Supplentary information 1

Accessible protocol for asymmetric hydroformylation of vinylarenes using formaldehyde

Tsumoru Morimoto,* Tetsuji Fujii, Kota Miyoshi, Gouki Makado, Hiroki Tanimoto,

Yasuhiro Nishiyama, and Kiyomi Kakiuchi

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST),

Ikoma, Nara 630-0192

morimoto@ms.naist.jp

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1. General considerations.

Nuclear magnetic resonance spectra were recorded on a 500 MHz spectrometer. Chemical shifts of ^{1}H NMR spectra are given in ppm using the solvent signal as the internal standard ($CDCl_3$, δ = 7.26 ppm). Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant in Hz, and integration. ^{13}C NMR chemical shifts are given in ppm using deuteriochloroform (77.0 ppm) as the internal standard. Infrared absorption peaks are reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained with ionization voltages of 70 eV. High performance liquid chromatography was conducted using an ultraviolet detector. Optical rotations were measured using a digital polarimeter.

2. Materials.

All commercial reagents were used as supplied or purified by standard techniques when necessary. Formalin, (-)-1,2-bis((2*R*,5*R*)-diphenylphospholano)ethane ((*R*,*R*)-Ph-bpe), its enantiomer ((*S*,*S*)-Ph-bpe), and 4-trifluoromethylstyrene (**13**) were purchased from Aldrich Chemical Co. Paraformaldehyde, which was purchased from Nacalai Tesque, Inc., was dried over P_2O_5 under a vacuum before use. Toluene (dehydrated) was purchased from Kanto Chemical Co. 1,1'-Bis(diphenylphosphino)-2,2'-biphenyl (BIPHEP) and (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane ((*S*,*S*)-BDPP) were purchased from Strem Chemicals Inc. 1,1'-(*S*)-Bis(diphenylphosphino)-2,2'-binaphthyl ((*S*)-BINAP), 4-methylstyrene (**5**), and 3-methylstyrene (**7**) were purchased from Tokyo Chemical Industry Co. 3-Methoxystyrene (**3**), 4-fluorostyrene (**9**), and 4-chlorostyrene (**11**) were purchased from Wako Pure Chemical Industries, Ltd. $[RhCl(cod)]_2$ was prepared using a previously reported method.[1] Vinylarenes **15**[2] and **17**[3] were synthesized along to the previous reports, respectively.

3. Representative procedure for the asymmetric hydroformylation of vinylarenes using formalin.

A 10 mL screw-capped vial containing a stirring bar was charged with $[RhCl(cod)]_2$ (2.47 mg, 0.005 mmol), (*R*,*R*)-Ph-bpe (1.0 mL of 12 mM toluene solution, 0.012 mmol), vinylarene (104.2 mg, 1 mmol), formalin (37%, 0.19 mL, 2.5 mmol), and toluene (3.8 mL) under nitrogen. The mixture was degassed and purged with nitrogen (three freeze-pump-thaw cycles). The vial containing the mixture was placed in a preheated oil bath at 80 °C and stirred for 10 h. The reaction mixture was diluted with ether (2 mL), and *n*-dodecane (50 mg) was then added as the internal standard for GC analysis. The conversion of vinylarene, the chemical yields of produced aldehydes, and the regioselectivity of the aldehydes (*branched*/*linear* raio) were determined by GC, because some of the produced aldehydes are volatile and are easily oxidized under the usual workup operations. After the GC analysis, methanol (5 mL) and $NaBH_4$ (37.8 mg, 1 mmol) were added to the mixture at 0 °C, and the resulting mixture was stirred at the same temperature until the aldehydes were completely consumed. After adding aqueous HCl (1.0 M, 20 mL) to the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and then concentrated in vacuo. All the eluent fractions after purification of the residue by column chromatography on silica gel were collected. The enantiomeric excess (ee%) of the branched alcohol was determined by HPLC using a chiral column stationary phase.

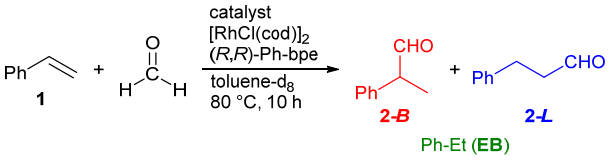
4. Measurement of ee% of branched aldehydes.

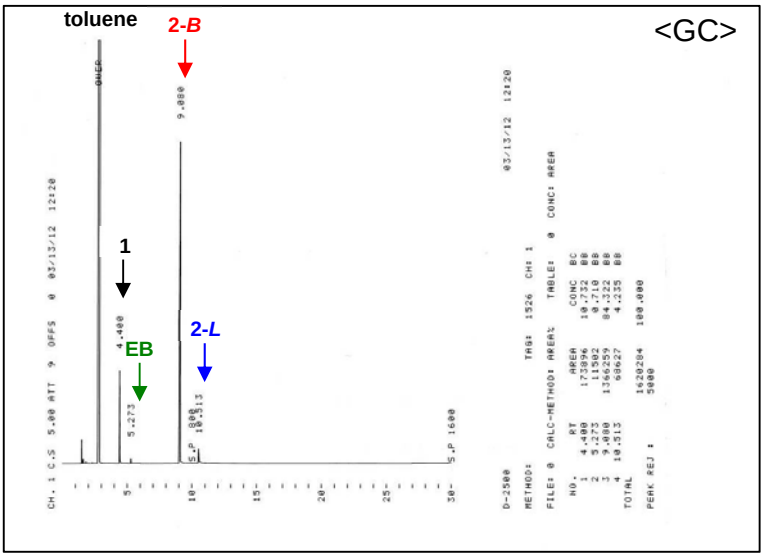
Enantiomeric excess (ee%) of branched aldehydes was determined by HPLC equipped with a chiral column stationary phase, after conversion to the corresponding alcohols.

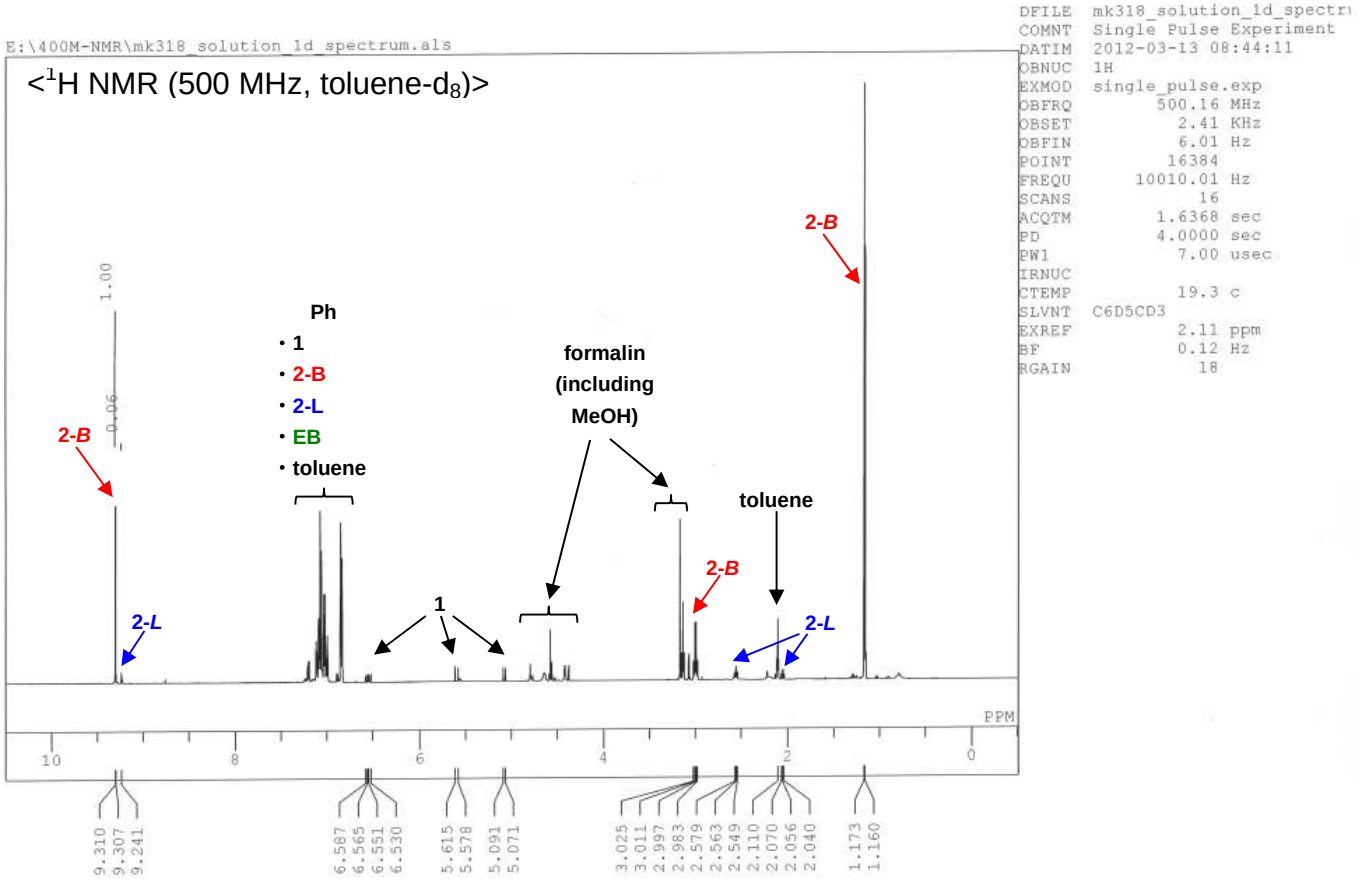
5. Determination of absolute configuration.

The absolute configurations of **2-*B***, **4-*B***, **6-*B***, **8-*B***, **10-*B***, **12-*B***, **14-*B***, **16-*B***, and **18-*B*** were assigned from specific optical rotation data for the purified corresponding *branched*-alcohols.

6. GC and ^{1}H NMR analyses of the catalytic reaction of styrene with formalin in toluene-d_8.



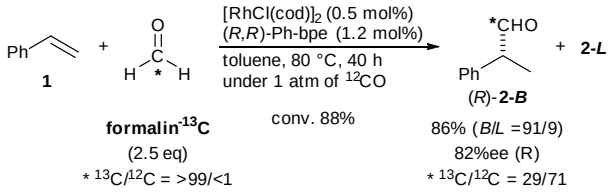




7. ^{13}C-Labeled Experimets (Scheme 3).

Reactions using ^{13}C-labeled formalin were run following the typical procedures. The incorporation (%) of ^{13}C was determined, after the produced aldehydes were converted to the corresponding alcohols, by comparing their ^{13}C-integration values with those of the corresponding unlabeled alcohols.

(a) Reaction of styrene with formaldehyde-^{13}C under 1atm of ^{12}CO (Figure A-iii).



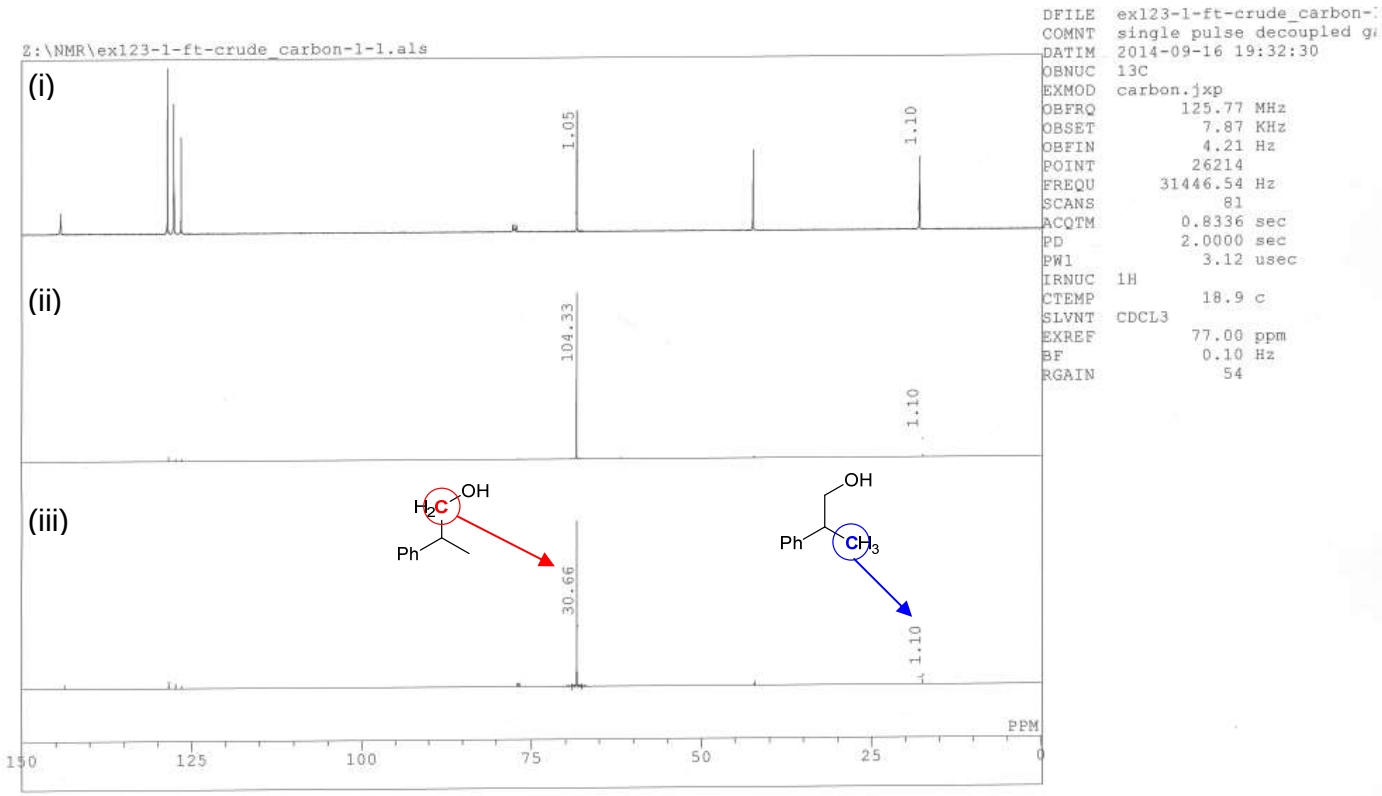
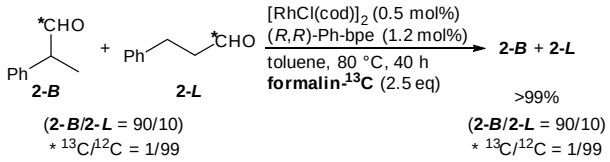


Figure A. ^{13}C NMR (500 MHz, $CDCl_3$) of alcohols derived from **2-*B*** formed in the reaction of styrene with (i) unlabeled formaldehyde; (ii) ^{13}C-labeled formaldehyde under N_2; (iii) ^{13}C-labeled formaldehyde under 1 atm of ^{12}CO.

