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A novel approach to fluoro-containing alkenes

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Abstract—A new and general one-pot transformation of aromatic aldehydes to fluorinated olefins containing $-CH{=}C(Cl)CF_3$ or $-CH{=}C(F)CClF_2$ moieties is described. Freons CCl_3CF_3 and CCl_2FCClF_2 were used as trifluoromethyl and difluoromethyl C_2-building blocks respectively. A proposed mechanism for the reaction is discussed. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Fluorine-containing drugs and pesticides have achieved an increasing interest in modern bioorganic chemistry due their remarkable biological activity.[1] Pharmaceutical and agricultural chemicals that contain di- and trifluoromethyl groups have been the subject of increased research activity in recent years. Extensive studies have been made to develop a cheaper and more efficient synthetic methodology for the introduction of the trifluoromethyl and difluoromethyl group into various organic compounds. Usage of new reagents and improved techniques for the selective introduction of fluorine has become a major target in fluoroorganic chemistry.

Synthetic pyrethroids containing the $CH{=}C(Cl)CF_3$ moiety were found the highly important.[2,3] Compounds containing this group are also widely used as synthetic precursors of trifluoromethylacetylenes in the synthesis of heterocycles bearing trifluoromethyl group.[4,5] 1,1,1-Trihalo-2,2,2-trifluoroethanes are usually employed as a trifluoromethyl C_2-synthon for the preparation of such alkenes due to their commercial availability. The classical route to 2-chloro-3,3,3-trifluoroprop-1-enylbenzenes is the reductive coupling of 1,1,1-trichloro-2,2,2-trifluoromethane (freon-113a) or $CHClBrCF_3$ (halothane)[6] with aldehydes. As a rule, literature approaches for the introduction of C-2 fluorinated fragments are based on the use of either phosphorus chemistry (Wittig approach)[7] or organometallic chemistry (demands equivalent quantities of metal reductants)[2,3,8–13] or on the combination of these two methods. Alternative procedures include the electroreductive coupling of freon-113a with aldehydes[14] An organomercury reagent also was suggested for the synthesis of such alkenes.[15]

Recently we have elaborated a novel synthesis of 1,1-dichlorostyrenes from benzaldehydes using a non-Wittig approach. The method is based on a new catalytic redox reaction between *N*-unsubstituted hydrazones and carbon tetrachloride in the presence of copper(I) chloride and aqueous ammonia, leading to the formation of the carbon–carbon double bond.[16,17] We also developed a one-pot technique for the transformation of aldehydes into the corresponding dichloroalkenes via hydrazones formed in situ.[18] The target dichlorostyrenes were obtained in high yields.

We propose that founded reaction has general significance and may be used for the preparation of various types of alkenes. An analogous approach can be applied to the synthesis of 3-chloro-2,3,3-trifluoroprop-1-enylbenzenes **1** and 2-chloro-3,3,3-trifluoroprop-1-enylbenzenes **2** in the case of chlorofluorocarbons CFC-113 and CFC-113a (Scheme 1). Now we report the results of our investigations on the use of CFC-113 and CFC-113a as difluoromethyl- and trifluoromethyl-containing C_2-building blocks for the preparation of fluorinated alkenes from aromatic aldehydes.

2. Results and discussion

2.1. Optimization of the reaction conditions

We started our investigation with the reaction between the hydrazone of *p*-nitrobenzaldehyde and freon-113. This hydrazone was chosen as a representative substrate due to its stability. Previously we had found optimal conditions for the reaction between CCl_4 and hydrazones (DMSO as

Keywords: catalysis; copper salts; fluoroalkenes; aromatic aldehydes; freons.

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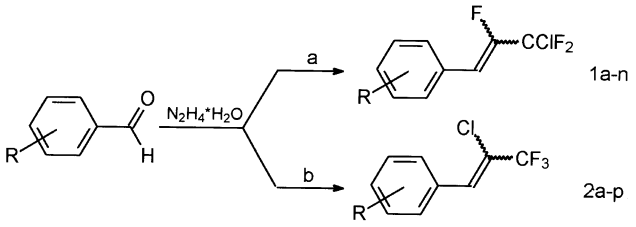
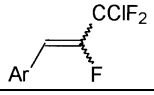
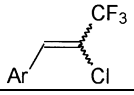


Scheme 1. a: Cu_2Cl_2, CCl_2F-$CClF_2$ (CFC-113); b: Cu_2Cl_2, CCl_3-CF_3 (CFC-113a).

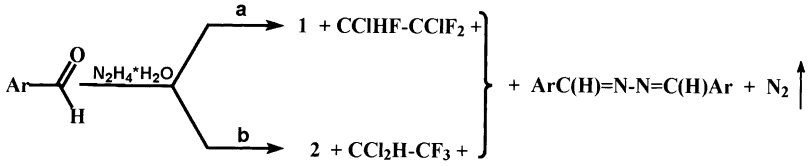
solvent, CuCl 10 mol% as catalyst and aqueous ammonia as base).[17] However, using these conditions, only traces of the desired fluorinated alkene **1a** were obtained. In our opinion, this difference can be explained by the lower oxidizing ability of freon-113 in comparison with CCl_4. We have suggested that the main factors affecting the yield of the target product are the nature of the solvent and base used. We proposed that the formation of a complexes between the copper salt, base and solvent molecules plays a significant role in the catalytic activity. A variety of bases such as amines, diamines, aminoalcohols, aminoacids, pyridines, potassium carbonate in some polar solvents: ethanol, acetonitrile, DMSO, DMF were tested. In most cases no reaction occurred and only traces of **1a** were obtained. The maximum yield of **1a** (39%) was obtained when the reaction was carried out in ethanol using 1,2-ethylenediamine as base. Previously we elaborated the one-pot technique for the synthesis of dichlorostyrenes without isolation of hydrazones.[18] It was found that yields of alkenes in general were better than those in sequential two-stage procedures. This approach was applied to the fluorinated alkene **1a** and the yield of **1a** was increased up to 63% by the one-pot technique.

