Acid-Promoted Reaction of Trifluoromethylated Allyl Alcohols with Arenes. Stereoselective Synthesis of CF₃-Alkenes and CF₃-Indanes

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Supporting Information

ABSTRACT: Reaction of 4-aryl-1,1,1-trifluorobut-3-en-2-ols [CF₃-allyl alcohols, ArCH═CHCH(OH)CF₃] with arenes under activation with anhydrous FeCl₃ or FSO₃H was studied. We found that the transformation led to trifluoromethylated alkenes [ArAr′CHCH═CHCF₃] or 1-trifluoromethylated indanes (CF₃-indanes). The formation of these two types of reaction products strongly depends on the nucleophilicity of the starting arene and the electrophilicity of cationic intermediates generated from CF₃-allyl alcohols under reaction conditions. Benzene, anisole, veratrole, and ortho-xylene lead exclusively to CF₃-alkenes with an E-configuration. More π-donating polymethylated arenes (pseudocumene, mesitylene) afford only CF₃-indanes with a predominantly cis-orientation of substituents at positions 1 and 3 of the indane ring. Meta- and para-xylene shows an intermediate behavior; they may form both CF₃-alkenes and/or CF₃-indanes. The mechanisms of the investigated transformations are discussed.

INTRODUCTION

Fluorinated organic compounds have significant theoretical and practical value in chemistry, biology, medicine, and material science. Incorporation of a fluorinated moiety into a molecule often changes such important parameters as lipophilicity, metabolic activity, and bioavailability. Trifluoromethylated alkenes (styrenes) are compounds of high practical interest. Some derivatives with such fragments have been widely used for organic light-emitting diodes (OLEDs) and other material chemistry applications. Some trifluoromethylated alkenes attract significant attention due to important biological activity and application in medicine. Incorporation of a CF₃ group permits one to design more potent drugs. For example, Tamoxifen (Nolvadex) is the well-known triarylethylene-type antiestrogenic drug, which is used in the therapy of breast cancer and for the treatment of menstrual disorders. Panomifene is a trifluoromethylated analogue of Tamoxifen (Figure 1). This drug demonstrated higher anticancer activity; however, quite important is the configuration of the double bond because only one diastereomer can be used.

The electron-withdrawing character of fluorinated groups is another advantage, which allows one to control the selectivity of transformations of fluorinated compounds. CF₃-substituted carbocations are very promising, but still very rare, fluorinated species exhibiting high electrophilicity and selectivity. The present work is a continuation of our investigations on the electrophilic activation of alkenes and alkynes. In a preliminary short communication, we showed that 4-phenyl-1,1,1-trifluorobut-3-en-2-ol 1a alkylated selected aromatics to afford E-4,4-diaryl-1,1,1-trifluorobut-2-enes 2 under action of various Bronsted or Lewis acids. The best results (highest yields of compounds 2) were obtained using 1 equiv of anhydrous iron trichloride FeCl₃ (Scheme 1).

Interaction of CF₃-alcohols 1 with Bronsted or Lewis acids proceeds through intermediate formation of various electrophilic species. Thus, coordination of oxygen with a Lewis acid or protonation with a Bronsted acid leads exclusively to CF₃-alkenes with an E-configuration. More π-donating polymethylated arenes (pseudocumene, mesitylene) afford only CF₃-indanes with a predominantly cis-orientation of substituents at positions 1 and 3 of the indane ring. Meta- and para-xylene shows an intermediate behavior; they may form both CF₃-alkenes and/or CF₃-indanes. The mechanisms of the investigated transformations are discussed.
alcohols 1 results in formation of CF₃-allyl cations A, having two resonance forms, A' and A'', with cationic centers on atoms C⁴ and C', respectively. Because of the electron-withdrawing character of the CF₃ group, these allyl cations react with arenes through form A'' to form a new C−C bond at C⁴ carbon. Intermediates B or C also possess highly electrophilic properties and may participate in reactions.

To study this reaction deeper and find its scope and limitations, we decided to investigate a set of CF₃-allyl alcohols 1a–f, bearing a CH₃ group instead of a CF₃ one, in reactions with arenes, heteroarenes, alkenes, alkynes, or with other organic compounds. To our surprise, reactions of tri- and tetrafluoromethylated allyl alcohols with various arenes under action of Brønsted or Lewis acids were found to give di-, tri-, and tetrafluoroalkylated products exclusively (predominantly C⁻ and C⁴ carbon). The latter may be considered as weaker electrophiles according to the results of DFT calculations, cation A¹ has an absolutely planar geometry. Similarly, species B¹ and C¹ are almost planar (see the Supporting Information). The C–O bond in intermediate C¹ is significantly elongated (1.636 Å) compared to a normal C–O bond in alcohols (1.43 Å). In the case of B¹, the C–O bond is only by 0.03 Å longer (1.464 Å) than that in the usual case.

Thus, the obtained calculated data revealed that the atom C⁴ must be the most reactive center in allyl cations; on the contrary, species B and C should react with nucleophiles with attack to the C² center. In other words, in the first case, the reaction may occur as an S₈,1⁻ process, but in the cases of species B and C, most probably, the reaction should result in the formation of products without an allylic rearrangement. Therefore, reaction conditions (temperature and polarity of solvent) can influence significantly the direction of the reaction to give different types of products.

