Supporting Information

Unsymmetrical Hybrid Ferrocene-Based Phosphine-Phosphoramidites: A New Class of Practical Ligands for Rh-Catalyzed Asymmetric Hydrogenation

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General Procedures: All synthetic reactions and manipulations were performed in a nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were reagent grade, dried and distilled before use following standard procedures. Dimethyl itaconate **9** and o-phenylene phosphorochloridite was purchased from Acros. chlorophosphites **3** and (*S_c*,*R_p*)-**2a** were prepared according the literature procedure.^{1, 2} Enamide **7** and methyl (*Z*)-acetamidocinnamate **11** were known compounds which were synthesized according to the literature procedure.^{3, 4} All other chemicals obtained commercially. Optical rotations were measured on a JASCO P-1020 high sensitive polarimeter. ¹H, ¹³C and ³¹P NMR spectra were recorded at room temperature on a BRUKER DEX 400 (400 MHz) spectrometers. Chemical shifts were determined relative to the residual solvent peaks (e.g. CH₂Cl₂, δ = 5.30 ppm for proton atoms, δ = 54.2 ppm for carbon atoms; H₃PO₄, δ = 0 ppm for phosphorus atoms). Enantiomeric excesses were determined by capillary GC analysis with a Chiral Select 1000 column (0.25mm x 30m) for **8**, with a γ-DEX-225 capillary column (0.25mm x 30m) for **10**, and with a CP-Chiralsil-L-Val column (0.25mm x 30m) for **12**.

Synthesis of key intermediate (*S_c*,*S_p*)-**2b**.

(*S*)-*N,N*-dimethyl-1-[(*R*)-2-trimethylsilyl-(*S*)-5-(diphenylphosphino)ferrocenyl]ethylamine **5** (1.03 g, 2.0 mmol)⁵ was sealed in an air-free tube with acetic anhydride (2.0

mL). The tube was heated to 100°C for 2 hours. After cooling to the room temperature, the reaction mixture was poured into 150 mL of 15% aqueous potassium carbonate with vigorous stirring. Oily material was extracted with Et₂O (30 mL x 2). The ether extract was washed with 5.0% HCl (20 mL x 2), 5.0 % K₂CO₃ (20 mL x 2), and brine (50 mL x 1), and then dried over Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography with hexanes/ethyl acetate (30/1 v/v) as eluent to give a viscous liquid. The resulting materials were then dissolved in a solution of 10 mL of 33 % aqueous H₂NMe in 20 mL of CH₃CN. The mixture was then placed in a 100 mL autoclave and heated at 70-80°C for 8 hours. The reaction mixture was diluted with 10 mL of CH₂Cl₂, and the solvent was evaporated. The residue was purified by silica gel column chromatography with hexanes/EtOAc (10/1 to 4/1 v/v) to give an orange viscous liquid (0.75 g), which was solidified on standing. The resulting solid was purified by rescrySTALLIZATION from 2-propanol to give 0.47 g of (*S*)-1-[(*R*)-2-trimethylsilyl-(*S*)-5-(diphenylphosphino)ferrocenyl]ethylamine **6** as a brown solid. $[\alpha]_D^{25}$ -366 (c 0.29, CH₂Cl₂); ¹H NMR (400 MHz, CD₂Cl₂): δ 0.32 (s, 9 H), 1.51 (d, *J* = 6.8 Hz, 3 H), 2.08 (s, 3 H), 3.58-3.65 (m, 1 H), 3.93 (s, 5 H), 4.01-4.02 (m, 1 H), 4.26-4.27 (m, 1 H), 7.24-7.58 (m, 10 H) ppm; ¹³C NMR (400 MHz, CD₂Cl₂): δ 1.82, 23.9, 35.1, 55.4, 70.3, 74.4, 74.9, 76.2, 77.4, 74.9, 76.2, 77.5, 106.2, 128.6, 129.8, 133.3, 136.0, 139.3, 141.2 ppm; ³¹P NMR (400 MHz, CD₂Cl₂): δ -23.7 ppm.

