Pd-Catalyzed Asymmetric Allylic Amination Using Aspartic Acid-Derived P-Chirogenic

Diaminophosphine Oxides: DIAPHOXs

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Supporting Information

Experimental Procedure for the Pd-Catalyzed Asymmetric Allylic Amination and Compound Characterization

General

Infrared (IR) spectra were recorded on a JASCO FT/IR 230 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ecp 400 spectrometer, operating at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 160 MHz. Chemical shifts in CDCl_3 , were reported downfield from TMS (= 0 ppm) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported downfield from TMS (= 0 ppm) or in the scale relative to the solvent signal [CHCl_3 (77.0 ppm)] as an internal reference. Optical rotations were measured on a JASCO P-1020 polarimeter. FAB mass spectra were measured on JMX-AX500. EI mass spectra were measured on JEOL GCmate. The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, PU-980; detector, UV-970, measured at 254 nm; column, DAICEL CHIRALPAK AD, DAICEL CHIRALPAK AD-H, DAICEL CHIRALCEL OD-H, DAICEL CHIRALCEL OJ; mobile phase, hexane–2-propanol or diisopropylamine–hexane–2-propanol; flow rate, 0.2–0.5 mL/min. Preligands **1a–d** were prepared according to the reported procedure, see ref 8a and 8b. Reactions were carried out in dry solvent under argon atmosphere. Other reagents were purified by the usual methods.

Pd-Catalyzed Asymmetric Allylic Amination of **2a** and **2b**

General Procedure

(1R)-N-Benzyl-1,3-diphenylpropenylamine (3a): To a stirred solution of **2a** (127 mg, 0.5 mmol), $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$ (1.8 mg, 0.005 mmol), **1a** (7.8 mg, 0.02 mmol), in CH_2Cl_2 (2 mL) was added BSA (0.370 mL, 1.5 mmol), and benzylamine

(0.165 mL, 1.5 mmol) at room temperature. After being stirred for 24 h, the reaction was concentrated under reduced pressure, and the obtained residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate = 20/1) to give **3a** as yellow oil (138 mg, 91%, 98% ee).

Characterization of New Compounds and Determination of the Enantiomeric Excess

Compound 2a: (Ohta et al. *Tetrahedron:Asymmetry* **2003**, *14*, 537.)

Compound 2b: Colorless oil. IR (neat) ν 3027, 2952, 1745, 1442, 1265, 938, 747, 699 cm⁻¹; ¹H NMR (CDCl₃): δ 1.80–1.89 (m, 1H), 1.96–2.06 (m, 1H), 2.33–2.39 (m, 2H), 2.57–2.62 (m, 2H), 2.69 (t, J = 7.6 Hz, 2H), 3.75 (s, 3H), 5.00–5.05 (m, 1H), 5.43 (ddt, J = 7.6 Hz, 15.6 Hz, 1.2 Hz, 1H), 5.80 (dt, J = 15.6 Hz, 6.8 Hz, 1H), 7.12–7.28 (m, 10H); ¹³C NMR (CDCl₃): δ 31.3, 33.9, 35.2, 36.0, 54.5, 78.5, 128.2, 128.2 (x 2), 128.3 (x 2), 128.3 (x 2), 128.4 (x 2), 134.5, 141.1, 141.4, 155.1; FAB-LRMS m/z 249 (M⁺–OCOOMe).

Compound 3a: (Ohta et al. *Tetrahedron:Asymmetry* **2003**, *14*, 537.)

Yellow oil. $[\alpha]_D^{25}$ –19.7 (c 0.15, CHCl₃, 98% ee (*R*)). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane = 15/85, flow rate: 0.4 mL/min, t_R 21.1 min [(*S*)-isomer] and 25.3 min [(*R*)-isomer], detection at 254 nm). The absolute configuration was determined by comparing the measured optical rotation with the literature data ($[\alpha]_D^{25}$ +21.0 (c 1.40, CHCl₃, 84% ee (*S*)).

Compound 3b: Yellow oil. IR (neat) ν 3060, 3026, 2925, 2835, 1667, 1600, 1494, 1450, 1217, 1146, 1011, 967, 745, 696 cm⁻¹; ¹H NMR (CDCl₃): δ 1.71 (br-s, 1H), 3.77 (s, 2H), 4.37 (d, J = 7.6 Hz, 1H), 6.16–6.17 (m, 1H), 6.30 (dd, J = 7.6 Hz, 16.0 Hz, 1H), 6.32–6.33 (m, 1H), 6.58 (d, J = 16.0 Hz, 1H), 7.19–7.42 (m, 11H); ¹³C NMR (CDCl₃): δ 43.6, 64.1, 106.9, 110.0, 126.3 (x 2), 127.3 (x 2), 127.3, 127.4, 128.4 (x 2), 128.5 (x 2), 130.4, 132.1, 136.7, 141.7, 142.4, 153.7; FAB-LRMS m/z 288 (M–H⁺); $[\alpha]_D^{24}$ –23.3 (c 0.40, CHCl₃, 96% ee). FAB-HRMS. Calcd for C₂₀H₁₈NO (M–H⁺): 288.1388. Found: 288.1373. The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 5/95, flow rate 0.5 mL/min, t_R 26.5 min (minor isomer) and 34.1 min (major isomer), detection at 254 nm).

Compound 3c: (Ohta et al. *Tetrahedron:Asymmetry* **2003**, *14*, 537.)

Colorless oil. $[\alpha]_D^{24}$ +12.4 (c 0.33, CHCl₃, 99% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OD-H, diisopropylamine/2-propanol/hexane 1/2/400, flow rate 0.25 mL/min, t_R 33.9 min (minor isomer) and 38.9 min (major isomer), detection at 254 nm).

Compound 3d: (Qian et al. *J. Organomet. Chem.* **1997**, *548*, 143.)

Yellow oil. $[\alpha]_D^{24}$ +9.5 (c 0.30, CHCl₃, 98% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD, 2-propanol/hexane 1/99, flow rate 0.5 mL/min, t_R 16.2 min (minor isomer) and 17.8 min (major isomer), detection at 254 nm).

Compound 3e: (Huet et al. *Bulletin de la Societe Chimique de France* **1964**, 960.)

Yellow oil. $[\alpha]_D^{24} +22.3$ (c 0.62, CHCl_3 , 94% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OD-H, diisopropylamine/2-propanol/hexane 1/2/400, flow rate 0.2 mL/min, t_R 30.2 min (minor isomer) and 33.7 min (major isomer), detection at 254 nm).

Compound 3f: (Hamada et al. *Tetrahedron Lett.* **1999**, 40, 7791.)

