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E- or Z-Selective synthesis of 4-fluorovinyl-1,2,3-triazoles with fluorinated second-generation Julia–Kocienski reagents†

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A highly modular approach to *N*-substituted 4-(1-fluorovinyl)triazoles is described. *In situ* desilylation and Cu-catalyzed ligation reaction of TMS-protected α-fluoropropargyl benzothiazole sulfone with aryl, alkyl, and metallocenyl azides furnished *second-generation* Julia–Kocienski reagents in good to excellent yields. Condensation reactions of these reagents with aldehydes can be tuned to yield *E* or *Z*-alkenes selectively. Under mild conditions with DBU as the base, reactions of aldehydes furnished *E*-alkenes as the major isomer. On the other hand, in condensation reactions with LHMDS as the base and in appropriate solvents, both aldehydes and ketones reacted to yield fluoroalkenes with *Z*-selectivity. Stereochemical assignment of *E*/*Z* olefins obtained in the reaction of a ketone with two Julia reagents was performed *via* X-ray crystallographic analysis and comparisons of NMR data. The method allows efficient and ready diversification of the *N*1-substituent and substituents at the double bond.

Introduction

The high modularity and 100% atom economy of the Huisgen ligation make this an attractive approach to obtain the triazole moiety.[1] As a class both 1,4- and 1,5-disubstituted 1,2,3-triazoles are highly valuable in a number of areas, from materials and polymer chemistry to pharmaceutics and medicine.[2] The complexation of the triazole ring has also been exploited in supramolecular chemistry.[3] The discovery of the Cu-catalyzed variant of the Huisgen ligation enabled facile and highly regioselective access to 4-substituted 1,2,3-triazoles.[4,5] This prompted the resurgence of the azide–alkyne cycloaddition, leading to a plethora of 1,2,3-triazole-derived structures. Fig. 1 shows some representative examples of 1,4-disubstituted 1,2,3-triazole-containing biologically active compounds,[6,7] as well as new macromolecules with valuable mechanical and/or thermal properties.[2d–f,8]

In the area of fluoroorganic chemistry,[9] we[10,11] and others[12] have been involved in the modular synthesis of variously functionalized fluoroolefins[10,13] using the Julia–Kocienski approach.[14] The effect of fluorine atom incorporation in pharmaceuticals is well established.[15] For example, *Z*- and *E*-fluorovinyl groups are hydrolytically stable isosteres of *trans* and *cis* peptide bonds, respectively.[16] Given the high modularity of the azide–alkyne cycloadditions (CuAAC) as well as the Julia–Kocienski olefination, we became interested in a facile approach for merging the pharmacologically interesting triazole and fluorovinyl moieties. We recently described an approach to 4-vinyl and 4-(α-fluorovinyl)-triazoles *via* the use of a building block containing a triple bond and an olefination handle. Although the synthesis of *N*-fluorovinyl triazoles[17] has been reported, our preliminary communication[11a] was, to the best of our knowledge, the first report on the synthesis of 4-(α-fluorovinyl)-triazoles.

In our preliminary communication[11a] we demonstrated that regioselectively difunctionalized triazoles, with readily varied *N*1 and vinyl substituents, could be accessed by a combination of the CuAAC and the Julia–Kocienski reactions. In that work we showed that triazole-substituted Julia–Kocienski reagents can be first obtained *via* a Cu-catalyzed azide–alkyne *click* ligation of propargyl and α-fluoropropargyl benzothiazole sulfones with one aryl and two alkyl azides. The resulting reagents then underwent olefination reactions with aldehydes and a ketone. Herein, we describe the broader generality of the azide–alkyne ligation reactions of α-fluoropropargyl benzothiazole sulfone with a larger series of azides, and the reactivity of these second-generation Julia–Kocienski reagents in olefinations with aldehydes and ketones. Notably, an evaluation of olefination conditions showed that the selectivity could be

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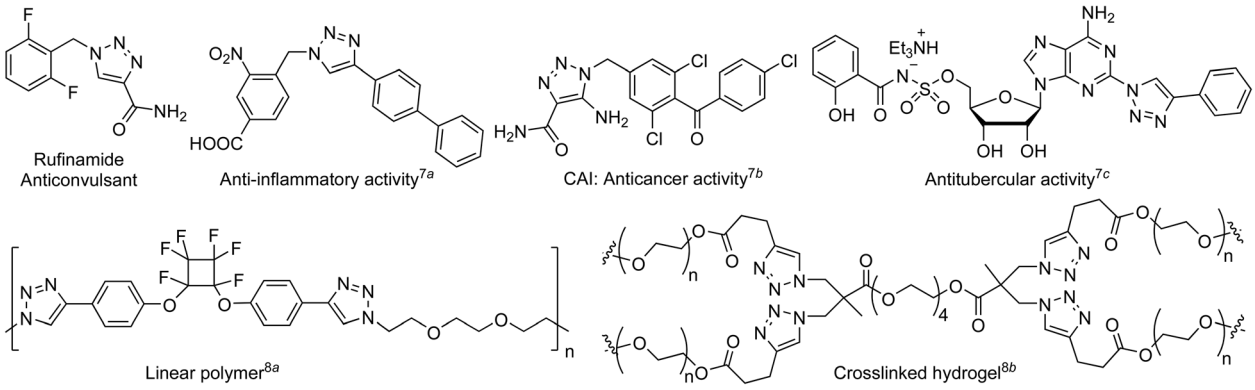


Fig. 1 Examples of 1,4-disubstituted 1,2,3-triazoles as biologically active compounds and as new macromolecules.

tuned to yield *E*- or *Z*-fluorovinyl triazoles as the major isomer in the Julia–Kocienski reactions. This adds to the overall modularity of this approach.

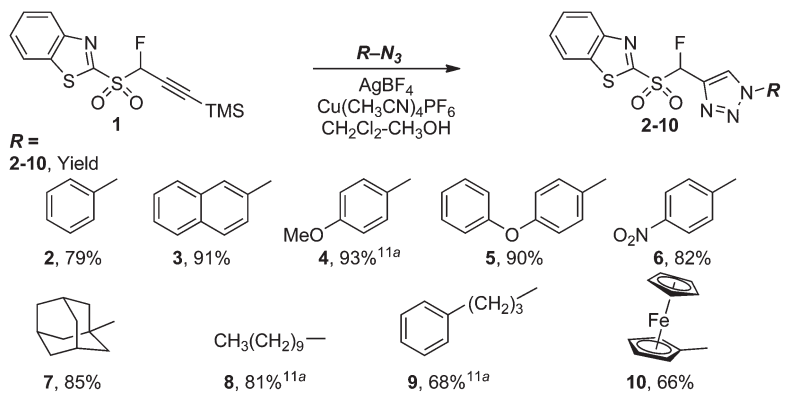
Results and discussion

In order to explore the generality of azide–alkyne ligation reactions leading to second-generation Julia–Kocienski reagents, TMS-protected α-fluoropropargyl benzothiazole sulfone **1**[11a,c] was deprotected *in situ* and subjected to ligation with a series of azides, following our published protocol[11a] (Scheme 1). It should be noted that the use of 1-phenyl-1*H*-tetrazol-5-yl propargyl sulfone (propargyl PT-sulfone) was also considered for the synthesis of comparable second-generation Julia–Kocienski reagents. The heteroaryl moiety can influence the selectivity in Julia–Kocienski olefinations,[14] *e.g.* olefinations of *n*-alkanals with alkyl PT-sulfones proceed with a superior selectivity as compared to benzothiazole-derived sulfones.[18] However, it has been reported that TMS-protected propargyl PT-sulfone is unstable.[19] This sulfone on reaction with benzaldehyde gave the enyne product in a low yield, plausibly due to its instability.[20] Because our protocol requires the initial fluorination of a TMS-protected propargyl heteroaryl sulfone, followed by CuAAC reactions, we chose the more stable benzothiazolyl derivative (Scheme 1).

Briefly, *in situ* alkyne deprotection with $AgBF_4$, followed by the $Cu(CH_3CN)_4PF_6$ mediated reaction with nine azides furnished the corresponding triazoles in 66–93% yields (**2–10**, Scheme 1). Azidobenzene and 1-azido-4-nitrobenzene gave triazole products **2** and **6** in 79% and 82% yield, respectively, whereas electron-rich aromatic azides gave triazoles **3–5** in slightly higher yields of 90–93%. 1-Azidoadamantane and 1-azidodecane gave products **7** and **8** in 85% and 81% yield, respectively, and 3-(azidopropyl)benzene gave triazole **9** in a slightly lower yield of 68%. Azidoferrocene reacted as well, to give product **10** in a respectable yield of 66%. Reactions were typically complete in 1.5–4 h, except in the case of 2-azidonaphthalene and 1-azido-4-nitrobenzene, where longer reaction times were required (19 h and 50 h, respectively).

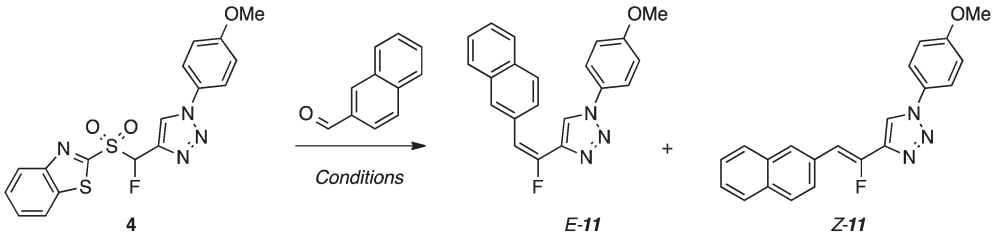
A screening of olefination conditions was then performed using *N*-*p*-methoxyphenyl triazolyl Julia–Kocienski reagent **4** and 2-naphthaldehyde (Table 1).

In our prior communication we have demonstrated that condensations of **4** and **9** with some aldehydes proceeded with *Z*-selectivity, in low-temperature LHMDS-mediated condensations in DMF–DMPU.[11a] In the present case as well, 2-naphthaldehyde reacted with **4** to furnish fluorovinyl triazole (*E*/*Z*)-**11** with high *Z*-selectivity (Table 1, entry 1, *E*/*Z* 7/93).



Scheme 1 Synthesis of fluoro(1-substituted-1*H*-1,2,3-triazol-4-yl)methyl 1,3-benzothiazol-2-yl sulfones **2–10** *via* the CuAAC reaction.

Table 1 Screening of olefination conditions



4 *E*-**11** *Z*-**11**

Entry	Base (molar equiv.)	Solvent	Additive (molar equiv.)	*T* (°C); time	**11**, Yield[a] (%), *E*/*Z*[b]
1	LHMDS (2.4)	DMF–DMPU[c]	—	−78; 3 min	76%, 7/93
2	LHMDS (2.4)	THF	$MgBr_2$ (1.8)	−78; 51 h	NR[d]
3	DBU (4.0)	DMF	—	−55; 3.5 h	NA,[e] 22/78
4	DBU (4.0)	DMF–DMPU[c]	—	−78; 24 h	Inc.,[f] 27/73
5	DBU (4.0)	THF	—	−78; 50 h	Inc.,[f] 63/37
6	DBU (4.0)	THF	—	rt; 10 h	77%, 77/23
7	DBU (4.0)	THF	—	50; 6 h	NA,[e] 77/23
8	DBU (4.0)	THF	—	Reflux; 2.5 h	74%, 78/22
9	DBU (4.0)	THF	$MgBr_2$ (1.8)	Reflux; 40 min	NA,[e] 69/31
10	DBU (4.0)	$CHCl_3$	—	Reflux; 4.5 h	NA,[e] 75/25

[a] Yields are of isolated and purified products. [b] *E*/*Z* olefin ratios in the crude reaction mixtures were determined by ^{19}F NMR prior to isolation. [c] DMF–DMPU 1 : 1 v/v. [d] Formation of products was not observed. [e] Products were not isolated. [f] Incomplete reaction and products were not isolated.

