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Asymmetric synthesis of β-aryl-β-trifluoromethyl-β-aminoarones via Mannich-type reactions of ketone enolates with chiral aryl CF_3-substituted *N-tert*-butanesulfinyl ketimines

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ABSTRACT

A method for the preparation of chiral β-aryl-β-trifluoromethyl-β-aminoarones has been developed involving the Mannich-type reactions of ketone-derivative enolates with chiral aryl CF_3-substituted *N-tert*-butanesulfinyl ketimines. This method tolerates a wide of aromatic ketones, giving the products in moderate to excellent yields (up to 91%) with good diastereoselectiveties (up to 93:7 dr). Acidic cleavage of the *tert*-butanesulfinyl group gave optically pure β-aryl-β-trifluoromethyl-β-aminoarones in excellent yields (up to 98%), which can be further transformed into CF_3-substituted aziridine derivatives.

1. Introduction

β-Amino ketones derivatives have received considerable attention because they are valuable building blocks for the synthesis of various pharmaceuticals and biologically active compounds.[1] Specifically, these aminoketones can be readily prepared and easily transformed into the corresponding γ-amino alcohols, β-amino esters and 1,3-diamines.[2] In the last two decades, a big challenge has also arisen from the progressively higher requirements on the enantiomeric purity of chiral ligands and therapeutic agents.[3] Consequently, the asymmetric synthesis of optically pure β-aminoketone derivatives become a crucial issue. Most recently, a Rh-catalyzed asymmetric hydrogenation of β-keto enamides as an efficient way to prepare enantiomerically pure β-amino ketones and their derivatives, γ-aryl amines was reported by Zhang's group.[4]

Fluorine-containing compounds are considered the particularly promising drug candidates because the introduction of fluorine-containing group often critically improves pharmacological properties of biologically active molecules (e.g., membrane permeability, hydrophobic binding stability against metabolic oxidation, etc.).[5] Thereinto, a lot of enantiomerically pure fluorine-containing β-aminocarbonyl compounds can be obtained via the organocatalytic and auxiliary-based asymmetric synthesis, but the yields of the target products are usually moderate.[6] For instance, Vovk's group succeeded in applying L-proline as organocatalyst to obtain β-aryl-β-trifluoromethyl-β-aminoketone derivatives via asymmetric Mannich reaction between aryl trifluoromethyl ketimines and acetone.[7] However, the synthesis of β-aryl-β-trifluoromethyl-β-amino ketones by auxiliary-based asymmetric nucleophilic addition of ketimines are rare due to the low electrophilicity and increased steric hindrance to nucleophilic attack on the C=N bond.

Chiral *N-tert*-butanesulfinamides developed by Ellman et al. are versatile reagents for the asymmetric synthesis of various classes of substituted amines, amino acids, amino alcohols, and diamines.[8] In recent years, *N-tert*-butanesulfinamide as a chiral auxiliary has been applied in the asymmetric synthesis of fluorine-containing amines.[9] For instance, Hu reported the asymmetric synthesis of α-difluoromethyl amines and chiral monofluoromethyl amines via the nucleophilic addition of difluoromethyl phenyl sulfone and fluoromethyl phenyl sulfone anion to *N-tert*-butanesulfinyl aldimines.[10] Our group reported the synthesis of enantio-pure α-trifluoromethyl α-propargyl sulfinamides by the addition of lithium acetylides to chiral CF_3-substituted (*S*)-*N-tert*-butanesulfinyl ketimines.[11] Recently, Pan reported the synthesis of β-trifluoromethylated β-amino ketones via addition of ketone-derivative enolates to trifluoromethylated *N-tert*-butanesulfinylimine with good chemical yields and excellent diastereoselectivities.[12] Considering that asymmetric construction of CF_3-substituted quaternary carbon

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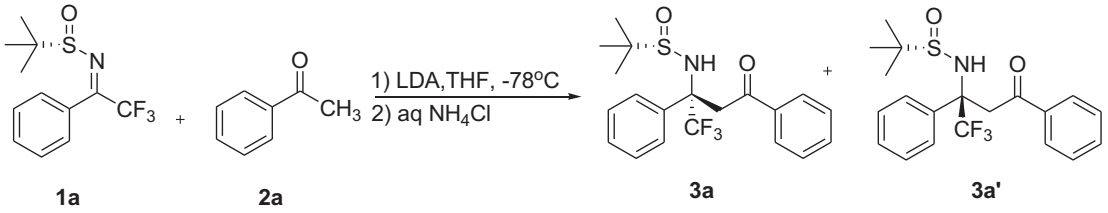
center is still a challenge and inspired by Pan's methodology, we here reported the synthesis of β-aryl-β-trifluoromethyl-β-aminoarones with good yields and high diastereoselectivities via nucleophilic additions of aromatic ketone enolates to chiral aryl CF_3-substituted *N-tert*-butanesulfinyl ketimines.

2. Result and discussion

The aryl CF_3-substituted (*S*)-*N-tert*-butanesulfinyl ketimines **1** were generated and isolated quickly prior to use (not fully characterized because of their low hydrostability).[13] Then the reaction of chiral ketimines and acetophenone **2a** in the presence of LDA was investigated. Firstly, the 1,2-addition reaction of ketimine **1a** with lithium acetophenone enolate, which prepared in advance from acetophenone **2a** and slightly excess of LDA at −78 °C was conducted in THF. The desired products **3a** and **3a′** were obtained in a good combined yield (81%) but in a moderate diastereoselectivity (73:27 dr) after 8 h (Table 1, entry 1). With the reduction of reaction time (2 h), the yield of the reaction was lowered to 69%, and no significant improvement for the diastereoselectivity (78:22 dr) was observed (entry 2). The reaction would not proceed or gave lower yield when dichloromethane (entry 4) or toluene (entry 3) was used as solvent. Further optimization of the reaction condition was carried out by changing the feeding order of starting materials. When LDA was slowly added into a solution of aryl CF_3-substituted (*S*)-*N-tert*-butanesulfinyl ketimines **1a** and acetophenone **2a** (entry 5) in THF, the desired products **3** were isolated in a moderate yield (60%) but in a higher diastereoselectivity (91:9 dr). The highest yield (90%) and a remaining diastereoselectivity (91%, 81:19 dr, entry 6) were achieved when 5.0 equiv of **2a** was used. It was noteworthy that the two adducts as diastereoisomers could be easily separated from each other by silica gel flash chromatography (entry 6).

