Electronic Supplementary Information

Enantioselective Addition of Terminal 1,3-Diynes to Aromatic Ketones Triggered by Cu-Hydroxycamphorsulfonamide Complexes

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Contents

1.General information:

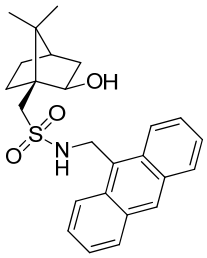
^{1}H, ^{13}C and ^{19}F were recorded on Varian Mercury Plus 400 instruments or Bruker AV 400 MHz at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm from the solvent resonance as the internal Me_4Si. MS were recorded on a VG-7070E or VG ZAB-HS spectrometer with the EI or ESI resource. Optical rotations were determined using an Autopol IV-T. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Melting points were measured on a WRS-1A digital melting point apparatus and are uncorrected. HPLC analyses were carried out on a Hewlett Packard Model HP 1200 instrument. X-ray structural analyses was conducted on the XtaLAB mini (600 W,SHINE, CCD, 75mn, 0.1 electorns/pixel/sec).

Materials:

Tetrahydrofuran (THF), diethyl ether and toluene were distilled from sodium /benzophenone prior to use; CH_2Cl_2 (DCM) and $ClCH_2CH_2Cl$ (DCE) were distilled from CaH_2. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. Ligands **I**–**VI** were synthesized by known method.[1] Substituted terminal 1,3-Diynes were synthesized by literature.[2] Dimethylzinc (1.2M solution in toluene) were purchased from ACROS Organics. Standard reagents and solvents were purified according to known procedures.

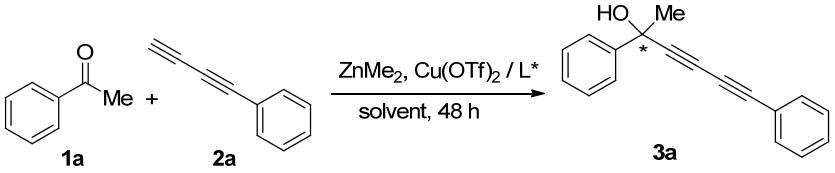
2. Preparation of Ligands:

Ligands **I**–**VI** were synthesized by known method.[1]



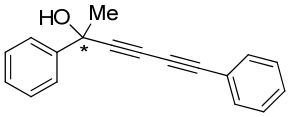
N-(anthracen-9-ylmethyl)-1-((1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]-heptan-1-yl)methanesulfonamide (IV): mp 167-169 °C; $[\alpha]_D^{20}$ -34.5 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.44 (1H, s), 8.29 (2H, d, *J* = 8.9 Hz), 8.00 (2H, d, *J* = 8.4 Hz), 7.60-7.56 (2H, m), 7.50-7.46 (2H, m), 5.29 (2H, d, *J* = 5.6 Hz), 4.95 (1H, t, *J* = 5.5 Hz), 3.98-3.94 (1H, m), 3.14 (2H, dd, *J* = 26.3 Hz, 8.7 Hz), 2.61 (1H, d, *J* = 13.7 Hz), 1.69-1.53 (5H, m), 1.02-0.95 (2H, m), 0.77 (3H, s), 0.47 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 131.5, 130.1, 129.4, 128.7, 127.1, 125.3, 123.4, 76.3, 52.9, 50.3, 48.5, 44.3, 39.4, 38.9, 30.3, 27.3, 20.2, 19.6; MS(ESI) m/z 446.2 $(M+Na)^+$; IR (neat) ν 3459, 3160, 3048, 2955, 2933, 2881, 1453, 1317, 1137, 1075, 1022, 878, 738, 568 cm^{-1}.

3. General procedure for the enantioselective addition of terminal 1,3-Diynes to aromatic ketones:

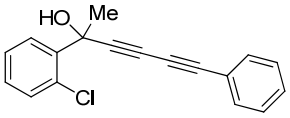


A CH_2Cl_2 solution (1.0 mL) of sulfonamide ligand **III** (7.46 mg, 0.02 mmol) and copper(II) triflate (7.22 mg, 0.02 mmol) was stirred at room temperature for 30 min to prepare the copper complex. Buta-1,3-diynylbenzene (65.5 mg, 0.52 mmol) and a 1.2M solution of dimethylzinc in toluene (0.5 mL, 0.6 mmol) were added to a dry flask at 0 °C under Ar_2 with stirring for 30 min. The copper complex was added to the flask containing $ZnMe_2$ and buta-1,3-diynylbenzene *via* a syringe and the homogeneous solution was stirred at 10 °C for 30 min, then acetophenone (23.5 μL, 0.2 mmol) was added. The mixture was allowed to stir at 10 °C for 48 h. The reaction

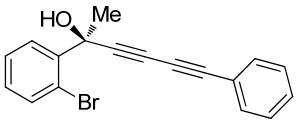
was quenched with 5% HCl solution. The product was extracted with ether (5 mL×3) washed with brine and dried over Na_2SO_4. The compound was purified *via* flash chromatography (silica gel) using 5% ethyl acetate in petroleum ether as eluent. The enantiomeric excess was determined by HPLC analysis on a Chiralcel OD-H IA or IB column.



2,6-Diphenylhexa-3,5-diyn-2-ol (3a): 94% yield, 77% ee; $[\alpha]_D^{20}$ +9.9 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.65 (2H, d, *J* = 7.7 Hz), 7.49 (2H, d, *J* = 7.4 Hz), 7.39-7.31 (6H, m), 3.06 (1H, br s), 1.82 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.8, 132.6, 129.4, 128.5, 128.0, 124.9, 121.5, 85.5, 79.4, 73.3, 70.5, 69.6, 33.0; MS(EI) m/z 245.5; IR (neat) ν 3398, 3060, 3030, 2963, 2929, 2235, 1598, 1446, 1261, 1158, 1094, 1067, 1024, 800, 758, 694 cm^{-1}; HPLC (DAICEL Chiralpak OD-H, Hexane / *i*-PrOH = 90 / 10, 0.8 mL / min, 254 nm) t_R (major) = 12.5 min, t_R (minor) = 18.7 min.

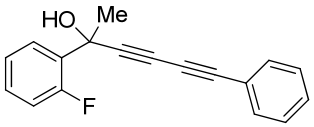


2-(2-Chlorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3b): 92% yield, 90% ee; $[\alpha]_D^{20}$ +5.8 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.74 (1H, d, *J* = 7.5 Hz), 7.48 (2H, d, *J* = 7.7 Hz), 7.42 (1H, d, *J* = 7.6 Hz), 7.36-7.29 (5H, m), 3.14 (1H, s), 1.99 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 140.4, 132.6, 131.9, 131.4, 129.3, 128.4, 127.0, 126.6, 121.5, 84.1, 79.6, 73.3, 69.4, 69.3, 29.4; MS(EI) m/z 279.6 ; IR (neat) ν 3445, 3063, 2960, 2918, 2849, 2235, 1434, 1264, 1037, 755, 688 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 95 / 5, 1.0 mL / min, 254 nm) t_R (major) = 10.7 min, t_R (minor) = 15.8 min.

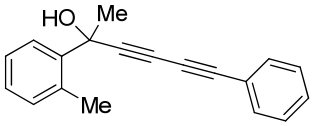


(S)-2-(2-bromophenyl)-6-phenylhexa-3,5-diyn-2-ol (3c): 91% yield, 90% ee; $[\alpha]_D^{20}$

+3.6 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.76 (1H, d, *J* = 7.7 Hz), 7.63 (1H, d, *J* = 7.8 Hz), 7.48 (2H, d, *J* = 7.2 Hz), 7.36-7.29 (4H, m), 7.18 (1H, t, *J* = 7.5 Hz), 3.22 (1H, s), 2.01 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 141.7, 134.9, 132.6, 129.5, 129.3, 128.4, 127.6, 126.9, 121.5, 121.1, 84.0, 79.6, 73.3, 70.2, 69.9, 29.5; MS(EI) m/z 323.7; IR (neat) ν 3401, 3061, 2962, 2929, 2235, 1489, 1443, 1260, 1093, 1027, 799, 755, 688 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 85 / 15, 1.0 mL / min, 254 nm) t_R (major) = 5.9 min, t_R (minor) = 7.5 min.

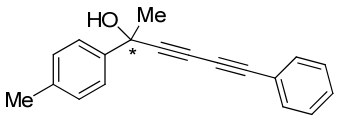


2-(2-Fluorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3d): 88% yield, 79% ee; $[\alpha]_D^{20}$ +7.4 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.65 (1H, t, *J* = 7.9 Hz), 7.48 (2H, d, *J* = 7.2 Hz), 7.36-7.30 (4H, m), 7.16 (1H, t, *J* = 7.6 Hz), 7.09 (1H, dd, *J* = 11.5 Hz, 8.4 Hz), 2.77 (1H, s), 1.94 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 160.1 (d, $^1J_{F\text{-}C}$ = 246.5 Hz), 132.6, 131.1 (d, $^3J_{F\text{-}C}$ = 10.5 Hz), 129.9 (d, $^3J_{F\text{-}C}$ = 8.6 Hz), 129.3, 128.4, 126.6 (d, $^2J_{F\text{-}C}$ = 22.1 Hz), 124.1 (d, $^4J_{F\text{-}C}$ = 3.4 Hz), 116.4 (d, $^2J_{F\text{-}C}$ = 22.1 Hz), 84.1, 79.6, 73.1, 69.0, 68.0, 30.2; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ -112.8 (1F, s); MS(EI) m/z 263.7; IR (neat) ν 3391, 3062, 2987, 2935, 2869, 2238, 1584, 1486, 1443, 1224, 1078, 754, 688 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 95 / 5, 1.0 mL / min, 254 nm) t_R (major) = 11.3 min, t_R (minor) = 15.4 min.

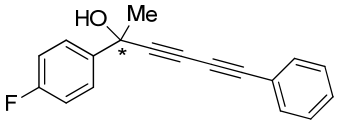


6-Phenyl-2-(o-tolyl)hexa-3,5-diyn-2-ol (3e): 60% yield, 71% ee; $[\alpha]_D^{20}$ +3.2 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.68-7.66 (1H, m), 7.48 (2H, d, *J* = 6.9 Hz), 7.35-7.29 (3H, m), 7.24-7.20 (3H, m), 2.83 (1H, s), 2.65 (3H, s), 1.90 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 141.3, 135.8, 132.6, 132.4, 129.3, 128.4, 128.0, 125.9, 121.6, 85.5, 79.5, 73.3, 70.2, 69.5, 30.7, 21.2; MS(EI) m/z 259.7; IR (neat) ν 3397, 3062, 3018, 2985, 2931, 2235, 1488, 1442, 1159, 1079, 1058, 912, 755, 726, 688 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm) t_R

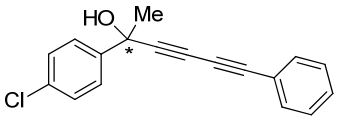
(major) = 9.1 min, t_R (minor) = 12.7 min.



6-Phenyl-2-(p-tolyl)hexa-3,5-diyn-2-ol (3f): 67% yield, 71% ee; $[\alpha]_D^{20}$ +11.7 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.54 (2H, d, *J* = 7.7 Hz), 7.49 (2H, d, *J* = 7.2 Hz), 7.36-7.29 (3H, m), 7.18 (2H, d, *J* = 7.7 Hz), 2.67 (1H, s), 2.35 (3H, s), 1.82 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 142.0, 137.7, 132.6, 129.3, 129.1, 128.4, 124.9, 121.6, 85.8, 79.2, 73.4, 70.3, 69.3, 32.9, 21.1; MS(EI) m/z 259.8; IR (neat) ν 3382, 3056, 3028, 2983, 2927, 2869, 2236, 1596, 1442, 1158, 1091, 917, 818, 755, 688, 578, 526 cm^{-1}; HPLC (DAICEL Chiralpak OD-H, Hexane / *i*-PrOH = 95 / 5, 0.8 mL / min, 254 nm) t_R (major) = 20.2 min, t_R (minor) = 31.4 min.

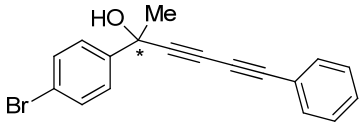


2-(4-Fluorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3g): 83% yield, 71% ee; $[\alpha]_D^{20}$ +17.8 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.65-7.62 (2H, m), 7.50 (2H, d, *J* = 6.9 Hz), 7.36-7.31 (3H, m), 7.06 (2H, t, *J* = 8.6 Hz), 2.41 (1H, s), 1.82 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 159.8 (d, $^1J_{F\text{-}C}$ = 236.5 Hz), 140.5 (d, $^4J_{F\text{-}C}$ = 3.4 Hz), 132.6, 129.4, 128.5, 126.8 (d, $^3J_{F\text{-}C}$ = 8.1 Hz), 121.4, 115.2 (d, $^2J_{F\text{-}C}$ = 22.1 Hz), 84.8, 79.7, 73.0, 70.1, 69.9, 33.1; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ -114.6 (1F, s); MS(EI) m/z 263.7; IR (neat) ν 3380, 3063, 2986, 2929, 2856, 2237, 1602, 1506, 1226, 1159, 1087, 836, 755, 688, 575, 525 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 95 / 5, 1.0 mL / min, 254 nm) t_R (major) = 12.0 min, t_R (minor) = 16.2 min.

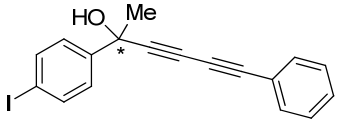


2-(4-Chlorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3h): 86% yield, 72% ee; $[\alpha]_D^{20}$ +11.7 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.59 (2H, d, *J* = 8.4 Hz), 7.50 (2H, d, *J* = 7.1 Hz), 7.38-7.31 (5H, m), 2.42 (1H, s), 1.81 (3H, s); ^{13}C-NMR ($CDCl_3$,

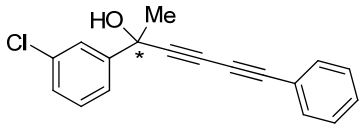
100 MHz) δ 143.2, 133.9, 132.6, 129.5, 128.6, 128.5, 126.4, 121.3, 84.6, 79.8, 72.9, 70.1, 70.0, 33.0; MS(EI) m/z 279.8; IR (neat) ν 3552, 3357, 3296, 3057, 2984, 2929, 2856, 2236, 1489, 1092, 1013, 829, 755, 688 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 95 / 5, 1.0 mL / min, 254 nm) t_R (major) = 16.7 min, t_R (minor) = 18.1 min.



2-(4-Bromophenyl)-6-phenylhexa-3,5-diyn-2-ol (3i): 80% yield, 65% ee; $[\alpha]_D^{20}$ +20.2 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.54-7.49 (6H, m), 7.38-7.31 (3H, m), 2.45 (1H, s), 1.81 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 143.8, 132.6, 131.5, 129.5, 128.5, 126.8, 122.0, 121.3, 84.5, 79.8, 72.9, 70.2, 70.0, 33.0; MS(EI) m/z 324.4; IR (neat) ν 3331, 3059, 2985, 2926, 2850, 2235, 1590, 1486, 1087, 1009, 823, 754, 688 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 80 / 20, 0.8 mL / min, 254 nm) t_R (major) = 7.2 min, t_R (minor) = 8.1 min.

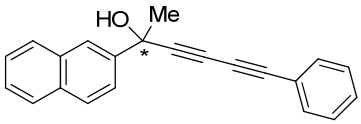


2-(4-Iodophenyl)-6-phenylhexa-3,5-diyn-2-ol (3j): 95% yield, 81% ee; $[\alpha]_D^{20}$ +10.5 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.71 (2H, d, *J* = 8.6 Hz), 7.50 (2H, d, *J* = 6.7 Hz), 7.41-7.31 (5H, m), 2.43 (1H, s), 1.80 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.5, 137.5, 132.6, 129.4, 128.5, 127.0, 121.3, 93.6, 84.5, 79.8, 72.9, 70.2, 70.0, 32.9; MS(ESI) m/z 355.0 $(M\text{-}OH)^+$; IR (neat) ν 3411, 3054, 2985, 2918, 2849, 2235, 1484, 1391, 1264, 1087, 1005, 820, 754, 739, 688 cm^{-1}; HPLC (DAICEL Chiralpak OD-H, Hexane / *i*-PrOH = 80 / 20, 0.8 mL / min, 254 nm) t_R (major) = 11.5 min, t_R (minor) = 24.0 min.

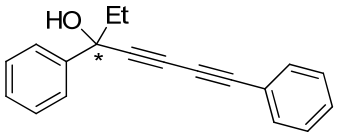


2-(3-Chlorophenyl)-6-phenylhexa-3,5-diyn-2-ol (3k): 92% yield, 70% ee; $[\alpha]_D^{20}$ +9.0 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.65 (1H, s), 7.53 (1H, d, *J* = 7.0

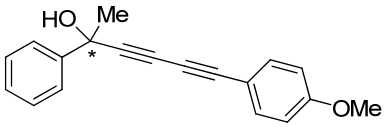
Hz), 7.50 (2H, d, *J* = 7.1 Hz), 7.37-7.28 (5H, m), 3.68 (1H, br s), 1.81 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 147.0, 134.4, 132.6, 129.7, 129.4, 128.5, 128.0, 125.3, 123.2, 121.4, 84.8, 79.6, 73.1, 69.9, 69.8, 33.1; MS(EI) m/z 279.9; IR (neat) ν 3295, 3060, 2918, 2849, 2236, 1433, 1264, 1037, 755, 688 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 70 / 30, 0.8 mL / min, 254 nm) t_R (major) = 5.1 min, t_R (minor) = 6.0 min.



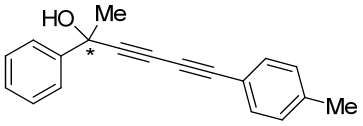
2-(Naphthalen-2-yl)-6-phenylhexa-3,5-diyn-2-ol (3l): 71% yield, 68% ee; $[\alpha]_D^{20}$ +2.5 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.12 (1H, s), 7.90-7.83 (3H, m), 7.74 (1H, d, *J* = 8.6 Hz), 7.52-7.49 (4H, m), 7.38-7.31 (3H, m), 2.58 (1H, s), 1.92 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 141.9, 133.1, 133.0, 132.6, 129.4, 128.5, 128.4, 128.4, 127.6, 126.4, 126.3, 123.5, 123.2, 121.5, 85.2, 79.6, 73.2, 70.7, 69.9, 32.8; MS(ESI) m/z 279.1 $(M\text{-}OH)^+$; IR (neat) ν 3538, 3384, 3057, 2984, 2928, 2859, 2236, 1598, 1489, 1442, 1187, 1127, 1084, 858, 818, 752, 688, 526, 477 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm) t_R (minor) = 7.7 min, t_R (major) = 21.1 min.



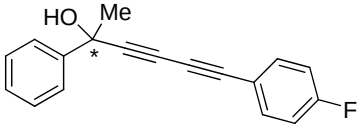
3,7-Diphenylhepta-4,6-diyn-3-ol (3m): 91% yield, 62% ee; $[\alpha]_D^{20}$ +11.0 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.62 (1H, d, *J* = 7.4 Hz), 7.51 (1H, d, *J* = 7.0 Hz), 7.39-7.31 (6H, m), 2.08-1.95 (2H, m), 0.99 (3H, t, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 143.7, 132.6, 129.4, 128.5, 128.3, 127.9, 125.5, 121.5, 84.6, 79.0, 74.5, 73.3, 70.6, 38.3, 9.1; MS(EI) m/z 259.6; IR (neat) ν 3396, 3061, 3030, 2964, 2928, 2235, 1446, 1261, 1094, 1067, 1024, 800, 758, 694 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm) t_R (major) = 4.3 min, t_R (minor) = 4.7 min.



6-(4-Methoxyphenyl)-2-phenylhexa-3,5-diyn-2-ol (3n): 90% yield, 80% ee; $[\alpha]_D^{20}$ +22.4 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.66 (2H, d, *J* = 7.6 Hz), 7.44 (2H, d, *J* = 8.7 Hz), 7.38 (2H, t, *J* = 7.5 Hz), 7.31 (1H, t, *J* = 7.2 Hz), 6.84 (2H, d, *J* = 8.7 Hz), 3.81 (3H, s), 2.50 (1H, s), 1.83 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 160.5, 144.8, 134.2, 128.4, 128.0, 124.9, 114.2, 113.4, 84.7, 79.9, 72.1, 70.6, 69.9, 55.3, 33.0; MS(EI) m/z 275.7; IR (neat) ν 3418, 3060, 2984, 2933, 2838, 2233, 1603, 1509, 1252, 1174, 1030, 831, 763, 699 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 90 / 10, 1.0 mL / min, 254 nm) t_R (major) = 10.2 min, t_R (minor) = 12.2 min.

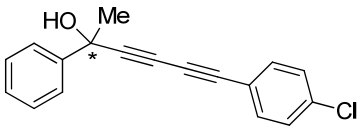


2-Phenyl-6-(p-tolyl)hexa-3,5-diyn-2-ol (3o): 82% yield, 70% ee; $[\alpha]_D^{20}$ +17.7 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.65 (2H, d, *J* = 7.7 Hz), 7.40-7.36 (4H, m), 7.31 (1H, t, *J* = 7.2 Hz), 7.12 (2H, d, *J* = 7.8 Hz), 2.54 (1H, s), 2.35 (3H, s), 1.83 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.8, 139.8, 132.5, 129.2, 128.4, 128.0, 124.9, 118.4, 85.0, 79.7, 72.6, 70.6, 69.8, 33.0, 21.6; MS(EI) m/z 259.6; IR (neat) ν 3415, 3029, 2958, 2928, 2870, 2234, 1602, 1509, 1448, 1286, 1180, 815, 763, 699, 527 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 80 / 20, 0.8 mL / min, 254 nm) t_R (major) = 5.8 min, t_R (minor) = 6.0 min.

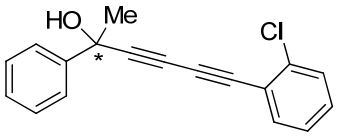


6-(4-Fluorophenyl)-2-phenylhexa-3,5-diyn-2-ol (3p): 77% yield, 62% ee; $[\alpha]_D^{20}$ +12.1 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.65 (2H, d, *J* = 7.3 Hz), 7.48 (2H, m), 7.38 (2H, t, *J* = 7.5 Hz), 7.30 (1H, t, *J* = 7.2 Hz), 7.02 (2H, t, *J* = 8.6 Hz), 2.91 (1H, br s), 1.83 (3H, m); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 163.1 (d, $^1J_{F\text{-}C}$ = 250.1 Hz), 145.0, 134.6 (d, $^3J_{F\text{-}C}$ = 8.6 Hz), 128.4, 127.9, 124.9, 117.7 (d, $^4J_{F\text{-}C}$ = 3.4 Hz),

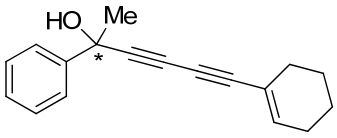
115.9 (d, $^{2}J_{F\text{-}C}$ = 22.1 Hz), 85.9, 78.1, 73.2, 70.3, 69.2, 33.1; ^{19}F-NMR ($CDCl_3$, 376 MHz) δ -108.4 (1F, s); MS(EI) m/z 263.6; IR (neat) ν 3359, 3061, 3029, 2985, 2931, 2237, 1598, 1505, 1232, 1155, 835, 699, 529 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 80 / 20, 1.0 mL / min, 254 nm) t_R (major) = 4.6 min, t_R (minor) = 5.0 min.



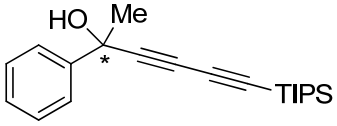
6-(4-Chlorophenyl)-2-phenylhexa-3,5-diyn-2-ol (3q): 79% yield, 66% ee; $[\alpha]_D^{20}$ +12.6 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.64 (2H, d, *J* = 7.5 Hz), 7.42-7.36 (4H, m), 7.32-7.28 (3H, m), 2.69 (1H, s), 1.82 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.8, 139.8, 132.5, 129.2, 128.4, 128.0, 124.9, 118.4, 85.0, 79.7, 72.6, 70.6, 69.8, 33.0, 21.6; MS(EI) m/z 279.6; IR (neat) ν 3554, 3375, 3060, 330, 2985, 2929, 2860, 2236, 1489, 1092, 1013, 826, 763, 699, 578, 524 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 90 / 10, 1.0 mL / min, 254 nm) t_R (major) = 6.2 min, t_R (minor) = 7.0 min.



6-(2-Chlorophenyl)-2-phenylhexa-3,5-diyn-2-ol (3r): 85% yield, 67% ee; $[\alpha]_D^{20}$ +12.1 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.65 (2H, d, *J* = 6.9 Hz), 7.52 (1H, d, *J* = 6.9 Hz), 7.39-7.38 (3H, m), 7.33-7.26 (2H, m), 7.21 (1H, t, *J* = 6.4 Hz), 2.61 (1H, s), 1.84 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.5, 137.0, 134.4, 130.3, 129.6, 128.5, 128.1, 126.6, 124.9, 121.7, 86.8, 78.0, 75.9, 70.6, 69.4, 32.9; MS(EI) m/z 279.6; IR (neat) ν 3391, 3063, 2983, 2963, 2917, 2849, 2235, 1435, 1093, 1067, 754, 698 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 90 / 10, 1.0 mL / min, 254 nm) t_R (major) = 6.3 min, t_R (minor) = 7.7 min.



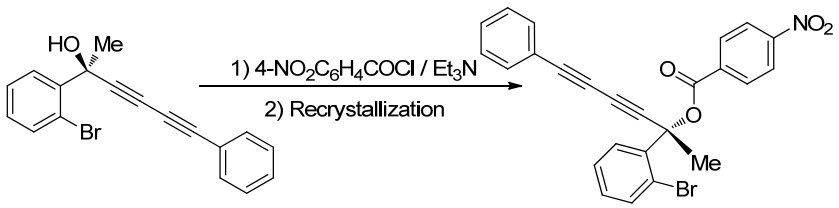
6-(Cyclohex-1-en-1-yl)-2-phenylhexa-3,5-diyn-2-ol (3s): 85% yield, 79% ee; $[\alpha]_D^{20}$ +16.5 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.62 (2H, d, *J* = 7.5 Hz), 7.35 (2H, t, *J* = 7.3 Hz), 7.29 (1H, d, *J* = 7.1 Hz), 6.29 (1H, m), 2.94 (1H, s), 2.14-2.09 (4H, m), 1.78 (3H, s), 1.63-1.56 (4H, m); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.9, 139.2, 128.4, 127.9, 124.9, 119.5, 84.4, 81.5, 70.7, 70.5, 69.9, 33.0, 28.6, 25.9, 22.1, 21.3; MS(EI) m/z 249.7; IR (neat) ν 3384, 3061, 3027, 2984, 2932, 2860, 2228, 1448, 1146, 1092, 1055, 919, 763, 699, 578 cm^{-1}; HPLC (DAICEL Chiralpak IB, Hexane / *i*-PrOH = 90 / 10, 1.0 mL / min, 254 nm) t_R (major) = 5.2 min, t_R (minor) = 5.5 min.



2-Phenyl-6-(triisopropylsilyl)hexa-3,5-diyn-2-ol (3t): 71% yield, 72% ee, $[\alpha]_D^{20}$ +6.1 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.62 (2H, d, *J* = 7.5 Hz), 7.37 (2H, t, *J* = 7.5 Hz), 7.30 (1H, d, *J* = 7.2 Hz), 2.53 (1H, s), 1.79 (3H, s), 1.09 (21H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 144.6, 128.4, 128.0, 124.9, 88.9, 85.6, 79.2, 70.4, 70.2, 32.9, 18.5, 11.3; MS(EI) m/z 283.1 (M-^{i}Pr); IR (neat) ν 3325, 2944, 2891, 2866, 2221, 2102, 1462, 1367, 1239, 1065, 921, 882, 763, 697, 678, 579 cm^{-1}; HPLC (DAICEL Chiralpak IA, Hexane / *i*-PrOH = 95 / 5, 1.0 mL / min, 254 nm) t_R (minor) = 4.7 min, t_R (major) = 5.0 min.

4. A large-scale addition, Further transformation, and X-ray Analysis:

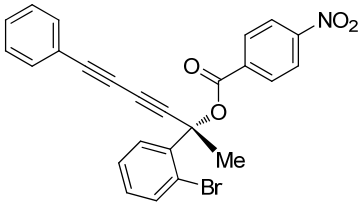
A CH_2Cl_2 solution (15.0 mL) of sulfonamide ligand **III** (112.0 mg, 0.3 mmol) and copper(II) triflate (108.3 mg, 0.3 mmol) was stirred at room temperature for 30 min to prepare the copper complex. Buta-1,3-diynylbenzene **2a** (982.5 mg, 7.8 mmol) and a 1.2M solution of dimethylzinc in toluene (7.5 mL, 9 mmol) were added to a dry flask at 0 °C under Ar_2 with stirring for 30 min. The copper complex was added to the flask containing $ZnMe_2$ and buta-1,3-diynylbenzene *via* a syringe and the homogeneous solution was stirred at 10 °C for 30 min, then 1-(2-bromophenyl)ethanone **1a** (593.9 mg, 3 mmol) was added. The mixture was allowed to stir at 10 °C for 48 h. The reaction was quenched with 5% HCl solution and extracted with ether (25 mL×3). The organic layer was washed with brine and dried over Na_2SO_4. The crude was purified *via* flash chromatography (silica gel) using ethyl acetate in petroleum ether (0–5%, *v*/*v*) as eluent to recover the buta-1,3-diynylbenzene (562.3 mg, 93%) and to afford the light yellow oil **3c** (923.5 mg, 95% yield and 90% ee).



3c, 90% ee

4, 76% yield, >99.99% ee

To a solution of **3c** (0.37 mmol, 120 mg) in CH_2Cl_2 (4 mL) was directly dropped a mixture of 4-nitrobenzoyl chloride (74 mg, 0.4 mmol, 1.1 equiv) and Et_3N (103 μL, 0.74 mmol, 2 eqiuv) in CH_2Cl_2 (2 mL) at 0 °C, then stirring was maintained for 48 h at room temperature. The resulting mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to afford the product**.** Recrystallization of this product from CH_2Cl_2/hexane furnished acicular crystal.



