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ORIGINAL PAPER

Incorporation of the pentafluorosulfanyl group through common synthetic transformations

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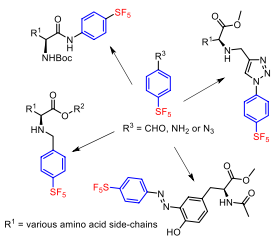
Abstract

The incorporation of $–SF_5$ group onto model amino acids has been achieved using commercially available synthons substituted with this group. This work investigates the influence of the $–SF_5$ group on a variety of common synthetic transformations utilized in fields of bioconjugation and drug development, namely, amide coupling, reductive amination, diazo-coupling, and CuAAC "click" reactions. The influence of the novel substituent on the success of these common transformations is presented, and alternative approaches for those which proved unsatisfactory are proposed herein.

Graphic abstract



Keywords Amines · Amino acids · Carboxylic acids · Michael addition · Drug research

Introduction

The $–SF_5$ group has remained largely unexplored in the literature, since its first reported synthesis by Silvey and Cady in 1950, likely due to concerns of the group's stability and the scarcity of $–SF_5$ synthetic building blocks [1]. However, in recent years, reports highlighting its unique physicochemical profile have renewed interest in the substituent.

The $–SF_5$ group demonstrates high chemical stability, resistant to hydrolysis under both strong acidic and basic conditions. Regarding steric demand, the $–SF_5$ group occupies a volume (49.2 cm^3 mol^{-1}), 1.5-fold that of the $–CF_3$ group and only slightly smaller than that of the *tert*-butyl group [2]. Much like the $–CF_3$ group, the presence of the multiple fluorine atoms renders it highly polar; for example, phenyl sulfur pentafluoride exerts a dipole moment of 3.44 Debye [3]. This dipole moment provides the group with a strong inductive electron-withdrawing effect. Despite this polarity, the $–SF_5$ group is also highly lipophilic with a hydrophobicity constant of $\pi = 1.51$, relative to the $–CF_3$ group with a hydrophobicity constant of $\pi = 1.09$ [4].

The $–SF_5$ groups' unique physicochemical parameters have resulted in its application within several fields, particularly medicinal chemistry as a $–CF_3$ alternative, affording numerous $–SF_5$ drug analogues with improved biological

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activities [5–9]. Furthermore, our group has recently discovered that the $–SF_5$ group, when incorporated on *para*- and *meta*-substituted nitroarenes, is capable of undergoing [^{18}F]\[^{19}F] radioisotopic exchange, suggesting its potential as a stable [^{18}F]F radiosynthon for application in Positron Emission Tomography [10].

A variety of reactions utilising both aryl and heterocyclic $–SF_5$ derivatives have been investigated previously, including traditional and vicarious nucleophilic aromatic substitution [11, 12], azo-coupling, dediazoniation, click chemistry, Sonogashira [13] and Negishi coupling [14], and Diels–Alder additions [15–17].

Current knowledge surrounding the $–SF_5$ group and its potential application remains very much in its infancy, indicating a significant gap in current literature. A more holistic understanding of the $–SF_5$ group influences on various commonly used synthetic transformations would provide valuable information for future research endeavours concerning the $–SF_5$ group. In this work, the effect of the aryl $–SF_5$ moiety on amide coupling, reductive amination, azo-coupling, and CuAAC "click" reactions have been investigated, to ascertain their feasibility as methods for incorporating aryl–SF_5 group into drugs and biomolecules.

Results and discussion

Pentafluorosulfanyl aniline in amide coupling

Amide coupling reactions have been applied extensively for the synthesis and modification of peptides, and are the most utilized transformation in the pharmaceutical industry [18]. In this work, *N*-BOC-protected model amino acids were used as carboxylic acid substrates for investigating the nucleophilicity of 4-(pentafluorosulfanyl)aniline in the context of amide coupling reactions. Amide coupling was first performed using HOBt and EDCI·HCl as coupling reagents, as shown in Scheme 1 (method a). Amide coupling products synthesized by this method were obtained as viscous yellow oils in relatively low yield (15–26%) following purification by column chromatography (Table 1).

Amide coupling reactions were monitored via TLC. Successful syntheses were confirmed by ^{1}H NMR spectra and with HRMS. ^{19}F NMR was used to ensure that the $–SF_5$ group had been conserved under the reaction conditions employed. A representative ^{19}F NMR spectrum of compound **3a** (Fig. 1) shows resonances at $\delta = 85.03$ and 63.40 ppm as a quintuplet and doublet, respectively. The resonances are indeed indicative of the $–SF_5$ group's presence [19].

The use of dimethylformamide (DMF) as a solvent was necessary to completely solubilise each compound in the reaction mixture, consequently, extensive washing of the reaction mixture to partition DMF, EDCI·HCl, and the *N*-acylurea by-product into the aqueous phase may have resulted in minor product loss. Employing alternative water-immiscible solvents such as dichloromethane could improve product recovery. However, this may be detrimental to the reaction itself [20].

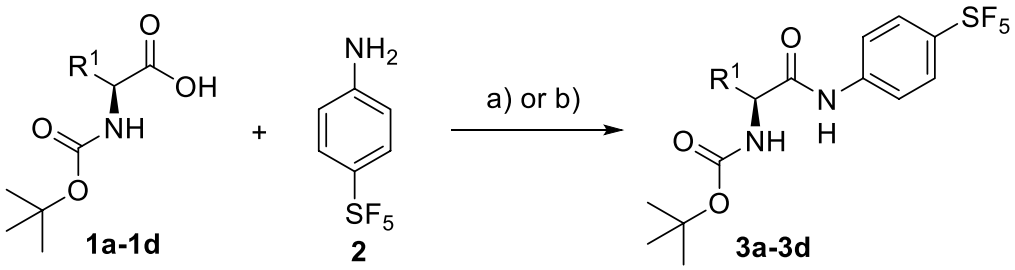
The progress of each reaction was monitored by TLC, which revealed the presence of unreacted amine precursor. Despite being the limiting reagent, unreacted aniline was present beyond 18 h of reaction. This occurrence was attributed to the slow consumption of the remaining amino acid

Table 1 Respective yields obtained of amide coupling products **3a**–**3d**

3	Amino acid R^1	Yield/%[a]	Yield/%[b]
a	Phe	19	44
b	Ala	15	36
c	Trp	26	38
d	Pro	21	41

[a]HOBt, EDCI·HCl, DMF, 18 h, r.t. [b]TMOS, PhMe, 36 h, 110 °C

Scheme 1



R^1 = Unique amino acid side chain

a) HOBt, EDCI·HCl, DMF, 18 h, r.t. b) TMOS, PhMe, 36 h, 110 °C.

