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Synthesis of bis(halovinyl)benzenes by catalytic olefination*

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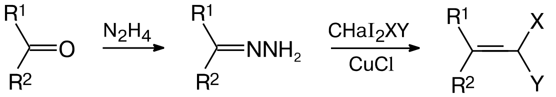
Catalytic olefination of hydrazines of terephthalic and isophthalic aldehydes with polyhaloalkanes afforded the corresponding *p*- and *m*-divinylbenzene derivatives bearing halogen atoms and various functional groups at the double bonds. Stereochemical features of the reaction were studied.

Key words: catalytic olefination, polyhaloalkanes, alkenes, dienes, organofluorine compounds.

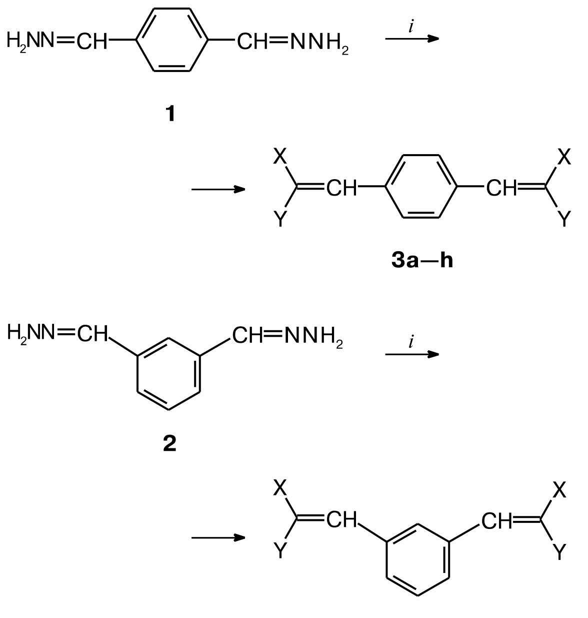
Divinylbenzenes and diethynylbenzenes[1] are widely used monomers for the synthesis of electrically conductive, fluorescent, and other oligomeric and polymeric materials possessing valuable physicochemical properties.[2] Thus, bis(2,2-dihalovinyl)benzenes are used for the synthesis of diethynylbenzenes and serve also as starting materials for tunable organic fluorophores.[1d,2c] Usually, mono- and bis(halovinyl)benzenes are prepared by the Wittig reaction from the corresponding dialdehydes, however, the significant drawback of this method is the use of either equimolar or excess amounts of organophosphorus and organometallic compounds.[3] An alternative approach towards these compounds is the catalytic olefination reaction (the Nenajdenko—Shastin reaction),[4,5] which is the reaction of *N*-unsubstituted hydrazones of aldehydes and ketones with polyhaloalkanes catalyzed by copper salts providing a variety of halogen-containing olefins, including functionalized ones (Scheme 1).

Scheme 1



In the present work, we describe olefination of dihydrazones of terephthalic (**1**) and isophthalic (**2**) aldehydes with polyhaloalkanes (Scheme 2).

Scheme 2



Reagent and conditions: *i*. $CHal_2XY$, CuCl (2 mol.%), base. Substituents X, Y, and olefination reagent ($CHal_2XY$) are given in Table 1.

We used polyhalomethanes $CBrCl_3$, CBr_4, and $CFBr_3$ (building blocks C-1); polyhaloethanes CF_3CBr_3, CF_3CCl_3, and CF_3CFBr_2 (building blocks C-2), as well as ethyl trichloroacetate and trichloroacetonitrile allowing synthesis of functionalized alkenes.

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Table 1. Synthesis of divinylbenzene derivatives by catalytic olefination reaction

