HETEROCYCLES, Vol. 103, No. 2, 2021, pp. 1011 - 1022. © 2021 The Japan Institute of Heterocyclic Chemistry
Received, 31st October, 2020, Accepted, 4th December, 2020, Published online, 18th December, 2020
DOI: 10.3987/COM-20-S(K)42

CATALYTIC ASYMMETRIC RING-OPENING OF σ-SYMMETRIC CYCLIC CARBONATES WITH CHIRAL AMINO SULFONAMIDE CATALYSTS

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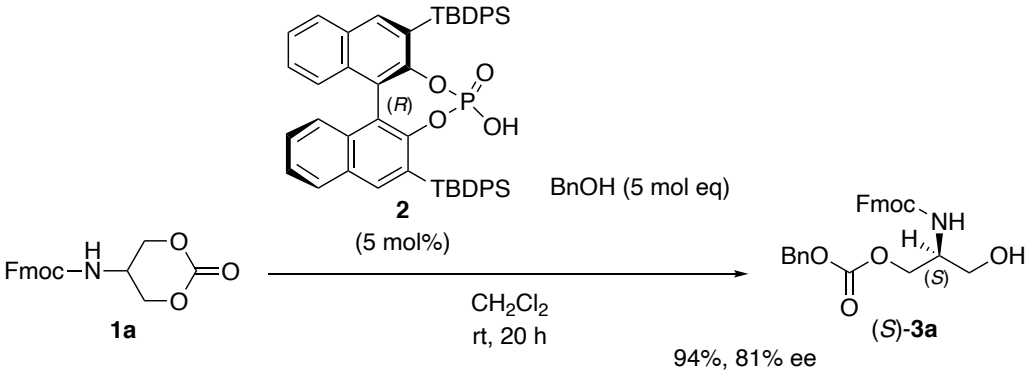
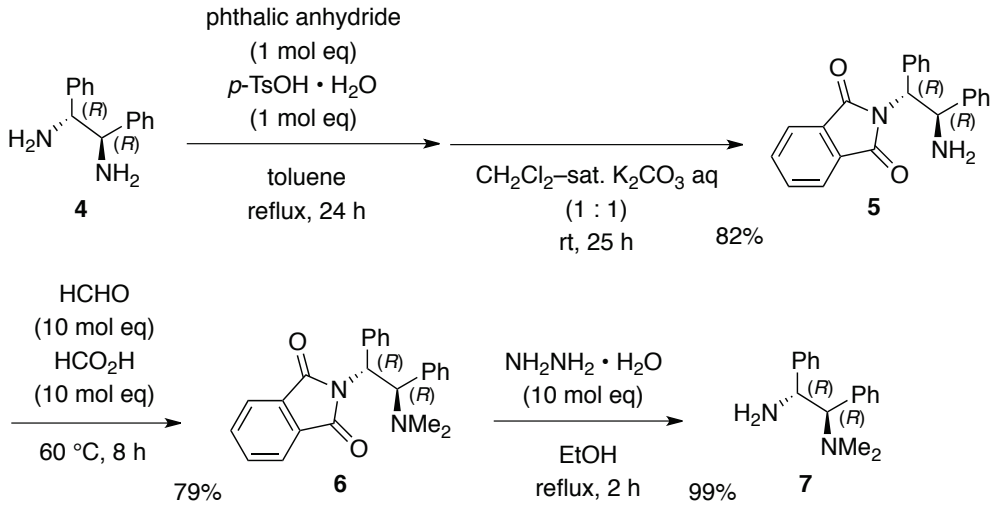
Abstract – Enantioselective ring-opening of σ-symmetric six-membered cyclic carbonates with benzyl alcohol catalyzed by 20 mol% of chiral amino sulfonamide catalysts afforded chiral acyclic carbonates in up to 79% ee.

Catalytic asymmetric desymmetrization is a general and convenient strategy for asymmetric synthesis.[1–7] We have developed several enzymatic or nonenzymatic catalytic asymmetric desymmetrizations of σ-symmetric compounds, such as 1,3-diesters,[8–10] cyclic anhydrides,[11–13] 1,3-diols,[10,14–17] and cyclic carbonates.[18] In the desymmetrization of σ-symmetric six-membered cyclic carbonate **1a**, a catalytic amount of BINOL-based phosphoric acid **2** was used as a chiral Brønsted acid catalyst. As a result, asymmetric ring-opening of **1a** with **2** afforded the acyclic carbonate (*S*)-**3a** in 94% yield with 81% ee as shown in Scheme 1.[19]