Under the optimized condition, the reactions were then investigated between various aromatic ketones with chiral aryl CF_3-substituted *N-tert*-butanesulfinyl ketimines. As shown in Table 2, the yields of the reaction were decreased by substituent on the

Table 1
Optimization of reaction conditions[a]

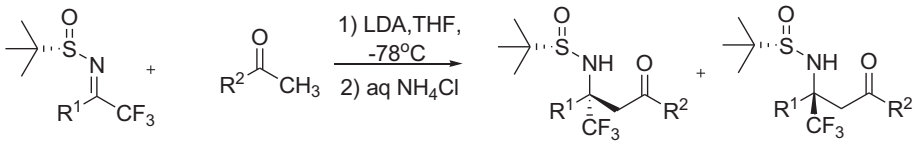


1a **2a** **3a** **3a'**

Entry	**2a** (equiv)	Solvent	Time (h)	Yield[b] (%)	dr[c]
1	1.7	THF	8	81	73:27
2	1.7	THF	2	64	78:22
3	1.7	Toluene	8	41	77:23
4	1.7	CH_2Cl_2	8	—[d]	—[d]
5	1.7	THF	8	60[e]	91:9
6	5	THF	4	90[e]	81:19

[a] All reactions were conducted with *N-tert*-butanesulfinyl ketimine **1a** (1 mmol), LDA (1.87 mmol), solvent (5 mL) unless stated otherwise.
[b] Isolated yield.
[c] Diastereomeric ratios were determined by ^{19}F NMR analysis of the crude reaction mixture.
[d] No reaction.
[e] LDA was slowly added into the mixture of sulfinyl ketimine **1a** and acetophenone **2a**.

Table 2
Asymmetric nucleophilic addition of ketones to chiral ketimines[a]



1 **2** **3** **3'**

Entry	R^1	R^2	Product	Yield[b] (%)	dr[c,d]
1	Ph (**1a**)	Ph (**2a**)	**3a**+**3a′**	91	81:19
2	Ph (**1a**)	4-MeC_6H_4 (**2b**)	**3b**+**3b′**	55	89:11
3	Ph (**1a**)	4-ClC_6H_4 (**2c**)	**3c**+**3c′**	69	85:15
4	Ph (**1a**)	4-$MeOC_6H_4$ (**2d**)	**3d**+**3d′**	47	93:7[e]
5	Ph (**1a**)	2-MeC_6H_4 (**2e**)	**3e**+**3e′**	72	80:20
6	4-$MeOC_6H_4$ (**1b**)	Ph (**2a**)	**3f**+**3f′**	56	71:29
7	4-$MeOC_6H_4$ (**1b**)	4-MeC_6H_4 (**2b**)	**3g**+**3g′**	62	70:30
8	4-$MeOC_6H_4$ (**1b**)	4-ClC_6H_4 (**2c**)	**3h**+**3h′**	63	72:28
9	4-$MeOC_6H_4$ (**1b**)	4-$MeOC_6H_4$ (**2d**)	**3i**+**3i′**	29	84:16
10	4-$MeOC_6H_4$ (**1b**)	2-MeC_6H_4 (**2e**)	**3j**+**3j′**	60	55:45
11	4-ClC_6H_4 (**1c**)	Ph (**2a**)	—[f]	—[f]	—[f]

[a] *N-tert*-Butanesulfinyl ketimine (1 mmol), arone (5 mmol), LDA (1.87 mmol), solvent (5 mL).
[b] Isolated yields.
[c] Diastereomeric ratios were determined by ^{19}F NMR analysis.
[d] Configurations were determined by X-ray crystallographic analysis.
[e] Only **3d** was collected.
[f] No reaction.

aromatic ring of ketones **2** (<80%) (Table 2, entries 1–5). Better diastereoselectivities were observed when the unsubstituted ketimines **1a** was reacted with arones (>80:20 dr, entries 1–5). Electron-rich arones gave higher diastereoselectivities but lower yields than those of electron-deficient arones (entries 3–4, 8–9). Starting from more hindered *o*-substituted arones **2e**, the adducts **3e**, **3e′**, **3j** and **3j′** were also obtained under the optimized condition (entries 5, 10). However, all attempts to carry out the reaction between *p*-chlorophenyl ketimine **1c** and arone **2a** were failed to give any desired product under the optimized or other reaction conditions (entry 11).

The absolute configuration of the addition product **3e** was determined by X-ray crystallographic analysis. The newly formed stereocenter is a (*S*)-configuration (Fig. 1).[14] The stereocenters of other corresponding major products were assigned by analogy, and (*Ss*,*S*)-**3a** was obtained as major diastereomer. Based on the outcome of configuration, the mechanism of asymmetric addition was suggested to proceed via a chelated transition state model in which the CF_3 and bulky *tert*-butanesulfinyl groups were stated in *e* bond.[13] Consequently, a π–π interaction may also exist between the two axial aromatic groups (Fig. 2). It is different from the addition of ketone enolates to sulfinylimine, which was proceeded via a non-chelated transition state model.[12,15]

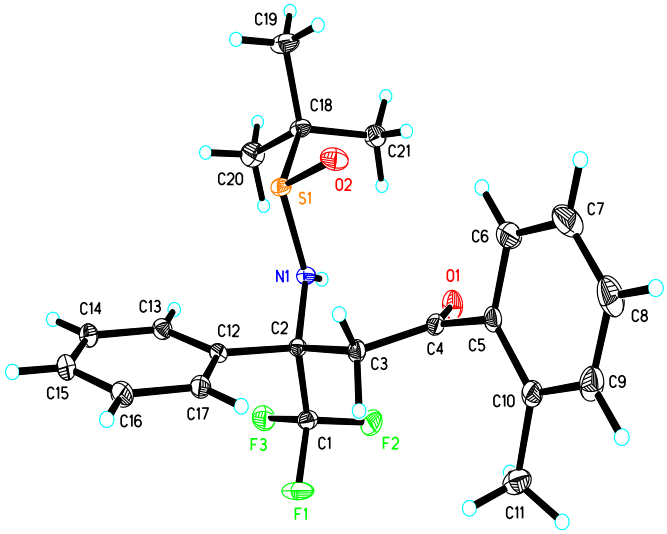


Fig. 1. X-ray crystal structure of (*Ss*,*S*)-**3e**.

