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Facile synthesis of (*E*)-β-(trifluoromethyl)styrenes from halothane (HCFC-123B1)

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ABSTRACT

A practical and convenient synthesis of (*E*)-β-(trifluoromethyl)styrenes has been achieved by the reaction of commercially available halothane (HCFC-123B1) and hydrazones prepared in advance *in situ*, in the presence of 1,2-ethylenediamine and a catalytic amount of $CuCl_2{\cdot}2H_2O$ at room temperature. The products showed acceptable to high yields and high to excellent stereoselectivity. This handy synthetic method provided easy access to a variety of (*E*)-β-(trifluoromethyl)styrenes.

1. Introduction

Considering the richness of the trifluromethylaryl moiety in biologically active molecules and functional materials, the selective introduction of trifluoromethyl (CF_3) substituents at specific positions of aromatic rings is an important synthetic transformation [1]. Thus, various methods for incorporating CF_3 into aromatic rings have recently been developed by many groups [2–6]. On the other hand, the corresponding selective introduction of trifluoromethyl (CF_3) substituents at specific positions in olefins has received relatively less attention so far. However, the approach toward such transformation also has gradually evolved over the last several years.

One of the traditional methods for the preparation of trifluoromethylated alkenes employs the Wittig- and/or Julia–Kocienski reaction involving carbonyl compounds (Scheme 1, Type I) [7–11]. However, this type of reaction has mainly two disadvantages: (i) low stereoselectivity and (ii) narrow scope of substrates (aromatic aldehydes are employed, in general). Another method involves the transition-metal-mediated coupling reaction (Type II) [12–28]. Taking the incessant emergence of well-elaborated procedures into account, it appears that the syntheses of trifluoromethylated alkenes have incorporated this methodology. As much as this type of reaction adequately addresses the issue of stereoselectivity, the use of relatively expensive reagents remains a major drawback. Besides the aforementioned methodologies, there also exists a different catalytic olefination reaction developed mainly by Nenajdenko et al. (type III) [29–32]. Specifically, his group has already reported the efficient synthesis of β-halo-β-(trifluoromethyl)styrenes [29]. Their method involves the initial formation of hydrazones of carbonyl compounds followed by the treatment with polyhalogenalkanes in the presence of a base and catalytic amount of copper salt. However, the development of the relevant β-(trifluoromethyl)styrenes remains unexplored. Therefore, we considered the use of halothane (HCFC-123B1) instead of the polyhalogenalkanes, employed by Nenajdenko et al., to afford the corresponding β-(trifluoromethyl)styrenes under similar reaction conditions [33]. We report herein the practical synthesis of β-(trifluoromethyl)styrenes using halothane as a trifluoroethylidene ($CF_3CH{=}$) source.

2. Results and discussion

4-Chloro-benzaldehyde (**1a**) was reacted with an excess amount of hydrazine hydrate (3.0 equiv.). The reaction readily proceeded to afford the corresponding hydrazone in quantitative yield for 10 min at room temperature and monitored using TLC. Then, 1,2-ethylenediamine (2.4 equiv.), halothane (2.0 equiv.), and

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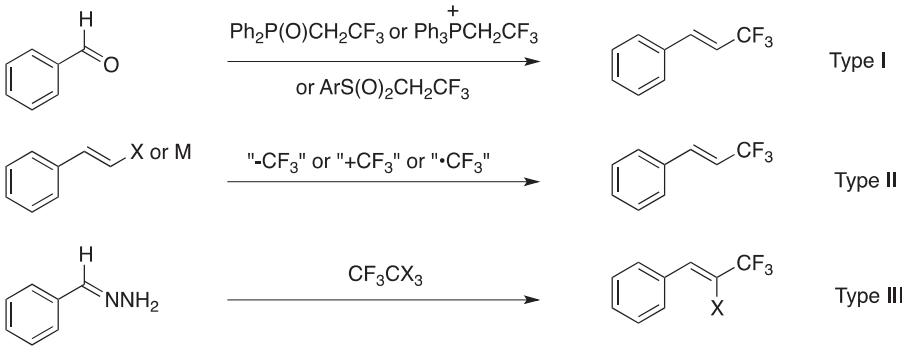
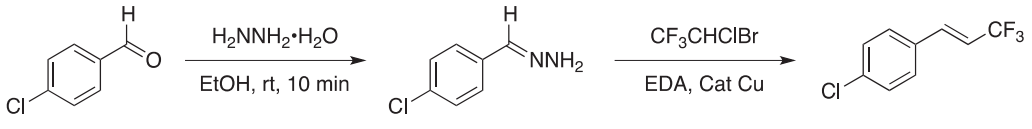


