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Copper(I)-catalyzed addition of trifluoromethylated benzyl radicals derived from aryltrifluoroethyl bromides to terminal olefins

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Abstract

Relatively unreactive aryltrifluoroethyl bromides were reacted with 1-octene in the presence of CuCl and 2,2′-bipyridyl at high temperatures. Trifluoromethylated benzyl radical was generated, and a diastereomer mixture of radical adducts was obtained with a (60–70):(40–30) diastereomer ratio. Ph_3SnH reduction of the adducts gave the corresponding hydrocarbons with an isolated trifluoromethyl group. The reactions with styrene or aromatic and aliphatic silyl enol ethers led to the formation of trifluorodiphenylbutene and β-trifluoromethylated ketones, respectively.

Keywords: Trifluoromethyl compound; Radical addition; Atom-transfer reaction; Cu(I) catalysts; Tin hydride reduction

1. Introduction

Synthesis of the compounds with a trifluoromethyl group [1] is an active area of organic synthesis due to their potential biological activities [2] and the utility as a structural subunit for the functional materials such as ferroelectric liquid crystals [3]. However, most of the reports deal with the synthesis of trifluoromethylated aromatics and heteroaromatics. As a new synthetic pathway for the compounds with an isolated trifluoromethyl group on a straight alkyl chain, which could be useful for a substructure of ferroelectric liquid crystals, we propose here an atom-transfer reaction of brominated precursors **1** with terminal olefins. In the reaction, trifluoromethylated benzyl radicals **2** are generated by single electron transfer from copper(I) (Cu(I)) catalyst (Scheme 1). Cu(I)-catalyzed radical generation from polyhaloalkanes is a well known process for the polyhalogenated compounds [4]. Since the more halogen substitution effectively lowers the energy level of the antibonding σ^*-orbital of C–X bond where an electron transfer occurs from Cu(I), the electrophilic radical reaction of highly halogenated substrates with electron-rich olefins is faster. In the case of aryltrifluoroethyl bromides **1**, the activating electron-withdrawing group for lowering the energy level of the σ^*_{C-Br}-orbital is only the trifluoromethyl group accompanied with a generally radical-stabilizing aryl group. Itoh and Nagashima et al. [5] reported the rate acceleration by CuCl/2,2′-dipyridyl complex for the radical cyclization of *N*-alkenyltrichloroacetamides. Although bromides **1** appear still less reactive than trichloroacetamides, this catalyst system could work also in the intermolecular reaction of bromides **1**.

We report here the atom-transfer radical reaction of aryltrifluoroethyl bromides **1** with some terminal olefins in the presence of Cu(I) amine complex and the following reduction of the product bromides into (trifluoromethyl)-aralkanes.

2. Experimental

^1H and ^{13}C NMR spectra were collected in $CDCl_3$ in the presence of TMS as an internal standard at 300 and 75.4 MHz, respectively unless otherwise noted. ^{19}F NMR spectra (282 MHz) were recorded in $CDCl_3$, and referenced based on internal $CF_3COOC_2H_5$ whose chemical shift was set at −75.75 ppm downfield (δ) from internal $CFCl_3$ in $CDCl_3$. Preparative HPLC was performed by a Jai JAIGEL 1H or 2H GPC column (20 mm ∅ × 600 mm) using a UV detector.

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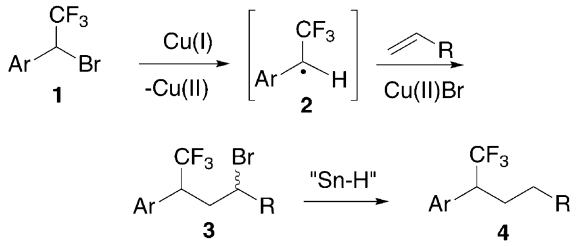


Scheme 1.

2.1. General method for the preparation of aryltrifluoroethylbromides

An equimolar mixture of trifluoroethanol **5**, triphenylphosphite, and NBS in CH_2Cl_2 was stirred at room temperature or under refluxing for several hours. The solvent was removed under reduced pressure, and then, the residue was chromatographed on a silica gel column (hexane–CH_2Cl_2) to give pure bromide **1**. The spectral data of known bromides **1b** and **d** were identical to the reported ones.

2.2. 1-(1-Bromo-2,2,2-trifluoroethyl)-4-chlorobenzene (*1b*)

As described above, from alcohol **5b** (3.50 g, 16.7 mmol), NBS (3.03 g, 17.0 mmol), and $(PhO)_3P$ (5.28 g, 17.0 mmol) in CH_2Cl_2 (20 ml), **1b** (2.36 g, 52%) was obtained as colorless oil by stirring the solution under refluxing for 5 h: spectral data were identical with those reported in [14].

2.3. 4-(1-Bromo-2,2,2-trifluoroethyl)toluene (*1c*)

As described above, from alcohol **5c** (5.77 g, 30.4 mmol), NBS (6.05 g, 34.0 mmol), and $(PhO)_3P$ (9.43 g, 30.4 mmol) in CH_2Cl_2 (40 ml) at room temperature, **1c** (2.53 g, 33%) was obtained as colorless oil by stirring the solution under refluxing for 10 h: ^{1}H NMR δ 2.366 (3H, s), 5.098 (1H, q, J = 7.5 Hz), 7.196 (2H, d, J = 4.2 Hz), 7.388 (2H, d, J = 4.2 Hz); ^{13}C NMR δ 21.22, 47.09 (q, J = 34 Hz), 123.44 (q, J = 278 Hz), 128.97, 129.57, 129.87, 140.21; ^{19}F NMR δ −71.1 (d, J = 8 Hz); MS *m/z* 252 (M^+). Anal. Calcd. for $C_9H_8BrF_3$: C, 42.72; H, 3.19. Found: C, 42.61; H, 3.11.

2.4. 4-(1-Bromo-2,2,2-trifluoroethyl)anisole (*1d*)

As described above, from alcohol **5d** (9.42 g, 47.2 mmol), NBS (8.90 g, 50.0 mmol), and $(PhO)_3P$ (15.5 g, 50.0 mmol) in CH_2Cl_2 (40 ml), **1d** (6.59 g, 54%) was obtained as colorless oil by stirring the solution at room temperature overnight: spectral data were identical with those reported in [15].

