Regiospecific Synthesis of 1,4,5-Trisubstituted-1,2,3-triazole via One-Pot Reaction Promoted by Copper(I) Salt

Yong-Ming Wu,* Juan Deng, Ya Li, Qing-Yun Chen

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Rd., Shanghai 200032, P. R. China
Fax +86(21)64166128; E-mail: ymwu@mail.sioc.ac.cn
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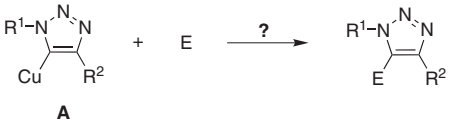
Abstracts: A method for the regiospecific synthesis of 1,4,5-trisubstituted-1,2,3-triazole catalyzed by copper(I) iodide was developed. This is the first example of a regiospecific synthesis of 5-iodo-1,4-disubstituted-1,2,3-triazole, which can be further elaborated to a range of 1,4,5-trisubstituted-1,2,3-triazole derivatives.

Key words: fluoroalkyl-1,4,5-trisubstituted-1,2,3-triazole, one-pot reaction, regiospecific synthesis, fluoroalkylazide, terminal alkyne, 1,3-dipolar cycloaddition

[1,2,3]-Triazoles have been widely used in pharmaceuticals, agrochemicals, dyes, photographic materials, and in corrosion inhibition.[1] For example, there are numerous reports in the literature including anti-HIV activity,[2] antimicrobial activity against Gram positive bacteria,[3] and selective β_3 adrenergic receptor agonism of triazole compounds.[4] Due to their potential usefulness, several synthetic methods have been developed for the construction of triazole frameworks. Among them, the most important and useful method is the 1,3-dipolar cycloaddition of azide with alkyne.[5] Two problems are, however, encountered in this transformation: (1) reactivity of the substrates, either alkynes or azides require be activation by an electron-withdrawing group, otherwise, the reaction must be carried out at a higher temperature; (2) the regioselectivity of the products, for unsymmetrical alkynes, a mixture of regioisomers is obtained in most cases. Since Sharpless reported a method of regioselective synthesis of 1,2,3-triazoles using Cu(I) salt as catalysis,[6a] this field has become more and more active, several groups have reported their results on this subject by employing different kinds of Cu(I) salts as catalyst recently.[6] We recently reported a method for the regioselective synthesis of fluoroalkylated 1,4-disubstituted-1,2,3-triazoles catalyzed by Cu(I) iodide.[7] In this paper, we would like to report a convenient method for the regiosepecific synthesis of 1,4,5-trisubstituted-1,2,3-triazoles by an one-pot reaction strategy.

Considering the proposed mechanism of Cu(I)-catalyzed reaction of organo-azides with terminal alkynes, an intermediate of Cu(I) salt of 1,2,3-triazole **A** was proposed.[6a,7] It is reasonable to suggest that the intermediate **A** could be trapped by electrophiles (Scheme 1).



A

Scheme 1

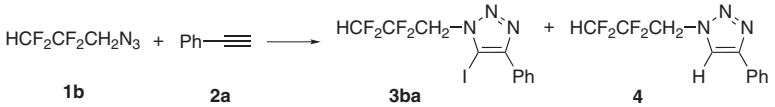
The reaction of 2,2,3,3-tetrafluoropropylazide **1b** with phenylacetylene **2a** (Scheme 2) under various conditions was examined. The results are summarized in Table 1.

When iodine was used as an electrophilic trapping reagent, two products were isolated, which were separated conveniently by flash column chromatography. The struc-

Table 1 Results of the Reaction of Organo-azide with Terminal Alkyne in the Presence of Electrophiles

Entry	Conditions[a]	Yield[b] (%)	
		3ba	**4**
1	CuI (1 equiv), I_2, CH_3CN, Et_3N (5 equiv)	42	48
2	CuI (1 equiv), I_2, THF, Et_3N (5 equiv)	42	19
3	CuI (1 equiv), ICl, CH_3CN, Et_3N (5 equiv)	50	30
4	CuI (1 equiv), ICl, THF, Et_3N (5 equiv)	80	14
5	CuI (0.2 equiv), ICl, THF, Et_3N (5 equiv)	14	6
6	CuI (0.1 equiv), ICl, THF, Et_3N (5 equiv)	4	trace
7	CuI (1 equiv), ICl, THF, Et_3N (1.2 equiv)	77	trace

[a] All reactions were performed at r.t.
[b] Isolated yield.