Yellow oil. $[\alpha]_D^{24} -8.4$ (c 0.70, CHCl_3 , 95% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 5/95, flow rate 0.5 mL/min, t_R 20.9 min (minor-isomer) and 28.6 min (major-isomer), detection at 254 nm).

Compound 3h: Yellow oil. IR (neat) ν 3060, 3026, 2923, 2853, 1495, 1454, 971, 745, 698 cm^{-1} ; ^1H NMR (CDCl_3): 1.67–1.83 (m, 2H), 2.39–2.44 (m, 2H), 2.50–2.64 (m, 2H), 2.74 (t, $J = 7.6$ Hz, 2H), 2.96–3.02 (m, 1H), 3.56 (d, $J = 13.2$ Hz, 1H), 3.73 (d, $J = 13.2$ Hz, 1H), 5.27 (dd, $J = 8.8$ Hz, 15.6 Hz, 1H), 5.56 (dt, $J = 15.6$ Hz, 6.8 Hz, 1H), 7.11–7.31 (m, 15H); ^{13}C NMR (CDCl_3): δ 32.3, 34.0, 35.8, 37.5, 51.1, 59.9, 125.6, 125.8, 126.7, 128.2 (x 2), 128.2 (x 2), 128.3 (x 2), 128.3 (x 2), 128.4 (x 2), 128.5 (x 2), 132.0, 133.5, 140.7, 141.7, 142.3; EI-LRMS m/z 355 (M^+); $[\alpha]_D^{24} -6.8$ (c 1.13, CHCl_3 , 52% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 1/99, flow rate 0.5 mL/min, t_R 28.0 min (major isomer) and 32.0 min (minor isomer), detection at 254 nm).

Pd-Catalyzed Asymmetric Allylic Amination of **5a–m**

General Procedure

Benzyl-(2-phenylcyclohex-2-enyl)-amine (6a): To a stirred solution of **5a** (72 mg, 0.3 mmol), $[\eta^3\text{-C}_3\text{H}_5\text{PdCl}]_2$ (1.1 mg, 0.003 mmol), **1a** (4.9 mg, 0.012 mmol) in CH_3CN (1.5 mL) was added BSA (0.23 mL, 0.9 mmol), and benzylamine (0.10 mL, 0.9 mmol) at room temperature. After being stirred for 17 h at the same temperature, the reaction was concentrated under reduced pressure, and the obtained residue was purified by flash column chromatography (SiO_2 , hexane/ethyl acetate 7/1) to give **6a** as yellow oil (76 mg, 93%, 96% ee).

Characterization of New Compounds and Determination of the Enantiomeric Excess

Compound 5a: (Hamada et al. *Tetrahedron Lett.* **2001**, 42, 1229.)

Compound 5b: (Hamada et al. *Tetrahedron Lett.* **2001**, 42, 1229.)

Compound 5c: Colorless oil. IR (neat) ν 2930, 2855, 1744, 1443, 1265, 980, 940, 700 cm^{-1} ; ^1H NMR (CDCl_3):

δ 1.54–1.65 (m, 1H), 1.72–1.89 (m, 3H), 1.99–2.08 (m, 1H), 2.17–2.30 (m, 2H), 2.48–2.56 (m, 1H), 3.73 (s, 3H), 5.69 (dd, J = 1.6 Hz, 7.2 Hz, 1H), 6.18 (dd, J = 6.0 Hz, 7.6 Hz, 1H), 7.23–7.34 (m, 5H); ^{13}C NMR (CDCl_3): δ 25.2, 26.5, 27.5, 30.6, 54.6, 78.7, 126.5, 126.8 (x 2), 128.1 (x 2), 134.9, 142.2, 142.3, 155.2; FAB-LRMS m/z 171 ($\text{M}^+ - \text{OCOOMe}$).

Compound 5d: Colorless oil. IR (neat) ν 2952, 1739, 1441, 1334, 1268, 972, 945, 916, 810 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.73–1.98 (m, 3H), 2.13–2.25 (m, 2H), 2.33–2.41 (m, 1H), 3.69 (s, 3H), 5.91 (t, J = 2.4 Hz, 1H), 6.45 (dd, J = 3.2 Hz, 5.2 Hz, 1H), 7.42–7.53 (m, 3H), 7.78–7.82 (m, 4H); ^{13}C NMR (CDCl_3): δ 17.0, 25.9, 28.8, 54.4, 71.4, 124.2, 124.3, 125.6, 125.9, 127.4, 127.8, 128.1, 132.2, 132.5, 133.3, 134.8, 136.9, 155.4; EI-LRMS m/z 313 (M^+).

Compound 5e: White Solid. Mp 33–34 $^\circ\text{C}$; IR (KBr) ν 2954, 1746, 1443, 1327, 1270, 1165, 1123, 1070, 766 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.71–1.84 (m, 2H), 1.86–1.94 (m, 1H), 2.10–2.24 (m, 2H), 2.32–2.40 (m, 1H), 3.73 (s, 3H), 5.75 (t, J = 3.2 Hz, 1H), 6.39 (dd, J = 3.2 Hz, 4.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl_3): δ 17.0, 25.9, 28.7, 54.6, 71.3, 124.2 (q, J = 270.3 Hz), 125.3 (x 2) (q, J = 3.8 Hz), 125.6 (x 2), 129.1 (q, J = 32.2 Hz), 133.8, 134.2, 143.2, 155.4; FAB-LRMS m/z 225 ($\text{M}^+ - \text{OCOOMe}$).

Compound 5f: Colorless oil. IR (neat) ν 2952, 1745, 1512, 1442, 1335, 1269, 1159, 962, 935, 916 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.66–1.81 (m, 2H), 1.83–1.92 (m, 1H), 2.08–2.20 (m, 2H), 2.22–2.35 (m, 1H), 3.72 (s, 3H), 5.70 (t, J = 3.2 Hz, 1H), 6.24 (dd, J = 2.8 Hz, 5.2 Hz, 1H), 6.96–7.02 (m, 2H), 7.27–7.34 (m, 2H); ^{13}C NMR (CDCl_3): δ 17.0, 25.8, 28.8, 54.6, 71.7, 115.2 (x 2) (d, J = 21.4 Hz), 127.4 (x 2) (d, J = 8.0 Hz), 132.9 (d, J = 235.9 Hz), 135.8 (d, J = 3.1 Hz), 155.8, 160.9, 163.3; FAB-LRMS m/z 175 ($\text{M}^+ - \text{OCOOMe}$).

