The acid free asymmetric intermolecular α-alkylation of aldehydes in fluorinated alcohols

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Supporting information

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General methods

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Commercial grade solvents and reagents were used without further purification.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

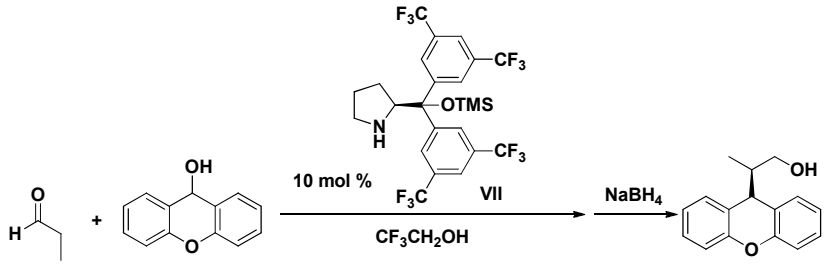
Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. The oil samples were examined under neat conditons.

High Resolution Mass (**HRMS**) spectra were obtained using Finnigan MAT95XP GC/HRMS (Thermo Electron Corporation).

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for 1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet).

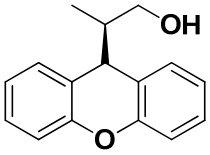
Enantioselectivities were determined HPLC analysis employing a Daicel Chiracel column at 25 ^{o}C. Optical rotation was measured using a JASCO P-1030 Polarimeter equipped with a sodium vapor lamp at 589 nm. Concentration is denoted as *c* and was calculated as grams per deciliters (g / 100 mL) whereas the solvent. Absolute configuration of the products was determined by comparison with known compounds.

General procedure for the organocatalytic enantioselective acid free alkylation of aldehydes in fluorinated alcohols:



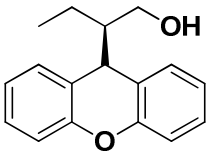
To a solution of xanthydrol (19.8 mg, 0.1 mmol) and (*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)(trimethylsilyloxy)methyl)pyrrolidine **VII** (6.0 mg, 0.01 mmol) in CF_3CH_2OH (0.5 mL) was added propanal (0.4 mmol). The resulting solution was stirred at room temperature or higher temperature for indicated time. Upon the completion of reaction as monitored by TLC, excessive $NaBH_4$ was then cautiously added to the yellow solution and stirred at room temperature for 0.5 h. The reaction was subsequently quenched with water (1 mL) and HCl (1M). The organic phase was separated and the aqueous solution was extracted with ethyl acetate (1 mL x 3). The combined organic phases were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting yellow oil was purified by preparative chromatography (hexane/ethyl acetate = 4 : 1) to afford the desired product in colorless oil. Both enantiomeric excess and diastereomeric ratio were determined by HPLC using chiral AS-H, AD-H or OD-H columns. The absolute configuration of the products was determined by optical rotation in comparison with the literature reported values.[1]

(*R*)-2-(9H-xanthen-9-yl)propan-1-ol



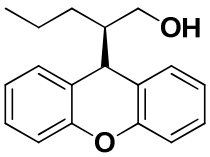
$[\alpha]_D^{20}$ = + 3.1 (*c* = 1.5, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min, t_{minor} = 11.9 min, t_{major} = 12.8 min.
^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.25-7.20 (m, 4H), 7.11-7.04 (m, 4H), 4.23 (d, *J* = 4.2 Hz, 1H), 3.57-3.42 (m, 2H), 2.04-1.95 (m, 1H), 0.64 (d, *J* = 6.9 Hz, 3H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ: 153.4, 153.1, 129.7, 128.8, 127.7, 127.5, 125.1, 123.3, 122.9, 122.5, 116.3, 116.2, 64.9, 45.1, 40.3, 12.0;
HRMS (ESI): calcd. for $C_{16}H_{17}O_2$ 241.1229 $[M+H]^+$, found 241.1238 $[M+H]^+$;
IR (thin film) ν/cm^{-1}: 3350, 2970, 1460, 1379, 1256, 1161, 1128.