(b) Reaction of a mixture of **2-*B*** and **2-*L*** with formaldehyde-^{13}C (Figure B-ii).

When a mixture of ^{13}C-unlabeled branched and linear aldehydes (*B*/*L* = 90/10) was reacted with formaldehyde-^{13}C, no scrambling at the formyl carbons of the recovered aldehydes was observed.



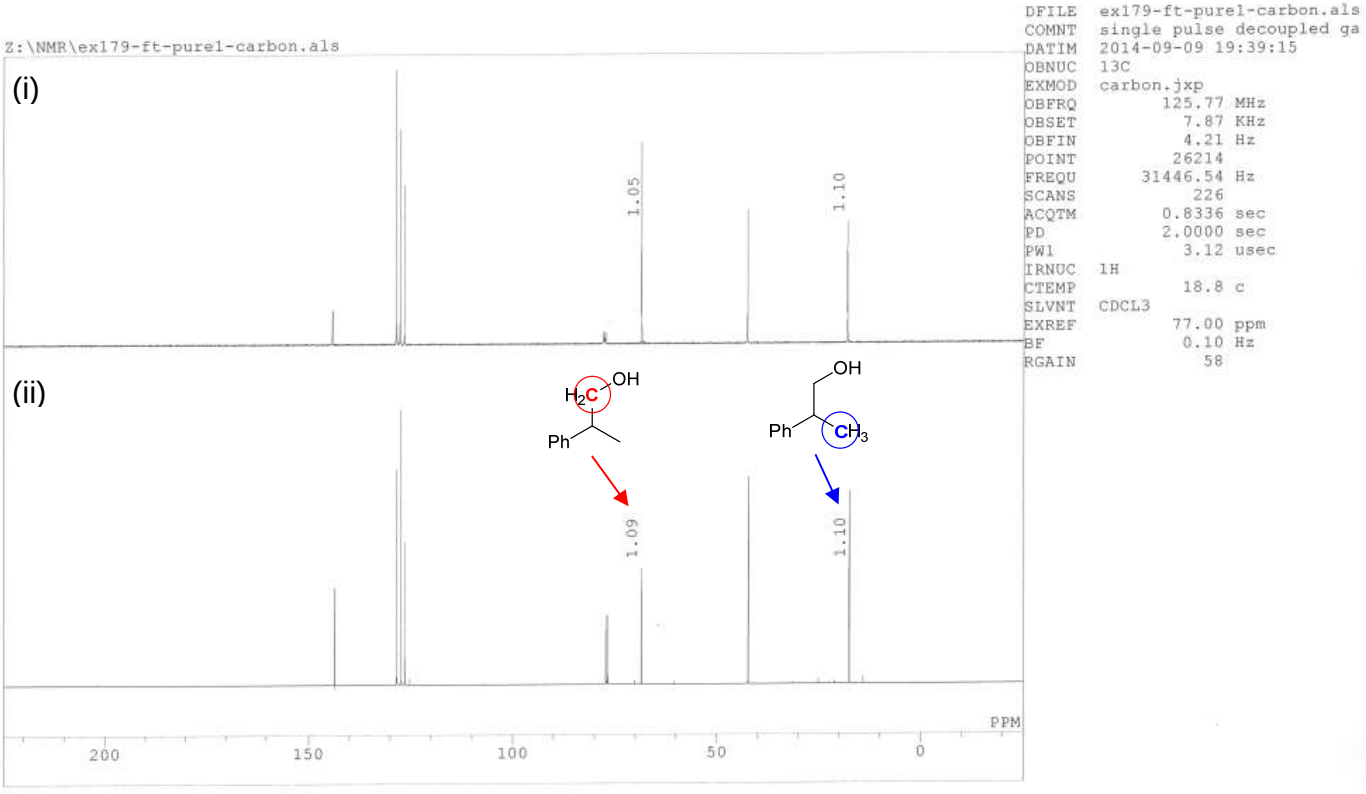
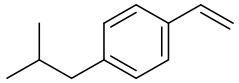


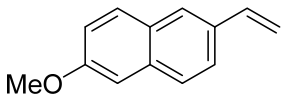
Figure B. ^{13}C NMR (500 MHz, $CDCl_3$) of alcohols derived from (i) the starting material; (ii) the recovered **2-*B*** in the reaction with ^{13}C-labeled formaldehyde.

8. Spectral data of vinylaenes 15 and 17.



15

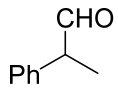
4-Isobutylstyrene (**15**).[2] Colorless oil; R_f 0.28 (hexane/Et_2O = 7/1); ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, *J* = 8.9 Hz, 6H), 1.82–1.90 (m, 1H), 2.46 (d, *J* = 6.7 Hz, 2H), 5.19 (d, *J* = 11.0 Hz, 1H), 5.71 (d, *J* = 17.7 Hz, 1H), 6.70 (dd, *J* = 17.7, 11.0 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 30.2, 45.1, 112.8, 125.9, 129.3, 135.0, 136.7, 141.5; IR (neat) ν 2954 s, 2921 s, 2867 m, 2846 m, 1903 w, 1807 w, 1680 w, 1630 m, 1609 w, 1565 w, 1510 m, 1464 m, 1405 m, 1383 m, 1366 m, 1338 w, 1317 w, 1285 w, 1202 w, 1167 w, 1119 w, 1080 w, 1017 w, 989 m, 902 s, 847 s, 804 s, 722 w, 642 w; MS(EI) *m*/*z* (relative intensity, %) 160 (M^+, 17), 118 (17), 117 (100), 115 (16), 91 (10); exact mass calcd for $C_{12}H_{16}$ 160.1252, found 160.1253.



17

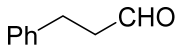
2-methoxy-6-vinylnaphthalene (**17**).[3] White solid; mp 90–92 °C ; R_f 0.31 (hexane/Et_2O = 100/1); ^1H NMR (500 MHz, $CDCl_3$) δ: 3.91 (s, 3H), 5.27 (d, *J* = 11.0 Hz, 1H), 5.82 (d, *J* = 17.7 Hz, 1H), 6.83-6.86 (m, 1H), 7.11-7.13 (m, 2H), 7.60-7.70 (m, 4H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 53.3, 105.8, 113.1, 118.9, 123.7, 126.2, 127.0, 128.9, 129.5, 132.9, 134.3, 136.9, 157.8; IR (KBr) ν 2962 m, 2938 m, 2906 m, 2837 w, 2050 w, 1936 w, 1816 w, 1785 w, 1715 w, 1626 s, 1597 s, 1505 m, 1780 s, 1462 s, 1454 m, 1428 m, 1403 m, 1390 s, 1370 m, 1337 m, 1297 w, 1269 s, 1240 s, 1196 s, 1175 s, 1162 s, 1117 m, 1029 s, 993 s, 963 m, 926 m, 893 s, 856 s, 815 s, 752 w, 706 w, 630 w; MS(EI) m/z (relative intensity, %) 184 (M^+,100), 169 (23), 141 (67), 139 (13), 115 (33) ; exact mass calcd for $C_{13}H_{12}O$ 184.0888, found 184.0888.

9. Spectral data of branched and linear aldehydes.



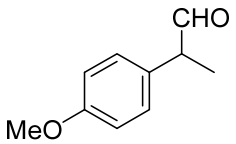
2-*B*

2-Phenylpropanal (**2-*B***). Colorless oil; R_f 0.32 (hexane/Et_2O = 7/1); ^{1}H NMR (500MHz, $CDCl_3$) δ 1.45 (d, *J* = 6.7 Hz, 3H), 3.64 (q, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 6.7 Hz, 2H), 7.31 (tt, *J* = 7.6, 2.0 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 9.70 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 53.0, 127.5, 128.3, 129.1, 137.7, 201.1; IR (neat) ν 2977 m, 2934 m, 2875 m, 2815 m, 2717 m, 2359 w, 1852 w, 1879 w, 1723 s, 1601 m, 1583 w, 1492 s, 1452 s, 1390 m, 1373 w, 1301 w, 1266 w, 1184 w, 1157 w, 1119 w, 1066 m, 1021 m, 999w, 912 w, 891 w, 864 s, 759 s; MS(EI) m/z (relative intensity, %) 136 (M^+, 15), 106 (29), 105 (100), 103 (13), 91 (14), 79 (22), 77 (19); exact mass calcd for $C_9H_{10}O$ 134.0732, found 134.0732.



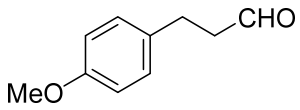
2-*L*

3-Phenylpropanal (**2-*L***). Colorless oil; R_f 0.28 (hexane/Et_2O = 7/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.79 (td, *J* = 7.6, 1.2 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 8.6 Hz, 3H), 7.31 (t, *J* = 7.3 Hz, 2H), 9.83 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 45.2, 126.2, 128.2, 128.5, 140.3, 201.5; IR (neat) ν 2926 w, 2893 w, 2825 w, 2724 w, 2360 w, 1951 w, 1885 w, 1724 s, 1603 w, 1584 w, 1496 m, 1454 m, 1407 m, 1389 m, 1359 w, 1269 w, 1180 w, 1082 w, 1057 w, 1030 w, 914 w, 854 w, 746 s, 700 s; MS(EI) m/z (relative intensity, %) 136 (M^+, 20), 118 (60), 117 (99), 105 (16), 103 (14), 92 (53), 91 (100), 79 (15), 78 (14), 77 (23), 65 (25), 51 (15); exact mass calcd for $C_9H_{10}O$ 134.0732, found 134.0731.



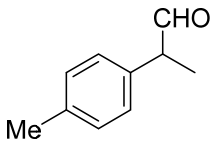
4-*B*

2-(4-Methoxyphenyl)propanal (**4-*B***).[4] Colorless oil; R_f 0.29 (hexane/Et_2O = 6/1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (d, *J* = 6.7 Hz, 3H), 3.59 (q, *J* = 6.9 Hz, 1H), 3.81 (s, 3H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 9.65 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 14.6, 52.1, 55.3, 114.5, 129.3, 159.0, 201.2; IR (neat) ν 2974 m, 2935 m, 2909 w, 2875 w, 2836 m, 2717 w, 1720 s, 1610 m, 1582 m, 1512 s, 1459 m, 1421 w, 1390 w, 1303 m, 1250 s, 1180 s, 1122 w, 1025 s, 892 w, 866 m, 830 s, 806 m, 726 w, 544 m; MS(EI) m/z (relative intensity, %) 164 (M^+,9), 136 (10), 135 (100), 105 (21), 103 (11), 91 (13), 79 (14), 77 (12); exact mass calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0841.



4-*L*

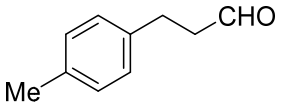
3-(4-Methoxyphenyl)propanal (**4-*L***).[5] Colorless oil; R_f 0.20 (hexane/Et_2O = 6/1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.76 (t, *J* = 7.6 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 3.79 (s, 3H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 9.82 (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 52.1, 55.3, 114.5, 129.4, 129.5, 159.0, 201.2; IR (neat) 2957 m, 2935 m, 2914 m, 2835 m, 2724 m, 1723 s, 1612 s, 1583 m, 1513 s, 1464 m, 1441 m, 1407 m, 1388 m, 1357 w, 1300 m, 1246 s, 1179 s, 1110 m, 1034 s, 862 m, 812 m, 768 m, 705 w, 665 w. ; MS(EI) m/z (relative intensity, %) 164 (M^+,26), 122 (10), 121 (100), 108 (25), 91 (13), 78 (10), 77 (16); exact mass EI calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0841.



6-*B*

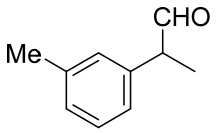
2-(4-Methylphenyl)propanal (**6-*B***).[6] Colorless oil; R_f 0.40 (hexane/Et_2O = 6/1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (d, *J* = 7.3 Hz, 3H), 2.35 (s, 3H), 3.60 (bq, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 9.66 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 14.6, 21.0, 52.5, 128.2, 129.7, 134.6, 137.2, 201.2; IR (neat) ν 2922 w, 2861 w, 2822 w, 2723 w, 1724 s, 1515 m, 1448 w, 1407 w, 1387 w, 1184 w, 1111 w, 1054 w, 861 w, 805 m, 653 w; MS(EI) m/z (relative intensity, %) 148

(M^+,9), 120 (10), 119 (100), 117 (15), 91 (28), 77 (10); exact mass EI calcd for $C_{10}H_{12}O$ 148.0888, found 148.0885.



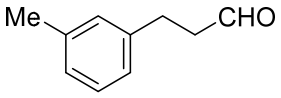
6-*L*

3-(4-Methylphenyl)propanal (**6-*L***).[6] Colorless oil; R_f 0.34 (hexane/Et_2O = 6/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 7.09-7.11 (m, 4H), 9.82 (s, 1H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 21.0, 27.7, 45.4, 128.1, 129.3, 135.8, 137.2, 201.8; IR (neat) ν 2977 m, 2933 w, 2874 w, 2812 w, 2716 w, 1902 w, 1724 s, 1513 s, 1453 m, 1417 w, 1388 w, 1186 w, 1121 w, 1030 w, 1019 m, 892 w, 865 w, 813 s, 719 w; MS(EI) m/z (relative intensity, %) 148 (M^+,63), 133 (18), 119 (14), 117 (11), 115 (13), 106 (43), 105 (100), 103 (15), 92 (52), 91 (50), 79 (20), 78 (10), 77 (29), 65 (13), 51 (12); exact mass EI calcd for $C_{10}H_{12}O$ 148.0888, found 148.0885.



