Tetrahedron 69 (2013) 9690–9700

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Imidazolium-based chiral ionic liquids: synthesis and application

Yumiko Suzuki [a,*], Junichiro Wakatsuki [b], Mariko Tsubaki [b], Masayuki Sato [b]

[a] Department of Materials & Life Sciences, Faculty of Science & Technology, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan
[b] School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Suruga-ku, Shizuoka 422-8526, Japan

ARTICLE INFO

Article history:
Received 9 August 2013
Received in revised form 4 September 2013
Accepted 5 September 2013
Available online 13 September 2013

Keywords:
Chiral ionic liquid
Chiral solvent
Imidazolium salt
Michael addition

ABSTRACT

Synthesis of chiral ionic liquids containing an imidazole nucleus and chiral centers on *N*-substituents is reported. [(2*S*,3*S*)-2,3-Dihydroxybutane-1,4-bis(3-butylimidazolium)]-[bis(trifluoromethanesulfonyl)amide]$_2$ and [(4*S*,5*S*)-2-phenyl-1,3-dioxolane-4,5-bis(1-methylimidazolium)]-[bis(trifluoromethanesulfonyl)amide]$_2$ induced enantioselectivity in the Michael addition of malonic esters to chalcones.

1. Introduction

Ionic liquids (ILs) are molten salts with melting points below 100 °C. The most common ILs are *N*,*N*-dialkylimidazolium, *N*-alkylpyridinium, and alkylammonium salts. In the last two decades, ILs have attracted considerable attention from various disciplines because of their unique and diverse properties, such as tunable miscibility, thermal stability, and high conductivity.[1,2] Since the report of Wilkes and co-workers on air- and water-stable molten imidazolium salts,[2] studies on syntheses, properties, and applications of ILs have increased substantially, and the use of ILs in organic synthesis has become widespread.

There are many reports of successful applications of ILs as solvents in asymmetric reactions. In most of these studies, chiral substrates, reagents, or both, or immobilized chiral catalysts were used as chiral sources.[3] Enantioselective synthesis may also be carried out by the use of chiral ionic liquids (CILs) as chiral sources. To date, successful syntheses through asymmetric induction by chiral solvents are rare.[4] The use of chiral solvents has been precluded because of their high cost and difficulties in their synthesis. However, because of their recyclability, ease of synthesis, and high degree of organization, CILs can be viable chiral solvents for effectively transferring their chiralities to reaction products. In fact, several examples of asymmetric induction by CILs have been reported in the literature.[5,6] This growing interest in the use of CILs as solvents for chiral induction has prompted us to commence the present study on the synthesis and application of chiral molten imidazolium salts.

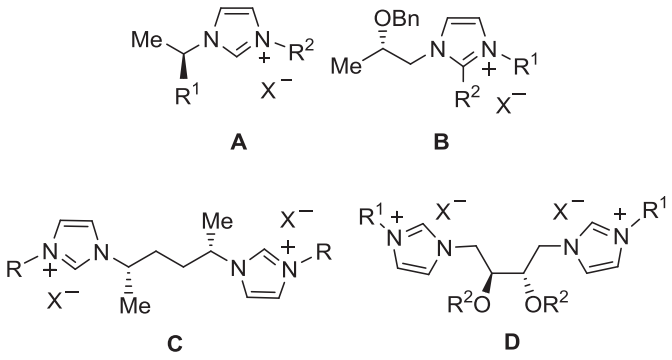
Herein, we describe the synthesis of novel imidazolium-based CILs, and their application as chiral solvents in Michael addition. The synthetic routes for the CILs are straightforward and all stereogenic centers in the newly-synthesized CILs were derived from those of 'chiral pool' precursors or commonly used chiral building blocks.

2. Results and discussion

We synthesized the following structural types of CILs: molecular structure with one imidazole nucleus bearing an asymmetric carbon atom α to the nitrogen atom on a *N*-substituent (**A**); molecular structure with one imidazole nucleus bearing an asymmetric carbon atom β to the nitrogen atom on a *N*-substituent (**B**); C_2-symmetric bisimidazolium salts bearing asymmetric carbon atoms α to the nitrogen atom of imidazoles (**C**); and C_2-symmetric bisimidazolium salts bearing asymmetric carbon atoms β to the nitrogen atom of imidazoles (**D**).

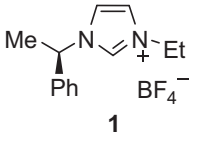
* Corresponding author. Tel./fax: +81 332383089; e-mail address: yumiko_suzuki@sophia.ac.jp (Y. Suzuki).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.09.017

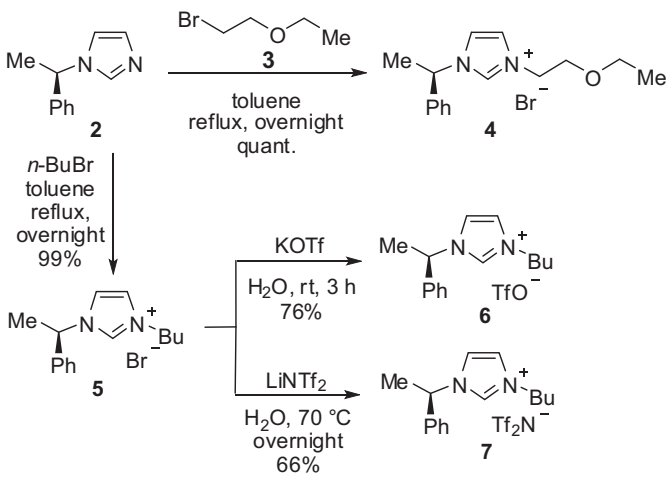


2.1. Synthesis of CIL A

The chiral imidazolium tetrafluoroborate **1** is a solid at room temperature, and its melting point is 90 °C.[7] Conversion of the counter anion of **1** to anions, such as trifluoromethanesulfonates, bis(trifluoromethanesulfonyl)amide, and methyl sulfonates, as well as the longer *N*-alkyl substituents was anticipated to lower the melting points of 1-(1-phenylethyl)imidazolium salts.



Imidazole **2** was prepared from (*R*)-(+)-1-phenylethylamine by reaction with glyoxal and formaldehyde.[7] The reaction of **2** with 2-bromoethyl ethyl ether **3** and *n*-butylbromide in toluene heated at reflux afforded CILs **4** and **5**, respectively (Scheme 1). The anion exchanges of **5** were carried out according to a method in the literature.[8] Treatment of **5** with potassium trifluoromethanesulfonate in water at 25 °C afforded CIL **6**. The anion exchange was confirmed by mass spectrometry and ^{19}F NMR spectroscopy. The signal for trifluoromethanesulfonate was observed at 149 *m*/*z* in the negative ion mode, and no peak for bromide was seen in FABMS. The chemical shift of trifluoromethanesulfonate was observed at −79.0 ppm in the ^{19}F NMR spectrum.

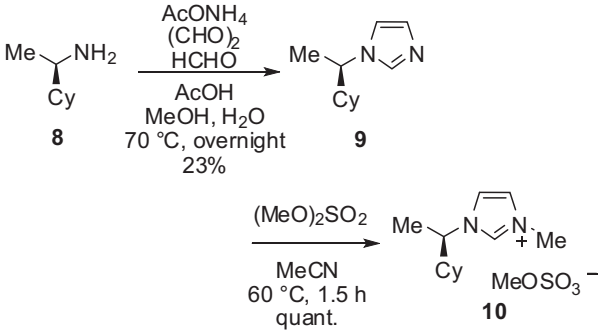


Scheme 1.

Compared with that of **5**, the ^{1}H NMR frequency of **6** is shifted upfield. In particular, the signal of the proton at the 2-position of the imidazole of **6** has a shift of 9.37 ppm, whereas that of **5** has a shift of 10.97 ppm. The lower chemical shifts of **6** were also observed in the ^{13}C NMR spectrum. It can be considered that the imidazole rings and the planar trifluoromethanesulfonate ions interact, and that electrons of oxygen atoms of triflate ions shield the imidazoles.

Reaction of **5** with lithium bis(trifluoromethanesulfonyl)imide produced CIL **7**. The ^{19}F NMR signal of **7** was observed at −78.9 ppm, and a peak at 280 *m*/*z* in the negative ion mode of the mass spectrum was assigned to the anion.

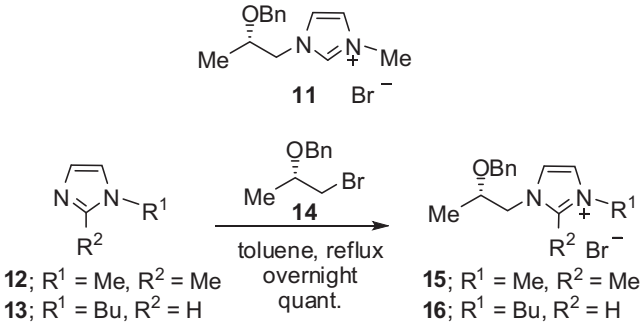
CIL **10** was synthesized from (*R*)-(−)-1-cyclohexylethylamine **8** in two steps (Scheme 2). First, the imidazole nucleus was constructed in the reaction of **8** with formaldehyde, glyoxal, and ammonium acetate, and then the resulting imidazole **9** was quaternized using dimethyl sulfonate to afford **10** as an oil.



Scheme 2.

2.2. Synthesis of CIL B

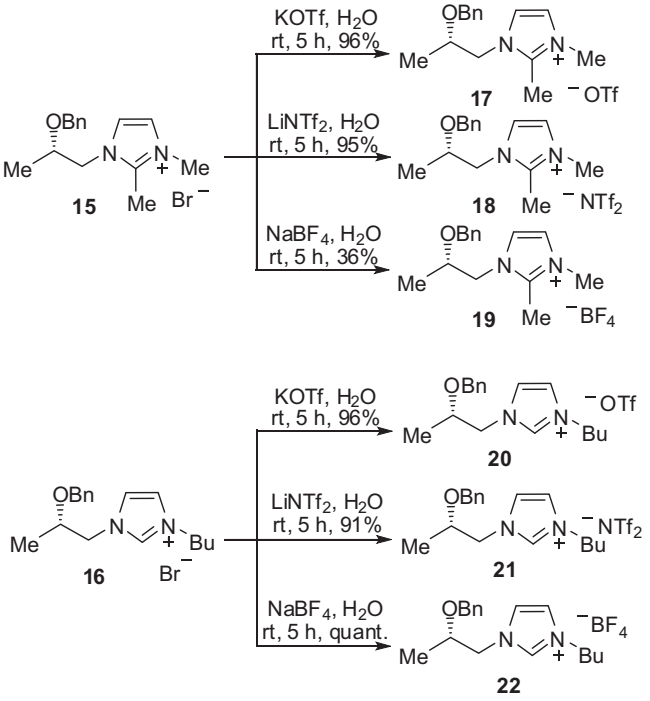
Bao's research group reported asymmetric Michael addition reaction using CIL **11** as a solvent and a chiral source (Scheme 3).[6b] They synthesized **11** by the reaction of 1-methylimidazole with **14**, which was prepared from (L)-(−)-ethyl lactate. The reaction of **14** with 1,2-dimethylimidazole (**12**) and 1-butylimidazole (**13**) afforded imidazolium salt **15** (a solid) and **16** (a liquid).



Scheme 3.

In an attempt to convert it into a liquid, **15** was treated with potassium trifluoromethanesulfonate in water (Scheme 4). The product **17**, however, was also a solid. The ^{1}H NMR frequency of **17** is also shifted upfield compared with that of **15**, as in the case of **5** and **6**. In particular, the signals of the 4,5-protons of the imidazole ring are shifted to 7.07–7.09 ppm from 7.54 to 7.71 ppm. The other anion exchange reactions of **15** were successfully carried out using lithium bis(trifluoromethanesulfonyl)imide and sodium tetrafluoroborate to afford CILs **18** and **19**, respectively. The isolated yield of **18** was low, presumably because of its high solubility in water

and the low efficiency of extraction with dichloromethane. Anion exchange of **16** was also performed to afford triflate **20**, bis(trifluoromethanesulfonyl)imide **21**, and tetrafluoroborate **22** in excellent yields (Scheme 4). All of the butylimidazolium salts **20**–**22** were obtained as oils. The anions of **17**–**22** were detected and confirmed by ^{1}H NMR and ^{19}F NMR spectroscopy, as well as by mass spectrometry.