1b **2a** **3ba** **4**

Scheme 2 Reaction of organo-azide with terminal alkyne in the presence of electrophiles.

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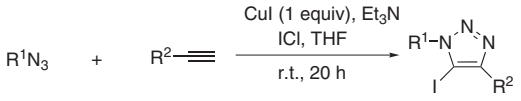
tures of them were easily determined by NMR and mass spectroscopy and were shown to be iodotriazole **3ba** and triazole **4**, respectively. The yields of **3ba** are not satisfactory probably due to the low electrophilicity of iodine in THF or acetonitrile (entries 1, 2). This yield was dramatically increased when ICl was used as an electrophile in THF (up to 80%, entry 4). A stoichiometric amount of CuI was required, otherwise, low conversion yields were observed (entries 5, 6); triethylamine is also required.

The scope of this transformation is partly revealed by the examples in Table 2 and Scheme 3. As can be seen in Table 2, it was found that the reaction can be adapted to many different substrates, the azide may be substituted by 2,2-dihydropolyfluoroalkyl groups (entry 1, 2, 3 etc.), benzyl group (entry 12, 13), and alkyl group (entry 14). The alkynes may be substituted by aromatic, alkyl, ester, and amide groups. The yield of this transformation is moderate to good.



1 **2** **3**

R^1	R^2
1a CF_3CH_3	**2a** Ph
1b $H(CF)_2CH_2$	**2b** *n*-C_4H_9
1c *n*-$C_6F_{13}CH_2$	**2c** CO_2-allyl
1d $PhCH_2$	**2d** CONH-allyl
1e *n*-C_8H_{17}	

Scheme 3 Synthesis of 5-iodo-1,4-disubstituted-1,2,3-triazoles.

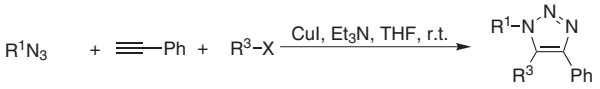
It was interesting to note that with two terminal triple bonds on the substrate, the reaction with two equivalents of azide, resulted in bis-1,2,3-triazole compound **5** in 76% yield (Scheme 4).

Other electrophiles were also examined in this trapping reaction. It was found that under the same reaction conditions, when 2.5 equivalents of allyl bromide were used as an electrophile, three products were obtained: the desired product 5-allyl-1,2,3-triazoles **7** (46%); as well as two additional products 5-iodo **3** (6%) and **4** (42%), **3** was formed by the reaction of Cu(I) salt intermediate of 1,2,3-triazole **A** with I_2 which was present as an impurity in Cu(I) iodide, while **4** was the hydrolysis product of **A**. It was interesting to note that in the presence of 4 Å molecular sieve a 63% yield of 5-allyl-1,4-disubstituted-1,2,3-triazole **7** was obtained. Acylation took place simultaneously when benzoyl chloride or acetyl chloride was added to the reaction system, the results are listed in Scheme 5 and Table 3. Unfortunately only moderate yields resulted, while other electrophiles such as trimethylsilyl chloride, ethyl chloroformate, methylsulfonyl

Table 2 Results of the Reaction of Azides with Terminal Alkynes

Entry	Azides (R^1)	Alkynes (R^2)	Product	Yield[a] (%)
1	CF_3CH_2	Ph	**3aa**	48
2	CF_3CH_2	C_4H_9	**3ab**	61
3	CF_3CH_2	CO_2-allyl	**3ac**	82
4	CF_3CH_2	CONH-allyl	**3ad**	73
5	$HCF_2CF_2CH_2$	Ph	**3ba**	77
6	$HCF_2CF_2CH_2$	C_4H_9	**3bb**	63
7	$HCF_2CF_2CH_2$	CO_2-allyl	**3bc**	74
8	$HCF_2CF_2CH_2$	CONH-allyl	**3bd**	74
9	$CF_3(CF_2)_5CH_2$	Ph	**3ca**	48
10	$CF_3(CF_2)_5CH_2$	CO_2-allyl	**3cc**	78
11	$CF_3(CF_2)_5CH_2$	CONH-allyl	**3cd**	81
12	$PhCH_2$	Ph	**3da**	72
13	$PhCH_2$	CO_2-allyl	**3dc**	72
14	C_8H_{17}	Ph	**3ea**	34

[a] Isolated yield.



