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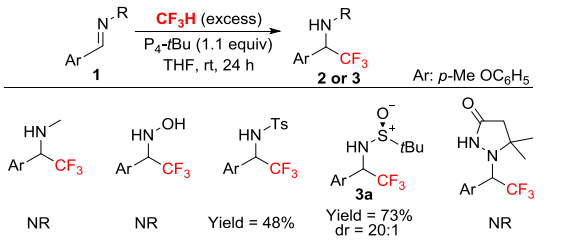
Here we have successfully demonstrated the first stereodivergent direct nucleophilic trifluoromethylation of *N*-sulfinylimines using the potent greenhouse gas "HFC-23, fluoroform" with organic-superbase or organometallic-base in high yields and selectivity.

Fluoroform (HFC-23, CF_3H and trifluoromethane) is a stable, nontoxic potent greenhouse gas (11,700-fold higher GWP than carbon dioxide) and formed as a by-product during the synthesis of poly tetrafluoroethylene (PTFE) in a huge amount, and it is a very good source for trifluoromethyl (CF_3) group.[1,2] Trifluoromethyltrimethylsilane (CF_3SiMe_3, Ruppert-Prakash reagent) is well known and most used nucleophilic trifluoromethylating reagent, but the production of CF_3SiMe_3 is expensive.[3,1d] To overcome this issue, fluoroform has attracted as an inexpensive source for nucleophilic trifluoromethylation. However, its high pK_a (27), low boiling point (−82 °C) and lability of the CF_3 anion made trifluoromethylation quite challenging.[2] In the past decades, fluoroform was successfully tamed by different methods. Initially, trifluoromethylation of the carbonyl compounds were disclosed by Shono, Normant and Langlois using an electrogenerated bases and strong bases, here the CF_3 anion was stabilized by trapping with DMF as a reservoir.[2a,c,g] Later on, Grushin demonstrated the productive trifluoromethylation of arylboronic acids, α-halo ketones and aryl halides from fluoroform-derived $CuCF_3$.[4] Thereafter, Prakash and co-workers tamed fluoroform with a common base (potassium hexamethyldisilazide; KHMDS) and solvents (THF, toluene and ether) in a stoichiometric manner.[2i] Our group also made valuable contributions using fluoroform *i.e.*, trifluoromethylation of aldehydes, sulfonyl fluorides, ketones and sulfides using catalytic or stoichiometric amount of organic-superbase (P_4-*t*Bu).[2k,p] In each case, stability of the substrate in the presence of a strong base played the crucial role.

In this context, α-trifluoromethyl amines have received ample attention in the literature as key building blocks for many active pharmacophores.[5] During the last two decades, nucleophilic trifluoromethylation of azomethines has increased significantly to synthesis of α-trifluoromethyl amines.[6] Prakash and co-workers pioneered the trifluoromethylation of diverse sulfinylimines with CF_3SiMe_3 in good yields and diastereoselectivities.[6c-e,k] Later on, several research groups developed the trifluoromethylation of different kinds of azomethine substrates with CF_3SiMe_3.[6] However, until now, there is no reported example of the trifluoromethylation of azomethine substrates using fluoroform. As part of our ongoing research program to develop the trifluoromethylation of various substrates using fluoroform, here we have reported the first stereodivergent trifluoromethylation of sulfinylimines with high diastereoselectivities (dr) and yields (up to 90%) by using fluoroform.



Scheme 1 Screening of the reaction of azomethines with CF_3H. Reaction conditions: azomethine (0.2 mmol), CF_3H (excess), P_4-*t*Bu (1.1 equiv) in THF (1.0 mL) at room temperature for 24 h. Yields were calculated by crude ^{19}F NMR with $PhCF_3$ as reference. NR - no reaction.

Initially our investigation started by screening various azomethine substrates using CF_3H in our best reported condition (reaction with organic-superbase (P_4-*t*Bu) in THF at room temperature).[2k] In this primary screening, *N*-tosylimine and *N*-sulfinylimine produced the desired trifluoromethylated products in moderate to good yields (*N*-tosyl; 48% and *N*-

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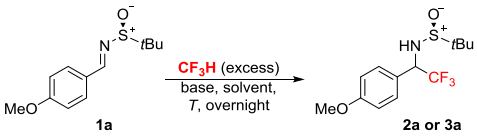
sulfinyl; 73% with 20:1 dr), whereas other azomethine substrates (aldoxime, *N*-methylimine and azomethine imine) failed to produce the desired products. Details were shown in Scheme 1.