As representative examples, the optically pure β-aryl-β-trifluoromethy-β-aminoarones **4a** and **4h** could be readily accessed with retention of configuration by cleaving the *N*-*tert*-butanesulfinyl group under mild acidic condition (4 M HCl in dioxane). As shown in Scheme 1, free β-phenyl-β-trifluoromethyl-β-aminoarone **4a** was obtained in high isolated yield (98%), and the substituted aminoarone **4h** was also obtained in good yield (88%).

Although the nucleophilicity of amino group was reduced by the geminal trifluoromethyl group, acylation of optically pure **4a** with benzoyl chloride could be smoothly underwent[16,17] to afford **5a** in yield of 94% with retention of configuration. Subsequently, we tried to construct an oxazine ring from **5a** by using phosphorus pentachloride as dehydrant because oxazine is a versatile synthon in heterocyclic chemistry and a skeleton found frequently in manifold biologically active compounds.[18] However, only aziridine derivative **7a** was obtained in 73% of yield when 2.5 equiv of phosphorus pentachloride (PCl_5) was used as shown in Scheme 2. A proposed mechanism for the formation of aziridine **7a** was shown in Scheme 3 where one molecule of hydrogen chloride was eliminated firstly to form the chloroimino intermediate **A**,[19] which then transferred to aziridine **7a** by intramolecular cyclization.

3. Conclusions

In summary, nucleophilic additions of ketone-derivative enolates to aryl CF_3-substituted *N*-*tert*-butanesulfinyl ketimines provided a general and efficient method for the asymmetric synthesis of β-aryl-β-trifluoromethyl-β-aminoarones. The product obtained could be further applied in the synthesis of valuable CF_3-substituted aziridine derivative in good yield.

4. Experimental section

4.1. General experiment methods

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere and all reagents were obtained from commercial suppliers and used without further purification. THF and hexane were distilled from sodium/benzophenone ketyl and toluene was distilled from sodium immediately before use. Standard column chromatography was performed on 300–400 mesh silica gel using flash column chromatography techniques. IR spectra of liquids were recorded as thin film on KBr plates. Melting points were determined on a Melt-Temp apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker AM-400 spectrometer with TMS as an internal standard. ^{19}F NMR spectra were recorded on Bruker AM-400 spectrometer with $CFCl_3$ as an external standard. ^{13}C NMR spectra were recorded on a Bruker 400 (101 MHz) spectrometer. High Resolution MS spectra were taken on Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS. Optical rotations were determined on a Rudolph Autopol III, automatic polarimeter using $CHCl_3$ as solvent.

4.2. Typical experimental procedure for addition reactions of ketone-derivative enolates to *N*-*tert*-butanesulfinyl ketimines

Into a flame-dried 25 mL Schlenk flask containing a solution of *N*-*tert*-butanesulfinyl ketimine (*S*)-**1a** (1.0 mmol) and ketone (5 mmol) in THF (5 mL) was slowly added a solution of LDA (0.94 mL, 1.87 mmol, 2 M solution in THF/heptane/ethylenebenzene) at −78 °C under N_2 atmosphere. After stirring at −78 °C for 4 h, saturated aqueous NH_4Cl solution (8 mL) and H_2O (10 mL) were added to quench the reaction, and the mixture was brought to room temperature. The resulting mixture was extracted with EtOAc (15 mL×3). The combined organic solution was dried over anhydrous Na_2SO_4. After removal of volatile solvents under

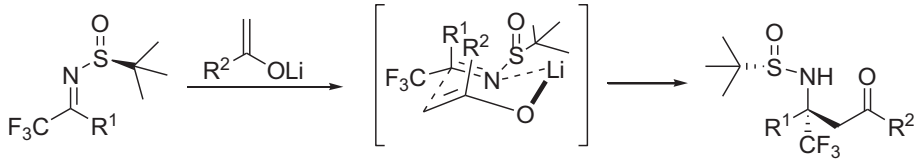
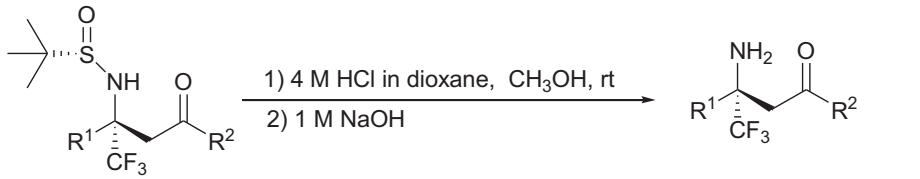
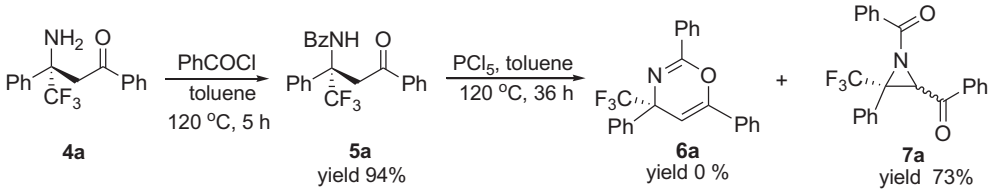


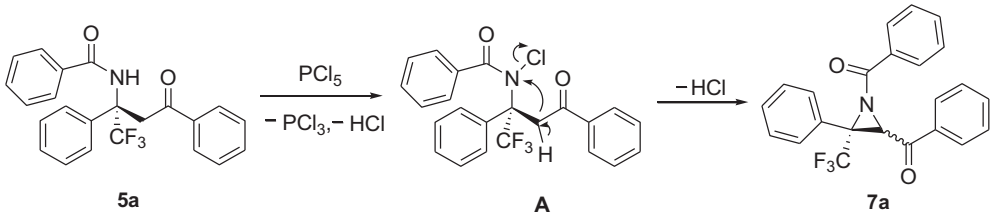
Fig. 2. Proposed mechanism for the asymmetric addition.