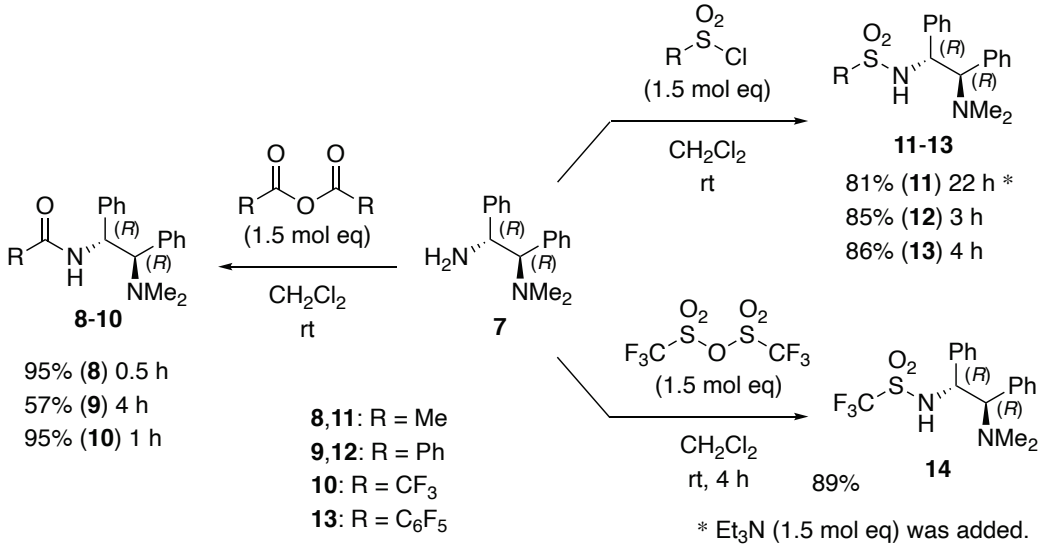


Scheme 1. Catalytic asymmetric ring-opening of σ-symmetric cyclic carbonate **1a** with chiral Brønsted acid catalyst **2**

Our interest in the asymmetric ring-opening of σ-symmetric cyclic carbonates led us to investigate amino sulfonamide catalysts obtained from the readily available chiral 1,2-diphenylethane-1,2-diamine. We here describe the first example of the use of chiral amino sulfonamide in the catalytic asymmetric ring-opening of σ-symmetric six-membered cyclic carbonates.



Scheme 2. Synthesis of chiral diamine **7**

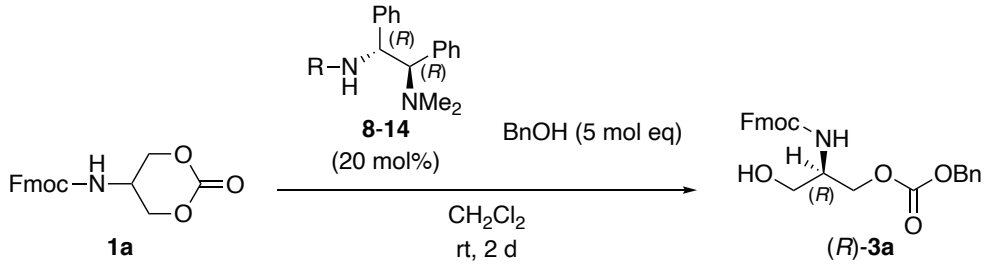


Scheme 3. Synthesis of chiral amine catalysts **8**–**14**

Chiral amino amides **8**–**10** and amino sulfonamides **11**–**14** were synthesized starting from (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (**4**). First, diamine **7** was synthesized as shown in Scheme 2.[20] (1*R*,2*R*)-1,2-Diphenylethane-1,2-diamine (**4**) was treated with phthalic anhydride in the presence of *p*-TsOH•H_2O to afford phthalimide **5**. Reductive amination of **5** using formaldehyde and formic acid gave

dimethylamine **6**. Then, deprotection of **6** with an excess amount of hydrazine monohydrate provided chiral diamine **7**. Conversion of **7** into chiral catalysts **8**–**14** was performed as shown in Scheme 3. Reaction of **7** with carboxylic anhydrides afforded chiral amino amide catalysts **8**–**10**, whereas reaction with sulfonyl chlorides or sulfonic anhydride provided chiral amino sulfonamide catalysts **11**–**14**.

We investigated catalytic asymmetric ring-opening of σ-symmetric cyclic carbonate **1a** bearing a Fmoc-amino group at the prochiral center with 5 equivalent of benzyl alcohol in the presence of 20 mol% of chiral catalysts **8**–**14** as shown in Table 1. The reaction of cyclic carbonate **1a** with chiral amino amide catalysts **8**–**10** in CH_2Cl_2 at room temperature for 2 d afforded the acyclic carbonate (*R*)-**3a** in 41–87% yields with 7–21% ee (Table 1, entries 1–3). On the other hand, in the presence of chiral amino sulfonamide catalysts **11**–**13**, the acyclic carbonate (*R*)-**3a** was obtained with higher enantioselectivities in the range of 64–69% ee than by the reaction with chiral amino amide catalysts **8**–**10** (Table 1, entries 4–6). However, chiral amino sulfonamide catalyst **14** with a trifluoromethylsulfonyl moiety gave (*R*)-**3a** in 42% yield with 37% ee (Table 1, entry 7). The enantiomeric excess values of acyclic carbonate (*R*)-**3a** were determined by means of HPLC analysis using a chiral stationary phase (CSP).

