Activation of Saturated Fluorocarbons to Synthesize Spirobiindanes, Monofluoroalkenes, and Indane Derivatives

HIGHLIGHTS

C(sp³)-F bond activation in general unactivated fluorocarbons

The activation of C(sp³)-F bonds in aliphatic gem-difluoroalkanes

The selective activation of inert C(sp³)-F bonds catalyzed by B(C₆F₅)₃

An intramolecular cascade defluorinative Friedel-Crafts cyclization

Wang et al., iScience 17, 132-143 July 26, 2019 © 2019 The Author(s). https://doi.org/10.1016/j.isci.2019.06.018
Activation of Saturated Fluorocarbons to Synthesize Spirobiindanes, Monofluoroalkenes, and Indane Derivatives

Jiandong Wang,1 Yuta Ogawa,1 and Norio Shibata1,2,3,*

SUMMARY
Fluorinated organic compounds are produced in abundance by the pharmaceutical and agrochemical industry, making such compounds attractive as building blocks for further functionalization. Unfortunately, activation of C(sp3)-F bond in saturated fluorocarbons, especially for aliphatic gem-difluoroalkanes, remains challenging. Here we describe the selective activation of inert C(sp3)-F bonds catalyzed by B(C6F5)3. In hexafluoro-2-propanol (HFIP), chemically robust aliphatic gem-difluorides are converted in high yields to the corresponding substituted 2,2,3,3-tetrahydro-1,1-spirobiindenes via a B(C6F5)3-catalyzed intramolecular cascade Friedel-Crafts cyclization, not requiring a silicon-based trapping reagent. However, in the absence of a hydrogen-bonding donor solvent such as HFIP, the aliphatic gem-difluorides preferentially engage in a defluorination/elimination process that provides monofluorinated alkenes in good yields. Furthermore, a series of substituted 1-alkyl-2,3-dihydro-1H-indenes was obtained in high yield from the B(C6F5)3-catalyzed defluorinative cyclization of aliphatic secondary monofluorides in HFIP. The protocol could inspire development of a new class of main-group Lewis acid-catalyzed C(sp3)-F bond activation in general unactivated fluorocarbons.

INTRODUCTION
The demand for the selective activation of C-F bonds is growing as a result of the increased availability of fluorinated compounds in the pharmaceutical and agrochemical industries (Amii and Uneyama, 2009; Ahrens et al., 2015; Kuehnel et al., 2013; Hamel and Paquin, 2018; Klare, 2017). Recently, remarkable progress has been made in the transition-metal-mediated heterolysis of C(sp2)-F bonds in aromatic and vinylic fluorocarbons (Ahrens et al., 2015; Kuehnel et al., 2013; Pike et al., 2017; Guo et al., 2015; Luo et al., 2018). However, the defluorinative functionalization of C(sp3)-F bonds in unactivated aliphatic fluorides is less frequently reported and still a challenging issue in synthetic organic chemistry (Stahl et al., 2013; Shen et al., 2015). Indeed, the notorious chemical robustness of C-F bonds not only stems from their thermodynamic stability—the C-F bond is among the strongest covalent single bonds that carbon can form—but also from kinetic factors because the fluoride moiety is neither a good leaving group nor a good Lewis base (O’Hagan, 2008; Nolte et al., 2012).

The direct abstraction of the fluoride moiety in inert C(sp3)-F bonds by p-block-based Lewis acids that exhibit high fluoride affinity has emerged as a promising strategy for the degradation of saturated fluorocarbons (Stahl et al., 2013; Shen et al., 2015), because of that the formation of covalent bonds between fluoride and main-group elements (e.g., B, Al, Si, and P), which are more stable than C-F bonds, may offer a thermodynamic driving force for the scission of the C-F bonds (Stahl et al., 2013). In addition, the stronger Lewis acidity of fluorophilic electrophiles is essential for the direct heterolytic cleavage of C(sp3)-F bonds, given the high activation barrier. The substitution of the fluoride in C(sp3)-F bonds to form C-H, C-C, and C-heteroatom bonds has been initiated by neutral, strong aluminum- and boron-based Lewis acids (Stahl et al., 2013; Greb, 2018; Morgan et al., 2013; Koerte et al., 2017; Ahrens et al., 2013; Jaiswal et al., 2017) or cationic species such as [CPh3]2+, [SiEt3]+, [iBu2Al]+, [Li(C6F5)3]2+, and even P(III) dications such as [bipy]PPh2+ bearing weakly coordinating counter anions such as [BF4]− (Stahl et al., 2013; Klahn et al., 2007; Gu et al., 2009; Forster et al., 2017; Douvis and Ozerov, 2008; Scott et al., 2005; Großekappenberg et al., 2015; Zhu et al., 2016; Chitnis et al., 2018).

In their seminal reports, Olah and co-workers described the cleavage of unactivated C(sp3)-F bonds initiated by boron-based Lewis acids, specifically the preferential abstraction of fluorides from aliphatic...
fluorohaloalkanes by boron trifluoride to generate the stable BF$_2^-$ anion and Friedel-Crafts-type alkylation products with excess arenes (Olah et al., 1957; Olah and Kuhn, 1964). Consistent with the greater stability of tertiary carbocations derived from tertiary aliphatic fluorides, Oshima and co-workers have reported that BF$_3$-OEt$_2$ catalyzes C-C bond couplings between silicon enolates and tertiary fluorides (Hirano et al., 2004). Subsequently, Stephan et al. have reported the splitting of unactivated C(sp$^3$)-F bonds using stoichiometric amounts of B(C$_6$F$_5$)$_3$ and a phosphine as frustrated Lewis pairs (FLPs) to produce [R$_3$PR']$_2$BF$_2$ (Caputo and Stephan, 2012). Alternatively, using catalytic amounts of B(C$_6$F$_5$)$_3$ with an excess of Et$_3$SiH, a C-H bond is formed at the expense of the corresponding C(sp$^3$)-F bond (Caputo and Stephan, 2012). Furthermore, HB(C$_6$F$_5$)$_2$ has been used to induce the direct C(sp$^3$)-F borylation of secondary and primary aliphatic fluoroalkanes via an initial dehydrofluorination and a subsequent borylation of the resulting olefin intermediates (Bamford et al., 2018). Recently, Moran and co-workers have reported the Friedel-Crafts reactions of tertiary fluoroalkanes with an excess of arenes (3.0–5.0 equiv.) catalyzed by B(C$_6$F$_5$)$_3$ in MeNO$_2$ under ambient atmosphere; interestingly, in this case the Lewis acid B(C$_6$F$_5$)$_3$ absorbs water to generate [(C$_6$F$_5$)$_2$B(OH)$_2$]$_n$, which then acts as a Brønsted acid (Dryzhakov and Moran, 2016; Dryzhakov et al., 2017; Beringhelli et al., 2001). Despite the general progress in this area, the development of alternative catalytic methods based on boron-based Lewis acids as fluorophilic electrophiles for the activation of inert C(sp$^3$)-F bonds in saturated fluorocarbons remains highly desirable.

The modification of C(sp$^3$)-F bonds in aliphatic gem-difluoroalkanes is much more difficult than in the corresponding saturated monofluoroalkanes because the strength of C-F bonds increases with the number of geminal fluoride atoms (Hamel and Paquin, 2018; O’Hagan, 2008). Indeed, in most cases, the fluorine moiety in gem-difluorides is found at activated benzylic, allylic, or propargylic positions (Figure 1A), as well as at the α-position of a carbonyl group or in gem-difluorocyclopropanes (Hamel and Paquin, 2018; Song et al., 2017). In a representative example of unactivated aliphatic gem-difluoroalkanes from Ozerov and co-workers, the ethylation of 1,1-difluorocyclopentane was observed together with the reduction side product cyclopentane (67:33) by gas chromatography-mass spectrometry analysis as one special case (Figure 1B) by using catalytic amounts of [Et$_2$Al][HCB$_1$H$_3$Br$_3$] in the presence of an excess amount of AIE$_3$ (Gu et al., 2009). In 2018, the group of Young reported two examples for the monodefluorination of an acyclic aliphatic gem-difluoromethylene group in 1,1-difluoroethane and 1,1-difluorodecane: using FLPs obtained from Al(C$_6$F$_5$)$_3$ and P(o-Tol)$_3$, the α-fluoroalkylphosphonium salts were generated in moderate yield (Figure 1C) (Mandal et al., 2018). Building upon our long-standing interest in the activation of inert C(sp$^3$)-F bonds (Haufe et al., 2012; Tanaka et al., 2016; Cui et al., 2018), we discovered in this study that a catalytic amount of the Lewis acid B(C$_6$F$_5$)$_3$ activated the C(sp$^3$)-F bond in aliphatic gem-difluoroalkanes of type 1 to selectively generate substituted 2,2',3,3'-tetrahydro-1,1'-spirobiindenyls (2) and monofluorinated alkenes (3) in good yield (Figure 1D). Moreover, this method was also used for the functionalization of the C(sp$^3$)-F bond in secondary monofluoroalkanes to C(sp$^3$)-C(sp$^3$) bonds in good yield. The use of hydrogen-bonding hexafluoro-2-propanol (HFIP) as the solvent was essential to induce the catalyst turnover for the defluorinative Friedel-Crafts alkylation.

RESULTS AND DISCUSSION
Optimization Study
Initially, based on the pioneering work of Olah and Stephan on the activation of C(sp$^3$)-F bonds in saturated monofluoroalkanes initiated by boron-based Lewis acids (Olah et al., 1957; Olah and Kuhn, 1964; Caputo and Stephan, 2012), we attempted to use stoichiometric amounts of BF$_3$-OEt$_2$ and B(C$_6$F$_5$)$_3$ (2.2 equiv.) to induce cleavage of the C(sp$^3$)-F bond in unactivated gem-difluoroalkane 1a (Table 1, entries 1 and 2). Although no reaction was detected upon using BF$_3$-OEt$_2$, the use of a stoichiometric amount of B(C$_6$F$_5$)$_3$ afforded 2,2',3,3'-tetrahydro-1,1'-spirobi[indene] (2) in 85% yield. This result was very encouraging, considering that examples of the activation of C(sp$^3$)-F bonds in inert aliphatic gem-difluoroalkanes are extremely rare (Figure 1) (Gu et al., 2009; Mandal et al., 2018). Subsequently, we turned our attention to the development of a catalytic B(C$_6$F$_5$)$_3$-induced cascade intramolecular Friedel-Crafts cyclization (Lan et al., 2006; Birman et al., 1999; Li et al., 2016; Zheng et al., 2018).

Recently, HFIP has attracted considerable attention as a solvent to promote Friedel-Crafts acylations and alkylations (Motiwala et al., 2015; Vekariya and Aube, 2016; Tang et al., 2018) owing to its unique properties, which include reduced nucleophilicity, a strong propensity to engage as a hydrogen-bonding donor, and the ability to stabilize cationic intermediates (Colomer et al., 2017). Indeed, intermolecular Friedel-Crafts alkylations by hydrogen-bonding interactions between activated benzylic C-F bonds and HFIP in the
absence of any Lewis or Brønsted acids has been reported by Paquin and co-workers (Champagne et al., 2014, 2015). Using a combination of the hydrogen-bonding-donor solvent HFIP and B(C6F5)3 (20 mol %) in the absence of any silicon-based trapping reagent, afforded the defluorinative Friedel-Crafts-type product 2a in 75% yield (Table 1, entry 5). It is worth noting here that moisture was strictly excluded in our method, owing to the hydrolysis of 1a under acidic conditions. When using “wet” HFIP, i.e., HFIP that was used as purchased under an atmosphere of argon without any precaution to exclude moisture, the corresponding hydrolysis product (1,5-diphenylpentan-3-one) was observed as the major product and 2a was obtained in only 27% yield (Table 1, entry 7). Upon adding H2O (2.2 equiv.), the intramolecular Friedel-Crafts transformation was completely suppressed, and the quantitative hydrolysis into a ketone was confirmed instead when prolonging the reaction time (Table 1, entry 9). Other reaction parameters, such as solvents, concentration, and temperature, were also investigated (for more details, see also Table S1). Finally, we were able to identify the optimal reaction conditions for the synthesis of spirobiindanes 2: B(C6F5)3 (20 mol %) in HFIP (0.05 M) at 50°C for 2 h (Table 1, entry 8). In the absence of B(C6F5)3, or when using other hydrogen-bonding solvents such as PrOH, CF3CH2OH, or (CF3)2PhOH, the reaction did not proceed (Table 1, entries 10–13). Unexpected results were obtained using 1,2-dichlorobenzene as the solvent. Indeed, the formation of
monofluoroalkene 3a, derived from the defluorination/elimination sequence of aliphatic gem-difluoroalkane 1a (Yanai et al., 2011; Yang et al., 2013; Surmont et al., 2009; Li et al., 2018; Drouin et al., 2018), was observed in good yield when conducting the reaction at very high temperatures (Table 1, entries 14, 17). Specifically, when the temperature was increased from 160°C to 220°C in a sealed tube, the yield of the elimination product 3a increased from 64% to 81% with good stereoselectivity (Z/E = 7.3:1), whereas no reaction was detected in the absence of B(C6F5)3 (entry 16). These results indicate that the increased reaction temperature is beneficial for the defluorination/elimination. Furthermore, after screening the reaction temperature, the yield of 3a was optimized under reflux for 24 h at 220°C (entry 19)

Table 1. Optimization of the Selective Cleavage of C(sp3)-F Bonds in Aliphatic gem-Difluoroalkanes

| Entry | Lewis Acids (Equiv.) | Solvent (0.1M) | T (°C) | t (h) | Yields (%) |
|-------|---------------------|----------------|--------|-------|------------|
|       |                     |                |        |       | 2a | 3a* |
| 1     | BF3·OEt2 (2.2)      | CH2Cl2         | RT     | 30    | NR | NR |
| 2     | B(C6F5)3 (2.2)      | CH2Cl2         | RT     | 30    | 85 | 0 |
| 3     | B(C6F5)3 (0.2)      | CH2Cl2         | RT     | 30    | Trace | 0 |
| 4     | B(C6F5)3 (0.2)      | (CF3)2CHOH     | RT     | 17    | 28 | 0 |
| 5     | B(C6F5)3 (0.2)      | (CF3)2CHOH     | 50     | 2     | 75 | 0 |
| 6     | B(C6F5)3 (0.1)      | (CF3)2CHOH     | 50     | 20    | 16 | 0 |
| 7     | B(C6F5)3 (0.2)      | (CF3)2CHOH$^+$ | 50     | 2     | 27 | 0 |
| 8     | B(C6F5)3 (0.2)      | (CF3)2CHOH$^-$ | 50     | 2     | 84 | 0 |
| 9     | B(C6F5)3 (0.2)      | (CF3)2CHOH$^{1+}$ | 50     | 2     | 0$^d$ | 0$^d$ |
|       |                     | iPrOH$^f$      | 50     | 2     | NR | NR |
| 11    | B(C6F5)3 (0.2)      | CF3CH2OH$^+$   | 50     | 2     | NR | NR |
| 12    | B(C6F5)3 (0.2)      | (CF3)2PhOH$^+$ | 50     | 2     | NR | NR |
| 13    | –                   | (CF3)2CHOH$^+$ | 50     | 2     | NR | NR |
| 14    | B(C6F5)3 (0.2)      | o-C6H4Cl2      | 160    | 3     | 0  | 64 |
| 15    | B(C6F5)3 (0.1)      | o-C6H4Cl2      | 160    | 3     | 0  | 30 |
| 16    | –                   | o-C6H4Cl2      | 160    | 3     | NR | NR |
| 17    | B(C6F5)3 (0.2)      | o-C6H4Cl2      | 220    | 3     | 0  | 81$^f$ |
| 18    | B(C6F5)3 (0.2)      | p-C6H4F2       | reflux | 3     | 0  | 75 |
| 19    | B(C6F5)3 (0.2)      | p-C6H4F2       | reflux | 24    | 0  | 87$^f$ |

*Determined by$^{19}$F NMR analysis using PhCF3 as the internal standard.

$^a$(CF3)2CHOH was used as purchased without any precaution to exclude moisture. The hydrolysis product 1,5-diphenylpentan-3-one was observed as the major product.

$^b$Concentration: 0.05 M.

$^c$The hydrolysis product 1,5-diphenylpentan-3-one was obtained in quantitative yield after 12 h at 50°C.

$^d$Z/E = 7.3:1.

$^e$Z/E = 7.1:1.
conditions to find an acceptable reaction temperature (for further details, see also Table S2) in the presence of B(C₆F₅)₃ (20 mol%), we discovered that stirring the reaction mixture in refluxing 1,4-difluorobenzene (boiling point 88–89°C) instead of using harsher reaction conditions (220°C) afforded 3a in 87% yield with good stereoselectivity (Z/E = 7.1:1).

**Substrate Scope**

With the optimized reaction conditions in hand, we explored the substrate scope (Figure 2). First, we examined intramolecular Friedel-Crafts reactions as shown in Figure 2A. For aliphatic gem-difluoroalkanes substituted with alkyl groups (1a-h), good to high yields were observed; in particular, gem-difluoroalkane 1f, bearing a methyl group at the C2 position of the benzene ring, generated the desired product (2f) in high yield (up to 90%). However, for methoxy-substituted gem-difluorides 1c and 1g, substantially lower yields were observed due to the presence of the electron-rich heteroatom acting as a Lewis base that is able to provide lone electron pairs to interact with the Lewis acid catalyst.

This unexpected donor-acceptor interaction between the oxygen atom and the electron-deficient boron moiety hampered the fluoride abstraction via the C(sp³)-F→B(C₆F₅)₃ interaction, leading to decreased yields. In contrast, gem-difluoroalkanes (1i-m) with a halogen (F, Cl, Br) group at the C2 or C4 position afforded acceptable yields (57–79%), whereas dialkyl-substituted substrates 1n and 1o furnished good to excellent product yields (up to 95%). Naphthyl-type 2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]naphthalene] 2p was also prepared in good yield (84%). Moreover, 4,6-dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2q and 4-bromo-4'-methyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2r were generated in moderate yields (42% and 59%, respectively). Six-membered spiro-compound 2s and five- or six-membered spiro-compound 2t were also prepared in high yields (up to 90%). As shown in Figure 2B, the substrate scope for the defluorination/elimination process was explored. When using symmetric substrates, the desired acyclic monofluoroalkenes (3a, 3e-g, 3j-k, 3n-o, 3u, and 3aa) were prepared in moderate to good yields (up to 84%) with good Z/E stereoselectivity.

Specifically, substrates with electron-donating substituents such as methyl, methoxy, or dialkyl groups on the benzene ring gave the desired products (3e-g and 3n-o) in moderate to good yields (51%–70%) in refluxing 1,4-difluorobenzene. Halogen groups were well tolerated in the elimination transformation, although an unexpected decrease in yield (38%) was observed for the preparation of bromo-substituted 3j, albeit that the stereoselectivity was high (Z/E = 25:1). In addition, benzylic gem-difluoroalkanes afforded 3bb and 3cc in merely low to moderate yields (41% and 25%, respectively), and only the Z-isomer is formed, even though the fluorinated moiety is located at the activated position and was thus expected to be removed more easily. For cyclic gem-difluoroalkanes (Strobach and Boswell, 1971), the formation of six-membered substrates was favored, i.e., 3dd and 3ee were prepared in 80% and 64% yield, respectively. Furthermore, the defluorination of large-ring-type gem-difluoroalkanes proceeded smoothly to afford the corresponding cyclic monofluoroalkenes 3gg and 3hh in good yields, albeit that the Z/E selectivity was low.

**B(C₆F₅)₃ Catalyzed Friedel-Crafts Reactions of Secondary Aliphatic Fluorides**

Although the cleavage of the C(sp³)-F bond in unactivated aliphatic monofluorides was expected to be easier than in the corresponding saturated gem-difluoroalkanes, the Friedel-Crafts alkylation of secondary monofluorinated alkanes was less successful (Hamel and Paquin, 2018; Stahl et al., 2013). Under the previously established optimal reaction conditions for the synthesis of spirobiindanes 2, using 20 mol % B(C₆F₅)₃ in HFIP, an intramolecular defluorinative cyclization of secondary fluorcarbon 4a was observed in good yield (90%; Figure 3A, entry 1). Subsequently, upon decreasing the catalyst loading to 2 mol %, the desired 1-phenethyl-2,3-dihydro-1H-indene (5a) was smoothly prepared (91%; Figure 3A, entry 5). However, in the absence of a Lewis-acidic catalyst, a reaction was not observed (Figure 3A, entry 6), which demonstrates the crucial importance of B(C₆F₅)₃ for abstraction of fluoride. Subsequently, we explored the substrate scope (Figure 3B) of this reaction. With long-chain symmetric substrates with electron-donating groups (4a-f), good to high yields were observed (70%–93%). Conversely, yields for the intramolecular Friedel-Crafts transformation of halogen-substituted monofluoroalkanes 5g-j were a bit lower (68%–80%). Similarly, 2,3-dimethyl- and 2,4-dimethyl-substituted 4k and 4l were converted into the cyclic products 5k and 5l in 50% and 67% yield, respectively, whereas the naphthyl-type product 5m was obtained in 79% yield. Miscellaneous monofluorides 4n-p furnished the desired alkyl-substituted indanes in moderate to good yields (44%–91%). Six-membered ring products 5r and 5s were also prepared in 82%–85% yield. However, benzylic secondary monofluoride 4q furnished 1-phenyl-2,3-dihydro-1H-indene (5q) in merely 29% yield. It should be noted that an increased yield (46%) for the synthesis of
Figure 2. Substrate Scope of the Defluorination of Aliphatic gem-Difluoroalkanes to Afford Spirobiindanes 2 and Monofluoroalkenes 3

(A) Intramolecular Friedel-Crafts reactions.

(B) Defluorination/elimination reactions.
was observed in the absence of a Lewis acid catalyst. Although intermolecular Friedel-Crafts alkylations of primary benzylic monofluoride using excess amounts of electrophiles in HFIP in the absence of acids have already been reported (Champagne et al., 2014), we have observed the first example of the functionalization of a secondary benzylic monofluoride such as 4q in the absence of any catalyst or additive (Figure 3B).

![Figure 3. Intramolecular Friedel-Crafts Cyclization of Secondary Monofluoroalkanes 4](image)

| Entry | B(C₅F₃)₃ (mol%) | HFIP (M) | Time (h) | Yields (%) |
|-------|-----------------|----------|----------|------------|
| 1     | 20              | 0.05     | 2        | 90         |
| 2     | 10              | 0.05     | 2        | 93         |
| 3     | 10              | 0.1      | 3        | 78         |
| 4     | 5               | 0.05     | 5        | 92         |
| 5     | 2               | 0.05     | 5        | 91         |
| 6     | 0               | 0.05     | 12       | 0          |

* Isolated yields

---

5q was prepared in 46% yield only in HFIP without B(C₅F₃)₃

**Figure 3. Intramolecular Friedel-Crafts Cyclization of Secondary Monofluoroalkanes 4**

(A) Optimization of reaction conditions.

(B) Substrate Scope.
We found that the donor-acceptor interactions between the fluorine moiety of C(sp³)-F bonds in unactivated aliphatic gem-difluoroalkanes, a weak Lewis base, and the strong Lewis acid \( \text{B(C}_6\text{F}_5\text{)}_3 \), is of vital importance; this is emphasized by the overwhelming chemoselectivity for the Friedel-Crafts cyclization of C(sp³)-F bonds rather than the cleavage of weaker C-halogen bonds or the removal of other good leaving groups (Table 2). Specifically, when using a stoichiometric amount of \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2 equiv.) in \( \text{CH}_2\text{Cl}_2 \) at room temperature for 30 h, gem-difluoroalkane 1a afforded only the desired 2,2,3,3-tetrahydro-1,1-sprirob[inden] 2a in 85% yield, whereas the formation of elimination product 3a was not observed. In contrast, the intramolecular Friedel-Crafts cyclization was not observed when using 1,5-diphenylpentan-3-one (1v), (3,3-dimethoxypentane-1,5-diyl) dibenzene (1w), (3,3-dichloropentane-1,5-diyl) dibenzene (1x), and (3,3-dibromopentane-1,5-diyl) dibenzene (1y) (Table 2, entries 1–5). Although the cleavage of C-OMe bonds of substrate 1w by \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2 equiv.) was observed, as the electron-rich heteroatom is a good Lewis base, only a complex mixture was found, and the formation of 2a was not observed (Table 2, entry 3).

