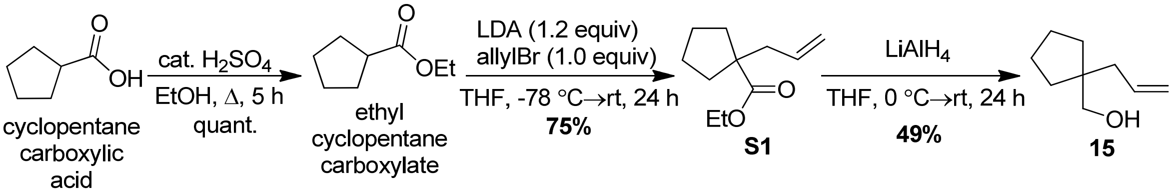
Experimental Supporting Information

General information: All reactions were performed under an argon atmosphere with stirring, unless otherwise noted. Bisoxazoline ligand 4,5-dihydro-2-(2-(4,5-dihydrooxazol-2-yl)propan-2-yl)oxazole, (achiral box) used to generate racemic samples for HPLC analysis, was synthesized using our previously reported procedure.[1] The 1,1-diphenylethylene **13a** was purchased from Aldrich and used without further purification. The 4,4'-(ethene-1,1-diyl)bis(methoxybenzene) **13b**, 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) **13c**, 3-methylene-2,3-dihydrobenzofuran **25** and 2-ethyl-3-methylene-1-tosylindoline **27** alkene acceptors were synthesized according to a previously reported procedures.[2] The MnO_2 used was obtained from Aldrich as an activated, <5 μm powder of 85% purity and used out of the bottle as supplied. All other reagents were purchased from Aldrich, Acros or Strem. Solvents were purified using a solvent filtration system purchased from Contour Glass Co (Irvine, California). $PhCF_3$ was purchased from Acros and distilled from CaH_2 prior to use. ^{1}H NMR spectra were recorded at 300, 400 or 500 MHz using Varian instruments. ^{13}C NMR data were recorded at 75 MHz. Coupling constants (*J*) are in hertz. Abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet, ABq = AB quartet, AX = AX quartet and br = broad. IR spectra were taken neat using a Nicolet-Impact 420 FTIR. Wave numbers in cm^{-1} are reported for characteristic peaks. High resolution mass spectra were obtained at SUNY, Buffalo's mass spec. facility on a ThermoFinnigan MAT XL spectrometer. Melting points were obtained on an electrothermal melting point apparatus and are reported uncorrected. X-ray structures were obtained at the X-ray crystallographic facilities at the University of Rochester. Optical rotations were obtained using a Rudolph Autopol I Polarimeter fitted with a micro cell with a 1 dm path length. Enantiomeric excess was determined by high performance liquid chromatography (HPLC) using Chiralpak AD-RH or Regis (*S*, *S*)-Whelk chiral analytical column (UV detection at 254nm).

Synthesis of substrates:

Substrates **1a**, **1b**, **3**, **5**, **7**, **9**, **17**, **20** and **22** were synthesized as previously reported.[3,4,5] Ethyl cyclopentane carboxylate was synthesized as previously reported.[6] Substrate **15** was synthesized via the following route, adapted from a previously reported procedure[7], starting from the commercially available cyclopentane carboxylic acid:



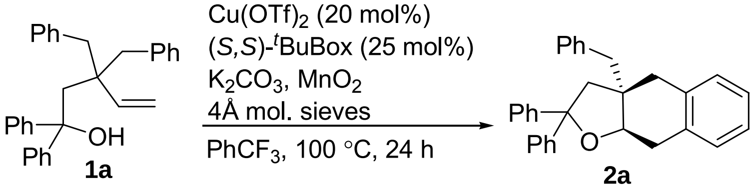
(1-Allylcyclopentyl)methanol (15)

Ethyl cyclopentane carboxylate was obtained via the previously reported method[6]: Cyclopentane carboxylic acid (2.85 mL, 3.00 g, 26.3 mmol) was dissolved in absolute ethanol (14 mL) at room temperature. To this mixture was added conc. sulfuric acid (0.33 mL) and then the reaction was refluxed for 5 hours. The reaction mixture was allowed to cool to room temperature and then excess ethanol was removed under reduced pressure and the remaining oil was slowly poured over crushed ice with stirring. The ester separated from the mixture as an oil and was isolated with a separatory funnel. The aqueous layer was then extracted with chloroform (2 x 20 mL). The combined organic layers were washed with water, sat. sodium bicarbonate and water (1 x 50 mL each). The combined organics were dried over anhydrous magnesium sulfate. Removal of solvents gave ethyl cyclopentane carboxylate quantitatively as a pale yellow, sweetly fragrant, volatile oil.

Adapted from a previous reported procedure[7]: Diisopropylamine (4.46 mL, 31.6 mmol, 1.2 equiv) was dissolved in THF (26 mL) at room temperature before placing the flask in a -78 °C bath. After stirring the mixture for 10 minutes 1.6 M ^{n}BuLi (19.7 mL, 31.5 mmol, 1.2 equiv) was added dropwise via syringe to the reaction mixture. After stirring the mixture for an additional 30 minutes ethyl cyclopentane carboxylate (3.74 g, 26.3 mmol, 1.0 equiv) was added dropwise via syringe. After stirring the mixture for an additional 30 minutes, allylbromide (2.29 mL, 26.3 mmol, 1.0 equiv) was added dropwise via syringe. The reaction mixture was then left to come to room temperature and stir overnight. The reaction was then quenched by the slow addition of sat. ammonium chloride solution (25 mL) and the organic layer was separated. The organics were then dried over anhydrous magnesium sulfate and the solvent removed *in vacuo* to give **S1** (3.59 g) in 75% crude yield as a clear oil.

Lithium aluminum hydride (2.10 g, 55.3 mmol, 2.8 equiv) was added in five portions to a solution of **S1** (3.59 g, 19.7 mmol, 1 equiv) in THF (105 mL) at 0 °C. The mixture was then stirred and allowed to come to room temperature overnight. The reaction was quenched with sat. ammonium chloride and the mixture was extracted with ethyl acetate (3 x 50 mL). The combined organics were dried over anhydrous magnesium sulfate and after filtration the solvents were removed *in vacuo* to give an oily residue which, when subjected to flash chromatography using hexanes-EtOAc 83 : 17, gave the pentenol **15** (1.36 g) in 49% yield as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95-5.77 (m, 1H), 5.12-5.03 (m, 2H), 3.40 (s, 2H), 2.16 (d, J = 6.9 Hz, 2H), 1.64-1.39 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 116.9, 69.0, 47.2, 42.0, 34.1, 25.2; IR (neat): 3361, 3075, 2951, 2868, 1639, 1453, 1039, 994, 912 cm^{-1}; LRMS (CI) calc'd for $[M-OH]^+$ C_9H_{15}: 123.2, found 123.2.

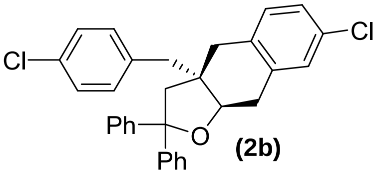
Representative procedure for the Cu(OTf)$_2$-catalyzed enantioselective intramolecular carboetherification:



(3a*R*,9a*R*)-3a-Benzyl-2,2-diphenyl-2,3,3a,4,9,9a-hexahydronaphtho[2,3-b]furan (2a)

*Excess moisture can adversely affect the enantioselectivity of these reactions. Care should be taken to maintain anhydrous conditions. Cu(OTf)$_2$ should either be obtained from a glove box or lightly flame dried under vacuum before use. Cu(OTf)$_2$ (9.4 mg, 0.026 mmol, 20 mol %) and (*S*,*S*)-^{t}Bu-Box ligand (9.6 mg, 0.033 mmol, 25 mol %) were placed in a 12 mL glass reaction tube with a stir bar and $PhCF_3$ (1.0 mL). The tube was then flushed with argon, capped and stirred at 60 °C for 2 h. The reaction mixture was allowed to cool to room temperature before K_2CO_3 (18.1 mg, 0.131 mmol, 1 equiv) and MnO_2 (33.9 mg, 0.390 mmol, 3 equiv) were added. Alcohol **1a** (54.4 mg, 0.130 mmol) dissolved in $PhCF_3$ (0.30 mL) was then added to the mixture followed by flame activated 4Å mol. sieves (~30 mg). The tube was flushed with argon again, capped and stirred at 100 °C for 24 h. The reaction was then allowed to cool to room temperature before being diluted with EtOAc (3 mL) and filtered through a pad of Celite (~5 g). The Celite was then rinsed with EtOAc (3 x 30 mL) and the combined filtrate was concentrated *in vacuo*. The residue was purified by prep TLC (SiO_2, 9 : 1 hexanes/Et_2O) to afford 51 mg (95% yield) of **2a** as a clear oil. *The same procedure is followed using the 4,5-dihydro-2-(2-(4,5-dihydrooxazol-2-yl)propan-2-yl)oxazole (achiral box), in order to generate racemic products used for analytical HPLC analysis. ^1H NMR data matched that previously reported by Chemler.[3] ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.35-7.20 (m, 7H), 7.10-7.04 (m, 3H), 7.03-6.99 (m, 3H), 6.70-6.67 (m, 2H), 4.40-4.38 (m, 1H), 3.13 (dd, J = 15.0, 3.2 Hz, 1H), 2.97 (dd, J = 13.2, 2.0 Hz, 1H), 2.73 (dd, J = 15.2, 3.2 Hz, 1H), 2.63 (d, J = 12.8 Hz, 1H), 2.48-2.44 (m, 2H), 2.38 (dd, J = 13.6, 1.6 Hz, 1H), 2.01 (d, J = 12.8 Hz, 1H); $[\alpha]_D^{19}$ = 98.9° (c = 0.14, $CHCl_3$); ee = >95%, determined by HPLC analysis [Chiralpak AD-RH, 57 : 43 MeCN/H_2O, 0.20 mL/min, λ = 254 nm, t(major) = 138.65 min, t(minor) = 153.09 min].

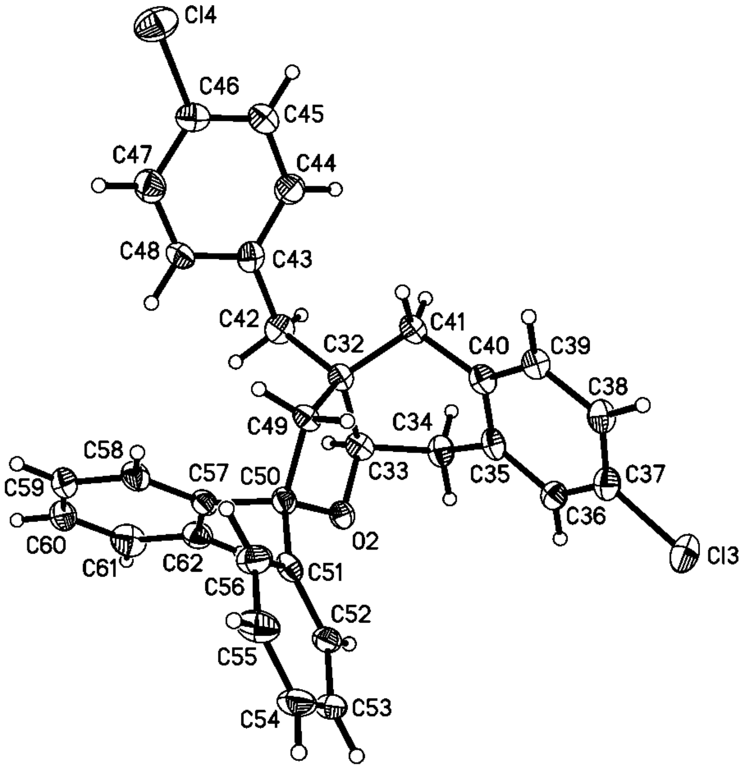
(3a*R*,9a*R*)-7-Chloro-3a-(4-chlorobenzyl)-2,2-diphenyl-2,3,3a,4,9,9a-hexahydronaphtho[2,3-b]furan (2b)



(2b)

^1H NMR data matched that previously reported by Chemler.[3] Tetrahydronaphthofuran **2b** was purified by flash chromatography (SiO_2, 100 : 0 - 80 : 20 gradient hexanes/EtOAc) to give (47 mg) obtained from the catalytic carboetherification of **1b** as a white solid (95% yield), mp 137-139 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 8.4, 1.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.28-7.23 (m, 3H), 7.19 (dd, J = 8.4, 2.4 Hz, 1H), 7.07-7.04 (m, 3H), 6.99-6.96 (m, 3H), 6.75-6.72 (m, 2H), 4.34 (t, J = 3.6 Hz, 1H), 3.10 (dd, J = 15.2, 3.2 Hz, 1H), 2.90 (d, J = 13.2 Hz, 1H), 2.66 (dd, J = 15.2, 3.2 Hz, 1H), 2.46 (ABq, J_{AB} = 14.0, $\Delta\nu$ = 29.5 Hz, 2H), 2.38 (ABq, J_{AB} = 13.2, $\Delta\nu$ = 23.9 Hz, 2H), 1.99 (d, J = 13.2 Hz, 1H); $[\alpha]_D^{19}$ = 112.1° (c = 0.43, $CHCl_3$); ee = >95%, determined by HPLC analysis [Chiralpak AD-RH, 62 : 38 MeCN/H_2O, 0.20 mL/min, λ = 254 nm, t(major) = 178.78 min, t(minor) = 197.52 min].

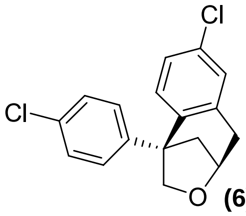
The X-ray crystal structure of **2b** (CCDC 985356) was used to establish 3a*R*, 9a*R* stereochemistry (C32 and C33 below, respectively). The structure was obtained by William W. Brennessel at the Crystallographic Facility at the University of Rochester.



(3a*R*,9a*R*)-3a-Benzyl-2,3,3a,4,9,9a-hexahydronaphtho[2,3-b]furan (4)

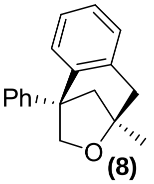
Tetrahydronaphthofuran **4** was purified by flash chromatography (SiO_2, 100 : 0 - 80 : 20 gradient hexanes/EtOAc) to give (28 mg) obtained from the catalytic carboetherification of **3** as a clear oil (71% yield). ^{1}H NMR data matched that previously reported by Chemler.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.07 (m, 9H), 4.12 (t, *J* = 4.4 Hz, 1H), 3.68-3.58 (m, 2H), 2.89 (dd, *J* = 15.2, 4.0 Hz, 1H), 2.80-2.69 (m, 3H), 2.57 (ABq, J_{AB} = 14.8, Δν = 52.8 Hz, 2H), 2.05-1.99 (m, 1H), 1.50-1.42 (m, 1H); $[\alpha]_D^{19.0}$ = 7.3° (*c* = 0.55, $CHCl_3$); ee = 70%, determined by HPLC analysis [Regis (*S*, *S*)-Whelk, 95 : 5 Hex./^{i}PrOH, 1.00 mL/min, λ = 254 nm, t(major) = 4.57 min, t(minor) = 3.97 min].

(1*S*,4*R*)-7-Chloro-1-(4-chlorophenyl)-1,2,4,5-tetrahydro-1,4-methanobenzo[d]oxepine (6)


(6)

Tetrahydrofuran **6** was purified by Prep TLC (SiO_2, 100 : 0 - 90 : 10 gradient hexanes/EtOAc) to give (34 mg) obtained from the catalytic carboetherification of **5** (reaction run at 120 °C) as a white solid (77% yield), mp 121-123 °C. ^1H NMR data matched that previously reported by Chemler.[3] ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.17-7.12 (m, 3H), 6.92 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.40 (d, *J* = 8.4 Hz, 1H), 4.81-4.78 (m, 1H), 4.26 (ABq, J_{AB} = 7.2, Δν = 43.0 Hz, 2H), 3.09 (s, 2H), 2.47 (d, *J* = 10.8 Hz, 1H), 2.33 (dd, *J* = 11.6, 6.8 Hz, 1H); $[\alpha]_D^{19.6}$ = -64.8° (*c* = 0.50, $CHCl_3$). ee = 82%, determined by HPLC analysis [Regis (*S*, *S*)-Whelk, 95 : 5 Hex./^{i}PrOH, 1.00 mL/min, λ = 254 nm, t(major) = 6.35 min, t(minor) = 5.53 min].

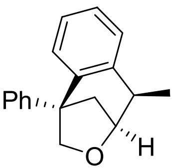
(1*S*,4*R*)-4-Methyl-1-phenyl-1,2,4,5-tetrahydro-1,4-methanobenzo[d]oxepine (8)


(8)

Tetrahydrofuran **8** was purified by Prep TLC (SiO_2, 100 : 0 - 90 : 10 gradient hexanes/EtOAc) to give (36 mg) obtained from the catalytic carboetherification of **7** (reaction run at 120 °C) as a white solid (99% yield), mp 126-128 °C. ^1H NMR data matched that previously reported by Chemler.[3] ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.36-7.31 (m, 1H), 7.24-7.19 (m, 2H), 7.15-7.11 (m, 2H), 6.98-6.94 (m, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 4.34 (ABq, J_{AB} = 7.2, Δν = 12.5 Hz, 2H), 3.10 (s, 2H), 2.38 (AXq, J_{AX} = 10.8, Δν = 143.6 Hz, 2H), 1.55 (s, 3H); $[\alpha]_D^{19.4}$ = -70.5° (*c* = 0.91, $CHCl_3$); ee = 84%, determined by HPLC analysis [Chiralpak AD-RH, 75 : 25 MeCN/H_2O, 1.00 mL/min, λ = 254 nm, t(major) = 4.65 min, t(minor) = 6.53 min].

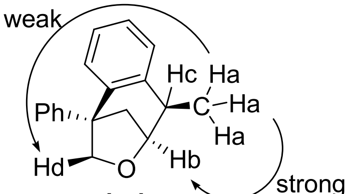
(1*S*,4*S*,5*S*)-5-Methyl-1-phenyl-1,2,4,5-tetrahydro-1,4-methanobenzo[d]oxepine (10)

Tetrahydrofurans **10** and **11** were purified by Prep TLC (SiO_2, 95 : 5 hexanes/Et_2O) to give (37 mg) obtained from the catalytic carboetherification of **9** (reaction run at 120 °C) as a clear oil [96% yield, **10 : 11** (1 : 1)]. They were separated by prep HPLC using 98 : 2 Hex./EtOAc (**10** eluted first) and **10** was a



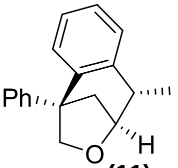
(10)

white crystalline solid, mp 179-181 °C. ^{1}H NMR data matched that previously reported by Chemler.[3] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42-7.27 (m, 4H), 7.24-7.21 (m, 2H), 7.16 (td, J = 7.2, 1.6 Hz, 1H), 6.95 (t, J = 8 Hz, 1H), 6.47 (dd, J = 8.0, 1.6 Hz, 1H), 4.51 (dd, J = 6.4, 2.4 Hz, 1H), 4.30 (ABq, J_{AB} = 6.8, Δν = 20.1 Hz, 2H), 3.16-3.11 (m, 1H), 2.58 (d, J = 10.8 Hz, 1H), 2.41 (dd, J = 11.2, 6.4 Hz, 1H), 1.46 (d, J = 7.2 Hz, 3H); $[\alpha]_D^{19.7}$ = -36.1° (c = 0.19, CHCl$_3$); ee = 94%, determined by HPLC analysis [Regis (S, S)-Whelk, 98 : 2 Hex./^{i}PrOH, 0.20 mL/min, λ = 254 nm, t(major) = 25.74 min, t(minor) = 23.91 min]. The relative stereochemistry of **10** was assigned by NOE and process of elimination (it was not **11**). Saturation of Ha revealed a strong enhancement of Hb but also a weak enhancement of Hd.



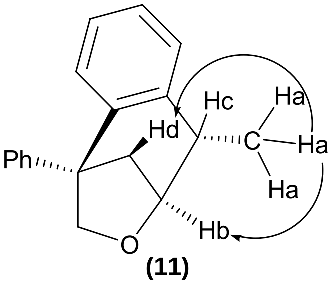
(10)

(1*S*,4*S*,5*R*)-5-Methyl-1-phenyl-1,2,4,5-tetrahydro-1,4-methanobenzo[d]oxepine (11)



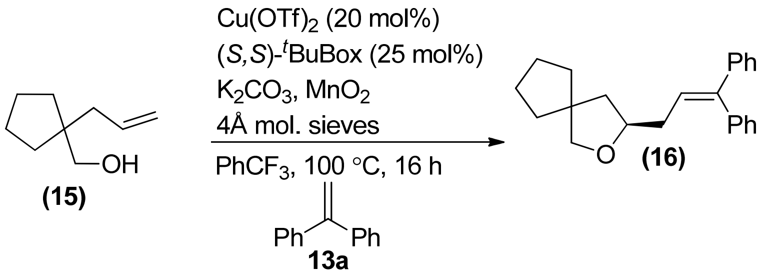
(11)

Tetrahydrofuran **11** was obtained as a clear oil. ^{1}H NMR data matched that previously reported by Chemler.[3] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43-7.31 (m, 4H), 7.25-7.20 (m, 2H), 7.15 (td, J = 7.2, 1.2 Hz, 1H), 6.95 (t, J = 8.4 Hz, 1H), 6.48 (d, J = 8.0 Hz, 1H), 4.50 (dd, J = 6.4, 2.8 Hz, 1H), 4.26 (ABq, J_{AB} = 7.2, Δν = 14.74 Hz, 2H), 3.19-3.14 (m, 1H), 2.61 (d, J = 11.6 Hz, 1H), 2.20 (dd, J = 11.2, 6.8 Hz, 1H), 1.31 (d, J = 6.8 Hz, 3H); $[\alpha]_D^{20.0}$ = -30.7° (c = 0.29, CHCl$_3$); ee = 94%, determined by HPLC analysis [Regis (S, S)-Whelk, 95 : 5 Hex./^{i}PrOH, 1.00 mL/min, λ = 254 nm, t(major) = 7.26 min, t(minor) = 5.22 min]. The relative stereochemistry of **11** was assigned by NOE. Saturation of Ha on diastereomer **III-11** showed strong enhancements of Hb and Hd but no enhancement of Hd.



(11)

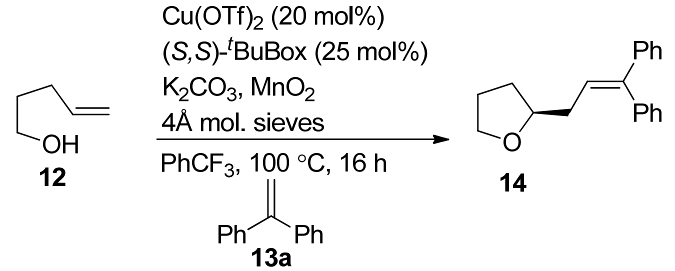
Representative procedure for the Cu(OTf)$_2$-catalyzed enantioselective intermolecular carboetherification:



(*R*)-3-(3,3-Diphenylallyl)-2-oxaspiro[4.4]nonane (16)

*Excess moisture can adversely affect the enantioselectivity of these reactions. Care should be taken to maintain anhydrous conditions. Cu(OTf)$_2$ should either be obtained from a glove box or lightly flame dried under vacuum before use. Cu(OTf)$_2$ (25.0 mg, 0.069 mmol, 20 mol %) and (*S,S*)-^{t}Bu-Box ligand (25.7 mg, 0.087 mmol, 25 mol %) were placed in a 12 mL glass reaction tube equipped with a stir bar. The mixture was dissolved in PhCF$_3$ (1.5 mL) and the tube was flushed with argon and capped. The mixture was stirred at 60 °C for 2 h then allowed to cool to room temperature. K$_2$CO$_3$ (47.3 mg, 0.342 mmol, 1 equiv), MnO$_2$ (90.1 mg, 1.03 mmol, 3 equiv) and 1,1-diphenylethylene **13a** (183 μL, 1.03 mmol, 3 equiv) were added to the reaction mixture. Alcohol **15** (48.3 mg, 0.342 mmol) was dissolved in PhCF$_3$ (0.5 mL) and added to the tube followed by additional PhCF$_3$ (1.4 mL). Flame-dried 4Å mol. sieves (~70 mg) were added directly to the tube while still hot. The tube was flushed with argon and capped and the reaction mixture was stirred at 100 °C for 16 h. The reaction was then allowed to cool to room temperature before being diluted with EtOAc (3 mL) and vacuum filtered through a pad of Celite (~5 g). The Celite was then rinsed with EtOAc (3 x 30 mL) and the combined filtrate was concentrated *in vacuo.*

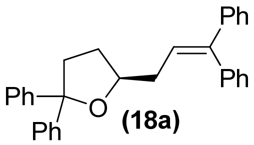
The residue was purified by Prep TLC (SiO_2, 92 : 8 hexanes/EtOAc) to give (41 mg) of **16** as a pale yellow oil (90% yield). $[\alpha]_D^{19.0}$ = -8.5° (*c* = 0.56, $CHCl_3$); ee = 82%, determined by HPLC analysis [Chiralpak AD-RH, 60 : 40 MeCN/H_2O, 0.75 mL/min, λ = 254 nm, t(major) = 33.07 min, t(minor) = 29.39 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2H), 7.32-7.30 (m, 1H), 7.26-7.17 (m, 7H), 6.14 (t, *J* = 7.6 Hz, 1H), 4.09-4.02 (m, 1H), 3.58 (ABq, J_{AB} = 8.0, Δν = 30.2 Hz, 2H), 2.45 (dt, *J* = 7.2, 6.8 Hz, 1H), 2.33 (dt, *J* = 7.6, 6.0 Hz, 1H), 1.88 (dd, *J* = 12, 6.4 Hz, 1H), 1.66-1.43 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.6, 140.0, 129.9, 128.2, 128.0, 127.2, 126.9, 125.6, 79.1, 78.6, 50.9, 44.8, 37.6, 36.7, 36.2, 24.7; IR (neat): 3056, 3024, 2950, 2859, 1599, 1494, 1444, 1362, 1052, 760 cm^{-1}; HRMS (EI) calc'd for $[M^{\cdot}]^+$ $C_{23}H_{26}O$: 318.1986, found 318.1978.



(*S*)-2-(3,3-Diphenylallyl)tetrahydrofuran (14)

The reaction followed the same procedure as above except this reaction was run at 0.08 M with respect to substrate, as opposed to the 0.1 M, in order to eliminate an undesired side product. Upon scale-up to 0.526 mmol of substrate this side product is unavoidable. The residue was purified by flash chromatography (SiO_2, 100 : 0 - 90 : 10 gradient hexanes/Et_2O) to afford 35 mg (92% yield) of **14** as a pale yellow oil. $[\alpha]_D^{18.0}$ = -7.4° (*c* = 0.39, $CHCl_3$); ee = 82%, determined by HPLC analysis [Chiralpak AD-RH, 60 : 40 MeCN/H_2O, 0.75 mL/min, λ = 254 nm, t(major) = 13.71 min, t(minor) = 12.69 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.2 Hz, 2H), 7.32-7.27 (m, 1H), 7.25-7.18 (m, 7H), 6.16 (t, *J* = 7.6 Hz, 1H), 3.97-3.83 (m, 2H), 3.73 (td, *J* = 7.0, 6.8 Hz, 1H), 2.42 (dt, *J* = 7.2, 6.8 Hz, 1H), 2.35-2.28 (m, 1H), 2.01-1.93 (m, 1H), 1.89-1.82 (m, 1H), 1.54-1.45 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.6, 140.1, 129.9, 128.2, 128.0, 127.3, 126.9, 125.7, 79.0, 67.8, 35.8, 30.9, 25.7; IR (neat): 3040, 3012, 2968, 2850, 1495, 1442, 1361, 1076, 759 cm^{-1}; HRMS (EI) calc'd for $[M^{\cdot}]^+$ $C_{19}H_{20}O$: 264.1516, found 264.1509.

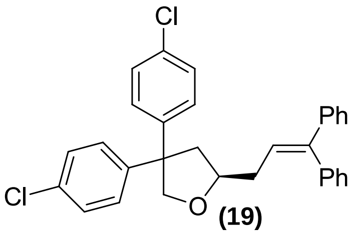
(*S*)-5-(3,3-Diphenylallyl)-2,2-diphenyltetrahydrofuran (18a)



(18a)

Tetrahydrofuran **18a** was purified by flash chromatography (SiO_2, 100 : 0 - 90 : 10 gradient hexanes/Et_2O) to give (55 mg) obtained from the catalytic carboetherification of **17** and **13a** as a clear oil (90% yield). $[\alpha]_D^{19.0}$ = 8.2° (*c* = 0.54, $CHCl_3$); ee = >95%, determined by HPLC analysis [Chiralpak AD-RH, 80 : 20 to 90 : 10 gradient MeOH/H_2O, 0.10 mL/min, λ = 254 nm, t(major) = 229.49 min, t(minor) = 225.11 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.40 (m, 4H), 7.36-7.14 (m, 16H), 6.22 (t, *J* = 7.2 Hz, 1H), 4.26-4.20 (m, 1H), 2.65-2.40 (m, 4H), 2.01-1.92 (m, 1H), 1.72-1.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 146.7, 143.1, 142.7, 140.1, 130.0, 128.2, 128.1, 128.0, 127.9, 127.3, 126.9, 126.6, 126.5, 125.8, 88.1, 78.7, 38.8, 36.3, 30.9; IR (neat): 3056, 3024, 2965, 1598, 1493, 1446, 1362, 1228, 1053, 915, 885, 759 cm^{-1}; HRMS (EI) calc'd for $[M^{\cdot}]^+$ $C_{31}H_{28}O$: 416.2139, found 416.2135.

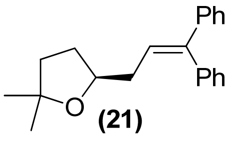
(*R*)-4,4-Bis(4-chlorophenyl)-2-(3,3-diphenylallyl)tetrahydrofuran (19)



(19)

Tetrahydrofuran **19** was purified by flash chromatography (SiO_2, 100 : 0 - 80 : 20 gradient hexanes/EtOAc) to give (53 mg) obtained from the catalytic carboetherification of **5** and **13a** as a pale orange oil (80% yield). $[\alpha]_D^{19.6}$ = -29.9° (*c* = 0.57, $CHCl_3$); ee = 80%, determined by HPLC analysis [Chiralpak AD-RH, 80 : 20 MeCN/H_2O, 1.00 mL/min, λ = 254 nm, t(major) = 19.49 min, t(minor) = 13.81 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.30 (m, 3H), 7.27-7.13 (m, 13H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.09 (t, *J* = 7.8 Hz, 1H), 4.27 (AXq, J_{AX} = 9.0, $\Delta\nu$ = 122 Hz, 2H), 4.19-4.08 (m, 1H), 2.58-2.35 (m, 3H), 2.26 (dd, *J* = 16.4, 12.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 143.8, 142.3, 139.8, 132.5, 132.3, 129.8, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.2, 127.1, 127.0, 124.7, 78.5, 55.3, 44.2, 36.0, 29.7; IR (neat): 3058, 3021, 2958, 2922, 2854, 1598, 1494, 1445, 1261, 1095, 1013, 820 cm^{-1}; HRMS (EI) calc'd for $[M^{\cdot}]^{+}$ $C_{31}H_{26}Cl_2O$: 484.1333, found 484.1355.

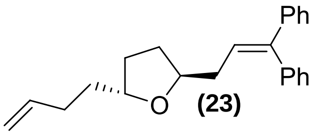
(*S*)-5-(3,3-Diphenylallyl)-2,2-dimethyltetrahydrofuran (21)



(21)

Tetrahydrofuran **21** was purified by flash chromatography (SiO_2, 95: 5 isochratic hexanes/ether) to give (62 mg) obtained from the catalytic carboetherification of **20** and **13a** as a colorless oil (84% yield). $[\alpha]_D^{20}$ = -21.74° (c = 1.0, $CHCl_3$); ee = 96%, determined by HPLC [Chiralpak AD-RH, 60 : 40 CH_3CN/H_2O, 0.5 mL/min, λ = 254 nm, t(major) = 22.96 min, t(minor) = 21.41 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.19 (m, 10H), 6.16 (t, J = 7.6 Hz, 1H), 4.10-4.04 (m, 1H), 2.49-2.42 (m, 1H), 2.34-2.26 (m, 1H), 2.05-1.98 (m, 1H), 1.74-1.60 (m, 3H), 1.25 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (75 Hz, $CDCl_3$): δ 143.1, 142.7, 140.1, 129.9, 128.1, 128.0, 127.2, 126.9, 125.6, 80.6, 78.2, 38.5, 36.5, 31.4, 29.2, 28.1; IR (neat): 3055, 3024, 2966, 1494, 1444, 1364, 1144, 1073, 760, 700 cm^{-1}; HRMS (EI) calcd for $[M]^{+}$ $C_{21}H_{24}O$: 292.1822, found: 292.1826.

(2*S*,5*S*)-2-(But-3-en-1-yl)-5-(3,3-diphenylallyl)tetrahydrofuran (23)

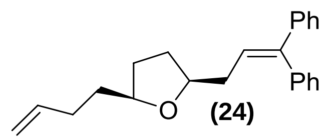


(23)

Tetrahydrofurans **23** and **24** were purified by Prep TLC (SiO_2, 100 : 0 to 95 : 5 gradient hexanes/EtOAc) to give (42 mg) obtained from the catalytic carboetherification of **22** and **13a** as a clear oil [90% yield, **23 : 24** (6 : 1)]. They were separated by prep HPLC using 98 : 2 Hex./EtOAc (**23** eluted first). $[\alpha]_D^{20.1}$ = -9.9° (*c* = 0.28, $CHCl_3$); ee = 86%, determined by HPLC analysis [Chiralpak AD-RH, 60 : 10 MeCN/H_2O, 0.75 mL/min, λ = 254 nm, t(major) = 25.31 min, t(minor) = 21.43 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 4H), 7.25-7.17 (m, 6H), 6.13 (t, *J* = 7.6 Hz, 1H), 5.89-5.78 (m, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 12.4 Hz, 1H), 4.10-4.03 (m, 1H), 3.96-3.89 (m, 1H), 2.42 (dt, *J* = 6.8, 6.4 Hz, 1H), 2.28 (dt, *J* = 6.8, 6.4 Hz, 1H), 2.17-1.96 (m, 4H), 1.75-1.63 (m, 1H), 1.56-1.44 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.7, 140.1, 138.5, 129.9, 128.2, 128.0, 127.3, 126.9, 125.7, 114.4, 78.4, 78.3, 36.1, 35.1, 31.9, 31.6, 30.5; IR (neat): 3057, 3022, 2928, 2857, 1491, 1438, 1361, 1071, 907, 755 cm^{-1}; HRMS (EI) calc'd for

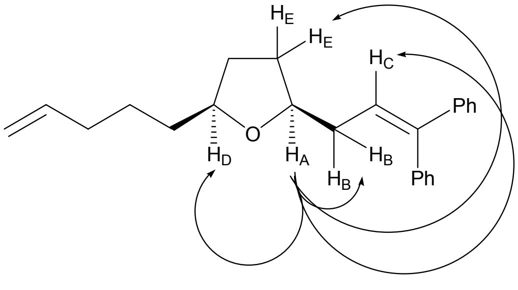
$[M^{\cdot}]^+$ $C_{23}H_{26}O$: 318.1978, found 318.1978. The relative stereochemistry of **23** was assigned by process of elimination (it was not **24**).