1 **6** **7**

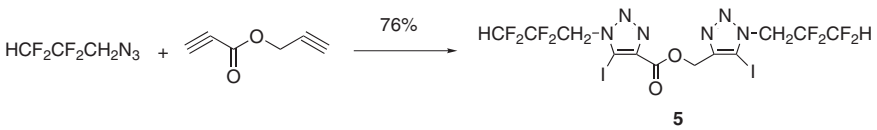
R^1	R^3-X
1b $HCF_2CF_2CH_2$	**6a** CH_2=$CHCH_2Br$,
1d $PhCH_2$	**6b** PhCOCl,
	6c CH_3COCl.

Scheme 5 Synthesis of 2,4,5-trisubstituted-1,2,3-triazoles.

chloride, benzyl bromide, and butyl bromide did not undergo a similar transformation under the same reaction conditions probably due to their low electrophilicity.

All compounds were characterized by ^1H NMR, ^{19}F NMR, IR spectroscopy, mass spectroscopy, and elemental analysis and their structure determined on the basis of our previous paper.[7]

Based on our previous paper,[7] the reaction mechanism for the formation of 1,4-disubstituted 1,2,3-triazole is that proposed in Scheme 6. Cu(I) first inserts into the terminal alkyne, forming copper(I) acetylide **I**, which then reacts with fluoroalkyl azide to form the intermediate of Cu(I) salt of 1,2,3-triazole **A**; this intermediate **A** is trapped by ICl and other electrophiles to form the final products **3** or **7**. As the catalyst Cu(I) iodide was transformed to Cu(I)



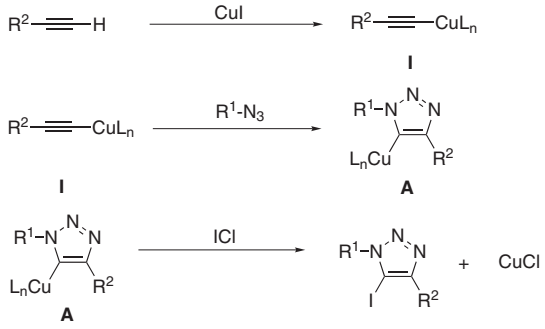
5

Scheme 4

Table 3 Results of Synthesis of 2,4,5-Trisubstituted-1,2,3-triazoles

Entry	Azide (R^1)	R^3-X	Product 7	Yield (%)
1	$HCF_2CF_2CH_2$		**7ba**	63[a]
2	$PhCH_2$		**7da**	62[a]
3	$HCF_2CF_2CH_2$	PhCOCl	**7bb**	57[a]
4	$PhCH_2$	PhCOCl	**7db**	61[a]
5	$HCF_2CF_2CH_2$	CH_3COCl	**7bc**	34[b]
6	$PhCH_2$	CH_3COCl	**7dc**	27[b]

[a] Isolated yield.
[b] Mixture with iodotriazole, determined by ^{1}H NMR.



Scheme 6 The mechanism of the synthesis of 1,4,5-trisubstituted-1,2,3-triazoles.

chloride, a stoichiometric amount of CuI was required in this reaction.

In conclusion, we have developed a convenient one-pot method for the regiospecific synthesis of 1,4,5-trisubstituted-1,2,3-triazoles catalyzed by Cu(I) iodide; this method can be used to synthesize different multiple substituted 1,2,3-triazole derivatives, which might be used in many different areas. This result also confirmed the existence of Cu(I) salt of 1,2,3-triazole **A**. Furthermore the iodo group of 5-iodo-1,2,3-triazole compounds have the potential to be transformed into a range of functional groups, and this research is ongoing.