For the gem-dibromoalkane 1y, the formation of an unexpected elimination product in 29% yield was detected, which was ascribed to the ability of the bromine to act as a good leaving group (Table 2, entry 5). In

Table 2. Control Experiments to Probe Reaction Mechanism

| Entry | X | Lewis Acids (Equiv.) | Solvent (0.1M) | T (°C) | t (h) | Yields (%) |
|-------|---|----------------------|----------------|--------|-------|------------|
| 1     | F | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2) | \( \text{CH}_2\text{Cl}_2 \) | RT     | 30    | 85         |
| 2     | 1v (C=O) | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2) | \( \text{CH}_2\text{Cl}_2 \) | RT     | 30    | NR        |
| 3     | MeO | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2) | \( \text{CH}_2\text{Cl}_2 \) | RT     | 30    | ND        |
| 4     | Cl | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2) | \( \text{CH}_2\text{Cl}_2 \) | RT     | 30    | NR        |
| 5     | Br | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2) | \( \text{CH}_2\text{Cl}_2 \) | RT     | 30    | 0         |
| 6     | F | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | (CF\(_3\))\(_2\)CHOH | 50     | 2     | 84         |
| 7     | 1v (C=O) | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | (CF\(_3\))\(_2\)CHOH | 50     | 2     | NR        |
| 8     | MeO | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | (CF\(_3\))\(_2\)CHOH | 50     | 2     | NR        |
| 9     | Cl | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | (CF\(_3\))\(_2\)CHOH | 50     | 2     | 0         |
| 10    | Br | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | (CF\(_3\))\(_2\)CHOH | 50     | 2     | 0         |
| 11    | Br | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | (CF\(_3\))\(_2\)CHOH | 50     | 2     | 0         |
| 12    | Br | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | (CF\(_3\))\(_2\)CHOH | 50     | 2     | 0         |
| 13    | F | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | p-C\(_6\)H\(_4\)F\(_2\) | reflux | 24    | 0         |
| 14    | MeO | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | p-C\(_6\)H\(_4\)F\(_2\) | reflux | 24    | 0         |
| 15    | Cl | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | p-C\(_6\)H\(_4\)F\(_2\) | reflux | 24    | Trace    |
| 16    | Br | \( \text{B(C}_6\text{F}_5\text{)}_3 \) (0.2) | p-C\(_6\)H\(_4\)F\(_2\) | reflux | 24    | 0         | 9         |

Mechanistic Investigations

We found that the donor-acceptor interactions between the fluorine moiety of C(sp³)-F bonds in unactivated aliphatic gem-difluoroalkanes, a weak Lewis base, and the strong Lewis acid \( \text{B(C}_6\text{F}_5\text{)}_3 \), is of vital importance; this is emphasized by the overwhelming chemoselectivity for the Friedel-Crafts cyclization of C(sp³)-F bonds rather than the cleavage of weaker C-halogen bonds or the removal of other good leaving groups (Table 2). Specifically, when using a stoichiometric amount of \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2 equiv.) in \( \text{CH}_2\text{Cl}_2 \) at room temperature for 30 h, gem-difluoroalkane 1a afforded only the desired 2,2,3,3-tetrahydro-1,1-sprirob[inden] 2a in 85% yield, whereas the formation of elimination product 3a was not observed. In contrast, the intramolecular Friedel-Crafts cyclization was not observed when using 1,5-diphenylpentan-3-one (1v), (3,3-dimethoxypentane-1,5-diyl) dibenzene (1w), (3,3-dichloropentane-1,5-diyl) dibenzene (1x), and (3,3-dibromopentane-1,5-diyl) dibenzene (1y) (Table 2, entries 1–5). Although the cleavage of C-OMe bonds of substrate 1w by \( \text{B(C}_6\text{F}_5\text{)}_3 \) (2.2 equiv.) was observed, as the electron-rich heteroatom is a good Lewis base, only a complex mixture was found, and the formation of 2a was not observed (Table 2, entry 3). For the gem-dibromoalkane 1y, the formation of an unexpected elimination product in 29% yield was detected, which was ascribed to the ability of the bromine to act as a good leaving group (Table 2, entry 5). In
addition, under optimized conditions of HFIP, the formation of C(sp³)-C(sp³) bonds was only detected for gem-difluoroalkane 1a, but not for the relatively weaker C(sp³)-OMe, C(sp³)-Cl, and C(sp³)-Br bonds (Table 2, entries 6–12). However, the unexpected elimination products (monochloroalkene 3x and monobromoalkene 3y) were formed in 63% and 81% yield, respectively (Table 2, entry 9 and 11). Interestingly, in the absence of B(C₆F₅)₃ but still using HFIP as solvent, the yields of elimination products 3x and 3y remained essentially unchanged (61% and 86%, respectively). In other words, it is the hydrogen-bonding interaction between HFIP and either the C(sp³)-Cl or C(sp³)-Br bonds rather than the interaction with Lewis acids B(C₆F₅)₃ that governs the elimination process. Similarly, under the standard reaction conditions for the defluorinative elimination of 1a, i.e., treatment with B(C₆F₅)₃ (20 mol %) in refluxing 1,4-difluorobenzene for 24 h, gem-difluoride 1a afforded the desired monofluorinated olefin 3a in 87% yield, whereas a reaction was not observed for the corresponding aliphatic halides and ketals, with the exception of (3,3-dibromo-pentane-1,5-diyl)dibenzene, which afforded the monobromoalkene elimination product in 9% yield (Table 2, entries 13–16). Therefore the synthesis of spirobiindanes and monofluoroalkenes from aliphatic gem-difluoroalkanes 1 catalyzed by B(C₆F₅)₃ proceeds from a C-F bond activation process.

Based on the results discussed above, a reaction mechanism of C-F bond cleavage induced by the C(sp³)-F → B(C₆F₅)₃ interaction is proposed in Figure 4A. In our opinion, two effects of HFIP favor the intramolecular Friedel-Crafts process. (1) The strong hydrogen-bonding interaction between the hydrogen-bonding donor solvent HFIP and the fluoride anion in [FB(C₆F₅)₃]⁻ reduces the Brønsted basicity of the fluoride anion (cf. intermediate III) (Lee et al., 2016; Liang et al., 2017), which would result in the suppression of the E1-type elimination. Indeed, it has already been reported that the Lewis basicity of the fluoride anion of CsF or tetra-n-butylammonium fluoride (TBAF) is decreased in tertiary alcohols or urea (Kim et al., 2006, 2008a, 2008b; Pfeifer et al., 2016). For instance, relative to anhydrous TBAF, the TBAF(t-BuOH)₄ complex significantly favors nucleophilic substitution over elimination pathways (Kim et al., 2008a, 2008b). (2) HFIP, with its high dielectric constant (ε = 15.7) and low nucleophilicity (Colomer et al., 2017), provides additional stabilization for several carbocation intermediates in the intramolecular Friedel-Crafts alkylation (e.g., Figure 4B, II, IV, and VI). In addition, the alternative and probable reaction pathway via further defluorinative cyclization of monofluoroalkene 3 with a C(sp²)-F bond was ruled out as shown in Figure 4B. This result also indicates that the selective C-F bond activation by B(C₆F₅)₃ is limited to C(sp³)-F bonds. For benzylic secondary monofluoride (1-fluoropropane-1,3-diyl)dibenzene (4q), the hydrogen bonding between the benzylic C(sp³)-F bond and HFIP could enable the heterolytic cleavage of the C-F bond to generate carbonium ion VIII in Figure 4C, followed by the formation of the C(sp³)-C(sp³) bond. Accordingly, it is reasonable to extrapolate that in the intramolecular cyclization of aliphatic gem-difluoroalkanes 1, the hydrogen-bonding interaction enhances the ability of the fluoride to act as a leaving group, thus promoting the generation of carbonium ion II via the removal of a fluoride anion at relative low reaction temperatures. Indeed, without HFIP, higher temperatures were beneficial for the defluorinative elimination to generate monofluoroalkene 3; the yield of 3a increases from 64% to 81% when the temperature is increased from 160°C to 220°C in 1,2-dichlorobenzene in a sealed tube (Table 1, entries 14 and 17). Therefore, a combination of the hydrogen-bonding donor solvent HFIP and a catalytic amount of B(C₆F₅)₃ promotes the cascade intramolecular Friedel-Crafts reactions of gem-difluorides 1. It also should be pointed out that the HF generated in situ from Friedel-Crafts cyclization might enhance the hydrogen-bonding interaction with C(sp³)-F bonds to improve further the ability of fluoride moiety to act as a leaving group, which would benefit the heterolytic cleavage of C(sp³)-F bonds induced by B(C₆F₅)₃. Indeed, the intramolecular Friedel-Crafts reaction of primary benzylic monofluoride was controlled only by hydrogen-bonding effect initiated by HFIP and HF generated in situ (Champagne et al., 2014).

In conclusion, the selective cleavage of C(sp³)-F bonds in unactivated aliphatic gem-difluoroalkanes 1 afforded substituted spirobiindanes 2 and monofluoroalkenes 3 in good yields. In addition, the intramolecular Friedel-Crafts cyclization of aliphatic secondary monofluoroalkanes 4 was also described. The C(sp³)-F → B(C₆F₅)₃ interaction was probed by control experiments by the use of the corresponding ketone, ketal, and other halide-substituted derivatives. Accordingly, the combination of the hydrogen-bonding donor solvent HFIP and a catalytic amount of the Lewis acid B(C₆F₅)₃ enables the selective functionalization of inert C(sp³)-C(sp³) bonds into C(sp³)-C(sp³) bonds.

Limitations of the Study

The substrates with electron-withdrawing groups such as CF₃ and nitro groups are not suitable, which is to support the Friedel-Crafts cyclization mechanism in Figure 4A. We also examined more reactive
iodo-substituted substrates, but complex mixtures were obtained. Although the corresponding F-, Cl-, and Br-substituted substrates are acceptable (2i, 2j, 2k, 2l, and 2m, Figure 2A), these results also show some limitation of this method.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.06.018.
ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI grants JP 18H02553 (KIBAN B) and JP 18H04401 (Middle Molecular Strategy).

AUTHOR CONTRIBUTIONS

N.S. conceived the concept. J.W. conducted and analyzed the experiments and synthesized compounds. Y.O. prepared the starting materials. N.S. designed and directed the project, and N.S. and J.W. wrote the manuscript. All authors contributed to discussions.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

Ahrens, M., Scholz, G., Braun, T., and Kemnitz, E. (2013). Catalytic hydrodefluorination of fluoromethanes at room temperature by silylium-like surface species. Angew. Chem. Int. Ed. 52, 5328–5332.

Ahrens, T., Kohlmann, J., Ahrens, M., and Braun, T. (2015). Functionalization of fluorinated molecules by transition-metal-mediated C-F bond activation to access fluorinated building blocks. Chem. Rev. 115, 931–972.

Amii, H., and Uneyama, K. (2009). C-F bond activation in organic synthesis. Chem. Rev. 109, 2119–2183.

Bamford, K.L., Chitnis, S.S., Qu, Z.-w., and Stephan, D.W. (2018). Interactions of C–F bonds with hydridoboranes: reduction, borylation and Friedel–Crafts Alkylation. Chem. Eur. J.

Birman, V.B., Rheingold, A.L., and Lam, K.-C. (1999). 1,1,2,2-Tetrafluorobenzene–n-dodecane: a novel, C2-symmetric chiral ligand. Tetrahedron Asymmetry 10, 125–131.

Caputo, C.B., and Stephan, D.W. (2012). Activation of allyl C-F bonds by B(C6F5)3: stoichiometric and catalytic transformations. Organometallics 31, 27–30.

Champagne, P.A., Benhassine, Y., Desroches, J., and Paquin, J.-F. (2014). Friedel–Crafts reaction of benzyl fluorides: selective activation of C-F bonds as enabled by hydrogen bonding. Angew. Chem. Int. Ed. 53, 18385–18393.

Champagne, P.A., Desroches, J., and Paquin, J.-F. (2015). Organic fluorne as a hydrogen-bond acceptor: recent examples and applications. Synthesis 47, 306–322.

Chitnis, S.S., LaFortune, J.H.W., Cummings, H., Liu, L.L., Andrews, R., and Stephan, D.W. (2018). Phosphorus coordination chemistry in catalysis: air stable P(III)-dication as lewis acid catalysts for the allylation of C-F bonds. Organometallics 37, 4540–4544.

Colomer, J., Chamberlain, A.E.R., Haughey, M.B., and Donohoe, T.J. (2017). Hexafluorosopropanol as a highly versatile solvent. Nat. Rev. Chem. 1, 0088.

Cui, B., Jia, S., Tokunaga, E., and Shibata, N. (2018). Defluorosilylation of fluoroarenes and fluoroalkanes. Nat. Commun. 9, 4393.

Dovirs, C., and Ozerov, O.V. (2008). Hydrodefluorination of perfluoroalkyl groups using silylum-carborane catalysts. Science 321, 1186–1190.

Drouin, M., Haral, J.-D., and Paquin, J.-F. (2018). Synthesis of monofluoroalkanes: a leap forward. Synthesis 50, 881–955.

Dryzhakov, M., and Moran, J. (2016). Autocatalytic Friedel–Crafts reactions of tertiary aliphatic fluorides initiated by B(allyl)F3/H2O: ACS Catal. 6, 3670–3673.

Dryzhakov, M., Richmond, E., Li, G., and Moran, J. (2017). Catalytic B(C6F5)3/H2O-promoted defluorative functionalization of tertiary aliphatic fluorides. J. Fluor. Chem. 193, 45–51.

Forster, F., Metzner, T.T., Inan, E., Hrobak, P., and Oestreicher, M. (2017). Cooperative Al–H bond activation in Dibal-H: catalytic generation of an aluminium-ion-like Lewis acid for hydrodefluorinated Friedel–Crafts alkylation. J. Am. Chem. Soc. 139, 16334–16343.

Grebl, L. (2018). Lewis superacids: classifications, candidates, and applications. Chem. Eur. J. 24, 17881–17896.

Großkaupenberg, H., Reißmann, M., Schmidtmann, M., and Müller, T. (2015). Quantitative assessment of the Lewis acidity of silylum ions. Organometallics 34, 4952–4958.

Gu, W., Haneline, M.R., Dovirs, C., and Ozerov, O.V. (2009). Carbon–carbon coupling of C(sp3)–F bonds using aluminium catalysis. J. Am. Chem. Soc. 131, 11203–11212.

Guo, W.-H., Min, Q.-Q., Gu, J.-W., and Zhang, X. (2015). Rhodium-catalyzed ortho-selective C-F bond borylation of polyfluoroarenes with Bpin-Bpin. Angew. Chem. Int. Ed. 54, 9075–9078.

Hamel, J.-D., and Paquin, J.-F. (2018). Activation of C-F bonds α to C=C multiple bonds. Chem. Commun. (Camb.) 54, 10224–10239.

Haufe, G., Suzuki, S., Yasui, H., Terada, C., Kitayama, T., Shiro, M., and Shibata, N. (2012). C-F bond activation of unactivated aliphatic fluorides: synthesis of fluoromethyl-3,5-dimethyl-2-oxazolidinones by desymmetrization of 2-Aryl-1,3-difluoro-2-propanol. Angew. Chem. Int. Ed. 51, 12275–12279.

Hirano, K., Fujita, K., Yorimitsu, H., Shinokubo, H., and Oshima, K. (2004). Boron trifluoride-catalyzed reaction of allyl fluoride with silyl enolate, allylsilane, and hydrosilane. Tetrahedron Lett. 45, 2555–2557.

Jaiswal, A.K., Goh, K.K.K., Sung, S., and Young, R.D. (2017). Aluminum-catalyzed cross-coupling of silylalkynes with aliphatic C-F bonds. Org. Lett. 19, 1934–1937.

Kim, D.W., Ahn, D.-S., Oh, Y.-H., Lee, S., Kim, D.H., Oh, Y.J., Lee, S., Kim, J.S., Ryu, J.S., Moon, D.H., et al. (2006). A new class of SN2 reactions catalyzed by protic solvents: facile fluorination for isotopic labeling of diagnostic molecules. J. Am. Chem. Soc. 128, 16394–16397.

Kim, D.W., Jeong, H.-J., Lim, S.T., Sohn, M.-H., Katzenellenbogen, J.A., and Chi, D.Y. (2008a). Facile nucleophilic fluorination reactions using tert-alcohols as a reaction medium: significantly enhanced reactivity of alkali metal fluorides and improved selectivity. J. Org. Chem. 73, 957–962.

Kim, D.W., Jeong, H.-J., Lim, S.T., and Sohn, M.-H. (2008b). Tetra(t-Buty1 AlcohOl)-coordinated fluoride as a facile fluoride source. Angew. Chem. Int Ed. 47, 8404–8406.

Received: April 14, 2019
Revised: June 3, 2019
Accepted: June 12, 2019
Published: July 26, 2019
Klahn, M., Fischer, C., Spannenberg, A., Rosenthal, U., and Kroising, I. (2007). Hydrodefluorination of non-activated C–F bonds by disobutylaluminiumhydride via the aluminium cation [−Bu2Al]+. Tetrahedron Lett. 48, 8900–8903.

Klare, H.F.T. (2017). Catalytic C–H arylation of unactivated C–H bonds by silylium ion-promoted C(sp2)–F bond activation. ACS Catal. 7, 6999–7002.

Koerte, L.A., Schwabedissen, J., Soffner, M., Blomeyer, S., Reuter, C.G., Vishnevskiy, Y.V., Neumann, B., Stammier, H.-G., and Mitzel, N.W. (2017). Tris(perfluorotolyl)borane–A boron Lewis superacid. Angew. Chem. Int. Ed. 56, 8578–8582.

Kuehnel, M.F., Lentz, D., and Braun, T. (2013). Synthesis of fluorinated building blocks by transition-metal-mediated hydrodefluorination reactions. Angew. Chem. Int. Ed. 52, 3329–3348.

Lan, K., Shan, Z., and Fan, S. (2006). Synthesis of spirobiindanes via bis-cyclization reaction of the 1,5-diaaryl-3-pentanones catalyzed by heteropoly acids. Tetrahedron Lett. 47, 4343–4345.

Lee, J.-W., Oliveira, M.T., Jang, H.B., Lee, S., Chi, D.Y., Kim, D.W., and Song, C.E. (2016). Hydrogen-bond promoted nucleophilic fluorination: concept, mechanism and applications in positron emission tomography. Chem. Soc. Rev. 45, 4638–4650.

Li, S., Zhang, J.-W., Li, X.-L., Cheng, D.-J., and Tan, B. (2016). Phosphoric acid-catalyzed asymmetric synthesis of SPINOL derivatives. J. Am. Chem. Soc. 138, 16561–16566.

Li, Y., Liu, J., Zhao, S., Du, X., Guo, M., Zhao, W., Tang, X., and Wang, G. (2018). Copper-catalyzed fluoroalcoholation of silyl enol ethers and ketones toward the synthesis of β-fluoroenones. Org. Lett. 20, 917–920.

Liang, S., Hammond, G.B., and Xu, B. (2017). Hydrogen bonding regulator for nucleophilic fluorination. Chem. Eur. J. 23, 17850–17861.

Luo, Z.-J., Zhao, H.-Y., and Zhang, X. (2018). Highly selective Pd-catalyzed direct C–F bond arylation of polyfluoroarenes. Org. Lett. 20, 2543–2546.

Mandal, D., Gupta, R., and Young, R.D. (2018). Selective monodefluorination and witig functionalization of gem-difluoromethyl groups to generate monofluoroalkanes. J. Am. Chem. Soc. 140, 10682–10686.

Morgan, M.M., Marwitz, A.J.V., Piers, W.E., and Parvez, M. (2013). Comparative Lewis acidity in fluoroarylboranes: B(o-HC2F5)3, B(p-HC2F5)3, and B(C6F5)3. Organometallics 32, 317–322.

Motwala, H.F., Vekariya, R.H., and Aube, J. (2015). Intramolecular Friedel-Crafts acylation reaction promoted by 1,1,1,3,3,3-Hexafluoro-2-propanol. Org. Lett. 17, 5484–5487.

Nolte, C., Ammer, J., and Mayr, H. (2012). Nucleofugality and nucleophilicity of fluoride in protic solvents. J. Org. Chem. 77, 3325–3335.

O’Hagan, D. (2008). Understanding organofluorine chemistry. An introduction to the C–F bond. Chem. Soc. Rev. 37, 308–319.

Olah, G.A., and Kuhn, S.J. (1964). Selective Friedel-Crafts reactions. I. Boron halide catalyzed halolkylation of benzene and alkylbenzenes with fluorohaloalkanes. J. Org. Chem. 29, 2317–2320.

Olah, G., Kuhn, I., and Olah, J. (1957). Aromatic substitution. III. Alkylation of aromatic compounds by the boron trifluoride-catalyzed reaction of alkyl fluorides. J. Chem. Soc. 1957, 2174–2176.

Pfeifer, L., Engle, K.M., Pidgeon, G.W., Sparkes, H.A., Thompson, A.L., Brown, J.M., and Gouverneur, V. (2016). Hydrogen-bonded homoeofluoride–diarylurea complexes: structure, reactivity, and coordinating power. J. Am. Chem. Soc. 138, 13314–13325.

Pike, S.D., Crimmin, M.R., and Chaplin, A.B. (2017). Organometallic chemistry using partially homoleptic fluoride–diarylurea complexes: Synthesis of 3,5-Diaryl-5-fluoropyrroles. Org. Lett. 55, 3615–3633.

Scott, V.J., Çelenlikçi-Çetin, R., and Ozerov, O.V. (2008). Room-temperature catalytic hydrodefluorination of C(sp2)–F bonds. J. Am. Chem. Soc. 127, 2852–2853.

Shen, Q., Huang, Y.-G., Liu, C., Xiao, J.-C., Chen, Q.-Y., and Guo, Y. (2015). Review of recent advances in CF bond activation of aliphatic fluorides. J. Fluorine Chem. 179, 14–22.

Song, X., Xu, C., and Wang, M. (2017). Transformations based on ring-opening of gem-difluorocyclopropanes. Tetrahedron Lett. 58, 1806–1816.

Stahl, T., Klare, H.F.T., and Oestreich, M. (2013). Main-group Lewis acids for C–F bond activation. ACS Catal. 3, 1578–1587.

Strobach, D.R., and Boswell, G.A., Jr. (1971). Synthesis of 1-fluorocycloalkanes. J. Org. Chem. 36, 818–820.

Surmont, R., Verniest, G., and Kimpe, N.D. (2009). Gold-catalyzed synthesis of 2-Aryl-3-fluoropyrroles. Org. Lett. 11, 2920–2923.

Tanaka, J., Suzuki, S., Tokunaga, E., Haufe, G., and Shibata, N. (2016). Asymmetric desymmetrization via metal-free C–F bond activation: synthesis of 3,5-Diaryl-5-fluoromethyloxazolidin-2-ones with quaternary carbon centers. Angew. Chem. Int. Ed. 55, 9432–9436.