Scheme 1. Previous synthesis of β-(trifluoromethyl)styrenes.

a catalytic amount of CuCl (20 mol%) were successively added to the reaction mixture. After the reaction mixture was stirred for 3 h at room temperature, a small amount of the target olefin molecules was observed along with the corresponding azine using GC–MS. However, the conversion of the hydrazone was only 30% while the unreacted hydrazone remained intact (entry 1). In order to improve the percent conversion, we continued to explore different reaction conditions. We observed that the input of a large amount of hydrazine hydrate (5.0 equiv.) yielded a significant enhancement in the conversion (entry 2). The use of a combination catalyst system containing CuCl and a ligand (PPh_3 or 1,10-phenanthroline) led to either a similar or reduced conversion (entries 3 and 4). Reducing the catalyst loading to 5 mol% did not essentially affect the conversion (entries 5 to 7). However, increasing the amount of 1,2-ethylenediamine improved the conversion (entry 9). By comparison, $CuCl_2{\cdot}2H_2O$ was no less effective than CuCl (entry 10). Taking easy handling of the catalyst into account, we hereafter adopted the use of $CuCl_2{\cdot}2H_2O$ instead of CuCl. It is noteworthy that the choice of solvent significantly influenced the conversion, with ethylene glycol proving to be the optimal reaction solvent. The use of ethylene glycol resulted in the complete conversion of the hydrazone substrate and adequate reduction in the quantities of byproducts. We opine that the hydrogen bonding between the solvent and chlorine presumably facilitated the β-elimination reaction in the cupper-chlorine intermediate [34]. Thus, we carried out the reaction under the above reaction conditions to obtain the desired product in 79% yield with a ratio of *E*/*Z* = 94/6 (entry 11). Compared with the complete conversion, the isolated yield was not as high as our expectation. We confirmed that the reaction itself proceeded neatly. One of the reasons for the reduced isolated yield was the difficulty in isolation owing to the volatility of the product (Table 1).

With an optimized procedure in hand, we examined the olefination of halothane using other aldehydes. For various benzaldehydes, acceptable to high yields (45–95%) and high to excellent (*E*)-stereoselectivity (93/7–98/2) were accomplished for the synthesis of styrene derivatives, regardless of the electronic nature of the substituents and substitution patterns on the benzene ring. It is noteworthy that the free hydroxyl group on the benzene ring did not necessarily retard the reaction albeit it led to acceptable yields (entries 3, 7 and 8). In fact, in these cases the reaction did not proceed as cleanly as other substrates. For both α- and β-naphthaldehyde, high yields and excellent (*E*)-stereoselectivity were also achieved (entries 11 and 12). On the other hand, attempts to employ undecanal as an aliphatic aldehyde and cinnamaldehyde as an α,β-unsaturated aldehyde under the same conditions yielded the complex reaction mixtures (entries 13 and 14). In addition, benzophenone as a ketone was also not suitable

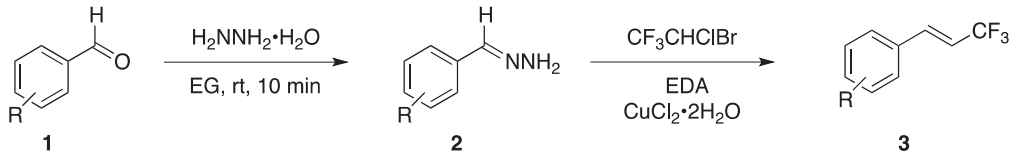
Table 1
Optimization of reaction conditions[a].