Having the results of theoretical prediction in hand, we started the investigation of synthetic possibilities of the reaction and their mechanism. FeCl₃-promoted reaction of CF₃-allyl alcohols 1 with benzene, isomeric xylenes, anisole, and veratrole gave highly regioselectively and stereoselectively CF₃-alkenes 2 (Table 2, and Scheme 3). The reaction proceeds as an S₈,1⁻ type process to form a new C−C bond at the C⁴ position of the starting alcohol. That can be explained by the electron-withdrawing action of the trifluoromethyl group making the

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**RESULTS AND DISCUSSION**

To estimate electronic properties of reaction intermediates, we performed DFT calculations of species A, B, and C, derived from starting alcohols 1a–f (Table 1). Charge distribution, contribution of the atomic orbital into the molecular orbital, and global electrophilicity indices ω were calculated. Because of the electron-withdrawing effect of the CF₃ group, cations A¹–A⁶ bear a greater positive charge on the carbon C⁴ compared to C² (Table 1). Apart from that, atom C⁴ has a larger LUMO contribution (31–35%) in cations A. Species B and C are characterized by a small positive charge on atom C² and a negative one on C⁴. The LUMO of B is localized mainly on the iron atom (see the Supporting Information). A higher contribution to the LUMO at carbon C⁴ compared to C² is observed for species C. Therefore, charge controlled reactions of species B and C should direct nucleophiles at carbon C². Among these three types of species, the cations A possess the highest electrophilic properties based on the ω values of 14.1–19.9 eV in comparison with ω = 6.7–7.5 eV for B and ω = 2.9–3.3 eV for C, correspondingly (Table 1). The latter may be considered as weaker electrophiles.
more preferable resonance form A" (Scheme 1). It should be noted that this reaction is 100% diastereoselective to form E-isomers 2 only (configurations were confirmed by NOESY; see the Supporting Information). In 1H NMR, values of constants \( J \) between protons at the carbon–carbon double bond are 15.6–15.7 Hz, which correspond to the E-configuration. This stereoechemical result can be explained by high steric demand of both the diarylmethyl group and the trifluoromethyl moiety attached to the formed double bond.

Methoxy substituted alcohols 1e,f afforded complex mixtures of oligomeric products in the same reactions under action of FeCl\(_3\) (at r.t.) or Brønsted superacid TfOH (at r.t. or –35 °C). It probably happened due to high \( \pi \)-nucleophilicity of

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**Table 1. Selected Electronic Characteristics and Calculated Geometries of Species A, B, and C**

<table>
<thead>
<tr>
<th>species</th>
<th>R in Ar</th>
<th>( E_{\text{HOMO}} ), eV</th>
<th>( E_{\text{LUMO}} ), eV</th>
<th>( \omega_r ), eV</th>
<th>( q(C_1^+) ), e</th>
<th>( q(C_2^+) ), e</th>
<th>( k(C_1^+) ) LUMO, %</th>
<th>( k(C_2^+) ) LUMO, %</th>
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<tbody>
<tr>
<td>A1</td>
<td>H</td>
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<td>–8.75</td>
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<td>24</td>
<td>35</td>
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<tr>
<td>A2</td>
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<tr>
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<td>–8.43</td>
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<td>–0.07</td>
<td>0.08</td>
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<td>32</td>
</tr>
<tr>
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<td>–0.06</td>
<td>0.08</td>
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<tr>
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<td>–8.56</td>
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<td>–0.10</td>
<td>0.10</td>
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<td>–0.11</td>
<td>35</td>
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<tr>
<td>B3</td>
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<td>–4.52</td>
<td>6.9</td>
<td>0.02</td>
<td>–0.11</td>
<td>35</td>
<td>35</td>
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<tr>
<td>B4</td>
<td>4-Cl</td>
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<td>–0.11</td>
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<td>–4.52</td>
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<td>–0.04</td>
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<tr>
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<td>–0.04</td>
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<td>–3.11</td>
<td>3.3</td>
<td>0.04</td>
<td>–0.02</td>
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<td>22</td>
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<td>–3.00</td>
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<td>0.04</td>
<td>–0.03</td>
<td>9</td>
<td>19</td>
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</tbody>
</table>

\(^a\)Global electrophilicity index \( \omega = (E_{\text{HOMO}} + E_{\text{LUMO}})/2 \). \(^b\)Natural charges. \(^c\)Contribution of atomic orbital into the molecular orbital. \(^d\)LUMO is mainly localized on iron atom.

**Table 2. Reaction of CF\(_3\)-allyl Alcohols 1 with Arenes, Leading to CF\(_3\)-alkenes 2**

<table>
<thead>
<tr>
<th>entry</th>
<th>starting materials</th>
<th>reaction products, E-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 1a) (R = H)</td>
<td>2a</td>
</tr>
<tr>
<td>2</td>
<td>( 1a) (R = H)</td>
<td>2b, 2c</td>
</tr>
<tr>
<td>3</td>
<td>( 1a) (R = H)</td>
<td>2d, 2e</td>
</tr>
<tr>
<td>4</td>
<td>( 1a) (R = H)</td>
<td>2f</td>
</tr>
<tr>
<td>5</td>
<td>( 1a) (R = H)</td>
<td>2g, 2h</td>
</tr>
<tr>
<td>6</td>
<td>( 1b) (R = 3-Me)</td>
<td>2i</td>
</tr>
<tr>
<td>7</td>
<td>( 1d) (R = 4-Cl)</td>
<td>2j</td>
</tr>
<tr>
<td>8</td>
<td>( 1d) (R = 4-Cl)</td>
<td>2k</td>
</tr>
<tr>
<td>9</td>
<td>( 1d) (R = 4-Cl)</td>
<td>2l</td>
</tr>
<tr>
<td>10</td>
<td>( 1e) (R = 3-MeO)</td>
<td>2m(8/1)</td>
</tr>
</tbody>
</table>

**Reactions conditions: A - FeCl\(_3\), CH\(_2\)Cl\(_2\), 20 °C, 1 h, molar ratio 1:FeCl\(_3\):ArH = 1:1:1.1; B - FSO\(_3\)H, CH\(_2\)Cl\(_2\), –75 °C, 2 h, molar ratio 1:FSO\(_3\)H:ArH = 1:80:3. **Mixture of para- (2d, 2l) and ortho- (2e, 2m) isomers was formed.
methoxylated aromatic rings trapping intermediate cationic species and leading the reaction into alternative routes at these conditions. We managed to involve CF3-allyl alcohols 1e,f in the reaction with arenes only at low temperature, −75 °C in superacid FSO3H (entries 10, 11, and see Scheme 6).

