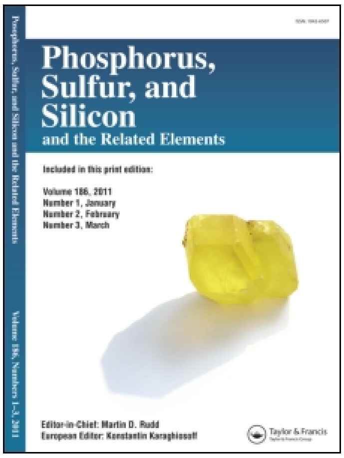

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REACTIONS OF PENTAFLUOROBENZENESULFONYL CHLORIDE WITH ALKENES IN THE PRESENCE OF A RUTHENIUM OR PALLADIUM COMPLEX

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The reactions of pentafluorobenzenesulfonyl chloride with styrenes in the presence of a ruthenium(II) phosphine complex and subsequent treatment with triethylamine were found to give (*E*)-1-aryl-2-(pentafluorobenzenesulfonyl)ethene in high yields. On the other hand, palladium catalyzed reactions of pentafluorobenzenesulfonyl chloride with styrenes in the presence of a base afforded modest yields of both (*E*)-1-aryl-2-(pentafluorophenyl)ethene and (*E*)-1-aryl-2-(pentafluorobenzenesulfonyl)ethene.

Keywords: Pentafluorobenzenesulfonyl chloride; catalytic reaction; perfluorophenylation; perfluorobenzenesulfonylation; ruthenium(II) complex; palladium complex

INTRODUCTION

Previously, we reported the reactions of alkane- and arenesulfonyl chlorides with alkene in the presence of a ruthenium(II) phosphine complex gave corresponding 1:1 adduct in high yield.[1] On the other hand, the reaction of perfluoroalkanesulfonyl chloride with alkene under similar conditions afforded 1:1 adduct with extrusion of sulfur dioxide in high yield, and therefore the reaction was found to be a convenient and an excellent method for the introduction of perfluoroalkyl group into an alkene.[2] Moreover, we recently reported that the reactions of alkane-, arene-, and perfluoroalkanesulfonyl chlorides with silyl enol ether in the presence of a ruthenium(II) complex gave corresponding β-keto sulfone[3] and perfluoroalkyl ketone, respectively[4]. In the course of our studies on the ruthe-

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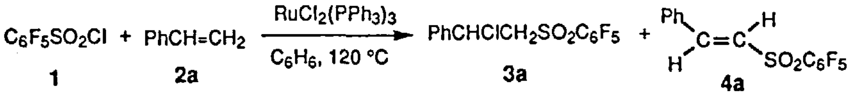
nium(II) catalyzed reactions of various sulfonyl chlorides with alkene and aromatic compound, we found that the ruthenium(II) catalyzed reactions of pentafluorobenzenesulfonyl chloride with aromatic and heteroaromatic compounds afforded pentafluorophenylated compound in good yield.[5] Now, we report here the reaction of pentafluorobenzenesulfonyl chloride with 1-alkene in the presence of a ruthenium(II) complex gives perfluorobenzenesulfonylated compound, and the palladium catalyzed reaction of pentafluorobenzenesulfonyl chloride with styrenes affords pentafluorobenzenesulfonylated compound together with pentafluorophenylated compound.

RESULTS AND DISCUSSION

When a solution of pentafluorobenzenesulfonyl chloride (**1**) (2.0 mmol), styrene (**2a**) (2.2 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in benzene (4.0 cm^3) was degassed and heated at 120 °C for 4 h, the reaction proceeded smoothly. The ^1H NMR spectrum[6] of the reaction mixture after removal the metal complex by flash column chromatography on Florisil with benzene indicated the formation of 1-chloro-2-pentafluorobenzenesulfonyl-1-phenylethane (**3a**) and (*E*)-1-pentafluorobenzenesulfonyl-2-phenylethene (**4a**) in almost 1:1 ratio. The compound **4a** may be formed by dehydrochlorination of **3a** once formed under the reaction conditions because we have found a similar dehydrochlorination catalyzed by the ruthenium(II) complex.[7] Since an attempt to separate these reaction products **3a** and **4a** by elution chromatography and/or gel permeation chromatography was failed, **3a** was converted to **4a** by treatment of the reaction mixture with triethylamine, and the yield was determined as the dehydrochlorinated compound **4a**.