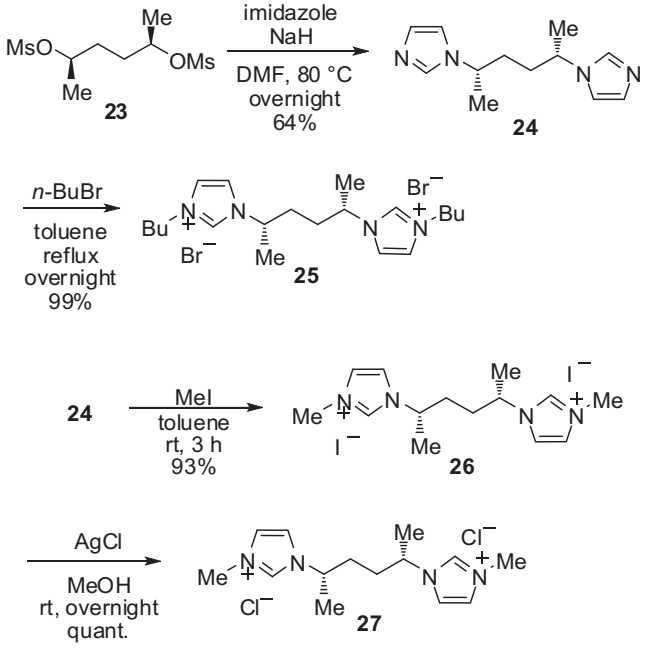
Scheme 4.

2.3. Synthesis of CIL C

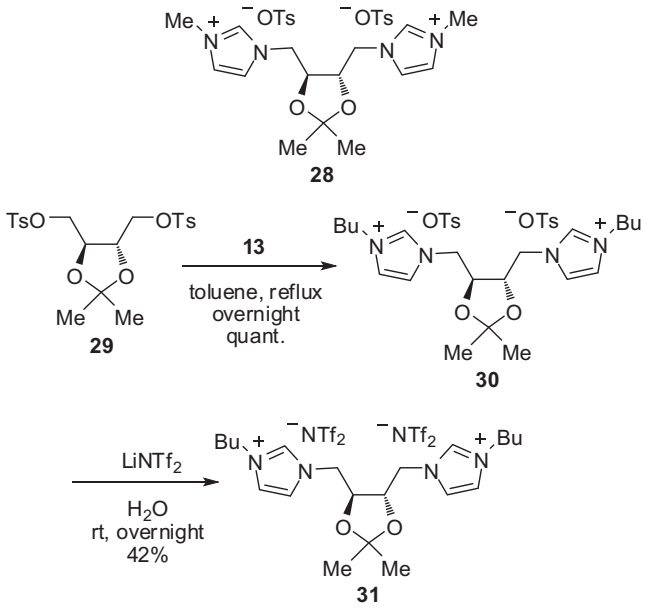
Dicationic ILs including bisimidazolium salts were first reported by Armstrong and his co-workers.[9] Their studies showed that this type of ILs have thermal stabilities greater than that of monocationic ILs. The C_2-symmetric CILs **25** and **27**, which are chiral bisimidazolium salts, were prepared as follows (Scheme 5). The reaction of mesylate **23**[10] with imidazole in the presence of NaH in DMF produced diimidazolylhexane **24**, which subsequently underwent quaternization by reaction with 1-bromobutane to afford bisimidazolium bromide **25** as an oil in excellent yield. On the other hand, treatment of **24** with iodomethane produced **26** as a solid, which was then quantitatively converted to an oily chloride **27** using AgCl. The anion exchange was confirmed by mass spectroscopy. Only a peak for chloride was observed at 35 *m*/*z* in the negative ion mode, and no peak for iodide was seen.

2.4. Synthesis of CIL D

The synthesis of chiral imidazolium salt **28** from **29** was reported by Dorta's group (Scheme 6).[11] Although **28** is solid, it was anticipated that the conversion of the counter anion and *N*-substituents would afford CILs having the chiral dioxolane (dimethylacetal) structures. The reaction of **29** with 1-butylimidazole produced the amorphous product **30**, which was then treated with lithium bis(trifluoromethanesulfonyl)imide in water to afford **31** as an oil (Scheme 6).

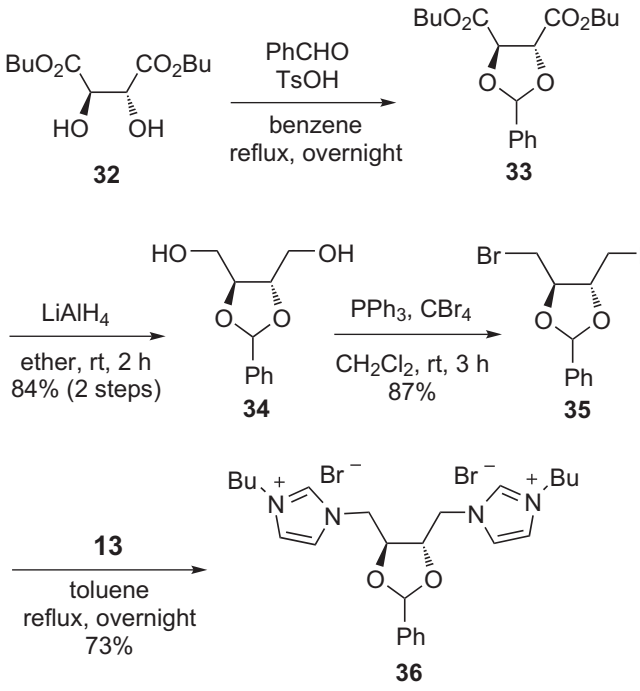


Scheme 5.

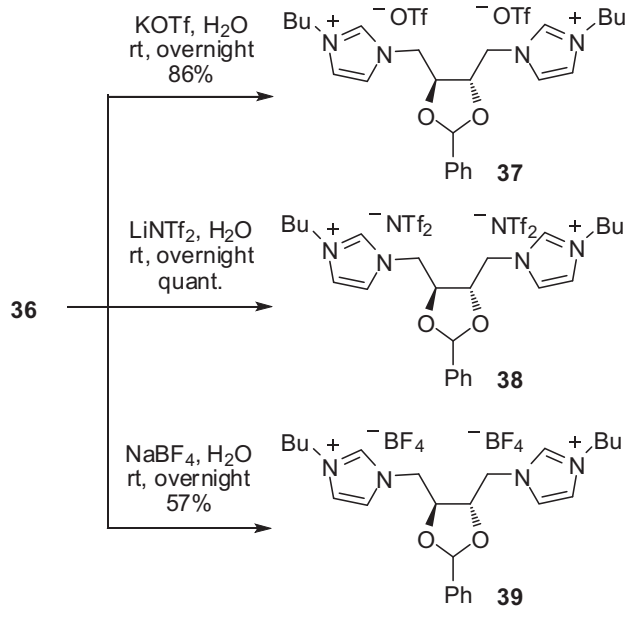


Scheme 6.

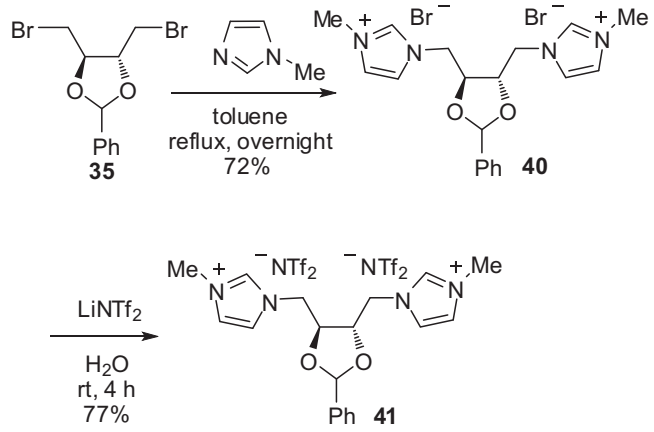
The CILs with benzylidene acetal moiety were synthesized from dibutyl-(L)-(+)-tartrate **32** (Schemes 7–9). After the formation of the acetal, dibutyl esters were reduced into hydroxyl groups, which were then converted into bromo groups to afford **35** (Scheme 7). The amorphous bromide **36** was obtained by the reaction of **35** with **13**. The anion exchange reactions of **36** were carried out to afford the triflate **37** and the bis(trifluoromethanesulfonyl)imide **38** as oils and tetrafluoroborate **39** as a solid (Scheme 8). The reaction of the bromide **35** with 1-metylimidazole afforded the amorphous imidazolium bromide **40**, which was then converted to the oily bis(trifluoromethanesulfonyl)imide **41** (Scheme 9). The anions of **37**–**39**, **41** were detected and confirmed by ^{1}H NMR, ^{19}F NMR, and mass spectra.



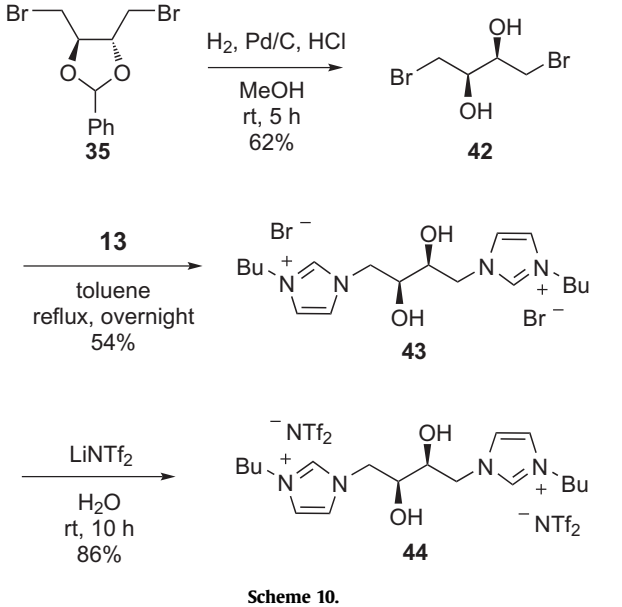
Scheme 7.



Scheme 8.



Scheme 9.



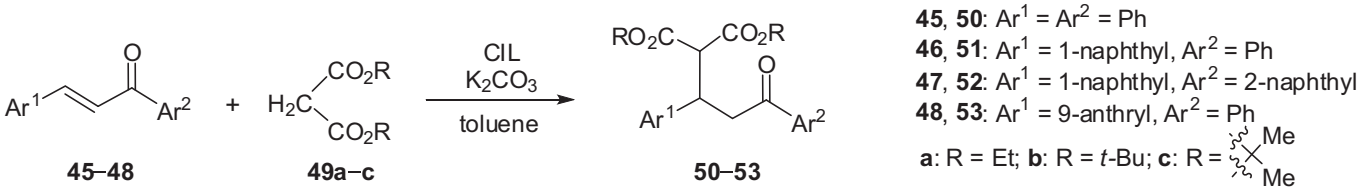
Scheme 10.

The C_2-symmetric CIL **44** was also synthesized from **35** (Scheme 10). After the benzylidene acetal of **35** was deprotected, the resulting **42** was subjected to a reaction with **13**. The product **43** was obtained as an amorphous solid. The anion of **43** was exchanged to bis(trifluoromethanesulfonyl)imide to afford **44** as an oil.

2.5. Michael addition in CIL A–D

Michael addition[11] of diethyl malonate **49a** to the chalcone **45** was examined (Table 1, entries 1–6). CILs were diluted with the co-solvent toluene to reduce their viscosity,[6b] and potassium carbonate was used as base. When the monoimidazolium-type CILs **A** and **B** (**5** and **11**, respectively) were used, the reaction showed no enantioselectivity (entries 1, 2). On the other hand, the bisimidazolium-type CILs **C** and **D** (**27**, **41**, and **44**) induced enantioselectivity to give **49a**,**b**[12] in 2–5% ee (entries 3–6). The enantiomeric excess was analyzed by HPLC using a Daicel CHIRALPAK AD or AD-H column (hexane/2-propanol=9/1). When CIL **41** was used, the enantiomer that was produced in excess was eluted faster. On the other hand, in the case of CIL **44**, the enantiomer that was obtained in excess was eluted later except for entries **12**, and **16**. (The absolute configurations of each enantiomer are unknown.) The use of chalcone derivatives **46**,[13] **47**,[14] and **48**[14], which have the bulkier aromatic substituents 1-naphthyl, 2-naphthyl, and 9-anthryl increased the enantioselectivities as a whole (3–14% ee, entries 7–12). In the case of the substrate **47** and **48**, however, the reaction rates were significantly decreased. The use of di-*tert*-butyl malonate **49b** and a cyclic ester Meldrum's acid **49c** as Michael addition donors also decreased the reaction rates (entries 13–20). In the reaction of **45**, the use of **49c** resulted in higher selectivities (12–13% ee, entries 15, 16) compared with that achieved with diethyl malonate **49a** (4% ee, entries 4, 6).