(*R*)-2-(9H-xanthen-9-yl)butan-1-ol



$[\alpha]_D^{20}$ = + 2.3 (*c* = 1.5, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min, t_{minor} = 10.9 min, t_{major} = 12.7 min.
^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.18-7.14 (m, 4H), 7.03-7.00 (m, 4H), 4.21 (d, *J* = 4.3 Hz, 1H), 3.51-3.42 (m, 2H), 1.69-1.63 (m, 1H), 1.53 (br, 1H), 1.31-1.23 (m, 1H), 1.05-0.96 (m, 1H), 0.74 (t, *J* = 7.5 Hz, 3H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ: 153.2 (2C), 129.5, 128.9, 127.6 (2C), 124.9, 123.7, 123.2, 123.0, 116.3, 62.1, 52.0, 39.3, 19.7, 12.1;
HRMS (ESI): calcd. for $C_{17}H_{19}O_2$ 255.1385 $[M+H]^+$, found 255.1373 $[M+H]^+$;
IR (thin film) ν/cm^{-1}: 3019, 2399, 2358, 1520, 1420, 1261, 1215, 1080, 1016.

(*R*)-2-(9H-xanthen-9-yl)pentan-1-ol



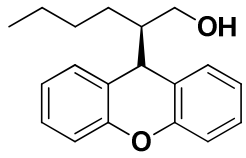
$[\alpha]_D^{20}$ = + 6.4 (*c* = 2.0, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min, t_{minor} = 9.7 min, t_{major} = 11.5 min.
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.19-7,13 (m, 4H), 7.03- 6.98 (m, 4H), 4.20 (d, *J* = 4.2 Hz, 1H), 3.45 (d, *J* = 5.7 Hz, 2H), 1.81-1.69 (m, 1H), 1.27-0.92 (m, 4H), 0.70 (t, *J* = 6.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.1, 129.5, 128.9, 127.6 (2C), 124.8, 123.8, 123.2, 123.0, 116.3 (2C), 62.6, 50.2, 39.4, 29.6, 26.5, 22.7, 13.9;

HRMS (ESI): calcd. for $C_{18}H_{21}O_2$ 269.1542 $[M+H]^+$, found 269.1543 $[M+H]^+$;

IR (thin film) ν/cm^{-1}: 2984, 2359, 1697, 1557, 1472, 1263.

(*R*)-2-(9H-xanthen-9-yl)hexan-1-ol



$[\alpha]_D^{20}$ = + 3.0 (*c* = 2.1, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min, t_{minor} = 8.8 min, t_{major} = 10.7 min.

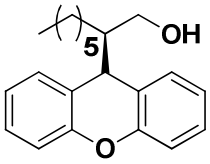
^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.19-7.14 (m, 4H), 7.03-6.99 (m, 4H), 4.20 (d, *J* = 4.2 Hz, 1H), 3.47-3.41 (m, 2H), 1.77-1.71 (m, 1H), 1.53 (s, 1H), 1.24-0.94 (m, 6H), 0.70 (t, *J* = 6.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 153.2 (2C), 129.5, 128.9, 127.6 (2C), 124.7, 123.7, 123.2, 123.0, 116.3 (2C), 62.5, 50.2, 39.3, 29.6, 26.5, 22.7, 13.9;

HRMS (ESI): calcd. for $C_{19}H_{23}O_2$ 283.1698 $[M+H]^+$, found 283.1689 $[M+H]^+$;

IR (thin film) ν/cm^{-1}: 3018, 2253, 1477, 1422, 1382, 1265, 1215.

(*R*)-2-(9*H*-xanthen-9-yl)octan-1-ol



$[\alpha]_D^{20}$ = + 2.5 (*c* = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:*i*-PrOH (95: 5), flow rate = 1 mL/min, t_{minor} = 7.8 min, t_{major} = 9.1 min.

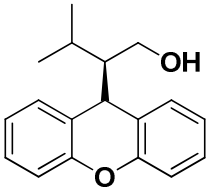
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.25-7.20 (m, 4H), 7.10-7.05 (m, 4H), 4.27 (d, *J* = 4.2 Hz, 1H), 1.85-1.78 (m, 1H), 1.28-1.12 (m, 11H), 0.82 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.21, 153.17, 129.50, 128.92, 127.59, 127.56, 124.76, 123.74, 123.20, 123.00, 116.29, 116.27, 62.54, 50.20, 39.37, 31.62, 29.32, 27.39, 26.80, 22.55, 14.02.

