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Sodium dithionite initiated addition of 1-bromo-1-chloro-2,2,2-trifluoroethane to allylaromatics Facile synthesis of conjugated dienes substituted with terminal CF_3 group

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Abstract

Sodium dithionite effectively promotes the addition of 1-bromo-1-chloro-2,2,2-trifluoroethane to the terminal double bond of allylbenzenes **1**. The reactions proceeded in MeCN/H_2O to give a 3:1 mole ratio of diastereoisomers of 1-(2-bromo-4-chloro-5,5,5-trifluoropentyl)benzenes **2** as the main products together with small amounts of its reductive debromination products **3**. Total yields of **2** and **3** were dependent on the nature of the aromatic ring substituents in **1**. Treatment of adducts **2** with DBU in refluxing hexanes resulted in double dehydrohalogenation affording, in good yields, conjugated dienes **4** (1,1,1-trifluoro-5-phenyl-2,4-pentadienes) terminated with the CF_3 group at the one end and the phenyl group at the opposite end. These dienes were found to be sufficiently reactive to undergo Diels-Alder condensation with active dienophiles to give trifluoromethylated carbocycles. The reactions of $CF_3CHClBr$ with allylheterocycles were less successful and lead to low yields of mixtures of hardly separable compounds or to polymeric resins.

Keywords: 1-Bromo-1-chloro-2,2,2-trifluoroethane; Radical addition; Sodium dithionite; Allylaromatics; Trifluoromethyl dienes

1. Introduction

The sodium dithionite initiated addition of perfluoroalkyl halides to the electron rich substrates like alkenes and alkynes, developed a long time ago by Huang [1,2], is a well-known procedure with numerous applications. Recently, this procedure has been successfully applied to the perfluoroalkylation of steroids [3], glycosides [4] and thioles [5]. This is a free radical process in which radical anions SO_2^{-}, existing in an equilibrium with dithionite anions $S_2O_4^{2-}$, abstract halogen from R_FX (X = I, Br) molecules to generate highly electrophilic perfluoroalkyl radicals. This method of generating perfluoroalkyl radicals posseses a number of advantages, i.e. aqueous medium (H_2O–CH_3CN mixture is usually used), very mild reaction conditions, simplicity and low cost of the initiator and the solvents.

We have found that sodium dithionite is also effective in generating $CF_3CHCl^{\bullet}$ radicals from 1-bromo-1-chloro-2,2,2-trifluoroethane ($CF_3CHClBr$), inexpensive and commercially available reagent known as an inhalation anaesthetic (Halothane®). In preceding papers we reported addition of 1-bromo-1-chloro-2,2,2-trifluoroethane to a number of vinyl ethers leading, after dehydrohalogenation, to valuable α,β-unsaturated carbonyl compounds substituted with the trifluoromethyl group [6,7]. The addition of $CF_3CHClBr$ to β-pinene occurred almost quantitatively and dehalogenation and reduction of the adduct gave a number of trifluoromethyl substituted terpenoids [8]. As an extension of these investigations, we studied the sodium dithionite initiated reactions of $CF_3CHClBr$ with a number of linear, branched and cyclic alkenes and in most cases good yields of the addition products were obtained [9]. However, the attempted reactions with styrene and other alkenes, in which the double bond is conjugated with an aromatic ring, totally failed. In contrast to the latter, allylbenzene and ring substituted allylbenzenes were found to be particularly reactive.

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In the present paper, we report the results of our studies on the addition of $CF_3CHClBr$ to numerous allylaromatics and allylheterocycles and dehydrohalogention reactions of the adducts, which lead to interesting conjugated dienes terminally substituted with the trifluoromethyl group.

2. Results and discussion

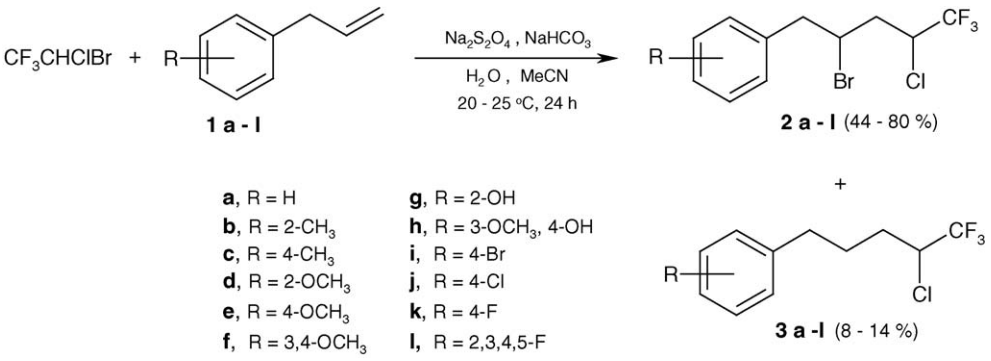
The reactions of 1-bromo-1-chloro-2,2,2-trifluoroethane with allylbenzenes **1** were carried out under typical conditions in a water–acetonitrile solution (1:1, v/v) in which sodium dithionite and sodium hydrogen carbonate (HBr scavanger) were suspended (the salts are only partially soluble in the reaction mixture). The reaction mixture was vigorously stirred at ambient temperature and organic substrates ($CF_3CHClBr$ and **1**) were added one by one. The reactions proceeded within the temperature range of 20–25 °C with evolution of carbon dioxide (formed by the reaction of SO_2 with $NaHCO_3$). In most cases, gas evolution ceased after 1 h but, to complete the reactions, stirring was continued overnight. The crude mixtures of products (after extraction with Et_2O) consisted of adducts **2** (4-bromo-2-chloro-1,1,1-trifluoro-5-phenylpentanes) as the main components together with small amounts of reductively debrominated compounds **3** and traces of unreacted alkenes **1** (Scheme 1). A 1:1 mole ratio of $Na_2S_2O_4$ to alkenes **1** was found to be necessary for the reactions to afford good yields of the products. Decreased $Na_2S_2O_4$/**1** ratio does not diminish formation of compounds **3** but resulted in lower total yields. As shown in Table 1, there is no clear evidence for the influence of electron donating substituents (Me, OMe, OH) on the total yields of compounds **2** and **3** and on their ratio. It may be, however, that the yields are increased by the presence of methoxy groups in the aromatic ring of **1f** (Table 1, entry 7). The relatively low yield of the reaction with 2-methoxyallylbenzene **1d** (entry 4) may be caused by steric reason. Electron withdrawing substituents, like halogens (entries 10–12) definitely decrease the reactivity of allylbenzenes **1j–1l** with increased formation of debrominated products. No reaction occurred with 4-nitroallylbenzene **1m** (entry 13) under any conditions. 1-Allylnaphthalene **1n** (entry 14) gave low yields of the adducts with increased amount of the debrominated compound **3n**. In this last case, decreased reactivity may be attributed to delocalisation of the electrons around large aromatic system and therefore decreased electron density at the allylic double bond.

Compounds **2** and **3** were isolated by column chromatography as inseparable mixtures (oils) and their ratios were determined from the integrated ^1H and ^{19}F NMR spectra and GC–MS analyses. In all cases, adducts **2** were found to be approximately 3:1 mixtures of two diastereoisomers. Two NMR signals for the CF_3 and CHCl groups appear in all spectra but, because of overlapping, it was not possible in every case to resolve all ^1H signals of the minor isomers (Table 2). The identity of minor compound **3** was confirmed by comparison of weak signals appearing in the NMR spectra of mixtures of products **2** + **3** with the spectra of pure compounds **3a**, **3k** and **3l** (see Section 3), which were obtained by treatment of the selected mixtures (**2a** + **3a**, **2k** + **3k** and **2l** + **3l**) with zinc metal in ethanol (Scheme 2). Not high yields of **3k** and **3l** may be attributed to a tar formation; no C–Cl bond reduction was observed.