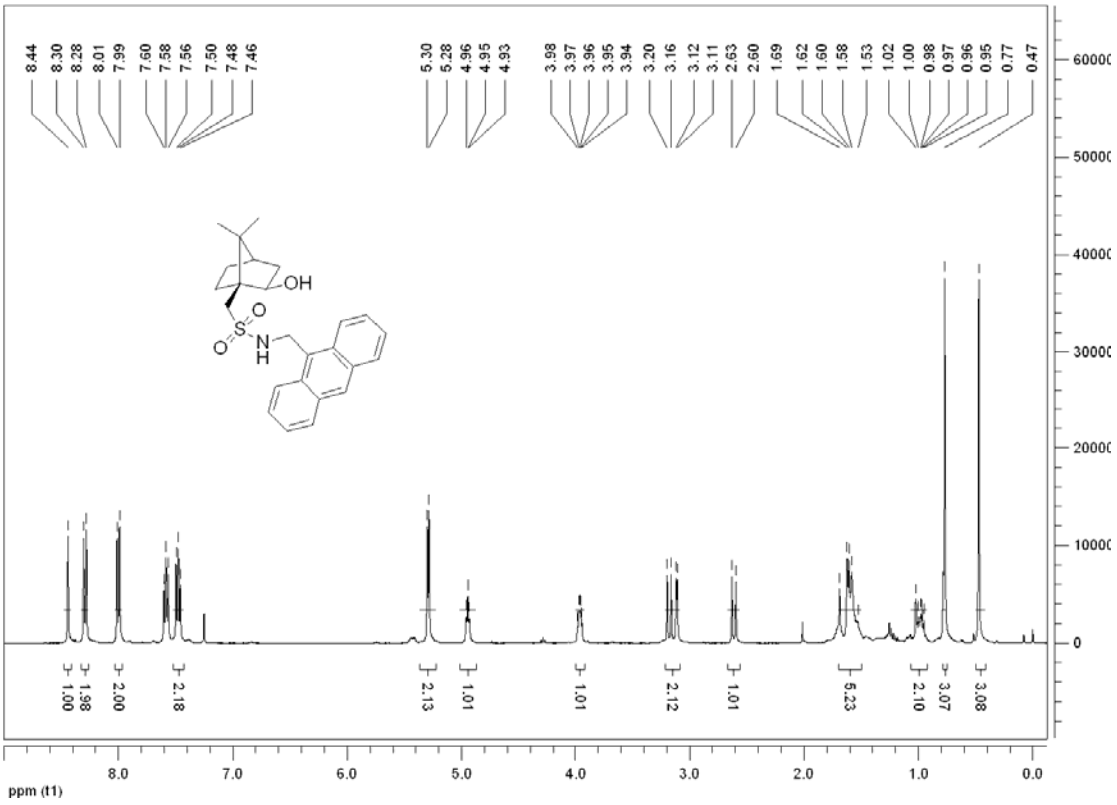
(S)-2-(2-bromophenyl)-6-phenylhexa-3,5-diyn-2-yl 4-nitrobenzoate (4): 133 mg, 76% yield, >99.99% ee; mp 164-165 ^{o}C; $[\alpha]_D^{20}$ -29.7 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.30-8.25 (4H, m), 8.05 (1H, d, *J* = 7.9 Hz), 7.59 (1H, d, *J* = 7.9 Hz), 7.51 (2H, d, *J* = 6.8 Hz), 7.43-7.32 (4H, m), 7.20 (1H, t, *J* = 7.6 Hz), 2.30 (3H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 162.2, 150.7, 138.1, 135.6, 135.3, 132.6, 131.2, 130.0, 129.6, 128.5, 127.6, 123.5, 121.2, 119.3, 80.8, 79.8, 78.3, 73.3, 72.9, 28.5; MS(ESI) m/z 473.0 $(M)^+$; IR (neat) ν 3442, 2918, 2850, 2242, 1729, 1523, 1348, 1266, 1091, 1055, 841, 762, 719 cm^{-1}.

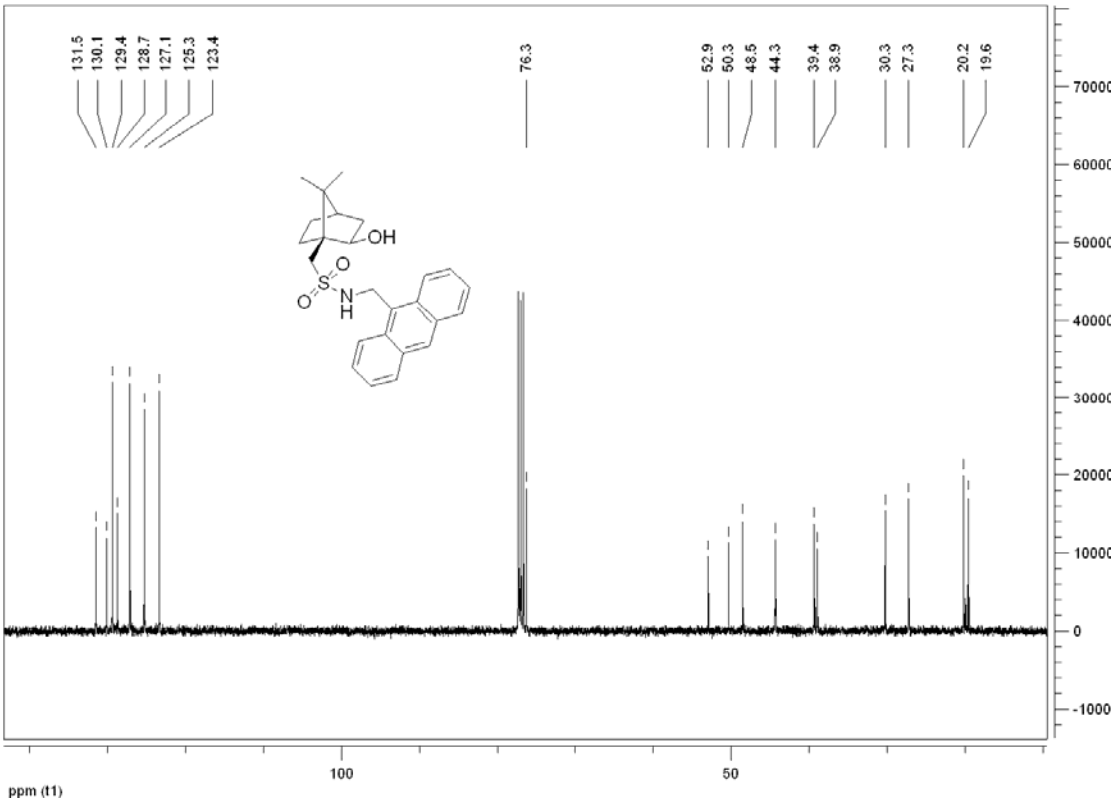
5. References

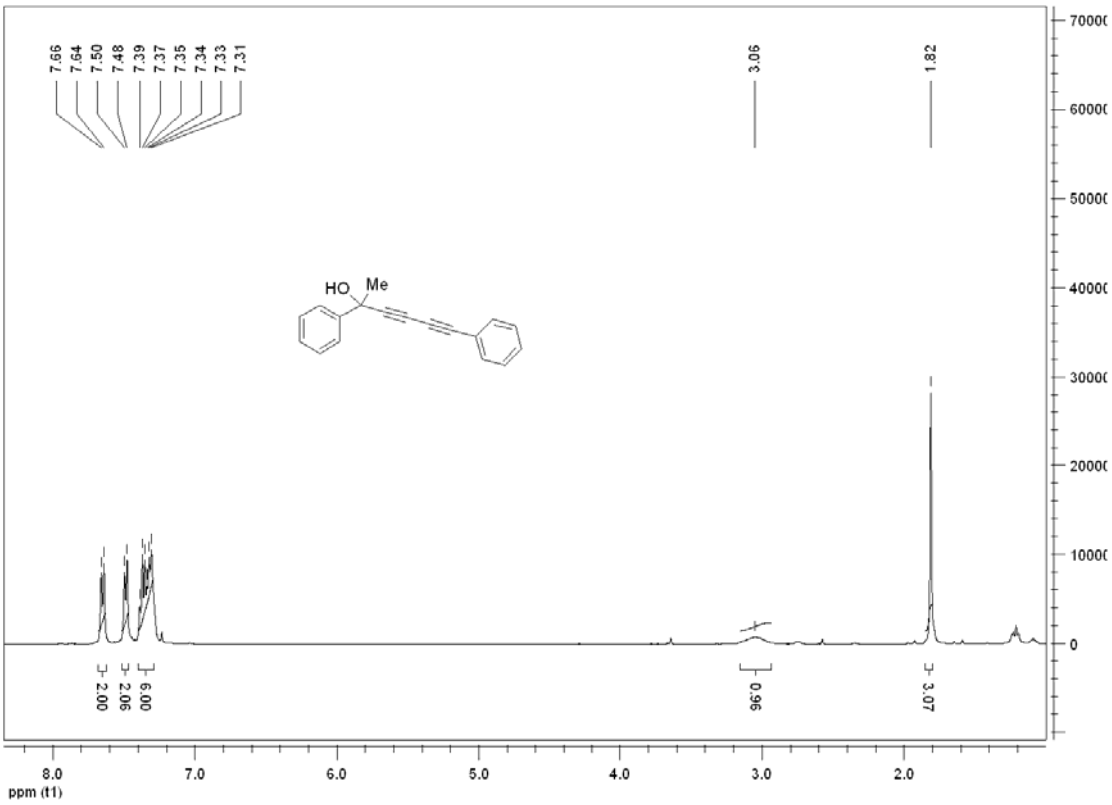
1 (*a*) D. J. Ramón, M. Yus, *Tetrahedron*, 1998, **54**, 5651–5666; (*b*) D. J. Ramón, M. Yus, *Chem. Eur. J.*, 2006, **12**, 4431–4445.

2 X.-W. Jiang, M. Rawat, W. D. Wulff, *J. Am. Chem. Soc.*, 2004, **126**, 5970–5971.

6. NMR Spectra and HPLC Charts for the Addition Adducts:



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7.37
7.35
7.34
7.33
7.31
3.06
1.82
HO
Me
2.00
2.06
6.00
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3.07
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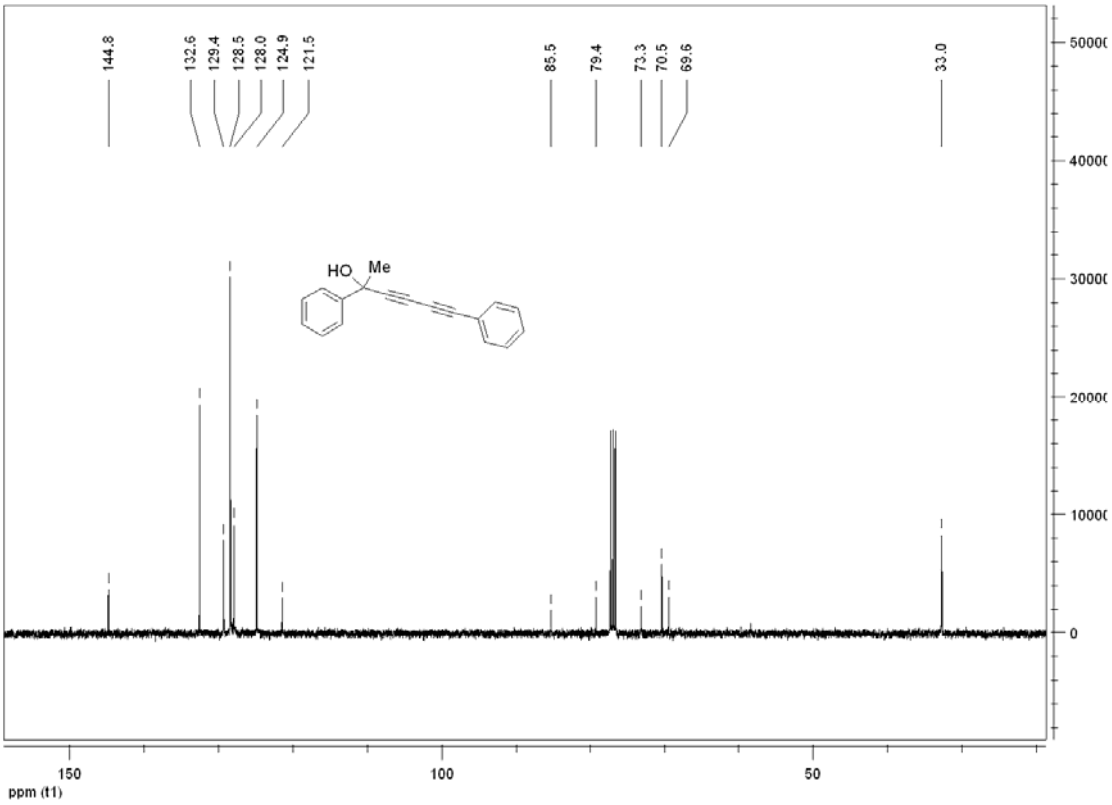
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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HO
Me
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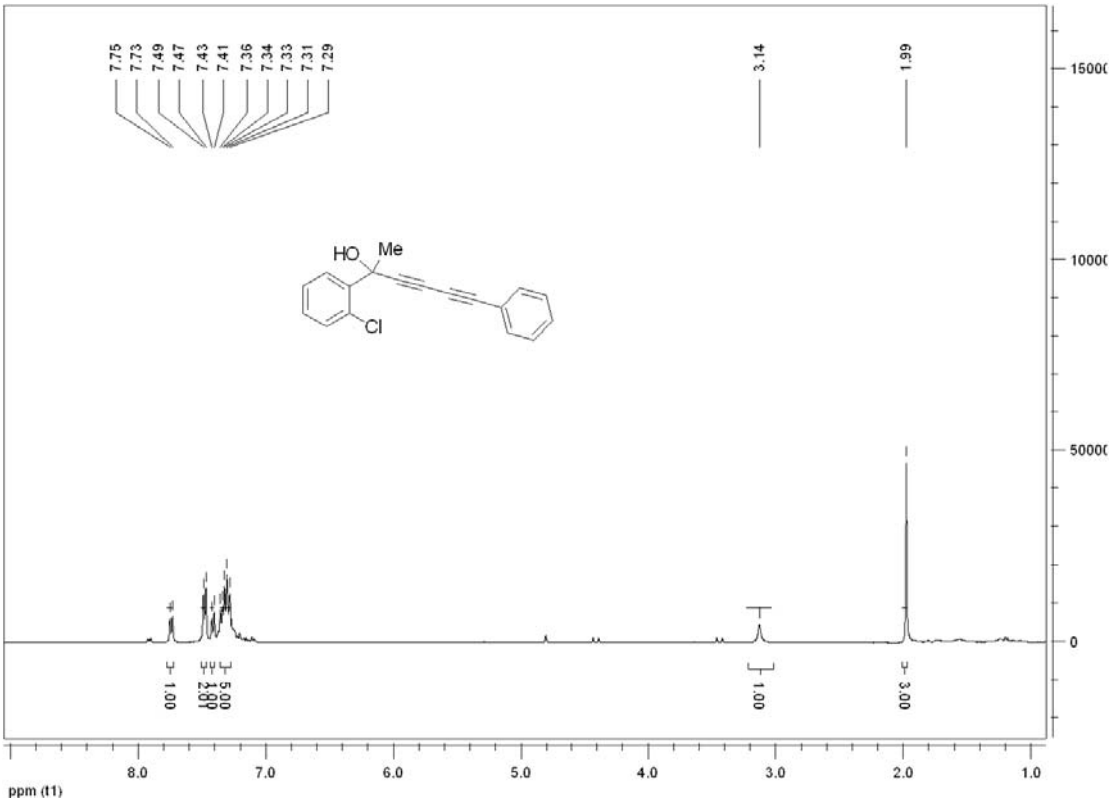
100
50
ppm (t1)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7.31
7.29
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HO
Me
Cl
1.00
2.00
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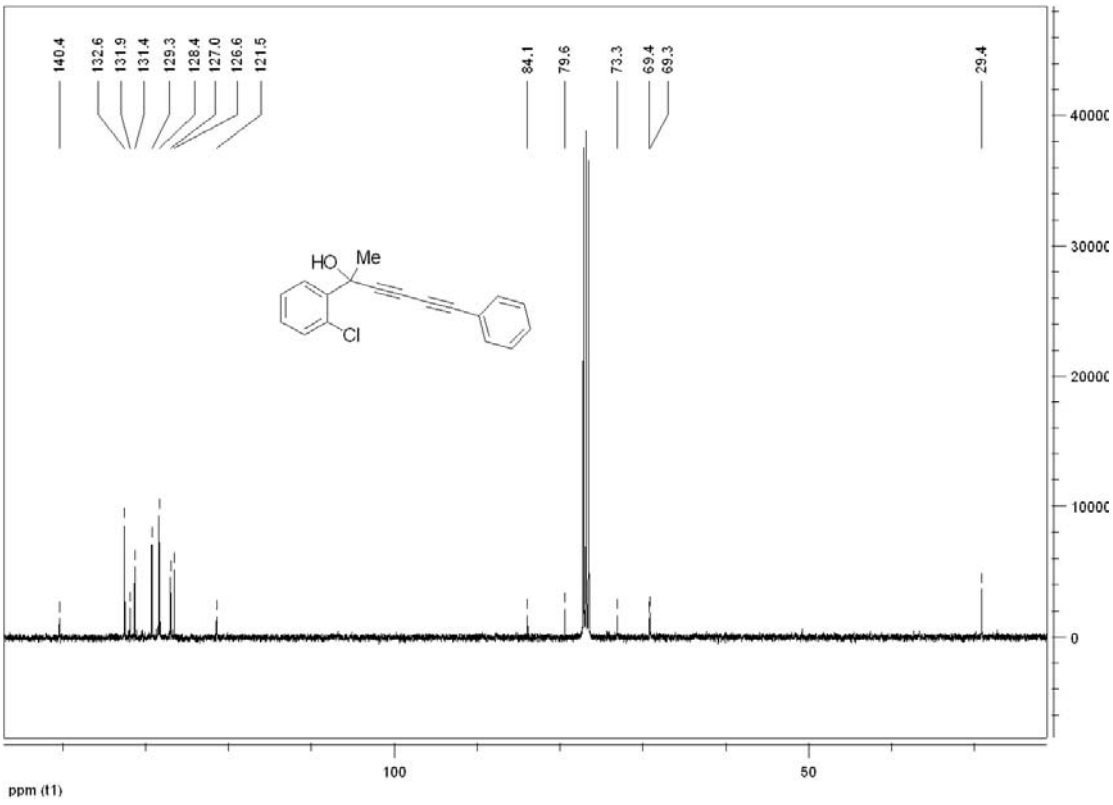
ppm (t1)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Me
Cl
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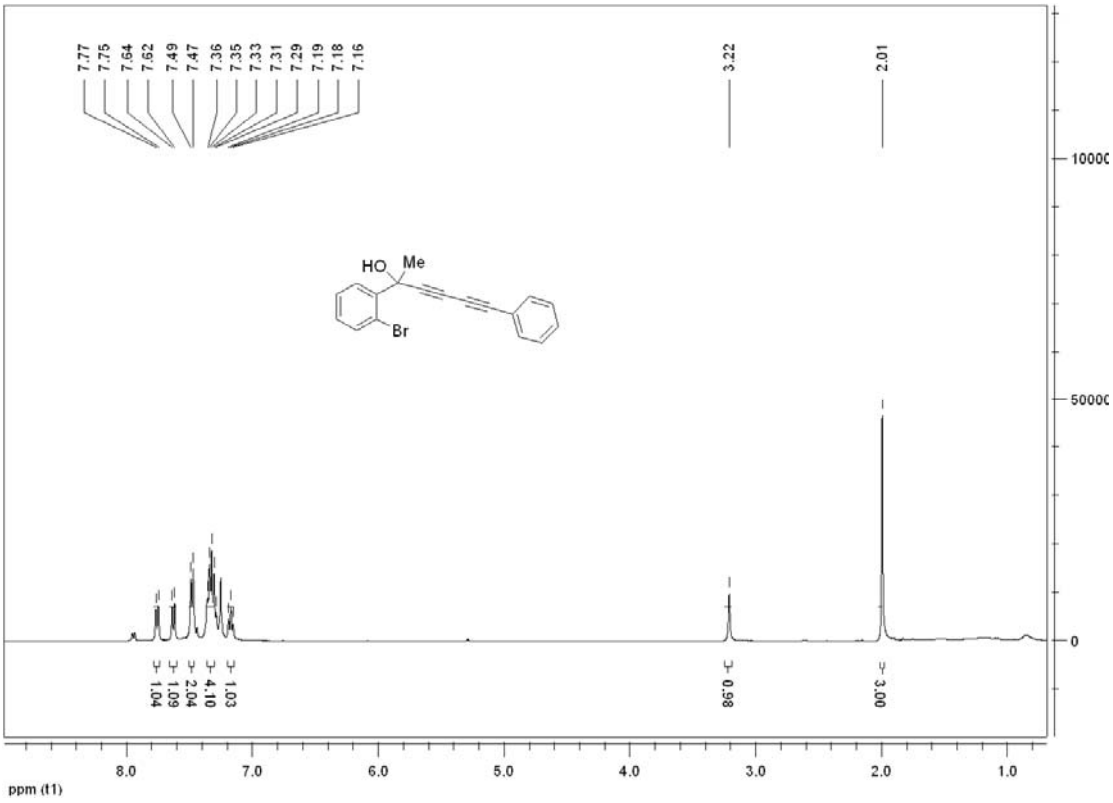
50
ppm (t1)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7.16
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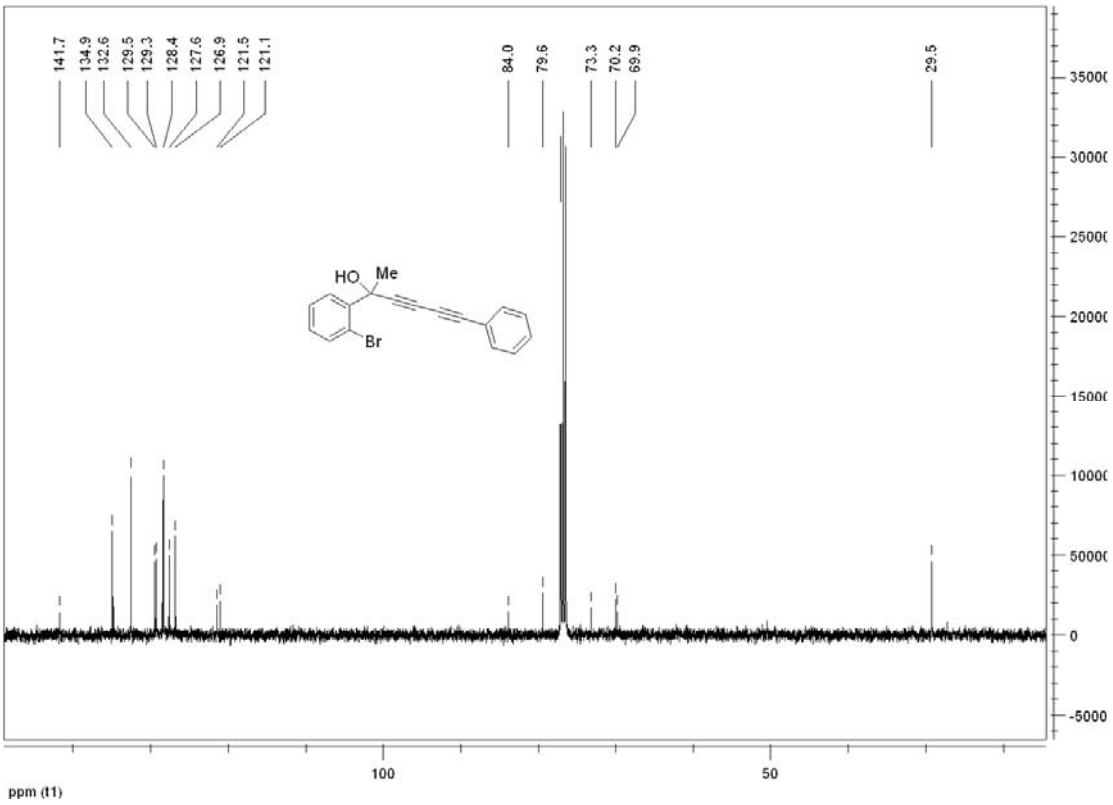
3.00
ppm (t1)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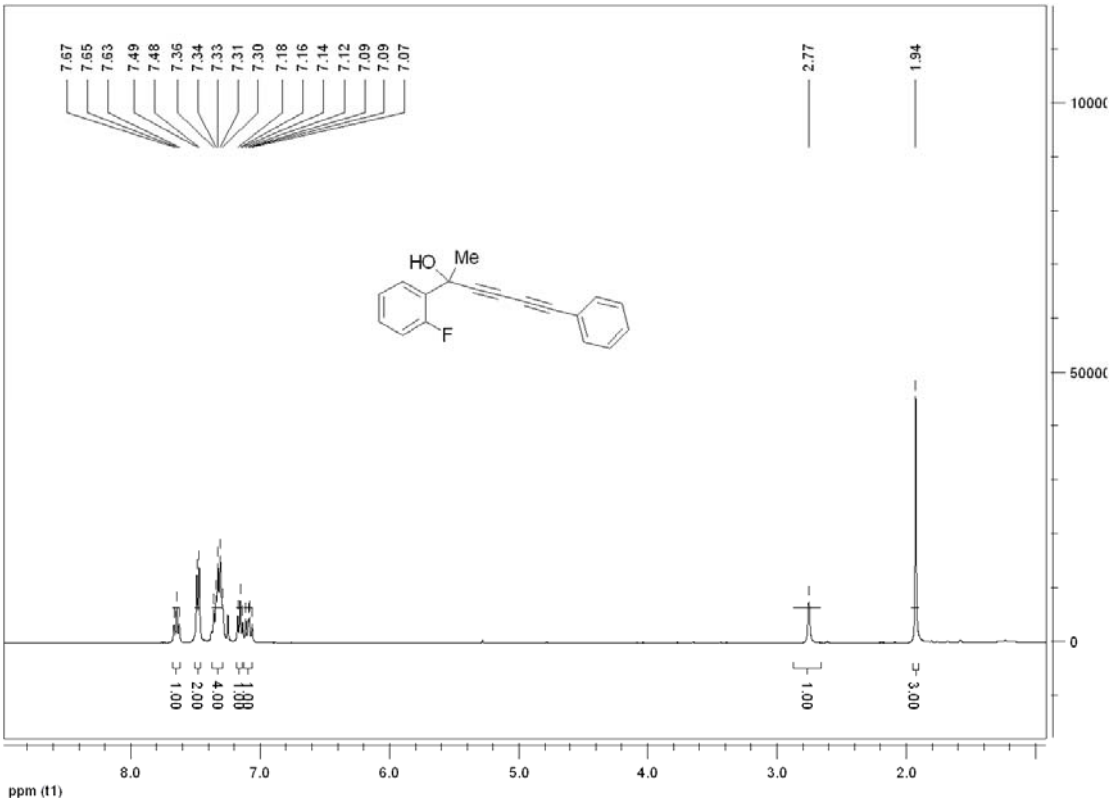
Me
Br
ppm (t1)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7.12
7.09
7.09
7.07
2.77
1.94
HO
Me
F
1.00
2.00
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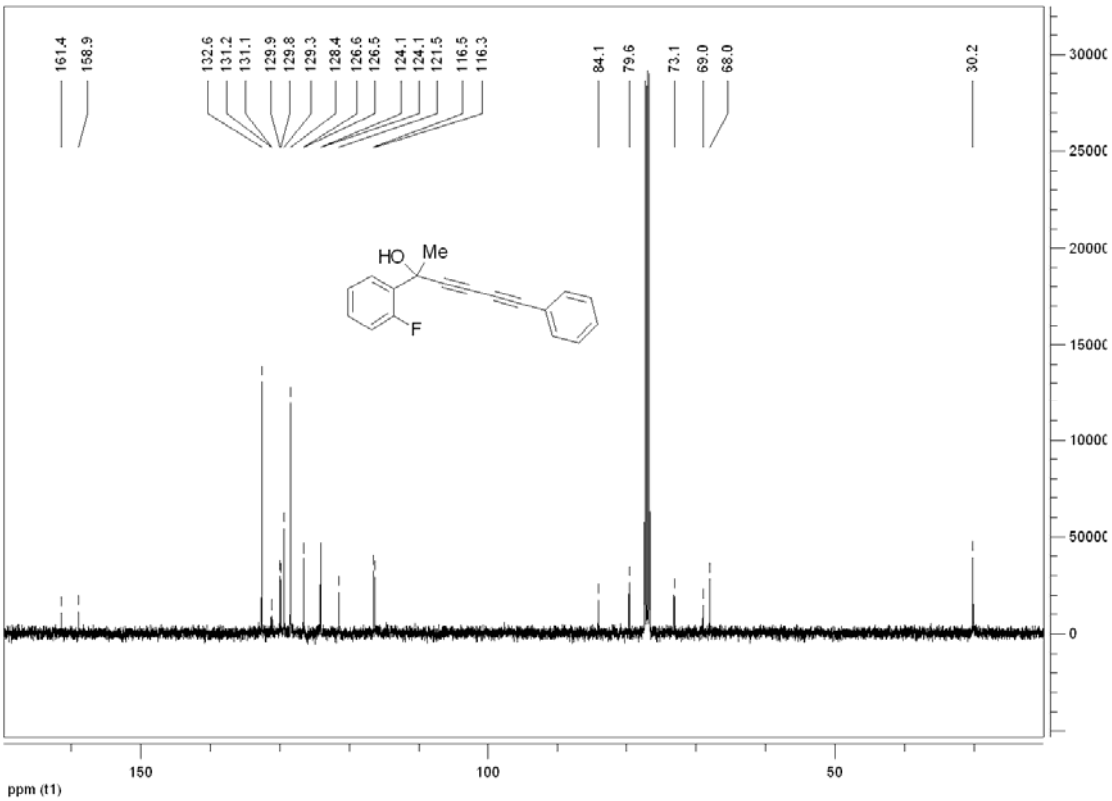
4.0
3.0
2.0
ppm (t1)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126.6
126.5
124.1
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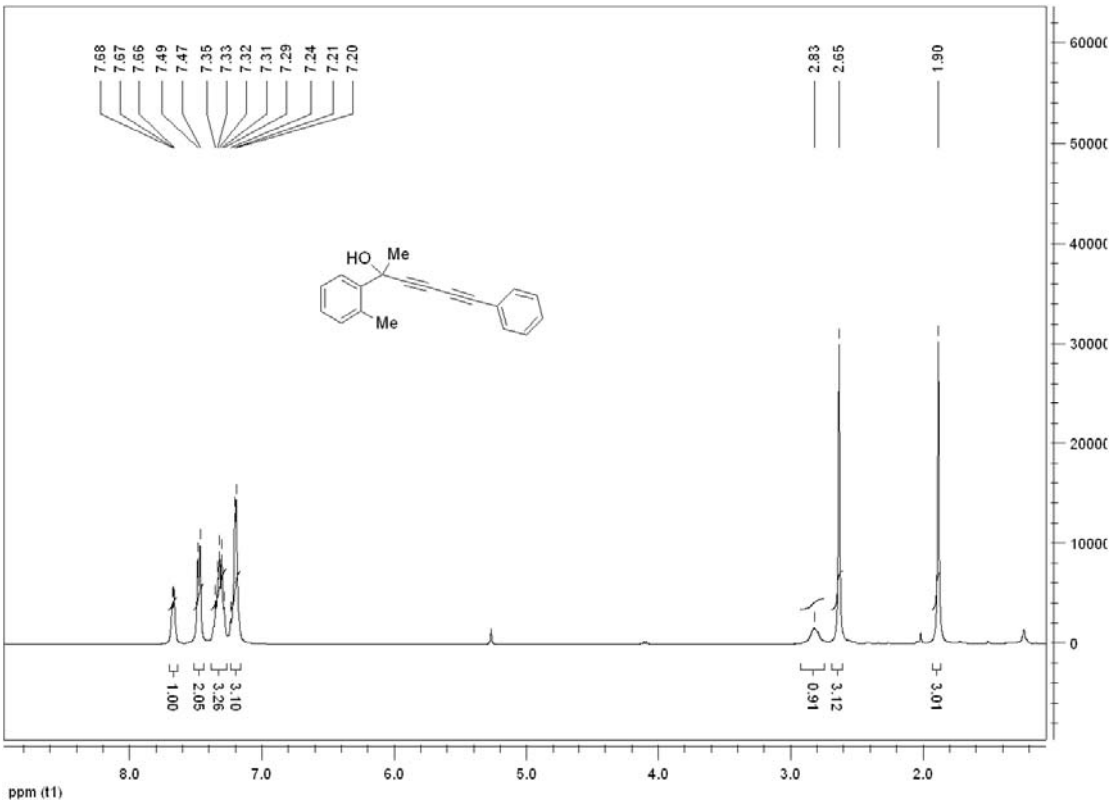
121.5
116.5
116.3
84.1
79.6
73.1
69.0
68.0
30.2
HO
Me
F
150
100
50
ppm (t1)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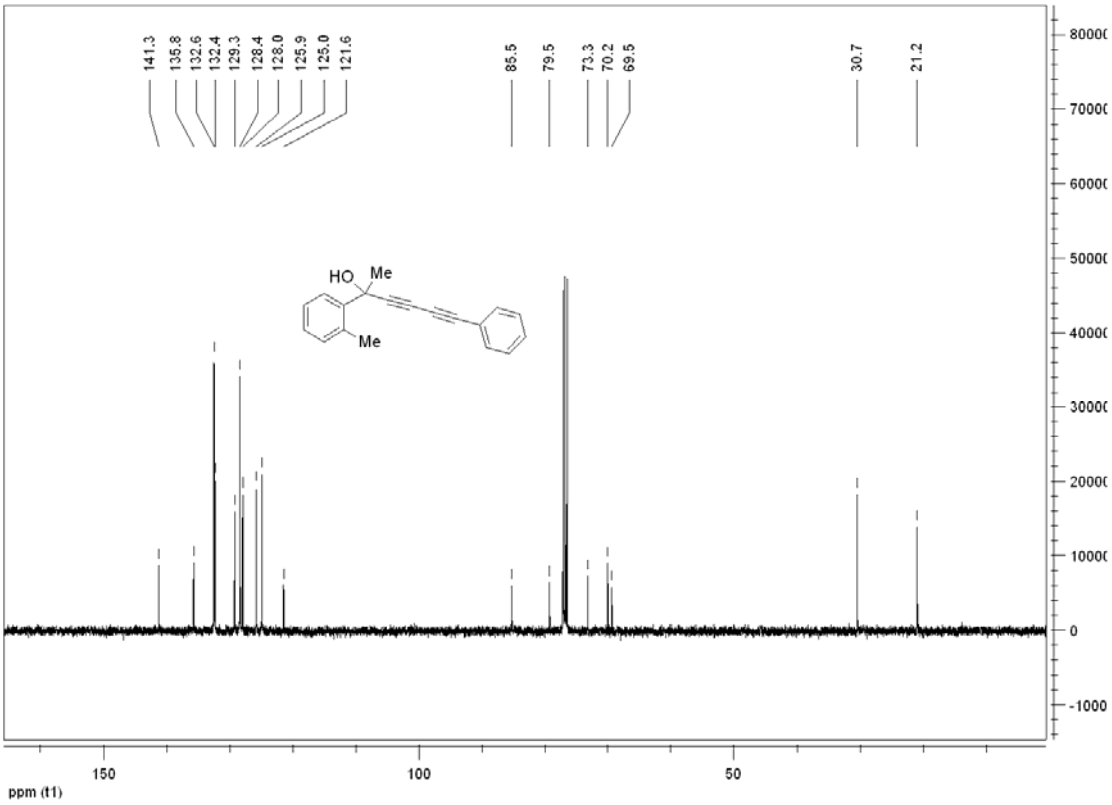
7.67
7.66
7.49
7.47
7.35
7.33
7.32
7.31
7.29
7.24
7.21
7.20
2.83
2.65
1.90
HO
Me
Me
1.00
2.05
3.26
3.10
0.91
3.12
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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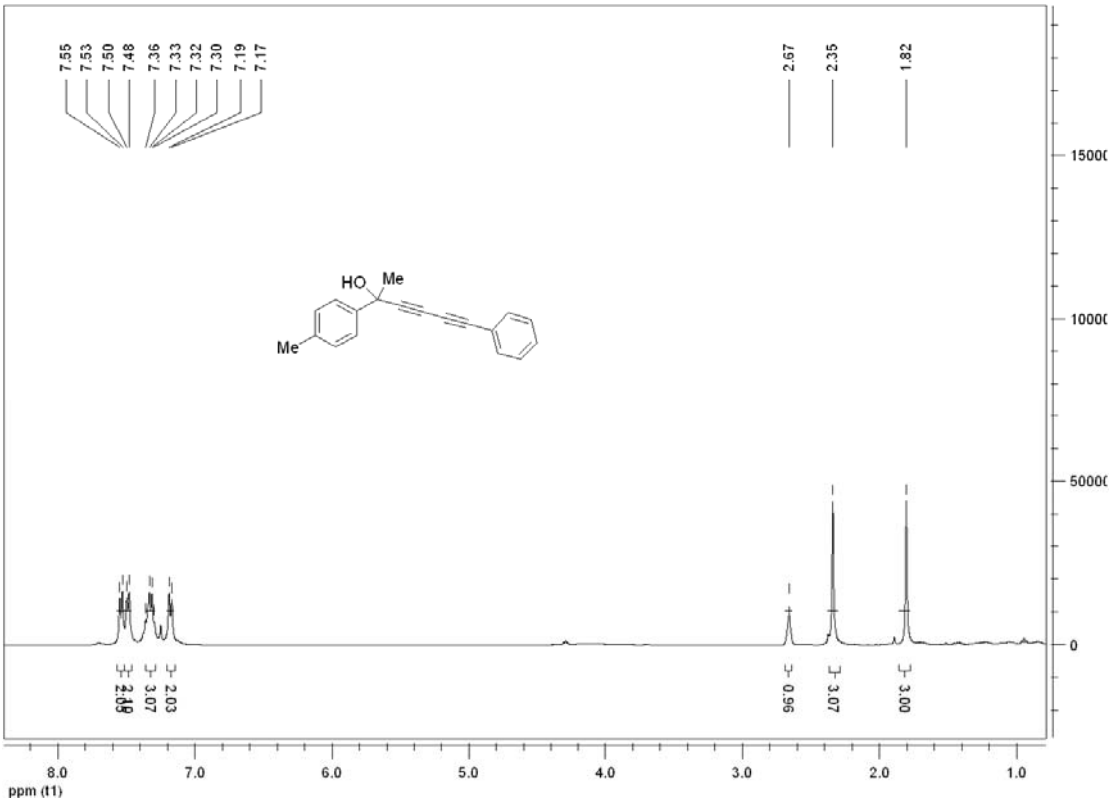
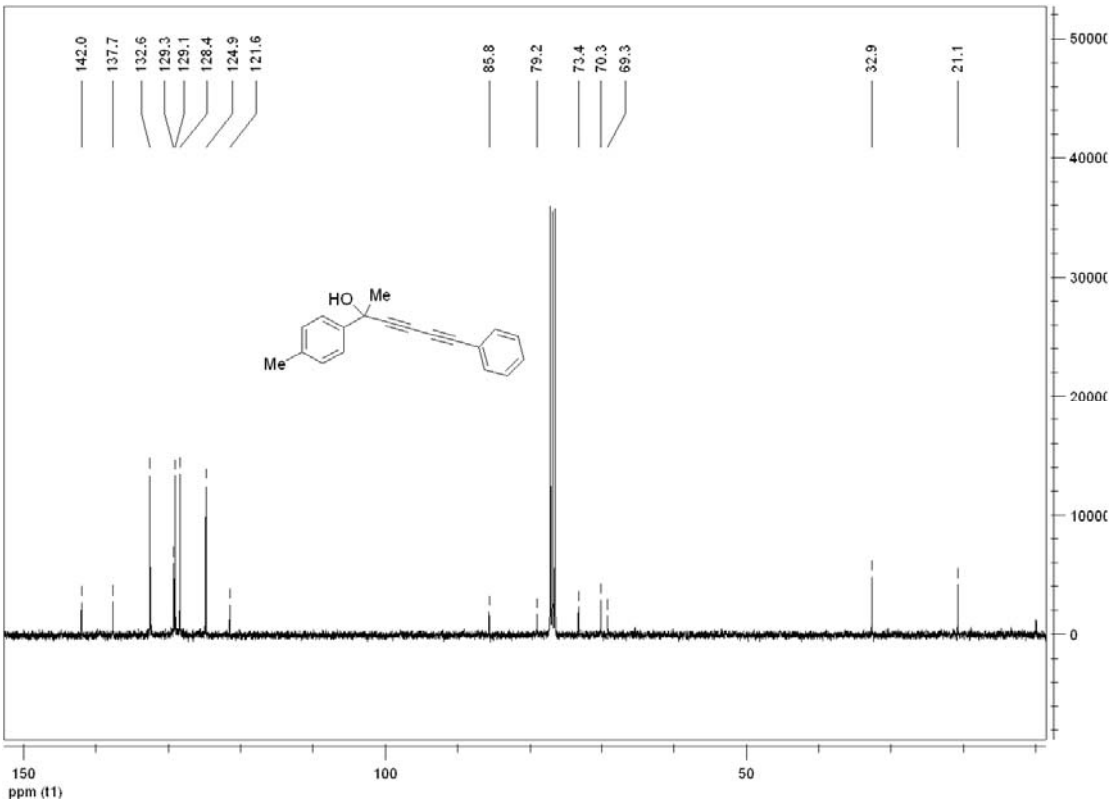
135.8
132.6
132.4
129.3
128.4
128.0
125.9
125.0
121.6
85.5
79.5
73.3
70.2
69.5
30.7
21.2
HO
Me
Me
150
100
50
ppm (t1)