2.5. 1-(1-Bromo-2,2,2-trifluoroethyl)naphthalene (*1e*)

As described above, from alcohol **5e** (4.76 g, 21.0 mmol), NBS (3.92 g, 22.0 mmol), and $(PhO)_3P$ (6.83 g, 22.0 mmol) in CH_2Cl_2 (30 ml) at room temperature, **1e** (3.89 g, 64%) was obtained as colorless solid by stirring the solution at room temperature overnight: mp 30–31 °C; ^{1}H NMR δ 6.093 (1H, q, J = 6.0 Hz), 7.44–7.695 (3H, m), 7.85–7.97 (4H, m); ^{13}C NMR δ 42.01 (q, J = 36 Hz), 121.87, 123.96 (q, J = 278 Hz), 125.41, 126.22, 127.32, 127.98, 129.27, 130.18, 130.57, 130.65, 133.70; ^{19}F NMR δ −69.2 (d, J = 6 Hz); MS *m/z* 288 (M^+). Anal. Calcd. for $C_{12}H_8BrF_3$: C, 49.86; H, 2.79. Found: C, 49.58; H, 2.73.

2.6. 4-(1-Bromo-2,2,2-trifluoroethyl)-1,1′-biphenyl (*1f*)

As described above, from alcohol **5f** (1.60 g, 6.3 mmol), NBS (1.25 g, 7.0 mmol), and $(PhO)_3P$ (2.17 g, 7.0 mmol) in CH_2Cl_2 (50 ml), **1f** (1.20 g, 60%) was obtained by stirring at room temperature overnight as colorless solid: mp 89–90 °C; ^{1}H NMR δ 5.178 (1H, q, J = 7.3 Hz), 7.35–7.49 (3H, m), 7.56–7.63 (6H, m); ^{13}C NMR d 46.89 (q, J = 34 Hz), 123.43 (q, J = 278 Hz), 127.17, 127.59, 127.91, 128.91, 129.53, 129.55, 131.63 (q, J = 1 Hz), 139.95, 142.98; ^{19}F NMR δ −71.2 (d, J = 7 Hz); MS *m/z* 314 (M^+). Anal. Calcd. for $C_{14}H_{10}BrF_3$: C, 53.36; H, 3.20. Found: C, 53.29; H, 3.17.

2.7. Radical reaction of arylbromotrifluoroethanes (*1*) with 1-octene

Bromide **1** was dissolved in 1,2-dichlorobenzene, and the solution was degassed by sonication under N_2 atmosphere. The solution was added into preliminarily degassed mixture of 1-octene, CuCl, and 2,2′-bipyridyl in 1,2-dichlorobenzene. The resulting solution was refluxed at 180 °C for 24 h. The cooled mixture was filtered. The solvent of the filtrate wad removed by distillation under reduced pressure. The residue was purified by preparative HPLC with a GPC column ($CHCl_3$) directly or after distillation under reduced pressure (150 °C, 5 mmHg).

2.8. 4-Bromo-1,1,1-trifluoro-2-phenyldecane (*3a*)

As described above, bromide **3a** was obtained as a mixture of **3a$_1$** and **3a$_2$** (66:34) from bromide **1a** (478 mg, 2.00 mmol), 1-octene (898 mg, 8.00 mmol), CuCl (20 mg, 0.20 mmol), 2,2′-bipyridyl (63 mg, 0.40 mmol), 1,2-dichlorobenzene (8 ml): 519 mg (74%); colorless oil; MS *m/z* 350 (M^+). Anal. Calcd. for $C_{16}H_{22}BrF_3$: C, 54.71; H, 6.31. Found: C, 55.03; H, 6.25. NMR signals for the diastereomers were assigned by comparison of spectra obtained from partly separated samples: **3a$_1$** (major component); ^{1}H NMR δ 0.855 (3H, t, J = 7.2 Hz), 1.22–1.56 (8H, m), 1.68–1.92 (2H, m), 2.25–2.40 (2H, m), 3.480 (1H, tt, J = 8.4, 5.1 Hz), 3.772 (1H, dqd, J = 9.3, 9.3, 5.4 Hz), 7.28–7.42 (5H, m); ^{13}C NMR δ 14.00, 22.49, 27.24, 28.57, 31.53, 37.83 (q, J = 1 Hz), 39.66, 48.71 (q, J = 27 Hz), 54.21, 120–135;[2] ^{19}F NMR δ −70.0 (d,

[2] No rigorous assignment was achieved because of the low S/N ratios of CF_3 carbon signals.

$J = 9$ Hz): **3a₂** (minor component); ^{1}H NMR δ 0.874 (3H, t, $J = 7.2$ Hz), 1.22–1.56 (8H, m), 1.68–1.92 (2H, m), 2.32–2.46 (1H, m), 2.586 (1H, dt, $J = 15.0$, 6.6 Hz), 3.607 (1H, qt, $J = 9.3$, 7.2 Hz), 4.001 (1H, tt, $J = 6.9$, 6.9 Hz), 7.28–7.42 (5H, m); ^{13}C NMR δ 14.01, 22.51, 27.05, 28.48, 31.55, 38.06, 39.16 (q, $J = 1$ Hz), 48.05 (q, $J = 27$ Hz), 54.06, 120–135 (see footnote 3); ^{19}F NMR δ −69.6 (d, $J = 9$ Hz).

2.9. 4-Bromo-2-(4-chlorophenyl)-1,1,1-trifluorodecane (3b)

As described above, bromide **3b** was obtained as a mixture of **3b₁** and **3b₂** (60:40) from bromide **1b** (544 mg, 2.00 mmol), 1-octene (898 mg, 8.00 mmol), CuCl (20 mg, 0.20 mmol), 2,2′-bipyridyl (63 mg, 0.40 mmol), 1,2-dichlorobenzene (8 ml): 673 mg (81%); colorless oil; MS *m/z* 384 (M^+). Anal. Calcd. for $C_{16}H_{21}BrClF_3$: C, 49.83; H, 5.49. Found: C, 49.48; H, 5.30. NMR signals for the diastereomers were assigned by comparison of spectra obtained from partly separated samples: **3b₁** (major component); ^{1}H NMR δ 0.861 (3H, t, $J = 6.8$ Hz) 1.23–1.52 (8H, m), 1.68–1.92 (2H, m), 2.17–2.40 (2H, m), 3.438 (1H, dddd, $J = 11.1$, 8.1, 5.4, 3.3 Hz), 3.766 (1H, dqd, $J = 11.7$, 9.3, 3.9 Hz), 7.19–7.42 (4H, m); ^{13}C NMR δ 14.00, 22.49, 28.49, 31.52, 37.70 (q, $J = 2$ Hz), 39.62, 48.22 (q, $J = 27$ Hz), 53.89, 120–135 (see footnote 3), 131.63 (q, $J = 2$ Hz); ^{19}F NMR δ −70.1 (d, $J = 9$ Hz): **3b₂** (minor component); ^{1}H NMR δ 0.878 (3H, t, $J = 6.6$ Hz), 1.23–1.64 (8H, m), 1.70–1.91 (2H, m), 2.17–2.40 (1H, m), 2.574 (1H, dt, $J = 14.9$, 6.2 Hz), 3.612 (1H, qt, $J = 9.0$, 6.9 Hz), 3.998 (1H, tt, $J = 7.8$, 6.0 Hz), 7.19–7.42 (4H, m); ^{13}C NMR δ 14.00, 22.51, 28.57, 31.52, 39.15 (q, $J = 2$ Hz), 38.25, 47.55 (q, $J = 27$ Hz), 53.90, 121–135 (see footnote 3), 133.22 (q, $J = 2$ Hz); ^{19}F NMR d −69.7 (d, $J = 9$ Hz).

