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Cooperative Lewis Acid—Onium Salt Catalysis as Tool for the Desymmetrization of *meso*-Epoxides

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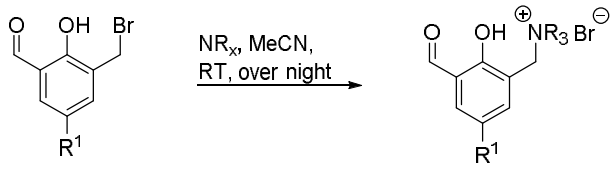
Experimental

All reactions were performed in oven-dried glassware (stored at 150 °C in an oven and afterwards heated to 630 °C for 5 minutes under vacuum using a heat-gun) and unless otherwise indicated under a positive pressure of nitrogen (0.2 bar). Liquids were added *via* syringe, solids were added neat against a flow of nitrogen. Solvents were removed by the use of a rotary-evaporator with a bath temperature of 40 °C and pressures between 10 and 700 mbar. Non-volatile compounds were dried *in vacuo* at 0.1 mbar. For work-up procedures and flash chromatography, distilled technical grade solvents were used. Dichloromethane (DCM), diethyl ether, tetrahydrofuran (THF), toluene and acetonitrile used for reactions and purification of the catalysts/ligands were dried under nitrogen using a solvent purification system. *n*-Hexane and *i*-propanol for HPLC were purchased in HPLC-quality and used without further purification. Acetic acid was distilled over P_2O_5 and LiBr was dried in a Kugelrohr-oven (0.1 mbar, 250 °C, overnight). The epoxides used in catalysis were prepared according to literature procedures (see below). All other laboratory chemicals were purchased from commercial suppliers and were used without purification unless otherwise indicated. Yields refer to purified compounds and are calculated in mol% of the starting material used. Expect as otherwise indicated, reactions were magnetically stirred and monitored by NMR-spectroscopy or thin layer-chromatography (TLC) using silica gel plates (silica gel 60 F254). Visualization occurred by fluorescence quenching under UV light and / or by staining with ceric ammonium molybdate. Flash-chromatography was performed on silica-gel 60 (40-63 μm particle size), using a moderate pressure applied *via* hand-pump or nitrogen-flow. In reactions and during catalysis where low temperatures are necessary a cryostatic temperature regulator was used. NMR spectra were recorded at room temperature on spectrometers operating at 700, 500, 400, 300 or 250 MHz (^{1}H), 125 or 75 MHz (^{13}C) and 376 MHz (^{19}F). Chemical shifts δ are referred in terms of ppm, coupling constants *J* are given in Hz. The following classify the multiplicity: *s* = singulet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet or unresolved, *br* = broad signal. Infrared spectra were recorded by the IR-service of the Universität Stuttgart on a *FT-IR* spectrometer with ATR unit and the signals are given by wavenumbers (cm^{-1}). Optical rotation was measured on a polarimeter operating at the sodium D line with a 100 mm path cell length. Melting points were measured using a melting point apparatus in open glass capillaries and are uncorrected. Mass spectra were obtained from the MS-service of the Universität Stuttgart and the methods used are stated below. The *er* values were determined by HPLC using a chiral stationary phase (methods are shown below).

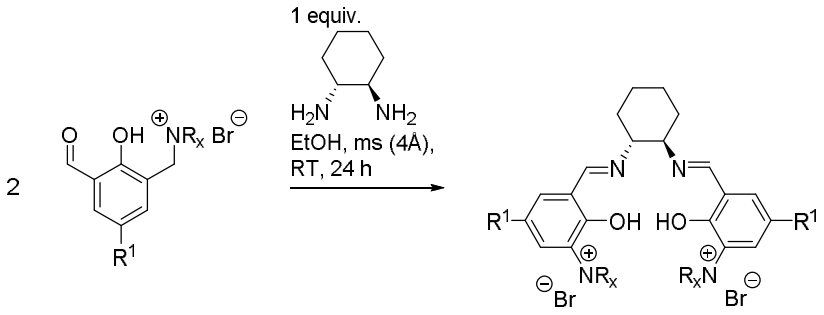
General Procedures

General Procedure for the Synthesis of Ammonium and Pyridinium Salts (GP1)



The aldehyde (1.0 equiv., 1.0 mmol) was dissolved in acetonitrile (1 mL of acetonitrile / 1.0 mmol of aldehyde) and the amine/pyridine-derivative (1.1 equiv.) was added. The mixture was stirred for 15 h, after which diethyl ether was added to cause precipitation (10 mL / 1.0 mmol aldehyde). The supernatant solvent was decanted and the precipitate was washed with diethyl ether three times and dried *in vacuo*.

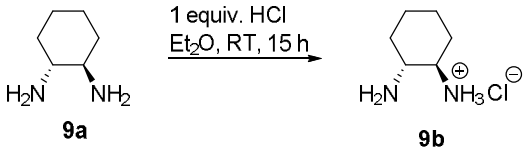
General Procedure for the Formation of the C_2-Symmetric Ligands (GP2)



This synthesis followed a published protocol.[1] Molecular sieves (4Å 100 mg/mmol) and the corresponding onium salt (2.0 equiv.) were added to a solution of (1*R*,2*R*)-(−)-diaminocyclohexane (1.0 equiv.) in ethanol at ambient temperature and the mixture was stirred for 24 hours. After filtration, ethanol was removed *in vacuo*. Subsequent repetitive azeotropic removal of residual ethanol with DCM gave the corresponding pure ligand.

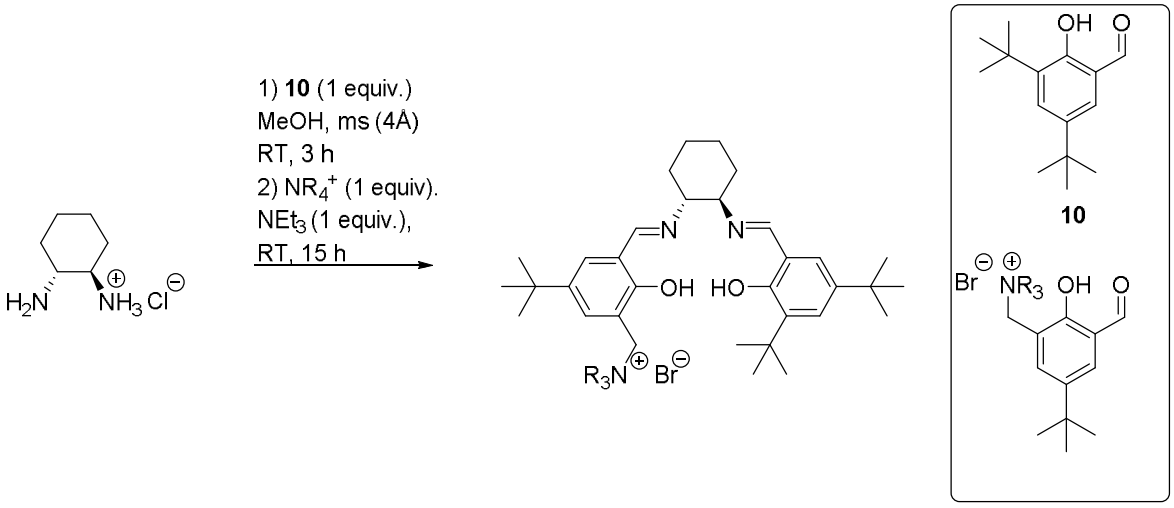
General Procedure for the Synthesis of the C_1-Symmetric Ligands (GP3)

Mono-Protonation of the Diaminocyclohexane[2]



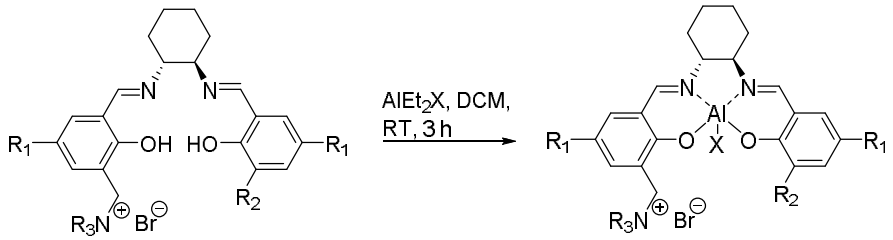
To a rapidly stirred solution of (1*R*,2*R*)-(−)-diaminocyclohexane (1.0 equiv.) in diethyl ether, HCl (1.0 equiv., 4 M in dioxane) was slowly added and the resulting mixture was stirred for 15 h at room temperature. The excessive solvent was removed *in vacuo* and the residue was washed three times with diethyl ether (10 mL). The obtained white powder was used without further purification.

Diimine Formation



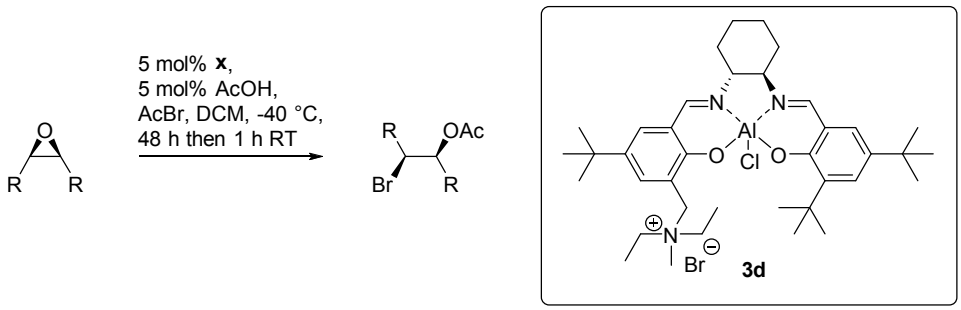
Similar to a literature protocol[2] the protonated diamine **9b** (1.0 equiv.) was dissolved in MeOH and molecular sieves (4Å) and aldehyde **10** (1.0 equiv. in MeOH) was added. The resulting mixture was stirred for three hours. A solution of the second aldehyde (1.0 equiv.) in MeOH was slowly given to the reaction and after 5 minutes NEt_3 (1.0 equiv.) was added dropwise. The yellow solution was stirred for additional 15 h. Afterwards the solvent was removed *in vacuo* and the residue was dissolved in toluene. After filtration over celite, repetitive azeotropic removal of residual toluene with DCM gave a yellow solid, which was washed with *n*-pentane till the washing phase showed no more yellow color. After removing the last residues of solvent under reduced pressure the ligands were obtained as bright yellow powders.

General Procedure for the *In-Situ-F*ormation of Catalysts (GP4)



A Schlenk-flask was charged with the respective ligand (0.01 mmol), which was dissolved in DCM (0.5 mL). After five minutes of stirring, a solution of the corresponding aluminum source (1.0 equiv., 0.01 mmol, 1.0 M in heptane) was added dropwise and the resulting solution was stirred for an additional three hours. The *in situ* formed catalysts were then directly used without further purification.

General Procedure for the Desymmetrization of Epoxides with Acetyl Bromide (GP5)



To a solution of the *in situ* generated catalyst **3d** (0.05 equiv. 0.01 mmol) in DCM (0.50 mL) the corresponding epoxide (1.00 equiv, 0.20 mmol), acetic acid (0.05 equiv., 0.01 mmol, 0.6 µL in 20.0 µL DCM as a stock solution) and acetyl bromide (10.00 equiv, 2.00 mmol, 245.9 mg, 149.0 µL) were successively added at –40 °C and the mixture was stirred for 48 h at this temperature. Afterwards the flask was removed from the cooling bath and the reaction mixture

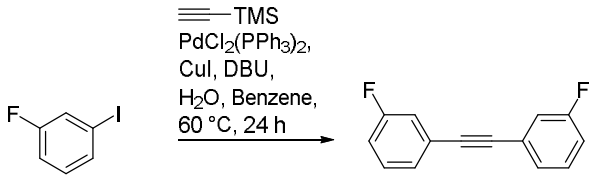
stirred for an additional hour at ambient temperature. The reaction was quenched by the addition of Hünig's base (0.2 mL) and the resulting mixture was diluted with DCM (2 mL) and filtered over a short pad of silica gel. The solvent was removed and the residue was purified by column chromatography (petrol ether/ethyl acetate 30:1) to obtain the desired products.

Substrate Synthesis

cis-Stilbene Oxide (1a)

Substrate **x** which was used throughout the reported investigation as the standard substrate was prepared according to literature known procedures starting from diphenyl acetylene.[3,4]

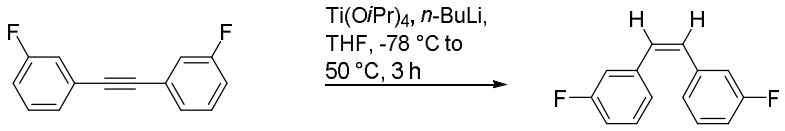
cis-2,3-Bis(3-fluorophenyl)oxirane (1b)



1b1

Intermediate **1b1** was synthesized using a literature known protocol.-[5] A dry Schlenk flask was charged with CuI (0.20 equiv., 1.0 mmol, 190.4 mg) and $PdCl_2(PPh_3)_2$ (0.12 equiv., 0.6 mmol, 442.2 mg) under a nitrogen atmosphere. Dry benzene (50 mmol) was added followed by 1-fluoro-3-iodobenzene (2.0 equiv., 10.0 mmol, 2.22 g, 1.16 mL), DBU (12.0 equiv., 60 mmol, 9.13 g, 8.96 mL) and trimethylsilylacetylene (1.0 equiv. 5.0 mmol, 491.1 mg, 0.71 mL). Water (0.8 equiv., 4.0 mmol, 72.0 mg, 72 µL) was added and the flask was wrapped in aluminum foil to protect it from light radiation. The reaction mixture was stirred at 60 °C for 24 h. Afterwards the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (25 mL) and stirred for ten minutes at ambient temperature. The phases were separated and the aqueous one extracted with diethyl ether three times (50 mL). The combined organic phases were washed with brine (100 mL), dried over Mg_2SO_4 and the solvent was removed under reduced pressure. Column chromatography (petrol ether) of the residue yielded the desired product **1b1** (0.98 g, 92%) as a white solid.

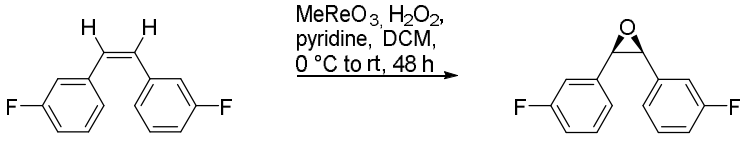
$C_{14}H_8F_2$, **MW**: 214.21 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)**: δ = 7.36-7.28 (*m*, 4H, Ar*H*), 7.25-7.22 (*m*, 1H, Ar*H*), 7.22-7.20 (*m*, 1H, Ar*H*), 7.10-7.03 (*m*, 2H, Ar*H*).



1b2

Synthesis of the (*Z*)-olefin **1b2** followed a known procedure procedure.[6] The alkyne **1b1** (1 equiv., 3.0 mmol, 0.64 g) was put into a dry Schlenk flask and dissolved in THF (20.0 mL). The mixture was cooled to −78 °C and $Ti(O^iPr)_4$ (2 equiv., 6.0 mmol, 1.71 g, 1.78 mL) followed by *n*-BuLi (6 equiv., 12.0 mmol, 0.67 g, 7.5 mL 15% in hexane) were added. The dark red solution was stirred at this temperature for 15 minutes and then heated to 50 °C. After 3 hours at this temperature the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (10.0 mL) and stirred for an additional 5 minutes. Afterwards the phases were separated and the aqueous one was extracted three times with diethyl ether (25 mL). The combined organic phases were washed with brine (50.0 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (petrol ether) of the residue yielded the desired olefin (0.52 g, 80%) a clear oil.

$C_{14}H_{10}F_2$, **MW**: 216.23 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)**: δ = 7.24-7.16 (*m*, 2H, Ar*H*), 7.02-6.96 (*m*, 2H, Ar*H*), 6.94-6.85 (*m*, 4H, Ar*H*), 6.59 (*s*, 2H, C*H*=C*H*).



1b

For the epoxidation of the olefin **1b2** a literature know procedure[7] was employed. A flask was charged with olefin **1b2** (1.00 equiv., 1.22 mmol), which was solved in DCM (2.5 mL) and cooled down to 0 °C. After stirring for 5 minutes at 0 °C $MeReO_3$ (2.5 mol%, 0.03 mmol, 7.6 mg), pyridine (0.15 equiv., 0.18 mmol, 14.5 mg, 14.8 µL) and H_2O_2 (1.50 equiv., 1.83 mmol, 207.5 mg,

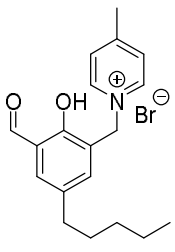
0.21 mL 30% in water) were added consecutively. The mixture was allowed to warm up to ambient temperature and rapidly stirred for 48 h. To quench the reaction MnO_2 (2.0 mg) was added and the mixture was diluted with DCM. After separation of the phases the aqueous one was extracted three times with DCM (2.00 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (petrol ether/ ethyl acetate 30:1) to yield the desired epoxide **1b** as a white solid (0.16 g, 57%).

$C_{14}H_{10}F_2O$, **MW**: 232.07 g/mol. **M.p.**: 65 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)**: δ = 7.20-7.14 (*m*, 2H, *o*-C*H*CF), 7.00-6.95 (*m*, 2H, *o*-C*H*), 6.91-6.82 (*m*, 4H, *p*-C*H*, *m*-C*H*), 4.35 (*s*, 2H, C*H*O). **^{13}C NMR (376 MHz, $CDCl_3$, 25 °C)**: δ = 163.9-161.4 (*d*, *J* = 246), 136.8 (*d*, *J* = 7.4), 129.7 (*d*, *J* = 8.2), 122.6 (*d*, *J* = 2.9), 114.9 (*d*, *J* = 21.0), 114.0 (*d*, *J* = 23), 59.3 (*d*, *J* = 2.2). **IR ($CHCl_3$)**: $\tilde{\nu}$ = 3071, 2984, 1589, 1446, 1221, 786, 690. **HRMS (EI) *m/z*:** calculated: 232.0700 ; measured: 232.0696.

Ligand Synthesis

Synthesis of the Onium Salts

1-(3-Formyl-2-hydroxy-5-pentylbenzyl)-4-methylpyridinium Bromide (11)



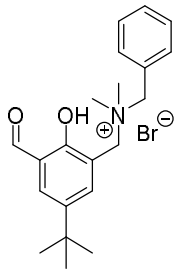
11

Pyridinium salt **11** was prepared according to **GP1**. The aldehyde (1.0 mmol, 0.30 g) was treated with 4-methylpyridine (1.1 mmol, 0.11 g, 0.11 mL). The desired compound **11** (0.37 g, 92%) was isolated as a light brown powder. [8]

$C_{19}H_{24}BrNO_2$, **MW**: 377.1 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)**: δ = 11.41 (*s*, 1H, Ar-O*H*), 9.86 (*s*, 1H, Ar-C*H*O), 9.40 (*d*, *J* = 6.7, 2H, *o*-Py-*H*), 8.39 (*d*, *J* = 2.0, 1H, Ar-*H*), 7.72 (*d*, *J* = 6.4, 2H, *m*-Py-*H*), 7.45 (*d*, *J* = 2.1, 1H, Ar-*H*), 6.24 (*s*, 2H, Ar-C*H*2-Py), 2.68–2.63 (*m*, 5H, Ar-CH_2-C_4H_9 and Py-CH_3), 1.68–1.58 (*m*, 2H, (CH_2)pentyl), 1.38–1.25 (*m*, 4H, (CH_2)pentyl), 0.89 (*t*, *J* = 6.8, 3H, CH_3).

