Asymmetric Synthesis of Both Enantiomers of α-Trifluoromethyl Substituted Homoallylamine

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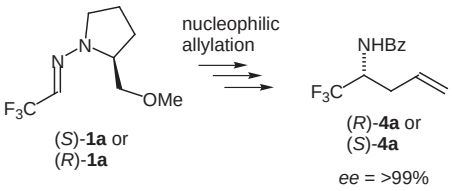
Abstract: An efficient asymmetric synthesis of both enantiomers of α-trifluoromethylated homoallylamine via nucleophilic allylation of trifluoroacetaldehyde SAMP- or RAMP-hydrazone, followed by benzoylation and SmI_2-promoted nitrogen-nitrogen single bond cleavage is described.

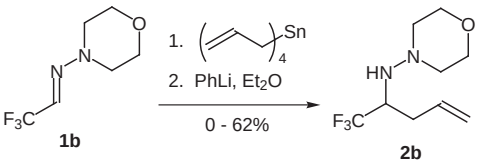
Key words: asymmetric synthesis, fluorine, hydrazone, allylation, amines

The asymmetric nucleophilic allylation of imino derivatives has received increasing attention in organic synthesis,[1,2] because the resulting enantio-enriched homoallylamines or hydrazines are promising precursors of β-amino substituted aldehydes, ketones, epoxides, and calboxylic acid derivatives. Although some reports recently described the asymmetric synthesis of α-alkyl, aryl or vinyl substituted α-trifluoromethylamines,[3] to the best of our knowledge, there is no report on the stereoselective allylation of α-trifluoromethylated imines or hydrazones leading to enantiopure α-trifluoromethylated homoallylamines despite their synthetic utility.[4,5] As a part of our studies directed towards the asymmetric synthesis of organofluorine compounds by means of the SAMP- or RAMP-hydrazone method,[6] we describe herein the first asymmetric synthesis of both enantiomers of α-trifluoromethylated homoallylamine (*R*)- or (*S*)-**4a** using trifluoroacetaldehyde SAMP- or RAMP-hydrazone (*S*)- or (*R*)-**1a** as a starting substrate (Scheme 1).



Scheme 1

For the screening of the allylation reaction of trifluoroacetaldehyde hydrazones, the reaction between trifluoroacetaldehyde morpholinohydrazone (**1b**) and tetraallyltin was first examined (Scheme 2). The results are summarized in Table 1.



Scheme 2

Table 1 Screening of the Reaction Conditions for the Allylation of Trifluoroacetaldehyde Morpholinohydrazone (**1b**)

Entry[a]	Tetraallyltin (equiv)	PhLi (equiv)	Yield of **2b** (%)[b]
1	3	3	7 (38)
2	1	4	21 (35)
3	2	8	47
4	3	12	62
5	3[c]	3	20 (15)
6[d]	0.3	0	0 (quant)

[a] The reaction was performed with hydrazone **1b** (1 mmol) in Et_2O (11 mL).
[b] Yields of isolated products. Values in parentheses stand for the recovered **1b**.
[c] Allyltriphenyltin was used in place of tetraallyltin.
[d] The reaction was carried out in the presence of 5 mol% of $Yb(OTf)_3$ in MeCN at r.t.

As shown in Scheme 2, treatment of tetraallyltin (3 equiv) with phenyllithium (12 equiv) at room temperature, followed by addition of trifluoroacetaldehyde morpholinohydrazone (**1b**) at –78 °C, gave the corresponding trifluoroacetaldehyde morpholinohydrazine **2b** in 62% yield (entry 4). The reaction of **1b** with three equivalents of tetraallyltin and PhLi, respectively, was extremely sluggish, providing only a trace amount of **2b** (entry 1). Employing tetraallyltin (1–2 equiv) and PhLi (4–8 equiv) produced **2b** in 21–47% yields along with recovered **1b** (entries 2 and 3). The use of allyltriphenyltin (3 equiv) in place of tetraallyltin with PhLi (3 equiv) was also ineffective, giving **2b** in 20% yield together with 15% of **1b** (entry 5). $Yb(OTf)_3$-catalyzed (5 mol%) allylation[7] with 0.3 equivalent of tetraallyltin in acetonitrile at room tempera-

