Supporting Information-I

Direct Organocatalytic Chemoselective Synthesis of Pharmaceutically Active Benzothiazole/Benzoxazole-Triazoles

Badaraita Gorachand, Pandhiti R. Lakshmi, and Dhevalapally B. Ramachary*

Catalysis Laboratory, School of Chemistry, University of Hyderabad, Central University (P.O.), Prof. CR Rao Road, Gachibowli, Hyderabad-500 046, Telangana, India
E-mail: ramsc@uohyd.ac.in and ramchary.db@gmail.com

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General Experimental Procedures for the OrgAKC Reactions

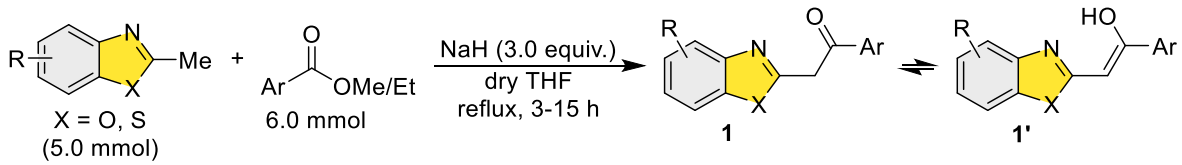
General Methods

The ^{1}H NMR and ^{13}C NMR spectra were recorded at 500, 400, 125 and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2, or CH_3) was determined by recording the DEPT-135 experiment and is given in parentheses. The coupling constants *J* are given in Hz. Column chromatography was performed using silica gel (particle size: 0.063−0.200 mm). High-resolution mass spectra were recorded on a micromass ESI-TOF MS. IR spectra were recorded on FT/IR-5300 and FT/IR-5700. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious $MACH_3$ diffractometer using graphite monochromated, Mo−Kα (λ = 0.71073 Å) radiation with CAD_4 software, or the X-ray intensity data were measured at 298 K on a SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo−Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates were used and compounds were visualized by irradiation with UV light and / or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL), followed by heating.

Materials: All solvents and commercially available chemicals were used as received without further purification unless otherwise stated.

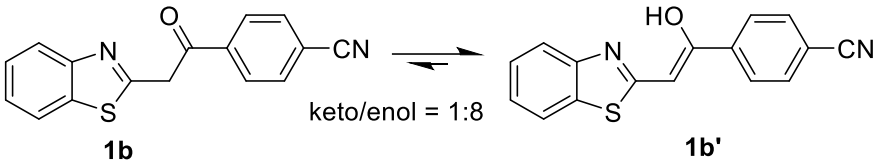
<u>Procedure A:</u> General procedure for the synthesis of compound 1:

The 2-acyl benzothiazole/benzoxazole derivatives of **1a-v** were synthesized by using literature procedures.[1a-e] Benzothiazole/benzoxazole-ketones **1b**, **1c**, **1e**, **1i**, **1k**, **1l**, **1p**, **1q**, **1r**, and **1v** are new compounds and given those analytical data herein.



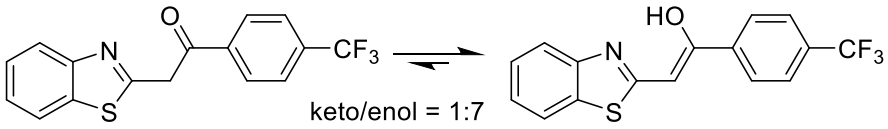
Sodium hydride (60 wt% in oil, 600 mg, 15.0 mmol, 3.0 equiv.) was added to THF (10 mL) solution of substituted 2-methyl benzothiazole or 2-methyl benzoxazole (5.0 mmol, 1.0 equiv.) and alkyl benzoate (6.0 mmol, 1.2 equiv.) at room temperature. The resulting reaction mixture was refluxed for 10-15 hours. After cooling to room temperature, aqueous NH_4Cl was added to the reaction mixture and extracted with diethyl ether (3 x 20 mL). The extracted organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/hexane, 0:10 to 1.5:8.5) to afford benzothiazole/benzoxazole-ketones **1** in 70-90% of yield.[1b]

(*Z*)-4-(2-(Benzo[*d*]thiazol-2-yl)-1-hydroxyvinyl)benzonitrile (**1b′**)**:** The title compound was prepared following **Procedure A** using base sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 90% (1.2 g). Mp: 182-184 °C. IR (neat): ν_{max} 2966, 2879, 1769, 1611, 1471, 1245, 1112, 1052, 838, 757, 728 and 614 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **1b'** δ 13.81 (1H, s), 7.95 (2H, d, J = 8.0 Hz), 7.85 (1H, d, J = 8.0 Hz), 7.81 (1H, d, J = 8.0 Hz), 7.71 (2H, d, J = 8.5 Hz), 7.49 (1H, m), 7.36-7.33 (1H, m), 6.42 (1H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1b'** δ 167.4 (C), 163.0 (C), 150.0 (C), 139.0 (C), 132.6 (2 x CH), 131.5 (C), 126.8 (CH), 126.3 (2 x CH), 124.7 (CH), 121.5 (CH), 120.3 (CH), 118.5 (C), 113.3 (C), 92.6 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{11}N_2OS$ 279.0592; Found 279.0592.



1b **1b'**

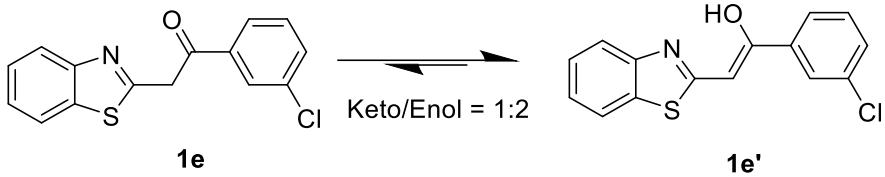
(*Z*)-2-(Benzo[*d*]thiazol-2-yl)-1-(4-(trifluoromethyl)phenyl)ethen-1-ol (**1c'**)**:** The title compound was prepared following **Procedure A** using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 90% (1.4 g). Mp: 160-162 °C. IR (neat): ν_{max} 2967, 2878, 1767, 1610, 1470, 1243, 1112, 1052, 838, 757, 728 and 614 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **1c'** δ 13.95 (1H, br s), 7.96 (2H, d, J = 8.0 Hz), 7.83 (1H, d, J = 8.0 Hz), 7.79 (1H, d, J = 8.0 Hz), 7.75 (2H, d, J =



1c **1c'**

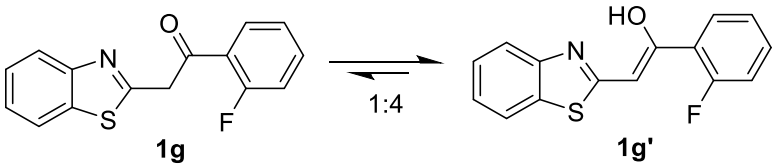
8.5 Hz), 7.46 (1H, td, *J* = 7.5, 1.0 Hz), 7.34 (1H, td, *J* = 7.5, 1.0 Hz), 6.41 (1H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): **1c'** δ 167.7 (C), 163.8 (C), 150.2 (C), 138.2 (C), 131.8 (C, q, *J* = 32.1 Hz), 131.5 (C), 126.7 (CH), 126.2 (2 x CH), 125.5 (2 x CH, q, $J_{C\text{-}F}$ = 3.75 Hz), 124.5 (CH), 123.9 (C, q, $J_{C\text{-}F}$ = 270.75 Hz), 121.5 (CH), 120.2 (CH), 92.0 (CH). ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.75, -63.23 (C, CF_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{11}F_3NOS$ 322.0513; Found 322.0513.

2-(Benzo[*d*]thiazol-2-yl)-1-(3-chlorophenyl)ethan-1-one (1e) and **(*Z*)-2-(Benzo[*d*]thiazol-2-yl)-1-(3-chlorophenyl)ethen-1-ol (1e'):** The title compound was prepared following **Procedure A** using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 80% (1.1 g). Mp: 139-141 °C. IR (neat): ν_{max} 3071, 1687, 1595, 1561, 1464, 1416, 1301, 1260, 1138, 895, 745, 718 and 665 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): for **1e** δ 8.08 (2H, br s), 7.98 (2H, d, *J* = 8.0 Hz), 7.49-7.46 (1H, m), 7.40-7.34 (3H, m), 4.84 (2H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1e** δ 192.9 (C), 163.4 (C), 152.2 (C), 137.2 (C), 135.6 (C), 135.2 (C), 133.8 (CH), 130.1 (CH), 126.8 (CH), 126.2 (CH), 125.3 (CH), 122.7 (CH), 121.5 (CH), 119.5 (CH), 43.5 (CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): for **1e'** δ 9.78 (1H, br s), 7.80 (1H, d, *J* = 8.0 Hz), 7.74 (1H, d, *J* = 8.0 Hz), 7.72 (1H, dt, *J* = 8.0, 1.5 Hz), 7.55 (1H, dd, *J* = 7.5, 1.0 Hz), 7.43 (2H, td, *J* = 8.0, 1.0 Hz), 7.29 (1H, td, *J* = 8.0, 1.0 Hz), 6.32 (1H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1e'** δ 169.9 (C), 167.6 (C), 165.4 (C), 149.3 (C), 137.0 (C), 134.6 (C), 133.5 (CH), 130.2 (CH), 129.7 (CH), 126.6 (CH), 126.1 (CH), 124.3 (CH), 124.0 (CH), 121.4 (CH), 91.0 (CH). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{10}ClNOSNa$ 310.0069; Found 310.0069.



1e **1e'**

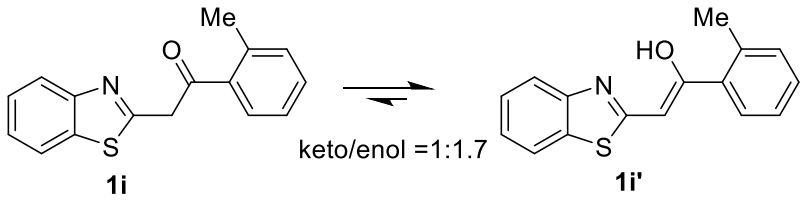
2-(Benzo[*d*]thiazol-2-yl)-1-(2-fluorophenyl)ethan-1-one (**1g)** and **(*Z*)-2-(Benzo[d]thiazol-2-yl)-1-(2-fluorophenyl)ethen-1-ol (1g'):** The title compound was prepared following **Procedure A** using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.0:9.0) and isolated as a yellow solid



1g **1g'**

compound. Yield: 70% (0.9 g). Mp: 63-65 °C. IR (neat): ν_{max} 2921, 1793, 1607, 1445, 1260, 1243, 1052, 816, 739, 726 and 667 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **1g** δ 8.01-7.95 (2H, m), 7.87 (1H, d, J = 8.0 Hz), 7.58-7.54 (1H, m), 7.47-7.42 (1H, m), 7.39-7.36 (1H, m), 7.27-7.24 (1H, m), 7.19-7.15 (1H, m), 4.83 (2H, d, $^5J_{C-F}$ = 2.5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): for **1g** δ 192.3 (C), 161.8 (C, d, $^1J_{C-F}$ = 264.0 Hz), 152.7 (C), 135.9 (C), 135.2 (CH, d, $^3J_{C-F}$ = 9.0 Hz), 131.1 (CH), 126.0 (CH), 125.1 (CH), 124.8 (CH), 124.6 (C), 124.4 (CH), 123.0 (CH), 122.9 (C), 116.9 (CH, d, $^2J_{C-F}$ = 23.0 Hz), 47.9 (CH_2, d, $^5J_{C-F}$ = 9.0 Hz). for **1g'** δ 13.99 (1H, br s), 7.97 (1H, td, J = 8.0, 1.5 Hz), 7.81 (1H, d, J = 8.0 Hz), 7.78 (1H, d, J = 8.0 Hz), 7.44 (1H, d, J = 8.0 Hz), 7.39 (1H, m), 7.30 (1H, t, J = 8.0 Hz), 7.24 (1H, t, J = 7.5 Hz), 7.12 (1H, dd, J = 12.0, 8.5 Hz), 6.58 (1H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): **1g'** δ 168.2 (C), 160.51 (C), 160.48 (C, d, $^1J_{C-F}$ = 252.0 Hz), 150.2 (C), 131.6 (C), 131.4 (CH, d, ^3J = 9.0 Hz), 129.4 (CH), 126.6 (CH), 124.4 (2 x CH), 123.0 (C), 121.5 (CH), 120.1 (CH), 116.3 (CH, d, $^2J_{C-F}$ = 24.0 Hz), 95.7 (CH, $^4J_{C-F}$ = 15.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.5, -111.0). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{11}FNOS$ 272.0542; Found 272.0542.

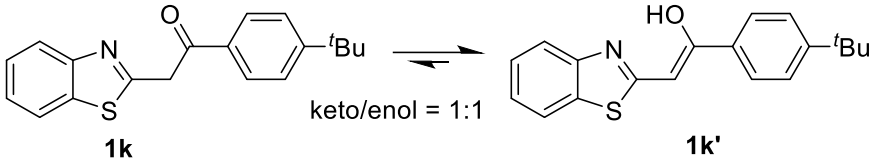
2-(Benzo[*d*]thiazol-2-yl)-1-(o-tolyl)ethan-1-one (1i) and **(*Z*)-2-(Benzo[*d*]thiazol-2-yl)-1-(o-tolyl)ethen-1-ol (1i′):** The title compound was prepared following **Procedure A** with using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow semi-solid compound. Yield: 85% (1.1 g). IR (neat): ν_{max} 3096, 2921, 1676, 1582, 1467, 1273, 1212, 1067, 881, 810, 758, 697 and 630 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **1i** δ 8.00 (1H, d, J = 8.0 Hz), 7.86 (1H, d, J = 7.0 Hz), 7.85 (1H, d, J = 8.5 Hz), 7.47-7.35 (3H, m), 7.32-7.28 (1H, m), 7.26-7.21 (1H, m), 4.76 (2H, s), 2.56 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1i** δ 197.1 (C), 163.7 (C), 152.7 (C), 136.0 (C), 135.9 (C), 132.3 (CH), 132.3 (CH), 131.2 (C), 129.3 (CH), 125.97 (CH), 125.90 (CH), 125.0 (CH), 122.9 (CH), 121.5 (CH), 46.2 (CH_2), 21.6 (CH_3). ^1H NMR (500 MHz, $CDCl_3$): for **1i'** δ 13.76 (1H, br s), δ 7.81 (1H, d, J = 8.5 Hz), 7.77 (1H, d, J = 8.0 Hz), 7.50 (1H, d, J = 8.0 Hz), 7.47-7.35 (1H, m), 7.32-7.28 (2H, m), 7.26-7.21 (2H, m), 5.95 (1H, s), 2.54 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1i'** δ 169.2 (C), 167.9 (C), 150.2 (C), 139.5 (C), 136.6 (C), 135.9 (C), 130.9 (CH), 129.4 (CH), 128.3 (CH), 126.4



1i 1i'

(CH), 125.7 (CH), 124.1 (CH), 121.4 (CH), 119.9 (CH), 94.6 (CH), 20.6 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}NOS$ 268.0796; Found 268.0796.

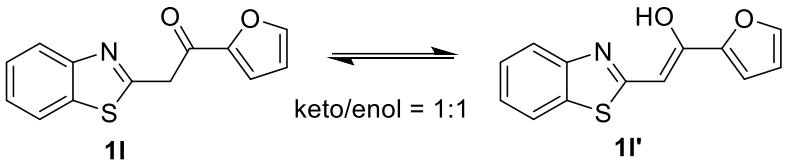
2-(Benzo[*d*]thiazol-2-yl)-1-(4-(*tert*-butyl)phenyl)ethan-1-one (1k) and **(*Z*)-2-(Benzo[*d*]thiazol 2-yl)-1-(4-(*tert*-butyl)phenyl)ethen-1-ol (1k′):** The title compound was prepared following



1k **1k'**

Procedure A with using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 70% (1.08 g). Mp: 120-123 °C. IR (neat): ν_{max} 3052, 2962, 1685, 1614, 1508, 1470, 1433, 1309, 1122, 1054, 855, 727 and 890 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **1k** δ 8.03-8.00 (3H, m), 7.80 (2H, d, *J* = 8.0 Hz), 7.79 (1H, d, *J* = 10.0 Hz), 7.42 (1H, td, *J* = 8.5, 1.5 Hz), 7.36 (1H, td, *J* = 7.0 Hz), 4.80 (2H, s), 1.33 (9H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1k** δ 193.7 (C), 165.7 (C), 157.7 (C), 153.8 (C), 133.2 (C), 131.9 (C), 128.7 (2 x CH), 125.9 (CH), 125.7 (2 x CH), 125.0 (CH), 122.8 (CH), 121.5 (CH), 43.8 (CH_2), 35.2 (C), 30.9 (3 x CH_3). ^1H NMR (500 MHz, $CDCl_3$): for **1k'** δ 13.79 (1H, br s), 7.86 (1H, d, *J* = 8.0 Hz), 7.86 (1H, d, *J* = 8.0 Hz), 7.50 (2H, dt, *J* = 7.5, 2.0 Hz), 7.47-7.44 (3H, m), 7.27 (1H, td, *J* = 8.0 Hz), 6.34 (1H, s), 1.35 (9H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1k'** δ 168.2 (C), 163.8 (C), 152.6 (C), 150.4 (C), 135.9 (C), 131.3 (C), 126.4 (CH), 125.7 (2 x CH), 125.5 (2 x CH), 124.0 (CH), 121.3 (CH), 119.8 (CH), 90.4 (CH), 34.8 (C), 31.2 (3 x CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}NOS$ 310.1266. Found 310.1260.