Table 1
Michael addition of malonate esters to chalcone derivatives in CILs



45–48 **49a–c** **50–53**

Entry	Ar^1	Ar^2	R	CIL	Conditions[a]	Yield %	ee %[b]
1	Ph	Ph	Et	**5**	rt, overnight	74	0
2	Ph	Ph	Et	**11**	rt, overnight	100[c]	0[c]
3	Ph	Ph	Et	**27**	rt, overnight	90	2
4	Ph	Ph	Et	**41**	rt, overnight	81	4
5	Ph	Ph	Et	**41**	0 °C, 2 days	33	5
6	Ph	Ph	Et	**44**	rt, overnight	100	4
7	1-Naphthyl	Ph	Et	**41**	rt, overnight	82	7
8	1-Naphthyl	Ph	Et	**44**	rt, overnight	82	10
9	1-Naphthyl	2-Naphtyl	Et	**41**	rt, 1 day	17	14
10	1-Naphthyl	2-Naphtyl	Et	**44**	rt, 1 day	34	3
11	9-Anthryl	Ph	Et	**41**	rt, 1 day	10	2
12	9-Anthryl	Ph	Et	**44**	rt, 1 day	4	11
13	Ph	Ph	*t*-Bu	**41**	rt, overnight	13	3
14	Ph	Ph	*t*-Bu	**44**	rt, overnight	35	4
15	Ph	Ph	$>CMe_2$	**41**	rt, 1 day	55	12
16	Ph	Ph	$>CMe_2$	**44**	rt, 1 day	28	13
17	1-Naphthyl	Ph	$>CMe_2$	**41**	rt, 3 days	40	8[d]
18	1-Naphthyl	Ph	$>CMe_2$	**44**	rt, 3 days	8	11[d]
19	1-Naphthyl	2-Naphtyl	$>CMe_2$	**41**	rt, 3 days	27	6
20	1-Naphthyl	2-Naphtyl	$>CMe_2$	**44**	rt, 3 days	12	8

[a] The reaction was conducted with chalcone derivatives (0.1 mmol), malonate esters (0.12 mmol), and K_2CO_3 (0.3 mmol), in CILs (1.0 mmol) and toluene (0.1 mL).
[b] Determined by HPLC.
[c] 96% yield, 25% ee, as reported.[6b]
[d] HPLC analysis was performed after conversion of **50c** to dimethyl 2-[1-(naphthalen-1-yl)-3-oxo-3-phenylpropyl]malonate.

3. Conclusion

We have shown the syntheses and spectroscopic characteristics of four structural types of CILs: monoimidazolium salts bearing an asymmetric carbon atom α to the nitrogen atom on a *N*-substituent (**A**); monoimidazolium salts bearing an asymmetric carbon atom β to the nitrogen atom on a *N*-substituent (**B**); C_2-symmetric bisimidazolium salts bearing asymmetric carbon atoms α to the nitrogen atoms of imidazoles (**C**); and C_2-symmetric bisimidazolium salts bearing asymmetric carbon atoms β to the nitrogen atoms of imidazoles (**D**). We also performed Michael addition using CILs **A**–**D** as solvents in order to evaluate their chiral-inducing abilities. The bisimidazolium-type CILs **C** and **D** were observed to have subtle but steady inducing effects. Notably, CILs **41** and **44** induce opposite selectivities, although both CILs come from the same chiral starting material **32** and have stereogenic centers with the same configurations. At present, the mechanism of the selectivity remains unclear and it is still quite a challenge to achieve high selectivity using chiral solvents. However, our result indicates that more efficient chiral solvents can be developed by designing CIL structures based on bis- or polyimidazolium salts, and that chiral ionic liquids can be used in asymmetric synthesis as green solvents/or catalysts. We believe that asymmetric induction by recyclable chiral solvents is the final frontier in asymmetric organic synthesis.

4. Experimental section

4.1. General

All of the chiral starting materials were used without purification.[15] The enantiomeric purities of CILs were not determined.

4.2. Synthesis of CIL A

*4.2.1. (R)-1-(1-Phenylethyl)-1H-imidazole (**2**).*[7] (*R*)-1-Phenylethylamine (2.6 mL, 20 mmol) and aqueous ammonia (2.8 mL, 40 mmol) were added to a mixture of formaldehyde (1.5 mL, 20 mmol) and glyoxal (2.3 mL, 20 mmol). The mixture was stirred at a reflux temperature overnight, and then the product was extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo to give the crude product, which was purified by silica gel chromatography (8% MeOH/CH_2Cl_2) to give **2** (1.6 g, 47%) as a brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.86 (3H, d, J=6.9 Hz, CH_3), 5.34 (1H, q, J=6.9 Hz, CH), 6.92 (1H, t, J=1.4 Hz, imidazole), 7.09 (1H, t, J=1.4 Hz, imidazole), 7.14 (2H, q, J=2.9 Hz, phenyl), 7.28–7.36 (3H, m, phenyl), 7.66 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 22.1, 56.7, 118.1, 126.1, 128.2, 129.0, 129.5, 136.2, 141.7; HRMS (FAB) m/z: MH^+, found 173.1094. $C_{11}H_{13}N_2$ requires 173.1079.

*4.2.2. (R)-1-(2-Ethoxyethyl)-3-(1-phenylethyl)imidazolium bromide (**4**).* 2-Bromoethylethylether (**3**) (0.14 mL, 3.2 mmol) was dropwisely added to a solution of imidazole **2** (0.37 g, 2.2 mmol) in toluene (3 mL). The mixture was stirred at a reflux temperature overnight to give the oily product insoluble to toluene. After decantation of the supernatant, the crude product was washed with toluene several times, and then the remaining solvent was evaporated in vacuo to give **4** (0.70 g, quant.) as a brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.53 (3H, t, J=7.5 Hz, CH_3CH_2), 2.05 (3H, d, J=7.3 Hz, CH_3CH), 3.52 (2H, q, J=7.5 Hz, CH_3CH_2), 3.84 (2H, t, J=4.5 Hz, CH_2N), 4.66 (2H, t, J=4.5 Hz, CH_2O), 5.82 (1H, q, J=7.3 Hz, CH), 7.04 (1H, t, J=1.8 Hz, imidazole), 7.40–7.42 (6H, m,

imidazole, phenyl), 10.86 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 15.1, 21.4, 50.1, 60.0, 66.8, 68.3, 120.4, 123.5, 127.0, 129.5, 136.3, 138.0; IR (neat) cm^{-1}: 1557, 1454, 1155, 1113; HRMS (FAB) m/z: M^+, found 245.1638. $C_{15}H_{21}N_2O$ requires 245.1654; $[\alpha]_D^{21}$ +1.45 (c 1.0, $CHCl_3$).

*4.2.3. (R)-1-Butyl-3-(1-phenylethyl)imidazolium bromide (**5**).* 1-Bromobutane (1.6 mL, 14.2 mmol) was dropwisely added to a solution of imidazole **2** (1.6 g, 9.5 mmol) in toluene (6 mL). The mixture was stirred at a reflux temperature overnight to give the oily product insoluble to toluene. After decantation of the supernatant, the crude product was washed with toluene several times, and then the remaining solvent was evaporated in vacuo to give **5** (0.70 g, quant.) as a brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.95 (3H, t, J=7.4 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.39 (2H, sext, J=7.4 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.85 (2H, quint, J=7.4 Hz, CH$_3$CH$_2$CH_2CH$_2$), 2.03 (3H, d, J=6.9 Hz, CH_3CH), 4.38 (2H, t, J=7.4 Hz, CH$_3$CH$_2$CH$_2$CH_2), 5.99 (1H, q, J=6.9 Hz, CH), 7.13 (1H, t, J=1.7 Hz, imidazole), 7.23 (1H, t, J=1.7 Hz, imidazole), 7.32–7.45 (5H, m, phenyl), 10.97 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.6, 19.6, 21.4, 32.2, 50.0, 59.8, 120.8, 122.3, 127.0, 129.4, 129.5, 136.4, 138.1; IR (neat) cm^{-1}: 3408, 2961, 1553, 1456, 1155; HRMS (FAB) m/z: M^+, found 229.1680. $C_{15}H_{21}N_2O$ requires 229.1705; $[\alpha]_D^{25}$ +18.33 (c 0.9, $CHCl_3$).

*4.2.4. (R)-1-Butyl-3-(1-phenylethyl)imidazolium trifluoromethanesulfonate (**6**).* A solution of **5** (0.31 g, 1.0 mmol) and potassium trifluoromethanesulfonate (0.29 g, 1.5 mmol) in water (2 mL) was stirred at room temperature overnight. The product was extracted with chloroform. The organic layer was dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo to give **6** (0.29 g, 76%) as a brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.93 (3H, t, J=7.4 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.34 (2H, sext, J=7.4 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.85 (2H, quint, J=7.4 Hz, CH$_3$CH$_2$CH_2CH$_2$), 1.96 (3H, d, J=6.9 Hz, CH_3CH), 4.23 (2H, t, J=7.4 Hz, CH$_3$CH$_2$CH$_2$CH_2), 5.70 (1H, q, J=6.9 Hz, CH), 7.20 (1H, t, J=1.7 Hz, imidazole), 7.30 (1H, t, J=1.7 Hz, imidazole), 7.35–7.41 (5H, m, phenyl), 9.37 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.4, 19.5, 20.9, 32.1, 50.1, 60.3, 120.8 (q, J=1300 Hz), 120.8, 122.2, 122.2, 126.9, 129.6, 135.7, 137.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.0; IR (neat) cm^{-1}: 1555, 1458, 1348, 1179, 1132, 1051; HRMS (FAB) m/z: M^+, found 229.1687. $C_{15}H_{21}N_2$ requires 229.1705; MS (FAB^-) m/z: 149; $[\alpha]_D^{26}$ +10.16 (c 1.2, $CHCl_3$).

*4.2.5. (R)-1-Butyl-3-(1-phenylethyl)imidazolium bis(trifluoromethanesulfonyl)amide (**7**).* A solution of **5** (0.31 g, 1.0 mmol) and lithium bis(trifluoromethanesulfonyl)imide (0.29 g, 1.0 mmol) in water (2 mL) was stirred overnight at 70 °C. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **6** (0.33 g, 66%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.97 (3H, t, J=7.4 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.38 (2H, sext, J=7.4 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.87 (2H, quint, J=7.4 Hz, CH$_3$CH$_2$CH_2CH$_2$), 1.97 (3H, d, J=6.9 Hz, CH_3CH), 4.22 (2H, t, J=7.4 Hz, CH$_3$CH$_2$CH$_2$CH_2), 5.70 (1H, d, J=6.9 Hz, CH), 7.12 (1H, t, J=1.7 Hz, imidazole), 7.19 (1H, t, J=1.7 Hz, imidazole), 7.32–7.35 (2H, m, phenyl), 7.41–7.45 (3H, m, phenyl), 9.01 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.3, 19.4, 20.8, 32.0, 50.1, 60.3, 119.9 (q, J=1250 Hz), 121.2, 122.6, 126.9, 129.7, 129.7, 134.5, 137.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −78.9; IR (neat) cm^{-1}: 1557, 1456, 1252, 1152, 1028; HRMS (FAB) m/z: M^+, found 229.1717. $C_{15}H_{21}N_2$ requires 229.1705; MS (FAB^-) m/z: 280; $[\alpha]_D^{26}$ +12.84 (c 1.0, $CHCl_3$).

*4.2.6. (R)-1-(1-Cyclohexylethyl)-1H-imidazole (**9**).* Glyoxal (0.72 mL, 9.7 mmol), an aqueous solution (1 mL) of ammonium acetate (0.75 g, 9.7 mmol), and a methanol (1 mL) solution of (*R*)-(−)-1-cyclohexylethylamine (**1**) (1.0 mL, 6.7 mmol) were added to a mixture of formaldehyde (0.72 mL, 9.7 mmol) in acetic acid (2.5 mL). The mixture was stirred overnight at 70 °C. After being cooled, the mixture was neutralized by adding a $NaHCO_3$ solution, and then the product was extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo to give the crude product, which was purified by silica gel chromatography (2% MeOH/CH_2Cl_2) to give **9** (0.28 g, 23%) as a pale brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.70–0.80 (1H, m, cyclohexyl), 0.90–1.00 (1H, m, cyclohexyl), 1.07–1.28 (3H, m, cyclohexyl), 1.30–1.36 (1H, m, cyclohexyl), 1.45 (3H, d, J=6.9 Hz, CH_3), 1.48–1.55 (1H, m, cyclohexyl), 1.60–1.70 (2H, m), 1.73–1.80 (2H, m, cyclohexyl), 3.83 (1H, quint, J=6.9 Hz, CH), 6.88 (1H, t, J=1.1 Hz, imidazole), 7.06 (1H, t, J=1.1 Hz, imidazole), 7.40 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 19.0, 25.9, 26.0, 26.2, 29.5, 29.9, 44.5, 58.9, 117.2, 129.0, 136.4; HRMS (FAB) m/z: MH^+, found 179.1569. $C_{11}H_{19}N_2$ requires179.1548; $[\alpha]_D^{23}$ −17.01 (c 1.0, $CHCl_3$).

