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Azulenes with aryl substituents bearing pentafluorosulfanyl groups: synthesis, spectroscopic and halochromic properties†

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Four regioisomeric azulenes bearing pentafluorosulfanylphenyl substituents have been prepared and characterised by various spectroscopic techniques. The absorption spectra are qualitatively similar in the visible region for all isomers, but upon protonation exhibit pronounced variation dependent on the connectivity within each molecule.

Introduction

Azulene (1) is a non-alternant, bicyclic aromatic compound that has an intense blue colour. Whilst it is isomeric with naphthalene, it has appreciably different properties such as an unusually large dipole for a hydrocarbon (1.08 D) and a HOMO to LUMO transition in the visible region.† By introducing substituents onto the azulene ring, the absorption spectrum may be perturbed such that a wide range of colours can be produced.‡ Thus, azulene derivatives have been employed as colorimetric sensors for a variety of analytes.§ Azulene derivatives have also found application in photovoltaics¶ and more broadly in organic electronics.¶¶ The azulene motif is also encountered in the context of medicinal chemistry.¶¶ Many azulene derivatives are reported to exhibit halochromism,¶¶ whereby the colour change on protonation may be rationalised in terms of protonation of either a substituent on the azulene, or of the five-membered ring of the azulene itself (Scheme 1). The protonated form contains a 6π e− tropilium cation, hence the seven-membered ring remains aromatic.

Although azulenes have been reported bearing a wide range of substituents (and hence exhibiting a wide range of colours to the naked eye), the pentafluorosulfanyl group remains unexplored in the context of azulene chemistry. Specifically, to our knowledge there have been no reports of azulenes with pentafluorosulfanyl-containing substituents. The SF₅ group, whilst known for many years, has been the focus of increasing research interest in recent years.¶¶ This may be ascribed in part to the commercial availability of SF₅-containing building blocks that were previously hard to access. In the life sciences, SF₅ substituents have been investigated as an alternative to CF₃. The unique combination of characteristics that an SF₅ group can impart includes high thermal, chemical and metabolic stability, a highly electron-withdrawing nature and a significant increase in lipophilicity. An SF₅ group also presents a larger steric demand compared to a CF₃ group. Aryl SF₅ groups in particular are inert to a variety of reaction conditions, including Brønsted acids and bases, hydrogenation and some organometallic reagents. From an environmental standpoint, it has been shown that aryl SF₅ compounds are susceptible to photodegradation¶¶ and can undergo microbial metabolism.¶¶ The SF₅ group has also been investigated in the context of materials chemistry, with reports on liquid crystals,¶¶ polymers,¶¶ and photophysical properties such as triboluminescence and fluorescence.¶¶ Theoretical studies on the SF₅ group have also been disclosed.¶¶

Results and discussion

In the present study, we have synthesised and characterised four novel isomeric azulenes bearing pentafluorosulfanyl/phenyl...
substituents; these have been accessed using cross coupling methodology. Azulene cross coupling methods that employ the azulene-containing substrate as either the nucleophilic or electrophilic cross coupling partner have been developed, as well as C–H activation approaches. We intended to employ commercially available SF₅-aryl bromides 2 and 3 as the electrophilic cross coupling components. Thus, we used the reported Ir-catalysed C–H borylation of azulene to prepare substrates 4 and 5. These underwent Suzuki–Miyaura coupling with 2 and 3, to give target SF₅-phenylazulenes 6–9 (Scheme 2).

Initial attempts at the Suzuki–Miyaura coupling to form 6 employed PPh₃ as the ligand and were unsuccessful. Instead, use of Buchwald’s bulky biaryl monodentate “SPhos” ligand allowed the synthesis of target azulenes 6–9. The products were characterised by various spectroscopic techniques, and the findings are described below.

