Supporting Information

Rhodium-catalyzed triazole-directed C-H bond functionalization of arenes with diazo compounds

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1. General information

Unless otherwise noted, all chemicals were obtained from commercial resources and were used without further purification. All reactions were carried out in a glass thick-wall tube with magnetic stirring under the atmosphere of N\textsubscript{2}. Thin layer chromatography (TLC) was performed on Huanghai GF254 silica gel coated plates and visualized by exposure to UV light (254 nm). Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR were recorded on Bruker spectrometers with CDCl\textsubscript{3} as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are referenced to residual solvent peaks (CHCl\textsubscript{3} in CDCl\textsubscript{3}: 7.26 ppm for \textsuperscript{1}H, 77.00 ppm for \textsuperscript{13}C). Data for \textsuperscript{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI+). All triazoles 1\textsuperscript{(1)} and diazo compounds 2\textsuperscript{(2)} were prepared according to the published procedures.

Reference


2. General procedure of Rh(III)-catalyzed alkylation of triazoles

1) General procedure for the synthesis of 3

1,2,3-Triazole 1 (0.2 mmol, 1.0 equiv), diazo compound 2 (0.44 mmol, 2.2 equiv), [Cp*RhCl\textsubscript{2}]\textsubscript{2} (0.005 mmol, 2.5 mol %), AgSbF\textsubscript{6} (0.02 mmol, 10 mol %), and 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford the desired products 3.

2) General procedure for the synthesis of 4

1,2,3-Triazole 1 (0.2 mmol, 1.0 equiv), diazo compound 2 (0.24 mmol, 1.2 equiv),
[Cp*RhCl₂]₂ (0.005 mmol, 2.5 mol%), AgSbF₆ (0.02 mmol, 10 mol%), and 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 2 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford the desired products 4.

3. X-ray diffraction analysis

The single crystals of compounds were grown by slow diffusion of their hexane solutions for 3a and 3x, methanol solution for A. Single-crystal X-ray diffraction data were collected at 150 K for 3x, and 273 K for 3a and A on a Siemens Smart/CCD area-detector diffractometer with a MoKα radiation (λ = 0.71073 Å) by using an ω-2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. The octyl group is severely disordered, which are not treated. CCDC Nos. 1844325 (A), 1844326 (3a), and 1844334 (3x).

(1) SMART-CCD Software, version 4.05; Siemens Analytical X-ray Instruments, Madison, WI, 1996.


4. Molecular structures of 3a and 3x
Figure S1. Molecular structures of 3a and 3x. Thermal ellipsoid plot drawn at 40% probability.

5. Characterization of data for the products
MeO

CO₂Me

CO₂Me

Me

N=N

Ph

tetramethyl 2,2′-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)dimalonate (3a)

White solid (89.5 mg, 88%); mp 139-141 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 1H), 7.43-7.37 (m, 3H), 7.36 (s, 2H), 7.32-7.30 (m, 2H), 5.62 (s, 2H), 4.57 (s, 2H), 3.64 (s, 12H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 143.2, 139.4, 134.5, 133.0, 129.8, 129.2, 128.8, 128.3, 128.0, 124.7, 54.5, 54.3, 52.8, 21.6; HRMS (ESI+) calcd for C₂₆H₂₇N₃O₈[M+Na]⁺ 532.1696, found 532.1690.

MeO

CO₂Me

CO₂Me

Me

N=N

Ph

tetramethyl 2,2′-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-1,3-phenylene)dimalonate (3b)

White solid (91.0 mg, 92%); mp 166-169 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 1.2 Hz, 1H), 7.56 (s, 1H), 7.48-7.45 (m, 2H), 7.41-7.37 (m, 3H), 7.33-7.30 (m, 2H), 5.63 (s, 2H), 4.59 (s, 2H), 3.64 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 143.1, 134.5, 133.3, 131.1, 129.3, 129.2, 129.1, 128.8, 128.0, 124.7, 54.7, 54.3, 52.8; HRMS (ESI+) calcd for C₂₅H₂₅N₃O₈ [M+Na]⁺ 518.1540, found 518.1534.

tetramethyl 2,2′-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methoxy-1,3-phenylene)
-dimalonate (3c)

White solid (100.8 mg, 96 %); mp 126-127 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (s, 1H), 7.42-7.37 (m, 3H), 7.31-7.29 (m, 2H), 7.12 (s, 2H), 5.62 (s, 2H), 4.57 (s, 2H), 3.84 (s, 3H), 3.64 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4, 159.7, 143.1, 134.6, 134.4, 129.2, 128.8, 128.0, 124.8, 123.5, 114.9, 55.5, 54.6, 54.3, 52.8; HRMS (ESI+) calcd for C$_{26}$H$_{27}$N$_3$O$_9$ [M+Na]$^+$ 548.1645, found 548.1640.

![3d](image)

tetramethyl 2,2’-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-fluoro-1,3-phemylene)-dimalonate (3d)

White solid (86.2 mg, 84 %); mp 136-168 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (s, 1H), 7.44-7.38 (m, 3H), 7.35 (s, 1H), 7.33-7.30 (m, 3H), 5.63 (s, 2H), 4.56 (s, 2H), 3.65 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.9, 162.5 (d, $J_{C-F} = 253.5$ Hz), 142.4, 135.4 (d, $J_{C-F} = 8.4$ Hz), 134.4, 129.2, 128.9, 128.0, 127.3 (d, $J_{C-F} = 3.4$ Hz), 124.8, 116.7 (d, $J_{C-F} = 23.2$ Hz), 54.5, 54.4, 53.0; $^{19}$F NMR (CDCl$_3$, 376 MHz) δ -110.1; HRMS (ESI+) calcd for C$_{25}$H$_{24}$FN$_3$O$_8$ [M+Na]$^+$ 536.1445, found 536.1440.

![3e](image)

tetramethyl 2,2’-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-chloro-1,3-phemylene)-dimalonate (3e)

White solid (64.2 mg, 61 %); mp 134-136 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (s, 1H), 7.48 (s, 1H), 7.43-7.38 (m, 3H), 7.32-7.29 (m, 2H), 7.12 (s, 2H), 5.63 (s, 2H), 4.56
(s, 2H), 3.67 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 142.2, 135.3, 134.8, 134.3, 129.7, 129.5, 129.2, 128.9, 128.0, 124.8, 54.4, 54.3, 53.0; HRMS (ESI+) calcd for C$_{25}$H$_{24}$ClN$_3$O$_8$ [M+Na]$^+$ 552.1150, found 552.1144.