Similarly, the reactions of **1** with some styrene derivatives and 1-alkenes were carried out in the presence of the ruthenium(II) complex, and the product was purified after converting it to dehydrochlorinated compound **4** by addition of triethylamine to the reaction mixture. In all the cases 1-aryl- or 1-alkyl-2-(pentafluorobenzenesulfonyl)ethene **4** was obtained as a sole product in high yield. The results are summarized in Table I.

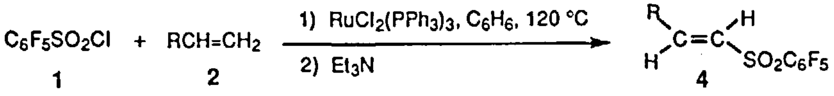


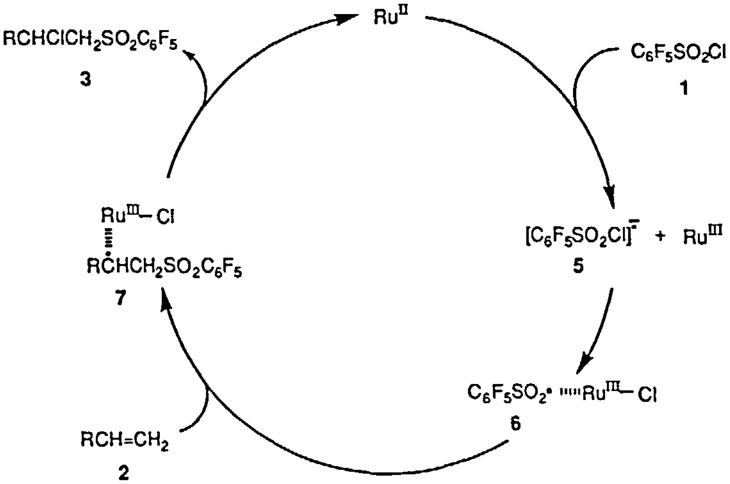
TABLE I Reactions of Pentafluorobenzenesulfonyl Chloride (1) with RCH=CH_2 (2) in the Presence of a Ruthenium(II) Complex.[a]

Run	*R in 2*		*Yield[b]/%*	
1	2a	C_6H_5	4a	85
2	2b	*p*-$CH_3C_6H_4$	4b	81
3	2c	*p*-ClC_6H_4	4c	83
4	2d	*m*-$NO_2C_6H_4$[c]	4d	86
5	2e	C_4H_9	4e	75
6	2f	C_6H_{13}	4f	62

[a] The reactions were carried out at 120 °C for 4 h in a degassed sealed tube containing pentafluorobenzenesulfonyl chloride (2.0 mmol), alkene (2.2 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in benzene (4.0 cm^3). The reaction mixture was treated with an excess amount of triethylamine. [b] Isolated yields. [c] Reaction time: 24 h.

