Supplementary Information

Design of bifunctional quaternary phosphonium salt catalysts for CO₂ fixation reaction with epoxides under mild conditions

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General Information

1H, 13C, and 31P NMR spectra were measured on a JEOL JNM-AL 400 NMR instrument (400 MHz for 1H NMR, 100 MHz for 13C NMR, and 162 MHz for 31P NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for 1H NMR, and CDCl₃ served as the internal standard (77.0 ppm) for 13C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. High-resolution mass spectra (HRMS) were measured on JEOL JMS-700N and JMS-700. Infrared spectra (IR) were measured on a JASCO FT/IR-4200 spectrometer. Optical rotations were measured on a JASCO P-2100 polarimeter. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AT and SPD-20A instruments using Daicel Chiralpak AS-3 or ID-3 (4.6 mm × 250 mm) columns. All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by the use of UV lamp (254 nm), or dyes such as KMnO₄. The products were purified by flash column chromatography on silica gel. Dehydrated tetrahydrofuran was purchased from Kanto Chemical.
Experimental Section


1-1. General Procedure for the Synthesis of Catalysts 3 (o-3, m-3, p-3).

Compounds 3a (o-3a, m-3a, p-3a) were prepared according to the literature.\(^1\)

1-1-1. Synthesis of compounds 3b (o-3b, m-3b, p-3b).

To a solution of 3a (8.0 mmol) in THF (15 mL) was added sodium hydride (9.6 mmol, 60% oil suspension) at 0 °C, and stirred for 10 min. To this reaction mixture was added chloromethyl methyl ether (10.4 mmol) at 0 °C, and then the solution was warmed to room temperature. After stirred for 2 h at room temperature, the mixture was quenched with saturated aqueous NH\(_4\)Cl. After evaporation to remove THF, organic compounds were extracted with ethyl acetate (15 mL x 3). The combined organic layer was dried over Na\(_2\)SO\(_4\) and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 100:1–30:1 as eluent) to afford 3b (89–93% yields).

\(\text{CH}_3\text{OMOM}\)

**o-3b**: 91% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.32\) (dt, \(J = 2.0, 7.8\) Hz, 1H), 7.14–7.28 (m, 6H), 7.07 (dt, \(J = 0.8, 7.2\) Hz, 1H), 5.06 (s, 2H), 3.32 (s, 3H), 2.17 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.4, 138.6, 136.7, 132.0, 131.1, 130.0, 129.5, 128.5, 127.2, 125.3, 121.9, 115.3, 94.9, 55.9, 20.0; IR (neat): 2953, 2927, 2901, 1479, 1223, 1195, 1151, 1077, 1011, 992, 921, 754, 743, 726 cm\(^{-1}\); HRMS (FAB) calcd for C\(_{15}\)H\(_{16}\)O\(_2\): 228.1150 ([M\(^+\)], found 228.1151.

\(\text{CH}_3\text{OMOM}\)

**m-3b**: 89% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.32\) (t, \(J = 7.6\) Hz, 1H), 7.22–7.26 (m, 4H), 6.96–7.04 (m, 3H), 5.20 (s, 2H), 3.50 (s, 3H), 2.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 157.0, 143.4, 141.6, 135.2, 130.3, 129.6,
129.0, 127.3, 125.7, 122.8, 117.3, 114.5, 94.5, 55.9, 20.4; IR (neat): 2953, 2930, 2899, 1599, 1581, 1476, 1182, 1150, 1078, 1037, 1006, 989, 922, 756, 727, 703 cm⁻¹; HRMS (FAB) calcd for C₁₁H₁₂O₂: 229.1229 ([M+H⁺]), found 229.1227.