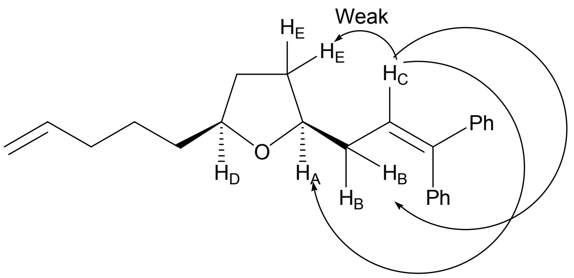
(2*R*,5*S*)-2-(But-3-en-1-yl)-5-(3,3-diphenylallyl)tetrahydrofuran (24)



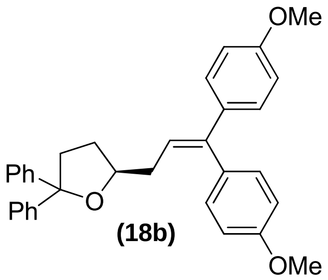
(24)

Tetrahydrofuran **24** was obtained as a clear oil. $[\alpha]_D^{19.2}$ = -2.6° (*c* = 0.16, $CHCl_3$). ee = 97%, determined by HPLC analysis [Chiralpak AD-RH, 60 : 40 MeCN/H_2O, 0.75 mL/min, λ = 254 nm, t(major) = 21.61 min, t(minor) = 23.11 min]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.36-7.29 (m, 2H), 7.25-7.18 (m, 6H), 6.14 (t, *J* = 7.2 Hz, 1H), 5.88-5.79 (m, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 8.0 Hz, 1H), 3.96-3.90 (m, 1H), 3.86-3.81 (m, 1H), 2.43 (dt, *J* = 6.8, 6.4 Hz, 1H), 2.31 (dt, *J* = 7.2, 6.4 Hz, 1H), 2.17-1.90 (m, 4H), 1.72-1.65 (m, 1H), 1.56-1.44 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 142.7, 140.1, 138.6, 130.0, 128.2, 128.0, 127.3, 126.9, 125.7, 114.4, 110.0, 78.9, 78.8, 36.2, 35.3, 31.0, 30.5, 29.8; IR (neat): 3062, 3025, 2916, 2856, 1495, 1446, 1367, 1078, 998, 907, 755 cm^{-1}; HRMS (EI) calc'd for $[M^{\cdot}]^+$ $C_{23}H_{26}O$: 318.1978, found 318.1973. The relative stereochemistry of **24** was assigned by NOE. In the first experiment, saturation of H_A showed strong enhancements of H_C and H_D. In a second experiment, saturation of H_C revealed a strong enhancement of H_A, a weak enhancement of H_E, but no enhancement of H_D. This data has led to our support of this structure for **24.**



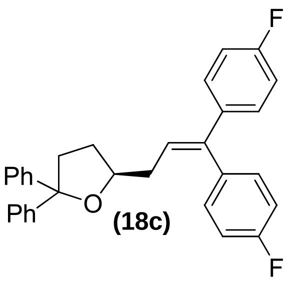


(*S*)-5-(3,3-Bis(4-methoxyphenyl)allyl)-2,2-diphenyltetrahydrofuran (18b)


(18b)

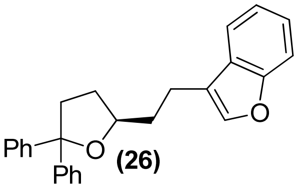
Tetrahydrofuran **18b** was purified by flash chromatography (SiO_2, 100 : 0 - 80 : 20 gradient hexanes/EtOAc) to give (60 mg) obtained from the catalytic carboetherification of **17** and **13b** as a pale yellow oil (88% yield). $[\alpha]_D^{19.9}$ = 4.6° (*c* = 0.85, $CHCl_3$); ee = >95%, determined by HPLC analysis [Chiralpak AD-RH, 65 : 35 MeCN/H_2O, 0.20 mL/min, λ = 254 nm, t(major) = 77.01 min, t(minor) = 73.07 min]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (td, *J* = 9.6, 1.2 Hz, 4H), 7.31-7.16 (m, 6H), 7.13-7.08 (m, 4H), 6.88 (d, *J* = 9.6 Hz, 2H), 6.79 (d, *J* = 10 Hz, 2H), 6.07 (t, *J* = 6.8 Hz, 1H), 4.26-4.18 (m, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.67-2.38 (m, 4H), 2.02-1.93 (m, 1H), 1.72-1.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 158.5, 147.1, 146.7, 142.2, 135.8, 132.6, 131.1, 128.4, 128.1, 127.9, 126.5, 125.9, 123.84, 113.5, 113.4, 88.1, 78.9, 55.2, 38.8, 36.3, 30.9; IR (neat): 3058, 3022, 2925, 2850, 1606, 1511, 1448, 1288, 1246, 1174, 1109, 1034, 833 cm^{-1}; HRMS (EI) calc'd for $[M^{\cdot}]^+$ $C_{33}H_{32}O_3$: 476.2343, found 476.2346.

(*S*)-5-(3,3-Bis(4-fluorophenyl)allyl)-2,2-diphenyltetrahydrofuran (18c)


(18c)

Tetrahydrofuran **18c** was purified by flash chromatography (SiO_2, 100 : 0 - 90 : 10 gradient hexanes/Et_2O) to give (44 mg) obtained from the catalytic carboetherification of **17** and **13c** as a pale yellow oil (70% yield). $[\alpha]_D^{19.5}$ = -4.5° (*c* = 0.98, $CHCl_3$); ee = >95%, determined by HPLC analysis [Chiralpak AD-RH, 65 : 35 MeCN/H_2O, 0.20 mL/min, λ = 254 nm, t(major) = 78.12 min, t(minor) = 74.75 min]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.42 (m, 4H), 7.34-6.92 (m, 14H), 6.16 (t, *J* = 7.2 Hz, 1H), 4.30-4.22 (m, 1H), 2.69-2.38 (m, 4H), 2.05-1.95 (m, 1H), 1.73-1.65 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1 (d, J_1 = 245 Hz), 161.9 (d, J_1 = 245 Hz), 147.0, 146.6, 141.2, 131.5 (d, J_3 = 8.03 Hz), 128.8 (d, J_3 = 6.9 Hz), 128.1, 128.0, 126.6, 126.1, 125.9, 125.8, 115.2 (d, J_2 = 21.75 Hz), 114.9 (d, J_2 = 21.75 Hz), 88.2, 78.6, 38.7, 36.3, 30.9; IR (neat): 3058, 2964, 2877, 1602, 1506, 1448, 1261, 1224, 1557, 1094, 1054, 912, 838, 797 cm^{-1}; HRMS (CI) calc'd for $[M+H]^+$ $C_{31}H_{27}OF_2$: 453.2026, found 453.2024.

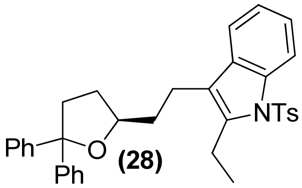
(*R*)-3-(2-(5,5-Diphenyltetrahydrofuran-2-yl)ethyl)benzofuran (26)



(26)

Tetrahydrofuran **26** was purified by flash chromatography (SiO_2, 100 : 0 - 90 : 10 gradient hexanes/EtOAc) to give (50 mg) obtained from the catalytic carboetherification of **17** and **25** as a clear oil (88% yield). $[\alpha]_D^{18.3}$ = 15.7° (*c* = 0.71, $CHCl_3$); ee = 94%, determined by HPLC analysis [Chiralpak AD-RH, 90 : 10 MeCN/H_2O, 0.65 mL/min, λ = 254 nm, t(major) = 17.87 min, t(minor) = 16.75 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.48-7.44 (m, 6H), 7.33-7.26 (m, 6H), 7.25-7.17 (m, 2H), 4.24-4.18 (m, 1H), 2.98-2.79 (m, 2H), 2.71-2.64 (m, 1H), 2.60-2.53 (m, 1H), 2.15-2.03 (m, 2H), 1.97-1.93 (m, 1H), 1.75-1.66 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 147.3, 146.7, 141.1, 128.3, 128.1, 128.0, 126.6, 126.5, 125.9, 125.8, 124.1, 122.2, 120.2, 119.7, 111.4, 88.0, 78.3, 38.8, 35.8, 31.4, 20.4; IR (neat): 3059, 3012, 2928, 2859, 1597, 1490, 1454, 1261, 1184, 1092, 1051, 858, 801, 747 cm^{-1}; HRMS (EI) calc'd for $[M^{\cdot}]^+$ $C_{26}H_{24}O_2$: 368.1774, found 368.1771.

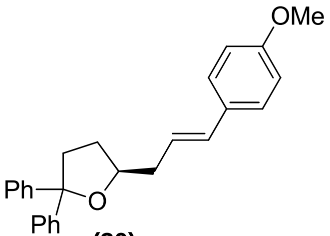
(*R*)-3-(2-(5,5-Diphenyltetrahydrofuran-2-yl)ethyl)-2-ethyl-1-tosyl-1H-indole (28)



(28)

Tetrahydrofuran **28** was purified by flash chromatography (SiO_2, 100 : 0 - 90 : 10 gradient hexanes/EtOAc) to give (66 mg) obtained from the catalytic carboetherification of **17** and **27** as a white solid (81% yield), required two columns to obtain pure compound **28**; $[\alpha]_D^{20}$ = 3.75° (c = 0.95, $CHCl_3$); ee = nd (enantiomers were unseparable); mp 47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 8.8 Hz, 2H), 7.49-7.41 (m, 4H), 7.32-7.19 (m, 8H), 7.06 (d, J = 8.4 Hz, 2H), 4.06-4.00 (m, 1H), 3.10-3.01 (m, 2H), 2.91-2.75 (m, 2H), 2.66-2.59 (m, 1H), 2.55-2.49 (m, 1H), 2.28 (s, 3H), 2.00-1.84 (m, 2H), 1.77-1.70 (m, 1H), 1.64-1.55 (m, 1H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 Hz, $CDCl_3$): δ 147.3, 146.7, 144.2, 139.3, 136.9, 135.9, 130.9, 129.5, 128.1, 128.0, 126.6, 126.5, 126.1, 125.8, 125.7, 123.9, 123.3, 120.7, 118.6, 115.4, 88.0, 77.9, 38.7, 36.6, 31.3, 21.5, 20.9, 19.9, 15.7; IR (neat): 3058, 2934, 2873, 1597, 1448, 1361, 1225, 1172, 1090, 1048, 811, 748, 703 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{35}H_{35}O_3NS$: 549.2332, found: 549.2335.

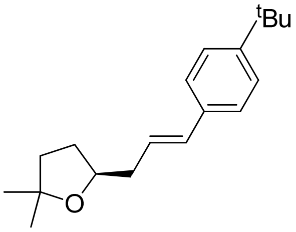
(*S*,E)-5-(3-(4-methoxyphenyl)allyl)-2,2-diphenyltetrahydrofuran (30)



(30)

Tetrahydrofuran **30** was purified by preparative TLC (SiO_2, 95 : 5 hexanes/ether, developed 2x) to give (25 mg) obtained from the catalytic carboetherification of **17** and **29a** as a colorless oil (46% yield). $[\alpha]_D^{19}$ = 8.30° (c = 0.6, $CHCl_3$); ee = >95%, determined by HPLC [Chiralpak AD-RH, 65 : 35 CH_3CN/H_2O, 0.5 mL/min, λ = 254 nm, t(major) = 31.22 min, t(minor) = 39.63 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.0 Hz, 4H), 7.32-7.25 (m, 6H), 7.22-7.17 (m, 2H), 6.85 (m, 2H), 6.41 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0 Hz, 7.2 Hz, 1H), 4.31-4.23 (m, 1H), 3.81 (s, 3H), 2.67-2.61 (m, 2H), 2.57-2.45 (m, 2H), 2.09-1.98 (m, 1H), 1.81-1.70 (m, 1H); ^{13}C NMR (75 Hz, $CDCl_3$): δ 158.8, 147.1, 146.6, 131.4, 130.5, 128.1, 128.0, 127.5, 127.1, 126.6, 126.5, 125.9, 124.6, 113.9, 88.2, 78.7, 55.3, 39.7, 38.8, 30.7; IR (neat): 3028, 2952, 2835, 1607, 1510, 1456, 1248, 1174, 1035, 701 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{26}H_{26}O_2$: 370.1947, found: 370.1933.

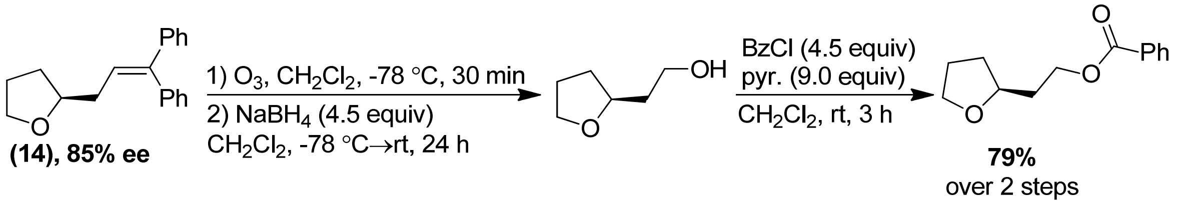
(*S*,E)-5-(3-(4-(tert-butyl)phenyl)allyl)-2,2-dimethyltetrahydrofuran (31)



(31)

Tetrahydrofuran **31** was purified by preparative TLC (SiO_2, 95 : 5 hexanes/ether, developed 2x) to give (35 mg) obtained from the catalytic carboetherification of **20** and **29b** as a colorless oil (42% yield). $[\alpha]_D^{19}$ = -21.73° (c = 0.55, $CHCl_3$); ee = 95%, determined by HPLC [Chiralpak AD-RH, 90 : 10 CH_3CN/H_2O, 0.5 mL/min, λ = 254 nm, t(major) = 35.61 min, t(minor) = 12.19 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 4H), 6.42 (d, J = 16.0 Hz, 1H), 6.18 (dt, J = 16.0 Hz, 7.6 Hz, 1H), 4.11-4.03 (m, 1H), 2.55-2.48 (m, 1H), 2.40-2.33 (m, 1H), 2.05-1.97 (m, 1H), 1.75-1.66 (m, 3H), 1.31 (s, 9H), 1.27 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (75 Hz, $CDCl_3$): δ 150.0, 134.9, 131.7, 125.9, 125.7, 125.4, 80.7, 78.1, 39.8, 38.4, 34.5, 31.3, 31.1, 29.2, 28.1; IR (neat): 2964, 2868, 1507, 1457, 1363, 1269, 1143, 1050, 967 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{19}H_{28}O$: 272.2146, found: 272.2140.

Conversion of **14** to the known compound (*S*)-2-(Tetrahydrofuran-2-yl)ethyl benzoate to establish absolute configuration.[8]



(*S*)-2-(Tetrahydrofuran-2-yl)ethyl benzoate:

Tetrahydrofuran **14** (35 mg, 0.132 mmol, 1 equiv) was dissolved in CH_2Cl_2 (2.0 mL) and the mixture placed, with stirring, in a -78 °C bath. After allowing the mixture to stir for 10 minutes a stream of O_3 gas was bubbled through until a deep blue color persisted even with removal of the gas stream. Once enough O_3 had been bubbled into the mixture the reaction was purged with a stream of argon gas. The mixture was then treated with sodium borohydride (23.0 mg, 0.608 mmol, 4.5 equiv) and allowed to stir and come to room temperature overnight. The reaction was then quenched with 1 M HCl (5 mL) and extracted with diethyl ether (3 x 10 mL). The combined organics were then dried over anhydrous sodium sulfate and the solvent removed *in vacuo* to give 131 mg of the crude alcohol product which was used in the next step without further purification.

Pyridine (0.097 mL, 1.20 mmol, 9 equiv) was added via syringe at room temperature to a solution of the crude alcohol from the previous step (131 mg) dissolved in CH_2Cl_2 (2.0 mL). The resulting mixture was allowed to stir for 20 minutes before benzoyl chloride (0.069 mL, 0.594 mmol, 4.5 equiv) was added drop wise via syringe. The mixture was then allowed to stir at room temperature for 3 hour before being quenched with water (5 mL) and then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were then washed with brine (15 mL) and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* gave the crude residue which was purified by flash chromatography 30% Et_2O in hexanes to give (*S*)-2-(tetrahydrofuran-2-yl)ethyl benzoate[8], 23.0 mg, as a colorless oil (79% yield over 2 steps).

$[\alpha]_D^{19.5}$ = 13.1° (c = 0.53, CH_2Cl_2). ^{1}H NMR data matched that previously reported by Matsubara.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 4.50-4.37 (m, 2H), 4.05-3.97 (m, 1H), 3.92-3.86 (m, 1H), 3.78-3.72 (m, 1H), 2.12-1.85 (m, 5H), 1.60-1.51 (m, 1H).

The absolute configuration of the 2-(tetrahydrofuran-2-yl)ethyl benzoate we obtained was assigned as (*S*) by comparing the optical rotation with the literature value of the known enantiomer.[8] [lit. (*R*)-2-(tetrahydrofuran-2-yl)ethyl benzoate: $[\alpha]_D^{26}$ = -14.7° (c = 2.21, CH_2Cl_2)].

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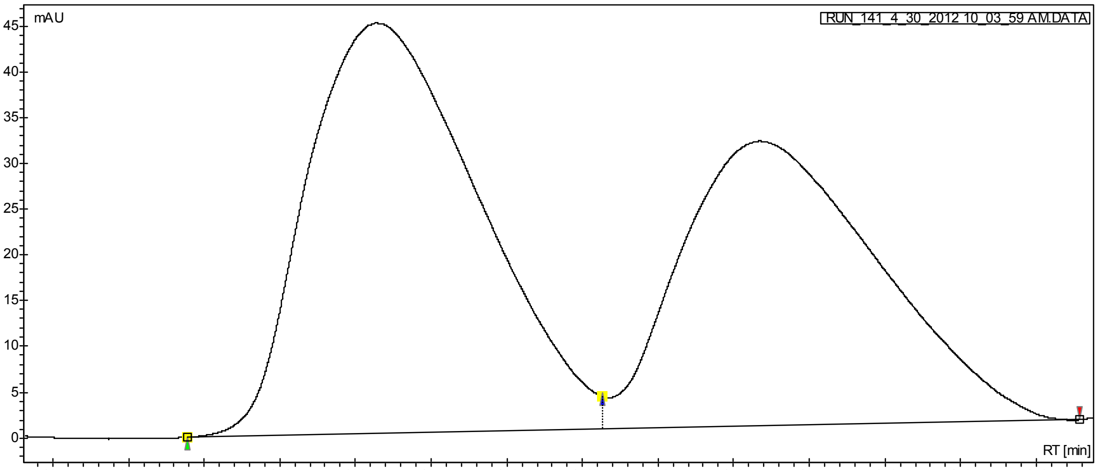
HPLC traces:



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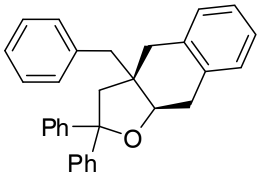
2	142.67	44.4



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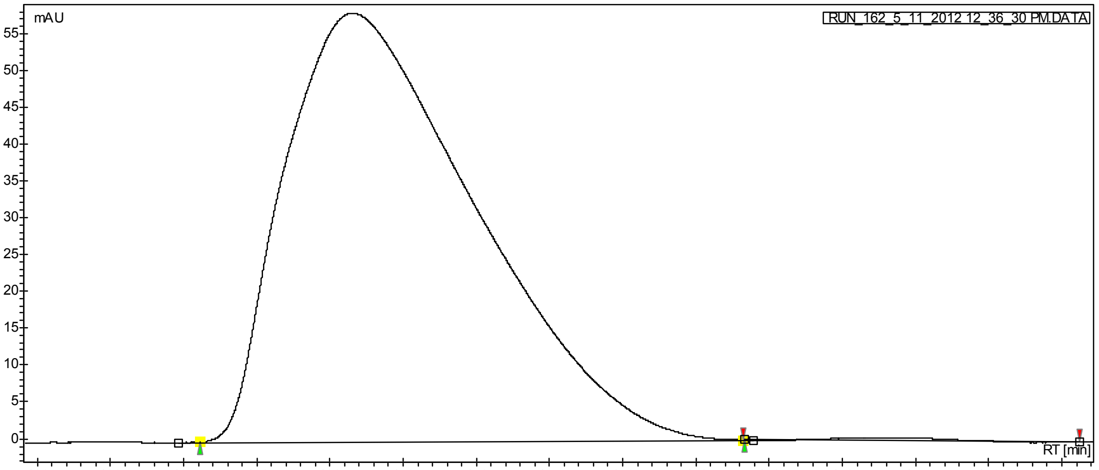

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1	138.65	99.7
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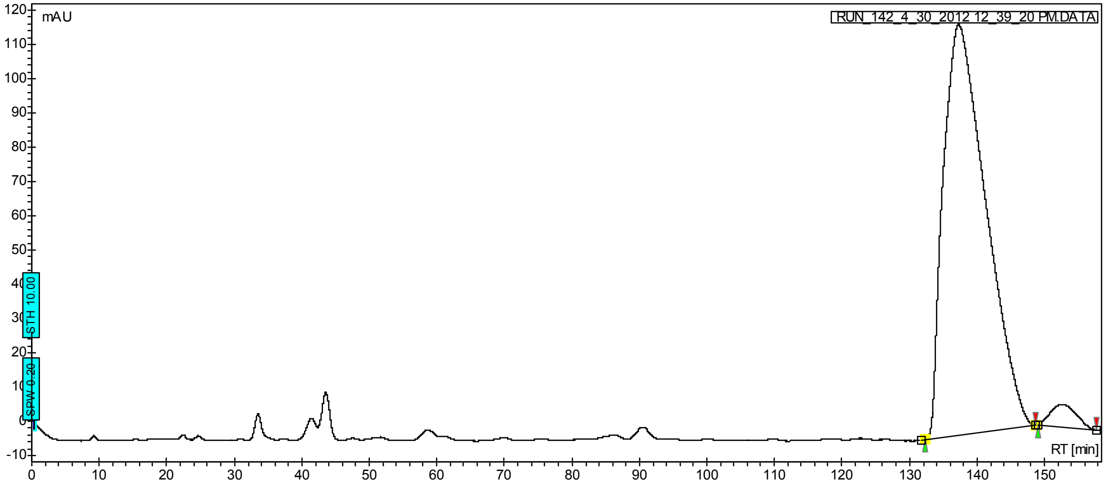
2a using (*S*,*S*)-^{i}Pr-box:



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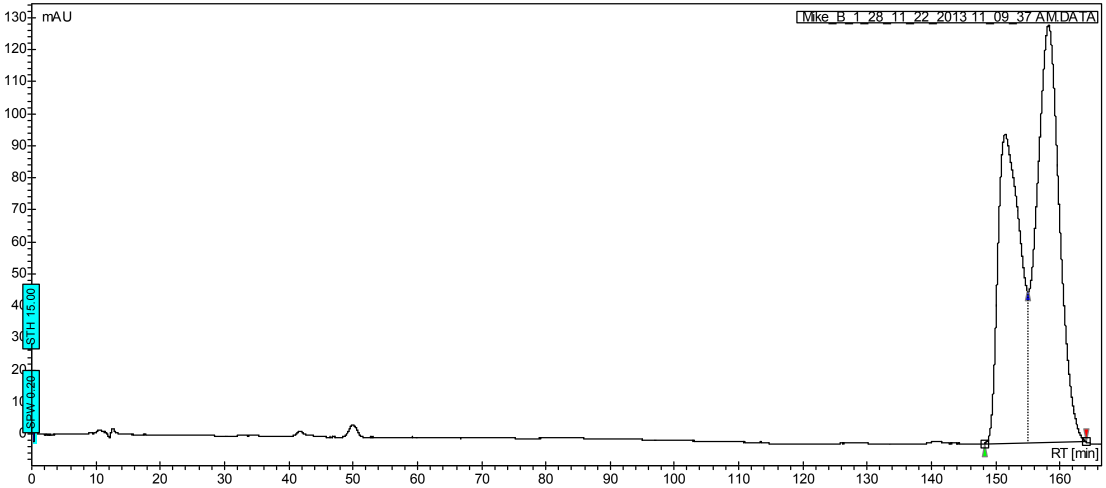
1	137.23	96.7
2	152.69	3.3

2a using (*S*)-^{i}Pr-QUINOX:



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1	151.47	42.0
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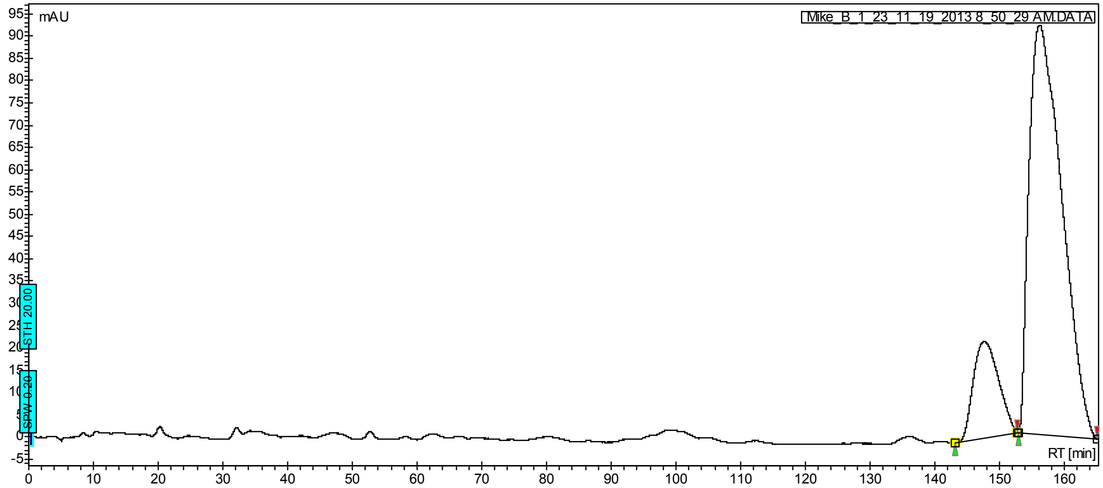
2a using (*R*,*R*)-Ph-box:



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1	147.54	15.4
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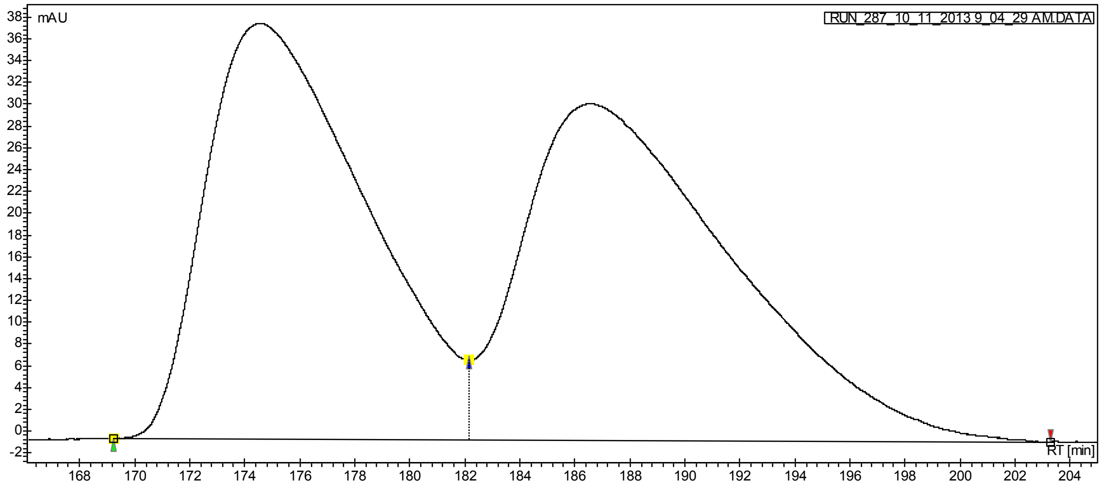

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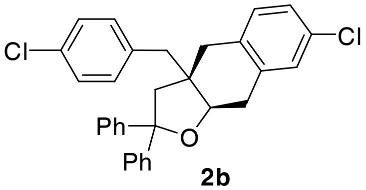

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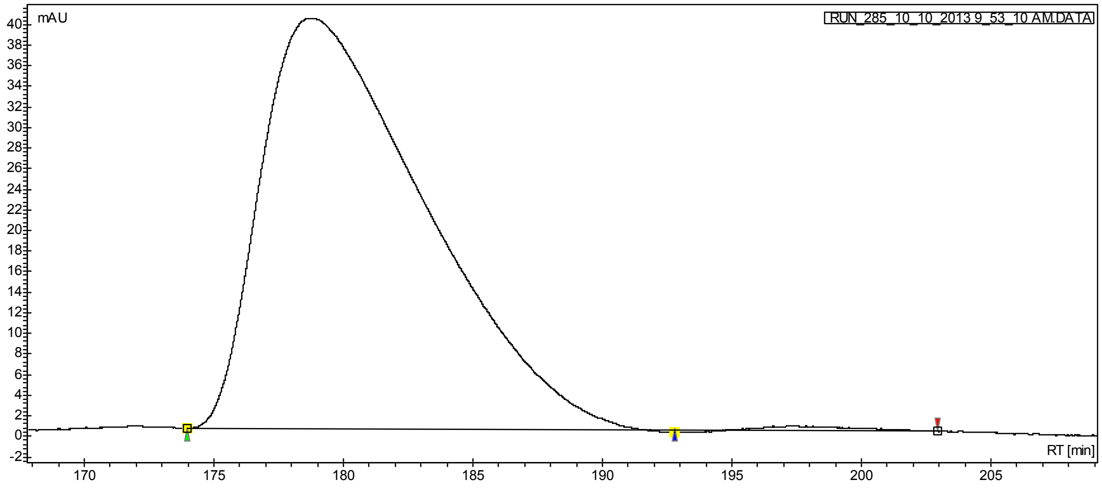

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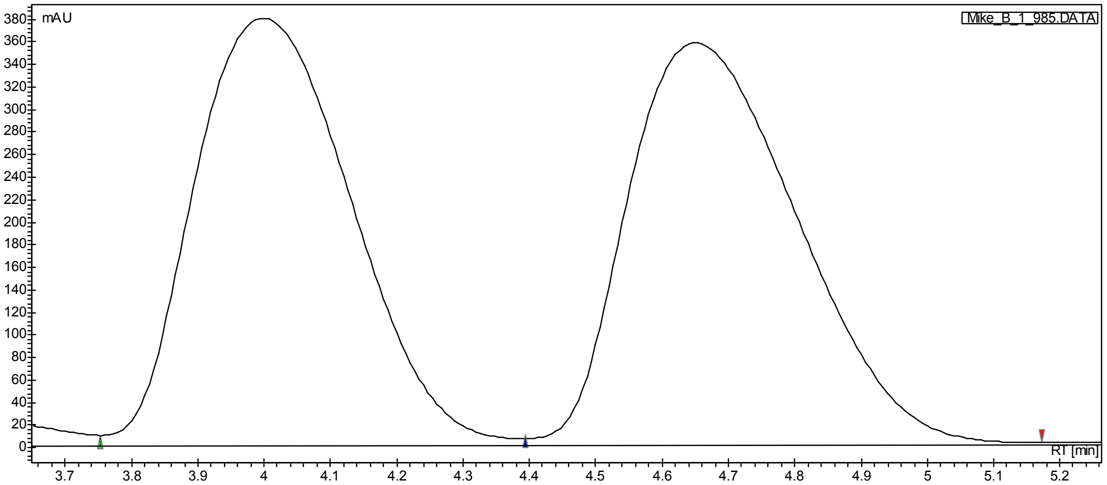

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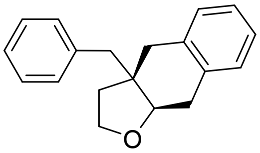

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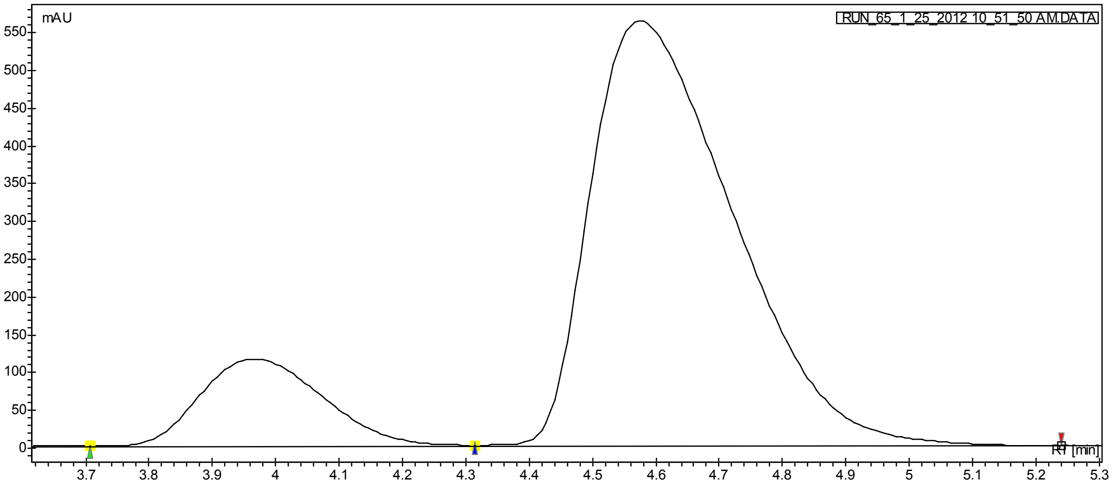

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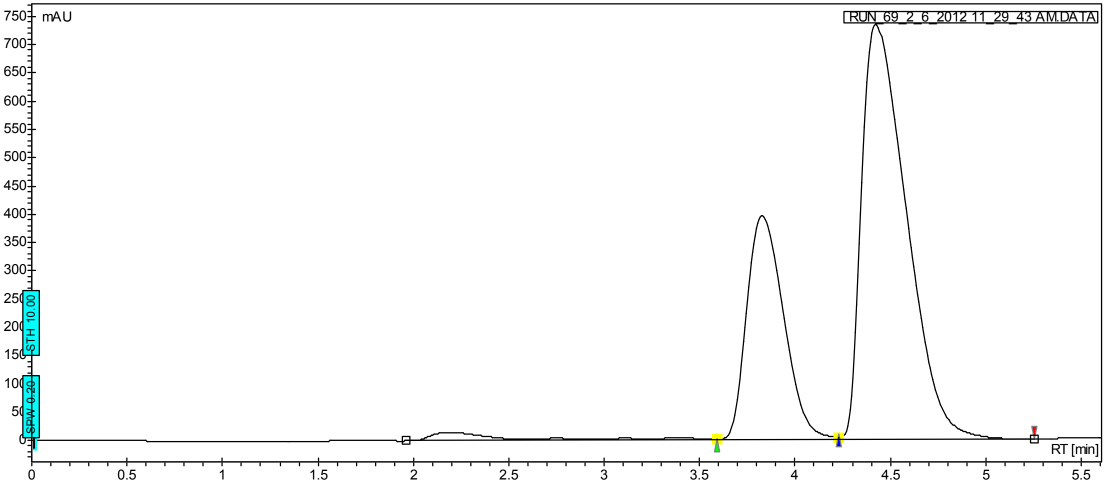
(4) using (*S*,*S*)-^{i}Pr-box:



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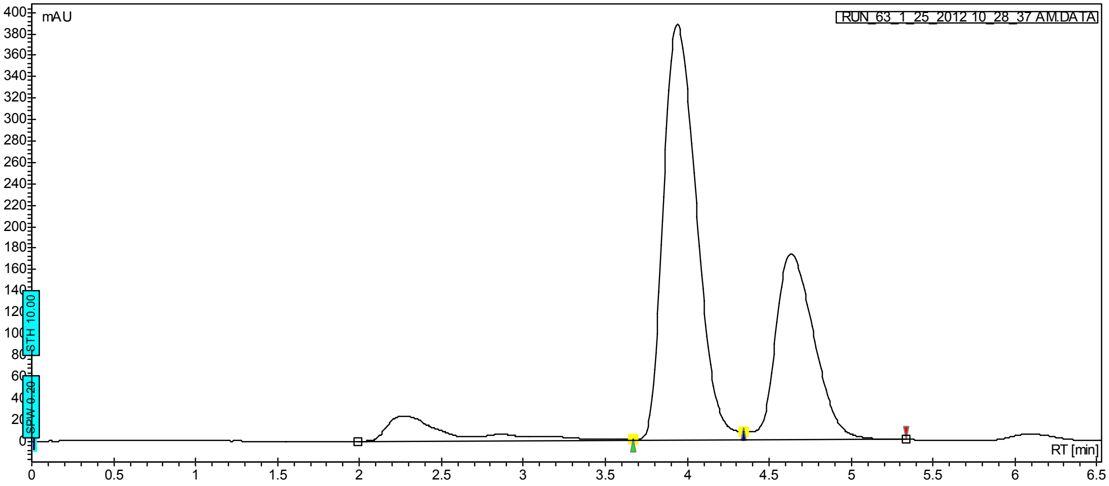

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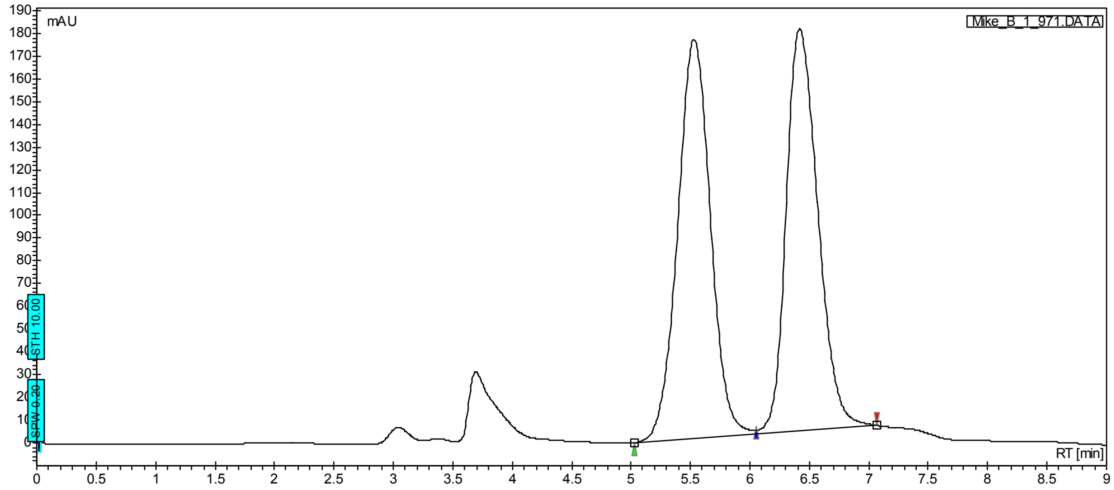

