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Regio- and stereo-specific preparation of (*E*)-1-aryl-3,3,3-trifluoro-1-iodo-propenes and their palladium-catalyzed reaction with terminal alkynes

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Abstract

A new type of iodo-containing trifluoromethylated building blocks were synthesized. The reaction of 1-aryl-3,3,3-trifluoropropynes **1** with lithium iodide in acetic acid at 75 °C gave (*E*)-1-aryl-3,3,3-trifluoro-1-iodo-propenes **2** in high yield, which undergo the palladium-catalyzed Sonogashira reaction with terminal alkynes afforded trifluoromethyl-containing 1,3-enynes in high yield.

Keywords: Trifluoromethyl; Stereospecific; Vinyl iodides; 1,3-Enynes; Sonogashira reaction

1. Introduction

Recently, trifluoromethylated compounds have received considerable attention and have been found diverse applications in the areas of materials science [1], agrochemistry and biomedical chemistry [2] due to their unique chemical, physical and biological properties [3]. Although various new approaches were recently proposed [4], the existing methods for direct trifluoromethylation of organic compounds do not always allow the introduction of a CF_3 group in required position of the target molecule [5]. As a result, the preparation and application of trifluoromethylated building blocks [6] is an alternative approach for constructing trifluoromethyl-substituted compounds. Among these blocks, trifluoromethylated building blocks bearing a vinyl iodide moiety are versatile intermediates owing to the active C–I bond, which are widely used as synthetic precursors of furan derivatives [7] and some macrolides [8]. The addition of trifluoropropynes with $LiAlH_4/I_2$ [6,9] or CF_3I to propynes [10], and the selective trifluoro-methylation [11] of 1,2-diiodoalkenes are usual methods for preparation of CF_3-containing vinyl iodides. However, most of the reported building blocks [12] are (*Z*)-isomer. Qing et al. [13] reported (*Z*)-isomer of CF_3-containing vinyl iodides which were prepared in NaI/AcOH system, and now we would like to describe the synthesis of analogical (*E*)-isomer in LiI/AcOH system.

The 1,3-enyne moiety is an important structural unit for biologically active [14] and natural compounds [15], and also new functional materials [16]. Therefore, the introduction of CF_3 group into 1,3-enynes is so attractive to chemists [10,13]. The generation of 1,3-enyne moiety from vinylic systems and terminal acetylenes is quite obvious by using a configuration-retention stereospecific procedure such as the Sonogashira methodology [17]. The 1,3-enynes bearing a trifluoromethyl group in double bond are key intermediates in preparation of trifluoromethyl-containing furans [18]. Such as 3,3,3-trifluoro-1-iodopropenes [10,13] and 3,3,3-trifluoro-2-iodopropenes [19] are often used to prepare them by coupling reaction with terminal alkynes.

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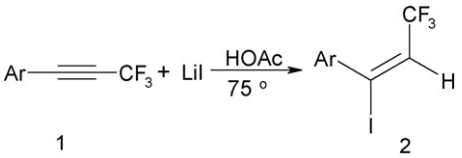
Herein, we wish to report a practical regio- and stereo-specific route to new building blocks: (*E*)-1-aryl-3,3,3-trifluoro-1-iodopropenes **2**, which were obtained from 1-aryl-3,3,3-trifluoropropynes **1** [20]. In addition, **1** can be conveniently prepared from commercially available 1,1,1-trichloro-2,2,2-trifluoroethane (freon-113a) [21]. In order to demonstrate synthetic utilities of the above building blocks and to prepare trifluoromethyl-containing 1,3-enynes, the palladium-catalyzed coupling reaction of (*E*)-1-aryl-3,3,3-trifluoro-1-iodopropenes with terminal alkynes was investigated.

2. Results and discussion

In 1992, Lu and co-workers [22] reported a stereospecifical reaction of 2-propynoic acids with lithium halides or sodium halides in acetic acid to give *Z*-isomers. Trifluoromethyl is also a strong electron-withdrawing group as carboxyl. However, when 1-aryl-3,3,3-trifluoropropynes **1** were treated with lithium iodide in acetic acid at 75 °C (Scheme 1), we were delighted to found that (*E*)-1-aryl-3,3,3-trifluoro-1-iodopropenes **2** were the exclusive products. At the same condition, the yields were very low if lithium iodide was substituted by sodium iodide.

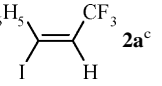
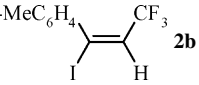
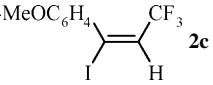
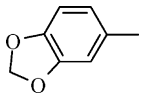
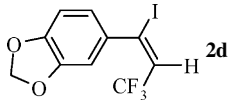
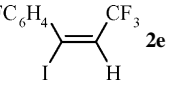
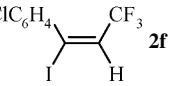
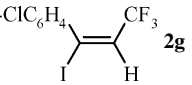
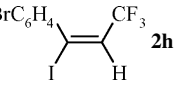
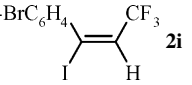
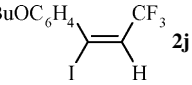
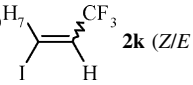
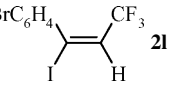
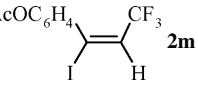
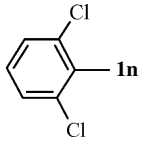
The reaction was monitored by ^{19}F NMR. A mixture of 1-aryl-3,3,3-trifluoropropynes **1** and lithium iodide (1.1 equiv.) in acetic acid was stirred and heated at 75 °C. With the proceeding of reaction, a new doublet peak (close—60 ppm) increased and the singlet peak (close—50 ppm) decreased. After 16 h, the singlet peak of the starting material disappeared completely. The mixture was poured into water and neutralized with solid K_2CO_3 until no CO_2 evolved, then extracted with ether, washed wish saturated $NaHSO_3$ solution and brine. The solvent was removed *in vacuo* after extracts were dried by $MgSO_4$. Purification of the residue and elution with 25:1 petroleum ether/ethyl acetate gave *E*-isomers **2** in high yields. The results were summarized in Table 1. The yields have not been affected by the electronic effects of substituents, all trifluoro-propynes with substituent groups of different electronic nature on aryl ring afforded satisfactory results. However, the steric hindrance of aryl group could notably reduce reaction yields.

