Title

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Non-Covalently Immobilized Chiral Imidazolidinone on Sulfated-Chitin: Reusable Heterogeneous Organocatalysts for Asymmetric Diels-Alder Reaction

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Abstract. A heterogeneous chiral imidazolodinone catalyst was synthesized by immobilization on a sulfated chitin through non-covalent ionic interactions. The chitin-based organocatalyst promoted the asymmetric Diels-Alder reaction with high enantioselectivity under heterogeneous conditions and was successfully reused multiple times without apparent loss of catalytic activity and enantioselectivity.

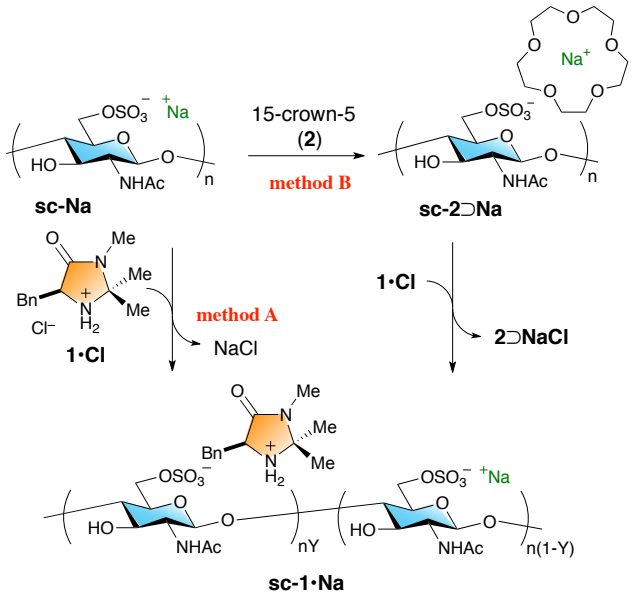
Keywords: Organocatalysis; heterogeneous catalysis; asymmetric Diels-Alder reaction; imidazolidinone; chitin

The development of polymer-immobilized chiral organocatalysts has attracted increasing attention owing to the advantages such as ready product separation, and catalyst reusability, due to which these catalysts are major contributors to green and sustainable chemistry.[1] The immobilization of organocatalysts has been typically performed by covalent attachment onto artificial polymer scaffolds, which generally requires time- and cost-intensive polymeric catalyst synthesis. In addition, the random conformation of the polymers and the chemical modifications for attaching the covalent linkages around the catalytically active sites often results in decreased catalytic activity and selectivity of the immobilized catalyst in comparison with the corresponding small molecule catalysts. Therefore, development of a simple immobilization method which uses readily accessible stereocontrolled polymer scaffolds and avoids chemical modification of the catalyst is necessary.

Chitin is the world's second most abundant biopolymer with global reserves of 10^{11} tons and is routinely extracted from crustacean shells, insect exoskeletons, and fungi.[2] It is chemically stable but is also degradable under specific conditions. It has poor solubility in common solvents and contains many functionalities which offer possibilities for modification. Furthermore, chitins tend to form a regular helical conformation in cristalin[3] and solution phases.[4] If these linear helical polymers are employed as solid supports for organocatalysts, their controlled regular structure is expected to provide a uniform stereocontrolled reaction field around the supported catalyst, which may minimalize the loss of catalytic activity due to immobilization. Indeed, the well-controlled helical conformation of the polymers has recently been proved effective for enhancing both the enantioselectivity and catalytic activity of the supported catalysts.[5]

With the anticipation that the use of the easily available chitin would further open up opportunities for the preparation of diverse and efficient polymer-based catalysts, we recently developed a novel chitin-based achiral supramolecular catalyst.[6] In that study, we took advantage of the ionic immobilization strategy for cationic catalysts,[7,8] where ionic interactions between organocatalysts and the synthetic polymer supports were used for catalyst preparation instead of the conventional covalent bonding linkages. As a result, we demonstrated the use of a reusable supramolecular catalyst in which flavinium and alkali metal cations were non-covalently assembled on anionic sulfated-chitin via ionic interactions without the chemical modification.[6] Due to the cooperative catalysis of the flavinium, alkali metal, and sulfated chitin, the heterogeneous supramolecular catalyst afforded superior catalytic activity for Baeyer-Villiger oxidation of ketones in comparison with the corresponding homogeneous flavinium catalyst. To apply this strategy to asymmetric organocatalysis, we report herein, the synthesis of the first set of chitin-immobilized chiral organocatalysts (**sc-1•Na**s) which use an anionic sulfated-chitin (**sc-Na**) as a scaffold and the commercially available chiral imidazolidinone (**1**) as a cationic organocatalyst module. Furthermore, we investigated the catalytic activity, enantioselectivity, and reusability of the prepared catalyst for catalyzing an asymmetric Diels-Alder reaction.