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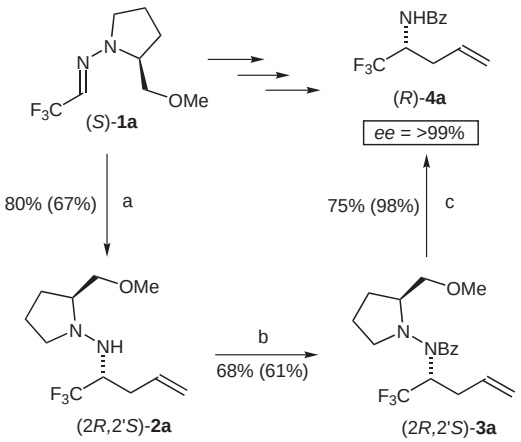
ture did not occur at all, and **1b** was recovered in quantitative yield (entry 6). With other allylic nucleophiles e.g., allylmagnesium bromide (3 equiv, –78 °C to r.t., overnight), only trace amount of **2b** was formed with 67% recovery of **1b**.

Next, in order to synthesize diastereo- and enantiomerically pure hydazines, the stereoselective allylation of trifluoroacetaldehyde SAMP- or RAMP-hydrazone (*S*)- or (*R*)-**1a** was carried out (Scheme 3).[8]



Scheme 3 *Reagents and conditions*: (a) tetraallyltin, PhLi, r.t., then –78 °C; (b) catalytic DMAP, Et_3N, PhCOCl, r.t.; (c) SmI_2, THF/DMPU, r.t.

When SAMP-hydrazone (*S*)-**1a** was treated with a mixture, obtained by the reaction between 3 equivalents of tetraallyltin and 12 equivalents of PhLi at room temperature, in Et_2O at –78 °C for 4 hours, the allylated hydrazine (2*R*,2′*S*)-**2a** was produced with high diastereoselectivty (93:7), and diastereomerically pure **2a** was easily obtained by flash column chromatography in 80% yield. Hydrazone (*R*)-**1a** also nicely underwent the allylation reaction to give (2*S*,2′*R*)-**2a** (>98% de) in 67% yield after column chromatography.

The obtained diastereomerically pure hydrazines **2a** were easily converted to the enantiopure homoallylamines. After benzoylation of SAMP- or RAMP-hydrazine **2a** with an excess amount of triethylamine and benzoyl chloride in the presence of a catalytic amount of DMAP at room temperature, respectively, SmI_2-induced cleavage of the nitrogen–nitrogen single bond of the hydrazides **3a** gave the corresponding enantiopure α-trifluoromethylated homoallylamines (*R*)- and (*S*)-**4a** in 75–98% yield with >99% ee without any detectable epimerization or racemization.[9] The benzoyl group is essential for the cleavage of nitrogen–nitrogen single bond of **3a**. Thus, treatment of SAMP-hydrazine **2a** with SmI_2 under the same conditions gave only a trace amount of homoallylamine **4a**, and hydrazine **2a** was recovered quantitatively.

In summary, we have achieved the first efficient asymmetric synthesis of both enantiomers of α-trifluoromethylated homoallylamine based on the nuleophilic allylation of trifluoroacetaldehyde SAMP- or RAMP-hydrazone (ee >99%).

Optical rotaions were measured in Uvasol grade $CHCl_3$ (Merck) on a HORIBA SEPA-300 instrument. HPLC was carried out using Daicel CHIRALCEL OD (Daicel, 0.46 cm ϕ × 25 cm) column on a Shimadzu LC-4A liquid chromatograph. Melting points were obtained on a Yanagimoto MP-S2 micro melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FT-IR 8100A spectrometer. ^{1}H NMR spectra were measured with a JEOL α-400 (400 MHz) FT-NMR spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. ^{13}C NMR spectra were obtained on a JEOL α-400 (100 MHz) FT-NMR spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. ^{19}F NMR spectra were recorded on a JEOL α-400 (376 MHz) FT-NMR spectrometer in $CDCl_3$ solution using trifluoroacetic acid as the external standard. Mass spectra were taken on a Hitachi QP 1000 spectrometer (70 eV). HRMS were measured on a JEOL JMS-700 mass spectrometer. SmI_2 (0.1 M THF solution) and tetraallyltin were purchased from Aldrich Chemical Co.

