Supporting Information

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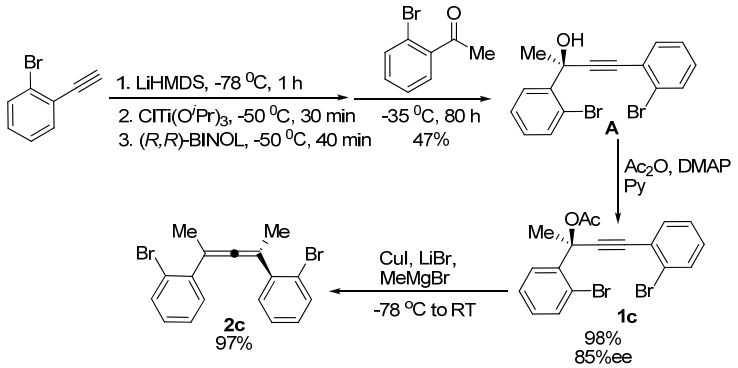
Method and Materials

General. Unless otherwise stated, reactions were performed using freshly purified solvents which were purified using solvent purification columns purchased from Glass Contour, Laguna Beach, CA. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Gas chromatography (GC) was performed on an HP 6890N autosampling GC with an HP-5 capillary column and equipped with a FID detector. Flash chromatography was performed with indicated solvents using silica gel (particle size 0.032-0.063m) purchased from Sorbent Technologies.^{1}H and ^{13}C NMR spectra were recorded on Varian Inova-400, 500 or Mercury-300 spectrometer. Chemical shift are reported relative to internal chloroform ($CDCl_3$: ^{1}H, δ = 7.27, ^{13}C, δ = 77.26). Coupling constants are in Hz and are reported as d (doublet), t (triplet), q (quartet). For signals having multiple coupling patterns, the coupling constant are listed in the same order as the pattern (e.g. dt, J = 2.0, 4.0; 2.0 is the coupling constant for the doublet and 4.0 is for the coupling constant for the triplet). ^{31}PNMR is using triphenylphosphine as external standard (CDCl3, δ = -6 ppm). HPLC analyses were carried out on a Shimadzu LC-2010A system. Optical rotations were measured on a Rudolph Research Analytical Autopol® IV Polarimeter (50/60 Hz). Infrared spectra were recorded on a Perkin- Elmer 1000 series FTIR. Mass spectra were acquired on a Shimadzu QP5000 GC/MS or Agilent technologies 1200 series LC/MS using indicated ionization methods.

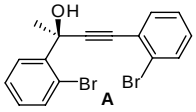
1. Syntheses of bisphosphine oxides

1.1 Procedure for the enantioselective synthesis of bis(bromobenzene)dimethylallene (Scheme 1). (Unoptimized)

Scheme 1



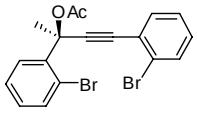
(*S*)-2,4-bis(2-bromophenyl)but-3-yn-2-ol (A). Following a known procedure,[1] an oven-dried Schlenk flask under a nitrogen atmosphere was charged with solution of 2-bromophenylacetylene (11 mmol, 2 g, 2.2 equiv) in 10 ml toluene. The flask was cooled to -78 °C. Lithium bis(trimethylsilyl)amide (10 mmol, 10 ml 1 M solution in THF, 2 equiv) was added into the flask drop-wise. The resulting solution was stirred at the same temperature for 1 h. After the flask was warmed to -50 °C (acetonitrile-dry ice bath) a 1 M solution of $Cl(TiO^{i}Pr)_3$ in toluene (10 mol, 10 ml, 2 equiv) was added drop-wise. The resulting yellow solution containing un-dissolved LiCl was stirred for 30 min maintaining the temperature around -50 °C. (*R*)-BINOL (1.5 mmol, 420.5 mg, 30 mol%) was directly added to the mixture under the protection of nitrogen. The flask was re-sealed and the reaction mixture was stirred for 40 min maintaining the temperature around -50 °C. Gradually the color of the reaction mixture turned orange. Bromophenylacetone (5 mmol, 1g, 1 equiv) was added slowly. The resulting mixture was warmed to -35 °C and stirred at the same temperature for 80 hours. The reaction was quenched by adding H_2O (2 ml) at a low temperature and diluted with Et_2O (10 ml). The reaction mixture was stirred at room temperature for 15 minutes, and then it was filtered through Celite. The collected phases were separated and the aqueous solution was extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting yellow oil was purified by flash chromatography on silica gel (100% hexane to 5% ethyl acetate in hexane) to give pure desired propargylic alcohol **A** (825 mg, 47% yield). The enantiomeric excess was determined after acylation.



Data for propargylic alcohol **A:**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.9, 1.7 Hz, 1H), 7.64 (dd, J = 7.9, 1.3 Hz, 1H), 7.57 (dd, J = 8.0, 1.3 Hz, 1H), 7.50 (dd, J = 7.6, 1.8 Hz, 1H), 7.36 (td, J = 7.6, 1.3 Hz, 1H), 7.26 (td, J = 7.6, 1.3 Hz, 1H), 7.14-7.21 (m, 2H), 3.28 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.5, 135.2, 133.7, 132.6, 129.9, 129.6, 127.8, 127.4, 127.2, 125.9, 125.0, 121.3, 96.2, 83.9, 70.5, 29.9; MS: ESI-MS (*m/z*): 362.9 $[M-H_2O]^+$, 402.9 $[M+Na]^+$; FTIR (neat) 2349, 1469, 1432, 1022, 753 cm^{-1}

[1] Cozzi, P. G. and Alesi, S., *Chem. Commun.*, **2004**, 2448-2449.

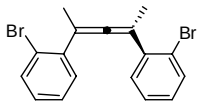


(*S*)-2,4-bis(2-bromophenyl)but-3-yn-2-yl acetate (1c): An oven-dried test tube with a Teflon-coated stir bar was charged with propargylic alcohol **A** (1.0 equiv, 2.17 mmol, 825 mg) and DMAP (20 mg, 0.07 equiv). Under nitrogen, pyridine (10 ml) and then acetic anhydride (4 equiv, 8.68 mmol, 891.7 mg, 0.825 ml) were added to the reaction solution. After stirring at rt for 12 h the reaction was quenched by adding saturated NH_4Cl (5 ml) slowly at 0 ^oC and diluted with Et_2O (30 ml). The reaction mixture was partitioned between Et_2O and water. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the resulting crude product was purified by flash chromatography on silica gel (100% hexane to 5% ethyl acetate in hexane) to give pure propargylic acetate **1c** (900 mg, 98%). The enantiomeric excess (ee) was determined to be 85% by chiral HPLC analysis (Chiracel OD-H column, 1% isopropanol in hexane, 0.5 mL/min, T_R=14.22 (major), 19.48 min).

Data for **1c**:

^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.59 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.36 (td, *J* = 7.9, 1.2 Hz, 1H), 7.29 (td, *J* = 7.7, 1.2 Hz, 1H), 7.21 (td, *J* = 7.9, 1.7 Hz, 1H), 7.16 (td, *J* = 7.6, 1.7 Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H).

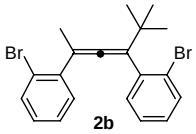
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 139.5, 135.6, 133.9, 132.6, 130.1, 130.0, 129.6, 127.6, 127.2, 126.0, 124.8, 119.3, 93.1, 86.2, 29.0, 21.5; FTIR (neat) 1748, 1469, 1426, 1366, 1231, 1023, 754 cm^{-1}. MS: ESI-MS (*m/z*): 362.9 $[M\text{-}OAc]^+$.



2,2'-(penta-2,3-diene-2,4-diyl)bis(bromobenzene) (2c): An oven-dried Schlenk flask (50 mL in volume) with a Teflon-coated stir bar was charged with CuI (10 equiv, 30 mmol, 5.7 g) and LiBr (10 equiv, 30 mmol, 2.6 g) under a nitrogen atmosphere. The flask was cooled to -78^oC. A solution of 3.0 M MeMgBr in THF (10 equiv, 30 mmol, 3 ml) was added to the flask drop-wise. The resulting solution was warmed up to 0 ^oC and stirred at the same temperature for 20 min. The flask was cooled to -78 ^oC, a solution of propargylic acetate **1c** in 5 ml THF (1 equiv, 3 mmol, 1.24 g) was added drop-wise to the reaction. The resulting mixture was allowed to warm to room temperature over 1 h and stirred at the same temperature for 2 h. The reaction was quenched by adding saturated aqueous NH_4Cl solution (10 ml) very carefully and slowly at 0 ^oC. (Caution: substantial gas evolution). The resulting mixture was diluted with Et_2O (30 ml) and stirred at room temperature for 5 minutes. The aqueous layer was separated and extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting yellow oil was purified by flash chromatography on silica gel (100% hexane to 2% ethyl acetate in hexane) to give pure 2,2'-(penta-2,3-diene-2,4-diyl)bis(bromobenzene) **2c** (1.1 g, 97% yield).

^1HNMR: (400, $CDCl_3$) δ = 7.31 (d, *J* = 6.4, 2H), 7.00 (m, 4H), 6.82, (t, *J* = 1.6, 2H), 1.88 (s, 6H); ^{13}CNMR:(100 $CDCl_3$) δ = 203.5, 140.0, 133.5, 130.0, 128.4, 127.4, 123.0, 100.9, 20.3; MS: EI-MS (*m/z*): 378 $[M]^+$, 299, 218, 203.

Similarly, **2,2'-(5,5-dimethylhexa-2,3-diene-2,4-diyl)bis(bromobenzene)** (**2b**) was synthesized according to this procedure but using CuCN and ^{t}BuLi.



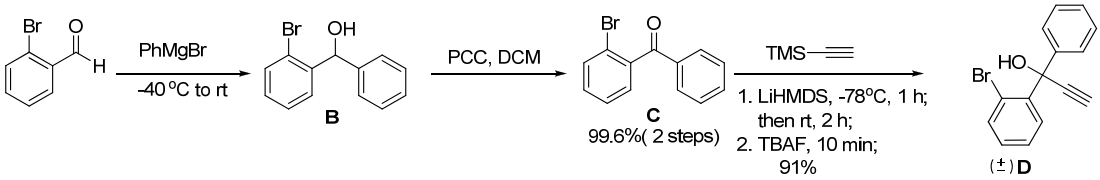
2b

^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.19-7.26 (m, 4H), 7.16 – 7.04 (m, 2H), 2.14 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.80, 140.53, 138.54, 133.15, 133.02, 131.52, 130.68, 128.41, 128.37, 127.36, 126.60, 125.37, 122.88, 113.70, 102.79, 36.34, 30.04, 19.69; MS: EI-MS (*m/z*): 363 $[M\text{-}^tBu]^+$; FTIR (neat) 2964, 1466, 1429, 1360, 1024, 745cm^{-1}

1.2 Procedure for the enantioselective preparation of bis(2-bromophenyl)diphenyllallene (2d).

Synthesis of 1-(2-bromophenyl)-1-phenylprop-2-yn-1-ol (**D**)

Scheme 2



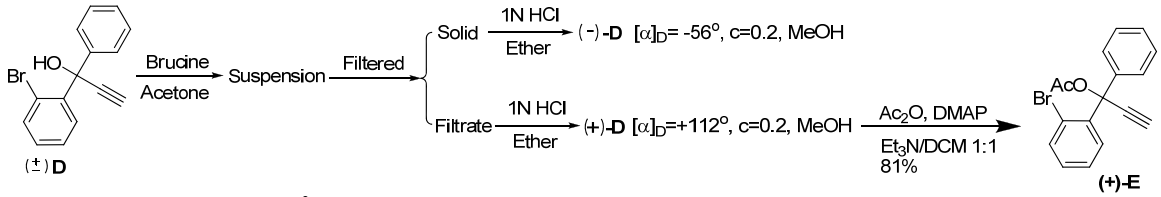
A solution of 2-bromobenzaldehyde (1 equiv, 15 mmol, 2.78 g,) in 50 ml THF under a N_2 atmosphere was cooled to -40 ^oC. PhMgBr (2 equiv, 30 mmol, 10 ml 3 M solution in THF) was added drop-wise. The resulting solution was then allowed to warm to room temperature and stirred at the same temperature for 1 h. The reaction was quenched by adding saturated aqueous NH_4Cl solution (10 ml) very slowly at 0 ^oC. The resulting solution was diluted with Et_2O (30 ml). The reaction mixture was stirred at room temperature for 5 minutes, and then separated. The aqueous solution was extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting yellow oil **B** was dissolved in 50 ml of DCM and transferred into a round bottom flask. Celite (5 g) and pyridinium chlorochromate (16 g, 5 equiv) were added and the resulting slurry was stirred at room temperature for 2 hours until the alcohol had been completely consumed as judged by TLC analysis. The reaction was diluted with 50 ml of diethyl ether causing substantial precipitation. The suspension was filtered through Celite, and the filtrate was concentrated under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel (100% hexane to 2% ethyl acetate in hexane) to give pure (2-bromophenyl)(phenyl)ketone **C** (4g, 99% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.67 – 7.62 (m, 1H), 7.63 – 7.56 (m, 1H), 7.43-7.48 (m, 2H), 7.41 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.38 – 7.31 (m, 2H).

A solution of trimethylsilyl acetylene (1.5 equiv, 15 mmol, 1.47 g) in 50 ml THF under a N_2 atmosphere was cooled to -78 ^oC. Lithium bis(trimethylsilyl)amide (15 mmol, 15 ml 1 M solution in THF, 1.5 equiv) was added drop-wise. The resulting solution was stirred at -78 ^oC for 1 h after which a solution of (2-bromophenyl)(phenyl)ketone **C** (1 equiv, 10 mmol, 2.61g) in THF (5 ml) was added into reaction solution. After addition, the resulting mixture was allowed to warm to room temperature and was stirred at the same temperature for 2 h. Tetra-*n*-butylammonium fluoride (TBAF, 2 equiv, 20 mmol, 20 ml of 1 M solution in THF) was added at room temperature and stirred at the same temperature for 10 minutes. The reaction was quenched by adding saturated aqueous NH_4Cl solution (10 ml) very slowly at 0 ^oC. The resulting solution was diluted with Et_2O (30 ml) and then separated. The aqueous solution was extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting yellow oil was purified by flash chromatography on silica gel (100% hexane to 5% ethyl acetate in hexane) to give pure 1-(2-bromophenyl)-1-phenylprop-2-yn-1-ol **D** (2.62 g, 91% yield; characterization data below).

Resolution of propargylic alcohol **D**.

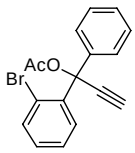
Scheme 3



Following a known procedure[3] an oven-dried round bottom flask (10 mL in volume) with a Teflon-coated stir bar was charged with racemic1-(2-bromophenyl)-1-phenylprop-2-yn-1-ol **D** (1 equiv, 1 mmol, 281 mg). Acetone (6 ml) was added into the flask followed by addition of brucine (1 equiv, 1 mmol, 395 mg). The resulting mixture was stirred at room temperature for 12 hours. During stirring the mixture first became nearly homogeneous and then a white precipitant formed. After 12 h, the mixture was filtered. The filtrate was treated with 1N HCl (10 ml) and diethyl ether (15 ml). The resulting mixture was stirred for 5 minutes and then separated. The aqueous solution was extracted with Et_2O (3 X 10 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. Removal of the solvent under reduced pressure provided the dextrorotatory enantiomer of **D** as a yellow oil (103 mg, 37% yield, $[\alpha]_D$= + 112^o, c=0.2 in MeOH). The solid was treated in an identical manner to provide the levorotatory enantiomer of **D** as a yellow oil (180 mg, 63% yield,).

Data for **D**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.22 (td, *J* = 7.6, 1.7 Hz, 1H), 3.24 (s, 1H), 2.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 141.7, 135.1, 129.9, 128.8, 128.6, 128.4, 127.5, 127.0, 122.1, 84.4, 76.6, 75.0; FTIR (neat) 3536, 3290, 1463, 1449, 1431, 1334, 1181, 1025, 980, 897, 756, 697, 662, 635 cm^{-1}; MS: ESI-MS (*m/z*): 270.9 $[M-H_2O]^+$, 556.9 $[2M-H_2O]^+$.

Optical Rotation: (+)-**D**: $[\alpha]_D$= + 112^o, c=0.2 in MeOH; (-)-**D**: $[\alpha]_D$= -56^o, c=0.2 in MeOH; Lit[2]: 100% optically active **D** $[\alpha]_D$= -114^o, c=0.2 in MeOH). See analysis of **E** and **1c** for analysis of ee by chiral shift reagent and HPLC, respectively.



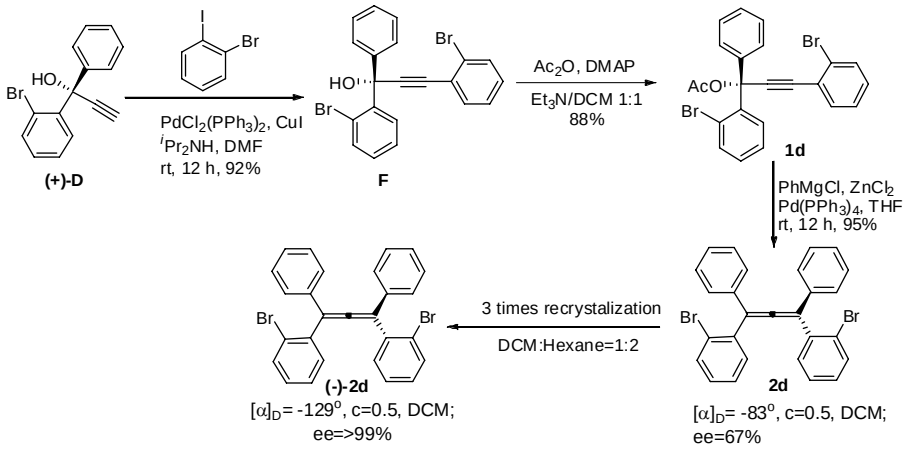
(+)-1-(2-bromophenyl)-1-phenylprop-2-ynyl acetate E: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.36 – 7.29 (m, 3H), 7.19 (td, *J* = 7.6, 1.6 Hz, 1H), 3.01 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =168.4, 140.7, 138.9, 135.6, 131.1, 130.1, 128.4, 128.3, 127.2, 127.0, 121.3, 81.7, 79.3, 29.5, 21.7; MS: ESI-MS (*m/z*): 270.9 $[M-OAc]^+$, 352.9 $[M+Na]^+$; FTIR (neat) 3286, 1755, 1466, 1366, 1228, 1027, 982, 757, 697 cm^{-1}

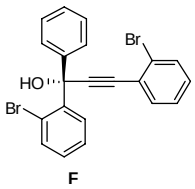
Enantiomer excess (ee) of **E** was determined to be ca. 75% by NMR analysis of its acetate in $CDCl_3$ with the chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-d-camphorato]europium(III), $Eu(hfc)_3$ (Aldrich, 99+%). (Spectra provided below.)

Synthesis of **1,3-bis(2-bromophenyl)-1,3-diphenylpropa-1,2-diene** (**Scheme 4**)

Scheme 4

[3] Toda, F. and Tanaka, K. *Tetrahedron. Lett*., **1981**, 4669-4672

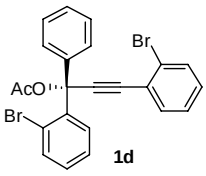




F

(*R*)-1,3-bis(2-bromophenyl)-1-phenylprop-2-yn-1-ol F: An oven-dried test tube (16 X 100 mm, 10 mL in volume) with a Teflon-coated stir bar was charged with enantiomerically enriched (+)-**D** (1 equiv, 0.58 mmol, 162 mg), CuI (6 mol%, 0.036 mmol, 7 mg) and $PdCl_2(PPh_3)_2$ (3 mol%, 0.018 mmol, 13 mg) under a nitrogen atmosphere. DMF (1 ml) was added into the tube and then $^iPr_2NEt$ (5 equiv, 2.9 mmol, 0.41 ml) and 1-bromo-2-iodobenzene (1.5 equiv, 0.807 mmol, 248 mg) were added sequentially. The resulting solution was stirred at the rt for 20 h until the starting terminal alkyne had been completely consumed as judged by NMR analysis (TLC could not resolve starting material and product). The reaction was quenched by adding saturated aqueous NH_4Cl solution (2ml) and diluted with Et_2O (5 ml). The resulting mixture was stirred at room temperature for 5 min and then separated. The aqueous solution was extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting yellow oil was purified by flash chromatography on silica gel (100% hexane to 5% ethyl acetate in hexane) to give pure 1,3-bis(2-bromophenyl)-1-phenylprop-2-yn-1-ol **F** (236 mg, 92% yield).

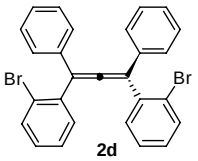
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.52 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.44 – 7.30 (m, 5H), 7.28 – 7.12 (m, 2H), 3.28 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 142.1, 135.1, 133.9, 132.7, 130.0, 129.8, 128.8, 128.5, 128.4, 127.42, 127.38, 127.2, 125.9, 124.9, 122.3, 94.4, 86.5, 75.6; MS: ESI-MS (*m/z*): 424.9 $[M-H_2O]^+$, 464.9 $[M+Na]^+$; FTIR (neat) 3533, 3061, 2361, 1469, 1449, 1434, 1336, 1162, 1123, 1056, 1026, 980, 896, 753, 697 cm^{-1}



1d

(*R*)-1,3-bis(2-bromophenyl)-1-phenylprop-2-ynyl acetate 1d: An oven-dried round bottom flask (10 mL in volume) with a Teflon-coated stir bar was charged with 1,3-bis(2-bromophenyl)-1-phenylprop-2-yn-1-ol **F** (1 equiv, 0.36 mmol, 158 mg) and DMAP (5mg, 0.1 equiv) under a N_2 atmosphere. DCM (2 ml) was added into the flask and followed by addition of Et_3N (2 ml). Acetic anhydride (20 equiv, 7.15 mmol, 0.68 ml) was added to the reaction solution slowly. The resulting solution was stirred at rt for 3 h until the starting material had been completely consumed as indicated by TLC analysis. The reaction was quenched by adding saturated aqueous NH_4Cl solution (3 ml) very slowly at 0 °C. The resulting solution was diluted with Et_2O (30 ml). The aqueous layer was separated and extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting solid was purified by flash chromatography on silica gel (100% hexane to 5% ethyl acetate in hexane) to give pure 1,3-bis(2-bromophenyl)-1-phenylprop-2-ynyl acetate **1d** (153 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.60 – 7.54 (m, 4H), 7.50 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.38 – 7.27 (m, 3H), 7.27 – 7.18 (m, 2H), 7.13-7.18 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 140.8, 139.5, 135.6, 133.9, 132.6, 131.2, 130.1, 130.0, 128.3, 128.2, 127.4, 127.2, 127.1, 126.0, 124.8, 121.5, 91.8, 89.2, 80.1, 21.8; MS: ESI-MS (*m/z*): 424.9[M-OAc]$^+$; FTIR (neat) 2361, 2343, 1752, 1468, 1364, 1224, 1178, 1026, 978, 754, 696, 668 cm^{-1}



2d

1,3-bis(2-bromophenyl)-1,3-diphenylpropa-1,2-diene 2d[4]

An oven-dried Schlenk flask (25 mL in volume) with a Teflon-coated stir bar was charged with freshly fused $ZnCl_2$ (2 equiv, 1.1 mmol, 150 mg) under a N_2 atmosphere. THF (4 ml) was added and then a solution of PhMgCl (2 equiv, 1.1 mmol, 0.55 ml of 2.0 M in ether) was added drop-wise. The resulting solution was stirred at room temperature for 15 min. The reaction mixture was cooled to -40 °C and a solution of $Pd(PPh_3)_4$ (5 mol%, 0.0275 mmol, 32 mg) in THF (1 ml) was added via cannula. A solution of 1,3-bis(2-bromophenyl)-1-phenylprop-2-ynyl acetate **1c** (1 equiv, 0.55 mmol, 266 mg) in THF (1 ml) was added to the reaction via syringe. The resulting mixture was allowed to warm to room temperature slowly and stirred at the same temperature for 12 h. The reaction was quenched by adding saturated aqueous NH_4Cl solution (5 ml) very slowly. The resulting solution was diluted with Et_2O (10 ml). The reaction mixture was stirred at room temperature for 5 min and then separated. The aqueous solution was extracted with Et_2O (3 X 10 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting solid was purified by flash chromatography on silica gel (100% hexane to 2% ethyl acetate in hexane) to give pure 1,3-bis(2-bromophenyl)-1,3-diphenylpropa-1,2-diene **2c** (262 mg, 95% yield, $[\alpha]_D$= -83°, c=0.5 in DCM). The enantiomer excess (ee) was

[4] Elsvier, C. J., Stehouwer, P. M., Westmijze, H. and Vermeer, P., *J. Org. Chem*. **1983**, 48, 1103-1105

determined to be 67% by chiral HPLC analysis (Chiracel OD-H column, 0.1% isopropanol in hexane, 1 mL/min, T_R: 11.7 min, 12.2 min (major)).

After recrystalized from DCM/Hexane (1:2) for 3 times, 100% optically pure enantiomer **(-)-2c** was obtained ($[\alpha]_D$= -129°, c=0.5 in DCM).

Spectra data of **2c**:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 2H), 7.46 – 7.32 (m, 12H), 7.23-7.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.0, 137.0, 135.3, 133.4, 132.3, 129.6, 128.9, 127.8, 127.8, 127.3, 124.6, 112.5; MS: EI-MS (*m/z*): 502 $[M]^+$; HPLC: Chiracel OD-H column, 0.1% isopropanol in hexane, 1 mL/min, T_R: 12.2 min. FTIR (neat) 3057, 2361, 2343, 1595, 1492, 1470, 1446, 1432, 1046, 1027, 908, 764, 746, 692, 596 cm^{-1}

The absolute stereochemistry of **2c** was confirmed by X-ray crystallography (Fig A).

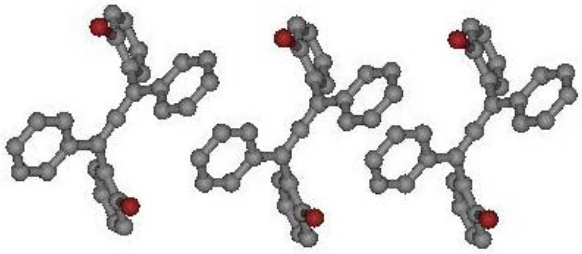
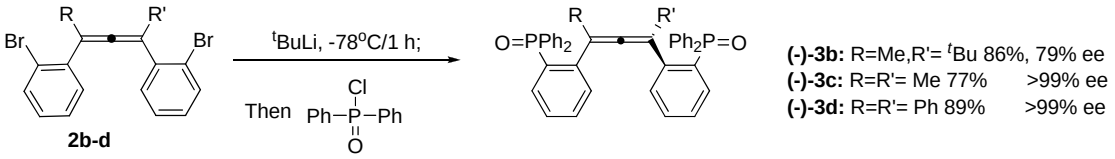


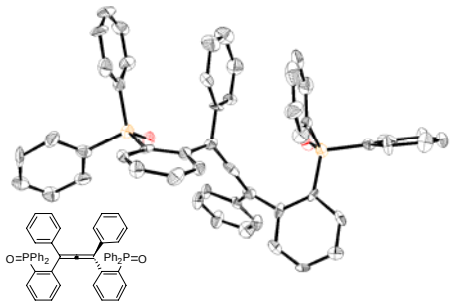
Figure A. Crystal structure of **2c**. Three molecules in the unit cell. Single crystals were grown by slow evaporation from a solution in hexanes/CH_2Cl_2.

1.3 General procedure for syntheses of 1,3-bis(2-(diphenylphosphoryl)phenyl)-1,3-dialkyl/diaryl propa-1,2-diene (Scheme E)

Scheme E



General procedure: An oven-dried round bottom flask (10 mL in volume) with a Teflon-coated stir bar was charged with **2** (1 equiv, 0.13 mmol, 66 mg) under a N_2 atmosphere. Diethyl ether (3 ml) was added and then the flask was cooled to -78 °C. ^{t}BuLi (5 equiv, 0.66 mmol, 0.39 ml 1.7 M solution in pentane) was added into the flask drop-wise. The resulting solution was stirred at -78 °C for 1 h before a solution of diphenylphosphinic chloride (4 equiv, 0.53 mmol, 124 mg) in ether (1 ml) was added to reaction via syringe. After addition, the resulting mixture was allowed to warm to room temperature and was stirred at the same temperature for 12 h. The reaction was quenched by adding saturated aqueous NH_4Cl solution (3 ml) very slowly at 0 °C. The resulting solution was diluted with ethyl acetate (10 ml) and then separated. The aqueous solution was extracted with ethyl acetate (3 X 10 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting solid was purified by flash chromatography on silica gel (100% ethyl acetate to 5% methanol in ethyl acetate) to give pure bisphosphine oxide.

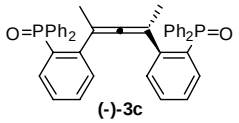


Data for **1,3-bis(2-(diphenylphosphoryl)phenyl)-1,3-diphenylpropa-1,2-diene (-)-3d**: yield: 89%,

$[\alpha]_D$= -83°, c=0.5 in DCM; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.11 (m, 24H), 7.07 – 6.85 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.6 (center C of allene), 112.5 (terminal C of allene). Other peaks cannot be interpreted because of the overlap; C-P coupling signals are overlapped with aryl-carbons; spectrum provided below); ^{31}P NMR (121 MHz, $CDCl_3$) δ 29.0; MS: ESI-MS (*m/z*): 745.1 $[M+H]^+$, 767.1 $[M+Na]^+$; HPLC: enantiomeric excess (ee) was determined by chiral HPLC analysis, >99% ee (Chiral OD-H column, 3% ethanol in hexane, 1 mL/min.T_R=25.8 min); FTIR (neat) 2924, 1438, 1130, 1035, 730, 694, 561, 540 cm^{-1}

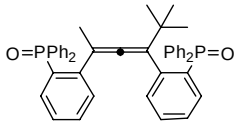
A single crystal suitable for X-ray diffraction was grown slow evaporation of a CH_2Cl_2/Tol (ca. 1:2) solution of **3d** (Fig B).

Fig B. X-ray structure of **3d**.