(*S*)-1-[(*R*)-2-trimethylsilyl-(*S*)-5-(diphenylphosphino)ferrocenyl]ethylamine **6** (125 mg, 0.25mmol) was dissolved in 5.0 mL of a 1.0 mol / L solution of tetrabutylammonium fluoride (TBAF) in THF. After 3 h reflux, the mixture was concentrated in vacuo to afford a red oil, which was extracted with Et₂O (10 mL x 20). the resulting organic layer was washed with water (10 mL x 2), and then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (modified by 2 % Et₃N) with hexanes/EtOAc/Et₃N (50/10/1 to 20/10/1 v/v/v) to give 98 mg (91.6% yield) of (*S_c*,*S_p*)-**2b** as an orange crystals. $[\alpha]_D^{25}$ -344 (c 0.23, CH₂Cl₂); ¹H NMR (400 MHz,

CD₂Cl₂): δ 0.88 (d, J = 6.4 Hz, 3 H), 2.44 (s, 3 H), 3.57-3.61 (m, 1 H), 4.24 (s, 1 H), 4.47 (s, 1 H), 7.18-7.53 (m, 10 H) ppm; ¹³C NMR (400 MHz, CD₂Cl₂): δ 22.7, 35.4, 69.1, 69.6, 70.0, 71.6, 74.8, 102.0, 128.8, 129.8, 133.4, 135.8, 138.5, 141.0 ppm; ³¹P NMR (400 MHz, CD₂Cl₂): δ -24.3 ppm. HRMS calcd for C₂₅H₂₆FeNP + H: 428.1160, found: 428.1155.

General procedure for the synthesis of ferrocene based phosphine-phosphoramidites **1**.

Chlorophosphite **3** (1.0 mmol) was dissolved in 4.0 mL of dried toluene, which was cooled to 0°C. A solution of (*S_c*,*R_p*)-**2a** or (*S_c*,*S_p*)-**2b** (427 mg, 1.0 mmol) and Et₃N (303 mg, 3.0 mmol) in 4.0 mL of toluene was added to above-solution during 30 minutes. The resulting mixture was standing at room temperature overnight. The precipitation was filtrated, and the solid was washed with toluene (5 mL x 1). The filtrate was collected, and concentrated under reduced pressure. Adding the n-hexane to the filtrate gave the yellow power **1**, which was sufficient pure for further use. An analytic sample was obtained by column chromatography purification (silica gel, hexanes / ethyl acetate = 4 / 1) to give yellow power **1**, which can be crystallized from hexane/acetate.

(*S_c*,*R_p*,*S_a*)-**1a**: $[\alpha]^{25}_{\text{D}}$ +253 (c 0.26, CH₂Cl₂); ¹H NMR (400 MHz, CD₃COCD₃): δ 1.74-1.75 (d, 3 H), 1.84-1.86 (d, 3 H), 3.92 (s, 1 H), 4.00 (s, 5H), 4.40-4.41 (m, 1 H), 4.62 (s, 1 H), 5.31-5.32 (m, 1 H), 6.85-6.87 (m, 1 H), 7.13-7.27 (m, 9 H), 7.42-7.65 (m, 8 H), 7.93-8.03 (m, 4 H); ¹H NMR (400 MHz, CD₃COCD₃): δ 19.5, 25.4, 52.5, 70.6, 70.9, 71.1, 73.0, 123.1, 123.4, 125.7, 125.9, 127.3, 127.4, 127.5, 128.5, 128.9, 129.2, 129.3, 129.7, 130.4, 131.1, 131.4, 133.2, 136.7, 136.9, 150.7, 151.8; ³¹P NMR (400 MHz, CD₃COCD₃): δ -25.0 (d, J = 125.6 Hz), 148.8 (d, J = 125.6 Hz). HRMS calcd for C₄₅H₃₇FeNO₂P₂: 741.1649, found: 741.1645.