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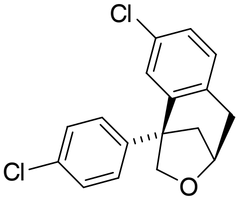
2	6.42	49.3



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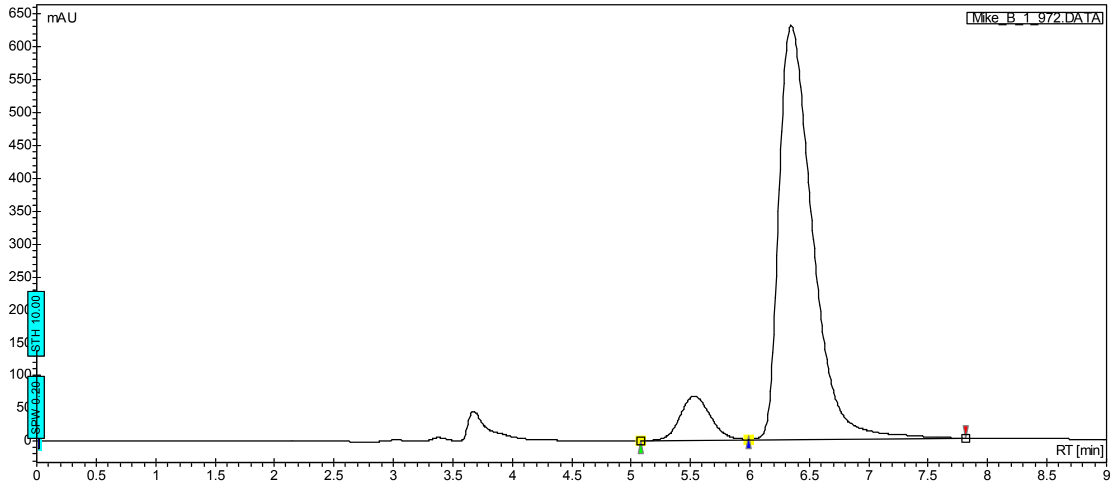

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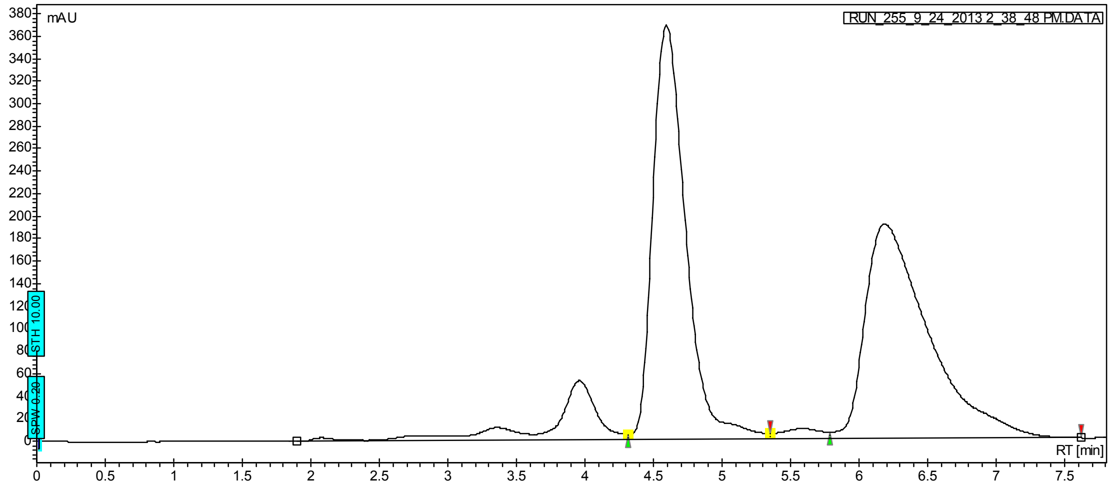

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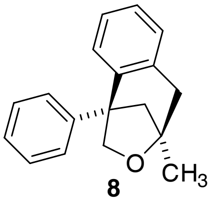

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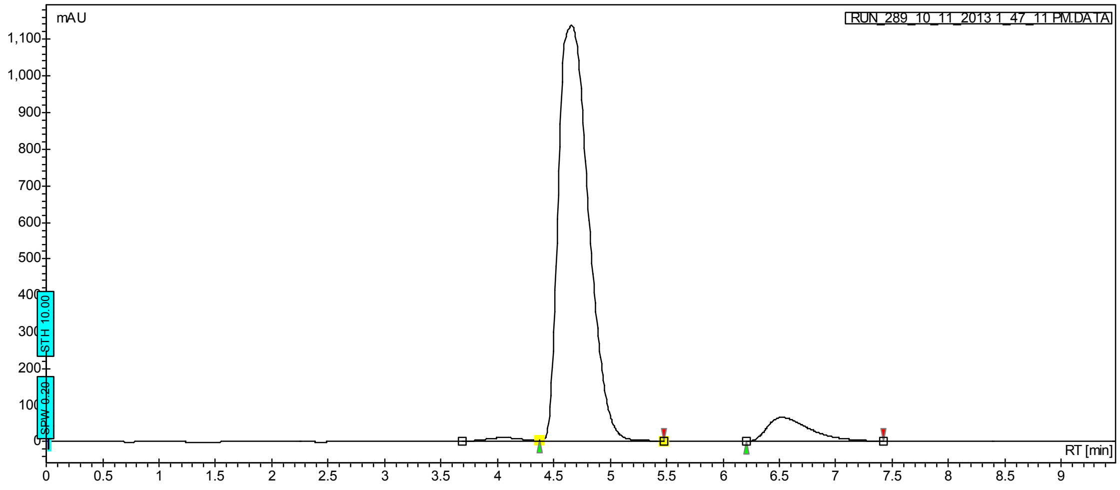

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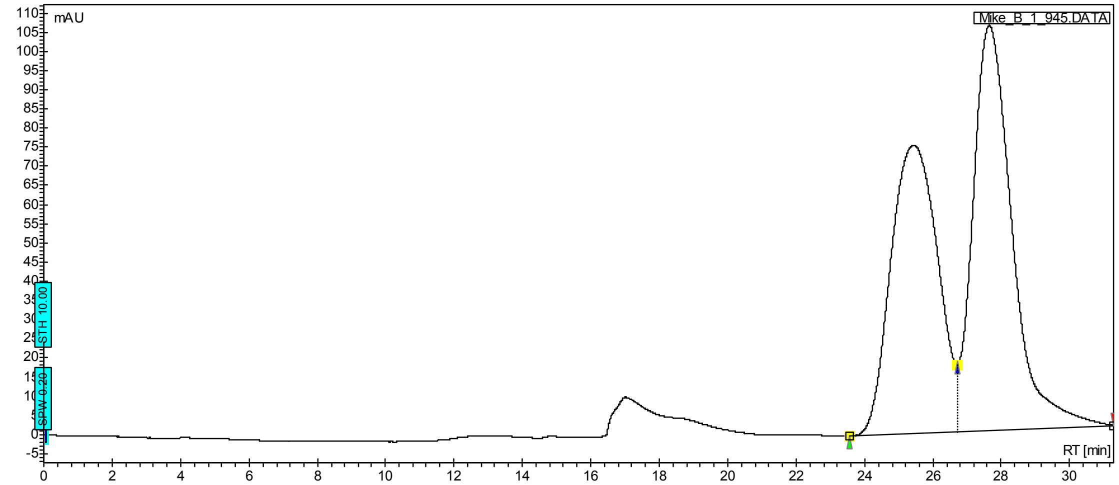

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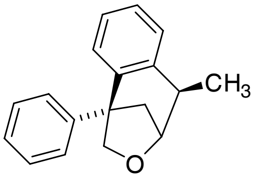

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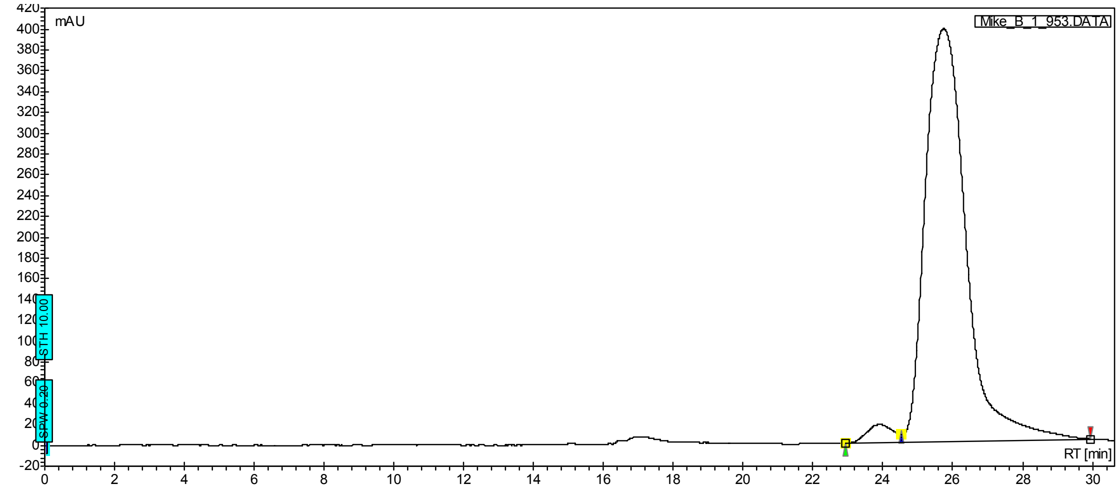

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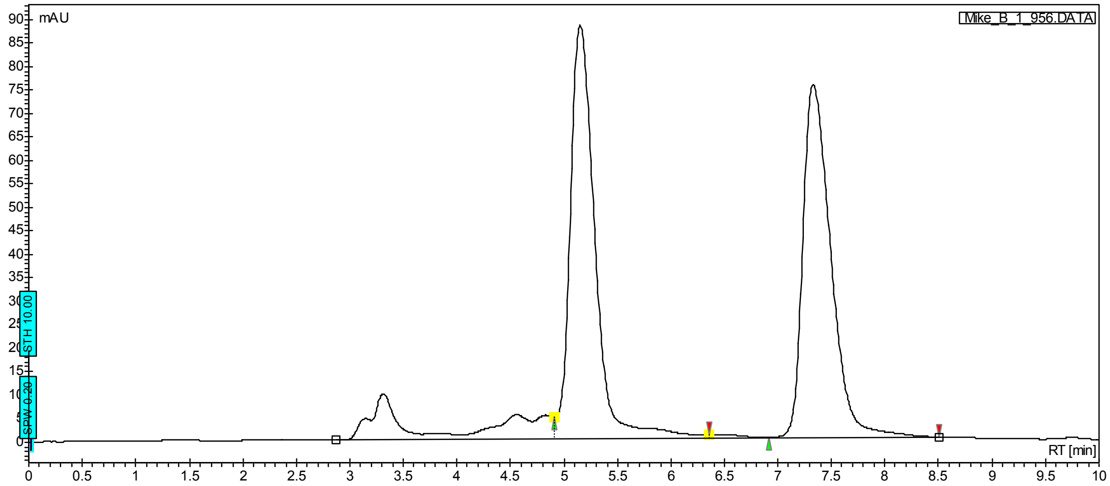

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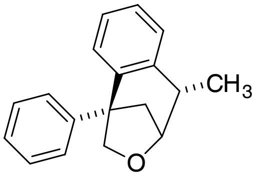

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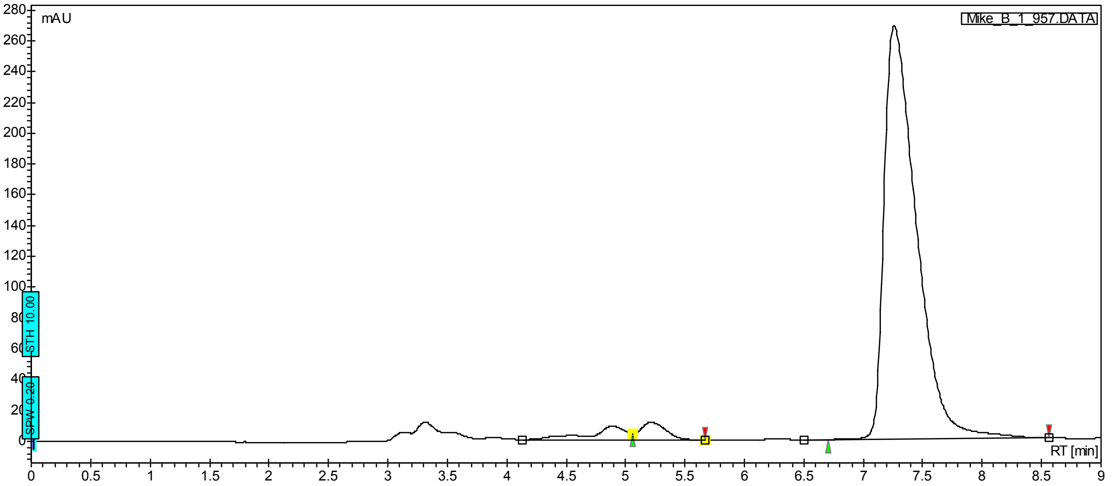

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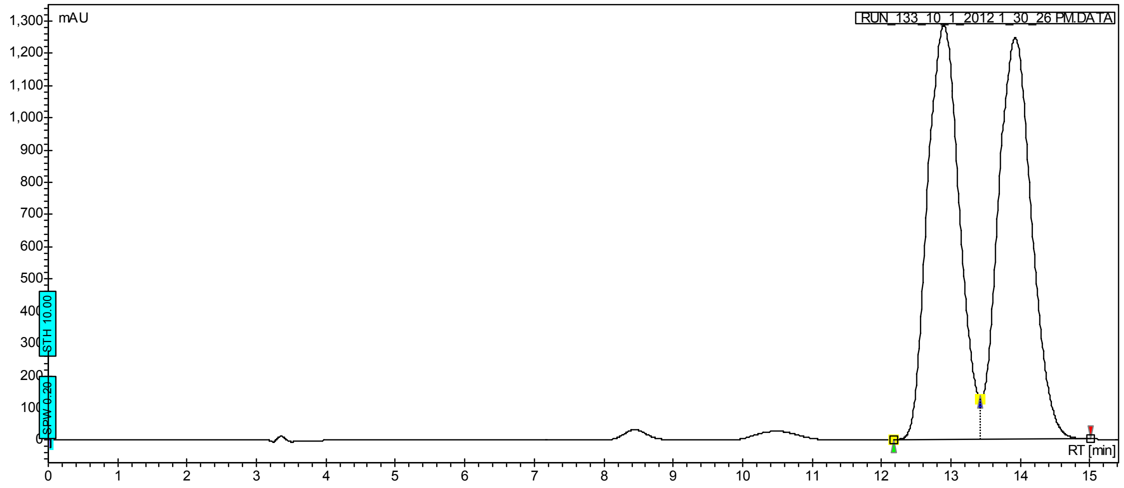

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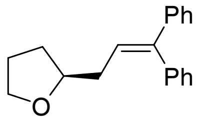

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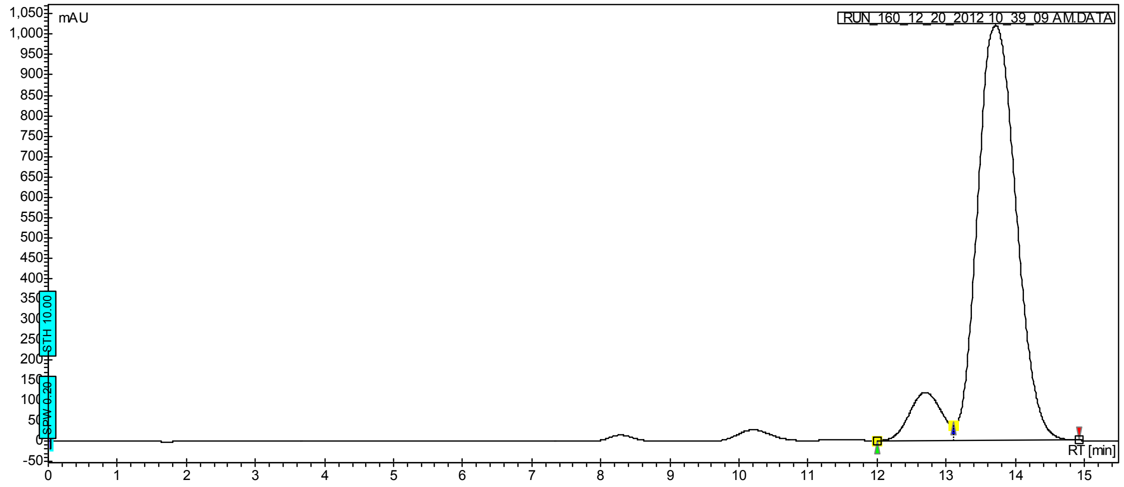

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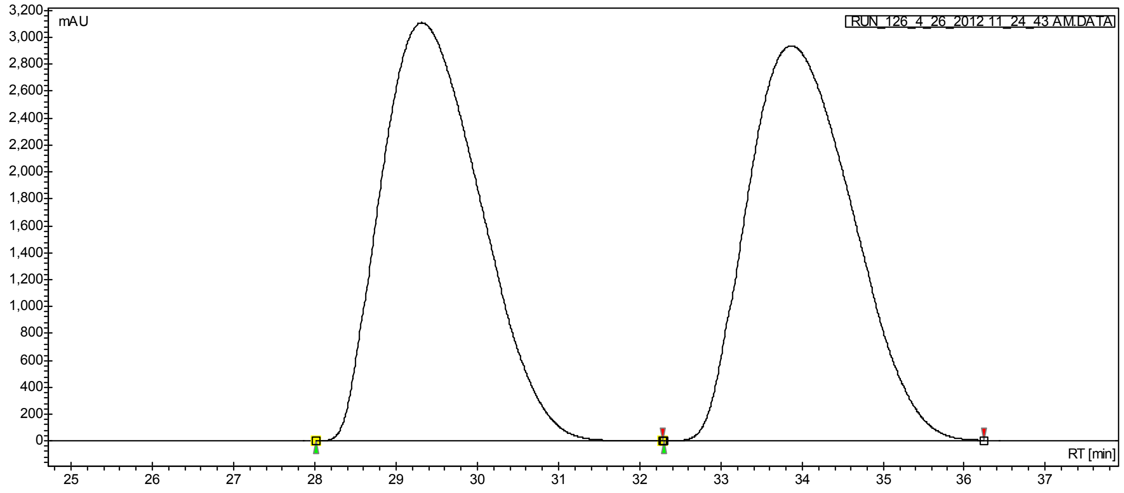
2	13.90	91.3



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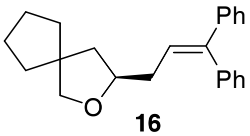

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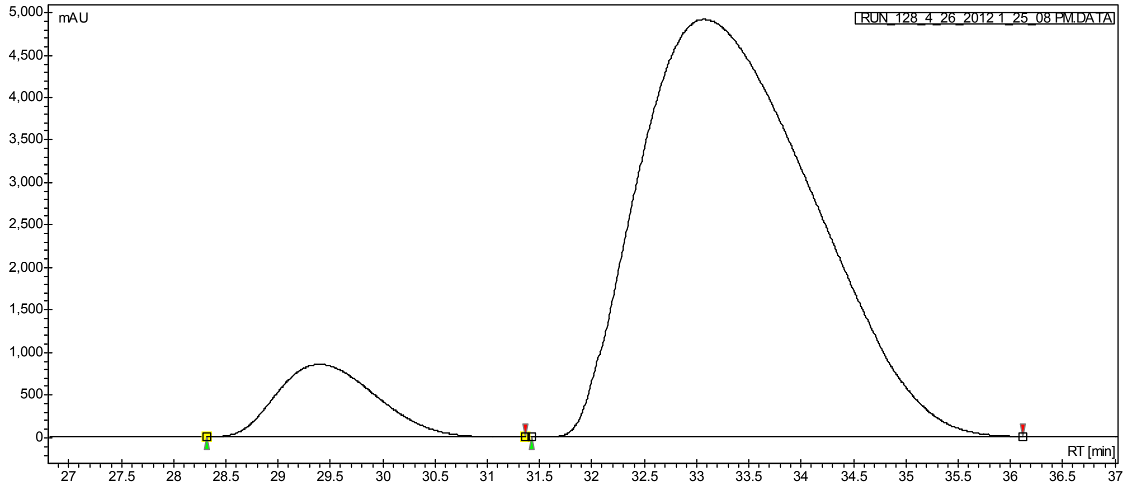

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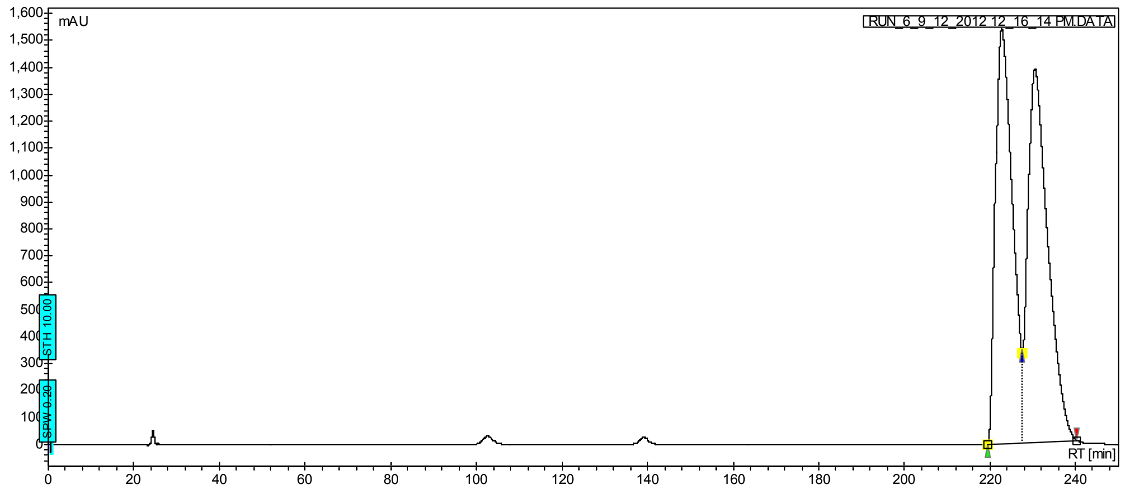

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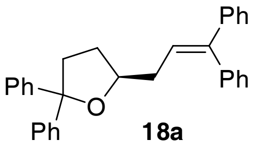

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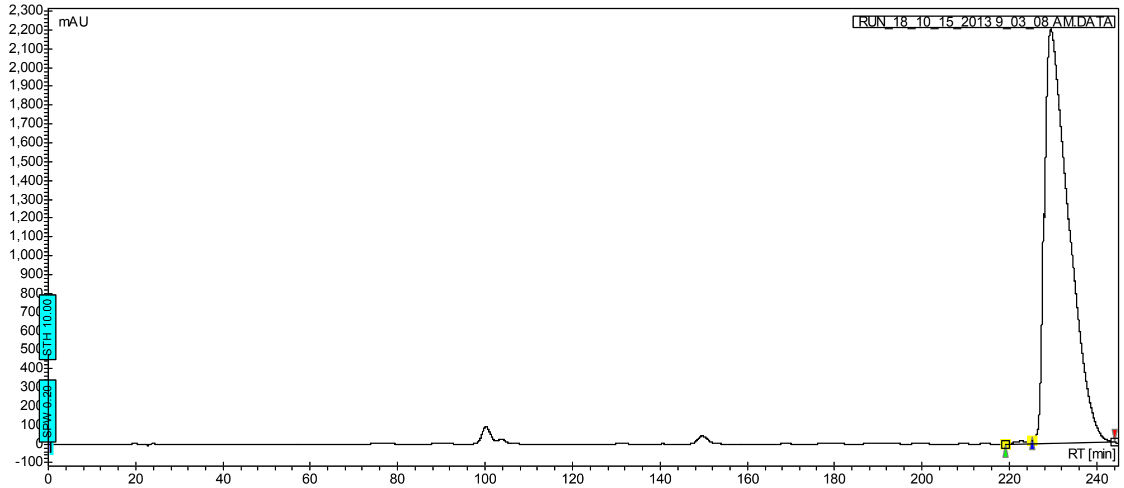

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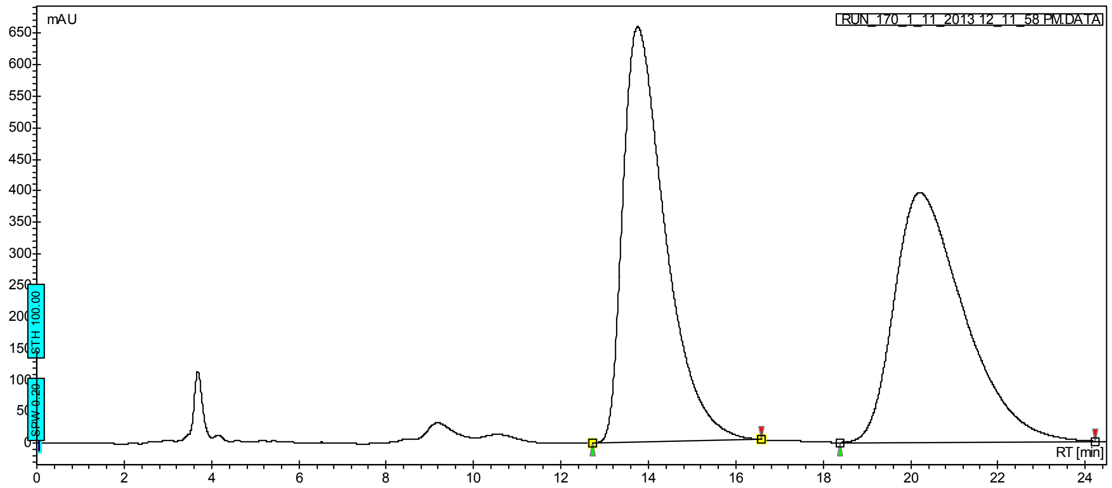

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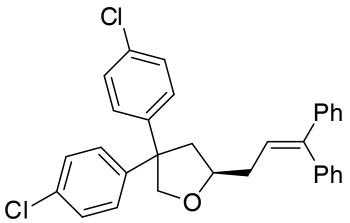

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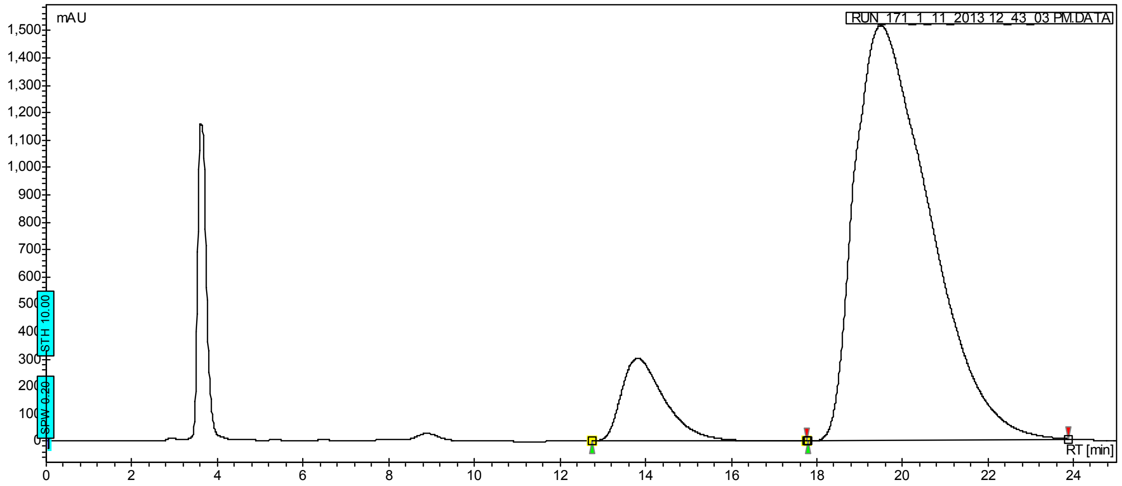

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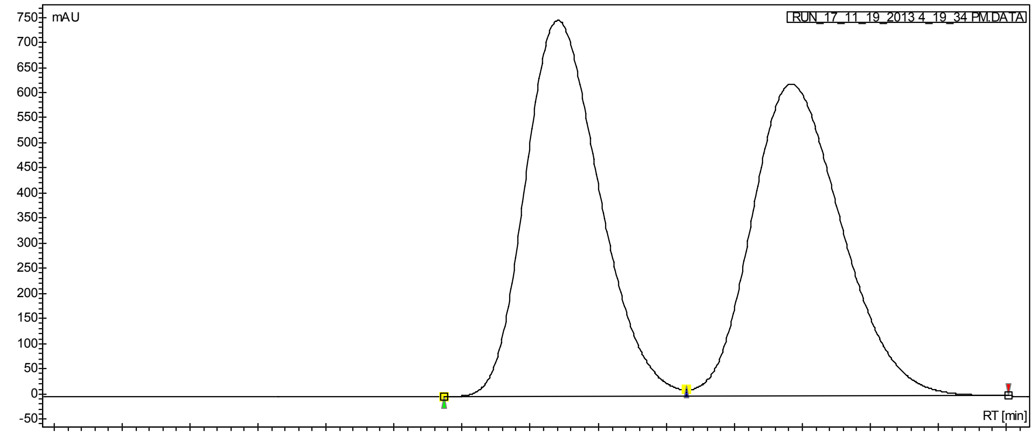

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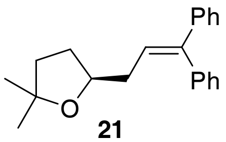

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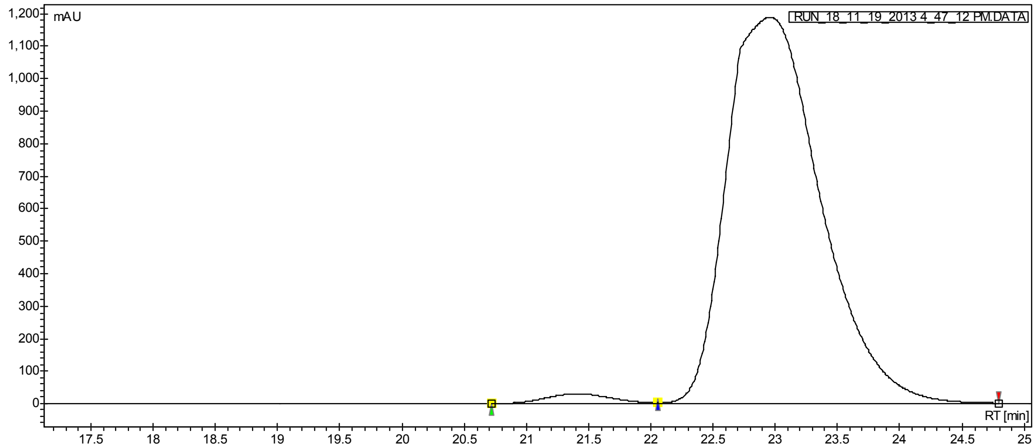

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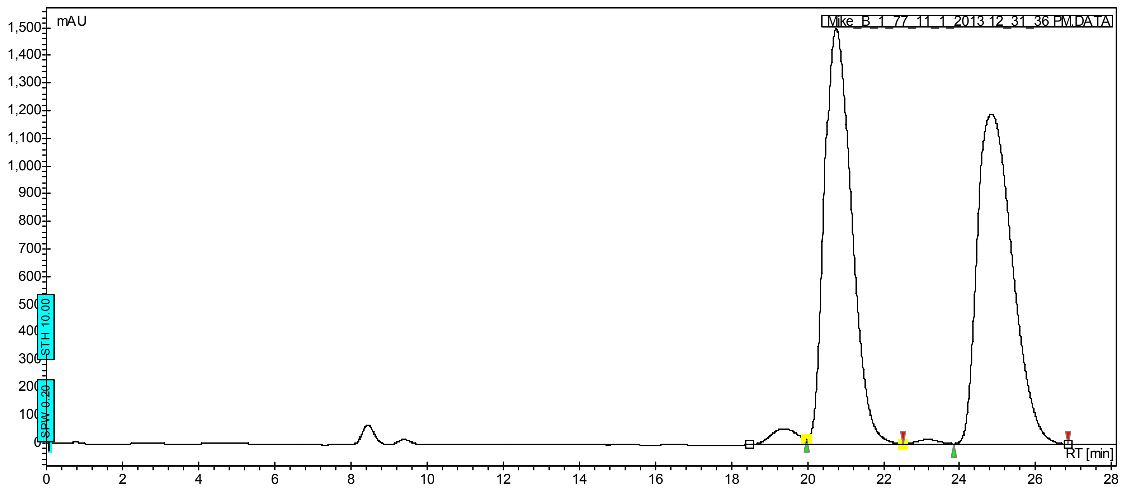

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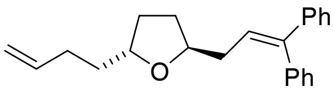

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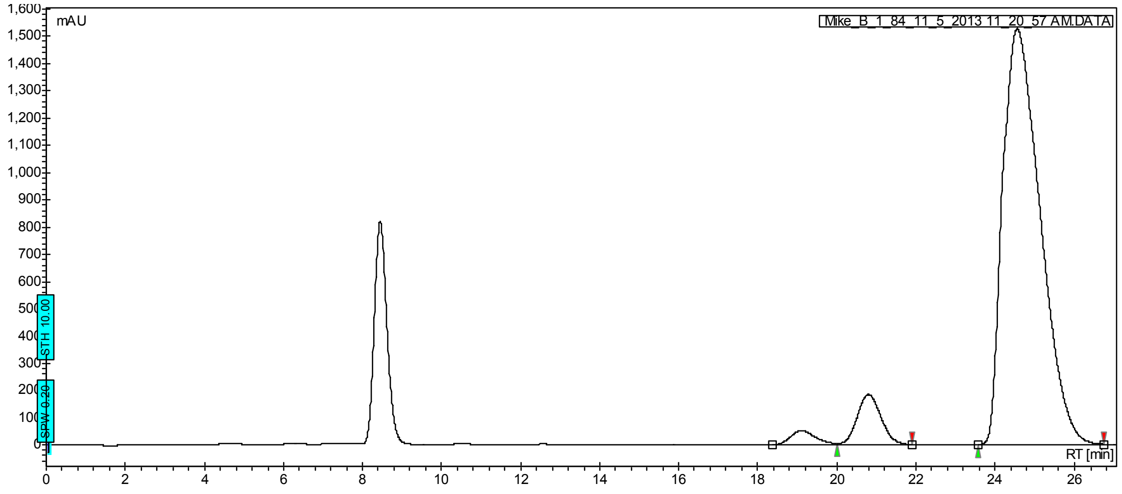

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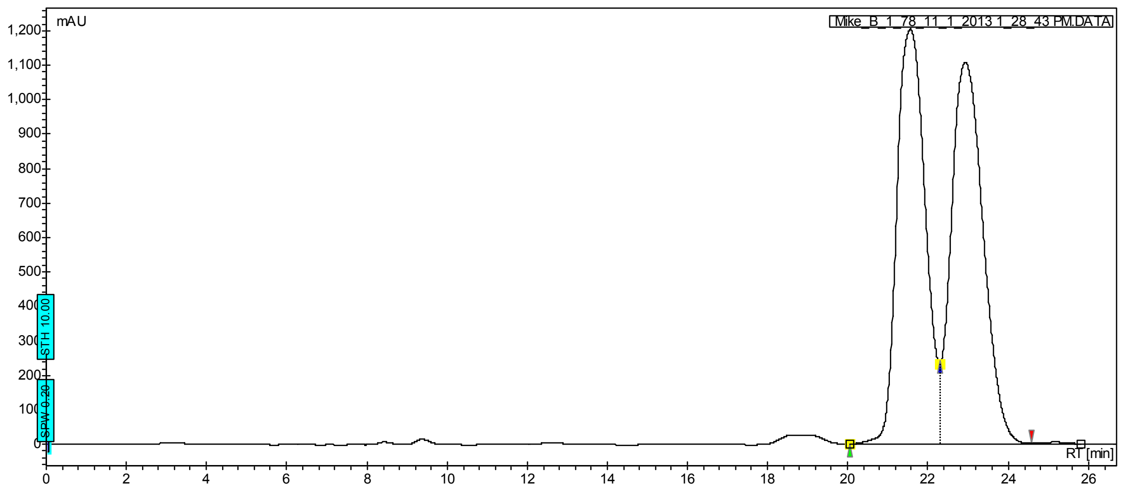

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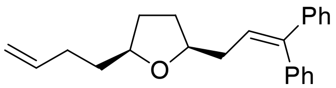