Dihyrazone	Olefination reagent	Product	X	Y	Yield (%)	Ratio of isomers*
1	$CBrCl_3$	**3a**	Cl	Cl	76	—
1	CBr_4	**3b**	Br	Br	55	—
1	CCl_3CO_2Et	**3c**	Cl	CO_2Et	25	72 : 28 (*Z*,*Z* : *Z*,*E*)
1	CCl_3CN	**3d**	Cl	CN	39	67 : 33 (*E*,*E* : *Z*,*E*)
1	$CFBr_3$	**3e**	F	Br	52	66 : 29 : 5 (*E*,*E* : *Z*,*E* : *Z*,*Z*)
1	CF_3CBr_3	**3f**	Br	CF_3	17	78 : 22 (*Z*,*Z* : *Z*,*E*)
1	CF_3CCl_3	**3g**	Cl	CF_3	24	67 : 33 (*Z*,*Z* : *Z*,*E*)
1	CF_3CFBr_2	**3h**	F	CF_3	69	86 : 14 (*Z*,*Z* : *Z*,*E*)
2	$CBrCl_3$	**4a**	Cl	Cl	73	—
2	CBr_4	**4b**	Br	Br	81	—
2	CCl_3CO_2Et	**4c**	Cl	CO_2Et	23	79 : 21 (*Z*,*Z* : *Z*,*E*)
2	CCl_3CN	**4d**	Cl	CN	40	73 : 27 (*E*,*E* : *Z*,*E*)
2	$CFBr_3$	**4e**	F	Br	34	58 : 37 : 5 (*E*,*E* : *Z*,*E* : *Z*,*Z*)
2	CF_3CBr_3	**4f**	Br	CF_3	48	83 : 17 (*Z*,*Z* : *Z*,*E*)
2	CF_3CCl_3	**4g**	Cl	CF_3	50	65 : 35 (*Z*,*Z* : *Z*,*E*)
2	CF_3CFBr_2	**4h**	F	CF_3	33	84 : 16 (*Z*,*Z* : *Z*,*E*)

* Configuration of isomers is given in parentheses.

The yields of target compounds **3**, **4** were found substantially dependent on reactivity of the staring polyhaloalkanes (Table 1). Earlier, we estimated the reactivity of different polyhaloalkanes using the global electrophilicity index.[6] The presence of the fluorine atoms in the starting reactant significantly decreases its activity, for example, in the case of less reactive freons. Nevertheless, the availability of the starting compounds, simplicity of both processing and isolation of the products are important advantages of catalytic olefination.

It is worthy to note that in the case of unsymmetrical alkenes ($X \neq Y$), a mixture of *E*,*E*-,*E*,*Z*-, and *Z*,*Z*-isomers can be formed. We showed previously that catalytic olefination is highly stereoselective and yields the least sterically strained alkenes. The content of minor isomer in some cases did not exceed 5%.[5o] Olefination of dialdehyde hydrazones **1** and **2** also favors formation of isomer bearing the aryl moiety and the most bulky substituent in *trans* position to each other. Note that comparing "monoalkenes", "dienes" **3**, **4** give slightly higher amount of the minor isomer due to statistical doubling of its content. Indeed, upon reaction, one molecule of *Z*,*Z*-isomer, one molecule of *E*,*E*-isomer, and two molecules of *Z*,*E*-isomer (*Z*,*E* and *E*,*Z*) are formed. NMR spectroscopy was used to determine the configuration and to assign the isomers. In the case of symmetric *E*,*E*- and *Z*,*Z*-isomers, the molecule has the greater degree of symmetry leading to simplification of the NMR spectra. Thus, in the ^{1}H NMR spectra of the major isomers of compounds **3**, the protons of the aromatic ring resonate as singlets. Both vinyl protons of compounds **3**, **4** also appear as singlets, the exception is the major dimers of fluorinated dienes **3e**, **4e** and **3h**, **4h** resonating as doublets with $J = 32.5—35.2$ Hz due to spin-spin coupling with the fluorine atoms, which indicated *E*,*E*-configuration for **3e**, **4e** and *Z*,*Z*-configuration for **3h**, **4h**. The spectra of minor isomers (*Z*,*Z* and *E*,*E*, respectively) show similar pattern with the only difference that the coupling constant is equal to 15.2—20.5 Hz. In the case of compounds **3c**,**d**,**f**,**g** and **4c**,**d**,**f**,**g**, the assignment of major isomer to *Z*,*Z*- or *E*,*E*-type was performed based on a comparison of the chemical shifts of the vinyl protons with published data.[5g,j,k] In spectra of unsymmetrical *E*,*Z*-isomers of compounds **3**, **4**, the vinyl proton signals are non-equivalent. Therefore, the aromatic protons of *para*-"dienes" **3** resonate as two separate doublets. It is of note that the isomer bearing the aryl moiety and the most bulky substituent in *cis*-positions at both double bonds was detected only for compounds **3e** and **4e**, however, content of this minor isomer did not exceed 5%.