Melting points and boiling points are uncorrected. IR spectra were obtained with a Perkin-Elmer 983G spectrometer as KBr disks. NMR spectra were recorded either on a Varian-360L or Bruker AM-300 spectrometer with $CDCl_3$ as solvent. Chemical shifts were reported in parts per million relative to TMS as an external standard ($\delta = 0$) for ^{1}H NMR spectra and $CFCl_3$ as an internal standard ($\delta = 0$) for ^{19}F NMR (upfield shift being designated as negative) spectra. Coupling constants are given in Hertz (Hz). Low- and high-resolution mass spectra were recorded on a Hewlett-Packard HP-5989A and a Finnigan MAT spectrometer, respectively. Elemental analyses were performed at this institute.

Compounds 3; Typical Procedure

Under a N_2 atmosphere, to a Schlenk tube, fluoroalkylazide (0.5 mmol), terminal alkyne (0.5 mmol), Et_3N (0.6 mmol), THF (5 mL), ICl (0.5 mmol), and CuI (0.5 mmol) were added successively. The mixture was stirred at r.t. for 20 h. After removal of the solvent, the crude product was purified by flash chromatography on a silica gel column (hexane–EtOAc, 5:1) as eluent.

5-Iodo-4-phenyl-1-(2,2,2-trifluoroethyl)-1*H*-[1,2,3]triazole (3aa)

White solid; mp 164–165 °C.

IR: 1100, 1189, 1400, 1447 cm^{-1}.

^{1}H NMR: $\delta = 5.10$ (q, $J = 8$ Hz, 2 H), 7.41–7.54 (m, 3 H), 7.93–7.98 (m, 2 H).

^{19}F NMR: $\delta = -69.71$ (t, $J = 8$ Hz, 3 F).

MS: *m*/*z* (%) = 353 (M^+, 7), 325 (42), 242 (41), 198 (51), 89 (100).

Anal. Calcd for $C_{10}H_7F_3IN_3$: C, 34.02; H, 2.00; N, 11.90; F, 16.14. Found: C, 34.03; H, 2.22; N, 11.91; F, 16.48.

4-Butyl-5-iodo-1-(2,2,2-trifluoroethyl)-1*H*-[1,2,3]triazole (3ab)

White solid; mp 57–58 °C.

IR: 1120, 1169, 1397, 1525, 2322, 2967, 3018 cm^{-1}.

^{1}H NMR: $\delta = 0.96$ (t, $J = 7$ Hz, 3 H), 1.34–1.47 (m, 2 H), 1.65–1.77 (m, 2 H), 2.70 (t, $J = 8$ Hz, 2 H), 5.99 (q, $J = 8$ Hz, 2 H).

^{19}F NMR: $\delta = -69.99$ (t, $J = 8$ Hz, 3 F).

MS: *m*/*z* (%) = 333 (M^+, 1), 262 (97), 206 (50), 178 (19), 136 (100).

Anal. Calcd for $C_8H_{11}F_3IN_3$: C, 28.85; H, 3.33; N, 12.62; F, 17.11. Found: C, 28.87; H, 3.35; N, 12.57; F, 17.20.

Allyl 5-Iodo-1-(2,2,2-trifluoroethyl)-1*H*-[1,2,3]triazole-4-carboxylate (3ac)

White solid; mp 103–104 °C.

IR: 1114, 1178, 1266, 1519, 1720, 2976, 3020 cm^{-1}.

^{1}H NMR: $\delta = 4.92$ (d, $J = 5$ Hz, 2 H), 5.11 (q, $J = 8$ Hz, 2 H), 5.34 (d, $J = 11$ Hz, 1 H), 5.48 (d, $J = 17$ Hz, 1 H), 6.00–6.14 (m, 1 H).

^{19}F NMR: $\delta = -69.61$ (t, $J = 8$ Hz, 3 F).

MS: *m*/*z* (%) = 360 ($M^+ - 1$, 4), 276 (7), 233 (15), 153 (49), 41 (100).

Anal. Calcd for $C_8H_7F_3IN_3O_2$: C, 26.61; H, 1.95; N, 11.64; F, 15.79. Found: C, 26.51; H, 2.18; N, 11.52; F, 15.29.

