α-Trifluoromethyl α-Ethoxy β-Vinyl Anions: Stereoselective Route to Hindered β-Ethoxy Allylic Alcohols and Crotonates

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Abstract: α-Trifluoromethyl β-bromo enol ethers **3** can be stereoselectively obtained through a sequential bromination-dehydrobromination of enol ethers **1**. Bromine-lithium exchange, followed by subsequent trapping with electrophiles gives access to new functionalized CF_3-enol ethers.

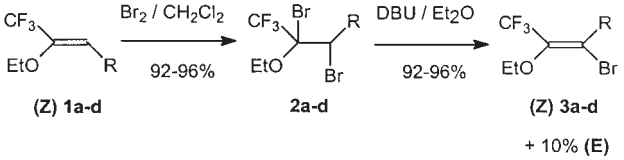
Key words: trifluoromethyl compounds, enol ether, vinyl bromide, halogen-metal exchange, allylic alcohols

As a part of our effort to explore the synthetic utility of CF_3-containing vinyl ethers **1**,[1] we have investigated the preparation of their organometallic derivatives. We recently reported that our first attempts to generate β-metalated vinyl ethers from **1**, by direct metalation with a strong base, failed: treatment of enol ethers with organolithium reagents resulted in no reaction from **1a**, and in an addition/elimination reaction from **1c**, leading to substituted trifluoromethyl alkenes.[2] We thus envisaged the preparation of these β-metalated vinyl ethers through halogen-lithium exchange in bromovinylic enol ethers.

In nonfluorinated systems, β-bromoenamines[3] and β-bromo enol ethers[4] have been reported in halogen-metal exchanges, and used as useful precursors of enolate equivalents, although these often undergo a rapid lithium ethoxide elimination leading to acetylenic compounds.[5] In fluorinated systems some halogen-metal exchanges have been studied from α–CF_3, β-alkoxy vinyl chlorides for the preparation of acetylenic compounds through a facile β-elimination.[6] However, an α-CF_3, β-ethoxy vinyl zinc reagent, generated from the corresponding vinyl bromide in the presence of TMEDA, has been described to be exceptionally stable, in contrast to its lithium counterpart, and has been used in palladium-catalyzed coupling reactions.[7]

We have now established that vinyllithium reagents can be generated from enol ethers, β to a CF_3 group. Herein we report the preparation of β-trifluoromethyl β-ethoxy vinylic bromides **3**, the halogen-lithium exchange, and the reactivity of β-metalated vinyl ethers towards electrophiles.

Trifluoromethyl-substituted (*Z*)-enol ethers **1** are readily available in large quantities through Wittig reaction of ethyl trifluoroacetate.[8] We first developed a procedure for the preparation of the previously unreported bromo enol ethers **3** through a bromination-dehydrobromination sequence. Addition of bromine to (*Z*)-enol ethers **1a–d** in dichloromethane proceeded slowly, taking several hours at room temperature (GC control), to form the dibromo adducts **2a–d.** These compounds are particularly stable. They can be isolated in high yields and with a high diastereoselectivity by short path distillation (Scheme 1, Table 1). Surprisingly, subsequent treatment with triethylamine did not provide the expected vinyl bromides, but resulted in the recovery of the dibromides **2a–d.** Addition of nucleophilic bases, such as morpholine or azides, to **2a–d** resulted mainly in complete debromination leading back to (*Z*)-enol ethers **1a–d.** Such halophilic debromination with amines, which act as nucleophiles, has already been observed from other CF_3-substituted dibromides.[7] However, when DBU in Et_2O was employed, the dehydrobromination of **2a–d** occurred leading to vinyl bromides **3a–d** in high yields (*Z/E* 90:10). The reaction could be performed in one pot from **1a–d**, provided Et_2O was added for the second step of the reaction.



1-3	R
a	CH_2CH_2Ph
b	$CH_2(CH_2)_4CH_3$
c	Ph
d	Cyclohexyl

Scheme 1

The determination of the configuration of tetrasubstituted alkenes is always problematic; the often used differences in ^{19}F chemical shifts and in $^3J_{CF}$ coupling constants[9] are too weak in this case to allow an unambiguous assignment, which was thus performed by homo and hetero NOE difference experiments. The *Z* configuration was assigned to the major isomer of **3a, 3b**, and **3d** by the observation of a $\{^{19}F\}$, ^1H NOE effect between CF_3 and the allylic protons (4% for **3a, 3b**, and 20% for **3d**). The *E* configuration was assigned to the minor isomer of **2c** by the observation of a 6% enhancement of *ortho* aromatic proton signal when OCH_2 was irradiated. Thus, assuming that the dehydrobromination is most likely *anti*, the addition of Br_2 to the double bond occurs preferentially in an *anti* manner, leading to the adducts **2a–d** and then to the *Z* isomer of **3a–d**, independently of the nature of the R group.