2.10. 4-Bromo-1,1,1-trifluoro-2-(4-methylphenyl)decane (3c)

As described above, bromide **3c** was obtained as a mixture of **3c₁** and **3c₂** (58:42) from bromide **1c** (504 mg, 2.00 mmol), 1-octene (898 mg, 8.00 mmol), CuCl (20 mg, 0.20 mmol), 2,2′-bipyridyl (63 mg, 0.40 mmol), 1,2-dichlorobenzene (8 ml): 494 mg (68%); colorless oil; MS *m/z* 364 (M^+). Anal. Calcd. for $C_{17}H_{24}BrF_3$: C, 55.90; H, 6.62. Found: C, 55.64; H, 6.59. NMR signals for the diastereomers were assigned by comparison of spectra obtained from partly separated samples: **3c₁** (major component); ^{1}H NMR δ 0.858 (3H, t, $J = 6.9$ Hz) 1.22–1.92 (8H, m), 1.64–1.92 (2H, m), 2.16–2.42 (2H, m), 3.438 (1H, dddd, $J = 11.1$, 8.1, 5.4, 3.3 Hz), 3.766 (1H, dqd, $J = 11.7$, 9.3, 3.9 Hz), 7.19–7.42 (4H, m); ^{13}C NMR δ 14.00, 22.49, 28.49, 31.52, 37.70 (q, $J = 2$ Hz), 39.62, 48.22 (q, $J = 27$ Hz), 53.89, 120–135 (see footnote 3), 131.63 (q, $J = 2$ Hz); ^{19}F NMR δ −70.1 (d, $J = 9$ Hz): **3c₂** (minor component); ^{1}H NMR δ 0.878 (3H, t, $J = 6.6$ Hz), 1.23–1.64 (8H, m), 1.70–1.91 (2H, m), 2.17–2.40 (1H, m), 2.574 (1H, dt, $J = 14.9$, 6.2 Hz), 3.612 (1H, qt, $J = 9.0$, 6.9 Hz), 3.998 (1H, tt, $J = 7.8$, 6.0 Hz), 7.19–7.42 (4H, m); ^{13}C NMR δ 14.00, 22.51, 28.57, 31.52, 39.15 (q, $J = 2$ Hz), 38.25, 47.55 (q, $J = 27$ Hz), 53.90, 121–135 (see footnote 3), 133.22 (q, $J = 2$ Hz); ^{19}F NMR δ −69.7 (d, $J = 9$ Hz).

2.11. 4-Bromo-1,1,1-trifluoro-2-(4-methyoxyphenyl)decane (3d)

As described above, bromide **3d** was obtained as a mixture of **3d₁** and **3d₂** (68:32) from bromide **1d** (536 mg, 2.00 mmol), 1-octene (898 mg, 8.00 mmol), CuCl (20 mg, 0.20 mmol), 2,2′-bipyridyl (63 mg, 0.40 mmol), 1,2-dichlorobenzene (8 ml): 229 mg (30%); colorless oil; MS *m/z* 380 (M^+). Anal. Calcd. for $C_{17}H_{24}BrF_3O$: C, 53.55; H, 6.34. Found: C, 53.17; H, 6.21. NMR signals for the diastereomers were assigned by comparison of spectra obtained from partly separated samples: **3d₁** (major component); ^{1}H NMR δ 0.858 (3H, t, $J = 6.9$ Hz) 1.22–1.92 (10H, m), 2.16–2.42 (2H, m), 3.383–3.603 (1H, m), 3.64–3.80 (1H, m), 3.807 (3H, s), 6.907 (2H, d, $J = 8.7$ Hz), 7.229 (2H, d, $J = 8.7$ Hz); ^{13}C NMR δ 14.00, 22.50, 27.28, 27.28, 31.54, 37.84 (q, $J = 2$ Hz), 39.67, 47.92 (q, $J = 27$ Hz), 54.37, 55.21, 114.21, 120–135 (see footnote 3), 159.62; ^{19}F NMR δ −70.3 (d, $J = 9$ Hz): $3d_2$ (minor component); ^{1}H NMR δ 0.874 (3H, t, $J = 7.2$ Hz), 1.23–1.64 (8H, m), 1.70–1.91 (2H, m), 2.17–2.40 (1H, m), 2.574 (1H, dt, $J = 14.9$, 6.2 Hz), 3.64–3.80 (1H, m), 3.802 (3H, s), 3.982 (1H, tt, $J = 7.8$, 6.0 Hz), 6.894 (2H, d, $J = 8.7$ Hz), 7.219 (2H, d, $J = 8.7$ Hz); ^{13}C NMR δ 14.00, 22.53, 27.04, 28.49, 31.57, 39.09 (q, $J = 2$ Hz), 39.67, 47.23 (q, $J = 26$ Hz), 54.02, 55.23, 114.25, 120–135 (see footnote 3), 159.57; ^{19}F NMR δ −70.1 (d, $J = 9$ Hz).

2.12. 4-Bromo-1,1,1-trifluoro-2-(1-naphthyl)decane (3e)

As described above, bromide **3e** was obtained as a mixture of **3e₁** and **3e₂** (64:36) from bromide **1e** (576 mg, 2.00 mmol), 1-octene (898 mg, 8.00 mmol), CuCl (20 mg, 0.20 mmol), 2,2′-bipyridyl (63 mg, 0.40 mmol), 1,2-dichlorobenzene (8 ml): 144 mg (18%); colorless oil; MS *m/z* 400 (M^+). Anal. Calcd. for $C_{20}H_{24}BrF_3O$: C, 59.86; H, 6.03. Found: C, 59.94; H, 5.94. NMR signals for the diastereomers were assigned by comparison of spectra obtained from partly separated samples: **3e₁** (major component); ^{1}H NMR δ 0.838 (3H, t, $J = 6.9$ Hz) 1.10–1.55 (8H, m), 1.60–1.80 (2H, m), 2.46–2.64 (2H, m), 3.514 (1H, tt, $J = 7.8$, 6.6 Hz), 4.838 (1H, dqd, $J = 9.0$, 9.0, 5.7 Hz), 7.46–7.62 (4H, m), 7.83–7.90 (2H, m), 8.236 (1H, d, $J = 8.7$ Hz); ^{13}C NMR δ 13.99, 22.48, 27.22, 28.56, 31.52, 38.72 (q, $J = 2$ Hz), 39.72, 41.66 (q, $J = 27$ Hz), 54.19, 120–135 (see footnote 3); ^{19}F NMR δ −69.8 (d, $J = 9$ Hz): **3e₂** (minor component); ^{1}H NMR δ 0.832 (3H, t, $J = 7.2$ Hz), 1.10–1.55 (8H, m), 1.70–1.91 (2H, m), 2.25–2.50 (1H, m), 2.574 (1H, ddd, $J = 15.0$, 7.5, 5.7 Hz), 4.132 (1H, tt, $J = 7.5$, 6.0 Hz), 4.61–4.76 (1H, m), 7.46–4.62

