Supporting Information

Synthesis of 1-Aryl-1H-1,2,3-triazoles through the One-pot Cascade Reactions of Alkynes with Aliphatic Azides and Allenic Ketones

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I. General Experimental Information

Reagents and solvents were purchased from commercial suppliers and used without further purification. 1-Aryl substituted allenic ketones were prepared through oxidation of the corresponding homopropargyl alcohols,\(^1\) which were prepared through zinc promoted propargylation of aldehydes.\(^2\) 1,4-Disubstituted allenic ketones were prepared from the reaction of \(^1\)-(triphenylphosphoranylidene)-2-propanone or \(^2\)-(triphenylphosphoranylidene)acetophenone with phenylacetyl chloride based on a literature procedure.\(^3\)

The \(^1\)H and \(^13\)C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm from the internal standard tetramethylsilane. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), etc. Coupling constants were given in hertz. High-resolution mass spectra (HRMS) were obtained via ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).
II. Experimental Procedures and Spectroscopic Data

1. Typical procedure for the synthesis of 4a and spectroscopic data of 4a-4gg

To a flask containing ethynyl-3-methylbenzene (1a, 56.1 mg, 0.55 mmol) and ethyl 4-azido-3-oxobutanoate (2, 85.5 mg, 0.5 mmol) in t-BuOH/H2O (5 mL, v/v = 1/1) were added CuSO4·5H2O (aqueous solution, 25 μL, 1 M, 0.025 mmol) and sodium ascorbate (9.9 mg, 0.05 mmol). The mixture was stirred at room temperature for 12 h. Upon completion as monitored by TLC, the flask was charged with 1-phenylbuta-2,3-dien-1-one (3a, 79.2 mg, 0.55mmol) and NaOH (40.0 mg, 1.0 mmol). The mixture was stirred at 80 °C for 1.5 h. After being cooled to room temperature, it was quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO2) using EtOAc/petroleum ether (v/v =1/5) as eluent to give 4a (128.0 mg, 64%). Other 1-aryl-1H-1,2,3-triazole derivatives 4b-4dd were obtained in a similar manner.

Ethyl 3-hydroxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4a)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (128.0 mg, 64%); Mp: 144-145°C. 1H NMR (400 MHz, CDCl3) δ: 1.47 (t, J = 7.2 Hz, 3H), 2.69 (s, 3H), 4.50 (q, J = 7.6 Hz, 2H), 6.93 (s, 1H), 7.20-7.16 (m, 2H), 7.25-7.22 (m, 3H), 7.32-7.28 (m, 1H), 7.40-7.37 (m, 2H), 7.70 (s, 1H), 7.81-7.78 (m, 2H), 12.08 (s, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.2, 24.3, 62.4, 112.4, 122.0, 122.9, 124.3, 125.8, 128.1, 128.0, 128.5, 128.7, 130.5, 136.5, 143.5, 144.6, 147.1, 158.7, 171.2. HRMS (ESI): calcd for C24H22N3O3 [M+H]+: 400.1656; found: 400.1663.

Ethyl 2'-bromo-3-hydroxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4b)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (143.1 mg, 60%); Mp: 168-169°C. 1H NMR (400 MHz, CDCl3) δ: 1.48 (t, J = 6.8 Hz, 3H), 2.69 (s, 3H), 4.52 (q, J = 7.2 Hz, 2H), 6.82 (s, 1H), 7.10 (7, J = 7.6 Hz, 1H), 7.31-7.18 (m, 3H), 7.38 (t, J = 7.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.89 (s, 1H), 12.07 (s, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.2, 24.3, 62.5, 113.2, 121.9, 122.6, 122.8, 124.5, 125.8, 127.2, 128.0, 128.7, 130.0, 130.6, 130.8, 132.4, 137.4, 143.2, 144.0, 146.5, 158.1, 171.2. HRMS (ESI): calcd for C24H21BrN3O3 [M+H]+: 478.0761; found: 478.0768.

Ethyl 3-hydroxy-4',5-dimethyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4c)
Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (130.1 mg, 63%). ¹H NMR(400 MHz, CDCl₃) δ:
1.47 (t, J = 6.8 Hz, 3H), 2.27 (s, 3H), 2.68 (s, 3H), 4.49 (q, J = 6.8 Hz, 2H), 6.92 (s, 1H), 7.08- 7.02 (m, 4H), 7.32-7.28 (m, 1H), 7.41-7.38 (m, 2H), 7.71 (s, 1H), 7.83-7.80 (m, 2H), 12.06 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 21.2, 24.4, 62.4, 112.1, 121.9, 122.9, 124.3, 125.8, 127.98, 128.0, 128.7, 129.3, 130.6, 133.5, 138.5, 144.7, 147.1, 158.8, 171.3. HRMS (ESI): calcd for C₂₅H₂₄N₃O₃ [M+H]^+: 414.1812; found: 414.1811.

Ethyl 3-hydroxy-3',4'-dimethoxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4d)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (149.6 mg, 65%); Mp: 170-171°C. ¹H NMR (400 MHz, CDCl₃) δ: 1.45 (t, J = 6.8 Hz, 3H), 2.67 (s, 3H), 3.65 (s, 3H), 3.79 (s, 3H), 4.47 (q, J = 6.8 Hz, 2H), 6.59 (d, J = 2.4 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.82 (dd, J₁ = 8.4 Hz, J₂ = 1.6 Hz, 1H), 7.30-7.26 (m, 1H), 6.93 (s, 1H), 7.39-7.35 (m, 2H), 7.67 (s, 1H), 7.78-7.76 (m, 2H), 12.08 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 24.4, 55.5, 55.9, 62.4, 111.0, 111.9, 120.9, 121.7, 122.5, 123.9, 125.8, 126.1, 127.7, 128.8, 130.4, 143.6, 144.2, 147.3, 148.7, 149.3, 159.0, 171.3. HRMS (ESI): calcd for C₂₆H₂₆N₃O₅ [M+H]^+: 508.0866; found: 508.0878.

Ethyl 2'-bromo-3-hydroxy-5'-methoxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4e)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (152.4 mg, 60%); Mp: 180-182°C. ¹H NMR (400 MHz, CDCl₃) δ: 1.48 (t, J = 7.2 Hz, 3H), 2.69 (s, 3H), 3.68 (s, 3H), 4.51 (q, J = 7.2 Hz, 2H), 6.65 (dd, J₁ = 8.8 Hz, J₂ = 2.8 Hz, 1H), 6.78 (d, J = 2.8 Hz, 1H), 7.41-7.29 (m, 4H), 6.82 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.90 (s, 1H), 12.08 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 24.3, 55.5, 62.5, 112.1, 113.2, 115.8, 116.5, 122.7, 124.4, 125.8, 128.0, 128.8, 130.5, 133.1, 138.0, 143.2, 143.9, 146.6, 158.2, 159.5, 171.2. HRMS (ESI): calcd for C₂₆H₂₃BrN₃O₄ [M+H]^+: 508.0866; found: 508.0878.