Encouraged by this result (Scheme 1, also see entry 1 in Table 1), we proceeded for further optimization studies with *N*-sulfinylimine **1** to make the reaction stereoselective. The reaction in catalytic amount of organic super base P_4-*t*Bu (0.2 equiv) with $(Me_3Si)_3N$ as an additive in THF resulted no reaction (Table 1, run 2). We then investigated the reaction in the presence of other bases such as potassium *tert*-butoxide and *in-situ* generated base ($(Me_3Si)_3N$ + CsF), but these reactions did not progress (Table 1, entries 3 and 4). Conversely, the reaction with KHMDS in THF at −78 °C progressed smoothly and gave an excellent yield of 91% with 2:1 diastereomeric ratio (Table 1, entry 8). To improve the diastereoselectivity we screened various solvents using KHMDS as a base, and finally found that toluene is the best solvent to furnish the desired product with good yield and excellent diastereoselectivity (dr 1: 20, Table 1, entry 10). After that, an attempt with P_4-*t*Bu base in toluene at −78 °C slightly increased the yield and further excellent diastereoselectivity (86%, dr 34:1, Table 1, entry 11) compared to entry 1 in Table 1. Noteworthy is the reaction in the presence of KHMDS which produced the (S_s, *S*) diastereomer whereas P_4-*t*Bu gave the (S_s, *R*) diastereomer exclusively. The configuration of these diastereomers were confirmed by the hydrolysis of CF_3-sulfinamides followed by a comparison with previous chiroptical data in the literature (see later part, Table 4).[6c]

Table 1 Optimization of solvent and base.[a]



Entry	Base (equiv)	Solvent	*T* [°C]	Yield [%][b]	dr[c]
1	P_4-*t*Bu (1.1)	THF	25	73	20:1
2[c]	P_4-*t*Bu (0.2)	THF	25	traces	-
3	*t*BuOK (2.0)	THF	−78	0	-
4	$(Me_3Si)_3N$ (1.5)[e]	THF/toluene	−78	0	-
5	KHMDS (1.5)	THF/toluene	−78	27	1:2
6	KHMDS (2.0)	THF/toluene	−78	80	1:2
7	KHMDS (2.5)	THF/toluene	−78	61	1:5
8	KHMDS (2.0)	THF	−78	91	2:1
9	KHMDS (2.0)	Et_2O	−78	71	1:20
10	KHMDS (2.0)	toluene	−78	84	1:20
11	P_4-*t*Bu (1.1)	toluene	−78	89	34:1

[a] Reaction conditions: **1a** (0.2 mmol), CF_3H (excess) in solvent (1.0 mL) at given temperature overnight. [b] Yields were calculated by crude ^{19}F NMR with the reference compound $PhCF_3$. [c] dr calculated from crude ^{19}F NMR. [d] $(Me_3Si)_3N$ (1.5 equiv) used as an additive. [e] 1.5 equiv of CsF was used

The phenomena of the reversal of diastereoselectivities are explained by the chelated and open transition states.[7] In the case of KHMDS, diastereoselectivity is explained by the formation of a chelated transition state **TS1** with (*S*)-*N*-sulfinylimine and KHMDS; subsequently, **TS1** transforms to **TS2**, resulting in an "*Re*" face attack to furnish predominately (S_s, *S*) CF_3-sulfinamides. In the P_4-*t*Bu trifluoromethylation reaction, fluoroform was deprotonated by base then naked "CF_3" anion was stabilized by the phosphazene counter ion. Furthermore, the phosphazene-stabilized "CF_3" anion has attacked *via* open transition state **TS3** which resulted in a less hindered "*Si*" face attack to afford exclusively (S_s, *R*) CF_3-sulfinamides (Figure 1).

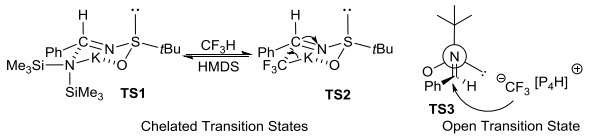
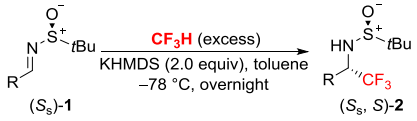


Figure 1 Transition states for trifluoromethylation reactions.