However, when the reaction was performed with LHMDS in THF and in the presence of $MgBr_2$, no product formation was observed even after 51 h (entry 2). We were now curious to assess whether condensations would proceed under milder conditions. Indeed, the use of DBU as the base in DMF at −55 °C gave (*E*/*Z*)-**11**, but with a lower *Z*-selectivity than the reaction with LHMDS (compare entry 3 to entry 1). A DBU-mediated reaction in DMF–DMPU at −78 °C gave selectivity comparable to entry 3, but the reaction was incomplete after 24 h (entry 4). We were pleased that these reactions could be tuned to *E*-selectivity upon changing the solvent to THF. However, this reaction was incomplete even after 50 h (entry 5, *E*/*Z* 63/37). When the reaction was performed at rt, *E*-selectivity improved and the reaction was complete within 10 h (entry 6, *E*/*Z* 77/23, 77% yield). Further increase in temperature to 50 °C gave the same *E*/*Z* ratio, but in a shorter reaction time (entry 7). At reflux, the reaction was complete in 2.5 h (entry 8, *E*/*Z* 78/22, 74% yield). In the presence of $MgBr_2$, the *E*/*Z* ratio dropped to 69/31 (entry 9). The reaction in $CHCl_3$ at reflux gave a similar *E*/*Z* ratio of 75/25 as compared to the reaction in THF, but a longer reaction time was required (compare entry 10 to entry 8).

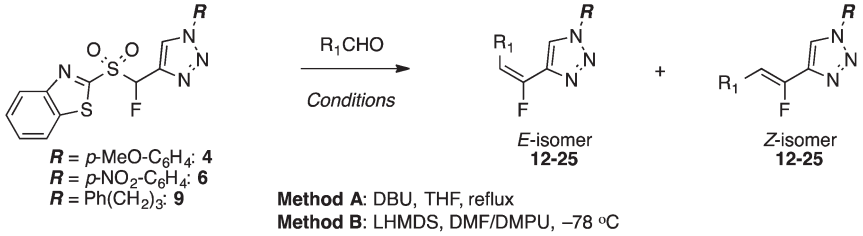
Having determined the conditions that allowed olefinations to be tuned towards *Z*- or *E*-selectivity, we next assessed the scope of condensations with regard to the carbonyl compound and the structure of the Julia–Kocienski reagent. For this, we performed condensation reactions with three Julia–Kocienski reagents **4**, **6**, and **9** under two sets of conditions, *i.e.* with DBU in refluxing THF (Method A, Table 2), and with LHMDS in DMF–DMPU at −78 °C (Method B, Table 2).

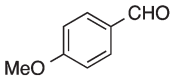
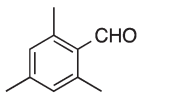
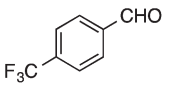
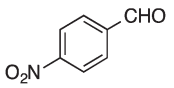
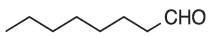
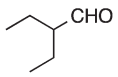
Under DBU-mediated conditions, all reactions proceeded with *E*-selectivity. Selectivity appears to depend on the aldehyde, and to a lesser extent on the triazole reagent. Good *E*-selectivity was observed with electron-rich aromatic aldehydes (entry 8 in Table 1 and entries 1–3 in Table 2), whereas *E*-selectivity was moderate to poor with an increasing electron deficiency in the aldehydes, and with alkanals (entries 5–14, Table 2). Alpha branching in the aldehyde did not alter the *E*/*Z* ratio (compare entry 9 to 12). In the case of aromatic aldehydes, yields were in the range of 74–87% (entry 8 in Table 1, and entries 1–3 and 6–8 in Table 2), except for the reaction of *p*-trifluoromethylbenzaldehyde with sulfone **4**, where product **16** was obtained in a moderate yield of 52% (entry 5). *n*-Octanal gave products in moderate (entries 9 and 11) to poor yields (entry 10). 2-Ethylbutanal reacted with sulfone **4** to give the product in 47% yield (entry 12), whereas reactions with sulfones **6** and **9** gave only traces of products (entries 13, 14). It is plausible that in the case of enolizable aldehydes, yields were low due to a competing aldol reaction. Consistent with this, yields were lower with 2-ethylbutanal compared to *n*-octanal, where steric hindrance likely results in slower addition of the Julia reagent to the aldehyde and in the subsequent spirocyclization.

LHMDS-mediated condensations proceeded with complementary *Z*-selectivity (Table 2). As with the DBU-mediated reactions, this selectivity depended on the structure of the aldehyde, and to a much lesser extent on that of the sulfone. Selectivity was good to excellent with electron-rich aldehydes and the sterically hindered 2-ethylbutanal, and moderate to good with electron-deficient aromatic aldehydes and *n*-octanal. These condensations were very fast and complete disappearance of the aldehyde was observed within 5 minutes at −78 °C.

Next, the reactivity of triazole-derived Julia–Kocienski reagents with ketones was tested as well. For this, *N*-*p*-methoxyphenyl (**4**), *N*-(3-phenylpropyl) (**9**), and *N*-ferrocenyl (**10**) derived reagents were reacted with three ketones. Table 3

Table 2 Tunable selectivity in condensations of sulfones **4, 6, and 9** with aldehydes



Entry	Sulfone	R_1-CHO	Product, yield,[a] % E/Z ratio[b] Method A	Method B
1	**4**		**12**, 80%, 81 : 19	**12**, 72%, 14 : 86[c]
2	**6**		**13**, 82%, 87 : 13	**13**, 62%, 19 : 81
3	**9**		**14**, 75%, 76 : 24	**14**, 90%, 7 : 93[c]
4	**9**		—[d]	**15**, 47%, 26 : 74[c]
5	**4**		**16**, 52%, 64 : 36	**16**, 77%, 30 : 70
6	**6**		**17**, 87%, 60 : 40	**17**, 73%, 15 : 85
7	**9**		**18**, 80%, 63 : 37	**18**, 72%, 20 : 80
8	**9**		**19**, 85%, 57 : 43	**19**, 76%, 38 : 62[c]
9	**4**		**20**, 61%, 57 : 43	**20**, 68%, 34 : 66[c]
10	**6**		**21**, 33%, 58 : 42	**21**, 61%, 32 : 68
11	**9**		**22**, 56%, 61 : 39	**22**, 63%, 36 : 64[c]
12	**4**		**23**, 47%, 54 : 46	**23**, 59%, 15 : 85[c]
13	**6**		**24**, 3%, 54 : 46	**24**, 68%, 12 : 88
14	**9**		**25**, 5%, 61 : 39	**25**, 57%, 19 : 81[c]

[a] Yields are of isolated and purified products. [b] E/Z olefin ratios in the crude reaction mixtures were determined by ^{19}F NMR prior to isolation. [c] Data reported in ref 11*a*. [d] Reaction was not performed.

shows yields, E/Z ratios, and ^{19}F chemical shifts of the products.

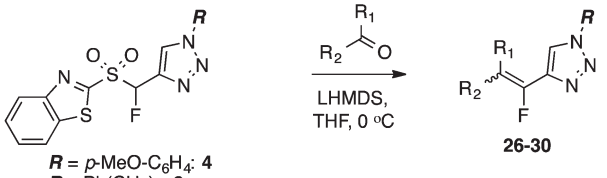
All reactions proceeded under LHMDS-mediated conditions, in THF at 0 °C, to give fluorovinyl triazoles **26–30** in 58–87% yields (Table 3). Initially, condensations were performed using conditions that were employed with aldehydes, *i.e.* with LHMDS in DMF–DMPU at −78 °C, but incomplete conversions of the starting ketone were observed. Complete conversions were achieved upon warming of the reaction mixture to room temperature; however, yields were lower in DMF–DMPU. For example, addition of LHMDS to a solution of acetophenone and **9** in DMF–DMPU at −78 °C with subsequent warming to room temperature gave (*E*/*Z*)-**29** in 63% yield. In comparison, a 77% yield was obtained when the reaction was performed in THF at 0 °C (entry 4). Stereoselectivity, on the other hand, was similar in both reactions.

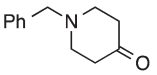
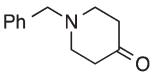
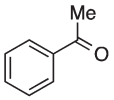
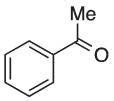
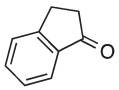
In order to assess the stereoselectivity of the condensations with acetophenone, the *E*/*Z* isomers produced in the reaction of *N*-(3-phenylpropyl) derived Julia–Kocienski reagent **9** (Table 3, entry 4) with acetophenone were chromatographically separated and the major isomer was crystallized. Analysis by X-ray diffraction[21] showed the stereochemistry of the major isomer to be *Z*-**29** (Fig. 2). The X-ray structure also confirmed regioselectivity of the azide–alkyne cycloaddition reaction.

The *Z*-stereoselectivity observed in the reaction of sulfone **9** with acetophenone is consistent with that observed in LHMDS-mediated reactions of aldehydes (Table 2, Method B). We assessed the stereochemistry in *E*-**28** and *Z*-**28**, formed by reaction of sulfone **4** with acetophenone (Table 3, entry 3), by comparing with the NMR characteristics of *E*- and *Z*-**29**.

Comparing the ^1H NMR spectra of *E*- and *Z*-**29**, a distinctive 1.11 ppm difference was observed in the chemical shifts of the H-5 triazolyl proton singlets, and the triazolyl proton resonance in *Z*-**29** (the major isomer) appeared most downfield in the spectrum (Table 4). The ^{19}F resonance of the major isomer of *Z*-**29** is more upfield shifted as compared to the *E*-isomer (see data in Table 3). Comparing the NMR data of *E*/*Z*-isomers of compound **29** to those of **28**, a similar 1.13 ppm difference was observed between the chemical shifts of the triazolyl H-5 proton singlets in the major and the minor isomers of olefins **28**. Also, the ^1H NMR of the major isomer showed an aromatic singlet as the most downfield shifted resonance. Furthermore, in the ^{19}F NMR, the major isomer in olefin mixture **28** produced the most upfield resonance. Due to the close structural similarities of (*E*/*Z*)-**28** and (*E*/*Z*)-**29** and the parallels in

Table 3 Condensations of sulfones **4, 9, and 10** with ketones



Entry	Sulfone	R_1R_2CO	Product, yield,[a] % isomer ratio[b]	^{19}F NMR δ[c] (ppm)
1	**4**		**26**, 87%, NA[d]	–121.99[d] ppm
2	**9**		**27**, 58%, NA	–121.52 ppm
3	**4**		**28**, 64%,[e] 28 : 72	–116.46 ppm (minor)[f] –116.57 ppm (major)[f]
4	**9**		**29**, 77%,[e] 20 : 80	–115.56 ppm (minor *E*-**29**)[g] –116.33 ppm (major *Z*-**29**)[g]
5	**10**		**30**, 58%, one isomer only[h]	–123.76 ppm

[a] Yields are of isolated and purified products. [b] Olefin isomer ratios in the crude reaction mixtures were determined by ^{19}F NMR prior to isolation. [c] Referenced to $CFCl_3$ as the internal standard; 282 MHz, $CDCl_3$ solvent. [d] Data reported in ref 11*a*. [e] Combined yields of *E*- and *Z*-isomers. [f] Stereochemistry of the isomers was assigned by comparison to compound **29** (see text). [g] Stereochemistry of the major isomer was assigned by X-ray crystallography (see text). [h] Stereochemistry was not assigned.