Having found the optimal reaction conditions, we tried to study the scope and limitations of the technique. A wide range of aromatic aldehydes was converted to the corre-

Table 1. Synthesis of fluorinated alkenes

Ar				
	Yield (%)	*Z*/*E* ratio[a]	Yield (%)	*Z*/*E* ratio[b]
4-$O_2NC_6H_4$, **a**	63	6/1	67	7/1
3-$O_2NC_6H_4$, **b**	43	4/1	57	3/1
4-ClC_6H_4, **c**	46	10/1	73	3/1
3-ClC_6H_4, **d**	48	11/1	57	4/1
4-$CH_3OC_6H_4$, **e**	49	19/1	56	10/1
4-BrC_6H_4, **f**	55	6/1	63	6/1
C_6H_5, **g**	39	13/1	27	6/1
4-NCC_6H_4, **h**	35	6/1	61	3/1
4-$CH_3C_6H_4$, **i**	66	16/1	72	6/1
4-FC_6H_4, **j**	36	13/1	34	4/1
2-FC_6H_4, **k**	33	4/1	32	3/1
2-ClC_6H_4, **l**	24	7/1	40	4/1
Terephthalaldehyde, **m**	19	86/13/1[c]	24	2/1[d]
1-Naphthyl, **n**	48	10/0	47	10/0
4-$Me_2NC_6H_4$, **o**	–	–	31	10/0
2-$CH_3OC_6H_4$, **p**	–	–	22	6/1
2-$CF_3C_6H_4$	–	–	Trace	–
2,6-$Cl_2C_6H_3$	–	–	–	–

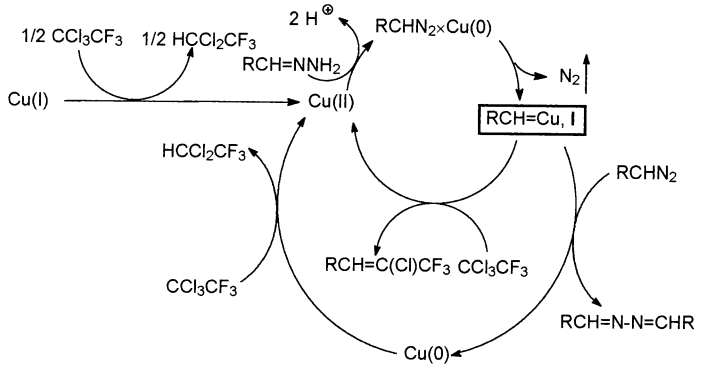
[a] The structure of isomers was established by comparison of $^3J_{H-F}$ ($J_{trans}\approx 34$ Hz$>J_{cis}\approx 20$ Hz).
[b] The structure of isomers was determined according by Fujita[8–10] and Dmowski.[19,20]
[c] Mixture of (*Z*,*Z*), (*Z*,*E*) and (*E*,*E*) isomers.
[d] Mixture of (*Z*,*Z*) and (*Z*,*E*) isomers.



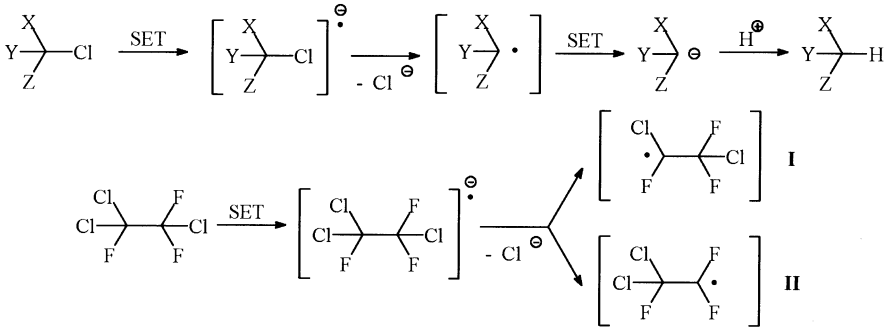
Scheme 2. a: Cu_2Cl_2, CCl_2F-$CClF_2$ (CFC-113); b: Cu_2Cl_2, CCl_3-CF_3 (CFC-113a).

Table 2.

Aldehyde	Yield (%)					
	Azine	Fluoroalkene **1**	Total	Azine	Fluoroalkene **2**	Total
4-$O_2NC_6H_4$	32	63	95	25	67	92
4-$CH_3C_6H_4$	27	66	93	24	72	96
4-$Me_2NC_6H_4$	92	0	92	65	31	96



Scheme 3.



Scheme 4.

sponding 3-chloro-2,3,3-trifluoroprop-1-enylbenzenes **1** and 2-chloro-3,3,3-trifluoroprop-1-enylbenzenes **2** bearing various substituents in the aromatic ring. In most cases the reaction proceeded smoothly to give the target products in good yield (Table 1).

2.2. Reaction mechanism

The synthesis of fluorinated alkenes **1** and **2** is accompanied by slow nitrogen evolution and formation of *sym*-azines of the aldehydes as by-products (Scheme 2). The total yield of dichlorostyrenes and azines is nearly quantitative (Table 2).

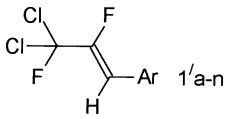
Recently we have proposed a mechanism of similar reactions of hydrazones with carbon tetrachloride. This mechanism and the formation of some key intermediates have been confirmed experimentally.[18] We believe that the reaction with freons proceeds in a similar manner which can also explain the formation of products obtained (alkenes and azines) from the corresponding hydrazones. The postulated key intermediate of the reaction of hydrazones with polyhalogenoalkanes is a copper–carbenoid complex **I** (Scheme 3).[21–27]

The first step of the catalytic cycle is the reaction of copper(II) with hydrazone to give the corresponding diazoalkane and two molecules of acid fixed by the base. The next step is the formation of a copper-carbene complex **I**. The reaction is accompanied by the evolution of one molecule of nitrogen. The complex **I** reacts with freon to give the target fluorinated alkene and to regenerate the catalyst (inside cycle). Another type of carbenoid complex **I** transformation is their reaction with diazoalkane to form the *sym*-azine (outside cycle).[28] The step of copper(0) oxidation complete the outside catalytic cycle. These two reactions (and two cycles of copper transformation) are competitive. Previously we studied the reaction of *p*-nitrophenyldiazomethane with CCl_4 and observed the formation of the corresponding alkene and *sym*-aldazine.[17] Also we showed that hydrazones dissolved in DMSO rapidly reacted with an equimolar quantity of $CuCl_2$ in the presence of aqueous ammonia. The corresponding *sym*-azines were isolated in nearly quantitative yield (>94%).

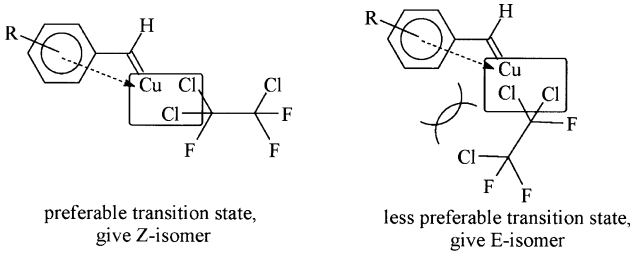
According to Schemes 3 and 4 freons CCl_3CF_3 and CCl_2FCClF_2 can also be converted to the corresponding partially reduced freons $CHCl_2CF_3$ and $CHClFCClF_2$, formed as a result of two single electron transfer (SET) steps. Previously in the reaction of hydrazones with CCl_4 we have detected chloroform as the result of similar reduction of CCl_4 in the reaction media.[17]

We calculated the results of two consistent single electron transfer on CCl_3CF_3 and CCl_2FCClF_2 and predicted the formation of two possible isomeric radicals $C_2Cl_2F_3$ (**I** and **II**) and corresponding hydrofluorocarbons $CClHFCClF_2$ and CCl_2FCHF_2 in the reaction with CFC-113 (Scheme 4).[†] Radical **I** is more stable than radical **II** (ΔH_{form}=5.6 kcal/mol). The chromato-mass-spectra of the reaction mixture confirmed the formation of $CClHFCClF_2$ and CCl_2FCHF_2 from CFC-113.[29] These data supported the proposed reaction mechanism.

