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Silver-Catalyzed Regioselective Cycloaddition of Isocyanides with Diazo Compounds: Access to 1,4-Disubstituted-1,2,3-triazoles

Shuai Wang, a Li-Jun Yang, a Jun-Liang Zeng, a Yan Zheng, a Jun-An Ma* a,b

a Department of Chemistry, Key Laboratory of Systems Bioengineering (the Ministry of Education), Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. of China.

b State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. of China.

*Email: majun_an68@tju.edu.cn
General information:

$^1$H, $^{13}$C and $^{19}$F NMR were recorded at Bruker AVANCE III 600 M spectrometer. Chemical shifts were reported in ppm from the solvent resonance as the internal standard (CDCl$_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; DMSO-d$_6$: $\delta_H = 2.50$ ppm, $\delta_C = 39.52$ ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Melting points (MP) were measured on a WRS-1A digital melting point apparatus and are uncorrected. X-ray structural analysis was conducted on the XtaLAB mini instrument.

Materials:

N,N-Dimethylformamide (DMF) was dried by CaH$_2$. Analytical thin layer chromatography was performed on 0.20 mm silica gel plates. Silica gel (200–300 mesh) was used for flash chromatography. All the isocyanides were prepared according to literatures.$^1$ 2,2,2-Trifluorodiazoethane (CF$_3$CHN$_2$) in different solutions was prepared as flows.

As shown in the figure: A solution of 6.1 g NaNO$_2$ in 15 mL water was added slowly to the stirring solution of 10.8 g of tritfluoroethylamine hydrochloride in 25 mL water.
at rt. And then the rapidly generated yellow gas was gradually blown off through a
drying tube (MgSO₄) into a gas absorber containing 100 mL anhydrous solvent
equipped with an ice bath. After about 2 hours later, there would be no gas bubbling
any more. Then the apparatus was removed carefully. Finally the concentration of the
stock solution was determined by ¹⁹F-NMR analysis with dispersion method.

**Experimental part**

**General procedure for the cycloaddition of diazo compound with isocyanides**

Isocyanobenzene (1a, 20.6 mg, 0.2 mmol), Ag₂CO₃ (5.5 mg, 0.02 mmol), 4Å MS
(25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was
sealed well and 2,2,2-trifluorodiazoethane (26.4 mg, 0.24 mmol, 12 μL of 0.02 M in
DMF) was added at room temperature. The reaction mixture was stirred at 40 °C for 6
h. After the reaction mixture was cooled down to room temperature, 10 mL water was
added and extracted with EtOAc (8 mL × 3). The organic phases were collected, dried
over anhydrous Na₂SO₄, and concentrated under reduced pressure. Purification by
flash chromatography on silica gel with petroleum ether / ethyl acetate (25:1, v:v)
afforded pure 1-phenyl-4-(trifluoromethyl)-1H-1,2,3-triazole (2a) as a white solid.

![Structural formula of 1-phenyl-4-(trifluoromethyl)-1H-1,2,3-triazole (2a).]

1-Phenyl-4-(trifluoromethyl)-1H-1,2,3-triazole (2a).

White solid (36.2 mg, mp: 76–78 °C, yield: 85%). ¹H NMR (600 MHz, CDCl₃) δ 8.33
(s, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H). ¹⁹F
NMR (565 MHz, CDCl₃) δ –61.18 (s). ¹³C NMR (150 MHz, CDCl₃) δ 139.55 (q, J =
39.5 Hz), 136.20, 130.12, 129.90, 121.71, 120.99, 120.44 (q, J = 267.9 Hz). HRMS
(ESI): calcd. for C₉H₆F₃N₃[M+Na]⁺: 236.0406, found: 236.0410. IR (KBr) ν 3105,
1596, 1571, 1505, 1380, 1335, 1256, 1134, 1042, 995, 852, 755, 687 cm⁻¹.
1-(4-Fluorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2b).

White solid (43.0 mg, mp: 83–85 ºC, yield: 93%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.31 (s, 1H), 7.77 - 7.73 (m, 2H), 7.30 - 7.24 (m, 2H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ –61.28 (s), –110.33 ~ –110.38 (m). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 163.14 (d, $J$ = 250.9 Hz), 139.73 (q, $J$ = 39.7 Hz), 132.54, 123.21 (d, $J$ = 8.8 Hz), 121.90, 120.41 (q, $J$ = 267.8 Hz), 117.19 (d, $J$ = 23.4 Hz). HRMS (ESI): calcd. for C$_9$H$_5$F$_4$N$_3$[M+Na]$^+$: 254.0312, found: 254.0313. IR (KBr) ν 3145, 3114, 1571, 1519, 1378, 1303, 1262, 1240, 1172, 1126, 1101, 1039, 996, 836 cm$^{-1}$.

1-(3-Fluorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2c).

White solid (38.8 mg, mp: 82–84 ºC, yield: 84%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.38 (s, 1H), 7.57 - 7.52 (m, 3H), 7.21 (ddd, $J$ = 11.5, 5.4, 3.2 Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ –61.39 (s), –108.99 ~ –109.04 (m). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 163.19 (d, $J$ = 249.8 Hz), 139.80 (q, $J$ = 39.6 Hz), 137.33 (d, $J$ = 10.0 Hz), 131.69 (d, $J$ = 8.9 Hz), 121.79, 120.34 (q, $J$ = 268.0 Hz), 116.89 (d, $J$ = 21.1 Hz), 116.35 (d, $J$ = 3.4 Hz), 108.88 (d, $J$ = 26.4 Hz). HRMS (ESI): calcd. for C$_9$H$_5$F$_4$N$_3$[M+Na]$^+$: 254.0312, found: 254.0312. IR (KBr) ν 3145, 3115, 1610, 1573, 1484, 1380, 1267, 1222, 1179, 1150, 1042, 977, 870, 848, 780, 679 cm$^{-1}$.

1-(2-Fluorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2d).

White solid (46.1 mg, mp: 55–57 ºC, yield: 90%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.39
(s, 1H), 8.02 – 7.94 (m, 1H), 7.54 – 7.48 (m, 1H), 7.42 – 7.31 (m, 2H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ –61.22 (s), –123.74 (ddd, $J = 11.4, 7.5, 2.4$ Hz). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 153.50 (d, $J = 251.5$ Hz), 139.48 (q, $J = 39.7$ Hz), 131.40 (d, $J = 8.0$ Hz), 125.68 (d, $J = 3.8$ Hz), 125.14, 124.55, 120.43 (q, $J = 267.9$ Hz), 117.35 (d, $J = 19.8$ Hz). HRMS (ESI): calcd. for C$_9$H$_5$F$_4$N$_3$[M+H]$^+$: 232.0492, found: 232.0496. IR (KBr) ν 3027, 1538, 1522, 1498, 1455, 1399, 1388, 1243, 1138, 1098, 1022, 937, 774, 672 cm$^{-1}$.

1-(3,5-Difluorophenyl)-4-(trifluoromethyl)-1$H$-1,2,3-triazole (2e).

White solid (40.3 mg, mp: 66–68 ºC, yield: 81%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.35 (s, 1H), 7.38 (dd, $J = 6.8, 2.0$ Hz, 2H), 6.99 (tt, $J = 8.5, 2.2$ Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ –61.48 (s), –105.12 (dd, $J = 8.6, 7.4$ Hz). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 163.66 (dd, $J = 252.2, 13.7$ Hz), 140.14 (q, $J = 40.0$ Hz), 137.81 (t, $J = 12.5$ Hz), 121.67 (d, $J = 2.5$ Hz), 120.19 (q, $J = 268.2$ Hz), 105.35 (t, $J = 25.2$ Hz), 104.89 – 104.57 (m). HRMS (ESI): calcd. for C$_9$H$_4$F$_5$N$_3$[M+H]$^+$: 250.0398, found: 250.0404. IR (KBr) ν 3122, 3074, 1616, 1514, 1500, 1480, 1428, 1379, 1268, 1233, 1171, 1136, 1029, 997, 977, 855 cm$^{-1}$.

1-(3,4-Difluorophenyl)-4-(trifluoromethyl)-1$H$-1,2,3-triazole (2f).

White solid (39.3 mg, mp: 85–87 ºC, yield: 79%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.38 (s, 1H), 7.72 – 7.67 (m, 1H), 7.53 (d, $J = 8.2$ Hz, 1H), 7.39 (q, $J = 8.8$ Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ –61.43 (s), –132.56 ~ –132.76 (m), –134.18 ~ –134.77 (m). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 151.74 (dd, $J = 35.7, 13.0$ Hz), 150.06 (dd, $J =$
35.3, 13.1 Hz), 139.86 (q, J = 39.7 Hz), 132.43 (dd, J = 7.8, 3.4 Hz), 121.97 (d, J = 2.3 Hz), 120.22 (q, J = 267.9 Hz), 118.86 (d, J = 18.9 Hz), 117.17 (dd, J = 6.7, 4.0 Hz), 111.31 (d, J = 21.8 Hz). **HRMS (ESI):** calcd. for C₉H₉F₅N₃[M+H]+: 250.0398, found: 250.0405. **IR (KBr)** ν 3149, 3115, 1622, 1576, 1527, 1479, 1380, 1282, 1260, 1225, 1210, 1176, 1122, 1040, 979, 879, 845, 821, 782, 746, 645, 605 cm⁻¹

1-(3-Chloro-4-fluorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2g).

