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Asymmetric Michael addition of α-fluoro-α-phenylsulfonyl ketones to nitroolefins catalyzed by phenylalanine-based bifunctional thioureas☆

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ABSTRACT

Phenylalanine-based bifunctional thiourea derivatives promoted the asymmetric Michael addition of α-fluoro-α-phenylsulfonyl ketones to nitroolefins, affording enantiomerically enriched fluorine-containing multifunctional molecules containing adjoining chiral fluorine-substituted quaternary and tertiary centers in good yields and enantioselectivities.

1. Introduction

Nowadays, the great importance of fluorine-containing compounds has been well recognized in kinds of fields such as material, medicinal, pharmaceutical and agrochemical science [1]. The introduction of the fluorine atom has almost become one of the routine practices in the studies of these sciences. Therefore, there has been a great demand for the development of more selective, safe and mild fluorination methods [2]. With the rapid development of organocatalysis over the past decade, the organocatalytic asymmetric synthesis of fluorinated molecules has received considerable attentions among organic chemists and impressive advancement has been achieved [3]. Particularly, the asymmetric addition reaction of fluorine-substituted monofluorinated nucleophiles to various electrophiles, with the concomitant formation of a new C–C bond and the construction of a chiral fluorinated center, has been one of the research focuses. For examples, α-fluoro-β-keto esters have been used as nucleophiles in asymmetric Michael additions with nitroolefins, *N*-alkyl maleimides and Mannich reactions [4]. Our group has also reported the asymmetric Robinson annulation between α-fluoro-β-keto esters and α,β-unsaturated ketones catalyzed by primary-secondary diamines to synthesize multiply substituted fluorinated chiral cyclohexenones with a fluorinated quaternary chiral center in excellent enantioselectivities [5].

Besides α-fluoro-β-keto esters, the use of α-nitro, cyano, ester, or acetyl-substituted fluoro(phenylsulfonyl)methanes as the nucleophile has been particularly intriguing due to their convertibility into a variety of functionalized monofluoromethylated compounds, which are crucial synthons for many valuable compounds in the pharmaceutical arena [4i–j,6]. Prakash et al. have achieved enantioselective and diastereoselective Michael additions of these fluorine containing (phenylsulfonyl)methane derivatives to chalcones using cinchona alkaloids-based bifunctional catalysts [4j,k]. In addition, their organocatalytic asymmetric Michael additions to α, β-unsaturated aldehydes have also been reported by Palomo [4h] and Córdova [4i]. Surprisingly, to the best of our knowledge, there has been no report on the organocatalyzed Michael addition of α-fluoro-α-phenylsulfonyl ketones to nitroolefins. Together with the rich chemistry of the nitro group [7], the multiply functionalized product of such an addition could have great potential in organic synthesis and related areas. Herein, we report our results on this kind of reaction using amino acid and cinchona alkaloid-derived bifunctional thiourea catalysts (Fig. 1).

2. Results and discussion

Initially, cinchona alkaloid based bifunctional catalyst **1**, the optimum catalyst in Prakash's study [4j], was examined in the model reaction of 2-fluoro-1-phenyl-2-(phenylsulfonyl)ethanone **3a** to (*E*)-(2-nitrovinyl)benzene **4a** in xylene at room temperature.

☆ Dedicated to Professor Wei-Yuan Huang on the occasion of his 90th birthday.

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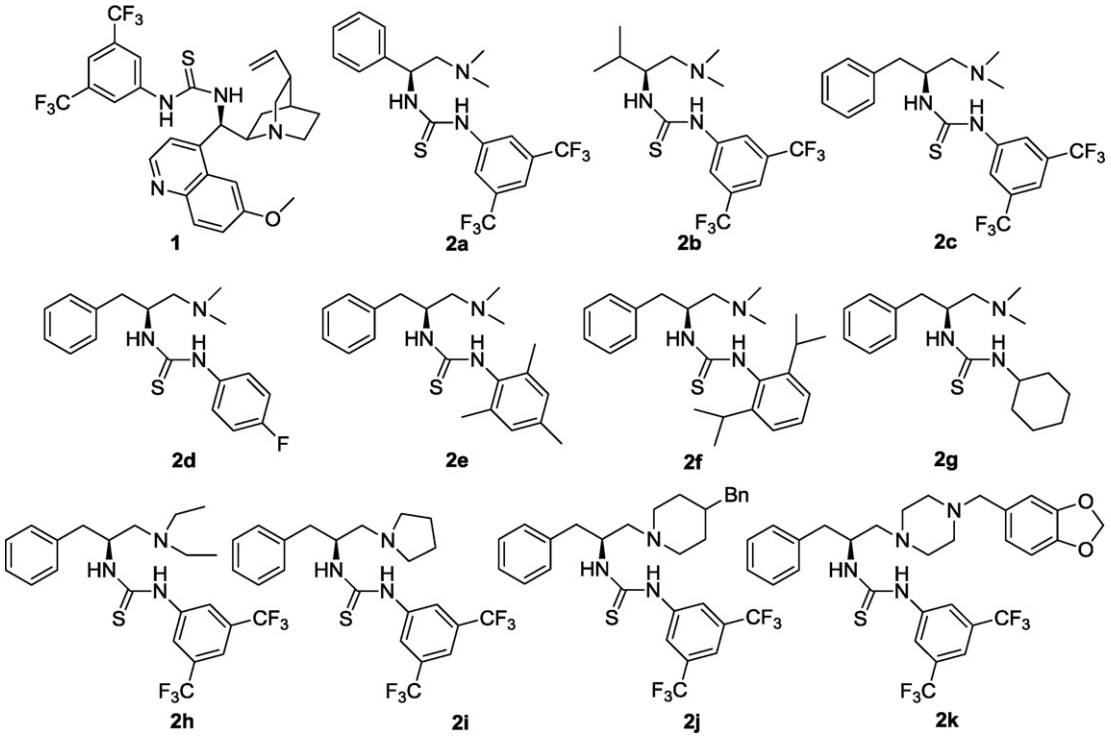