![3f](image)

tetramethyl 2,2'-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-bromo-1,3-phenylene)-dimalonate (3f)

White solid (90.5 mg, 79 %); mp 140–142 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.71 (s, 2H), 7.48 (s, 1H), 7.41–7.36 (m, 3H), 7.30–7.28 (m, 2H), 5.61 (s, 2H), 5.53 (s, 2H), 3.63 (s, 12H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.9, 142.2, 134.9, 134.3, 132.3, 130.3, 129.2, 128.9, 128.0, 124.8, 123.4, 54.4, 54.3, 53.0; HRMS (ESI+) calcd for C$_{25}$H$_{24}$BrN$_3$O$_8$ [M+Na]$^+$ 596.0639, found 596.0632.

![3g](image)

tetramethyl 2,2'-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-(methoxycarbonyl)-1,3-phenylene)dimalonate (3g)

White solid (59.7 mg, 54 %); mp 123–125 °C; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 8.21 (s, 2H), 7.53 (s, 1H), 7.42–7.36 (m, 3H), 7.31 (d, $J = 7.8$ Hz, 2H), 5.63 (s, 2H), 4.63 (s, 2H), 3.92 (s, 3H), 3.65 (s, 12H); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 170.7, 168.5, 145.0, 138.2, 136.9, 136.5, 133.7, 133.0, 131.9, 131.5, 130.7, 127.5, 57.4, 57.1, 55.6, 55.1; HRMS (ESI+) calcd for C$_{27}$H$_{27}$N$_3$O$_{10}$ [M+Na]$^+$ 576.1589, found 576.1584.
tetramethyl 2,2’-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-cyano-1,3-phenylene)dimalonate (3h)
White solid (26.0 mg, 25 %); mp 156-159 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.90 (s, 2H), 7.54 (s, 1H), 7.42-7.38 (s, 3H), 7.31 (d, J = 7.2 Hz, 2H), 5.63 (s, 2H), 4.60 (s, 2H), 3.67 (s, 12H); ¹³C NMR (150 MHz, CDCl₃) δ 170.2, 144.1, 138.5, 137.3, 136.7, 135.5, 131.9, 131.8, 130.7, 127.6, 120.4, 116.1, 57.2, 56.9, 55.8; HRMS (ESI+) calcd for C₂₆H₂₄N₄O₈ [M+Na]⁺ 543.1486, found 543.1474.

tetramethyl 2,2’-(2-(1-octyl-1H-1,2,3-triazol-4-yl)-1,3-phenylene) dimalonate (3i)
White solid (80.9 mg, 78 %); mp 86-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.60 (d, J = 2.4 Hz, 2H), 7.51-7.47 (m, 1H), 4.62 (s, 2H), 4.44 (t, J = 7.2 Hz, 2H), 3.70 (s, 12H), 2.00-1.93 (m, 2H), 1.35-1.27 (m, 10H), 0.88 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 142.6, 133.2, 131.3, 129.3, 129.2, 124.5, 54.7, 52.9, 50.6, 31.7, 30.3, 29.1, 29.0, 26.4, 22.6, 14.1; HRMS (ESI+) calcd for C₂₆H₃₅N₃O₈ [M+Na]⁺ 540.2322, found 540.2315.

tetramethyl 2,2’-(5-methyl-2-(1-octyl-1H-1,2,3-triazol-4-yl)-1,3-phenylene)-
**dimalonate (3j)**

White solid (94.6 mg, 89 %); mp 78-79 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (s, 1H), 7.40 (s, 2H), 4.60 (s, 2H), 4.43 (t, $J = 6.8$ Hz, 2H), 3.70 (s, 12H), 2.43 (s, 3H), 1.98-1.94 (m, 2H), 1.35-1.27 (m, 10H), 0.88 (t, $J = 6.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.7, 142.6, 139.2, 132.9, 132.9, 128.5, 124.5, 54.5, 52.9, 50.5, 31.7, 30.3, 29.1, 29.0, 26.4, 22.6, 21.6, 14.1; HRMS (ESI+) calcd for C$_{27}$H$_{37}$N$_3$O$_8$ [M+Na]$^+$ 554.2478, found 554.2473.

![Structure 3j](image)

**tetramethyl 2,2-(5-methoxy-2-(1-octyl-1H,1,2,3-triazol-4-yl)-1,3-phenylene)-dimalinate (3k)**

White solid (103.7 mg, 95 %); mp 78-80 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (s, 1H), 7.16 (s, 2H), 4.60 (s, 2H), 4.43 (t, $J = 7.2$ Hz, 2H), 3.86 (s, 3H), 3.70 (s, 12H), 1.99-1.94 (m, 2H), 1.35-1.27 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.4, 159.6, 142.5, 134.3, 124.6, 123.7, 114.9, 55.5, 54.6, 52.9, 50.5, 31.7, 30.3, 29.1, 28.9, 26.4, 22.6, 14.0; HRMS (ESI+) calcd for C$_{27}$H$_{37}$N$_3$O$_9$ [M+Na]$^+$ 570.2428, found 570.2422.

![Structure 3k](image)

**tetramethyl 2,2-(5-fluoro-2-(1-octyl-1H,1,2,3-triazol-4-yl)-1,3-phenylene)-dimalinate (3l)**

White solid (78.4 mg, 73 %); mp 92-94 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (s, 1H), 7.37 (s, 1H), 7.34 (s, 1H), 4.58 (s, 2H), 4.43 (t, $J = 7.2$ Hz, 2H), 3.69 (s, 12H), 1.96-1.93
(m, 2H), 1.33-1.25 (m, 10H), 0.86 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.0, 162.4 (d, $J_{C-F}$ = 247.2 Hz), 141.8, 135.3 (d, $J_{C-F}$ = 8.4 Hz), 127.5 (d, $J_{C-F}$ = 3.4 Hz), 124.7, 116.7 (d, $J_{C-F}$ = 23.0 Hz); $^{19}$F NMR (CDCl$_3$, 376 MHz) δ -110.3; HRMS (ESI+) calcd for C$_{26}$H$_{34}$FN$_3$O$_8$ [M+Na]$^+$ 558.2222, found 558.2215.

tetramethyl 2,2-(5-methyl-2-(1-phenethl-1H-1,2,3-triazol-4-yl)-1,3-phenylene)dimalomate (3m)