Scheme 1. Preparation of β-aryl-β-trifluoromethyl-β-aminoarones.



Scheme 2. Preparation of oxazine with **4a**.



Scheme 3. Proposed mechanism for the formation of aziridine **7a**.

reduced pressure, the crude product was purified by silica gel column chromatography (petroleum ether/EtOAc, 6:1).

*4.2.1. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-4-oxo-2,4-diphenylbutan-2-yl)propane-2-sulfinamide(**3a**).* Yellow oil, yield 74%, $[\alpha]_D^{35}$ +312.7 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J*=7.8 Hz, 2H), 7.69 (d, *J*=7.4 Hz, 2H), 7.56 (t, *J*=7.2 Hz, 1H), 7.42 (dt, *J*=15.2, 7.6 Hz, 5H), 6.52 (s, 1H), 4.05 (AB, *J*=17.1 Hz, 1H), 3.94 (AB, *J*=17.1 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 136.0, 133.6, 132.7, 128.2, 127.8, 127.5, 127.4, 127.1, 124.4 (q, *J*=287.9 Hz), 65.0 (q, *J*=27.3 Hz), 55.9, 40.5, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.5; IR (KBr, cm^{-1}): 3227, 3056, 2953, 2917, 2872, 1686, 1598, 1356, 1251, 1167, 1073, 836; HRMS[M+H^+]: calcd for $C_{20}H_{23}F_3NO_2S$: 398.1396, found: 398.1402.

*4.2.2. (S)-2-Methyl-N-((R)-1,1,1-trifluoro-4-oxo-2,4-diphenylbutan-2-yl)propane-2-sulfinamide(**3a′**).* Pale yellow oil, yield 17%, $[\alpha]_D^{34}$ −330.8 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89–8.04 (m, 2H), 7.57 (dd, *J*=10.6, 4.2 Hz, 1H), 7.49–7.54 (m, 2H), 7.46 (t, *J*=7.7 Hz, 2H), 7.32–7.40 (m, 3H), 5.22 (s, 1H), 4.36 (AB, *J*=18.5 Hz, 1H), 4.26 (AB, *J*=18.5 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 136.1, 135.7, 132.7, 127.8, 127.7, 127.6, 127.0, 125.7, 124.3 (q, *J*=286.8 Hz), 63.9 (q, *J*=26.4 Hz), 56.1, 39.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.9; IR (KBr, cm^{-1}): 3289, 3072, 2967, 2919, 2869, 1685, 1585, 1352, 1251, 1163, 1074, 821; HRMS[M+H^+]: calcd for $C_{20}H_{23}F_3NO_2S$: 398.1396, found: 398.1412.

*4.2.3. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-4-oxo-2-phenyl-4-p-tolylbutan-2-yl)propane-2-sulfinamide (**3b**).* Pale yellow oil, yield 49%, $[\alpha]_D^{33}$ +86.0 (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.79–7.88 (m, 2H), 7.69 (d, *J*=6.5 Hz, 2H), 7.41 (d, *J*=5.4 Hz, 3H), 7.25 (d, *J*=7.1 Hz, 2H), 6.57 (s, 1H), 4.00 (AB, *J*=16.9 Hz, 1H), 3.86 (AB, *J*=17.0 Hz, 1H), 2.39 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 144.8, 134.7, 134.5, 129.4, 129.1, 128.4, 128.3, 128.2, 125.4 (q, *J*=287.9 Hz), 66.1 (q, *J*=27.3 Hz), 56.9, 30.8, 22.7, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.1; IR (KBr, cm^{-1}): 3233, 3056, 2965, 2913, 2872, 1679, 1606, 1355, 1224, 1169, 1074, 799; HRMS[M+H^+]: calcd for $C_{21}H_{25}F_3NO_2S$: 412.1553, found: 412.1564.

*4.2.4. (S)-2-Methyl-N-((R)-1,1,1-trifluoro-4-oxo-2-phenyl-4-p-tolylbutan-2-yl)propane-2-sulfinamide (**3b′**).* Colorless oil, yield 6%, $[\alpha]_D^{33}$ −82.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J*=8.2 Hz, 2H), 7.48 (dd, *J*=6.4, 2.6 Hz, 2H), 7.36 (m, 1H), 7.34 (d, *J*=2.8 Hz, 2H), 7.25 (d, *J*=3.2 Hz, 2H), 5.27 (s, 1H), 4.29 (AB, *J*=18.4 Hz, 1H), 4.21 (AB, *J*=18.4 Hz, 1H), 2.40 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 144.6, 137.2, 134.3, 129.4, 128.8, 128.5, 128.2, 126.8, 125.0 (q, *J*=286.8 Hz), 65.1 (q, *J*=26.3 Hz), 57.1, 29.7, 22.5, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.8. IR (KBr, cm^{-1}): 3289, 3064, 2967, 2925, 2857, 1681, 1605, 1353, 1251, 1166, 1074, 799; HRMS [M+Na^+]: calcd for $C_{21}H_{24}F_3NO_2SNa$: 434.1372, found: 434.1379.