Compounds **2** were found to be resistant to medium strong bases like pyridine and triethylamine but on treatment with DBU (1,8-diazabicyclo[5.4.0]undece-7-ene) they undergo double dehydrohalogenation (–HBr and –HCl) to give conjugated dienes **4** (1,1,1-trifluoro-5-phenyl-2,4-pentadienes) in high yields (Scheme 3 and Table 1). Thus, heating mixtures of **2** and **3** and DBU in refluxing hexanes resulted in mixtures of **4** and **3** from which, pure dienes **4** were easily separated by simple crystallisation; in only few cases additional purification was required. The ^1H NMR spectra of dienes **4** (Table 3) revealed that they are formed exclusively as the *trans,trans*-form ($^{trans}J_{HH}$ = ca. 15 Hz).

Compound **2g** substituted with the hydroxy group in the *ortho*-position in the aromatic ring, unlike all other adducts **2**, did not undergo dehydrohalogenation under basic condition but, instead, intermolecular nucleophilic substitution occured to give 2,3-dihydrobenzofuran derivative **5** (Table 1, entry 7).

Reactions of 1-bromo-1-chloro-2,2,2-trifluoroethane with allylheterocycles were much less successful. The reactions with 2-allylpyridine (**6**) and 3-allylpyridine (**10**), even with an excess of $CF_3CHClBr$ and prolonged reaction time, gave only low yields of products. In case of **6** (Scheme 4), a mixture of three compounds was obtained which were tentatively identified as **7**, **8** and **9** (GC–MS analysis only). In case of **10**, a 4:1 mixture of compounds **11** and **12** (Scheme 5) was obtained with total yield



Scheme 1.

Table 1
$Na_2S_2O_4$ initiated addition of $CF_3CHClBr$ to allylaromatics and dehydrohalogenation of the adducts with DBU

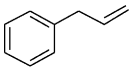
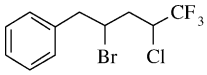
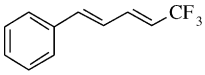
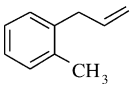
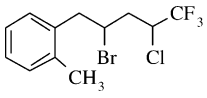
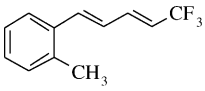
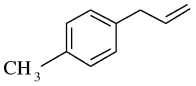
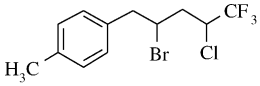
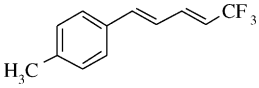
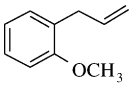
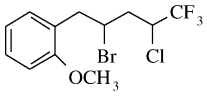
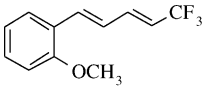
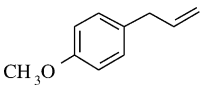
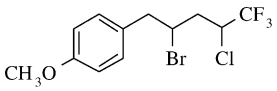
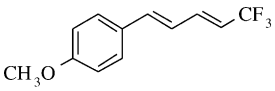
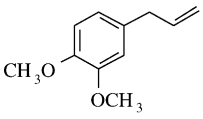
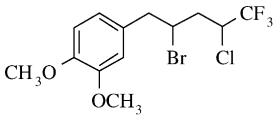
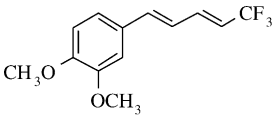
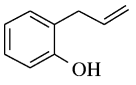
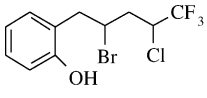
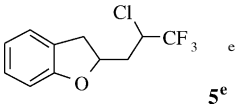
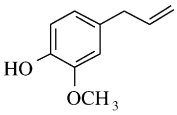
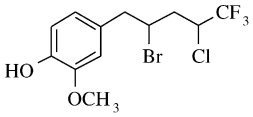
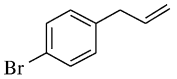
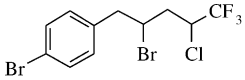
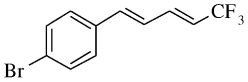
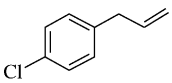
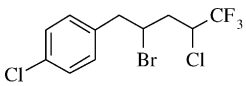
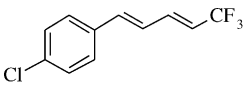
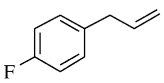
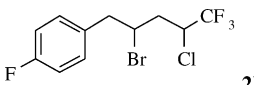
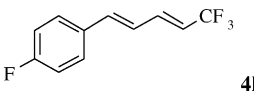
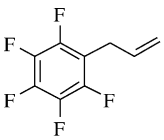
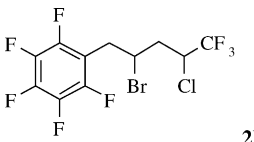
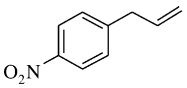
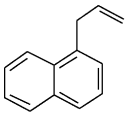
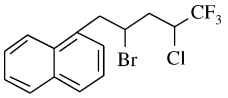
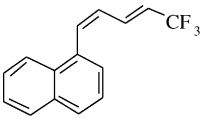
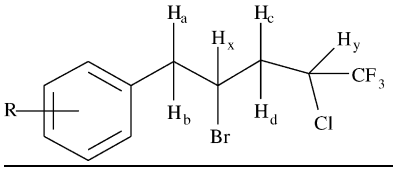
Entry	Substrate	Addition of $CF_3CHClBr$[a]		Dehydrohalogenation[b]	
		Product	Yield (%)[c]	Product	Yield (%)[c]
1	 **1a**	 **2a**	77 (incl. 13% **3a**)[d]	 **4a**	73
2	 **1b**	 **2b**	65 (incl. 8.5% **3b**)[d]	 **4b**	89
3	 **1c**	 **2c**	58 (incl. 9% **3c**)[d]	 **4c**	98
4	 **1d**	 **2d**	52 (incl. 6% **3d**)[d]	 **4d**	50
5	 **1e**	 **2e**	71 (incl. 8% **3e**)[d]	 **4e**	80
6	 **1f**	 **2f**	80 (incl. 13% **3f**)[d]	 **4f**	70
7	 **1g**	 **2g**	63 (incl. 14% **3g**)[d]	 **5**[e]	52
8	 **1h**	 **2h**	64 (incl. 12% **3h**)[d]		
9	 **1i**	 **2i**	67 (incl. 10% **3i**)[d]	 **4i**	91
10	 **1j**	 **2j**	59 (incl. 8% **3j**)[d]	 **4j**	94
11	 **1k**	 **2k**	44 (incl. 10% **3k**)[d]	 **4k**	44
12	 **1l**	 **2l**	50 (incl. 28% **3l**)[d]		
13	 **1m**	No reaction	0		

Table 1 (*Continued*)

Entry	Substrate	Addition of $CF_3CHClBr$[a]		Dehydrohalogenation[b]	
		Product	Yield (%)[c]	Product	Yield (%)[c]
14	 **1n**	 **2n**	30 (incl. 16% **3n**)[d]	 **4n**	53

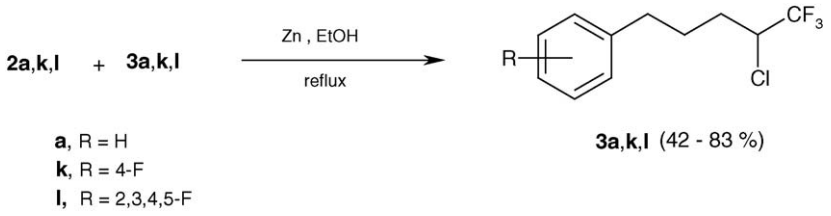
[a] Reaction conditions: $CF_3CHClBr$/allylAr/$Na_2S_2O_4$/Na_2HCO_3 ratio = 2:1:1:3; solvents: H_2O/MeCN = 1:1; temperature: 20–25 °C; time: 24 h.
[b] Reaction conditions: DBU/**2** ratio = 3:1; solvent: hexanes; temperature: reflux; time: 12–18 h.
[c] Isolated total yields of **2** and **3**.
[d] GLC estimate.
[e] Reaction conditions: EtONa/EtOH, r.t.: 12 h.