The structure and configuration of products was confirmed by ^1H NMR and ^{19}F NMR spectra. The vinyl hydrogen is a quartet peak in ^1H NMR spectra and coupling constant (7.3 Hz) is a typical value for $^3J_{F-H}$ of ArCI = $CHCF_3$. The $-CF_3$ group is a doublet peak in ^{19}F NMR spectra and coupling constant is also 7.3 Hz which is a typical value for $^3J_{F-H}$. Therefore, the product was assigned to be ArCI = $CHCF_3$. Following the method [11] of stereospecific reduction of C–I bond, we reduced the ArCI = $CHCF_3$ **2(a, c, j, k)**. Only single isomer was obtained when **2(a, c, j)** were reduced, and the coupling

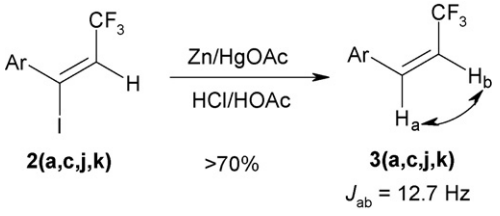


Scheme 1.

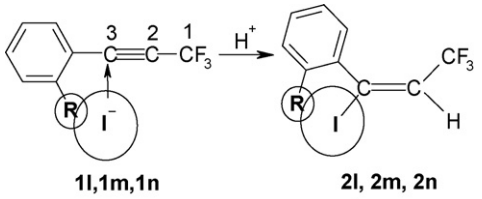
Table 1
The addition reaction of **1** with LiI in AcOH

Entry	**1** Ar=	Product **2**[a]	Yield (%)[b]
1	C_6H_5 **1a**	 **2a**[c]	81
2	*p*-MeC_6H_4 **1b**	 **2b**	86
3	*p*-$MeOC_6H_4$ **1c**	 **2c**	80
4	 **1d**	 **2d**	85
5	*p*-FC_6H_4 **1e**	 **2e**	92
6	*p*-ClC_6H_4 **1f**	 **2f**	89
7	*m*-ClC_6H_4 **1g**	 **2g**	72
8	*p*-BrC_6H_4 **1h**	 **2h**	90
9	*m*-BrC_6H_4 **1i**	 **2i**	78
10	*p*-$BuOC_6H_4$ **1j**	 **2j**	82
11	1-Naphthyl **1k**	 **2k** (*Z*/*E* = 38:62)	14
12	*o*-BrC_6H_4 **1l**	 **2l**	Trace
13	*o*-$AcOC_6H_4$ **1m**	 **2m**	Trace
14	 **1n**		No reaction

[a] All compounds were corfirmed by NMR, IR and MS.
[b] Yields were based on 1.
[c] The spectra data of this compoud are same to reference.



Scheme 2.

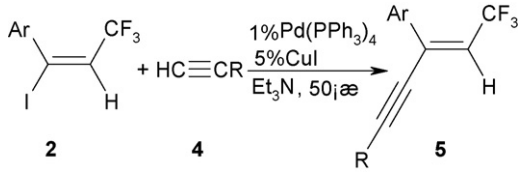


Scheme 3.

constant ($^3J_{H–H}$) of H_a and H_b in reduced product **3(a, c, j)** is 12.7 Hz (Scheme 2), which means *cis*-vinyl protons in double bond ($^3J_{H–H}$ of *tran* > 16 Hz [23]). On the basis of above results, the *E*-configuration was designated to **2**. The ^{1}H NMR and ^{19}F NMR spectra of **2a** are same to the reported [11]. Taniguchi et al. [24] had pointed that the *Z*-isomer converted to *E*-isomer under the condition of high temperature and long reaction time. Actually, *Z*-isomer could be obviously detected by ^{19}F NMR during the reaction. The weak doublet peak of *Z*-isomer in about −64 ppm disappeared completely at last.

In our reaction system, furan ring were opened when 1-furyl-3,3,3-trifluoropropynes reacted with HI. In addition, we have not obtained the addition results of 1-pyridyl-3,3,3-trifluoropropynes and 1-alkyl-3,3,3-trifluoropropynes because they cannot be prepared by conventional method [20]. It was noteworthy that the mixture of *Z*- and *E*-**2k** was obtained in 14% yield when Ar– is 1-naphthyl. We think the steric hindrance of 1-naphthyl caused low yield and low stereoselectivity. In order to prove our viewpoint, trifluoropropynes bearing *ortho*-substituted phenyl were applied to this reaction system. In entry 12, 13, Ar– is *o*-Br–Ph–, *o*-CH_3COO–Ph–, when we monitored the reaction with ^{19}F NMR, only a very weak doublet peak brought out and the singlet peak of material never disappeared. In entry 14, both *ortho*-positions of Ar– are occupied by chlorine atom, no product was monitored.

Although Lu and co-workers [22] had discussed the mechanism of regio- and stereo-specific addition of carbon-carbon triple bond, we think the trace product of **2l**, **2m**, **2n** owing to the steric hindrance between R group and iodide anion when iodide anion regio-specifically attack C-3 carbon atom of the electrondeficient carbon–carbon triple bond (Scheme 3).