7.55
7.53
7.50
7.48
7.36
7.33
7.32
7.30
7.19
7.17
2.67
2.35
1.82
HO
Me
Me
15000
10000
5000
0
2.48
3.07
2.03
0.96
3.07
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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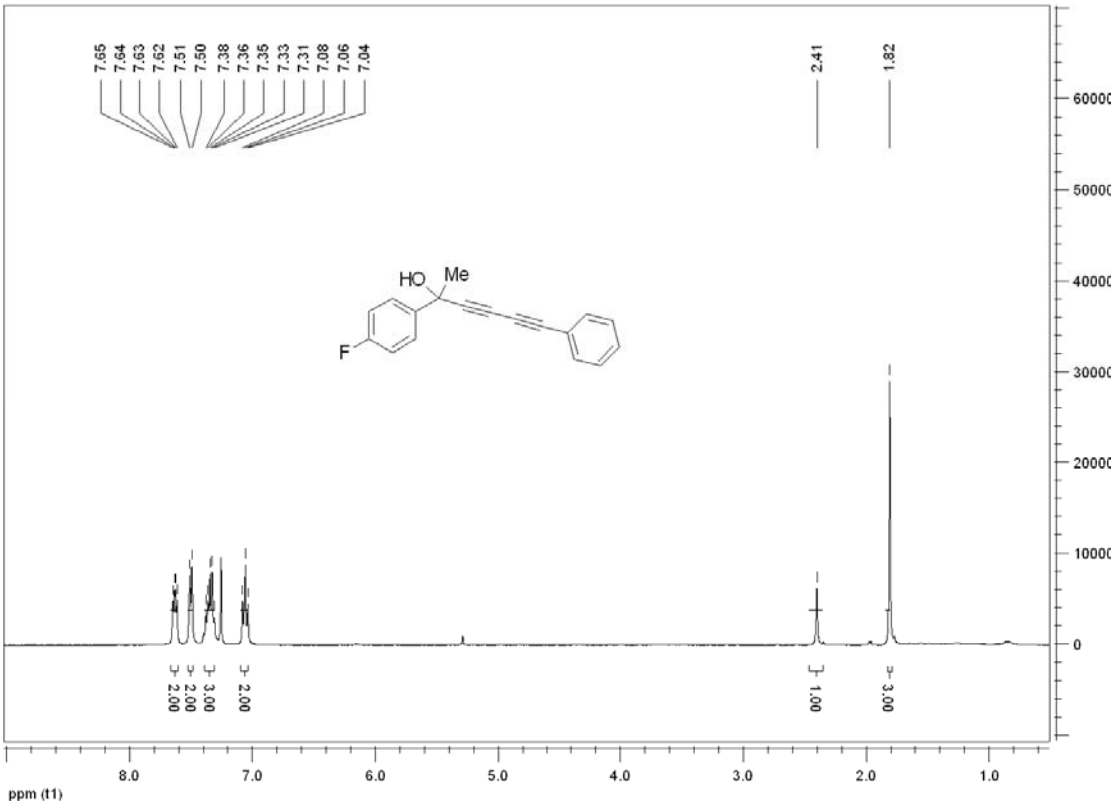
132.6
129.3
129.1
128.4
124.9
121.6
85.8
79.2
73.4
70.3
69.3
32.9
21.1
HO
Me
Me
50000
40000
30000
20000
10000
0
150
100
50
ppm (t1)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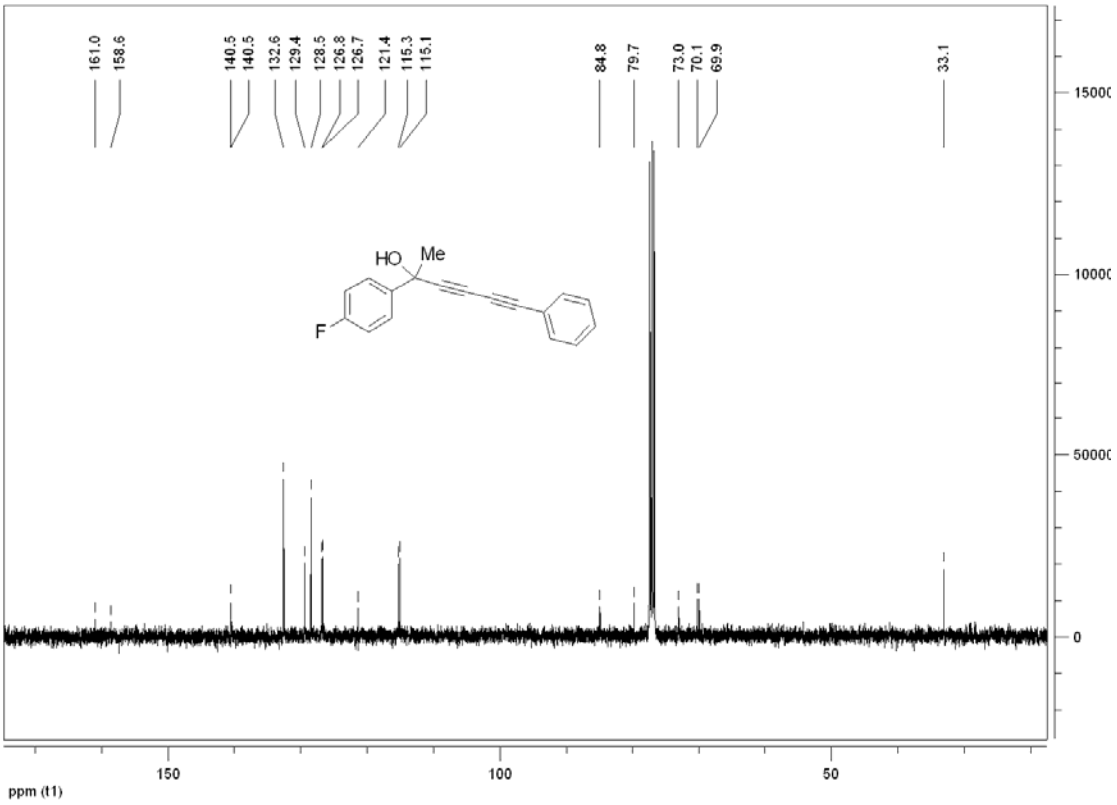
7.50
7.38
7.36
7.35
7.33
7.31
7.08
7.06
7.04
2.41
1.82
HO
Me
F
2.00
2.00
3.00
2.00
1.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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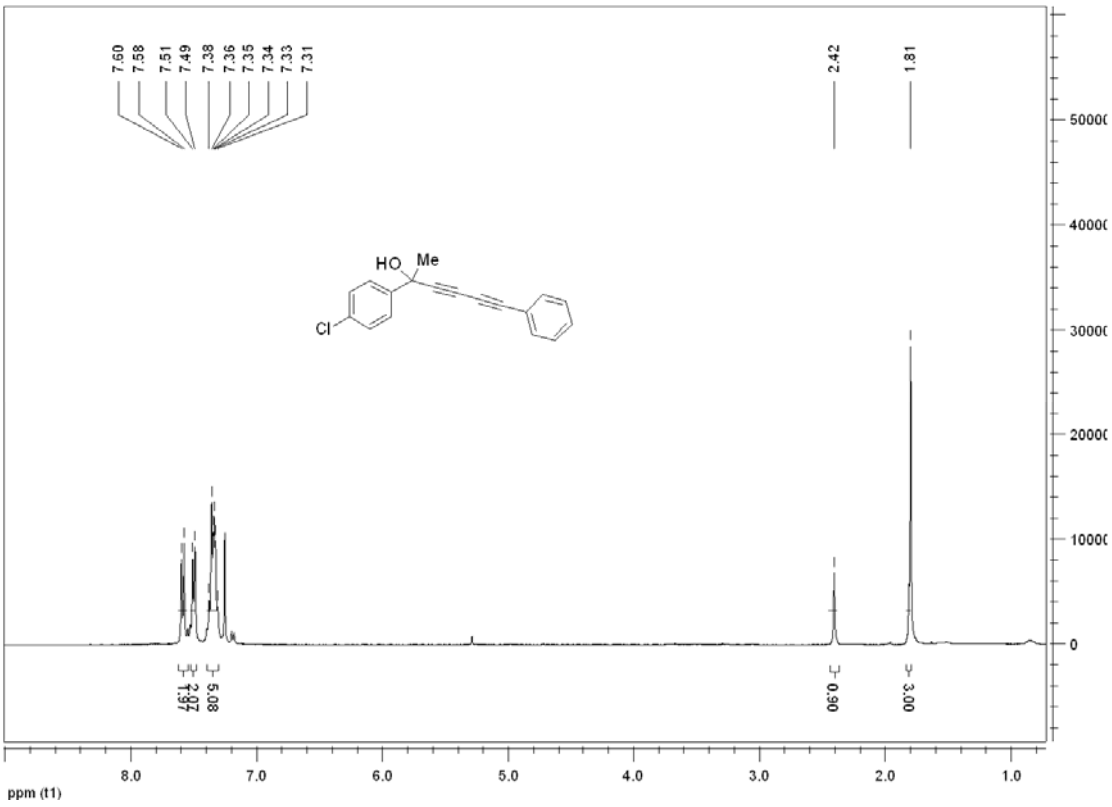
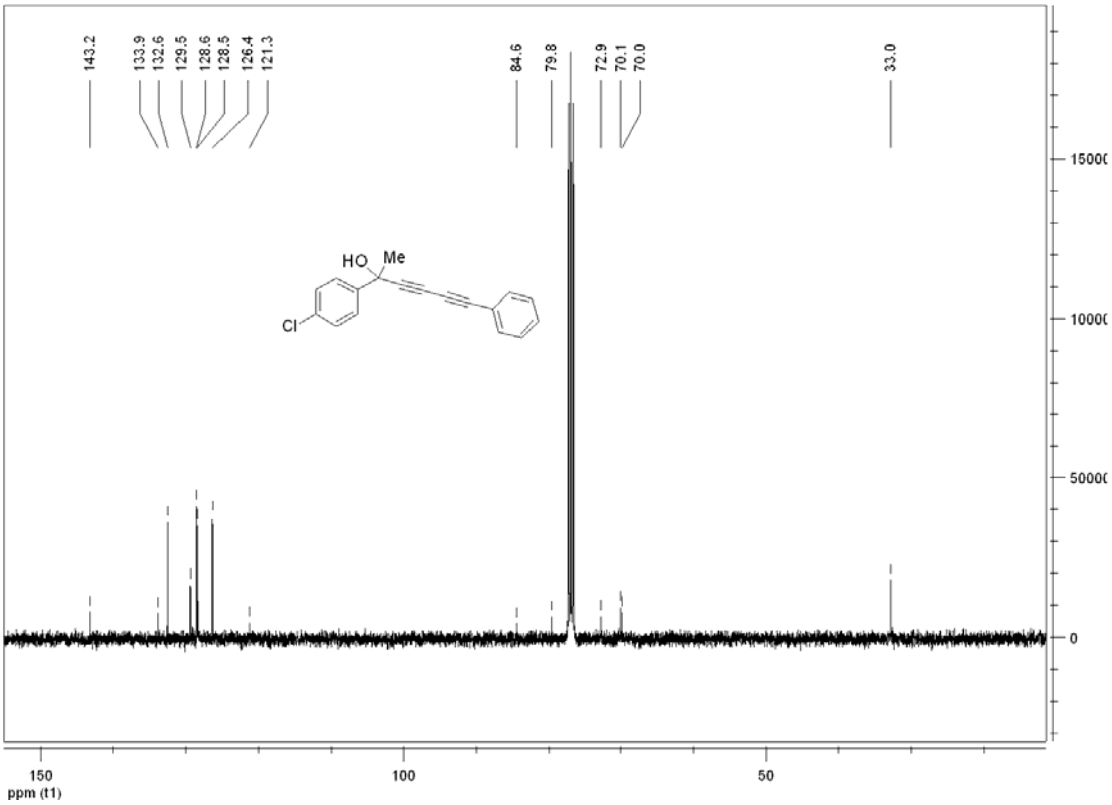
158.6
140.5
140.5
132.6
129.4
128.5
126.8
126.7
121.4
115.3
115.1
84.8
79.7
73.0
70.1
69.9
33.1
HO
Me
F
150
100
50
ppm (t1)


7.60
7.58
7.51
7.49
7.38
7.36
7.35
7.34
7.33
7.31
2.42
1.81
HO
Me
Cl
7.97
5.08
0.90
3.00
ppm (t1)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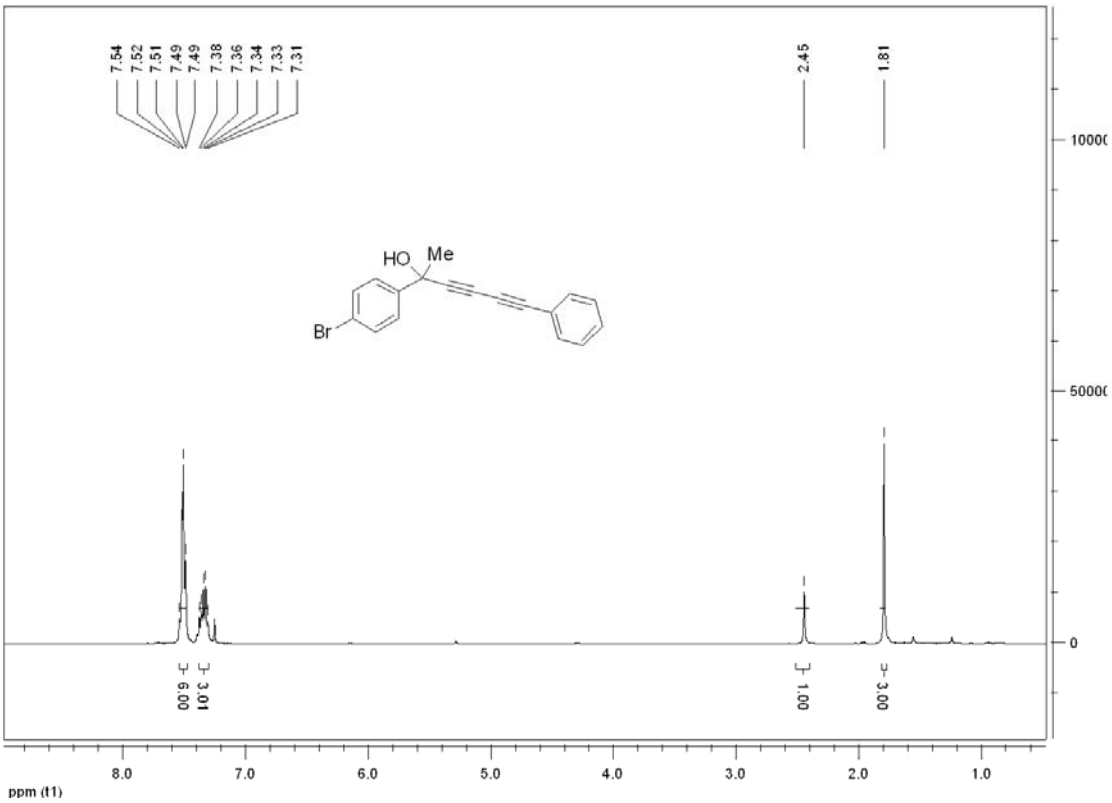
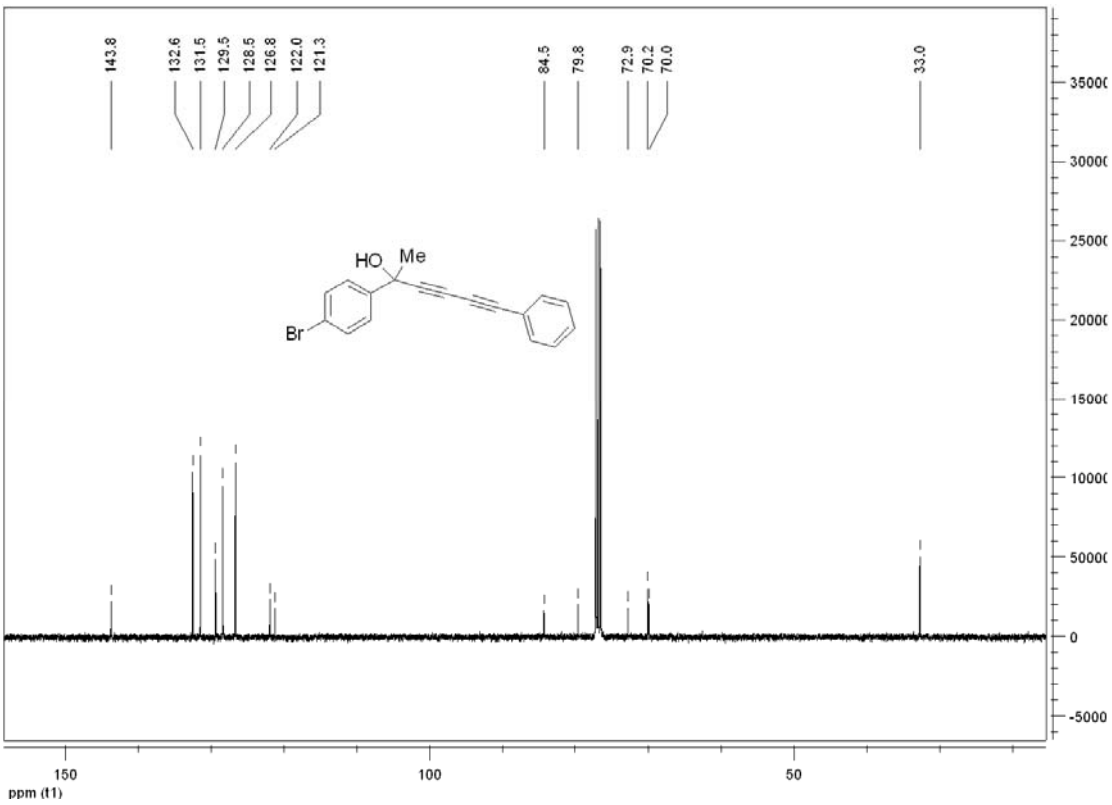
133.9
132.6
129.5
128.6
128.5
126.4
121.3
84.6
79.8
72.9
70.1
70.0
33.0
HO
Me
Cl
ppm (t1)