In summary, olefination of dihydrazones of terephthalic and isophthalic aldehydes allows development of simple and versatile pathway towards halogenated 1,3- and 1,4-divinylbenzenes, including the corresponding fluorinated compounds and functionalized derivatives. These dienes are of great interest for the synthesis of polymers using, for example, the Suzuki cross-coupling reaction; the synthesis of fluorinated polymers based on compounds **3e**,**f** and **4e**,**f** is particularly promising. Functionalized alkenes **3c**,**d** and **4c**,**d** may serve as unique building blocks in the synthesis of heterocycles, which, in turn, can be used in design of coordination polymers and supramolecular structures.

Experimental

^{1}H and ^{13}C NMR spectra were run on a Bruker AMX 400 spectrometer (working frequencies of 400.1 and 100.6 MHz, respectively) in $CDCl_3$; chemical shifts are given in the δ scale relative to Me_4Si (internal standard). ^{19}F NMR spectra were recorded on a Bruker AM 300 instrument (working frequencies of 282.4 MHz). IR spectra were recorded using Carl Zeiss UR-20 and IR 200 spectrophotometers in neat (for liquids) and in Nujol (for solids). TLC was performed on Merck 60 F_{254} plates; for visualization of the spots, acidified $KMnO_4$ solution and UV irradiation were used. Column chromatography was performed on a silica gel (63—200 mesh, Merck). In the NMR spectra of the minor *E*-isomers, only characteristic signals, non-coincided with the signals of major *Z*-isomer, are given.

The starting hydrazones of terephthalic and isophthalic aldehydes were synthesized by a known procedure.[5p] ^{1}H NMR spectra of compounds **3a**,[5q] **3b**,[1d] and **4c**[3b] are in agreement with the published data.

Synthesis of divinylbenzenes 3, 4 (general procedure). Terephthalic aldehyde dihydrazone (**1**) or isophthalic aldehyde dihydrazone (**2**) (0.810 g, 5 mmol) was added in small portion over a period of 2 h to a mixture of DMSO (20 mL), the corresponding base (25 mmol), CuCl (0.01 g, 2 mol.%), and the corresponding polyhaloalkane(25 mmol). The reaction mixture was stirred at room temperature for 24 h, poured into water (300 mL), extracted with dichloromethane (3×50 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo*. Column chromatography of the residue (silica gel, elution with appropriate dichloromethane—hexane mixtures) afforded the title product. The isomeric mixtures were not separated into individual isomers.

1,4-Bis(2,2-dichlorovinyl)benzene (3a) was synthesized by a reaction of hydrazone **1** with $CBrCl_3$ using concentrated aqueous ammonia as a base. Yield 1.023 g (76%), colorless crystals, m.p. 77—78 °C (*cf.* Ref. 1d: 77—78 °C). ^{1}H NMR ($CDCl_3$), δ: 6.86 (s, 2 H, C=C$\underline{\mathrm{H}}$); 7.57 (s, 4 H, Ar).

1,4-Bis(2,2-dibromovinyl)benzene (3b) was synthesized by a reaction of hydrazone **1** with CBr_4 using concentrated aqueous ammonia as a base. Yield 1.219 g (55%), colorless crystals, m.p. 97—98 °C (*cf.* Ref. 1d: 98—99 °C). ^{1}H NMR ($CDCl_3$), δ: 7.48 (s, 2 H, C=C$\underline{\mathrm{H}}$); 7.58 (s, 4 H, Ar).

1,4-Bis(2-chloro-3-ethoxy-3-oxopropenyl)benzene (3c) was synthesized by a reaction of **1** with CCl_3CO_2Et using triethylamine as a base. Yield 0.425 g (25%), colorless heavy oil. A mixture of *Z,Z*- and *Z,E*-isomers in a 72 : 28 ratio. Found (%): C, 56.12; H, 4.80. $C_{16}H_{16}Cl_2O_4$. Calculated (%): C, 55.99; H, 4.70.

