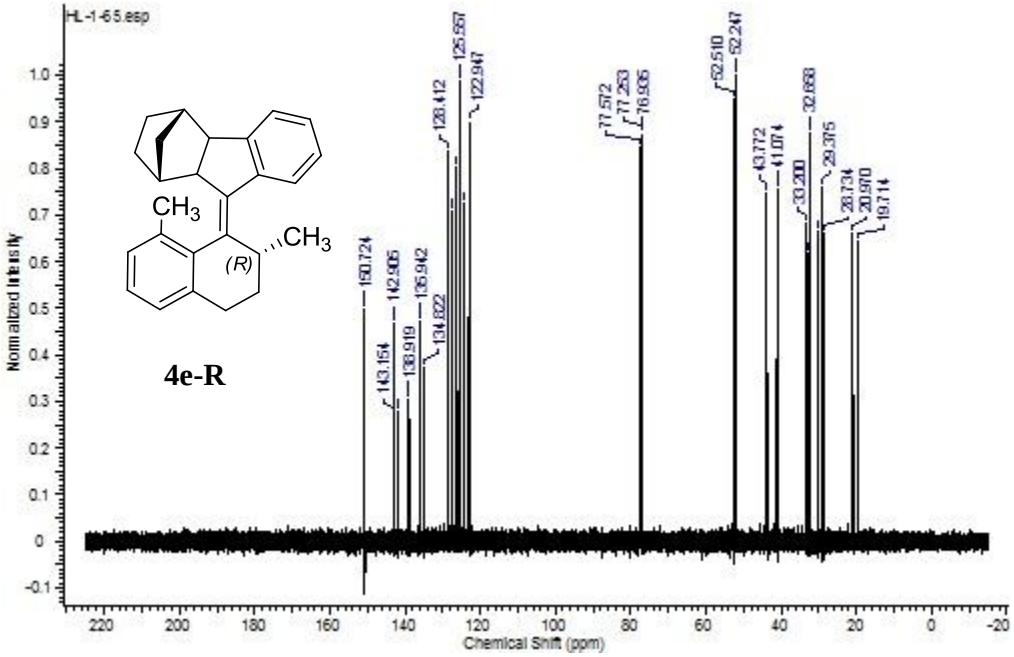
123.026
123.776
92.618
82.016
77.730
77.305
76.880
39.975
31.799
25.747
20.977
Normalized Intensity
Chemical Shift (ppm)


20110326-hl_1_65_Proton-002.esp
CH3
CH3
(R)
4e-R
Normalized Intensity
Chemical Shift (ppm)
1.00 3.49 2.00 0.94 1.04 0.88 0.91 1.14 2.48 3.05 2.00 2.46 3.48 1.38 1.60 1.32 1.03


HL-1-65.esp
CH3
CH3
(R)
4e-R
150.724
143.154
142.905
138.919
136.942
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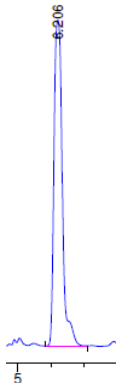
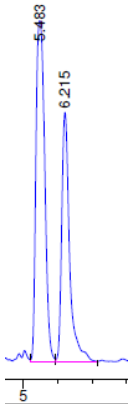
128.412
125.567
122.947
77.572
77.253
76.936
52.510
52.247
43.772
41.074
33.200
32.868
29.375
28.734
20.970
19.714
Normalized Intensity
Chemical Shift (ppm)

HPLC Trace of 3R-**6ea**



Signal 1: DAD1 C, Sig=235,8 Ref=360,100

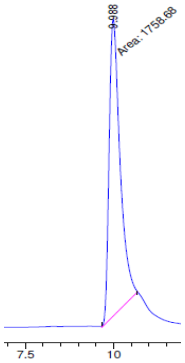
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.206	VV	0.2727	4.99027e4	2900.76587	100.0000



Signal 1: DAD1 C, Sig=235,8 Ref=360,100

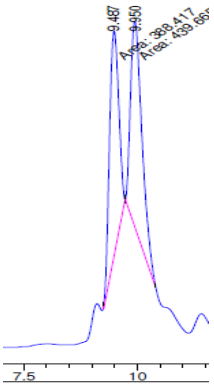
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.483	VV	0.2824	4.93260e4	2814.83618	59.9458
2	6.215	VV	0.2429	3.29583e4	2057.67480	40.0542

HPLC trace of **4e-R**



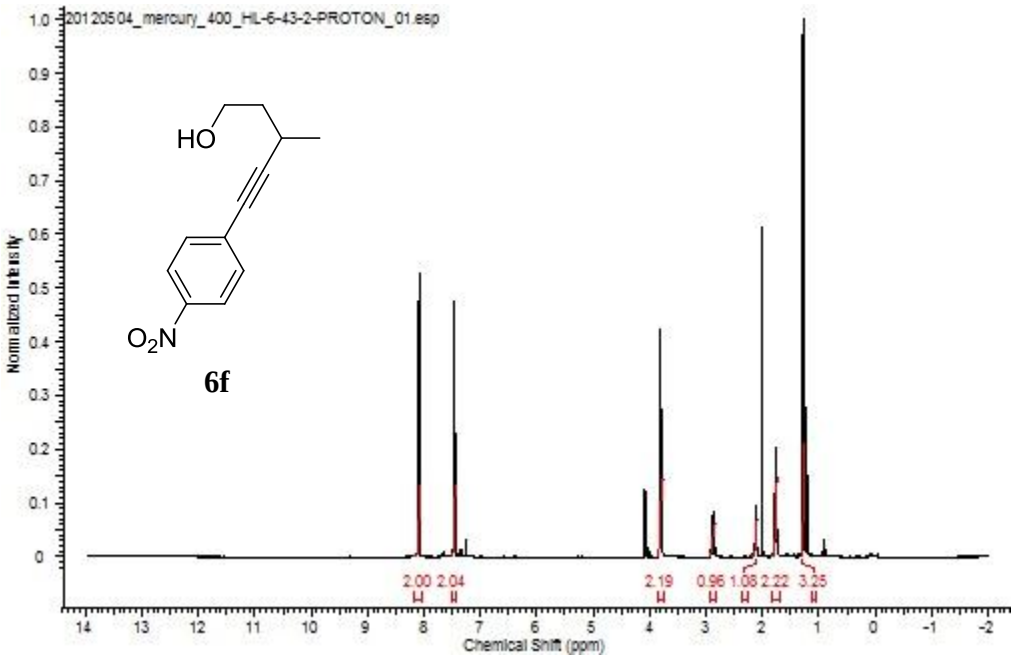
Signal 1: DAD1 E, Sig=269,16 Ref=360,100

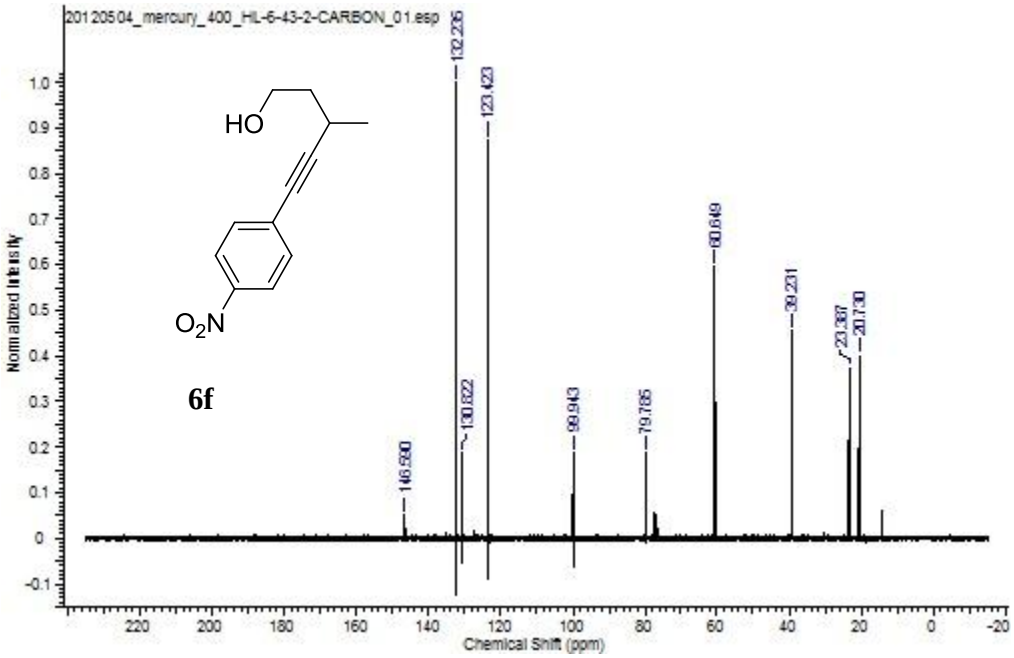
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.988	MM	0.3591	1758.67615	81.61610	100.0000

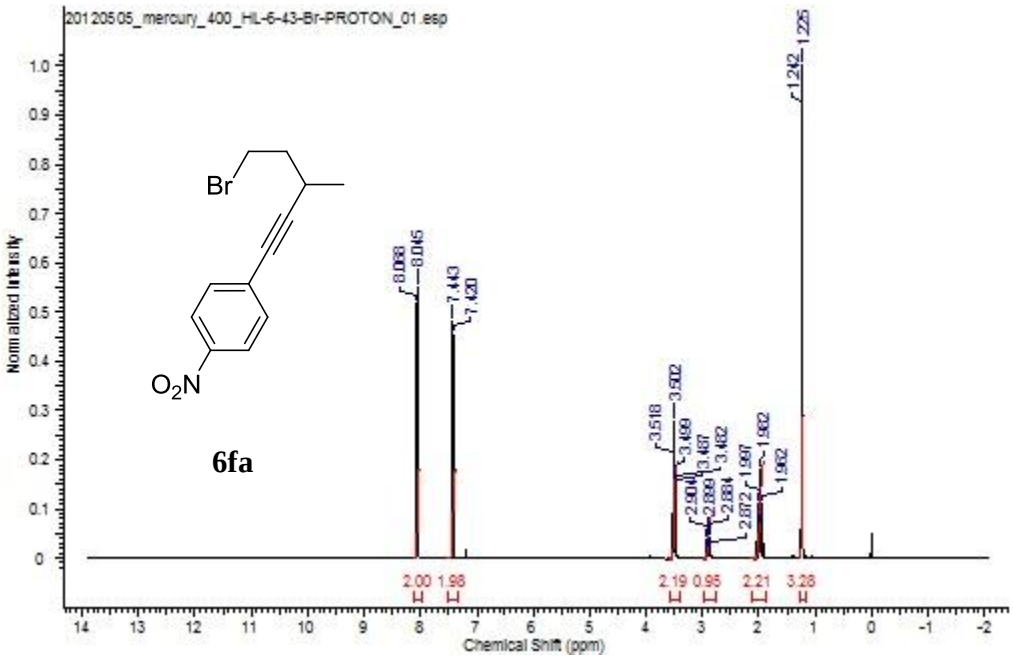


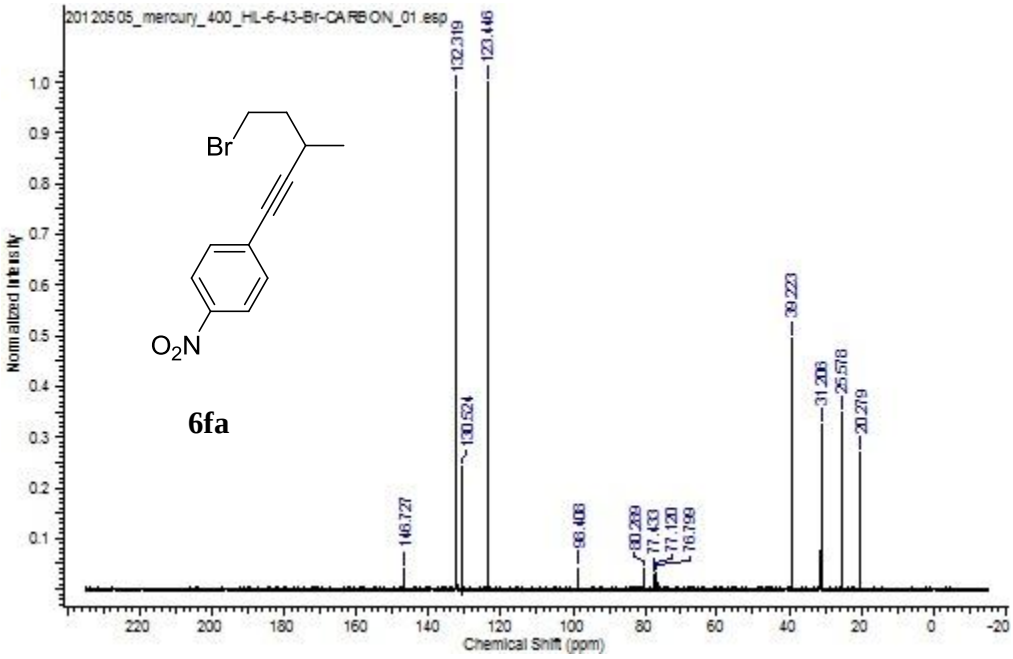
Signal 1: DAD1 E, Sig=269,16 Ref=360,100

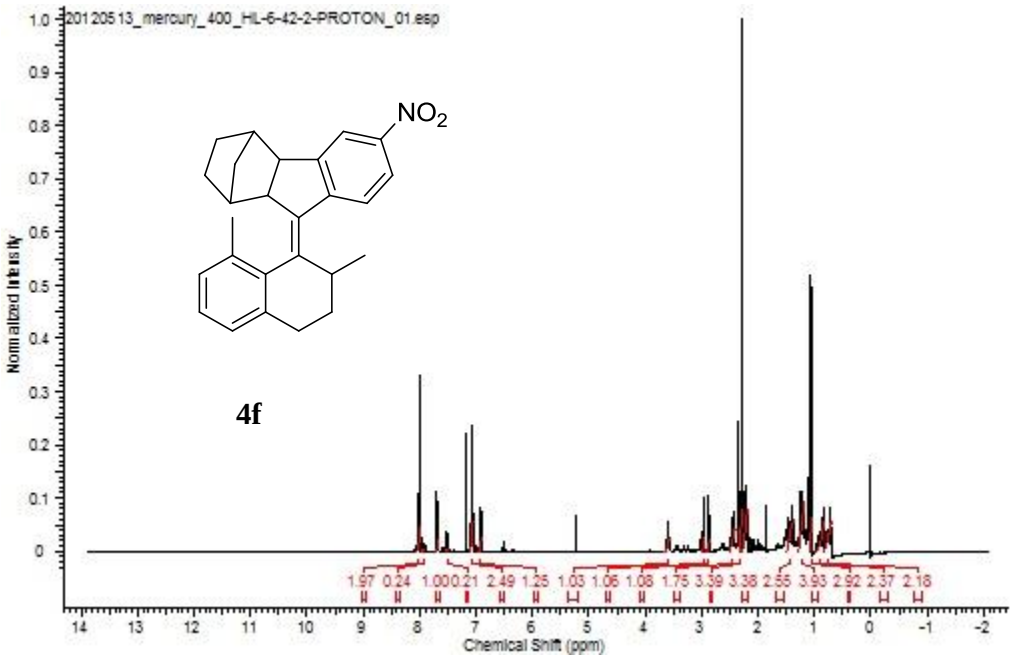
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.487	MM	0.2360	388.41684	27.43240	46.9056
2	9.950	MM	0.2924	439.66516	25.06434	53.0944

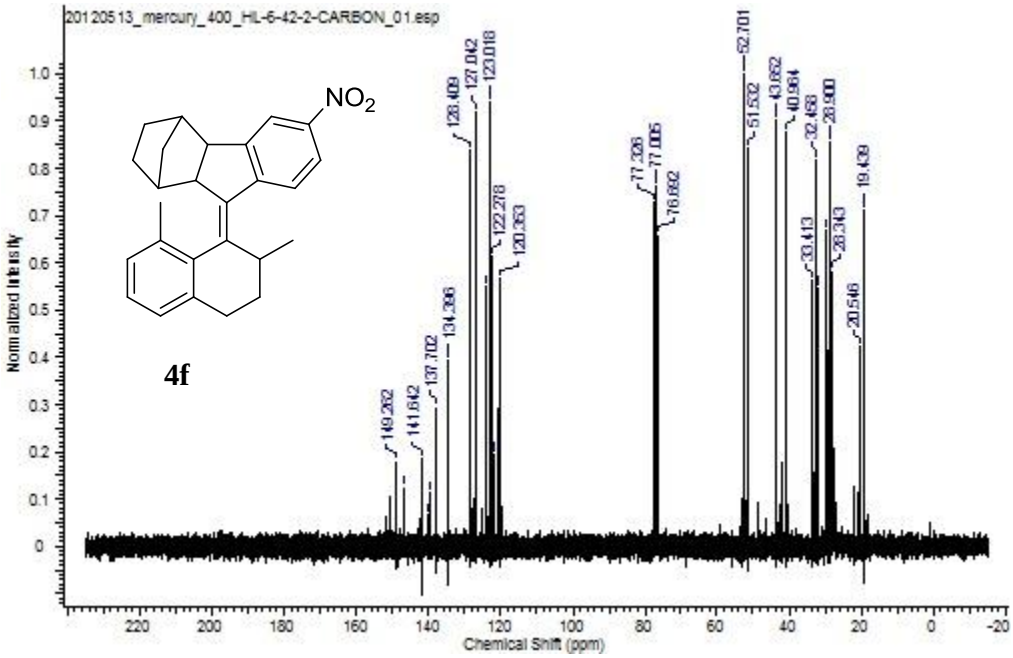

20120504_mercury_400_HIL-6-43-2-PROTON_01.esp
HO
O2N
6f
2.00 2.04
2.19
0.96 1.08 2.22 3.25
Normalized Intensity
Chemical Shift (ppm)

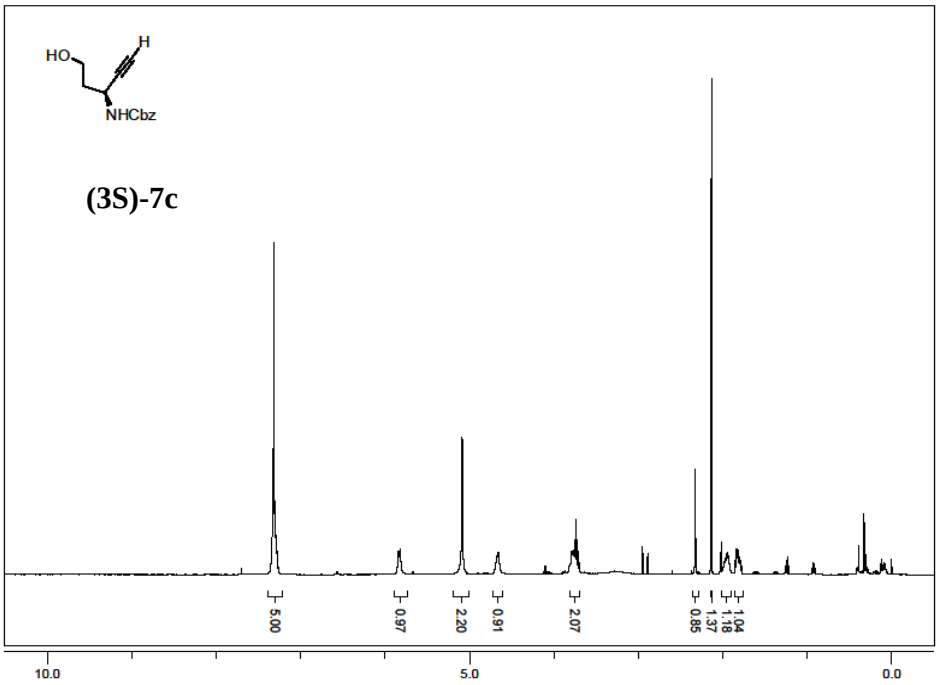

20120504_mercury_400_HIL-6-43-2-CARBON_01.esp
HO
O2N
6f
132.226
123.423
130.822
146.590
99.943
79.785
60.649
39.231
23.387
20.730
Normalized Intensity
Chemical Shift (ppm)

