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Regio- and stereoselective synthesis of chiral (αS)-(Z)-trifluoromethyl-β-aryl-enamines

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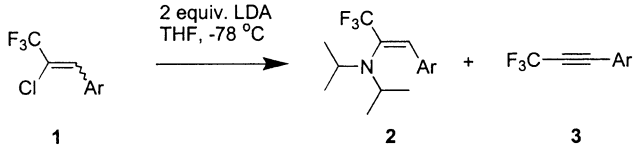
Abstract—Chiral (αS)-(Z)-trifluoromethyl-β-aryl-enamines were regio and stereoselectiveally prepared in excellent yields by the one pot reaction of 2-aryl-1-chloro-1-trifluoromethylethlene with lithium (αS)-(α-methylbenzyl) benzylamide. A mechanism involving elimination and addition processes is discussed.

1. Introduction

Recently, there has been a growing interest in the asymmetric synthesis of organic molecules bearing a fluorinated group due to their significant biological activity.[1] For example, a new class of potent non-nucleoside transcriptase inhibitor, efavirenz, which bears a trifluoromethyl group has shown excellent results for the treatment of AIDS.[2] Syntheses and applications of chiral fluorinated building blocks are efficient methods for construction of optically active fluorinated target molecules by carbon–carbon bond formation.[3] Enamines are versatile building blocks in organic synthesis and their chemistry has been well documented.[4–6] Fluorine-containing enamines have been prepared and utilized for the synthesis of biologically activity compounds.[7] Several methods reported for the preparation of α-trifluoromethylated enamines suffer from critical reaction conditions and low stereoselectivity, or difficulty in availability of the starting materials, which include Wittig reaction of trifluoroacetamides,[8] amination of fluoroketones,[9] and addition of amines to fluoroalkynes.[10] To the best of our knowledge, there are few reports of the synthesis of chiral trifluoromethyl enamines in the literature.[11] Therefore, it is of great value to develop a facile method for the preparation of chiral α-trifluoromethyl enamines. Here, we disclose a concise regio- and stereoselective synthesis of (αS)-(Z)-trifuromethylenamines.

2. Results and discussion

It is known that 1-chloro-2-aryl-1-trifluoromethylethylenes **1** can be conveniently prepared from the reaction of commercially available trichlorotrifluoroethane with aryl aldehydes in high yields.[12] Initially, we tried to synthesise trifluoromethyl phenylacetylene by dechlorination of 1-chloro-2-phenyl-1-trifluoromethylethylene with a lithium diisopropylamide. To our surprise, the expected 1-phenyl-trifluoromethylacetylene was isolated in a small quantity and a 60% yield of a mixture of (Z) and (E)-α-CF_3-β-phenyl-enamine was obtained. This result suggested to us that it might be possible to prepare a trifluoromethyl-enamine via the reaction of 1-chloro-2-aryl-1-trifluoro-methylethylenes **1** with a lithium dialkylamide. We found that 2 equiv. of the lithium diisopropylamide drove the reaction to completion and α-trifluoromethyl enamines **2** were isolated in high yields. The configuration of the double bond was assigned as Z by comparing its ^{19}F NMR and ^{1}H



Scheme 1.

Table 1. Reaction of 1-chloro-2-aryl-1-trifluoromethylethylenes with LDA

Entry	Aryl	^{19}F NMR of **2**	Yield of **2** (%)[a]	Ratio of Z/E[b]
1	Ph	−16.7, −11	60 **2a**	80:20[c]
2	Ph	−16.7	98 **2a**	100:0[d]
3	*p*-Cl-C_6H_4	−15	73 **2b**	100:0[d]
4	*p*-CH_3O- C_6H_4	−17	80 **2c**	100:0[d]
5	*p*-CH_3-C_6H_4	–	Polymer	–

[a] Isolated yield.
[b] Determined by ^{19}F NMR.
[c] Reaction was carried out using 1 equiv. of LDA.
[d] Reaction was carried out using 2 equiv. of LDA.

Keywords: trifluoromethyl enamines; stereoselection; lithium amide; Michael addition.

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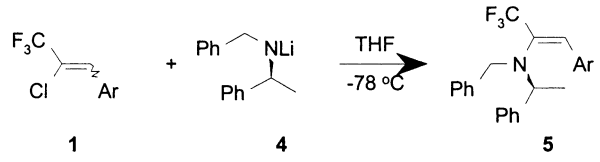


1 4 5

Scheme 2.