*4.2.5. (S)-N-((S)-4-(4-Chlorophenyl)-1,1,1-trifluoro-4-oxo-2-phenylbutan-2-yl)-2-methylpropane-2-sulfinamide (**3c**).* Yellow oil, yield 59%, $[\alpha]_D^{34}$ +232.8 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J*=8.4 Hz, 2H), 8.01 (d, *J*=6.2 Hz, 2H), 7.78 (dd, *J*=7.2, 4.7 Hz, 5H), 6.76 (s, 1H), 4.37 (AB, *J*=17.1 Hz, 1H), 4.26 (AB, *J*=17.2 Hz, 1H), 1.77 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 140.2, 135.3, 134.3, 129.5, 129.2, 129.0, 128.4, 128.4, 125.2 (q, *J*=287.9 Hz), 65.7 (q, *J*=27.3 Hz), 57.0, 41.3, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.5; IR (KBr, cm^{-1}): 3248, 3056, 2967, 2908, 2960, 1686, 1580, 1352, 1221, 1167, 1076, 833; HRMS[M+H^+]: calcd for $C_{20}H_{22}ClF_3NO_2S$: 432.1006, found: 432.1017.

*4.2.6. (S)-N-((R)-4-(4-Chlorophenyl)-1,1,1-trifluoro-4-oxo-2-phenylbutan-2-yl)-2-methylpropane-2-sulfinamide (**3c′**).* Colorless

oil, yield 10%, $[\alpha]_D^{33}$ −242.6 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J*=2.4 Hz, 2H), 7.46–7.51 (m, 2H), 7.43 (d, *J*=1.6 Hz, 2H), 7.37 (d, *J*=1.2 Hz, 2H), 7.27 (d, *J*=9.5 Hz, 1H), 5.10 (s, 1H), 4.32 (AB, *J*=18.5 Hz, 1H), 4.20 (AB, *J*=18.5 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 140.2, 136.9, 135.0, 129.5, 129.1, 129.0, 128.7, 126.7, 124.9 (q, *J*=286.8 Hz), 64.8 (q, *J*=27.3 Hz), 57.2, 40.4, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.1; IR (KBr, cm^{-1}): 3282, 3065, 2968, 2919, 2869, 1687, 1580, 1344, 1251, 1165, 1077, 824; HRMS[M+Na^+]: calcd for $C_{20}H_{21}ClF_3NO_2SNa$: 454.0826, found: 454.0832.

*4.2.7. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-4-(4-methoxyphenyl)-4-oxo-2-phenylbutan-2-yl)propane-2-sulfinamide (**3d**).* Yellow oil, yield 31%, $[\alpha]_D^{24}$ +192.5 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83–7.87 (m, 2H), 7.59–7.64 (m, 2H), 7.32–7.37 (m, 3H), 6.84–6.88 (m, 2H), 6.57 (s, 1H), 3.89 (AB, *J*=16.7 Hz, 1H), 3.80 (s, 3H), 3.74 (AB, *J*=16.7 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 164.1, 130.8, 130.6, 130.0, 129.1, 128.5, 128.4, 125.4 (q, *J*=285.0 Hz), 113.9, 66.3 (q, *J*=27.3 Hz), 57.1, 55.5, 25.0, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.2; IR (KBr, cm^{-1}): 3215, 3068, 2964, 2926, 2856, 1671, 1598, 1368, 1253, 1171, 1026, 809; HRMS[M+H^+]: calcd for $C_{21}H_{25}F_3NO_3S$: 428.1502, found: 428.1520.

*4.2.8. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-4-oxo-2-phenyl-4-o-tolylbutan-2-yl)propane-2-sulfinamide (**3e**).* White solid, yield 58%, mp 111–113 °C, $[\alpha]_D^{35}$ +147.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.60 (m, 2H), 7.52 (d, *J*=7.8 Hz, 1H), 7.35–7.36 (m, 1H), 7.35 (d, *J*=1.7 Hz, 1H), 7.29–7.32 (m, 1H), 7.19 (d, *J*=8.9 Hz, 3H), 6.52 (s, 1H), 3.85 (s, 2H), 2.37 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 138.4, 137.8, 134.5, 131.9, 131.6, 129.3, 128.6, 128.4, 127.8, 126.8, 125.8, 125.4 (q, *J*=287.9 Hz), 65.9 (q, *J*=28.3 Hz), 57.0, 44.6, 22.8, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.8; IR (KBr, cm^{-1}): 3232, 3060, 2962, 2923, 2851, 1687, 1595, 1393, 1214, 1167, 1073, 909, 738; HRMS[M+H^+]: calcd for $C_{21}H_{25}F_3NO_2S$: 412.1553, found: 412.1571.

*4.2.9. (S)-2-Methyl-N-((R)-1,1,1-trifluoro-4-oxo-2-phenyl-4-o-tolylbutan-2-yl)propane-2-sulfinamide (**3e′**).* Pale yellow oil, yield 14%, $[\alpha]_D^{34}$ −249.2 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J*=7.7 Hz, 1H), 7.41–7.51 (m, 2H), 7.32 (dt, *J*=5.6, 3.6 Hz, 4H), 7.23 (t, *J*=7.6 Hz, 1H), 7.12 (dd, *J*=33.6, 5.3 Hz, 1H), 5.15 (s, 1H), 4.25 (AB, *J*=18.6 Hz, 1H), 4.09 (AB, *J*=18.6 Hz, 1H), 2.30 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 138.4, 137.5, 137.2, 132.1, 131.8, 128.8, 128.5, 128.2, 126.8, 125.8, 124.9 (q, *J*=286.8 Hz), 65.0 (q, *J*=26.3 Hz), 57.1, 53.1, 43.1, 22.5, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.0; IR (KBr, cm^{-1}): 3289, 3060, 2982, 2917, 2876, 1690, 1601, 1343, 1251, 1167, 1074, 910, 741; HRMS[M+H^+]: calcd for $C_{21}H_{25}F_3NO_2S$: 412.1553, found: 412.1563.