A plausible reaction mechanism for these perfluorobenzenesulfonylations is given in Scheme 1. The electron-transfer reaction between pentafluorobenzenesulfonyl chloride **1** and the ruthenium(II) catalyst affords anion radical **5** of compound **1**, which cleaves homolytically to give pentafluorobenzenesulfonyl radical **6** and Ru^{III}-Cl. The pentafluorobenzenesulfonyl radical **6** adds to the terminal carbon atom of alkene **2** to give carbon radical **7**. The subsequent chlorine-atom abstraction by radical **7** from Ru^{III}-Cl species affords 1:1 adduct **3**, and the ruthenium(II) catalyst is regenerated. Radicals **6** and **7** are considered to be confined in the coordination sphere of the ruthenium complex.[8] Dehydrochlorination from the adduct **3** is partly occurring in the presence of the ruthenium(II) complex to give *E*-1-aryl-2-(pentafluorobenzenesulfonyl)ethene **4**.[7]

The ruthenium(II) catalyzed reaction of **1** with styrene was also carried out at 240 °C expecting the extrusion of sulfur dioxide from the radical **6** to form pentafluorophenyl radical and which adds to styrene forming 1-chloro-2-pentafluorophenyl-1-phenylethane and/or 1-pentafluorophenyl-2-phenylethene under the reaction conditions. Because, we have found that the ruthenium(II) catalyzed reaction of **1** with aromatic and heteroaromatic compounds afforded pentafluorophenylated compound with extrusion of sulfur dioxide.[5] However, no such expected reaction product was detected in the reaction mixture and resinous polymeric compounds formed together with **4a**. The results imply that pentafluorophenyl radical does not form from radical **6** under the reaction conditions, and two reasons are considered that sulfur dioxide does not eliminate from pentafluorobenzenesulfonyl radical **6** under the reaction conditions. One reason is that the pentafluorophenyl radical is an unstable σ-radical compared with sulfonyl radical **6**, and therefore the formation of phenyl radical is very difficult by



SCHEME 1

extrusion of sulfur dioxide from **6**. Another reason is that the reactivity of pentafluorobenzenesulfonyl radical **6** toward alkene is very high so that the addition reaction of radical **6** to alkene proceeds very rapidly before sulfur dioxide eliminates from the radical **6** in contrast to the results found in the reactions of **1** with aromatic and heteroaromatic compounds. Anyway, it was found that chlorine atom and pentafluorobenzenesulfonyl group preferentially adds to an alkene in the ruthenium(II) catalyzed reaction of **1** with alkene.

Then, the reaction of **1** with alkenes was studied in the presence of a palladium complex and a base since Miura *et al.* reported that the palladium catalyzed reaction of arenesulfonyl chloride with alkene in the presence of a palladium complex, a phase transfer catalyst, and a base accompanied extrusion of sulfur dioxide to give arylated compound.[9] When the reaction of pentafluorobenzenesulfonyl chloride **1** (2.0 mmol) with styrene (10.0 mmol) in the presence of dichlorobis(benzonitrile)palladium (0.05 mmol), potassium carbonate (3.0 mmol), and benzyl(trioctyl)ammonium chloride (0.3 mmol) was carried out in *m*-xylene at 140 °C for 4 h, (*E*)-1-pentafluorophenyl-2-phenylethene **8a** formed together with (*E*)-1-pentafluorobenzenesulfonyl-2-phenylethene **4a**. The result shows that elimination of sulfur dioxide from **1** proceeds when a palladium catalyst is employed, though the yields were low. To improve the yield of pentafluorophenylated product **8a**, the reactions of pentafluorobenzenesulfonyl chloride **1** with styrene were examined under various conditions by using several palladium complexes and several organic bases in some aromatic solvents. The results are summarized in Table II. As shown in Run 11, the best result for the formation of perfluorophenylated compound **8a** was obtained when dichlorobis(benzonitrile)palladium, 2,6-di-*tert*-butylpyridine, and *m*-xylene were employed, although the yield was not good enough in this case too.