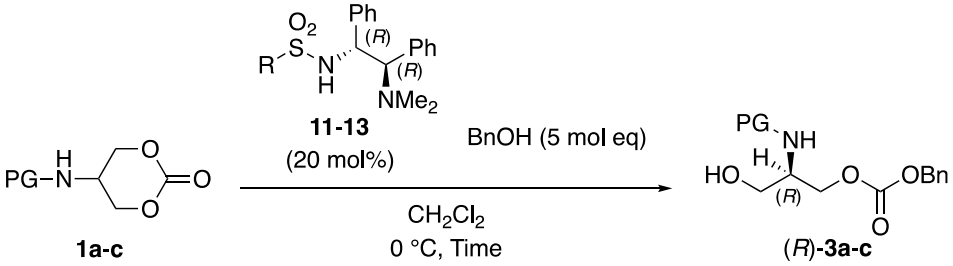


Entry	Catalyst	R	Yield (%) [a]	ee (%) [b]
1	**8**	COMe	87	21
2	**9**	COPh	75	21
3	**10**	$COCF_3$	41	7
4	**11**	SO_2Me	41	69
5	**12**	SO_2Ph	72	66
6	**13**	$SO_2C_6F_5$	99	64
7	**14**	SO_2CF_3	42	37

a) Isolated yields.
b) Determined by HPLC (CHIRALPAK AD-H, *n*-hexane/EtOH = 1 : 1, 1.0 mL/min, 254 nm) analysis.

Table 1. Catalytic asymmetric ring-opening of σ-symmetric cyclic carbonate **1a** with chiral amino amides catalysts **8**–**10** and amino sulfonamides catalysts **11**–**14**

In order to improve the enantioselectivity of (*R*)-**3a**, the ring-opening of cyclic carbonate **1a** catalyzed by chiral amino sulfonamide catalysts **11**–**13** was investigated at 0 °C as shown in Table 2. Compared to the result at room temperature (Table 1, entries 4–6), (*R*)-**3a** was obtained in relatively lower yield (12–26%) but with higher enantioselectivity (71–75% ee) in the reaction of cyclic carbonates **1a** using chiral amino sulfonamide catalysts **11**–**13** (Table 2, entries 1–3). Then, the reaction time was prolonged to enhance the yield of (*R*)-**3a**. As a result, the yield of (*R*)-**3a** was improved up to 75% without loss of enantioselectivity in the reaction catalyzed by chiral amino sulfonamide catalyst **11** (Table 2, entries 4 and 5). In the case of σ-symmetric cyclic carbonates **1b** and **1c**, which bear different protective groups (Cbz and Boc), the ring-opening reaction furnished (*R*)-**3b** (61% yield, 79% ee) and (*R*)-**3c** (59% yield, 74% ee), respectively (Table 2, entries 6 and 7).



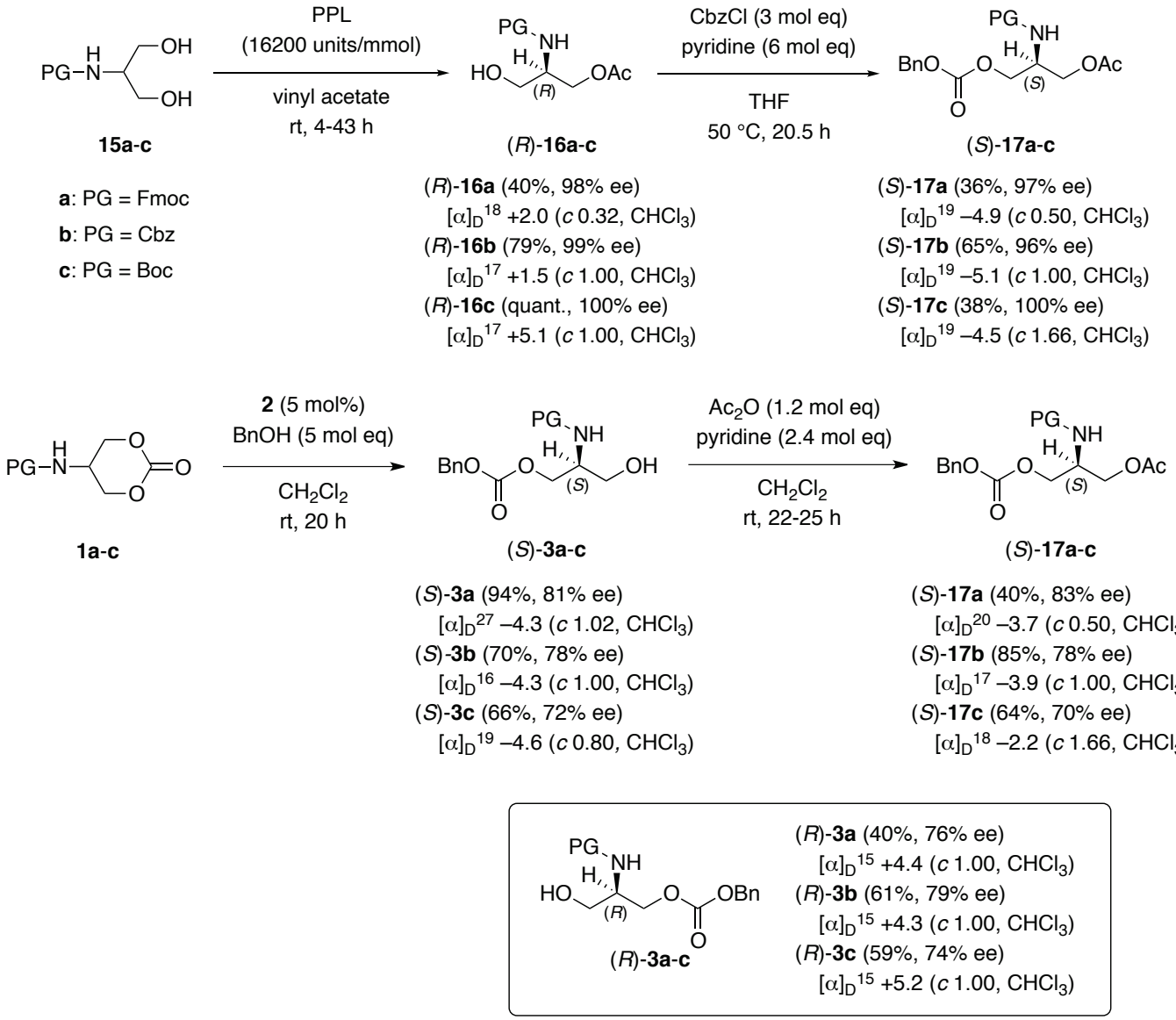
Entry	1	R	11-13	R	Time (d)	Yield (%) [a]	ee (%) [b]
1	**1a**	Fmoc	**11**	Me	2	12 [(*R*)-**3a**]	75
2	**1a**	Fmoc	**12**	Ph	2	18 [(*R*)-**3a**]	71
3	**1a**	Fmoc	**13**	C_6F_5	2	26 [(*R*)-**3a**]	72
4	**1a**	Fmoc	**11**	Me	5	40 [(*R*)-**3a**]	76
5	**1a**	Fmoc	**11**	Me	7	75 [(*R*)-**3a**]	75
6	**1b**	Cbz	**11**	Me	7	61 [(*R*)-**3b**]	79
7	**1c**	Boc	**11**	Me	7	59 [(*R*)-**3c**]	74