7.54
7.52
7.51
7.49
7.49
7.38
7.36
7.34
7.33
7.31
2.45
1.81
HO
Me
Br
6.00
3.01
1.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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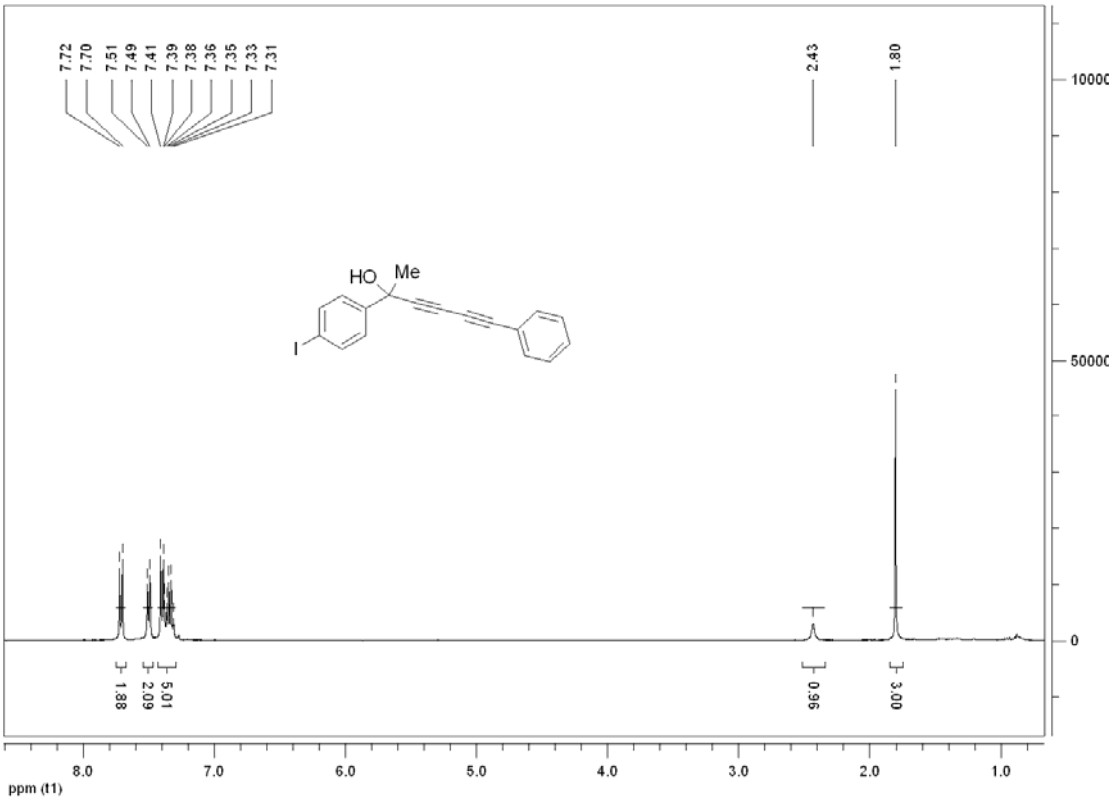
131.5
129.5
128.5
126.8
122.0
121.3
84.5
79.8
72.9
70.2
70.0
33.0
HO
Me
Br
150
100
50
ppm (t1)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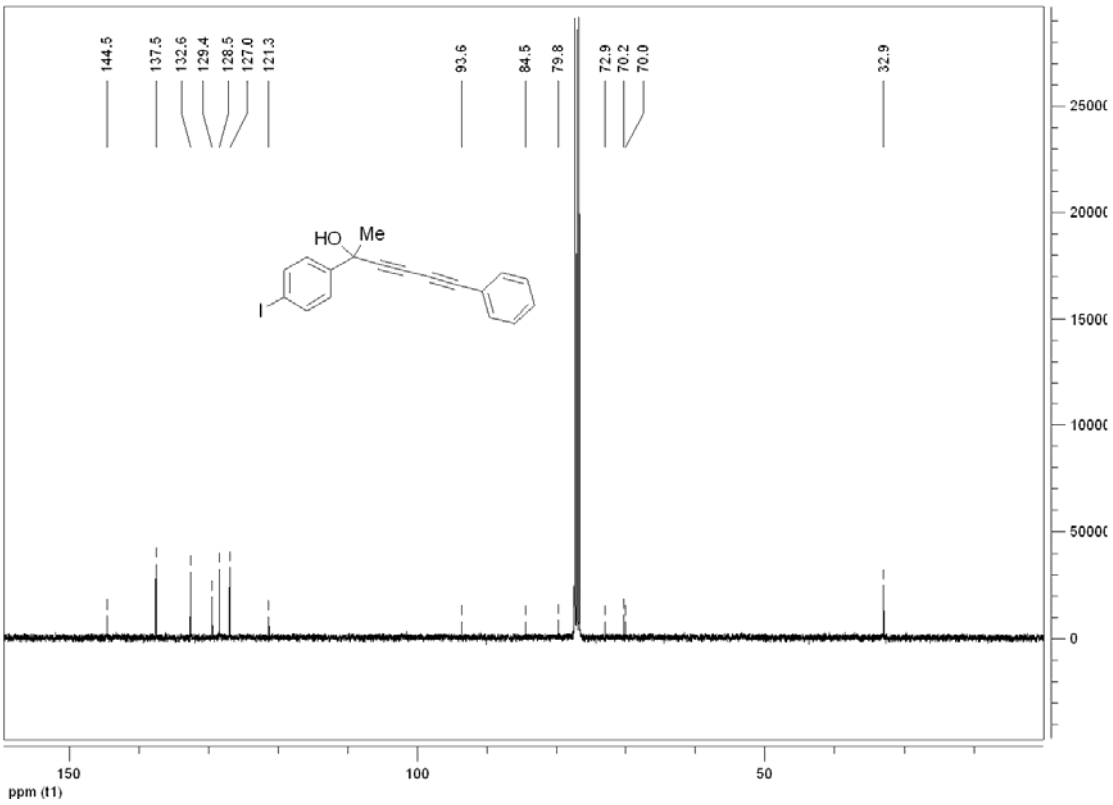
7.70
7.51
7.49
7.41
7.39
7.38
7.36
7.35
7.33
7.31
2.43
1.80
HO
Me
I
1.88
2.09
5.01
0.96
3.00
ppm (t1)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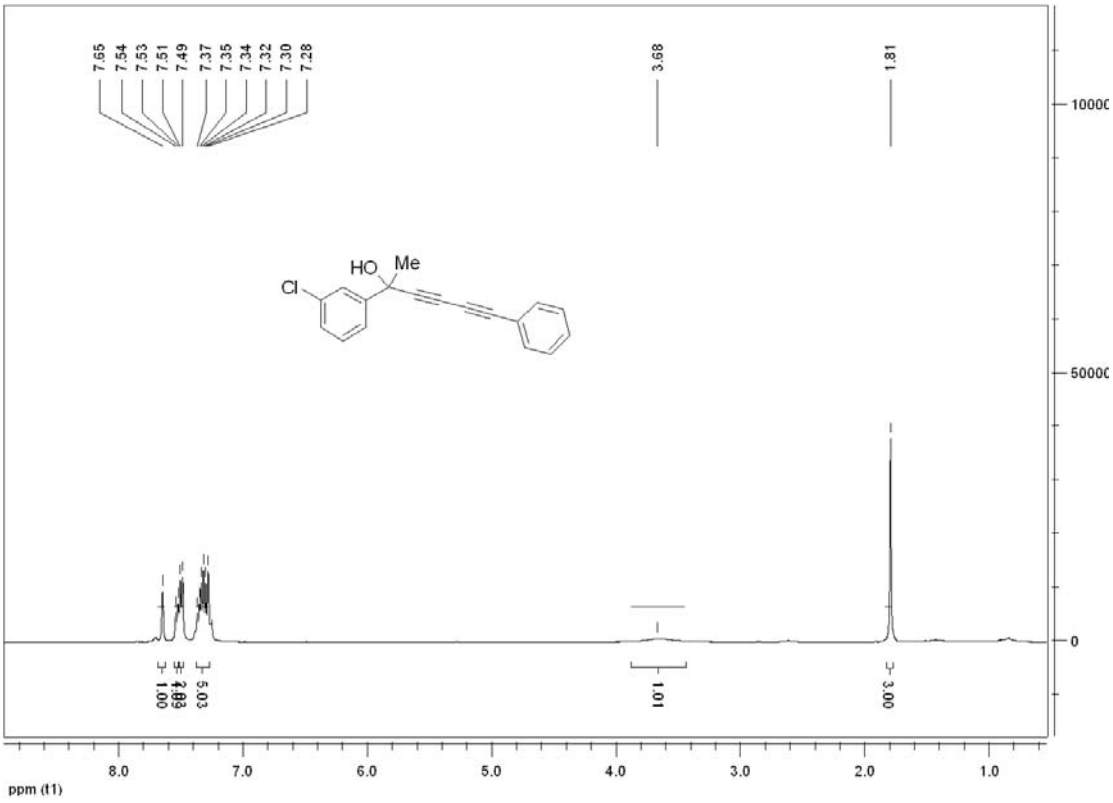
137.5
132.6
129.4
128.5
127.0
121.3
93.6
84.5
79.8
72.9
70.2
70.0
32.9
HO
Me
I
ppm (t1)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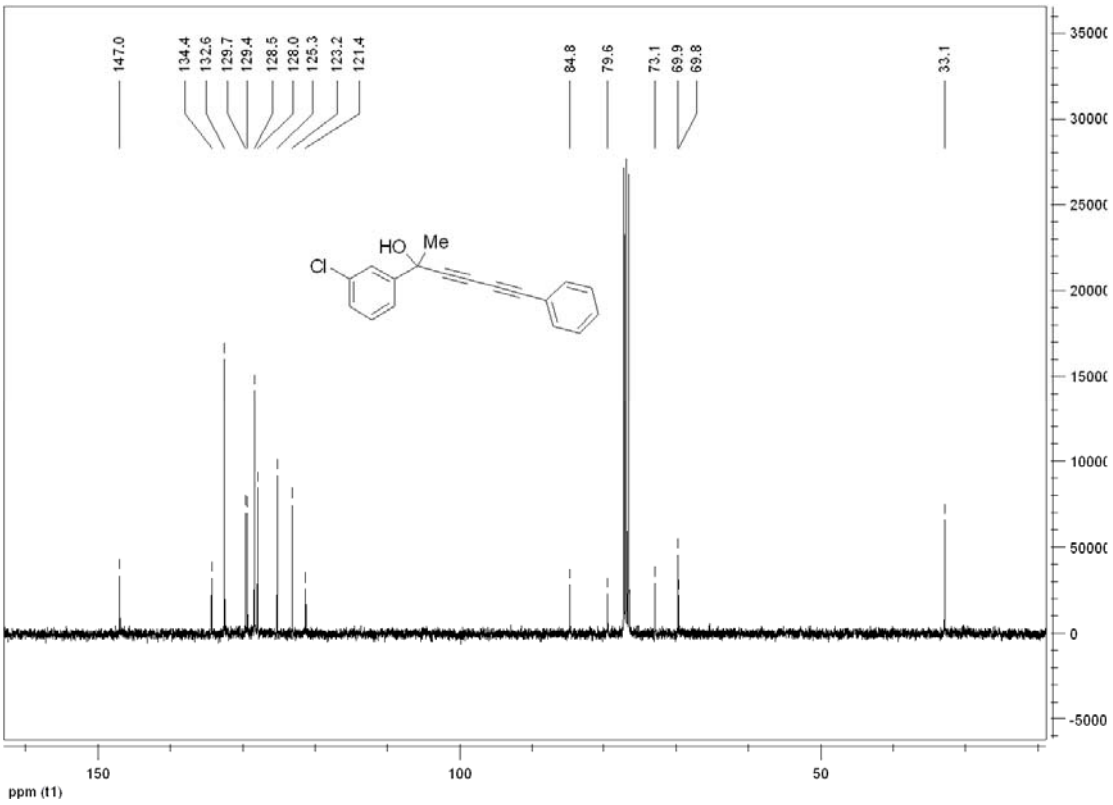
7.54
7.53
7.51
7.49
7.37
7.35
7.34
7.32
7.30
7.28
3.68
1.81
HO
Me
Cl
10000
50000
0
1.00
3.03
1.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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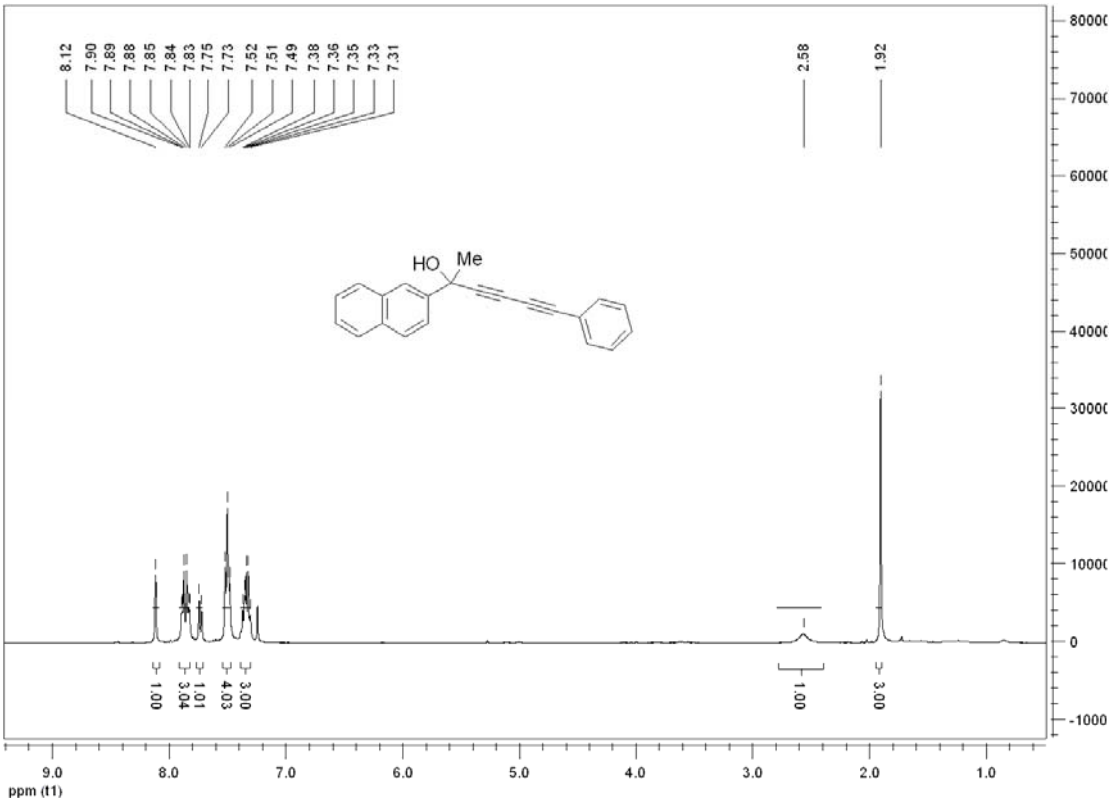
134.4
132.6
129.7
129.4
128.5
128.0
125.3
123.2
121.4
84.8
79.6
73.1
69.9
69.8
33.1
HO
Me
Cl
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
100
50
ppm (t1)


8.12
7.90
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7.88
7.85
7.84
7.83
7.75
7.73
7.52
7.51
7.49
7.38
7.36
7.35
7.33
7.31
2.58
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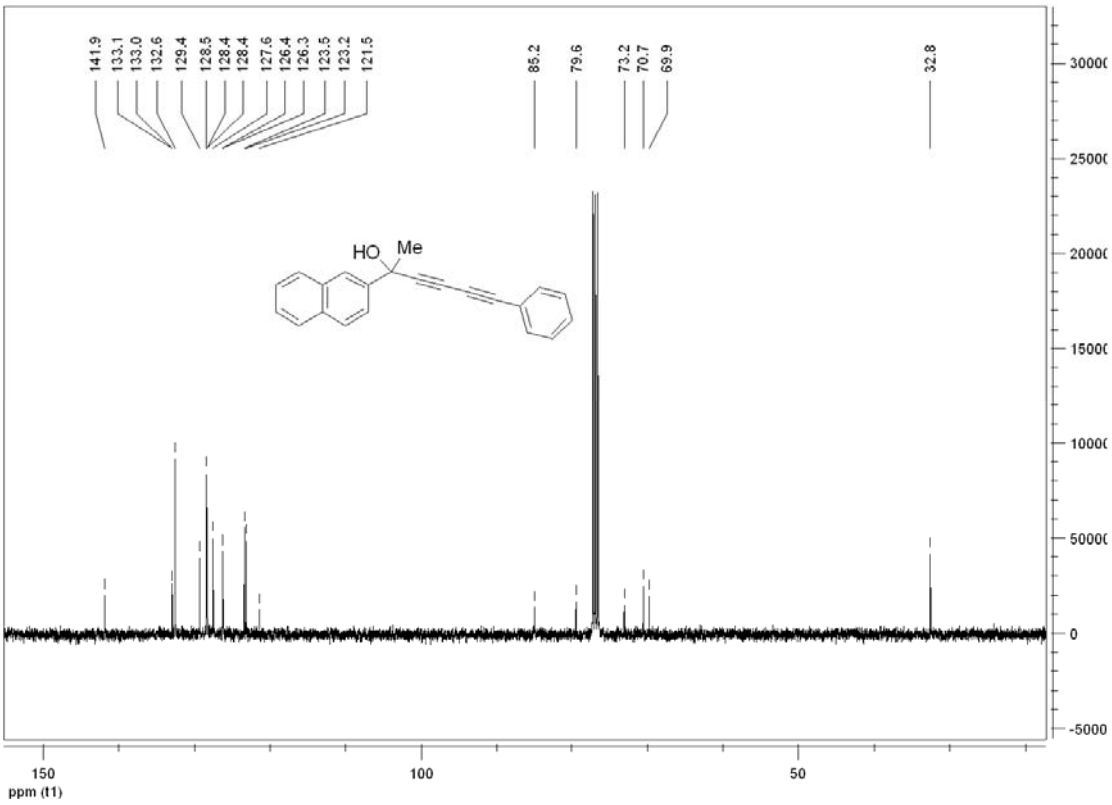
HO
Me
1.00
3.04
1.01
4.03
3.00
1.00
3.00
ppm (t1)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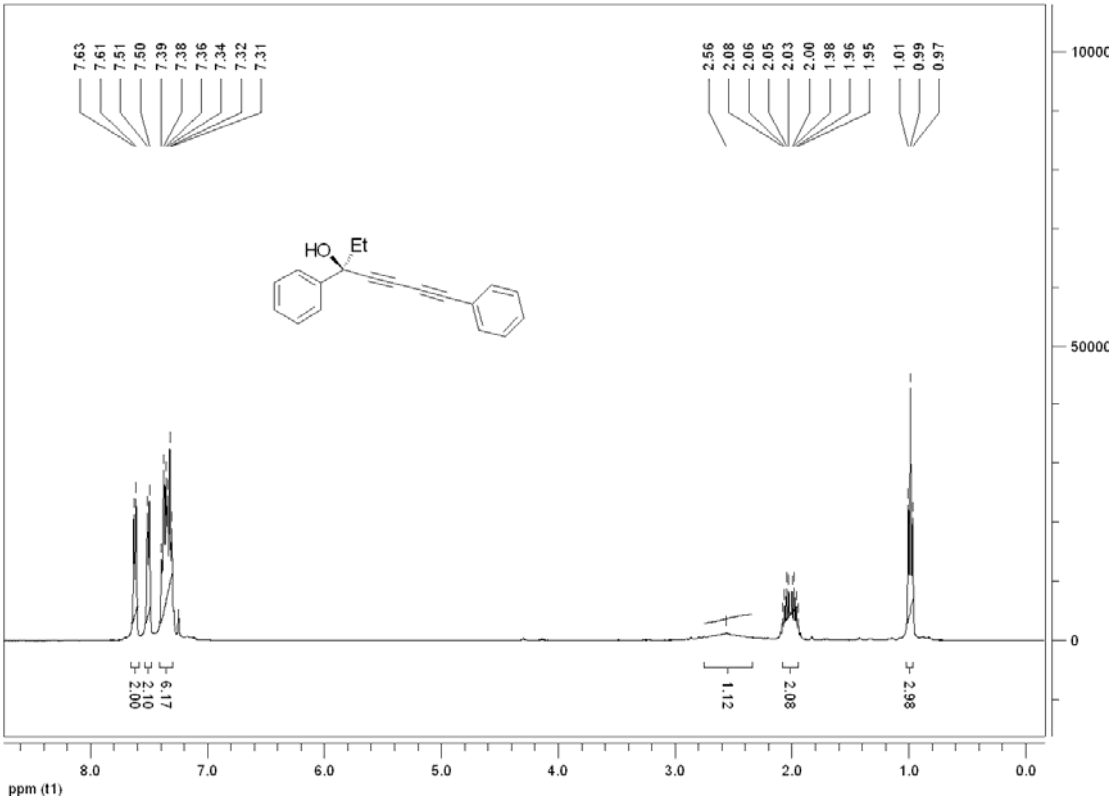
133.0
132.6
129.4
128.5
128.4
128.4
127.6
126.4
126.3
123.5
123.2
121.5
85.2
79.6
73.2
70.7
69.9
32.8
HO
Me
ppm (t1)