NMR spectra were acquired for 6–9, and the aromatic region of the ¹H-NMR spectra for the four products are shown in Fig. 1. All spectra have been fully assigned based on data from 2D NMR experiments (see ESI†). The plane of symmetry in isomer 6 gives rise to the simplest of the four spectra. The four proton environments on the azulene ring (H1/3, H4/8, H5/7 and H6, see Scheme 2 for numbering) are observed as a 2H singlet, 2H doublet, 2H double doublet and 1H triplet respectively, this being typical for a 2-substituted azulene. While isomer 7 no longer possesses a plane of symmetry, it is nevertheless still a 2-substituted azulene, and the same multiplicities for the azulene protons are observed as for 6. Indeed, the chemical shifts are near-identical, despite the differing location of the –SF₅ group. For isomers 8 and 9, substitution at the azulene 1-position means the internal plane of symmetry of the azulene core is broken, so 7 distinct azulene proton environments are observed. H4 and H8 were differentiated by means of NOESY correlations between H8 and H2’ for both 8 and 9. For meta-disubstituted isomers 7 and 9, the SF₅ coupling is present for H2’, which is observed as a double doublet (apparent triplet).

In the ³¹F NMR spectra for all four isomers 6–9, the fluorines are observed as a 4F doublet and a 1F quintet. As –SF₅ groups have octahedral geometry at sulfur, the two distinct fluorine environments correspond to the four equatorial and one axial (i.e. trans to carbon) fluorines, respectively. The observed equivalence of the four equatorial fluorines indicates free rotation of the C–S bond on the NMR timescale.

In the ¹H–¹³C-NMR spectra, the SF₅ ipso carbons (C4’ for 6 and 8; C3’ for 7 and 9) exhibit JCF coupling, and the SF₅ ortho carbons (C3/5’ for 6 and 8; C2’/4’ for 7 and 9) exhibit JHF coupling. Due to the presence of four equatorial and one axial fluorine, such coupling would be expected to lead to a quintet of doublets. In fact, all signals in the ¹³C spectra that exhibit splitting are simply quintets, i.e. only coupling to the equatorial fluorines is observed. The JCF couplings are in the range 16.5–16.9 Hz, whereas the JHF couplings are 4.2–4.9 Hz. A survey of ¹³C-NMR data for reported SF₅-containing compounds shows that such quintet splittings are commonly observed. The lack of doublet splitting is often not discussed; it has been stated that for the axial fluorine, values of JCFax < 2 Hz and JHFax < 1 Hz are typical, and so such coupling is often not observable.

Of the four isomers, we were able to grow crystals of 7 of sufficient quality for analysis by X-ray diffraction. The structure obtained is shown in Fig. 2. Azulene 7 crystallised in the monoclinic space group P2₁/c. The dihedral angles between the azulene and the phenyl ring are appreciably different for the two molecules in the unit cell, being 8.3(5)° and 22.6(5)° respectively. The FCF₅-S-C dihedral angles are 38.4(3)° and 44.5(3)°, with the equatorial fluorines staggered with respect to the phenyl ring. C–S bond lengths are 1.802(3) Å and 1.804(3) Å. The geometry at sulfur is slightly distorted away from a perfect octahedron; the equatorial fluorine atoms of the SF₅ group adopt an “umbrella” shape, canting toward the axial fluorine with FCF₅-S-F₅ angles less than perpendicular (in the range 87.2(1)° to 87.7(1)°). All these observations are in keeping with those previously reported for other aryl-SF₅ molecules.

Fig. 3 shows the packing arrangement in the unit cell to be of a herringbone pattern. The two molecules in the unit cell are...
aligned in a head-to-head fashion, but they are not coplanar. Rather the two planes defined by the seven-membered rings of the two azulenes intersect at an angle of 60.0° (see ESI†).

UV-visible region absorption spectra for 6–9 were acquired in CH₂Cl₂, and the data for the visible region are shown in Fig. 4 (see ESI† for full data). The solutions of the four isomers are very similar in colour. In the visible region 6–9 all have the greatest absorbance in the green-to-red region, hence appear to be blue. Azulenes often exhibit halochromic behaviour, and upon adding excess trifluoroacetic acid to the solutions of 6–9, spectroscopic changes were observed. For the azulenes substituted at the 1-position (8 and 9), an increase in absorbance between 600–700 nm was noted; this was most pronounced for 9, with the appearance of a new absorbance maximum at λₘₐₓ = 636 nm. This resulted in only a subtle colour change (Fig. 5). In contrast, protonation of 6 and 7 resulted in pronounced colour changes, the solutions turning yellow-brown and red, respectively. This may be attributed to the appearance of new absorbance peaks in the blue region (peak at λₘₐₓ = 409 nm for 6, and a shoulder approximately the same wavelength for 7).