a) Isolated yields.
b) Determined by HPLC analysis.

Table 2. Catalytic asymmetric ring-opening of σ-symmetric cyclic carbonates **1a**–**c** with chiral amino sulfonamide catalysts **11**–**13**

The absolute configurations of acyclic carbonates (*R*)-**3a**–**c** were determined by their chemical conversion to the known chiral compounds and comparison of their specific rotations (Scheme 4). Based on the data in the literature,[21] PPL (porcine pancreatic lipase)-catalyzed desymmetrizations of *N*-protected serinols **15a**–**c** with vinyl acetate afforded chiral monoacetates (*R*)-(+)-**16a**–**c**. Treatment of (*R*)-(+)-**16a**–**c** with CbzCl in the presence of pyridine furnished acyclic carbonates (*S*)-(–)-**17a**–**c**. On the other hand, acyclic

carbonates (–)-**3a**–**c**, obtained by the asymmetric ring-opening of **1a**–**c** with BINOL-based chiral phosphoric acid **2**,[18] was acetylated with acetic anhydride in the presence of pyridine. As a result, (–)-**17a**–**c** were obtained and the absolute configuration was determined to be *S* by comparison of the observed sign of their specific rotations to the sign of the above-mentioned (*S*)-(–)-**17a**–**c**. Therefore, the absolute configurations of (–)-**3a**–**c** were determined to be *S* by the chemical correlation. Consequently, the absolute configurations of (+)-**3a**–**c**, which were obtained as the major enantiomers in the asymmetric ring-opening catalyzed by chiral amino amide catalysts **8**–**10** and chiral amino sulfonamide catalysts **11**–**14**, were established to be *R*.



Scheme 4. Determination of the absolute configurations of acyclic carbonates **3a**–**c**

Although the mechanistic details of the asymmetric ring-opening of σ-symmetric cyclic carbonates **1a**–**c** are unclear, it is reasonable to assume that the chiral amino sulfonamide catalyst **11** activates cyclic

carbonates **1a**–**c** and benzyl alcohol simultaneously in the first step (**A**),[11,12] as shown in Figure 1. The asymmetric ring opening (**B**)[18] induced by enantioselective activation of one of the ether oxygens would yield chiral (*R*)-**3a**–**c**.

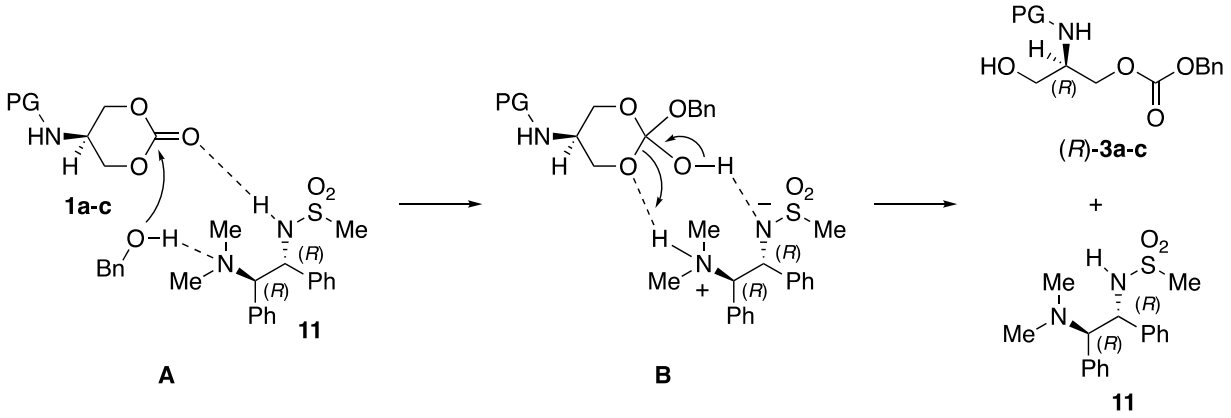


Figure 1. A plausible activation mode for the catalytic asymmetric ring-opening of σ-symmetric cyclic carbonates **1a**–**c** with chiral amino sulfonamide catalyst **11**

In conclusion, a novel approach to the catalytic asymmetric ring-opening of σ-symmetric cyclic carbonates **1a**–**c** in the presence of chiral amino sulfonamide catalysts **11**–**14** is presented. Further investigations to elucidate the mechanism of the asymmetric desymmetrization of cyclic carbonates are currently under way in our labolatory.