(*S_c*,*R_p*,*R_a*)-**1b**: $[\alpha]^{25}_{\text{D}}$ +181 (c 0.31, CH₂Cl₂); ¹H NMR (400 MHz, CD₂Cl₂): δ 1.68-1.69 (d, 3 H), 1.90-1.91 (d, 3 H), 3.87 (s, 5 H), 4.13 (s, 1 H), 4.41-4.42 (m, 1 H), 4.53 (s, 1 H), 5.05-5.10 (m, 1 H), 6.10-6.12 (d, 1 H), 7.16-7.37 (m, 15 H), 7.58-7.60 (m, 3 H), 7.79-7.81 (m, 1 H), 7.88-7.94 (m, 2 H) ppm; ¹³C NMR (400 MHz, CD₂Cl₂):

δ 19.9, 27.8, 70.3, 70.5, 71.4, 73.0, 76.2, 122.9, 123.2, 125.0, 125.3, 126.5, 126.6, 127.4, 128.3, 128.8, 128.9, 129.0, 129.8, 130.1, 130.8, 133.1, 133.3, 133.4, 136.1, 136.3, 139.7, 142.1, 150.3, 151.2 ppm; ^{31}P NMR (400 MHz, CD_2Cl_2): δ -26.4, 151.3 ppm. HRMS calcd for $\text{C}_{45}\text{H}_{37}\text{FeNO}_2\text{P}_2$: 741.1649, found: 741.1647.

(S_c, S_p, R_a) -**1c**: $[\alpha]^{25}_{\text{D}} -16$ (c 0.03, CH_2Cl_2); ^1H NMR (400 MHz, CD_2Cl_2): δ 1.36-1.38 (d, 3 H), 2.24-2.25 (d, 3 H), 3.80 (s, 1 H), 4.10 (s, 5 H), 4.27 (s, 1 H), 4.39 (s, 1 H), 5.05-5.15 (m, 1H), 7.19-7.42 (m, 15 H), 7.54-7.56 (m, 3 H), 7.89-8.00 (m, 4 H) ppm; ^{13}C NMR (400 MHz, CD_2Cl_2): δ 23.3, 28.1, 70.1, 70.6, 71.1, 71.6, 74.8, 99.4, 122.7, 125.3, 125.5, 126.8, 127.4, 127.5, 128.6, 128.8, 129.0, 129.1, 129.9, 130.9, 131.0, 131.5, 132.1, 133.1, 133.3, 135.9, 136.2, 141.0, 150.3, 151.2 ppm. ^{31}P NMR (400 MHz, CD_2Cl_2): δ -23.3, 148.7 ppm. HRMS calcd for $\text{C}_{45}\text{H}_{37}\text{FeNO}_2\text{P}_2$: 741.1649, found: 741.1647.

(S_c, S_p, S_a) -**1d**: $[\alpha]^{25}_{\text{D}} +398$ (c 0.20, CH_2Cl_2); ^1H NMR (400 MHz, CD_2Cl_2): δ 1.41-1.43 (d, 3 H), 2.12-2.13 (d, 3 H), 3.89 (s, 1 H) 4.03 (s, 5 H), 4.40 (s, 1 H), 4.71 (s, 1 H), 5.00-5.15 (m, 1 H), 7.18-7.54 (m, 18 H), 7.93-8.01 (m, 4 H) ppm; ^{13}C NMR (400 MHz, CD_2Cl_2): δ 23.1, 28.9, 70.1, 70.7, 72.3, 72.7, 74.4, 98.7, 122.8, 125.3, 125.5, 126.9, 127.5, 128.6, 128.7, 129.0, 129.1, 129.9, 130.8, 131.1, 131.5, 132.1, 133.2, 133.4, 136.0, 136.2, 141.2, 150.4, 151.2 ppm; ^{31}P NMR (400 MHz, CD_2Cl_2): δ -22.5, 149.9 ppm. HRMS calcd for $\text{C}_{45}\text{H}_{37}\text{FeNO}_2\text{P}_2$: 741.1649, found: 741.1641.

(S_c, R_p) -**1e**: $[\alpha]^{25}_{\text{D}} +376$ (c 0.29, CH_2Cl_2); ^1H NMR (400 MHz, CD_2Cl_2): δ 1.74-1.76 (d, 3 H), 1.90-1.91 (d, 3 H), 3.94 (s, 5 H), 4.35-4.36 (m, 1 H), 4.51 (s, 1 H), 5.05-5.15 (m, 1 H), 6.37-6.39 (m, 1 H), 7.11-7.39 (m, 15 H), 7.59-7.61 (m, 2H) ppm; ^{13}C NMR (400 MHz, CD_2Cl_2): δ 19.3, 25.6, 70.1, 70.5, 71.3, 72.7, 76.1, 95.6, 122.2, 123.0, 124.6, 125.1, 128.0, 128.5, 128.7, 128.8, 129.5, 129.9, 130.0, 130.1, 131.4, 132.1, 132.8, 132.9, 136.2, 136.5, 139.4, 151.7, 153.3 ppm; ^{31}P NMR (400 MHz, CD_2Cl_2): δ -24.9 (d, $J = 110.8$ Hz), 150.0 (d, $J = 110.8$ Hz) ppm. HRMS calcd for $\text{C}_{37}\text{H}_{33}\text{FeNO}_2\text{P}_2$: 641.1336, found: 641.1328.