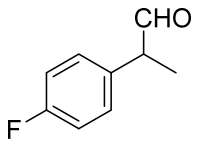
8-*B*

2-(3-Methylphenyl)propanal (**8-*B***).[7] Colorless oil; R_f 0.34 (hexane/Et_2O = 6/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (d, *J* = 7.1 Hz, 3H), 2.36 (s, 3H), 3.60 (q, *J* = 7.1 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 7.02 (s, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 9.68 (s, 1H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 14.6, 21.4, 53.0, 125.3, 128.3, 129.0, 129.1, 137.6, 138.8, 201.2; IR (neat) ν 2977 m, 2933 m, 2873 w, 2812 m, 2718 w, 1722 s, 1605 m, 1589 w, 1489 m, 1455 m, 1389 w, 1304 w, 1160 w, 1115 w, 1096 w, 1067 w, 1027 w, 996 w, 905 m, 878 s, 833 w, 784 s, 703 s, 663 w; MS(EI) m/z (relative intensity, %) 148 (M^+,13), 120 (13), 119 (100), 117 (15), 91 (29), 77 (12); exact mass EI calcd for $C_{10}H_{12}O$ 148.0888, found 148.0888.



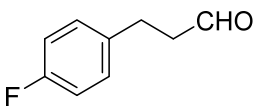
8-*L*

3-(3-Methylphenyl)propanal (**8-*L***).[8] Colorless oil; R_f 0.30 (hexane/Et_2O = 6/1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.77 (t, J = 7.3 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 6.99-7.02 (m, 3H), 7.18 (t, J = 7.3 Hz, 1H), 9.82 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 28.0, 45.3, 125.3, 127.0, 128.5, 129.1, 138.2, 140.2, 201.7; IR (neat) ν 2921 m, 2864 m, 2824 m, 2723 m, 1725 s, 1609 m, 1590 w, 1488 m, 1450 m, 1407 m, 1388 m, 1359 w, 1276 w, 1171 w, 1095 w, 1057 w, 909 w, 847 w, 783 m, 754 w, 700 s; MS(EI) m/z (relative intensity, %) 148 (M^+,70), 120 (15), 119 (29), 117 (14), 115 (14), 106 (69),105 (100), 103 (18), 92 (62), 91 (76), 79 (24), 78 (12), 65 (17), 51 (15); exact mass EI calcd for $C_{10}H_{12}O$ 148.0888, found 148.0888.



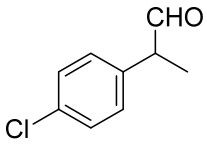
10-*B*

2-(4-Fluorophenyl)propanal (**10-*B***).[4] Colorless oil; R_f 0.34 (hexane/Et_2O = 6/1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.43 (d, J = 6.7 Hz, 3H), 3.63 (bq, J = 6.7 Hz, 1H), 7.06-7.08 (m, 2H), 7.17-7.18 (m, 2H), 9.66 (d, J = 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 52.1, 115.9 (d, $J_{C\text{-}F}$ = 21.1 Hz), 129.8 (d, $J_{C\text{-}F}$ = 8.6 Hz), 133.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 161.2, 163.1, 200.7; IR (neat) ν 2979 w, 2937 w, 2878 w, 2818 w, 2721 w, 1891 w, 1723 s, 1651 w, 1602 m, 1509 s, 1456 w, 1417 w, 1390 w, 1372 w, 1296 w, 1224 s, 1160 m, 1097 w, 1027 w, 1015 w, 896 w, 867 w, 834 w, 720 w, 656 w, 619 w ; MS(EI) m/z (relative intensity, %) 152 (M^+,8), 123 (100), 103 (48), 77 (18) ; exact mass calcd for C_9H_9FO 152.0637, found 152.0634.



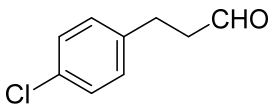
10-*L*

3-(4-Fluorophenyl)propanal (**10-*L***).[9] Colorless oil; R_f 0.23 (hexane/Et_2O = 6/1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.77 (t, J = 7.3 Hz, 2H), 2.93 (t, J = 7.6 Hz, 2H), 6.97-6.99 (m, 2H), 7.15-7.16 (m, 2H), 9.82 (d, J = 1.2 Hz, 1H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 27.1, 45.3, 115.2 (d, $J_{C\text{-}F}$ = 21.1 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8.6 Hz), 135.9 (d, $J_{C\text{-}F}$ = 3.8 Hz), 160.4, 162.3, 201.3; IR (neat) ν 2930 w, 2890 w, 2827 m, 2727 m, 1890 w, 1724 s, 1601 m, 1509 s, 1447 w, 1408 m, 1389 m, 1358 w, 1300 w, 1221 s, 1159 m, 1099 m, 1057 w, 1016 w, 899 w, 865 m, 821 s, 781 m, 756 w, 666 w; MS(EI) m/z (relative intensity, %) 152 (M^+,40), 123 (11), 110 (44), 109 (100), 113 (17), 96 (34), 83 (19), 77 (14), 75 (11); exact mass calcd for C_9H_9FO 152.0637, found 152.0633.



12-*B*

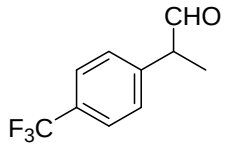
2-(4-Chlorophenyl)propanal (**12-*B***).[4] Colorless oil; R_f 0.31 (hexane/Et_2O = 7/1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.44 (d, J = 7.3 Hz, 3H), 3.63 (q, J = 6.9 Hz, 1H), 7.14-7.15 (m, 2H), 7.33-7.35 (m, 2H), 9.66 (d, J = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 52.3, 129.6, 133.5, 136.1, 200.5; IR (neat) ν 2978 m, 2935 m, 2875 m, 2817 m, 2720 m, 1895 w, 1725 s, 1685 m, 1594 w, 1492 s, 1457 m, 1409 s, 1372 m, 1295 w, 1261 m, 1181 m, 1093 s, 1027 m, 1014 s, 896 m, 864 m, 825 s, 769 m, 718 m, 676 w, 637 w, 529 s; MS(EI) m/z (relative intensity, %) 168 (M^+,9), 141 (31), 139 (100), 104 (10), 103 (65), 77 (34), 51 (12); exact mass calcd for C_9H_9ClO 168.0342, found 168.0341.



12-*L*

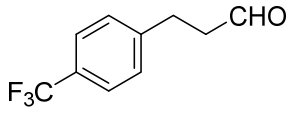
3-(4-Chlorophenyl)propanal (**12-*L***).[9] Colorless oil; R_f 0.19 (hexane/Et_2O = 7/1), ^1H NMR (500 MHz, $CDCl_3$) δ 2.78 (t, J = 7.3 Hz, 2H), 2.93 (t, J = 7.6 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.6 Hz, 3H), 9.82 (d, J = 1.2 Hz, 1H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 27.4, 45.1, 128.7, 129.7, 132.0, 138.8, 201.5; IR (neat) ν 2929 w, 2896 w, 2825 m, 2725 m, 1900 w, 1723s, 1598 w, 1492 s, 1448 w, 1407 m,

1388 m, 1358 w, 1266 w, 1179 w, 1091 s, 1057 w, 1014 m, 902 w, 862 m, 805 m, 720 w, 657 w, 609 w; MS(EI) m/z (relative intensity, %)168 (M^+,48), 133 (58), 127 (33), 126 (25), 125 (100), 115 (14), 114 (10), 112 (29), 105 (14), 103 (35), 91 (52), 89 (22), 77 (43), 75 (16), 63 (12), 55 (14), 51 (23), 50 (14) ; exact mass calcd for C_9H_9ClO 168.0342, found 168.0343.



14-*B*

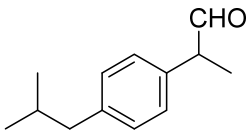
2-(4-Trifluoromethylphenyl)propanal (**14-*B***). Colorless oil; R_f 0.38 (hexane/Et_2O = 2/1); ^1H NMR ($CDCl_3$) δ 1.49 (d, J = 7.3 Hz, 3H), 3.73 (q, J = 7.3 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 9.70 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 52.7, 124.0 (q, $J_{C\text{-}F}$ = 272.5 Hz), 125.9 (q, $J_{C\text{-}F}$ = 3.5 Hz), 128.7, 129.8 (q, $J_{C\text{-}F}$ = 32.6 Hz), 141.8, 200.1; IR (neat) ν 2982 w, 2939 w, 2881 w, 2822 w, 2770 w, 2722 w, 2647 w, 2360 w, 2340 w, 1791 w, 1727 s, 1618 m, 1585 w, 1517 w, 1456 w, 1420 w, 1392 w, 1374 w, 1326 s, 1250 w, 1166 s, 1124 s, 1069 s, 1016 m, 955 w, 896 w, 865 w, 837 m, 787 w, 733 w, 668 w, 634 w, 605 m; MS(EI) m/z (relative intensity, %) 202 (M^+, 8), 174 (20), 173 (100), 159 (12), 153 (36), 133 (66), 127 (18), 105 (19), 103 (13), 77 (13); exact mass calcd for $C_{10}H_9F_3O$ 202.0605, found 202.0605.



14-*L*

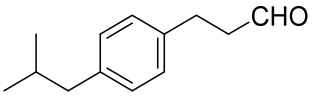
3-(4-Trifluoromethylphenyl)propanal (**14-*L***). Colorless oil; R_f 0.26 (hexane/Et_2O = 2/1); ^1H NMR ($CDCl_3$) δ 2.82 (bt, J = 7.3 Hz, 2H), 3.01 (t, J = 7.3 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H), 9.82 (t, J = 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8, 44.8, 124.2 (q, $J_{C\text{-}F}$ = 272.5 Hz), 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 128.6, 128.7 (q, $J_{C\text{-}F}$ = 32.6 Hz), 144.5, 200.7; IR (neat) ν 2936 w, 2899 w, 2828 w, 2728 w, 2348 w, 1922 w, 1725 s, 1618 m, 1585 w, 1444 w, 1419 m, 1390 w, 1326 s, 1273 w, 1163 s, 1113 s, 1068 s, 1019 m, 903 w, 864 w, 841 w, 822 w, 731 w, 689 w, 602 w; MS(EI) m/z

(relative intensity, %) 202 (M^+, 56), 183 (16), 160 (100), 159 (56), 153 (18), 151 (12), 146 (26), 145 (13), 133 (68), 127 (25), 119 (10), 115 (15), 109 (37), 105 (27), 103 (18), 91 (90), 77 (21), 75 (14), 63 (15), 57 (10), 56 (16), 55 (18), 51 (17), 50 (10); exact mass calcd for $C_{10}H_9F_3O$ 202.0605, found 202.0605.



16-*B*

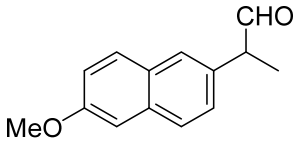
2-(4-Isobutylphenyl)propanal (**16-*B***).[10] Colorless oil; R_f 0.42 (hexane/Et_2O = 6/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (d, J = 6.7 Hz, 6H), 1.43 (d, J = 7.1 Hz, 3H), 1.82-1.90 (m, 1H), 2.47 (d, J = 7.3 Hz, 2H), 3.61 (q, J = 7.1 Hz, 1H), 7.12 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 9.67 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 22.3, 30.2, 45.0, 52.6, 128.0, 129.8, 134.8, 141.0, 201.3; IR (neat) ν 2955 s, 2931 s, 2868 s, 2848 m, 2813 m, 2716 m, 1723 s, 1635 w, 1512 m, 1464 m, 1420 m, 1384 m, 1366 m, 1282 w, 1167 w, 1125 w, 1068 w, 1027 m, 1019 m, 892 m, 865 m, 844 m, 797 m, 743 w, 717 m, 658 w, 631 w; MS(EI) m/z (relative intensity, %) 190 (M^+,16), 162 (25), 161 (100), 119 (66), 118 (13), 117 (31),115 (16), 105 (28), 91 (47), 77 (13), 57 (22); exact mass EI calcd for $C_{13}H_{18}O$ 190.1358, found 190.1359.



16-*L*

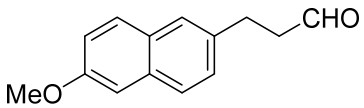
3-(4-Isobutylphenyl)propanal (**16-*L***).[11] Colorless oil; R_f 0.29 (hexane/Et_2O = 6/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (d, J = 6.7 Hz, 6H), 1.82-1.86 (m, 1H), 2.44 (d, J = 7.1 Hz, 2H), 2.77 (td, J = 7.5, 1.5 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H), 7.08-7.09 (m, 4H), 9.82 (t, J = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 27.7, 30.2, 45.0, 45.3, 128.0, 129.3, 137.4, 139.7, 201.8; IR (neat) ν 2954 s, 2924 s, 2867 s, 2848 m, 2819 m, 2719 m, 2360 w, 1902 w, 1725 s, 1513 m, 1465 m, 1452 m, 1408 m, 1384 m, 1365 m, 1280 w, 1208 w, 1167 m, 1116 m, 1082 w, 1056 w, 1021 w, 921 w, 862 m, 792 m, 769 w, 668 w;

MS(EI) m/z (relative intensity, %) 190 (M^+,52), 148 (20), 147 (100), 134 (10), 133 (29), 129 (11),119 (10), 117 (16), 115 (13), 106 (12), 105 (74), 104 (32), 103 (10), 92 (116), 91 (56), 77 (12); exact mass EI calcd for $C_{13}H_{18}O$ 190.1358, found 190.1357.