Compound 5g: Colorless oil. IR (neat) ν 2953, 1745, 1611, 1583, 1443, 1336, 1260, 976, 919, 783 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.68–1.91 (m, 3H), 2.09–2.24 (m, 2H), 2.29–2.37 (m, 1H), 3.74 (s, 3H), 5.70 (t, J = 3.2 Hz, 1H), 6.34 (dd, J = 3.2 Hz, 4.8 Hz, 1H), 6.90–6.96 (m, 1H), 7.03–7.07 (m, 1H), 7.10–7.13 (m, 1H), 7.23–7.29 (m, 1H); ^{13}C NMR (CDCl_3): δ 16.9, 25.8, 28.7, 54.6, 71.4, 112.7 (d, J = 21.8 Hz), 113.9 (d, J = 21.0 Hz), 121.3 (d, J = 2.6 Hz), 129.8 (d, J = 8.4 Hz), 133.4 (d, J = 120.5 Hz), 142.0 (d, J = 7.7 Hz), 155.4, 161.7, 164.1; FAB-LRMS m/z 249 ($\text{M}^+ - \text{H}$), 175 ($\text{M}^+ - \text{OCOOMe}$).

Compound 5h: Colorless oil. IR (neat) ν 2952, 1746, 1488, 1443, 1336, 1266, 963, 918, 758 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.68–1.87 (m, 2H), 1.95–2.08 (m, 2H), 2.15–2.35 (m, 2H), 3.67 (s, 3H), 5.66 (t, J = 4.4 Hz, 1H), 6.14 (dd, J = 3.6 Hz, 4.4 Hz, 1H), 6.99–7.10 (m, 2H), 7.20–7.25 (m, 2H); ^{13}C NMR (CDCl_3): δ 17.4, 25.6, 28.6, 54.5, 72.8 (d, J = 3.4 Hz), 115.5 (d, J = 22.9 Hz), 123.9 (d, J = 3.5 Hz), 128.0 (d, J = 14.1 Hz), 128.7 (d, J = 8.1 Hz), 130.3 (d, J = 4.2 Hz), 133.2 (d, J = 291.3 Hz), 155.3, 158.8, 161.2; FAB-LRMS m/z 249 ($\text{M}^+ - \text{H}$), 175 ($\text{M}^+ - \text{OCOOMe}$).

Compound 5i: Colorless oil. IR (neat) ν 2953, 1739, 1607, 1514, 1442, 1255, 1037, 914 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.68–1.90 (m, 3H), 2.10–2.22 (m, 2H), 2.27–2.35 (m, 1H), 3.72 (s, 3H), 3.80 (s, 3H), 5.72 (t, J = 3.2 Hz, 1H), 6.23 (dd, J = 3.2 Hz, 5.2 Hz, 1H), 6.85 (dt, J = 8.8 Hz, 2.8 Hz, 2H), 7.29 (dt, J = 8.8 Hz, 2.4 Hz, 2H); ^{13}C NMR (CDCl_3): δ 17.0, 25.8, 28.9, 54.5, 55.2, 71.7, 113.7 (x 2), 126.8 (x 2), 130.2, 132.2, 134.2, 155.5, 158.8; EI-LRMS m/z 262 (M^+).

Compound 5j: Colorless oil. IR (neat) ν 2939, 1734, 1577, 1437, 1260, 773 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.66–1.89 (m, 3H), 2.10–2.23 (m, 2H), 2.28–2.36 (m, 1H), 3.69 (s, 3H), 3.79 (s, 3H), 5.74 (t, J = 3.2 Hz, 1H), 6.32 (t, J = 3.2 Hz, 5.2 Hz,

1H), 6.79 (dd, $J = 2.4$ Hz, 8.4 Hz, 1H), 6.90–6.95 (m, 2H), 7.22 (dd, $J = 8.0$ Hz, 8.0 Hz, 1H); ^{13}C NMR (CDCl_3): δ 17.0, 25.8, 28.8, 54.5, 55.1, 71.6, 111.4, 112.8, 118.2, 129.3, 131.9, 134.8, 141.2, 155.4, 159.6; EI-LRMS m/z 262 (M^+).

Compound 5k: (Mori et al, *J. Am. Chem. Soc.* **2003**, 125, 9801.)

Compound 5l: Colorless oil. IR (neat) ν 2952, 1744, 1442, 1335, 1266, 961, 693 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.60–1.88 (m, 4H), 1.96–2.03 (m, 1H), 2.12–2.26 (m, 2H), 3.68 (d, $J = 17.2$ Hz, 1H), 3.74 (t, $J = 3.2$ Hz, 1H), 3.81 (d, $J = 17.2$ Hz, 1H), 6.07 (dd, $J = 3.6$ Hz, 4.0 Hz, 1H), 7.16–7.30 (m, 10H); ^{13}C NMR (CDCl_3): δ 16.9, 25.9, 28.4, 54.7, 69.6, 126.2, 126.4 (x 2), 127.2, 128.5 (x 2), 129.4, 133.2, 135.3, 137.5, 155.6; FAB-LRMS m/z 183 ($\text{M}^+ - \text{OCOOMe}$).

Compound 5m: White solid. Mp: 51–54 $^\circ\text{C}$; IR (KBr) ν 2952, 2931, 1743, 1442, 1265, 982, 945, 919, 759 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.64–1.82 (m, 2H), 1.86–1.99 (m, 2H), 2.08–2.32 (m, 2H), 3.79 (s, 3H), 5.33 (t, $J = 4.4$ Hz, 1H), 6.43 (dd, $J = 4.0$ Hz, 4.4 Hz, 1H), 7.26–7.30 (m, 3H), 7.39–7.42 (m, 2H); ^{13}C NMR (CDCl_3): δ 17.5, 25.7, 28.2, 54.7, 72.7, 88.0, 88.6, 112.0, 123.3, 128.0, 128.2 (x 2), 131.5 (x 2), 139.9, 155.5; EI-LRMS m/z 256 (M^+).

Compound 6a: Yellow oil. IR (neat) ν 3025, 2931, 2858, 2828, 1494, 1453, 1106, 1070, 757, 697 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.60–1.88 (m, 4H), 1.96–2.03 (m, 1H), 2.12–2.26 (m, 2H), 3.68 (d, $J = 17.2$ Hz, 1H), 3.74 (t, $J = 3.2$ Hz, 1H), 3.81 (d, $J = 17.2$ Hz, 1H), 6.07 (dd, $J = 3.6$ Hz, 4.0 Hz, 1H), 7.16–7.30 (m, 10H); ^{13}C NMR (CDCl_3): δ 17.8, 26.2, 27.5, 51.3, 51.9, 126.1 (x 2), 126.7, 126.8, 128.2 (x 2), 128.3 (x 2), 128.3 (x 2), 128.5, 139.6, 140.5, 141.1; EI-LRMS m/z 264 ($\text{M}^+ + 1$), 262 ($\text{M}^+ - 1$); $[\alpha]_{\text{D}}^{22} -116.5$ (c 0.71, CHCl_3 , 96% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD, 2-propanol/hexane 1/9, flow rate 0.3 mL/min, t_{R} 13.0 min (major isomer) and 15.0 min (minor isomer), detection at 254 nm).