White solid (97.3 mg, 93 %); mp 116-118 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (s, 2H), 7.29-7.27 (m, 3H), 7.23-7.19 (m, 1H), 7.12-7.10 (2H), 4.68 (t, J = 6.8 Hz, 2H), 4.48 (s, 2H), 3.69 (s, 12H), 3.28 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.6, 142.3, 139.2, 137.0, 132.9, 129.0, 129.9, 128.9, 128.7, 128.3, 127.1, 124.9, 54.4, 52.8, 51.9, 36.7, 21.5; HRMS (ESI+) calcd for C$_{27}$H$_{31}$N$_3$O$_8$ [M+Na]$^+$ 546.1847, found 546.1842.

tetramethyl 2,2-(5-methoxy-2-(1-phenethl-1H-1,2,3-triazol-4-yl)-1,3-phenylene)dimalomate (3n)

White solid (102.3 mg, 95 %); mp 137-138 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29-7.26 (m, 3H), 7.23-7.20 (m, 1H), 7.14 (s, 2H), 7.11 (d, J = 6.8 Hz, 2H) 4.68 (t, J = 6.8 Hz, 2H), 4.47 (s, 2H), 3.84 (s, 3H), 3.69 (s, 12H), 3.28 (t, J = 6.8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.4, 159.6, 142.2, 137.0, 134.3, 128.9, 128.7, 127.1, 125.0, 123.5, 114.9, 58.4, 555.4, 54.5, 52.9, 51.9, 36.7, 18.4; HRMS (ESI+) calcd for C$_{27}$H$_{29}$N$_3$O$_9$ [M+Na]$^+$ 562.1802, found 562.1796.
tetramethyl 2,2-(5-fluoro-2-(1-phenethyl-1H-1,2,3-triazol-4-yl)-1,3-phenylene)dimalonate (3o)

White solid (70.0 mg, 66 %); mp 118-119 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J$ = 9.2 Hz, 2H), 7.31 (s, 1H), 7.30-7.26 (m, 2H), 7.24-7.20 (m, 1H), 7.11 (d, $J$ = 7.2, 2H), 4.70 (t, $J$ = 6.8, 2H), 4.46 (s, 2H), 3.71 (s, 12H), 3.29 (t, $J$ = 6.8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.0, 162.3 (d, $J_{C-F}$ = 247 Hz), 141.5, 136.9, 135.3 (d, $J_{C-F}$ = 8.0 Hz), 128.9, 128.8 (d, $J_{C-F}$ = 24.0 Hz), 127.3 (d, $J_{C-F}$ = 3.0 Hz), 127.1, 125.1, 116.7 (d, $J_{C-F}$ = 23.0 Hz), 54.4, 53.1, 52.0, 36.7; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ -110.4; HRMS (ESI+) calcd for C$_{26}$H$_{26}$FN$_3$O$_8$ [M+Na]$^+$ 550.1602, found 550.1596.

tetramethyl 2,2'-(3-(1-benzyl-1H-1,2,3-triazol-4-yl)thiophene-2,4-diyl)-dimalonate (3p)

White solid (73.1 mg, 73 %); mp 140-142 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (s, 1H), 7.59 (s, 1H), 7.43-7.37 (m, 3H), 7.33-7.31 (m, 2H), 5.60 (s, 2H), 5.11 (s, 1H), 4.87 (s, 1H), 3.72 (s, 6H), 3.68 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.2, 167.5, 140.9, 134.5, 132.1, 130.8, 130.6, 129.2, 128.8, 128.1, 126.2, 123.5, 54.3, 53.2, 52.9, 51.7, 51.6; HRMS (ESI+) calcd for C$_{23}$H$_{23}$N$_3$O$_8$S [M+Na]$^+$ 524.1104, found 524.1098.
tetramethyl 2,2’-(2-(1-phenyl-1H-1,2,3-triazol-4-yl)-1,3-phenylene)dimalonate (3q)
White solid (58.1 mg, 59 %); mp 190-193 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.10 (s, 1H), 7.83-7.80 (m, 2H), 7.59-7.55 (m, 2H), 7.50-7.46 (m, 1H), 7.45 (s, 2H), 4.70 (s, 2H), 3.72 (s, 12H), 2.45 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.63, 143.41, 139.53, 136.86, 133.0, 129.9, 129.0, 127.9, 122.9, 120.5, 54.7, 52.9, 21.6; HRMS (ESI+) calcd for C₂₅H₂₅N₃O₈ [M+Na]^+ 518.1534, found 518.1528.

dimethyl 2,2’-(5-methyl-2-(1-(p-tolyl)-1H-1,2,3-triazol-4-yl)-1,3-phenylene)-dimalonate (3r)
White solid (62.7 mg, 62 %); mp 198-200 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.04 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.44 (s, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.70 (s, 2H), 3.71 (s, 12H), 2.45 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.7, 143.3, 139.5, 139.2, 134.6, 133.0, 130.4, 130.1, 128.0, 122.8, 120.4, 54.6, 52.9, 21.6, 21.2; HRMS (ESI+) calcd for C₂₆H₂₇N₃O₈ [M+Na]^+ 532.1696, found 532.1690.
1H-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)dimalonate (3r')
White solid (28.6 mg, 22 %); mp 178-179 °C; 1H NMR (CDCl₃, 400 MHz) δ 7.88 (s, 1H), 7.52 (s, 1H), 7.41 (s, 2H), 7.34 (s, 2H), 4.79 (s, 1H), 4.70 (s, 2H), 3.74 (s, 3H), 3.71 (s, 12H), 2.48 (s, 3H), 2.44 (s, 3H); 13C NMR (CDCl₃, 100 MHz) δ 168.6, 168.0, 142.8, 140.9, 139.6, 133.7, 133.3, 131.1, 130.1, 128.5, 127.8, 127.3, 126.3, 54.8, 53.1, 52.9, 52.0, 21.6, 21.4; HRMS (ESI+) calcd for C₃₁H₃₃N₃O₁₂ [M+Na]⁺ 662.1962, found 662.1954.