2-(Benzo[*d*]thiazol-2-yl)-1-(furan-2-yl)ethan-1-one (1l) and **(*Z*)-2-(Benzo[*d*]thiazol-2-yl)-1-**

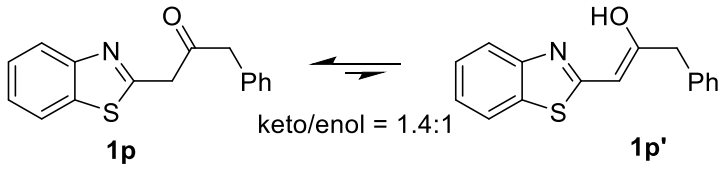


1l **1l'**

(furan-2-yl)ethen-1-ol (1l′): The title compound was prepared following **Procedure A** with using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 85% (1.03 g). Mp: 86-88 °C. IR (neat): ν_{max} 2922, 1612, 1553, 1508, 1469, 1357, 1266, 1122, 1054, 854, 815, 722 and 753 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **1l** δ 8.00 (1H, d, *J* = 8.0 Hz), 7.85 (1H, d, *J* = 8.0 Hz), 7.73-7.70 (1H, m), 7.47-7.44 (1H, m), 7.42-7.35 (2H,

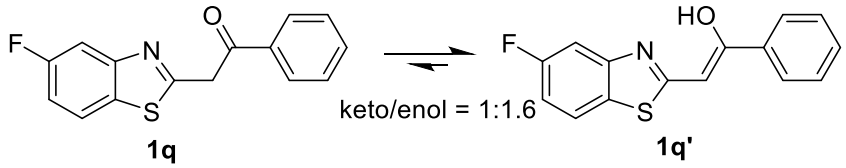
m), 6.67-6.56 (1H, m), 4.67 (2H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1l** δ 182.6 (C), 167.2 (C), 162.8 (C), 150.1 (C), 147.3 (CH), 135.9 (C), 126.5 (CH), 125.9 (CH), 122.9 (CH), 121.5 (CH), 118.8 (CH), 112.8 (CH), 43.5 (CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): for **1l'** δ 7.73-7.70 (1H, m), 7.64-7.63 (1H, m), 7.50 (1H, br s), 7.42-7.35 (1H, m), 7.27-7.24 (1H, m), 6.96 (1H, d, *J* = 8.5 Hz), 6.52-6.51 (1H, m), 6.52 (1H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1l'** δ 159.1 (C), 152.7 (C), 151.6 (C), 148.8 (C), 144.1 (CH), 130.3 (C), 125.1 (CH), 123.9 (CH), 121.4 (CH), 118.9 (CH), 112.1 (CH), 111.6 (CH), 89.5 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{10}NO_2S$ 244.0432; Found 244.0430.

1-(Benzo[*d*]thiazol-2-yl)-3-phenylpropan-2-one (1p) and **(*Z*)-1-(Benzo[*d*]thiazol-2-yl)-3-phenylprop-1-en-2-ol (1p′):** The title compound was prepared following **Procedure A** with using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a semi-solid compound. Yield: 80% (1.07 g). IR (neat): ν_{max} 3064, 1737, 1687, 1498, 1438, 1369, 1273, 1209, 1179, 1063, 997, 786, 733 and 696 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): for **1p** δ 8.00 (1H, d, *J* = 8.0 Hz), 7.75 (1H, d, *J* = 8.0 Hz), 7.69 (1H, td, *J* = 9.0 Hz), 7.40-7.38 (1H, m), 7.35-7.32 (2H, m), 7.29-7.26 (1H, m), 7.25-7.22 (2H, m), 4.24 (2H, s), 3.89 (2H, s). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): for **1p** δ 202.1 (C), 172.3 (C), 162.8 (C), 152.8 (C), 133.2 (C), 129.6 (2 x CH), 128.9 (2 x CH), 127.4 (CH), 126.1 (CH), 125.2 (CH), 122.9 (CH), 121.6 (CH), 49.9 (CH_2), 46.6 (CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): for **1p'** δ 13.52 (1H, br s), 7.46 (2H, td, *J* = 7.5, 2.0 Hz), 7.40-7.38 (1H, m), 7.35-7.32 (2H, m), 7.29-7.26 (2H, m), 7.25-7.22 (2H, m), 5.56 (1H, s), 3.65 (2H, s). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): for **1p'** δ 176.7 (C), 149.6 (C), 136.6 (C), 135.8 (C), 130.7 (C), 129.4 (2 x CH), 128.6 (2 x CH), 126.9 (CH), 126.4 (CH), 124.0 (CH), 121.4 (CH), 119.3 (CH), 92.7 (CH), 42.7 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}NOS$ 268.0796; Found 268.0796.



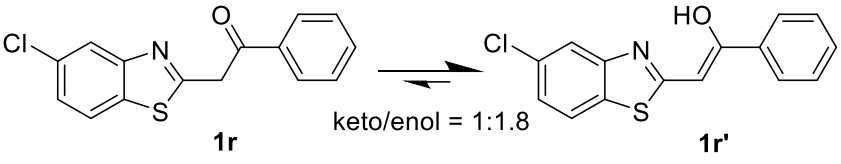
1p 1p'

2-(5-Fluorobenzo[*d*]thiazol-2-yl)-1-phenylethan-1-one (1q) and **(*Z*)-2-(5-Fluorobenzo[*d*]thiazol-2-yl)-1-phenylethen-1-ol (1q')**



The title compound was prepared following **Procedure A** using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 85% (1.15 g). Mp: 171-172 °C. IR (neat): ν_{max} 3397, 1605, 1572, 1456, 1425, 1262, 1155, 1119, 745 and 688 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): for **1q** δ 8.12 (1H, d, J = 7.5 Hz), 7.79 (1H, dd, J = 9.0, 5.0 Hz), 7.60 (1H, q, J = 7.5 Hz), 7.52-7.47 (2H, m), 7.45-7.44 (2H, m), 7.15 (1H, td, J = 9.0, 2.5 Hz), 4.83 (2H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1q** δ 193.9 (C), 165.3 (C), 161.7 (C, d, $^{1}J_{C\text{-}F}$ = 242.5 Hz), 153.4 (C, d, $^{3}J_{C\text{-}F}$ = 12.5 Hz), 135.7 (C), 133.9 (CH), 129.5 (C), 128.9 (2 x CH), 128.6 (2 x CH), 122.2 (CH, d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 113.9 (CH, d, $^{2}J_{C\text{-}F}$ = 25.0 Hz), 109.0 (CH, d, $^{2}J_{C\text{-}F}$ = 23.7 Hz), 43.8 (CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): for **1q'** δ 13.40 (1H, br s), 8.08 (1H, d, J = 7.5 Hz), 7.87-7.86 (2H, m), 7.70-7.68 (1H, m), 7.52-7.47 (1H, m), 7.45 (2H, m), 7.05 (1H, td, J = 9.0, 2.5 Hz), 6.35 (1H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **1q'** δ 170.5 (C), 166.2 (C), 162.1 (C, d, $^{1}J_{C\text{-}F}$ = 242.5 Hz), 151.9 (C, d, $^{3}J_{C\text{-}F}$ = 12.5 Hz), 134.4 (C), 131.3 (C), 130.5 (CH), 128.55 (2 x CH), 125.9 (2 x CH), 121.9 (CH, d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 112.5 (CH, d, $^{2}J_{C\text{-}F}$ = 25.0 Hz), 106.7 (CH, d, $^{2}J_{C\text{-}F}$ = 25.0 Hz), 91.1 (CH). ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.41, -116.0 (*C*-F). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{11}FNOS$ 272.0545; Found 272.0544.

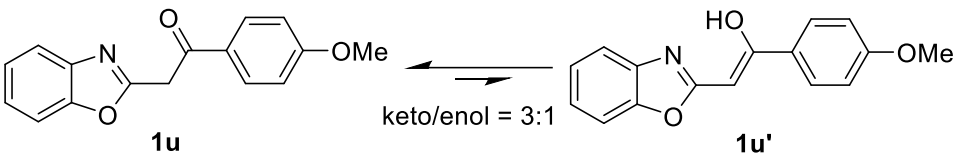
2-(5-Chlorobenzo[*d*]thiazol-2-yl)-1-phenylethan-1-one (1r) and **(*Z*)-2-(5-Chlorobenzo[*d*]thiazol-2-yl)-1-phenylethen-1-ol (1r'):**



The title compound was prepared following **Procedure A** using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 87% (1.2 g). Mp: 174-176 °C. IR (neat): ν_{max} 3370, 1694, 1597, 1453, 1417, 1261, 1156, 710 and 563 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): for **1r** δ 7.99 (1H, br s), 7.88-7.82 (2H, m), 7.79 (1H, d, J = 8.5 Hz), 7.64-7.61 (1H, m), 7.46-7.44 (2H, m), 7.36 (1H, dd, J = 8.5, 1.5 Hz), 6.36 (1H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz,

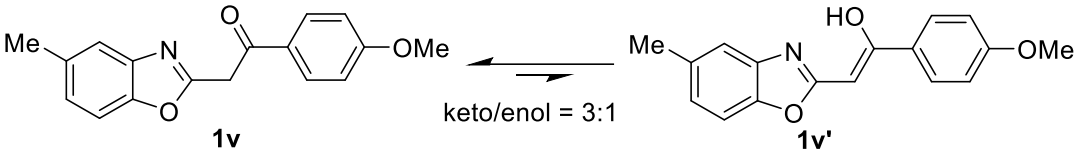
$CDCl_3$, DEPT-135): for **1r** δ 193.9 (C), 165.5 (C), 153.5 (C), 135.7 (C), 134.2 (C), 134.0 (CH), 132.1 (C), 128.7 (2 x CH), 125.6 (CH), 122.8 (CH), 122.2 (CH), 122.0 (2 x CH), 43.8 (CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): for **1r'** δ 13.67 (1H, br s), 8.08 (1H, d, J = 8.0 Hz), 7.88-7.82 (2H, m), 7.69 (1H, d, J = 8.5 Hz), 7.53-7.50 (1H, m), 7.46-7.44 (2H, m), 6.36 (1H, dd, J = 8.5, 2.0 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, DEPT-135): for **1r'** δ 169.9 (C), 165.2 (C), 151.9 (C), 134.3 (C), 132.6 (C), 130.6 (CH), 130.0 (C), 128.9 (CH), 128.6 (2 x CH), 125.9 (2 x CH), 124.5 (CH), 120.2 (CH), 91.0 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{11}ClNOS$ 288.0250; Found 288.0249.

2-(Benzo[*d*]oxazol-2-yl)-1-(4-methoxyphenyl)ethan-1-one (**1u**) and **(*Z*)-2-(Benzo[*d*]oxazol-2-yl)-1-(4-methoxyphenyl)ethen-1-ol** (**1u'**): The title compound was prepared following



Procedure A using sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1:9) and isolated as a yellow solid compound. Yield 70% (0.9 g). Mp: 65-68 ℃. IR (neat): ν_{max} 3360, 1681, 1601, 1511, 1257, 1169 and 734 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): for **1u** δ 8.03 (2H, dt, J = 9.0, 2.0 Hz), 7.70 (1H, dd, J = 6.0, 3.0 Hz), 7.50 (1H, dd, J = 6.5, 3.5 Hz), 7.31 (1H, d, J = 6.0 Hz), 7.30 (1H, d, J = 6.0 Hz), 6.95 (2H, dt, J = 9.0, 2.0 Hz), 4.58 (2H, s), 3.866 (3H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): for **1u** δ 190.8 (C), 164.1 (C), 160.8 (C), 151.2 (C), 141.2 (C), 131.0 (2 x CH), 128.7 (C), 124.9 (CH), 124.3 (CH), 119.9 (CH), 114.0 (2 x CH), 110.6 (CH), 55.5 (OCH_3), 39.4 (CH_2). ^{1}H NMR (500 MHz, $CDCl_3$): for **1u'** δ 7.83 (2H, dt, J = 9.0, 2.0 Hz), 7.58 (1H, d, J = 7.5 Hz), 7.46 (1H, d, J = 8.0 Hz), 7.29 (1H, dd, J = 7.0, 1.0 Hz), 7.26 (1H, dd, J = 7.5, 1.0 Hz), 6.95 (2H, dt, J = 9.0, 2.0 Hz), 6.10 (1H, s), 3.86 (3H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): for **1u'** δ 166.3 (C), 166.0 (C), 161.6 (C), 148.6 (C), 139.9 (C), 127.5 (2 x CH), 126.5 (C), 124.5 (CH), 123.8 (CH), 117.6 (CH), 113.9 (2 x CH), 110.1 (CH), 82.1 (CH), 55.4 (OCH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}NO_3$ 268.0974; Found 268.0979. and *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{13}NO_3Na$ 290.0793; Found 290.0795.

1-(4-Methoxyphenyl)-2-(5-methylbenzo[*d*]oxazol-2-yl)ethan-1-one (**1v**) and **(*Z*)-1-(4-Methoxyphenyl)-2-(5-methylbenzo[*d*]oxazol-2-yl)ethen-1-ol** (**1v'**): The title compound was prepared following **Procedure A** using



sodium hydride, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield 76% (1.0 g). Mp: 70-73 °C. IR (neat): ν_{max} 3005, 1671, 1596, 1573, 1260, 1164, 994, 831, and 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **1v** δ 8.03 (2H, dt, J = 9.0, 2.5 Hz), 7.48 (1H, s), 7.37 (1H, d, J = 8.5, Hz), 7.12 (1H, dd, J = 8.5, 2.0 Hz), 6.95 (2H, dt, J = 9.0, 2.5 Hz), 4.56 (2H, s), 3.87 (3H, s), 2.45 (3H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): for **1v** δ 190.9 (C), 164.1 (C), 160.8 (C), 149.5 (C), 141.4 (C), 134.1 (C), 131.0 (2 x CH), 128.0 (CH), 128.7 (CH), 126.0 (C), 119.8 (CH), 114.0 (2 x CH), 55.5 (OCH_3), 39.4 (CH_2), 21.4 (CH_3). ^1H NMR (500 MHz, $CDCl_3$): for **1v'** δ 7.84 (2H, dt, J = 9.0, 2.0 Hz), 7.37 (1H, d, J = 8.5 Hz), 7.33 (1H, d, J = 8.5 Hz), 7.05 (1H, dd, J = 8.5, 2.0 Hz), 6.95 (2H, dt, J = 9.0, 2.5 Hz), 6.08 (1H, s), 4.56 (2H, s), 3.86 (CH_3), 2.46 (CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): for **1v'** δ 166.15 (C), 166.10 (C), 161.5 (C), 146.8 (C), 139.9 (C), 134.4 (C), 127.4 (2 x CH), 126.6 (C), 124.8 (CH), 117.6 (CH), 113.9 (2 x CH), 109.4 (CH), 82.2 (CH), 55.4 (OCH_3), 21.5 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{16}NO_3$ 282.1130; Found 282.1135.

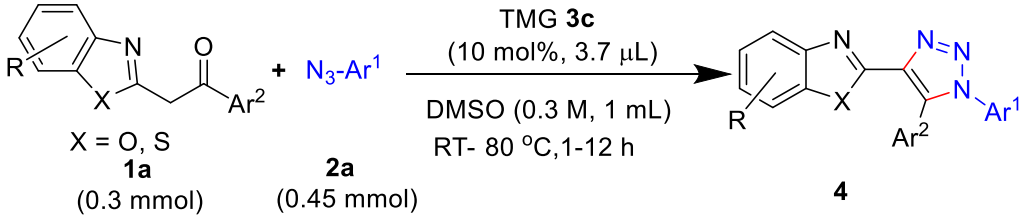
<u>Procedure B</u>: General procedure for the synthesis of aryl/alkyl azides 2.