18-*B*

2-(6-Methoxynaphthalen-2-yl)propanal (**18-*B***).[10] White solid; mp 105-106°C (hexane/AcOEt); R_f 0.32 (hexane/Et_2O = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (s, 3H), 3.90-3.93 (m, 1H), 3.95 (s, 3H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.21 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 8.01 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.40 (d, *J* = 1.8 Hz, 1H), 9.86 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.6, 55.4, 105.7, 119.7, 124.7, 127.1, 127.8, 130.1, 131.1, 132.6, 137.3, 159.7, 197.9; IR (neat) ν 2968 w, 2938 w, 2843 w, 1922 w, 1791 w, 1725 w, 1674 s, 1621 s, 1602 s, 1479 s, 1439 m, 1412 m, 1389 m, 1359 m, 1332 m, 1274 s, 1203 s, 1166 s, 1122 m, 1069 m, 1020 s, 963 m, 948 m, 920 m, 897 s, 860 s, 820 s, 742 m, 671 m, 658 m, 604 m; MS(EI) m/z (relative intensity, %) 214 (M^+,1), 200 (49), 186 (13), 185 (100), 157 (45), 142 (18), 128 (10), 114 (23); exact mass EI calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0993.

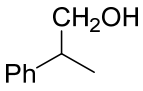


18-*L*

3-(6-Methoxynaphthalen-2-yl)propanal (**18-*L***). White solid; mp 40 °C (hexane/AcOEt); R_f 0.17 (hexane/Et_2O = 7/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.83 (bt, *J* = 7.6 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H), 3.90 (s, 3H), 7.11-7.13 (m, 2H), 7.27 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.54 (s, 1H), 7.66 (dd, *J* = 8.6, 4.6 Hz, 2H), 9.83 (t, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 45.2, 55.2, 105.6, 118.9, 126.2, 127.0, 127.3, 128.0, 128.9, 129.0, 133.1, 135.4, 157.3, 201.6; IR (neat).2965 m, 2937 m, 2893 m, 2843 m, 2732 w, 2049 w, 1920 w, 1728 s, 1632 s, 1605 s, 1505 s, 1485 s, 1455 s, 1414 m, 1392 s, 1345 m,

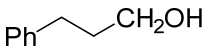
1260 s, 1229 s, 1175 s, 1160 s, 1121 m, 1064 w, 1027 s, 980 w, 963 w, 932 w, 895 s, 855 s, 818 s, 756 w, 714 w, 684 w, 665 w, 611 w; MS(EI) m/z (relative intensity, %) 214 (M^+,52), 172 (22), 171 (100), 158 (21), 141 (12), 128 (29), 115 (16); exact mass EI calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0994.

10. Spectral data of branched and linear alcohols.



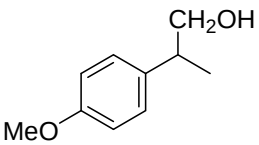
reductant of **2-*B***

2-Phenylpropan-1-ol (reductant of **2-*B***). Colorless oil; R_f 0.38 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (d, J = 7.3 Hz, 3H), 1.46 (s, 1H), 2.94-2.97 (m, 1H), 3.70 (d, J = 6.7 Hz, 2H), 7.23-7.25 (m, 3H), 7.34 (dd, J = 9.8, 5.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.6, 42.4, 68.7, 126.7, 127.5, 128.6, 143.6; IR (neat) ν 2962 s, 2929 s, 2874 s, 1946 w, 1871 w, 1805 w, 1748 w, 1602 w, 1583 w, 1493 s, 1452 s, 1393 m, 1230 w, 1192 w, 1156 w, 1091 w, 1068 m, 1034 s, 1013 s, 974 w, 935 w, 912 w, 842 w, 760 s, 700 s; MS(EI) m/z (relative intensity, %) 136 (M^+, 16), 106 (29), 105 (100), 103 (13), 91 (14), 79 (22), 77 (19); exact mass EI calcd for $C_9H_{12}O$ 136.0888, found 136.0885.



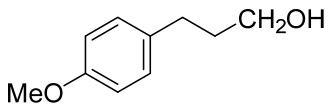
reductant of **2-*L***

3-Phenylpropan-1-ol (reductant of **2-*L***). Colorless oil; R_f 0.34 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (s, 1H), 1.87-1.93 (m, 2H), 2.72 (t, J = 7.6 Hz, 2H), 3.68 (t, J = 3.7 Hz, 2H), 7.18-7.31 (m, 5H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 32.0, 34.2, 62.3, 125.8, 128.3, 128.4, 141.8; IR (neat) ν 2939 s, 2863 s, 1946 w, 1874 w, 1806 w, 1750 w, 1603 m, 1496 s, 1473 m, 1454 s, 1379 m, 1350 m, 1229 w, 1154 w, 1059 s, 1031 s, 917 m, 850 w, 808 w, 745 s, 699 s; MS(EI) m/z (relative intensity, %) 136 (M^+, 21), 118 (60), 117 (97), 105 (16), 103 (14), 92 (53), 91 (100), 79 (15), 78 (14), 77 (23), 65 (26), 51 (15); exact mass EI calcd for $C_9H_{12}O$ 136.0888, found 136.0887.



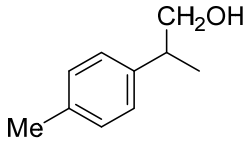
reductant of **4-*B***

2-(4-Methoxyphenyl)propan-1-ol (reductant of **4-*B***).[5] Colorless oil; R_f 0.25 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, J = 6.7 Hz, 3H), 1.37 (s, 1H), 2.91 (td, J = 13.9, 6.9 Hz, 1H), 3.63-3.70 (m, 2H), 3.80 (s, 3H), 6.88 (td, J = 5.8, 3.5 Hz, 2H), 7.16 (td, J = 5.8, 3.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 41.5, 55.3, 68.8, 114.0, 128.4, 135.4, 158.3; IR (neat) ν 2959 s, 2931 s, 2875 s, 2835 s, 2054 w, 1882 w, 1612 s, 1583 m, 1512 s, 1463 s, 1420 m, 1378 m, 1301 s, 1276 m, 1247 s, 1179 s, 1119 m, 1075 m, 1037 s, 1017 s, 974 w, 933 w, 884 w, 829 s, 808 w, 728 w, 688 w; MS(EI) m/z (relative intensity, %) 166 (M^+,11), 136 (10), 135 (100), 105 (19), 91 (10), 79 (11); exact mass EI calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.0992.



reductant of
4-*L*

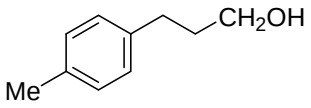
3-(4-Methoxyphenyl)propan-1-ol (reductant of **4-*L***).[12] Colorless oil; R_f 0.17 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 1H), 1.83-1.89 (m, 2H), 2.65 (t, J = 7.6 Hz, 2H), 3.66 (q, J = 5.9 Hz, 2H), 3.79 (s, 3H), 6.84 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 31.1, 34.4, 55.2, 62.2, 113.8, 129.3, 133.8, 157.7; IR (neat) ν 2937 s, 2861 s, 2837 s, 2596 w, 2543 w, 2481 w, 2424 w, 2058 w, 1883 w, 1767 w, 1612 s, 1583 m, 1512 s, 1464 s, 1299 s, 1245 s, 1178 s, 1110 m, 1035 s, 912 m, 839 m, 811 m, 785 m, 745 w, 700 w, 637 w; MS(EI) m/z (relative intensity, %) 166 (M^+,20), 122 (11), 121 (100), 77 (12); exact mass EI calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.0992.



reductant of
6-*B*

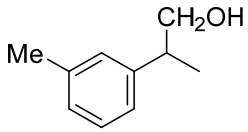
2-(4-Methylphenyl) propan-1-ol (reductant of **6-*B***).[5] Colorless oil; R_f 0.29 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, J = 6.7 Hz, 3H), 1.40 (s, 1H), 2.33 (s, 3H), 2.90-2.93 (m, 1H), 3.68 (d, J = 5.5 Hz, 2H), 7.12-7.16 (m, 4H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 17.6, 21.0, 42.0, 68.7, 127.3,

129.3, 136.2, 140.5; IR (neat) ν 2961 s, 2923 s, 2873 s, 2731 w, 1897 w, 1793 w, 1648 w, 1514 s, 1455 s, 1417 m, 1379 m, 1335 m, 1308 w, 1233 w, 1186 w, 1108 m, 1076 m, 1038 s, 1013 s, 974 m, 937 w, 883 w, 814 s, 721 m, 630 w; MS(EI) m/z (relative intensity) 150 (M^+,14), 120 (12), 119 (100) , 117 (14), 91 (23); exact mass EI calcd for $C_{10}H_{12}O$ 150.1045, found 150.1045.



reductant of
6-*L*

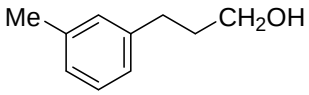
3-(4-Methylphenyl)propan-1-ol (reductant of **6-*L***).[13] Colorless oil; R_f 0.24 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 1H), 1.84-1.90 (m, 2H), 2.32 (s, 3H), 2.66 (t, J = 7.6 Hz, 2H), 3.66 (q, J = 6.1 Hz, 2H), 7.09-7.12 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 31.6, 34.3, 62.3, 128.3, 129.1, 135.3, 138.7; IR (neat) ν 2858 s, 2731 m, 2593 w, 2301 w, 1898 w, 1794 w, 1576 w, 1515 s, 1453 s, 1380 m, 1350 m, 1213 m, 1159 m, 1112 m, 1043 s, 912 m, 862 w, 836 m, 805 s, 780 m, 746 w; MS(EI) m/z (relative intensity, %) 150 (M^+,44), 132 (31), 131 (12), 119 (16) , 118 (11), 117 (100) , 115 (12), 106 (40), 105 (98), 103 (13), 91 (48), 79 (21), 77 (27), 65 (11); exact mass EI calcd for $C_{10}H_{14}O$ 150.1045 , found 150.1044.



reductant of
8-*B*

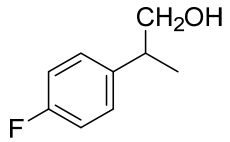
2-(3-Methylphenyl)propan-1-ol (reductant of **8-*B***).[14] Colorless oil; R_f 0.29 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, J = 6.7 Hz, 3H), 1.46 (s, 1H), 2.35 (s, 3H), 2.90-2.92 (m, 1H), 3.68 (d, J = 6.7 Hz, 2H), 7.04 (t, J = 7.3 Hz, 3H), 7.20-7.24 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.6, 21.5, 42.4, 68.7, 124.4, 127.4, 128.2, 128.5, 138.2, 143.6; IR (neat) ν 2922 s, 2873 s, 2731 w, 1936 w, 1864 w, 1778 w, 1677 w, 1607 s, 1589 m, 1489 s, 1455 s, 1377 s, 1334 m, 1246 m, 1214 m, 1162 m, 1102 m, 1080 m, 1031 s, 976 m, 934 w, 911 m, 880 m, 860 w, 783 s, 703 s, 666 m, 616 m; MS(EI) m/z

(relative intensity) 150 (M^+, 18), 120 (22), 119 (100), 117 (15), 105 (10), 91 (27), 77 (10) ; exact mass EI calcd for $C_{10}H_{14}O$ 150.1045, found 150.1046.



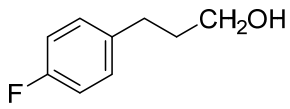
reductant of
8-*L*

3-(3-Methylphenyl)propan-1-ol (reductant of **8-*L***).[15] Colorless oil; R_f 0.20 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88 (tt, J = 7.6, 5.9 Hz, 2H), 2.33 (s, 3H), 2.67 (t, J = 7.6 Hz, 2H), 3.67 (td, J = 5.9, 3.0 Hz, 2H), 7.00-7.01 (m, 3H), 7.18 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 32.0, 34.2, 62.3, 125.4, 126.6, 128.3, 129.2, 137.9, 141.7; IR (neat) ν 2938 s, 2863 s, 2734 w, 1608 m, 1589 m, 1487 m, 1453 m, 1377 m, 1348 m, 1250 w, 1226 w, 1170 w, 1096w, 1055 s, 934 w, 913 w, 884 w, 781 m, 736 m, 699 s ; MS(EI) m/z (relative intensity) 150 (M^+, 41), 132 (15), 131 (11), 119 (17), 118 (10), 117 (83), 115 (14), 107 (10), 106 (100), 105 (61), 103 (14), 92 (10), 91 (82), 79 (20), 78 (11), 77 (29), 65 (12) ; exact mass EI calcd for $C_{10}H_{14}O$ 150.1045 , found 150.1044 .



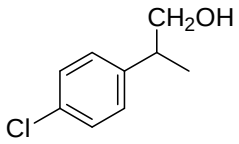
reductant of
10-*B*

2-(4-Fluorophenyl)propan-1-ol (reductant of **10-*B***).[16] Colorless oil; R_f 0.33 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (d, J = 6.7 Hz, 3H), 1.64 (s, 1H), 2.90-2.93 (m, 1H), 3.63-3.66 (m, 2H), 7.00 (t, J = 8.6 Hz, 2H), 7.19 (td, J = 8.6, 3.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.7, 41.6, 68.6, 115.3 (d, $J_{C\text{-}F}$ = 21.1 Hz), 128.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 139.3 (d, $J_{C\text{-}F}$ = 4.8 Hz), 160.6, 162.5; IR (neat) ν 2964 s, 2932 s, 2876 s, 2721 w, 2579 w, 2435 w, 2046 w, 1887 w, 1764 w, 1644 w, 1603 s, 1509 s, 1463 s, 1417 m, 1381 m, 1299 m, 1223 s, 1159 s, 1100 m, 1073 m, 1038 s, 1013 s, 975 m, 936 w, 884 w, 834 s, 744 w, 722 m, 693 m, 629 w, 554 s, 837 s ; MS(EI) m/z (relative intensity) 154 (M^+, 12), 124 (14), 123 (100), 103 (45), 77 (13) ; exact mass EI calcd for $C_9H_{11}FO$ 154.0794, found 154.0796.



