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Catalytic asymmetric β-hydrogen transfer reduction of α-trifluoromethyl aromatic ketones with diethylzinc

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ABSTRACT

The catalytic asymmetric β-hydrogen transfer reduction of α-trifluoromethyl ketones using diethylzinc as the β-hydrogen donor was developed with the use of phosphinamide chiral ligand. The corresponding alcohol products were afforded in good yields with up to 73% ee. This method was successfully applied to the chemo- and enantioselective reduction of α-methyl/trifluoromethyl diketone, affording 88% yield and 70% ee of the fluorinated hydroxylketone product.

1. Introduction

Trifluoromethylated organic compounds play a significant role in medicinal and agrochemical products due to their particular properties and reactivities.[1–7] The ever-increasing demand of enantiomerically enriched trifluoromethylated compounds has dramatically promoted the development of their asymmetric syntheses.[3,8–13] Among the developed methodologies, the enantioselective reduction of trifluoromethyl ketones is of great value and many types of approaches have been reported, such as asymmetric transition metal-catalyzed hydrogenations,[14–19] biocatalyzed reductions,[20–24] chiral organometallic reagents reductions,[25–28] asymmetric borane reductions,[29–33] and asymmetric β-hydrogen transfer reductions.[34–36]

Compared with other asymmetric reduction transformations, asymmetric β-hydrogen transfer reduction of trifluoromethyl ketones is underdeveloped with few examples.[34–36] In 2002, Yong and Chong introduced a chiral organomagnesium amide as a hydrogen source in the asymmetric β-hydrogen transfer reduction of α-trifluoromethyl ketones, affording the corresponding α-trifluoromethyl secondary alcohol products with up to 96% ee and up to 95% yield.[36] However, due to the high reactivity of the diorganomagnesium reagent, a stoichiometric amount of chiral amide ligand and a low temperature (−78 °C) were required to achieve high enantioselectivity. Diethylzinc is as a well-known β-hydrogen donor and was used in the reduction of trifluoromethyl ketones by Higashiyama et al.[37] some other groups also found that trifluoromethyl ketones could be reduced by diethylzinc,[38–41] but the asymmetric version of the β-hydrogen transfer reduction of α-trifluoromethyl ketones with diethylzinc has never been reported.

As already known, the selective reduction of a targeted functional group in the presence of other reducible functional group is of great interest in organic synthesis. Until recently, only a few methods for the chemo- and enantioselective reduction of methyl/trifluoromethyl diketone have been developed because both the α-methyl carbonyl group and the α-trifluoromethyl carbonyl group are very similar in chemical properties and are easy to reduce simultaneously.[17,42–46] As a consequence, it remains challenging to develop an efficient method for the chemo- and enantioselective reduction of methyl/trifluoromethyl diketone.

We have been interested in 1,2-diamino phosphinamide chiral ligand catalyzed diorganozinc reagents that participate in asymmetric reactions.[47–52] This type of chiral ligands also shows high efficiency in organocatalyzed asymmetric reactions.[53–56] As part of our ongoing interest in developing efficient asymmetric reactions, we herein report the first asymmetric β-hydrogen transfer reduction of α-trifluoromethyl ketones with diethylzinc catalyzed by a 1,2-diamino phosphinamide chiral ligand derived from (1*R*,2*R*)-1,2-diphenylethylenediamine and its application in the chemo- and enantioselective reduction of methyl/trifluoromethyl diketone.

2. Results and discussion

In our previous studies, inspired by Ishihara's pioneering work on the development of conjugated Lewis acid–base catalysts,[57–61] several highly efficient 1,2-diamino phosphinamide chiral ligands derived from quinidine, (1*R*,2*R*)-1,2-diaminocyclohexane, and

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(1*R*,2*R*)-1,2-diphenylethylenediamine **1**–**4** were developed and applied in the catalytic asymmetric addition reactions of a variety of aromatic aldehydes and ketones with diethylzinc reagent, affording the corresponding addition alcohol products with excellent yields and enantioselectivities.[47–51] However, when trifluoromethylketone was used as the substrate, these ligands provided reduction alcohol product **5a** as the main product and only a small amount of addition product **8** could be observed. The experimental results are listed in Table 1.