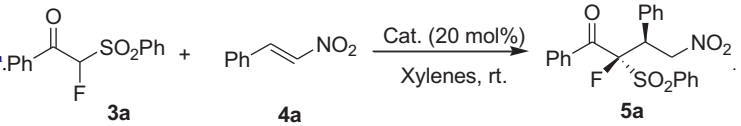
Fig. 1. Structures of the catalysts studied.

Although a good yield and excellent diastereoselectivity were gained, the enantioselectivity was not satisfactory (Table 1, entry 1). Based on our recent efforts on the development of organocatalysts from easily available chiral amino acids, several other thiourea catalysts **2a**–**2k** were synthesized and examined [7]. Variation in the chiral amino acid skeletons revealed that phenylalanine-derived catalyst **2a** is slightly better than phenylglycine-derived **2b** and isoleucine-derived **2c**, in terms of enantioselectivity (Table 1, entries 2–4). While changing the substituents on the benzene ring of the group (thiourea moiety) to electron-donating and bulky ones could lead to much improved enantioselectivities, the yields decreased dramatically (Table 1, entries 4–8). Pleasingly, further structural optimization by increasing the steric hindrance of tertiary amine moiety gave rise to the best catalyst **2k**, providing the desired product **5a** in high enantioselectivity and with good yield and excellent diastereoselectivity (Table 1, entry 12). Notably, all the catalysts with different structures gave the same excellent d.r. value of 20:1.

Next, different solvents were tested with the optimal catalyst **2k** (Table 2). In spite that the reaction performed in carbon tetrachloride proceeded faster and gave higher yields, a slight drop in the enantioselectivity was observed (Table 2, entries 3). In contrast, more polar chlorine-containing solvents dichloromethane, chloroform or MTBE gave extremely low yields being the lower conversion of reactants (Table 2, entries 4–6). While the use of toluene or a co-solvent of carbon tetrachloride and xylenes failed to provide better results, the use of pure *m*-xylene led to somewhat improved overall results (Table 2, entries 7–8).

Table 1

Screening of catalysts[a].

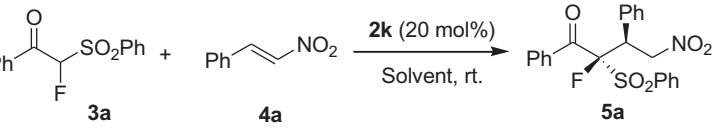


Entry	Cat.	Yield of **5a**/%[b]	*dr*. of **5a**[c]	*ee*. of **5a**/%[d]
1	**1**	85	20:1	70
2	**2a**	80	20:1	55
3	**2b**	75	20:1	60
4	**2c**	90	20:1	64
5	**2d**	70	20:1	68
6	**2e**	30	20:1	82
7	**2f**	33	20:1	89
8	**2g**	66	20:1	60
9	**2h**	95	20:1	73
10	**2i**	90	20:1	68
11	**2j**	95	20:1	75
12	**2k**	75	20:1	93

[a] Unless otherwise noted, the reaction was carried out with **3a** (0.1 mmol), **4a** (0.15 mmol), catalyst (20 mol%) and solvent (0.5 mL) at room temperature for 3 days.
[b] Isolated yield.
[c] Determined by ^{19}F NMR.
[d] Determined by HPLC.

Table 2

Screening of solvents[a].

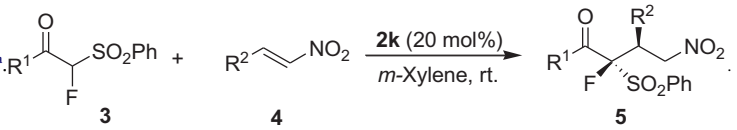


Entry	Solvent	Time/h	Yield/%[b]	*dr.*[c]	*ee.*/%[d]
1	Xylenes	72	75	20:1	93
2	Toluene	72	50	20:1	90
3	CCl_4	48	95	20:1	90
4	$CHCl_3$	72	14	20:1	ND
5	CH_2Cl_2	72	10	20:1	ND
6	MTBE	72	10	20:1	ND
7	Xylenes/CCl_4(2:1)	72	90	20:1	90
8	*m*-Xylene	72	80	20:1	94
9	*o*-Xylene	72	85	20:1	92
10	*p*-Xylene	72	85	20:1	93

[a] Unless otherwise noted, the reaction was carried out with **3a** (0.1 mmol), **4a** (0.15 mmol), catalyst (20 mol%) and solvent (0.5 mL) at room temperature.
[b] Isolated yield.
[c] Determined by ^{19}F NMR.
[d] Determined by HPLC.