(-)-3c

(2,2'-(penta-2,3-diene-2,4-diyl)bis(2,1-phenylene))bis(diphenylphosphine oxide) 3c: yield: 77%. $[\alpha]_D$= -162°, c=0.1 in DCM, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 8H), 7.50 – 7.36 (m, 10H), 7.32 (td, *J* = 7.5, 2.9 Hz, 4H), 7.23 – 7.17 (m, 4H), 7.10 (dd, *J* = 7.3, 4.1 Hz, 2H), 1.39 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8 (center C of allene), 101.7 (terminal C of allene), 21.5 (Me). Other peaks could not be interpreted because of spectral overlap; C-P coupling signals are overlapped with aryl-carbons; spectrum provided below); ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.9; MS:LC-APCI-MS (*m/z*): 621.3 $[M+H]^+$; FTIR (neat) 3055, 2362, 2343, 1587, 1560, 1466, 1437, 1196, 1129, 1116, 1105, 730, 720, 695, 544, 526 cm^{-1}; HPLC: enantiomer excess (ee) was determined by chiral HPLC analysis, >99% ee after recrystalization from 70% ee product in DCM and hexane (Chiral OD-H column, 4% ethanol in hexane, 1 mL/min, T_R=31.4 min).

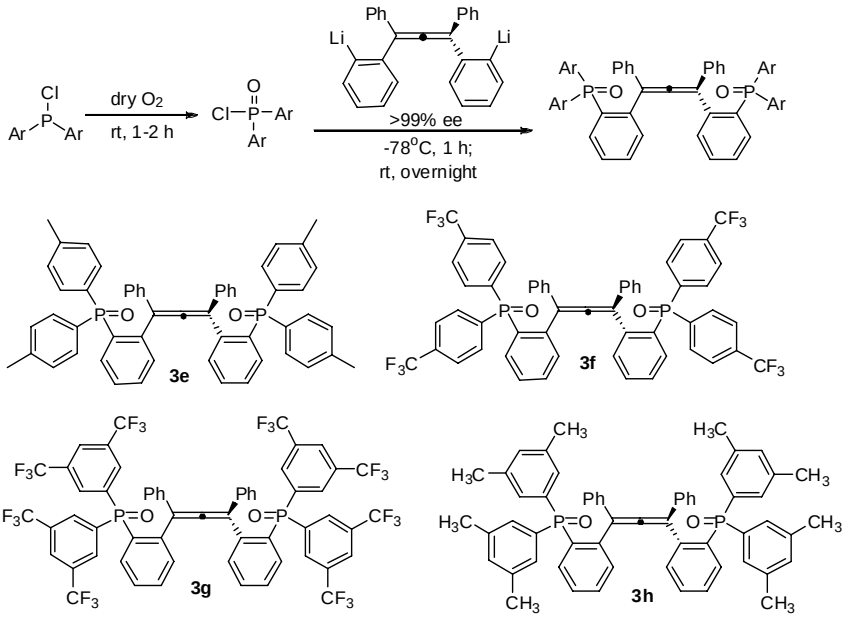


(2,2'-(5,5-dimethylhexa-2,3-diene-2,4-diyl)bis(2,1-phenylene))bis(diphenylphosphine oxide) 3b: yield:86%, ^{1}H, ^{13}C and ^{31}P NMR spectra indicated a ca. 2:1 ratio, presumably atropisomers; see attached spectra). Purified product was one peak by reverse phase HPLC (C_{18} column).

$[\alpha]_D$= -44°, c=0.1 in DCM; ^{1}H NMR (400 MHz, $CDCl_3$) shows two sets of protons (around 2:1). δ 7.91 (dd, *J* = 7.6, 4.3 Hz), 7.64 – 6.94 (m), 6.88 (t, *J* = 7.1 Hz), 6.78 (dd, *J* = 11.6, 7.4 Hz), 6.33 (dd, *J* = 7.3, 4.8 Hz), 1.94 (s), 1.62 (s), 1.31 (s), 1.05 (s); ^{13}C NMR (75 MHz, $CDCl_3$) there are two sets of ^{13}C signals. δ 201.56, 201.31 (center C of allene), 114.55, 113.84, 105.52, 104.98 (terminal C of allene), 37.37, 36.32, 30.76, 30.45(t-Butyl carbons), 22.33, 20.50 (Methyl carbon). Other peaks cannot be interpreted because of the overlap; C-P coupling signals are overlapped with aryl-carbons); ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.10, 30.97, 30.88, 27.50. (Four ^{31}P signals); MS: LC-APCI-MS (*m/z*): 663.3$[M+H]^+$; FTIR (neat) 2950, 1560, 1437, 1201, 1116, 743, 719, 696, 544 cm^{-1}

1.4 General procedure for syntheses of 1,3-bis(2-(diarylphosphoryl)phenyl)-1,3-diphenylpropa-1,2-diene (Scheme 6)

Scheme 6

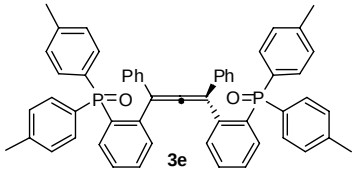


This procedure was modified from the literature.[5] An oven-dried test tube with a Teflon-coated stir bar was charged with diarylchlorophosphine (4 equiv, 0.4 mmol) under a N_2 atmosphere. Dried benzene (1 ml) was added via syringe and oxygen was bubbled through the reaction solution at RT with the following apparatus: An oxygen tank was connected to an empty flask; the outlet of that flask was connected to a bubbler containing H_2SO_4 (to dry the O_2; the empty flask was a safety precaution in case back pressure forced H_2SO_4 out of the bubbler). The outlet of the bubbler was split with a T-joint, one arm of which was connected to the reaction flask via a needle submerged in the reaction mixture. The second branch was equipped with a clamp to adjust flow. The outlet from the reaction flask was connected to a small trap with silicon oil for monitoring gas flux. The oxygen cylinder was opened and the delivery pressure was adjusted to a slow rate through the reaction mixture (1-2 bubbles/second through the silicon oil-filled bubbler). Gas was introduced for 1-2 hours before transfer. Another oven-dried test tube with a Teflon-coated stir bar was charged with (-)-1,3-bis(2-bromophenyl)-1,3-diphenylpropa-1,2-diene **2c** (1 equiv, 0.1 mmol) under a N_2 atmosphere. Diethyl ether (1 ml) was added and then the tube was cooled down to -78°C. ^{t}BuLi (3 equiv, 0.3 mmol, 1.7 M solution in pentane) was added into the tube drop-wise via syringe. The resulting solution was stirred at -78 °C for 1 hour. And then the solution of fresh-made diarylphosphinic chloride (4 equiv, 0.4 mmol) in benzene (1 ml) was transferred into reaction via cannula syringe. After addition, the resulting mixture was allowed to warm to room temperature and was stirred at the same

[5] Wu, H.; Yu, J.; Spencer, J. B., *Org. Lett*. **2004**, *6*, 4675-4678.

temperature for 12 h. The reaction was quenched by adding saturated aqueous NH_4Cl solution (2 ml) very slowly at 0 ^oC. The resulting solution was diluted with ethyl acetate (10 ml) and then separated. The aqueous solution was extracted with ethyl acetate (3 X 10 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting solid was purified by flash chromatography on silica gel (100% ethyl acetate to 5% methanol in ethyl acetate) to give pure bisphosphine oxides (**3e-3h**).

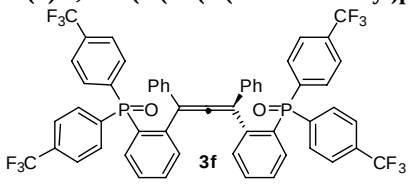
(*S*)-1,3-bis(2-(dip-tolylphosphoryl)phenyl)-1,3-diphenylpropa-1,2-diene 3e: yield: 33%



3e

$[\alpha]_D$= –58^o, c=0.1 in DCM; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 7.7, 6.6 Hz, 2H), 7.42 (dd, *J* = 7.4, 7.5 Hz, 2H), 7.36 – 7.19 (m, 11H), 6.89-6.95 (m, 14H), 6.82 (d, *J* = 7.1 Hz, 3H), 2.23 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ =206.5 (center C of allene), 112.5 (terminal carbon of allene), 21.7, 21.4 (two methyl carbons). Other peaks cannot be interpreted because of spectral overlap; C-P coupling signals are overlapped with aryl-carbons; see spectra below). ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.7; MS: ESI-MS (*m/z*): 801.4 $[M+H]^+$, 823.4 $[M+Na]^+$; FTIR (neat) 3054, 2922, 2364, 1602, 1492, 1446, 1187, 1115, 807, 764, 729, 694, 659, 537 cm^{-1}.

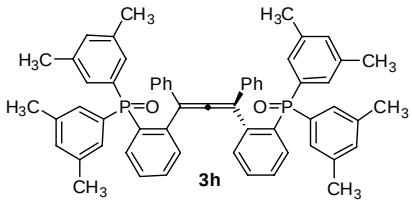
(*S*)-1,3-bis(2-(bis(4-(trifluoromethyl)phenyl)phosphoryl)phenyl)-1,3-diphenylpropa-1,2-diene 3f: yield:61%,



3f

$[\alpha]_D$= –60^o, c=0.5 in DCM; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.52 (m, 14H), 7.52 – 7.35 (m, 6H), 7.16 (d, *J* = 6.4 Hz, 4H), 6.96-7.07 (m, 6H), 6.82 (d, *J* = 7.1 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.9 (center C of allene), 112.2 (terminal C of allene), Other peaks cannot be interpreted because of spectral overlap; C-P and C-F coupling signals are overlapped with aryl-carbons; see spectra below); ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.54, -63.60; MS: EI-MS (*m/z*): 1017.15 $[M+H]^+$, 1039.05 $[M+Na]^+$; FTIR (neat) 2361, 2343, 1399, 1322, 1169, 1130, 1062, 1018, 836, 711, 668, 543 cm^{-1}.

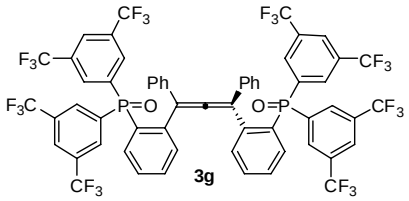
Data for 1,3-bis(2-(bis(3,5-dimethylphenyl)phosphoryl)phenyl)-1,3-diphenylpropa-1,2-diene 3g: yield:58%



3h

$[\alpha]_D$= –360^o, c=0.1 in $CHCl_3$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.65 (m, 2H), 7.46 (dt, *J* = 25.6, 7.3 Hz, 2H), 7.31 – 7.21 (m, 4H), 7.11 (d, *J* = 12.5 Hz, 4H), 7.00 – 6.72 (m, *J* = 27.3, 14.2 Hz, 18H), 2.14 (s, 12H), 2.08 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.8 (center C of allene), 112.6 (terminal C of allene), 21.50, 21.47 (two methyl carbons). Other peaks cannot be interpreted because of spectral overlap; C-P coupling signals are overlapped with aryl-carbons; see spectra below); ^{31}P NMR (121 MHz, $CDCl_3$) δ 29.94; MS: ESI-MS (*m/z*): 857.30 $[M+H]^+$, 879.35 $[M+Na]^+$; FTIR (neat) 3410, 2921, 2361, 2343, 1638, 1274, 1131, 850, 727, 691, 576 cm^{-1}

Data for **1,3-bis(2-(bis(3,5-bis(trifluoromethyl)phenyl)phosphoryl)phenyl)-1,3-diphenylpropa-1,2-diene 3h**: yield:35%

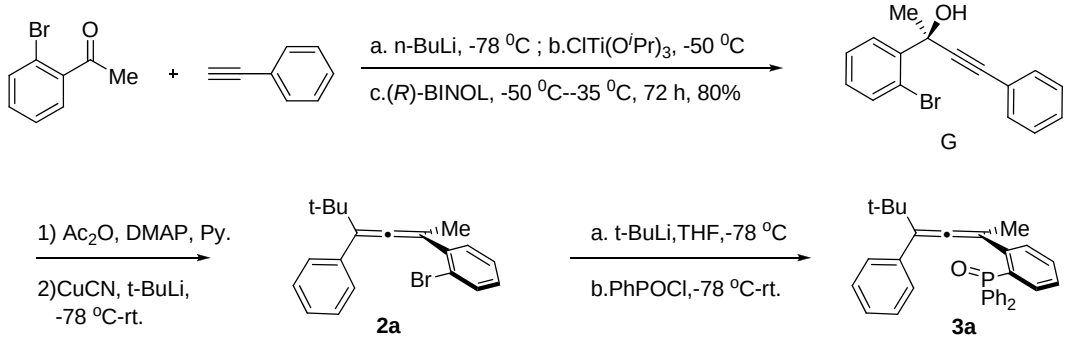


3g

$[\alpha]_D$= –32^o, c=0.5 in DCM; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.69 (m, 14H), 7.50-7.61 (m, 6H), 6.98 – 6.76 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.1 (center C of allene), 112.0 (terminal C of allene). Other peaks cannot be interpreted because of spectral overlap; C-P and C-F coupling signals are overlapped with aryl-carbons; see spectra below); ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.48; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.35, -63.37; MS: ESI-MS (*m/z*): 1289.00 $[M+H]^+$, 1311.00 $[M+Na]^+$; FTIR (neat) 2365, 1280, 1132 cm^{-1}.

1.5 The procedure for syntheses of (*R*)-(2-(5,5-dimethyl-4-phenylhexa-2,3-dien-2-yl)phenyl)diphenylphosphine oxide (3a)

(Scheme 7)



(*S*)-2-(2-bromophenyl)-4-phenylbut-3-yn-2-ol (G)

An oven-dried Schlenk flask (15 mL in volume) with a Teflon-coated stir bar was charged with a solution of 2-bromophenylacetylene (3.2 mmol, 326.4mg, 1.6 equiv) in 2 ml toluene under N_2. The flask was cooled to -78 ^oC. *n*-Butylithium solution (3 mmol, 1.2 ml 2.5M solution in Hexane, 1.5 equiv) was added into the flask drop-wise. The resulting solution was stirred at the same temperature for 1 h. After the flask was warmed to -50 ^oC by transferring it to an acetonitrile-dry ice bath, a 1 M solution of $Cl(TiO^iPr)_3$ in toluene (3 mol, 3ml, 1.5 equiv) was added drop-wise to the reaction mixture. The resulting yellow solution containing un-dissolved LiCl was stirred for 30 minutes maintain the temperature around -50 ^oC. (*R, R*)-BINOL (0.5 mmol, 143 mg, 25 mol %) was directly added to the mixture under the protection of nitrogen. The flask was re-sealed and the reaction mixture was stirred for 40 min maintaining the temperature around -50 ^oC. Gradually the color of the reaction mixture turned orange. Bromophenylacetone (2 mmol, 400mg, 1 equiv) was added slowly. The resulting mixture was warmed to -35^oC and stirred at the same temperature for 72 hours. The reaction was quenched by adding H_2O (2 ml) at a low temperature and diluted with Et_2O (10 ml). The reaction mixture was stirred at room temperature for 15 minutes, and then it was filtered through Celite. The collected phases were separated and the aqueous solution was extracted with Et_2O (3 X 20 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting yellow oil was purified by flash chromatography on silica gel (100% hexane to 5% ethyl acetate in hexane) to give pure desired propargylic alcohol **G** (482 mg, 70% ee, 80% yield).

$[\alpha]_D$= -6.8^o, c=0.15 in $CHCl_3$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.44-7.46 (m, 2H), 7.34 (dd, *J* = 7.6, 8.0 Hz, 1H), 7.28-7.31 (m, 3H), 7.17 (dd, *J* = 7.2, 7.1 Hz, 1H), 3.20 (s, 1H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.0, 135.2, 131.9, 129.4, 128.7, 128.5, 127.8, 127.1, 122.8, 121.4, 91.8, 85.1, 70.2, 29.9; MS: EI-MS (*m/z*): 285[M-OH]$^+$, 221, 185, 178; HPLC condition: Chiracel OD-H column, 1% isopropanol in hexane, 0.5 mL/min, T_R= 50.2 (major), 56.9 min.

(*R*)-1-bromo-2-(5,5-dimethyl-4-phenylhexa-2,3-dien-2-yl)benzene (2a)

An oven-dried test tube with a Teflon-coated stir bar was charged with propargylic alcohol **G** (1.0 equiv, 2 mmol, 614 mg) and DMAP (24 mg, 0.1 equiv). Under nitrogen, pyridine (4 ml) and then acetic anhydride (2 equiv, 4 mmol, 400 mg) were added to the reaction solution. After stirring at room temperature for 12 hours the reaction was quenched by adding saturated NH_4Cl (5 ml) slowly at 0 ^oC and diluted with Et_2O (30 ml). The reaction mixture was partitioned between Et_2O and water. The organic layer was separated and the aqueous solution was extracted with Et_2O (3 X 20 ml). The organic phases were combined and washed with brine, dried over $MgSO_4$. After removal of the solvent under reduced pressure, the resulting crude product was directly used for the next step. To the suspension of CuCN (890 mg, 10 mmol) in THF (10 mL), t-Butyl Lithium (1.7 M, 10 mmol) was added drop wise at -40 ^oC. After completion of addition, a solution of above acylation product in 10 mL THF was added into the solution at -78 ^oC. the mixture was slowly warmed up to room temperature for overnight. The reaction was quenched with saturated NH_4Cl solution, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting oil was purified by flash chromatography on silica gel (100% hexane to 1% ethyl acetate in hexane) to give desired allene product **2a** (650 mg, 71 % ee, 95% yield in two steps).

$[\alpha]_D$= –67.4^o, c=0.49 in $CHCl_3$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.26-7.36 (m, 7H), 7.10-7.13 (dt, *J* = 9.2, 4.8 Hz, 1H), 2.13 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 201.5, 141.2, 138.1, 133.3, 130.5, 129.8, 128.4, 127.9, 127.5, 126.7, 122.9, 115.8, 101.6, 35.4, 30.3, 20.9; MS: EI-MS (*m/z*): 342[M]$^+$, 285, 261, 203; HPLC condition: Chiracel OJ-H column, 1% isopropanol in hexane, 1 mL/min, T_R= 4.5 (major), 6.6 min.

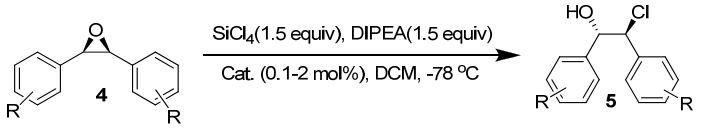
(*R*)- (2-(5,5-dimethyl-4-phenylhexa-2,3-dien-2-yl)phenyl)diphenylphosphine oxide (3a)

An oven-dried round bottom flask (10 mL in volume) with a Teflon-coated stir bar was charged with **2a** (1 equiv, 0.5 mmol, 170.66 mg) under a N_2 atmosphere. Diethyl ether (3 ml) was added and then the flask was cooled to -78 ^oC. ^{t}BuLi (1.5 equiv, 0.75 mmol, 0.44 ml 1.7 M solution in pentane) was added into the flask drop-wise through septum by syringe. The resulting solution was stirred at -78 ^oC for 1 hour. A solution of diphenylphosphinic chloride (1.1 equiv, 0.55 mmol, 130.24 mg) in ether (1 ml) was added to the reaction, and the resulting mixture was allowed to warm up room temperature and was stirred at the same temperature for 12 h. The reaction was quenched by adding saturated aqueous NH_4Cl solution (3 ml) very slowly at 0 ^oC. The resulting solution was diluted with ethyl acetate (10 ml) and then separated. The aqueous solution was extracted with ethyl acetate (3 X 10 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting solid was purified by flash chromatography on silica gel (50-100% ethyl acetate in hexane to 15% methanol in ethyl acetate) to give pure monophosphine oxide **3a** (199 mg, 86%, 70% ee).

$[\alpha]_D$= + 30.1^o, c=0.26 in $CHCl_3$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 5.6, 9.6 Hz, 1H), 7.25-7.51 (m, 11H), 7.19 (m, 3H), 7.11 (td, *J* = 1.6, 6.4 Hz, 2H), 6.94 (m, 2H), 1.78 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 201.1, 145.5, 145.3, 137.0, 135.0, 134.8, 132.3, 131.5, 131.3, 130.0, 128.7, 128.5, 128.3, 128.1, 127.7, 126.8, 126.6, 126.5, 115.4, 102.5, 35.6, 30.1, 23.3; MS: EI-MS (*m/z*): 462[M]$^+$, 406, 405, 249; HPLC condition: Chiracel OD-H column, 10% isopropanol in hexane, 1 mL/min, T_R= 5.2 (major), 5.8 min.

2. Representative procedure for epoxide opening with chiral bisphosphine oxides

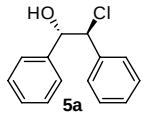
Scheme 8



Procedure I (0.1 mol% catalyst)**:** An oven-dried test tube (16 X 100 mm, 10 mL in volume) with a Teflon-coated stir bar was charged with *cis*-stilbene oxide (1 equiv, 0.1 mmol) under an atmosphere of N_2. A solution of bisphosphine oxide in DCM (0.1 mol%, 0.5 ml, 0.002

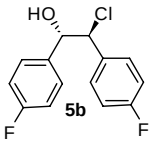
M solution) was added by syringe. $^{i}Pr_2NEt$ (1.5 equiv, 0.15 mmol, 26 µl) was added and then the tube was cooled to -78 °C. A solution of $SiCl_4$ (1.5 equiv, 0.15 mmol, 1.0 M solution in DCM) was added into the flask drop-wise by syringe. The resulting solution was stirred at -78 °C for the indicated time. The reaction was quenched by adding propylene oxide (0.1 ml) followed by adding saturated aqueous $NaHCO_3$ solution (0.7 ml) and saturated aqueous KF/KH_2PO_4 solution (0.7 ml) at -78 °C.[6] The resulting solution was warmed to room temperature and diluted with ether (3 ml). The aqueous solution was separated and extracted with ether (3 X 10 ml). The organic phases were combined and washed with brine, dried over magnesium sulfate and filtered. After removal of the solvent under reduced pressure, the resulting oil was purified by flash chromatography on silica gel (100% hexane to 2% ethyl acetate in hexane) to give pure chlorohydin product.[7]

Procedure II (2 mol% catalyst)**:** An oven-dried test tube (16 X 100 mm, 10 mL in volume) with a Teflon-coated stir bar was charged with bisphosphine oxide catalyst (2 mol%, 0.002 mmol) and *cis*-stilbene oxide (1 equiv, 0.1 mmol) under an atmosphere of N_2. DCM (5 mL) and dried $^{i}Pr_2NEt$ (1.5 equiv, 0.15 mmol, 26 µl) were added and the tube was cooled to –78 °C. A solution of $SiCl_4$ (1.5 equiv, 0.15 mmol, 1.0 M solution in DCM) was added into the flask drop-wise via syringe. The resulting solution was stirred at -78 °C for the indicated time. The product was isolated as in procedure 1.



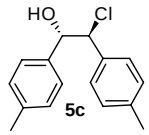
(1*S*,2*S*)-2-chloro-1,2-diphenylethanol 5a[9]: this compound was prepared by following procedure **I** using catalyst **3d**. Reaction time is 12-16 h at -78 °C. Colorless liquid, yield: 97%, ee: 94%.

$[\alpha]_D$= +21.2°, c=1.0 in $EtOH_3$; ^{1}HNMR: ($CDCl_3$) δ = 7.08-7.25 (m, 10H), 5.00 (d, J = 8.4), 4.94 (d, J = 8.4); HPLC: ee:94% , Chiral OD-H column, 3% isopropanol in hexane, 1 mL/min.T_R: 23.8 min (major) and 26.4 min (minor); MS: ESI-MS (*m/z*): 216[M-OH]$^+$.



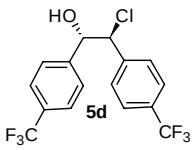
(*1S,2S*)-2-chloro-1,2-bis(4-fluorophenyl)ethanol 5b[10]: this compound was prepared by following procedure **I** using catalyst **3d**. Catalyst loading was 0.1 mol% (0.5 ml of 0.002 M solution in DCM). Reaction time is 36 h at -78 °C. Colorless liquid, yield: 96%, ee: 93%.

$[\alpha]_D$= –4.0°, c=0.85 in $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.14 (m, 2H), 7.05-7.07 (m, 2H), 6.90-6.95 (m, 4H), 4.53 (d, *J* = 8.4 Hz, 1H), 4.90 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =161.87 (d, *J* = 247), 161.76 (d, *J* = 247), 134.5 (d, *J* = 3.3), 133.6 (d, *J* = 3.8), 130.0 (d, *J* = 8.1), 128.9 (d, *J* = 8.2), 115.6 (d, *J* = 21), 115.3 (d, *J* = 21), 78.6, 70.0; MS: ESI-MS (*m/z*): 251.0 [M-HO]$^+$, 233.0 [M-Cl]$^+$; HPLC condition: Chiracel AD-H column, 3% isopropanol in hexane, 0.5 mL/min. T_R=:26.1 min (major), and 28.2 min (minor).



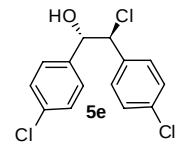
(*1S,2S*)-2-chloro-1,2-dip-tolylethanol 5c[10]**:** this compound was prepared by following procedure **I** using catalyst **3d**. Catalyst loading was 0.1 mol% (0.5 ml of 0.002 M solution in DCM). Reaction time is 12 h at -78 °C. Colorless liquid, yield: 92%, ee: 89%.

$[\alpha]_D$= –37°, c=0.8 in $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.01 (m, 4H), 4.98 (d, *J* = 8.0 Hz, 1H), 4.91 (d, *J* = 7.9 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.5, 138.0, 136.3, 135.3, 129.2, 129.0, 128.1, 127.1, 78.5, 70.9, 21.2; MS: ESI-MS (*m/z*): 243.0 [M-HO]$^+$, 225.1 [M-Cl]$^+$; HPLC: condition: Chiracel AD-H column, 10% isopropanol in hexane, 0.5 mL/min. T_R = 9.7 min (major), and 10.7 min (minor).



(*1S,2S*)-2-chloro-1,2-bis(4-(trifluoromethyl)phenyl)ethanol 5d[10]: this compound was prepared by following procedure **II** using catalyst **3d**. Catalyst loading was 2 mol% (2 ml DCM). Reaction time is 36 h at -78 °C. Colorless liquid, yield: 89%, ee: 87%.

$[\alpha]_D$= –11.9°, c=0.65 in $CHCl_3$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.04 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 142.5, 141.3, 131.2 (m), 130.8 (m), 128.7, 127.6, 125.8 (m), 125.1 (m), 125.1, 125.0, 78.1, 69.0; MS: ESI-MS (*m/z*): 392.0 [M+Na]$^+$, 374 [M-OH+ Na]$^+$; HPLC condition: Chiracel AD-H column, 10% isopropanol in hexane, 0.5 mL/min. T_R = 6.4 min (minor) and 8.5 min (major).

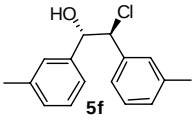


(1*S*,2*S*)-2-chloro-1,2-bis(4-chlorophenyl)ethanol 5e[14]: this compound was prepared by following procedure **I** using catalyst **3d**. Catalyst loading was 0.1 mol% (0.5 ml of 0.002 M solution in DCM). Reaction time is 36 h at -78 °C. Colorless liquid, yield: 89%, ee: 82%.

$[\alpha]_D$= –50.2°, c=0.85 in $CHCl_3$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 4.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.1,

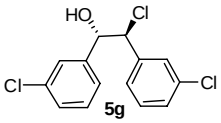
[6] Denmark, S. E.; Barsanti, P. A.; Beutner, G. L. Wilson, T. W. *Adv. Synth. Catal.* **2007**, *349*, 567.
[7] We found that the quality of the $SiCl_4$ was important. Clear solution without obvious precipitants worked well. Lower ee's were observed when the $SiCl_4$ showed evidence of hydrolysis.
[9] Denmark, S. E.; Barsant, P. A.; Wong, K.-T.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63*, 2428.
[10] Tao, B.; Lo, M.-C.; Fu, G. *J. Am. Chem. Soc*. **2001**, *123*, 353.

136.1, 134.8, 134.4, 129.6, 128.9, 128.7, 128.6, 78.3, 69.6; MS: ESI-MS (*m/z*): 284.9 $[M-H_2O]^+$, 306.0 $[M-H_2O+Na]^+$; HPLC condition, Chiracel AD-H column, 3% isopropanol in hexane, 0.5 mL/min. T_R= :10.5 min (minor) ,and 12.7 min (major).



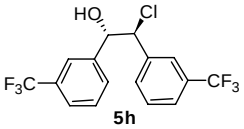
(1*S*,2*S*)-2-chloro-1,2-dim-tolylethanol 5f: this compound was prepared by following procedure **I** using catalyst **3d**. Catalyst loading was 0.2 mol% (1 ml of 0.002 M solution in DCM). Reaction time is 36 h at -78 ^oC. Colorless liquid, yield: 89%, ee: 91%.

^1H NMR (400 MHz, $CDCl_3$) δ 7.18 – 6.94 (m, 7H), 6.88 (d, *J* = 7.4 Hz, 1H), 4.99 (d, *J* = 7.9 Hz, 1H), 4.93 (d, *J* = 7.9, 2.8 Hz, 1H), 2.99 (d, *J* = 2.9 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ = 139.0, 138.2, 137.96, 137.92, 129.5, 129.1, 128.8, 128.4, 128.2, 127.7, 125.3, 124.3, 78.7, 71.0, 21.6, 21.5; MS: ESI-MS (*m/z*): 243.0 $[M-H_2O]^+$, 225.0 $[M-Cl]^+$; HPLC: ee: 91% , Chiral OD-H column, 2% isopropanol in hexane, 0.5 mL/min. T_R:20 min (major) and 23 min (minor); FTIR (neat) 3426, 3025, 2921, 2361, 1608, 1489, 1456, 1260, 1155, 1057, 775, 724, 702, 639 cm^{-1}



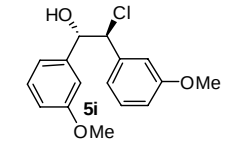
(1*S*,2*S*)-2-chloro-1,2-bis(3-chlorophenyl)ethanol 5g: this compound was prepared by following procedure **II** using catalyst **3d** 2 mol% DCM(2 ml) was used. Reaction time is 12 h at -78 ^oC. Colorless liquid, yield: 96%; ee: 90 %.