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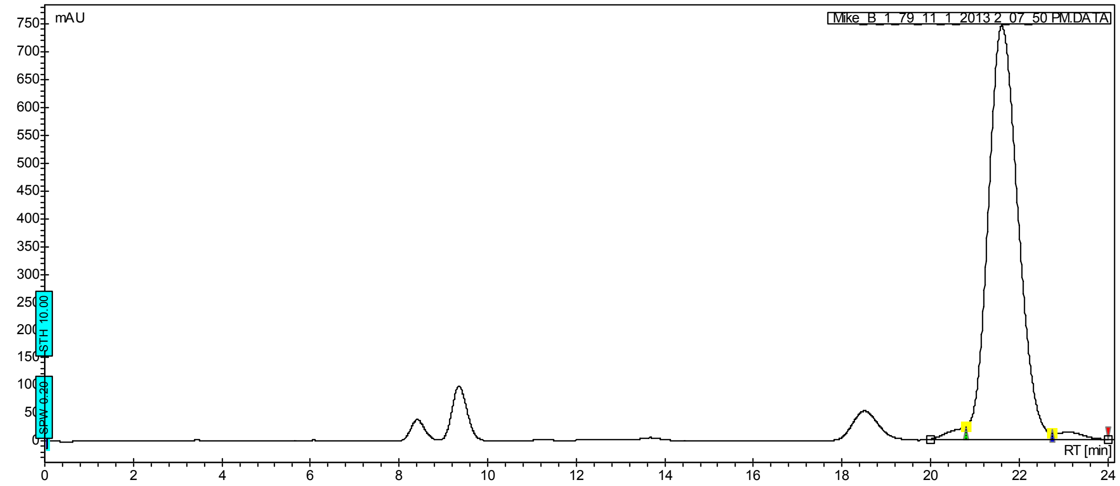

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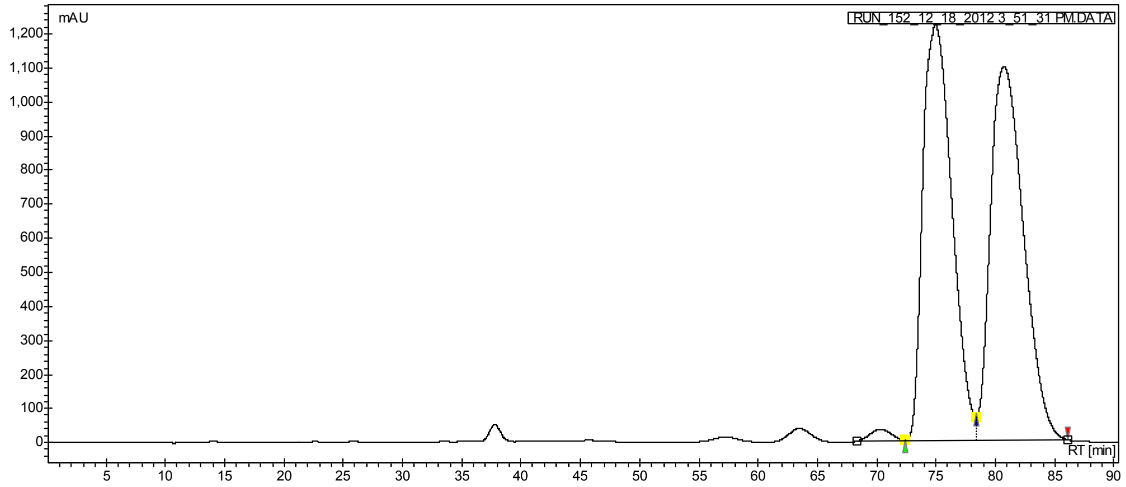

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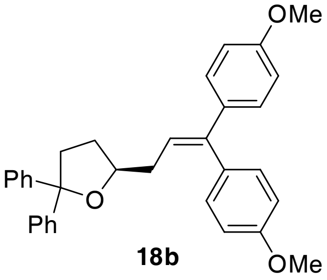

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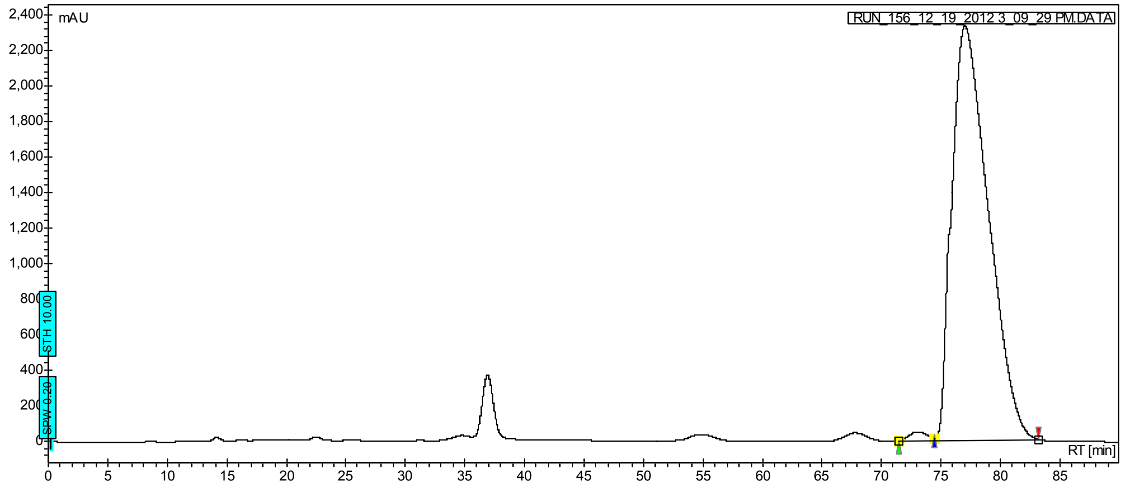

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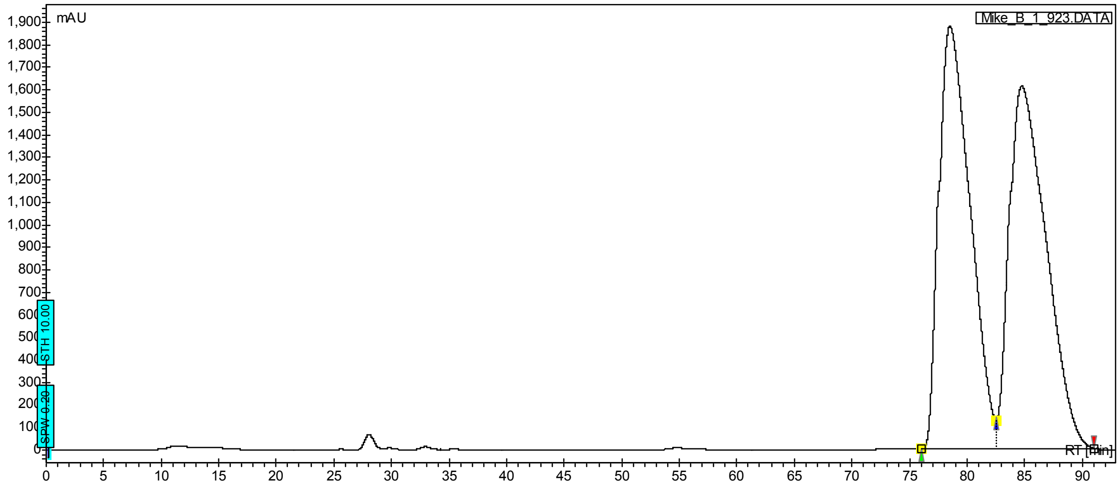

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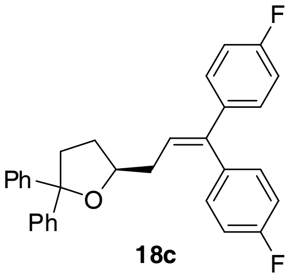
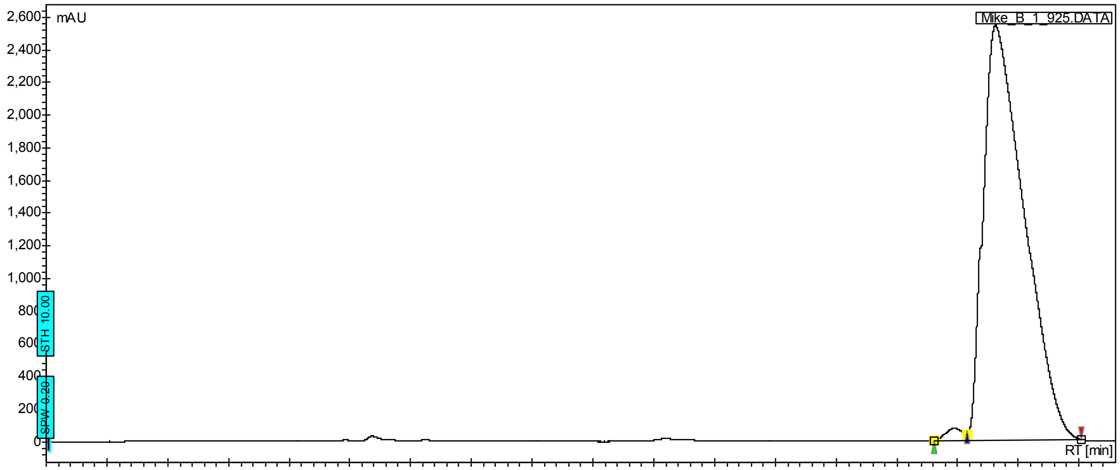
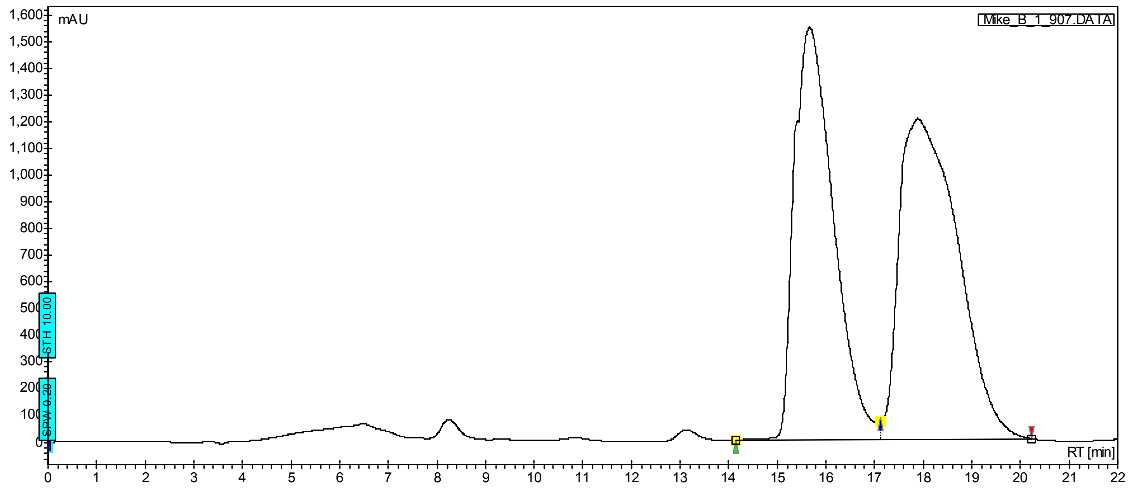
1	78.52	49.5
2	84.77	50.5



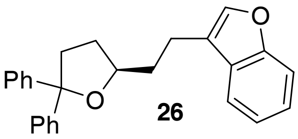
18c



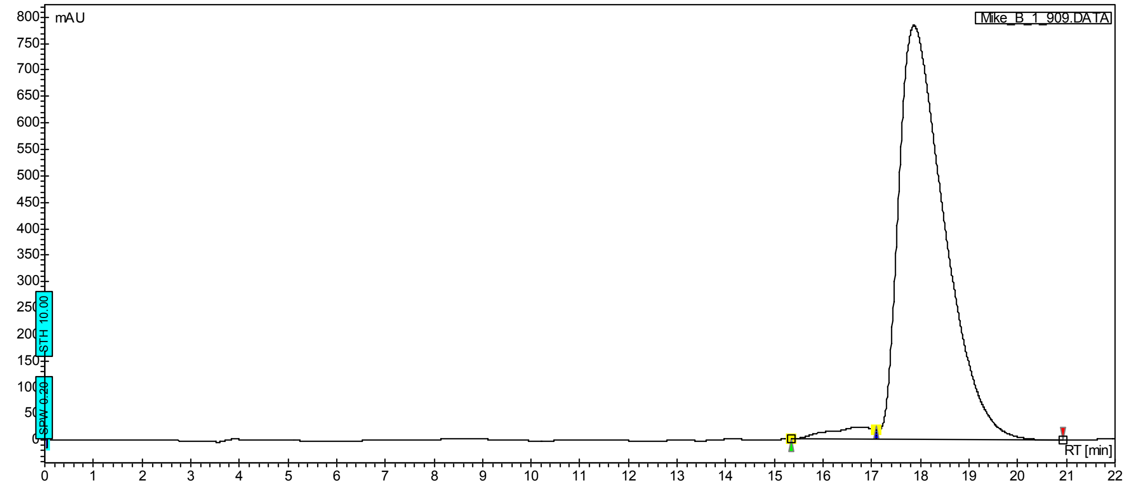
#	Time **[min]**	Area **[%]**
1	74.75	1.2
2	78.12	98.8



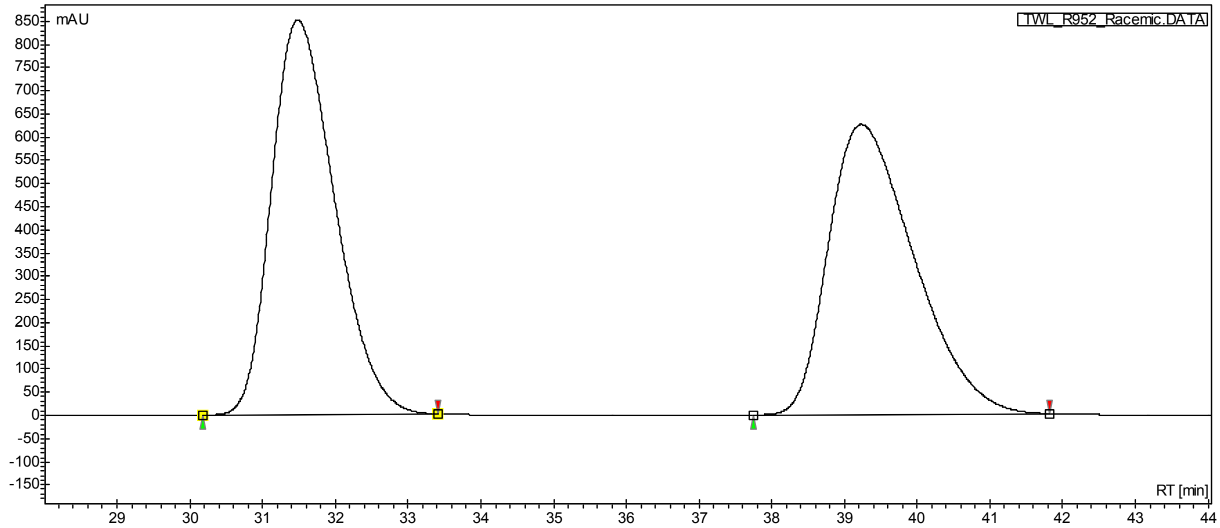
#	Time **[min]**	Area **[%]**
1	15.66	46.3
2	17.89	53.7



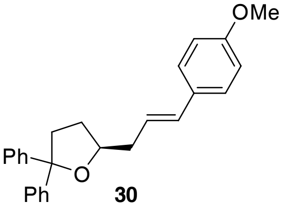
26



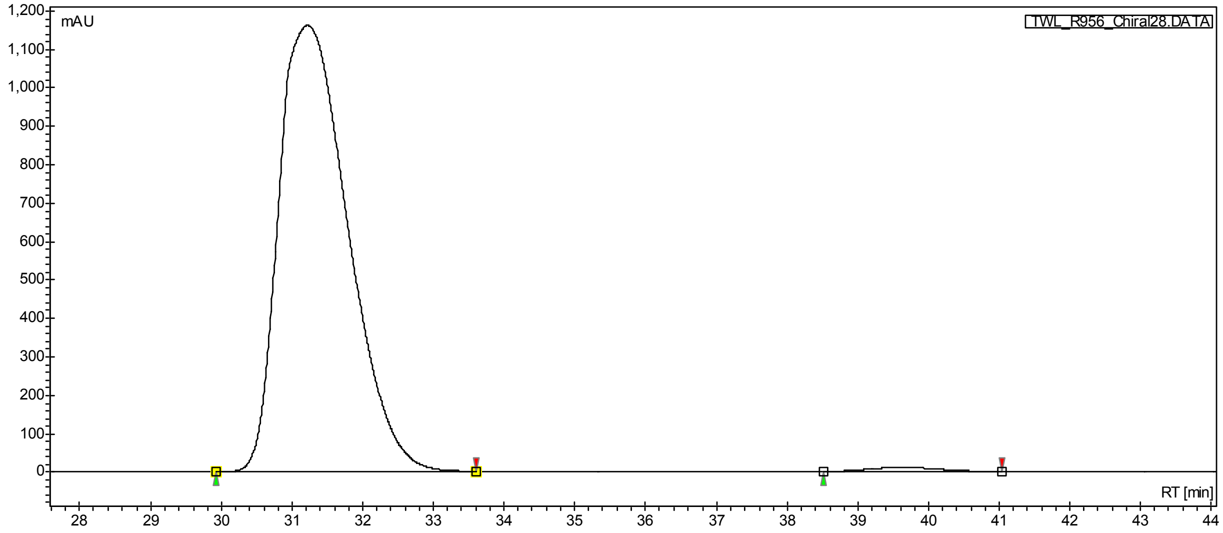
#	Time **[min]**	Area **[%]**
1	16.75	2.9
2	17.87	97.1



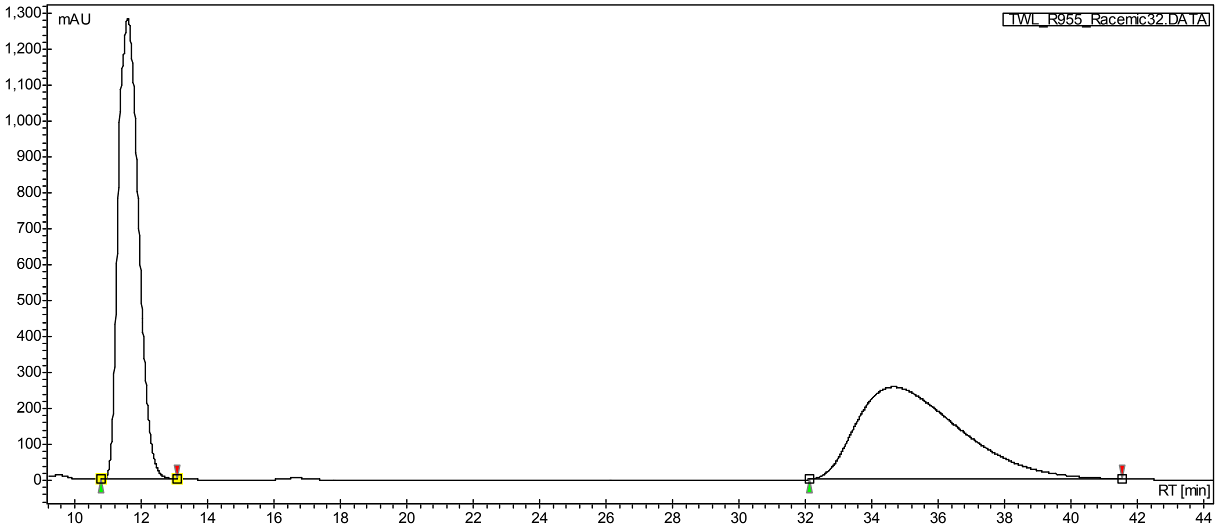
#	Time **[min]**	Area **[%]**
1	31.48	50.2
2	39.23	49.8



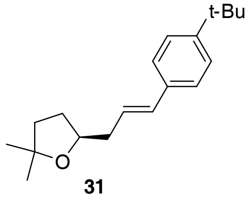
30



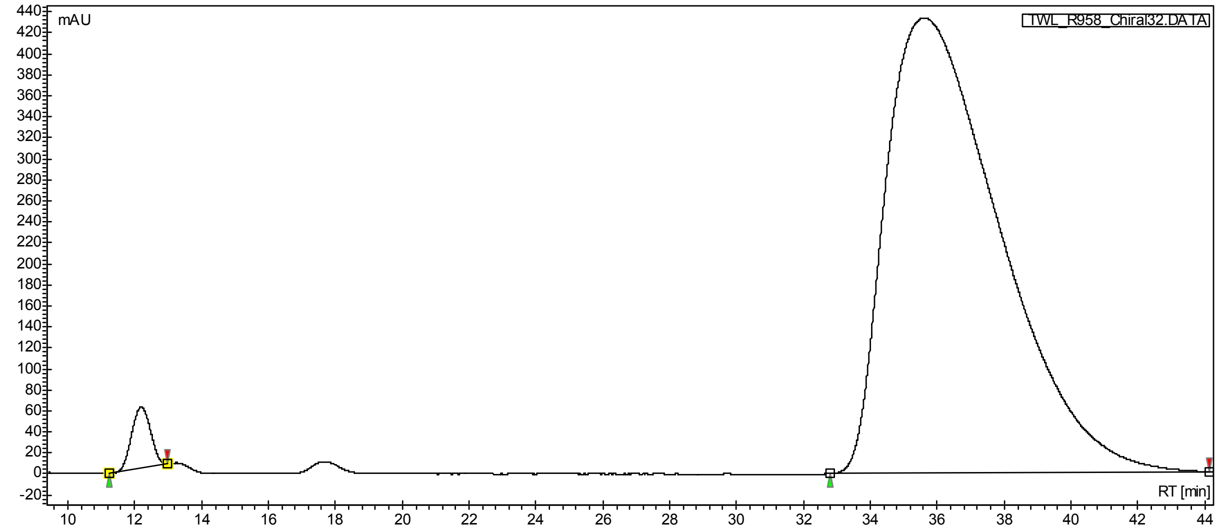
#	Time **[min]**	Area **[%]**
1	31.22	99.1
2	39.63	0.9



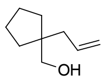
#	Time **[min]**	Area **[%]**
1	11.59	49.4
2	34.67	50.6



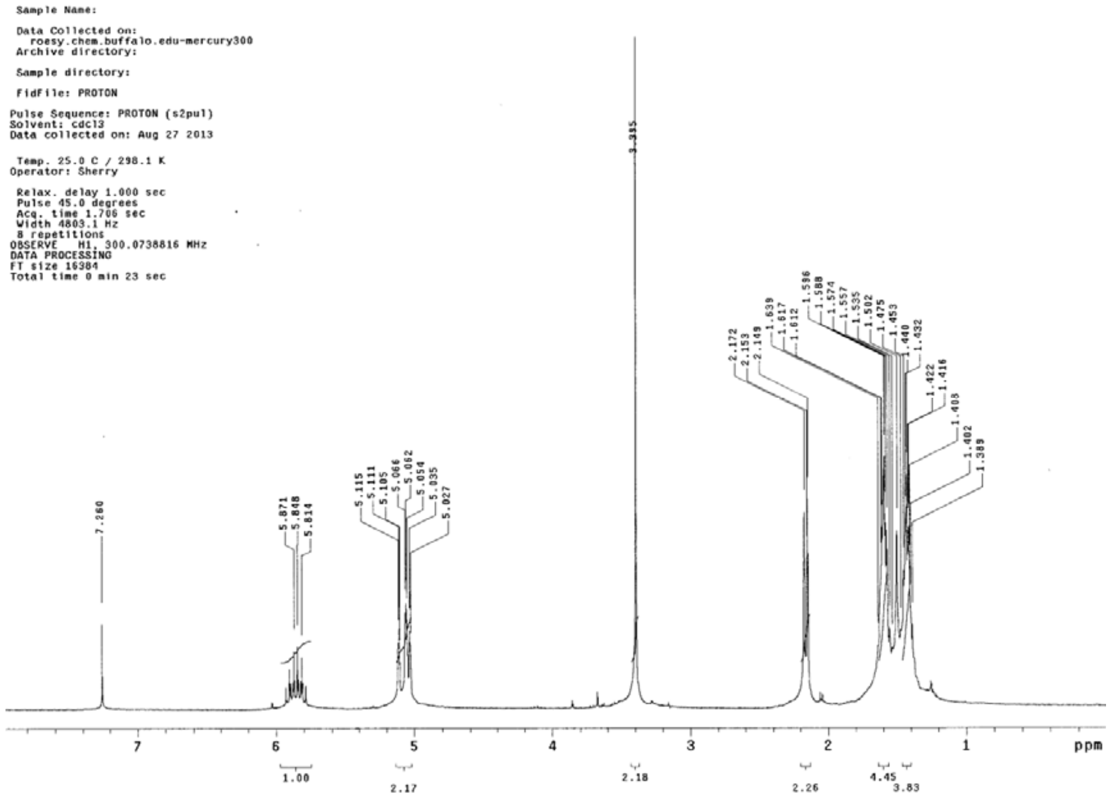
31



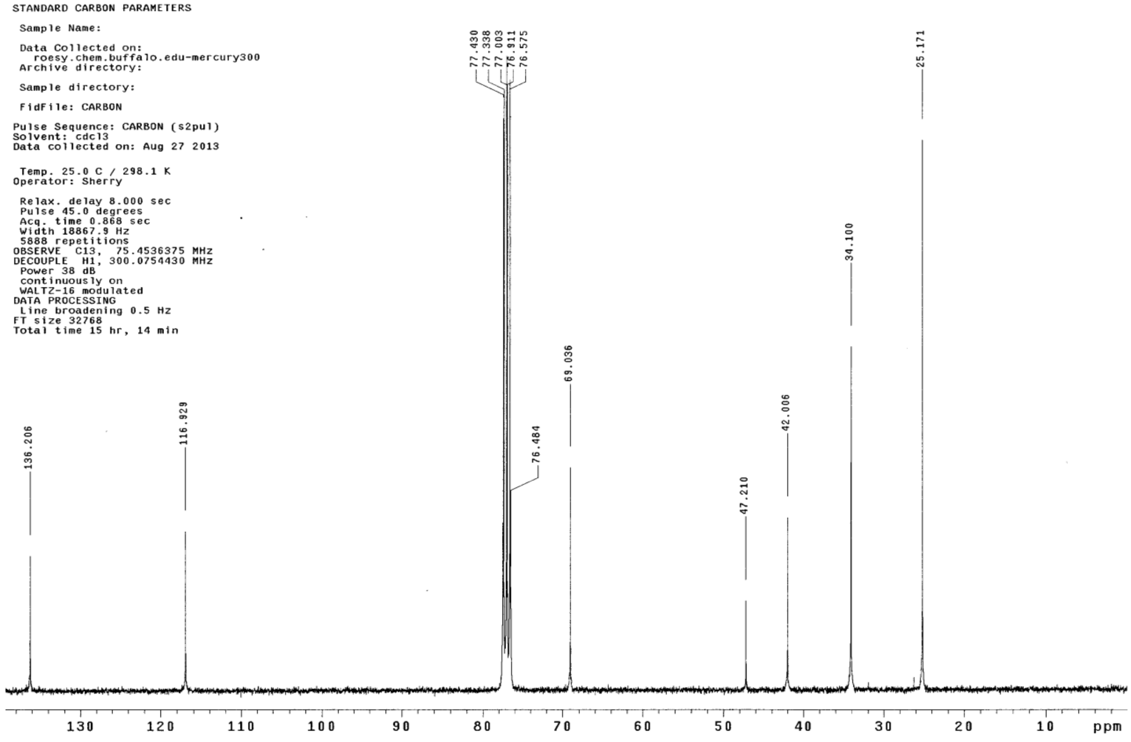
#	Time **[min]**	Area **[%]**
1	12.19	2.2
2	35.61	97.8



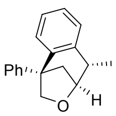
15



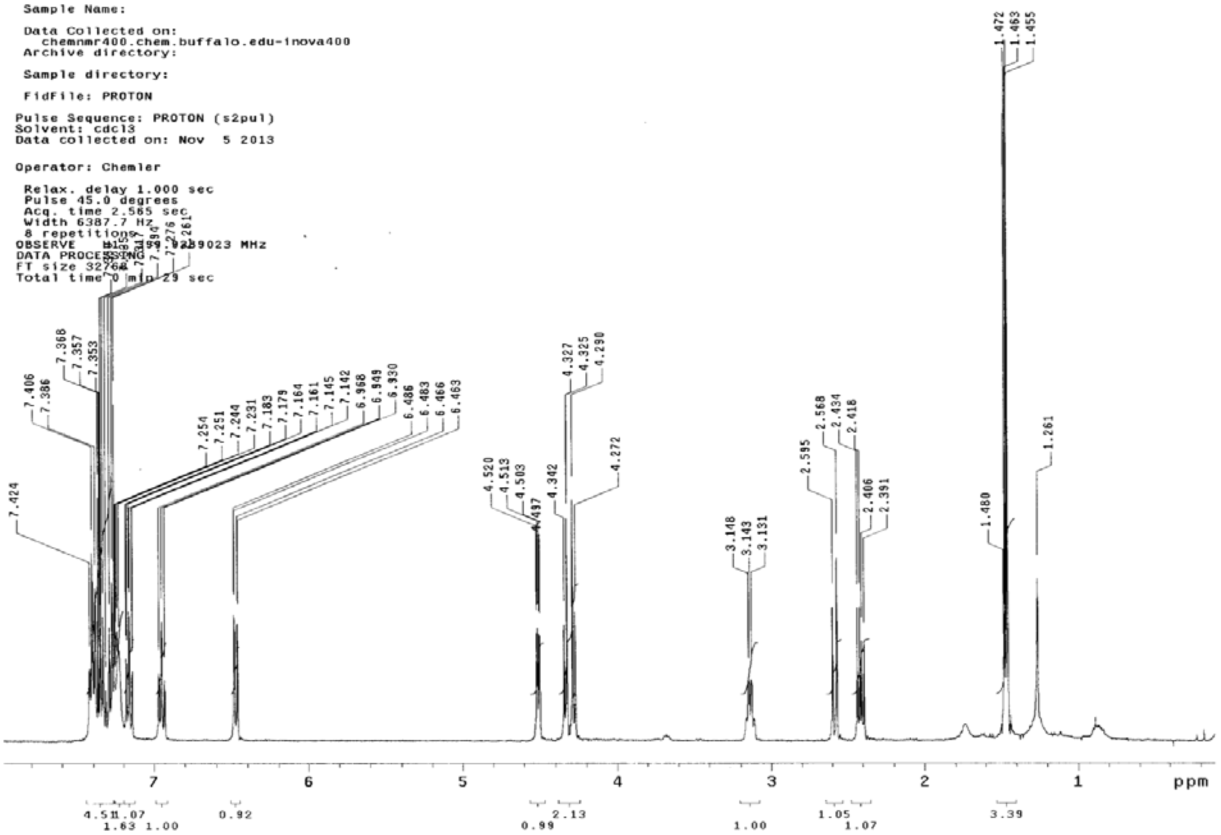
```
Sample Name:

 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 27 2013

 Temp. 25.0 C / 298.1 K
Operator: Sherry

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.706 sec
 Width 4803.1 Hz
 8 repetitions
OBSERVE   H1, 300.0738816 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec
```



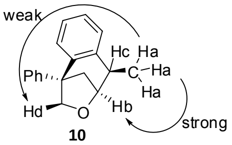
```
STANDARD CARBON PARAMETERS

 Sample Name:

 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 27 2013

 Temp. 25.0 C / 298.1 K
Operator: Sherry

 Relax. delay 8.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 5888 repetitions
OBSERVE  C13, 75.4536375 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 14 min
```



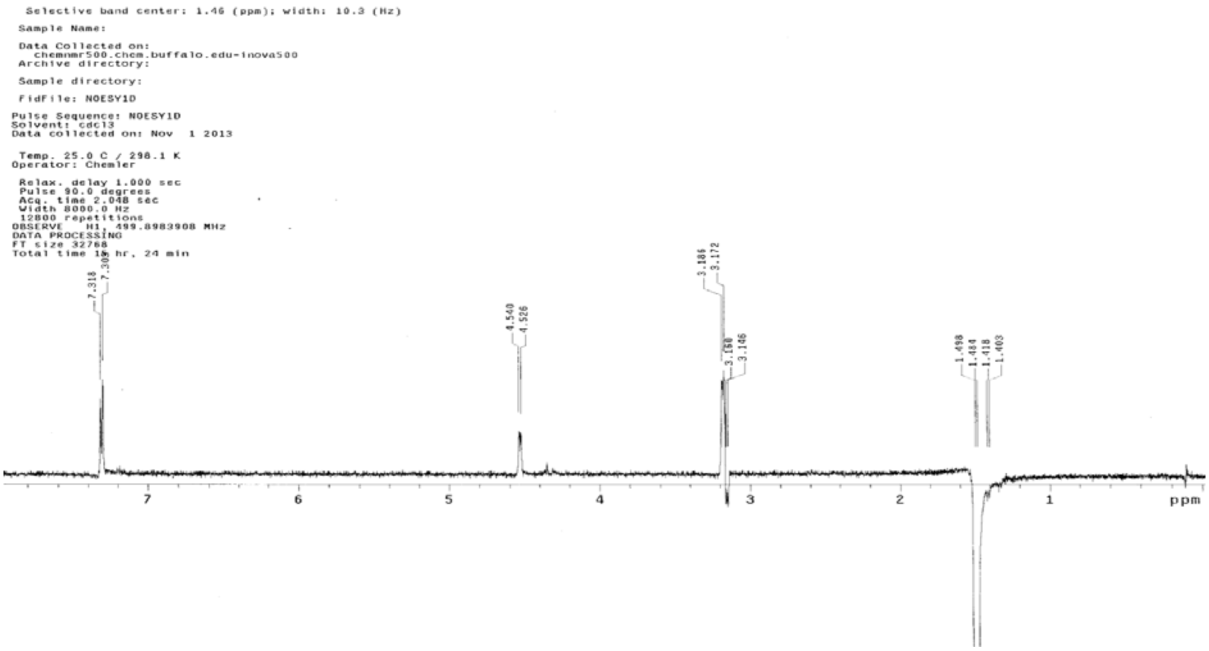
11



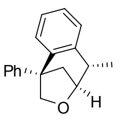
```
Sample Name:

Data Collected on:
  chemnmr400.chem.buffalo.edu-inova400
Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov  5 2013

Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE   H1, 399.[illegible]9023 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
```



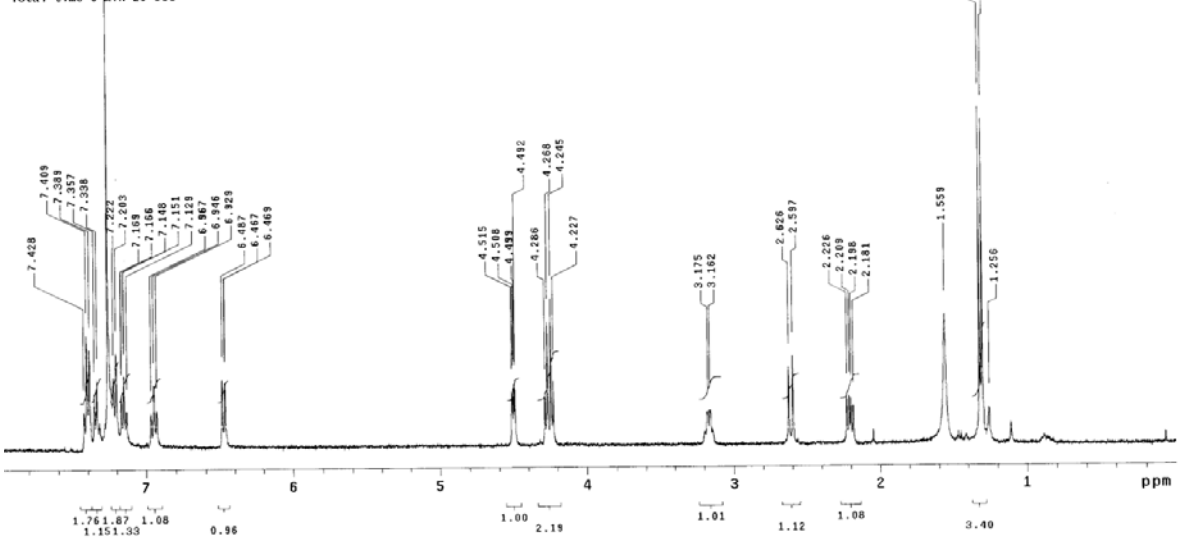
10



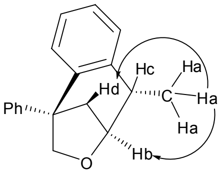
```
Selective band center: 1.46 (ppm); width: 10.3 (Hz)

Sample Name:

Data Collected on:
  chemnmr500.chem.buffalo.edu-inova500
Archive directory:

Sample directory:

FidFile: NOESY1D

Pulse Sequence: NOESY1D
Solvent: cdcl3
Data collected on: Nov  1 2013

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
12800 repetitions
OBSERVE   H1, 499.8983908 MHz
DATA PROCESSING
FT size 32768
Total time 15 hr, 24 min
```