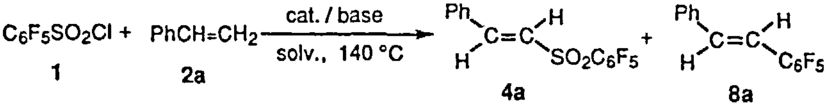


TABLE II Reactions of Pentafluorobenzenesulfonyl Chloride (**1**) with Styrene (**2a**) in the Presence of a Palladium Complex and a Base[a]

Run	*Catalyst*	*Base*	*Solvent*	*Yields* [b]/%	
				4a	*8a*
1	$PdCl_2(PhCN)_2$[c]	K_2CO_3	*m*-xylene	3	9
2	$PdCl_2(CH_3CO_2)_2$[d]	DTBP[e]	*m*-xylene	5	29
3	$PdCl_2(PhCN)_2$[d]	DTBP	*m*-xylene	26	26
4	$PdCl_2(PPh_3)_2$	DTBP	*m*-xylene	trace	3
5	$Pd(PPh_3)_4$	DTBP	*m*-xylene	19	18
6	$PdCl_2(PhCN)_2$	Et_3N	*m*-xylene	trace	3
7	$PdCl_2(PhCN)_2$	2,6-lutidine	*m*-xylene	31	0
8	$PdCl_2(PhCN)_2$	DPP[f]	*m*-xylene	3	8
9	$PdCl_2(PhCN)_2$	DTBP	benzonitrile	33	3
10	$PdCl_2(PhCN)_2$	DTBP	*p*-cymene[g]	6	29
11	$PdCl_2(PhCN)_2$	DTBP	*m*-xylene	25	39

[a] The reactions were carried out at 140 °C for 4 h in a degassed sealed tube containing pentafluorobenzenesulfonyl chloride (2.0 mmol), styrene (10.0 mmol), palladium catalyst (0.05 mmol), base (2.2 mmol), and solvent (4.0 cm^3). [b] Isolated yields. [c] Phase-transfer catalyst, $Bz(Oct)_3NCl$ (0.3 mmol), was added. [d] Triphenylphosphine (0.1 mmol) was added. [e] DTBP: 2,6-Di-*tert*-butylpyridine. [f] DPP: 2,6-Diphenylpyridine. [g] Reaction temperature: 160 °C.

Then, the reactions of pentafluorobenzenesulfonyl chloride **1** with several styrene derivatives **2** were carried out in the presence of dichlorobis(benzonitrile)palladium, 2,6-di-*tert*-butylpyridine, and *m*-xylene at 140 °C for 4 h, and the results are summarized in Table III. As shown in Table III, (*E*)-1-aryl-2-(pentafluorophenyl)ethene **8** formed together with (*E*)-1-aryl-2-(pentafluorobenzenesulfonyl)ethene **4**, although the yield was low.

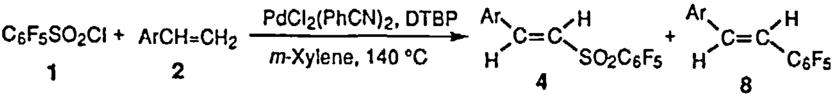


TABLE III Reactions of Pentafluorobenzenesulfonyl Chloride (**1**) with $RCH=CH_2$ (**2**) in the Presence of a Dichlorobis(benzonitrile)palladium and DTBP[a]

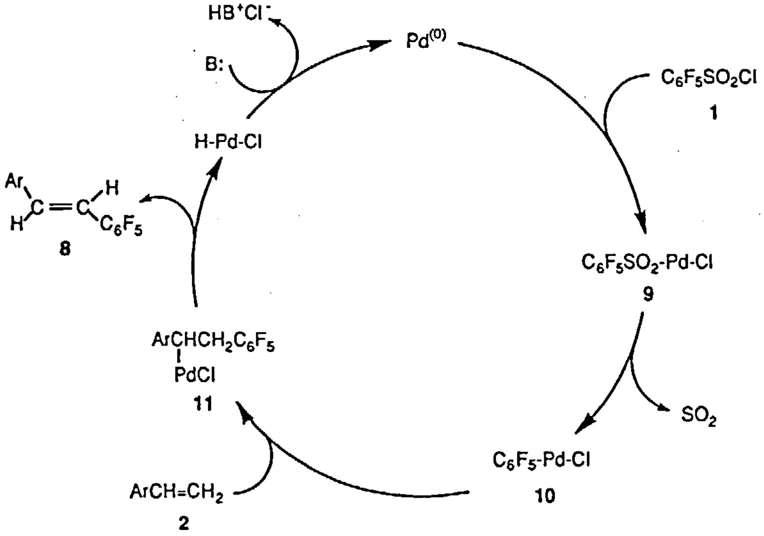
Run	*R in 2*		*Yields*[b]*/%*			
1	2a	C_6H_5	4a	25	8a	39
2	2a	C_6H_5[c]	4a	11	8a	28
3	2b	p-$CH_3C_6H_4$	4b	4	8b	11
4	2c	p-ClC_6H_4	4c	10 (16)	8 c	18 (29)
5	2d	m-$NO_2C_6H_4$[d]	4d	26 (50)	8d	13 (25)