Chiral imidazolidinones (**1**) developed by MacMillan are versatile cationic organocatalysts for diverse asymmetric transformations including asymmetric Diels-Alder reactions, 1,3-dipolar cycloadditions, Friedel-Crafts alkylations and so on,[9] and a series of these catalysts are commercially available.[10] Owing to the typical challenges faced in the recovery and reuse of these catalysts, several approaches for immobilizing imidazolidinone derivatives onto solid supports have been developed.[7d,11] However, these immobilization processes often suffer from tedious synthetic routes, low selectivities, and efficiencies. Despite the many advances in this area, the development of a facile approach which provides eco-friendly immobilized heterogeneous chiral imidazolidinone catalysts with high enantioselectivity and catalytic activity remains a challenge.



Scheme 1. Synthesis of **sc-1•Na** via ion-exchange reaction between **1•Cl** and **sc-Na**.

The chitin-immobilized imidazolidinone catalysts **sc-1•Na**s were readily prepared by an ion-exchange reaction between **1•Cl** and 6-*O*-sulfated chitin (**sc-Na**), which was synthesized by the simple sulfation of commercially available chitin (Scheme 1)[12] and the results for the synthesis are summarized in Table 1. The ion-exchange reaction between **1•Cl** and lyophilized **sc-Na** (degree of sulfation, D.S. = 0.99 equiv., Supporting Information) was first carried out under heterogeneous conditions by soaking **sc-Na** in a MeOH solution of **1•Cl** for 30 min, according to the procedure used for the preparation of chitin-immobilized flavinium catalyst (entries 1 and 2 in Table 1, method A in Scheme 1).[6] Since the obtained supramolecular **sc-1•Na** showed moderate solubility in H_2O, the amount of immobilized **1** (degree of immobilization, D.I.) was estimated by NMR analysis in D_2O. When 0.16 and 10 equivs. of (*S*)-**1•Cl** were used in MeOH (0.08 M), **sc-1•Na**s with 11% D.I. (**sc-1**$^{S}_{0.11}$**•Na**) and 50% D.I. (**sc-1**$^{S}_{0.50}$**•Na**) were obtained, respectively (entries 1 and 2). To achieve complete exchange the Na^+ ion of **sc-Na** with **1**, we prepared **sc-2⊃Na** by complexation of **sc-Na** with 15-crown-5 (**2**) and attempted the ion-exchange reaction between (*S*)-**1•Cl** and **sc-2⊃Na** in H_2O under homogeneous conditions (method B in Scheme 1). After stirring an aqueous solution of (*S*)-**1•Cl** and **sc-2⊃Na** for 15 min, the reaction mixture was washed with Et_2O and the residue was reprecipitated in EtOH to afford **sc-1**$^{S}_{0.97}$**•Na** with 97% D.I. (entry 3 in Table 1). Importantly, this immobilization experiment was reproducible (entries 3 and 4). Similarly, the use of (*R*)-**1•Cl** afforded poly-**1•2**$^{R}_{0.96}$ without a significant difference of D.I. (entry 5). The ^{1}H NMR spectra of (*S*)-**2•Cl**, poly-**1•Na**, poly-**1•2**$^{S}_{0.98}$, and **sc-1**$^{R}_{0.96}$**•Na** in D_2O revealed that the immobilization occurred without any decomposition of **1** or the sulfated chitin (Figure 1A (a-d)). Figure 1B shows the photographs and SEM images of **sc-Na** (f and h) and **sc-1**$^{S}_{0.97}$**·Na** (g and i). After immobilization of **1**, the original microfibers of the lyophilized sulfated chitin grew slightly, but the three-dimensional sponge-like scaffold with relatively large surface area remained without any significant change (Figure 1B (h and i)). Interestingly, the diastereomeric pair, **sc-1**$^{S}_{0.97}$**•Na**, and **sc-1**$^{R}_{0.96}$**•Na** showed nearly identical signals,