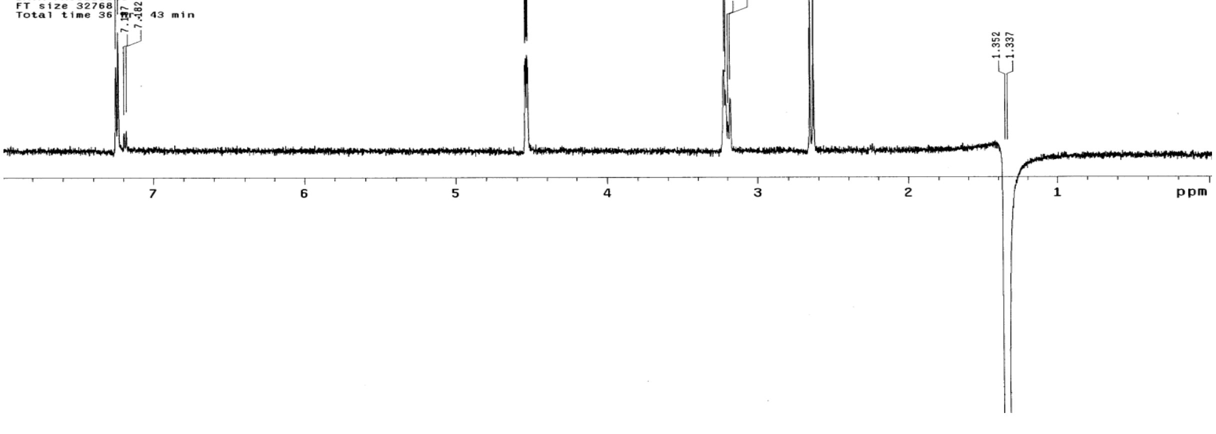
11



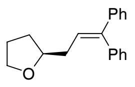
```
Sample Name:

 Data Collected on:
   chemnmr400.chem.buffalo.edu-inova400
 Archive directory:

 Sample directory:

 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 27 2013

Operator: Chemler

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.565 sec
 Width 6387.7 Hz
 8 repetitions
OBSERVE   H1, 399.9389023 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
```



11



```
 Selective band center: 3.96 (ppm); width: 30.0 (Hz)
 Selective band center: 1.34 (ppm); width: 9.3 (Hz)

 Sample Name:

 Data Collected on:
   nmr500c.chem.buffalo.edu-inova500
 Archive directory:

 Sample directory:

 FidFile: NOESY1D

Pulse Sequence: NOESY1D
Solvent: cdcl3
Data collected on: Nov 14 2013

 Temp. 25.0 C / 298.1 K
Operator: Chemler

 Relax. delay 1.000 sec
 Pulse 90.0 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 11872 repetitions
OBSERVE   H1, 499.8983908 MHz
DATA PROCESSING
FT size 32768
Total time 36 hr, 43 min
```



14

Sample Name:

Data Collected on:
  chemnmr400.chem.buffalo.edu-inova400
Archive directory:

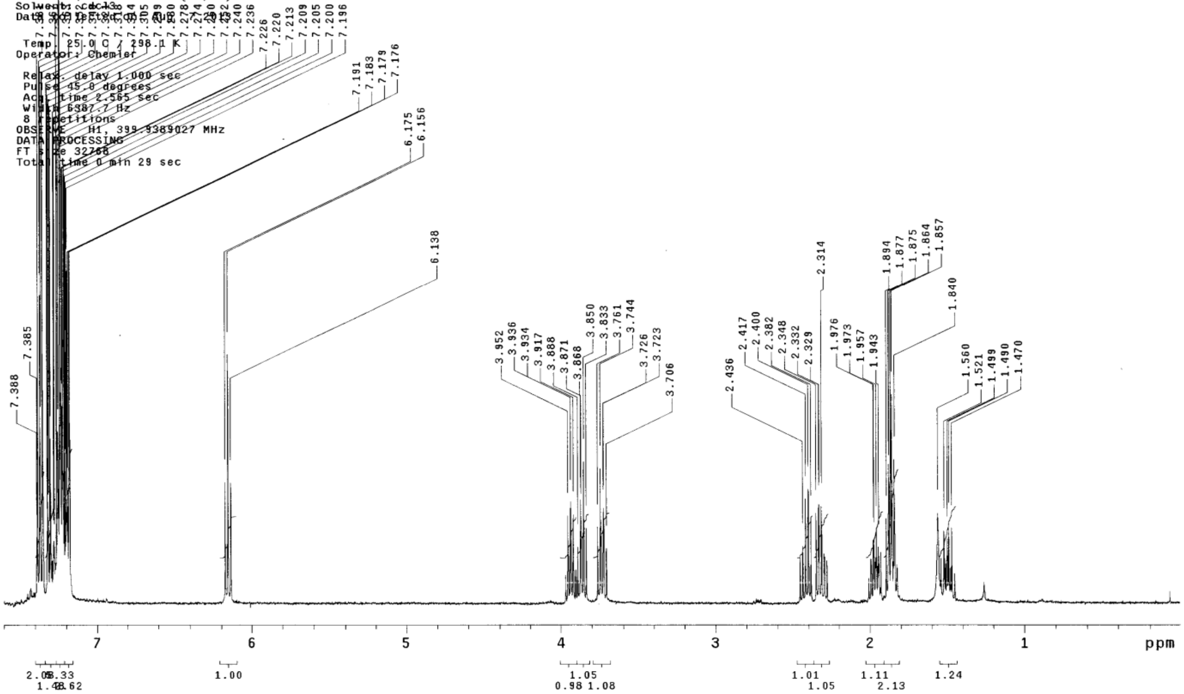
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 7 2013

Temp. 25.0 C / 298.1 K
Operator: Chemier

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
  roesy.chem.buffalo.edu-mercury300
Archive directory:

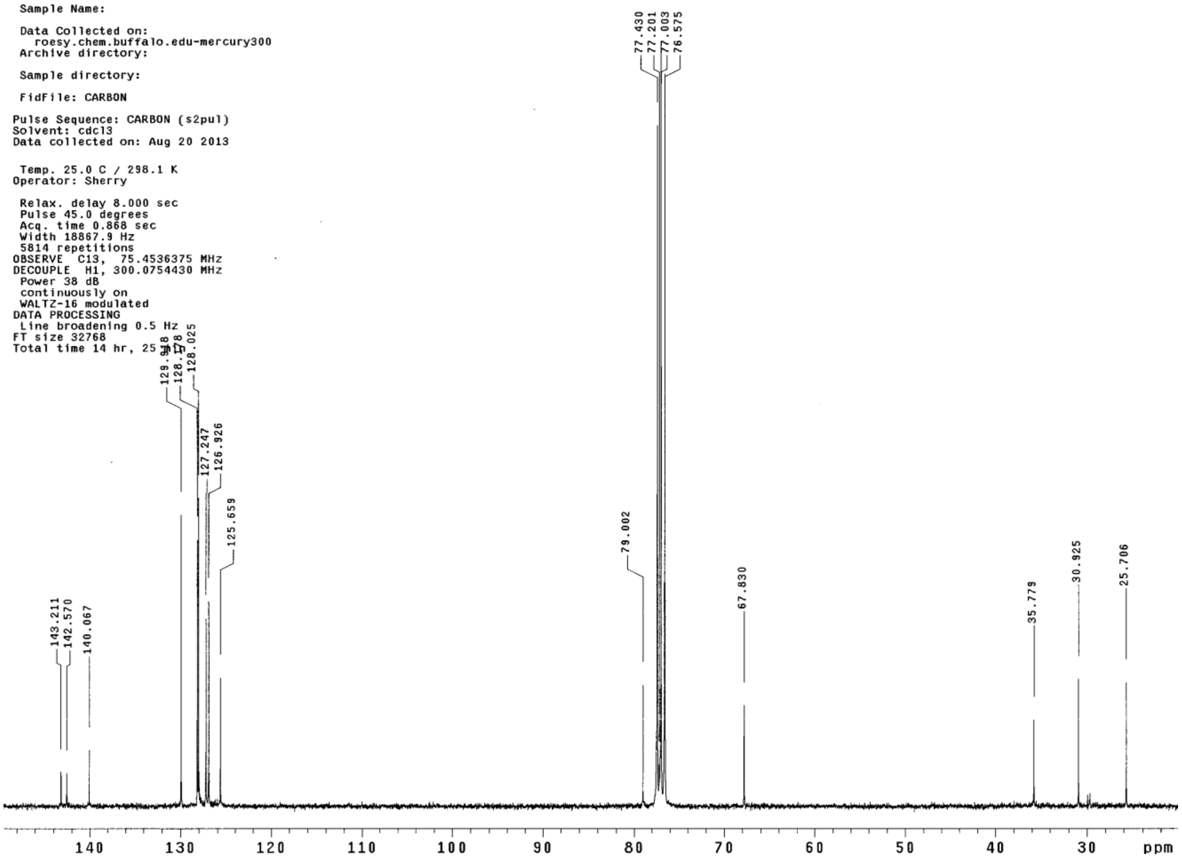
Sample directory:

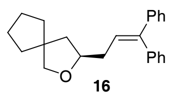
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 20 2013

Temp. 25.0 C / 298.1 K
Operator: Sherry

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
5814 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 14 hr, 25 min





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Sample Name:

Data Collected on:
 chemnmr400.chem.buffalo.edu-inova400
Archive directory:

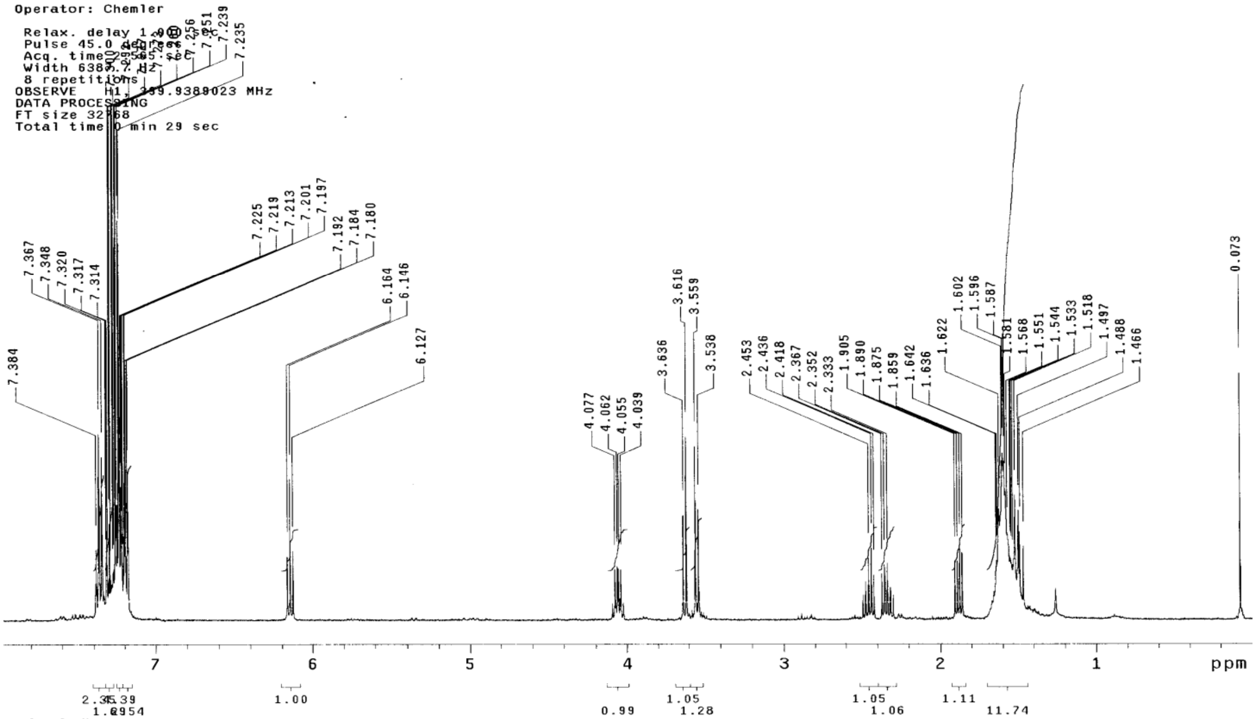
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 5 2013

Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time [illegible] sec
Width 638[illegible].7 Hz
8 repetitions
OBSERVE H1, [illegible]9.938[illegible]023 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



Sample Name:

Data Collected on:
 roesy.chem.buffalo.edu-mercury300
Archive directory:

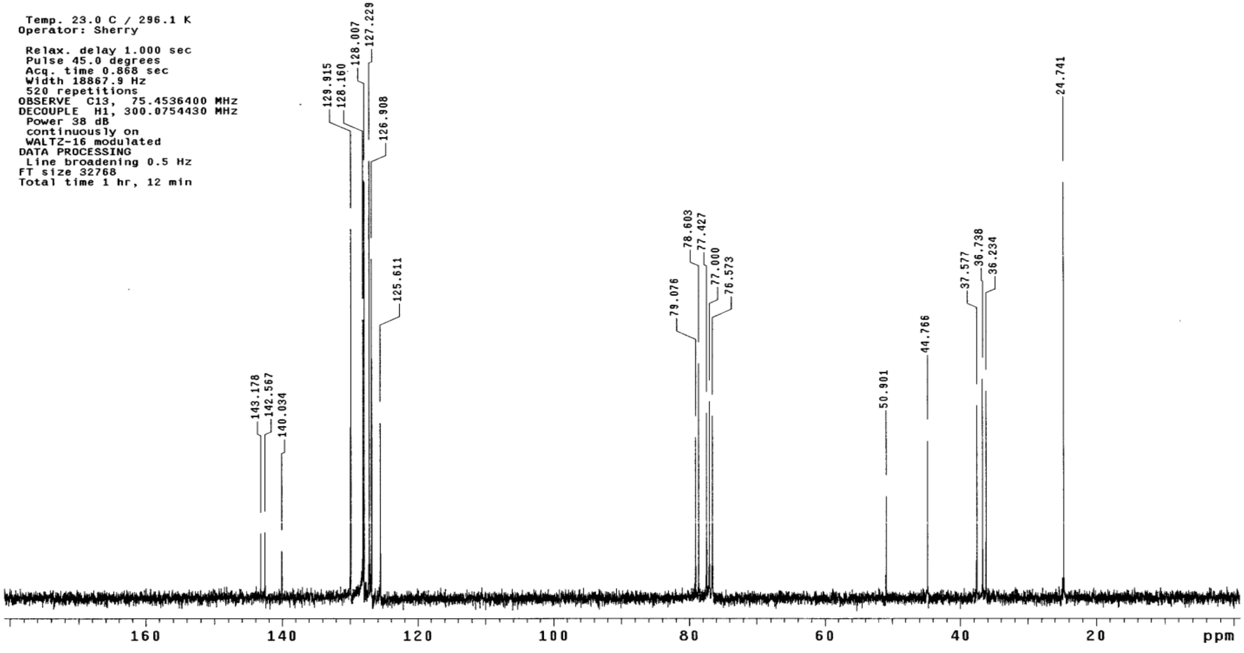
Sample directory:

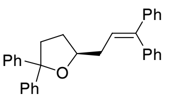
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 9 2012

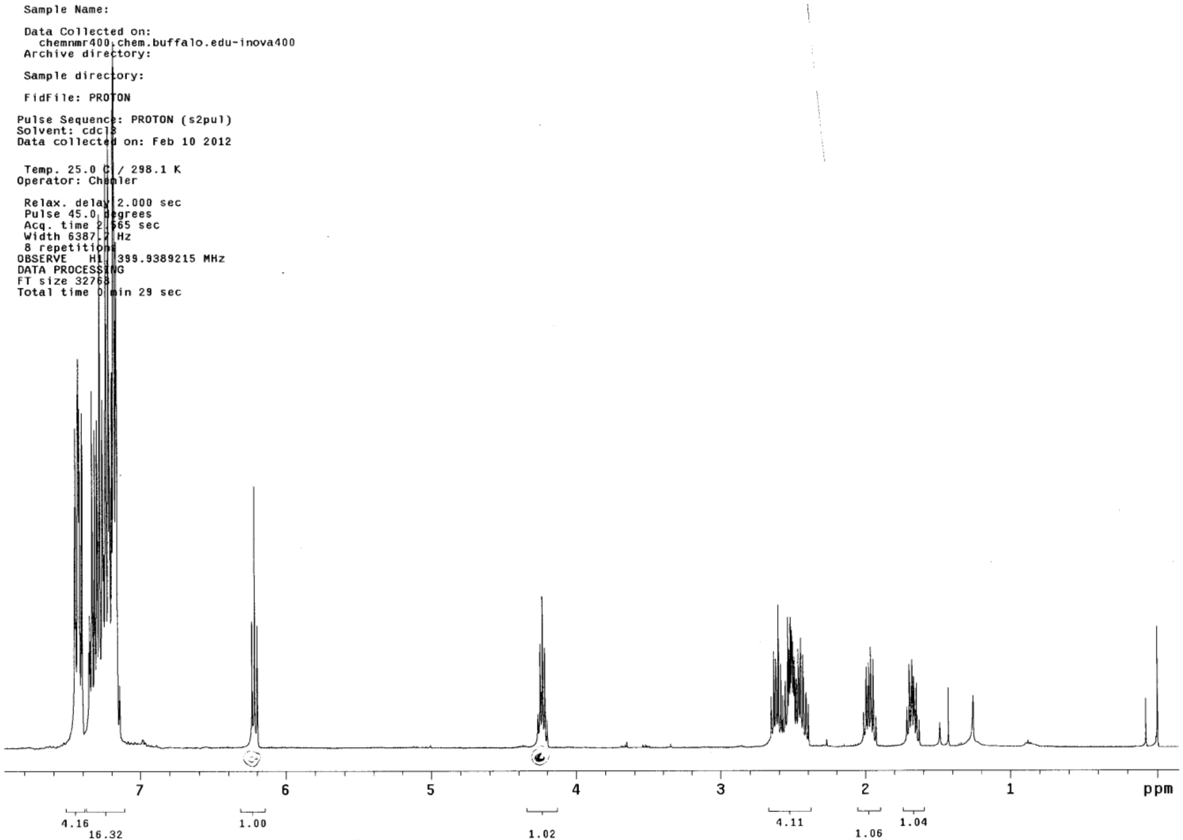
Temp. 23.0 C / 296.1 K
Operator: Sherry

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
520 repetitions
OBSERVE C13, 75.4536400 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 12 min





18a



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

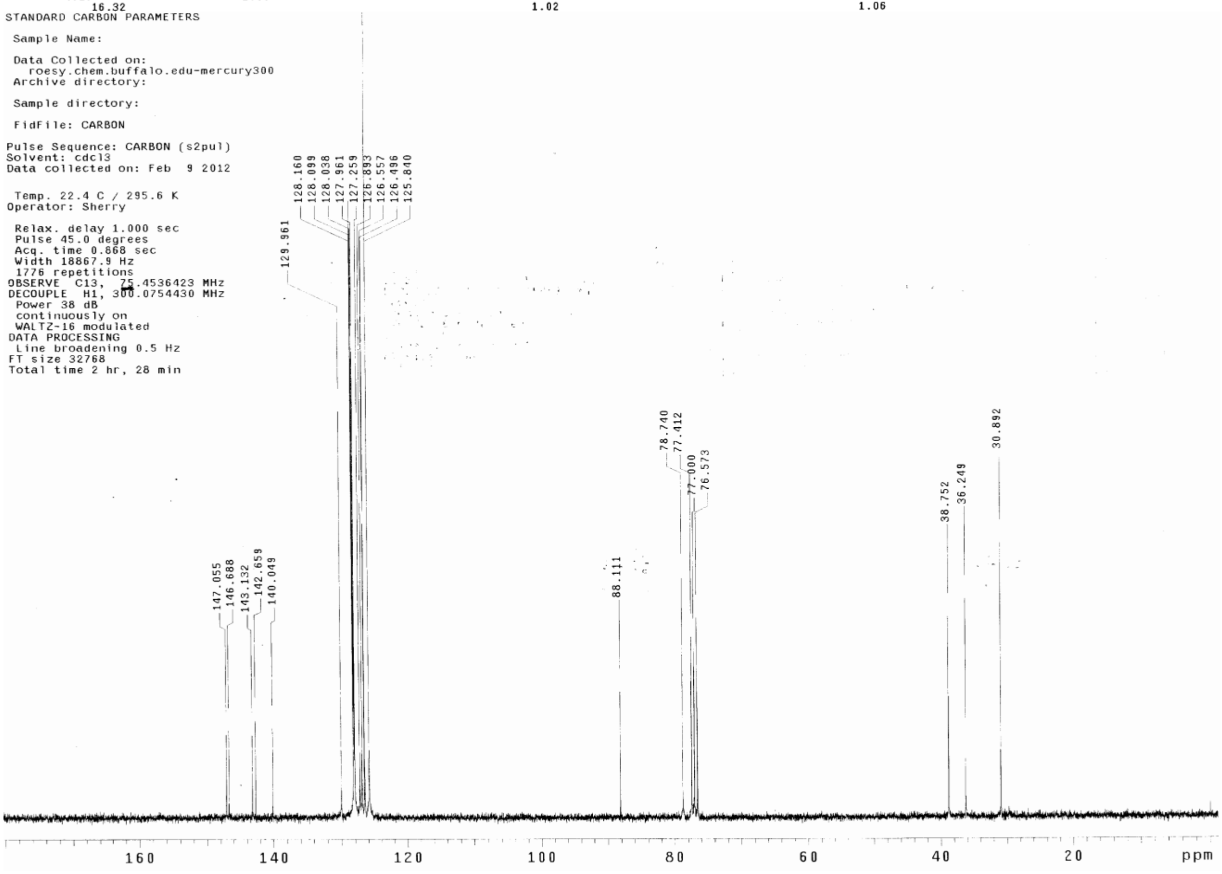
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 10 2012

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389215 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

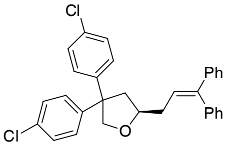
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 9 2012

Temp. 22.4 C / 295.6 K
Operator: Sherry

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1776 repetitions
OBSERVE C13, 75.4536423 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 2 hr, 28 min



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STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

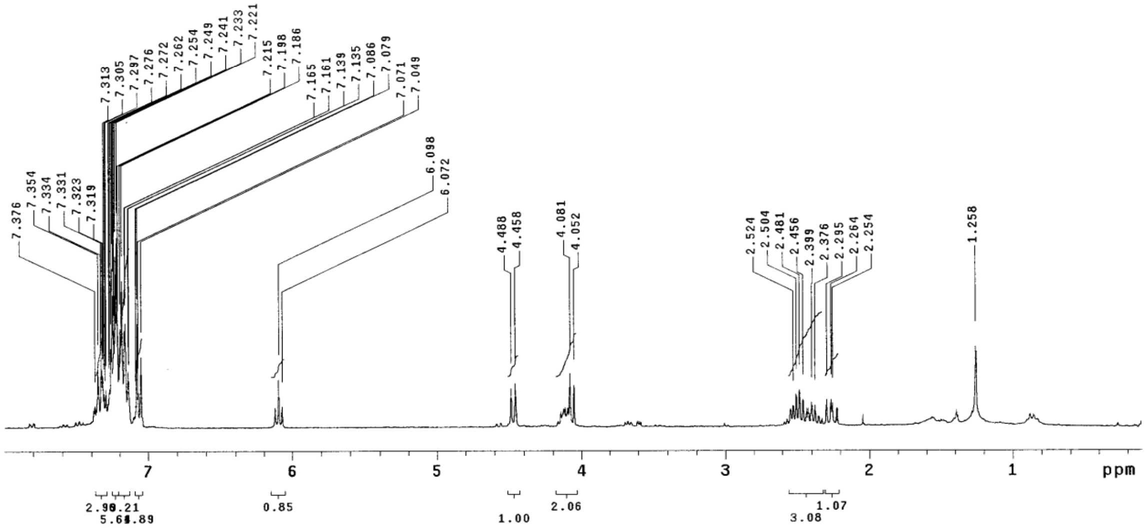
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 24 2013

Temp. 25.0 C / 298.1 K
Operator: Sherry

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.0738816 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec



Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

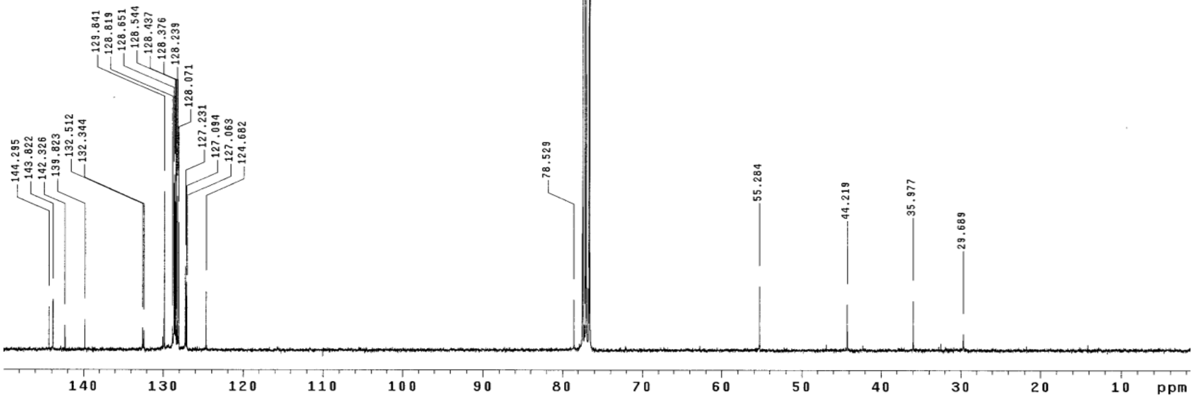
Sample directory:

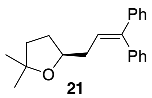
FidFile: CARBON

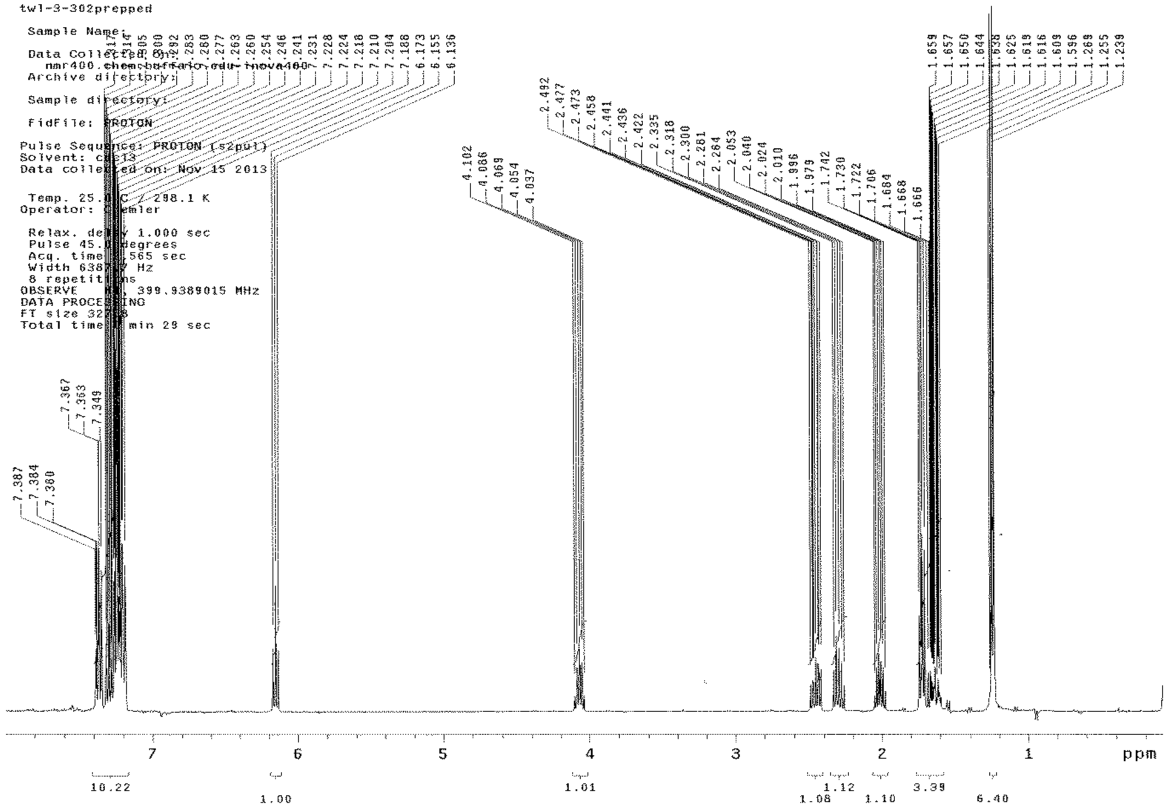
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 23 2013

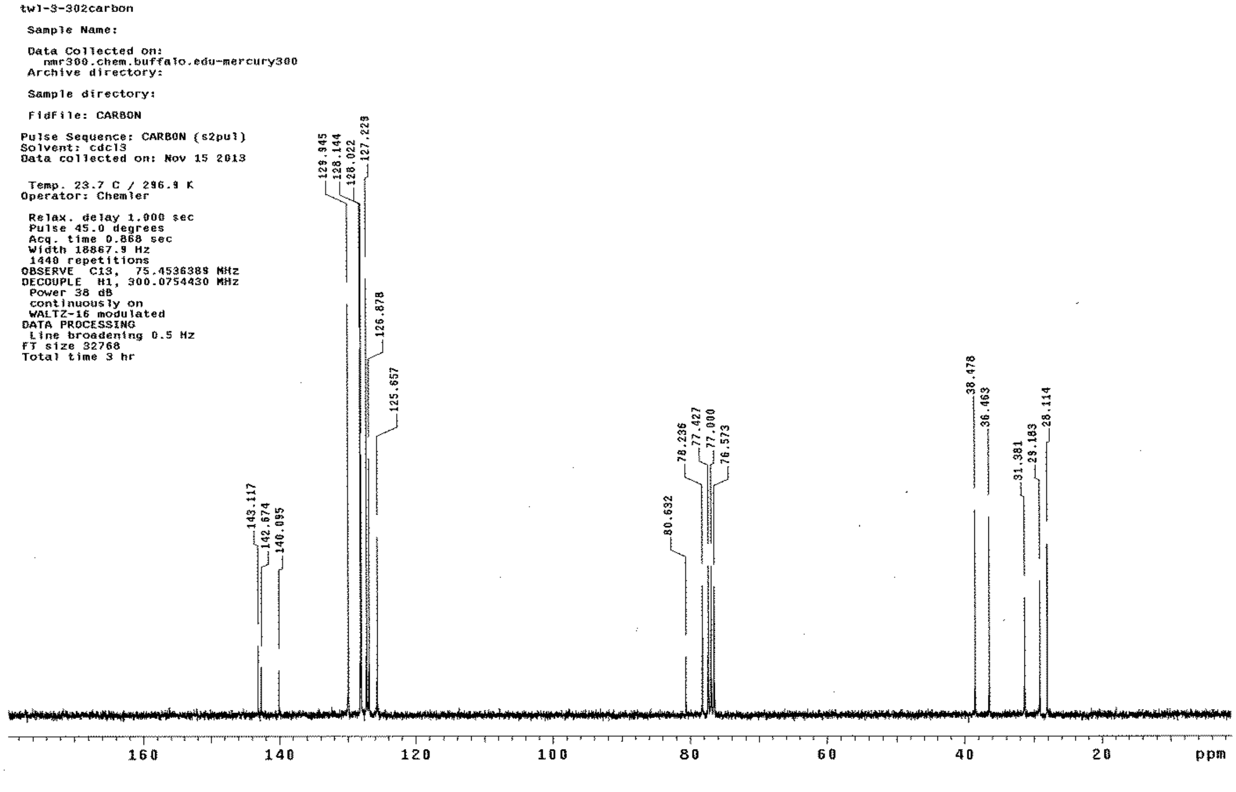
Temp. 23.4 C / 296.6 K
Operator: Sherry

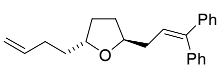
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
5952 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 14 min



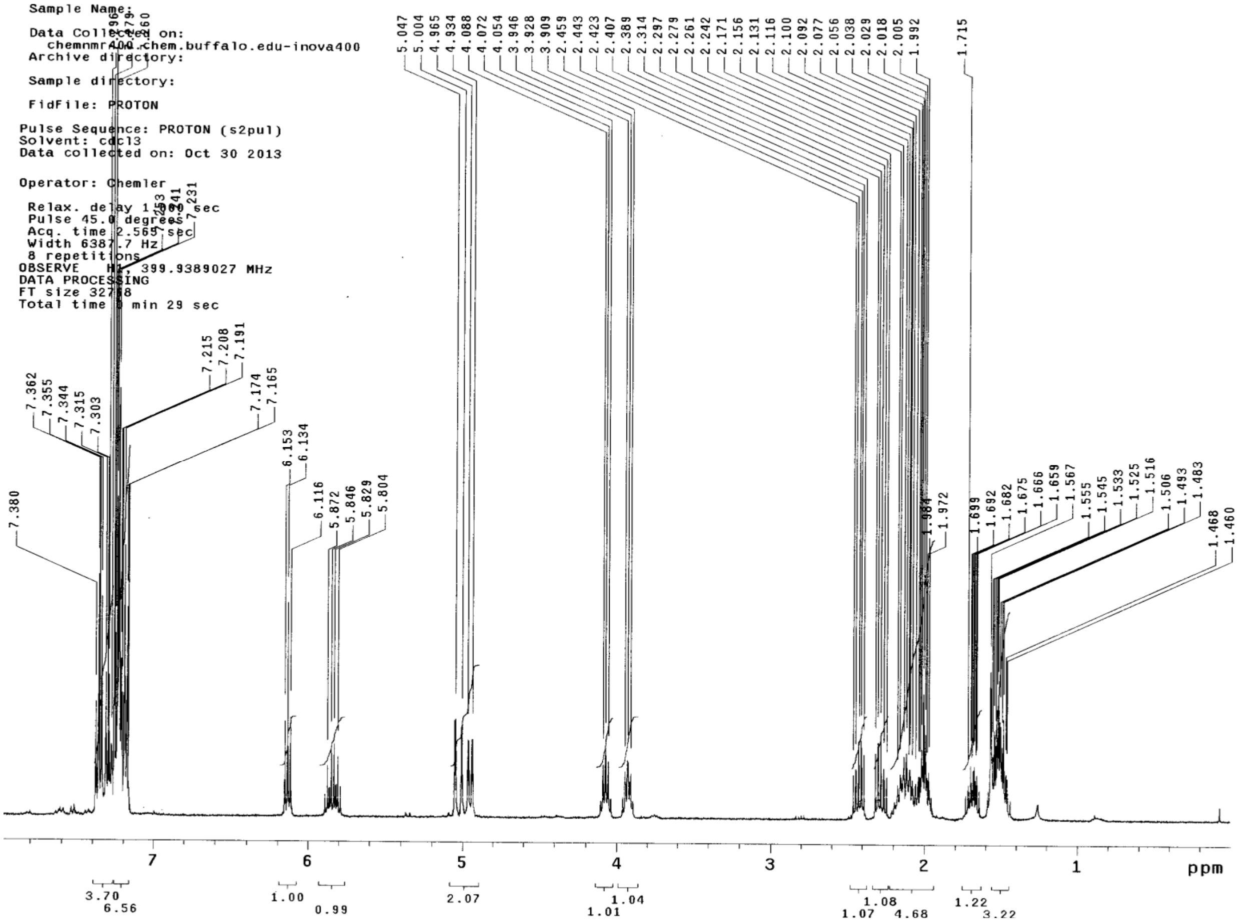

21


twl-3-302prepped
Sample Name:
Data Collected on:
nmr400.chem.buffalo.edu-nova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 15 2013
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389015 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
7.387
7.384
7.380
7.367
7.363
7.349
7.314
7.305
7.300
7.292
7.283
7.280
7.277
7.263
7.260
7.254
7.246
7.241
7.231
7.228
7.224
7.218
7.210
7.204
7.188
6.173
6.155
6.136
4.102
4.086
4.069
4.054
4.037
2.492
2.477
2.473
2.458
2.441
2.436
2.422
2.335
2.318
2.300
2.281
2.264
2.053
2.040
2.024
2.010
1.996
1.979
1.742
1.730
1.722
1.706
1.684
1.668
1.666
1.659
1.657
1.650
1.644
1.638
1.625
1.619
1.616
1.609
1.596
1.269
1.255
1.239
7
6
5
4
3
2
1
ppm
10.22
1.00
1.01
1.08
1.12
1.10
3.39
6.40


twl-3-302carbon
Sample Name:
Data Collected on:
nmr300.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 15 2013
Temp. 23.7 C / 296.9 K
Operator: Chemler
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1440 repetitions
OBSERVE C13, 75.4536389 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 3 hr
143.117
142.674
140.095
129.945
128.144
128.022
127.229
126.878
125.657
80.632
78.236
77.427
77.000
76.573
38.478
36.463
31.381
29.183
28.114
160
140
120
100
80
60
40
20
ppm