Scheme 4.

Table 2
The Sonogashira reaction of **2** with terminal alkynes **4**

Entry	**2** Ar=	**4** R=	Product **5**	Yield (%)
1	*p*-ClC_6H_4	$CH_2N(CH_2CH_3)_2$	**5a**	81
2	*p*-ClC_6H_4	CH_2OH	**5b**	77
3	*p*-ClC_6H_4	C_6H_5	**5c**	82
4	*p*-ClC_6H_4	$C(CH_3)_2OH$	**5d**	88
5	*p*-$MeOC_6H_4$	$CH_2N(CH_2CH_3)_2$	**5e**	88
6	*p*-$MeOC_6H_4$	CH_2OH	**5f**	78
7	*p*-$MeOC_6H_4$	C_6H_5	**5g**	89
8	*p*-$MeOC_6H_4$	$C(CH_3)_2OH$	**5h**	74
9	*p*-$BuOC_6H_4$	$CH_2N(CH_2CH_3)_2$	**5i**	98
10	*p*-$BuOC_6H_4$	CH_2OH	**5j**	86
11	*p*-$BuOC_6H_4$	C_6H_5	**5k**	96
12	*p*-BrC_6H_4	$CH_2N(CH_2CH_3)_2$	**5l**	95
13	*p*-BrC_6H_4	CH_2OH	**5m**	96
14	*p*-MeC_6H_4	$CH_2N(CH_2CH_3)_2$	**5n**	66
15	*p*-MeC_6H_4	CH_2OH	**5o**	52
16	*p*-MeC_6H_4	C_6H_5	**5p**	96

The corresponding *E*-isomers of **2l**, **2m** had not been separated because of the too less products.

In order to develop synthetic utilities of these building blocks, we applied them to research their coupling reaction (Scheme 4). The Sonogashira reaction of **2** with terminal alkynes **4** in the presence of $Pd(PPh_3)_4$ and CuI in triethylamine at 50 °C afforded trifluoromethyl-containing 1,3-enynes **5** in high yield. The results were summarized in Table 2. Significant influence of electronic effects of Ar and R on yields had not been observed. Only in the case of entry 15 (Ar=*p*-MeC_6H_4, R=CH_2OH), the yield was not as high as the others.

It is well known that the reactivity of sp^2 species is vinyl iodide > aryl bromide ≫ aryl chloride in coupling reaction [17]. So, **2h** and **2f** reacted with 1.0 equiv. of terminal alkynes afforded target products **5**. However, the bromide atom on aryl was also substituted by alkynyl when **2h** or **2i** was treated with 1.5 equiv. of terminal alkynes. Compare with **2**, the chemical shift of vinyl proton in **5** decreased in ^{1}H NMR and ^{19}F NMR, and the coupling constant of $^3J_{F–H}$ increased.

3. Conclusion

In summary, we have investigated the regio- and stereo-specific addition reaction of 1-aryl-3,3,3-trifluoropropyne **1** with HI in LiI/AcOH system. (*E*)-1-Aryl-3,3,3-trifluoro-1-iodopropenes **2** were prepared in high yields by this addition reaction. The vinyl iodides **2** were used to prepare trifluoromethyl-containing 1,3-enynes **5** by palladium-catalyzed coupling reaction with terminal alkynes.

4. Experimental

^{1}H NMR and ^{13}C NMR were determined in a $CDCl_3$ solution with a Bruker Avance300 (300 M Hz) spectrometer using tetramethylsilane as the internal standard. ^{19}F NMR spectra were also obtained in a $CDCl_3$ solution on Bruker Avance300 (282.2 MHz) spectrometer using $CFCl_3$ as external standard. All chemical shifts (δ) were expressed in parts per

million, and coupling constants (*J*) were given in Hertz. Mass spectra were obtained using EI at 70 eV. IR spectra were recorded on a Bruker Equinox 55 spectrometer.

4.1. General procedure for addition of 1-aryl-3,3,3-trifluoropropynes with LiI in AcOH

A mixture of 1-phenyl-3,3,3-trifluoropropynes **1a** (240 mg, 1.4 mmol) and lithium iodide (218 mg, 1.6 mmol) in acetic acid (1.5 mL) was stirred at 75 °C, while the mixture was monitored by TLC and ^{19}F NMR. After 16 h, water (8 mL) was added. The mixture was neutralized with solid K_2CO_3 until no CO_2 evolved and then extracted with ether (3× 15 mL), washed with saturated $NaHSO_3$ solution and brine. The extracts were dried by $MgSO_4$, and the solvent was removed *in vacuo*. Purification of the residue by silica-gel column chromatography eluted with 25:1 petroleum ether/ethyl acetate gave product **2a**.

*4.1.1. (E)-1-Iodo-1-phenyl-3,3,3-trifluoropropene (E)-**2a***

Yield 81% (pale yellow oil). IR (thin film): 2928, 1631, 1306, 1266, 1133 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (q, J = 7.3 Hz, 1H, $CHCF_3$), 7.28 (s, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.2, 120.4, 124.1, 126.0, 128.0, 128.4, 138.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ −60.10 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 298 (M^+, 16), 171 (100), 151 (52), 127(7); Anal. Calcd for $C_9H_6F_3I$: C, 36.27; H, 2.03. Found: C, 36.38; H, 2.11.

*4.1.2. (E)-1-Iodo-1-p-tolyl-3, 3, 3-trifluoropropene (E)-**2b***

Yield 86% (pale yellow oil). IR (thin film): 2925, 1628, 1599, 1303, 1264, 1129 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H, CH_3), 6.53 (q, J = 7.3 Hz, 1H, $CHCF_3$), 7.15 (d, J = 8.2 Hz, 2H, Ph), 7.40 (d, J = 8.2 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 111.6, 119.8, 123.4, 125.8, 128.2,139.2, 140.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.89 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 312 (M^+, 100), 185 (12), 165 (46), 115 (48); Anal. Calcd for $C_{10}H_8F_3I$: C, 38.49; H, 2.58. Found: C, 38.61; H, 2.65.