*4.2.7. (R)-3-(1-Cyclohexylethyl)-1-methylimidazolium methylsulfonate (**10**).* A solution of **9** (0.54 g, 3.0 mmol) and dimethyl sulfonate (0.29 mL, 3.0 mmol) in acetonitrile (6 mL) was stirred at 70 °C for 1.5 h. The solvent was evaporated off. The oily residue was washed with diethyl ether and dried in vacuo to give **10** (0.97 g, quant.) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.88–1.02 (2H, m, cyclohexyl), 1.08–1.33 (4H, m, cyclohexyl), 1.55 (3H, d, J=6.9 Hz, CH_3CH), 1.59–1.78 (5H, m, cyclohexyl), 3.74 (3H, s, CH_3O), 4.04 (3H, s, CH_3N), 4.28 (1H, quint, J=6.9 Hz, CH), 7.19 (1H, t, J=1.7 Hz, imidazole), 7.35 (1H, t, J=1.7 Hz, imidazole), 9.56 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 18.1, 25.6, 25.7, 25.8, 29.1, 29.2, 36.5, 43.4, 54.5, 62.3, 120.4, 124.0, 136.8; IR (neat) cm^{-1}: 2928, 1557, 1450, 1165, 1043, 843; HRMS (FAB) m/z: M^+, found 193.1715. $C_{12}H_{21}N_2$ requires 193.1705; $[\alpha]_D^{25}$ −2.99 (c 0.8, CH_3OH).

4.3. Synthesis of CIL B

4.3.1. Ethyl (S)-2-(benzyloxy)propionate.[6b] Sodium hydride (60% in oil, 3.8 g, 94.4 mmol) and (L)-(−)-ethyl lactate (**1**) (10.0 mL, 85.8 mmol) were added to a solution of benzyl bromide (12.5 mL, 103 mmol) in THF/DMF (50 mL/50 mL). The mixture was stirred at 70 °C for 3 h. The product was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (30% AcOEt/hexane) to give the product (16.2 g, 91%) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.28 (3H, t, J=7.4 Hz, CH_3CH$_2$), 1.43 (3H, d, J=6.9 Hz, CH_3CH), 4.04 (1H, q, J=6.9 Hz, CH), 4.16–4.25 (2H, m, CH$_3$CH_2), 4.44 (1H, d, J=12.0 Hz, PhCH_2), 4.69 (1H, d, J=12.0 Hz, PhCH_2), 7.27–7.37 (5H, m, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 14.3, 18.8, 60.9, 72.1, 74.1, 127.9, 128.1, 128.5, 137.7, 173.3.

4.3.2. (S)-2-Benzyloxypropan-1-ol.[6b] Ethyl (*S*)-2-(benzyloxy)propionate (16.2 g, 77.8 mmol) was added dropwisely to a suspension of $LiAlH_4$ (3.2 g, 77.8 mmol) in dry diethyl ether (200 mL) with ice-cooling. The mixture was stirred at room temperature for 2 h, neutralized with saturated ammonium chloride solution, and then filtered. The filtrate was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (AcOEt/hexane: 1/8) to give the product (3.7 g, quant.) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.19 (3H, d, J=6.7 Hz, CH_3), 2.04 (1H, t, J=3.7 Hz, OH), 3.48–3.53 (1H, m, CH), 3.60–3.72 (2H, m, CH_2OH), 4.49 (1H, d, J=11.6 Hz, PhCH_2), 4.66 (1H, d, J=11.6 Hz, PhCH_2), 7.27–7.37 (5H, m, phenyl); ^{13}C NMR

(126 MHz, $CDCl_3$) δ: 16.3, 66.1, 70.9, 75.8, 127.7, 127.9, 127.9, 128.5, 138.7.

*4.3.3. (S)-Benzyl 1-bromo-2-propyl ether (**14**).*[6b] Triphenylphosphine (49.1 g, 182 mmol) and NBS (33.0 g, 182 mmol) were added to a solution of (*S*)-2-benzyloxypropan-1-ol (15.1 g, 90.8 mmol) in dichloromethane (200 mL) with ice-cooling. The mixture was stirred at room temperature overnight, and poured into water. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (20% AcOEt/hexane) to give **14** (17.7 g, 85%) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.33 (3H, d, J=6.7 Hz, CH_3), 3.39 (1H, dd, J=4.9, 10.4 Hz, CH_2Br), 3.46 (1H, dd, J=4.9, 10.4 Hz, CH_2Br), 3.73–3.76 (1H, m, CH), 4.59 (2H, s, PhCH_2), 7.27–7.38 (5H, m, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 19.2, 36.8, 71.2, 74.3, 127.9, 128.6, 138.4.

*4.3.4. (S)-1-(2-Benzyloxypropyl)-2,3-dimethylimidazolium bromide (**15**).* 1,2-Dimethylimidazole (**12**) (0.14 mL, 1.38 mmol) was added dropwisely to a solution of **14** (0.21 g, 0.92 mmol) in toluene (5 mL). The mixture was stirred at reflux temperature overnight. The crude product was washed with toluene, and the remaining solvent and the starting materials were distilled off using a glass tube oven to give **15** (0.29 g, quant.) as a colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.35 (3H, d, J=6.1 Hz, CH_3CH), 2.61 (3H, s, 2-CH_3), 3.88 (3H, s, CH_3N), 3.95–3.97 (1H, m, CH), 4.06 (1H, dd, J=14.0, 9.1 Hz, CH_2CH), 4.25 (1H, d, J=14.0 Hz, PhCH_2), 4.58–4.60 (2H, m, CH_2CH, PhCH_2), 7.10 (2H, dd, J=1.8, 6.7 Hz, phenyl), 7.27–7.31 (3H, m, phenyl), 7.54 (1H, d, J=1.8 Hz, imidazole), 7.71 (1H, d, J=1.8 Hz, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 10.9, 17.0, 35.9, 53.7, 71.0, 73.6, 122.3, 122.4, 127.9, 128.0, 128.5, 137.6, 144.7; IR (neat) cm^{-1}: 1533, 1454, 1024; HRMS (FAB) m/z: M$^+$, found 245.1637 $C_{15}H_{21}N_2O$ requires 245.1648; MS (FAB$^-$) m/z: 79, 81; $[\alpha]_D^{25}$ +35.24 (c 1.0, $CHCl_3$).

*4.3.5. (S)-1-(2-Benzyloxypropyl)-3-butylimidazolium bromide (**16**).* 1-Butylimidazole (**13**) (2.6 g, 21.0 mmol) was added dropwisely to a solution of **14** (3.2 g, 14.0 mmol) in toluene (15 mL). The mixture was stirred at reflux temperature overnight. The crude product was washed with toluene, and the remaining solvent was evaporated in vacuo to give **16** (4.8 g, quant.) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.97 (3H, t, J=7.3 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.32 (3H, d, J=6.1 Hz, CH_3CH), 1.36–1.39 (2H, sext, J=7.3 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.88 (2H, quint, J=7.9, CH$_3$CH$_2$CH_2CH$_2$), 4.03–4.06 (1H, m, CH), 4.22–4.29 (4H, m, CH$_3$CH$_2$CH$_2$CH_2, CH_2CH), 4.36 (1H, d, J=11.6 Hz, PhCH_2), 4.63 (1H, d, J=11.6 Hz, PhCH_2), 4.78 (1H, dd, J=2.4, 14.0 Hz, CH_2CH), 7.10 (1H, s, imidazole), 7.14–7.34 (5H, m, phenyl), 7.37 (1H, s, imidazole), 10.62 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.5, 16.7, 19.4, 32.1, 49.8, 54.4, 70.8, 73.2, 121.6, 123.6, 127.8, 127.9, 128.5, 136.9, 137.6; IR (neat) cm^{-1}: 1533, 1454, 1024; HRMS (FAB) m/z: M$^+$, found 273.1967. $C_{16}H_{23}N_2O$ requires 273.1961; MS (FAB$^-$) m/z: 79, 81; $[\alpha]_D^{26}$ +41.48 (c 1.1, $CHCl_3$).

*4.3.6. (S)-1-(2-Benzyloxypropyl)-2,3-dimethylimidazolium trifluoromethanesulfonate (**17**).* A solution of **15** (0.46 g, 1.5 mmol) and potassium trifluoromethanesulfonate (0.58 g, 3.0 mmol) in water (5 mL) was stirred at room temperature overnight. The product was extracted with chloroform. The organic layer was dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo to give **17** (0.29 g, 76%) as a yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.29 (3H, d, J=6.3 Hz, CH_3CH), 2.45 (3H, s, 2-CH_3), 3.72 (3H, s, CH_3N), 3.83–3.88 (1H, m, CH), 3.97 (1H, dd, J=9.2, 11.5 Hz, CH_2CH), 4.21 (1H, d, J=11.5 Hz, PhCH_2), 4.24 (1H, dd, J=2.9, 11.5 Hz, CH_2CH), 4.55 (1H, d, J=11.5 Hz, PhCH_2), 7.07–7.09 (2H, m, imidazole), 7.28–7.30 (5H, m, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 10.0, 16.8, 35.3, 53.5, 71.1, 73.5, 102.8 (q, J=1273 Hz), 122.1, 128.0, 128.1, 128.5, 137.6, 144.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.0; IR (neat) cm^{-1}: 1541, 1456, 1261, 1148, 1028; HRMS (FAB) m/z: M$^+$, found 245.1630. $C_{15}H_{21}N_2O$ requires 245.1648; MS (FAB$^-$) m/z: 149; $[\alpha]_D^{26}$ +36.80 (c 1.0, $CHCl_3$).

*4.3.7. (S)-1-(2-Benzyloxypropyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide (**18**).* A solution of **15** (1.3 g, 4.2 mmol) and lithium bis(trifluoromethanesulfonyl)imide (1.8 g, 6.3 mmol) in water (10 mL) was stirred at room temperature for 5 h. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **18** (2.1 g, 95%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.30 (3H, d, J=5.7 Hz, CH_3CH), 2.47 (3H, s, 2-CH_3), 3.75 (3H, s, CH_3N), 3.85–3.89 (1H, m, CH), 3.98 (1H, dd, J=9.2, 14.3 Hz, CH_2CH), 4.20 (1H, d, J=12.0 Hz, PhCH_2), 4.32 (1H, dd, J=2.9, 14.3 Hz, CH_2CH), 4.55 (1H, d, J=12.0 Hz, PhCH_2), 7.07–7.10 (2H, m, phenyl), 7.27–7.30 (2H, m, phenyl), 7.32 (1H, d, J=1.7 Hz, imidazole), 7.39 (1H, d, J=1.7 Hz, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 9.8, 16.7, 35.1, 53.6, 71.1, 73.2, 119.9 (q, J=1278 Hz), 121.2, 121.9, 122.0, 128.1, 128.5, 137.6, 144.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.4; IR (neat) cm^{-1}: 1564, 1454, 1049, 1026; HRMS (FAB) m/z: M$^+$, found 245.1637. $C_{15}H_{21}N_2O$ requires 245.1648; MS (FAB$^-$) m/z: 280; $[\alpha]_D^{26}$ +26.48 (c 1.0, $CHCl_3$).

*4.3.8. (S)-1-(2-Benzyloxypropyl)-2,3-dimethylimidazolium tetrafluoroborate (**19**).* A solution of **15** (0.31 g, 1.0 mmol) and sodium tetrafluoroborate (0.17 g, 1.5 mmol) in water (2 mL) was stirred at room temperature for 5 h. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **19** (0.12 g, 36%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.28 (3H, d, J=6.3 Hz, CH_3CH), 2.41 (3H, s, 2-CH_3), 3.68 (3H, s, CH_3N), 3.79–3.84 (1H, m, CH), 3.93 (1H, dd, J=14.3, 9.2 Hz, CH_2CH), 4.14 (1H, dd, J=2.3, 14.3 Hz, CH_2CH), 4.20 (1H, d, J=11.5 Hz, PhCH_2), 4.55 (1H, d, J=11.5 Hz, PhCH_2), 7.07–7.09 (3H, m, phenyl), 7.16 (1H, d, J=2.3 Hz, imidazole), 7.27–7.29 (3H, m, phenyl, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 10.0, 16.8, 35.2, 53.4, 71.0, 73.6, 122.0, 122.2, 127.9, 128.0, 128.5, 137.7, 144.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −152.9; IR (neat) cm^{-1}: 1564, 1454, 1049, 1026; HRMS (FAB) m/z: M$^+$, found 245.1679. $C_{15}H_{21}N_2O$ requires 245.1648; MS (FAB$^-$) m/z: 87; $[\alpha]_D^{25}$ +41.47 (c 1.0, $CHCl_3$).