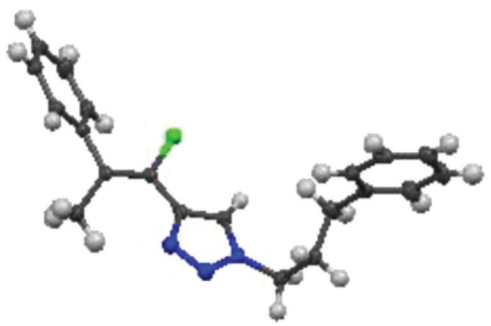


Fig. 2 Crystal structure of the major isomer of fluorovinyl triazole **29** (C, black; H, grey; F, green; N, blue).

the NMR spectra, the major isomer of **28** was assigned a *Z*-geometry and the minor isomer a *E*-geometry. The condensation product from indanone (**30**) is structurally very different to postulate the olefin stereochemistry by such comparisons. Moreover, because formation of only one isomer was detected, comparison of chemical shifts was not possible.

Table 4 Chemical shifts of the H-5 proton resonance in the major and minor isomers of compounds **28** and **29**

Compound	Triazolyl H-5 resonance[a]	$\Delta\delta$[b] ppm
Major isomer of **28**	8.04 ppm	1.13
Minor isomer of **28**	6.91 ppm	
Z-**29**	7.65 ppm	1.11
E-**29**	6.54 ppm	

[a] Obtained at 500 MHz in $CDCl_3$. [b] δ ppm of the major isomer – δ ppm of the minor isomer.

Conclusions

In conclusion, a highly modular approach to *N*-substituted 4-(1-fluorovinyl)triazoles has been developed, where the *N*1-substituent as well as substituents at the double bond can be readily varied. Cu-catalyzed azide–alkyne ligation reactions of TMS-protected α-fluoropropargyl benzothiazole sulfone, a Julia–Kocienski reagent, proceed with aryl, alkyl, or metallocenyl azides to give triazole-derived second-generation Julia–Kocienski reagents in good to excellent yields. Condensation reactions of triazole-derived Julia–Kocienski reagents with aldehydes are tunable and proceed with either *E*-selectivity under mild DBU-mediated conditions in THF at reflux, or with *Z*-selectivity in low temperature LHMDS-mediated reactions in DMF–DMPU. Ketones react in the presence of LHMDS in THF to give tetrasubstituted olefins. In the cases studied, where both isomers were formed in reactions with ketones, *E*- and *Z*-fluorovinyl triazoles were separable under chromatographic conditions. This method offers high flexibility for diversification of *N*1 and vinyl substituents.

Experimental section

General experimental considerations

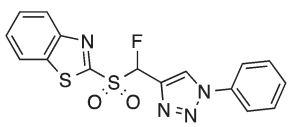
THF was distilled over $LiAlH_4$ and then over sodium, toluene was distilled over sodium, and CH_2Cl_2 was distilled over $CaCl_2$. DMF and DMPU were obtained from commercial sources and were used without further purification. For reactions performed under a nitrogen atmosphere, glassware was dried with a heat gun under vacuum. LDA (2.0 M solution in heptane–THF–EtPh) and LHMDS (1.0 M in THF) were obtained from commercial sources. All other reagents were obtained from commercial sources and were used as received. 1-Azidoadamantane and *N*-fluorobenzenesulfonimide (NFSI) are commercially available. Synthesis of 2-[1-fluoro-3-(trimethylsilyl) prop-2-ynylsulfonyl]benzo[*d*]thiazole (**1**) was first reported in our preliminary communication,[11a] we then reported an improved method.[11c] Syntheses of 2-{fluoro[1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl]methylsulfonyl}benzo[*d*]-thiazole (**4**), 2-[(1-decyl-1*H*-1,2,3-triazol-4-yl)fluoromethylsulfonyl]benzo[*d*]-thiazole (**8**) and 2-{fluoro[1-(3-phenylpropyl)-1*H*-1,2,3-triazol-4-yl]methylsulfonyl}benzo[*d*]-thiazole (**9**) have been reported in our preliminary communication.[11a] 1-Azido-4-phenoxy-

benzene,[22a] 1-azido-4-nitrobenzene,[22a] azidobenzene,[22,23] 2-azidonaphthalene,[23] azidoferrocene,[24] 1-azido-4-methoxybenzene,[11a,22] 3-(azidopropyl)benzene,[11a] and 1-azidodecane[11a] were synthesized *via* literature methods. Thin layer chromatography was performed on glass-backed silica gel plates (250 μm). Column chromatographic purifications were performed on 200–300 mesh silica gel. ^{1}H NMR spectra were recorded at 500 MHz and were referenced to the residual protio solvent. ^{13}C NMR spectra were recorded at 125 MHz and were referenced to the carbon resonance of the deuterated solvent. ^{19}F NMR spectra were recorded at 282 MHz with $CFCl_3$ as the internal standard. Chemical shifts (δ) are reported in parts per million and coupling constants (J) are in hertz (Hz). HRMS data were obtained using a TOF analyzer, the ionization modes are specified under each compound heading.

Synthesis of triazoles

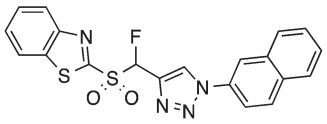
General procedure. To a stirring solution of azide (1 molar equiv.) in 4 : 1 (v/v) CH_2Cl_2–MeOH (28.0 mL mmol^{-1} of azide), 2-[1-fluoro-3-(trimethylsilyl)prop-2-ynylsulfonyl]benzo[*d*]thiazole **1** (1.10–1.50 molar equiv.), $Cu(CH_3CN)_4PF_6$ (0.20 molar equiv.) and $AgBF_4$ (0.20 molar equiv.) were sequentially added. The stirring was continued at room temperature until TLC showed the disappearance of the azide. The solvents were evaporated under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel. The quantities of azides and fluoropropargyl sulfone **1**, reaction times, eluting solvents for chromatography, product yields, R_f values, and spectroscopic characterization data are provided under the individual compound headings.

*2-{[Fluoro(1-phenyl-1H-1,2,3-triazol-4-yl)methyl]sulfonyl}benzo[d]thiazole (**2**).*



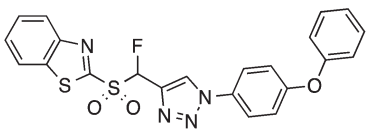
Prepared from azidobenzene (60.0 mg, 0.500 mmol) and sulfone **1** (206 mg, 0.630 mmol, 1.26 molar equiv.), in a reaction time of 4 h. Chromatography was performed using 20% EtOAc in hexanes and compound **2** was obtained as an off-white solid (148 mg, 79%). R_f (40% EtOAc in hexanes) = 0.45. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, 1H, Ar-H, J = 1.4 Hz), 8.32 (d, 1H, Ar-H, J = 8.3 Hz), 8.07 (d, 1H, Ar-H, J = 8.3 Hz), 7.78 (d, 2H, Ar-H, J = 7.4 Hz), 7.71 (t, 1H, Ar-H, J = 7.5 Hz), 7.66 (t, 1H, Ar-H, J = 7.6 Hz), 7.58 (t, 2H, Ar-H, J = 7.6 Hz), 7.52 (t, 1H, Ar-H, J = 7.4 Hz), 7.02 (d, 1H, CHF, $^2J_{FH}$ = 46.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 153.1, 137.8, 136.6, 136.0 (d, $^2J_{CF}$ = 24.3 Hz), 130.2, 129.9, 128.9, 128.3, 126.2, 124.0, 122.6, 121.2, 96.0 (d, $^1J_{CF}$ = 219.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −165.6 (d, $^2J_{FH}$ = 45.8 Hz). HRMS (ESI) calcd for $C_{16}H_{12}FN_4O_2S_2$ $[M + H]^+$ 375.380, found 375.379.

*2-{[Fluoro(1-(naphthalen-2-yl)-1H-1,2,3-triazol-4-yl)methyl]sulfonyl}benzo[d]thiazole (**3**).*



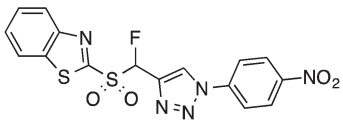
Prepared from 2-azidonaphthalene (85.0 mg, 0.500 mmol) and sulfone **1** (206 mg, 0.630 mmol, 1.26 molar equiv.) in a reaction time of 19 h. Chromatography was performed using 20% EtOAc in hexanes and compound **3** was obtained as an off-white solid (194 mg, 91%). R_f (40% EtOAc in hexanes) = 0.50. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (d, 1H, Ar-H, J = 1.8 Hz), 8.32 (d, 1H, Ar-H, J = 8.3 Hz), 8.22 (d, 1H, Ar-H, J = 1.9 Hz), 8.06 (d, 1H, Ar-H, J = 8.3 Hz), 8.04 (d, 1H, Ar-H, J = 8.8 Hz), 7.96–7.93 (m, 2H, Ar-H), 7.90 (dd, 1H, Ar-H, J = 8.8, 2.3 Hz), 7.72–7.59 (m, 4H, Ar-H), 7.06 (d, 1H, CHF, $^2J_{FH}$ = 46.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 153.1, 137.8, 136.1 (d, $^2J_{CF}$ = 24.3 Hz), 133.9, 133.4, 133.3, 130.5, 128.9, 128.6, 128.2, 127.9, 127.7, 126.6, 126.2, 124.2, 122.6, 119.4, 119.0, 96.1 (d, $^1J_{CF}$ = 220.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −165.5 (d, $^2J_{FH}$ = 45.8 Hz). HRMS (ESI) calcd for $C_{20}H_{14}FN_4O_2S_2$ $[M + H]^+$ 425.0537, found 425.0541.

*2-{[Fluoro(1-(4-phenoxyphenyl)-1H-1,2,3-triazol-4-yl)methyl]sulfonyl}benzo[d]thiazole (**5**).*



Prepared from 1-azido-4-phenoxybenzene (20.0 mg, 0.095 mmol) and sulfone **1** (total 46.6 mg, 0.143 mmol, 1.50 molar equiv.; 0.095 mmol were added initially and 0.048 mmol after 45 min) in a reaction time of 2 h 45 min. Chromatography was performed using CH_2Cl_2 and compound **5** was obtained as a white solid (39.7 mg, 90%). R_f (40% EtOAc in hexanes) = 0.52. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, 1H, Ar-H, J = 1.9 Hz), 8.33 (d, 1H, Ar-H, J = 8.3 Hz), 8.07 (d, 1H, Ar-H, J = 7.8 Hz), 7.72–7.65 (m, 4H, Ar-H), 7.41 (t, 2H, Ar-H, J = 8.1 Hz), 7.21 (t, 1H, Ar-H, J = 7.4 Hz), 7.16 (d, 2H, Ar-H, J = 8.8 Hz), 7.09 (d, 2H, Ar-H, J = 7.8 Hz), 7.01 (d, 1H, CHF, $^2J_{FH}$ = 46.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.9, 158.9, 156.2, 153.1, 137.8, 135.9 (d, $^2J_{CF}$ = 23.8 Hz), 131.6, 130.3, 128.9, 128.2, 126.2, 124.6, 124.1, 122.9, 122.6, 119.9, 119.4, 96.0 (d, $^1J_{CF}$ = 220.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −165.7 (d, $^2J_{FH}$ = 45.8 Hz). HRMS (ESI) calcd for $C_{22}H_{16}FN_4O_3S_2$ $[M + H]^+$ 467.0642, found 467.0646.