Table 3

Study on the reaction scope with different **3** and **4**[a].



Entry	R^1	R^2	Time/h	Yield/%[b]	*dr.*[c]	*ee.*/%[d]
1	C_6H_5, (**3a**)	C_6H_5, (**4a**)	72	80(**5a**)	20:1	94
2	CH_3, (**3b**)	C_6H_5, (**4a**)	72	90(**5b**)	6:1	96
3	C_6H_5, (**3a**)	*p*-FC_6H_4, (**4b**)	72	88(**5c**)	14:1	89
4	C_6H_5, (**3a**)	*p*-BrC_6H_4, (**4c**)	48	90(**5d**)	17:1	90
5	C_6H_5, (**3a**)	*p*-$CH_3C_6H_4$, (**4d**)	72	85(**5e**)	20:1	90
6	C_6H_5, (**3a**)	*p*-$CH_3OC_6H_4$, (**4e**)	72	82(**5f**)	10:1	93
7	C_6H_5, (**3a**)	*p*-PhC_6H_4, (**4f**)	72	89(**5g**)	20:1	90
8	C_6H_5, (**3a**)	*p*-$NO_2C_6H_4$, (**4g**)	72	70(**5h**)	14:1	91
9	C_6H_5, (**3a**)	*o*-BrC_6H_4, (**4h**)	72	90(**5i**)	15:1	87
10	C_6H_5, (**3a**)	*m*-BrC_6H_4, (**4i**)	72	85(**5j**)	15:1	86
11	C_6H_5, (**3a**)	1-Naphthyl, (**4j**)	72	85(**5k**)	20:1	92
12	C_6H_5, (**3a**)	2-Furyl, (**4k**)	72	93(**5l**)	20:1	91
13	C_6H_5, (**3a**)	2-Thienyl, (**4l**)	72	82(**5m**)	16:1	91
14	C_6H_5, (**3a**)	*n*-Bu, (**4m**)	72	90(**5n**)	5:1	90
15	C_6H_5, (**3a**)	*i*-Pr, (**4n**)	72	70(**5o**)	20:1	91

[a] Unless otherwise noted, the reaction was carried out with **3** (0.3 mmol), **4** (0.45 mmol), catalyst (20 mol%) and solvent (3.0 mL) at room temperature.
[b] Isolated yield.
[c] Determined by ^{19}F NMR.
[d] Determined by HPLC.

Interestingly, the *dr.* value in all these cases examined also remained excellent without negligible changes.

With the optimized reaction conditions in hand, a selected spectrum of different substrates was examined to test the scope of this reaction (Table 3). Alkyl ketone derivative **3b** ($R^1 = CH_3$) also participated in the reaction well to give the adduct **5b** in excellent yield and enantioselectivity, albeit with a diminished diastereoselectivity of 6:1 (Table 3, entry 2). With regard to different olefins **4**, when R^2 was an aryl group, substrates with electron-donating/withdrawing substituents on the benzene ring were generally well tolerated, though slight drops in *dr.* and *ee.* values were observed (Table 3, entries 3–11). Heterocyclic substrates **4k** and **4l** also gave comparably good results (Table 3, entries 12–13). Notably, alkyl substituted nitroolefins also proved to be highly applicable to the reaction system: the bulkier **4n** (R^2 = *i*-Pr) was much more favored over **4m** (R^2 = *n*-Bu) in terms of *dr.* value while both gave excellent *ee.* values (Table 3, entries 14–15). It is also worth mentioning that the excellent diastereoselectivities obtained in most cases in our system poses a sharp contrast to Lu's work [4c] dealing with the addition of α-fluoro-β-keto esters to nitroolefins, where only modest *dr.* values (no more than 6:1) were obtained in most cases. The absolute configuration of the major isomer of **5d** was determined by X-ray crystallographic analysis (Fig. 2), and the others were assigned by analogy assuming a similar mechanism was followed [8]. A possible transition state model was proposed to explain the stereochemical results of the Michael addition. Thus,

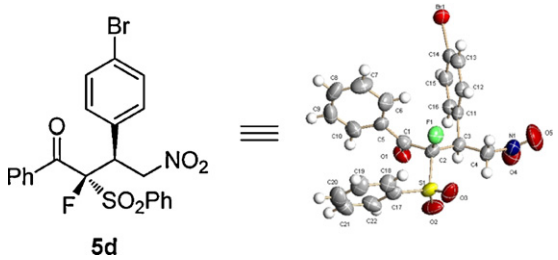
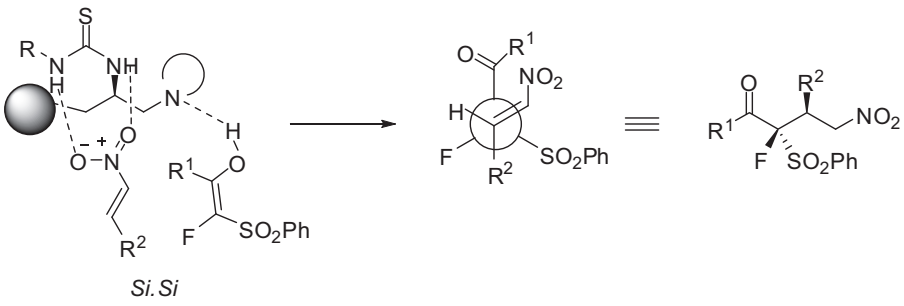
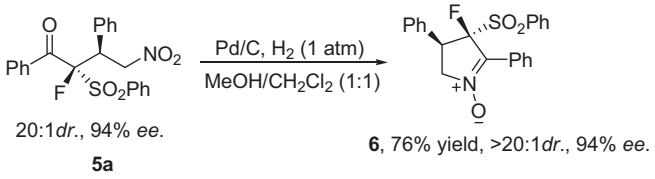


