Supporting Information

Design and Synthesis of Chiral *N*-Chloro- Imidodicarbonates: Application to Asymmetric Chlorination of Silyl Enol Ethers

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Experimental

(1*S*,2*S*,3*S*,5*R*)-2,6,6-Trimethyl-bicyclo[3.1.1]heptan-3-chloroformate (5b): The title compound was obtained as a colorless oil in quantitative yield by following the same procedure of **5a** starting from (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheol **4b**. $[\alpha]_{\text{D}}^{25} +48.2$ (*c* 1.5, CH₂Cl₂); IR (KBr, cm⁻¹): 691, 843, 867, 1167, 1454, 1775 (CO), 2919; ¹H NMR (400 MHz, CDCl₃): δ 0.93 (s, 3H), 1.09 (d, *J* = 10.4 Hz, 1H), 1.16 (d, *J* = 7.2 Hz, 3H), 1.24 (s, 3H), 1.75-1.95 (m, 2H),

1.95-2.10 (m, 1H), 2.15-2.30 (m, 1H), 2.30-2.45 (m, 1H), 2.55-2.70 (m, 1H), 5.0-5.2 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.4, 23.8, 27.2, 33.2, 35.1, 38.1, 41.0, 43.3, 47.3, 83.8, 150.4.

(1*S*,2*R*,5*S*)-6,6-dimethyl-bicyclo[3.1.1]hept-2-yl-methyl chloroformate (5c): To a stirred solution of triphosgene (2.37 g, 7.98 mmol) in 30 mL of toluene was dropwise added a solution of pyridine (2.37 mL, 29.22 mmol) in 15 mL toluene at 0 °C under argon atmosphere. After stirring for 10 min at this temperature, a solution of (1*S*,2*R*,5*S*)-6,6-(-)-myrtanol **4c** (3.0 g, 19.5 mmol) in 45 mL of toluene was slowly added through a dropping funnel. The reaction mixture was allowed to come at ambient temperature and stirred. After 6h, 50 mL of water was added and extracted with toluene (2×50 mL). Combined organic layers were washed with water (50 mL), brine (50 mL), dried over Na_2SO_4 and evaporated under reduced pressure to afford the title compound as colorless oil in quantitative yield (4.14 g). This was directly used for the next step without further purification. $[\alpha]_{\text{D}}^{25}$ -12.37 (*c* 1.0, CH_2Cl_2); IR (KBr, cm^{-1}): 689, 770, 810, 846, 1143, 1470, 1778 (CO), 2919; ^1H NMR (400 MHz, CDCl_3): δ 0.86-1.10 (m, 1H), 0.99 (s, 3H), 1.20 (s, 3H), 1.40-1.51 (m, 1H), 1.82-2.10 (m, 5H), 2.30-2.43 (m, 1H), 2.43-2.52 (m, 1H), 4.20-4.32 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 17.1, 22.1, 24.6, 26.7, 31.7, 38.8, 40.0, 41.6, 75.3, 149.7.

(1*S*,2*S*,3*S*,5*R*)-2,6,6-trimethyl-bicyclo[3.1.1]hept-3-yl carbamate (6b): The title compound was obtained as a white solid in quantitative yield by following the same procedure of **6a**. mp 127-131 °C; $[\alpha]_{\text{D}}^{25}$ +40.41 (*c* 1.0, CH_2Cl_2); IR (KBr, cm^{-1}): 1052, 1359, 1387, 1606, 1690 (CO), 2909, 3449; ^1H NMR (400 MHz, CDCl_3): δ 0.96 (s, 3H), 1.03 (d, *J* = 10.0 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.22 (s, 3H), 1.65-1.75 (m, 1H), 1.75-1.85 (m, 1H), 1.85-1.95 (m, 1H), 1.95-2.15

(m, 1H), 2.25-2.45 (m, 1H), 2.45-2.70 (m, 1H), 4.55 (br s, 2H), 4.85-5.02 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.5, 23.7, 27.4, 33.5, 35.9, 38.2, 41.2, 43.7, 47.5, 74.8, 157.3; Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{NO}_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.87; H, 9.93; N, 6.95.