*4.1.3. (E)-1-Iodo-1-(4-methoxyphenyl)-3,3,3-trifluoropropene (E)-**2c***

Yield 80% (pale yellow oil). IR (thin film): 2960, 1604, 1257, 1126 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 6.56 (q, J = 7.3 Hz, 1H, $CHCF_3$), 6.85 (d, J = 8.6 Hz, 2H, Ph), 7.30 (d, J = 8.6 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 113.5, 119.6, 123.3, 128.8, 129.2, 133.0, 160.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ −57.54 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 328 (M^+, 6), 201 (100), 181 (22), 132 (26); Anal. Calcd for $C_{10}H_8F_3IO$: C, 36.61; H, 2.46. Found: C, 36.73; H, 2.55.

*4.1.4. (E)-1-Iodo-1-(3-benzo [1,3] dioxol-5-yl)-3,3,3-trifluoropropene (E)-**2d***

Yield 85% (pale yellow oil). IR (thin film): 2902, 1633, 1487, 1240, 1145 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.00 (s, 2H, OCH_2O). 6.02 (q, J = 7.3 Hz, 1H, $CHCF_3$), 6.80 (m, 3H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 101.8, 114.3, 120.8, 124.1, 128.9, 129.5, 130.2, 133.4, 148.4, 152.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ −57.66 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 342 (M^+, 6), 215 (100), 146 (32); Anal. Calcd for $C_{10}H_6F_3IO_2$: C, 35.11; H, 1.77. Found: C, 35.31; H, 1.87.

*4.1.5. (E)-1-Iodo-1-(4-fluorophenyl)-3,3,3-trifluoropropene (E)-**2e***

Yield 92% (pale yellow oil). IR (thin film): 2934, 1683, 1310,1266, 1135 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (q, J = 7.3 Hz, 1H, $CHCF_3$), 7.22 (m, 2H, Ph), 7.74 (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.4, 119.0, 122.6, 127.6, 129.3, 132.0, 163.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ −109.03 (s, 1F), −68.72 (d, J = 7.3 Hz, 3F,); MS (EI, 70 eV) *m/z*: 316 (M^+, 16), 189 (100), 120 (28); Anal. Calcd for $C_9H_5F_4I$: C, 34.20; H, 1.59. Found: C, 34.31; H, 1.66.

*4.1.6. (E)-1-Iodo-1-(4-chlorophenyl)-3,3,3-trifluoropropene (E)-**2f***

Yield 89% (pale yellow oil). IR (thin film): 2928, 1675, 1307, 1263, 1133 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.56 (q, J = 7.3 Hz, 1H, $CHCF_3$), 7.35 (d, J = 8.6 Hz, 2H, Ph), 7.43 (d, J = 8.6 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.3, 124.0, 127.5, 128.4, 130.5, 135.7, 136.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ −60.24 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 333 (M + 1, 33), 332 (M^+, 100), 205 (12), 185 (52), 169 (32), 136 (18); Anal. Calcd for $C_9H_5ClF_3I$: C, 32.51; H, 1.52. Found: C, 32.63; H, 1.60.

*4.1.7. (E)-1-Iodo-1-(3-chlorophenyl)-3,3,3-trifluoropropene (E)-**2g***

Yield 72% (pale yellow oil). IR (thin film): 2922, 1629, 1302, 1265, 1134 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.58 (q, J = 7.3 Hz, 1H, $CHCF_3$), 7.34 (m, 3H, Ph), 7.47 (s, 1H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.5, 124.4, 127.6, 128.5, 129.2, 129.6, 129.9, 130.2, 134.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ −60.36 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 333 (M + 1, 38), 332 (M^+, 100), 205 (40), 185 (75), 169 (52), 136 (18). Anal. Calcd for $C_9H_5ClF_3I$: C, 32.51; H, 1.52. Found: C, 32.66; H, 1.63.

*4.1.8. (E)-1-Iodo-1-(4-bromophenyl)-3,3,3-trifluoropropene (E)-**2h***

Yield 90% (pale yellow oil). IR (thin film): 2920, 1630, 1484, 1213, 1134 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.56 (q, J = 7.3 Hz, 1H, $CHCF_3$), 7.36 (d, J = 8.6 Hz, 2H, Ph), 7.50 (d, J = 8.6 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.6, 123.3, 124.6, 129.7, 131.7, 133.9, 134.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ −60.27 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 376/378 (M^+, 90), 249/251 (5), 170 (100), 101 (22); Anal. Calcd for $C_9H_5BrF_3I$: C, 28.68; H, 1.34. Found: C, 28.70; H, 1.39.

*4.1.9. (E)-1-Iodo-1-(3-bromophenyl)-3,3,3-trifluoropropene (E)-**2i***

Yield 78% (pale yellow oil). IR (thin film): 2981, 1630, 1562, 1264, 1132 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.58 (q, J = 7.3 Hz, 1H, $CHCF_3$), 7.36 (m, 3H, Ph), 7.63 (s, 1H, Ph);

^{13}C NMR (75 MHz, $CDCl_3$): δ 120.0, 123.8, 127.2, 128.4, 129.1, 129.5, 129.8, 130.1,134.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ −60.37 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 376/378 (M^+, 15), 249/251 (60), 170 (100), 101 (28); Anal. Calcd for $C_9H_5BrF_3I$: C, 28.68; H, 1.34. Found: C, 28.74; H, 1.43.