7.63
7.61
7.51
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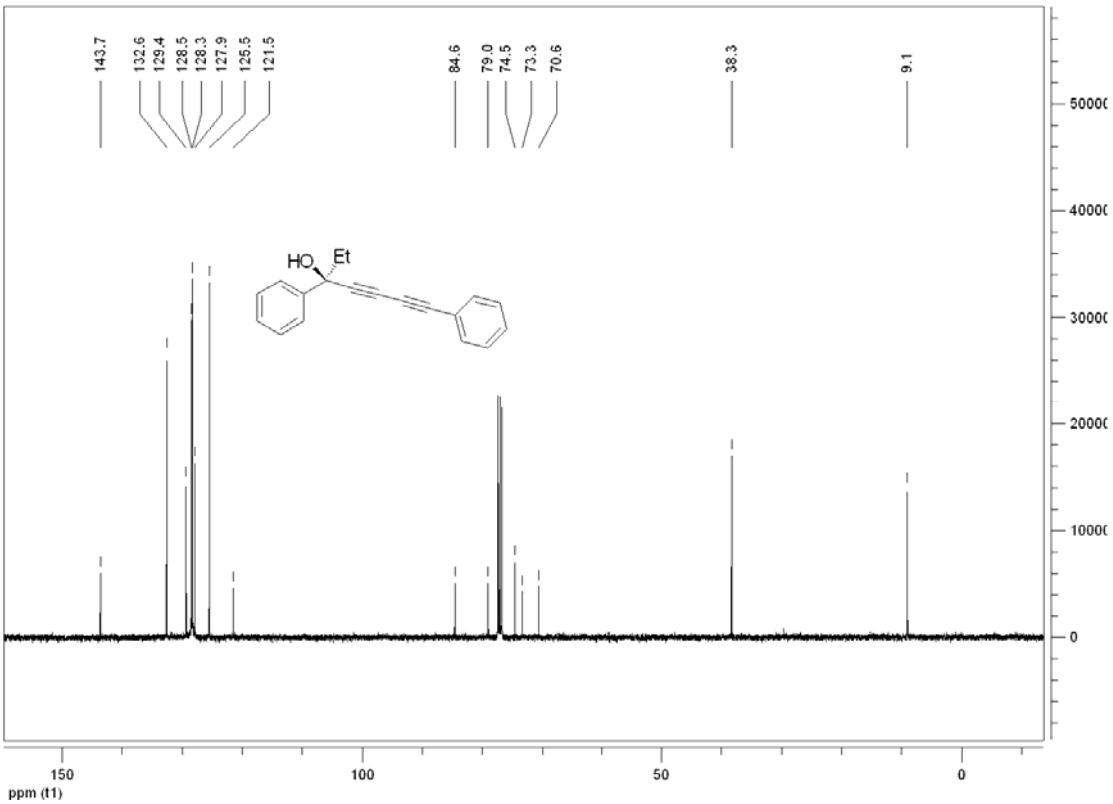
7.39
7.38
7.36
7.34
7.32
7.31
2.56
2.08
2.06
2.05
2.03
2.00
1.98
1.96
1.95
1.01
0.99
0.97
HO
Et
2.00
2.10
6.17
1.12
2.08
2.98
ppm (t1)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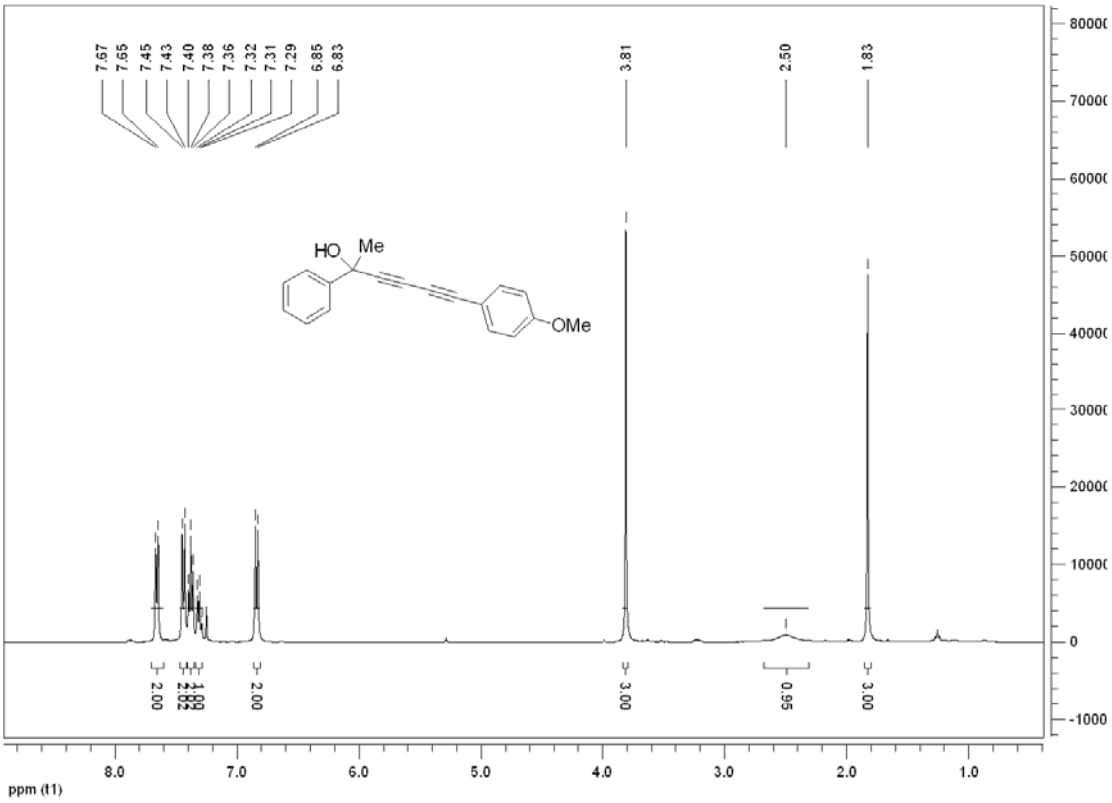
132.6
129.4
128.5
128.3
127.9
125.5
121.5
84.6
79.0
74.5
73.3
70.6
38.3
9.1
HO
Et
ppm (t1)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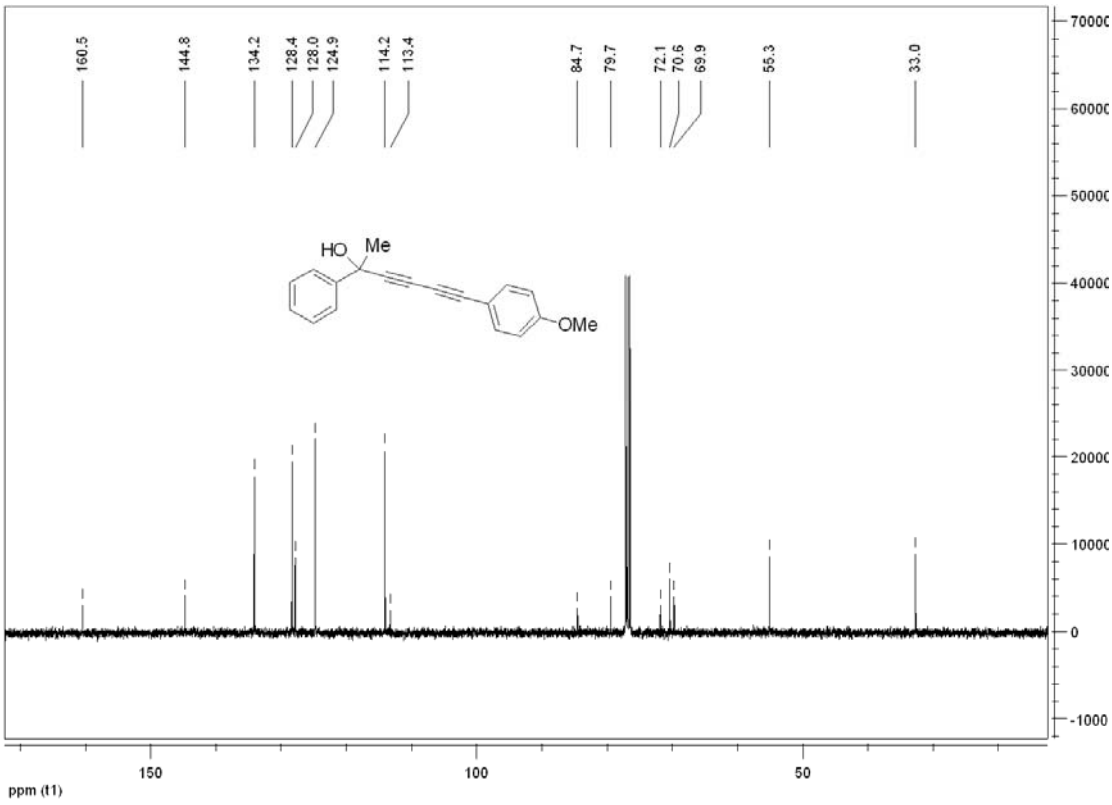
7.36
7.32
7.31
7.29
6.85
6.83
3.81
2.50
1.83
HO
Me
OMe
2.00
2.00
3.00
0.95
3.00
ppm (t1)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128.4
128.0
124.9
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113.4
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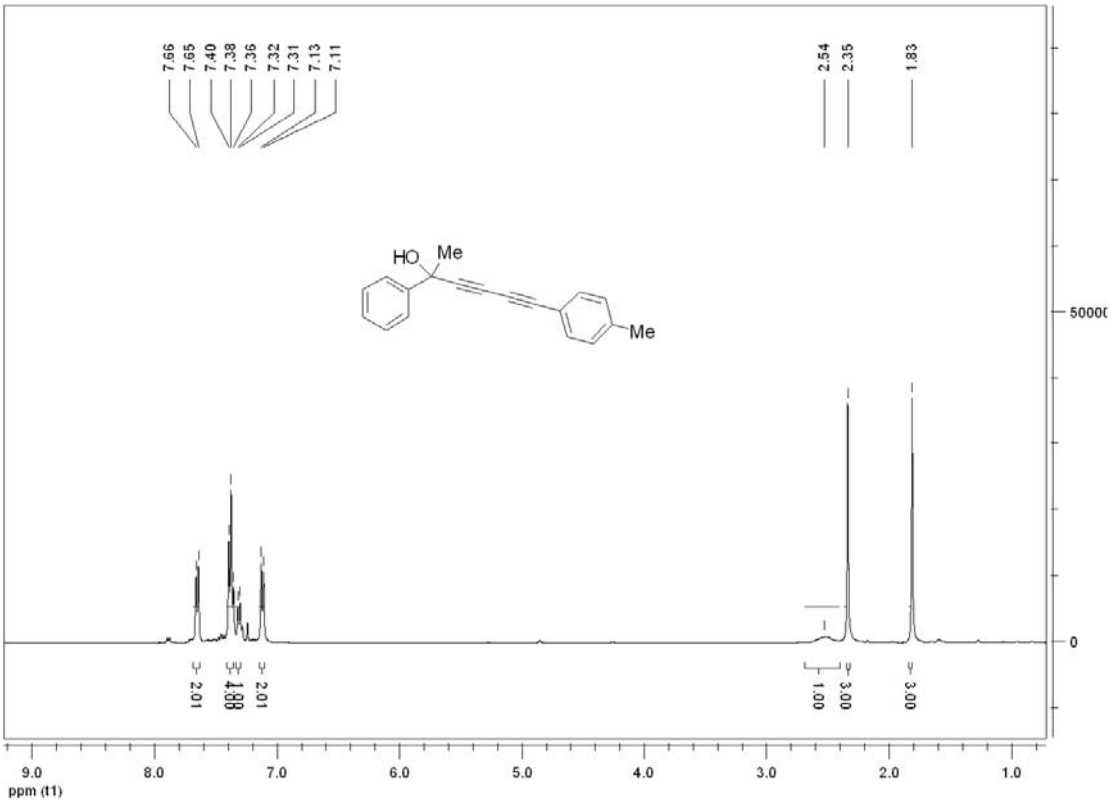
79.7
72.1
70.6
69.9
55.3
33.0
HO
Me
OMe
ppm (t1)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7.36
7.32
7.31
7.13
7.11
2.54
2.35
1.83
HO
Me
Me
5000
0
2.01
4.08
2.01
1.00
3.00
3.00
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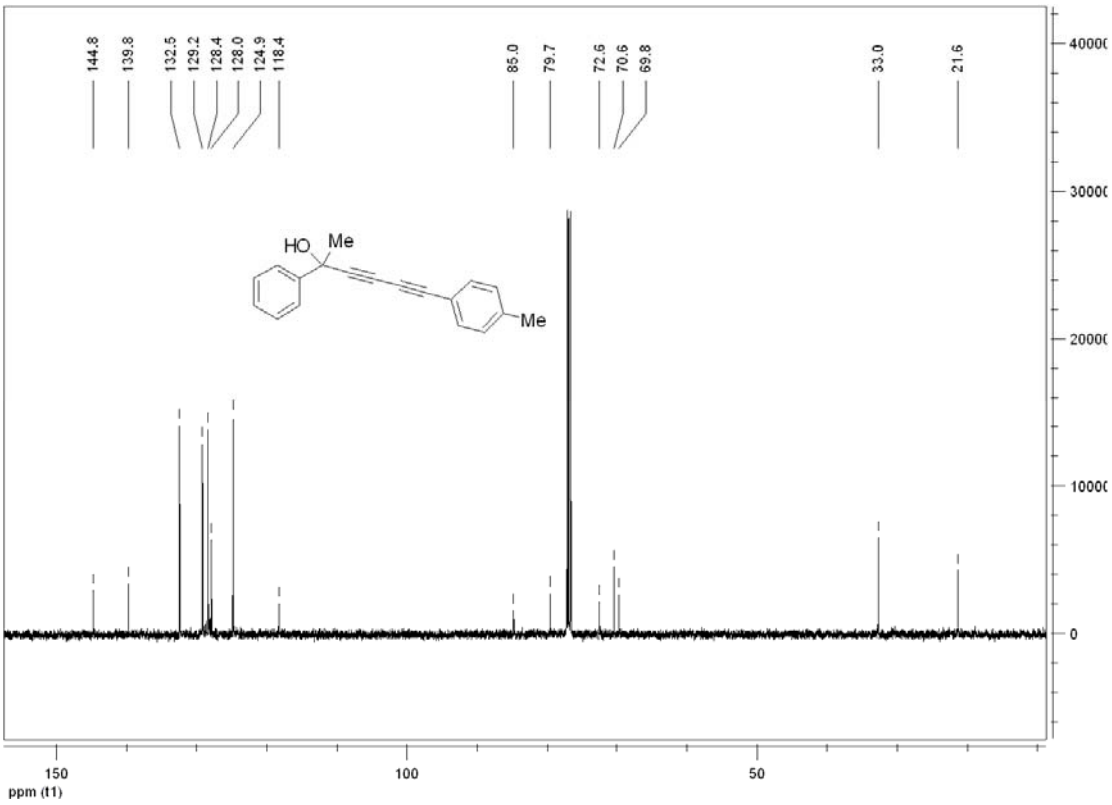
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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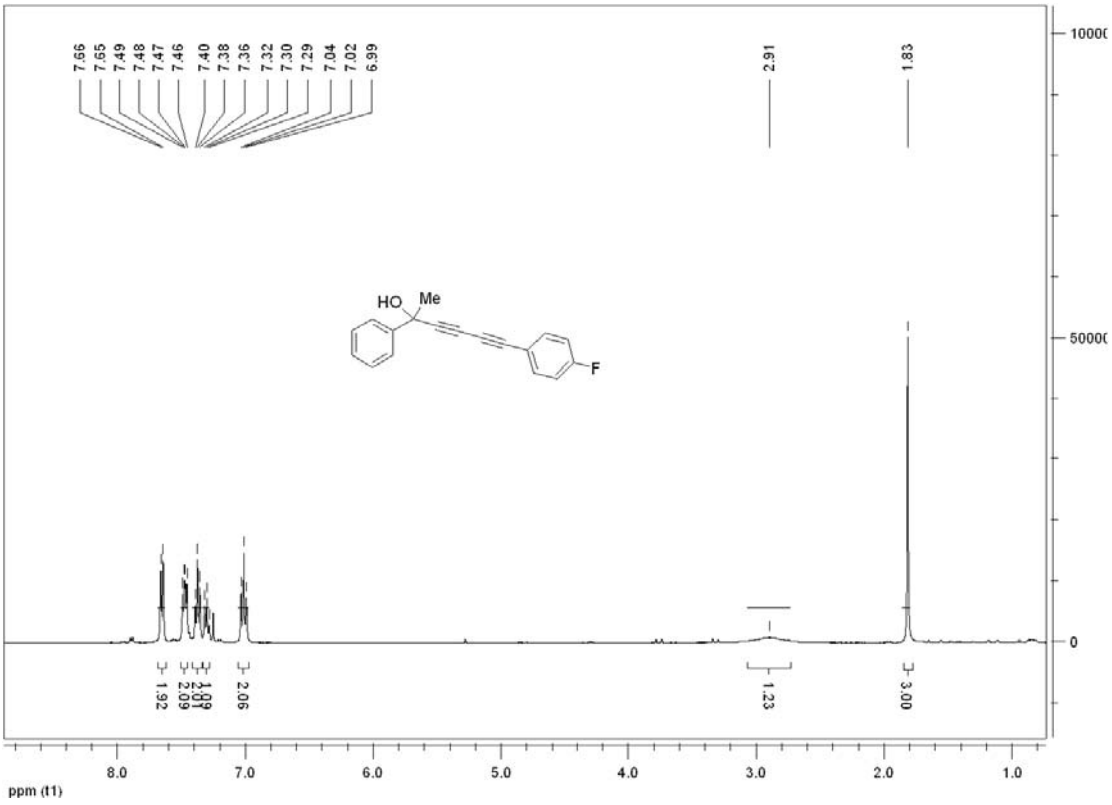
139.8
132.5
129.2
128.4
128.0
124.9
118.4
85.0
79.7
72.6
70.6
69.8
33.0
21.6
HO
Me
Me
40000
30000
20000
10000
0
150
100
50
ppm (t1)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7.48
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7.46
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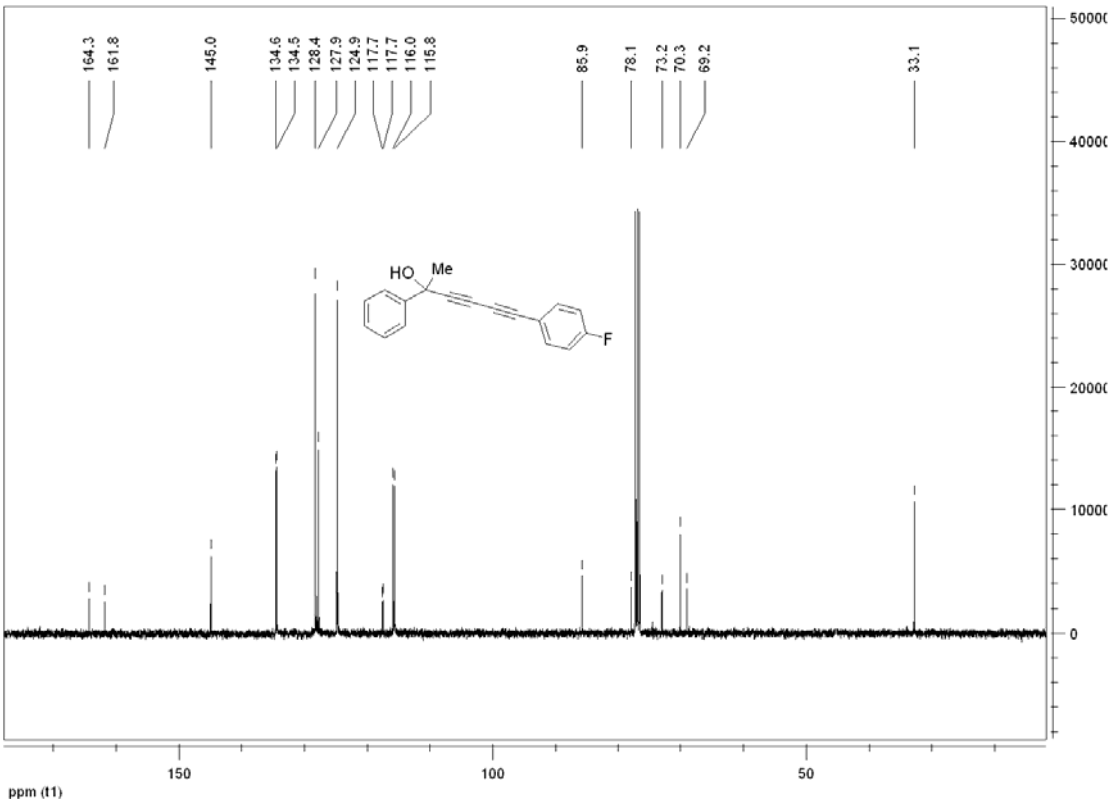
7.38
7.36
7.32
7.30
7.29
7.04
7.02
6.99
2.91
1.83
HO
Me
F
1.92
2.09
3.09
2.06
1.23
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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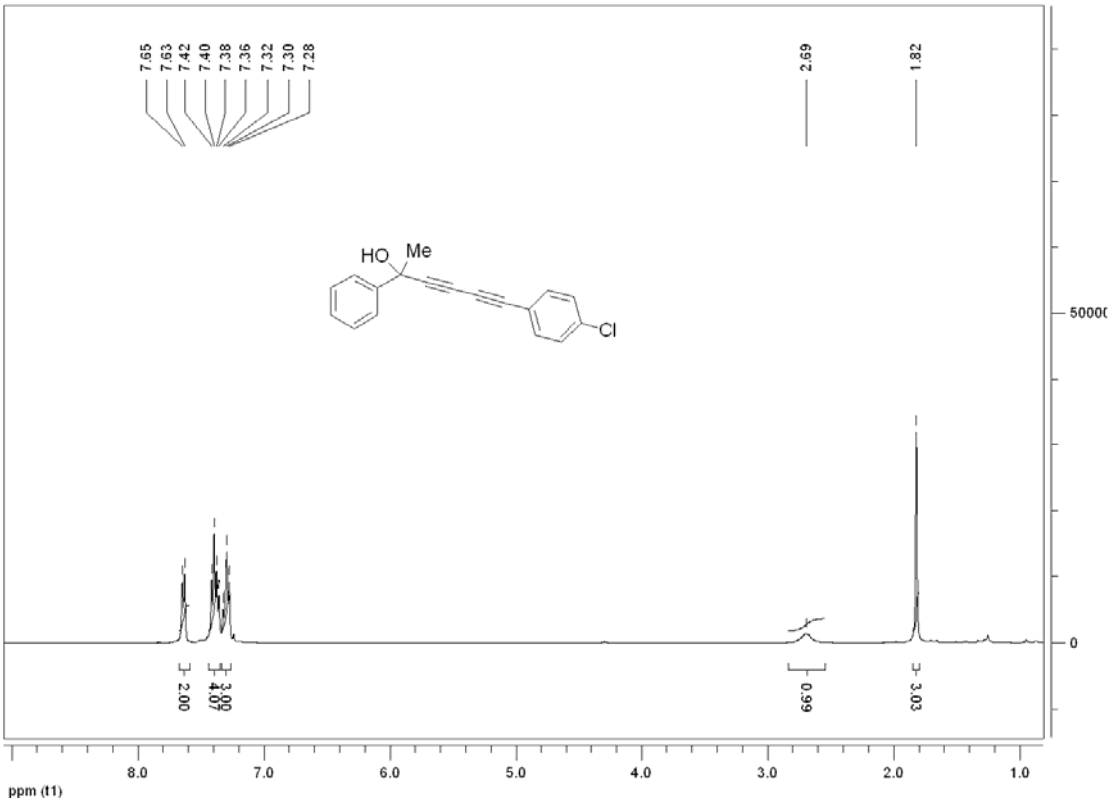
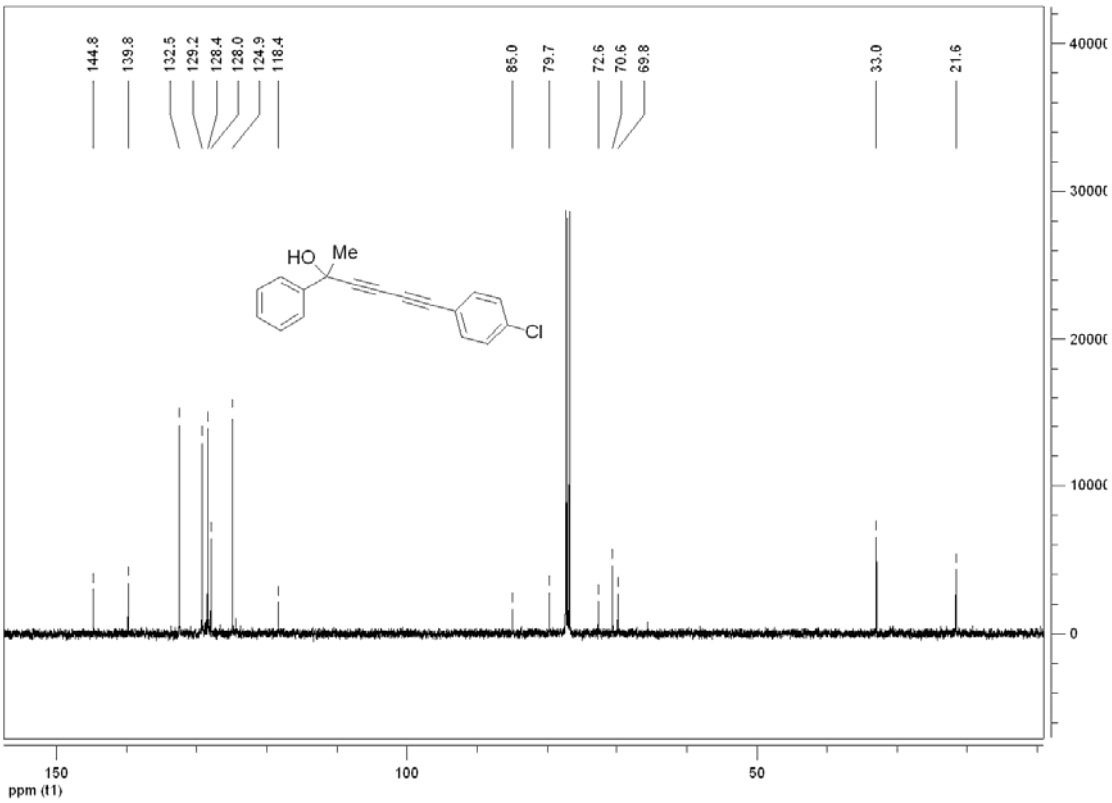
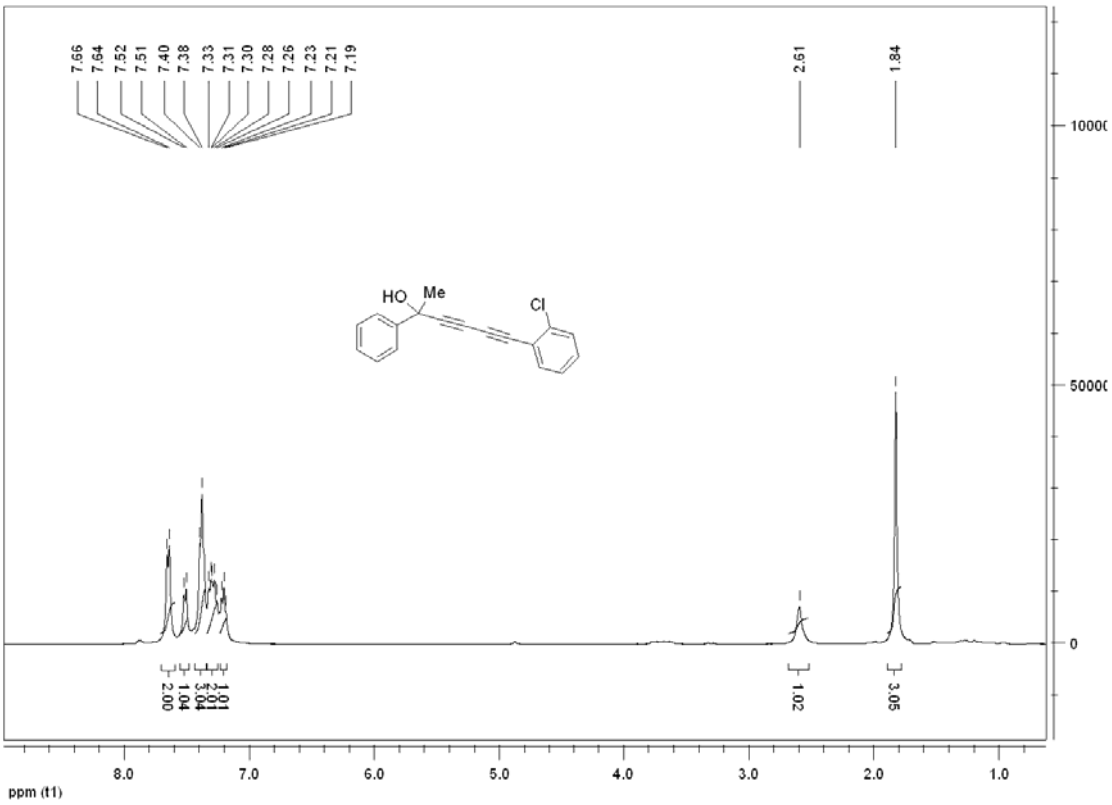
134.6
134.5
128.4
127.9
124.9
117.7
117.7
116.0
115.8
85.9
78.1
73.2
70.3
69.2
33.1
HO
Me
F
150
100
50
ppm (t1)



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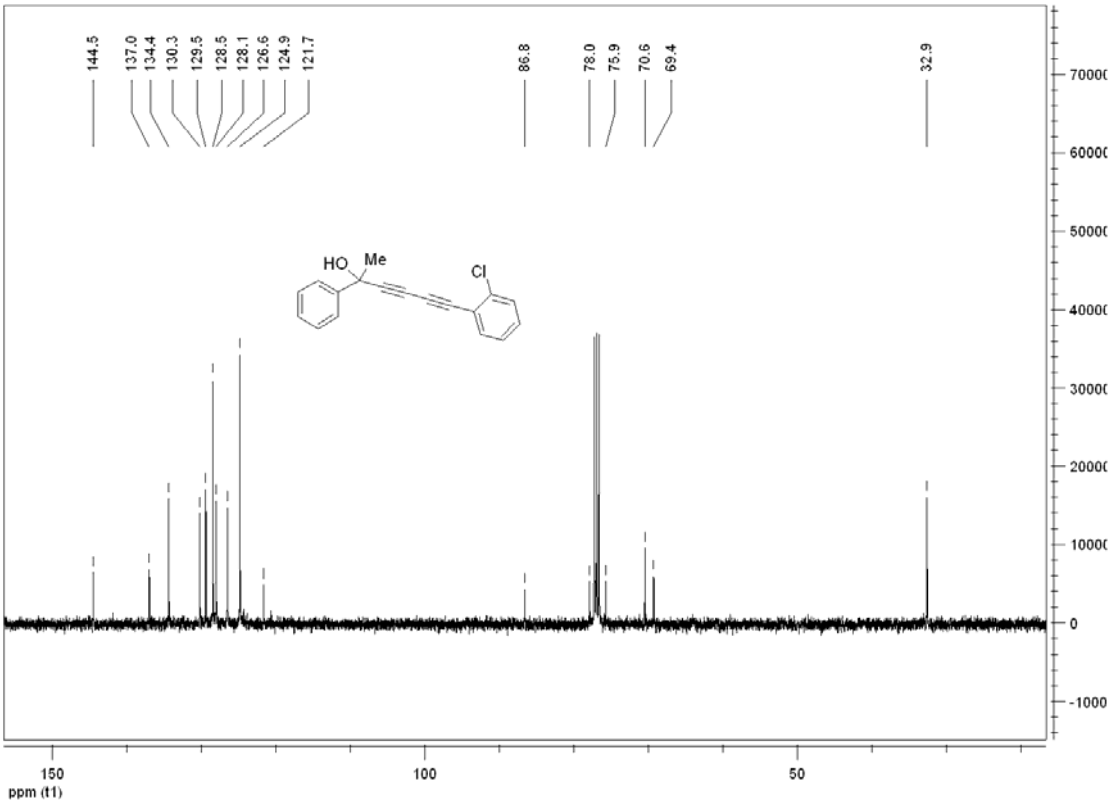
7.40
7.38
7.33
7.31
7.30
7.28
7.26
7.23
7.21
7.19
2.61
1.84
HO
Me
Cl
2.00
1.04
3.04
2.01
1.02
3.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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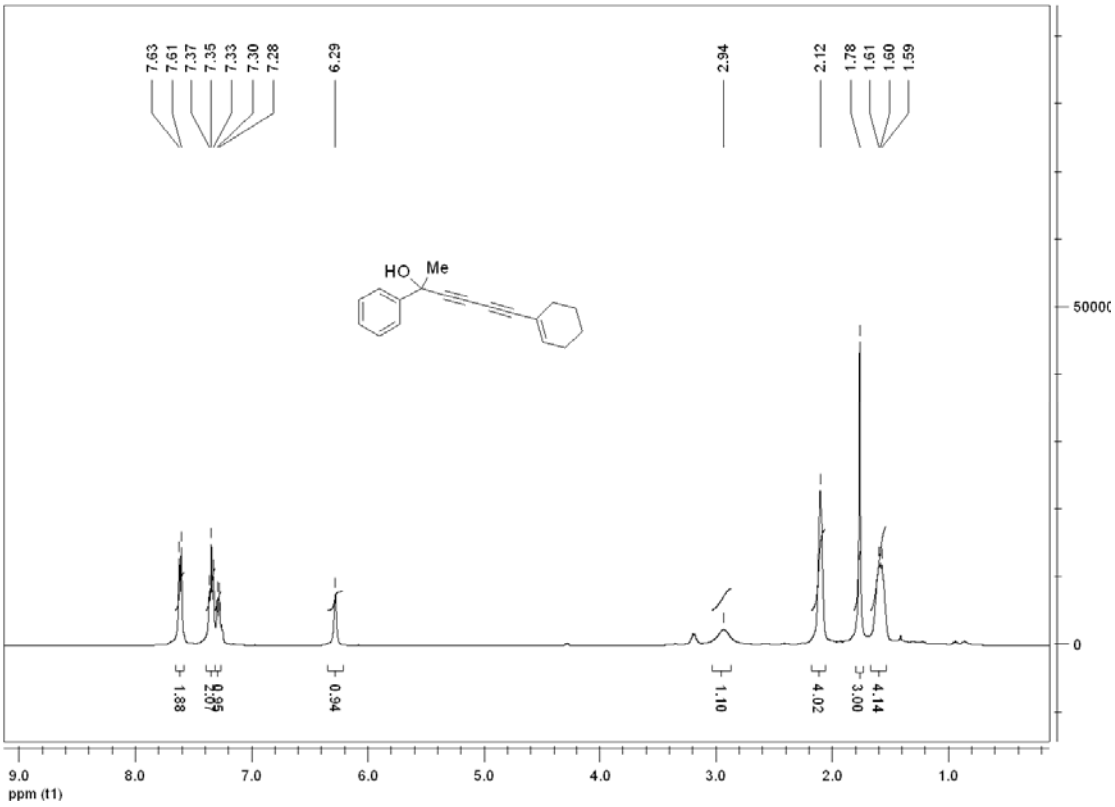
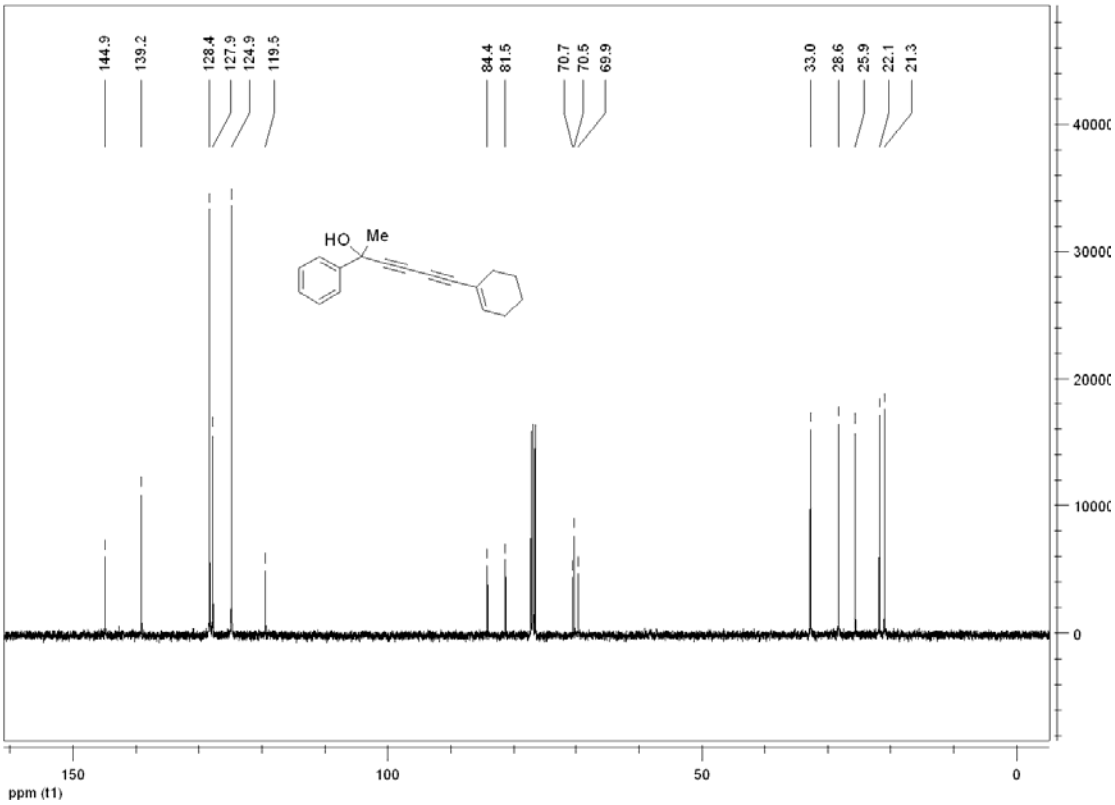
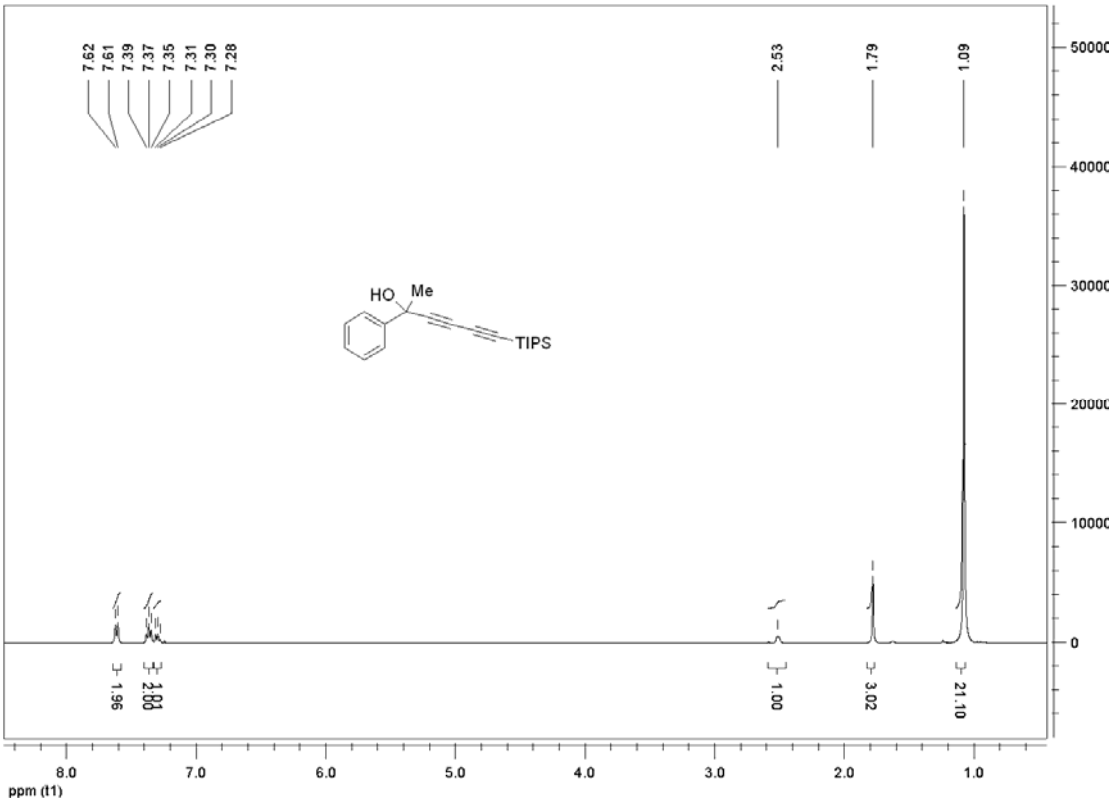
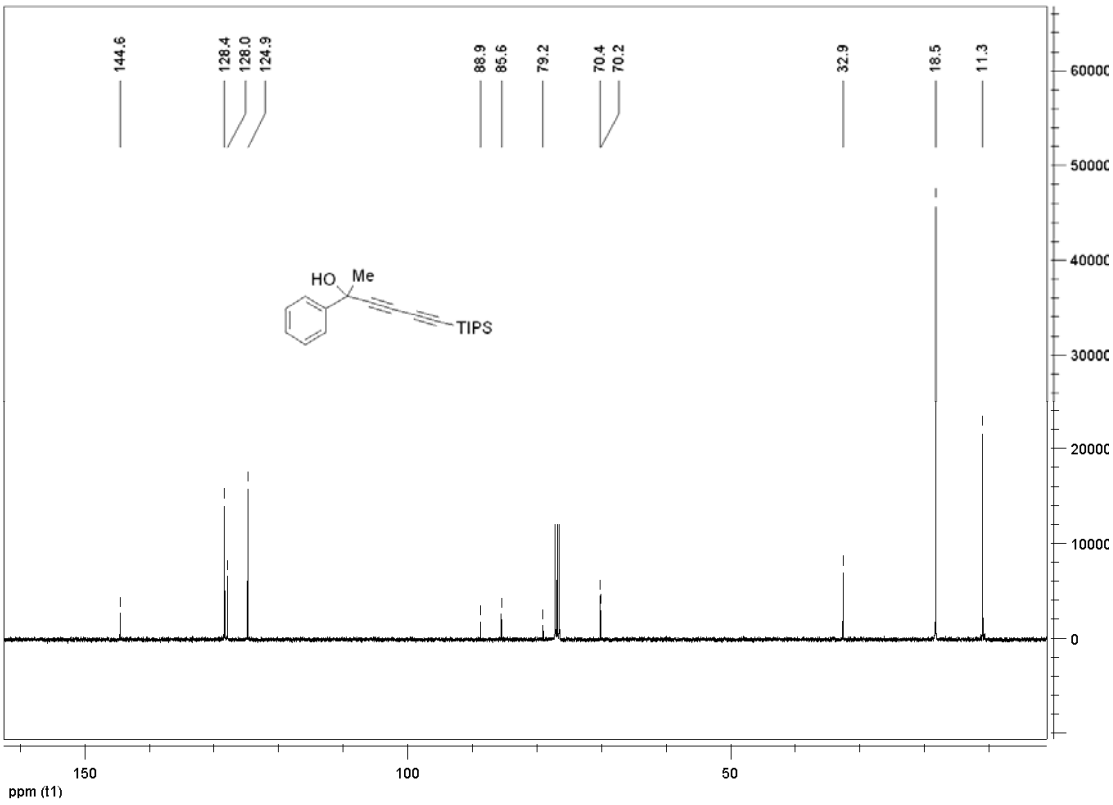
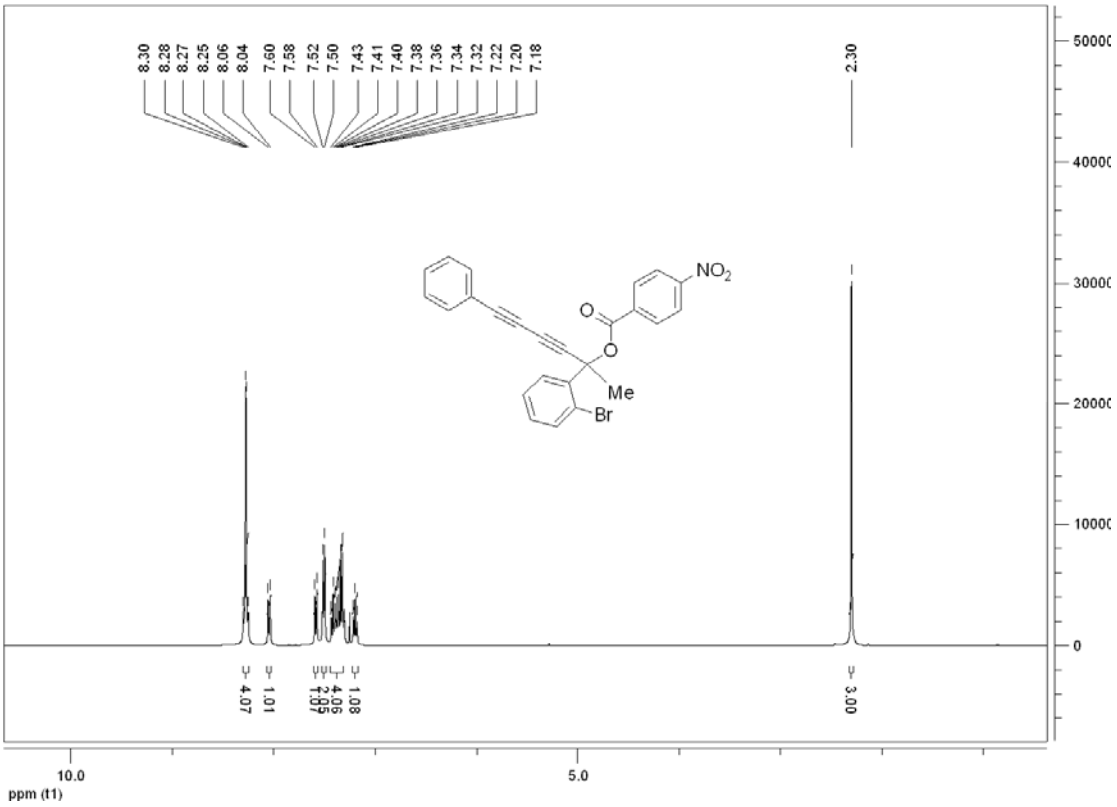
134.4
130.3
129.5
128.5
128.1
126.6
124.9
121.7
86.8
78.0
75.9
70.6
69.4
32.9
HO
Me
Cl
150
100
50
ppm (t1)