Table 2
NMR data of compounds **2**

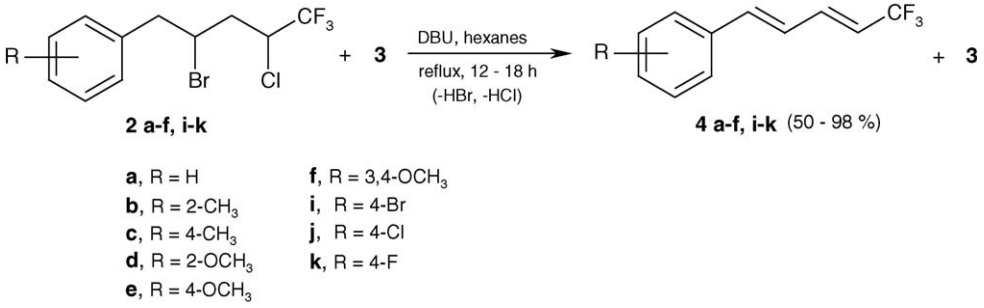


Compound, R	Chemical shift (δ, ppm)[a,b]							Coupling constants (J, Hz)								
	H_a	H_b	H_x	H_c	H_d	H_y	CF_3	H_aH_b	H_aH_x	H_bH_x	H_cH_d	H_cH_x	H_cH_y	H_dH_x	H_dH_y	H_yF
2a, H	3.20 dd	3.32 dd	4.43 dtd	2.19 ddd	2.32 ddd	4.54 dqd	−75.0 d	14.3	6.9	7.3	15.0	2.4	11.4	11.4	2.4	6.6
	3.20[c]	3.20[c]	4.35 dtd	2.44 dt	2.60 dt	n.f.	−74.0 d	14.3	n.f.	n.f.	15.2	n.f.	7.6	6.3	n.f.	6.1
2b, 2-CH_3	3.19 dd	3.38 dd	4.43 dtd	2.20 ddd	2.38 ddd	4.55 dqd	−75.0 d	14.4	7.3	7.3	15.0	2.2	11.5	11.3	2.2	6.6
	n.f.	n.f.	4.31 dtd	2.50 dt	2.63 dt	n.f.	−74.5 d	n.f.	n.f.	n.f.	15.1	n.f.	7.5	6.2	n.f.	6.5
2c, 4-CH_3	3.14 dd	3.29 dd	4.38 dtd	2.19 ddd	2.30 ddd	4.53 dqd	−75.0 d	14.3	7.1	7.2	15.0	2.4	11.5	11.3	2.4	6.6
	3.14	3.14	4.33 dtd	2.43 dt	2.59 dt	n.f.	−74.4 d	n.f.	n.f.	n.f.	15.1	n.f.	7.5	6.3	n.f.	6.4
2d, 2-CH_3O	3.23 dd	3.32 dd	4.52 dtd	2.18 ddd	2.33 ddd	4.56 dqd	−75.0 d	13.9	7.1	7.1	15.0	2.3	11.5	11.5	2.3	6.6
	3.14 dd	3.27 dd	4.36[c]	2.43 dt	2.57 ddd	n.f.	−74.7 d	14.0	7.7	5.7	15.0	n.f.	7.5	7.01	n.f.	6.5
2e, 4-CH_3O	3.13 dd	3.32 dd	4.38 dtd	2.18 ddd	2.29 ddd	4.54 dqd	−75.0 d	14.4	7.1	7.1	15.0	2.5	11.4	11.1	2.5	6.6
	3.13	3.13	4.31 dtd	2.41 dt	2.59 dt	n.f.	−74.4 d	n.f.	n.f.	n.f.	15.2	n.f.	7.6	6.25	n.f.	6.4
2f, 3,4-CH_3O	3.13 dd	3.29 dd	4.40 dtd	2.20 ddd	2.30 ddd	4.54 dqd	−75.0 d	14.3	7.1	7.01	15.0	2.4	11.3	11.2	2.5	6.6
	n.f.	n.f.	4.34 dt	2.42 dt	2.59 dt	n.f.	−74.4 d	n.f.	n.f.	n.f.	15.1	n.f.	7.6	6.3	n.f.	6.5
2g, 2-OH	3.26 dd	3.32 dd	4.53 dtd	2.24 ddd	2.36 ddd	4.60 dqd	−75.0 d	14.0	7.1	7.2	15.0	2.4	11.4	11.4	2.4	7.6
	3.18 dd	3.26	4.43 dt	2.43 dt	2.61 dt	n.f.	−74.6 d	14.2	7.7	n.f.	15.1	n.f.	7.5	6.3	n.f.	6.1
2h, 3-CH_3OH	3.11 dd	3.27 dd	4.36 dtd	2.19 ddd	2.29 ddd	4.53 dqd	−75.0 d	14.3	7.3	7.1	15.0	2.5	11.4	11.2	2.6	6.6
4-OH	n.f.	n.f.	4.32 dt	2.41 dt	2.59 dt	n.f.	−74.0 d	n.f.	n.f.	n.f.	15.1	n.f.	7.6	6.3	n.f.	6.5
2j, 4-Cl	3.18 dd	3.26 dd	4.38 dtd	2.18 ddd	2.32 ddd	4.53 dqd	−75.0 d	14.4	6.6	7.5	15.0	2.3	11.4	11.4	2.3	6.8
	3.08 dd	3.20	4.30 dt	2.44 dt	2.59 dt	n.f.	−74.4 d	14.5	8.5	n.f.	15.1	n.f.	7.6	6.3	n.f.	6.3
2k, 4-F	3.18 dd	3.27 dd	4.38 dtd	2.19 ddd	2.32 ddd	4.53 dqd	−75.0 d	14.4	6.6	7.4	15.0	2.4	11.5	11.4	2.3	6.4
	3.10 dd	3.20	4.30 dt	2.44 dt	2.59 dt	n.f.	−74.4 d	14.4	8.2	n.f.	15.1	n.f.	7.5	6.3	n.f.	6.5
2l, 1,2,3,4,5-F	3.30 dd	3.38 dd	4.41 dtd	2.24 ddd	2.44 ddd	4.51 dqd	−75.0 d	14.9	5.8	8.6	14.8	2.3	11.4	11.5	2.5	6.2
	n.f.	n.f.	4.34	2.54 dt	2.65 dt	n.f.	−74.6 d	n.f.	n.f.	n.f.	15.1	n.f.	7.6	6.3	n.f.	6.2
2n, 1-Naftyl	3.62 dd	3.82 dd	4.54 dtd	2.24 ddd	2.46 ddd	4.62 dqd	−75.0 d	14.5	7.5	7.1	15.0	2.3	11.6	11.4	2.2	6.6
	3.68 dd	n.f.	4.36[c] dt	2.56 dt	2.68 dt	[c]	−74.5 d	14.5	6.5	n.f.	15.3	n.f.	7.6	6.2	n.f.	6.4

n.f.: not found.
[a] Spectra of all compounds **2** exhibit the expected signals of the aromatic ring protons and the substituents R protons.
[b] For each compound, the upper row contains NMR data for the major diastereoisomer and the lower row for the minor diastereoisomer.
[c] The signal is overlapped by the signal of the major diastereoisomer.



Scheme 2.

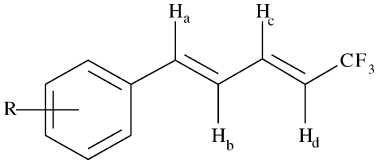


Scheme 3.

of 28%. The reactions of $CF_3CHClBr$ with 2-allylfuran and 2-allylthiofuran resulted in a polymeric tar.