Fig. 2. ORTEP structure of compound **5d**.



Scheme 1. Proposed transition-state structure.



Scheme 2. Conversion of **5a** to **6**.

the bifunctional chiral thiourea catalyst activated the nitroolefin through H-bonding. The α-fluoro-α-phenylsulfonyl ketone attacked the nitroolefin from the *Si* face leading the Michael product of the 2*S*, 3*S* configuration (Scheme 1).

Nitrones have attracted growing interests among synthetic chemists due to their successful applications as building blocks in the synthesis of various natural and biologically active compounds [9,10]. As an illustration of the utility of the present reaction, the Michael adduct **5a** was transformed to pyrrolidine-type nitrone product **6** via a single simple hydrogenation step. The densely functionalized cyclic nitrone **6** was obtained in good yield, and with no decrease in *dr*. and *ee*. values (Scheme 2).

3. Conclusion

In summary, we have reported the organocatalyzed asymmetric Michael addition of α-fluoro-α-phenylsulfonyl ketones to nitroolefins to afford enantiomerically enriched fluorine-containing multifunctional molecules containing adjoining fluorine-substituted quaternary and tertiary centers. Using readily available phenylalanine-based bifunctional thiourea derivatives as the catalysts, the desired products were obtained with good to excellent yield and stereoselectivity.

4. Experimental

Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers and purified by standard techniques. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a DPX-300 or Varian EM-360 (300 MHz) and DPX-400 (100 MHz) with TMS as the internal standard. ^{19}F NMR spectra were recorded at 282 MHz with $CFCl_3$ as the external standard. Analytical high-performance liquid chromatography (HPLC) was carried out on WATERS equipment using a chiral column. Melting points were determined on a SGW X-4 apparatus, and are uncorrected. Optical rotations were measured on a JASCO P-1030 Polarimeter at λ = 589 nm. IR spectra were recorded on a NicoletbAV-360 instrument. Elementary analysis was taken on a Vario EL III elementary analysis instrument. LRMS and HRMS analyses were performed on API 200 LC/MS system (Applied Biosystems Co. Ltd.) or APEXIII(7.0 T) FTMS mass spectrometer, respectively.

4.1. General procedure for the Michael addition catalyzed by 2*k*

The solution of **2k** (6 mg, 0.01 mmol), **3a** (14 mg, 0.05 mmol) and **4a** (10 mg, 0.07 mmol) in *m*-xylene (0.5 mL) was stirred at room temperature and monitored by TLC. After completion (72 h), the mixture was purified by flash chromatography (dichloromathane/petro ether: 1/1) to provide white solid product **5a** 17 mg, in 80% yield.

4.1.1. 2-Fluoro-4-nitro-1,3-diphenyl-2-(phenylsulfonyl)butan-1-one 5*a*

White solid; Mp: 90–92 °C; $[\alpha]_D^{25}$ = 45.1 (*c* = 1.34 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83–7.77 (m, 2H), 7.66–7.56 (m, 1H), 7.51–7.37 (m, 3H), 7.34–7.10 (m, 9H), 5.69–5.56 (m, 1H), 5.30–5.17 (m, 1H), 4.74–4.64 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −145.72 (d, *J* = 17.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7 (d, *J* = 25.2 Hz), 135.3, 135. 2, 134.3, 134.0, 131.6, 130.7, 129.7, 129.5, 129.5, 129.3, 129.1, 110.5 (d, *J* = 240.9 Hz), 75.3 (d, *J* = 5.2 Hz), 47.4 (d, *J* = 22.2 Hz); IR (KBr) ν 2933, 1675, 1560, 1453, 1331, 1158 cm^{-1}; ESI-MS (*m*/*z*): 450.0 (M + 23)$^+$; HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{18}NO_5FS$: 427.0890; found: 427.0892 [M]$^+$; HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.8 mL/min; t_R = 32.0 min (minor enantiomer), 37.8 min (major enantiomer).

