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Mild and metal-free trifluoromethylation and pentafluoroethylation of *gem*-difluoroalkenes with $TMSCF_3$ and $TMSCF_2CF_3$

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ABSTRACT

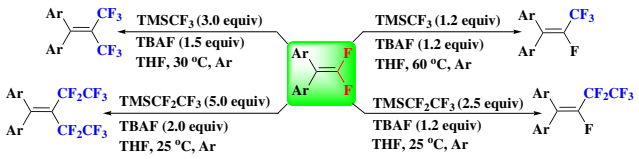
A direct and efficient approach for the trifluoromethylation and pentafluoroethylation of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_3$ and $TMSCF_2CF_3$ in the presence of TBAF was developed. The reactions proceeded smoothly under mild reaction conditions to give the corresponding monotrifluoromethylated, bistrifluoromethylated, monopentafluoroethylated and bispentafluoroethylated products in fair to good yields, respectively, without the addition of metal catalyst.

1. Introduction

Trifluoromethylated alkenes are useful structural motifs that have been widely used in pharmaceuticals, agrochemicals as well as material science.[1] Therefore, a variety of methods for nucleophilic, electrophilic, and radical trifluoromethylation of alkenes with various trifluoromethylating reagents have been developed over the past few years.[2] However, drawbacks of these methods are the use of expensive Togni's or Umemoto's reagents, transition-metal catalysts and the handling of gaseous CF_3X.[3]

(Trifluoromethyl)trimethylsilane ($TMSCF_3$), known as Ruppert–Prakash reagent, is a powerful and versatile reagent for facile introduction of the trifluoromethyl moiety into organic molecules.[4] In 2011, Bräse reported an efficient method for the trifluoromethylation of alkenyl iodides and bromides using a system of $TMSCF_3$/CuI/KF.[5] Buchwald developed a palladium-catalyzed trifluoromethylation of various cyclohexenyl triflates and nonaflates with $TMSCF_3$ and a variety of trifluoromethylated cyclohexenes were obtained in good to high yields.[6] Yu described a copper-catalyzed trifluoromethylation of internal olefins, α-oxoketene dithioacetals, using $Cu(OH)_2$ as a catalyst and $TMSCF_3$ as a trifluoromethylating reagent to afford the corresponding multifunctionalized tetrasubstituted CF_3 olefins and trifluoromethylated *N*-heterocycles.[7]

gem-Difluoroalkenes have unique reactivities toward nucleophiles, which render them more useful in organic synthesis.[8] It is well-known that the trifluoromethyl anion could be generated in situ from $TMSCF_3$ in combination with KF.[9] Although the 'naked' trifluoromethyl carbanion is unstable and easily decomposes at room temperature,[4a] we expected that the nucleophilic trifluoromethylation of the polarized *gem*-difluoroalkenes with the active CF_3 anion species might take place. A survey of the literature reveals that trifluoromethylation of C–F bond of arenes and alkenes with trifluoromethylating reagents has been scarcely reported.[10] In continuation of our interest in the cleavage and functionalization of the C–F bond,[11] in this paper, we report a straightforward method for the trifluoromethylation (pentafluoroethylation) of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_3$ ($TMSCF_2CF_3$) in the presence of TBAF under mild reaction conditions (Scheme 1). In addition, we also report a novel Pd-catalyzed trifluoromethylation of *N*-(α-fluorovinyl)azoles with $TMSCF_3$ (Scheme 6).



Scheme 1. Trifluoromethylation and pentafluoroethylation of *gem*-difluoroalkenes.

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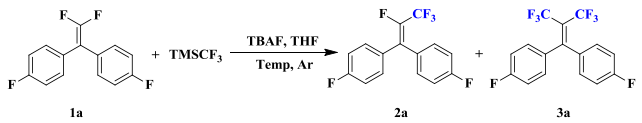
2. Results and discussion

Our initial investigations focused on the reaction between 4,4′-(2,2-difluoroethene-1,1-diyl)bis(fluorobenzene) **1a** and $TMSCF_3$ using TBAF as fluoride source (Table 1). The results indicated that the amounts of $TMSCF_3$, TBAF and reaction temperature had significant effects on the yields and ratios of two types of products, monotrifluoromethylated product **2a** and bistrifluoromethylated product **3a**. However, no matter what the reaction conditions were, a mixture of **2a** and **3a** along with the recovered starting material **1a** were obtained. Further decreasing the amount of $TMSCF_3$ to 1.0 equiv or increasing the amount of $TMSCF_3$ to 4.0 equiv, respectively, could not provide the sole product (**2a** or **3a**) (entries 2 and 6). Fortunately, the mixture of **2a** and **3a** could be separated by column chromatography. Consequently, the optimal reaction conditions for the synthesis of **2a** are as follows: 1.2 equiv of $TMSCF_3$, 1.2 equiv of TBAF, and THF as the solvent at 60 °C (entry 3). The optimal reaction conditions for the synthesis of **3a** are as follows: 3.0 equiv of $TMSCF_3$, 1.5 equiv of TBAF, and THF as the solvent at 30 °C (entry 15).

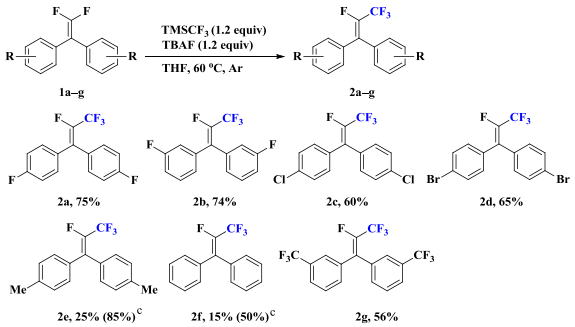
Table 1
Optimization of the reaction conditions for the synthesis of **2a** and **3a**[a]



Entry	$TMSCF_3$ (equiv)	TBAF (equiv)	Temp (°C)	Yield **2a**[b] (%)	Yield **3a**[b] (%)
1	0.5	1.2	60	14	0
2	1.0	1.2	60	63	17
3	1.2	1.2	60	85	15
4	2.0	1.2	60	80	20
5	3.0	1.2	60	72	28
6	4.0	1.2	60	69	31
7	1.2	1.2	30	65	27
8	1.2	1.0	60	81	17
9	1.2	1.5	60	76	20
10	3.0	1.2	10	65	2
11	3.0	1.2	20	63	31
12	3.0	1.2	30	59	43
13	3.0	1.2	40	53	38
14	3.0	1.2	50	69	31
15	3.0	1.5	30	34	56
16	3.0	2.0	30	41	52

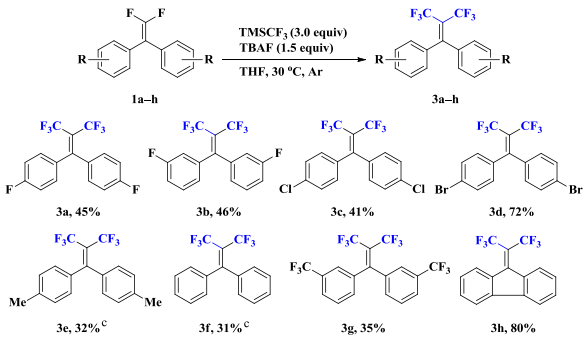
[a] Reaction conditions: **1a** (1.0 mmol), THF (5 mL), Ar, 1 h.
[b] Yields determined by GC analysis and based on **1a**.