\[ \text{p-3b: 93% yield; } ^{1} \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.20–7.27 (m, 6H), 7.08 (d, } J = 8.8 \text{ Hz, } 2\text{H), 5.22 (s, } 2\text{H), 3.52 (s, } 3\text{H), 2.28 (s, } 3\text{H); } ^{13} \text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 156.2, 141.4, 135.5, 135.4, 130.24, 130.22, 129.8, 127.0, 125.7, 115.8, 94.5, 56.0, 20.5; IR (neat): 2952, 2929, 2898, 1611, 1514, 1482, 1230, 1150, 1077, 1010, 994, 836, 761, 731 \text{ cm}^{-1}; \text{HRMS (FAB) calcd for C}_{11}\text{H}_{12}\text{O}: 229.1229 ([M+H⁺]), found 229.1230. \]

1-1-2. Synthesis of compounds 3c (o-3c, m-3c, p-3c).

A mixture of 3b (5.0 mmol), N-bromosuccinimide (NBS) (5.5 mmol), and 2,2’-azobis(isobutyronitrile) (AIBN) (0.25 mmol) in benzene (20 mL) was heated at 80 °C for 3 h. After cooled to room temperature, water was added to this reaction mixture. Organic compounds were extracted with ethyl acetate (10 mL x 3). The combined organic layer was dried over Na₂SO₄ and concentrated. The residue was then dissolved in a combined solvent of dichloromethane (5 mL) and methanol (5 mL). To this solution was added p-toluenesulfonic acid monohydrate (5.0 mmol), and the mixture was heated at 45 °C for 3 h. After cooled to room temperature, water was added to this reaction mixture and the mixture was evaporated to remove methanol. Organic compounds were extracted with dichloromethane (10 mL x 3). The combined organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 30:1–10:1 as eluent) to afford 3c (73–76% yields).

\[ \text{o-3c: 76% yield; } ^{1} \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.60 (dd, } J = 2.0, 7.6 \text{ Hz, } 1\text{H), 7.38–7.46 (m, } 2\text{H), 7.26–7.35 (m, } 2\text{H), 7.22 (dd, } J = 1.6, 8.0 \text{ Hz, } 1\text{H), 7.00–7.04 (m, } 2\text{H), 4.70 (s, } 1\text{H), 4.44 (d, } J = 10.0 \text{ Hz, } 1\text{H), 4.32 (d, } J = 10.0 \text{ Hz, } 1\text{H); } ^{13} \text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 152.5, 137.2, 136.0, 131.2, 131.1, 130.3, 129.7, 129.1, 125.9, 120.6, 115.8, 31.4; IR (neat): 3512, 3428, 3060, 1475, 1443, 1220, 1198, 1177, 752 \text{ cm}^{-1}; \text{HRMS (FAB) calcd for C}_{13}\text{H}_{12}\text{BrO: 263.0072 ([M+H⁺]), found 263.0065.} \]
**m-3c**: 74% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.51–7.54 (m, 1H), 7.29–7.39 (m, 3H), 7.23–7.26 (m, 1H), 6.99–7.02 (m, 1H), 6.92–6.94 (m, 1H), 6.86–6.89 (m, 1H), 4.48 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.2, 141.7, 141.5, 135.0, 130.9, 130.2, 129.6, 128.5, 128.0, 121.6, 116.0, 114.5, 32.3; IR (neat): 3367, 3062, 1584, 1475, 1442, CBrO calcd for CDCl$_3$ Hz), 131.9, 130.3, 130.17

**p-3c**: 73% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.50–7.53 (m, 1H), 7.31–7.36 (m, 4H), 7.22–7.25 (m, 1H), 6.92 (d, $J$ = 8.8 Hz, 2H), 4.96 (br, 1H), 4.47 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 154.9, 141.6, 135.2, 132.7, 130.9, 130.5, 130.3, 128.5, 127.7, 115.2, 32.5; IR (neat): 3352, 3062, 3030, 1612, 1516, 1482, 1218, 1173, 835, 759 cm$^{-1}$; HRMS (FAB) calcd for C$_{13}$H$_{11}$BrO: 261.9993 ([M]$^+$), found 261.9992.