[a] The reactions were carried out at 140 °C for 4 h in a degassed sealed tube containing pentafluorobenzenesulfonyl chloride (2.0 mmol), styrene derivatives (10.0 mmol), dichlorobis(benzonitrile)palladium (0.05 mmol), 2,6-di-*tert*-butylpyridine (2.2 mmol), and *m*-xylene (4.0 cm^3). [b] Isolated yields. In parentheses are the yields determined by GC. [c] Reaction temperature: 180 °C. [d] Reaction time: 24 h.

The reaction mechanism of the perfluorophenylation is shown in Scheme 2. The oxidative addition of pentafluorobenzenesulfonyl chloride **1** to the palladium(0) catalyst, which is considered to be formed in the reaction media, affords $C_6F_5SO_2$-Pd-Cl **9** which eliminates sulfur dioxide giving C_6F_5-Pd-Cl species **10**. Insertion of carbon-carbon double bond of styrene derivative to the carbon-palladium bond of **10** affords intermediate **11**, and the subsequent β-elimination of H-Pd-Cl from **11** affords (*E*)-1-aryl-2-(pentafluorophenyl)ethene **8**. The palladium(0) catalyst is regenerated by the reaction of base to the palladium hydrochloride species H-Pd-Cl, and the catalytic cycle is achieved as in the Heck reaction.[10] (*E*)-1-Aryl-2-(pentafluorobenzenesulfonyl)ethene **4** is considered to be formed by the insertion of styrene derivative to the $C_6F_5SO_2$-Pd-Cl species **9**, before sulfur dioxide eliminates from **9**, affording $ArCH(PdCl)CH_2SO_2C_6F_5$ and the subsequent reactions similar to the formation of **8**.

EXPERIMENTAL

M.p.s were determined on a Yamato MP21 apparatus and were uncorrected. IR spectra were determined on a Hitachi 260–10 spectrometer with samples either neat liquides or KBr disks. ^1H or ^{13}C NMR spectra were determined on a JEOL JNM-EX 400 and a JEOL JNM-LA 500 FT NMR spectrometers at 400 or 100 and 500 or 125 MHz, respectively, using Me_4Si as an internal standard, and *J*-values are given in Hz. ^{19}F NMR spectra were taken on a JEOL JNM-EX 400 FT NMR spectrometer at 376 MHz using $CFCl_3$ as an internal standard. Mass



SCHEME 2

spectra were measured on a JEOL JMS-AX 500 spectrometer by electron impact (EI) at 70 eV. Gas-liquid chromatography (GLC) were performed using a Hitachi G-3000 gas chromatograph with OV-1 (10%) 25 m capillary column. Gel-permeation chromatography (GPC) was performed using a JAI LC-08 and JAI LC-908 liquid chromatograph with two JAIGEL-1H columns (20 mm × 600 mm) with chloroform as eluent.