4.1.2. 3-Fluoro-5-nitro-4-phenyl-3-(phenylsulfonyl)pentan-2-one 5*b*

White solid; Mp: 115–116 °C; $[\alpha]_D^{27}$ = 93.4 (*c* = 1.03 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89–7.72 (m, 3H), 7.63–7.54 (m, 2H), 7.34–7.19 (m, 3H), 7.16–7.04 (m, 2H), 5.50–5.42 (m, 1H), 5.23–5.06 (m, 1H), 4.57–4.37 (m, 1H), 1.87 (d, *J* = 5.9 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −148.42 (d, *J* = 8.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5 (d, *J* = 27.7 Hz), 135.5, 134.2, 131.4, 130.5, 129.6, 129.4, 129.2, 129.1, 107.6 (d, *J* = 236.4 Hz), 74.9 (d, *J* = 5.9 Hz), 46.2 (d, *J* = 22.5 Hz), 28.7; IR (KBr) ν 3066, 1728, 1560, 1497, 1449, 1332, 1160 cm^{-1}; ESI-MS (*m*/*z*): 388.1 (M + 23)$^+$; HRMS (EI): *m*/*z*: calcd. for $C_{17}H_{16}NO_5FS$: 365.0733; found: 365.0738 [M]$^+$; HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.7 mL/min; t_R = 17.9 min (minor enantiomer), 19.1 min (major enantiomer).

4.1.3. 2-Fluoro-3-(4-fluorophenyl)-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one 5*c*

Colorless oil; $[\alpha]_D^{25}$ = 36.6 (*c* = 1.28 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.53–7.34 (m, 5H), 7.30–7.11 (m, 4H), 6.91 (t, *J* = 8.8 Hz, 2H), 5.60–5.46 (m, 1H), 5.27–5.07 (m, 1H), 4.80–4.65 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −111.67 (s, 1F), −147.57 (d, *J* = 20.5 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3 (d, *J* = 24.2 Hz), 163.1 (d, *J* = 249.4 Hz), 135.3, 135.1 (d, *J* = 4.4 Hz), 134.3, 131.6 (d, *J* = 8.8 Hz), 130.6, 129.6, 129.5, 129.3, 128.3, 127.4 (d, *J* = 2.8 Hz), 116.1 (d, *J* = 21.4 Hz), 110.3 (d, *J* = 241.2 Hz), 75.4 (d, *J* = 5.3 Hz), 46.7 (d, *J* = 22.6 Hz); IR (film) ν 3065, 1677, 1597, 1561, 1511, 1448,

1336, 1161 cm^{-1}; ESI-MS (*m*/*z*): 468.0 $(M + 23)^+$; HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{17}NO_5F_2S$: 445.0796; found: 445.0788 $[M]^+$; HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.7 mL/min; t_R = 32.5 min (minor enantiomer), 45.3 min (major enantiomer).

4.1.4. 2-Fluoro-3-(4-bromophenyl)-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one **5d**

White solid; Mp: 130–132 °C; $[\alpha]_D^{23}$ = 27.5 (*c* = 1.20 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.54–7.18 (m, 9H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.56–5.39 (m, 1H), 5.22–5.07 (m, 1H), 4.82–4.61 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −147.57 (d, *J* = 20.5 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0 (d, *J* = 24.0 Hz), 135.3, 135.0 (d, *J* = 4.2 Hz), 134.4, 134.3, 132.2, 131.4, 130.8, 130.6, 129.6 (d, *J* = 8.8 Hz), 129.3, 128.4, 123.7, 110.4 (d, *J* = 241.6 Hz), 75.2 (d, *J* = 4.8 Hz), 47.0 (d, *J* = 22.1 Hz); IR (KBr) ν 2924, 1677, 1595, 1561, 1448, 1338, 1161 cm^{-1}; ESI-MS (*m*/*z*): 528.1 $(M + 23)^+$; HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{17}NO_5FSBr$: 504.9995; found: 504.9996 $[M]^+$; HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.9 mL/min; t_R = 48.9 min (minor enantiomer), 84.8 min (major enantiomer).

4.1.5. 2-Fluoro-4-nitro-1-phenyl-2-(phenylsulfonyl)-3-p-tolylbutan-1-one **5e**

Colorless oil; $[\alpha]_D^{27}$ = 43.9 (*c* = 1.38 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 6.9 Hz, 1H), 7.52–7.30 (m, 5H), 7.29–7.15 (m, 2H), 7.11–6.91 (m, 4H), 5.67–5.49 (m, 1H), 5.28–5.10 (m, 1H), 4.74–4.55 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −146.23 (d, *J* = 11.5 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6 (d, *J* = 24.4 Hz), 139.2, 135.3 (d, *J* = 24.4 Hz), 135.2, 134.4, 134.0, 130.7, 129.8, 129.7, 129.6, 129.5, 129.2, 128.5, 128.2, 110.2 (d, *J* = 240.6 Hz), 75.5 (d, *J* = 5.1 Hz), 47.1 (d, *J* = 22.5 Hz), 21.1; IR (film) ν 2924, 1677, 1596, 1558, 1448, 1159 cm^{-1}; ESI-MS (*m*/*z*): 464.1 $(M + 23)^+$; HRMS (EI): *m*/*z*: calcd. for $C_{23}H_{20}NO_5FS$: 441.1046; found: 441.1042 $[M]^+$; HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.6 mL/min; t_R = 26.2 min (minor enantiomer), 44.1 min (major enantiomer).

