

Supporting Information for our Manuscript titled

“First Example of Memory of Chirality in Carbenium Ion Chemistry” (No.ol005795T)

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The characterization data and/or HPLC traces for **6**, **7**, **8**, **9**, **10**, and **11** were described below.

(4S)-3-Benzoyl-2,2-dimethyloxazolidine-4-carboxylic acid (6): >99.9%ee; $[\alpha]_D^{21} -72.2$ (c 1.1, methanol); mp 118-123_ (uncorrected); $^1\text{H-NMR}$ (CDCl_3) δ 1.68 (br s, 3H), 1.80 (br s, 3H), 4.12-4.30 (m, 2H), 4.45 (br s, 1H), 7.39 (s, 5H); IR (neat) 3448, 2990, 1748, 1597, 1433, 1209, 841, 700 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.38; H, 5.91; N, 5.56.

Optical purity (**6**) was determined by CSP HPLC method; Daicel Chiralpak AD (0.46 cm ϕ x 25 cm), *n*-hexane/ethanol=9:1 containing 0.1% trifluoroacetic acid, wavelength: 210nm, flow rate: 1.0mL/min, retention time:11min for (*S*)-isomer, 13.5min for (*R*)-isomer.

3-Benzoyl-4-methoxy-2,2-dimethyloxazolidine (7): 39%ee; $[\alpha]_D^{26} -9.5$ (c 1.2, methanol); mp 99-101_ (uncorrected); $^1\text{H-NMR}$ (CDCl_3) δ 1.66 (s, 3H), 1.81 (s, 3H), 3.07 (s, 3H), 3.90 (dd, $J=5.0$ and 1.8Hz, 1H), 4.05 (d, $J=5.0$ Hz, 1H), 4.78 (d, $J=1.8$ Hz, 1H), 7.35-7.48 (m, 3H), 7.52-7.60 (m, 2H); IR (neat) 2984, 2830, 2361, 1640, 1397, 1076, 841 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.41; H, 7.36; N, 5.87.

Optical purity (**7**) were determined by CSP HPLC method; Daicel Chiralpak AD (0.46 cm ϕ x 25 cm), *n*-hexane/ethanol=15:1, wavelength : 210nm, flow rate: 1.0mL/min, retention time:9min_for (*R*)-**7**, 13min for (*S*)-**7**.

(4R,5R)-3-Benzoyl-2,2,5-trimethyloxazolidine-4-carboxylic acid (8): $[\alpha]_D^{20} -158.0$ (c 1.0, methanol); mp 162-163_ (uncorrected); $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ 1.36 (d, $J=4.9$ Hz, 3H), 1.60 (s, 3H), 1.67 (s, 3H), 4.10-4.24 (m, 2H), 7.33-7.46 (m, 5H); IR (neat) 2986, 2940, 1744, 1576, 1418, 1258 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.96; H, 6.48; N, 5.32.

(4R,5R)-3-Benzoyl-4-methoxy-2,2,5-trimethyloxazolidine ((4R,5R)-9): $[\alpha]_D^{23} -11.6$ (c 1.2, methanol); mp 71-72_ (uncorrected); $^1\text{H-NMR}$ (CDCl_3) δ 1.34 (d, $J=6.5$ Hz, 3H), 1.72 (s, 6H), 2.92 (s, 3H), 4.23 (qd, $J=6.6$ and 2.1Hz, 1H), 4.70 (br s, 1H), 7.35-7.52 (m, 5H); IR (neat) 2984, 2938, 2830, 1655, 1389, 1078 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.34; H, 7.66; N, 5.68.

(4S,5R)-3-Benzoyl-4-methoxy-2,2,5-trimethyloxazolidine ((4S,5R)-10): $[\alpha]_D^{22} +4.3$ (c 1.4, methanol); colorless oil; $^1\text{H-NMR}$ (CDCl_3) δ 1.30 (d, $J=6.3$ Hz, 3H), 1.67 (s, 3H), 1.79 (s, 3H), 2.98 (s, 3H), 4.17 (qd, $J=6.3$ and 3.0Hz, 1H), 4.67 (br s, 1H), 7.35-7.52 (m, 5H); IR (neat) 2984, 2938, 2836, 1647, 1391, 1078 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.68; H, 7.83; N, 5.64.

(4R,5S)-3-Benzoyl-2,2,5-trimethyloxazolidine-4-carboxylic acid (11): $[\alpha]_D^{20} -102.0$ (c 1.0, methanol); mp 168-171_ (uncorrected); $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ 1.12 (d, $J=5.1$ Hz, 3H), 1.61 (s, 3H), 1.80 (s, 3H), 4.22 (d, $J=6.2$ Hz, 1H), 4.49 (dq, $J=6.2$ and 5.1Hz, 1H), 7.25-7.50 (m, 5H); IR (neat) 2982, 2938, 1738, 1576, 1439, 1226, 1103, 746, 700 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.80; H, 6.44; N, 5.30.

(4S,5S)-3-Benzoyl-4-methoxy-2,2,5-trimethyloxazolidine ((4S,5S)-9): $[\alpha]_D^{23} +11.0$ (c 1.0, methanol); mp 70-72_ (uncorrected); $^1\text{H-NMR}$ (CDCl_3) δ 1.34 (d, $J=6.5$ Hz, 3H), 1.73 (s, 6H), 2.92 (s, 3H), 4.23 (qd, $J=6.6$ and 2.1Hz, 1H), 4.70 (br s, 1H), 7.35-7.52 (m, 5H); IR (neat) 2980, 2936, 2878, 1644, 1412, 1254, 1084 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.25; H, 7.69; N, 5.62.

(4R,5S)-3-Benzoyl-4-methoxy-2,2,5-trimethyloxazolidine ((4R,5S)-10): $[\alpha]_D^{24} -4.1$ (c 1.0, methanol); colorless oil; $^1\text{H-NMR}$ (CDCl_3) δ 1.30 (d, $J=6.3$ Hz, 3H), 1.67 (s, 3H), 1.79 (s, 3H), 2.98 (s, 3H), 4.17 (qd, $J=6.3$ and 3.0Hz, 1H), 4.67 (br s, 1H), 7.35-7.52 (m, 5H); IR (neat) 2984, 2938, 2836, 1651, 1391, 1076 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.15; H, 7.60; N, 5.60.

Diastereomeric ratio of **9/10** was determined by HPLC method; YMC-Pack SIL (0.46cm ϕ x 15cm), *n*-hexane/2-propanol=25:1, wavelength : 210nm, flow rate: 1.0mL/min, retention time: 5.2min for (4*R*,5*R*)-**9** and (4*S*,5*S*)-**9**, 7.1min for (4*S*,5*R*)-**10** and (4*R*,5*S*)-**10**.

Optical purity (**9** or **10**) could be determined by CSP HPLC method; Daicel Chiralpak AD (0.46cm ϕ x 25cm), *n*-hexane/ethanol=30:1, wavelength : 210nm, flow rate: 1.0mL/min, retention time: 8.0min for (4*R*,5*R*)-**9** , 8.8min for (4*R*,5*S*)-**10**, 11.6min for (4*S*,5*S*)-**9**, 12.3min for (4*S*,5*R*)-**10**.