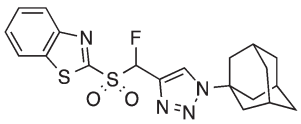
*2-{[Fluoro(1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methyl]sulfonyl}benzo[d]thiazole (**6**).*



Prepared from 1-azido-4-nitrobenzene (425 mg, 2.59 mmol) and sulfone **1** (932 mg, 2.85 mmol, 1.10 molar equiv.) in a reaction time of 50 h. Chromatography was performed using 40% EtOAc in hexanes and compound **6** was obtained as a

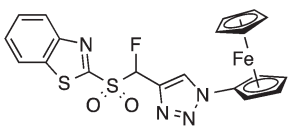
yellow solid (889.8 mg, 82%). R_f (40% EtOAc in hexanes) = 0.47. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.57 (s, 1H, Ar-H), 8.47 (d, 2H, Ar-H, J = 8.8 Hz), 8.41 (d, 1H, Ar-H, J = 8.3 Hz), 8.36 (d, 1H, Ar-H, J = 7.4 Hz), 8.30 (d, 2H, Ar-H, J = 8.8 Hz), 7.81–7.76 (m, 2H, Ar-H), 7.72 (d, 1H, CHF, $^2J_{FH}$ = 43.3 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.8, 152.2, 147.2, 140.2, 137.3, 136.4 (d, $^2J_{CF}$ = 23.8 Hz), 128.8, 128.3, 126.1, 125.5, 125.3, 123.6, 121.3, 95.9 (d, $^1J_{CF}$ = 217.4 Hz). ^{19}F NMR (282 MHz, DMSO-d_6): δ −172.0 (d, $^2J_{FH}$ = 42.7 Hz). HRMS (ESI) calcd for $C_{16}H_{11}FN_5O_4S_2$ $[M + H]^+$ 420.0231, found 420.0223.

2-{[(1-(Adamantan-1-yl)-1H-1,2,3-triazol-4-yl]fluoromethyl]sulfonyl}benzo[d]thiazole (7).



Prepared from 1-azidoadamantane (177 mg, 1.00 mmol) and sulfone **1** (409 mg, 1.25 mmol, 1.25 molar equiv.) in a reaction time of 4 h. Chromatography was performed with CH_2Cl_2 and compound **7** was isolated as a white solid (367 mg, 85%). R_f (40% EtOAc in hexanes) = 0.53. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, 1H, Ar-H, J = 8.3 Hz), 8.12 (s, 1H, Ar-H), 8.02 (d, 1H, Ar-H, J = 7.8 Hz), 7.66–7.59 (m, 2H, Ar-H), 6.93 (d, 1H, CHF, $^2J_{FH}$ = 46.5 Hz), 2.25–2.23 (m, 9H), 1.80–1.74 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.2, 153.0, 137.7, 134.1 (d, $^2J_{CF}$ = 21.5 Hz), 128.7, 128.1, 126.1, 122.5, 122.3, 96.4 (d, $^1J_{CF}$ = 219.2 Hz), 61.0, 43.0, 35.9, 29.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ −163.8 (d, $^2J_{FH}$ = 45.8 Hz). HRMS (ESI) calcd for $C_{20}H_{22}FN_4O_2S_2$ $[M + H]^+$ 433.1163, found 433.1169.

*2-{[(1-Ferrocenyl-1H-1,2,3-triazol-4-yl)fluoromethyl]sulfonyl}benzo[d]thiazole (**10**).*



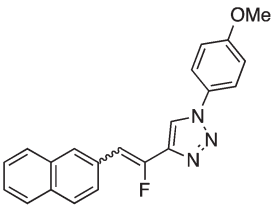
Prepared from azidoferrocene (160 mg, 0.710 mmol) and sulfone **1** (279 mg, 0.850 mmol, 1.20 molar equiv.) in a reaction time of 4 h. Chromatography was performed using 20% EtOAc in hexanes and compound **10** was obtained as a yellowish solid (226 mg, 66%). R_f (40% EtOAc in hexanes) = 0.52. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33–8.32 (m, 2H, Ar-H), 8.07 (d, 1H, Ar-H, J = 7.8 Hz), 7.72–7.63 (m, 2H, Ar-H), 6.97 (d, 1H, CHF, $^2J_{FH}$ = 46.5 Hz), 4.88–4.879 (m, 2H, Ar-H), 4.33 (t, 2H, Ar-H, J = 1.8 Hz), 4.25 (s, 5H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 153.1, 137.8, 135.2 (d, $^2J_{CF}$ = 24.3 Hz), 128.9, 128.2, 126.2, 125.5, 122.6, 96.1 (d, $^1J_{CF}$ = 219.7 Hz), 93.3, 70.6, 67.4, 62.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ −165.7 (d, $^2J_{FH}$ = 45.8 Hz). HRMS (ESI) calcd for $C_{20}H_{16}FFeN_4O_2S_2$ $[M + H]^+$ 483.0043, found 483.0048.

General procedures for condensations of sulfones 4, 6, and 9 with aldehydes

Method A: DBU-mediated condensations. To a stirring solution of the aldehyde (1 molar equiv.) and sulfone (1.2–1.7 molar equiv., see specific compound headings for the stoichiometry) in THF (20 mL mmol^{-1} of aldehyde), DBU (4 molar equiv.) in THF (8 mL mmol^{-1} of aldehyde) was added. The reaction mixture was stirred at reflux and monitored for the disappearance of the aldehyde. If the disappearance of sulfone was observed prior to consumption of the aldehyde, more sulfone was added to the reaction mixture and the reaction was continued at reflux. Upon complete consumption of the aldehyde, the solvent was removed under reduced pressure. The product E/Z ratio was determined by ^{19}F NMR, prior to purification by column chromatography. The combined E/Z product mixture was purified by column chromatography over silica gel. The quantities of reactants and solvents, reaction times, eluting solvents for chromatography, product yields, R_f values, and spectroscopic data are provided under the individual compound headings.

Method B: LHMDS-mediated condensations. A stirring solution of aldehyde (1 molar equiv.) and sulfone (1.2 molar equiv.) in 1 : 1 (v/v) DMF–DMPU (15.2 mL mmol^{-1} of aldehyde) was cooled to −78 °C (dry ice/iPrOH), under a nitrogen atmosphere. LHMDS (1.0 M solution in THF, 2.40 molar equiv.) was then added to the mixture. The reaction mixture was stirred at −78 °C for 5 min, saturated aq. NH_4Cl was added, and the mixture was poured into EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×). The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The product E/Z ratio was determined by ^{19}F NMR, prior to purification by column chromatography. The combined E/Z product mixture was purified by column chromatography over silica gel. The quantities of reactants and solvents, eluting solvents for chromatography, product yields, R_f values, and spectroscopic data are provided under the individual compound headings.

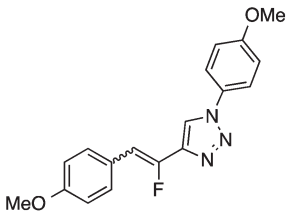
*(E/Z)-4-[1-Fluoro-2-(naphthalen-2-yl)vinyl]-1-(4-methoxyphenyl)-1H-1,2,3-triazole (**11**).*



Prepared by Method B using 2-naphthaldehyde (20.0 mg, 0.128 mmol), sulfone **4** (62.3 mg, 0.154 mmol, 1.2 molar equiv.) and LHMDS (0.307 mL, 0.307 mmol, 2.4 molar equiv.), in 1 : 1 (v/v) DMF–DMPU (2.0 mL). The E/Z ratio was determined to be 7/93. Chromatography was performed using 20% EtOAc in hexanes and E/Z-**11** was obtained as a white solid (33.4 mg, 76%). R_f (20% EtOAc in hexanes) = 0.23. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (s, 1H, Ar-H, Z-isomer), 8.05 (s, 1H, Ar-H, Z-isomer), 7.96 (s, 1H, Ar-H, E-isomer), 7.87–7.78 (m, 4H, Ar-H, both E- and Z-isomers), 7.68 (d, 2H, Ar-H, J = 8.5 Hz, Z-isomer), 7.59 (d, 1H, Ar-H, J = 8.5 Hz, E-isomer), 7.55 (d, 2H, Ar-H, J = 8.6 Hz, E-isomer), 7.50–7.46 (m, 2H, Ar-H, both E- and Z-isomers), 7.05 (d, 2H, Ar-H, J = 8.2 Hz, Z-isomer),

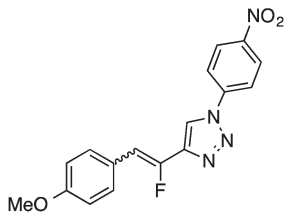
6.99 (d, 2H, Ar-H, J = 8.9 Hz, *E*-isomer), 6.98 (d, 1H, CHF, $^3J_{FH}$ = 41.2 Hz, *Z*-isomer), 6.78 (d, 1H, CHF, $^3J_{FH}$ = 22.3 Hz, *E*-isomer), 3.89 (s, 3H, CH_3, *Z*-isomer), 3.85 (s, 3H, CH_3, *E*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ −105.98 (d, $^3J_{FH}$ = 24.4 Hz, *E*-isomer), −118.47 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{21}H_{17}FN_3O$ $[M + H]^+$ 346.1350, found 346.1334.

*(E/Z)-4-[1-Fluoro-2-(4-methoxyphenyl)vinyl]-1-(4-methoxyphenyl)-1H-1,2,3-triazole (**12**).*



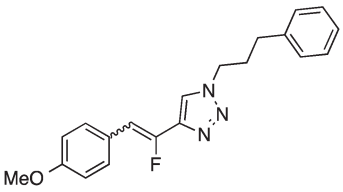
Prepared by Method A using 4-methoxybenzaldehyde (68.1 mg, 0.500 mmol), sulfone **4** (total 283.1 mg, 0.700 mmol, 1.4 molar equiv.; 0.6 mmol was added first and 0.1 mmol was added after 4.5 h), and DBU (304.5 mg, 2.00 mmol, 4.0 molar equiv.) in THF (14 mL), in a reaction time of 6.5 h. The *E*/*Z* ratio was determined to be 81/19. Chromatography was performed using 20% EtOAc in hexanes and *E*/*Z*-**12** was obtained as a white solid (130.1 mg, 80%). R_f (20% EtOAc in hexanes) = 0.22. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 1H, Ar-H, *Z*-isomer), 7.81 (s, 1H, Ar-H, *E*-isomer), 7.66 (d, 2H, Ar-H, J = 9.2 Hz, *Z*-isomer), 7.61–7.57 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 7.46 (d, 2H, Ar-H, J = 8.8 Hz, *E*-isomer), 7.04 (d, 2H, Ar-H, J = 9.2 Hz, *Z*-isomer), 7.01 (d, 2H, Ar-H, J = 9.2 Hz, *E*-isomer), 6.92 (d, 2H, Ar-H, J = 8.8 Hz, *Z*-isomer), 6.87 (d, 2H, Ar-H, J = 8.8 Hz, *E*-isomer), 6.75 (d, 1H, CHF, $^3J_{FH}$ = 41.4 Hz, *Z*-isomer), 6.57 (d, 1H, CHF, $^3J_{FH}$ = 23.0 Hz, *E*-isomer), 3.88 (s, 3H, CH_3, *Z*-isomer), 3.86 (s, 3H, CH_3, *E*-isomer), 3.84 (s, 3H, CH_3, *Z*-isomer), 3.81 (s, 3H, CH_3, *E*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ −108.51 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −121.54 (d, $^3J_{FH}$ = 42.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{18}H_{17}FN_3O_2$ $[M + H]^+$ 326.1299, found 326.1304.