White solid (45.1 mg, mp: 70–72 ºC, yield: 85%). **¹H NMR** (600 MHz, CDCl₃) δ 8.32 (s, 1H), 7.87 (dd, J = 6.1, 2.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.36 (t, J = 8.5 Hz, 1H). **¹⁹F NMR** (565 MHz, CDCl₃) δ –61.36 (s), –111.19 ~ –114.89 (m). **¹³C NMR** (150 MHz, CDCl₃) δ 158.72 (d, J = 253.5 Hz), 139.95 (q, J = 39.8 Hz), 132.80, 123.75, 123.13 (d, J = 19.4 Hz), 121.89 (d, J = 2.5 Hz), 120.96 (d, J = 7.7 Hz), 120.26 (q, J = 268.0 Hz), 118.10 (d, J = 23.0 Hz). **HRMS (ESI):** calcd. for C₉H₉ClF₄N₃[M+H]+: 266.0103, found: 266.0109. **IR (KBr)** ν 3143, 3108, 1603, 1566, 1511, 1455, 1407, 1373, 1277, 1256, 1181, 1126, 1065, 1040, 980, 879, 830, 750, 720 cm⁻¹.

1-(4-Chlorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2h).

White solid (39.0 mg, mp: 126–128 ºC, yield: 79%). **¹H NMR** (600 MHz, CDCl₃) δ 8.33 (s, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H). **¹⁹F NMR** (565 MHz, CDCl₃) δ –61.29 (s). **¹³C NMR** (150 MHz, CDCl₃) δ 139.80 (q, J = 39.7 Hz), 135.87, 134.74, 130.33, 122.23, 121.70, 120.35 (q, J = 268.0 Hz). **HRMS (ESI):** calcd. for C₉H₅ClF₃N₃[M+Na]+: 270.0016, found: 270.0015. **IR (KBr)** ν 3005, 1555, 1507, 1446, 1397, 1256, 1142, 1040, 933 cm⁻¹.
1-(3-Chlorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2i).

White solid (40.0 mg, mp: 79–81 °C, yield: 81%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.32 (s, 1H), 7.80 (s, 1H), 7.66 (d, $J = 7.4$ Hz, 1H), 7.51 (q, $J = 8.0$ Hz, 2H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ −61.29 (s). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 139.78 (q, $J = 39.7$ Hz), 136.99, 135.96, 131.24, 130.00, 121.75, 121.27, 120.27 (q, $J = 267.9$ Hz), 118.96. HRMS (ESI): calcd. for C$_9$H$_5$ClF$_3$N$_3$[M+Na]$^+$: 270.0016, found: 270.0022. IR (KBr) ν 3139, 3113, 1600, 1579, 1566, 1423, 1420, 1384, 1243, 1199, 1162, 1033, 976, 866, 847, 776, 743, 669 cm$^{-1}$.

1-(2-Chlorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2j).

Oil (32.6 mg, yield: 66%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.24 (s, 1H), 7.53 – 7.49 (m, 2H), 7.41 (dt, $J = 23.9$, 7.2 Hz, 2H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ −61.14 (s). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 138.73 (q, $J = 39.6$ Hz), 133.91, 131.77, 130.99, 128.76, 128.26, 127.87, 125.43 (d, $J = 2.6$ Hz), 120.42 (q, $J = 267.9$ Hz). HRMS (ESI): calcd. for C$_9$H$_5$ClF$_3$N$_3$[M+Na]$^+$: 270.0016, found: 270.0018. IR (KBr) ν 3023, 1532, 1500, 1441, 1372, 1301, 1243, 1141, 1037, 931 cm$^{-1}$.

1-(3,4-Dichlorophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2k).

White solid (42.3 mg, mp: 97–99 °C, yield: 75%). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.38 (s, 1H), 7.91 (s, 1H), 7.64 (s, 2H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ −61.37 (s). $^{13}$C
**NMR** (150 MHz, CDCl$_3$) δ 139.96 (q, $J = 39.8$ Hz), 135.20, 134.45, 134.26, 131.85, 122.83, 121.76 (d, $J = 2.6$ Hz), 120.21 (q, $J = 268.0$ Hz), 119.95. **HRMS (ESI):** calcd. for C$_9$H$_5$Cl$_2$F$_3$N$_3$[M+Na]$^+$: 303.9627, found: 303.9631. **IR (KBr)** ν 3112, 1568, 1488, 1440, 1400, 1373, 1263, 1177, 1137, 1040, 1014, 977, 882, 852, 817, 741, 675 cm$^{-1}$.

**1-(4-Bromophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2l).**

White solid (39.4 mg, mp: 139–141 °C, yield: 68%). **$^1$H NMR** (600 MHz, CDCl$_3$) δ 8.33 (s, 1H), 7.69 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.6$ Hz, 2H). **$^{19}$F NMR** (565 MHz, CDCl$_3$) δ –61.28 (s). **$^{13}$C NMR** (150MHz, CDCl$_3$) δ 139.82 (q, $J = 39.6$ Hz), 135.22, 133.31, 123.77, 122.42, 121.62. 120.34 (q, $J = 267.9$ Hz). **HRMS (ESI):** calcd. for C$_9$H$_5$BrF$_3$N$_3$[M+Na]$^+$: 313.9511, found: 313.9517. **IR (KBr)** ν 3135, 3027, 1561, 1278, 1253, 1212, 1201, 1143, 1111, 1022, 996, 832 cm$^{-1}$

**1-(4-Iodophenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2m).**

White solid (35.3 mg, mp: 159–161 °C, yield: 52%). **$^1$H NMR** (600 MHz, CDCl$_3$) δ 8.31 (s, 1H), 7.90 (d, $J = 7.9$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H). **$^{19}$F NMR** (565 MHz, CDCl$_3$) δ –61.25 (s). **$^{13}$C NMR** (150 MHz, CDCl$_3$) δ 139.88 (q, $J = 39.7$ Hz), 139.29, 135.92, 122.49, 121.46, 120.34 (q, $J = 267.8$ Hz), 95.12. **HRMS (ESI):** calcd. for C$_9$H$_5$I$_3$N$_3$[M+H]$^+$: 339.9553, found: 339.9560. **IR (KBr)** ν 3136, 3106, 1588, 1564, 1493, 1374, 1256, 1168, 1135, 1040, 989, 851, 821, 748 cm$^{-1}$

**4-(Trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2n).**
White solid (47.8 mg, mp: 139–141 °C, yield: 85%). \( ^1H \text{ NMR} \) (600 MHz, DMSO) \( \delta \) 9.72 (s, 1H), 8.18 (d, \( J = 8.5 \) Hz, 2H), 7.97 (d, \( J = 8.6 \) Hz, 2H). \( ^19F \text{ NMR} \) (565 MHz, DMSO) \( \delta \) –60.28 (s), –61.55 (s). \( ^{13}C \text{ NMR} \) (150 MHz, DMSO) \( \delta \) 138.80, 138.08 (q, \( J = 38.8 \) Hz), 129.76 (q, \( J = 32.6 \) Hz), 127.30 (q, \( J = 3.7 \) Hz), 124.70, 123.76 (q, \( J = 272.4 \) Hz), 121.29, 120.68 (q, \( J = 267.3 \) Hz). \text{HRMS (ESI)}: calcd. for \( \text{C}_{10}\text{H}_5\text{F}_6\text{N}_3\text{[M+Na]}^+ \): 304.0280, found: 304.0286. \text{IR (KBr)} \( \nu \) 3145, 3112, 1572, 1525, 1380, 1336, 1260, 1175, 1071, 1038, 994, 847 cm\(^{-1} \).

1-(4-Ethoxycarbonylphenyl)-4-(trifluoromethyl)-1\(H\)-1,2,3-triazole (2o).

White solid (49.6 mg, mp: 126–128 °C, yield: 87%). \( ^1H \text{ NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 8.45 (s, 1H), 8.21 (d, \( J = 8.6 \) Hz, 2H), 7.85 (d, \( J = 8.6 \) Hz, 2H), 4.40 (q, \( J = 7.1 \) Hz, 2H), 1.40 (t, \( J = 7.2 \) Hz, 3H). \( ^19F \text{ NMR} \) (565 MHz, CDCl\(_3\)) \( \delta \) –61.36 (s). \( ^{13}C \text{ NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 165.23, 139.87 (q, \( J = 39.8 \) Hz), 139.19, 131.71, 131.51, 121.74, 120.45, 120.31 (q, \( J = 268.0 \) Hz), 61.70, 14.30. \text{HRMS (ESI)}: calcd. for \( \text{C}_{12}\text{H}_10\text{F}_3\text{N}_3\text{O}_2\text{[M+H]}^+ \): 286.0798, found: 286.0801. \text{IR (KBr)} \( \nu \) 3143, 3112, 2996, 1714, 1568, 1376, 1286, 1257, 1145, 1038, 001, 851, 769 cm\(^{-1} \).