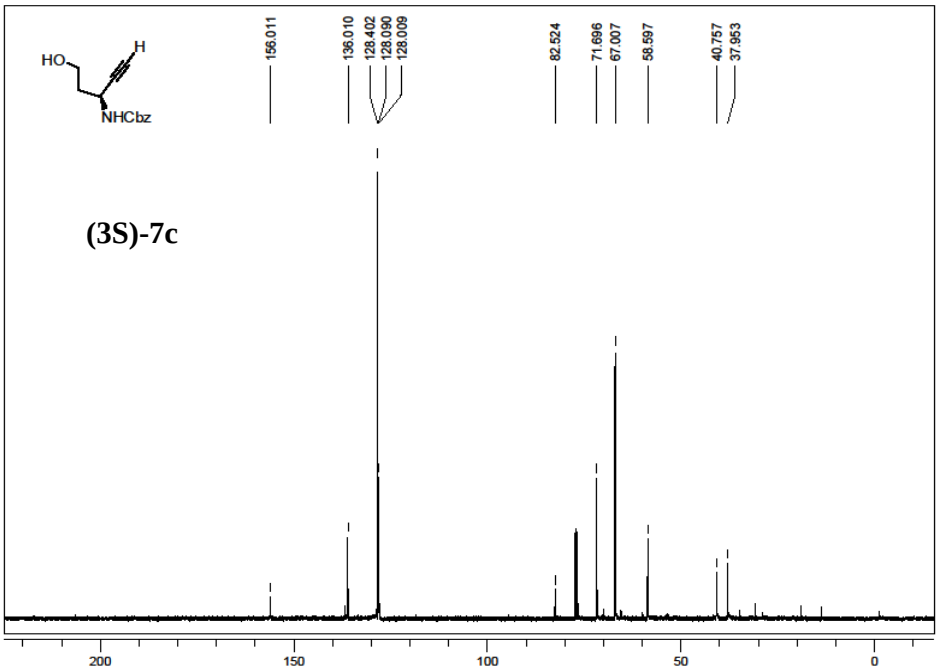

20120505_mercury_400_HIL-6-43-Br-PROTON_01.esp
Br
O_2N
6fa
8.068
8.045
7.443
7.420
3.518
3.502
3.499
3.487
3.482
2.904
2.899
2.884
2.872
1.997
1.992
1.962
1.225
1.242
2.00 1.98
2.19 0.95
2.21 3.28
Normalized Intensity
Chemical Shift (ppm)

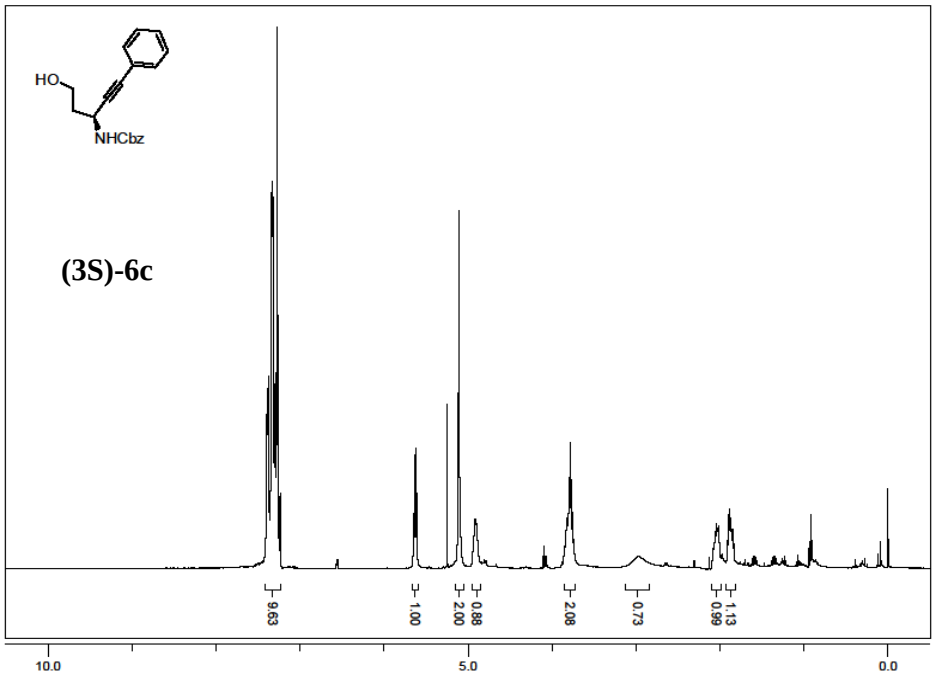

20120505_mercury_400_HIL-6-43-Br-CARBON_01.esp
Br
O_2N
6fa
132.319
123.446
130.524
146.727
98.408
80.289
77.433
77.120
76.799
39.223
31.206
25.578
20.279
Normalized Intensity
Chemical Shift (ppm)

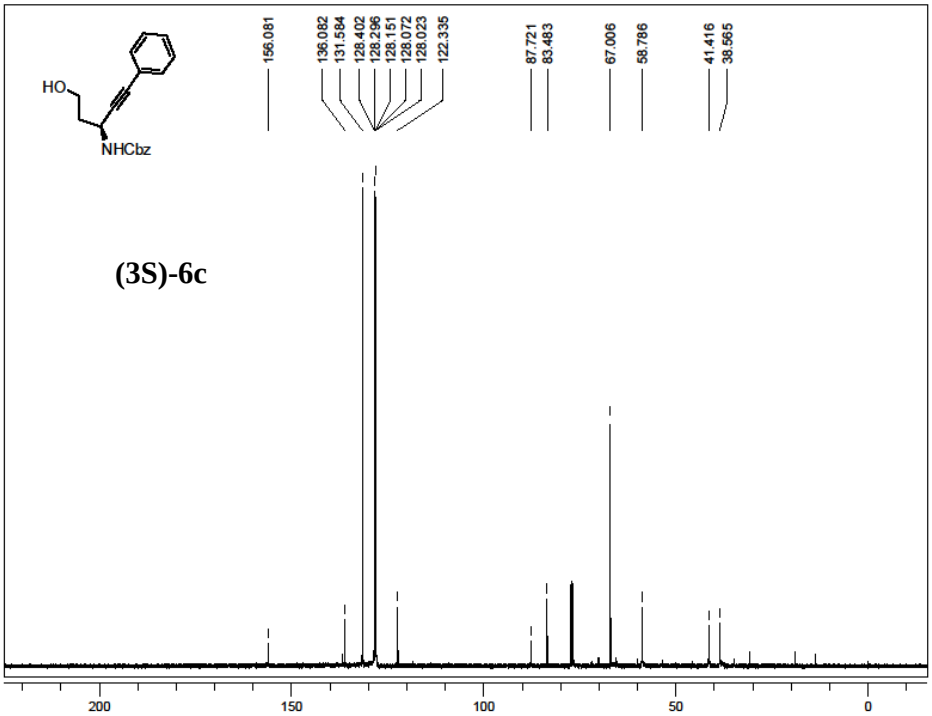

20120513_mercury_400_HIL-6-42-2-PROTON_01.esp
NO2
4f
Normalized Intensity
Chemical Shift (ppm)
1.97 0.24 1.00 0.21 2.49 1.25 1.03 1.06 1.08 1.75 3.39 3.38 2.55 3.93 2.92 2.37 2.18

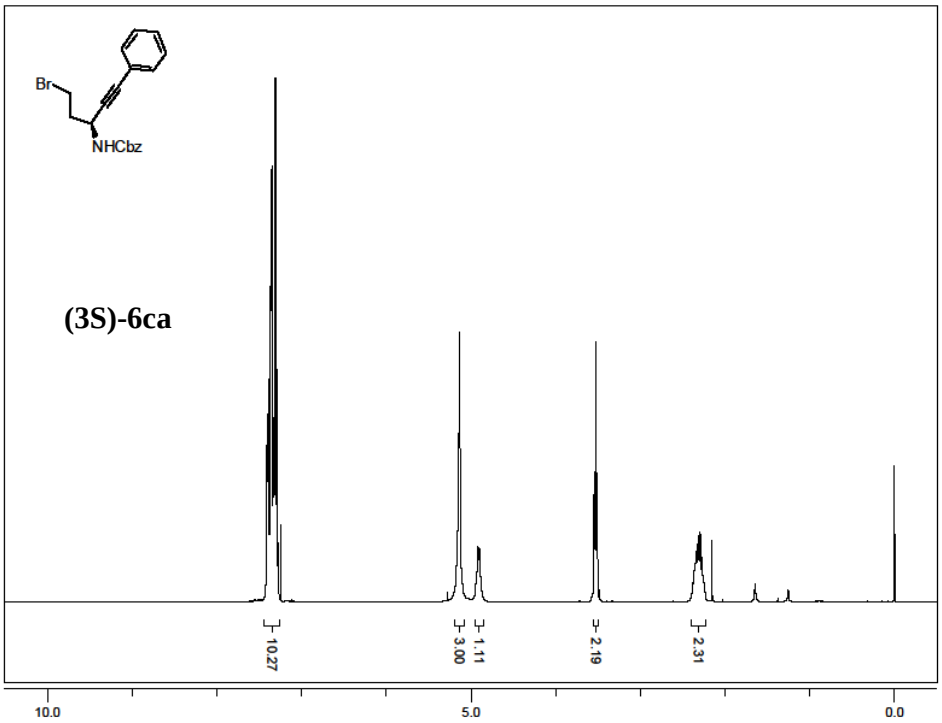

20120513_mercury_400_HIL-6-42-2-CARBON_01.esp
NO2
4f
Normalized Intensity
Chemical Shift (ppm)
149.262
141.642
137.702
134.396
128.409
127.042
123.016
122.278
120.353
77.326
77.005
76.682
52.701
51.532
43.652
40.964
32.468
33.413
28.900
28.343
20.546
19.439

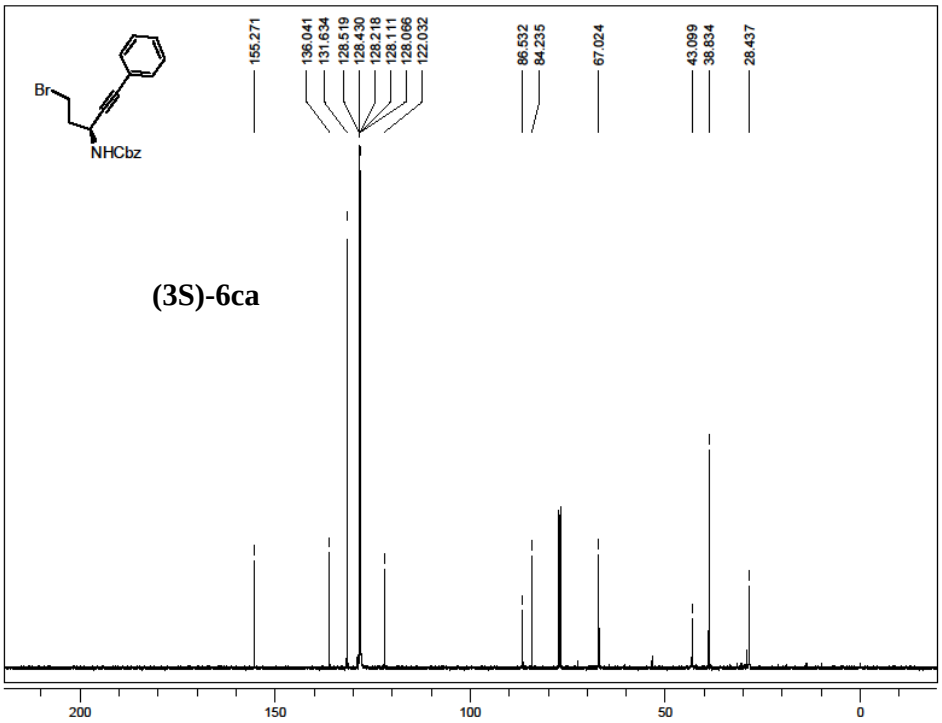

HO
H
NHCbz
(3S)-7c
5.00
0.97
2.20
0.91
2.07
0.85
1.37
1.18
1.04
10.0
5.0
0.0

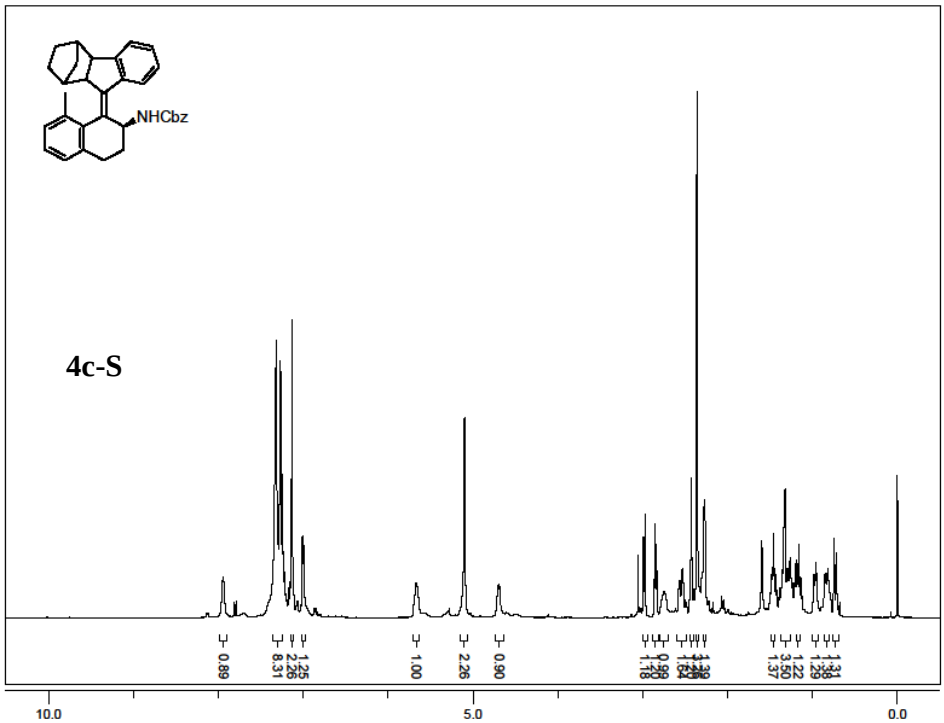

HO
H
NHCbz
(3S)-7c
156.011
136.010
128.402
128.090
128.009
82.524
71.696
67.007
58.597
40.757
37.953
200
150
100
50
0

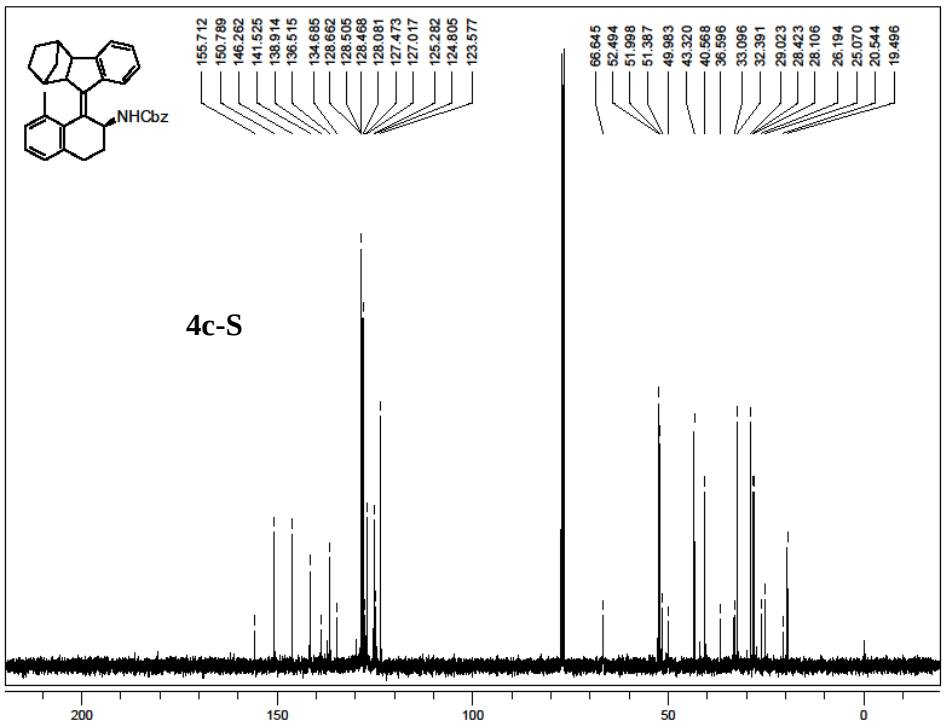

HO
NHCbz
(3S)-6c
9.63
1.00
2.00
0.88
2.08
0.73
0.99
1.13
10.0
5.0
0.0


HO
NHCbz
(3S)-6c
156.081
136.082
131.584
128.402
128.296
128.151
128.072
128.023
122.335
87.721
83.483
67.006
58.786
41.416
38.565
200
150
100
50
0

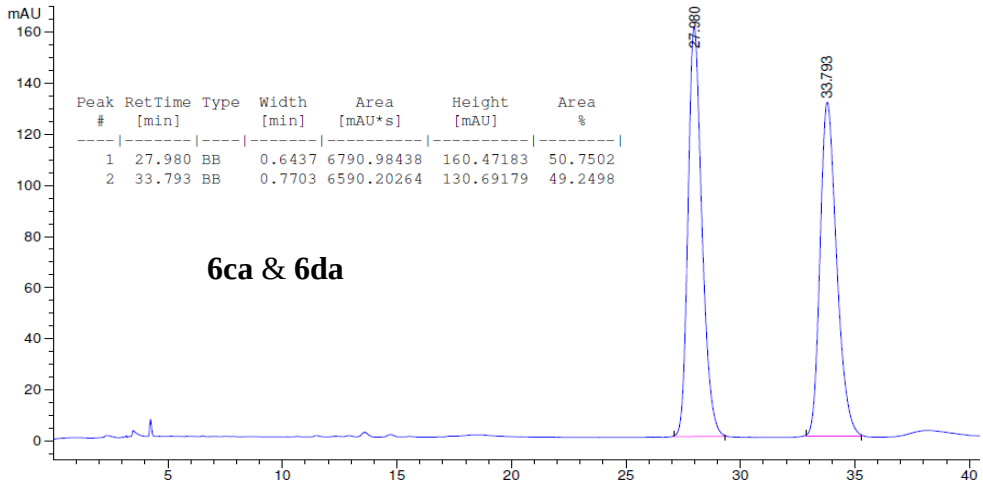

Br
NHCbz
(3S)-6ca
10.27
3.00
1.11
2.19
2.31
10.0
5.0
0.0

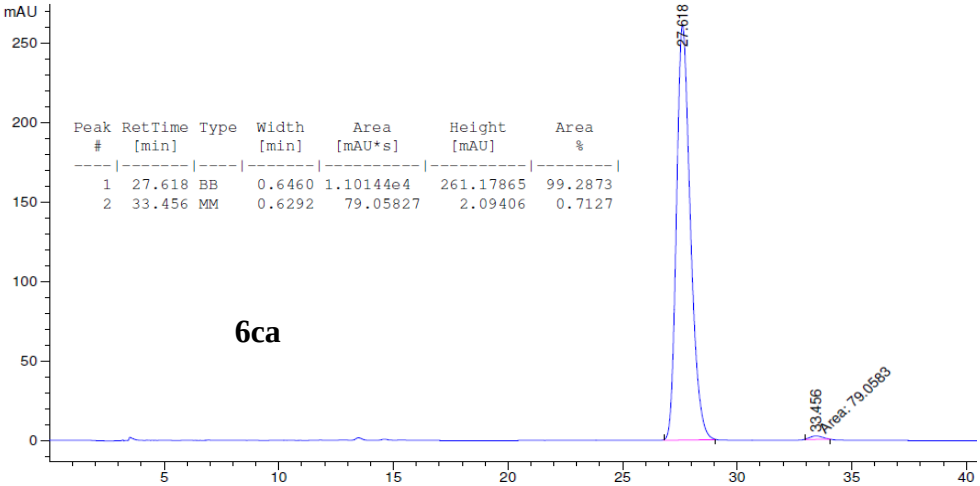

Br
NHCbz
(3S)-6ca
155.271
136.041
131.634
128.519
128.430
128.218
128.111
128.066
122.032
86.532
84.235
67.024
43.099
38.834
28.437
200
150
100
50
0