Z,Z-isomer. ^{1}H NMR ($CDCl_3$), δ: 1.38 (t, 6 H, CH_3, *J* = 7.1 Hz); 4.34 (q, 4 H, CH_2, *J* = 7.1 Hz), 7.87 (s, 6 H, =CH—, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.2 (CH_3); 62.7 (CH_2); 123.5 (C=$\underline{\mathrm{C}}$—Cl); 130.6 (CH, Ar); 134.4 ((C_{quat})Ar); 135.8 ($\underline{\mathrm{C}}$=C—Cl); 163.1 (CO_2Et).

E,Z-isomer. ^{1}H NMR ($CDCl_3$), δ: 1.19 (t, 6 H, CH_3, *J* = 7.1 Hz), 4.21 (q, 4 H, CH_2, *J* = 7.1 Hz), 7.17 (s, 1 H, =CH—), 7.34 (d, 2 H, Ar, *J* = 8.3 Hz), 7.80 (d, 2 H, Ar, *J* = 8.3 Hz), 7.85 (s, 1 H, =CH—). ^{13}C NMR ($CDCl_3$), δ: 13.7 (CH_3); 62.4 (CH_2); 123.0 (C=$\underline{\mathrm{C}}$—Cl); 124.0 (C=$\underline{\mathrm{C}}$—Cl); 128.7 (CH, Ar); 130.5 (CH, Ar); 133.3 ((C_{quat})Ar); 135.5 ((C_{quat})Ar); 135.9 ($\underline{\mathrm{C}}$=C—Cl), 136.0 ($\underline{\mathrm{C}}$=C—Cl); 163.1 (CO_2Et). Found (%): C, 56.12; H, 4.80. $C_{16}H_{16}Cl_2O_4$. Calculated (%): C, 55.99; H, 4.70.

1,4-Bis(2-chloro-2-cyanovinyl)benzene (3d) was synthesized by a reaction of hydrazone **1** with CCl_3CN using triethylamine as a base. Yield 0.502 g (40%), colorless crystals. A mixture of *E,E*- and *Z,E*-isomers in a ratio of 67 : 33. Found (%): C, 57.96; H, 2.47. $C_{12}H_6Cl_2N_2$. Calculated (%): C, 57.86; H, 2.43.

E,E-isomer. ^{1}H NMR ($CDCl_3$), δ: 7.39 (s, 2 H, C=C$\underline{\mathrm{H}}$); 7.79 (s, 4 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 102.4 (C=$\underline{\mathrm{C}}$—Cl); 114.7 (CN); 129.3 (CH, Ar); 130.9 ((C_{quat})Ar); 143.7 ($\underline{\mathrm{C}}$H=C).

E,Z-isomer. ^{1}H NMR($CDCl_3$), δ: 6.74 (s, 1 H, =CH—); 7.38 (s, 1 H, =CH—); 7.68 (d, 2 H, Ar, *J* = 8.6 Hz); 7.81 (d, 2 H, Ar, *J* = 8.6 Hz).

1,4-Bis(2-bromo-2-fluorovinyl)benzene (3e) was synthesized by a reaction of hydrazone **1** with $CFBr_3$ using concentrated aqueous ammonia as a base. Yield 0.844 g (52%), colorless crystals. A mixture of *E,E*-, *Z,E*-, and *Z,Z*-isomers in a ratio of 66 : 29 : 5. Found (%): C, 37.19; H, 1.94. $C_{10}H_6Br_2F_2$. Calculated (%): C, 37.07; H, 1.87. IR, ν/cm^{-1}: 1647 (C=C).

E,E-isomer. ^{1}H NMR ($CDCl_3$), δ: 5.98 (d, 2 H, C=C$\underline{\mathrm{H}}$, *J* = 33.1 Hz), 7.39 (s, 4 H, C_6H_4). ^{19}F NMR ($CDCl_3$), δ: –67.30 (d, *J* = 33.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 112.7 (d, $\underline{\mathrm{C}}$=C—F, *J* = 5.9 Hz); 128.3 (d, (CH)Ar, *J* = 7.3 Hz); 132.0 (d, (C_{quat})Ar, *J* = 1.8 Hz); 134.5 (d, C=$\underline{\mathrm{C}}$—F, *J* = 332.3 Hz).

