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Cyclopropene activation via I(I)/I(III) catalysis: Proof of principle and application in direct tetrafluorination

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ABSTRACT

Preliminary validation of cyclopropene activation by an I(I)/I(III) catalysis manifold is disclosed to enable the direct tetrafluorination of 3,3-diarylcyclopropenes. This transformation occurs through the *in situ* generation of ArI(III)F_2, with inexpensive iodobenzene, amine·HF complexes and Selectfluor® serving as catalyst, fluoride source and oxidant, respectively. Leveraging this approach, it has been possible to generate four C(sp^3)-F bonds in a single operation (up to 44%). A Hammett study revealed that the reaction has a very narrow tolerance window with respect to the *p*-substituent of the aryl groups. Through a process of reaction deconstruction, a mechanism involving two discrete catalytic processes is proposed. Whereas the first cycle results in the ring opening fluorination of the 3,3-diarylcyclopropene, the second proceeds via a fluorination/phenonium ion rearrangement to liberate a tetrafluorinated diarylethane. This study adds hypervalent iodine catalysis to the plenum of strategies that facilitate cyclopropene activation.

1. Introduction

Von Baeyer's 1886 treatise on ring strain is totemic in the evolution of structural analysis [1]. With the advent of hybridization, interrogating, describing and ultimately harnessing ring strain has been extended to penetrate all facets of organic reaction design [2]. Contemporary discussions now extend beyond Baeyer's original cycloalkane series and allow the behavior of small, unsaturated ring systems to be predicted and rationalized *post facto*. Cyclopropenes are ubiquitous in this regard due to the distortion from the idealized C(sp^2)-geometry, which manifests itself in a strain energy of 228 kJ mol^{-1} (Fig. 1, top) [3]. It logically follows that strategies to leverage this valuable C_3-unit in synthesis by direct activation of the strained π-bond have been intensively pursued [4]. A diverse arsenal of methods has evolved that traverses the polar and radical chemistry landscapes, enabling formal addition events and facilitating ring-cleavage (Fig. 1, center) [5].

In contrast to metal-based π-acid catalysis strategies [6], cyclopropene activation via an I(I)/I(III) cycle remains conspicuously underdeveloped [7]. This is surprising given the effectiveness of hypervalent iodine species in functionalizing alkenes and the inexpensive nature of aryl iodide organocatalysts [8]. To explore the competency of I(III) intermediates in activating 3,3-diaryl cyclopropenes (**I**), a formal tetrafluorination sequence to generate diarylethanes was envisaged [9]. Should reactivity parallels exist, then the formation of the *geminal*-difluoride **II** would be convincing evidence.

This electron rich styrene would then be a competent substrate for a second *geminal* difluorination (**III**) to enable formation of four C(sp^3)-F bonds in a single operation. If successful, this strategy would add I(III) species to the rich tapestry of catalytically active species for cyclopropene activation. Furthermore, it would address the obstinate challenge of internal alkenes in I(I)/I(III)-based difluorination chemistry [10–12].

2. Results & discussion

To advance our working hypothesis, 3,3-diaryl cyclopropenes (**I**) were investigated as readily available starting materials (Fig. 1, left). It was envisaged that exposure of **I** to an *in situ* generated $ArIF_2$ species [13,14], would induce an activation/displacement sequence to furnish alkene **II** via two discrete C–F bond forming events: this would broadly emulate π-bond activation observed with certain coinage metal catalysts [15]. Moreover, the intermediary alkene (**II**)

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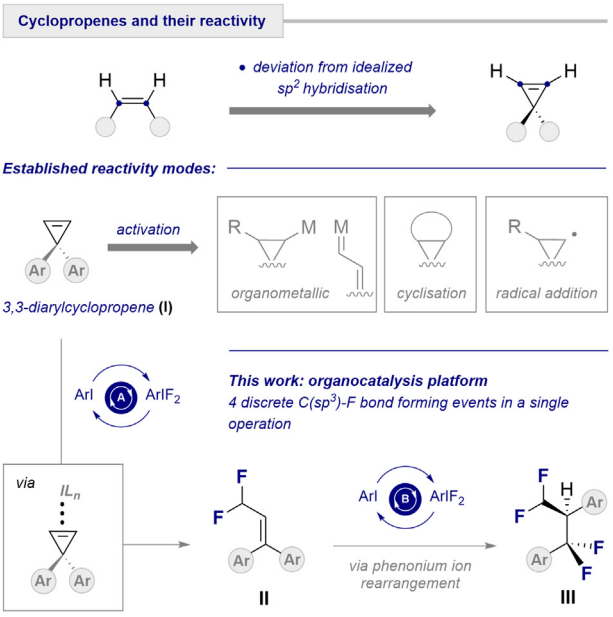


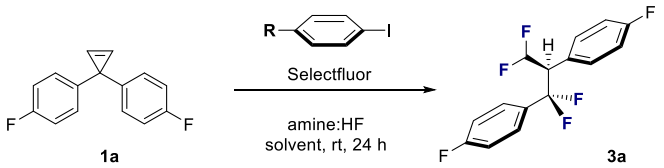
Fig. 1. Cyclopropenes, selected activation modes and a catalysis platform to enable the direct tetrafluorination of 3,3-diaryl cyclopropenes via I(I)/I(III) catalysis.

would be susceptible to a second difluorination process, enabling the net tetrafluorination (**III**) in a single operation where the regioselectivity would be dictated by phenonium ion rearrangement [16].

A process of reaction optimization was conducted using inexpensive aryl iodide organocatalysts (Table 1, **1a** → **3a**). In the presence of a suitable oxidant and fluoride source the requisite ArI(III)F_2 would be generated *in situ*, thereby mitigating the need to prepare stoichiometric quantities of this species. Based on previous success, Selectfluor® was leveraged as an oxidant [17], in combination with various $NEt_3 \cdot 3HF$ and $Pyr \cdot (HF)_x$ mixtures to explore the impact of changes in Brønsted acidity on reaction efficiency [18]. Initially, *p*-TolI was investigated (30 mol%) with Selectfluor® (3 eq.) and using an amine:HF ratio of 1:5 (for full details see the ESI) in $CHCl_3$ at ambient temperature (entry 1). Although this amine:HF ratio was ineffective in the title reaction, steadily increasing the HF component from 1:6 to 1:7 translated into meaningful advances (8% and 30%, entries 2 and 3, respectively). A control reaction in the absence of iodobenzene confirmed that, although degradation of **1a** partially competes, the generation of the tetrafluorinated product **3a** only occurs under the auspices of an I(I)/I(III) catalysis platform (entry 4). This is pertinent given a previous report by Lal that Selectfluor®/HF combinations can enable direct *vicinal* fluorination of electron rich alkenes [19]. Reducing the reaction time to 20 h (entry 5) led to a moderate yield enhancement, but this could not be further improved by increasing the amine:HF ratio to 1:8 (entry 6). A short catalyst screen (entries 7–9) proved to be ineffective, but a further yield enhancement was noted upon changing to iodobenzene in the presence of an amine:HF ratio of 1:8 (entry 10, 44%). A slight reduction in yield was noted when the reaction was performed with Olah's reagent (entry 11). Modifying the reaction media did not have a positive impact on the reaction outcome (entries 12–14), and control reactions in the absence of the HF source and Selectfluor® did not generate product **3a** (entries 15 and 16, respectively). Finally, substituting Selectfluor® for *m*CPBA proved to be detrimental (entry 17).