(1S,2R,5S)-6,6-dimethyl-bicyclo[3.1.1]hept-2-yl-methyl carbamate (6c): The title compound was obtained as a white solid in quantitative yield by following the same procedure of **6a**. mp 80-83 °C; $[\alpha]_{\text{D}}^{25}$ -11.42 (*c* 1.0, CH_2Cl_2); IR (KBr, cm^{-1}): 1059, 1344, 1404, 1641, 1703 (CO), 1729, 2924, 3443; ^1H NMR (200 MHz, CDCl_3): δ 0.92 (d, *J* = 9.6 Hz, 1H), 0.99 (s, 3H), 1.18 (s, 3H), 1.30-1.65 (m, 1H), 1.70-2.15 (m, 5H), 2.20-2.5 (m, 2H), 4.00 (d, *J* = 7.8 Hz, 2H), 4.61 (br s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 18.5, 23.2, 25.8, 27.9, 32.9, 38.5, 40.4, 41.2, 42.9, 69.5, 157.7; Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{NO}_2$: C, 69.97; H, 9.71; N, 7.10. Found: C, 70.18; H, 9.95; N, 6.93.

(1S,2S,3S,5R)-2,6,6-trimethyl-bicyclo[3.1.1]hept-3-yl imidodicarbonate OR imidodicarboxylic acid-(1S,2S,3S,5R)-2,6,6-trimethyl-bicyclo[3.1.1]hept-3-yl ester (1b): This compound was obtained as a gummy liquid in 20% yield by following the same procedure of **1a**. $[\alpha]_{\text{D}}^{25}$ +49.8 (*c* 0.7, CH_2Cl_2); IR (KBr, cm^{-1}): 1099, 1171, 1499, 1561, 1784 (CO), 2931, 3446; ^1H NMR (400 MHz, CDCl_3): δ 0.95 (s, 6H), 1.02 (d, *J* = 9.6 Hz, 2H), 1.12 (d, *J* = 7.6 Hz, 6H), 1.22 (s, 6H), 1.70-1.80 (m, 2H), 1.80-1.87 (m, 2H), 1.87-2.0 (m, 2H), 2.05-2.20 (m, 2H), 2.30-2.45 (m, 2H), 2.55-2.70 (m, 2H), 5.0-5.15 (m, 2H), 7.0 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.4 (2C), 23.8 (2C), 27.4 (2C), 33.4 (2C), 35.7 (2C), 38.2 (2C), 41.1 (2C), 43.6 (2C), 47.4 (2C), 76.3 (2C), 150.9 (2C); Anal. Calcd for $\text{C}_{22}\text{H}_{35}\text{NO}_4$: C, 69.99; H, 9.34; N, 3.71. Found: C, 70.15; H, 9.25; N, 3.82

(1*S*,2*R*,5*S*)-6,6-dimethyl-bicyclo [3.1.1]hept-2-ylmethyl imidodicarbonate OR imidodicarboxylic acid-(1*S*,2*R*,5*S*)-6,6-dimethyl-bicyclo[3.1.1]hept-2-ylmethyl ester (1c):

The title compound was prepared in 30% yield as a gummy liquid by following the same procedure of **1a**. $[\alpha]_D^{25}$ -9.29 (*c* 1.2, CH₂Cl₂); IR (KBr, cm⁻¹): 1096, 1193, 1530, 1714, 1730 (CO), 1781(CO), 2917; ¹H NMR (200 MHz, CDCl₃): δ 0.85-1.10 (m, 2H), 0.94 (s, 6H), 1.18 (s, 6H), 1.30-1.65 (m, 4H), 1.70-2.10 (m, 8H), 2.20-2.55 (m, 4H), 4.11 (d, *J* = 7.8 Hz, 4H), 6.95 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 18.3 (2C), 23.1 (2C), 25.7 (2C), 27.7 (2C), 32.8 (2C), 38.5 (2C), 40.1 (2C), 41.1 (2C), 42.7 (2C), 70.3 (2C), 150.9 (2C); Anal. Calcd for C₂₂H₃₉NO₄ + 0.5 H₂O: C, 68.36; H, 9.39; N, 3.62. Found: C, 68.42; N, 9.50; N, 3.51.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl imidotricarbonate OR (1*R*,2*S*,5*R*)-(-)-menthyl imidotricarbonate (7): White solid, mp 61-62 °C; $[\alpha]_D^{25}$ -62.77 (*c* 1.0, CH₂Cl₂); IR (KBr, cm⁻¹): 772, 950, 1095, 1273, 1735 (CO), 1768 (CO), 1812 (CO), 2957; ¹H NMR (400 MHz, CDCl₃): δ 0.75-0.95 (m, 3H), 0.79 (d, *J* = 6.8 Hz, 9H), 0.90 (d, *J* = 7.2 Hz, 9H), 0.92 (d, *J* = 6.8 Hz, 9H), 0.95-1.11 (m, 6H), 1.27-1.40 (m, 3H), 1.40-1.55 (m, 3H), 1.65-1.75 (m, 6H), 1.87-2.05 (m, 3H), 2.05-2.20 (m, 3H), 4.65-4.85 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 15.0 (3C), 19.8 (3C), 21.0 (3C), 22.0 (3C), 24.8 (3C), 30.3 (3C), 33.1 (3C), 39.3 (3C), 45.9 (3C), 77.7 (3C), 148.7 (3C); Calcd for C₃₃H₅₇NO₆: C, 70.30; H, 10.19; N, 2.48. Found: C, 70.19; H, 10.27; N, 2.39.