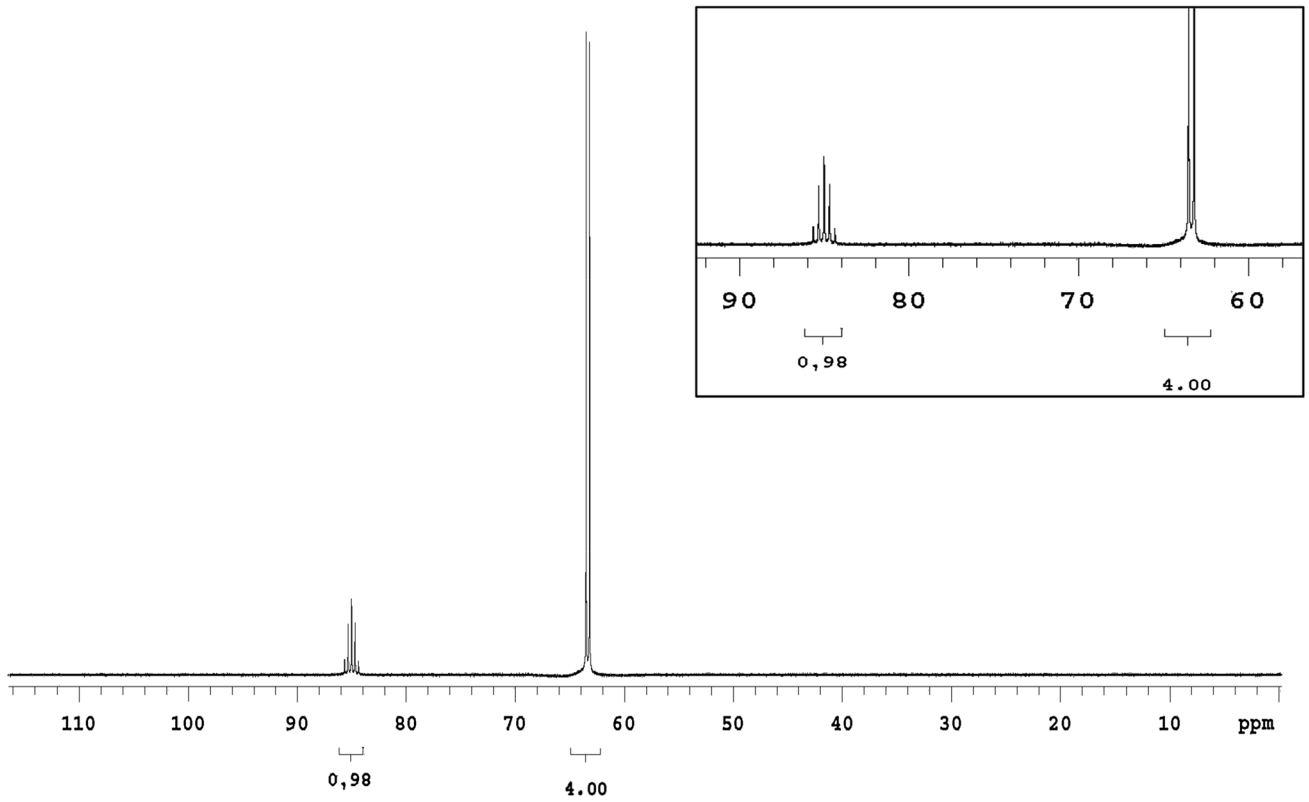


Fig. 1 ^{19}F NMR of compound **3a**, showing resonances at $\delta = 85.03$ and 63.40 ppm as a quintuplet and doublet, respectively

precursor available for coupling through competitive side reactions, namely the formation of the *N*-acylurea by-product. In typical HOBt/EDCI coupling reactions, the amine is sufficiently nucleophilic to outcompete EDCI·HCl before its rearrangement into the *N*-acylurea. However, it is not the case for this reaction, as the electron-withdrawing effect of the $–SF_5$ group is likely to have hindered the reactivity of the amine. The poor yields obtained by this method warranted the investigation of alternative synthetic approaches towards the desired products.

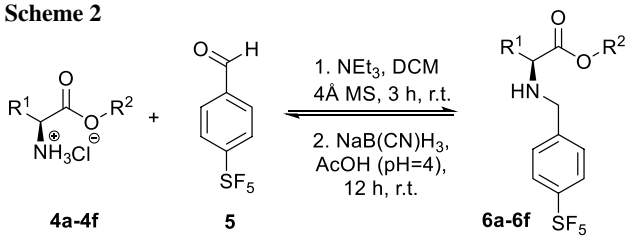
To further optimise the synthesis of compounds **3a**–**3d**, tetramethyl orthosilicate (TMOS) was investigated as a coupling reagent as recently demonstrated by Braddock et al. [21]. This method (method b) was attractive because of its ability to facilitate amide coupling with electron-poor aniline derivatives. To further maximise coupling efficiency, reactions were conducted in high concentrations using toluene as a solvent and heated to reflux in the presence of a 2.5 molar equiv. of TMOS.

Completely anhydrous conditions were required to avoid hydrolysis of the *N*-Boc group, particularly given the reaction requirement for high temperatures and prolonged reaction times. Reflux of the reaction mixture at 110 °C, with a large excess of TMOS and under a nitrogen atmosphere, proved effective for minimising the occurrence of competitive hydrolysis. Yields obtained for amide coupling products using the TMOS method were a substantial improvement over the EDCI/HOBT coupling method (36–44%) mentioned previously. Furthermore, unlike the HOBt/EDCI case, the TMOS process does not generate by-products such as the *N*-acylurea; therefore, reaction times could be extended to 36 h without the occurrence of precursor-consuming side reactions. A 36 h reaction time was necessary based on the poor nucleophilicity of 4-(pentafluorosulfanyl)aniline (**2**), and this parameter was used with all the amino acid substrates. Longer reaction times were not employed as TLC analysis of the crude mixtures started to reveal the formation of other by-products, likely attributed to either hydrolysis or thermal decomposition.

Pentafluorosulfanyl benzaldehyde in reductive aminations

Similarly, to the previously described amide coupling reaction, model amino acids were used as amine-bearing substrates to investigate the reactivity of 4-(pentafluorosulfanyl)-benzaldehyde in reductive amination reactions under typical conditions. Reductive amination was achieved through the condensation of 4-(pentafluorosulfanyl)benzaldehyde with several C-protected amino acid esters. The subsequent imine

Scheme 2



R^1 = Unique amino acid side chain
R^2 = Ester protective group

Table 2 Respective yields obtained of reductive amination products **6a–6f**

6	Amino acid R^1	R^2	Yield/%
a	Gln	*t*-Bu	77
b	Tyr	Me	81
c	Ser	Bz	69
d	Cys	Et	72
e	Trp	Me	67
f	Pro	Bz	82

intermediates were reduced using $NaB(CN)H_3$ under mildly acidic conditions to yield the respective secondary amine products, as shown in Scheme 2. Reductive amination reactions afforded seven novel amino acid analogues in modest-to-high yields (Table 2). Reductive amination products were all obtained as viscous oils, except **6d** which rapidly dimerised upon exposure to air to form a light-yellow solid. Products **6a**, **6b** formed white crystalline solids after prolonged storage.

To approximately assess the by-product formation, reaction mixtures were monitored by TLC, all of which indicated an absence of aldehyde precursor after 2.5 h. Reaction times were extended from 40 min to 3 h to maximise imine formation. Additionally, 4 Å molecular sieve was employed to remove water from the reaction mixture, thereby promoting equilibriums favourability towards the desired imine product. These synthetic modifications also proved successful in minimising the generation of benzyl alcohol by-product.