^1H NMR (400 MHz, $cdcl_3$) δ 7.32 – 7.07 (m, 6H), 7.02 – 6.98 (td, *J* = 1.4, 7.8 Hz , 1H), 6.92 – 6.88 (td, *J* = 1.4, 7.8 Hz, 1H), 4.99 – 4.79 (m, 2H), 3.01 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 140.6, 139.5, 134.6, 134.5, 129.9, 129.7, 129.2, 128.8, 128.3, 127.2, 126.4, 125.4, 78.1, 69.3; MS: ESI-MS (*m/z*): 284.9 $[M-H_2O]^+$, 306.0 $[M-H_2O+Na]^+$; HPLC: Chiral OD-H column, 3% isopropanol in hexane, 0.5 mL/min. T_R:30 min (minor) and 40.6 min (major); FTIR (neat) 3420, 2923, 2852, 2360, 1575, 1477, 1432, 1190, 1080, 884, 764, 694 cm^{-1}



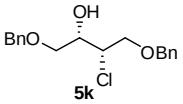
(1*S*,2*S*)-2-chloro-1,2-bis(3-(trifluoromethyl)phenyl)ethanol 5h: this compound was prepared by following procedure **II** using catalyst **3d**. DCM (2 ml) was used. Reaction time is 48 h at -78 ^oC. Colorless solid, yield: 91%, ee: 88 %.

^1H NMR (400 MHz, $cdcl_3$) δ 7.51 (dd, *J* = 15.8, 7.5 Hz, 2H), 7.36 (m, 4H), 7.29 – 7.24 (m, 2H), 4.99 (s, 2H), 3.07 (s, br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 138.3, 131.5(q, *J* = 1.2 Hz), 131.1 (q, *J* = 32 Hz), 130.9 (q, *J* = 32 Hz), 130.4 (q, *J* = 1.2 Hz), 129.2, 129.0, 125.8 (q, *J* = 3.7 Hz), 125.5 (q, *J* = 3.7 Hz), 125.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 3.8 Hz),123.9 (q, *J* = 272 Hz), 123.8 (q, *J* = 272 Hz), 78.4, 69.1; MS: ESI-MS (*m/z*): 351.0 $[M-H_2O]^+$, 374.0 $[M-H_2O+Na]^+$; HPLC: Chiral AD-H column, 8% isopropanol in hexane, 0.5 mL/min. T_R:6.5 min (minor) and 7.2 min (major); FTIR (neat) 3417, 2923, 1451, 1331, 1167, 1127, 1074, 906, 812, 701 cm^{-1}



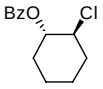
(*1S,2S*)-2-chloro-1,2-bis(3-methoxyphenyl)ethanol 5i: this compound was prepared by following procedure **I** using catalyst **3d**. Catalyst loading was 0.2 mol% (1 ml of 0.002 M solution in DCM). Reaction time is 16 h at -78 ^oC. Colorless liquid, ee: 88%, yield: 95%.

$[\alpha]_D$= –17.5^o, c=0.8 in $CHCl_3$; ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 – 7.27 (m, 2H), 6.70 – 6.80 (m, 6H), 4.97 (d, *J* = 5.4 Hz, 1H), 4.92 (d, *J* = 5.6 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 159.65, 159.62, 140.6, 139.4, 129.6, 129.4, 120.6, 119.6, 114.4, 114.3, 113.8, 112.5, 78.8, 70.6, 55.5, 55.4. MS: ESI-MS (m/z): 275.0 $[M-HO]^+$, 257.1 $[M-Cl]^+$. HPLC condition, Chiracel AD-H column, 15% isopropanol in hexane, 0.5 mL/min. T_R = 13.2 min (major), 14.3 min (minor).



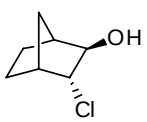
(2*S*,3*S*)-1,4-bis(benzyloxy)-3-chlorobutan-2-ol 5k[9]: this compound was prepared by following procedure **II** using 2 mol% catalyst **3d**. DCM (2 ml) was used. Reaction time is 36 h at -78 ^oC. Colorless liquid, yield: 90%, ee: 60%

$[\alpha]_D$=+2.3^o, c=1.33 in EtOH. ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 10H), 4.64 – 4.49 (m, 4H), 4.31 – 4.23 (td, *J* = 6.1, 2.5 Hz, 1H), 4.18 (td, *J* = 6.1, 2.5 Hz, 1H), 3.85 (ddd, *J* = 10.2, 6.2, 1.6 Hz, 1H), 3.76 (ddd, *J* = 10.2, 5.5, 1.6 Hz, 1H), 3.66 – 3.53 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 137.7, 128.74, 128.70, 128.16, 128.09, 128.02, 127.99, 73.8, 73.74, 7.8, 71.3, 70.3, 61.0; HPLC condition, Chiral OD-H column, 4% ethanol in hexane, 1mL/min. T_R:21.8 min (major) and 25.2 min (minor); FTIR (neat) 3443, 3064, 3031, 2919, 2865, 1722, 1496, 1454, 1364, 1207, 1102, 1028, 737, 698 cm^{-1}



(1*S*,2*S*)-2-chlorocyclohexyl benzoate 5l[9]: this compound was prepared from alcohol, which was generated by following procedure **I** using catalyst **3d**. Reaction time is 1 h at -78 ^oC. Colorless liquid, yield: 95%

^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.03-5.08 (m, 1H), 4.00-4.06 (m, 1H), 2.41 – 2.11 (m, 2H), 1.90 – 1.68 (m, 3H), 1.58 – 1.29 (m, 3H); ^{13}C NMR (126 MHz, $cdcl_3$) δ =165.9, 133.2, 130.5, 129.9, 128.6, 76.6, 60.8, 34.9, 30.9, 24.6, 23.4; HPLC: ee was determined from benzoate **5l**: 29% , Chiral OD-H column, 0.2% isopropanol in hexane, 1mL/min. T_R: 12.4 min(major) and 13.8 min(minor); FTIR (neat) 2920, 2361, 2343, 1720, 1450, 1267, 1108, 710 cm^{-1}.

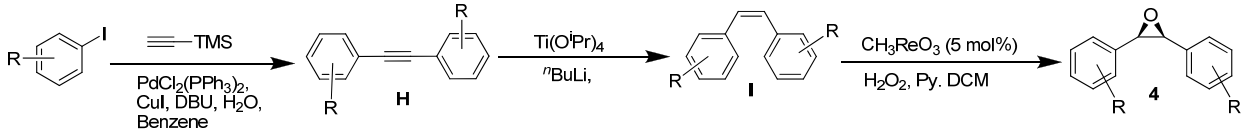


(1*S,2*R**,3*R**,4*R**)-3-chlorobicyclo[2.2.1]heptan-2-ol**: this compound was prepared by following procedure **I** using catalyst **3c**. Catalyst loading was 0.1 mol% (0.5 ml of 0.002 M solution in DCM). Reaction time is 36 h at -78 ^oC. Colorless liquid, yield: 76%, ee: 50%.

$[\alpha]_D$= –18.6°, c=0.19 in $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02-4.06 (m, 2H), 2.36 (m, 1H), 2.32 (m, 1H), 2.24 (t, *J* = 4.4 Hz, 1H), 2.16 (dd, *J* = 8.8, 10.4 Hz, 1H), 1.68 (m, 1H), 1.53(m, 1H), 1.11 (quintet, *J* = 10.4 Hz, 1H), 1.10 (quintet, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 80.8, 61.4, 48.4, 42.0, 41.3, 25.3, 24.7. GC condition: Astec Chiraldex G-TA, 100 °C, 1.60 mL/min carrier gas flow. T_R= 29.5 min (major), 31.9 min (minor).

3. Representative procedure for synthesis of diaryepoxide. (Scheme 8)

Scheme 8

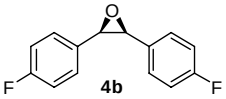


The first intermediate **H** was synthesized according to the known procedure.[11] Thus, an oven-dried test tube (16 X 100 mm, 10 mL in volume) with a Teflon-coated stir bar was charged with CuI (10 mol%, 0.1 mmol, 19 mg) and $PdCl_2(PPh_3)_2$ (63 mol%, 0.06 mmol, 42 mg) under a N_2 atmosphere. Benzene (5 ml) was added into the tube and then iodobenzene (1 equiv, 1 mmol), H_2O (0.4 equiv, 0.4 mmol, 7.2 mg) and DBU (6 equiv, 6 mmol, 0.897 ml) were added sequentially by syringe. Trimethylsilylacetylene (0.5 equiv, 0.5 mmol, 49 mg) was added last. The test tube was packaged by aluminum foil to protect from light. The resulting solution was heated to 60 °C and stirred at the same temperature for 12-24 hours until the starting material had been completely consumed as judged by TLC analysis. The reaction was quenched by adding saturated aqueous NH_4Cl (2ml) and diluted with Et_2O (3 ml). The resulting mixture was stirred at room temperature for 5 minutes, and then separated. The aqueous solution was extracted with Et_2O (3 X 10 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting crude product was purified by flash chromatography on silica gel (100% hexane to 1% ethyl acetate in hexane) to give pure coupling products **H**.

A know procedure[12] is followed for the second step. An oven-dried test tube (16 X 100 mm, 10 mL in volume) with a Teflon-coated stir bar was charged with the diarylalkyne **H** (1 equiv, 0.45 mmol) under a N_2 atmosphere. THF (2 ml) was added and the tube was cooled to -78 °C. $Ti(O^iPr)_4$ (2 equiv, 0.9 mmol, 0.263 ml) was added and then ^{n}BuLi (4 equiv, 1.8 mmol, 2.9 M in hexane, 0.62 ml) was added drop-wise. The resulting solution was warmed up to -50 °C and stirred at the same temperature for 2-4 h.[13] The reaction was quenched by adding saturated aqueous NH_4Cl solution (2 ml) and diluted with Et_2O (3 ml). The resulting mixture was stirred at room temperature for 5 minutes, and then separated. The aqueous solution was extracted with Et_2O (3 X 10 ml). The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting crude product was purified by flash chromatography on silica gel (100% hexane to 1% ethyl acetate in hexane) to give pure cis olefins **I**.

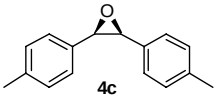
The last epoxidation step was using CH_3ReO_3 as catalyst.[10] An oven-dried test tube (16 X 100 mm, 10 mL in volume) with a Teflon-coated stir bar was charged with the diarylalkene **I** (1 equiv, 0.8 mmol) and then DCM (2 ml) was added. The test tube was cooled to 0 °C, CH_3ReO_3 (5 mmol%, 0.04 mmol, 10 mg) was added into this solution, and then pyridine (13 mol%, 9 µl) and H_2O_2 (3 equiv, 2.4 mmol, 100µl) were added. The test tube was capped with a rubber septum and sealed. The resulting solution was warmed up to room temperature and stirred at the same temperature for 40-48 h. The reaction was quenched by adding 15 mg of MnO_2 slowly and carefully. The resulting mixture was filtered through celite and rinsed by 5 ml of DCM. The organic phases were combined, washed with brine, and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the resulting crude product was purified by flash chromatography on silica gel (100% hexane to 5% ethyl acetate in hexane) to give pure epoxide products **4**.

***cis-2,3-bis(4-fluorophenyl)oxirane* 4b**[10].



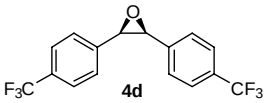
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.12 (m, 4H), 6.85- 6.89 (m, 4H), 4.31 (s, 2H).
MS: ESI-MS (*m/z*): 233.1 $[M+H]^+$, 255.1 $[M+Nal]^+$.

***cis*--2,3-dip-tolyloxirane 4c**[10].



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, *J* = 8.0 Hz, 4H), 6.98 (d, *J* = 8.0 Hz, 4H), 4.29 (s, 2H), 2.24 (s, 6H).
MS: ESI-MS (*m/z*): 225.1 $[M+H]^+$.
.

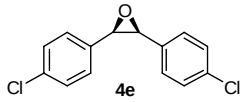
***cis*-2,3-bis(4-(trifluoromethyl)phenyl)oxirane 4d**[10].



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.2 Hz, 4H), 7.25 (d, *J* = 8.2 Hz, 4H), 4.43 (s, 2H).
MS: ESI-MS (*m/z*): 333.0 $[M+H]^+$, 374.0 $[M+H_2O+Nal]^+$.
.

[11] Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett*, **2002, *2***, *4* 3199.
[12] Lara-Ochoa, F. and Espinosa-Perez, G., *Tetrahedron Lett*. **2007**, 48, 7007-7010.
[13] For electron-deficient arylalkynes, some over-reduced products (alkanes) were observed.

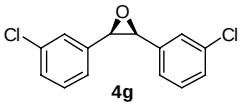
***cis*-2,3-bis(4-chlorophenyl)oxirane 4e**[14].



4e

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.5 Hz, 4H), 7.10 (d, *J* = 8.5 Hz, 4H), 4.33 (s, 2H).
MS: ESI-MS (*m/z*): 265.0 $[M+H]^+$.

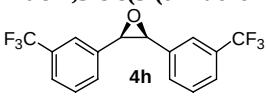
***cis*-2,3-bis(3-chlorophenyl)oxirane 4g**.



4g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 2.0 Hz, 2H), 7.10-7.16 (m, 4H), 7.05- 7.00 (m, 2H), 4.32 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 136.2, 134.2, 129.5, 128.2, 127.2, 125.1, 59.3.
FTIR (neat) 2981, 2361, 1600, 1574, 1480, 1426, 1357, 1182, 1076, 907, 781, 724, 692, 682, 599 cm^{-1}

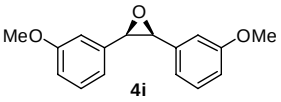
***cis*-2,3-bis(3-(trifluoromethyl)phenyl)oxirane 4h.**



4h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 - 7.37 (m, 4H), 7.28-7.35 (m, 4H), 4.44 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 135.0 (s), 130.7 (q, *J* = 32.6 Hz), 130.2 (s), 128.7 (s), 124.8 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 275.0 Hz), 123.8 (q, *J* = 4.0), 59.31 (s).
MS: ESI-MS (*m/z*): 333.0 $[M+H]^+$, 374.0 $[M+H_2O+Na]^+$.
FTIR (neat) 2363, 1448, 1332, 1282, 1156, 1120, 1095, 1071, 812, 704 cm^{-1}

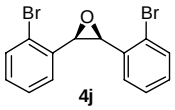
***cis*-2,3-bis(3-methoxylphenyl)oxirane 4i**.



4i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (t, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.71- 6.73 (m, 4H), 4.32 (s, 2H), 3.68 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 136.3, 129.1, 119.7, 113.9, 112.5, 59.9, 55.3.
MS: ESI-MS (*m/z*): 257.1 $[M+H]^+$.

***cis*-2,3-bis(2-bromophenyl)oxirane 4j**.



4j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 2H), 4.58 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 133.5, 132.4, 129.4, 128.9, 126.6, 123.0, 60.9.
MS: ESI-MS (*m/z*): 354.9, 352.9 $[M+H]^+$.

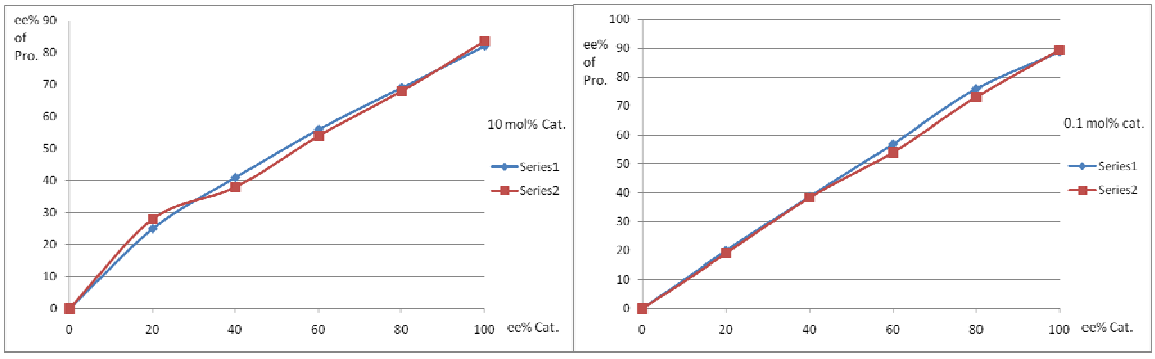
4. Catalyst recovery experiment.

Catalyst **3d** was recovered from reaction, purified by PTLC. (Yield: 94%)

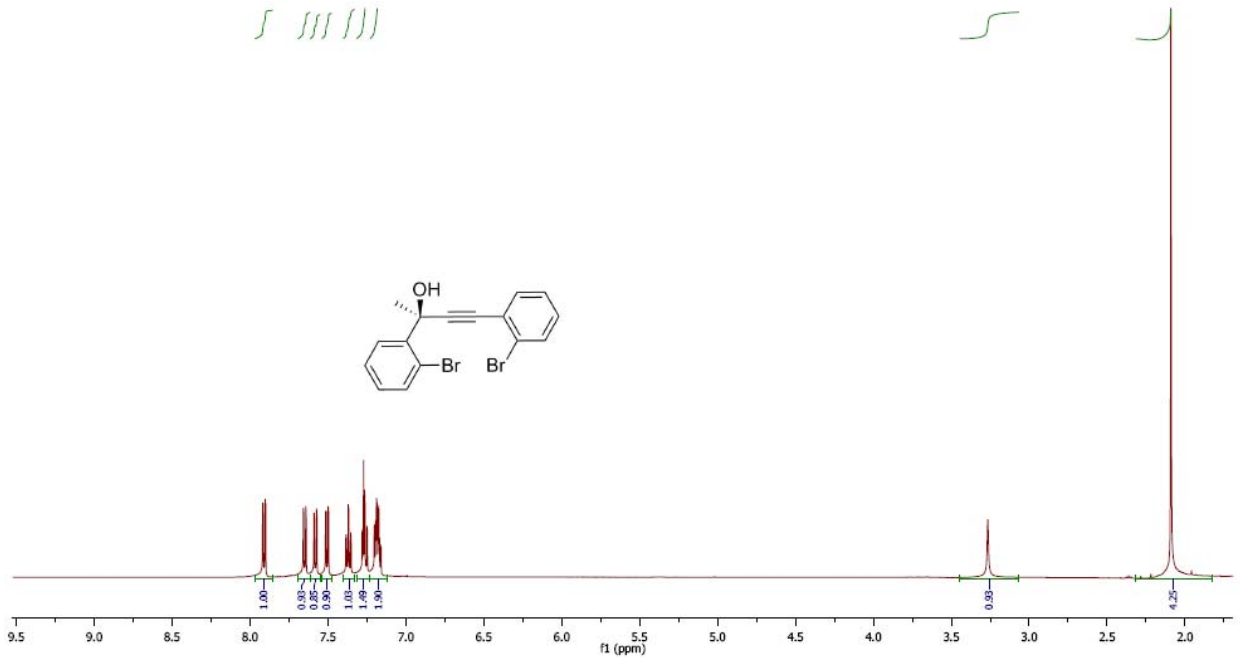
According to procedure **II**, (1R,2R)-2-chloro-1,2-diphenylethanol was synthesized by using this recovered catalyst **3d**. Enantiomeric excess (ee) was determined by chiral HPLC analysis, 90% ee (Chiral OD-H column, 2% isopropanol in hexane, 1 mL/min.). $[\alpha]_D$= -83°, c=0.5 in DCM.

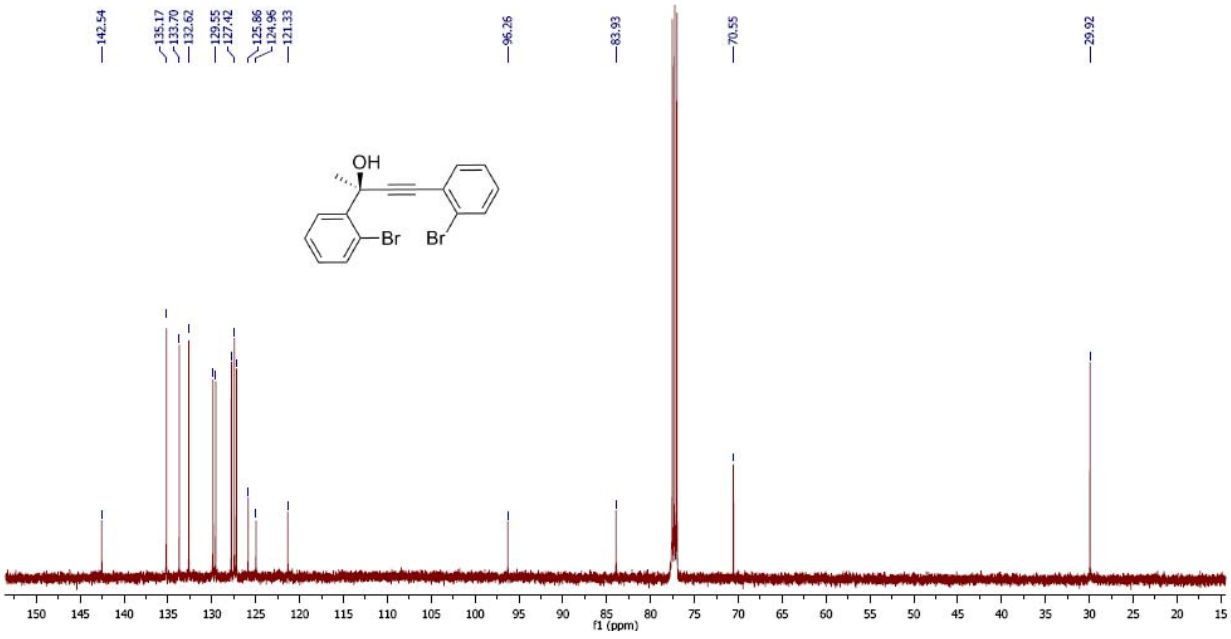
5. Non-linear effect experiments of Catalyst 3d.

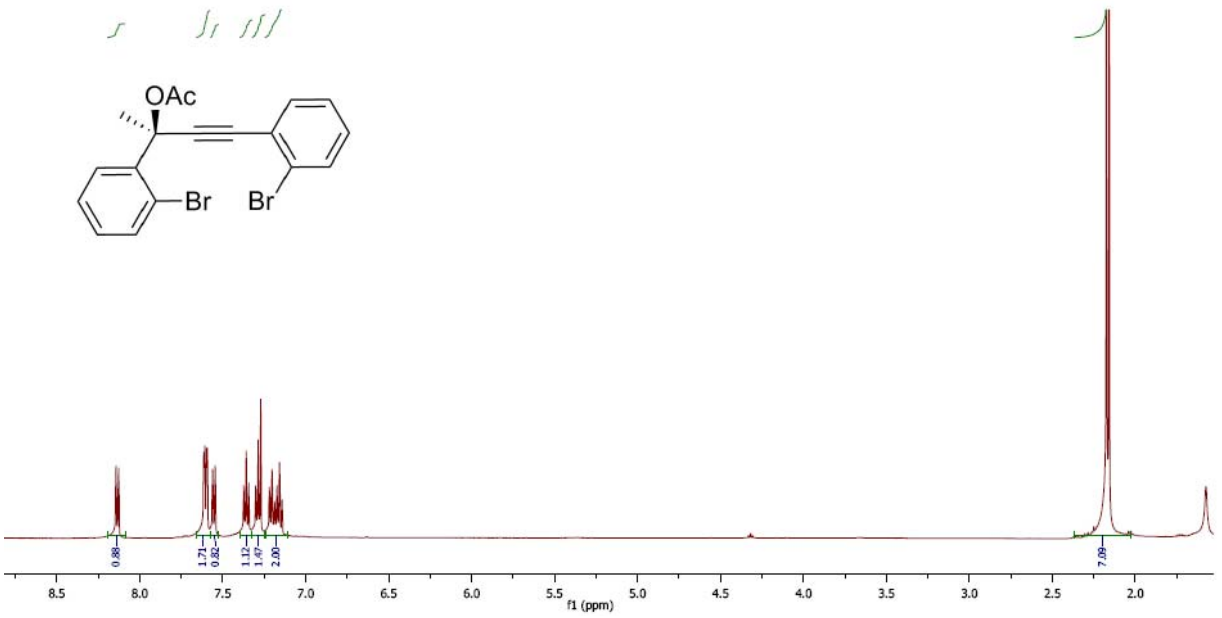
Catalysts **3d** with different enantiomer excess (20%, 40%, 60%, 80%, 100%) were used in this experiment. Two different catalyst loading (0.1 mol% and 10 mol%) reactions were investigated. Each data point represents the average of two experiments (shown separately here).

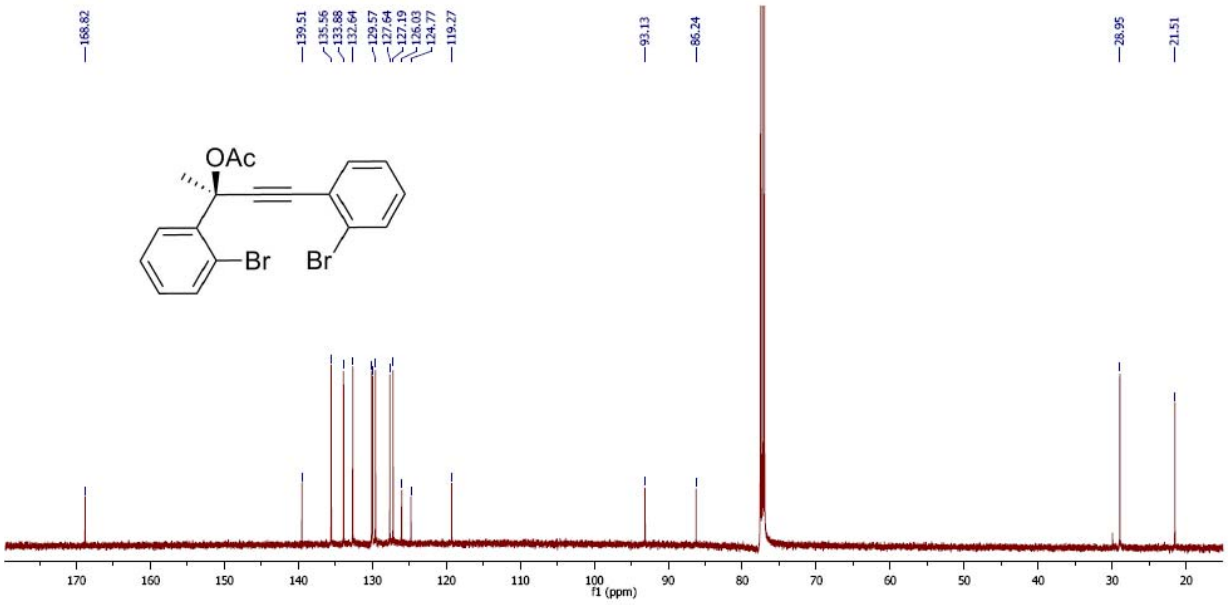


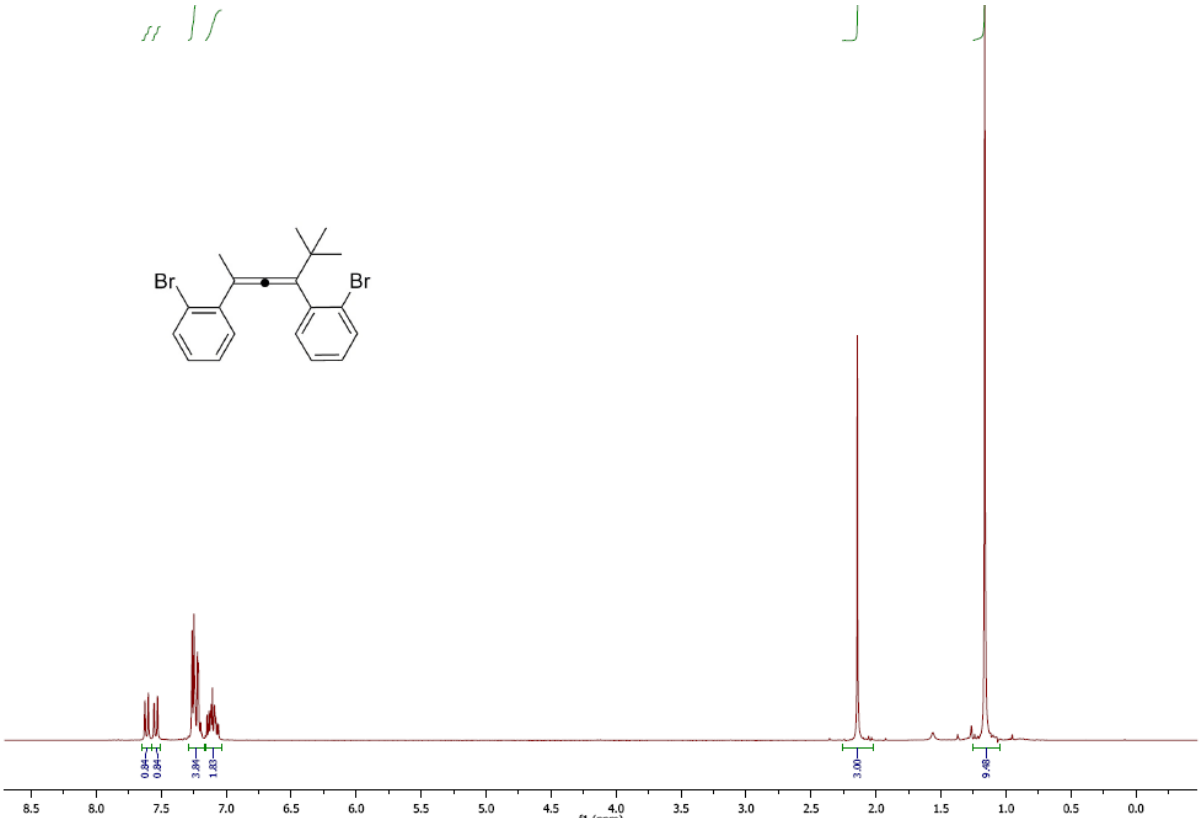
[14] Takenaka, N.; Sarangthem, R. S.; Captain, B. *Angew. Chem. Int. Ed.* **2008**, *47*, 9708.