EXPERIMENTAL

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained with a JASCO FT/IR-6200 IR Fourier transform spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded with a Bruker AV500 spectrometer. Chemical shifts are given in δ values (ppm) using TMS as an internal standard. HRMS (ESI) data were recorded with a Waters LCT Premier spectrometer. Elemental combustion analyses were performed with a J-SCIENCE LAB JM10. Optical rotations were recorded with a JASCO digital polarimeter P-2200. All reactions were monitored by TLC employing 0.25 mm silica gel plates (Merck 5715; 60 F_{254}). Column chromatography was carried out on silica gel [Silica Gel 60N (Kanto Chemical) or Silica Gel PSQ 60B (Fuji Silysia Chemical)]. Chiral-stationary-phase HPLC analyses were performed using a JASCO PU-980 or PU-2080 apparatus equipped with a JASCO UV/VIS detector. Anhydrous CH_2Cl_2 was used as purchased from Kanto Chemical. All other reagents were used as purchased.

2-[(1*R*,2*R*)-2-Amino-1,2-diphenylethyl]isoindoline-1,3-dione (5)[22]

To a solution of **4** (2.00 g, 9.42 mmol) and phthalic anhydride (1.40 g, 9.42 mmol) in anhydrous toluene (9.4 mL) was added *p*-toluenesulfonic acid monohydrate (1.80 g, 9.42 mmol) at rt. After being refluxed for 24 h, the reaction mixture was cooled to rt and filtered. The resultant solid was washed with toluene (60 mL) and *n*-hexane (60 mL). Then, the solid was dissolved in CH_2Cl_2 (60 mL) and sat. K_2CO_3 aq (60 mL) was added and stirred at rt for 25 h. The reaction mixture was separated and the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography [Silica Gel PSQ 60B: $CHCl_3$–MeOH (20:1)] to afford **5** (2.65 g, 82%).

White solid; mp 130–132 °C; $[\alpha]_D^{19}$ +97.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.64 (brs, 2H), 5.32 (d, *J* = 11.0 Hz, 1H), 5.41 (d, *J* = 11.0 Hz, 1H), 7.09–7.17 (m, 4H), 7.17–7.23 (m, 2H), 7.25–7.29 (m, 2H), 7.37–7.41 (m, 2H), 7.68–7.73 (m, 2H), 7.82–7.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.0, 62.9, 123.3, 127.3, 127.4, 127.7, 128.3, 128.4, 129.1, 131.9, 134.0, 137.9, 143.0, 168.9; IR (KBr) 3061, 3031, 1765, 1707, 719, 698 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{18}N_2O_2Na$: 365.1266; found: 365.1236. Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.14; H, 5.35; N, 8.19%.

2-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]isoindoline-1,3-dione (6)

A mixture of **5** (1.50 g, 4.38 mmol), formaldehyde solution (37%, 3.6 mL, 43.8 mmol), and formic acid (1.7 mL, 43.8 mmol) was stirred at 60 °C for 8 h. After cooling the reaction mixture to rt, sat. $NaHCO_3$ aq (13 mL) was added and then extracted with $CHCl_3$ (3 x 13 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography [Silica Gel PSQ 60B: *n*-hexane–AcOEt (3:1)] to afford **6** (1.28 g, 79%).

Pale yellow solid; mp 210–212 °C; $[\alpha]_D^{19}$ –111.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (s, 6H), 5.21 (d, *J* = 12.3 Hz, 1H), 5.97 (d, *J* = 12.3 Hz, 1H), 7.05–7.10 (m, 1H), 7.13–7.18 (m, 3H), 7.18–7.28 (m, 4H), 7.52–7.55 (m, 2H), 7.66–7.71 (m, 2H), 7.83 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.8, 54.9, 65.9, 123.1, 127.2, 127.6, 127.7, 128.3, 129.6, 132.7, 133.7, 137.5, 168.6; IR (KBr) 2970, 1764, 1710, 717, 701 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{22}N_2O_2Na$: 393.1579; found: 393.1574. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.83; H, 6.06; N, 7.49%.

(1*R*,2*R*)-N^1,N^1-Dimethyl-1,2-diphenylethane-1,2-diamine (7)

To a solution of **6** (1.27 g, 3.43 mmol) in EtOH (6.8 mL) was added hydrazine monohydrate (80%, 2.10 mL, 34.3 mmol) at rt. After being refluxed for 2 h, the reaction mixture was cooled to rt and Et_2O (100 mL) was added and filtered. The filtrate was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to afford **7** (815 mg, 99%).