HRMS (ESI): calcd. for $C_{21}H_{27}O_2$ 311.2011 $[M+H]^+$, found 311.2014 $[M+H]^+$;

IR (thin film) ν/cm^{-1}: 3016, 2399, 1477, 1458, 1256, 1215, 1096, 1016.

(*R*)-3-methyl-2-(9H-xanthen-9-yl)butan-1-ol



$[\alpha]_D^{20}$ = + 3.3 (*c* = 1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min, t_{minor} = 9.6 min, t_{major} = 11.3 min.

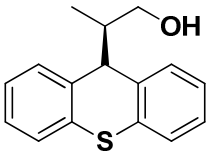
^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.28-7.21 (m, 4H), 7.13-7.08 (m, 4H), 4.32 (d, *J* = 4.6 Hz, 1H), 3.64 (s, 2H), 1.89 -1.83 (m, 1H), 1.00 (d, *J* = 7.0 Hz, 3H), 0.72 (d, *J* = 6.8, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 153.2 (2C), 129.3, 128.8,127.8, 127.6, 125.1, 124.9,123.4, 123.2, 116.6,116.4, 60.6, 56.3, 39.0, 26.1, 23.0, 18.7;

HRMS (ESI): calcd. for $C_{18}H_{21}O_2$ 269.1542 $[M+H]^+$, found 269.1531 $[M+H]^+$;

IR (thin film) ν/cm^{-1}: 3387, 2972, 1458, 1381, 1215, 1126, 1029.

(*R*)-2-(9H-thioxanthen-9-yl)propan-1-ol



$[\alpha]_D^{20}$ = - 15.6 (*c* = 1.9, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:*i*-PrOH (95: 5), flow rate = 1 mL/min, t_{minor} = 11.5 min, t_{major} = 12.0 min.

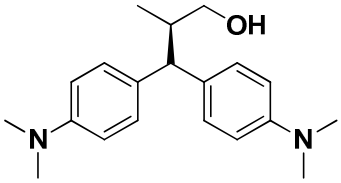
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.36-7.33 (m, 2H), 7.27- 7.24 (m, 1H), 7.20-7.09 (m, 5H), 3.89 (d, *J* = 9.96 Hz, 1H), 3.37 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.24 (dd, *J* = 10.8, 5.0 Hz, 1H), 2.28 - 2.15 (m, 1H), 0.75 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 132.9, 132.8, 132.2, 129.6, 127.2, 127.1, 126.5, 126.4, 126.3, 126.0, 65.7, 51.8, 34.9, 15.7;

HRMS (ESI): calcd. for $C_{16}H_{17}OS$ 257.1000 $[M+H]^+$, found 257.1003 $[M+H]^+$;

IR (thin film) ν/cm^{-1}: 3019, 2399, 1520, 1464, 1215, 1096, 1022.

(*R*)-2-(3,6-bis(dimethylamino)-9*H*-xanthen-9-yl)propan-1-ol



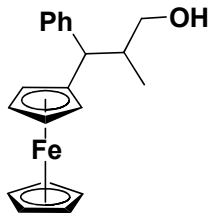
$[\alpha]_D^{20}$ = -16.9 (*c* = 1.7, $CHCl_3$). The enantiomeric excess was determined by HPLC with Chiralpack OD-H column at 220 nm; eluent: hexane:i-PrOH (85: 15), flow rate = 1 mL/min, t_{major} = 10.2 min, t_{minor} = 15.9 min.