To check our hypothesis about the possibility to redirect the reaction, we studied more carefully the reaction with more nucleophilic arenes (xylene, pseudocumene, and mesitylene) and thiophene. Surprisingly, in the case of FeCl3 activation reaction of alcohols 1a,d with para-xylene, we observed not only formation of alkenes 2n,o but also of CF3-indanes 3a,b, which were isolated as minor products (Scheme 3). The corresponding trifluoromethylated indanes were isolated as cis-isomers; their configuration was established using NOESY correlations (Figure 3).

The appearance of compounds 3 reveals the participation of carbon C2 from the initial CF3-allyl alcohols 1 (see Scheme 3) in reaction with such x-donating arenes. The formation of indanes 3 can be explained by a two-step electrophilic substitution at the para-xylene ring. The first step of the reaction is the formation of an allyl substituted arene; however, this is not the alkene 2 because our additional experiments showed that alkenes 2 cannot be cyclized to indanes 3 due to electron-withdrawing destabilization of the formed carbocation by the trifluoromethyl group (Scheme 8). It is quite interesting that, in this reaction, trifluoromethylated alcohols perform as 1,3-dicationic synthons.

The indane (indene) fragment is a very important structural unit of a large number of bioactive and pharmaceutically interesting molecules as well as modern catalysts for polymerization. 2-Trifluoromethylated indanes are an important type of indane derivatives, which have shown different biological activities: antiemetic (neurokinin receptor type 1 agonist) and anticancer (pyruvate dehydrogenase kinase (PDHK) inhibitor, growth factor receptor tyrosine kinase inhibitor). Apart from that, recently, we have shown that the trans-1,3-diaryl-1-trifluoromethyl indane scaffold is a new core for cannabinoid receptor ligand design. However, so far, the existing approaches to trifluoromethylated indanes have some restrictions. The synthesis proposed in this investigation is quite straightforward to construct highly desirable CF3-indanes 3 from CF3-alcohols 1 and arene in a one-pot sequence.

The reaction of 1b with para- and meta-xylene provided exclusively the corresponding trifluoromethylated indanes in moderate yields (Scheme 4). In the case of para-xylene, we observed stereoselective formation of indane 3c having a cis-configuration, whereas, in the case of meta-xylene, a mixture of cis-/trans-isomers 3d in the ratio of 1:3 was formed. These stereochemical observations can be explained by the more hindered structure of 3c, having an additional methyl group in position 4 of the indane core.

More striking results were obtained with highly nucleophilic pseudocumene and mesitylene (Scheme 5). Alcohols 1a–d gave in the reaction with pseudocumene exclusively cis-indanes 3e–h. Reactions with mesitylene led to cis-, trans-indanes 3e,g,h (Scheme 5). Formation of these types of indanes showed that a shift of the methyl group in the mesitylene ring takes place (Scheme 5). These results can be explained by protonation of intermediate alkene D; the next step is electrophilic cyclization in cation E, followed by migration of methyl group in species F and elimination of a proton from the aryl ring, leading finally to indanes 3.

Analogously to FeCl3-promoted synthesis of indanes (Schemes 3–5), alcohol 1f can be activated with fluorosulfonic acid to form in the reaction with pseudocumene stereoselectively only cis-indane 3i (Scheme 6). The reaction depends significantly on the reactivity and nature of the aromatic substrate. For example, in the case of reaction with anisole, we observed no formation of indane. Two products 2p and 4a (Scheme 6) were isolated. The first step of the reaction in the case of 4a is participation of atom C2. However, 2p is the result of attack of anisole at C4. These observations can be explained by the higher polarization of the anisole molecule having a nonactivated meta-atom. Therefore, the formation of noncylized products is more favorable in this case.

![Scheme 3](image_url)

**Scheme 3**

![Figure 3](image_url)

**Figure 3.** Selected NOESY correlations for cis- and trans-indanes 3 (blue: H-H correlations; green: H-F correlations).

![Scheme 4](image_url)

**Scheme 4**

![cis-,trans-3d (42%) cis- : trans- 1 : 3](image_url)

![cis-3c (28%)](image_url)
Stereochemical structures of cis- and trans-indanes 3a–i were determined by NOESY correlations (Figure 3). To have the final confirmation of the configuration, X-ray data for a single crystal of compound cis-3g were obtained (Figure 4). 1H NMR spectra can be also used to determine the configuration. Proton H3 of cis-isomers 3 has a resonance signal at 4.48–4.55 ppm as a doublet with J 10.2–10.6 Hz; the same proton of trans-isomers appears as a pseudotriplet at 4.56–4.60 ppm with J 8.6–8.7 Hz. Despite the predominant formation of cis-isomers 3, DFT calculations have shown that the differences between Gibbs energies of cis- and trans-isomers 3a and 3d are 6.4 and 9.6 kJ/mol, correspondingly, in favor of the trans-isomers (see the Supporting Information). Therefore, the formation of cis-indanes is a kinetically controlled process.

We also studied the FeCl3-promoted reaction of CF3-alcohols 1 with thiophene (Scheme 7). It is well-known that thiophene is highly activated toward electrophiles and also rather stable in acidic media compared to other five-membered heterocycles. Another important feature of thiophene chemistry is connected with the significant strain that appeared when an additional five-membered ring is condensed with the thiophene fragment, making such a reaction unfavorable. Therefore, we expected the absence of indane formation in the case of the reaction with thiophene.

This assumption was found in very good agreement with experiment. When the ratio of alcohols 1 and thiophene was 1 to 1, mixtures of mono-5 and bis-alkylated products 6 were formed in good total yield (Scheme 7). The reaction proceeds highly stereoselectively and regioselectively in terms of thiophene substitution (only electrophilic substitution in the α-position is observed) and alcohols 1 (reaction at C4 carbon).