Our investigation showed that the poor yield and enantioselectivity of the alcohol reduction product were afforded when using chiral ligands **1**, **2a**, and **2b** (Table 1, entries 1–3). In addition, (1*R*,2*R*)-1,2-diaminocyclohexane derived chiral ligand **3** gave a nearly racemic reduction product with moderate yield (entry 4). Interestingly, 90% yield and 48% ee value of alcohol reduction product were obtained when using (1*R*,2*R*)-1,2-diphenylethylenediamine derived *N*-monosubstituted **4a** (entry 5). We wondered if we could develop a better chiral 1,2-diamino phosphinamide ligand for the catalytic asymmetric β-hydrogen transfer reduction by further ligand structure modification. With *N*-nonsubstituted ligand **4b**, both the yield and ee value of the reduction product decreased to 34% and 19%, respectively (entry 6). With *N*,*N*-dialkylated chiral ligands **4c** and **4d**, the desired reduction products were obtained in moderate yields, but the corresponding ee values were low with opposite configurations (entries 7 and 8). However, as shown in entries 9–14, increasing the size of the *N*-monosubstituent had a positive effect on the yield and ee value of the reduction product. The best result was obtained with a Bn group as the *N*-substituent, giving the reduction product with 95% yield and 57% ee value.

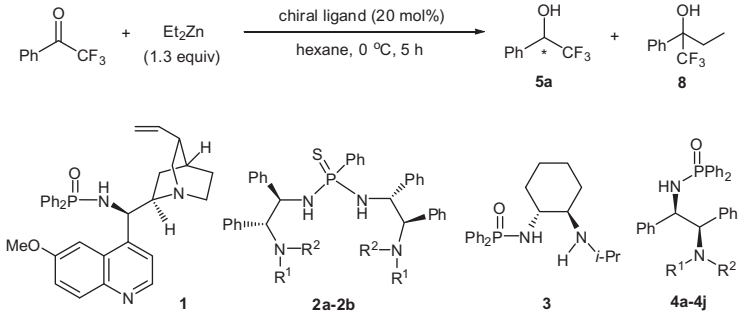
In order to further enhance the enantioselectivity of the asymmetric β-H transfer reduction reaction, various reaction conditions such as the amount of diethylzinc reagent, the loading of chiral ligand, reaction solvent, time, and temperature were also evaluated with the optimized chiral ligand **4j** in hand and the experimental results are listed in Table 2.

When diethylzinc reagent was increased from 1.3 equiv to 3.0 equiv, the yield of the desired product slightly increased but the ee value dropped significantly (Table 2, entries 1–3). With only 0.8 equiv of diethylzinc, both the yield and ee value of the product decreased (entry 4). When the loading of chiral ligand **4j** was increased to 30 mol %, both the yield and ee value increased slightly to 98% and 58%, respectively (entry 5). Changing the solvent from hexane to toluene increased the enantioselectivity to 60% (entries 5–8). Lowering the temperature to −10 °C enhanced the ee value to 62% (entry 9). When −20 °C was used and the reaction mixture was stirred for 48 h, the ee value of the product was optimized to 73% with 88% yield (entry 10). Further lowering the reaction temperature to −50 °C, meant the reaction did not happen at all (entry 11). On the basis of the above experimental data, the optimized reaction conditions were in toluene at −20 °C for 48 h using 30 mol % of **4j** as the chiral ligand and 1.3 equiv of diethylzinc reagent as the β-hydrogen donor.

We next evaluated the effectiveness of the optimized catalytic system in the catalytic asymmetric β-H transfer reduction of varied α-trifluoromethyl ketones with diethylzinc, and the results are summarized in Table 3.