With the optimized conditions in hand (Table 1, entries 3 and 15), we next examined the scope of the novel nucleophilic trifluoromethylation of different 1,1-diaryl-2,2-difluoroethenes with $TMSCF_3$ (Schemes 2 and 3). Most substrates could afford monotrifluoromethylated alkenes **2a**–**g** or bistrifluoromethylated alkenes **3a**–**h** in moderate to good yields, respectively. However, the reaction efficiency of the bistrifluoromethylation of *gem*-difluoroalkenes was lower than that of the monotrifluoromethylation. Generally, *gem*-difluoroalkenes bearing electron-withdrawing group gave the desired products in higher yields than substrates bearing electron-donating or neutral groups with 1.2 equiv of $TMSCF_3$ (e.g., the isolated yields of **2e** and **2f** were very low, Scheme 2). To obtain satisfactory yields, the amounts of $TMSCF_3$ was increased to 3.0 equiv and 5.0 equiv, respectively (**2e**, **2f** and **3e**, **3f**). The reaction of 9-(difluoromethylene)-9*H*-fluorene **1h** with $TMSCF_3$ could provide bistrifluoromethylated alkene **3h** as a sole product with 80% yield.



[a] Reaction conditions: **1a–g** (1.0 mmol), $TMSCF_3$ (1.2 mmol), TBAF (1 M in THF, 1.2 mmol), THF (5 mL), 60 °C, 0.5–1 h, Ar. [b] Isolated yields (some products are volatile and are lost during the chromatographic purification and rotary evaporation). [c] 3.0 mmol $TMSCF_3$ was used.

Scheme 2. Monotrifluoromethylation of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_3$.[a,b]



[a] Reaction conditions: **1a–h** (1.0 mmol), $TMSCF_3$ (3.0 mmol), TBAF (1 M in THF, 1.5 mmol), THF (5 mL), 30 °C, 0.5–1 h, Ar. [b] Isolated yields (some products are volatile and are lost during the chromatographic purification and rotary evaporation). [c] 5.0 mmol $TMSCF_3$ was used.

Scheme 3. Bistrifluoromethylation of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_3$.[a,b]

The CF_3CF_2-substituted moiety serves as a useful structural element in many pharmaceuticals and agrochemicals. Much recent attention has been devoted to the development of new methods for the construction of $C_{vinyl}–CF_2CF_3$ bonds.[12] Encouraged by the success in the mono- and bis-trifluoromethylation of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_3$, we next attempted to pentafluoroethylate *gem*-difluoroalkenes with $TMSCF_2CF_3$. Thus, the pentafluoroethylation of 1,1-diaryl-2,2-difluoroethenes **1a** with $TMSCF_2CF_3$ in the presence of TBAF was selected as a model reaction to optimize the reaction conditions (Table 2). The behaviour of $TMSCF_2CF_3$ towards **1a** is almost the same as that observed previously with $TMSCF_3$. Generally, a mixture of monopentafluoroethylated product **4a** and bispentafluoroethylated product **5a** was observed. After screening of a number of reaction conditions, the optimal reaction conditions for the synthesis of **4a** (or **5a**) are as follows: 2.5 (or 5.0) equiv of $TMSCF_2CF_3$, 1.2 (or 2.0) equiv of TBAF, and THF as the solvent at 25 °C (entries 3 and 12).

Next, the scope of this novel pentafluoroethylation reaction was investigated by treatment of different 1,1-diaryl-2,2-difluoroethenes with $TMSCF_2CF_3$ under the aforementioned optimized reaction conditions (Table 2, entries 3 and 12).

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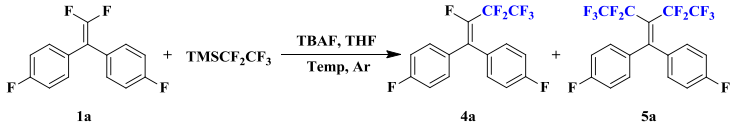
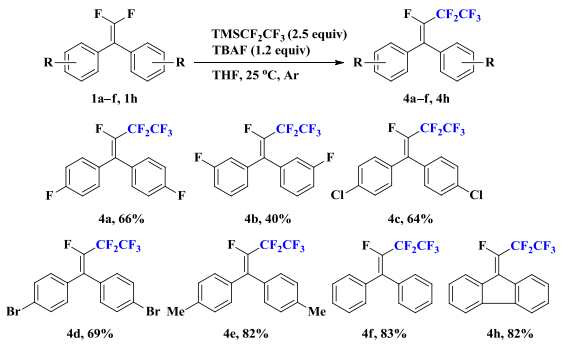
Table 2
Optimization of the reaction conditions for the synthesis of **4a** and **5a**[a]



Entry	$TMSCF_2CF_3$ (equiv)	TBAF (equiv)	Temp (°C)	Yield **4a**[b] (%)	Yield **5a**[b] (%)
1	1.0	1.2	25	48	0
2	2.0	1.2	25	75	8
3	2.5	1.2	25	83	7
4	2.5	1.2	0	38	0
5	2.5	1.2	10	41	0
6	2.5	1.2	40	82	8
7	2.5	1.0	25	69	5
8	2.5	1.5	25	77	12
9	3.0	1.2	25	53	47
10	4.0	1.2	25	49	51
11	5.0	1.2	25	46	54
12	5.0	2.0	25	42	58
13	5.0	2.0	40	44	55

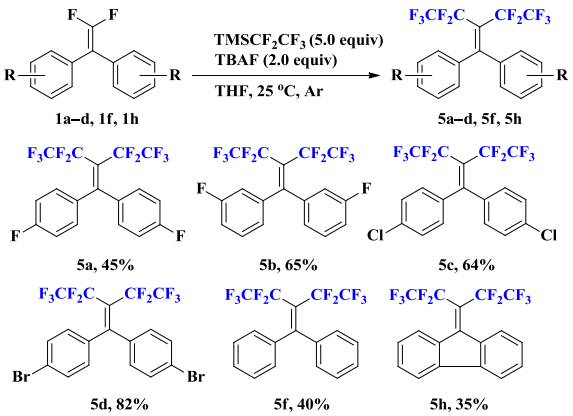
[a] Reaction conditions: **1a** (1.0 mmol), THF (5 mL), Ar, 1 h.
[b] Yields determined by GC analysis and based on **1a**.

As shown in Schemes 4 and 5, both monopentafluoroethylation and bispentafluoroethylation reaction proceeded smoothly and afforded the corresponding products in 35–83% yields. Additionally, the structure of **4h** was confirmed by X-ray crystallographic analysis (Fig. 1).