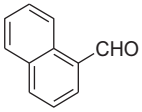
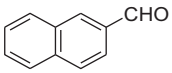


Entry	$CF_3CHClBr$ (equiv.)	$H_2NNH_2{\cdot}H_2O$ (equiv.)	EDA[b] (equiv.)	Cat. Cu (mol%)	Temp. (°C)	Time (h)	**2**-Conv.[c] (%)
1	2	3	2.4	CuCl (20)	r.t.	3	30
2	2	5	2.4	CuCl (20)	r.t.	3	60
3	2	5	2.4	CuCl (20), PPh_3 (20)	r.t.	3	63
4	2	5	2.4	CuCl (20), Phen[d] (20)	r.t.	3	40
5	6	5	2.4	CuCl (20)	0-r.t.	3	76
6	6	5	2.4	CuCl (10)	0-r.t.	3	73
7	6	5	2.4	CuCl (5)	0-r.t.	3	79
8	6	5	2.4	CuCl (5)	0	5	72
9	6	5	4.4	CuCl (5)	0-r.t.	3	87
10	6	5	4.4	$CuCl_2{\cdot}2H_2O$ (5)	0-r.t.	3	84
11[e]	6	5	4.4	$CuCl_2{\cdot}2H_2O$ (5)	0-r.t.	1	100 (79)[f,g]

[a] **1a** (1.0 equiv.) and hydrazine-monohydride were used.
[b] 1,2-Ethylenediamine.
[c] Determined using GC–MS.
[d] 1,10-Phenanthroline.
[e] Ethylene glycol was used instead of ethanol as a solvent.
[f] Isolated yield.
[g] *E*/*Z* = 94/6 as a diastereomer ratio determined using ^{19}F NMR.

Table 2
Scope of substrates for the reaction involving various aldehydes[a].



Entry	Aldehyde	3	Yield (%)[b]	E/Z[c]
1	4-Cl	**3a**	79	94/6
2	4-OMe	**3b**	46	93/7
3	4-OH	**3c**	54	93/7
4	4-NO_2	**3d**	95	98/2
5	4-CN	**3e**	67	97/3
6	4-Ph	**3f**	95	98/2
7	3-OH	**3g**	58	95/5
8	2-OH	**3h**	45	98/2
9	3,4-OMe	**3i**	54	97/3
10	3,5-Me	**3j**	74	98/2
11		**3k**	80	98/2
12		**3l**	72	99/1
13	Undecanal	**3m**	CM[d]	–
14	Cinnamaldehyde	**3n**	CM[d]	–
15	Benzophenone	**3o**	0[e,f]	–

[a] Reaction was carried out using **1** (1.0 equiv.), $H_2NNH_2{\cdot}H_2O$ (5.0 equiv.), $CF_3CHClBr$ (6.0 equiv.), EDA (1,2-ethylenediamine, 4.4 equiv.), and $CuCl_2{\cdot}2H_2O$ (5 mol%) in ethyleneglycol (EG).
[b] Isolated yield.
[c] Determined using ^{19}F NMR or GC–MS.
[d] Complex mixture.
[e] Corresponding hydrazone (**2o**) was prepared at 100 °C.
[f] No reaction.

for this reaction, thereby leading to the recovering of the corresponding hydrazone in quantitative yield (entry 15). Although the reaction mechanism of this reaction was not fully elucidated, we presumed that it should be similar to that prescribed by Nenajdenko et al., involving the corresponding Cu–carbene intermediate [31] (Table 1).

3. Conclusion

We developed a convenient synthetic route for obtaining (*E*)-β-(trifluoromethyl)styrene derivatives in acceptable to high yields with high to excellent stereoselectivity. The substrates required for this reaction were easily available and inexpensive; moreover, the procedure involved was simple and convenient. Although several attractive preparations of (*E*)-β-(trifluoromethyl)styrene derivatives have already been reported so far, we believe that our method will fulfill the need of the research community, and serve as a convenient synthetic tool.

4. Experimental

Infrared (IR) spectra are reported in cm^{-1}. ^1H, ^{19}F and ^{13}C NMR spectra were measured in $CDCl_3$ solutions. Chemical shifts were given by δ relative to that of an internal Me_4Si (TMS) for ^1H NMR and ^{13}C NMR spectra and hexafluorobenzene (C_6F_6) for ^{19}F NMR spectra.