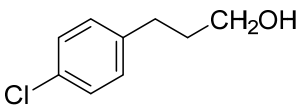
reductant of
10-*L*

3-(4-Fluorophenyl)propan-1-ol (reductant of **10-*L***).[9] Colorless oil; R_f 0.25 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, J = 6.7 Hz, 3H), 1.37 (s, 1H), 2.89-2.92 (m, 1H), 3.63-3.70 (m, 2H), 3.80 (s, 3H), 6.88 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 34.3, 62.0, 115.1(d, $J_{C\text{-}F}$ = 20.2 Hz), 129.7(d, $J_{C\text{-}F}$ = 7.7 Hz), 137.3(d, $J_{C\text{-}F}$ = 3.8 Hz), 160.3, 162.2; IR (neat) ν 2939 s, 2865 s, 1887 w, 1767 w, 1600 m, 1509 s, 1477 m, 1453 m, 1416 m, 1396 m, 1353 m, 1295 m, 1221 s, 1158 s, 1099 m, 1042 s, 1015 s, 912 m, 849 s, 821 s, 788 m, 757 m, 702 m; MS(EI) m/z (relative intensity, %) 154 (M^+,18), 136 (57), 135 (84), 110 (20), 109 (100), 103 (11), 83 (19), 77 (10); exact mass EI calcd for $C_9H_{11}FO$ 154.0794, found 154.0797.



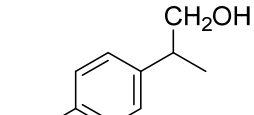
reductant of
12-*B*

2-(4-Chlorophenyl)propan-1-ol (reductant of **12-*B***).[16] Colorless oil; R_f 0.39 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, J = 7.3 Hz, 3H), 1.53 (s, 1H), 2.91-2.94 (m, 1H), 3.66-3.68 (m, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.5, 41.8, 68.5, 128.7, 128.8, 132.3, 142.2; IR (neat) ν 2963 s, 2929 s, 2875, 2360 w, 2341 w, 1896 w, 1715 w, 1646 w, 1595 w, 1571 w, 1493 s, 1462 w, 1410 s, 1380 m, 1338 m, 1232 w, 1181 w, 1091 s, 1075 m, 1039 s, 1012 s, 975 m, 938 w, 896 m, 825 s, 787 w, 767 w, 719 w, 669 w, 620 w; MS(EI) m/z (relative intensity, %) 170 (M^+,14), 141 (33), 140 (15), 139 (100), 103 (60), 77 (27); exact mass EI calcd for $C_9H_{11}ClO$ 170.0498, found 170.0498.



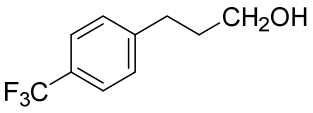
reductant of
12-*L*

3-(4-Chlorophenyl)propan-1-ol (reductant of **12-*L***).[9] Colorless oil; R_f 0.33 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.43 (s, 1H), 1.86 (tt, *J* = 7.6, 5.8 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 3.66 (t, *J* = 5.8 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ: 31.4, 34.0, 62.0, 128.4, 129.7, 131.5, 140.2; IR (neat) ν 2940 s, 2865 s, 2583 w, 2288 w, 1896 w, 1781 w, 1717 w, 1650 w, 1597 m, 1574 w, 1491 s, 1454 s, 1407 s, 1380 m, 1350 m, 1229 m, 1202 w, 1177 m, 1159 m, 1092 s, 1056 s, 1015 s, 913 m, 862 w, 835 m, 799 m, 764 w, 746 w, 714 m, 700 m, 660 m, 630 m; MS(EI) m/z (relative intensity, %) 170 (M^+,15), 152 (21), 127 (17), 125 (51), 118 (10), 117 (100), 115 (13), 103 (15), 91 (24), 89 (13), 77 (19); exact mass EI calcd for $C_9H_{11}ClO$ 170.0498, found 170.0497.



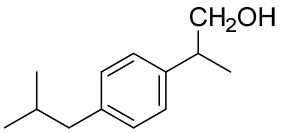
reductant of
14-*B*

2-(4-Trifluoromethylphenyl)propan-1-ol (reductant of **14-*B***).[10] Colorless oil; R_f 0.31 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (d, *J* = 6.7 Hz, 3H), 1.43 (s, 1H), 3.02-3.05 (m, 1H), 3.74 (d, *J* = 6.7 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.4, 42.3, 68.3, 124.2 (q, $J_{C\text{-}F}$ = 271.5 Hz), 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 127.8, 128.9 (q, $J_{C\text{-}F}$ = 32.7 Hz), 148.0; IR (neat) ν 2967 m, 2934 m, 2879 m, 2646 w, 1919 w, 1800 w, 1673 w, 1619 m, 1585 w, 1457 m, 1420 m, 1383 m, 1327 , s, 1238 w, 1164 s, 1122 s, 1069 s, 1045 s, 1015 s, 976 w, 953 w, 897 w, 883 w, 838 s, 750 w, 726 w, 660 w, 643 w, 607 m; MS(EI) m/z (relative intensity, %) 204 (M^+, 8), 174 (83), 173 (100), 172 (11), 159 (21), 155 (21), 154 (62), 153 (57), 151 (12), 134 (11), 133 (85), 127 (26), 105 (59), 77 (14); exact mass EI calcd for $C_{10}H_{11}F_3O$ 204.0762, found 204.0761.



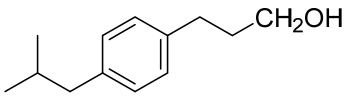
reductant of
14-*L*

3-(4-Trifluoromethylphenyl)propan-1-ol (reductant of **14-*L***). Colorless oil; R_f 0.16 (hexane/AcOEt = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 1H), 1.90-1.92 (m, 2H), 2.78 (t, *J* = 7.9 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 31.9, 33.8, 61.9, 124.3 (q, $J_{C\text{-}F}$ = 269.2 Hz), 125.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 128.3(q, $J_{C\text{-}F}$ = 33.6 Hz), 128.7, 145.9; IR (neat) ν 2942 s, 2870 s, 2646 w, 1919 w, 1801 w, 1618 m, 1584 s, 1473 w, 1451 w, 1418 m, 1327 s, 1240 w, 1163 s, 1122 s, 1068 s, 1046 s, 1019 s, 954 w, 915 w, 845 m, 816 m, 730 w, 635 m, 615 m; MS(EI) m/z (relative intensity, %) 204 (M^+, 1), 186 (48), 160 (13), 159 (26), 133 (13), 118 (10), 117 (100), 115 (11), 109 (17), 91 (29); exact mass EI calcd for $C_{10}H_{11}F_3O$ 204.0762, found 204.0763.



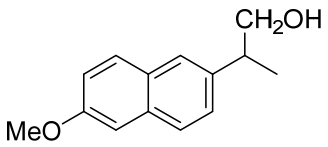
reductant of
16-*B*

2-(4-Isobutylphenyl)propan-1-ol (reductant of **16-*B***).[10] Colorless oil; R_f 0.34 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J* = 11.0 Hz, 6H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.44 (d, *J* = 4.9 Hz, 1H), 1.81-1.89 (m, 1H), 2.45 (d, *J* = 6.7 Hz, 2H), 2.90-2.93 (m, 1H), 3.68 (d, *J* = 7.3 Hz, 2H), 7.10-7.14 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.6, 22.4, 30.2, 42.0, 45.0, 68.8, 127.1, 129.4, 140.0, 140.7; IR (neat) ν 2922 s, 2723 w, 1899 w, 1790 w, 1633 w, 1512 s, 1464 s, 1420 s, 1382 s, 1366 s, 1335 m, 1282 m, 1219 m, 1186 m, 1167 m, 1112 m, 1070 m, 1037 s, 1012 s, 975 m, 920 w, 883 m, 843 s, 798 s, 707 m, 645 m; MS(EI) m/z (relative intensity, %) 192 (M^+,16), 162 (15), 161 (100), 119 (39), 117 (16), 105 (13), 91 (21), 57 (10); exact mass EI calcd for $C_{13}H_{20}O$ 192.1514 , found 192.1517.



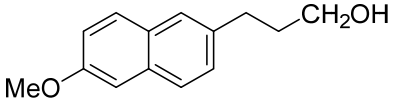
reductant of
16-*L*

3-(4-Isobutylphenyl)propan-1-ol (reductant of **16-*L***). Colorless oil; R_f 0.23 (hexane/AcOEt = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (d, J = 6.7 Hz, 6H), 1.46 (s, 1H), 1.81-1.85 (m, 1H), 1.86-1.91 (m, 2H), 2.44 (d, J = 7.3 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 3.67 (t, J = 6.7 Hz, 2H), 7.06-7.11 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 30.2, 31.6, 34.3, 45.0, 62.4, 128.1, 129.1, 138.9, 139.2; IR (neat) ν 2951 s, 2867 s, 2731 w, 2601 w, 1899 w, 1791 w, 1723 w, 1679 w, 1614 w, 1512 s, 1464 s, 1418 s, 1382 s, 1365 s, 1279 m, 1211 m, 1166 m, 1116 m, 1059 s, 916 m, 882 m, 846 m, 809 m, 792 m; MS(EI) m/z (relative intensity) 192 (M^+,32), 149 (73), 132 (16), 131 (100), 117 (22), 116 (11), 115 (12), 105 (28), 104 (10), 91 (37); exact mass EI calcd for $C_{13}H_{20}O$ 192.1514 , found 192.1513.



reductant of
18-*B*

2-(6-Methoxynaphthalen-2-yl)propan-1-ol (reductant of **18-*B***).[10] White solid; mp 98–100°C (hexane/AcOEt); R_f 0.34 (hexane/Et_2O = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (d, J = 6.7 Hz, 3H), 3.05-3.12 (m, 1H), 3.77 (d, J = 7.3 Hz, 2H), 3.91 (s, 3H), 7.11-7.15 (m, 2H), 7.33-7.35 (m, 1H), 7.61 (s, 1H), 7.70-7.71 (m, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 17.6, 42.3, 55.3, 68.6, 105.6, 118.9, 125.9, 126.2, 127.2, 129.0, 129.1, 133.5, 138.6, 157.4; IR (neat) ν 2963 m, 2935 m, 2910 m, 2877 m, 2837 m, 2049 w, 1919 w, 1765 w, 1710 w, 1635 m, 1605 s, 1502 m, 1486 m, 1455 m, 1413 m, 1392 m, 1360 m, 1349 m, 1322 w, 1262 s, 1213 s, 1163 s, 1124 m, 1092 w, 1048 s, 1029 s, 959 m, 926 m, 890 m, 854 s, 831 w, 814 s, 752 m, 683 m, 663 m, 620 m; MS(EI) m/z (relative intensity, %) 216 (M^+,24), 186 (14), 185 (100), 170 (16), 154 (11), 153 (11), 141 (14), 115 (12); exact mass EI calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1148.

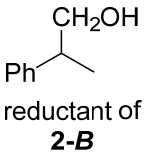


reductant of
18-*L*

3-(6-Methoxynaphthalen-2-yl)propan-1-ol (reductant of **18-*L***). White solid.; mp 98–100°C (hexane/AcOEt); R_f 0.28 (hexane/Et_2O = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.74 (s, 1H), 1.92-1.95 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.88 (s, 3H), 7.10-7.11 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.54 (s, 1H), 7.65 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 28.1, 45.3, 55.3, 105.6, 118.9, 126.3, 127.1, 127.4, 128.9, 129.0, 133.1, 133.4, 157.4, 201.7; IR (neat) ν 2963 s, 2932 s, 2857 s, 2617 w, 2421 w, 2052 w, 1921 w, 1775 w, 1712 w, 1635 s, 1604 s, 1504 s, 1485 s, 1462 s, 1416 s, 1392 s, 1344 m, 1297 m, 1263 s, 1229 s, 1196 s, 1161 s, 1116 m, 1029 s, 1008 s, 962 s, 929 s, 890 s, 853 s, 816 s, 784 m, 757 m, 748 m, 686 m, 661 s, 612 m; MS(EI) m/z (relative intensity, %) 216 (M^+,46), 172 (45), 171 (100), 141 (11), 128 (29), 115 (12); exact mass EI calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1151.

11. HPLC Charts of Reductants of Aldehydes 2-*B*, 4-*B*, 6-*B*, 8-*B*, 10-*B*, 12-*B*, 14-*B*, 16-*B*, and 18-*B*.

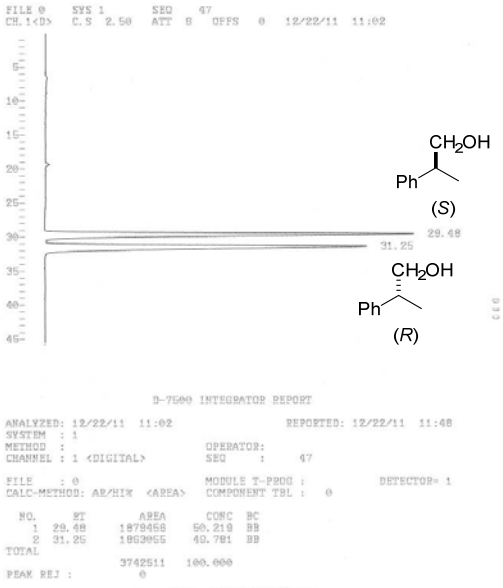
2-Phenylpropan-1-ol (reductant of **2-*B***) (Table 1).