[†] DFT technique (TAINA program, D. N. Laikov, Moscow State University), PBE 96 functional and the basis of triple-zeta quality.



Scheme 5.



Scheme 6.

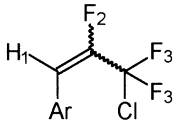
More detailed investigation of the reaction mixture by ^{19}F NMR and chromato-mass-spectrometry showed that in the reaction with CCl_2FCClF_2 traces of the *Z*-isomer of abnormal products **1′** are also formed (<2% by ^{19}F NMR) (Scheme 5). We assume that these compounds are formed as a result of SET on radical **II** and subsequent loss of fluorid ion, just as normal products **1** were formed as a result of SET on radical **I** and subsequent loss of chlorid ion. The ratio of **1** and **1′** alkenes are corresponded the relative stability of radicals **I** and **II**. In the case of reaction of CCl_2FCClF_2 with 1-naphthylcarbaldehyde we observed about 7% of the abnormal product (by ^{19}F NMR), whereas in the reaction with CCl_3CF_3 abnormal products **1′** are not obtained.

The reaction is very sensitive to steric hindrance. We found that the yields of alkenes **1** and **2** are generally lower in the case of aldehydes bearing substituents in the *ortho*-positions. Some *ortho*-substituted aldehydes do not give the target alkenes in this reaction (Table 1). Thus, alkene **2p** was isolated in only 22% yield in the reaction with CCl_3CF_3 however no product was obtained in the reaction with CCl_2FCClF_2, probably because the $CClF_2$ group is more bulky than the CF_3 moiety.

The reaction proceeds stereoselectively and the *Z*-isomers are formed preferentially (Table 1). We found that the *Z*/*E* ratio depends on the electronic nature and position of substituents in the aromatic ring. The steric hindrance of the polyhalogenoalkane also affects the stereoselectivity. Generally, the reaction proceeds more stereoselectively in the case of CCl_2FCClF_2 and for electron rich aldehydes. These data supported the mechanism of reaction. The copper atom in the proposed key intermediate of the reaction (the copper–carbenoid complex **I**) may also be coordinated with the π-orbitals of the aromatic ring. In the case of electron-donating substituents such interaction is more effective and one side of the intermediate is less accessible for the attack by freon. For example, in the case of the reaction of 4-dimethylaminobenzaldehyde having a strongly electron-donating substituent and 1-naphthylcarbaldehyde only the *Z*-alkenes were obtained. Possible transition states are given on Scheme 6.

The ^1H and ^{19}F chemical shifts and coupling constants for

Table 3. ^1H, ^{19}F chemical shifts, ^1H–^{19}F and ^{19}F–^{19}F coupling constants (Hz) for 3-chloro-2,3,3-trifluoroprop-1-enylbenzenes



Aryl	^1H Chemical shifts[a]		^{19}F Chemical shifts[b]				Coupling constants[b]			
	H_1 in *Z*	H_1 in *E*	*Z* Isomer of **1**		*E* Isomer of **1**		*Z* Isomer of **1**		*E* Isomer of **1**	
			F_2	F_3	F_2	F_3	$H–F_2$	$F_2–F_3$	$H–F_2$	$F_2–F_3$
4-$O_2NC_6H_4$	6.42	6.68	−124.93	−62.40	−118.65	−58.62	33.75	14.65	19.37	14.65
3-$O_2NC_6H_4$	6.46	6.73	−126.18	−62.40	−119.43	−58.67	33.60	16.50	19.20	13.75
4-ClC_6H_4	6.32	6.64	−128.97	−61.92	−121.55	−58.52	34.8	17.87	20.85	13.75
3-ClC_6H_4	6.19	6.52	−127.47	−61.92	−122.82	−58.35	34.45	16.50	20.08	13.80
4-$CH_3OC_6H_4$	6.19	6.54	−132.70	−60.99	−124.02	−58.12	35.65	16.49	21.62	13.75
4-BrC_6H_4	6.19	6.48	−128.33	−61.65	−121.00	−58.24	34.69	16.50	20.32	13.75
C_6H_5	6.17	6.50	−129.65	−61.35	−122.42	−57.98	35.19	16.50	21.06	13.75
4-NCC_6H_4	6.31	6.60	−124.95	−62.25	−118.84	−58.54	33.96	16.50	19.83	13.75
4-$CH_3C_6H_4$	6.22	6.56	−130.72	−61.18	−123.16	−58.02	35.69	16.50	21.06	13.75
4-FC_6H_4[c]	6.23	6.55	−130.90	−61.73	−122.32	−58.41	34.94	16.50	20.57	13.75
2-FC_6H_4[d]	6.56	6.52	−128.05	−61.88	−119.47	−59.55	35.20	16.50	19.82	13.75
2-ClC_6H_4	6.69	6.55	−129.32	−61.44	−120.53	−58.30	34.20	16.50	19.33	13.75
Terephthal aldehyde[e]	6.20[f]	6.52[g]	−127.59[f]	−61.81[f]	−120.93[g]	−58.38[g]	34.70	16.50[f]	20.57	13.75[g]
1-Naphthyl	6.99	–	−129.79	−61.12	–	–	32.71	16.50	–	–

[a] ^1H NMR (376.29 MHz, $CDCl_3$).
[b] ^{19}F NMR (376.29 MHz, $CDCl_3/CFCl_{3int}$).
[c] Also were obtained signals of fluorine in ring with shift −112.78 (*Z*) and −115.04 (*E*).
[d] Also were obtained signals of fluorine in ring with shift −117.93 (*Z*) and −119.47 (*E*).
[e] Obtained as mixture of (*Z*,*Z*), (*Z*,*E*) and (*E*,*E*) isomers 86/13/1 by ^{19}F NMR spectra.
[f] In (*Z*,*Z*) isomer of **1m**.
[g] In (*Z*,*E*) isomer of **1m**.