For halogen-metal exchange reactions, treatment of vinyl bromides **3a,b,d** (*Z/E* 90:10) with *t*-BuLi in THF at –78 °C, and further hydrolysis, resulted in the formation of (*E*)-**1a,b,d**, accompanied by 10% of (*Z*)-**1a,b,d**, indicating the stereoselective formation of the anionic intermediate with retention of configuration of the double bond in

Table 1. Compounds **2a–d** and **3a–d** Prepared[a]

Product	Yield (%)	^{1}H NMR ($CDCl_3$) δ^b, J(Hz)	^{13}C NMR ($CDCl_3$) δ^b, J_{C-F} (Hz)	^{19}F NMR ($CDCl_3$/$CFCl_3$) $\delta Z/\delta E$	IR (KBr/film $\nu_{C=C}$ (cm^{-1})
2a	92	1.2 (t, *J*=7.2, 3H), 2.2–2.4 (m, 1H) 2.6–2.8 (m, 2H), 3.0–3.2 (m, 1H), 3.8 (q, *J* = 7.2, 2H), 4.3 (dd, *J* = 10.2, 1.5, C*H*Br), 7.1–7.4 (m, 5H)	15.1/14.0, 33.4, 36.4, 53.2 (*C*-Br), 66.1, 101.2 (q, ^2J = 30, CCF_3), 121.1 (q, ^1J = 290, CF_3), 126.3, 128.5, 128.6, 140.0	–67.3 (90:10)[c]	
2b	96	0.9 (m, 3H), 1.1–1.4 (m, 8H), 1.6 1 –2.0 (m, 1H), 2.1–2.4 (m, 1H), 3.8 (q, *J* = 7, 2H), 4.3/4.4 (major/minor) (dd, *J* = 10.2, *J* = 1.7, C*H*Br)	3.8, 14.1, 22.7, 27.5, 28.4, 31.7, 34.7, 54.3 (CBr), 66.9, 101.8 (q, ^2J = 30, CCF_3), 121.1 (q, ^1J = 290, CF_3)	–67.7/–67.75 (90:10)	
2c	94	1.25 (t, *J* = 7, 3H), 3.85 (q, *J* = 7, 2H), 5.40/5.45 (major/minor) (s, CHBr), 7.2–7.6 (m, 5H)	14.5, 51.3 (CBr), 67.0, 99.3 (q, ^2J = 30, *C*CF_3), 120.9 (q, ^1J = 290, CF_3), 128.1, 129.4, 129.9, 138.1.	–68/–68.2 (90:10)	
2d	90	1.1–1.7 (m, 10H), 1.3 (t, *J* = 7, CH_3), 2.4 (m, 1H), 3.9 (m, 2H), 4.3/4.4 (major/minor) (s, CHBr)	14.7, 26.0, 26.4, 28.6, 33.1, 41.7, 59.6, 67.0, 102.8 (q, ^2J = 30, CCF_3), 121.2 (q, ^1J = 291, CF_3), 138.2	–66.7 (90:10)[c]	
3a	92.5	1.12 (*Z*)/0.9 (t, *J* = 7.4, 3H), 2.6 –2.7 (m, 4H), 3.64 (*Z*)/3.15 (q, *J* = 7.4, 2H), 7.0–7.26 (m, 5H)	15.0 (*Z*)/15.2, 34.8 (*Z*)/33.7, 37.3 (*Z*)/37.4, 69.6/70.3, 121,1 (*Z*)/121.2 (q, ^1J = 278, CF_3), 126.0 (*Z*)/119.0 (q, ^3J=3/3.5, *C*CCF_3), 126.4, 128.3, 128.4, 128.5, 139.6, 140.9, 141.8 (*Z*)/142.2 (q, ^2J = 33.5/33, *C*CF_3)	–62.5/–63.1 (*Z*/*E* 90:10)	1647
3b	92.50.9 (*Z*)/l.0 (t, *J* = 7, 3H), 1.15 (m, 7H), 1.2 (m, 2H), 1.5 (m, 2H), 2.5 (*Z*)/2.45 (bt, *J* = 7.5/7, 2H), 3.75 (*Z*)/3.5 (q, *J* = 7, 2H)		14.1, 15.3, 22.6, 28.2, 28.6, 31.6, 35.2, 69.7, 121.0 (q, ^1J = 278, CF_3), 127.8 (q, ^3J = 3, *C*CCF_3), 142.0 (q, ^2J = 33.6, *C*CF_3)	–62.2/–63.1 (*Z*/*E* 90:10)	1641
3c	96	1.47 (*Z*)/1.0 (t, *J* = 7, 3H), 4.2 (*Z*)/3.65 (q, *J* = 7, 2H), 7.3–7.6 (m, 5H)	15.6 (*Z*)/14.8, 70.0 (*Z*)/70.3, 120.5 (*Z*)/121.2 (q, ^1J = 278, CF_3), 121.4 (*Z*)/117.6 (q, ^3J = 3.4/2.7, *C*CCF_3), 128.2, 128.7, 129.4, 135.9, 141.9/ 142.7, (q, ^2J = 33/33.5, *C*CF_3)	–61.2/–63.2 (*Z*/*E* 90:10)	1640
3d	92.5	1.2–1.25 (m, 3H), 1.35 (*Z*)/1.33 (t, *J* = 7/7.1, 3H), 1.4–1.8 (m, 10H), 2.6–2.9 (m, 1H, C*H*), 3.9 (*Z*)/3.8 (q, *J* = 7.1/7)	15.3, 25.7, 25.8, 25.9, 31.9 (*Z*)/31.3, 40.9 (*Z*)/41.1, 69.6 (*Z*)/70.7, 121.7 (*Z*)/125.4 (q, ^1J = 278, CF_3), 134.8 (*Z*)/131.4 (q, ^3J = 3.6/3.1, *C*CCF_3), 140.4 (*Z*)/140.2 (q, ^2J = 33, *C*CF_3)	–60.4/–61.9 (*Z*/*E* 90:10)	1641