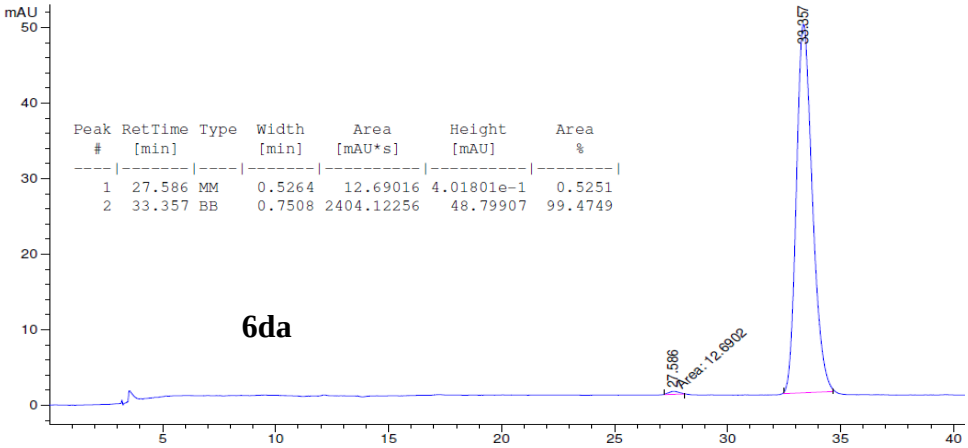

NHCbz
4c-S
0.89
6.31
2.26
1.25
1.00
2.26
0.90
1.18
0.99
0.98
1.37
3.50
1.22
1.29
1.38
1.31
10.0
5.0
0.0


NHCbz
4c-S
155.712
150.789
146.262
141.525
138.914
136.515
134.685
128.662
128.505
128.468
128.081
127.473
127.017
125.282
124.805
123.577
66.645
52.494
51.998
51.387
49.983
43.320
40.568
36.596
33.096
32.391
29.023
28.423
28.106
26.194
25.070
20.544
19.496
200
150
100
50
0

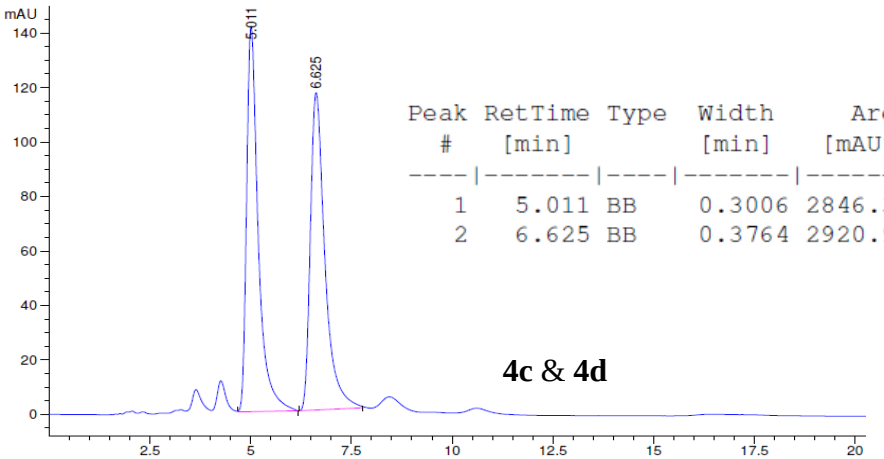
HPLC trace of (3S)-**6ca** and (3R)-**6da**



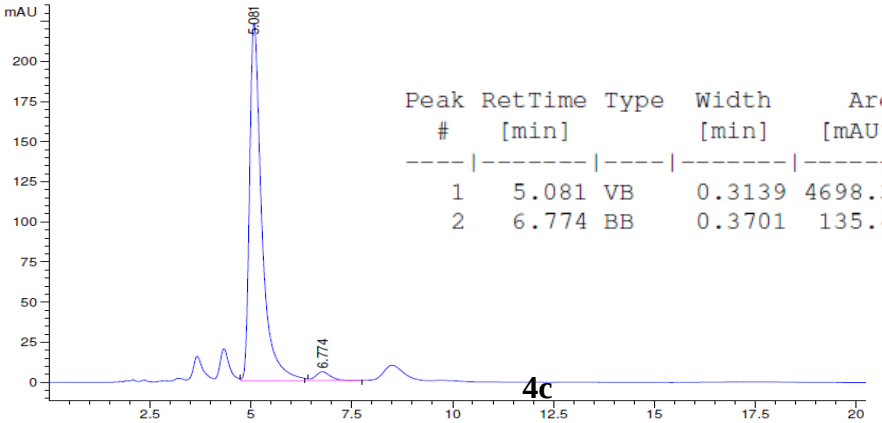




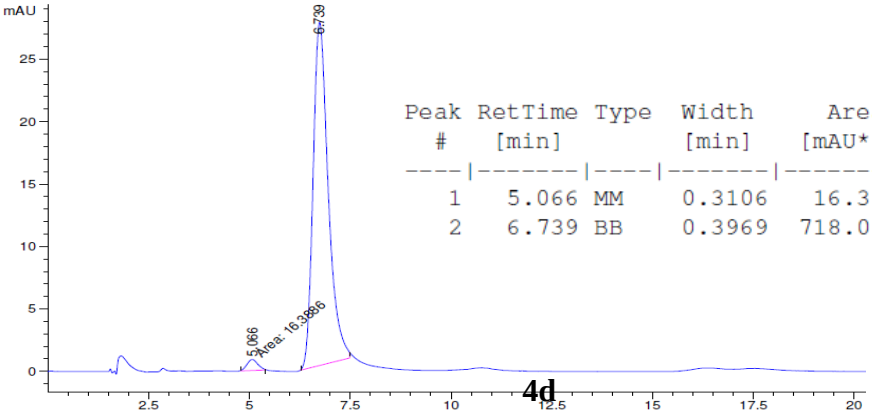
HPLC trace of **4c-S** and **4d-R**



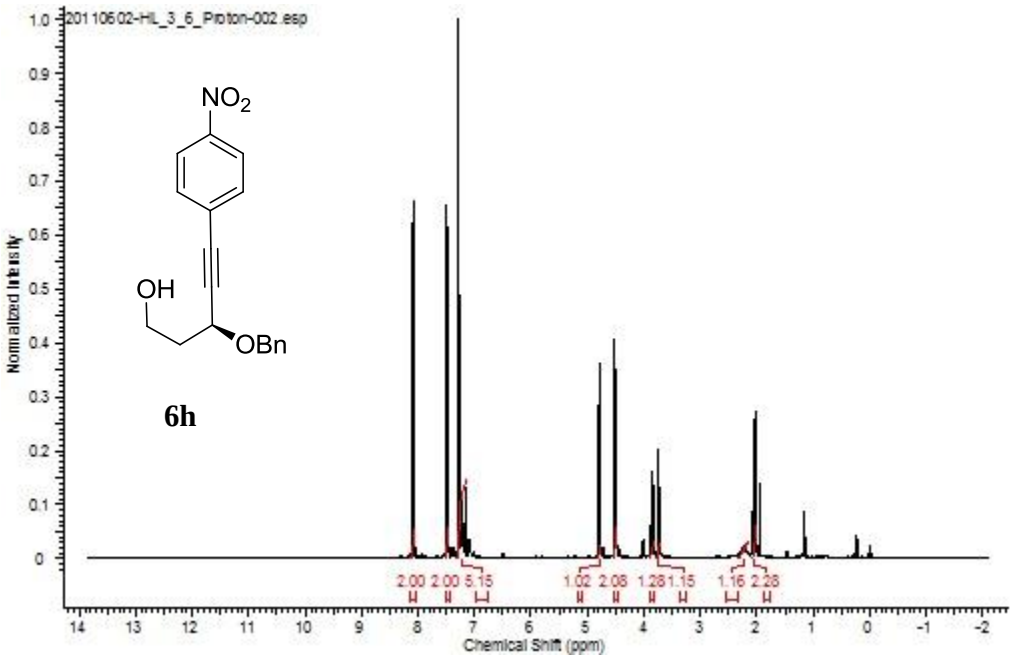
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.011	BB	0.3006	2846.35937	141.56934	49.3536
2	6.625	BB	0.3764	2920.92041	116.52809	50.6464

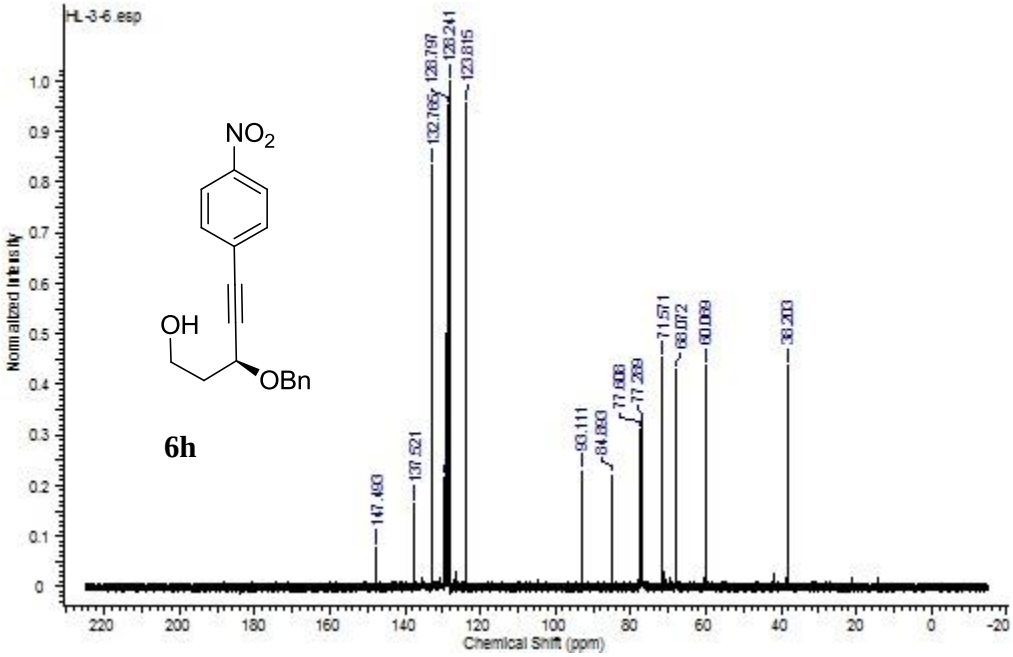


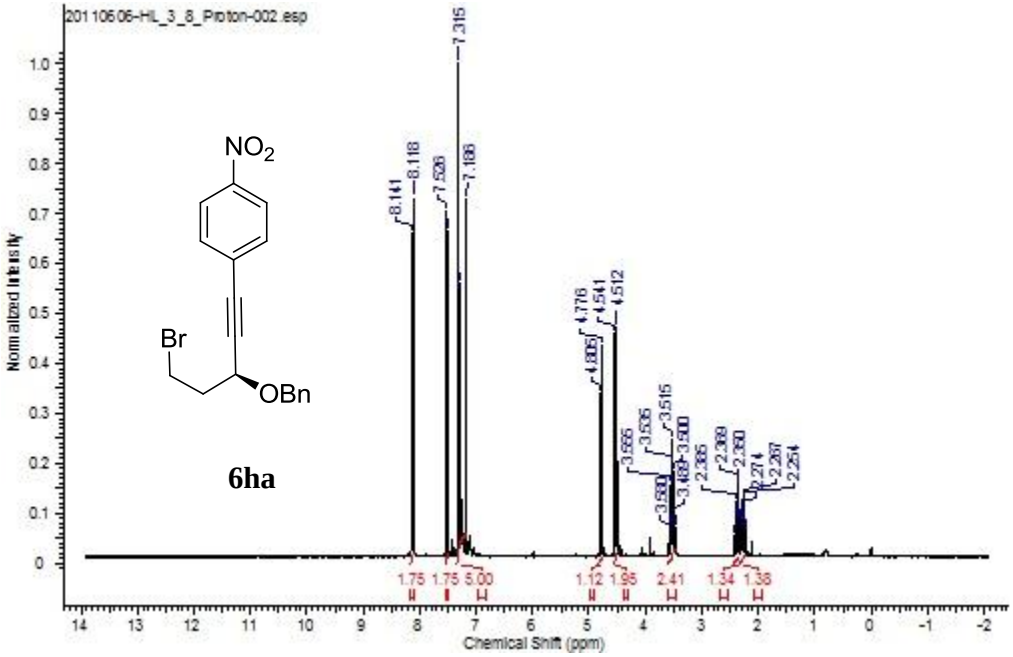
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.081	VB	0.3139	4698.32715	222.92935	97.1983
2	6.774	BB	0.3701	135.42508	5.48362	2.8017

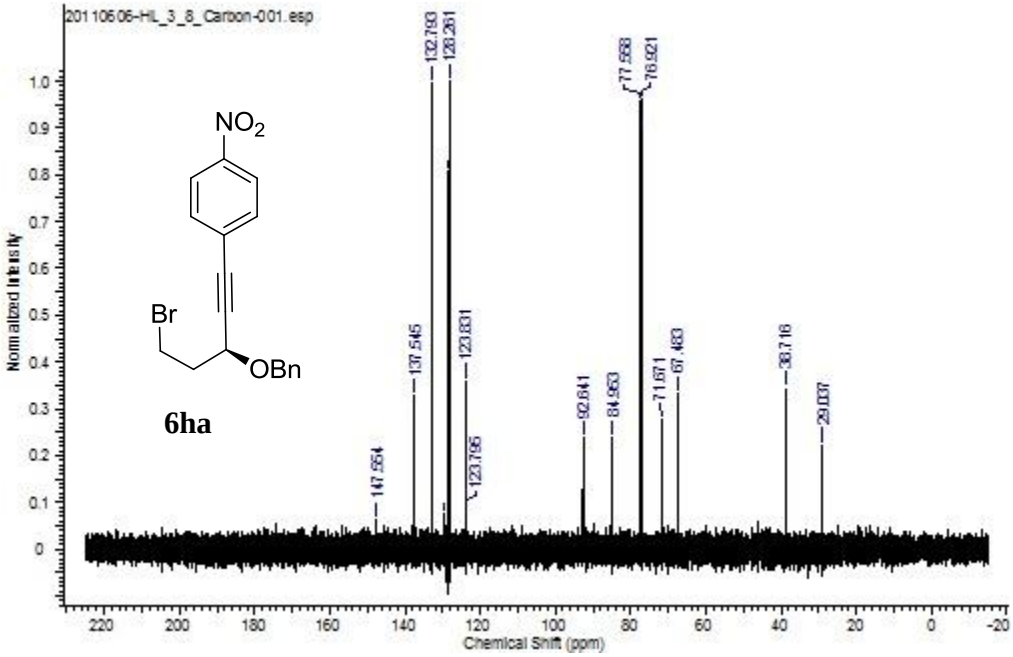


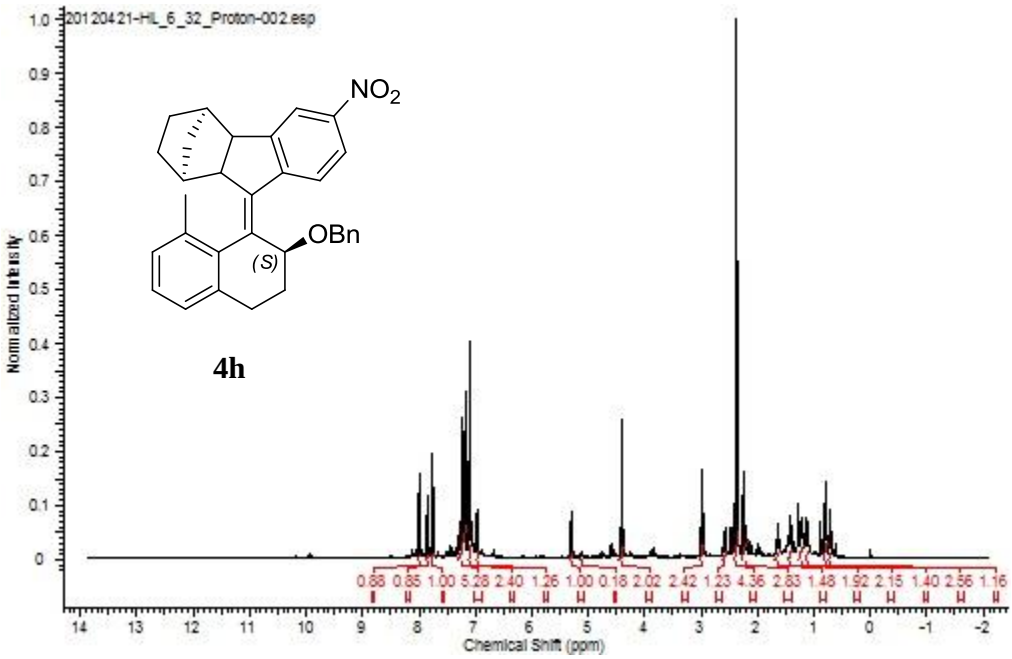
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.066	MM	0.3106	16.38861	8.79379e-1	2.2313
2	6.739	BB	0.3969	718.09088	27.48118	97.7687

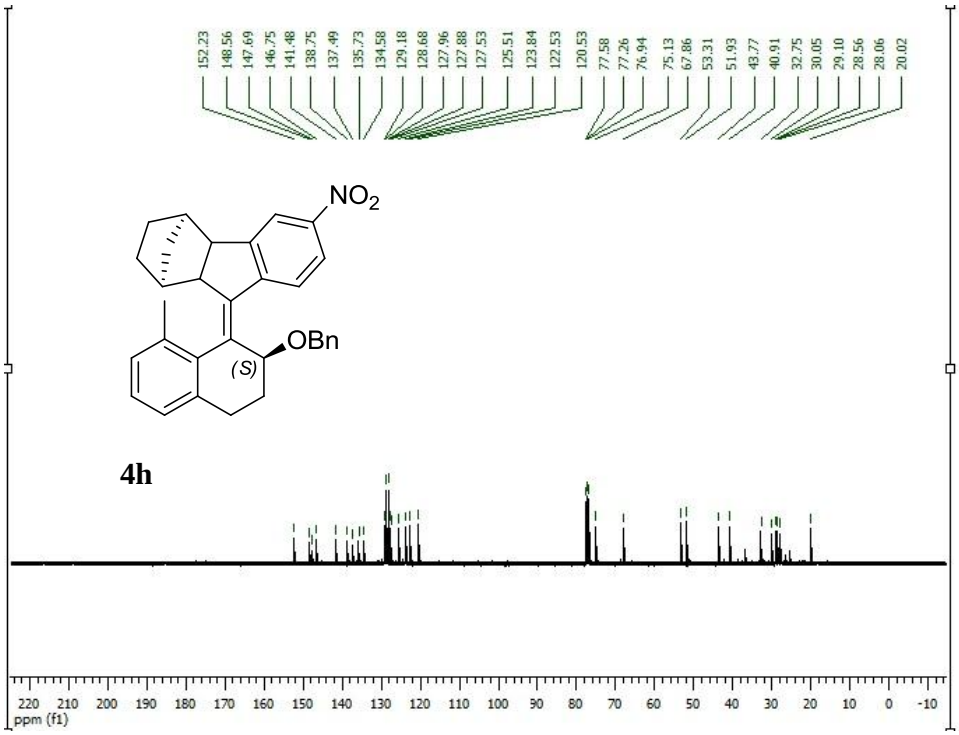

20110602-HL_3_6_Proton-002.esp
NO2
OH
OBn
6h
2.00 2.00 5.15 1.02 2.08 1.28 1.15 1.16 2.28
Normalized Intensity
Chemical Shift (ppm)