The aryl/alkyl-azide derivatives were synthesized using literature procedures.[2]

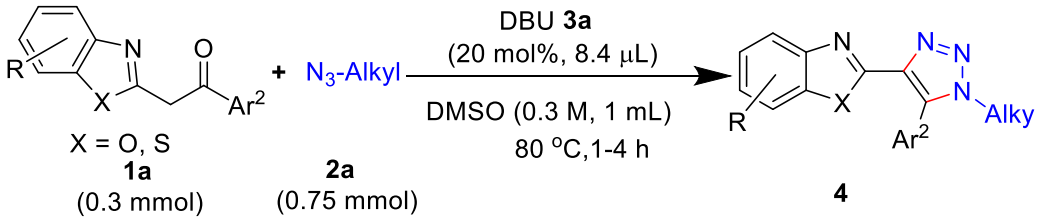
To a solution of substituted aniline (4.31 mmol, 1.0 equiv.) in H_2O (7.84 mL) was added ice (4.0 g) and followed by dropwise addition of 12 N conc. hydrochloric acid (1.57 mL) at 0 °C. Subsequently, a solution of $NaNO_2$ (0.32 g, 4.70 mmol, 1.09 equiv.) in water (4.89 mL) was added dropwise over 10 min with constant stirring. After stirring the reaction mixture for 15 min at 0 °C, a solution of NaN_3 (0.31 g, 4.70 mmol, 1.09 equiv.) in water (4.89 mL) was added dropwise to this mixture and it was allowed to stir at room temperature for 2-3 h. The crude reaction mixture was extracted with Et_2O (3 x 15 mL). The obtained organic layers were washed with saturated aqueous $NaHCO_3$ (3 x 15 mL), and brine (25 mL), treated with anhydrous Na_2SO_4, filtered and the solvents

were concentrated under reduced pressure. The crude product **2** was further purified through column chromatography on silica gel (eluent: Hexane) and obtained aryl/alkyl azides **2a-2p**, in 80-99% yields. The vinyl azides **2q**, **2r**,[3] benzyl azide **2s**,[4] and **2t**,[5] was synthesized by using the reported methods.

Procedure Ca: **General Procedure for the TMG-Catalysed Regioselective [3+2] Cycloaddition Reactions**: To an ordinary glass vial equipped with a magnetic stirring bar were added 0.3 mmol of **1**, 1.5 equiv. of aryl azide **2** and 0.03 mmol of tetramethyl guanidine **3c** (3.7µL, 0.1 equiv.) in 1.0 mL of DMSO (0.3 M). The reaction mixture was allowed to stir until complete consumption of **1** (monitored by TLC) at room temperature. The corresponding product **4** was purified by column chromatography (silica gel: 100-200 mesh; eluent: EA/hexanes).

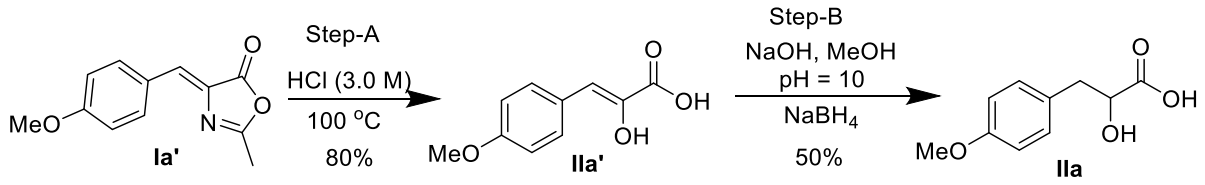


Procedure Cb: **General Procedure for the DBU-Catalysed Regioselective [3+2] Cycloaddition Reactions**: To an ordinary glass vial or sealed tube equipped with a magnetic stirring bar were added 0.3 mmol of **1**, 2.5 equiv. of alkyl azide **2** and 0.06 mmol of DBU **3a** (8.4 µL, 0.2 equiv.) in 1.0 mL of DMSO (0.3 M). The reaction mixture was allowed to stir at 80 °C until complete consumption of **1** (monitored by TLC) at room temperature. The corresponding product **4** was purified by column chromatography (silica gel: 100-200 mesh; eluent: EA/hexanes).

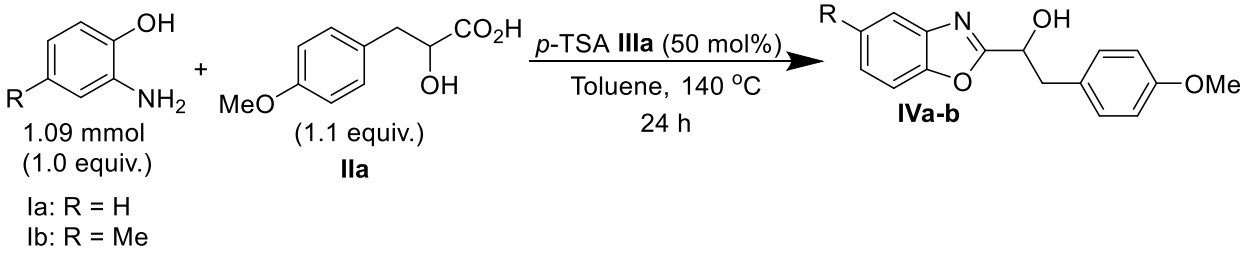


Procedure D: **General procedure for the synthesis of intermediate II:**

Step-A:[6] To a 100 mL round-bottom flask equipped with a magnetic stir bar, **Ia'** (2.01 g, 9.25 mmol) and 3.0 M HCl (54 mL) were added. The reaction mixture was heated to 100 °C for 8 h, cooled to room temperature, filtered, and residue was washed with water. The desired acid was obtained as a pale yellow solid **IIa'** after recrystallization (MeOH/H_2O) (1.44 g, 80% yield). IR (neat): ν_{max} 3441, 2957, 1712, 1610, 1510, 1231, 1176, 1073, 1030, 822 and 770 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 7.71 (2H, d, J = 8.5 Hz), 6.88 (2H, d, J = 9.0 Hz), 6.46 (1H, s), 3.79 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD, DEPT-135): δ 168.7 (C), 160.6 (C), 140.6 (C), 132.3 (2 x CH), 129.1 (C), 114.8 (2 x CH), 111.9 (CH), 55.8 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{10}O_4Na$ 217.0477; Found 217.0481.

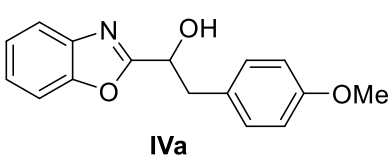


Step-B:[7] A mixture of NaOH (0.326 g, 8.1 mmol, 1.1 equiv.) and 16 mL methanol solution was prepared and brought to pH = 10 at 0 °C, then **IIa'** (1.44 g, 7.41 mmol) was added to the solution, after 10-15 minutes, $NaBH_4$ (0.422 g, 11.11 mmol, 1.5 equiv.) was added in portions. The solution was stirred overnight at room temperature, acidified with 1M HCl, saturated with NaCl, and extracted with EtOAc (10 mL) for five times. The combined organic layers were dried over Na_2SO_4, evaporated, and the crude product was column chromatographed on SiO_2 (MeOH and $CHCl_3$ (1:10) as eluent) to afford **IIa** as a white solid (0.727 g, 50% yield). Mp: 129-131 °C. IR (neat): ν_{max} 3443, 2958, 1713, 1510, 1250, 1177, 1074, 765, and 747 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 7.06 (2H, d, J = 8.5 Hz), 6.71 (2H, d, J = 8.5 Hz), 4.17 (1H, dd, J = 7.0, 4.5 Hz), 3.64 (3H, s), 2.92 (1H, dd, J = 13.5, 4.0 Hz), 2.73 (1H, dd, J = 14.0, 8.0 Hz). ^{13}C NMR (125 MHz, CD_3OD, DEPT-135): δ 177.3 (C), 160.0 (C), 131.6 (2 x CH), 130.8 (C), 114.7 (2 x CH), 73.0 (CH), 55.7 (OCH_3), 40.8 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{12}O_4Na$ 219.0633; Found 219.0637.



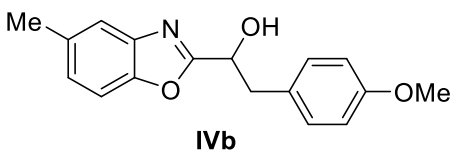
<u>Procedure E:</u> General procedure for the synthesis of intermediate IV:[8]

Using a Dean-Stark apparatus, in a 25 mL round-bottom flask equipped with a magnetic stir bar, **Ia** (1.09 mmol, 1.0 equiv.), **IIa** (1.199 mmol 1.1 equiv.), *p*-TSA **III** (104.19 mg, 0.547 mmol, 0.5 equiv.) and 2.0 mL of toluene was added and refluxed at 140 °C until the completion of the reaction was monitored by TLC. The reaction mixture was cooled to rt and toluene was evaporated under reduced pressure. The desired crude reaction mixture was loaded onto silica gel column and eluted using ethyl acetate/hexanes (0:10 to 1.5:8.5) to obtain as a brown solid of **1-(benzo[d]oxazol-2-yl)-2-(4-methoxyphenyl)ethan-1-ol (IVa):** Yield: 53% (155 mg). Mp: 128-130 °C. IR (neat): ν_{max} 3486, 2909, 1719, 1611, 1511, 1300, 1240, 1109, 823 and 772 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (1H, dd, J = 7.0, 3.5 Hz), 7.53 (1H, dd, J = 6.5, 2.5 Hz), 7.37-7.32 (2H, m), 7.13 (2H, d, J = 8.5 Hz), 6.81 (2H, d, J = 8.5 Hz), 5.15 (1H, dd, J = 8.0, 5.0 Hz), 3.77 (3H, s), 3.32 (1H, dd, J = 14.0, 5.0 Hz), 3.20 (1H, dd, J = 14.0, 5.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 166.7 (C), 158.6 (C), 150.7 (C), 140.4 (C), 130.5 (2 x CH), 128.0 (C), 125.2 (CH), 124.5 (CH), 120.1 (CH), 114.0 (2 x CH), 110.8 (CH), 69.1 (CH), 55.2 (OCH_3), 41.0 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}NO_3$ 270.1130; Found 270.1135.



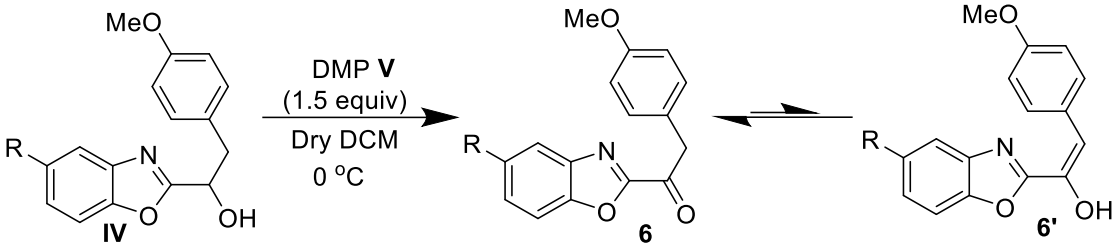
IVa

2-(4-Methoxyphenyl)-1-(5-methylbenzo[d]oxazol-2-yl)ethan-1-ol (IVb): Yield: 50% (154 mg). Mp: 129-131 °C. IR (neat): ν_{max} 3276, 2914, 1736, 1608, 1508, 1241, 1034, 802 and 554 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 (1H, s), 7.38 (1H, d, J = 8.5 Hz), 7.13 (1H, d, J = 9.0 Hz), 7.11 (2H, d, J = 8.5 Hz), 6.79 (2H, d, J = 8.5 Hz), 5.11 (1H, dd, J = 7.5, 5.0 Hz), 3.75 (3H, s), 3.59 (1H, br s), 3.30 (1H, dd, J = 14.0, 5.0 Hz), 3.18 (1H, dd, J = 14.0, 5.0 Hz), 2.44 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 167.0 (C), 158.6 (C), 149.0 (C), 140.6 (C), 134.4 (C), 130.5 (2 x CH), 128.2 (C), 126.3 (CH), 120.0 (CH), 114.0 (2 x CH), 110.1 (CH), 69.1 (CH), 55.2 (OCH_3), 41.0 (CH_2), 21.4 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{18}NO_3$ 284.1287; Found 284.1287.



IVb

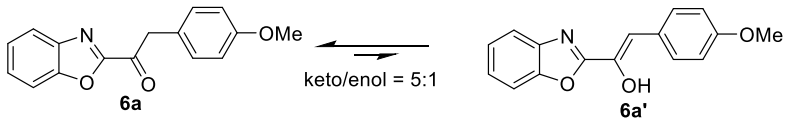
<u>Procedure F:</u> General procedure for the synthesis of ketones 6:[9]



R = H, Me
(0.8 mmol, 1.0 equiv.)

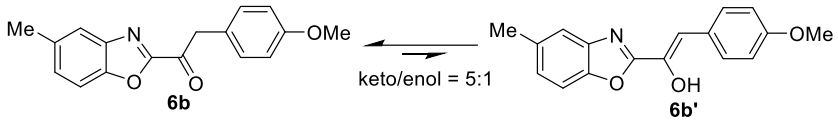
Dess–Martin periodinane (DMP) **V** (500 mg, 1.23 mmol, 1.5 equiv.) was added in portions to a stirred solution of **IV** (0.8 mmol, 1.0 equiv.) in anhydrous DCM (2 mL) at 0 °C. The solution was stirred at 25 °C for 2 h. The reaction mixture was diluted with EtOAc (20 mL) and quenched by the addition of 1:1 (v/v) aqueous $Na_2S_2O_3$/$NaHCO_3$ (25 mL) and stirred for 10 min. The organic layer was washed with H_2O (30 mL), saturated with aqueous NaCl, followed by concentration under reduced pressure, purified by column chromatography using ethyl acetate/hexanes (0:10 to 0.5:9.5), and isolated as a yellow solid compound.

1-(Benzo[d]oxazol-2-yl)-2-(4-methoxyphenyl)ethan-1-one (6a) and **(*Z*)-1-(benzo[d]oxazol-2-yl)-2-(4-methoxyphenyl)ethen-1-ol (6a'):** The title compound was prepared following



Procedure F, purified by column chromatography using ethyl acetate/hexanes (0:10 to 0.5:9.5) and isolated as a yellow solid compound. Yield 50% (111.3 mg). Mp: 80-82 °C. IR (neat): ν_{max} 3096, 2930, 1703, 1599, 1510, 1249, 1160, 1017, 751 and 703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **6a** δ 7.91 (1H, d, J = 8.0 Hz), 7.64 (1H, d, J = 8.0 Hz), 7.52 (1H, t, J = 8.0 Hz), 7.46 (1H, t, J = 8.0 Hz), 7.32 (2H, d, J = 8.5 Hz), 6.87 (2H, d, J = 8.5 Hz), 4.45 (2H, s), 3.78 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **6a** δ 187.5 (C), 159.0 (C), 157.1 (C), 151.0 (C), 140.6 (C), 130.9 (2 x CH), 128.6 (CH), 125.7 (CH), 124.6 (C), 122.4 (CH), 114.2 (2 x CH), 112.0 (CH), 55.2 (OCH_3), 45.0 (CH_2). ^1H NMR (500 MHz, $CDCl_3$): for **6a'** δ 9.90 (1H, s), 7.82 (2H, d, J = 8.5 Hz), 7.72-7.00 (1H, m), 7.52 (1H, t, J = 8.0 Hz), 7.37-7.35 (1H, m), 6.94 (2H, d, J = 8.5 Hz), 6.59 (H, br s), 3.85 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **6a'** δ 161.2 (C), 159.2 (C), 151.4 (C), 141.0 (C), 136.4 (C), 131.2 (2 x CH), 127.4 (C), 125.5 (CH), 124.8 (CH), 119.7 (CH), 114.1 (2 x CH), 110.7 (CH), 109.4 (CH), 55.2 (OCH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{14}NO_3$ 268.0974; Found 268.0973 and $C_{16}H_{13}NO_3Na$ 290.0793; Found 290.0794.