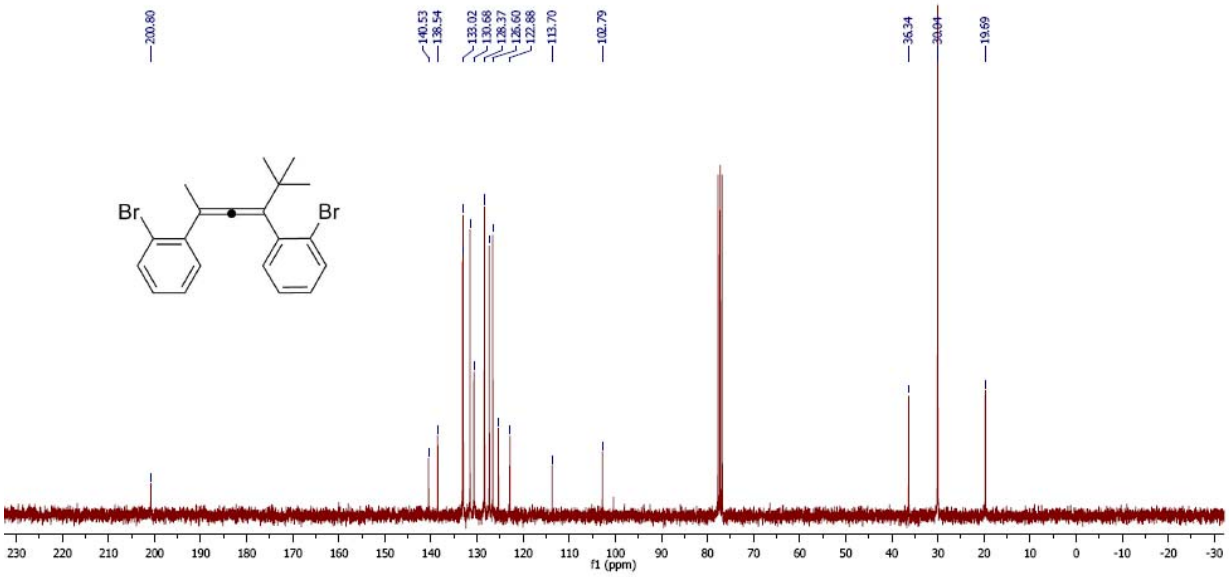

OH
Br
Br
1.00
0.93
0.85
0.90
1.03
1.49
1.90
0.93
4.25
f1 (ppm)

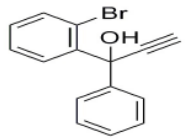

142.54
135.17
133.70
132.62
129.55
127.42
125.86
124.96
121.33
96.26
83.93
70.55
29.92
OH
Br
Br
f1 (ppm)

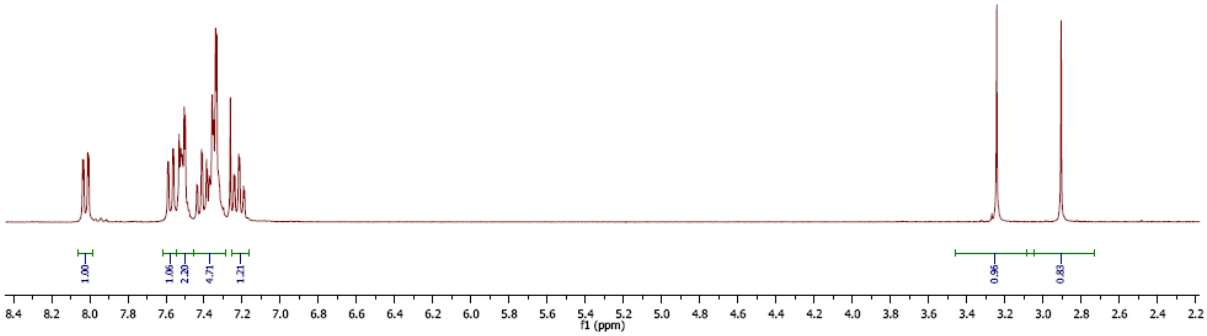

OAc
Br
Br
0.88
1.71
0.82
1.12
1.47
2.00
7.09
f1 (ppm)

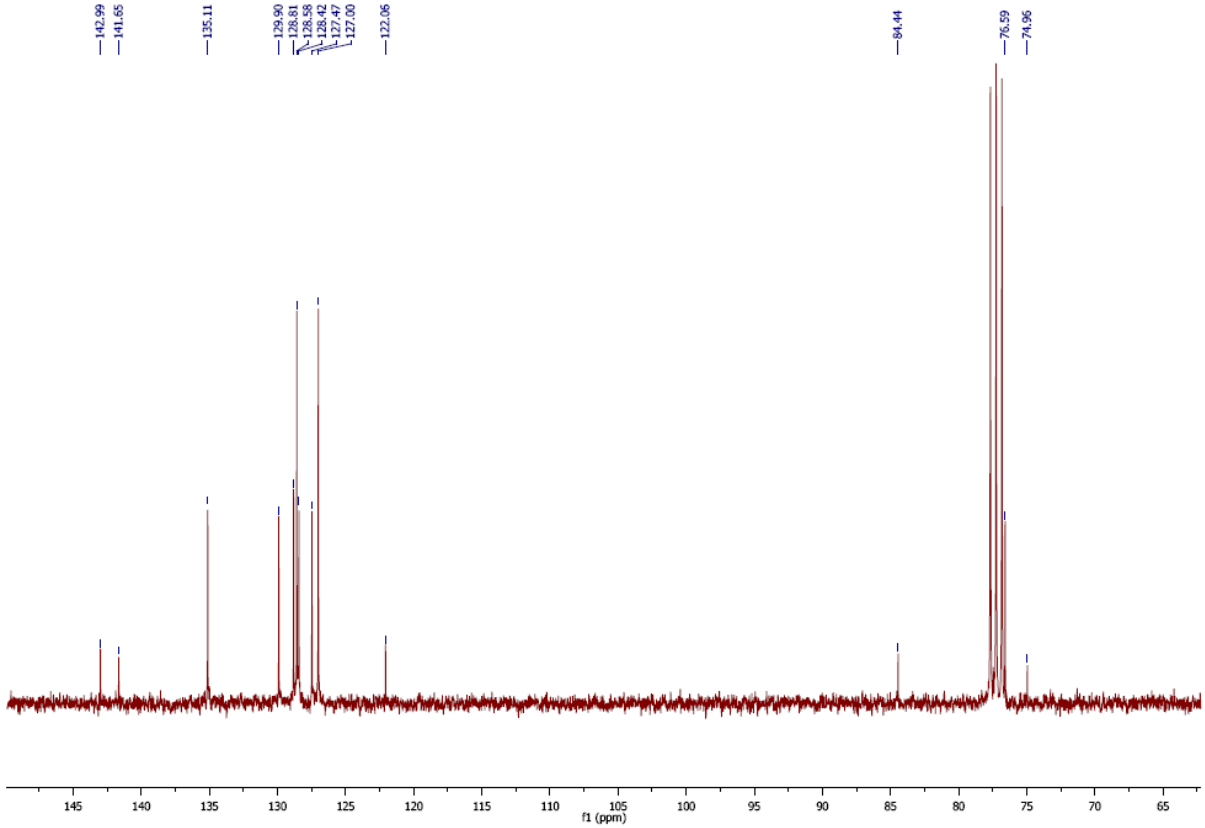

168.82
139.51
135.56
133.88
132.64
129.57
127.64
127.19
126.03
124.77
119.27
93.13
86.24
28.95
21.51
OAc
Br
Br
f1 (ppm)

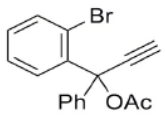

Br
Br
0.84
0.84
3.84
1.83
3.00
9.48
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


200.80
140.53
138.54
133.02
130.68
128.37
126.60
122.88
113.70
102.79
36.34
30.04
19.69
Br
Br
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

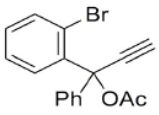

Br
OH

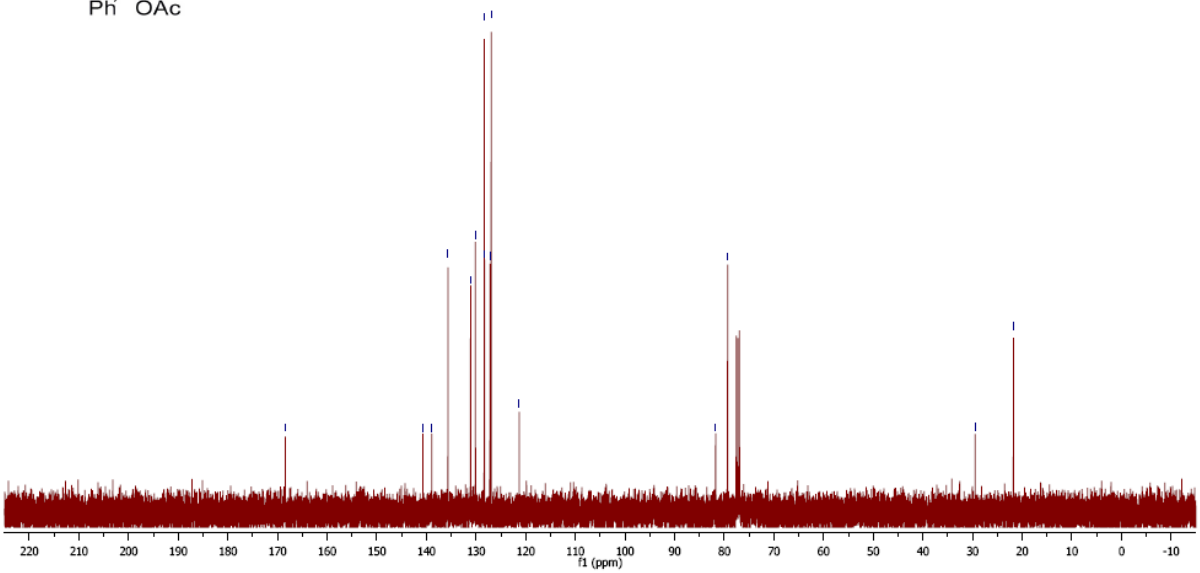

1.00
1.06
2.20
4.71
1.21
0.96
0.88
f1 (ppm)

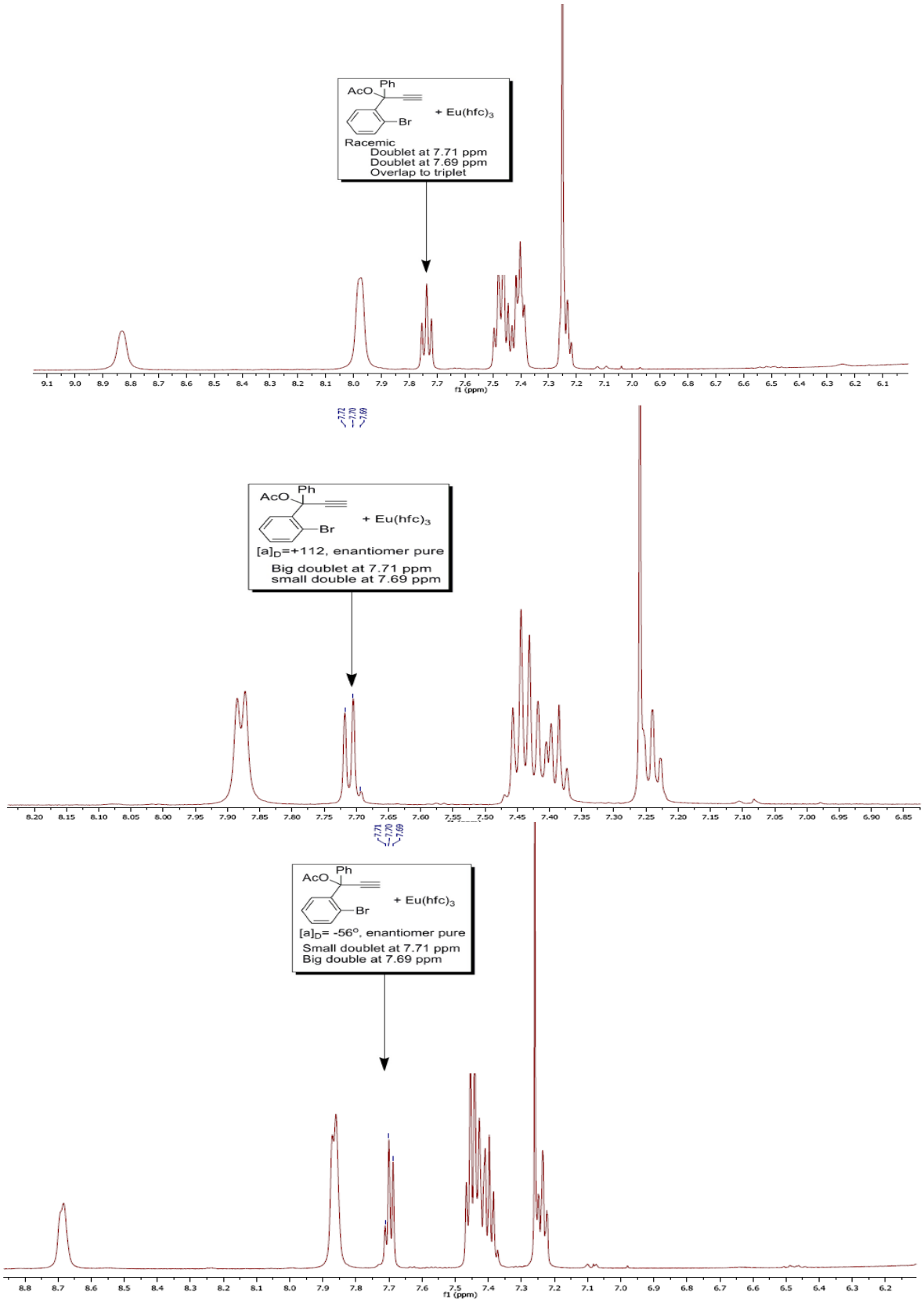

142.99
141.65
135.11
129.90
128.81
128.58
128.42
127.47
127.00
122.06
84.44
76.59
74.96
f1 (ppm)

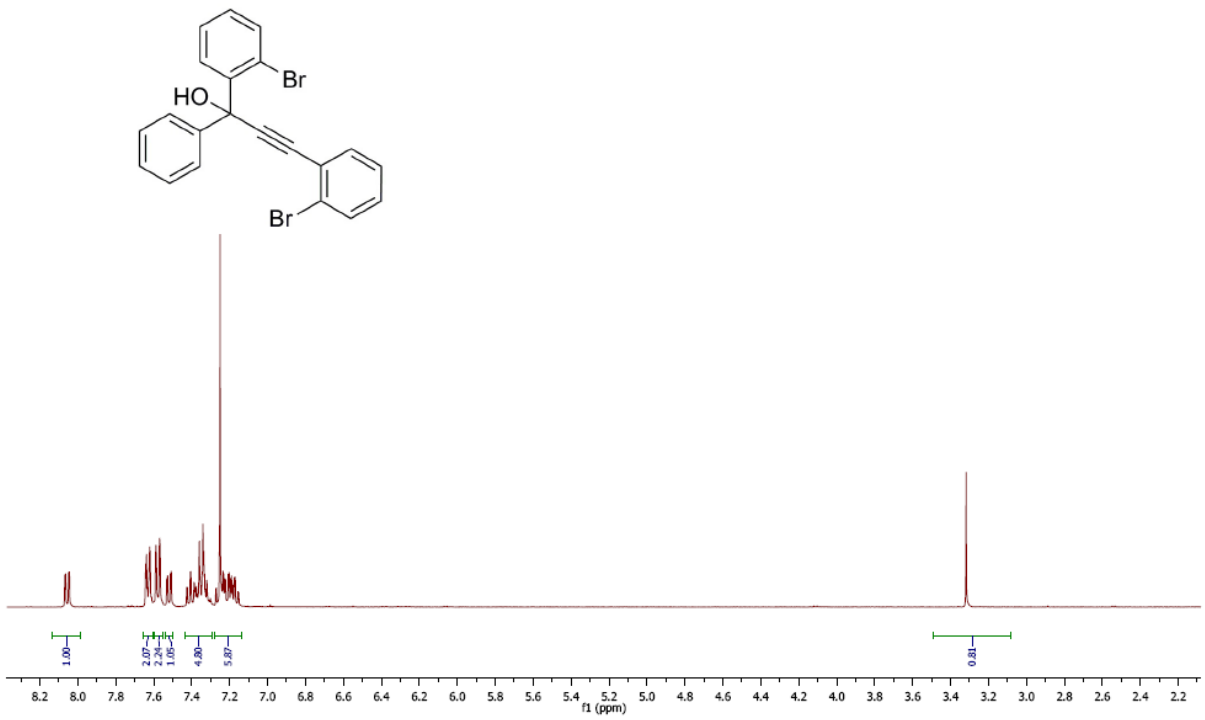

Br
Ph
OAc

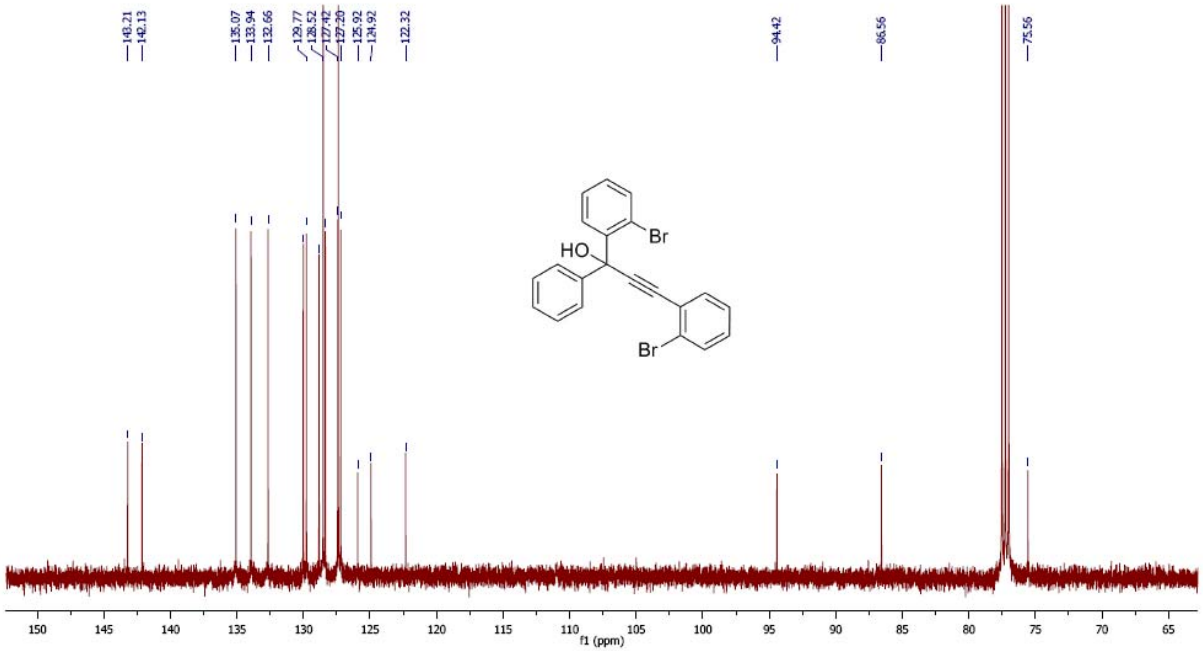
1.00
1.02
3.21
3.38
1.06
0.72
3.46
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)
168.43
140.71
138.94
135.65
128.34
126.94
121.30
81.74
79.32
29.48
21.74

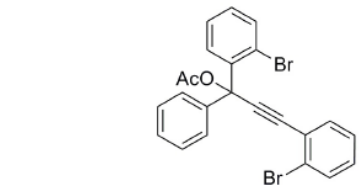

Br
Ph
OAc

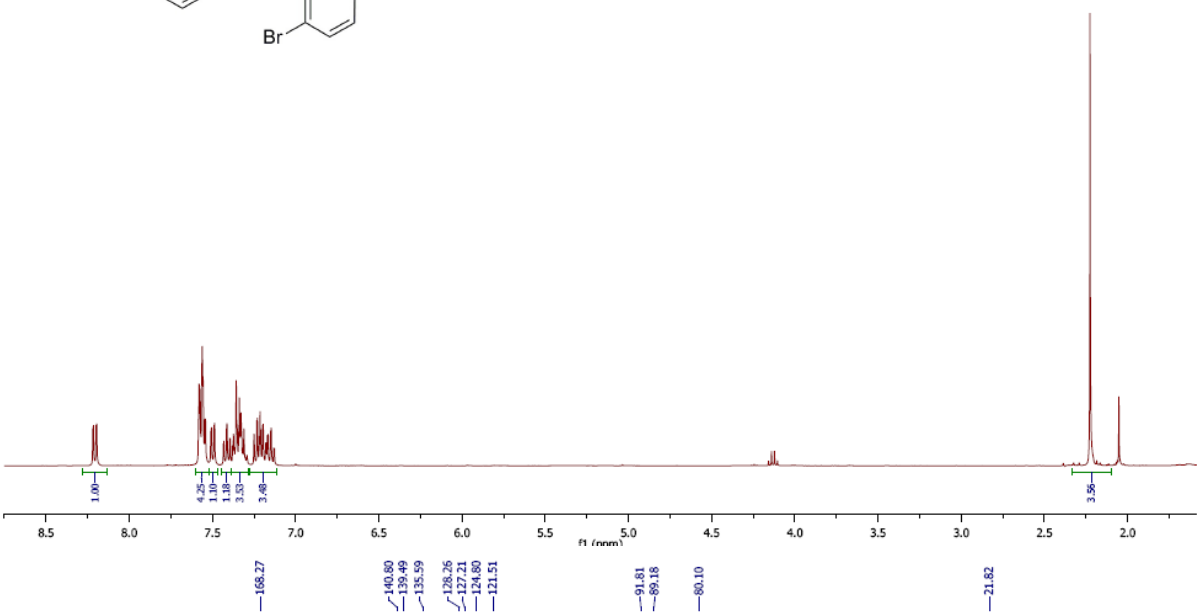

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AcO
Ph
Br
+ Eu(hfc)3
Racemic
Doublet at 7.71 ppm
Doublet at 7.69 ppm
Overlap to triplet
f1 (ppm)
AcO
Ph
Br
+ Eu(hfc)3
[a]D=+112, enantiomer pure
Big doublet at 7.71 ppm
small double at 7.69 ppm
AcO
Ph
Br
+ Eu(hfc)3
[a]D= -56°, enantiomer pure
Small doublet at 7.71 ppm
Big double at 7.69 ppm

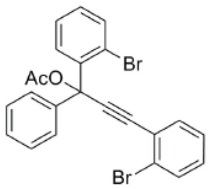

HO
Br
Br
1.00
2.07
2.24
1.05
4.80
5.87
0.81
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2
f1 (ppm)


143.21
142.13
135.07
133.94
132.66
129.77
128.52
127.42
127.20
125.92
124.92
122.32
94.42
86.56
75.56
HO
Br
Br
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65
f1 (ppm)

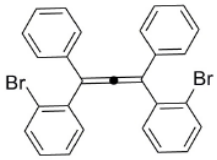

AcO
Br
Br

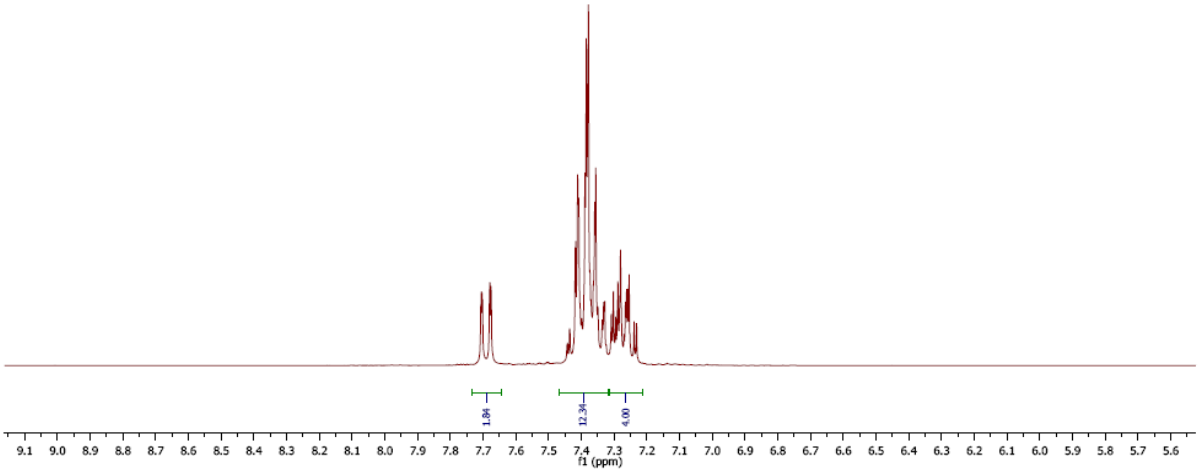

1.00
4.25
1.10
1.18
3.33
3.48
3.56
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

168.27
140.80
139.49
135.59
128.26
127.21
124.80
121.51
91.81
89.18
80.10
21.82

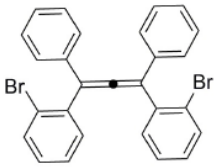

AcO
Br
Br

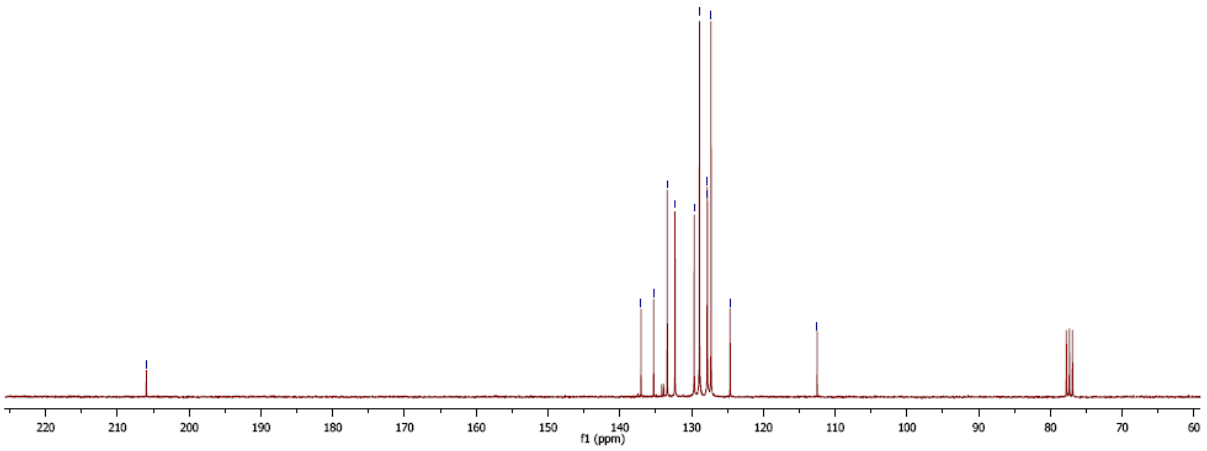
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

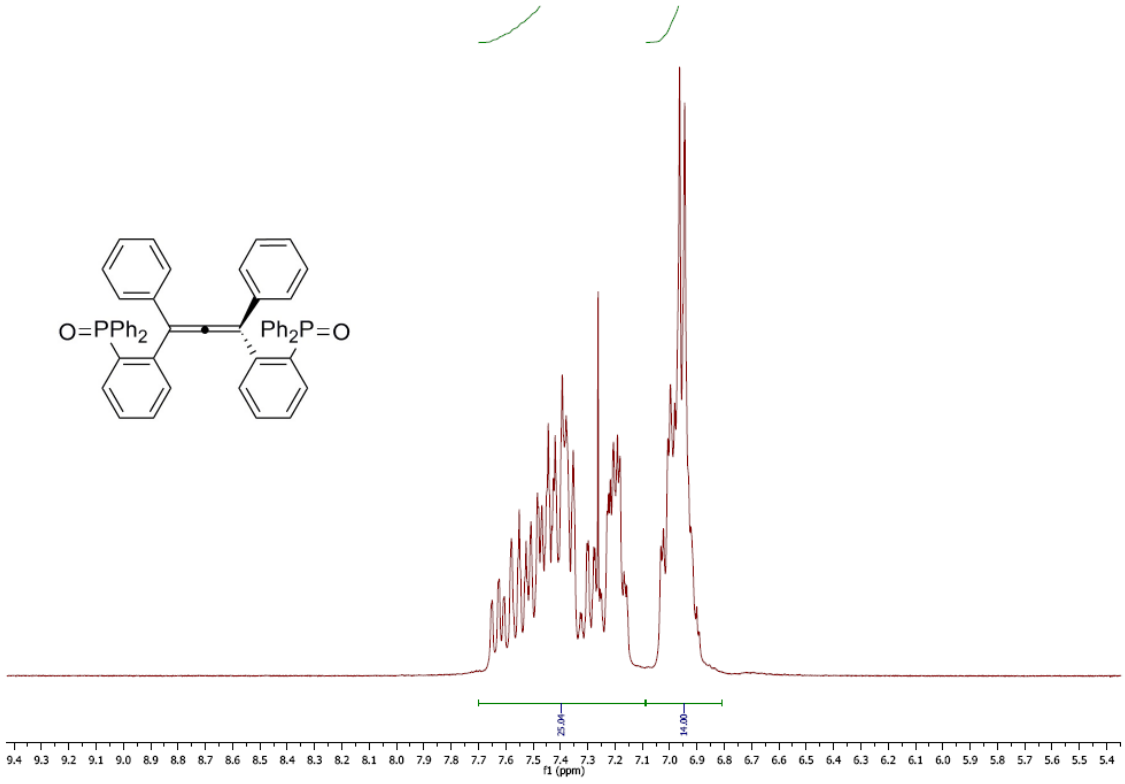

Br
Br

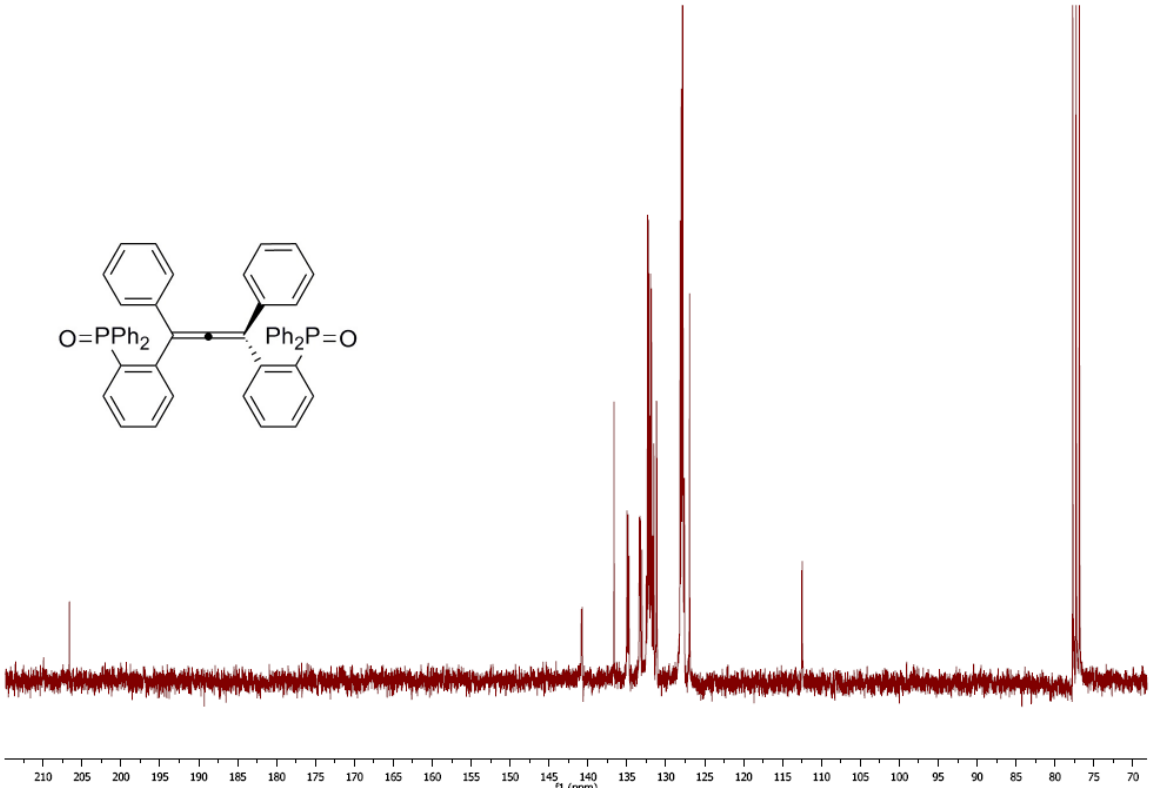

1.84
12.34
4.00
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6
f1 (ppm)

