



Chiral bifunctional thiourea-catalyzed enantioselective aldol reaction of trifluoroacetaldehyde hemiacetal with aromatic ketones

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ABSTRACT

In the presence of saccharide-derived bifunctional amine-thiourea catalysts, the direct aldol condensation of trifluoroacetaldehyde methyl hemiacetal with aromatic ketones proceeds to produce (*R*)- β -hydroxy β -trifluoroalkyl ketones in low to moderate yields with good enantioselectivities.

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1. Introduction

Over the past decade, the need for environmentally friendly and metal-free reactions has led to great progress in the organocatalyst-mediated asymmetric synthesis. Numerous chiral organocatalysts have been designed, and a variety of new asymmetric reactions have been developed in organic synthesis [1,2]. Of the promising organocatalysts, chiral bifunctional amine-thioureas have been proved to be powerful and have been applied successfully in many asymmetric catalytic reactions [3,4], such as Strecker reactions, Michael and Friedel-Crafts additions, as well as Pictet–Spengler and nitro Mannich condensations. Nevertheless, little progress has been made in the development of chiral thiourea-catalyzed asymmetric aldol reactions, and only one report by Hiemstra [5] has addressed nitromethane as nucleophilic species to react with aromatic aldehydes.

On the other hand, the asymmetric synthesis of chiral trifluoromethyl-substituted secondary and tertiary alcohols has attracted considerable attention due to the occurrence of this moiety found in a number of biologically active compounds [6–9]. In the context, one attractive strategy is the asymmetric addition of carbon nucleophiles to prochiral trifluoromethyl carbonyl compounds. For example, trifluoroacetaldehyde and derivatives are very important prochiral substrates, and have been used in many

asymmetric reactions [10–12]. However, only several limited reports involved the asymmetric aldol condensation of trifluoroacetaldehyde and derivatives with ketones. Mikami et al. presented the asymmetric aldol reaction of ketone-derived vinyl ethers or silyl enol ethers with trifluoroacetaldehyde catalyzed by a chiral binaphthol-derived titanium catalyst [13–15]. Funabiki and coworkers developed another asymmetric transformation of chiral ketimines with easily handling trifluoroacetaldehyde ethyl hemiacetal instead of trifluoroacetaldehyde gas [16–19]. In addition, several research groups also disclosed the asymmetric aldol condensations of (a)cyclo alkyl ketones with trifluoroacetaldehyde hemiacetal by the use of chiral organocatalysts [20–23]. However, to the best of our knowledge, no direct enantioselective aldol reactions of aromatic ketones with trifluoroacetaldehyde hemiacetal have been reported [24]. Design of new chiral bifunctional organocatalysts [25–27] as well as development of asymmetric reactions for the synthesis of chiral trifluoromethyl-containing functionalized compounds [28–32] has been of our interest and research objective. As part of our ongoing studies, herein we would like to provide our preliminary results on chiral bifunctional amine-thiourea-promoted direct enantioselective aldol reaction of trifluoroacetaldehyde methyl hemiacetal with aromatic ketones.

2. Results and discussion

Bifunctional chiral amine-thioureas have been demonstrated as effective promoters for activation of nucleophilic ketone species