[a] Reaction conditions: **1a–f**, **1h** (1.0 mmol), $TMSCF_2CF_3$ (2.5 mmol), TBAF (1 M in THF, 1.2 mmol), THF (5 mL), 25 °C, 0.5–1 h, Ar. [b] Isolated yields (some products are volatile and are lost during the chromatographic purification and rotary evaporation).

Scheme 4. Monopentafluoroethylation of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_2CF_3$.[a,b]



[a] Reaction conditions: **1a–d**, **1f**, **1h** (1.0 mmol), $TMSCF_2CF_3$ (5.0 mmol), TBAF (1 M in THF, 2.0 mmol), THF (5 mL), 25 °C, 0.5–1 h, Ar. [b] Isolated yields (some products are volatile and are lost during the chromatographic purification and rotary evaporation).

Scheme 5. Bispentafluoroethylation of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_2CF_3$.[a,b]

Inspired by the observed reactivity of $TMSCF_3$ towards *gem*-difluoroalkenes, we next extended the substrates to several *N*-(α-fluorovinyl)azoles. Unfortunately, the C–F bonds in *N*-(α-fluorovinyl)azoles are less reactive under the abovementioned optimized reaction conditions and the nucleophilic vinylic substitution reaction (S_NV) could not take place. Therefore, we used 1-(1-fluoro-2,2-diphenylvinyl)-1*H*-imidazole **1i** as a model substrate to reinvestigate the reaction conditions (Table 3). The results indicated that the reactivity of the C–F bond in **1i** toward $TMSCF_3$ was very low. For example, no trifluoromethylated product **6i** was observed in absence of metal catalyst (entry 1). Both Ni and Pd salts could catalyze the trifluoromethylation of **1i** with $TMSCF_3$, however, their catalytic activity was not very high and the desired product **6i** was obtained in moderate yield along with small amounts of C–N bond cleavage product **3f** (bistrifluoromethylated product) (such as entries 4, 7–12). Based on these experiments, the relatively optimal reaction conditions were established as follows: 5.0 equiv of

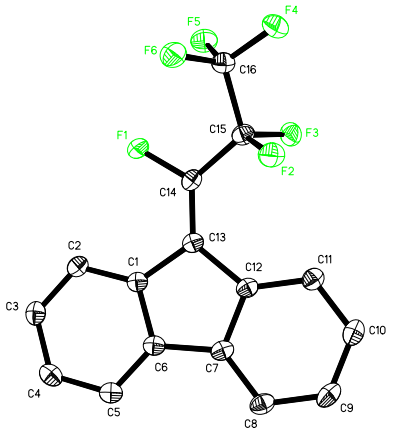
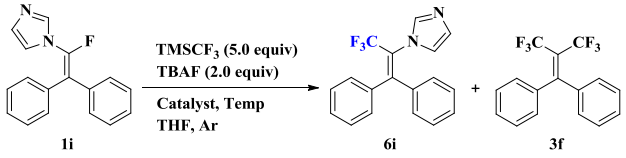


Fig. 1. Crystal structure of compound **4h**.

Table 3
Optimization of the reaction conditions for the synthesis of **6i**[a]



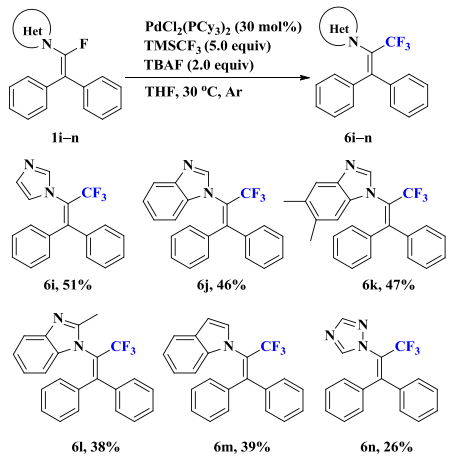
1i 6i 3f

Entry	Catalyst (mol %)	Temp (°C)	Yield **6i** (%)	Yield **3f** (%)[b]
1	None	60	0	0
2	$NiCl_2$(dppe) (30)	60	3	56
3	$NiCl_2(PCy_3)_2$ (30)	60	31	10
4	$NiCl_2$(dppp) (30)	60	50	16
5	$NiCl_2(PCy_3)_2$ (30)	30	37	15
6	$NiCl_2$(dppe) (30)	30	37	63
7	$NiCl_2$(dppp) (30)	30	49	11
8	$NiBr_2(PPh_3)_2$ (30)	30	51	12
9	$PdCl_2$(dppe) (30)	30	48	7
10	$PdCl_2(CH_3CN)_2$ (30)	30	49	11
11	$PdCl_2(PCy_3)_2$ (30)	30	60	20
12	$PdCl_2(PCy_3)_2$ (20)	30	50	15

[a] Reaction conditions: **1i** (1.0 mmol), $TMSCF_3$ (5.0 mmol), TBAF (1 M in THF, 2.0 mmol), THF (5 mL), Ar, 1 h.
[b] Yields referred to the desired product **6i**. Yields determined by GC analysis and based on **1i**.

$TMSCF_3$, 2.0 equiv of TBAF, 0.3 equiv of $PdCl_2(PCy_3)_2$ and THF as the solvent at 30 °C (entry 11).

To determine the limitations of this method, we applied this Pd-catalyzed trifluoromethylation reaction to several additional *N*-(α-fluorovinyl)azoles. As shown in Scheme 6, substrates **1i**–**n** could react with $TMSCF_3$ in presence of 30 mol% $PdCl_2(PCy_3)_2$ and afforded slightly lower yields of trifluoromethylated *N*-vinylazoles (**6i**–**n**). The lack of reactivity and incomplete conversions displayed by these substrates (**1i**–**n**) might be ascribed to the fact that the electron-donating inductive effect exerted by the azole nitrogen atom makes C–F bond relatively unreactive.



[a] Reaction conditions: **1i–n**, (1.0 mmol), $TMSCF_3$ (5.0 mmol), $PdCl_2(PCy_3)_2$ (0.3 mmol), TBAF (1 M in THF, 2.0 mmol), THF (5 mL), 30 °C, 0.5–1 h, Ar.
[b] Isolated yields.

Scheme 6. Trifluoromethylation of 1-(1-fluoro-2,2-diarylvinyl)-1*H*-azoles with $TMSCF_3$.[a,b]

3. Conclusions

In summary, we have developed an efficient method for the trifluoromethylation and pentafluoroethylation of 1,1-diaryl-2,2-difluoroethenes with $TMSCF_3$ and $TMSCF_2CF_3$ without the addition of the metal catalyst. The reactions proceeded smoothly and furnished the corresponding monotrifluoromethylated, bistrifluoromethylated, monopentafluoroethylated and bispentafluoroethylated alkenes in fair to good yields, respectively, under four different reaction conditions. In addition, we also developed a novel Pd-catalyzed trifluoromethylation of *N*-(α-fluorovinyl) azoles with $TMSCF_3$. These protocols provide convenient and alternative approaches for the direct construction of C_{vinyl}–CF_3 and C_{vinyl}–CF_2CF_3 bonds from the fluoroalkenes.