4.1.6. 2-Fluoro-3-(4-methoxyphenyl)-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one **5f**

White solid; Mp: 84–85 °C; $[\alpha]_D^{25}$ = 42.5 (*c* = 1.20 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.48–7.33 (m, 5H), 7.23–7.21 (m, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 5.59–5.50 (m, 1H), 5.25–5.10 (m, 1H), 4.74–4.53 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −146.39 (d, *J* = 17.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6 (d, *J* = 24.2 Hz), 160.2, 135.2, 134.5, 134.0, 130.9, 130.6, 129.6, 129.5, 129.2, 128.2, 123.2, 114.4, 110.3 (d, *J* = 240.0 Hz), 75.5 (d, *J* = 4.4 Hz), 55.24, 46.7 (d, *J* = 22.5 Hz); IR (KBr) ν 2926, 1677, 1611, 1557, 1448, 1255 cm^{-1}; ESI-MS (*m*/*z*): 480.1 $(M + 23)^+$; HRMS (EI): *m*/*z*: calcd. for $C_{23}H_{20}NO_6FS$: 457.0995; found: 457.0993 $[M]^+$; HPLC separation conditions: Chiralcel OD-H, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.8 mL/min; t_R = 31.8 min (major enantiomer), 50.4 min (minor enantiomer).

4.1.7. 3-(Biphenyl-4-yl)-2-fluoro-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one **5g**

White solid; Mp: 125–126 °C; $[\alpha]_D^{25}$ = 29.4 (*c* = 0.78 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.48–7.39 (m, 11H), 7.35–7.30 (m, 1H), 7.24 (d, *J* = 8.6 Hz, 4H), 5.59–5.51 (m, 1H), 5.26–5.20 (m, 1H), 4.83–4.73 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −146.51 (d, *J* = 16.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5 (d, *J* = 24.1 Hz), 142.1, 139.9, 135.2, 134.4, 134.1, 130.7, 130.5, 130.2, 129.6, 129.5, 129.2, 128.9, 127.8, 127.6, 127.0, 110.4 (d, *J* = 241.4 Hz), 75.4 (d, *J* = 4.3 Hz), 47.2 (d, *J* = 22.8 Hz); IR (KBr) ν 2923, 1677, 1595, 1556, 1448, 1334, 1158 cm^{-1}; ESI-MS (*m*/*z*): 526.2 $(M + 23)^+$; HRMS (EI): *m*/*z*: calcd. for $C_{28}H_{22}NO_5FS$: 503.1203; found: 503.1099 $[M]^+$; HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.9 mL/min; t_R = 57.3 min (minor enantiomer), 86.9 min (major enantiomer).

4.1.8. 2-Fluoro-4-nitro-3-(4-nitrophenyl)-1-phenyl-2-(phenylsulfonyl)butan-1-one **5h**

Red oil; $[\alpha]_D^{28}$ = 30.4 (*c* = 1.10 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (AB, *J* = 8.7 Hz, 2H), 7.76 (AB, *J* = 8.7 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50–7.37 (m, 7H), 7.23 (t, *J* = 8.4 Hz, 1H), 5.57–5.48 (m, 1H), 5.29–5.17 (m, 1H), 4.99–4.87 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −1447.68 (d, *J* = 16.1 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5 (d, *J* = 23.8 Hz), 148.3, 139.1, 135.6, 134.7, 134.0, 130.7, 129.6, 129.5, 129.4, 128.5, 123.9, 110.3 (d, *J* = 243.4 Hz), 74.9 (d, *J* = 21.4 Hz), 47.0 (d, *J* = 21.5 Hz); IR (film) ν 3071, 1676, 1596, 1561, 1448, 1349, 1160 cm^{-1}; ESI-MS (*m*/*z*): 495.1 $(M + 23)^+$; HRMS (ESI): *m*/*z*: calcd. for $C_{22}H_{17}N_2O_7FSNa$: 495.0633; found: 495.0639 $[M + 23]^+$; HPLC separation conditions: Chiralcel ASH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.8 mL/min; t_R = 96.8 min (major enantiomer), 129.0 min (minor enantiomer).

4.1.9. 3-(2-Bromophenyl)-2-fluoro-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one **5i**

Colorless oil; $[\alpha]_D^{26}$ = -51.9 (*c* = 1.14 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.67–7.42 (m, 6H), 7.34–7.25 (m, 2H), 7.14–7.01 (m, 3H), 6.06–5.85 (m, 1H), 5.35–5.20 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −146.56 (s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8 (d, *J* = 24.9 Hz), 135.7, 135.6 (d, *J* = 4.4 Hz), 134.2, 134.1, 133.4, 132.1, 131.2, 130.5, 129.8 (d, *J* = 8.1 Hz), 129.6, 128.3, 128.2, 128.1, 127.6, 109.4 (d, *J* = 240.7 Hz), 75.8 (d, *J* = 5.9 Hz), 45.3 (d, *J* = 23.5 Hz); IR (film) ν 3020, 1711, 1561, 1445, 1376, 1216, 756 cm^{-1}; ESI-MS (*m*/*z*): 528.0 $(M + 23)^+$; HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{17}NO_5FSBr$: 504.9995; found: 504.9991 $[M]^+$; HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.8 mL/min; t_R = 29.9 min (minor enantiomer), 44.4 min (major enantiomer).