White solid; mp 41–43 °C; $[\alpha]_D^{19}$ +50.1 (*c* 1.00, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (brs, 2H), 2.22 (s, 6H), 3.64 (d, *J* = 10.5 Hz, 1H), 4.44 (d, *J* = 10.5 Hz, 1H), 6.97–7.01 (m, 2H), 7.02–7.07 (m, 1H), 7.08–7.13 (m, 3H), 7.14–7.18 (m, 2H), 7.20–7.24 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.9, 55.6, 75.2, 126.81, 126.84, 127.3, 127.96, 128.04, 129.8, 133.8, 143.3; IR (KBr) 3388, 3315, 2965, 752, 707 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{20}N_2Na$: 263.1524; found: 263.1532.

***N*-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]acetamide (8)**

To a solution of **7** (70.6 mg, 0.294 mmol) in anhydrous CH_2Cl_2 (1 mL) was added acetic anhydride (42 μL, 0.441 mmol) at rt under an argon atmosphere. After stirring for 0.5 h, sat. $NaHCO_3$ aq (13 mL) was added and then extracted with $CHCl_3$ (3 x 13 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography [Silica Gel PSQ 60B: $CHCl_3$–MeOH (15:1)] and the resulting solid was washed with sat. K_2CO_3 aq to afford **8** (79.0 mg, 95%).

Colorless plates ($CHCl_3$–*n*-hexane); mp 114–116 °C; $[\alpha]_D^{19}$ +108.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.16 (s, 6H), 3.64 (d, *J* = 10.8 Hz, 1H), 5.12 (dd, *J* = 4.2, 10.8 Hz, 1H), 7.01–7.12 (m, 8H), 7.18–7.28 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.5, 40.7, 54.4, 73.4, 126.7, 127.3, 127.6, 127.7, 127.9, 129.7, 132.6, 141.1, 170.1; IR (KBr) 3245, 2960, 1646, 1556, 753, 700 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{22}N_2ONa$: 305.1630; found: 305.1629.

***N*-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]benzamide (9)**

White solid; mp 130–132 °C; $[\alpha]_D^{20}$ +188.4 (*c* 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (s, 6H), 3.78 (d, *J* = 10.9 Hz, 1H), 5.26 (dd, *J* = 3.2, 10.9 Hz, 1H), 7.03–7.08 (m, 1H), 7.08–7.13 (m, 4H), 7.16–7.20 (m, 2H), 7.22–7.30 (m, 3H), 7.44–7.55 (m, 3H), 7.87–7.91 (m, 2H), 8.06 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.7, 54.9, 73.7, 126.8, 127.1, 127.3, 127.7, 127.8, 127.9, 128.5, 129.8, 131.4, 132.3, 134.7, 141.0, 167.2; IR (KBr) 3277, 1644, 1525, 755, 702 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{24}N_2ONa$: 367.1786; found: 367.1817.

***N*-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]-2,2,2-trifluoroacetamide (10)**

White solid; mp 110–112 °C; $[\alpha]_D^{19}$ +97.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.19 (s, 6H), 3.74 (d, *J* = 11.1 Hz, 1H), 5.07 (d, *J* = 11.0 Hz, 1H), 7.04–7.16 (m, 7H), 7.24–7.30 (m, 3H), 8.34 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.5, 54.8, 73.2, 115.9 (q, $^1J_{C,F}$ = 288.4 Hz), 127.1, 127.5, 128.0, 128.1, 128.3, 129.7, 131.2, 138.6, 157.0 (q, $^2J_{C,F}$ = 37.1 Hz); IR (KBr) 3324, 2945, 1714, 1180, 752, 702, 570 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{19}F_3N_2ONa$: 359.1347; found: 359.1339.

***N*-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]methansulfonamide (11)**

To a solution of **7** (290 mg, 1.21 mmol) and methanesulfonyl chloride (140 μL, 1.81 mmol) in anhydrous CH_2Cl_2 (20 mL) was added triethylamine (252 μL, 1.81 mmol) at rt under an argon atmosphere. After stirring for 22 h, sat. $NaHCO_3$ aq (15 mL) was added and then extracted with $CHCl_3$ (3 x 20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography [Silica Gel PSQ 60B: $CHCl_3$–MeOH (9:1)], then purified a second time by column chromatography [Silica Gel PSQ 60B: $CHCl_3$–MeOH (30:1)] to afford **11** (312 mg, 81%).

White solid; mp 253–255 °C; $[\alpha]_D^{20}$ +61.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 6H), 2.40 (s, 3H), 3.65 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 11.2 Hz, 1H), 6.70 (brs, 1H), 7.04–7.07 (m, 2H), 7.09–7.28 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.1, 42.0, 57.3, 72.8, 127.81, 127.83, 127.9, 128.4, 128.6, 129.8, 131.0, 138.5; IR (KBr) 3167, 3019, 2902, 1684, 1659, 1381, 1336, 1180, 778, 713 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{22}N_2O_2SNa$: 341.1300; found: 341.1296. Anal. Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.12; H, 6.96; N, 8.80. Found: C, 63.87; H, 6.89; N, 8.91%.

***N*-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]benzenesulfonamide (12)**

Colorless plates ($CHCl_3$–*n*-hexane); mp 142–143 °C; $[\alpha]_D^{21}$ +74.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08 (s, 6H), 3.55 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 6.87–6.95 (m, 8H), 7.16–7.20 (m, 3H), 7.25–7.28 (m, 2H), 7.38–7.41 (m, 1H), 7.57–7.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 57.4, 73.4, 127.16, 127.25, 127.65, 127.72, 127.8, 128.3, 128.4, 129.8, 131.0, 132.0, 137.8, 140.3; IR (KBr) 3172, 2939, 2789, 1452, 1349, 1173 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{24}N_2O_2SNa$: 403.1456; found: 403.1447. Anal. Calcd for $C_{22}H_{24}N_2O_2S$: C, 69.44; H, 6.36; N, 7.36. Found: C, 69.33; H, 6.40; N, 7.14%.