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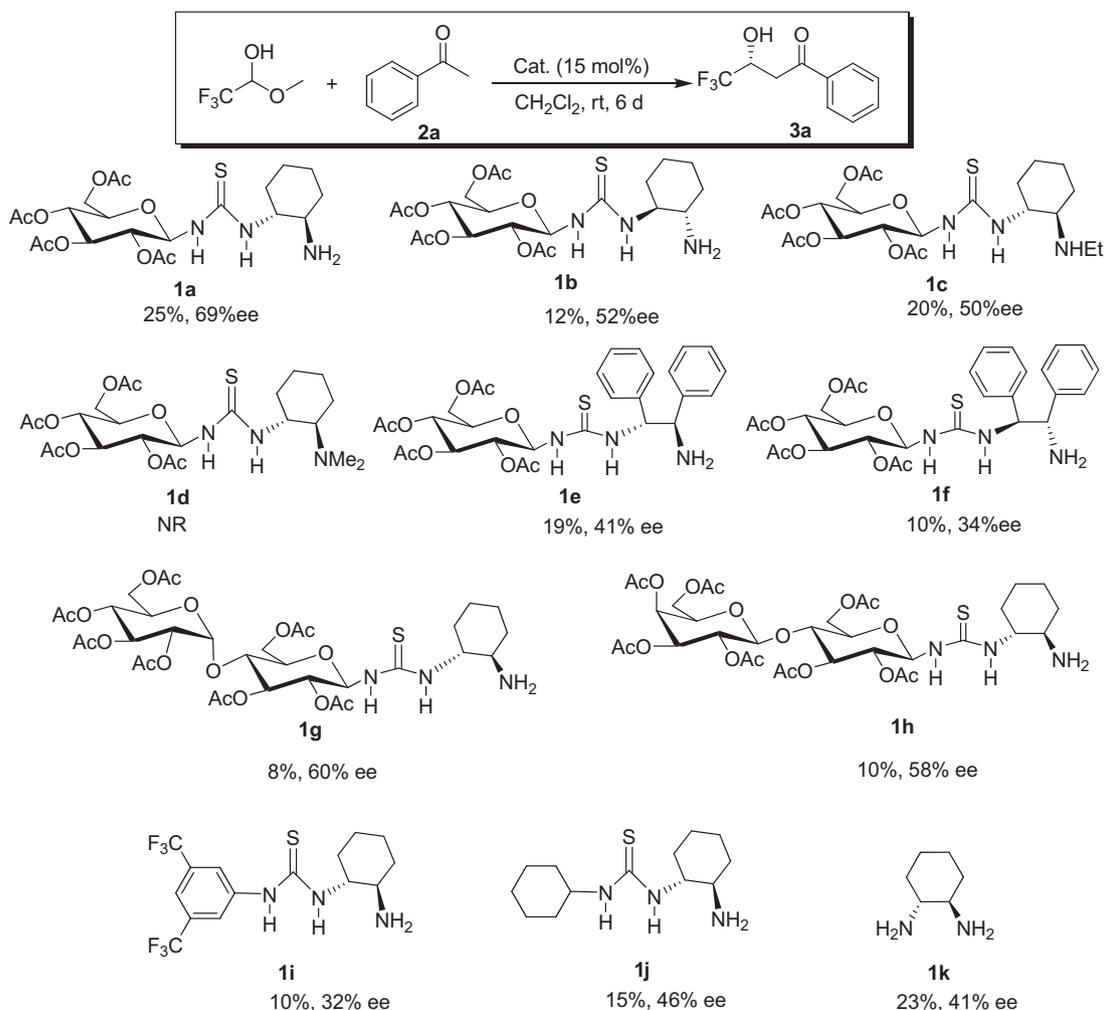


Fig. 1. Screening of the bifunctional amine-thiourea catalysts.

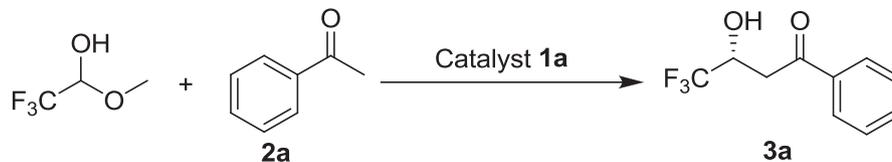
involving an enamine intermediate. Accordingly, our investigation began by screening these organocatalysts to evaluate their ability to promote aldol condensation of acetophenone **2a** with trifluoroacetaldehyde methyl hemiacetal at room temperature. As shown in Fig. 1, several bifunctional primary and secondary amine-thioureas (**1a–c** and **1e–f**) were tested, the desired product **3a** was obtained in low yields with moderate to good enantioselectivities. However, no reaction occurred when tertiary amine-thiourea **1d** was used as organocatalyst. The experimental results also showed that the (*R,R*)-configuration of 1,2-diamine matched the β -D-glucopyranose to give the relatively high stereoselectivity (**1a** and **1e** vs. **1b** and **1f**, respectively). In addition, a comparison between the results obtained using catalysts **1a–b** and **1e–f** indicates that the (1*R*,2*R*)-cyclohexanediamine moiety leads to better results than the (1*R*,2*R*)-1,2-diphenylethylenediamine moiety. Maltose and lactose-derived primary amine-thioureas **1g** and **1h** gave the good enantioselectivities, albeit with poor yields. The two chiral primary amine-thioureas **1i** and **1j** without sugar motif were evaluated in this aldol reaction. The product was obtained with lower enantioselectivity. These results demonstrated that the carbohydrate motif could play a cooperative role in the stereochemistry control for this title reaction. Interestingly, (1*R*,2*R*)-cyclohexanediamine **1k** directly promoted this condensation reaction to give the desired product in 23% yield with 41% ee.