Figure 4. Molecular structure of cis-3g (ellipsoid contour of probability levels is 50%).
The reaction can be performed more selectively to provide exclusively either compound 5 or 6. For example, the reaction of 1d with an excess of thiophene (5 equiv) gave selectively only 5d, but in the case of the use of 0.5 equiv of thiophene, adduct 6d was obtained solely (Scheme 7). The E-configuration of double bonds in alkenes 5 or 6 was confirmed by NMR (see the Supporting Information). It should be noted that compounds 6 may be formed as mixtures of meso- and dl-isomers, but it is difficult to determine their ratio due to overlapping of signals of isomers in 1H and 19F NMR spectra (see the Supporting Information).

Summarizing the discussed reactions (Table 2, Schemes 3–7), one may conclude that acid-promoted reaction of alcohols 1 with arenes can proceed by several pathways with participation of both reactive centers at carbons C1 and/or C2 (Scheme 1). Formation of indanes 3 (Schemes 3–6) and products of double arylation 4a (Scheme 6) reveal the participation at the first step of the reaction of atom C2 of starting alcohol 1. Alkylation of arenes (Table 2, Scheme 3) and thiophene (Scheme 7) may be explained through intermediate generating of an allyl cation reacting highly predominantly at atom C4 (Scheme 2). However, involvement of atom C2 in reactions may prove that species other than A also take part in these transformations. Most probably these particles have structures B and C (Scheme 2), derived from alcohols 1 under coordination of FeCl3 on hydroxyl group oxygen or by protonation of this oxygen. Indeed, it should be difficult to eliminate the hydroxyl group from initial alcohol 1 to generate allyl cation A due to powerful electron-withdrawing properties of group CF3. Intermediates B and C may participate in the reaction medium and react with rather nucleophilic electron rich arenes.

On the basis of experimental results and theoretical calculations, we proposed a possible reaction mechanism including multiple pathways of CF3-allyl alcohols 1 with arenes under action of Lewis or Brønsted acids (Scheme 8). Species B and C, having enough electrophilic center on C2, react with rather π-donating arenes, such as xylenes, pseudocumene, and mesitylene, forming compounds D. Further protonation of the formed alkene leads to cation E (Scheme 8), which may react in two different pathways. The first direction is intramolecular cyclization into indanes 3. This route is realized when the adjacent ortho-position is quite reactive. Another pathway is the reaction with one more arene molecule, leading to compounds 4 (Scheme 8). It should be noted that compounds 2 in FeCl3- or FSO3H-promoted reactions are not cyclized into indanes 3 and do not give 4 with arenes, due to deactivation of the double bond to protonation in alkenes 2 by the electron-withdrawing CF3 group. Directions of all of these transformations of alcohols 1 into different products 2–4 depend on the electrophilicity of species A, B, C and nucleophilicity of arenes. In some cases, mixed mechanism can be realized, for example, the reaction of 1 with para-xylene, giving mixtures of compounds 2 and 3 (Scheme 3).

**CONCLUSIONS**

In conclusion, we have studied the acid-promoted reaction of 4-aryl-1,1,1-trifluorobut-3-en-2-ols (CF3-allyl alcohols) with arenes. It was found that the most efficient activators of this reaction are anhydrous FeCl3 and FSO3H. The reaction affords efficient stereoselective synthesis of trifluoromethylated alkenes (up to 75%) and indanes (up to 81%): only E-CF3-alkenes and predominantly cis-CF3-indanes are formed. Short reaction times, good yields, and simplicity of the reaction procedure are significant advantages of the method. A possible reaction mechanism includes three types of electrophilic species derived from starting alcohols. The formation of two types of reaction

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**Scheme 7**

![Scheme 7](image)

**Scheme 8. Possible Mechanism of Acid-Promoted Reaction of 1 with Arenes**

![Scheme 8](image)

Anhydrous FeCl₃ (0.3 mmol) was added to a solution of alcohol 1 (0.3 mmol) and arene (0.32 mmol) or thiophene (0.34 mmol) in anhydrous dichloromethane (1 mL). The mixture was stirred at room temperature for 1 h and then quenched with a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted with CHCl₃ (3 × 50 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by preparative TLC on silica gel, using petroleum ether or petroleum ether–EtOAc mixtures (95:5 to 9:1) as an eluent.

General Procedure for the Reaction of 1 with Arenes in FSO₃H. Synthesis of 2, 3, 4. Alcohol 1 (0.26 mmol) was added to a mixture of FSO₃H (at −75 °C) (1 mL), CH₂Cl₂ (1–3 mL) with benzene (0.69 mL), or another arene (0.28 mmol). The reaction mixture was magnetically stirred for 2 h. The reaction mixture was poured into frozen concentrated aqueous HCl (10 mL), diluted with water (20 mL), and then extracted with chloroform (2 × 40 mL). The extracts were combined, washed with water, a saturated aqueous solution of NaHCO₃, and water again, and dried over Na₂SO₄. The solvent was distilled off under reduced pressure. The crude mixture was purified by preparative TLC on silica gel, using petroleum ether–EtOAc mixtures (9:1 as an eluent).

(E)-1,1,1-Trifluoro-4-(3,4-dimethylphenyl)-4-phenylbut-2-ene (2a).

In this case, the reaction was performed with the compound 1a (0.3 mmol) and benzene (14.8 mmol). Yield 50 mg, 65%. Colorless oil. H NMR (CDCl₃, 400 MHz) δ ppm: 2.22 (6H, 2CH₃), 4.78 (m, 1H), 5.52 (dqd, 1H, J = 15.6 Hz, JH₂ = 6.4 Hz, JF₂ = 1.7 Hz), 6.88 (ddq, 1H, J = 15.6 Hz, J = 6.8 Hz, JF₂ = 2.0 Hz), 6.90–6.92 (m, 1H), 6.95 (s, 1H), 7.11 (1H, J = 7.6 Hz), 7.17–7.19 (m, 2H), 7.25–7.36 (m, 3H). 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.60 (dt, CF₂ JF₂ = 6.4 Hz, JF₂ = 2.0 Hz).