1-(4-Acetylphenyl)-4-(trifluoromethyl)-1\(H\)-1,2,3-triazole (2p).

White solid (43.3 mg, mp: 198–200 °C, yield: 85%). \( ^1H \text{ NMR} \) (600 MHz, DMSO) \( \delta \) 9.71 (s, 1H), 8.17 (d, \( J = 8.4 \) Hz, 2H), 8.11 (d, \( J = 8.5 \) Hz, 2H), 2.64 (s, 3H). \( ^19F \text{ NMR} \) (565 MHz, DMSO) \( \delta \) –59.99 (s). \( ^{13}C \text{ NMR} \) (150 MHz, DMSO) \( \delta \) 196.95, 138.87, 137.91 (q, \( J = 38.7 \) Hz), 137.16, 130.03, 124.54, 120.63 (q, \( J = 267.4 \) Hz), 120.58, 26.86 (q, \( J = 8.8 \) Hz). \text{HRMS (ESI)}: calcd. for \( \text{C}_{11}\text{H}_8\text{F}_3\text{N}_3\text{O}[\text{M+Na}]^+ \): 278.0512, found: 278.0513. \text{IR (KBr)} \( \nu \) 3106, 3070, 1683, 1601, 1515, 1459, 1403, 1364, 1259, 8-8
1145, 1083, 1038, 994, 846, 802, 760, 620, 592 cm\(^{-1}\)

1-(4-Nitrophenyl)-4-(trifluoromethyl)-1\textsubscript{H}-1,2,3-triazole (2q).

White solid (42.3 mg, mp: 193–195 °C, yield: 82%). \(^{1}\text{H} \text{NMR} (600 \text{ MHz, DMSO}) \delta 9.78 (s, 1H), 8.46 (d, \(J = 8.0 \text{ Hz, 2H})\), 8.25 (d, \(J = 8.3 \text{ Hz, 2H})\). \(^{19}\text{F NMR} (565 \text{ MHz, DMSO}) \delta -60.15 (s)\). \(^{13}\text{C NMR} (150 \text{ MHz, DMSO}) \delta 147.38, 140.13, 138.05 (q, \(J = 38.7 \text{ Hz}\), 125.49, 124.98, 121.47, 120.52 (q, \(J = 267.7 \text{ Hz}\)). **HRMS (ESI):** calcd. for C\(_9\)H\(_5\)F\(_3\)N\(_4\)O\(_2\)[M+H]\(^+\): 259.0437, found: 259.0444. **IR (KBr)** \(\nu\) 3121, 3092, 1528, 1396, 1350, 1294, 1262, 1150, 1114, 860 cm\(^{-1}\).

![Image](image1)

1-(3-Nitrophenyl)-4-(trifluoromethyl)-1\textsubscript{H}-1,2,3-triazole (2r).

White solid (48.0 mg, mp: 142–144 °C, yield: 93%). \(^{1}\text{H} \text{NMR} (600 \text{ MHz, DMSO}) \delta 9.76 (s, 1H), 8.74 (s, 1H), 8.39 (d, \(J = 7.6 \text{ Hz, 1H})\), 8.32 (d, \(J = 7.7 \text{ Hz, 1H})\), 7.88 (td, \(J = 8.2, 2.1 \text{ Hz, 1H})\). \(^{19}\text{F NMR} (565 \text{ MHz, DMSO}) \delta -60.34 (s)\). \(^{13}\text{C NMR} (150 \text{ MHz, DMSO}) \delta 148.40, 137.97 (q, \(J = 38.7 \text{ Hz}\), 136.51, 131.48, 126.58, 124.75, 123.85, 120.50 (q, \(J = 267.4 \text{ Hz}\), 115.43. **HRMS (ESI):** calcd. for C\(_{12}\)H\(_{10}\)F\(_3\)N\(_3\)O\(_2\)[M+H]\(^+\): 259.0437, found: 259.0441. **IR (KBr)** \(\nu\) 3149, 3120, 3068, 1574, 1539, 1495, 1381, 1352, 1297, 1261, 1180, 1141, 1040, 1010, 976, 902, 869, 844, 814, 751, 667 cm\(^{-1}\).

![Image](image2)

1-(2-Methoxyphenyl)-4-(trifluoromethyl)-1\textsubscript{H}-1,2,3-triazole (2s).

White solid (38.8 mg, mp: 63–65 °C, yield: 80%). \(^{1}\text{H} \text{NMR} (600 \text{ MHz, CDCl\(_3\}) \delta 8.43
(s, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.13 (t, J = 8.3 Hz, 2H), 3.92 (s, 3H). ¹⁹F NMR (565 MHz, CDCl₃) δ -61.00 (s). ¹³C NMR (150 MHz, CDCl₃) δ 151.06, 138.52 (q, J = 39.4 Hz), 131.08, 125.56, 125.44, 124.51, 121.52, 120.74 (q, J = 267.6 Hz), 112.48, 56.21. HRMS (ESI): calcd. for C₁₀H₈F₃N₃O[M+Na]+: 266.0512, found: 266.0515. IR (KBr) ν 3175, 2947, 1605, 1569, 1510, 1477, 1380, 1258, 1234, 1139, 1029, 981, 940, 837, 762, 673 cm⁻¹.

![Chemical structure of 1-(3-Methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2t).]

1-(3-Methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2t).

White solid (46.2 mg, mp: 63–65 ºC, yield: 95%). ¹H NMR (600 MHz, CDCl₃) δ 8.32 (s, 1H), 7.44 (t, J = 8.2 Hz, 1H), 7.32 (t, J = 2.2 Hz, 1H), 7.26 (dd, J = 8.0, 1.3 Hz, 1H), 7.03 (dd, J = 8.4, 1.9 Hz, 1H), 3.88 (s, 3H). ¹⁹F NMR (565 MHz, CDCl₃) δ –61.25 (s). ¹³C NMR (150 MHz, CDCl₃) δ 160.84, 139.49 (q, J = 39.5 Hz), 137.23, 130.90, 121.76, 120.47 (q, J = 267.8 Hz), 115.55, 112.77, 106.93, 55.76. HRMS (ESI): calcd. for C₁₀H₈F₃N₃O[M+H]+: 244.0692, found: 266.0699. IR (KBr) ν 3121, 3011, 1610, 1573, 1483, 1449, 1410, 1376, 1211, 1150, 1066, 1018, 972, 921, 822 cm⁻¹.

![Chemical structure of 1-(4-Methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2u).]

1-(4-Methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2u).

White solid (39.3 mg, mp: 121–123 ºC, yield: 81%). ¹H NMR (600 MHz, CDCl₃) δ 8.23 (s, 1H), 7.61 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H). ¹⁹F NMR (565 MHz, CDCl₃) δ –61.18 (s). ¹³C NMR (150 MHz, CDCl₃) δ 160.65, 139.34 (q, J = 39.4 Hz) 129.56, 122.67, 121.75, 120.54 (q, J = 267.8 Hz), 115.09, 55.75. HRMS (ESI): calcd. for C₁₀H₈F₃N₃O[M+Na]+: 266.0512, found: 266.0517. IR (KBr) ν 3104, 1568, 1517, 1466, 1425, 1380, 1261, 1174, 1137, 1043, 826 cm⁻¹.
1-(3,5-Dimethoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2v).
White solid (39.2 mg, mp: 65–67 ºC, yield: 72%).

\[ ^1H \text{NMR} \ (600 \text{ MHz, CDCl}_3) \delta 8.31 \text{ (s, 1H), } 6.87 \text{ (s, 2H), } 6.54 \text{ (s, 1H), } 3.85 \text{ (s, 6H)}. \]
\[ ^19F \text{NMR} \ (565 \text{ MHz, CDCl}_3) \delta -61.24. \]
\[ ^13C \text{NMR} \ (150 \text{ MHz, CDCl}_3) \delta 161.69, 139.35 \text{ (q, } J = 39.5 \text{ Hz), } 137.61, 121.78, 120.40 \text{ (q, } J = 267.8), 101.27, 99.33, 55.81. \]

HRMS (ESI): calcd. for C\textsubscript{11}H\textsubscript{10}F\textsubscript{3}N\textsubscript{3}O [M+H]\textsuperscript{+}: 274.0798, found: 274.0804.

IR (KBr) \: \nu 3113, 3010, 1616, 1495, 1462, 1377, 1231, 1210, 1150, 1062, 1020, 976, 924, 826, 675 \text{ cm}^{-1}.