*4.3.9. (S)-1-(2-Benzyloxypropyl)-3-butylimidazolium trifluoromethanesulfonate (**20**).* A solution of **16** (0.38 g, 1.1 mmol) and potassium trifluoromethanesulfonate (0.20 g, 1.7 mmol) in water (2 mL) was stirred at room temperature for 5 h. The product was extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo to give **20** (0.43 g, 96%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.95 (3H, t, J=7.4 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.28 (3H, d, J=6.3 Hz, CH_3CH), 1.33 (2H, sext, J=7.4 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.83 (2H, quint, J=7.4 Hz, CH$_3$CH$_2$CH_2CH$_2$), 3.94–3.97 (1H, m, CH), 4.14–4.17 (3H, m, CH$_3$CH$_2$CH$_2$CH_2, CH_2CH), 4.33 (1H, d, J=12.0, PhCH_2), 4.53 (1H, dd, J=2.9, 14.3 Hz, CH_2CH), 4.62 (1H, d, J=12.0 Hz, PhCH_2), 7.13 (1H, t, J=1.7 Hz, imidazole), 7.20 (2H, d, J=7.4 Hz, phenyl), 7.30–7.32 (3H, m, phenyl), 7.35 (1H, t, J=1.7 Hz, imidazole), 9.47 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.3, 16.5, 19.3, 31.9, 49.7, 54.3, 70.7, 73.0, 120.7 (q, J=1273 Hz), 121.9, 123.5, 127.8, 127.9, 128.5, 136.4, 137.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.0; IR (neat) cm^{-1}: 1564, 1454, 1256, 1223, 1155, 1028; HRMS (FAB) m/z: M$^+$, found 273.1951. $C_{16}H_{23}N_2O$ requires 273.1961; MS (FAB$^-$) m/z: 149; $[\alpha]_D^{27}$ +37.17 (c 1.1, $CHCl_3$).

*4.3.10. (S)-1-(2-Benzyloxypropyl)-3-butylimidazolium bis(trifluoromethanesulfonyl)amide (**21**).* A solution of **16** (0.38 g, 1.1 mmol) and lithium bis(trifluoromethanesulfonyl)imide (0.49 g, 1.7 mmol) in water (2 mL) was stirred at room temperature for 5 h. The product

was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **21** (0.54 g, 91%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.95 (3H, t, J=7.4 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.26 (3H, d, J=6.3 Hz, CH_3CH), 1.33 (2H, sext, J=7.4 Hz CH$_3$CH_2CH$_2$CH$_2$), 1.80 (2H, quint, J=7.4 Hz, CH$_3$CH$_2$CH_2CH$_2$), 3.88–3.95 (1H, m, CH), 4.06 (1H, dd, J=7.9, 14.0 Hz, CH_2CH), 4.13 (3H, m, CH$_3$CH$_2$CH$_2$CH_2, CH_2CH), 4.31 (1H, d, J=12.0 Hz, PhCH_2), 4.38 (1H, dd, J=2.9, 14.3 Hz, CH_2CH), 4.62 (1H, d, J=12.0 Hz, PhCH_2), 7.15 (1H, t, J=1.7 Hz, imidazole), 7.19 (2H, dd, J=2.3, 8.0 Hz, phenyl), 7.30–7.32 (4H, m, phenyl, imidazole), 8.76 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.3, 16.4, 19.3, 31.9, 49.9, 54.6, 70.8, 72.9, 119.9 (q, J=1273 Hz), 121.8, 123.7, 127.9, 128.1, 128.6, 135.7, 137.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.4; IR (neat) cm^{-1}: 1564, 1454, 1348, 1182, 1134, 1051; HRMS (FAB) m/z: M^+, found 273.1954. $C_{16}H_{23}N_2O$ requires 273.1961; MS (FAB$^-$) m/z: 280; $[\alpha]_D^{26}$ +29.16 (c 1.4, $CHCl_3$).

*4.3.11. (S)-1-(2-Benzyloxypropyl)-3-butylimidazolium tetrafluoroborate (**22**).* A solution of **16** (0.91 g, 2.7 mmol) and sodium tetrafluoroborate (0.46 g, 4.1 mmol) in water (10 mL) was stirred at room temperature for 5 h. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **22** (1.0 g, quant.) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.94 (3H, t, J=7.4 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.28 (3H, d, J=6.3 Hz, CH_3CH), 1.34 (2H, sext, J=8.0 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.84 (2H, quint, J=8.0 Hz, CH$_3$CH$_2$CH_2CH$_2$), 3.95–4.01 (1H, m, CH), 4.15–4.21 (3H, m, CH$_3$CH$_2$CH$_2$CH_2, CH_2CH), 4.33 (1H, d, J=11.5 Hz, PhCH_2), 4.58–4.62 (2H, m, PhCH_2, CH_2CH), 7.14 (1H, t, J=1.7 Hz, imidazole), 7.20 (2H, d, J=8.0 Hz, phenyl), 7.26–7.33 (3H, m, phenyl), 7.36 (1H, t, J=1.7 Hz, imidazole), 9.79 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.4, 16.6, 19.4, 32.0, 49.8, 54.4, 70.8, 73.2, 121.6, 123.6, 127.8, 127.9, 128.5, 136.7, 137.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −151.9; IR (neat) cm^{-1}: 1539, 1454, 1364, 1179, 1134, 1051; HRMS (FAB) m/z: M^+, found 273.1962. $C_{16}H_{23}N_2O$ requires 273.1961; MS (FAB$^-$) m/z: 87; $[\alpha]_D^{25}$ +39.95 (c 1.0, $CHCl_3$).

4.4. Synthesis of CIL C

*4.4.1. (2R,5R)-Hexanediol dimethanesulfonate (**23**).*[10] Triethylamine (12.4 mL, 87.9 mmol) and mesyl chloride (4.9 mL, 62.8 mmol) were added to a solution of (2*R*,5*R*)-2,5-hexanediol (3.0 mL, 25.1 mmol) in dichloromethane (75 mL) with ice-cooling. The mixture was stirred at room temperature for 4 h, and then neutralized by addition of hydrochloric acid. The product was extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (2% MeOH/CH_2CL_2) to give **23** (6.9 g, quant.) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.42 (6H, d, J=6.1 Hz, CH_3CH), 1.75–1.86 (4H, m, CH$_2$), 3.02 (6H, s, CH$_3$S), 4.86–4.89 (2H, m, CH).

*4.4.2. (2S,5S)-2,5-Di(1-imidazolyl)hexane (**24**).* Imidazole (1.4 g, 21.0 mmol) and sodium hydride (0.84 g, 21.0 mmol) were added to a solution of **23** (1.9 g, 6.9 mmol) in DMF (20 mL) with ice-cooling. The mixture was stirred at 80 °C overnight, and then poured into water. The product was extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (2% MeOH/CH_2CL_2) to give **24** (0.97 g, 64%) as a yellow solid; ^{1}H NMR 1.41–1.50 (8H, m, CH$_3$, CH$_2$), 1.60–1.68 (2H, m, CH$_2$), 4.07–4.12 (2H, m, CH), 6.81 (2H, t, J=1.2 Hz, imidazole), 7.07 (2H, t, J=1.2 Hz, imidazole), 7.45 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.4, 16.6, 19.4, 32.0, 49.8, 54.4, 70.8, 73.2, 121.6, 123.6, 127.8, 127.9, 128.5, 136.7, 137.6; IR (neat) cm^{-1}: 1497, 1223, 1078; HRMS (FAB) m/z: MH^+, found 219.1608. $C_{12}H_{19}N_4$ requires 219.1610; MS (FAB$^-$) m/z: 87; $[\alpha]_D^{25}$ −22.59 (c 1.0, $CHCl_3$).

*4.4.3. [(2S,5S)-Hexane-2,5-bis(3-butylimidazolium)][bromide]$_2$ (**25**).* n-Butylbromide (14 μl, 0.013 mmol) was added dropwisely to a solution of **24** (11 mg, 0.05 mmol) in toluene (2 mL). The mixture was stirred at reflux temperature overnight. The crude product was washed with toluene, and the remaining solvent was evaporated in vacuo to give **25** (24 mg, 99%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.98 (6H, t, J=7.3 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.39 (4H, sext, J=7.3 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.60 (6H, d, J=6.7 Hz, CH$_3$C), 1.90 (4H, quint, J=6.7 Hz, CH$_3$CH$_2$CH_2CH$_2$), 2.08–2.14 (4H, m, CH_2CH), 4.26–4.35 (4H, m, CH$_3$CH$_2$CH$_2$CH_2), 5.04–5.06 (2H, m, CH), 7.26 (2H, t, J=1.8 Hz, imidazole), 8.03 (2H, t, J=1.8 Hz, imidazole), 10.19 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.5, 19.6, 21.8, 32.1, 32.8, 50.0, 57.0, 121.5, 122.1, 135.7; IR (neat) cm^{-1}: 3397, 1557, 1456, 1163; HRMS (FAB) m/z: M^+, found 332.2913. $C_{20}H_{36}N_4$ requires 332.2940; MS (FAB$^-$) m/z: 79, 81; $[\alpha]_D^{24}$ −10.77 (c 1.0, $CHCl_3$).

*4.4.4. [(2S,5S)-Hexane-2,5-bis(3-metylimidazolium)][iodide]$_2$ (**26**).* Methyl iodide (1.44 mL, 21.6 mmol) was added dropwisely to a solution of **24** (0.59 g, 2.7 mmol) in toluene (10 mL) with ice-cooling. The mixture was stirred at 80 °C for 3 h. The crude product was washed with toluene, and the remaining solvent was evaporated in vacuo to give **26** (1.26 g, 93%) as a yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.60 (6H, d, J=6.9 Hz, CH_3CH), 2.15 (4H, dd, J=2.3, 4.6 Hz, CH$_2$), 4.02 (6H, s, CH$_3$N), 4.88–4.95 (2H, m, CH), 7.18 (2H, t, J=1.7 Hz, imidazole), 7.78 (2H, t, J=1.7 Hz, imidazole), 9.85 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 18.8, 31.2, 34.4, 55.5, 119.1, 122.6, 134.3; IR (neat) cm^{-1}: 3393, 3082, 1553, 1456, 1165; HRMS (FAB) m/z: $[MI]^+$, found 375.1042. $C_{14}H_{24}N_4I$ requires 375.1046; MS (FAB$^-$) m/z: 127; $[\alpha]_D^{26}$ +4.09 (c 1.0, CH_3OH).

*4.4.5. [(2S,5S)-Hexane-2,5-bis(3-metylimidazolium)][chloride]$_2$ (**27**).* Silver chloride (1.4 g, 9.6 mmol) was added dropwisely to a solution of **26** (0.81 g, 1.6 mmol) in methanol (10 mL). The mixture was stirred room temperature overnight. The resulting AgI was filtered off and the filtrate was evaporated in vacuo to give **27** (0.51 g, quant.) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.55 (6H, d, J=6.9 Hz, CH_3CH), 1.69–1.94 (4H, m, CH$_2$), 3.92 (6H, s, CH$_3$N), 4.56 (2H, sext, J=6.9 Hz, CH), 7.58 (2H, t, J=1.7 Hz, imidazole), 7.70 (2H, t, J=1.7 Hz, imidazole), 9.07 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 20.8, 32.1, 36.0, 56.2, 120.6, 123.8, 136.5; IR (neat) cm^{-1}: 3366, 1668, 1558, 1167; HRMS (FAB) m/z: $[MCl]^+$, found 283.1692. $C_{14}H_{24}N_4Cl$ requires 283.1684; MS (FAB$^-$) m/z: 35; $[\alpha]_D^{26}$ +4.09 (c 1.0, CH_3OH).