In order to increase the reaction rate and enantioselectivity, variation of other reaction parameters were undertaken. The results were listed in Table 1. A change of the solvent had an

important effect on the stereoselection (Table 1, entries 1–10). The reaction provided 25–31% yields and good enantioselectivities in low polar solvents, such as arenes and chlorinated alkanes (Table 1, entries 1, 2, and 8–10). No product was observed in coordinating solvents and high polar solvents (Table 1, entries 3–7). Among the solvents tested, CH_2Cl_2 was found to be the best with respect to catalytic activity and asymmetric induction. Subsequently, a preliminary screen of additives was carried out (Table 1, entries 11–16). No reaction occurred in the presence of molecular sieves. The use of organic acids and bases did not have a significant effect on the reaction rate and stereoselection. To our delight, an increase of yields was observed by using H_2O as the additive. The water might accelerate the reaction by facilitating the interconversion of the different intermediates of the catalytic cycle. Further optimization of temperature, the loading of the additive and the catalyst was finished (Table 1, entries 17–25). The good results were attained when 15 mol% of thiourea **1a** and 5 mol% of H_2O were employed at room temperature.

Under the optimized experimental conditions, the scope of the reaction was explored (Table 2). It was found that ketones **2a–h** with electron-neutral or -withdrawing groups on aromatic rings were used, the reactions proceeded to give modest yields and good enantioselectivities (Table 2, entries 1–7). However, the presence of electron-donating substituents on aromatic rings decreased the reaction rate and lower yield was obtained for these ketone substrates (Table 2, entries 8 and 9). In addition, heteroaromatic methyl ketone **2j** was also viable substrate to afford the desired

Table 1
Optimization of reaction conditions in the presence of **1a**.



Entry	Solvent	Additive	Temperature (°C)	Time (d)	Yield (%) ^a	Ee (%) ^b
1	CH ₂ Cl ₂	–	25	6	25	69
2	Toluene	–	25	6	30	65
3	Et ₂ O	–	25	6	NR	–
4	THF	–	25	6	NR	–
5	CH ₃ CN	–	25	6	NR	–
6	DMF	–	25	6	NR	–
7	DMSO	–	25	6	NR	–
8	ClCH ₂ CH ₂ Cl	–	25	6	24	65
9	CHCl ₃	–	25	6	31	65
10	Benzene	–	25	6	30	65
11	CH ₂ Cl ₂	5 Å MS (10 mol%)	25	6	NR	–
12	CH ₂ Cl ₂	PhCO ₂ H (10 mol%)	25	6	17	60
13	CH ₂ Cl ₂	CF ₃ CO ₂ H (10 mol%)	25	6	10	60
14	CH ₂ Cl ₂	ⁱ Pr ₂ NEt (10 mol%)	25	6	12	59
15	CH ₂ Cl ₂	Pyridine (10 mol%)	25	6	NR	–
16	CH ₂ Cl ₂	H ₂ O (10 mol%)	25	6	45	68
17	CH ₂ Cl ₂	H ₂ O (5 mol%)	25	6	45	68
18	CH ₂ Cl ₂	H ₂ O (1 mol%)	25	6	38	60
19	CH ₂ Cl ₂	H ₂ O (5 mol%)	25	8	45	68
20	CH ₂ Cl ₂	H ₂ O (5 mol%)	25	4	40	68
21	CH ₂ Cl ₂	H ₂ O (5 mol%)	25	3	40	68
22	CH ₂ Cl ₂	H ₂ O (5 mol%)	10	6	15	68
23	CH ₂ Cl ₂	H ₂ O (5 mol%)	40	6	46	68
24 ^c	CH ₂ Cl ₂	H ₂ O (5 mol%)	25	6	45	68
25 ^d	CH ₂ Cl ₂	H ₂ O (5 mol%)	25	6	42	65

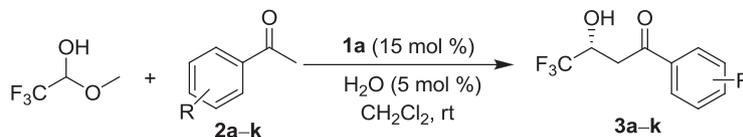
^a Isolated yield. NR: no reaction.

^b The ee values were determined by HPLC. The absolute configuration was assigned according to Refs. [15–19].