To expand the reaction beyond the *p*-F derivative **3a**, a small series of modified 3,3-diarylcyclopropenes were generated

Table 1
Identification and optimization of the catalysis conditions.[a]



Entry	Amine:HF ratio	Catalyst	Solvent	Conversion[b]	Yield[b]
1	1:5	*p*-Me	$CHCl_3$	74%	<5%
2	1:6	*p*-Me	$CHCl_3$	>95%	8%
3	1:7	*p*-Me	$CHCl_3$	>95%	30%
4	1:7	-	$CHCl_3$	27%	<5%
5[c]	1:7	*p*-Me	$CHCl_3$	>95%	33%
6	1:8	*p*-Me	$CHCl_3$	>95%	27%
7[c]	1:7	*p*-CO_2Me	$CHCl_3$	44%	<5%
8[c]	1:7	*p*-*t*Bu	$CHCl_3$	93%	12%
9[c]	1:7	*p*-H	$CHCl_3$	90%	11%
10[c]	**1:8**	***p*-H**	**$CHCl_3$**	**>95%**	**44%**
11[c]	1:9.23	*p*-H	$CHCl_3$	>95%	41%
12[c]	1:8	*p*-H	DCM	>95%	33%
13[c]	1:8	*p*-H	HFIP	>95%	10%
14	1:8	*p*-H	toluene	16%	<5%
15	-	*p*-H	$CHCl_3$	24%	<5%
16[d]	1:8	*p*-H	$CHCl_3$	32%	<5%
17[e]	1:8	*p*-H	$CHCl_3$	90%	<5%

[a] Standard reaction conditions: *p*-fluorodiphenylcyclopropene (0.2 mmol), catalyst (30 mol%), Selectfluor® (3.0 eq.), amine:HF source (0.5 mL), solvent (0.5 mL), 24 h, ambient temperature.
[b] Determined by ^{19}F NMR using α,α,α-trifluorotoluene as an internal standard.
[c] Reaction time decreased to 20 h.
[d] Reaction in absence of Selectfluor®.
[e] Reaction using *m*CPBA.

following established literature procedures (see compounds **1a-f**, Fig. 3) [20]. Gratifyingly, compounds **1d**, **1e** and **1f** were isolated as solids and it was possible to unequivocally establish their structure by single crystal X-ray analysis (Fig. 2). Selected structural data for these 3,3-diarylcyclopropenes are summarized in Table 2 [21–23].

In the solid state, similar bond distances and angles are observed for all three compounds. However, the packing diagrams reveal very different intermolecular non-covalent interactions between the constituent molecules. For example, the *p*-Cl derivative **1e** forms a linear chain of alternating crystallographically independent molecules (A and B) along the *a*-axis: this is enabled by C–H ⋯ π interactions between the cyclopropene rings (C2A-H2A ⋯ C3B 2.898 Å; C2B–H2B⋯C3A 2.830 Å). Additional C–H ⋯ π interactions between the aryl rings and cyclopropene rings supported by C–H ⋯ Cl interactions between the chlorine atom and the aromatic units (aryl or cyclopropene) consolidate the formation of this chain and lead to a well-defined 3D network (for more details see the ESI file). It is interesting to note that no classical π ⋯ π interactions between the aromatic rings were observed.

Replacing the chlorine with bromine resulted in a significant change in the packing diagram of compound **1f**. No direct C–H ⋯ π interactions between the cyclopropene rings or classical π ⋯ π interactions between the aryl rings were observed. Instead, a mixture of non-covalent interactions (C–H ⋯ π, π ⋯ π and C–H⋯Br) between the cyclopropene rings and the *p*-bromo-phenyl substituents result in linear chains along the *b*-axis. These chains are further supported by additional Br ⋯ π interactions. Similarly, no interactions between the cyclopropene units are observed in the packing diagram of compound **1d**, where the cyclopropene units are surrounded by four adjacent methoxy groups and additionally stabilized by two C–H ⋯ π contacts.

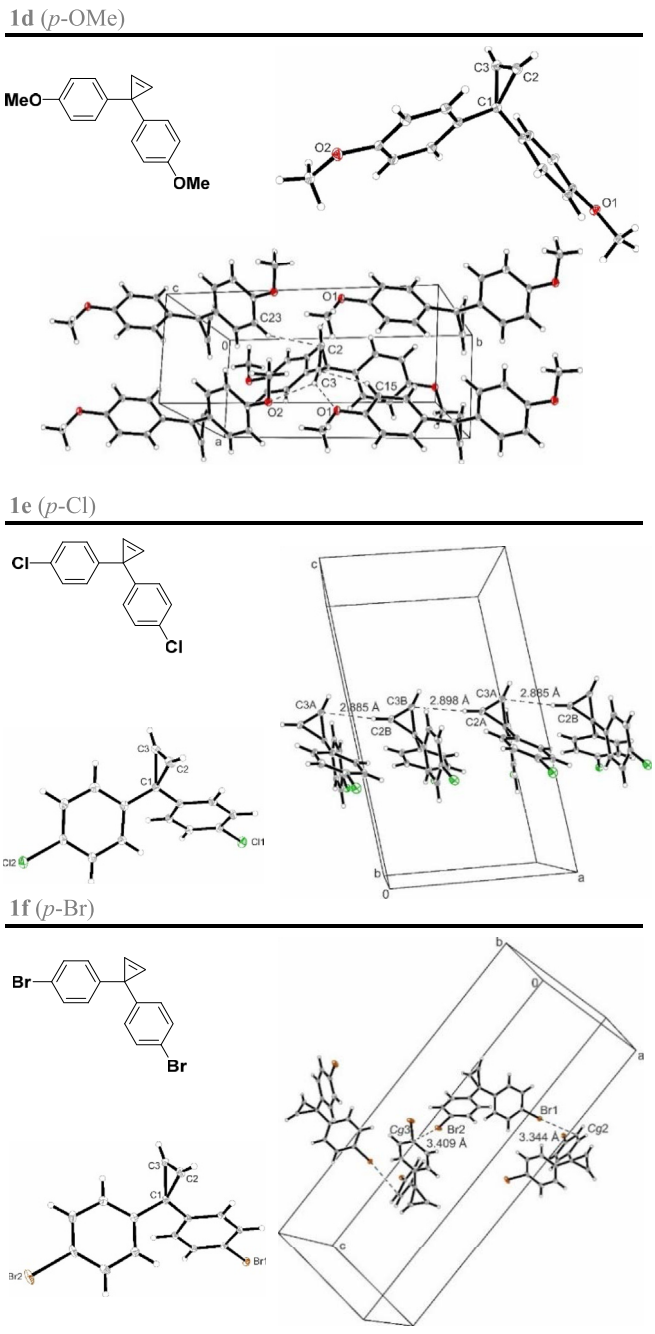


Fig. 2. X-ray structural analyses of 3,3-diarylcyclpropenes. Top **1d** (*p*-OMe) (CCDC 2165452); middle; **1e** (*p*-Cl) (CCDC 2165453) and bottom; **1f** (*p*-Br) (CCDC 2165454). Thermal ellipsoids are shown at 30% probability.