4.1. (E)-1-(4-chlorophenyl)-3,3,3-trifluoropropene (*3a*) [14]

A 25 mL two-neck flask equipped with a magnetic stir bar, a stopcock and a three-way stopcock, was charged with 3.0 mL of ethylene glycol, $H_2NNH_2{\cdot}H_2O$ (73.0 μL, 1.50 mmol, 5.0 equiv.), 4-chlorobenzardehyde **1a** (42.0 mg, 0.299 mmol, 1.0 equiv.) and stirred at room temperature for 10 min until the complete consumption of **1a** (checked by TLC and GC–MS) and generation of the corresponding hydrazone. To this mixture was added $CF_3CHClBr$ (190.0 μL, 1.80 mmol, 6.0 equiv.), 1,2-ethylenediamine (88.0 μL, 1.32 mmol, 4.4 equiv.). The flask was then immersed in an ice bath. To this mixture was added $CuCl_2{\cdot}2H_2O$ (2.6 mg, 0.017 mmol, 0.05 equiv.) and the resulting mixture was stirred for 1 h at room temperature. To the mixture was added distilled water (5 mL), and the resulting mixture was extracted with Et_2O (5 mL) three times. The combined solution was dried over sodium sulphate, concentrated *in vacuo* then the residual oil was purified by chromatography on silica gel column [hexane as an eluent] to give **3a** as colorless oil (48.9 mg).

Colorless oil: Yield 79% (48.9 mg, *E*/*Z* = 94/6); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.50–7.30 (m, 4*H*), 7.09 (d, *J* = 16.0 Hz, 1*H*), 6.17 (dq, *J* = 16.0, 6.7 Hz, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 136.4 (q, *J* = 6.2 Hz), 136.0, 131.9, 129.1, 128.7, 123.5 (q, *J* = 268.6 Hz), 116.4 (q, *J* = 34.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.6 (d, *J* = 6.7 Hz); GC–MS (EI, *m*/*z*, 70 eV) 206 (100, $M^+[^{35}Cl]$), 208 (33, $M^+[^{37}Cl]$), 171 (25), 151 (48), 137 (12), 101 (16), 75 (16), 51 (8).

*4.2. (E)-1-(4-methoxyphenyl)-3,3,3-trifluoropropene (**3b**) [14]*

White solid; Yield 46% (38.1 mg, *E*/*Z* = 93/7); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (d, *J* = 8.8 Hz, 2*H*), 7.09 (d, *J* = 16.2 Hz, 1*H*), 6.91 (d, *J* = 8.8 Hz, 2*H*), 6.06 (dq, *J* = 16.2, 6.6 Hz, 1*H*), 3.84 (s, 3*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 161.0, 137.1 (q, *J* = 6.3 Hz), 129.0, 126.1, 123.9 (q, *J* = 268.9 Hz), 114.3, 113.4 (q, *J* = 33.8 Hz), 55.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.1 (d, *J* = 6.6 Hz); GC–MS (EI, *m*/*z*, 70 eV) 202 (100), 187 (17), 183 (10), 159 (5), 151 (7), 139 (13), 119 (8), 109 (34), 89 (5), 63 (6).

*4.3. (E)-1-(4-hydroxyphenyl)-3,3,3-trifluoropropene (**3c**) [18]*

Pale yellow oil: yield 54% (50.0 mg, *E*/*Z* = 93/7); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (d, *J* = 8.3 Hz, 2*H*), 7.07 (d, *J* = 16.1 Hz, 1*H*), 6.84 (d, *J* = 8.3 Hz, 2*H*), 6.05 (dq, *J* = 16.1, 6.4 Hz, 1*H*), 4.49 (bs, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 157.0, 137.0 (q, *J* = 7.0 Hz), 129.3, 126.4, 123.9 (q, *J* = 268.9 Hz), 115.8, 113.6 (q, *J* = 34.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.2 (d, *J* = 6.4 Hz); GC–MS (EI, *m*/*z*, 70 eV) 188 (100, M^+), 169 (15), 138 (21), 119 (25), 91 (11), 63 (8).

*4.4. (E)-1-(4-nitrophenyl)-3,3,3-trifluoropropene (**3d**) [13]*

White solid: yield 95% (123.6 mg, *E*/*Z* = 98/2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, *J* = 8.4 Hz, 2*H*), 7.64 (d, *J* = 8.4 Hz, 2*H*), 7.23 (d, *J* = 16.3 Hz, 1*H*), 6.37 (dq, *J* = 16.3, 6.5 Hz, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 148.5, 139.5, 135.4 (q, *J* = 6.9 Hz), 128.3, 124.2, 122.8 (q, *J* = 269.8 Hz), 120.1 (q, *J* = 34.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −65.3 (d, *J* = 6.5 Hz); GC–MS (EI, *m*/*z*, 70 eV) 217 (60, M^+), 187 (22), 151 (100), 109 (22), 102 (16), 75 (10), 51 (8).