***N*-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]-2,3,4,5,6-pentafluorobenzenesulfonamide (13)**

Colorless needles ($CHCl_3$–*n*-hexane); mp 216–218 °C; $[\alpha]_D^{20}$ +144.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 6H), 3.70 (d, *J* = 11.2 Hz, 1H), 4.92 (d, *J* = 11.2 Hz, 1H), 6.91–6.99 (m, 3H), 7.00–7.05 (m, 4H), 7.17–7.25 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.1, 57.6, 72.5, 116.6, 116.71, 116.72, 116.74, 116.9, 127.8, 128.0, 128.1, 128.3, 129.7, 130.4, 136.06, 136.09, 136.12, 136.16, 136.20, 136.24, 136.3, 138.09, 138.13, 138.2, 138.3, 138.4, 142.4, 143.1, 143.18, 143.21, 143.25, 143.3, 144.4, 145.22, 145.25, 145.28, 145.32, 145.35; IR (KBr) 3195, 2943, 1649, 1518, 1498, 1382, 766, 702 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{19}F_5N_2O_2SNa$: 493.0985; found: 493.0952. Anal. Calcd for $C_{22}H_{19}F_5N_2O_2S$: C, 56.17; H, 4.07; N, 5.95. Found: C, 56.01; H, 4.06; N, 6.01%.

***N*-[(1*R*,2*R*)-2-(Dimethylamino)-1,2-diphenylethyl]-1,1,1-trifluoromethanesulfonamide (14)**

White solid; mp 186–188 °C; $[\alpha]_D^{19}$ +34.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 6H), 3.69 (d, *J* = 11.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 7.03–7.07 (m, 2H), 7.10–7.19 (m, 5H), 7.23–7.29 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 58.1, 73.6, 119.5 (q, $^1J_{C,F}$ = 321.8 Hz), 128.0, 128.08, 128.14, 128.3, 129.8, 130.0, 137.7; IR (KBr) 3036, 1276, 1201, 1171, 927, 703, 625, 603, 515 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{19}F_3N_2O_2SNa$: 395.1017; found: 395.0996. Anal. Calcd for $C_{17}H_{19}F_3N_2O_2S$: C, 54.83; H, 5.14; N, 7.52. Found: C, 54.62; H, 5.12; N, 7.53%.

Catalytic Asymmetric Ring-Opening of σ-Symmetric Cyclic Carbonates: Typical Procedure

To a solution of cyclic carbonate **1a** (45.0 mg, 0.133 mmol) and chiral amino sulfonamide catalyst **11** (8.4 mg, 0.0265 mmol) in anhydrous CH_2Cl_2 (1.8 mL) was added BnOH (67 μL, 0.663 mmol) at 0 °C under an argon atmosphere. After stirring for 7 d, 1N HCl (10 mL) was added and then extracted with $CHCl_3$ (3 x 15 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography [Silica Gel PSQ 60B: *n*-hexane–AcOEt (3:2 to 1:1 to 1:2)] to afford (*R*)-**3a** (44.5 mg, 75%, 75% ee). The enantiomeric excess of (*R*)-**3a** was determined by HPLC analysis [CHIRALPAK AD-H, *n*-hexane–EtOH (1:1); flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 10.72 min, t_R (minor) = 14.85 min].

(9*H*-Fluoren-9-yl)methyl (*R*)-{1-{[(Benzyloxy)carbonyl]oxy}-3-hydroxypropan-2-yl}carbamate [(*R*)-3a]

White solid (76% ee); mp 73–75 °C; $[\alpha]_D^{16}$ +4.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (brs, 1H), 3.60–3.74 (m, 2H), 3.92–4.01 (m, 1H), 4.19 (t, *J* = 6.7 Hz, 1H), 4.22–4.34 (m, 2H), 4.40 (d, *J* = 6.8 Hz, 2H), 5.16 (s, 2H), 5.28 (d, *J* = 8.3 Hz, 1H), 7.30 (dt, *J* = 0.7, 7.4 Hz, 2H), 7.33–7.41 (m, 7H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.1, 51.4, 61.5, 66.2, 66.9, 70.1, 120.0, 125.0, 127.1, 127.7, 128.5, 128.7, 128.8, 134.7, 141.3, 143.71, 143.74, 155.3, 156.2; IR (KBr) 3319, 2961, 1744, 1690, 1541, 1269 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{26}H_{25}NO_6Na$: 470.1580; found: 470.1563.

Benzyl (*R*)-{1-{[(Benzyloxy)carbonyl]oxy}-3-hydroxypropan-2-yl}carbamate [(*R*)-3b]

79% ee, HPLC analysis [TCI Chiral BP-S, *n*-hexane–EtOH (5:1); flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 8.94 min, t_R (minor) = 20.95 min].