7.63
7.61
7.37
7.35
7.33
7.30
7.28
6.29
2.94
2.12
1.78
1.61
1.60
1.59
HO
Me
1.88
2.07
0.94
1.10
4.02
3.00
4.14
50000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


144.9
139.2
128.4
127.9
124.9
119.5
84.4
81.5
70.7
70.5
69.9
33.0
28.6
25.9
22.1
21.3
HO
Me
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)






8.30
8.28
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8.25
8.06
8.04
7.60
7.58
7.52
7.50
7.43
7.41
7.40
7.38
7.36
7.34
7.32
7.22
7.20
7.18
2.30
NO2
O
O
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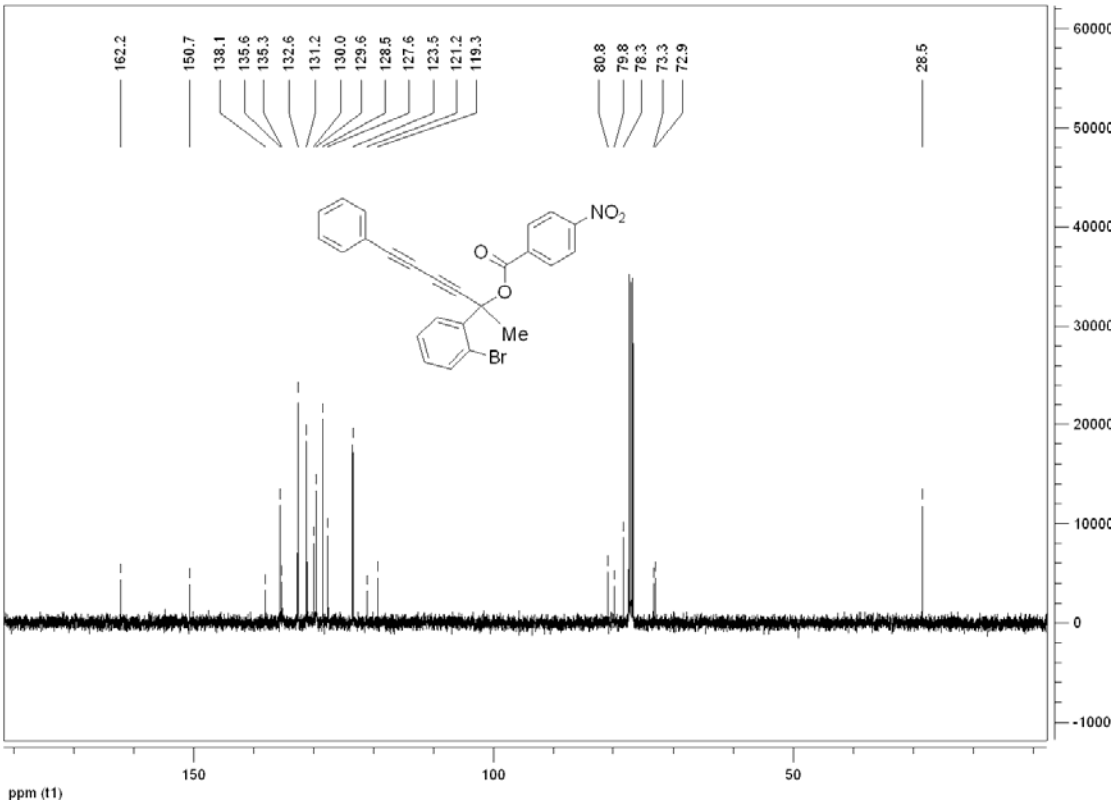
Br
4.07
1.01
2.05
2.07
1.08
3.00
10.0
5.0
ppm (t1)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150.7
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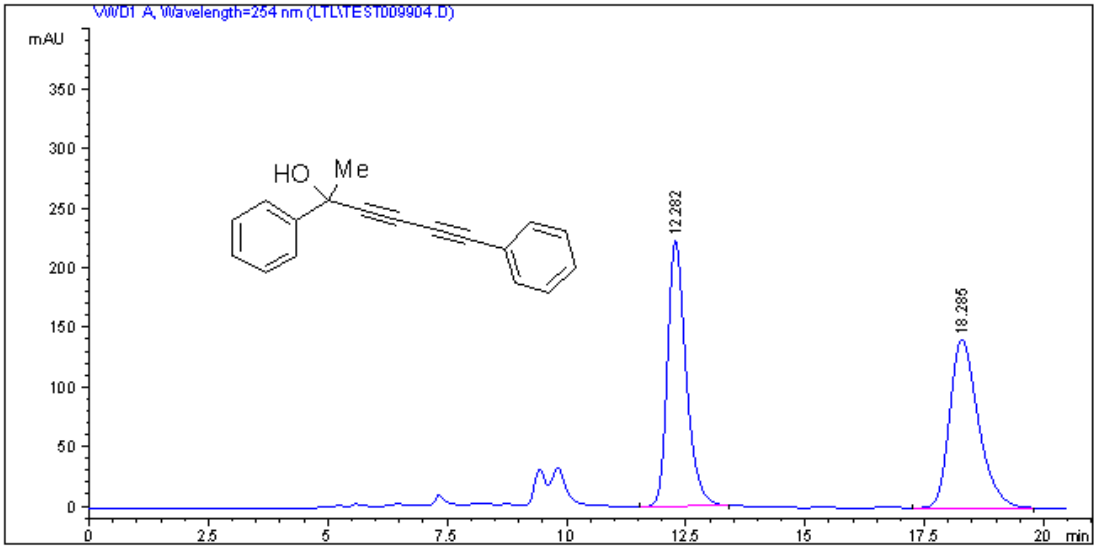
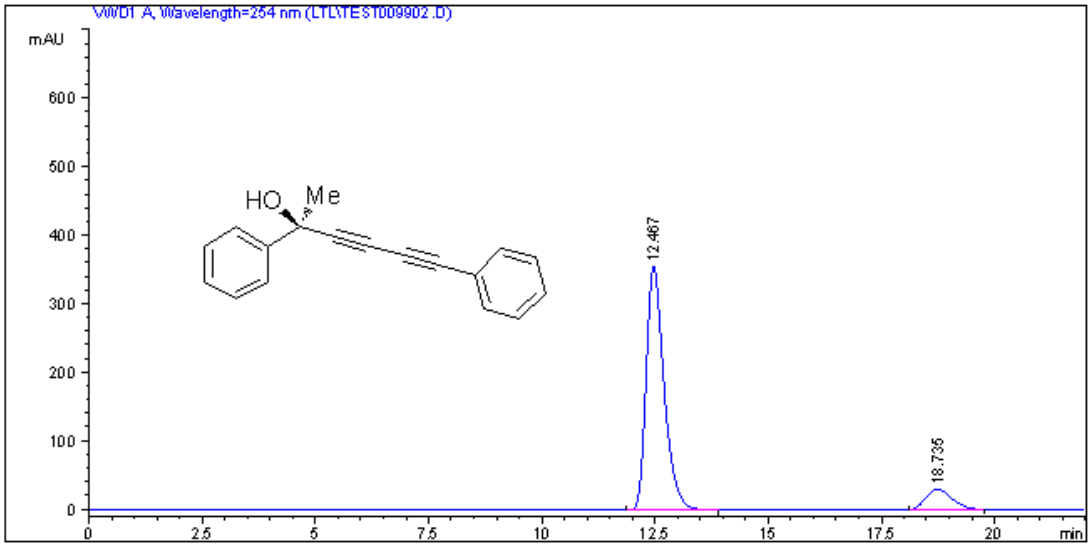
135.6
135.3
132.6
131.2
130.0
129.6
128.5
127.6
123.5
121.2
119.3
80.8
79.8
78.3
73.3
72.9
28.5
NO2
O
O
Me
Br
150
100
50
ppm (t1)

Sample Info : 254nm, OD-H, i-PrOH:Hexane = 10:90, 0.8 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

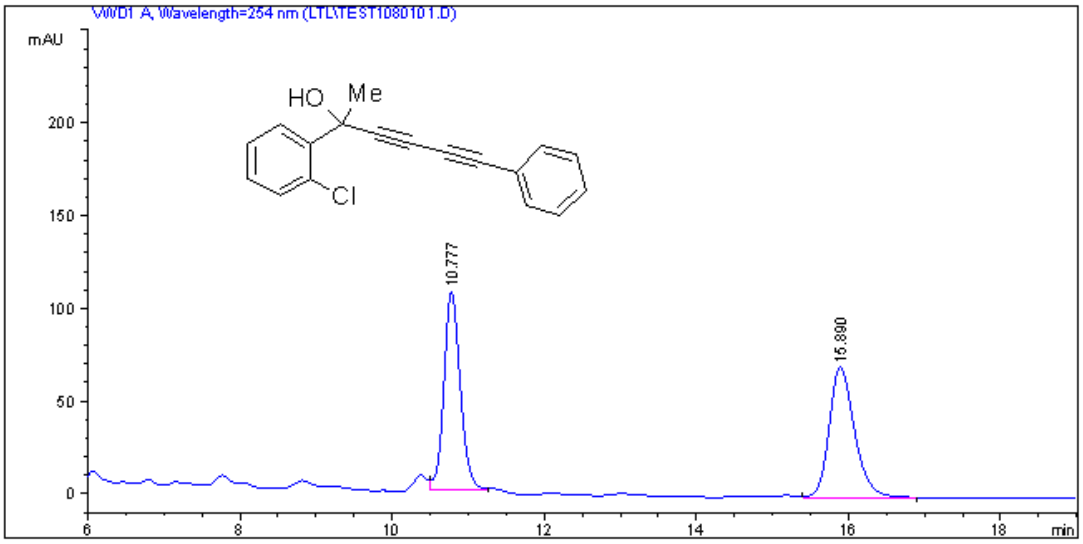
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.282	BB	0.4103	6028.77637	222.80725	50.5104
2	18.285	VB	0.6400	5906.93213	141.47630	49.4896



Signal 1: VWD1 A, Wavelength=254 nm

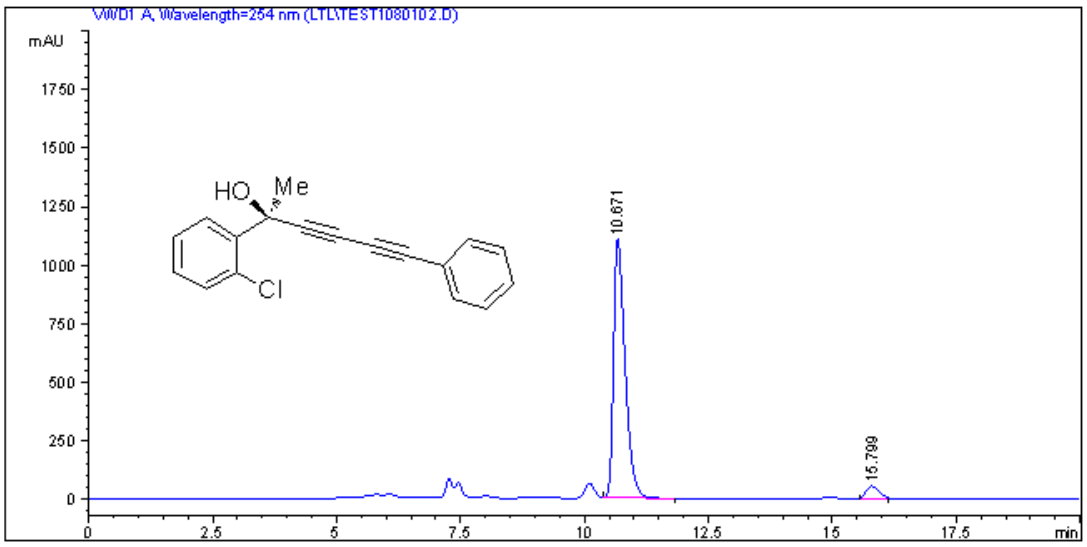
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.467	BB	0.4182	9776.57129	355.69666	88.6844
2	18.735	BBA	0.6180	1247.42883	30.71000	11.3156

Sample Info : 254nm, IB, i-PrOH : Hexane = 5:95, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

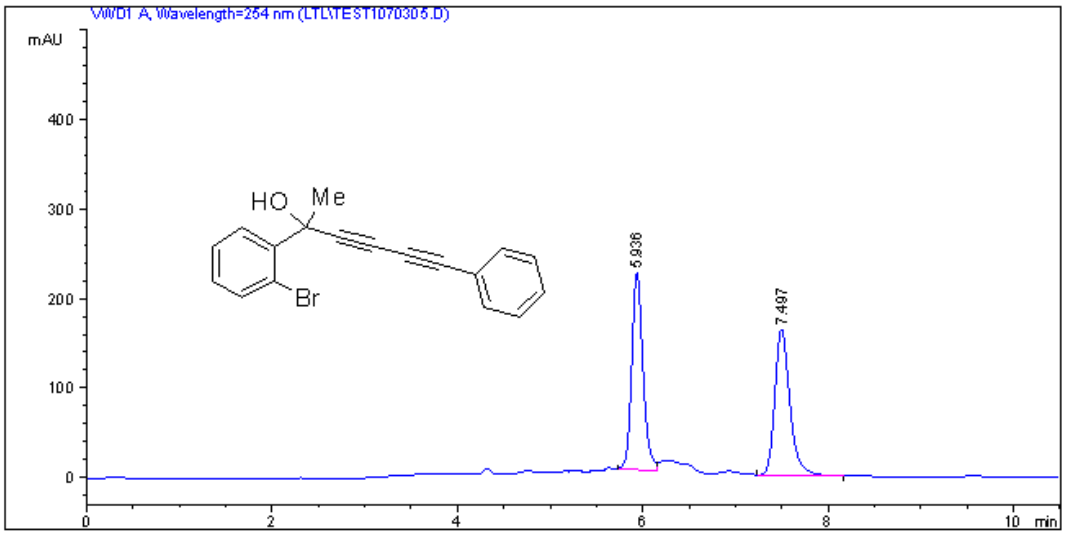
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.777	VB	0.2285	1599.69360	106.86388	49.6088
2	15.890	VB	0.3527	1624.91992	70.30116	50.3912



Signal 1: VWD1 A, Wavelength=254 nm

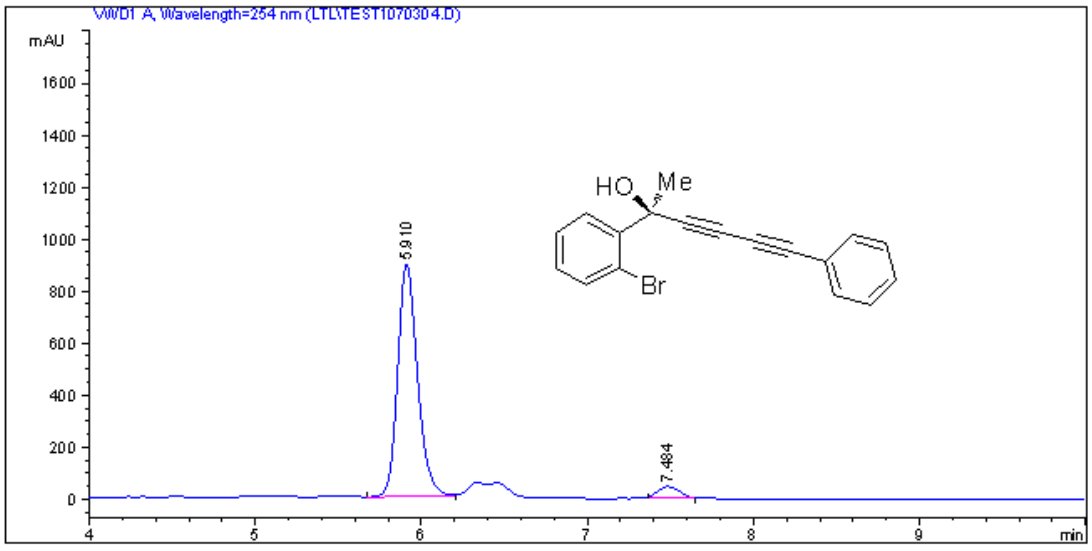
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.671	BB	0.2448	1.78097e4	1104.86743	94.8293
2	15.799	PM	0.3130	971.10297	51.71267	5.1707

Sample Info : 254nm, IB, i-PrOH : Hexane =15:85, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

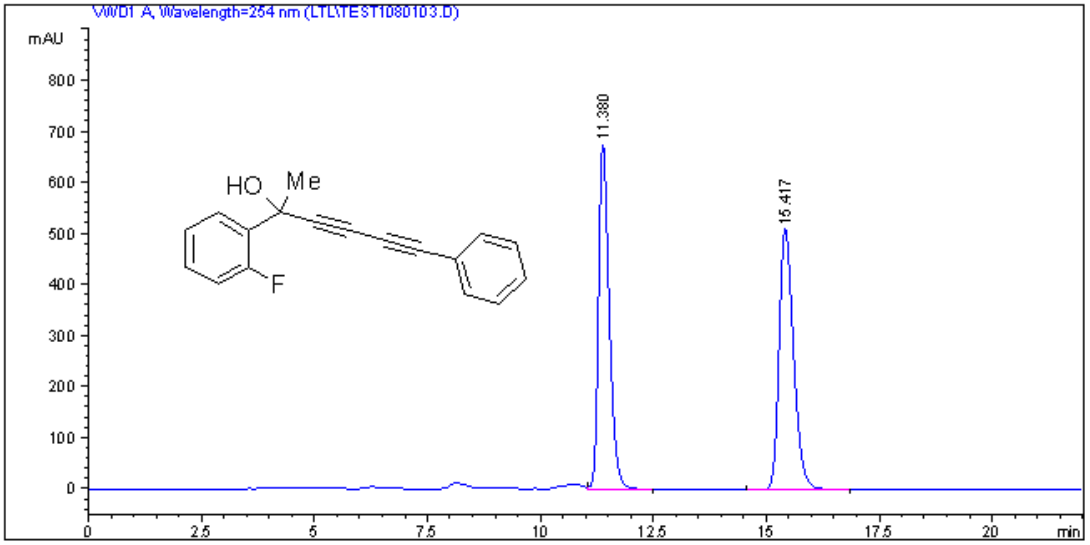
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.936	BV	0.1290	1856.68982	220.00349	50.1957
2	7.497	VV	0.1725	1842.21179	163.10420	49.8043



Signal 1: VWD1 A, Wavelength=254 nm

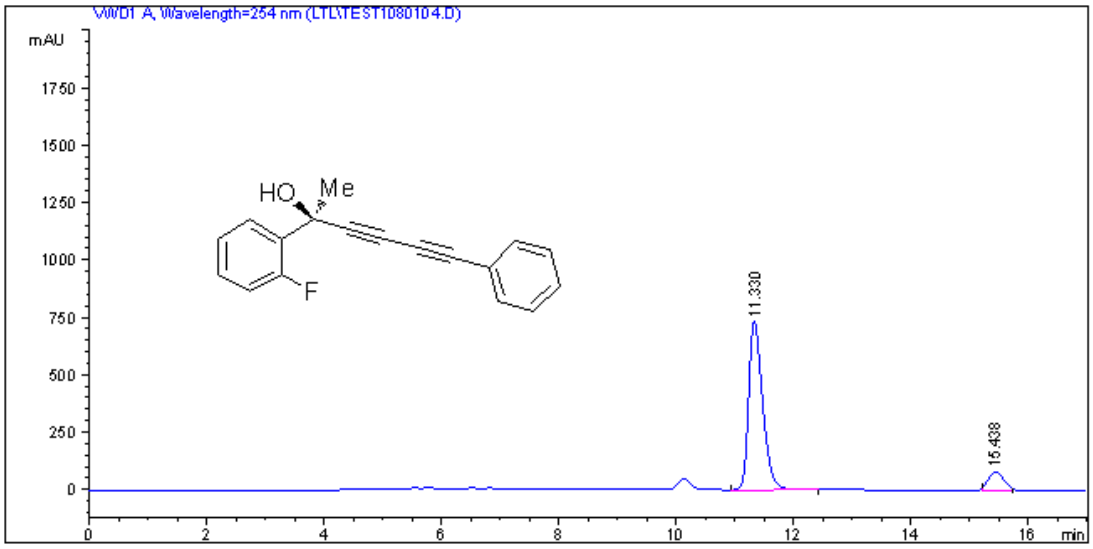
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.910	VV	0.1275	7440.18799	895.13458	94.9761
2	7.484	PM	0.1494	393.56369	43.89990	5.0239

Sample Info : 254nm, IB, i-PrOH : Hexane = 5:95, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

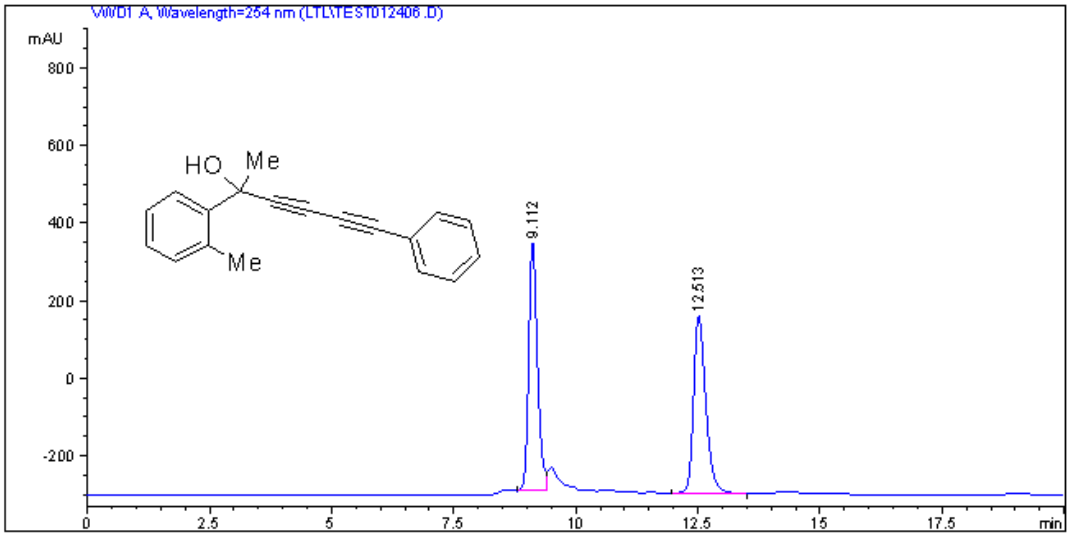
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.380	VB	0.2529	1.11873e4	675.52533	49.5217
2	15.417	BB	0.3435	1.14033e4	510.63538	50.4783



Signal 1: VWD1 A, Wavelength=254 nm

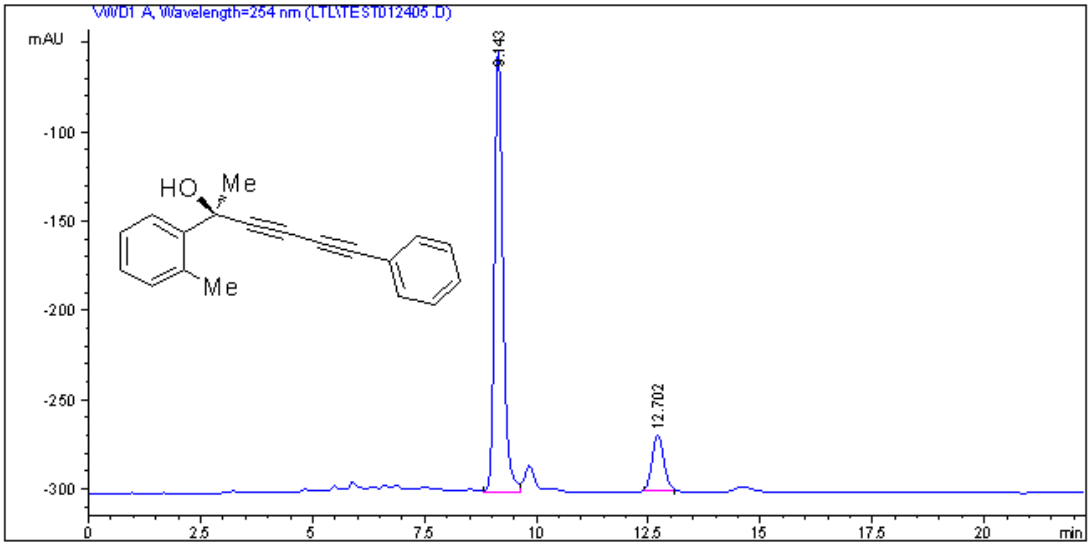
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.330	BB	0.2532	1.21559e4	732.73633	89.2175
2	15.438	MM	0.3091	1469.12659	79.21481	10.7825

Sample Info : 254nm. IB. i-PrOH : Hexane = 20:80. 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

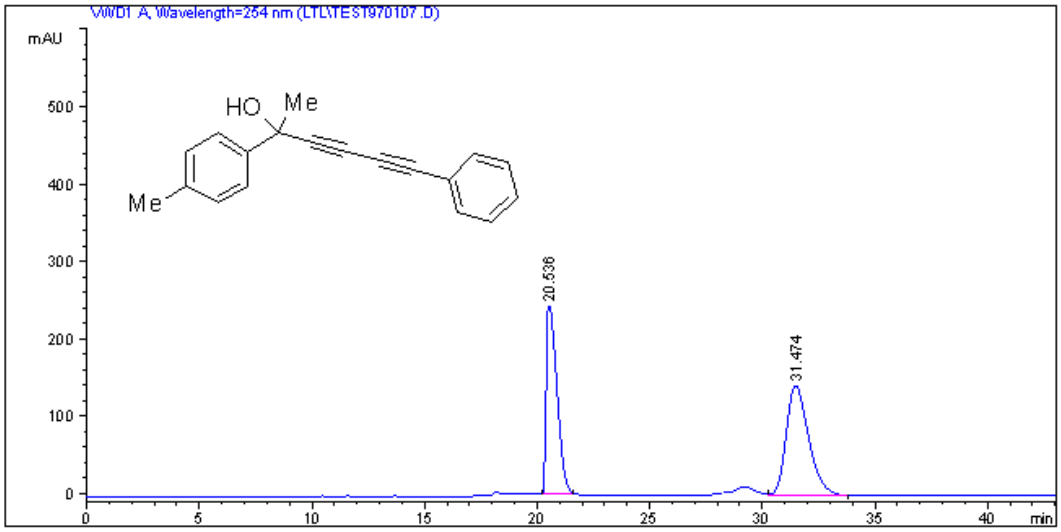
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.112	VV	0.1916	8040.36133	640.34326	50.0424
2	12.513	BB	0.2672	8026.75195	457.81573	49.9576