Me_iPrO₂C₃O₂iPrN₃C₃O₂iPrN₃Ph₃

2,2'-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene) dimalonate (3s)
White solid (77 mg, 62 %); mp 119-121 °C; 1H NMR (500 MHz, CDCl₃) δ 7.50 (s, 1H), 7.38-7.34 (m, 5H), 7.30-7.28 (m, 2H), 5.60 (s, 2H), 5.50-4.93 (m, 4H), 4.48 (s, 2H), 2.38 (s, 3H), 1.18 (d, J = 6.0 Hz, 12H), 1.13 (d, J = 6.0 Hz, 12H); 13C NMR (125 MHz, CDCl₃) δ 167.8, 143.4, 138.7, 134.6, 133.1, 129.6, 129.2, 128.7, 128.3, 127.9, 124.7, 130.4, 129.6, 128.6, 126.6, 124.6, 123.1, 120.6, 119.2, 54.8, 52.9, 21.6, 21.5, 21.4; HRMS (ESI+) calcd for C₃₄H₄₃N₅O₈ [M+Na]⁺ 644.2942, found 644.2938.

MeEtO₂C₄O₂EtN₃C₄O₂EtN₃Ph₃

2,2’-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene) dimalonate (3t)
White solid (101.4 mg, 90 %); mp 95-97 °C; 1H NMR (CDCl₃, 400 MHz) δ 7.48 (s, 1H), 7.42-7.37 (m, 5H), 7.32-7.30 (m, 2H), 5.62 (s, 2H), 4.54 (s, 2H), 4.15-4.03 (m,


8H), 2.40 (s, 3H), 1.18 (t, J = 7.2 Hz, 12H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 168.2, 143.3, 139.1, 134.5, 133.1, 129.2, 128.8, 128.3, 128.0, 124.7, 61.7, 54.9, 54.3, 21.6, 13.9; HRMS (ESI+) calcd for C$_{30}$H$_{35}$N$_3$O$_8$ [M+Na]$^+$ 588.2316, found 588.2309.

diethyl 2,2′-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)bis(2-(methylsulfonyl)acetate (3u)

Tautomer (1:1.6); white solid (90.6 mg, 78 %); mp 168-171 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.93 (s, 1H), 7.87 (s, 1H), 7.86, 7.78 (both s, 1H), 7.42-7.31 (m, 5H), 5.65 (s, 2H), 4.93, 4.92 (both s, 2H), 4.31-4.09 (both m, 4H), 2.89, 2.85 (both s, 6H), 2.49, 2.48 (both s, 3H), 1.24, 1.21 (both t, J = 7.2 Hz, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 164.9, 164.5, 142.2, 142.1, 140.1, 139.9, 134.6, 134.4, 131.6, 131.5, 131.3, 131.0, 129.3, 129.2, 129.0, 128.9, 128.0, 127.1, 126.7, 69.6, 69.4, 63.0, 54.6, 54.5, 40.1, 39.6, 21.7, 21.6, 13.9; HRMS (ESI+) calcd for C$_{26}$H$_{31}$N$_3$O$_8$S$_2$ [M+Na]$^+$ 600.1451, found 600.1445.

diethyl 2,2′-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)bis(3-oxobutanoate) (3v)

$^1$H NMR spectrum is complicated due to tautomerization (The ratio of two tautomers: 1/7).

Light yellow oil (82.0 mg, 81 %); $^1$H NMR (400 MHz, CDCl$_3$ ) for the major tautomer: δ 12.80, 12.77 (both s, 2H), 7.43-7.33 (m, 3H), 7.19-7.17 (m, 1H), 7.11-7.08 (m, 2H), 7.00 (s, 2H), 5.52 (s, 1H), 5.52 (s, 1H), 4.02-3.87 (m, 4H), 2.40 (s, 3H), 1.78, 1.77 (both s, 3H), 1.75, 1.66 (both s, 3H); 1.01 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); $^1$H
NMR (400 MHz, CDCl$_3$) for the minor tautomer: $\delta$ 7.29 (s, 3H), 7.15 (s, 1H), 6.95 (d, $J = 6.8$ Hz, 4H), 5.57, 5.56 (both s, 2H), 5.22 (s, 1H), 5.26 (s, 1H), 4.24-4.09 (m, 4H), 2.40 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H), 1.22 (t, $J = 7.2$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 202.7, 202.4, 174.4, 174.0, 173.5, 173.3, 172.0, 171.8, 169.1, 168.9, 146.0, 145.9, 145.0, 144.9, 138.8, 138.7 138.2, 138.0, 135.7, 135.6, 135.5, 135.2, 135.1, 134.7, 134.6, 132.6, 132.4, 132.3, 131.8, 130.6, 130.5, 129.2, 129.1, 128.5, 127.6, 127.6, 127.5, 127.3, 123.2, 123.1, 103.6, 103.5, 103.1, 103.0, 61.9, 61.8, 61.4, 60.6, 60.4, 60.3, 60.1, 54.1, 53.8, 53.7, 29.7, 29.6, 29.4, 26.9, 21.3, 21.2, 20.1, 20.0, 19.8, 14.2, 14.1, 14.0, 13.9; HRMS (ESI+) calcd for C$_{28}$H$_{31}$N$_3$O$_6$ [M+Na]$^+$ 528.2105, found 528.2096.

diethyl 2,2’-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)bis(3-oxo-3-phenylpropanoate) (3w).

$^1$H NMR spectrum is complicated due to tautomerization (The ratio of two tautomers: 1/7).

Yellow solid (108.8 mg, 86 %); mp 106-109 °C; $^1$H NMR (400 MHz, CDCl$_3$) for the major tautomer: 7.86 (d, $J = 6.8$ Hz, 2H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.43-7.39 (m, 2H), 7.65 (s, 1H), 7.33-7.24 (m, 6H), 7.22-7.17 (m, 2H), 7.11-7.09 (m, 3H), 7.01 (s, 1H), 5.51 (s, 1H), 5.42, 5.41 (both s, 2H), 4.14-3.78 (m, 4H), 2.18, 2.11 (both s, 3H), 1.03 (t, $J = 6.8$ Hz, 6H); $^1$H NMR (400 MHz, CDCl$_3$) for the minor tautomer: $\delta$ 13.37 (s, 1H), 13.36 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.33-7.24 (m, 2H), 7.14 (s, 3H), 7.00-6.97 (m, 2H), 6.94-6.88 (m, 4H), 6.78 (s, 1H), 6.72 (s, 1H), 6.02, 5.85 (both s, 2H), 5.39, 5.38 (both s, 2H), 4.14-3.78 (m, 4H), 2.06 (s, 3H), 2.05 (s, 3H), 0.88 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 194.9, 194.8, 194.0, 193.9, 172.8, 172.7, 170.4, 169.5, 169.2, 168.8, 145.0, 143.9, 143.8, 139.9, 139.7, 138.9, 135.1, 134.1, 134.0, 133.4, 133.2, 133.0, 130.0, 129.2,
128.9, 128.7, 127.9, 127.3, 124.7, 124.6, 123.1, 123.0, 103.4, 103.4, 77.4, 77.1, 76.8, 61.6, 61.4, 61.3, 61.1, 60.9, 57.8, 54.4, 54.2, 54.1, 54.0, 29.7, 26.9, 21.5, 21.4, 21.2, 14.1, 14.0; HRMS (ESI+) calcd for C_{38}H_{35}N_{3}O_{6} [M+Na]^+ 652.2418, found 652.2416.

diethyl 2,2'-((5-methyl-1H-1,2,3-triazol-4-yl)-1,3-phenylene)bis(3-oxo-3-phenylpropanoate) (3x).