Ethyl 2-(4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4f)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (149.7 mg, 69%); Mp: 151-152°C. ¹H NMR (400 MHz, CDCl₃) δ: 1.48 (t, J = 7.2 Hz, 3H), 2.69 (s, 3H), 4.50 (q, J = 7.2 Hz, 2H), 6.93 (s, 1H), 7.17-7.15 (m,
2H), 7.25-7.22 (m, 3H), 7.36-7.33 (m, 2H), 7.68 (s, 1H), 7.74-7.70 (m, 2H), 12.10 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.4, 62.5, 112.4, 121.9, 122.9, 124.3, 127.1, 128.1, 128.5, 128.6, 128.9, 133.8, 136.4, 143.7, 144.6, 146.0, 158.6, 171.2. HRMS (ESI): calcd for C$_{24}$H$_{22}$ClN$_3$O$_3$ [M+H]$^+$: 434.1266; found: 434.1276.

**Ethyl 2'-bromo-2-(4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5'-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4g)**

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (165.3 mg, 61%); Mp: 177-179°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.47 (t, $J = 6.8$ Hz, 3H), 2.68 (s, 3H), 3.67 (s, 3H), 4.50 (q, $J = 7.2$ Hz, 2H), 6.65 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 1H), 6.77 (d, $J = 3.2$ Hz, 1H), 6.81 (s, 1H), 7.32 (d, $J = 8.8$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.90 (s, 1H), 12.11 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.4, 55.5, 62.6, 112.1, 113.2, 115.9, 116.5, 122.5, 122.8, 124.5, 127.0, 128.9, 129.1, 133.1, 133.7, 138.0, 143.4, 143.8, 145.5, 158.1, 158.5, 171.2. HRMS (ESI): calcd for C$_{24}$H$_{22}$BrClN$_3$O$_3$ [M+H]$^+$: 542.0477; found: 542.0473.

**Ethyl 2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4h)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (142.2 mg, 68%); Mp: 154-155°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.47 (t, $J = 7.6$ Hz, 3H), 2.69 (s, 3H), 4.49 (q, $J = 7.6$ Hz, 2H), 6.92 (s, 1H), 7.08-7.04 (m, 2H), 7.18-7.16 (m, 2H), 7.24-7.22 (m, 3H), 7.66 (s, 1H), 7.76-7.73 (m, 2H), 12.10 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.4, 62.5, 112.4, 115.7 (d, $^2$J$_{C,F} = 21.6$ Hz), 121.9, 122.6, 124.3, 126.8 (d, $^4$J$_{C,F} = 2.9$ Hz), 127.5 (d, $^3$J$_{C,F} = 7.4$ Hz), 128.1, 128.5, 136.5, 143.6, 144.6, 146.2, 158.7, 162.6 (d, $^1$J$_{C,F} = 245.8$ Hz), 171.2. HRMS (ESI): calcd for C$_{24}$H$_{21}$FN$_3$O$_3$ [M+H]$^+$: 418.1561; found: 418.1562.

**Ethyl 2'-bromo-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4i)**

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (153.8 mg, 62%); Mp: 171-172°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.48 (t, $J = 7.2$ Hz, 3H), 2.69 (s, 3H), 4.51 (q, $J = 6.8$ Hz, 2H), 6.81 (s, 1H), 7.12-7.04 (m, 3H), 7.26-7.19 (m, 2H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.75-7.72 (m, 2H), 7.85 (s, 1H), 12.10 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.3, 62.5, 113.2, 115.7 (d, $^2$J$_{C,F} = 21.8$ Hz), 121.9, 122.4, 122.7, 124.5, 126.7 (d, $^4$J$_{C,F} = 2.3$ Hz), 127.2, 127.5 (d, $^3$J$_{C,F} = 8.5$ Hz), 129.9, 130.8, 132.4, 137.4, 143.2, 143.9, 145.7, 158.1,
162.6 (d, $J_{C,F} = 245.6$ Hz), 171.2. HRMS (ESI): calcd for C$_{24}$H$_{20}$BrF$_3$N$_3$O$_3$ [M+H]$^+$: 496.0667; found: 496.0678.

**Ethyl 2'-bromo-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5'-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4j)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (147.3 mg, 56%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.47 (t, $J = 7.2$ Hz, 3H), 2.69 (s, 3H), 3.68 (s, 3H), 4.50 (q, $J = 7.2$ Hz, 2H), 6.66 (dd, $J_1 = 8.8$ Hz, $J_2 = 3.6$ Hz, 1H), 6.77 (d, $J = 2.8$ Hz, 1H), 6.81 (s, 1H), 7.05-7.09 (m, 2H), 7.33 (d, $J = 8.8$ Hz, 1H), 7.72-7.76 (m, 2H), 7.86 (s, 1H), 12.10 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.2, 24.3, 55.5, 62.6, 112.1, 113.2, 115.7 (d, $J_{C,F} = 21.3$ Hz), 115.9, 116.5, 122.5, 122.6, 124.4, 126.7 (d, $J_{C,F} = 3.8$ Hz), 127.5 (d, $J_{C,F} = 7.8$ Hz), 133.1, 138.1, 143.3, 143.8, 145.7, 158.1, 158.5, 162.6 (d, $J_{C,F} = 245.5$ Hz), 171.2. HRMS (ESI): calcd for C$_{25}$H$_{22}$BrF$_3$N$_3$O$_3$ [M+H]$^+$: 526.0772; found: 526.0777.

**Ethyl 2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4k)**

Eluent: ethyl acetate/petroleum ether (1/8); Brown solid (169.7 mg, 71%); Mp: 162-164°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.46 (t, $J = 7.2$ Hz, 3H), 2.68 (s, 3H), 4.49 (q, $J = 7.6$ Hz, 2H), 6.92 (s, 1H), 7.17-7.14 (m, 2H), 7.24-7.21 (m, 3H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.70 (s, 1H), 12.11 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.2, 24.4, 62.5, 112.4, 121.9, 124.3, 123.0, 127.3, 128.1, 128.53, 128.56, 129.5, 131.9, 136.4, 143.7, 144.6, 146.1, 158.6, 171.2. HRMS (ESI): calcd for C$_{25}$H$_{21}$BrN$_3$O$_3$ [M+H]$^+$: 478.0761; found: 478.0770.