(4H, m), 7.83–7.90 (2H, m), 8.144 (1H, d, $J = 8.4$ Hz); ^{13}C NMR δ 13.99, 22.48, 27.07, 28.40, 31.43, 38.53, 40.11 (q, $J = 2$ Hz), 40.90 (q, $J = 26$ Hz), 54.62, 55.23, 120–135 (see footnote 3); ^{19}F NMR δ −68.3 (d, $J = 9$ Hz).

2.13. 4-[3-Bromo-1-(trifluoromethyl)nonyl]-1,1′-biphenyl (3f)

As described above, bromide **3f** was obtained as a mixture of **3f$_1$** and **3f$_2$** (68:32) from bromide **1f** (576 mg, 2.00 mmol), 1-octene (898 mg, 8.00 mmol), CuCl (20 mg, 0.20 mmol), 2,2′-bipyridyl (63 mg, 0.40 mmol), 1,2-dichlorobenzene (8 ml): 147 mg (35%); colorless oil; MS *m/z* 426 (M^+). Anal. Calcd. for $C_{22}H_{26}BrF_3$: C, 61.83; H, 6.13. Found: C, 61.51; H, 5.99. NMR signals for the diastereomers were assigned by comparison of spectra obtained from partly separated samples: **3f$_1$** (major component); ^{1}H NMR δ 0.852 (3H, t, $J = 7.2$ Hz), 1.20–1.55 (8H, m), 1.65–1.95 (2H, m), 2.20–2.47 (2H, m), 3.549 (1H, dtd, $J = 10.8$, 5.4, 3.3 Hz), 3.824 (1H, dqd, $J = 9.3$, 9.3, 5.4 Hz), 7.33–7.62 (5H, m); ^{13}C NMR δ 14.00, 22.49, 27.26, 28.60, 31.53, 37.82 (t, $J = 2$ Hz), 36.69, 48.42 (q, $J = 27$ Hz), 54.27, 125–142 (see footnote 3); ^{19}F NMR δ −69.9 (d, $J = 9$ Hz): **3e$_2$** (minor component); ^{1}H NMR δ 0.870 (3H, t, $J = 6.6$ Hz), 1.20–1.55 (8H, m), 1.65–1.95 (2H, m), 2.25–2.50 (1H, m), 2.619 (1H, dt, $J = 15.0$, 6.6 Hz), 3.659 (1H, qt, $J = 9.3$, 7.2 Hz), 4.044 (1H, tt, $J = 7.2$, 6.3 Hz), 7.33–7.62 (5H, m); ^{13}C NMR δ 14.02, 22.53, 27.06, 28.51, 31.53, 38.11, 39.19 (q, $J = 2$ Hz), 47.73 (q, $J = 26$ Hz), 54.08, 125–145 (see footnote 3); ^{19}F NMR δ −69.5 (d, $J = 9$ Hz).

2.14. 1,1,1-Trifluoro-2-phenyldecane (4a)

A mixture of bromide **3a** (351 g, 1.0 mmol) and Ph_3SnH (702 mg, 2.0 mmol) was mixed without solvent, and the resulting mixture was heated at 90 °C for 8 h. The mixture was distilled in a glass tube oven (140 °C, 5 mmHg) to obtain 4a: 270 mg (quantity); colorless oil; ^{1}H NMR δ 0.858 (3H, t, $J = 6.6$ Hz), 1.13–1.27 (12H, m), 1.79–2.04 (2H, m), 3.202 (1H, dqd, $J = 10.8$, 9.6, 4.2 Hz), 7.24–7.39 (5H, m); ^{13}C NMR δ 14.06, 22.64, 26.69, 28.6 (q, $J = 2$ Hz), 29.16, 29.20, 29.21, 31.77, 50.08 (q, $J = 26$ Hz), 127.05 (q, $J = 280$ Hz), 128.00, 128.58, 129.01, 135.03 (q, $J = 2$ Hz); ^{19}F NMR δ −70.3 (d, $J = 9$ Hz); MS *m/z* 272 (M^+). Anal. Calcd. for $C_{16}H_{23}F_3$: C, 70.56; H, 8.51. Found: C, 70.20; H, 8.42.

2.15. 2-(4-Chlorophenyl)-1,1,1-trifluorodecane (4b)

As described above, a mixture of bromide **3b** (246 mg, 0.5 mmol) and Ph_3SnH (351 mg, 1.0 mmol) was mixed without solvent, and the resulting mixture was heated at 90 °C for 5 h. The mixture was distilled in a glass tube oven (140 °C, 5 mmHg) to obtain 4b: 154 mg (quantity); colorless oil; ^{1}H NMR δ 0.860 (3H, t, $J = 6.6$ Hz), 1.09–1.27 (12H, m), 1.74–1.87 (1H, m), 1.92–2.03 (1H, m), 3.188 (2H, dqd, $J = 11.1$, 9.3, 3.9 Hz), 7.207 (2H, d, $J = 8.7$ Hz), 7.328 (1H, d, $J = 8.7$ Hz); ^{13}C NMR δ 14.06, 22.64, 26.69, 28.60 (q, $J = 2$ Hz), 29.16, 29.20, 29.21, 31.77, 50.08 (q, $J = 26$ Hz), 127.05 (q, $J = 280$ Hz), 128.00, 128.58, 129.10, 135.03 (q, $J = 2$ Hz); ^{19}F NMR δ −70.3 (d, $J = 9$ Hz); MS *m/z* 306 (M^+). Anal. Calcd. for $C_{16}H_{22}ClF_3$: C, 62.64; H, 7.23. Found: C, 62.26; H, 6.93.