Tang, R.-J., Milcent, T., and Crousse, B. (2018). Bisulfitic salt-catalyzed Friedel-Crafts benzylation of amines with benzyl alcohols. J. Org. Chem. 83, 14001–14009.

Vekariya, R.H., and Aube, J. (2016). Hexafluoro-2-propanol-promoted intermolecular Friedel-crafts acylation reaction. Org. Lett. 18, 3534–3537.

Yanai, H., Okada, H., Sato, A., Okada, M., and Taguchi, T. (2011). Copper-free defluorinative alkylation of allylic difluorides through Lewis acid-mediated C–F bond activation. Tetrahedron Lett. 52, 2997–3000.

Yang, T.-P., Lin, J.-H., Chen, Q.-Y., and Xiao, J.-C. (2013). A novel reaction of gem-difluorocyclopropyl ketones with nitrites leading to 2-fluoropyrroles. Chem. Commun. (Camb.) 49, 9833–9835.

Zheng, Z., Cao, Y., Cheng, Q., Han, Z., Ding, J., Luo, C., Wang, Z., Zhu, D., Zhou, Q.-L., and Ding, K. (2018). Chiral cyclohexyl-fused spirobiindanes: practical synthesis, ligand development, and asymmetric catalysis. J. Am. Chem. Soc. 140, 10376–10381.

Zhu, J., Pérez, M., Caputo, C.B., and Stephan, D.W. (2016). Use of trifluoromethyl groups for catalytic benzylation and alkylation with subsequent hydrodefluorination. Angew. Chem. Int. Ed. 55, 1417–1421.
Supplemental Information

Activation of Saturated Fluorocarbons to Synthesize Spirobiindanes, Monofluoroalkenes, and Indane Derivatives

Jiandong Wang, Yuta Ogawa, and Norio Shibata
Supplemental Figures

Figure S1. $^1$H NMR spectrum of 2a, related to Figure 2

Figure S2. $^{13}$C NMR spectrum of 2a, related to Figure 2
**Figure S3.** $^1$H NMR spectrum of 2b, related to Figure 2

**Figure S4.** $^{13}$C NMR spectrum of 2b, related to Figure 2
**Figure S5.** $^1$H NMR spectrum of 2c, related to Figure 2

![NMR spectrum](image)

**Figure S6.** $^{13}$C NMR spectrum of 2c, related to Figure 2

![NMR spectrum](image)
Figure S7. $^1$H NMR spectrum of 2d, related to Figure 2

Figure S8. $^{13}$C NMR spectrum of 2d, related to Figure 2
Figure S9. $^1$H NMR spectrum of 2e, related to Figure 2

![Figure S9](image)

Figure S10. $^{13}$C NMR spectrum of 2e, related to Figure 2

![Figure S10](image)
Figure S11. $^1$H NMR spectrum of 2f, related to Figure 2

Figure S12. $^{13}$C NMR spectrum of 2f, related to Figure 2
Figure S13. $^1$H NMR spectrum of 2g, related to Figure 2

Figure S14. $^{13}$C NMR spectrum of 2g, related to Figure 2
Figure S15. $^1$H NMR spectrum of 2h, related to Figure 2

Figure S16. $^{13}$C NMR spectrum of 2h, related to Figure 2
Figure S17. GC-MS analysis of 2h, related to Figure 2
Figure S18. $^1$H NMR spectrum of $2i$, related to Figure 2

Figure S19. $^{13}$C NMR spectrum of $2i$, related to Figure 2
Figure S20. $^1$H NMR spectrum of 2j, related to Figure 2

Figure S21. $^{13}$C NMR spectrum of 2j, related to Figure 2
Figure S22. $^1$H NMR spectrum of $2k$, related to Figure 2

Figure S23. $^{13}$C NMR spectrum of $2k$, related to Figure 2
Figure S24. $^1$H NMR spectrum of 2l, related to Figure 2

![Figure S24. $^1$H NMR spectrum of 2l, related to Figure 2](image)

Figure S25. $^{13}$C NMR spectrum of 2l, related to Figure 2

![Figure S25. $^{13}$C NMR spectrum of 2l, related to Figure 2](image)
Figure S26. ¹H NMR spectrum of 2m, related to Figure 2

Figure S27. ¹³C NMR spectrum of 2m, related to Figure 2
Figure S28. $^1$H NMR spectrum of 2n, related to Figure 2

Figure S29. $^{13}$C NMR spectrum of 2n, related to Figure 2
Figure S30. $^1$H NMR spectrum of 2o, related to Figure 2

![Figure S30. $^1$H NMR spectrum of 2o, related to Figure 2](image)

Figure S31. $^{13}$C NMR spectrum of 2o, related to Figure 2

![Figure S31. $^{13}$C NMR spectrum of 2o, related to Figure 2](image)
Figure S32. $^1$H NMR spectrum of 2p, related to Figure 2

Figure S33. $^{13}$C NMR spectrum of 2p, related to Figure 2
Figure S34. $^1$H NMR spectrum of 2q, related to Figure 2

Figure S35. $^{13}$C NMR spectrum of 2q, related to Figure 2
Figure S36. $^1$H NMR spectrum of 2r, related to Figure 2

Figure S37. $^{13}$C NMR spectrum of 2r, related to Figure 2
Figure S38. $^1$H NMR spectrum of 2s, related to Figure 2

Figure S39. $^{13}$C NMR spectrum of 2s, related to Figure 2
Figure S40. $^1$H NMR spectrum of 2t, related to Figure 2

Figure S41. $^{13}$C NMR spectrum of 2t, related to Figure 2
Figure S42. $^1$H NMR spectrum of 3a, related to Figure 2

Figure S43. $^{13}$C NMR spectrum of 3a, related to Figure 2
Figure S44. $^{19}$F NMR spectrum of 3a, related to Figure 2

Figure S45. $^1$H NMR spectrum of 3e, related to Figure 2
**Figure S46.** $^{13}$C NMR spectrum of 3e, related to Figure 2

**Figure S47.** $^{19}$F NMR spectrum of 3e, related to Figure 2
Figure S48. $^1$H NMR spectrum of 3f, related to Figure 2

![Figure S48. $^1$H NMR spectrum of 3f, related to Figure 2](image)

Figure S49. $^{13}$C NMR spectrum of 3f, related to Figure 2

![Figure S49. $^{13}$C NMR spectrum of 3f, related to Figure 2](image)
Figure S50. $^{19}$F NMR spectrum of 3f, related to Figure 2

Figure S51. $^1$H NMR spectrum of 3g, related to Figure 2
Figure S52. $^{13}$C NMR spectrum of 3g, related to Figure 2.

Figure S53. $^{19}$F NMR spectrum of 3g, related to Figure 2.
**Figure S54.** $^1$H NMR spectrum of 3n, related to Figure 2

**Figure S55.** $^{13}$C NMR spectrum of 3n, related to Figure 2
Figure S56. $^{19}$F NMR spectrum of $3n$, related to Figure 2

Figure S57. $^1$H NMR spectrum of $3o$, related to Figure 2
Figure S58. $^{13}$C NMR spectrum of 3o, related to Figure 2

Figure S59. $^{19}$F NMR spectrum of 3o, related to Figure 2
Figure S60. $^1$H NMR spectrum of 3j, related to Figure 2

Figure S61. $^{13}$C NMR spectrum of 3j, related to Figure 2
Figure S62. $^{19}$F NMR spectrum of 3j, related to Figure 2

Figure S63. $^1$H NMR spectrum of 3k, related to Figure 2
Figure S64. $^{13}$C NMR spectrum of 3k, related to Figure 2

Figure S65. $^{19}$F NMR spectrum of 3k, related to Figure 2
Figure S66. $^1$H NMR spectrum of 3u, related to Figure 2

Figure S67. $^{13}$C NMR spectrum of 3u, related to Figure 2
Figure S68. $^{19}$F NMR spectrum of 3u, related to Figure 2

Figure S69. $^1$H NMR spectrum of 3aa, related to Figure 2
Figure S70. $^{19}$F NMR spectrum of 3aa, related to Figure 2

Figure S71. $^1$H NMR spectrum of 3bb, related to Figure 2
Figure S72. $^{19}$F NMR spectrum of 3bb, related to Figure 2

Figure S73. $^1$H NMR spectrum of 3cc, related to Figure 2
Figure S74. $^{19}$F NMR spectrum of 3cc, related to Figure 2

Figure S75. $^1$H NMR spectrum of 3dd, related to Figure 2
Figure S76. $^{19}$F NMR spectrum of 3dd, related to Figure 2

Figure S77. $^1$H NMR spectrum of 3ee, related to Figure 2
Figure S78. $^{19}$F NMR spectrum of 3ee, related to Figure 2

Figure S79. $^1$H NMR spectrum of 3ff, related to Figure 2
Figure S80. $^{13}$C NMR spectrum of 3ff, related to Figure 2

Figure S81. $^{19}$F NMR spectrum of 3ff, related to Figure 2
Figure S82. $^1$H NMR spectrum of 3gg, related to Figure 2

Figure S83. $^{13}$C NMR spectrum of 3gg, related to Figure 2
Figure S84. $^{19}$F NMR spectrum of 3gg, related to Figure 2

Figure S85. $^1$H NMR spectrum of (Z)-3hh, related to Figure 2
Figure S86. $^{13}$C NMR spectrum of (Z)-3hh, related to Figure 2

Figure S87. $^{19}$F NMR spectrum of (Z)-3hh, related to Figure 2
Figure S88. $^{19}$F NMR spectrum of 3hh, related to Figure 2
Figure S89. $^1$H NMR spectrum of 5a, related to Figure 3

Figure S90. $^{13}$C NMR spectrum of 5a, related to Figure 3
Figure S91. $^1$H NMR spectrum of 5b, related to Figure 3

Figure S92. $^{13}$C NMR spectrum of 5b, related to Figure 3
Figure S93. $^1$H NMR spectrum of $5c$, related to Figure 3

Figure S94. $^{13}$C NMR spectrum of $5c$, related to Figure 3
**Figure S95.** $^1$H NMR spectrum of 5d, related to Figure 3

**Figure S96.** $^{13}$C NMR spectrum of 5d, related to Figure 3
Figure S97. $^1$H NMR spectrum of 5e, related to Figure 3

Figure S98. $^{13}$C NMR spectrum of 5e, related to Figure 3
Figure S99. $^1$H NMR spectrum of 5f, related to Figure 3

Figure S100. $^{13}$C NMR spectrum of 5f, related to Figure 3
Figure S101. \(^1\)H NMR spectrum of 5g, related to Figure 3

Figure S102. \(^{13}\)C NMR spectrum of 5g, related to Figure 3
Figure S103. $^1$H NMR spectrum of $5h$, related to Figure 3

Figure S104. $^{13}$C NMR spectrum of $5h$, related to Figure 3
Figure S105. $^1$H NMR spectrum of 5i, related to Figure 3

Figure S106. $^{13}$C NMR spectrum of 5i, related to Figure 3
Figure S107. $^1$H NMR spectrum of 5j, related to Figure 3

Figure S108. $^{13}$C NMR spectrum of 5j, related to Figure 3
Figure S109. $^1$H NMR spectrum of 5k, related to Figure 3

Figure S110. $^{13}$C NMR spectrum of 5k, related to Figure 3
Figure S111. $^1$H NMR spectrum of 5l, related to Figure 3

Figure S112. $^{13}$C NMR spectrum of 5l, related to Figure 3
Figure S113. $^1$H NMR spectrum of 5m, related to Figure 3

Figure S114. $^{13}$C NMR spectrum of 5m, related to Figure 3
Figure S115. $^1$H NMR spectrum of 5n, related to Figure 3

Figure S116. $^{13}$C NMR spectrum of 5n, related to Figure 3
Figure S117. $^1$H NMR spectrum of 5o, related to Figure 3

Figure S118. $^1$H NMR spectrum of 5p, related to Figure 3
Figure S119. $^{13}$C NMR spectrum of 5p, related to Figure 3

Figure S120. $^1$H NMR spectrum of 5q, related to Figure 3
Figure S121. $^1$H NMR spectrum of 5r, related to Figure 3

Figure S122. $^1$H NMR spectrum of 5s, related to Figure 3
Figure S123. $^1$H NMR spectrum of unknown gem-difluoride 1b, related to Figure 2

Figure S124. $^{13}$C NMR spectrum of unknown gem-difluoride 1b, related to Figure 2
Figure S125. $^{19}$F NMR spectrum of unknown gem-difluoride 1b, related to Figure 2

Figure S126. $^1$H NMR spectrum of unknown gem-difluoride 1c, related to Figure 2
Figure S127. $^{13}$C NMR spectrum of unknown gem-difluoride 1c, related to Figure 2

Figure S128. $^{19}$F NMR spectrum of unknown gem-difluoride 1c, related to Figure 2
Figure S129. $^1$H NMR spectrum of unknown gem-difluoride 1d, related to Figure 2

Figure S130. $^{13}$C NMR spectrum of unknown gem-difluoride 1d, related to Figure 2
**Figure S131.** $^{19}$F NMR spectrum of unknown *gem*-difluoride 1d, related to Figure 2

![Figure S131](image1)

**Figure S132.** $^1$H NMR spectrum of unknown *gem*-difluoride 1e, related to Figure 2

![Figure S132](image2)
Figure S133. $^{13}$C NMR spectrum of unknown gem-difluoride 1e, related to Figure 2

Figure S134. $^{19}$F NMR spectrum of unknown gem-difluoride 1e, related to Figure 2
Figure S135. $^1$H NMR spectrum of unknown *gem*-difluoride 1f, related to Figure 2

Figure S136. $^{13}$C NMR spectrum of unknown *gem*-difluoride 1f, related to Figure 2
Figure S137. $^{19}\text{F}$ NMR spectrum of unknown gem-difluoride 1f, related to Figure 2

Figure S138. $^1\text{H}$ NMR spectrum of unknown gem-difluoride 1g, related to Figure 2
Figure S139. $^{13}$C NMR spectrum of unknown gem-difluoride 1g, related to Figure 2

Figure S140. $^{19}$F NMR spectrum of unknown gem-difluoride 1g, related to Figure 2
Figure S141. $^1$H NMR spectrum of unknown *gem*-difluoride 1h, related to Figure 2

Figure S142. $^{13}$C NMR spectrum of unknown *gem*-difluoride 1h, related to Figure 2
Figure S143. $^{19}$F NMR spectrum of unknown gem-difluoride 1h, related to Figure 2

Figure S144. $^1$H NMR spectrum of unknown gem-difluoride 1i, related to Figure 2
**Figure S145.** $^{13}$C NMR spectrum of unknown *gem*-difluoride 1i, related to Figure 2

**Figure S146.** $^{19}$F NMR spectrum of unknown *gem*-difluoride 1i, related to Figure 2
**Figure S147.** $^1$H NMR spectrum of unknown gem-difluoride 1j, related to Figure 2

**Figure S148.** $^{13}$C NMR spectrum of unknown gem-difluoride 1j, related to Figure 2
Figure S149. $^{19}$F NMR spectrum of unknown gem-difluoride 1j, related to Figure 2

Figure S150. $^1$H NMR spectrum of unknown gem-difluoride 1k, related to Figure 2
Figure S151. $^{13}$C NMR spectrum of unknown gem-difluoride 1k, related to Figure 2

Figure S152. $^{19}$F NMR spectrum of unknown gem-difluoride 1k, related to Figure 2
Figure S153. $^1$H NMR spectrum of unknown gem-difluoride 1I, related to Figure 2

Figure S154. $^{13}$C NMR spectrum of unknown gem-difluoride 1I, related to Figure 2
Figure S155. $^{19}$F NMR spectrum of unknown gem-difluoride 1l, related to Figure 2

Figure S156. $^1$H NMR spectrum of unknown gem-difluoride 1m, related to Figure 2
Figure S157. $^{13}$C NMR spectrum of unknown gem-difluoride 1m, related to Figure 2

Figure S158. $^{19}$F NMR spectrum of unknown gem-difluoride 1m, related to Figure 2
Figure S159. $^1$H NMR spectrum of unknown gem-difluoride 1n, related to Figure 2

Figure S160. $^{13}$C NMR spectrum of unknown gem-difluoride 1n, related to Figure 2
Figure S161. $^{19}F$ NMR spectrum of unknown gem-difluoride 1n, related to Figure 2

Figure S162. $^1H$ NMR spectrum of unknown gem-difluoride 1o, related to Figure 2
**Figure S163.** $^{13}$C NMR spectrum of unknown *gem*-difluoride 1o, related to Figure 2

**Figure S164.** $^{19}$F NMR spectrum of unknown *gem*-difluoride 1o, related to Figure 2
Figure S165. $^1$H NMR spectrum of unknown gem-difluoride 1p, related to Figure 2

Figure S166. $^{13}$C NMR spectrum of unknown gem-difluoride 1p, related to Figure 2
Figure S167. $^{19}$F NMR spectrum of unknown \textit{gem}-difluoride 1p, related to Figure 2

Figure S168. $^1$H NMR spectrum of unknown \textit{gem}-difluoride 1q, related to Figure 2
Figure S169. $^{13}$C NMR spectrum of unknown *gem*-difluoride 1q, related to Figure 2

Figure S170. $^{19}$F NMR spectrum of unknown *gem*-difluoride 1q, related to Figure 2
Figure S171. $^1$H NMR spectrum of unknown gem-difluoride 1r, related to Figure 2

Figure S172. $^{13}$C NMR spectrum of unknown gem-difluoride 1r, related to Figure 2
Figure S173. $^{19}$F NMR spectrum of unknown gem-difluoride 1r, related to Figure 2

Figure S174. $^1$H NMR spectrum of unknown gem-difluoride 1s, related to Figure 2
Figure S175. $^{13}$C NMR spectrum of unknown gem-difluoride 1s, related to Figure 2

Figure S176. $^{19}$F NMR spectrum of unknown gem-difluoride 1s, related to Figure 2
Figure S177. $^1$H NMR spectrum of unknown *gem*-difluoride 1t, related to Figure 2

Figure S178. $^{13}$C NMR spectrum of unknown *gem*-difluoride 1t, related to Figure 2
Figure S179. $^{19}$F NMR spectrum of unknown gem-difluoride 1t, related to Figure 2

Figure S180. $^1$H NMR spectrum of unknown gem-difluoride 1u, related to Figure 2
**Figure S181.** $^{13}$C NMR spectrum of unknown *gem*-difluoride 1u, related to Figure 2

![$^{13}$C NMR spectrum](image1.png)

**Figure S182.** $^{19}$F NMR spectrum of unknown *gem*-difluoride 1u, related to Figure 2

![$^{19}$F NMR spectrum](image2.png)
**Figure S183.** $^1$H NMR spectrum of unknown gem-difluoride 1cc, related to Figure 2

**Figure S184.** $^{13}$C NMR spectrum of unknown gem-difluoride 1cc, related to Figure 2
Figure S185. $^{19}$F NMR spectrum of unknown gem-difluoride 1cc, related to Figure 2

Figure S186. $^1$H NMR spectrum of unknown gem-difluoride 1ee, related to Figure 2
Figure S187. $^{13}$C NMR spectrum of unknown *gem*-difluoride 1ee, related to Figure 2

Figure S188. $^{19}$F NMR spectrum of unknown *gem*-difluoride 1ee, related to Figure 2
**Figure S189.** $^1$H NMR spectrum of unknown *gem*-difluoride 1hh, related to Figure 2

**Figure S190.** $^{13}$C NMR spectrum of unknown *gem*-difluoride 1hh, related to Figure 2
Figure S191. $^{19}$F NMR spectrum of unknown gem-difluoride 1hh, related to Figure 2.
Figure S192. $^1$H NMR spectrum of unknown secondary monofluoride 4a, related to Figure 3

Figure S193. $^{13}$C NMR spectrum of unknown secondary monofluoride 4a, related to Figure 3
Figure S194. $^{19}$F NMR spectrum of unknown secondary monofluoride 4a, related to Figure 3

Figure S195. $^1$H NMR spectrum of unknown secondary monofluoride 4b, related to Figure 3
Figure S196. $^{13}$C NMR spectrum of unknown secondary monofluoride 4b, related to Figure 3

Figure S197. $^{19}$F NMR spectrum of unknown secondary monofluoride 4b, related to Figure 3
Figure S198. $^1$H NMR spectrum of unknown secondary monofluoride 4c, related to Figure 3

Figure S199. $^{13}$C NMR spectrum of unknown secondary monofluoride 4c, related to Figure 3
Figure S200. $^{19}$F NMR spectrum of unknown secondary monofluoride 4c, related to Figure 3

Figure S201. $^1$H NMR spectrum of unknown secondary monofluoride 4d, related to Figure 3
Figure S202. $^{13}$C NMR spectrum of unknown secondary monofluoride 4d, related to Figure 3

![13C NMR spectrum of unknown secondary monofluoride 4d](image)

Figure S203. $^{19}$F NMR spectrum of unknown secondary monofluoride 4d, related to Figure 3

![19F NMR spectrum of unknown secondary monofluoride 4d](image)
Figure S204. $^1$H NMR spectrum of unknown secondary monofluoride 4e, related to Figure 3

Figure S205. $^{13}$C NMR spectrum of unknown secondary monofluoride 4e, related to Figure 3
Figure S206. $^{19}$F NMR spectrum of unknown secondary monofluoride 4e, related to Figure 3

Figure S207. $^1$H NMR spectrum of unknown secondary monofluoride 4f, related to Figure 3
Figure S208. $^{13}$C NMR spectrum of unknown secondary monofluoride 4f, related to Figure 3

Figure S209. $^{19}$F NMR spectrum of unknown secondary monofluoride 4f, related to Figure 3
Figure S210. $^1$H NMR spectrum of unknown secondary monofluoride 4g, related to Figure 3

Figure S211. $^{13}$C NMR spectrum of unknown secondary monofluoride 4g, related to Figure 3
Figure S212. $^{19}\text{F}$ NMR spectrum of unknown secondary monofluoride 4g, related to Figure 3

Figure S213. $^{1}\text{H}$ NMR spectrum of unknown secondary monofluoride 4h, related to Figure 3
Figure S214. $^{13}$C NMR spectrum of unknown secondary monofluoride 4h, related to Figure 3

Figure S215. $^{19}$F NMR spectrum of unknown secondary monofluoride 4h, related to Figure 3
Figure S216. $^1$H NMR spectrum of unknown secondary monofluoride 4i, related to Figure 3

Figure S217. $^{13}$C NMR spectrum of unknown secondary monofluoride 4i, related to Figure 3
**Figure S218.** $^{19}\text{F}$ NMR spectrum of unknown secondary monofluoride 4i, related to Figure 3

**Figure S219.** $^{1}\text{H}$ NMR spectrum of unknown secondary monofluoride 4j, related to Figure 3
**Figure S220.** $^{13}$C NMR spectrum of unknown secondary monofluoride 4j, related to Figure 3

![$^{13}$C NMR spectrum of unknown secondary monofluoride 4j](image)

**Figure S221.** $^{19}$F NMR spectrum of unknown secondary monofluoride 4j, related to Figure 3

![$^{19}$F NMR spectrum of unknown secondary monofluoride 4j](image)
Figure S222. $^1$H NMR spectrum of unknown secondary monofluoride 4k, related to Figure 3

Figure S223. $^{13}$C NMR spectrum of unknown secondary monofluoride 4k, related to Figure 3
Figure S224. $^{19}$F NMR spectrum of unknown secondary monofluoride 4k, related to Figure 3

Figure S225. $^1$H NMR spectrum of unknown secondary monofluoride 4l, related to Figure 3
Figure S226. $^{13}$C NMR spectrum of unknown secondary monofluoride 4I, related to Figure 3

Figure S227. $^{19}$F NMR spectrum of unknown secondary monofluoride 4I, related to Figure 3
Figure S228. $^1$H NMR spectrum of unknown secondary monofluoride 4m, related to Figure 3