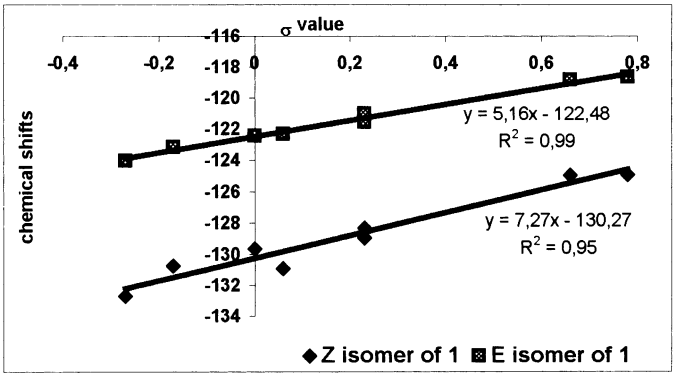


Figure 1. Dependence of chemical shifts of F(2) from Hammett constants.

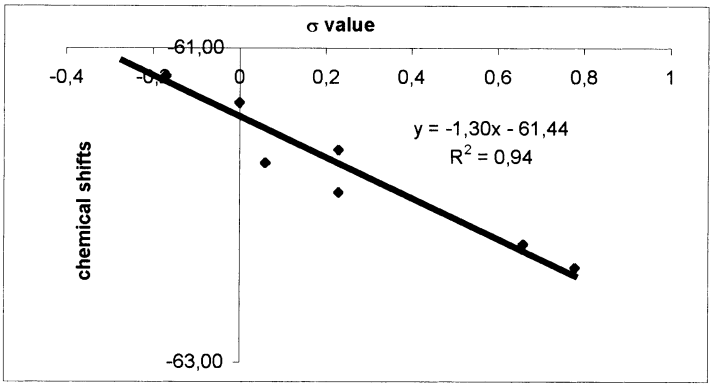


Figure 2. Dependence of chemical shifts of F(3) in *Z*-isomer of **1** from Hammett constants.

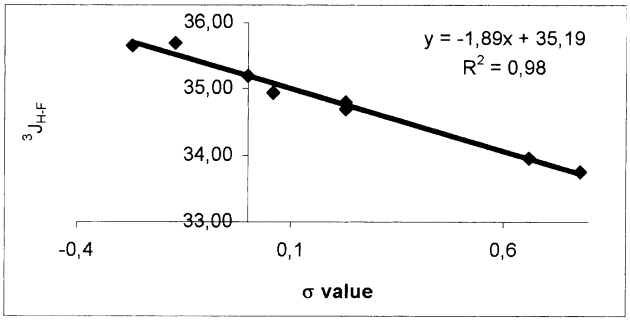


Figure 3. Coupling constants H–F_2 in *Z*-isomer of **1**.

the fluoro-alkenes **1a**–**n** are given in Table 3. The spectrum of the four-spin system CH═CF($CClF_2$) comprising the substituents on the ethylenic bond in **1** was interpreted as AMX_2. The identification of the hydrogen atoms in the two isomers was established on the basin of the values of their coupling constants with the vinylic fluorine,[30–32] thus the *trans* relationship giving rise to the larger coupling $^3J_{H-F}$ of approximately 34 Hz (Fig. 3), while the *cis* coupling $^3J_{H-F}$ was approximately 20 Hz (Fig. 4).

The chemical shifts of the vinylic and allylic fluorine and coupling constants $^3J_{H-F}$ showed linear correlations with Hammett substituent parameters for the *para*-substituents when the σ values were used (Figs. 1–4). A less satisfactory relationship was observed for *E*-isomers of alkenes **1** than that for *Z*-isomers.

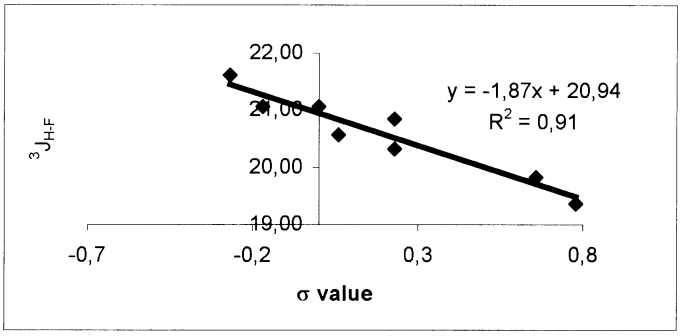


Figure 4. Coupling constants H–F_2 in *E*-isomer of **1**.

3. Conclusion

A new general stereoselective synthesis of 3-chloro-2,3,3-trifluoroprop-1-enylbenzenes and 2-chloro-3,3,3-trifluoroprop-1-enylbenzenes has been developed. The target alkenes were prepared in good yield, from readily available and inexpensive starting materials in a simple one-pot procedure. The present approach proves to be a versatile and advantageous alternative to classical routes to the 2-chloro-3,3,3-trifluoroprop-1-enylbenzenes.

4. Experimental

4.1. General

Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on a Varian VXR-400 and Bruker AM 400C spectrometers in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer. Column chromatography was performed on silica gel (63–200 mesh, Merck). Mass-spectra were recorded on a HP5890 mass spectrometer with the 5989x-G detector.

4.2. General procedure for 3-chloro-2,3,3-trifluoroprop-1-enylbenzenes

A solution of aromatic aldehyde (10 mmol) in EtOH (50 mL) was added dropwise to a solution of 100% $N_2H_4{\cdot}H_2O$ (10 mmol, 0.49 mL) in EtOH (50 mL) and the mixture was stirred until aldehyde disappeared (TLC monitoring). Then freshly purified copper(I) chloride (1 mmol, 100 mg) and ethylenediamine (3.4 mL) were added. After 10 min 1,1,2-trichloro-1,2,2-trifluoroethane (6 mL) was added dropwise at 20°C. The reaction mixture was stirred for 24 h, EtOH was evaporated in vacuo and residue was quenched with hydrochloric acid (5%) (300 mL) and extracted with CH_2Cl_2 (3×50 mL). The extracts were dried over sodium sulfate, dichloromethane was evaporated in vacuo and the residue was purified by column chromatography (hexane). *E*- and *Z*-isomeric mixture of alkenes **1** and **2** could not be separated by column chromatography.

2-Chloro-3,3,3-trifluoroprop-1-enylbenzenes were similarly prepared using 1,1,1-trichloro-2,2,2-trifluoroethane.

All new compounds gave satisfactory 400 MHz ^{1}H and 100 MHz ^{13}C NMR and IR spectral data. ^{19}F and selected ^{1}H NMR data for minor isomers **1a**–**n** are reported in Table 3. Most signals of the minor isomers of **1** and **2** usually overlapped with the signals of major isomers. Physical data for compounds **1a**–**n** and **2a**–**p** are as follows.