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.16-7.13 (m, 4H), 6.67-6.64 (m, 4H), 3.58 (dd, *J* = 10.8, 4.1 Hz, 1H), 3.50 (d, *J* = 10.8 Hz, 1H), 3.41 (dd, *J* = 10.8, 5.7 Hz, 1H), 2.88 (s, 6H), 2.87 (s, 6H), 2.49- 2.40 (m, 1H), 1.62-1.54 (m, 1H), 0.94 (d, *J* = 6.7, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 149.0, 148.9, 132.9 (2C), 128.5, 128.3, 113.1, 112.9, 67.2, 53.7, 40.8 (2C), 39.6, 16.4;

HRMS (ESI): calcd. for $C_{20}H_{29}N_2O$ 313.2280 $[M+H]^+$, found 313.2280 $[M+H]^+$;

IR (thin film) ν/cm^{-1}: 3019, 2399, 1612, 1518, 1476, 1422, 1215, 1018.



Both enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpack OD-H column at 220 nm, eluent: hexane:i-PrOH (95: 5), 1.0 mL/min; diastereomer 1: t_{minor} = 15.0 min, t_{major} = 22.3 min, diastereomer 2: t_{minor} = 20.4 min, t_{major} = 28.0 min.

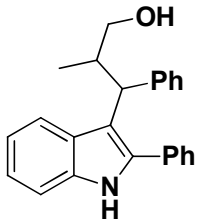
^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.30-7.18 (m, 5H), 4.11-3.97 (m, 4H), 3.73 (s, 2H), 3.67 (s, 2H), 3.43-3.30 (m, 3H), 2.07-1.90 (m, 1H), 1.52 (br s, 1H), 0.83 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 144.6, 128.7, 128.2, 126.4, 92.2, 70.0, 68.6, 68.2, 67.1, 66.7, 66.6, 49.3, 42.7, 16.2.

HRMS (ESI): calcd. for $C_{24}H_{31}OFe$ 391.1724$[M+H]^+$, found 391.1716 $[M+H]^+$;

IR (thin film) ν/cm^{-1}: 3053, 2961, 1720, 1265, 1026, 739, 704.

2-methyl-3-phenyl-3-(2-phenyl-1H-indol-3-yl)propan-1-ol



The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 220 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 0.5 mL/min, diastereomer 1: t_{minor} = 50.5 min, t_{major} = 98.6 min, diastereomer 2: t_{major} =80.2 min, t_{minor} = 94.2 min.

^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.97 (br s, 1H), 7.88-7.83 (m, 1H), 7.43-7.24 (m, 8H), 7.18-7.04 (m, 5H), 4.06-4.04 (m, 1H), 3.51-3.46 (m, 1H), 3.33-3.26 (m, 1H), 2.89-2.82 (m, 1H), 1.13-1.00 (m, 1H), 0.85 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 144.7, 136.2, 136.1, 133.3, 129.2, 128.7, 128.5, 128.4, 128.3, 127.6, 126.0, 121.9, 121.2, 119.7, 114.8, 111.0, 66.7, 46.1, 38.6,15.9.

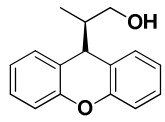
HRMS (ESI): calcd. for $C_{24}H_{24}NO$ 342.1858 $[M+H]^+$, found 342.1871 $[M+H]^+$;

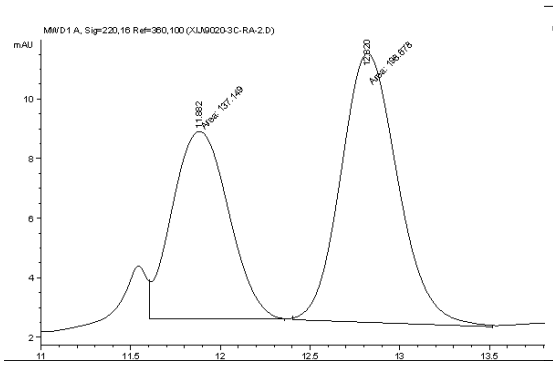
IR (thin film) ν/cm^{-1}: 3400, 2967, 2930, 1597, 1454, 1265, 1030, 735, 702.