2-(4-Methoxyphenyl)-1-(5-methylbenzo[d]oxazol-2-yl)ethan-1-one (**6b**) and **(*Z*)-2-(4-methoxyphenyl)-1-(5-methylbenzo[d]oxazol-2-yl)ethen-1-ol** (**6b'**): The title compound was prepared following **Procedure F**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 0.5:9.5) and isolated as a yellow solid compound. Yield 50.5% (117.3 mg). Mp: 80-82 °C. IR (neat): ν_{max} 2998, 1759, 1703, 1602, 1514, 1245, 1176, 1017, and 814 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): for **6b** δ 7.68 (1H, s), 7.48 (1H, d, J = 8.5 Hz), 7.33-7.30 (1H, m), 7.30 (2H, d, J = 8.5 Hz), 6.86 (2H, d, J = 8.5 Hz), 4.42 (2H, s), 3.77 (3H, s), 2.45 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **6b** δ 187.5 (C), 158.9 (C), 157.2 (C), 149.2 (C), 140.8 (C), 135.8 (C), 130.9 (2 x CH), 130.0 (CH), 124.7 (C), 121.9 (CH), 114.2 (2 x CH), 111.3 (CH), 55.2 (OCH_3), 44.9 (CH_2), 21.5 (CH_3). ^1H NMR (500 MHz, $CDCl_3$): for **6b'** δ 9.88 (1H, s), 7.82 (2H, d, J = 8.0 Hz), 7.47-7.45 (1H, m), 7.39 (1H, d, J = 8.0 Hz), 7.15 (1H, d, J = 8.5 Hz), 6.93 (2H, d, J = 8.0 Hz), 6.56 (1H, s), 3.84 (3H, s), 2.46 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): for **6b'** δ 161.3 (C), 159.1 (C), 149.5 (C), 141.2 (C), 136.5 (C), 134.7 (C), 131.1 (2 x CH), 127.5 (C), 126.5 (CH), 119.6 (CH), 114.0 (2 x CH), 109.9 (CH), 109.2 (CH), 55.2 (OCH_3), 21.5 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{16}NO_3$ 282.1130; Found 282.1130.



<u>Procedure G:</u> General Procedure for the TMG-Catalysed Regioselective [3+2]-Cycloaddition Reactions for the Synthesis of 7: To an ordinary 5.0 mL round bottom flask equipped with a magnetic stirring bar were added 0.3 mmol of ketones **6**, 2.5 equiv. of alkyl azide **2** and 0.06 mmol of TMG **3c** (7.5 µL, 0.2 equiv.) in 1.0 mL of DMSO (0.3 M). The reaction mixture was allowed to stir at 80 °C until complete consumption of ketones **6** (monitored by TLC). The corresponding click products **7** was purified by column chromatography (silica gel: 100-200 mesh; eluent: EA/hexanes).

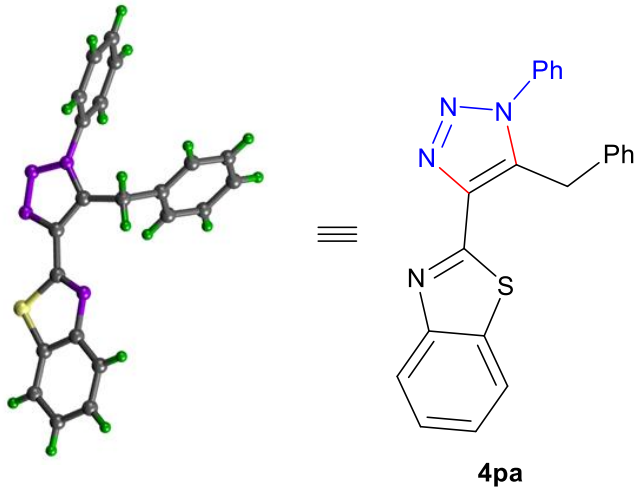


Figure-S1: The X-ray crystal structure of compound 2-(5-benzyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole **4pa**.

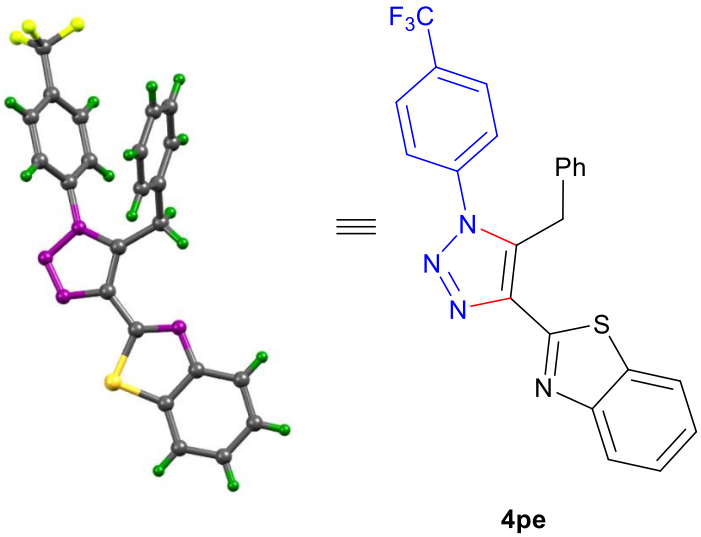
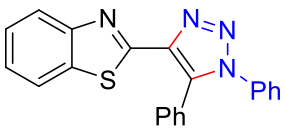


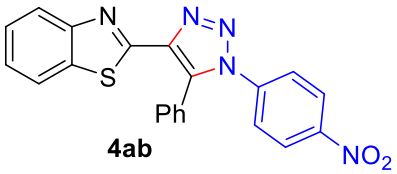
Figure-S2: The X-ray crystal structure of compound 2-(5-benzyl-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole **4pe**.

2-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4aa): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a light brown solid compound. Yield: 99% (105.2 mg). Mp: 130-133 °C. IR (neat): ν_{max} 1590, 1492, 1454, 1308, 1150, 1077, 993, 760, 692 and 586 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (1H, d, J = 8.0 Hz), 7.86 (1H, d, J = 8.0 Hz), 7.46-7.43 (3H, m), 7.41-7.37 (6H, m), 7.36-7.36 (3H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.7 (C), 153.7 (C), 140.0 (C), 135.9 (2 x C), 134.8 (C), 130.7 (2 x CH), 129.9 (CH), 129.3 (CH), 129.2 (2 x CH), 128.4 (2 x CH), 125.9 (CH), 125.7 (C), 125.2 (CH), 125.1 (2 x CH), 123.5 (CH), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{15}N_4S$ 355.1017; Found 355.1017.



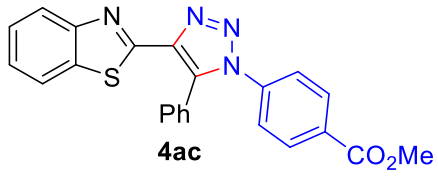
4aa

2-(1-(4-Nitrophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ab): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 99% (118.6 mg). Mp: 199-202 °C. IR (neat): ν_{max} 1593, 1516, 1341, 1286, 993, 947, 852, 749, 726, 691 and 487 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (2H, d, J = 9.0 Hz), 7.94 (1H, d, J = 8.5 Hz), 7.88 (1H, d, J = 8.0 Hz), 7.55-7.52 (3H, m), 7.49-7.47 (4H, m), 7.44 (1H, t, J = 7.5 Hz), 7.37 (1H, d, J = 8.0 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 157.9 (C), 153.7 (C), 147.5 (C), 140.75 (C), 140.70 (C), 135.9 (C), 134.9 (C), 130.4 (2 x CH), 130.5 (CH), 128.9 (2 x CH), 126.1 (CH), 125.5 (CH), 125.3 (2 x CH), 125.1 (C), 124.7 (2 x CH), 123.6 (CH), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}N_5O_2S$ 400.0868; Found 400.0868.



4ab

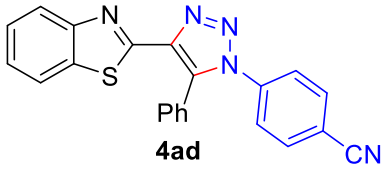
Methyl 4-(4-(benzo[*d*]thiazol-2-yl)-5-phenyl-1*H*-1,2,3-triazol-1-yl)benzoate (4ac): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as pale-yellow solid compound. Yield: 98% (121.3 mg). Mp: 161-163 °C. IR (neat): ν_{max} 1715, 1602, 1477, 1276, 1100, 993, 9951, 770, 753, 694, and 534 cm^{-}



4ac

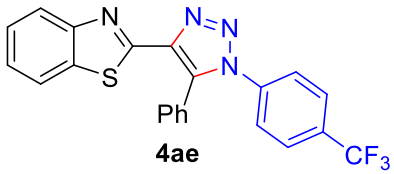
[1]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07-8.04 (2H, m), 7.94-7.92 (1H, m), 7.88-7.85 (1H, m), 7.49-7.46 (3H, m), 7.43-7.41 (5H, m), 7.37-7.32 (1H, m), 3.91 (3H, s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, DEPT-135): δ 165.7 (C, O-*C*=O), 158.3 (C), 153.7 (C), 140.3 (C), 139.4 (C), 135.9 (C), 134.9 (C), 130.7 (C), 130.7 (2 x CH), 130.6 (2 x CH), 130.1 (CH), 128.6 (2 x CH), 125.9 (CH), 125.4 (C), 125.3 (CH), 124.7 (2 x CH), 123.5 (CH), 121.4 (CH), 52.3 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{17}N_4O_2S$ 413.1072; Found 413.1075.

4-(4-(Benzo[*d*]thiazol-2-yl)-5-phenyl-1*H*-1,2,3-triazol-1-yl)benzonitrile (4ad): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow solid compound. Yield: 99% (112.6 mg). Mp: 218 °C. IR (neat): ν_{max} 2920, 1738, 1601, 1502, 1312, 1075, 991, 995, 945, 841, 765, 694, 563 and 534 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (1H, d, *J* = 8.0 Hz), 7.87 (1H, d, *J* = 7.5 Hz), 7.68 (2H, d, *J* = 9.0 Hz), 7.54-7.42 (8H, m), 7.39-7.35 (1H, m). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, DEPT-135): δ 157.9 (C), 153.6 (C), 140.6 (C), 139.3 (C), 135.9 (C), 134.9 (C), 133.2 (2 x CH), 130.6 (2 x CH), 130.5 (CH), 128.8 (2 x CH), 126.1 (CH), 125.4 (CH), 125.3 (2 x CH), 125.1 (C), 123.6 (CH), 121.4 (CH), 117.5 (C), 113.1 (C). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{13}N_5SNa$ 402.0789; Found 402.0788.



4ad

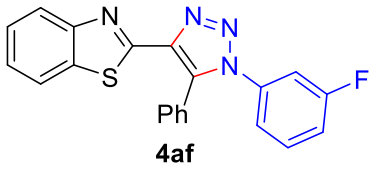
2-(5-Phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ae): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as an off-white solid compound. Yield: 91% (125.4 mg). Mp: 158-161 °C. IR (neat): ν_{max} 1612, 1518, 1422, 1319, 1167, 1117, 1063, 992, 946, 856, 753, 694, 692 and 606 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (1H, d, *J* = 8.5 Hz), 7.88 (1H, dd, *J* = 8.0, 1.5 Hz), 7.67 (2H, d, *J* = 7.0 Hz), 7.52-7.42 (8H, m), 7.38-7.36 (1H, m). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.2 (C), 153.7 (C), 140.5 (C), 138.8 (C), 135.9 (C), 134.9 (C), 131.3 (C, q, $^{2}J_{C-F}$ = 32.5 Hz), 130.7 (2 x CH), 130.3 (CH), 128.9 (2 x CH), 126.5 (2 x CH, q, $^{3}J_{C-F}$ = 3.75 Hz), 126.1 (CH), 125.4 (CH), 125.3 (C), 125.2 (2 x CH), 123.6 (CH), 123.4 (C, q, $^{1}J_{C-F}$ = 270.0



4ae

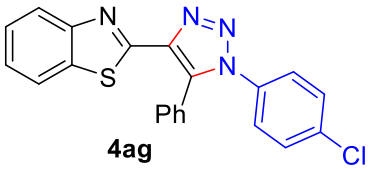
Hz), 121.4 (CH). ^{19}F NMR (470 MHz, $CDCl_3$): -62.74 (C, *C*F_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{14}F_3N_4S$ 423.0891; Found 423.0888.

2-(1-(3-Fluorophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4af): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0.10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 98% (109.5 mg). Mp: 131-133 °C. IR (neat): ν_{max} 1599, 1522, 1492, 1451, 1217, 1138, 1074, 947, 863, 784, 760, 709, 690 and 674 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (1H, dt, J = 8.4, 0.4 Hz), 7.88 (1H, dt, J = 8.0, 0.8 Hz), 7.51-7.40 (6H, m), 7.38-7.32 (2H, m), 7.15-7.10 (3H, m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, DEPT-135): δ 162.4 (C, d, $^1J_{C\text{-}F}$ = 247.0 Hz), 158.3 (C), 153.7 (C), 140.2 (C), 137.2 (C, d, $^3J_{C\text{-}F}$ = 10.0 Hz), 135.9 (C), 134.9 (C), 130.6 (2 x CH), 130.5 (CH), 130.2 (CH), 128.6 (2 x CH), 126.0 (CH), 125.4 (C), 125.3 (CH), 123.5 (CH), 121.4 (CH), 120.7 (CH, d, $^2J_{C\text{-}F}$ = 3.0 Hz), 116.4 (CH, d, $^3J_{C\text{-}F}$ = 3.0 Hz), 112.7 (CH, d, $^2J_{C\text{-}F}$ = 5.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): -109.85 (*C*-F). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{13}FN_4SNa$ 395.0743; Found 395.0743.



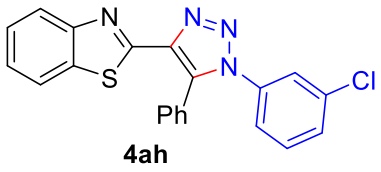
4af

2-(1-(4-Chlorophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ag): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 99% (115.5 mg). Mp: 150-153 °C. IR (neat): ν_{max} 1492, 1475, 1312, 1287, 1089, 945, 822, 757, 696 and 524 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (1H, dd, J = 7.0, 1.0 Hz), 7.87 (1H, dd, J = 8.0, 0.5 Hz), 7.49-7.41 (6H, m), 7.38-7.34 (3H, m), 7.30-7.25 (2H, m). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.4 (C), 153.7 (C), 140.2 (C), 135.9 (C), 135.3 (C), 134.9 (C), 134.5 (C), 130.7 (2 x CH), 130.1 (CH), 129.5 (2 x CH), 128.6 (2 x CH), 126.2 (2 x CH), 126.0 (CH), 125.4 (C), 125.3 (CH), 123.5 (CH), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}ClN_4S$ 389.0628; Found 389.0625.



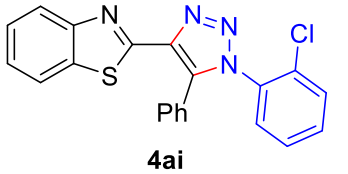
4ag

2-(1-(3-Chlorophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ah): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 93% (108.5 mg). Mp: 151-154 °C. IR (neat): ν_{max} 1688, 1629, 1514, 1453, 1382, 1347, 1191, 1120, 905, 724 and 647 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (1H, d, J = 8.5 Hz), 7.88 (1H, d, J = 8.0 Hz), 7.51-7.41 (8H, m), 7.39-7.35 (1H, m), 7.32-7.29 (1H, m), 7.16 (1H, d, J = 8.0 Hz). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 158.3 (C), 153.6 (C), 140.2 (C), 136.9 (C), 135.9 (C), 135.0 (C), 134.8 (C), 130.6 (3 x CH), 130.2 (C), 130.2 (CH), 129.5 (CH), 128.7 (2 x CH), 126.0 (CH), 125.3 (2 x CH), 123.5 (CH), 123.1 (CH), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}ClN_4S$ 389.0628; Found 389.0630.



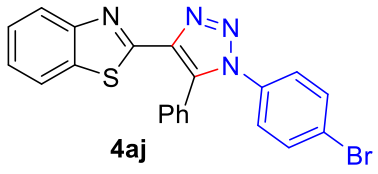
4ah

2-(1-(2-Chlorophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ai): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 60% (70 mg). Mp: 130-143 °C. IR (neat): ν_{max} 1519, 1480, 1441, 1281, 1080, 993, 949, 759, 727 and 692 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (1H, d, J = 8.0 Hz), 7.89 (1H, d, J = 8.0 Hz), 7.48-7.33 (11H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.7 (C), 153.7 (C), 139.3 (C), 137.8 (C), 134.9 (C), 133.8 (C), 131.9 (C), 131.6 (CH), 130.5 (CH), 130.2 (2 x CH), 129.9 (CH), 129.5 (CH), 128.2 (2 x CH), 127.6 (CH), 125.9 (CH), 125.3 (CH), 125.1 (C), 123.5 (CH), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}ClN_4S$ 389.0628; Found 389.0627.