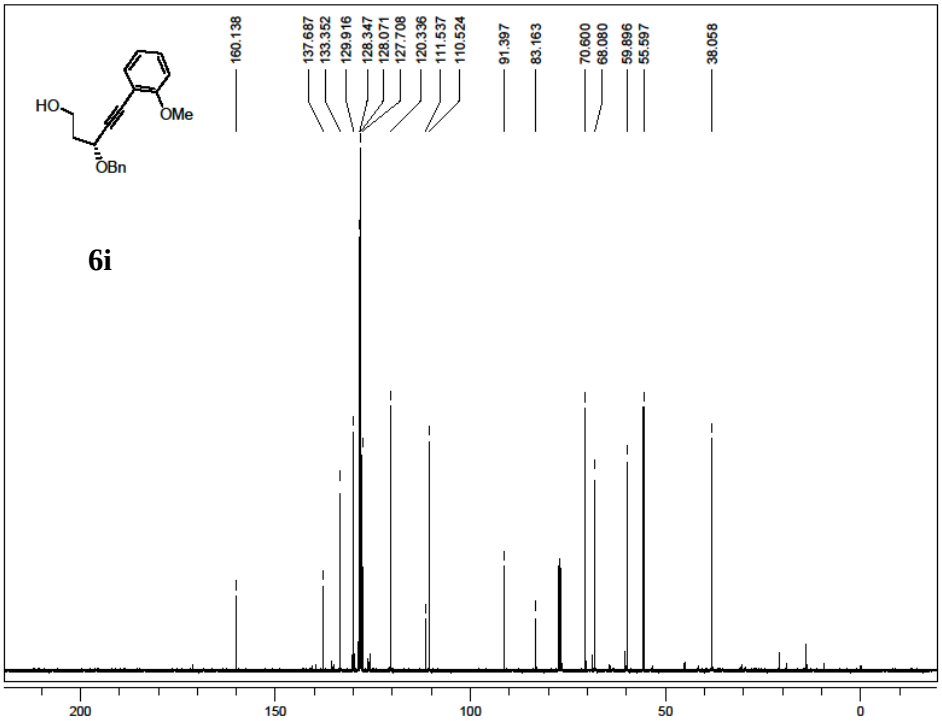

HL-3-6.esp
NO2
OH
OBn
6h
147.493
137.521
132.765
128.797
128.241
123.815
90.111
84.893
77.608
77.289
71.571
68.072
60.069
38.203
Normalized Intensity
Chemical Shift (ppm)

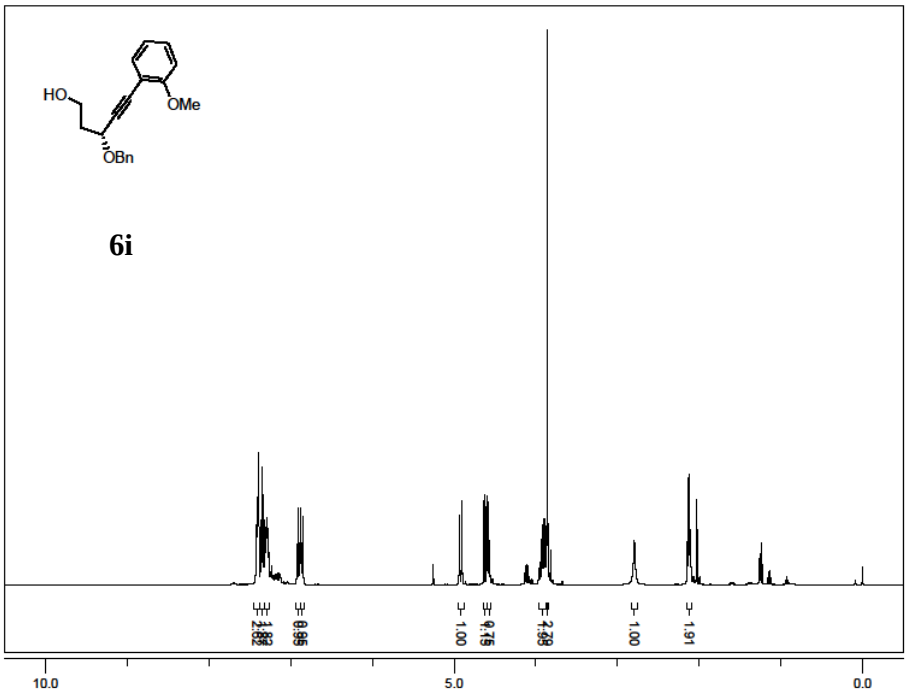

20110606-HIL_3_8_Proton-002.esp
NO2
Br
OBn
6ha
Normalized Intensity
Chemical Shift (ppm)

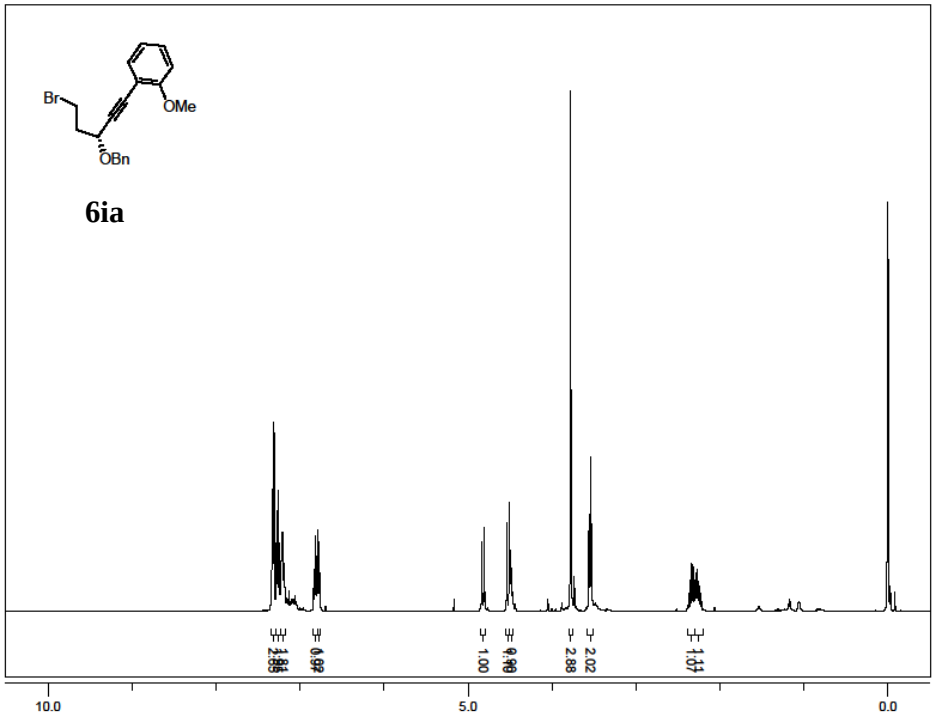

20110606-HIL_3_8_Carbon-001.esp
NO2
Br
OBn
6ha
Normalized Intensity
Chemical Shift (ppm)

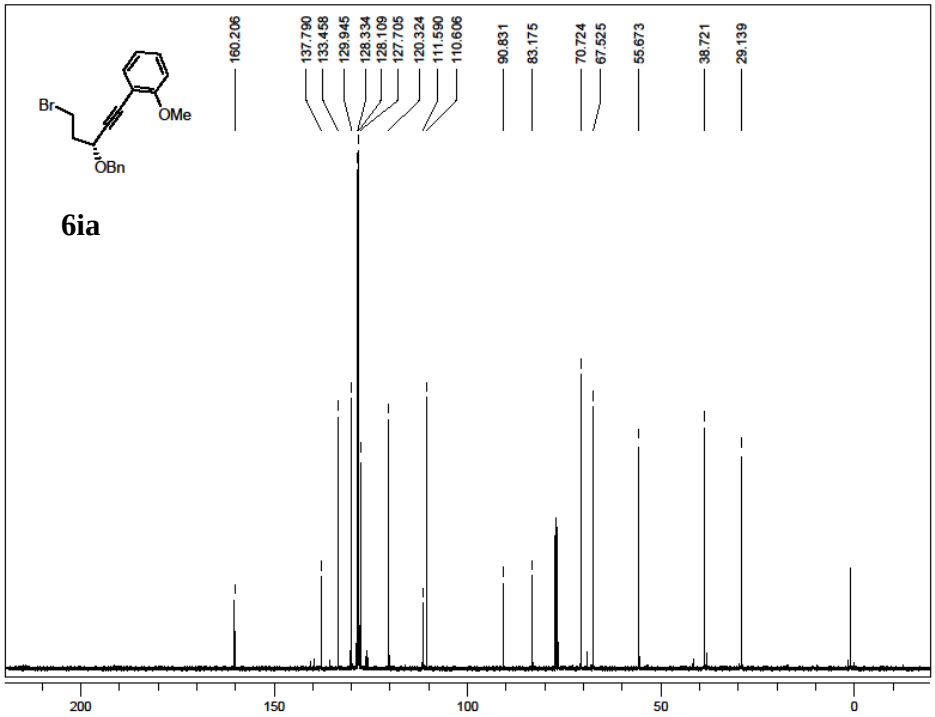

20120421-HIL_6_32_Proton-002.esp
NO2
OBn
(S)
4h
Normalized Intensity
Chemical Shift (ppm)
0.88 0.85 1.00 5.28 2.40 1.26 1.00 0.18 2.02 2.42 1.23 4.36 2.83 1.48 1.92 2.15 1.40 2.56 1.16

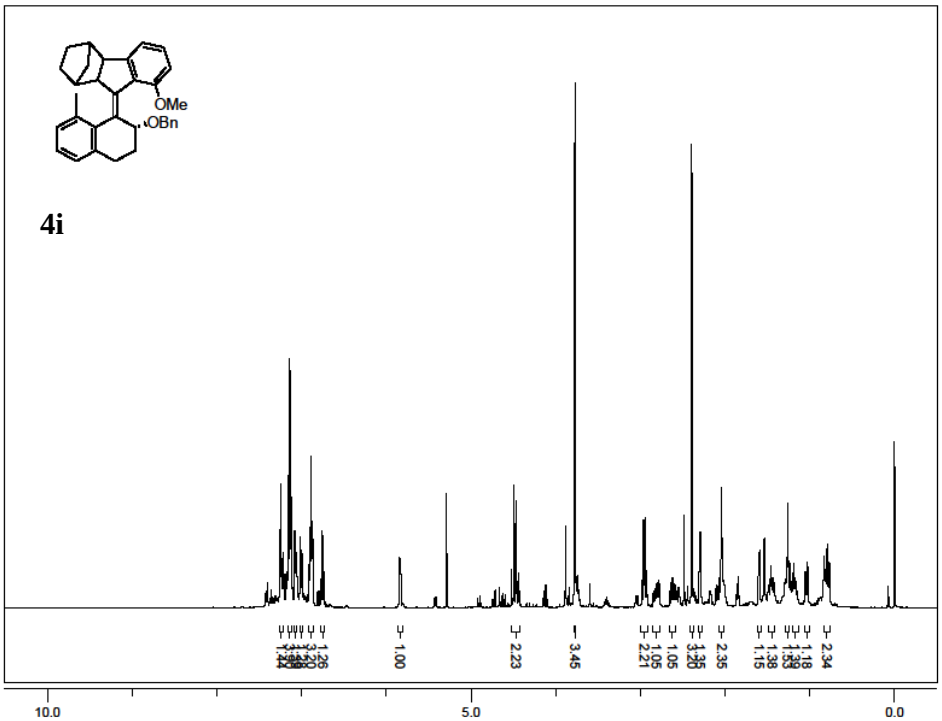

152.23 148.56 147.69 146.75 141.48 138.75 137.49 135.73 134.58 129.18 128.68 127.96 127.88 127.53 125.51 123.84 122.53 120.53 77.58 77.26 76.94 75.13 67.86 53.31 51.93 43.77 40.91 32.75 30.05 29.10 28.56 28.06 20.02
NO2
OBn
(S)
4h
ppm (f1)


HO
OMe
OBn
6i
160.138
137.687
133.352
129.916
128.347
128.071
127.708
120.336
111.537
110.524
91.397
83.163
70.600
68.080
59.896
55.597
38.058
200
150
100
50
0


HO
OMe
OBn
6i
1.00
1.00
1.91
10.0
5.0
0.0


Br
OMe
OBn
6ia
10.0
5.0
0.0


160.206
137.790
133.458
129.945
128.334
128.109
127.705
120.324
111.590
110.606
90.831
83.175
70.724
67.525
55.673
38.721
29.139
Br
OMe
OBn
6ia
200
150
100
50
0


OMe
OBn
4i
1.00
2.23
3.45
2.21
1.05
3.20
3.35
2.35
1.15
1.38
1.18
2.34
10.0
5.0
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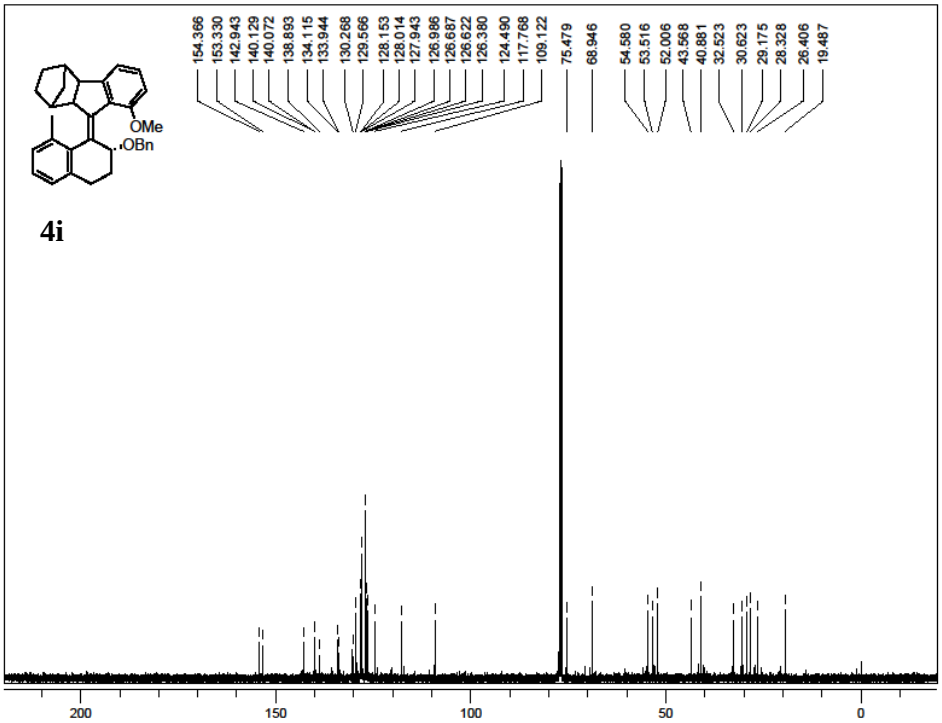
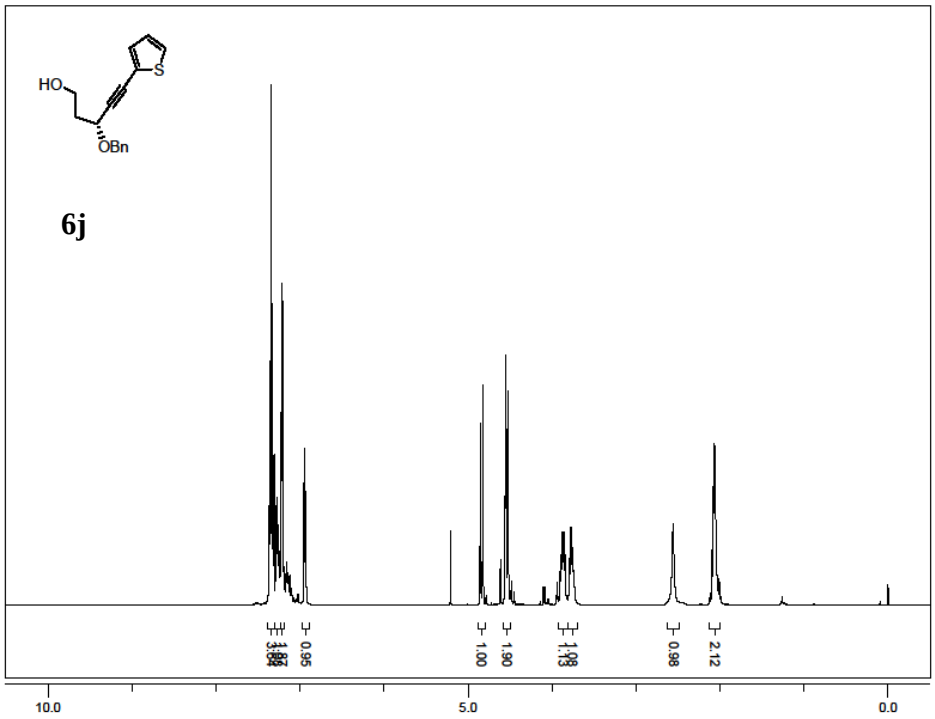

OMe
OBn
4i
154.366
153.330
142.943
140.129
140.072
138.893
134.115
133.944
130.268
129.566
128.153
128.014
127.943
126.986
126.687
126.622
126.380
124.490
117.768
109.122
75.479
68.946
54.580
53.516
52.006
43.568
40.881
32.523
30.623
29.175
28.328
26.406
19.487
200
150
100
50
0