4. Experimental

4.1. General information

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. THF was freshly dried and stored over activated 4 Å molecular sieves under argon. The products were purified by column chromatography over silica gel (300–400 mesh size). Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz and 100 MHz, respectively) using TMS as internal standard. The ^{19}F NMR was obtained using a Bruker AM-400 spectrometer (376 MHz) with $CDCl_3$ as the NMR solvent. Gas chromatography-mass spectra (GC–MS) were recorded on HP 5973 MSD with 6890 GC. High resolution mass spectra (HRMS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer.

4.2. Synthesis of compounds 1a–h and 1i–n

Compounds **1a**–**h** were prepared according to the literature procedure.[13] Compounds **1i**–**n** were prepared according to the literature procedure.[11a]

4.3. General procedure for the synthesis of compounds 2a–g

Under an argon atmosphere, a 25 mL of dried round-bottom flask was charged with *gem*-difluoroalkenes **1a**–**g** (1.0 mmol), $TMSCF_3$ (170.6 mg, 1.2 mmol), and THF (5 mL). The mixture was stirred at 25 °C for 5 min, and then TBAF (1.2 mmol, 1.2 mL, 1.0 M in dry THF) was added dropwise to the mixture. The mixture was stirred at 60 °C for 0.5–1 h (TLC). After the consumption of **1a**–**g**, the reaction mixture was quenched with H_2O (5 mL), and subsequently extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was washed with brine (2×10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel (*n*-hexane as eluent) to provide the corresponding products **2a**–**g**.

*4.3.1. 4,4′-(Perfluoroprop-1-ene-1,1-diyl)bis(fluorobenzene) (**2a**).* Colourless liquid. Yield: 75%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27–7.17 (m, 4H), 7.09–7.01 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 164.1 (d, $^1J_{CF}$=247.5 Hz), 162.9 (dd, $^1J_{CF}$=248.8 Hz, $^6J_{CF}$=1.2 Hz), 160.9, 142.3 (dq, $^1J_{CF}$=261.7 Hz, $^2J_{CF}$=37.3 Hz), 131.7–131.4 (m), 131.4–131.2 (m), 131.0, 130.2–127.7 (m), 126.9–126.8 (m), 119.4 (qd, $^1J_{CF}$=271.5 Hz, $^2J_{CF}$=41.4 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.3 (d, *J*=9.8 Hz, 3F), −111.2 to −111.3 (m, 1F), −112.1 to −112.2 (m, 1F), −128.0 (q, *J*=9.4 Hz, 1F) ppm. HRMS (EI): calcd for $C_{15}H_8F_6$ $[M]^+$ 302.0530, found 302.0531.

*4.3.2. 3,3′-(Perfluoroprop-1-ene-1,1-diyl)bis(fluorobenzene) (**2b**).* Colourless liquid. Yield: 74%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.30 (m, 2H), 7.19–7.15 (m, 1H), 7.06–6.97 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, $^1J_{CF}$=244.8 Hz), 161.2 (d,

$^1J_{CF}$=244.6 Hz), 155.7–149.9 (m), 141.6 (d, $^3J_{CF}$=6.9 Hz), 134.5 (d, $^3J_{CF}$=8.1 Hz), 128.8 (d, $^3J_{CF}$=8.2 Hz), 128.3 (d, $^3J_{CF}$=8.0 Hz), 124.2–124.1 (m), 122.5, 115.4 (dq, $^2J_{CF}$=29.4 Hz, $^3J_{CF}$=3.5 Hz), 114.5, 114.3, 114.0 (d, $^4J_{CF}$=1.5 Hz), 113.6 (d, $^2J_{CF}$=40.9 Hz), 97.6–94.1 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.6 (d, *J*=9.4 Hz, 3F), −112.1–−112.2 (m, 2F), −126.0 (q, *J*=9.4 Hz, 1F) ppm. HRMS (EI): calcd for $C_{15}H_8F_6$ $[M]^+$ 302.0530, found 302.0532.

*4.3.3. 4,4′-(Perfluoroprop-1-ene-1,1-diyl)bis(chlorobenzene) (**2c**).* Colourless liquid. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J*=8.4 Hz, 2H), 7.36 (d, *J*=8.4 Hz, 2H), 7.23 (d, *J*=8.4 Hz, 2H), 7.18 (d, *J*=8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5 (dq, $^1J_{CF}$=262.8 Hz, $^2J_{CF}$=37.2 Hz), 135.4, 135.3, 133.1, 132.4–132.3 (m), 130.9, 130.8, 128.8, 128.7, 126.9–126.7 (m), 119.2 (qd, $^1J_{CF}$=272.1 Hz, $^2J_{CF}$=41.4 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.3 (d, *J*=9.8 Hz, 3F), −126.6 (q, *J*=9.8 Hz, 1F) ppm. HRMS (EI): calcd for $C_{15}H_8Cl_2F_4$ $[M]^+$ 333.9910, found 333.9915.

*4.3.4. 4,4′-(Perfluoroprop-1-ene-1,1-diyl)bis(bromobenzene) (**2d**).* Colourless liquid. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J*=8.4 Hz, 2H), 7.45 (d, *J*=8.4 Hz, 2H), 7.11 (d, *J*=8.4 Hz, 2H), 7.06 (d, *J*=8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5 (dq, $^1J_{CF}$=262.9 Hz, $^2J_{CF}$=37.4 Hz), 133.5, 132.8, 131.8, 131.7, 131.4, 131.3, 131.2–131.1 (m), 126.7 (dq, $^2J_{CF}$=10.6 Hz, $^3J_{CF}$=2.5 Hz), 119.2 (qd, $^1J_{CF}$=272.0 Hz, $^2J_{CF}$=41.3 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.3 (d, *J*=9.8 Hz, 3F), −126.3 (q, *J*=9.8 Hz, 1F) ppm. HRMS (EI): calcd for $C_{15}H_8Br_2F_4$ $[M]^+$ 425.8888, found 425.8882.

*4.3.5. 4,4′-(Perfluoroprop-1-ene-1,1-diyl)bis(methylbenzene) (**2e**).* 426.6 mg (3.0 mmol) $TMSCF_3$ was used. Colourless liquid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.12 (m, 6H), 7.10–7.08 (m, 2H), 2.36 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6 (dq, $^1J_{CF}$=258.5 Hz, $^2J_{CF}$=37.3 Hz), 139.1, 138.6, 137.3–136.8 (m), 132.6–132.5 (m), 131.7–131.6 (m), 131.5, 129.6, 129.5, 129.0, 119.6 (qd, $^1J_{CF}$=271.5 Hz, $^2J_{CF}$=41.9 Hz), 21.3, 21.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.1 (d, *J*=10.2 Hz, 3F), −129.6 (q, *J*=10.0 Hz, 1F) ppm. HRMS (EI): calcd for $C_{17}H_{14}F_4$ $[M]^+$ 294.1032, found 294.1033.