The rest of the analytical data were in compliance to the literature known values.[8]

N-Benzyl-1-(5-(*tert*-butyl)-3-formyl-2-hydroxyphenyl)-*N*,*N*-dimethylmethylammonium Bromide (12)



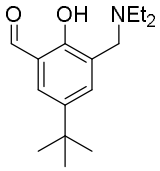
12

Ammonium salt **12** was prepared according to **GP1**. The aldehyde (3.7 mmol, 1.00 g) was treated with *N,N*-Dimethylbenzylamine (4.1 mmol, 0.55 g, 0.61 mL). The desired compound **12** (1.42 g, 95%) was isolated as a light brown powder.

$C_{21}H_{28}BrNO_2$, **MW**: 405.13 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)**: δ = 11.60 (*s*, 1H, Ar-O*H*), 9.95 (*s*, 1H, Ar-C*H*O), 8.39 (*d*, *J* = 1.8, 1H, *m*-Ar*H*), 7.74 (*d*, *J* = 1.8, 2H, Ar*H*), 7.65 (*d*, *J* = 7.0, 2H, Ar*H*), 7.56-7.48 (*m*, 3H, Ar*H*), 5.14 (*s*, 2H, C*H*2), 4.99 (*s*, 2H, CH_2), 3.15 (*s*, 6H, N(CH_3)$_2$), 1.39 (*s*, 9H, C(CH_3)$_3$).

The rest of the analytical data were in compliance to the literature known values.[9]

5-(*tert*-Butyl)-3-((diethylamino)methyl)-2-hydroxybenzaldehyde (13)[10]

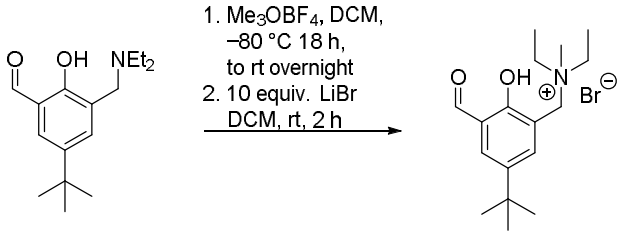


13

The synthesis of **13** followed a literature known protocol.[10] Ethanol (15.0 mL) and 5-(*tert*-butyl)-2-hydroxybenzaldehyde (1.0 equiv., 15.1 mmol, 2.69 g) were mixed and a solution of formaldehyde in water (35%, 1.5 equiv., 22.7 mmol, 1.84 g, 1.84 mL) followed by diethylamine (1.5 equiv., 22.7 mmol, 1.66 g, 2.37 mL) were added. The mixture was heated to reflux for 24 h. The solvent was removed *in vacuo* and the residue diluted by DCM (20 mL). After drying over $MgSO_4$ and removal of the DCM the crude product was purified by column chromatography (petrol ether/ethyl acetate 10:1, followed by the addition of 5% NEt_3 to the eluent). The desired pure aldehyde (2.19 g, 55%) was obtained as yellow oil.

$C_{16}H_{25}NO_2$, **MW**: 263.19 g/mol. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)**: δ = 12.21 (*bs*, 1H, Ar-O*H*), 10.42 (*s*, 1H, C*H*O), 7.65 (*d*, *J* = 2.5,1H, *m*-Ar*H*), 7.25 (*d*, *J* = 2.5, 1H, *m*-Ar*H*), 3.81 (*s*, 2H, CH_2), 2.65 (*q*, *J* = 7.2, 4H, NCH_2), 1.28 (*s*, 9H, C(CH_3)$_3$), 1.13 (*t*, *J* = 7.2, 6H, NCH$_2$CH_3). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C)**: δ = 191.2, 160.5, 141.6, 132.2, 123.8, 123.5, 122.6, 56.6, 46.6, 34.2, 31.5, 11.3. **IR ($CHCl_3$)**: $\tilde{\nu}$ = 2965, 2870, 1677, 1476, 1215, 962, 742, 611. **HRMS (ESI) *m/z*:** calculated: 264.1958; measured: 264.1940.

N-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-*N*-diethyl-*N*-methylammonium Bromide (14)

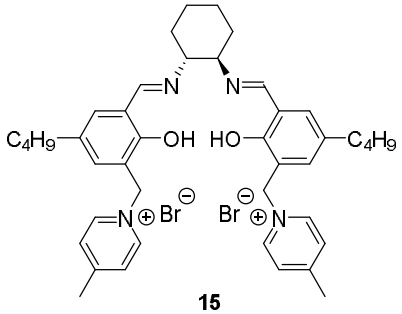


13 **14**

In a dried Schlenk-flask trimethyloxoniumtetrafluoroborate (0.97 equiv., 1.94 mmol, 0.29 g) was dissolved in dry DCM (25.0 mL) and cooled down –80 °C. At this temperature a solution of aldehyde **x** (1.00 equiv., 2.00 mmol, 0.53 g) in DCM (5.0 mL) was added dropwise to the reaction and the resulting solution stirred for 8 hours. The mixture was warmed up to ambient temperature overnight and quenched by the addition of MeOH (1.0 mL). The resulting solution was stirred for 30 minutes at ambient temperature, and freed of the solvent *in vacuo*. The crude product was diluted by DCM (5.0 mL) and carefully layered with *n*-hexanes (5.0 mL). After 12 h at -20 °C fridge crystals were obtained. These were collected by filtration and dissolved in DCM (25.0 mL) and lithium bromide (10 equiv., 19.4 mmol, 1.68 g) was added. Afterwards the mixture was stirred for 2 h at ambient temperature. The precipitated salt was removed by filtration and the remaining solvent under reduced pressure to yield the pure bromide salt **14** (0.61 g, 85%) as a white powder.

$C_{17}H_{28}BrNO_2$, **MW**: 357.13 g/mol. **M.p.:** 173.1-178.5 °C **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)**: δ = 11.63 (*s*, 1H, Ar-O*H*), 9.93 (*s*, 1H, C*H*O), 8.50 (*d*, *J* = 2.4, *m*-Ar*H*), 7.70 (*d*, *J* = 2.4, *m*-Ar*H*), 4.99 (*s*, 2H, NCH_2Ar), 3.75-3.45 (*m*, *J* = 7.1, 4H, N(CH_2CH$_3$)$_2$), 3.19 (*s*, 3H, NCH_3), 1.49-1.42 (*t*, *J* = 7.3, 6H, N(CH$_2$CH_3)$_2$), 1.38 (*s*, 9H, C(CH_3)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C)**: δ = 196.9, 158.7, 144.4, 141.6, 133.0, 120.4, 115.6, 58.5, 55.9, 31.4, 8.5. **IR ($CHCl_3$)**: $\tilde{\nu}$ = 3421, 2959, 1649, 1476, 1061, 723. **HRMS (ESI) *m/z*:** calculated: 278.2115; measured: 278.2110.

(*R,R*)-(−)-*N,N'*-Bis(3-pentyl-5-(pyridinium-1-ylmethyl)salicylidene)-1,2-cyclohexanediamine dibromide (15)[8]



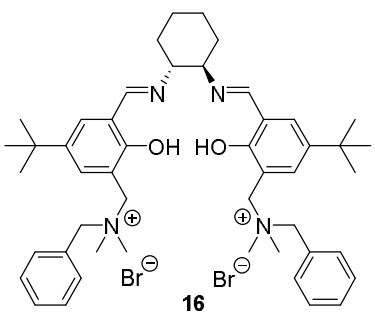
15

Ligand **15** was prepared according to **GP2** with aldehyde **11** (2.0 equiv., 0.9 mmol, 328.0 mg) and (1*R*,2*R*)-1,2-diaminocyclohexane (1.0 equiv., 0.45 mmol, 51.4 mg as a dark yellow powder (329.3 mg, 91%).[8]

$C_{42}H_{54}Br_2N_4O_2$, **MW**: 804.26 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)**: δ = 14.13 (*b*, 2H, Ar-O*H*), 9.44 (*d*, *J* = 9.7, 4H, *o*-Py-*H*), 8.41 (*tt*, *J* = 7.9, 1.4, 2H, *p*-Py-*H*), 8.32 (*s*, 2H, Ar-C*H*=N-Cy), 7.94 (*t*, *J* = 7.2, 4H, *m*-Py-*H*), 7.81 (*d*, *J* = 2.2, 2H, Ar-*H*), 7.13 (*d*, *J* = 1.9, 2H, Ar-*H*), 6.09 (*m*, 4H, Ar-CH_2-Py), 3.41 (*m*, 2H, Cy-*H*N=CHR)), 2.51 (*m*, 4H, Ar-CH_2-C_4H_9), 1.98–1.85 (*m*, 4H, Cy-H_2), 1.72–1.43 (*m*, 10H, Cy-H_2 und (CH_2)pentyl), 1.33–1.25 (*m*, 8H, (CH_2)pentyl), 0.86 (*t*, *J* = 6.7, 6H, (CH_3)pentyl).

The rest of the analytical data were in compliance to the literature known values. [8]

(*R,R*)-(+)-*N,N'*-Bis(3-*tert*-butyl-5-((*N*-benzyl-*N,N*-dimethylammonium)-1-ylmethyl)-salicylidene)-1,2-cyclohexadiamine dibromide (16)[9]



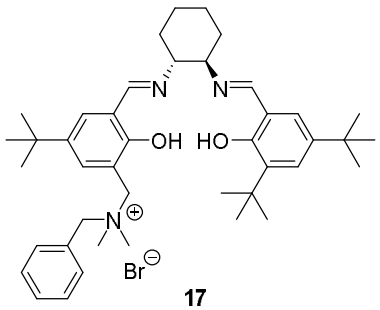
16

Ligand **16** was prepared according to **GP2** with aldehyde **12** (2.0 equiv., 0.84 mmol, 341.6 mg) and (1*R*,2*R*)-1,2-diaminocyclohexane (1.0 equiv., 0.42 mmol, 48.0 mg) as a yellow powder (345.6 mg, 92%).

$C_{42}H_{54}Br_2N_4O_2$, **MW**: 888.36 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)**: δ = 14.04 (*bs*, 2H, Ar-O*H*), 8.37 (*s*, 2H, Ar-C*H*=N), 7.87 (*s*, 2H, Ar-*H*), 7.66 (*m*, 4H, Ar-*H*), 7.48-7.37 (*m*, 6H, Ar-*H*), 7.31 (*bs*, 2H, Ar-*H*), 5.10-4.95 (*m*, 6H, ArCH_2), 4.86 (*m*, 2H, ArCH_2), 3.41 (*m*, 2H, Cy-C*H*), 3.11 (*s*, 6H, NCH_3), 3.07 (*s*, 6H, NCH_3), 1.99-1.84 (*m*, 4H, Cy-CH_2), 1.51-1.38 (*m*, 4H, cy-CH_2), .123 (*s*, 18H, C(CH_3)$_3$).

The rest of the analytical data were in compliance to the literature known values.[9]

N-Benzyl-1-(3-((*E*)-(((1*R*,2*R*)-2-(((*E*)-3,5-di-*tert*-butyl-2-hydroxybenzyliden)amino)Cy)imino)methyl)-2-hydroxy-5-*tert*-butyl-benzyl)-*N*,*N*-dimethylammonium bromide (17)

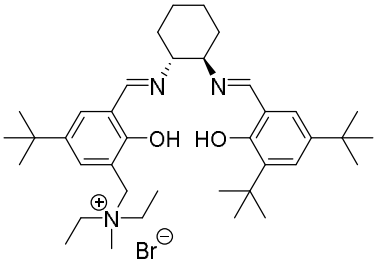


17

Ligand **17** was prepared according to **GP3** using HCl (1.0 equiv., 1.43 mmol, 0.71 mL 2M in Et_2O), to protonate (1*R*,2*R*)-1,2-diaminocyclohexane (1.0 equiv., 1.43 mmol, 0.16 g) in Et_2O (10.0 mL). For the condensation the hydrochloride **9b** (1.0equiv., 0.98 mmol, 0.15 g) was dissolved in 10.0 mL of MeOH and 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.1 equiv., 1.08 mmol, 0.25 g), ammonium bromide **12** (1.0 equiv., 0.98 mmol, 0.25 g) and triethylamine (2.0 equiv., 1.96 mmol, 0.20 g, 0.27 mL) were added subsequently (each one dissloved in 3.00 mL of MeOH). The desired ligand **17** (0.85 mmol, 0.61 g, 85%) was obtained as a bright yellow solid.

$C_{42}H_{60}BrN_3O_2$, MW: 717.39 g/mol. **M.p.:** 218.2-220.7 °C decomposition. **$[\alpha]^{20}D$ (c = 0.10 mg/mL, DCM):** +198.0. **^{1}H NMR (500 MHz, CDCl3, 24 °C):** δ = 14.21 (*s*, 1H, Ar-O*H*), 13.55 (*s*, 1H, Ar-O*H*), 8.29 (*s*, 1H, Ar-C*H*-N), 8.21 (*s*, 1H, Ar-C*H*-N), 7.75 (*d*, *J* = 2.60, 1H, Ar-*H*), 7.60 (*d*, *J* = 7.66, 2H, Ar-*H*), 7.45-7.33(*m*, 3H, Ar-*H*), 7.27 (*d*, *J* = 2.69, 1H, Ar-*H*), 7.22 (*d*, *J* = 2.39, 1H, Ar-*H*), 6.91 (*d*, *J* = 2.60, 1H, Ar-*H*), 5.03-4.71 (*m*, 4H, N-C*H2*-Ar), 3.03 (*s*, 6H, N-C*H3*), 1.89-1.49 (*m*, 8H, Cy-*H2*), 1.33 (*s*, 9H, *t*Bu*H*), 1.19 (*s*, 9H, *t*Bu-*H*), 1.17 (*s*, 9H, *t*Bu*H*). **^{13}C NMR (75 MHz, CDCl3, 25 °C):** δ =165.7, 164.8, 159.8, 158.0, 141.8, 140.2,136.7, 136.1 ,133.4, 131.2, 130.7, 129.2, 127.6, 127.1, 125.8, 118.3, 117.8, 114.8, 72.4, 71.5, 68.2,62.7, 49.1, 48.9, 35.0, 34.1, 34.1, 33.5, 32.7, 31.5, 31.4, 31.3, 31.0, 29.4, 29.4, 24.3, 24.2. **IR (solid):** $\tilde{\nu}$ = 3399, 2954, 2863, 2181, 1629, 1476, 1477, 1441, 1362, 923, 861, 730. **HRMS (ESI) *m/z*:** calculated 638.4680; measured: 638.4689.

N-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-2-(((*E*)-3,5-di-*tert*-butyl-2-hydroxybenzylidene)amino)methyl)-2-hydroxybenzyl)-*N*-diethyl-*N*-methylammonium Bromide (18)



18

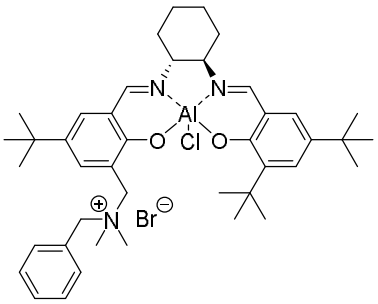
Ligand **18** was prepared according to **GP3** using HCl (1.0 equiv., 0.33 mmol, 82.4 µL, 4M in 1,4-dioxane), to protonate (1*R*,2*R*)-1,2-diaminocyclohexane (1.0 equiv., 0.33 mmol, 38.4 mg) in Et_2O (1.0 mL). For the condensation the hydrochloride **9b** was dissolved in MeOH (2.0 ml) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.1 equiv., 0.36 mmol, 85.0 mg), ammonium bromide **14** (1.0 equiv., 0.33 mmol, 118.1 g) and triethylamine (2.0 equiv., 0.66 mmol, 66.7 mg, 91.4 µL) were added subsequently (each one dissolved in 0.5 mL of MeOH). The desired ligand **18** (0.28 mmol, 190.0 mg, 86%) was obtained as a bright yellow solid.

$C_{38}H_{60}BrN_3O_2$, MW: 669.39 g/mol. **M.p.:** 155.1-165.1 °C decomposition. **$[\alpha]^{20}D$ (c = 0.18 mg/mL, DCM):** +313.5. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 14.31 (*s*, 1H, ArO*H*), 13.60 (*s*,

1H, ArO*H*), 8.36 (*s*, 1H, C*H*=N), 8.29 (*s*, 1H, C*H*=N), 7.81 (*d*, *J* = 2.3, Ar*H*), 7.35 (*d*, *J* = 2.4, Ar*H*), 7.28 (*d*, *J* = 2.3, Ar*H*), 7.00 (*d*, *J* = 2.4, Ar*H*), 4,85-4.57 (*m*, 2H, CH_2N), 3.81-3.24 (*m*, 4H, N(CH_2CH$_3$)$_2$), 3.10 (*s*, 3H, NCH_3), 2.03 (*m*, 1H, Cy*H*), 1.91 (*m*, 3H, Cy*H*), 1.72 (*m*, 2H, Cy*H*), 1.49 (*m*, 2H, Cy*H*), 1.39 (*m*, 15H, C(CH_3)$_3$, N(CH$_2$CH_3)$_3$), 1.26 (*m*, 18H, C(CH_3)$_3$). **^{13}C NMR (75 MHz, CDCl$_3$, 25 °C):** δ = 165.9, 164.9, 160.0, 158.1, 141.9, 140.4, 136.9, 136.1, 131.3, 127.2, 125.9, 118.4, 117.9, 114.7, 72.5, 71.7, 59.7, 56.0, 55.8, 35.2, 34.24, 34.20, 33.6, 32.8, 31.6, 31.4, 29.5, 24.46, 24.43, 8.5. **IR (CHCl$_3$):** $\tilde{\nu}$ = 3411, 2954, 2864, 1630, 1477, 1036, 731. **HRMS (ESI) *m/z*:** calculated: 590.4680; measured: 590.4699.

Catalysis

Isolation of Catalyst 3c



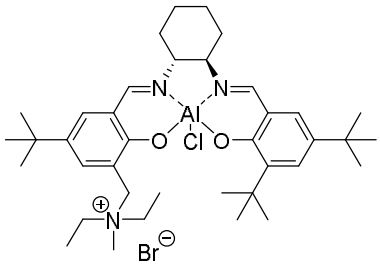
3c

Catalyst **3c** was formed as mentioned in **GP3**. To a solution of ligand **17** (1.0 equiv., 0.056 mmol, 40.1 mg) in DCM was given AlEt$_2$Cl (1.1 equiv., 0.061 mmol, 7.4 mg, 61 µL, 1M in heptane). This mixture was stirred for 48 h. To the solution was added dry *n*-pentane to percipitate the catalyst. The percipitate was washed twice with dry *n*-pentane and dried under reduced pressure to yield the desired catalyst as a yellow solid (33.1 mg, 76%).

C$_{42}$H$_{58}$AlBrClN$_3$O$_2$, MW: 779.28 g/mol. **M.p.:**>200 °C decomposition. **^{1}H NMR (400 MHz, CDCl3, 25 °C):** δ = 8.44 (*s*, 1H, C*H*N), 8.32 (*s*, 1H, C*H*N), 8.12 (*m*, 1H, Ar*H*), 7.69-7.42 (*m*, 7H, Ar*H*), 7.20 (*d*, *J* = 2.5, Ar*H*), 5.30-5.20 (*m*, 1H, NC*H*Ph), 5.18-5.06 (*m*, 1H, NC*H*Ph), 5.05-4.85 (*m*, 2H, NCH_2Ar), 3.64 (*m*, 2H, Cy*H*), 3.14 (*s*, 3H, NCH_3), 3.11 (*s*, 3H, NCH_3), 2.55 (*m*, 2H, Cy*H*), 2.10 (*m*, 2H, Cy*H*), 1.59 (*s*, 9H, *t*Bu*H*), 1.55-1.48 (*m*, 4H, Cy*H*), 1.36 (*s*, 9H, *t*Bu*H*), 1.33 (*s*, 9H,

*t*Bu*H*). **^{13}CNMR (75 MHz, CDCl3, 25 °C):** δ = 165.9 (*m*), 162.2, 161.8, 140.2, 140.0, 139.5, 139.2, 133.8, 133.3, 131.1, 130.6, 129.2, 128.3, 127.9, 119.1, 118.6, 118.3, 67.6, 64.8, 63.8, 63.4, 48.9, 48.5, 35.5, 34.1, 34.0, 31.2, 31.1, 29.7, 27.8, 27.6, 24.0, 23.8. **IR ($CHCl_3$):** $\tilde{\nu}$ = 2952, 2864, 1636, 1557, 1473, 1361, 1258, 865, 844, 705, 595. **HRMS (ESI) m/z:** calculated for $[M]^+$ $C_{42}H_{58}AlClN_2O_2$: 698.4027; measured: 698.4009.