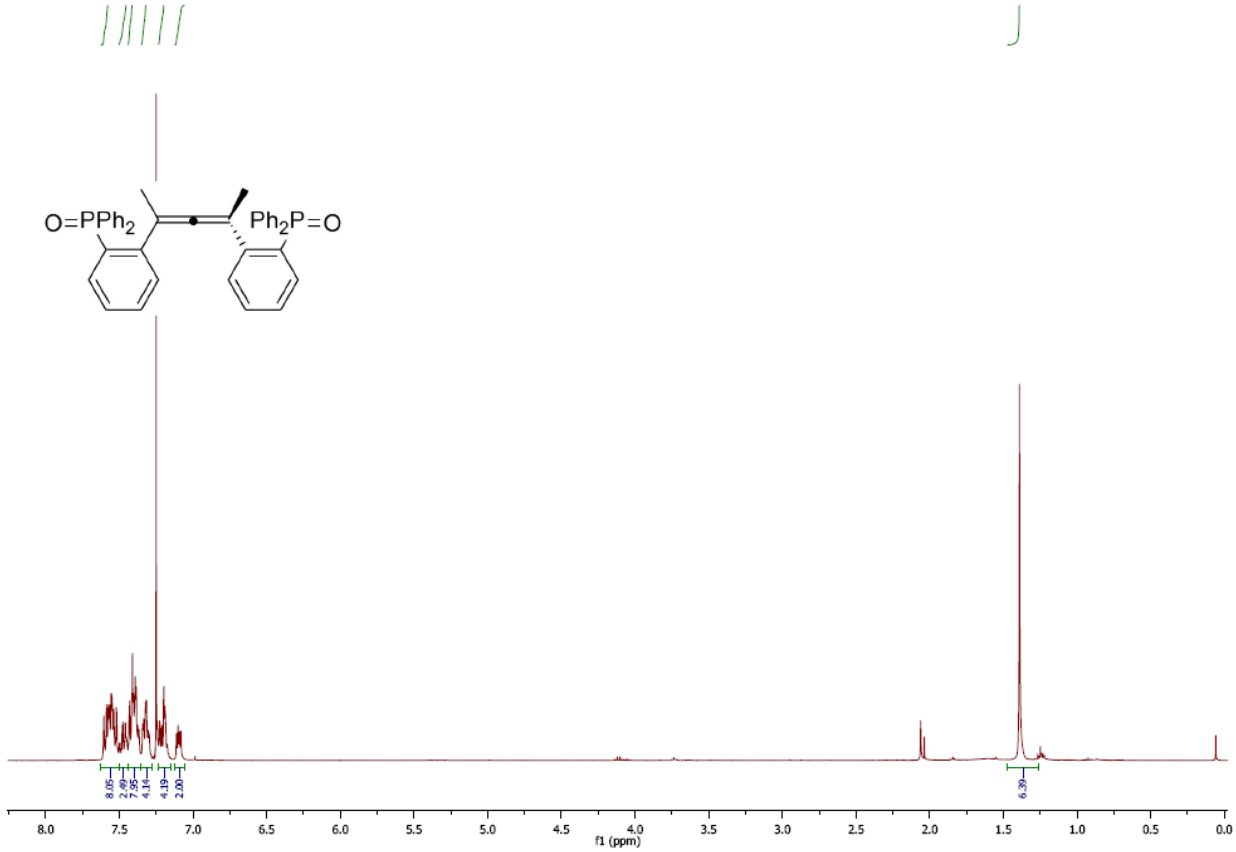

205.96
137.04
135.28
133.39
132.30
127.81
127.28
124.62
112.50

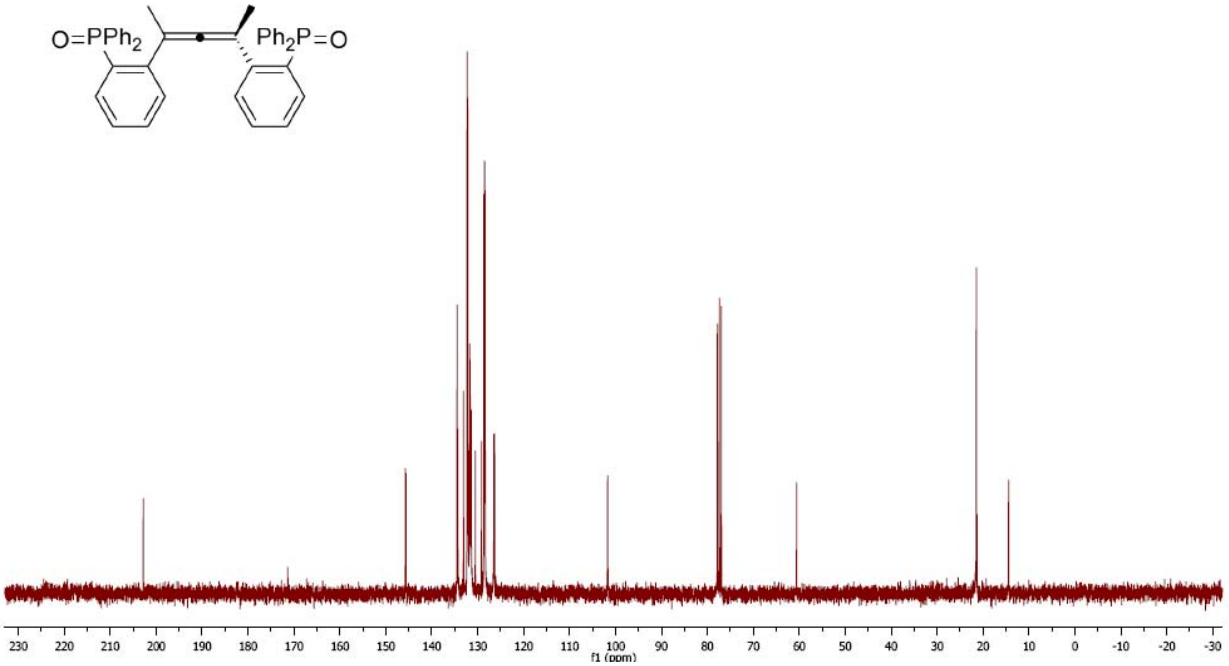

Br
Br

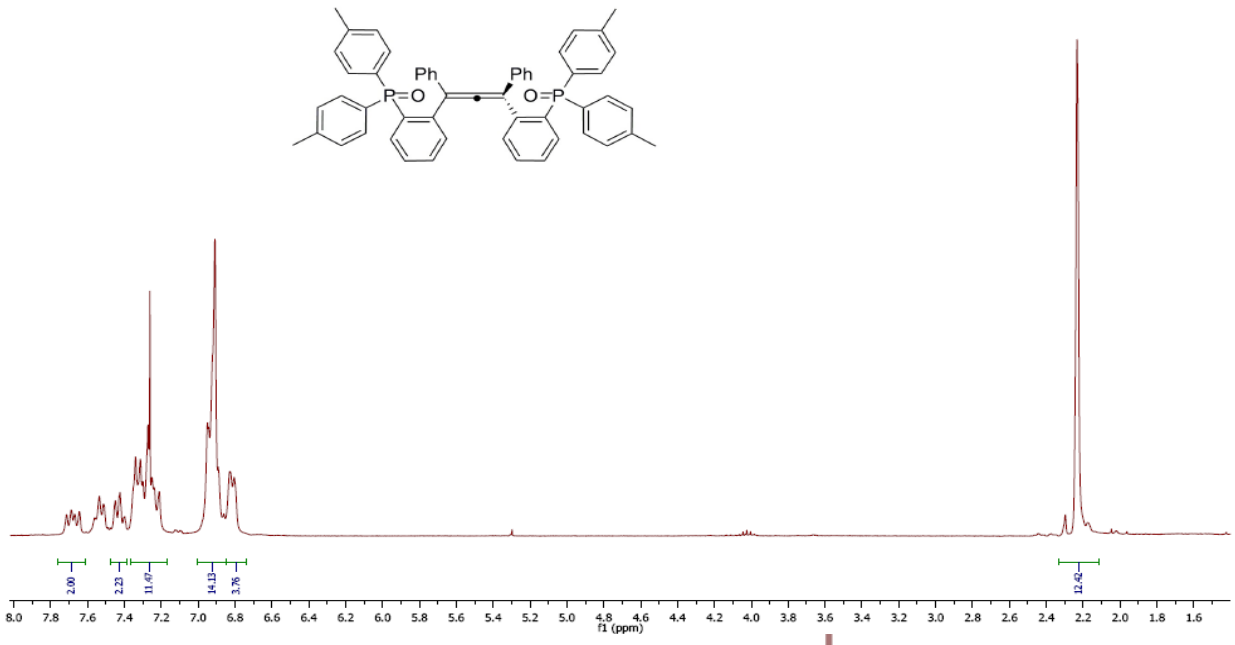

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60
f1 (ppm)

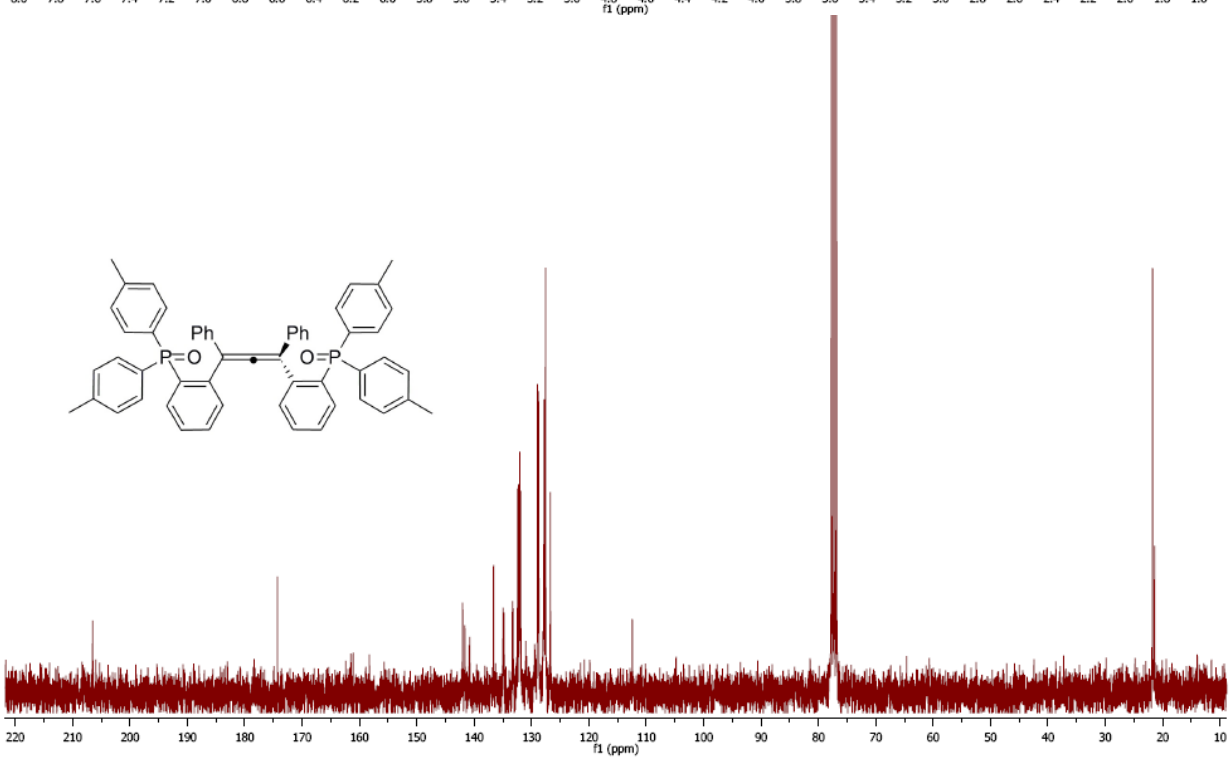

O=PPh2
Ph2P=O
25.04
14.00
9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4
f1 (ppm)

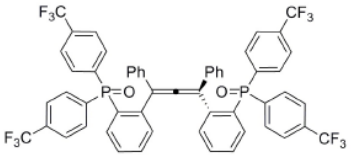

O=PPh2
Ph2P=O
210 205 200 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70

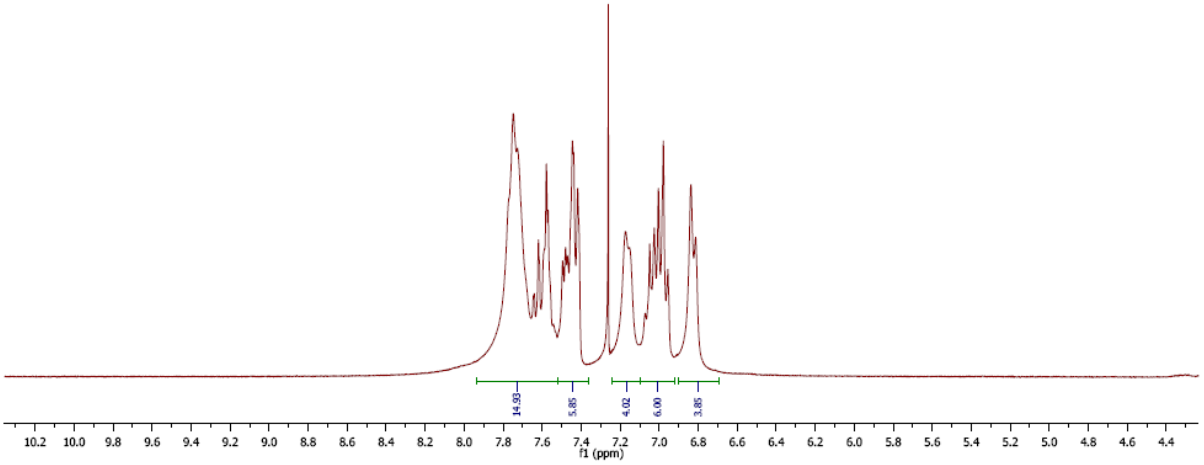

O=PPh2
Ph2P=O
8.06
2.89
7.95
4.14
4.19
2.00
6.39
f1 (ppm)

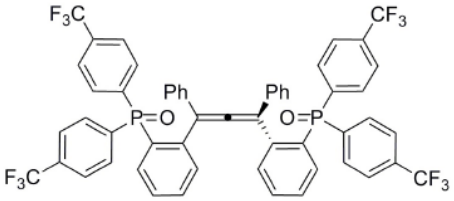

O=PPh2
Ph2P=O
f1 (ppm)


Ph
Ph
P=O
O=P
2.00
2.23
11.47
14.13
3.76
12.42
f1 (ppm)


Ph
Ph
P=O
O=P
f1 (ppm)

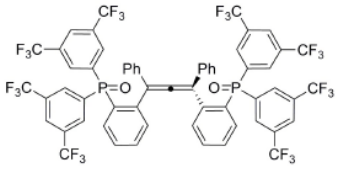

F3C
CF3
Ph
Ph
P=O
O=P
F3C
CF3

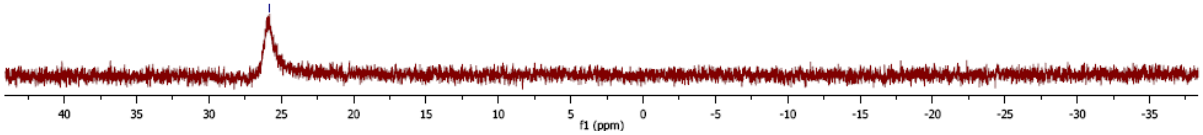

14.93
5.85
4.02
6.00
3.85
f1 (ppm)


F3C
CF3
Ph
Ph
P=O
O=P
F3C
CF3

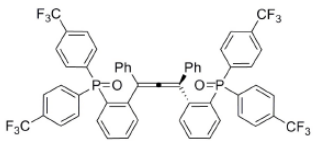
f1 (ppm)

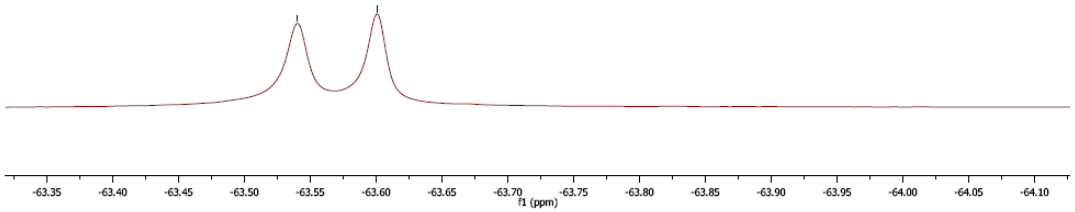
^{31}P NMR (121 MHz, $CDCl_3$) δ 25.80.

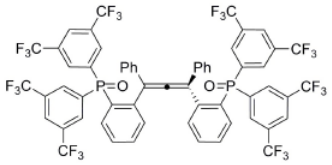


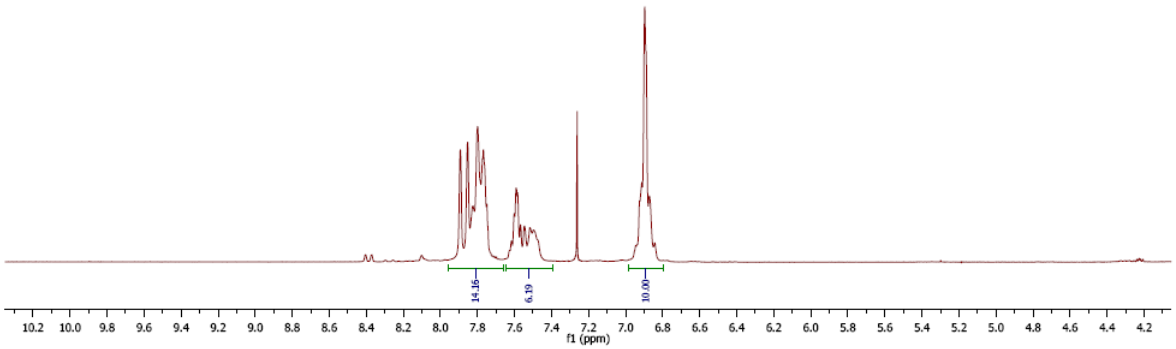


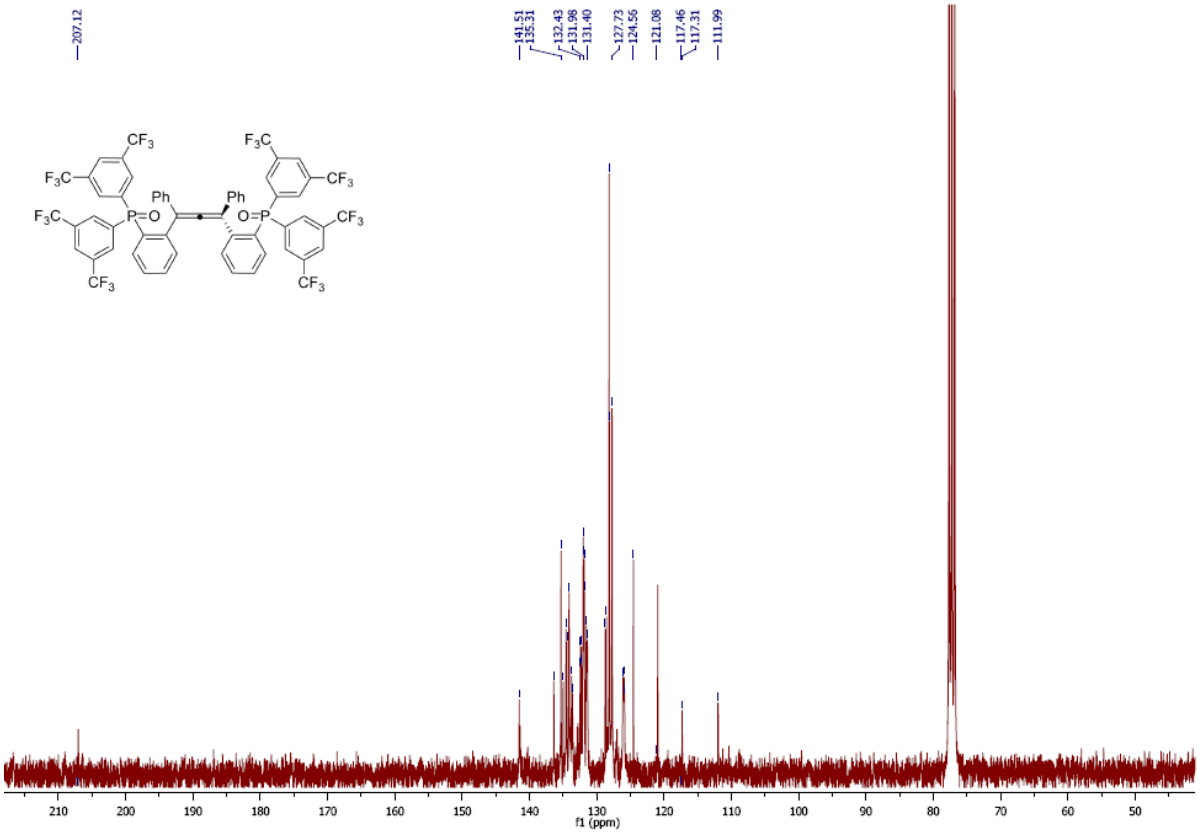
^{19}F NMR (282 MHz, $CDCl_3$) δ -63.54, -63.60.



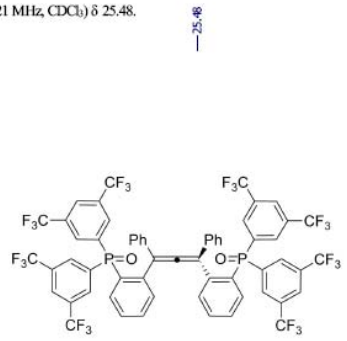


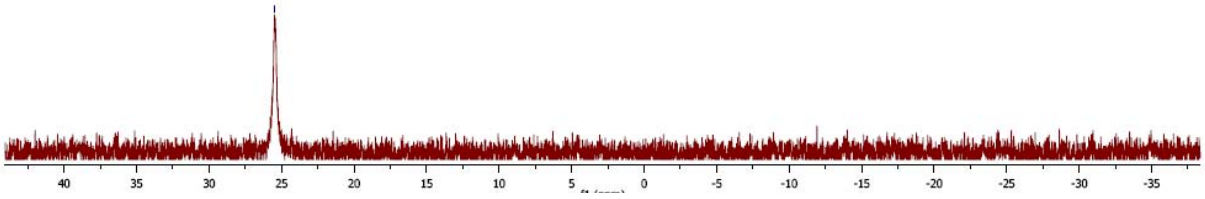

CF3
F3C
Ph
Ph
P=O
O=P
F3C
CF3
CF3
CF3


14.16
6.19
10.00
f1 (ppm)

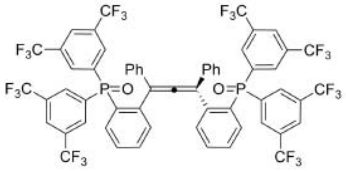

207.12
141.51
135.31
132.43
131.98
131.40
127.73
124.56
121.08
117.46
117.31
111.99
f1 (ppm)

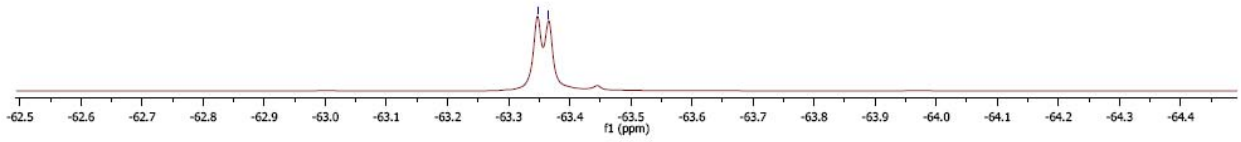
^{31}P NMR (121 MHz, $CDCl_3$) δ 25.48.

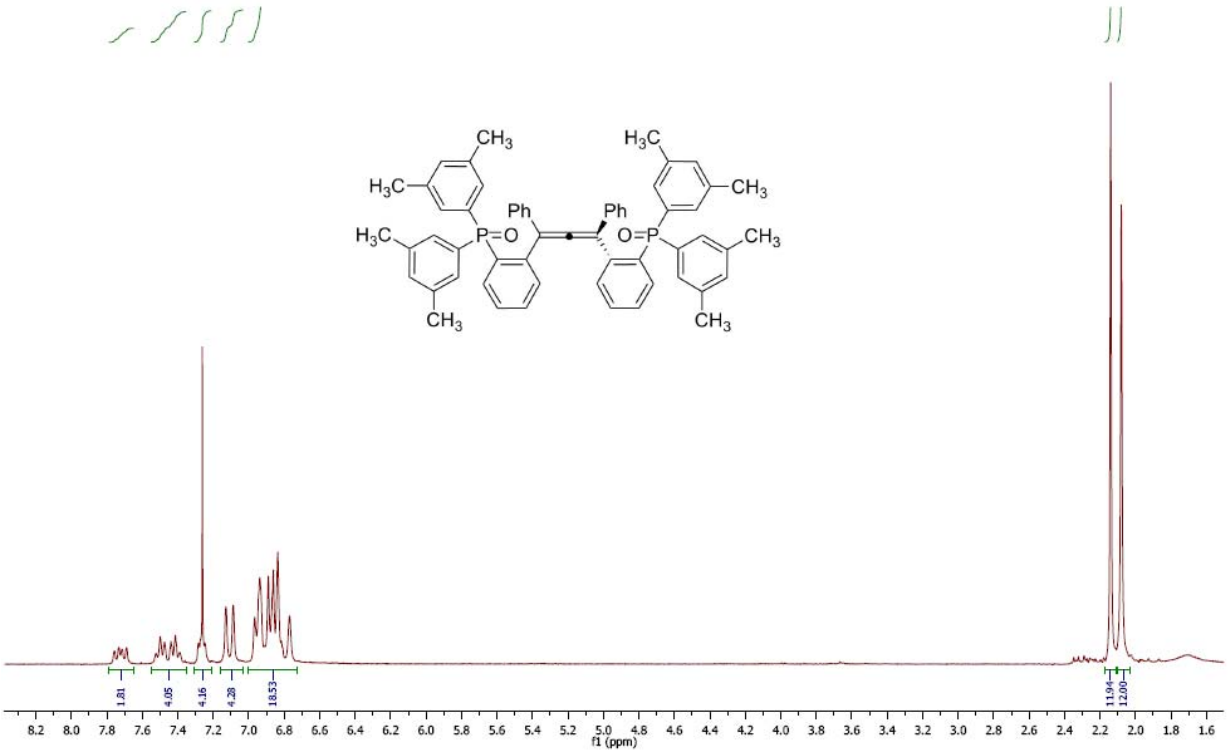


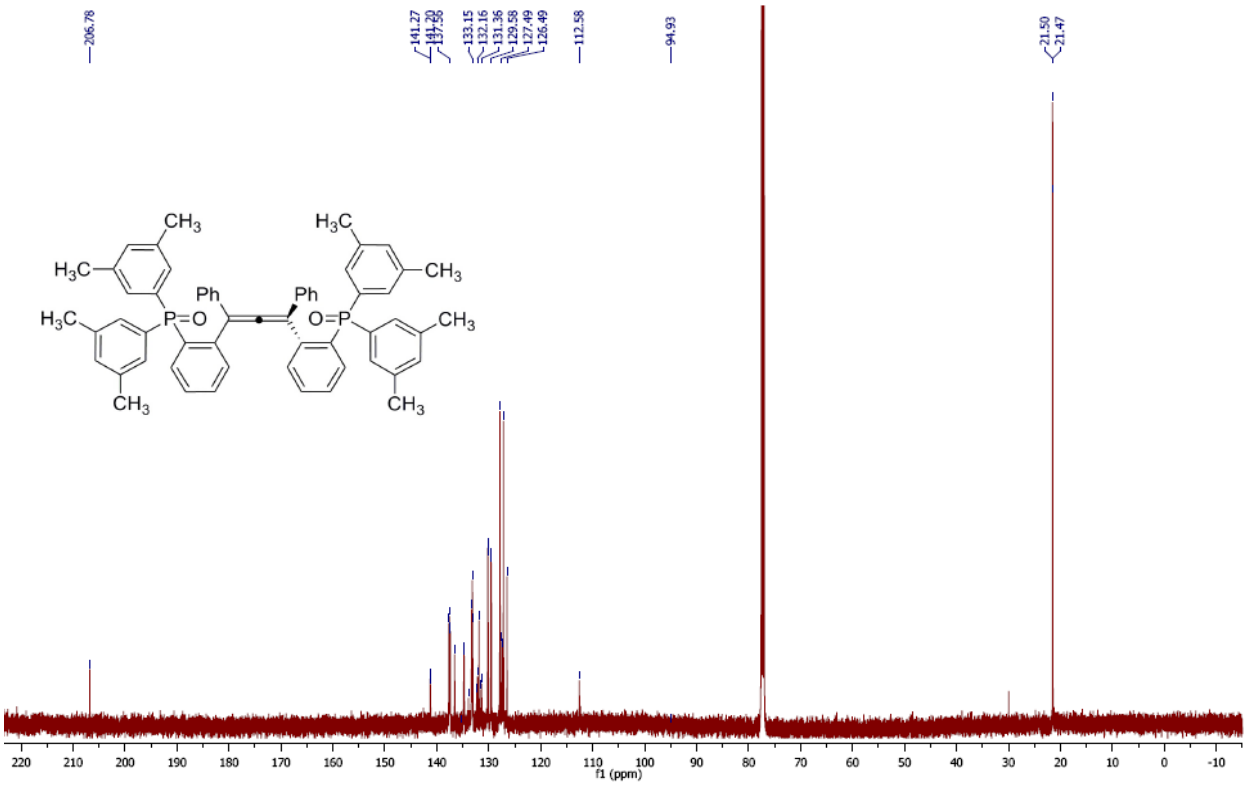


^{19}F NMR (282 MHz, $CDCl_3$) δ -63.35, -63.37.