*4.3.6. (Perfluoroprop-1-ene-1,1-diyl)dibenzene (**2f**).* 426.6 mg (3.0 mmol) $TMSCF_3$ was used. Colourless liquid. Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.43 (m, 3H), 7.41–7.39 (m, 3H), 7.37–7.35 (m, 2H), 7.31–7.29 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1 (dq, $^1J_{CF}$=260.0, $^2J_{CF}$=37.2 Hz), 135.2, 135.1, 134.5, 134.4, 129.6, 129.5, 129.0, 128.7, 128.4, 119.5 (qd, $^1J_{CF}$=273.5 Hz, $^2J_{CF}$=37.3 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.4 (d, *J*=10.2 Hz, 3F), −128.8 (q, *J*=9.8 Hz, 1F) ppm. HRMS (EI): calcd for $C_{15}H_{10}F_4$ $[M]^+$ 266.0719, found 266.0720.

*4.3.7. 3,3′-(Perfluoroprop-1-ene-1,1-diyl)bis((trifluoromethyl)benzene) (**2g**).* Colourless liquid. Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.63 (m, 3H), 7.58–7.49 (m, 3H), 7.46–7.36 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6 (dq, $^1J_{CF}$=264.4 Hz, $^2J_{CF}$=37.5 Hz), 140.9, 135.1–135.0 (m), 134.3–134.2 (m), 132.9, 132.7–132.6 (m), 132.3, 131.8–130.7 (m), 129.3, 129.2, 129.1, 126.2–126.1 (m), 125.6 (q, $^3J_{CF}$=5.8 Hz), 123.4 (q, $^3J_{CF}$=3.7 Hz), 123.7 (q, $^1J_{CF}$=270.8 Hz), 123.6 (q, $^1J_{CF}$=270.8 Hz), 118.9 (qd, $^1J_{CF}$=272.2 Hz, $^2J_{CF}$=41.1 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.9 (s, 6F), −64.6 (d, *J*=9.4 Hz, 3F), −125.1 (q, *J*=10.0 Hz, 1F) ppm. HRMS (EI): calcd for $C_{17}H_8F_{10}$ $[M]^+$ 402.0466, found 402.0468.

4.4. General procedure for the synthesis of compounds 3a–h

Under an argon atmosphere, a 25 mL of dried round-bottom flask was charged with *gem*-difluoroalkenes **1a**–**h** (1.0 mmol), $TMSCF_3$ (426.6 mg, 3.0 mmol), and THF (5 mL). The mixture was stirred at 30 °C for 5 min, and then TBAF (1.5 mmol, 1.5 mL, 1.0 M in dry THF) was added dropwise to the mixture. The mixture was stirred at 30 °C for 0.5–1 h (TLC). After the consumption of **1a**–**h**, the reaction mixture was quenched with H_2O (5 mL), and subsequently extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was washed with brine (2×10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel (*n*-hexane as eluent) to provide the corresponding products **3a**–**h**.

*4.4.1. 4,4′-(3,3,3-Trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl) bis(fluorobenzene) (**3a**).* Colourless liquid. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.15 (m, 4H), 7.11–7.07 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^1J_{CF}$=249.9 Hz), 158.1–158.0 (m), 135.1–135.0 (m), 130.9–130.8 (m), 121.5 (q, $^1J_{CF}$=274.2 Hz), 118.2 (q, $^2J_{CF}$=22.0 Hz), 115.6 (d, $^2J_{CF}$=21.9 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −55.3 (s, 6F), −110.0–−110.1 (m, 2F) ppm. HRMS (EI): calcd for $C_{16}H_8F_8$ $[M]^+$ 352.0498, found 352.0499.

*4.4.2. 3,3′-(3,3,3-Trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl) bis(fluorobenzene) (**3b**).* Colourless liquid. Yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.24 (m, 2H), 7.13–7.00 (m, 2H), 7.00–6.83 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, $^1J_{CF}$=246.9 Hz), 140.3 (d, $^3J_{CF}$=7.7 Hz), 130.2 (d, $^3J_{CF}$=8.2 Hz), 124.5 (d, $^4J_{CF}$=2.8 Hz), 121.2 (q, $^1J_{CF}$=272.9 Hz), 117.0 (d, $^2J_{CF}$=21.0 Hz), 116.5–116.2 (m), 115.8 (d, $^2J_{CF}$=21.1 Hz), 115.6–115.4 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −55.6 (s, 6F), −111.7–−111.8 (m, 2F) ppm; HRMS (EI): calcd for $C_{16}H_8F_8$ $[M]^+$ 352.0499, found 352.0500.

*4.4.3. 4,4′-(3,3,3-Trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl) bis(chlorobenzene) (**3c**).* Colourless liquid. Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J*=8.4 Hz, 4H), 7.11 (d, *J*=8.4 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 137.1, 136.5, 130.0, 128.8, 121.4 (q, $^1J_{CF}$=276.8 Hz), 119.1 (q, $^2J_{CF}$=30.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −55.3 (s, 6F) ppm. HRMS (EI): calcd for $C_{16}H_8Cl_2F_6$ $[M]^+$ 383.9907, found 383.9903.

*4.4.4. 4,4′-(3,3,3-Trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl) bis(bromobenzene) (**3d**).* Colourless liquid. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J*=8.5 Hz, 4H), 7.01 (d, *J*=8.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 131.8, 130.6, 130.1, 124.8, 121.4 (q, $^1J_{CF}$=276.9 Hz), 118.8 (q, $^2J_{CF}$=31.5 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −55.3 (s, 6F) ppm. HRMS (EI): calcd for $C_{16}H_8Br_2F_6$ $[M]^+$ 473.8876, found 473.8877.

*4.4.5. 4,4′-(3,3,3-Trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl) bis(methylbenzene) (**3e**).* 710.8 mg (5.0 mmol) $TMSCF_3$ was used. Colourless liquid. Yield: 32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16–7.14 (m, 4H), 7.04–7.02 (m, 4H), 2.36 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 136.8, 129.5, 129.0, 128.9, 128.8, 121.9 (q, $^1J_{CF}$=274.3 Hz), 117.1–116.8 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −55.0 (s, 6F) ppm. HRMS (EI): calcd for $C_{18}H_{14}F_6$ $[M]^+$ 344.1000, found 344.1001.

*4.4.6. (3,3,3-Trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl)dibenzene (**3f**).* 710.8 mg (5.0 mmol) $TMSCF_3$ was used. Colourless liquid. Yield: 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.34 (m, 6H), 7.20–7.18 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3–160.2 (m), 139.3, 129.7, 128.5, 128.2, 125.7, 121.8 (q, $^1J_{CF}$=274.8 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −55.2 (s, 6F) ppm. HRMS (EI): calcd for $C_{16}H_{10}F_6$ $[M]^+$ 316.0687, found 316.0685.