*(E/Z)-4-[1-Fluoro-2-(4-methoxyphenyl)vinyl]-1-(4-nitrophenyl)-1H-1,2,3-triazole (**13**).*



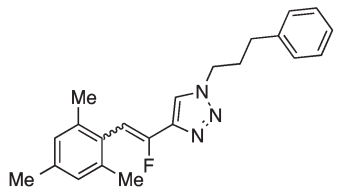
Prepared by Method A using 4-methoxybenzaldehyde (20.5 mg, 0.150 mmol), sulfone **6** (75.5 mg, 0.180 mmol, 1.2 molar equiv.), and DBU (91.3 mg, 0.600 mmol, 4.0 molar equiv.), in THF (4.3 mL), in a reaction time of 3 h. The *E*/*Z* ratio was determined to be 87/13. Chromatography was performed using CH_2Cl_2 and *E*/*Z*-**13** was obtained as a pale yellow solid (41.9 mg, 82%). R_f (20% EtOAc in hexanes) = 0.29. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (s, 1H, Ar-H, *Z*-isomer), 9.31 (s, 1H, Ar-H, *E*-isomer), 8.49–8.46 (m, Ar-H, 2H, both *E*- and *Z*-isomers), 8.30–8.27 (m, Ar-H, 2H, both *E*- and *Z*-isomers), 7.64 (d, 2H, Ar-H, J = 8.8 Hz, *Z*-isomer), 7.46 (d, 2H, Ar-H, J = 8.8, *E*-isomer), 7.01 (d, 2H, Ar-H, J = 8.7 Hz, *Z*-isomer), 6.90 (d, 2H, Ar-H, J = 8.7 Hz, *E*-isomer), 6.783 (d, 1H, CHF, $^3J_{FH}$ = 24.0 Hz, *E*-isomer), 6.778 (d, 1H, CHF, $^3J_{FH}$ = 40.1 Hz, *Z*-isomer), 3.80 (s, 3H, *Z*-isomer), 3.75 (s, 3H, *E*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ −109.57 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −122.23 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{17}H_{14}FN_4O_3$ $[M + H]^+$ 341.1044, found 341.1043.

*(E/Z)-4-[1-Fluoro-2-(4-methoxyphenyl)vinyl]-1-(3-phenylpropyl)-1H-1,2,3-triazole (**14**).*



Prepared by Method A using 4-methoxybenzaldehyde (20 mg, 0.15 mmol), sulfone **9** (total 106.5 mg, 0.26 mmol, 1.7 molar equiv.; 0.21 mmol was added first and 0.05 mmol was added after 8 h), and DBU (91.3 mg, 0.60 mmol, 4.0 molar equiv.), in THF (4.2 mL), in a reaction time of 20 h. The *E*/*Z* ratio was determined to be 76/24. Chromatography was performed using 20% EtOAc in hexanes and *E*/*Z*-**14** was obtained as a white solid (38.2 mg, 75%). R_f (20% EtOAc in hexanes) = 0.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 1H, Ar-H, *Z*-isomer), 7.58 (d, 2H, Ar-H, J = 8.8 Hz, *Z*-isomer), 7.39 (d, 2H, Ar-H, J = 8.8 Hz, *E*-isomer), 7.38 (s, 1H, *E*-isomer), 7.33–7.18 (m, Ar-H, 3H, *E*-isomer and 5H *Z*-isomer), 7.14 (d, 2H, Ar-H, J = 7.8 Hz, *E*-isomer), 6.91 (d, 2H, Ar-H, J = 8.8 Hz, *Z*-isomer), 6.85 (d, 2H, Ar-H, J = 8.3 Hz, *E*-isomer), 6.67 (d, 1H, CHF, $^3J_{FH}$ = 41.4 Hz, *Z*-isomer), 6.52 (d, 1H, CHF, $^3J_{FH}$ = 22.6 Hz, *E*-isomer), 4.39 (t, 2H, CH_2, J = 6.9 Hz, *Z*-isomer), 4.32 (t, 2H, CH_2, J = 6.9 Hz, *E*-isomer), 3.83 (s, 3H, CH_3, *Z*-isomer), 3.80 (s, 3H, CH_3, *E*-isomer), 2.69 (t, 2H, CH_2, J = 7.4 Hz, *Z*-isomer), 2.63 (t, 2H, CH_2, J = 7.4 Hz, *E*-isomer), 2.29 (quint, 2H, CH_2, J = 7.2 Hz, *Z*-isomer), 2.23 (quint, 2H, CH_2, J = 7.4 Hz, *E*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ −108.20 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −121.30 (d, $^3J_{FH}$ = 42.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{20}H_{21}FN_3O$ $[M + H]^+$ 338.1663, found 338.1667.

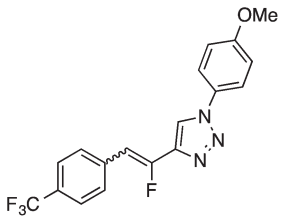
*(E/Z)-4-(1-Fluoro-2-mesitylvinyl)-1-(3-phenylpropyl)-1H-1,2,3-triazole (**15**).*



Prepared by Method B using 2,4,6-trimethylbenzaldehyde (15.0 mg, 0.10 mmol), sulfone **9** (50.4 mg, 0.12 mmol, 1.2 molar equiv.), and LHMDS (0.240 mL, 0.242 mmol, 2.4 molar equiv.), in 1 : 1 (v/v) DMF–DMPU (1.52 mL). The *E*/*Z* ratio was determined to be 26/74. Chromatography was performed using 20% EtOAc in hexanes and *E*/*Z*-**15** was obtained

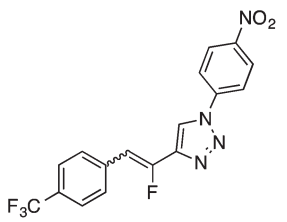
as a white solid (16.7 mg, 47%). R_f (20% EtOAc in hexanes) = 0.45. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (s, 1H, Ar-H, *Z*-isomer), 7.33–7.19 (m, Ar-H, 3H *E*-isomer and 5H *Z*-isomer), 7.07 (d, 2H, Ar-H, J = 7.3 Hz, *E*-isomer), 6.92 (s, 2H, Ar-H, both *E*- and *Z*-isomers), 6.76 (d, 1H, CHF, $^3J_{FH}$ = 41.5 Hz, *Z*-isomer), 6.59 (s, 1H, Ar-H, *E*-isomer), 6.36 (d, 1H, CHF, $^3J_{FH}$ = 18.5 Hz, *E*-isomer), 4.40 (t, 2H, CH_2, J = 7.1 Hz, *Z*-isomer), 4.17 (t, 2H, CH_2, J = 6.8 Hz, *E*-isomer), 2.71 (t, 2H, CH_2, J = 7.3 Hz, *Z*-isomer), 2.49 (t, 2H, CH_2, J = 7.3 Hz, *E*-isomer), 2.33–2.27 (m, 3H *E*-isomer and 11H *Z*-isomers), 2.15 (s, 6H, *E*-isomer, $2CH_3$), 2.10 (quint, 2H, *E*-isomer, J = 7.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −114.17 (d, $^3J_{FH}$ = 18.3 Hz, *E*-isomer), −115.50 (d, $^3J_{FH}$ = 42.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{22}H_{25}FN_3$ $[M + H]^+$ 350.2027, found 350.2034.

*(E/Z)-4-{1-Fluoro-2-[4-(trifluoromethyl)phenyl]vinyl}-1-(4-methoxyphenyl)-1H-1,2,3-triazole (**16**).*



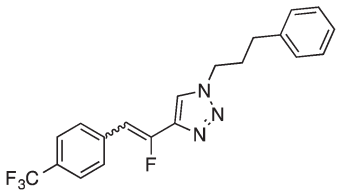
Prepared by Method A using 4-(trifluoromethyl)benzaldehyde (20.0 mg, 0.115 mmol), sulfone **4** (55.8 mg, 0.138 mmol, 1.2 molar equiv.), and DBU (70.0 mg, 0.460 mmol, 4.0 molar equiv.), in THF (3.2 mL), in a reaction time of 4 h. The *E*/*Z* ratio was determined to be 64/36. Chromatography was performed using 10% EtOAc in hexanes and *E*/*Z*-**16** was obtained as a white solid (21.6 mg, 52%). R_f (10% EtOAc in hexanes) = 0.21. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H, Ar-H, *Z*-isomer), 7.94 (s, 1H, Ar-H, *E*-isomer), 7.75 (d, 2H, Ar-H, J = 8.3 Hz, *Z*-isomer), 7.68 (d, 2H, Ar-H, J = 7.8 Hz, *E*-isomer), 7.65 (d, 2H, Ar-H, J = 7.4 Hz, *Z*-isomer), 7.62–7.58 (m, Ar-H, 4H *E*-isomer and 2H *Z*-isomer), 7.05 (d, 2H, Ar-H, J = 8.8 Hz, *Z*-isomer), 7.03 (d, 2H, Ar-H, J = 9.2 Hz, *E*-isomer), 6.86 (d, 1H, CHF, $^3J_{FH}$ = 40.5 Hz, *Z*-isomer), 6.61 (d, 1H, CHF, $^3J_{FH}$ = 23.0 Hz, *E*-isomer), 3.89 (s, 3H, CH_3, *Z*-isomer), 3.87 (s, 3H, CH_3, *E*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.17 (CF_3, both *E*- and *Z*-isomers), −103.52 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −116.10 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{18}H_{14}F_4N_3O$ $[M + H]^+$ 364.1068, found 364.1068.

*(E/Z)-4-{1-Fluoro-2-[4-(trifluoromethyl)phenyl]vinyl}-1-(4-nitrophenyl)-1H-1,2,3-triazole (**17**).*



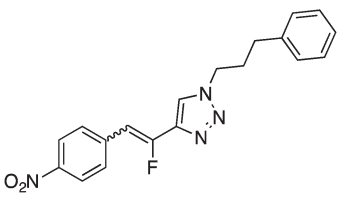
Prepared by Method A using 4-(trifluoromethyl)benzaldehyde (15.0 mg, 0.086 mmol), sulfone **6** (43.0 mg, 0.103 mmol, 1.2 molar equiv.), and DBU (52.0 mL, 0.344 mmol, 4.0 molar equiv.), in THF (2.5 mL), in a reaction time of 4 h. The *E*/*Z* ratio was determined to be 60/40. Chromatography was performed using 50% CH_2Cl_2 in hexanes and *E*/*Z*-**17** was obtained as a white solid (28.5 mg, 87%). R_f (10% EtOAc in hexanes) = 0.19. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48–8.44 (m, Ar-H, 2H, both *E*- and *Z*-isomers), 8.26 (s, 1H, Ar-H, *Z*-isomer), 8.17 (s, 1H, Ar-H, *E*-isomer), 8.03 (d, 2H, Ar-H, J = 8.8 Hz, *Z*-isomer), 7.97 (d, 2H, Ar-H, J = 8.8 Hz, *E*-isomer), 7.77 (d, 2H, Ar-H, J = 7.8 Hz, *Z*-isomer), 7.66–7.60 (m, Ar-H, 4H *E*-isomer and 2H *Z*-isomer), 6.92 (d, 1H, CHF, $^3J_{FH}$ = 40.1 Hz, *Z*-isomer), 6.69 (d, 1H, CHF, $^3J_{FH}$ = 23.0 Hz, *E*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.20 (CF_3, both *E*- and *Z*-isomers), −104.80 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −116.81 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{17}H_{10}F_4N_4NaO_2$ $[M + Na]^+$ 401.0632, found 401.0616.