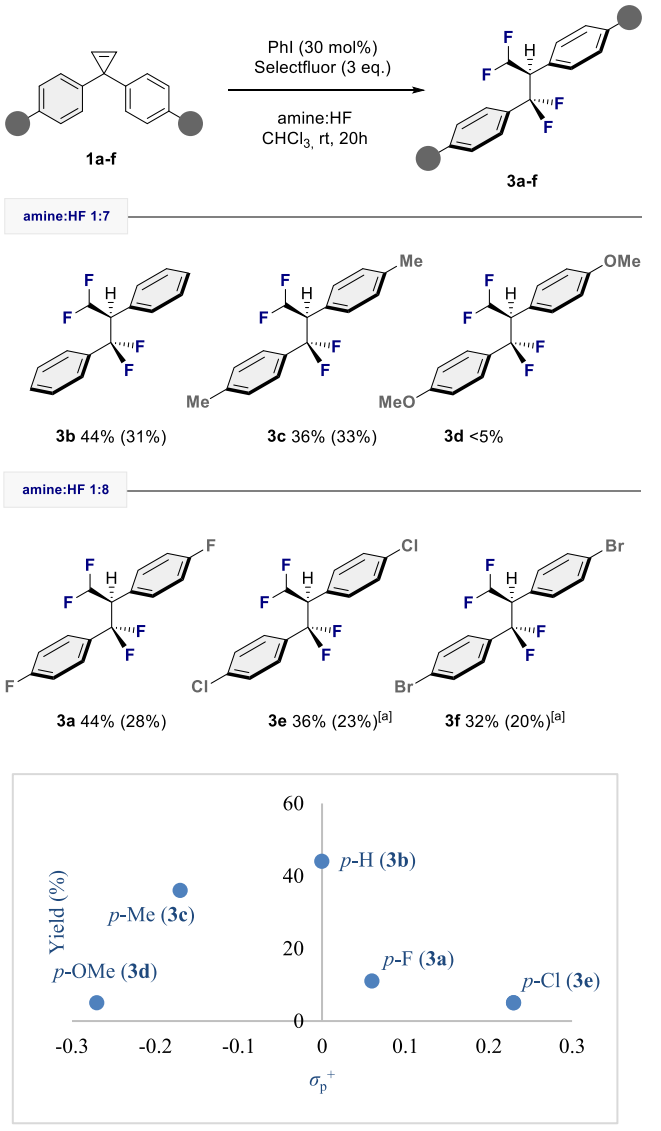


Fig. 3. Top: Tetrafluorination of cyclopropenes **1a-f** to access the tetrafluorides **3a-f**. Yield determined by ^{19}F NMR using α,α,α-trifluorotoluene as an internal standard. Isolated yields in parentheses. [a] Temperature increased to 50 °C. Bottom: A plot of the NMR yields of various substrates exposed to the reaction conditions with an amine:HF ratio of 1:7, versus the σ_p^+ value of the aryl *p*-substituent.

When exploring the reactivity of selected 3,3-diarylcyclopropenes (**1a-f**), two sets of conditions which differ slightly in the amine:HF ratio were identified (Fig. 3). Whereas the *para*-H, -Me and -OMe substrates could be processed to the desired products with an amine:HF ratio of 1:7, the halogen series (*p*-F, -Cl and -Br) required an amine:HF ratio of 1:8. Employing the general catalysis conditions, the unsubstituted diarylethane product **3b** could be smoothly generated in 44% yield (Fig. 3). Installing a *p*-Me substituent did not impact reactivity at all, enabling **3c** to be synthesized in 36% yield. However, electron rich *p*-OMe groups suppressed the reaction completely (**3d**, <5%). This may be a consequence of C(sp^2)-F fluorination of the anisole ring [24], which inhibits reactivity. Regrettably, it was not possible to isolate side products and thus this remains conjecture. To complement the *p*-F species (**3a**), the corresponding *p*-Cl (**3e**) and *p*-Br (**3f**) products

Table 2
Core bond lengths (Å) and angles (°) in the 3,3-diarylcyclopropenes **1d**, **1e** and **1f**.

	1d (*p*-OMe)	1e (*p*-Cl)[a]	1f (*p*-Br)
C1–C2	1.508 (3)	1.515(6)/1.515(6)	1.513 (4)
C1–C3	1.513 (4)	1.517(6)/1.518(6)	1.517 (4)
C2–C3	1.285 (4)	1.278(6)/1.279(6)	1.280 (4)
C1–C11	1.511 (4)	1.518(6)/1.512(5)	1.504 (4)
C1–C21	1.511 (4)	1.506(5)/1.510(5)	1.508 (4)
C2–C1–C3	50.3 (2)	49.9(3)/49.9(3)	49.9 (2)
C1–C2–C3	65.0 (2)	65.1(3)/65.2(3)	65.2 (2)
C1–C3–C2	64.6 (2)	65.0(3)/64.9(3)	64.8 (2)
C11–C1–C21	117.8 (3)	117.4(4)/116.9(4)	116.7 (2)

[a] two independent molecules in the asymmetric unit.

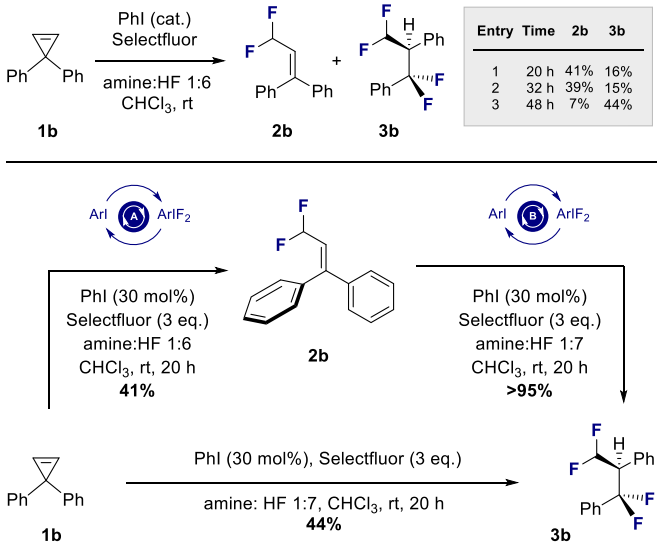
were generated in 36% and 32%. Although the 3,3-diaryl cyclopropane scaffolds **1a-c** were well tolerated under the general catalysis conditions, modifications to the electronic nature of the aryl rings proved challenging. This is immediately apparent from inspection of the Hammett study (NMR yield vs. substituent σ_p^+ value) shown in Fig. 3 (bottom), which reveals a very narrow reactivity window.

Since the working hypothesis hinged on the initial formation of alkene **II** (see Fig. 1), a process of reaction deconstruction was initiated [25]. To that end, the unsubstituted diphenylcyclopropene **1b** was exposed to the reaction conditions, albeit with tempered Brønsted acidity to mitigate activation of the intermediate alkene by an I(III) species (Scheme 1). Employing an amine:HF ratio of 1:6, the desired alkene **2b** was generated in 41% yield after 20 h. Phenonium ion rearrangement could not be completely mitigated with 16% of the tetrafluorinated product **3b** being generated. Extending the reaction time to 48 h led to an inversion of the product ratio and favored the formation of **3b** in 44% yield. Interestingly, isolation of **2b** and re-exposure to standard reaction conditions afforded **3c** in almost quantitative NMR yield (Scheme 1, bottom). In addition to supporting the formation of **2** as an intermediate in the transformation, these experiments underscore the challenging nature of cyclopropene activation and indicate that the efficiency of the process is determined by the initial activation/*geminal* difluorination sequence (catalytic cycle A) and not the second cycle (B).

Reaction profile monitoring by ^{1}H and ^{19}F NMR spectroscopy also provided a convenient and operationally facile platform to substantiate the intermediacy of **II** in this process (Fig. 4). After 20 h, the predominant generation of compound **2b** is evident (green boxes). The consumption of this alkene and subsequent generation of compound **3b** are in-line with the working hypothesis.

The remarkable efficiency of the *geminal* difluorination of intermediate **2b** was unexpected, given previous results involving internal alkenes in I(I)/I(III) catalysis. Cognizant of the report by Lal that electron rich 1,1-diarylethylenes undergo direct, *vicinal* fluorination with Selectfluor® and HF [19], control reactions were performed to establish (i) that a catalytic cycle is operational, and (ii) to delineate the impact of the difluoromethyl group (Table 3).

The preferential formation of the *geminal*-difluoride (as opposed to the *vicinal* product) demonstrates that the process is distinct from the uncatalyzed study reported by Lal [19]. To



Scheme 1. Deconstructing the tetrafluorination of cyclopropenes.