reductant of **2-*B***

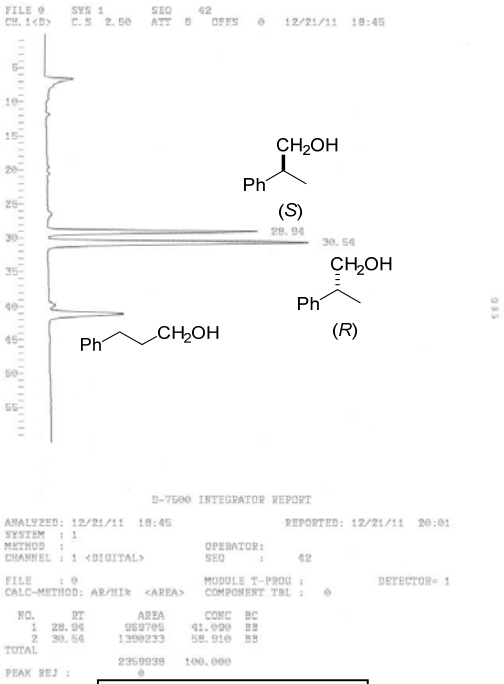
The ee was determined on an AS-H column (*n*-hexane/2-propanol = 99/1, flow = 0.5 mL/min, detection at 254 nm), with enantiomers eluting at 29.5 (*S*) and 31.3 (*R*) min. $[\alpha]_D^{32}$ +2.0° (c 1.0, $CHCl_3$) for 18%ee (*R*) (Table 1, entry 1); +4.7° (c 1.0, $CHCl_3$) for 52%ee (*R*) (Table 1, entry 2); +4.2° (c 0.57, $CHCl_3$) for 37%ee (*R*) (Table 1, entry 3); +12.7° (c 1.1, $CHCl_3$) for 81%ee (*R*) (Table 1, entry 4); +13.5° (c 1.0, $CHCl_3$) for 90%ee (*R*) (Table 1, entry 5); -13.5° (c 1.1, $CHCl_3$) for 90%ee (*S*) (Table 1, entry 6); +14.1° (c 1.0, $CHCl_3$) for 93%ee (*R*) (Table 1, entry 7); lit. $[\alpha]_D^{22}$ +17° (neat) for 100%ee (*R*).[17]

racemate



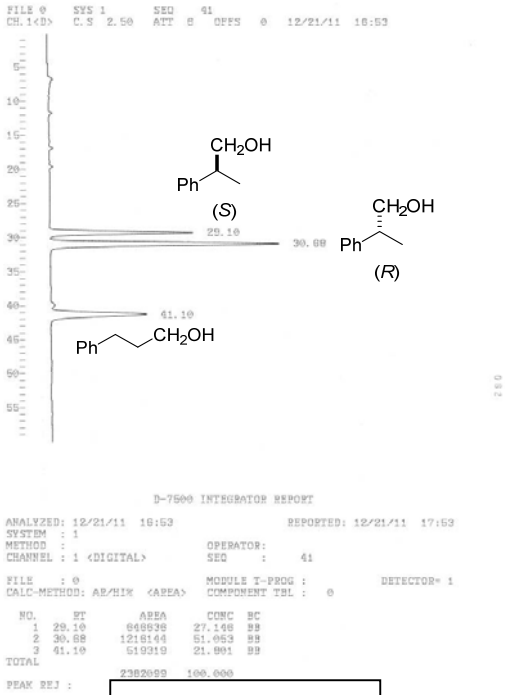
(*S*) : area 50.219%
(*R*) : area 49.781%

Table 1, entry 1



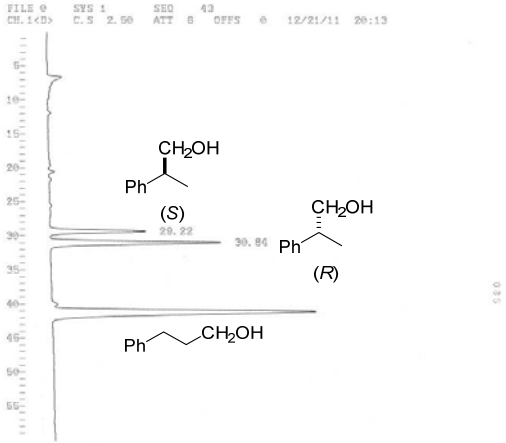
(*S*) : area 41.090%
(*R*) : area 58.910%

Table 1, entry 2



(*S*) : area 21.228%
(*R*) : area 78.772%

Table 1, entry 3



D-7500 INTEGRATOR REPORT

ANALYZED: 12/21/11 20:13 REPORTED: 12/21/11 21:14
SYSTEM : 1
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 43

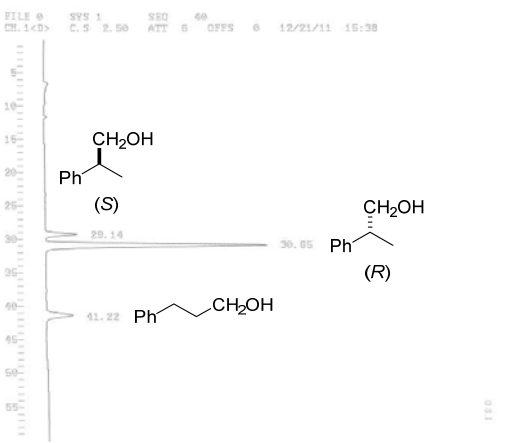
FILE : 0 MODULE T-PROG : DETECTOR= 1
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
1	29.22	392217	31.436	BB
2	30.84	855462	68.564	BB
TOTAL		1247679	100.000	

PEAK REJ : 0

(*S*) : area 31.436%
(*R*) : area 68.564%

Table 1, entry 4



D-7500 INTEGRATOR REPORT

ANALYZED: 12/21/11 15:38 REPORTED: 12/21/11 16:38
SYSTEM : 1
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 40

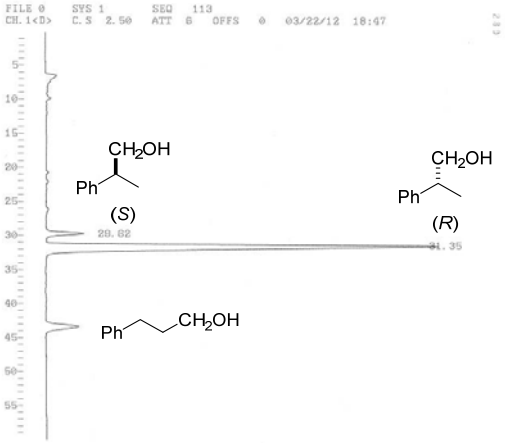
FILE : 0 MODULE T-PROG : DETECTOR= 1
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
1	29.14	123371	9.475	BB
2	30.85	1178767	82.877	BB
3	41.22	120100	8.448	BB
TOTAL		1422278	100.000	

PEAK REJ : 0

(*S*) : area 9.475%
(*R*) : area 90.525%

Table 1, entry 5



D-7500 INTEGRATOR REPORT

ANALYZED: 03/22/12 18:47 REPORTED: 03/22/12 21:02
SYSTEM : 1
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 113

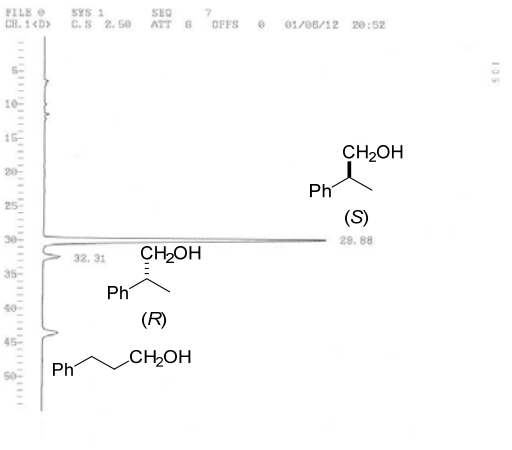
FILE : 0 MODULE T-PROG : DETECTOR= 1
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
1	29.62	139870	5.059	BB
2	31.35	2624875	94.941	BB
TOTAL		2764745	100.000	

PEAK REJ : 0

(*S*) : area 5.059%
(*R*) : area 94.941%

Table 1, entry 6



D-7500 INTEGRATOR REPORT

ANALYZED: 01/06/12 20:52 REPORTED: 01/06/12 21:47
SYSTEM : 1
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 7

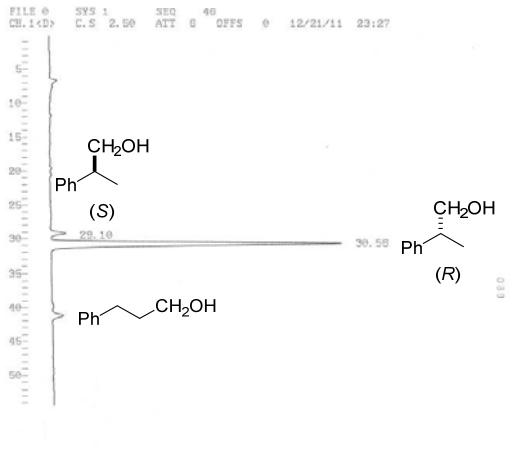
FILE : 0 MODULE T-PROG : DETECTOR= 1
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
1	29.88	1413399	95.476	BB
2	32.31	66976	4.524	BB
TOTAL		1480375	100.000	

PEAK REJ : 0

(*S*) : area 95.476%
(*R*) : area 4.524%

Table 1, entry 7



D-7500 INTEGRATOR REPORT

ANALYZED: 12/21/11 23:27 REPORTED: 12/22/11 00:22
SYSTEM : 1
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 46

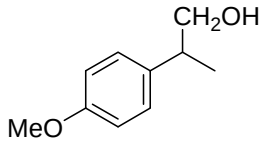
FILE : 0 MODULE T-PROG : DETECTOR= 1
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
1	29.10	55597	3.455	BB
2	30.56	1553102	96.545	BB
TOTAL		1608699	100.000	

PEAK REJ : 0

(*S*) : area 3.455%
(*R*) : area 96.545%

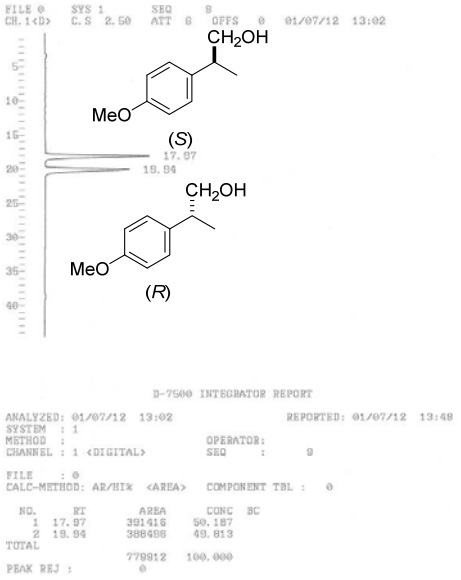
2-(4-Methoxyphenyl)propanal (**4-*B***) (Table 2, entries 1 and 2).



reductant of **4-*B***

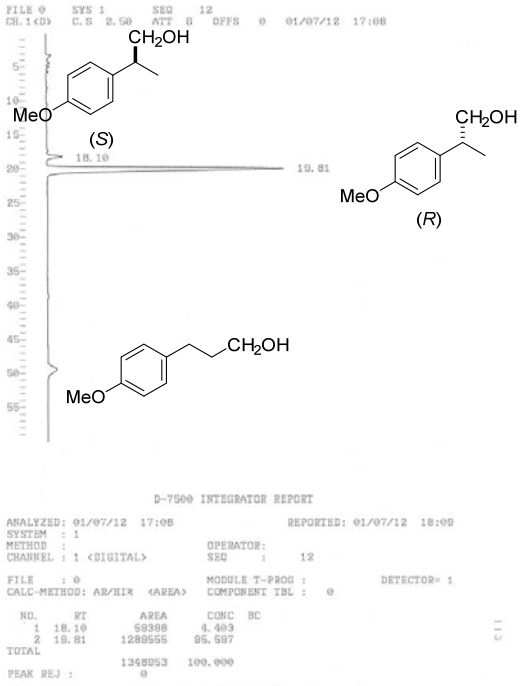
The ee was determined on an AS-H column (*n*-hexane/2-propanol = 97/3, flow = 1.0 mL/min, detection at 254 nm), with enantiomers eluting at 18.0 (*S*) and 20.0 (*R*) min. $[\alpha]_D^{26}$ +18.0° (c 1.0, $CHCl_3$) for 91%ee (*R*) (Table 2, entry 1); +18.2° (c 1.1, $CHCl_3$) for 95%ee (*R*) (Table 2, entry 2); lit. $[\alpha]_D^{23}$ -15.5° (c 2.1, $CHCl_3$) for 100% ee (*S*).[16]

racemate



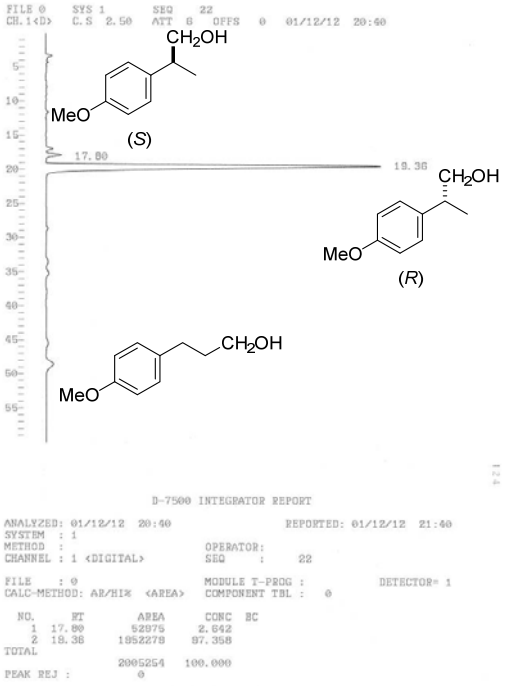
(*S*) : area 50.187%
(*R*) : area 49.813%

Table 2, entry 1



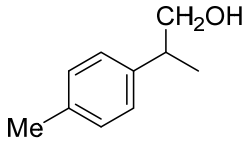
(*S*) : area 4.403%
(*R*) : area 95.597%

Table 2, entry 2



(*S*) : area 2.642%
(*R*) : area 97.358%

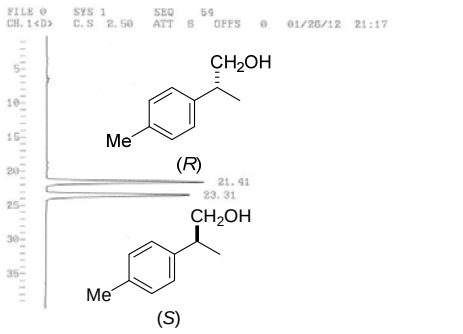
2-(4-Methylphenyl) propan-1-ol (reductant of **6-*B***) (Table 2, entries 3 and 4).