E,Z-isomer. ^{1}H NMR ($CDCl_3$), δ: 5.99 (d, 1 H, C=C$\underline{\mathrm{H}}$, *J* = 32.8 Hz); 6.66 (d, 1 H, C=C$\underline{\mathrm{H}}$, *J* = 15.2 Hz), 7.41 (d, 2 H, Ar, *J* = 8.3 Hz), 7.50 (d, 2 H, Ar, *J* = 8.3 Hz). ^{19}F NMR ($CDCl_3$), δ: –64.71 (d, *J* = 15.2). ^{13}C NMR ($CDCl_3$), δ: 111.4 (d, $\underline{\mathrm{C}}$=C—F, *J* = 24.5 Hz); 128.5 (d, (CH)Ar, *J* = 7.3 Hz); 128.5 (d, (CH)Ar, *J* = 7.3 Hz); 128.6 (d, *J* = 3.3 Hz).

Z,Z-isomer. ^{1}H NMR ($CDCl_3$), δ: 6.67 (d, 2 H, C=C$\underline{\mathrm{H}}$, *J* = 15.3 Hz); 7.51 (s, 4 H, Ar).

1,4-Bis(2-bromo-3,3,3-trifluoroprop-1-enyl)benzene (3f) was synthesized by a reaction of dihydrazone **1** with CF_3CBr_3 using concentrated aqueous ammonia as a base. Yield 0.353 g (17%), colorless oil. A mixture of *Z,Z*- and *Z,E*-isomers in a ratio of 78 : 22. Found (%): C, 34.12; H, 1.51. $C_{12}H_6Br_2F_6$. Calculated (%): C, 33.99; H, 1.43.

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.64 (d, 2 H, C=C$\underline{\mathrm{H}}$, *J* = 1.0 Hz); 7.64 (s, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$), δ: 111.0 (q, C=$\underline{\mathrm{C}}$—CF_3, *J* = 37.0); 120.8 (q, CF_3, *J* = 271.9 Hz); 129.7, 133.4 (q, $\underline{\mathrm{C}}$=C—CF_3, *J* = 5.1 Hz); 134.0.

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.38 (d, 2 H, Ar, *J* = 8.3 Hz); 7.54 (s, 1 H, =CH—); 7.62 (s, 1 H, =CH—); 7.77 (d, 2 H, Ar, *J* = 8.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 111.7 (q, C=$\underline{\mathrm{C}}$—CF_3, *J* = 38.0 Hz); 117.4 (q, C=$\underline{\mathrm{C}}$—CF_3, *J* = 34.0 Hz); 120.4 (q, CF_3, *J* = 273.7 Hz); 128.5 (q, Ar, *J* = 1.8 Hz); 129.6; 129.8; 136.7 (q, $\underline{\mathrm{C}}$=C—CF_3, *J* = 7.0 Hz); 140.5 (q, Ar, *J* = 2.6 Hz). Remaining signals are coincide with the signals of *Z,Z*-isomer.

1,4-Bis(2-chloro-3,3,3-trifluoroprop-1-enyl)benzene (3g) was synthesized by a reaction of dihydrazone **1** with CF_3CCl_3 using ethylenediamine as a base. Yield 24%, colorless oil. A mixture of *Z,Z*- and *Z,E*-isomers in a ratio of 67 : 33. Found (%): C, 43.14; H, 1.85. $C_{12}H_6Cl_2F_6$. Calculated (%): C, 43.01; H, 1.80. IR, ν/cm^{-1}: 1650 (C=C).

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.07 (d, 2 H, =CH—, *J* = 1.0 Hz); 7.56 (br.s, 4 H, Ar). ^{13}C NMR spectrum of the isomeric mixture ($CDCl_3$), δ: 120.9 (d, =$\underline{\mathrm{C}}$(Cl)CF_3, *J* = 36.6 Hz); 120.9 (q, CF_3, *J* = 271.6 Hz); 129.7 (d, *J* = 4.6 Hz), 130.1, 133.2.

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.02 (s, 1 H, =CH—); 7.06 (s, 1 H, =CH—); 7.13 (d, 2 H, Ar, *J* = 8.2 Hz); 7.50 (d, 2 H, Ar, *J* = 8.2 Hz).