**Ethyl 2'-bromo-2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4l)**

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (147.3 mg, 53%); Mp: 165-166°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.48 (t, $J = 7.6$ Hz, 3H), 2.69 (s, 3H), 4.51 (q, $J = 7.6$ Hz, 2H), 6.82 (s, 1H), 7.12-7.08 (m, 1H), 7.26-7.18 (m, 2H), 7.50-7.46 (m, 3H), 7.64 (d, $J = 7.6$ Hz, 2H), 7.89 (s, 1H), 12.11 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.2, 24.3, 62.6, 113.2, 121.8, 121.9, 122.6, 122.7, 124.5, 127.2, 127.3, 129.5, 129.9, 130.8, 131.9, 132.4, 137.3, 143.3, 143.9, 145.5, 158.0, 171.2. HRMS (ESI): calcd for C$_{26}$H$_{20}$Br$_2$N$_3$O$_3$ [M+H]$^+$: 555.9866; found: 555.9876.
**Ethyl 2-((4-(bromophenyl))-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-4'-(trifluoromethyl) [1,1'-biphenyl]-4-carboxylate (4m)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (160.2 mg, 66%); Mp: 169-170°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.48 (t, $J = 6.8$ Hz, 3H), 2.70 (s, 3H), 4.51 (q, $J = 7.2$ Hz, 2H), 6.90 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.52-7.49 (m, 4H), 7.86-7.66 (m, 2H), 7.80 (s, 1H), 12.14 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.4, 62.7, 113.0, 121.9, 122.1, 122.9, 124.2, 127.9 (q, $^1J_{CF} = 270.0$ Hz), 125.5 (q, $^3J_{CF} = 3.4$ Hz), 127.3, 128.6, 129.3, 130.2 (q, $^2J_{CF} = 33.3$ Hz), 131.9, 140.2, 143.0, 144.0, 146.3, 158.5, 171.1. HRMS (ESI): calcd for C$_{25}$H$_{20}$BrF$_3$N$_3$O$_3$ [M+H]$^+$: 546.0635; found: 546.0631.

**Ethyl 3-hydroxy-5-methyl-2-(4-(m-tolyl))-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4n)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (130.5 mg, 63%); Mp: 120-122 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.47 (t, $J = 7.2$ Hz, 3H), 2.37 (s, 3H), 2.69 (s, 3H), 4.50 (q, $J = 7.6$ Hz, 2H), 6.93 (s, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.18-7.16 (m, 2H), 7.25-7.22 (m, 3H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.66 (s, 1H), 7.69 (s, 1H), 12.07 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 21.4, 24.4, 62.4, 112.4, 122.0, 122.87, 122.93, 124.3, 126.5, 128.1, 128.5, 128.7, 128.9, 129.1, 130.2, 136.5, 138.4, 143.5, 144.6, 147.1, 158.7, 171.2. HRMS (ESI): calcd for C$_{25}$H$_{24}$N$_3$O$_3$ [M+H]$^+$: 414.1812; found: 414.1823.

**Ethyl 2'-bromo-3-hydroxy-5-methyl-2-(4-(m-tolyl))-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4o)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (147.6 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.48 (t, $J = 7.2$ Hz, 3H), 2.37 (s, 3H), 2.69 (s, 3H), 4.51 (q, $J = 7.2$ Hz, 2H), 6.81 (s, 1H), 7.11-7.07 (m, 2H), 7.28-7.17 (m, 3H), 7.47 (dd, $J_1 = 8.4$ Hz, $J_2 = 0.8$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.64 (s, 1H), 7.88 (s, 1H), 12.09 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 21.4, 24.3, 62.5, 113.2, 121.9, 122.6, 122.8, 122.9, 124.5, 126.4, 127.2, 128.6, 129.8, 129.9, 130.3, 130.8, 132.4, 137.4, 138.4, 143.2, 144.0, 146.6, 158.1, 171.2. HRMS (ESI): calcd for C$_{25}$H$_{23}$BrN$_3$O$_3$ [M+H]$^+$: 492.0917; found: 492.0927.

**Ethyl 2'-bromo-3-hydroxy-5'-methoxy-5-methyl-2-(4-(m-tolyl))-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4p)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (187.9 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$:
1.46 (t, J = 7.6 Hz, 3H), 2.36 (s, 3H), 2.68 (s, 3H), 3.67 (s, 3H), 4.49 (q, J = 7.6 Hz, 2H), 6.64 (dd, J₁ = 8.8 Hz, J₂ = 3.2 Hz, 1H), 6.78 (d, J = 2.8 Hz, 1H), 6.81 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.32-7.24 (m, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.65 (s, 1H), 7.90 (s, 1H), 12.09 (s, 1H). 13C NMR (100 MHz, CDCl₃) δ: 14.2, 21.4, 24.3, 55.5, 62.5, 112.1, 113.2, 115.8, 116.5, 122.67, 122.70, 122.9, 124.4, 126.4, 128.7, 128.8, 130.4, 133.0, 138.1, 138.4, 143.2, 143.9, 146.7, 158.2, 158.5, 171.2. HRMS (ESI): calcd for C₂₅H₂₅BrN₃O₄ [M+H]^+: 522.1023; found: 522.1033.

Ethyl 2'-bromo-3-hydroxy-5-methyl-2-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4q)

Eluent: ethyl acetate/petroleum ether (1/3). Brown solid (172.2 mg, 70%); Mp: 145-146°C. ¹H NMR (400 MHz, CDCl₃) δ: 1.47 (t, J = 7.0 Hz, 3H), 2.34 (s, 3H), 2.68 (s, 3H), 4.49 (q, J = 7.2 Hz, 2H), 6.81 (s, 1H), 7.10-7.06 (m, 1H), 7.22-7.17 (m, 4H), 7.46 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.85 (s, 1H), 12.09 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 21.3, 24.3, 62.5, 113.2, 121.9, 122.3, 122.8, 124.5, 125.7, 127.2, 127.7, 129.4, 129.9, 130.8, 132.4, 137.4, 137.8, 143.1, 143.9, 146.6, 158.1, 171.2. HRMS (ESI): calcd for C₂₅H₂₅BrN₃O₃ [M+H]^+: 492.0917; found: 492.0925.

Ethyl 2'-bromo-3-hydroxy-5'-methoxy-2-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4r)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (147.9 mg, 55%); Mp: 162-163°C. ¹H NMR (400 MHz, CDCl₃) δ: 1.47 (t, J = 7.2 Hz, 3H), 2.68 (s, 3H), 3.67 (s, 3H), 3.81 (s, 3H), 4.50 (q, J = 6.8 Hz, 2H), 6.65 (dd, J₁ = 8.8 Hz, J₂ = 3.2 Hz, 1H), 6.77 (d, J = 3.2 Hz, 1H), 6.81 (s, 1H), 6.92 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.79 (s, 1H), 12.06 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 24.3, 55.3, 55.5, 62.5, 112.2, 113.2, 114.2, 115.8, 116.6, 121.8, 122.7, 123.2, 124.4, 127.1, 133.1, 138.1, 143.1, 143.9, 146.4, 158.2, 158.5, 159.5, 171.2. HRMS (ESI): calcd for C₂₆H₂₅BrN₃O₅ [M+H]^+: 538.0972; found: 538.0980.

Ethyl 3-hydroxy-2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4s)

Eluent: ethyl acetate/petroleum ether (1/1). Yellow solid (138.1 mg, 78%); Mp: 120-121°C. ¹H NMR (400 MHz, CDCl₃) δ: 1.47 (t, J = 7.2 Hz, 3H), 2.68 (s, 3H), 2.77 (s, 1H), 4.49 (q, J = 7.6 Hz, 2H), 4.73 (s, 2H),
6.90 (s, 1H), 7.14-7.09 (m, 2H), 7.25-7.21 (m, 3H), 7.46 (s, 1H), 12.08 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.3, 56.4, 62.4, 112.4, 121.9, 124.3, 125.1, 128.0, 128.51, 128.53, 136.4, 143.6, 144.6, 146.9, 158.6, 171.2. HRMS (ESI): calcd for C$_{19}$H$_{20}$N$_3$O$_4$ [M+H]$^+$: 354.1448; found: 354.1442.