Although 6–9 differ only in their positions of substitution (that is to say, they are isomers), they differ markedly in their spectroscopic responses to Brønsted acid. There are precedents for this phenomenon. Wang, He and co-workers have studied azulenes bearing thienyl substituents;23 Hawker and co-workers have studied azulenes bearing diketopyrrolopyrrole substituents;24 and Murai, Takai and co-workers have studied analogues of 6 and 8 with a –CF₃ group in the place of the –SF₅ group.25 In each case a more significant change in absorption maxima (and hence colour) is observed for the isomer with the substituent(s) aligned with...
(instead of orthogonal to) the dipole of the azulene core, i.e. at the azulene 2-position.

To gain further insight into the properties of 6–9, the structures were modelled by DFT, using the BP86 functional. Both the neutral and protonated structures were modelled in the gas phase and then corrected for dispersion and a dichloromethane solvent environment (see ESI† for full computational details). For [8 + H]⁺ and [9 + H]⁺, protonation at either the azulene 1-position or 3-position would give rise to a tropylium cation, as per Scheme 1. Both regioisomeric cations were modelled, and for both [8 + H]⁺ and [9 + H]⁺, the isomer protonated at the 3-position was found to be the more stable by 3.9 kcal mol⁻¹. The alternative of protonation at the 1-position involves rehybridisation of C1 to sp³, and hence conjugation between the seven membered ring and the phenyl substituent is lost (see ESI†). The cases of [6 + H]⁺ and [7 + H]⁺ are more straightforward, since the site of protonation is unambiguous. Of the four (neutral) isomers 6–9, the most stable were 2-substituted isomers 6 and 7, having the same free energy, whereas 8 and 9 were higher in free energy by 1.0 and 1.1 kcal mol⁻¹, respectively. For the corresponding protonated structures, larger free energy differences were calculated. [7 + H]⁺ was found to be the most stable isomer, with [6 + H]⁺ higher in free energy by 0.6 kcal mol⁻¹. In contrast, the 1-substituted isomers [8 + H]⁺ and [9 + H]⁺ were +4.1 and +3.9 kcal mol⁻¹ above [7 + H]⁺, respectively.

Table 1  Computed HOMO and LUMO energies [eV] for SF₅ substituted azulene species 6–9, and dipole magnitude (Debye, D)

<table>
<thead>
<tr>
<th></th>
<th>E_HOMO</th>
<th>E_LUMO</th>
<th>ΔE_LUMO-HOMO</th>
<th>Dipole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>−5.093</td>
<td>−3.157</td>
<td>1.936</td>
<td>6.30</td>
</tr>
<tr>
<td>7</td>
<td>−5.051</td>
<td>−3.170</td>
<td>1.880</td>
<td>5.43</td>
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<tr>
<td>8</td>
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<td>−3.087</td>
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<tr>
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<td>−4.980</td>
<td>−3.113</td>
<td>1.867</td>
<td>6.13</td>
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<tr>
<td>Protonated</td>
<td></td>
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<tr>
<td>[6 + H]⁺</td>
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<td>−7.525</td>
<td>2.022</td>
<td>20.63</td>
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<tr>
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<td>−7.472</td>
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<td>−9.603</td>
<td>−7.735</td>
<td>1.869</td>
<td>21.15</td>
</tr>
</tbody>
</table>

The calculated frontier molecular orbitals for 6–9 are shown in Fig. 6. It can be seen that for the 2-substituted azulenes 6 and 7, the HOMO is localised entirely on the azulene ring system; the positions of the orbital lobes and nodes are extremely similar to those of azulene (1) itself.26 For the 1-substituted azulenes 8 and 9, the HOMO also extends onto the phenyl ring. In contrast, the LUMOs of 7, 8 and 9 are localised primarily on the SF₅ substituent. The only isomer having C₂ symmetry, 6, has a LUMO that deviates from this trend, with the orbital lobes and nodes on the azulene rings of 6 again resembling those of the corresponding MO of the parent unsubstituted azulene 1. The MOs of the protonated forms were also determined (see ESI†). The calculated HOMO and LUMO energies for 6–9 and their protonated forms, as well as their calculated dipole moments, are shown in Table 1.