*(E/Z)-4-{1-Fluoro-2-[4-(trifluoromethyl)phenyl]vinyl}-1-(3-phenylpropyl)-1H-1,2,3-triazole (**18**).*



Prepared by Method A using 4-(trifluoromethyl)benzaldehyde (20 mg, 0.115 mmol), sulfone **9** (57.0 mg, 0.14 mmol, 1.2 molar equiv.), and DBU (70.0 mg, 0.46 mmol, 4.0 molar equiv.), in THF (3.2 mL), in a reaction time of 4 h. The *E*/*Z* ratio was determined to be 63/37. Chromatography was performed using 50% CH_2Cl_2 in hexanes and *E*/*Z*-**18** was obtained as a white solid (34.2 mg, 80%). R_f (10% EtOAc in hexanes) = 0.35. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, 2H, Ar-H, J = 8.3 Hz, *Z*-isomer), 7.69 (s, 1H, Ar-H, *Z*-isomer), 7.62 (d, 2H, Ar-H, J = 7.4 Hz, both *E*- and *Z*-isomers), 7.57 (d, 2H, Ar-H, J = 8.3 Hz, *E*-isomer), 7.53 (s, 1H, Ar-H, *E*-isomer), 7.34–7.21 (m, 3H, Ar-H, both *E*- and *Z*-isomers), 7.19 (d, 2H, J = 7.4 Hz, *Z*-isomer), 7.15 (d, 2H, Ar-H, J = 7.4 Hz, *E*-isomer), 6.78 (d, 1H, CHF, $^3J_{FH}$ = 40.5 Hz, *Z*-isomer), 6.55 (d, 1H, CHF, $^3J_{FH}$ = 23.0 Hz, *E*-isomer), 4.41 (t, 2H, J = 7.1 Hz, *Z*-isomer), 4.36 (t, 2H, CH_2, J = 7.1 Hz, *E*-isomer), 2.69 (t, 2H, J = 7.4 Hz, *Z*-isomer), 2.64 (t, 2H, CH_2, J = 7.4 Hz, *E*-isomer), 2.30 (quint, 2H, J = 7.4 Hz, *Z*-isomer), 2.25 (quint, 2H, CH_2, J = 7.4 Hz, *E*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.14 (s, CF_3), −102.93 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −115.81 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{20}H_{18}F_4N_3$ $[M + H]^+$ 376.1431, found 376.1427.

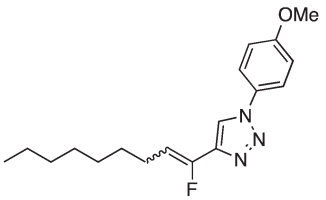
*(E/Z)-4-[1-Fluoro-2-(4-nitrophenyl)vinyl]-1-(3-phenylpropyl)-1H-1,2,3-triazole (**19**).*



Prepared by Method B using 4-nitrobenzaldehyde (75.6 mg, 0.50 mmol), sulfone **9** (249.9 mg, 0.60 mmol, 1.2 molar equiv.), and LHMDS (1.20 mL, 1.20 mmol, 2.4 molar equiv.),

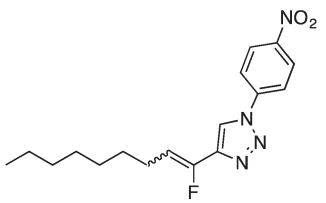
in 1 : 1 (v/v) DMF–DMPU (7.6 mL). The *E*/*Z* ratio was determined to be 38/62. Chromatography was performed using 40% EtOAc in hexanes and *E*/*Z*-**19** was obtained as a white solid (133.9 mg, 76%). R_f (20% EtOAc in hexanes) = 0.12. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, 2H, Ar-H, J = 8.8 Hz, *Z*-isomer), 8.17 (d, 2H, Ar-H, J = 8.8 Hz, *E*-isomer), 7.75 (d, 2H, Ar-H, J = 8.3 Hz, *Z*-isomer), 7.74 (d, 2H, Ar-H, J = 8.3 Hz, *E*-isomer), 7.72 (s, 1H, Ar-H, *Z*-isomer), 7.64 (s, 1H, Ar-H, *E*-isomer), 7.33–7.29 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 7.25–7.22 (m, 1H, Ar-H, both *E*- and *Z*-isomers), 7.21–7.16 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 6.82 (d, 1H, CHF, $^3J_{FH}$ = 39.6 Hz, *Z*-isomer), 6.55 (d, 1H, CHF, $^3J_{FH}$ = 23.5 Hz, *E*-isomer), 4.42 (t, 2H, J = 7.1 Hz, *Z*-isomer), 4.38 (t, 2H, CH_2, J = 7.4 Hz, *E*-isomer), 2.71–2.65 (m, 2H, both *E*- and *Z*-isomers), 2.34–2.25 (m, 2H, both *E*- and *Z*-isomers). ^{19}F NMR (282 MHz, $CDCl_3$): δ −100.64 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −113.37 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{19}H_{18}FN_4O_2$ $[M + H]^+$ 353.1408, found 353.1411.

*(E/Z)-4-(1-Fluoronon-1-en-1-yl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (**20**).*



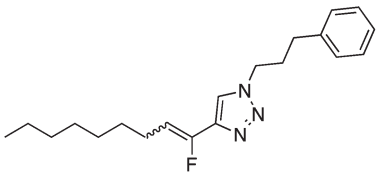
Prepared by Method B using *n*-octanal (20.0 mg, 0.160 mmol), sulfone **4** (76.8 mg, 0.190 mmol, 1.2 molar equiv.), and LHMDS (0.384 mL, 0.384 mmol, 2.4 molar equiv.), in 1 : 1 (v/v) DMF–DMPU (2.4 mL). The *E*/*Z* ratio was determined to be 34/66. Chromatography was performed using 20% EtOAc in hexanes and *E*/*Z*-**20** was obtained as a colorless semi-solid (34.7 mg, 68%). R_f (20% EtOAc in hexanes) = 0.40. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H, Ar-H, *E*-isomer), 7.86 (s, 1H, Ar-H, *Z*-isomer), 7.65–7.62 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 7.04–7.02 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 5.85 (dt, 1H, CHF, $^3J_{FH}$ = 39.1, $^3J_{HH}$ = 7.8 Hz, *Z*-isomer), 5.54 (dt, 1H, CHF, $^3J_{FH}$ = 22.6, $^3J_{HH}$ = 8.3 Hz, *E*-isomer), 3.87 (s, 3H, both *E*- and *Z*-isomers), 2.66 (q, 2H, J = 7.4 Hz, *E*-isomer), 2.30 (q, 2H, J = 7.2 Hz, *Z*-isomer), 1.50 (quint, 2H, J = 7.4 Hz, both *E*- and *Z*-isomers), 1.40–1.26 (m, 8H, both *E*- and *Z*-isomers), 0.90–0.86 (m, 3H, both *E*- and *Z*-isomers). ^{19}F NMR (282 MHz, $CDCl_3$): δ −115.56 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −124.67 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{18}H_{25}FN_3O$ $[M + H]^+$ 318.1976, found 318.1983.

*(E/Z)-4-(1-Fluoronon-1-en-1-yl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (**21**).*



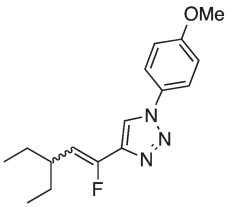
Prepared by Method B using *n*-octanal (20.0 mg, 0.160 mmol), sulfone **6** (79.7 mg, 0.19 mmol, 1.2 molar equiv.), and LHMDS (0.380 mL, 0.380 mmol, 2.4 molar equiv.), in 1 : 1 (v/v) DMF–DMPU (2.2 mL). The *E*/*Z* ratio was determined to be 32/68. Chromatography was performed using 20% EtOAc in hexanes and *E*/*Z*-**21** was obtained as a pale yellow solid (32.5 mg, 61%). R_f (20% EtOAc in hexanes) = 0.48. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45–8.42 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 8.14 (s, 1H, Ar-H, *E*-isomer), 8.05 (s, 1H, Ar-H, *Z*-isomer), 8.01–7.97 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 5.93 (dt, 1H, CHF, $^3J_{FH}$ = 39.0 Hz, $^3J_{HH}$ = 7.8 Hz, *Z*-isomer), 5.62 (dt, 1H, CHF, $^3J_{FH}$ = 22.9 Hz, $^3J_{HH}$ = 8.3 Hz, *E*-isomer), 2.68 (q, 2H, CH_2, J = 7.7 Hz, *E*-isomer), 2.32 (q, 2H, CH_2, J = 7.5 Hz, *Z*-isomer), 1.50 (quint, 2H, CH_2, J = 7.2 Hz, both *E*- and *Z*-isomers), 1.41–1.29 (m, 8 H, both *E*- and *Z*-isomers), 0.88 (app q, 3H, CH_3, J = 6.8 Hz, both *E*- and *Z*-isomers). ^{19}F NMR (282 MHz, $CDCl_3$): δ −116.23 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −125.21 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{17}H_{22}FN_4O_2$ $[M + H]^+$ 333.1721, found 333.1719.

*(E/Z)-4-(1-Fluoronon-1-en-1-yl)-1-(3-phenylpropyl)-1H-1,2,3-triazole (**22**).*



Prepared by Method B using *n*-octanal (20.0 mg, 0.160 mmol), sulfone **9** (79.1 mg, 0.19 mmol, 1.2 molar equiv.), and LHMDS (0.380 mL, 0.380 mmol, 2.4 molar equiv.), in DMF–DMPU (v/v) (2.2 mL). The *E*/*Z* ratio was determined to be 36/64. Chromatography was performed using 20% EtOAc in hexanes and *E*/*Z*-**22** was obtained as a pale yellow solid (32.9 mg, 63%). R_f (20% EtOAc in hexanes) = 0.2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 1H, Ar-H, *E*-isomer), 7.48 (s, 1H, Ar-H, *Z*-isomer), 7.31 (t, 2H, Ar-H, J = 7.4 Hz, both *E*- and *Z*-isomers), 7.22 (t, 1H, Ar-H, J = 7.1 Hz, both *E*- and *Z*-isomers), 7.19–7.17 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 5.77 (dt, 1H, CHF, $^3J_{FH}$ = 39.1 Hz, $^3J_{HH}$ = 7.8 Hz, *Z*-isomer), 5.48 (dt, 1H, CHF, $^3J_{FH}$ = 22.6 Hz, $^3J_{HH}$ = 8.1 Hz, *E*-isomer), 4.38–4.34 (m, 2H, both *E*- and *Z*-isomers), 2.67 (q, 2H, J = 7.1 Hz, both *E*- and *Z*-isomers), 2.60 (q, 2H, J = 7.7 Hz, *E*-isomer), 2.30–2.23 (m, 2H *E*-isomer and 4H *Z*-isomer), 1.49–1.43 (m, 2H, both *E*- and *Z*-isomers), 1.37–1.23 (m, 8H, both *E*- and *Z*-isomers), 0.90–0.86 (m, 3H, CH_3, both *E*- and *Z*-isomers). ^{19}F NMR (282 MHz, $CDCl_3$): δ −115.34 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −124.51 (d, $^3J_{FH}$ = 36.6 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{20}H_{28}FN_3Na$ $[M + Na]^+$ 352.2159, found 352.2161.