*4.4.6. [(4S,5S)-2,2-Dimethyl-1,3-dioxolane-4,5-bis(1-methylene-3-butylimidazolium)][p-toluenesulfonate]$_2$ (**30**).* 1-Butylimidazole (0.37 g, 3.0 mmol) was added dropwisely to a solution of **28**[11] (0.50 g, 1.0 mmol) in toluene (5 mL). The mixture was stirred at reflux temperature overnight. The crude product was washed with toluene, and the remaining solvent was evaporated in vacuo to give **30** (0.72 g, quant.) as a brown amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.85 (6H, t, J=7.3 Hz, CH_3CH$_2$CH$_2$CH$_2$), 1.23 (4H, sext, J=7.3 Hz, CH$_3$CH_2CH$_2$CH$_2$), 1.31 (6H, s, CH$_3$), 1.72 (4H, quint, J=7.3 Hz, CH$_3$CH$_2$CH_2CH$_2$), 2.32 (6H, s, tosyl), 4.11 (4H, m, CH$_3$CH$_2$CH$_2$CH_2), 4.26 (2H, dt, J=14.3, 2.3 Hz, CH), 4.62 (2H, dd, J=14.3, 2.3 Hz, CH$_2$), 4.94 (2H, d, J=14.3 Hz, CH$_2$), 7.24 (2H, s, imidazole), 7.63 (2H, s, 8.0 Hz, imidazole), 9.64 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.4, 19.5, 21.4, 27.0, 31.9, 49.9, 50.3, 75.9, 111.4, 121.6, 123.9, 125.9, 128.8, 137.8, 139.5, 143.6; IR (neat) cm^{-1}: 1564, 1456, 1186, 1119, 1032, 1011; HRMS (FAB) m/z: $[MTsO]^+$, found

547.2964. $C_{28}H_{43}N_4O_5S$ requires 547.2943; MS (FAB^-) *m*/*z*: 171; $[\alpha]_D^{22}$ −27.03 (*c* 0.3, CH_3OH).

*4.4.7. [(4S,5S)-2,2-Dimethyl-1,3-dioxolane-4,5-bis(1-methylene-3-butylimidazolium)][bis(trifluoromethanesulfonyl)amide]$_2$ (**31**).* A solution of **30** (0.71 g, 0.99 mmol) and lithium bis(trifluoromethanesulfonyl)imide (0.86 g, 3.0 mmol) in water (3 mL) was stirred at room temperature overnight. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **31** (0.39 g, 42%) as a yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.94 (6H, t, *J*=7.4 Hz, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.27–1.41 (10H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$, CH$_3$), 1.85 (4H, quint, *J*=7.4 Hz, CH$_3$CH$_2$C*H*$_2$CH$_2$), 4.17–4.18 (2H, m, CH), 4.22 (4H, t, *J*=7.4 Hz, CH$_3$CH$_2$CH$_2$C*H*$_2$), 4.41 (2H, dd, *J*=14.3, 6.9 Hz, CH$_2$), 4.64 (2H, d, *J*=14.3 Hz, CH$_2$), 7.59 (4H, d, *J*=1.7 Hz, imidazole), 8.85 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 12.4, 19.0, 25.9, 31.7, 49.6, 50.4, 75.8, 111.6, 119.8 (q, *J*=1278 Hz), 122.4, 123.3, 136.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.5; IR (neat) cm^{-1}: 1562, 1464, 1346, 1179, 1132, 1051; HRMS (FAB) *m*/*z*: M^+, found 375.2761. $C_{21}H_{36}N_4O_2$ requires 375.2838. $[MNTf_2]^+$, found 656.2005. $C_{23}H_{36}N_5O_6S_2F_6$ requires 656.2011; MS (FAB^-) *m*/*z*: 280; $[\alpha]_D^{25}$ −18.50 (*c* 0.9, $CHCl_3$).

*4.4.8. (4S,5S)-1,3-Dioxolane-2-phenyl-4,5-dimethanol (**34**).* Benzaldehyde (81.2 mL, 800 mmol) and *p*-toluenesulfonic acid (1.9 mL, 10 mmol) were added to a solution of dibutyl-(L)-(+)-tartrate **31** in benzene (100 mL). The reaction flask was fitted with a Dean–Stark water separator and the mixture was stirred at reflux temperature overnight. After the neutralization with saturated $NaHCO_3$ solution, the solvent was evaporated off. The product was extracted with diethyl ether and the organic layer was dried over $MgSO_4$, filtered, and concentrated. The remaining benzaldehyde was distilled off in vacuo to give crude **32** (46g) as a yellow oil.

The crude **33** (46 g) was added dropwisely to a suspension of $LiAlH_4$ (12.4 g, 300 mmol) in dry diethyl ether (200 mL) with ice-cooling. The mixture was stirred at room temperature for 2 h, neutralized with saturated ammonium chloride solution, and then filtered. The filtrate was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (20% AcOEt/hexane) to give **34** (17.6 g, 84% in 2 steps) as a yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 2.13–2.18 (2H, m, OH), 3.75–3.90 (4H, m, CH$_2$), 4.18 (2H, td, *J*=4.9, 1.8 Hz, CH), 5.98 (1H, s, PhC*H*), 7.39–7.40 (3H, m, phenyl), 7.48 (2H, dd, *J*=2.4, 6.7 Hz, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 62.3, 62.4, 78.7, 79.6, 103.9, 126.8, 128.6, 129.8, 137.2.

*4.4.9. (4R,5R)-4,5-Bis(bromomethyl)-2-phenyl-1,3-dioxolane (**34**).* Triphenylphosphine (3.1 g, 11.5 mmol) and tetrabromomethane (4.9 g, 14.4 mmol) were added to a solution of **33** (1.0 g, 4.8 mmol) in dichloromethane (30 mL) with ice-cooling. The mixture was stirred at room temperature for 3 h, and neutralized with saturated $NaHCO_3$ solution. The product was extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (AcOEt/hexane: 1:8) to give **35** (1.4 g, 87%) as a colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 3.58–3.65 (4H, m, CH$_2$), 4.36–4.41 (2H, m, CH), 6.07 (1H, s, PhC*H*), 7.39–7.40 (3H, m, phenyl), 7.50–7.52 (2H, m, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 32.3, 32.8, 79.1, 80.1, 104.4, 127.0, 128.7, 130.0, 136.6.

*4.4.10. [(4S,5S)-2-Phenyl-1,3-dioxolane-4,5-bis(1-methylene-3-butylimidazolium)][bromide]$_2$ (**36**).* 1-Butylimidazole (1.6 g, 12.6 mmol) was added dropwisely to a solution of **35** (1.4 g, 4.2 mmol) in toluene (20 mL). The mixture was stirred at reflux temperature overnight. The crude product was washed with toluene, and the remaining solvent was evaporated in vacuo to give **36** (1.8 mg, 73%) as a brown amorphous solid; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.56–0.62 (6H, m, C*H*$_3$CH$_2$CH$_2$CH$_2$), 0.98–1.01 (4H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$), 1.47–1.55 (4H, m, CH$_3$CH$_2$C*H*$_2$CH$_2$), 3.91–4.00 (4H, m, CH$_3$CH$_2$CH$_2$C*H*$_2$), 4.35 (2H, d, *J*=38.9 Hz, CH), 4.73–4.88 (4H, m, C*H*$_2$CH), 6.09 (1H, s, PhC*H*), 7.02–7.04 (3H, m, phenyl), 7.09–7.10 (2H, m, phenyl), 7.29 (1H, s, imidazole), 7.34 (1H, s, imidazole), 7.68 (1H, s, imidazole), 7.95 (1H, s, imidazole), 9.54 (1H, s, imidazole), 9.80 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.3, 19.2, 31.7, 49.7, 76.4, 103.1, 121.8, 123.6, 124.0, 126.7, 128.3, 129.7, 135.2, 136.6, 136.8; IR (neat) cm^{-1}: 3401, 2959, 1560, 1458, 1163, 1072; HRMS (FAB) *m*/*z*: $[MBr^{79}]^+$, found 503.2003. $C_{25}H_{36}N_4O_2Br^{79}$ requires 503.2016. $[MBr^{81}]^+$, found 505.1980. $C_{25}H_{36}N_4O_2Br^{81}$ requires 505.2005; MS (FAB^-) *m*/*z*: 79, 81; $[\alpha]_D^{24}$ −55.65 (*c* 1.0, CH_3OH).

*4.4.11. [(4S,5S)-2-Phenyl-1,3-dioxolane-4,5-bis(1-methylene-3-butylimidazolium)][trifluoromethanesulfonate]$_2$ (**37**).* A solution of **16** (0.60 g, 1.0 mmol) and potassium trifluoromethanesulfonate (0.36 g, 3.0 mmol) in water (3 mL) was stirred at room temperature overnight. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **20** (0.62 g, 86%) as a brown oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.89–0.93 (6H, m, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.32–1.39 (4H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$), 1.82–1.87 (4H, m, CH$_3$CH$_2$C*H*$_2$CH$_2$), 4.14–4.18 (4H, m, CH$_3$CH$_2$CH$_2$C*H*$_2$), 4.47 (2H, td, *J*=7.3, 1.8 Hz, CH), 4.62 (1H, dd, *J*=14.6, 5.5 Hz, C*H*$_2$CH), 4.79 (1H, dd, *J*=14.6, 1.8 Hz, C*H*$_2$CH), 4.89 (1H, q, *J*=7.3 Hz, C*H*$_2$CH), 5.05 (1H, dd, *J*=14.6, 1.8 Hz, C*H*$_2$CH), 6.11 (1H, s, PhC*H*), 7.17 (2H, d, *J*=1.8 Hz, imidazole), 7.37–7.44 (5H, m, phenyl), 7.54 (1H, s, imidazole), 7.74 (1H, s, imidazole), 9.33 (1H, s, imidazole), 9.46 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 12.5, 19.0, 31.6, 31.6, 49.5, 49.5, 49.9, 50.4, 77.0, 103.7, 120.6 (q, *J*=1250 Hz), 122.3, 122.5, 123.2, 123.4, 126.7, 128.2, 129.7, 135.9, 136.6, 136.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.0; IR (neat) cm^{-1}: 1560, 1460, 1252, 1223, 1157, 1028; HRMS (FAB) *m*/*z*: M^+, found 573.2336. $C_{26}H_{36}F_3N_4O_5S$ requires 573.2353; MS (FAB^-) *m*/*z*: 149; $[\alpha]_D^{27}$ −45.59 (*c* 1.0, CH_3OH).

*4.4.12. [(4S,5S)-2-Phenyl-1,3-dioxolane-4,5-bis(1-methylene-3-butylimidazolium)][bis(trifluoromethanesulfonyl)amide]$_2$ (**38**).* A solution of **36** (0.60 g, 1.0 mmol) and lithium bis(trifluoromethanesulfonyl)imide (0.86 g, 3.0 mmol) in water (3 mL) was stirred at room temperature overnight. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **38** (0.98 g, quant.) as a yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.79–0.84 (6H, m, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.19–1.24 (4H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$), 1.64–1.77 (4H, m, CH$_3$CH$_2$C*H*$_2$CH$_2$), 3.98–4.07 (4H, m, CH$_3$CH$_2$CH$_2$C*H*$_2$), 4.28–4.40 (3H, m, CH$_2$, CH), 4.49–4.52 (2H, m, CH$_2$), 4.68 (1H, d, *J*=13.7 Hz, CH), 6.02 (1H, s, PhC*H*), 7.25–7.38 (8H, m, phenyl, imidazole), 7.47 (1H, s, imidazole), 8.48 (1H, s, imidazole), 8.66 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 12.3, 19.1, 31.6, 31.7, 50.8, 50.8, 51.3, 51.9, 77.0, 103.8, 119.9 (q, *J*=1273 Hz), 122.4, 122.6, 123.1, 126.6, 128.2, 129.7, 135.8, 136.5, 136.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.4; IR (neat) cm^{-1}: 1562, 1464, 1346, 1182, 1132, 1053; HRMS (FAB) *m*/*z*: $[MNTf_2]^+$, found 704.2000. $C_{27}H_{36}F_6N_5O_6S_2$ requires 704.2011; MS (FAB^-) *m*/*z*: 280; $[\alpha]_D^{25}$ −37.44 (*c* 1.3, CH_3OH).