*4.1.10. (E)-1-Iodo-1-(4-butoxyphenyl)-3,3,3-trifluoropropene (E)-**2j***

Yield 82% (pale yellow oil). IR (thin film): 2960, 1604, 1507, 1261, 1133 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, J = 7.4 Hz, 3H, CH_3). 1.49 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.76 (m, 2H, $OCH_2CH_2CH_2CH_3$), 3.96 (t, J = 6.5 Hz, 2H, OCH_2CH_2 CH_2CH_3), 6.56 (q, J = 7.3 Hz, 1H, $CHCF_3$), 6.83 (d, 2H, J = 8.7 Hz, Ph), 7.27 (d, 2H, J = 8.7 Hz, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 19.2, 31.2, 67.7, 113.9, 119.5, 123.2, 128.7, 129.3, 132.7, 160.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ −57.50 (d, J = 7.3 Hz); MS (EI, 70 eV) *m/z*: 370 (M^+, 11), 243 (100), 174 (26); Anal. Calcd for $C_{13}H_{14}F_3IO$: C, 42.18; H, 3.81. Found: C, 42.24; H, 3.85.

*4.1.11. (Z/E)-1-Iodo-1-(naphthalen-1-yl)-3,3,3-trifluoropropene (Z/E)-**2k***

Yield 14% (pale yellow oil). IR (thin film): 2965, 1609, 1521, 1267, 1135 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.57 (d, J = 7.3 Hz, 0.62H, $CHCF_3$), 6.91 (q, J = 7.3 Hz, 0.38H, $CHCF_3$), 7.42 (m, 2H), 7.58(m, 2H), 7.88(m, 2H), 7.99(m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −60.49 (d, J = 7.3 Hz, 1.86 F), −59.25 (d, J = 7.3 Hz, 1.14 F); MS (EI, 70 eV) *m/z*: 348 (M^+, 18), 221 (100), 152 (23); Anal. Calcd for $C_{13}H_8F_3I$: C, 44.85; H, 2.32. Found: C, 44.89; H, 2.29.

4.2. General procedure for reduction of (E)-1-aryl-3,3,3-trifluoro-1-iodopropenes in AcOH

(*E*)-ArCI = $CHCF_3$ (5 mmol), Zn (1.2 g, 20 mmol), and AgOAc (0.1 g, 0.6 mmol) were mixed together in AcOH (10 mL). Under vigorous stirring 1 mL of concentrated HCl (37%) was added dropwise over a 5 min period. The mixture was further stirred for 5 min, and then was filtered. The filtrate was mixed with 30 mL of hexane and 10 mL of H_2O. The organic layer was separated, and the water solution was extracted with hexane (20 mL × 3). The combined organic solution was washed with water (10 mL × 3), dried, and concentrated. Purification of the residue by flash column chromatography gave product **3**.

*4.2.1. (Z)-1-Phenyl-3,3,3-trifluoropropene (Z)-**3a***

Yield 76% (pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.75 (dq, J = 7.3 Hz, 12.7Hz, $CHCF_3$), 6.92 (d, J = 12.7 Hz, 1H, CH=$CHCF_3$), 7.36 (m, 5H, PH).

*4.2.2. (Z)-1-(4-Methoxyphenyl)-3,3,3-trifluoropropene (Z)-**3c***

Yield 82% (pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3H, OCH_3), 5.64 (dq, J = 7.3 Hz, 12.7 Hz, $CHCF_3$), 6.83 (d, J = 12.7 Hz, 1H, CH = $CHCF_3$), 6.91 (d, J = 8.7 Hz, 2H, Ph), 7.40 (d, J = 8.7 Hz, 2H, Ph).

*4.2.3. (Z)-1-(4-Butoxyphenyl)-3, 3, 3-trifluoropropene (Z)-**3j***

Yield 91% (pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03 (t, J = 7.4 Hz, 3H, CH_3), 1.55 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.82 (m, 2H, $OCH_2CH_2CH_2CH_3$), 4.02 (t, J = 6.5 Hz, 2H, OCH_2 $CH_2CH_2CH_3$), 5.67 (dq, J = 7.3 Hz, 12.7 Hz, $CHCF_3$), 6.84 (d, J = 12.7 Hz, 1H, CH = $CHCF_3$), 6.93 (d, J = 8.7 Hz, 2H, Ph), 7.42 (d, J = 8.7 Hz, 2H, Ph).

*4.2.4. (Z/E)-1-(Naphthalen-1-yl)-3,3,3-trifluoropropene (Z/E)-**3k***

Yield 77% (pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$): 5.68 (dq, J = 7.3 Hz, 12.7 Hz, 0.62H, $CHCF_3$), 6.02 (dq, J = 7.3 Hz, 16.5 Hz, 0.38H, $CHCF_3$), 6.86 (d, J = 12.7 Hz, 0.62H, CH = $CHCF_3$), 7.12 (d, J = 16.5 Hz, 0.38H, CH = $CHCF_3$), 7.40 (m, 2H), 7.57 (m, 2H), 7.86 (m, 2H), 7.98 (m, 1H).

4.3. General procedure for preparation of (E)-2-aryl-3-trifluoromethyl-1,3-enynes 5

To a three-necked, round-bottomed flask were added (*E*)-1-aryl-1-iodo-3,3,3-trifluoropropene **2** (1 mmol), terminal alkyne **3** (1.5 mmol), CuI (0.05 mmol), $Pd(PPh_3)_4$ (0.01 mmol), and triethylamine (6 mL) under nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 8 h and then filtered. The filtrate was concentrated and flash chromatographed on silica gel (hexanes/ether = 10:1) to yield **5**.