4.2.1. 1-[3-Chloro-2,3,3-trifluoro-1-propenyl]-4-nitrobenzene 1a. The title compound was obtained as a 6:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless crystals, mp 36–37°C. R_f (Hexane) 0.20. IR (Nujol) (ν, cm^{-1}) 1700 (C═C), 1530 (NO_2). $C_9H_5ClF_3NO_2$ (251.6): calcd C 42.97, H 2.00, found C 43.24, H 2.04. *Major isomer* **1a**: ^{1}H NMR ($CDCl_3$) δ 6.42 (d, J=33.8 Hz, 1H), 7.73 (d, J=8.8 Hz, 2H), 8.26 (d, J=8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 107.57, 120.01 (J=288.4, 41.2 Hz), 123.73, 130.29 (J=7.6, 3.1 Hz), 135.91, 147.68 (J=3.1 Hz), 149.93 (J=271.6, 32.1 Hz). MS (EI, 70 eV); *m*/*z* (%): 251 (63) [M$^+$], 216 (59) [M$^+$−Cl], 170 (100) [M$^+$−Cl–NO_2], 169 (100) [M$^+$−Cl–H–NO_2].

4.2.2. 1-[3-Chloro-2,3,3-trifluoro-1-propenyl]-3-nitrobenzene 1b. The title compound was obtained as a 4:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.25. IR (Nujol) (ν, cm^{-1}) 1710 (C═C), 1540 (NO_2). $C_9H_5ClF_3NO_2$ (251.6): calcd C 42.97, H 2.00, found C 43.00, H 2.16. *Major isomer* **1b**: ^{1}H NMR ($CDCl_3$) δ 6.46 (d, J=33.6 Hz, 1H), 7.63 (dd, J=7.8, 7.8 Hz, 1H), 7.91 (d, J=7.8 Hz, 1H), 8.22 (d, J=7.8 Hz, 1H), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 107.53 (J=7.6, 4.6 Hz), 120.2 (J=285, 42 Hz), 124.04 (J=2 Hz), 124.27 (J=7.7 Hz), 129.93, 135.17 (J=7.7 Hz), 135.48, 148.5, 149.85 (J=262, 30 Hz).

4.2.3. 1-Chloro-4-[3-chloro-2,3,3-trifluoro-1-propenyl]-benzene 1c. The title compound was obtained as a 10:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.55. IR (Nujol) (ν, cm^{-1}) 1710 (C═C). $C_9H_5Cl_2F_3$ (241.0): calcd C 44.85, H 2.09, found C 44.84, H 2.21. *Major isomer* **1c**: ^{1}H NMR ($CDCl_3$) δ 6.32 (d, J=34.8 Hz, 1H), 7.23 (d, J=8.7 Hz, 2H), 7.39 (d, J=8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 108.39 (J=7.6, 3.7 Hz), 124.27 (J=286.4, 41.3 Hz), 128.25 (J=3.7 Hz), 129.12, 130.90 (J=7.6 Hz), 135.49 (J=3.7 Hz), 148.44 (J=262, 30 Hz). MS (EI, 70 eV); *m*/*z* (%): 240 (38) [M$^+$], 205 (100) [M$^+$−Cl], 185 (88) [M$^+$−Cl–HF], 169 (43) [M$^+$−2Cl].

4.2.4. 1-Chloro-3-[3-chloro-2,3,3-trifluoro-1-propenyl]-benzene 1d. The title compound was obtained as a 11:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.50. IR (Nujol) (ν, cm^{-1}) 1700 (C═C). $C_9H_5Cl_2F_3$ (241.0): calcd C 44.85, H 2.09, found C 44.84, H 2.56. *Major isomer* **1d**: ^{1}H NMR ($CDCl_3$) δ 6.19 (d, J=34.5 Hz, 1H), 7.22–7.26 (m, 2H), 7.33 (dt, J=6.7, 1.7 Hz, 1H), 7.47 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 108.30 (J=7.6, 4.6 Hz), 120.42 (J=288.4, 41.2 Hz), 127.78 (J=6.1 Hz), 129.50, 129.57, 130.03, 131.45 (J= 3.1 Hz), 134.84, 148.91 (J=270.1, 32.0 Hz).

4.2.5. 1-[3-Chloro-2,3,3-trifluoro-1-propenyl]-4-methoxy benzene 1e. The title compound was obtained as a 19:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.35. IR (Nujol) (ν, cm^{-1}) 1700 (C═C). $C_{10}H_8ClF_3O$ (236.6): calcd C 50.76, H 3.41, found C 50.64, H 3.60. *Major isomer* **1e**: ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 3H), 6.19 (d, J=35.7 Hz, 1H), 6.84 (d, J=8.7 Hz, 2H), 7.44 (d, J=8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 55.23, 109.18 (J=7.6, 4.6 Hz), 114.28, 120.93 (J=288.4, 41.2 Hz), 122.40(J=3.1 Hz), 131.33(J=7.6 Hz), 146.83 (J=264.0, 32.0 Hz), 160.48 (J=3.1 Hz). MS (EI, 70 eV); *m*/*z* (%): 236 (35) [M$^+$], 201 (100) [M$^+$−Cl], 181 (54) [M$^+$−Cl–HF].

4.2.6. 1-Bromo-4-[3-chloro-2,3,3-trifluoro-1-propenyl]-benzene 1f. The title compound was obtained as a 6:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.75. IR (Nujol) (ν, cm^{-1}) 1700 (C═C). $C_9H_5BrClF_3$ (285.5): calcd C 37.86, H 1.77,

found C 37.80, H 2.00. *Major isomer* **1f**: ^{1}H NMR ($CDCl_3$) δ 6.19 (d, J=34.7 Hz, 1H), 7.32 (d, J=8.7 Hz, 2H), 7.43 (d, J=8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 108.48 (J=7.6 Hz, J=3.1 Hz), 120.50 (J=288.4, 41.2 Hz), 123.82 (J=4.6 Hz), 128.66 (J=3.1 Hz), 131.08 (J=7.6 Hz), 131.54, 148.51 (J=268.6, 32.0 Hz). MS (EI, 70 eV); *m/z* (%): 286 (29) [M^+], 251 (20) [M^+-Cl], 170 (100) [$M^+-Cl-Br$], 169 (39) [$M^+-Cl-H-Br$].

4.2.7. [3-Chloro-2,3,3-trifluoro-1-propenyl]benzene 1g. The title compound was obtained as a 93:7 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil, bp 84°C/18 torr. R_f (Hexane) 0.85. IR (Nujol) (ν, cm^{-1}) 1700 (C=C). $C_9H_6ClF_3$ (206.6): calcd C 52.32, H 2.93, found C 52.33, H 2.98. *Major isomer* **1g**: ^{1}H NMR ($CDCl_3$) δ 6.17 (d, J=35.2 Hz, 1H), 7.21–7.25 (m, 3H), 7.40 (dd, J=7.8, 1.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 109.53 (J=7.6, 3.1 Hz), 120.75 (J=288.4, 41.2 Hz), 128.86, 129.55 (J=3.1 Hz), 129.76 (J=7.6 Hz), 130.02 (J=3.1 Hz), 148.17 (J=267.0, 32.0 Hz).