*4.4.13. [(4S,5S)-2-Phenyl-1,3-dioxolane-4,5-bis(1-methylene-3-butylimidazolium)][tetrafluoroborate]$_2$ (**39**).* A solution of **36** (0.60 g, 1.0 mmol) and sodium tetrafluoroborate (0.34 g, 3.0 mmol) in water (3 mL) was stirred at room temperature overnight. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **39** (0.34 g, 57%) as a yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 0.88–0.92 (6H, m, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.24–1.35 (4H, m,

$CH_3CH_2CH_2CH_2$), 1.74–1.86 (4H, m, $CH_3CH_2CH_2CH_2$), 4.10–4.25 (4H, m, $CH_3CH_2CH_2CH_2$), 4.47–4.84 (6H, m, CH_2, CH), 6.09 (1H, s, PhC*H*), 7.34–7.44 (5H, m, phenyl), 7.62 (2H, s, imidazole), 7.64 (1H, s, imidazole), 7.67 (1H, s, imidazole), 7.76 (1H, s, imidazole), 8.95 (1H, s, imidazole), 9.07 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 12.5, 19.1, 31.7, 49.4, 49.4, 49.9, 50.3, 76.9, 103.6, 122.3, 122.5, 123.2, 123.5, 126.7, 128.2, 129.7, 135.9, 136.6, 136.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −150.9; IR (neat) cm^{-1}: 2961, 1562, 1462, 1167, 1049; HRMS (FAB) *m*/*z*: $[MBF_4]^+$, found 511.2844. $C_{25}H_{36}BF_4N_4O_2$ requires 511.2862; MS (FAB^-) *m*/*z*: 87; $[\alpha]_D^{23}$ −60.26 (*c* 1.2, CH_3OH).

*4.4.14. (S)-1-(2-Benzyloxypropyl)-2,3-dimethylimidazolium bromide (**40**).* 1-Methylimidazole (1.9 mL, 24.6 mmol) was added dropwisely to a solution of **35** (2.7 g, 8.2 mmol) in toluene (20 mL). The mixture was stirred at reflux temperature overnight. The crude product was washed with toluene, and the remaining solvent and the starting materials were distilled off using a glass tube oven to give **40** (3.0 g, 72%) as a brown amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.88 (3H, s, CH_3), 3.94 (3H, s, CH_3), 4.40–4.45 (2H, m, CH_2), 4.55–4.63 (3H, m, CH_2, CH), 4.70 (1H, dd, *J*=2.3, 14.3 Hz, CH), 5.95 (1H, s, PhC*H*), 7.30–7.41 (5H, m, phenyl), 7.70–7.72 (2H, m, imidazole), 7.80 (1H, t, *J*=1.7 Hz, imidazole), 7.84 (1H, t, *J*=1.7 Hz, imidazole), 9.15 (1H, s, imidazole), 9.19 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 35.7, 50.0, 50.4, 77.0, 103.8, 123.2, 123.4, 123.5, 123.6, 126.9, 128.3, 129.8, 136.0, 137.3, 137.6; IR (neat) cm^{-1}: 3401, 3065, 1562, 1456, 1169, 1072; HRMS (FAB) *m*/*z*: M^+, found 339.1818. $C_{19}H_{24}N_4O_2$ requires 339.1899. $[MBr^{79}]^+$, found 419.1072. $C_{19}H_{24}N_4O_2Br^{79}$ requires 419.1077. $[MBr^{81}]^+$, found 421.1050. $C_{19}H_{24}N_4O_2Br^{81}$ requires 421.1064; $[\alpha]_D^{25}$ −62.29 (*c* 1.2, CH_3OH).

*4.4.15. [(4S,5S)-2-Phenyl-1,3-dioxolane-4,5-bis(1-methylene-3-methylimidazolium)][bis(trifluoromethanesulfonyl)amide]$_2$ (**41**).* A solution of **40** (2.9 g, 5.8 mmol) and lithium bis(trifluoromethanesulfonyl)imide (5.0 g, 17.4 mmol) in water (20 mL) was stirred at room temperature for 4 h. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The solvent was evaporated in vacuo to give **37** (4.0 g, 77%) as a brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.82 (3H, s, CH_3), 3.85 (3H, s, CH_3), 4.39 (2H, d, *J*=6.9 Hz, CH_2), 4.50 (2H, dd, *J*=14.3, 6.9 Hz, CH_2), 4.58 (1H, dd, *J*=14.3, 12.0 Hz, CH), 4.66 (1H, d, *J*=12.0 Hz, CH), 5.94 (1H, s, PhC*H*), 7.32–7.40 (5H, m, phenyl), 7.69–7.70 (2H, m, phenyl), 7.72 (1H, t, *J*=1.7 Hz, imidazole), 7.74 (1H, t, *J*=1.7 Hz, imidazole), 9.05 (1H, s, imidazole), 9.08 (1H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 133.8, 33.9, 48.4, 49.0, 75.5, 75.5, 102.5, 118.3 (q, *J*=1273 Hz), 119.6, 121.5, 121.7, 122.1, 122.2, 125.2, 126.8, 128.3, 134.4, 137.1, 137.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −80.1; IR (neat) cm^{-1}: 1562, 1456, 1346, 1173, 1132, 1049; HRMS (FAB) *m*/*z*: M^+, found 339.1836. $C_{19}H_{24}N_4O_2$ requires 339.1899. $[MNTf_2]^+$, found 620.1075. $C_{21}H_{24}N_5O_6S_2F_6$ requires 620.1072; MS (FAB^-) *m*/*z*: 280; $[\alpha]_D^{25}$ −39.73 (*c* 1.2, CH_3OH).

*4.4.16. (2R,3R)-1,4-Dibromobutane-2,3-diol (**42**).* Palladium carbon (5%, 60 mg) and several drops of hydrochloric acid were added to a solution of **35** (1.0 g, 4.8 mmol) in methanol (50 mL). The mixture was stirred at room temperature for 3 h under H_2 atmosphere and filtered. The filtrate was concentrated. Then the residue was purified by silica gel chromatography (AcOEt/hexane: 1:2) to give **42** (0.26 g, 62%) as a colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.56 (2H, d, *J*=5.2 Hz, OH), 3.50 (2H, dd, *J*=10.3, 5.2 Hz, CH_2), 3.55 (2H, dd, *J*=10.3, 5.2 Hz, CH_2), 3.99 (2H, dt, *J*=5.2, 5.2 Hz, CH).; ^{13}C NMR (126 MHz, $CDCl_3$) δ: 34.7, 71.5.

*4.4.17. [(2S,3S)-2,3-Dihydroxybutane-1,4-bis(3-butylimidazolium)][bromide]$_2$ (**43**).* 1-Butylimidazole (1.8 g, 12.6 mmol) was added dropwisely to a solution of **42** (1.2 g, 4.8 mmol) in toluene (20 mL). The mixture was stirred at reflux temperature overnight. The crude product was washed with toluene, and the remaining solvent was evaporated off. The residue was purified by silica gel chromatography (4% methanol/dichloromethane) to give **43** (1.6 mg, 66%) as a brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.90–0.94 (6H, m, $CH_3CH_2CH_2CH_2$), 1.31–1.42 (4H, m, $CH_3CH_2CH_2CH_2$), 1.87 (4H, quint, *J*=7.4, $CH_3CH_2CH_2CH_2$), 4.24 (4H, t, *J*=7.4 Hz, $CH_3CH_2CH_2CH_2$), 4.31–4.35 (2H, m, CH), 4.52 (2H, dd, *J*=14.3, 8.6 Hz, CH_2CH), 4.65 (2H, dd, *J*=14.3, 2.9 Hz, CH_2CH), 5.08 (2H, d, *J*=5.7, OH), 7.33 (2H, s, imidazole), 7.89 (2H, s, imidazole), 9.59 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.6, 19.6, 31.9, 49.9, 52.9, 69.9, 121.5, 124.1, 136.8; IR (neat) cm^{-1}: 3088, 1562, 1456, 1161, 1120, 1070; HRMS (FAB) *m*/*z*: $[M]^+$, found 335.2448. $C_{18}H_{32}N_4O_2$ requires 335.2447. $[MBr^{79}]^+$, found 415.1684. $C_{18}H_{32}N_4O_2Br^{79}$ requires 415.1703. $[MBr^{81}]^+$, found 417.1675. $C_{18}H_{32}N_4O_2Br^{81}$ requires 417.1690; $[\alpha]_D^{26}$ −11.41 (*c* 1.0, CH_3OH).

*4.4.18. [(2S,3S)-2,3-Dihydroxybutane-1,4-bis(3-butylimidazolium)][bis(trifluoromethanesulfonyl)amide]$_2$ (**44**).* A solution of **43** (1.5 g, 1.6 mmol) and lithium bis(trifluoromethanesulfonyl)imide (1.4 g, 4.9 mmol) in water (5 mL) was stirred at room temperature for 6 h. The product was extracted with chloroform. The organic layer was washed with brine, dried over $NaSO_4$, and filtered. The filtrate was concentrated and purified by silica gel chromatography (4% methanol/dichloromethane) to give **44** (1.5 g, quant.) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.96 (6H, t, *J*=7.4 Hz, $CH_3CH_2CH_2CH_2$), 1.36 (4H, sext, *J*=7.4 Hz, $CH_3CH_2CH_2CH_2$), 1.86 (4H, quint, *J*=7.4 Hz, $CH_3CH_2CH_2CH_2$), 3.95 (2H, dd, *J*=2.9, 9.2 Hz, CH), 4.22 (4H, t, *J*=7.4 Hz, $CH_3CH_2CH_2CH_2$), 4.29 (2H, dd, *J*=9.2, 14.3 Hz, CH_2), 4.37 (2H, dd, *J*=2.9, 14.3 Hz, CH_2), 7.58 (2H, t, *J*=1.7 Hz, imidazole), 7.61 (2H, t, *J*=1.7 Hz, imidazole), 8.87 (2H, s, imidazole); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.6, 19.6, 31.9, 49.9, 52.9, 69.9, 119.8 (q, *J*=1273 Hz), 122.3, 123.1, 136.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −79.9; IR (neat) cm^{-1}: 3501, 1564, 1464, 1346, 1180, 1130, 1051; HRMS (FAB) *m*/*z*: $[MNTf_2]^+$, found 616.1675. $C_{20}H_{32}N_5O_6S_2$ requires 616.1693; MS (FAB^-) *m*/*z*: 280; $[\alpha]_D^{27}$ −7.71 (*c* 1.3, CH_3OH).

4.5. General procedure for Michael addition in CIL

Chalcone (0.1 mmol), malonate esters (0.12 mmol), and K_2CO_3 (0.3 mmol) were added to a mixture of CIL (1.1 mmol) and toluene (0.1 mL). The mixture was stirred at room temperature, and then the crude product was extracted by washing the CIL layer with diethyl ether several times. The extracts were combined and concentrated. The residue was purified by silica gel chromatography (20% ethyl acetate/hexane) to obtain Michael adducts.

*4.5.1. Diethyl 2-(3-oxo-1,3-diphenylpropyl)malonate (**50a**).*[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.99 (3H, t, *J*=7.2 Hz, CH_3CH_2), 1.23 (3H, t, *J*=7.2 Hz, CH_3CH_2), 3.45 (1H, q, *J*=9.2 Hz, CH_3CH_2), 3.54 (1H, dd, *J*=16.0, 4.6 Hz, CH_3CH_2), 3.82 (1H, d, *J*=9.2 Hz, EtO_2CCH), 3.94 (2H, q, *J*=7.1 Hz, CH_3CH_2), 4.17–4.20 (3H, m, PhC*H*, $PhCOCH_2$), 7.14–7.17 (1H, m, phenyl), 7.21–7.27 (4H, m, phenyl), 7.41 (2H, t, *J*=7.7 Hz, phenyl), 7.51 (1H, t, *J*=7.7 Hz, phenyl), 7.89 (2H, d, *J*=6.9 Hz, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.9, 14.1, 40.9, 42.7, 57.7, 61.5, 61.8, 127.2, 128.2, 128.3, 128.5, 128.6, 133.2, 136.9, 140.5, 167.9, 168.5, 197.6; Analytical chiral HPLC: Daicel CHIRALPAK AD column, 0.46×25 cm, hexane/2-propanol=9/1, 1.0 mL min^{-1}, 19.9 min, 33.0 min.

*4.5.2. Diethyl 2-[1-(naphthalen-1-yl)-3-oxo-3-phenylpropyl]malonate (**51a**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.88 (3H, t, *J*=7.3 Hz, CH_3CH_2), 1.19 (3H, t, *J*=7.3 Hz, CH_3CH_2), 3.73 (2H, q, *J*=6.9 Hz, CH_3CH_2), 3.87 (2H, q, *J*=6.9 Hz, CH_3CH_2), 4.03 (1H, d, *J*=8.5, EtO_2CCH), 4.10–4.23 (2H, m, $PhCOCH_2$), 5.14–5.16 (1H, m, NaphC*H*), 7.35–7.54 (7H, m, aromatic), 7.70 (1H, d, *J*=8.5 Hz, aromatic), 7.81 (1H, d, *J*=8.5 Hz, aromatic), 7.88 (2H, dd, *J*=8.5, 1.8 Hz, aromatic),

8.30 (1H, d, J=8.5 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.7, 14.1, 38.8, 42.4, 57.2, 61.5, 61.7, 123.5, 125.2, 125.7, 126.4, 128.2, 128.6, 128.9, 133.0, 131.6, 132.5, 133.1, 136.8, 168.0, 168.7, 197.7; HRMS (FAB) m/z: M^+, found 418.1767. $C_{26}H_{26}O_5$ requires 418.1780; Analytical chiral HPLC: Daicel CHIRALPAK AD column, 0.46×25 cm, hexane/2-propanol=9/1, 1.0 mL min^{-1}, 22.1 min, 34.9 min.