The L-tryptophan derivative was obtained with the lowest yield among the reductive amination products, on account of the imine intermediates participation in a Pictet–Spengler side reaction through tryptophan's imidazole ring. The addition of acid to the reaction mixture is necessary to ensure protonation of the imine and subsequent hydride attack. However, in the case of L-tryptophan methyl ester, the addition of acid has a catalytic effect promoting a Pictet–Spengler side reaction (Scheme 3). To minimise the occurrence of the 1,2,3,4-tetrahydro-*β*-carboline by-product, the reductive amination reactions were performed in a step-wise procedure whereby the imine was first allowed to form in situ as indicated by TLC. At that point, acetic acid and sodium cyanoborohydride were added to the reaction mixture in rapid succession to minimise the time that the imine spends in its protonated state prior to reduction. This ensured a maximal proportion of the iminium ion salt underwent reduction rather than acid catalyzed cyclisation through tryptophan's imidazole ring.

This side reaction is likely to have been promoted by the high electrophilicity of the transient imine carbon resulting from the $-SF_5$ groups electron-withdrawing effect. This effect is evident from the work of Wang et al. [22], who investigated the use of 1,1,1,3,3,3-trifluoroisopropyl alcohol as a catalytic solvent for the synthesis of 1,2,3,4-tetrahydro-*β*-carbolines. From this research, it was observed that when aromatic aldehydes bearing electron-withdrawing groups, such as 4-nitro, underwent condensation with L-tryptophan methyl ester, 1,2,3,4-tetrahydro-*β*-carbolines were obtained exclusively. On the other hand, aldehydes bearing donating groups in the *para* position, such as 4-methoxybenzaldehyde, demonstrated exclusive favourability for the alternative imine product.

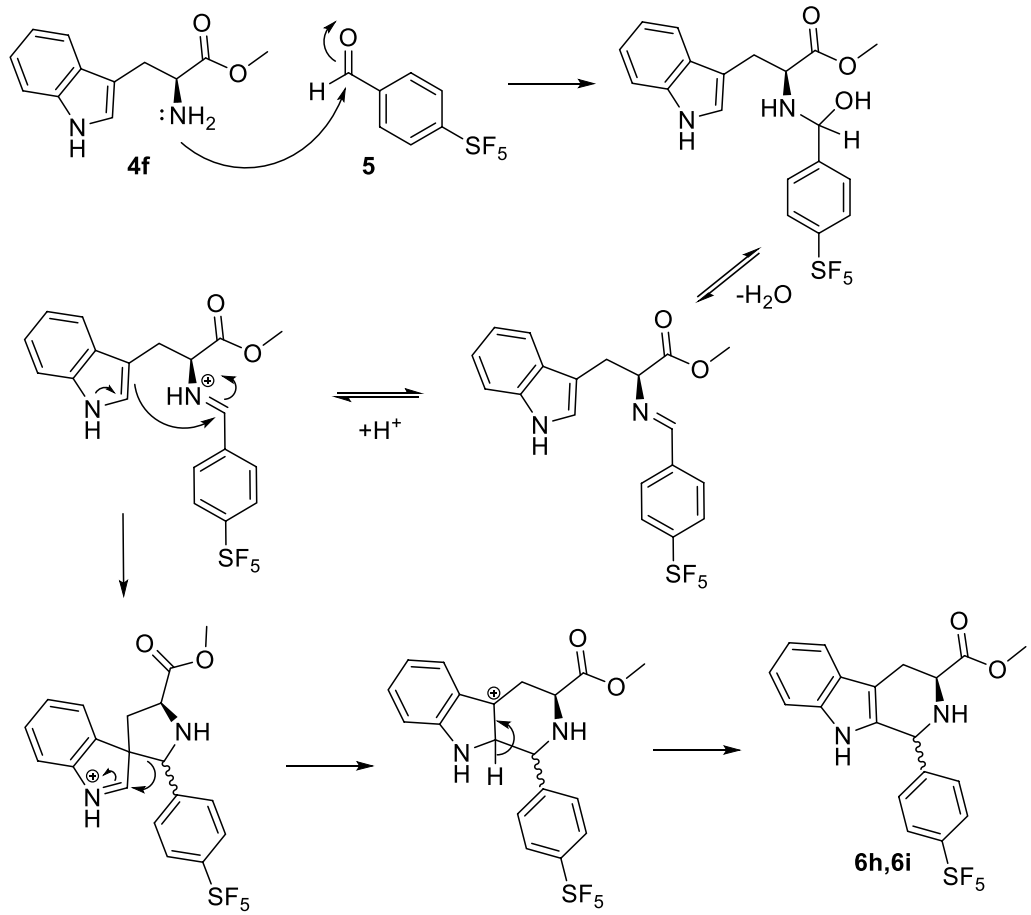
An alternative approach to amine functionalisation was also investigated using pentafluorosulfanyl ethene, originally believed to be capable of undergoing a Michael addition owing to the electron-withdrawing effect of the $-SF_5$ group. However, this withdrawing effect occurs inductively rather than through a resonance-based modality. Thus, ethene sulfanyl pentafluoride is incapable of forming the resonance stabilised carbanion intermediate required for a Michael addition to occur.

Pentafluorosulfanyl phenylazide for CuAAC

The Cu-catalyzed Azide–Alkyne Cycloaddition (CuAAC) has been used extensively as a bioconjugation method, on account of its impressive selectivity and reaction rate. Additionally, the 1,4-triazole rings function as an amide bioisostere, allowing for the biologically discrete modification of peptides, thus warranting the investigation of 4-(pentafluorosulfanyl)phenyl azide and the feasibility for its application in CuAAC reactions. Ye et al. [23] have reported the CuAAC reaction between gaseous 1-pentafluorosulfanyl acetylene and phenyl azide, obtaining the subsequent 1,4-triazole in 83% yield. In future, we would also like to investigate 4-(pentafluorosulfanyl)phenylacetylene and its participation in CuAAC reactions with various azides.

In this work, the CuAAC reaction was performed between methyl (2*S*)-3-phenyl-2-[(prop-2-yn-1-yl)amino]propanoate (**8**) and 4-(pentafluorosulfanyl)phenyl azide (**10**) using $Cu(OAc)_2$ and sodium ascorbate as catalysts (Scheme 4). Compound **8** was obtained by *N*-alkylation of L-phenylalanine methyl ester with propargyl bromide.