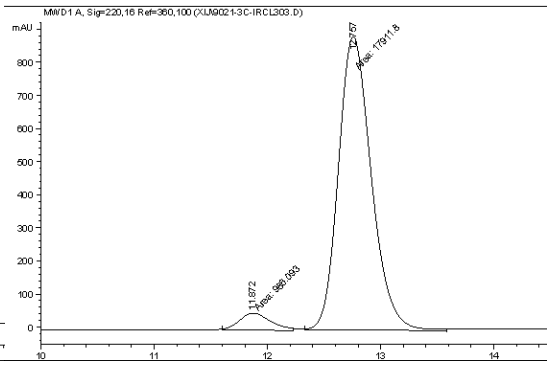
References

1. (a) Cozzi, P. G.; Benfatti, F.; Zoli, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 1313. (b) Benfatti, F.; Benedetto, E.; Cozzi, P. G. *Chem. Asian J.* **2010**, *5*, 2047. (c) Benfatti, F.; Benedetto, E.; Cozzi, P. G. *Chem. Eur. J.* **2010**, *5*, 9. (d) Benfatti, F.; Capdevila, M. G.; Benedetto, E.; Zoli, L.; Cozzi, P. G. *Chem. Commun.* **2009**, 5919. (e) Ho, X. H. ; Mho, S. ; Kang, H.; Jang, H. Y. *Eur. J. Org. Chem.* **2010**, 4436. (f) Bauer, J. O.; Stiller, J.; Marqués-López, E.; Strohfeldt, K.; Christmann, M.; Strohmann, C. *Chem. Eur. J.* **2010**, *16*, 12553. (g) Xiao, J.; Zhao, K.; Loh, T. P. *Chem. Asian J.* **2011**, *6*, 2890.

Representative HPLC Spectra







Signal 1: MWD1 A, Sig=220,16 Ref=360,100

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1	11.882	MM	0.3633	137.14928	6.29207	40.8392
2	12.820	MM	0.3667	198.67805	9.03095	59.1608

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

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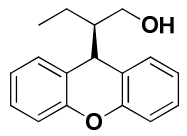
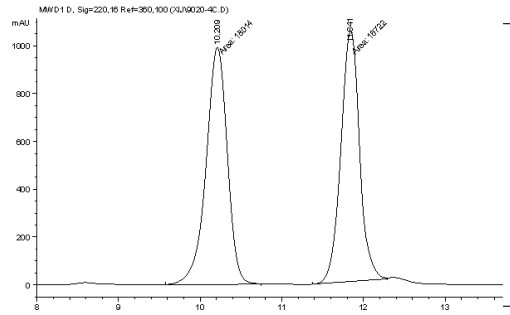
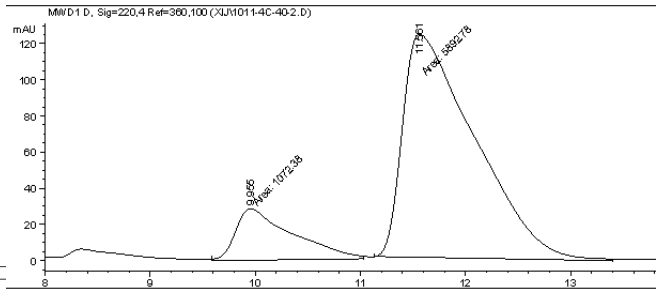




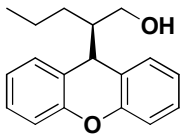


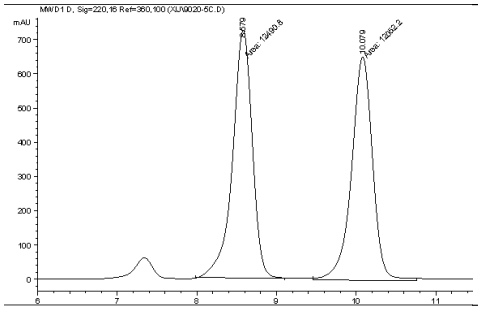
Signal 1: MWD1 D, Sig=220,16 Ref=360,100

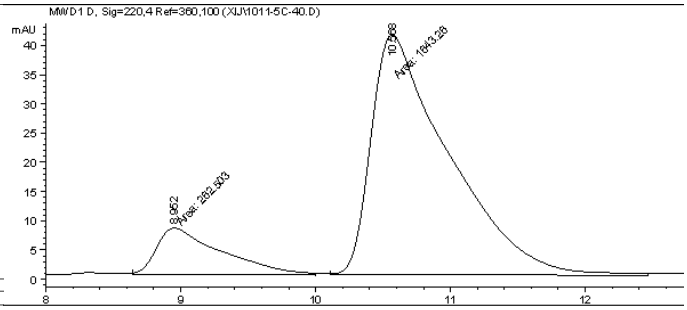
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.209	MM	0.3026	1.80140e4	992.18854	51.8598
2	11.841	MM	0.2657	1.67220e4	1048.99866	48.1402