Table 2. Reaction of 1-chloro-2-aryl-1-trifluoromethylethylenes with lithium (α*S*)-(α-methylbenzyl)benzylamide

Entry	Aryl	^{19}F NMR of **5**	Yield of **5** (%)[a]	Ratio of *Z*/*E*[b]
1	Ph	−17.5	85 **5a**	100:0
2	*p*-CH_3O-C_6H_4	−17.0	95 **5b**	100:0
3	*p*-CH_3-C_6H_4	−17. 3	89 **5c**	100:0
4	*p*-CH_3-C_6H_4	−17.3, −13.0	86 **5c**	80:20[c]
5	*p*-F-C_6H_4	−17.0	95 **5d**	100:0
6	*p*-Cl-C_6H_4	−17.0	85 **5e**	100:0
7	*p*-Br-C_6H_4	−17.3	94 **5f**	100:0

[a] Isolated yield.
[b] Determined by ^{19}F NMR.
[c] Reaction was carried out using 1 equiv. of lithium (α*S*)-(α-methylbenzyl)benzylamide.

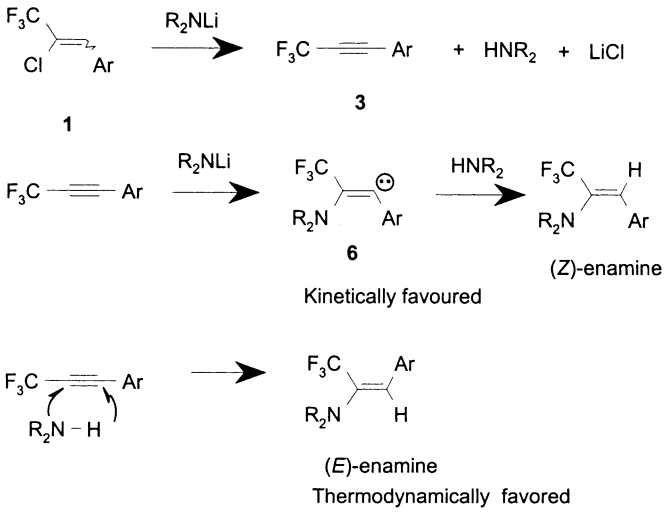
NMR spectroscopic data with those reported in the literature.[11] Extension of the reaction to substrates with electron-withdrawing (entry 3) or electron-donating (entry 4–5) groups in the aromatic ring also stereoselectively gave (*Z*)-α-trifluoromethylenamines **2** in high yield (Table 1, Scheme 1).

It has been reported that the stereoselective Michael addition of enantiomerically pure ammonia equivalents to an α,β-unsaturated ester is an efficient method for the asymmetric synthesis of chiral β-amino acids. Lithium (α-methylbenzyl)benzylamide **4** is an extremely useful chiral ammonia equivalent.[13] The amide **4** is particularly attractive because it is readily available and inexpensive and the two *N*-benzyl groups are easy removable by hydrogenolysis.

Thus, treatment of (α*S*)-(α-methylbenzyl)benzylamine in THF at −78°C with butyllithium generated a solution of lithium (α*S*)-(α-methylbenzyl)benzylamide to which was added 1-chloro-2-aryl-1-trifluoromethylethylene **1**. Standard work up generated (α*S*)-1-trifluromethylenamines **5** in high yield. All reactions afforded (*Z*)-enamines **5**. Reactions of various substrates are summarized in Table 2 (Scheme 2).

We envisaged that the unusual reaction was composed of elimination and addition processes. The first equivalent of lithium amide eliminated HCl from **1** to yield 1-aryl-trifluoromethylacetylenes **3**. The second equivalent of lithium amide added under kinetic control since the enamines possessed the (*Z*)-configuration irrespective of the bulkiness of substituents of the double bond. To confirm this suggestion, 1-aryl-trifluoromethylacethylenes **3** were directly treated with 1 equiv. of lithium amide for 0.5–1 h. The desired (*Z*)-enamines were also obtained stereoselectivelly in high yield as the one pot procedure. Bumgardner has rationalized the stereochemistry of substituted trifluoromethyl ethylene, generated by the nucleophilic addition of trifluoromethyl acetylene, to the secondary orbital interaction of the LUMO (π^*CF_3) and HOMO π' of vinyl fragment.[14] According to the Bumgardner's theory, it can depicted that the nucleophilic addition of lithium amide to trifluoromethyl acetylene **3** would give kinetically favoured (*Z*)-configuration product **5** due to the secondary orbital interaction of π^*CF_3(LUMO)−π'(HOMO) of the lone pair of electronic anion of vinyl fragment in transition state **6** (Scheme 3). Thus, if the reaction was performed with 1 equiv. of lithium amide, the stereoselectivity would be decreased. The generated amine could take part in a *cis* addition with acetylenes **3** to yield (*E*)-enamines. This hypothesis was demonstrated in entry 1 (Table 1) and entry 4 (Table 2), where the reactions carried out with 1 equiv. of lithium amide gave a mixture of (*Z*) and (*E*)-enamines.