2-Chloro-3,4-dihydro-2H-naphthalen-1-one (9a):¹ The title compound was obtained in 88% yield according to the general procedure for chlorination of silyl enol ether. Light yellow oil; IR (KBr, cm⁻¹): 523, 618, 742, 802, 893, 1219, 1307, 1455, 1601, 1694 (CO), 2931; ¹H NMR (200

MHz, CDCl₃): δ 2.35-2.70 (m, 2H), 2.85-3.10 (m, 1H), 3.10-3.30 (m, 1H), 4.63 (dd, J = 4.0, 7.6 Hz, 1H), 7.15-7.40 (m, 2H), 7.52 (t, J = 7.5 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): δ 26.3, 32.4, 59.8, 127.1, 128.5, 128.7, 130.4, 134.1, 143.1, 190.8. Enantiomeric excess was determined to be 22% ee from TMS-enol ether **8a** and 4% ee from TBDMS-enol ether **8b** by HPLC analysis with a Chiracel OD-H column (4.6 mm ϕ ×150 mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210 nm.

2-Chloro-1-phenyl-pentan-1-one (9e): The title compound was obtained in 91% yield according to the general procedure for chlorination of silyl enol ether. Light yellow oil; IR (KBr, cm⁻¹): 688, 966, 1213, 1276, 1449, 1597, 1694 (CO), 2963; ¹H NMR (200 MHz, CDCl₃): δ 0.98 (t, J = 7.3 Hz, 3H), 1.35-1.70 (m, 2H), 1.85-2.20 (m, 2H), 5.13 (dd, J = 5.9, 7.9 Hz, 1H), 7.35-7.65 (m, 3H), 8.00 (dd, J = 1.6, 7.2 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 13.5, 19.4, 35.5, 57.5, 128.7 (2C), 128.8 (2C), 133.6, 134.5, 193.6. Enantiomeric excess was determined to be 32% ee by HPLC analysis with a Chiracel OD-H column (4.6 mm ϕ ×150 mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210 nm.

2-Chloro-1-(4-chloro-phenyl)-propan-1-one (9f): The title compound was obtained in 89% yield according to the general procedure for chlorination of silyl enol ether. Colorless oil; IR (KBr, cm⁻¹): 526, 771, 844, 955, 1093, 1249, 1402, 1489, 1591, 1695 (CO), 2984; ¹H NMR (200 MHz, CDCl₃): δ 1.74 (d, J = 6.7 Hz, 3H), 5.18 (q, J = 6.6 Hz, 1H), 7.47 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 19.7, 52.6, 129.0 (2C), 130.4 (2C), 132.4, 140.2, 192.4. Enantiomeric excess was determined to be 32% ee by HPLC analysis with a

Chiracel OD-H column (4.6 mm ϕ ×150 mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210 nm.

2-Chloro-1-(4-methoxy-phenyl)-propan-1-one (9g): The title compound was obtained in 81% yield according to the general procedure for chlorination of silyl enol ether. Colorless oil; IR (KBr, cm^{-1}): 613, 769, 844, 955, 1029, 1173, 1252, 1511, 1602, 1685 (CO), 2981; ^1H NMR (200 MHz, CDCl_3): δ 1.70 (d, J = 6.4 Hz, 3H), 5.22 (q, J = 6.6 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 8.00 (d, J = 8.9 Hz, 2H); ^{13}C NMR (50 MHz, CDCl_3): δ 19.9, 52.5, 55.3, 113.8 (2C), 126.6, 131.1 (2C), 163.8, 192.0. Enantiomeric excess was determined to be 20% ee by HPLC analysis with a Chiracel OD-H column (4.6 mm ϕ ×150 mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210 nm.