(E)-1,1,1-Trifluoro-4-(3,4-dimethylphenyl)-4-phenylbut-2-ene (2b).

Yield 46 mg, 75%. Colorless oil. H NMR (CDCl₃, 400 MHz) δ ppm: 2.26 (6H, 2CH₃), 4.78 (m, 1H), 5.52 (dqd, 1H, J = 15.6 Hz, JH₂ = 6.4 Hz, J = 1.7 Hz), 6.88 (ddq, 1H, J = 15.6 Hz, J = 6.8 Hz, JF₂ = 2.0 Hz), 6.90–6.92 (m, 1H), 6.95 (s, 1H), 7.11 (1H, J = 7.6 Hz), 7.17–7.19 (m, 2H), 7.25–7.36 (m, 3H). 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.60 (dt, CF₂ JF₂ = 6.4 Hz, JF₂ = 2.0 Hz).

(E)-1,1,1-Trifluoro-4-(2-methylphenyl)-4-phenylbut-2-ene (2c).

Yield 48 mg, 56%. Colorless oil. H NMR (CDCl₃, 400 MHz) δ ppm: 2.22 (3H, 3CH₃), 2.33 (s, 3H, CH₃), 4.98 (m, 1H), 5.36 (dqd, 1H, J = 15.6 Hz, JF₂ = 6.4 Hz, J = 1.8 Hz), 6.87 (ddq, 1H, J = 15.6 Hz, J = 6.0 Hz, JH₂ = 2.0 Hz), 6.95–7.03 (m, 3H), 7.11–7.13 (m, 2H), 7.24–7.34 (m, 3H). 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.53 (dt, CF₂ JF₂ = 6.4 Hz, JF₂ = 2.0 Hz).

(E)-1,1,1-Trifluoro-4-(4-methylphenyl)-4-phenylbut-2-ene (2d).

Yield 50 mg, 58%. Colorless oil. H NMR (CDCl₃, 400 MHz) δ ppm: 3.80 (s, 3H, CH₃), 4.79–4.81 (m, 1H), 5.49 (dqd, 1H, J = 15.6 Hz, JF₂ = 6.4 Hz, J = 1.6 Hz), 6.85 (ddq, 1H, J = 15.6 Hz, J = 6.8 Hz, JF₂ = 4.0 Hz), 6.89 (d, 2H, J = 8.5 Hz), 7.08 (d, 2H, J = 8.5 Hz), 7.16 (d, 2H, J = 7.2 Hz), 7.24–7.36 (m, 3H). 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.63 dt (CF₂ JF₂ = 6.4 Hz, JF₂ = 2.0 Hz).

(E)-1,1,1-Trifluoro-4-(2-naphthalenyl)-4-phenylbut-2-ene (2e).

Yield 12 mg, 14%. Pale yellow oil. H NMR (CDCl₃, 400 MHz) δ ppm: 7.38 (s, 3H, CH₃), 5.25–5.26 (m, 1H), 5.44 (dqd, 1H, J = 15.6 Hz, JF₂ = 6.4 Hz, J = 1.5 Hz), 6.85 (ddq, 1H, J = 15.6 Hz, J = 6.4 Hz, JF₂ = 2.0 Hz), 6.88–6.95 (m, 1H), 7.04 (dd, 1H, J = 7.5 Hz, JF₂ = 1.3 Hz), 7.16–7.18 (m, 2H), 7.22–7.33 (m, 4H). 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.55 (dt, CF₂ JF₂ = 6.4 Hz, JF₂ = 2.0 Hz).

(E)-1,1,1-Trifluoro-4-(3,4-dimethylphenyl)-4-phenylbut-2-ene (2f).

Yield 46 mg, 48%. Colorless solid, mp 67–68 °C (MeOH). H NMR (CDCl₃, 400 MHz) δ ppm: 3.82 (s, 3H, CH₃), 3.87 (s, 3H, CH₃), 4.79 (m, 1H), 5.50 (dqd, 1H, J = 15.6 Hz, JF₂ = 6.3 Hz, J = 1.2 Hz), 6.65 (d, 1H, J = 1.6 Hz), 6.70 (d, 1H, J = 8.2 Hz, J = 1.6 Hz), 6.84 (d, 1H, J = 8.2 Hz), 6.84 (d, 1H, J = 15.6 Hz, J = 6.8 Hz, JF₂ = 2.0 Hz), 7.16 (d, 2H, J = 7.2 Hz), 7.25–7.36 (m, 3H). 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.63 dt (CF₂ JF₂ = 6.3 Hz, JF₂ = 2.0 Hz).

(E)-1,1,1-Trifluoro-4-(3,4-dimethylphenyl)-4-(3-methylphenyl)-but-2-ene (2g).