HO
S
OBn
6j
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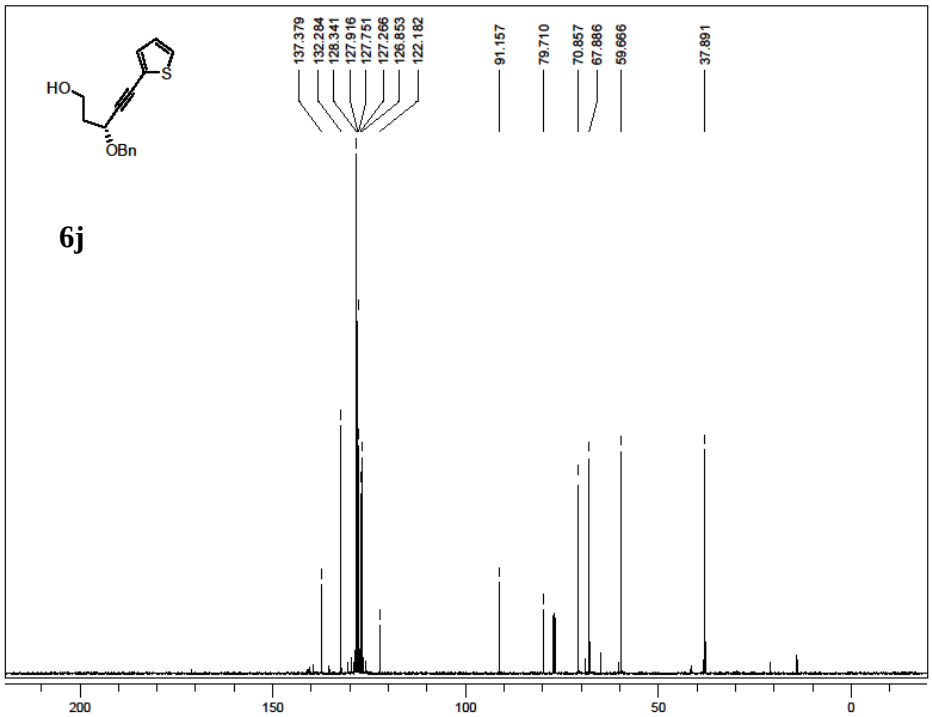
1.00
1.60
0.98
2.12
10.0
5.0
0.0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S
OBn
6j
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132.284
128.341
127.916
127.751
127.266
126.853
122.182
91.157
79.710
70.857
67.886
59.666
37.891
200
150
100
50
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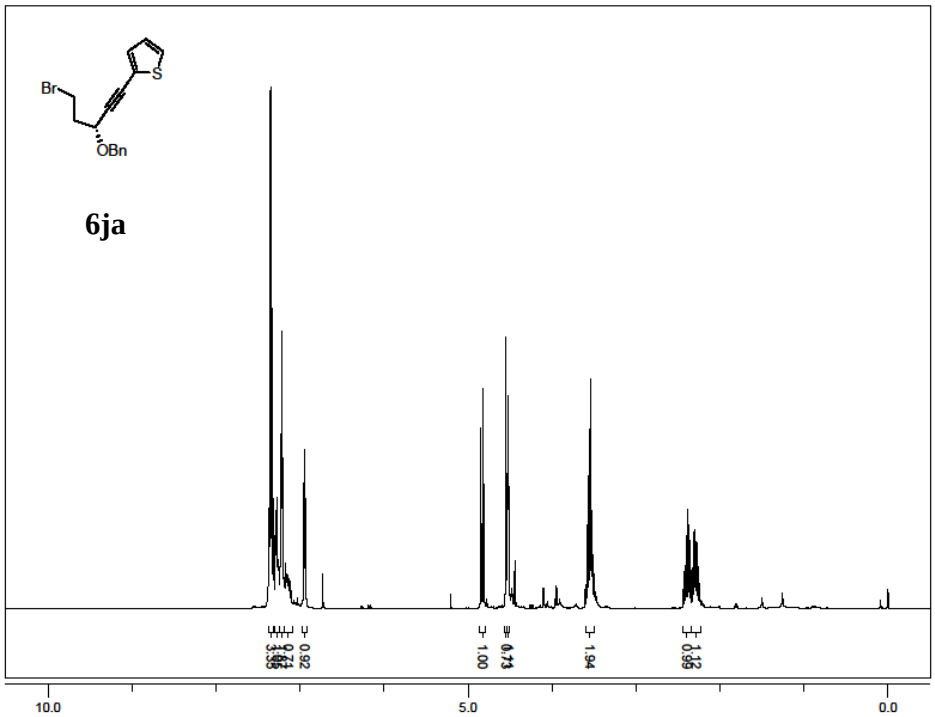
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S
OBn
6ja
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5.0
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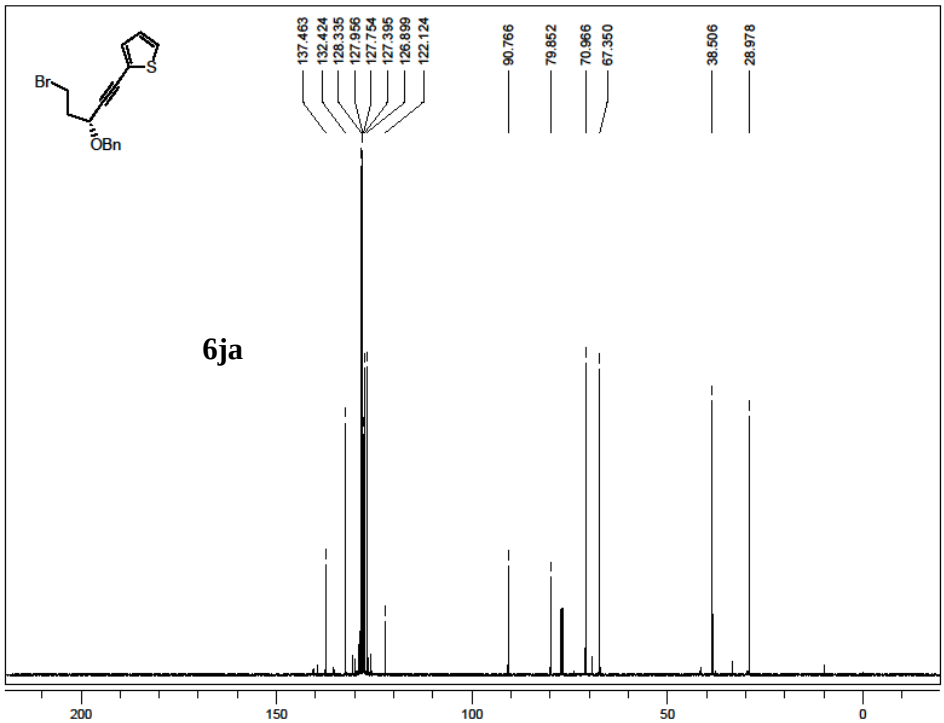
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S
OBn
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132.424
128.335
127.956
127.754
127.395
126.899
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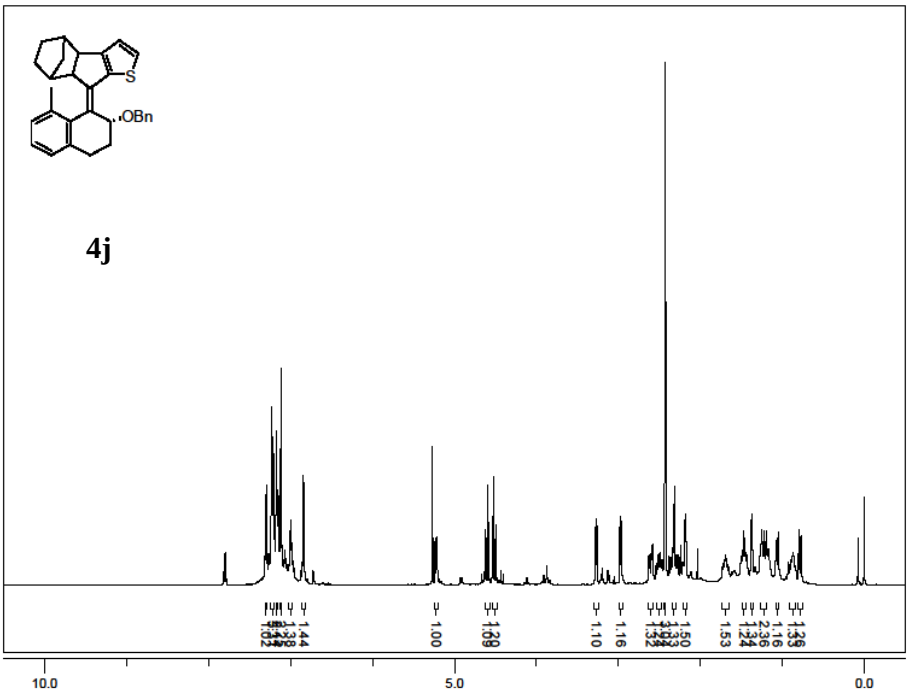
79.852
70.966
67.350
38.506
28.978
6ja
200
150
100
50
0


S
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4j
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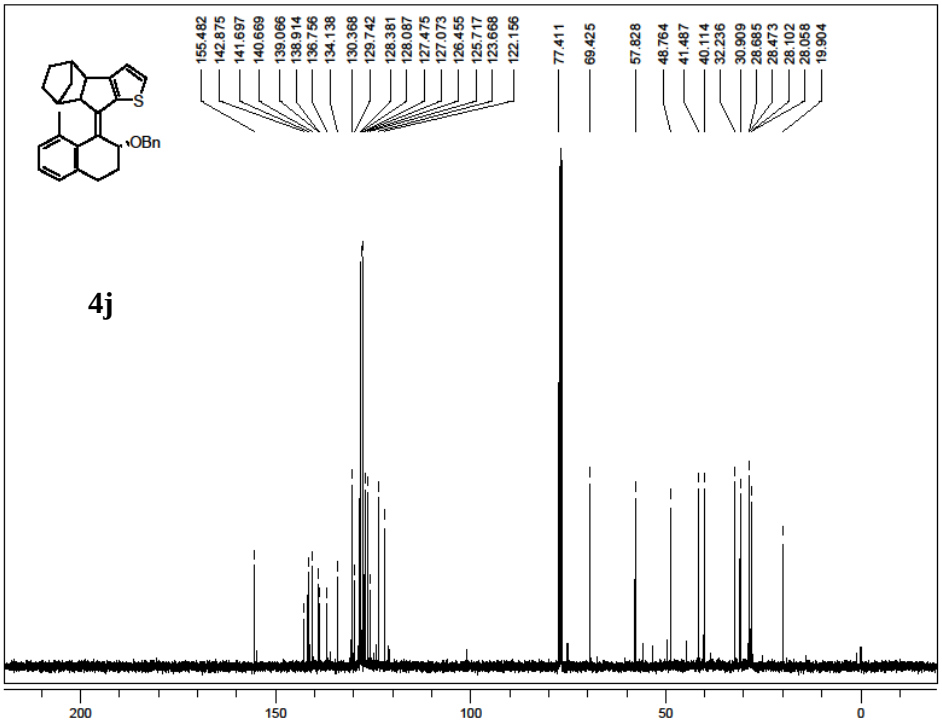
1.00
1.10
1.16
1.50
1.53
10.0
5.0
0.0


S
OBn
4j
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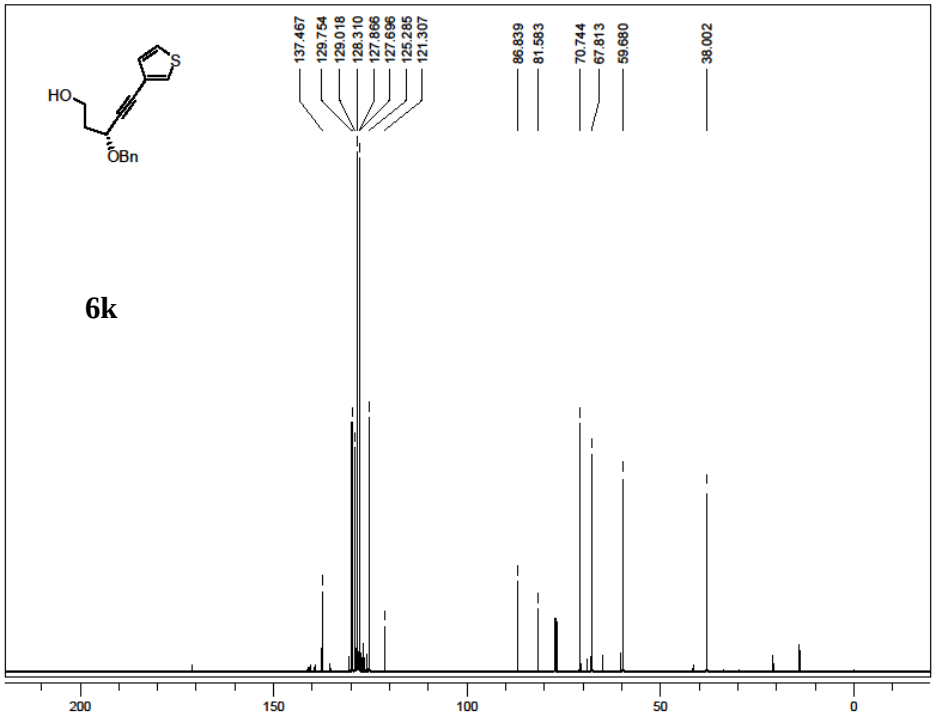
142.875
141.697
140.669
139.066
138.914
136.756
134.138
130.368
129.742
128.381
128.087
127.475
127.073
126.455
125.717
123.668
122.156
77.411
69.425
57.828
48.764
41.487
40.114
32.236
30.909
28.685
28.473
28.102
28.058
19.904
200
150
100
50
0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127.866
127.696
125.285
121.307
86.839
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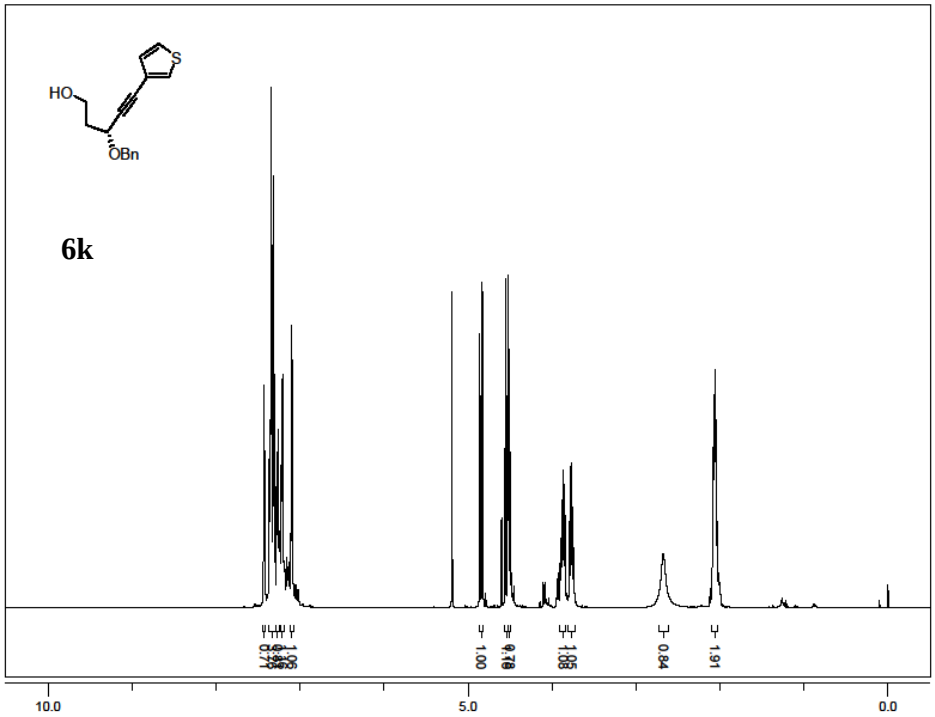
70.744
67.813
59.680
38.002
HO
S
OBn
6k
200
150
100
50
0


HO
S
OBn
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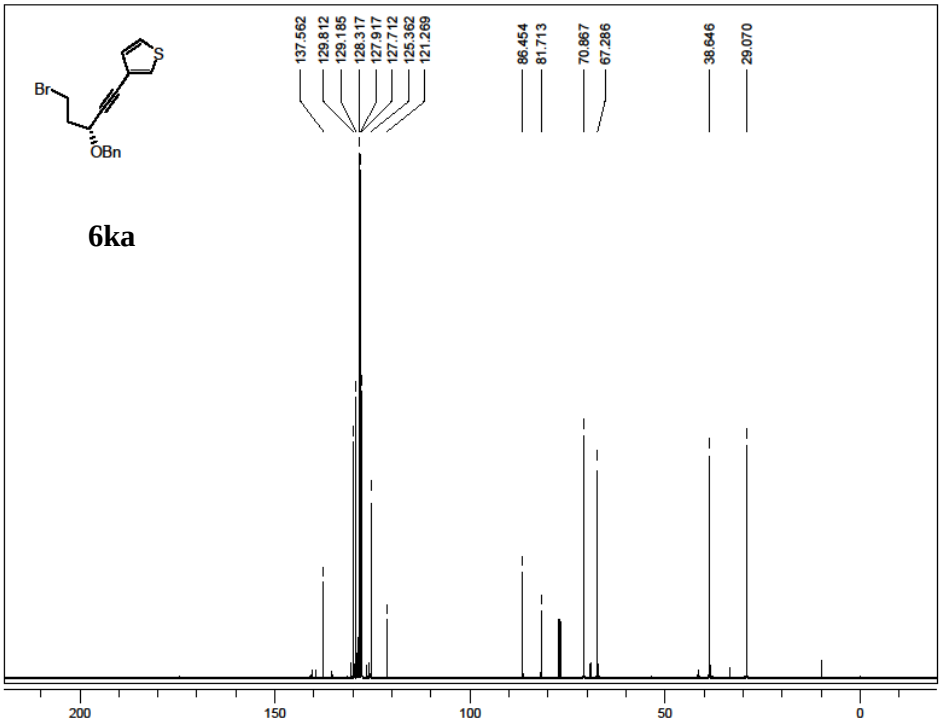
0.84
1.91
10.0
5.0
0.0


Br
S
OBn
6ka
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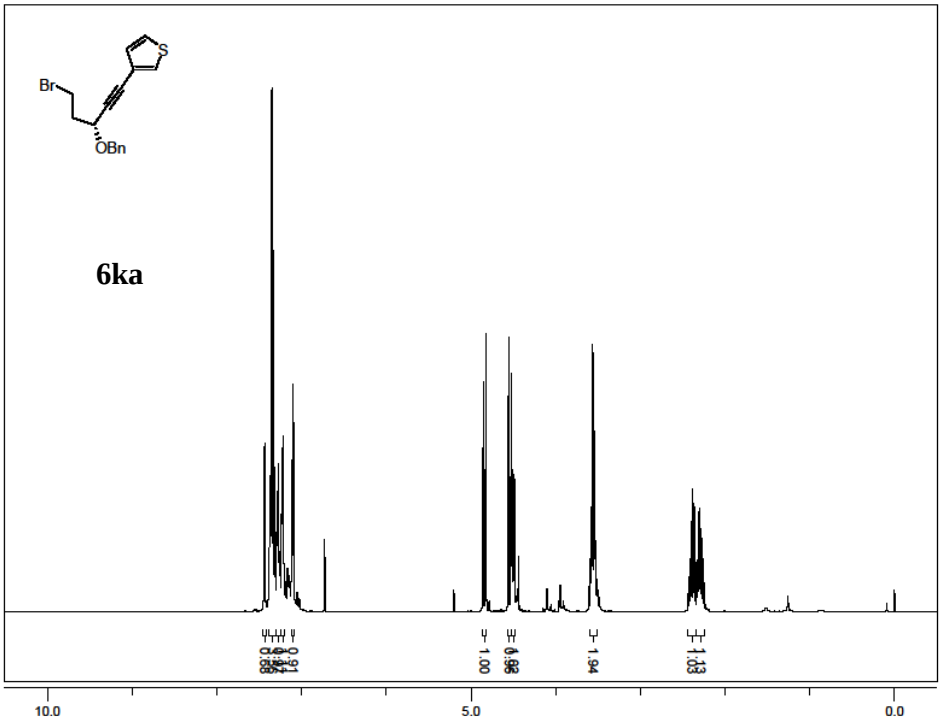
129.185
128.317
127.917
127.712
125.362
121.269
86.454
81.713
70.867
67.286
38.646
29.070
200
150
100
50
0