4ai

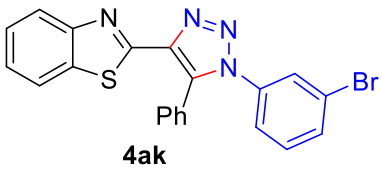
2-(1-(4-Bromophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4aj): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 93% (120.9 mg). Mp: 158-160 °C. IR (neat): ν_{max} 1484, 1367, 1217, 991, 946, 838, 819, 755, 726 and 519 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$):



4aj

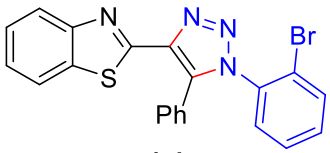
δ 7.94 (1H, d, J = 9.0 Hz), 7.88 (1H, dd J = 8.0, 0.8 Hz), 7.55-7.50 (2H, m), 7.49-7.47 (1H, m), 7.45-7.41 (5H, m), 7.36 (1H, td, J = 7.6, 1.2 Hz), 7.24-7.20 (2H, m). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 158.4 (C), 153.7 (C), 140.2 (C), 135.9 (C), 135.0 (C), 134.9 (C), 132.5 (2 x CH), 130.7 (2 x CH), 130.2 (CH), 128.7 (2 x CH), 126.5 (2 x CH), 126.0 (CH), 125.4 (C), 125.3 (CH), 123.5 (CH), 123.4 (C), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}BrN_4S$ 433.0123; Found 433.0127.

2-(1-(3-Bromophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ak): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 98% (127.4 mg). Mp: 144-147 °C. IR (neat): ν_{max} 1582, 1479, 1429, 1298, 1248, 1072, 1039, 997, 947, 794, 764, 750 and 611 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (1H, d, J = 7.6 Hz), 7.89 (1H, dd, J = 7.2, 0.8 Hz), 7.57-7.54 (1H, m), 7.57-7.54 (1H, m), 7.51-7.35 (6H, m), 7.37 (1H, td, J = 7.2, 1.2 Hz), 7.27-7.18 (2H, m). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 158.3 (C), 153.7 (C), 140.2 (C), 137.0 (C), 135.9 (C), 134.9 (C), 134.4 (CH), 130.7 (2 x CH), 130.4 (CH), 130.2 (CH), 128.7 (2 x CH), 128.2 (CH), 126.0 (CH), 125.3 (CH), 123.6 (2 x CH), 123.6 (C), 122.7 (C), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{13}BrN_4SNa$ 454.9942; Found 454. 9939.



4ak

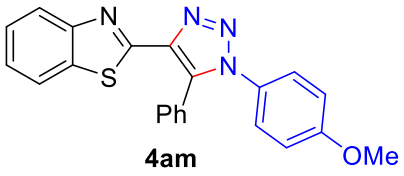
2-(1-(2-Bromophenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4al): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white-yellow solid compound. Yield: 60% (80.0 mg). Mp: 154-159 °C. IR (neat): ν_{max} 1624, 1573, 1509, 1354, 1233, 1218, 1124, 915, 799, 726, 714, 685 and 656 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (1H, d, J = 8.0 Hz), 7.89 (1H, d, J = 8.0, Hz), 7.66 (1H, d, J = 7.5 Hz), 7.48 (2H, d, J = 7.5 Hz), 7.45-7.39 (4H, m), 7.38-7.33 (4H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.7 (C), 153.7 (C), 139.3 (C), 137.6 (C), 135.5 (C), 134.9 (C), 133.7 (CH), 131.9 (CH), 130.4 (2 x CH), 129.9 (CH), 129.7 (2 x CH), 128.2 (2 x CH), 125.9 (CH), 125.3 (CH), 125.2 (C), 123.5 (CH),



4al

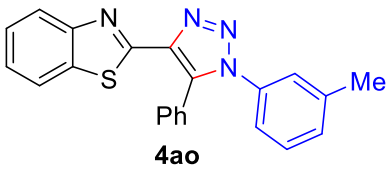
121.8 (C), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}BrN_4S$ 433.0123; Found 433.0122.

2-(1-(4-Methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4am): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 70% (80.73 mg). Mp: 190-193 °C. IR (neat): ν_{max} 1511, 1476, 1447, 1366, 1250, 1229, 1043, 946, 832, 766, 692 and 578 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (1H, d, J = 8.0 Hz), 7.87 (1H, d, J = 8.0 Hz), 7.47-7.39 (6H, m), 7.37-7.33 (1H, m), 7.27-7.24 (2H, m), 6.88 (2H, dd, J = 12.0, 3.0 Hz), 3.81 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.1 (C), 158.9 (C), 153.8 (C), 139.9 (C), 136.0 (C), 134.9 (C), 130.7 (2 x CH), 129.8 (CH), 129.1 (C), 128.4 (2 x CH), 126.6 (2 x CH), 125.93 (CH), 125.91 (C), 125.2 (CH), 123.5 (CH), 121.4 (CH), 114.4 (2 x CH), 55.5 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}N_4OS$ 385.1123; Found 385.1121.



4am

2-(5-Phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4an): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a yellow-solid compound. Yield: 70% (77.37 mg). Mp: 197-200 °C. IR (neat): ν_{max} 1510, 1367, 1228, 995, 946, 818, 764, 693, and 584 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (1H, d, J = 8.0 Hz), 7.86 (1H, d, J = 8.0 Hz), 7.46-7.38 (6H, m), 7.36-7.33 (1H, m), 7.25-7.16 (4H, m), 2.36 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.8 (C), 153.7 (C), 139.9 (C), 139.5 (2 x C), 135.9 (C), 134.9 (C), 133.6 (C), 130.7 (2 x CH), 129.8 (2 x CH), 129.8 (2 x CH), 128.4 (CH), 125.9 (CH), 125.2 (2 x CH), 124.9 (CH), 123.5 (CH), 121.4 (CH), 21.1 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{16}N_4SNa$ 391.0993; Found 391.0994.



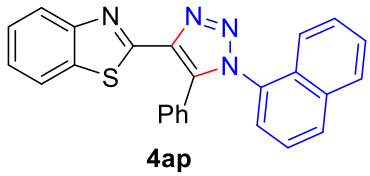
4an

2-(5-Phenyl-1-(*m*-tolyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ao): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to

4ao

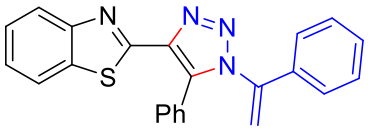
1.5:8.5) and isolated as a pale-yellow solid. Yield: 88% (97.3 mg). Mp: 197-200 °C. IR (neat): ν_{max} 1475, 1435, 1294, 1272, 1093, 1040, 946, 868, 783, 730 and 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (1H, d, J = 8.0 Hz), 7.86 (1H, d, J = 8.0 Hz), 7.47-7.32 (7H, m), 7.24-7.19 (3H, m), 7.02 (1H, d, J = 7.2 Hz), 2.33 (3H, s). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 158.7 (C), 153.7 (C), 139.9 (C), 139.5 (C), 135.99 (C), 135.54 (C), 134.9 (C), 130.7 (2 x CH), 130.1 (CH), 129.8 (CH), 128.9 (CH), 128.4 (2 x CH), 125.9 (CH), 125.8 (C), 125.8 (CH), 125.2 (CH), 123.5 (CH), 122.1 (CH), 121.3 (CH), 21.2 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}N_4S$ 369.1174; Found 369.1174.

2-(1-(Naphthalen-1-yl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ap): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 93% (112.8 mg). Mp: 145-149 °C. IR (neat): ν_{max} 1595, 1510, 1471, 1418, 1313, 1272, 1126, 958, 944, 917, 798 and 758 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (2H, d, J = 8.0 Hz), 7.92-7.90 (2H, m), 7.65-7.50 (4H, m), 7.47-7.42 (2H, m), 7.40-7.36 (3H, m), 7.31-7.27 (1H, m), 7.23-7.20 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.9 (C), 153.8 (C), 139.4 (C), 138.2 (C), 134.9 (C), 133.9 (C), 132.2 (C), 130.7 (CH), 130.1 (2 x CH), 129.8 (CH), 129.7 (C), 128.2 (CH), 128.2 (2 x CH), 127.9 (CH), 127.0 (CH), 126.0 (CH), 125.6 (CH), 125.4 (C), 125.3 (CH), 124.8 (CH), 123.5 (CH), 122.3 (CH), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{17}N_4S$ 405.1174; Found 405.1175.



4ap

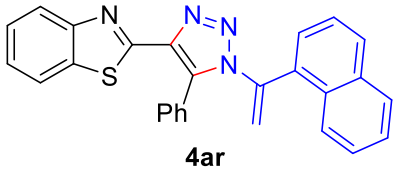
2-(5-Phenyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4aq): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid. Yield: 61% (69.6 mg). Mp: 159-161 °C. IR (neat): ν_{max} 1640, 1595, 1518, 1475, 1448, 1413, 1343, 1114, 1010, 947, 912, 773, 765 and 695 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (1H, d, J = 8.0 Hz), 7.86 (1H, J = 7.5 Hz), 7.45-7.40 (3H, m), 7.36-7.21 (4H, m), 7.29-7.21 (3H, m), 7.11 (2H, dd, J = 8.0, 1.5 Hz), 5.87 (1H, s), 5.60 (1H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.6 (C), 153.7 (C), 142.4 (C), 139.6 (C), 136.8 (C), 134.9 (C),



4aq

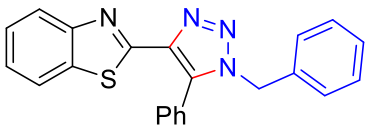
134.7 (C), 130.2 (2 x CH), 129.8 (CH), 129.4 (CH), 128.5 (2 x CH), 128.1 (2 x CH), 125.9 (CH), 125.8 (2 x CH), 125.6 (C), 125.2 (CH), 123.5 (CH), 121.4 (CH), 115.3 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{17}N_4S$ 381.1174; Found 381.1173.

2-(1-(1-(Naphthalen-1-yl)vinyl)-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ar): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 80% (103.3 mg). Mp: 177-180 °C. IR (neat): ν_{max} 1688, 1628, 1543, 1478, 1434, 1282, 1227, 1015, 946, 898, 808, 753, 721 and 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (1H, d, *J* = 8.0 Hz), 7.88 (1H, *J* = 8.0 Hz), 7.76-7.70 (3H, m), 7.48-7.41 (6H, m), 7.37-7.33 (2H, m), 7.30-7.25 (3H, m), 6.01 (1H, s), 5.64 (1H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.8 (C), 153.8 (C), 142.4 (C), 139.7 (C), 137.1 (C), 134.9 (C), 133.5 (C), 132.9 (C), 132.0 (C), 130.1 (2 x CH), 129.9 (CH), 128.6 (CH), 128.5 (CH), 128.2 (2 x CH), 127.6 (CH), 127.1 (CH), 126.7 (CH), 126.0 (CH), 125.7 (CH), 125.97 (C), 125.3 (CH), 123.6 (CH), 122.8 (CH), 121.4 (CH), 115.8 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{19}N_4S$ 431.1330; Found 431.1332.



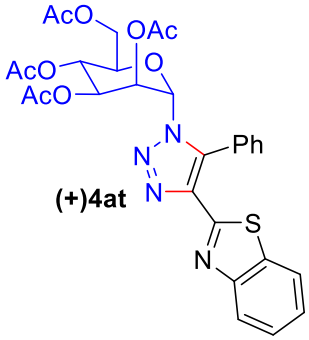
4ar

2-(1-Benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4as): The title compound was prepared following **Procedure Cb** employing catalyst **3a** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 74% (82.0 mg). Mp: 118-121 °C. IR (neat): ν_{max} 1594, 1521, 1449, 1433, 1311, 1229, 1119, 964, 937, 819, 765, 730 and 693 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (1H, d, *J* = 3.0 Hz), 7.83 (1H, *J* = 2.5 Hz), 7.54 (1H, tt, *J* = 7.5, 1.0 Hz), 7.49-7.46 (2H, m), 7.39 (1H, td, *J* = 8.0, 1.0 Hz), 7.35-7.32 (3H, m), 7.28-7.26 (3H, m), 7.07-7.05 (2H, m), 5.49 (2H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 158.6 (C), 153.6 (C), 140.1 (C), 136.6 (C), 134.8 (C), 134.7 (C), 130.3 (2 x CH), 130.2 (CH), 128.8 (4 x CH), 128.3 (CH), 127.5 (2 x CH), 125.9 (CH), 125.8 (C), 125.1 (CH), 123.4 (CH), 121.4 (CH), 52.2 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}N_4S$ 369.1174; Found 369.1174.

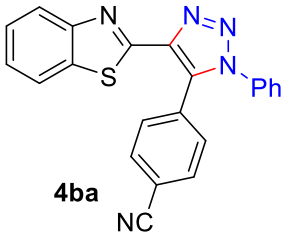


4as

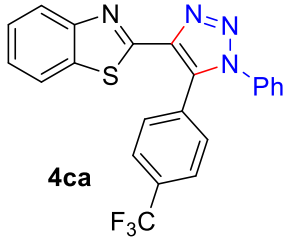
(2*R*,3*R*,5*S*,6*S*)-2-(Acetoxymethyl)-6-(4-(benzo[*d*]thiazol-2-yl)-5-phenyl-1*H*-1,2,3-triazol-1 yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (4at): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 76% (138.7 mg). Mp: 95-97 °C. $[\alpha]_D^{25}$ = (+) 78.2 (*c* = 0.1, MeOH). IR (neat): ν_{max} 1746, 1712, 1437, 1367, 1325, 1218, 1125, 1053, 950, 732 and 699 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.92-7.89 (2H, m), 7.68-7.66 (2H, m), 7.61-7.55 (3H, m), 7.44-7.41 (1H, m), 7.39-7.36 (1H, m), 6.37 (1H, dd, *J* = 9.5, 4.0 Hz), 5.84 (1H, dd, *J* = 9.0, 2.0 Hz), 5.80 (1H, d, *J* = 1.5 Hz), 5.45 (1H, t, *J* = 10.0 Hz), 4.35 (1H, dd, *J* = 12.0, 5.5 Hz), 4.26-4.23 (1H, m), 4.05 (1H, dd, *J* = 12.5, 2.5 Hz), 2.14 (3H, s), 2.10 (3H, s), 2.08 (3H, s), 2.03 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 170.3 (C), 169.7 (C), 169.6 (C), 169.3 (C), 158.1 (C), 153.7 (C), 140.0 (C), 137.5 (C), 134.9 (C), 130.7 (2 x CH), 130.7 (CH), 128.8 (2 x CH), 126.0 (CH), 125.4 (CH), 124.6 (C), 123.6 (CH), 121.4 (CH), 82.0 (CH), 71.8 (CH), 69.2 (CH), 69.1 (CH), 66.0 (CH), 61.9 (CH_2), 20.6 (3 x CH_3), 20.5 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{29}N_4O_9S$ 609.1655; Found 609.1656.



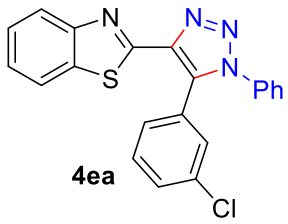
4-(4-(Benzo[*d*]thiazol-2-yl)-1-phenyl-1*H*-1,2,3-triazol-5-yl)benzonitrile (4ba): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 96% (109.2 mg). Mp: 159-162 °C. IR (neat): ν_{max} 2234, 1591, 1454, 1435, 1313, 1272, 1161, 994, 948, 814, 841, 759, 730, 690 and 592 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (1H, d, *J* = 7.5 Hz), 7.89 (1H, d, *J* = 8.5 Hz), 7.69 (2H, d, *J* = 8.5 Hz), 7.63 (2H, d, *J* = 8.5 Hz), 7.50-7.44 (4H, m), 7.41-7.38 (1H, m), 7.33-7.31 (2H, m). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.4 (C), 153.7 (C), 140.4 (C), 135.6 (C), 134.9 (C), 133.8 (C), 131.9 (2 x CH), 131.6 (2 x CH), 130.6 (C), 129.9 (CH), 129.6 (2 x CH), 126.2 (CH), 125.6 (CH), 125.3 (2 x CH), 123.5 (CH), 121.6 (CH), 118.1 (C), 113.6 (C). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{14}N_5S$ 380.0970; Found 380.0971.



2-(1-Phenyl-5-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ca): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 82% (103.9 mg). Mp: 178-180 °C. IR (neat): ν_{max} 1623, 1594, 1553, 1493, 1434, 1322, 1156, 1130, 1067, 949, 843, 759, 730, 688 and 615 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (1H, d, J = 8.0 Hz), 7.90 (1H, d, J = 8.0 Hz), 7.67-7.63 (4H, m), 7.48-7.42 (4H, m), 7.38 (1H, td, J = 7.5, 1.0 Hz), 7.34-7.32 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.6 (C), 153.7 (C), 140.3 (C), 135.7 (C), 134.9 (C), 134.3 (C), 131.7 (C, q, $^{2}J_{C-F}$ = 32.5 Hz), 131.3 (2 x CH), 129.7 (CH), 129.6 (C), 129.5 (2 x CH), 126.1 (CH), 125.5 (CH), 125.3 (2 x CH), 125.2 (2 x CH, q, $^{3}J_{C-F}$ = 3.75 Hz), 123.7 (C, q, $^{1}J_{C-F}$ = 270.1 Hz), 123.5 (CH), 121.5 (CH). ^{19}F NMR (376 MHz, $CDCl_3$): -62.86 (C, CF_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{14}F_3N_4S$ 423.0891; Found 423.0884.