*4.3.1. (E)-4-(4-Chlorophenyl)-N,N-diethyl-6,6,6-trifluorohex-4-en-2-yl-1-amine (E)-**5a***

Yield 81% (pale yellow oil). IR (film): 2972, 2821, 2219, 1622, 1491, 1267, 1135, 839, 729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, J = 5.7Hz, 6H, CH_3), 2.60 (q, J = 5.7 Hz, 4H, CH_2CH_3), 3.73 (s, 2H, CH_2N), 6.27 (q, J = 7.5Hz, 1H, $CHCF_3$), 7.37 (d, J = 8.6 Hz, 2H, Ph), 7.57 (d, J = 8.6 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.4, 41.2, 47.2, 78.7, 97.8, 120.6, 124.2, 127.8, 128.6, 130.5, 135.8, 136.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.21 (d, J = 7.5 Hz); MS (EI, 70 eV) *m/z*: 316 (M + 1, 33), 315 (M^+, 100), 285 (32); Anal. Calcd for $C_{16}H_{17}ClF_3N$: C, 60.86; H, 5.43; N, 4.44. Found: C, 60.74; H, 5.49; N, 4.38.

*4.3.2. (E)-4-(4-Chlorophenyl)-6,6,6-trifluorohex-4-en-2-yl-1-ol (E)-**5b***

Yield 77% (pale yellow oil). IR (thin film): 3364, 2924, 2865, 2237, 1624, 1491, 1268, 817, 729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 1H, OH), 4.55 (s, 2H, CH_2OH), 6.30 (q, J = 7.5 Hz, 1H, $CHCF_3$), 7.57 (d, J = 8.6 Hz, 2H, Ph), 7.38 (d, J = 8.6 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.2, 79.2, 99.1, 121.4, 124.0, 127.8, 128.7, 130.6, 135.9, 136.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.48 (d, J = 7.5 Hz); MS (EI, 70 eV) *m/z*: 261 (M^+ 1, 23), 260 (M^+, 68), 243 (100); Anal. Calcd for $C_{12}H_8ClF_3O$: C, 55.30; H, 3.09; Found: C, 55.42; H, 3.16.

*4.3.3. (E)-1-Phenyl-3-(4-chlorophenyl)-5,5,5-trifluoropent-3-en-1-yl (E)-**5c***

Yield 82% (pale yellow oil). IR (thin film): 3061, 2926, 2204, 1620, 1489, 1270, 836, 755, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.34 (q, J = 7.5 Hz, 1H, $CHCF_3$), 7.35 (m, 5H, Ph), 7.56 (d, J = 8.5 Hz, 2H, Ph), 7.67 (d, J = 8.5 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.8, 93.8, 119.8, 126.5, 128.3, 128.7, 129.0, 129.2, 130.8, 131.7, 132.3, 135.7, 136.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.38 (d, J = 7.5 Hz); MS (EI, 70 eV) *m/z*: 307 (M + 1, 41), 306 (M^+, 100), 271 (28); Anal. Calcd for $C_{17}H_{10}ClF_3$: C, 66.57; H, 3.29; Found: C, 66.48; H, 3.35.

*4.3.4. (E)-5-(4-Chlorophenyl)-7,7,7-trifluoro-2-methylhept-5-en-3-yl-2-ol (E)-**5d***

Yield 88% (pale yellow oil). IR (thin film): 3389, 2984, 2223, 1623, 1492, 1358, 1268, 1134, 814, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.63 (s, 6H, CH_3), 2.05 (s, 1H, OH), 6.29 (q, J = 7.5 Hz, 1H, $CHCF_3$), 7.38 (d, J = 8.5 Hz, 2H, Ph), 7.56 (d, J = 8.5 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.4, 65.2, 79.0, 98.8, 121.4, 124.2, 127.5, 128.4, 130.3, 135.7, 136.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.47 (d, J = 7.5 Hz); MS (EI, 70 eV) *m/z*: 289 (M + 1, 37), 288 (M^+, 86), 261 (100); Anal. Calcd for $C_{14}H_{12}ClF_3O$: C, 58.25; H, 4.19; Found: C, 58.17; H, 4.11.

*4.3.5. (E)-4-(4-Methoxyphenyl)-N,N-diethyl-6,6,6-trifluorohex-4-en-2-yl-1-amine (E)-**5e***

Yield 88% (pale yellow oil). IR (thin film): 2971, 2820, 2218, 1610, 1513, 1362, 1271, 1105, 835, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, J = 5.7Hz, 6H, CH_3), 2.58 (q, J = 5.7 Hz, 4H, CH_2CH_3), 3.63 (s, 2H, CH_2N), 3.83 (s, 3H, OCH_3), 6.02 (q, J = 8.7 Hz, 1H, $CHCF_3$), 6.89 (d, J = 8.7 Hz, 2H, Ph), 7.39 (d, J = 8.7 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.9, 40.8, 47.0, 54.7, 84.7, 88.8, 113.5, 120.5, 123.8, 127.1, 129.3, 133.8, 159.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ −56.15 (d, J = 8.7 Hz); MS (EI, 70 eV) *m/z*: 311 (M^+, 65), 280 (100), 251 (24); Anal. Calcd for $C_{17}H_{20}F_3NO$: C, 65.58; H, 6.47; N, 4.50. Found: C, 65.47; H, 6.41; N, 4.45.

*4.3.6. (E)-4-(4-Methoxyphenyl)-6,6,6-trifluorohex-4-en-2-yl-1-ol (E)-**5f***

Yield 78% (pale yellow oil). IR (thin film): 3401, 2934, 2844, 2052, 1610, 1513, 1463, 1271, 1111, 831, 679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.88 (s, 1H, OH), 3.83 (s, 3H, OCH_3), 4.43 (s, 2H, CH_2OH), 6.05 (q, J = 8.7Hz, 1H, $CHCF_3$), 6.90 (d, J = 8.8 Hz, 2H, Ph), 7.39 (d, J = 8.8 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.4, 54.8, 85.0, 91.6, 113.8, 120.9, 124.1, 126.9, 129.7, 133.9, 160.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ −56.16 (d, J = 8.7 Hz); MS (EI, 70 eV) *m/z*: 256 (M^+, 65), 239 (100), 208(63); Anal. Calcd for $C_{13}H_{11}F_3O_2$: C, 60.94; H, 4.33; Found: C, 60.82; H, 4.42.