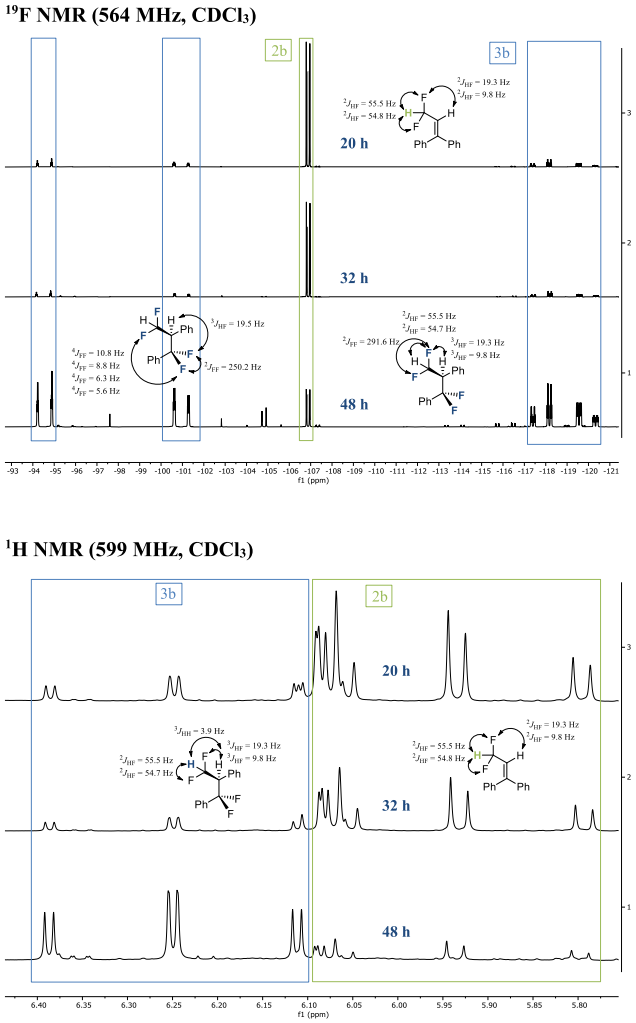


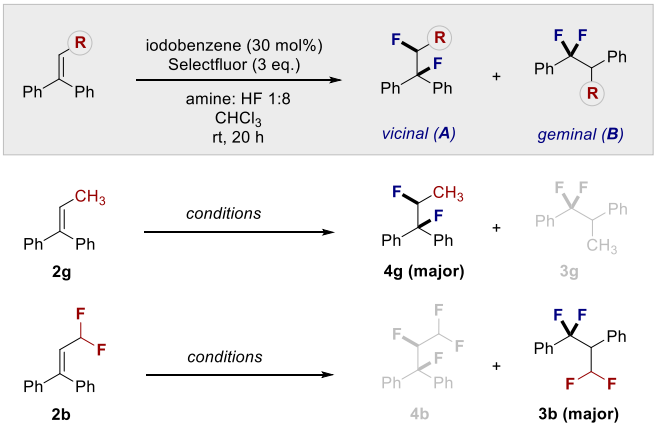
Fig. 4. Upper: Selected region of the ^{19}F NMR spectrum after 20, 32 and 48 h. Lower: Selected region of the ^{1}H NMR spectrum after 20, 32 and 48 h. In all cases, the reaction aliquots were quenched prior to analysis.

investigate the effect of the *gem*-difluoromethyl group, substrates bearing R = CH_3 (**2g**) and R = CHF_2 (**2b**) were independently exposed to the reaction conditions with and without catalyst [10f]. In the presence of the catalyst, the *vicinal* and *geminal* products were formed in 70% (**4g**) and 20% (**3g**), respectively. The control experiment in the absence of iodobenzene also favored formation of the *vicinal* product in >95% (**4g**), with only traces (<5%) of the *geminal* product (**3g**) detected. In contrast, substituting R = CH_3 by R = CHF_2 (**2b**) led to a complete reversal of circumstances. Not only was the catalyst clearly required, but the dominant product formed was the *geminal* product **3b** (>95% yield).

3. Conclusion

In summary, an I(I)/I(III) catalysis platform has been leveraged to enable the activation of 3,3-diaryl cyclopropenes with concomitant formation of four C(sp^3)-F bonds in a single operation. *In situ* generation of $ArIF_2$, through Selectfluor®-mediated oxidation of inexpensive iodobenzene, provides a key species that is common to two consecutive catalytic processes (Fig. 5). In the initial catalytic cycle (cycle A), fluorinative ring opening of the cyclopropene (**I**) generates a 1,1-diaryl alkene bearing a difluoromethyl group (**II**). Following a second activation process, a tertiary fluoride centre is

Table 3
The role of CHF_2 in regulating the regioselectivity of the process.[a]



Entry	R	Catalyst	Yield A[b]	Yield B[b]
1	CH_3	PhI	70% (**4g**)	20% (**3g**)
2	CH_3	-	>95% (**4g**)	<5% (**3g**)
3	CHF_2	PhI	<5% (**4b**)	>95% (**3b**)
4	CHF_2	-	<5% (**4b**)	<5% (**3b**)

[a] Standard reaction conditions: alkene (0.2 mmol), iodobenzene (30 mol%), Selectfluor® (3.0 eq.), amine:HF source (1:8, 0.5 mL), $CHCl_3$ (0.5 mL), 20 h, ambient temperature.
[b] Determined by ^{19}F NMR using α,α,α-trifluorotoluene as an internal standard.

generated prior to phenonium ion rearrangement [16,26] which, in turn, liberates the PhI catalyst. A final C(sp^3)-F bond forming event furnishes the product **III**. Through a process of reaction deconstruction, the involvement of species **II** as an intermediate is proposed, and these data suggest that cyclopropene activation is challenging (cycle A). In contrast, the difluorinative rearrangement of **II** to **III** is facile and high yielding. Brønsted acidity is a critical parameter in the net process with an amine:HF ratio of 1:7 required for the *p*-H, -Me and -OMe series, and 1:8 required for the halogenated series. Finally, the importance of the β-CF_2H motif in intermediate **II** in ensuring *geminal* fluorination is demonstrated: replacement with β-CH_3 enables (uncatalyzed) *vicinal* difluorination. Despite the narrow reactivity window observed, it is envisaged that this study will stimulate interest in merging the reactivity of small, unsaturated rings with main group catalysis to facilitate sequential C(sp^3)-F forming events.

4. Experimental section

All commercially available reagents were purchased as reagent grade from *Sigma Aldrich, Merck*, *Alfa Aesar*, *TCI, BLDpharm* or *abcr* and were used without further purification unless otherwise stated. Where indicated tetrahydrofuran and dichloromethane were dried by a solvent purification system including columns packed with molecular sieves and aluminium oxide. All reactions with HF were run in Teflon® vials. Solvents for extractions or chromatographic purifications were bought as technical grade and distilled on a rotary evaporator prior to use. For analytical thin layer chromatography, glass plates coated with SiO_2-60 F254 were used from *Merck*. They were visualised with UV-light (254 nm) or with $KMnO_4$ or CAM solution. Column chromatography was performed using silica gel (40–63 μm, *VWR Chemicals*). NMR measurements were performed on a *Bruker AV300, AV400, Agilent DD2 500* or an *Agilent DD2* 600 by the NMR service department of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster.

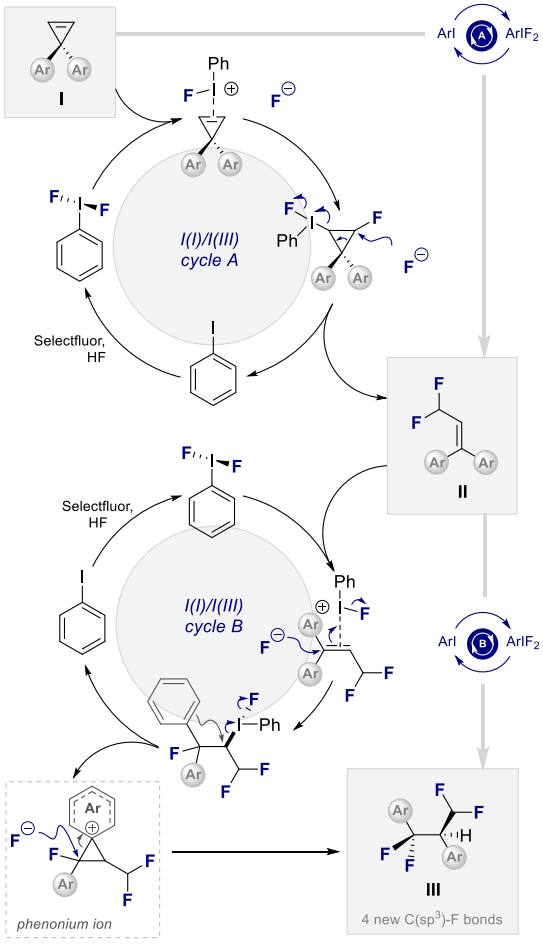


Fig. 5. Postulated catalytic cycle.