23



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

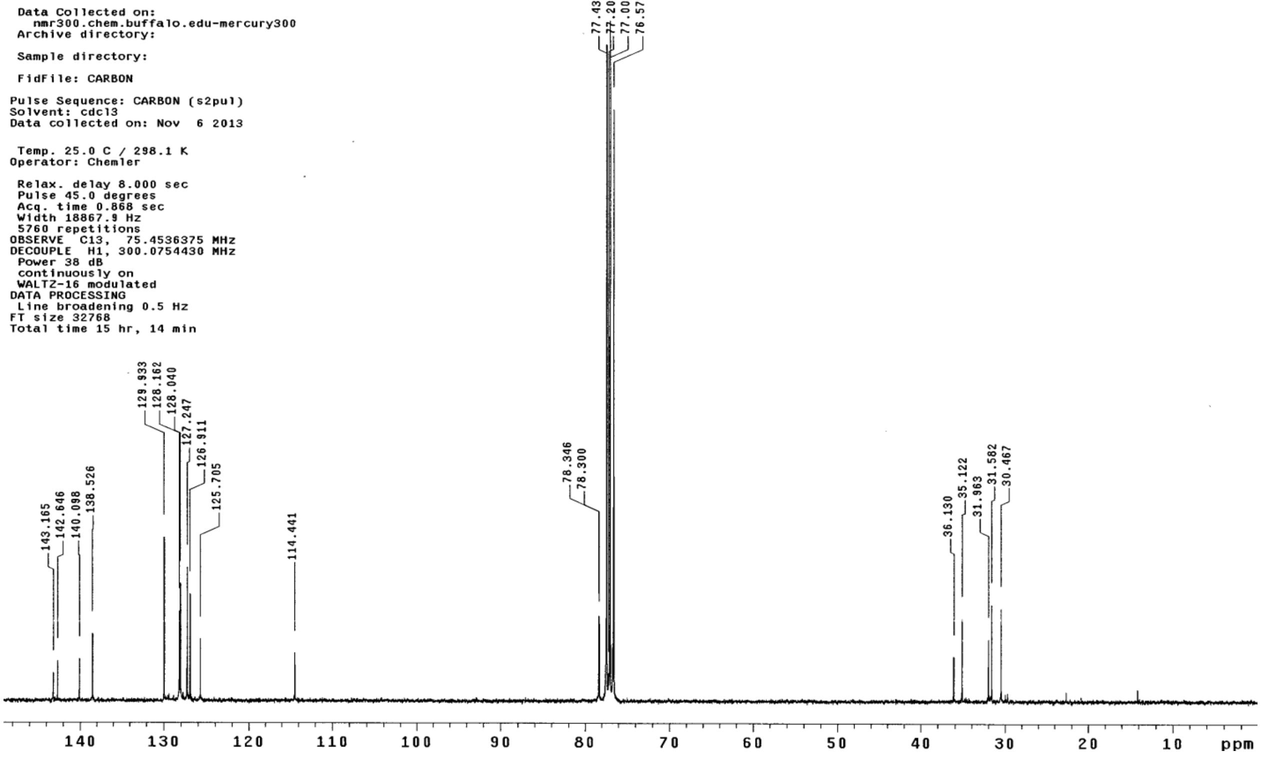
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 30 2013

Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



Sample Name:

Data Collected on:
nmr300.chem.buffalo.edu-mercury300
Archive directory:

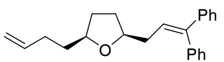
Sample directory:

FidFile: CARBON

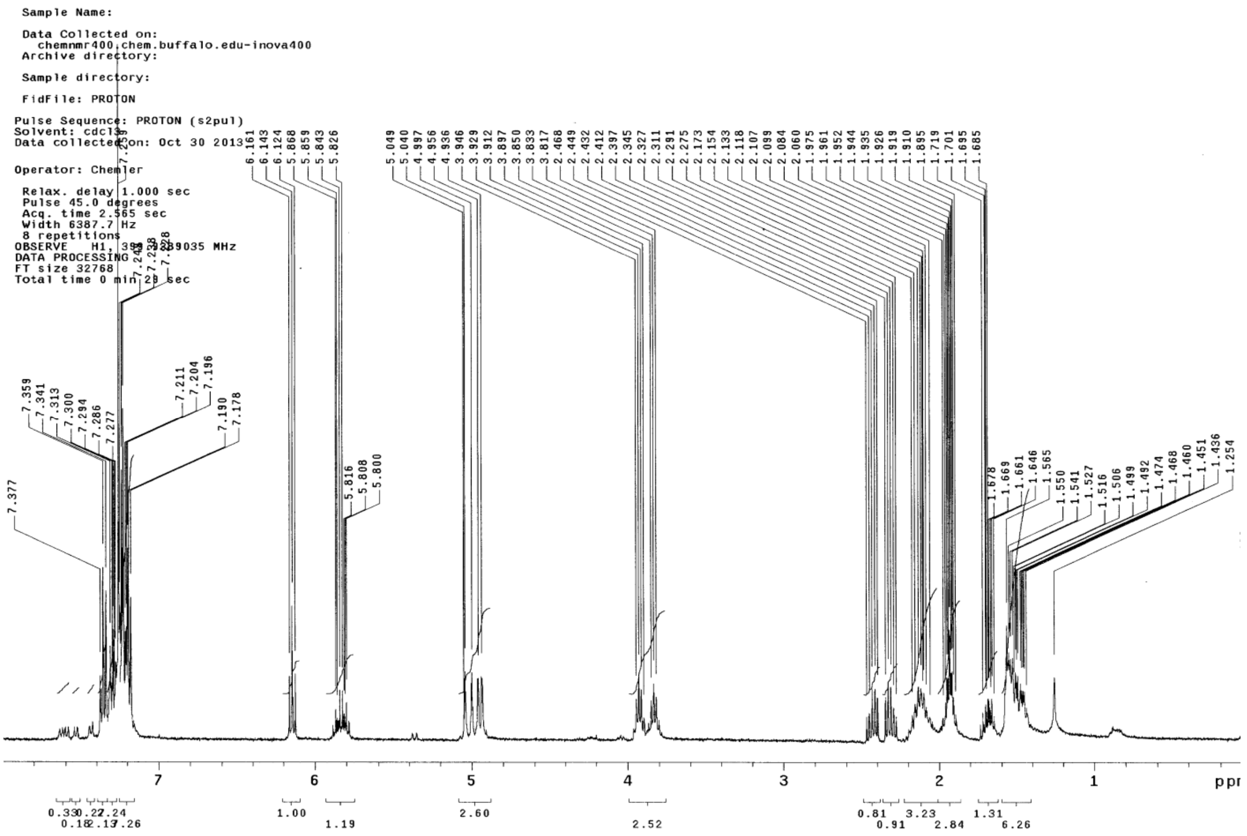
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 6 2013

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
5760 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 14 min



24



Sample Name:

Data Collected on:
  chemnmr400.chem.buffalo.edu-inova400
Archive directory:

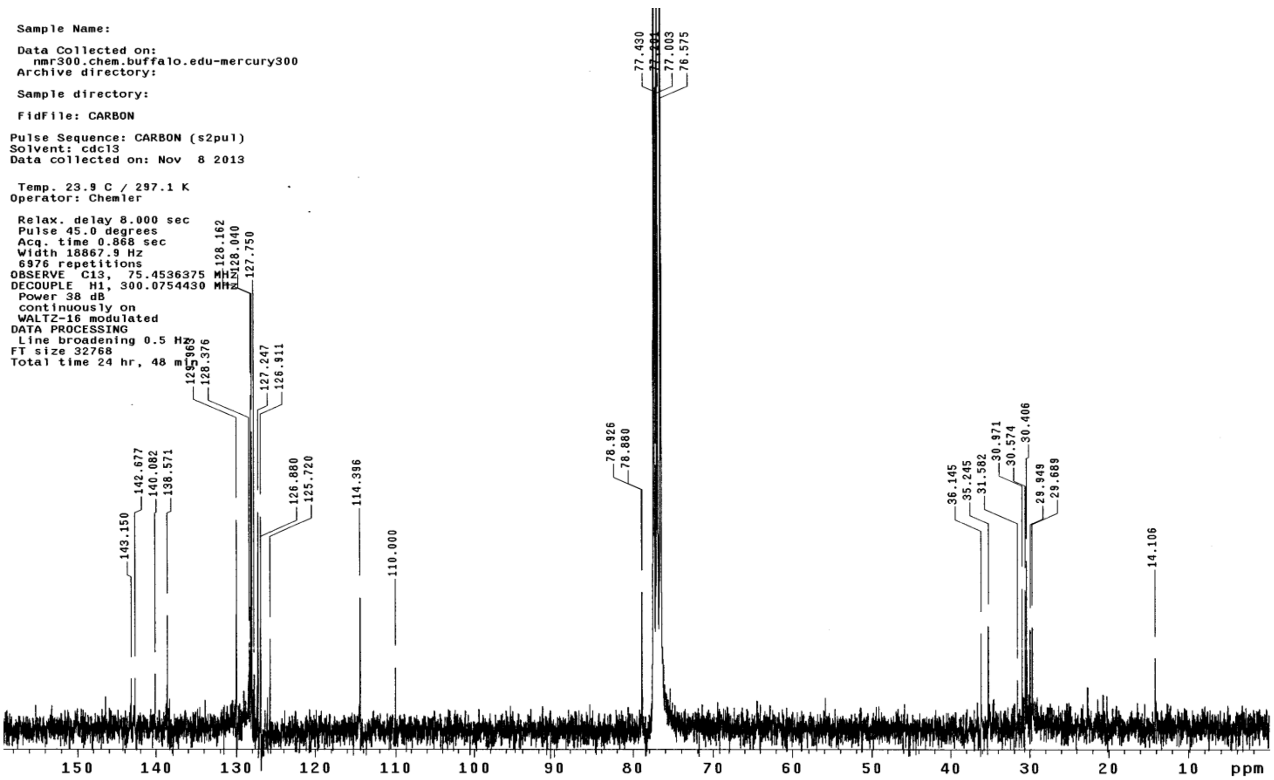
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 30 2013

Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9239035 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



Sample Name:

Data Collected on:
  nmr300.chem.buffalo.edu-mercury300
Archive directory:

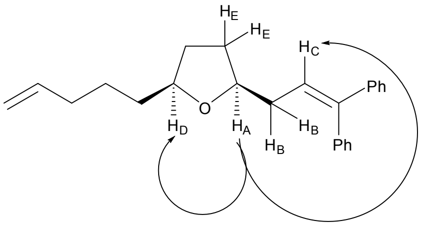
Sample directory:

FidFile: CARBON

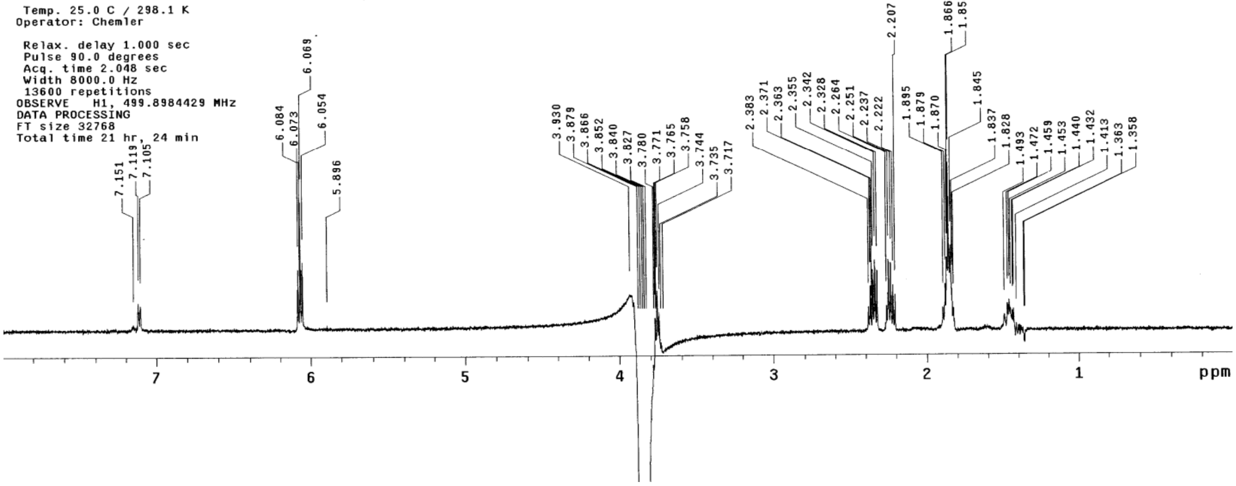
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 8 2013

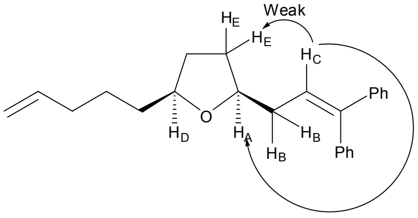
Temp. 23.9 C / 297.1 K
Operator: Chemler

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
6976 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 24 hr, 48 min

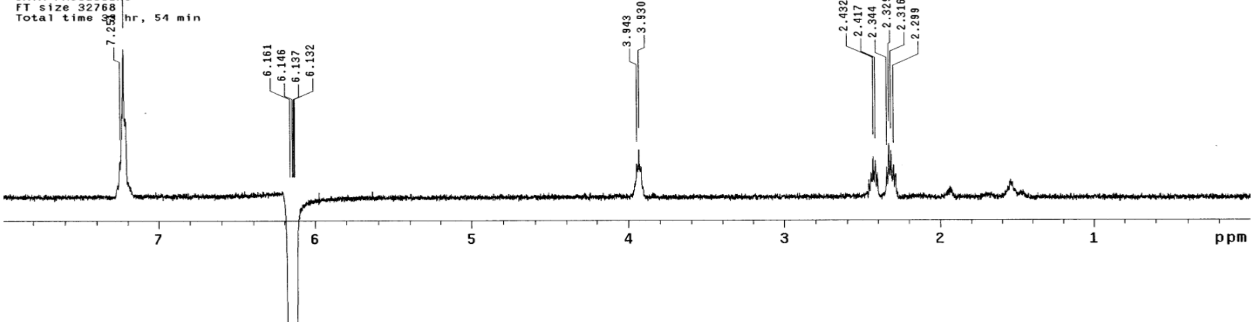


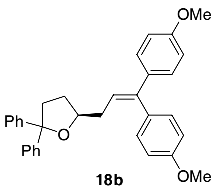
```
 Selective band center: 3.86 (ppm); width: 32.5 (Hz)

 Sample Name:

 Data Collected on:
   nmr500c.chem.buffalo.edu-inova500
 Archive directory:

 Sample directory:

 FidFile: NOESY1D

Pulse Sequence: NOESY1D
Solvent: cdcl3
Data collected on: Nov 20 2013

 Temp. 25.0 C / 298.1 K
Operator: Chemler

 Relax. delay 1.000 sec
 Pulse 90.0 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 13600 repetitions
OBSERVE   H1, 499.8984429 MHz
DATA PROCESSING
FT size 32768
Total time 21 hr, 24 min
```



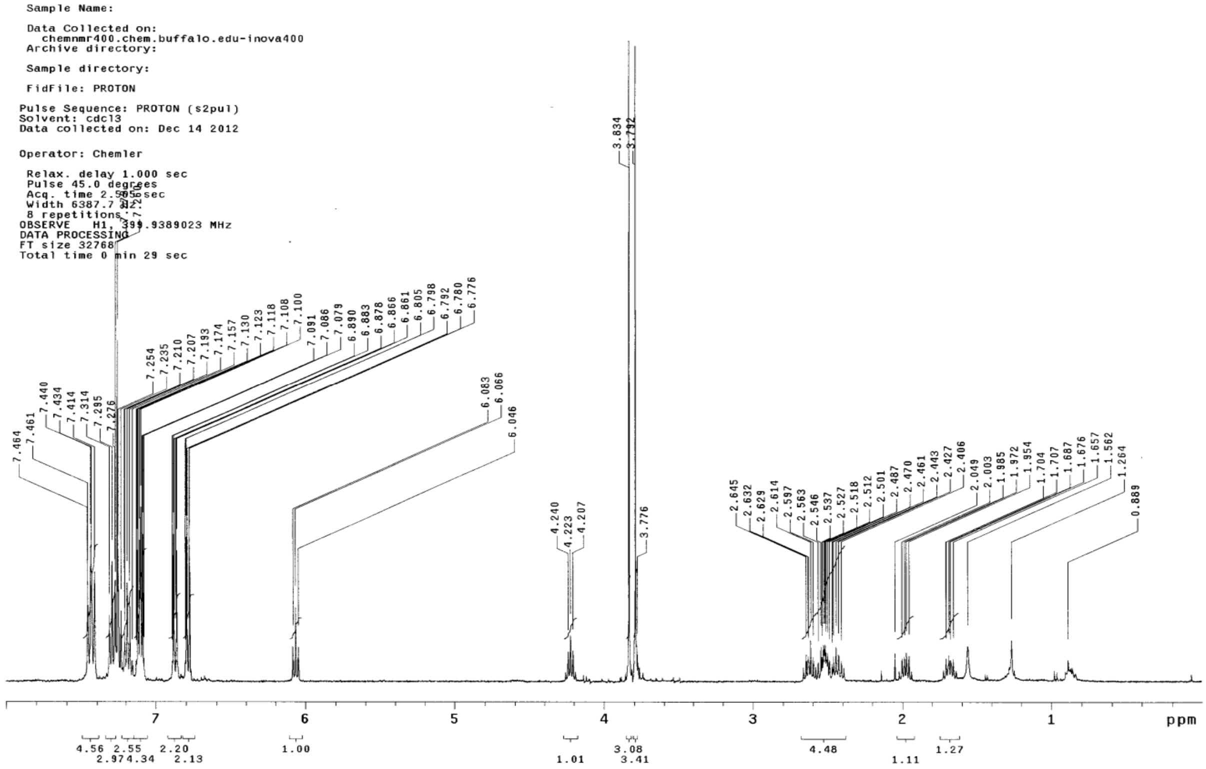


```
 Selective band center: 6.15 (ppm); width: 16.5 (Hz)

 Sample Name:

 Data Collected on:
   nmr500c.chem.buffalo.edu-inova500
 Archive directory:

 Sample directory:

 FidFile: NOESY1D

Pulse Sequence: NOESY1D
Solvent: cdcl3
Data collected on: Nov 22 2013

 Temp. 25.0 C / 298.1 K
Operator: Chemler

 Relax. delay 1.000 sec
 Pulse 90.0 degrees
 Acq. time 2.048 sec
 Width 8000.0 Hz
 14784 repetitions
OBSERVE   H1, 499.8984040 MHz
DATA PROCESSING
FT size 32768
Total time 33 hr, 54 min
```





18b



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

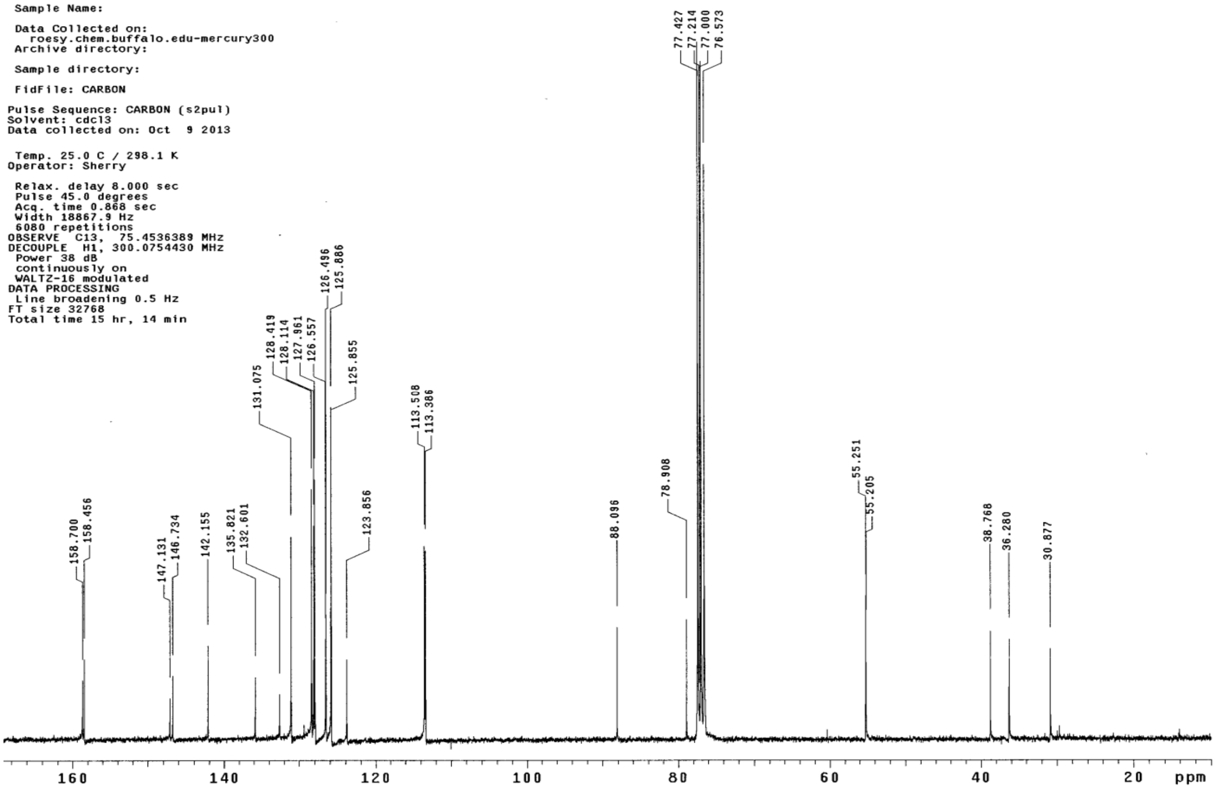
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 14 2012

Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.505 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389023 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

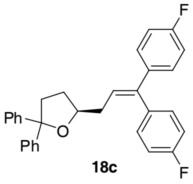
Sample directory:

FidFile: CARBON

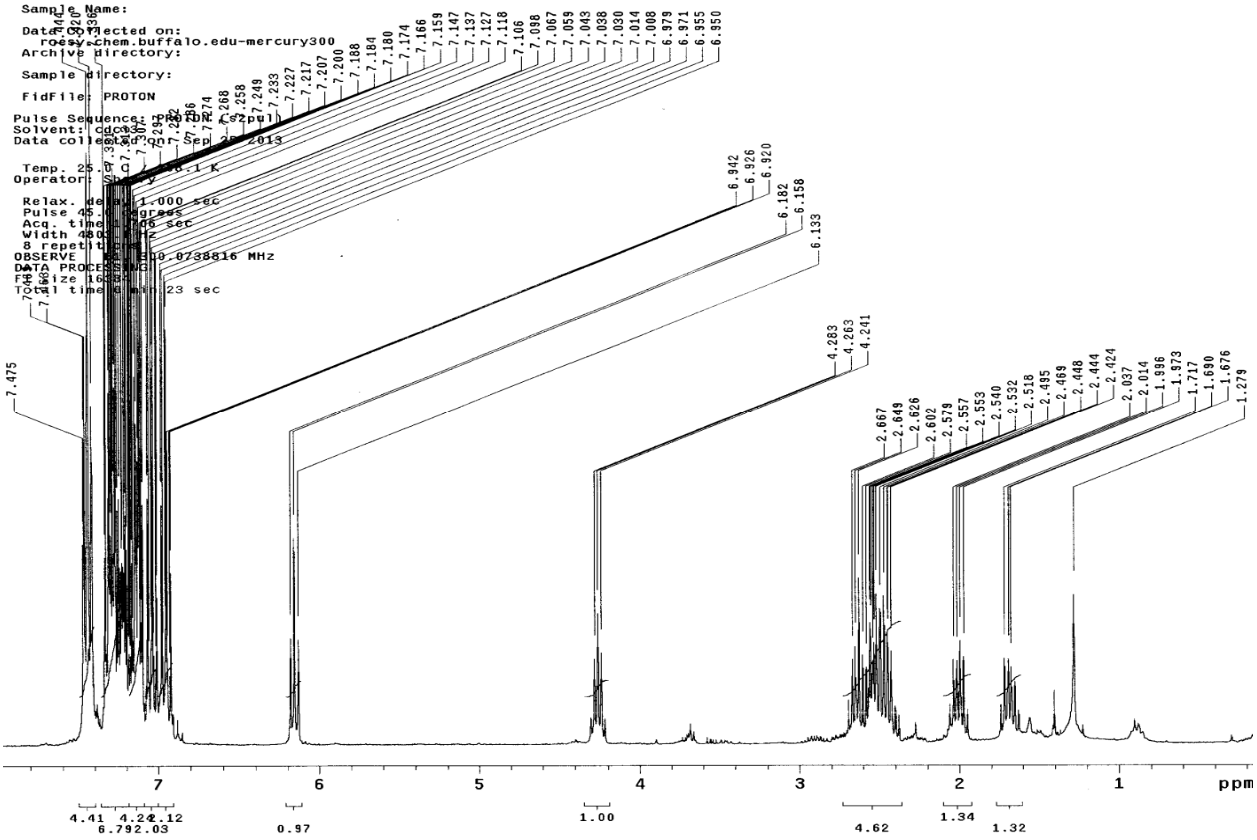
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 9 2013

Temp. 25.0 C / 298.1 K
Operator: Sherry

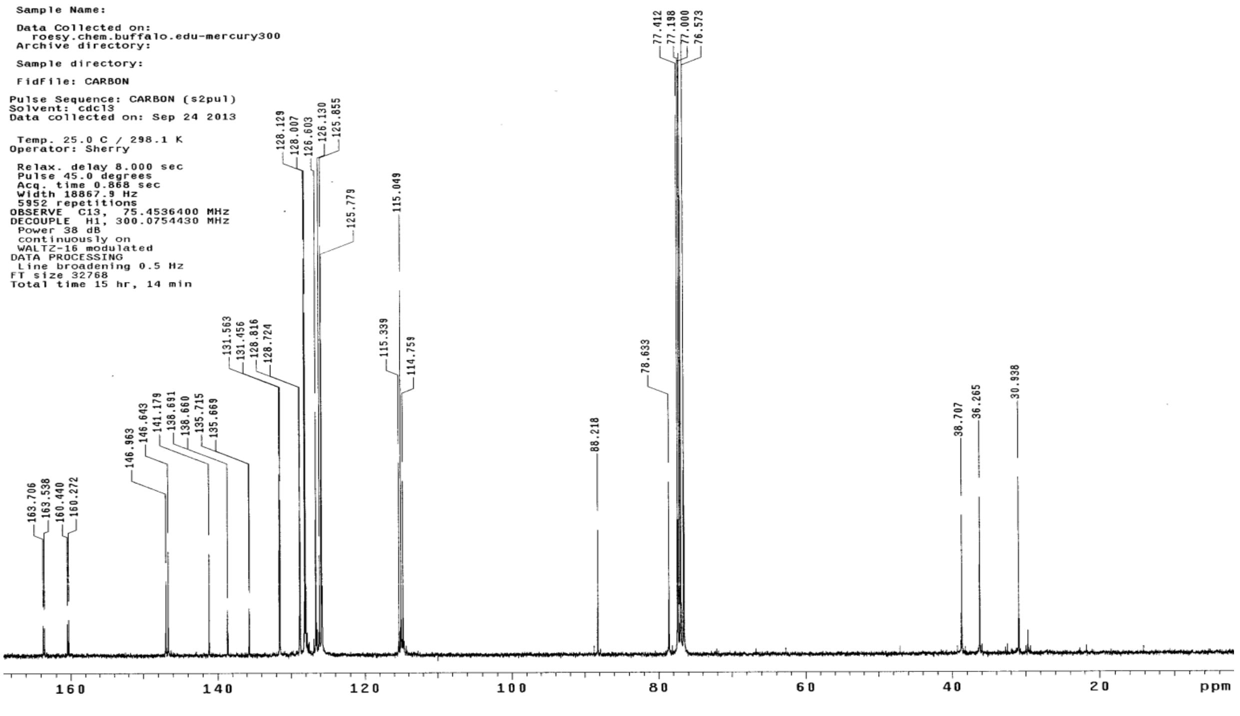
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
6080 repetitions
OBSERVE C13, 75.4536389 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 14 min



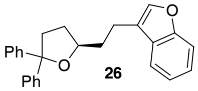
18c



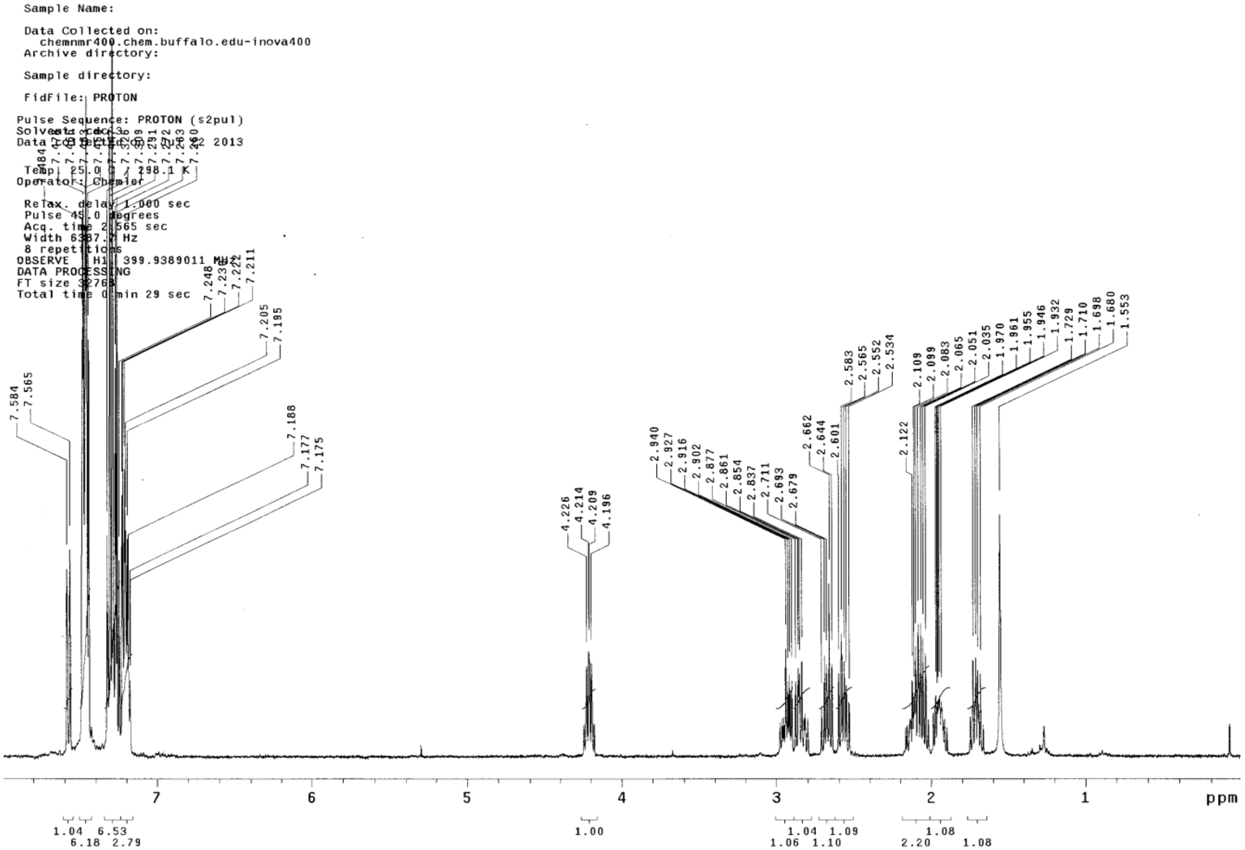
```
 Sample Name:

 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 2[illegible] 2013

 Temp. 25.0 C / 298.1 K
Operator: Sherry

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time [illegible]06 sec
 Width 480[illegible] Hz
 8 repetitions
OBSERVE  [illegible] 300.0738816 MHz
DATA PROCESSING
FT size 163[illegible]
Total time [illegible] min 23 sec
```



```
STANDARD CARBON PARAMETERS

 Sample Name:

 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 24 2013

 Temp. 25.0 C / 298.1 K
Operator: Sherry

 Relax. delay 8.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 5952 repetitions
OBSERVE  C13,  75.4536400 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 14 min
```



26



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

Sample directory:

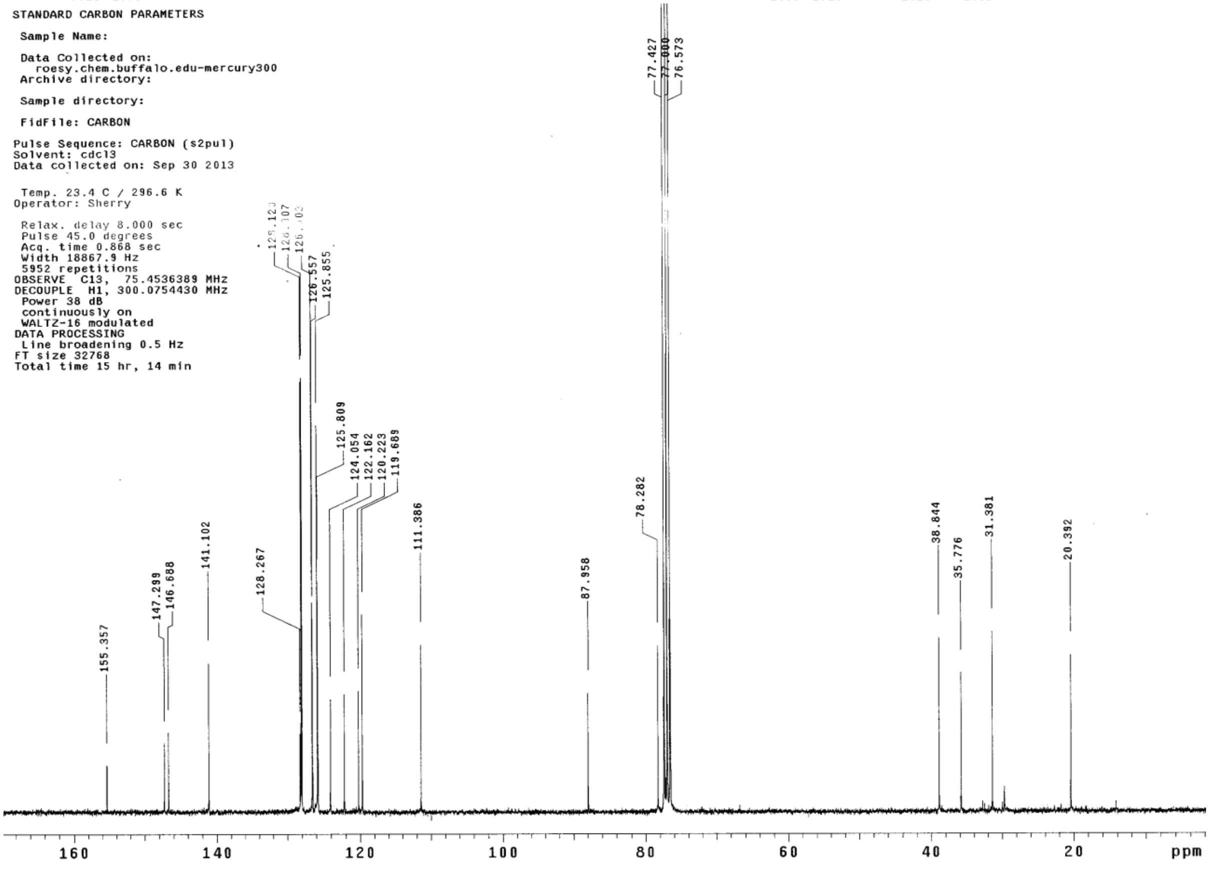
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: [illegible] 22 2013

Temp. 25.0 C / 298.1 K
Operator: Chemier

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389011 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec

STANDARD CARBON PARAMETERS



Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

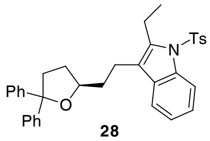
Sample directory:

FidFile: CARBON

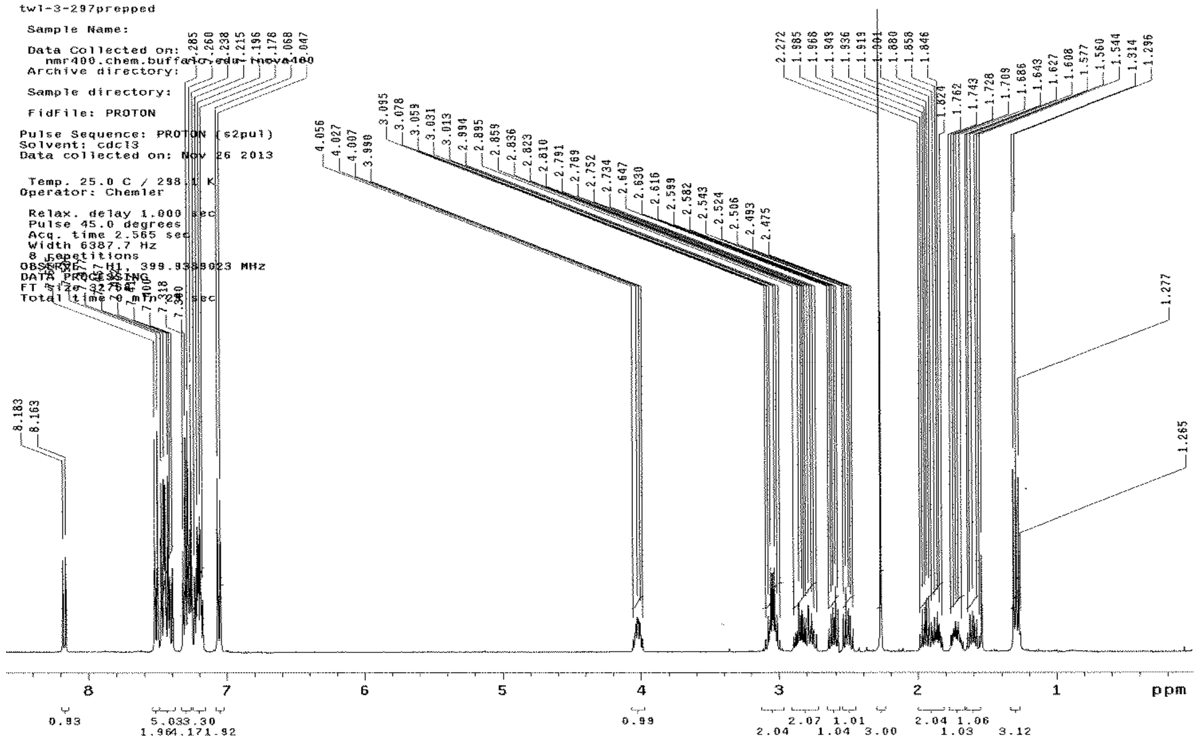
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 30 2013