Br
S
OBn
6ka
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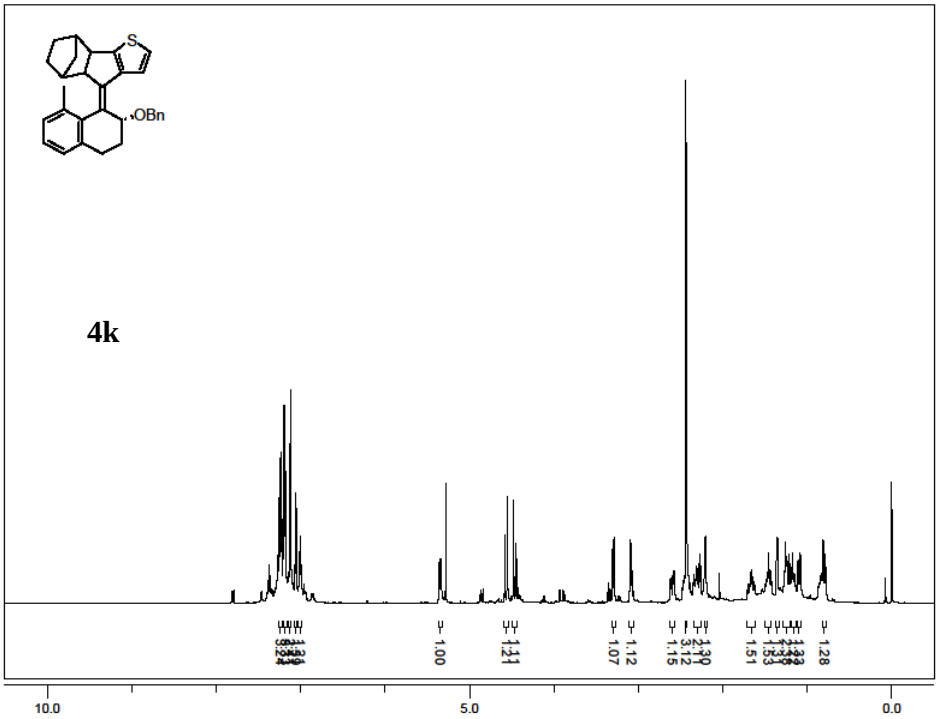
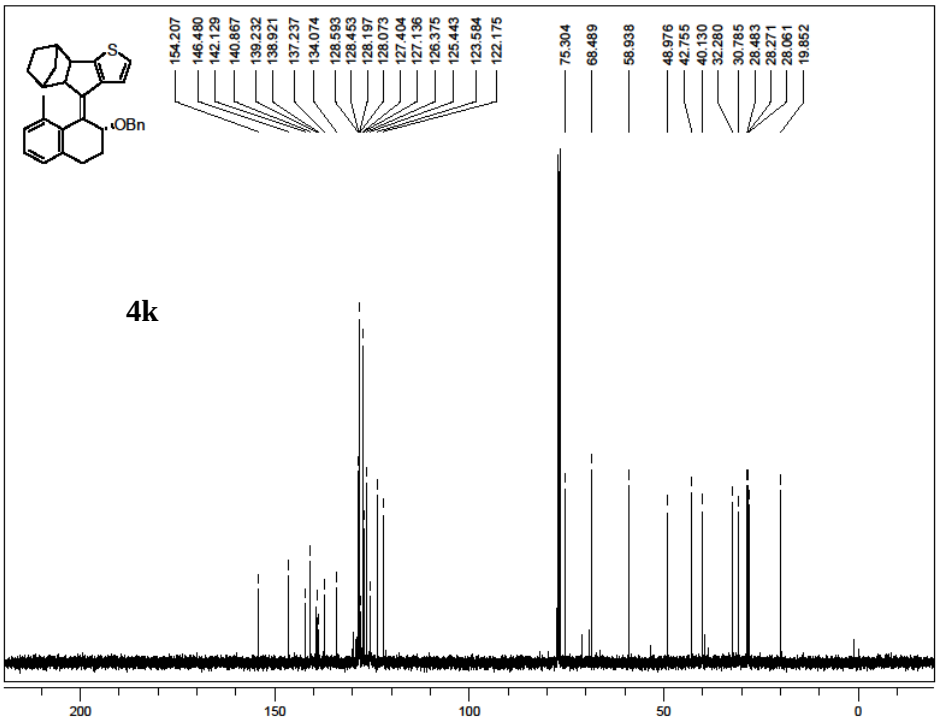
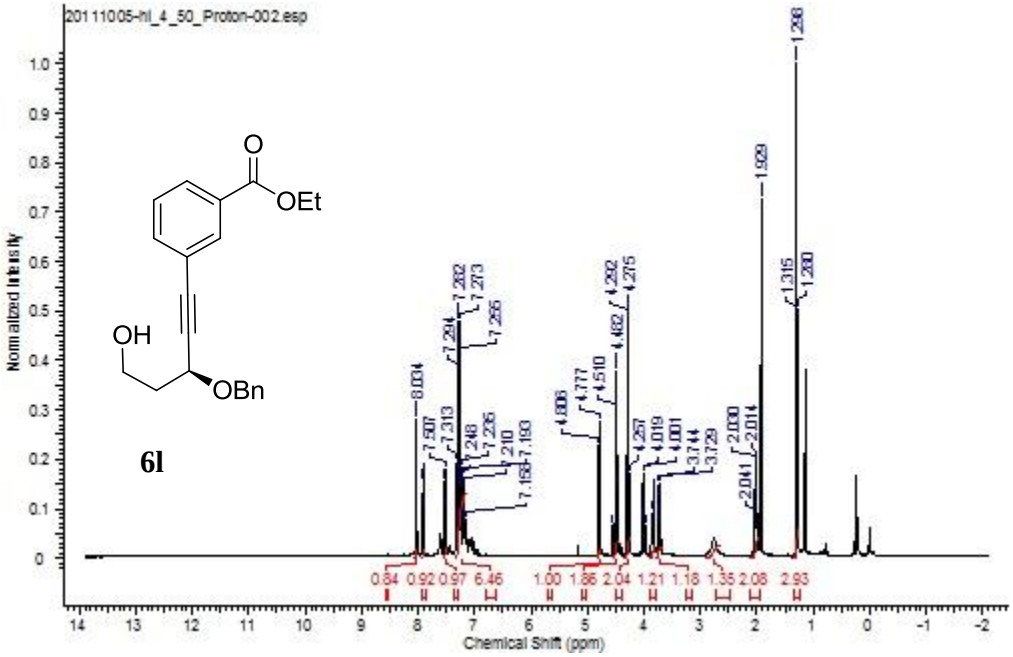
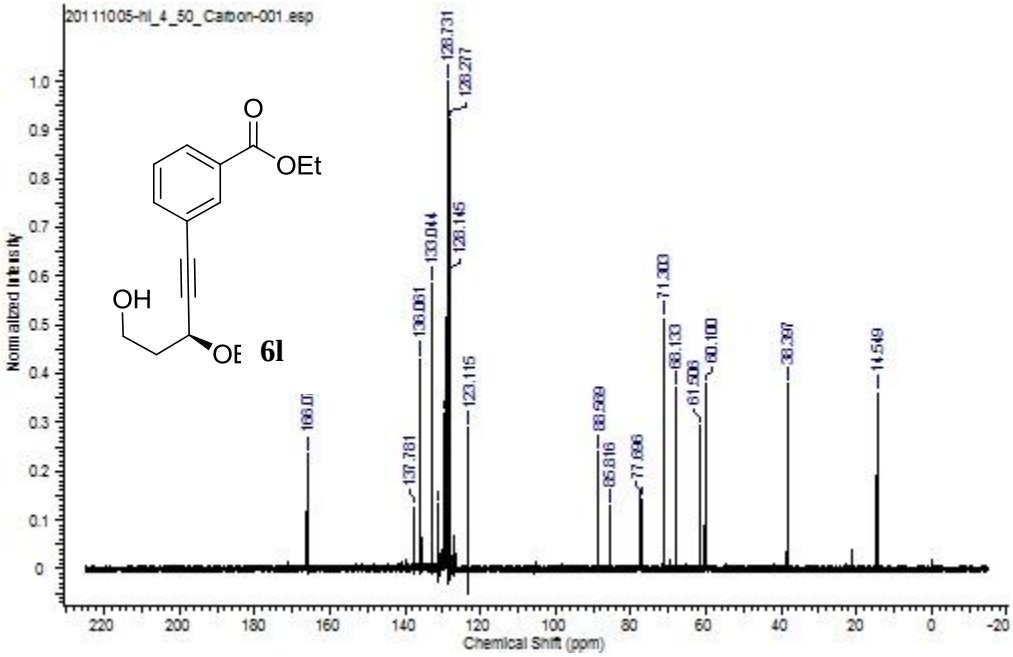
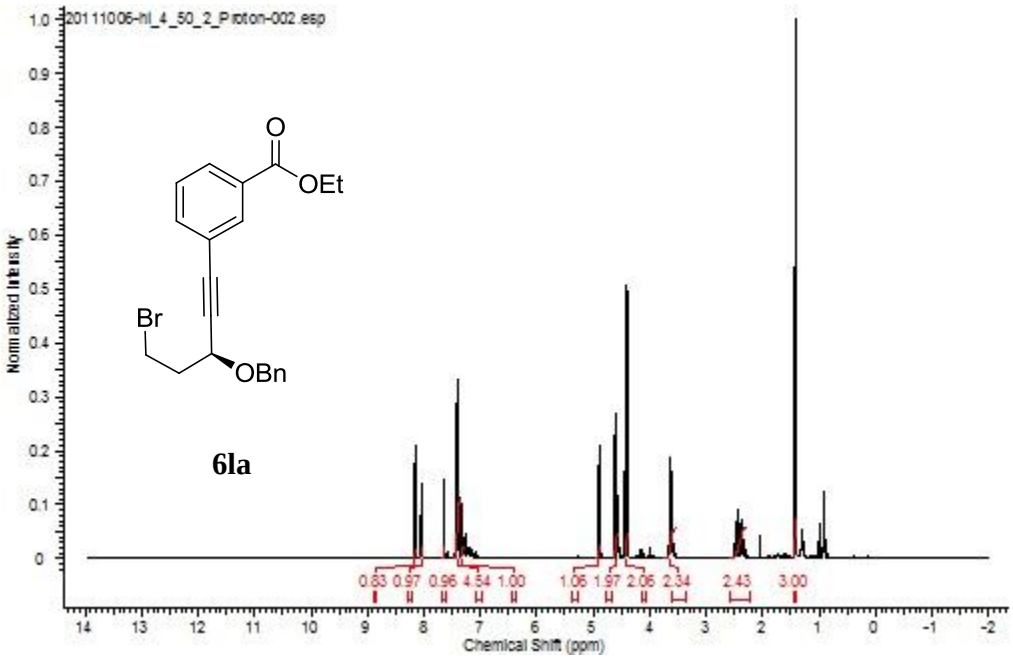
1.94
1.03
10.0
5.0
0.0

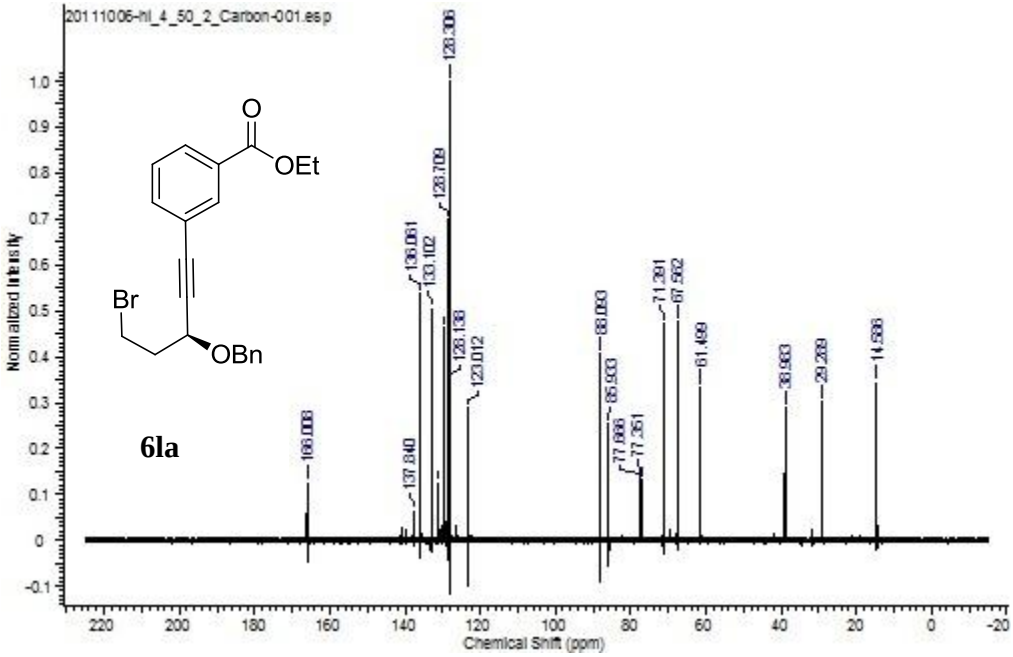

S
OBn
4k
1.00
1.11
1.07
1.12
1.15
1.51
1.28
10.0
5.0
0.0

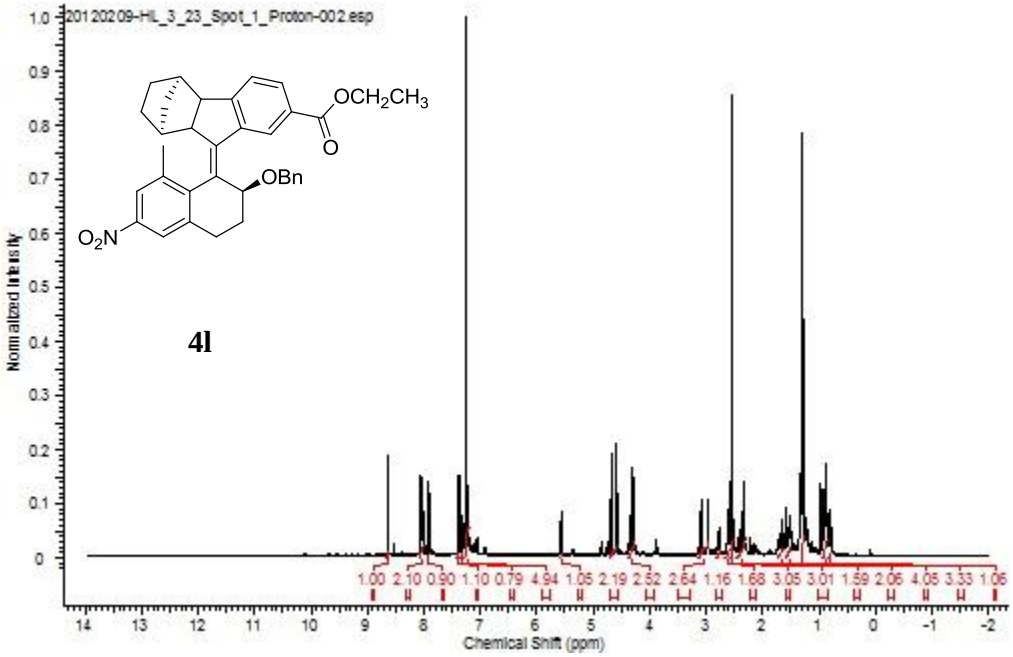

S
OBn
4k
154.207
146.480
142.129
140.867
139.232
138.921
137.237
134.074
128.593
128.453
128.197
128.073
127.404
127.136
126.375
125.443
123.584
122.175
75.304
68.489
58.938
48.976
42.755
40.130
32.280
30.785
28.483
28.271
28.061
19.852
200
150
100
50
0

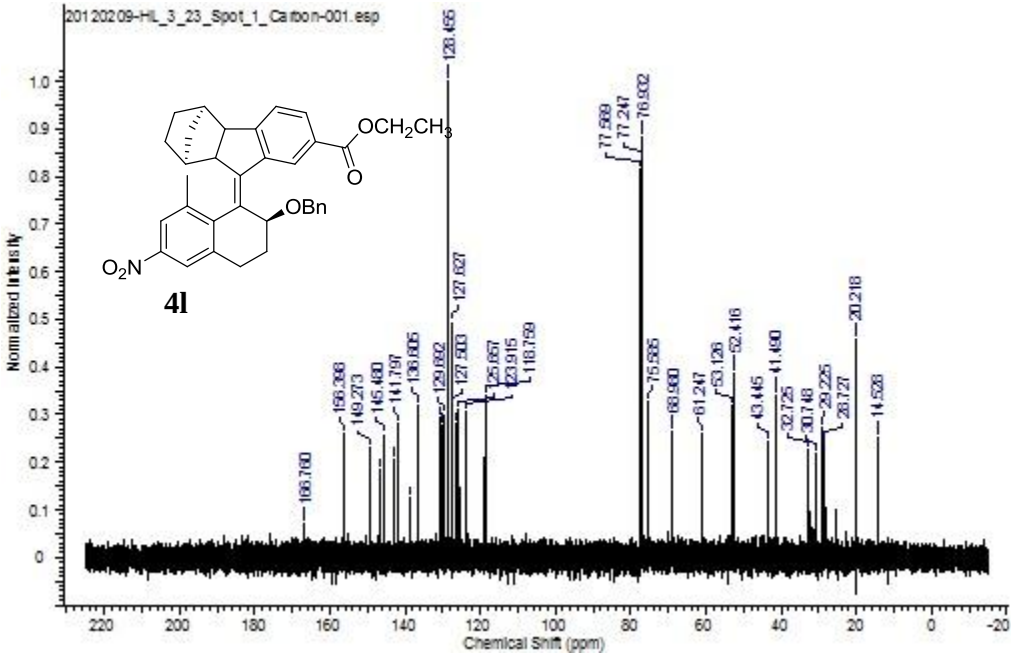

20111005-hl_4_50_Proton-002.esp
Normalized Intensity
Chemical Shift (ppm)
O
OEt
OH
OBn
6l
0.84 0.92 0.97 6.46 1.00 1.86 2.04 1.21 1.18 1.35 2.08 2.93


20111005-hl_4_50_Carbon-001.esp
Normalized Intensity
Chemical Shift (ppm)
O
OEt
OH
OE
6l


20111006-hl_4_50_2_Proton-002.esp
O
OEt
Br
OBn
6la
0.83 0.97 0.96 4.54 1.00 1.06 1.97 2.06 2.34 2.43 3.00
Normalized Intensity
Chemical Shift (ppm)


20111006-hl_4_50_2_Carbon-001.esp
O
OEt
Br
OBn
6la
166.008
137.840
136.061
133.102
128.706
128.709
128.138
123.012
88.093
85.903
77.966
77.351
71.291
67.562
61.499
38.963
29.289
14.536
Normalized Intensity
Chemical Shift (ppm)


20120209-HL_3_23_Spot_1_Proton-002.esp
OCH2CH3
O
OBn
O2N
4l
Normalized Intensity
Chemical Shift (ppm)
1.00 2.10 0.90 1.10 0.79 4.94 1.05 2.19 2.52 2.64 1.16 1.68 3.05 3.01 1.59 2.06 4.05 3.33 1.06


20120209-HL_3_23_Spot_1_Carbon-001.esp
OCH2CH3
O
OBn
O2N
4l
Normalized Intensity
Chemical Shift (ppm)
166.760
156.366
149.273
145.480
141.797
136.605
129.892
128.495
127.627
127.503
125.657
123.915
118.759
77.569
77.247
76.932
75.585
68.900
61.247
53.126
52.416
43.445
41.490
32.725
30.748
29.225
28.727
20.216
14.528

Crystal Structure Information

Compound **4a-S**

Cif file name: d12141

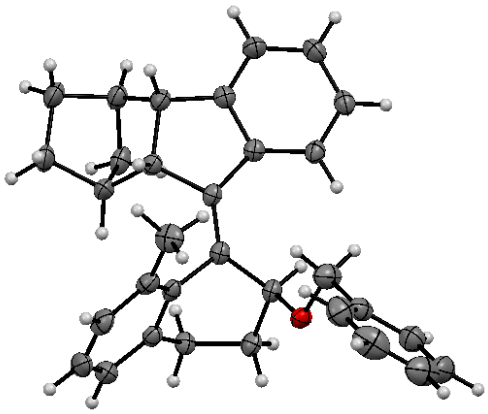


Table 1. Crystal data and structure refinement for d12141.

Identification code	d12141	
Empirical formula	C32 H32 O	
Formula weight	432.58	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.2613(6) Å	α= 90°.
	b = 14.1399(10) Å	β= 90°.
	c = 16.2722(9) Å	γ = 90°.
Volume	2361.0(3) $Å^3$	
Z	4	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.542 mm^{-1}	
F(000)	928	
Crystal size	0.18 x 0.16 x 0.15 mm^3	
Theta range for data collection	4.14 to 66.57°.	
Index ranges	-12<=h<=11, -16<=k<=16, -16<=l<=19	
Reflections collected	15493	

Independent reflections	4075 [R(int) = 0.0385]
Completeness to theta = 66.57°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9231 and 0.9087
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4075 / 0 / 305
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0921
R indices (all data)	R1 = 0.0403, wR2 = 0.0940
Absolute structure parameter	-0.1(3)
Largest diff. peak and hole	0.246 and -0.188 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d12141. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1690(1)	-244(1)	1119(1)	26(1)
O(1A)	1799(13)	-101(10)	552(10)	27(5)
C(1)	4849(2)	510(1)	479(1)	23(1)
C(2)	6303(2)	535(1)	695(1)	26(1)
C(3)	6682(2)	1361(2)	1265(1)	32(1)
C(4)	8142(2)	1260(2)	1485(1)	39(1)
C(5)	8837(2)	1546(2)	674(1)	38(1)
C(6)	7702(2)	1742(2)	87(1)	32(1)
C(7)	7035(2)	794(1)	-121(1)	28(1)
C(8)	5972(2)	860(1)	-752(1)	27(1)
C(9)	6127(2)	1039(2)	-1586(1)	33(1)
C(10)	5052(2)	1036(2)	-2102(1)	35(1)
C(11)	3830(2)	844(1)	-1780(1)	31(1)
C(12)	3667(2)	668(1)	-953(1)	27(1)
C(13)	4732(2)	692(1)	-417(1)	24(1)
C(14)	6702(2)	2194(1)	670(1)	34(1)
C(15)	3917(2)	389(1)	1057(1)	23(1)
C(16)	2466(2)	593(1)	959(1)	24(1)
C(17)	1994(2)	1307(1)	1605(1)	28(1)
C(18)	3091(2)	1691(1)	2142(1)	26(1)
C(19)	3853(2)	879(1)	2494(1)	25(1)
C(20)	4144(2)	789(2)	3323(1)	32(1)
C(21)	4775(2)	-19(2)	3597(1)	37(1)
C(22)	5095(2)	-723(2)	3058(1)	35(1)
C(23)	4850(2)	-644(1)	2213(1)	29(1)
C(24)	4244(2)	182(1)	1932(1)	23(1)
C(25)	5214(2)	-1448(2)	1655(1)	40(1)
C(26)	1914(2)	-976(2)	553(1)	41(1)
C(27)	976(2)	-1759(2)	733(1)	33(1)
C(28)	-338(2)	-1650(2)	564(1)	42(1)
C(29)	-1202(2)	-2378(2)	739(1)	49(1)

C(30)	-779(3)	-3190(2)	1074(2)	55(1)
C(31)	509(3)	-3325(2)	1252(2)	57(1)
C(32)	1393(3)	-2604(2)	1079(1)	46(1)

Table 3. Bond lengths [Å] and angles [°] for d12141.