The chemical shifts were referenced to the residual solvent peak as the internal standard (7.26 ppm for $CDCl_3$, 2.50 ppm for DMSO-d_6 for ^1H NMR and 77.16 ppm for $CDCl_3$ for ^{13}C NMR). The multiplicity is abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (heptet), m (multiplet) and br (broad). The given assignments are supported by additional 1D and 2D NMR experiments. The melting points were determined on a *Büchi* B-545 melting point apparatus with open glass capillaries. The IR measurements were performed on a *Perkin-Elmer* 100 FT-*IR* spectrometer and the intensities of the bands are assigned as follows: *w* (weak), *m* (medium), *s* (strong). High resolution mass spectrometry was performed by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster on a Bruker Daltonics MicroTof (HRMS-ESI), a Triplequad TSQ 7000 (MS-EI), Triplequad Quattro Micro GC (GC-EI-MS), a Qp5050 Single Quad (GC-EI-MS) or a LTQ Orbitap LTQ XL (HRMS-APCI).

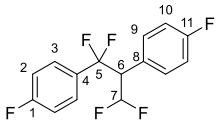
General Procedure A: Unless stated otherwise, a Teflon® vial was equipped with a 1 cm stirring bar followed by the addition of cyclopropene (0.20 mmol, 1.00 eq.), iodobenzene (12.2 mg, 0.06 mmol, 0.30 eq.) and $CHCl_3$ (0.5 mL). The mixture was stirred and the stated amine:HF mixture was added (0.5 mL) via syringe. After stirring for 1 min, Selectfluor® (213 mg, 0.60 mmol, 3.00 eq.) was added in one portion. The reaction vessel was then sealed with a Teflon® screw cap. After stirring (350 rpm) at ambient temperature for the stated time, DCM (2 mL) was added to dilute the reaction and a saturated aqueous solution of $NaHCO_3$ (2 mL) was carefully added via a long glass pipette to partially quench the

reaction. The mixture was poured into an Erlenmeyer flask charged with 100 mL of a saturated aqueous solution of $NaHCO_3$ (CAUTION, evolution of CO_2!). The Teflon® vial was rinsed with DCM and the solution transferred into another flask with a saturated aqueous solution of $NaHCO_3$ to guarantee the removal of excess HF. The organics were extracted with DCM (3 × 30 mL) and the combined organic layers were dried over $MgSO_4$ before the solvent was carefully removed under reduced pressure. An internal standard (α-,α-,α-trifluorotoluene) was added to the crude residue and the yield was determined by ^{19}F NMR spectroscopy relative to the internal standard. The NMR sample was then recombined with the crude residue and purified by column chromatography to furnish the desired product.

HF·amine sources: $Et_3N{\cdot}3HF$ = amine:HF/1:3.0. $Pyr{\cdot}(HF)_x$ (Olah's reagent) = amine:HF/1:9.23 (calculated based on the physical data provided by the supplier, Sigma-Aldrich). Stock solutions of larger volumes were prepared and stored in polyethylene containers at −20 °C:

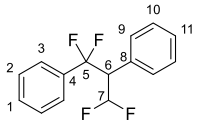
amine:HF/1:4.5	0.159 mL of $Pyr{\cdot}(HF)_x$ and 0.341 mL of $Et_3N{\cdot}3HF$
amine:HF/1:5	0.211 mL of $Pyr{\cdot}(HF)_x$ and 0.289 mL of $Et_3N{\cdot}3HF$.
amine:HF/1:6.0	0.295 mL of $Pyr{\cdot}(HF)_x$ and 0.205 mL of $Et_3N{\cdot}3HF$.
amine:HF/1:7	0.365 mL of $Pyr{\cdot}(HF)_x$ and 0.135 mL of $Et_3N{\cdot}3HF$.
amine:HF/1:7.5	0.402 mL of $Pyr{\cdot}(HF)_x$ and 0.098 mL of $Et_3N{\cdot}3HF$.
amine:HF/1:8	0.430 mL of $Pyr{\cdot}(HF)_x$ and 0.070 mL of $Et_3N{\cdot}3HF$.

(3,3-difluoroprop-1-ene-1,1-diyl)dibenzene (2b) [27]**:** Compound **2b** was prepared according to a General Procedure **A** with an amine:HF ratio of 1:6 using cycloprop-2-ene-1,1-diyldibenzene (**1a**) (38.5 mg, 0.20 mmol, 1.00 eq.) and a reaction time of 20 h. The reaction was run six times and prior to purification by column chromatography (SiO_2, 100% *n*-pentane) yielding product as a clear oil (247 mg, 1.07 mmol, 45%). R_f = 0.41 (100% *n*-pentane). ^1H NMR (400 MHz, DMSO-d_6, 299 K): δ [ppm] = 7.47 (m, 3H), 7.38 (m, 3H), 7.29–7.26 (m, 2H), 7.18 (m, 2H), 6.35 (q, *J* = 8.0 Hz, 1H), 6.09 (td, *J* = 55.3 Hz, *J* = 7.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6): δ [ppm] = −105.65 (dd, $^2J_{HF}$ = 55.3, $^3J_{HF}$ = 8.3 Hz). GC-EI-MS: Retention: 8.06–8.08 min, *m/z*: 230.09 ($[M]^+$, calcd. for $C_{15}H_{12}F_2^+$: 230.16).



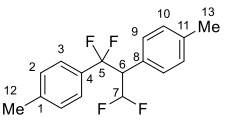
4,4'-(1,1,3,3-tetrafluoropropane-1,2-diyl)*bis*(fluorobenzene) (3a):