4.1.10. 3-(3-Bromophenyl)-2-fluoro-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one **5j**

Colorless oil; $[\alpha]_D^{26}$ = −34.1 (*c* = 1.03 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.51–7.24 (m, 9H), 7.18–7.02 (m, 2H), 5.59–5.43 (m, 1H), 5.25–5.04 (m, 1H), 4.79–4.57 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −147.68 (s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1 (d, *J* = 24.0 Hz), 135.5, 135.1 (d, *J* = 4.2 Hz), 134.3, 134.2, 133.9, 132.9, 132.5, 130.6, 130.5, 129.6 (d, *J* = 14.0 Hz), 129.3, 128.4, 128.3, 123.0, 110.2 (d, *J* = 242.8 Hz), 75.2 (d, *J* = 4.5 Hz), 47.0 (d, *J* = 22.0 Hz); IR (film) ν 3020, 1720, 1562, 1446, 1216, 758 cm^{-1}; ESI-MS (*m*/*z*): 528.1 $(M + 23)^+$; HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{17}NO_5FSBr$: 504.9995; found: 505.0000 $[M]^+$; HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.8 mL/min; t_R = 23.2 min (major enantiomer), 41.0 min (minor enantiomer).

4.1.11. 2-Fluoro-3-(naphthalen-2-yl)-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one **5k**

Colorless oil; $[\alpha]_D^{25}$ = −52.2 (*c* = 2.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.87–7.78 (m, 4H), 7.73–7.62 (m, 2H), 7.55–7.45 (m, 4H), 7.39–7.30 (m, 1H), 7.27–7.08 (m, 6H), 5.98 (d, *J* = 14.3 Hz, 1H), 5.78–5.70 (m, 1H), 5.43 (dd, *J* = 2.7, 14.1 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −145.30 (d, *J* = 8.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2 (d, *J* = 25.0 Hz), 135.5, 135.4, 134.0, 133.2, 130.9, 130.0, 129.6, 129.5, 129.4, 128.9, 128.7, 128.2, 127.2, 126.4, 125.4, 124.9, 123.0, 110.1 (d, *J* = 243.4 Hz), 76.2 (d, *J* = 5.3 Hz), 40.2

(d, J = 22.9 Hz); IR (film) ν 3064, 1677, 1596, 1556, 1448, 1336, 1159 cm^{-1}; ESI-MS (m/z): 500.1 $(M + 23)^+$; HRMS (EI): m/z: calcd. for $C_{26}H_{20}NO_5FS$: 477.1046; found: 477.1043 $[M]^+$; HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.7 mL/min; t_R = 34.4 min (minor enantiomer), 62.4 min (major enantiomer).

4.1.12. 2-Fluoro-3-(furan-2-yl)-4-nitro-1-phenyl-2-(phenylsulfonyl)butan-1-one **5l**

Red oil; $[\alpha]_D^{26}$ = 54.2 (c = 1.40 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 7.9 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.57–7.44 (m, 3H), 7.44–7.31 (m, 2H), 7.27–7.18 (m, 3H), 6.33–6.19 (m, 2H), 5.67 (d, J = 14.1 Hz, 1H), 5.28–5.08 (m, 1H), 4.89–4.68 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −144.81 (d, J = 7.1 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8 (d, J = 24.1 Hz), 145.2, 143.7, 135.6, 134.9 (d, J = 4.5 Hz), 134.0, 133.9, 130,8, 129.5, 129.4, 129.3, 128.2, 112.0, 111.0, 108.1 (d, J = 241.4 Hz), 73.8 (d, J = 4.5 Hz), 41.7 (d, J = 23.5 Hz); IR (film) ν 1724, 1679, 1561 cm^{-1}; ESI-MS (m/z): 440.1 $(M + 23)^+$; HRMS (EI): m/z: calcd. for $C_{20}H_{16}NO_6FS$: 417.0682; found: 417.0680 $[M]^+$; HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.6 mL/min; t_R = 17.7 min (major enantiomer), 37.1 min (minor enantiomer).

4.1.13. 2-Fluoro-4-nitro-1-phenyl-2-(phenylsulfonyl)-3-(thiophen-2-yl)butan-1-one **5m**

Red oil; $[\alpha]_D^{25}$ = 35.6 (c = 1.50 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.53–7.43 (m, 5H), 7.30–7.14 (m, 3H), 6.96 (d, J = 3.2, 1H), 6.89–6.79 (m, 1H), 5.69–5.55 (m, 1H), 5.27–5.15 (m, 1H), 5.10–4.97 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −144.83 (d, J = 18.4 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1 (d, J = 25.5 Hz), 135.5, 135.1 (d, J = 4.3 Hz), 134.2, 133.4, 130.6, 129.6, 129.5, 129.5, 129.4, 128.3, 127.3, 127.2, 109.6 (d, J = 242.4 Hz), 76.5 (d, J = 4.3 Hz), 43.4 (d, J = 22.7 Hz); IR (film) ν 3066, 1677, 1596, 1561, 1448, 1342, 1160 cm^{-1}; ESI-MS (m/z): 456.1 $(M + 23)^+$; HRMS (EI): m/z: calcd. for $C_{20}H_{16}NO_5FS_2$: 433.0454; found: 433.0449 $[M]^+$; HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.6 mL/min; t_R = 21.2 min (major enantiomer), 42.3 min (minor enantiomer).