Yield 46 mg, 48%. Pale yellow oil. H NMR (CDCl₃, 400 MHz) δ ppm: 3.82 (s, 3H, CH₃), 3.82 (s, 3H, CH₃), 4.79 (m, 1H), 5.50 (dqd, 1H, J = 15.6 Hz, JF₂ = 6.3 Hz, J = 1.2 Hz), 6.65 (d, 1H, J = 1.6 Hz), 6.70 (d, 1H, J = 8.2 Hz, J = 1.6 Hz), 6.84 (d, 1H, J = 8.2 Hz), 6.84 (d, 1H, J = 15.6 Hz, J = 6.8 Hz, JF₂ = 2.0 Hz), 7.16 (d, 2H, J = 7.2 Hz), 7.25–7.36 (m, 3H). 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.63 dt (CF₂ JF₂ = 6.3 Hz, JF₂ = 2.0 Hz).
**E-(4-Chlorophenyl)-1,1-trifluoro-4-(4,4-dimethylphenyl)but-2-ene (2h).** Yield 46 mg; 56%. Yellow oil. **1H NMR** (CDCl₃, 400 MHz) δ ppm: 2.18 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 4.93–4.94 (m, 1H), 5.34 (dqd, 1H, J = 15.8 Hz, J₁₂ = 6.3 Hz, J = 1.7 Hz), 6.82 (ddq, 1H, J = 15.8 Hz, J = 5.9 Hz, J₂₃ = 2.0 Hz), 6.91 (d, 1H, J = 8.3 Hz), 7.01 (m, 2H), 7.03 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.4 Hz). **13C NMR** (CDCl₃, 100 MHz) δ ppm: 19.6 (CH₃), 21.1 (CH₃), 48.2 (C₂), 120.7 (q, C₁₃), J²₃ = 36.3 Hz, 123.3 (q, C₁₅, J²₃ = 269.6 Hz), 127.2, 128.3, 129.0, 130.0, 133.6, 136.2, 137.2, 139.1, 142.3 (q, C₁₇, J²₃ = 6.3 Hz). **19F NMR** (CDCl₃, 376 MHz) δ ppm: −63.61 (dt, CF₂Br₂ = 6.3 Hz, J₂₃ = 2.2 Hz). MS (GC–MS–EI), m/z (Irel, %): 324/326 (83/28) [M⁺], 309/311 (100/33), 289 (52), 274 (77), 255 (8), 212 (12), 197 (19), 178 (15), 146 (12), 125 (14), 101 (16), 77 (15), 51 (S). **HRMS (ESI):** C₂₃H₂₁ClF₂O₂ found 357.0865 [M + H]⁺; calcld. 357.0865 [M + H]⁺.

**E-(4-Chlorophenyl)-1,1-trifluoro-4-(3,4-dimethylphenyl)but-2-ene (2j).** Yield 40 mg; 43%. Pale yellow oil. **1H NMR** (CDCl₃, 400 MHz) δ ppm: 2.18 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 4.93–4.94 (m, 1H), 5.34 (dqd, 1H, J = 15.8 Hz, J₁₂ = 6.3 Hz, J = 1.7 Hz), 6.82 (ddq, 1H, J = 15.8 Hz, J = 5.9 Hz, J₂₃ = 2.0 Hz), 6.91 (d, 1H, J = 8.3 Hz), 7.01 (m, 2H), 7.03 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.4 Hz). **13C NMR** (CDCl₃, 100 MHz) δ ppm: 19.6 (CH₃), 21.1 (CH₃), 48.2 (C₂), 120.7 (q, C₁₃), J²₃ = 36.3 Hz, 123.3 (q, C₁₅, J²₃ = 269.6 Hz), 127.2, 128.3, 129.0, 130.0, 133.6, 136.2, 137.2, 139.1, 142.3 (q, C₁₇, J²₃ = 6.3 Hz). **19F NMR** (CDCl₃, 376 MHz) δ ppm: −63.61 (dt, CF₂Br₂ = 6.3 Hz, J₂₃ = 2.2 Hz). MS (GC–MS–EI), m/z (Irel, %): 324/326 (83/28) [M⁺], 309/311 (100/33), 289 (52), 274 (77), 255 (8), 212 (12), 197 (19), 178 (15), 146 (12), 125 (14), 101 (16), 77 (15), 51 (S). **HRMS (ESI):** C₂₃H₂₁ClF₂O₂ found 357.0865 [M + H]⁺; calcld. 357.0869 [M + H]⁺.

**E-(4-Chlorophenyl)-1,1-trifluoro-4-(4-(2,5-dimethylphenyl)but-2-ene (2l).** Yield 40 mg; 47%. Colorless oil. **1H NMR** (CDCl₃, 400 MHz) δ ppm: 2.19 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 4.97–4.98 (m, 1H), 5.37 (dqd, 1H, J = 15.6 Hz, J₁₂ = 6.4 Hz, J = 1.2 Hz), 6.86 (ddq, 1H, J = 15.6 Hz, J = 6.0 Hz, J₂₃ = 2.0 Hz), 6.87 (s, 1H), 7.01 (d, 1H, J = 7.8 Hz), 7.08 (d, 2H, J = 7.8 Hz), 7.36 (d, 2H, J = 7.4 Hz), 7.24–7.34 (m, 3H). **13C NMR** (CDCl₃, 100 MHz) δ ppm: 19.3 (CH₃), 21.3 (CH₃), 49.1 (C₁), 120.5 (q, C₁₇, J²₃ = 33.4 Hz), 123.4 (q, C₁₅, J²₃ = 269.5 Hz), 127.1, 128.0, 128.8, 129.0, 129.1, 130.9, 133.5, 135.9, 139.1, 140.1, 142.8 (q, C₁₃, J²₃ = 6.3 Hz). **19F NMR** (CDCl₃, 376 MHz) δ ppm: −63.69 (dt, CF₂Br₂ = 6.3 Hz, J₂₃ = 2.0 Hz). MS (GC–MS–EI), m/z (Irel, %): 290 (80) [M⁺], 275 (100), 255 (63), 235 (6) (212), 255 (7), 192 (24), 193 (20), 184 (26), 178 (31), 165 (20), 143 (22), 115 (40), 103 (20), 91 (35), 77 (20), 65 (8), 51 (10). **HRMS (ESI):** C₂₃H₂₁F₂O₂ found 357.0865 [M + H]⁺; calcld. 357.0869 [M + H]⁺.