*4.5.3. Diethyl 2-[1-(naphthalen-1-yl)-3-(naphthalen-2-yl)-3-oxopropyl]malonate (**52a**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.90 (3H, t, J=7.4 Hz, CH_3CH_2), 1.20 (3H, t, J=7.4 Hz, CH_3CH_2), 3.88–3.91 (4H, m, CH_3CH_2), 4.08–4.23 (3H, m, EtO_2CCH, 2-NaphCH_2), 5.22–5.24 (1H, m, 1-NaphCH), 7.37 (1H, t, J=7.4 Hz, aromatic), 7.47 (2H, t, J=6.8 Hz, aromatic), 7.69 (1H, d, J=7.9 Hz, aromatic), 7.81–7.93 (8H, m, aromatic), 8.08 (1H, dt, J=12.7, 5.2 Hz, aromatic), 8.33 (1H, d, J=8.5 Hz, aromatic); Analytical chiral HPLC: Daicel CHIRALPAK AD column, 0.46×25 cm, hexane/2-propanol=9/1, 0.8 mL min^{-1}, 40.5 min, 52.3 min.

*4.5.4. Diethyl 2-(1-(anthracen-9-yl)-3-oxo-3-phenylpropyl)malonate (**53a**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.18–1.21 (6H, m, CH_3CH_2), 3.36–3.47 (2H, m, CH_3CH_2), 3.79 (1H, dd, J=17.5, 6.1 Hz, PhCOCH_2), 3.98 (1H, dd, J=17.5, 4.9 Hz, PhCOCH_2), 4.13–4.18 (2H, m, CH_3CH_2), 4.59 (1H, d, J=11.6 Hz, EtO_2CCH), 6.03–6.07 (1H, m, ArCH), 7.28 (2H, t, J=8.0 Hz, aromatic), 7.34–7.52 (5H, m, aromatic), 7.77 (2H, d, J=8.0 Hz, aromatic), 7.85 (1H, d, J=7.9 Hz, aromatic), 7.95 (1H, d, J=8.0 Hz, aromatic), 8.29–8.31 (2H, m, aromatic), 8.76 (1H, d, J=9.2 Hz, aromatic); HRMS (FAB) m/z: M^+, found 468.1922. $C_{30}H_{28}O_5$ requires 468.1937; Analytical chiral HPLC: Daicel CHIRALPAK AD column, 0.46×25 cm, hexane/2-propanol=9/1, 1.0 mL min^{-1}, 32.7 min, 42.5 min.

*4.5.5. Di-tert-butyl 2-(3-oxo-1,3-diphenylpropyl)malonate (**50b**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.18 (9H, s, CH_3C), 1.46 (9H, s, CH_3C), 3.39 (1H, dd, J=15.5, 9.7 Hz, CH_2), 3.50 (1H, dd, J=15.5, 4.0 Hz, CH_2), 3.63 (1H, d, J=9.7 Hz, CH), 4.06 (1H, td, J=15.5, 4.0 Hz, CH), 7.12-7.15 (1H, m, phenyl), 7.19-7.25 (4H, m, phenyl), 7.40 (2H, t, J=7.4 Hz, phenyl), 7.51 (1H, t, J=7.4 Hz, phenyl), 7.88 (2H, dd, J=8.0, 1.1 Hz, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 27.6, 28.0, 40.9, 43.4, 59.4, 81.6, 82.1, 127.0, 128.2, 128.3, 128.6, 128.6, 133.0, 137.0, 140.8, 167.1, 167.9, 197.9; Analytical chiral HPLC: Daicel CHIRALPAK AD column, 0.46×25 cm, hexane/2-propanol=9/1, 1.0 mL min^{-1}, 22.7 min, 36.9 min.

*4.5.6. 2,2-Dimethyl-5-(3-oxo-1,3-diphenylpropyl)-1,3-dioxane-4,6-dione (**50c**).*[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.35 (3H, s, CH_3), 1.68 (3H, s, CH_3), 3.60 (1H, dd, J=19.0, 5.0 Hz, PhCOCH_2), 4.29 (1H, dd, J=19.0, 10.5 Hz, PhCOCH_2), 4.34 (1H, d, J=3.5 Hz, CH), 4.47–4.51 (1H, m, Ph CH), 7.25–7.28 (1H, m, phenyl), 7.32 (2H, t, J=8.5 Hz, phenyl), 7.42 (2H, d, J=7.5 Hz, phenyl), 7.47 (2H, t, J=8.5 Hz, phenyl), 7.56–7.59 (2H, t, J=7.5 Hz, phenyl), 8.00 (2H, d, J=8.5 Hz, phenyl); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 28.0, 28.2, 40.0, 40.9, 49.4, 105.4, 127.9, 128.2, 128.8, 128.9, 129.0, 133.6, 136.7, 140.1, 165.4, 165.6, 199.2; HRMS (FAB) m/z: M^+, found 353.1414. $C_{21}H_{21}O_5$ requires 353.1389; Analytical chiral HPLC: Daicel CHIRALPAK AD-H column, 0.46×15 cm, hexane/2-propanol=9/1, 0.8 mL min^{-1}, 20.1 min, 29.6 min.

*4.5.7. 2,2-Dimethyl-5-[1-(naphthalen-1-yl)-3-oxo-3-phenylpropyl]-1,3-dioxane-4,6-dione (**51c**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.62 (3H, s, CH_3), 1.68 (3H, s, CH_3), 3.82 (1H, dd, J=18.0, 6.0 Hz, PhCOCH_2), 4.06 (1H, dd, J=18.0, 9.5 Hz, PhCOCH_2), 4.16 (1H, d, J=2.5 Hz, CH), 5.39–5.43 (1H, m, ArCH), 7.43–7.48 (3H, m, aromatic), 7.51–7.62 (3H, m, aromatic), 7.71 (1H, d, J=7.5 Hz, aromatic), 7.79 (1H, d, J=8.5 Hz, aromatic), 7.88 (1H, d, J=7.5, aromatic), 7.98 (2H, d, J=7.0 Hz, aromatic), 8.29 (1H, d, J=8.5 Hz, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 27.6, 28.3, 33.7, 39.9, 49.4, 105.3, 122.7, 125.3, 125.6, 126.0, 127.1, 128.2, 128.3, 128.7, 129.3, 131.1, 133.6, 134.2, 136.6, 137.4, 164.8, 166.2, 199.2; HRMS (FAB) m/z: M^+, found 402.1460. $C_{25}H_{22}O_5$ requires 402.1467.

The obtained **50c** was converted to dimethyl 2-[1-(naphthalen-1-yl)-3-oxo-3-phenylpropyl]malonate for HPLC analysis as follows: Ring-opening reaction with methanol in refluxing toluene to a carboxylic acid (monoester) and esterification with diazomethane; Analytical chiral HPLC: Daicel CHIRALPAK AD-H column, 0.46×15 cm, hexane/2-propanol=9/1, 1.0 mL min^{-1}, 31.6 min, 34.1 min.

*4.5.8. 2,2-Dimethyl-5-(1-(naphthalen-1-yl)-3-(naphthalen-2-yl)-3-oxopropyl)-1,3-dioxane-4,6-dione (**52c**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.64 (3H, s, CH_3), 1.69 (3H, s, CH_3), 3.97 (1H, dd, J=18.0, 5.5 Hz, 2-NaphCOCH_2), 4.16–4.21 (2H, m, CH, 2-NaphCOCH_2), 5.45–5.48 (1H, m, 1-NaphCH), 7.47–7.62 (5H, m, aromatic), 7.77 (1H, d, J=7.5 Hz, aromatic), 7.81 (1H, d, J=8.5 Hz, aromatic), 7.89–7.92 (4H, m, aromatic), 8.03 (1H, dd, J=8.5, 2.0 Hz, aromatic), 8.32 (1H, d, J=8.5 Hz, aromatic), 8.52 (1H, s, aromatic); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 27.6, 28.4, 34.0, 39.9, 49.5, 105.3, 122.7, 123.9, 125.3, 125.6, 126.0, 126.9, 127.1, 127.9, 128.3, 128.6, 128.7, 129.3, 129.8, 130.2, 131.1, 132.5, 133.9, 134.2, 135.8, 137.4, 164.8, 166.2, 199.3; HRMS (FAB) m/z: M^+, found 452.1614. $C_{29}H_{29}O_5$ requires 452.1624; Analytical chiral HPLC: Daicel CHIRALPAK AD-H column, 0.46×15 cm, hexane/2-propanol=9/1, 1.0 mL min^{-1}, 27.8 min, 41.6 min.

References and notes

1. (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083; (b) Rogers, R. D.; Voth, G. A. *Acc. Chem. Res.* **2007**, *40*, 1077–1078; (c) Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40*, 1079–1086; (d) Giernoth, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 5608–5609.
2. Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965–967.
3. Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A.-C.; Plaquevent, J.-C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081–3093.
4. (a) Seebach, D.; Oei, H. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 634–636; (b) Laarhoven, W. H.; Cuppen, T. J. M. *J. Chem. Soc., Chem. Commun.* **1977**, 47a–47a; (c) Ulbert, O.; Szarka, Á.; Halasi, S.; Somogyi, B.; Belafi-Bako, K.; Gubicza, L. *Biotechnol. Tech.* **1999**, *13*, 299–302; (d) Verbit, L.; Halvert, T. R.; Patterson, R. B. *J. Org. Chem.* **1975**, *40*, 1649–1650.
5. For reviews see: (a) Baudequin, C.; Bregeon, D. J.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A.-C. *Tetrahedron: Asymmetry* **2005**, *16*, 3921–3945; (b) Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281–292; (c) Chen, X.; Li, X.; Hu, A.; Wang, F. *Tetrahedron: Asymmetry* **2008**, *19*, 1–14; (d) Payagala, T.; Armstrong, D. W. *Chirality* **2012**, *24*, 17–25.
6. (a) Pegot, B.; Vo-Thanh, G.; Gori, D.; loupy, A. *Tetrahedron Lett.* **2004**, *45*, 6425–6428; (b) Wang, Z.; Wang, Q.; Zhang, Y.; Bao, W. *Tetrahedron Lett.* **2005**, *46*, 4657–4660; (c) Ding, J.; Desikan, V.; Han, X.; Xiao, T. L.; Ding, R.; Jenks, W. S.; Armstrong, D. W. *Org. Lett.* **2005**, *7*, 335–337; (d) Schulz, P. S.; Müller, N.; Bösmann, A.; Wasserscheid, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1293–1295.
7. Bao, W.; Wang, Z.; Li, Y. *J. Org. Chem.* **2003**, *68*, 591–593.
8. Singh, R. P.; Manandhar, S.; Shreeve, J. M. *Synthesis* **2003**, 1579–1585.
9. (a) Anderson, J. L.; Ding, R.; Ellern, A.; Armstrong, D. W. *J. Am. Chem. Soc.* **2005**, *127*, 593–604; (b) Han, X.; Armstrong, D. W. *Org. Lett.* **2005**, *7*, 4205–4208.
10. Meca, L.; Cisarova, I.; Dvorak, D. *Organometallics* **2003**, *22*, 3703–3709.
11. For selected examples of Michael addition using ionic liquids as catalysts or solvents see: (a) Luo, S.; Mi, X.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J.-P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3093–3097; (b) Ni, B.; Zhang, Q.; Headley, A. D. *Green Chem.* **2007**, *9*, 737–739; (c) Mečiarová, M.; Toma, S. *Chem.—Eur. J.* **2007**, *13*, 1268–1272.
12. Machado, M. Y.; Dorta, R. *Synthesis* **2005**, 2473–2475.
13. Chong, J. M.; Shen, L.; Taylor, N. J. *J. Am. Chem. Soc.* **2000**, *122*, 1822–1823.
14. Robinson, T. P.; Hubbard, R. B., IV; Ehlers, T. J.; Arbiser, J. L.; Goldsmith, D. J.; Bowen, J. P. *Bioorg. Med. Chem.* **2005**, *13*, 4007–4013.
15. Huang, K.; Breitbach, Z. S.; Armstrong, D. W. *Tetrahedron: Asymmetry* **2006**, *17*, 2821–2832.
16. Mizukami, S.; Kihara, N.; Endo, T. *Tetrahedron Lett.* **1993**, *34*, 7437–7440.