[a] Satisfactory microanalyses obtained: C ± 0.3, H + 0.2 (except for compound **3b**).
[b] δ of major isomer unless otherwise indicated.
[c] GC ratio (no separation in ^{19}F NMR).

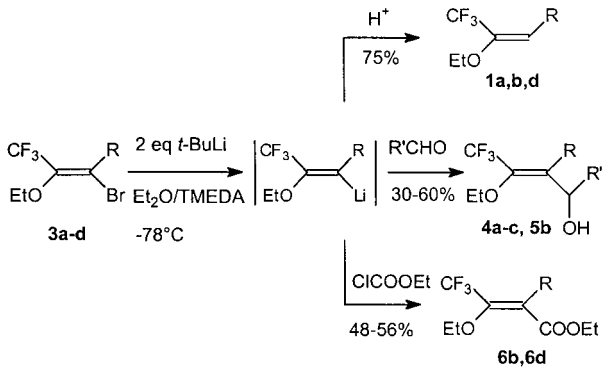
the starting vinyl bromides (Scheme 2, Table 2). It is noteworthy that even the minor (*E*)-isomer where Br and OEt are *trans*, provides quantitatively enol ether **1** without formation of acetylenic compounds. However our attempts to quench the β-lithiated enol ethers with other electrophiles (aldehydes, TMSCl) failed, the only products being enol ethers **1**, even when the electrophiles were introduced a few seconds after *t*-BuLi. This suggests that the formation of **1** is not the result of protonation, but of a very rapid reductive process involving the solvent. Reactions were thus performed in Et_2O instead of THF. Under these conditions, the main process was the β-elimination of lithium ethoxide, leading to acetylenic compounds.[10] Finally the addition of TMEDA allowed the condensation to occur. Thus, addition of two equivalents of *t*-BuLi to vinyl bromides **3a, b** (*Z*/*E* 90:10) in Et_2O at –78 °C, in the presence of one equivalent of TMEDA, followed by rapid quenching with one equivalent of benzaldehyde, afforded 50% of allylic alcohols **4a, b** (*Z*/*E* 90:10), accompanied by about 20% of (*Z*,*E*)-**1a, b** (Scheme 2, Table 3). The *E* configuration was assigned to the minor isomer of **4a** and **4b** by the observation of a {^{19}F},^{1}H NOE effect (4%) between CF_3 and the *H*-COH proton.