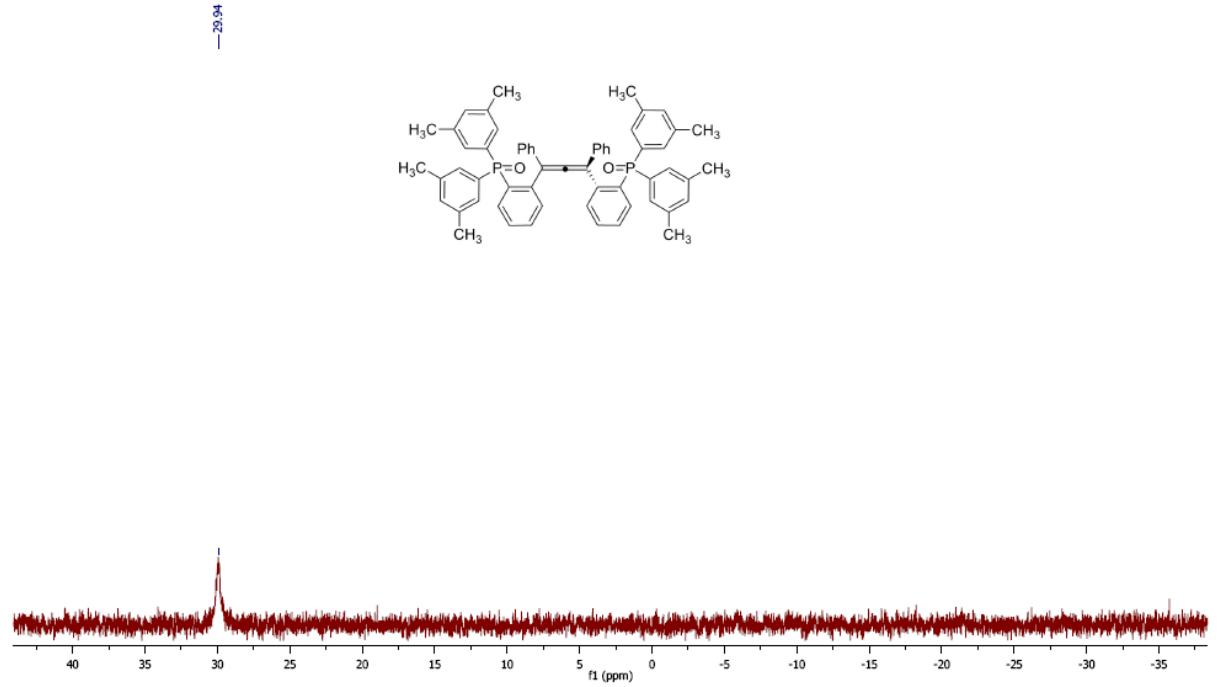


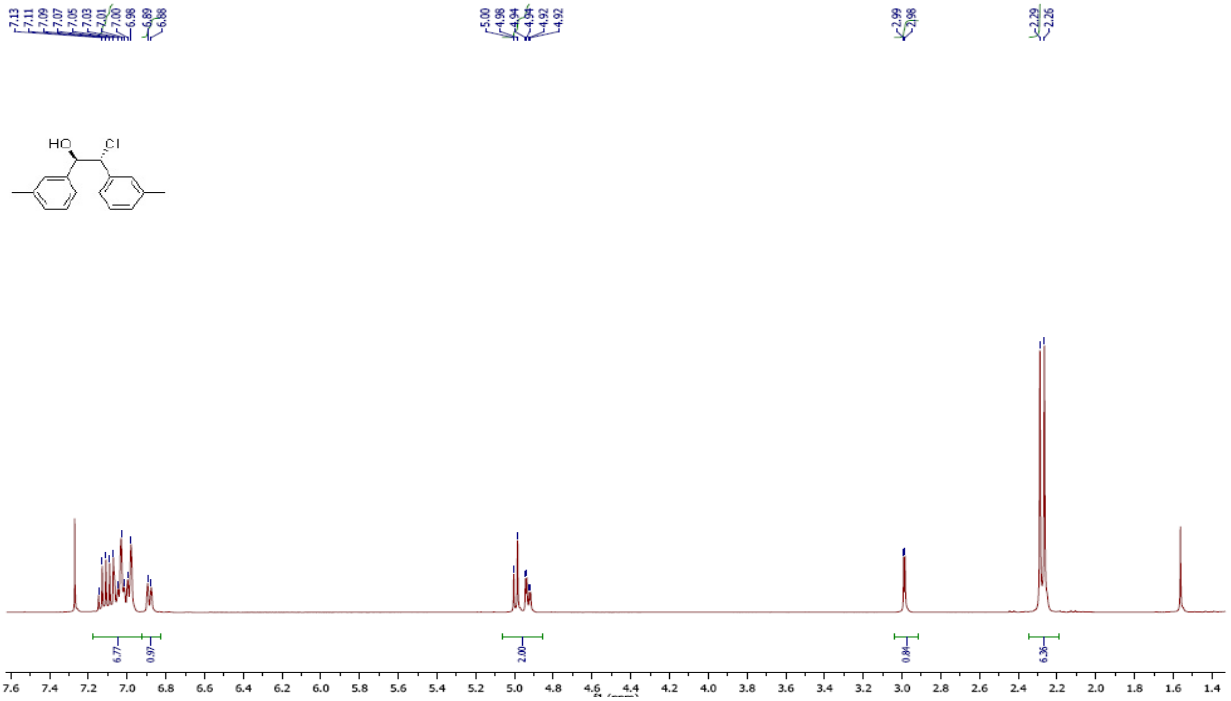


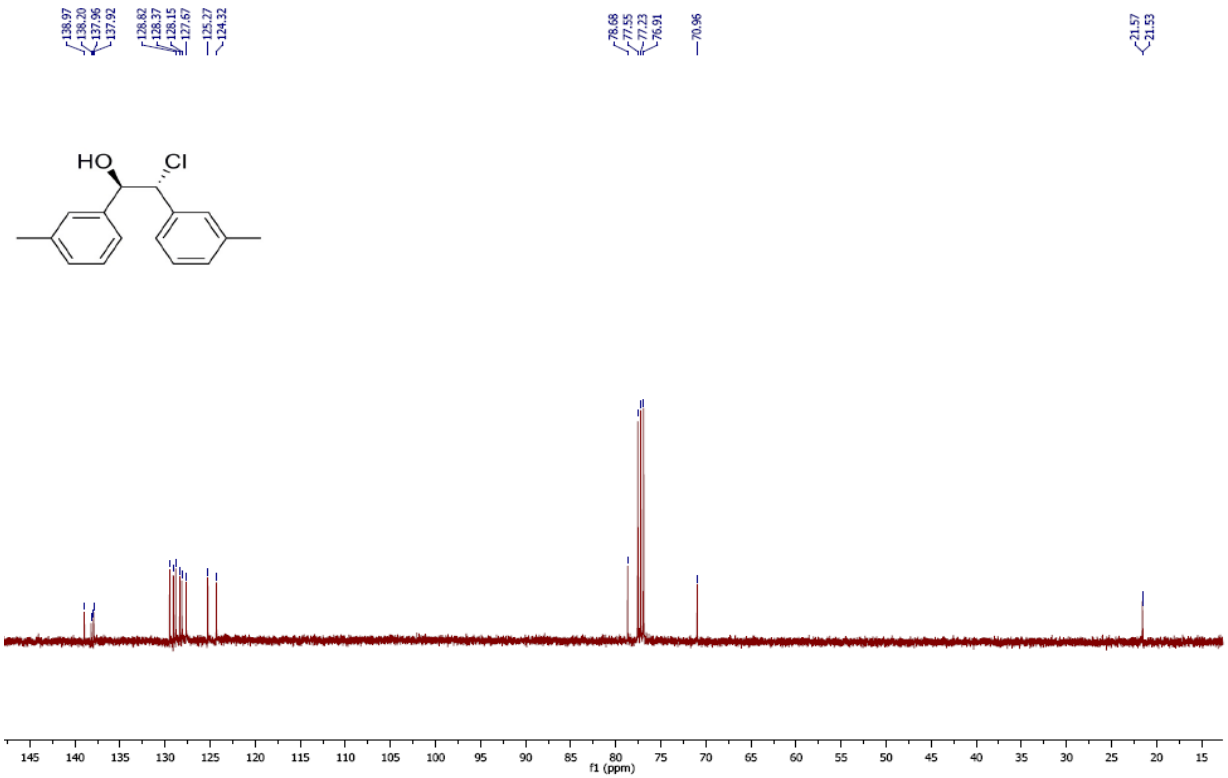

CH3
H3C
H3C
P=O
Ph
Ph
O=P
H3C
CH3
CH3
CH3
1.81
4.05
4.16
4.28
18.53
11.94
12.00
f1 (ppm)

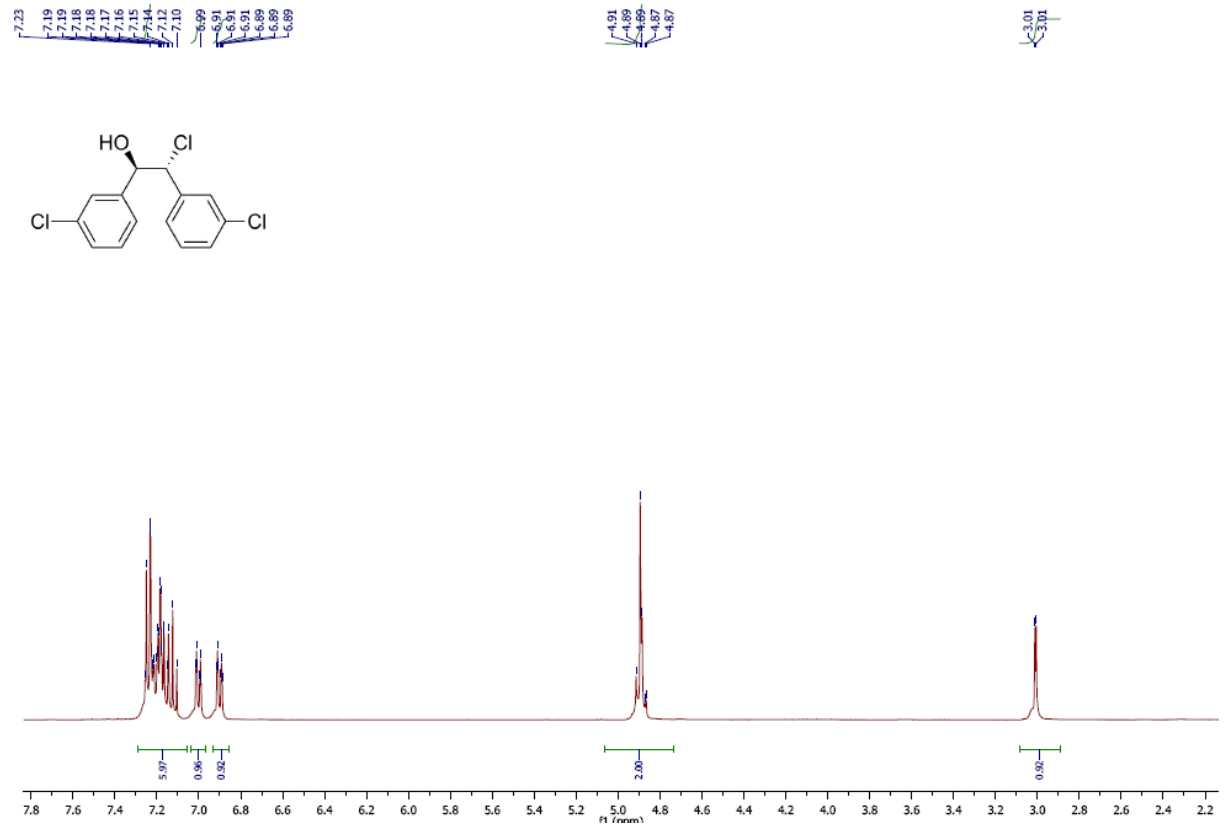

206.78
141.27
141.20
137.58
133.15
132.16
131.36
129.58
127.49
126.49
112.58
94.93
21.50
21.47
CH3
H3C
H3C
P=O
Ph
Ph
O=P
H3C
CH3
CH3
CH3
f1 (ppm)

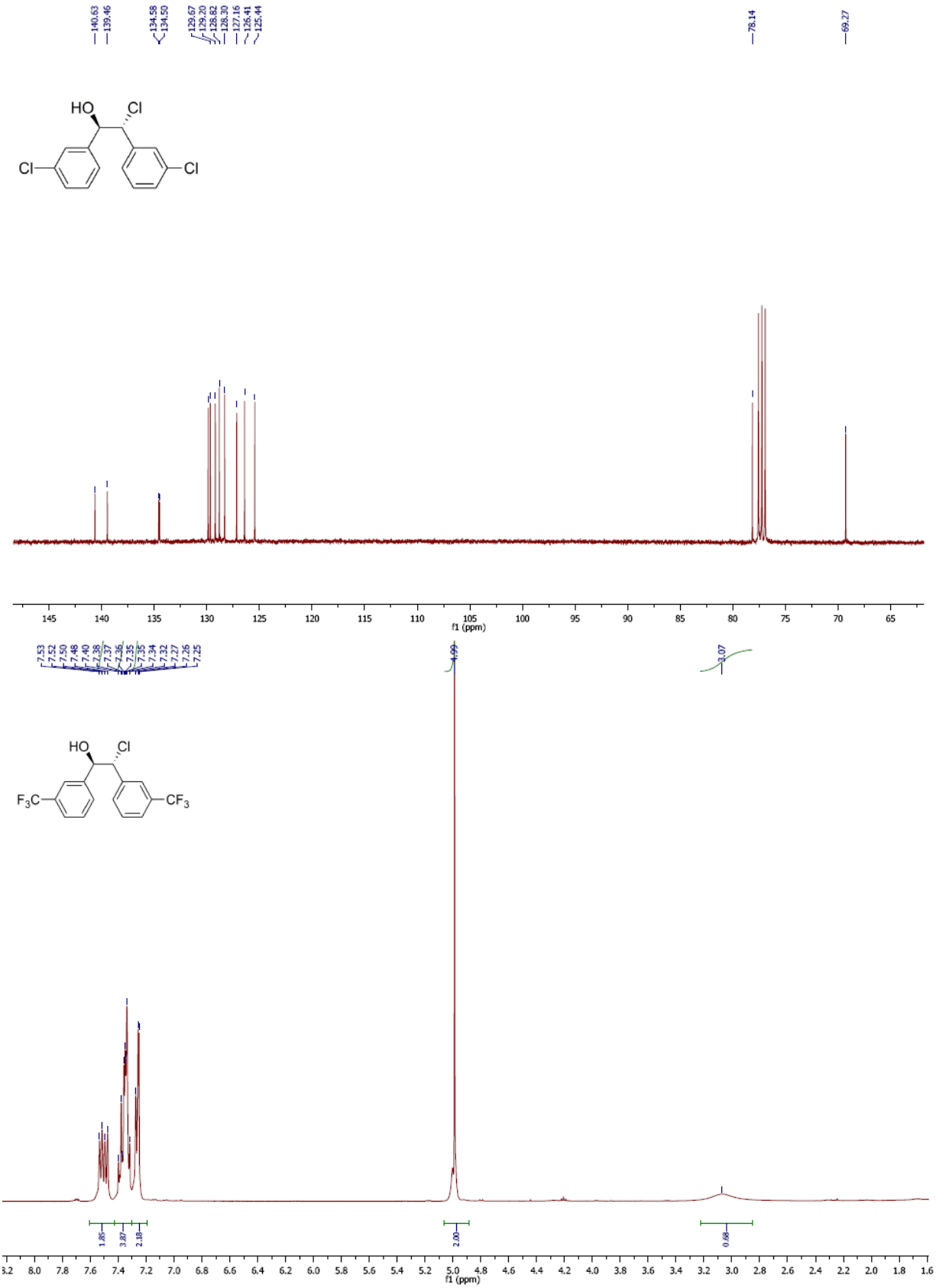
^{31}P NMR (121 MHz, $CDCl_3$) δ 29.94.

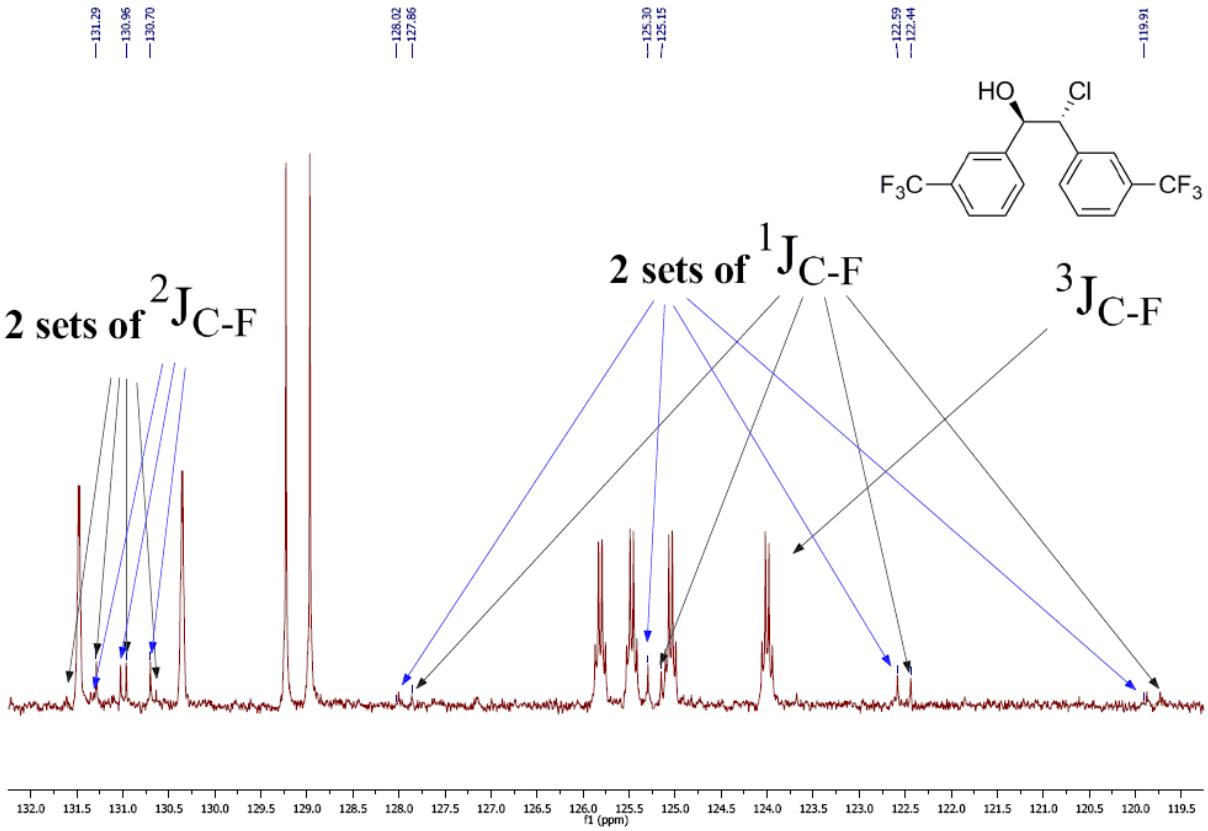


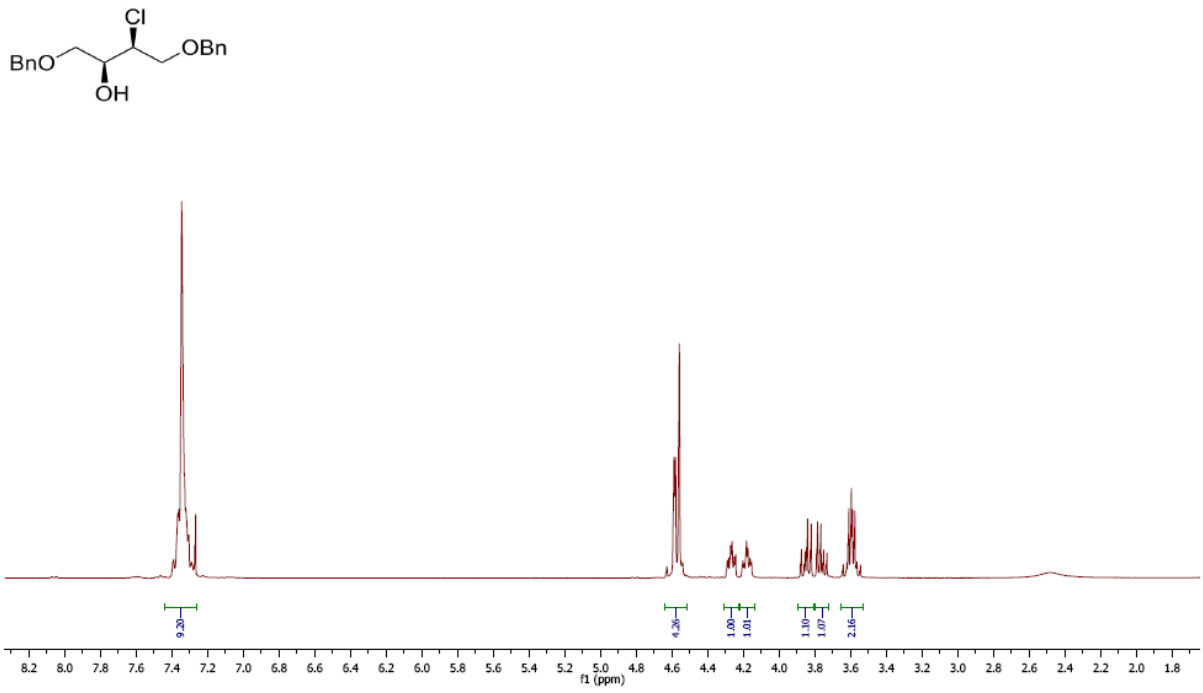


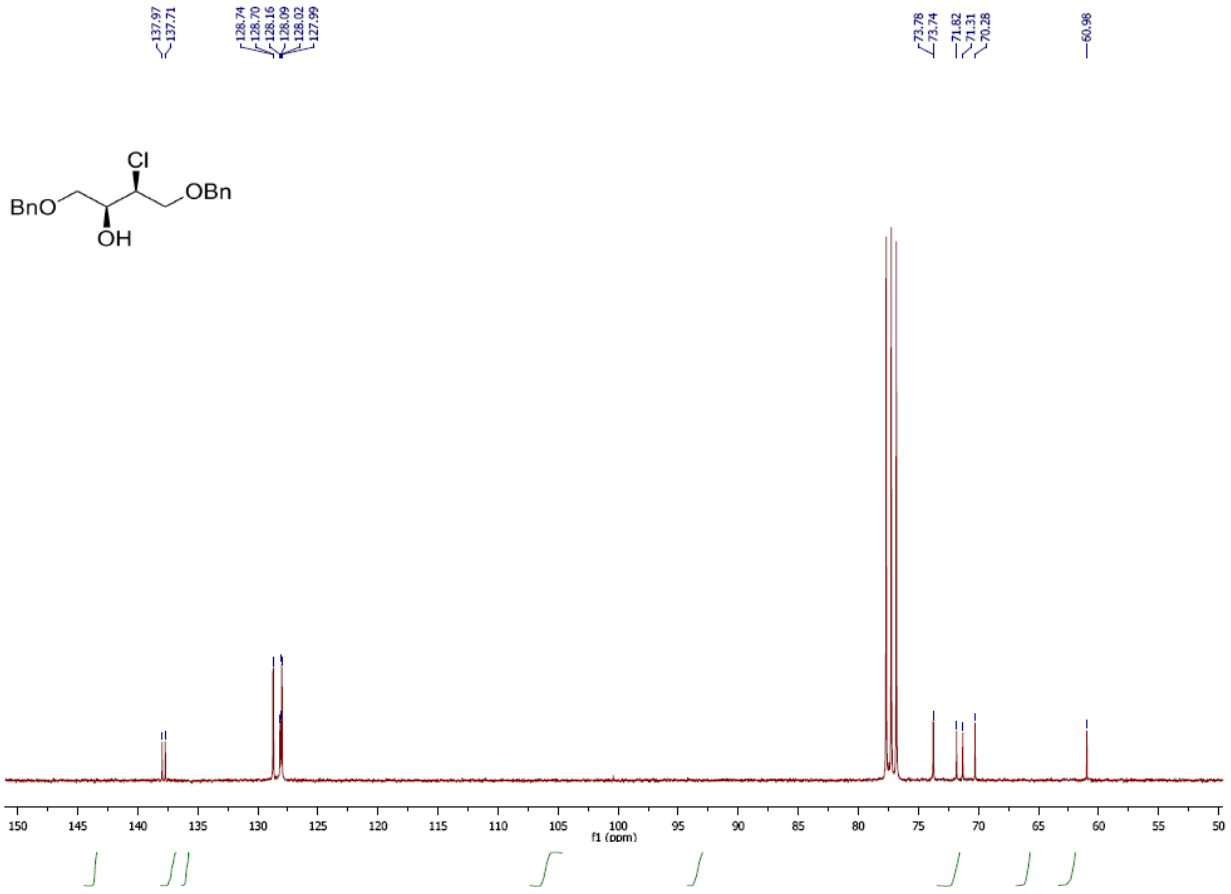

138.97
138.20
137.96
137.92
128.82
128.37
128.15
127.67
125.27
124.32
78.68
77.55
77.23
76.91
70.96
21.57
21.53
HO
Cl
f1 (ppm)

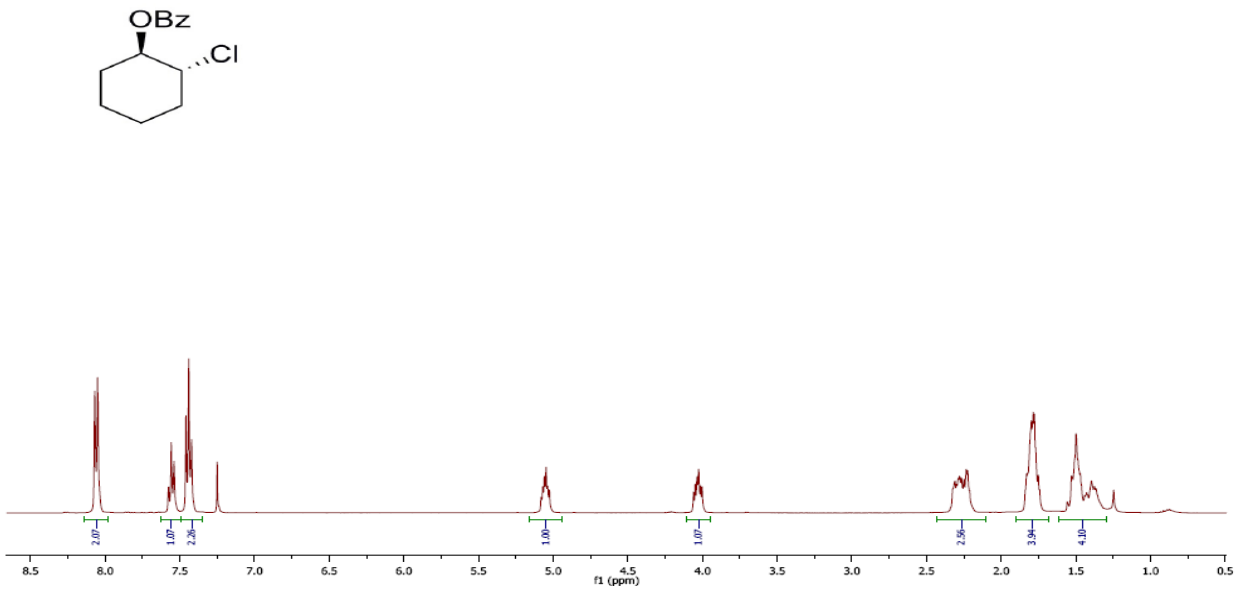

7.23
7.19
7.19
7.18
7.18
7.17
7.16
7.15
7.14
7.12
7.10
6.99
6.91
6.91
6.91
6.89
6.89
6.89
4.91
4.89
4.89
4.87
4.87
3.01
3.01
HO
Cl
Cl
Cl
5.97
0.96
0.92
2.00
0.92
f1 (ppm)