Table 2 Substrate scope in presence of KHMDS.[a]



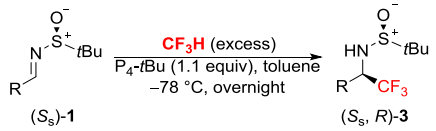
Entry	R	Sulfinamide (S_s, *S*)	Yield (%)[b]	dr[c]
1	4-$OCH_3C_6H_4$	**2a**	79 (84)	1:20
2	Ph	**2b**	60 (72)	1:18
3	4-ClC_6H_4	**2c**	60 (68)	1:18
4	4-$NO_2C_6H_4$	**2d**	45 (48)	1:2
5	^{t}Bu	**2e**	55 (61)	1:4
6	4-$CF_3C_6H_4$	**2f**	42 (48)	1:5
7	4-BrC_6H_4	**2g**	52 (56)	1:13
8	4-$N(Me)_2C_6H_4$	**2h**	70 (78)	1:14
9	2-Napthyl	**2i**	78 (83)	1:13
10	3,4-$(OCH_3)_2C_6H_3$	**2j**	74 (81)	1:14
11	3-$CF_3C_6H_4$	**2k**	36 (40)	1:5
12	3-$OCH_3C_6H_4$	**2l**	64 (70)	1:11
13	2-$OCH_3C_6H_4$	**2m**	61 (66)	1:9
14	4-$CH_3C_6H_4$	**2n**	68 (68)	1:8
15	2-$CH_3C_6H_4$	**2o**	45 (48)	1:7
16	Styrenyl	**2p**	34 (35)	1:13
17	1-Napthyl	**2q**	78 (79)	1:7

[a] Reaction conditions: azomethine (0.2 mmol), CF_3H (excess), KHMDS in toluene (2.0 equiv) in toluene (1.0 mL) at −78 °C overnight. [b] Yields are isolated yields of total diastereomeric mixture and yields in parentheses were calculated by crude ^{19}F NMR with reference $PhCF_3$. [c] Diastereomeric ratios were determined by ^{19}F NMR spectroscopy of the crude reaction mixture.

Having the optimized trifluoromethylation reaction conditions in hand, we next screened the substrate scope of (*S*)-*N*-sulfinylimines **1** in the presence of KHMDS (−78 °C in toluene, Table 2). Most of the (*S*)-*N*-sulfinylimine substrates **1** having different electronic properties were tolerated to produce good yields with moderate to excellent diastereoselectivities (S_s, *S*). The imines with an electron-donating group **1a** (4-OCH_3) and **1h** (4-$N(Me)_2$) produced the corresponding trifluoromethylated sulfinamides in excellent yields (**2a**: 79%; **2h**: 70%) with high diastereoselectivities (dr 1:20 and 1:14, Table 2, entries 1 and 8). The electron-withdrawing group substituted (*S*)-*N*-sulfinylimines **1d** (4-NO_2), **1f** (4-CF_3) and **1k** (3-CF_3) furnished the desired products **2d** (45%), **2f** (42%) and **2k** (36%) in moderate yields with average diastereoselectivities (dr up to 1:5, Table 2, entries 4, 6 and 11). The halogen-substituted (*S*)-*N*-

sulfinylimines **1c** (4-Cl) and **1g** (4-Br) tolerated the reaction well and afforded CF_3-sulfinamides in good yields **2c** (60%) and **2g** (52%) with high selectivities (dr 1:18 and 1:13, Table 2, entries, 3 and 7). The *tert*-butyl (*S*)-*N*-sulfinylimine **1e** proceeded the reaction with moderate yield **2e** (55%) and diastereoselectivity (dr 1:4, Table 2, entry 5), whereas α, β-unsaturated sulfinylimine **1p** furnished the corresponding product in low yield **2p** (34%) with very good diastereoselectivity (dr 1:13, Table 2, entry 16). We have observed the slight decrease in diastereoselectivity, when the substitution was present at the ortho position of the phenyl ring in (*S*)-*N*-sulfinylimine **1o** (2-CH_3) and **1q** (napthyl) in Table 2, entries 13 and 17. These phenomena can be explained by steric hindrance of the group present at the *ortho* position which disturbs the chelated transition state.