Compound 6b: Yellow oil. IR (neat) ν 2929, 2860, 1494, 1456, 1444, 1110, 758, 697 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.83 (t, $J = 7.2$ Hz, 3H), 1.16–1.37 (m, 4H), 1.39 (br-s, 1H), 1.58–1.70 (m, 1H), 1.72–1.81 (m, 2H), 1.86–1.93 (m, 1H), 2.12–2.24 (m, 2H), 2.48 (dd, $J = 6.8$ Hz, 11.6 Hz, 1H), 2.63 (dd, $J = 7.2$ Hz, 11.6 Hz, 1H), 3.70 (m, 1H), 6.04 (t, $J = 4.0$ Hz, 1H), 7.22–7.39 (m, 5H); ^{13}C NMR (CDCl_3): δ 13.9, 17.9, 20.4, 26.1, 27.8, 32.3, 47.3, 53.1, 126.1 (x 2), 126.8, 128.3, 128.4 (x 2), 139.6, 141.2; EI-LRMS m/z 229 (M^+); $[\alpha]_{\text{D}}^{21} -123.7$ (c 0.63, CHCl_3 , 95% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OD-H, 2-propanol/hexane 5/95, flow rate 0.4 mL/min, t_{R} 17.3 min (minor isomer) and 20.5 min (major isomer), detection at 254 nm).

Compound 6c: Yellow oil. IR (neat) ν 2980, 2933, 2862, 1739, 1444, 1196, 759, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.22 (t, $J = 7.2$ Hz, 3H), 1.58–1.64 (m, 1H), 1.74–1.86 (m, 4H), 2.10–2.25 (m, 2H), 3.33 (d, $J = 17.2$ Hz, 1H), 3.38 (d, $J = 17.2$ Hz, 1H), 3.80 (m, 1H), 4.12 (q, $J = 7.2$ Hz, 2H), 6.04 (t, $J = 3.6$ Hz, 1H), 7.22–7.41 (m, 5H); ^{13}C NMR (CDCl_3): δ 14.1, 17.7, 26.0, 27.6, 48.4, 52.2, 60.5, 126.2 (x 2), 126.9, 128.3 (x 2), 128.8, 139.3, 141.0, 172.3; EI-LRMS m/z 259 (M^+); $[\alpha]_{\text{D}}^{20} -121.5$ (c 0.86, CHCl_3 , 96% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD, 2-propanol/hexane 2/98, flow rate 0.4 mL/min, t_{R} 19.0 min (*S* isomer) and 22.8 min (*R* isomer), detection at 254 nm). The absolute configuration was determined by comparing the measured optical rotation with the literature data, after conversion into the corresponding *p*-toluenesulfonamide ($[\alpha]_{\text{D}}^{19} -84.8$ (c 1.66, MeOH, 96% ee),

Literature data (Hamada et al. *Tetrahedron Lett.* **2001**, 42, 1297.) $[\alpha]_D^{25} +84.2$ (c 1.59, MeOH, 97% ee (*R*)).

Compound 6d: Colorless oil. IR (neat) ν 2930, 2852, 1682, 1494, 1325, 1289, 1251, 1116, 768, 755, 696 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.58–1.67 (m, 1H), 1.73–1.92 (m, 3H), 2.14–2.19 (m, 2H), 2.43 (ddd, $J = 2.8$ Hz, 6.0 Hz, 11.2 Hz, 2H), 2.54 (ddd, $J = 3.2$ Hz, 6.0 Hz, 11.2 Hz, 2H), 3.35 (ddd, $J = 2.8$ Hz, 6.0 Hz, 10.4 Hz, 2H), 3.48 (ddd, $J = 3.2$ Hz, 6.0 Hz, 10.4 Hz, 2H), 3.73–3.75 (m, 1H), 6.12 (dt, $J = 2.0$ Hz, 4.0 Hz, 1H), 7.17–7.35 (m, 5H); ^{13}C NMR (CDCl_3): δ 20.4, 22.5, 26.0, 49.0, 59.9 (x 2), 67.5 (x 2), 126.1, 126.6, 127.5, 130.0, 130.5, 139.2, 142.0, 142.1; EI-LRMS m/z 243 (M^+); $[\alpha]_D^{21} -54.5$ (c 0.55, CHCl_3 , 97% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 1/99, flow rate 0.2 mL/min, t_R 32.0 min (minor isomer) and 37.6 min (major isomer), detection at 254 nm).

Compound 6e: Yellow oil. IR (neat) ν 3059, 3026, 2929, 2844, 1600, 1495, 1453, 1101, 758, 694 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.97–2.04 (m, 1H), 2.19–2.28 (m, 1H), 2.41–2.50 (m, 1H), 2.58–2.68 (m, 1H), 3.73 (d, $J = 12.8$ Hz, 1H), 3.84 (d, $J = 12.8$ Hz, 1H), 4.29–4.32 (m, 1H), 6.21 (dd, $J = 0.8$ Hz, 2.4 Hz, 1H), 7.20–7.43 (m, 10H); ^{13}C NMR (CDCl_3): δ 30.2, 31.1, 51.2, 62.7, 126.2 (x 2), 126.8, 127.1, 128.3 (x 2), 128.4 (x 2), 128.4 (x 2), 129.0, 135.6, 140.5, 144.1; EI-LRMS m/z 249 (M^+); $[\alpha]_D^{21} -32.5$ (c 0.61, CHCl_3 , 93% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD, 2-propanol/hexane 5/95, flow rate 0.4 mL/min, t_R 12.8 min (major isomer) and 17.2 min (minor isomer), detection at 254 nm).

Compound 6f: White solid; IR (KBr) ν 2951, 2846, 2804, 1452, 1349, 1251, 1116, 1069, 1025, 767, 690 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.83–1.90 (m, 1H), 2.12–2.20 (m, 1H), 2.42–2.56 (m, 6H), 3.56–3.68 (m, 4H), 4.21–4.28 (m, 1H), 6.29–6.31 (m, 1H), 7.20–7.32 (m, 3H), 7.67–7.70 (m, 2H); ^{13}C NMR (CDCl_3): δ 22.0, 31.9, 48.3, 67.5 (x 2), 70.7 (x 2), 126.4 (x 2), 126.9, 128.0 (x 2), 130.1, 136.4, 141.3; EI-LRMS m/z 229 (M^+); $[\alpha]_D^{21} +48.1$ (c 0.79, CHCl_3 , 99% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK OJ, 2-propanol/hexane 1/99, flow rate 0.2 mL/min, t_R 42.7 min (minor isomer) and 61.1 min (major isomer), detection at 254 nm).