Scheme 3



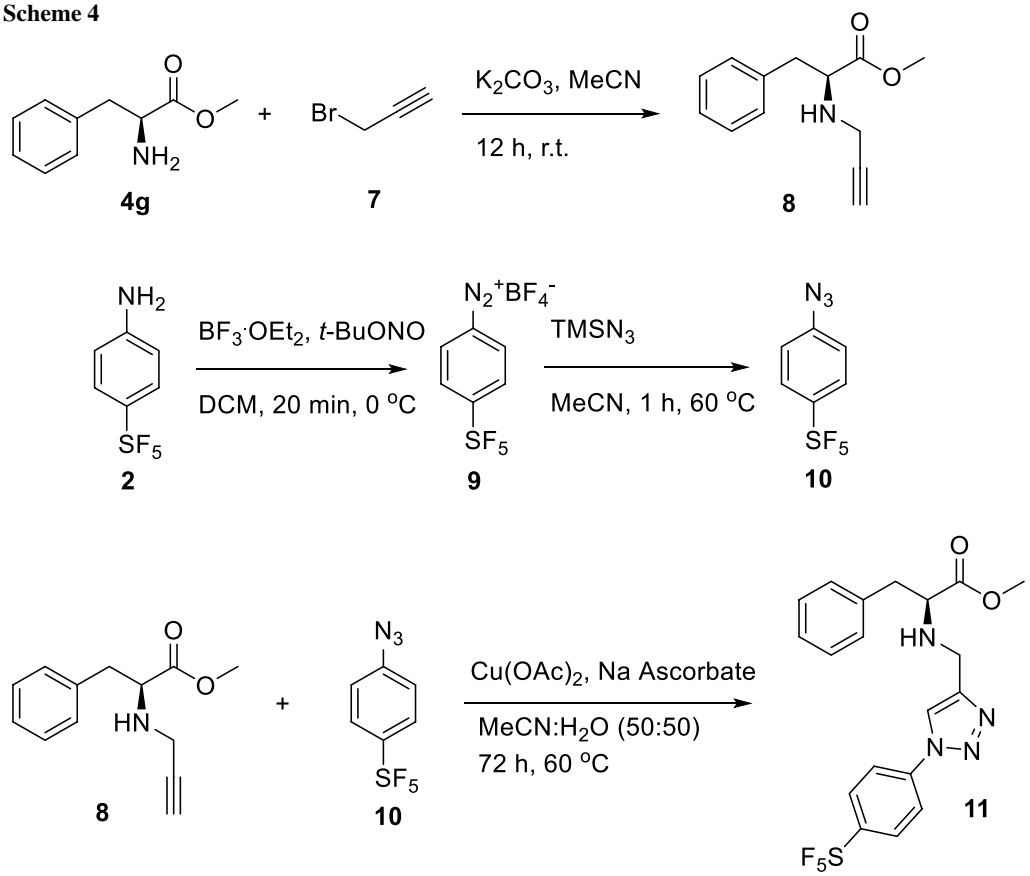
Initial attempts to synthesize the 4-(pentafluorosulfanyl)phenyl azide entailed the reaction of the corresponding aniline with a large excess of $NaNO_2$ in HCl, with the resulting diazonium chloride salt intermediate undergoing in situ reaction with an excess of NaN_3 to form the azide product. However, these attempts proved unsuccessful as the intermediate diazonium chloride lacked stability in the aqueous reaction media, readily undergoing an undesired nucleophilic substitution reaction to form the corresponding phenolic by-product.

To address this instability, 4-(pentafluorosulfanyl)-phenyl diazonium salt was prepared with a tetrafluoroborate counter-cation from the corresponding amine using the procedure described by Okazaki et al. [13], whereby $BF_3{\cdot}OEt_2$, *tert*-BuONO, and acetonitrile are utilized to serve as a Lewis acid, N_2 source, and solvent, respectively. Unlike the chloride counter-cation, the tetrafluoroborate diazonium salt could be easily isolated by filtration and stored at room temperature for short periods without decomposing. In this way, 4-(pentafluorosulfanyl)phenyl diazonium tetrafluoroborate (**9**) was obtained in a yield of 87% and could be used to synthesize the azide product by reaction with trimethylsilyl azide (Scheme 4). Due to the explosive nature of azide derivatives, the product **10** was stored in solution as a safety precaution; the yield was assumed to be quantitative.

The CuAAC click reaction was performed in a mixture of water and acetonitrile (50:50) which was allowed to proceed for 72 h at 60 °C before TLC finally indicated the complete consumption of the azide precursor. The subsequent click product **11** was obtained as a brown viscous oil. The successful synthesis of the desired product was advocated by the presence of a characteristic singlet peak at 7.51 ppm, indicating the triazole's lone proton. Purification of the crude product by column chromatography afforded the final product in a yield of 61%.

The slow reaction rate exhibited in the cycloaddition was primarily attributed to the diminished reactivity of 4-(pentafluorosulfanyl)phenyl azide due to the reduced electron density around the azide group provided by the $–SF_5$ groups inductive effect and delocalisation within the aromatic ring. The detrimental influence of these factors in CuAAC reactions is supported by the work of Golas et al. [24], who reported a clear negative correlation between azide reactivity and both increased electron-withdrawing

Scheme 4



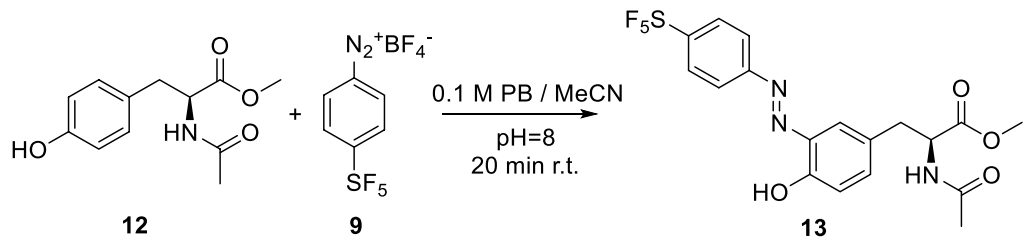
effect and steric hindrance of their substituents. Inversely, alkynes substituted with electron-withdrawing groups exhibit higher reactivity through the increased acidity of the terminal C_{sp}-H proton, thus encouraging its deprotonation before coordinating with the copper ligand, a rate-determining step in the CuAAC mechanism [25]. Notwithstanding this, Huang et al. [26] reported a successful one-pot CuAAC reaction between aliphatic azides bearing a terminal –SF_5 group and a variety of alkyne functionalised compounds, achieving yields ranging between 57 and 91% after 18 h at 60 °C. The success of the CuAAC reactions utilising aliphatic azides under similar conditions further highlights the detrimental influence of the electron-withdrawing aryl –SF_5 moiety on the azide group and its subsequent reactivity towards its alkyne click partner.

Pentafluorosulfanyl phenyl diazonium salt in azo coupling

The azo-coupling reaction has been investigated extensively as a method for the bioconjugation of prosthetic groups with the phenolic side chains of tyrosine residues. The appealing stability of the SF_5-substituted tetrafluoroborate diazonium salt **9** prompted its use in a diazo-coupling reaction with *N*-acyl protected tyrosine methyl ester, whereby the model amino acids' phenolic side chain was used as a target for chemo-selective bioconjugation (Scheme 5).