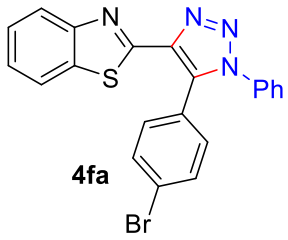
2-(5-(4-Chlorophenyl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4da): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale yellow solid compound. Yield: 81% (94.5 mg). Mp: 150-153 °C. IR (neat): ν_{max} 1594, 1495, 1476, 1455, 1267, 1091, 1074, 947, 848, 830, 756, 730, 688 and 612 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (1H, d, J = 8.0 Hz), 7.89 (1H, d, J = 8.0 Hz), 7.45-7.41 (6H, m), 7.39-7.36 (3H, m), 7.34-7.32 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.7 (C), 153.7 (C), 140.0 (C), 136.1 (C), 135.8 (C), 134.9 (C), 134.7 (C), 132.1 (2 x CH), 129.6 (CH), 129.4 (2 x CH), 128.7 (2 x CH), 126.0 (CH), 125.3 (CH), 125.2 (2 x CH), 124.2 (C), 123.5 (CH), 121.5 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}ClN_4S$ 389.0628; Found 389.0627.



2-(5-(3-Chlorophenyl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ea): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 84% (98 mg). Mp: 175-178 °C. IR

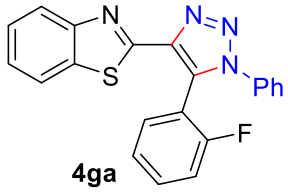
(neat): ν_{max} 1591, 1562, 1493, 1436, 1283, 1155, 1073, 951, 882, 788, 760, 628 and 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (1H, d, J = 8.0 Hz), 7.90 (1H, d, J = 8.0 Hz), 7.63-7.62 (1H, m), 7.45-7.41 (5H, m), 7.39-7.35 (3H, m), 7.33-7.29 (1H, m), 7.28-7.27 (1H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.5 (C), 153.7 (C), 140.2 (C), 135.8 (C), 134.9 (C), 134.4 (C), 134.3 (C), 130.9 (CH), 130.0 (CH), 129.6 (CH), 129.6 (CH), 129.4 (2 x CH), 128.8 (CH), 127.5 (C), 126.1 (CH), 125.4 (CH), 125.2 (2 x CH), 123.6 (CH), 121.5 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}ClN_4S$ 389.0628; Found 389.0629.

2-(5-(4-Bromophenyl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4fa): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white-yellow solid compound. Yield: 90% (117 mg). Mp: 208-210 °C. IR (neat): ν_{max} 1591, 1493, 1476, 1452, 1434, 1272, 1157, 1067, 1037, 946, 831, 758, 731 and 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (1H, dt, J = 8.0, 1.0 Hz), 7.91 (1H, dt, J = 8.0, 1.0 Hz), 7.53 (2H, td, J = 7.5, 2.5 Hz), 7.45-7.41 (4H, m), 7.39-7.35 (3H, m), 7.34-7.25 (2H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.7 (C), 153.7 (C), 140.0 (C), 135.8 (C), 134.9 (C), 134.7 (C), 132.3 (2 x CH), 131.7 (2 x CH), 129.6 (CH), 129.5 (2 x CH), 126.0 (CH), 125.4 (CH), 125.2 (2 x CH), 124.7 (C), 124.5 (C), 123.5 (CH), 121.5 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}BrN_4S$ 433.0123; Found 433.0123.



4fa

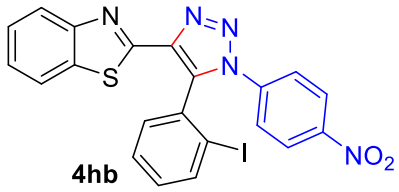
2-(5-(2-Fluorophenyl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ga): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale yellow solid. Mp: 162-164 °C. Yield: 60% (67 mg). IR (neat): ν_{max} 1593, 1477, 1452, 1432, 1236, 1104, 949, 917, 816, 761, 725 and 689 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90-7.88 (2H, m), 7.51-7.47 (2H, m), 7.43-7.34 (7H, m), 7.26-7.26 (1H, m), 7.12-709 (1H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 159.9 (C, d, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 158.2 (C), 153.8 (C), 141.2 (C), 136.0 (C), 134.8 (C), 132.5 (CH, d, $^{4}J_{C\text{-}F}$ = 1.25 Hz), 132.4 (CH, d, $^{3}J_{C\text{-}F}$ = 8.75 Hz), 130.4 (C), 129.5 (CH), 129.3 (2 x CH), 125.9 (CH), 125.3 (CH), 124.5 (2 x CH), 124.2 (CH, d, $^{3}J_{C\text{-}F}$ = 3.75 Hz), 123.5 (CH), 121.4 (CH),



4ga

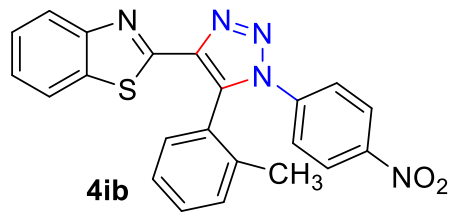
116.0 (CH, d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 114.5 (C, d, $^{2}J_{C\text{-}F}$ = 13.75 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): -110.31 (*C*-F). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}FN_4S$ 373.0923; Found 373.0926.

2-(5-(2-Iodophenyl)-1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (**4hb**): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0.0:1.0 to 1.5:8.5) and isolated as a brown solid compound. Yield: 58% (91.4 mg). Mp:122-125 °C. IR (neat): ν_{max} 1638, 1578, 1503, 1472, 1428, 1347, 1274, 1239, 1039, 1015, 911, 782, 743 and 635 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$ +$MeOD_4$): δ 8.31-8.27 (2H, m), 8.02-7.92 (2H, m), 7.89-7.84 (1H, m), 7.67-7.61 (2H, m), 7.59-7.52 (1H, m), 7.50-7.44 (2H, m), 7.42-7.40 (1H, m), 7.38-7.32 (1H, m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$+$MeOD_4$, DEPT-135): δ 156.8 (C), 153.3 (C), 147.6 (C), 141.2 (C), 140.5 (C), 139.9 (CH), 137.8 (C), 134.6 (C), 132.2 (CH), 132.0 (CH), 131.1 (C), 128.8 (CH), 126.2 (CH), 125.5 (CH), 124.7 (4 x CH), 123.4 (CH), 121.4 (CH), 99.7 (C). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{13}IN_5O_2S$ 525.9835; Found 525.9841.



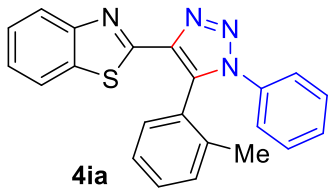
4hb

2-(1-(4-Nitrophenyl)-5-(*o*-tolyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (**4ib**)**:** The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (:10 to 1.5:8.5) and isolated as a light brown solid compound. Yield: 61% (75.6 mg). Mp: 159-162 °C. IR (neat): ν_{max} 1593, 1525, 1496, 1474, 1434, 1344, 1275, 1160, 1113, 991, 946, 849, 762 and 683 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24-8.22 (2H, m), 8.95 (1H, d, *J* = 8.0 Hz), 7.84 (1H, d, *J* = 7.5 Hz), 7.56 (2H, d, *J* = 8.0 Hz), 7.52-7.49 (1H, m), 7.45-7.43 (1H, m), 7.38-7.30 (4H, m), 2.01 (3H, s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, DEPT-135): δ 176.3 (C), 153.6 (C), 147.5 (C), 141.6 (C), 140.9 (C), 138.2 (C), 135.6 (C), 134.8 (C), 131.1 (CH), 131.0 (CH), 130.7 (CH), 126.7 (CH), 126.2 (CH), 125.5 (CH), 125.3 (C), 124.8 (2 x CH), 124.1 (2 x CH), 123.7 (CH), 121.4 (CH), 19.7 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{16}N_5O_2S$ 414.1025; Found 414.1026.



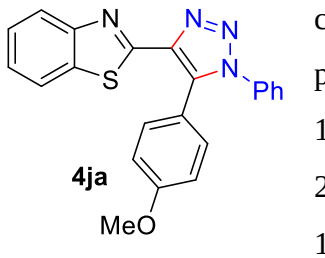
4ib

2-(1-Phenyl-5-(*o*-tolyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ia): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes ():10 to 1.5:8.5) and isolated as a light brown compound. Yield: 50% (55.3 mg). Mp: 185-189 °C. IR (neat): ν_{max} 1593, 1494, 1436, 1364, 1434, 1225, 994, 945, 759, 732 and 689 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (1H, d, J = 8.0 Hz), 7.83 (1H, d, J = 7.5, 1.0 Hz), 7.45-7.40 (2H, m), 7.38-7.34 (6H, m), 7.33-7.30 (1H, m), 7.28-7.27 (2H, m), 2.05 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.1 (C), 153.7 (C), 140.9 (C), 138.3 (C), 136.2 (C), 135.7 (C), 134.7 (C), 130.9 (CH), 130.7 (CH), 130.4 (CH), 129.6 (2 x CH), 129.2 (CH), 126.3 (CH), 126.0 (CH), 125.9 (C), 125.2 (CH), 124.1 (2 x CH), 123.6 (CH), 121.4 (CH), 19.8 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}N_4S$ 369.1174; Found 369.1173.



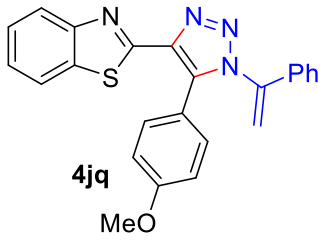
4ia

2-(5-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ja): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid. Yield: 94% (108.4 mg). Mp: 199-201 °C. IR (neat): ν_{max} 1613, 1598, 1492, 1464, 1449, 1295, 1254, 1175, 1016, 945, 834, 755, 685, and 588 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (1H, d, J = 8.0 Hz), 7.88 (1H, t, J = 7.0 Hz), 7.44-7.26 (9H, m), 6.92 (2H, dd, J = 8.5, 3.0 Hz), 3.80 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.7 (C), 158.9 (C), 153.7 (C), 139.8 (C), 136.2 (C), 136.0 (C), 134.9 (C), 132.2 (2 x CH), 129.3 (2 x CH), 129.3 (CH), 125.9 (CH), 125.22 (2 x CH), 125.18 (CH), 123.5 (CH), 121.4 (CH), 117.5 (C), 113.9 (2 x CH), 55.3 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}N_4OS$ 385.1123; Found 385.1125.



4ja

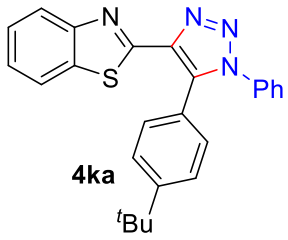
2-(5-(4-Methoxyphenyl)-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4jq): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a pale-yellow solid compound. Yield: 80% (98.5 mg). Mp: 115-118 °C. IR (neat): ν_{max} 1612, 1489, 1437, 1349, 1254, 1178, 945, 834, 765, 727, and 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (1H, d, J = 8.0 Hz), 7.87 (1H, d, J = 8.0 Hz), 7.44-7.38 (3H, m), 7.37-7.33



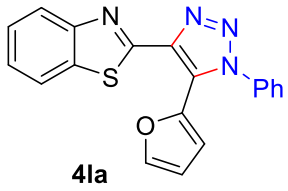
4jq

(1H, m), 7.27-7.23 (3H, m), 7.13 (2H, dd, *J* = 8.0, 1.5 Hz), 6.83 (2H, d, *J* = 8.5 Hz), 5.89 (1H, d, *J* = 0.5 Hz), 5.58 (1H, d, *J* = 1.0 Hz), 3.79 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): *δ* 160.7 (C), 158.9 (C), 153.8 (C), 142.6 (C), 139.4 (C), 136.9 (C), 134.9 (C), 134.8 (C), 131.7 (2 x CH), 129.5 (CH), 128.6 (2 x CH), 126.0 (CH), 125.8 (2 x CH), 125.2 (CH), 123.5 (CH), 121.4 (CH), 117.5 (C), 115.4 (CH_2), 113.8 (2 x CH), 55.3 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}N_4OS$ 411.1280; Found 411.1281.

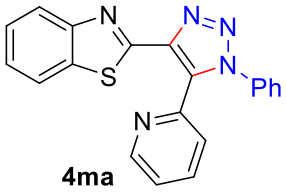
2-(5-(4-(*tert*-Butyl)phenyl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ka): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a brown solid compound. Yield: 87% (107.1 mg). Mp: 169-171 °C. IR (neat): ν_{max} 2956, 1594, 1491, 1456, 1313, 1074, 995, 947, 831, 758, 727, 694, 600, and 551 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.98 (1H, d, *J* = 8.0 Hz), 7.88 (1H, dd, *J* = 8.0, 0.5 Hz), 7.45-7.43 (1H, m), 7.42-7.39 (7H, m), 3.36-7.34 (3H, m), 1.34 (9H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): *δ* 158.9 (C), 153.7 (C), 153.2 (C), 139.9 (C), 136.2 (C), 136.1 (C), 134.9 (C), 130.4 (2 x CH), 129.3 (CH), 129.2 (2 x CH), 125.9 (CH), 125.4 (2 x CH), 125.2 (2 x CH), 125.2 (CH), 123.5 (CH), 122.4 (C), 121.4 (CH), 34.8 (C), 31.1 (3 x CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{23}N_4S$ 411.1643; Found 411.1641.



2-(5-(Furan-2-yl)-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4la): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a light brown solid compound. Yield: 96% (99 mg). Mp: 198-200 °C. IR (neat): ν_{max} 1595, 1560, 1495, 1455, 1434, 1358, 1222, 1152, 1014, 954, 754, 727 and 591 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.08 (1H, d, *J* = 8.0 Hz), 7.94 (1H, d, *J* = 8.0 Hz), 7.76 (1H, dd, *J* = 8.0, 0.5 Hz), 6.57 (1H, d, *J* = 8.5, 1.5 Hz), 7.52-7.45 (6H, m), 7.43-7.39 (1H, m), 7.39-7.38 (1H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): *δ* 158.8 (C), 153.8 (C), 144.4 (CH), 139.5 (C), 139.2 (C), 137.0 (C), 134.9 (C), 129.7 (CH), 129.0 (2 x CH), 126.9 (C), 126.1 (CH), 125.4 (CH), 125.2 (2 x CH), 123.4 (CH), 121.5 (CH), 116.5 (CH), 111.7 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{13}N_4OS$ 345.0810; Found 345.0808.

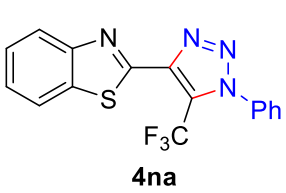


2-(1-Phenyl-5-(pyridin-2-yl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ma): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as light brown solid. Yield: 85% (90.6 mg). Mp: 145-149 ºC. IR (neat): ν_{max} 1588, 1493, 1441, 1289, 1157, 1081, 951, 792, 755 and 726 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (1H, d, J = 4.5 Hz), 7.93-7.90 (3H, m), 7.83 (1H, td, J = 8.0, 1.5 Hz), 7.45-7.34 (8H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 158.6 (C), 153.7 (C), 149.7 (CH), 146.1 (C), 140.4 (C), 136.4 (C), 136.2 (CH), 134.9 (C), 134.8 (C), 129.2 (CH), 129.0 (2 x CH), 127.1 (CH), 125.9 (CH), 125.3 (CH), 125.0 (2 x CH), 124.1 (CH), 123.4 (CH), 121.4 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{14}N_5S$ 356.0970; Found 356.0970.



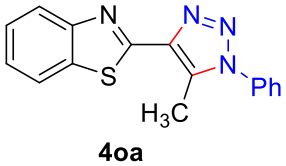
4ma

2-(1-Phenyl-5-trifluoromethyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4na): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a solid brown compound. Mp: 120-123 °C. Yield: 96% (99.4 mg). IR (neat): ν_{max} 1593, 1496, 1428, 1345, 1253, 1144, 1129, 954, 757, 728 and 683 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (1H, d, J = 8.0 Hz), 7.99 (1H, d, J = 8.0 Hz), 7.65-7.58 (3H, m), 7.57-7.53 (3H, m). 7.49-7.46 (1H, m). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 155.9 (C), 153.9 (C), 142.3 (C), 135.7 (C), 135.4 (C), 131.0 (CH), 129.5 (2 x CH), 126.5 (CH), 126.1 (CH), 125.7 (2 x CH), 125.3 (C), 124.1 (CH), 121.7 (CH), 119.3 (C, q, $^{1}J_{C\text{-}F}$ = 269.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.4. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{10}F_3N_4S$ 347.0578; Found 347.0577.