As shown in Table 3, the reactions between diethylzinc and *p*-F, Cl, Me substituted aryl α-trifluoromethyl ketones gave the corresponding reduction products **5b**–**5d** in over 70% yield with over 60% enantioselectivity (Table 3, entries 2–4). When the aromatic group was 2-naphthyl, the desired product was afforded with 87% yield and 40% ee value. When one fluorine atom of the trifluoromethyl group was replaced by a chloride atom, the desired

Table 1
Evaluation of 1,2-diamino phosphinamide chiral ligands in the catalytic asymmetric β-H transfer reduction of α-trifluoromethyl ketone with diethylzinc[a]



Entry	Ligand	R^1	R^2	Yield[b] of **5a** (%)	ee[c] of **5a** (%)	Config.[d]	Ratio of **5a**:**8**[e]
1	**1**	–	–	13	17	(*S*)	65:35
2	**2a**	Me	*i*-Pr	18	11	(*S*)	79:21
3	**2b**	H	Cbz	17	10	(*S*)	77:23
4	**3**	–	–	60	2	(*R*)	94:6
5	**4a**	H	*i*-Pr	90	48	(*R*)	97:3
6	**4b**	H	H	34	19	(*R*)	87:13
7	**4c**	Me	Me	60	10	(*S*)	94:6
8	**4d**	Me	Et	50	11	(*S*)	94:6
9	**4e**	H	Et	76	50	(R)	96:4
10	**4f**	H	CH_2*i*-Pr	96	51	(*R*)	98:2
11	**4g**	H	Bu	80	51	(*R*)	96:4
12	**4h**	H	CH_2Bu	86	52	(*R*)	96:4
13	**4i**	H	*c*-Hex	92	53	(*R*)	97:3
14	**4j**	H	Bn	95	57	(*R*)	98:2

[a] Unless otherwise noted, all reactions were carried out in 1 mmol scale.
[b] Isolated yields.
[c] Determined by chiral GC analysis.
[d] The configuration was determined by comparing the sign of specific rotation value with the literature value.
[e] The ratio was determined by ^{19}F NMR spectroscopic analysis of unpurified reaction products.

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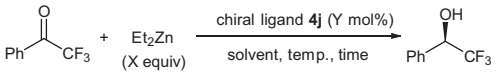
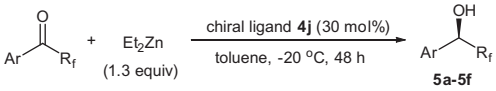
Table 2
Optimization of reaction conditions for the catalytic asymmetric β-H transfer reduction of trifluoroacetophenone with diethylzinc using chiral ligand **4j**[a]

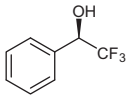
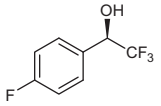
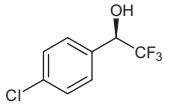
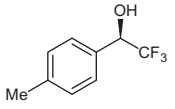
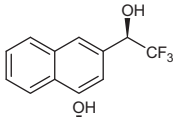
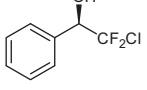


Entry	X	Y	Solvent	Time (h)	Temp (°C)	Yield[b] (%)	ee[c] (%)
1	1.3	20	Hexane	5	0	95	57
2	2.0	20	Hexane	5	0	96	44
3	3.0	20	Hexane	5	0	99	22
4	0.8	20	Hexane	5	0	42	55
5	1.3	30	Hexane	5	0	98	58
6	1.3	30	CH_2Cl_2	5	0	86	51
7	1.3	30	Toluene	5	0	96	60
8[d]	1.3	30	Toluene	5	0	95	58
9	1.3	30	Toluene	12	−10	76	62
10	1.3	30	Toluene	48	−20	88	73
11	1.3	30	Toluene	48	−50	N.R.[e]	—

[a] Unless otherwise noted, all reactions were carried out on a 1 mmol scale.
[b] Isolated yields.
[c] Determined using chiral GC analysis.
[d] Et_2Zn (1.0 mol/L in toluene) was used.
[e] No reaction after 48 h.