Table 1. Immobilization of cationic **1** on anionic **sc-Na**

Entry	Sulfated chitin	Catalyst (equiv.)	Product	D.I.[a] (Y, equiv.)	Yield (%)
1[b]	**sc-Na**	(*S*)-**1•Cl** (0.16)	**sc-1**$^{S}_{0.11}$**•Na**	0.11	96
2[b]	**sc-Na**	(*S*)-**1•Cl** (10)	**sc-1**$^{S}_{0.50}$**•Na**	0.50	97
3[c]	**sc-2⊃Na**	(*S*)-**1•Cl** (20)	**sc-1**$^{S}_{0.97}$**•Na**	0.97	90
4[c]	**sc-2⊃Na**	(*S*)-**1•Cl** (20)	**sc-1**$^{S}_{0.98}$**•Na**	0.98	90
5[c]	**sc-2⊃Na**	(*R*)-**1•Cl** (20)	**sc-1**$^{R}_{0.96}$**•Na**	0.96	78
6[b,d]	**sc**$_{0.55}$**-Na**	(*S*)-**1•Cl** (5.5)	**sc**$_{0.55}$**-1**$^{S}_{0.15}$**•Na**	0.15	95

[a] Determined by ^{1}H NMR. [b] Immobilization was carried out heterogeneously by soaking **sc-Na** in a solution of **1•Cl** in MeOH (0.08 M) for 30 min at ca. 25 ˚C. [c] The immobilization was carried out homogeneously by mixing **sc-2⊃Na** (0.08 M) and **1•Cl** in H_2O for 15 min at ca. 25 ˚C. [d] **sc**$_{0.55}$**-Na** was used.

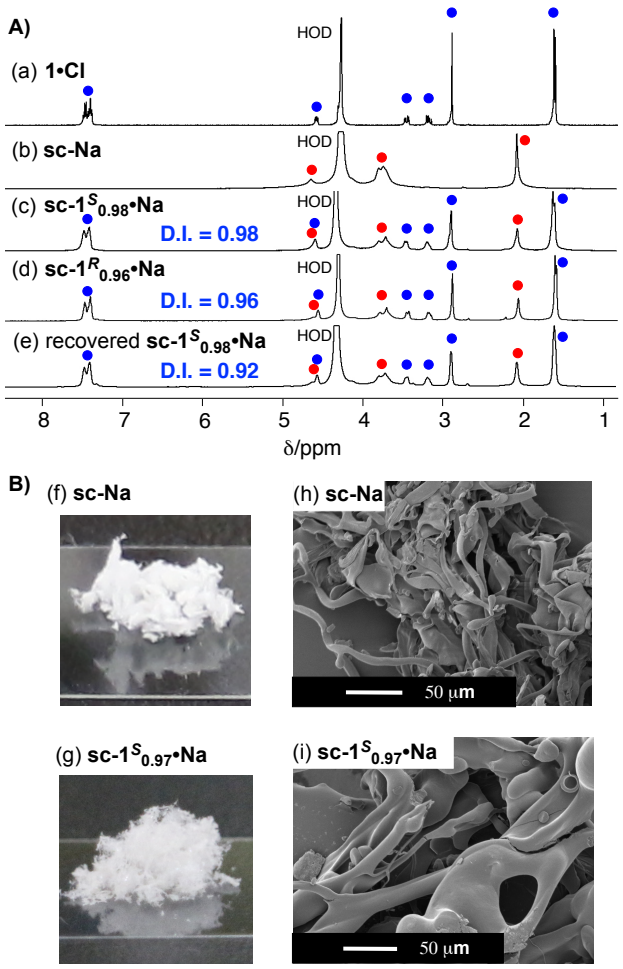
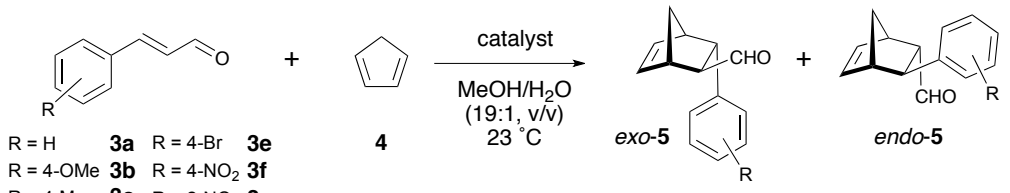


Figure 1. (A) ^{1}H NMR spectra (500 MHz, D_2O, 80 ˚C) of **1•Cl** (a), **sc-Na** (b), **sc-1$^S_{0.98}$•Na** (c), **sc-1$^R_{0.96}$•Na** (d), and recovered **sc-1$^S_{0.98}$•Na** collected after the asymmetric Diels-Alder reaction (Entry 10 in Table 2). (B) Photographs (f,g) and SEC images (h,i) of **sc-Na** and **sc-1$^S_{0.97}$•Na**.

which suggested that the chirality of chitin may not significantly affect the inherent chirality of **1**. The supramolecular catalyst, **sc$_{0.55}$-1$^S_{0.15}$•Na** was also prepared from partially sulfated **sc$_{0.55}$-Na** (D.S. = 0.55 equiv, entry 6).