Diazo-coupling entailed the dropwise addition of the diazonium salt in acetonitrile to a solution of the model amino acid in a solution of acetonitrile and phosphate buffer (1:1). The diazo-coupling product **13** precipitated from

Scheme 5



solution immediately upon adding the solution containing the diazonium salt. The $–SF_5$ group was highly advantageous in this case as it significantly promoted the electrophilicity of the diazonium salt, allowing for reaction time as short as 20 min. Furthermore, the lipophilic nature of the phenyl $–SF_5$ moiety allowed the product to precipitate from the polar solvent mixture readily. *N*-Acyl protection of the tyrosine derivative **12** was necessary to prevent the formation of the triazene by-product. The product was isolated by filtration and washed with ethyl acetate to afford the pure final product in a yield of 79%. The azo-coupling product demonstrated an intense orange colour, a common characteristic among azo-bridged compounds. The successful synthesis was indicated by ^{1}H NMR and confirmed by HRMS.

Conclusions

From the results obtained, it is apparent that the electronic effects of the $–SF_5$ group have a substantial influence on the reactions investigated for introducing the group onto model amino acids. 4-(Pentaflurosulfanyl)aniline used in amide coupling reactions lacked the nucleophilicity necessary for efficient coupling to be achieved. The reaction rate of amide coupling by the EDCI/HOBt method was hindered to such an extent that amino acid precursor was consumed preferentially to form the *N*-acylurea by-product. Tetramethyl orthosilicate (TMOS) was employed as an alternative coupling reagent in an attempt to optimise the rate of amide coupling reactions. Amide coupling by this method afforded modest improvements in yield; however, prolonged reaction times of up to 36 h were necessary even at elevated concentration and temperature.

Similarly, the CuAAC reaction performed in this work also appears to have been hindered by the substantial electronic effects of the aryl–SF_5 moiety, whereas present on the azide counterpart. Future attempts using click chemistry to incorporate the $–SF_5$ group onto biomolecules should instead aim to utilise $–SF_5$ functionalised terminal alkynes for cycloaddition with azide-modified biomolecules. In turn, this strategy could exploit this electron-withdrawing effect advantageously to facilitate a CuAAC reaction with the same exemplary rate kinetics and selectivity as those reported in the literature.

Reductive amination reactions proved effective, as the $–SF_5$ group's electron-withdrawing effect rendered 4-(pentafluorosulfanyl)benzaldehyde highly electrophilic, affording the reductive amination products in moderate-to-high yields (67–84%). Much like the reductive amination reaction, the electronic effects imposed by the aryl–SF_5 moiety proved beneficial for increasing the electrophilicity and subsequent reactivity of the diazonium salt in the azo-coupling reaction, allowing for rapid introduction of the aryl–SF_5 moiety via the model tyrosine phenolic side chain.

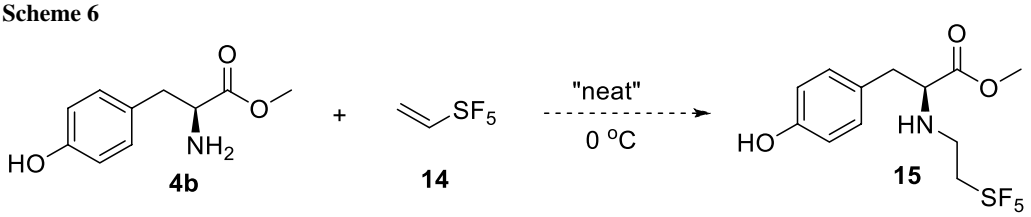
Experimental

All chemical reagents and AR grade or analytical grade solvents were acquired from commercial sources, such as Sigma-Aldrich, Merck, and Fluorochem. All reactions were monitored using TLC Silica gel 60 F_{254} with UV detection at 254 nm and stained with either iodine or ninhydrin reagent. Automated column chromatography was performed using LC-Prep. Solvents were removed under reduced pressure using a Buchi Rotavapor rotary evaporator. High-resolution mass spectra were obtained using an Agilent 6510 Q-TOF Mass Spectrometer (ESI). ^{1}H NMR, ^{13}CNMR, and ^{19}F NMR spectra were recorded on an Agilent 500 54 premium shielded spectrometer 500 MHz (500 MHz ^{1}H, 125 MHz ^{13}C, 470.29 MHz ^{19}F) in deuterated chloroform ($CDCl_3$).

Synthesis of amide coupling products 3a–3d

General procedure A: To a solution of 110 mg 4-(pentafluorosulfanyl)aniline (0.5 mmol) in 10 cm^3 anhydrous DMF was added *N*-Boc protected amino acid (0.505 mmol), 105 mg EDCI (0.55 mmol), and 65 mg HOBt (0.55 mmol) in a closed vessel under nitrogen atmosphere. The reaction was allowed to proceed overnight at room temperature with stirring. The solution was quenched with 20 cm^3 of water and extracted with $CHCl_3$ (3×20 cm^3); the organic layers were then combined and washed with water (2×30 cm^3). The organic layer was dried with anhydrous $MgSO_4$ and concentrated in vacuo to provide the crude product, which was purified by column chromatography using EtOAc:hexane (30:70) as the eluent to afford the pure product.

Scheme 6



General procedure B: To nitrogen flushed round-bottom flask fitted with a reflux condenser, and drying tube was added 110 mg 4-(pentafluorosulfanyl)aniline (0.5 mmol) and *N*-Boc protected amino acid (0.5 mmol) followed by 1 cm^3 dry toluene and tetramethyl orthosilicate (250% mol), the reaction mixture was then heated to 100 °C and allowed to reflux for 36 h. The reaction mixture was then quenched with 10 cm^3 water and extracted with DCM (3×10 cm^3). The combined organic layers were washed with 30 cm^3 1 N HCl, followed by 30 cm^3 saturated $NaHCO_3$. The organic layer was then dried with 30 cm^3 saturated NaCl solution and anhydrous $MgSO_4$ and concentrated under reduced pressure to provide the crude product, which was purified by column chromatography using EtOAc:hexane (30:70) as eluent to afford the pure product.

***tert*-Butyl *N*-[(1*S*)-1-[[4-(pentafluoro-λ⁶-sulfanyl)-phenyl]carbamoyl]-2-phenylethyl]carbamate (3a, $C_{20}H_{25}F_5N_2O_3S$)** Compound **3a** was synthesized using procedure B, as a yellow oil (98 mg, 0.22 mmol, 44%). $R_f = 0.22$ in EtOAc:hexane (3:7); HRMS (EI): *m/z* calcd for $C_{20}H_{24}F_5N_2O_3S$ $[M–H]^-$ 465.1271, found 465.1301; ^{1}H NMR ($CDCl_3$): $\delta = 7.60$ (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H) 7.29–7.18 (m, 5H), 4.83–4.80 (m, 1H), 3.02 (m, 2H), 1.63 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 28.26$, 37.91, 118.94, 126.85, 127.24, 128.90, 129.18, 129.28, 136.19, 140.08, 170.18 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 85.03$ (m, $J = 150$ Hz, 1F), 63.40 (d, $J = 150$ Hz, 4F) ppm.