*4.2.10. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxo-4-phenylbutan-2-yl)propane-2-sulfinamide (**3f**).* White solid, yield 40%, mp 145–146 °C,$[\alpha]_D^{35}$ +346.9 (*c* 0.7, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, *J*=4.9 Hz, 2H), 8.04 (d, *J*=6.0 Hz, 2H), 7.94 (d, *J*=4.5 Hz, 2H), 7.71 (d, *J*=2.9 Hz, 1H), 7.39 (d, *J*=5.8 Hz, 2H), 7.00 (s, 1H), 4.48 (AB, *J*=17.1 Hz, 1H), 4.33 (AB, *J*=17.1 Hz, 1H), 4.28 (s, *J*=2.7 Hz, 3H), 1.76 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 160.0, 137.2, 133.7, 130.1, 130.0, 128.8, 128.7, 125.5 (q, *J*=285.8 Hz), 113.7, 65.3 (q, *J*=26.8 Hz), 56.9, 55.3, 41.5, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.5; IR (KBr, cm^{-1}): 3227, 3060, 2962, 2916, 2848, 1687, 1609, 1356, 1256, 1164, 1072, 833; HRMS[M+H^+]: calcd for $C_{21}H_{25}F_3NO_3S$: 428.1502, found: 428.1518.

*4.2.11. (S)-2-Methyl-N-((R)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxo-4-phenylbutan-2-yl)propane-2-sulfinamide(**3f′**).* Pale yellow oil, yield 16%, $[\alpha]_D^{35}$ −357.5 (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J*=7.6 Hz, 2H), 7.76 (d, *J*=7.3 Hz, 1H), 7.66 (t, *J*=7.6 Hz, 2H), 7.59 (d, *J*=8.6 Hz, 2H), 7.07 (d, *J*=8.8 Hz, 2H), 5.36 (s, 1H), 4.51 (AB, *J*=18.5 Hz, 1H), 4.39 (AB, *J*=18.5 Hz, 1H), 3.99 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 159.7, 136.8, 133.7, 128.7, 128.0, 125.5 (q, *J*=285.8 Hz), 113.9, 64.6 (q, *J*=26.3 Hz), 57.1, 55.2, 40.3, 22.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.0; IR (KBr, cm^{-1}): 3276, 3061, 2964, 2919, 2845, 1685, 1604, 1344, 1253, 1160, 1075, 828; HRMS[M+H^+]: calcd for $C_{21}H_{25}F_3NO_3S$: 428.1502, found: 428.1514.

*4.2.12. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxo-4-p-tolylbutan-2-yl)propane-2-sulfinamide (**3g**).* White solid, yield 43%, mp 134–136 °C,$[\alpha]_D^{34}$ +91.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J*=8.1 Hz, 2H), 7.79 (d, *J*=8.6 Hz, 2H), 7.45–7.48 (m, 2H), 7.13 (d, *J*=8.9 Hz, 2H), 6.81 (s, 1H), 4.19 (AB, *J*=16.8 Hz, 1H), 4.02 (s, 3H), 3.95 (s, *J*=16.8 Hz, 1H), 2.61 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 160.0, 144.8, 134.7, 130.1, 130.0, 129.5, 128.3, 125.6 (q, *J*=287.9 Hz), 113.7, 65.7 (q, *J*=27.3 Hz), 56.9, 55.3, 41.3, 22.8, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.3; IR (KBr, cm^{-1}): 3223, 3047, 2958, 2917, 2848, 1675, 1601, 1356, 1253, 1165, 1073, 821; HRMS[M+H^+]: calcd for $C_{22}H_{27}F_3NO_3S$: 442.1658, found: 442.1677.

*4.2.13. (S)-2-Methyl-N-((R)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxo-4-p-tolylbutan-2-yl)propane-2-sulfinamide (**3g′**).* Colorless oil, yield 19%, $[\alpha]_D^{35}$ −108.4 (*c* 0.1, $CHCl_3$); NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J*=8.3 Hz, 2H), 7.31 (d, *J*=8.8 Hz, 2H), 7.04–7.19 (m, 2H), 6.68–6.92 (m, 2H), 5.17 (s, 1H), 4.17 (AB, *J*=18.3 Hz, 1H), 4.09 (AB, *J*=18.3 Hz, 1H), 3.69 (s, 3H), 2.32 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 158.7, 143.6, 133.3, 128.4, 128.0, 127.1, 127.1, 124.1 (q, *J*=284.7 Hz), 112.9, 63.70 (q, *J*=26.6 Hz), 56.0, 54.2, 39.1, 21.5, 20.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.9; IR (KBr, cm^{-1}): 3276, 3064, 2962, 2917, 2840, 1682, 1608, 1351, 1252, 1156, 1075, 829; HRMS[M+Na^+]: calcd for $C_{22}H_{26}F_3NO_3SNa$: 464.1478, found: 464.1487.

*4.2.14. (S)-N-((S)-4-(4-Chlorophenyl)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxobutan-2-yl)-2-methylpropane-2-sulfinamide (**3h**).* White solid, yield 45%, mp 129–131 °C, $[\alpha]_D^{34}$ −367.0 (*c* 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85–7.95 (m, 2H), 7.57 (d, *J*=8.8 Hz, 2H), 7.40–7.50 (m, 2H), 6.86–7.03 (m, 2H), 6.45 (s, 1H), 3.99 (AB, *J*=17.0 Hz, 1H), 3.84 (AB, *J*=17.0 Hz, 1H), 3.83 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 160.1, 140.3, 135.5, 129.9, 129.6, 129.1, 125.4 (q, *J*=282.8 Hz), 126.0, 113.7, 65.4 (q, *J*=27.3 Hz), 56.9, 55.3, 29.7, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −74.1; IR (KBr, cm^{-1}): 3346, 2917, 2870, 1658, 1378, 1262, 1098, 1025, 800; HRMS [M+Na^+]: calcd for $C_{21}H_{23}ClF_3NO_3SNa$: 484.0932, found: 484.0952.