Signal 1: VWD1 A, Wavelength=254 nm

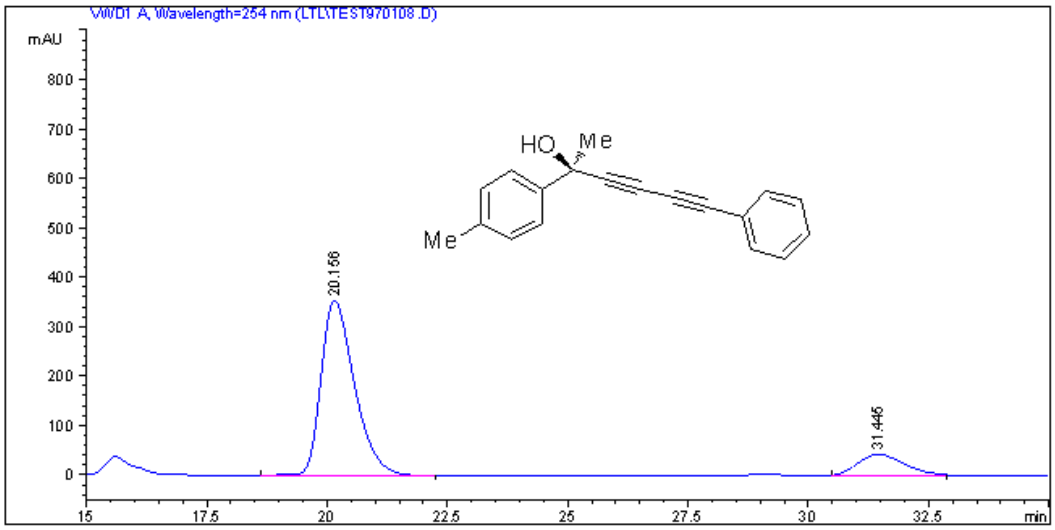
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.143	VV	0.2009	3260.36060	246.46223	85.6533
2	12.702	MM	0.2949	546.09961	30.86733	14.3467

Sample Info : 254nm, OD-H, i-PrOH : Hexane =5:95, 0.8 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

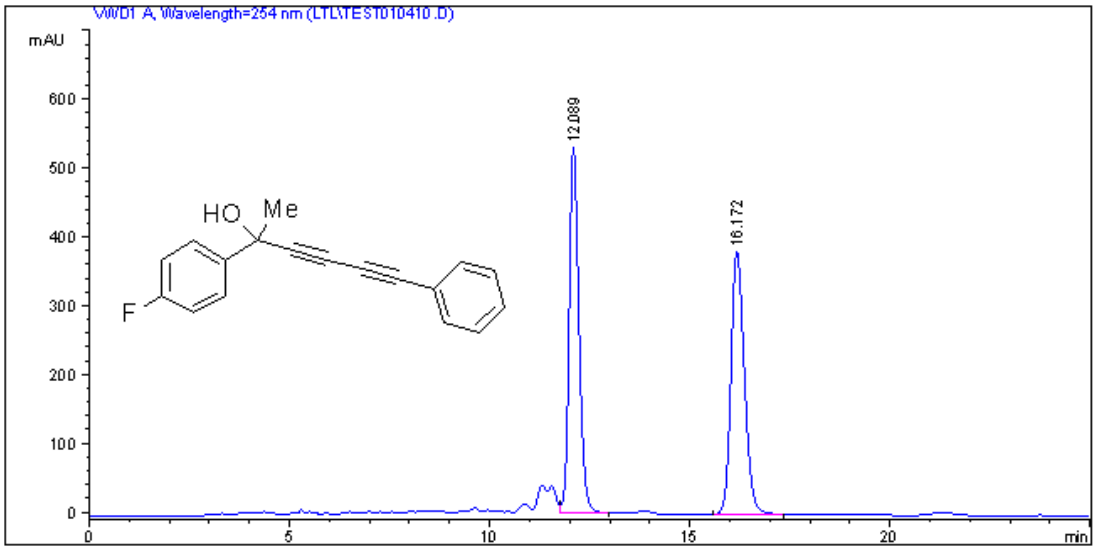
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.536	PM	0.6805	9921.72852	243.00238	50.2495
2	31.474	VB	1.0532	9823.19629	141.98685	49.7505



Signal 1: VWD1 A, Wavelength=254 nm

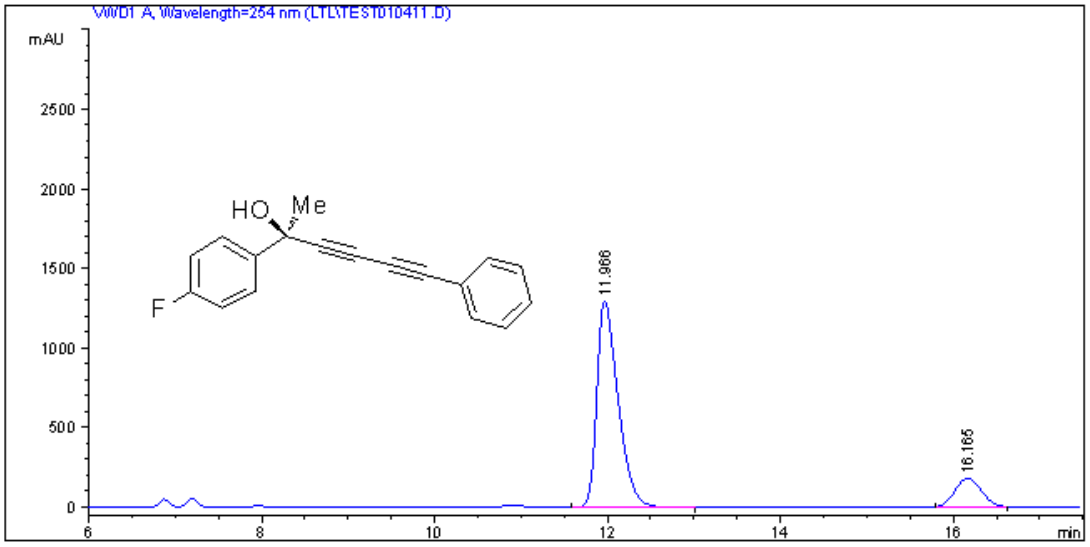
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.156	BB	0.7439	1.70995e4	354.10083	85.8087
2	31.445	MM	1.1094	2827.96802	42.48532	14.1913

Sample Info : 254nm,IB, i-PrOH : Hexane = 5:95, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

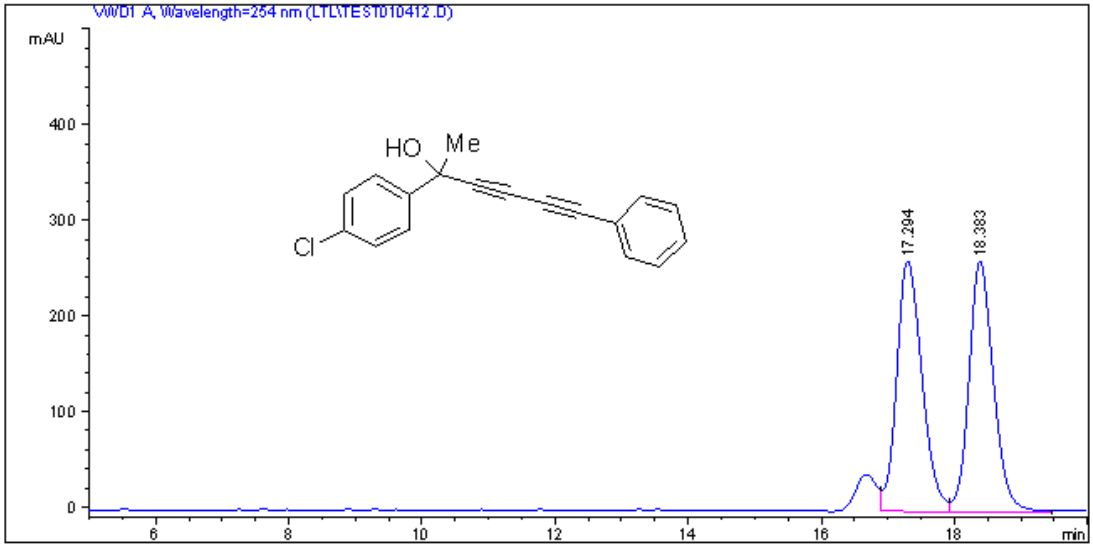
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.089	VB	0.2594	9023.03906	531.11072	50.3720
2	16.172	BB	0.3573	8889.76660	382.10690	49.6280



Signal 1: VWD1 A, Wavelength=254 nm

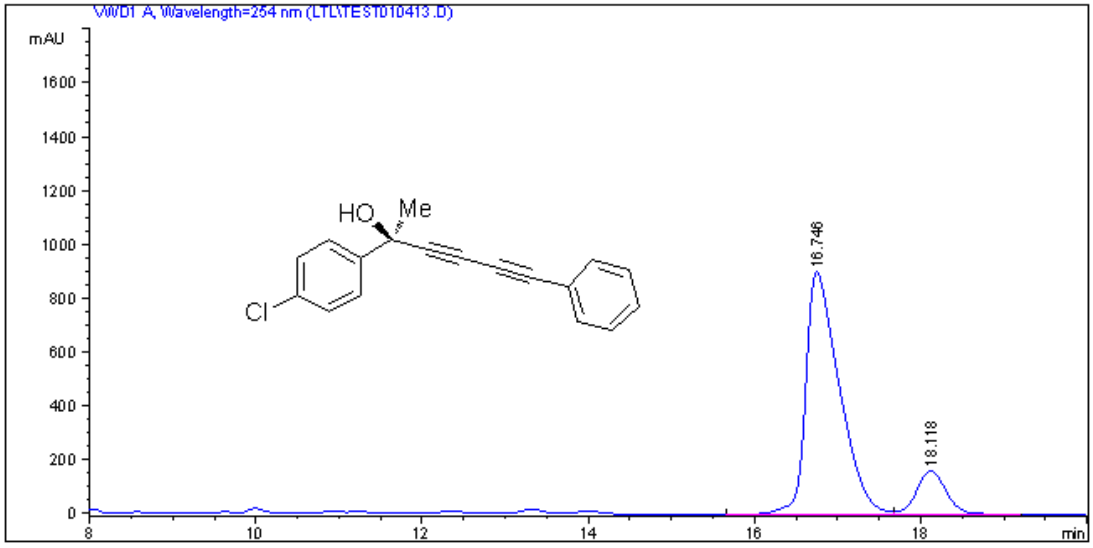
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.966	VB	0.2582	2.23129e4	1301.65479	85.4606
2	16.165	BBA	0.3365	3796.07324	178.77954	14.5394

Sample Info : 254nm,IB, i-PrOH : Hexane = 5:95, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

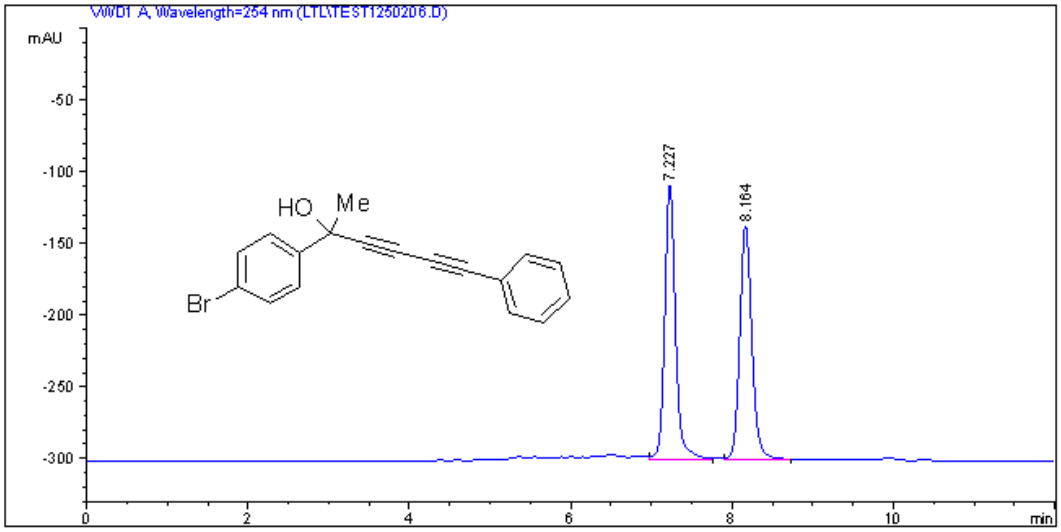
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.294	VV	0.4119	6924.96436	261.83704	50.8728
2	18.383	VB	0.3878	6687.33643	262.26413	49.1272



Signal 1: VWD1 A, Wavelength=254 nm

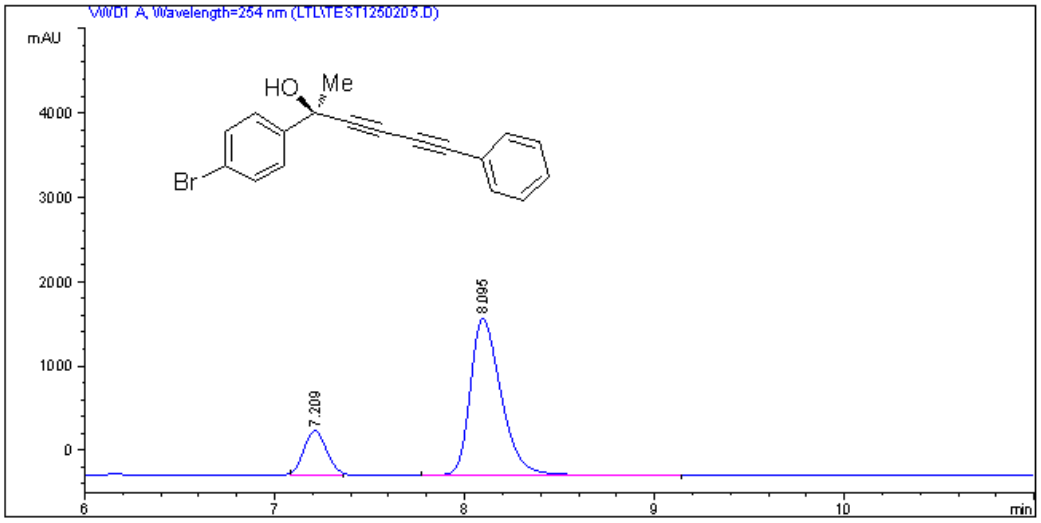
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.746	BV	0.4117	2.51384e4	900.29480	86.4132
2	18.118	VB	0.3815	3952.52905	160.77248	13.5868

Sample Info : 254nm, IB, i-PrOH : Hexane = 20:80, 0.8 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

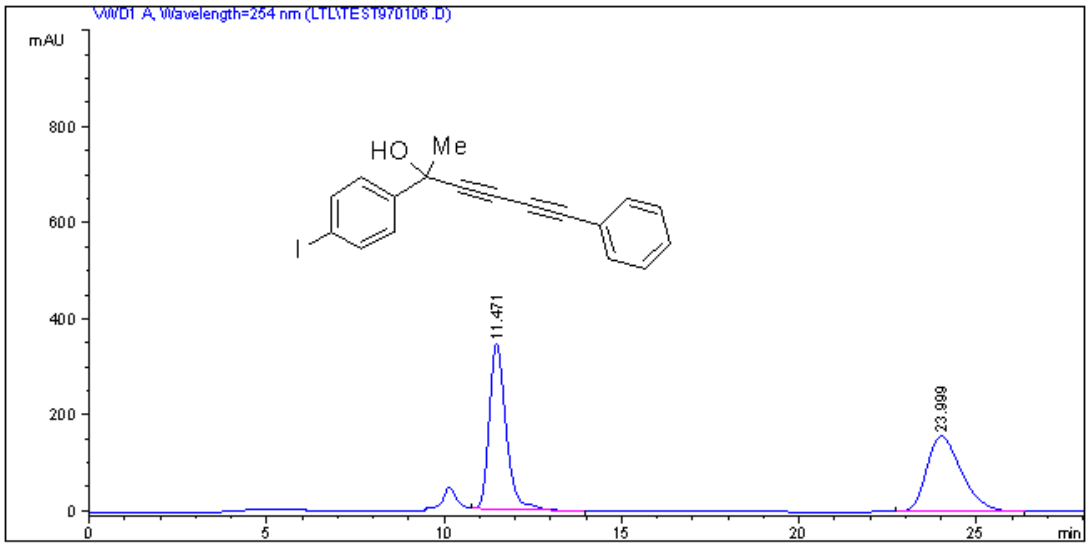
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.227	BBA	0.1388	1715.82678	190.15863	50.4731
2	8.164	BB	0.1588	1683.66382	162.45650	49.5269



Signal 1: VWD1 A, Wavelength=254 nm

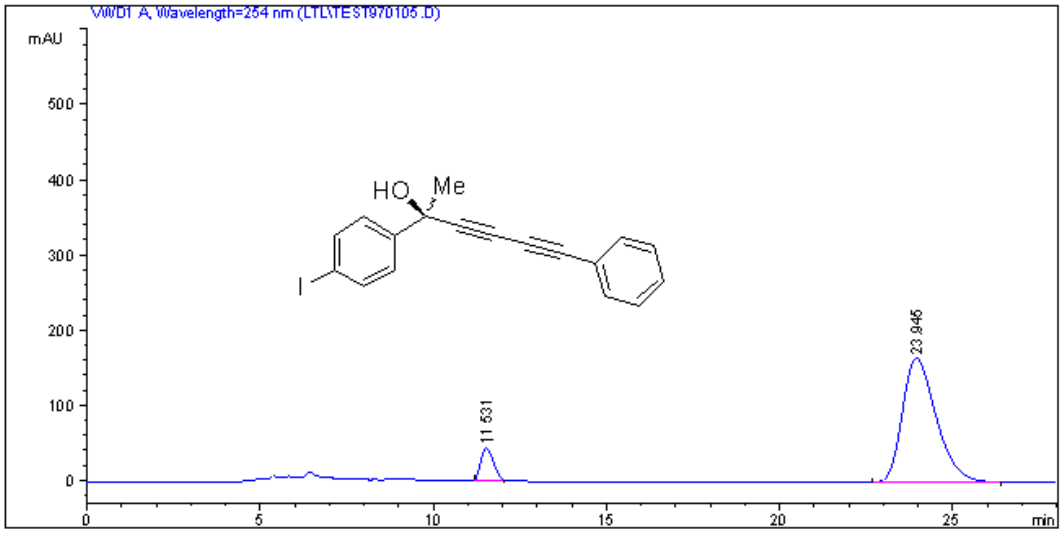
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.209	MM	0.1415	4567.57812	537.92682	17.7920
2	8.095	VV	0.1731	2.11045e4	1860.79565	82.2080

Sample Info : 254nm, OD-H, i-PrOH : Hexane =20:80, 0.8 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

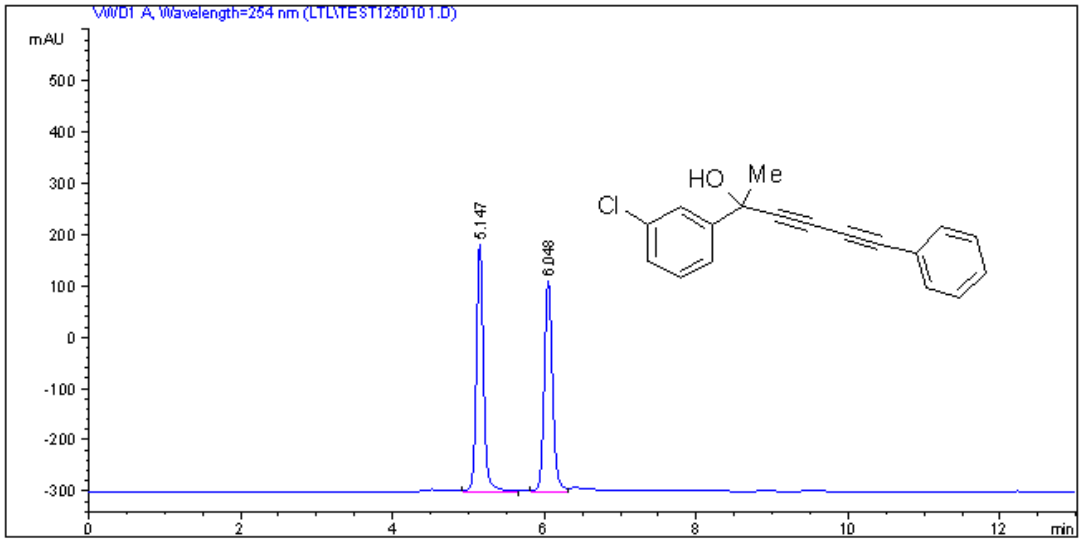
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.471	BB	0.4998	1.12254e4	342.97769	50.9495
2	23.999	BB	1.0532	1.08070e4	157.62984	49.0505



Signal 1: VWD1 A, Wavelength=254 nm

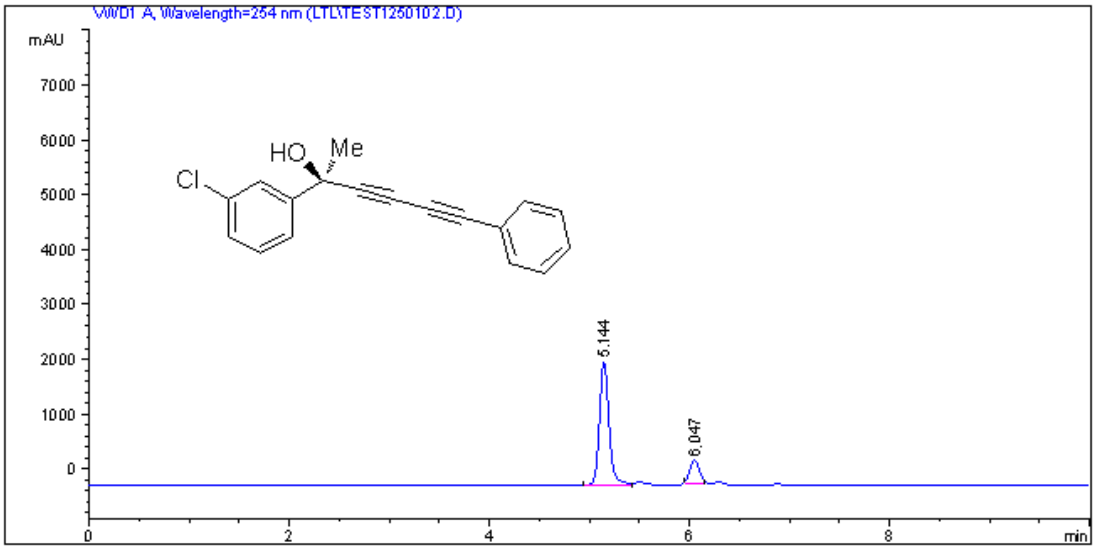
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.531	MM	0.4304	1125.42065	43.57665	9.1415
2	23.945	BB	1.0386	1.11857e4	164.95369	90.8585

Sample Info : 254nm, IB, i-PrOH : Hexane = 30:70, 0.8 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

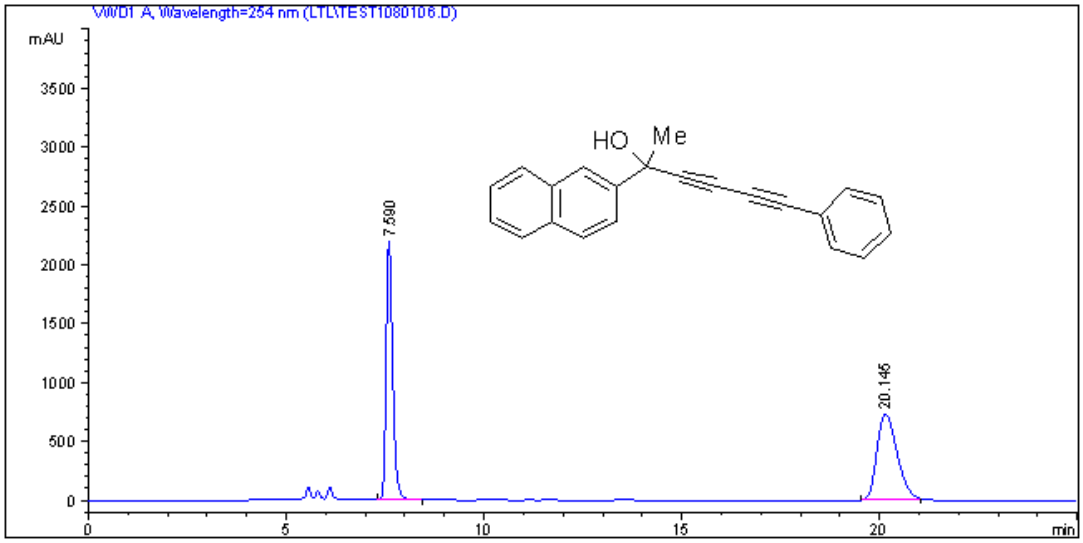
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.147	VV	0.1005	3196.92187	483.32996	50.5334
2	6.048	VV	0.1164	3129.43115	411.24179	49.4666



Signal 1: VWD1 A, Wavelength=254 nm

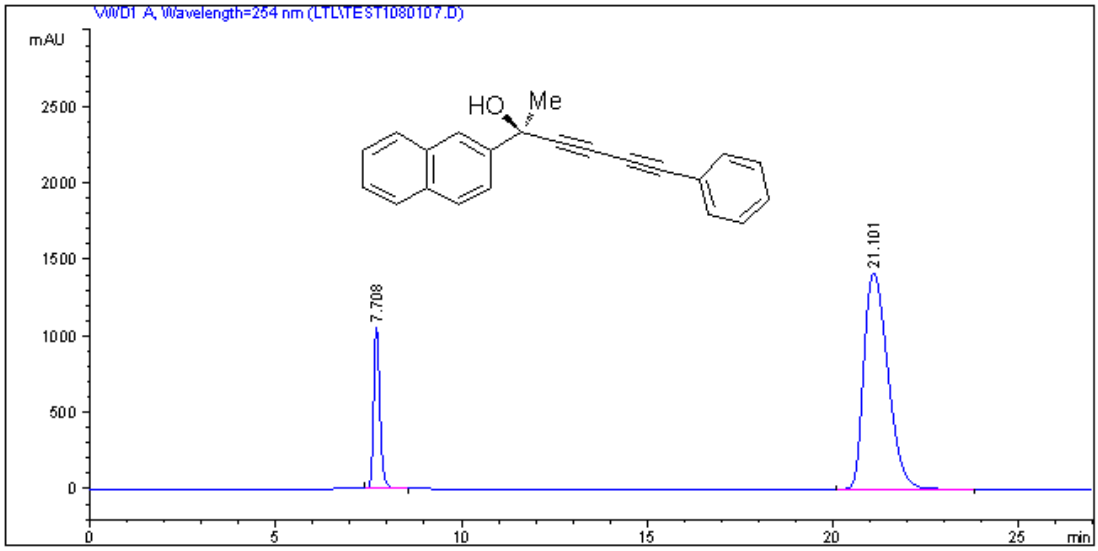
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.144	VV	0.1019	1.51117e4	2243.08691	84.8266
2	6.047	MM	0.1086	2703.10596	414.73950	15.1734

Sample Info : 254nm, IB, i-PrOH : Hexane = 20:80, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

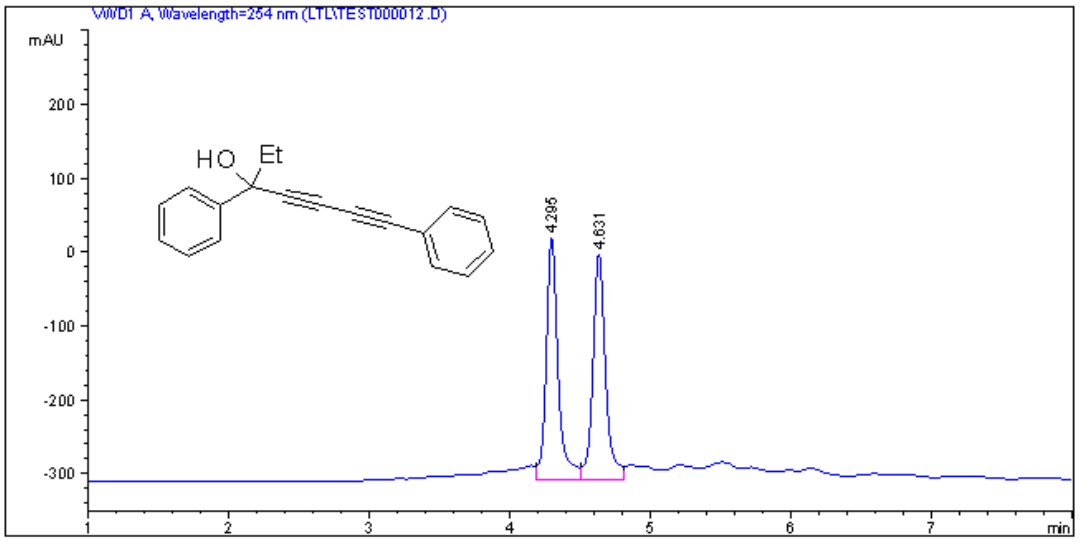
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.590	VV	0.1779	2.55515e4	2197.47607	49.4328
2	20.145	BBA	0.5577	2.61379e4	732.21826	50.5672



Signal 1: VWD1 A, Wavelength=254 nm

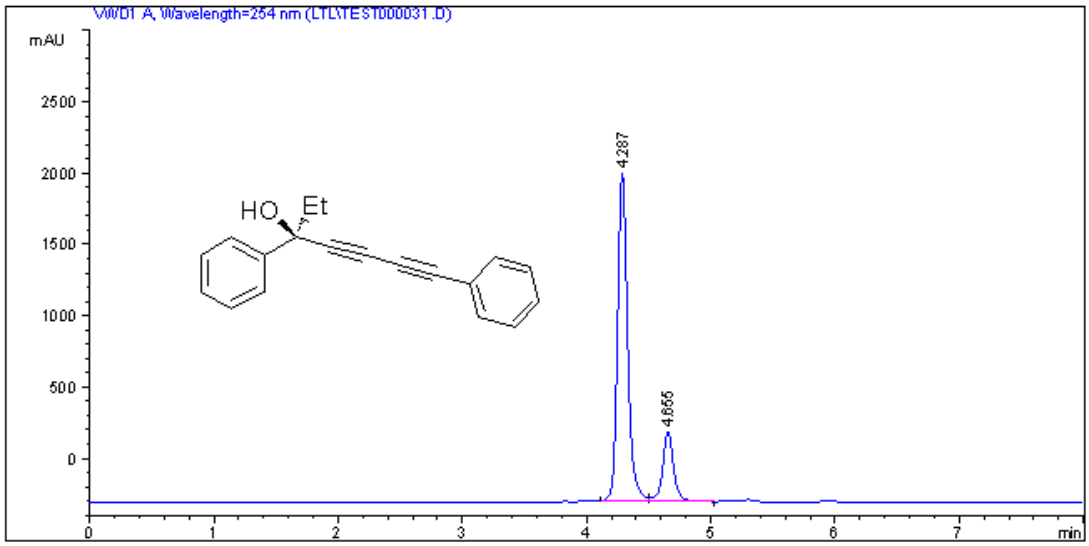
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.708	VV	0.1754	1.21775e4	1055.33875	16.0573
2	21.101	BB	0.7138	6.36601e4	1415.83521	83.9427

Sample Info : 254nm, IB, i-PrOH : Hexane =20:80, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