***tert*-Butyl *N*-[(1*S*)-1-[[4-(pentafluoro-λ⁶-sulfanyl)phenyl]carbamoyl]ethyl]carbamate (3b, $C_{14}H_{19}F_5N_2O_3S$)** Compound **3b** was synthesized using procedure B, as a yellow oil (38 mg, 0.18 mmol, 36%). $R_f = 0.16$ in EtOAc:hexane (1:1); HPLC: $t_R = 6$ min 27 s; HRMS (EI): *m/z* calcd for $C_{14}H_{18}F_5N_2O_3S$ $[M–H]^-$ 389.0958, found 389.0948; ^{1}H NMR ($CDCl_3$): $\delta = 7.64$ (d, $J = 10$ Hz, 2H), 7.56 (d, $J = 10$ Hz, 2H), 4.84–4.82 (m, 1H), 1.48 (s, 9H), 1.44 (d, $J = 7$ Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 28.30$, 118.80, 126.87, 126.91, 171.17 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 85.16$ (m, $J = 150$ Hz, 1F), 63.40 (d, $J = 150$ Hz, 4F) ppm.

***tert*-Butyl *N*-[(1*S*)-2-(1*H*-indol-3-yl)-1-[[4-(pentafluoro-λ⁶-sulfanyl)phenyl]carbamoyl]ethyl]carbamate (3c, $C_{22}H_{24}F_5N_3O_3S$)** Compound **3c** was synthesized using procedure B, as a white solid (96 mg, 0.19 mmol, 38%). $R_f = 0.38$ in EtOAc:hexane (3:7); HRMS (EI): *m/z* calcd for $C_{22}H_{25}F_5N_3O_3S$ $[M+H]^+$ 506.1531, found 506.1545; ^{1}H NMR ($CDCl_3$): $\delta = 7.66$ (d, $J = 8$ Hz, 1H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.38 (m, 3H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 3.38 (dd, $J = 5$, 14 Hz, 1H), 3.26 (dd, $J = 7.5$, 14 Hz, 1H), 1.43 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 28.42$, 109.21, 111.50, 118.85, 119.10, 120.25, 122.75, 123.41, 126.99, 150.45, 170.58 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 85.17$ (m, $J = 149.5$ Hz, 1F), 63.43 (d, $J = 149.5$ Hz, 4F) ppm.

***tert*-Butyl 2-[[4-(pentafluoro-λ⁶-sulfanyl)phenyl]carbamoyl]pyrrolidine-1-carboxylate (3d, $C_{16}H_{21}F_5N_2O_3S$)** Compound **3d** was synthesized using procedure B, as a yellow oil (46 mg, 0.205 mmol, 41%). $R_f = 0.32$ in EtOAc:hexane (3:7); HPLC: $t_R = 6$ min 35 s; HRMS (EI): *m/z* calcd for $C_{16}H_{22}F_5N_2O_3S$ $[M+H]^+$ 417.1266, found 417.1268; ^{1}H NMR ($CDCl_3$): $\delta = 7.59$ (m, 2H), 7.55 (m, 2H), 4.54–4.48 (m, 1H), 3.52–3.43 (m, 1H), 3.42–3.32 (m, 1H), 2.52–2.40 (m, 1H) 2.06–1.88 (m, 3H), 1.50 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 24.61$, 27.35, 28.41, 47.34, 60.53, 62.93, 81.25, 118.69, 126.79, 141.13, 163.27, 170.44 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 85.45$ (m, $J = 149.5$ Hz, 1F), 63.42 (d, $J = 149.5$ Hz, 4F) ppm.

Synthesis of reductive amination products 6a–6f

To a nitrogen flushed reaction vessel was added C-protected amino acid methyl ester hydrochloride (1.1 mmol) dissolved in 15 cm^3 anhydrous DCM. NEt_3 (1.1 mmol, 153 mm^3) was added dropwise to the vessel, and the reaction was allowed to stir for 20 min. After 20 min, 232 mg 4-(pentafluorosulfanyl)benzaldehyde (1 mmol) was added dropwise to the reaction vessel followed by 440 mg $NaB(CN)H_3$ (7 mmol) and a few drops of glacial acetic acid. The reaction was allowed to proceed overnight at room temperature with stirring. Upon confirmation of reaction completion via TLC, the reaction was quenched with 20 cm^3 saturated $NaHCO_3$ and then extracted with $CHCl_3$ (3×10 cm^3), dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:hexane (1:1) as eluent to afford the final product.

***tert*-Butyl (2*S*)-4-carbamoyl-2-[[[4-(pentafluoro-λ⁶-sulfanyl)-phenyl]methyl]amino]butanoate (6a, $C_{16}H_{23}F_5N_2O_3S$)** Compound **6a** was obtained as a white solid (324.2 mg, 0.77 mmol, 77%). $R_f = 0.26$ in EtOAc:hexane (1:1); HPLC: $t_R = 6$ min 34 s; HRMS (EI): *m/z* calcd for $C_{16}H_{24}F_5N_2O_3S$ $[M+H]^+$ 419.1428, found 419.1415; ^{1}H NMR ($CDCl_3$): $\delta = 7.69$ (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8$ Hz, 2H), 3.88 (d, $J = 14$ Hz, 1H), 3.65 (d, $J = 14$ Hz, 1H), 3.11 (m, 2H), 3.07–2.31 (m, 2H), 1.48 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 23.12$, 28.04, 29.48, 45.11, 60.01, 82.01, 126.54, 128.83, 175.49 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 84.83$ (m, $J = 150$ Hz, 1F), 63.02 (d, $J = 149.5$ Hz, 4F) ppm.

Methyl (2*S*)-3-(4-hydroxyphenyl)-2-[[[4-(pentafluoro-λ⁶-sulfanyl)phenyl]methyl]amino]propanoate (6b, $C_{17}H_{18}F_5NO_3S$) Compound **6b** was obtained as a white solid (333.7 mg, 0.81 mmol, 81%). $R_f = 0.32$ in EtOAc:hexane (3:7); HPLC: $t_R = 5$ min 3 s; HRMS (EI): *m/z* calcd for

$C_{17}H_{19}F_5NO_3S$ $[M+H]^+$ 412.1000, found 412.0999; ^1H NMR ($CDCl_3$): $\delta = 7.64$ (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8$ Hz, 2H), 7.01 (d, $J = 8$ Hz, 2H), 6.74 (d, $J = 8$ Hz, 2H), 3.87 (d, $J = 14$ Hz, 1H), 3.68 (s, 3H), 3.65 (d, $J = 14$ Hz, 1H), 3.44 (t, $J = 6.5$ Hz, 1H), 2.92 (dd, $J = 6$, 13.5 Hz, 1H), 2.86 (dd, $J = 7.5$, 13.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 38.84$, 51.06, 51.84, 62.09, 115.32, 125.89, 125.93, 125.96, 128.16, 129.05, 130.41, 143.65, 154.54, 174.98 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 84.95$ (m, $J = 150$ Hz, 1F), 63.02 (d, $J = 150$ Hz, 4F) ppm.