O(1)-C(26)	1.405(3)
O(1)-C(16)	1.451(2)
C(1)-C(15)	1.353(3)
C(1)-C(13)	1.484(2)
C(1)-C(2)	1.534(2)
C(2)-C(3)	1.541(3)
C(2)-C(7)	1.568(2)
C(2)-H(2A)	1.0000
C(3)-C(14)	1.525(3)
C(3)-C(4)	1.546(3)
C(3)-H(3A)	1.0000
C(4)-C(5)	1.553(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.532(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(14)	1.537(3)
C(6)-C(7)	1.542(3)
C(6)-H(6A)	1.0000
C(7)-C(8)	1.501(2)
C(7)-H(7A)	1.0000
C(8)-C(9)	1.391(3)
C(8)-C(13)	1.404(3)
C(9)-C(10)	1.386(3)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.386(3)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.380(3)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.398(3)
C(12)-H(12A)	0.9500
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900

C(15)-C(24)	1.490(2)
C(15)-C(16)	1.525(2)
C(16)-C(17)	1.536(3)
C(16)-H(16)	1.0000
C(17)-C(18)	1.524(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.503(2)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.387(3)
C(19)-C(24)	1.404(3)
C(20)-C(21)	1.386(3)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.368(3)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.402(3)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.399(3)
C(23)-C(25)	1.503(3)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.496(3)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-C(28)	1.385(3)
C(27)-C(32)	1.388(3)
C(28)-C(29)	1.388(3)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.344(4)
C(29)-H(29A)	0.9500
C(30)-C(31)	1.366(4)
C(30)-H(30A)	0.9500
C(31)-C(32)	1.394(4)
C(31)-H(31A)	0.9500

C(32)-H(32A)	0.9500

C(26)-O(1)-C(16)	113.15(15)
C(15)-C(1)-C(13)	130.41(16)
C(15)-C(1)-C(2)	122.05(16)
C(13)-C(1)-C(2)	107.44(14)
C(1)-C(2)-C(3)	113.66(15)
C(1)-C(2)-C(7)	106.08(14)
C(3)-C(2)-C(7)	102.19(15)
C(1)-C(2)-H(2A)	111.5
C(3)-C(2)-H(2A)	111.5
C(7)-C(2)-H(2A)	111.5
C(14)-C(3)-C(2)	101.91(14)
C(14)-C(3)-C(4)	101.85(16)
C(2)-C(3)-C(4)	108.30(17)
C(14)-C(3)-H(3A)	114.5
C(2)-C(3)-H(3A)	114.5
C(4)-C(3)-H(3A)	114.5
C(3)-C(4)-C(5)	102.98(15)
C(3)-C(4)-H(4A)	111.2
C(5)-C(4)-H(4A)	111.2
C(3)-C(4)-H(4B)	111.2
C(5)-C(4)-H(4B)	111.2
H(4A)-C(4)-H(4B)	109.1
C(6)-C(5)-C(4)	103.16(15)
C(6)-C(5)-H(5A)	111.1
C(4)-C(5)-H(5A)	111.1
C(6)-C(5)-H(5B)	111.1
C(4)-C(5)-H(5B)	111.1
H(5A)-C(5)-H(5B)	109.1
C(5)-C(6)-C(14)	101.39(16)
C(5)-C(6)-C(7)	108.51(16)
C(14)-C(6)-C(7)	101.51(15)
C(5)-C(6)-H(6A)	114.6
C(14)-C(6)-H(6A)	114.6
C(7)-C(6)-H(6A)	114.6

C(8)-C(7)-C(6)	114.74(16)
C(8)-C(7)-C(2)	104.23(14)
C(6)-C(7)-C(2)	103.35(15)
C(8)-C(7)-H(7A)	111.3
C(6)-C(7)-H(7A)	111.3
C(2)-C(7)-H(7A)	111.3
C(9)-C(8)-C(13)	120.89(17)
C(9)-C(8)-C(7)	126.63(17)
C(13)-C(8)-C(7)	112.46(15)
C(10)-C(9)-C(8)	119.95(18)
C(10)-C(9)-H(9A)	120.0
C(8)-C(9)-H(9A)	120.0
C(11)-C(10)-C(9)	119.53(17)
C(11)-C(10)-H(10A)	120.2
C(9)-C(10)-H(10A)	120.2
C(12)-C(11)-C(10)	120.89(18)
C(12)-C(11)-H(11A)	119.6
C(10)-C(11)-H(11A)	119.6
C(11)-C(12)-C(13)	120.64(17)
C(11)-C(12)-H(12A)	119.7
C(13)-C(12)-H(12A)	119.7
C(12)-C(13)-C(8)	118.04(16)
C(12)-C(13)-C(1)	132.13(17)
C(8)-C(13)-C(1)	109.71(15)
C(3)-C(14)-C(6)	94.58(15)
C(3)-C(14)-H(14A)	112.8
C(6)-C(14)-H(14A)	112.8
C(3)-C(14)-H(14B)	112.8
C(6)-C(14)-H(14B)	112.8
H(14A)-C(14)-H(14B)	110.3
C(1)-C(15)-C(24)	122.01(16)
C(1)-C(15)-C(16)	126.33(16)
C(24)-C(15)-C(16)	110.95(15)
O(1)-C(16)-C(15)	111.22(14)
O(1)-C(16)-C(17)	103.86(14)
C(15)-C(16)-C(17)	111.11(14)

O(1)-C(16)-H(16)	110.2
C(15)-C(16)-H(16)	110.2
C(17)-C(16)-H(16)	110.2
C(18)-C(17)-C(16)	113.18(15)
C(18)-C(17)-H(17A)	108.9
C(16)-C(17)-H(17A)	108.9
C(18)-C(17)-H(17B)	108.9
C(16)-C(17)-H(17B)	108.9
H(17A)-C(17)-H(17B)	107.8
C(19)-C(18)-C(17)	109.32(15)
C(19)-C(18)-H(18A)	109.8
C(17)-C(18)-H(18A)	109.8
C(19)-C(18)-H(18B)	109.8
C(17)-C(18)-H(18B)	109.8
H(18A)-C(18)-H(18B)	108.3
C(20)-C(19)-C(24)	120.51(18)
C(20)-C(19)-C(18)	123.61(17)
C(24)-C(19)-C(18)	115.86(15)
C(21)-C(20)-C(19)	119.35(19)
C(21)-C(20)-H(20A)	120.3
C(19)-C(20)-H(20A)	120.3
C(22)-C(21)-C(20)	120.29(17)
C(22)-C(21)-H(21A)	119.9
C(20)-C(21)-H(21A)	119.9
C(21)-C(22)-C(23)	121.89(18)
C(21)-C(22)-H(22A)	119.1
C(23)-C(22)-H(22A)	119.1
C(24)-C(23)-C(22)	117.84(18)
C(24)-C(23)-C(25)	122.97(16)
C(22)-C(23)-C(25)	119.17(17)
C(23)-C(24)-C(19)	119.95(16)
C(23)-C(24)-C(15)	125.16(17)
C(19)-C(24)-C(15)	114.86(16)
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5

C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(1)-C(26)-C(27)	108.14(16)
O(1)-C(26)-H(26A)	110.1
C(27)-C(26)-H(26A)	110.1
O(1)-C(26)-H(26B)	110.1
C(27)-C(26)-H(26B)	110.1
H(26A)-C(26)-H(26B)	108.4
C(28)-C(27)-C(32)	118.4(2)
C(28)-C(27)-C(26)	120.4(2)
C(32)-C(27)-C(26)	121.2(2)
C(27)-C(28)-C(29)	119.9(2)
C(27)-C(28)-H(28A)	120.0
C(29)-C(28)-H(28A)	120.0
C(30)-C(29)-C(28)	120.7(2)
C(30)-C(29)-H(29A)	119.6
C(28)-C(29)-H(29A)	119.6
C(29)-C(30)-C(31)	121.2(2)
C(29)-C(30)-H(30A)	119.4
C(31)-C(30)-H(30A)	119.4
C(30)-C(31)-C(32)	119.0(3)
C(30)-C(31)-H(31A)	120.5
C(32)-C(31)-H(31A)	120.5
C(27)-C(32)-C(31)	120.8(2)
C(27)-C(32)-H(32A)	119.6
C(31)-C(32)-H(32A)	119.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for d12141. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	24(1)	28(1)	28(1)	-3(1)	3(1)	-6(1)
C(1)	21(1)	20(1)	27(1)	2(1)	-2(1)	-1(1)
C(2)	22(1)	30(1)	27(1)	4(1)	-1(1)	-1(1)
C(3)	23(1)	48(1)	26(1)	-1(1)	0(1)	-8(1)
C(4)	26(1)	56(1)	34(1)	6(1)	-9(1)	-10(1)
C(5)	22(1)	53(1)	39(1)	6(1)	-4(1)	-6(1)
C(6)	24(1)	40(1)	32(1)	7(1)	-4(1)	-8(1)
C(7)	21(1)	36(1)	29(1)	3(1)	-1(1)	1(1)
C(8)	26(1)	28(1)	26(1)	0(1)	-1(1)	0(1)
C(9)	28(1)	42(1)	29(1)	3(1)	2(1)	-5(1)
C(10)	38(1)	44(1)	23(1)	1(1)	-2(1)	-3(1)
C(11)	31(1)	34(1)	28(1)	-2(1)	-6(1)	0(1)
C(12)	23(1)	28(1)	30(1)	-4(1)	-3(1)	-2(1)
C(13)	24(1)	21(1)	26(1)	2(1)	-2(1)	-1(1)
C(14)	25(1)	34(1)	43(1)	-2(1)	-8(1)	-5(1)
C(15)	22(1)	19(1)	27(1)	2(1)	-3(1)	-1(1)
C(16)	21(1)	24(1)	27(1)	1(1)	-3(1)	-2(1)
C(16A)	21(1)	24(1)	27(1)	1(1)	-3(1)	-2(1)
C(17)	23(1)	28(1)	33(1)	1(1)	-4(1)	3(1)
C(18)	26(1)	23(1)	28(1)	-1(1)	-2(1)	0(1)
C(19)	19(1)	29(1)	27(1)	4(1)	0(1)	-4(1)
C(20)	29(1)	42(1)	26(1)	-1(1)	0(1)	0(1)
C(21)	30(1)	56(1)	26(1)	9(1)	-4(1)	4(1)
C(22)	25(1)	42(1)	38(1)	14(1)	-4(1)	7(1)
C(23)	21(1)	32(1)	34(1)	9(1)	1(1)	1(1)
C(24)	18(1)	26(1)	26(1)	6(1)	-1(1)	-3(1)
C(25)	44(1)	32(1)	43(1)	6(1)	-1(1)	10(1)
C(26)	43(1)	38(1)	42(1)	-8(1)	8(1)	-11(1)
C(26A)	43(1)	38(1)	42(1)	-8(1)	8(1)	-11(1)
C(27)	38(1)	31(1)	29(1)	-5(1)	4(1)	-9(1)
C(28)	42(1)	48(1)	35(1)	2(1)	-1(1)	-4(1)

C(29)	38(1)	65(2)	46(1)	-13(1)	3(1)	-18(1)
C(30)	66(2)	44(1)	55(1)	-14(1)	14(1)	-22(1)
C(31)	87(2)	32(1)	51(1)	3(1)	6(1)	-5(1)
C(32)	53(2)	41(1)	46(1)	-6(1)	-3(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for d12141.

	x	y	z	U(eq)
H(2A)	6606	-85	920	32
H(3A)	6094	1447	1749	39
H(4A)	8356	601	1641	46
H(4B)	8385	1688	1941	46
H(5A)	9379	2118	753	45
H(5B)	9394	1026	467	45
H(6A)	7933	2137	-402	38
H(7A)	7688	299	-270	34
H(9A)	6969	1163	-1803	40
H(10A)	5152	1165	-2671	42
H(11A)	3094	833	-2135	37
H(12A)	2823	530	-745	33
H(14A)	7024	2784	926	41
H(14B)	5848	2305	404	41
H(16)	2284	837	393	29
H(16A)	2540	1046	489	29
H(17A)	1562	1842	1323	34
H(17B)	1338	998	1961	34
H(18A)	3673	2098	1810	31
H(18B)	2722	2078	2593	31
H(20A)	3914	1275	3698	39
H(21A)	4986	-83	4163	45
H(22A)	5496	-1282	3261	42
H(25A)	4927	-1307	1094	59
H(25B)	4792	-2030	1845	59
H(25C)	6162	-1533	1661	59
H(26A)	2821	-1208	604	50
H(26B)	1783	-742	-14	50
H(26C)	2652	-1095	931	50
H(26D)	2248	-1125	-3	50

H(28A)	-647	-1078	327	50
H(29A)	-2102	-2301	620	59
H(30A)	-1387	-3679	1190	66
H(31A)	797	-3902	1490	68
H(32A)	2291	-2691	1200	56

Table 6. Torsion angles [°] for d12141.

C(15)-C(1)-C(2)-C(3)	-62.6(2)
C(13)-C(1)-C(2)-C(3)	114.32(16)
C(15)-C(1)-C(2)-C(7)	-174.08(16)
C(13)-C(1)-C(2)-C(7)	2.8(2)
C(1)-C(2)-C(3)-C(14)	-77.24(18)
C(7)-C(2)-C(3)-C(14)	36.59(18)
C(1)-C(2)-C(3)-C(4)	175.85(15)
C(7)-C(2)-C(3)-C(4)	-70.31(17)
C(14)-C(3)-C(4)-C(5)	-33.8(2)
C(2)-C(3)-C(4)-C(5)	73.2(2)
C(3)-C(4)-C(5)-C(6)	-1.8(2)
C(4)-C(5)-C(6)-C(14)	36.5(2)
C(4)-C(5)-C(6)-C(7)	-69.9(2)
C(5)-C(6)-C(7)-C(8)	-174.84(16)
C(14)-C(6)-C(7)-C(8)	78.86(18)
C(5)-C(6)-C(7)-C(2)	72.36(18)
C(14)-C(6)-C(7)-C(2)	-33.93(17)
C(1)-C(2)-C(7)-C(8)	-2.3(2)
C(3)-C(2)-C(7)-C(8)	-121.59(16)
C(1)-C(2)-C(7)-C(6)	117.98(15)
C(3)-C(2)-C(7)-C(6)	-1.34(18)
C(6)-C(7)-C(8)-C(9)	70.4(3)
C(2)-C(7)-C(8)-C(9)	-177.35(19)
C(6)-C(7)-C(8)-C(13)	-111.34(18)
C(2)-C(7)-C(8)-C(13)	0.9(2)
C(13)-C(8)-C(9)-C(10)	-1.1(3)
C(7)-C(8)-C(9)-C(10)	177.0(2)
C(8)-C(9)-C(10)-C(11)	-0.7(3)
C(9)-C(10)-C(11)-C(12)	0.9(3)
C(10)-C(11)-C(12)-C(13)	0.8(3)
C(11)-C(12)-C(13)-C(8)	-2.5(3)
C(11)-C(12)-C(13)-C(1)	-178.16(19)
C(9)-C(8)-C(13)-C(12)	2.7(3)
C(7)-C(8)-C(13)-C(12)	-175.69(16)

C(9)-C(8)-C(13)-C(1)	179.26(18)
C(7)-C(8)-C(13)-C(1)	0.9(2)
C(15)-C(1)-C(13)-C(12)	-9.9(3)
C(2)-C(1)-C(13)-C(12)	173.55(19)
C(15)-C(1)-C(13)-C(8)	174.22(18)
C(2)-C(1)-C(13)-C(8)	-2.3(2)
C(2)-C(3)-C(14)-C(6)	-56.78(16)
C(4)-C(3)-C(14)-C(6)	55.07(17)
C(5)-C(6)-C(14)-C(3)	-56.35(17)
C(7)-C(6)-C(14)-C(3)	55.45(16)
C(13)-C(1)-C(15)-C(24)	178.07(18)
C(2)-C(1)-C(15)-C(24)	-5.8(3)
C(13)-C(1)-C(15)-C(16)	-12.5(3)
C(2)-C(1)-C(15)-C(16)	163.65(16)
C(26)-O(1)-C(16)-C(15)	-64.2(2)
C(26)-O(1)-C(16)-C(17)	176.20(16)
C(1)-C(15)-C(16)-O(1)	122.41(19)
C(24)-C(15)-C(16)-O(1)	-67.15(18)
C(1)-C(15)-C(16)-C(17)	-122.41(19)
C(24)-C(15)-C(16)-C(17)	48.03(19)
O(1)-C(16)-C(17)-C(18)	123.94(16)
C(15)-C(16)-C(17)-C(18)	4.3(2)
C(16)-C(17)-C(18)-C(19)	-52.0(2)
C(17)-C(18)-C(19)-C(20)	-129.52(19)
C(17)-C(18)-C(19)-C(24)	49.0(2)
C(24)-C(19)-C(20)-C(21)	-2.9(3)
C(18)-C(19)-C(20)-C(21)	175.56(17)
C(19)-C(20)-C(21)-C(22)	-0.6(3)
C(20)-C(21)-C(22)-C(23)	2.5(3)
C(21)-C(22)-C(23)-C(24)	-0.8(3)
C(21)-C(22)-C(23)-C(25)	-179.4(2)
C(22)-C(23)-C(24)-C(19)	-2.7(3)
C(25)-C(23)-C(24)-C(19)	175.84(18)
C(22)-C(23)-C(24)-C(15)	179.60(17)
C(25)-C(23)-C(24)-C(15)	-1.9(3)
C(20)-C(19)-C(24)-C(23)	4.6(3)

C(18)-C(19)-C(24)-C(23)	-173.98(16)
C(20)-C(19)-C(24)-C(15)	-177.48(17)
C(18)-C(19)-C(24)-C(15)	3.9(2)
C(1)-C(15)-C(24)-C(23)	-65.7(3)
C(16)-C(15)-C(24)-C(23)	123.42(19)
C(1)-C(15)-C(24)-C(19)	116.55(19)
C(16)-C(15)-C(24)-C(19)	-54.4(2)
C(16)-O(1)-C(26)-C(27)	-174.77(16)
O(1)-C(26)-C(27)-C(28)	71.0(2)
O(1)-C(26)-C(27)-C(32)	-108.4(2)
C(32)-C(27)-C(28)-C(29)	-0.1(3)
C(26)-C(27)-C(28)-C(29)	-179.48(19)
C(27)-C(28)-C(29)-C(30)	0.1(3)
C(28)-C(29)-C(30)-C(31)	0.0(4)
C(29)-C(30)-C(31)-C(32)	-0.1(4)
C(28)-C(27)-C(32)-C(31)	-0.1(3)
C(26)-C(27)-C(32)-C(31)	179.3(2)
C(30)-C(31)-C(32)-C(27)	0.1(4)

Symmetry transformations used to generate equivalent atoms:

Compound **4f**

Cif file name: **d12160**

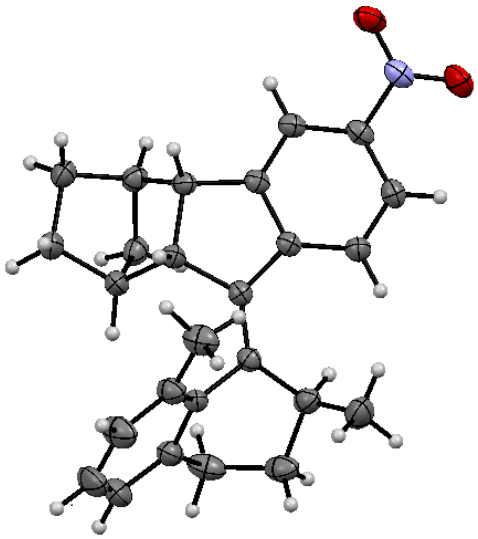


Table 1. Crystal data and structure refinement for d12160.