![1H NMR spectrum of unknown secondary monofluoride 4m](image)

Figure S229. $^{13}$C NMR spectrum of unknown secondary monofluoride 4m, related to Figure 3

![13C NMR spectrum of unknown secondary monofluoride 4m](image)
Figure S230. $^{19}$F NMR spectrum of unknown secondary monofluoride 4m, related to Figure 3

Figure S231. $^1$H NMR spectrum of unknown secondary monofluoride 4n, related to Figure 3
Figure S232. $^{13}$C NMR spectrum of unknown secondary monofluoride 4n, related to Figure 3

Figure S233. $^{19}$F NMR spectrum of unknown secondary monofluoride 4n, related to Figure 3
**Figure S234.** $^1$H NMR spectrum of unknown secondary monofluoride 4p, related to Figure 3

**Figure S235.** $^{13}$C NMR spectrum of unknown secondary monofluoride 4p, related to Figure 3
Figure S236. $^{19}$F NMR spectrum of unknown secondary monofluoride 4p, related to Figure 3

Figure S237. $^1$H NMR spectrum of unknown secondary monofluoride 4r, related to Figure 3
Figure S238. $^{13}$C NMR spectrum of unknown secondary monofluoride 4r, related to Figure 3

Figure S239. $^{19}$F NMR spectrum of unknown secondary monofluoride 4r, related to Figure 3
Figure S240. $^1$H NMR spectrum of unknown secondary monofluoride 4s, related to Figure 3

Figure S241. $^{13}$C NMR spectrum of unknown secondary monofluoride 4s, related to Figure 3
Figure S242. $^{19}$F NMR spectrum of unknown secondary monofluoride 4s, related to Figure 3
Figure S243. $^1$H-NMR spectra copy of crude reaction mixture: Using (CF$_3$)$_2$CHOH as purchased without precaution to exclude moisture, related to Table 1 (entry 7)
**Figure S244.** $^1$H-NMR spectrum of 1v, related to Table 2

![Figure S244](image1)

**Figure S245.** $^1$H-NMR spectrum of 1w, related to Table 2

![Figure S245](image2)
Figure S246. $^1$H-NMR spectrum of 1x, related to Table 2

Figure S247. $^1$H-NMR spectrum of 1y, related to Table 2
**Figure S248.** $^1$H-NMR spectrum of 3x, related to Table 2

**Figure S249.** $^1$H-NMR spectrum of 3y, related to Table 2
Figure S250. $^{13}$C-NMR spectrum of 3y, related to Table 2
Figure S251. $^1$H-NMR spectrum of crude reaction mixture of (3,3-dichloropentane-1,5-diyldibenzene (1x) and (CF$_3$)$_2$CHOH, related to Table 2.
Figure S252. $^1$H-NMR spectrum of crude reaction mixture of (3,3-dibromopentane-1,5-diyl)dibenzene (1y) and (CF$_3$)$_2$CHOH, related to Table 2.
Figure S253: $^1$H-NMR spectra copy of crude reaction mixture of (3,3-dibromopentane-1,5-diyl)dibenzene(1y)/B(C$_6$F$_5$)$_3$/p-C$_6$H$_4$F$_2$, related to Table 2.
Table S1. Optimization of B(C₆F₅)₃ induced defluorinative Friedel-Crafts cyclization, related to Table 1.

| Entry | B(C₆F₅)₃ (equiv) | Solvent         | Concentration | Temperature (°C) | Time (h) | Yields (%) |
|-------|------------------|-----------------|---------------|-----------------|----------|------------|
| 1     | 2.2              | CH₂Cl₂          | 0.1 M         | RT              | 30       | 85         |
| 2     | 1.1              | CH₂Cl₂          | 0.1 M         | RT              | 30       | 31         |
| 3     | 0.2              | CH₂Cl₂          | 0.1 M         | RT              | 30 Trace | Trace      |
| 4     | 0.2              | CH₂Cl₂          | 0.2 M         | 100⁰a           | 2        | Trace      |
| 5     | 0.2              | CH₂Cl₂          | 2.0 M         | 100⁰a           | 2 Trace  | Trace      |
| 6     | 0.5              | MeNO₂           | 2.0 M         | RT              | 30 Trace | Trace      |
| 7     | 0.2              | (CF₃)₂CHOH      | 2.0 M         | 100⁰a           | 2        | 54         |
| 8     | 0.2              | (CF₃)₂CHOH      | 0.25 M        | 100⁰a           | 2        | 53         |
| 9     | 0.1              | (CF₃)₂CHOH      | 0.25 M        | 100⁰a           | 2        | 41         |
| 10    | 0.05             | (CF₃)₂CHOH      | 0.25 M        | 100⁰a           | 2 Trace  | 25         |
| 11    | ---              | (CF₃)₂CHOH      | 0.25 M        | 100⁰a           | 2 Trace  | Trace      |
| 12    | 0.2              | (CF₃)₂CHOH/DCM  | 0.25 M        | 100⁰a           | 2 Trace  | Trace      |
|       |                  | (1:9)           |               |                 |          |            |
| 13    | 0.2              | (CF₃)₂CHOH      | 0.125 M       | 100⁰a           | 2        | 71         |
| 14    | 0.2              | (CF₃)₂CHOH      | 0.125 M       | 100⁰a           | 2        | 0b         |
|       |                  |                 |               |                 |          |            |
| 15    | 0.2              | (CF₃)₂CHOH      | 0.125 M       | 50              | 2        | 75         |
| 16    | 0.2              | (CF₃)₂CHOH      | 0.1 M         | 50              | 2        | 77         |
| 17    | 0.2              | (CF₃)₂CHOH      | 0.1 M         | RT              | 17       | 28         |
| 18    | 0.1              | (CF₃)₂CHOH      | 0.1 M         | 50              | 20       | 16         |
| 19    | 0.2              | (CF₃)₂CHOH      | 0.05 M        | 50              | 2        | 84         |
| 20    | 0.2              | (CF₃)₂CHOH      | 0.05 M        | 50c             | 2        | 83         |
| 21    | 0.2              | (CF₃)₂CHOH₆     | 0.05 M        | 50              | 2        | 27b        |
| 22    | 0.2              | (CF₃)₂CHOH      | 0.05 M        | 50              | 12       | 0b         |
|       |                  |                 |               |                 |          |            |
| 23    | ---              | (CF₃)₂CHOH      | 0.05 M        | 50              | 2 Trace  | Trace      |
| 24    | 0.2              | Solkane-365     | 0.05 M        | 50              | 2 Trace  | Trace      |
| 25    | 0.2              | iPrOH           | 0.05 M        | 50              | 2 Trace  | Trace      |
| 26    | 0.2              | 1,4-dioxane     | 0.05 M        | 50              | 2 Trace  | Trace      |
| 27    | 0.2              | CF₃CH₂OH        | 0.05 M        | 50              | 2 Trace  | Trace      |
| 28    | 0.2              | (CF₃)₂PhOH      | 0.05 M        | 100             | 2 Trace  | Trace      |
Sealed tube. The hydrolysis product 1,5-diphenylpentan-3-one was obtained in quantitative yield. The reaction was conducted under microwave conditions. (CF₃)₂CHOH was used as purchased, without any precaution to exclude moisture. 1,5-diphenylpentan-3-one was observed as major product.

**Table S2.** Optimization of conditions for the synthesis of monofluoroalkenes, related to Table 1.

| Entry | B(C₆F₅)₃ (equiv) | Solvent | Concentration | Temperature (°C) | Time (h) | Yield (a) (%) | Z/E (b) |
|-------|-----------------|---------|---------------|------------------|----------|---------------|---------|
| 1     | 0.2             | o-C₆H₄Cl₂ | 0.1 M         | 100              | 3        | 45            | 5.9:1   |
| 2     | 0.2             | o-C₆H₄Cl₂ | 0.1 M         | 160              | 3        | 70            | 6.9:1   |
| 3     | 0.1             | o-C₆H₄Cl₂ | 0.1 M         | 160              | 3        | 30            | 6.3:1   |
| 4     | 0.2             | o-C₆H₄Cl₂ | 0.1 M         | 160              | 6        | 64            | 6.2:1   |
| 5     | ---             | o-C₆H₄Cl₂ | 0.1 M         | 160              | 3        | NR            | ---     |
| 6     | 0.2             | o-C₆H₄Cl₂ | 0.25 M        | 180¹           | 3        | 67            | 5.9:1   |
| 7     | 0.2             | o-C₆H₄Cl₂ | 0.25 M        | 160              | 3        | 52            | 6.3:1   |
| 8     | 0.1             | o-C₆H₄Cl₂ | 0.25 M        | 160              | 3        | 43            | 7.5:1   |
| 9     | 0.2             | o-C₆H₄Cl₂ | 0.05 M        | 160              | 3        | 71            | 5.6:1   |
| 10    | 0.2             | o-C₆H₄Cl₂ | 0.1 M         | 220²           | 3        | 81            | 7.3:1   |
| 11    | 0.2             | m-C₆H₄Cl₂ | 0.1 M         | 160              | 3        | 13            | ---     |
| 12    | 0.2             | Nitrobenzene | 0.1 M     | 160              | 3        | 23            | 6.5:1   |
| 13    | 0.2             | DMF      | 0.1 M         | reflux           | 3        | NR            | ---     |
| 14    | 0.2             | DMSO     | 0.1 M         | 160              | 3        | NR            | ---     |
| 15    | 0.2             | o-C₆H₄F₂ | 0.1 M         | reflux           | 3        | 75            | 6.9:1   |
| 16    | 0.2             | o-C₆H₄F₂ | 0.1 M         | reflux           | 24       | 87            | 7.1:1   |

—aDetermined by ¹⁹F NMR analysis using PhCF₃ as the internal standard. —bThe reaction was conducted under microwave conditions. —cSealed tube.
Transparent Methods

General information
All reactions were performed in oven-dried and flame-dried glassware (10 mL) under a positive pressure of argon atmosphere unless mentioned otherwise. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or KMnO$_4$ in ethanol/heat. Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 63-210 μm). The $^1$H-NMR (300 MHz), $^{19}$F-NMR (282 MHz), $^{13}$C-NMR (125 MHz or 75 MHz) spectra for solution in CDCl$_3$ were recorded on a Bruker Avance 500, a Varian Mercury 300 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from internal TMS (δ = 0.00) for $^1$H-NMR. CeF$_6$ [δ = −162.2 (CDCl$_3$)] was used as an internal standard for $^{19}$F-NMR. Mass spectra were recorded on a SHIMAZU LCMS-2010EV (ESI-MS and APCI-MS) and SHIMADZU GCMS-QP5050A (EI-MS) using GC capillary column HYDRODEX-β-TBDAc (length: 25 m, i.d.: 0.25 mm). Helium was used as a carrier gas. Initial temperature: 50 °C, increase temperature at a rate: 40 °C/min until final temperature (230 °C), hold temperature for 15 min at 230 °C. Solvent delay: 3.0 minutes. High resolution mass spectrometry (HRMS) was recorded on a Waters, GCT Premier (EI-MS) with a TOF analyzer. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Melting points were recorded on a BUCHI M-565.

Super dehydrated solvents such as CH$_2$Cl$_2$, 1,4-dioxane and 1,2-dichlorobenzene (water max 0.001%) were purchased from Wako Pure Chemical Industries, Ltd. and used under argon atmosphere. 1,4-difluorobenzene and 1,1,1,3,3,3-hexafluoropropan-2-ol was purchased from Tokyo Chemical Industry Co., Ltd., and were drying and distilled from 4Å molecule sieves under argon atmosphere, and were stored in glove box. Tis(pentafluorophenyl)borane was purchased from Tokyo Chemical Industry Co., Ltd. (>98.0%, stored under Ar), and was used and stored in glove box with argon atmosphere.
Experimental Procedures

The preparation of spirobiindanes 2a-2t, related to Figure 2.

General procedure for the intramolecular Friedel-Craft reaction of gem-difluoroalkanes: In a flame-dried test tube (10 mL), gem-difluoroalkanes 1 (0.1 mmol) were added to a solution of $\text{B(C}_6\text{F}_5)_3$ (20 mol%) in dry HFIP (2.0 mL) at room temperature in a glovebox filled with argon. Subsequently, the tube was sealed with a rubber septum, removed from the glovebox and stirred at 50 °C for 2-4 h under a positive pressure of argon with a balloon. The resulting mixture was allowed to cool to room temperature and washed with water, extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, filtered, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel using $n$-hexane as the eluent to afford the desired spirobiindanes 2a-2t in good yields.

2,2',3,3'-Tetrahydro-1,1'-spirobi[indene] 2a

![Structure of 2a](image)

(3,3-Difluoropentane-1,5-diyl)dibenzene 1a (26.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel ($n$-hexane) to give 2a (18.8 mg, 84%) as a colorless oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.34–7.24 (m, 2H), 7.24–7.08 (m, 4H), 6.99–6.86 (m, 2H), 3.10–2.94 (m, 4H), 2.34–2.23 (m, 2H), 2.25–2.10 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.4, 143.7, 126.65, 126.63, 124.3, 123.4, 60.7, 40.5, 30.8. MS (EI, $m/z$) 220 [M$^+$]

6,6'-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2b

![Structure of 2b](image)

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) 1b (28.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel ($n$-hexane) to give 2a (17.3 mg, 69%) as a white solid, mp = 84–86 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.19 (d, $J$ = 7.6 Hz, 2H), 7.08–6.98 (m, 2H), 6.78 (s, 2H), 2.99 (dd, $J$ = 8.0, 6.0 Hz, 4H), 2.39–2.16 (m, 8H), 2.23–2.08 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.6, 144.7, 136.2, 127.5, 124.1, 124.0, 60.6, 40.8, 30.5, 21.3. IR (KBr): 2929, 2852, 1490, 1459, 1380, 809 cm$^{-1}$. HRMS (El) calcd. for C$_{19}$H$_{20}$ [M$^+$]: 248.1565 found
4,4'-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) 1c (32.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2c (9.7 mg, 27%) as a white solid, mp = 129–131 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.17 (d, $J$ = 8.2 Hz, 2H), 6.75 (dd, $J$ = 8.2, 2.5 Hz, 2H), 6.49 (d, $J$ = 2.4 Hz, 2H), 3.72 (s, 6H), 2.98–2.83 (m, 4H), 2.34–2.21 (m, 2H), 2.24–1.95 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.0, 151.7, 135.7, 124.8, 112.8, 108.7, 61.2, 55.4, 40.9, 30.1. IR (KBr): 2937, 2832, 1614, 1479, 1364, 1284, 821 cm$^{-1}$. MS (EI, m/z) 280 [M$^+$]. HRMS (EI) calcd. for C$_{19}$H$_{20}$O$_2$ $^+$ [M$^+$]: 280.1463 found 280.1466.

6,6'-Diethyl-2,2',3,3'-tetrahydro-1,1'-spirob[indene] 2d

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(ethylbenzene) 1d (31.5 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2d (17.6 mg, 62%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.23–7.16 (m, 2H), 7.04 (d, $J$ = 7.6 Hz, 2H), 6.79 (s, 2H), 2.98–2.86 (m, 4H), 2.57 (q, $J$ = 7.5 Hz, 4H), 2.31–2.03 (m, 4H), 1.17 (t, $J$ = 7.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.6, 142.8, 141.1, 126.2, 124.0, 122.9, 60.6, 40.7, 30.4, 28.8, 15.9. IR (KBr): 2960, 2933, 2852, 1482, 1463, 1373, 885, 813 cm$^{-1}$. MS (EI, m/z) 276 [M$^+$]. HRMS (EI) calcd. for C$_{21}$H$_{24}$O$_2$ $^+$ [M$^+$]: 276.1878 found 276.1884.

6,6'-Dibutyl-2,2',3,3'-tetrahydro-1,1'-spirob[indene] 2e

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(butylbenzene) 1e (37.2 mg, 0.1 mmol) was added to a solution of
tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2e (19.7 mg, 59%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.19 (d, $J$ = 7.6 Hz, 2H), 7.05–6.96 (m, 2H), 6.77 (s, 2H), 2.99–2.86 (m, 4H), 2.54–2.46 (m, 4H), 2.37–2.24 (m, 2H), 2.21–2.12 (m, 2H), 1.53–1.44 (m, 4H), 1.30 (dq, $J$ = 14.5, 7.2 Hz, 4H), 0.88 (t, $J$ = 7.3 Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.6, 141.5, 141.1, 126.8, 123.9, 123.5, 60.6, 40.8, 35.6, 34.0, 30.5, 22.5, 13.9. IR (KBr): 2948, 2925, 2860, 1606, 1488, 1454, 1378, 829, 732 cm$^{-1}$. MS (EI, m/z) 332 [M$^+$]. HRMS (EI) calcd. for C$_{25}$H$_{32}$+ [M$^+$]: 332.2504 found 332.2519.

4,4’-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2f

2,2’-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) 1f (28.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2f (22.8 mg, 90%) as a white solid, mp = 89–90 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.11–6.99 (m, 4H), 6.76 (d, $J$ = 7.2 Hz, 2H), 2.95–2.89 (m, 4H), 2.34–2.25 (m, 8H), 2.22–2.04 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.3, 142.5, 133.5, 127.4, 126.8, 120.7, 61.1, 40.3, 29.3, 19.1. IR (KBr): 2937, 2848, 1590, 1494, 1376, 782, 765 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{20}$+ [M$^+$]: 248.1565 found 248.1567.

4,4’-Dimethoxy-2,2’,3,3’-tetrahydro-1,1’-spirobi[indene] 2g

2,2’-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) 1g (32.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2g (10.5 mg, 37%) as a white solid, mp = 107-109 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.13 (t, $J$ = 7.8 Hz, 2H), 6.71 (d, $J$ = 8.1 Hz, 2H), 6.57 (d, $J$ = 7.5 Hz, 2H), 3.87 (s, 6H), 2.99–2.81 (m, 4H), 2.30–2.21 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 155.7, 152.3, 142.5, 133.5, 127.4, 126.8, 120.7, 61.1, 108.1, 60.8, 55.2, 40.4, 27.4. IR (KBr): 2952, 2840, 1687, 1463, 1315, 1255, 775 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{20}$O$_2$+ [M$^+$]: 280.1463 found 280.1460.
5,5'-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spiro[indene] 2h

3,3'-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) 1h (28.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2h (19.6 mg, 78%) as a colorless oil. The isolated 2h was obtained with impure isomers (ratio about 9:1, based on integrals of methyl peak in ¹H-NMR, and GC-MS analysis). ¹H NMR (300 MHz, CDCl₃) δ 7.10 (s, 2H), 6.96 (d, J = 7.7 Hz, 2H), 6.82 (d, J = 7.7 Hz, 2H), 2.99–2.87 (m, 4H), 2.33–2.23 (m, 8H), 2.22–2.16 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 147.6, 143.9, 136.2, 127.4, 125.0, 123.0, 59.9, 40.7, 30.7, 21.2. IR (KBr): 3004, 2940, 2948, 1610, 1490, 1448, 1376, 809, 771 cm⁻¹. MS (EI, m/z) 248 [M⁺]. HRMS (EI) calcd. for C₁₉H₂₀F₂⁺ [M⁺]: 248.1565 found 248.1577.

4,4'-Difluoro-2,2',3,3'-tetrahydro-1,1'-spiro[indene] 2i

2,2'-(3,3-Difluoropentane-1,5-diyl)bis(fluorobenzene) 1i (29.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2i (14.9 mg, 57%) as a white solid, mp = 96–97 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.15–7.08 (m, 2H), 6.96–6.86 (m, 2H), 6.70 (d, J = 7.5 Hz, 2H), 3.13–2.97 (m, 4H), 2.35 (ddd, J = 11.6, 7.5, 2.0 Hz, 2H), 2.26–2.16 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.19 (d, J = 246.6 Hz), 153.50 (d, J = 5.6 Hz), 129.55 (d, J = 18.3 Hz), 128.75 (d, J = 6.9 Hz), 118.96 (d, J = 3.3 Hz), 113.43 (d, J = 20.6 Hz), 61.6, 40.5, 26.70. IR (KBr): 2944, 1614, 1585, 1455, 1241 cm⁻¹. HRMS (EI) calcd. for C₁₇H₁₄F₂⁺ [M⁺]: 256.1064 found 256.1057.
4,4'-Dibromo-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2j

2,2'-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) 1j (41.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2j (30.1 mg, 79%) as a white solid, mp = 100-102 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.37–7.31 (m, 2H), 7.03 (t, J = 7.7 Hz, 2H), 6.85 (d, J = 7.5 Hz, 2H), 3.07–2.99 (m, 4H), 2.33–2.25 (m, 2H), 2.24–2.14 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 151.9, 143.9, 130.1, 128.7, 122.2, 119.9, 63.2, 39.8, 32.3. IR (KBr): 2940, 1565, 1442, 1307, 775, 678 cm⁻¹. MS (El, m/z) 375 [M⁺]. HRMS (EI) calcd. for C₁₇H₁₄Br₂⁺ [M⁺]: 375.9462 found 375.9452.

4,4'-Dichloro-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2k

2,2'-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) 1k (32.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2k (23.3 mg, 77%) as a white solid, mp = 116-118 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.19 (d, J = 7.9 Hz, 2H), 7.09 (t, J = 7.6 Hz, 2H), 6.80 (d, J = 7.4 Hz, 2H), 3.15–2.96 (m, 4H), 2.34 (ddd, J = 11.7, 7.3, 4.2 Hz, 2H), 2.26–2.17 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 151.9, 141.7, 130.6, 128.4, 126.9, 121.6, 62.6, 39.9, 30.1. IR (KBr): 2937, 2844, 1590, 1459, 1415, 1099, 817, 725 cm⁻¹. HRMS (El) calcd. for C₁₇H₁₄Cl₂⁺ [M⁺]: 288.0473 found 288.0481.

6,6'-Dibromo-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2l

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) 1l (41.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture...
was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2l (24.4 mg, 64%) as a white solid, mp = 142–144 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.32 (dd, $J = 8.0$, 1.8 Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 1.5$ Hz, 2H), 2.96 (dd, $J = 8.2$, 6.0 Hz, 4H), 2.32–2.23 (m, 2H), 2.24–2.16 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 152.0, 142.5, 129.9, 126.4, 126.0, 120.4, 60.8, 40.6, 30.3. IR (KBr): 2944, 2840, 1583, 1479, 1396, 1064, 809, 638 cm$^{-1}$. HRMS (EI) calcd. for Chemical Formula: C$_{17}$H$_{14}$Br$_2$ $^{[M^+]}$: 375.9462 found 375.9454.

6,6'-Dichloro-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2m

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) 1m (32.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2m (18.9 mg, 65%) as a white solid, mp = 116–118 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.25–7.14 (m, 4H), 6.87 (d, $J = 1.3$ Hz, 2H), 2.97 (dd, $J = 8.4$, 5.9 Hz, 4H), 2.35–2.14 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 151.6, 141.9, 132.4, 127.1, 125.5, 123.5, 60.8, 40.6, 30.2. IR (KBr): 2937, 2844, 1590, 1415, 1459, 1099, 877, 725 cm$^{-1}$. MS (EI, $m/z$) 288 [M$^+$]. HRMS (EI) calcd. for Chemical Formula: C$_{17}$H$_{14}$Cl$_2$ $^{[M^+]}$: 288.0473 found 288.0476.