Signal 1: MWD1 D, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.955	MM	0.6241	1072.38330	28.63899	15.3964
2	11.561	MM	0.7954	5892.77881	123.48148	84.6036





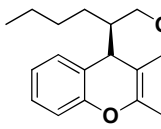


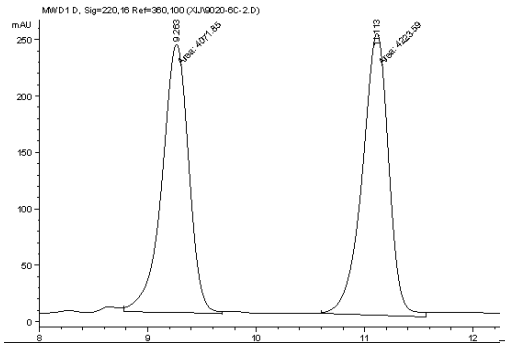
Signal 1: MWD1 D, Sig=220,16 Ref=360,100

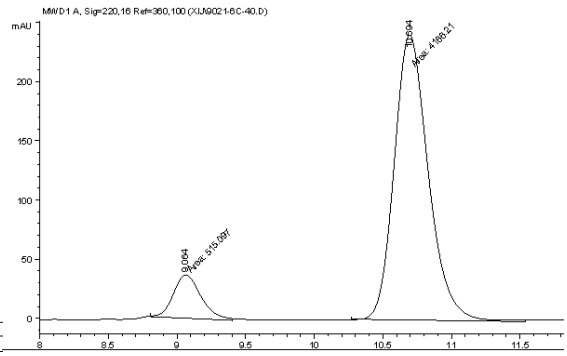
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.579	MM	0.2871	1.24908e4	725.05658	50.8937
2	10.079	MM	0.3074	1.20522e4	653.40631	49.1063

Signal 1: MWD1 D, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.952	MM	0.5507	262.50311	7.94413	13.7742
2	10.568	MM	0.6675	1643.26123	41.03031	86.2258





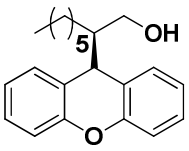


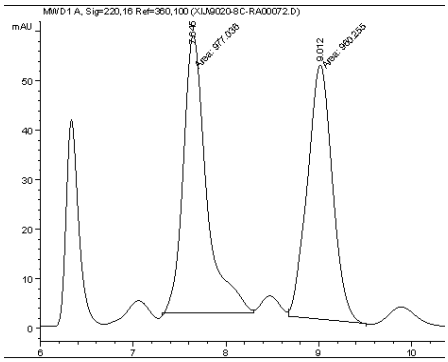
Signal 1: MWD1 D, Sig=220,16 Ref=360,100

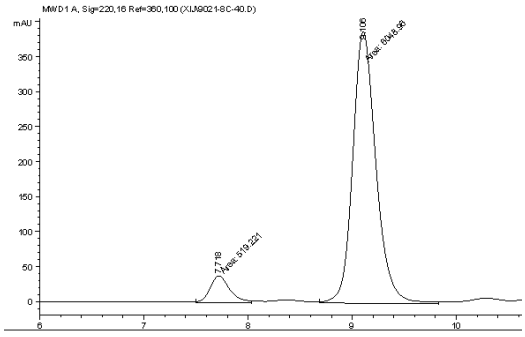
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.263	MM	0.2852	4071.84595	237.93983	49.0854
2	11.113	MM	0.2817	4223.58984	249.85394	50.9146

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.064	MM	0.2345	515.09698	36.61646	11.0033
2	10.694	MM	0.2879	4166.21240	241.18961	88.9967