Allyl 5-Iodo-1-(2,2,2-trifluoroethyl)-1*H*-[1,2,3]triazole-4-carboxamide (3ad)

White solid; mp 120–121 °C.

IR: 1117, 1178, 1265, 1557, 1652, 2961, 3399 cm^{-1}.

^{1}H NMR: $\delta = 4.09$ (t, $J = 8$ Hz, 2 H), 5.54 (q, $J = 8$ Hz, 2 H), 5.21 (d, $J = 11$ Hz, 1 H), 5.30 (d, $J = 17$ Hz, 1 H), 5.85–5.99 (m, 1 H), 7.25–7.39 (br, 1 H).

^{19}F NMR: $\delta = -69.71$ (t, $J = 8$ Hz, 3 F).

MS: *m*/*z* (%) = 360 (M^+, 8), 276 (11), 233 (40), 205 (34), 150 (67), 56 (100).

Anal. Calcd for $C_8H_8F_3IN_4O$: C, 26.69; H, 2.24; N, 15.56; F, 15.83. Found: C, 26.67; H, 2.39; N, 15.50; F, 15.67.

5-Iodo-4-phenyl-1-(2,2,3,3-tetrafluoropropyl)-1*H*-[1,2,3]triazole (3ba)

White solid; mp 152–153 °C.

IR: 1093, 1236, 1538 cm^{-1}.

^{1}H NMR: $\delta = 5.07$ (t, $J = 13$ Hz, 2 H), 6.04 (tt, $J_1 = 3$ Hz, $J_2 = 53$ Hz, 1 H), 7.42–7.55 (m, 3 H), 7.92–7.99 (m, 2 H).

^{19}F NMR: $\delta = -136.87$ (d, $J = 52$ Hz, 2 F), –118.68 (t, $J = 12$ Hz, 2 F).

MS: *m*/*z* (%) = 385 (M^+, 3), 366 (1), 357 (32), 230 (51), 89 (100).

Anal. Calcd for $C_{11}H_8F_4IN_3$: C, 34.31; H, 2.09; N, 10.91; F, 19.73. Found: C, 34.16; H, 2.17; N, 10.97; F, 19.88.

4-Butyl-5-iodo-1-(2,2,3,3-tetrafluoropropyl)-1*H*-[1,2,3]triazole (3bb)
White solid; mp 67–68 °C.

IR: 1107, 1235, 1437, 2966 cm^{-1}.

^1H NMR: δ = 0.96 (t, *J* = 7 Hz, 3 H), 1.32–1.46 (m, 2 H), 1.62–1.76 (m, 2 H), 2.70 (t, *J* = 8 Hz, 2 H), 4.94 (t, *J* = 13 Hz, 2 H), 5.98 (tt, J_1 = 3 Hz, J_2 = 53 Hz, 1 H).

^{19}F NMR: δ = –137.14 (d, *J* = 53 Hz, 2 F), –119.10 (t, *J* = 13 Hz, 2 F).

MS: *m*/*z* (%) = 346 (M^+ – 19, 2), 294 (100), 238 (42), 210 (39), 168 (98).

Anal. Calcd for $C_9H_{12}F_4IN_3$: C, 29.61; H, 3.31; N, 11.51; F, 20.82. Found: C, 29.23; H, 3.28; N, 11.32; F, 20.87.

Allyl 5-Iodo-1-(2,2,3,3-tetrafluoropropyl)-1*H*-[1,2,3]triazole-4-carboxylate (3bc)
White solid; mp 75–76 °C.

IR: 1108, 1226, 1518, 1718, 3012 cm^{-1}.

^1H NMR: δ = 4.89–4.92 (m, 2 H), 5.07 (t, *J* = 14 Hz, 2 H), 5.31–5.51 (m, 2 H), 5.81–6.18 (m, 2 H).

^{19}F NMR: δ = –136.19 (d, *J* = 52 Hz, 2 F), –117.96 (t, *J* = 14 Hz, 2 F).

MS: *m*/*z* = 393 (M^+).