$^1$H NMR spectrum is complicated due to tautomerization (The ratio of two tautomers: 1/5.3).

White solid (98.9 mg, 76 %); mp 104-106 °C; $^1$H NMR (400 MHz, CDCl$_3$ ) for the major tautomer: $\delta$ 7.80 (d, $J = 7.2$ Hz, 2H), 7.69 (d, $J = 7.6$ Hz, 1H), 7.45-7.40 (m, 2H), 7.35-7.29 (m, 4H), 7.21-7.12 (m, 3H), 7.04 (s, 1H), 6.26, 5.93, 5.45 (s, 2H), 4.33 (t, $J = 7.2$ Hz, 1H), 4.26-3.93 (m, 5H), 2.23, 2.16, 2.09 (all s, 3H), 1.83-1.71 (m, 2H), 0.80 (t, $J = 6.4$ Hz, 3H); $^1$H NMR (400 MHz, CDCl$_3$ ) for the minor tautomer: $\delta$ 13.43 (s, 1H), 13.41 (s, 1H), 8.07 (d, $J = 7.6$ Hz, 2H), 7.75 (d, $J = 7.6$ Hz, 2H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.45-7.40 (m, 1H), 7.35-7.29 (m, 2H), 7.00-6.95 (m, 4H), 6.76 (d, $J = 14.0$ Hz, 2H), 4.26-3.93 (m, 6H), 2.08 (s, 3H), 1.61-1.55 (m, 3H), 0.78 (t, $J = 6.4$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 195.1, 194.8, 194.0, 193.9, 172.9, 172.8, 170.1, 169.4, 169.3, 169.2, 168.9, 168.8, 144.6, 144.4, 143.5, 139.9, 139.7, 138.8, 135.8, 135.4, 135.1, 134.1, 133.5, 133.2, 133.0, 132.9, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 127.9, 127.8, 127.5, 127.4, 124.5, 122.8, 122.7, 103.8, 103.6, 61.7, 61.6, 61.4, 61.3, 61.1, 58.2, 58.1, 57.9, 57.8, 50.6, 50.4, 50.2, 31.8, 31.7, 30.2, 28.9, 26.4, 26.3, 22.6, 21.6, 21.5, 21.2, 14.1, 14.0; HRMS (ESI+) calcd for C$_{39}$H$_{45}$N$_{5}$O$_{6}$ [M+Na]$^+$ 674.3201, found 674.3203.
dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methylphenyl)malonate (4a)

Pale yellow oil (28.8 mg, 38 %); 1H NMR (CDCl3, 400 MHz) δ 7.62 (s, 1H), 7.38-7.35 (m, 4H), 7.34-7.30 (m, 3H), 7.16 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 5.57 (s, 2H), 5.54 (s, 1H), 3.72 (s, 6H), 2.37 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 169.3, 147.1, 138.6, 134.6, 130.6, 130.3, 129.5, 129.2, 129.1, 128.8, 128.2, 127.5, 122.0, 54.2, 54.1, 52.8, 21.3. HRMS (ESI+) calcd for C21H23N3O4 [M+Na]+ 402.1424, found 402.1411.

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)phenyl)malonate (4b)

Pale yellow oil (23.4 mg, 32 %); 1H NMR (CDCl3, 400 MHz) δ 7.66 (s, 1H), 7.57-7.54 (m, 1H), 7.50-7.48 (m, 1H), 7.40-7.34 (m, 5H), 7.32-7.31 (s, 2H), 5.59 (s, 2H), 5.54 (s, 1H), 3.72 (s, 6H); 13C NMR (CDCl3, 100 MHz) δ 169.1, 147.0, 134.5, 130.8, 130.3, 129.9, 129.6, 129.2, 128.8, 128.6, 128.3, 128.1, 122.2, 54.3, 54.2, 52.8; HRMS (ESI+) calcd for C20H19N3O4 [M+Na]+ 388.1268, found 388.1260.

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methoxyphenyl)malonate (4c)

Yellow oil (26.9 mg, 34 %); 1H NMR (CDCl3, 400 MHz) δ 7.58 (s, 1H), 7.42-7.37 (m, 4H), 7.33-7.31 (m, 2H), 7.10-7.09 (d, J = 1.2 Hz, 1H), 6.92-6.88 (d, J = 8.8 Hz, 2.8 Hz, 1H), 5.57 (s, 2H), 5.51 (s, 1H), 3.83 (s, 3H), 3.72 (s, 6H); 13C NMR (CDCl3, 100 MHz) δ 169.1, 159.6, 146.9, 130.8, 129.1, 128.8, 128.2, 121.7, 115.1, 114.1, 55.4, 54.3, 54.2, 52.8; HRMS (ESI+) calcd for C21H21N3O5 [M+Na]+ 418.1373, found 418.1360.
dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-fluorophenyl)malonate (4d)
Pale yellow oil (24.5 mg, 32%); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.63 (s, 1H), 7.48-7.44 (m, 1H), 7.43-7.38 (m, 3H), 7.36-7.30 (m, 3H), 7.06 (td, $J = 8.4, 2.8$ Hz, 1H), 5.58 (s, 2H), 5.49 (s, 1H), 3.73 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 168.6, 162.4 ($J_{C-F} = 246.6$ Hz), 146.2, 134.4, 133.0 ($d, J_{C-F} = 8.3$ Hz), 131.4 ($d, J_{C-F} = 8.3$ Hz), 129.2, 128.9, 128.2, 126.6 ($J_{C-F} = 3.2$ Hz), 122.2, 117.0 ($d, J_{C-F} = 22.9$ Hz), 115.6 ($d, J_{C-F} = 21.4$ Hz), 54.3, 54.1, 53.0; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ -112.1; HRMS (ESI+) calcd for C$_{20}$H$_{18}$FN$_3$O$_4$ [M+Na]$^+$ 406.1179, found 406.1174.