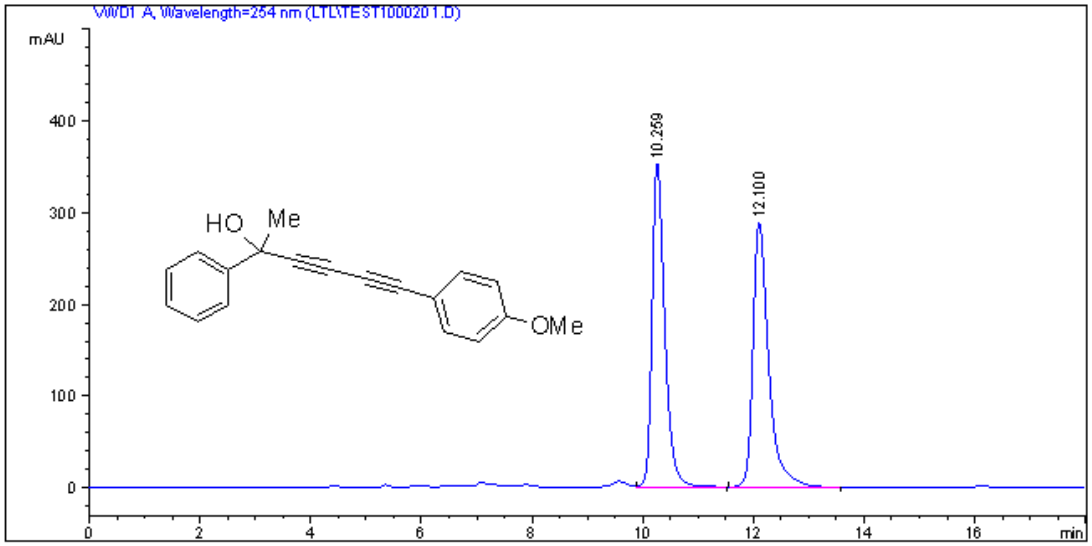
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.295	VV	0.0883	1950.89331	328.32309	50.0862
2	4.631	VV	0.0957	1944.17786	306.92432	49.9138



Signal 1: VWD1 A, Wavelength=254 nm

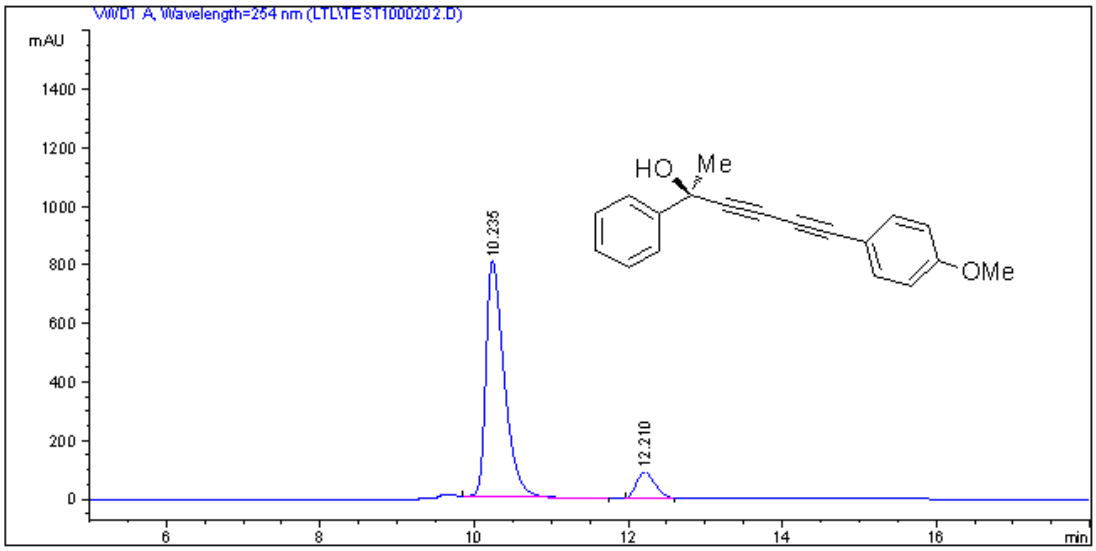
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.287	BV	0.0864	1.30219e4	2302.07959	81.0791
2	4.655	VV	0.0944	3038.82959	488.27237	18.9209

Sample Info : 254nm, IB, i-PrOH : Hexane =10:90, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

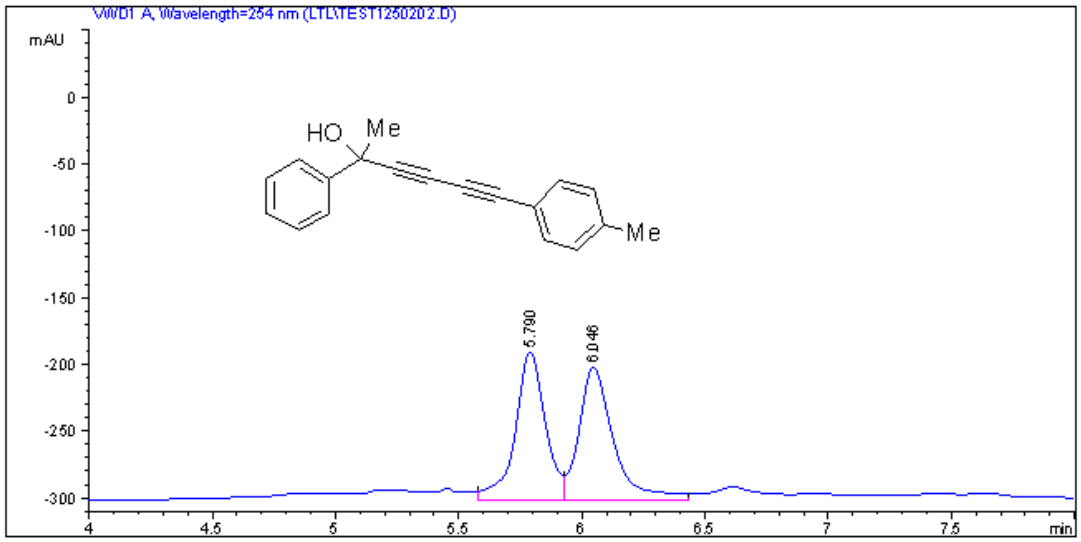
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.259	VB	0.2417	5641.81055	353.19366	49.6486
2	12.100	BB	0.2967	5721.67676	288.78970	50.3514



Signal 1: VWD1 A, Wavelength=254 nm

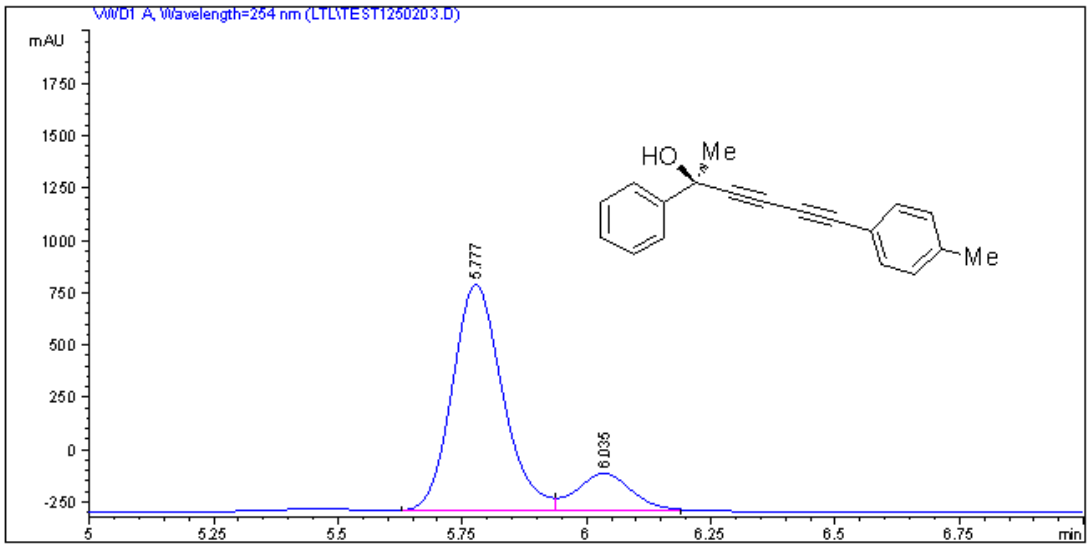
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.235	BBA	0.2481	1.31732e4	803.36218	89.7490
2	12.211	PM	0.2818	1504.61536	88.97887	10.2510

Sample Info : 254nm, IB, i-PrOH : Hexane = 20:80, 0.8 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

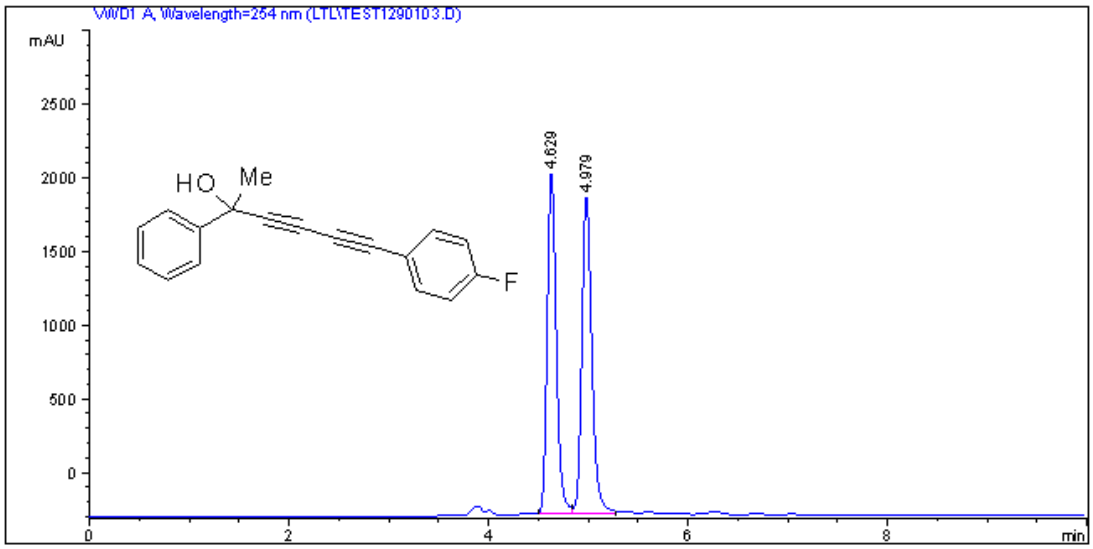
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.790	BV	0.1266	941.12756	110.95915	49.3123
2	6.046	VV	0.1425	967.37872	99.58524	50.6877



Signal 1: VWD1 A, Wavelength=254 nm

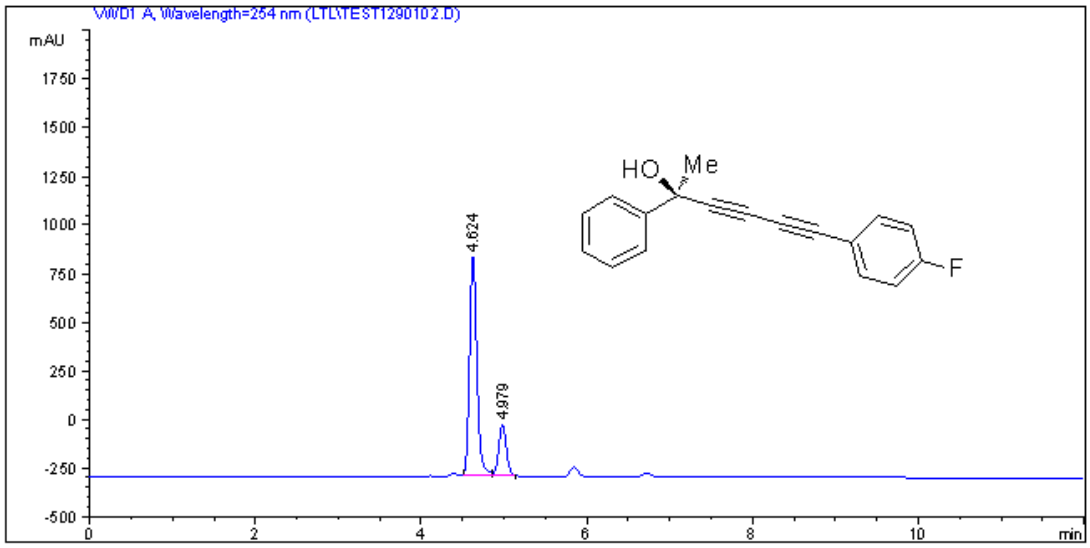
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.777	BV	0.1080	7586.21826	1082.22449	84.8561
2	6.035	VBA	0.1152	1353.88464	177.45412	15.1439

Sample Info : 254nm, IB, i-PrOH : Hexane = 20:80, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

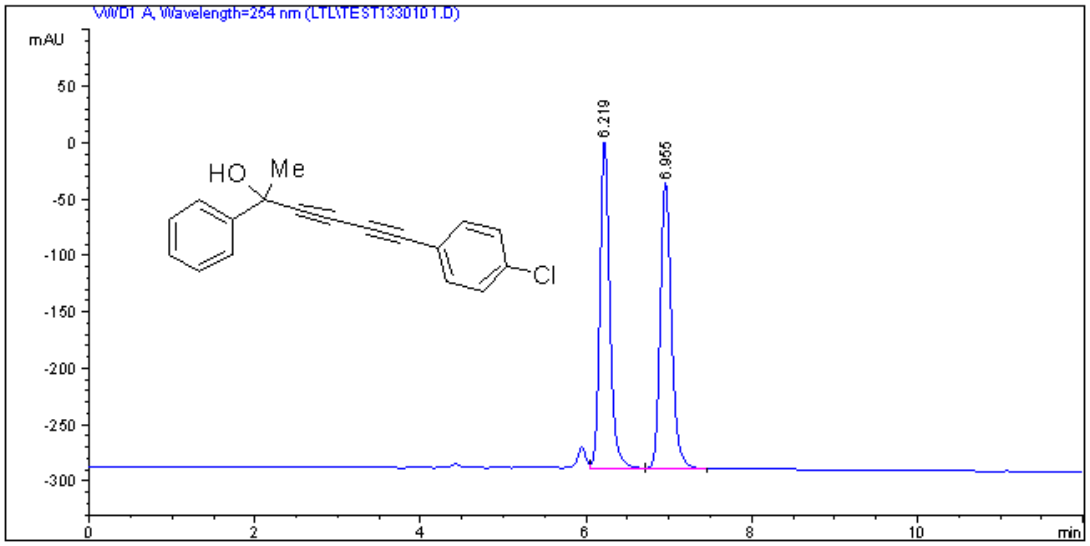
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.629	BV	0.0971	1.46067e4	2309.36890	49.3091
2	4.979	VBA	0.1062	1.50160e4	2149.70557	50.6909



Signal 1: VWD1 A, Wavelength=254 nm

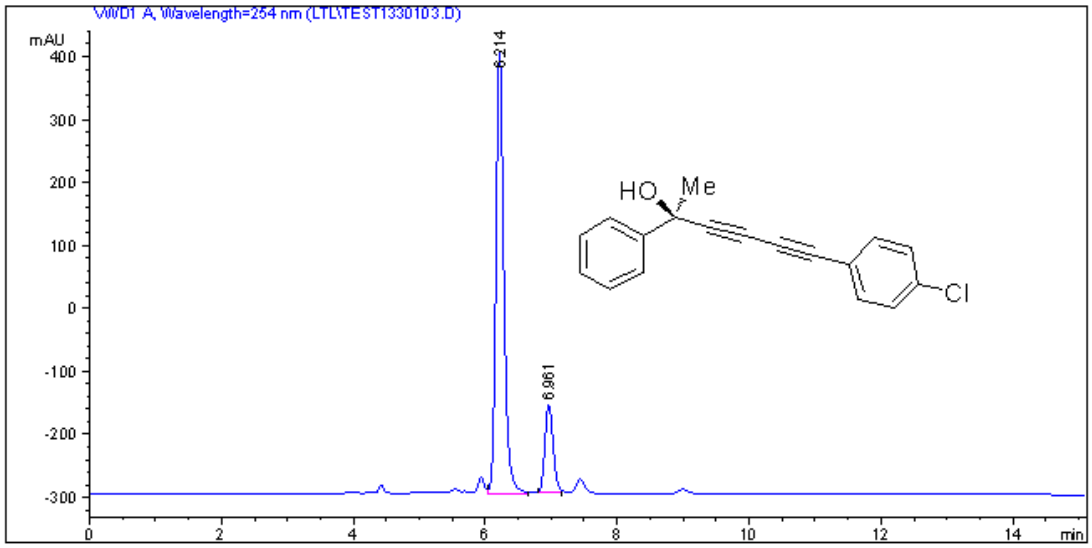
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.624	BV	0.0953	6956.14404	1127.69421	81.0143
2	4.979	VBA	0.0982	1630.17432	258.91681	18.9857

Sample Info : 254nm, IB, i-PrOH : Hexane = 10:90, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

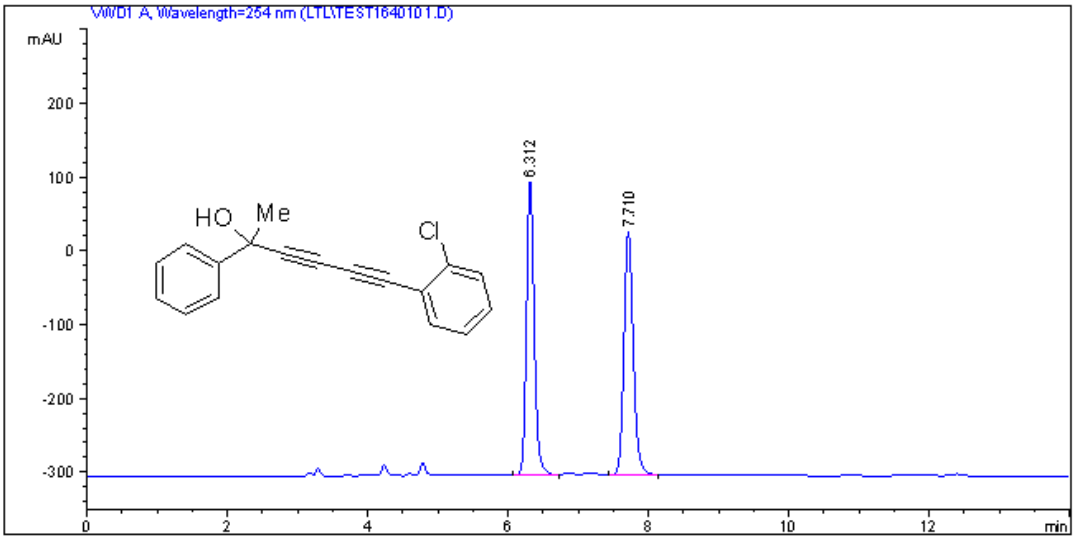
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.219	VV	0.1265	2418.20972	289.79160	50.2775
2	6.955	VB	0.1437	2391.51685	253.07774	49.7225



Signal 1: VWD1 A, Wavelength=254 nm

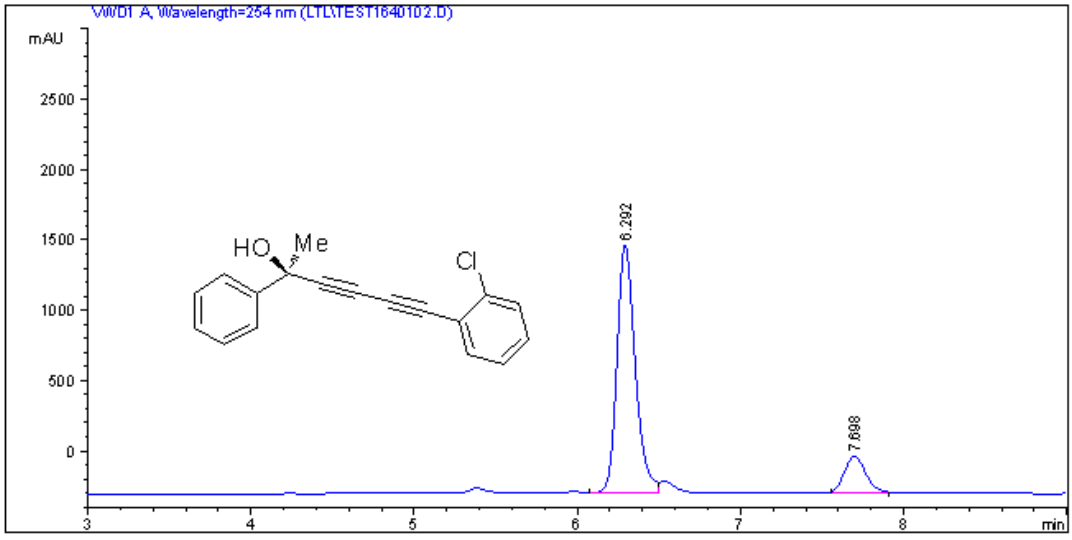
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.214	VBA	0.1264	5838.34668	700.03992	82.9353
2	6.961	BBA	0.1348	1201.29150	138.30208	17.0647

Sample Info : 254nm, IB, i-PrOH : Hexane =10:90, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

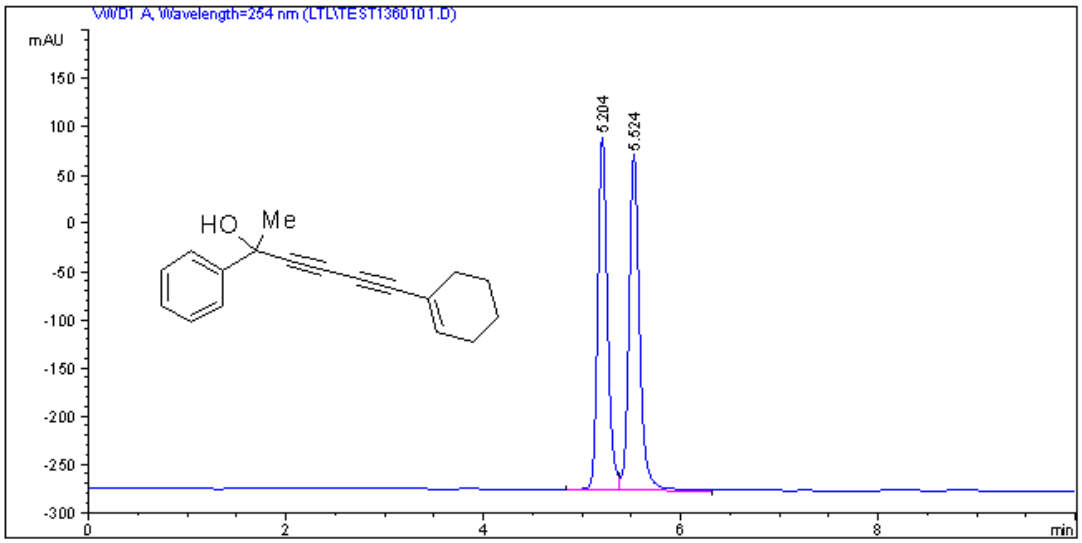
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.312	BV	0.1175	3072.30518	399.05151	49.9672
2	7.710	VBA	0.1437	3076.33740	330.01743	50.0328



Signal 1: VWD1 A, Wavelength=254 nm

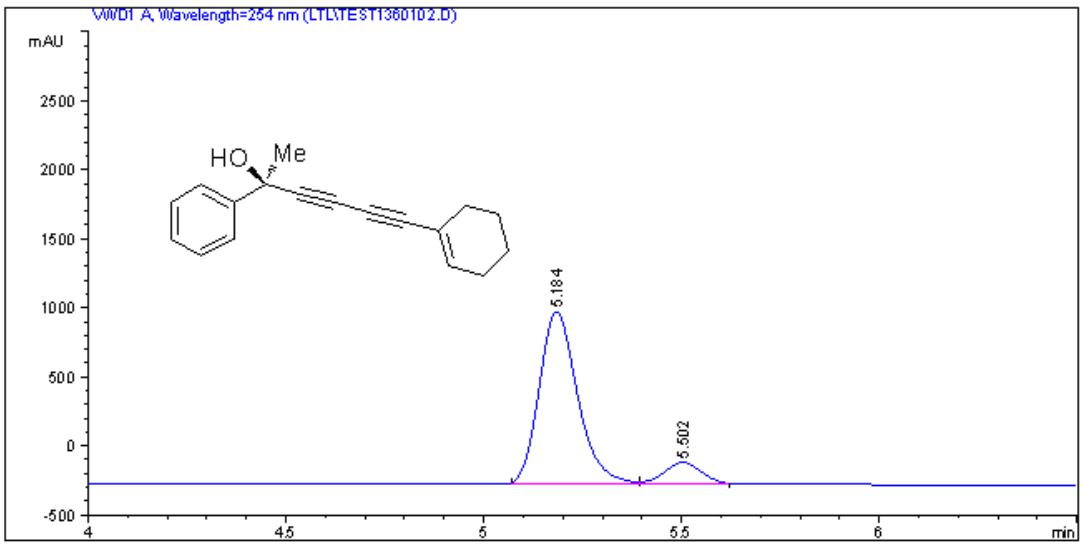
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.292	VV	0.1204	1.38310e4	1768.05591	85.5481
2	7.698	BBA	0.1398	2336.51855	256.43332	14.4519

Sample Info : 254nm, IB, i-PrOH : Hexane = 10:90, 1.0 mL/min



Signal 1: VWD1 A, Wavelength=254 nm

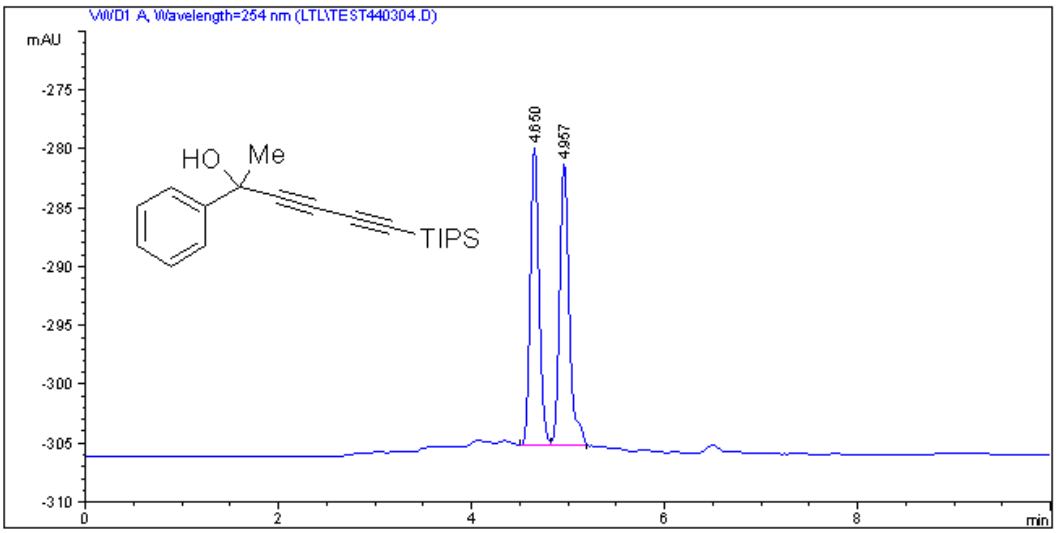
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.204	VV	0.1052	2525.16260	366.32806	49.1025
2	5.524	VV	0.1124	2617.47192	348.42822	50.8975



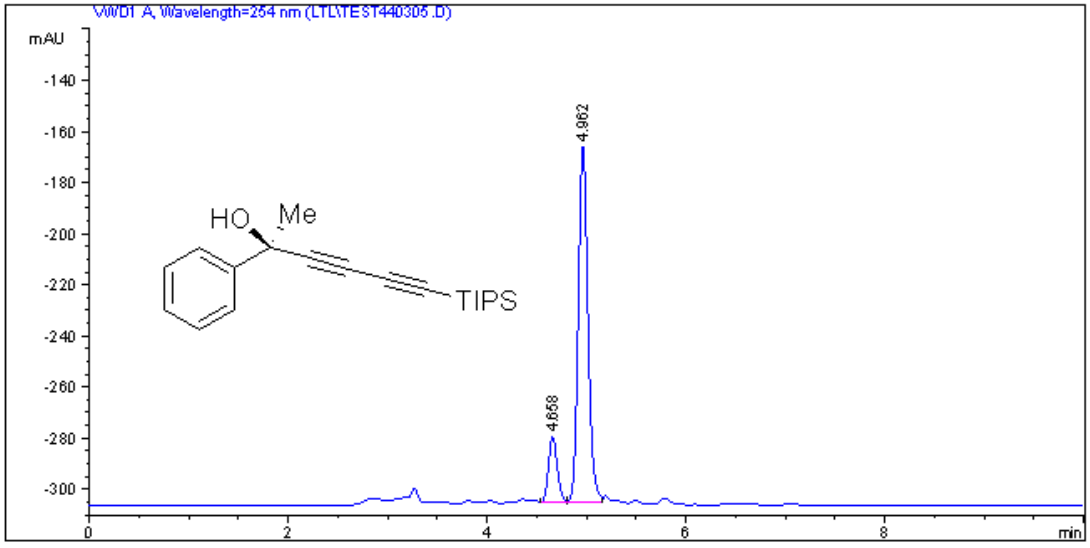
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.184	BV	0.1033	8379.56641	1245.06824	89.4064
2	5.502	VBA	0.1000	992.87726	153.94943	10.5936

Sample Info : 254nm,IA, i-PrOH : Hexane =5:95, 1.0mL/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.650	BV	0.0969	159.38727	25.25359	49.0439
2	4.957	VBA	0.1058	165.60150	23.84807	50.9561



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.658	BV	0.0949	157.09421	25.59127	14.2985
2	4.962	VV	0.1036	941.58051	139.36656	85.7015

7. Basic crystal data for the product 4

CCDC 830329 contains the supplementary crystallographic data for the product **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 110524

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 110524

```
Bond precision:  C-C = 0.0055 A          Wavelength=0.71073

Cell:            a=7.0214(6)     b=16.2366(16)     c=19.0401(18)
                 alpha=90        beta=90           gamma=90
Temperature:     294 K

                 Calculated                Reported
Volume           2170.6(3)                 2170.6(3)
Space group      P 21 21 21                P2(1)2(1)2(
Hall group       P 2ac 2ab                 ?
Moiety formula   C25 H16 Br N O4           ?
Sum formula      C25 H16 Br N O4           C25 H16 Br N O4
Mr               474.29                    474.30
Dx,g cm-3        1.451                     1.451
Z                4                         4
Mu (mm-1)        1.925                     1.925
F000             960.0                     960.0
F000'            959.28
h,k,lmax         9,21,24                   9,21,24
Nref             2841[ 4973]               4940
Tmin,Tmax        0.482,0.583               0.391,0.615
Tmin'            0.312

Correction method= MULTI-SCAN

Data completeness= 1.74/0.99      Theta(max)= 27.500

R(reflections)= 0.0435( 3161)     wR2(reflections)= 0.1187( 4940)

S = 1.012                 Npar= 281
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT035_ALERT_1_B No _chemical_absolute_configuration info given . ?

Alert level C

Datablock 110524 - ellipsoid plot