**E-(4-Chlorophenyl)-1,1-trifluoro-4-(4-(2,5-dimethylphenyl)but-2-ene (2n).** Yield 58 mg; 69%. Pale yellow oil. **1H NMR** (CDCl₃, 400 MHz) δ ppm: 2.17 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 4.94–4.95 (m, 1H), 5.35 (dqd, 1H, J = 15.6 Hz, J₁₂ = 6.4 Hz, J = 1.2 Hz), 6.79–6.85 (m, 1H), 6.83 (s, 1H), 7.01–7.09 (m, 4H), 7.29 (d, 2H, J = 4.8 Hz). **13C NMR** (CDCl₃, 100 MHz) δ ppm: 19.3 (CH₃), 21.3 (CH₃), 48.5 (C₁), 120.8 (q, C₁₃, J²₃ = 33.6 Hz), 123.3 (q, C₁₅, J²₃ = 269.5 Hz), 128.2, 128.9, 129.0, 130.3, 130.1, 133.0, 133.2, 136.0, 138.9, 140.2 (q, C₁₇, J²₃ = 6.2 Hz). **19F NMR** (CDCl₃, 376 MHz) δ ppm: −63.59 (dt, CF₂Br₂ = 6.0 Hz, J₂₃ = 2.0 Hz). MS (GC–MS–EI), m/z (Irel, %): 324/326 (87/31) [M⁺], 309/311 (100/33), 289 (43), 274 (20), 255 (24), 212 (12), 197 (19), 184 (26), 178 (31), 165 (20), 143 (22), 115 (40), 103 (20), 91 (35), 77 (20), 65 (8), 51 (10). **HRMS (ESI):** C₂₃H₂₁F₂O₂ found 357.0865 [M + H]⁺; calcld. 357.0869 [M + H]⁺.
rel-(1R,3S)-1-(Trifluoromethyl)-4,7-dimethyl-3-(3-methylphenyl)-indane (cis-3d). Obtained in a mixture with indane cis-3d. C14 H21 F3 Na found 323.1330 [M+Na+]; calcd. 323.1330.

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19F NMR (CDCl₃, 376 MHz) δ ppm: −66.90 (d, CF₂JF₂ = 9.7 Hz). MS (GC-MS, EI), m/z (Irel., %): 318 (50) [M⁺], 304 (100), 286 (22), 197 (5), 158 (17), 89 (1). HRMS (ESI): C₆H₄F₂Na⁺ found 341.1490 [M + Na⁺]; calcld. 341.1493.

19F NMR (CDCl₃, 376 MHz) δ ppm: −69.93 (d, CF₂JF₂ = 9.5 Hz). MS (GC-MS, EI), m/z (Irel., %): 420 (30) [M⁺], 227 (100), 212 (6), 169 (5), 139 (3). HRMS (ESI): C₆H₄F₂O₄ found 431.1829 [M + H⁺]; calcld. 431.1834.

19F NMR (CDCl₃, 376 MHz) δ ppm: −69.93 (d, CF₂JF₂ = 9.5 Hz). MS (GC-MS, EI), m/z (Irel., %): 420 (30) [M⁺], 227 (100), 212 (6), 169 (5), 139 (3). HRMS (ESI): C₆H₄F₂O₄ found 431.1829 [M + H⁺]; calcld. 431.1834.

Yield 52 mg, 60%. Pale yellow oil. 1H NMR (CDCl₃, 400 MHz) δ ppm: 1.90 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 2.28–2.31 (m, 1H), 2.34 (s, 3H, CH₃), 2.98 (dt, 1H, J = 14.3 Hz, J = 10.4 Hz). 13C NMR (CDCl₃, 100 MHz) δ ppm: 16.2 (CH₃), 19.7 (CH₃), 19.8 (q, CF₂JF₂ = 3.4 Hz). 35.6 (q, C₁JF₂ = 19.8 Hz). 47.6 (q, C₁JF₂ = 28.8 Hz). 48.1 (C₁), 127.6 (q, CF₂J₃C₂ = 280.2 Hz). 128.4, 129.4, 131.4, 131.8, 131.9, 133.4, 134.1 (q, CF₂JF₂ = 1.9 Hz). 138.0, 140.3, 144.7. 19F NMR (CDCl₃, 376 MHz) δ ppm: −66.94 (d, CF₂JF₂ = 9.7 Hz). MS (GC-MS, EI), m/z (Irel., %): 318 (50) [M⁺], 304 (100), 286 (22), 197 (5), 158 (17), 142 (5), 129 (7), 117 (7), 105 (5), 91 (5). HRMS (ESI): C₆H₄F₂ClNa⁺ found 341.1488 [M + Na⁺]; calcld. 341.1493.

Yield 52 mg, 70% (from pseudocumene), 40 mg, 45% (from mesitylene). Pale yellow oil. 1H NMR (CDCl₃, 400 MHz) δ ppm: 1.90 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 2.28–2.31 (m, 1H), 2.34 (s, 3H, CH₃), 2.98 (dt, 1H, J = 14.3 Hz, J = 10.4 Hz). 13C NMR (CDCl₃, 100 MHz) δ ppm: 16.2 (CH₃), 19.7 (CH₃), 19.8 (q, CF₂JF₂ = 3.4 Hz). 35.6 (q, C₁JF₂ = 19.8 Hz). 47.6 (q, C₁JF₂ = 28.8 Hz). 48.1 (C₁), 127.6 (q, CF₂J₃C₂ = 280.2 Hz). 128.4, 129.4, 131.4, 131.8, 131.9, 133.4, 134.1 (q, CF₂JF₂ = 1.9 Hz). 138.0, 140.3, 144.7. 19F NMR (CDCl₃, 376 MHz) δ ppm: −66.94 (d, CF₂JF₂ = 9.7 Hz). MS (GC-MS, EI), m/z (Irel., %): 338/340 (69/23) [M⁺], 323/325 (100/35), 303 (15), 269 (20), 254 (7), 226 (12), 143 (5), 101 (10). HRMS (ESI): C₆H₄F₂ClNa⁺ found 361.1514 [M + Na⁺]; calcld. 361.1517.

19F NMR (CDCl₃, 376 MHz) δ ppm: −66.86 (d, CF₂JF₂ = 9.8 Hz). MS (GC-MS, EI), m/z (Irel., %): 334 (73) [M⁺], 319 (73), 303 (10), 250 (8), 226 (100), 211 (11), 157 (23), 142 (9), 125 (15), 89 (6). HRMS (ESI): C₆H₄F₂NClO₄ found 357.1439 [M + Na⁺]; calcld. 357.1442.