1-(p-Tolyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2w).
White solid (25.4 mg, mp: 95–97 ºC, yield: 56%).

\[ ^1H \text{NMR} \ (600 \text{ MHz, CDCl}_3) \delta 8.27 \text{ (s, 1H), } 7.59 \text{ (d, } J = 8.3 \text{ Hz, 2H), } 7.34 \text{ (d, } J = 8.1 \text{ Hz, 2H), } 2.42 \text{ (s, 3H)}. \]
\[ ^19F \text{NMR} \ (565 \text{ MHz, CDCl}_3) \delta -61.20. \]
\[ ^13C \text{NMR} \ (150 \text{ MHz, CDCl}_3) \delta 140.22, 139.45 \text{ (q, } J = 39.6 \text{ Hz), } 133.98, 130.59, 121.61, 120.88, 120.54 \text{ (q, } J = 267.2 \text{ Hz), } 21.18. \]

HRMS (ESI): calcd. for C\textsubscript{10}H\textsubscript{8}F\textsubscript{3}N\textsubscript{3}[M+Na]\textsuperscript{+}: 250.0563, found: 250.0566.

IR (KBr) \: \nu 3111, 3049, 1569, 1522, 1379, 1259, 1166, 1134, 1041, 994, 853, 818 \text{ cm}^{-1}.

1-(3,5-Dimethylphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2x).
White solid (36.2 mg, mp: 63–65 ºC, yield: 75%).

\[ ^1H \text{NMR} \ (600 \text{ MHz, CDCl}_3) \delta 8.21 \text{ (s, 1H), } 7.22 \text{ (s, 2H), } 6.99 \text{ (s, 1H), } 2.26 \text{ (s, 6H)}. \]
\[ ^19F \text{NMR} \ (565 \text{ MHz, CDCl}_3) \delta -61.25. \]
\[ ^13C \text{NMR} \ (150 \text{ MHz, CDCl}_3) \delta 140.12, 139.26 \text{ (q, } J = 39.4 \text{ Hz), } 136.09, 131.34, \]
121.72 (d, \(J = 2.6\) Hz), 120.54 (q, \(J = 267.7\) Hz), 118.59, 21.14. **HRMS (ESI):** calcd. for \(C_{11}H_{10}F_{3}N_{3}[M+H]^+\): 242.0900, found: 242.0905. **IR (KBr)** ν 3144, 3113, 1618, 1597, 1571, 1489, 1436, 1378, 1290, 1255, 1225, 1169, 1133, 1036, 988, 945, 896, 846 cm\(^{-1}\)

![Molecule Structure](image)

**1-(o-Tolyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2y).**

Oil (32.7 mg, yield: 72%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.09 (s, 1H), 7.44 (t, \(J = 7.4\) Hz, 1H), 7.38 (d, \(J = 7.5\) Hz, 1H), 7.34 (t, \(J = 7.5\) Hz, 1H), 7.30 (d, \(J = 7.6\) Hz, 1H), 2.19 (s, 3H). \(^{19}\)F NMR (565 MHz, CDCl\(_3\)) \(\delta\) –61.04 (s). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 138.78 (q, \(J = 39.5\) Hz), 135.53, 133.77, 131.77, 130.71, 127.15, 125.97, 124.84, 120.56 (q, \(J = 267.8\) Hz), 17.70. **HRMS (ESI):** calcd. for \(C_{10}H_8F_3N_3[M+H]^+\): 250.0563, found: 250.0570. **IR (KBr)** ν 3121, 3099, 1567, 1522, 1441, 1422, 1399, 1379, 1263, 1200, 1173, 1122, 1019, 987, 877, 815, 760 cm\(^{-1}\).

![Molecule Structure](image)

**1-([1,1'-Biphenyl]-2-yl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2z).**

White solid (38.2 mg, mp: 67–69 °C, yield: 66%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.64 (dd, \(J = 15.5, 7.7\) Hz, 2H), 7.56 (t, \(J = 7.3\) Hz, 2H), 7.47 (s, 1H), 7.32 (p, \(J = 6.0\) Hz, 3H), 7.10 – 7.04 (m, 2H). \(^{19}\)F NMR (565 MHz, CDCl\(_3\)) \(\delta\) –61.22 (s). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 138.66 (q, \(J = 39.5\) Hz), 137.37, 136.69, 134.23, 131.36, 130.79, 129.02, 128.91, 128.50, 128.45, 126.63, 125.34 (d, \(J = 2.6\) Hz), 120.33 (q, \(J = 267.8\) Hz). **HRMS (ESI):** calcd. for \(C_{15}H_{10}F_3N_3[M+Na]^+\): 312.0719, found: 312.0720. **IR (KBr)** ν 3146, 3114, 1592, 1565, 1506, 1486, 1465, 1447, 1435, 1423, 1394, 1295, 1261, 1230, 1131, 1084, 1037, 1009, 997, 979, 910, 840, 780, 765, 737 cm\(^{-1}\).
1-(Naphthalen-1-yl)-4-(trifluoromethyl)-1\textit{H}-1,2,3-triazole (2a’).

White solid (46.3 mg, mp: 94–96 °C, yield: 88\%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.24 (s, 1H), 8.05 (dd, $J = 8.7, 7.3$ Hz, 1H), 7.96 (d, $J = 8.1$ Hz, 1H), 7.60 (t, $J = 5.2$ Hz, 1H), 7.59 – 7.53 (m, 3H), 7.51 (d, $J = 8.4$ Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ –60.89 (s). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 138.98 (q, $J = 39.6$ Hz), 134.22, 132.63, 131.32, 128.55, 128.42, 128.28, 127.46, 125.86, 125.00, 123.92, 121.74, 120.61 (q, $J = 267.9$ Hz). HRMS (ESI): calcd. for C$_{13}$H$_8$F$_3$N$_3$[M+H]$^+$: 264.0743, found: 264.0749. IR (KBr) $\nu$ 3134, 3100, 1599, 1567, 1376, 1269, 1148, 1038, 985, 861, 803, 772, 741 cm$^{-1}$.

1-(1-Phenylethyl)-4-(trifluoromethyl)-1\textit{H}-1,2,3-triazole (2b’).

White solid (20.8 mg, mp: 54–56 °C, yield: 43\%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.71 (s, 1H), 7.40 (dd, $J = 15.5, 8.3$ Hz, 3H), 7.30 (d, $J = 7.0$ Hz, 2H), 5.87 (q, $J = 6.8$ Hz, 1H), 2.03 (d, $J = 7.0$ Hz, 3H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ –61.08 (s). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 138.97 (q, $J = 39.3$ Hz), 138.78, 129.45, 129.24, 126.77, 122.07, 120.60 (q, $J = 267.7$ Hz), 61.19, 21.35. HRMS (ESI): calcd. for C$_{11}$H$_{10}$F$_3$N$_3$[M+Na]$^+$: 264.0719, found: 264.0718. IR (KBr) $\nu$ 3141, 3104, 3033, 3005, 1566, 1496, 1455, 1384, 1259, 1229, 1157, 1041, 994, 855, 778, 749, 706 cm$^{-1}$.

1-Cyclohexyl-4-(trifluoromethyl)-1\textit{H}-1,2,3-triazole (2c’).
White solid (12.3 mg, mp: 34–36 °C, yield: 28%). \(^1\)H NMR (600 MHz, CDCl\(_3\) \(\delta\) 7.83 (s, 1H), 4.51 (tt, \(J = 11.8, 3.8\) Hz, 1H), 2.25 (dd, \(J = 13.2, 1.8\) Hz, 2H), 1.96 (dd, \(J = 10.9, 3.0\) Hz, 2H), 1.77 (ddd, \(J = 25.0, 12.6, 3.6\) Hz, 3H), 1.53 – 1.45 (m, 2H), 1.35 – 1.26 (m, 1H). \(^{19}\)F NMR (565 MHz, CDCl\(_3\) \(\delta\) –61.06 (s). \(^{13}\)C NMR (150 MHz, CDCl\(_3\) \(\delta\) 138.72 (q, \(J = 39.2\) Hz), 120.91, 120.81 (q, \(J = 267.6\) Hz), 60.93, 33.63, 25.18, 25.16. HRMS (ESI): calcd. for C\(_9\)H\(_{12}\)F\(_3\)N\(_3\)[M+Na]\(^+\): 242.0876, found: 242.0881. IR (KBr) \(\nu\) 3119, 2961, 1537, 1440, 1212, 1147, 1030, 990, 889, 766 cm\(^{-1}\).