**Ethyl 2'-bromo-3-hydroxy-2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4t)**

Eluent: ethyl acetate/petroleum ether (1/1). Yellow solid (159.8 mg, 74%); Mp: 129-130°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.46 (t, $J = 6.8$ Hz, 3H), 2.66 (s, 3H), 2.82 (s, 1H), 4.49 (q, $J = 6.8$ Hz, 2H), 4.65 (s, 2H), 6.78 (s, 1H), 7.10-7.06 (m, 1H), 7.17-7.14 (m, 2H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.61 (s, 1H), 11.97 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.2, 56.4, 62.5, 113.3, 121.9, 122.7, 124.5, 124.7, 127.1, 129.9, 130.7, 132.4, 137.3, 143.1, 143.9, 146.5, 158.0, 171.1. HRMS (ESI): calcd for C$_{19}$H$_{19}$BrN$_3$O$_4$ [M+H]$^+$: 432.0553; found: 432.0560.

**Ethyl 2'-bromo-5'-fluoro-3-hydroxy-2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4u)**

Eluent: ethyl acetate/petroleum ether (1/1). White solid (171.0 mg, 76%); Mp: 135-136°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.47 (t, $J = 6.8$ Hz, 3H), 2.67 (s, 3H), 2.70 (s, 1H), 4.50 (q, $J = 6.8$ Hz, 2H), 4.71 (s, 2H), 6.76 (s, 1H), 6.83-6.86 (m, 1H), 6.95 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.8$ Hz, 1H), 7.39-7.42 (m, 1H), 7.68 (s, 1H), 12.08 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.2, 56.5, 62.6, 113.6, 116.3 (d, $^4J_{C,F} = 3.9$ Hz), 117.2 (d, $^2J_{C,F} = 22.3$ Hz), 118.1 (d, $^2J_{C,F} = 22.4$ Hz), 122.6, 124.1, 124.8, 133.7 (d, $^3J_{C,F} = 8.1$ Hz), 139.2 (d, $^3J_{C,F} = 8.4$ Hz), 142.6, 143.4, 146.5, 157.8, 161.3 (d, $^1J_{C,F} = 247.6$ Hz), 171.0. HRMS (ESI): calcd for C$_{19}$H$_{18}$BrFNN$_3$O$_4$ [M+H]$^+$: 450.0459; found: 450.0470.

**Ethyl 3-hydroxy-2-(4-(hydroxy(phenyl)methyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4v)**

Eluent: ethyl acetate/petroleum ether (1/2). White solid (150.6 mg, 70%); Mp: 140-142°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.44 (t, $J = 7.2$ Hz, 3H), 2.65 (s, 3H), 3.52 (s, 1H), 4.46 (q, $J = 7.6$ Hz, 2H), 5.93 (s, 1H), 6.87 (s, 1H), 7.04-7.02 (m, 2H), 7.14 (s, 1H), 7.28-7.18 (m, 8H), 11.99 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.3, 26.4, 68.9, 112.5, 121.9, 124.0, 124.1, 126.78, 127.8, 128.0, 128.36, 128.44, 128.5, 136.4, 141.9, 143.6, 144.6, 150.7, 158.5, 171.2. HRMS (ESI): calcd for C$_{23}$H$_{24}$N$_3$O$_4$ [M+H]$^+$: 430.1761;
found: 430.1767.

**Ethyl 2-(4-(2-(2-bromophenyl)-1-hydroxyethyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-4’-(trifluoromethyl)-[1,1’-biphenyl]-4-carboxylate (4w)**

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (203.5 mg, 69%); Mp: 88-90°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.46 (d, $J = 7.2$ Hz, 3H), 2.67 (s, 3H), 2.94-2.99 (m, 1H), 3.21-3.25 (m, 1H), 3.74 (s, 1H), 4.49 (q, $J = 7.6$ Hz, 2H), 5.30 (s, 1H), 6.87 (s, 1H), 7.07 (t, $J = 7.2$ Hz, 1H), 7.25-7.20 (m, 3H), 7.31 (s, 1H), 7.49-7.44 (m, 4H), 12.07 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.1, 24.3, 33.1, 62.6, 71.9, 113.1, 121.6, 124.0, 125.4 (q, $^{3}J_{C-F} = 3.2$ Hz), 126.6 (q, $^{1}J_{C-F} = 271.4$ Hz), 127.5, 127.6, 128.5, 128.8, 130.4 (q, $^{2}J_{C-F} = 31.0$ Hz), 132.5, 140.2, 142.2, 142.9, 143.9, 158.5, 171.1. HRMS (ESI): calcd for C$_{27}$H$_{23}$BrF$_3$N$_5$O$_4$ [M+H]$^+$: 590.0897; found: 590.0906.

**Ethyl 2-(4-benzyl-1H-1,2,3-triazol-1-yl)-3-hydroxy-3’,4’-dimethoxy-5-methyl-[1,1′-biphenyl]-4-carboxylate (4x)**

Eluent: ethyl acetate/petroleum ether (1/3). White solid (151.7 mg, 64%); Mp: 100-101°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.45 (t, $J = 7.2$ Hz, 3H), 2.65 (s, 3H), 3.58 (s, 3H), 3.85 (s, 3H), 4.06 (s, 2H), 4.47 (q, $J = 7.2$ Hz, 2H), 6.48 (s, 1H), 6.74 (s, 2H), 6.88 (s, 1H), 7.07-7.05 (m, 3H), 7.23-7.14 (m, 3H), 11.95 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.2, 24.3, 31.9, 55.78, 55.82, 62.3, 110.9, 111.0, 120.8, 123.8, 124.9, 126.3, 128.4, 128.5, 129.1, 143.3, 144.3, 148.7, 149.3, 158.8, 171.2. HRMS (ESI): calcd for C$_{27}$H$_{28}$N$_3$O$_5$ [M+H]$^+$: 474.2023; found: 474.2030.

**Ethyl 3-hydroxy-5,6-dimethyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1′-biphenyl]-4-carboxylate (4y)**

Eluent: ethyl acetate/petroleum ether (1/8). Yellow oil (119.9 mg, 56%); Mp: 133-135°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.46 (t, $J = 7.6$ Hz, 3H), 2.04 (s, 3H), 2.35 (s, 3H), 2.58 (s, 3H), 4.50 (q, $J = 7.2$ Hz, 2H), 7.09-7.06 (m, 3H), 7.25-7.19 (m, 4H), 7.45 (d, $J = 7.2$ Hz, 1H), 7.50 (s, 1H), 7.56 (s, 1H), 10.79 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.2, 17.7, 19.4, 21.4, 62.3, 115.4, 122.61, 122.64, 122.8, 126.4, 127.6, 127.9, 128.2, 128.6, 128.7, 128.8, 130.3, 136.3, 138.4, 141.4, 144.7, 146.7, 153.9, 170.6. HRMS (ESI): calcd for C$_{26}$H$_{26}$N$_3$O$_3$ [M+H]$^+$: 428.1969; found: 428.1979.