In summary, we have developed a stereoselective method for the preparation of (*Z*)-1-trifluoromethylenamines in a one pot reaction. The reactions involved elimination of HCl from of 2-aryl-1-chloro-1-trifluoromethylethlense with the first equivalent of lithium amide and kinetically controlled addition of a second equivalent of lithium



Scheme 3.

amide to the resulting acetylene, giving a stereoselective access to the corresponding (*Z*)-enamines in high yield. Reaction of 2-aryl-1-chloro-1-trifluoromethylethlene with 2 equiv. of lithium (α*S*)-(α-methylbenzyl)benzylamide gave exclusively (α*S*)-(Z)-trifluoromethylenamines which could be useful trifluoromethyl containing building blocks for the preparation of optically active compounds bearing a trifluoromethyl group.

3. Experimental

^{1}H NMR spectra were recorded on 300 MHz spectrometers with TMS as an internal standard. ^{19}F NMR spectra were obtained on a 56.8 MHz spectrometer with trifluoroacetic acid (δ 0.00) as an external standard; downfield shifts were designated negative. IR spectra were taken on a Shimadzu 440-IR spectrometer, and mass spectra were obtained using EI ionization at 70 eV. All reactions were routinely monitored with the aid of TLC or ^{19}F NMR spectroscopy.

3.1. General procedure for synthesis of (*Z*)-enamines 2 and 5

n-Butyllithium (3.6 mmol, 1.8 M in hexane) was added to a solution of diisopropylamine or (α*S*)-(α-methylbenzyl)-benzylamine (3.9 mmol) in anhydrous THF (40 mL) at −20°C for 30 min under an argon atmosphere. The mixture was then cooled to −78°C. 1-Chloro-2-aryl-1-trifluoro-methylethylene (1.8 mmol) **1** in THF (10 mL) was added dropwise over 1 h, and then allowed to warm to room temperature. Water (150 mL) was added and the mixture was extracted several times with diethyl ether and the combined organic layers were dried over anhydrous sodium sulphate. After removal of solvent, the residue was subjected to flash chromatography on silica gel eluting with ethyl acetate/petroleum ether (1/100) to give the enamines as colourless oils.

3.1.1. (*Z*)-1-Disopropylamino-2-phenyl-1-trifluoromethyl-ethylene (2a). Found: C, 66.35; H, 7.42; N, 5.80. $C_{15}H_{20}F_3N$ requires C, 66.40; H, 7.43; N, 5.16%. ν_{max}(liquid film) 2972, 1258, 1159, 1114 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −16.7 (3F, s, C*F*$_3$); δ_H (300 MHz, $CDCl_3$) 1.11 (12H, d, *J*=6.5 Hz, 2×(*Me*)$_2$CH), 3.56–3.58 (2H, m, 2×(Me)$_2$C*H*), 6.93 (1H, s, =CH), 7.33–7.51 (3H, m, Ph-*H*), 7.95–7.99 (2H, m, Ph-*H*); *m*/*z* (EI) 271 (23, MH$^+$), 256 (90), 214 (100); HRMS (EI): M$^+$, found 271.1589. $C_{15}H_{20}F_3N$ requires 271.1585.

3.1.2. (*Z*)-1-Disopropylamino-2-(*p*-chloro)phenyl-1-trifluoromethylethylene (2b). Found: C, 60.02; H, 6.42; N, 4.63. $C_{15}H_{19}ClF_3N$ requires C, 58.92; H, 6.26; N, 4.58%. ν_{max}(liquid film) 2928, 1257, 1156, 1112 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −15.0 (3F, s, C*F*$_3$); δ_H (300 MHz, $CDCl_3$) 1.13 (12H, d, *J*=6.6 Hz, 2×(*Me*)$_2$CH), 3.56–3.59 (2H, m, 2×(Me)$_2$C*H*), 7.04 (1H, s, =CH), 7.39–7.41 (3H, m, Ph-*H*); *m*/*z* (EI) 307 (6, MH$^+$), 290 (97), 248 (100); HRMS (EI): M$^+$, found 305.1154, 305.1137. $C_{15}H_{19}ClF_3N$ requires 305.1158, 307.1129.