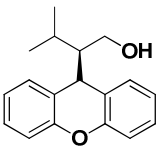


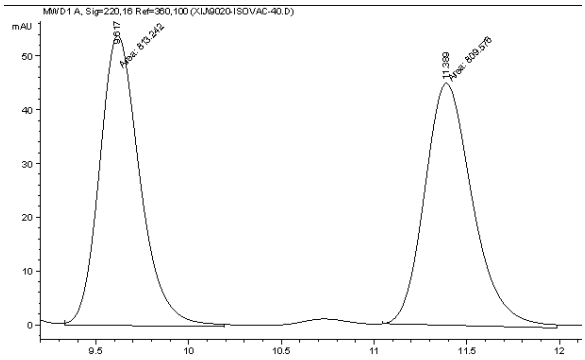
Signal 1: MWD1 A, Sig=220,16 Ref=360,100

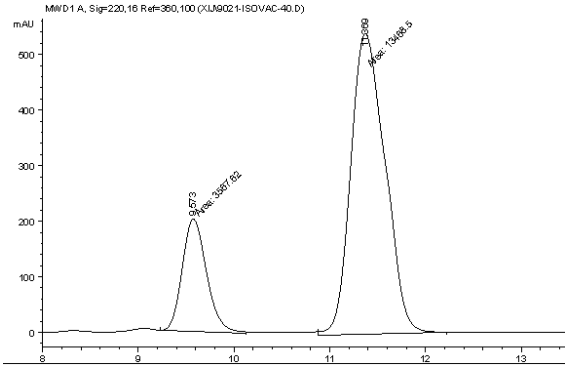
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.645	MM	0.2906	977.03583	56.04145	50.4331
2	9.012	MM	0.3110	960.25507	51.46384	49.5669

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.718	MM	0.2240	519.22058	38.63672	7.9051
2	9.106	MM	0.2594	6048.95557	388.72278	92.0949





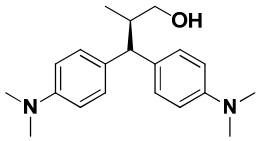


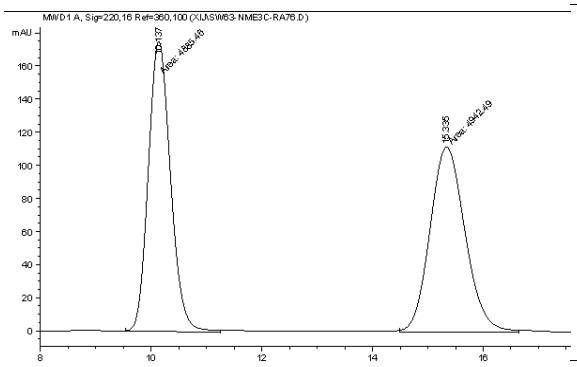
Signal 1: MWD1 A, Sig=220,16 Ref=360,100

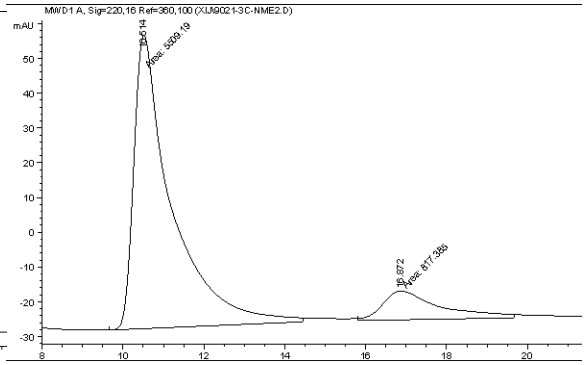
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.617	MM	0.2510	813.24207	53.99939	50.1129
2	11.389	MM	0.2998	809.57648	45.00978	49.8871

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.573	MM	0.2942	3567.61987	202.09833	20.9415
2	11.369	MM	0.4150	1.34685e4	540.95123	79.0585