*4.3.7. (E)-1-Phenyl-3-(4-methoxyphenyl)-5,5,5-trifluoropent-3-en-1-yl (E)-**5g***

Yield 89% (pale yellow oil). IR (thin film): 2962, 2840, 2206, 1611, 1512, 1259, 837, 756, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 3H, OCH_3), 6.15 (q, J = 8.7 Hz, 1H, $CHCF_3$), 6.93 (d, J = 8.8 Hz, 2H, Ph), 7.36 (m, 3H, Ph), 7.49 (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 54.8, 88.8, 93.6, 114.0, 120.8, 122.2, 124.3, 127.2, 128.4, 129.1, 129.7, 131.9, 134.7, 160.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ −56.12 (d, J = 8.7 Hz); MS (EI, 70 eV) *m/z*: 302 (M^+, 65), 271 (100), 69 (12); Anal. Calcd for $C_{18}H_{13}F_3O$: C, 71.52; H, 4.33; Found: C, 71.38; H, 4.41.

*4.3.8. (E)-5-(4-Methoxyophenyl)-7,7,7-trifluoro-2-methylhept-5-en-3-yl-2-ol (E)-**5h***

Yield 74% (pale yellow oil). IR (thin film): 3400, 2983, 2937, 2220, 1610, 1512, 1463, 1364, 1253, 837 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.56 (s, 6H, CH_3), 1.63 (s, 1H, OH), 3.84 (s, 3H, OCH_3), 6.02 (q, J = 8.7 Hz, 1H, $CHCF_3$), 6.90 (d, J = 8.8 Hz, 2H, Ph), 7.39 (d, J = 8.8 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.5, 54.8, 65.3, 85.2, 91.8, 113.9, 121.1, 124.2, 127.0, 129.8, 133.9, 160.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ −56.13 (d, J = 8.7 Hz); MS (EI, 70 eV) *m/z*: 284 (M^+, 65), 267 (100), 236 (55); Anal. Calcd for $C_{15}H_{15}F_3O_2$: C, 63.38; H, 5.32; Found: C, 63.26; H, 5.19.

*4.3.9. (E)-4-(4-Butoxyphenyl)-N,N-diethyl-6,6,6-trifluorohex-4-en-2-yl-1-amine (E)-**5i***

Yield 98% (pale yellow oil). IR (thin film): 2968, 2363, 1611, 1511, 1270, 1109 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, J = 7.3 Hz, 3H, $OCH_2CH_2CH_2CH_3$), 1.07 (t, J = 5.7 Hz, 6H, NCH_2CH_3), 1.46 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.73 (m, 2H, OCH_2 $CH_2CH_2CH_3$), 2.53 (q, J = 5.7 Hz, 4H, NCH_2CH_3), 3.58 (s, 2H, CH_2N), 3.93 (t, J = 6.5 Hz, 2H, OCH_2CH_2 CH_2CH_3), 5.99 (q, J = 8.7 Hz, 1H, $CHCF_3$), 6.85 (d, J = 8.8 Hz, 2H, Ph), 7.38 (d, J = 8.8 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.5, 13.7, 19.1, 31.1, 41.1, 47.3, 67.5, 84.9, 89.6, 113.8, 120.5, 124.2, 127.3, 129.6, 134.3, 159.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ −55.93 (d, J = 8.7 Hz); MS (EI, 70 eV) *m/z*: 354 (M + 1, 20), 353 (M^+, 100), 221 (18); Anal. Calcd for $C_{20}H_{26}F_3NO$: C, 67.97; H, 7.42; N, 3.96. Found: C, 68.02; H, 7.49; N, 3.92.

*4.3.10. (E)-4-(4-Butoxyphenyl)-6,6,6-trifluorohex-4-en-2-yl-1-ol (E)-**5j***

Yield 86% (pale yellow oil). IR (thin film): 3345, 2961, 2206, 1611, 1511, 1271, 1131 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, J = 7.3 Hz, 3H, CH_3). 1.52 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.80 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.89 (s, 1H, OH), 3.99 (t, J = 6.5 Hz, 2H, $OCH_2CH_2CH_2CH_3$), 4.45 (s, 2H, CH_2OH), 6.06 (q, J = 8.7 Hz, 1H, $CHCF_3$), 6.89 (d, J = 8.8 Hz, 2H, Ph), 7.39 (d, J = 8.8 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 19.2, 31.2, 51.4, 67.7, 85.2, 91.8, 114.1, 121.5, 124.4, 126.8, 129.7, 133.9, 160.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ −55.95 (d, J = 8.7 Hz); MS (EI, 70 eV) *m/z*: 298 (M^+, 100), 279 (28), 243 (23); Anal. Calcd for $C_{16}H_{17}F_3O_2$: C, 64.42; H, 5.74; Found: C, 64.38; H, 5.66.

*4.3.11. (E)-1-Phenyl-3-(4-butoxyphenyl)-5,5,5-trifluoropent-3-en-1-yl (E)-**5k***

Yield 96% (pale yellow oil). IR (thin film): 3060, 2960, 2206, 1611, 1511, 1267, 1131 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.06 (t, J = 7.3 Hz, 3H, CH_3), 1.59 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.86 (m, 2H, $OCH_2CH_2CH_2CH_3$), 4.04 (t, J = 6.5 Hz, 2H, OCH_2CH_2 CH_2CH_3), 6.20 (q, J = 8.7 Hz, 1H, $CHCF_3$), 6.99 (d, J = 8.8 Hz, 2H, Ph), 7.41 (m, 3H, Ph), 7.55 (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 19.2, 31.2, 67.6, 89.0, 93.9, 114.1, 120.8, 122.1, 124.5, 127.2, 128.4, 129.2, 129.9, 131.8, 134.6, 160.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ −55.91 (d, J = 8.7 Hz); MS (EI, 70 eV) *m/z*: 344 (M^+, 28), 289 (100), 181 (17); Anal. Calcd for $C_{21}H_{19}F_3O$: C, 73.24; H, 5.56; Found: C, 73.12; H, 5.63.