White solid; mp 56–58 °C; $[\alpha]_D^{15}$ +4.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (brs, 1H), 3.63 (dd, *J* = 4.0, 10.5 Hz, 1H), 3.71 (dd, *J* = 3.5, 11.1 Hz, 1H), 3.93–4.00 (m, 1H), 4.25 (dd, *J* = 5.7, 11.0 Hz, 1H), 4.31 (dd, *J* = 4.9, 11.1 Hz, 1H), 5.09 (s, 2H), 5.15 (s, 2H), 5.29 (d, *J* = 8.3 Hz, 1H), 7.29–7.40 (m,

10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.4, 61.5, 66.2, 67.0, 70.1, 128.1, 128.2, 128.4, 128.5, 128.65, 128.72, 134.8, 136.1, 155.2, 156.2; IR (KBr) 3506, 3317, 1733, 1685, 1542, 1274 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{21}NO_6Na$: 382.1267; found: 382.1276.

***tert*-Butyl (*R*)-{1-{[(Benzyloxy)carbonyl]oxy}-3-hydroxypropan-2-yl}carbamate [(*R*)-3c]**

74% ee, HPLC analysis [CHIRALPAK AD-H, *n*-hexane–EtOH (3:1); flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 7.90 min, t_R (minor) = 10.16 min].

Colorless oil; $[\alpha]_D^{17}$ +5.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.60 (brs, 1H), 3.59–3.66 (m, 1H), 3.67–3.73 (m, 1H), 3.86–3.94 (m, 1H), 4.24 (dd, *J* = 5.7, 11.0 Hz, 1H), 4.31 (dd, *J* = 4.9, 10.9 Hz, 1H), 4.99–5.06 (m, 1H), 5.17 (s, 2H), 7.33–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3, 50.9, 61.6, 66.4, 70.0, 80.0, 128.4, 128.65, 128.70, 134.8, 155.2, 155.7; IR (neat) 3388, 2977, 1748, 1519, 1268, 1168 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{23}NO_6Na$: 348.1423; found: 348.1389.

REFERENCES AND NOTES

1. M. S. Manna and S. Mukherjee, *Org. Biomol. Chem.*, 2015, **13**, 18.
2. A. Borissov, T. Q. Davies, S. R. Ellis, T. A. Fleming, M. S. W. Richardson, and D. J. Dixon, *Chem. Soc. Rev.*, 2016, **45**, 5474.
3. J. Merad, M. Candy, J.-M. Pons, and C. Bressy, *Synthesis*, 2017, **49**, 1938.
4. T. Suzuki, *Tetrahedron Lett.*, 2017, **58**, 4731.
5. M. Inai, T. Asakawa, and T. Kan, *Tetrahedron Lett.*, 2018, **59**, 1343.
6. N. Di Iorio, S. Crotti, and G. Bencivenni, *Chem. Rec.*, 2019, **19**, 2095.
7. J. Sietmann and J. M. Wiest, *Angew. Chem. Int. Ed.*, 2020, **59**, 6964.
8. S. Tamai, S. Miyauchi, C. Morizane, K. Miyagi, H. Shimizu, M. Kume, S. Sano, M. Shiro, and Y. Nagao, *Chem. Lett.*, 1994, **23**, 2381.
9. S. Sano, K. Hayashi, T. Miwa, T. Ishii, M. Fujii, H. Mima, and Y. Nagao, *Tetrahedron Lett.*, 1998, **39**, 5571.
10. S. Sano, T. Miwa, K. Hayashi, K. Nozaki, Y. Ozaki, and Y. Nagao, *Tetrahedron Lett.*, 2001, **42**, 4029.
11. T. Honjo, S. Sano, M. Shiro, and Y. Nagao, *Angew. Chem. Int. Ed.*, 2005, **44**, 5838.
12. T. Honjo, T. Tsumura, S. Sano, Y. Nagao, K. Yamaguchi, and Y. Sei, *Synlett*, 2009, 3279.
13. S. Sano, M. Kamura, A. Nakamura, S. Kitaike, and M. Nakao, *Heterocycles*, 2016, **93**, 391.
14. S. Sano, M. Nakao, M. Takeyasu, T. Honjo, and Y. Nagao, *Lett. Org. Chem.*, 2006, **3**, 764.
15. T. Honjo, M. Nakao, S. Sano, M. Shiro, K. Yamaguchi, Y. Sei, and Y. Nagao, *Org. Lett.*, 2007, **9**,

509.

16. S. Sano, M. Nakao, M. Takeyasu, C. Yamamoto, S. Kitaike, Y. Yoshioka, and Y. Nagao, *Open Org. Chem. J.*, 2009, **3**, 22.
17. S. Sano, T. Tsumura, N. Tanimoto, T. Honjo, M. Nakao, and Y. Nagao, *Synlett*, 2010, 256.
18. S. Sano, T. Tsumura, M. Horibe, and M. Nakao, *Synlett*, 2013, **24**, 2302.
19. As described below, the absolute configurations of chiral acyclic carbonate (*S*)-(–)-**3a**–**c** were unequivocally determined not in reference 18, but in this paper.
20. M. Shang, X. Wang, S. M. Koo, J. Youn, J. Z. Chan, W. Yao, B. T. Hastings, and M. Wasa, *J. Am. Chem. Soc.*, 2017, **139**, 95.
21. J. Y. Choi and R. F. Borch, *Org. Lett.*, 2007, **9**, 215.
22. H. Yue, H. Huang, G. Bian, H. Zong, F. Li, and L. Song, *Tetrahedron: Asymmetry*, 2014, **25**, 170.