(S_c, R_p) -**1f**: $[\alpha]^{25}_{\text{D}} +163$ (c 0.17, CH_2Cl_2); ^1H NMR (400 MHz, CD_2Cl_2): δ 1.54-1.56 (d, 3 H), 1.72-1.73 (d, 3 H), 3.93 (s, 5 H), 4.34-4.35 (m, 1 H), 4.46 (s, 1 H), 5.22-5.24 (m, 1 H), 6.37-6.39 (m, 1 H), 6.69-6.83 (m, 3 H), 7.06-7.62 (m, 10 H) ppm; ^{13}C NMR

(400 MHz, CD₂Cl₂): δ 20.2, 24.5, 70.1, 70.6, 71.3, 73.0, 111.3, 111.4, 121.8, 121.9, 128.1, 128.4, 128.7, 128.8, 129.9, 132.9, 133.1, 136.2, 136.4, 139.0, 141.2, 147.2, 147.4 ppm; ³¹P NMR (400 MHz, CD₂Cl₂): δ -25.3 (d, J = 106.0 Hz), 147.8 (d, J = 106.0 Hz) ppm. HRMS calcd for C₃₁H₂₉FeNO₂P₂: 565.1023, found: 565.1011.

General procedure for asymmetric hydrogenation and determination of enantiomeric excesses.

In a nitrogen-filled glovebox, a stainless steel autoclave was charge with Rh(COD)₂BF₄ (4.0 mg, 1 x 10⁻² mmol) and ferrocenylphosphine-phosphoramidite ligands **1** (1.1 x 10⁻² mmol) in 3 mL of a degassed solvent. After stirring for 10 min at room temperature. A substrate (10 mmol) in 5 mL of same solvents was added to the reaction mixture, and then the hydrogenation was performed at room temperature under a H₂ pressure of 10 bar for indicated times. The reaction mixture was passed through a short silica gel column to remove the catalyst. After evaporating the solvent, the crude reaction mixture was subjected into the ¹H NMR to determine the conversion. The enantiomeric excesses and yields of hydrogenation products were measured by capillary GC directly without any further purification.

Arylamines:

N-acetyl-1-phenylethylamine **8a** (R = H) was obtained as a colorless crystalline solid (1.50 g, 92% yield). ¹H NMR (CDCl₃) δ 1.48 (d, 3 H), 1.97 (s, 3 H), 5.10-5.14 (m, 1 H), 5.85 (b, 1 H), 7.25-7.36 (m, 5 H). The ee's were determined by GC analysis (Supelco Chiral select 1000 column, 30m x 0.25mm, 15 psi, 130°C) $t(S)$ =16.9, $t(R)$ =18.4. The absolute configuration was determined by comparing the GC retention times with GC data in the literature.⁶

N-acetyl-1-(4-fluorophenyl)ethylamine **8b** (R = F) was obtained as a colorless crystalline solid (1.72 g, 95% yield). ¹H NMR (CDCl₃) δ 1.47 (d, 3 H), 1.98 (s, 3 H),

5.09-5.12 (m, 1 H), 5.68 (b, 1 H), 6.99-7.04 (m, 2 H), 7.27-7.30 (m, 2 H). The ee's were determined by GC analysis (Supelco Chiral select 1000 column, 30m x 0.25mm, 15 psi, 140°C) $t(S)$ =12.6, $t(R)$ =13.7. The absolute configuration was determined by comparing the GC retention times with GC data in the literature.⁶