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-chlorophenyl)malonate (4e)
Pale yellow oil (31.9 mg, 40%); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.66 (s, 1H), 7.57-7.56 (d, $J = 2.4$ Hz, 1H), 7.44-7.38 (m, 4H), 7.34-7.32 (m, 3H), 5.58 (s, 2H), 5.53 (s, 1H), 3.74 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 168.6, 146.1, 134.5, 134.3, 132.4, 130.7, 130.1, 129.2, 129.0, 128.9, 128.6, 128.2, 122.3, 54.3, 54.0, 53.0; HRMS (ESI+) calcd for C$_{20}$H$_{18}$ClN$_3$O$_4$ [M+Na]$^+$ 422.0884, found 422.0878.

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-4-methylphenyl)malonate (4f)
White solid (72.0 mg, 95 %); mp 112-114 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.66 (s, 1H), 7.45-7.37 (m, 4H), 7.33-7.32 (m, 3H), 7.20 (d, \(J = 8.0\) Hz, 1H ), 5.58 (s, 2H), 5.47 (s, 1H), 3.71 (s, 6H), 2.34 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 169.3, 147.1, 138.2, 134.5, 130.3, 129.7, 129.5, 129.2, 128.8, 128.2, 127.8, 122.2, 54.2, 53.9, 52.8, 21.0; HRMS (ESI+) calcd for C\(_{21}\)H\(_{21}\)N\(_3\)O\(_4\) [M+Na]\(^+\) 402.1424, found 402.1399.

![Diagram 4g](image)

**dimethyl 2-(5-methyl-1H-1,2,3-triazol-4-yl)phenylmalonate (4g)**

Yellow oil (29.0 mg, 35 %); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.67 (s, 1H), 7.47 (d, \(J = 8.8\) Hz), 7.13 (d, \(J = 2.8\) Hz, 1H), 6.93 (dd, \(J = 8.8, 2.8\) Hz, 1H), 5.50 (s, 1H), 4.39 (t, \(J = 7.2\) Hz), 3.84 (s, 3H), 3.74 (s, 6H), 1.96-1.91 (m, 2H), 1.35-1.25 (m, 10 H), 0.88 (t, \(J = 6.4\) Hz); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 169.0, 159.5, 146.4, 132.0, 130.9, 123.3, 121.7, 115.1, 114.2, 55.4, 54.2, 52.9, 50.4, 31.7, 30.3, 29.1, 29.0, 26.5, 22.6, 14.1; HRMS (ESI+) calcd for C\(_{22}\)H\(_{31}\)N\(_3\)O\(_5\) [M+Na]\(^+\) 440.2156, found 440.2148.

![Diagram 4h](image)

**dimethyl 2-(5-methyl-2-(1-phenethyl-1H-1,2,3-triazol-4-yl)phenyl)malonate (4h)**

Yellow oil (22.8 mg, 29 %); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.34 (s, 1H), 7.37-7.28 (m, 4H), 7.25-7.23 (m, 1H), 7.18 (dd, \(J = 8, 0.8\) Hz, 1H ), 5.36 (s,1H), 4.65 (t, \(J = 6.8\) Hz, 2H), 3.74 (s, 6H), 3.26 (t, \(J = 6.8\) Hz, 2H), 2.38 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 169.2, 146.2, 138.5, 137.1, 130.2, 129.6, 129.3, 128.9, 128.8, 127.7, 127.1, 122.5, 53.9, 52.8, 51.8, 36.8, 21.4; HRMS (ESI+) calcd for C\(_{22}\)H\(_{23}\)N\(_3\)O\(_4\) [M+Na]\(^+\) 416.1587, found 416.1581.
**diethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methylphenyl)malonate (4i)**

Yellow liquid (35.0 mg, 43 %); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.64 (s, 1H), 7.41-7.36 (m, 5H), 7.33-7.30 (m, 2H), 5.57 (s, 2H), 5.40 (s, 1H), 4.20-4.12 (m, 4H), 2.37 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 168.7, 147.1, 138.5, 134.6, 130.7, 130.3, 129.5, 129.2, 129.1, 128.8, 127.6, 122.0, 61.7, 54.5, 54.2, 21.3, 14.0; HRMS (ESI+) calcd for C$_{23}$H$_{25}$N$_3$O$_4$ [M+Na]$^+$ 430.1737, found 430.1743.

**ethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methylphenyl)-2-(methylsulfonyl) acetate (4j)**

Yellow oil (33.9 mg, 41 %); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.78 (s, 1H), 7.73 (s, 1H), 7.41-7.32 (m, 6H), 7.24 (d, $J = 8.0$ Hz, 1H), 6.58 (d, 1H), 5.60 (d, $J = 14.8$ Hz, 1H), 5.57 (d, $J = 14.8$ Hz, 1H), 4.35-4.18 (m, 2H), 3.05 (s, 3H), 2.41 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 165.5, 147.2, 138.8, 134.4, 131.0, 130.6, 129.9, 129.2, 128.9, 128.7, 128.2, 125.8, 122.6, 68.6, 62.7, 54.4, 40.3, 21.4, 13.9; HRMS (ESI+) calcd for C$_{21}$H$_{23}$N$_3$O$_4$S [M+Na]$^+$ 436.1307, found 436.1301.

**ethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methylphenyl)-2-(dimethoxyphosphoryl) acetate (4k)**
Yellow solid (23.9 mg, 27 %); mp 134-136 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.75 (s, 1H), 7.71 (s, 1H), 7.40-7.31 (m, 6H), 7.15 (d, $J = 8.0$ Hz, 1H), 5.61, 5.56 (d, $J = 14.8$ Hz, both 1H), 5.30 (d, $J_{HP} = 8.0$ Hz, 2H), 4.23-4.41 (m, 2H), 3.69 (d, $J_{HP} = 10.8$ Hz, 3H), 3.56 (d, $J_{HP} = 10.8$ Hz, 3H), 2.38 (s, 3H), 1.20 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 167.8, 146.9, 138.6 (d, $J_{CP} = 3.0$ Hz), 134.5, 131.1 (d, $J_{CP} = 5.0$ Hz), 130.0, 129.2, 129.1 (d, $J_{CP} = 3.0$ Hz), 128.9, 128.4 (d, $J_{CP} = 8.0$ Hz) 128.2, 127.5 (d, $J_{CP} = 8.0$ Hz), 122.5, 62.0, 58.4, 53.8(d, $J_{CP} = 6.0$ Hz), 53.7 (d, $J_{CP} = 6.0$ Hz), 46.7 (d, $J_{CP} = 136.0$ Hz), 21.4, 14.0; $^{31}$P NMR (CDCl$_3$, 162 MHz) δ 22.2; HRMS (ESI+) calcd for C$_{22}$H$_{26}$N$_3$O$_5$P [M+Na]$^+$ 466.1502, found 466.1491.