The electrochemical behaviour of 6–9 was studied using cyclic voltammetry to determine the oxidation potentials (Fig. 7). All cyclic voltammograms (CVs) were acquired in dry acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte, at a scan rate of 100 mV s⁻¹ (see ESI† for full details). Three scans were taken for each run (the CVs in Fig. 7 show plots for the first and third scans only). The small quantities of 6 and 8 available necessitated that these CVs were acquired at a lower concentration than for 7 and 9. All four isomers exhibited an oxidation peak in the first scan; key electrochemical parameters...
In contrast to the above, the CVs for 8 and 9 show scans 1 and 3 to be essentially identical. Being substituted at the azulene 1-position, 8 and 9 would not be expected to be good substrates for electropolymerisation, as the azulene 1- and 3-positions are where the union of monomers usually occurs. Nevertheless, it seems the oxidised forms of 8 and 9 also do not decompose to give other electrochemically active products. We have previously studied the characteristics of azulenes that exhibit such superimposable CVs and have found that some substituents at the azulene 1-position can confer stability on the radical cation. Such a characteristic is potentially beneficial for the application of azulene derivatives in various contexts such as photovoltaics and organic electronics. However, this effect is not general for all groups at the azulene 1-position, so the identification of m- and p-pentafluorosulfonylphenyl as substituents having this effect may be significant.

It is illuminating to compare the data we have gathered for 6–9 with literature data on analogues of 6–9 bearing other electron-withdrawing groups in the place of the –SF5 group. As described in the Introduction, in many cases SF5-containing compounds have been compared with their CF3 analogues, with various differences in their properties being noted. In the present case, –CF3 analogues have previously been reported for 6, 7, 8, 9, 15a,16d. The halochromic properties have been studied for the –CF3 analogues of 6 and 8, with the same trend being observed in both cases: no significant colour change upon protonation of 8 or its –CF3 analogue, but a significant colour change upon protonation of 6 or its –CF3 analogue. For 6 the new peak with \( \lambda_{\text{max}} = 409 \text{ nm} \) leads to a brown colour, whereas for its –CF3 analogue a reported new peak with \( \lambda_{\text{max}} = 427 \text{ nm} \) leads to a yellow colour. The only data reported for all four –CF3 analogues are NMR data, which may be compared with the data for 6–9. For instance, the \(^1\)H-NMR spectrum of 6 and its –CF3 analogue are almost identical, with the only significant difference being that the –SF5 ortho protons are more deshielded than those in the –CF3 analogue (\( \Delta \delta \) 0.12 ppm). The same trend is observed when comparing 7–9 with their respective –CF3 analogues—the chemical shifts of the azulenyln protons hardly vary, and only the protons on the phenyl ring show any significant changes. This indicates that while the –SF5 group exerts a greater inductive electron-withdrawing effect than the –CF3 group, and hence perturbs the chemical shifts of the phenylene protons, it is too far removed to influence significantly the shielding of the azulenyln protons. A second informative comparison is between 6 and 8 and their nitro analogues. (Comparisons cannot be made for 7 and 9 as their nitro analogues have not been reported.) Here, the \(^1\)H-NMR spectra of the nitro analogues exhibit significantly more deshielded phenyl protons, as a consequence of the mesomeric and inductive electron-withdrawing effect of the nitro group. Some minor changes to the chemical shifts of the azulenyln protons is too far removed to influence significantly the shielding of the azulenyln protons. A second informative comparison is between 6 and 8 and their nitro analogues. In these cases,
while the phenyl proton resonances differ significantly in the presence or absence of the SF₅ group, the variations in the chemical shifts of the azulenyl protons are again minor (Δδ values between 0.01 and 0.08 ppm are observed for the various positions on the azulene rings). Considering the above observations as a whole, it appears that for phenylazulenes the presence of an electron withdrawing group on the phenyl ring greatly influences the electronics of the phenyl ring, but its effect on the electronics of the azulene ring is attenuated in comparison.