Allylation of Trifluoroacetaldehyde SAMP-Hydrazone (*S*)-1a; (2*R*,2′*S*)-2-[2′-(Methoxymethyl)pyrrolidin-1′-yl]amino-1,1,1-trifluoropent-4-ene [(2*R*,2′*S*)-2a]; Typical Procedure

A solution of PhLi (5.7 mL of a 1.06 M cyclohexane–Et_2O solution, 6 mmol) was slowly added to an anhyd Et_2O solution (10 mL) of tetraallyltin (0.424 g, 1.5 mmol) at r.t. under argon. After the reaction mixture was stirred at r.t. for 1 h and cooled to –78 °C, an anhyd Et_2O solution (1 mL) of trifluoroacetaldehyde SAMP-hydrazone (*S*)-**1a** (0.105 g, 0.5 mmol) was slowly added at –78 °C. After stirring at –78 °C for 4 h, the resulting mixture was quenched with a cold sat. aq $NaHCO_3$ solution (50 mL), and the precipitate formed was removed by suction filtration with hexane (30 mL). The mixture was extracted with Et_2O (2 × 30 mL), dried (Na_2SO_4), and the solvent was removed under reduced pressure. After the isomer ratio of the products was determined by ^{19}F NMR, the residue was purified by flash chromatography on silica gel (hexane–Et_2O, 10:1) to give hydrazine **2a** (80%, 0.102 g); yield: 80%; R_f 0.28 (hexane–Et_2O, 10:1); $[\alpha]_D^{21}$ –34.8 (*c* = 0.97, $CHCl_3$).

IR (KBr): 3293, 2977, 1645, 1458, 1379, 1273, 1173, 1125, 920, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50–1.59 (m, 1 H, $CH_2CH_AH_BCH$), 1.64–1.77 (m, 2 H, $CH_{A'}H_{B'}CH_AH_BCH$), 1.86–1.95 (m, 1 H, $CH_{A'}H_{B'}CH_2CH$), 2.25–2.33 (m, 1 H, CH_AH_B), 2.42–2.49 (m, 1 H, CH_AH_B) 2.43 (q, *J* = 8.78 Hz, 1 H, NCH_AH_B), 2.63–2.70 (m, 1 H, NCH_AH_B), 2.70 (m, 1 H, CF_3CH), 3.30 (br s, 1 H, NH), 3.35 (s, 3 H, OCH_3), 3.38 (AB quartet, *J* = 9.27, 5.37 Hz, 1 H, CH_AH_BO), 3.44–3.49 (m, 1 H, NCH), 3.47 (AB quartet, *J* = 9.27, 5.37 Hz, 1 H, CH_AH_BO), 5.12 (ddt, *J* = 9.75, 1.71, 1,71 Hz, 1 H, $CH=CH_AH_B$), 5.16 (ddt, *J* = 17.08, 1.71, 1.71 Hz, 1 H, $CH=CH_AH_B$), 5.85 (ddt, *J* = 17.08, 9.75, 7.31 Hz, 1 H, $CH=CH_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.92 (s), 26.19 (s), 32.61 (s), 57.45 (s), 58.98 (s), 61.09 (q, J_{CF} = 25.91 Hz), 66.58 (s), 75.14 (s), 126.21 (q, J_{CF} = 282.30 Hz), 133.60 (s).

^{19}F NMR ($CDCl_3$): δ = 3.41 (d, J_{FH} = 7.63 Hz, 3 F).

MS (EI): *m*/*z* (%) = 252.0 (M^+, 7.9), 207.0 ($M^+ - CH_2OCH_3$, 100.0), 129.0 ($M^+ - CF_3CHCH_2CHCH_2$, 8.1).

HRMS (CI): *m*/*z* calcd for $C_{11}H_{19}ON_2F_3$ (M + H), 253.1529; found, 253.1520.

(2*S*,2′*R*)-2-[(2′-Methoxymethyl)pyrrolidin-1′-yl]amino-1,1,1-trifluoropent-4-ene [(2*S*,2′*R*)-2a]
This compound was prepared staring from (*R*)-**1a** according to the above typical procedure; yield: 67%; R_f 0.25 (hexane–Et_2O, 10:1); $[\alpha]_D^{22}$ +43.62 (*c* = 0.96, $CHCl_3$).