^c 20 mol% of **1a** was used.

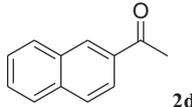
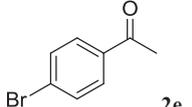
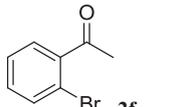
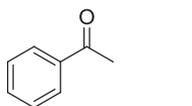
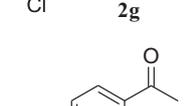
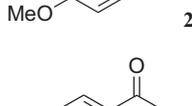
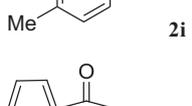
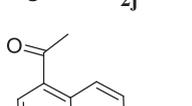
^d 10 mol% of **1a** was used.

Table 2
Enantioselective aldol reaction of trifluoroacetaldehyde methyl hemiacetal with aromatic ketones.



Entry	Ketone	Time (d)	Yield (%) ^a	Ee (%) ^b
1		5	45	68
2		4	54	59
3		5	49	64

Table 2 (Continued)

Entry	Ketone	Time (d)	Yield (%) ^a	Ee (%) ^b
4	 2d	5	42	57
5	 2e	5	38	60
6	 2f	6	36	60
7	 2g	6	42	60
8	 2h	6	20	62
9	 2i	6	13	58
10	 2j	6	35	50
11	 2k	10	–	–

^a Isolated yield.

^b The ee values were determined by HPLC. The absolute stereochemistry of products **3b–j** was assigned on the basis of analogy with **3a** studies.

product **3j** in moderate yield and enantioselectivity (entry 10). Surprisingly, no reaction was observed in the reaction of 1-naphthyl methyl ketone **2h** with trifluoroacetaldehyde methyl hemiacetal (Table 2, entries 11 vs. 4).

The stereogenic center of 4,4,4-trifluoro-1-phenyl-3-hydroxy-1-butanones (**3a**), which was generated by **1a**-catalyzed asymmetric aldol condensation of trifluoroacetaldehyde hemiacetal

with **2a**, was determined to be *R* by the comparison to the reported values such as the optical rotation and the retention time of HPLC using a chiral stationary phase [15–19]. The absolute stereochemistry of other products **3b–j** was assigned on the basis of analogy with **3a** studies. These results show that the *Re*-face of the in situ generated trifluoroacetaldehyde was predominantly approached by the enamine intermediate formed from ketone and the primary

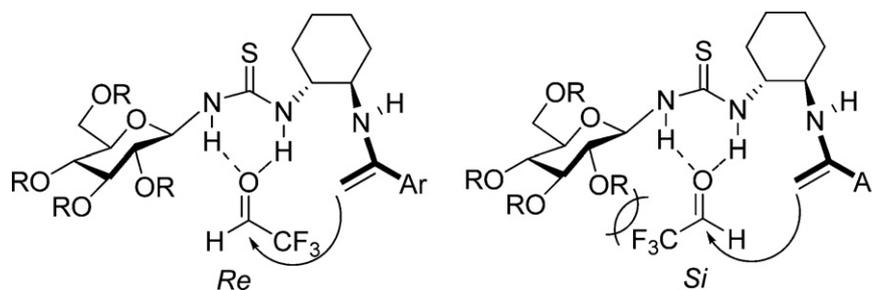


Fig. 2. TS structures for the formation of the *R* and *S* enantiomers.

amine group of the bifunctional thiourea catalyst. The attack of the enamine to the Si-face of the trifluoroacetaldehyde was restricted by the thiourea scaffold of the catalyst (Fig. 2).

3. Conclusions

We have developed an enantioselective organocatalytic direct aldol reaction of trifluoroacetaldehyde methyl hemiacetal with a series of aromatic ketones by the use of bifunctional amine-thiourea catalysts derived from commercially available saccharides and chiral diamines. This direct condensation proceeds to produce (*R*)- β -hydroxy β -trifluoroalkyl ketones in low to moderate yields (13–54%) with good enantioselectivities (50–68% ee). Further investigation of the reaction mechanism, the improvement of this reaction rate and enantioselectivity are ongoing in our laboratories and will be reported in due course.