Temp. 23.4 C / 296.6 K
Operator: Sherry

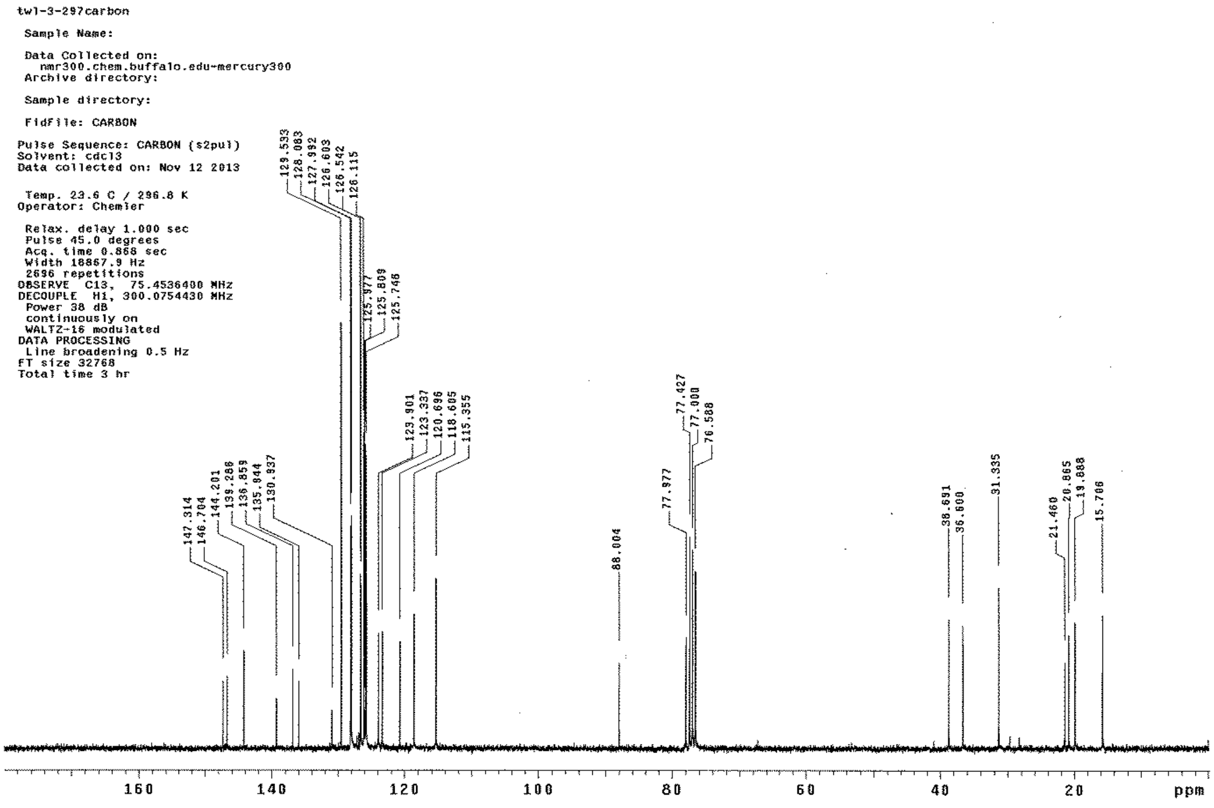
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
5952 repetitions
OBSERVE C13, 75.4536389 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 14 min



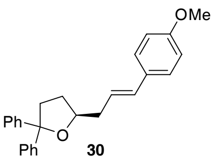
28



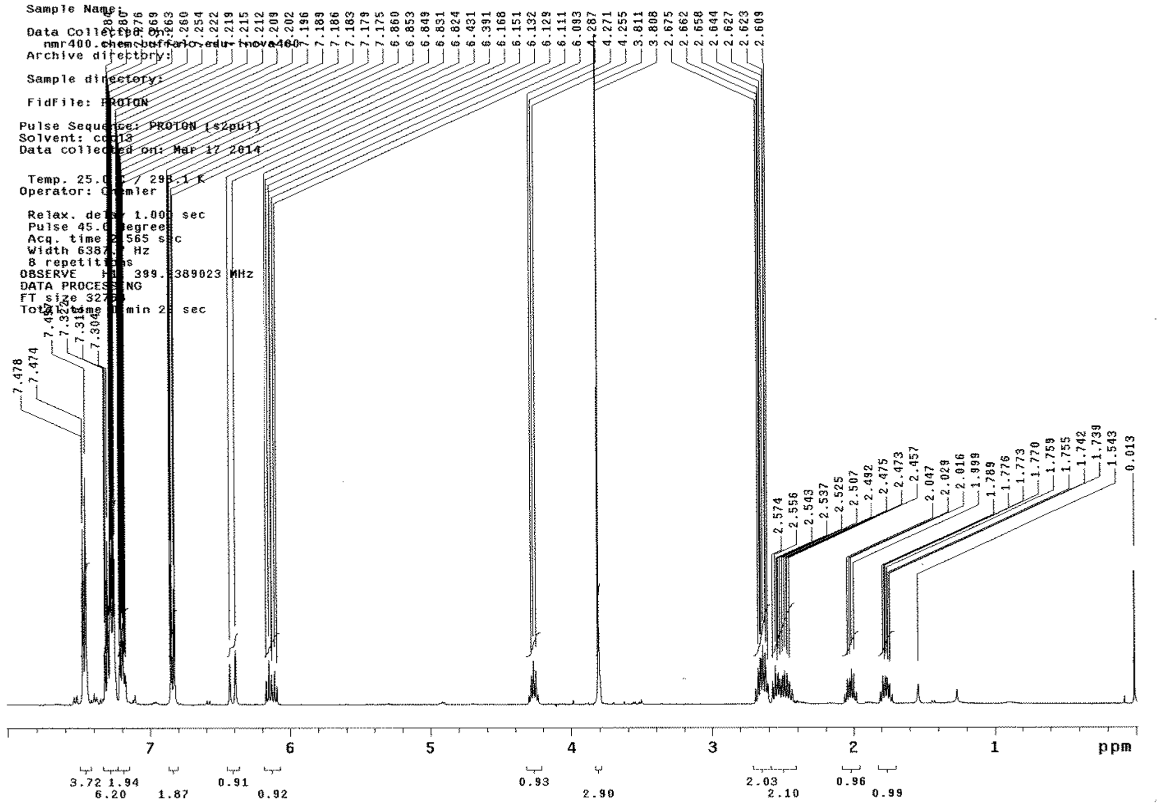
```
twl-3-297prepped
 Sample Name:
 Data Collected on:
  nmr400.chem.buffalo.edu-inova400
 Archive directory:
 Sample directory:
 FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 26 2013
 Temp. 25.0 C / 298.1 K
Operator: Chemler
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.565 sec
 Width 6387.7 Hz
 8 repetitions
OBSERVE  H1, 399.9359023 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
```



```
twl-3-297carbon
 Sample Name:
 Data Collected on:
  nmr300.chem.buffalo.edu-mercury300
 Archive directory:
 Sample directory:
 FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 12 2013
 Temp. 23.6 C / 296.8 K
Operator: Chemler
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 2696 repetitions
OBSERVE  C13, 75.4536400 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 3 hr
```



30



twl-4-072prepped

Sample Name:

Data Collected on:
nmr400.chem.buffalo.edu-inova400
Archive directory:

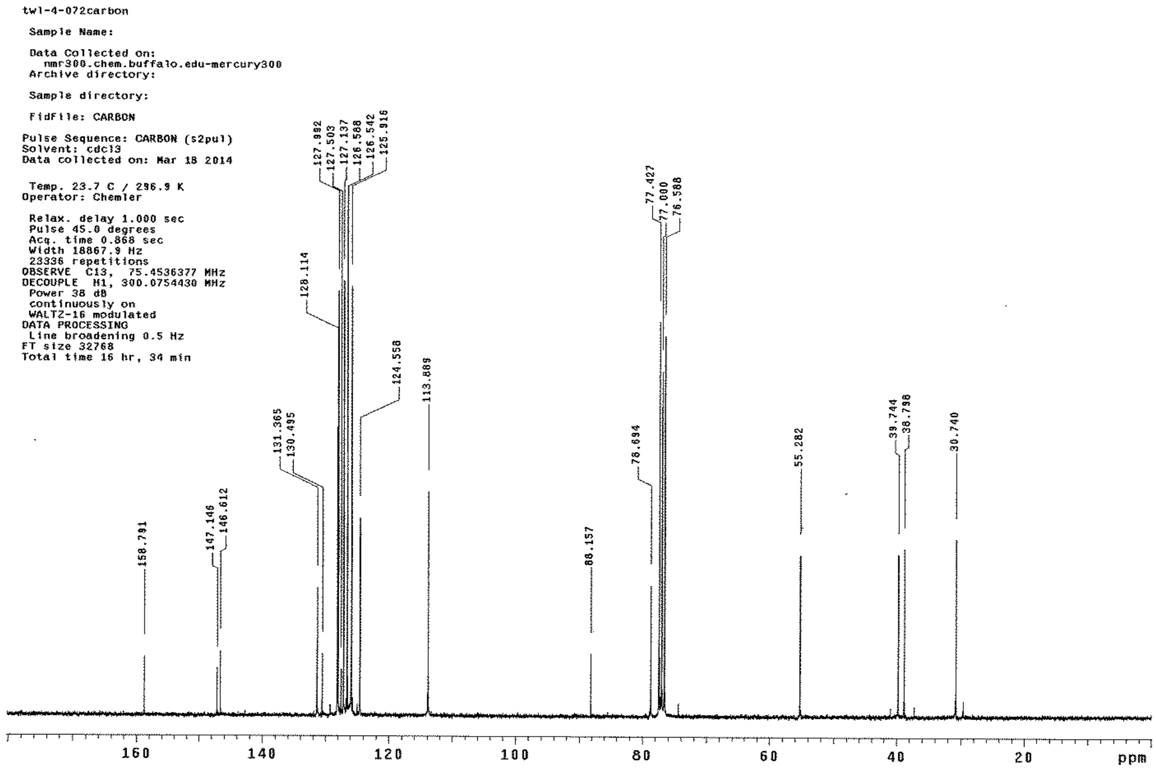
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 17 2014

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.[illegible] Hz
8 repetitions
OBSERVE H1, 399.[illegible]389023 MHz
DATA PROCESSING
FT size 32768
Total time [illegible] min 2[illegible] sec



twl-4-072carbon

Sample Name:

Data Collected on:
nmr300.chem.buffalo.edu-mercury300
Archive directory:

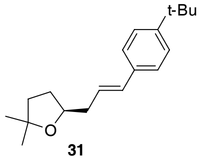
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 18 2014

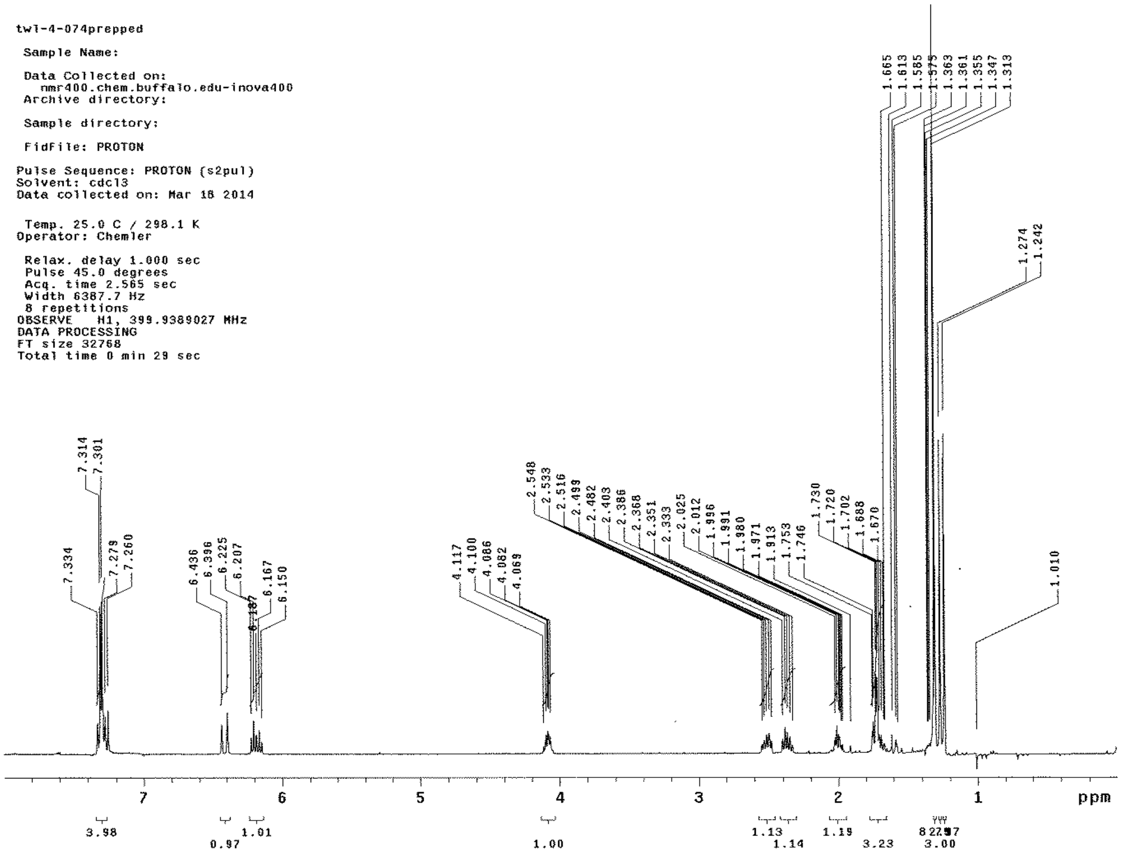
Temp. 23.7 C / 296.9 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
23336 repetitions
OBSERVE C13, 75.4536377 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 16 hr, 34 min

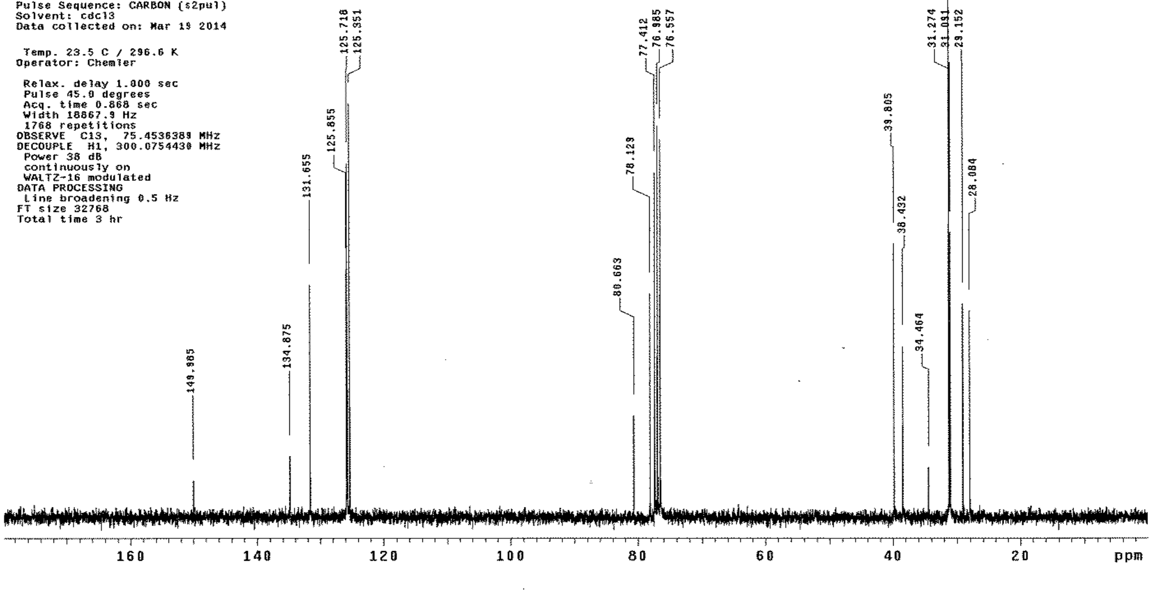


31

```
twl-4-074prepped

 Sample Name:

 Data Collected on:
   nmr400.chem.buffalo.edu-inova400
 Archive directory:

 Sample directory:

 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 18 2014


 Temp. 25.0 C / 298.1 K
Operator: Chemler

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.565 sec
 Width 6387.7 Hz
 8 repetitions
OBSERVE   H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
```



```
twl-4-074carbon

 Sample Name:

 Data Collected on:
   nmr300.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 19 2014


 Temp. 23.5 C / 296.6 K
Operator: Chemler

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 1768 repetitions
OBSERVE  C13,  75.4536389 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 3 hr
```



SUPPORTING INFORMATION

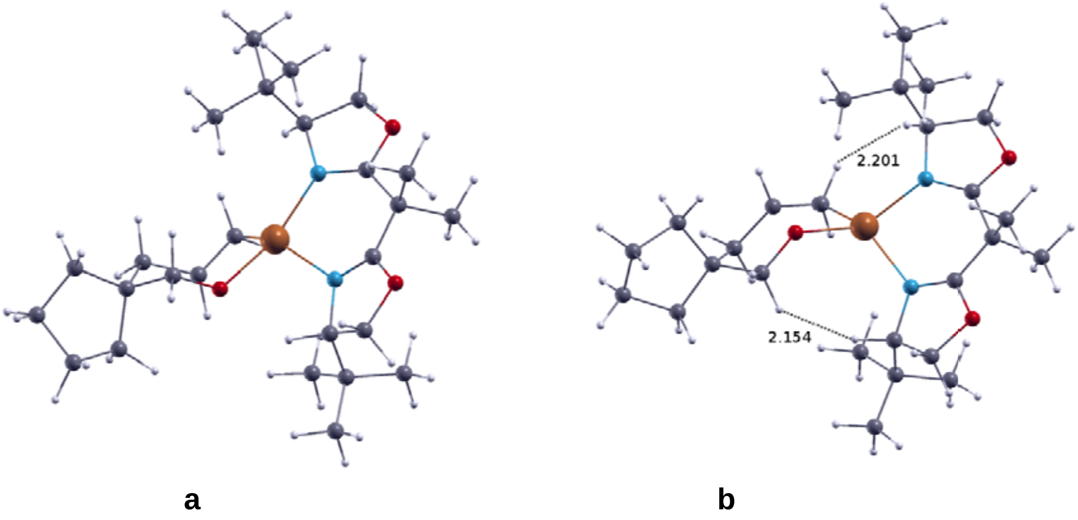
Enantioselective Copper-Catalyzed Intra- and Intermolecular Carboetherification of Unactivated Alkenes

COMPUTATIONAL DETAILS

Unrestricted Density Functional Theory (DFT) calculations (geometry optimizations, vibrational frequencies) were carried out at the hybrid Generalized Gradient Approximation (GGA) level using the Gaussian 09 software.[1] The UB3LYP[2] functional was coupled with a 6-31+G(d) basis set[3] applied on all atoms (*i.e.*, H, C, N, O, Cu). Trifluorotoluene (ε = 9.18) was employed in the experiment; however parameters for this solvent are not available in Gaussian. Because of this the solvation free energy (ΔG_{solv}) was computed using the default Polarizable Continuum Model (PCM) in Gaussian and parameters for dichloromethane (ε = 8.93).[4] We have previously used parameters for 1,2-dichloroethane (ε = 10.13) to model trifluorotoluene[5], but since its dielectric constant is closer to dichloromethane, we employ the latter solvent here instead. Tests revealed that the relative energies of species which may be important in the reaction mechanism did not change much when geometry optimizations and frequency calculations were carried out in solution. For this reason, we chose to calculate the solvation free energy by carrying out single point calculations on geometries which were stationary points in the gas phase. The thermochemical data was obtained for 373.15 K, in accordance with the experimental conditions. Analysis of vibrational frequencies showed that the optimized structures had all real normal modes, whereas the transition states possessed only one imaginary frequency. The Intrinsic Reaction Coordinate (IRC) method[6] was employed to find the initial coordinates of the product species, which result from considering the path of steepest descent for each transition state (TS). The geometries found in this way were then confirmed to be minima of the potential energy surface. The spin density and Natural Bond Order (NBO) analysis using NBO 3.1[7] version for Gaussian were performed at the UB3LYP/6-31+G(d) level of theory for the pro-S (aka major) and pro-R (aka minor) transition states. Plots visualizing the spin density were prepared with the Avogadro (1.1.0)[8] open source molecular editor and visualizer, using Cartesian coordinates of the gas phase species. The so-called tetrahedral twist angle (θ_{TTA}) is used to define the angle between two planes: the first containing two nitrogen atoms of bis(oxazoline) ligand and the Cu atom; the second contains the carbon atom boded to Cu (which belongs to the 6-member heterocyclic ring in a chair conformation), the O atom bonded to Cu (also in the ring), and Cu (see Fig 1). θ_{TTA} was measured using the Mercury 2.4 program.[9]

The basis set superposition error (BSSE) was calculated via the Counterpoise method.[10] The major transition state was used to estimate the BSSE, with its structure being split into two fragments. These were chosen based on the last step of the mechanism, *i.e.*, the C-[Cu] homolysis step of the carboetherification. Frontier Density Surfaces (FDS) were visualized for both transition states using WebMO.[11] These plots are obtained from the magnitudes of the gradient of the electron density maps for the molecular orbitals available for attack by an electrophile, nucleophile, or a radical. Furthermore an electrostatic potential map was created to illustrate the charge distribution for both transition states in vacuum and dichloromethane. This in addition to the electrophilic MO, nucleophilic MO, and radical FDS can be used as an aid to describe the electronic structure of the transition states. Below we use the term "iso values MO and ED" in order to refer to the isosurface value used to plot the molecular orbitals and electron density, respectively. The electron density colored by the electrostatic potential in Figure 7 was calculated using the Amsterdam Density Functional (ADF) program package,[12] the B3LYP functional and a small frozen core ATZP (augmented triple-zeta basis sets with added polarization functions from the ADF basis set library) on the geometries optimized with the Gaussian program code. Herein, we provide the electrostatic potential calculated with ADF because of the powerful visualization capabilities provided by the ADF-GUI (graphical user interface).

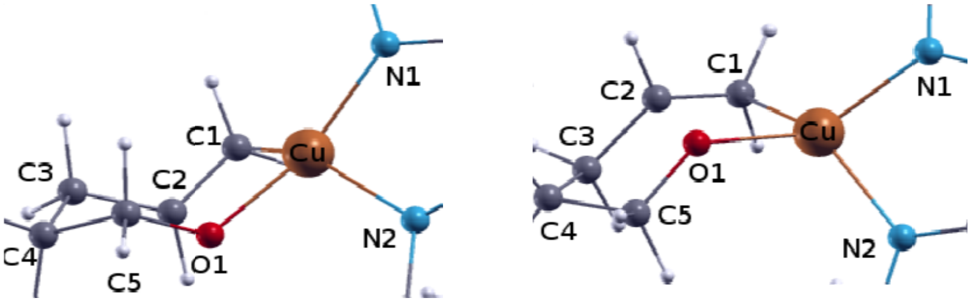
TRANSITION STATE ANALYSIS



$\Delta\Delta G^{\ddagger}$=1.59 kcal/mol and %ee = 79.1

Fig. 1 Structural representation of the major (a) and minor (b) transition states. H – H distances of less than or equal to 2.2 Å are shown, *i.e.*, one between a substrate terminal alkene H and a ligand backbone

H as well as one between a substrate carbon H and a ligand backbone H. The color code for atoms is as follows: H – white, O – red, N – blue, C – gray, and Cu – orange-bronze.



Cu-C1: 2.126 Å
Cu-O1: 1.951 Å
Cu-N1: 2.015 Å
Cu-N2: 2.099 Å
C1-C2: 1.409 Å
C2-C3: 1.501 Å
C3-C4: 1.547 Å
C4-C5: 1.539 Å
C5-O1: 1.418 Å

(a)

Cu-C1: 2.138 Å
Cu-O1: 1.942 Å
Cu-N1: 2.027Å
Cu-N2: 2.116 Å
C1-C2: 1.407 Å
C2-C3: 1.500 Å
C3-C4: 1.546 Å
C4-C5: 1.543 Å
C5-O1: 1.410 Å

(b)

Fig. 2 A zoomed-in view of the first coordination shell around the Cu atom for the major (a) and minor (b) transition states.

Natural Bond Order Analysis

The NBO orbital analysis shows that for the major transition state in vacuum the Cu – C bonding orbital is composed from the atomic orbitals of the first C of the (1-allylcyclopentyl)methanol ligand and the metal center. This NBO is singly occupied (β-spin) and formed due to an overlap between the C p orbital and the Cu d orbital. Both orbitals contribute about 50% to this NBO. The overlap-weighted natural atomic orbital bond order indicates that there is about (30%) overlap between these orbitals. Not surprisingly the addition of the solvent via single-point calculations does not influence this analysis. Also although it appears that there is no bonding orbital between the Cu and the O atom the second most important overlap is between these two atoms. A similar situation is found for the interaction of the metal center with the N atoms. Despite a 17 degree difference between θ_{TTA} calculated for both transition states (see below) the NBO analysis for the major TS is very comparable to the results obtained for the minor TS.

Spin density

The most important contributions computed for the major and minor transition states in vacuum and solvent are presented in Table 1, and illustrated in Fig 2 a – d with the iso value set to 0.0005 au.

Table 1. Spin densities of major and minor transition states.

Major TS (vacuum)			**Minor TS (vacuum)**		
Atom	Description	Percentage	Atom	Description	Percentage
Cu	–	45.1 %	Cu	–	46.0 %
C1	connecting Cu with CYPN through propane	27.2 %	C1	connecting Cu with CYPN through propane	27.7 %
O1	connecting Cu with CYPN through methyl	22.1%	O1	connecting Cu with CYPN through methyl	24.1 %
N1 + N2	connecting Cu with 5-membered heterocyclic rings	3.48 + 2.54 = 6.02 %	N1 + N2	connecting Cu with 5-membered heterocyclic rings	2.58 + 1.44 = 4.02 %
Major TS (dichloromethane)			**Minor TS (dichloromethane)**		
Cu	–	46.1 %	Cu	–	47.3 %
C1	connecting Cu with CYPN through propane	26.3 %	C1	connecting Cu with CYPN through propane	26.9 %
O1	connecting Cu with CYPN through methyl	21.1 %	O1	connecting Cu with CYPN through methyl	22.5 %
N1 + N2	connecting Cu with 5-membered heterocyclic rings	3.72 + 2.63 = 6.35 %	N1 + N2	connecting Cu with 5-membered heterocyclic rings	2.80 + 1.60 = 4.40 %

CYPN – cyclopentyl

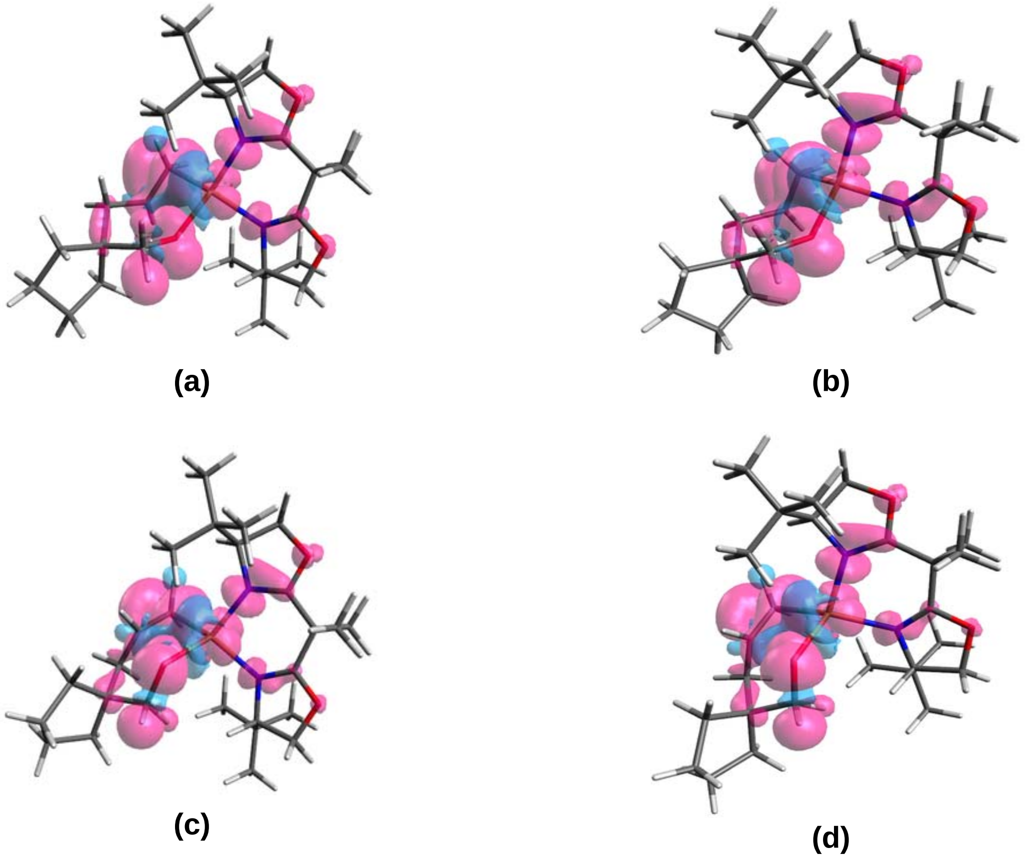

(a) (b) (c) (d)

Fig. 3 Spin Densities for the major transition state in vacuum (a) and in dichloromethene (b), and for minor transition state in vacuum (c) and in dichloromethane (d).

It was found that 93% of the SOMO resides on Cu (46%), O1 (21%) and C1 (26%) for the major TS. In the case of the minor TS 97% of the SOMO also resides on these atoms however its composition is slightly different, *i.e.*, Cu (47%), O1 (23%) and C1 (27%). Hence it is fair to state that these two transition states highly resemble one another. The most striking difference found between the major and minor TS is the relationship between N-Cu and O-Cu bond distances and their corresponding $N_{LP} \rightarrow Cu_{LP^*}$ and $O_{LP} \rightarrow Cu_{LP^*}$ NBO donor-acceptor stabilization energies (Table 2).

Table 2. Selected β-spin NBO donor-acceptor stabilization energies and bond distances for major and minor transition states. Each NBO is labeled as: BD – bond, LP – valence lone pair, and the asterisk indicates a non-Lewis orbital.

	Donor → acceptor	E_{NBO} (kcal/mol)	Corresponding bond distance (Å)
Major TS	$C2\text{-}O1_{(BD)} \rightarrow Cu_{(LP^*)}$	16.21	2.049
	$O1_{(LP)} \rightarrow Cu_{(LP^*)}$	28.46	1.951
	$N1_{(LP)} \rightarrow Cu_{(LP^*)}$	30.65	2.015
	$N2_{(LP)} \rightarrow Cu_{(LP^*)}$	20.32	2.099
Minor TS	$C2\text{-}O1_{(BD)} \rightarrow Cu_{(LP^*)}$	13.34	2.044
	$O1_{(LP)} \rightarrow Cu_{(LP^*)}$	13.67	1.942
	$N1_{(LP)} \rightarrow Cu_{(LP^*)}$	26.28	2.029
	$N2_{(LP)} \rightarrow Cu_{(LP^*)}$	14.27	2.116

The NBO donor - acceptor stabilization energy (E_{NBO}) reveals that C2-O1 contributes about 16 kcal/mol, whereas the same bond in the minor TS contributes almost 3 kcal/mol less towards E_{NBO}. Moreover, N(1,2) → Cu is very comparable for both transition states. However, the O1→Cu gives about 50% more NBO stabilization energy in the major TS as compared to the minor TS.

An analysis of the Wiberg bond indices[13] (WIB) showed that within the major TS about 68% of the C1-Cu and 45% of C2-O1 bond is formed (see Table3). In order to obtain a percentage of the formed bond first the relative variation of the WIB has to be calculated as:[14]

$$\Delta BO_{A-B} = (W_{A-B}^{TS} - W_{A-B}^{R})/(W_{A-B}^{IntP} - W_{A-B}^{R}) \qquad [1]$$

where W is the total WIB for a given bond, A-B, in the NAO basis (i.e., $\sum W_{A-B}(\alpha) + W_{A-B}(\beta)$). The superscripts *R, TS,* and *IntP* refer to reactant, transition state, and intermediate product, respectively.

Since the C1-Cu and C2-O1 bonds are not present in the starting material their WIB indexes are 0. Therefore Eq. (1) may be simplified to:

$$\Delta BO_{A-B} = (W_{A-B}^{TS})/(W_{A-B}^{IntP}) \qquad [2]$$

Hence the percentage evolution (%EV)[15] for a given A-B bond order is obtained as shown below:

$$\%EV = 100\Delta BO_{A-B} \qquad [3]$$

Note that for the O1-Cu bond Eq. (1) has to be used, and the WIB is assumed to be 1. In this case the percentage indicates how much of this bond is broken.

Table 3. $\Delta\mathrm{BO}_{A\text{-}B}$ and total WIB for the intermediate product and the major transition state obtained in vacuum.

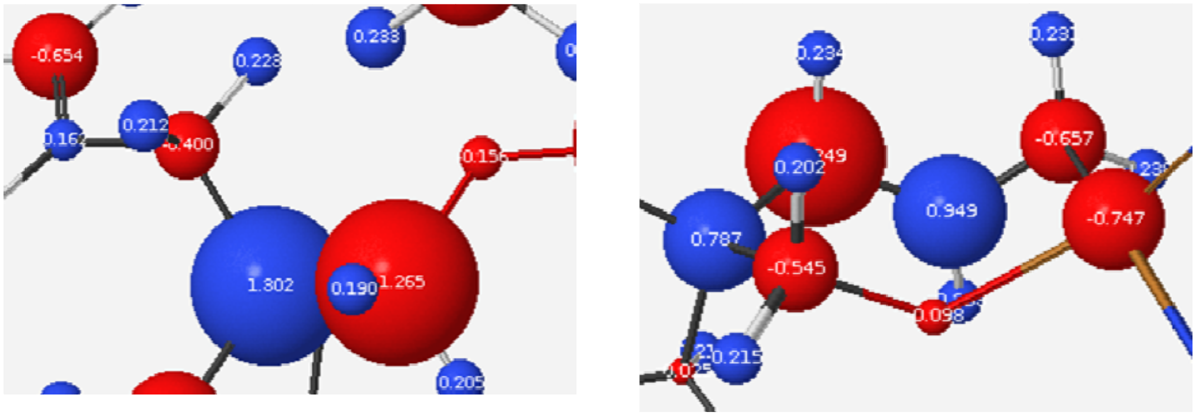
	Major TS	**Intermediate Product**
$\mathrm{WIB}_{C1\text{-}Cu}$	0.1965	0.2897
$\mathrm{WIB}_{C2\text{-}O1}$	0.1775	0.3984
$\mathrm{WIB}_{O1\text{-}Cu}$	0.1844	0.1015
$\Delta\mathrm{BO}_{C1\text{-}Cu}$	0.6783	—
$\Delta\mathrm{BO}_{C2\text{-}O1}$	0.4455	—
$\Delta\mathrm{BO}_{O1\text{-}Cu}$	0.9077	—

The results computed with inclusion of solvent do not have a significant effect on the WIB values. Hence the $\Delta\mathrm{BO}_{A\text{-}B}$ and corresponding percentages are very similar.

Taken all together (*i.e.*, NBO, WBI, E_{NBO}, etc.) it seems that the major TS is preferred, due to a highly stabilizing NBO donor-acceptor energy for O1→Cu, which may be related to the formation of the C2-O1 bond and breaking of the Cu-O1 bond.

Mulliken charges

In order to illustrate the change in the charge distribution that occurs when the carboetherification reaction progresses from the starting material (SM) to the major TS the Mulliken charges were computed in dichloromethane, see Figure 4. It is important to note that results obtained in vacuum are very similar.