reductant of **6-*B***

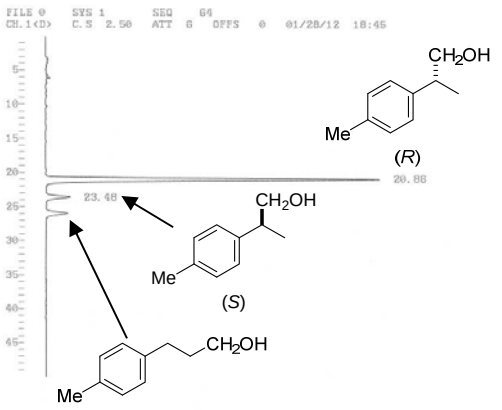
The ee was determined on an AD-H column (*n*-hexane/2-propanol = 99/1, flow = 1.0 mL/min, detection at 254 nm), with enantiomers eluting at 21.4 (*R*) and 23.3 (*S*) min. $[\alpha]_D^{26}$ +15.1° (c 1.0, $CHCl_3$) for 86%ee (*R*) (Table 2, entry 3); +16.7° (c 0.97, $CHCl_3$) for 91%ee (*R*) (Table 2, entry 4); lit. $[\alpha]_D^{23}$ -15.5° (c 2.1, $CHCl_3$) for 100%ee (S).[5]

racemate



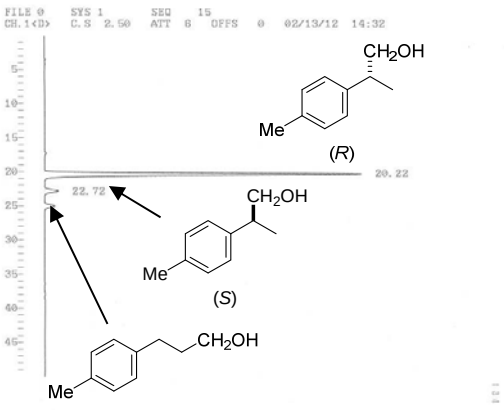
(*R*) : area 49.973%
(*S*) : area 50.027%

Table 2, entry 3



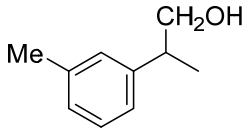
(*R*) : area 92.762%
(*S*) : area 7.238%

Table 2, entry 4



(*R*) : area 95.399%
(*S*) : area 4.601%

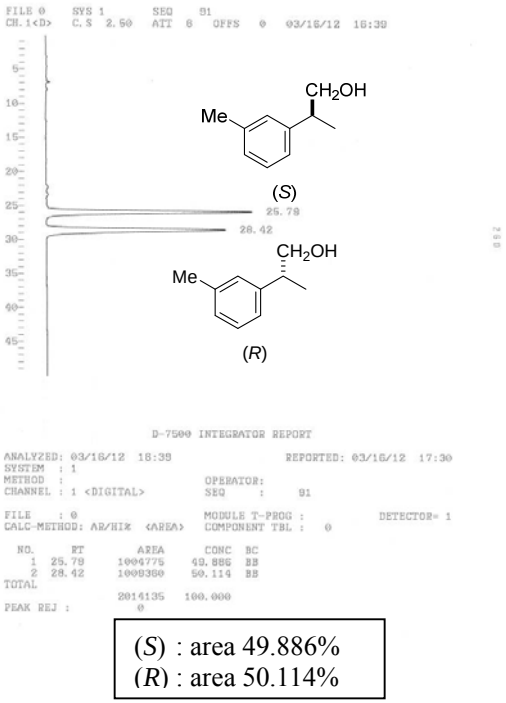
2-(3-Methylphenyl)propan-1-ol (reductant of **8-*B***) (Table 2, entries 5 and 6).



reductant of **8-*B***

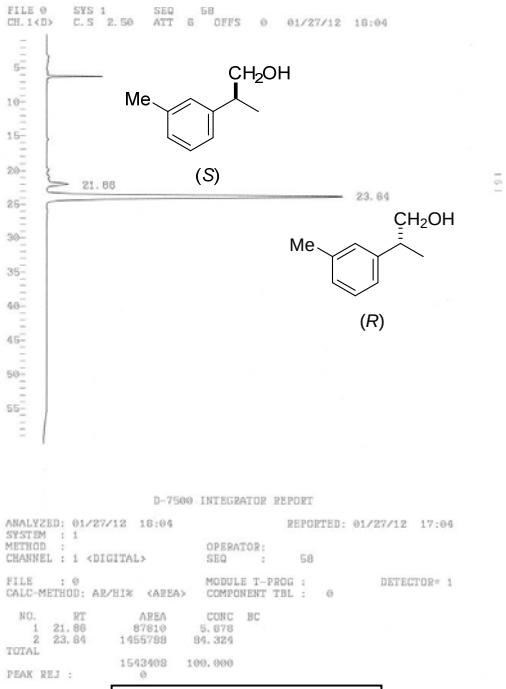
The ee was determined on an AD-H column (*n*-hexane/2-propanol = 99/1, flow = 1.0 mL/min, detection at 254 nm), with enantiomers eluting at 25.8 (*S*) and 28.4 (*R*) min. $[\alpha]_D^{26}$ +14.4° (c 1.0, $CHCl_3$) for 89%ee (*R*) (Table 2, entry 5); +16.7° (c 0.97, $CHCl_3$) for 94%ee (*R*) (Table 2, entry 6); lit. $[\alpha]_D^{20}$ -8.2° for 55%ee (*S*).[18]

racemate



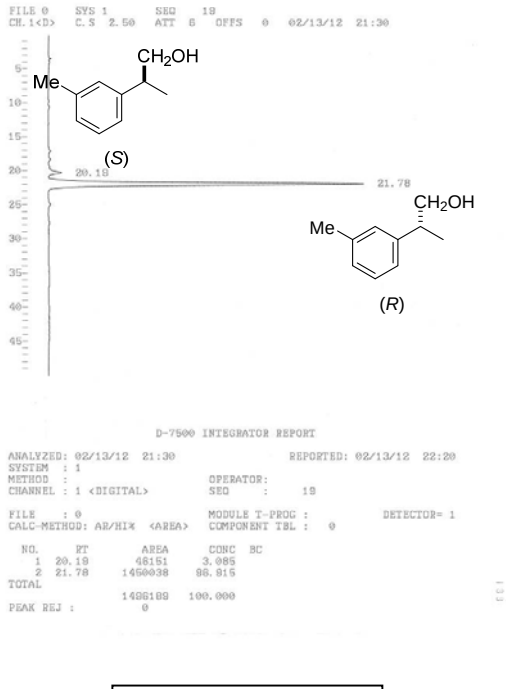
(*S*) : area 49.886%
(*R*) : area 50.114%

Table 2, entry 5



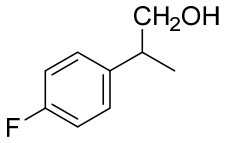
(*S*) : area 5.676%
(*R*) : area 94.324%

Table 2, entry 6



(*S*) : area 3.085%
(*R*) : area 96.915%

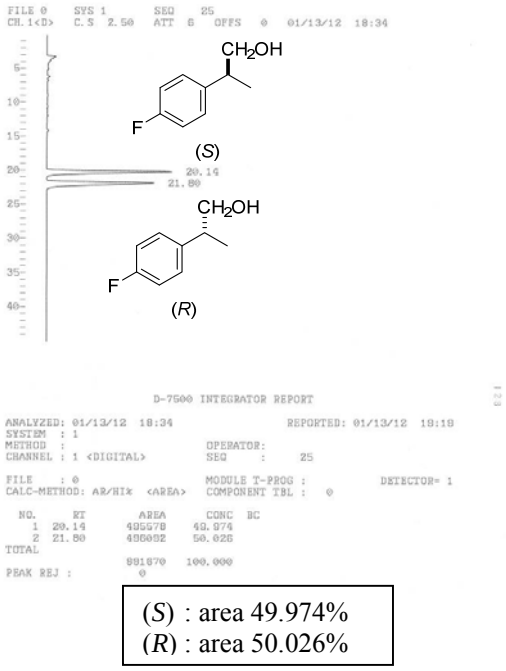
2-(4-Fluorophenyl)propan-1-ol (reductant of **10-*B***) (Table 2, entries 7 and 8).



reductant of **10-*B***

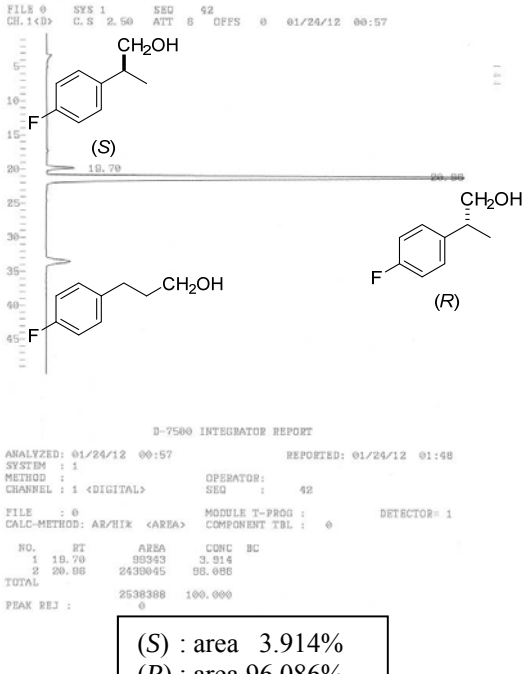
The ee was determined on an AS-H column (*n*-hexane/2-propanol = 99/1, flow = 1.0 mL/min, detection at 254 nm), with enantiomers eluting at 20.1 (*S*) and 21.8 (*R*) min. $[\alpha]_D^{26}$ +11.5° (c 1.0, $CHCl_3$) for 92%ee (*R*) (Table 2, entry 7); +11.0° (c 1.1, $CHCl_3$) for 95%ee (*R*) (Table 2, entry 8); lit. $[\alpha]_D^{20}$ -17.9° for 77%ee (*S*).[18]

racemate



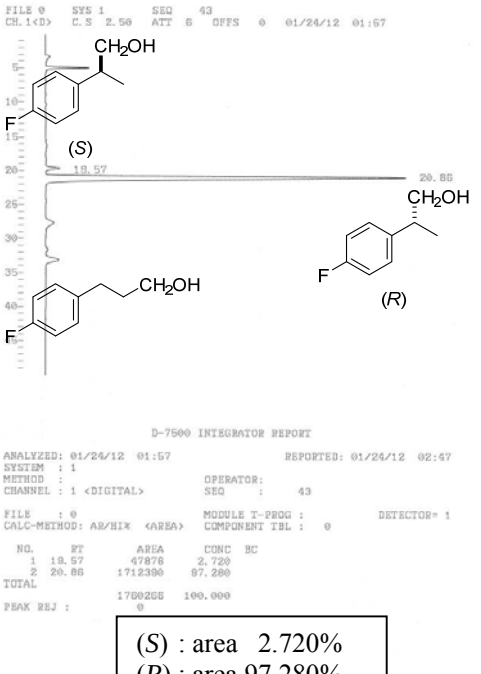
(*S*) : area 49.974%
(*R*) : area 50.026%

Table 2, entry 7



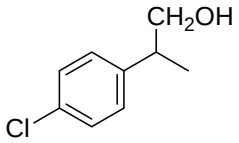
(*S*) : area 3.914%
(*R*) : area 96.086%

Table 2, entry 8



(*S*) : area 2.720%
(*R*) : area 97.280%

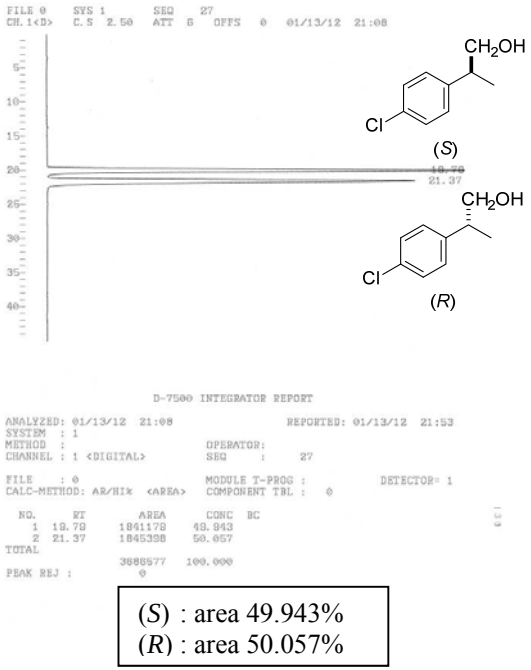
2-(4-Chlorophenyl)propan-1-ol (reductant of **12-*B***) (Table 2, entries 9 and 10).



reductant of **12-*B***

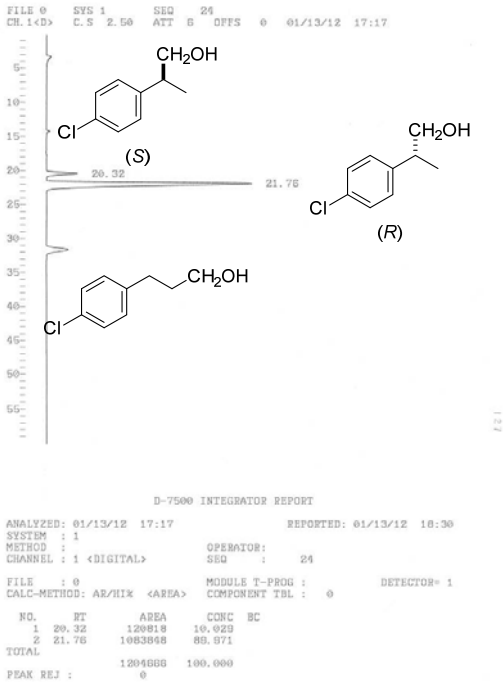
The ee was determined on an AS-H column (*n*-hexane/2-propanol = 99/1, flow = 1.0 mL/min, detection at 254 nm), with enantiomers eluting at 19.7 (*S*) and 21.4 (*R*) min. $[\alpha]_D^{32}$ +12.9° (c 1.0, $CHCl_3$) for 80%ee (*R*) (Table 2, entry 9); +12.9° (c 1.2, $CHCl_3$) for 92%ee (*R*) (Table 2, entry 10); lit. $[\alpha]_D^{23}$ -14.1° (c 0.8, $CHCl_3$) for 100% ee (*S*).[16]

racemate



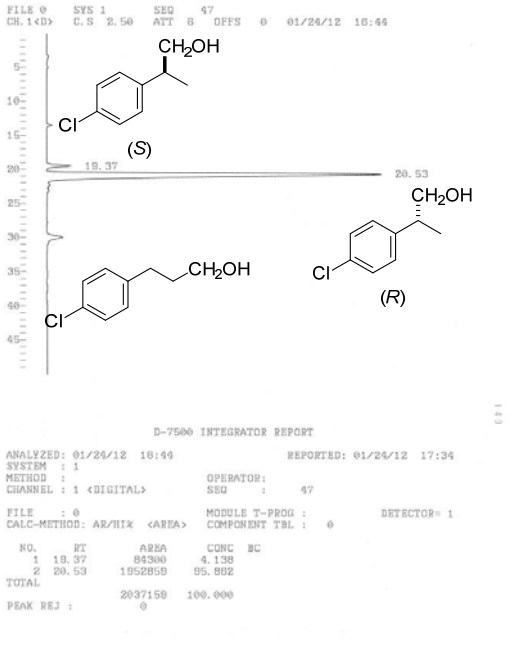
(*S*) : area 49.943%
(*R*) : area 50.057%