1-1-3. **Synthesis of catalysts 3 (o-3, m-3, p-3).**

A mixture of 3c (3.0 mmol) and triphenylphosphine (9.0 mmol) in toluene (10 mL) was heated at 110 °C for 12 h. After cooled to room temperature, the resulting white precipitate was collected by filtration. Although the collected compound 3 as a white solid was almost pure, the white solid 3 was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 30:1–10:1 as eluent) to afford 3 (86–89% yields).

**o-3**: 88% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.18 (s, 1H), 7.73–7.77 (m, 3H), 7.64 (d, $J$ = 8.0 Hz, 1H), 7.53–7.59 (m, 6H), 7.33 (t, $J$ = 7.6 Hz, 1H), 7.18–7.23 (m, 6H), 7.09–7.15 (m, 3H), 6.91 (d, $J$ = 8.0 Hz, 1H), 6.48 (t, $J$ = 7.6 Hz, 1H), 5.96 (d, $J$ = 8.0 Hz, 1H), 5.04–5.12 (m, 1H), 4.51–4.60 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 153.1, 140.9 (m), 134.9 (d, $J$ = 2.5 Hz), 133.6 (d, $J$ = 9.9 Hz), 131.9, 130.3, 130.17 (d, $J$ = 12.3 Hz), 130.15, 129.1, 129.0 (d, $J$ = 3.3 Hz), 127.7 (d, $J$ = 3.3 Hz), 126.2, 126.1, 119.7, 117.6 (m), 116.8, 116.7, 29.2 (d, $J$ = 48.6 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ = 21.1; IR (neat): 3057, 2991, 2964, 2196, 1437, 1109, 919, 720, 687 cm$^{-1}$; HRMS (FAB) calcd for C$_{31}$H$_{26}$OP: 445.1721 ([M]$^+$), found 445.1722.

**m-3**: 86% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.83 (s, 1H), 7.72–7.77 (m, 3H), 7.52–7.58 (m, 6H), 7.16–7.40 (m, 9H), 7.09 (t, $J$ = 7.6 Hz, 1H), 6.88–6.99
(m, 3H), 5.88 (dd, J = 1.0, 7.6 Hz, 1H), 5.20 (br, 2H); \(^{13}\)C NMR (100 MHz, CD\(_3\)OD): \(\delta =\) 159.0, 145.4, 142.2, 136.5, 135.2 (d, J = 9.9 Hz), 132.1 (m), 131.4 (d, J = 12.3 Hz), 131.0, 130.2, 129.2, 126.4 (m), 121.0, 119.2, 118.3, 117.1, 115.8, 29.2 (d, J = 47.8 Hz); \(^{31}\)P NMR (162 MHz, CD\(_3\)OD): \(\delta =\) 21.3; IR (neat): 3173, 3060, 2889, 2201, 1583, 1473, 1438, 1198, 1110, 917, 753, 725, 687 cm\(^{-1}\); HRMS (FAB) calcd for C\(_{31}\)H\(_{26}\)OP: 445.1721 ([M]\(^+\)), found 445.1722.

\(\text{p-3:} 89\% \text{ yield;} \quad ^1H \text{ NMR (400 MHz, CDCl}_3): \(\delta =\) 8.98 (s, 1H), 7.72–7.77 (m, 3H), 7.53–7.58 (m, 6H), 7.10–7.31 (m, 9H), 7.03 (d, J = 8.8 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.31 (d, J = 8.4 Hz, 2H), 5.02 (d, J = 14.4 Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta =\) 157.3, 144.0 (d, J = 5.8 Hz), 135.0 (d, J = 2.5 Hz), 133.8 (d, J = 9.9 Hz), 131.9 (m), 130.1 (d, J = 12.4 Hz), 129.6, 129.4, 128.8 (d, J = 3.3 Hz), 128.4 (d, J = 12.4 Hz), 127.5 (d, J = 3.3 Hz), 124.9 (d, J = 8.2 Hz), 117.4, 116.6, 116.4, 28.6 (d, J = 47.0 Hz); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta =\) 21.5; IR (neat): 3145, 3059, 2197, 1610, 1517, 1482, 1437, 1265, 1111, 917, 720, 687 cm\(^{-1}\); HRMS (FAB) calcd for C\(_{31}\)H\(_{26}\)OP: 445.1721 ([M]\(^+\)), found 445.1722.