4,4',6,6'-Tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2n

4,4'-(3,3-Difluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) 1n (31.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2n (26.5 mg, 95%) as a white solid, mp = 149–150 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 6.84 (s, 2H), 6.59 (s, 2H), 2.87 (t, $J = 7.6$ Hz, 4H), 2.28 (s, 6H), 2.25–1.94 (m, 10H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.6, 139.5, 136.4, 133.2, 128.4, 121.3, 120.9, 60.9, 40.6, 28.9, 21.2, 19.0. IR (KBr): 2917, 2848, 1594, 1459, 1099, 877, 725 cm$^{-1}$. MS (EI, $m/z$) 276 [M$^+$]. HRMS (EI) calcd. for C$_{21}$H$_{24}$ $^{[M^+]}$: 276.1878 found 276.1886.
4,4',5,5'-Tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2o

3,3'-(3,3-Difluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) 1o (31.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2o (23.7 mg, 85%) as a white solid, mp = 140–141 °C. ¹H NMR (300 MHz, CDCl₃) δ 6.95 (d, J = 7.6 Hz, 2H), 6.69 (d, J = 7.6 Hz, 2H), 2.93 (dd, J = 11.6, 6.0 Hz, 4H), 2.25–2.24 (m, 8H), 2.22 (s, 6H), 2.19–2.10 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 148.1, 142.7, 134.6, 132.1, 128.4, 120.4, 61.1, 40.6, 29.7, 19.6, 15.9. IR (KBr): 2996, 2933, 2857, 1605, 1475, 1452, 1373 cm⁻¹. HRMS (EI) calcd. for C₂₁H₂₄⁺ [M⁺]: 276.1878 found 276.1879.

2,2',3,3'-Tetrahydro-1,1'-spiro[cyclopenta[b]naphthalene] 2p

2,2'-(3,3-Difluoropentane-1,5-diyl)dinaphthalene 1p (36.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2l (28.6 mg, 84%) as a white solid. M.p 49-51 °C ¹H NMR (300 MHz, CDCl₃) δ 7.82–7.75 (m, 4H), 7.65 (d, J = 7.8 Hz, 2H), 7.38–7.25 (m, 6H), 3.24–3.14 (m, 4H), 2.47–2.33 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 149.8, 143.0, 133.2, 133.1, 127.8, 127.4, 125.1, 124.9, 122.3, 121.6, 59.9, 41.3, 30.5. IR (KBr): 2996, 2848, 1598, 1448, 1259 cm⁻¹. MS (El, m/z) 320 [M⁺] HRMS (El) calcd. for C₂₅H₂₀⁺ [M⁺]: 320.1565 found 320.1568.

4,6-Dimethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2q

1-(3,3-Difluoro-5-phenylpenty)-2,4-dimethylbenzene 1q (28.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture
was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2q (10.8 mg, 42%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.28 (d, $J = 6.6$ Hz, 1H), 7.25–7.14 (m, 2H), 6.95 (d, $J = 6.9$ Hz, 1H), 6.85 (s, 1H), 6.58 (s, 1H), 3.03–2.85 (m, 4H), 2.36–2.24 (m, 5H), 2.23 (s, 3H), 2.20–2.12 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.7, 150.4, 143.8, 139.6, 136.6, 133.3, 128.6, 126.6, 126.5, 124.3, 123.5, 121.3, 60.9, 40.7, 40.4, 39.9, 29.1, 21.2, 19.1. IR (KBr): 2937, 2852, 1610, 1479, 1463, 850, 754, 730 cm$^{-1}$. MS (EI, m/z) 248 [M$^+$]. HRMS (EI) calcd. for C$_{19}$H$_{20}$+ [M$^+$]: 248.1565 found 248.1567.

4-Bromo-4'-methyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] 2r

1-Bromo-2-(3,3-difluoro-5-(o-tolyl)pentyl)benzene 1r (35.3 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2r (24.3 mg, 69%) as a white solid, mp = 83–85 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.34 (d, $J = 7.8$ Hz, 1H), 7.10–7.03 (m, 3H), 6.85 (d, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 7.1$ Hz, 1H), 3.06–2.98 (m, 2H), 2.98–2.90 (m, 2H), 2.32–2.21 (m, 5H), 2.26–2.16 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 152.7, 149.6, 143.9, 142.3, 133.7, 129.6, 128.5, 127.7, 122.3, 120.6, 119.8, 62.2, 40.3, 39.5, 32.2, 29.3, 19.1. IR (KBr): 3075, 2932, 2848, 1598, 1486, 1438, 750, 615 cm$^{-1}$. HRMS (EI) calcd. for C$_{18}$H$_{17}$Br+ [M$^+$]: 312.0514 found 312.0517.

3,3',4,4'-Tetrahydro-2H,2'H-1,1'-spirobi[naphthalene] 2s

(4,4-Difluoroheptane-1,7-diyl) dibenzene 1s (28.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2s (22.7 mg, 90%) as a white solid, mp = 56–58 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.12–6.99 (m, 6H), 6.77 (d, $J = 7.5$ Hz, 2H), 2.96–2.87 (m, 4H), 2.16–2.10 (m, 2H), 1.94–1.83 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 146.7, 137.1, 130.2, 128.5, 125.7, 125.2, 42.9, 38.8, 30.3, 19.5. IR (KBr): 2952, 2852, 1579, 1479, 1448 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{20}$+ [M$^+$]: 248.1565 found 248.1571.
2,3,3',4'-Tetrahydro-2'H-spiro[indene-1,1'-naphthalene] 2t

(3,3-Difluorohexane-1,6-diyl)dibenzene 1t (27.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2t (21.7 mg, 88%) as a colorless oil. 

1H NMR (300 MHz, CDCl₃) δ 7.26 (t, J = 6.9 Hz, 2H), 7.08–6.99 (m, 4H), 6.84 (dd, J = 14.5, 7.3 Hz, 2H), 2.94–2.84 (m, 4H), 2.36–2.25 (m, 2H), 1.95–1.84 (m, 4H).

13C NMR (126 MHz, CDCl₃) δ 152.9, 144.2, 143.6, 137.1, 129.0, 128.6, 126.6, 126.4, 125.8, 125.6, 124.2, 124.2, 52.4, 43.1, 36.2, 30.2, 30.1, 20.6. IR (KBr): 2937, 2840, 1592, 1563, 1450, 1307 cm⁻¹. HRMS (EI) calcd. for C₁₈H₁₈F₂⁺ [M⁺]: 234.1409 found 234.1411.

General procedure for the preparation of monofluoroalkene 3, related to Figure 2.

In a flame-dried test tube, gem-difluoroalkanes 1 (0.1 mmol) were added to a solution of B(C₆F₅)₃ (20 mol%) in dry 1,4-difluorobenzene (1.0 mL) at room temperature in a glovebox filled with argon. Subsequently, the tube was sealed with a rubber septum, removed from the glovebox and heated to reflux for 24-48 h under a positive pressure of argon with a balloon. The resulting mixture was allowed to cool to room temperature and washed with water, extracted with CH₂Cl₂, dried over Na₂SO₄, filtered, and then concentrated in vacuo.

The residue was purified by column chromatography on silica gel using n-hexane as the eluent to give the desired monofluoroalkene 3.

(3-Fluoropent-2-ene-1,5-diyl)dibenzene 3a

(3,3-Difluoropentane-1,5-diyl)dibenzene 1a (26.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 2a (20.3 mg, 84%) as a colorless oil. The ratio for Z/E isomers (7.1:1) was determined by 19F-NMR. (Z)-3a: 1H NMR (300 MHz, CDCl₃) δ 7.28–7.15 (m, 8H), 7.12 (d, J = 6.8 Hz, 2H), 4.68 (dt, J = 36.8, 7.6 Hz, 1H), 3.41 (d, J = 7.5 Hz, 2H), 2.87–2.81 (m, 2H), 2.53 (dt, J = 16.2, 6.1 Hz, 2H); 13C NMR (126 MHz, CDCl₃) δ 159.0 (d, J = 254.5 Hz), 140.7, 140.5 (d, J = 1.7 Hz), 128.4, 128.4, 128.3, 128.2, 126.1, 125.9, 104.6 (d, J = 15.2 Hz), 33.9 (d, J = 27.5 Hz), 32.5 (d, J = 1.0 Hz), 29.8 (d, J = 5.9 Hz); 19F NMR (282 MHz, CDCl₃) δ -110.7 (dt, J = 36.2, 17.5 Hz, 1F). IR (KBr): 3087, 3023, 2933, 2852, 1710, 1610, 1486, 1452, 1068, 943 cm⁻¹. MS (El, m/z) 240 [M⁺]. HRMS (El) calcd. for C₁₇H₁₇F⁺ [M⁺]: 240.1314,
found 240.1325.

4,4′-(3-Fluoropent-2-ene-1,5-diyl)bis(butylbenzene) 3e

4,4′-(3,3-Difluoropentane-1,5-diyl)bis(butylbenzene) 1e (37.2, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3e (24.5 mg, 69%) as a colorless oil. The ratio for Z/E isomers (10.0:1) was determined by 19F-NMR. (Z)-3e: 'H NMR (300 MHz, CDCl3) δ 7.18–6.97 (m, 8H), 4.66 (dt, J = 36.9, 7.5 Hz, 1H), 3.36 (d, J = 7.4 Hz, 2H), 2.80 (t, J = 7.7 Hz, 2H), 2.65–2.54 (m, 6H), 1.58–1.51 (m, 4H), 1.35 (dd, J = 14.6, 7.3 Hz, 4H), 0.92 (t, J = 7.2 Hz, 6H). 13C NMR (126 MHz, CDCl3) δ 159.02 (d, J = 254.2 Hz), 140.6, 140.5, 137.9, 137.74 (d, J = 1.5 Hz), 128.41, 128.40, 128.3, 128.1, 104.77 (d, J = 15.2 Hz), 35.3, 35.2, 34.07 (d, J = 27.4 Hz), 33.75 (d, J = 2.3 Hz), 32.1, 29.4, 29.3, 22.42, 22.40, 14.00, 13.98. 19F NMR (282 MHz, CDCl3) δ -111.3 (dt, J = 36.9, 17.2 Hz, 1F). IR (KBr): 3012, 2956, 2925, 2857, 1511, 1452, 1378, 1112, 798 cm⁻¹. HRMS (EI) calcd. for C25H33F13 [M⁺]: 352.2566, found 352.2569.

2,2′-(3-Fluoropent-2-ene-1,5-diyl)bis(methylbenzene) 3f

2,2′-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) 1f (28.8, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3f (17.3 mg, 60%) as a colorless oil. The ratio for Z/E isomers (9.1:1) was determined by 19F-NMR. (Z)-3f: 'H NMR (300 MHz, CDCl3) δ 7.23–7.06 (m, 8H), 4.64 (dt, J = 36.9, 7.4 Hz, 1H), 3.39 (d, J = 7.4 Hz, 2H), 2.84–2.77 (m, 2H), 2.49–2.38 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 159.12 (d, J = 254.6 Hz), 138.9, 138.70 (d, J = 1.5 Hz), 136.2, 135.9, 130.2, 130.1, 128.8, 128.6, 126.32 (d, J = 4.5 Hz), 126.2, 126.07, 126.05, 103.9 (d, J = 15.2 Hz), 32.9 (d, J = 27.6 Hz), 30.00 (d, J = 14.6 Hz), 27.7 (d, J = 5.8 Hz), 19.3, 19.2; 19F NMR (282 MHz, CDCl3) δ -110.17 (dt, J = 36.2, 17.8 Hz, 1F). IR (KBr): 3056, 2921, 2877, 1710, 1594, 14886, 1255, 1145, 1101, 738 cm⁻¹. MS (EI, m/z) 268 [M⁺]. HRMS (EI) calcd. for C19H21F1 [M⁺]: 268.1627, found 268.1633.
2,2’-(3-Fluoropent-2-ene-1,5-diyl)bis(methoxybenzene) 3g

2,2’-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) 1g (32.0, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3g (15.9 mg, 53%) as a colorless oil. The ratio for Z/E isomers (5.8:1) was determined by $^{19}$F-NMR. (Z)-3g: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.26–7.16 (m, 4H), 6.94–6.72 (m, 4H), 4.69 (dt, $J = 37.4$, 7.5 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.38 (d, $J = 7.4$ Hz, 2H), 2.85–2.79 (m, 2H), 2.51–2.40 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.69 (d, $J = 254.1$ Hz), 157.4, 157.1, 130.0, 129.3, 129.2, 128.9, 127.3, 127.0, 120.39, 120.32, 110.13, 110.03, 103.41 (d, $J = 15.0$ Hz), 55.26, 55.16, 32.22 (d, $J = 27.4$ Hz), 27.44 (d, $J = 1.4$ Hz), 24.01 (d, $J = 6.3$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -110.32 (dt, $J = 37.4$, 17.3 Hz, 1F). IR (KBr): 3019, 2952, 2832, 1702, 1602, 1486, 1459, 1243, 1108, 1025 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{21}$FO$_2$ [M$^+$]: 300.1526, found 300.1532.

4,4’-(3-Fluoropent-2-ene-1,5-diyl)bis(1,3-dimethylbenzene) 3n

4,4’-(3,3-Difluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) 1n (31.6, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3g (15.0 mg, 50%) as a colorless oil. The ratio for Z/E isomers (9.1:1) was determined by $^{19}$F-NMR. (Z)-3n: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.03–6.84 (m, 6H), 4.60 (dt, $J = 37.1$, 7.4 Hz, 1H), 3.34 (d, $J = 7.4$ Hz, 2H), 2.81–2.74 (m, 2H), 2.45–2.34 (m, 2H), 2.28 (s, 6H), 2.26 (s, 3H), 2.24 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.01 (d, $J = 254.1$ Hz), 136.0, 135.9, 135.68, 135.66, 135.64, 135.63, 131.0, 130.9, 128.7, 128.5, 126.6, 126.5, 103.99 (d, $J = 15.2$ Hz), 32.95 (d, $J = 27.5$ Hz), 29.6, 27.25 (d, $J = 5.8$ Hz), 20.90, 20.89, 19.22, 19.13. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -110.37 (dt, $J = 37.0$, 17.7 Hz, 1F). IR (KBr): 3019, 2952, 2832, 1702, 1602, 1486, 1459, 1243, 1108, 1025 cm$^{-1}$. HRMS (EI) calcd. for C$_{21}$H$_{25}$F$^+$ [M$^+$]: 296.1940, found 296.1954.
3,3′-(3-Fluoropent-2-ene-1,5-diyl)bis(1,2-dimethylbenzene) 3o

3,3′-(3,3-Difluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) 1o (31.6, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3o (20.5 mg, 70%) as a colorless oil. The ratio for Z/E isomers (8.7:1) was determined by \(^{19}\)F-NMR. (Z)-3o: \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.02–6.94 (m, 6H), 4.62 (dt, \(J = 37.1, 7.4 \)Hz, 1H), 3.41 (d, \(J = 7.3 \)Hz, 2H), 2.86–2.81 (m, 2H), 2.49–2.39 (m, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 158.8 (d, \(J = 254.3 \)Hz), 138.8, 138.63 (d, \(J = 1.5 \)Hz), 136.9, 136.84, 134.81, 134.4, 127.99, 127.98, 126.9, 126.6, 125.44, 125.43, 104.14 (d, \(J = 15.1 \)Hz), 33.16 (d, \(J = 27.5 \)Hz), 30.8, 28.40 (d, \(J = 5.6 \)Hz), 20.7, 20.6, 14.9. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ -109.43 (dt, \(J = 37.1, 17.7 \)Hz). IR (KBr): 3016, 2917, 1702, 1583, 1452, 1382, 1132, 732, 779 cm\(^{-1}\). MS (El, \(m/z\)) 296 [M]+. HRMS (El) calcd. for C\(_{21}\)H\(_{25}\)F\(_2\)+: 296.1940, found 296.1949.

2,2′-(3-Fluoropent-2-ene-1,5-diyl)bis(bromobenzene) 3j

2,2′-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) 1j (41.5, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3j (15.1 mg, 38%) as a colorless oil. The ratio for Z/E isomers (25:1) was determined by \(^{19}\)F-NMR. (Z)-3j: \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.52 (dd, \(J = 7.8, 4.5 \)Hz, 2H), 7.24–7.02 (m, 6H), 4.69 (dt, \(J = 36.6, 7.5 \)Hz, 1H), 3.49 (d, \(J = 7.5 \)Hz, 2H), 3.06–2.93 (m, 2H), 2.62–2.46 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 159.24 (d, \(J = 255.9 \)Hz), 139.8, 139.78 (d, \(J = 1.8 \)Hz), 132.8, 132.6, 130.7, 130.1, 127.9, 127.7, 127.4, 124.34, 124.29, 103.31 (d, \(J = 14.8 \)Hz), 33.1, 32.21 (d, \(J = 27.4 \)Hz), 30.4 (d, \(J = 5.9 \)Hz); \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ -108.96 (dt, \(J = 36.4, 18.1 \)Hz). IR (KBr): 3015, 2917, 1702, 1583, 1452, 1382, 1132, 732, 779 cm\(^{-1}\). HRMS (El) calcd. for C\(_{17}\)H\(_{15}\)Br\(_2\)F\(_2\)+: [M]+: 395.9525, found 395.9547.
2,2’-(3-Fluoropent-2-ene-1,5-diy)bis(chlorobenzene) 3k

```
\[
\begin{array}{c}
\text{Cl} \\
| \\
\text{F} \\
| \\
\text{Cl}
\end{array}
\]
```

2,2’-(3,3-Difluoropentane-1,5-diy)bis(chlorobenzene) 1k (32.9 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3k (18.1 mg, 55%) as a colorless oil. The ratio for Z/E isomers (8.6:1) was determined by $^{19}$F-NMR. (Z)-3k: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.42–7.26 (m, 2H), 7.23–7.04 (m, 6H), 4.68 (dt, J = 36.5, 7.6 Hz, 1H), 3.49 (d, J = 7.5 Hz, 2H), 2.99–2.85 (m, 2H), 2.52 (dt, J = 17.9, 7.6 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.34 (d, J = 255.8 Hz), 138.16, 138.11, 138.0, 133.87, 133.85, 130.7, 130.0, 129.5, 129.3, 127.7, 127.4, 126.8, 103.18 (d, J = 14.8 Hz), 32.07 (d, J = 27.4 Hz), 30.5, 27.72 (d, J = 6.1 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -109.22 (dt, J = 36.4, 18.1 Hz, 1F). IR (KBr): 3072, 2911, 1706, 1565, 1463, 1438, 1141, 1041, 757 cm$^{-1}$. HRMS (EI) calcd. for C$_{17}$H$_{15}$Cl$_2$F$_2$+[M$^+$]: 308.0535, found 308.0558.

4,4’-(3-Fluoropentane-1,5-diy)bis(fluorobenzene) 3u

```
\[
\begin{array}{c}
\text{F} \\
| \\
\text{Cl} \\
| \\
\text{F}
\end{array}
\]
```

4,4’-(3,3-Difluoropentane-1,5-diy)bis(fluorobenzene) 1u (29.6 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3u (14.9 mg, 52%) as a colorless oil. The ratio for Z/E isomers (11.1:1) was determined by $^{19}$F-NMR. (Z)-3u: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.17–7.07 (m, 2H), 7.02–6.86 (m, 6H), 4.60 (dt, J = 36.6, 7.7 Hz, 1H), 3.33 (d, J = 7.6 Hz, 2H), 2.82 (dd, J = 14.6, 7.3 Hz, 2H), 2.52–2.44 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 161.43 (d, J = 243.8 Hz), 161.32 (d, J = 243.6 Hz), 158.78 (d, J = 254.9 Hz), 136.22, 136.19, 136.07 (d, J = 3.0 Hz), 136.06 (d, J = 2.9 Hz), 129.75 (d, J = 41.2 Hz), 129.69 (d, J = 41.2 Hz), 115.2, 115.1, 115.08, 115.00, 104.95 (d, J = 15.1 Hz), 34.05 (d, J = 27.4 Hz), 31.6, 28.95 (d, J = 6.0 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -110.75 (dt, J = 36.6, 17.7 Hz, 1F), -117.18--117.34 (m, 1F), -117.43--117.68 (m, 1F). IR (KBr): 3045, 2929, 2857, 1710, 1606, 1519, 1430, 1153, 1089, 806 cm$^{-1}$. HRMS (EI) calcd. for C$_{17}$H$_{15}$F$_3$+[M$^+$]: 276.1126, found 276.1139.
(2-Fluoroprop-1-ene-1,3-diyldibenzene 3aa (Nahra et al., 2015)

![Image of 3aa structure]

(2,2-Difluoropropane-1,3-diyldibenzene 1aa (23.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3aa (11.0 mg, 50%) as a colorless oil. The ratio for Z/E isomers (16.6:1) was determined by $^{19}$F-NMR. (Z)-3aa: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.55–7.40 (m, 2H), 7.37–7.17 (m, 8H), 5.52 (d, $J$ = 38.8 Hz, 1H), 3.65 (d, $J$ = 17.0 Hz, 2H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -100.15 (dt, $J$ = 38.7, 17.0 Hz); MS (EI, m/z) 212 [M$^+$]

(Z)-(1-Fluoroprop-1-ene-1,3-diyldibenzene 3bb (Yang et al., 2013)

![Image of 3bb structure]

(1,1-Difluoropropane-1,3-diyldibenzene 1bb (23.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give Z-3bb (8.8 mg, 41%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.54–7.44 (m, 2H), 7.37–7.19 (m, 8H), 5.60 (dt, $J$ = 36.4, 7.7 Hz, 1H), 3.65 (d, $J$ = 7.7 Hz, 2H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -121.09 (d, $J$ = 36.4 Hz, 1F); MS (EI, m/z) 212 [M$^+$]

(Z)-(1-Fluoropent-1-en-1-yl)benzene 3cc (Zhang et al., 2009)

![Image of 3cc structure]

(1,1-Difluoropentyldibenzene 1cc (18.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give Z-3cc (4.2 mg, 25%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.50 (dd, $J$ = 8.2, 1.4 Hz, 2H), 7.47–7.29 (m, 3H), 5.40 (dt, $J$ = 37.6, 7.6 Hz, 1H), 2.27–2.20 (m, 2H), 1.56–1.47 (m, 2H), 0.97 (t, $J$ = 7.4 Hz, 3H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -121.38 (d, $J$ = 37.6 Hz); MS (EI, m/z) 164 [M$^+$]
4-Fluoro-1,2,3,6-tetrahydro-1′-biphenyl 3dd (Vandamme and Paquin, 2017)

(4,4-Difluorocyclohexyl)benzene 3dd (19.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give Z-3dd (15.6 mg, 82%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.38–7.28 (m, 2H), 7.28–7.16 (m, 3H), 5.30–5.23 (m, 1H), 2.84–2.74 (m, 1H), 2.29–2.21 (m, 4H), 2.02–1.89 (m, 2H); ¹⁹F NMR (282 MHz, CDCl₃) δ -103.35–-103.72 (m, 1F); MS (EI, m/z) 176 [M]+

1-Fluoro-4-pentylcyclohex-1-ene 3ee (Vandamme et al., 2017)

1,1-Difluoro-4-pentylcyclohexane 1ee (19.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 24 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give Z-3ee (11.1 mg, 64%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 5.17–5.10 (m, 1H), 2.23–2.09 (m, 3H), 1.84–1.80 (m, 1H), 1.71–1.62 (m, 1H), 1.52–1.46 (m, 1H), 1.40–1.20 (m, 9H), 0.88 (t, J = 6.8 Hz, 3H); ¹⁹F NMR (282 MHz, CDCl₃) δ -103.59–-103.77 (m, 1F); MS (EI, m/z) 170 [M]+

1-Fluoro-2-phenylcyclohept-1-ene 3ff

1,1-Difluoro-2-phenylcycloheptane 1ff (21.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3ff with 1-fluoro-7-phenylcyclohept-1-ene 3ff' in a 3.3:1 ratio, (9.4 mg, 45%) as a colorless oil. 1-fluoro-2-phenylcyclohept-1-ene 3ff: ¹H NMR (300 MHz, CDCl₃) δ 7.42–7.26 (m, 5H), 2.63–2.48 (m, 2H), 2.49–2.36 (m, 2H), 1.86–1.70 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 159.30 (d, J = 258.1 Hz), 139.5, 127.97, 127.91, 126.33, 118.73 (d, J = 11.5 Hz), 31.79 (d, J = 29.6 Hz), 31.54 (d, J = 6.3 Hz),
31.2, 26.97 (d, $J = 1.6$ Hz), 24.67 (d, $J = 3.3$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -94.81 (t, $J = 17.0$ Hz, 1F).