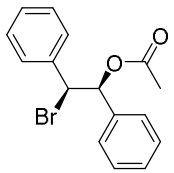
In situ formation of catalyst 3d



3d

Catalyst **3d** was formed as mentioned in **GP3**. To a solution of ligand **x** (1.0 equiv., 0.01 mmol, 6.7 mg) in DCM was added $AlEt_2Cl$ (1.0 equiv., 0.01 mmol, 1.0 mg, 10 µL, 1M in *n*-heptane). The catalyst was used without further purification.

(1*S*,2*S*)-2-Bromo-1,2-diphenylethyl acetate (4a)



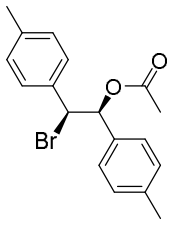
4a

Acetate **4a** was prepared according to **GP4** using stilbenoxide (1.0 equiv., 0.2 mmol, 39.3 mg) and isolated by column chromatography (petrol ether/ ethyl acetate 30:1) as a white solid (56.1 mg,

88%, *er* 92:8). The enantiomeric ratio was determined by HPLC: Chiralcel AD-H, *n*-hexane/ *i*PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 14.8 min (major enantiomer) 16.4 min (minor enantiomer).

$C_{16}H_{15}BrO_2$, MW: 319.20 g/mol. **M.p.:** 65.0 °C. **$[\alpha]^{20}D$ (c = 0.21 mg/mL, DCM):** +107.1. **^1H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.24-7.15 (*m*, 8H, Ar*H*), 7.14-7.08 (*m*, 2H, Ar*H*), 6.22 (*d*, 1H, C*H*Br), 5.17 (*d*, *J* = 9.4, 1H, C*H*O), 2.17 (*s*, 3H, CH_3-CO). **^{13}C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.8, 137.8, 136.8, 128.8, 128.7, 128.62, 128.59, 128.4, 127.5, 78.7, 56.8, 21.3. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3056, 3031, 2969, 1742, 1369, 1223, 1021, 758, 697, 611, 537. **HRMS (ESI) *m/z*:** calculated for $[M+Na]^+$ $C_{16}H_{15}BrO_2Na$: 343.0129; measured: 343.0122.

(1*S*,2*S*)-2-Bromo-1,2-di-*p*-tolylethyl acetate (4b)

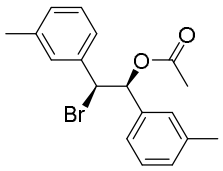


4b

Acetate **4b** was prepared according to **GP4** using 2,3-di-*p*-tolyloxirane (1.0 equiv. 0.2 mmol, 44.9 mg) and isolated by column chromatography (petrol ether/ ethyl acetate 30:1) as a colorless oil (61.2 mg, 88%, er 91:9). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 10.35 min (major enantiomer) 14.35 min (minor enantiomer).

$C_{18}H_{19}BrO_2$, MW: 347.25 g/mol. **$[\alpha]^{20}D$ (c = 0.16 g/100mL, DCM):** +98.9. **^1H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.14-7.09 (*m*, 2H, Ar*H*), 7.05-6.96 (*m*, 6H, Ar*H*), 6.21 (*d*, *J* = 9.5, 1H, C*H*Br), 5.18 (*d, J* = 9.3, 1H, C*H*O), 2.26 (*s*, 3H, ArCH_3), 2.24 (*s*, 3H, ArCH_3), 2.14 (*s*, 3H, CH_3-CO). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.8, 138.6, 138.4, 135.1, 133.9, 129.3, 129.1, 128.5, 127.5, 78.4, 57.0, 21.3. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3027, 2922, 1741, 1370, 1224, 1019, 814, 727, 523. **HRMS (EI) *m/z*:** Calculated for $[M]^+$ $C_{18}H_{19}BrO_2$: 346.0568; found: 346.0568.

(1*S*,2*S*)-2-Bromo-1,2-di-*m*-tolylethyl acetate (4c)

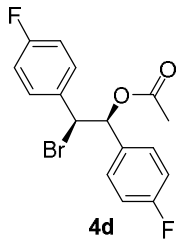


4c

Acetate **4c** was prepared according to **GP4** using 2,3-di-*m*-tolyloxirane (1.0 equiv. 0.2 mmol, 44.9 mg) and isolated by coloumn chromatography (petrol ether/ ethyl acetate 30:1) as a colorless oil, (59.1 mg, 85%, er 91:9). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm 10.67 min (major enantiomer) 15.36 min (minor enantiomer).

$C_{18}H_{19}BrO_2$, MW: 347.25 g/mol. **[α]^{20}D (c = 0.18 g/100 mL, DCM):** +101.7. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.08-6.87 (*m*, 8H, Ar*H*), 6.18 (*d*, *J* = 9.3, 1H, C*H*Br), 5.12 (*d, J* = 9.3, 1H, C*H*O), 2.23 (*s*, 3H, ArCH_3), 2.20 (*s*, 3H, ArCH_3), 2.13 (*s*, 3H, CH_3-CO). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.8, 138.2, 138.0, 137.8, 136.8, 129.5, 129.31, 129.29, 128.4, 128.19, 128.17, 125.7, 124.6, 78.5, 57.1, 21.42, 21.37, 21.26. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3024, 2921, 1742, 1370, 1222, 1024, 787, 710, 463.**HRMS (EI) *m/z*:** Calculated for $[M]^+$ $C_{18}H_{19}BrO_2$: 346.0568; measured: 346.0571.

(1*S*,2*S*)-2-Bromo-1,2-bis(4-fluorophenyl)ethyl acetate (4d)



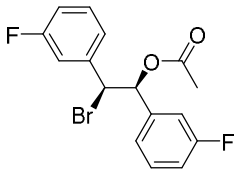
4d

Acetate **4d** was prepared according to **GP4** using 2,3-bis(4-fluorophenyl)oxirane (1.0 equiv. 0.2 mmol, 46.5 mg) and isolated by column chromatography (petrol ether/ ethyl acetate 30:1)as a

colorless oil (63.2 mg, 91%, er 95:5). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 13.92 min (major enantiomer) 19.04 min (minor enantiomer).

$C_{16}H_{13}BrF_2O_2$, MW: 355.18 g/mol. **[α]^{20}D (c = 0.24 g/100mL, DCM):** +114.9. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.24-7.17 (*m*, 2H, Ar*H*), 7.15-7.07 (*m*, 2H, Ar*H*), 6.97-6.87 (*m*, 4H, Ar*H*), 6.19 (*d*, *J* = 9.3, 1H, C*H*Br), 5.15 (*d, J* = 9.3, 1H, C*H*O), 2.19 (*s*, 3H, CH_3-CO). **^{19}F NMR (376 MHz, $CDCl_3$, 25 °C):** δ = –112.1 to –112.2 (*m*), –112.4 to –112.6 (*m*). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.5, 163.8 (*d*, *J* = 9.0), 161.3 (*d*, *J* = 9.4), 133.4 (*d*, *J* = 3.7), 132.4 (*d*, *J* = 3.1), 130.3 (*d*, *J* = 8.7), 129.1 (*d*, *J* = 8.1), 115.7, 115.52, 115.46, 115.3, 77.9, 55.3, 21.0. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3075, 1741, 1605, 1509, 1218, 1159, 1028, 834, 735, 529. **HRMS (EI) *m/z*:** Calculated for $[M]^+$ $C_{16}H_{13}BrF_2O_2$: 354.0067; measured: 354.0066.

(1*S*,2*S*)-2-Bromo-1,2-bis(3-fluorophenyl)ethyl acetate (4e)



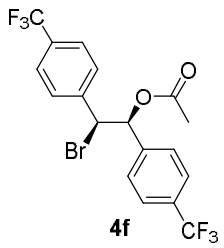
4e

Acetate **4e** was prepared according to **GP4** using 2,3-bis(3-fluorophenyl)oxirane (1.0 equiv. 0.2 mmol, 46.5 mg) and isolated by coloumn chromatography (petrol ether/ ethyl acetate 30:1) as a colurless oil (65.3 mg, 92%, er 96:4). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 14.03 min (major enantiomer) 19.84 min (minor enantiomer).

$C_{16}H_{13}BrF_2O_2$, MW: 355.18 g/mol. **[α]^{20}D (c = 0.15 g/100mL, DCM):** +106.2. **^{1}H NMR (500 MHz, $CDCl_3$, 24 °C):** δ = 7.25-7.15 (*m*, 2H, Ar*H*), 7.06-6.98 (*m*, 2H, Ar*H*), 6.97-6.88 (*m*, 4H, Ar*H*), 6.18 (*d*, *J* = 8.9, 1H, C*H*Br), 5.12 (*d, J* = 9.0, 1H, C*H*O), 2.20 (*s*, 3H, CH_3-CO). **^{19}F NMR (376 MHz, $CDCl_3$, 25 °C):** δ = –112.01 to –112.07 (*m*), –112.11 to –112.2 (*m*). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 170.0, 163.8 (*d*, *J* = 9.8), 161.4 (*d*, *J* = 9.5), 139.9 (*d*, *J* = 7.3), 130.2 (*d*, *J* = 8.6), 130.0 (*d*, *J* = 8.0), 124.3 (*d*, *J* = 3.3), 123.3 (*d*, *J* = 3.0), 116.0 (*d*, *J* = 20.7), 115.93 (*d*, *J* = 5.9), 115.88 (*d*, *J* = 2.0), 115.7 (*d*, *J* = 7.4), 114.3 (*d*, *J* = 22.7), 77.7, 55.0, 21.1. **IR ($CHCl_3$):**

$\tilde{\nu}$ = 3065, 1746, 1593, 1449, 1223, 906, 727, 715, 481. **HRMS (ESI) *m/z*:** Calculated for $[M]^+$ $C_{16}H_{13}BrF_2O_2$: 354.0067; measured: 354.0061.

(1*S*,2*S*)-2-Bromo-1,2-bis(4-(trifluoromethyl)phenyl)ethyl acetate (4f)

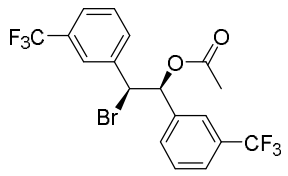


4f

Acetate **4f** was prepared according to **GP4** using 2,3-bis(4-(trifluoromethyl)phenyl)oxirane (1.0 equiv. 0.2 mmol, 66.5 mg) and isolated by coloumn chromatography (petrol ether/ ethyl acetate 30:1) as a colorless oil (81.0 mg, 89%, *er* 95.5:4.5,). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 14.40 min (major enantiomer) 18.24 min (minor enantiomer).

$C_{18}H_{13}BrF_6O_2$, MW: 455.19 g/mol. **$[\alpha]^{20}D$ (c = 0.35 g/100mL, DCM):** +76.6. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.51-7.41 (*m*, 4H, Ar*H*), 7.37-7.29 (*m*, 2H, Ar*H*), 7.27-7.19 (*m*, 2H, Ar*H*), 6.21 (*d*, *J* = 8.6, 1H, C*H*Br), 5.16 (*d, J* = 8.6, 1H, C*H*O), 2.15 (*s*, 3H, CH_3-CO). **^{19}F NMR (376 MHz, $CDCl_3$, 25 °C):** δ = -62.83, -62.84. **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.5, 141.2, 140.2, 131.3 (*d*, *J* = 5.1), 131.0 (*d*, *J* = 5.1), 129.1, 127.9, 125.8 (*m*), 125.6 (*m*), 125.1 (*d*, *J* = 8.8), 122.4 (*d*, *J* = 8.6), 77.5, 54.4, 21.1. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3077, 2961, 1747, 1322, 1223, 1165, 1111, 1067, 1018, 846, 607. **HRMS (EI) *m/z*:** Calculated for $[M-F]^+$ $C_{18}H_{13}BrF_5$: 435.0019; measured: 435.0023.

(1*S*,2*S*)-2-Bromo-1,2-bis(3-(trifluoromethyl)phenyl)ethyl acetate (4g)

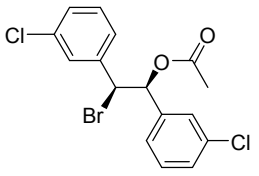


4g

Acetate **4g** was prepared according to **GP4** using 2,3-bis(3-(trifluoromethyl)phenyl)oxirane (1.0 equiv. 0.2 mmol, 66.5 mg) and isolated by coloumn chromatography (petrol ether/ ethyl acetate 30:1) as a colorless oil (74.6 mg, 82%, *er* 88:12). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 14.08 min (minor enantiomer) 15.52 min (major enantiomer).

$C_{18}H_{13}BrF_6O_2$, MW: 455.19 g/mol. **[α]^{20}D (c = 0.15 g/100 mL, DCM):** +71.8. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.56-7.48 (*m*, 2H, Ar*H*), 7.47-7.28 (*m*, 6H, Ar*H*), 6.24 (*d*, *J* = 8.2, 1H, C*H*Br), 5.19 (*d, J* = 8.2, 1H, C*H*O), 2.21 (*s*, 3H, CH_3-CO). **^{19}F NMR (376 MHz, $CDCl_3$, 25 °C):** δ = -62.95, -62.98. **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.4, 138.1, 137.2, 131.8, 131.5-130.4 (*m*), 130.7, 129.2, 128.9, 125.8-125.4 (*m*), 124.9 (*d*, *J* = 9.3), 124.1-123.9 (*m*), 122.2 (*d*, *J* = 9.3), 77.6, 54.4, 20.5. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3069, 2961, 1747, 1326, 1222, 1163, 1119, 1073, 1033, 806, 699, 662. **HRMS (EI) *m/z*:** Calculated for [M-F]$^{+}$: 435.0019; measured: 435.0019.

(1*S*,2*S*)-2-Bromo-1,2-bis(3-chlorophenyl)ethyl acetate (4h)



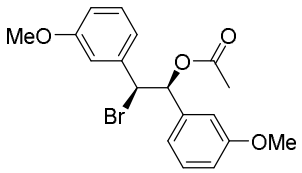
4h

Acetate **4h** was prepared according to **GP4** using 2,3-bis(3-chlorophenyl)oxirane (1.0 equiv. 0.2 mmol, 53.0 mg) and isolated by coloumn chromatography (petrol ether/ ethyl acetate 30:1) as a colorless oil (69.1 mg, 89%, er 90.5:9.5). The enantiomeric ratio was determined by HPLC:

Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 14.30 min (major enantiomer) 18.16 min (minor enantiomer).

$C_{16}H_{13}BrCl_2O_2$, MW: 388.08 g/mol. **[α]^{20}D (c = 0.17 g/100 mL, DCM):** +61.9. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.25-7.02 (*m*, 7H, Ar*H*), 6.96-6.91 (*m*, 1H, Ar*H*), 6.10 (*d*, *J* = 8.8, 1H, C*H*Br), 5.03 (*d, J* = 8.8, 1H, C*H*O), 2.14 (*s*, 3H, CH_3-CO). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.5, 139.4, 138.5, 134.53, 134.51, 129.9, 129.7, 129.1, 129.0, 128.9, 127.4, 126.8, 125.8, 77.6, 54.9, 21.1. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3064, 1744, 1575, 1430, 1371, 1219, 1028, 882, 787, 732, 693, 671, 465. **HRMS (EI) *m/z*:** Calculated for $[M]^+$ $C_{16}H_{13}BrCl_2O_2$: 385.9476; measured: 385.9489.

(1*S*,2*S*)-2-Bromo-1,2-bis(3-methoxyphenyl)ethyl acetate (4i)



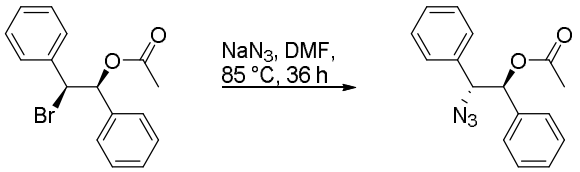
4i

Acetate **4i** was prepared according to **GP4** using 2,3-bis(3-methoxyphenyl)oxirane (1.0 equiv. 0.2 mmol, 44.9 mg) and isolated by coloumn chromatography (petrol ether/ ethyl acetate 10:1) as a colorless oil (64.5 mg, 85%, er 91:9). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 25.87 min (major enantiomer) 39.52 min (minor enantiomer).

$C_{18}H_{19}BrO_4$, MW: 379.25 g/mol. **[α]^{20}D (c = 0.15 g/100 mL, DCM):** +76.6. **^{1}H NMR (500 MHz, $CDCl_3$, 24 °C):** δ = 7.16-7.06 (*m*, 2H, Ar*H*), 6.87-6.64 (*m*, 6H, Ar*H*), 6.23 (*d*, *J* = 9.5, 1H, C*H*Br), 5.15 (*d, J* = 9.3, 1H, C*H*O), 3.73 (*s*, 3H, OCH_3), 3.68 (*s*, 3H, OCH_3), 2.18 (*s*, 3H, CH_3-CO). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.9, 159.6, 159.4, 139.2, 138.3, 129.6, 129.4, 121.0, 119.8, 114.5, 114.2, 113.1, 78.4, 56.7, 55.4, 55.3, 21.2. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3002, 2960, 2835, 1743, 1600, 1586, 1491, 1455, 1435, 1371, 1261, 1219, 1152, 1027, 873, 785, 712, 698, 487. **HRMS (EI) *m/z*:** Calculated for $[M]^+$ $C_{18}H_{19}BrO_4$: 378.0467; found: 378.0462.

Derivatization

(1*S*,2*R*)-2-Azido-1,2-diphenylethyl acetate (6)

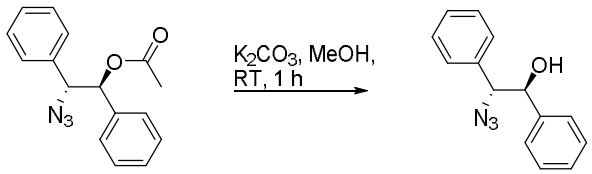


4a **6**

The synthesis of **6** was inspired by a literature known procedure.[11] The protected bromohydrin **x** (1.0 equiv., 0.25 mmol, 80.4 mg; 91:9 *er*) was dissolved in dry DMF (0.35 mL) and sodium azide (1.5 equiv., 0.38 mmol, 24.6 mg) was added. The mixture was heated to 85 °C and stirred at that temperature for 36 h. The reaction was quenched by the addition of water (2.00 mL) and extracted three times with Et_2O (10.00 mL). The combined organic phases were washed with brine (20 mL) three times, dried over $MgSO_4$ and the solvent was removed under reduced pressure. After workup the desired compound was obtained as a colorless oil (64.0 mg, 90%, 87:13 *er*). The enantiomeric ratio was determined by HPLC: Chiralcel ODH, ^{n}hexane/^{i}PrOH (99/1), 0.8 mL min^{-1}, 210 nm, 15.25 min (major enantiomer) 18.24 min (minor enantiomer).