3.1.3. (*Z*)-1-Disopropylamino-2-(*p*-methoxyl)phenyl-1-trifluoromethylethylene (2c). Found: C, 63.73; H, 7.30; N, 4.69. $C_{16}H_{22}F_3NO$ requires C, 63.77; H, 7.36; N, 4.65%. ν_{max}(liquid film) 2974, 1607, 1511, 1253, 1154, 1106 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −17.0 (3F, s, C*F*$_3$); δ_H (300 MHz, $CDCl_3$) 1.11 (12H, d, *J*=6.5 Hz, 2×(*Me*)$_2$CH), 3.56–3.59 (2H, m, 2×(Me)$_2$C*H*), 3.82 (3H, s, C*H*$_3$O), 6.85 (1H, s, =C*H*), 6.86 (2H, d, *J*=8.9 Hz, Ph-*H*), 7.91–7.94 (3H, m, Ph-*H*), 7.97 (2H, m); *m*/*z* (EI) 301 (51, MH$^+$), 286 (100); HRMS (EI): M$^+$, found 271.1589. $C_{15}H_{20}F_3N$ requires 271.1585.

3.1.4. (*Z*)-1-{*N*-Benzyl-*N*-[(1*S*)-phenylethyl]}amino-2-phenyl-1-trifluoromethylethylene (5a). Found: C, 75.69; H, 6.01 N, 4.01. $C_{24}H_{22}F_3N$ requires C, 75.57; H, 5.81; N, 3.67%. $[\alpha]_D^{20}$=+173 (*c*=1.5, $CHCl_3$); ν_{max}(liquid film) 1259, 1160, 1112 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −17.5 (3F, s, C*F*$_3$); δ_H (300 MHz, $CDCl_3$) 1.48 (3H, d, *J*=6.9 Hz, C*H*$_3$CH), 3.75 (1H, d, *J*=14.5 Hz, PhC*H*$_A$H$_B$), 4.10 (1H, d, *J*=14.5 Hz, PhCH$_A$*H*$_B$), 4.50 (1H, q, *J*=6.8 Hz, CH$_3$C*H*), 6.64 (1H, s, =C*H*), 7.15–7.45 (15H, m, 3×Ph-*H*); *m*/*z* (EI) 381 (3, MH$^+$), 277(68), 105 (100); HRMS (EI): M$^+$, found 381.1698. $C_{24}H_{22}F_3N$ requires 381.1704.

3.1.5. (*Z*)-1-{*N*-Benzyl-*N*-[(1*S*)-phenylethyl]}amino-2-(*p*-methoxyl)phenyl-1-trifluoromethylethylene (5b). Found: C, 73.00; H, 6.08; F, 14.05; N, 3.40. $C_{25}H_{24}F_3NO$ requires C, 72.98; H, 5.88; F, 13.85; N, 3.40%. $[\alpha]_D^{20}$=+162 (*c*=1.0, $CHCl_3$); ν_{max}(Nujol) 1607, 1512, 1253, 1155, 1108 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −17.0 (3F, s, C*F*$_3$); δ_H (300 MHz, $CDCl_3$) 1.41 (3H, d, *J*=6.8 Hz, C*H*$_3$CH), 3.79 (3H, s, C*H*$_3$O), 3.75 (1H, d, *J*=14.5 Hz, PhC*H*$_A$H$_B$), 4.10 (1H, d, *J*=14.5 Hz, PhCH$_A$*H*$_B$), 4.40 (1H, q, *J*=6.8 Hz, CH$_3$C*H*), 6.59 (1H, s, =C*H*), 6.71 (2H, d, *J*=8.8 Hz, Ph-*H*), 6.95–7.10 (2H, m, Ph-*H*), 7.10–7.21 (5H, m, Ph-*H*), 7.35–7.38 (5H, m, Ph-*H*); *m*/*z* (EI) 412 (23 MH$^+$), 307 (52), 105 (100); HRMS (EI): M$^+$, found 411.1794. $C_{25}H_{24}F_3NO$ requires 411.1796.