1-fluoro-7-phenylcyclohept-1-ene 3ff: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.25–7.14 (m, 5H), 5.59 (dt, $J = 23.9$, 6.4 Hz, 1H), 3.86–3.75 (m, 1H), 2.20–2.11 (m, 2H), 2.07–1.92 (m, 2H), 1.63–1.43 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 162.30 (d, $J = 246.3$ Hz), 141.05 (d, $J = 1.4$ Hz), 128.4, 127.7, 126.4, 108.24 (d, $J = 23.3$ Hz), 47.96 (d, $J = 28.0$ Hz), 32.28 (d, $J = 9.3$ Hz), 27.1, 24.1, 22.22 (d, $J = 11.4$ Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -94.26 (dd, $J = 23.8$, 13.0 Hz, 1F). IR (KBr): 3016, 2933, 2861, 1681, 1594, 1490, 1442, 1351, 1176, 1022, 750, 698 cm$^{-1}$. HRMS (EI) calcd. for C$_{13}$H$_{15}$F$^+$ [M$^+$]: 190.1158, found 190.1168.

1,1-Difluorocycloclooctadecene 1gg (20.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 48 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 3gg (14.9 mg, 71%) as a colorless oil. The ratio for Z/E isomers (3.3:1) was determined by $^{19}$F-NMR. (Z)-3gg: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.55 (dt, $J = 37.8$, 7.8 Hz, 1H), 2.28–2.19 (m, 1H), 2.19–2.11 (m, 3H), 1.39–1.26 (m, $J = 12.0$ Hz, 16H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.1 (d, $J = 252.5$ Hz), 107.2 (d, $J = 15.9$ Hz), 31.7 (d, $J = 28.4$ Hz), 26.2 (d, $J = 1.7$ Hz), 25.9, 25.7, 25.2, 24.6, 24.65, 24.61, 22.9, 22.87 (d, $J = 4.4$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -112.85 (dt, $J = 37.8$, 21.6 Hz, 1F). (E)-3gg: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.96 (dt, $J = 23.4$, 8.2 Hz, 1H), 2.35–2.30 (m, 2H), 2.02–1.95 (m, 2H), 1.65–1.41 (m, 16H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.0 (d, $J = 244.9$ Hz), 106.7 (d, $J = 21.7$ Hz), 27.1 (d, $J = 2.1$ Hz), 26.9 (d, $J = 22.7$ Hz), 24.6, 24.4, 24.2, 23.9, 23.55, 22.58 (d, $J = 9.4$ Hz), 22.13, 21.93. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -106.15—-106.71 (m, 1F). IR (KBr): 2921, 2857, 1695, 1452, 1068 cm$^{-1}$. HRMS (EI) calcd. for C$_{12}$H$_{21}$F$^+$ [M$^+$]: 184.1627, found 184.1646.

1,1-Difluorocyclopentadecane 1hh (24.6, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (10.1 mg, 20 mol%) in dry 1,4-difluorobenzene (1.0 ml). And the resulting mixture was refluxed for 48 h under argon atmosphere. The $^{19}$F-NMR showed that the Z/E ratio was 3:1. Then the purification by column chromatography on silica gel (n-hexane) to give 3hh (18.8 mg, 80% yield)
as a colorless oil. The ratio for \( Z/E \) isomers (3.0:1) was determined by \( ^{19} \text{F}-\text{NMR}. \) \( \text{(Z)-3hh:} \) \( ^{1} \text{H NMR (300 MHz, CDCl}_3 \) δ 4.45 (dt, \( J = 38.6, 7.3 \text{ Hz, 1H}), 2.26–2.17 (m, 1H), 2.20–1.93 (m, 3H), 1.53–1.45 (m, 3H), 1.44–1.30 (m, 19H); \( ^{13} \text{C NMR (126 MHz, CDCl}_3 \) δ 159.30 (d, \( J = 252.9 \text{ Hz), 105.96 (d, J = 16.2 \text{ Hz}), 31.43 \text{ (d, J = 28.0 \text{ Hz), 28.55 (d, J = 1.4 \text{ Hz), 27.2, 27.1, 27.0, 26.96, 26.90, 26.89, 26.87, 26.8, 25.6, 25.1, 22.7 \text{ (d, J = 4.7 \text{ Hz);} \} ^{19} \text{F NMR (282 MHz, CDCl}_3 \) δ -111.35 (dt, \( J = 38.7, 19.4 \text{ Hz, 1F). IR (KBr): 2925, 2861, \} \text{1706, 1448, 1340 cm}^{-1}. \) \( \text{MS (EI, m/z}^{226} \text{ [M]+. HRMS (EI) calcd. for} \text{ C}_{15} \text{H}_{27} \text{F}^{+} \text{ [M]+:} 226.2097, \) \text{ found 226.2088.}

**General procedure for Friedel-Crafts reaction of secondary monofluoroalkanes 4, related to Figure 3.**

In a flame-dried test tube, monofluoroalkanes \( 4a-4s \) (0.1 mmol) were added to a solution of \( \text{B(C}_6 \text{F}_5)_3 \) (2 mol%) in dry HFIP (2.0 mL) at room temperature in a glovebox filled with argon. Subsequently, the tube was sealed with a rubber septum, removed from the glovebox and stirred at 50 °C for 2-4 h under a positive pressure of argon with a balloon. The resulting mixture was allowed to cool to room temperature and washed with water, extracted with CH\(_2\)Cl\(_2\), dried over Na\(_2\)SO\(_4\), filtered and then concentrated in vacuo. The residue was purified by column chromatography on silica gel using \( n \)-hexane as the eluent to give the desired substituted indane derivatives \( 5a-5s. \)

1-Phenethyl-2,3-dihydro-1\( H \)-indene \( 5a \) (Khalaf and Roberts, 1972)

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

(3-Fluoropentane-1,5-diyl)dibenzene \( 4a \) (24.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry \( \text{CF}_3\text{CHOH (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give \( 5a \) (20.5 mg, 91%) as a colorless oil. \( ^{1} \text{H NMR (300 MHz, CDCl}_3 \) δ 7.40–7.28 (m, 2H), 7.28–7.18 (m, 4H), 7.18–7.07 (m, 3H), 3.15–3.04 (m, 2H), 2.78–2.67 (m, 2H), 1.91–1.80 (m, 1H), 1.74–1.60 (m, 4H). \( ^{13} \text{C NMR (126 MHz, CDCl}_3 \) δ 140.9, 140.5, 137.0, 129.2, 129.1, 128.8, 128.2, 125.9, 125.6, 125.5, 43.3, 39.5, 29.7, 26.4, 19.1. MS -EI: 222.

4-Methyl-1-(2-methylphenethyl)-2,3-dihydro-1\( H \)-indene \( 5b \)

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

2,2’-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) \( 4b \) (27.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry \( \text{CF}_3\text{CHOH (2.0 ml). And the resulting mixtuure was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel
(n-hexane) to give 5a (22.5 mg, 85%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.20–7.09 (m, 4H), 7.11–6.99 (m, 3H), 3.08–3.00 (m, 2H), 2.81–2.69 (m, 2H), 2.60–2.55 (m, 1H), 2.37 (s, 3H), 2.24 (s, 3H), 1.96–1.88 (m, 1H), 1.88–1.74 (m, 1H), 1.72–1.64 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.7, 139.2, 136.5, 136.3, 135.4, 130.3, 130.2, 127.2, 126.7, 126.0, 125.6, 125.1, 40.5, 38.3, 26.8, 25.7, 19.7, 19.6, 18.9. IR(KBr): 3016, 2857, 2933, 1587, 1490, 1455, 1371, 1033, 782, 740 cm$^{-1}$. MS-EI: 250. HRMS (EI) calcd. for C$_{19}$H$_{22}$+ [M]+: 250.1722, found 250.1720.

6-Methyl-1-(4-methylphenethyl)-2,3-dihydro-1H-indene 5c

![Structure of 5c]

4,4′-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) 4c (27 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5c (22.9 mg, 90%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.18–7.03 (m, 5H), 7.03–6.94 (m, 2H), 3.07 (dd, $J$ = 13.2, 4.3 Hz, 1H), 2.99 (dt, $J$ = 14.8, 4.7 Hz, 1H), 2.75–2.62 (m, 2H), 2.55–2.49 (m, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.92–1.77 (m, 1H), 1.73–1.56 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.5, 138.0, 135.3, 134.8, 133.9, 129.4, 129.09, 129.04, 128.95, 126.56, 42.96, 39.59, 29.37, 26.33, 21.11, 21.07, 19.28. IR(KBr): 3012, 2857, 2937, 1614, 1498, 1442, 802 cm$^{-1}$. MS-EI: 250, HRMS (EI) calcd. for C$_{19}$H$_{22}$+ [M]+: 250.1722, found 250.1715.

6-Ethyl-1-(4-ethylphenethyl)-2,3-dihydro-1H-indene 5d

![Structure of 5d]

4,4′-(3-Fluoropentane-1,5-diyl)bis(ethylbenzene) 4d (29.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 3 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5c (26.6 mg, 93%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.22–7.06 (m, 4H), 7.08–6.95 (m, 3H), 3.09–3.00 (m, 2H), 2.72–2.55 (m, 7H), 1.92–1.80 (m, 1H), 1.77–1.58 (m, 3H), 1.29–1.17 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 141.7, 141.3, 140.4, 138.2, 134.2, 129.1, 129.0, 128.3, 127.7, 125.3, 43.0, 39.6, 29.4, 28.5, 28.5, 26.5, 19.2, 15.8, 15.7. IR(KBr): 3012, 2933, 2865, 1614, 1508, 1452, 1052, 835, 809 cm$^{-1}$. EI-MS: 278. HRMS (EI) calcd. for C$_{21}$H$_{26}$+ [M]+: 278.2035, found 278.2036.
6-Butyl-1-(4-butylphenethyl)-2,3-dihydro-1H-indene 5e

4,4’-(3-Fluoropentane-1,5-diyl)bis(butylbenzene) 4e (35.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5e (28.8 mg, 86%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.13–7.10 (m, 4H), 7.04–6.98 (m, 3H), 3.13–2.95 (m, 2H), 2.78–2.49 (m, 7H), 1.93–1.81 (m, 1H), 1.74–1.51 (m, 7H), 1.43–1.27 (m, 4H), 0.98–0.85 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 140.4, 140.3, 140.1, 138.2, 134.2, 129.1, 128.9, 128.8, 128.3, 125.9, 43.1, 39.7, 35.5, 35.3, 35.2, 33.9, 33.8, 29.4, 29.3, 22.5, 22.4, 19.2, 14.1; IR (KBr): 3008, 2937, 2857, 1610, 1508, 1455, 1375, 806, 838 cm⁻¹. MS (EI, m/z) 334 [M⁺]. HRMS (EI) calcd. for C₂₅H₃₄⁺ [M⁺]: 334.2661, found 334.2663.

6-Methoxy-1-(4-methoxyphenethyl)-2,3-dihydro-1H-indene 5f

4,4’-(3-Fluoropentane-1,5-diyl)bis(methoxybenzene) 4f (30.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5f (12.4 mg, 44%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.13 (d, J = 8.5 Hz, 2H), 7.04–7.01 (m, 1H), 6.86 (d, J = 8.5 Hz, 2H), 6.74–6.69 (m, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 3.09–2.95 (m, 2H), 2.73–2.67 (m, 2H), 1.87–1.82 (m, 1H), 1.68–1.59 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 157.8, 157.2, 141.6, 133.0, 130.1, 129.9, 129.1, 113.7, 113.6, 111.9, 55.3, 55.2, 42.4, 39.9, 28.9, 26.5, 19.4. IR (KBr): 3004, 2915, 2840, 1610, 1519, 1508, 1455, 1375, 806, 838 cm⁻¹. MS (EI, m/z) 282 [M⁺]. HRMS (EI) calcd. for C₁₉H₂₂O₂⁺ [M⁺]: 282.1620, found 282.1622.

4-Bromo-1-(2-bromophenethyl)-2,3-dihydro-1H-indene 5g

2,2’-(3-Fluoropentane-1,5-diyl)bis(bromobenzene) 4g (40.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5g (32.9 mg, 80%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.58 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.29–7.18 (m, 2H), 7.09–7.04 (m, 1H), 7.00 (t, J = 7.8 Hz, 1H), 3.32–3.14 (m,
2H), 3.04–2.82 (m, 2H), 2.73–2.57 (m, 1H), 2.06–1.90 (m, 1H), 1.88–1.74 (m, 1H), 1.74–1.55 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.9, 139.7, 136.3, 133.0, 131.9, 130.1, 128.3, 127.9, 127.2, 126.7, 125.7, 124.9, 43.3, 37.7, 30.4, 25.4, 18.7. IR (KBr): 3056, 2933, 2873, 1554, 1434, 1135, 1037, 808, 777, 719 cm$^{-1}$. HRMS (EI) calcd. for C$_{17}$H$_{16}$Br$_2$: [M$^+$]: 377.9619, found 377.9622.

4-Chloro-1-(2-chlorophenethyl)-2,3-dihydro-1H-indene 5h

![Chemical structure](image)

2,2'-((3-Fluorophenyl-1,5-diyl)bis(chlorobenzene) 4h (31.1 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5h (21.8 mg, 75%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.44–7.35 (m, 1H), 7.28–7.12 (m, 5H), 7.07 (t, $J = 7.7$ Hz, 1H), 3.28–3.14 (m, 2H), 2.98–2.79 (m, 2H), 2.70–2.60 (m, 1H), 1.99–1.77 (m, 2H), 1.70–1.58 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.7, 138.1, 134.8, 134.4, 134.3, 131.8, 129.7, 127.9, 127.6, 126.7, 126.5, 126.2, 124.9, 40.9, 37.7, 27.4, 24.5, 18.4; IR (KBr): 3056, 2933, 2873, 1594, 1563, 1444, 1143, 1051, 773, 682 cm$^{-1}$. MS (EI, m/z 290 [M$^+$]). HRMS (EI) calcd. for C$_{17}$H$_{16}$Cl$_2$: 290.0629, found 290.0642.

6-Fluoro-1-(4-fluorophenethyl)-2,3-dihydro-1H-indene 5i

![Chemical structure](image)

4,4'-((3-Fluorophenyl-1,5-diyl)bis(fluorobenzene) 4i (27.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF$_3$)$_2$CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5i (17.6 mg, 68%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.21–7.12 (m, 2H), 7.08–6.94 (m, 3H), 6.87–6.75 (m, 2H), 3.08–2.95 (m, 2H), 2.76–2.65 (m, 2H), 1.93–1.76 (m, 1H), 1.73–1.56 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 161.4 (d, $J = 243.8$ Hz), 160.8 (d, $J = 242.8$ Hz), 142.1 (d, $J = 6.5$ Hz), 136.1 (d, $J = 3.3$ Hz), 132.5 (d, $J = 2.9$ Hz), 130.49 (d, $J = 7.7$ Hz), 130.3, 115.1 (d, $J = 21.1$ Hz), 114.8 (d, $J = 21.1$ Hz), 112.9 (d, $J = 21.1$ Hz), 42.29, 39.7, 29.0, 26.3, 19.3. IR (KBr): 3041, 2925, 2869, 1602, 1511, 1459, 1153, 1128, 813, 730 cm$^{-1}$. MS-EL: 258. HRMS (EI) calcd. for C$_{17}$H$_{16}$F$_2$: [M$^+$]: 258.1220, found 258.1225.
4-Fluoro-1-(2-fluorophenethyl)-2,3-dihydro-1H-indene 5j

2,2′-(3-Fluoropentane-1,5-diyl)bis(fluorobenzene) 4j (27.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5j (17.6 mg, 68%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.21–7.11 (m, 2H), 7.10–6.99 (m, 4H), 6.85 (t, J = 8.6 Hz, 1H), 3.17–3.04 (m, 2H), 2.91–2.75 (m, 2H), 2.65–2.56 (m, 1H), 1.95–1.83 (m, 1H), 1.82–1.74 (m, 1H), 1.63–1.54 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 161.4 (d, J = 244.8 Hz), 160.7 (d, J = 243.3 Hz), 142.8 (d, J = 4.7 Hz), 131.5 (d, J = 5.1 Hz), 127.8 (d, J = 8.1 Hz), 127.5 (d, J = 16.0 Hz), 126.1 (d, J = 8.9 Hz), 124.6, 124.3 (d, J = 3.1 Hz), 123.83 (d, J = 3.5 Hz), 115.3 (d, J = 22.4 Hz), 111.9 (d, J = 22.1 Hz), 38.0, 36.3, 25.8, 22.06 (d, J = 4.3 Hz), 17.8. IR (KBr): 3031, 2933, 2857, 1579, 1498, 1457, 1234, 879, 773, 755 cm⁻¹. HRMS (EI) calcd. for C₁₇H₁₆F₂⁺ [M⁺]: 258.1220, found 258.1225.

1-(2,4-Dimethylphenethyl)-4,6-dimethyl-2,3-dihydro-1H-indene 5k

4,4′-(3-Fluoropentane-1,5-diyl)bis(1,3-dimethylbenzene) 4k (29.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5j (14.1 mg, 50%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.06 (d, J = 7.6 Hz, 1H), 7.01 (s, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.90 (s, 1H), 6.87 (s, 1H), 3.08–2.95 (m, 2H), 7.23–2.65 (m, 2H), 2.57–2.45 (m, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 2.03–1.87 (m, 1H), 1.85–1.71 (m, 1H), 1.70–1.57 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 140.7, 136.3, 136.2, 136.1, 135.5, 134.4, 132.3, 131.1, 130.1, 128.2, 127.1, 126.2, 40.1, 38.3, 26.6, 25.5, 20.96, 20.93, 19.68, 19.63, 18.9. IR (KBr): 3031, 2925, 2861, 1612, 1500, 1452, 1027, 852, 813 cm⁻¹. MS-EI: 278. HRMS (EI) calcd. for C₂₁H₂₆⁺ [M⁺]: 278.2035, found 278.2041.
1-(3,4-Dimethylphenethyl)-4,5-dimethyl-2,3-dihydro-1H-indene 5l

3,3’-(3-Fluoropentane-1,5-diyl)bis(1,2-dimethylbenzene) 4l (29.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5j (25.2 mg, 67%) as a white solid, mp = 97-98 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.08–7.02 (m, 3H), 7.02–6.96 (m, 2H), 3.13 (dd, J = 13.5, 4.2 Hz, 1H), 3.02 (dd, J = 10.3, 4.8 Hz, 1H), 2.80–2.72 (m, 2H), 2.66–2.50 (m, 1H), 2.31 (s, 6H), 2.28 (s, 3H), 2.15 (s, 3H), 2.01–1.89 (m, 1H), 1.86–1.72 (m, 1H), 1.67–1.55 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 139.1, 138.6, 136.9, 135.2, 134.8, 134.7, 133.7, 128.3, 127.7, 127.1, 126.1, 125.0, 41.2, 38.4, 27.5, 25.4, 20.8, 20.5, 19.1, 15.3, 15.1. IR (KBr): 3016, 2937, 2861, 1590, 1471, 1378, 777, 725 cm⁻¹. HRMS (EI) calcd. for C₂₁H₂₆⁺ [M⁺]: 278.2035, found 278.2059.

1-(2-(Naphthalen-2-yl)ethyl)-2,3-dihydro-1H-cyclopenta[b]naphthalene 5m

2,2’-(3-Fluoropentane-1,5-diyl)dinaphthalene 4m (34.2 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5m (25.7 mg, 79%) as a sticky semi-solid. ¹H NMR (300 MHz, CDCl₃) δ 8.31 (d, J = 8.5 Hz, 1H), 7.94–7.80 (m, 4H), 7.77 (s, 1H), 7.70–7.61 (m, 1H), 7.61–7.53 (m, 2H), 7.52–7.40 (m, 3H), 7.28–7.20 (m, 1H), 3.91 (d, J = 11.5 Hz, 1H), 3.41 (d, J = 14.2 Hz, 1H), 3.09–2.87 (m, 3H), 2.24–2.06 (m, 1H), 2.02–1.78 (m, 2H), 1.75–1.58 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 138.7, 135.2, 133.9, 133.5, 132.6, 132.0, 131.6, 128.9, 128.3, 128.0, 127.6, 127.5, 127.4, 127.2, 126.3, 126.0, 125.9, 125.2, 124.6, 122.7, 40.5, 35.0, 30.1, 24.4, 17.3. IR (KBr): 3052, 3012, 2925, 2865, 1673, 1600, 1513, 1450, 1373, 1268, 850, 738 cm⁻¹. HRMS (EI) calcd. for C₂₅H₂₂⁺ [M⁺]: 322.1722, found 322.1718.

1-Benzyl-2,3-dihydro-1H-indene 5n (Adamczyk et al., 1984)

(2-Fluorobutane-1,4-diyl)dibenzene 4n (22.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was
stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5m (20.0 mg, 91%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.36–7.24 (m, 5H), 7.22–7.10 (m, 4H), 3.14–2.81 (m, 5H), 2.19–2.08 (m, 1H), 2.03–1.82 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 146.6, 136.6, 136.2, 129.0, 128.9, 128.4, 126.8, 126.1, 125.7, 125.6, 40.7, 37.7, 30.3, 29.7. MS (EI, m/z) 208 [M]+

1-Butyl-2,3-dihydro-1H-indene 5o (Adamczyk et al., 1984)

(3-Fluorohexyl)benzene 4o (19.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 5 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5o (10.9 mg, 62%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.24–7.05 (m, 4H), 2.87–2.68 (m, 3H), 1.97–1.80 (m, 2H), 1.75–1.61 (m, 3H), 1.58–1.28 (m, 3H), 0.95 (t, J = 7.6 Hz, 3H). MS (EI, m/z) 174 [M]+

1-Isopentyl-2,3-dihydro-1H-indene 5p

(3-Fluoro-6-methylheptyl)benzene 4p (20.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5p (7.5 mg, 39%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.18–7.07 (m, 2H), 7.07–6.95 (m, 2H), 2.91–2.68 (m, 3H), 1.92–1.63 (m, 5H), 1.58–1.37 (m, 2H), 0.97 (d, J = 6.5 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 142.1, 136.9, 129.1, 128.6, 125.4, 125.3, 46.8, 35.1, 29.7, 27.1, 25.4, 23.9, 21.5, 19.3; IR (KBr): 3006, 2937, 2869, 1725, 1573, 1490, 1454, 1365, 748 cm⁻¹. MS (EI, m/z) 188 [M]+. HRMS (EI) calcd. for C₁₄H₂₀ [M]+: 188.1565 found 188.1564.