Compound 6g: Yellow oil. IR (neat) ν 3025, 2922, 2848, 1598, 1493, 1444, 1126, 1101, 1075, 1029, 756, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.43–1.55 (m, 1H), 1.73–1.80 (m, 4H), 1.98–2.10 (m, 2H), 2.21–2.29 (m, 1H), 2.47–2.56 (m, 1H), 3.65 (d, $J = 11.2$ Hz, 1H), 3.71 (d, $J = 11.2$ Hz, 1H), 3.83 (dd, $J = 2.0$ Hz, 6.4 Hz, 1H), 6.04 (dd, $J = 5.6$ Hz, 8.0 Hz, 1H), 7.19–7.31 (m, 10H); ^{13}C NMR (CDCl_3): δ 25.4, 27.1, 27.6, 30.6, 51.7, 59.7, 126.3 (x 2), 126.4, 126.7, 128.0 (x 2), 128.2 (x 2), 128.2 (x 2), 131.9, 140.7, 144.6, 146.6; EI-LRMS m/z 277 (M^+); $[\alpha]_D^{23} -17.0$ (c 1.26, CHCl_3 , 83% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 5/95, flow rate 0.4 mL/min, t_R 9.7 min (major isomer) and 10.7 min (minor isomer), detection at 254 nm).

Compound 6h: Yellow oil. IR (neat) ν 3056, 3025, 2930, 2858, 1505, 1495, 1455, 1105, 1074, 807, 744, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.63–1.92 (m, 4H), 2.02–2.09 (m, 1H), 2.16–2.33 (m, 2H), 3.73 (d, $J = 13.2$ Hz, 1H), 3.84 (d, $J = 13.2$ Hz, 1H), 3.84–3.87 (m, 1H), 6.21 (t, $J = 4.0$ Hz, 1H), 7.17–7.28 (m, 5H), 7.42–7.45 (m, 3H), 7.65 (s, 1H), 7.71–7.80 (m, 3H); ^{13}C NMR (CDCl_3): δ 17.7, 26.3, 27.2, 51.2, 51.3, 124.4, 124.9, 125.5, 125.9, 126.8, 127.4, 127.8, 128.0, 128.2 (x 2),

128.4 (x 2), 129.2, 132.5, 138.2, 139.3, 140.4; EI-LRMS m/z 313 (M^+); $[\alpha]_D^{22}$ -109.9 (c 0.77, $CHCl_3$, 94% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 5/95, flow rate 0.4 mL/min, t_R 37.6 min (minor isomer) and 48.8 min (major isomer), detection at 254 nm).

Compound 6i: Colorless oil. IR (neat) ν 3028, 2934, 2861, 1614, 1455, 1327, 1164, 1121, 1069, 844, 699 cm^{-1} ; 1H NMR ($CDCl_3$): δ 1.62–1.86 (m, 3H), 2.01–2.07 (m, 1H), 2.13–2.29 (m, 2H), 3.68 (d, J = 13.2 Hz, 1H), 3.67–3.73 (m, 1H), 3.82 (d, J = 13.2 Hz, 1H), 6.14 (t, J = 4.0 Hz, 1H), 7.14–7.29 (m, 5H), 7.36 (d, J = 4.0 Hz, 2H), 7.50 (d, J = 4.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 17.4, 26.2, 27.0, 51.1, 51.4, 124.3 (q, J = 270.4 Hz), 125.1 (x 2) (q, J = 3.8 Hz), 126.3 (x 2), 126.9, 128.3 (x 2), 128.3 (x 2), 128.7 (q, J = 32.1 Hz), 130.3, 138.7, 140.3, 144.7; EI-LRMS m/z 331 (M^+); $[\alpha]_D^{21}$ -67.2 (c 1.39, $CHCl_3$, 93% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 5/95, flow rate 0.4 mL/min, t_R 14.7 min (minor isomer) and 17.7 min (major isomer), detection at 254 nm).

Compound 6j: Yellow oil. IR (neat) ν 3026, 2931, 2859, 2830, 1601, 1506, 1454, 1226, 1159, 838, 738 cm^{-1} ; 1H NMR ($CDCl_3$): δ 1.60–1.86 (m, 4H), 1.98–2.04 (m, 1H), 2.10–2.26 (m, 2H), 3.67–3.74 (m, 1H), 3.67 (d, J = 13.2 Hz, 1H), 3.82 (d, J = 13.2 Hz, 1H), 6.00 (t, J = 4.0 Hz, 1H), 6.95 (tt, J = 3.2 Hz, 8.8 Hz, 2H), 7.17–7.30 (m, 7H); ^{13}C NMR ($CDCl_3$): δ 17.6, 26.1, 27.2, 51.2, 51.8, 115.0 (x 2) (d, J = 21.0 Hz), 126.8, 127.6 (x 2) (d, J = 7.7 Hz), 128.2 (x 2), 128.3 (x 2), 128.4, 137.1 (d, J = 3.0 Hz), 139.5 (d, J = 180. Hz), 160.7, 163.1; EI-LRMS m/z 281 (M^+); $[\alpha]_D^{21}$ -89.5 (c 0.68, $CHCl_3$, 91% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 1/99, flow rate 0.4 mL/min, t_R 22.7 min (major isomer) and 28.0 min (minor isomer), detection at 254 nm).

Compound 6k: Yellow oil. IR (neat) ν 3027, 2932, 2860, 2829, 1609, 1581, 1486, 1453, 1440, 1265, 1171, 1159, 781, 741, 697 cm^{-1} ; 1H NMR ($CDCl_3$): δ 1.60–1.72 (m, 2H), 1.76–1.86 (m, 1H), 1.99–2.05 (m, 1H), 2.12–2.28 (m, 2H), 3.64–3.68 (m, 1H), 3.69 (d, J = 13.2 Hz, 1H), 3.83 (d, J = 13.2 Hz, 1H), 6.10 (t, J = 4.4 Hz, 1H), 6.89–7.07 (m, 3H), 7.19–7.30 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 17.4, 26.1, 27.0, 51.2, 51.6, 112.9 (d, J = 21.8 Hz), 113.4 (d, J = 21.0 Hz), 121.6 (d, J = 2.7 Hz), 126.8, 128.2 (x 2), 128.2 (x 2), 129.3, 129.5 (d, J = 8.4 Hz), 139.4 (d, J = 172.8 Hz), 143.5 (d, J = 7.3 Hz), 161.7, 164.1; EI-LRMS m/z 281 (M^+); $[\alpha]_D^{20}$ -99.6 (c 0.71, $CHCl_3$, 93% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 4/96, flow rate 0.4 mL/min, t_R 14.5 min (minor isomer) and 17.4 min (major isomer), detection at 254 nm).