1,4-Bis(2,3,3,3-tetrafluoroprop-1-enyl)benzene (3h) was synthesized by a reaction of dihydrazone **1** with CF_3CFBr_2 using ethylenediamine as a base. Yield 1.040 g (69%), colorless crystals, m.p. 42—45 °C. A mixture of *Z,Z*- and *Z,E*-isomers in a ratio of 84 : 16. Found (%): C, 47.81; H, 1.95. $C_{12}H_6F_8$. Calculated (%): C, 47.70; H, 2.00.

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 6.44 (d, 2 H, C=C$\underline{\mathrm{H}}$, *J* = 35.2 Hz); 7.61 (s, 4 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 110.7, 118.8 (qd, CF—$\underline{\mathrm{C}}F_3$, *J* = 271.3 Hz, *J* = 41.3 Hz); 129.4, 130.1, 130.2, 130.9, 145.9 (dq, $\underline{\mathrm{C}}$F—CF_3, *J* = 269.4 Hz, *J* = 38.7 Hz).

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 6.82 (d, 1 H, C=C$\underline{\mathrm{H}}$, *J* = 20.5 Hz); 7.34 (d, 2 H, Ar, *J* = 8.1 Hz); 7.58 (d, 2 H, Ar, *J* = 8.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 129.7, 129.8.

1,3-Bis(2,2-dichlorovinyl)benzene (4a) was synthesized by a reaction of dihydrazone **2** with $CBrCl_3$ using concentrated aqueous ammonia as a base. Yield 0.974 g (73%), colorless crystals, m.p. 48—49 °C. IR, ν/cm^{-1}: 1612. ^{1}H NMR ($CDCl_3$), δ: 6.87 (s, 2 H, C=C$\underline{H}$); 7.39 (dd, 1 H, Ar, *J* = 7.0 Hz, *J* = 8.7 Hz); 7.47—7.51 (m, 2 H, Ar), 7.73—7.76 (m, 1 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 121.7 (CH=$\underline{C}$$Cl_2$); 127.9 ($\underline{C}$H=$CCl_2$); 128.5 (Ar); 133.5 (($C_{quat}$)Ar). Found (%): C, 44.82; H, 2.26. $C_{10}H_6Cl_4$. Calculated (%): C, 43.01; H, 1.80.

1,3-Bis(2,2-dibromovinyl)benzene (4b) was synthesized by a reaction of dihydrazone **2** with CBr_4 using concentrated aqueous ammonia as a base. Yield 1.776 g (81%), colorless crystals, m.p. 60—61 °C (*cf.* Ref. 3b: 58—59 °C). ^{1}H NMR ($CDCl_3$), δ: 7.38 (dd, 1 H, Ar, *J* = 7.1 Hz, *J* = 8.5 Hz); 7.47—7.51 (m, 2 H, Ar), 7.48 (s, 2 H, C=C$\underline{H}$); 7.73—7.75 (m, 1 H, Ar).

1,3-Bis[2-(2-chloro-3-ethoxy-3-oxopropenyl)]benzene (4c) was synthesized by a reaction of dihydrazone **2** with CCl_3CO_2Et using triethylamine as a base. Yield 0.389 g (23%), colorless viscous oil. A mixture of *Z,Z*- and *Z,E*-isomers in a ratio of 79 : 21. Found (%): C, 56.15; H, 4.79. $C_{16}H_{16}Cl_2O_4$. Calculated (%): C, 55.99; H, 4.70.

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 1.35 (t, 6 H, CH_3, *J* = 7.1 Hz); 4.31 (q, 4 H, CH_2, *J* = 7.1 Hz); 7.43 (t, 1 H, Ar, *J* = 7.9 Hz); 7.80 (dd, 2 H, Ar, *J* = 7.9 Hz, *J* = 1.4 Hz); 7.86 (s, 2 H, =CH—); 8.25 (s, 1 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.0 (CH_3), 62.5 (CH_2), 123.0 (C=$\underline{C}$—Cl), 128.6, 131.7, 132.1, 133.1, 135.8 ($\underline{C}$=C—Cl), 162.8 (CO_2Et).