N-acetyl-1-(4-chlorophenyl)ethylamine **8c** (R = Cl) was obtained as a colorless crystalline solid (1.88 g, 95% yield). ¹H NMR (CDCl₃) δ 1.47 (d, 3 H), 1.99 (s, 1 H), 5.07-5.11 (m, 1 H), 5.68 (b, 1 H), 7.23-7.31 (m, 4 H). The ee's were determined by GC analysis (Supelco Chiral select 1000 column, 30m x 0.25mm, 15 psi, 150°C) $t(S)$ =23.7, $t(R)$ =25.1. The absolute configuration was determined by comparing the GC retention times with GC data in the literature.⁶

N-acetyl-1-(4-bromophenyl)ethylamine **8d** (R = Br) was obtained as a colorless crystalline solid (2.20 g, 91% yield). ¹H NMR (CDCl₃) δ 1.45 (d, 3 H), 1.98 (s, 3 H), 5.05-5.08 (m, 1 H), 5.79 (b, 1 H), 7.17-7.19 (d, 2 H), 7.44-7.46 (d, 2 H). The ee's were determined by GC analysis (Supelco Chiral select 1000 column, 30m x 0.25mm, 15 psi, 150°C) $t(S)$ =42.1, $t(R)$ =44.7. The absolute configuration was determined by comparing the GC retention times with GC data in the literature.⁶

N-acetyl-1-(4-trifluoromethylphenyl)ethylamine **8e** (R = CF₃) was obtained as a colorless crystalline solid (2.22 g, 97% yield). ¹H NMR (CDCl₃) δ 1.50 (d, 3 H), 2.01 (s, 3 H), 5.14-5.18 (m, 1 H), 5.72 (b, 1 H), 7.42-7.44 (d, 2 H), 7.58-7.60 (d, 2 H). The ee's were determined by GC analysis (Supelco Chiral select 1000 column, 30m x 0.25mm, 15 psi, 150°C) $t(S)$ =9.6, $t(R)$ =10.4. The absolute configuration was determined by comparing the GC retention times with GC data in the literature.⁶

Methylsuccinic acid dimethyl ester

Methylsuccinic acid dimethyl ester **10** was obtained as a colorless oil (1.42 g, 89% yield). ¹H NMR (CDCl₃) δ 1.23 (d, 3 H), 2.38-2.44 (m, 1 H), 2.72-2.78 (m, 1 H), 2.92-2.94 (m, 1 H), 3.68 (s, 3 H), 3.70 (s, 3 H). The ee's were determined by GC analysis (Supelco γ -DEX 225 column, 30m x 0.25mm, 60 pka, 80 °C) $t(S)$ =26.5,

$t(R)$ =28.1 or by GC analysis (Supelco γ -DEX 225 column, 30m x 0.25mm, 10 psi, 80 °C) $t(S)$ =23.1, $t(R)$ =25.7. The absolute configuration was determined by comparing the GC retention times with GC data in the literature.⁷

α -Amino Ester

Methyl 2-acetamido-3-phenylpropionate **12** was obtained as slightly brown crystalline solid (2.12 g, 96% yield). ¹H NMR (CDCl₃) δ 1.98 (s, 3 H), 3.07-3.18 (m, 2 H), 3.73 (s, 3 H), 4.86-4.91 (m, 1 H), 5.97 (b, 1 H), 7.08-7.10 (m, 2 H), 7.25-7.32 (m, 3 H). The ee's were determined by GC analysis (CP-Chiralsil-L-Val column, 30m x 0.25mm, 15 psi, 160 °C) $t(S)$ =11.0, $t(R)$ =12.1. The absolute configuration was determined by comparing the GC retention times with GC data in the literature.⁸

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10125.

1H NMR HU-9 IN CDCL3 2004/08/17

¹H NMR HU-3 IN CD₂CL₂ 2004/07/08

¹³C NMR HU-3 IN CD₂CL₂ 2004/07/08

31P NMR HU-3 IN CD2CL2 2004/07/08

¹³C NMR HU-1 IN CD₂CL₂ 2004/07/08

31P NMR HU-1 IN CD2CL2 2004/07/08

¹³C NMR (HU31-1 IN ACETON-d6)

31P NMR (HU31-1 IN ACETON-d6)

¹³C NMR (HU08-8# IN CH₂CL₂-d₂)

^{31}P NMR HU-8 in CD_2Cl_2

¹³C NMR (HU08-7# IN CH₂CL₂-d₂)