Ag\(_2\)CO\(_3\) (0.04 mmol, 0.10 equiv), isocyanide \(\text{I} (0.40 \text{ mmol, 1.0 equiv), 4Å MS (100.0 mg, and trifluoromethylbenzene (0.4 mmol, 1.0 equiv) were added into a 10.0 mL Schlenk tube. The tube was sealed well and diazo compound (0.48 mmol, 1.2 equiv) in DMF (1.0 mL) was added. The reaction mixture was conducted at 40 °C for 6.0 h, and cooled at room temperature. A little sample (~ 40 \(\mu\)L) was used for the \(^{19}\)F NMR spectroscopic analysis and the determination of yield (2d\(^+\): 26%). To the reaction mixture was added sodium hydride (0.8 mmol, 2.0 equiv) at 0 °C. After stirring for 1 h at the same temperature, I\(_2\) (0.88 mmol, 2.2 equiv) was added and stirred overnight at room temperature. The reaction was quenched with water and extracted with ether (8.0 mL \(\times\) 3). The organic phases were collected, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. Purification by flash chromatography on silica gel (hexane / ethyl acetate =50:1) afforded the corresponding iodonitrile: 1-(\(tert\)-butyl)-5-iodo-4-(trifluoromethyl)-1H-1,2,3-triazole, white solid (26.8 mg, mp: 84–86 °C, yield: 21%). \(^1\)H NMR (400 MHz, CDCl\(_3\) \(\delta\) 1.17 (s, 9H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\) \(\delta\) –59.46 (s). \(^{13}\)C NMR (100 MHz, CDCl\(_3\) \(\delta\) 126.57, 120.31 (q, \(J = 267.4\) Hz), 54.12, 29.89. IR (KBr) \(\nu\) 3445, 3179, 2975, 2925, 1581, 1418, 1141, 971, 768, 610, 432 cm\(^{-1}\). HRMS (EI): calcd. for C\(_7\)H\(_9\)F\(_3\)IN\(_3\)[M]\(^+\): 318.9788, found: 318.9793.
Ethyl 1-phenyl-1H-1,2,3-triazole-4-carboxylate (2e’).

White solid (31.2 mg, mp: 83–85 °C, yield: 72%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.51 (s, 1H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 7.7$ Hz, 2H), 7.45 (t, $J = 7.4$ Hz, 1H), 4.41 (q, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 160.64, 140.84, 136.38, 129.95, 129.52, 125.59, 120.81, 61.48, 14.34.

Ethyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate (2f’).

White solid (41.0 mg, mp: 110–112 °C, yield: 83%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.41 (s, 1H), 7.62 (d, $J = 8.9$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 4.42 (q, $J = 7.1$ Hz, 2H), 3.84 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 160.77, 160.40, 140.69, 129.76, 125.65, 122.50, 114.98, 61.47, 55.74, 14.39.

Ethyl 1-($p$-tolyl)-1H-1,2,3-triazole-4-carboxylate (2g’).

White solid (39.3 mg, mp: 96–98 °C, yield: 85%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (s, 1H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 4.45 (q, $J = 7.1$ Hz, 2H), 2.43 (s, 3H), 1.43 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.64, 140.63, 139.70, 134.03, 130.37, 125.49, 120.62, 61.36, 21.09, 14.30.

Ethyl 1-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (2h’).
White solid (37.3 mg, mp: 170–172 °C, yield: 74%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.50 (s, 1H), 7.72 (d, \(J = 8.7\) Hz, 2H), 7.52 (d, \(J = 8.7\) Hz, 2H), 4.45 (q, \(J = 7.1\) Hz, 2H), 1.42 (t, \(J = 7.1\) Hz, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 160.57, 141.17, 135.55, 134.95, 130.27, 125.53, 122.10, 61.70, 14.43.

![Ethyl 1-(3-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate (2i’).](image)

White solid (31.9 mg, mp: 142–144°C, yield: 61%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.66 (s, 2H), 8.37 (d, \(J = 8.0\) Hz, 1H), 8.22 (d, \(J = 7.8\) Hz, 1H), 7.81 (t, \(J = 8.1\) Hz, 1H), 4.48 (q, \(J = 7.0\) Hz, 2H), 1.45 (t, \(J = 7.0\) Hz, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 160.29, 149.13, 141.63, 137.22, 131.40, 126.38, 125.58, 124.12, 115.80, 61.93, 14.44.

![Tert-butyl 1-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (2j’).](image)

White solid (36.9 mg, mp: 169–171 °C, yield: 66%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.43 (s, 1H), 7.70 (d, \(J = 8.6\) Hz, 2H), 7.48 (d, \(J = 8.6\) Hz, 2H), 1.58 (s, 9H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.66, 142.29, 135.23, 134.98, 130.11, 125.20, 122.01, 82.69, 28.25. HRMS (ESI): calcd. for C\(_{13}\)H\(_{14}\)ClN\(_3\)O\(_2\)[M+Na]\(^+\): 302.0667, found: 302.0668. IR (KBr) ν 3408, 3145, 3110, 2983, 2935, 1713, 1543, 1498, 1400, 1264, 1038, 836, 800, 516 cm\(^{-1}\).

![1-Phenyl-4-(trimethylsilyl)-1H-1,2,3-triazole (2k’).](image)
White solid (13.9 mg, mp: 96–98 ºC, yield: 32%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (s, 1H), 7.73 (d, \(J = 7.7\) Hz, 2H), 7.50 (t, \(J = 7.7\) Hz, 2H), 7.41 (t, \(J = 7.4\) Hz, 1H), 0.37 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.45, 137.21, 129.78, 128.58, 127.25, 120.92, –1.01. HRMS (ESI): calcd. for C\(_{11}\)H\(_{15}\)N\(_3\)Si[M+Na]\(^+\): 240.0927, found: 240.0930. IR (KBr) \(\nu\) 3444, 3137, 2957, 2226, 1674, 1399, 1245, 1207, 839, 749, 687, 513 cm\(^{-1}\).

![Diagram](https://example.com/diagram.png)

1-(\(p\)-Tolyl)-4-(trimethylsilyl)-1\(^H\)-1,2,3-triazole (2l').

White solid (16.2 mg, mp: 95–97 ºC, yield: 35%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (s, 1H), 7.60 (d, \(J = 7.8\) Hz, 2H), 7.29 (d, \(J = 7.8\) Hz, 2H), 2.40 (s, 3H), 0.37 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.25, 138.61, 134.94, 130.26, 127.23, 120.82, 21.19, –1.00. HRMS (ESI): calcd. for C\(_{12}\)H\(_{17}\)N\(_3\)Si[M+Na]\(^+\): 254.1084, found: 254.1090. IR (KBr) \(\nu\) 3130, 3046, 2959, 2226, 1721, 1519, 1249, 1205, 842, 815, 755, 517 cm\(^{-1}\).

![Diagram](https://example.com/diagram.png)

1-(4-Chlorophenyl)-4-(trimethylsilyl)-1\(^H\)-1,2,3-triazole (2m').

White solid (20.6 mg, mp: 123–125 ºC, yield: 41%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (s, 1H), 7.69 (d, \(J = 6.9\) Hz, 2H), 7.48 (d, \(J = 6.8\) Hz, 2H), 0.37 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.86, 135.73, 134.32, 129.98, 127.09, 122.04, –1.03. HRMS (ESI): calcd. for C\(_{11}\)H\(_{14}\)ClN\(_3\)Si[M+Na]\(^+\): 274.0538, found: 274.0539. IR (KBr) \(\nu\) 3448, 3117, 2980, 2902, 2231, 1677, 1502, 1248, 1201, 1038, 983, 840, 761, 514 cm\(^{-1}\).
1-(3,5-Dimethoxyphenyl)-4-(trimethylsilyl)-1H-1,2,3-triazole (2n').
Colorless oil (23.3 mg, yield: 42%). \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.90 (s, 1H), 6.87 (s, 2H), 6.47 (s, 1H), 3.82 (s, 6H), 0.35 (s, 9H). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 161.52, 147.32, 138.65, 127.36, 100.36, 99.31, 55.76, –1.06. HRMS (ESI): calcd. for C\(_{13}\)H\(_{19}\)N\(_3\)O\(_2\)Si[\( \text{M+Na}^+ \)]: 300.1139, found: 300.1140. IR (KBr) ν 3122, 3005, 2958, 2843, 1608, 1492, 1203, 1157, 1065, 843, 759, 632 cm\(^{-1}\).

1-(3-Nitrophenyl)-4-(trimethylsilyl)-1H-1,2,3-triazole (2o').
White solid (19.9 mg, mp: 107–109 ºC, yield: 38%). \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.58 (s, 1H), 8.28 (d, \( J = 8.1 \) Hz, 1H), 8.21 (d, \( J = 8.0 \) Hz, 1H), 8.07 (s, 1H), 7.74 (t, \( J = 8.2 \) Hz, 1H), 0.39 (s, 9H). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 149.00, 148.58, 137.94, 131.05, 127.07, 126.43, 123.03, 115.44, –1.08. HRMS (ESI): calcd. for C\(_{11}\)H\(_{14}\)N\(_4\)O\(_2\)Si[\( \text{M+Na}^+ \)]: 285.0778, found: 285.0782. IR (KBr) ν 3742, 3125, 2961, 1743, 1698, 1535, 1399, 1349, 1248, 840, 735, 667 cm\(^{-1}\).

Methyl 2-methoxy-5-(4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)benzoate (2p').
White solid (45.2 mg, mp: 126–128 ºC, yield: 75%). \( ^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.30 (s, 1H), 8.10 (d, \( J = 2.8 \) Hz, 1H), 7.86 (dd, \( J = 9.0, 2.8 \) Hz, 1H), 7.13 (d, \( J = 9.0 \) Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H). \( ^{19}\)F NMR (565 MHz, CDCl\(_3\)) \( \delta \) –61.24 (s). \( ^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 165.09, 159.93, 139.54 (q, \( J = 39.6 \) Hz), 128.89, 126.22,
124.43, 121.79 (d, $J = 2.5$ Hz), 121.09, 120.40 (q, $J = 267.8$ Hz), 113.42, 56.60, 52.53. 