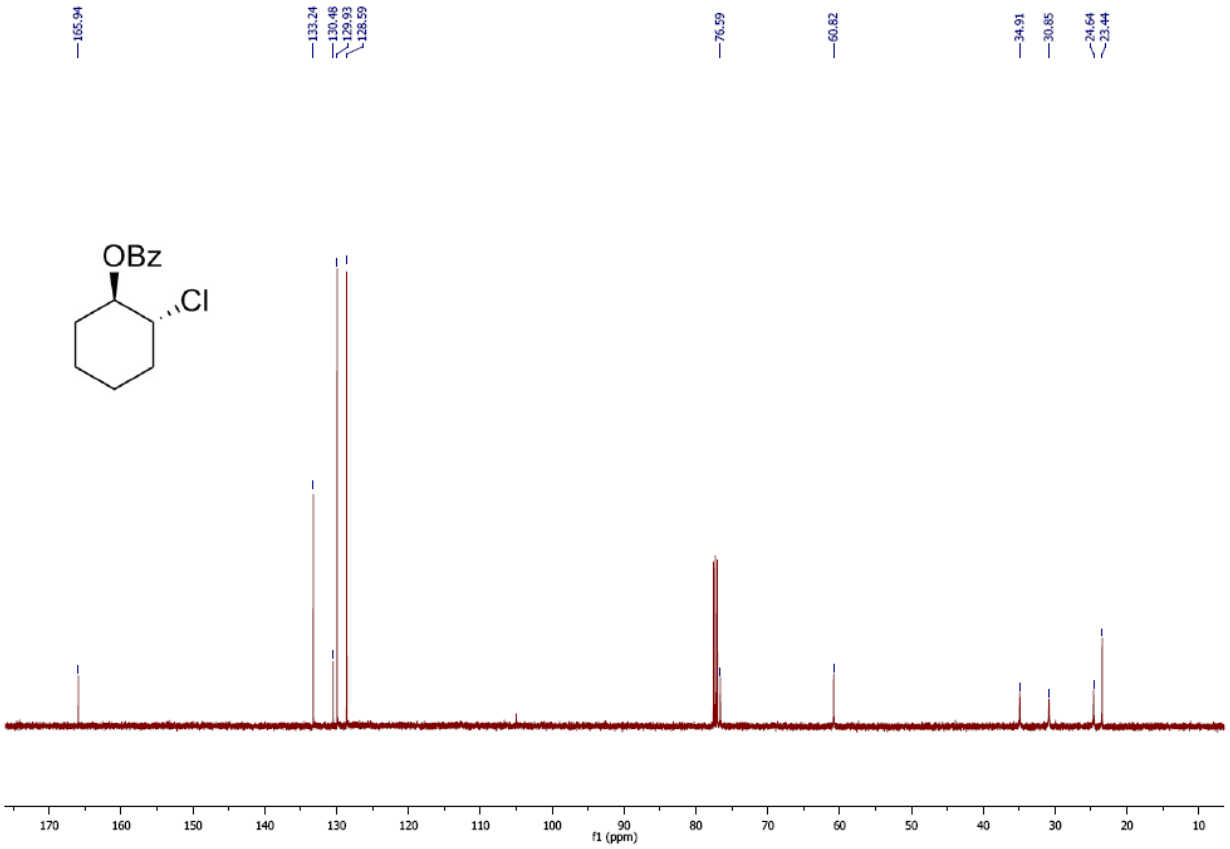

140.63
139.46
134.58
134.50
129.67
129.20
128.82
128.30
127.16
126.41
125.44
78.14
69.27
HO
Cl
Cl
Cl
f1 (ppm)
7.53
7.52
7.50
7.48
7.40
7.38
7.37
7.36
7.35
7.35
7.34
7.32
7.27
7.26
7.25
4.99
3.07
HO
Cl
F3C
CF3
1.85
3.87
2.18
2.00
0.68
f1 (ppm)

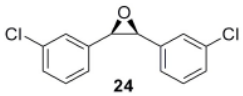

131.29
130.96
130.70
128.02
127.86
125.30
125.15
122.59
122.44
119.91
HO
Cl
F3C
CF3
2 sets of 2JC-F
2 sets of 1JC-F
3JC-F
f1 (ppm)


Cl
BnO
OBn
OH
9.20
4.26
1.00
1.01
1.10
1.07
2.16
f1 (ppm)

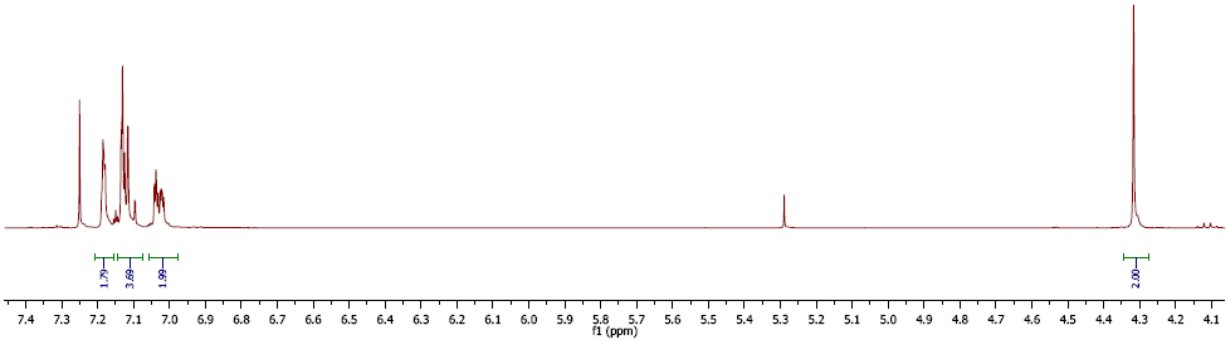

137.97
137.71
128.74
128.70
128.16
128.09
128.02
127.99
73.78
73.74
71.82
71.31
70.28
60.98
Cl
BnO
OBn
OH
f1 (ppm)

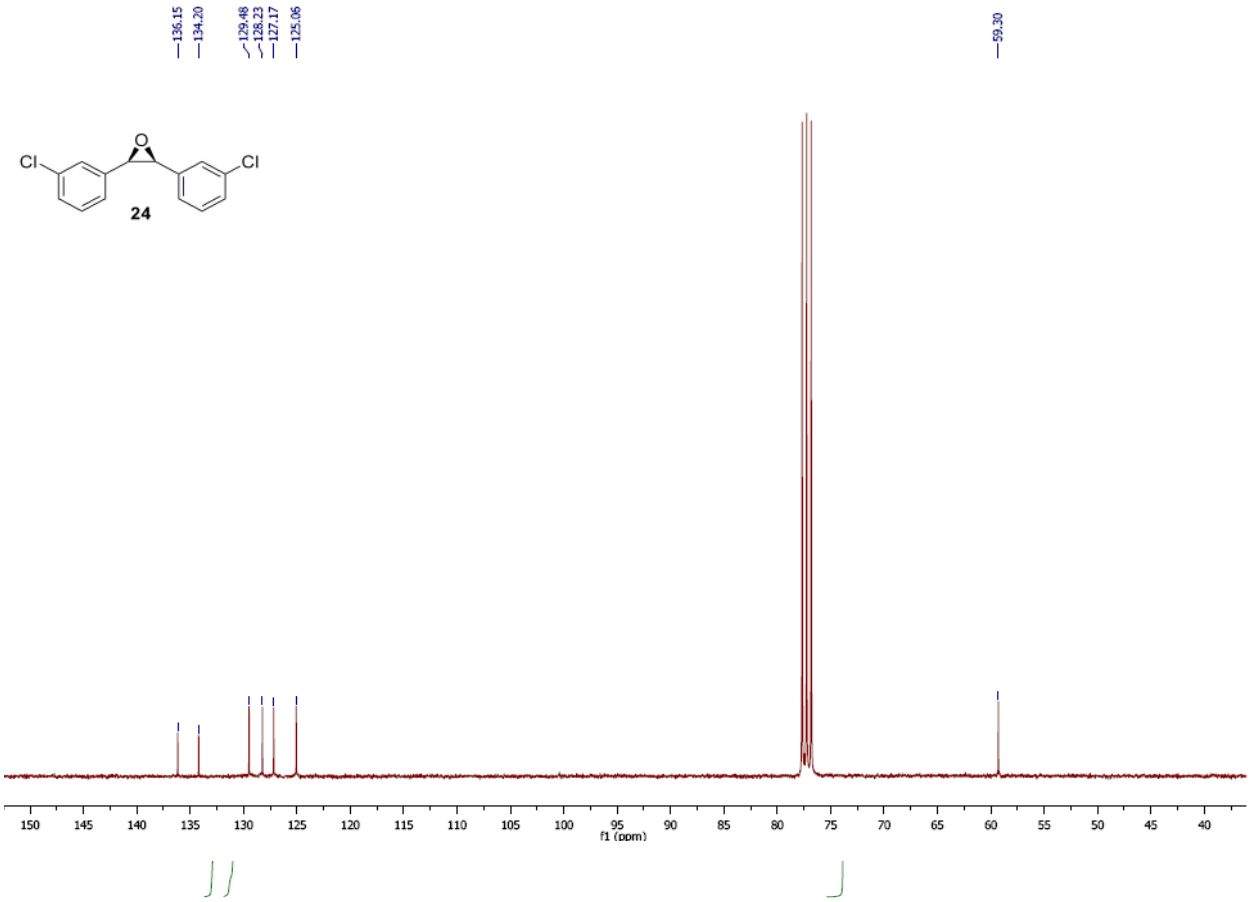

OBz
Cl
2.07
1.07
2.26
1.00
1.07
2.56
3.94
4.10
f1 (ppm)

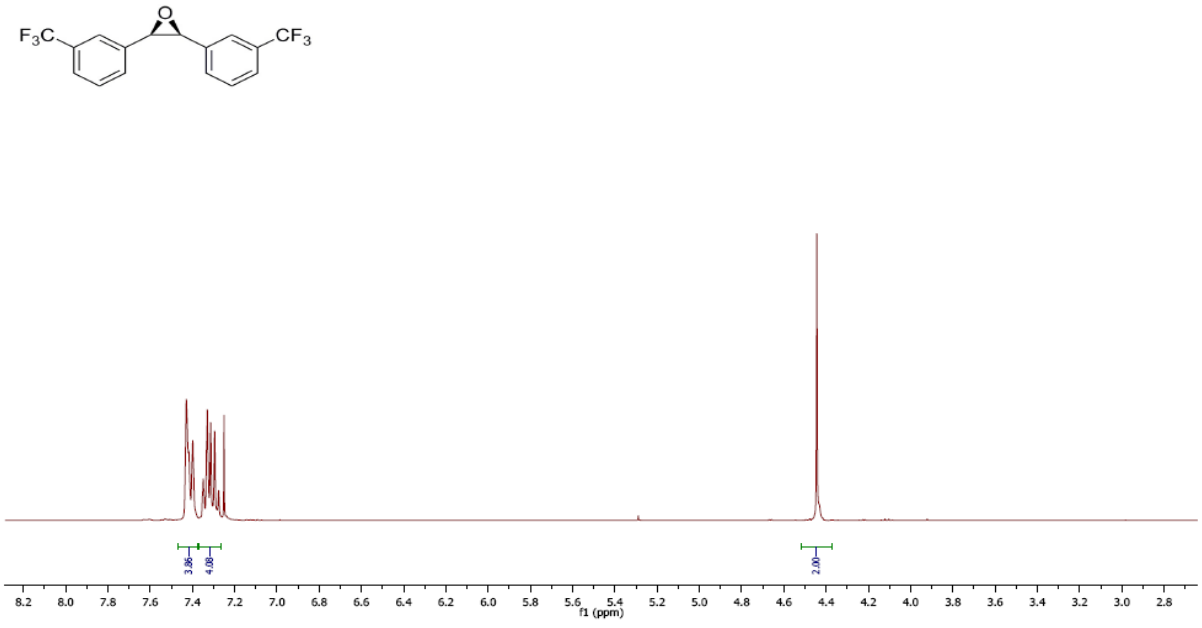

165.94
133.24
130.48
129.93
128.59
76.59
60.82
34.91
30.85
24.64
23.44
OBz
Cl
f1 (ppm)

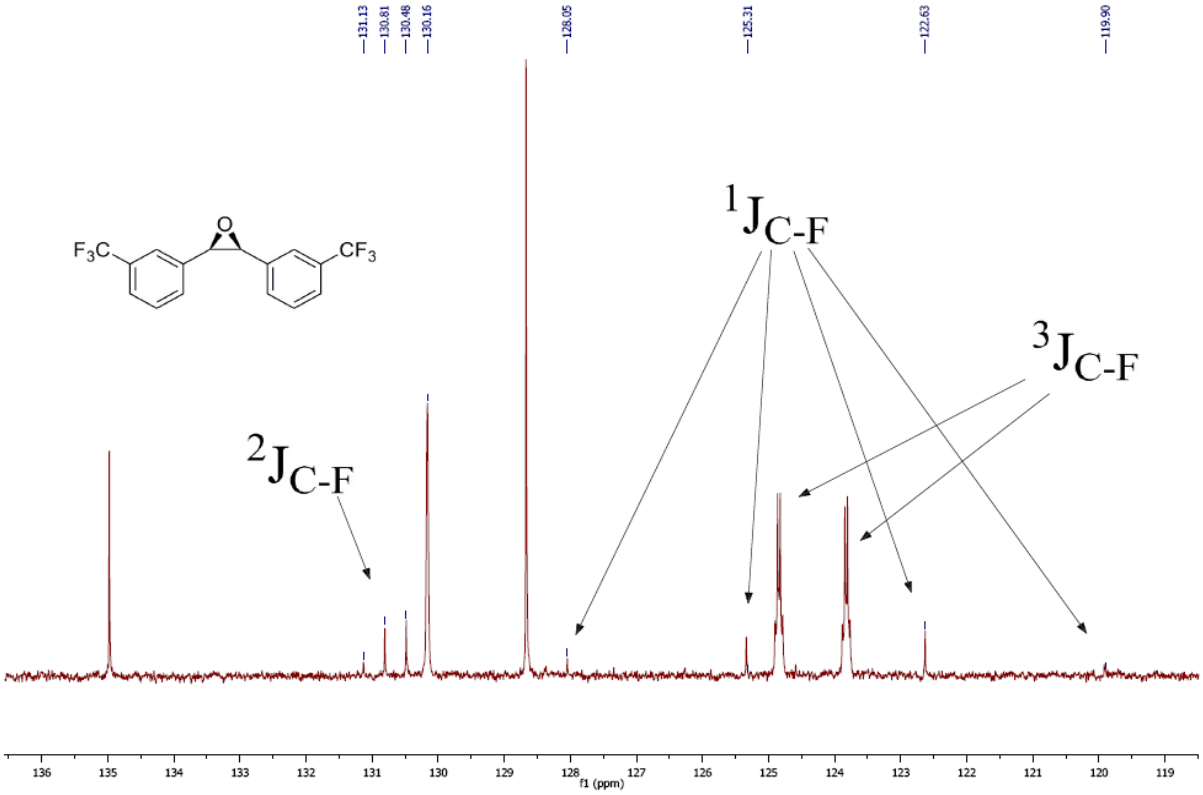

Cl
O
Cl

24


1.79
3.89
1.99
2.00
f1 (ppm)


136.15
134.20
129.48
128.23
127.17
125.06
59.30
Cl
Cl
O
24
f1 (ppm)


F3C
CF3
O
3.86
4.08
2.00
f1 (ppm)


131.13
130.81
130.48
130.16
128.05
125.31
122.63
119.90
F3C
CF3
O
1JC-F
3JC-F
2JC-F
136
135
134
133
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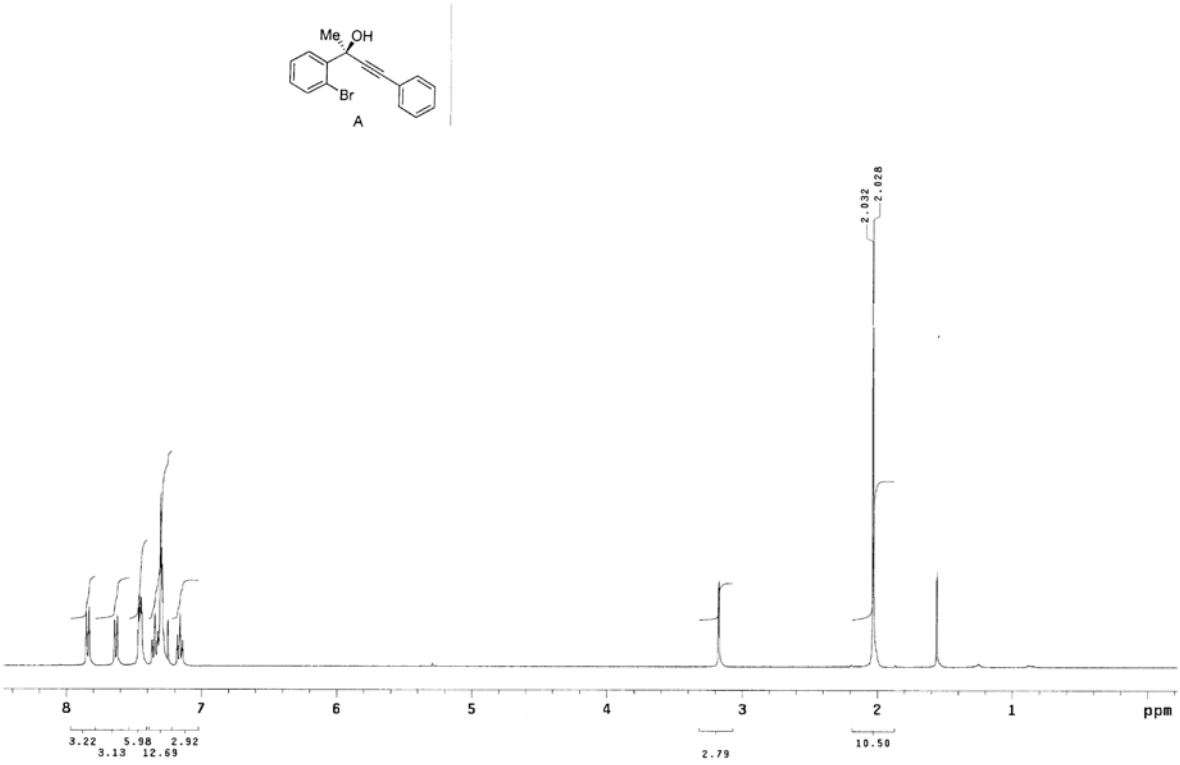
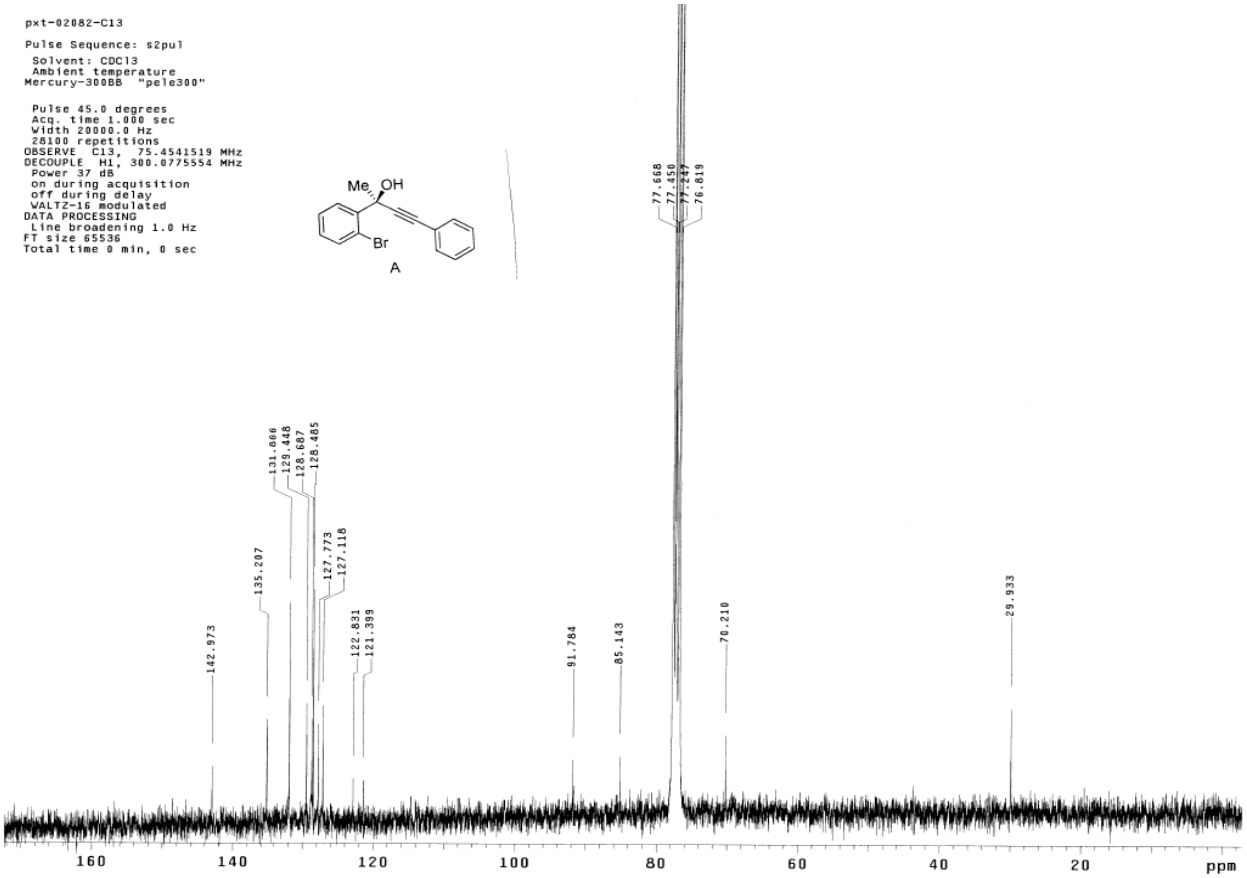
131
130
129
128
127
126
125
124
123
122
121
120
119
f1 (ppm)


Me
OH
Br
A
2.032
2.028
8
7
6
5
4
3
2
1
ppm
3.22
5.98
2.92
3.13
12.69
2.79
10.50

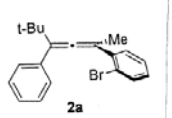

pxt-02082-C13
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "pele300"
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 20000.0 Hz
28100 repetitions
OBSERVE C13, 75.4541519 MHz
DECOUPLE H1, 300.0775554 MHz
Power 37 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 0 min, 0 sec
Me
OH
Br
A
77.668
77.450
77.247
76.819
131.066
129.448
128.687
128.485
127.773
127.118
122.831
121.399
142.973
135.287
91.784
85.143
76.210
29.933
160
140
120
100
80
60
40
20
ppm

pxt-02049

File: Proton

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-400 "pele400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6396.4 Hz
16 repetitions
OBSERVE H1, 399.7793055 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 21 sec



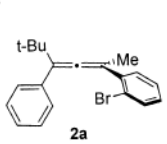
2a

Std proton

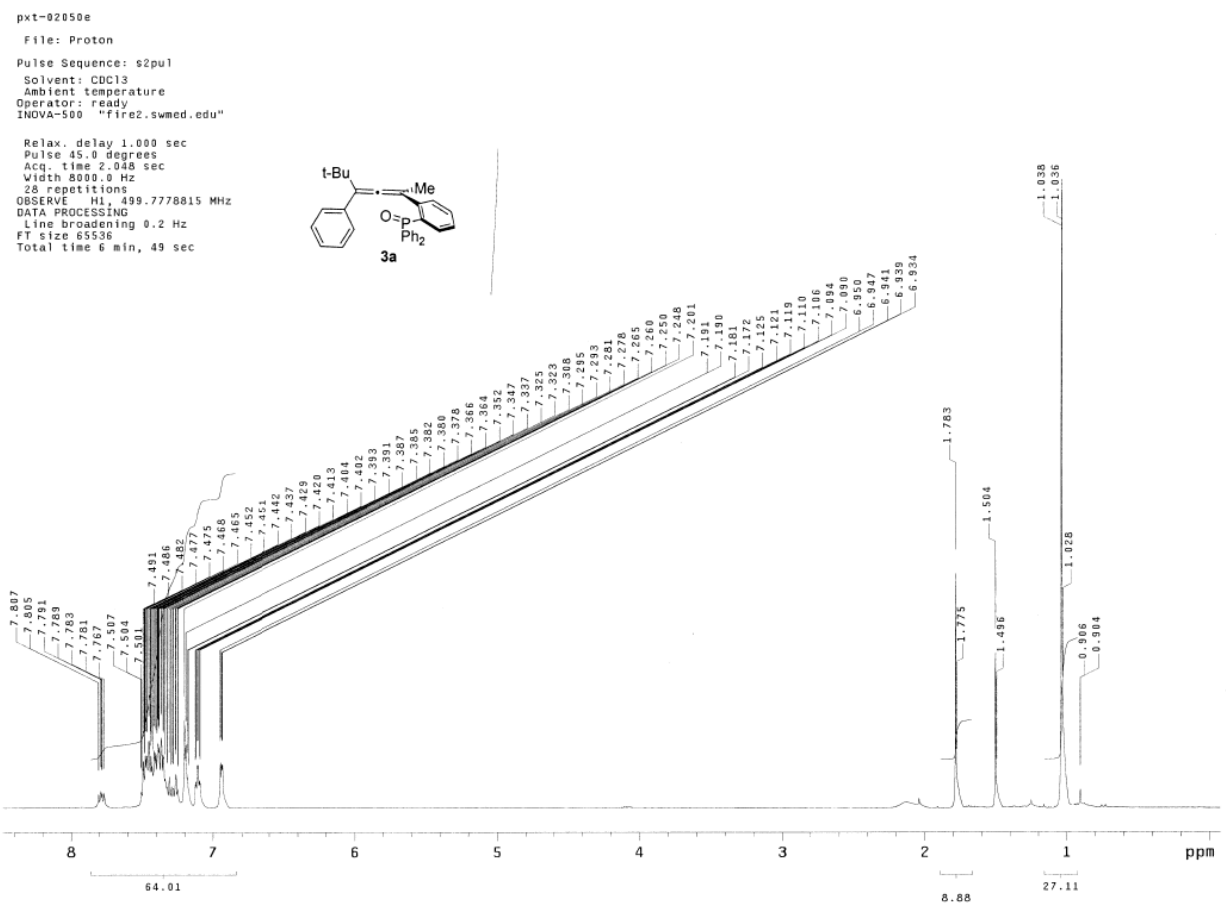
File: pxt-02049-C13

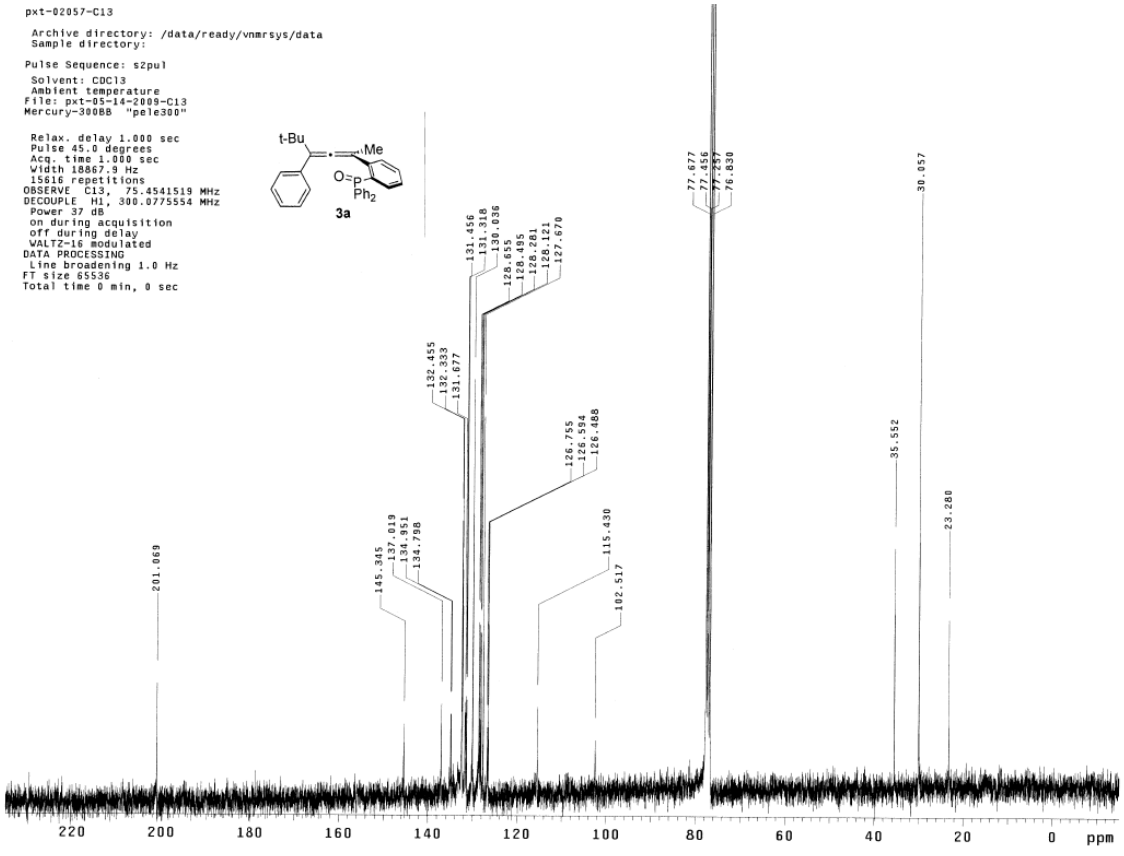
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
File: pxt-02049-C13
INOVA-400 "pele400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24125.5 Hz
132 repetitions
OBSERVE C13, 100.5245623 MHz
DECOUPLE H1, 399.7813047 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 4 hr, 29 min, 25 sec



2a


pxt-02050e
File: Proton
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Operator: ready
INOVA-500 "fire2.swmed.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
28 repetitions
OBSERVE H1, 499.7778815 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 6 min, 49 sec
t-Bu
Me
O=P
Ph2
3a
ppm
64.01
8.88
27.11

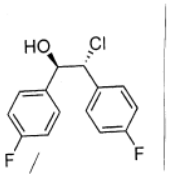

pxt-02057-C13
Archive directory: /data/ready/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: pxt-05-14-2009-C13
Mercury-300BB "pele300"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
15616 repetitions
OBSERVE C13, 75.4541519 MHz
DECOUPLE H1, 300.0775554 MHz
Power 37 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 0 min, 0 sec
t-Bu
Me
O=P
Ph2
3a
ppm