![4l](image)

**diisopropyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-5-methylphenyl)malonate (4l)**

Yellow oil (22.6 mg, 26 %); $^1$H NMR (CDCl$_3$, 600 MHz) δ 7.65 (s, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.40-7.39 (m, 4H), 7.31 (d, $J = 6.6$ Hz, 2H), 7.15 (d, $J = 7.8$ Hz, 1H), 5.57 (s, 2H), 5.27 (s, 1H), 5.08-5.02 (m, 2H), 2.37 (s, 3H), 1.23 (t, $J = 6.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ 168.7, 147.1, 138.5, 134.6, 130.7, 130.3, 129.5, 129.2, 129.1, 128.8, 127.6, 122.0, 61.7, 54.5, 54.2, 21.3, 14.0; HRMS (ESI+) calcd for C$_{25}$H$_{29}$N$_3$O$_4$ [M+Na]$^+$ 458.2050, found 458.2045.

![4m](image)

**dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-3-fluorophenyl)malonate (4m)**

White solid (40.6 mg, 53 %); mp 94-96 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.77 (s, $J = 3.0$ Hz, 1H), 7.39-7.30 (m, 7H), 7.12-7.09 (s, 1H), 5.77 (s, 1H), 5.59 (s, 2H), 3.73 (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.6, 162.5 (d, $J_{CF} = 245.9$ Hz), 142.5, 137.1,
136.4 (d, $J_{CF} = 2.3$ Hz), 132.1 (d, $J_{CF} = 9.3$ Hz), 131.8, 131.4, 130.7, 128.2 (d, $J_{CF} = 3.2$ Hz), 127.3 (d, $J_{CF} = 10.1$ Hz), 121.4 (d, $J_{CF} = 14.4$ Hz), 118.0, (d, $J_{CF} = 23.1$ Hz), 57.2 (d, $J_{CF} = 2.3$ Hz), 56.9, 55.5; $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$ -112.3; HRMS (ESI+) calcd for C$_{20}$H$_{18}$FN$_3$O$_4$ [M+Na]$^+$ 406.1174, found 406.1169.

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-3-methylphenyl)malonate (4n)
Pale yellow oil (54.6 mg, 72 %); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.43 (s, 1H), 7.41-7.35 (m, 4H), 7.33-7.29 (m, 3H), 7.25-7.23 (s, 1H), 5.62 (s, 2H), 4.65 (s, 1H), 3.63 (s, 6H), 2.11 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 144.5, 138.5, 134.7, 132.8, 130.5, 130.0, 129.2, 128.9, 128.8, 127.9, 126.5, 123.5, 54.8, 54.2, 52.7, 21.0; HRMS (ESI+) calcd for C$_{21}$H$_{21}$N$_3$O$_4$ [M+Na]$^+$ 402.1430, found 402.1424.

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-3-formylphenyl)malonate (4o)
Pale yellow oil (35.4 mg, 45 %); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.73 (s, 1H), 8.00 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.85 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.61 (s, 1H), 7.44-7.38 (m, 4H), 7.35-7.31 (m, 2H), 5.66 (s, 2H), 4.79 (s, 1H), 3.67 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.2, 168.3, 141.1, 135.8, 134.9, 134.2, 133.6, 133.5, 129.5, 129.3, 129.0, 128.1, 128.0, 125.2, 54.5, 53.7, 53.0; HRMS (ESI+) calcd for C$_{21}$H$_{19}$N$_3$O$_5$ [M+Na]$^+$ 416.1228, found 416.1217.
dimethyl 2-(2-(1-benzyl-5-iodo-1H-1,2,3-triazol-4-yl)phenyl)malonate (4p)

White solid (51.1 mg, 52%); mp 159-162 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.62 (d, $J = 8.0$ Hz, 1H), 7.48-7.44 (m, 1H), 7.36-7.26 (m, 7H), 5.68 (s, 2H), 5.08 (s, 1H), 3.68 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 150.7, 134.2, 132.6, 130.7, 130.1, 129.7, 129.5, 129.0, 128.8, 128.6, 128.1, 127.8, 54.6, 54.1, 52.8; HRMS (ESI+) calcd for C$_{20}$H$_{18}$N$_3$O$_4$ [M+Na]$^+$ 514.0238, found 514.0234.

White solid (42.4 mg, 48%); mp 131-133 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.46-7.44 (m, 1H), 7.31-7.18 (m, 7H), 7.07 (td, $J = 8.0$, 1.2 Hz, 1H), 7.02-6.94 (m, 5H), 5.44 (s, 2H), 5.37 (s, 1H), 3.58 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.0, 144.2, 135.8, 135.4, 132.3, 130.8, 130.6, 129.8, 129.5, 129.4, 129.0, 128.8, 128.6, 128.2, 127.9, 127.4, 126.8, 54.2, 52.7, 52.2; HRMS (ESI+) calcd for C$_{26}$H$_{23}$N$_3$O$_4$ [M+Na]$^+$ 464.1582, found 464.1581.

6. Mechanistic experiments

6.1 Synthesis of 1,2,3-triazole coordinated cyclometalated intermediate A
A mixture of \([\text{Cp}^*\text{RhCl}_2]_2\) (0.05 mmol, 1.0 equiv.), 1a (0.2 mmol, 2.0 equiv.), NaOAc (0.11 mmol, 2.2 equiv.) and 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 24 h. The reaction mixture was then cooled to room temperature and filtered through Celite pad. The solid residue was washed with DCM three times. The combined filtrate was concentrated under reduced pressure and the crude mixture was kept for recrystallization from DCM/Et₂O at room temperature to obtain a red orange crystal A identified by x-ray diffraction study.