*4.2.15. (S)-N-((R)-4-(4-Chlorophenyl)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxobutan-2-yl)-2-methylpropane-2-sulfinamide (**3h′**).* Pale yellow oil, yield 17%, $[\alpha]_D^{32}$ −350.0 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.93 (m, 2H), 7.41–7.50 (m, 2H), 7.38 (d, *J*=8.8 Hz, 2H), 6.84–6.92 (m, 2H), 5.05 (s, 1H), 4.29 (AB, *J*=18.5 Hz, 1H), 4.16 (AB, *J*=18.5 Hz, 1H), 3.80 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.8, 140.2, 135.0, 129.4, 129.0, 128.7, 128.0, 126.1 (q, *J*=286.8 Hz), 114.0, 64.5 (q, *J*=26.3 Hz), 57.1, 55.2, 30.9, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.4; IR (KBr, cm^{-1}): 3289, 3065, 2962, 2917, 2835, 1688, 1592, 1354, 1253, 1163, 1079, 826; HRMS [M+H^+]: calcd for $C_{21}H_{24}ClF_3NO_3S$: 462.1112, found: 462.1130.

*4.2.16. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-2,4-bis(4-methoxyphenyl)-4-oxobutan-2-yl)propane-2-sulfinamide (**3i**).* Yellow solid, yield 24%, mp 87–88 °C, $[\alpha]_D^{35}$ +228.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89–7.98 (m, 2H), 7.59 (d, *J*=8.6 Hz, 2H), 6.95 (s, 2H), 6.92 (d, *J*=1.1 Hz, 2H), 6.68 (s, 1H), 3.94 (AB, *J*=16.6 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.73 (AB, *J*=16.5 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 164.1, 159.9, 130.6, 130.1, 130.0, 129.9, 125.6 (q, *J*=284.8 Hz), 113.9, 113.7, 65.9 (q, *J*=26.3 Hz), 56.9, 55.6, 55.2, 41.1, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.5; IR (KBr, cm^{-1}): 3211, 3072, 2958, 2916, 2843, 1666, 1601,

1360, 1252, 1167, 1072, 833; HRMS[M+H$^+$]: calcd for $C_{22}H_{27}F_3NO_4S$: 458.1607, found: 458.1621.

*4.2.17. (S)-2-Methyl-N-((R)-1,1,1-trifluoro-2,4-bis(4-methoxyphenyl)-4-oxobutan-2-yl)propane-2-sulfinamide(**3i'**).* Yellow oil, yield 5%, $[\alpha]_D^{34}$ +243.2 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J*=9.0 Hz, 2H), 7.39 (d, *J*=8.6 Hz, 2H), 6.93 (d, *J*=8.9 Hz, 2H), 6.86 (d, *J*=9.0 Hz, 2H), 5.30 (s, 1H), 4.22 (AB, *J*=18.2 Hz, 1H), 4.14 (AB, *J*=18.2 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 164.0, 159.7, 130.4, 129.9, 129.1, 128.1, 125.1 (q, *J*=286.8 Hz), 113.9, 113.9, 64.8 (q, *J*=27.3 Hz), 57.1, 55.5, 55.2, 40.0, 22.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.0; IR (KBr, cm^{-1}): 3260, 3068, 2970, 2931, 2847, 1670, 1602, 1356, 1254, 1167, 1075, 820; HRMS[M+H$^+$]: calcd for $C_{22}H_{27}F_3NO_4S$: 458.1607, found: 458.1626.

*4.2.18. (S)-2-Methyl-N-((S)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxo-4-o-tolylbutan-2-yl)propane-2-sulfinamide (**3j**).* White solid, yield 33%, mp 109–111 °C, $[\alpha]_D^{35}$ −96.3 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.58 (m, 3H), 7.37 (d, *J*=7.5 Hz, 1H), 7.24–7.28 (m, 2H), 6.93 (d, *J*=9.2 Hz, 2H), 6.65 (s, 1H), 3.87–3.92 (m, 2H), 3.83 (s 3H), 2.45 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 160.1, 138.6, 137.8, 131.9, 131.5, 130.0, 127.8, 126.2, 125.8, 125.5 (q, *J*=288.9 Hz), 113.7, 65.4 (q, *J*=27.3 Hz), 56.8, 55.3, 44.6, 22.8, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −74.1; IR (KBr, cm^{-1}): 3242, 3068, 2965, 2921, 2851, 1679, 1613, 1348, 1256, 1165, 1072, 830; HRMS[M+H$^+$]: calcd for $C_{22}H_{27}F_3NO_3S$: 442.1658, found: 442.1672.

*4.2.19. (S)-2-Methyl-N-((R)-1,1,1-trifluoro-2-(4-methoxyphenyl)-4-oxo-4-o-tolylbutan-2-yl)propane-2-sulfinamide (**3j'**).* Pale yellow oil, yield 27%, $[\alpha]_D^{31}$ −81.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J*=7.7, 1.1 Hz, 1H), 7.41 (d, *J*=8.8 Hz, 2H), 7.35 (dd, *J*=7.5, 1.3 Hz, 1H), 7.27 (d, *J*=7.6 Hz, 1H), 7.21 (d, *J*=7.6 Hz, 1H), 6.87–6.91 (d, *J*=8.0 Hz, 2H), 5.20 (s, 1H), 4.26 (AB, *J*=18.6 Hz, 1H), 4.09 (AB, *J*=18.6 Hz, 1H), 3.78 (s, 3H), 2.37 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 159.8, 138.4, 137.6, 132.1, 131.8, 129.0, 128.2, 128.1, 125.8, 125.0 (q, *J*=285.8 Hz), 113.9, 64.7 (q, *J*=27.3 Hz), 57.1, 55.2, 42.9, 22.5, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.2; IR (KBr, cm^{-1}): 3283, 3060, 2967, 2922, 2848, 1690, 1610, 1350, 1253, 1162, 1074, 829; HRMS[M+H$^+$]: calcd for $C_{22}H_{27}F_3NO_3S$: 442.1658, found: 442.1678.