*4.3.12. (E)-4-(4-Bromophenyl)-N,N-diethyl-6,6,6-trifluorohex-4-en-2-yl-1-amine (E)-**5l***

Yield 95% (pale yellow oil). IR (thin film): 2972, 2819, 2361, 2221, 1626, 1485, 1272, 1131 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, J = 5.7 Hz, 6H, CH_3), 2.56 (q, J = 5.7 Hz, 4H, CH_2CH_3), 3.61 (s, 2H, CH_2N), 6.12 (q, J = 8.5 Hz, 1H, $CHCF_3$), 7.30 (d, J = 8.4 Hz, 2H, Ph), 7.53 (d, J = 8.4 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.6, 41.4, 47.4, 84.1, 91.4, 120.4, 122.6, 124.0, 129.7, 131.4, 133.8, 134.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.50 (d, J = 8.5 Hz); MS (EI, 70 eV) *m/z*: 361/359 (M^+, 45), 221 (40); Anal. Calcd for $C_{16}H_{17}BrF_3N$: C, 53.35; H, 4.76; N, 3.89. Found: C, 53.42; H, 4.85; N, 3.85.

*4.3.13. (E)-4-(4-Bromophenyl)-6,6,6-trifluorohex-4-en-2-yl-1-ol (E)-**5m***

Yield 96% (pale yellow oil). IR (thin film): 3274, 2968, 2363, 1486, 1511, 1274, 1109 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.80 (s, 1H, OH), 4.46 (s, 2H, CH_2OH), 6.15 (q, J = 8.5 Hz, 1H, $CHCF_3$), 7.29 (d, J = 8.4 Hz, 2H, Ph), 7.54 (d, J = 8.4 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.3, 84.0, 93.1, 120.5, 123.5, 124.0,129.7,131.5, 133.8, 134.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.52 (d, J = 8.5 Hz); MS (EI, 70 eV) *m/z*: 306/304 (M^+, 100), 287/285 (30); Anal. Calcd for $C_{12}H_8BrF_3O$: C, 47.24; H, 2.64; Found: C, 47.36; H, 2.71.

*4.3.14. (E)-N,N-Diethyl-6,6,6-trifluoro-4-p-tolylhex-4-en-2-yl-1-amine (E)-**5n***

Yield 66% (pale yellow oil). IR (thin film): 2972, 2220, 1618, 1512, 1269, 1132 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.14 (t, J = 5.7 Hz, 6H, CH_2CH_3), 2.40 (s, 3H, $PhCH_3$), 2.64 (q, J = 5.7 Hz, 4H, CH_2CH_3), 3.76 (s, 2H, CH_2N), 6.28 (q, J = 7.7 Hz, 1H, $CHCF_3$), 7.20 (d, J = 8.2 Hz, 2H, Ph), 7.56 (d, J = 8.2 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.6, 21.2, 41.4, 47.4, 79.5, 97.1, 120.3, 126.6, 128.8, 129.3, 132.6, 133.2, 140.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.14 (d, J = 7.7 Hz); MS (EI, 70 eV) *m/z*: 296 (M + 1, 20), 295 (M^+, 100); Anal. Calcd for $C_{17}H_{20}F_3N$: C, 69.13; H, 6.83; N, 4.74. Found: C, 69.06; H, 6.94; N, 4.68.

*4.3.15. (E)-6,6,6-Trifluoro-4-p-tolylhex-4-en-2-yl-1-ol (E)-**5o***

Yield 52% (pale yellow oil). IR (thin film): 3364, 2928, 2363, 1709, 1616, 1512, 1271, 1129 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 1H, OH), 2.41 (s, 3H, $PhCH_3$), 4.57 (s, 2H, CH_2OH), 6.31 (q, J = 7.7 Hz, 1H, $CHCF_3$), 7.23 (d, J = 8.2 Hz, 2H, Ph), 7.56 (d, J = 8.2 Hz, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 51.5, 80.0, 98.7, 120.8, 124.6, 126.6, 129.4, 131.9, 132.6, 140.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.16 (d, J = 7.7 Hz); MS (EI, 70 eV) *m/z*: 240 (M^+, 8), 223 (44), 208 (25); Anal. Calcd for $C_{13}H_{11}F_3O$: C, 65.00; H, 4.62; Found: C, 64.89; H, 4.54.

*4.3.16. (E)-5,5,5-Trifluoro-1-phenyl-3-p-tolylpent-3-en-1-yl (E)-**5p***

Yield 96% (pale yellow oil). IR (thin film): 3058, 2958, 2206, 1709, 1616, 1490, 1268, 1129 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.46 (s, 3H, $PhCH_3$), 6.39 (q, J = 7.7 Hz, 1H, $CHCF_3$), 7.29 (d, J = 8.2 Hz, 2H, Ph), 7.45 (m, 4H, Ph), 7.60 (m, 3H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 88.6, 92.8, 119.5, 126.5, 128.3, 128.7, 129.0, 129.2, 131.5, 131.7, 132.3, 132.7, 140.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.11 (d, J = 7.7 Hz); MS (EI, 70 eV) *m/z*: 286 (M^+, 100), 271 (34). Anal. Calcd for $C_{18}H_{13}F_3$: C, 75.51; H, 4.58; Found: C, 75.43; H, 4.63.

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