31P NMR (HU08-7# IN CH2CL2-d2)

¹³C NMR HU-2 IN CD₂CL₂

¹³C NMR HU-3 IN CD₂CL₂

^{31}P NMR HU-3 IN CDCl_3

¹³CNMR (HU15-2# IN CD₂CL₂)

31PNM (HU15-2# IN CD2CL2)

1H NMR HU-6 IN CDCL3 2004/08/17

1H NMR HU-5 IN CDCL3 2004/08/16

1H NMR HU-7 IN CDCl3 2004/08/17

¹H NMR HU-2 IN CDCL₃ 2004/08/16

1H NMR HU-1 IN CDCL3 2004/08/16

1H NMR HU-1 IN CDCL3 2004/08/19

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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.929	VV	0.5656	1.21757e6	2.72328e4	50.02639
2	18.495	VV	0.4517	1.21628e6	3.58597e4	49.97361

Totals : 2.43385e6 6.30925e4

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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.281	BV	0.4506	2.49655e5	8918.55469	19.20523
2	18.185	VB	0.4324	1.05028e6	3.22132e4	80.79477

Totals : 1.29993e6 4.11317e4

(Entry 1, Table 1)

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Area Percent Report
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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.373	MM	0.2377	1640.99963	115.07597	0.21296
2	18.257	BB	0.4080	7.68924e5	2.66981e4	99.78704

Totals : 7.70565e5 2.68132e4

8a

(Entry 2, Table 1)

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Area Percent Report
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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.069	BB	0.3052	6.06507e4	3141.38745	55.27041
2	17.564	BB	0.3211	4.90837e4	2375.35718	44.72959

Totals : 1.09734e5 5516.74463

8a

(Entry 3, Table 1)

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

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Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.337	BB	0.3451	3.95936e5	1.69170e4	99.79217
2	17.594	MM	0.2611	824.59546	52.63436	0.20783

Totals : 3.96761e5 1.69696e4

8a

(Entry 4, Table 1)

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.685	MM	0.3157	5403.47021	285.29062	8.70202
2	18.253	PB	0.3325	5.66909e4	2661.30542	91.29798

Totals : 6.20944e4 2946.59604

8a

(Entry 5, Table 1)

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

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Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.307	BV	0.5883	1.79593e5	4965.56152	9.29955
2	18.466	VP	0.5232	1.75161e6	4.30014e4	90.70045

Totals : 1.93120e6 4.79870e4

8a

(Entry 6, Table 1)

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.787	BV	0.4839	1.18481e6	3.38898e4	89.05410
2	17.849	VP	0.3048	1.45628e5	7424.37646	10.94590

Totals : 1.33044e6 4.13142e4

8a

(Entry 7, Table 1)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.358	MM	0.2261	809.72888	59.67658	0.20743
2	18.025	BB	0.3601	3.89550e5	1.62237e4	99.79257

Totals : 3.90360e5 1.62834e4

8a

(Entry 8, Table 1)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	16.250	MM	0.3065	3447.45972	187.48569	0.36252
2	18.264	BB	0.4292	9.47522e5	2.99450e4	99.63748

Totals : 9.50969e5 3.01325e4

8a

(Entry 9, Table 1)

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	12.716	PV	0.2209	4.70909e4	3332.15430	49.54712
2	13.595	VB	0.2357	4.79518e4	3183.25610	50.45288

Totals : 9.50427e4 6515.41040

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	12.593	MM	0.2173	3587.28467	275.08548	0.69398
2	13.675	VB	0.2805	5.13327e5	2.81762e4	99.30602

Totals : 5.16914e5 2.84513e4

(Entry 10, Table 1)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	23.994	PV	0.3879	1.57373e4	628.89972	49.16295
2	25.210	VB	0.4056	1.62732e4	613.27643	50.83705

Totals : 3.20104e4 1242.17615

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	23.719	MM	0.3267	1646.22314	83.97400	0.59210
2	25.072	VB	0.4334	2.76384e5	9910.14648	99.40790

Totals : 2.78030e5 9994.12048

(Entry 11, Table 1)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	42.876	BV	0.7635	1.77294e5	3473.26099	49.43877
2	44.963	VB	0.7112	1.81319e5	3837.56299	50.56123