4.3. Typical experimental procedure for acidic cleavage of *tert*-butanesulfinyl group

To a solution of sulfinamide (0.4 mmol) in methanol (0.5 M) was added HCl (0.25 mL, 4.0 M in 1,4-dioxane). The reaction mixture was stirred at room temperature for 2 h and diluted with EtOAc (10 mL) after which a NaOH aqueous solution (1 M) was carefully added dropwise to adjust the pH of the mixture to 8. The organic layer was removed and the aqueous layer was extracted with EtOAc (15 mL×2). The organic layers were combined and dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by chromatography (silica gel, petroleum ether/EtOAc, 10:1).

*4.3.1. (S)-3-Amino-4,4,4-trifluoro-1,3-diphenylbutan-1-one (**4a**).* Colorless oil, yield 98%, $[\alpha]_D^{34}$ +161.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.82 (m, 2H), 7.46 (d, *J*=7.6 Hz, 2H), 7.41 (t, *J*=7.4 Hz, 1H), 7.28 (t, *J*=7.8 Hz, 2H), 7.13–7.23 (m, 3H), 4.02 (AB, *J*=17.5 Hz, 1H), 3.43 (AB, *J*=17.5 Hz, 1H), 2.43 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 138.0, 137.0, 133.7, 128.8, 128.4, 128.2, 127.9, 126.6, 1256.2 (q, *J*=284.8 Hz), 61.3 (q, *J*=26.3 Hz), 42.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.9; IR (KBr, cm^{-1}): 3395, 3330, 2925, 1686, 1590, 1319, 1276, 1154, 747, 695; HRMS[M+H$^+$]: calcd for $C_{16}H_{15}F_3NO$: 294.1100, found: 294.1103.

*4.3.2. (S)-3-Amino-1-(4-chlorophenyl)-4,4,4-trifluoro-3-(4-methoxyphenyl)butan-1-one(**4h**).* Yellow oil, yield 88%, $[\alpha]_D^{34}$ −192.0 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J*=5.4 Hz, 2H), 7.47 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.5 Hz, 2H), 6.86 (d, *J*=8.8 Hz, 2H), 4.05 (AB, *J*=17.3 Hz, 1H), 3.49 (AB, *J*=17.3 Hz, 1H), 3.77 (s, 3H), 2.46 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 159.4, 140.1, 135.4, 129.7, 129.4, 129.0, 127.8, 126.2 (q, *J*=285.8 Hz), 113.8, 60.9 (q, *J*=26.3 Hz), 55.2, 42.7; ^{19}F MNR (376 MHz, $CDCl_3$) δ −79.1; IR (KBr, cm^{-1}): IR (KBr, cm^{-1}): 3398, 3333, 3061, 2938, 2841, 1687, 1592, 1407, 1258, 1099, 734, 639; HRMS [M+H$^+$]: calcd for $C_{17}H_{16}ClF_3NO_2$: 358.0816, found: 358.0826.

*4.3.3. Preparation of (S)-N-(1,1,1-trifluoro-4-oxo-2,4-diphenylbutan-2-yl)benzamide (**5a**).* To a solution of (*S*)-3-amino-4,4,4-trifluoro-1,3-diphenylbutan-1-one **4a** (150 mg, 0.51 mmol) in dry toluene (2 mL), benzoyl chloride (144 mg, 1.02 mmol) was added. The reaction mixture was boiled for 5 h, followed 15 mL of H_2O was added to quench the reaction. The organic layer was removed and the aqueous layer was extracted with EtOAc (10 mL×2). The organic layers were combined and dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by chromatography (silica gel, petroleum ether/EtOAc, 3:1).

*4.3.4. (S)-N-(1,1,1-Trifluoro-4-oxo-2,4-diphenylbutan-2-yl)benzamide (**5a**).* Yellow oil, yield 94%, $[\alpha]_D^{23}$ −209.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.95 (d, *J*=1.5 Hz, 2H), 7.93 (d, *J*=1.3 Hz, 1H), 7.55–7.62 (m, 4H), 7.39–7.53 (m, 7H), 4.44 (AB, *J*=16.4 Hz, 1H), 3.87 (AB, *J*=16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 166.6, 136.7, 136.12, 134.3, 133.7, 131.8, 128.7, 128.6, 128.6, 128.5, 128.2, 127.1, 125.8, 125.4 (q, *J*=286.0 Hz), 64.2 (q, *J*=28.1 Hz), 39.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −71.3; IR (KBr, cm^{-1}): 3341, 3063, 2921, 1689, 1521, 1167, 908, 733; HRMS[M+H$^+$]: calcd for $C_{23}H_{19}F_3NO_2$: 398.1362, found: 398.1373.

4.4. Procedure for (*S*)-2,4,6-triphenyl-4-(trifluoromethyl)-4*H*-1,3-oxazine (7a)

To a solution of amide **5a** (292 mg, 0.73 mmol) in dry toluene (10 mL), phosphorus pentachloride (380 mg, 1.83 mmol) was added and the reaction mixture was boiled for 48 h. Then 20 mL of H_2O was added to quench the reaction, the organic layer was removed and the aqueous layer was extracted with EtOAc (15 mL×2). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by chromatography (silica gel, petroleum ether/EtOAc, 20:1).

*4.4.1. (S)-2,4,6-Triphenyl-4-(trifluoromethyl)-4H-1,3-oxazine (**7a**).* Yellow oil, yield 73%, $[\alpha]_D^{34}$ +140.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J*=7.1 Hz, 2H), 7.96 (d, *J*=7.2 Hz, 2H), 7.81 (d, *J*=7.2 Hz, 2H), 7.64 (dd, *J*=15.4, 7.6 Hz, 2H), 7.42–7.56 (m, 7H), 5.96 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 166.2, 138.2, 136.0, 133.7, 132.7, 129.1, 129.0, 129.0, 128.7, 128.6, 128.5, 127.4, 125.9, 124.1 (q, *J*=283.1 Hz), 88.3, 84.2 (q, *J*=27.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −69.7; IR (KBr, cm^{-1}): 3064, 2913, 2843, 1696, 1654, 1447, 1252, 1169, 1070, 1025, 691; HRMS calcd for $C_{23}H_{17}F_3NO_2$ [M+H$^+$]: 396.1206, found: 396.1209.

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