Identification code	d12160	
Empirical formula	C26 H27 N O2	
Formula weight	385.49	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6278(3) Å	α= 98.774(2)°.
	b = 9.9460(3) Å	β= 99.335(2)°.
	c = 11.6593(4) Å	γ = 110.505(1)°.
Volume	1005.06(6) $Å^3$	
Z	2	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.624 mm^{-1}	
F(000)	412	
Crystal size	0.22 x 0.17 x 0.15 mm^3	

Theta range for data collection	5.53 to 66.61°.
Index ranges	-11<=h<=9, -11<=k<=11, -13<=l<=13
Reflections collected	9686
Independent reflections	3360 [R(int) = 0.0230]
Completeness to theta = 66.61°	94.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6609
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3360 / 0 / 267
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1305
R indices (all data)	R1 = 0.0508, wR2 = 0.1320
Largest diff. peak and hole	0.524 and -0.215 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d12160. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3272(2)	6237(2)	3238(1)	41(1)
O(2)	3695(2)	4488(2)	2203(1)	51(1)
N(1)	3397(2)	5040(2)	3095(1)	33(1)
C(1)	2762(2)	2245(2)	6993(1)	24(1)
C(2)	2447(2)	3385(2)	7838(1)	27(1)
C(3)	854(2)	2778(2)	8113(2)	32(1)
C(4)	710(2)	3991(2)	9019(2)	37(1)
C(5)	551(2)	5114(2)	8270(2)	33(1)
C(6)	651(2)	4422(2)	7031(2)	29(1)
C(7)	2316(2)	4559(2)	7120(1)	26(1)
C(8)	2663(2)	4076(2)	5954(1)	25(1)
C(9)	2799(2)	4826(2)	5042(2)	27(1)
C(10)	3192(2)	4239(2)	4050(1)	27(1)
C(11)	3441(2)	2939(2)	3942(2)	29(1)
C(12)	3298(2)	2195(2)	4853(1)	28(1)
C(13)	2897(2)	2750(2)	5875(1)	24(1)
C(14)	-177(2)	2774(2)	6964(2)	33(1)
C(15)	2816(2)	989(2)	7259(1)	25(1)
C(16)	2685(2)	-341(2)	6345(2)	34(1)
C(17)	1579(3)	-1780(2)	6573(2)	43(1)
C(18)	522(2)	-1494(2)	7342(2)	43(1)
C(19)	1509(2)	-524(2)	8525(2)	32(1)
C(20)	1309(2)	-843(2)	9617(2)	43(1)
C(21)	2382(3)	14(2)	10651(2)	54(1)
C(22)	3636(3)	1170(2)	10591(2)	51(1)
C(23)	3868(2)	1538(2)	9510(2)	36(1)
C(24)	2765(2)	699(2)	8469(1)	26(1)
C(25)	5320(2)	2774(2)	9512(2)	43(1)
C(26)	4237(3)	-411(2)	6356(2)	48(1)

Table 3. Bond lengths [Å] and angles [°] for d12160.

O(1)-N(1)	1.227(2)
O(2)-N(1)	1.224(2)
N(1)-C(10)	1.465(2)
C(1)-C(15)	1.348(2)
C(1)-C(13)	1.477(2)
C(1)-C(2)	1.532(2)
C(2)-C(3)	1.546(2)
C(2)-C(7)	1.565(2)
C(2)-H(2A)	1.0000
C(3)-C(14)	1.531(3)
C(3)-C(4)	1.538(2)
C(3)-H(3A)	1.0000
C(4)-C(5)	1.551(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.536(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(14)	1.535(2)
C(6)-C(7)	1.545(2)
C(6)-H(6A)	1.0000
C(7)-C(8)	1.500(2)
C(7)-H(7A)	1.0000
C(8)-C(9)	1.386(2)
C(8)-C(13)	1.406(2)
C(9)-C(10)	1.383(2)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.386(2)
C(11)-C(12)	1.382(2)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.404(2)
C(12)-H(12A)	0.9500
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900

C(15)-C(24)	1.487(2)
C(15)-C(16)	1.520(2)
C(16)-C(26)	1.518(3)
C(16)-C(17)	1.547(3)
C(16)-H(16A)	1.04(2)
C(17)-C(18)	1.531(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.504(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.385(3)
C(19)-C(24)	1.402(2)
C(20)-C(21)	1.383(3)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.365(3)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.396(3)
C(22)-H(22A)	0.9500
C(23)-C(24)	1.397(2)
C(23)-C(25)	1.503(3)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800

O(2)-N(1)-O(1)	123.54(14)
O(2)-N(1)-C(10)	118.41(15)
O(1)-N(1)-C(10)	118.04(14)
C(15)-C(1)-C(13)	128.73(14)
C(15)-C(1)-C(2)	123.52(14)
C(13)-C(1)-C(2)	107.67(13)
C(1)-C(2)-C(3)	113.32(13)
C(1)-C(2)-C(7)	106.01(12)

C(3)-C(2)-C(7)	102.30(13)
C(1)-C(2)-H(2A)	111.6
C(3)-C(2)-H(2A)	111.6
C(7)-C(2)-H(2A)	111.6
C(14)-C(3)-C(4)	101.67(14)
C(14)-C(3)-C(2)	101.66(13)
C(4)-C(3)-C(2)	108.38(14)
C(14)-C(3)-H(3A)	114.5
C(4)-C(3)-H(3A)	114.5
C(2)-C(3)-H(3A)	114.5
C(3)-C(4)-C(5)	103.39(14)
C(3)-C(4)-H(4A)	111.1
C(5)-C(4)-H(4A)	111.1
C(3)-C(4)-H(4B)	111.1
C(5)-C(4)-H(4B)	111.1
H(4A)-C(4)-H(4B)	109.0
C(6)-C(5)-C(4)	103.00(13)
C(6)-C(5)-H(5A)	111.2
C(4)-C(5)-H(5A)	111.2
C(6)-C(5)-H(5B)	111.2
C(4)-C(5)-H(5B)	111.2
H(5A)-C(5)-H(5B)	109.1
C(14)-C(6)-C(5)	101.52(13)
C(14)-C(6)-C(7)	101.93(13)
C(5)-C(6)-C(7)	107.35(13)
C(14)-C(6)-H(6A)	114.8
C(5)-C(6)-H(6A)	114.8
C(7)-C(6)-H(6A)	114.8
C(8)-C(7)-C(6)	114.63(13)
C(8)-C(7)-C(2)	104.19(12)
C(6)-C(7)-C(2)	103.43(13)
C(8)-C(7)-H(7A)	111.4
C(6)-C(7)-H(7A)	111.4
C(2)-C(7)-H(7A)	111.4
C(9)-C(8)-C(13)	121.42(15)
C(9)-C(8)-C(7)	126.21(14)

C(13)-C(8)-C(7)	112.34(13)
C(10)-C(9)-C(8)	117.96(15)
C(10)-C(9)-H(9A)	121.0
C(8)-C(9)-H(9A)	121.0
C(9)-C(10)-C(11)	122.32(15)
C(9)-C(10)-N(1)	118.89(15)
C(11)-C(10)-N(1)	118.77(15)
C(12)-C(11)-C(10)	119.40(15)
C(12)-C(11)-H(11A)	120.3
C(10)-C(11)-H(11A)	120.3
C(11)-C(12)-C(13)	120.16(15)
C(11)-C(12)-H(12A)	119.9
C(13)-C(12)-H(12A)	119.9
C(12)-C(13)-C(8)	118.74(14)
C(12)-C(13)-C(1)	131.45(14)
C(8)-C(13)-C(1)	109.66(13)
C(3)-C(14)-C(6)	94.63(13)
C(3)-C(14)-H(14A)	112.8
C(6)-C(14)-H(14A)	112.8
C(3)-C(14)-H(14B)	112.8
C(6)-C(14)-H(14B)	112.8
H(14A)-C(14)-H(14B)	110.3
C(1)-C(15)-C(24)	121.61(14)
C(1)-C(15)-C(16)	124.46(14)
C(24)-C(15)-C(16)	113.28(13)
C(26)-C(16)-C(15)	111.06(16)
C(26)-C(16)-C(17)	110.48(16)
C(15)-C(16)-C(17)	110.66(14)
C(26)-C(16)-H(16A)	109.4(12)
C(15)-C(16)-H(16A)	108.4(11)
C(17)-C(16)-H(16A)	106.7(12)
C(18)-C(17)-C(16)	112.17(15)
C(18)-C(17)-H(17A)	109.2
C(16)-C(17)-H(17A)	109.2
C(18)-C(17)-H(17B)	109.2
C(16)-C(17)-H(17B)	109.2

H(17A)-C(17)-H(17B)	107.9
C(19)-C(18)-C(17)	107.47(16)
C(19)-C(18)-H(18A)	110.2
C(17)-C(18)-H(18A)	110.2
C(19)-C(18)-H(18B)	110.2
C(17)-C(18)-H(18B)	110.2
H(18A)-C(18)-H(18B)	108.5
C(20)-C(19)-C(24)	120.26(17)
C(20)-C(19)-C(18)	123.91(17)
C(24)-C(19)-C(18)	115.62(15)
C(21)-C(20)-C(19)	119.85(18)
C(21)-C(20)-H(20A)	120.1
C(19)-C(20)-H(20A)	120.1
C(22)-C(21)-C(20)	119.88(18)
C(22)-C(21)-H(21A)	120.1
C(20)-C(21)-H(21A)	120.1
C(21)-C(22)-C(23)	121.95(19)
C(21)-C(22)-H(22A)	119.0
C(23)-C(22)-H(22A)	119.0
C(22)-C(23)-C(24)	118.26(17)
C(22)-C(23)-C(25)	118.66(17)
C(24)-C(23)-C(25)	123.03(16)
C(23)-C(24)-C(19)	119.68(15)
C(23)-C(24)-C(15)	124.67(15)
C(19)-C(24)-C(15)	115.64(14)
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(16)-C(26)-H(26A)	109.5
C(16)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(16)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for d12160. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	43(1)	44(1)	48(1)	27(1)	15(1)	22(1)
O(2)	75(1)	54(1)	33(1)	20(1)	25(1)	26(1)
N(1)	29(1)	38(1)	32(1)	16(1)	7(1)	10(1)
C(1)	22(1)	26(1)	23(1)	6(1)	5(1)	8(1)
C(2)	32(1)	26(1)	25(1)	8(1)	8(1)	13(1)
C(3)	40(1)	29(1)	37(1)	13(1)	20(1)	17(1)
C(4)	49(1)	38(1)	36(1)	13(1)	21(1)	24(1)
C(5)	38(1)	34(1)	34(1)	8(1)	13(1)	20(1)
C(6)	32(1)	30(1)	29(1)	7(1)	7(1)	16(1)
C(7)	30(1)	23(1)	26(1)	7(1)	7(1)	11(1)
C(8)	22(1)	25(1)	26(1)	7(1)	5(1)	8(1)
C(9)	24(1)	25(1)	31(1)	10(1)	5(1)	8(1)
C(10)	22(1)	32(1)	26(1)	12(1)	4(1)	7(1)
C(11)	29(1)	35(1)	25(1)	8(1)	8(1)	12(1)
C(12)	31(1)	28(1)	28(1)	8(1)	9(1)	14(1)
C(13)	22(1)	25(1)	25(1)	7(1)	5(1)	8(1)
C(14)	29(1)	31(1)	40(1)	4(1)	13(1)	12(1)
C(15)	26(1)	26(1)	23(1)	6(1)	5(1)	10(1)
C(16)	48(1)	30(1)	26(1)	8(1)	8(1)	18(1)
C(17)	62(1)	29(1)	32(1)	6(1)	4(1)	13(1)
C(18)	37(1)	35(1)	48(1)	17(1)	1(1)	4(1)
C(19)	32(1)	32(1)	38(1)	14(1)	13(1)	14(1)
C(20)	52(1)	41(1)	46(1)	20(1)	28(1)	18(1)
C(21)	87(2)	44(1)	32(1)	17(1)	27(1)	20(1)
C(22)	74(2)	44(1)	26(1)	8(1)	8(1)	14(1)
C(23)	46(1)	32(1)	27(1)	9(1)	7(1)	12(1)
C(24)	32(1)	25(1)	26(1)	9(1)	10(1)	14(1)
C(25)	44(1)	40(1)	36(1)	9(1)	-1(1)	9(1)
C(26)	66(1)	53(1)	45(1)	16(1)	23(1)	40(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for d12160.

	x	y	z	U(eq)
H(2A)	3273	3843	8586	32
H(3A)	583	1802	8336	39
H(4A)	1628	4450	9686	44
H(4B)	-199	3591	9346	44
H(5A)	-440	5217	8240	40
H(5B)	1386	6093	8600	40
H(6A)	229	4790	6360	35
H(7A)	3055	5573	7547	32
H(9A)	2627	5715	5097	32
H(11A)	3706	2562	3248	35
H(12A)	3473	1307	4787	34
H(14A)	-1253	2511	7016	39
H(14B)	-114	2138	6250	39
H(16A)	2210(20)	-250(20)	5506(19)	40
H(17A)	955	-2450	5798	52
H(17B)	2177	-2278	6976	52
H(18A)	-89	-1000	6950	51
H(18B)	-185	-2436	7458	51
H(20A)	435	-1649	9656	51
H(21A)	2247	-201	11401	64
H(22A)	4372	1741	11307	61
H(25A)	5351	2867	8691	64
H(25B)	6196	2563	9864	64
H(25C)	5361	3697	9983	64
H(26A)	4893	465	6135	72
H(26B)	4118	-1297	5783	72
H(26C)	4703	-446	7157	72

Table 6. Torsion angles [°] for d12160.

C(15)-C(1)-C(2)-C(3)	-62.6(2)
C(13)-C(1)-C(2)-C(3)	114.39(14)
C(15)-C(1)-C(2)-C(7)	-174.02(15)
C(13)-C(1)-C(2)-C(7)	2.99(16)
C(1)-C(2)-C(3)-C(14)	-76.52(16)
C(7)-C(2)-C(3)-C(14)	37.14(15)
C(1)-C(2)-C(3)-C(4)	176.85(13)
C(7)-C(2)-C(3)-C(4)	-69.49(16)
C(14)-C(3)-C(4)-C(5)	-34.27(17)
C(2)-C(3)-C(4)-C(5)	72.35(17)
C(3)-C(4)-C(5)-C(6)	-0.96(18)
C(4)-C(5)-C(6)-C(14)	35.78(17)
C(4)-C(5)-C(6)-C(7)	-70.76(16)
C(14)-C(6)-C(7)-C(8)	79.71(16)
C(5)-C(6)-C(7)-C(8)	-174.04(13)
C(14)-C(6)-C(7)-C(2)	-33.04(15)
C(5)-C(6)-C(7)-C(2)	73.21(15)
C(1)-C(2)-C(7)-C(8)	-3.59(16)
C(3)-C(2)-C(7)-C(8)	-122.54(13)
C(1)-C(2)-C(7)-C(6)	116.57(13)
C(3)-C(2)-C(7)-C(6)	-2.38(15)
C(6)-C(7)-C(8)-C(9)	72.7(2)
C(2)-C(7)-C(8)-C(9)	-174.97(15)
C(6)-C(7)-C(8)-C(13)	-109.21(16)
C(2)-C(7)-C(8)-C(13)	3.09(17)
C(13)-C(8)-C(9)-C(10)	-0.8(2)
C(7)-C(8)-C(9)-C(10)	177.13(15)
C(8)-C(9)-C(10)-C(11)	0.4(2)
C(8)-C(9)-C(10)-N(1)	-177.81(13)
O(2)-N(1)-C(10)-C(9)	-177.57(15)
O(1)-N(1)-C(10)-C(9)	3.0(2)
O(2)-N(1)-C(10)-C(11)	4.1(2)
O(1)-N(1)-C(10)-C(11)	-175.30(15)
C(9)-C(10)-C(11)-C(12)	-0.2(2)

N(1)-C(10)-C(11)-C(12)	178.00(14)
C(10)-C(11)-C(12)-C(13)	0.4(2)
C(11)-C(12)-C(13)-C(8)	-0.7(2)
C(11)-C(12)-C(13)-C(1)	-175.63(15)
C(9)-C(8)-C(13)-C(12)	0.9(2)
C(7)-C(8)-C(13)-C(12)	-177.25(14)
C(9)-C(8)-C(13)-C(1)	176.88(14)
C(7)-C(8)-C(13)-C(1)	-1.29(18)
C(15)-C(1)-C(13)-C(12)	-9.1(3)
C(2)-C(1)-C(13)-C(12)	174.11(16)
C(15)-C(1)-C(13)-C(8)	175.64(16)
C(2)-C(1)-C(13)-C(8)	-1.17(17)
C(4)-C(3)-C(14)-C(6)	55.15(15)
C(2)-C(3)-C(14)-C(6)	-56.66(14)
C(5)-C(6)-C(14)-C(3)	-55.87(14)
C(7)-C(6)-C(14)-C(3)	54.87(14)
C(13)-C(1)-C(15)-C(24)	175.77(15)
C(2)-C(1)-C(15)-C(24)	-7.9(2)
C(13)-C(1)-C(15)-C(16)	-14.1(3)
C(2)-C(1)-C(15)-C(16)	162.21(15)
C(1)-C(15)-C(16)-C(26)	102.38(19)
C(24)-C(15)-C(16)-C(26)	-86.79(18)
C(1)-C(15)-C(16)-C(17)	-134.54(17)
C(24)-C(15)-C(16)-C(17)	36.3(2)
C(26)-C(16)-C(17)-C(18)	142.63(17)
C(15)-C(16)-C(17)-C(18)	19.2(2)
C(16)-C(17)-C(18)-C(19)	-61.1(2)
C(17)-C(18)-C(19)-C(20)	-127.66(19)
C(17)-C(18)-C(19)-C(24)	47.0(2)
C(24)-C(19)-C(20)-C(21)	-2.5(3)
C(18)-C(19)-C(20)-C(21)	171.9(2)
C(19)-C(20)-C(21)-C(22)	-0.1(3)
C(20)-C(21)-C(22)-C(23)	0.9(4)
C(21)-C(22)-C(23)-C(24)	0.8(3)
C(21)-C(22)-C(23)-C(25)	-176.6(2)
C(22)-C(23)-C(24)-C(19)	-3.4(3)

C(25)-C(23)-C(24)-C(19)	173.96(17)
C(22)-C(23)-C(24)-C(15)	177.42(17)
C(25)-C(23)-C(24)-C(15)	-5.2(3)
C(20)-C(19)-C(24)-C(23)	4.3(3)
C(18)-C(19)-C(24)-C(23)	-170.60(16)
C(20)-C(19)-C(24)-C(15)	-176.47(16)
C(18)-C(19)-C(24)-C(15)	8.7(2)
C(1)-C(15)-C(24)-C(23)	-63.2(2)
C(16)-C(15)-C(24)-C(23)	125.70(18)
C(1)-C(15)-C(24)-C(19)	117.60(18)
C(16)-C(15)-C(24)-C(19)	-53.52(19)

Symmetry transformations used to generate equivalent atoms: