

**Enantioselective Assembly of Tertiary Stereocenters via Multicomponent
Chemoselective Cross-Coupling of Geminal Chloro(iodo)alkanes**

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GENERAL METHODS

General procedures ----- 3

Materials ----- 3

Instrumentation ----- 3

PREPARATION OF SUBSTRATES

Representative procedure of synthesis geminal dihalide substrate -----4

SYNTHESIS OF DOUBLE CROSS-COUPLING PRODUCTS

Representative procedure for the generation of coupling product ----- 8

Determination of absolute configuration ----- 12

References ----- 38

$^1\text{H}/^{13}\text{C}/^{19}\text{F}$ Spectra ----- 39

GENERAL METHODS

General Procedures

All reactions were generally performed in glove box or in dried glassware under an atmosphere of dry N_2 . Reaction mixtures were stirred magnetically unless otherwise indicated and monitored by thin layer chromatography (TLC) on Merck precoated glass-backed silica gel 60 F-254 0,25 mm plates with visualization by fluorescence quenching at 254 nm. TLC plates were stained using potassium permanganate. Chromatography purification of products (flash column chromatography) was performed on silica gel 60 (70-230 mesh, Merck) using a forced flow of eluent at 0.3-0.5 bar. Concentration of reaction product solutions and chromatography fractions under reduced pressure was performed by rotary evaporation at 35-45°C at the appropriate pressure and then at rt, ca. 10 mmHg (vacuum pump) unless otherwise indicated.

Materials

All chemicals, including dry solvents were purchased from Aldrich, Fluka, Acros, TCI, Merck, Strem, DiaminoPharm or Alfa Aesar and used as such unless stated otherwise. Yields given refer to chromatographically purified compounds unless otherwise demonstrated.

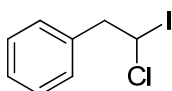
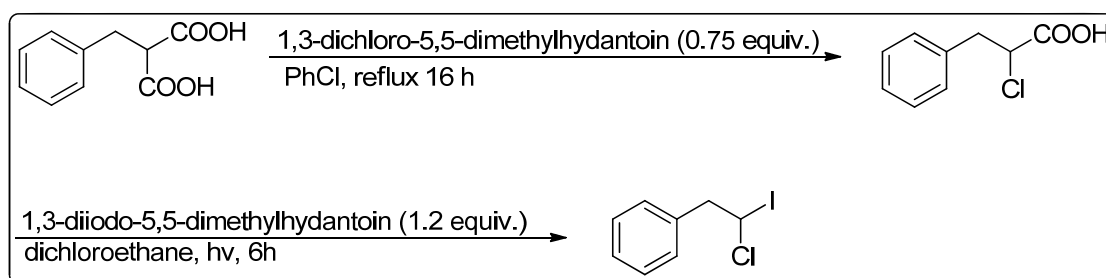
Instrumentation

Infrared (IR) spectra were recorded on a FTIR-Bruker spectrophotometer and reported as wavenumber (cm^{-1}) of the absorption maxima for the range between 4000 cm^{-1} and 400 cm^{-1} with only major peaks reported. 1H NMR spectra was recorded on Bruker 500 MHz, 400 MHz, 300 MHz and 200 MHz spectrometer. ^{13}C NMR spectra was recorded on Bruker 125 MHz, 100 MHz, 75 MHz and 50 MHz spectrometer. ^{19}F NMR spectra was recorded on Bruker 188 MHz. 1H NMR chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane (with the $CHCl_3$ peak at 7.26 ppm used as standard). ^{13}C NMR chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane (with the central peak of $CHCl_3$ at 77.16 ppm used as standard). ^{19}F NMR chemical shifts are expressed in parts per million (δ) (with the C_6F_6 peak at -164.9 ppm used as standard). All ^{13}C and ^{19}F spectra were measured with complete proton decoupling. NMR coupling constants (J) are reported in Hertz (Hz), and splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplet; t, triplet; q, quartet; m, multiplet. High resolution mass

spectrometric measurements (HRMS) were performed by the Waters LCT Premier and Bruker maxis impact with APCI solid probe. Enantiomeric excess were determined by HPLC analysis on Shimadzu HPLC units including the following instruments: pump, LC-20AT; detector, SPD-M20A; column, Daicel chiralcel OJ-H or OD-H. Optical rotations were recorded on a polarimeter (Optical Activity LTD).

PREPARATION OF SUBSTRATES

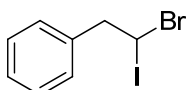
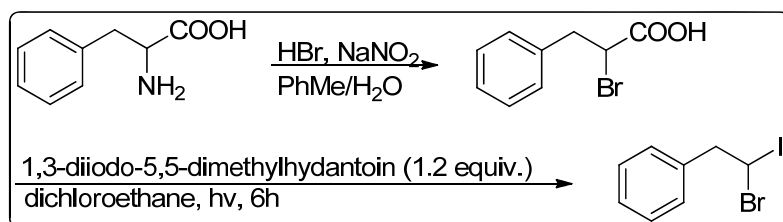
Representative procedure of synthesis geminal dihalide substrate



(2-chloro-2-iodoethyl)benzene

In a 100 mL round bottom flask, benzyl malonic acid (1.16 g, 6 mmol) 1,3-dichloro-5,5-dimethylhydantoin (886 mg, 4.5 mmol) and PhCl 18 mL were charged at room temperature under N₂ flow. The mixture was heated to reflux and stirred for 16 h. The reaction mixture was then cooled to room temperature. After evaporating the solvent, the mixture was directly subjected to flash column chromatography using hexanes/EtOAc as eluent and obtained the desired Chloro-acid intermediate as yellow color oil, which was subjected to iodo-decarboxylation process followed by reported procedure¹.

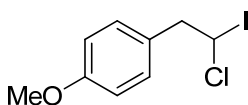
85%; Yellow oil; IR (neat) 3030, 3015, 699, 417; ¹H NMR (CDCl₃, 400 MHz): δ 7.30-7.22 (m, 5H), 5.79-5.76 (t, *J* = 13.6 Hz, 1H), 3.67-3.51 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 137.4, 129.4, 128.7, 128.5, 127.7, 52.8, 29.6; HRMS (APCI) calcd for C₈H₈NaClI [M + Na]⁺: 288.9257; found: 288.9230.



(2-bromo-2-iodoethyl)benzene

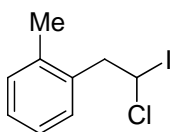
In a 100 mL round bottom flask, 48% HBr (4.08g, 24.2 mmol), water 2 mL and PhMe 6 mL were charged at 15 °C under N₂ flow. The mixture was cooled down to 0 °C and phenylalanine (1g, 6 mmol) was added. The reaction mixture was cooled to -5 °C. A solution of NaNO₂ (543 mg, 7.9 mmol) in water 1mL was added dropwise to the reaction mixture. After the addition, the reaction mixture was brought to room temperature and stirred for another 3 h. The organic phase was separated and diluted with 10 mL toluene which subsequently washed with water (10 mL) then brine (10 mL). The organic phase was then dried over MgSO₄ and evaporated to produce the desired Bromo-acid intermediate which was subjected to next step (iodo-decarboxylation) without further purification.

80%; Yellow oil; IR (neat) 3020, 3007, 698, 402; ¹H NMR (CDCl₃, 400 MHz): δ 7.31-7.19 (m, 5H), 5.53-5.50 (t, *J* = 7.2 Hz, 1H), 3.67-3.51 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 137.4, 129.4, 128.7, 128.5, 127.7, 52.8, 29.6; HRMS (APCI) calcd for C₈H₈NaBrI [M + Na]⁺: 332.8752; found: 332.8750.



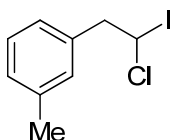
1-(2-chloro-2-iodoethyl)-4-methoxybenzene

76%; Yellow oil; IR (neat) 3031, 3015, 704, 414; ¹H NMR (CDCl₃, 400 MHz): δ 7.14-6.82 (m, 4H), 5.73-5.70 (t, *J* = 6.8 Hz, 1H), 3.77 (s, 3H), 3.60-3.43 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 159.1, 130.5, 129.6, 129.4, 114.0, 55.3, 51.9, 30.8; HRMS (APCI) calcd for C₉H₁₀OClI [M]⁺: 295.9465; found: 295.9467.



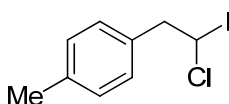
1-(2-chloro-2-iodoethyl)-2-methylbenzene

86%; Yellow oil; IR (neat) 3029, 3012, 701, 418; ^1H NMR (CDCl_3 , 400 MHz): δ 7.25-7.20 (m, 4H), 5.83-5.80 (t, $J = 7.0$ Hz, 1H), 3.78-3.60 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 136.4, 136.0, 130.8, 130.3, 127.9, 126.3, 50.2, 28.8, 19.7.



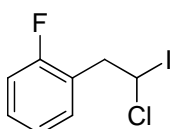
1-(2-chloro-2-iodoethyl)-3-methylbenzene

84%; Yellow oil; IR (neat) 3028, 3011, 698, 416; ^1H NMR (CDCl_3 , 200 MHz): δ 7.31-7.08 (m, 4H), 5.86-5.79 (t, $J = 6.0$ Hz, 1H), 3.74-3.54 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 138.3, 137.3, 130.1, 128.5, 128.4, 126.4, 52.8, 29.8, 21.4; HRMS (APCI) calcd for $\text{C}_9\text{H}_{10}\text{ClI}$ $[\text{M}]^+$: 279.9516; found: 279.9456.



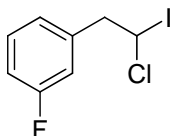
1-(2-chloro-2-iodoethyl)-4-methylbenzene

85%; Yellow oil; IR (neat) 3031, 3013, 699, 420; ^1H NMR (CDCl_3 , 300 MHz): δ 7.15 (s, board, 4H), 5.80-5.76 (t, $J = 6.9$ Hz, 1H), 3.67-3.49 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 137.3, 134.3, 129.3, 129.2, 52.3, 30.2, 21.2.



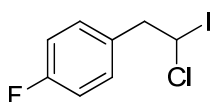
1-(2-chloro-2-iodoethyl)-2-fluorobenzene

82%; Yellow oil; IR (neat) 3024, 3012, 697, 415; ^1H NMR (CDCl_3 , 300 MHz): δ 7.35-7.02 (m, 4H), 5.90-5.85 (t, $J = 6.4$ Hz, 1H), 3.77-3.58 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 131.8 (d, $J = 4.2$ Hz), 129.6 (d, $J = 8.2$ Hz), 124.1 (d, $J = 21.5$ Hz), 115.6 (d, $J = 21.5$ Hz), 46.5, 27.3; ^{19}F NMR (CDCl_3 , 188 MHz): δ -121.0.



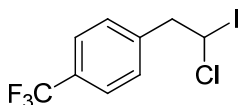
1-(2-chloro-2-iodoethyl)-3-fluorobenzene

84%; Yellow oil; IR (neat) 3027, 3014, 696, 413; ^1H NMR (CDCl_3 , 200 MHz): δ 7.38-6.96 (m, 4H), 5.85-5.78 (t, $J = 7.0$ Hz, 1H), 3.74-3.52 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 130.2 (d, $J = 8.2$ Hz), 125.0, 116.6 (d, $J = 21.4$ Hz), 114.9 (d, $J = 20.9$ Hz), 52.2, 28.2; ^{19}F NMR (CDCl_3 , 188 MHz): δ -115.9; HRMS (APCI) calcd for $\text{C}_8\text{H}_7\text{NaFCII}$ $[\text{M}+\text{Na}]^+$: 306.9163; found: 306.9196.



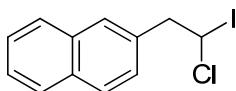
1-(2-chloro-2-iodoethyl)-4-fluorobenzene

90%; Yellow oil; IR (neat) 3020, 3011, 698, 411; ^1H NMR (CDCl_3 , 200 MHz): δ 7.28-7.00 (m, 4H), 5.82-5.75 (t, $J = 6.0$ Hz, 1H), 3.71-3.48 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 131.2 (d, $J = 8.1$ Hz), 115.8 (d, $J = 21.4$ Hz), 51.7, 29.6; ^{19}F NMR (CDCl_3 , 188 MHz): δ -117.6; HRMS (APCI) calcd for $\text{C}_8\text{H}_7\text{NaFCII}$ $[\text{M}+\text{Na}]^+$: 306.9163; found: 306.9160.



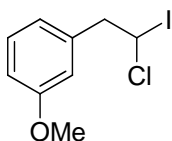
1-(2-chloro-2-iodoethyl)-4-(trifluoromethyl)benzene

91%; Yellow oil; IR (neat) 3024, 3008, 697, 409; ^1H NMR (CDCl_3 , 300 MHz): δ 7.61-7.35 (m, 4H), 5.84-5.79 (t, $J = 6.3$ Hz, 1H), 3.76-3.59 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 141.0, 129.8, 125.6 (q, $J = 4.1$ Hz), 52.0, 27.5; ^{19}F NMR (CDCl_3 , 188 MHz): δ -65.8; HRMS (APCI) calcd for $\text{C}_9\text{H}_9\text{OF}_3\text{CII}$ $[\text{M}+\text{H}_2\text{O}]^+$: 351.9339; found: 351.9336.



2-(2-chloro-2-iodoethyl)naphthalene

79%; Yellow oil; IR (neat) 3033, 3012, 702, 422; ^1H NMR (CDCl_3 , 200 MHz): δ 7.89-7.35 (m, 7H), 5.97-5.90 (t, $J = 6.0$ Hz, 1H), 3.92-3.70 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 135.2, 133.4, 128.4, 128.3, 127.8, 127.1, 126.4, 126.1, 52.8, 29.5; HRMS (APCI) calcd for $\text{C}_{12}\text{H}_{10}\text{ClI}$ $[\text{M}]^+$: 315.9510; found: 315.9542.



1-(2-chloro-2-iodoethyl)-3-methoxybenzene

77%; Yellow oil; IR (neat) 3025, 3014, 700, 423; ^1H NMR (CDCl_3 , 300 MHz): δ 7.68-6.59 (m, 4H), 5.97-5.92 (t, $J = 7.2$ Hz, 1H), 3.85-3.58 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 140.0, 135.9, 130.2, 117.6, 114.5, 55.5, 50.8, 26.6; HRMS (APCI) calcd for $\text{C}_9\text{H}_{10}\text{OClI}$ $[\text{M}]^+$: 295.9465; found: 295.9467.

SYNTHESIS OF DOUBLE CROSS-COUPLING PRODUCTS

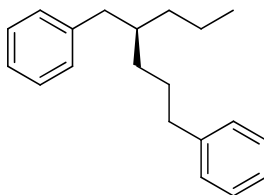
Representative procedure for the generation of **3b**.

1. Preparing of *n*-propyl-9BBN stock solution. In a glove box, 9-BBN dimer (1.22g, 5 mmol) *i*-Pr₂O (7 mL) was added in turn to a hydrogenation reactor. The reactor was capped and removed from the glove box. Propene gas was filled in the reactor and the reaction mixture was stirred under 5 atmospheres at room temperature (r.t.). After 16 hours, the reactor was taken back to the glove box and the reaction mixture was diluted with *i*-Pr₂O to furnish a 1 M solution. Next, a portion of the solution (2 mL, 2 mmol) was added to a solution of KO^tBu (179 mg, 1.6 mmol) in *i*-BuOH (148 mg, 2 mmol) in a 10-mL vial. The resulting mixture was stirred at r.t. for at least 45 mins, extra *i*-Pr₂O was added to make the solution with 0.5 M concentration.

2. Preparing of benzenepropyl-9BBN stock solution.

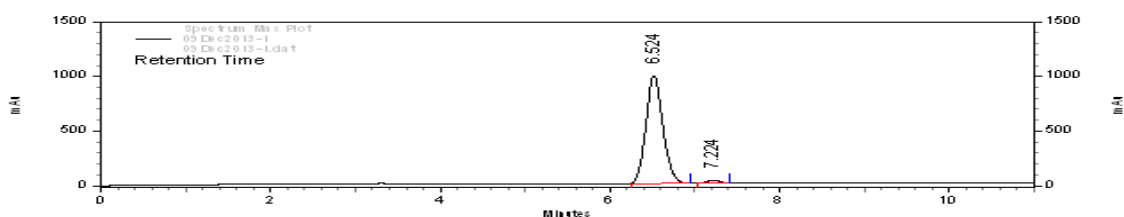
In a glovebox, 9-BBN dimer (244 mg, 1 mmol), *i*-Pr₂O (2 mL), and the Allyl benzene (260 mg, 2.2 mmol) were added in turn to a 10-mL vial and stirred for 24 h at room temperature. Next, this reaction mixture was added to a solution of KO^tBu (156 mg, 1.4 mmol) in *i*-BuOH (148 mg, 2.0 mmol) in a 10-mL vial. The resulting mixture was stirred at r.t. for at least 45 mins, extra *i*-Pr₂O was added to make the solution with 0.5 M concentration.

A solution of NiCl₂.glyme (11.0 mg, 0.050 mmol) and ligand **2** (14.4 mg, 0.06 mmol) in *i*-Pr₂O (1 mL) in a 20-mL vial was stirred at r.t. for 2 h. Next, geminal iodide-chloride electrophile **1a** (133 mg, 0.5 mmol) was added followed by 5.5 mL of *i*-Pr₂O, and then the solution of the activated *n*-propyl-9BBN (1.3 mL, 0.65 mmol) which contains KO^tBu (0.5 mmol) and *i*-BuOH (0.65 mmol) was added. After 24 h stirring, activated benzenepropyl-9BBN solution (2 mL, 1mmol) which contains KO^tBu (0.7 mmol) and *i*-BuOH (1 mmol) was added and the reaction mixture was stirred for another 48 h at r.t. before filtering through a silica gel, eluting with Et₂O (30 mL). The solvent was removed by rotary evaporation, and the residue was purified by chromatography using an eluent of hexane/dichloromethane. The product ((*S*)-(2-propylpentane-1,5-diyl)dibenzene), was obtained as a colorless oil (113 mg, 85%).

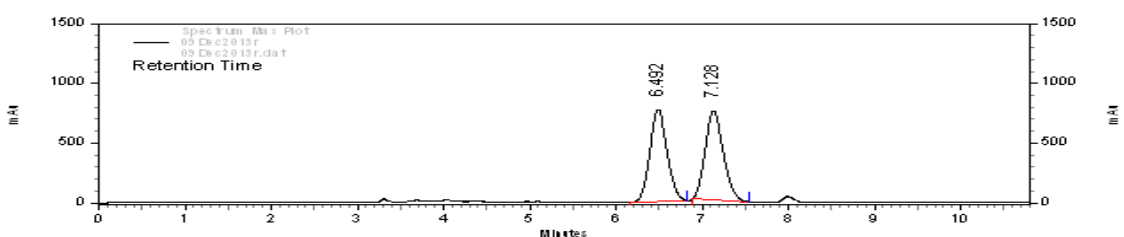


(S)-(2-propylpentane-1,5-diyl)dibenzene

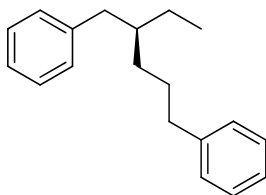
85%; Colorless oil; $[\alpha]_D^{25} + 12.5$ (c 1.0, CHCl₃, 96% ee); IR (neat) 3027, 1321, 998, 746; ¹H NMR (CDCl₃, 200 MHz): δ 7.32-7.08 (m, 10H), 2.63-2.56 (m, 4H), 1.74-1.59 (m, 3H), 1.31-1.27 (m, 6H), 0.93 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (CDCl₃, 50 MHz): δ 143.0, 141.7, 129.2, 128.4, 128.3, 128.1, 125.6, 125.5, 40.5, 39.4, 36.3, 35.5, 32.8, 28.6, 19.7, 14.4; HRMS (APCI) calcd for C₂₀H₂₇ [M]⁺: 267.2113; found: 267.2102; HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 1.5/98.5, 1.0 mL/min, 190 nm) t₁ = 6.5 min (major), t₂ = 7.2 min (minor).



Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
6.524	13676632	98.066	98692.7	97.499
7.224	269725	1.934	2531.6	2.501
Totals	13946357	100.000	1012243	100.000

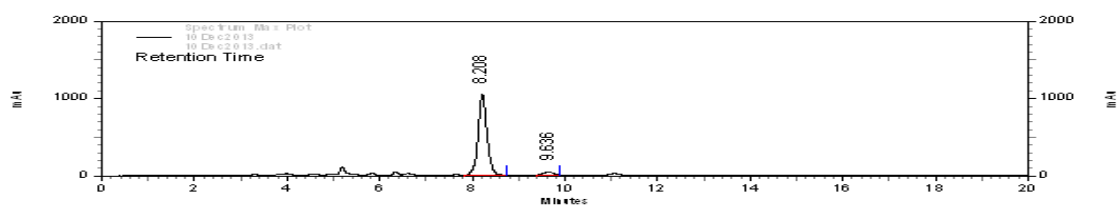


Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
6.492	10684829	49.436	77176.7	50.836
7.128	10928440	50.564	74637.6	49.164
Totals	21613269	100.000	1518143	100.000

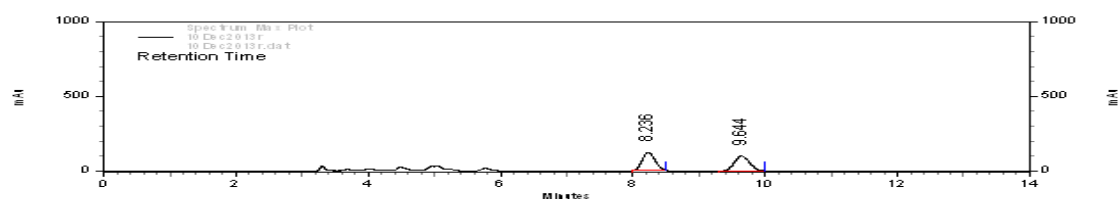


(S)-(2-ethylpentane-1,5-diyl)dibenzene

79%; Colorless oil; $[\alpha]_D^{25} + 9.1$ (*c* 1.0, CHCl₃, 92% ee); IR (neat) 3028, 1314, 1092, 768; ¹H NMR (CDCl₃, 400 MHz): δ 7.24-7.08 (m, 10H), 2.54-2.48 (m, 3H), 1.62-1.57 (m, 4H), 1.23-1.20 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 142.8, 141.7, 129.2, 128.4, 128.2, 128.1, 125.6, 125.5, 41.2, 40.1, 36.3, 32.3, 28.6, 25.4, 10.8; HRMS (APCI) calcd for C₁₉H₂₅ [M]⁺: 253.1956; found: 253.1960; HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 1.5/98.5, 1.0 mL/min, 190 nm) t₁ = 8.2 min (major), t₂ = 9.6 min (minor).



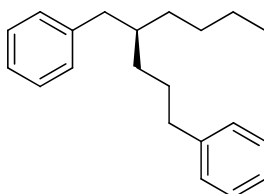
Retention Time	Area	Area Percent	Height
8.208	13704878	95.137	1040035
9.636	550654	3.863	39713
Totals	14255532	100.000	1079749



Retention Time	Area	Area Percent	Height
8.236	1620901	50.361	120687
9.644	1597652	49.639	99783
Totals	3218553	100.000	220470

Determination of absolute configuration

The absolute configuration of the double cross-coupling product obtained with ligand (*R,R*)-**2** was determined to be (*S*) by comparison to the reported optical rotation².

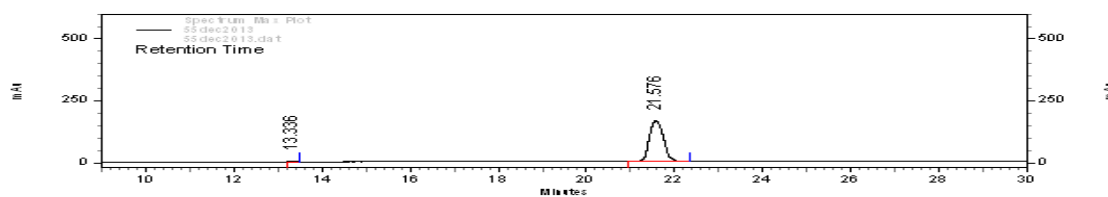


This result: $[\alpha]_D^{25} + 7.9$ (*c* 1.0, CHCl₃, 98% ee)

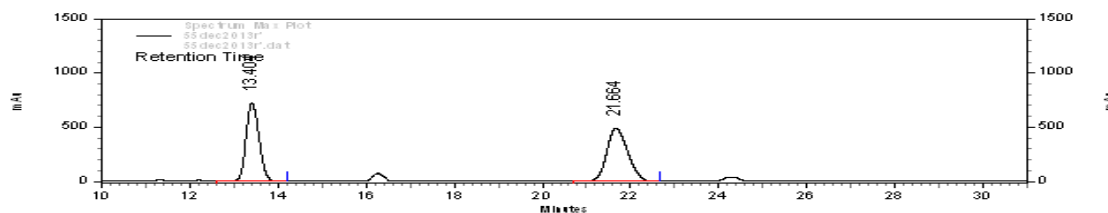
Reference 2: $[\alpha]_D^{22} + 8.5$ (*c* 1.0, CHCl₃, 93% ee)

(*S*)-(2-butylpentane-1,5-diyldibenzene)²

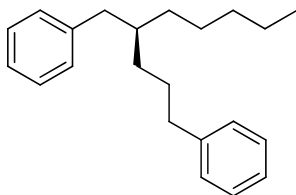
80%; $[\alpha]_D^{25} + 7.9$ (*c* 1.0, CHCl₃, 98% ee); ¹H NMR (CDCl₃, 200 MHz): δ 7.33-7.12 (m, 10H), 2.61-2.53 (m, 4H), 1.76-1.56 (m, 3H), 1.38-1.26 (m, 7H), 0.95-0.81 (m, 4H); ¹³C NMR (CDCl₃, 50 MHz): δ 142.9, 141.7, 129.2, 128.3, 128.2, 128.1, 125.6, 125.5, 40.5, 39.5, 36.3, 32.8, 28.8, 28.5, 23.0, 14.1; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 13.3 min (minor), t₂ = 21.6 min (major).



Retention Time	Area	Area Percent	Height	
13.336	32379	0.887	3315	1.987
21.576	3617526	99.113	163538	98.013
Totals	3649905	100.000	166853	100.000

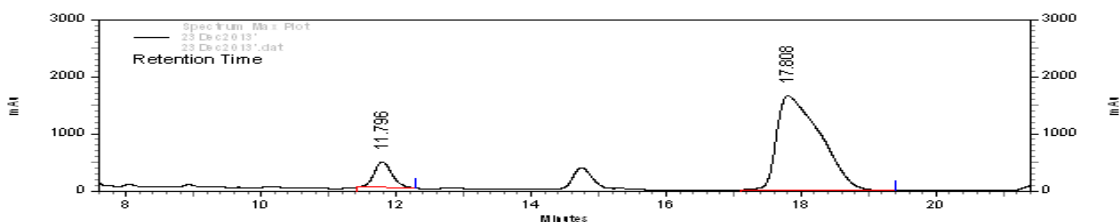


Retention Time	Area	Area Percent	Height	
13.404	14824646	48.237	722319	59.788
21.664	15909105	51.763	485604	40.202
Totals	30732751	100.000	1207923	100.000

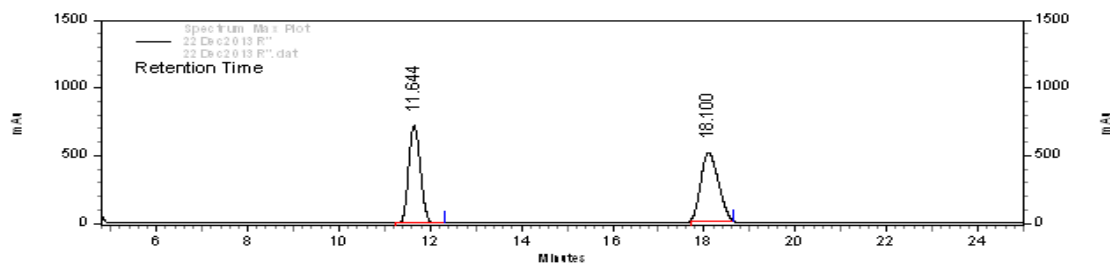


(S)-(2-pentylpentane-1,5-diyl)dibenzene

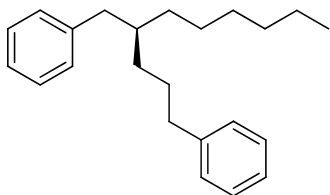
81%; Colorless oil; $[\alpha]_D^{25} + 6.7$ (c 1.0, CHCl_3 , 80% ee); IR (neat) 3019, 1300, 982, 708; ^1H NMR (CDCl_3 , 300 MHz): δ 7.28-7.10 (m, 10H), 2.57-2.50 (m, 4H), 1.60-1.58 (m, 3H), 1.34-1.22 (m, 11H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 142.6, 141.3, 129.1, 128.3, 128.1, 128.0, 125.5, 125.4, 40.4, 39.5, 36.2, 32.9, 32.6, 32.1, 28.4, 26.1, 22.6, 14.0; HRMS (APCI) calcd for $\text{C}_{22}\text{H}_{31}$ $[\text{M}+1]^+$: 295.2426; found: 295.2429. HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0.2/99.8, 1.0 mL/min, 190 nm) $t_1 = 11.8$ min (minor), $t_2 = 17.8$ min (major).



Retention Time	Area	Area Percent	Height	
11.796	8409734	10.227	450330	21.430
17.808	73817469	89.773	1651030	78.570
Totals	82227203	100.000	2101360	100.000

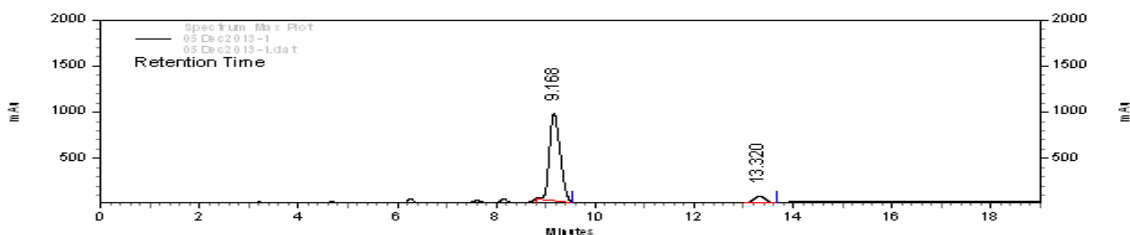


Retention Time	Area	Area Percent	Height	
11.644	12813448	48.628	719005	58.848
18.100	13536232	51.372	502800	41.152
Totals	26349680	100.000	1221805	100.000

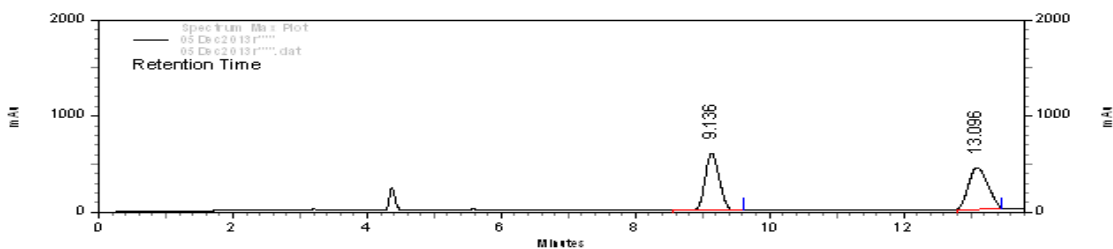


(S)-(2-hexylpentane-1,5-diyl)dibenzene

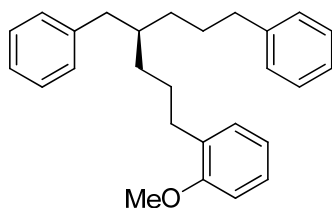
83%; Colorless oil; $[\alpha]_D^{25}$ - 3.2 (*c* 1.0, CHCl₃, 89% ee); IR (neat) 3020, 1294, 987, 729; ¹H NMR (CDCl₃, 200 MHz): δ 7.33-7.12 (m, 10H), 2.62-2.54 (m, 4H), 1.70-1.55 (m, 4H), 1.38-1.27 (m, 12H), 0.93 (t, *J* = 6.1 Hz, 3H); ¹³C NMR (CDCl₃, 50 MHz): δ 142.8.0, 141.7, 129.2, 128.4, 128.2, 128.1, 125.6, 40.5, 39.6, 36.3, 33.1, 32.8, 31.9, 29.7, 28.5, 26.5, 22.7, 14.1; HRMS (APCI) calcd for C₂₃H₃₃ [M+]⁺: 309.2582; found: 309.2589. HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0.5/99.5, 1.0 mL/min, 190 nm) t₁ = 9.2 min (major), t₂ = 13.3 min (minor).



Retention Time	Area	Area Percent	Height
9.168	14259245	94.508	938157
13.320	828689	5.492	59455
Totals	15087934	100.000	997612

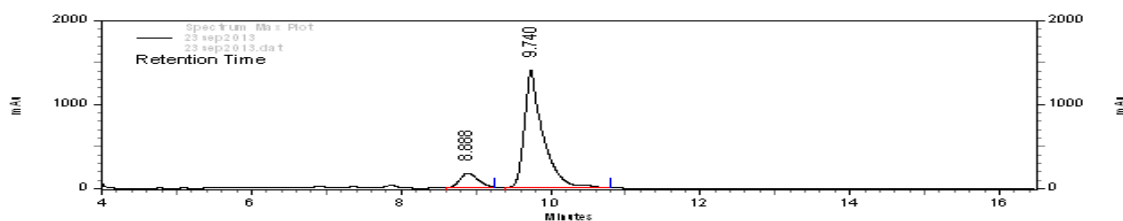


Retention Time	Area	Area Percent	Height
9.136	8301800	49.169	587014
13.096	8582537	50.831	430213
Totals	16884337	100.000	1017227

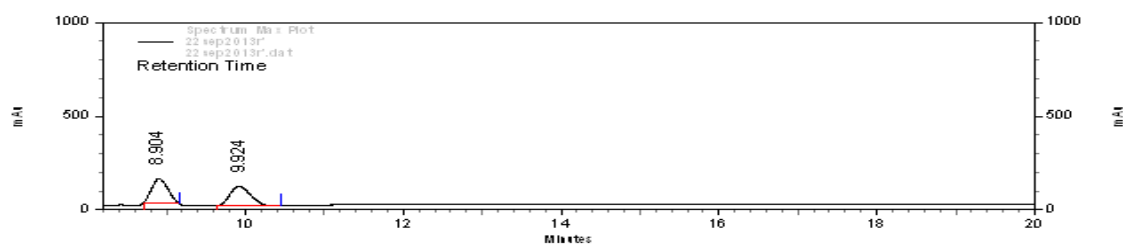


(S)-2-(2-(3-(2-methoxyphenyl)propyl)pentane-1,5-diyl)dibenzene

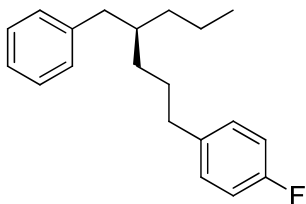
68%; Colorless oil; $[\alpha]_D^{25}$ - 14.6 (*c* 1.0, CHCl₃, 78% ee); IR (neat) 3017, 1287, 1011, 705; ¹H NMR (CDCl₃, 200 MHz): δ 7.35-6.77 (m, 14H), 3.85 (s, 3H), 2.64-2.48 (m, 6H), 1.73-1.59 (m, 5H), 1.39-1.26 (m, 4H); ¹³C NMR (CDCl₃, 50 MHz): δ 157.4, 142.8, 141.6, 131.2, 129.8, 129.3, 128.4, 128.3, 128.1, 126.9, 125.6, 125.5, 120.3, 110.2, 55.3, 40.4, 39.3, 32.9, 32.7, 30.5, 28.5, 26.8; HRMS (APCI) calcd for C₂₇H₃₃O [M+1]⁺: 373.2531; found: 373.2516. HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 1.5/98.5, 1.0 mL/min, 190 nm) t₁ = 8.9 min (minor), t₂ = 9.7 min (major).



Retention Time	Area	Area Percent	Height
8.888	2894026	10.807	171796
9.740	23885945	89.193	1402401
Totals	26779971	100.000	1574197

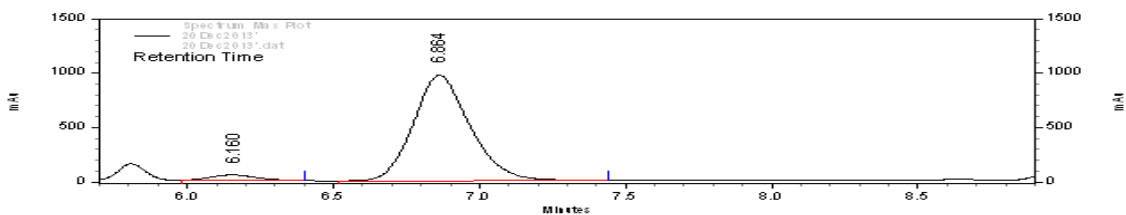


Retention Time	Area	Area Percent	Height
8.904	1850823	51.796	131440
9.924	1722458	48.204	98433
Totals	3573281	100.000	229873

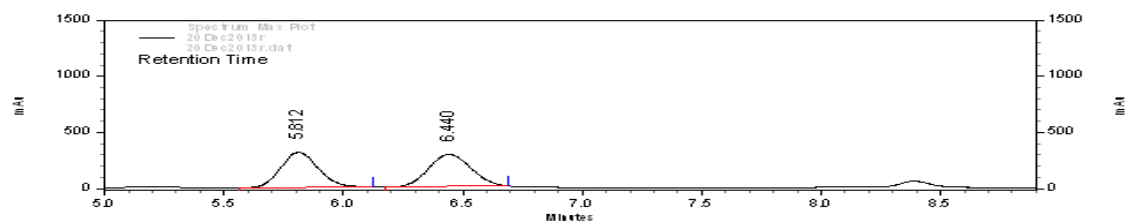


(S)-1-(4-benzylheptyl)-4-fluorobenzene

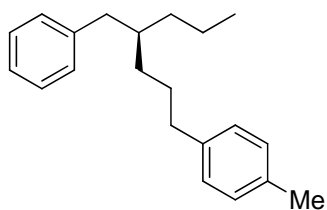
81%; Colorless oil; $[\alpha]_D^{25} + 10.3$ (*c* 1.0, CHCl₃, 92% ee); IR (neat) 3040, 3012, 1491, 1452, 798; ¹H NMR (CDCl₃, 400 MHz): δ 7.25-6.90 (m, 9H), 2.55-2.43 (m, 4H), 1.66-1.55 (m, 3H), 1.29-1.19 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 162.4 (d, *J* = 241.3 Hz), 141.6, 138.4 (d, *J* = 3.1 Hz), 129.7 (d, *J* = 7.7 Hz), 129.2, 128.3 (d, *J* = 15.8 Hz), 125.6, 115.0 (d, *J* = 20.9 Hz), 40.5, 39.4, 35.6, 35.4, 35.1, 32.6, 31.5, 29.0, 28.6, 19.7, 14.4; ¹⁹F NMR (CDCl₃, 188 MHz): δ -121.4; HRMS (APCI) calcd for C₂₀H₂₆F [M+]⁺: 285.2019; found: 285.2023; HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 1.5/98.5, 1.0 mL/min, 190 nm) t₁ = 6.2 min (minor), t₂ = 6.9 min (major).



Retention Time	Area	Area Percent	Height	
6.160	539273	3.958	49174	4.814
6.864	13085748	96.042	972288	95.186
Totals	13625021	100.000	1021462	100.000

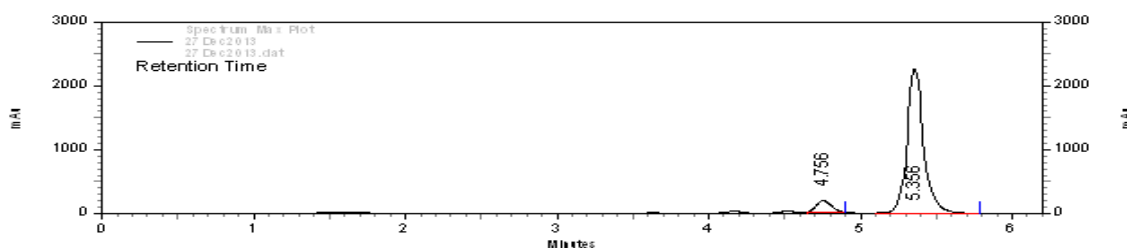


Retention Time	Area	Area Percent	Height	
5.812	3417457	49.177	313649	52.176
6.440	3531887	50.823	287487	47.824
Totals	6949344	100.000	601136	100.000

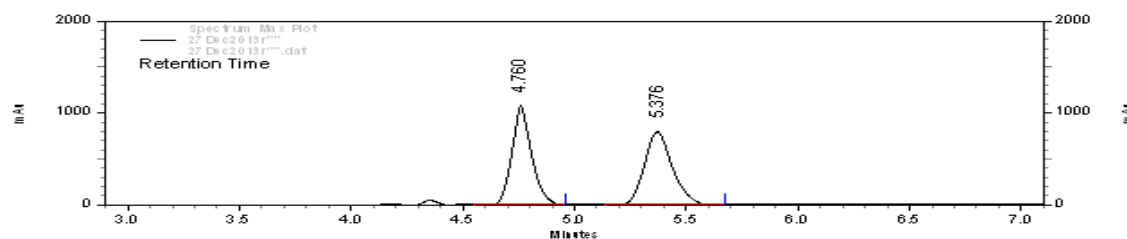


(S)-1-(4-benzylheptyl)-4-methylbenzene

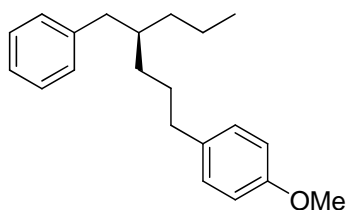
85%; Colorless oil; $[\alpha]_D^{25} + 20.6$ (c 1.0, CHCl_3 , 87% ee); IR (neat) 3044, 3011, 1495, 1453, 799; ^1H NMR (CDCl_3 , 200 MHz): δ 7.29-7.08 (m, 9H), 2.58-2.51 (m, 4H), 2.36 (s, 3H), 1.56-1.35 (m, 3H), 1.34-1.27 (m, 6H), 0.91 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 142.1, 139.9, 135.1, 129.2, 128.9, 128.2, 128.1, 40.5, 39.4, 35.9, 35.5, 32.9, 28.8, 21.0, 19.7, 14.5; HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{29}$ $[\text{M}+1]^+$: 281.2269; found: 281.2273. HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 4/96, 1.0 mL/min, 190 nm) $t_1 = 4.8$ min (minor), $t_2 = 5.4$ min (major).



Retention Time	Area	Area Percent	Height
4.756	1229157	6.614	180391
5.356	17355870	93.386	2251890
Totals	18585027	100.000	2432281

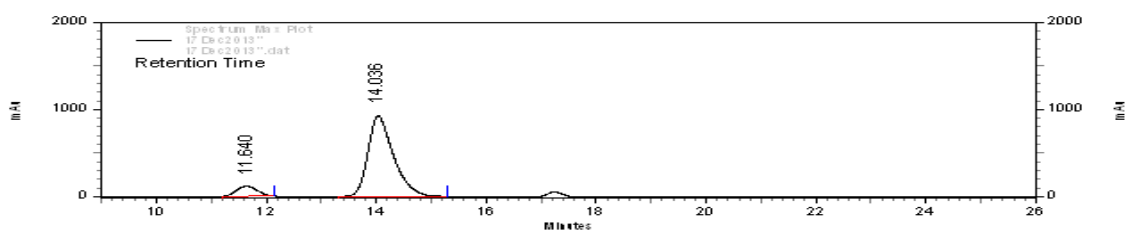


Retention Time	Area	Area Percent	Height
4.760	6484724	48.905	1078324
5.376	6775040	51.095	793433
Totals	13259764	100.000	1871757

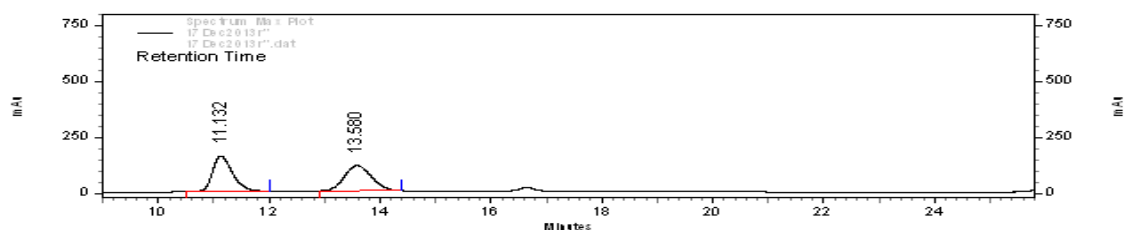


(S)-1-(4-benzylheptyl)-4-methoxybenzene

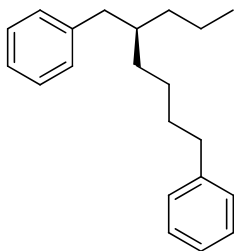
88%; Colorless oil; $[\alpha]_D^{25} + 10.1$ (c 1.0, CHCl_3 , 82% ee); IR (neat) 3042, 3016, 1493, 1450, 792; ^1H NMR (CDCl_3 , 400 MHz): δ 7.24-6.77 (m, 9H), 3.76 (s, 3H), 2.57-2.44 (m, 4H), 1.66-1.55 (m, 3H), 1.28-1.15 (m, 6H), 0.94 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 157.6, 141.7, 134.9, 129.2, 129.1, 128.1, 125.5, 113.7, 55.3, 40.5, 39.4, 35.5, 35.3, 32.7, 28.8, 19.7, 14.4; HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{29}\text{O}$ $[\text{M}+1]^+$: 297.2218; found: 297.2173. HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 1.5/98.5, 1.0 mL/min, 190 nm) $t_1 = 11.6$ min (minor), $t_2 = 14.0$ min (major).



Retention Time	Area	Area Percent	Height
11.640	299875.7	9.158	114143
14.036	2974624.2	90.842	930236
Totals	32744999	100.000	1044379

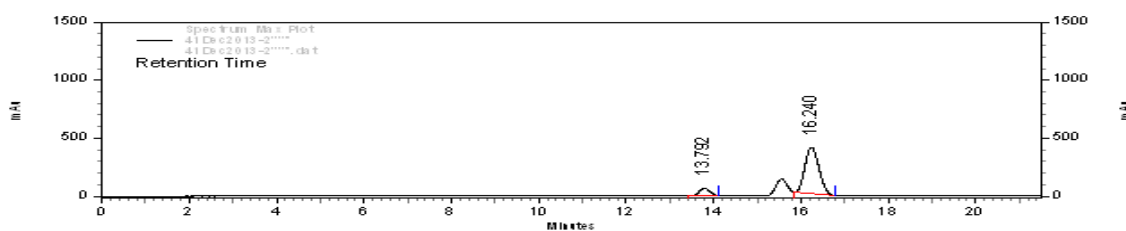


Retention Time	Area	Area Percent	Height
11.132	387334.0	50.253	156274
13.580	383436.4	49.747	112251
Totals	7707704	100.000	268525

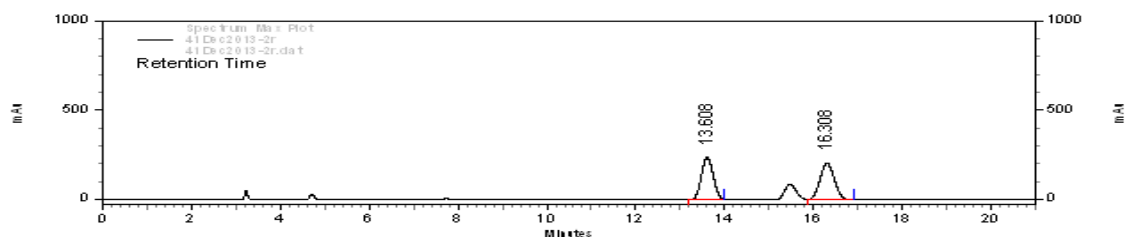


(S)-(2-propylhexane-1,6-diyl)dibenzene

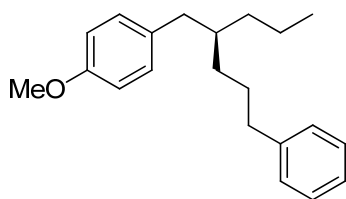
81%; Colorless oil; $[\alpha]_D^{25} + 7.4$ (c 1.0, CHCl_3 , 78% ee); IR (neat) 3040, 3017, 1490, 1452, 799; ^1H NMR (CDCl_3 , 400 MHz): δ 7.24-7.08 (m, 10H), 2.58-2.48 (m, 4H), 1.60-1.50 (m, 4H), 1.32-1.18 (m, 7H), 0.84 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 142.7, 141.6, 129.1, 128.3, 128.1, 128.0, 125.4, 125.3, 40.4, 39.3, 35.8, 35.4, 32.8, 31.7, 26.1, 19.6, 14.3; HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{29}$ $[\text{M}+1]^+$: 281.2245; found: 281.2254. HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 1/99, 1.0 mL/min, 190 nm) $t_1 = 13.8$ min (minor), $t_2 = 16.2$ min (major).



Retention Time	Area	Area Percent	Height
13.792	1132423	11.145	67064
16.240	9027985	88.855	400655
Totals	10160408	100.000	467719

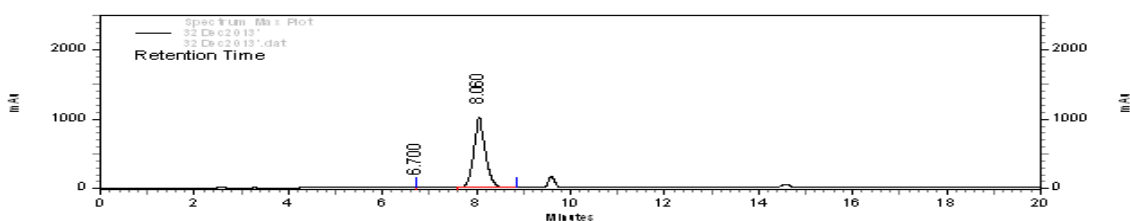


Retention Time	Area	Area Percent	Height
13.608	4305038	49.296	234438
16.308	4427962	50.704	201651
Totals	8733000	100.000	436089

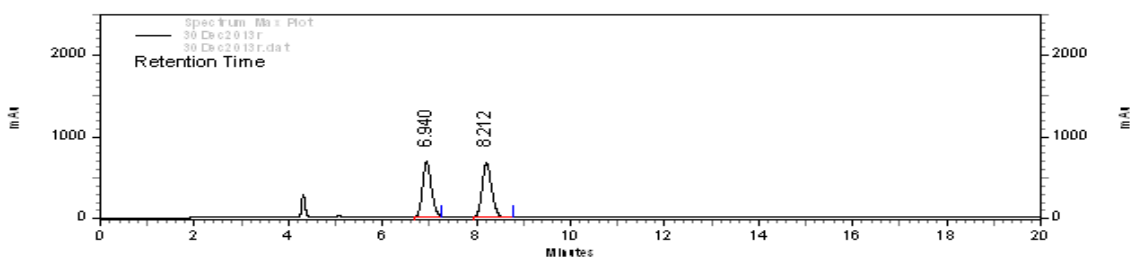


(S)-1-methoxy-4-(5-phenyl-2-propylpentyl)benzene

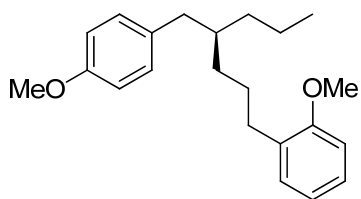
82%; Colorless oil; $[\alpha]_D^{25} + 5.4$ (c 1.0, CHCl_3 , >99% ee); IR (neat) 3029, 3015, 1458, 704; ^1H NMR (CDCl_3 , 200 MHz): δ 7.34-6.80 (m, 9H), 3.81 (s, 3H), 2.61-2.47 (m, 4H), 1.71-1.36 (m, 9H), 0.91 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 157.5, 142.8, 133.7, 130.0, 128.4, 128.2, 125.6, 113.5, 55.2, 39.5, 36.3, 35.5, 32.7, 28.6, 19.7, 14.4; HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{29}\text{O}$ $[\text{M}+1]^+$: 297.2218; found: 297.2220; HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 4/96, 1.0 mL/min, 190 nm) $t_1 = 6.7$ min (minor), $t_2 = 8.1$ min (major).



Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
6.700	0	0.000	0	0.000
8.060	16967386	100.000	1010643	100.000
Totals	16967386	100.000	1010643	100.000

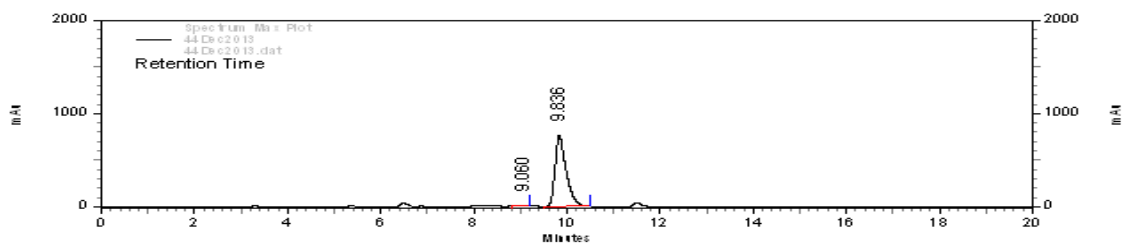


Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
6.940	8828168	49.264	677877	50.550
8.212	9091832	50.736	663117	49.450
Totals	17920000	100.000	1340994	100.000

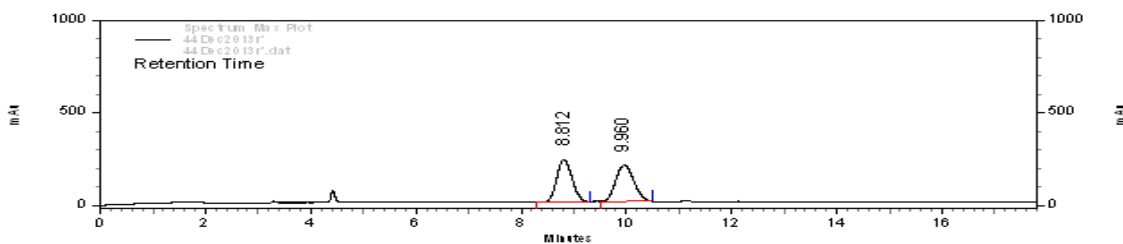


(S)-1-methoxy-2-(4-(4-methoxybenzyl)heptyl)benzene

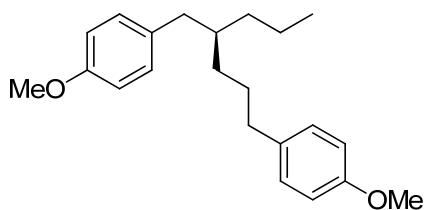
88%; Colorless oil; $[\alpha]_D^{25} + 16.7$ (c 1.0, CHCl_3 , >99% ee); IR (neat) 3044, 3017, 1464, 731; ^1H NMR (CDCl_3 , 200 MHz): δ 7.27-6.82 (m, 8H), 3.85 (s, 3H), 3.82 (s, 3H), 2.51-2.48 (m, 4H), 1.72-1.23 (m, 9H), 0.92 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 134.1, 131.5, 130.1, 129.8, 126.8, 120.3, 113.5, 110.2, 55.2, 39.5, 35.4, 32.9, 30.5, 26.8, 19.7, 14.5; HRMS (APCI) calcd for $\text{C}_{22}\text{H}_{31}\text{O}_2$ $[\text{M}+1]^+$: 327.2324; found: 327.2320; HPLC (Daicel Chiralcel OJ-H, i -PrOH/hexane = 2/98, 1.0 mL/min, 190 nm) $t_1 = 9.1$ min (minor), $t_2 = 9.8$ min (major).



Spectrum Max Plot Results					
Retention Time	Area	Area Percent	Height		
9.060	32291	0.255	4642		0.601
9.836	12635003	99.745	768148		99.399
Totals	12667294	100.000	772790		100.000

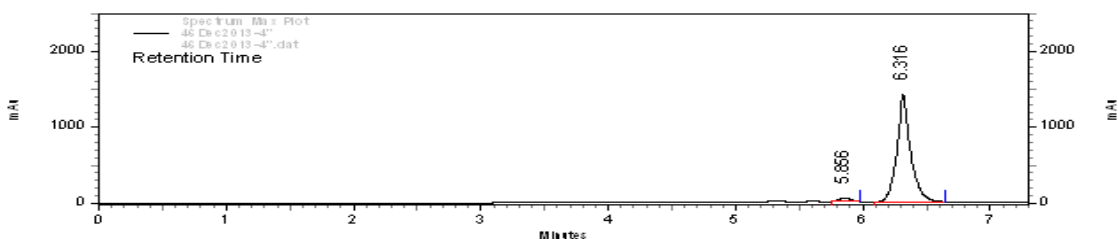


Spectrum Max Plot Results					
Retention Time	Area	Area Percent	Height		
8.812	4674004	49.944	231025		54.225
9.960	4684441	50.056	195022		45.775
Totals	9358445	100.000	426047		100.000

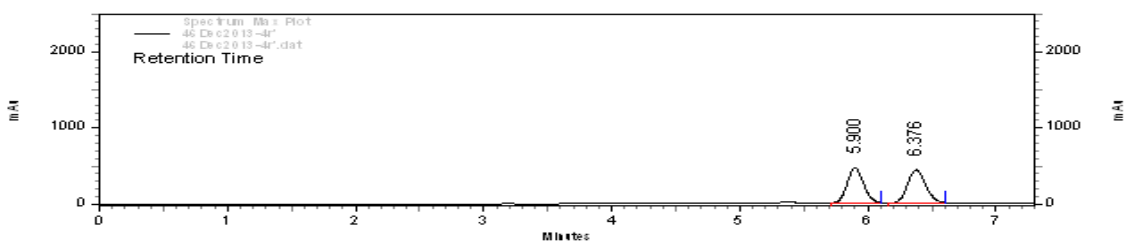


(S)-4,4'-(2-propylpentane-1,5-diyl)bis(methoxybenzene)

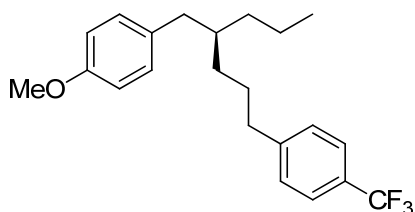
87%; Colorless oil; $[\alpha]_D^{25} + 12.9$ (c 1.0, CHCl_3 , 94% ee); IR (neat) 3062, 3013, 1467, 722; ^1H NMR (CDCl_3 , 300 MHz): δ 7.06-6.77 (m, 8H), 3.78 (s, 6H), 2.49-2.40 (m, 4H), 1.62-1.18 (m, 9H), 0.86 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 134.8, 133.8, 129.9, 129.1, 113.5, 113.4, 55.1, 39.4, 35.3, 35.2, 32.5, 28.7, 19.6, 14.3; HRMS (APCI) calcd for $\text{C}_{22}\text{H}_{31}\text{O}_2$ $[\text{M}+1]^+$: 327.2324; found: 327.2320. HPLC (Daicel Chiralcel OD-H, i -PrOH/hexane = 2/98, 1.0 mL/min, 190 nm) $t_1 = 5.9$ min (minor), $t_2 = 6.3$ min (major).



Retention Time	Area	Area Percent	Height	
5.856	304071	2.785	42003	2.869
6.316	10613184	97.215	1422228	97.131
Totals	10917255	100.000	1464231	100.000

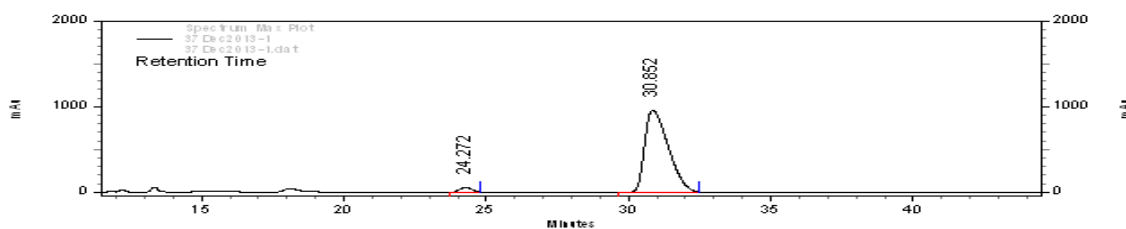


Retention Time	Area	Area Percent	Height	
5.900	4074350	48.954	466404	51.748
6.376	4248490	51.046	434895	48.252
Totals	8322840	100.000	901299	100.000

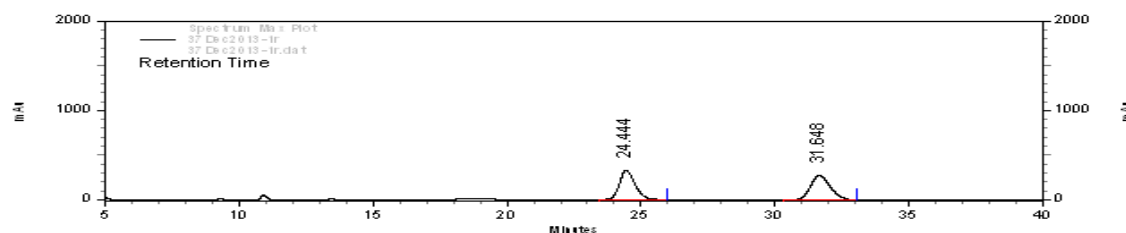


(S)-1-methoxy-4-(2-propyl-5-(4-(trifluoromethyl)phenyl)pentyl)benzene

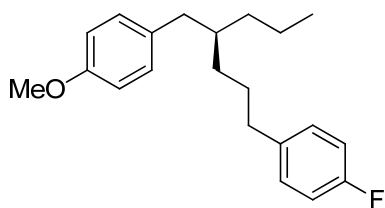
82%; Colorless oil; $[\alpha]_D^{25} + 8.6$ (*c* 1.0, CHCl₃, 95% ee); IR (neat) 3031, 3018, 1457, 709; ¹H NMR (CDCl₃, 400 MHz): δ 7.48-6.75 (m, 8H), 3.75 (s, 3H), 2.58-2.35 (m, 4H), 1.61-1.17 (m, 9H), 0.84 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 157.7, 146.9, 133.5, 130.0, 128.7, 127.8, 125.2 (q, *J* = 3.7 Hz), 113.5, 55.3, 55.2, 39.4, 36.0, 35.5, 32.5, 28.2, 19.8, 14.4; ¹⁹F NMR (CDCl₃, 188 MHz): δ -65.5; HRMS (APCI) calcd for C₂₂H₂₇OF₃ [M]⁺: 364.2014; found: 364.2037. HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 24.3 min (minor), t₂ = 30.9 min (major).



Retention Time	Area	Area Percent	Height
24.272	1496687	2.677	52130
30.852	54413412	97.323	953369
Totals	55910099	100.000	1005499

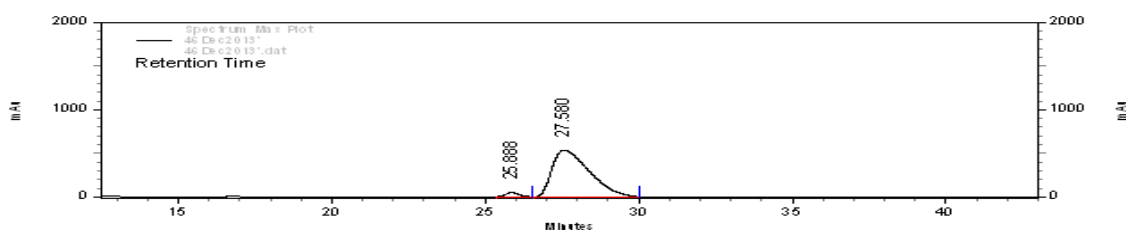


Retention Time	Area	Area Percent	Height
24.444	12967234	49.364	321676
31.648	13301378	50.636	266340
Totals	26268612	100.000	588016

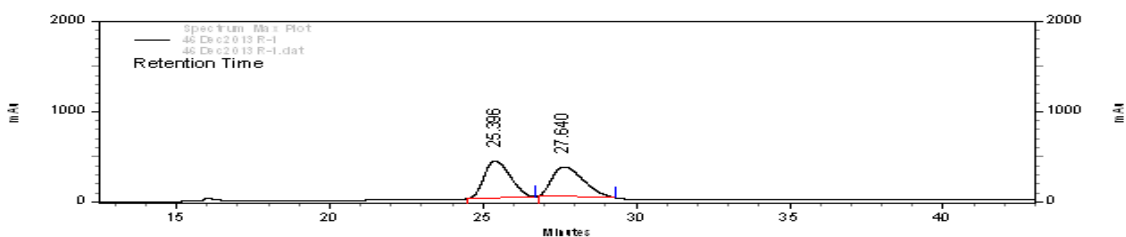


(S)-1-fluoro-4-(4-(4-methoxybenzyl)heptyl)benzene

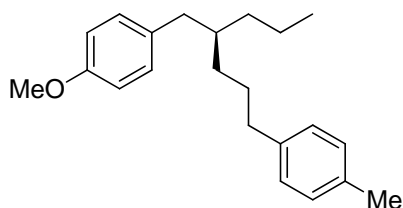
85%; Colorless oil; $[\alpha]_D^{25} + 3.1$ (c 1.0, CHCl_3 , 94% ee); IR (neat) 3040, 3021, 1462, 723; ^1H NMR (CDCl_3 , 400 MHz): δ 7.06-6.76 (m, 8H), 3.76 (s, 3H), 2.48-2.39 (m, 4H), 1.61-1.15 (m, 9H), 0.84 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 162.6 (d, $J = 380.1$ Hz), 138.3, 133.5, 129.9, 129.6 (d, $J = 7.7$ Hz), 114.9 (d, $J = 20.9$ Hz), 113.4, 55.1, 39.4, 39.3, 35.4, 35.3, 32.4, 28.5, 19.6, 14.3; ^{19}F NMR (CDCl_3 , 188 MHz): δ -121.4; HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{27}\text{FO}$ $[\text{M}]^+$: 314.2040; found: 314.2034; HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 1/99, 1.0 mL/min, 190 nm) $t_1 = 25.9$ min (minor), $t_2 = 27.6$ min (major).



Retention Time	Area	Area Percent	Height
25.888	1435957	3.106	48041
27.580	44799732	96.894	532145
Totals	46235689	100.000	580186

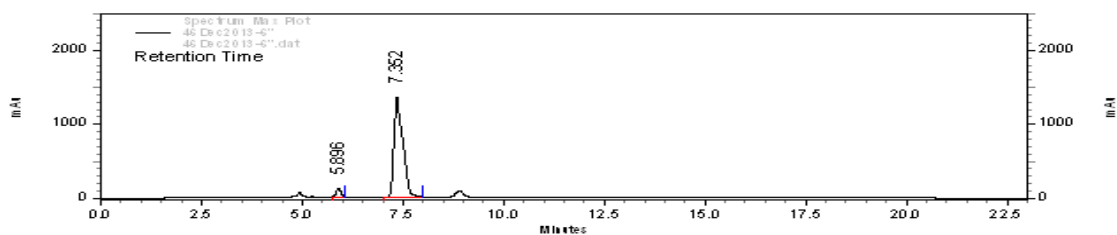


Retention Time	Area	Area Percent	Height
25.396	23961701	50.586	405245
27.640	23406756	49.414	329244
Totals	47368457	100.000	734489

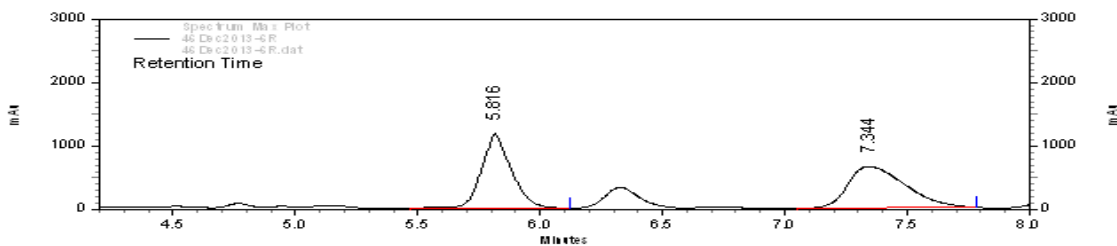


(S)-1-methoxy-4-(2-propyl-5-(p-tolyl)pentyl)benzene

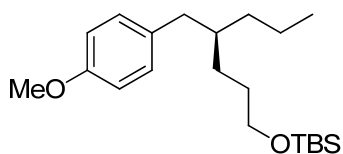
86%; Colorless oil; $[\alpha]_D^{25} + 10.1$ (c 1.0, CHCl_3 , 92% ee); IR (neat) 3043, 3017, 1459, 711; ^1H NMR (CDCl_3 , 400 MHz): δ 7.05-6.76 (m, 8H), 3.76 (s, 3H), 2.49-2.41 (m, 4H), 2.29 (s, 3H), 1.55-1.16 (m, 9H), 0.83 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 157.6, 139.9, 134.9, 133.8, 129.9, 128.8, 128.1, 113.4, 55.1, 39.4, 35.7, 35.3, 32.6, 28.6, 20.9, 19.6, 14.3; HRMS (APCI) calcd for $\text{C}_{22}\text{H}_{30}\text{O}$ $[\text{M}]^+$: 310.2291; found: 310.2278; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 1/99, 1.0 mL/min, 190 nm) $t_1 = 5.9$ min (minor), $t_2 = 7.4$ min (major).



Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
5.896	888981	4.140	112674	7.712
7.352	20582338	95.860	1348361	92.288
Totals	21471319	100.000	1461035	100.000

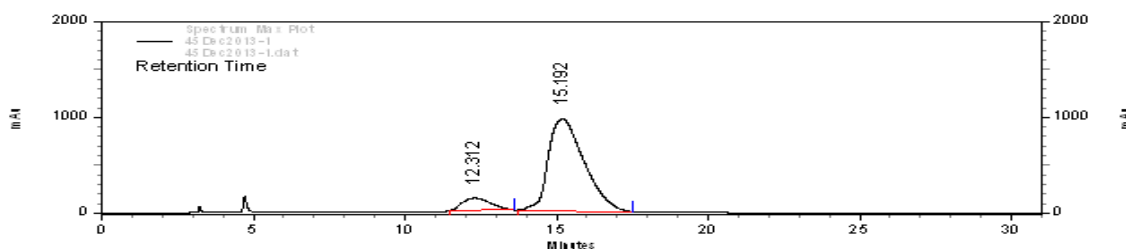


Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
5.816	9924809	48.291	1171455	64.147
7.344	10627128	51.709	654759	35.853
Totals	20551937	100.000	1826214	100.000

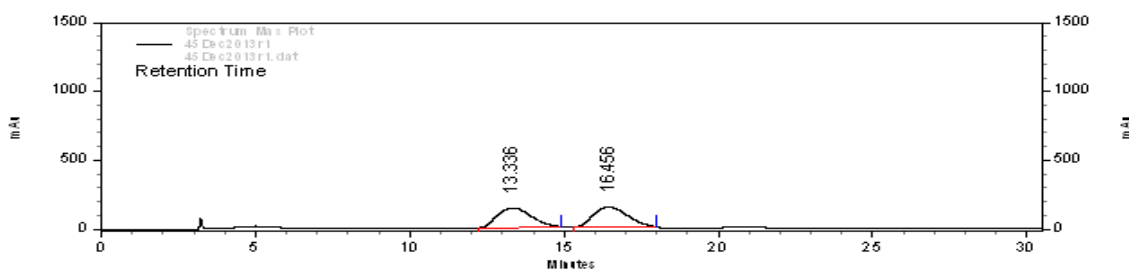


(S)-tert-butyl((4-(4-methoxybenzyl)heptyl)oxy)dimethylsilane

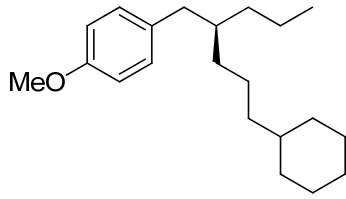
80%; Colorless oil; $[\alpha]_D^{25} + 9.4$ (c 1.0, CHCl₃, 81% ee); IR (neat) 3020, 3007, 1458, 708; ¹H NMR (CDCl₃, 400 MHz): δ 7.08-6.80 (m, 4H), 3.80 (s, 3H), 3.60 (t, *J* = 6.0 Hz, 2H), 2.50-2.47 (m, 2H), 1.63-1.21 (m, 9H), 0.89-0.84 (m, 12H), 0 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 157.6, 133.7, 130.0, 113.5, 63.6, 55.2, 39.5, 39.4, 35.4, 29.9, 29.8, 26.0, 19.7, 14.4, -5.3; HRMS (APCI) calcd for C₂₁H₃₉O₂Si [M+1]⁺: 351.2719; found: 351.2750; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 12.3 min (minor), t₂ = 15.2 min (major).



Retention Time	Area	Area Percent	Height	
12.312	8380830	9.638	128368	11.817
15.192	78574063	90.362	957942	88.183
Totals	86954893	100.000	1086310	100.000

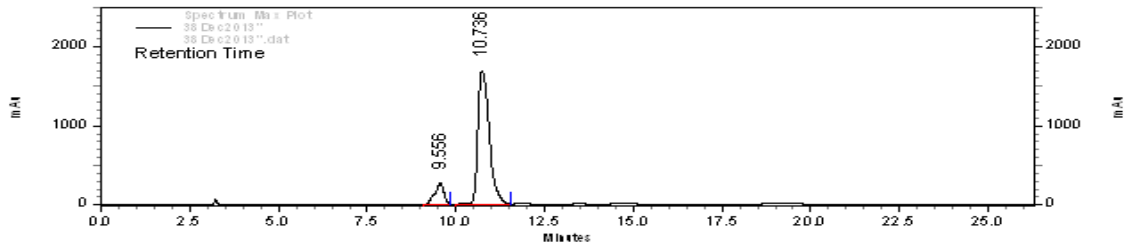


Retention Time	Area	Area Percent	Height	
13.336	10807591	48.723	140712	48.984
16.456	11373924	51.277	146550	51.016
Totals	22181515	100.000	287262	100.000

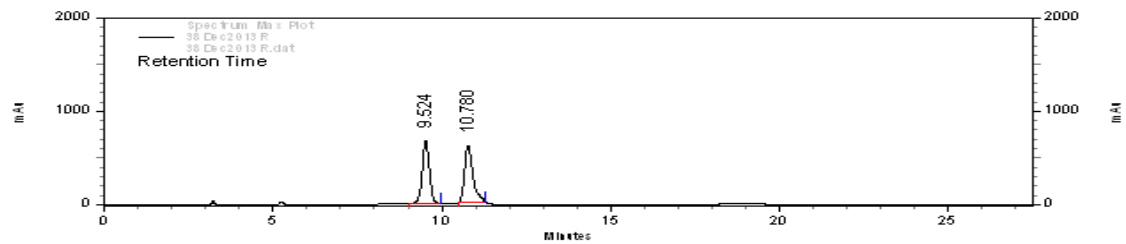


(S)-1-(5-cyclohexyl-2-propylpentyl)-4-methoxybenzene

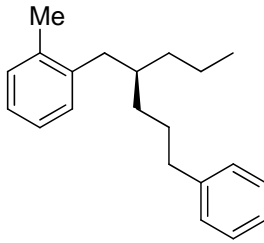
84%; Colorless oil; $[\alpha]_D^{25} + 3.9$ (c 1.0, CHCl₃, 78% ee); IR (neat) 3029, 3011, 1462, 705; ¹H NMR (CDCl₃, 400 MHz): δ 7.02-6.77 (m, 4H), 3.80 (s, 3H), 2.43-2.40 (m, 2H), 1.65-1.29 (m, 6H), 1.10-1.05 (m, 14H), 0.84-0.80 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz): 157.6, 133.9, 130.0, 113.5, 55.3, 55.1, 39.6, 37.9, 37.6, 35.5, 33.5, 33.4, 26.8, 26.5, 23.7, 19.8, 14.5; HRMS (APCI) calcd for C₂₁H₃₄O [M]⁺: 302.2604; found: 302.2589; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 9.6 min (minor), t₂ = 10.7 min (major).



Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
9.556	4677062	10.995	262943	13.457
10.736	37859173	89.005	1690977	86.543
Totals	42536235	100.000	1953920	100.000

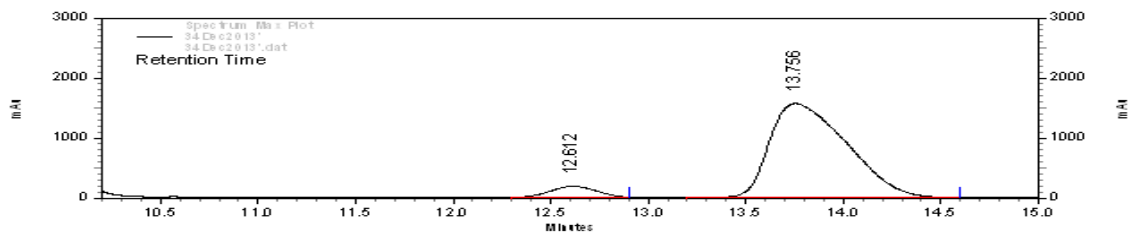


Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
9.524	9975756	48.503	668591	52.278
10.780	10591708	51.497	610321	47.722
Totals	20567464	100.000	1278912	100.000

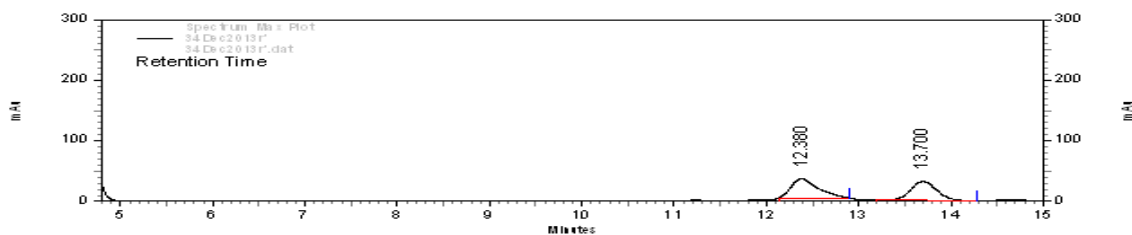


(S)-1-methyl-2-(5-phenyl-2-propylpentyl)benzene

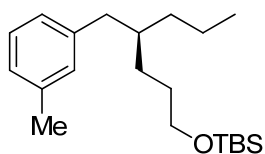
78%; Colorless oil; $[\alpha]_D^{25} + 9.8$ (c 1.0, CHCl_3 , 87% ee); IR (neat) 3046, 3013, 1452, 978, 709; ^1H NMR (CDCl_3 , 400 MHz): δ 7.27-7.01 (m, 9H), 2.61-2.49 (m, 3H), 2.27, (s, 3H), 1.68-1.47-1.26 (m, 10H), 0.87 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 142.8, 139.9, 136.2, 130.2, 130.1, 128.4, 128.2, 125.7, 125.6, 38.1, 38.0, 36.6, 35.8, 33.1, 28.6, 19.7, 14.5; HPLC (Daicel Chiralcel OD-H, i -PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) $t_1 = 12.6$ min (minor), $t_2 = 13.8$ min (major).



Retention Time	Area	Area Percent	Height	
12.612	297582.7	6.464	181680	10.377
13.756	4305858.3	93.536	1569031	89.623
Totals	46034410	100.000	1750711	100.000

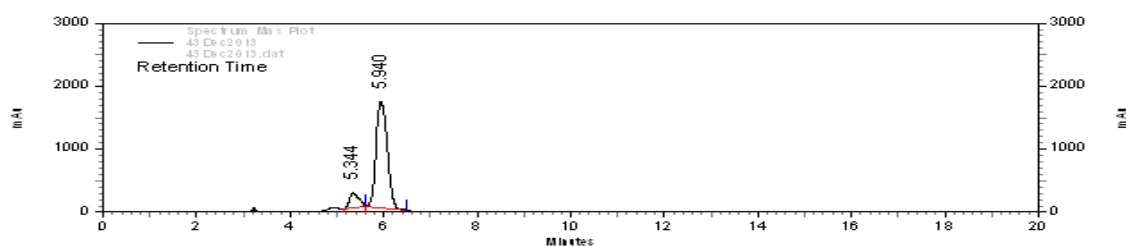


Retention Time	Area	Area Percent	Height	
12.380	654158	51.818	31572	50.412
13.700	608247	48.182	31056	49.588
Totals	1262405	100.000	62628	100.000

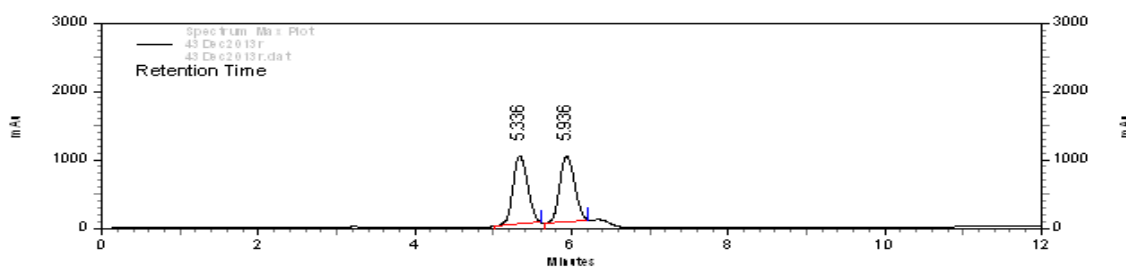


(S)-tert-butyl dimethyl((4-(3-methylbenzyl)heptyl)oxy)silane

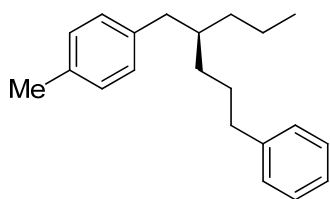
84%; Colorless oil; $[\alpha]_D^{25} + 5.7$ (c 1.0, CHCl₃, 80% ee); IR (neat) 3037, 3019, 1448, 1415, 708; ¹H NMR (CDCl₃, 400 MHz): δ 7.14-6.90 (m, 4H), 3.54 (t, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 3H), 1.64-1.30 (m, 9H), 1.19-0.84 (m, 12H), 0 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 140.1, 131.3, 130.5, 128.2, 63.5, 39.8, 35.4, 29.8, 28.9, 26.0, 18.4, 14.4, -5.2; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 5.3 min (minor), t₂ = 5.9 min (major).



Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
5.344	3182253	10.191	236108	12.350
5.940	28044414	89.809	1675773	87.650
Totals	31226667	100.000	1911881	100.000

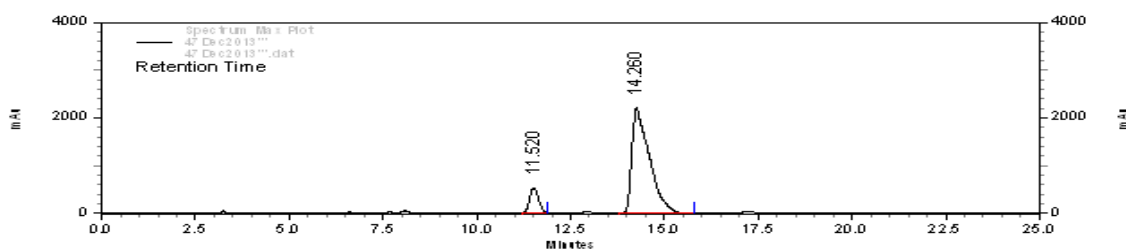


Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
5.336	12995113	50.494	996087	50.924
5.936	12740632	49.506	959956	49.076
Totals	25735745	100.000	1956043	100.000

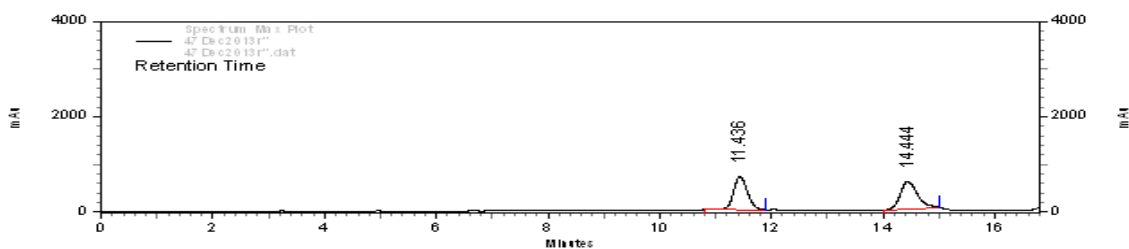


(S)-1-methyl-4-(5-phenyl-2-propylpentyl)benzene

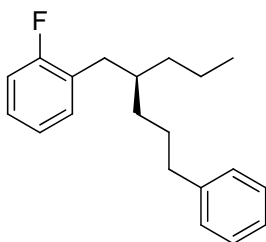
86%; Colorless oil; $[\alpha]_D^{25} + 8.2$ (*c* 1.0, CHCl₃, 78% ee); IR (neat) 3056, 3014, 1456, 989, 794; ¹H NMR (CDCl₃, 300 MHz): δ 7.29-6.99 (m, 9H), 2.57-2.46 (m, 4H), 2.32, (s, 3H), 1.68-1.23 (m, 9H), 0.87 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ 142.8, 138.4, 134.2, 128.9, 128.7, 128.3, 128.1, 125.5, 39.9, 39.3, 36.2, 35.4, 32.7, 28.5, 20.9, 19.6, 14.3; HRMS (APCI) calcd for C₂₁H₂₉ [M+1]⁺: 281.2269; found: 281.2268; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 11.5 min (minor), t₂ = 14.3 min (major).



Retention Time	Area	Area Percent	Height
11.520	8741593	10.887	530765
14.260	71551465	89.113	2207285
Totals	80293058	100.000	2738050

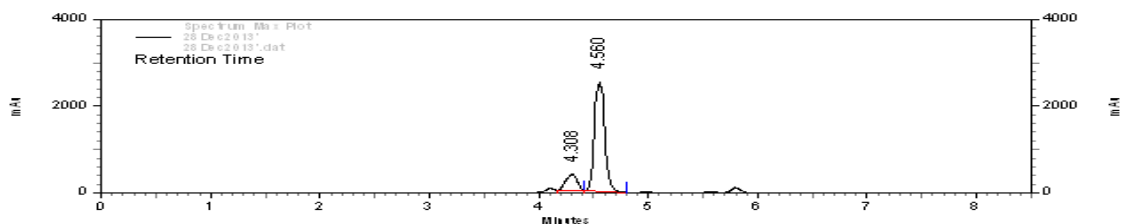


Retention Time	Area	Area Percent	Height
11.436	11784640	49.315	691236
14.444	12111811	50.685	570537
Totals	23896451	100.000	1261773

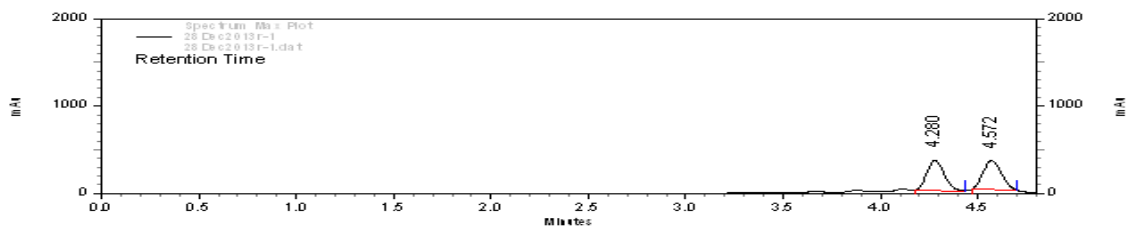


(S)-1-fluoro-2-(5-phenyl-2-propylpentyl)benzene

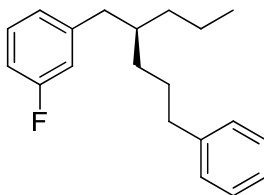
83%; Colorless oil; $[\alpha]_D^{25}$ -3.5 (*c* 1.0, CHCl₃, 72% ee); IR (neat) 3031, 3011, 1441, 793; ¹H NMR (CDCl₃, 200 MHz): δ 7.32-6.96 (m, 9H), 2.60-2.53 (m, 4H), 1.73-1.27 (m, 9H), 0.90 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ 131.4, 128.3(*d*, *J* = 11.3 Hz), 127.2 (*d*, *J* = 8.1 Hz), 125.4, 123.5, 115.2 (*d*, *J* = 23.3 Hz), 38.2, 36.1, 35.5, 33.5, 32.8, 28.3, 19.5, 14.3; ¹⁹F NMR (CDCl₃, 188 MHz): δ -121.6; HRMS (APCI) calcd for C₂₀H₂₆F [M+1]⁺: 285.2019; found: 285.2009; HPLC (Daicel Chiralcel OJ-H, *i*-PrOH/hexane = 4/96, 1.0 mL/min, 190 nm) t₁ = 4.3 min (minor), t₂ = 5.6 min (major).



Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
4.308	2625446	13.801	364344	12.619
4.560	16397801	86.199	2522831	87.381
Totals	19023247	100.000	2887175	100.000

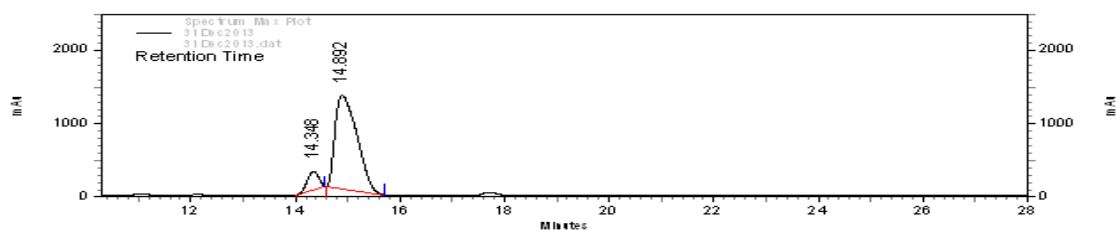


Spectrum Max Plot Results				
Retention Time	Area	Area Percent	Height	
4.280	2097213	48.762	343067	50.682
4.572	2203700	51.238	333838	49.318
Totals	4300913	100.000	676905	100.000

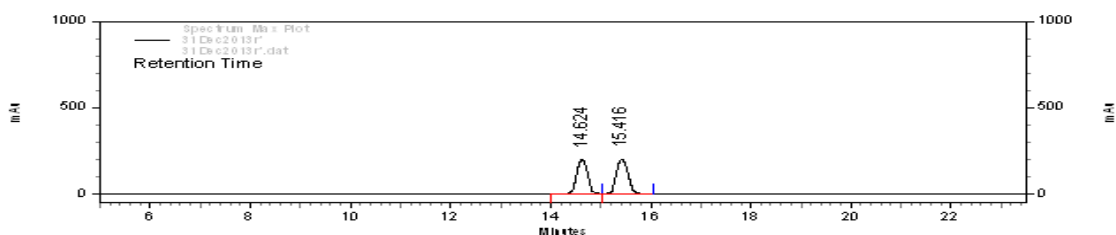


(S)-1-fluoro-3-(5-phenyl-2-propylpentyl)benzene

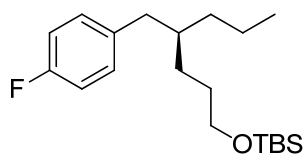
80%; Colorless oil; $[\alpha]_D^{25} + 3.0$ (c 1.0, CHCl₃, 82% ee); IR (neat) 3028, 3009, 1492, 786; ¹H NMR (CDCl₃, 200 MHz): δ 7.28-6.82 (m, 9H), 2.57-2.43 (m, 4H), 1.70-1.25 (m, 9H), 0.90 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ 129.5 (d, *J* = 10 Hz), 128.4 (d, *J* = 5.1 Hz), 125.6, 124.9, 116.1 (d, *J* = 20.3 Hz), 112.7 (d, *J* = 25.0 Hz), 40.4, 39.3, 36.2, 35.4, 32.7, 28.5, 19.7, 14.4; ¹⁹F NMR (CDCl₃, 188 MHz): δ -117.4; HRMS (APCI) calcd for C₂₀H₂₆F [M+1]⁺: 285.2019; found: 285.2020; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 14.3 min (minor), t₂ = 14.9 min (major).



Retention Time	Area	Area Percent	Height
14.348	3787793	9.151	249020
14.892	37604913	90.849	1286264
Totals	41392706	100.000	1535284

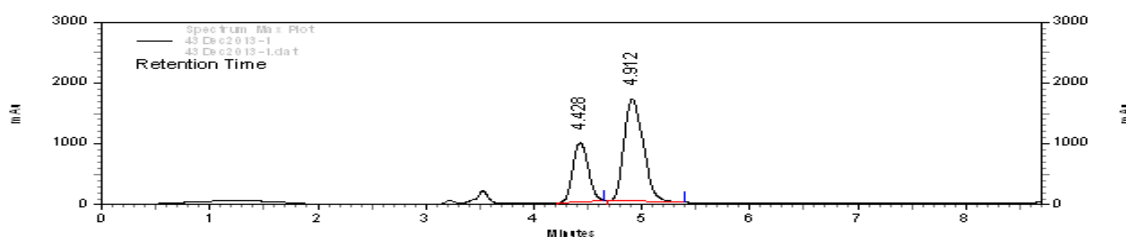


Retention Time	Area	Area Percent	Height
14.624	3049876	48.071	197419
15.416	3294635	51.929	198428
Totals	6344511	100.000	395847

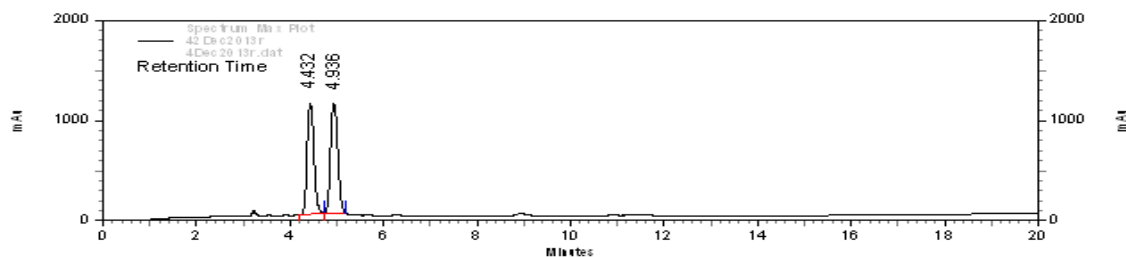


(S)-tert-butyl((4-(4-fluorobenzyl)heptyl)oxy)dimethylsilane

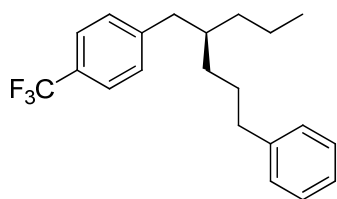
79%; Colorless oil; $[\alpha]_D^{25}$ - 5.6 (*c* 1.0, CHCl₃, 38% ee); IR (neat) 3021, 3018, 1487, 704; ¹H NMR (CDCl₃, 200 MHz): δ 7.13-6.91 (m, 4H), 3.59 (t, *J* = 6.0 Hz, 2H), 2.53-2.49 (m, 2H), 1.64-1.24 (m, 9H), 0.92 (m, 12H), 0 (s, 6H); ¹³C NMR (CDCl₃, 50 MHz): δ 130.4 (d, *J* = 7.7 Hz), 115.0 (d, *J* = 20.8 Hz), 63.6, 39.7, 39.3, 35.4, 29.8, 29.0, 25.9, 19.7, 14.3, -5.2; ¹⁹F NMR (CDCl₃, 188 MHz): δ -121.5; HRMS (APCI) calcd for C₂₀H₃₆FOSi [M+1]⁺: 339.2514; found: 339.2507. HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0.1/99.9, 1.0 mL/min, 190 nm) t₁ = 4.4 min (minor), t₂ = 4.9 min (major).



Retention Time	Area	Area Percent	Height
4.428	9524812	31.243	963420
4.912	20961140	68.757	1683248
Totals	30485952	100.000	2646668

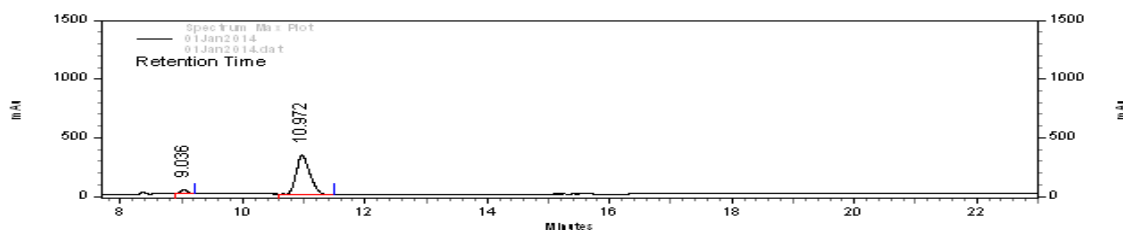


Retention Time	Area	Area Percent	Height
4.432	11194952	48.774	1103869
4.936	11757519	51.226	1089071
Totals	22952471	100.000	2192940

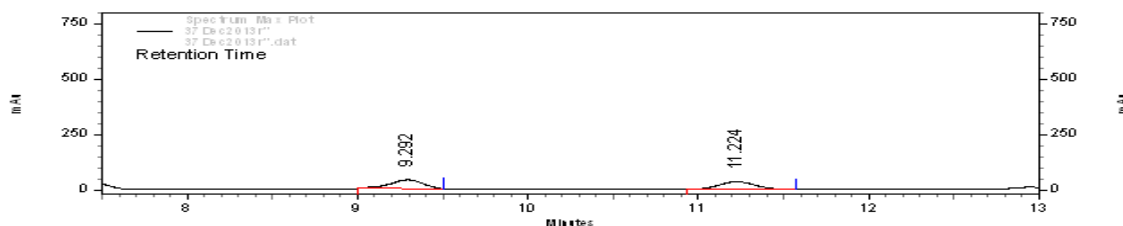


(S)-1-(5-phenyl-2-propylpentyl)-4-(trifluoromethyl)benzene

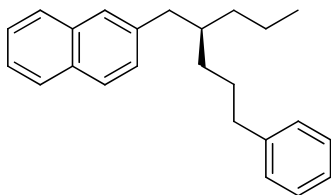
81%; Colorless oil; $[\alpha]_D^{25}$ -20.2 (*c* 1.0, CHCl₃, 89% ee); IR (neat) 3065, 3010, 1498, 766; ¹H NMR (CDCl₃, 300 MHz): δ 7.55-7.10 (m, 9H), 2.57-2.51 (m, 4H), 1.69-1.20 (m, 9H), 0.86 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ 145.7, 142.4, 136.4, 129.4 (d, *J* = 10.9 Hz), 128.2 (d, *J* = 7.3 Hz), 126.0, 124.9 (q, *J* = 3.7 Hz), 40.2, 39.2, 36.0, 35.3, 32.4, 28.3, 19.5, 14.2; ¹⁹F NMR (CDCl₃, 188 MHz): δ -65.5; HRMS (APCI) calcd for C₂₁H₂₅F₃ [M]⁺: 334.1908; found: 334.1926. HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) t₁ = 9.0 min (minor), t₂ = 11.0 min (major).



Retention Time	Area	Area Percent	Height
9.036	303647	5.732	33566
10.972	4993843	94.268	331632
Totals	5297490	100.000	365198

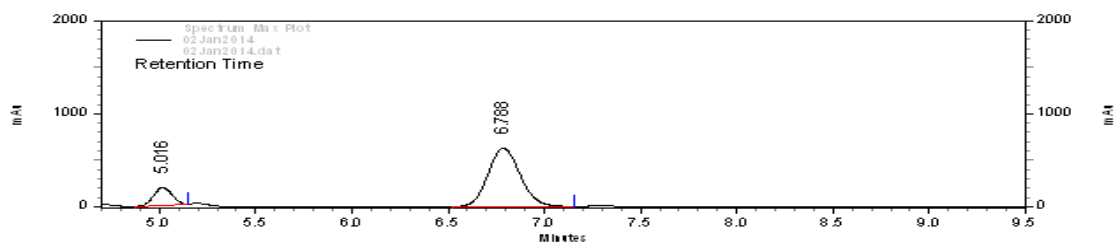


Retention Time	Area	Area Percent	Height
9.292	539726	51.454	39415
11.224	509229	48.546	34169
Totals	1048955	100.000	73584

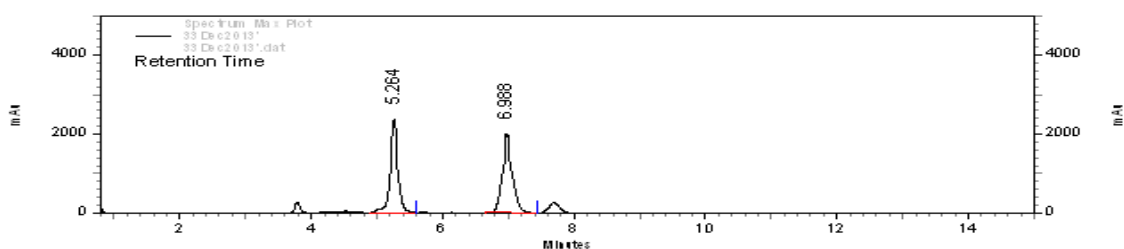


(S)-2-(5-phenyl-2-propylpentyl)naphthalene

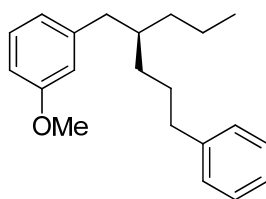
58%; Yellow oil; $[\alpha]_D^{25} + 7.8$ (c 1.0, CHCl₃, 71% ee); IR (neat) 3065, 3010, 1498, 766; ¹H NMR (CDCl₃, 200 MHz): δ 7.85-7.14 (m, 12H), 2.73-2.54 (m, 4H), 1.83-1.32 (m, 9H), 0.91 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (CDCl₃, 50 MHz): δ 142.8, 139.3, 133.5, 131.9, 128.4, 128.2, 128.0, 127.6, 127.4, 127.3, 125.8, 125.6, 125.0, 40.7, 39.4, 36.3, 35.6, 32.9, 28.6, 19.8, 14.5; HRMS (APCI) calcd for C₂₄H₂₈ [M]⁺: 316.2191; found: 316.2166; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 4/96, 1.0 mL/min, 190 nm) t₁ = 5.0 min (minor), t₂ = 6.8 min (major).



Retention Time	Area	Area Percent	Height
5.016	1234119	14.541	188269
6.788	7252974	85.459	625023
Totals	8487093	100.000	813292

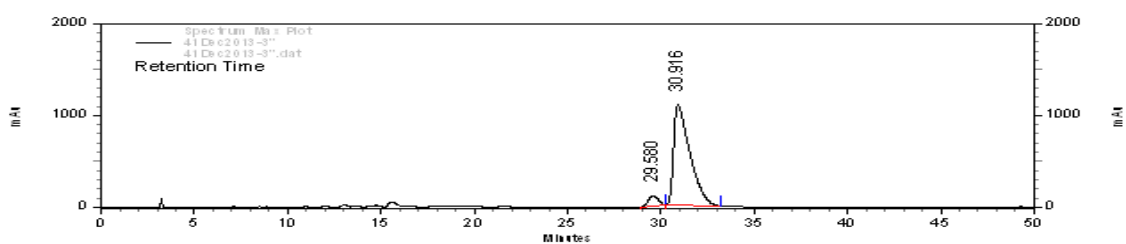


Retention Time	Area	Area Percent	Height
5.264	18870726	48.232	2377895
6.988	20254033	51.768	2004106
Totals	39124759	100.000	4382001

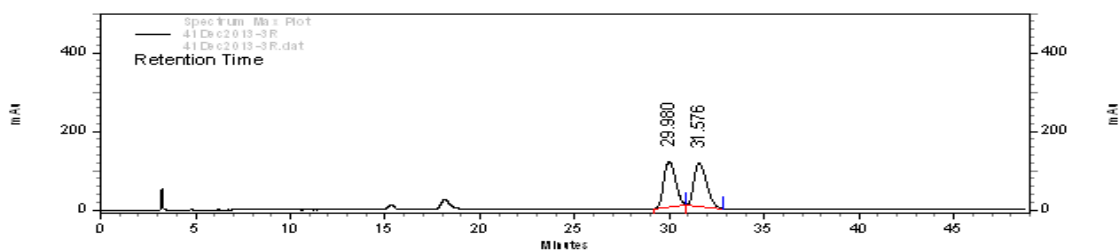


(S)-1-methoxy-3-(5-phenyl-2-propylpentyl)benzene

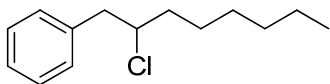
78%; Colorless oil; $[\alpha]_D^{25} + 4.4$ (c 1.0, CHCl_3 , 88% ee); IR (neat) 3045, 3020, 1457, 792; ^1H NMR (CDCl_3 , 300 MHz): δ 7.27-6.6 (m, 9H), 3.76 (s, 3H), 2.53-2.50 (m, 4H), 1.80-1.24 (m, 9H), 0.89 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 157.8, 140.3, 129.8, 128.3, 128.1, 125.5, 116.9, 112.3, 55.3, 38.5, 37.4, 36.1, 35.5, 32.8, 28.4, 19.5, 14.3; HRMS (APCI) calcd for $\text{C}_{21}\text{H}_{29}\text{O}$ $[\text{M}+1]^+$: 297.2218; found: 297.2210. HPLC (Daicel Chiralcel OD-H, i -PrOH/hexane = 0/100, 1.0 mL/min, 190 nm) $t_1 = 29.6$ min (minor), $t_2 = 30.9$ min (major).



Retention Time	Area	Area Percent	Height	
29.580	4228575	5.983	114326	9.467
30.916	6645318	94.017	1093342	90.533
Totals	70681893	100.000	1207668	100.000

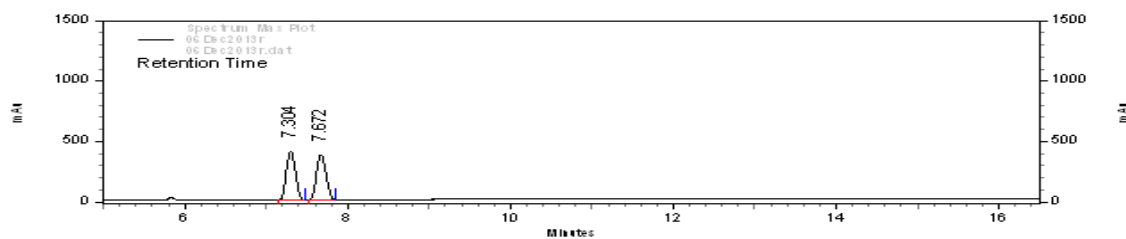


Retention Time	Area	Area Percent	Height	
29.980	4896767	49.593	116079	51.515
31.576	4977156	50.407	109251	48.485
Totals	9873923	100.000	225330	100.000



(2-chlorooctyl)benzene

90%; Colorless oil; IR (neat) 3019, 1416, 783, 405; ^1H NMR (CDCl_3 , 300 MHz): δ 7.19-7.13 (m, 5H), 4.35-4.20 (m, 1H), 3.36-3.12 (m, 2H), 1.81-1.55 (m, 3H), 1.40-1.25 (m, 7H), 0.88 (t, $J = 6.8$ Hz 3H); ^{13}C NMR (CDCl_3 , 100 MHz): 139.7, 128.9, 128.3, 126.6, 47.4, 39.4, 38.9, 31.5, 29.5, 28.3, 22.5, 13.9; HRMS (APCI) calcd for $\text{C}_{14}\text{H}_{21} [\text{M}-\text{Cl}]^+$: 189.1643; found: 189.1628; HPLC (Daicel Chiralcel OD-H, *i*-PrOH/hexane = 0.2/99.8, 1.0 mL/min, 190 nm) $t_1 = 7.3$ min, $t_2 = 7.7$ min (racemic).



Retention Time	Area	Area Percent	Height	
7.304	3073.510	50.633	3992.78	52.028
7.672	2996.657	49.367	3681.50	47.972
Totals	6070.167	100.000	7674.28	100.000

References

- Kulbitski, K., Nisnevich, G. & Gandelman, M. Metal-free efficient, general and facile iododecarboxylation method with biodegradable co-products. *Adv. Synth. Catal.* **353**, 1438-1442 (2011).
- Saito, B. & Fu, G. C. Enantioselective alkyl-alkyl Suzuki cross-couplings of unactivated homobenzylic halides. *J. Am. Chem. Soc.* **130**, 6694-6695 (2008).

$^1\text{H}/^{13}\text{C}/^{19}\text{F}$ Spectra