Compound 6l: Yellow oil. IR (neat) ν 3027, 2931, 2859, 2832, 1487, 1449, 1235, 1203, 1104, 759, 698 cm^{-1} ; 1H NMR ($CDCl_3$): δ 1.62–1.72 (m, 1H), 1.79–1.92 (m, 3H), 2.21–2.26 (m, 2H), 3.62 (d, J = 12.8 Hz, 1H), 3.71 (d, J = 12.8 Hz, 1H), 3.70–3.74 (m, 1H), 5.94 (t, J = 3.6 Hz, 1H), 6.98–7.10 (m, 4H), 7.15–7.25 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 18.7, 25.9, 28.2, 50.8, 53.3 (d, J = 3.0 Hz), 115.4 (d, J = 22.9 Hz), 123.9 (d, J = 3.1 Hz), 126.6, 128.1 (x 2), 128.2 (x 2), 128.3, 129.5 (d, J = 14.5 Hz), 130.4 (d, J = 4.2 Hz), 131.1 (d, J = 1.9 Hz), 138.5 (d, J = 421.7 Hz), 158.8, 161.2; EI-LRMS m/z 281 (M^+); $[\alpha]_D^{22}$ -109.4 (c 1.04, $CHCl_3$, 98% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 5/95, flow rate 0.4 mL/min, t_R 14.2 min (major isomer) and 17.7 min (minor isomer), detection at 254 nm).

Compound 6m: Yellow oil. IR (neat) ν 3027, 2931, 2857, 2832, 1606, 1508, 1456, 1282, 1248, 1179, 1038, 771, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.60–1.73 (m, 3H), 1.76–1.86 (m, 1H), 1.95–2.03 (m, 1H), 2.08–2.33 (m, 2H), 3.67 (d, $J = 12.8$ Hz, 1H), 3.66–3.70 (m, 1H), 3.79 (s, 3H), 3.81 (d, $J = 12.8$ Hz, 1H), 5.98 (t, $J = 3.6$ Hz, 1H), 6.78–6.84 (m, 2H), 7.17–7.28 (m, 5H); ^{13}C NMR (CDCl_3): δ 17.7, 26.1, 27.3, 51.3, 51.8, 55.2, 113.7 (x 2), 126.7, 127.0, 127.1 (x 2), 128.2 (x 2), 128.3 (x 2), 133.4, 138.7, 140.4, 158.6; EI-LRMS m/z 262 (M^+); $[\alpha]_{\text{D}}^{22} -107.6$ (c 0.68, CHCl_3 , 91% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OD-H, diisopropylamine/2-propanol/hexane 0.5/1/200, flow rate 0.3 mL/min, t_{R} 46.4 min (major isomer) and 55.4 min (minor isomer), detection at 254 nm).

Compound 6n: Yellow oil. IR (neat) ν 2932, 2858, 2831, 1598, 1577, 1488, 1455, 1285, 1203, 1168, 1051, 774, 697 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.62–1.88 (m, 3H), 1.95–2.02 (m, 1H), 2.10–2.27 (m, 2H), 3.68 (d, $J = 13.6$ Hz, 1H), 3.68–3.72 (m, 1H), 3.77 (s, 3H), 3.81 (d, $J = 13.6$ Hz, 1H), 6.06 (t, $J = 4.0$ Hz, 1H), 6.78 (dd, $J = 2.4$ Hz, 8.4 Hz, 1H), 6.85–6.90 (m, 2H), 7.17–7.28 (m, 5H); ^{13}C NMR (CDCl_3): δ 17.8, 26.1, 27.4, 51.3, 52.0, 55.1, 111.7, 112.5, 118.6, 126.8, 128.2 (x 2), 128.2 (x 2), 128.7, 129.2, 139.5, 140.4, 142.7, 159.6; EI-LRMS m/z 262 (M^+); $[\alpha]_{\text{D}}^{22} -87.2$ (c 1.12, CHCl_3 , 93% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALCEL OJ, 2-propanol/hexane 5/95, flow rate 0.3 mL/min, t_{R} 32.5 min (minor isomer) and 37.4 min (major isomer), detection at 254 nm).

Compound 6o: Yellow oil. IR (neat) ν 2928, 2855, 1471, 1456, 1254, 1102, 1055, 837, 773 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.05 (s, 6H), 0.89 (s, 9H), 1.55–1.72 (m, 4H), 1.83–1.87 (m, 1H), 1.96–2.07 (m, 2H), 3.20–3.25 (m, 1H), 3.72 (d, $J = 13.2$ Hz, 1H), 3.90 (d, $J = 13.2$ Hz, 1H), 4.13 (dd, $J = 1.2$ Hz, 12.8 Hz, 1H), 4.20 (dd, $J = 1.6$ Hz, 12.8 Hz, 1H), 5.72–5.77 (m, 1H), 7.21–7.37 (m, 5H); ^{13}C NMR (CDCl_3): δ -5.4, -5.3, 18.1, 18.4, 25.2, 26.0 (x 3), 27.1, 51.4, 52.2, 66.3, 125.1, 126.7, 128.1 (x 2), 128.2 (x 2), 138.7, 141.1; FAB-LRMS m/z 332 (MH^+); $[\alpha]_{\text{D}}^{22} -31.7$ (c 0.70, CHCl_3 , 72% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD, 2-propanol/hexane 5/95, flow rate 0.3 mL/min, t_{R} 10.8 min (major isomer) and 14.8 min (minor isomer), detection at 254 nm).

Compound 6p: Yellow oil. IR (neat) ν 3024, 2932, 2858, 1633, 1495, 1449, 1069, 961, 748, 692 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.43–1.67 (m, 3H), 1.82–1.92 (m, 1H), 2.06–2.28 (m, 3H), 3.53–3.57 (m, 1H), 3.81 (d, $J = 13.2$ Hz, 1H), 3.96 (d, $J = 13.2$ Hz, 1H), 5.95 (t, $J = 4.0$ Hz, 1H), 6.27 (d, $J = 16.4$ Hz, 1H), 6.62 (d, $J = 16.4$ Hz, 1H), 7.16–7.39 (m, 10H); ^{13}C NMR (CDCl_3): δ 16.9, 25.9, 26.3, 49.4, 51.7, 124.9, 126.1 (x 2), 126.9, 127.0, 128.4 (x 2), 128.5 (x 2), 128.6 (x 2), 130.7, 132.9, 137.5, 137.7, 140.5; FAB-LRMS m/z 290 (MH^+); $[\alpha]_{\text{D}}^{22} -57.3$ (c 1.04, CHCl_3 , 94% ee). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/9, flow rate 0.5 mL/min, t_{R} 19.8 min (minor isomer) and 25.0 min (major isomer), detection at 254 nm).