*4.5. (E)-1-(4-cyanophenyl)-3,3,3-trifluoropropene (**3e**) [15]*

White solid: yield 67% (40.7 mg, *E*/*Z* = 97/3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, *J* = 8.2 Hz, 2*H*), 7.56 (d, *J* = 8.2 Hz, 2*H*), 7.13 (dm, *J* = 16.3 Hz, 1*H*), 6.32 (dq, *J* = 16.3, 6.5 Hz, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 137.6, 135.9 (q, *J* = 6.3 Hz), 132.7, 128.0, 122.9 (q, *J* = 268.9 Hz), 119.4 (q, *J* = 34.4 Hz), 118.2, 113.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.1 (d, *J* = 6.5 Hz); GC–MS (EI, *m*/*z*, 70 eV) 197 (100, M^+), 176 (20), 147 (30), 128 (17), 101 (10), 75 (12), 51 (7).

*4.6. (E)-1-(4-biphenyl)-3,3,3-trifluoropropene (**3f**) [14]*

Pale yellow solid: yield 95% (64.7 mg, *E*/*Z* = 98/2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (t, *J* = 7.9 Hz, 4*H*), 7.54 (d, *J* = 7.9 Hz, 2*H*), 7.46 (t, *J* = 7.9 Hz, 2*H*), 7.39 (d, *J* = 7.9 Hz, 1*H*), 7.19 (d, *J* = 16.0 Hz, 1*H*), 6.24 (dq, *J* = 16.0, 6.4 Hz, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 142.8, 140.1, 137.2 (q, *J* = 6.9 Hz), 132.3, 128.9, 128.0, 127.8, 127.5, 127.0, 123.7 (q, *J* = 268.9 Hz), 115.7 (q, *J* = 33.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.5 (d, *J* = 6.4 Hz); GC–MS (EI, *m*/*z*, 70 eV) 248 (100, M^+), 227 (6), 178 (21), 152 (8), 99 (3), 76 (4), 51 (2).

*4.7. (E)-1-(3-hydroxyphenyl)-3,3,3-trifluoropropene (**3g**) [18]*

Pale yellow solid: yield 58% (44.7 mg, *E*/*Z* = 95/5); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.35 (m, 1*H*), 7.09 (d, *J* = 16.2 Hz, 1*H*), 7.03 (d, *J* = 7.7 Hz, 1*H*), 6.92 (s, 1*H*), 6.85 (d, *J* = 7.8 Hz, 1*H*), 6.17 (dq, *J* = 16.2, 6.5 Hz, 1*H*), 4.88 (s, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 155.6, 137.2 (q, *J* = 6.8 Hz), 135.1, 130.2, 123.5 (q, *J* = 268.9 Hz), 120.5, 117.1, 116.3 (q, *J* = 34.3 Hz), 114.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.7 (d, *J* = 6.5 Hz); GC–MS (EI, *m*/*z*, 70 eV) 188 (100, M^+), 167 (11), 149 (12), 140 (12), 119 (14), 109 (10), 91 (13), 63 (7).

*4.8. (E)-1-(2-hydroxyphenyl)-3,3,3-trifluoropropene (**3 h**) [16]*

Pale yellow oil: yield 45% (31.7 mg, *E*/*Z* = 98/2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.30 (m, 2*H*), 7.24 (d, *J* = 7.5 Hz, 1*H*), 6.96 (t, *J* = 7.5 Hz, 1*H*), 6.78 (d, *J* = 7.5 Hz, 1*H*), 6.38 (q, *J* = 15.9, 6.3 Hz, 1*H*), 5.09 (bs, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 154.1, 132.8 (q, *J* = 6.9 Hz), 131.0, 129.0, 123.9 (q, *J* = 268.9 Hz), 121.2, 120.8, 116.8 (q, *J* = 33.8 Hz), 116.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.6 (d, *J* = 4.1 Hz); GC–MS (EI, *m*/*z*, 70 eV) 188 (71, M^+), 167 (39), 149 (100), 118 (55), 91 (24), 63 (13), 51 (10).