Table 3
Enantioselective reduction of trifluoromethyl ketones with diethylzinc catalyzed by chiral ligand **4j**[a]



Entry	Product	Number	Yield[b] (%)	ee[c] (%)
1		**5a**	88	73
2		**5b**	75	61
3		**5c**	71	60
4		**5d**	70	61
5		**5e**	87	40
6		**5f**	86	71

[a] Unless otherwise noted, all reactions were carried out in 1 mmol scale.
[b] Isolated yield.
[c] Determined by chiral GC.

product was afforded with 86% yield and 71% ee value (Table 3, entry 6).

Further investigation showed that acetophenone did not react with diethylzinc under the reaction conditions (Fig. 1a). When a 1:1 mixture of acetophenone and α-trifluoromethyl ketone was treated with diethylzinc under the reaction conditions, only

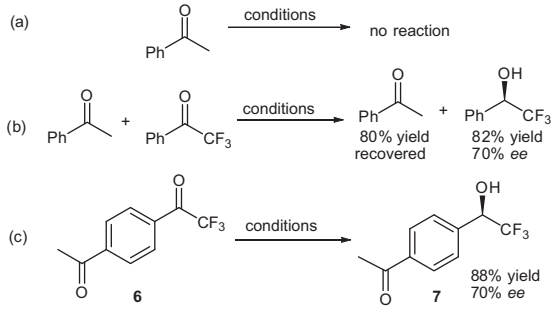


Figure 1. Chemo- and enantioselective reduction of methyl/trifluoromethyl diketone **6**. Conditions: ligand **4j** (30 mol %), Et_2Zn (1.3 equiv), toluene as solvent, −20 °C, 48 h.

α-trifluoromethyl ketone was reduced. The reduction alcohol product was obtained with 82% yield and 70% ee value and 80% yield of acetophenone was recovered (Fig. 1b). These results indicated that this method selectively reduced the α-trifluoromethyl carbonyl group in the presence of an α-methyl carbonyl group. Next, we applied the method in the chemo- and enantioselective reduction of **6** containing both α-trifluoromethyl carbonyl and α-methyl carbonyl groups (Fig. 1c). Compound **6** was chemo- and enantioselectively reduced and the corresponding product of fluorinated chiral hydroxyketone **7** was afforded with 88% yield and 70% ee value.

Based on Ishihara's conjugate Lewis acid–base double activated transition state model[57] and our experimental results, a plausible transition state is proposed as shown in Figure 2.

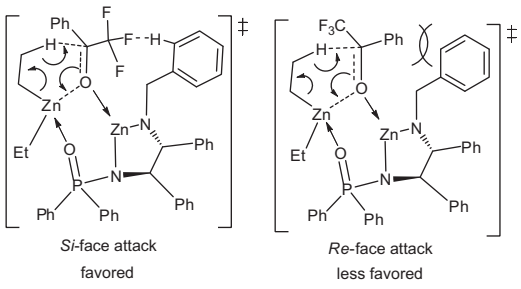


Figure 2. Proposed transition states.

The zinc metal center of the 1,2-diamino phosphinamide–Zn(II) complex serves as a Lewis acid to active the carbonyl group of α-trifluoromethyl ketone and the P=O moiety of the complex serves as a Lewis base to coordinate the diethylzinc reagent, after which β-H of the diethylzinc reagent could be transferred to the carbonyl group of trifluoromethyl ketone via a six-membered ring transition state. The (*R*)-product was formed via *Si*-face attack of trifluoromethyl ketone, which should be highly preferred without steric repulsion between the Bn group of chiral metallic complex and the Ph group of trifluoromethyl ketone. In addition, the Ar–H···F–C interaction could help to stabilize the *Si*-face attack transition state.[36]

3. Conclusion

In conclusion, with the use of diethylzinc as a β-hydrogen donor, we developed an efficient catalytic asymmetric β-H transfer reduction of α-trifluoromethyl aromatic ketones. Chiral ligand structure modification gave us 1,2-diamino phosphinamide **4j** as

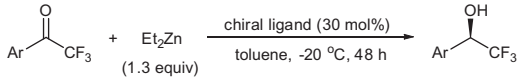
the best catalyst, which afforded good yields and up to 73% ee value of the resulting α-trifluoromethyl alcohol products. This method was successfully applied in the chemo- and enantioselective reduction of α-methyl/trifluoromethyl diketone and a possible transition state was also proposed.