(a) (b)

Fig. 4 Mulliken charges for the starting material (a) and the major transition state (b) obtained in dichloreomethane. Red indicates negative charge, while blue positive charge.

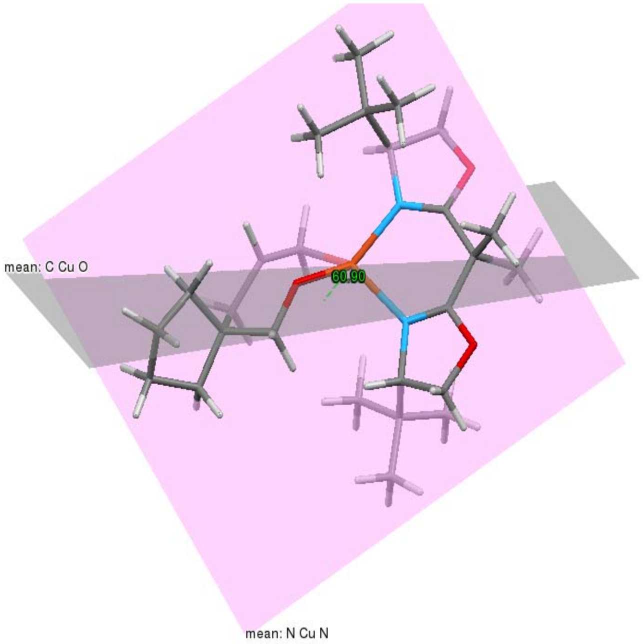
Additionally Table 4 contains values of Mulliken charges for the most important atoms obtained for SM and major TS as well as for the minor TS in both environments.

Table 4. Mulliken charges for select atoms of the major and minor transition states obtained in vacuum and dichloreomethane.

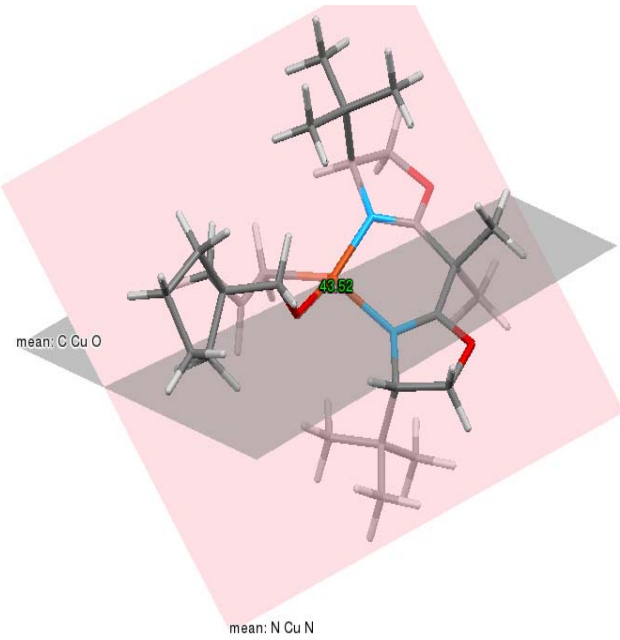
	Vacuum			**Dichloromethane**		
Atom	SM	Major TS	Minor	SM	Major TS	Minor
C1	-0.641	-0.604	-0.782	-0.654	-0.657	-0.829
C2	+0.197	+0.927	+1.193	+0.162	+0.949	+1.222
O1	-0.127	-0.795	-0.032	-0.156	-0.098	-0.079
C5	+ 1.310	-0.551	-0.156	1.302	-0.545	-0.140

Tetrahedral twist angle

For the major TS the value of the tetrahedral twist angle is 43.52 degrees, so about 16.5 degrees less than a perfect tetrahedron whereas the minor TS has θ_{TTA}=60.90 degrees, which is only slightly more than the twist angle for T_d.



(a)



(b)

Fig. 5 Graphic representation of the tetrahedral twist angles: θ_{TTA} = 60.9° and 43.5°, for the minor (a) and major (b) transition states, respectively.

Basis Set Supper Position Error (BSSE)

The BSSE for the 6-31+G(d) basis set (ΔE_{BSSE}=2.7 kcal/mol) obtained at 0K in vacuum is about an order of magnitude smaller than the BSSE computed using the 6-31G(d) basis set. In fact, combining the 6-31G(d) with a different basis set on the metal center reduced the BSSE, but not as significantly. In particular the 6-31G(d) was applied to all atoms except Cu for which two different small-core effective core-potential (ECP) and corresponding basis sets were employed. The BSSE calculated using the following levels of theory B3LYP/6-31G(d)[Cu-LL2DZ] (where LL2DZ stands for Las Alamos LAN2DZ[12]) and B3LYP/6-31G(d)[Cu-SRSC] (where SRSC denotes Stuttgart RSC 1997 EPC[12]) were ΔE_{BSSE}=8.0 kcal/mol and ΔE_{BSSE}=7.0 kcal/mol, respectively. Hence using the 6-31+G(d) basis set not only reduces the BSSE but also is recommended for ionic and/or species with unpaired electron(s) since this basis set includes diffuse basis functions.

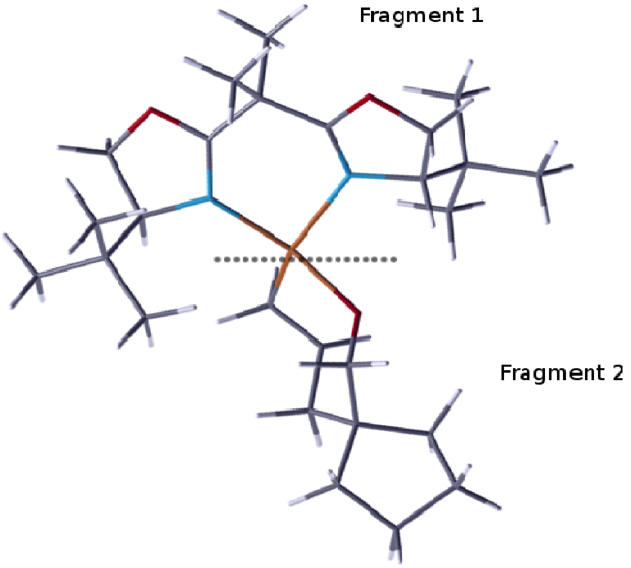
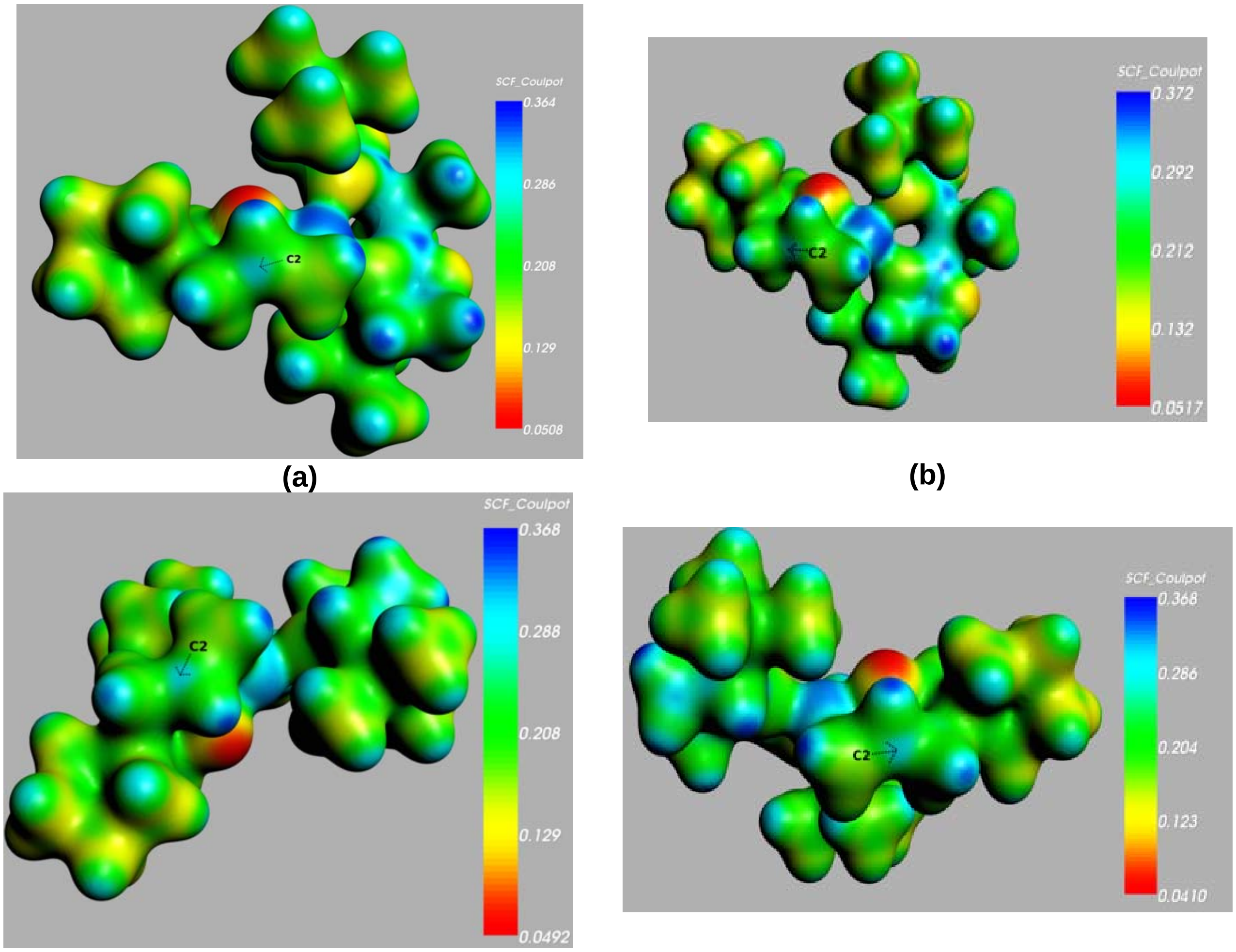


Fig. 6 Graphic representation of fragments used to calculate the BSSE. The gray dotted line indicates where the major TS was “cut” in order to define two counterpoise fragments.

MOLECULAR PROPERTIES

Images of the electrostatic potential, electrophilic, nucleophilic and radical FDS, for the major and minor transition states in vacuum and dichloromethane are shown below.



(a) (b)

(c) (d)

Fig. 7 Electrostatic potentials for the: a) major TS in vacuum, b) major TS in dichloromethane, and the c) minor transition state in vacuum, and d) minor TS in dichloromethane. The isosurface for the electron density was 0.03 au, and the color bar illustrates the value of the electrostatic potential.

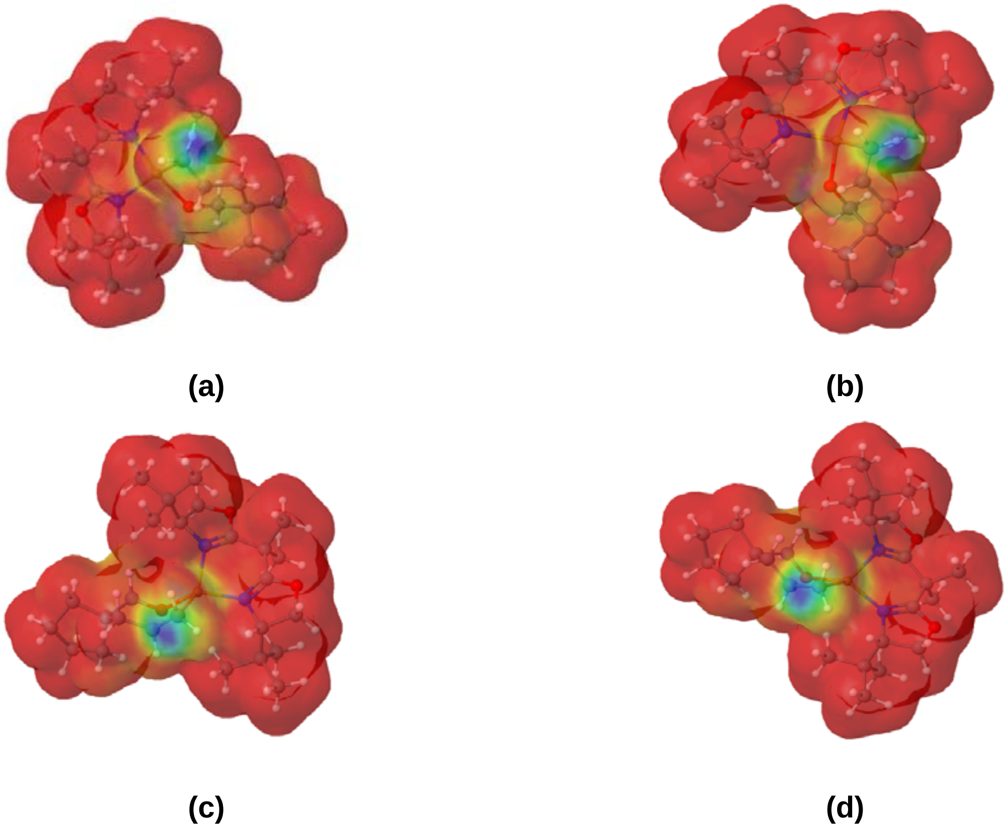
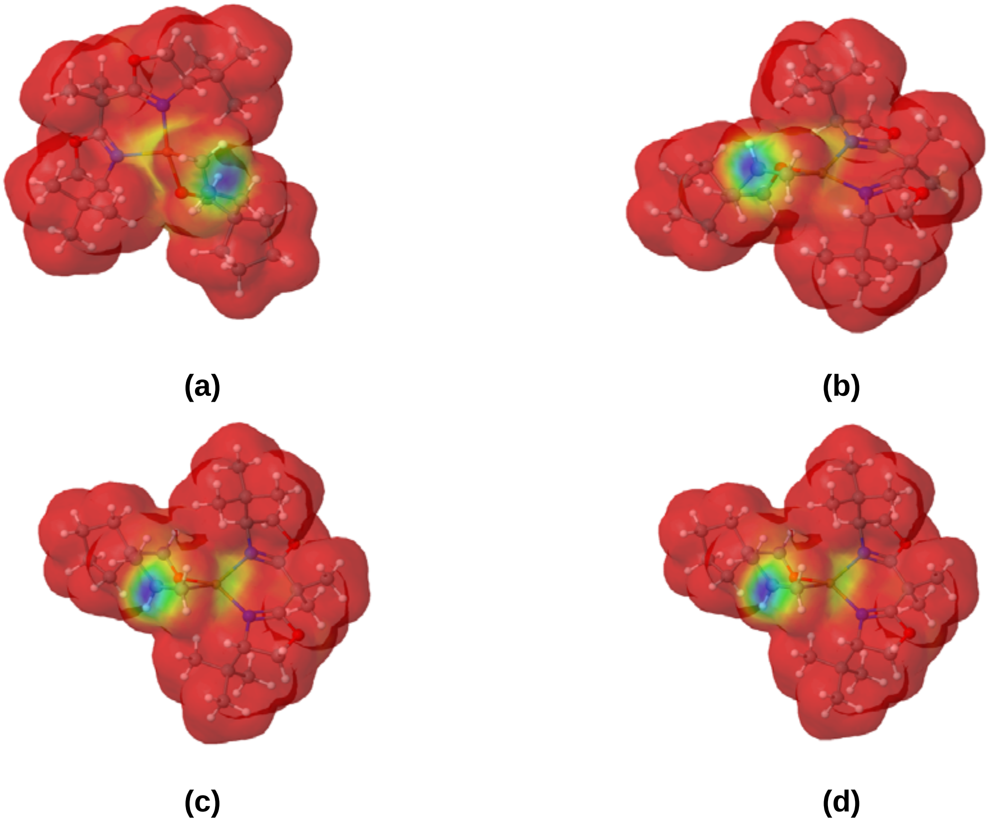


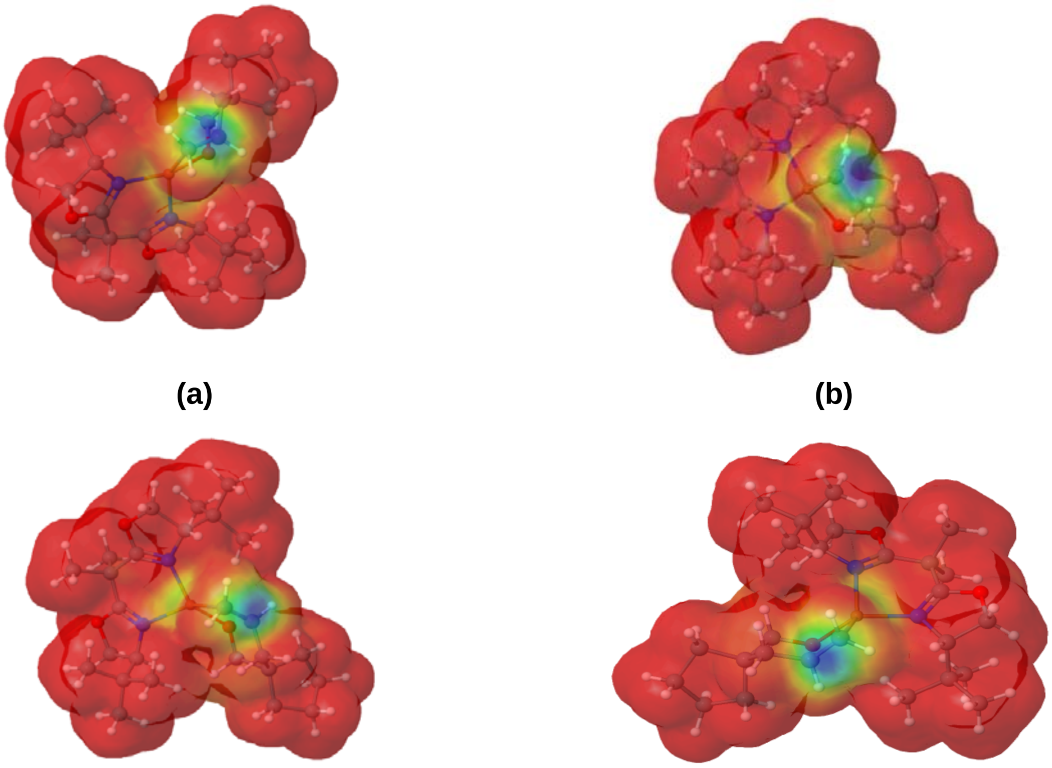
Fig. 8 Electrophilic MO FDS of the: a) major TS in vacuum, b) major TS in dichloromethane, and the c) minor transition state in vacuum, and d) minor TS in dichloromethane. Iso values MO and ED are set to 0.05 and 0.003 au. The blue color indicates the most susceptible regions to be attacked by an electrophile.



(a) (b)

(c) (d)

Fig. 9 Nucleophilic MO FDS of the: a) major TS in vacuum, b) major TS in dichloromethane, and the c) minor transition state in vacuum, and d) minor TS in dichloromethane. Iso values MO and ED are set to 0.05 and 0.003 au. The blue color indicates the most susceptible regions to be attacked by a nucleophile.



(a)

(b)

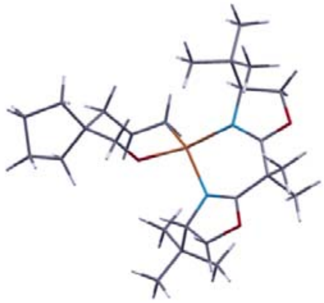
(c)

(d)

Fig. 10 Radical FDS of the: a) major TS in vacuum, b) major TS in dichloromethane, and the c) minor transition state in vacuum, and d) minor TS in dichlormorthane. Iso values MO and ED are set to 0.05 and 0.003 au. The blue color indicates the most susceptible regions to be attacked by a radical.

CARTESIAN COORDINATES

$[C_{26}H_{45}CuN_2O_3]^+$ (Major TS)

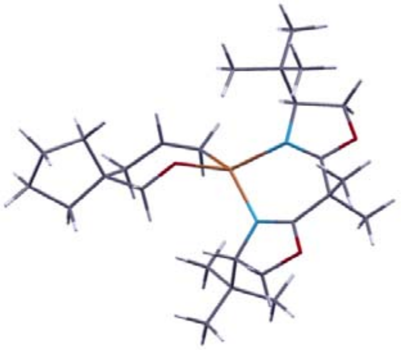


C	0.00000000	0.00000000	0.00000000
C	1.27421500	0.45748700	0.38872600
C	2.31183200	-0.45012700	0.98344100
C	2.93609300	0.16960400	2.25621500
C	1.69784400	0.64694800	3.03623500
O	0.88071500	1.40712900	2.16166100
Cu	-0.94393400	0.93043500	1.66215100
N	-2.75236900	0.04396800	1.73092100
C	-3.87874700	0.64631600	1.93500800
O	-4.98260000	-0.01963900	1.57321300
C	-4.54761700	-1.22658600	0.88155500
C	-3.05867000	-1.34627200	1.26394700
H	-2.45310000	-1.55050100	0.37700600
C	-2.73895200	-2.44671700	2.32972400
C	-1.24555300	-2.40766600	2.70586900
H	-0.60396800	-2.56247900	1.83064800
H	-1.02030100	-3.20645100	3.42140100
H	-0.96653500	-1.45859500	3.17708400
C	-3.03993500	-3.81995800	1.68964000
H	-2.45814000	-3.97146500	0.77164500
H	-4.09997500	-3.94893800	1.44311800
H	-2.77340600	-4.62334500	2.38506800
C	-3.57990100	-2.27156900	3.60934000
H	-3.36684000	-1.31861600	4.10680100
H	-3.34198300	-3.06940400	4.32141500
H	-4.65759100	-2.32424900	3.41725600
H	-4.70853900	-1.06120600	-0.18772200
H	-5.18252700	-2.04156900	1.22497200
C	-4.18278300	1.97567900	2.60247500
C	-2.96038600	2.84326500	2.82087400
N	-1.79506900	2.74388700	2.28730100
C	-1.01395300	3.95763000	2.66496200
C	-1.88322200	4.55898800	3.79211700
O	-3.17309300	3.89023800	3.63298700
H	-2.06519500	5.63016600	3.71664300
H	-1.52076900	4.31900800	4.79586800
C	-0.74463000	4.91167800	1.45601500
C	-2.04932000	5.48040000	0.86459900
H	-2.70615000	4.68392000	0.49640400
H	-1.81941500	6.13098200	0.01337300
H	-2.61349700	6.08385000	1.58522800
C	0.01652600	4.15103300	0.35299700
H	-0.60065600	3.35815900	-0.08491500
H	0.93256600	3.69677200	0.74487100
H	0.29196400	4.83881500	-0.45466000
C	0.14755200	6.06641600	1.96056100
H	-0.34254500	6.66979900	2.73376500
H	0.39250100	6.74227200	1.13357800

H	1.09221100	5.69088600	2.37320000
H	-0.04604600	3.62162500	3.04615000
C	-5.17533800	2.78488900	1.71501900
H	-4.75783000	2.97522700	0.72122700
H	-5.39276000	3.74312000	2.19275300
H	-6.10847600	2.22929800	1.60155100
C	-4.85440000	1.66189800	3.97251000
H	-4.16924100	1.13264800	4.64247400
H	-5.74196000	1.04460600	3.81678700
H	-5.15402000	2.59561400	4.45247500
H	1.15962900	-0.21631200	3.45984200
H	1.98849500	1.29563400	3.87711700
C	3.89678000	1.35905400	1.94227100
C	5.04836500	1.22953500	2.95495400
C	5.24083400	-0.29066600	3.06791100
C	3.79841400	-0.83762100	3.08109800
H	3.73097300	-1.85867200	2.68838400
H	3.42562600	-0.87624600	4.11451600
H	5.81434000	-0.59320600	3.95038600
H	5.78086700	-0.66203300	2.18658200
H	4.75173300	1.64476600	3.92856300
H	5.95225000	1.76110100	2.63870000
H	3.38433400	2.32635100	1.98754300
H	4.29882700	1.25772500	0.92450100
H	3.08738600	-0.62789600	0.22529600
H	1.85878700	-1.42133400	1.21894300
H	1.63134300	1.39535200	-0.02713700
H	-0.20384200	-1.06554000	0.07543900
H	-0.52503300	0.52651700	-0.79788500

$[C_{26}H_{45}CuN_2O_3]^+$ (Minor TS)

C	0.00000000	0.00000000	0.00000000
C	-1.35624900	-0.62968200	0.11620200
C	-2.47425100	-0.25095900	-0.64881400
H	-3.20860100	-1.00945200	-0.90558400
H	-2.36380000	0.56231600	-1.36630000
Cu	-3.37034100	0.76448300	1.00551500
O	-1.72176100	0.27842000	1.91032300
C	-0.50630300	0.94995800	2.15760400
C	0.62241600	0.22213600	1.39721900
C	1.94218800	1.05478200	1.37097500
C	3.06139200	0.11112500	1.85521200
C	2.33425800	-0.83213300	2.82556200
C	1.00650500	-1.11802000	2.10117300
H	1.16875900	-1.90282500	1.34894100
H	0.21568900	-1.47561700	2.77005200
H	2.14700200	-0.31860700	3.77912200
H	2.89689600	-1.74361500	3.05373000
H	3.89792500	0.64932400	2.31317900
H	3.46718100	-0.46418800	1.01215200
H	1.85186000	1.90275500	2.06484900
H	2.14396700	1.48130900	0.38148900



H	-0.54781900	2.00462700	1.84591600
H	-0.32048800	0.93163700	3.24289900
N	-5.31925500	0.20951000	0.97055600
C	-6.32536100	0.97777600	1.22574000
O	-7.53549400	0.50914100	0.89361200
C	-7.32982500	-0.73934000	0.17333600
C	-5.85809400	-1.09745100	0.47258800
H	-5.33516800	-1.35123200	-0.45377300
C	-5.66176700	-2.28455400	1.47270100
C	-4.16176700	-2.52545700	1.72955900
H	-3.62862900	-2.74786600	0.79708000
H	-4.03344000	-3.39023700	2.39042500
H	-3.67675600	-1.67132000	2.21259700
C	-6.24469200	-3.55432800	0.81291500
H	-5.77187700	-3.75711800	-0.15648900
H	-7.32743900	-3.49384500	0.65495300
H	-6.06381700	-4.42354400	1.45465400
C	-6.36620100	-2.02459800	2.81841300
H	-5.94967900	-1.14942200	3.32948300
H	-6.22690500	-2.88497000	3.48219900
H	-7.44691500	-1.87676900	2.70804400
H	-7.52113600	-0.53736900	-0.88446400
H	-8.06397700	-1.45097900	0.54754100
C	-6.39003200	2.31592200	1.93862300
C	-5.05562200	3.02208900	2.07267600
N	-3.91043200	2.73362200	1.56013700
C	-2.99145500	3.87699100	1.84596100
C	-3.77311300	4.66103700	2.92274400
O	-5.13099500	4.14742000	2.80243500
H	-3.82029000	5.73836800	2.76974000
H	-3.43567000	4.45001800	3.94165900
C	-2.62000500	4.69829500	0.56833000
C	-3.85837300	5.34981800	-0.07825000
H	-4.58435500	4.59697500	-0.40581800
H	-3.55845300	5.92026400	-0.96426000
H	-4.36825900	6.04801900	0.59527700
C	-1.94566400	3.77659800	-0.46525300
H	-2.63062300	2.99923400	-0.81972300
H	-1.05435300	3.29154200	-0.04945800
H	-1.62536800	4.35855300	-1.33685700
C	-1.61128000	5.79047400	0.98468900
H	-2.03751500	6.50924400	1.69441100
H	-1.29037200	6.36032600	0.10562400
H	-0.71362300	5.35614900	1.44284200
H	-2.06596000	3.47381900	2.26542000
C	-7.34658100	3.26998900	1.16312900
H	-6.98795700	3.45222000	0.14482800
H	-7.41390200	4.22589400	1.68654500
H	-8.34295800	2.82808200	1.10617100
C	-6.96932400	2.04729200	3.36173200
H	-6.30213700	1.40880500	3.94958500
H	-7.94241400	1.55757100	3.27849700

H	-7.09758100	2.99562900	3.88778300
H	-1.38128300	-1.61064000	0.58369700
H	-0.07214600	0.94637000	-0.55068100
H	0.63409200	-0.67285200	-0.59517900

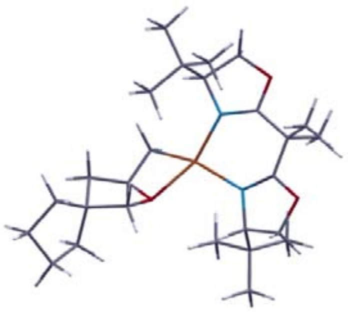
$C_{27}H_{45}CuF_3N_2O_6S$ (tBu-SM, 4-coord)

C	0.00000000	0.00000000	0.00000000
C	0.46916600	-1.47689400	0.11621500
C	1.88510400	-1.49416900	0.75972600
H	1.78512100	-1.14602300	1.80447700
H	2.22804800	-2.54101400	0.80414600
O	2.78704600	-0.68222700	0.06118300
Cu	4.60775900	-0.91992700	0.09264000
N	5.12249900	1.06921200	0.04967100
C	6.17520100	1.53386700	-0.51945400
O	6.14921800	2.83763000	-0.86201100
C	4.78262800	3.29285000	-0.62024700
C	4.17934200	2.19707700	0.28462600
H	3.19473400	1.87880100	-0.06675900
C	4.04989300	2.59150000	1.79313100
C	3.57206700	1.38205200	2.61881700
H	2.64529700	0.96568400	2.21300000
H	3.38407500	1.69416100	3.65353600
H	4.32255300	0.58735300	2.64552700
C	2.98395300	3.70487400	1.88913600
H	2.01843300	3.36717100	1.49228200
H	3.27199700	4.61639500	1.35016100
H	2.83151900	3.98546300	2.93783600
C	5.38392900	3.09611200	2.37844500
H	6.15338300	2.31769200	2.34993400
H	5.24259200	3.37114400	3.43020000
H	5.76634200	3.98476400	1.86090400
H	4.29173700	3.36322200	-1.59620700
H	4.84757800	4.28287900	-0.17065900
C	7.50188500	0.83903000	-0.77127500
C	7.35847600	-0.65877900	-0.96432100
N	6.31228800	-1.40036300	-0.86877000
C	6.69020300	-2.79784600	-1.23364400
C	8.23137800	-2.71152800	-1.25961600
O	8.50651200	-1.27527000	-1.28048100
H	8.70621400	-3.13785600	-2.14318100
H	8.68378900	-3.11380600	-0.35051800
C	6.00667500	-3.28979800	-2.54617300
C	6.39207900	-2.42374700	-3.76058100
H	6.07922000	-1.38189000	-3.62612400
H	5.89623000	-2.80087400	-4.66286500
H	7.47156500	-2.43403100	-3.95571400
C	4.47629400	-3.26400300	-2.36482200
H	4.09366800	-2.24493800	-2.24295300
H	4.16734700	-3.84800700	-1.48967100
H	3.98382400	-3.69469600	-3.24508300

C	6.44500300	-4.75079900	-2.78594100
H	7.52438600	-4.84248400	-2.95750800
H	5.94037500	-5.15409700	-3.67176100
H	6.18384500	-5.38953200	-1.93324200
H	6.37167900	-3.45027900	-0.41819000
C	8.19007300	1.43226800	-2.02856500
H	7.57141300	1.30338400	-2.92321000
H	9.14793300	0.93465600	-2.19262200
H	8.36545000	2.50014300	-1.88447800
C	8.39560300	1.08098200	0.48577200
H	7.96382200	0.60634400	1.37128900
H	8.49509700	2.15667100	0.66020100
H	9.38989200	0.66233500	0.30815800
O	4.83386800	-2.40223500	1.51573500
S	6.07797300	-2.37427000	2.38615100
C	5.40195500	-3.03988800	4.00778700
F	6.38747100	-3.11618000	4.91626800
F	4.88072600	-4.26540100	3.83914200
F	4.44284700	-2.23074400	4.48800700
O	6.53564300	-1.00525800	2.69207900
O	7.10301900	-3.34724300	1.97033700
C	0.48268000	-2.20316600	-1.26347700
C	-0.05681300	-3.62043100	-0.99666100
C	-1.12919300	-3.38638700	0.08056800
C	-0.47475100	-2.34824300	1.01372500
H	-1.20996200	-1.74486100	1.55903600
H	0.12236500	-2.86806500	1.77593100
H	-1.42663100	-4.30151800	0.60679000
H	-2.03204900	-2.96791900	-0.38537600
H	0.73731500	-4.26616800	-0.59557300
H	-0.44726200	-4.10671300	-1.89908500
H	1.48345600	-2.19494200	-1.70842400
H	-0.18696100	-1.68785300	-1.96353200
H	0.70414300	0.53679900	-0.64597900
H	0.08212500	0.45312700	1.00159700
C	-1.40300300	0.20703600	-0.50358200
C	-1.73433500	0.89406400	-1.60292300
H	-2.77022500	1.02191900	-1.90878000
H	-0.97840900	1.35644400	-2.23636500
H	-2.20564400	-0.23211900	0.09172200

$[C_{26}H_{45}CuN_2O_3]^+$ (tBu-Pdt-1) Major

C	0.00000000	0.00000000	0.00000000
C	1.31579900	0.53961900	0.50373300
C	2.39277300	-0.45132600	0.94661500
C	3.06164500	0.22049000	2.16688600
C	1.81914500	0.80290100	2.85572500
H	1.28820700	0.03634800	3.43609500
H	2.03399400	1.65781400	3.50545400
O	0.96566600	1.27494500	1.77936700
C	4.07496100	1.33976300	1.76681500
C	5.19429300	1.26697600	2.81900000



C	5.33002700	-0.24299500	3.06854200
C	3.86894700	-0.73716800	3.10172800
H	3.76994500	-1.78514900	2.79780500
H	3.48070700	-0.66947300	4.12754200
H	5.87706700	-0.48599300	3.98545800
H	5.87043800	-0.70840300	2.23356300
H	4.88596200	1.77455000	3.74421500
H	6.12358100	1.73961700	2.48376100
H	3.60398300	2.32775100	1.70085100
H	4.49434500	1.11879500	0.77612500
H	3.09853600	-0.66764300	0.13824300
H	1.92702600	-1.39876900	1.24733800
H	1.72874800	1.31219300	-0.15244100
Cu	-1.10315400	0.93014400	1.40814300
N	-2.80168000	-0.16143000	1.64371800
C	-3.96516200	0.36128000	1.84218600
O	-5.02392900	-0.39192700	1.51244600
C	-4.50421800	-1.58330900	0.84921600
C	-3.00662500	-1.58101700	1.22044500
H	-2.39065300	-1.76697600	0.33671700
C	-2.59964900	-2.61535600	2.32218000
C	-1.11089700	-2.44671900	2.68216500
H	-0.46666000	-2.59044700	1.80747500
H	-0.82150100	-3.19285500	3.43087500
H	-0.90396400	-1.45667400	3.10350400
C	-2.80125600	-4.03015900	1.73682500
H	-2.21502900	-4.17249600	0.82030700
H	-3.85054600	-4.24514900	1.50392500
H	-2.47247800	-4.78523300	2.45936500
C	-3.44325600	-2.45510300	3.60209400
H	-3.30235800	-1.46853800	4.05814400
H	-3.13837900	-3.20192300	4.34348300
H	-4.51491200	-2.59987100	3.42355600
H	-4.68488600	-1.46018500	-0.22259300
H	-5.07363900	-2.43337600	1.22150300
C	-4.35057500	1.69279300	2.45986900
C	-3.17252100	2.60574500	2.74292600
N	-1.97791200	2.57139500	2.26249800
C	-1.27878300	3.82458200	2.68037300
C	-2.22076500	4.35704500	3.78278200
O	-3.46656200	3.63080700	3.55544200
H	-2.45168300	5.41949800	3.72246400
H	-1.88691500	4.11136200	4.79507300
C	-1.01978300	4.81545900	1.49813100
C	-2.33294800	5.32124600	0.86912300
H	-2.92442800	4.49913500	0.45033100
H	-2.10825000	6.00952500	0.04683900
H	-2.96161600	5.86807400	1.58143400
C	-0.17338100	4.13029900	0.40831200
H	-0.71730900	3.30820600	-0.07181000
H	0.75964200	3.72860700	0.81690000
H	0.08067500	4.85380400	-0.37463100

C	-0.21678200	6.00910500	2.05977000
H	-0.76877300	6.56747900	2.82515500
H	0.01829700	6.71501400	1.25557700
H	0.73332900	5.68105200	2.49974500
H	-0.30744800	3.54507700	3.09873500
C	-5.30146500	2.45167900	1.48498500
H	-4.81908600	2.63553700	0.51974000
H	-5.58757200	3.41105800	1.92299900
H	-6.20350500	1.85913700	1.31778600
C	-5.10597100	1.38971600	3.78738500
H	-4.45490800	0.88969600	4.51180000
H	-5.96388200	0.74546100	3.58431500
H	-5.46152400	2.32269500	4.22854200
H	-0.09479500	-1.08563100	0.05736800
H	-0.31475000	0.37387000	-0.97858400

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