$C_{16}H_{15}N_3O_2$, MW: 281.32 g/mol. **[α]^{20}D (c = 0.18 g/100 mL, DCM):** +36.6. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.35-7.29 (*m*, 6H, Ar*H*), 7.26-7.18 (*m*, 4H, Ar*H*), 5.95 (*d*, *J* = 6.5, 1H, C*H*N), 4.90 (*d*, *J* = 6.5, 1H, C*H*O), 2.00 (*s*, 3H, CH_3CO). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.5, 136.2, 135.7, 128.76, 128.74, 128.6, 128.3, 127.91, 127.86, 77.6, 69.1, 21.0. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3065, 2101, 1744, 1371, 1222, 1026, 761, 699. **HRMS (EI) *m/z*:** Calculated for [M-$C_7H_6BrN_3$]$^+$ $C_9H_9O_2$: 149.0603; measured: 149.0606.

(1*S*,2*R*)-2-Azido-1,2-diphenylethylethan-1-ol (7)



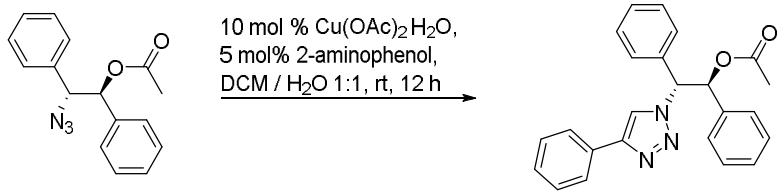
6 **7**

Azido acetate **6** (1.0 equiv., 0.06 mmol, 16.9 mg) was dissolved in a mixture of water and methanol (1:4, 0.30 mL), potassium carbonate (2.0 equiv., 0.12 mmol, 16.6 mg) was added and the resulting mixture was stirred for one hour at ambient temperature. The mixture was extracted three times with diethyl ether (2.0 mL). The combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure. Column chromatography of the crude product yielded the desired azido alcohol (15.4 mg, 91%) as colorless oil.

$C_{14}H_{13}N_3O$, MW: 239.28 g/mol. **$[\alpha]^{20}D$ (c = 0.13 g/100 mL, DCM):** –61.2. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.37-7.27 (*m*, 6H, Ar*H*), 7.26-7.20 (*m*, 4H, Ar*H*), 4.80 (*d*, *J* = 6.6, 1H, C*H*N), 4.66 (*d*, *J* = 6.6, 1H, C*H*O), 2.09 (*bs*, 1H, O*H*).

The rest of the analytical data were in compliance to the literature known values. [11]

(1*S*,2*R*)-1,2-Diphenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl acetate (8)



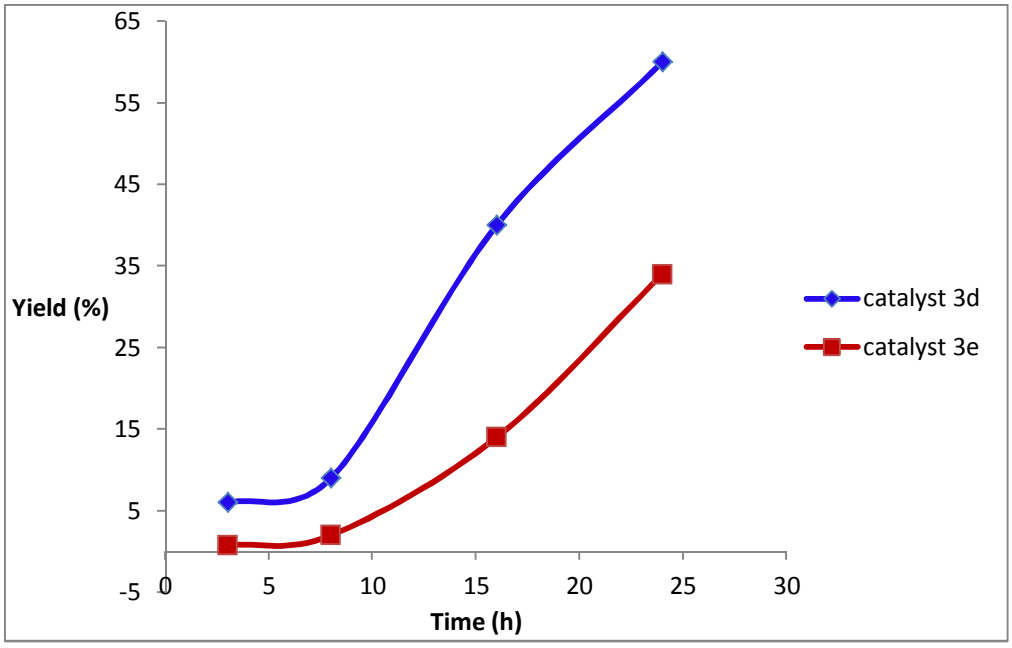
6 **8**

The synthesis of molecule **8** was in analogy to a literature known method.[12,13] Azido acetate **6** (1.00 equiv., 0.100 mmol, 28.1 mg), copper (II) acetate (0.10 equiv., 0.010 mmol, 2.0 mg) and 2-aminophenol (0.05 equiv., 0.005 mmol, 0.5 mg) were dissolved in DCM (0.2 mL) and mixed with water (0.2 mL). Phenyl acetylene (1.00 equiv., 0.100 mmol, 10.2 mg, 9.5 µL) was added dropwise

and the mixture was stirred for 12 hours at ambient temperature. Afterwards the reaction was extracted three times with DCM (2.0 mL) and the combined organic phases were washed with brine (3.0 mL) and dried over sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (petrol ether/ethyl acetate 5:1) to yield the desired product **7** as a white solid (29.9 mg, 89%).

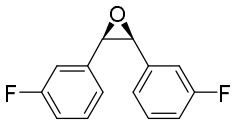
$C_{24}H_{21}N_3O_2$, MW: 383.45 g/mol. **M.p.:** 135.1-138.5 °C. **$[\alpha]^{20}D$ (c = 0.13 g/100 mL, DCM):** –15.3. **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ = 7.69(*d*, *J* = 7.5, 2H, Ar*H*), 7.56 (*m*, 2H, Ar*H*), 7.55 (*s*, 1H, C*H*N_3), 7.41-7.33 (*m*, 5H, Ar*H*), 7.31-7.28 (*m*, 3H, Ar*H*), 6.83 (*d*, *J* = 9.1, 1H, C*H*N(CN)), 5.86 (*d*, *J* = 9.0, 1H, C*H*O), 1.92 (*s*, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$, 25 °C):** δ = 169.2, 147.5, 136.6, 135.4, 130.5, 129.3, 129.04, 128.97, 128.89, 128.7, 128.5, 128.3, 127.2, 125.8, 119.8, 75.5, 69.2, 20.9. **IR ($CHCl_3$):** $\tilde{\nu}$ = 3125, 3083, 3033, 1737, 1370, 1301, 1025, 766, 698, 560. **HRMS (ESI) *m/z*:** Calculated for $[M+Na]^+$ $C_{24}H_{21}N_3O_2$: 406.1526; measured: 406.1517.

Kinetic Comparison between catalysts 3d and 3e



Spectral data

cis-2,3-Bis(fluorophenyl)oxirane (1b)



1b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PROCNO                 1

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RG                 182.64
DW                 62.400 usec
DE                  6.50 usec
TE                 296.0 K
D1              1.00000000 sec
TD0                    1

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PLW1          12.00000000 W

F2 - Processing parameters
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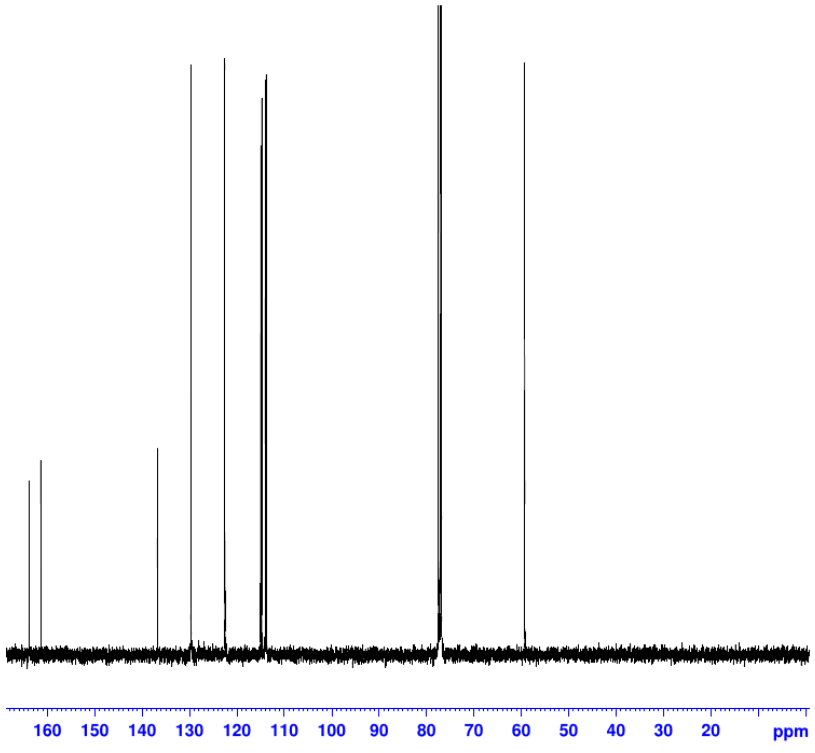
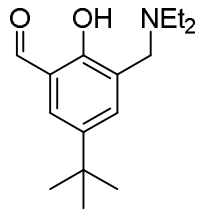
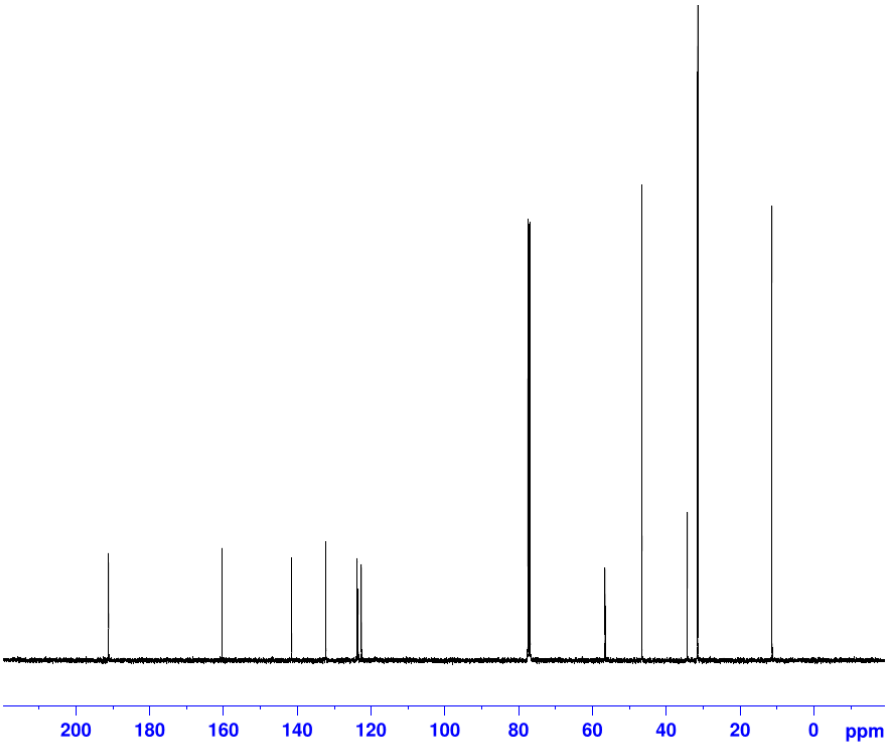


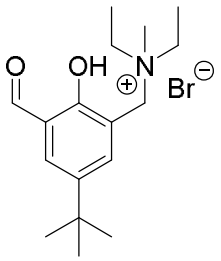
5-(*tert*-Butyl)-3-((diethylamino)methyl)-2-hydroxybenzaldehyde (13)



13



***N*-(5-(*tert*-Butyl)-3-formyl-2-hydroxybenzyl)-*N*-diethyl-*N*-methylammonium Bromide (14)**



14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SOLVENT               CDC13
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DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894966 sec
RG                    205.35
DW                    62.400 usec
DE                     6.50 usec
TE                    296.0 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
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PLW1           12.00000000 W

F2 - Processing parameters
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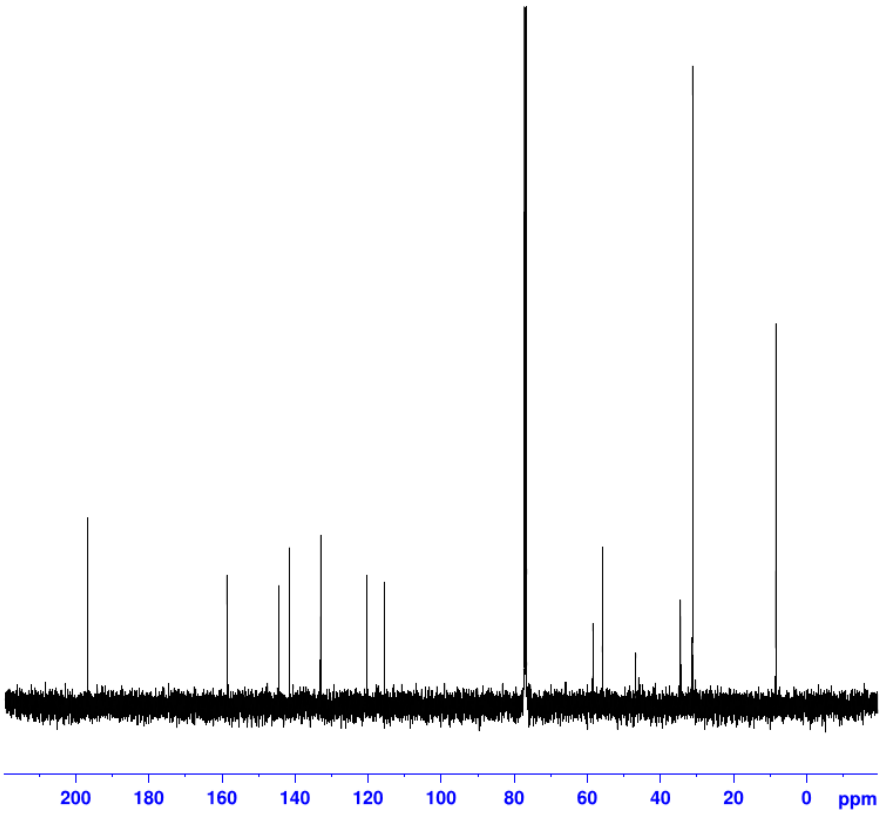
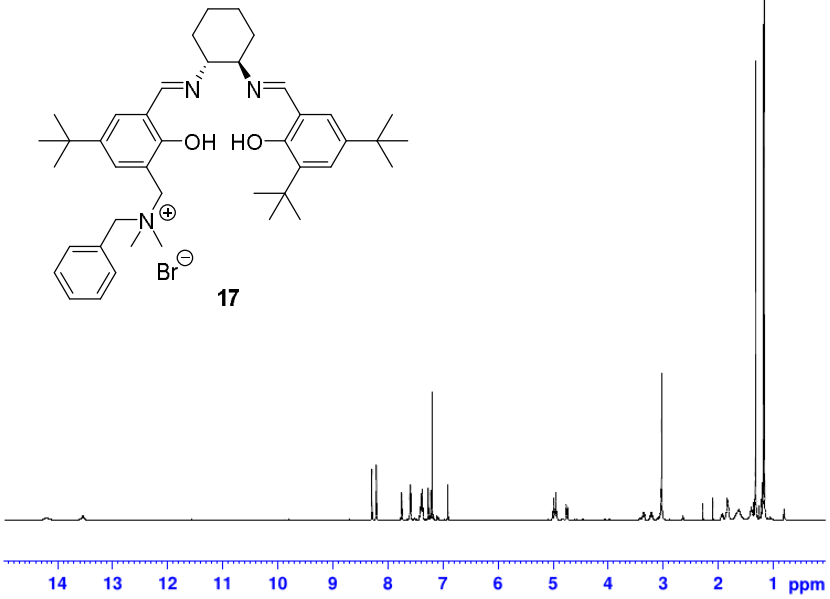


***N*-Benzyl-1-(3-((*E*)-(((1*R*,2*R*)-2-(((*E*)-3,5-di-*tert*-butyl-2-hydroxybenzyliden)amino)Cy)imino)methyl)-2-hydroxy-5-*tert*-butyl-benzyl)-*N*,*N*-dimethylammonium bromide (17)**

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DW                   48.400 usec
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TD0                          1

======== CHANNEL f1 ========
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F2 - Processing parameters
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PC                       1.00
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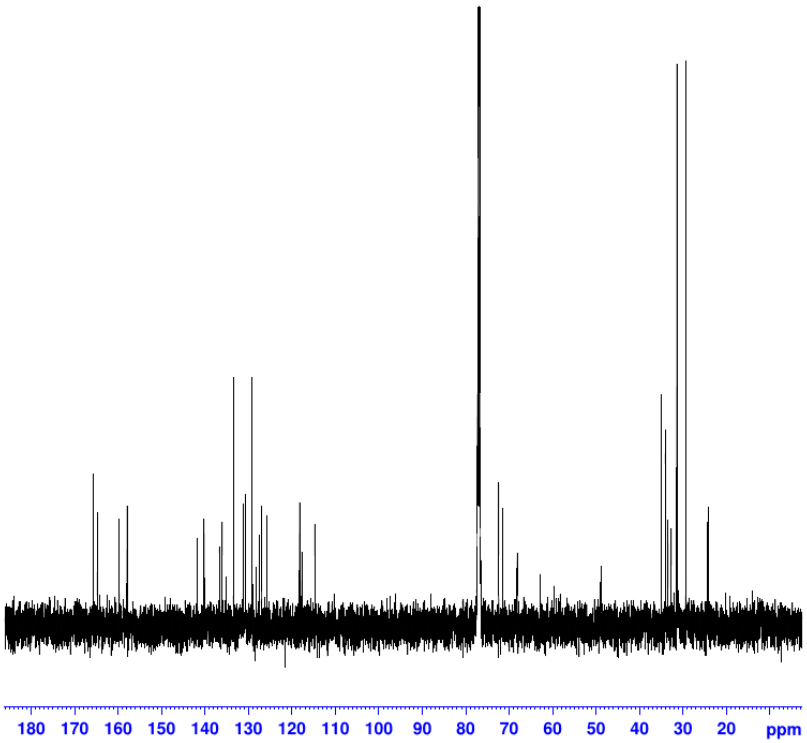


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SOLVENT               CDCl3
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DS                        4
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AQ                0.9961972 sec
RG                     2890
DW                   15.200 usec
DE                   10.00 usec
TE                   296.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
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P1                       10.20 usec
PL1                       1.50 dB
PL1W             51.74793243 W
SFO1             125.7761482 MHz

======== CHANNEL f2 ========
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NUC2                        1H
PCPD2                   100.00 usec
PL2                       1.00 dB
PL12                     19.99 dB
PL13                     21.00 dB
PL2W             19.75309753 W
PL12W             0.24925002 W
PL13W             0.19753097 W
SFO2             500.1550006 MHz

F2 - Processing parameters
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WDW                         EM
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GB           0
PC                       1.40
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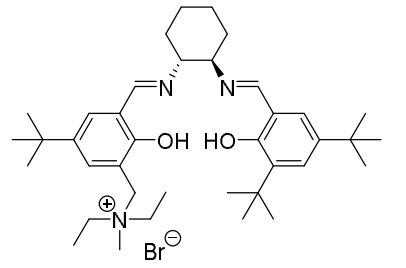
***N*-(5-(*tert*-Butyl)-3-((*E*)-(((1*R*,2*R*)-2-(((*E*)-3,5-di-*tert*-butyl-2-hydroxybenzylidene)amino)methyl)-2-hydroxybenzyl)-*N*-diethyl-*N*-methylammonium Bromide (18)**



18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FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                182.64
DW                62.400 usec
DE                 6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

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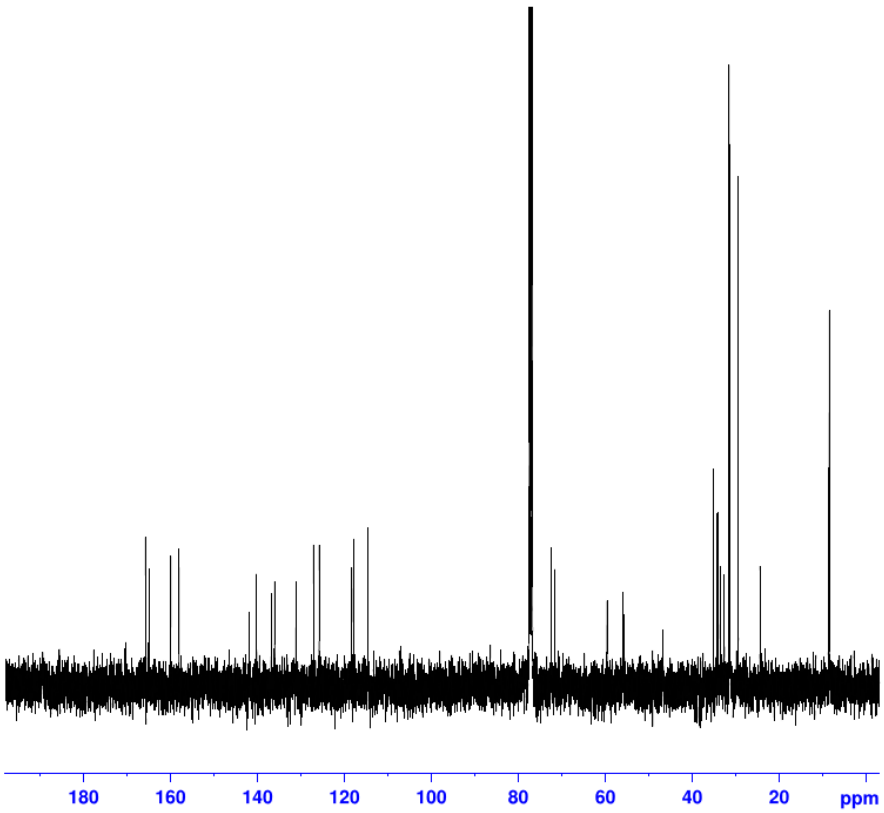
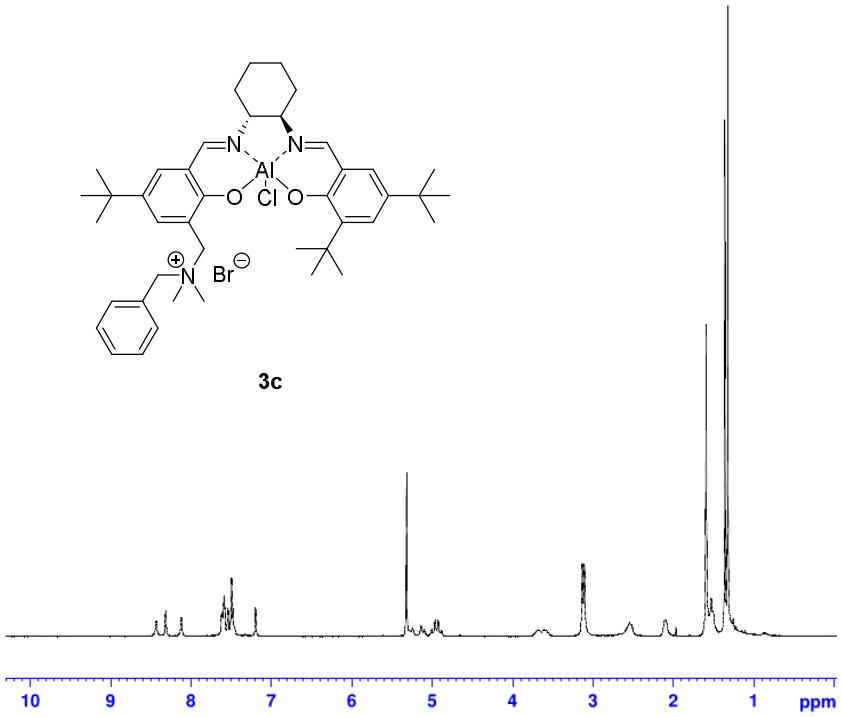
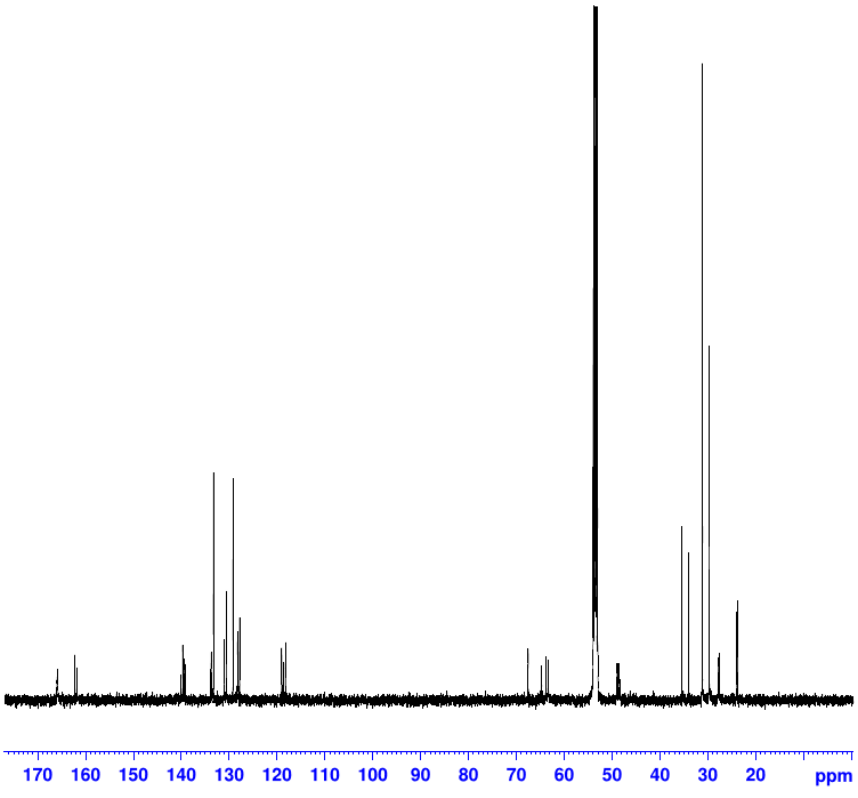


Catalyst 3c



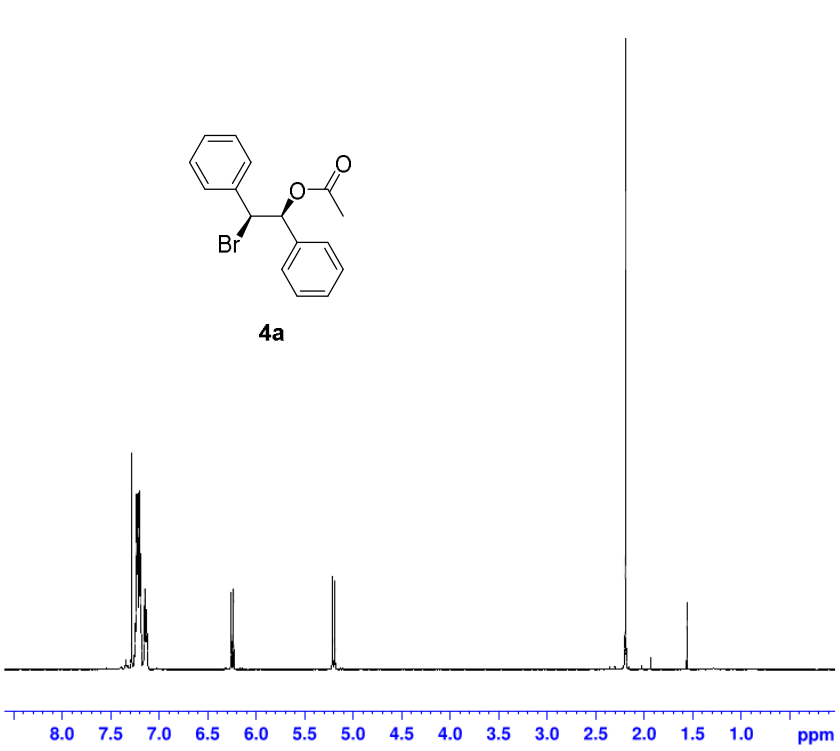
3c

```
Current Data Parameters
NAME                  34-Sy087
EXPNO                      130
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20150310
Time                     11.09
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      32768
SOLVENT                CD2C12
NS                         16
DS                          2
SWH                6188.119 Hz
FIDRES             0.188846 Hz
AQ                 2.6477044 sec
RG                       456
DW                    80.800 usec
DE                     8.00 usec
TE                    296.7 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       11.05 usec
PL1                      -2.00 dB
PL1W               37.02396774 W
SFO1              300.1318534 MHz

F2 - Processing parameters
SI                       16384
SF                300.1300106 MHz
WDW                         EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```

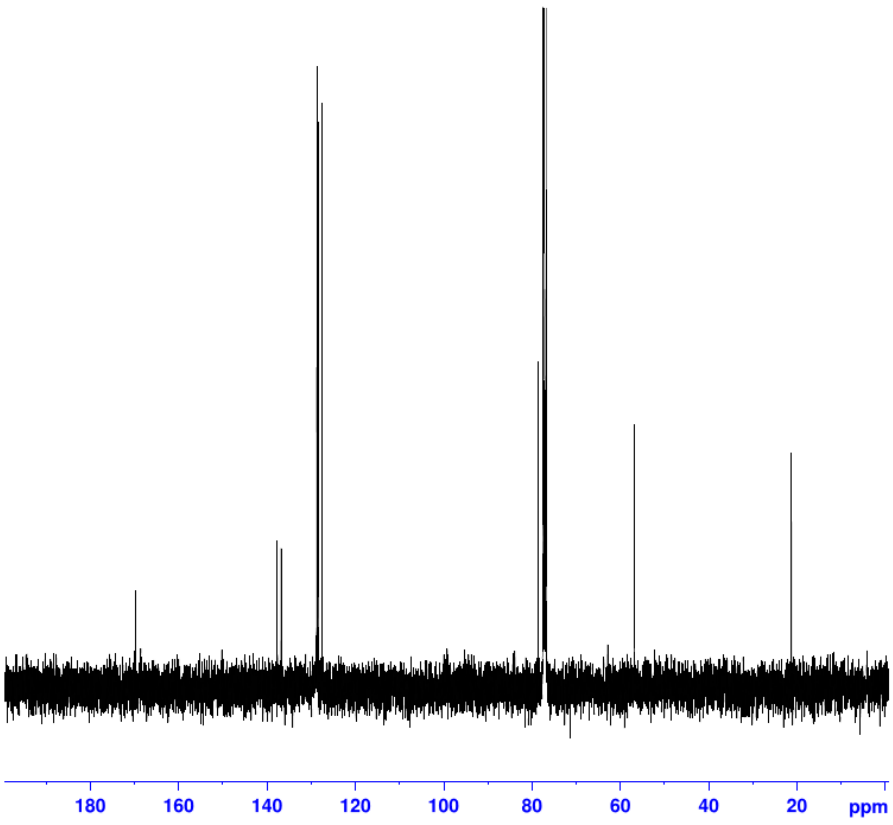



```
Current Data Parameters
NAME                  34-Sy087
EXPNO                      111
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20150311
Time                     23.22
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                CD2C12
NS                        8192
DS                           4
SWH               32894.738 Hz
FIDRES             0.501934 Hz
AQ                 0.9961972 sec
RG                        2890
DW                    15.200 usec
DE                     10.00 usec
TE                    296.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.20 usec
PL1                       1.50 dB
PL1W              51.74793243 W
SFO1             125.7761482 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                   100.00 usec
PL2                       1.00 dB
PL12                     19.99 dB
PL13                     21.00 dB
PL2W              19.75309753 W
PL12W              0.24925002 W
PL13W              0.19753097 W
SFO2             500.1550006 MHz

F2 - Processing parameters
SI                       32768
SF                125.7635626 MHz
WDW                         EM
SSB          0
LB                        1.00 Hz
GB           0
PC                        1.40
```

(1S,2S)-2-Bromo-1,2-diphenylethyl acetate (4a)

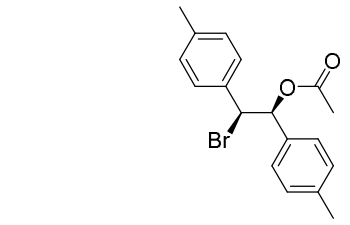



```
NAME      Stillbenprodukt
EXPNO                 530
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160728
Time                1.45
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                 205.35
DW                 62.400 usec
DE                  6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1024708 MHz
NUC1                  1H
P1                 13.70 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                 65536
SF            400.1000000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



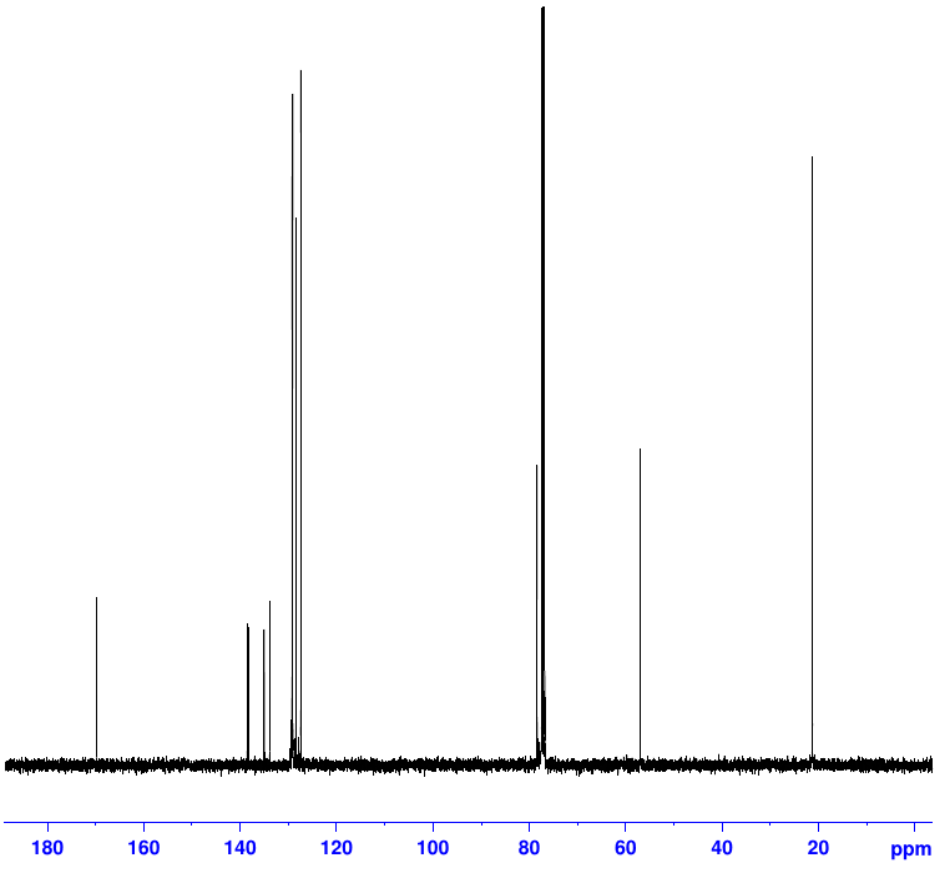
(1S,2S)-2-Bromo-

1,2-di-p-tolylethyl acetate (4b)



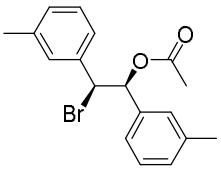
4b


```
Current Data Parameters
NAME                  pMepaper
EXPNO                      690
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20160706
Time                     18.16
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDC13
NS                         16
DS                          2
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                      139.45
DW                      62.400 usec
DE                       6.50 usec
TE                      296.0 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1024708 MHz
NUC1                        1H
P1                       13.70 usec
PLW1               12.00000000 W

F2 - Processing parameters
SI                      65536
SF                 400.1000097 MHz
WDW                        EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```



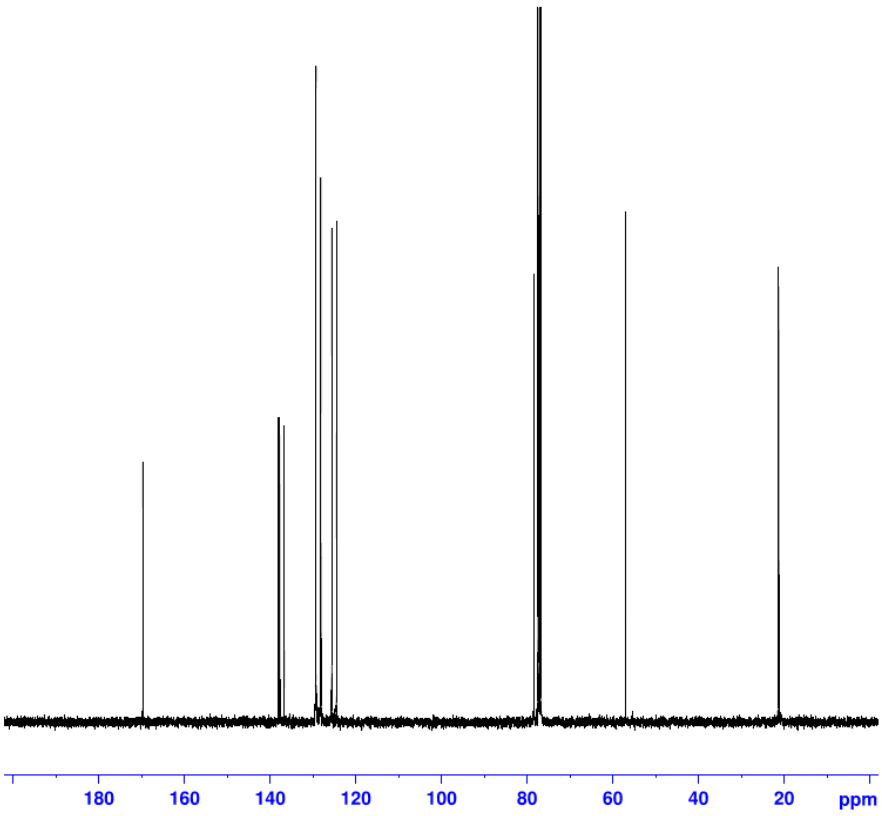
(1S,2S)-2-

Bromo-1,2-di-m-tolylethyl acetate (4c)

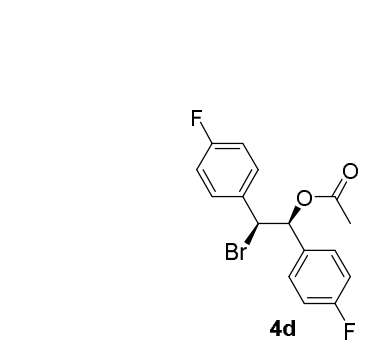


4c


```
Current Data Parameters
NAME                  mMepaper
EXPNO                      660
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20160706
Time                     17.55
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894966 sec
RG                        90.96
DW                       62.400 usec
DE                        6.50 usec
TE                       296.0 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.1024708 MHz
NUC1                        1H
P1                       13.70 usec
PLW1               12.00000000 W