2.16. 1,1,1-Trifluoro-2-(4-methylphenyl)decane (4c)

As described above, a mixture of bromide **3c** (182 mg, 0.5 mmol) and Ph_3SnH (351 mg, 1.0 mmol) was mixed without solvent, and the resulting mixture was heated at 90 °C for 5 h. The mixture was distilled in a glass tube oven (140 °C, 5 mmHg) to obtain **4c**: 130 mg (91%); colorless oil; ^{1}H NMR δ 0.858 (3H, t, $J = 6.9$ Hz), 1.13–1.27 (12H, m), 1.78–1.87 (1H, m), 1.89–2.02 (1H, m), 2.336 (3H, s), 3.161 (1H, dqd, $J = 11.1$, 9.3, 4.2 Hz), 7.154 (4H, s); ^{13}C NMR δ 14.05, 21.08, 22.63, 26.72, 28.60 (q, $J = 2$ Hz), 29.19, 29.24, 29.24, 31.80, 49.42 (q, $J = 26$ Hz), 127.12 (q, $J = 279$ Hz), 128.87, 129.29, 131.95 (q, $J = 2$ Hz), 137.70; ^{19}F NMR δ −69.6 (d, $J = 9$ Hz); MS *m/z* 322 (M^+). Anal. Calcd. for $C_{17}H_{25}F_3$: C, 71.30; H, 8.80. Found: C, 70.93; H, 8.80.

2.17. 1,1,1-Trifluoro-2-(4-methoxyphenyl)decane (4d)

As described above, a mixture of bromide **3d** (114 mg, 0.3 mmol) and Ph_3SnH (211 mg, 0.6 mmol) was mixed without solvent, and the resulting mixture was heated at 90 °C for 9 h. The mixture was distilled in a glass tube oven (140 °C, 5 mmHg) to obtain 4d: 91 mg (quantity); colorless oil; ^{1}H NMR δ 0.860 (3H, t, $J = 6.8$ Hz), 1.13–1.26 (12H, m), 1.76–1.88 (1H, m), 1.91–2.01 (1H, m), 3.150 (1H, dqd, $J = 11.1$, 9.6, 3.9 Hz), 3.798 (3H, s), 6.881 (2H, d, $J = 9.0$ Hz), 7.190 (3H, d, $J = 9.0$ Hz); ^{13}C NMR δ 14.06, 22.62, 26.68, 28.55 (q, $J = 2$ Hz), 29.17, 29.20, 29.24, 31.78, 49.20 (q, $J = 26$ Hz), 55.16, 113.95, 126.91 (q, $J = 2$ Hz), 127.12 (q, $J = 280$ Hz), 130.02, 159.27; ^{19}F NMR δ −70.7 (d, $J = 9$ Hz); MS *m/z* 302 (M^+). Anal. Calcd. for $C_{17}H_{25}F_3$: C, 67.53; H, 8.33. Found: C, 67.35; H, 8.15.

2.18. 1,1,1-Trifluoro-2-(1-naphthyl)decane (4e)

As described above, a mixture of bromide **3e** (80 mg, 0.2 mmol) and Ph_3SnH (140 mg, 0.4 mmol) was mixed without solvent, and the resulting mixture was heated at 90 °C for 11 h. The mixture was distilled in a glass tube oven (160 °C, 5 mmHg) to obtain **4d**: 0.058 g (90%); colorless oil; ^{1}H NMR δ 0.831 (3H, t, $J = 6.6$ Hz), 1.00–1.30 (12H, m), 1.96–2.08 (1H, m), 2.11–2.25 (1H, m), 4.15–4.34 (1H, m), 7.41–7.66 (4H, m), 7.835 (1H, d, $J = 8.1$ Hz), 7.886 (1H, d, $J = 8.5$ Hz), 8.062 (1H, d, $J = 8.4$ Hz); ^{13}C NMR δ 14.05, 22.58, 26.68, 29.10, 29.15, 29.36, 29.44, 31.71, 42.76

(q, $J = 26$ Hz), 122–135 (see footnote 3), 122.56, 125.32, 125.60, 126.84, 128.50, 129.09, 129.14, 131.24 (q, $J = 2$ Hz), 136.13, 136.19; ^{19}F NMR δ −69.6 (d, $J = 9$ Hz); MS *m/z* 322 (M^+). Anal. Calcd. for $C_{20}H_{25}F_3$: C, 74.51; H, 7.82. Found: C, 74.18; H, 7.48.

2.19. 4-[1-(Trifluoromethyl)nonyl]-1,1'-biphenyl (**4f**)

As described above, a mixture of bromide **3f** (85 mg, 0.2 mmol) and Ph_3SnH (140 mg, 0.4 mmol) was mixed without solvent, and the resulting mixture was heated at 90 °C for 9 h. The mixture was distilled in a glass tube oven (160 °C, 5 mmHg) to obtain **4d**: 70 mg (quantity); colorless oil; ^{1}H NMR δ 0.857 (3H, t, $J = 6.9$ Hz), 1.14–1.35 (12H, m), 1.885 (1H, ddt, $J = 14.1$, 10.8, 7.5 Hz), 2.012 (1H, dtd, $J = 14.1$, 7.8, 4.5 Hz), 3.249 (1H, dqd, $J = 10.8$, 9.6, 4.5 Hz), 7.30–7.61 (9H, m); ^{13}C NMR δ 14.07, 22.62, 26.73, 28.61 (q, $J = 2$ Hz), 29.18, 29.23, 31.78, 49.75 (q, $J = 26$ Hz), 127.05 (q, $J = 280$ Hz), 127.06, 127.28, 127.40, 128.77, 129.12, 129.39, 133.99 (q, $J = 2$ Hz), 136.18; ^{19}F NMR δ −70.2 (d, $J = 9$ Hz); MS *m/z* 348 (M^+). Anal. Calcd. for $C_{22}H_{27}F_3$: C, 75.83; H, 7.81. Found: C, 76.04; H, 7.41.

2.20. (E)-1,1,1-Trifluoro-2,4-diphenyl-3-butene (**8**)

A freshly degassed mixture of bromide **1a** (478 mg, 2 mmol), CuCl (20 mg, 0.2 mmol), 2,2′-bipyridyl (63 mg, 0.4 mmol), and styrene (833 mg, 8 mmol) in 1,2-dichlorobenzene (8 ml) was refluxed under nitrogen for 24 h. After filtration of the mixture, the solvent was removed under reduced pressure. The residue was distilled (200 °C/5 mmHg) and finally olefin **8** was isolated by GPC ($CHCl_3$) as colorless oil: 412 mg (79%); ^{1}H NMR δ 4.129 (1H, qd, $J = 9.0$, 8.4 Hz), 6.447 (1H, dd, $J = 15.9$, 8.4 Hz), 6.582 (1H, d, $J = 15.9$ Hz), 7.15–7.38 (10H, m); ^{13}C NMR δ 53.41 (q, $J = 28$ Hz), 122.61 (q, $J = 2$ Hz), 126.04 (q, $J = 281$ Hz), 126.53, 128.14, 128.22, 128.60, 128.82, 128.98, 134.70 (q, $J = 2$ Hz), 135.48, 136.12; ^{19}F NMR δ −69.4 (d, $J = 9$ Hz); MS *m/z* 262 (M^+). Anal. Calcd. for $C_{16}H_{13}F_3$: C, 73.27; H, 5.00. Found: C, 72.94; H, 4.90.