4na

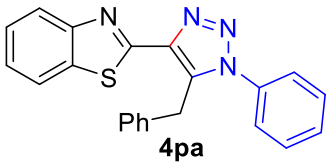
2-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4oa): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: Mp: 135-137 °C. 99% (86.8 mg). IR (neat): ν_{max} 1596, 1579, 1501, 1454, 1431, 1342, 1312, 1264, 1101, 1070, 957, 754, 716 and 692 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (1H, d, J = 8.0 Hz), 7.94 (1H, d, J = 8.0 Hz), 7.61-7.53 (5H, m), 7.50 (1H, m). 7.39 (1H, m), 2.81 (3H, s). $^{13}C\{^{1}H\}$



4oa

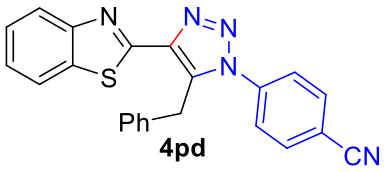
NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.3 (C), 153.9 (C), 139.9 (C), 135.6 (C), 134.4 (C), 133.3 (C), 129.8 (CH), 129.6 (2 x CH), 126.0 (CH), 125.13 (2 x CH), 125.08 (CH), 122.9 (CH), 121.6 (CH), 10.3 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}N_4S$ 293.0861; Found 293.0862.

2-(5-Benzyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4pa): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0.0:1.0 to 1.5:8.5) and isolated as a white solid. Mp: 174-176 °C. Yield: 78% (86.2 mg). IR (neat): ν_{max} 1594, 1505, 1452, 1431, 1344, 1259, 1141, 1071, 964, 783, 764, 717 and 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (1H, d, *J* = 8.5 Hz), 7.96 (1H, d, *J* = 8.0 Hz), 7.54-7.51 (1H, m), 7.49-7.7.46 (3H, m), 7.42-7.39 (1H, m), 7.30-7.28 (2H, m), 7.14-7.12 (3H, m), 6.99-6.97 (2H, m), 4.7 (2H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 159.9 (C), 154.0 (C), 140.2 (C), 136.6 (C), 136.0 (C), 135.7 (C), 134.6 (C), 130.1 (CH), 129.4 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 126.8 (CH), 126.1 (CH), 125.9 (2 x CH), 125.2 (CH), 123.2 (CH), 121.7 (CH), 29.0 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}N_4S$ 369.1174; Found 369.1175.



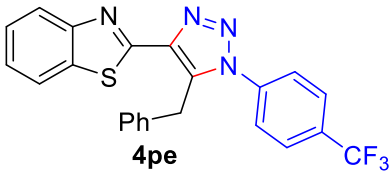
4pa

4-(4-(Benzo[*d*]thiazol-2-yl)-5-benzyl-1*H*-1,2,3-triazol-1-yl)benzonitrile (4pd): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid. Mp: 159-162 ºC. Yield: 93% (109.8 mg). IR (neat): ν_{max} 2230, 1600, 1508, 1453, 1439, 1414, 1268, 1069, 957, 841, 753, 724 and 693 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (1H, d, *J* = 8.0 Hz), 7.96 (1H, d, *J* = 8.5 Hz), 7.75 (2H, d, *J* = 8.5 Hz), 7.49-7.45 (3H, m), 7.43-7.39 (1H, m), 7.18-7.16 (3H, m), 6.99-6.98 (2H, m), 4.76 (2H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 159.2 (C), 153.9 (C), 140.9 (C), 139.1 (C), 136.0 (C), 135.8 (C), 134.5 (C), 133.4 (2 x CH), 128.8 (2 x CH), 128.2 (2 x CH), 127.1 (CH), 126.2 (2 x CH), 126.2 (CH), 125.4 (CH), 123.2 (CH), 121.7 (CH), 117.4 (C), 113.9 (C), 29.1 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}N_5S$ 394.1126; Found 394.1127.



4pd

2-(5-Benzyl-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4pe): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Mp: 162-165 °C. Yield: 92% (120.4 mg). IR (neat): ν_{max} 1614, 1599, 1573, 1521, 1454, 1319, 1263, 1166, 1128, 1107, 1054, 960, 845 and 766 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (1H, d, J = 8.0 Hz), 7.96 (1H, d, J = 8.0 Hz), 7.74 (2H, d, J = 8.0 Hz), 7.49-7.40 (4H, m), 7.18-7.16 (3H, m), 7.01-6.99 (2H, m), 4.74 (2H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 159.5 (C), 153.9 (C), 140.7 (C), 138.5 (C), 136.3 (C), 135.9 (C), 134.6 (C), 132.1 (C, q, $^{2}J_{C-F}$ = 32.5 Hz), 128.7 (2 x CH), 128.3 (2 x CH), 127.0 (CH), 126.6 (2 x CH, q, $^{3}J_{C-F}$ = 3.75 Hz), 126.2 (CH), 126.1 (2 x CH), 125.4 (CH), 123.4 (C, q, $^{1}J_{C-F}$ = 271.2 Hz), 123.3 (CH), 121.7 (CH), 29.1 (CH_2). ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.77 (C, CF_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{16}F_3N_4S$ 437.1048; Found 437.1051.

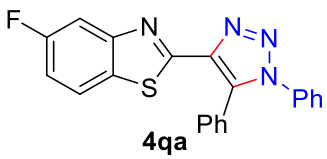


4pe

2-(5-Benzyl-1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4pn): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 89% (102.12 mg). Mp: 162-165 °C. IR (neat): ν_{max} 1601, 1515, 1493, 1452, 1311, 1272, 1074, 957, 819, 753, 726 and 692 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (1H, d, J = 8.0 Hz), 7.96 (1H, d, J = 7.5 Hz), 7.47 (1H, td, J = 8.0, 1.0 Hz), 7.40 (1H, td, J = 8.0, 1.0 Hz), 7.28-7.25 (2H, m), 7.18-7.13 (5H, m), 7.02-7.00 (2H, m), 4.67 (2H, s), 2.44 (3H, s). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 160.1 (C), 154.0 (C), 140.4 (C), 140.1 (C), 136.8 (C), 136.0 (C), 134.6 (C), 133.1 (C), 129.9 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 126.7 (CH), 126.0 (CH), 125.7 (2 x CH), 125.1 (CH), 123.1 (CH), 121.6 (CH), 29.0 (CH_2), 21.3 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{19}N_4S$ 383.1330; Found 383.1327.

4pn

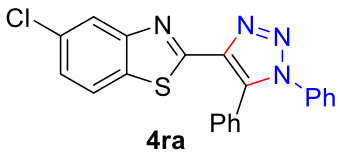
2-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)-5-fluorobenzo[*d*]thiazole (4qa): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid



4qa

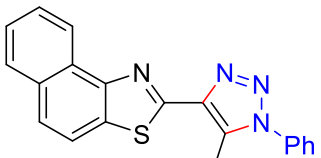
compound. Yield: 99% (110.6 mg). Mp: 212-214 °C. IR (neat): ν_{max} 1569, 1495, 1418, 1264, 1148, 1123, 996, 965, 762, 732 and 699 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (1H, dd, J = 9.0, 5.0 Hz), 7.61 (1H, dd, J = 9.5, 2.0 Hz), 7.49-7.39 (8H, m), 7.35-7.33 (2H, m), 7.13 (1H, td, J = 8.5, 2.0 Hz). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 161.7 (C, d, $^{1}J_{C\text{-}F}$ = 241.2 Hz), 161.3 (C), 154.7 (C, d, $^{2}J_{C\text{-}F}$ = 12.5 Hz), 139.8 (C), 136.2 (C), 136.0 (C), 130.7 (2 x CH), 130.2 (C, d, $^{4}J_{C\text{-}F}$ = 1.3 Hz), 130.0 (CH), 129.4 (CH), 129.3 (2 x CH), 128.5 (2 x CH), 125.6 (C), 125.2 (2 x CH), 122.0 (CH, d, ^{3}J = 10.0 Hz), 113.9 (CH, d, $^{2}J_{C\text{-}F}$ = 23.7 Hz), 109.5 (CH, d, $^{2}J_{C\text{-}F}$ =23.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): -116.23 (*C*-F). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}FN_4S$ 373.0923; Found 373.0927.

5-Chloro-2-(1,5-diphenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]thiazole (4ra): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 99% (115.5 mg). Mp: 231-233 °C. IR (neat): ν_{max} 1594, 1521, 1443, 1432, 1282, 1060, 994, 968, 949, 893, 794, 761, 687 and 593 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (1H, d, J = 1.5 Hz), 7.79 (1H, d, J = 8.5 Hz), 7.49-7.39 (8H, m), 7.34-7.32 (3H, m). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 160.8 (C), 154.7 (C), 139.7 (C), 136.3 (C), 136.0 (C), 133.2 (C), 132.1 (C), 130.7 (2 x CH), 130.1 (CH), 129.5 (CH), 129.4 (2 x CH), 128.5 (2 x CH), 125.7 (CH), 125.6 (C), 125.2 (2 x CH), 123.3 (CH), 122.2 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{14}ClN_4S$ 389.0628; Found 389.0631.



4ra

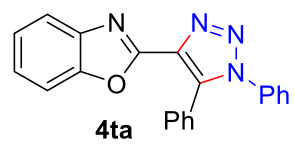
2-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)naphtho[1,2-*d*]thiazole (4sa): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 99% (120.1 mg). Mp: 212-214 °C. IR (neat): ν_{max} 1593, 1495, 1449, 1362, 1264, 1077, 997, 955, 899, 814, 770, 733, 694, and 554 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (1H, d, J = 8.0 Hz), 7.91 (1H, d, J = 9.0 Hz), 7.90 (1H, d, J = 7.5 Hz), 7.78 (1H, 1H, d, J = 8.5 Hz), 7.60-7.57 (3H, m), 7.55-7.45 (4H, m), 7.43-7.38 (5H, m). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 157.9 (C), 150.1 (C), 140.3 (C), 136.2 (C), 135.6 (C), 131.9 (C), 131.6 (C), 133.0 (2 x CH),



4sa

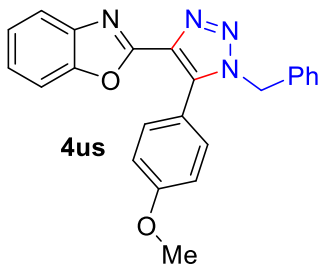
129.8 (CH), 129.34 (CH), 129.32 (2 x CH, C), 128.7 (C), 128.2 (2 x CH), 127.9 (CH), 126.8 (CH), 126.0 (2 x CH), 125.2 (2 x CH), 123.8 (CH), 118.9 (CH). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{17}N_4S$ 405.1174; Found 405.1179.

2-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)benzo[*d*]oxazole (4ta): The title compound was prepared following **Procedure Ca** employing catalyst **3c**, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 99% (110.6 mg). Mp: 212-214 °C. IR (neat): ν_{max} 1636, 1589, 1493, 1450, 1239, 1057, 995, 922, 764, 744, 690, 611, and 572 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.73-7.71 (1H, m), 7.57-7.55 (1H, m), 7.49-7.41 (8H, m), 7.35-7.31 (4H, m). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 156.0 (C), 150.4 (C), 141.6 (C), 138.2 (C), 135.9 (C), 134.7 (C), 130.5 (2 x CH), 130.1 (CH), 129.6 (CH), 129.4 (2 x CH), 128.6 (2 x CH), 125.4 (C), 125.4 (CH), 125.3 (2 x CH), 124.6 (CH), 120.5 (CH), 110.8 (CH). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{14}N_4ONa$ 361.1065; Found 361.1071.



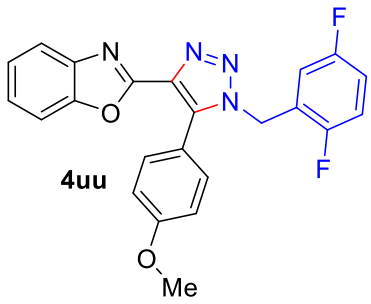
4ta

2-(1-Benzyl-5-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]oxazole (4us): The title compound was prepared following **Procedure Cb** employing catalyst **3a** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 1.5:8.5) and isolated as a white solid compound. Yield: 90% (103.2 mg). Mp: 121-123 °C. IR (neat): ν_{max} 1498, 1452, 1248, 904, 722 and 648 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.68-7.66 (1H, m), 7.52-7.50 (1H, m), 7.32-7.26 (7H, m), 7.09-7.08 (2H, m), 7.00 (2H, d, J = 9.0 Hz), 5.51 (2H, s), 3.89 (3H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 160.9 (C), 156.3 (C), 150.2 (C), 141.5 (C), 138.6 (C), 134.8 (C), 134.5 (C), 131.5 (2 x CH), 128.8 (2 x CH), 128.3 (CH), 127.3 (2 x CH), 125.1 (CH), 124.4 (CH), 120.3 (CH), 117.3 (C), 114.2 (2 x CH), 110.7 (CH), 55.3 (CH_3), 52.11 (CH_2). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{19}N_4O_2$ 381.1508; Found 381.1505.



4us

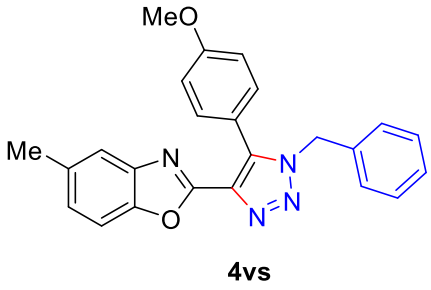
2-(1-(2,5-Difluorobenzyl)-5-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)benzo[*d*]oxazole (4uu):



4uu

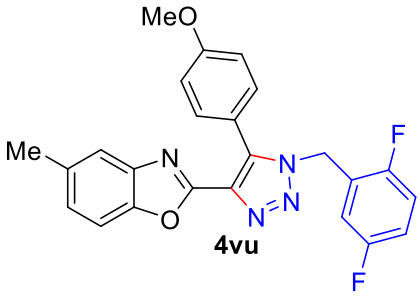
The title compound was prepared following **Procedure Cb** employing catalyst **3a** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 2.0:8.0) and isolated as a white solid compound. Yield: 87% (109.2 mg). Mp: 115-117 °C. IR (neat): ν_{max} 1499, 1454, 1379, 1254, 903 and 723 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (1H, dd, J = 6.5, 2.0 Hz), 7.52 (1H, dd, J = 7.5, 1.5 Hz), 7.33 (2H, d, J = 9.0 Hz), 7.32-7.28 (2H, m), 7.02 (2H, d, J = 9.0 Hz), 7.00-6.97 (2H, m), 6.78-6.75 (1H, m), 5.54 (2H, s), 3.89 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 161.2 (C), 158.7 (C, dd, $^{1}J_{C\text{-}F}$, $^{4}J_{C\text{-}F}$ = 242.5, 2.5 Hz), 156.0 (C), 155.7 (C, dd, $^{1}J_{C\text{-}F}$, $^{4}J_{C\text{-}F}$ = 242.5, 2.5 Hz), 150.2 (C), 141.5 (C), 138.8 (C), 134.5 (C), 131.3 (2 x CH), 125.2 (CH), 124.5 (CH), 123.63 (C, dd, $^{2}J_{C\text{-}F}$, $^{3}J_{C\text{-}F}$ = 16.2, 7.5 Hz), 120.3 (CH), 116.9 (CH, t, J = 8.7 Hz), 116.8 (C), 116.7 (CH, t, J = 8.7 Hz), 115.9 (CH, dd, $^{2}J_{C\text{-}F}$, $^{3}J_{C\text{-}F}$ = 25.0, 2.5 Hz), 114.4 (2 x CH), 110.7 (CH), 55.4 (CH_3), 45.39 (CH_2, d, $^{3}J_{C\text{-}F}$ = 5.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): -117.13 (F, d, J = 17.39 Hz), -123.62 (F, d, J = 17.39 Hz). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{17}F_2N_4O_2$ 419.1320; Found 419.1322.