4. Experimental section

4.1. General methods

All experiments were carried out in dried glassware with magnetic stirring under an atmosphere of dry nitrogen. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra are recorded in $CDCl_3$ solutions using a 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm, δ) relative to $CDCl_3$ (δ 7.26 for ^{1}H NMR), or $CDCl_3$ (δ 77.0 for ^{13}C NMR). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Commercial reagents were used as received unless otherwise indicated. All solvents were purified and dried prior to use according to the literature.[62] Optical rotations were measured on a polarimeter and specific rotations are reported as follows: $[\alpha]_D^T$ (c g/100 mL, solvent). GC analysis was performed using Chiral column. Chiral 1,2-diamino phosphinamide ligands **1**,[49] **2a–2b**,[51] **3**,[47] **4a–4i**,[50] **4j**,[52] compound **6**,[46] and **8**[38] were prepared according to the literature.

4.2. Typical procedure for the catalytic asymmetric β-hydrogen transfer reduction of α-trifluoromethyl ketone



To a solution of chiral phosphinamide chiral ligand (0.3 mmol) in toluene (1.3 mL), Et_2Zn (1.3 mL, 1 M in n-hexane, 1.3 mmol) was added and the resulting mixture was stirred for 10 min at 0 °C under an atmosphere of nitrogen. Next, the reaction mixture was cooled to −20 °C, and α-trifluoromethyl ketone (1.0 mmol) was added dropwise. After being stirred for 48 h, the reaction was quenched by saturated NH_4Cl solution (15 mL) and the mixture was extracted with EtOAc (15 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give a residue, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to give the corresponding product.

4.2.1. (*R*)-2,2,2-Trifluoro-1-phenylethanol 5a[63]

Colorless oil, 155 mg (88% yield); the 73% ee value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 11.5 min (minor, *S*), t_R = 12.0 min (major, *R*)]. $[\alpha]_D^{30.5}$ = −16.1 (c 0.50, CH_2Cl_2) {literature[63] $[\alpha]_D^{25}$ = −13.1 (c 0.28, CH_2Cl_2) for 60% ee (*R*)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.73 (s, 1H), 5.02 (q, J = 6.6 Hz, 1H), 7.38–7.53 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.9 (q, J = 32.2 Hz), 124.3 (q, J = 281.0 Hz), 127.5, 128.6, 129.6, 134.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.2 (d, J = 6.7 Hz, 3F).

4.2.2. (*R*)-2,2,2-Trifluoro-1-(4-fluorophenyl)ethanol 5b[63]

Colorless oil, 146 mg (75% yield); the 61% ee value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 11.2 min (minor, *S*), t_R = 12.3 min (major, *R*)]. $[\alpha]_D^{29.5}$ = −16.5 (c 0.50, CH_2Cl_2) {literature[63] $[\alpha]_D^{19}$ = −11.5 (c 0.07, CH_2Cl_2) for 45% ee (*R*)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.12 (s, 1H), 5.01 (q, J = 6.5 Hz, 1H), 7.00–7.17 (m, 2H), 7.35–7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.2 (q, J = 32.2 Hz), 115.6 (d, J = 21.9 Hz), 124.1 (q, J = 282.1 Hz), 129.3 (d, J = 8.2 Hz), 129.7, 163.4 (d, J = 248.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.6 (d, J = 6.7 Hz, 3F), −112.4 (m, 1F).