Catalyst o-4 was synthesized from a known compound o-4a\(^2\) in a similar manner for the synthesis of catalysts 3.

o-4: 85\% yield; \(^1H \text{ NMR (400 MHz, CDCl}_3): \(\delta =\) 7.76–7.80 (m, 3H), 7.55–7.60 (m, 6H), 7.17–7.36 (m, 10H), 7.10 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.71 (t, J = 7.6 Hz, 1H), 6.04 (d, J = 7.2 Hz, 1H), 5.30–5.40 (m, 1H), 4.52 (dd, J = 14.4, 14.4 Hz, 1H), 3.71 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta =\) 155.7, 140.0 (d, J = 5.8 Hz), 135.0, 134.0 (d, J = 9.9 Hz), 131.4 (d, J = 3.3 Hz), 130.9 (m), 130.7, 130.2 (d, J = 13.1 Hz), 129.6, 128.8 (d, J = 3.2 Hz), 128.2 (d, J = 3.3 Hz), 126.5 (d, J = 9.0 Hz), 120.9, 117.8 (d, J = 5.8 Hz), 117.0 (d, J = 4.9 Hz), 111.0, 55.8, 29.5 (d, J = 46.9 Hz); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta =\) 21.6; IR (neat):
3055, 3006, 2963, 2836, 2173, 1481, 1436, 1263, 1231, 1110, 996, 923, 752, 722, 689 cm\(^{-1}\); HRMS (FAB) calcd for C\(_{32}\)H\(_{20}\)OP: 459.1878 ([M\(^+\)], found 459.1879.

1-3. Synthesis of catalyst \(\text{o-5}\).

Catalyst \(\text{o-3}\) was transformed into the corresponding phosphonium hydroxide by passing through an ion-exchange resin (amberlyst A26, OH\(^-\) form) in methanol. The resulting phosphonium hydroxid was then treated with HI (1.3 equiv, 55%) in methanol at room temperature. Solvent was removed and the residue was purified by flash column chromatography on silica gel (dichloromethane/methanol = 30:1–10:1 as eluent) to afford \(\text{o-5}\) (81% yield).

\(\text{o-5}\): \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 8.02 (br, 1H), 7.74–7.78 (m, 3H), 7.54–7.60 (m, 7H), 7.35 (t, \(J = 7.6\) Hz, 1H), 7.11–7.25 (m, 9H), 6.93 (d, \(J = 7.2\) Hz, 1H), 6.52 (t, \(J = 7.6\) Hz, 1H), 5.97 (d, \(J = 7.2\) Hz, 1H), 4.94–5.03 (m, 1H), 4.60–4.69 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 152.6, 140.6 (d, \(J = 5.8\) Hz), 135.1 (d, \(J = 2.4\) Hz), 133.8 (d, \(J = 9.9\) Hz), 131.9 (d, \(J = 3.3\) Hz), 130.3 (d, \(J = 12.4\) Hz), 129.3, 129.2 (d, \(J = 4.1\) Hz), 127.9 (d, \(J = 3.3\) Hz), 126.3, 126.2, 126.1, 120.2, 117.6 (d, \(J = 3.3\) Hz), 116.8, 29.3 (d, \(J = 48.6\) Hz); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) = 21.1; IR (neat): 3171, 3057, 2924, 2194, 1484, 1438, 1109, 916, 750, 722, 687 cm\(^{-1}\); HRMS (FAB) calcd for C\(_{31}\)H\(_{26}\)OP: 445.1721 ([M\(^+\)], found 445.1722.