Compound 6q: Yellow oil. IR (neat) ν 3027, 2934, 2859, 1647, 1489, 1453, 1068, 755, 690 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.55–1.60 (m, 1H), 1.68–1.88 (m, 3H), 1.92–1.97 (m, 1H), 2.08–2.24 (m, 2H), 3.32–3.38 (m, 1H), 3.86 (d, $J = 13.2$ Hz, 1H), 3.96 (d, $J = 13.2$ Hz, 1H), 6.32 (t, $J = 4.0$ Hz, 1H), 7.22–7.41 (m, 10H); ^{13}C NMR (CDCl_3): δ 18.8, 26.1, 28.1, 51.1, 54.2, 88.6, 89.5, 123.5, 124.0, 126.8, 127.9, 128.2 (x 2), 128.2 (x 2), 128.3 (x 2), 131.4 (x 2), 137.6, 140.8; FAB-LRMS m/z 288 (MH^+); $[\alpha]_{\text{D}}^{25} -24.5$ (c 0.78, CHCl_3 , 80% ee). The enantiomeric excess was determined by HPLC analysis

(DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/9, flow rate 0.5 mL/min, t_R 9.7 min (major isomer) and 21.0 min (minor isomer), detection at 254 nm).

Compound 8: (Mori et al. *J. Org. Chem.* **2004**, 69, 1837.)

Compound 10: Yellow oil. IR (neat) ν 2974, 2928, 1488, 1441, 1243, 1116, 1063, 1040, 937, 804 cm^{-1} ; ^1H NMR (CDCl_3): δ 1.07 (t, $J = 7.2$ Hz, 3H), 1.14 (t, $J = 7.2$ Hz, 3H), 1.55–1.63 (m, 2H), 1.68–1.88 (m, 3H), 2.06–2.22 (m, 2H), 2.61 (dd, $J = 6.4$ Hz, 12.0 Hz, 1H), 2.78 (dd, $J = 4.8$ Hz, 12.0 Hz, 1H), 3.37–3.48 (m, 2H), 3.54–3.62 (m, 3H), 4.49 (dd, $J = 4.8$ Hz, 6.4 Hz, 1H), 5.92 (d, $J = 5.2$ Hz, 1H), 5.93 (d, $J = 5.2$ Hz, 1H), 5.94 (t, $J = 4.0$ Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 6.85 (dd, $J = 1.6$ Hz, 8.0 Hz, 1H), 6.90 (d, $J = 1.6$ Hz, 1H); ^{13}C NMR (CDCl_3): δ 15.1, 15.2, 17.9, 26.0, 27.8, 49.6, 53.3, 61.8, 61.9, 100.8, 102.1, 106.8, 108.0, 119.4, 127.4, 135.6, 139.0, 146.4, 147.6; EI-LRMS m/z 333 (M^+); $[\alpha]_{\text{D}}^{21} -92.3$ (c 0.78, CHCl_3 , 97% ee (*S*)). The enantiomeric excess was determined by HPLC analysis (DAICEL CHIRALPAK AD, 2-propanol/hexane 5/95, flow rate 0.4 mL/min, t_R 17.1 min [(*S*)-isomer] and 33.8 min [(*R*)-isomer], detection at 254 nm). The absolute configuration was determined by comparing the measured optical rotation with the literature data, after conversion into compound **7** ($[\alpha]_{\text{D}}^{22} -97.8$ (c 1.42, CHCl_3 , 97% ee (*S*)), Literature data (Mori et al. *J. Org. Chem.* **2004**, 69, 1837.) $[\alpha]_{\text{D}}^{25} -85.7$ (c 0.58, CHCl_3 , 99% ee (*S*)).

^{13}C NMR Spectra for Purity Documentation. (S-10 ~ S-25)

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EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 24

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K-TM-08-18-13C

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OBSET 536.00 KHz
OBFIN 362.3 Hz
POINT 65536
FREQU 25188.9 Hz
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EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

S-10

DFILE E:\02\YKBT-2-6-BCM.NMF;1
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OBFTN 5500.0 Hz
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BF 1.20 Hz
RGAIN 24

5c.als
YK-TM-15-31-13C

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SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

S-11

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 FREQU 25188.9 Hz
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 PD 1.500 sec
 PW1 3.5 us
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 CTEMP 21.4 c
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 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 5d

:\\1\5e.als
 K-TM-14-22-13C

DFILE E:\\1\5e.als
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 POINT 65536
 FREQU 25188.9 Hz
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 CTEMP 22.5 c
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 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 5e

S 12

K-TM-13-39-13C

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 FREQU 25188.9 Hz
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 CTEMP 21.5 c
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 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 5f

\\1\5g.als
 K-TM-14-12-13C

DFILE E:\1\5g.als
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 FREQU 25188.9 Hz
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 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 21.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 5g

S-13

DFILE E:\1\5h.als
 COMNT YK-TM-14-38-13C
 DATIM 28-JAN-2005 19:27:28
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 137
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 21.5 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 5h

\\No.11\YK-TN-11-050723-5i-13C_1.als
 K-TN-11-050723-5i-13C

DFILE E:\\No.11\\YK-TN-11-050723
 COMNT YK-TN-11-050723-5i-13C
 DATIM 23-JUL-2005 14:09:29
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 361.1 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 50
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 22.9 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 28

¹³C of 5i

S-14

YK-TM-14-10-13C

DFILE E:\5j.als
 COMNT Yk-TM-14-10-13C
 DATIM 27-JAN-2005 20:03:41
 OBNUC 13C
 EXMOD single pulse dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 57
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 21.5 c
 SLVNT CDCL3
 EKREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

YK-TM-14-33-13C_1.als
 K-TM-14-33-13C

DFILE E:\YK-TM-14-33-13C_1.als
 COMNT YK-TM-14-33-13C
 DATIM 26-JAN-2005 20:51:27
 OBNUC 13C
 EXMOD single pulse dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 181
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 20.9 c
 SLVNT CDCL3
 EKREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

S-15

kya03-06-product-cabon

DFILE E:\03\51.als
COMNT ykya03-06-product-cabon
DATIM
OBNUC 13C
EXMOD SINGL-BCM
OBFREQ 100.40 MHz
OBSET 130.00 KHz
OBFIN 5500.0 Hz
POINT 32768
FREQU 27100.3 Hz
SCANS 128
ACQTM 1.209 sec
PD 3.700 sec
PW1 4.9 us
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23