***tert*-butyl-(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl imidodicarbonate (10a):** To a stirred suspension of NaH (0.12 g, 60% in oil, 3.01 mmol) in dry THF (15 mL) under argon, was dropwise added a solution of carbamate **6a** (0.50 g, 2.51 mmol) in dry THF (15 mL) at 0 °C. The reaction mixture was slowly allowed to come at rt (25 °C) and stirred for 2 h. The reaction mixture was again cooled at 0 °C. A solution of BOC-anhydride (0.60 g, 2.76 mmol) in dry THF (15 mL) was rapidly added at 0 °C and stirred. After 15 min, the reaction was quenched with aqueous saturated NH_4Cl solution (15 mL). The reaction mixture was extracted with diethyl ether (4×15 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated to give the crude product **10a**. Flash chromatography over silica- gel column (diethyl ether: petroleum ether = 6:94) yielded 0.30 g (40%) as a gummy liquid. $[\alpha]_{\text{D}}^{33}$ -61.25 (c 0.4, CH_2Cl_2); IR (KBr, cm^{-1}): 777, 1096, 1154, 1369, 1527, 1711 (CO), 1719 (CO), 2956; ^1H NMR (200 MHz, CDCl_3): δ 0.77 (d, J = 7.0 Hz, 3H), 0.88 (d, J = 7.0 Hz,

3H), 0.89 (d, $J = 6.3$ Hz, 3H), 0.85-1.15 (m, 3H), 1.20-1.45(m, 2H), 1.48 (s, 9H), 1.55-1.75 (m, 2H), 1.75-2.15 (m, 2H), 4.65 (dt, $J = 4.4, 10.8$ Hz, 1H), 6.82 (br s 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 16.2, 20.7, 21.9, 23.2, 26.0, 27.9 (3C), 31.2, 34.0, 40.8, 46.9, 75.9, 82.2, 149.5, 150.6; Anal. Calcd for $\text{C}_{16}\text{H}_{29}\text{NO}_4$: C, 64.18; H, 9.76; N, 4.68. Found: C, 63.93; H, 9.57; N, 4.43.

***N*-acetyl carbamic acid-(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl ester (10b)**: Freshly distilled acetyl chloride (0.18 mL, 2.51 mmol) was added to a stirred solution of carbamate **6a** (0.50 g, 2.51 mmol) in dry toluene (5 mL) under argon. The resulting solution was stirred at 80 °C for 2 h. The reaction mixture was cooled to room temperature and quenched with saturated aqueous NaHCO_3 solution (10 mL). After extraction with diethyl ether (3×10 mL), the combined organic layers were washed with water (20 mL), brine (15 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the crude product. Flash chromatography over silica- gel column (diethyl ether: petroleum ether =10:90) yielded 0.46 g (75 %) of **10b** as a white solid. mp 91-92 °C; $[\alpha]_{\text{D}}^{33} -77.85$ (c 0.4, CH_2Cl_2); IR (KBr, cm^{-1}): 1012, 1163, 1229, 1508, 1702 (CO), 1753 (CO), 2958, 3291; ^1H NMR (200 MHz, CDCl_3): δ 0.77 (d, $J = 7.0$ Hz, 3H), 0.89 (d, $J = 7.0$ Hz, 3H), 0.91 (d, $J = 6.4$ Hz, 3H), 0.85-1.25 (m, 3H), 1.25-1.55 (m, 2H), 1.55-1.75 (m, 2H), 1.75-1.90 (m, 1H), 1.90-2.15 (m, 1H), 2.42 (s, 3H), 4.61 (dt, $J = 4.4, 10.8$ Hz, 1H), 7.47 (br s, 1H); ^{13}C NMR (50 MHz, CDCl_3): δ 16.3, 20.6, 21.9, 23.4, 24.0, 26.2, 31.3, 34.0, 40.8, 46.9, 76.6, 151.8, 172.4; Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_3$: C, 64.70; H, 9.61; N, 5.80. Found: C, 64.85; H, 9.70; N, 5.68.