All solvents were distilled and stored under nitrogen. Pentafluorobenzenesulfonyl chloride from Fluorochem was used without further purification. Styrene, *m*-nitrostyrene, and 1-hexene from Wako Chemicals, *p*-methylstyrene, *p*-chlorostyrene, *p*-xylene, and 1-octene from Tokyo Kasei Chemicals were distilled and stored under nitrogen. 2,6-Lutidine and 2,6-diphenylpyridine from Tokyo Kasei Chemicals, and 2,6-di-*tert*-butylpyridine from Aldrich Chemicals were used without further purification. Dichlorotris(triphenylphosphine)ruthenium(II)[11] (mp 133.0–135.5 °C; lit. mp 132–134 °C), dichlorobis(benzonitrile) palladium(II)[12] (mp 125.5–127.0 °C), and tetrakis(triphenylphosphine)-palladium(0)[13] were prepared by the method described in the literature. Palladium acetate(II) from Wako Chemicals and dichlorobis(triphenylphosphine)palladium(II) from Aldrich Chemicals were used without further purification.

General Procedure for the Reaction of Pentafluorobenzenesulfonyl Chloride with Alkenes in the Presence of a Ruthenium(II) Complex

A solution containing pentafluorobenzenesulfonyl chloride (**1**) (533 mg, 2.0 mmol), alkene (**2**) (2.2 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (20 mg, 0.02 mmol) in dry benzene (4.0 cm^3) was degassed by a freeze-pump-thaw cycle, sealed in an ampoule, and heated at 120 °C for 4 h. After addition of excess amount of triethylamine (506 mg, 5.0 mmol) to the reaction mixture at room temperature, the mixture was subjected to short-column chromatography on silica-gel with benzene-hexane (1:1) as eluent to remove the metal complex. The products were isolated from the reaction mixture by use of GPC and/or column chromatography over silica-gel (Wakogel C-60), and were identified by IR, NMR and MS spectroscopy.

General Procedure for the Reaction of Pentafluorobenzenesulfonyl Chloride with Styrenes in the Presence of a Palladium Complex

A solution containing pentafluorobenzenesulfonyl chloride (**1**) (533 mg, 2.0 mmol), styrene derivatives (**2**) (10.0 mmol), and a palladium complex (20 mmg, 0.05 mmol) in *m*-xylene (4.0 cm^3) was degassed by a freeze-pump-thaw cycle, sealed in an ampoule, and heated at 140 °C for an adequate time. The reaction mixture was subjected to short-column chromatography on silica-gel with hexane or benzene as eluent to remove the metal complex. The products were isolated from the reaction mixture by use of GPC and/or column chromatography over silica-gel (Wakogel C-60), and were identified by IR, NMR and MS spectroscopy. The physical and spectral data for the compounds obtained are as follows.

(*E*)-1-Pentafluorobenzenesulfonyl-2-phenylethene (**4a**): mp 117.0–118.0 °C; IR (KBr) 3060, 1340, and 1140 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10 (1H, d, *J* = 15.6 Hz), 7.42–7.56 (5H, m), and 7.84 (1H, d, *J* = 15.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 126.1, 129.2, 129.5, 131.6, 132.4, and 147.1; ^{19}F NMR (376 MHz, CDCl$_3$) δ 136.3 (2F, m), 144.6 (1F, tt, *J* = 20.7 and 6.8 Hz), and 158.5 (2F, m); MS (*m/z*) 334 (M$^+$), 269, 250, 167, 103, 102, and 77. Calcd for $C_{14}H_7O_2SF_5$: C, 50.31; H, 2.11. Found: C, 50.53; H, 1.93.