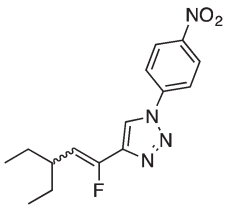
*(E/Z)-4-(3-Ethyl-1-fluoropent-1-en-1-yl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (**23**).*



Prepared by Method B using 2-ethylbutanal (15.0 mg, 0.15 mmol), sulfone **4** (72.8 mg, 0.18 mmol, 1.2 molar equiv.),

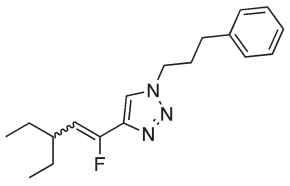
and LHMDS (0.360 mL, 0.360 mmol, 2.4 molar equiv.), in DMF–DMPU (v/v) (2.2 mL). The *E*/*Z* ratio was determined to be 15/85. Chromatography was performed using 20% EtOAc in hexanes and *E*/*Z*-**23** was obtained as a colorless semi-solid (25.7 mg, 59%). R_f (20% EtOAc in hexanes) = 0.39. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H, Ar-H, *E*-isomer), 7.87 (s, 1H, Ar-H, *Z*-isomer), 7.66–7.62 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 7.03 (d, 2H, Ar-H, J = 8.8 Hz, both *E*- and *Z*-isomers), 5.61 (dd, 1H, CHF, $^3J_{FH}$ = 39.1 Hz, $^3J_{HH}$ = 10.6 Hz, *Z*-isomer), 5.27 (dd, 1H, CHF, $^3J_{FH}$ = 24.0 Hz, $^3J_{HH}$ = 11.0 Hz, *E*-isomer), 3.87 (s, 3H, both *E*- and *Z*-isomers), 3.31–3.23 (m, 1H, *E*-isomer), 2.57–2.49 (m, 1H, *Z*-isomer), 1.60–1.52 (m, 2H, both *E*- and *Z*-isomers), 1.40–1.30 (m, 2H, both *E*- and *Z*-isomers), 0.93 (t, 6H, J = 7.6 Hz, both *E*- and *Z*-isomers). ^{19}F NMR (282 MHz, $CDCl_3$): δ −114.37 (d, $^3J_{FH}$ = 21.4 Hz, *E*-isomer), −124.68 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{16}H_{21}FN_3O$ $[M + H]^+$ 290.1663, found 290.1666.

*(E/Z)-4-(3-Ethyl-1-fluoropent-1-en-1-yl)-1-(4-nitrophenyl)-1H-1,2,3-triazole (**24**).*



Prepared by Method B using 2-ethylbutanal (15.0 mg, 0.15 mmol), sulfone **6** (75.5 mg, 0.18 mmol, 1.2 molar equiv.), and LHMDS (0.360 mL, 0.360 mmol, 2.4 molar equiv.), in DMF–DMPU (v/v) (2.0 mL). The *E*/*Z* ratio was determined to be 12/88. Chromatography was performed using 20% EtOAc in hexanes and compound *E*/*Z*-**24** was obtained as a pale yellow solid (31.0 mg, 68%). R_f (20% EtOAc in hexanes) = 0.53. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, 2H, Ar-H, J = 8.9 Hz, both *E*- and *Z*-isomers), 8.14 (s, 1H, Ar-H, *E*-isomer), 8.05 (s, 1H, Ar-H, *Z*-isomer), 8.01–7.98 (m, 2H, Ar-H, both *E*- and *Z*-isomers), 5.70 (dd, 1H, CHF, $^3J_{FH}$ = 39.4 Hz, $^3J_{HH}$ = 10.4 Hz, *Z*-isomer), 5.35 (dd, 1H, CHF, $^3J_{FH}$ = 24.0 Hz, $^3J_{HH}$ = 11.1 Hz, *E*-isomer), 3.34–3.24 (m, 1H, *E*-isomer), 2.59–2.51 (m, 1H, *Z*-isomer), 1.64–1.54 (m, 2H, both *E*- and *Z*-isomers), 1.41–1.32 (m, 2H, both *E*- and *Z*-isomers), 0.93 (t, 6H, J = 7.5 Hz, both *E*- and *Z*-isomers). ^{19}F NMR (282 MHz, $CDCl_3$): δ −114.94 (d, $^3J_{FH}$ = 24.4 Hz, *E*-isomer), −125.07 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{15}H_{18}FN_4O_2$ $[M + H]^+$ 305.1408, found 305.1414.

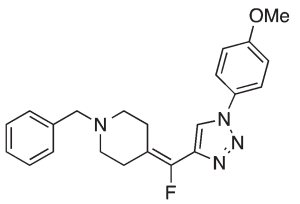
*(E/Z)-4-(3-Ethyl-1-fluoropent-1-en-1-yl)-1-(3-phenylpropyl)-1H-1,2,3-triazole (**25**).*



Prepared by Method B using 2-ethylbutanal (20.0 mg, 0.20 mmol), sulfone **9** (100.0 mg, 0.24 mmol, 1.2 molar equiv.), and LHMDS (0.480 mL, 0.480 mmol, 2.4 molar equiv.), in DMF–DMPU (v/v) (3.0 mL). The *E*/*Z* ratio was determined to be 19/81. Chromatography was performed using 20% EtOAc in hexanes and compound *E*/*Z*-**25** was obtained as a white solid (34.5 mg, 57%). R_f (20% EtOAc in hexanes) = 0.21. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H, Ar-H, *E*-isomer), 7.49 (s, 1H, Ar-H, *Z*-isomer), 7.31 (t, 2H, Ar-H, J = 7.4 Hz, both *E*- and *Z*-isomers), 7.22 (t, 1H, Ar-H, J = 7.4 Hz, both *E*- and *Z*-isomers), 7.18 (d, 2H, Ar-H, J = 7.4 Hz, both *E*- and *Z*-isomers), 5.53 (dd, 1H, CHF, $^3J_{FH}$ = 39.6 Hz, $^3J_{HH}$ = 10.1 Hz, *Z*-isomer), 5.21 (dd, 1H, CHF, $^3J_{FH}$ = 23.7 Hz, $^3J_{HH}$ = 11.3 Hz, *E* isomer), 4.36 (t, 2H, CH_2, J = 7.1 Hz, both *E*- and *Z*-isomers), 3.22–3.14 (m, 1H, CH, *E*-isomer), 2.67 (t, 2H, CH_2, J = 7.4 Hz, both *E*- and *Z*-isomers), 2.54–2.46 (m, 1H, CH, *Z*-isomer), 2.31–2.23 (m, 2H, CH_2, both *E*- and *Z*-isomers), 1.57–1.50 (m, 2H, CH_2, both *E*- and *Z*-isomers), 1.37–1.26 (m, 2H, CH_2, both *E*- and *Z*-isomers), 0.93–0.88 (m, 6H, $2CH_3$, both *E*- and *Z*-isomers). ^{19}F NMR (282 MHz, $CDCl_3$): δ −113.99 (d, $^3J_{FH}$ = 24.4 Hz, *E*-isomer), −124.55 (d, $^3J_{FH}$ = 39.7 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{18}H_{25}FN_3$ $[M + H]^+$ 302.2027, found 302.2031.

General procedure for condensations of sulfones 4, 9, and 10 with ketones. A stirring solution of the ketone (1 molar equiv.) and sulfone (1.2–1.3 molar equiv.) in THF (12 mL mmol^{-1} of ketone, except for compound **30**, see below) was cooled to 0 °C under a nitrogen atmosphere. LHMDS (2.40 molar equiv. in every case and 4.0 molar equiv. for compound **30**, see below) was added to the mixture. The reaction mixture was then stirred at 0 °C and was monitored for the disappearance of the ketone. Saturated aq. NH_4Cl was added and the mixture was poured into EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×). The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The product *E*/*Z* ratio was determined by ^{19}F NMR, prior to purification by column chromatography. The combined *E*/*Z* product mixture was isolated by column chromatography over silica gel. The quantities of reactants and solvents, reaction times, eluting solvents for chromatography, product yields, R_f values, and spectroscopic data are provided under the individual compound headings.

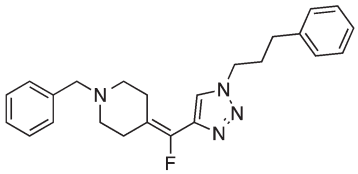
*1-Benzyl-4-{fluoro[1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl]-methylene}piperidine (**26**).*[11a]



Prepared from 1-benzylpiperidin-4-one (20.0 mg, 0.11 mmol), sulfone **4** (56.6 mg, 0.14 mmol, 1.3 molar equiv.), and LHMDS (0.260 mL, 0.260 mmol, 2.4 molar equiv.), in THF (1.3 mL), in a reaction time of 5 min. Chromatography was performed using 40% EtOAc in hexanes to obtain compound **26** as a semi-solid (36.2 mg, 87%). R_f (30% EtOAc in hexanes) = 0.20.

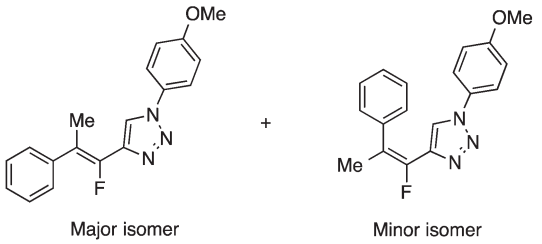
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H, Ar-H), 7.63 (d, 2H, Ar-H, J = 9.3 Hz), 7.36–7.32 (m, 4H, Ar-H), 7.28–7.25 (m, 1H, Ar-H), 7.02 (d, 2H, Ar-H, J = 8.3 Hz), 3.87 (s, 3H, CH_3), 3.57 (s, 2H, CH_2), 3.00 (t, 2H, CH_2, J = 4.9 Hz), 2.59–2.54 (m, 6H, $3CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2, four resonances at 143.4, 143.2, 142.9, 141.6 (two doublets for 2C), 138.4, 130.4, 129.4 (2C), 128.4 (2C), 127.3, 122.4 (2C), 119.9, 118.9 (d, J_{CF} = 15.1 Hz), 115.0 (2C), 63.1, 55.8, 54.3, 53.8, 27.0 (d, J_{CF} = 4.6 Hz), 26.2 (d, J_{CF} = 7.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −121.99 (s). HRMS (ESI) calcd for $C_{22}H_{24}FN_4O$ $[M + H]^+$ 379.1929, found 379.1924.