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2,5-Bis(E)-4,4,4-trifluoro-1-phenylbut-2-en-1-yl)thiophene (6a). Yield 14 mg, 10%. Yellow oil. 1H NMR (CDCl₃, 400 MHz) δ ppm: 3.92–4.93 (m, 2H), 5.55–5.64 (m, 2H), 6.65 (d, 2H, J = 1.5 Hz), 6.73–6.81 (m, 2H), 7.10–7.22 (m, 4H), 7.29–7.37 (m, 6H). 13C NMR (CDCl₃, 100 MHz) δ ppm: 45.4 (CH₃), 120.3 (q, C′, Jc= 33.7 Hz), 123.1 (q, C′, Jc= 269.7 Hz), 125.7, 125.7, 128.8, 129.1, 140.5, 141.5 (q, C″, Jc= 6.3 Hz), 144.3. 19F NMR (CDCl₃, 376 MHz) δ ppm: 48.1 (CF₃), 46.8 (CF₂), 135.9, 135.9, 138.9, 138.9, 140.8 (q, C″′, Jc= 6.3 Hz), 144.0. 31P NMR (CDCl₃, 202 MHz) δ ppm: 45.2 (m, 1Ph). MS (GC-MS, EI), m/z (Irel., %): 425 (78) [M]+, 357 (99), 267 (100), 183 (82), 165 (40), 133 (10), 115 (36), 91 (25), 77 (12), 45 (13). HRMS (ESI): C₉H₇F₃SδF found 591.0501 [M+Ag]+; calc 591.0509.

2,5-Bis(E)-4,4,4-trifluoro-1-(3-methylphenyl)but-2-en-1-yl)thiophene (6b). Yield 12 mg, 18%. Yellow oil. 1H NMR (CDCl₃, 400 MHz) δ ppm: 2.34 (s, 6H, 2CH₃), 4.87–4.88 (m, 2H), 5.54–5.64 (m, 2H), 6.64 (d, 2H, J = 0.9 Hz), 6.73–6.81 (m, 2H), 7.00–7.04 (m, 4H), 7.11 (d, 2H, J = 7.3 Hz), 7.22–7.25 (m, 2H). 13C NMR (CDCl₃, 100 MHz) δ ppm: 21.6 (CH₃), 48.4 (C′), 120.1 (q, C′′, Jc= 33.7 Hz), 123.2 (q, C′′, Jc= 269.7 Hz), 125.3, 125.5, 125.6, 128.9, 129.0, 138.3, 140.5, 141.6 (q, C″′, Jc= 6.4 Hz), 144.4. 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.808 (m, CF₃), −63.813 (m, CF₂). MS (GC–MS, EI), m/z, (Irel., %): 408 (82) [M]+, 465 (10), 385 (8), 281 (100), 248 (7), 197 (48), 179 (12), 114 (12) (91). HRMS (ESI): C₁₉H₁₉F₃SδF found 587.0417 [M+Ag]+; calc 587.0397.

2,5-Bis(E)-4,4,4-trifluoro-1-(4-methylphenyl)but-2-en-1-yl)thiophene (6c). Yield 28 mg, 42%. Yellow oil. 1H NMR (CDCl₃, 400 MHz) δ ppm: 2.34 (s, 6H, 2CH₃), 4.87–4.88 (m, 2H), 5.54–5.62 (m, 2H), 6.63 (d, 2H, J = 1.4 Hz), 6.72–6.79 (m, 2H), 7.08–7.10 (m, 4H). 13C NMR (CDCl₃, 100 MHz) δ ppm: 21.6 (CH₃), 48.1 (C′), 120.1 (q, C′′, Jc= 33.7 Hz), 125.5 (q, C′′, Jc= 269.7 Hz), 125.4, 125.5, 128.2, 129.7, 137.5, 137.6, 141.7 (q, C″′, Jc= 6.3 Hz), 144.5. 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.80 (m, CF₃), −63.82 (m, CF₂). MS (GC–MS, EI), m/z, (Irel., %): 480 (65) [M]+, 465 (14), 411 (10), 385 (8), 281 (100), 248 (8), 197 (43), 179 (15), 164 (12), 129 (16), 105 (11), 91 (5). HRMS (ESI): C₂₁H₂₁F₃SδF found 587.0408 [M+Ag]+; calc 587.0397.

2,5-Bis(E)-(1-chlorophenyl)-4,4,4-trifluorobut-2-en-1-yl)thiophene (6d). Yield 12 mg, 18%. Yellow oil. 1H NMR (CDCl₃, 400 MHz) δ ppm: 2.34 (s, 6H, 2CH₃), 4.87–4.88 (m, 2H), 5.54–5.58 (m, 2H), 6.68 (d, 2H, J = 1.6 Hz), 6.9 J = 1.1 Hz), 6.65 (d, 2H, J = 2.1 Hz), 6.74 (dd, 2H, J = 1.6 Hz, J = 6.9 Hz), 6.73–6.76 (m, 4H). 7.12–7.15 (m, 4H). 7.31–7.34 (m, 4H). 13C NMR (CDCl₃, 100 MHz) δ ppm: 47.7 (C₁), 120.8 (q, C′, Jc= 33.9 Hz), 123.0 (q, C′, Jc= 269.8 Hz), 125.8, 125.9, 129.3, 129.6, 133.8, 134.9, 140.8 (q, C″, Jc= 6.3 Hz), 144.0. 19F NMR (CDCl₃, 376 MHz) δ ppm: −63.926 (m, CF₃), −63.928 (m, CF₂). MS (GC–MS, EI), m/z, (Irel., %): 520/522/524 (44/31/7) [M]+, 485/487 (12/4), 301/303 (100/38), 266 (8), 217 (31), 183 (9), 164 (22), 149 (9), 115 (10), 45 (6). HRMS (ESI): C₁₉H₁₉F₃SδF found 562.9312 [M+Ag]+; calc 562.9299.

2 ACCESS TO ASSOCIATED CONTENT

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Crystallographic data (CIF)

1H, 13C, and 31P spectra of compounds, X-ray data, and computational details (PDF)

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Notes

The authors declare no competing financial interest.