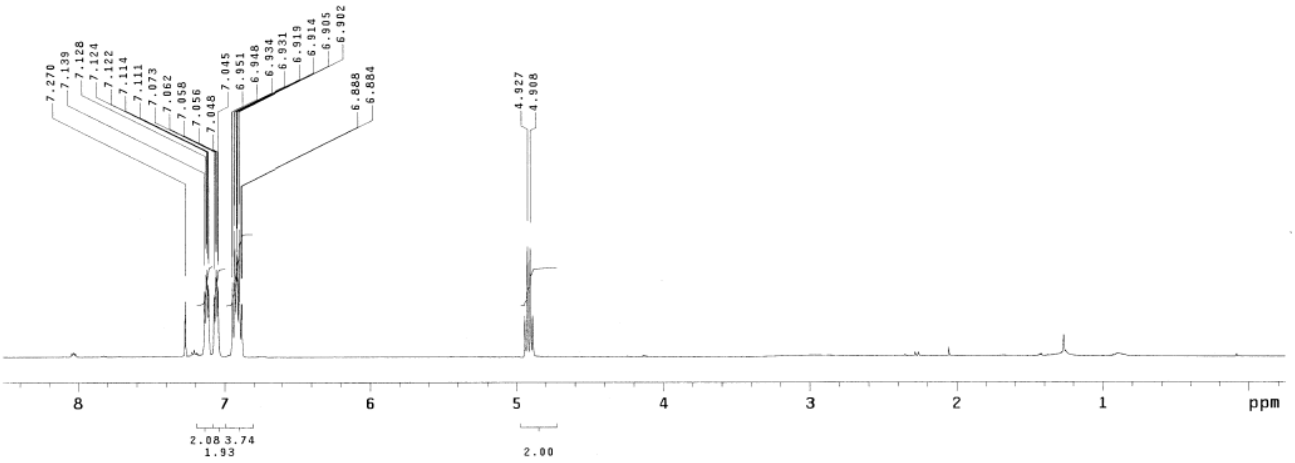
pxt-02293

File: Proton

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-500 "fire2.swmed.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
20 repetitions
OBSERVE H1, 499.7778753 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 21 sec



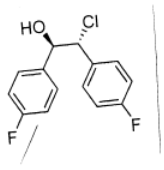


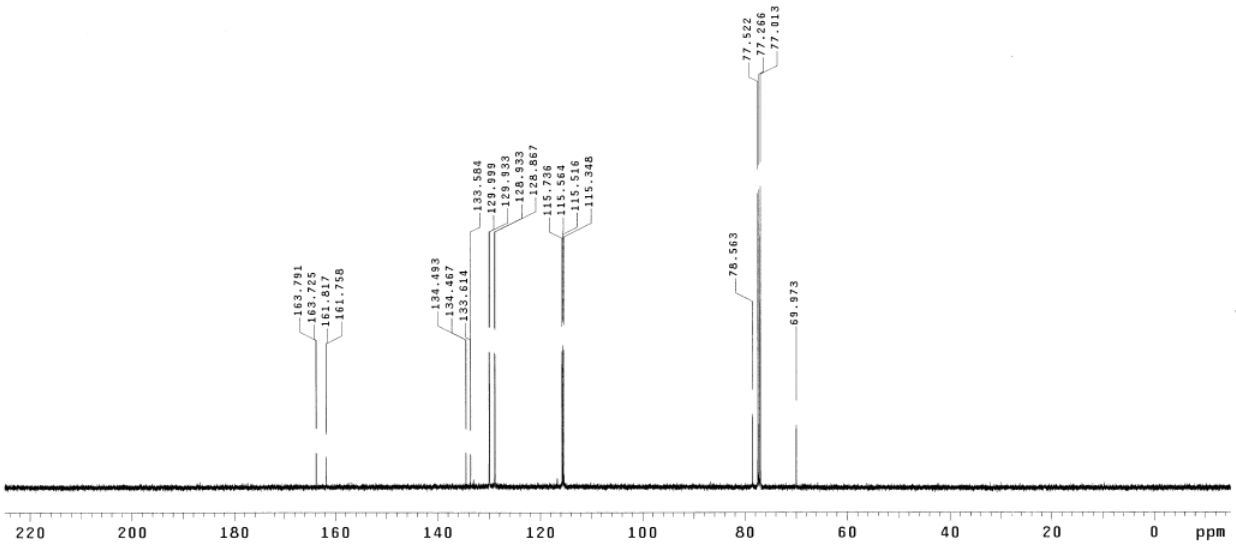
Standard Carbon

File: Carbon

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-500 "fire2.swmed.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
2376 repetitions
OBSERVE C13, 125.6692167 MHz
DECOUPLE H1, 499.7803743 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 38 hr, 29 min, 22 sec



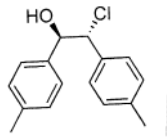


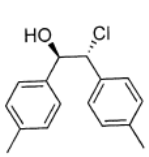
pxt-03033

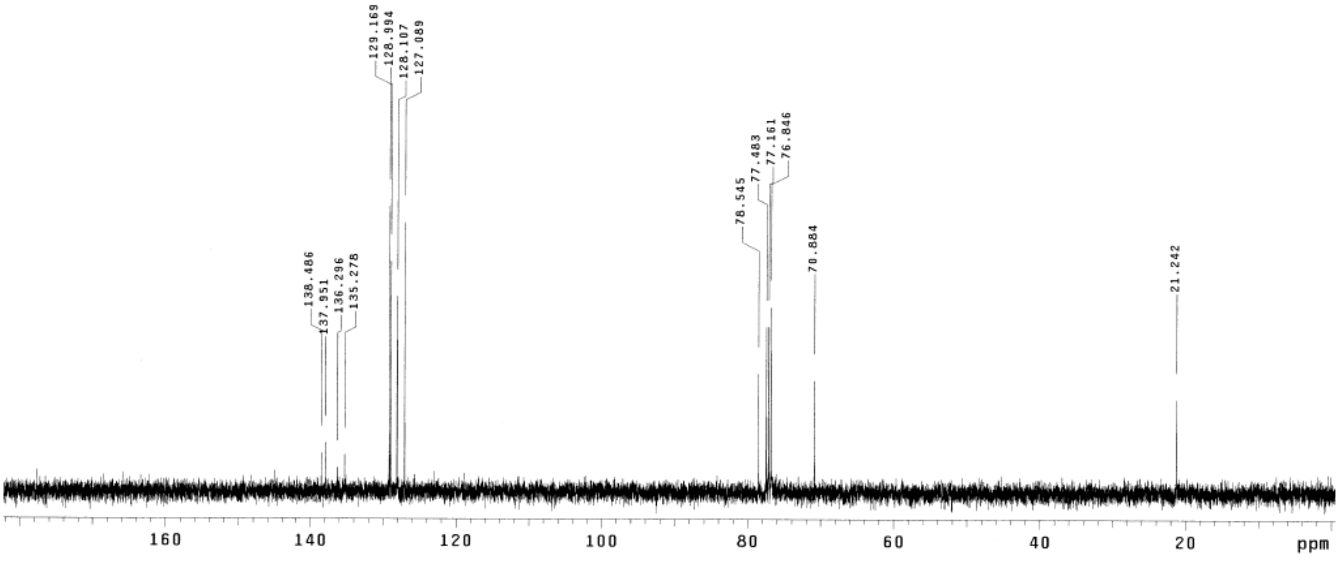
File: Proton

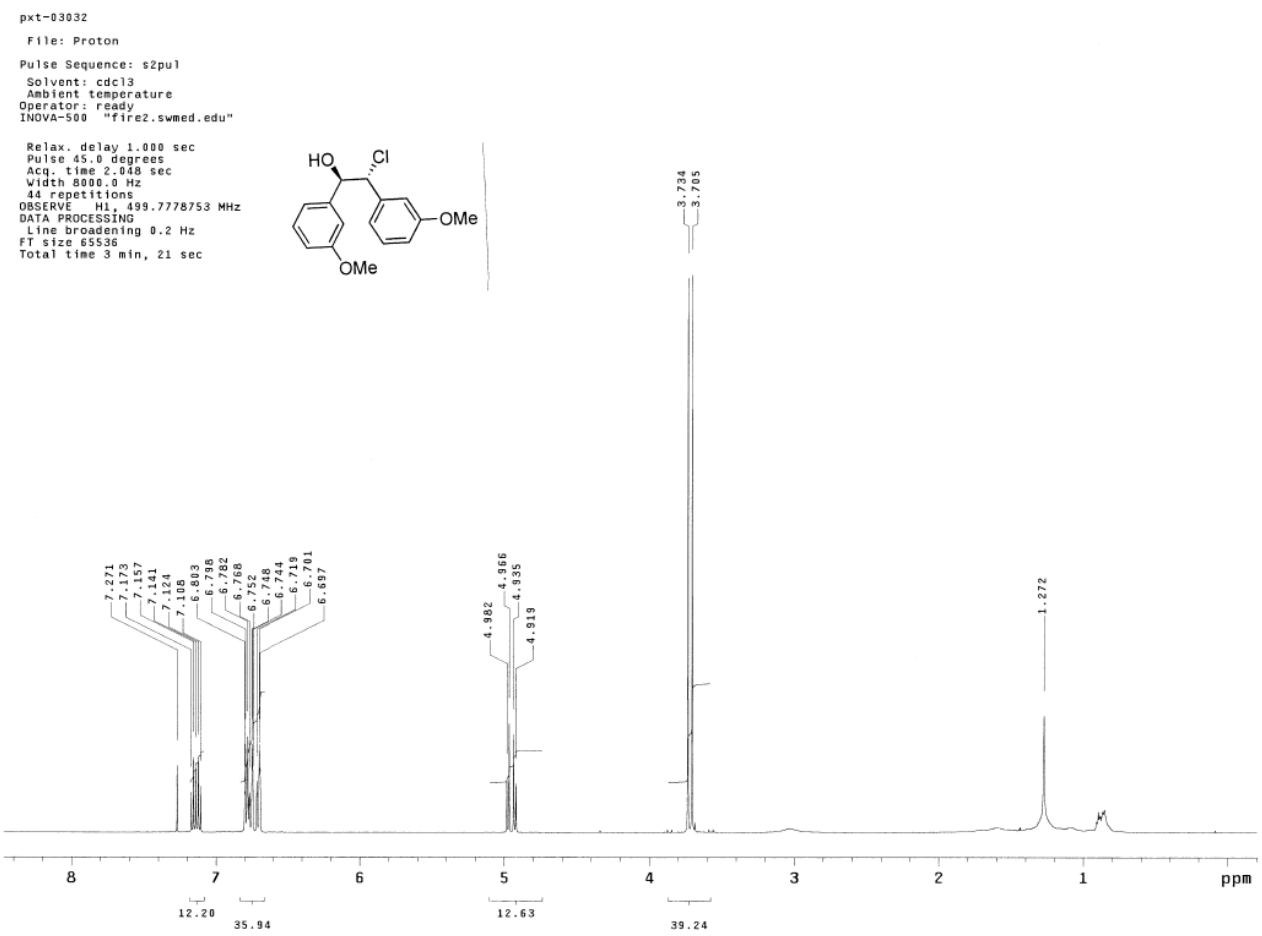
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 50.0 C / 323.1 K
Operator: ready
INOVA-400 "pele400"

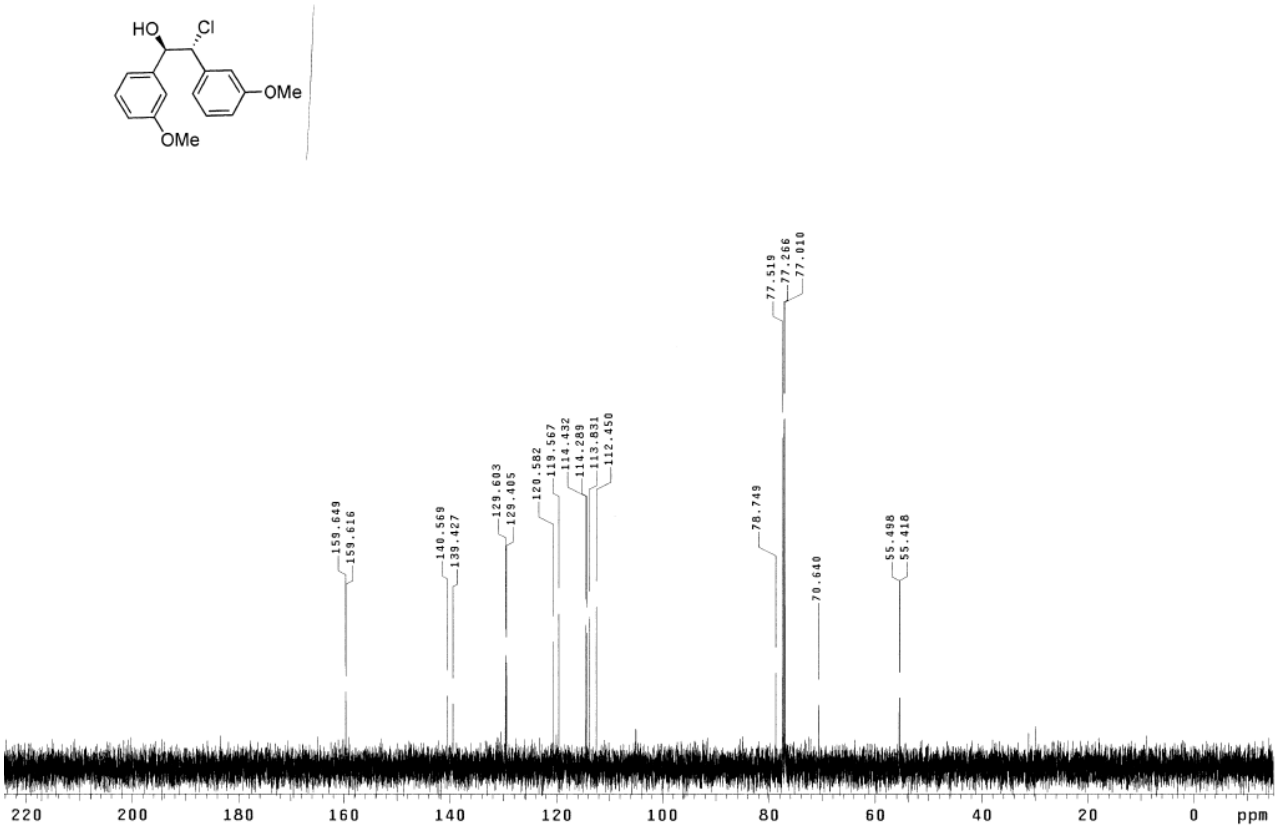
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6396.4 Hz
48 repetitions
OBSERVE H1, 399.7793055 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 21 sec







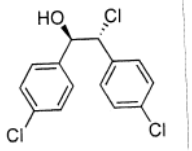

pxt-03032
File: Proton
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-500 "fire2.swmed.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
44 repetitions
OBSERVE H1, 499.7778753 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 21 sec
HO
Cl
OMe
OMe
7.271
7.173
7.157
7.141
7.124
7.108
6.803
6.798
6.782
6.768
6.752
6.748
6.744
6.719
6.701
6.697
4.982
4.966
4.935
4.919
3.734
3.705
1.272
8
7
6
5
4
3
2
1
ppm
12.20
35.94
12.63
39.24

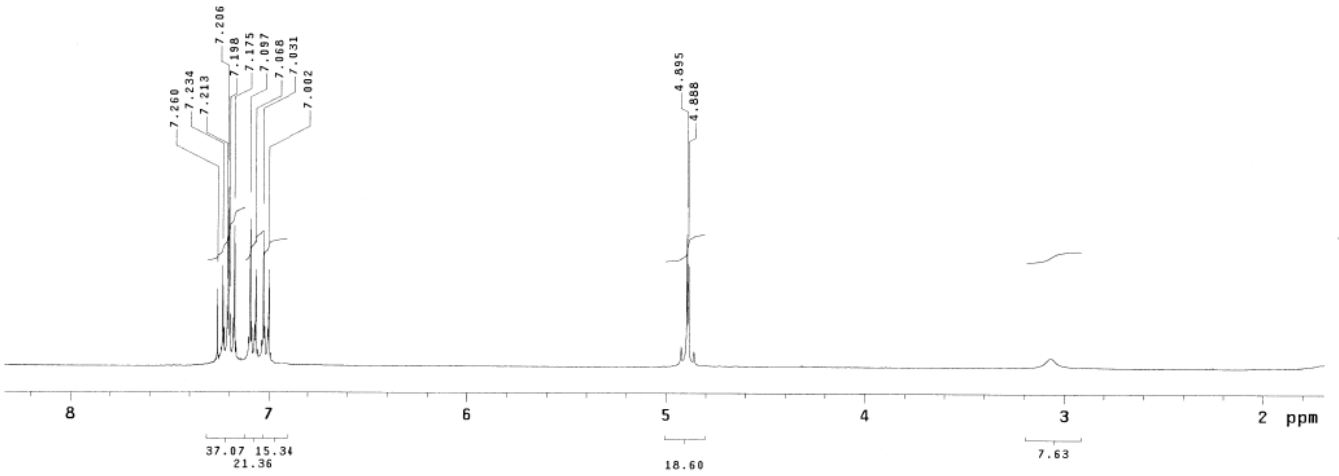

HO
Cl
OMe
OMe
159.649
159.616
140.569
139.427
129.603
129.405
120.582
119.567
114.432
114.289
113.831
112.450
77.519
77.266
77.010
78.749
70.640
55.498
55.418
220
200
180
160
140
120
100
80
60
40
20
0
ppm

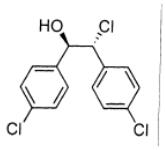
pxt-03029

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "pele300"

Relax. delay 2.000 sec
Pulse 73.6 degrees
Acq. time 1.998 sec
Width 5805.0 Hz
40 repetitions
OBSERVE H1, 300.0759987 MHz
DATA PROCESSING
FT size 32768
Total time 4 min, 40 sec





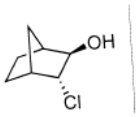


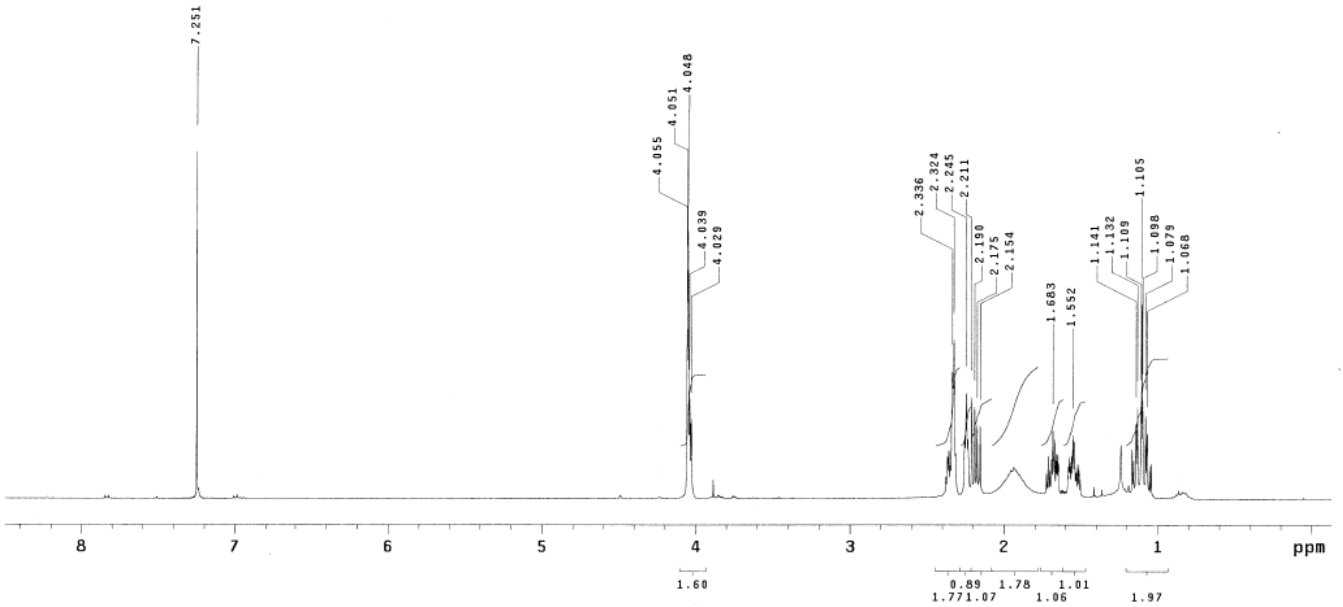
pxt-03035-1

File: Proton

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-400 "pele400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6396.4 Hz
40 repetitions
OBSERVE H1, 399.7793055 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 21 sec

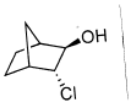


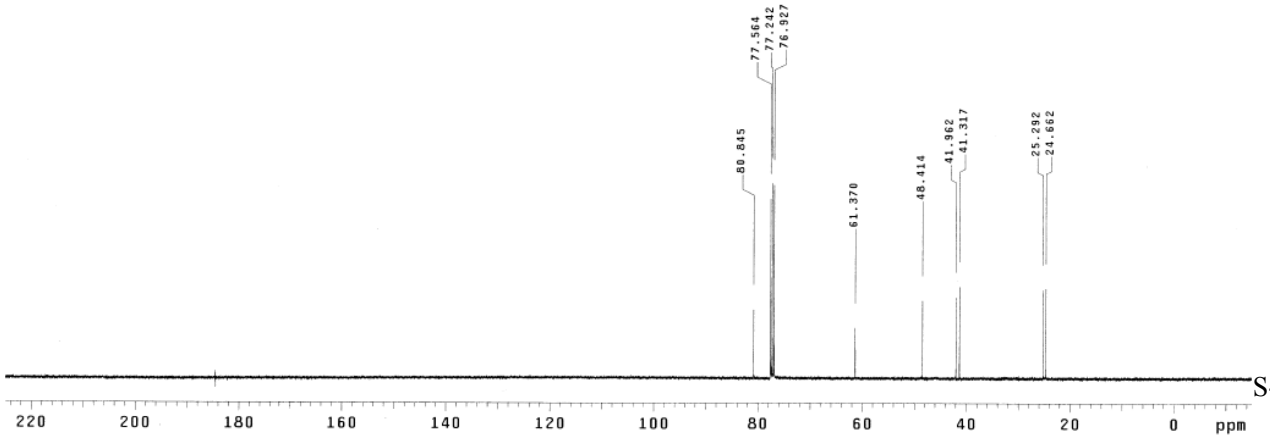


File: Carbon

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-400 "pele400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24125.5 Hz
14280 repetitions
OBSERVE C13, 100.5245623 MHz
DECOUPLE H1, 399.7813047 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 64 hr, 9 min, 0 sec



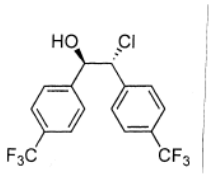


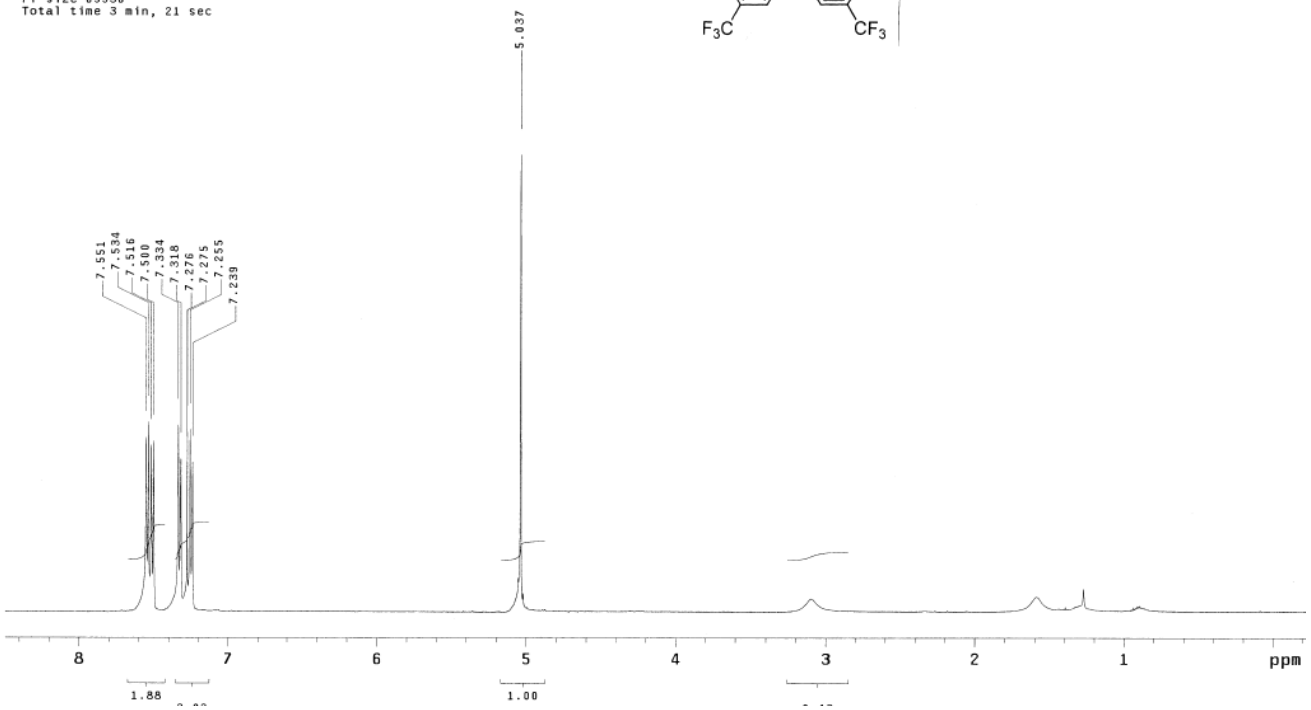
pxt-03036

File: Proton

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-500 "fire2.swmed.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7778753 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 3 min, 21 sec



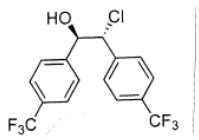


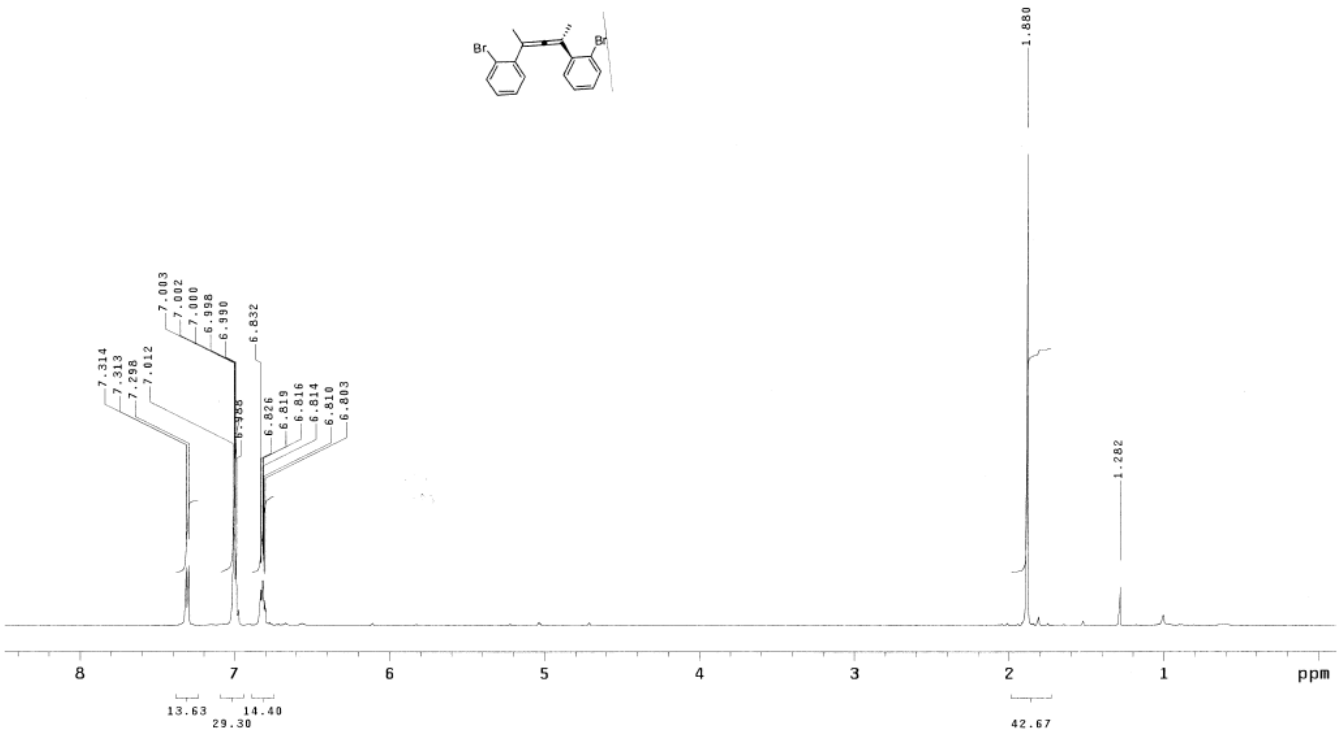
Standard Carbon

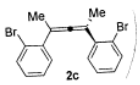
File: Carbon

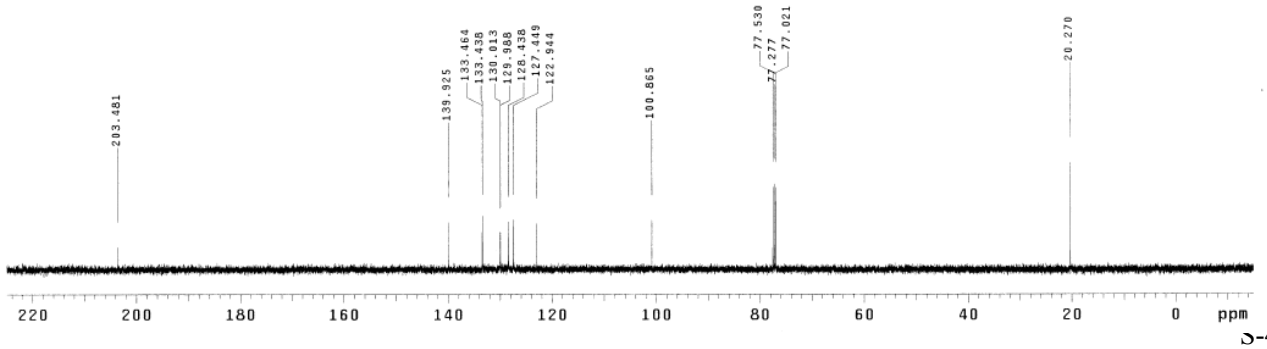
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: ready
INOVA-500 "fire2.swmed.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
764 repetitions
OBSERVE C13, 125.6692167 MHz
DECOUPLE H1, 499.7803743 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 38 hr, 29 min, 22 sec




Br
Br
7.314
7.313
7.298
7.012
7.003
7.002
7.000
6.998
6.990
6.832
6.826
6.819
6.816
6.814
6.810
6.803
1.880
1.282
8
7
6
5
4
3
2
1
ppm
13.63
14.40
29.30
42.67


Me
Me
Br
Br
2c


203.481
139.925
133.464
133.438
130.013
129.988
128.438
127.449
122.944
100.865
77.530
77.277
77.021
26.270
220
200
180
160
140
120
100
80
60
40
20
0
ppm