2-(Morpholin-1′-yl)amino-1,1,1-trifluoropent-4-ene (2b)
This compound was prepared starting from **1b** following the above typical procedure; yield: 62%; R_f 0.23 (hexane–Et_2O, 10:1).

IR (KBr): 3278, 2859, 1646, 1453, 1358, 1275, 1113, 878 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.09 (ddd, *J* = 14.64, 9.50, 9.50 Hz, 1 H, CH_AH_B), 2.38 (br, 1 H, NH), 2.40–2.45 (m, 1 H, CH_AH_B), 2.54–2.59 (m, 4 H, CH_2NCH_2), 3.17–3.24 (m, 1 H, CF_3CH), 3.58–3.65 (m, 4 H, CH_2OCH_2), 5.12–5.15 (m, 2 H, CH=CH_2), 5.65–5.73 (m, 1 H, C*H*=CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.96 (s), 56.32 (s), 58.28 (q, J_{CF} = 28.12 Hz), 66.12 (s), 120.55 (s), 125.62 (q, J_{CF} = 284.50 Hz), 132.42 (s).

^{19}F NMR ($CDCl_3$): δ = 1.85 (d, J_{FH} = 6.11 Hz, 3 F).

MS (EI): *m*/*z* (%) = 224.0 (M^+, 8.7), 101.0 (M^+ – $CF_3CHCH_2CHCH_2$, 100.0).

HRMS (CI): *m*/*z* calcd for $C_9H_{16}ON_2F_3$ (M + H), 225.1216; found, 225.1210.

Benzoylation of SAMP-Hydrazine 2a; (2*R*,2′*S*)-*N*-[2′-(Methoxymethyl)pyrrolidin-1′-yl]]-*N*-(1,1,1-trifluoropent-4-en-2-yl)benzamide [(2*R*,2′*S*)-3a]; Typical Procedure
A mixture of SAMP-hydrazine (2*R*,2′*S*)-**2a** (0.179 g, 0.709 mmol), benzoyl chloride (0.996 g, 7.09 mmol), Et_3N (0.716 g, 7.09 mmol), and a catalytic amount of DMAP (1 crystal) in CH_2Cl_2 (2 mL) was stirred at r.t. for 3 d under argon. The resultant mixture was quenched with a sat. aq $NaHCO_3$ solution (50 mL), extracted with Et_2O (3 × 30 mL), washed with a sat. aq $NaHCO_3$ solution (2 × 30 mL), and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane–Et_2O, 20:1, followed by hexane–Et_2O, 5:1) to give the hydrazide **3a** (68%, 0.173 g); yield: 68%; R_f 0.13 (hexane–Et_2O, 5:1); $[\alpha]_D^{22}$ –39.06 (*c* = 1.00, $CHCl_3$).

IR (KBr): 2979, 1667, 1601, 1447, 1348, 1321, 1173, 1120, 924, 702 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.52–1.90 (m, 4 H, CH_2CH_2), 2.77–2.88 (m, 1 H, NCH_AH_B), 3.07 (s, 1 H, NCH_AH_B), 3.14–3.20 (m, 1 H, CH_AH_B), 3.22–3.27 (m, 1 H, CH_AH_B), 3.36 (s, 3 H, OCH_3), 3.44–3.53 (m, 1 H, NCH), 3.48 (AB quartet, *J* = 9.52, 4.15 Hz, 1 H, CH_AH_BO), 3.79–3.83 (m, 1 H, CH_AH_BO), 4.19 (m, 1 H, CF_3CH), 5.13 (dd, *J* = 16.34, 1.22 Hz, 1 H, CH=CH_AH_B), 5.17 (dd, *J* = 9.27, 1.22 Hz, 1 H, CH=CH_AH_B), 5.59 (ddt, *J* = 16.34, 9.27, 6.83 Hz, 1 H, C*H*=CH_2), 7.32–7.51 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.31 (s), 27.95 (s), 30.48 (s), 54.87 (s), 58.60 (s), 62.43 (q, J_{CF} = 28.67 Hz), 63.46 (s), 74.65 (s), 124.31 (q, J_{CF} = 265.20 Hz), 126.13 (s), 128.60 (s), 129.65 (s), 131.65 (s), 136.33 (s), 171.09 (s).