Compound **3a** was prepared according to a General Procedure **A** with an amine:HF ratio of 1:8 using 4,4'-(cycloprop-2-ene-1,1-diyl) *bis*(fluorobenzene) (**1a**) (45.6 mg, 0.20 mmol, 1.00 eq.) and a reaction time of 20 h. The crude mixture was purified by column chromatography (SiO_2, 100% *n*-pentane) yielding the product as a clear oil (16.8 mg, 0.06 mmol, 28%). R_f = 0.25 (100% *n*-pentane). FT-IR ($\tilde{\nu}$ = cm^{-1}): 1900 (w), 1609 (m), 1512 (s), 1388 (w), 1373 (w), 1322 (w), 1303 (w), 1233 (s), 1197 (w), 1163 (s), 1135 (s), 1093 (m), 1056 (s), 1017 (m), 990 (m), 971 (m), 941 (w), 876 (w), 838 (s), 822 (s), 790 (s), 759 (m), 732 (w), 675 (w). ^1H NMR (600 MHz, $CDCl_3$, 299 K): δ [ppm] = 7.24 (m, 2H, H–C3), 7.19 (m, 2H, H–C9), 7.00 (m, 4H, H–C2, H–C10), 6.34 (dddd, $^2J_{HF}$ = 55.4 Hz, $^2J_{HF}$ = 54.5 Hz, $^3J_{HH}$ = 3.6 Hz, *J* = 1.0 Hz, 1H, H–C7), 3.71 (app. ttd, $^3J_{HF}$ = 19.9 Hz, $^3J_{HF}$ = 9.8 Hz, $^3J_{HH}$ = 3.6 Hz, 1H, H–C6. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ [ppm] = 164.3 (dt, $^1J_{CF}$ = 250.3 Hz, $^5J_{CF}$ = 1.8 Hz, C1), 162.6 (d, $^1J_{CF}$ = 248.6 Hz, C11), 132.5 (dq, $^3J_{CF}$ = 8.3 Hz, $^4J_{CF}$ = 1.6 Hz, C9), 131.3 (td, $^2J_{CF}$ = 26.7 Hz, $^4J_{CF}$ = 3.0 Hz, C4), 127.7 (dt, $^3J_{CF}$ = 8.7 Hz, $^3J_{CF}$ = 6.4 Hz, C3), 125.7–125.6 (m, C8), 120.9 (td, $^1J_{CF}$ = 249.8 Hz, $^3J_{CF}$ = 6.8 Hz, C5), 115.8 (d, $^2J_{CF}$ = 19.3 Hz, C10), 115.6 (d, $^2J_{CF}$ = 19.9 Hz, C2), 113.5 (m, C7) 57.4 (tt, $^2J_{CF}$ = 25.8 Hz, $^2J_{CF}$ = 20.8 Hz, C6). ^{19}F NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −93.2 to −93.8 (m, 1F, F^a-C5), −100.6 to −101.2 (m, 1F, F^b-C5), −110.1 to −110.1 (m, 1F, F–C1), −112.9 (tt, $^3J_{HF}$ = 8.5 Hz, $^4J_{HF}$ = 5.2 Hz, 1F, F–C11), −118.1 (app. dddt, $^2J_{FF}$ = 292.4 Hz, $^2J_{HF}$ = 54.5 Hz, $^4J_{FF}$ = 9.6 Hz, $^4J_{FF}$ = 5.6 Hz, 1F, F^a-C7), −120.9 (ddddd, $^2J_{FF}$ = 291.8 Hz, $^2J_{HF}$ = 55.4 Hz, $^3J_{HF}$ = 20.1 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.2 Hz, 1F, F^b-C7). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −93.5 (dddd, $^2J_{FF}$ = 251.3 Hz, $^4J_{FF}$ = 9.8 Hz, $^4J_{FF}$ = 5.2 Hz, F–C5, 1F, F^a-C5), −100.9 (ddd, $^2J_{FF}$ = 251.2 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.6 Hz, 1F, F^b-C5), −110.1 (dd, $^6J_{FF}$ = 2.9 Hz, $^6J_{FF}$ = 2.2 Hz, 1F, F–C1), −112.9 (s, 1F, F–C11), −118.1 (ddd, $^2J_{FF}$ = 292.4 Hz, $^4J_{FF}$ = 9.7 Hz, $^4J_{FF}$ = 5.6 Hz, 1F, F^a-C7), −120.2 (ddd, $^2J_{FF}$ = 292.4 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.2 Hz, 1F, F^b-C7). GC-EI-MS: Retention: 7.38–7.45 min, *m/z*: 304.0681 ($[M]^+$, calcd. for $C_{15}H_{10}F_6^+$: 304.0687).



(1,1,3,3-tetrafluoropropane-1,2-diyl)dibenzene (3b):

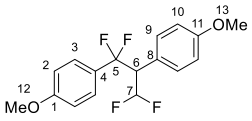
Compound **3b** was prepared according to a General Procedure **A** with an amine:HF ratio of 1:7 using cycloprop-2-ene-1,1-diyldibenzene (**1b**) (38.5 mg, 0.20 mmol, 1.00 eq.) and a reaction time of 20 h. The crude mixture was purified by column chromatography (SiO_2, 100% *n*-pentane) yielding the product as a clear oil (16.8 mg, 0.06 mmol, 31%). R_f = 0.15 (100% *n*-pentane). FT-IR ($\tilde{\nu}$ = cm^{-1}): 1606 (w), 1498 (w), 1453 (w), 1387 (w), 1373 (w), 1319 (w), 1255 (w), 1198 (w), 1156 (w), 1136 (m), 1078 (m), 1046 (m), 1003 (w), 988 (w), 968 (w), 920 (w), 871 (w), 836 (w), 822 (w), 760 (m), 734 (w), 717 (m), 695 (s), 668 (m). ^1H NMR (600 MHz, $CDCl_3$, 299 K): δ [ppm] = 7.38–7.25 (m, 8H, H-C^{Ar}), 7.34–7.25 (m, 2H, H-C^{Ar}), 7.22 (m, 2H, H–C9), 6.35 (ddd, $^2J_{HF}$ = 55.3 Hz, $^2J_{HF}$ = 54.7 Hz, $^3J_{HH}$ = 3.9 Hz, 1H, H–C7), 3.75 (app. heptd, $^3J_{HF}$ = 10.5, $^3J_{HF}$ = 10.2 Hz, $^3J_{HF}$ = 10.1 Hz, *J* = 10.0, $^3J_{HF}$ = 9.6 Hz, *J* = 9.1, $^3J_{HH}$ = 3.9 Hz, 1H, H–C6). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ [ppm] = 135.2 (t, $^2J_{CF}$ = 26.0 Hz, C4), 130.6 (d, $^4J_{CF}$ = 1.6 Hz, C9), 130.1 (t, $^4J_{CF}$ = 1.6 Hz, C2), 129.9 (s, C8) 128.5 (s, C1), 128.4 (s, C10), 128.2 (s, C11), 125.4 (t, $^3J_{CF}$ = 6.4 Hz, C3), 121.7 (m, C5) 114.2 (t, $^1J_{CF}$ = 243.8 Hz, C7), 58.0 (t, $^2J_{CF}$ = 21.2 Hz, 1C, C6). ^{19}F NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −94.5 (dddd, $^2J_{FF}$ = 250.2 Hz, $^3J_{HF}$ = 10.7 Hz, $^4J_{FF}$ = 10.7 Hz, $^4J_{FF}$ = 5.6 Hz, 1F, F^a-C5), −100.8 (dddd, $^2J_{FF}$ = 250.4 Hz, $^3J_{HF}$ = 19.5 Hz, $^4J_{FF}$ = 7.6 Hz, $^4J_{FF}$ = 7.4 Hz, 1F, F^b-C5), −117.8 (app. dddt, $^2J_{FF}$ = 291.4 Hz, $^2J_{HF}$ = 54.7 Hz, $^4J_{FF}$ = 10.8 Hz, $^3J_{HF}$ = 10.0 Hz, $^4J_{FF}$ = 6.5 Hz, 1F, F^a-C7), −119.8 (ddddd, $^2J_{FF}$ = 291.6 Hz, $^2J_{HF}$ = 55.5 Hz, $^3J_{HF}$ = 19.3 Hz, $^4J_{FF}$ = 8.8 Hz, $^4J_{FF}$ = 5.7 Hz, 1F, F^b-C7). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −94.5 (ddd, $^2J_{FF}$ = 250.2 Hz, $^4J_{FF}$ = 10.8 Hz, $^4J_{FF}$ = 5.6 Hz, 1F, F^a-C5), −100.8 (ddd, $^2J_{FF}$ = 250.2 Hz, $^4J_{FF}$ = 8.8 Hz, $^4J_{FF}$ = 6.3 Hz, 1F, F^b-C5), −117.7 (ddd, $^2J_{FF}$ = 291.5 Hz, $^4J_{FF}$ = 10.8 Hz, $^4J_{FF}$ = 6.4 Hz, 1F, F^a-C7), −119.8 (ddd, $^2J_{FF}$ = 291.4 Hz, $^4J_{FF}$ = 8.8 Hz, $^4J_{FF}$ = 5.6 Hz, 1F, F^b-C7). GC-EI-MS: Retention: 7.52–7.59 min, *m/z*: 268.0870 ($[M]^+$, calcd. for $C_{15}H_{12}F_4^+$: 268.0875).