**HRMS (ESI):** calcd. for C$_{12}$H$_{10}$F$_3$N$_3$O$_3$[M+Na]$^+$: 324.0566, found: 324.0566. **IR (KBr)** $\nu$ 3113, 2960, 1687, 1614, 1510, 1323, 1262, 1194, 1138, 1044, 1018, 983, 912, 847, 822, 785, 747 cm$^{-1}$.

**The preparation of Mesalazine-derived 1,2,3-triazole**

To a solution of 2$p'$ (0.29 mmol, 87.3 mg) in methanol (5.0 mL) was added 2 N aqueous sodium hydroxide solution (4.5 mL) and the mixture heated at reflux for 1.5 h. The reaction was cooled to ambient temperature, filtered and the filtrate concentrated in vacuo to remove the methanol. The residual aqueous phase was washed with diethyl ether, acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. The organic extracts were dried (MgSO$_4$) and the solvent removed in vacuo to give 2-methoxy-5-(4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)benzoic acid as a white solid (82.7 mg), which was used without further purification.

A solution of boron tribromide (0.66 mmol) in dichloromethane (1.0 mL) was added dropwise to a solution of 2-methoxy-5-(4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)-benzoic acid (82.7 mg, 0.29 mmol) in dried dichloromethane (2.0 mL) under argon at 0 °C. The reaction was stirred for 1 hour at 0 °C and allowed to warm to ambient temperature and stirred for further 16 hours. It was then poured into ice water and extracted with dichloromethane then with ethyl acetate. The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate and the aqueous phase acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. The ethyl acetate extracts were dried (MgSO$_4$) and concentrated under reduced pressure. Purification by flash chromatography on silica gel afforded the corresponding product.
2-Hydroxy-5-(4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)benzoic acid (3).
White solid [75.2 mg, mp: 222–224 °C, yield: 95% (two steps)]. $^1$H NMR (600 MHz, DMSO) $\delta$ 9.55 (s, 1H), 8.28 (d, $J = 2.3$ Hz, 1H), 8.04 (dd, $J = 8.7$, 1.8 Hz, 1H), 7.19 (d, $J = 8.8$ Hz, 1H), 7.19 (s, 1H). $^{19}$F NMR (565 MHz, DMSO) $\delta$ –59.83 (s). $^{13}$C NMR (150 MHz, DMSO) $\delta$ 170.68, 161.37, 137.51 (q, $J = 38.4$ Hz), 128.14, 127.79, 124.31, 122.77, 120.70 (q, $J = 267.3$ Hz), 118.62, 113.90. HRMS (ESI): calcd. for C$_{10}$H$_6$F$_3$N$_3$O$_3$[M-H]: 272.0288, found: 272.0289. IR (KBr) $\nu$ 3247, 3053, 3011, 2955, 1660, 1613, 1502, 1312, 1260, 1182, 1022, 1000, 982, 903,843, 822, 773 cm$^{-1}$.

1-(Adamantan-1-yl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2q').
White solid (28.2 mg, mp: 148–150 °C, yield: 52%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.90 (s, 1H), 2.26 (d, $J = 19.4$ Hz, 6H), 2.23 (s, 3H) 1.79 (q, $J = 12.5$ Hz, 6H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ –60.96 (s). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 138.06 (q, $J = 38.8$ Hz), 120.87 (q, $J = 267.5$ Hz), 119.80, 60.91, 43.00, 35.81, 29.50. HRMS (ESI): calcd. for C$_{13}$H$_{16}$F$_3$N$_3$[M+Na]: 294.1189, found: 294.1190. IR (KBr) $\nu$ 3146, 3109, 2914, 2859, 1566, 1453, 1380, 1308, 1253, 1227, 1196, 1161, 1135, 1053, 1016, 983 cm$^{-1}$.

(2S,3R,5S,6R)-6-(Acetoxymethyl)-3-(4-(trifluoromethyl)-1H-1,2,3-triazol-1-yl)tetrhydro-2H-pyran-2,4,5-triyl triacetate (2r').

S-20
White solid (34.5 mg, mp: 174–176 °C, yield: 37%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.93 (s, 1H), 6.20 (d, $J = 7.8$ Hz, 1H), 5.80 (t, $J = 8.8$ Hz, 1H), 5.22 (t, $J = 8.5$ Hz, 1H), 4.72 (t, $J = 8.5$ Hz, 1H) 4.39 (d, $J = 9.5$ Hz, 1H), 4.17 (d, $J = 11.9$ Hz, 1H), 4.08 (d, $J = 5.0$ Hz, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.87 (s, 3H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ –61.20 (s). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.57, 169.68, 169.14, 168.02, 139.19 (q, $J = 39.8$ Hz), 123.90, 120.25 (q, $J = 268.2$ Hz), 91.59, 73.25, 72.07, 68.18, 63.36, 61.47, 20.76, 20.60, 20.54, 20.24. HRMS (ESI): calcd. for C$_9$H$_{12}$F$_3$ N$_3$[M+Na]$^+$: 490.1044, found: 490.1045. IR (KBr) ν 2995, 1770, 1759, 1383, 1245, 1103, 1056, 764, 750 cm$^{-1}$.

**Pd-catalyzed arylation of 1,4-disubstituted 1,2,3-triazoles:**

**Typical Preparative Procedure A**

1-(3-methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole 2t (36.4 mg, 0.15 mmol, 1.0 equiv), Pd(Ph$_3$P)$_2$Cl$_2$ (5.26 mg, 0.05 equiv), tetrabutylammonium acetate (90.3 mg, 2.0 equiv) were added into a 10.0 mL Schlenk tube under Ar atmosphere. 1.0 mL of NMP was then added, followed by the addition of aryl bromine (1.5 equiv), and the reaction mixture was stirred at 100°C for 2 h. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (10 mL), washed twice with 10 mL portions of water and brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 15:1) afforded the corresponding product.

**Typical Preparative Procedure B**

1-(3-methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (36.4 mg, 0.15 mmol, 1.0 equiv), Pd(OAc)$_2$ (1.34 mg, 0.04 equiv), PCy$_3$ (3.36 mg, 0.08 equiv), chlorobenzene or aryl trifluoromethanesulfonate (1.50 equiv), and K$_2$CO$_3$ (41.4 mg, 2.0 equiv) were added into a 10.0 mL Schlenk tube under Ar atmosphere. 1.0 mL of PhMe was then added and the reaction mixture was stirred for 22 h. at 120 °C. Et$_2$O (5.0 mL) and H$_2$O (5.0 mL) were added to the cold reaction mixture. The separated aqueous phase
was extracted with Et₂O (2 × 5.0 mL). The combined organic layers were washed with aqueous NH₄Cl (5.0 mL), H₂O (5.0 mL) and brine (5.0 mL), dried over Na₂SO₄ and concentrated in vacuum. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 15:1) afforded the corresponding product.

![Chemical Structure Image]

1-(3-Methoxyphenyl)-5-phenyl-4-(trifluoromethyl)-1H-1,2,3-triazole (4a).
Prepared according to Procedure A, white solid (41.0 mg, mp: 82–84 ºC, yield: 86%).

¹H NMR (600 MHz, CDCl₃) δ 7.46 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.8 Hz, 3H), 6.95 (d, J = 8.3 Hz, 1H), 6.84 (s, 1H), 6.81 (d, J = 7.9 Hz, 1H), 3.71 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 160.23, 137.31, 136.53, 136.43 (q, J = 38.3 Hz), 130.45, 130.25, 129.85, 128.99, 124.77, 120.94 (q, J = 268.7 Hz), 117.32, 115.98, 110.75, 55.59. HRMS (ESI): calcd. for C₁₆H₁₂F₃N₃O₂[M+Na]+: 342.0825, found: 342.0824. IR (KBr) ν 3064, 2957, 2926, 2833, 1597, 1488, 1455, 1427, 1377, 1246, 1147, 1030, 987, 863, 831, 770 cm⁻¹.

![Chemical Structure Image]

1-(3-Methoxyphenyl)-5-(naphthalen-2-yl)-4-(trifluoromethyl)-1H-1,2,3-triazole (4b).
Prepared according to Procedure B, white solid (39.3 mg, mp: 101–103 ºC, yield: 71%).

¹H NMR (600 MHz, CDCl₃) δ 7.85 (dd, J = 18.1, 9.0 Hz, 4H), 7.60 – 7.54 (m, 2H), 7.25 – 7.18 (m, 2H), 6.93 (dd, J = 8.6, 1.6 Hz, 2H), 6.83 – 6.80 (m, 1H), 3.68 (s, 3H).