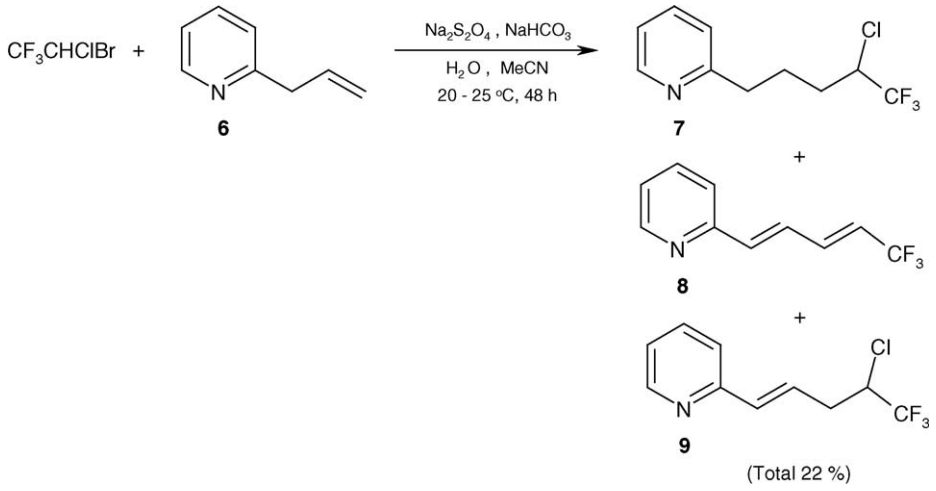
Dienes, terminally substituted with the trifluoromethyl group have been previously synthesized by the ene reactions of trifluoromethyl carbonyl compounds followed by dehydration of the resultant homoallylic alcohols [10,11]. Such dienes were reported to be sufficiently reactive to undergo Diels-Alder condensation with active dienophiles to give trifluoromethylated cyclohexenes, albeit the reaction of **4a** with maleic anhydride gave only 23% yield of the cycloadduct [11]. With the aim to check the reactivity of dienes **4**, cycloaddition reactions of **4a**, **4e** and **4f** were carried out. The reaction of **4a** with maleic anhydride gave adduct **13** as the only product in 33% yield, while from the dimethoxy substituted diene **4f**, a 46% yield of a mixture of the expected adduct **14** and aromatized compound **15** was obtained (Scheme 6). Similarly, cycloaddition of methoxy substituted diene **4e** with diethyl acetylenedicarboxylate resulted in a mixture of normal and aromatized adducts **16** and **17** in over 80% total yield (Scheme 7). These results confirm the effectiveness of trifluoromethyl substituted dienes **4** as components of the 2 + 4 cycloaddition reactions. The presence of electron donating substituents in the aromatic ring of these dienes enhances their reactivity.

Table 3
NMR data of compounds **4**

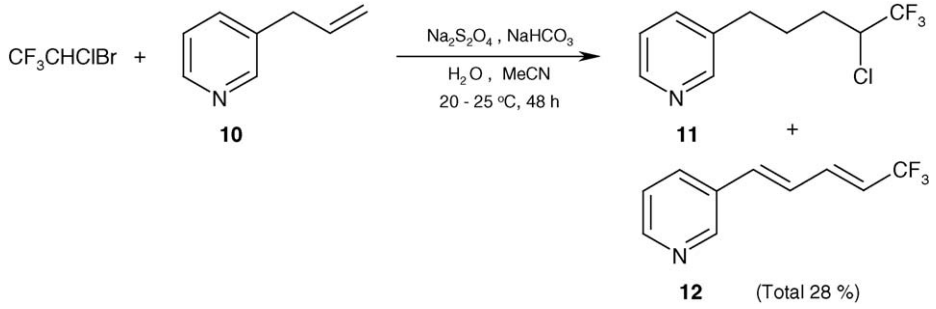


Compound, R	Chemical shift (δ, ppm)[a,b]					Coupling constants (J, Hz)			
	H_a	H_b	H_c	H_d	CF_3	H_aH_b	H_bH_c	H_cH_d	H_dF
4a, H	6.75 dd	6.81 d	6.90 ddq	5.79 dq	−63.7 d	15.6	10.0	15.3	7.0
4b, 2-CH_3	6.68 dd	7.06 d	6.94 ddq	5.79 dq	−63.7 d	15.4	10.8	15.4	7.1
4c, 4-CH_3	6.72 dd	6.79 d	6.89 ddq	5.76 dq	−63.6 d	15.5	10.0	15.3	7.0
4d, 2-CH_3O	[e]	[e]	6.96 ddq	6.03 dq	−62.7 d		10.6	15.3	7.4
4e, 4-CH_3O	6.74 dd	6.74 d	6.86[c]	5.72 dq	−63.5 d	15.6	10.6	15.3	7.0
4f, 3,4-CH_3O	6.64 dd	6.76 d	6.89[c]	5.76 dq	−63.5 d	15.6	10.5	15.4	7.0
4i, 4-Br	[d]	[d]	6.88 ddq	5.82 dq	−63.7 d	15.3	10.2	15.3	7.0
4j, 4-Cl	[e]	[e]	[e]	6.10 dq	−62.9 d			15.3	7.3
4k, 4-F	[e]	[e]	[e]	6.00 dq	−62.9 d			15.5	7.3
4e, Ar = 1-naphtyl	7.57[c]	7.13 dd	7.29 ddq	6.16 dq	−62.8 d	15.3	10.7	15.3	7.3

[a] Spectra of all compounds **4** exhibit the expected signals of the aromatic ring protons and the substituents R protons.
[b] Signals of H_a, H_b and H_c protons appear as the ABX system.
[c] Overlapped by signals of the phenyl ring protons.

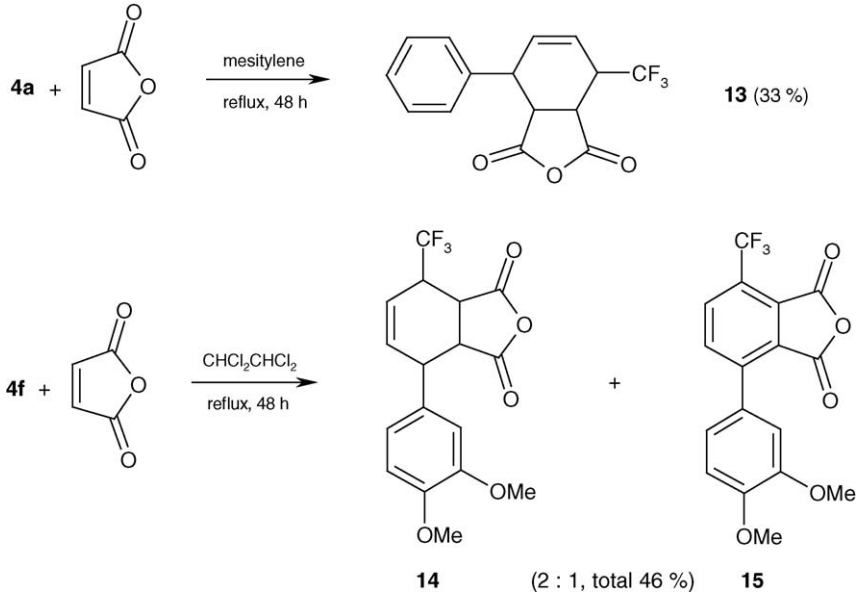


Scheme 4.

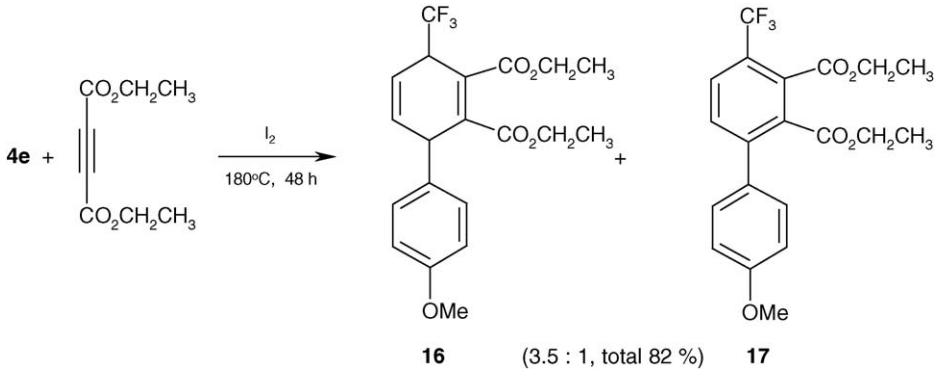


Scheme 5.