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 1.12 (t, 3 H, CH_3, *J* = 7.1 Hz); 4.16 (q, 2 H, CH_2, *J* = 7.1 Hz); 7.17 (s, 1 H, =CH—); 7.28 (d, 1 H, Ar, *J* = 7.6 Hz); 7.35 (t, 1 H, Ar, *J* = 7.6 Hz); 7.72 (d, 1 H, Ar, *J* = 7.6 Hz); 7.73 (s, 1 H, =CH—). ^{13}C NMR ($CDCl_3$), δ: 13.5 (CH_3), 62.1 (CH_2), 123.0 (C=$\underline{C}$—Cl), 124.0 (C=$\underline{C}$—Cl), 128.3, 129.8, 130.1, 130.7, 132.8, 134.1, 136.0 ($\underline{C}$=C—Cl), 162.9 (CO_2Et).

1,3-Bis(2-chloro-2-cyanovinyl)benzene (4d) was synthesized by a reaction of dihydrazone **2** with CCl_3CN using triethylamine as a base. Yield 0.479 g (39%), colorless solid, m.p. 71—73 °C. A mixture of *E,E*- and *Z,E*-isomers in a ratio of 73 : 27. IR, ν/cm^{-1}: 1698 (C=C), 2220 (CN). Found (%): C, 57.94; H, 2.49. $C_{12}H_6Cl_2N_2$. Calculated (%): C, 57.86; H, 2.43.

E,E-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.39 (s, 2 H, C=C$\underline{H}$); 7.54—7.58 (m, 1 H, Ar); 7.77 (t, 2 H, Ar, *J* = 7.7 Hz); 7.80—7.85 (m, 1 H, Ar); 8.07 (s, 1 H, Ar). ^{13}C NMR spectrum of the isomeric mixture ($CDCl_3$), δ: 101.7 (C=$\underline{C}$—Cl); 101.8 (C=$\underline{C}$—Cl); 114.2 (CN); 115.5 (CN); 128.6, 129.3, 129.4, 129.7, 129.8, 130.1, 130.5, 131.7, 131.9, 132.0, 132.2, 132.3, 140.5, 140.6, 143.5 ($\underline{C}$H=C); 143.6 ($\underline{C}$H=C).

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.37 (s, 1 H, =CH—); 7.65—7.69 (m, 1 H, Ar).

1,3-Bis(2-bromo-2-fluorovinyl)benzene (4e) was synthesized by a reaction of dihydrazone **2** with $CFBr_3$ using aqueous ammonia as a base. Yield 0.542 g (34%), colorless oil. A mixture of *E,E*-, *Z,E*-, and *Z,Z*-isomers in a ratio of 58 : 37 : 5. Found (%): C, 37.21; H, 1.91. $C_{10}H_6Br_2F_2$. Calculated (%): C, 37.07; H, 1.87. IR, ν/cm^{-1}: 1652 (C=C).

E,E-Isomer. ^{1}H NMR ($CDCl_3$), δ: 5.97 (d, 2 H, C=C$\underline{H}$, *J* = 32.5 Hz); 7.31—7.43 (m, 4 H, Ar). ^{19}F NMR spectrum of the isomeric mixture ($CDCl_3$), δ: –68.1 (d, *J* = 32.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 111.2 (d, $\underline{C}$=C—F, *J* = 24.3 Hz); 112.6 (d, $\underline{C}$=C—F, *J* = 6.3 Hz); 127.3 (d, *J* = 2.0 Hz); 127.4 (d, *J* = 2.0 Hz); 127.5 (d, *J* = 1.5 Hz); 127.5; 127.6; 127.8 (d, *J* = 3.0 Hz); 127.8; 127.9 (d, *J* = 3.0 Hz); 128.0 (d, *J* = 2.6 Hz); 128.5; 128.7; 129.0; 130.3 (d, C=$\underline{C}$—F, *J* = 339.1 Hz); 132.0; 132.7; 132.9 (d, *J* = 4.8 Hz); 135.3 (d, C=$\underline{C}$—F, *J* = 316.2 Hz); 136.0.

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 5.99 (d, 1 H, C=C$\underline{H}$, *J* = 32.5 Hz); 6.65 (d, 1 H, C=C$\underline{H}$, *J* = 14.9 Hz); 7.52 (s, 1 H, Ar). ^{19}F NMR ($CDCl_3$), δ: –68.1 (d, 1 F, *J* = 32.5 Hz); –65.6 (d, 1 F, *J* = 14.9 Hz).