4. Experimental

4.1. General information

NMR was recorded on Varian Mercury Plus 500 instruments at 500 MHz (^1H NMR) and 125 MHz (^{13}C NMR). Chemical shifts were reported in ppm down field from internal Me_4Si . ^{19}F NMR (376 MHz) spectra were recorded on a Bruker ARX400 instrument in CDCl_3 solutions using CFCl_3 as the internal standard. HPLC analyses were carried out on a Hewlett Packard Model HP 1200 instrument. Optical rotations were determined using an Autopol IV-T. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Tetrahydrofuran (THF), diethyl ether, toluene and benzene were distilled from sodium/benzophenone prior to use; CH_2Cl_2 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, CHCl_3 , CH_3CN , DMSO and DMF were distilled from CaH_2 . All purchased reagents were used without further purification. All of bifunctional amine-thiourea catalysts were synthesized according to the literatures [25–27].

4.2. General procedure for catalyzed aldol reaction

Trifluoroacetaldehyde methyl hemiacetal (130 mg, 1.0 mmol), acetophenone **2a** (180 mg, 1.5 mmol), catalyst **1a** (75.5 mg, 0.15 mmol), and H_2O (1.0 mg, 0.05 mmol) were placed in a 5 mL vial equipped with a Tefloncoated stir bar. Dichloromethane (2 mL) was added under air. The vial was capped with a white polyethylene stopper, and the resulting mixture was stirred at room temperature for 5 days. Then the reaction solution was concentrated in vacuo, and the crude was purified by flash chromatography to afford the desired product **3a** [15–19].

Other products **3b–d**, and **3h–i** [15–19,24], as known compounds, were prepared according to the abovementioned procedure.

4.2.1. (*R*)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one ((*R*)-**3a**)

98.1 mg (45% yield), $[\alpha]_D^{20} + 12.2^\circ$ (c1.0, CHCl_3). 68% ee was determined by HPLC analysis [Daicel Chirapak OD-H, *i*-PrOH/hexane (5/95), 254 nm, 0.8 mL/min, $t_R = 26.5$ min (*S*), 28.3 min (*R*)]. ^1H NMR (500 MHz, CDCl_3) δ 3.35 (dd, $J = 18.1$ Hz, 1H), 3.43 (dd, $J = 18.1$ Hz, 1H), 3.70 (d, $J = 2.95$ Hz, 1H), 4.68–4.73 (m, 1H), 7.27–7.753 (m, 2H), 7.62–7.65 (m, 1H), 7.84–7.97 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 38.2, 67.1 (q, $J = 32.0$ Hz), 124.7 (q, $J = 280.4$ Hz), 128.2, 128.8, 133.2, 136.0, 198.1. ^{19}F NMR (376 MHz, CDCl_3) δ -79.26 (d, $J = 6.92$ Hz, 3F). IR (KBr) ν 3442, 1697, 1605, 1519, 1167, 1104, 1049, 753, 706 cm^{-1} .

4.2.2. (*R*)-4,4,4-trifluoro-3-hydroxy-1-(naphthalen-2-yl)butan-1-one ((*R*)-**3d**)

42%, $[\alpha]_D^{20} + 18.2^\circ$ (c1.0, CHCl_3). 57% ee was determined HPLC analysis [Daicel Chirapak OD-H, *i*-PrOH/hexane (5/95), 254 nm, 0.8 mL/min, $t_R = 22.20$ min (major), 41.63 min (minor)]. ^1H NMR (500 MHz, CDCl_3) δ 3.42–3.62 (m, 2H), 3.67–3.77 (m, 1H), 4.72–4.86 (m, 1H), 7.57–7.71 (m, 2H), 7.88–7.97 (m, 2H), 7.97–8.07 (m, 2H), 8.45–8.54 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 38.3, 67.3 (q, $J = 31.8$ Hz), 123.4 (q, $J = 280.6$ Hz), 127.2, 128.8, 129.1, 129.7, 130.4, 132.4, 133.3, 136.0, 197.4. ^{19}F NMR (376 MHz, CDCl_3) δ -79.20 (d, $J = 6.90$ Hz, 3F). IR (KBr) ν 34382, 1690, 1608, 1520, 1160, 1106, 1047, 756, 704 cm^{-1} .