The vinylic anion generated from **3b** could also be condensed with propanal and ethyl chloroformate leading to allylic alcohol and α,β-ethylenic ester, **5b** (*Z*/*E* 90:10) and (*Z*)-**6b** respectively (60%), with again (*Z*,*E*)-**1b** as byproduct. The *Z* configuration of **6b** was determined by the observation of a {^{19}F},^{1}H NOE effect between CF_3 and the

Table 2. Compounds **1a, b, d** Prepared[a]

Product	Yield (%)	^{1}H NMR ($CDCl_3$)[1] δ, J (Hz)	^{3}C NMR ($CDCl_3$)[1] δ (*E*/*Z*), J_{C-F} (Hz)	^{9}F NMR ($CDCl_3$/$CFCl_3$) δ	IR (KBr/film) $\nu_{C=C}$ (cm^{-1})
1a	74	1.25 (t, J = 7, 3H), 2.5 (m, 2H), 2.7 (m, 2H), 3.7 (q, J = 7, 2H), 4.85 (*E*)/5.65 (t, J = 7.8, 1H), 7.2 (m, 5H)	14.3, 26.9 (*E*)/26.8, 36.7, 64.4 (*E*)/69.8, 106.8 (q, ^3J = 3, CCF_3), 120.0 (q, ^1J = 266, CF_3), 127.0, 128.2, 128.7, 141.1, 143.9 (q, ^2J = 33, CCF_3)	–65.2/–69.5 (*E*/*Z* 90:10)	1669
1b	75	0.9 (m, 3H), 1.3 (m, 11H), 2.15 (m, 2H), 3.7 (q, J = 7, 2H), 4.9 (*E*)/5.6 (t, J = 8, 1H)	14.0, 14.3, 22.6 (*E*)/22.4, 24.9, 28.7, 30.3, 31.6, 64.3 (*E*)/69.7, 108.4 (q, ^3J = 2, $CCCF_3$), 120.0 (q, ^1J = 275, CF_3), 143.5 (q, ^2J = 33, CCF_3)	–65.3/–69.5 (*E*/*Z* 90:10)	1669

[a] Satisfactory microanalyses obtained: C ± 0.3, H ± 0.2.



	R	PhCHO	C_2H_5CHO	$ClCO_2Et$
a	CH_2CH_2Ph	**4a** (56%)		
b	$CH_2(CH_2)_4CH_3$	**4b** (50%)	**5b** (60%)	**6b** (56%)
c	Ph	**4c** (30%)		
d	Cyclohexyl			**6d** (48%)

Scheme 2

allylic CH_2 protons. This formation of only one isomer can be explained by a different reactivity of the two isomeric vinyl anions towards ethyl chloroformate. The condensation reaction is not dependent on steric hindrance: from the bulky vinyl bromide **3d**, ester **6d** could be obtained in similar yield. The same stereoselective formation of the (*Z*)-isomer was observed. The reaction of **3c** with *t*-BuLi and a further quenching with benzaldehyde, allowed the isolation of the allylic alcohol **4c** but with a lower yield (30%). Unidentified side product mixture is the result of expected competitive reactions: in the presence of a phenyl substituent, starting material and reduction or condensation products could undergo a carbolithiation as already described from **1c**.[2]

In conclusion, we have developed a stereoselective synthesis of β-trifluoromethyl β-ethoxy vinyl bromides, from which vinyl lithium reagents have been generated and used successfully for condensation with electrophiles. By this way we describe a stereoselective preparation of (*E*)-enol ethers **1**, which were not until now accessible, and which could find the same synthetic utility as the (*Z*)-isomer.[10] Furthermore, we have synthesized new hindered trifluoromethyl-containing allylic alcohols and ethyl crotonates. The high stereoselectivity, the presence of a latent carbonyl group and another functionality, make these tetrasubstituted olefins new valuable CF_3-containing synthons.