(2,2-Dimethyl-propionyl)-carbamic acid-(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl ester (10c): To a stirred suspension of NaH (0.12 g 60 % in oil, 3.01 mmol) in dry THF (10 mL) under argon, was dropwise added a solution of carbamate **6a** (0.50 g, 2.51 mmol) and pivaloyl

chloride (0.34 mL, 2.76 mmol) in dry THF (10 mL) at 0 °C. The reaction mixture was stirred at rt (25 °C) for 9h and quenched with saturated aqueous NH₄Cl solution (10 mL). The product was extracted with diethyl ether (3×10 mL). Combined organic layers were washed with water (20 mL), brine (15 mL), dried over anhydrous Na₂SO₄ and evaporated to afford the crude product. Flash chromatography over silica-gel column (diethyl ether: petroleum ether = 14:86) gave pure 0.43 g of **10c** (60%) as a white solid. mp 75-80 °C; [α]_D³³ -71.18 (*c* 0.4, CH₂Cl₂); IR (KBr, cm⁻¹): 1012, 1164, 1229, 1508, 1701 (CO), 1753 (CO), 2958, 3290; ¹H NMR (200 MHz, CDCl₃): δ 0.78 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 6H), 0.5-1.40 (m, 3H), 1.23 (s, 9H), 1.45-1.75 (m, 4H), 1.75-1.95 (m, 1H), 1.95-2.15 (m, 1H), 4.69 (dt, *J* = 4.5, 10.9 Hz, 1H), 7.50 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 16.0, 20.5, 21.7, 23.0, 25.8, 26.8 (3C), 31.1, 33.8, 39.9, 40.6, 46.7, 76.1, 150.6, 175.0; Anal. Calcd for C₁₆H₂₉NO₃: C, 67.81; H, 10.31; N, 4.94. Found: C, 68.04; H, 10.73, N, 4.86.

***tert*-butyl-(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl-*N*-chloroimidodicarbonate (11a):**

The title compound was obtained as a gummy liquid by following the same procedure of **2a**. IR (KBr, cm⁻¹): 747, 1106, 1147, 1231, 1370, 1759 (CO), 2958; ¹H NMR (200 MHz, CDCl₃): δ 0.77 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.85-1.35 (m, 3H), 1.53 (s, 9H), 1.45-1.80 (m, 4H), 1.80-2.15 (m, 2H), 4.69 (dt, *J* = 4.4, 10.8 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): δ 16.0, 20.5, 21.7, 23.1, 25.9, 27.6 (3C), 31.2, 33.9, 40.4, 46.6, 79.5, 85.4, 149.4, 150.8.

***N*-acetyl-*N*-chloro carbamic acid-(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl ester (11b):**

The title compound was obtained as a gummy liquid by following the same procedure of **2a**. IR (KBr, cm⁻¹): 615, 753, 948, 1097, 1210, 1264, 1738 (CO), 2958; ¹H NMR (200 MHz, CDCl₃): δ

0.79 (d, $J = 7.0$ Hz, 3H), 0.92 (d, $J = 7.0$ Hz, 3H), 0.93 (d, $J = 6.4$ Hz, 3H), 0.85-1.35 (m, 3H), 1.35-1.8 (m, 4H), 1.80-2.05 (m, 1H), 2.05-2.17 (m, 1H), 2.59 (s, 3H), 4.69 (dt, $J = 4.4, 10.9$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3): δ 16.2, 20.6, 21.8, 23.3, 26.1, 26.2, 31.4, 33.9, 40.4, 46.8, 80.1, 151.8, 168.0.

***N*-chloro-(2,2-Dimethyl-propionyl)-carbamic acid-(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl ester (11c):** The title compound was obtained as a gummy liquid by following the same procedure of **2a**. IR (KBr, cm^{-1}): 952, 1078, 1262, 1460, 1483, 1739 (CO), 2958; ^1H NMR (200 MHz, CDCl_3): δ 0.78 (d, $J = 6.9$ Hz, 3H), 0.90 (d, $J = 6.9$ Hz, 3H), 0.92 (d, $J = 6.1$ Hz, 3H), 0.85-1.50 (m, 5H), 1.35 (s, 9H), 1.50-1.80 (m, 2H), 1.80-2.20 (m, 2H), 4.66 (dt, $J = 4.3, 10.8$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3): δ 16.1, 20.6, 21.8, 23.3, 26.1, 27.7 (3C), 31.3, 33.9, 40.4, 44.1, 46.9, 79.7, 153.9, 181.0.