2-(1-Benzyl-5-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-5-methylbenzo[*d*]oxazole (4vs): The title compound was prepared following **Procedure Cb** employing catalyst **3a** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 2.0:8.0) and isolated as a white solid compound. Yield: 90% (106.2 mg). Mp: 99-101 °C. IR (neat): ν_{max} 1498, 1455, 1261, 1159, 1029, 800 and 748 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (1H, s), 7.36 (1H, d, J = 8.5 Hz), 7.29-7.26 (5H, m), 7.11-7.07 (3H, m), 6.99 (2H, d, J = 8.5 Hz), 5.50 (2H, s), 3.89 (3H, s), 2.43 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.9 (C), 156.3 (C), 148.4 (C), 141.7 (C), 138.4 (C), 134.9 (C), 134.6 (C), 134.2 (C), 131.5 (2 x CH), 128.8 (2 x CH), 128.3 (CH), 127.3 (2 x CH), 126.2 (CH), 120.2 (CH), 117.4 (C), 114.2 (2 x CH), 109.9 (CH), 55.3 (CH_3), 52.1 (CH_2), 21.3 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{21}N_4O_2$ 397.1665; Found 397.1665.



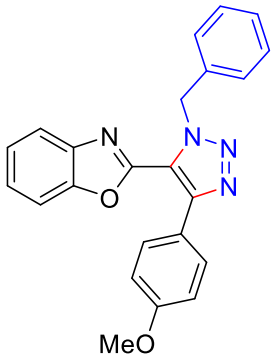
4vs

2-(1-(2,5-Difluorobenzyl)-5-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-5-methylbenzo[*d*]oxazole (4vu): The title compound was prepared following **Procedure Cb** employing catalyst **3a** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 2.0:8.0) and isolated as a white solid compound. Yield: 88% (113.8 mg). Mp: 99-101 °C. IR (neat): ν_{max} 1497, 1433, 1296, 1251, 1161, 1030, 905, 801, and 723 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (1H, m), 7.38 (1H, d, J = 8.5, Hz), 7.32 (2H, d, J = 9.0 Hz), 7.11 (1H, d, J = 8.5, Hz), 7.01 (2H, d, J = 9.0 Hz), 7.99-6.96 (2H, m), 6.78-6.74 (1H, m), 5.54 (2H, s), 3.89 (3H, s), 2.43 (3H, s). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, DEPT-135): δ 161.1 (C), 158.7 (C, dd, $^{1}J_{C\text{-}F}$, $^{4}J_{C\text{-}F}$ = 242.0, 1.0 Hz), 155.6 (C, dd, $^{1}J_{C\text{-}F}$, $^{4}J_{C\text{-}F}$ = 243.0, 2.0 Hz), 156.1 (C), 148.5 (C), 141.7 (C), 138.7 (C), 134.6 (C), 134.3 (C), 131.3 (2 x CH), 126.4 (CH), 123.7 (C, dd, $^{2}J_{C\text{-}F}$, $^{3}J_{C\text{-}F}$ = 16.0, 8.0 Hz), 120.2 (CH), 116.9 (C), 116.9 (CH, br t, J = 8.7 Hz), 116.6 (CH, br t, J = 8.7 Hz), 115.9 (CH, dd, $^{2}J_{C\text{-}F}$, $^{3}J_{C\text{-}F}$ = 25.0, 4.0 Hz), 114.4 (2 x CH), 110.0 (CH), 55.3 (CH_3), 45.3 (CH_2, d, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 21.4 (CH_3). ^{19}F NMR (370 MHz, $CDCl_3$): -117.16 (F, d, J = 17.7 Hz), -123.64 (F, d, J = 17.7 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{19}F_2N_4O_2$ 433.1476; Found 433.1481.



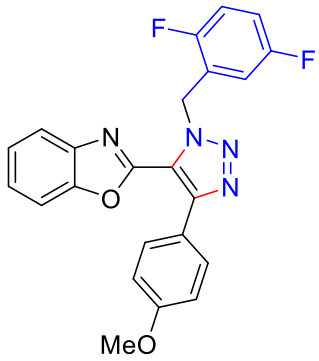
4vu

2-(1-Benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-5-yl)benzo[*d*]oxazole (7as): The title compound was prepared following **Procedure G** employing catalyst **3c** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 0.5:9.5) and isolated as a white solid compound. Yield: 55% (63 mg). Mp: 109-111 °C. IR (neat): ν_{max} 1613, 1534, 1496, 1247, 1178, 1063, 905 and 728 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (1H, d, J = 7.5 Hz), 7.76 (2H, d, J = 8.5 Hz), 7.49 (1H, d, J = 6.0 Hz), 7.41-7.40 (2H, m), 7.35 (2H, d, J = 6.5 Hz), 7.26-7.24 (3H, m), 6.97 (2H, d, J = 8.5 Hz), 6.14 (2H, s), 3.87 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.3 (C), 153.3 (C), 150.0 (C), 149.0 (C), 141.1 (C), 135.1 (C), 130.2 (2 x CH), 128.7 (2 x CH), 128.3 (CH), 128.1 (2 x CH), 126.2 (CH), 125.1 (CH), 122.5 (C), 121.1 (C), 120.5 (CH), 113.99 (2 x CH), 110.9 (CH), 55.3 (CH_3), 53.8 (CH_2). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}N_4O_2$ 383.1508; Found 383.1504.



7as

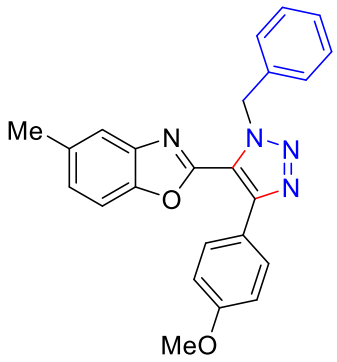
2-(1-(2,5-Difluorobenzyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-5-yl)benzo[*d*]oxazole (7au):



7au

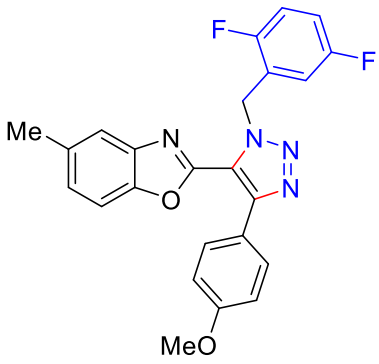
The title compound was prepared following **Procedure G** employing catalyst **3c** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 0.5:9.5) and isolated as a white solid compound. Yield: 60% (75 mg). Mp: 110-112 °C. IR (neat): ν_{max} 1536, 1346, 1246, 1178, 903 and 726 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (2H, d, J = 8.5 Hz), 7.81-7.79 (1H, m), 7.35-7.51 (1H, m), 7.43-7.39 (2H, m), 7.04-7.01 (1H, m), 7.00 (2H, d, J = 8.5 Hz), 6.96-6.91 (1H, m), 6.87-6.83 (1H, m), 6.18 (2H, s), 3.88 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.4 (C), 158.7 (C, dd, $^{1}J_{C\text{-}F,}$ $^{4}J_{C\text{-}F}$ = 242.5, 2.5 Hz), 156.2 (C, dd, $^{1}J_{C\text{-}F,}$ $^{4}J_{C\text{-}F}$ = 243.7, 2.5 Hz), 152.9 (C), 150.0 (C), 148.9 (C), 140.1 (C), 130.3 (2 x CH), 126.4 (CH), 125.2 (CH), 124.1 (C, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 17.5, 8.75 Hz), 122.2 (C), 121.3 (C), 120.6 (CH), 116.7 (CH, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 15.0, 8.75 Hz), 116.5 (CH, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 15.0, 8.75 Hz), 115.9 (CH, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 15.0, 8.75 Hz), 113.9 (2 x CH), 110.9 (CH), 55.3 (OCH_3), 47.4 (CH_2, d, $^{3}J_{C\text{-}F}$ = 3.75 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): -117.2 (F, d, J = 18.8 Hz), -123.60 (F, d, J = 18.8 Hz). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{17}F_2N_4O_2$ 419.1320; Found 419.1322.

2-(1-Benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-5-yl)-5-methylbenzo[*d*]oxazole (7bs): The title compound was prepared following **Procedure G** employing catalyst **3c** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 0.5:9.5) and isolated as a white solid compound. Yield: 56% (66 mg). Mp: 108-110 °C. IR (neat): ν_{max} 1535, 1497, 1247, 1178, 1063, 904 and 726 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (2H, d, J = 9.0 Hz), 7.61 (1H, s), 7.36-7.33 (3H, m), 7.26-7.24 (3H, m), 7.14 (1H, d, J = 8.5 Hz), 6.96 (2H, d, J = 8.5 Hz), 6.12 (2H, s), 3.86 (3H, s), 2.50 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.2 (C), 153.3 (C), 148.8 (C), 148.2 (C), 141.3 (C), 135.2 (2 x C), 130.2 (2 x CH), 128.7 (2 x CH), 128.3 (CH), 128.1 (2 x CH), 127.4 (CH), 122.5 (C), 121.2 (C), 120.3 (CH), 113.8 (2 x CH), 110.2 (CH), 55.3 (OCH_3), 53.7 (CH_2), 21.5 (CH_3). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{21}N_4O_2$ 397.1665; Found 397.1664.



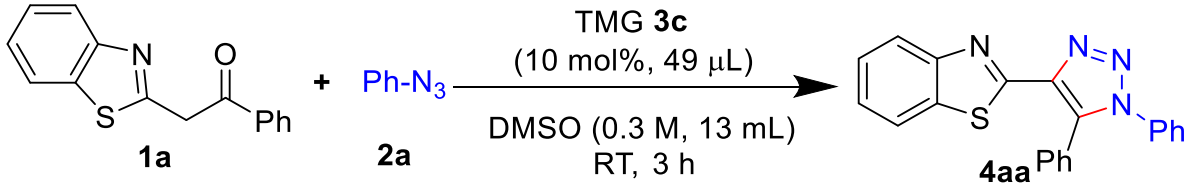
7bs

2-(1-(2,5-Difluorobenzyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-5-yl)-5-methylbenzo[*d*]oxazole (7bu): The title compound was prepared following **Procedure G** employing catalyst **3c** at 80 °C, purified by column chromatography using ethyl acetate/hexanes (0:10 to 0.5:9.5) and isolated as a white solid compound. Yield: 62% (80 mg). Mp: 109-112 °C.



7bu

IR (neat): ν_{max} 1613, 1533, 1346, 1248, 1178, 903 and 724 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (2H, d, J = 8.5 Hz), 7.58 (1H, s), 7.38 (1H, d, J = 8.5 Hz), 7.21 (1H, d, J = 8.5 Hz), 7.03-7.02 (1H, m), 6.99 (2H, d, J = 8.5 Hz), 6.95-6.90 (1H, br m), 6.86-6.82 (1H, br m), 6.16 (2H, s), 3.87 (3H, s), 2.49 (3H, s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, DEPT-135): δ 160.4 (C), 158.6 (C, dd, $^{1}J_{C\text{-}F,}$ $^{4}J_{C\text{-}F}$ = 242.5, 1.25 Hz), 156.2 (C, dd, $^{1}J_{C\text{-}F,}$ $^{4}J_{C\text{-}F}$ = 242.5, 2.5 Hz), 152.9 (C), 148.7 (C), 148.2 (C), 141.2 (C), 135.2 (C), 130.2 (2 x CH), 127.5 (CH), 124.1 (C, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 17.5, 7.5 Hz), 122.2 (C), 121.4 (C), 120.4 (CH), 116.6 (CH, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 17.5, 7.5 Hz), 116.4 (CH, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 17.5, 7.5 Hz), 115.9 (CH, dd, $^{2}J_{C\text{-}F,}$ $^{3}J_{C\text{-}F}$ = 21.2, 3.75 Hz), 113.9 (2 x CH), 110.3 (CH), 55.3 (OCH_3), 47.4 (CH_2, d, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 21.5 (CH_3). ^{19}F NMR (470 MHz, $CDCl_3$): -117.7 (F, d, J = 14.1 Hz), -123.64 (F, d, J = 18.8 Hz). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}F_2N_4O_2$ 433.1476; Found 433.1479.



<u>Procedure H</u>: The Gram-Scale Synthesis of the OrgAKC Reactions: In an ordinary 50 mL round bottom flask equipped with a magnetic stir bar, 2-(benzo[*d*]thiazol-2-yl)-1-phenylethan-1-one **1a** (1.0 g, 3.95 mmol, 1.0 equiv.), phenyl azide **2a** (0.715 g, 6.0 mmol, 1.5 equiv.), and DMSO (0.3 M, 13.0 mL) were added. After 5 minutes, TMG **3c** (49 µL, 0.395 mmol, 0.1 equiv.) was added to the reaction mixture and stirred at room temperature for 3 h. The crude reaction mixture was worked up with aq. NH_4Cl solution and the aqueous layer were extracted with

dichloromethane (2 × 30 mL). The combined organic layers were dried and concentrated under reduced pressure. Pure click product **4aa** (1.33 g, 95%) was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate 0:10 to 1.5:8.5).

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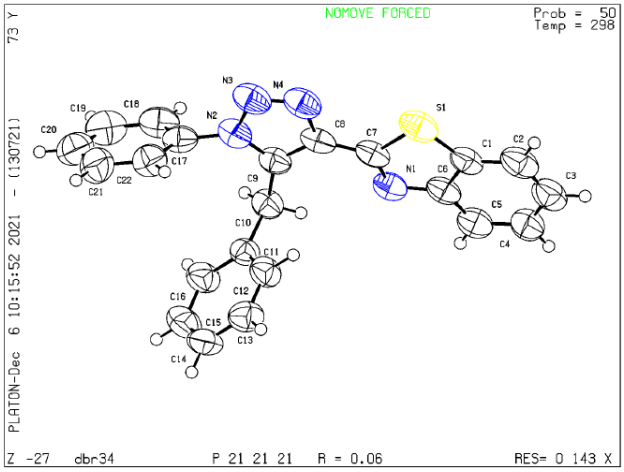
X-Ray Single Crystal Data for 4pa. The ellipsoid contour % Probability Levels are 50%

Crystalized from Dichloromethane-Hexane; $C_{22}H_{16}N_4S$; Mr = 368.45; orthorhombic; space group = *P 21 21 21*; A clear whiteish white crystal of 0.2x0.15x0.1 mm^3 was used.

Table S1. Crystal data and structural refinement for **4pa** (2384641)

```
Bond precision:   C-C = 0.0078 A          Wavelength=0.71073

Cell:             a=5.8739(2)     b=12.2152(6)     c=25.4655(13)
                  alpha=90        beta=90          gamma=90
Temperature:      298 K

                  Calculated                  Reported
Volume            1827.17(14)                 1827.17(14)
Space group       P 21 21 21                  P 21 21 21
Hall group        P 2ac 2ab                   P 2ac 2ab
Moiety formula    C22 H16 N4 S                C22 H16 N4 S
Sum formula       C22 H16 N4 S                C22 H16 N4 S
Mr                368.45                      368.45
Dx,g cm-3         1.339                       1.339
Z                 4                           4
Mu (mm-1)         0.191                       0.191
F000              768.0                       768.0
F000'             768.73
h,k,lmax          6,14,30                     6,14,30
Nref              3217[ 1891]                 3183
Tmin,Tmax         0.966,0.981                 0.380,1.000
Tmin'             0.963

Correction method= # Reported T Limits: Tmin=0.380 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.68/0.99        Theta(max)= 25.027

R(reflections)= 0.0557( 1866)                wR2(reflections)=
                                             0.1083( 3183)
S = 0.907                   Npar= 244
```

Ellipsoid plot for **4pa**



X-Ray Single Crystal Data for 4pe. The ellipsoid contour % Probability Levels are 50%

Crystalized from Dichloromethane-Hexane; $C_{23}H_{15}F_3N_4S$; Mr = 436.45; orthorhombic; space group = *P 21 21 21*; A clear whiteish white crystal of 0.2x0.15x0.1 mm^3 was used.

Table S2. Crystal data and structural refinement for **4pe** (2384642)

Bond precision: C-C = 0.0079 A Wavelength=0.71073

Cell: a=6.3340(2) b=12.0464(5) c=26.3054(10)
alpha=90 beta=90 gamma=90

Temperature: 295 K

	Calculated	Reported
Volume	2007.15(13)	2007.15(13)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C23 H15 F3 N4 S	C23 H15 F3 N4 S
Sum formula	C23 H15 F3 N4 S	C23 H15 F3 N4 S
Mr	436.45	436.45
Dx,g cm-3	1.444	1.444
Z	4	4
Mu (mm-1)	0.207	0.207
F000	896.0	896.0
F000'	896.93	
h,k,lmax	8,15,33	8,15,33
Nref	4485[2593]	4137
Tmin,Tmax	0.963,0.980	0.566,1.000
Tmin'	0.959	

Correction method= # Reported T Limits: Tmin=0.566 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.60/0.92 Theta(max)= 27.235

R(reflections)= 0.0642(3350) wR2(reflections)= 0.1950(4137)

S = 1.099 Npar= 280

Ellipsoid plot for **4pe**