F2 - Processing parameters
SI                      65536
SF                  400.1000458 MHz
WDW                        EM
SSB                 0
LB                        0.30 Hz
GB                  0
PC                        1.00
```

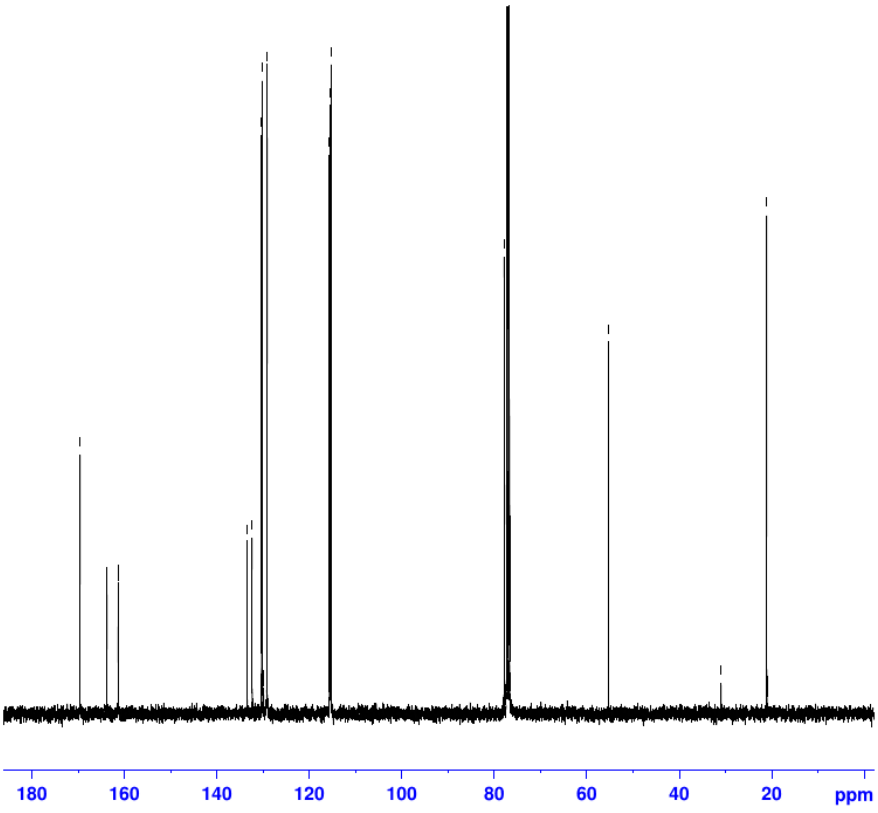


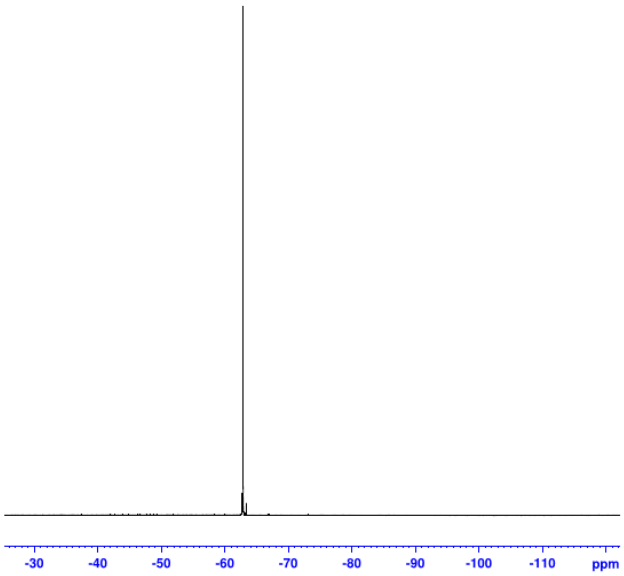
(1S,2S)-2-Bromo-1,2-bis(4-fluorophenyl)ethyl acetate (4d)



4d

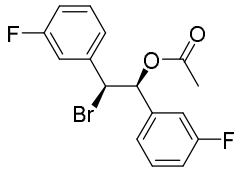

```
Current Data Parameters
NAME                  pFpaper
EXPNO                     650
PROCNO                      1

F2 - Acquisition Parameters
Date_               20160706
Time                   17.50
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894966 sec
RG                    124.07
DW                    62.400 usec
DE                     6.50 usec
TE                    296.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             400.1024708 MHz
NUC1                       1H
P1                      13.70 usec
PLW1            12.00000000 W

F2 - Processing parameters
SI                    65536
SF               400.1000399 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```



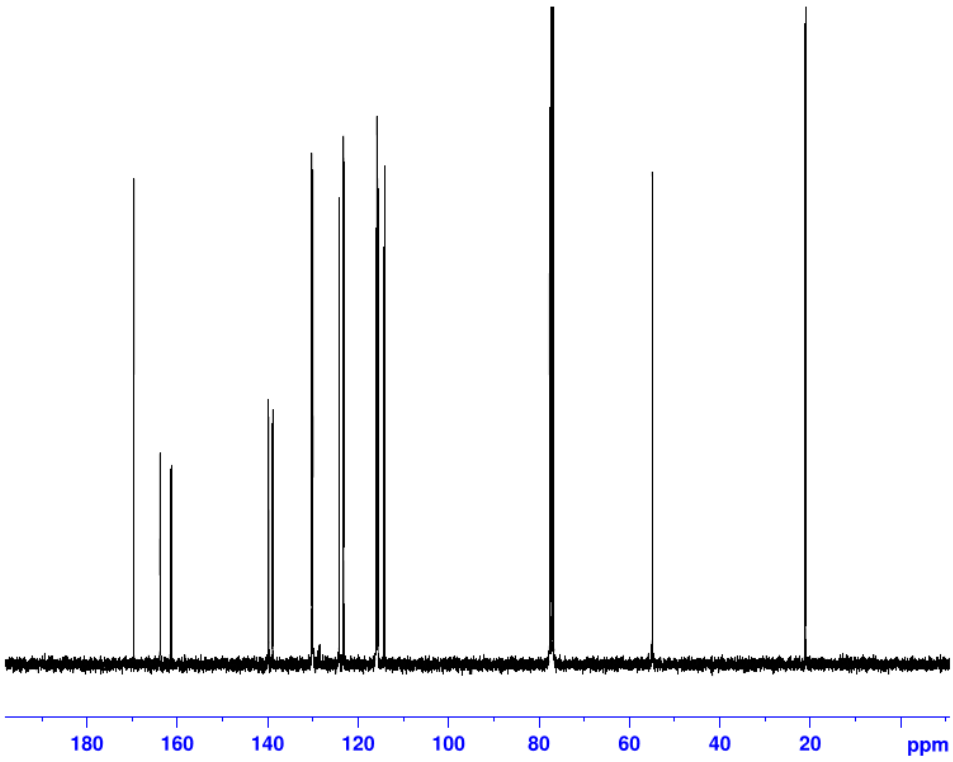


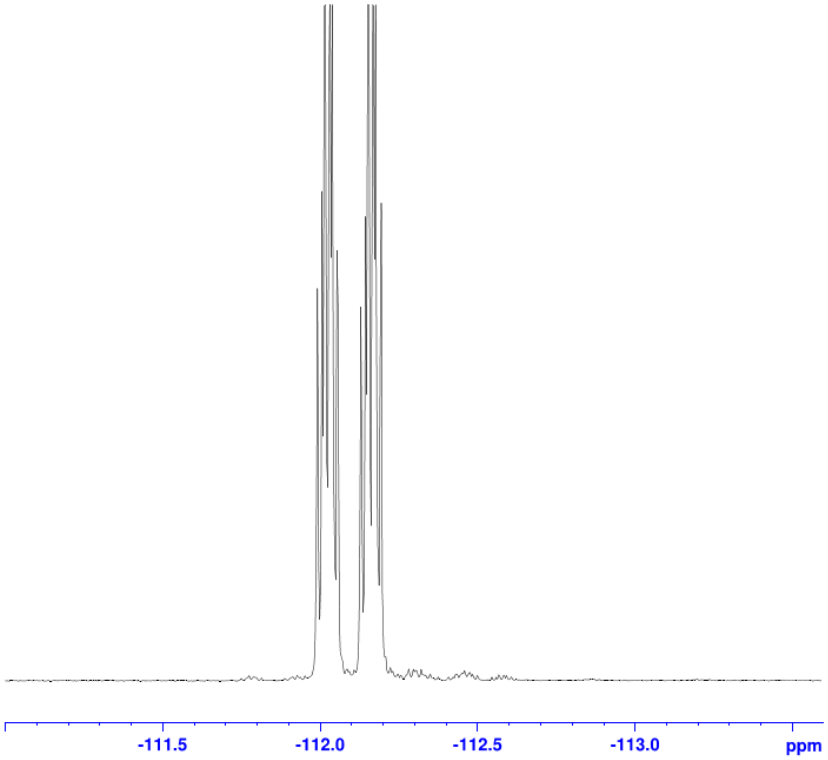

```
Current Data Parameters
NAME                  2G-Sy419
EXPNO                      670
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160628
Time                    18.07
INSTRUM                 spect
PROBHD   5 mm PABBO BA/
PULPROG                 zgflqn
TD                      131072
SOLVENT                 CDCl3
NS                          16
DS                           4
SWH                  89285.711 Hz
FIDRES                0.681196 Hz
AQ                    0.7340532 sec
RG                       205.35
DW                        5.600 usec
DE                        6.50 usec
TE                       296.0 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1          376.4324910 MHz
NUC1                     19F
P1                     14.65 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                       65536
SF            376.4701380 MHz
WDW                        EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```

(1S,2S)-2-Bromo-1,2-bis(3-fluorophenyl)ethyl acetate (4e)



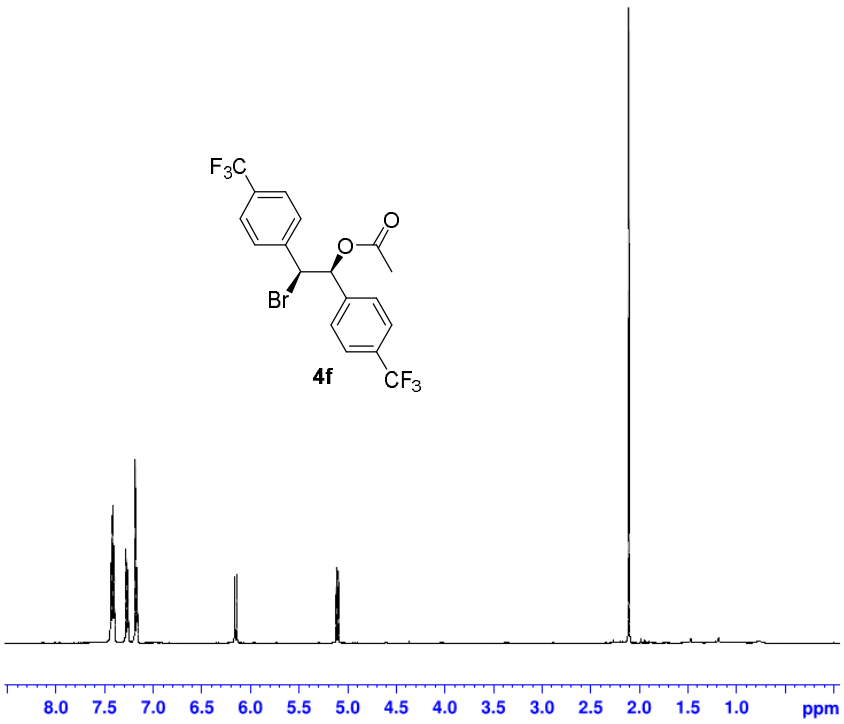
4e



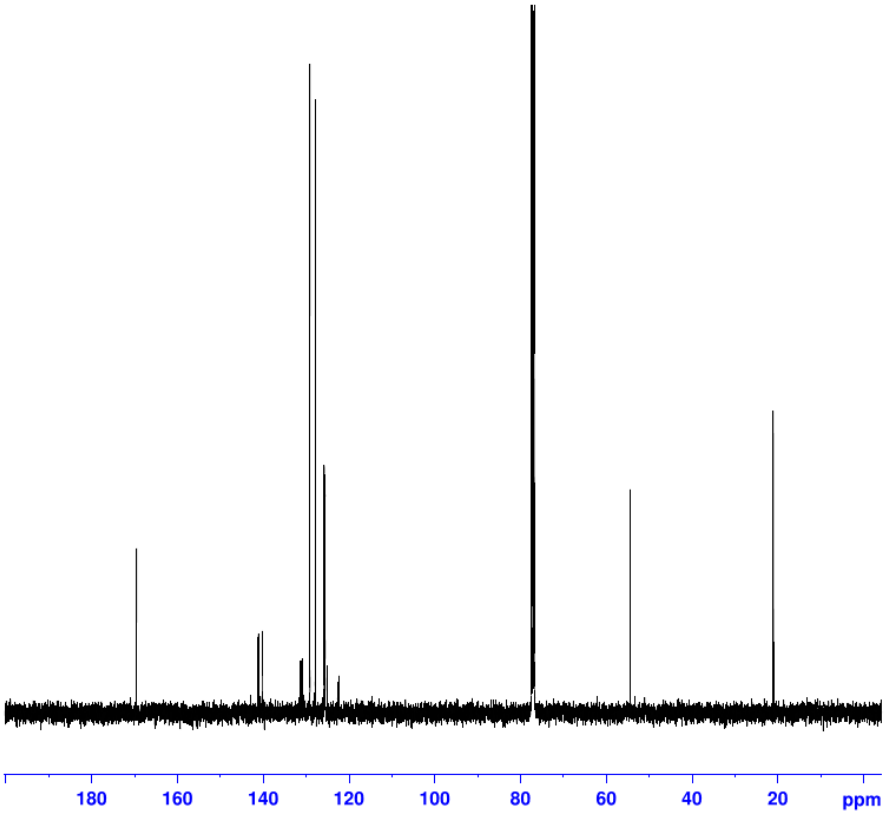


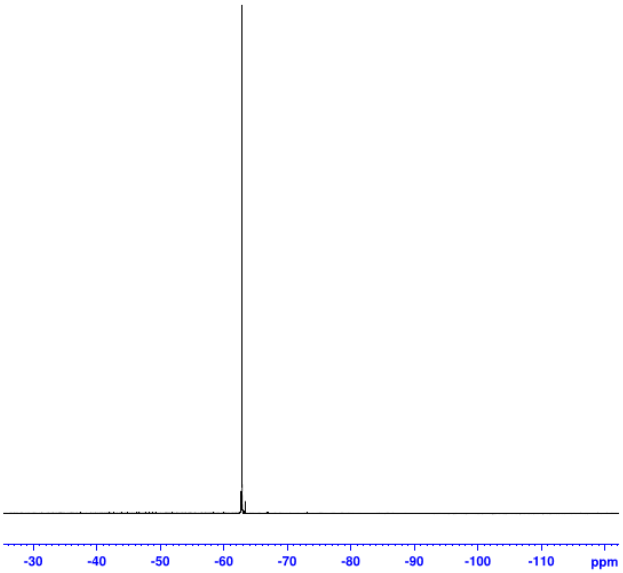

```
Current Data Parameters
NAME          mFProdukt
EXPNO               291
PROCNO                1

F2 - Acquisition Parameters
Date_          20160623
Time              12.41
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgflqn
TD              131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG               205.35
DW                5.600 usec
DE                6.50 usec
TE               296.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        376.4324910 MHz
NUC1               19F
P1               14.65 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                65536
SF          376.4701380 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

(1S,2S)-2-Bromo-1,2-bis(4-(trifluoromethyl)phenyl)ethyl acetate (4f)



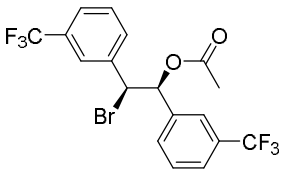

```
NAME            20-Sy419
EXPNO                310
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160601
Time               14.23
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                205.35
DW                62.400 usec
DE                 6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1024708 MHz
NUC1                  1H
P1                 13.70 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                 65536
SF            400.1000392 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```





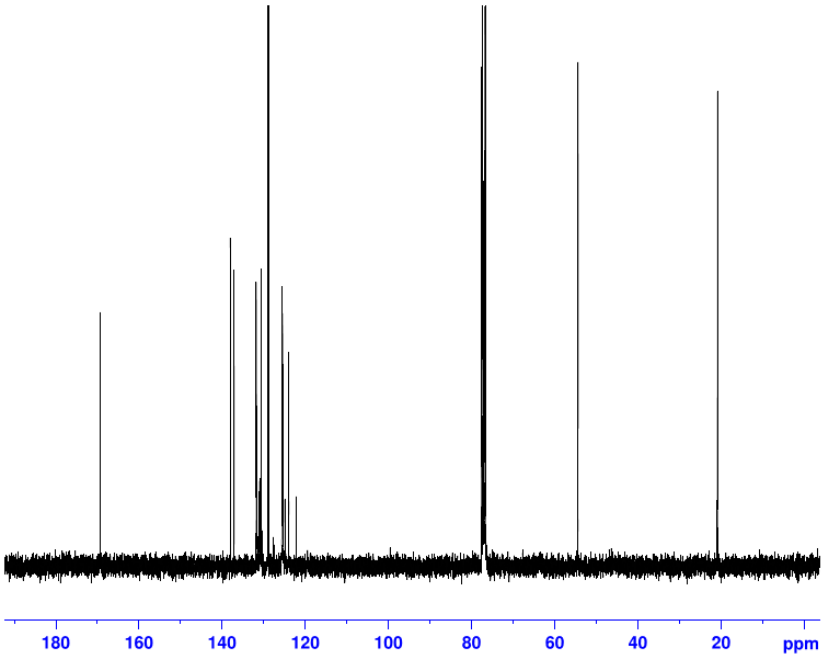

```
Current Data Parameters
NAME                  20-Sy419
EXPNO                      670
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160628
Time                   18.07
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zgflqn
TD                     131072
SOLVENT                CDCl3
NS                         16
DS                          4
SWH                89285.711 Hz
FIDRES             0.681196 Hz
AQ                 0.7340532 sec
RG                    205.35
DW                   5.600 usec
DE                    6.50 usec
TE                   296.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              376.4324910 MHz
NUC1                      19F
P1                      14.65 usec
PLW1             20.00000000 W