Benzyl (2*S*)-3-hydroxy-2-[[[4-(pentafluoro-λ^6-sulfanyl)phenyl]methyl]amino]propanoate (6c, $C_{17}H_{18}F_5NO_3S$) Compound **6c** was obtained as a yellow oil (284.3 mg, 0.69 mmol, 69%). $R_f = 0.60$ in EtOAc:hexane (3:7); HPLC: $t_R = 5$ min 23 s; HRMS (EI): *m/z* calcd for $C_{17}H_{19}F_5NO_3S$ $[M+H]^+$ 412.1000, found 412.0994; ^1H NMR ($CDCl_3$): $\delta = 7.69$ (d, $J = 8.5$ Hz, 2H), 7.4 (d, $J = 8.5$ Hz, 2H), 7.38–7.34 (m, 5H), 5.19 (s, 2H), 3.95 (d, $J = 14$ Hz, 1H), 3.82 (dd, $J = 4.5$, 11 Hz, 1H), 3.76 (d, $J = 13.5$ Hz, 3H), 3.68 (dd, $J = 6$, 10.5 Hz, 1H), 3.45 (t, $J = 5.5$ Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 51.10$, 61.94, 62.64, 67.04, 126.04, 126.06, 126.1, 128.18, 128.23, 128.52, 128.63 128.52, 135.25, 143.22, 172.66 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 84.65$ (m, $J = 150$ Hz, 1F), 63.02 (d, $J = 149.5$ Hz, 4F) ppm.

Ethyl (2*S*)-2-[[[4-(pentafluoro-λ^6-sulfanyl)phenyl]methyl]amino]-3-sulfanylpropanoate (6d, $C_{12}H_{18}F_5NO_2S_2$) Compound **6d** was obtained as a yellow oil (263.08 mg, 0.72 mmol, 72%). $R_f = 0.71$ in EtOAc:hexane (3:7); HPLC: $t_R = 4$ min 55 s; HRMS (EI): *m/z* calcd for $C_{12}H_{17}F_5NO_2S_2$ $[M+H]^+$ 366.0610, found 366.0608; ^1H NMR ($CDCl_3$): $\delta = 7.71$ (d, $J = 9$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 4.27–4.19 (m, 2H), 3.95 (d, $J = 14$ Hz, 1H), 3.76 (d, $J = 14$ Hz, 1H), 3.43 (t, $J = 5.5$ Hz, 1H), 3.16 (dd, $J = 11$ Hz, 1H), 3.13 (dd, $J = 11$ Hz, 1H), 1.37–1.25 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 51.10$, 61.93, 63.63, 67.04, 126.04, 126.10, 128.18, 128.23, 128.51, 128.63, 135.24, 143.22, 172.58 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 84.79$ (m, $J = 149.5$ Hz, 1F), 63.01 (d, $J = 149.5$ Hz, 4F) ppm.

Methyl (2*S*)-3-(1*H*-indol-3-yl)-2-[[[4-(pentafluoro-λ^6-sulfanyl)phenyl]methyl]amino]propanoate (6e, $C_{20}H_{19}F_5N_2O_2S$) Compound **6e** was obtained as a colourless oil (291 mg, 0.67 mmol, 67%). $R_f = 0.635$ in EtOAc:hexane (1:1); HPLC: $t_R = 5$ min 27 s; HRMS (EI): *m/z* calcd for $C_{20}H_{20}F_5N_2O_2S$ $[M+H]^+$ 447.1165, found 447.1168; ^1H NMR ($CDCl_3$): $\delta = 7.58$ (d, $J = 8.5$ Hz, 2H), 7.55 (d, $J = 8$ Hz, 2H), 7.36 (d, $J = 8$ Hz, 1H), 7.27 (d, $J = 8$. Hz, 1H), 7.20 (t, $J = 7$ Hz, 1H), 7.10 (t, $J = 7$ Hz, 1H), 7.03 (s, 1H), 3.87 (d, $J = 14$ Hz, 1H), 3.66 (s, 3H), 3.60 (d, $J = 13$ Hz, 1H), 3.22 (dd, $J = 5.5$, 14.5 Hz, 1H), 3.12 (dd, $J = 7$, 14.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 22.72$, 30.99, 52.61, 53.78, 67.10, 73.19, 74.86, 124.91, 124.94, 124.98, 126.03, 126.06, 126.10, 127.89, 128.33, 128.84, 128.89, 135.33, 142.84, 143.54, 175.01 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 84.99$ (m, $J = 149.5$ Hz, 1F), 63.03 (d, $J = 149.5$ Hz, 4F) ppm.

Benzyl (2*S*)-1-[[4-(pentafluoro-λ^6-sulfanyl)phenyl]methyl]-pyrrolidine-2-carboxylate (6f, $C_{19}H_{20}F_5NO_2S$) Compound **6f** was obtained as a yellow oil (345.57 mg, 0.82 mmol, 82% yield). $R_f = 0.68$ in EtOAc:hexane (3:7); HPLC: $t_R = 8$ min 0 s; HRMS (EI): *m/z* calcd for $C_{19}H_{21}F_5NO_2S$ $[M+H]^+$ 422.1208, found 422.1209; ^1H NMR ($CDCl_3$): $\delta = 7.69$ (d, $J = 9$ Hz, 2H), 7.51–5.08 (m, 5.39–5.08 (m, 2H), 4.06 (d, $J = 14.5$ Hz, 1H), 3.98 (d, $J = 13.5$ Hz, 1H), 3.57 (d, $J = 13.5$ Hz, 1H), 3.44 (d, $J = 13.5$ Hz, 1H), 3.00–1.68 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 27.81$, 50.96, 61.34, 61.81, 126.00, 126.04, 128.29, 143.63, 174.99 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 84.70$ (m, $J = 149.5$ Hz, 1F), 63.03 (d, $J = 149.5$ Hz, 4F) ppm.

Methyl (2*S*)-3-phenyl-2-[(prop-2-yn-1-yl)amino]propanoate (8, $C_{13}H_{15}NO_2$) To a nitrogen flushed vessel was added 1.116 g L-phenylalanine methyl ester hydrochloride (5.18 mmol) in 20 cm^3 anhydrous CH_3CN followed by 1.79 g K_2CO_3 (13 mmol). In a separate flask, 615 mg propargyl bromide (392 mm^3, 5.18 mmol) was dissolved in 10 cm^3 anhydrous CH_3CN. The propargyl bromide solution was added dropwise to the reaction vessel and the reaction was allowed to proceed for 12 h at room temperature. After 12 h, the reaction was checked with TLC and quenched with 60 cm^3 of water, the aqueous layer was extracted with $CHCl_3$ (3×20 cm^3), and the organic layers combined, dried with anhydrous $MgSO_4$. The solvent was removed in vacuo to give compound **8** as a yellow oil (923 mg, 4.25 mol, 82%). The product was used in the next reaction step without further purification. $R_f = 0.55$ in EtOAc:hexane (1:1); HRMS (EI): *m/z* calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$ 218.1176, found 218.1151; ^1H NMR ($CDCl_3$): $\delta = 7.31$–7.19 (m, 5H), 3.68 (s, 3H), 3.43 (d, $J = 17$ Hz, 2H), 3.37 (d, $J = 17$ Hz, 1H), 3.11–2.84 (m, 2H), 2.19 (t, $J = 2.5$ Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 36.81$, 39.43, 51.81, 61.12, 71.79, 81.17, 126.86, 128.50, 129.17, 136.84, 174.28 ppm.