*4.9. (E)-1-(3,4-dimethoxyphenyl)-3,3,3-trifluoropropene (**3i**) [16]*

Colorless oil: yield 54% (37.7 mg, *E*/*Z* = 97/3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.08 (d, *J* = 16.0 Hz, 1*H*), 7.02 (d, *J* = 7.8 Hz, 1*H*), 6.96 (s, 1*H*), 6.86 (d, *J* = 7.8 Hz, 1*H*), 6.07 (dq, *J* = 16.0, 6.5 Hz, 1*H*), 3.91 (s, 6*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 150.6, 149.0, 137.2 (q, *J* = 6.9 Hz), 126.0, 123.7 (q, *J* = 268.3 Hz), 121.4, 113.1 (q, *J* = 33.8 Hz), 110.8, 109.1, 55.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.1 (d, *J* = 6.5 Hz); GC–MS (EI, *m*/*z*, 70 eV) 232 (100, M^+), 217 (24), 189 (11), 169 (6), 149 (12), 125 (14), 91 (7), 51 (4).

*4.10. (E)-1-(3,5-dimethyphenyl)-3,3,3-trifluoropropene (**3j**)*

Colorless oil: yield 74% (55.2 mg, *E*/*Z* = 98/2); IR (ATR) 1666, 1603, 1331, 1269, 1257, 1108, 969, 822, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30–7.00 (m, 4*H*), 6.17 (dq, *J* = 16.0, 6.7 Hz, 1*H*), 2.33 (s, 6*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 138.5, 137.9 (q, *J* = 6.2 Hz), 133.3, 131.7, 125.4, 123.7 (q, *J* = 268.6 Hz), 115.4 (q, *J* = 34.2 Hz), 21.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.5 (d, *J* = 6.7 Hz); GC–MS (EI, *m*/*z*, 70 eV) 200 (100, M^+), 185 (55), 165 (21), 131 (23), 115 (19), 91 (9), 77 (5), 51 (4); anal. calcd. for $C_{11}H_{11}F_3$: C, 65.99; H, 5.54. Found: C, 66.13; H, 5.29%.

*4.11. (E)-1-(1-naphthyl)-3,3,3-trifluoropropene (**3k**) [21]*

Colorless oil: yield 80% (58.8 mg, *E*/*Z* = 98/2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90–7.82 (m, 4*H*), 7.60 (dm, *J* = 8.6 Hz, 1*H*), 7.56–7.48 (m, 2*H*), 7.32 (dm, *J* = 16.0 Hz, 1*H*), 6.32 (dq, *J* = 16.0, 6.4 Hz, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 135.2 (q, *J* = 6.9 Hz), 133.6, 131.1, 131.0, 130.2, 128.8, 126.9, 126.3, 125.4, 124.8, 123.4 (q, *J* = 269.5 Hz), 123.2, 118.8 (q, *J* = 33.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.5 (d, *J* = 6.4 Hz); GC–MS (EI, *m*/*z*, 70 eV) 222 (50, M^+), 201 (20), 183 (10), 153 (100), 126 (4), 101 (4), 76 (5).

*4.12. (E)-1-(2-naphthyl)-3,3,3-trifluoropropene (**3l**) [21]*

White solid: yield 72%, 53.0 mg (*E*/*Z* = 99/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85–7.72 (m, 4*H*), 7.56 (d, *J* = 8.6 Hz, 1*H*), 7.55–7.45 (m, 2*H*), 7.29 (d, *J* = 16.0 Hz, 1*H*), 6.30 (dq, *J* = 16.0, 6.4 Hz, 1*H*); ^{13}C NMR ($CDCl_3$, 101 MHz) 137.7 (q, *J* = 6.8 Hz), 134.0, 133.2, 130.8, 129.1, 128.8, 128.4, 127.8, 127.1, 126.8, 123.7 (q, *J* = 268.9 Hz), 123.1, 116.0 (q, *J* = 33.8 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −64.4 (d, *J* = 6.4 Hz); GC–MS (EI, *m*/*z*, 70 eV) 222 (100, M^+), 201 (24), 172 (8), 152 (27), 127 (4), 76 (4).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.07.018.