1-Phenyl-2,3-dihydro-1H-indene 5q (Léonard and Chirik, 2018)

(1-Fluoropropane-1,3-diyl)dibenzene 4q (21.4 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)₂CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5q (5.7 mg, 29%) as a colorless oil. Under the same condition in the absence of tris(pentafluorophenyl)borane, the desired 5q was isolated in 46% yield (9.1 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.16 (m, 8H), 6.96 (d, J = 7.3 Hz, 1H), 4.35 (t, J = 8.3 Hz, 1H), 3.05–2.97 (m, 2H), 2.66–2.56 (m,
1H), 2.15–1.99 (m, 1H); MS (EI, m/z) 194 [M]^+

1-Ethyl-1,2,3,4-tetrahydronaphthalene 5r (Michelet et al., 2014)

(4-Fluorohexyl)benzene 4r (18.0 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)_2CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5q (13.4 mg, 82%) as a colorless oil. ^1H NMR (300 MHz, CDCl₃) δ 7.25–7.04 (m, 4H), 2.81–2.62 (m, 3H), 1.95–1.67 (m, 4H), 1.65–1.49 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); MS (EI, m/z) 160 [M]^+

1-Butyl-1,2,3,4-tetrahydronaphthalene 5s (Adamczyk, et al., 1984)

(4-Fluoroctyl)benzene 4s (20.8 mg, 0.1 mmol) was added to a solution of tris(pentafluorophenyl)borane (1.0 mg, 2 mol%) in dry (CF₃)_2CHOH (2.0 ml). And the resulting mixture was stirred at 50 °C for 2 h under argon atmosphere. The purification by column chromatography on silica gel (n-hexane) to give 5s (16.1 mg, 85%) as a colorless oil. ^1H NMR (300 MHz, CDCl₃) δ 7.20–7.05 (m, 4H), 2.80–2.66 (m, 3H), 1.90–1.78 (m, 2H), 1.73–1.63 (m, 3H), 1.62–1.49 (m, 1H), 1.44–1.25 (m, 4H), 0.93 (t, J = 6.9 Hz, 3H); MS (EI, m/z) 188 [M]^+

Synthesis of unkown gem-difluorides 1b-1u, 1cc, 1ee and 1hh, related to Figure 2.

For the preparation of substrates 1b-1u, to a solution of corresponding ketone (1.0 mmol) in dry 1,2-dichloroethane at room temperature, was slowly added (diethylamino)sulfur trifluoride (DAST, 2.5 mmol). The resulting mixture was stirred at 60 ºC, monitored by TLC and upon the completion of the reaction at the same temperature. After cooling to room temperature, the mixture was diluted with CH₂Cl₂, and then washed with water and brine. After drying over Na₂SO₄, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane/ CH₂Cl₂) to afford desired 1b-1u in 28% to 57% yields, as shown in the following.

4,4’-(3,3-Difluoropentane-1,5-diyl)bis(methylbenzene) 1b

White solid, mp = 64–65 ºC, 33% yield. ^1H NMR (300 MHz, CDCl₃) δ 7.20–6.84 (m, 8H), 2.84–2.68 (m, 4H),
2.32 (s, 6H), 2.23–2.04 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.5, 135.7, 129.2, 128.2, 124.2 (t, $J = 241.3$ Hz), 38.6 (t, $J = 25.2$ Hz), 28.1 (t, $J = 5.0$ Hz), 21.1. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -99.18 (quintet, $J = 16.4$ Hz, 2F). IR (KBr): 3016, 2937, 2877, 1523, 1434, 1378, 1184, 1052, 908, 815, 742 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{22}$F$_2$+ [M+] 288.1690, found 288.1688.

4,4’-(3,3-Difluoropentane-1,5-diyl)bis(methoxybenzene) 1c

White solid, mp = 54–55 °C, 28% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.10 (d, $J = 8.5$ Hz, 4H), 6.84 (d, $J = 8.6$ Hz, 4H), 3.79 (s, 6H), 2.82–2.72 (m, 4H), 2.17–1.98 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 157.9, 132.6, 129.1, 124.2 (t, $J = 241.3$ Hz), 113.9, 55.2, 38.6 (t, $J = 25.2$ Hz), 27.6 (t, $J = 5.0$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -99.16 (quintet, $J = 16.5$ Hz, 2F). IR (KBr): 3008, 2937, 2877, 1523, 1434, 1378, 1184, 1052, 908, 815, 742 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{22}$F$_2$O$_2$+ [M+] 320.1588, found 320.1587.

4,4’-(3,3-Difluoropentane-1,5-diyl)bis(ethylbenzene) 1d

White solid, mp = 35–36 °C, 33% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.18–6.97 (m, 8H), 2.80–2.71 (m, 4H), 2.62 (q, $J = 7.6$ Hz, 4H), 2.29–2.12 (m, 4H), 2.62–2.46 (m, 4H), 2.26–2.07 (m, 4H), 1.67–1.53 (m, 4H), 1.35 (dq, $J = 14.5$, 7.3 Hz, 4H), 0.92 (t, $J = 7.3$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.1, 137.8, 128.2, 128.0, 124.2 (t, $J = 241.3$ Hz), 38.5 (t, $J = 25.3$ Hz), 28.4, 28.11 (t, $J = 4.9$ Hz), 15.6. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -99.09 (quintet, $J = 16.4$ Hz, 2F). IR (KBr): 3008, 2937, 2877, 1523, 1434, 1378, 1184, 1052, 908, 815, 742 cm$^{-1}$. HRMS (EI) calcd. for C$_{21}$H$_{26}$F$_2$O$_2$+ [M+] 316.2003, found 316.2000.

4,4’-(3,3-Difluoropentane-1,5-diyl)bis(butylbenzene) 1e

White solid, mp = 30–31 °C, 36% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.25–7.06 (m, 8H), 2.80–2.69 (m, 4H), 2.62–2.46 (m, 4H), 2.26–2.07 (m, 4H), 1.67–1.53 (m, 4H), 1.35 (dq, $J = 14.5$, 7.3 Hz, 4H), 0.92 (t, $J = 7.3$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.8, 137.8, 128.5, 128.1, 124.2 (t, $J = 241.3$ Hz), 38.49 (t, $J = 25.2$ Hz), 35.2, 33.7, 28.11 (t, $J = 4.6$ Hz), 22.3, 13.9. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -99.07 (quintet, $J = 16.4$ Hz, 2F). IR (KBr): 3012, 2956, 2861, 1517, 1455, 1375, 1199, 1153, 1056, 813 cm$^{-1}$. HRMS (EI) calcd. for C$_{25}$H$_{34}$F$_2$O$_2$+ [M+] 372.2629, found 372.2625.
2,2’-(3,3-Difluoropentane-1,5-diyld)bis(methylbenzene) 1f

White solid, mp = 52–53 °C, 32% yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.24–7.09 (m, 8H), 2.87–2.77 (m, 4H), 2.33 (s, 6H), 2.23–2.04 (m, 4H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 138.7, 135.9, 130.3, 128.7, 126.4, 126.2, 124.2 (t, \(J = 241.5\) Hz), 37.2 (t, \(J = 25.3\) Hz), 25.8 (t, \(J = 5.0\) Hz), 19.1. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ -99.98 (quintet, \(J = 16.4\) Hz, 2F). IR (KBr): 3019, 2937, 2869, 1494, 1461, 1380, 1299, 1199, 1157, 1064, 750 cm\(^{-1}\). HRMS (EI) calcd. for C\(_{19}\)H\(_{22}\)F\(_2\) [M\(^+\)] 288.1690, found 288.1692.

2,2’-(3,3-Difluoropentane-1,5-diyld)bis(methoxybenzene) 1g

White solid, mp = 89–90 °C, 45% yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.25–7.13 (m, 4H), 6.88 (dd, \(J = 15.3, 7.8\) Hz, 4H), 3.83 (d, \(J = 0.8\) Hz, 6H), 2.87–2.75 (m, 4H), 2.22–2.11 (m, 4H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 157.4, 129.7, 129.1, 127.4, 125.1 (t, \(J = 241.0\) Hz), 120.4, 110.1, 55.1, 36.2 (t, \(J = 25.2\) Hz), 23.7 (t, \(J = 5.4\) Hz). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ -98.23 (quintet, \(J = 16.4\) Hz, 2F). IR (KBr): 3019, 2960, 2940, 2844, 1598, 1492, 1457, 1448, 1367, 1243, 1151, 1108, 1052, 844 cm\(^{-1}\). HRMS (EI) calcd. for C\(_{19}\)H\(_{22}\)F\(_2\)O\(_2\) [M\(^+\)] 320.1588, found 320.1587.

3,3’-(3,3-Difluoropentane-1,5-diyld)bis(methylbenzene) 1h

White solid, mp = 44–45°C, 30% yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.23–7.12 (m, 2H), 7.09–6.94 (m, 6H), 2.85–2.73 (m, 4H), 2.33 (s, 6H), 2.28–2.07 (m, 4H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 140.5, 138.1, 129.1, 128.4, 126.9, 125.2, 124.21 (t, \(J = 241.3\) Hz), 38.49 (t, \(J = 25.3\) Hz), 28.45 (t, \(J = 5.1\) Hz), 21.3. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ -99.24 (quintet, \(J = 16.3\) Hz, 2F). IR (KBr): 3035, 2956, 2929, 1610, 1448, 1378, 1301, 1203, 1151, 1070, 779 cm\(^{-1}\). HRMS (EI) calcd. for C\(_{19}\)H\(_{22}\)F\(_2\)O\(_2\) [M\(^+\)] 320.1588, found 320.1587.

2,2’-(3,3-Difluoropentane-1,5-diyld)bis(fluorobenzene) 1i

Colorless oil, 55% yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.25–7.14 (m, 4H), 7.12–6.99 (m, 4H), 2.92–2.79 (m, 4H), 2.28–2.12 (m, 4H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 161.1 (d, \(J = 245.1\) Hz), 130.5 (d, \(J = 4.9\) Hz), 128.1 (d, \(J = 8.1\) Hz), 127.4 (d, \(J = 15.6\) Hz), 124.1 (d, \(J = 3.6\) Hz), 124.0 (t, \(J = 241.6\) Hz), 115.3 (d, \(J = 21.9\) Hz), 36.8 (t, \(J = 25.2\) Hz), 22.2 (td, \(J = 5.4, 2.8\) Hz). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ -99.87 (quintet, \(J = 16.4\) Hz,
2F), -117.30—119.91 (m, 2F). IR (KBr): 3052, 2937, 2869, 1589, 1494, 1454, 1228, 1195, 1060, 752 cm⁻¹. HRMS (EI) calcd. for C₁₇H₁₆F₄⁺ [M⁺] 296.1188, found 296.1194.

2,2’-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) 1j

White solid, mp = 58–59 °C, 50% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 4.0 Hz, 4H), 7.09 (dt, J = 8.9, 4.4 Hz, 2H), 3.06–2.92 (m, 4H), 2.27–2.13 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 139.8, 132.9, 130.4, 128.0, 127.7, 124.2, 124.0 (t, J = 241.9 Hz), 36.5 (t, J = 25.3 Hz), 29.2 (t, J = 5.3 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -99.18 (quintet, J = 16.3 Hz, 2F). IR(KBr): 3060, 2933, 1565, 1475, 1438, 1297, 1211, 1155, 1025, 744 cm⁻¹. HRMS (EI) calcd. for C₁₇H₁₆Br₂F₂⁺ [M⁺] 328.0597, found 328.0604.

2,2’-(3,3-Difluoropentane-1,5-diyl)bis(chlorobenzene) 1k

Colorless oil, 56% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.36 (dd, J = 7.3, 1.6 Hz, 2H), 7.34–7.13 (m, 6H), 3.02–2.93 (m, 4H), 2.28–2.08 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 138.1, 133.8, 130.4, 129.6, 127.8, 127.0, 124.1 (t, J = 241.8 Hz), 36.3 (t, J = 25.4 Hz), 26.7 (t, J = 5.3 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -99.35 (quintet, J = 16.3 Hz, 2F). IR(KBr): 3060, 2933, 2869, 1592, 1569, 1477, 1299, 1199, 1126, 1157, 1024, 759 cm⁻¹. HRMS (EI) calcd. for C₁₇H₁₆Cl₂F₂⁺ [M⁺] 415.9587, found 415.9589.

4,4’-(3,3-Difluoropentane-1,5-diyl)bis(bromobenzene) 1l

Yellow Solid, mp = 74–76 °C, 26% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, J = 8.3 Hz, 4H), 7.06 (d, J = 8.3 Hz, 4H), 2.83–2.64 (m, 4H), 2.27–2.03 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 139.4, 131.6, 130.0, 123.7 (t, J = 241.7 Hz), 120.0, 38.3 (t, J = 25.3 Hz), 27.8 (t, J = 5.1 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -99.70 (quintet, J = 16.1 Hz, 2F). IR(KBr): 3025, 2971, 2925, 2867, 1492, 1455, 1402, 1267, 1193, 1068, 1010, 844, 736 cm⁻¹. HRMS (EI) calcd. for C₁₇H₁₆Br₂F₂⁺ [M⁺] 415.9587, found 415.9583.
4,4’-(3,3-Difluoropentane-1,5-diyld)bis(chlorobenzene) \textbf{1m}

Yellow Solid, mp = 54–55 °C, 41% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J$ = 8.4 Hz, 4H), 7.10 (d, $J$ = 8.3 Hz, 4H), 2.86–2.72 (m, 4H), 2.24–1.99 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.9, 132.0, 129.6, 128.6, 123.7 (t, $J$ = 241.7 Hz), 38.38 (t, $J$ = 25.3 Hz), 27.81 (t, $J$ = 5.0 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -99.66 (quintet, $J$ = 16.4 Hz, 2F). IR (KBr): 3027, 2937, 2889, 1490, 1455, 1407, 1384, 1159, 1095, 1014, 815, 757 cm$^{-1}$. HRMS (EI) calcd. for C$_{17}$H$_{16}$Cl$_2$F$_2$ $^+$$[M^+]$ 328.0597, found 328.0606.

4,4’-(3,3-Difluoropentane-1,5-diyld)bis(1,3-dimethylbenzene) \textbf{1n}

White Solid, mp = 66–68 °C, 29% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.08–6.92 (m, 6H), 2.87–2.72 (m, 4H), 2.29 (s, 12H), 2.19–1.98 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 135.9, 135.7, 135.6, 131.1, 128.6, 126.8, 124.3 (t, $J$ = 241.4 Hz), 37.3 (t, $J$ = 25.3 Hz), 25.4 (t, $J$ = 5.0 Hz), 20.8, 19.1. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -99.82 (quintet, $J$ = 16.5 Hz, 2F). IR (KBr): 3002, 2948, 2879, 1614, 1502, 1461, 1376, 1270, 1189, 1047, 840, 761 cm$^{-1}$. HRMS (EI) calcd. for C$_{21}$H$_{26}$F$_2$ $^+$$[M^+]$ 316.2003, found 316.2013.

3,3’-(3,3-Difluoropentane-1,5-diyld)bis(1,2-dimethylbenzene) \textbf{1o}

White Solid, mp = 76–77 °C, 41% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.12–6.98 (m, 6H), 2.87–2.75 (m, 4H), 2.28 (s, 6H), 2.22 (s, 6H), 2.24–2.04 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.6, 137.1, 134.4, 128.1, 126.8, 125.6, 124.29 (t, $J$ = 241.4 Hz), 37.56 (t, $J$ = 25.3 Hz), 26.65 (t, $J$ = 4.9 Hz), 20.7, 14.9. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -99.97 (quintet, $J$ = 16.5 Hz, 2F). IR (KBr): 3001, 2948, 2892, 1585, 1467, 1440, 1386, 1186, 1031, 823, 773 cm$^{-1}$. HRMS (EI) calcd. for C$_{21}$H$_{26}$F$_2$ $^+$$[M^+]$ 316.2003, found 316.1998.

2,2’-(3,3-Difluoropentane-1,5-diyld)dinaphthalene

White Solid, mp = 110–112 °C, 48% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.82–7.70 (m, 6H), 7.60 (s, 2H), 7.52–7.39 (m, 4H), 7.32 (dd, $J$ = 8.4, 1.5 Hz, 2H), 3.09–2.97 (m, 4H), 2.50–2.21 (m, 4H). $^{13}$C NMR (126
MHz, CDCl$_3$ δ 138.0, 133.5, 132.0, 128.1, 127.6, 127.4, 126.9, 126.0, 125.4, 124.23 (t, $J = 241.5$ Hz), 38.37 (t, $J = 25.3$ Hz), 28.71 (t, $J = 5.0$ Hz). $^{19}$F NMR (282 MHz, cdcl$_3$) δ -98.91 (quintet, $J = 16.2$ Hz, 2F).

IR (KBr): 2937, 1598, 1508, 1458, 1365, 1295, 1155, 1102, 1066, 817 cm$^{-1}$. HRMS (EI) calcd. for C$_{25}$H$_{22}$F$_2$+ [M$^+$] 360.1690, found 360.1696.

1-(3,3-Difluoro-5-phenylpentyl)-2,4-dimethylbenzene 1p

![Chemical Structure]

Colorless oil, 48% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.34–7.26 (m, 2H), 7.25–7.12 (m, 3H), 7.07–6.94 (m, 3H), 2.85–2.64 (m, 4H), 2.29 (s, 6H), 2.22–1.97 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.6, 135.9, 135.7, 135.6, 131.1, 128.6, 128.5, 126.8, 126.2, 124.2 (t, $J = 241.4$ Hz), 38.4 (t, $J = 25.3$ Hz), 37.3 (t, $J = 25.2$ Hz), 28.5 (t, $J = 5.0$ Hz), 25.4 (t, $J = 5.0$ Hz), 20.8, 19.1. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -99.53 (m, 2F).

IR(KBr): 3027, 2944, 2869, 1504, 1450, 1382, 1305, 1199, 1159, 811 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{22}$F$_2$+ [M$^+$] 288.1690, found 288.1697.

1-Bromo-2-(3,3-difluoro-5-(o-tolyl)pentyl)benzene 1r

![Chemical Structure]

Yellow oil, 44% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.54 (d, $J = 7.8$ Hz, 1H), 7.29–7.22 (m, 2H), 7.21–7.07 (m, 5H), 3.04–2.90 (m, 2H), 2.90–2.76 (m, 2H), 2.33 (s, 3H), 2.28–2.00 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 139.8, 138.7, 135.9, 132.9, 130.4, 130.3, 128.6, 128.1, 127.7, 126.4, 126.2, 124.2, 124.1 (t, $J = 241.6$ Hz), 37.0 (t, $J = 25.2$ Hz), 36.6 (t, $J = 25.4$ Hz), 29.3 (t, $J = 5.3$ Hz), 25.8 (t, $J = 5.1$ Hz), 19.1. $^{19}$F NMR (282 MHz, cdcl$_3$) δ -99.51 (quintet, $J = 16.3$ Hz, 2F). HRMS (EI) calcd. for C$_{18}$H$_{19}$BrF$_2$+ [M$^+$] 352.0638, found 352.0639.

(4,4-Difluoroheptane-1,7-diyl)dibenzene 1s

![Chemical Structure]

Yellow oil, 35% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.34–7.23 (m, 4H), 7.23–7.10 (m, 6H), 2.65–2.50 (m, 4H), 1.95–1.63 (m, 8H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.4, 128.3, 128.3, 125.9, 125.1 (t, $J = 240.4$ Hz), 35.7 (t, $J = 25.5$ Hz), 35.3, 23.9 (t, $J = 4.5$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -97.85 (m, 2F).IR(KBr): 3023, 2952, 2857, 1604, 1492, 1454, 1322, 1091, 752 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{22}$F$_2$+ [M$^+$] 288.1690, found 288.1692.
(3,3-Difluorohexane-1,6-diyl)dibenzene \textbf{1t}

\begin{center}
\includegraphics[width=0.2\textwidth]{diagram1t}
\end{center}

Colorless oil, 29% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.37 – 7.24 (m, 4H), 7.24 – 7.08 (m, 6H), 2.85 – 2.72 (m, 2H), 2.71 – 2.58 (m, 2H), 2.25 – 2.00 (m, 2H), 1.98 – 1.70 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.4, 140.6, 128.5, 128.4, 128.3, 128.2, 126.1, 125.9, 124.6 (t, $J = 240.9$ Hz), 38.2 (t, $J = 25.5$ Hz), 35.9 (t, $J = 25.3$ Hz), 35.3, 28.41 (t, $J = 5.0$ Hz), 24.05 (t, $J = 4.5$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -98.67 (quintet, $J = 16.1$ Hz, 2F). IR(KBr): 3027, 2952, 2857, 1606, 1496, 1454, 1321, 1205, 1149, 746 cm$^{-1}$. HRMS (EI) calcd. for C$_{18}$H$_{20}$F$_2$ $[M^+]$ 274.1533, found 274.1539.

4,4’-(3,3-Difluoropentane-1,5-diyl)bis(fluorobenzene) \textbf{1u}

\begin{center}
\includegraphics[width=0.2\textwidth]{diagram1u}
\end{center}

Colorless oil, 57% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.24 – 7.07 (m, 4H), 7.08 – 6.95 (m, 4H), 2.87 – 2.71 (m, 4H), 2.28 – 2.05 (m, 4H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.4 (d, $J = 244.0$ Hz), 136.1 (d, $J = 3.2$ Hz), 129.6 (d, $J = 7.9$ Hz), 123.8 (t, $J = 241.5$ Hz), 115.3 (d, $J = 21.2$ Hz), 38.6 (t, $J = 25.3$ Hz), 27.6 (t, $J = 5.0$ Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -99.66 (qunitet, $J = 16.4$ Hz, 2F), -116.94 – -117.21 (m, 1F). IR(KBr): 2877, 2929, 1608, 1517, 1454, 1311, 1228, 1157, 1054, 829 cm$^{-1}$. HRMS (EI) calcd. for C$_{17}$H$_{16}$F$_4$ $[M^+]$ 296.1188, found 296.1191.

(1,1-Difluoropentyl)benzene \textbf{1cc}

\begin{center}
\includegraphics[width=0.2\textwidth]{diagram1cc}
\end{center}

To a solution of 1-phenylpentan-1-one (1.0 mmol) in CH$_2$Cl$_2$ (1.0 mL) at room temperature, was slowly added 4-tert-butyl-2,6-dimethylphenylsulfur trifluoride (Fluolead, 2.0 mmol) and hydrogen fluoride pyridine (around 70% HF, 0.4 equiv). (Umemoto et al., 2010) The resulting mixture was stirred for 36 hours and was diluted with CH$_2$Cl$_2$, and then washed with saturated Na$_2$CO$_3$ aqueous solution and brine. After drying over Na$_2$SO$_4$, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane) to afford desired \textbf{3cc} in 80% yields, as a colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.45 – 7.30 (m, 5H), 2.25 – 2.03 (m, 2H), 1.48 – 1.31 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 137.5 (t, $J = 26.7$ Hz), 129.4 (d, $J = 1.6$ Hz), 128.3, 124.9 (t, $J = 6.3$ Hz), 123.1 (t, $J = 241.9$ Hz), 38.8 (t, $J = 27.4$ Hz), 24.5 (t, $J = 4.0$ Hz), 22.3, 13.8. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -95.44 (t, $J = 16.2$ Hz). HRMS (EI) calcd. for C$_{11}$H$_{14}$F$_2^+$ $[M^+]$ 184.1064, found 184.1068.
1,1-Difluoro-4-pentylcyclohexane 1ee

![Chemical structure](image)

To a solution of 4-pentylcyclohexan-1-one (1.0 mmol) in dry CH$_2$Cl$_2$ at -40 °C, was slowly added DAST ((diethylamino)sulfur trifluoride, 2.0 mmol). The resulting mixture was slowly warmed to room temperature with 2-3 hours. And the reaction mixture was monitored by TLC and upon the completion of the reaction at the same temperature and was diluted with CH$_2$Cl$_2$, and then washed with water and brine. After drying over Na$_2$SO$_4$, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane/CH$_2$Cl$_2$) to afford desired 3ee in 72% yield, as a colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ 2.19–1.95 (m, 2H), 1.77–1.54 (m, 4H), 1.35–1.10 (m, 11H), 0.88 (t, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 123.9 (dd, $J$ = 241.5, 239.6 Hz), 35.6 (d, $J$ = 3.2 Hz), 33.6 (d, $J$ = 22.2 Hz), 33.4 (d, $J$ = 22.2 Hz), 32.0, 28.9 (d, $J$ = 9.5 Hz), 26.8, 22.6, 14.1. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -91.32 (d, $J$ = 233.2 Hz, 1F), -101.18—102.71 (m, 1F). HRMS (EI) calcd. for C$_{11}$H$_{20}$F $^{[M-F]}$ 171.1544, found 171.1548.