Catalyst (S)-6 was synthesized from a known compound (S)-6\(_a\) \(^3\) in a similar manner for the synthesis of catalysts 3.
(S)-6b: 96% yield; [α]²⁵_D = −150.5 (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 8.05 (d, J = 8.4 Hz, 1H), 7.95 (t, J = 7.6 Hz, 2H), 7.89 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.52 (dt, J = 0.8, 7.6 Hz, 1H), 7.30–7.39 (m, 3H), 7.22–7.25 (m, 2H), 6.94 (d, J = 8.8 Hz, 1H), 4.76 (s, 1H), 4.38 (d, J = 10.0 Hz, 1H), 4.29 (d, J = 10.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 151.3, 136.5, 133.7, 133.5, 132.9, 130.5, 130.3, 130.0, 129.1, 128.24, 128.16, 127.9, 127.4, 127.1, 126.9, 126.1, 124.4, 123.7, 117.8, 115.7, 31.9; IR (neat): 3511, 3419, 3056, 1619, 1596, 1380, 1202, 1172, 1145, 1128, 907, 817, 748, 728 cm⁻¹; HRMS (FAB) calcd for C₂₁H₁₅BrO: 362.0306 ([M⁺]), found 362.0299.

(S)-6: 85% yield; [α]²⁶_D = −13.5 (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 8.89 (br, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.74–7.80 (m, 3H), 7.61–7.68 (m, 4H), 7.40–7.48 (m, 7H), 7.13–7.28 (m, 9H), 6.88–6.95 (m, 2H), 6.59 (d, J = 8.4 Hz, 1H), 4.57–4.69 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 136.2 (d, J = 7.4 Hz), 134.9 (d, J = 3.3 Hz), 133.6 (d, J = 9.9 Hz), 133.3, 133.2 (d, J = 2.5 Hz), 133.0 (d, J = 2.5 Hz), 130.1 (d, J = 12.3 Hz), 129.9, 128.3, 128.1 (m), 127.8, 127.3, 126.7, 126.53, 126.47, 124.8 (d, J = 8.3 Hz), 123.6, 122.6, 120.1, 117.6, 116.8, 115.4, 30.5 (d, J = 48.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ = 19.6; IR (neat): 3056, 2193, 1436, 1274, 1108, 920, 822, 727, 687 cm⁻¹; HRMS (FAB) calcd for C₃₉H₃₆OP: 545.2034 ([M⁺]), found 545.2033.

1-5. Synthesis of catalyst (S)-7.

Catalyst (S)-7 was synthesized from a known compound (S)-7a in a similar manner for the synthesis of catalysts 3.

(S)-7: 80% yield; [α]²⁵_D = −120.5 (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 8.03 (d, J = 9.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.68–7.75 (m, 4H), 7.43–7.53 (m, 7H), 7.19–7.33 (m, 9H), 7.15 (d, J = 9.2 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 4.80 (dd, J = 14.8, 15.2 Hz, 1H), 4.67 (dd, J = 14.8, 15.2 Hz, 1H), 3.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 154.5, 135.2 (d, J = 8.2 Hz), 135.0 (d, J = 3.3 Hz), 133.8 (d, J = 9.1 Hz), 133.0 (d, J = 2.4 Hz), 132.8 (m), 130.7, 130.1 (d,
\( J = 12.4 \text{ Hz})\), 128.7, 128.6 (d, \( J = 3.3 \text{ Hz})\), 128.4 (d, \( J = 2.5 \text{ Hz})\), 128.2, 128.0, 127.6, 126.6, 126.5, 126.3, 125.0 (d, \( J = 8.2 \text{ Hz})\), 123.9 (d, \( J = 6.8 \text{ Hz})\), 118.5, 117.8, 116.9, 113.2, 55.8, 30.0 (d, \( J = 48.6 \text{ Hz})\); \( ^{31}P \text{ NMR (162 MHz, CDCl}_3\)): \( \delta = 20.4 \); \( \text{IR (neat):} \ 3056, 2841, 2178, 1436, 1264, 1254, 1108, 1083, 921, 908, 816, 724 \text{ cm}^{-1}; \) HRMS (FAB) calcd for \( \text{C}_{40}\text{H}_{32}\text{OP}\): 559.2191 ([M]+), found 559.2193.