Anal. Calcd for $C_9H_8F_4IN_3O_2$: C, 27.50; H, 2.05; N, 10.69; F, 19.33. Found: C, 27.44; H, 2.28; N, 10.62; F, 19.40.

Allyl 5-Iodo-1-(2,2,3,3-tetrafluoropropyl)-1*H*-[1,2,3]triazole-4-carboxamide (3bd)
White solid; mp 114–115 °C.

IR: 1117, 1258, 1557, 1646, 2959, 3382 cm^{-1}.

^1H NMR: δ = 4.07–4.13 (m, 2 H), 5.05 (t, *J* = 14 Hz, 2 H), 5.19–5.33 (m, 2 H), 5.80–6.18 (m, 2 H).

^{19}F NMR: δ = –136.12 (d, *J* = 53 Hz, 2 F), –117.95 (t, *J* = 14 Hz, 2 F).

MS: *m*/*z* (%) = 392 (M^+, 11), 265 (47), 237 (31), 182 (100), 51 (38).

Anal. Calcd for $C_9H_9F_4IN_4O$: C, 27.57; H, 2.31; N, 14.29; F, 19.38. Found: C, 27.71; H, 2.37; N, 14.14; F, 19.14.

5-Iodo-4-phenyl-1-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1*H*-[1,2,3]triazole (3ca)
White solid; mp 164–165 °C.

IR: 1139, 1209, 3024 cm^{-1}.

^1H NMR: δ = 5.20 (t, *J* = 14 Hz, 2 H), 7.40–7.60 (m, 3 H), 7.92–8.03 (m, 2 H).

^{19}F NMR: δ = –126.36 (2 F), –123.27, –122.92 (4 F), –121.91 (2 F), –115.14 (2 F), –80.96 (3 F).

MS: *m*/*z* (%) = 603 (M^+, 1), 575 (20), 448 (29), 242 (35), 89 (100).

Anal. Calcd for $C_{15}H_7F_{13}IN_3$: C, 29.87; H, 1.17; N, 6.97; F, 40.95. Found: C, 29.91; H, 1.46; N, 7.14; F, 41.03.

Allyl 5-Iodo-1-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1*H*-[1,2,3]triazole-4-carboxylate (3cc)
White solid; mp 133–134 °C.

IR: 1140, 1229, 1522, 1730 cm^{-1}.

^1H NMR: δ = 4.94–4.97 (m, 2 H), 5.21 (t, *J* = 14 Hz, 2 H), 5.36–5.50 (m, 2 H), 5.05–6.17 (m, 1 H).

^{19}F NMR: δ = –126.10 (2 F), –122.83 (4 F), –121.79 (2 F), –114.77 (2 F), –81.00 (3 F).

MS: *m*/*z* = 611 (M^+).

Anal. Calcd for $C_{13}H_7F_{13}IN_3O_2$: C, 25.55; H, 1.15; N, 6.88; F, 40.42. Found: C, 25.57; H, 1.09; N, 6.92; F, 40.60.

Allyl 5-Iodo-1-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1*H*-[1,2,3]triazole-4-carboxamide (3cd)
White solid; mp 114–115 °C.

IR: 1151, 1200, 1556, 1655, 3421 cm^{-1}.

^1H NMR: δ = 4.10 (t, *J* = 6 Hz, 2 H), 5.15 (t, *J* = 14 Hz, 2 H), 5.21 (d, *J* = 9 Hz, 1 H), 5.30 (d, *J* = 17 Hz, 1 H), 5.86–6.10 (m, 1 H), 7.25–7.39 (br, 1 H).

^{19}F NMR: δ = –123.12 (2 F), –122.83 (4 F), –121.91 (2 F), –115.13 (2 F), –80.96 (3 F).

MS: *m*/*z* (%) = 610 (M^+, 13), 591 (3), 526 (10), 483 (25), 455 (35), 400 (81), 80 (56), 56 (100).

Anal. Calcd for $C_{13}H_8F_{13}IN_4O$: C, 25.59; H, 1.32; N, 9.18; F, 40.48. Found: C, 25.64; H, 1.36; N, 9.10; F, 40.60.

1-Benzyl-5-iodo-4-phenyl-1*H*-[1,2,3]triazole (3da)
White solid; mp 128–129 °C.