2.21. 1,1,1-Trifluoro-2,4-diphenyl-4-butanone (**9**)

A freshly degassed mixture of bromide **1a** (478 mg, 2 mmol), CuCl (20 mg, 0.2 mmol), 2,2′-bipyridyl (63 mg, 0.4 mmol), and acetophenone trimethylsilyl enol ether (1.537 g, 8 mmol) in 1,2-dichlorobenzene (8 ml) accompanied with molecular sieves 4A (2 g) was stirred in a sealed tube at 180 °C for 33 h. After filtration of the mixture, the solvent was removed under reduced pressure. Then, the residue was dissolved to a mixture of Et_2O (5 ml), AcOH (5 ml), 12 M HCl (1 ml). The mixture was stirred at room temperature overnight. The mixture was extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4, and the solvents were removed under reduced pressure. Pure ketone **9** was obtained by distillation (150 °C/5 mmHg) followed by GPC ($CHCl_3$) as colorless oil: 521 mg (94%); mp 63–4 °C; ^{1}H NMR δ 3.592 (1H, dd, $J = 18.0$, 4.5 Hz), 3.704 (1H, dd, $J = 18.0$, 9.9 Hz), 4.248 (1H, qdd, $J = 10.0$, 9.9, 4.5 Hz), 7.25–7.47 (7H, m), 7.565 (1H, tt, $J = 7.5$, 1.5 Hz), 7.90–7.94 (2H, m); ^{13}C NMR δ 38.25 (q, $J = 2$ Hz), 44.76 (q, $J = 27$ Hz), 126.94 (q, $J = 279$ Hz), 128.01, 128.27, 128.67, 128.70, 129.01, 131.53, 134.56 (q, $J = 2$ Hz), 136.26, 195.25; ^{19}F NMR δ −70.21 (d, $J = 11$ Hz); MS *m/z* 278 (M^+). Anal. Calcd. for $C_{16}H_{13}F_3O$: C, 69.06; H, 4.71. Found: C, 68.93; H, 4.64.

2.22. 1,1,1-Trifluoro-2-phenyl-4-nonanone (**10**)

As described as above a mixture of bromide **2a** (478 mg, 2 mmol), CuCl (20 mg, 0.2 mmol), 2,2′-bipyridyl (63 mg, 0.4 mmol), and 2-heptanone trimethylsilyl enol ether (1.489 g, 8 mmol) in 1,2-dichlorobenzene (8 ml) accompanied with molecular sieves 4A (2 g) ketone **10** as colorless oil: 257 mg (48%); ^{1}H NMR δ 0.835 (3H, t, $J = 7.5$ Hz), 1.04–1.25 (4H, m), 1.483 (2H, tt, $J = 7.8$, 7.5 Hz), 2.277 (1H, dt, $J = 16.5$, 7.2 Hz), 2.392 (1H, dt, $J = 16.5$, 7.5 Hz), 3.039 (2H, d, $J = 6.9$ Hz), 4.031 (1H, qt, $J = 9.5$, 6.9 Hz), 7.28–7.39 (5H, m); ^{13}C NMR δ 13.76, 22.29, 23.14, 31.08, 42.03 (q, $J = 2$ Hz), 43.30, 44.59 (q, $J = 28$ Hz), 126.74 (q, $J = 279$ Hz), 128.26, 128.63, 128.91, 134.47 (q, $J = 2$ Hz), 206.26; ^{19}F NMR δ −70.5 (d, $J = 9$ Hz); MS *m/z* 272 (M^+). Anal. Calcd. for $C_{15}H_{19}F_3O$: C, 66.16H, 7.03. Found: C, 65.88; H, 6.92.

3. Results and discussion

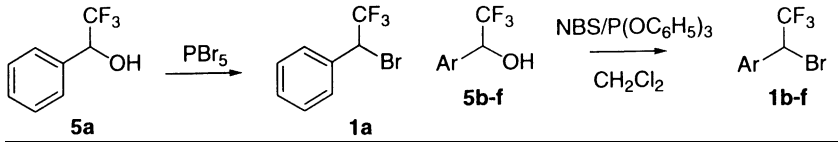
3.1. Preparation of aryltrifluoroethylbromides (**1**)

While bromotrifluorophenylethane **1a** is a known compound, the bromination of the corresponding alcohol **5a** with PBr_5 [6] was sluggish and, in some cases, unexpected reduction of bromide was observed. We modified the procedure for bromination of the starting materials **5b–f** to obtain bromides **1b–f** (Table 1). The reaction of alcohols **5b–f** with triphenyl phosphite and NBS in CH_2Cl_2 [7] at room temperature or under refluxing gave the bromides **1b–f** in moderate yields.

3.2. Cu(I) catalyzed radical reaction of aryltrifluoroethyl bromides

Radical reaction of bromide **1a** with an excess amount of 1-octene was examined in various reaction conditions (Table 2). The reaction conditions previously used by Burton and Kehoe [8], i.e. CuCl with ethanolamine as an additive in *t*-BuOH, resulted in low yield (29%) of the atom-transfer product **3a**. Use of DMF as solvent gave a complex mixture of olefins **6**. While employing Itoh's catalyst system (CuCl/2,2′-bipyridyl) [5] was not so successful for the reaction of

Table 1
Preparation of substituted aryltrifluoroethyl bromides **1**



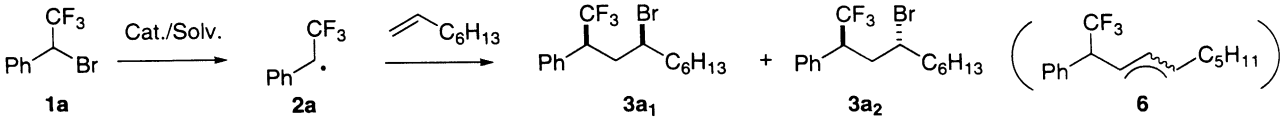
5a **1a** **5b-f** **1b-f**

Entry	Ar	Product	Yield (%)
1	4-Cl–C_6H_4Cl–	**1b**	52
2	4-CH_3Cl–C_6H_4Cl–	**1c**	33
3	4-CH_3OCl–C_6H_4Cl–	**1d**	54
4	1-naphthyl–	**1e**	64
5	4-C_6H_5Cl–C_6H_4Cl–	**1f**	60