4,4'-(1,1,3,3-tetrafluoropropane-1,2-diyl)*bis*(methylbenzene) (3c):

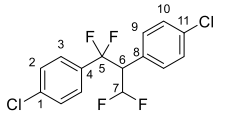
Compound **3c** was prepared according to a General Procedure **A** with an amine:HF ratio of 1:7 using 4,4'-(Cycloprop-2-ene-1,1-diyl) *bis*(fluorobenzene) (**1c**) (44.1 mg, 0.20 mmol, 1.00 eq.) and a reaction time of 20 h. The crude mixture was purified by column chromatography (SiO_2, 100% *n*-pentane) yielding the product as a clear oil (19.6 mg, 0.07 mmol, 33%).

R_f = 0.16 (100% *n*-pentane). FT-IR ($\tilde{\nu}$ = cm^{-1}): 2925 (m), 2855 (w), 1618 (w), 1518 (m), 1456 (m), 1386 (m), 1316 (m), 1259 (m), 1189 (m), 1161 (m), 1135 (s), 1098 (s), 1055 (s), 1024 (s), 989 (m), 969 (m), 874 (m), 817 (s), 802 (s), 774 (s), 747 (m), 727 (m), 701 (w), 677 (m). ^{1}H NMR (500 MHz, $CDCl_3$, 299 K): δ [ppm] = 7.18 (m, 2H), 7.14–7.12 (m, 2H), 7.11 (m, 2H), 7.09 (m, 2H), 6.29 (td, $^2J_{HF}$ = 54.9 Hz, $^2J_{HH}$ = 3.8 Hz, 1H, H–C7), 3.77–3.64 (m, 1H, H–C6), 2.33 (s, 3H, H–C12), 2.32 (s, 3H, H–C13). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 299 K): δ [ppm] = 140.2 (s, C1), 138.4 (s, C11), 132.7 (t, $^2J_{CF}$ = 25.6 Hz, C4), 130.6 (d, $^4J_{CF}$ = 1.5 Hz, C9), 129.3 (s, C10), 129.0 (s,C2), 127.1–127.0 (m, C8), 125.5 (t, $^3J_{CF}$ = 6.3 Hz, C3), 114.4 (t, $^1J_{CF}$ = 243.4 Hz, C7), 57.80 (t, $^2J_{CF}$ = 20.8 Hz, C6), 21.4 (C12), 21.3 (C13). ^{19}F NMR (470 MHz, $CDCl_3$, 299 K): δ [ppm] = −93.9 (dtd, $^2J_{FF}$ = 250.3 Hz, $^3J_{HF}$ = 10.7 Hz, $^4J_{FF}$ = 6.8 Hz, F^a-C5), −99.4 (ddt, $^2J_{FF}$ = 251.0 Hz, $^3J_{HF}$ = 17.5 Hz, $^4J_{FF}$ = 7.7 Hz, F^b-C5), −117.8 (dddt, $^2J_{FF}$ = 290.8 Hz, $^2J_{HF}$ = 54.8 Hz, $^4J_{FF}$ = 10.2 Hz, $^4J_{FF}$ = 6.7 Hz, F^a-C7), −119.9 (dddt, $^2J_{FF}$ = 290.4 Hz, $^2J_{HF}$ = 55.5 Hz, $^3J_{HF}$ = 19.7 Hz, $^4J_{FF}$ = 7.5 Hz, F^b-C7). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$, 299 K): δ [ppm] = −93.9 (ddd, $^2J_{FF}$ = 250.2 Hz, $^4J_{FF}$ = 10.5 Hz, $^4J_{FF}$ = 5.9 Hz, F^a-C5), −99.4 (dt, $^2J_{FF}$ = 250.0 Hz, $^4J_{FF}$ = 7.5 Hz, F^b-C5), −117.8 (ddd, $^2J_{FF}$ = 290.8 Hz, $^4J_{FF}$ = 10.3 Hz, $^4J_{FF}$ = 6.7 Hz, F^a-C7), −119.9 (dt, $^2J_{FF}$ = 290.7 Hz, $^4J_{FF}$ = 7.3 Hz, F^b-C7). GC-EI-MS: Retention: 8.29–8.31 min, *m/z*: 296.1184 ([M]$^+$, calcd. for $C_{17}H_{16}F_4^+$: 296.1183).



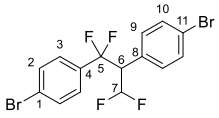
Attempted synthesis of 4,4'-(1,1,3,3-tetrafluoropropane-1,2-diyl)*bis*(methoxybenzene) (3d):

4,4'-(Cycloprop-2-ene-1,1-diyl)*bis*(methoxybenzene) (**1d**) (50.5 mg, 0.20 mmol, 1.00 eq.) was subjected to reaction conditions consistent with General Procedure A with an amine:HF ratio of 1:7 and a reaction time of 20 h. No product formation was observed.



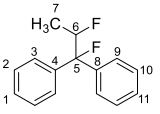
4,4'-(1,1,3,3-tetrafluoropropane-1,2-diyl)*bis*(chlorobenzene) (3e):

Compound **3e** was prepared according to General Procedure **A** with an amine:HF ratio of 1:8 using 4,4'-(cycloprop-2-ene-1,1-diyl) *bis*(chlorobenzene) (**1e**) (52.2 mg, 0.20 mmol, 1.00 eq.) at 50 °C and a reaction time of 20 h. The crude mixture was purified by column chromatography (SiO_2, 100% *n*-pentane) yielding the product as a clear oil (15.6 mg, 0.05 mmol, 23%). R_f = 0.19 (100% *n*-pentane). FT-IR ($\tilde{\nu}$ = cm^{-1}): 2928 (w), 1907 (w), 1604 (m), 1495 (s), 1416 (m), 1403 (m), 1389 (m), 1373 (m), 1324 (m), 1306 (m), 1254 (m), 1197 (m), 1162 (m), 1137 (s), 1092 (s), 1061 (s), 1017 (s), 989 (m), 970 (m), 946 (w), 872 (m), 826 (s), 805 (s), 772 (m), 756 (s), 737 (s), 703 (w), 673 (w). ^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ [ppm] = 7.33–7.30 (m, 2H, H–C3), 7.29–7.26 (m, 2H, H–C10), 7.21–7.18 (m, 2H, H–C2), 7.15 (m, 2H, H–C9), 6.33 (td, $^2J_{HF}$ = 55.3 Hz, $^3J_{HH}$ = 3.6 Hz, 1H, H–C7), 3.78–3.62 (m, 1H, H–C6). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ [ppm] = 136.7 (t, $^3J_{CF}$ = 2.2 Hz, C8), 135.2 (C11), 133.7 (t, $^2J_{CF}$ = 26.4 Hz, C4), 132.2–131.9 (m, C9), 129.0 (C10), 128.9 (C2), 128.1 (C5), 127.0 (t, $^3J_{CF}$ = 6.3 Hz, C3), 116.0–111.6 (m, C7), 57.9–56.7 (m, C6). ^{19}F NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −94.0 (dtd, $^2J_{FF}$ = 252.1 Hz, $^3J_{HF}$ = 9.8 Hz, $^4J_{FF}$ = 5.1 Hz, F^a-C5), −101.3 (dddd, $^2J_{FF}$ = 252.1 Hz, $^3J_{HF}$ = 19.9 Hz, $^4J_{FF}$ = 9.9 Hz, $^4J_{FF}$ = 5.6 Hz, F^b-C5), −117.9 (dddt, $^2J_{FF}$ = 292.9 Hz, $^2J_{HF}$ = 54.4 Hz, $^4J_{FF}$ = 9.6 Hz, $^4J_{FF}$ = 5.6 Hz, F^a-C7), −120.0 (ddddd, $^2J_{FF}$ = 292.4 Hz, $^2J_{HF}$ = 55.3 Hz, $^3J_{HF}$ = 19.8 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.2 Hz, F^b-C7). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = 94.0 (ddd, $^2J_{FF}$ = 252.1 Hz, $^4J_{FF}$ = 9.6 Hz, $^4J_{FF}$ = 5.2 Hz, F^a-C5), −101.3 (ddd, $^2J_{FF}$ = 252.1 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.5 Hz, F^b-C5), −117.9 (ddd, $^2J_{FF}$ = 292.9 Hz, $^4J_{FF}$ = 9.6 Hz, $^4J_{FF}$ = 5.6 Hz, F^a-C7), −120.0 (ddd, *J* = 292.9, 10.0, 5.2 Hz, F^b-C7). GC-EI-MS: Retention: 8.84–8.86 min, *m/z*: 336.00877 ([M]$^+$, calcd. for $C_{15}H_{10}Cl_2F_4^+$: 336.00902).