**Ethyl 4-benzyl-2-hydroxy-5,6-dimethyl-3-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)benzoate (4z)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (128.2 mg, 58%); Mp: 110-112 °C. $^1$H NMR (400
MHZ, CDCl₃) δ: 1.45 (t, J = 7.2 Hz, 3H), 2.18 (s, 3H), 2.38 (s, 3H), 2.57 (s, 3H), 3.84 (s, 2H), 4.48 (q, J = 7.2 Hz, 2H), 6.95-6.93 (m, 2H), 7.22-7.12 (m, 4H), 7.28 (dd, J₁ = 8.0 Hz, J₂ = 8.0 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.59 (s, 1H), 7.65 (s, 1H), 10.97 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 16.4, 19.7, 21.5, 34.9, 62.4, 113.9, 122.9, 123.2, 123.9, 126.3, 126.6, 128.0, 128.6, 128.7, 128.8, 130.4, 138.4, 138.7, 141.8, 142.4, 147.2, 154.8, 171.0. HRMS (ESI): calcd for C₂₇H₃₈N₅O₃ [M+H]⁺: 442.2125; found: 442.2129.

**Ethyl 5-benzyl-3-hydroxy-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4aa)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (127.1 mg, 52%). ¹H NMR (400 MHz, CDCl₃) δ: 1.21 (t, J = 6.8 Hz, 3H), 2.38 (s, 3H), 4.34 (q, J = 6.8 Hz, 2H), 4.47 (s, 2H), 6.95 (s, 1H), 7.17-7.11 (m, 5H), 7.24-7.21 (m, 4H), 7.32-7.28 (m, 3H), 7.56 (d, J = 7.2 Hz, 1H), 7.67 (s, 1H), 7.72 (s, 1H), 11.95 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 13.8, 21.4, 41.9, 62.4, 122.7, 122.8, 122.9, 124.9, 126.2, 126.5, 128.1, 128.2, 128.53, 128.56, 128.59, 128.7, 128.8, 130.4, 136.4, 138.5, 140.3, 144.7, 147.3, 158.8, 170.6. HRMS (ESI): calcd for C₃₁H₂₈N₅O₃ [M+H]⁺: 490.2125; found: 490.2130.

**Ethyl 6-benzyl-2-hydroxy-4-methyl-3-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)benzoate (4bb)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (113.5 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ: 1.17 (t, J = 7.2 Hz, 3H), 2.16 (s, 3H), 2.43 (s, 3H), 4.29 (q, J = 7.2 Hz, 2H), 4.40 (s, 2H), 6.05 (s, 1H), 7.08 (d, J = 7.6 Hz, 2H), 7.23-7.17 (m, 2H), 7.36-7.28 (m, 3H), 7.71 (d, J = 7.6 Hz, 1H), 7.80 (s, 1H), 7.98 (s, 1H), 12.02 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 13.8, 18.2, 21.5, 41.8, 62.3, 111.3, 122.5, 122.9, 124.1, 125.4, 126.1, 126.6, 128.2, 128.5, 128.8, 129.0, 130.4, 138.6, 140.5, 142.5, 144.4, 147.4, 158.4, 170.8. HRMS (ESI): calcd for C₂₆H₂₆N₃O₃ [M+H]⁺: 428.1969; found: 428.1977.

**Ethyl 4-benzyl-3-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-2-hydroxy-6-methylbenzoate (4cc)**

Eluent: ethyl acetate/petroleum ether (1/8). Yellow oil (147.6 mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ: 1.45 (t, J = 7.6 Hz, 3H), 2.61 (s, 3H), 3.83 (s, 2H), 4.46 (q, J = 7.2 Hz, 2H), 6.01 (s, 1H), 6.94-6.92 (m, 2H), 7.16-7.13 (m, 3H), 7.55-7.53 (m, 3H), 7.68-7.66 (m, 2H), 12.02 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.2, 24.4, 37.8, 62.3, 111.7, 121.9, 123.2, 124.6, 126.5, 127.4, 128.5, 128.8, 129.57, 129.6, 130.7, 131.9, 138.4, 143.7, 144.9, 146.1, 158.3, 171.3. HRMS (ESI): calcd for C₂₃H₂₃BrN₃O₃ [M+H]⁺: 492.0917; found: 492.0923.

**Ethyl 2-hydroxy-6-methyl-4-phenethyl-3-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)benzoate (4dd)**

S11
Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (141.5 mg, 64%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.46 (t, $J = 7.2$ Hz, 3H), 2.43 (s, 3H), 2.64 (s, 3H), 2.69 (t, $J = 7.6$ Hz, 2H), 2.83 (t, $J = 7.6$ Hz, 2H), 4.47 (q, $J = 7.2$ Hz, 2H), 6.78 (s, 1H), 6.95-6.94 (m, 2H), 7.22-7.16 (m, 4H), 7.34 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.2$ Hz, 1H), 7.38 (s, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.74 (s, 1H), 11.97 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 21.5, 24.3, 33.7, 37.0, 62.2, 111.2, 122.9, 123.4, 123.8, 126.2, 126.5, 128.5, 28.6, 128.7, 128.8, 130.5, 138.4, 140.6, 143.2, 145.5, 147.2, 158.2, 171.3. HRMS (ESI): calcd for C$_{27}$H$_{28}$N$_3$O$_3$ [M+H]$^+$: 442.2125; found: 442.2131.

**Ethyl 3-hydroxy-3',4'-dimethoxy-5-methyl-2-(4-(thiophen-3-yl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4ee)**

Eluent: ethyl acetate/petroleum ether (1/3). White soild (158.4 mg, 68%); Mp: 160-161°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.46 (t, $J = 6.8$ Hz, 3H), 2.69 (s, 3H), 3.68 (s, 3H), 3.83 (s, 3H), 4.50 (q, $J = 6.8$ Hz, 2H), 6.61 (d, $J = 2.0$ Hz, 1H), 6.85-6.76 (m, 2H), 6.94 (s, 1H), 7.36-7.34 (m, 1H), 7.41-7.39 (m, 1H), 7.57 (s, 1H), 7.65 (dd, $J_1 = 2.8$ Hz, $J_2 = 1.2$ Hz, 1H), 12.07 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 24.4, 55.78, 55.87, 62.4, 110.9, 111.0, 111.9, 120.9, 121.2, 121.7, 122.6, 123.9, 125.9, 126.2, 128.9, 131.6, 143.5, 143.6, 144.2, 148.7, 149.3, 159.0, 171.2. HRMS (ESI): calcd for C$_{24}$H$_{24}$N$_3$O$_3$S [M+H]$^+$: 466.1431; found: 466.1435.