In conclusion, sodium dithionite initiated addition of $CF_3CHClBr$ to allylaromatics, followed by dehydrohalogenation of the adducts, provides an easy and effective way to dienes with terminal CF_3 groups. These dienes were found to be sufficiently reactive to undergo Diels-Alder condensation with active dienophiles to give trifluoromethylated carbocycles. The reaction is, however, less or not applicable for the addition of $CF_3CHClBr$ to allylheterocycles.



Scheme 6.



Scheme 7.

3. Experimental

Melting points were determined in capillaries and boiling points were measured during distillation; both are uncorrected. ^{1}H NMR and ^{19}F NMR spectra were recorded with a Varian 400 spectrometer, both in $CDCl_3$ or C_2D_6CO (compounds **4**) solutions. Chemical shifts are quoted in ppm from internal TMS for ^{1}H nuclei and from internal $CFCl_3$ for ^{19}F nuclei. GLC analyses were performed with a Shimadzu GC-14A Chromatograph using a 3.5 m × 2 mm column packed with 5% silicone oil SE-52 on Chromosorb. GC–MS analyses were performed with a Hewlett-Packard 5890 apparatus (30 m capillary column, HP-5 oil). Mass spectra of pure compounds were obtained with an AMD-604 spectrometer and IR spectra with a Perkin-Elmer Spectrum 2000 instrument.

1-Bromo-1-chloro-2,2,2-trifluoroethane was a commercial reagent (FLUKA). Allylbenzenes **1a–1l**, allylnaphthalene **1n** and allylpyridines **1o–1p** were prepared by allylation of the adequate magnesium aryl bromides with allylbromide [12–15].

3.1. General procedure for the reactions of $CF_3CHClBr$ with allylbenzenes

Sodium dithionite (2.1 g, 10 mmol [85%]) and sodium hydrogen carbonate (2.52 g, 30 mmol) were suspended in a water–acetonitrile solution (1:1, 40 ml). The reaction mixture was stirred vigorously at ambient temperature and allylbenzene **1** (10 mol) and 1-bromo-1-chloro-2,2,2-trifluoroethene (3.95 g, 20 mol) were added one by one. Gas evolution (CO_2) occurred which ceased after about 1 h. Stirring was continued for 24 h at ambient temperature then water (30 ml) was added, the reaction mixture was extracted with diethyl ether (3 × 40 ml) and the combined extracts were dried over $MgSO_4$. The crude mixtures of products obtained after removal of the solvent were purified by column chromatography (silica gel, hexanes or hexanes–ethanol, 4:1) to give mixtures of **2** and **3** as colorless oils. Total yields of the products are shown in Table 1 and the NMR data for compounds **2** (two diastereoisomers in a 3:1–4:1 ratio) are collected in Table 2. The MS data for compounds **2** are given below.

MS (EI, 70 eV): *m/z* (rel. int., ion):

(2-Bromo-4-chloro-5,5,5-trifluoropentyl)benzene (**2a**): 318, 316, 314 (5, 22, 17, M^+); 237, 235 [9, 24 (M-Br)$^+$]; 117 (13, $PhCH_2CH{=}CH^+$); 91 (100, $PhCH_2^+$).

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-2-methylbenzene (**2b**): 332, 330, 328 (2, 8, 6, M^+); 249, 251 [6, 2 (M-Br)$^+$]; 131 (4); 117 (5); 105 [100 $(C_8H_9)^+$]; 91 (5, $PhCH_2^+$).

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-4-methylbenzene (**2c**): 332, 330, 328 (2, 7, 5, M^+); 249, 251 [4, 2 (M-Br)$^+$]; 131 (6); 117 (5); 105 [100 $(C_8H_9)^+$]; 91 (4, $PhCH_2^+$).

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-2-methoxybenzene (**2d**): 348, 346, 344 (3, 14, 11, M^+); 267, 265 [3, 8 (M-Br)$^+$]; 229 (4); 121 [100 $(C_8H_9O)^+$]; 91 (34, $PhCH_2^+$).

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-4-methoxybenzene (**2e**): 348, 346, 344 (7, 29, 22, M^+); 267, 265 [7, 19 (M-Br)$^+$]; 147 (4); 121 [100 $(C_8H_9O)^+$].

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-3,4-dimethoxybenzene (**2f**): 378, 376, 374 (5, 20, 16, M^+); 297, 295 [8, 4 (M-Br)$^+$]; 178 (3); 151 [100 $(C_9H_{11}O_2)^+$].

2-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-phenol (**2g**): 334, 332, 330 (1, 6, 4, M^+); 252, 250 [6, 4 (M-HBr)$^+$]; 133 (12); 119 (8); 107 [100 $(C_6H_7O)^+$].

4-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-2-methoxyphenol (**2h**): 364, 362, 360 (2, 8, 6, M^+); 283, 281 [3, 8 (M-Br)$^+$]; 164 (4); 137 [100 $(C_8H_9O_2)^+$].

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-4-bromobenzene (**2i**): 396, 394, 392 (16, 35, 18, M^+); 315, 313 [8, 6 (M-Br)$^+$]; 171 (99); 169 [100 $(C_7H_6Br)^+$]; 116 (4).

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-4-chlorobenzene (**2j**): 352, 350, 348 (4, 9, 5, M^+); 269, 271 [4, 2 (M-Br)$^+$]; 181 (3); 131 (16); 127 (32); 125 [100 $(C_7H_6Cl)^+$].

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-4-fluorobenzene (**2k**): 336, 334, 332 (2, 8, 6, M^+); 255, 253 [1, 4 (M-Br)$^+$]; 147 (1); 135 (8); 109 [100 $(C_7H_6F)^+$].

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)-2,3,4,5,6-pentafluorobenzene (**2l**): 408, 406, 404 (3, 11, 9, M^+); 327, 325 [7, 21 (M-Br)$^+$]; 207 (5); 181 [100 $(C_7H_2F_5)^+$].

1-(2-Bromo-4-chloro-5,5,5-trifluoropentyl)naphthalene (**2n**): 368, 366, 364 (5, 18, 14, M^+); 287, 285 [3, 5 (M-Br)$^+$]; 249 (2); 153 (6); 141 [100 $(C_{11}H_9)^+$].

3.2. Reductive debromination of selected compounds **2**

Zinc powder (1.2 g, 18 mmol) was added to a solution of a mixture of compounds **2** and **3** (6.4 mmol, **2/3** ratio as in Table 1) in ethanol (50 ml) and the reaction mixture was

refluxed for 12 h. After cooling to ambient temperature, brine (100 ml) was added, organic oil was extracted with diethyl ether (4 × 40 ml) and the combined extracts were dried over $MgSO_4$. The crude product obtained after removal of the solvent was purified by column chromatography (silica gel, hexanes or hexanes–ethanol) to give compounds **3** as colorless oils (GLC purity 91–94%).

(4-Chloro-5,5,5-trifluoropentyl)benzene (**3a**)—yield: 83%. ^{1}H NMR δ: 1.7–1.9 (complex AB system, CH_2); 2.00 (m, CH_2); 2.66 (m, Ph*CH*$_2$); 4.06 (dqd, $^3J_{HH}$ = 10.1 Hz, $^3J_{HF}$ = 6.6 Hz, $^3J_{HH}$ = 3.0 Hz, *CH*ClCF$_3$); 7.18 (m, 1H, Ph); 7.21 (m, 2H, Ph); 7.30 (m, 2H, Ph); ^{19}F NMR δ: −75.2 (d, $^3J_{HF}$ = 6.6 Hz, CF_3); MS (EI, 70 eV): *m/z* (rel. int., ion): 238, 236 (7, 22, M^+); 117 (3, $C_9H_9^+$); 105 (5, $PhCH_2CH_2^+$); 91 (100, $PhCH_2^+$). HRMS—found: 236.05783. Calculated for $C_{11}H_{12}ClF_3$: 236.05796.