4.2.8. 4-[3-Chloro-2,3,3-trifluoro-1-propenyl]benzonitrile 1h. The title compound was obtained as a 6:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.10. IR (Nujol) (ν, cm^{-1}) 2240 (CN), 1700(C=C). $C_{10}H_5ClF_3N$ (231.60): calcd C 51.86, H 2.18, found C 52.07, H 2.55. *Major isomer* **1h**: ^{1}H NMR ($CDCl_3$) δ 6.31 (d, J=34.0 Hz, 1H), 7.59 (d, J=8.9 Hz, 2H), 7.63 (d, J=8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 107.90 (J=7.6, 4.6 Hz), 112.93 (J=3.0 Hz), 120.07 (J=289.9, 41.2 Hz), 130.08 (J=7.6 Hz), 132.03, 132.48, 134.15(J=4.6 Hz), 149.94 (J=273.2, 32.1 Hz.

4.2.9. 1-[3-Chloro-2,3,3-trifluoro-1-propenyl]-4-methylbenzene 1i. The title compound was obtained as a 16:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil, bp 87°C/15 torr. R_f (Hexane) 0.85. IR (Nujol) (ν, cm^{-1}) 1700 (C=C). $C_{10}H_8ClF_3$ (220.6): calcd C 54.44, H 3.65, found C 53.76, H 3.82. *Major isomer* **1i**: ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H), 6.22 (d, J=35.7 Hz, 1H), 7.12 (d, J=8.1 Hz, 2H), 7.37 (d, J=8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.32, 109.46 (J=7.6, 4.6 Hz), 120.82 (J=286.9, 41.2 Hz), 127.00 (J=4.6 Hz), 129.57, 129.69 (J=7.6 Hz), 140.59, 148.33 (J=265.6, 32.0 Hz).

4.2.10. 1-[3-Chloro-2,3,3-trifluoro-1-propenyl]-4-fluorobenzene 1j. The title compound was obtained as a 13:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil, bp 87°C/15 torr. R_f (Hexane) 0.60. IR (Nujol) (ν, cm^{-1}) 1700 (C=C), 1240 (Ar–F). $C_9H_5ClF_4$ (224.6): calcd C 48.13, H 2.24, found C 48.29, H 2.54. *Major isomer* **1j**: ^{1}H NMR ($CDCl_3$) δ 6.23 (d, J=34.9 Hz, 1H), 7.02 (dd, J=8.7, 8.7 Hz, 2H), 7.48 (dd, J=8.7, 5.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 108.46 (J=7.6, 4.6 Hz), 116.02 (J=22.9 Hz), 131.70 (J=9.2, 7.6 Hz), 132.06 (J=9.2 Hz), 120.65 (J=288.4, 42.7 Hz), 147.91 (J=267.0, 32.1 Hz), 162.68 (J=250.3, 22.9 Hz).

4.2.11. 1-[3-Chloro-2,3,3-trifluoro-1-propenyl]-2-fluorobenzene 1k. The title compound was obtained as a 4:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil, bp 87°C/15 torr. R_f (Hexane) 0.60. IR (Nujol) (ν, cm^{-1}) 1700 (C=C), 1240 (Ar–F). $C_9H_5ClF_4$ (224.6): calcd C 48.13, H 2.24, found C 48.36, H 2.58. *Major isomer* **1k**: ^{1}H NMR ($CDCl_3$) δ 6.56 (d, J=35.2 Hz, 1H), 7.00–7.35 (m, 3H), 7.74 (dd, J=7.9, 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 101.41 (J=7.6, 4.6 Hz), 115.57 (J=22.9 Hz), 120.62 (J=288.4, 41.2 Hz), 124.50 (J=3.1 Hz), 130.32 (J=13.7 Hz), 131.28 (J=6.1, 3.1 Hz), 131.78 (J=9.2 Hz), 149.23 (J=267.0, 30.5 Hz), 160.39 (J=253.3 Hz).

4.2.12. 1-Chloro-2-[3-chloro-2,3,3-trifluoro-1-propenyl]-benzene 1l. The title compound was obtained as a 7:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.60. IR (Nujol) (ν, cm^{-1}) 1700 (C=C). $C_9H_5Cl_2F_3$ (241.0): calcd C 44.85, H 2.09, found C 44.37, H 2.33. *Major isomer* **1l**: ^{1}H NMR ($CDCl_3$) δ 6.69 (d, J=34.2 Hz, 1H), 7.15–7.19 (m, 2H), 7.28–7.33 (m, 1H), 7.61–7.70 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 105.50 (J=3.1 Hz), 120.46 (J=288.4, 41.2 Hz), 127.05, 129.80, 130.47, 130.67 (J=10.7 Hz), 132.92, 134.18, 149.11 (J= 270.1, 32.1 Hz).

4.2.13. 1,4-Bis[3-chloro-2,3,3-trifluoro-1-propenyl]benzene 1m. The title compound was obtained as a 86/13/1 mixture of (*Z*,*Z*), (*Z*,*E*) and (*E*,*E*) isomers (by ^{19}F NMR spectra) after purification. Colourless crystals, mp 52–53°C. R_f (Hexane) 0.70. IR (Nujol) (ν, cm^{-1}) 1700 (C=C). $C_{12}H_6Cl_2F_6$ (335.1): calcd C 43.01, H 1.80, found C 43.03, H 1.90. *Major isomer* **1m**: ^{1}H NMR ($CDCl_3$) δ 6.20 (d, J=34.7 Hz, 2H), 7.45 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 108.74 (J=7.6, 3.1 Hz), 120.61 (J=288.4, 41.2 Hz), 130.11 (J=7.6 Hz), 130.95, 149.01 (J=268.6, 32.0 Hz).

4.2.14. 1-[3-Chloro-2,3,3-trifluoro-1-propenyl]naphthalene 1n. Colourless oil. R_f (Hexane) 0.85. $C_{13}H_8ClF_3$ (256.7): calcd C 60.84, H 3.14, found C 60.55, H 3.05. ^{1}H NMR ($CDCl_3$) δ 6.99 (d, J=32.7 Hz, 1H), 7.43–7.53 (m, 3H), 7.73–7.89 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 106.38 (J=4.6 Hz), 120.94 (J=288.4, 41.2 Hz), 123.06, 125.19, 126.05, 126.78, 128.03 (J=9.2 Hz), 128.77, 129.83, 131.18, 133.53, 148.93 (J=265.5, 32.0 Hz). MS (EI, 70 eV); *m/z* (%): 256 (80) [M^+], 221 (47) [M^+-Cl], 201 (100) [$M^+-Cl-H-F$], 171 (91) [M^+-CClF_2],152 (17) [$M^+-F-CClF_2$].