F2 - Processing parameters
SI                       65536
SF                376.4701380 MHz
WDW                         EM
SSB         0
LB                       0.30 Hz
GB          0
PC                       1.00
```

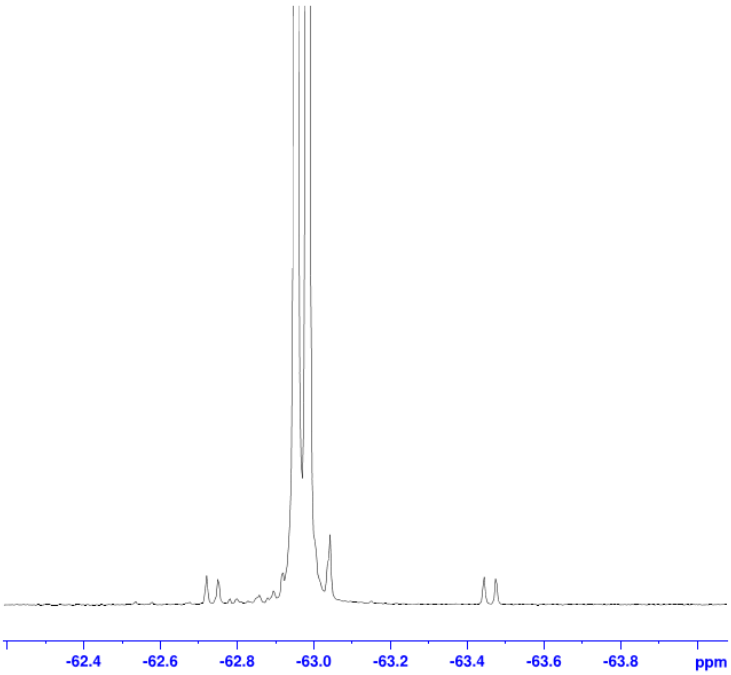
(1S,2S)-2-Bromo-1,2-bis(3-(trifluoromethyl)phenyl)ethyl acetate (4g)



4g

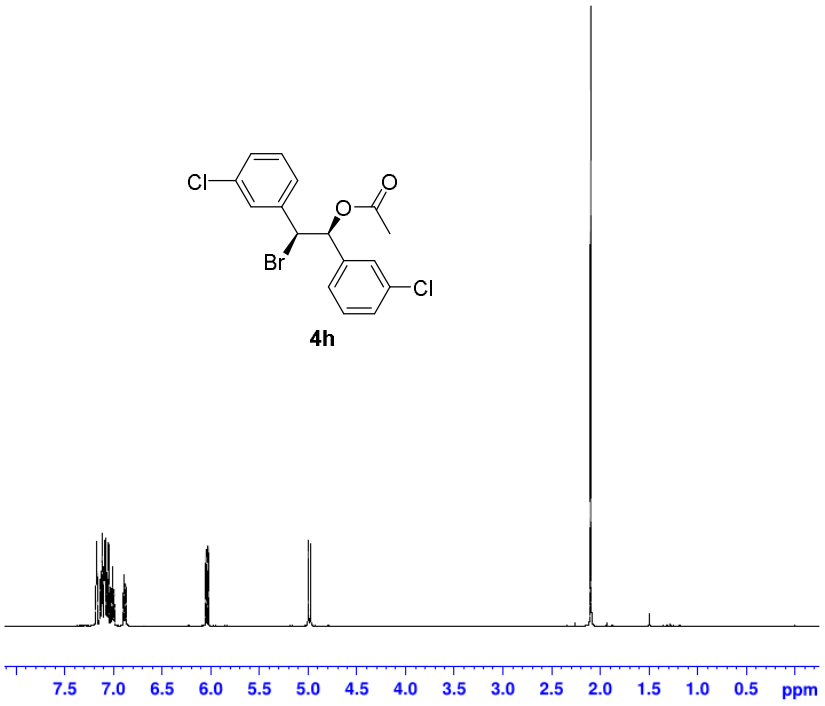

```
Current Data Parameters
NAME                  20-Sy418
EXPNO                      300
PROCNO                       1

F2 - Acquisition Parameters
Date_               20160601
Time                   14.17
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                 4.0894966 sec
RG                    182.64
DW                    62.400 usec
DE                     6.50 usec
TE                    296.0 K
D1              1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1            400.1024708 MHz
NUC1                      1H
P1                     13.70 usec
PLW1           12.00000000 W

F2 - Processing parameters
SI                    65536
SF              400.1000400 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



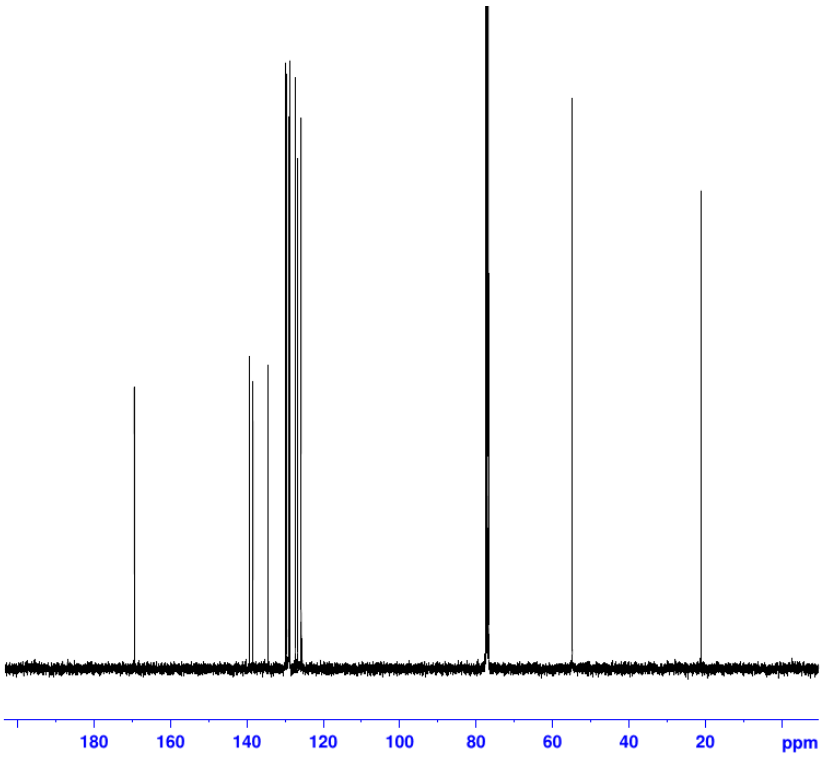



```
Current Data Parameters
NAME                  20-Sy418
EXPNO                      660
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20160628
Time                     18.03
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                zgflqn
TD                     131072
SOLVENT                  CDCl3
NS                           16
DS                            4
SWH                89285.711 Hz
FIDRES              0.681196 Hz
AQ                  0.7340532 sec
RG                     205.35
DW                      5.600 usec
DE                      6.50 usec
TE                     296.0 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               376.4324910 MHz
NUC1                       19F
P1                       14.65 usec
PLW1              20.00000000 W

F2 - Processing parameters
SI                       65536
SF                 376.4701380 MHz
WDW                         EM
SSB          0
LB                        0.30 Hz
GB           0
PC                       1.00
```

(1S,2S)-2-Bromo-1,2-bis(3-chlorophenyl)ethyl acetate (4h)

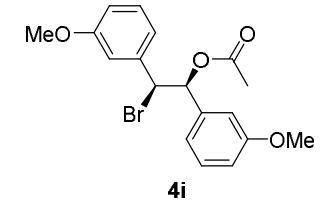



```
Current Data Parameters
NAME          mClSubstrat
EXPNO                 100
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160623
Time              10.57
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894966 sec
RG               124.07
DW               62.400 usec
DE                6.50 usec
TE               296.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         400.1024708 MHz
NUC1               1H
P1               13.70 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI               65536
SF           400.1000403 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```



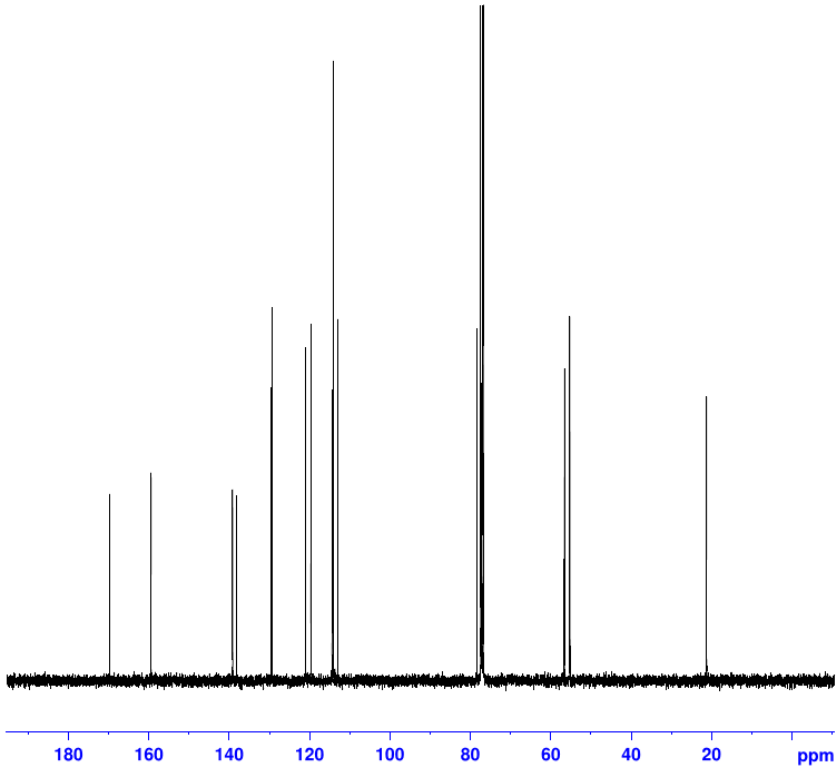

```
Data Parameters
    mClSubstrat
            100
              1

uisition Parameters
        20160623
           10.57
           spect
 5 mm PABBO BB/
           zg30
          65536
          CDCl3
             16
              2
        8012.820 Hz
        0.122266 Hz
       4.0894966 sec
          124.07
          62.400 usec
           6.50 usec
          296.0 K
     1.00000000 sec
              1

 CHANNEL f1 ========
    400.1024708 MHz
             1H
          13.70 usec
    12.00000000 W

cessing parameters
          65536
    400.1000403 MHz
              EM
 0
          0.30 Hz
 0
          1.00
```

(1S,2S)-2-Bromo-1,2-bis(3-methoxyphenyl)ethyl acetate (4i)

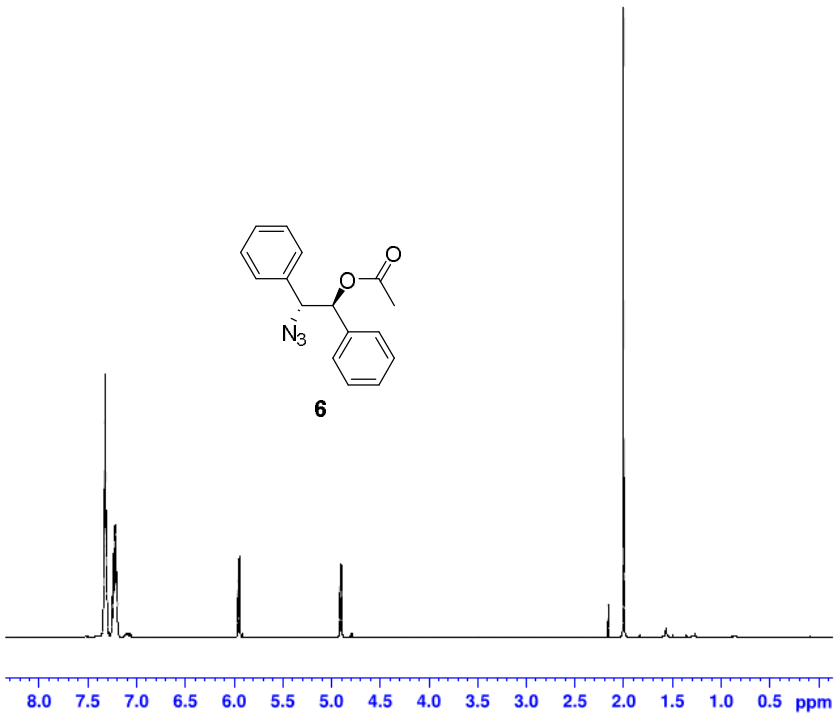


4i


```
Current Data Parameters
NAME          mOMeSubstrat
EXPNO                  110
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160623
Time              11.02
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ             4.0894966 sec
RG                124.07
DW                62.400 usec
DE                 6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         400.1024708 MHz
NUC1               1H
P1                13.70 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                65536
SF           400.1000000 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



(1S,2R)-2-Azido-1,2-diphenylethyl acetate (6)




```
Current Data Parameters
NAME                   Azid
EXPNO                   590
PROCNO                    1

F2 - Acquisition Parameters
Date_           20160727
Time                2.16
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                 124.07
DW                 62.400 usec
DE                  6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1024708 MHz
NUC1                  1H
P1                 13.70 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                 65536
SF            400.1000103 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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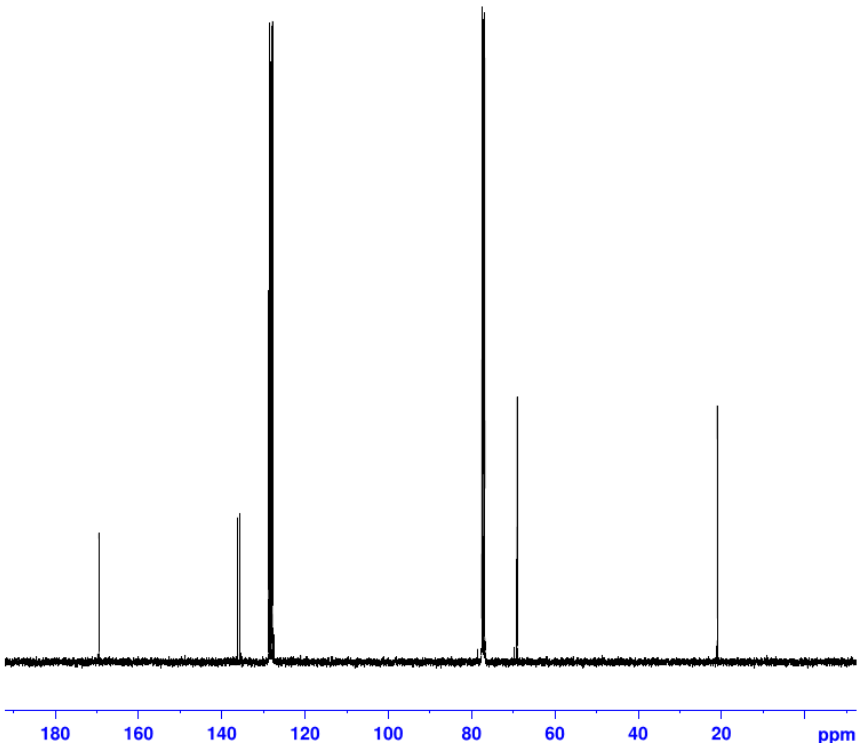
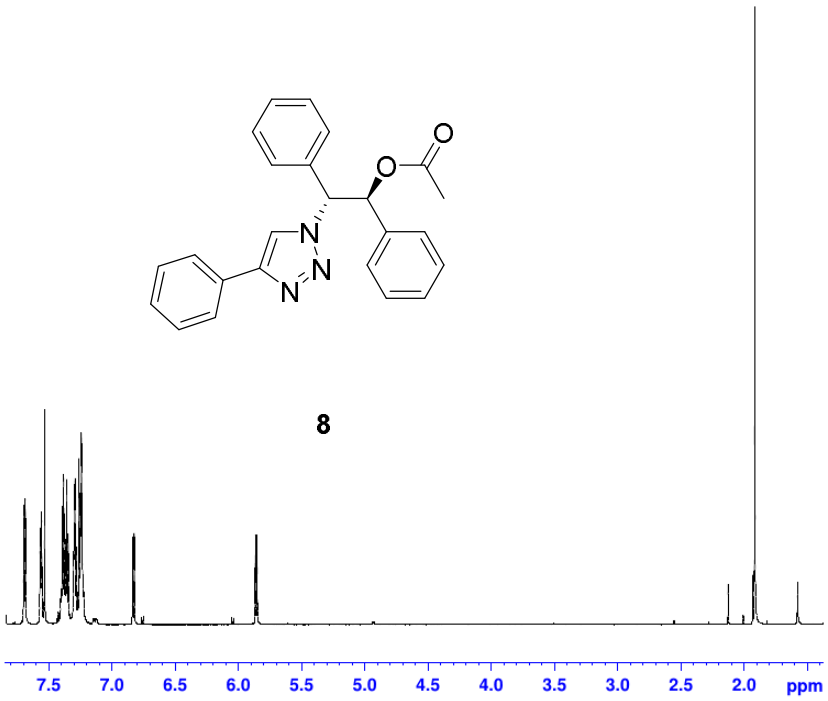


(1S,2R)-1,2-Diphenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl acetate (8)




```
Current Data Parameters
NAME        Funk-Triazol
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160728
Time              13.58
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           14097.744 Hz
FIDRES         0.215115 Hz
AQ            2.3243935 sec
RG               102.49
DW               35.467 usec
DE                6.50 usec
TE               298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         700.3643250 MHz
NUC1                 1H
P1                11.00 usec
PLW1         25.11899948 W

F2 - Processing parameters
SI                65536
SF           700.3600168 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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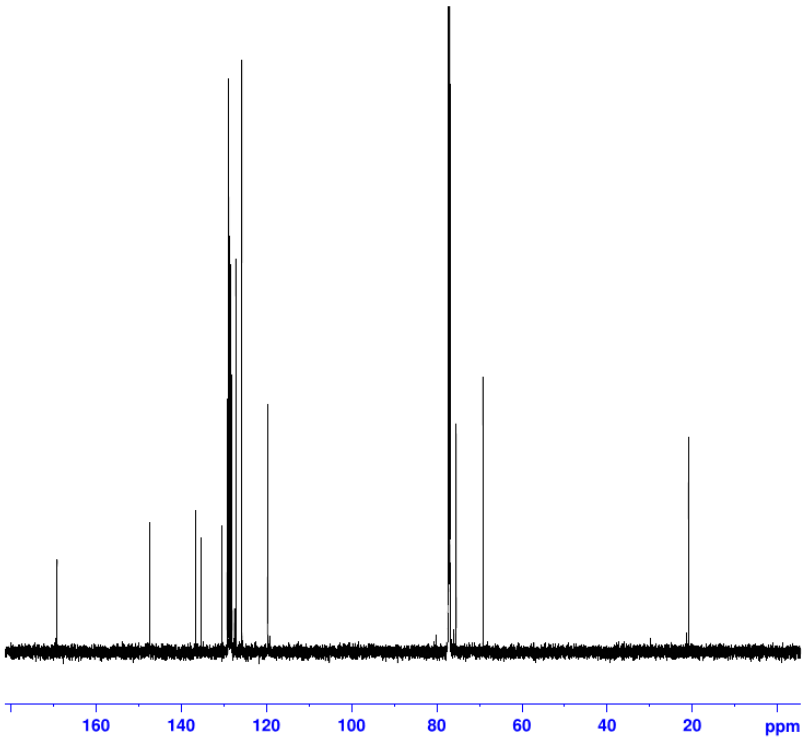
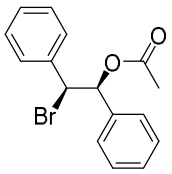


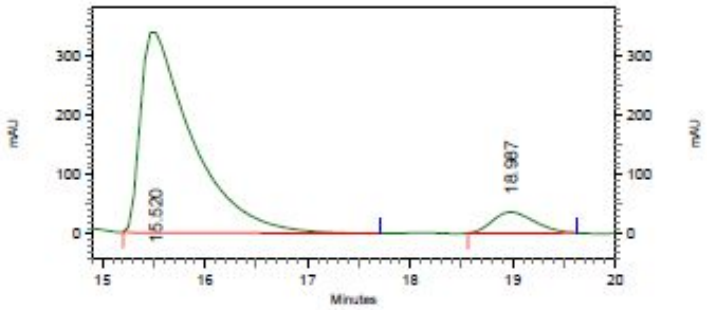
HPLC-Data

Compound:



4a

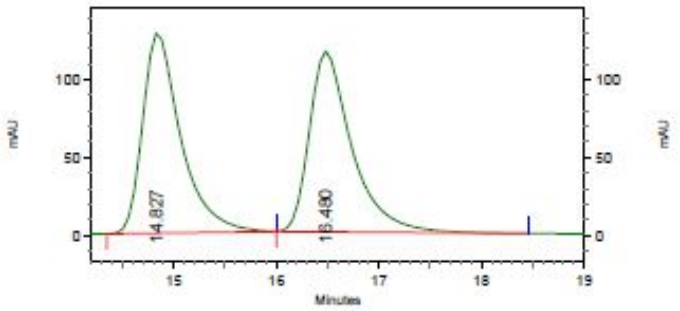
Column: Chiralpak AD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
15.520	1346436	47157783	92.124
18.987	142557	4031931	7.876
Totals	1488993	51189714	100.000