2. General Reaction Procedure.

2-1. General procedure for the reaction of styrene oxide 1a with \( \text{CO}_2 \) (Table 1).

To a mixture of styrene oxide 1a (2.0 mmol) and catalyst (0.020 mmol, 1 mol %) was added 1,3,5-trimethoxybenzene (0.10 mmol) as an internal standard. The reaction mixture was heated at 60 °C for 24 h under \( \text{CO}_2 \) atmosphere (1atm, using a balloon). After cooled to room temperature, the reaction solution (50 \( \mu \text{L})\) was added to an NMR tube, and diluted by CDCl\(_3\) (0.50 mL). The yield of a cyclic carbonate 2a was determined by \(^1H \text{ NMR analysis based on 1,3,5-trimethoxybenzene as an internal standard.}

2-2. General procedure for the reaction of epoxides 1 with \( \text{CO}_2 \) catalyzed by \( o\-5 \) (Table 2 and Scheme 4).

A mixture of epoxide 1 (2.0 mmol) and \( o\-5 \) (0.020 mmol, 1 mol %) was heated at 60 °C for 24 h under \( \text{CO}_2 \) atmosphere (1atm, using a balloon). After cooled to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1–3:1 as eluent) to afford cyclic carbonate 2.

2a:\(^5 \) Spectral data completely matched with reported data.\(^5 \) \( ^1\text{H NMR (400 MHz, CDCl}_3\)): \( \delta = 7.35–7.48 \) (m, 5H), 5.68 (dd, \( J = 7.6, 8.4 \text{ Hz, 1H})\), 4.81 (dd, \( J = 8.0, 8.8 \text{ Hz, 1H})\), 4.35 (dd, \( J = 8.0, 8.4 \text{ Hz, 1H})\); \( ^{13}C \text{ NMR (100 MHz, CDCl}_3\)): \( \delta = 154.8, 135.7, 129.6, 129.1, 125.8, 77.9, 71.1. \)

2b:\(^5 \) Spectral data completely matched with reported data.\(^5 \) \( ^1\text{H NMR (400 MHz, CDCl}_3\)): \( \delta = 7.34–7.39 \) (m, 2H), 7.12–7.17 (m, 2H), 5.67 (dd, \( J = 8.0, 8.4 \text{ Hz, 1H})\), 4.81 (dd, \( J = 8.4, 8.4 \text{ Hz, 1H})\), 4.33 (dd, \( J = 7.6, 8.8 \text{ Hz, 1H})\); \( ^{13}C \text{ NMR (100 MHz, CDCl}_3\)): \( \delta = 163.2 \) (d, \( J = 248 \text{ Hz})\), 154.6, 131.5 (d, \( J = 3.3 \text{ Hz})\), 128.0 (d, \( J = 8.3 \text{ Hz})\), 116.1 (d, \( J = 22.3 \text{ Hz})\), 77.3, 71.0.
2c: Spectral data completely matched with reported data.\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.43\) (d, \(J = 8.0\) Hz, 2H), 7.31 (d, \(J = 8.0\) Hz, 2H), 5.66 (dd, \(J = 7.6, 8.0\) Hz, 1H), 4.81 (dd, \(J = 8.0, 8.8\) Hz, 1H), 4.31 (dd, \(J = 7.6, 8.8\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.5, 135.5, 134.2, 129.3, 127.2, 77.2, 70.9\).

2d: Spectral data completely matched with reported data.\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 4.68–4.75\) (m, 1H), 4.53 (dd, \(J = 8.0, 8.4\) Hz, 1H), 4.07 (dd, \(J = 7.2, 8.4\) Hz, 1H), 1.77–1.86 (m, 1H), 1.62–1.71 (m, 1H), 1.36–1.57 (m, 2H), 0.99 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.0, 76.8, 69.3, 35.7, 17.6, 13.4\).