References

[1] I. Ojima, J. Org. Chem. 78 (2013) 6358–6383.
[2] P. Chen, G. Liu, Synthesis 45 (2013) 2919–2939.
[3] T. Liang, C.N. Neumann, T. Ritter, Angew. Chem. Int. Ed. 52 (2013) 8214–8264.
[4] H. Liu, Z. Gu, X. Jiang, Adv. Synth. Catal. 355 (2013) 617–626.
[5] X.-F. Wu, H. Neumann, M. Beller, Chem. Asian J. 7 (2012) 1744–1754.
[6] T. Besset, C. Schneider, D. Cahard, Angew. Chem. Int. Ed. 51 (2012) 5048–5050.

[7] D.O. Ayeni, S.K. Mandal, B. Zajc, Tetrahedron Lett. 54 (2013) 6008–6011.
[8] A. Hafner, T.S. Fischer, S. Bräse, Eur. J. Org. Chem. (2013) 7996–8003.
[9] T. Hanamoto, N. Morita, K. Shindo, Eur. J. Org. Chem. (2003) 4279–4283.
[10] T. Kobayashi, T. Eda, O. Tamura, H. Ishibashi, J. Org. Chem. 67 (2002) 3156–3159.
[11] T. Umemoto, Y. Gotoh, Bull. Chem. Soc. Jpn. 64 (1991) 2008–2010.
[12] J. Yin, Y. Li, R. Zhang, K. Jin, C. Duan, Synthesis 46 (2014) 607–612.
[13] P. Xu, A. Abdukader, K. Hu, Y. Cheng, C. Zhu, Chem. Commun. 50 (2014) 2308–2310.
[14] Y. Li, L. Wu, H. Neumann, M. Beller, Chem. Commun. 49 (2013) 2628–2630.
[15] Y. Yasu, T. Koike, M. Akita, Chem. Commun. 49 (2013) 2037–2039.
[16] T. Patra, A. Deb, S. Manna, U. Sharma, D. Maiti, Eur. J. Org. Chem. (2013) 5247–5250.
[17] T. Besset, D. Cahard, X. Pannecoucke, J. Org. Chem. 79 (2013) 413–418.
[18] Z. Li, Z. Cui, Z.-Q. Liu, Org. Lett. 15 (2013) 406–409.
[19] M. Presset, D. Oehlrich, F. Rombouts, G.A. Molander, J. Org. Chem. 78 (2012) 12837–12843.
[21] H. Egami, R. Shimizu, M. Sodeoka, Tetrahedron Lett. 53 (2012) 5503–5506.
[22] H. Lin, X. Dong, Y. Li, Q. Shen, L. Lu, Eur. J. Org. Chem. (2012) 4675–4679.
[23] Z. He, T. Luo, M. Hu, Y. Cao, J. Hu, Angew. Chem. Int. Ed. 51 (2012) 3944–3947.
[24] A.T. Parsons, T.D. Senecal, S.L. Buchwald, Angew. Chem. Int. Ed. 51 (2012) 2947–2950.
[25] C.-P. Zhang, J. Cai, C.-B. Zhou, X.-P. Wang, X. Zheng, Y.-C. Gu, J.-C. Xiao, Chem. Commun. 47 (2011) 9516–9518.
[26] J. Xu, D.-F. Luo, B. Xiao, Z.-J. Liu, T.-J. Gong, Y. Fu, L. Liu, Chem. Commun. 47 (2011) 4300–4302.
[27] E.J. Cho, S.L. Buchwald, Org. Lett. 13 (2011) 6552–6555.
[28] T. Liu, Q. Shen, Org. Lett. 13 (2011) 2342–2345.
[29] A.A. Goldberg, V.M. Muzalevskiy, A.V. Shastin, E.S. Balenkova, V.G. Nenajdenko, J. Fluorine Chem. 131 (2010) 384–388.
[30] V.G. Nenajdenko, G.N. Varseev, A.V. Shastin, E.S. Balenkova, J. Fluorine Chem. 126 (2005) 907–913.
[31] V.N. Korotchenko, A.V. Shastin, V.G. Nenajdenko, E.S. Balenkova, Tetrahedron 57 (2001) 7519–7527.
[32] X. Wang, Y. Xu, Y. Deng, Y. Zhou, J. Feng, G. Ji, Y. Zhang, J. Wang, Chem. Eur. J. 20 (2014) 961–965.
[33] W. Dmowski, J. Fluorine Chem. 132 (2011) 504–511.
[34] J. Ruan, J.A. Iggo, N.G. Berry, J. Xiao, J. Am. Chem. Soc. 132 (2011) 16689–16699.