**Ethyl 3-hydroxy-4',5-dimethyl-2-(4-(thiophen-3-yl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4ff)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (128.1 mg, 61%); Mp: 100-101°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.47 (t, $J = 7.2$ Hz, 3H), 2.27 (s, 3H), 2.68 (s, 3H), 4.49 (q, $J = 6.8$ Hz, 2H), 6.91 (s, 1H), 7.05 (dd, $J_1 = 11.6$ Hz, $J_2 = 8.4$ Hz, 4H), 7.36-7.34 (m, 1H), 7.43-7.41 (m, 1H), 7.61 (s, 1H), 7.66 (dd, $J_1 = 3.6$ Hz, $J_2 = 1.6$ Hz, 1H), 12.05 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 21.2, 24.4, 62.4, 112.1, 121.1, 121.9, 122.6, 124.3, 126.0, 126.1, 128.0, 129.3, 131.8, 133.5, 138.5, 134.3, 143.4, 144.7, 158.8, 171.3. HRMS (ESI): calcd for C$_{23}$H$_{22}$N$_3$O$_3$S [M+H]$^+$: 420.1376; found: 420.1380.

**Ethyl 3-hydroxy-4',5-dimethyl-2-(4-(pyridin-3-yl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4gg)**

Eluent: ethyl acetate/petroleum ether (1/2). Yellow oil (22.3 mg, 11%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.48
(t, J = 6.8 Hz, 3H), 2.28 (s, 3H), 2.68 (s, 3H), 4.51 (q, J = 6.8 Hz, 2H), 6.93 (s, 1H), 7.05 (s, 4H), 7.37-7.34 (m, 1H), 7.78 (s, 1H), 8.23-8.20 (m, 1H), 8.55(d, J = 3.6 Hz, 1H), 8.93 (s, 1H), 12.05 (s, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.2, 21.2, 24.4, 62.4, 112.1, 121.7, 123.2, 123.7, 124.3, 128.0, 129.3, 133.1, 133.4, 138.6, 143.7, 144.0, 144.7, 147.1, 149.1, 158.7, 171.3. HRMS (ESI): calcd for C_{27}H_{27}N_{3}O_{3} [M+H]^+: 415.1765; found: 415.1775.

2. Typical procedure for the synthesis of 7a and spectroscopic data of 7a-7e.

To a flask containing 4b (238.5 mg, 0.5 mmol) and K_{2}CO_{3} (138.0 mg, 1 mmol) in CH_{3}CN (5 mL) was added CH_{3}I (355.0 mg, 2.5 mmol). The mixture was stirred at 80 °C for 2 h. After being cooled to room temperature, it was quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na_{2}SO_{4} and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_{2}) using EtOAc/petroleum ether (v/v =1/8 ) as eluent to give 7a (223.4 mg, 91%). 7b-7e were obtained in a similar manner.

Ethyl 2'-bromo-3-methoxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (7a)

Eluent: ethyl acetate/petroleum ether (1/8). White solid (223.9 mg, 91%); Mp: 109-111°C. 1H NMR (400 MHz, CDCl3) δ: 1.42 (t, J = 6.8 Hz, 3H), 2.45 (s, 3H), 3.52 (s, 3H), 4.47 (q, J = 6.8 Hz, 2H), 7.05 (s, 1H), 7.08 (dd, J_{1} = 8.4 Hz, J_{2} = 2.0 Hz, 1H), 7.18 (dd, J_{1} = 7.6 Hz, J_{2} = 7.2 Hz, 1H), 7.22 (dd, J_{1} = 7.2 Hz, J_{2} = 1.6 Hz, 1H), 7.28 (dd, J_{1} = 7.2 Hz, J_{2} = 7.2 Hz, 1H), 7.37 (dd, J_{1} = 7.6 Hz, J_{2} = 7.6 Hz, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 7.2 Hz, 2H), 7.93 (s, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.3, 19.5, 61.8, 62.9, 122.4, 122.7, 125.6, 127.1, 127.4, 128.1, 128.2, 128.8, 129.5, 129.8, 130.2, 131.1, 132.3, 137.3, 138.5, 140.9, 146.8, 152.3, 166.7. HRMS (ESI): calcd for C_{26}H_{25}BrN_{3}O_{3} [M+H]^+: 492.0917; found: 492.0924.

Ethyl 2'-bromo-2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-3-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (7b)

Eluent: ethyl acetate/petroleum ether (1/5). White solid (262.2 mg, 92%); Mp: 123-124°C. 1H NMR (400 MHz, CDCl3) δ: 1.41 (t, J = 6.8 Hz, 3H), 2.43 (s, 3H), 3.50 (s, 3H), 4.45 (q, J = 7.2 Hz, 2H), 7.04 (s, 1H), 7.07 (dd, J_{1} = 7.6 Hz, J_{2} = 1.6 Hz, 1H), 7.21-7.15 (m, 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.91 (s, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.3, 19.5, 61.8, 63.0, 121.9,
122.4, 122.8, 127.1, 127.2, 127.3, 128.1, 129.2, 129.5, 129.8, 131.1, 131.9, 132.3, 137.3, 138.6, 140.8, 145.8, 152.2, 166.6. HRMS (ESI): calcd for C_{26}H_{25}BrN_{3}O_{3} [M+H]^+: 570.0022; found: 570.0023.

**Ethyl 2'-bromo-3-methoxy-5-methyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (7c)**

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (225.2 mg, 89%); Mp: 99-101°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.44 (t, $J = 8.0$ Hz, 3H), 2.37 (s, 3H), 2.45 (s, 3H), 3.51 (s, 3H), 4.48 (qd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 2H), 7.06 (s, 1H), 7.14-7.07 (m, 2H), 7.25-7.18 (m, 2H), 7.28 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.6$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.64 (s, 1H), 7.91 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.3, 19.5, 21.3, 61.7, 62.8, 122.4, 122.6, 122.7, 126.3, 127.1, 127.4, 128.0, 128.7, 128.9, 129.4, 129.8, 130.1, 131.1, 132.3, 137.3, 138.4, 138.5, 140.9, 146.8, 152.2, 166.7. HRMS (ESI): calcd for C$_{26}$H$_{25}$BrN$_{3}$O$_{3}$ [M+H]$^+$: 506.1079; found: 506.1075.

**Ethyl 2-(4-benzyl-1H-1,2,3-triazol-1-yl)-2'-bromo-3-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (7d)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (227.7 mg, 90%); Mp: 89-91°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.38 (t, $J = 7.2$ Hz, 3H), 2.39 (s, 3H), 3.49 (s, 3H), 3.97 (s, 2H), 4.42 (q, $J = 7.2$ Hz, 2H), 6.95 (d, $J = 7.2$ Hz, 2H), 6.98 (s, 1H), 7.22-7.07 (m, 6H), 7.28 (s, 1H), 7.43 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.3, 19.4, 31.7, 61.7, 62.9, 122.4, 124.8, 126.3, 127.0, 127.8, 128.3, 128.4, 129.6, 129.7, 130.9, 132.2, 137.3, 138.2, 138.9, 140.9, 146.4, 152.3, 166.7. HRMS (ESI): calcd for C$_{26}$H$_{25}$BrN$_{3}$O$_{3}$ [M+H]$^+$: 506.1074; found: 506.1068.