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 6.67 (d, 2 H, C=C$\underline{H}$, *J* = 14.9 Hz); 7.62 (s, 1 H, Ar).

1,3-Bis(2-bromo-3,3,3-trifluoroprop-1-enyl)benzene (4f) was synthesized by a reaction of dihydrazone **2** with CF_3CBr_3 using concentrated aqueous ammonia as a base. Yield 1.045 g (48%), colorless oil. A mixture of *Z,Z*- and *Z,E*-isomers in a ratio of 83 : 17. Found (%): C, 34.15; H, 1.49. $C_{12}H_6Br_2F_6$. Calculated (%): C, 33.99; H, 1.43.

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.54 (d, 1 H, Ar, *J* = 7.9 Hz); 7.65 (s, 2 H, C=C$\underline{H}$); 7.75 (dd, 2 H, Ar, *J* = 7.9 Hz, *J* = 1.5 Hz); 8.13 (s, 1 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 111.0 (q, C=$\underline{C}$—CF_3, *J* = 37.2 Hz); 120.8 (q, CF_3, *J* = 271.6 Hz); 128.6, 130.0; 131.0; 132.9; 133.6 (q, $\underline{C}$=C—CF_3, *J* = 4.8 Hz).

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.34 (d, 1 H, Ar, *J* = 7.4 Hz); 7.43—7.51 (m, 1 H, Ar); 7.70 (t, 1 H, Ar, *J* = 7.4 Hz); 7.91 (s, 1 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 110.9 (q, C=$\underline{C}$—CF_3, *J* = 37.2 Hz); 120.4 (q, CF_3, *J* = 274.2 Hz), 128.6; 129.0; 129.6; 130.4; 131.3; 133.1; 140.4 (q, *J* = 2.2 Hz).

1,3-Bis(2-chloro-3,3,3-trifluoroprop-1-enyl)benzene (4g) was synthesized by a reaction of dihydrazone **2** with CF_3CCl_3 using ethylenediamine as a base. Yield 0.832 g (50%), colorless oil. A mixture of *Z,Z*- and *Z,E*-isomers in a ratio of 65 : 35. Found (%): C, 43.12; H, 1.86. $C_{12}H_6Cl_2F_6$. Calculated (%): C, 43.01; H, 1.80.

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.34 (s, 2 H, C=C$\underline{H}$); 7.53 (t, 1 H, Ar, *J* = 7.8 Hz); 7.75 (dd, 2 H, Ar, *J* = 7.8 Hz, *J* = 1.2 Hz); 8.13 (s, 1 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 120.7 (q, CF_3, *J* = 272.0 Hz); 120.8 (q, C=$\underline{C}$—CF_3, *J* = 36.9 Hz); 128.7; 129.0; 129.6; 129.8 (q, *J* = 4.4 Hz); 130.4; 130.9; 131.3; 131.8; 132.1; 133.1; 136.0 (q, $\underline{C}$=C—CF_3, *J* = 1.9 Hz).

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 7.26—7.30 (m, 1 H, Ar); 7.30 (s, 1 H, C=C$\underline{H}$); 7.47 (t, 1 H, Ar, *J* = 7.8 Hz); 7.67 (s, 1 H, Ar); 7.70 (t, 1 H, Ar, *J* = 7.8 Hz).

1,3-Bis(2,3,3,3-tetrafluoroprop-1-enyl)benzene (4h) was synthesized by a reaction of dihydrazone **2** with CF_3CFBr_2 using ethylenediamine as a base. Yield 0.491 g (33%), colorless oil. IR, ν/cm^{-1}: 1702 (C=C).

Z,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 6.44 (d, 2 H, C=C$\underline{H}$, *J* = 35.2 Hz). ^{19}F NMR ($CDCl_3$), δ: –73.0 (d, *J* = 10.6 Hz); –131.4 (dq, *J* = 35.2 Hz, *J* = 10.6 Hz).

E,Z-Isomer. ^{1}H NMR ($CDCl_3$), δ: 6.89 (d, 1 H, C=C$\underline{H}$, *J* = 20.3 Hz).

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