Having prepared a series of chitin-immobilized catalysts, we turned attention to studying their catalytic activity. We began with the evaluation of the catalysis of the Diels-Alder reaction between **3a** and **4** in MeOH/H_2O at 23 ˚C, which is known to proceed in an asymmetric fashion with the use of **1•Cl** (entry 1, Table 2),[9a] using **sc-1•Na**s, and were pleased to see that the reaction proceeded in an asymmetric fashion. A series of **sc-1•Na**s with different D.I. successfully promoted the catalytic asymmetric Diels-Alder reaction under heterogeneous conditions, and furnished the corresponding exo- and endo-(*2S*)-**5a** in high enantioselectivity (entries 2-4 in Table 2). Both catalytic activity and enantioselectivity appeared to be dependent on D.I. and increased with increasing D.I., and as a result, **sc-1$^S_{0.97}$•Na** provided the highest level of enantioselectivity (exo 91% ee, endo 92% ee, entry 4). While immobilization of homogeneous chiral catalysts onto solid supports is often known to result in a decrease of their inherent enantioselectivity, it is noteworthy that the catalytic activity and enantioselectivity of heterogeneous **sc-1$^S_{0.97}$•Na** was almost comparable to that of the unsupported homogeneous catalyst **1•Cl** (entry 1). Interestingly, **Sc$_{0.55}$-1$^S_{0.15}$•Na** (D.S. = 0.55 equiv) showed a relatively lower enantioselectivity than that of the corresponding **sc-1$^S_{0.11}$•Na** (D.S. = 0.99 equiv, entries 2 and 5). The observed D.I. and D.S. effects suggested that the high catalytic activity and enantioselectivity of **sc-1$^S_{0.97}$•Na** originates from its high degree of the structural uniformity. **Sc-1$^R_{0.96}$•Na** which immobilizes (*R*)-**1** gave the exo- and endo-(*2R*)-**5** with almost comparable enantioselectivity (exo 88% ee, endo 90% ee) to its diastereomeric isomer **sc-1$^S_{0.97}$•Na** without significant match-mismatch effect (entry 6). The chirality of chitin did not seriously affect the chiral reaction field of **1**, as revealed by the ^{1}H NMR measurement (Figure 1A (c and d)). Therefore, **sc-Na** can be used as a universal support for (*R*)- and (*S*)-**1** without consideration of the match-mismatch effects. The weak and loose ionic interactions of the organocatalyst with the chiral sulfated chitin likely prevents a significant decrease of the inherent enantioselectivity of the well-designed organocatalyst.

Table 2. Asymmetric Diels-Alder reaction catalyzed by **sc-1•Na**[a]



R = H **3a** R = 4-Br **3e**
R = 4-OMe **3b** R = 4-NO_2 **3f**
R = 4-Me **3c** R = 2-NO_2 **3g**
R = 4-Cl **3d**