4.2.3. (*R*)-1-(4-bromophenyl)-4,4,4-trifluoro-3-hydroxybutan-1-one ((*R*)-**3e**)

38%, $[\alpha]_D^{20} + 21.4^\circ$ (c1.0, CHCl_3). 60% ee was determined HPLC analysis [Daicel Chirapak OD-H, *i*-PrOH/hexane (5/95), 254 nm, 0.8 mL/min, $t_R = 15.50$ min (major), 16.78 min (minor)]. ^1H NMR (500 MHz, CDCl_3) δ 3.21–3.45 (m, 2H), 3.62–3.78 (m, 1H), 4.65–4.79 (m, 1H), 7.57–7.73 (m, 2H), 7.33–7.41 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 38.3, 66.90 (q, $J = 32.0$ Hz), 123.3 (q, $J = 280.0$ Hz), 126.1, 129.5, 129.7, 132.2, 134.7, 196.4. ^{19}F NMR (376 MHz, CDCl_3) δ -79.18 (d, $J = 6.87$ Hz, 3F). IR (KBr) ν 3448, 1701, 1600, 1522, 1170, 1112, 1052, 758, 702 cm^{-1} . MS (ESI): m/z 295.7 $[\text{M}-1]^+$, 296.9 $[\text{M}]^+$, 297.9 $[\text{M}+1]^+$.

4.2.4. (*R*)-1-(2-bromophenyl)-4,4,4-trifluoro-3-hydroxybutan-1-one ((*R*)-**3f**)

36%, $[\alpha]_D^{20} + 3.4^\circ$ (c1.0, CH_2Cl_2). 60% ee was determined HPLC analysis [Daicel Chirapak OD-H, *i*-PrOH/hexane (5/95), 254 nm, 0.8 mL/min, $t_R = 17.49$ min (minor), 31.14 min (major)]. ^1H NMR (400 MHz, CDCl_3) δ 3.35–3.69 (m, 3H), 4.69–4.71 (m, 1H), 7.36–7.46 (m, 2H), 7.51 (d, $J = 7.3$ Hz 1H), 7.67 (d, $J = 7.8$ Hz 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 42.3, 67.1 (d, $J = 32.5$ Hz), 119.0, 127.7, 129.0, 132.6, 134.1, 140.0, 200.68. ^{19}F NMR (300 MHz, CDCl_3) δ -79.34 (d, $J = 6.70$ Hz, 3F). IR (KBr) ν 3423, 1702, 1403, 1279, 1170, 1127, 1052, 760 cm^{-1} . MS (ESI): m/z 296.8 $[\text{M}]^+$.

4.2.5. (*R*)-1-(3-chlorophenyl)-4,4,4-trifluoro-3-hydroxybutan-1-one ((*R*)-**3g**)

42%, $[\alpha]_D^{20} + 3.0^\circ$ (c1.0, CH_2Cl_2). 60% ee was determined HPLC analysis [Daicel Chirapak OD-H, *i*-PrOH/hexane (5/95), 254 nm, 0.8 mL/min, $t_R = 14.36$ min (minor), 18.00 min (major)]. ^1H NMR (400 MHz, CDCl_3) δ 3.32–3.39 (m, 3H), 4.72–4.73 (m, 1H), 7.48 (t, 1H), 7.63 (d, 1H), 7.87 (d, 1H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.5, 67.1, 126.3, 128.3, 134.0, 135.4, 137.6, 196.0. ^{19}F NMR (300 MHz, CDCl_3) δ -79.26 (d, $J = 6.75$ Hz, 3F). IR (KBr) ν 3420, 1696, 1629, 1423, 1280, 1169, 1122, 801, 563 cm^{-1} . MS (ESI): m/z 252.3 $[\text{M}]^+$.

4.2.6. (*R*)-4,4,4-trifluoro-3-hydroxy-1-(thiophen-2-yl)butan-1-one ((*R*)-**3j**)

35%, $[\alpha]_D^{20} + 2.2^\circ$ (c1.0, CH_2Cl_2). 50% ee was determined HPLC analysis [Daicel Chirapak AS-H, *i*-PrOH/hexane (5/95), 254 nm, 0.8 mL/min, $t_R = 17.81$ min (minor), 23.56 min (major)]. ^1H NMR (400 MHz, CDCl_3) δ 3.30–3.35 (m, 2H), 3.54 (s, 1H), 4.70 (s, 1H), 7.21 (s, 1H), 7.76–7.81 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 38.7, 67.2 (d, $J = 32.6$ Hz), 128.4, 133.1, 135.1, 143.1, 190.0. ^{19}F NMR (300 MHz, CDCl_3) δ -79.29 (d, $J = 6.45$ Hz, 3F). IR (KBr) ν 3438, 1645, 1559, 1514, 1416, 1280, 1169, 1126, 491 cm^{-1} . MS (ESI): m/z 223.9 $[\text{M}]^+$.

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