1a at room temperature, higher reaction temperatures (24 h refluxing in 1,2-dichlorobenzene; 180 °C) improved the yield of the products **3a$_{1,2}$** up to 74% along with contamination of a small amount of chlorinated products. The mixture of **3a** was also obtained by using tetraethylenediamine (TMEDA) as an additive in somewhat lower yield although it was reported that TMEDA was superior to 2,2′-bipyridyl for the addition of CCl_4 to styrene [9]. Other copper catalysts were also used. To avoid formation of a small amount of halogen-mixed products (chlorinated products), CuBr is better, whereas the yield (63%) was lower than the reaction with CuCl. Based on the reaction mechanism that involves the initial electron transfer from Cu(I) catalyst to bromide **1**, the presence of Cu(I) is required. Interestingly, $CuCl_2$ [10] was also effective presumably because a Cu(I) species was generated by the reduction of Cu(II) in situ. CuI was not a superior catalyst. Since bromide **3a** was converted into the corresponding iodide in low yield at 180 °C on treatment with CuI in a blank experiment, CuI exchange halogen with bromides **1a** and/or **3a** to give the corresponding unstable iodides, which decompose to unidentified byproducts at high reaction temperature (180 °C). In the low-boiling temperature solvents such as 1,2-dichloroethane (bp 83 °C), the reaction of **1a** was sluggish (34% yield; 7 days) although the product ratio (**3a$_1$**:**3a$_2$**) was improved up to 84:16. This suggests that the radical addition reaction occurs selectively at low temperature. However, at the higher temperatures, the products equilibrated to afford the (60–70):(40–30) mixture of **3a$_1$** and **3a$_2$**. Actually, when a 73:27 diastereomer mixture of **3a** was heated in refluxing 1,2-dichlorobenzene for 26 h in the presence of CuCl (0.1 equivalents) and 2,2′-bipyridyl (0.2 equivalents), it was converted into a 66:34 diastereomer mixture.

The related aryltrifluoroethyl bromides **1b–f** were also reacted with 1-octene in the presence of CuCl (0.1 equivalents) and 2,2′-bipyridyl (0.2 equivalents) in refluxing 1,2-dichlorobenzene as shown in Table 3. Electron-withdrawing 4-chlorophenyl derivative **1b** is a superior electron acceptor and gave the product **3b** in 81% yield in a shorter reaction time (4 h). *p*-Tolyl derivative **1c** reacted with 1-octene in a comparable yield to that of the reaction of **1a**, whereas electron-

Table 2
Cu(I)-catalyzed radical reaction of **1a** with 1-octene

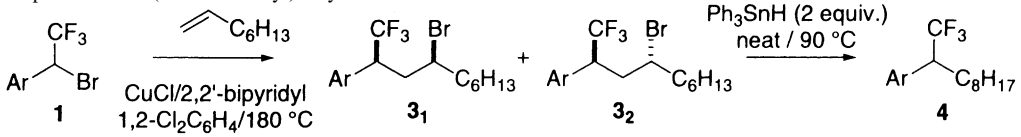


1a **2a** **3a$_1$** **3a$_2$** **6**

Entry	Substrate ratio (**1a**:1-octene)	Products	Catalysts (mol%)	Solvent	Temperature (°C)	Reaction time	Yield (%)	Product ratio (**3a$_1$**:**3a$_2$**)
1	1:2	**3a$_1$** + **3a$_2$**	CuCl (3); $H_2NCH_2CH_2OH$ (50)	*t*-BuOH	120[a]	3 days	29	67:33
2	1:2	**6**	CuCl (3); $H_2NCH_2CH_2OH$ (50)	DMF	160[a]	3 days	41	–
3	1:4	**3a$_1$** + **3a$_2$**	CuCl (10); 2,2′-bipyridyl (20)	1,2-$Cl_2C_6H_4$	180[b]	24 h	74	64:36
4	1:4	**3a$_1$** + **3a$_2$**	CuCl (10); TMEDA (20)	1,2-$Cl_2C_6H_4$	180[b]	24 h	47	67:33
5	1:4	**3a$_1$** + **3a$_2$**	CuBr (10); 2,2′-bipyridyl (20)	1,2-$Cl_2C_6H_4$	180[b]	24 h	62	64:36
6	1:4	**3a$_1$** + **3a$_2$**	$CuCl_2$ (10); 2,2′-bipyridyl (20)	1,2-$Cl_2C_6H_4$	180[b]	24 h	63	66:34
7	1:4	**3a$_1$** + **3a$_2$**	CuCl (10); 2,2′-bipyridyl (20)	1,2-$Cl_2C_6H_4$	180[b]	24 h	53	63:37
8	1:4	**3a$_1$** + **3a$_2$**	CuCl (10); 2,2′-bipyridyl (20)	$ClCH_2CH_2Cl$	83[b]	7 days	34	84:16

[a] Reaction was conducted in a sealed tube.
[b] Reaction was carried out under refluxing condition.

Table 3
Preparation of 1-(trifluoromethyl)nonylarenes 4

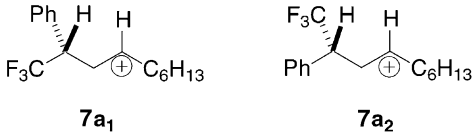


Entry	Ar	1	Products (yield (%))	Product ratio ($3a_1$:$3a_2$)	4	Yield (%)
1	C_6H_5–	**1a**	$3a_1 + 3a_2$ (74)	64:36	**4a**	Quantity
2	4-Cl–C_6H_4–	**1b**	$3b_1 + 3b_2$ (81)	60:40	**4b**	Quantity
3	4-CH_3–C_6H_4–	**1c**	$3c_1 + 3c_2$ (68)	58:42	**4c**	91
4	4-CH_3O–C_6H_4–	**1d**	$3d_1 + 3d_2$ (30)	68:32	**4d**	Quantity
5	1-naphthyl–	**1e**	$3e_1 + 3e_2$ (18)	64:36	**4e**	90
6	4-C_6H_4–C_6H_4–	**1f**	$3f_1 + 3f_2$ (35)	68:32	**4f**	Quantity

rich *p*-anisyl (**1d**), α-naphthyl (**1e**), and 4-diphenyl (**1f**) derivatives were less reactive substrates. The brominated products **3a–f** were reduced by heating at 90 °C with a twofold amount of Ph_3SnH to the corresponding trifluoroarylnonanes **4a–f** in high yields as shown in Table 3.