4-(Pentafluorosulfanyl)phenyldiazonium tetrafluoroborate (9) To a solution of 480 mg 4-(pentafluorosulfanyl)aniline (2.2 mmol) in 10 cm^3 DCM cooled over an ice bath was added 470 mg $BF_3{\cdot}OEt_2$ (410 mm^3, 3.3 mmol) dropwise, followed by the dropwise addition of 390 mm^3 *t*-BuONO (3.3 mmol). The reaction was allowed to proceed at 0 °C for 20 min, while being covered from excessive light. The resulting precipitate was isolated via vacuum filtration, washed with Et_2O (2×10 cm^3), and allowed to air dry to afford the final product as a white solid (607 mg, 1.9 mmol, 87%). IR (ATR): $\bar{\nu} = 2924$, 2852, 2309, 1574, 1418, 1304,

1053, 858 (S-F), 768 cm^{-1}. IR spectrum is consistent with those reported in the literature.

4-(Pentafluorosulfanyl)phenyl azide (10) In a two-neck round-bottom flask containing 317 mg 4-(pentafluorosulfanyl)phenyl diazonium tetrafluoroborate (1 mmol) was added 10 cm^3 anhydrous MeCN, and the solution was cooled to 0 °C with an ice bath under a nitrogen atmosphere. $TMSN_3$ (146 mm^3, 1.1 mmol) was then added dropwise to the solution over 5 min. The reaction mixture was then heated at 60 °C for approximately 1 h. Excess $TMSN_3$ was then removed by rotary evaporation, and the product was stored dissolved in the original 10 cm^3 of MeCN as an orange solution. The yield was assumed to be quantitative and the product was used without further purification. $R_f = 0.95$ in EtOAc:hexane (1:1).

Methyl (2*S*)-2-[[[1-[4-(pentafluorosulfanyl)phenyl]-1,2,3-triazol-4-yl]methyl]amino]-3-phenylpropanoate (11, $C_{19}H_{19}F_5N_4O_2S$) To a solution of 4-(pentafluorosulfanyl)phenyl azide (**10**, approx. 1 mmol) and 217 mg methyl (2*S*)-3-phenyl-2-[(prop-2-yn-1-yl)amino]propanoate (1 mmol) in 10 cm^3 MeCN was added 18 mg $Cu(OAc)_2$ (0.1 mmol) dissolved in 5 cm^3 H_2O shortly followed by 40 mg sodium ascorbate (0.2 mmol) dissolved in 5 cm^3 H_2O to afford a homogenous green solution. The reaction temperature was brought to 60 °C and allowed to proceed for 3 days and monitored via TLC. The reaction mixture was concentrated by rotary evaporation to remove MeCN and then extracted with $CHCl_3$ (2×10 cm^3). The organic layers were combined, washed with saturated NaCl solution, and dried with anhydrous $MgSO_4$. The organic layer was then concentrated in vacuo. The crude product was then purified via column chromatography to afford the pure product as a golden yellow oil (283 mg, 0.61 mmol, 61%). $R_f = 0.19$ in EtOAc:hexane (40:60); HRMS (EI): *m/z* calcd. for $C_{19}H_{20}F_5N_4O_2S$ $[M+H]^+$ 463.1222, found 463.1229; ^{1}H NMR ($CDCl_3$): $\delta = 7.91$ (d, $J = 11.5$ Hz, 2H), 7.76 (d, $J = 8.5$, 2H), 7.53 (s, 1H), 7.31–7.19 (m, 5H), 5.30 (s, 2H), 4.05 (d, $J = 14.5$ Hz, 1H), 3.88 (d, $J = 14.5$ Hz, 1H), 3.71 (s, 3H), 3.55 (dd, $J = 5.5$, 8 Hz, 1H), 3.05 (dd, $J = 5.5$, 13.5 Hz, 1H), 2.87 (dd, $J = 8.5$, 13.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 39.72$, 43.23, 51.99, 62.21, 119.61, 119.89, 126.78, 127.76, 128.45, 137.62, 148.48, 174.73 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 83.22$ (m, $J = 149.5$ Hz, 1F) 63.13 (d, $J = 149.5$ Hz, 4F) ppm.

Methyl (2*S*)-2-acetamido-3-[4-hydroxy-3-[(1E)-2-[4-(pentafluorosulfanyl)phenyl]diazen-1-yl]phenyl]propanoate (13, $C_{18}H_{18}F_5N_3O_4S$) In a two-neck round-bottom flask 237 mg *N*-acyl L-tyrosine methyl ester (1 mmol) was suspended in 5 cm^3 0.1 M Na_2HPO_4 followed by 5 cm^3 MeCN and stirred until completely dissolved. 4-(Pentafluorosulfanyl)phenyl diazonium tetrafluoroborate (317 mg, 1 mmol) dissolved in 5 cm^3 MeCN was then added dropwise to the reaction mixture. The reaction was allowed to proceed for a further 20 min at which point the precipitate that formed was isolated via vacuum filtration, washed with cold deionised water (2×10 cm^3), and allowed to air dry. Compound **13** was obtained as a bright orange solid (368 mg, 0.79 mmol, 79%). $R_f = 0.35$ in EtOAc:hexane (40:60); HRMS (EI): *m/z* calcd for $C_{18}H_{17}F_5N_3O_4S$ $[M-H]^-$ 466.0865, found 466.0864; ^{1}H NMR ($CDCl_3$): $\delta = 7.93$ (m, 4H), 7.26 (s, 1H), 7.15 (d $J = 8.5$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 1H), 5.99 (d, $J = 7.5$ Hz, 1H), 4.93 (d, $J = 8$ Hz, 1H), 3.77 (1H), 3.23 (dd, $J = 6$, 14.5 Hz, 1H) 3.14 (dd, $J = 6$, 14.5 Hz, 1H), 2.06 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 23.23$, 36.96, 52.52, 53.22, 118.64, 122.24, 127.39, 127.39, 134.11, 135.49, 137.27, 151.89, 169.61, 171.99 ppm; ^{19}F NMR ($CDCl_3$): $\delta = 83.45$ (m, $J = 149.5$ Hz, 1F), 63.01 (d, $J = 149.5$ Hz, 4F) ppm.

Attempted use of ethenesulfanyl pentafluoride as a Michael acceptor

The high volatility of ethene sulfanyl pentafluoride (**14**) (Scheme 6) required the use of a closed system, pressurised with nitrogen and ice bath in order to minimise the evaporative loss of precursor. Partly unsurprisingly, TLC of the reaction mixture indicated that product formation did not occur, despite the strong electron-withdrawing effect of the $-SF_5$ group.

In a further attempt to obtain the Michael-type product, a microfluidic platform was utilized to perform test reactions across a temperature range of 20–100 °C, using DMSO as the solvent. The closed environment of the microfluidic system is advantageous as it ensures that no volatile reagents are lost and provides a high surface/volume ratio that typically allows for more efficient and homogeneous heating. However, also in these conditions, no conjugation product was detected. These results indicate that the $-SF_5$ group's inductive effect is not sufficient by itself to provide a Michael-type addition product.

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Declarations

Conflict of interest The authors declare no competing financial interest.

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