*4.4.7. 3,3′-(3,3,3-Trifluoro-2-(trifluoromethyl)prop-1-ene-1,1-diyl) bis((trifluoromethyl)benz-ene) (**3g**).* Colourless liquid. Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.61 (m, 3H), 7.57–7.50 (m, 3H),

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7.44–7.35 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8 (q, $^2J_{CF}$=37.4 Hz), 141.2 (q, $^2J_{CF}$=37.4 Hz), 131.8, 131.7, 131.2 (q, $^3J_{CF}$=4.7 Hz), 131.1–131.0 (m), 125.0–123.7 (m), 123.5, 119.4 (q, $^1J_{CF}$=272.0 Hz), 119.0 (q, $^1J_{CF}$=272.0 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −55.5 (s, 6F), −62.9 (s, 6F) ppm. HRMS (EI): calcd for $C_{18}H_8F_{12}$ $[M]^+$ 452.0434, found 452.0435.

*4.4.8. 9-(Perfluoropropan-2-ylidene)-9H-fluorene (**3h**).* Yellow liquid. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J=8.0 Hz, 2H), 7.56 (d, J=7.2 Hz, 2H), 7.43 (t, J=7.6 Hz, 2H), 7.28 (d, J=8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 142.7, 135.0, 132.4, 128.6–128.4 (m), 128.2, 122.1 (q, $^1J_{CF}$=269.3 Hz), 119.8, 114.9–113.5 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −56.0 (s, 6F) ppm. HRMS (EI): calcd for $C_{16}H_8F_6$ $[M]^+$ 314.0530, found 314.0531.

4.5. General procedure for the synthesis of compounds 4a–f, 4h

Under an argon atmosphere, a 25 mL of dried round-bottom flask was charged with *gem*-difluoroalkenes **1a**–**f**, **1h** (1.0 mmol), $TMSCF_2CF_3$ (480.5 mg, 2.5 mmol), and THF (5 mL). The mixture was stirred at 25 °C for 5 min, then TBAF (1.2 mmol, 1.2 mL, 1.0 M in dry THF) was added dropwise to the mixture. The mixture was stirred at 25 °C for 0.5–1 h (TLC). After the consumption of **1a**–**g**, **1h**, the reaction mixture was quenched with H_2O (5 mL), and subsequently extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was washed with brine (2×10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel (*n*-hexane as eluent) to provide the corresponding products **4a**–**f**, **4h**.

*4.5.1. 4,4′-(Perfluorobut-1-ene-1,1-diyl)bis(fluorobenzene) (**4a**).* White solid. Mp: 42.7–43.2 °C. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.17 (m, 4H), 7.08–7.00 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{CF}$=247.4 Hz), 162.9 (d, $^1J_{CF}$=249.2 Hz), 142.0 (dt, $^1J_{CF}$=258.2 Hz, $^2J_{CF}$=27.1 Hz), 131.5 (d, $^3J_{CF}$=5.6 Hz), 131.4 (d, $^3J_{CF}$=5.7 Hz), 131.3 (d, $^4J_{CF}$=2.7 Hz), 131.2 (d, $^4J_{CF}$=2.7 Hz), 129.9–128.3 (m), 118.4 (qtd, $^1J_{CF}$=285.8 Hz, $^2J_{CF}$=36.6 Hz, $^3J_{CF}$=3.5 Hz), 115.5 (d, $^2J_{CF}$=21.6 Hz), 115.4 (d, $^2J_{CF}$=21.7 Hz), 112.4–106.9 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −83.1–−83.2 (m, 3F), −111.1–−111.2 (m, 1F), −112.4–−112.5 (m, 1F), −113.3–−113.4 (m, 2F), −125.7–−125.8 (m, 1F) ppm. HRMS (EI): calcd for $C_{16}H_8F_8$ $[M]^+$ 352.0498, found 352.0497.

*4.5.2. 3,3′-(Perfluorobut-1-ene-1,1-diyl)bis(fluorobenzene) (**4b**).* Colourless liquid. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.28 (m, 2H), 7.11–6.93 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, $^1J_{CF}$=245.4 Hz), 162.5 (d, $^1J_{CF}$=246.4 Hz), 142.7 (dt, $^1J_{CF}$=261.0 Hz, $^2J_{CF}$=27.2 Hz), 136.6 (d, $^3J_{CF}$=7.9 Hz), 135.5 (d, $^4J_{CF}$=4.5 Hz), 135.4 (d, $^4J_{CF}$=4.6 Hz), 130.0 (d, $^3J_{CF}$=8.2 Hz), 129.9 (d, $^2J_{CF}$=8.4 Hz), 129.3 (d, $^2J_{CF}$=10.8 Hz), 125.3–125.2 (m), 125.1–125.0 (m), 118.3 (qtd, $^1J_{CF}$=285.9 Hz, $^2J_{CF}$=36.3 Hz, $^3J_{CF}$=3.5 Hz), 116.7–116.3 (m), 116.3 (d, $^2J_{CF}$=21.1 Hz), 115.9 (d, $^2J_{CF}$=20.8 Hz), 111.9–106.7 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −83.1–−83.2 (m, 3F), −112.1–−112.2 (m, 1F), −112.3–−112.4 (m, 1F), −113.8–−113.9 (m, 2F), −123.9–−124.0 (m, 1F) ppm. HRMS (EI): calcd for $C_{16}H_8F_8$ $[M]^+$ 352.0498, found 352.0502.

*4.5.3. 4,4′-(Perfluorobut-1-ene-1,1-diyl)bis(chlorobenzene) (**4c**).* Colourless liquid. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.31 (m, 4H), 7.21–7.13 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2 (dt, $^1J_{CF}$=260.0 Hz, $^2J_{CF}$=26.8 Hz), 135.4, 135.1, 133.3, 132.1, 132.0, 130.8, 130.7, 128.8, 128.7, 118.3 (qtd, $^1J_{CF}$=285.7 Hz, $^2J_{CF}$=36.7 Hz, $^3J_{CF}$=3.5 Hz), 112.3–106.4 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −82.9–−83.0 (m, 3F), −113.3–−113.4 (m, 2F), −124.4–−124.5 (m, 1F) ppm. HRMS (EI): calcd for $C_{16}H_8Cl_2F_6$ $[M]^+$ 383.9907, found 383.9908.

*4.5.4. 4,4′-(Perfluorobut-1-ene-1,1-diyl)bis(bromobenzene) (**4d**).* White solid. Mp: 33.1–33.6 °C. Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J=8.4 Hz, 2H), 7.49 (d, J=8.8 Hz, 2H), 7.13 (d, J=7.6 Hz, 2H), 7.07 (d, J=8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2 (dt, $^1J_{CF}$=260.3 Hz, $^2J_{CF}$=26.9 Hz), 133.7 (d, $^4J_{CF}$=1.3 Hz), 133.0 (d, $^3J_{CF}$=4.6 Hz), 131.8, 131.7, 131.0, 130.9, 129.6 (d, $^2J_{CF}$=11.0 Hz), 123.8 (d, $^4J_{CF}$=1.2 Hz), 123.3, 118.3 (qtd, $^1J_{CF}$=285.9 Hz, $^2J_{CF}$=36.5 Hz, $^3J_{CF}$=3.4 Hz), 112.3–106.4 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −82.9–−83.0 (m, 3F), −113.3–−113.4 (m, 2F), −124.1–−124.3 (m, 1F) ppm. HRMS (EI): calcd for $C_{16}H_8Br_2F_6$ $[M]^+$ 475.8856, found 475.8864.