6.2 H/D exchange experiment

![H/D exchange reaction diagram]

1-benzyl-4-phenyl-1H-1,2,3-triazole 1b (0.2 mmol, 1.0 equiv.), \([\text{Cp}^*\text{RhCl}_2]_2\) (0.005 mmol, 2.5 mol %), AgSbF₆ (0.02 mmol, 10 mol %), 1,2-dichloroethane (2.0 mL) and D₂O (0.2 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford a mixture of 1b and \(d_2\)-1b. The deuterated ratio was calculated based on \(^1\text{H}\) NMR analysis.

\(^1\text{H}\) NMR Spectrum of 1b and \(d_2\)-1b in CDCl₃ at 400 MHz
1-benzyl-4-phenyl-1H-1,2,3-triazole 1a (0.2 mmol, 1.0 equiv.), dimethyl 2-diazo-
malonate (0.3 mmol, 1.5 equiv.), [Cp*RhCl₂]₂ (0.005 mmol, 2.5 mol %), AgSbF₆ (0.02
mmol, 10 mol %), 1,2-dichloroethane (2.0 mL) and D₂O (0.2 mL) were added into an
oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C
for 12 h. The solvent was then removed under reduced pressure, and the residue was
purified by silica gel chromatography using petroleum ether/ethyl acetate to afford the
isolated product d₂-1a, d₁-4a and dₙ-3a. The deuterated ratio was calculated from ¹H
NMR analysis.
'H NMR Spectrum of \( \text{d}_2\text{-}1\text{a} \) in CDCl\(_3\) at 400 MHz

\[ \text{H NMR Spectrum of } \text{d}_1\text{-}4\text{a} \text{ in CDCl}_3 \text{ at 400 MHz} \]
**6.3 Intermolecular competition experiments between 1c and 1e**

1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole 1c (0.1 mmol, 1.0 equiv.), 1-benzyl-4-(4-chlorophenyl)-1H-1,2,3-triazole 1e (0.1 mmol, 1.0 equiv.), dimethyl 2-diazaalkanolate (0.22 mmol, 2.2 equiv.), \([\text{Cp}^*\text{RhCl}_2]_2\) (0.005 mmol, 2.5 mol %), AgSbF$_6$ (0.02 mmol, 10 mol %), 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford a mixture of 3e and 3c. The ratio was calculated from $^1$H NMR analysis.
$^1$H NMR Spectrum of 3c and 3e in CDCl$_3$ at 400 MHz
7. $^1$H and $^{13}$C NMR Spectra of products

$^1$H NMR Spectrum of 3a in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3a in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3b in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3b in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3c in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3c in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3d in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3d in CDCl$_3$ at 100 MHz
\[^{19}\text{F NMR Spectrum of 3d in CDCl}_3 \text{ at 376 MHz}\]
$^1$H NMR Spectrum of 3e in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3e in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3f in CDCl$_3$ at 500 MHz

$^{13}$C NMR Spectrum of 3f in CDCl$_3$ at 125 MHz
$^1$H NMR Spectrum of 3g in CDCl$_3$ at 600 MHz

$^{13}$C NMR Spectrum of 3g in CDCl$_3$ at 150 MHz
$^{1}$H NMR Spectrum of 3h in CDCl$_3$ at 600 MHz

$^{13}$C NMR Spectrum of 3h in CDCl$_3$ at 150 MHz
$^1$H NMR Spectrum of 3i in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3i in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3j in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3j in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3k in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3k in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3l in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3l in CDCl$_3$ at 100 MHz
$^{19}$F NMR Spectrum of 3l in CDCl$_3$ at 376 MHz
$^1$H NMR Spectrum of 3m in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3m in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3n in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3n in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3o in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3o in CDCl$_3$ at 100 MHz
$^{19}\text{F NMR Spectrum of } 3\text{o in CDCl}_3 \text{ at 376 MHz}$
$^1$H NMR Spectrum of 3p in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3p in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3q in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3q in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3r in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3r in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3r’ in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3r’ in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3s in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3s in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3t in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3t in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3u in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3u in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3v in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3v in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3w in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3w in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 3x in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 3x in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4a in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4a in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4b in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4b in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4c in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4c in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4d in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4d in CDCl$_3$ at 100 MHz
$^{19}$F NMR Spectrum of 4d in CDCl$_3$ at 376 MHz
\(^1\)H NMR Spectrum of 4e in CDCl\(_3\) at 400 MHz

\(^{13}\)C NMR Spectrum of 4e in CDCl\(_3\) at 100 MHz
$^1$H NMR Spectrum of 4f in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4f in CDCl$_3$ at 100 MHz
\(^1^H\) NMR Spectrum of 4g in CDCl\(_3\) at 400 MHz

\(^1^C\) NMR Spectrum of 4g in CDCl\(_3\) at 100 MHz
$^1$H NMR Spectrum of 4h in CDCl$_3$ at 400 MHz
$^{13}$C NMR Spectrum of 4h in CDCl$_3$ at 100 MHz

$^1$H NMR Spectrum of 4i in CDCl$_3$ at 400 MHz
$^{13}$C NMR Spectrum of 4i in CDCl$_3$ at 100 MHz

$^1$H NMR Spectrum of 4j in CDCl$_3$ at 400 MHz
$^{13}$C NMR Spectrum of 4j in CDCl$_3$ at 100 MHz

$^1$H NMR Spectrum of 4k in CDCl$_3$ at 400 MHz
$^{13}$C NMR Spectrum of 4k in CDCl$_3$ at 100 MHz

$^{31}$P NMR Spectrum of 4k in CDCl$_3$ at 162 MHz
\(^1\)H NMR Spectrum of 4l in CDCl\textsubscript{3} at 400 MHz

\(^{13}\)C NMR Spectrum of 4l in CDCl\textsubscript{3} at 100 MHz
$^1$H NMR Spectrum of 4m in CDCl$_3$ at 600 MHz

$^{13}$C NMR Spectrum of 4m in CDCl$_3$ at 150 MHz
$^{19}$F NMR Spectrum of 4m in CDCl$_3$ at 376 MHz
$^1$H NMR Spectrum of 4n in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4n in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4o in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4o in CDCl$_3$ at 100 MHz
$^1$H NMR Spectrum of 4p in CDCl$_3$ at 400 MHz

$^{13}$C NMR Spectrum of 4p in CDCl$_3$ at 100 MHz
1H NMR Spectrum of 4q in CDCl₃ at 400 MHz

13C NMR Spectrum of 4q in CDCl₃ at 100 MHz