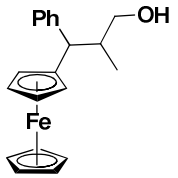


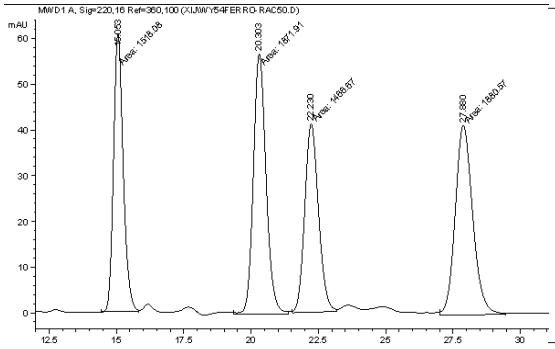
Signal 1: MWD1 A, Sig=220,16 Ref=360,100

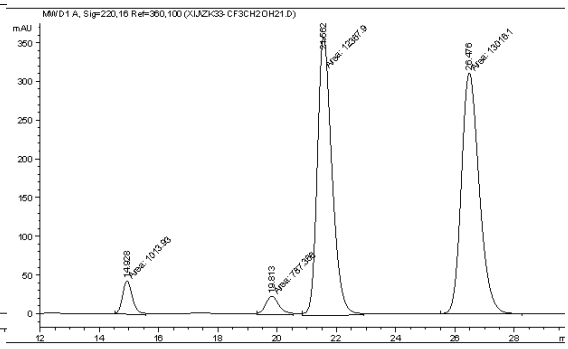
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.137	MM	0.4649	4885.45508	175.15433	49.7098
2	15.335	MM	0.7361	4942.49023	111.90463	50.2902

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.514	MM	1.0863	5509.19043	84.52453	87.0801
2	16.872	MM	1.6439	817.38525	8.28724	12.9199





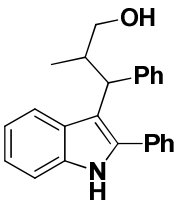


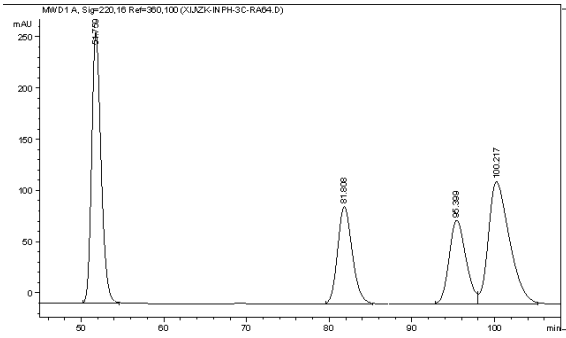
Signal 1: MWD1 A, Sig=220,16 Ref=360,100

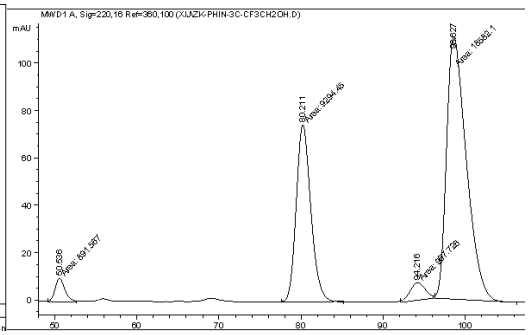
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.053	MM	0.4159	1518.08289	60.83552	22.5327
2	20.303	MM	0.5476	1871.91272	56.97300	27.7846
3	22.230	MM	0.5929	1466.66650	41.22790	21.7696
4	27.880	MM	0.7553	1880.57166	41.49514	27.9131

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.928	MM	0.3911	1013.92987	43.20525	3.7297
2	19.813	MM	0.5463	787.36572	24.02043	2.8963
3	21.562	MM	0.5725	1.23679e4	360.06619	45.4948
4	26.476	MM	0.6971	1.30161e4	311.20190	47.8793







Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.759	BB	1.2184	2.08910e4	264.24548	32.0318
2	81.808	BB	1.9026	1.17098e4	94.96300	17.9545
3	95.399	BV	2.1886	1.15421e4	81.48060	17.6973
4	100.217	VB	2.6803	2.10766e4	119.11897	32.3164

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.536	MM	1.4461	891.56726	10.27521	2.9983
2	80.211	MM	2.0708	9294.45313	74.80637	31.2567
3	94.216	MM	2.1704	967.72577	7.43123	3.2544
4	98.627	MM	2.7940	1.85821e4	110.84552	62.4906