Totals : 3.58613e5 7310.82397

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	42.093	MM	0.5883	2662.38867	75.43184	0.52028
2	44.694	VB	0.7751	5.09061e5	9350.76367	99.47972

Totals : 5.11723e5 9426.19551

(Entry 12, Table 1)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	9.694	PV	0.1730	1.00654e5	9103.98145	49.35275
2	10.399	VV	0.1793	1.03294e5	8906.95801	50.64725

Totals : 2.03948e5 1.80109e4

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	9.589	MM	0.1583	1469.23523	154.65553	0.40884
2	10.391	BB	0.1948	3.57898e5	2.84355e4	99.59116

Totals : 3.59368e5 2.85902e4

(Entry 13, Table 1)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	26.508	VV	0.3563	6.15499e4	2050.14307	50.45456
2	28.120	VV	0.4050	6.04409e4	1762.76086	49.54544

Totals : 1.21991e5 3812.90393

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	23.855	PV	0.3999	4.93377e4	1845.49988	48.62985
2	25.300	VB	0.4645	5.21179e4	1632.26416	51.37015

Totals : 1.01456e5 3477.76404

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	26.209	PB	0.3717	1.02086e5	3922.11572	99.94584
2	28.709	MM	0.1172	55.32235	7.86523	0.05416

Totals : 1.02141e5 3929.98096

10

(Entry 2, Table 2)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	25.940	PB	0.4467	2.06120e5	6218.82324	99.94363
2	28.622	MM	0.1960	116.25592	9.88805	0.05637

Totals : 2.06237e5 6228.71129

10

(Entry 3, Table 2)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	23.469	PB	0.3637	1.60310e5	6078.02783	99.93291
2	25.617	MM	0.1740	107.62737	10.30633	0.06709

Totals : 1.60418e5 6088.33416

(Entry 4, Table 2)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	23.517	PB	0.3473	1.36471e5	5465.92627	99.80572
2	25.573	MM	0.2194	265.64938	20.17566	0.19428

Totals : 1.36737e5 5486.10192

(Entry 5, Table 2)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	26.020	PB	0.3967	1.57254e5	5201.35449	99.93055
2	28.753	MM	0.1918	109.28680	9.49835	0.06945

Totals : 1.57363e5 5210.85284

10

(Entry 6, Table 2)

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	23.600	PB	0.3250	1.05568e5	4579.34570	99.53799
2	25.612	MM	0.2578	489.99408	31.67931	0.46201

Totals : 1.06058e5 4611.02502

10

(Entry 7, Table 2)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount   :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	11.020	PV	0.1340	5.81961e4	6928.67236	49.99280
2	12.096	VB	0.1373	5.82129e4	6706.73242	50.00720

Totals : 1.16409e5 1.36354e4

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount   :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	11.212	MM	0.1283	1846.22705	239.74133	1.17623
2	12.439	BB	0.1664	1.55115e5	1.34626e4	98.82377

Totals : 1.56961e5 1.37023e4

(Entry 1, Table 3)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	11.228	MM	0.0983	409.65564	69.43178	0.49330
2	12.346	BB	0.1495	8.26347e4	9136.36328	99.50670

Totals : 8.30443e4 9205.79506

12 (Entry 2, Table 3)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	11.204	MM	0.1384	377.58975	45.45784	0.07062
2	12.560	PB	0.2666	5.34300e5	2.52749e4	99.92938

Totals : 5.34677e5 2.53203e4

12 (Entry 3, Table 3)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	11.148	MM	0.0594	38.78903	10.88327	0.03980
2	12.144	PB	0.1759	9.74169e4	9477.95898	99.96020

Totals : 9.74557e4 9488.84225

12 (Entry 4, Table 3)

```

=====
                        Area Percent Report
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Sample Amount  :      1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	11.110	MM	0.1769	310.34482	29.23577	0.06747
2	12.439	PB	0.2476	4.59637e5	2.39785e4	99.93253

Totals : 4.59947e5 2.40077e4

12 (Entry 5, Table 3)

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: FID1 B,

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	11.267	MM	0.1119	572.63593	85.32590	0.51407
2	12.427	BB	0.1671	1.10820e5	1.08547e4	99.48593

Totals : 1.11392e5 1.09400e4