1,1-Difluorocyclopentadecane 1hh

![Chemical structure](image)

To a solution of cyclopentadecanone (1.0 mmol) in CH$_2$Cl$_2$ (1.0 mL) at room temperature, was slowly added 4-tert-butyl-2,6-dimethylphenylsulfur trifluoride (Fluolead, 2.0 mmol) and hydrogen fluoride pyridine (around 70% HF, 0.4 equiv). (Umemoto et al., 2010) The resulting mixture was stirred for 48 hours and was diluted with CH$_2$Cl$_2$, and then washed with saturated Na$_2$CO$_3$ aqueous solution and brine. After drying over Na$_2$SO$_4$, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane) to afford desired 3hh in 66% yields, as a colorless semi-solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.93–1.79 (m, 4H), 1.53–1.37 (m, 12H), 1.37–1.24 (m, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 126.5 (t, $J$ = 239.8 Hz), 34.5 (t, $J$ = 25.5 Hz), 26.9, 26.7, 26.4, 26.3, 26.3, 21.3 (t, $J$ = 5.5 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -90.88 (quintet, $J$ = 15.5 Hz, 2F). IR(KBr): 2929, 2862, 1448, 1085, 1037 cm$^{-1}$. HRMS (EI) calcd. for C$_{15}$H$_{28}$F $^{[M-F]}$ %, 227.2170 found 227.2179.
General procedure for preparation of aliphatic fluoride 4a-4s, related to Figure 3.

To a solution of aliphatic secondary alcohol (1.0 mmol) in dry CH$_2$Cl$_2$ at -78 °C, was slowly added (diethylamino)sulfur trifluoride (DAST, 1.3 mmol). The resulting mixture was slowly warmed to room temperature with 2-3 hours. And the reaction mixture was monitored by TLC and upon the completion of the reaction at the same temperature (around 2-3 hours) and was diluted with CH$_2$Cl$_2$, and then washed with water and brine. After drying over Na$_2$SO$_4$, the solvent was removed under reduced pressure, and the residue was subject to chromatography on silica gel (hexane/CH$_2$Cl$_2$) to afford desired 4a-4s in 41% to 90% yields as shown in the following.

(3-Fluoropentane-1,5-diyl)dibenzene 4a

\[
\begin{align*}
&\text{F} \\
&\text{C-C-C-C-C} \\
&\text{C-C-C-C-C}
\end{align*}
\]

Colorless oil, 82% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.40–7.24 (m, 4H), 7.23–7.02 (m, 6H), 4.61–4.39 (m, 1H, $^2$J$_{H\cdot F}$ = 49.4 Hz), 2.87–2.62 (m, 4H), 2.02–1.76 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.4, 128.4, 125.9, 92.7 (d, $^3$J = 168.2 Hz), 37.0 (d, $^3$J = 20.9 Hz), 31.4 (d, $^3$J = 4.3 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -183.61–184.34 (m, 1F). IR (KBr): 3031, 2940, 2865, 1606, 1490, 1442, 1164, 1037, 754, 698 cm$^{-1}$. HRMS (EI) calcd. for C$_{17}$H$_{19}$F$_{19}$+ [M$^+$]: 242.1471, found 242.1469.

2,2’-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) 4b

\[
\begin{align*}
&\text{Me} \\
&\text{C-C-C-C-C} \\
&\text{C-C-C-C-C} \\
&\text{Me}
\end{align*}
\]

Colorless oil, 87% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.22–7.01 (m, 8H), 4.62–4.37 (m, 1H, $^2$J$_{H\cdot F}$ = 49.3 Hz), 2.99–2.75 (m, 2H), 2.75–2.55 (m, 2H), 2.31 (s, 6H), 2.06–1.74 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 139.6, 135.8, 130.2, 128.8, 126.1, 126.0, 93.1 (d, $^4$J = 168.5 Hz), 35.7 (d, $^4$J = 21.0 Hz), 31.4 (d, $^4$J = 4.3 Hz), 20.9. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -181.50–185.19 (m, 1F). IR (KBr): 3019, 2937, 2877, 1598, 1486, 1455, 1378, 1168, 1025, 738 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{23}$F$_{19}$+ [M$^+$]: 270.1784 found 270.1783.

4,4’-(3-Fluoropentane-1,5-diyl)bis(methylbenzene) 4c

\[
\begin{align*}
&\text{Me} \\
&\text{C-C-C-C-C} \\
&\text{C-C-C-C-C} \\
&\text{Me}
\end{align*}
\]

Colorless oil, 80% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.18–6.96 (m, 8H), 4.62–4.37 (m, 1H, $^2$J$_{H\cdot F}$ = 49.3 Hz), 2.87–2.70 (m, 2H), 2.69–2.56 (m, 2H), 2.32 (s, 6H), 2.12–1.77 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.3, 135.3, 129.1, 128.3, 92.8 (d, $^3$J = 168.0 Hz), 37.1 (d, $^3$J = 20.9 Hz), 30.9 (d, $^3$J = 4.4 Hz), 20.9. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -177.86–191.48 (m, 1F). IR (KBr): 3008, 2940, 2861, 1515, 1442, 1375, 1041, 892, 806 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{23}$F$_{19}$+ [M$^+$]: 270.1784 found 270.1789.
4,4’-(3-Fluoropentane-1,5-diyl)bis(ethylbenzene) 4d

Colorless oil, 87% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.20–6.98 (m, 8H), 4.68–4.39 (m, 1H, $^2$J$_{HF}$ = 49.3 Hz), 2.92–2.58 (m, 8H), 2.16–1.79 (m, 4H), 2.16–1.79 (m, 4H), 1.23 (t, $^1$J$_{CH}$ = 7.6 Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.8, 138.6, 128.3, 127.9, 92.8 (d, $^2$J$_{CD}$ = 168.0 Hz), 37.1 (d, $^1$J$_{CH}$ = 20.9 Hz), 30.9 (d, $^1$J$_{CH}$ = 4.4 Hz), 28.4, 15.7.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -178.72–187.28 (m, 1F). IR (KBr): 3016, 2498, 2873, 1519, 1438, 1378, 1037, 898, 838 cm$^{-1}$. HRMS (EI) calcd. for C$_{21}$H$_{27}$F$_2$ $^+$/[M$^+$]: 298.2097 found 298.2098.

4,4’-(3-Fluoropentane-1,5-diyl)bis(butylbenzene) 4e

Colorless oil, 78% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.16–6.97 (m, 8H), 4.62–4.39 (m, 1H, $^2$J$_{HF}$ = 49.3 Hz), 2.86–2.71 (m, 2H), 2.69–2.49 (m, 6H), 2.01–1.86 (m, 4H), 1.66–1.53 (m, 4H), 1.43–1.21 (m, 4H), 0.92 (t, $^1$J$_{CH}$ = 7.3 Hz, 6H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.5, 138.5, 128.4, 128.2, 92.8 (d, $^2$J$_{CD}$ = 168.0 Hz), 37.0 (d, $^1$J$_{CH}$ = 20.9 Hz), 35.2, 33.7, 30.9 (d, $^1$J$_{CH}$ = 4.5 Hz), 22.3, 13.9. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -172.31–193.10 (m, 1F). IR (KBr): 3019, 2940, 2857, 1511, 1455, 1375, 1045, 902, 825 cm$^{-1}$. HRMS (EI) calcd. for C$_{25}$H$_{35}$F$_2$ $^+$/[M$^+$]: 354.2723 found 354.2726.

4,4’-(3-Fluoropentane-1,5-diyl)bis(methoxybenzene) 4f

Colorless oil, 70% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.09 (d, $^1$J$_{CH}$ = 8.5 Hz, 2H), 6.83 (d, $^1$J$_{CH}$ = 8.5 Hz, 2H), 4.60–4.35 (m, 1H, $^2$J$_{HF}$ = 49.3 Hz), 3.79 (s, 6H), 2.75–2.61 (m, 4H), 1.99–1.67 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 157.7, 133.4, 129.3, 113.7, 92.6 (d, $^2$J$_{CD}$ = 167.8 Hz), 55.2 (s), 37.2 (d, $^2$J$_{CD}$ = 20.9 Hz), 30.4 (d, $^2$J$_{CD}$ = 4.4 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -172.79–190.80 (m, 1F). IR (KBr): 2940, 2836, 1610, 1587, 1523, 1459, 1303, 1240, 1172, 1033, 829 cm$^{-1}$. HRMS (EI) calcd. for C$_{19}$H$_{23}$FO$_2$ $^+$/[M$^+$]: 302.1682 found 302.1687.

2,2’-(3-Fluoropentane-1,5-diyl)bis(bromobenzene) 4g

White solid, mp = 36–37 °C, 52% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.53 (d, $^1$J$_{CH}$ = 7.9 Hz, 2H), 7.32–7.13
(m, 4H), 7.13–6.97 (m, 2H), 4.68–4.43 (m, 1H, \(^2J_{HF} = 49.3\) Hz), 3.09–2.81 (m, 4H), 2.03–1.75 (m, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 140.6, 132.8, 131.8, 127.7, 127.5, 124.3, 92.6 (d, \(J = 169.1\) Hz), 35.0 (d, \(J = 20.9\) Hz), 31.8 (d, \(J = 4.5\) Hz). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -174.86–190.11 (m, 1F). IR (KBr): 3060, 2944, 2833, 1698, 1562, 1455, 1022, 881, 655 cm\(^{-1}\). HRMS (EI) calcd. for C\(_{17}\)H\(_{17}\)BrF\(_2\)\([M^+]\): 397.9681 found 397.9685.

2,2’-(3-Fluoropentane-1,5-diyl)bis(chlorobenzene) 4h

![Structure of 4h]

Colorless oil, 86% yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.48–7.29 (m, 2H), 7.28–7.02 (m, 6H), 4.63–4.41 (m, 1H, \(^2J_{HF} = 49.3\) Hz), 3.03–2.95 (m, 4H), 2.02–1.74 (m, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 138.9, 133.8, 130.5, 129.5, 127.5, 126.8, 92.7 (d, \(J = 169.0\) Hz), 34.9 (d, \(J = 20.9\) Hz), 29.3 (d, \(J = 4.6\) Hz). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -179.97–189.12 (m, 1F). IR (KBr): 3068, 2933, 2869, 1575, 1448, 1475, 1378, 1134, 1045, 892, 750, 678 cm\(^{-1}\). HRMS (EI) calcd. for C\(_{17}\)H\(_{17}\)Cl\(_2\)F\(_3\)\([M^+]\): 310.0691 found 310.0696.

4,4’-(3-Fluoropentane-1,5-diyl)bis(fluorobenzene) 4i

![Structure of 4i]

Colorless oil, 75% yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.21–7.06 (m, 4H), 7.03–6.87 (m, 4H), 4.58–4.33 (m, 1H, \(^2J_{HF} = 49.1\) Hz), 2.78–2.60 (m, 4H), 2.06–1.75 (m, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 161.31 (d, \(J = 243.6\) Hz), 136.95 (d, \(J = 3.2\) Hz), 129.75 (d, \(J = 7.8\) Hz), 115.19 (d, \(J = 21.1\) Hz), 92.30 (d, \(J = 168.5\) Hz), 37.10 (d, \(J = 21.0\) Hz), 30.57 (d, \(J = 4.4\) Hz) \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -117.85 (s, 2F), -180.69–190.67 (m, 1F). IR (KBr): 3031, 2940, 2861, 1610, 1502, 1438, 1232, 1037, 829 cm\(^{-1}\). HRMS (EI) calcd. for C\(_{17}\)H\(_{17}\)Cl\(_2\)F\(_3\)\([M^+]\): 278.1282 found 278.1288.
4,4’-(3-Fluoropentane-1,5-diyldiyl)bis(1,3-dimethylbenzene) 4k

![Chemical structure](image)

Semi-solid, 65% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.07–6.91 (m, 6H), 4.66–4.41 (m, 1H, $^2$J$_{H\!-\!F}$ = 49.4 Hz), 2.83–2.72 (m, 2H), 2.70–2.56 (m, 2H), 2.29 (s, 6H), 2.27 (s, 6H), 1.99–1.67 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 136.6, 135.7, 135.5, 131.1, 128.8, 126.6, 93.2 (d, $^2$J$_{C\!-\!F}$ = 168.3 Hz), 35.9 (d, $^2$J$_{C\!-\!F}$ = 21.0 Hz), 28.3 (d, $^2$J$_{C\!-\!F}$ = 4.2 Hz), 20.9, 19.1. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -182.74–183.43 (m, 1F). IR (KBr): 3008, 2952, 2819, 1606, 1515, 1448, 1375, 1037, 862, 813 cm$^{-1}$. HRMS (EI) calcd. for C$_{21}$H$_{27}$F$_4$ [M$^+$]: 298.2097, found 298.2094.

3,3’-(3-Fluoropentane-1,5-diyldiyl)bis(1,2-dimethylbenzene) 4l

![Chemical structure](image)

White solid, mp = 36–38 °C, 77% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.06–6.83 (m, 6H), 4.66–4.44 (m, 1H, $^2$J$_{H\!-\!F}$ = 49.1 Hz), 3.01–2.80 (m, 2H), 2.75–2.60 (m, 2H), 2.21 (s, 6H), 1.96–1.64 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.5, 136.9, 134.4, 127.9, 126.9, 125.4, 93.2 (d, $^2$J$_{C\!-\!F}$ = 168.2 Hz), 36.1 (d, $^2$J$_{C\!-\!F}$ = 20.8 Hz), 29.4 (d, $^2$J$_{C\!-\!F}$ = 3.8 Hz), 20.7, 14.9. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -173.12–190.67 (m, 1F). IR (KBr): 3019, 2937, 1594, 1455, 1375, 1172, 1029, 889 cm$^{-1}$. HRMS (EI) calcd. for C$_{21}$H$_{27}$F$_4$ [M$^+$]: 298.2096, found 298.2094.

2,2’-(3-Fluoropentane-1,5-diyldinaphthalene 4m

![Chemical structure](image)

White solid, mp = 90–92 °C, 41% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.89–7.68 (m, 6H), 7.60 (s, 2H), 7.49–7.37 (m, 4H), 7.31 (d, $^2$J$_{H\!-\!F}$ = 8.4 Hz), 4.65–4.47 (m, 1H, $^2$J$_{H\!-\!F}$ = 49.3 Hz), 3.08–2.83 (m, 4H), 2.12–1.87 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 138.8, 133.5, 131.9, 128.0, 127.5, 127.3, 127.1, 126.4, 125.9, 125.2, 92.6 (d, $^2$J$_{C\!-\!F}$ = 168.2 Hz), 36.8 (d, $^2$J$_{C\!-\!F}$ = 21.0 Hz), 31.5 (d, $^2$J$_{C\!-\!F}$ = 4.3 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -182.84–185.18 (m, 1F). IR (KBr): 3062, 2940, 1639, 1587, 1511, 1060, 862, 732 cm$^{-1}$. HRMS (EI) calcd. for C$_{25}$H$_{23}$F$_4$ [M$^+$]: 342.1784, found 342.1786.

(2-Fluorobutane-1,4-diyldibenzene 4n

![Chemical structure](image)
White solid, mp = 30–31 °C, 70% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.34–7.23 (m, 4H), 7.24–7.11 (m, 6H), 4.87–4.60 (m, 1H, ²J₉₋₈ = 48.8 Hz), 3.06–2.80 (m, 3H), 2.76–2.59 (m, 1H), 2.02–1.80 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 129.3, 128.4, 126.5, 125.9, 93.5 (d, J = 171.3 Hz), 41.6 (d, J = 21.4 Hz), 36.4 (d, J = 20.9 Hz), 31.3 (d, J = 4.2 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -180.42—181.31 (m, 1F). IR (KBr): 3031, 2952, 2865, 1598, 1498, 1442, 1072, 838, 738, 694 cm⁻¹. HRMS (El) calcd. for C₁₇H₁₇F⁺ [M⁺]: 228.1314 found 228.1317.

(3-Fluoro-6-methylheptyl)benzene 4p

Colorless oil, 55% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.32–7.03 (m, 5H), 4.58–4.34 (m, 1H, ²J₉₋₈ = 49.3 Hz), 2.87–2.59 (m, 2H), 2.06–1.75 (m, 2H), 1.72–1.44 (m, 3H), 1.42–1.15 (m, 2H), 0.90 (s, 3H), 0.87 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 141.6, 128.43, 128.40, 125.8, 93.8 (d, J = 167.5 Hz), 36.9 (d, J = 21.1 Hz), 34.0 (d, J = 4.3 Hz), 33.0 (d, J = 20.7 Hz), 31.4 (d, J = 4.3 Hz), 27.9, 22.4 (d, J = 6.3 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -177.27—184.97 (m, 1F). IR (KBr): 3023, 2944, 2864, 1590, 1494, 1463, 1382, 1060, 741, 698 cm⁻¹. HRMS (El) calcd. for C₁₅H₂₁F⁺ [M⁺]: 208.1627 found 208.1635

(4-Fluoroheptyl)benzene 4r

Colorless oil, 70% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.24 (m, 2H), 7.23–7.13 (m, 3H), 4.59–4.28 (m, 1H, ²J₉₋₈ = 49.3 Hz), 2.65 (t, J = 7.3 Hz, 2H), 1.89–1.45 (m, 6H), 0.95 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 142.1, 128.3, 128.2, 125.7, 95.5 (d, J = 167.4 Hz), 35.6, 34.2 (d, J = 21.0 Hz), 28.0 (d, J = 21.5 Hz), 26.9 (d, J = 4.1 Hz), 9.4 (d, J = 5.8 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -181.54—182.72 (m, 1F). IR (KBr): 3027, 2933, 2819, 1606, 1494, 1463, 1363, 1097, 944, 709 cm⁻¹. HRMS (El) calcd. for C₁₃H₁₇F⁺ [M⁺]: 180.1314 found 180.1322.

(4-Fluorooctyl)benzene 4s

Colorless oil, 53% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.24 (m, 2H), 7.22–7.15 (m, 3H), 4.58–4.37 (m, 1H, ²J₉₋₈ = 49.3 Hz), 2.64 (t, J = 7.3 Hz, 2H), 1.82–1.45 (m, 6H), 1.44–1.22 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 142.1, 128.3, 128.2, 125.7, 94.3 (d, J = 166.8 Hz), 35.6, 34.8 (d, J = 11.5 Hz), 34.6 (d, J = 11.7 Hz), 27.2 (d, J = 4.4 Hz), 26.9 (d, J = 4.2 Hz), 22.5, 13.9. ¹⁹F NMR (282 MHz, CDCl₃) δ -180.40—181.34 (m, 1F). IR (KBr): 3019, 2937, 2865, 1602, 1494, 1448, 1378, 1022, 764, 690 cm⁻¹. HRMS
(EI) calcd. for C_{14}H_{21}F^+ [M^+] : 208.1627 found 208.1622

**Synthesis of compound 1v-y, 3x and 3y, related to Table 2.**

In Table 2, substrates such as 1,5-diphenylpentan-3-one (1v), (3,3-dimethoxypentane-1,5-diyldibenzene (1w), (3,3-dichloropentane-1,5-diyldibenzene (1x), (3,3-dibromopentane-1,5-diyldibenzene (1y) and elimination product (3-chloropent-2-ene-1,5-diyldibenzene (3x), were known compounds, and were synthesized followed literature report (Blümel et al., 2018; Takeda et al., 1997; Mukaiyama et al., 1973). (3-bromopent-2-ene-1,5-diyldibenzene (3y) was new compound, as yellow oil. The Z/E ratio (10:1) was determined by $^1$H-NMR. HRMS (EI) calcd. for C_{17}H_{17}Br^+ [M^+]: 300.0514, found 300.0518. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.32–7.15 (m, 8H), 7.06 (d, $J = 6.8$ Hz, 2H), 5.72 (t, $J = 7.0$ Hz, 1H), 3.48 (d, $J = 6.9$ Hz, 2H), 2.93–2.83 (m, 2H), 2.83–2.71 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.4, 139.2, 128.6, 128.4, 128.34, 128.31, 128.13, 128.12, 126.1, 126.0, 43.4, 37.5, 34.4. IR (KBr): 3019, 2921, 2844, 1654, 1598, 1490, 1452, 1081, 686 cm$^{-1}$. 
Supplemental References

Nahra, F., Patrick, S.R., Bello, D., Brill, M., Obled, A., Cordes, D.B., Slawin, A.M.Z., O’Hagan, D., and Nolan, S.P. (2015). Hydrofluorination of Alkynes Catalysed by Gold Bifluorides. ChemCatChem 7, 240-244.

Yang, M.-H., Matikonda, S. S., and Altman, R. A. (2013). Preparation of Fluoroalkenes via the Shapiro Reaction: Direct Access to Fluorinated Peptidomimetics. Org. Lett. 15, 3894-3897.

Zhang, W., Huang, W., and Hu, J. (2009). Highly Stereoselective Synthesis of Monofluoroalkenes from α-Fluorosulfoximines and Nitrones. Angew. Chem. Int. Ed. 48, 9858-9861.

Vandamme, M., and Paquin, J.-F. (2017). Eliminative Deoxofluorination Using XtalFluor-E: A One-Step Synthesis of Monofluoroalkenes from Cyclohexanone Derivatives. Org. Lett. 19, 3604-3607.

Khalaf, A. A., and Roberts, R. M. (1972). Friedel-Crafts cycloalkylations of certain mono- and diphenyl-substituted alcohols and alkyl chlorides. J. Org. Chem. 37, 4227.

Adamczyk, M., Watt, D. S., and Netzel, D. A. (1984). Synthesis of biological markers in fossil fuels. 2. Synthesis and carbon-13 NMR studies of substituted indans and tetralins. J. Org. Chem. 49, 4226-4237.

Léonard, N. G., and Chirik, P. J. (2018). Air-Stable α-Diimine Nickel Precatalysts for the Hydrogenation of Hindered, Unactivated Alkenes. ACS Catal. 8, 342-348.

Michelet, B., Bour, C., and Gandon, V. (2014). Gallium-Assisted Transfer Hydrogenation of Alkenes. Chem. Eur. J. 20, 14488-14492.

Umemoto, T., Singh, R. P., Xu, Y., and Saito, N. (2010). Discovery of 4-tert-Butyl-2,6-dimethylphenylsulfur Trifluoride as a Deoxofluorinating Agent with High Thermal Stability as Well as Unusual Resistance to Aqueous Hydrolysis, and Its Diverse Fluorination Capabilities Including Deoxofluoro-Arylsulfinylation with High Stereoselectivity. J. Am. Chem. Soc. 132, 18199-18205.

Blümel, M., Nagasawa, S., Blackford, K., Hare, S.R., Tantillo, D.J., and Sarpong, R. (2018). Rearrangement of Hydroxylated Pinene Derivatives to Fenchone-Type Frameworks: Computational Evidence for Dynamically-Controlled Selectivity. J. Am. Chem. Soc. 140, 9291-9298.

Takeda, T., Sasaki, R., Yamauchi, S., and Fujiwara, T. (1997). Transformation of ketones and aldehydes to gem-dihalides via hydrazones using copper(II) halides. Tetrahedron 53, 557-566.

Mukaiyama, T., Imamoto, T., and Kobayashi, S. (1973). Convenient method for the hydrolysis of vinyl chlorides to ketones. Chem. Lett. 2, 261-264.