Table 3 Substrate scope in presence of P_4-*t*Bu Base.[a]



(S_s)-**1** (S_s, *R*)-**3**

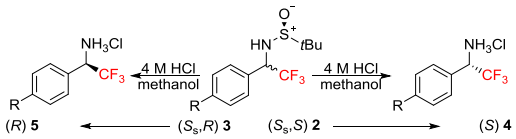
Entry	R	Sulfinamide (S_s, *R*)	Yield (%)[b]	dr[c]
1	4-$OCH_3C_6H_4$	**3a**	85 (89)	34:1
2	Ph	**3b**	64(66)	23:1
3	4-ClC_6H_4	**3c**	79 (83)	41:1
4	^{t}Bu	**3e**	61 (61)	49:1
5	4-$CF_3C_6H_4$	**3f**	80 (89)	21:1
6	4-BrC_6H_4	**3g**	80 (84)	24:1
7	4-$N(Me)_2C_6H_4$	**3h**	79 (84)	6:1
8	2-Napthyl	**3i**	75 (80)	20:1
9	3,4-$(OCH_3)_2C_6H_3$	**3j**	87 (90)	44:1
10	3-$CF_3C_6H_4$	**3k**	86 (96)	23:1
11	3-$OCH_3C_6H_4$	**3l**	81 (88)	63:1
12	2-$OCH_3C_6H_4$	**3m**	88 (89)	23:1
13	4-$CH_3C_6H_4$	**3n**	96 (97)	48:1
14	2-$CH_3C_6H_4$	**3o**	70 (75)	35:1
15	Styrenyl	**3p**	79 (92)	14:1
16	1-Napthyl	**3q**	70 (71)	13:1

[a] Reaction conditions: azomethine (0.2 mmol), CF_3H (excess), P_4-*t*Bu in hexane (1.1 equiv) in toluene (1.0 mL) at −78 °C overnight. [b] Yields are isolated yields of total diastereomeric mixture and yields in parentheses were calculated by crude ^{19}F NMR with reference $PhCF_3$. [c] Diastereomeric ratios were determined by ^{19}F NMR spectroscopy of the crude reaction mixture.

We also examined the generality of trifluoromethylation reaction with (*S*)-*N*-sulfinylimines **1** in the presence of P_4-*t*Bu base and the results were summarized in Table 3. The trifluoromethylation of (*S*)-*N*-sulfinylimines with P_4-*t*Bu base proceeded well for all the kind of substrates to furnish the corresponding CF_3-sulfinamides in excellent yields and diastereoselectivities (S_s, *R*; Table 3) including (*S*)-*N*-sulfinylimine **1f** (4-CF_3). Substrate **1** with various donating groups (**1a**: OCH_3; **1j**: di-OCH_3) and halogen substituents (**1c**: 4-Cl; **1g**: 4-Br) exhibited good reactivity and produced the expected products in good yields **3a** (85%), **3j** (87%), **3c** (79%) and **3g** (80%) with very high diastereoselectivities (dr up to 44:1, Table 3, entries 1, 3, 6 and 9). Gratifyingly, *tert*-butyl (*S*)-*N*-sulfinylimine substrate **1e** also tolerated the reaction well to afford the desired product **3e** in 61% yield with excellent diastereoselectivity (dr 49:1, Table 3, entry 4). More interestingly, the (*S*)-*N*-sulfinylimine having the electron-withdrawing group **1f** (4-CF_3) furnished the corresponding trifluoromethylated product **3f** in 80% yield with excellent selectivity (dr 21:1, Table 3, entry 5). In the case of P_4-*t*Bu, we observed that substrates with different electron properties did not show the any significant differences in yields and diastereoselectivities.