¹⁹F NMR (565 MHz, CDCl₃) δ –58.97 (s). ¹³C NMR (150 MHz, CDCl₃) δ
160.29, 137.39, 137.38, 136.65 (q, \( J = 38.0 \) Hz), 136.61, 133.69, 132.81, 130.27, 128.86, 128.55, 127.97, 127.93, 127.24, 126.04, 122.02, 121.02 (q, \( J = 268.8 \) Hz), 117.32, 115.88, 110.91, 55.57. **HRMS (ESI):** calcd. for C\(_{20}\)H\(_{14}\)F\(_3\)N\(_3\)O[M+Na]\(^+\): 392.0981, found: 392.0985. **IR (KBr)** \( \nu \) 3056, 3006, 2962, 1493, 1472, 1262, 1197, 1162, 1134, 1092, 843 cm\(^{-1}\).

1-(3-Methoxyphenyl)-5-(4-methoxyphenyl)-4-(trifluoromethyl)-1\(H\)-1,2,3-triazole (4c).

Prepared according to Procedure A, oil (37.8 mg, yield: 73%). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \( \delta \) 7.24 (d, \( J = 7.8 \) Hz, 1H), 7.14 (d, \( J = 8.7 \) Hz, 2H), 6.93 (dd, \( J = 8.4, 1.9 \) Hz, 1H), 6.88 (d, \( J = 8.8 \) Hz, 2H), 6.85 (t, \( J = 2.2 \) Hz, 1H), 6.78 (dd, \( J = 7.9, 1.1 \) Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H). **\(^1\)F NMR** (565 MHz, CDCl\(_3\)) \( \delta \) –59.14 (s). **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \( \delta \) 161.19, 160.34, 137.33, 136.80, 136.23 (q, \( J = 37.9 \) Hz), 131.30, 130.24, 121.10 (q, \( J = 268.6 \) Hz), 117.46, 116.64, 115.89, 114.55, 111.00, 55.66, 55.48. **HRMS (ESI):** calcd. for C\(_{17}\)H\(_{14}\)F\(_3\)N\(_3\)O\(_2\)[M+Na]\(^+\): 372.0930, found: 372.0935. **IR (KBr)** \( \nu \) 3076, 2961, 2931, 2841, 1613, 1584, 1512, 1494, 1469,1451, 1443, 1386, 1252, 1157, 1090,1032, 989, 863, 834, 780 cm\(^{-1}\).

1-(3-Methoxyphenyl)-5-(4-nitrophenyl)-4-(trifluoromethyl)-1\(H\)-1,2,3-triazole (4d)

Prepared according to Procedure B, white solid (35.4 mg, mp: 128–130 °C, yield: 65%). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \( \delta \) 8.27 (d, \( J = 8.7 \) Hz, 2H), 7.47 (d, \( J = 8.6 \) Hz, 2H), 7.30 (t, \( J = 8.2 \) Hz, 1H), 7.01 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 6.88 (s, 1H), 6.73 (dd, \( J = 2.0 \) Hz, 1H), 6.73 (d, \( J = 8.8 \) Hz, 1H). **HRMS (ESI):** calcd. for C\(_{17}\)H\(_{15}\)F\(_3\)N\(_3\)O\(_2\)[M+Na]\(^+\): 372.0930, found: 372.0935. **IR (KBr)** \( \nu \) 3076, 2961, 2931, 2841, 1613, 1584, 1512, 1494, 1469,1451, 1443, 1386, 1252, 1157, 1090,1032, 989, 863, 834, 780 cm\(^{-1}\).
7.9, 0.9 Hz, 1H), 3.77 (s, 3H). \( ^{19}F\) NMR (565 MHz, CDCl\(_3\)) \( \delta \) –59.03 (s). \( ^{13}C\) NMR (150 MHz, CDCl\(_3\)) \( \delta \) 160.59, 148.97, 137.05 (q, \( J \) = 38.7 Hz), 135.94, 135.14, 131.25, 131.11, 130.66, 124.16, 120.63 (q, \( J \) = 268.9 Hz), 117.34, 116.17, 111.38, 55.76. **HRMS (ESI):** calcd. for C\(_{16}H_{11}F_{3}N_{4}O_{3}\) [M+Na]\(^+\): 387.0675, found: 387.0679. **IR (KBr)** \( \nu \) 3117, 3015, 2967, 2845, 1609, 1520, 1493, 1443, 1388, 1345, 1290, 1242, 1201, 1168, 1132, 1077, 1044, 1005, 858, 770, 700, 680 cm\(^{-1}\).

![Chemical structure](image)

**4-(1-(3-Methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazol-5-yl)benzonitrile** (4e).

Prepared according to Procedure A, white solid (28.5 mg, mp: 99–101 °C, yield: 55%). \( ^{1}H\) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.70 (d, \( J \) = 8.3 Hz, 2H), 7.40 (d, \( J \) = 8.2 Hz, 2H), 7.30 (t, \( J \) = 8.2 Hz, 1H), 7.00 (dd, \( J \) = 8.4, 2.2 Hz, 1H), 6.85 (t, \( J \) = 2.1 Hz, 1H), 6.73 (dd, \( J \) = 7.8, 1.2 Hz, 1H), 3.76 (s, 3H). \( ^{19}F\) NMR (565 MHz, CDCl\(_3\)) \( \delta \) –59.04 (s). \( ^{13}C\) NMR (150 MHz, CDCl\(_3\)) \( \delta \) 160.53, 136.88 (q, \( J \) = 38.5 Hz), 135.97, 135.41, 132.68, 130.66, 130.59, 129.46, 120.64 (q, \( J \) = 268.9 Hz), 117.74, 117.31, 116.15, 114.56, 111.25, 55.72. **HRMS (ESI):** calcd. for C\(_{17}H_{11}F_{3}N_{4}O\) [M+Na]\(^+\): 367.0777, found: 367.0778. **IR (KBr)** \( \nu \) 2963, 2925, 2839, 2228, 1610, 1590, 1469, 1443, 1388, 1258, 1200, 1173, 1159, 1138, 1076, 1047, 1013, 993, 875, 840 cm\(^{-1}\).

![Chemical structure](image)

**1-(4-(1-(3-Methoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazol-5-yl)phenyl)ethane (4f).**

Prepared according to Procedure B, white solid (44.4 mg, mp: 91–93 °C, yield: 82%).
**1H NMR** (600 MHz, CDCl₃) δ 7.95 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.0 Hz, 1H), 6.95 (dd, J = 8.4, 2.0 Hz, 1H), 6.84 (t, J = 2.1 Hz, 1H), 6.73 (dd, J = 7.9, 1.2 Hz, 1H), 3.72 (s, 3H), 2.59 (s, 3H). **19F NMR** (565 MHz, CDCl₃) δ –59.06 (s). **13C NMR** (150 MHz, CDCl₃) δ 197.19, 160.43, 138.36, 136.77 (q, J = 38.4 Hz), 136.28, 130.45, 130.26, 129.31, 128.75, 120.79 (q, J = 268.7 Hz), 117.36, 116.05, 111.14, 55.69, 26.81. **HRMS (ESI)**: calcd. for C₁₈H₁₄F₃N₃O₂[M+Na]⁺: 384.0930, found: 384.0933. **IR (KBr)** ν 3058, 3014, 1688, 1606, 1498, 1475, 1425, 1260, 1202, 1165, 1132, 1095, 1067, 1038, 843 cm⁻¹.

**1-Phenyl-5-(2,2,2-trifluoroethyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (5)** was also detected when excessive CF₃CHN₂ were used

Ag₂CO₃ (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide 1 (20.6 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg) were added into a 10.0 mL Schlenk tube. The tube was sealed well and 2,2,2-trifluorodiazooethane in DMF (178 mg, 2.0 M, 8.0 equiv) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 25:1) afforded the corresponding product 2 (23.4 mg, yield: 55%) and the product 5 (7.1 mg, yield: 12%).

White solid (mp: 102–104 ºC). **1H NMR** (600 MHz, CDCl₃) δ 7.63 (dd, J = 16.3, 8.4 Hz, 3H), 7.42 (d, J = 7.2 Hz, 2H), 3.67 (q, J = 9.1 Hz, 2H). **19F NMR** (565 MHz, CDCl₃) δ –61.02 (d, J = 3.7 Hz, 3F), –64.35 (dt, J = 9.2, 4.4 Hz, 3F). **13C NMR** (150 MHz, CDCl₃) δ 138.26 (q, J = 38.7 Hz), 134.45, 131.43, 130.20, 127.56, 126.50, 123.36 (q, J = 278.1 Hz), 120.61 (q, J = 268.7 Hz), 28.62 (q, J = 33.6 Hz). **HRMS**
(ESI): calcd. for C_{11}H_{7}F_{6}N_{3}[M+Na]^{+}: 318.0436, found: 318.0440. IR (KBr) ν 3105, 3075, 2994, 2958, 1761, 1558, 1530, 1467, 1426, 1396, 1368, 1251, 1164, 1141, 1115, 1091, 997, 909, 844, 771, 699, 651 cm\(^{-1}\).