4.2.3. (*R*)-1-(4-Chlorophenyl)-2,2,2-trifluoroethanol 5c[63]

Colorless oil, 150 mg (71% yield); the 60% ee value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 10.9 min (minor, *S*), t_R = 11.7 min (major, *R*)]. $[\alpha]_D^{30.6}$ = −10.8 (c 0.50, CH_2Cl_2) {literature[63] $[\alpha]_D^{25}$ = −18.3 (c 0.13, CH_2Cl_2) for 51% ee (*R*)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.01 (s, 1H), 5.01 (q, J = 6.6 Hz, 1H), 7.34–7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.1 (q, J = 32.0 Hz), 124.1 (q, J = 283.5 Hz), 128.8, 129.6, 132.4, 135.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.5 (d, J = 6.8 Hz, 3F).

4.2.4. (*R*)-2,2,2-Trifluoro-1-*p*-tolylethanol 5d[63]

Colorless oil, 133 mg (70% yield); the 61% ee value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 10.1 min (minor, *S*), t_R = 10.6 min (major, *R*)]. $[\alpha]_D^{28.5}$ = −14.7 (c 0.50, CH_2Cl_2) {literature[63] $[\alpha]_D^{25}$ = −12.7 (c 0.18, CH_2Cl_2) for 68% ee (*R*)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.87 (br, 1H), 4.98 (m, 1H), 7.16–7.30 (m, 2H), 7.33–7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 72.6 (q, J = 31.8 Hz), 124.4 (q, J = 281.1 Hz), 127.4, 129.3, 131.1, 139.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.4 (d, J = 6.9 Hz, 3F).

4.2.5. (*R*)-2,2,2-Trifluoro-1-(naphthalen-2-yl)ethanol 5e[63]

White solid, 197 mg (87% yield); the 40% ee value was determined by Chiral GC Chirasil Dex CB [column temperature: 165 °C, t_R = 15.0 min (minor, *S*), t_R = 15.5 min (major, *R*)]. $[\alpha]_D^{29.9}$ = −11.8 (c 1.00, CH_2Cl_2) {literature[63] $[\alpha]_D^{25}$ = −24.7 (c 0.21, CH_2Cl_2) for 75% ee (*R*)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.34 (s, 1H), 5.16 (q, J = 6.8 Hz, 1H), 7.48–7.68 (m, 3H), 7.80–8.05 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 73.0 (q, J = 31.8 Hz), 124.4, 124.5 (q, J = 280.0 Hz), 126.6, 126.9, 127.4, 127.8, 128.3, 128.6, 131.4, 133.0, 133.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −77.6 (d, J = 6.7 Hz, 3F).

4.2.6. (*R*)-2-Chloro-2,2-difluoro-1-phenylethanol 5f[64]

Colorless oil, 166 mg (86% yield); the 71% ee value was determined by Chiral GC Chirasil Dex CB [column temperature: 125 °C, t_R = 24.0 min (minor, *S*), t_R = 24.4 min (major, *R*)]. $[\alpha]_D^{30.1}$ = −9.1 (c 0.50, $CHCl_3$) {literature[64] $[\alpha]_D^{21}$ = −13.8 (c 1.01, $CHCl_3$) for 73% ee (*R*)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.07 (s, 1H), 5.07 (t, J = 6.6 Hz, 1H), 7.32–7.62 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 77.6, 127.8, 128.4, 129.0 (t, J = 297.0 Hz), 129.5, 131.9, 134.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.3 (dd, J = 7.4, 164.0 Hz, 1F), −64.3 (dd, J = 8.4, 164.0 Hz, 1F).

4.2.7. (*R*)-1-(4-(2,2,2-Trifluoro-1-hydroxyethyl)phenyl)ethanone 7[46]

White solid, 179 mg (82% yield); the 70% ee value was determined by Chiral GC Chirasil Dex CB [column temperature: 165 °C, t_R = 15.9 min (minor, *S*), t_R = 16.4 min (major, *R*)]. $[\alpha]_D^{30.2}$ = −13.1 (c 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (s, 3H), 3.21 (s, 1H), 5.11 (m, 1H), 7.50–7.65 (m, 2H), 7.90–8.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 72.2 (q, J = 32.1 Hz), 124.1 (q, J = 282.3 Hz), 127.7, 128.5, 137.7, 139.2, 198.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ −78.2 (d, J = 6.4 Hz, 3F).

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