4

exo-**5**

endo-**5**

Entry	Catalyst (mol%)	Product	Time (h)	Yield[b] (%)	*Exo*:*endo*[c]	*Ee*[d] (*exo*, %)	*Ee*[e] (*endo*, %)
1	(*S*)-**1•Cl** (5)	**5a**	72	74	1.3:1	90 (2*S*)	91 (2*S*)
2	**sc-1**$^{S}_{0.11}$**•Na** (5)	**5a**	72	47	1.1:1	88 (2*S*)	86 (2*S*)
3	**sc-1**$^{S}_{0.89}$**•Na** (5)	**5a**	72	50	1.2:1	90 (2*S*)	90 (2*S*)
4	**sc-1**$^{S}_{0.97}$**•Na** (5)	**5a**	72	66	1.2:1	91 (2*S*)	92 (2*S*)
5	**sc**$_{0.03}$**-1**$^{R}_{0.35}$**•Na** (5)	**5a**	72	59	1.1:1	84 (2*S*)	79 (2*S*)
6	**sc-1**$^{R}_{0.98}$**•Na** (5)	**5a**	72	60	1.2:1	88 (2*R*)	90 (2*R*)
7	**sc-1**$^{S}_{0.98}$**•Na** (20)	**5a**	24	82[e]	1.2:1[e]	91 (2*S*)[e]	93 (2*S*)[e]
8	**sc-1**$^{S}_{0.98}$**•Na** (20), 1[e]	**5a**	24	91	1.2:1	91 (2*S*)	93 (2*S*)
9	2[e] reuse	**5a**	24	81	1.2:1	90 (2*S*)	90 (2*S*)
10	3[e] reuse	**5a**	24	81	1.2:1	91 (2*S*)	91 (2*S*)
11	4[e] reuse	**5a**	24	80	1.2:1	91 (2*S*)	93 (2*S*)
12	5[e] reuse	**5a**	24	79	1.2:1	90 (2*S*)	91 (2*S*)
13	**sc-1**$^{S}_{0.97}$**•Na** (20)	**5b**	72	80	1.3:1	93[f]	94[f]
14	**sc-1**$^{S}_{0.97}$**•Na** (20)	**5c**	48	77	1.3:1	90[f]	92[f]
15	**sc-1**$^{S}_{0.97}$**•Na** (20)	**5d**	24	73	1.2:1	93[f]	95[f]
16	**sc-1**$^{S}_{0.97}$**•Na** (20)	**5e**	24	75	1.2:1	88[f]	96[f]
17[g]	**sc-1**$^{S}_{0.98}$**•Na** (20)	**5f**	24	63	1.2:1	89[f]	91[f]
18[g]	**sc-1**$^{S}_{0.97}$**•Na** (20)	**5g**	48	61	1:1.7	89[f]	95[f]

[a] Conditions: **3** (0.5 M), **4** (3 equiv.), catalyst (5–20 mol%), MeOH/H_2O (19:1, v/v), 23 ˚C, 24–72 h. Catalyst loading of the polymeric catalysts was calculated based on the amount of the immobilized **1**. [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by ^{1}H NMR after reaction with (1*R*,2*R*)-*N*-(4-toluenesulfonyl)-1,2-diphenylethylene-1,2-diamine (TsDPEN). [e] Average of two runs. [f] Determined by chiral HPLC measurement using Daicel Chiralpak IA-3 or IB-3 column after the products were converted to the corresponding alcohols with $NaBH_4$. [g] Conditions: **3** (0.42 M), **4** (3 equiv.), catalyst (20 mol%), MeOH/DMF/H_2O (19:4:1, v/v), 23 ˚C, 24–48 h.

With the use of 20 mol% of **sc-1**$^{S}_{0.98}$**•** the asymmetric reaction proceeded efficiently to afford the product in 81% yield along with the highest ee (exo 91% ee, endo 93% ee, entry 7). After reaction completion, **sc-1**$^{S}_{0.98}$**•Na** was easily separable by simple filtration of the reaction mixture, due to the insolubility of **sc-1•Na**s in common organic solvents such as MeOH, EtOH, DMSO, CH_3CN, 1,4-dioxane, THF, EtOAc, Et_2O, hexane, CH_2Cl_2, and $CHCl_3$. The ^{1}H NMR spectrum of the recovered **sc-1**$^{S}_{0.98}$**•Na** indicated that 92% of **1** remained intact without major dissociation (Fig. 1(e)). Since the cationic **1** is tightly attached onto anionic sulfated chitin through ionic interactions, the recovered **sc-1**$^{S}_{0.98}$**•Na** could be reused at least 5 times without significant loss of the catalytic activity and enantioselectivity (entries 8-12 in Table 2). Using substituted cinnamaldehydes bearing electron-donating and withdrawing, OMe, Me, Cl, Br, and NO_2 groups (**3b-g**), the catalytic asymmetric Diels-Alder reaction proceeded successfully and delivered the corresponding products **5b-g** in good yields and high enantioselectivities (entries 13-18 in Table 2).

In conclusion, we developed a facile approach for preparation of a recyclable heterogeneous asymmetric organocatalyst from commercially available chiral imidazolidinone **1** and the abundantly available chitin, which could perform asymmetric Diels-Alder reactions under the heterogeneous conditions without decreasing the inherent catalytic activity and enantioselectivity of the parent homogeneous catalyst **1**. This is the first example of a non-covalently immobilized asymmetric organocatalyst on a chitin derivative. Although the catalytic activity and selectivity may not reach a satisfactory level for practical applications at this stage, these findings not only demonstrates the possibility for use of the naturally occurring chitin, but also provides a novel strategy for heterogeneous catalyst design, which will enable access to novel recyclable and practical asymmetric organocatalysts, which fulfill the requirements of green and sustainable chemistry.