^{19}F NMR chemical shifts are reported in ppm, negative upfield relative to internal $CFCl_3$, ^{1}H NMR and ^{13}C NMR chemical shifts are reported in ppm, positive downfield relative to internal TMS; spectra were recorded in $CDCl_3$ at 200 MHz (Bruker AC 200) and 400 MHz (Bruker ARX 400). IR (cm^{-1}, neat) were recorded on a Perkin–Elmer 841 spectrophotometer. Column chromatography were performed on silica gel (70–230 or 230–400 Mesh SDS). GC analyses were obtained using SE-30 column (25 m). Elemental analyses were performed by the Service de Microanalyses of the Faculté de Pharmacie, Châtenay-Malabry.

Et_2O was purified by distillation from sodium ketyl. All aldehydes and chloroformate were distilled before use. *t*-BuLi is available from Acros.

Enol ethers (*Z*)**-1a**, (*Z*)**-1c** and procedure for preparation of (*Z*)**-1b** have already been described.[8]

2,3-Dibromo-2-ethoxy-1,1,1-trifluoro-5-phenylpentane (2a); Typical Procedure:

A solution of Br_2 (1.65 g, 10.3 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of fluoroalkyl enol ether **1a** (2.48 g, 10.2 mmol) in CH_2Cl_2 (20 mL) at 0°C. When the addition was complete the mixture was allowed to warm to r.t. and stirred for a further 12 h in the absence of light. The mixture was then washed with sat. $NaHCO_3$ (20 mL), dried ($MgSO_4$) and evaporated to give a pale yellow oil. **2a** was obtained after distillation as a mixture (90:10) of diastereoisomers (3.87 g, 92%); bp 110°C/1.2 Torr (bulb-to-bulb).

3-Bromo-2-ethoxy-1,1,1-trifluoro-5-phenylpent-2-eue (3a); Typical Procedure:

DBU (1.2 g, 8 mmol) was added to a stirred solution of the 2,3-dibromo-2-ethoxy-1,1,1-trifluoro-5-phenylpentane (**2a**) (2.83 g, 7 mmol)

Table 3. Compounds **4a–c, 5b, 6b** and **6d** Prepared[a]

Product	Yield (%)	^{1}H NMR ($CDCl_3$) δZ (major), J (Hz)	^{13}C NMR ($CDCl_3$) δZ (major), $J_{C\text{-}F}$ (Hz)	^{19}F NMR ($CDCl_3$/$CFCl_3$) δ	IR (KBr/Film) $\nu_{C=C}$, $\nu_{C=O}$ or ν_{OH} (cm^{-1})
4a	56	1.3 (t, J = 7, 3H), 1.5 (bs, 1H, OH), 2.4 (m, 2H), 2.7 (m, 2H) 3.8 (m, AB system, J = 7, J = 7, 2H), 6.0 (s, 1H), 7.0–7.6 (m, 10H)	15.3, 28.5, 37.0, 70.1 (q, ^4J = 1), 71.6 (*C*-OH), 122.0 (q, ^1J = 278, CF_3), 126.0, 127.1, 128.0, 129.0, 136.7 (q, ^3J = 2.5, *C*CF_3), 140.5 (q, ^2J = 33), 141,5, 141.6 (q, J = 1, CF_3), 141.6	–62.1/–58.2 (*Z*/*E* 90:10)	1656, 3457
4b	50	0.8 (m, 3H), 1.2 (m, 11H), 2.0 (m, 2H), 2.5 (d, J = 5, OH), 3.6 and 3.7 (m, AB system, J = 7.3, J = 7, 2H), 5.7 (d, J = 5, 1H), 7.3 (m, 5H)	13.9, 15.0, 22.5, 26.9, 29.6, 30.1, 31.2, 69.8 (q, ^4J = 1), 71.5 (*C*OH), 122.0 (q, J = 278, CF_3), 125.7, 127.3, 128.2, 137.9 (q, ^3J = 2.7, *C*CCF_3), 140.3 (q, ^2J = 32, *C*CF_3), 141.9 (q, ^4J = 1, *C*OH)	–61.9/–58.2 (*Z*/*E* 90:10)	1673, 3451
4c	30	1.3 (t, J = 7, 3H), 2.2 (d, J = 8, OH), 4.0 (m, AB system, J = 7, J = 7, 2H), 6.0 (d, J = 8, 1H), 6.75 (m, 2H), 7.2 (m, 8H)	15.4, 70.2 (q, ^4J = 1), 71.3 (*C*OH), 122.0 (q, ^1J = 279, CF_3), 125.8, 127.6, 127.7, 128.1, 129.6, 131.9, 137.0 (q, ^3J = 2.5, *C*CCF_3), 140.8 (q, ^2J = 32, *C*CF_3), 141.2	–60.6 (*Z*)	1656, 3460
5b	60	0.8 (m, 3H), 0.95 (t, J = 7, 3H), 1.2 (m, 11H), 1.6 (m, 2H), 2.0 (m, 2H + 1H), 3.7 (m, AB system, J = 7, J = 7, 2H), 4.4 (*Z*)/4.5 (m, 1H)	10.4, 14.1, 15.3, 22.7, 26.5, (q, J= 2), 29,1, 29.9, 30.5 (q, J = 1.5), 31.6, 70.5 (q, J = 2), 72.6 (*C*oH), 120.0 (q, ^1J = 278, CF_3), 138.6 (q, ^3J = 2.7, *C*CCF_3), 139.5 (q, ^2J = 32, *C*CF_3)	–61.9/–59.0 (*Z*/*E* 90:10)	1656, 3448
6b	56	0.87 (t, J = 7, 3H), 1.25 (m, 14H), 2.3 (m, 2H), 3.7 (q, J = 7), 4.2 (q, J = 7)	13.9, 14.1, 15.0, 22.4, 27.5 (q, J = 2), 28.2, 28.8, 61.2, 70.8, 121.0 (q, ^1J = 278, CF_3), 130.0 (q, ^3J = 2.7, *C*CCF_3), 143.0 (q, ^2J = 32, *C*CF_3), 167.2	–63.6 (*Z*)	668, 1734
6d	48	1.3 (m, 12H), 1.6 (m, 4H), 2.5 (m, 1H), 3.8 (q, J = 7, CH_2O), 4.2 (q, J = 7, CH_2O)	14.2, 15.0, 25.5, 26.0, 31.3, 36.5, 61.0, 70.5, 121.5 (q, ^1J = 279, CF_3), 135.1 (q, ^3J = 2.3, *C*CCF_3), 140.5 (q, ^2J = 34, *C*CF_3), 166.4 (C=O)	–62.2 (*Z*)	1662, 1733