Spurred by these results, the obtained (S_s, *S*)-sulfinamides **2** and (S_s, *R*)-sulfinamides **3** in the presence of KHMDS and P_4-*t*Bu were further hydrolyzed with 4 M HCl in dioxane, and endured the corresponding enantiopure α-trifluoromethyl amines with good yields. These results were outlined in Table 4. The absolute configuration of these compounds was determined by comparing with the chiroptical values of previously reported compounds.[6c]

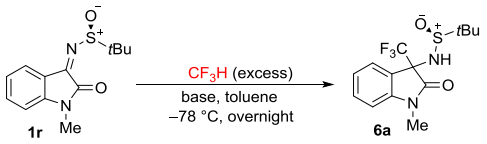
Table 4 Hydrolysis of CF_3-sulfinamides **2** and **3**.[a]



Entry	R	(*S*)-amine; Yield [b,d]	*ee*	(*R*)-amine; Yield [b,d]	*ee*
1	OCH_3	**4a**: 82%	99%	**5a**: 92%	99%
2	H	**4b**: 91%	99%	**5b**: 93%	99%
3	Cl	**4c**: 87%	99%	**5c**: 94%	99%
4	CF_3	**4f**: 70%	97%	**5f**: 94%	99%

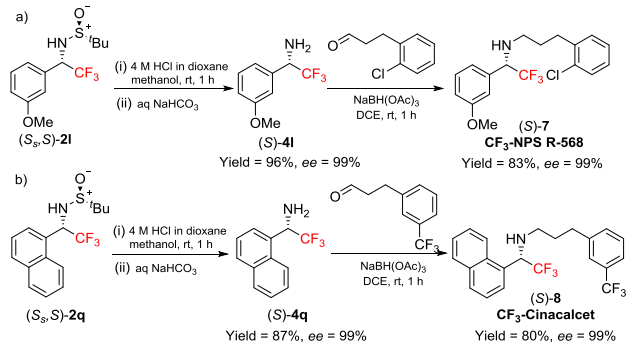
[a] Reaction conditions: sulfinamide (0.2 mmol), 4 M HCl in dioxane (0.4 mmol) in methanol (4 mL) at room temperature. [b] Configurations were determined by comparison with reported values of optical rotations. [c] Optical rotations were measured in methanol. [d] Yields are isolated yields.

To explore our methodology, we examined the isatin-derived ketimines using our optimized conditions (Scheme 2). Previously, Xu and co-workers reported that a reaction using CF_3SiMe_3 furnished corresponding CF_3-derivatives in 66% yield with poor selectivity (dr 1:4).[8] In our case, the KHMDS base produced the desired product in low yield (39%), but the reaction in the presence of P_4-*t*Bu resulted in good yield (79%), in both cases selectivity was poor (dr 1:1.2, Scheme 2). The extensive screening of solvents and substituents were summarized in supporting information (Table S1, SI). Further screening is ongoing in our laboratory to improve the diastereoselectivity and yield with CF_3SiMe_3.



Scheme 2 Trifluoromethylation of Isatin-derived ketimines.

With these results in hand, we have successfully prepared the trifluoromethylated drug analogues NPS R-568 (**7**; Scheme 3a) and Cinacalcet (**8**; Scheme 3b). Initially, the desulfonylation of the compounds (S_s, *S*)-**2l** and (S_s, *S*)-**2q** furnished the desired enantiopure α-trifluoromethyl amines in good yields (**4l**: 96%; **4q**: 87%, Scheme 3). Further, these compounds were treated with corresponding aldehydes for reductive amination in the presence of sodium triacetoxyborohydride to afford the required trifluoromethylated drug analogues in quantitative yields (**7**: 83%; **8**: 80%) and enantioselectivities (**7**: 99%; **8**: 99%).



Scheme 3 Preparation of CF_3 drug analogues. a) NPS R-568; b) Cinacalcet.

In conclusion, we have synthesized enantio-rich α-trifluoromethyl amines in a stereodivergent manner by the inexpensive potent greenhouse gas "fluoroform".[9] The trifluoromethylation of (*S*)-*N*-sulfinylimines in the presence of KHMDS produced (S_s, *S*)-trifluoromethylated *N*-sulfinamides whereas the P_4-*t*Bu super base furnished (S_s, *R*)-trifluoromethylated *N*-sulfinamides. This phenomenon was explained by the formation of chelated and non-chelated transition states with bases. By this methodology we successfully synthesized the enantiopure trifluoromethylated analogues of known drugs Cinacalcet and NPS R-568 in high yields. These enantio-rich α-trifluoromethyl amines are very useful precursors for the preparation of chiral ligands and biologically active compounds.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

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