Experimental Section

Typical procedure for synthesis of sc-1•Na (method A). **Sc-Na** (206 mg, 0.686 mmol) was soaked in a solution of **1•Cl** in MeOH (80 mM, 43.3 mL, 3.5 mmol) for 30 min at room temperature. The insoluble polymer was collected by filtration, and soaked again in a solution of **1•Cl** in MeOH (80 mM, 42.4 mL, 3.4 mmol) for 30 min at room temperature. The resulted white polymer was then collected by filtration, and washed with MeOH (14 mL), and dried *in vacuo* at room temperature, giving **sc-1$^{S}_{0.50}$•Na** (264 mg, 97%) as a white powder. These results are summarised in Table 1 and the ^{1}H NMR spectra are shown in Figure S1.

Spectroscopic data of **sc-1$^{S}_{0.50}$•Na**: White powder. IR (KBr, cm^{-1}): 3448, 1714, 1655, 1559, 1382, 1216, 1004, 811, 756. ^{1}H NMR (500 MHz, D_2O, 80 ˚C): δ 7.55-7.33 (m, 2.5H, Ar*H*), 4.62 (br, 1H, -C*H*(O-)$_2$), 4.58-4.53 (m, 0.5H, PhCH$_2$C*H*-), 4.38-4.01 (2H, CH_2, overlapped with HOD), 3.95–3.52 (br, m, 4H, C*H*), 3.45 (dd, J = 12, 4.6 Hz, 0.5H, PhC*H*$_2$-), 3.18 (dd, J = 15, 8.7 Hz, 0.5H, PhC*H*$_2$-), 2.89 (s, 1.5H, -NC*H*$_3$), 2.07 (s, 2.73H, -COC*H*$_3$), 1.62 (s, 1.5H, -NC(N)C*H*$_3$), 1.60 (s, 1.5H, -NC(N)C*H*$_3$). Anal. Calcd (%) for $C_{14.32}H_{21.33}N_2Na_{0.49}O_{8.38}S_{0.99}$: C, 43.15; H, 5.39; N, 7.03. Found: C, 43.39; H, 5.16; N, 7.07.

Typical procedure for synthesis of sc-1•Na (method B). 15-Crown-5 (1.09 g, 4.95 mmol) was added to an aqueous solution of **sc-Na** (83 mM, 20.0 mL, 1.7 mmol), and the mixture was stirred for 2 h at room temperature. The resulted aqueous solution was washed with Et_2O (100 mL), and lyophilized to give **sc-2⊃Na** (1.29 g, 83%) as a white powder. An aqueous solution of **sc-2⊃Na** (78 mM, 4.30 mL, 0.34 mmol) was prepared, and to this was added **1•Cl** (1.71 g, 6.7 mmol). After the mixture was stirred for 15 min at room temperature, the obtained polymer complex was precipitated in EtOH (216 mL), collected by filtration, washed with EtOH (1.9 mL), and dried *in vacuo* to give **sc-1$^{S}_{0.98}$•Na** (149 mg, 90%) as a white powder. These results are summarised in Table 1 and the ^{1}H NMR spectra are shown in Figure S1.

Spectroscopic data of **sc-1$^{S}_{0.98}$•Na**: White powder. IR (KBr, cm^{-1}): 3446, 1715, 1653, 1558, 1396, 1218, 1008, 809, 753. ^{1}H NMR (500 MHz, D_2O, 80 ˚C): δ 7.66-7.19 (m, 4.9H, Ar*H*), 4.78-4.52 (m, 1.98H, -C*H*(O-)$_2$, PhCH$_2$C*H*-), 4.51-4.03 (2H, CH_2, overlapped with HOD), 3.90–3.53 (m, 4H, Ar*H*), 3.47 (br, 0.98H, PhC*H*$_2$-), 3.20 (br, 0.98H, PhC*H*$_2$-), 2.89 (s, 2.94H, -NC*H*$_3$), 2.07 (s, 2.73H, -COC*H*$_3$), 1.63 (s, 2.94H, -NC(N)C*H*$_3$), 1.60 (s, 2.94H, -NC(N)C*H*$_3$). Anal. Calcd (%) for $C_{20.56}H_{30.45}N_{2.96}Na_{0.01}O_{8.86}S_{0.99}$: C, 50.11; H, 6.23; N, 8.41. Found: C, 49.82; H, 6.41; N, 8.35.

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