References:

1. Zhang, Y.; Shibatomi, K.; Yamamoto, H. *J. Am. Chem. Soc.* **2004**, *126*, 15038-15039.

NMR Spectrum:

Compound 5a: ¹H-Spectra (CDCl₃, 400 MHz)

Compound 5a: ¹³C-Spectra (CDCl₃, 100 MHz)

Compound 5a: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 5b: ¹H-Spectra (CDCl₃, 400 MHz)

Compound 5b: ^{13}C -Spectra (CDCl_3 , 100 MHz)

Compound 5b: DEPT-135-Spectra (CDCl_3 , 100 MHz)

Compound 5c: ¹H-Spectra (CDCl₃, 400 MHz)

Compound 5c: ¹³C-Spectra (CDCl₃, 100 MHz)

Compound 6a: ¹H-Spectra (CDCl₃, 200 MHz)

Compound 6a: ¹³C-Spectra (CDCl₃, 50 MHz)

Compound 6a: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 6b: ¹H-Spectra (CDCl₃, 400 MHz)

Compound 6b: ^{13}C -Spectra (CDCl_3 , 100 MHz)

Compound 6b: DEPT-135-Spectra (CDCl_3 , 100 MHz)

Compound 6c: ^1H -Spectra (CDCl₃, 200 MHz)

Compound 6c: ^{13}C -Spectra (CDCl₃, 100 MHz)

Compound 1a: ^1H -Spectra (CDCl_3 , 200 MHz)

Compound 1a: ^{13}C -Spectra (CDCl_3 , 50 MHz)

Compound 1a: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 1b: ¹H-Spectra (CDCl₃, 400 MHz)

Compound 1c: ¹H-Spectra (CDCl₃, 200 MHz)

Compound 1c: ¹³C-Spectra (CDCl₃, 100 MHz)

Compound 7: ¹H-Spectra (CDCl₃, 400 MHz)

Compound 7: ¹³C-Spectra (CDCl₃, 100 MHz)

Compound 2a: ^1H -Spectra (CDCl₃, 200 MHz)

Compound 2a: ^{13}C -Spectra (C₆D₆, 100 MHz)

Compound 2a: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 10a: ¹H-Spectra (CDCl₃, 200 MHz)

Compound 10a: ^{13}C -Spectra (CDCl₃, 100 MHz)

Compound 10a: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 10b: ^1H -Spectra (CDCl₃, 200 MHz)

Compound 10b: ^{13}C -Spectra (CDCl₃, 50 MHz)

Compound 10b: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 10c: ¹H-Spectra (CDCl₃, 200 MHz)

Compound 10c: ^{13}C -Spectra (CDCl₃, 100 MHz)

Compound 10c: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 11a: ^1H -Spectra (CDCl₃, 200 MHz)

Compound 11a: ^{13}C -Spectra (CDCl₃, 50 MHz)

Compound 11b: ^{13}C -Spectra (CDCl₃, 50 MHz)

Compound 11b: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 11c: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 9a: ¹H-Spectra (CDCl₃, 200 MHz)

Compound 9a: ^{13}C -Spectra (CDCl_3 , 50 MHz)

Compound 9a: DEPT-135-Spectra (CDCl_3 , 100 MHz)

Compound 9c: ^1H -Spectra (CDCl₃, 200 MHz)

Compound 9c: ^{13}C -Spectra (CDCl₃, 50 MHz)

Compound 9c: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 9c: ¹H-Spectra (CDCl₃, 200 MHz)

Compound 9e: ^{13}C -Spectra (CDCl₃, 50 MHz)

Compound 9e: DEPT-135-Spectra (CDCl₃, 100 MHz)

Compound 9f: ^1H -Spectra (CDCl_3 , 200 MHz)

Compound 9f: ^{13}C -Spectra (CDCl_3 , 50 MHz)

Compound 9g: ^{13}C -Spectra (CDCl_3 , 50 MHz)

Compound 9g: DEPT-135-Spectra (CDCl_3 , 100 MHz)

HPLC-Chromatogram of 9a: Chiracel OD-H column(4.6mm ϕ $\times$ 150mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210nm

HPLC-Chromatogram of 9b, obtained from enol ether 8b: Chiracel OD-H column(4.6mm ϕ $\times$ 150mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210nm

HPLC-Chromatogram of 9c/9d: Chiracel OD-H column(4.6mm ϕ $\times$ 150mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210nm

HPLC-Chromatogram of 9e: Chiracel OD-H column(4.6mm ϕ $\times$ 150mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210nm

HPLC-Chromatogram of 9f: Chiracel OD-H column(4.6mm ϕ $\times$ 150mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210nm

HPLC-Chromatogram of 9g: Chiracel OD-H column(4.6mm ϕ $\times$ 150mm), 0.5% *i*-PrOH/hexanes (isocratic), 1mL/min, 210nm