3.1.6. (*Z*)-1-{*N*-Benzyl-*N*-[(1*S*)-phenylethyl]}amino-2-(*p*-methyl)phenyl-1-trifluoromethylethylene (5c). $[\alpha]_D^{20}$=+105.6 (*c*=3.0, $CHCl_3$); ν_{max}(Nujol) 1259, 1157, 1110 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −17.3 (3F, s, CF_3); δ_H (300 MHz, $CDCl_3$) 1.46 (3H, d, *J*=6.8 Hz, C*H*$_3$CH), 2.36 (3H, s, C*H*$_3$-Ph), 3.77 (1H, d, *J*=14.5 Hz, PhC*H*$_A$H$_B$), 4.11 (1H, d, *J*=14.5 Hz, PhCH$_A$*H*$_B$), 4.77 (1H, q, *J*=6.7 Hz, CH$_3$C*H*), 6.62 (1H, s, =C*H*), 7.13–7.16 (14H, m, Ph-*H*); *m*/*z* (EI) 395 (16MH$^+$), 291 (42), 105 (100); HRMS (EI): M$^+$, found 395.1865. $C_{25}H_{24}F_3N$ requires 395.1860.

3.1.7. (*Z*)-1-{*N*-Benzyl-*N*-[(1*S*)-phenylethyl]}amino-2-(*p*-fluoro)phenyl-1-trifluoromethylethylene (5d). Found: C, 72.19; H, 5.11; N, 3.98. $C_{24}H_{21}F_4N$ requires C, 72.17; H, 5.30; N, 3.51%. $[\alpha]_D^{20}$=+166.5 (*c*=2.5, $CHCl_3$); ν_{max}(Nujol) 1509, 1260, 1229, 1158, 1112 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −17.0 (3F, s, CF_3); δ_H (300 MHz, $CDCl_3$) 1.45 (3H, d, *J*=6.8 Hz, C*H*$_3$CH), 3.75 (1H, d, *J*=14.5 Hz, PhC*H*$_A$H$_B$), 4.10 (1H, d, *J*=14.5 Hz, PhCH$_A$*H*$_B$), 4.50 (1H, q, *J*=6.7 Hz, CH$_3$C*H*), 6.58 (1H, s, =C*H*), 7.05–7.22 (14H, m, Ph-*H*); *m*/*z* (EI) 399 (4, MH$^+$), 105 (100); HRMS (EI): M$^+$, found 399.1605. $C_{24}H_{21}F_4N$ requires 399.1610.

3.1.8. (*Z*)-1-*N*-Benzyl-*N*-[(1*S*)-phenylethyl]}amino-2-(*p*-chloro)phenyl-1-trifluoromethylethylene (5e). $[\alpha]_D^{20}$=

+156.5 (c=2.4, $CHCl_3$); ν_{max}(Nujol) 1510, 1260, 1229, 1158, 1112 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −17.0 (3F, s, CF_3); δ_H (300 MHz, $CDCl_3$) 1.45 (3H, d, J=6.8 Hz, CH_3CH), 3.75 (1H, d, J=14.5 Hz, $PhCH_AH_B$), 4.10 (1H, d, J=14.5 Hz, $PhCH_AH_B$), 4.51 (1H, q, J=6.7 Hz, CH_3CH), 6.56 (1H, s, =CH), 7.10–7.16 (14H, m, Ph-H); m/z (EI) 415 (6, MH^+), 410 (40), 105 (100); HRMS (EI): M^+, found 415.1305. $C_{24}H_{21}ClF_3N$ requires 415.1315.

3.1.9. (*Z*)-1-{*N*-Benzyl-*N*-[(1*S*)-phenylethyl]}amino-2-(*p*-bromo)phenyl-1-trifluoromethylethylene (5f). $[\alpha]_D^{20}$= +127.7 (c=2.5, $CHCl_3$); ν_{max}(Nujol) 1259, 1161, 1112 (CF_3) cm^{-1}; δ_F (56.8 MHz, $CDCl_3$) −17.3 (3F, s, CF_3); δ_H (300 MHz, $CDCl_3$) 1.48 (3H, d, J=6.8 Hz, CH_3CH), 3.75 (1H, d, J=14.5 Hz, $PhCH_AH_B$), 4.10 (1H, d, J=14.5 Hz, $PhCH_AH_B$), 4.50 (1H, q, J=6.7 Hz, CH_3CH), 6.61(1H, s, =CH), 7.06–7.16 (12H, m, Ph-H); 7.26–7.28 (2H, m, Ph-H); m/z (EI) 461 (0.5MH^+, ^{81}Br), 459 (0.5MH^+, ^{79}Br), 277 (24), 105 (100); HRMS (EI): M^+, found 461.0743 (^{81}Br), 459.0811 (^{79}Br). $C_{24}H_{21}BrF_3N$ requires 461.0747 (^{81}Br), 459.0810 (^{79}Br).

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