4.2.15. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-nitrobenzene 2a. The title compound was obtained as a 7:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Pale yellow crystals, mp 63–64°C (lit.[4] 64–65°C). R_f (Hexane) 0.25. *Major isomer* **2a**: ^{1}H NMR ($CDCl_3$) δ 7.32 (s, 1H), 7.79 (d, J=8.8 Hz, 2H), 8.23 (d, J=8.8 Hz, 2H). *Minor isomer* **2a**: ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 1H).

4.2.16. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-3-nitrobenzene 2b. The title compound was obtained as a 3:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Pale yellow oil. R_f (Hexane) 0.30. IR (Nujol) (ν, cm^{-1}) 1620 (C=C), 1540 (NO_2). $C_9H_5ClF_3NO_2$ (251.6): calcd C 42.97, H 2.00, found C 42.62, H 1.99. *Major isomer* **2b**: ^{1}H NMR ($CDCl_3$) δ 7.29 (s, 1H), 7.57 (d, J=8.1 Hz, 1H), 7.92 (d, J=8.1 Hz, 1H), 8.16 (dd, J=8.1, 1.2 Hz, 1H), 8.48 (dd, J=1.2, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 120.36 (J=271.6 Hz), 122.11 (J=36.6 Hz), 124.17, 124.35, 128.52, 129.66, 132.89, 135.44, 148.08. *Minor isomer* **2b**: ^{1}H

NMR ($CDCl_3$) δ 7.22 (s, 1H), 7.49 (d, J=7.5 Hz, 2H), 8.03 (br.s, 1H), 8.09–8.13 (m, 1H).

4.2.17. 1-Chloro-4-[2-chloro-3,3,3-trifluoro-1-propenyl]-benzene 2c. The title compound was obtained as a 4:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.85. *Major isomer* **2c**: ^{1}H NMR ($CDCl_3$) δ 7.07 (s, 1H), 7.20 (d, J=8.7 Hz, 2H), 7.48 (d, J=8.7 Hz, 2H). *Minor isomer* **2c**: ^{1}H NMR ($CDCl_3$) δ 7.03 (d, J=8.4 Hz, 2H), 7.17 (d, J=8.4 Hz, 2H).

4.2.18. 1-Chloro-3-[2-chloro-3,3,3-trifluoro-1-propenyl]-benzene 2d. The title compound was obtained as a 4:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.85. IR (Nujol) (ν, cm^{-1}) 1660 (C=C). $C_9H_5Cl_2F_3$ (241.0): calcd C 44.85, H 2.09, found C 44.73, H 2.08. *Major isomer* **2d**: ^{1}H NMR ($CDCl_3$) δ 7.06 (s, 1H), 7.18–7.24 (m, 2H), 7.40 (d, J=7.2 Hz, 1H), 7.54 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 120.83 (J=36.6 Hz), 121.00 (J=271.6 Hz), 127.99, 129.32 (J=4.6 Hz), 128.30, 129.63, 129.78, 130.06, 134.67. *Minor isomer* **2d**: ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 1H).

4.2.19. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-methoxy-benzene 2e. The title compound was obtained as a 10:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.40. IR (Nujol) (ν, cm^{-1}) 1610 (C=C). $C_{10}H_8ClF_3O$ (236.6): calcd C 50.76, H 3.41, found C 50.67, H 3.37. *Major isomer* **2e**: ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 3H), 6.76 (d, J=8.7 Hz, 2H), 7.04 (s, 1H), 7.52 (d, J=8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 54.94, 113.94, 116.32 (J=36.6 Hz), 121.26 (J=271.6 Hz), 123.99, 130.04 (J= 4.6 Hz), 131.80, 161.05. *Minor isomer* **2e**: ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 3H), 6.71 (d, J=8.5 Hz, 2H), 7.00 (s, 1H), 7.07 (d, J=8.5 Hz, 2H).

4.2.20. 1-Bromo-4-[2-chloro-3,3,3-trifluoro-1-propenyl]-benzene 2f. The title compound was obtained as a 6:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.85. IR (Nujol) (ν, cm^{-1}) 1650 (C=C). $C_9H_5BrClF_3$ (285.5): calcd C 37.86, H 1.77, found C 37.53, H 1.84. *Major isomer* **2f**: ^{1}H NMR ($CDCl_3$) δ 7.09 (s, 1H), 7.41–7.44 (br.d, J=1.8 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ 120.01 (J=36.6 Hz), 120.77 (J=271.6 Hz), 124.44, 131.27, 131.51, 131.82, 135.75. *Minor isomer* **2f**: ^{1}H NMR ($CDCl_3$) δ 6.98 (s, 1H), 7.03 (d, J=8.4 Hz, 2H), 7.35 (d, J=8.4 Hz, 2H).

4.2.21. [2-Chloro-3,3,3-trifluoro-1-propenyl]benzene 2g. The title compound was obtained as a 6:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.90. *Major isomer* **2g**: ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 1H), 7.28–7.33 (m, 3H), 7.58–7.62 (m, 2H). *Minor isomer* **2g**: ^{1}H NMR ($CDCl_3$) δ 7.11 (s).

4.2.22. 4-[2-Chloro-3,3,3-trifluoro-1-propenyl]benzo-nitrile 2h. The title compound was obtained as a 3:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless crystals, mp 69–70°C. R_f (Hexane) 0.15. IR (Nujol) (ν, cm^{-1}) 2240 (CN), 1660 (C=C). $C_{10}H_5ClF_3N$ (231.60): calcd C 51.86, H 2.18, found C 51.61, H 2.14. *Major isomer* **2h**: ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 1H), 7.62 (d, J=8.4 Hz, 2H), 7.72 (d, J=8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 113.09, 117.78, 120.17 (J=271.6 Hz), 121.98 (J=36.6 Hz), 128.93, 130.00, 131.92, 135.43. *Minor isomer* **2h**: ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 1H), 7.28 (d, J=8.2 Hz, 2H), 7.55 (d, J=8.2 Hz, 2H).