2e: Spectral data completely matched with reported data.\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.74–5.84\) (m, 1H), 5.04–5.13 (m, 2H), 4.69–4.77 (m, 1H), 4.53 (dd, \(J = 8.0, 8.8\) Hz, 1H), 4.07 (dd, \(J = 7.6, 8.4\) Hz, 1H), 2.14–2.32 (m, 2H), 1.90–1.99 (m, 1H), 1.73–1.83 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.8, 136.0, 115.9, 76.2, 69.1, 32.7, 28.4\).

2f: Spectral data completely matched with reported data.\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 4.93–4.99\) (m, 1H), 4.60 (dd, \(J = 8.4, 8.8\) Hz, 1H), 4.42 (dd, \(J = 6.0, 8.8\) Hz, 1H), 3.72–3.80 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.3, 74.3, 66.8, 43.9\).

2g: Spectral data completely matched with reported data.\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.31\) (t, \(J = 7.6\) Hz, 2H), 7.02 (t, \(J = 7.6\) Hz, 1H), 6.91 (d, \(J = 8.0\) Hz, 2H), 5.00–5.06 (m, 1H), 4.62 (dd, \(J = 8.4, 8.8\) Hz, 1H), 4.54 (dd, \(J = 6.0, 8.8\) Hz, 1H), 4.24 (dd, \(J = 4.0, 10.4\) Hz, 1H), 4.15 (dd, \(J = 4.0, 10.4\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 157.7, 154.7, 129.6, 121.9, 114.6, 74.1, 66.8, 66.2\).

2i: Spectral data completely matched with reported data.\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 4.52\) (d, \(J = 8.8\) Hz, 1H), 4.16 (d, \(J = 8.4\) Hz, 1H), 3.73 (d, \(J = 11.6\) Hz, 1H), 3.59 (d, \(J = 12.4\) Hz, 1H), 1.64 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 153.8, 81.7, 72.0, 48.2, 23.0\).
2-3. General procedure for the kinetic resolution of epoxides 1 with CO$_2$ catalyzed by (S)-6 or (S)-7 (Scheme 5).

A mixture of epoxide 1 (2.0 mmol) and (S)-6 or (S)-7 (0.020 mmol, 1 mol %) was heated at 50 °C for 12 h (or 20 h) under CO$_2$ atmosphere (1 atm, using a balloon). After cooled to room temperature, the reaction mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1–3:1 as eluent) to afford cyclic carbonate 2h with recovery of 1h.

Scheme 6

1h:[$\alpha$]$^D_{29}$ = +16.3 (c = 1.6, EtOH; 31% ee) [lit.$^{6a}$ [$\alpha$]$^{25}_D$ = +41.4 (c = 1.1, EtOH; 95% ee (S))], HPLC analysis: Daicel Chiralpak ID-3, haxane/2-propanol = 20:1, flow rate = 0.5 mL/min, 254 nm; retention time: 10.5 min (minor) and 11.3 min (major). Spectral data completely matched with reported data.$^6$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.27 (t, $J$ = 8.4 Hz, 4H), 7.05 (d, $J$ = 7.2 Hz, 4H), 6.98 (t, $J$ = 7.2 Hz, 2H), 3.97 (dd, $J$ = 4.0, 16.0 Hz, 1H), 3.87 (dd, $J$ = 4.4, 16.0 Hz, 1H), 3.22–3.26 (m, 1H), 2.79 (dd, $J$ = 3.6, 5.2 Hz, 1H), 2.57 (dd, $J$ = 3.2, 5.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 147.9, 129.3, 121.7, 121.0, 53.8, 50.3, 45.9.