1-(4-Chloro-5,5,5-trifluoropentyl)-4-fluorobenzene (**3k**)—yield: 42%. ^{1}H NMR δ: 1.6–1.85 (complex AB system, CH_2); 1.98 (m, CH_2); 2.64 (m, Ph*CH*$_2$); 4.07 (dqd, $^3J_{HH}$ = 9.9 Hz, $^3J_{HF}$ = 6.5 Hz, $^3J_{HH}$ = 3.1 Hz, *CH*ClCF$_3$); 6.98 (tm, $^3J_{HF}$ = $^3J_{HH}$ = 8.8 Hz, 2H, Ph); 7.10 (ddm, $^3J_{HH}$ = 8.8. Hz, $^4J_{HF}$ = 5.5 Hz, 2H, Ph); ^{19}F NMR δ: −75.1 (d, $^3J_{HF}$ = 6.5 Hz, CF_3); −117.6 (tt, $^3J_{HF}$ = 8.8 Hz, $^4J_{HF}$ = 5.5 Hz, 1F$_{arom}$); MS (EI, 70 eV): *m/z* (rel. int., ion): 256, 254 (5, 15, M^+); 218 [1 (*M*-HCl)$^+$]; 135 (4, $C_9H_8F^+$); 109 [100 (C_7H_6F)$^+$]. HRMS—found: 254.04759. Calculated for $C_{11}H_{11}ClF_4$: 254.04854.

1-(4-Chloro-5,5,5-trifluoropentyl)-2,3,4,5,6-pentafluorobenzene (**3l**)—yield: 50%. ^{1}H NMR δ: 1.7–1.9 (m, CH_2); 2.00 (m, CH_2); 2.02 (m, 2H, CH_2); 2.77 (m, Ph*CH*$_2$); 4.10 (dqd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HF}$ = 6.6 Hz, $^3J_{HH}$ = 3.2 Hz, *CH*ClCF$_3$); ^{19}F NMR δ: −75.2 (d, $^3J_{HF}$ = 6.6 Hz, CF_3); −144.6 (dd, $^3J_{FF}$ = 21.9 Hz, $^4J_{FF}$ = 8.6 Hz, 2F$_{arom}$); −157.3 (t, $^3J_{FF}$ = 20.7 Hz, 1F$_{arom}$); −162.7 (td, $^3J_{FF}$ = average 21.3 Hz, $^4J_{FF}$ = 8.6 Hz, 2F). MS (EI, 70 eV): *m/z* (rel. int., ion): 328, 326 (4, 13, M^+); 290 [2 (*M*-HCl)$^+$]; 207 (6, $C_9H_4F_5^+$); 181 [100 ($C_7H_2F_5$)$^+$]; HRMS—found: 326.01058. Calculated for $C_{11}H_7F_8Cl$: 326.01085.

3.3. General procedure for dehydrohalogenation of compounds 2

A mixture of compounds **2** and **3** (12–25 mmol, **2/3** ratio as in Table 1) was dissolved in hexane (50–100 ml) and 3 equivalents of DBU was added dropwised. A precipitate was immediately formed. After refluxing for 12–18 h, the mixture was cooled to ambient temperature and 5% hydrochloric acid (20 ml) was added. The hexane layer was separated, washed with 5% HCl followed by brine and dried over $MgSO_4$. Evaporation of the solvent gave solid (in most cases) or oily (**4b**, **4d** and **4k**) material. Recrystallization of solid products from hexane or hexane–ethanol gave pure compounds **4a**–**4c**, **4e**, **4f**, **4i**, **4j** and **4n** as white crystals. Liquid compounds **4b**, **4d** and **4k** were purified by column chromatography (silica gel, hexane or hexane–ethanol). Isolated yields and melting points of compounds **4** are collected in Table 1. The MS data and elemental analyses are given below.

(*E*,*E*-5,5,5-Trifluoropenta-1,3-dienyl)benzene (**4a**): mp 32–33 °C. MS (EI, 70 eV): *m/z* (rel. int., ion): 198 (99, M^+); 179 [10 (*M*-F)$^+$]; 177 (21); 129 [100 (*M*-CF$_3$)$^+$]. Analysis—found: C, 66.8%, H, 4.4%, F, 28.2%. Calculated for $C_{11}H_9F_3$ (198.18): C, 66.7; H, 4.6; F, 28.7%.

1-Methyl-2-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)benzene (**4b**): colorless liquid, GLC purity 90% (7% of **3b**). MS (EI, 70 eV): *m/z* (rel. int., ion): 212 (84, M^+); 197 [19 (*M*-CH$_3$)$^+$]; 193 [6 (*M*-F)$^+$]; 177 [32 (*M*-CH$_3$-HF)$^+$]; 143 [62 (*M*-CF$_3$)$^+$]; 128 [35 (*M*-CF$_3$-CH$_3$)$^+$]; 115 (9). HRMS—found: 212.08089. Calculated for $C_{12}H_{11}F_3$: 212.08129.

1-Methyl-4-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)benzene (**4c**): mp 80–83 °C. MS (EI, 70 eV): *m/z* (rel. int., ion): 212 (96, M^+); 197 [24 (*M*-CH$_3$)$^+$]; 193 [7 (*M*-F)$^+$]; 177 [42 (*M*-CH$_3$-HF)$^+$]; 143 [100 (*M*-CF$_3$)$^+$]; 128 [68 (*M*-CF$_3$-CH$_3$)$^+$]; 115 (13). Analysis—found: C, 67.7; H, 4.95; F, 26.6%. Calculated for $C_{12}H_{11}F_3$ (212, 21): C, 67.9; H, 5.2; F, 26.9%.

1-Methoxy-2-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)benzene (**4d**): colorless liquid, GLC purity 94% (3% of **3d**). MS (EI, 70 eV): *m/z* (rel. int., ion): 228 (100, M^+); 209 [8 (*M*-F)$^+$]; 177 [9 (*M*-OCH$_3$-HF)$^+$]; 159 [55 (*M*-CF$_3$)$^+$]. HRMS—found: 228.07610. Calculated for $C_{12}H_{11}F_3O$: 228.07620.

1-Methoxy-4-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)benzene (**4e**): mp 76–78 °C. MS (EI, 70 eV): *m/z* (rel. int., ion): 228 (100, M^+); 209 [8 (*M*-F)$^+$]; 159 [59 (*M*-CF$_3$)$^+$]; 144 [29, *M*-CF$_3$-CH$_3$)$^+$]. Analysis—found: C, 63.2: H, 4.7; F, 24.9%. Calculated for $C_{12}H_{11}F_3O$ (228.21): C, 63.2; H, 4.9; F, 25.0%.

1,2-Dimethoxy-4-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)-benzene (**4f**): mp 79–80 °C. MS (EI, 70 eV): *m/z* (rel. int., ion): 258 (100, M^+); 239[10 (*M*-F)$^+$]; 227 [16 (*M*-OCH$_3$)$^+$]; 189 [75 (*M*-CF$_3$)$^+$]; 174 [13 (*M*-CF$_3$-CH$_3$)$^+$]; 158 [13 (*M*-CF$_3$-OCH$_3$)$^+$]. Analysis—found: C, 60.5; H, 4.8; F, 22.2%. Calculated for $C_{13}H_{13}F_3O_2$ (258): C, 60.5; H, 5.1; F, 22.1%.

1-Bromo-4-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)benzene (**4i**): mp 43–45 °C. MS (EI, 70 eV): *m/z* (rel. int., ion): 278, 276 (65, M^+); 209 [3 (*M*-CF$_3$)$^+$]; 197 [40 (*M*-Br)$^+$]; 177 [100 (*M*-Br-HF)$^+$]; 171 [22]; 169 [22]; 128 [76 (*M*-CF$_3$-Br)$^+$]. Analysis—found: C, 47.5; H, 2.7; F, 20.2%. Calculated for $C_{11}H_8F_3Br$ (277.08): C, 47.7; H, 2.9; F, 20.6%.

1-Chloro-4-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)benzene (**4j**): mp 43–44 °C. MS (EI, 70 eV): *m/z* (rel. int., ion): 232, 234 (61, M^+); 197 [54 (*M*-Cl)$^+$]; 177 [100 (*M*-HF-Cl)$^+$]; 163 [26 (*M*-CF$_3$)$^+$]; 128 [84 (*M*-CF$_3$-Cl)$^+$]; 127 [54 (*M*-CF$_3$-HCl)$^+$]. Analysis—found: C, 56.3; H, 3.2; F, 24.0%. Calculated for $C_{11}H_8F_3Cl$ (232.63): C, 56.8; H, 3.5; F, 24.5%.