4.1.14. 2-Fluoro-3-(nitromethyl)-1-phenyl-2-(phenylsulfonyl)heptan-1-one **5n**

Colorless oil; $[\alpha]_D^{25}$ = 65.1 (c = 1.30 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (AB, J = 7.3 Hz, 2H), 7.78–7.65 (m, 3H), 7.65–7.45 (m, 3H), 7.41–7.26 (m, 2H), 5.64–5.92 (m, 1H), 4.69–4.62 (m, 1H), 3.51–3.22 (m, 1H), 1.94–1.58 (m, 1H), 1.56–1.36 (m, 6H), 0.97–0.68 (m, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −148.27 (d, J = 7.1 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1 (d, J = 24.2 Hz), 135.4, 135.3, 134.2, 130.1, 129.8, 129.7, 129.3, 128.5, 111.4 (d, J = 241.1 Hz), 75.4 (d, J = 5.9 Hz), 41.7 (d, J = 17.7 Hz), 28.8 (d, J = 3.8 Hz), 28.65, 22.5, 13.6; IR (film) ν 2960, 1678, 1596, 1555, 1448, 1335, 1161 cm^{-1}; ESI-MS (m/z): 430.1 $(M + 23)^+$; HRMS (EI): m/z: calcd. for $C_{20}H_{22}NO_5FS$: 407.1203; found: 407.1192 $[M]^+$; HPLC separation conditions: Chiralcel ASH, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.5 mL/min; t_R = 75.3 min (major enantiomer), 78.7 min (minor enantiomer).

4.1.15. 2-Fluoro-4-methyl-3-(nitromethyl)-1-phenyl-2-(phenylsulfonyl)pentan-1-one **5o**

Colorless oil; $[\alpha]_D^{27}$ = 85.2 (c = 0.90 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 2H), 7.84–7.63 (m, 3H), 7.58–7.53 (m, 3H), 7.39–7.34 (m, 2H), 5.69 (d, J = 15.5 Hz, 1H), 4.76–4.65 (m, 1H), 3.58–3.44 (m, 1H), 2.32–2.13 (m, 1H), 0.86–0.80 (m, 6H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −149.81 (d, J = 7.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4 (d, J = 25.5 Hz), 135.5, 135.3 (d, J = 4.5 Hz) 134.1, 134.0, 131.1, 130.1 (d, J = 8.7 Hz), 129.3, 128.4, 111.4 (d, J = 241.4 Hz), 72.5 (d, J = 6.7 Hz), 46.3 (d, J = 21.0 Hz), 28.1 (d, J = 3.4 Hz), 20.5, 18.9 (d, J = 2.3 Hz); IR (film) ν 2970, 1677, 1596, 1557, 1469, 1448, 1335, 1160 cm^{-1}; ESI-MS (m/z): 416.1 $(M + 23)^+$; HRMS (ESI): m/z: calcd. for $C_{19}H_{20}NO_5FSNa$: 416.0938; found: 416.0937 $[M]^+$; HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 9:1 hexane:*i*-PrOH, 0.7 mL/min; t_R = 12.5 min (major enantiomer), 17.6 min (minor enantiomer).

4.1.16. 4-Fluoro-3,5-diphenyl-4-(phenylsulfonyl)-3,4-dihydro-2H-pyrrole 1-oxide **6**

To the solution of **5a** (40 mg, 0.1 mmol) in the mixture of methanol (1 mL) and dichloromethane (1 mL) at room temperature was added palladium on carbon (4 mg, 10% by weight). And the reaction mixture was stirred for 48 h under a balloon H_2 atmosphere and then filtered through celite, which was subsequently washed with dichloromethane three times. The filtrate was concentrated in vacuo and then separated by flash chromatography (ethyl acetate/dichloromathane/petro ether:1/1/3) to provide white solid product **6** 28 mg, in 71% yield.

White solid; Mp: 120 °C. $[\alpha]_D^{27}$ = −62.5 (c = 0.90 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.39–7.30 (m, 3H), 7.17–7.17 (m, 5H), 7.10 (t, J = 7.6 Hz, 1H), 4.93–4.86 (m, 1H), 4.66 (d, J = 8.0 Hz, 1H), 4.41 (d, J = 4.3 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −145.45 (d, J = 5.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 134.5 (d, J = 6.5 Hz), 134.1, 130.5, 130.4, 129.2, 128.8, 128.7, 128.4, 128.0, 127.8, 127.7, 126.4, 114.1 (d, J = 238.4 Hz), 69.0, 42.0 (d, J = 19.8 Hz); IR (film) ν 3064, 1575, 1548, 1495, 1446, 1379, 1326, 1155, 1083 cm^{-1}; ESI-MS (m/z): 396.2 $(M + 1)^+$, 418.1 $(M + 23)^+$; HRMS (EI): m/z: calcd. for $C_{22}H_{18}NO_3FS$: 395.0991; found: 395.0999 $[M]^+$; HPLC separation conditions: Chiralcel OD, 20 °C, 254 nm, 4:1 hexane:*i*-PrOH, 0.7 mL/min; t_R = 21.6 min (major enantiomer), 25.7 min (minor enantiomer).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.05.029.

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