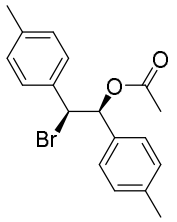
racemic reference:



UV Results

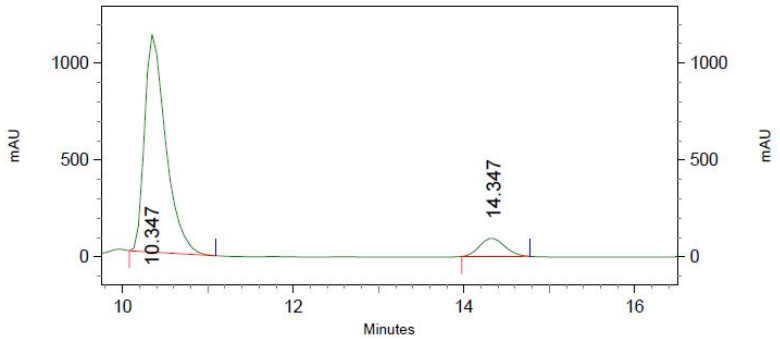
Retention Time	Height	Area	Area %
14.827	513632	13260877	49.89
16.480	464398	13318650	50.11
Totals	978030	26579527	100.00

Compound:



4b

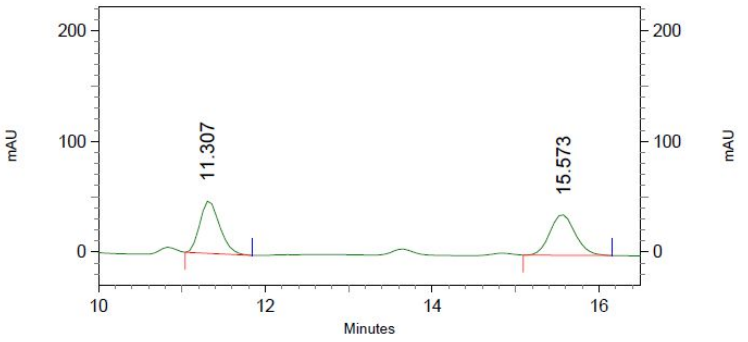
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
10.347	4492260	77367288	90.938
14.347	370879	7709562	9.062
Totals			
	4863139	85076850	100.000

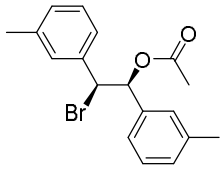
Nearlz racemic reference:



UV Results

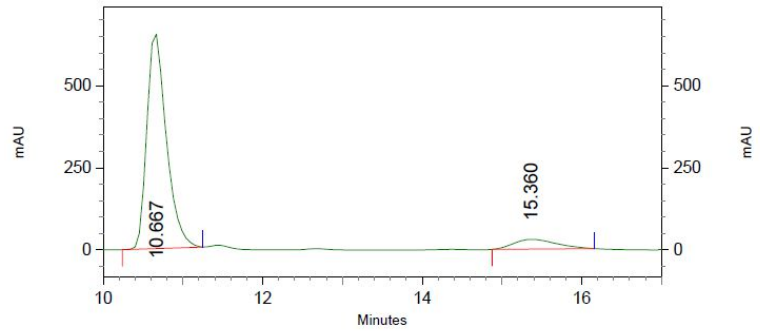
Retention Time	Height	Area	Area %
11.307	188458	3127539	50.22
15.573	146288	3100341	49.78
Totals			
	334746	6227880	100.00

Compound:



4c

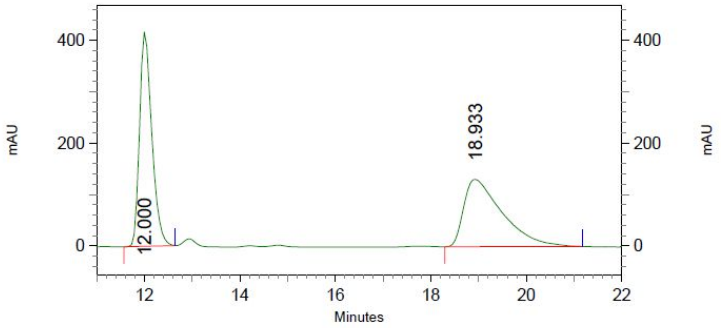
Column: Chiralpak AD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
10.667	2610094	44430257	91.064
15.360	117901	4359939	8.936
Totals	2727995	48790196	100.000

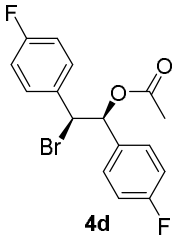
Nearly racemic reference:



UV Results

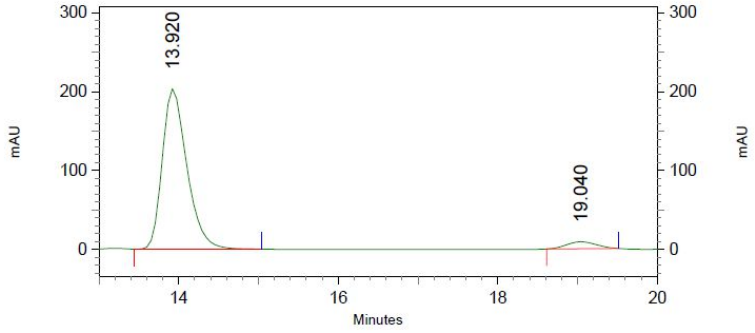
Retention Time	Height	Area	Area %
12.000	1668576	29796439	50.37
18.933	524630	29356079	49.63
Totals	2193206	59152518	100.00

Compound:



4d

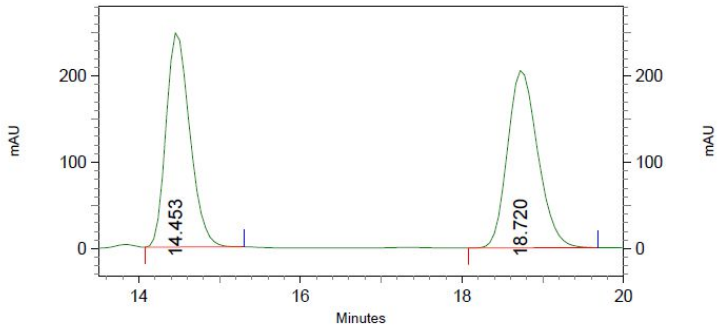
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
13.920	813604	17411643	94.937
19.040	36007	928589	5.063
Totals	849611	18340232	100.000

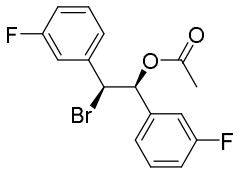
Nearly racemic reference:



UV Results

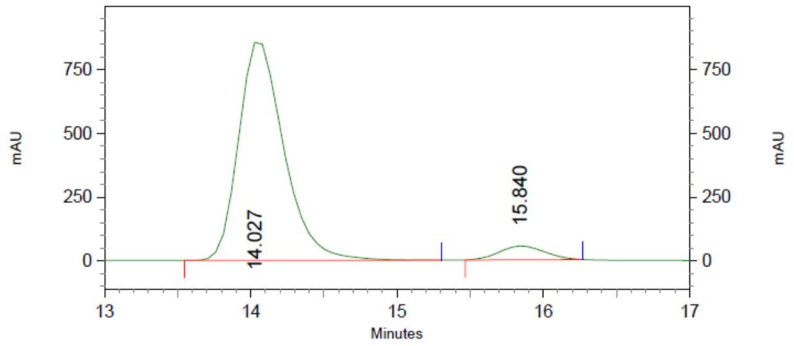
Retention Time	Height	Area	Area %
14.453	993132	20312733	48.66
18.720	821618	21427976	51.34
Totals	1814750	41740709	100.00

Compound:



4e

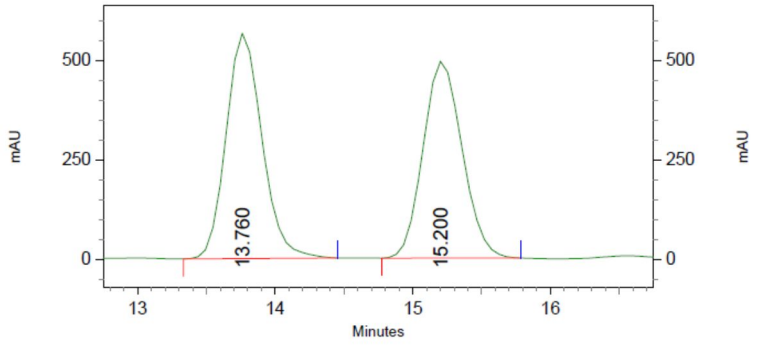
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
14.027	3413688	73698155	94.078
15.840	215675	4639405	5.922
Totals	3629363	78337560	100.000

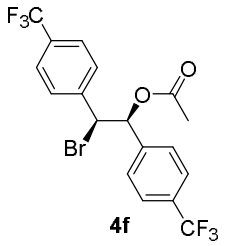
Nearly racemic reference:



UV Results

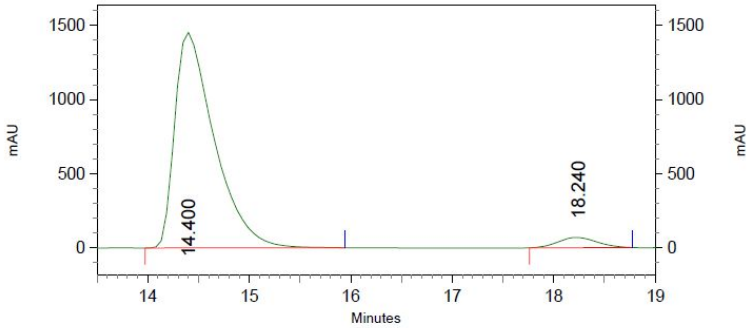
Retention Time	Height	Area	Area %
13.760	2262824	40968349	51.18
15.200	1976611	39077373	48.82
Totals	4239435	80045722	100.00

Compound:



4f

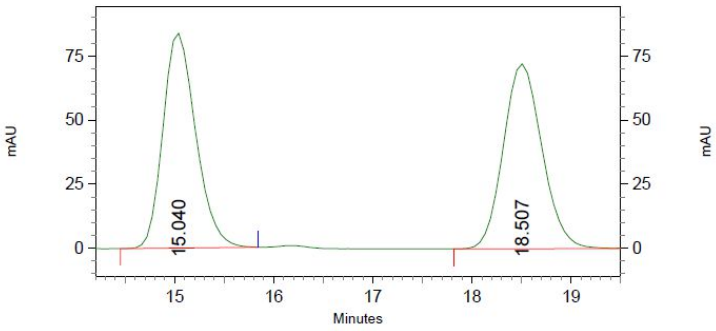
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
14.400	5811915	157193049	95.579
18.240	275301	7271085	4.421
Totals	6087216	164464134	100.000

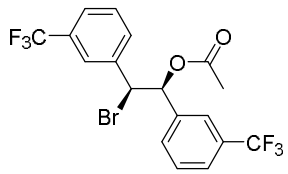
racemic reference:



UV Results

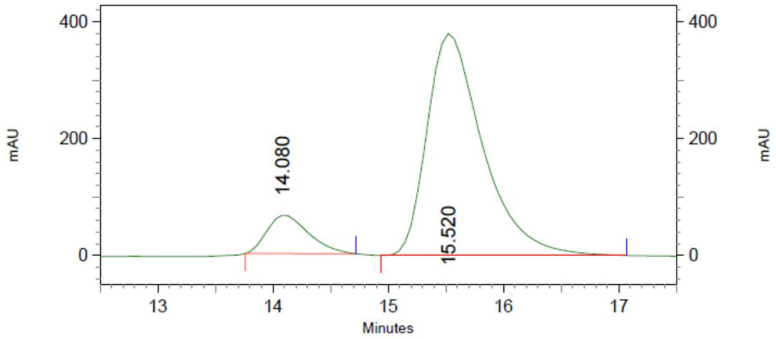
Retention Time	Height	Area	Area %
15.040	335288	7725863	49.69
18.507	288448	7821882	50.31
Totals	623736	15547745	100.00

Compound:



4g

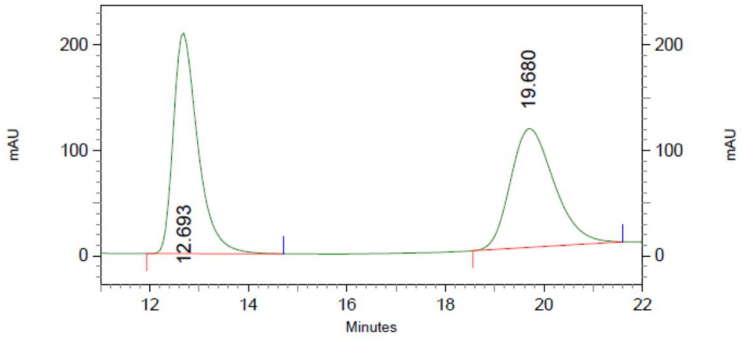
Column: Chiralpak AD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
14.080	263188	6609920	11.492
15.520	1518072	50909700	88.508
Totals			
	1781260	57519620	100.000

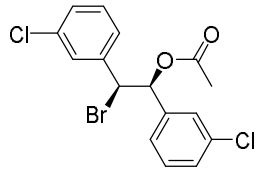
Nearly racemic reference:



UV Results

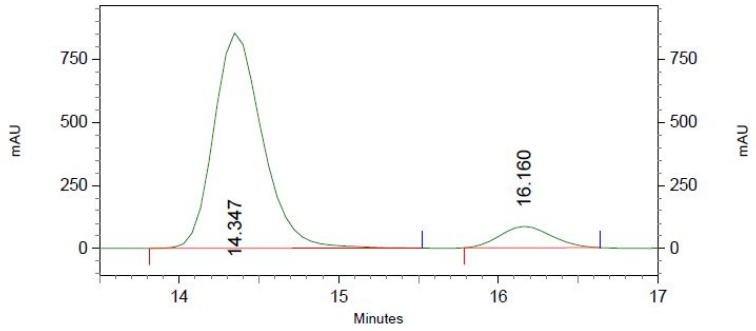
Retention Time	Height	Area	Area %
12.693	837791	28962984	51.03
19.680	450190	27790330	48.97
Totals			
	1287981	56753314	100.00

Compound:



4h

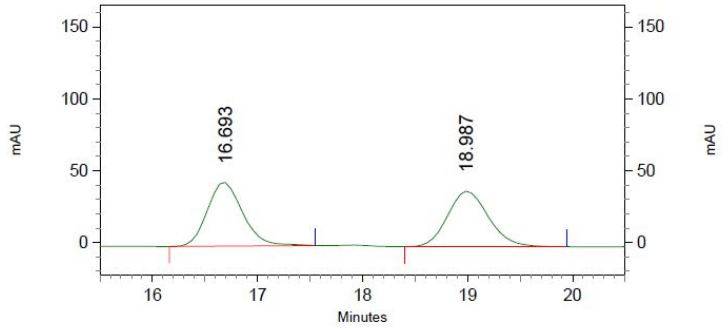
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
14.347	3412492	71859481	90.476
16.160	337445	7564735	9.524
Totals	3749937	79424216	100.000

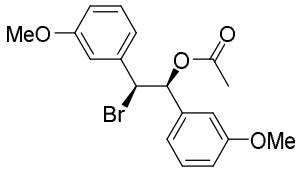
racemic reference:



UV Results

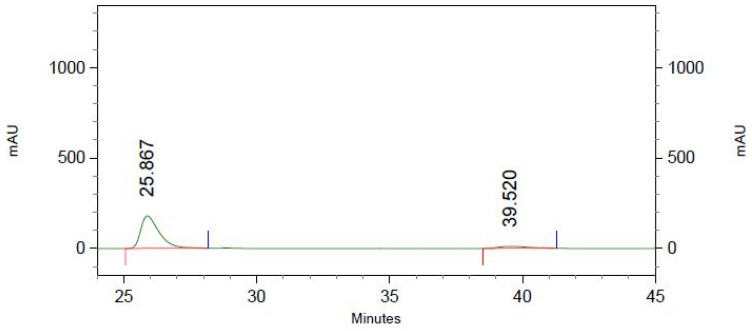
Retention Time	Height	Area	Area %
16.693	177351	4160776	49.85
18.987	154765	4185488	50.15
Totals	332116	8346264	100.00

Compound:



4i

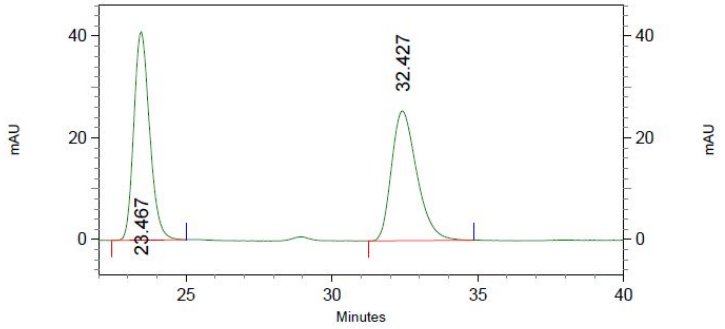
Column: Chiralpak OD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
25.867	718298	34460743	90.878
39.520	44211	3459189	9.122
Totals	762509	37919932	100.000

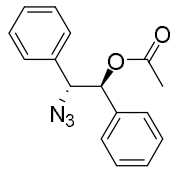
Racemic reference:



UV Results

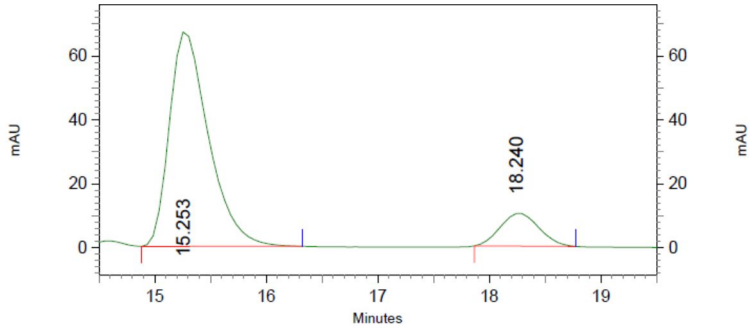
Retention Time	Height	Area	Area %
23.467	164224	6190078	50.12
32.427	102146	6160773	49.88
Totals	266370	12350851	100.00

Compound:



6

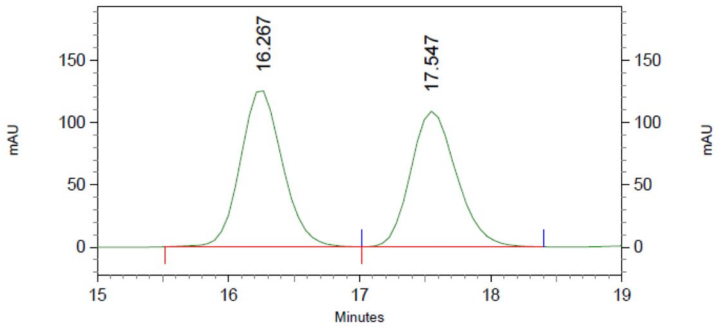
Column: Chiralpak AD-H
Method: *n*-Hexane/*i*-PrOH (99/1), 0.8 ml/min, 210 nm



UV Results

Retention Time	Height	Area	Area Percent
15.253	268318	6550666	86.939
18.240	40636	984118	13.061
Totals	308954	7534784	100.000

Nearly racemic reference:



UV Results

Retention Time	Height	Area	Area %
16.267	499721	11202000	51.54
17.547	434799	10531090	48.46
Totals	934520	21733090	100.00

References

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