Conclusions

In summary, we have synthesised and characterised the first azulene derivatives containing pentafluorosulfanylphenyl groups. These were accessed in one step from known azulenylboron species 4 and 5, by coupling with commercially available SF₅-containing bromoarenes 2 and 3. Ordinarily, the absorption spectra of azulene derivatives are usually profoundly influenced by the nature and position of the substituents on the azulene rings. However, in the present case the absorption spectra of isomers 6–9 are all very similar in the visible region. The spectroscopic response of isomers 6–9 to protonation varies appreciably, with significant absorbances in the blue region for [6 + H⁺] and [7 + H⁺] leading to observable changes in colour.

The fact that 6 and 7 exhibit a response to a stimulus (increase in [H⁺]) is suggestive of possible applications in chemical sensing. The pattern of the 2-substituted azulenes 6–7 having differing characteristics to the 1-substituted azulenes 8–9 was also observed in the electrochemical study, where 6 and 7 underwent electropolymerisation, but 8 and 9 did not. We anticipate that the commercial availability of an increasing number of SF₅-containing building blocks will allow for the preparation of further SF₅-containing azulenes with time.

Experimental

General synthetic methods

Reactions were carried out under an atmosphere of nitrogen unless stated otherwise. Petrol refers to petroleum ether, bp 40–60 °C. TLCs were performed using aluminium-backed plates precoated with Alugram® SIL G/UV or aluminium backed plates precoated with Alugram® ALOX N/UV 254 nm and visualised by UV light (254 nm) and/or curcumin followed by gentle warming. All solvents used in Suzuki–Miyaura couplings were dried by UV light (254 nm) and/or curcumin followed by gentle warming. All solvents used in Suzuki–Miyaura couplings were washed with pentane, then ethyl acetate. In instances additional chromatography was required, eluting with pentane, then ethyl acetate.

General procedure for Suzuki–Miyaura couplings

To a degassed solution of azulenylboronate 4 or 5 (1.0 eq.) and pentafluorosulfanyl aryl bromide 2 or 3 (2.0 eq.) in dioxane (5.0 mL), were added K₂CO₃ (1.5 eq.), Pd(OAc)₂ (5 mol%) and SPhos (10 mol%). The resulting mixture was heated at 80 °C under an N₂ atmosphere. The reaction mixture was allowed to cool and CH₂Cl₂ (50 mL) and water (25 mL) were added, transferred to a separating funnel and shaken. The organic layer was separated, washed with water (2 × 25 mL), and then the combined aqueous extracts were back extracted with CH₂Cl₂ (50 mL). The combined organic layers were washed with brine (25 mL), and passed through phase separating filter paper, and the solvent removed under reduced pressure. Purification of the crude product was carried out using silica column chromatography with petrol and ethyl acetate (9:1) as eluent. In some instances additional chromatography was required, eluting with pentane, then ethyl acetate.

(4-(Azulen-2-yl)phenyl)pentafluoro-λ⁵-sulfane (6). The general procedure was employed, using 4 (23 mg, 0.089 mmol), 2 (50 mg, 0.18 mmol) K₂CO₃ (18 mg, 0.13 mmol), Pd(OAc)₂ (1 mg, 0.004 mmol) and SPhos (4 mg, 0.009 mmol) for 21 h, to give 6 as a blue oil (15 mg, 0.045 mmol, 51%). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.34 (2H, J = 9.6 Hz), 8.00 (2H, d, J = 8.4 Hz), 7.83 (2H, d, J = 8.8 Hz), 7.67 (2H, s), 7.58 (1H, t, J = 9.9 Hz), 7.21 (2H, app t, J = 9.7 Hz); ¹³C (126 MHz, CDCl₃) δ (ppm) 153.3 (p, J = 16.7 Hz) 147.2, 141.4, 140.0, 137.8, 137.3, 127.7, 126.7 (p, J = 4.5 Hz), 124.3, 114.9; ¹⁹F NMR (471 MHz, CDCl₃) δ (ppm) 84.8 (1F, p, J = 150.4 Hz), 63.0 (4F, d, J = 150.4 Hz); IR (neat) 2962, 1575, 1404, 1213, 1098, 820, 800, 737 cm⁻¹; ASAP-MS (+ve) m/z caled for [C₁₆Hₑ₁F₅S]+ 330.0496; found 330.0505; caled for [C₁₆H₁₁F₅S + H]+ 331.0574; found 331.0580.