*4.5.5. 4,4′-(Perfluorobut-1-ene-1,1-diyl)bis(methylbenzene) (**4e**).* Colourless liquid. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.14 (m, 6H), 7.11–7.07 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 138.4, 137.3, 132.8–132.7 (m), 131.6, 131.5, 129.5–129.4 (m), 129.1, 129.0, 128.9, 120.4–119.7 (m), 112.6–106.7 (m), 21.3, 21.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −82.9–−83.0 (m, 3F), −113.0–−113.1 (m, 2F), −127.3–−127.5 (m, 1F) ppm. HRMS (EI): calcd for $C_{18}H_{14}F_6$ $[M]^+$ 344.1000, found 344.1001.

*4.5.6. (Perfluorobut-1-ene-1,1-diyl)dibenzene (**4f**).* White solid. Mp: 42.7–43.2 °C. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.14 (m, 6H), 7.11–7.07 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3 (dt, $^1J_{CF}$=256.0 Hz, $^2J_{CF}$=26.7 Hz), 139.1, 138.4, 137.3, 132.8, 131.6–131.4 (m), 129.5–129.4 (m), 129.1, 129.0, 128.9, 120.4–116.8 (m), 112.6–106.7 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −82.9–−83.0 (m, 3F), −113.0–−113.1 (m, 2F), −127.3–−127.4 (m, 1F) ppm. HRMS (EI): calcd for $C_{16}H_{10}F_6$ $[M]^+$ 316.0687, found 316.0689.

*4.5.7. 9-(Perfluoropropylidene)-9H-fluorene (**4h**).* White solid. Mp: 52.0–52.8 °C. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J=8.0 Hz, 1H), 7.83 (d, J=8.0 Hz, 1H), 7.67 (d, J=7.2 Hz, 2H), 7.44–7.38 (m, 2H), 7.34–7.25 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 143.4 (d, $^2J_{CF}$=32.1 Hz), 141.7 (d, $^3J_{CF}$=4.1 Hz), 140.0, 135.4, 132.0–131.9 (m), 130.4, 130.3, 130.2, 130.1, 128.3, 127.8, 127.6, 127.4, 127.2–127.0 (m), 126.1–125.9 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −83.1–−83.2 (m, 3F), −114.6–−114.7 (m, 2F), −117.8–−117.9 (m, 1F) ppm. HRMS (EI): calcd for $C_{16}H_8F_6$ $[M]^+$ 314.0530, found 314.0534.

4.6. General procedure for the synthesis of compounds 5a–d, 5f, 5h

Under an argon atmosphere, a 25 mL of dried round-bottom flask was charged with *gem*-difluoroalkenes **1a**–**d**, **1f**, **1h** (1.0 mmol), $TMSCF_2CF_3$ (961.0 mg, 5.0 mmol), and THF (5 mL). The mixture was stirred at 25 °C for 5 min, and then TBAF (2.0 mmol, 2.0 mL, 1.0 M in dry THF) was added dropwise to the mixture. The mixture was stirred at 25 °C for 0.5–1 h (TLC). After the consumption of **1a**–**d**, **1f**, **1h**, the reaction mixture was quenched with H_2O (5 mL), and subsequently extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was washed with brine (2×10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel (*n*-hexane as eluent) to provide the corresponding products **5a**–**d**, **5f**, **5h**.

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*4.6.1. 4,4′-(3,3,4,4,4-Pentafluoro-2-(perfluoroethyl)but-1-ene-1,1-diyl)bis(fluorobenzene) (**5a**).* Colourless liquid. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.05 (m, 4H), 7.01–6.96 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, $^1J_{CF}$=248.1 Hz), 128.9 (d, $^3J_{CF}$=8.4 Hz), 120.5–112.0 (m), 116.2 (d, $^2J_{CF}$=21.8 Hz), 116.2–116.0 (m), 115.7–114.9 (m), 115.1 (d, $^2J_{CF}$=21.9 Hz), 109.3–102.9 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.6–−81.7 (m, 6F), −101.4 (s, 4F), −112.2–−112.3 (m, 2F) ppm. HRMS (EI): calcd for $C_{18}H_8F_{12}$ $[M]^+$ 452.0434, found 452.0435.

*4.6.2. 3,3′-(3,3,4,4,4-Pentafluoro-2-(perfluoroethyl)but-1-ene-1,1-diyl)bis(fluorobenzene) (**5b**).* Colourless liquid. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.16 (m, 2H), 6.96–6.89 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, $^1J_{CF}$=246.4 Hz), 141.2 (d, $^3J_{CF}$=7.6 Hz), 129.7 (d, $^3J_{CF}$=8.2 Hz), 125.2–124.5 (m), 123.0–118.8 (m), 122.3, 115.5 (d, $^2J_{CF}$=20.9 Hz), 113.9 (d, $^2J_{CF}$=23.6 Hz), 112.3–108.9 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.8 (s, 6F), −102.4 (s, 4F), −112.4–−112.5 (m, 2F) ppm. HRMS (EI): calcd for $C_{18}H_8F_{12}$ $[M]^+$ 452.0434, found 452.0435.

*4.6.3. 4,4′-(3,3,4,4,4-Pentafluoro-2-(perfluoroethyl)but-1-ene-1,1-diyl)bis(chlorobenzene) (**5c**).* Colourless liquid. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J*=8.4 Hz, 4H), 7.04 (d, *J*=8.0 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7–163.6 (m), 138.0, 134.9, 130.2–128.2 (m), 128.3, 128.0, 120.0–117.0 (m), 114.5–111.8 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.7 (s, 6F), −101.9 (s, 4F) ppm. HRMS (EI): calcd for $C_{18}H_8Cl_2F_{10}$ $[M]^+$ 483.9843, found 483.9839.

*4.6.4. 4,4′-(3,3,4,4,4-Pentafluoro-2-(perfluoroethyl)but-1-ene-1,1-diyl)bis(bromobenzene) (**5d**).* White solid. Mp: 60.3–60.9 °C. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J*=8.4 Hz, 4H), 6.97 (d, *J*=8.4 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6–163.5 (m), 138.3, 131.8–131.7 (m), 131.3, 128.2, 123.0, 123.5–119.3 (m), 114.0–108.7 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.5–−81.6 (m, 6F), −101.8–−101.9 (m, 4F) ppm. HRMS (EI): calcd for $C_{18}H_8Br_2F_{10}$ $[M]^+$ 573.8813, found 573.8813.

*4.6.5. (3,3,4,4,4-Pentafluoro-2-(perfluoroethyl)but-1-ene-1,1-diyl)dibenzene (**5f**).* Colourless liquid. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.24 (m, 6H), 7.12 (d, *J*=7.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1 (t, $^3J_{CF}$=3.4 Hz), 140.1, 129.4–128.2 (m), 128.1, 127.8, 126.6, 120.6–114.8 (m), 112.5–109.0 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.4–−81.6 (m, 6F), −101.7–−101.8 (m, 4F) ppm. HRMS (EI): calcd for $C_{18}H_{10}F_{10}$ $[M]^+$ 416.0623, found 416.0622.