4,4'-(1,1,3,3-tetrafluoropropane-1,2-diyl)*bis*(bromobenzene) (3f)

Compound **3f** was prepared according to General Procedure **A** with an amine:HF ratio of 1:8 using 4,4'-(cycloprop-2-ene-1,1-diyl) *bis*(bromobenzene) (**1f**) (70.0 mg, 0.20 mmol, 1.00 eq.) at 50 °C and a reaction time of 20 h. The crude mixture was purified by column chromatography (SiO_2, 100% *n*-pentane) yielding the product as a clear oil (16.6 mg, 0.04 mmol, 20%). R_f = 0.16 (100% *n*-pentane). FT-IR ($\tilde{\nu}$ = cm^{-1}): 2931 (w), 1597 (m), 1492 (m), 1412 (w), 1399 (m), 1324 (w), 1253 (m), 1197 (w), 1162 (m), 1138 (m), 1098 (m), 1074 (s), 1013 (m), 989 (m), 970 (m), 822 (m), 802 (m), 749 (m), 727 (w), 688 (w). ^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ [ppm] = 7.50–7.46 (m, 2H, H–C2), 7.45–7.41 (m, 2H, H–C9), 7.14–7.11 (m, 2H, H–C3), 7.09 (m, 2H, H–C10), 6.32 (td, $^2J_{HF}$ = 54.5 Hz, $^3J_{HH}$ = 3.6 Hz, 1H, H–C7), 3.68 (app. ttd, $^3J_{HF}$ = 19.8 Hz, $^3J_{HF}$ = 9.7 Hz, $^3J_{HH}$ = 3.4 Hz, 1H, H–C6). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ [ppm] = 134.1 (t, $^2J_{CF}$ = 26.3 Hz, C4), 132.4–132.2 (m, C9), 132.0 (C10), 131.8 (C2), 128.7–128.5 (m, C8), 127.2 (t, $^3J_{CF}$ = 6.3 Hz, C3), 125.1–125.0 (m, C1), 123.4 (C11), 120.7 (m, C5), 116.4–111.1 (m, C7), 58.0–56.9 (m, C6). ^{19}F NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −94.1 (dtd, $^2J_{FF}$ = 252.3 Hz, $^3J_{HF}$ = 9.8 Hz, $^4J_{FF}$ = 5.2 Hz, F^a-C5), −101.4 (dddd, $^2J_{FF}$ = 252.2 Hz, $^3J_{HF}$ = 19.9 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.6 Hz, F^b-C5), −117.9 (dddt, $^2J_{FF}$ = 292.9 Hz, $^2J_{HF}$ = 54.4 Hz, $^4J_{FF}$ = 9.5 Hz, $^4J_{FF}$ = 5.6 Hz, F^a-C7), −120.0 (ddddd, $^2J_{FF}$ = 292.6 Hz, $^2J_{HF}$ = 55.3 Hz, $^3J_{HF}$ = 19.8 Hz, $^4J_{FF}$ = 9.9 Hz, $^4J_{FF}$ = 5.2 Hz, F^b-C7). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −94.1 (ddd, $^2J_{FF}$ = 252.3 Hz, $^4J_{FF}$ = 9.6 Hz, $^4J_{FF}$ = 5.2 Hz, F^a-C5), −101.4 (ddd, $^2J_{FF}$ = 252.3 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.6 Hz, F^b-C5), −117.9 (ddd, $^2J_{FF}$ = 292.9 Hz, $^4J_{FF}$ = 9.5 Hz, $^4J_{FF}$ = 5.6 Hz, F^a-C7), −120.0 (ddd, $^2J_{FF}$ = 292.9 Hz, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 5.2 Hz, F^b-C7). GC-EI-MS: Retention: 9.51–9.53 min, *m/z*: 425.90640 ([M]$^+$, calcd. for $C_{15}H_{10}Br_2F_4^+$: 425.90600).



(1,2-difluoropropane-1,1-diyl)dibenzene (4g):

Compound **4g** was prepared according to General Procedure **A** without the addition of catalyst, with an amine:HF ratio of 1:7 using prop-1-ene-1,1-diyldibenzene (**2g**) (38.9 mg, 0.20 mmol, 1.00 eq.) and a reaction time of 20 h. The crude mixture was purified by column chromatography (SiO_2, 100% *n*-pentane) yielding the product as a clear oil (43.1 mg, 0.19 mmol, 95%). $R_f = 0.16$ (100% pentane). FT-IR ($\tilde{\nu} = cm^{-1}$): 3064 (w), 2926 (m), 2855 (w), 1601 (w), 1494 (m), 1450 (s), 1381 (m), 1332 (w), 1236 (w), 1205 (w), 1155 (m), 1087 (s), 1069 (s), 1034 (w), 992 (m), 972 (s), 932 (m), 905 (s), 879 (m), 763 (s), 750 (s), 718 (m), 696 (s), 657(s). ^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ [ppm] = 7.53–7.50 (m, 2H, H-C^{Ar}), 7.44–7.41 (m, 2H, H-C^{Ar}), 7.38 (m, 4H, H-C^{Ar}), 7.35–7.29 (m, 2H, H-C^{Ar}), 5.47 (ddq, $^2J_{HF} = 45.6$ Hz, $^3J_{HF} = 18.6$ Hz, $^3J_{HH} = 6.4$ Hz, 1H, H–C6), 1.39 (ddd, $^3J_{HF} = 23.9$ Hz, $^3J_{HH} = 6.3$ Hz, $^4J_{HF} = 1.5$ Hz, 3H, H–C7). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ [ppm] = 140.9 (dd, $J = 22.6, 3.2$ Hz, C^{Ar}), 140.0 (d, $J = 23.6$ Hz, C^{Ar}), 128.4 (dd, $J = 32.3, 1.0$ Hz, C^{Ar}), 128.2 (dd, $J = 20.6, 1.6$ Hz, C^{Ar}), 126.3 (dd, $J = 8.6, 2.0$ Hz, C^{Ar}), 125.7 (dd, $J = 8.7, 1.3$ Hz, C^{Ar}), 98.5 (dd, $^1J_{CF} = 182.3$ Hz, $^2J_{CF} = 20.9$ Hz, C5), 91.3 (dd, $^1J_{CF} = 180.2$ Hz, $^2J_{CF} = 27.6$ Hz, C6), 15.13 (dd, $^2J_{CF} = 23.3$, $^3J_{CF} = 4.8$ Hz, C7). ^{19}F NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −164.2 (t, $^3J_{FF} = 14.1$ Hz, F–C5), −182.2 to −182.5 (m, F–C6). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$, 299 K): δ [ppm] = −164.2 (d, $^3J_{FF} = 14.0$ Hz, F–C5), −182.4 (d, $^3J_{FF} = 14.0$ Hz, F–C6). GC-EI-MS: Retention: 7.85–7.87 min, *m/z*: 232.10595 ([M]$^+$, calcd. for $C_{15}H_{14}F_2^+$: 232.10581).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2022.132925.

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