IR: 1155, 1230, 1446, 3031 cm^{-1}.

^1H NMR: δ = 5.72 (s, 2 H), 7.32–7.53 (m, 8 H), 7.94–8.00 (m, 2 H).

MS: *m*/*z* (%) = 361 (M^+, 2), 234 (6), 206 (39), 91 (100).

Anal. Calcd for $C_{15}H_{12}IN_3$: C, 49.88; H, 3.35; N, 11.63. Found: C, 49.79; H, 3.42; N, 11.65.

Allyl 1-Benzyl-5-iodo-1*H*-[1,2,3]triazole-4-carboxylate (3dc)
White solid; mp 85–86 °C.

^1H NMR: δ = 4.87–4.89 (m, 2 H), 5.29–5.33 (m, 1 H), 5.41–5.48 (m, 1 H), 5.68 (s, 2 H), 5.99–6.10 (m, 1 H), 7.25–7.31 (m, 2 H), 7.32–7.37 (m, 3 H).

MS: *m*/*z* (%) = 369 (M^+, 1), 242 (13), 91 (100).

Anal. Calcd for $C_{13}H_{12}IN_3O_2$: C, 42.30; H, 3.28; N, 11.38. Found: C, 42.23; H, 3.27; N, 11.30.

5-Iodo-1-octyl-4-phenyl-1*H*-[1,2,3]triazole (3ea)
White solid; mp 76–77 °C.

IR: 1153, 1227, 1447, 2919 cm^{-1}.

^1H NMR: δ = 0.90 (m, 3 H), 1.23–1.45 (m, 10 H), 1.95–2.00 (m, 2 H), 4.45 (t, *J* = 7 Hz, 2 H), 7.41–7.51 (m, 3 H), 7.93–7.97 (m, 2 H).

MS: *m*/*z* (%) = 383 (M^+, 6), 243 (100), 228 (41), 116 (88), 91 (54).

Anal. Calcd for $C_{16}H_{22}IN_3$: C, 50.14; H, 5.49; N, 10.96. Found: C, 50.25; H, 5.69; N, 10.85.

5-Iodo-1-(2,2,3,3-tetrafluoropropyl)-1*H*-[1,2,3]triazol-4-ylmethyl 5-iodo-1-(2,2,3,3-tetrafluoropropyl)-1*H*-[1,2,3]triazole-4-carboxylate (5)
White solid; mp 185–186 °C.

IR: 1100, 1202, 1423, 1513, 1741, 3015 cm^{-1}.

^1H NMR: δ = 5.20–5.41 (m, 4 H), 5.50 (s, 2 H), 6.37–6.78 (m, 2 H).

^{19}F NMR: δ = –139.09 (d, *J* = 52 Hz, 4 F), –121.11, –120.77 (m, 4 F).

MS: *m*/*z* (%) = 675 (M^+ + 1, 1), 519 (15), 336 (27), 308 (98), 294 (83), 167 (80), 80 (64), 51 (100).

Anal. Calcd for $C_{12}H_8F_8I_2N_6O_2$: C, 21.38; H, 1.20; N, 12.47; F, 22.55. Found: C, 21.41; H, 1.32; N, 12.45; F, 22.75.

Compounds 7; Typical Procedure

Under an N_2 atmosphere, to a Schlenk tube, fluoroalkylazide (0.5 mmol), terminal alkyne (0.5 mmol), Et_3N (0.6 mmol), THF (5mL), electrophile (1.25 mmol) and CuI (0.5 mmol) were added successively. The mixture was stirred at r.t. for 20 h. After removal of solvent, the crude product was purified by flash chromatography on a silica gel column (hexane–EtOAc, 5:1).

5-Allyl-4-phenyl-1-(2,2,3,3-tetrafluoropropyl)-1*H*-[1,2,3]triazole (7ba)

White solid; mp 70–71 °C.

^{1}H NMR: δ = 3.66–3.70 (m, 2 H), 4.88 (t, *J* = 14 Hz, 2 H), 4.99 (d, *J* = 17 Hz, 1 H), 5.28 (d, *J* = 10 Hz, 1 H), 5.88–6.03 (m, 1 H), 6.04 (tt, J_1 = 53 Hz, J_2 = 3 Hz, 1 H), 7.36–7.51 (m, 3 H), 7.62–7.70 (m, 2 H).