**Ethyl 2'-bromo-3,5'-dimethoxy-5-methyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (7e)**

Eluent: ethyl acetate/petroleum ether (1/5). White solid (249.3 mg, 93%); Mp: 120-121°C. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.39 (t, $J = 6.8$ Hz, 3H), 2.33 (s, 3H), 2.42 (s, 3H), 3.50 (s, 3H), 3.62 (s, 3H), 4.44 (qd, $J_1 = 6.8$ Hz, $J_2 = 1.2$ Hz, 2H), 6.60 (dd, $J_1= 8.8$ Hz, $J_2 = 2.8$ Hz, 1H), 6.76 (d, $J = 2.8$ Hz, 1H), 7.03 (s, 1H), 7.07 (d, $J = 8.0$ Hz, 1H), 7.23 (dd, $J_1 = 7.2$ Hz, $J_2 = 7.2$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.63 (s, 1H), 7.92 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 14.3, 19.5, 21.3, 55.4, 61.7, 62.9, 112.6, 116.2, 116.3, 122.7, 126.3, 127.4, 127.9, 128.7, 128.9, 129.5, 130.1, 132.9, 138.0, 138.5, 140.8, 146.9,
152.3, 158.4, 166.6. HRMS (ESI): calcd for C_{27}H_{27}BrN_{3}O_{4} [M+H]^+: 536.1179; found: 536.1185.

3. Typical procedure for the synthesis of 8a and spectroscopic data of 8a-8e.

A suspension of Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), Ph$_3$P (11.2 mg, 0.04 mmol), K$_2$CO$_3$ (138.0 mg, 1.0 mmol) and 7a (245.5 mg, 0.5 mmol) in toluene (3 mL) was stirred at 120 ºC under N$_2$ for 24 h. Upon completion, it was cooled to room temperature, treated with H$_2$O (10 mL). The resulting mixture was then extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine (2×10 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether, v/v = 1/8) to afford 8a (185.0 mg, 90%) as a white solid. Other triazolophenanthidine derivatives 8b-8e were obtained in a similar manner.

**Ethyl 11-methoxy-9-methyl-3-phenyl-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8a)**

Eluent: ethyl acetate/petroleum ether (1/8). White solid (185.4 mg, 90%); Mp: 191-192°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.45 (t, $J = 7.2$ Hz, 3H), 2.48 (s, 3H), 4.01 (s, 3H), 4.50 (q, $J = 6.8$ Hz, 2H), 7.32 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.6$ Hz, 1H), 7.55-7.47 (m, 4H), 7.72-7.70 (m, 2H), 7.98 (s, 1H), 8.03 (d, $J = 7.6$ Hz, 1H), 8.23 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.3, 19.5, 61.8, 63.4, 120.4, 122.9, 123.4, 123.8, 123.9, 125.2, 126.9, 127.7, 128.78, 128.82, 129.2, 129.8, 131.9, 132.2, 134.3, 140.9, 148.2, 167.1. HRMS (ESI): calcd for C$_{25}$H$_{22}$N$_3$O$_3$ [M+H]$^+$: 412.1656; found: 412.1659.

**Ethyl 3-(4-bromophenyl)-11-methoxy-9-methyl-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8b)**

Eluent: ethyl acetate/petroleum ether (1/8). White solid (217.6 mg, 89%); Mp: 198-201 ºC. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.46 (t, $J = 8.0$ Hz, 3H), 2.53 (s, 3H), 4.09 (s, 3H), 4.52 (q, $J = 6.8$ Hz, 2H), 7.45 (dd, $J_1 = 8.0$ Hz, $J_2 = 7.6$ Hz, 1H), 7.64-7.61 (m, 3H), 7.71-7.68 (m, 2H), 8.07 (d, $J = 8.8$ Hz, 1H), 8.08 (s, 1H), 8.37 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.3, 19.5, 61.8, 63.4, 120.5, 122.8, 123.1, 123.6, 123.8, 123.9, 125.2, 127.2, 127.9, 128.9, 129.4, 131.3, 131.5, 132.1, 134.5, 139.8, 148.4, 167.1. HRMS (ESI): calcd for C$_{25}$H$_{21}$BrN$_3$O$_3$ [M+H]$^+$: 490.0761; found: 490.0766.

**Ethyl 11-methoxy-9-methyl-3-(m-tolyl)-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8c)**

Eluent: ethyl acetate/petroleum ether (1/8). White solid (198.2 mg, 93%); Mp: 184-185 ºC. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.46 (t, $J = 7.2$ Hz, 3H), 2.46 (s, 3H), 2.53 (s, 3H), 4.10 (s, 3H), 4.52 (q, $J = 7.2$ Hz, 2H),
7.33 (d, J = 7.6 Hz, 1H), 7.46-7.40 (m, 2H), 7.62-7.52 (m, 3H), 8.08 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.3, 19.5, 21.4, 61.7, 63.4, 120.4, 123.1, 123.4, 123.9, 124.1, 125.2, 126.8, 127.0, 127.7, 128.6, 128.8, 129.2, 129.6, 130.5, 131.9, 132.1, 134.2, 138.6, 141.1, 148.3, 167.2. HRMS (ESI): calcd for C_{26}H_{24}N_{3}O_{3} [M+H]^+: 426.1812; found: 426.1821.

**Ethyl 3-benzyl-11-methoxy-9-methyl-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8d)**

Eluent: ethyl acetate/petroleum ether (1/5). White solid (196.1 mg, 92%); Mp: 174-176°C. 1H NMR (400 MHz, CDCl3) δ: 1.45 (t, J = 8.0 Hz, 3H), 2.46 (s, 3H), 4.08 (s, 3H), 4.59 (d, J = 7.2 Hz, 2H), 4.63 (s, 2H), 7.17-7.14 (m, 1H), 7.28-7.23 (m, 4H), 7.45-7.38 (m, 2H), 7.86 (s, 1H), 7.90-7.89 (m, 1H), 8.11 (d, J = 7.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.3, 19.4, 33.3, 61.7, 63.4, 120.3, 122.9, 123.2, 123.9, 124.2, 125.0, 126.5, 126.6, 128.25, 128.33, 128.62, 128.64, 129.1, 131.9, 134.1, 137.9, 138.7, 148.1, 167.1. HRMS (ESI): calcd for C_{26}H_{24}N_{3}O_{3} [M+H]^+: 426.1812; found: 426.1817.