(*E*)-1-Pentafluorobenzenesulfonyl-2-(4'-tolyl)ethene (**4b**): mp 136.0–137.0 °C; IR (KBr) 3060, 2930, 1340, and 1150 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.40 (3H, s), 7.04 (1H, d, *J* = 15.2 Hz), 7.25 (2H, d, *J* = 8.1 Hz), 7.44 (2H, d, *J* = 8.1 Hz), and 7.80 (1H, d, *J* = 15.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.7, 124.7, 128.8, 129.2, 130.0, 143.3, and 147.1; ^{19}F NMR (376 MHz, CDCl$_3$) δ 136.4 (2F, m), 145.0 (1F, tt, *J* = 20.7 and 7.0 Hz), and 158.6 (2F, m); MS (*m/z*) 348 (M$^+$), 283, 269, 167, 117, 116, and 91. Calcd for $C_{15}H_9O_2SF_5$: C, 51.73; H, 2.60. Found: C, 51.85; H, 2.37.

(*E*)-1-(4'-Chlorophenyl)-2-pentafluorobenzenesulfonylethene (**4c**): mp 143.5–144.5 °C; IR (KBr) 3060, 1340, and 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (1H, d, *J* = 15.6 Hz), 7.43 (2H, d, *J* = 8.8 Hz), 7.49 (2H, d, *J* = 8.8 Hz), and 7.79 (1H, d, *J* = 15.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.5, 129.7, 130.0, 130.2, 138.5, and 145.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ 136.3 (2F, m), 144.2 (1F, m), and 158.3 (2F, m); MS (*m/z*) 368 (M^+), 304, 167, and 136. Calcd for $C_{14}H_6O_2SF_5Cl$: C, 45.61; H, 1.64. Found: C, 45.66; H, 1.46.

(*E*)-1-Pentafluorobenzenesulfonyl-2-(3'-nitrophenyl)ethene (**4d**): mp 124.5–125.5 °C; IR (KBr) 3100, 1540, 1350, 1150, and 900 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (1H, d, *J*= 15.4 Hz), 7.90 (1H, d, *J* = 15.4 Hz), 7.67–8.35 (3H, m), and 8.43 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.3, 126.3, 129.3, 130.6, 133.3, 134.7, 143.9, and 148.8 ; ^{19}F NMR (376 MHz, $CDCl_3$) δ 136.0 (2F, m), 143.4 (1F, tt, *J* = 20.7 and 6.8 Hz), and 158.0 (2F, m); MS (*m/z*) 379 (M^+), 315, 298, 215, 146, 118, and 102. Calcd for $C_{14}H_6NO_4SF_5$: C, 44.34; H, 1.59; N, 3.69. Found: C, 44.31; H, 1.40; N, 3.70.

(*E*)-1-Pentafluorobenzenesulfonyl-1-hexene (**4e**): pale yellow oil; IR (neat) 2975, 2950, 1520, 1500, 1350, 1300, 1160, 1100, and 990 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (3H, t, *J* = 7.3 Hz), 1.36 (2H, sext, *J* = 7.3 Hz), 1.50 (2H, quint, *J* = 7.3 Hz), 2.33 (2H, tt, *J* = 7.3 and 7.3 Hz), 6.57 (1H, d, *J* = 14.2 Hz), and 7.21 (1H, dt, *J*= 14.4 and 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 22.1, 29.4, 31.4, 129.6, and 152.6; MS (m/z) 314 (M^+), 285, 259, 215, 167, and 117. HRMS Calcd for $C_{12}H_{11}O_2SF_5$: 314.0400. Found: *m/z* 314.0318.

(*E*)-1-Pentafluorobenzenesulfonyl-1-octene (**4f**): pale yelow oil; IR (neat) 2950, 1520, 1500, 1350, 1300, 1160, 1100, and 990 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.25–1.35 (6H, m), 1.50 (2H, quint, *J* = 7.2 Hz), 2.33 (2H, tt, *J* = 7.2 and 7.2 Hz), 6.57 (1H, d, *J* = 15.1 Hz), and 7.21 (1H, dt, *J* = 15.1 and 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 22.4, 27.3, 28.7, 31.4, 31.7, 129.6, and 152.6; MS (*m/z*) 343 (M^+ + 1), 285, 259, 215, and 167. HRMS Calcd for $C_{14}H_{15}O_2SF_5$: 342.0712. Found: 342.0775.