¹³C of 51

E:\5m.als
KYA-PH-ETHYNYL-SUBST-CARBON

DFILE E:\5m.als
COMNT KYA-PH-ETHYNYL-SUBST-CARBON
DATIM
OBNUC 13C
EXMOD SINGL-BCM
OBFREQ 100.40 MHz
OBSET 130.00 KHz
OBFIN 5500.0 Hz
POINT 32768
FREQU 27100.3 Hz
SCANS 256
ACQTM 1.209 sec
PD 3.700 sec
PW1 4.9 us
IRNUC 1H
CTEMP 28.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23

¹³C of 5m

S-16

DFILE E:\03\6a.als
 COMNT YKYA03-26-PRO-CARBON
 DATIM
 OBNUC 13C
 EXMOD SINGL-BCM
 OBFRQ 100.40 MHz
 OBSET 130.00 KHz
 OBFIN 5500.0 Hz
 POINT 32768
 FREQU 27100.3 Hz
 SCANS 256
 ACQTM 1.209 sec
 PD 3.700 sec
 PW1 4.9 us
 IRNUC 1H
 CTEMP 28.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 23

:6b.als
 K-TM-11-25-13C

DFILE E:\6b.als
 COMNT YK-TM-11-25-13C
 DATIM 24-JAN-2005 20:49:40
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 101
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 20.9 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26

S-17

DFILE E:\1\6c.als
 COMNT YK-TM-15-19-13C
 DATIM 24-FEB-2005 21:11:03
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 134
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 22.3 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 6c

:\\6d.als
 K-TM-11-24-13C

DFILE E:\\6d.als
 COMNT YK-TM-11-24-13C
 DATIM 25-JAN-2005 17:43:04
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 280
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 20.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26

¹³C of 6d

S-18

DFILE E:\6e.als
COMNT YK-TM-12-14-13C
DATIM 25-JAN-2005 17:16:37
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.00 MHz
OBSET 536.00 KHz
OBFIN 362.3 Hz
POINT 65536
FREQU 25188.9 Hz
SCANS 101
ACQTM 2.602 sec
PD 1.500 sec
PW1 3.5 us
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 26

: \6f.als
KYA-5-MOR-CARB

DFILE E:\6f.als
COMNT KYA-5-MOR-CARB
DATIM
OBNUC 13C
EXMOD SINGL-BCM
OBFRQ 100.40 MHz
OBSET 130.00 KHz
OBFIN 5500.0 Hz
POINT 32768
FREQU 27100.3 Hz
SCANS 256
ACQTM 1.209 sec
PD 3.700 sec
PW1 4.9 us
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 23

5-19

DFILE E:\1\6g.als
 COMMT YK-TM-15-12-13C
 DATIM 27-JAN-2005 22:26:57
 OBNUC 13C
 EGMOD single_pulse dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 102
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTMP 21.4 c
 SLVNT CDCL3
 EKREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 6g

:\\6h.als
 K-TM-13-36-13C

DFILE E:\\6h.als
 COMMT YK-TM-13-36-13C
 DATIM 27-JAN-2005 19:35:45
 OBNUC 13C
 EGMOD single_pulse dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 155
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTMP 21.5 c
 SLVNT CDCL3
 EKREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 6h

5-20

DFILE E:\1\61.als
COMNT YK-TM-14-24-13C
DATIM 29-JAN-2005 17:26:28
OBNUC 13C
EXMOD single pulse dec
OBFRQ 100.00 MHz
OBSET 536.00 KHz
OBFIN 362.3 Hz
POINT 65536
FREQU 25188.9 Hz
SCANS 101
ACQTM 2.602 sec
PD 1.500 sec
PW1 3.5 us
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 26

E:\1\6j.als
K-TM-13-37-13C

DFILE E:\1\6j.als
COMNT YK-TM-13-37-13C
DATIM 28-JAN-2005 20:01:30
OBNUC 13C
EXMOD single pulse dec
OBFRQ 100.00 MHz
OBSET 536.00 KHz
OBFIN 362.3 Hz
POINT 65536
FREQU 25188.9 Hz
SCANS 178
ACQTM 2.602 sec
PD 1.500 sec
PW1 3.5 us
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

S-21

DFILE E:\6k.als
 COMNT YK-TM-14-15-13C
 DATIM 15-DEC-2004 12:04:14
 OBNUC 13C
 EXMOD single pulse dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 51
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 22.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 6k

DFILE E:\1\61.als
 COMNT YK-TM-14-39-13C
 DATIM 28-JAN-2005 20:12:32
 OBNUC 13C
 EXMOD single pulse dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 85
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 21.5 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

¹³C of 6l

S-22

R-TM-14-13-13C

DFILE E:\6m.als
 COMNT YK-TM-14-13-13C
 DATIM 16-DEC-2004 11:50:30
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 40
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 23.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26

:\\1\6n.als
 K-TM-14-16-13C

DFILE E:\\1\6n.als
 COMNT YK-TM-14-16-13C
 DATIM 29-JAN-2005 17:38:25
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 64
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 22.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26

S-23

DFILE E:\60.als
 COMNT YK-TM-14-33-13C
 DATIM 26-JAN-2005 20:51:27
 OBNUC 13C
 EXMOD single pulse dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 181
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 20.9 c
 SLVNT CDCL3
 EKREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

:\\03\\6p.als
 tyk03-03-purepro-carbon

DFILE E:\\03\\6p.als
 COMNT tyk03-03-purepro-carbon
 DATIM
 OBNUC 13C
 EXMOD SINGL-BCM
 OBFRQ 100.40 MHz
 OBSET 130.00 KHz
 OBFIN 5500.0 Hz
 POINT 32768
 FREQU 27100.3 Hz
 SCANS 128
 ACQTM 1.209 sec
 PD 3.700 sec
 PW1 4.9 us
 IRNUC 1H
 CTEMP 23.1 c
 SLVNT CDCL3
 EKREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 23

S-24

DFILE E:\03\6q.als
 COMNT YKYA03-27-PRO-CARBON
 DATIM
 OBNUC 13C
 EXMOD SINGL-BCM
 OBFRQ 100.40 MHz
 OBSET 130.00 KHz
 OBFIN 5500.0 Hz
 POINT 32768
 FREQU 27100.3 Hz
 SCANS 256
 ACQTM 1.209 sec
 PD 3.700 sec
 PW1 4.9 us
 IRNUC 1H
 CTEMP 28.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 23

E:\1\10.als
 K-TM-15-28-13C

DFILE E:\1\10.als
 COMNT YK-TM-15-28-13C
 DATIM 10-MAR-2005 20:29:34
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.00 MHz
 OBSET 536.00 KHz
 OBFIN 362.3 Hz
 POINT 65536
 FREQU 25188.9 Hz
 SCANS 80
 ACQTM 2.602 sec
 PD 1.500 sec
 PW1 3.5 us
 IRNUC 1H
 CTEMP 22.3 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 25

S-25