*1-Benzyl-4-{fluoro[1-(3-phenylpropyl)-1H-1,2,3-triazol-4-yl]-methylene}piperidine (**27**).*



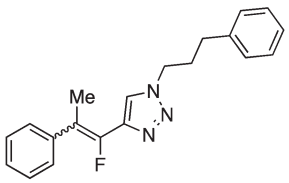
Prepared from 1-benzylpiperidin-4-one (20.0 mg, 0.11 mmol), sulfone **9** (52.8 mg, 0.13 mmol, 1.2 molar equiv.), and LHMDS (0.264 mL, 0.264 mmol, 2.4 molar equiv.), in THF (1.3 mL), in a reaction time of 2 h. Chromatography was performed using 20% EtOAc in hexanes to obtain compound **27** as an off-white semi-solid (25.0 mg, 58%). R_f (20% EtOAc in hexanes) = 0.23. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H, Ar-H), 7.36–7.25 (m, 7H, Ar-H), 7.22 (t, 1H, Ar-H, J = 7.4 Hz), 7.18 (d, 2H, Ar-H, J = 7.8 Hz), 4.36 (t, 2H, CH_2, J = 6.9 Hz), 3.55 (s, 2H, CH_2), 2.94 (t, 2H, CH_2, J = 4.8 Hz), 2.66 (t, 2H, CH_2, J = 7.6 Hz), 2.56–2.52 (m, 6H), 2.26 (quint, 2H, CH_2, J = 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.8 (d, J_{CF} = 227.9 Hz), 142.7 (d, J_{CF} = 40.3 Hz), 140.3, 138.8, 129.4 (2C), 128.9 (2C), 128.7 (2C), 128.4 (2C), 127.2, 126.7, 121.6, 118.5 (d, J_{CF} = 14.8 Hz), 63.2, 54.4, 53.9, 49.7, 32.8, 31.7, 27.2 (d, J_{CF} = 4.6 Hz), 26.3 (d, J_{CF} = 7.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −121.52 (s). HRMS (ESI) calcd for $C_{24}H_{28}FN_4$ $[M + H]^+$ 391.2293, found 391.2298.

*(E/Z)-4-(1-Fluoro-2-phenylprop-1-en-1-yl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (**28**).*



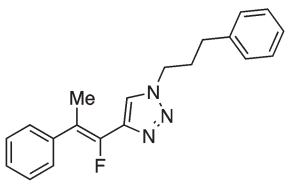
Prepared from acetophenone (20.0 mg, 0.17 mmol), sulfone **4** (80.9 mg, 0.20 mmol, 1.2 molar equiv.), and LHMDS (0.410 mL, 0.410 mmol, 2.4 molar equiv.), in THF (2.0 mL), in a reaction time of 15 min. The major/minor isomer ratio was determined to be 72 : 28. Chromatography was performed using 20% EtOAc in hexanes and compound *E*/*Z*-**28** was obtained as a white solid (33.0 mg, 64%). *Major isomer*: R_f (20% EtOAc in hexanes) = 0.27. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (s, 1H, Ar-H), 7.67 (d, 2H, Ar-H, J = 8.8 Hz), 7.50 (d, 2H, Ar-H, J = 7.8 Hz), 7.41 (t, 2H, Ar-H, J = 7.6 Hz), 7.31 (t, 1H, Ar-H, J = 7.4 Hz), 7.04 (d, 2H, Ar-H, J = 9.2 Hz), 3.87 (s, 3H, CH_3), 2.57 (d, 3H, CH_3, J = 3.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.2, four resonances at 145.8, 143.9, 143.7, 143.4 (two doublets for 2C), 138.6, 130.3, 128.5 (d, 2C, J_{CF} = 4.1 Hz), 128.4 (2C), 127.5, 122.4 (2C), 120.5, 118.0 (d, J_{CF} = 12.4 Hz), 115.1 (2C), 55.9, 17.5 (d, J_{CF} = 3.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −116.57 (s). *Minor isomer*: R_f (20% EtOAc in hexanes) = 0.22. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.32 (m, 5H, Ar-H), 7.27–7.25 (m, 2H, Ar-H), 6.94 (d, 2H, Ar-H, J = 9.2 Hz), 6.91 (s, 1H, Ar-H), 3.83 (s, 3H, CH_3), 2.21 (d, 3H, CH_3, J = 3.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1, 145.9 (d, J_{CF} = 240.8 Hz), 141.5 (d, J_{CF} = 35.0 Hz), 139.4 (d, J_{CF} = 7.3 Hz), 130.2, 129.2 (2C), 128.8 (d, 2C, J_{CF} = 2.7 Hz), 128.1, 122.3 (2C), 120.6 (d, J_{CF} = 5.1 Hz), 119.7 (d, J_{CF} = 19.2 Hz), 114.9 (2C), 55.8, 17.8 (d, J_{CF} = 6.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −116.46 (s). HRMS (ESI) calcd for $C_{18}H_{17}FN_3O$ $[M + H]^+$ 310.1350, found 310.1353.

*(E/Z)-4-(1-Fluoro-2-phenylprop-1-en-1-yl)-1-(3-phenylpropyl)-1H-1,2,3-triazole (**29**).*



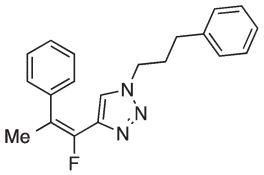
Prepared from acetophenone (20.0 mg, 0.17 mmol), sulfone **9** (83.2 mg, 0.20 mmol, 1.2 molar equiv.), and LHMDS (0.410 mL, 0.410 mmol, 2.4 molar equiv.), in THF (2.0 mL), in a reaction time of 30 min. The major/minor isomer ratio was determined to be 80 : 20. Chromatography was performed using 20% EtOAc in hexanes to obtain the major isomer *Z*-**29** as a white solid (33.0 mg, 60%), and the minor isomer *E*-**29** as a white solid (9.2 mg, 17%). Analysis of the major isomer by X-ray diffraction showed *Z* stereochemistry of the alkene (crystals were obtained by slow evaporation from a solution in methylene chloride).

*Major isomer Z-**29**.*



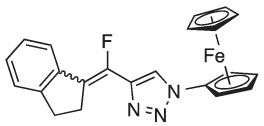
R_f (20% EtOAc in hexanes) = 0.20. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (s, 1H, Ar-H), 7.48 (d, 2H, Ar-H, J = 7.4 Hz), 7.39 (t, 2H, Ar-H, J = 7.6 Hz), 7.33–7.28 (m, 3H, Ar-H), 7.24–7.19 (m, 3H, Ar-H), 4.40 (t, 2H, CH_2, J = 7.1 Hz), 2.69 (t, 2H, CH_2, J = 7.4 Hz), 2.52 (d, 3H, CH_3, J = 3.2 Hz), 2.30 (quint, 2H, CH_2, J = 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1 (d, J_{CF} = 233.9 Hz), 143.0 (d, J_{CF} = 39.4 Hz), 140.2, 138.6, 128.9 (2C), 128.6 (2C), 128.4 (d, 2C, J_{CF} = 4.1 Hz), 128.3 (2C), 127.5, 126.6, 122.3 (d, J_{CF} = 2.3 Hz), 117.4 (d, J_{CF} = 13.3 Hz), 49.7, 32.6, 31.8, 17.4 (d, J_{CF} = 4.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −116.33 (s).

*Minor isomer E-**29**.*



R_f (20% EtOAc in hexanes) = 0.10. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.31 (m, 3H, Ar-H), 7.28 (t, 2H, Ar-H, J = 7.4 Hz), 7.22–7.19 (m, 3H, Ar-H), 7.06 (d, 2H, Ar-H, J = 7.4 Hz), 6.54 (s, 1H, Ar-H), 4.15 (t, 2H, CH_2, J = 6.7 Hz), 2.48 (t, 2H, CH_2, J = 7.4 Hz), 2.18 (d, 3H, CH_3, J = 4.1 Hz), 2.07 (quint, 2H, CH_2, J = 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1 (d, J_{CF} = 241.2 Hz), 141.0 (d, J_{CF} = 33.4 Hz), 140.2, 139.6 (d, J_{CF} = 7.3 Hz), 129.1 (2C), 128.82 (2C), 128.77 (d, 2C, J_{CF} = 2.7 Hz), 128.6 (2C), 127.9, 126.6, 122.6 (d, J_{CF} = 5.5 Hz), 119.3 (d, J_{CF} = 19.7 Hz), 49.4, 32.4, 31.6, 17.7 (d, J_{CF} = 6.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −115.56 (s). HRMS (ESI) calcd for $C_{20}H_{20}FN_3Na$ $[M + Na]^+$ 344.1533, found 344.1536.

*(E) or (Z)-4-[(2,3-Dihydro-1H-inden-1-ylidene)fluoromethyl]-1-ferrocenyl-1H-1,2,3-triazole (**30**).*



Prepared from 1-indanone (20.0 mg, 0.15 mmol), sulfone **10** (87.0 mg, 0.18 mmol, 1.2 molar equiv.), and LHMDS (total 0.600 mL, 0.600 mmol, 4.0 molar equiv.; 2.4 molar equiv. was added first and 1.6 molar equiv. was added after 2 h), in THF (5.0 mL), in a reaction time of 4 h. Chromatography was performed using 20% EtOAc in hexanes, with a stepwise increase to 40% EtOAc in hexanes, and compound **30** was obtained as a yellow-orange solid (35.1 mg, 58%). R_f (40% EtOAc in hexanes) = 0.48. Formation of only one isomer was detected by ^{1}H and ^{19}F NMR, and olefin stereochemistry was not determined. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, 1H, Ar-H, J = 6.8 Hz), 7.90 (s, 1H), 7.32 (d, 1H, Ar-H, J = 6.4 Hz), 7.29–7.24 (m, 2H), 4.88 (t, 2H, J = 1.9 Hz), 4.30 (t, 2H, J = 1.9 Hz), 4.25 (s, 5H), 3.34 (td, 2H, J = 6.8; 2.4 Hz), 3.17 (br t, 2H, J = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.8, 143.9 (d, $^1J_{CF}$ = 236.2 Hz), 143.6 (d, J_{CF} = 38.0 Hz), 139.1 (d, J_{CF} = 2.7 Hz), 128.4 (d, J_{CF} = 2.3 Hz), 127.0, 126.0 (d, J_{CF} = 14.2 Hz), 125.1, 124.0 (d, J_{CF} = 11.0 Hz), 120.2, 93.7, 70.5, 67.0, 62.4, 31.3, 28.3 (d, J_{CF} = 5.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −123.76 (s). HRMS (ESI) calcd for $C_{22}H_{19}FFeN_3$ $[M + H]^+$ 400.0907, found 400.0944.

Single-crystal X-ray diffraction for (*Z*)-29

The intensity data for (*Z*)-**29** were measured using a KappaCCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, ϕ–ω scans) at 100 (1) K. The data were not corrected for absorption. Details of the solution and refinements for $C_{20}H_{20}FN_3$ (*Z*-**29**) are as follows. The crystals of (*Z*)-**29**, with approximate dimensions 0.10 × 0.28 × 0.30 mm, were monoclinic with a space group of *P*2/*c*. The final unit-cell constants of (*Z*)-**29** were a = 18.306(4), b = 5.6030(11), c = 16.578(3) Å, β = 101.41(3)°, V = 1666.8(6) Å^3, Z = 4, ρ = 1.281 g cm^{-1}, μ = 0.085 mm^{-1}, formula weight = 321.39. The structure of Z-**29** was solved using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97. The hydrogen atoms were calculated with the riding model in the structure-factor calculations, but their parameters were not refined. The final discrepancy indices, 2.95 < θ < 27.47°, were R = 0.0610 (calculated on F for 2290 reflections) and R_w = 0.1395 (calculated on F^2 for all 3804 reflections) with 219 parameters varied. The major peaks of the final difference map are −0.29 and +0.22 e Å^3.

Acknowledgements

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