(*E*)-1-Pentafluorophenyl-2-phenylethene (**8a**): mp 136.0–137.0 °C (139.5–140°C[14]) ; IR (KBr) 1520, 1490, 1000, and 960 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.98 (1H, d, *J* = 17.0 Hz), 7.43 (1H, d, *J* = 17.0 Hz), and 7.3–7.6 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.7, 126.9, 128.9, 129.0, 136.5, and 137.2; MS (*m/z*) 270(M^+), 250, 219, and 201.

(*E*)-1-Pentafluorophenyl-2-(4'-tolyl)ethene (**8b**): mp 132.0–133.0 °C (143 °C[15]); IR (KBr) 1520, 1490, 1000, 960, and 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 6.93 (1H, d, *J* = 17.1 Hz), 7.20 (2H, d, *J* = 8.3 Hz), 7.41 (1H, d, *J* = 17.1 Hz), and 7.43 (2H, d, *J*=8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ

21.3, 111.7, 126.9, 129.3, 129.6, 133.7, and 139.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ 163.6 (2F, td, $J = 20.7$ and 7.0 Hz), 157.5 (1F, t, $J = 20.7$ Hz), 143.4 (2F, dd, $J = 20.7$ and 7.0 Hz); MS (*m/z*) 284 (M^+), 269, 250, and 219.

(*E*)-1-(4'-Chlorophenyl)-2-pentafluorophenylethene (**8c**): mp 100.0–101.0 °C (102–104 °C^{16}); IR (KBr) 1520, 1500, 1130, 1010, 970, and 930 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (1H, d, $J = 16.7$ Hz), 7.35 (2H, d, $J = 8.7$ Hz), 7.37 (1H, d, $J = 16.7$ Hz), and 7.45 (2H, d, $J = 8.7$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.1, 114.0, 127.3, 128.3, 128.7, and 129.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ 163.2 (2F, td, $J = 20.7$ and 7.0 Hz), 156.4 (1F, t, $J = 20.7$ Hz), 143.1 (2F, dd, $J = 20.7$ and 7.0 Hz); MS (*m/z*) 304 (M^+), 284, 269, 250, and 219.

(*E*)-1-Pentafluorophenyl-2-(3'-nitrophenyl)ethene (**8d**): mp 106.0–107.0 °C; IR (KBr) 1520, 1500, 1350, 1000, and 970 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (1H, d, $J = 17.1$ Hz), 7.48 (1H, d, $J = 17.1$ Hz), 7.58 (1H, t, $J = 7.8$ Hz), and 7.83 (1H, d, $J = 7.8$ Hz), 8.18 (1H, d, $J = 7.8$ Hz), and 8.38 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.8, 121.4, 123.3, 129.9, 132.6, 134.5, 138.2, and 148.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ 182.2 (2F, td, $J = 20.7$ and 6.8 Hz), 174.5 (1F, t, $J = 20.7$ Hz), 161.9 (2F, dd, $J = 20.7$ and 6.8 Hz) ; MS (*m/z*) 315 (M^+), 269, 250, and 219. Calcd for $C_{14}H_6NO_2F_5$: C, 53.35; H, 1.92; N, 4.44. Found: C, 53.10; H, 1.71; N, 4.37.

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[6] ^{1}H NMR (400 MHz, $CDCl_3$) of the reaction mixture: δ 4.10 (2H, d, $J = 7.3$ Hz), 5.41 (1H, d, $J = 7.3$ Hz), and 7.25–7.60 (5H, m) corresponding to **3a**; and δ 7.10 (1H, d, $J = 15.6$ Hz), 7.42–7.56 (5H, m), and 7.84 (1H, d, $J = 15.6$ Hz) corresponding to **4a**. The product ratio of **3a**:**4a** was determined to be almost 1:1 by the integral ratio of the ^{1}H NMR spectrum.

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