1-Fluoro-4-(*E*,*E*-5,5,5-trifluoropenta-1,3-dienyl)benzene (**4k**): colorless liquid, GLC purity 80% (15% of **3k**). MS (EI, 70 eV): *m/z* (rel. int., ion): 216 (50, M^+); 197 [7 (*M*-F)$^+$]; 147 [100 (*M*-CF$_3$)$^+$]; 127 [26 (*M*-CF$_3$-HF)$^+$]; [109 (96, C_7H_6F)$^+$, **3k**]. HRMS—found: 216.05656. Calculated for $C_{11}H_8F_4$: 216.05621.

1-(*E*,*E*-5,5,5-Trifluoropenta-1,3-dienyl)naphthalene (**4n**): mp 50–52 °C. MS (EI, 70 eV): *m/z* (rel. int., ion): 248 (74, M^+); 229 [4 (*M*-F)$^+$]; 179 [100 (*M*-CF$_3$)$^+$]. Analysis—found: C, 72.1; H, 4.2; F, 22.6%. Calculated for $C_{15}H_{11}F_3$ (248.24): C, 72.6; H, 4.5; F, 23.0%.

3.4. Preparation of 2-(2-chloro-3,3,3-trifluoropropyl)-2,3-dihydrobenzofuran (**5**)

Compound **2g** (1.5 g, 4.5 mmol) was added to ethanolic sodium ethoxide (4.6 mmol) solution and the reaction mixture was stirred at ambient temperature for 24 h. The reaction was quenched with 5% hydrochloric acid (15 ml) and the organic material was extracted with ether (2 × 30 ml), the extract was washed with 5% hydrochloric acid followed by water and dried over Na_2SO_4. The crude product obtained after evaporation of the solvent was purified by column chromatography (silica gel, hexanes–ethanol, 4:1) to give **5** as colorless oil (0.6 g, two diastereoisomers in a 3.8:1 ratio). Yield: 52%, GLC purity: 90%. Major isomer: ^{1}H NMR: 2.38 (narrow AB system, $^2J_{HH}$ = 14.5 Hz, 2H, CH_2CHCl); 2.90 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 7.0 Hz, 1H); 3.38 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 9.0 Hz, 1H); 4.36 (dq, $^3J_{HH}$ = 7.8 Hz, $^3J_{HF}$ = 6.5 Hz, 1H, CHCl); 5.00 (dq, $^3J_{HH}$ = 9.0 and 7.0 Hz, 1H); 6.79 (m, 1H, arom.); 6.87 (m, 1H, arom.); 7.15 (m, 2H, arom.). ^{19}F NMR: −74.65 (d, $^3J_{HF}$ = 6.5 Hz, CF_3). Minor isomer: ^{1}H NMR: ca. 2.4 (overlapped by signal of the major isomer, 2H), ca. 2.9 (overlapped, 1H); 3.34 (dd, $^2J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 9.0 Hz, 1H); 4.54 (dqd, $^3J_{HH}$ = 11.8 Hz, $^3J_{HF}$ = 6.5 Hz, $^3J_{HH}$ = 2.1 Hz, 1H, CHCl); 5.07 (m, 1H). ^{19}F NMR: −75.5 (d, $^3J_{HF}$ = 6.5 Hz, CF_3). HRMS—found: 250.03628. Calculated for $C_{11}H_{10}ClF_3O$: 250.03723.

3.5. Reaction of $CF_3CHClBr$ with 2-allylpyridine

2-Allylpyridine (**6**) (0.23 g, 2.3 mmol), $CF_3CHClBr$ (0.92 g, 4.7 mmol), $Na_2S_2O_4$ (0.5 g, 2.3 mmol) and $NaHCO_3$ (0.57 g, 6.9 mmol) were reacted in a MeCN–H_2O solution as in Section 3.1. GLC analysis of an aliquot taken after 24 h showed only partial conversion of **6**. Additional portion of $Na_2S_2O_4$ (0.25 g) and $CF_3CHClBr$ (0.46 g) were added and the reaction was continued for another 24 h and worked up. An oily product obtained after column chromatography (0.23 g, total yield 22%) consisted of compounds **7**–**9** in a 1:2:2 ratio (GC–MS identification only).

GC–MS: *m/z* (rel. int., ion):

2-(4-Chloro-5,5,5-trifluoropentyl)pyridine (**7**): 202 [100 (*M*-Cl)$^+$]; 182 [30 (*M*-Cl-HF)$^+$]; 120 [60 ($C_8H_{10}N$)$^+$]; 106 [20 (C_7H_8N)$^+$]; 93 [50 (C_6H_7N)$^+$]; 78 [15 (C_5H_4N)$^+$].

2-(5,5,5-Trifluoropenta-1,3-dienyl)pyridine (**8**): 199 (40, M^+); 180 [8 (*M*-F)$^+$]; 130 [100 (*M*-CF_3)$^+$]; 78 [10 (C_5H_4N)$^+$].

2-(4-Chloro-5,5,5-trifluoropent-1-enyl)pyridine (**9**): 237, 235 (7, 20, M^+); 200 [33 (*M*-Cl)$^+$]; 180 [10 (*M*-Cl-HF)$^+$]; 130 [25 (*M*-Cl-CF_3)$^+$]; 118 [100 ($C_8H_8N^+$]; 78 [12 (C_5H_4N)$^+$].

3.6. Reaction of $CF_3CHClBr$ with 3-allylpyridine

3-Allylpyridine (**10**) (0.74 g, 6.2 mmol), $CF_3CHClBr$ (2.45 g, 12 mol), $Na_2S_2O_4$ (1.3 g, 6.2 mmol) and $NaHCO_3$ (1.56 g, 18.6 mmol) were reacted as in Section 3.5. The crude mixture of products, obtained after extraction with Et_2O and removal of the solvent, was treated with DBU (2.8 g, 18 mmol) in hexanes as described in Section 3.3 and purified by column chromatography (silica gel, hexanes–AcOEt, 5:1) to give a yellowish oil (0.36 g, total yield 28%) consisted of inseparable compounds **11** and **12** in a 4:1 ratio (^{19}F NMR estimate).

3-(4-Chloro-5,5,5-trifluoropentyl)pyridine (**11**): ^{1}H NMR: 1.80 (m, 2H); 2.02 (m, 2H); 2.67 (m, 2H); 4.10 (dqd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HF}$ = 6.6 Hz, $^3J_{HH}$ = 3.0 Hz, 1H, CHCl). ^{19}F NMR: −75.2 (d, $^3J_{HF}$ = 6.6 Hz, CF_3). GC–MS: *m/z* (rel. int., ion): 239, 237 (10, 30, M^+); 106 [6 (C_7H_8N)$^+$]; 92 [100 (C_6H_6N)$^+$].

3-(5,5,5-Trifluoropenta-1,3-dienyl)pyridine (**12**): ^{1}H NMR: 5.68 (dq, $^3J_{HH}$ = 15.2 Hz, $^3J_{HF}$ = 6.9 Hz, 1H, H_4); 6.91 (ddq, $^3J_{HH}$ = 15.2 and 10.6 Hz, $^4J_{HF}$ = 2.1 Hz, 1H, H_3). ^{19}F NMR: −64.0 (dd, $^3J_{HF}$ = 6.9 Hz, $^4J_{HF}$ = 2.1 Hz, CF_3). GC–MS: *m/z* (rel. int., ion): 199 (60, M^+); 180 [6 (*M*-F)$^+$]; 130 [100 (*M*-CF_3)$^+$]; 103 (15, $C_7H_5N^+$); 77 [12 (C_5H_3N)$^+$].

The ^{1}H NMR signals of the pyridine ring protons of both **11** and **12** and of two vinylic protons of **12** appeared within the range of 6.8–8.7 ppm and overlapped each other.