2h:[$\alpha$]$^D_{29}$ = +16.3 (c = 1.6, EtOH; 31% ee) [lit.$^{6a}$ [$\alpha$]$^{25}_D$ = +41.4 (c = 1.1, EtOH; 95% ee (S))], HPLC analysis: Daicel Chiralpak AS-3, haxane/2-propanol = 3:1, flow rate = 0.5 mL/min, 254 nm; retention time: 39.1 min (minor) and 43.2 min (major). Spectral data completely matched with reported data.$^6$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.29 (t, $J$ = 8.8 Hz, 4H), 7.03 (t, $J$ = 7.2 Hz, 2H), 6.97 (d, $J$ = 7.2 Hz, 4H), 4.92–4.99 (m, 1H), 4.45 (dd, $J$ = 8.4, 8.8 Hz, 1H), 4.17 (dd, $J$ = 6.8, 8.8 Hz, 1H), 4.11 (dd, $J$ = 6.0, 15.6 Hz, 1H), 4.01 (dd, $J$ = 6.0, 15.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 154.4, 147.4, 129.5, 122.4, 121.0, 74.5, 67.3, 54.1.

1j: HPLC analysis: Daicel Chiralpak IC-3, haxane/2-propanol = 10:1, flow rate = 0.5 mL/min, 254 nm; retention time: 12.7 min (minor) and 14.0 min (major). Spectral data completely matched with reported data.$^6$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.23–7.38 (m, 10H), 5.46 (s, 1H), 3.74 (dd, $J$ = 2.8, 11.2 Hz, 1H), 3.46 (dd, $J$ = 5.6, 11.6 Hz, 1H), 3.20–3.24 (m, 1H), 2.79 (dd, $J$ = 4.4, 4.8 Hz, 1H), 2.61 (dd, $J$ = 2.8, 5.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 141.84, 141.76, 128.4, 127.6, 127.5, 127.0, 126.9, 83.9, 69.5, 50.9, 44.4.
2j: HPLC analysis: Daicel Chiralpak IB-3, haxane/2-propanol = 3:1, flow rate = 0.5 mL/min, 254 nm; retention time: 24.7 min (minor) and 29.3 min (major). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.25–7.37 (m, 10H), 5.42 (s, 1H), 4.82–4.87 (m, 1H), 4.51 (dd, $J$ = 8.4, 8.4 Hz, 1H), 4.44 (dd, $J$ = 5.8, 8.2 Hz, 1H), 3.74 (dd, $J$ = 4.0, 10.8 Hz, 1H), 3.61 (dd, $J$ = 3.4, 11.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.0, 141.1, 141.0, 128.5, 128.4, 127.73, 127.66, 126.7, 126.6, 84.1, 74.9, 67.7, 66.2; IR (neat): 3062, 3029, 2919, 2868, 1791, 1493, 1453, 1389, 1165, 1125, 1103, 1087, 1040, 1027, 742, 697 cm$^{-1}$; HRMS (EI) calcd for C$_{17}$H$_{16}$O$_4$: 284.1049 ([M]$^+$), found 284.1048.

3. Determination of Absolute Configurations of 1h and 2h.

The absolute configuration of major stereoisomer of 1h was confirmed by comparison of the optical rotation with the literature value.$^{6a}$ 1h: $[\alpha]^{20}_D$ = +16.3 ($c$ = 1.6, EtOH; 31% ee) [lit.$^{6a}$ $[\alpha]^{25}_D$ = +41.4 ($c$ = 1.1, EtOH; 95% ee ($S$))]. Based on the configuration of 1h, absolute configuration of major stereoisomer of 2h was determined as R.
4. X-ray diffraction analysis of catalyst o-3.

Catalyst o-3 was recrystallized from chloroform/hexane. Data of X-ray diffraction were collected by a Rigaku Varimax Saturn724+ diffractometer using multi-layer mirror monochromated MoKα (λ = 0.71075 Å) radiation. The structure was solved by direct methods and expanded using Fourier techniques. Some hydrogen atoms were refined isotropically and the rest were refined using the riding model.

The crystallographic data of o-3·CHCl₃ were summarized in the following table.

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The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1480807). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request/cif.
References


HPLC charts
S-25