4.2.23. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-methyl-benzene 2i. The title compound was obtained as a 6:1 mixture of *Z*–*E* isomers 6:1 after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.85. IR (Nujol) (ν, cm^{-1}) 1650 (C=C). $C_{10}H_8ClF_3$ (220.6): calcd C 54.44, H 3.65, found C 54.40, H 3.53. *Major isomer* **2i**: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 7.08 (s, 1H), 7.10 (br.s, 2H), 7.49 (d, J=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.21, 118.18 (J= 36.6 Hz), 121.15 (J=271.6 Hz), 129.03, 129.33, 130.03, 130.55 (J=4.6 Hz), 140.60. *Minor isomer* **2i**: ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 7.07 (s, 1H).

4.2.24. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-4-fluoro-benzene 2j. The title compound was obtained as a 4:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.75. IR (Nujol) (ν, cm^{-1}) 1660 (C=C), 1240 (Ar–F). $C_9H_5ClF_4$ (224.6): calcd C 48.13, H 2.24, found C 48.14, H 2.65. *Major isomer* **2j**: ^{1}H NMR ($CDCl_3$) δ 7.01 (dd, J=8.8, 8.8 Hz, 2H), 7.15 (s, 1H), 7.62 (dd, J=8.8, 5.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 115.80 (J=21.4 Hz), 120.91 (J=271.6 Hz), 127.74 (J=3.1 Hz), 128.91 (J=26.0 Hz), 129.46 (J=4.6 Hz), 132.05 (J= 7.6 Hz), 163.45 (J=251.8 Hz). *Minor isomer* **2j**: ^{1}H NMR ($CDCl_3$) δ 6.95 (dd, J=8.7, 8.7 Hz, 2H).

4.2.25. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-2-fluoro-benzene 2k. The title compound was obtained as a 3:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.75. IR (Nujol) (ν, cm^{-1}) 1660 (C=C), 1240 (Ar–F). $C_9H_5ClF_4$ (224.6): calcd C 48.13, H 2.24, found C 48.37, H 2.42. *Major isomer* **2k**: ^{1}H NMR ($CDCl_3$) δ 7.02 (dd, J=9.7, 8.7 Hz, 1H), 7.11 (d, J=7.4 Hz, 1H), 7.28–7.31 (m, 1H), 7.40 (s, 1H), 7.90 (ddd, J=7.4, 7.4, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 115.67 (J=22.9 Hz), 119.51 (J=45.8 Hz), 120.90 (J= 271.6 Hz), 123.32, 124.07 (J=3.1 Hz), 127.76 (J=7.6 Hz), 129.71, 131.85 (J=9.2 Hz), 160.68 (J=251.8 Hz). *Minor isomer* **2k**: ^{1}H NMR ($CDCl_3$) δ6.97 (dd, J=8.7, 8.7 Hz, 1H.

4.2.26. 1-Chloro-2-[2-chloro-3,3,3-trifluoro-1-propenyl]-benzene 2l. The title compound was obtained as a 4:1 mixture of *Z*–*E* isomers after purification (by ^{1}H NMR). Colourless oil. R_f (Hexane) 0.85. IR (Nujol) (ν, cm^{-1}) 1660 (C=C). $C_9H_5Cl_2F_3$ (241.0): calcd C 44.85, H 2.09, found C 44.57, H 2.25. *Major isomer* **2l**: ^{1}H NMR ($CDCl_3$) δ 7.21–7.24 (m, 2H), 7.33–7.36 (m, 1H), 7.47 (s, 1H), 7.72–7.74 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 120.62 (J= 271.6 Hz), 126.54, 126.64, 128.06 (J=4.6 Hz), 129.71, 129.85 (J=35.1 Hz), 130.25, 130.85, 134.08. *Minor isomer* **2l**: ^{1}H NMR ($CDCl_3$) δ 7.13 (s, 1H).

4.2.27. 1,4-Bis[2-chloro-3,3,3-trifluoro-1-propenyl]benzene 2m. Colourless oil. R_f (Hexane) 0.80. IR (Nujol) (ν, cm^{-1}) 1650 (C=C). ^{1}H NMR ($CDCl_3$) δ 7.07 (d, J=1.0 Hz, 2H), 7.56 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 120.92 (J=36.6 Hz), 120.95 (J=271.6 Hz), 129.69 (J=4.6 Hz), 130.13, 133.18.

4.2.28. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]naphthalene 2n. Colourless oil. R_f (Hexane) 0.85. IR (Nujol) (ν, cm^{-1}) 1660 (C=C). ^1H NMR ($CDCl_3$) δ 6.94 (s, 1H), 7.28–7.32 (m, 3H), 7.62–7.67 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 123.40, 124.96, 126.28, 126.86, 127.20, 128.75, 129.98. MS (EI, 70 eV); *m/z* (%): 256 (67) [M^+], 221 (100) [M^+-Cl], 201 (82) [$M^+-Cl-H-F$], 152 (64) [$M^+-Cl-CF_3$]. $C_{13}H_8ClF_3$ (256.7): calcd C 60.84, H 3.14, found C 61.07, C 3.05.

4.2.29. 4-[(1*Z*)-2-Chloro-3,3,3-trifluoro-1-propenyl]-*N*,*N*-dimethylaniline 2o. Colourless crystals, mp 74.5–75°C. R_f (Hexane) 0.30. IR (Nujol) (ν, cm^{-1}) 1610 (C=C). ^1H NMR ($CDCl_3$) δ 2.89 (s, 6 H), 6.56 (d, J=8.7 Hz, 2H), 7.02 (s, 1H), 7.56 (d, J=8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 39.80, 111.33, 113.17 (J=36.6 Hz), 118.98, 121.59 (J=271.6 Hz), 130.40 (J=4.6 Hz), 131.77, 151.28. $C_{11}H_{11}ClF_3N$ (249.7): calcd C 52.92, H 4.44, found C 53.05, C 4.43.

4.2.30. 1-[2-Chloro-3,3,3-trifluoro-1-propenyl]-2-methoxybenzene 2p. The title compound was obtained as a 6:1 mixture of *Z*–*E* isomers after purification (by ^1H NMR). Colourless oil. R_f (Hexane) 0.40. IR (Nujol) (ν, cm^{-1}) 1610 (C=C). $C_{10}H_8ClF_3O$ (236.6): calcd C 50.76, H 3.41, found C 50.40, H 3.19. *Major isomer* **2p**: ^1H NMR ($CDCl_3$) δ 3.68 (s, 3H), 6.75 (d, J=8.4 Hz, 1H), 6.86 (dd, J=7.7, 7.4 Hz, 1H), 7.23 (dd, J=8.4, 7.4 Hz, 1H), 7.52 (s, 1H), 7.80 (d, J=7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 55.29, 110.52, 119.07 (J=36.6 Hz), 120.20, 120.38, 121.15 (J=271.6 Hz), 126.05 (J=4.6 Hz), 129.54, 131.44, 157.73. *Minor isomer* **2p**: ^1H NMR ($CDCl_3$) δ 3.66 (s, 3H), 7.14 (s, 1H).

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