^{19}F NMR ($CDCl_3$): δ = 7.66 (d, J_{FH} = 7.63 Hz, 3 F).

MS (EI) *m*/*z* (%) = 356.0 (M^+, 1.4), 311.0 (M^+ – CH_2OCH_3, 100.0), 251.0 (M^+ – PhCO, 23.6), 105.0 (PhCO, 78.4).

(2*S*,2′*R*)-*N*-[2′-(Methoxymethyl)pyrrolidin-1′-yl]-*N*-1,1,1-trifluoropent-4-en-2-yl)benzamide [(2*S*,2′*R*)-3a]
This compound was prepared starting from (2*S*,2′*R*)-**2a** following the above typical procedure; yield: 61%; R_f 0.16 (hexane–Et_2O, 5:1); $[\alpha]_D^{22}$ +45.40 (*c* = 0.98, $CHCl_3$).

SmI_2-Induced Cleavage of the N–N Single Bond of SAMP-Hydrazide 3a; (*R*)-*N*-(1,1,1-Trifluoropent-4-en-2-yl)benzamide [(*R*)-4a]; Typical Procedure
A THF solution of SmI_2 (13.6 mL, 0.1 M, 1.4 mmol) was slowly added to a THF solution (3.1 mL) of SAMP-hydrazide (2*R*,2′*S*)-**3a** (0.161 g, 0.45 mmol) in the presence of DMPU (0.78 mL) at r.t. under argon. After 30 min the reaction mixture was quenched with a sat. aq $NaHCO_3$ solution (50 mL), extracted with CH_2Cl_2 (3 × 30 mL), and dried (Na_2SO_4). After the solvent was removed under reduced pressure, the residue was purified by flash chromatography on silica gel (hexane–Et_2O, 5:1) to give the amide **4a** (75%, 0.082 g); yield: 75%; R_f 0.13 (hexane–Et_2O, 5:1); mp 153.0–154.5 °C; $[\alpha]_D^{22}$ +6.65 (*c* = 1.01, $CHCl_3$).

IR (KBr): 3281, 1647, 1537, 1375, 1264, 1179, 1103, 924, 708 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.35–2.43 (m, 1 H, CH_AH_B), 2.56–2.63 (m, 1H, CH_AH_B), 4.83–4.93 (m, 1 H, CF_3CH), 5.13 (ddt, *J* = 8.05, 1.47, 1.47 Hz, 1 H, CH=CH_AH_B), 5.15 (ddt, *J* = 14.40, 1.47, 1.47 Hz, 1 H, CH=CH_AH_B), 5.73 (ddt, *J* = 14.40, 9.76, 8.05 Hz, 1 H, C*H*=CH_2), 6.04 (d, *J* = 9.27 Hz, 1 H, NH), 7.38–7.41 (m, 2 H, C_6H_5-H_m), 7.46–7.50 (m, 1 H, C_6H_5-H_p), 7.69–7.72 (m, 2 H, C_6H_5-H_o).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.87 (s), 49.88 (q, J_{CF} = 30.32 Hz), 119.68 (s), 125.08 (q, J_{CF} = 243.15 Hz), 127.05 (s), 128.65 (s), 131.43 (s), 131.07 (s), 133.41 (s), 167.33 (s).

^{19}F NMR ($CDCl_3$): δ = 2.60 (d, J_{FH} = 7.63 Hz, 3 F).

MS (EI): *m*/*z* (%) = 243.0 (M^+, 13.6), 202.0 (M^+ – CH_2CHCH_2, 0.8), 105.0 (PhCO, 100.0).

(*S*)-*N*-(1,1,1-Trifluoro-4-penten-2-yl)benzamide [(*S*)-4a]
This compound was prepared staring from (2*S*,2′*R*)-**3a** according to the above typical procedure; yield: 98%; R_f 0.13 (hexane–Et_2O, 5:1); mp 148.8–151.0 °C; $[\alpha]_D^{22}$ –3.36 (*c* = 1.02, $CHCl_3$).

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