[a] Satisfactory microanalyses obtained: C × 0.3, H × 0.2.

in anhyd Et_2O (25mL) at r.t. under argon. After 30 min the solution was filtered through Celite and evaporated to give a brown oil which was further purified by chromatography (CH_2Cl_2) to give **3a** (*Z*/*E* 90:10) (2.09 g, 92.5%) as a colorless oil.

(*E*)-2-Ethoxy-1,1,1-trifluoro-5-phenylpent-2-ene (1a); Typical Procedure:

1.5 M *t*-BuLi in hexanes (0.6 mL, 0.92 mmol) was added to a solution of **3a** (*Z*/*E* 90:10)(150 mg, 4.6×10^{-4} mol) in THF at –78 °C under argon. The solution was stirred for a further 15 min at –78 °C and allowed to warm to r.t. before hydrolysis with sat. NH_4Cl. The mixture was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic phases were dried ($MgSO_4$) and evaporated to give a yellow oil which was purified by chromatography (silica gel, pentane/Et_2O 90:10) to give **1a** (*E*/*Z* 90:10) (84 mg, 75%). Same results were obtained when the reaction was performed in Et_2O (15 mL)/TMEDA (53 mg, 1 equiv).

2-Ethoxy-1,1,1-trifluoro-3-[hydroxy(phenyl)methyl]-5-phenylpent-2-ene (4a); Typical Procedure:

1.5 M *t*-BuLi in hexanes (0.6 mL, 0.92 mmol) was added to a solution of **3a** (150 mg, 4.6×10^{-4} mol) in Et_2O in the presence of TMEDA (57 mg, 4.6×10^{-4} mol) at –78 °C under argon. After 1 min at –78 °C the benzaldehyde (43 mg, 4.6×10^{-4} mol) was added. The solution was stirred for a further 15 min at –78 °C and was allowed to warm to r.t. The mixture was quenched with sat. NH_4Cl and extracted with CH_2Cl_2 (2 × 25 mL). The combined organic phases were dried ($MgSO_4$) and evaporated to give a mixture of **4a** and **1a** (70:30). These products were then separated by chromatography (silica gel, pentane/Et_2O 80:20) to give (*Z*/*E*-**1a** (22 mg, 20%) and **4a** (*Z*/*E* 90:10)(90 mg, 56%).

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