^{19}F NMR: δ = –137.36 (d, *J* = 51 Hz, 2 F), –119.68 (t, *J* = 14 Hz, 2 F).

MS: *m*/z (%) = 299 (M^+, 23), 270 (86), 170 (78), 156 (42), 129 (100), 115 (52), 89 (45), 77 (31).

Anal. Calcd for $C_{14}H_{13}F_4N_3$: C, 56.19; H, 4.38; N, 14.04; F, 25.39. Found: C, 56.01; H, 4.36; N, 13.91; F, 25.40.

5-Allyl-1-benzyl-4-phenyl-1*H*-[1,2,3]triazole (7da)

Colorless liquid.

^{1}H NMR: δ = 3.43–3.48 (m, 2 H), 4.93 (d, *J* = 17 Hz, 1 H), 5.17 (d, *J* = 10 Hz, 1 H), 5.55 (s, 2 H), 5.76–5.91 (m, 1 H), 7.17–7.22 (m, 2 H), 7.30–7.49 (m, 6 H), 7.66–7.72 (m, 2 H).

^{13}C NMR: δ = 27.05, 52.12, 117.71, 127.22, 127.87, 128.33, 128.67, 128.99, 130.34, 131.39, 132.27, 135.06, 145.86.

MS: *m*/*z* (%) = 275 (M^+, 8), 246 (2), 156 (100), 91 (82), 77 (18), 57 (96).

HRMS: *m*/*z* calcd for $C_{18}H_{17}N_3$, 275.1422; found 275.1417.

4-Benzoyl-5-phenyl-3-(2,2,3,3-tetrafluoropropyl)-3*H*-[1,2,3]triazole (7bb)

White solid; mp 118–119 °C.

^{1}H NMR: δ = 5.33 (t, *J* = 14 Hz, 2 H), 5.91 (tt, J_1 = 53 Hz, J_2 = 3 Hz, 1 H), 7.17–7.30 (m, 5 H), 7.36–7.42 (m, 2 H), 7.44–7.51 (m, 1 H), 7.66–7.70 (m, 2 H).

^{19}F NMR: δ = –135.86 (d, *J* = 53 Hz, 2 F), –118.83 (t, *J* = 15 Hz, 2 F).

MS: *m*/*z* (%) = 363 (M^+, 2), 335 (8), 218 (10), 105 (100), 89 (17), 77 (50).

Anal. Calcd for $C_{18}H_{13}F_4N_3O$: C, 59.51; H, 3.61; N, 11.57; F, 20.92. Found: C, 59.30; H, 3.62; N, 11.57; F, 21.00.

(4-Benzoyl-3-benzyl-5-phenyl-3*H*-[1,2,3]triazole (7db)

White solid; mp 64–65 °C.

^{1}H NMR: δ = 5.76 (s, 2 H), 7.15–7.26 (m, 10 H), 7.37–7.45 (m, 3 H), 7.47–7.54 (m, 2 H).

MS: *m*/*z* (%) = 339 (M^+, 2), 310 (1), 105 (19), 91 (100), 77 (23).

Anal. Calcd for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38. Found: C, 77.65; H, 5.04; N, 12.30.

4-Acetyl-5-phenyl-3-(2,2,3,3-tetrafluoropropyl)-3H-[1,2,3]triazole (7bc)

^{1}H NMR: δ = 2.82 (s, 3 H), 5.40 (t, *J* = 14 Hz, 2 H), 5.96 (tt, J_1 = 52 Hz, J_2 = 3 Hz, 1 H), 7.40–7.60 (m, 5 H).

^{19}F NMR: δ = –136.53 (d, *J* = 52 Hz, 2 F), –119.59 (t, *J* = 14 Hz, 2F).

4-Acetyl-3-benzyl-5-phenyl-3H-[1,2,3]triazole (7dc)

^{1}H NMR: δ = 2.12 (s, 3 H), 5.87 (s, 2 H), 7.28–7.54 (m, 10 H).

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