**Ethyl 6,11-dimethoxy-9-methyl-3-(m-tolyl)-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8e)**

Eluent: ethyl acetate/petroleum ether (1/5). White solid (207.5 mg, 91%); Mp: 193-194°C. 1H NMR (400 MHz, CDCl3) δ: 1.44 (t, J = 7.6 Hz, 3H), 2.42 (s, 3H), 2.47 (s, 3H), 3.88 (s, 3H), 4.07 (s, 3H), 4.50 (q, J = 7.2 Hz, 2H), 6.93 (dd, J1 = 8.8 Hz, J2 = 2.4 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.39 (dd, J1 = 7.6 Hz, J2 = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.54 (s, 1H), 7.62 (s, 1H), 7.88 (s, 1H), 7.99 (d, J = 8.8 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ: 14.3, 19.4, 21.4, 55.5, 61.7, 63.3, 106.7, 116.50, 116.54, 120.4, 124.0, 124.9, 125.6, 126.7, 127.8, 128.6, 128.7, 129.4, 130.5, 132.0, 132.3, 134.0, 138.5, 139.8, 148.2, 160.1, 167.1. HRMS (ESI): calcd for C_{27}H_{26}N_{3}O_{4} [M+H]^+: 456.1918; found: 456.1920.

**III. Control experiments (I)**

1. Reaction of 1a with 2 leading to the formation of intermediate A

To a flask containing 4-azido-3-oxobutanoate (2, 171.2 mg, 1.0 mmol) and ethynylbenzene (1a, 102.0 mg, 1.0 mmol) in t-BuOH/H2O (4 mL) were added CuSO4·5H2O (aqueous solution, 1 M, 50 μL, 0.05 mmol) and sodium ascorbate (19.8 mg, 0.1 mmol). The resulting mixture was stirred at room temperature for 12 h. Then, it was diluted with cold water (15 mL) and 10% aqueous ammonia (2 mL). After being stirred for another 5 min, it was extracted with dichloromethane (3×5 mL). The combined organic phases were dried, filtered and concentrated under reduced pressure. The residue was purified by column chromatography over
silica gel using ethyl acetate/petroleum ether (v/v = 1:2) as eluent to give 3-oxo-4-(4-phenyl-1H-1,2,3-triazol-1-yl)butanoate as a mixture of ketone and enol tautomers (4/1) (A, 235.1 mg, 85%).

3-Oxo-4-(4-phenyl-1H-1,2,3-triazol-1-yl)butanoate (A)

Eluent: ethyl acetate/petroleum ether (1/2). Yellow oil (235.1 mg, 85%). ¹H NMR (400 MHz, CDCl₃), Enol tautomer: δ: 1.27 (t, J = 6.8 Hz, 3H), 4.20 (q, J = 6.8 Hz, 2H), 5.02 (s, 1H), 5.11 (s, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.85 (d, J = 9.2 Hz, 2H), 7.89 (s, 1H, 12.17 (s, 1H). Ketone tautomer: δ: 1.29 (t, J = 7.2 Hz, 3H), 3.58 (s, 2H), 4.22 (q, J = 7.2 Hz, 2H), 5.43 (s, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.84 (d, J = 9.2 Hz, 2H), 7.86 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.1, 14.11, 46.5, 58.1, 60.7, 62.1, 91.4, 120.5, 121.3, 125.8, 128.4, 128.41, 128.9, 130.3, 148.4, 166.4, 194.5. HRMS (ESI): calcd for C₁₄H₁₆N₃O₃ [M+H]+: 274.1186; found: 274.1189.

2. Reaction of A with 3a leading to the formation of 4a

To a flask containing 3-oxo-4-(4-phenyl-1H-1,2,3-triazol-1-yl)butanoate (A, 136.5 mg, 0.5 mmol) and 1-phenylbuta-2,3-dien-1-one (3a, 72.0 mg, 0.5 mmol) were added NaOH (40.0 mg, 1.0 mmol). The mixture was stirred at 80 °C for 1.5 h. After being cooled to room temperature, it was quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (SiO₂) using EtOAc/petroleum ether (v/v =1/5) as eluent to give 4a (157.6 mg, 79%).

IV. Control experiments (II)

1. Preparation of 5 from the reaction of 2 and 3a

To a flask containing 4-azido-3-oxobutanoate (2, 85.6 mg, 0.5 mmol) and 1-phenylbuta-2,3-dien-1-one (3a, 72.0 mg, 0.5 mmol) in t-BuOH/H₂O (5 mL, v/v = 1/1) were added NaOH (40.0 mg, 1.0 mmol). The mixture was stirred 80 °C for 2 h. Upon completion, it was quenched with aqueous NH₄Cl and extracted with ethyl acetate (3×5 mL). The combined organic phases were dried, filtered and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (v/v = 1/30) as eluent to give ethyl 2-azido-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (5, 92.2 mg, 31%).

Ethyl 2-azido-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (5)
Eluent: ethyl acetate/petroleum ether (1/30). Yellow solid (92.2 mg, 31%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.44 (t, $J$ = 7.2 Hz, 3H), 2.54 (s, 3H), 4.46 (q, $J$ = 7.2 Hz, 2H), 6.68 (s, 1H), 7.46-7.37 (m, 5H), 12.15 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 14.2, 23.9, 62.1, 111.6, 123.1, 124.4, 128.1, 128.2, 129.2, 137.1, 137.8, 139.1, 157.8, 171.8. HRMS (ESI): calcd for C$_{16}$H$_{16}$N$_3$O$_3$ [M+H]$^+$: 298.1186; found: 298.1193.

2. Preparation of 4a from the reaction of 5 and 1a

To a flask containing ethynyl-3-methylbenzene (1a, 56.1 mg, 0.55 mmol) and ethyl 2-azido-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (5, 148.5 mg, 0.5 mmol) in t-BuOH/H$_2$O (5 mL, v/v = 1/1) were added CuSO$_4$·5H$_2$O (aqueous solution, 1 M, 25 µL, 0.025 mmol) and sodium ascorbate (9.9 mg, 0.05 mmol). The mixture was stirred at room temperature for 12 h. Upon completion, it was cooled to room temperature, quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (SiO$_2$) using EtOAc/petroleum ether (v/v = 1/5) as the eluent to give 4a (73.8 mg, 37%).
III. Copies of 1H and 13C NMR spectra of 4a-4gg
\[ \text{HO} \quad \text{N} \quad \text{CH}_3 \]

\[ \text{4t} \]
S65
4y

(3-CH₃)Ph

N=N

OH

Ph

CH₃

CH₃

CO₂Et
4ee
IV. Copies of $^1$H and $^{13}$C NMR spectra of 7a-7e
V. Copies of $^1$H and $^{13}$C NMR spectra of 8a-8e
\begin{figure}
\centering
\includegraphics[width=\textwidth]{nmr_spectrum.png}
\caption{NMR spectrum of compound 8c.}
\end{figure}
VI. Copies of $^1$H and $^{13}$C NMR spectra of A and 5
VII. X-ray crystal structure and data of 4n

![Chemical structure of 4n](image)

**Figure 1** The X-ray crystal structure of 4n

**X-ray structure determination.** Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a CHCl₃ solution of 4n. Crystal data collection and refinement parameters of 4n are summarized in Table 1. Intensity data were collected at 290 K on a SuperNova Dual diffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. The crystallographic data (excluding structure factors) for 4n has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1536564 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
**Table 1** Crystallographic data and structure refinement results of 3g

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VIII. References