Cross-coupling experiment of the cycloadduct 2a with CF\(_3\)CHN\(_2\)

Ag\(_2\)CO\(_3\) (5.50 mg, 0.02 mmol, 0.10 equiv), cycloadduct 2a (42.6 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg) were added into a 10.0 mL Schlenk tube. The tube was sealed well and CF\(_3\)CHN\(_2\) in DMF (44.0 mg, 0.20 M, 2.0 equiv) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After cooling the tube to room temperature, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. Purification by flash chromatography on silica gel afforded the product. The \(^1\)H NMR spectrogram of product indicated this reaction could not undergo and the starting reagent 2a was 99% recovered.

General procedure for isotopic labeling experiments

The preparation of CF\(_3\)CH(D)N\(_2\)

As shown in the figure: A solution of 610 mg NaNO\(_2\) in 1.5 mL deuterium oxide was added slowly to the stirring solution of 1.08 g of tritfluoroethylamine hydrochloride in 2.5 mL deuterium oxide at rt. And then the rapidly generated yellow gas was gradually blown off through a drying tube (MgSO\(_4\)) into a gas absorber containing 10.0 mL anhydrous solvent equipped with an ice bath. After about 0.5 hour later, there would be no gas bubbling any more. Then the apparatus was removed carefully. Add the PhCF\(_3\) (25 uL) to 1.0 mL of DMF solvent (containing CF\(_3\)CH(D)N\(_2\)) and then detected by NMR. From the CF\(_3\)CH(D)N\(_2\)–\(^{19}\)F NMR spectrogram, the concentration of CF\(_3\)CH(D)N\(_2\) in DMF is 0.22 mmol/mL. Combined the CF\(_3\)CH(D)N\(_2\)–\(^{19}\)F NMR spectrogram and the CF\(_3\)CH(D)N\(_2\)–\(^1\)H NMR spectrogram, the ratio of hydrogen to deuterium of CF\(_3\)CH(D)N\(_2\) is 76:24.
The Procedure for the cycloaddition of CF₃CH(D)N₂ with 3-methoxyphenyl isocyanide

Having the CF₃CH(D)N₂ in hand, we then undergo the silver-catalyzed cycloaddition. Ag₂CO₃ (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide (20.6 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg) were added into a 10.0 mL Schlenk tube. The tube was sealed well and CF₃CH(D)N₂ (26.4 mg, 1.2 equiv) in DMF was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 25:1) afforded the product. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring is 78:22 by ¹H NMR, which is almost identical to that in CF₃CH(D)N₂.

The Procedure for the cycloaddition of N₂CH(D)CO₂Et (H/D = 15/85) with
4-chlorophenyl isocyanide

Ag₂CO₃ (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide (26.5 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well and N₂CH(D)CO₂Et (H/D = 15/85), 27.4 mg, 0.24 mmol, 1.2 equiv) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 5:1) afforded the product. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring is 80:20 by ¹H NMR analysis.

The Procedure for the cross-over cycloaddition of N₂CH(D)CO₂Et (H/D = 15/85) and N₂CHCO₂Bu' with 4-chlorophenyl isocyanide

Ag₂CO₃ (5.50 mg, 0.02 mmol, 0.10 equiv), isocyanide (26.5 mg, 0.20 mmol, 1.0 equiv), isocyanide (26.5 mg, 0.20 mmol, 1.0 equiv), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well and N₂CH(D)CO₂Et (H/D = 15/85), 27.4 mg, 0.24 mmol, 1.2 equiv) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 5:1) afforded the product. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring is 80:20 by ¹H NMR analysis.
equiv), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well. \( \text{N}_2\text{CH(D)CO}_2\text{Et (H/D = 15/85, 13.7 mg, 0.12 mmol)} \) and \( \text{N}_2\text{CHCO}_2\text{Bu}^t \) (17.0 mg, 0.12 mmol) was added. The reaction mixture was conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL \( \times 3 \)) to remove most of DMF. The organic phases were collected, dried over \( \text{Na}_2\text{SO}_4 \), and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 8:1) afforded the corresponding products. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring was analyzed by \(^1\text{H} \text{NMR.}\)
The Procedure for the cross-over control experiment

Ethyl 1-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (H/D = 80/20, 25.0 mg, 0.1 mmol) and tert-butyl 1-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (28.0 mg, 0.1 mmol), Ag₂CO₃ (5.50 mg, 0.02 mmol, 0.10 equiv), 4Å MS (25.0 mg), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. The tube was sealed well and conducted at 40 °C for 6.0 h. After the reaction was completed, 5.0 mL water was added and extracted with EtOAc (8.0 mL × 3) to remove most of DMF. The organic phases were collected, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether / ethyl acetate = 8:1) recovered the corresponding triazoles in quantitative yields. The ratio of hydrogen to deuterium at the 5-position of the 1,2,3-triazole ring was analyzed by ¹H NMR.
The research of interaction between isocyanide and Ag(I)

AgOAc (0.1 equiv) can also promote this reaction well and 1-(3,5-Dimethoxyphenyl)-4-(trifluoromethyl)-1H-1,2,3-triazole (2v) was obtained in 58% yield. In view of the poor solubility of Ag₂CO₃ in DMF, AgOAc was chosen as the catalyst to do NMR and IR experiments to study the interaction between isocyanide and Ag(I).

1-Isocyano-3,5-dimethoxybenzene (0.4 mmol, 65.2 mg) was dissolved in 0.5 mL DMF-d₇ in NMR tube, then AgOAc (1 equiv) was added to tube. After 10 minutes, interaction between isocyanide and Ag(I) was detected by $^{13}$C NMR.
1-isocyano-3,5-dimethoxybenzene in DMF-d$_7$ –$^{13}$C NMR

1-isocyano-3,5-dimethoxybenzene and Ag(I) in DMF-d$_7$ –$^{13}$C NMR
1-Isocyano-3,5-dimethoxybenzene (0.2 mmol, 32.6 mg), AgOAc (55 mg, 0.2 mmol), and DMF (1.0 mL) were added into a 10.0 mL Schlenk tube. After stirring for 10 minutes, the interaction between isocyanide and Ag(I) was detected by IR (KBr).

![1-isocyano-3,5-dimethoxybenzene-IR](image1)

![1-isocyano-3,5-dimethoxybenzene and AgOAc in DMF-IR](image2)


NMR Spectra of Products

2a-\(^1\)H NMR

2a-\(^{19}\)F NMR
$2c$-$^1$H NMR

$2c$-$^{19}$F NMR
2c-^{13}C NMR

2d-^{1}H NMR
2e-\(^1\)H NMR

2e-\(^19\)F NMR
2e-$^{13}$C NMR

2f-$^1$H NMR
$2g^{-13}H$ NMR

$2g^{-19}F$ NMR
$2i$-$^{13}$C NMR

$2j$-$^1$H NMR
$2k^-^1H$ NMR

$2k^-^{19}F$ NMR
$2k^{-13C}$ NMR

$2l^{-1H}$ NMR
$^{20}$-13C NMR

$^{2p}$-1H NMR
2q-¹H NMR

2q-¹⁹F NMR
$2q^{-13C}$ NMR

$2r^{-1H}$ NMR
2s-$^{13}$C NMR

2t-$^1$H NMR
2u-¹H NMR

2u-¹⁹F NMR
2u-$^{13}$C NMR

2v-$^1$H NMR
$^{29}$F NMR

$^{13}$C NMR
$2x^{-19}F$ NMR

$2x^{-13}C$ NMR

S-72
$2z$-$^{19}$F NMR

$2z$-$^{13}$C NMR
$2a^*-^{13}\text{C NMR}$

$2b^*-^{1}\text{H NMR}$
2b'-19F NMR

2b'-13C NMR
$2e^*-\text{H NMR}$

$2e^*-\text{F NMR}$
$2c\textsuperscript{\ell-13C}$ NMR

$2d\textsuperscript{\ell-1H}$ NMR
2d'-$^{19}$F NMR

2d'-$^{13}$C NMR
2$^\ddagger$-$^1$H NMR

2$^\ddagger$-$^{13}$C NMR
$2^g$-$^1$H NMR

$2^g$-$^{13}$C NMR
$^{1}H$ NMR

$^{13}C$ NMR
$2\text{H}^1$ NMR

$2\text{H}^1$ NMR

$2\text{H}^1$ NMR

$2\text{H}^1$ NMR
$2n^{-1}^1H$ NMR

$2n^{-1}^{13}C$ NMR
$2\tau^-\text{H NMR}$

$2\tau^-\text{F NMR}$
$^{3}$-^{19}F NMR

$^{3}$-^{13}C NMR
4b-$^19$F NMR

4b-$^{13}$C NMR
4e-\textsuperscript{1}H NMR

4e-\textsuperscript{19}F NMR
$^{13}$C NMR
X-Ray Analysis for the product 2a

CCDC 1024377 contains the supplementary crystallographic data for the product 2a. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
X-Ray Analysis for the product 5

CCDC 1024379 contains the supplementary crystallographic data for the product 5. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.