3.7. Reactions of compounds ***4*** with dienophiles

3.7.1. Reaction of ***4a*** with maleic anhydride

Diene **4a** (1.48 g, 7.5 mmol), maleic anhydride (0.78 g, 8 mmol) and mesitylene (1 ml) were heated at reflux for 48 h. After cooling to ambient temperature, the reaction mixture was dissolved in ethyl acetate, the solution was washed with water (removal of maleic anhydride), dried over $MgSO_4$. A solid material obtained after removal of the solvents was purified by column chromatography (silica gel, hexanes–ethanol, 4:1) to give compound **13** as brownish solid (0.74 g, yield: 33%).

4-Phenyl-7-trifluoromethyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (**13**): mp 165–168 °C. ^{1}H NMR (in acetone-d_6): 3.72 (m, 1H); 4.02 (m, 1H); 4.14 (dd, $^3J_{HH}$ = 9.2, 6.8 Hz, 1H); 4.24 (dd, $^3J_{HH}$ = 9.2, 6.2 Hz, 1H); 6.30 (m, 1H); 6.72 (m, 1H); 7.32 (m, 2H, arom.); 7.40 (m, 3H, arom.). ^{19}F NMR (in acetone-d_6): −61.9 ($^3J_{HF}$ = 10.3 Hz, CF_3). MS (EI): *m/z* (rel. int., ion): 296 (35, M^+); 268 [10 (*M*-CO)$^+$]; 224 [18 (*M*-C_2O_3)$^+$]; 223 [26 (*M*-C_2HO_3)$^+$]; 198 [75 (*M*-$C_4H_2O_3$)$^+$]; 183 (12); 155 (30); 129 (100, $C_{10}H_9^+$). Analysis—found: C, 60.9; H, 3.7; F, 19.2%. Calculated for $C_{15}H_{11}F_3O_3$ (296.24): C, 60.8; H, 3.7; F, 19.4%.

3.7.2. Reaction of ***4f*** with maleic anhydride

Compound **4f** (0.52 g, 2 mmol), maleic anhydride (0.25 g, 2.5 mmol) and $CHCl_2CHCl_2$ (1 ml) were heated at reflux for 48 h and worked up as above. Purification of the crude product by column chromatography (silica gel, hexanes–ethyl acetate, 3:2) gave a 2:1 mixture of compounds **14** and **15** (^{19}F NMR estimate) as yellowish solid (mp 134–138 °C, 0.33 g, total yield: 46%).

4-(3,4-Dimethoxyphenyl)-7-trifluoromethyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (**14**): ^{1}H NMR: 3.26 (m, 1H); 3.69 (m, 2H); 3.81 (dd, $^3J_{HH}$ = 8.6, 6.8 Hz, 1H); 3.87 (s, CH_3); 3.89 (s, CH_3); 6.21 (ddd, $^3J_{HH}$ = 9.4, 3.3, 2.2 Hz, 1H, vinylic); 6.48 (dm, $^3J_{HH}$ = 9.4 Hz, 1H, vinylic); 6.75 (d, $^3J_{HH}$ = 2.2 Hz, 1H, arom.); 6.82 (dd, $^3J_{HH}$ = 8.2, 2.0 Hz, 1H, arom.); 6.88 (d,

$^3J_{HH}$ = 8.2 Hz, 1H, arom.). ^{19}F NMR: −66.5 (d, $^3J_{HF}$ = 9.7 Hz, CF_3). GC–MS: *m/z* (rel. int., ion): 356 (100, M^+); 328 [25 (M-CO)$^+$]; 297 [12 (M-CO-OCH_3)$^+$]; 283 [58 (M-CO_3H)$^+$]; 189 (62, $C_{12}H_{13}O_2^+$); 128 (23, $C_{10}H_8^+$). HRMS—found: 356.08805. Calculated for $C_{17}H_{15}F_3O_5$: 356.08716.

4-(3,4-Dimethoxyphenyl)-7-trifluoromethyl-isobenzofuran-1,3-dione (**15**): ^{1}H NMR: 3.94 (s, CH_3); 3.97 (s, CH_3); 7.02 (d, $^3J_{HH}$ = 8.3 Hz, 1H, arom.); 7.12 (d, $^3J_{HH}$ = 2.06 Hz, 1H, arom.); 7.16 (dd, $^3J_{HH}$ = 8.3, 2.06 Hz, 1H, arom.); 7.96 (d, $^3J_{HH}$ = 8.1 Hz, 1H, vinylic); 8.14 (d, $^3J_{HH}$ = 8.1 Hz, 1H, vinylic). ^{19}F NMR: −61.92 (s, CF_3). GC–MS: *m/z* (rel. int., ion): 352 (100, M^+); 280 (8); 237 (6); 193 (12). HRMS—found: 352.05671. Calculated for $C_{17}H_{11}F_3O_5$: 352.05586.

*3.7.3. Reaction of **4e** with acetylenedicarboxylic acid diethyl ester*

Compound **4e** (1.14 g, 5 mmol), diethyl acetylenedicarboxylate (0.89 g, 5 mmol) and catalytic amount of iodine (1–2 mg) were heated and stirred at 170–180 °C for 48 h. Purification of the crude product by column chromatography (silica gel, hexanes–ethanol, 4:1) gave a 3.5:1 mixture of compounds **16** and **17** (^{19}F NMR estimate) as yellow oil (1.62 g, total yield: 82%).

3-(4-Methoxyphenyl)-6-trifluoromethylcyclohexa-1,4-diene-1,2-dicarboxylic acid diethyl ester (**16**): ^{1}H NMR: 1.07 (t, $^3J_{HH}$ = 7.15 Hz, CH_3); 1.28 (t, $^3J_{HH}$ = 7.15 Hz, CH_3); 3.79 (s, OCH_3); 4.05 (q, $^3J_{HH}$ = 7.15 Hz, CH_2); 4.09 (q, $^3J_{HH}$ = 7.15 Hz, CH_2); 4.26 (qd, $^3J_{HF}$ = 7.2 Hz, $^3J_{HH}$ = 3.3 Hz, 1H, $CHCF_3$); ca. 4.3 (1H, overlapped by the signal at 4.26); 5.80 (ddd, $^3J_{HH}$ = 10.0 and 3.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, vinylic); 6.04 (ddd, $^3J_{HH}$ = 10.0 and ca. 4 Hz, $^4J_{HH}$ = ca. 1 Hz, 1H, vinylic); 6.85 (d, $^3J_{HH}$ = 8.8 Hz, 2H, arom.); 7.16 (d, $^3J_{HH}$ = 8.8 Hz, 2H, arom.).^{19}F NMR: −68.6 (d, $^3J_{HF}$ = 7.2 Hz, CF_3). GC–MS: *m/z* (rel. int., ion): 398 (8, M^+); 352 [14 (M-C_2H_5OH)$^+$]; 283 [67 ($C_{17}H_{15}O_4$)$^+$]; 255 [100 ($C_{16}H_{15}O_3$)$^+$]; 237 (12); 209 (8); 168 (8); 139 (12); 108 (12). HRMS—found: 398.13434. Calculated for $C_{20}H_{21}F_3O_5$: 398.13411.

4′-Methoxy-4-trifluoromethylbiphenyl-2,3-dicarboxylic acid diethyl ester (**17**): ^{1}H NMR: 1.03 (t, $^3J_{HH}$ = 7.15 Hz, CH_3); 1.38 (t, $^3J_{HH}$ = 7.15 Hz, CH_3); 3.85 (s, OCH_3); 4.09 (q, $^3J_{HH}$ = 7.15 Hz, CH_2); 4.39 (q, $^3J_{HH}$ = 7.15 Hz, CH_2); 6.95 (d, $^3J_{HH}$ = 8.8 Hz, 2H); 7.27 (d, $^3J_{HH}$ = 8.8 Hz, 2H); 7.78 (d, $^3J_{HH}$ = 8.6 Hz, 1H); 7.85 (d, $^3J_{HH}$ = 8.6 Hz, 1H). ^{19}F NMR: −59.8 (s, CF_3). GC–MS: *m/z* (rel. int., ion): 396 (100, M^+); 368 [4 (M-CO)$^+$]; 351 (12); 303 (33); 283 (17); 207 (12). HRMS—found: 396.12013. Calculated for $C_{20}H_{19}F_3O_5$: 396.11846.

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