Table 2, entry 9



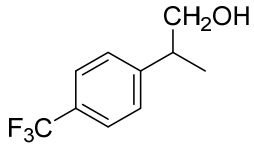
(*S*) : area 10.029%
(*R*) : area 89.971%

Table 2, entry 10



(*S*) : area 4.138%
(*R*) : area 95.862%

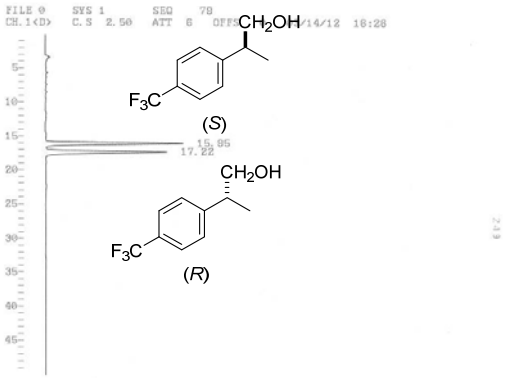
2-(4-Trifluoromethylphenyl)propan-1-ol (reductant of **14-*B***) (Table 2, entries 11 and 12).



reductant of **14-*B***

The ee was determined on an AS-H column (*n*-hexane/2-propanol = 99/1, flow = 0.5 mL/min, detection at 254 nm), with enantiomers eluting at 16.0 (*S*) and 17.2 (*R*) min. $[\alpha]_D^{26}$ +8.2° (c 1.2, $CHCl_3$) for 62%ee (*R*) (Table 2, entry 11); +8.5° (c 1.1, $CHCl_3$) for 67%ee (*R*) (Table 2, entry 12); lit. $[\alpha]_D^{23}$ -15.2° (c 0.51, $CHCl_3$) for 100% ee (*S*).[10]

racemate



D-7500 INTEGRATOR REPORT

ANALYZED: 03/14/12 16:26 REPORTED: 03/14/12 17:16
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 78

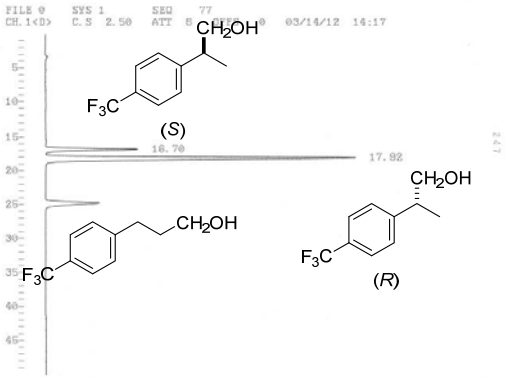
FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
1	15.95	440794	49.735	
2	17.22	445483	50.265	
TOTAL		886277	100.000	

PEAK REJ : 0

(*S*) : area 49.735%
(*R*) : area 50.265%

Table 2, entry 11



D-7500 INTEGRATOR REPORT

ANALYZED: 03/14/12 14:17 REPORTED: 03/14/12 15:21
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 77

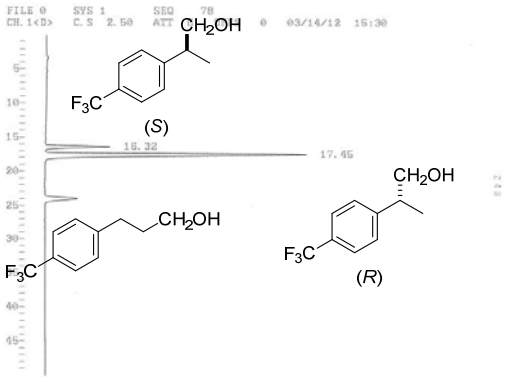
FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
1	16.70	312373	18.989	
2	17.92	1332884	81.011	
TOTAL		1645057	100.000	

PEAK REJ : 0

(*S*) : area 18.989%
(*R*) : area 81.011%

Table 2, entry 12



D-7500 INTEGRATOR REPORT

ANALYZED: 03/14/12 15:30 REPORTED: 03/14/12 16:20
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 78

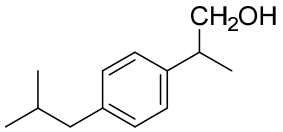
FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
1	16.32	200724	16.285	
2	17.45	1031847	83.715	
TOTAL		1232571	100.000	

PEAK REJ : 0

(*S*) : area 16.285%
(*R*) : area 83.715%

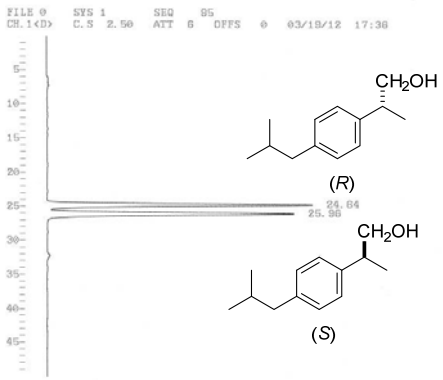
2-(4-Isobutylphenyl)propan-1-ol (reductant of **16-*B***) (Scheme 2, upper).



reductant of
16-*B*

The ee was determined on an AD-H column (*n*-hexane/2-propanol = 99/1, flow = 1.0 mL/min, detection at 254 nm), with enantiomers eluting at 24.6 (*R*) and 26.0 (*S*) min. $[\alpha]_D^{26}$ -20.2° (c 0.97, $CHCl_3$) for 87%ee (*S*) (Scheme 2, upper); lit. $[\alpha]_D^{20}$ +17.5° (c 1.60, $CHCl_3$) for 100% ee (*R*).[10]

racemate



D-7500 INTEGRATOR REPORT

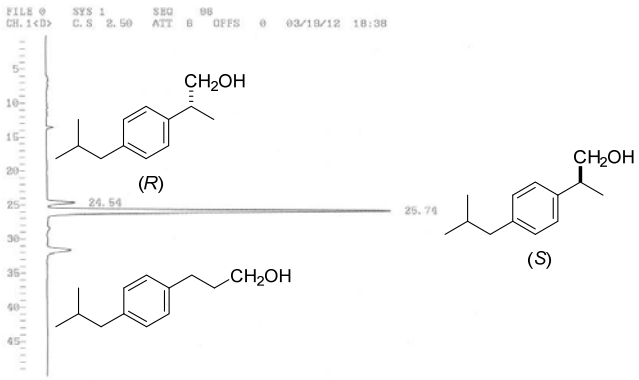
ANALYZED: 03/19/12 17:36 REPORTED: 03/19/12 18:26
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 95

FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
1	24.64	1178948	49.919	BV
2	25.96	1183793	50.081	VB
TOTAL		2362741	100.000	
PEAK REJ :		0		

(*R*) : area 49.919%
(*S*) : area 50.081%

Scheme 2, upper



D-7500 INTEGRATOR REPORT

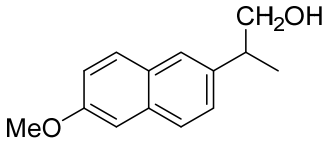
ANALYZED: 03/19/12 18:38 REPORTED: 03/19/12 20:04
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 96

FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
1	24.54	113270	6.636	
2	25.74	1593612	93.364	
TOTAL		1706882	100.000	
PEAK REJ :		0		

(*R*) : area 6.636%
(*S*) : area 93.364%

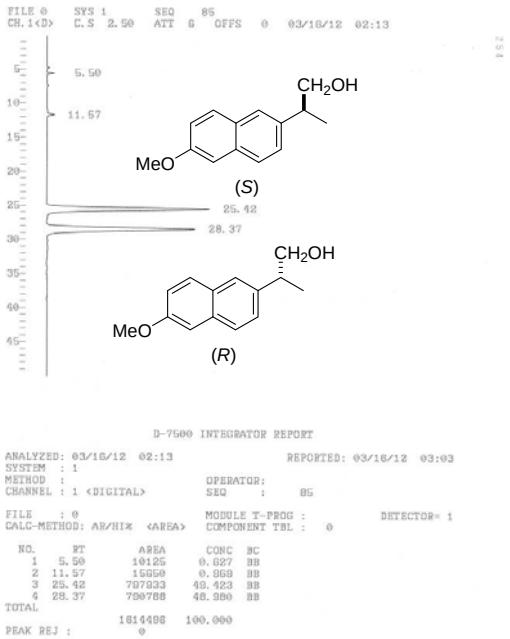
2-(6-Methoxynaphthalen-2-yl)propan-1-ol (reductant of **18-*B***) (Scheme 2, lower).



reductant of **18-*B***

The ee was determined on an AD-H column (*n*-hexane/2-propanol = 97/3, flow = 1.0 mL/min, detection at 254 nm), with enantiomers eluting at 25.4 (*S*) and 28.4 (*R*) min. $[\alpha]_D^{26}$ -18.8° (c 1.0, $CHCl_3$) for 91%ee (*S*) (Scheme 2, lower); lit. $[\alpha]_D^{24}$ +18.5°(c 1.00, $CHCl_3$) for 100% ee (*R*).[10]

racemate



D-7500 INTEGRATOR REPORT

ANALYZED: 03/16/12 02:13 REPORTED: 03/16/12 03:03
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 85

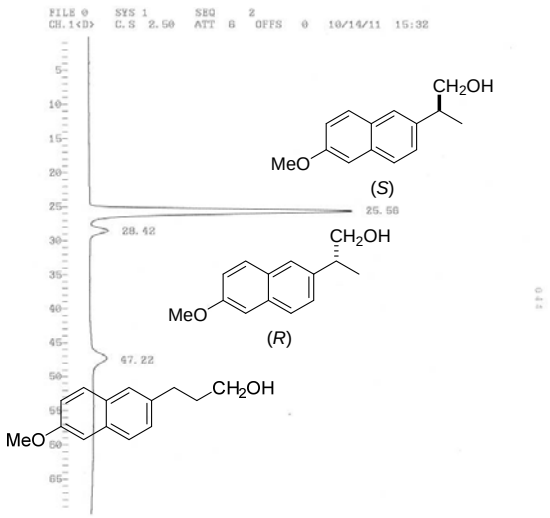
FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
1	5.50	10125	0.627	BB
2	11.57	15950	0.969	BB
3	25.42	797933	49.423	BB
4	28.37	790788	48.980	BB
TOTAL		1614496	100.000	

PEAK REJ : 0

(*S*) : area 50.225%
(*R*) : area 49.775%

Scheme 2, lower



D-7500 INTEGRATOR REPORT

ANALYZED: 10/14/11 15:32 REPORTED: 10/14/11 16:42
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 2

FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
1	25.56	2138677	91.224	BB
2	28.42	97188	4.146	BB
3	47.22	108548	4.630	BB
TOTAL		2344414	100.000	

PEAK REJ : 0

(*S*) : area 95.383%
(*R*) : area 4.617%

12. References:

(1) G. Giordano, R. H. Crabtree, *Inorg*. *Synth*., 1979, **19**, 218–220.

(2) C. R. Smith and T. V. RajanBabu, *Tetrahedron*, 2010, **66**, 1102–1110.

(3) E. Alacid and C. Nájera, *J*. *Org*. *Chem*., 2008, **73**, 2315–2322.

(4) T. Baumann, H. Vogt and S. Bräse, *Eur*. *J*. *Org*. *Chem*., **2007**, 266–282.

(5) M. Kimura and M. Seki, *Tetrahedron Lett*., 2004**, 45**, 3219–3223.

(6) S. Hoffmann, M. Nicoletti and B. List, *J*. *Am*. *Chem*. *Soc*., 2006, **128**, 40, 13074–13075.

(7) A. G. Panda, M. D. Bhor, S. S. Ekbote and B. M. Bhanage, *Catal*. *Lett*., 2009, **131**, 649–655.

(8) M. van de Sande and H. J. Gais, *Chem*. *Eur*. *J*., 2007, **13**, 1784–1795.

(9) B. M. Nestl, S. M. Glueck, M. Hall, W. Kroutil, R. Stuermer, B. Hauser and K. Faber, *Eur*. *J*. *Org*. *Chem*., **2006**, 4573 – 4577.

(10) J. A. Friest, Y. Maezato, S. Broussy, P. Blum and D. B. Berkowitz, *J*. *Am*. *Chem*. *Soc*., 2010, **132**, 5930–5931.

(11) C. G. Frost and B. C. Hartley, *Org*. *Lett*., 2007, **9**, 4259–4261.

(12) B. S. Bodnar and P. F. Vogt, *J*. *Org*. *Chem*., 2009, **74**, 2598–2600.

(13) F. K. Cheung, C Lin, F. Minissi, A. L. Crivillé, M. A. Graham, D. J. Fox and M. Wills, *Org*. *Lett*., 2007, **9**, 4659–4662.

(14) J. S. Yadav, A. K. Basak and P. Srihari, *Tetrahedron Lett*., 2007, **48**, 2841–2843.

(15) N. A. Sheddan and J. Mulzer, *Org*. *Lett*., 2005, **7**, 5115–5118.

(16) S. E. Denmark and N. S. Werner, *J*. *Am*. *Chem*. *Soc*., 2010, **132**, 3612–3620.

(17) This reagent is commercially available from Aldrich (# 461407).

(18) C. Mazet and D. Gérard, *Chem*. *Commun*., 2011, **47**, 298–300.