3.3. Stereochemistry determination of adducts *3a–f* with NOESY spectra

The ^1H NMR spectra of all products **3a–f** show characteristic coupling pattern in the region between δ 2.0 and δ 4.3 assignable to H1–H4 to identify the two diastereomers. The NOESY spectrum of the minor isomer $\mathbf{3a_2}$ showed cross peaks between H1 (δ 3.60) and H4 (δ 4.00) while no cross peak was found in that of the major isomer $\mathbf{3a_1}$. MM2 molecular mechanics calculation [11] [3] was performed for each two possible conformers (Fig. 1). Conformer $\mathbf{3a_{1}}_{syn}$ [4] was 4.4 kcal/mol more stable than $\mathbf{3a_{1}}_{anti}$ due to unfavorable CF_3–Br alignment. However, energy difference of $\mathbf{3a_{2}}_{syn}$ and $\mathbf{3a_{2}}_{anti}$ was small (0.3 kcal/mol). Accordingly, the plausible stable conformation of the major isomer is $\mathbf{3a_{1}}_{syn}$ in which NOE between H1 and H4 is not expected. On the other hand, that between H1 and H4 in the minor isomer $\mathbf{3a_{2}}_{syn}$ is expected. The major isomer $\mathbf{3a_{1}}_{syn}$ is slightly more stable (1.5 kcal/mol) than the minor one $\mathbf{3a_{2}}_{syn}$, and the product ratios reflect this energy difference. Since equilibration of **3a** is slow at lower temperatures, the stereoselectivity is much better, e.g. 84:16 for the adduct obtained at 83 °C (Table 2, entry 8), than estimated one based on the relative thermodynamic stabilities. This kinetic preference to give $\mathbf{3a_1}$ is explained by considering the conformation of carbocation intermediate **7a** which would be given by oxidation of the formed radical intermediate **2a** with Cu(II)BrX (X = Cl or Br). Approach of Br^- from an open face (β-face in Scheme 2) to favorable cation conformer $\mathbf{7a_1}$ leads to the major product $\mathbf{3a_1}$. On the other hand, approach of Br^- from the open face (β-face in Scheme 2) of unfavorable $\mathbf{7a_2}$, which is 0.8 kcal/mol less stable than $\mathbf{7a_1}$ at the level of semi-empirical MNDO/PM3 calculation [12],[5] leads to the minor $\mathbf{3a_2}$.



Scheme 2.

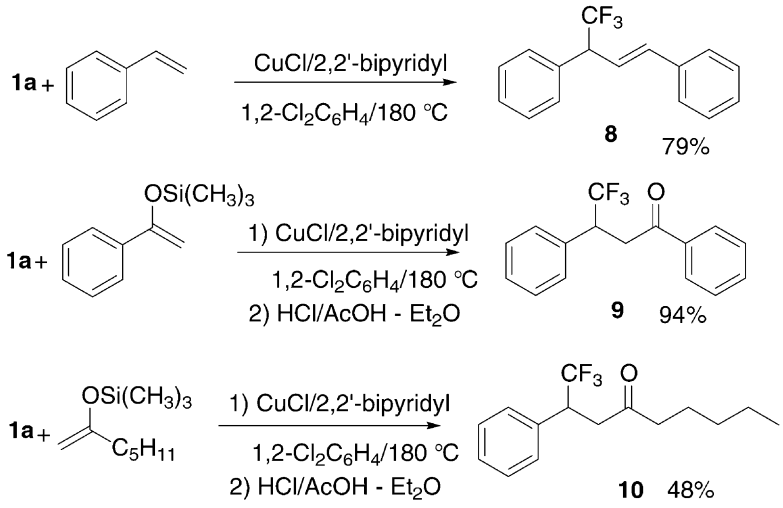
3.4. Radical reactions of bromide *1a* with other olefins

The radical reactions of bromide **1a** with several electron-rich olefins (4 M amount) in the presence of CuCl (0.1 equivalents) and 2,2′-dipyridyl (0.2 equivalents) in refluxing 1,2-dichlorobenzene were attempted and the results were shown in Scheme 3. The reaction with styrene gave no brominated products, but the obtained product was trifluorodiphenylbutene 8 in 79% yield. This shows that a stable diphenylallyl cation formed by the oxidation of the radical intermediate with Cu(II) species after addition of electron-deficient alkyl radical to styrene. As we previously reported [13], silyl enol ethers are good acceptors for the electron-deficient polyhalogenated alkyl radicals. Both aryl and alkyl silyl enol ethers reacted with bromide **1a** in the presence of CuCl. Since some unidentified trimethylsilyl species remained in the reaction mixture, the reaction mixture was treated with hydrochloric acid to give the desired ketones 9 and 10, respectively. However, because of the labile nature of ketone silyl acetal at high temperature, the formation of a small amount of ester was only confirmed by GC–MS analysis. Instead, the major product was a mixture of trifluoro-α-phenethyl radical dimers.

[3] MM2 calculations were performed using a software package Cache® Release 3.7 (Cache Scientific, Inc.).

[4] The suffixes *syn*/*anti* indicate stereochemistry between phenyl and 1-bromohexyl groups.

[5] Semi-empirical MNDO/PM3 calculation was performed using a software package Cache® Release 3.7 (Cache Scientific, Inc.).



Scheme 3.

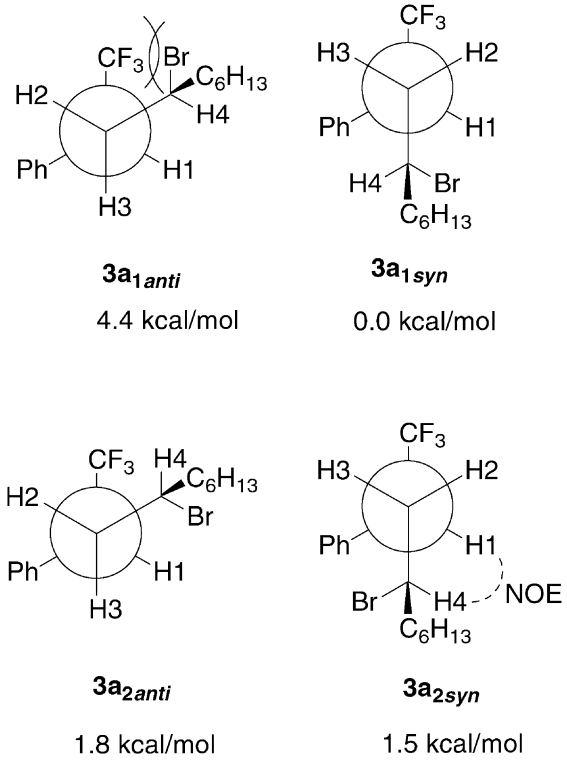


Fig. 1. Possible conformers of $\mathbf{3a_{1,2}}$ and the MM2 relative energies.

4. Conclusion

We have demonstrated that only a trifluoromethyl group is required for activation of a bromide to generate a trifluoromethylated benzyl radical in the presence of amine-coordinated CuCl catalyst. Terminal olefins as well as silyl enol ethers trapped the generated radical. Reduction of the brominated products with Ph_3SnH gave a class of compounds with an isolated trifluoromethyl group on a long straight alkyl chain, which may be important substructure for the ferroelectric liquid crystals.

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