(3-(Azulen-2-yl)phenyl)pentafluoro-λ⁵-sulfane (7). The general procedure was employed, using 4 (23 mg, 0.089 mmol), 3 (50 mg, 0.18 mmol) K₂CO₃ (18 mg, 0.13 mmol), Pd(OAc)₂ (1 mg, 0.004 mmol) and SPhos (4 mg, 0.009 mmol) for 22 h, to give 7 as a blue solid (13 mg, 0.039 mmol, 44%). m. p. 240–242 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 8.34 (2H, d, d, J = 9.6 Hz), 8.31 (1H, app t, J = 1.9 Hz), 8.07 (1H, d, J = 7.7 Hz), 7.72 (1H, dd, J = 8.3, 2.2 Hz), 7.67 (2H, s), 7.59 (1H, t, J = 9.5 Hz), 7.55 (1H, app t, J = 8.0 Hz), 7.22 (2H, app t, J = 9.7 Hz); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 154.9 (p, J = 16.8 Hz), 147.6, 141.5, 137.8, 137.6,
137.1, 130.5, 129.3, 125.3 (p, J = 4.4 Hz), 125.1 (p, J = 4.2 Hz), 124.3, 114.6. 1H NMR (471 MHz, CDCl3) δ 84.6 (1F, p, J = 150.8 Hz), 62.6 (4F, d, J = 150.3 Hz). IR (neat) 2922, 2853, 1571, 1535, 1463, 1452, 1420, 914, 890, 817, 737 cm⁻¹; ASAP-MS (+ve) m/z calcd for (C16H11F5S)+, 330.0496; found 330.0501; calcd for (C16H11F5S+ + H)+, 331.0574; found 331.0580.

(4-(Azulen-1-yl)phenyl)pentfluoro-λ6-sulfane (8). The general procedure was employed, using 3 (31 mg, 0.12 mmol), 2 (69 mg, 0.24 mmol), K2CO3 (25 mg, 0.18 mmol), Pd(OAc)2 (1.4 mg, 0.0061 mmol) and SPhos (5 mg, 0.012 mmol) for 17 h to give 8 as a blue oil (9 mg, 0.027 mmol, 22%). 1H NMR (500 MHz, CDCl3) δ 135.9, 135.4, 129.6, 128.9, 126.4 (ppm) 152.1 (p, J = 9.5 Hz), 7.237 (1H, app t, J = 9.3 Hz), 7.46 (1H, d, J = 3.9 Hz), 7.243 (1H, app t, J = 9.5 Hz), 7.20 (1H, app t, J = 9.5 Hz); 13C NMR (126 MHz, CDCl3) δ (ppm) 85.4 (1F, p, J = 150.4 Hz), 62.8 (4F, d, J = 150.1 Hz), 8.03 (1H, d, J = 3.9 Hz), 8.01 (1H, app t, J = 1.9 Hz), 7.77–7.73 (2H, m), 7.66 (1H, t, J = 9.9 Hz), 7.58 (1H, t, J = 8.0 Hz), 7.47 (1H, d, J = 3.9 Hz), 7.24 (2H, app t, J = 9.9 Hz); 13C NMR (126 MHz, CDCl3) δ (ppm) 154.5 (p, J = 16.5 Hz), 142.1, 138.8, 138.7, 137.9, 137.2, 135.7, 135.2, 129.1, 129.0, 127.1 (t, J = 4.6 Hz), 124.3, 124.00, 123.6 (p, J = 4.7 Hz), 117.9; 15N NMR (471 MHz, CDCl3) δ (ppm) 84.8 (1F, p, J = 150.0 Hz), 62.8 (4F, d, J = 149.7 Hz); IR (neat) 2965, 2925, 2857, 1601, 1576, 1395, 822, 792, 777, 743, 691, 662, 647 cm⁻¹; ASAP-MS (+ve) m/z calcd for (C16H11F5S)+, 330.0496; found 330.0503; calcd for (C16H11F5S+ + H)+, 331.0574; found 331.0577.

Conflicts of interest

There are no conflicts to declare.

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