*4.6.6. 9-(Perfluoropentan-3-ylidene)-9H-fluorene (**5h**).* White solid. Mp: 72.8–73.5 °C. Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J*=8.0 Hz, 2H), 7.56 (d, *J*=7.2 Hz, 2H), 7.42–7.38 (m, 2H), 7.26–7.20 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 135.5, 132.2, 130.7–130.4 (m), 128.7–128.5 (m), 128.3–128.2 (m), 128.0, 120.7–120.5 (m), 119.6, 117.6–116.8 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −74.8–−74.9 (m, 6F), −96.9 (s, 4F) ppm. HRMS (EI): calcd for $C_{18}H_8F_{10}$ $[M]^+$ 414.0466, found 414.0462.

4.7. General procedure for the synthesis of compounds 6i–n

Under an argon atmosphere, a 25 mL of dried round-bottom flask was charged with fluoroalkenes **1i**–**n** (1.0 mmol), $TMSCF_3$ (710.2 mg, 5.0 mmol), $PdCl_2(PCy_3)_2$ (221.5 mg, 0.3 mmol), and THF (5 mL). The mixture was stirred at 30 °C for 5 min, then TBAF (2.0 mmol, 2.0 mL, 1.0 M in dry THF) was added dropwise to the mixture. The mixture was stirred at 30 °C for 0.5–1 h (TLC). After the consumption of **1i**–**n**, the reaction mixture was quenched with H_2O (5 mL), and subsequently extracted with CH_2Cl_2 (3×20 mL). The combined organic layer was washed with brine (2×10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel (hexane/dichloromethane/Et_3N=10/1/0.1) to provide the corresponding products **6i**–**n**.

*4.7.1. 1-(3,3,3-Trifluoro-1,1-diphenylprop-1-en-2-yl)-1H-imidazole (**6i**).* White solid. Mp: 67.6–68.5 °C. Yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.41 (m, 4H), 7.32–7.30 (m, 2H), 7.21–7.15 (m, 3H), 7.03 (s, 2H), 6.91–6.89 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 150.7, 137.6, 137.1, 129.2, 129.1, 128.7, 128.6, 128.5, 128.3, 128.1, 121.3 (q, $^1J_{CF}$=273.6 Hz), 121.7, 121.5–121.1 (m) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.0 (s, 3F) ppm. HRMS (EI): calcd for $C_{18}H_{13}F_3N_2$ $[M]^+$ 314.1031, found 314.1029.

*4.7.2. 1-(3,3,3-Trifluoro-1,1-diphenylprop-1-en-2-yl)-1H-benzo[d]imidazole (**6j**).* White solid. Mp: 85.4–86.1 °C. Yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.74–7.72 (m, 1H), 7.48–7.39 (m, 6H), 7.33–7.24 (m, 2H), 7.10–6.99 (m, 3H), 6.87–6.85 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6 (q, $^3J_{CF}$=2.4 Hz), 143.8, 142.7, 137.4, 137.0, 129.4, 129.3, 128.8, 128.7, 128.4, 128.3, 127.7, 124.0, 122.9, 121.7 (q, $^1J_{CF}$=274.3 Hz), 120.0 (q, $^2J_{CF}$=33.9 Hz), 120.4, 110.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −59.3 (s, 3F) ppm. HRMS (EI): calcd for $C_{22}H_{15}F_3N_2$ $[M]^+$ 364.1187, found 364.1186.

*4.7.3. 5,6-Dimethyl-1-(3,3,3-trifluoro-1,1-diphenylprop-1-en-2-yl)-1H-benzo[d]imidazole (**6k**).* White solid. Mp: 92.2–93.1 °C. Yield: 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.47–7.37 (m, 6H), 7.18 (s, 1H), 7.06–6.98 (m, 3H), 6.85–6.83 (m, 2H), 2.37 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 143.1, 141.4, 137.5, 137.1, 133.6, 133.3, 131.8, 129.3, 128.8, 128.4, 128.3, 127.8, 121.9 (q, $^1J_{CF}$=272.6 Hz), 120.4, 110.8, 20.7, 20.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ −59.1 (s, 3F). HRMS (EI): calcd for $C_{24}H_{19}F_3N_2$ $[M]^+$ 392.1500, found 392.1501.

*4.7.4. 2-Methyl-1-(3,3,3-trifluoro-1,1-diphenylprop-1-en-2-yl)-1H-benzo[d]imidazole (**6l**).* White solid. Mp: 79.8–80.9 °C. Yield: 38%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.63 (m, 1H), 7.47–7.45 (m, 3H), 7.40–7.26 (m, 5H), 7.13–7.10 (m, 1H), 7.03–6.99 (m, 2H), 6.83–6.81 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9–154.8 (m), 151.6, 142.4, 142.3, 137.4, 137.3, 137.1, 129.6, 129.3, 128.7, 128.4, 127.6, 123.3, 122.7, 121.6 (q, $^1J_{CF}$=273.2 Hz), 120.0 (q, $^2J_{CF}$=34.8 Hz), 119.3, 110.6, 45.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −58.4 (s, 3F). HRMS (EI): calcd for $C_{23}H_{17}F_3N_2$ $[M]^+$ 378.1344, found 378.1343.

*4.7.5. 1-(1-Fluoro-2,2-diphenylvinyl)-1H-indole (**6m**).* Yellow oil. Yield: 39%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.43 (m, 6H), 7.28–6.98 (m, 9H), 6.69–6.60 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6 (q, $^3J_{CF}$=2.4 Hz), 143.9, 142.9, 137.5, 137.0, 134.8, 129.4, 129.3, 128.8, 128.7, 128.4, 128.3, 127.7, 124.0, 122.9, 121.7 (q, $^1J_{CF}$=274.3 Hz), 120.4, 120.0 (q, $^2J_{CF}$=33.9 Hz), 110.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −59.3 (s, 3F) ppm. HRMS (EI): calcd for $C_{23}H_{16}F_3N$ $[M]^+$ 363.1235, found 363.1236.

*4.7.6. 1-(3,3,3-Trifluoro-1,1-diphenylprop-1-en-2-yl)-1H-1,2,4-triazole (**6n**).* White solid. Mp: 99.2–100.1 °C. Yield: 26%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.62 (m, 1H), 7.42–7.36 (m, 5H), 7.18–7.14 (m, 3H), 7.00–6.97 (m, 2H), 6.21–6.20 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4 (q, $^3J_{CF}$=6.3 Hz), 141.2, 138.0, 137.2, 133.1, 129.0, 128.9, 128.7 (q, $^4J_{CF}$=1.8 Hz), 128.4, 128.3, 128.1, 125.2 (q, $^2J_{CF}$=33.6 Hz), 121.6 (q, $^1J_{CF}$=274.1 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ −59.1 (s, 3F) ppm. HRMS (EI): calcd for $C_{17}H_{12}F_3N_3$ $[M]^+$ 315.0983, found 315.0984.

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Supplementary data

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