Supporting Information-I

Organocatalytic Enone-Azide [3+2]-Cycloaddition: Synthesis of Functionally Rich C/N-Double Vinyl 1,2,3-Triazoles

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz 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 Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. 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 CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker 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 Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of p-anisaldehyde (23 mL), conc. H2SO4 (35mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. Starting materials **1a-g**,[1] and **8**[2] were synthesized based on the previous literature methods.

General Experimental Procedures:

Procedure A: General procedure for the DBU-catalyzed domino [3+2]-cycloaddition reactions in DMSO: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.10 mmol of DBU (**3e**) in DMSO (1.0 mL), was added 0.75 mmol of azides (**2** or **5**) and 0.5 mmol of corresponding enones (**1** or **8**) and the reaction mixture was stirred at 25 °C for 0.5-6.0 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure click products were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure B: General procedure for the DDQ oxidation of 4aa: In a 10 mL round bottom flask equipped with a magnetic stirring bar, to 0.5 mmol of compound **4aa** was added 5.0 mL of dry toluene as a solvent and then DDQ (2 equiv., 1.0 mmol) was added. The reaction mixture were refluxed for 48 h, the crude product was purified by column chromatography on silica gel (hexane/EtOAc) to afford the oxidized product **11**.

Procedure C: General procedure for the hydrogenation of 11: In a 10 mL round bottomed flask, a solution of 0.5 mmol of **11** in dry methanol (5 mL) was taken followed by addition of Pd/C (10 mol%). The reaction mixture was purged with nitrogen gas followed by hydrogen gas. The reaction mixture was allowed to stir at 25 °C under the pressure of a hydrogen gas

filled balloon for 3 h. The crude reaction mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The concentrate was subjected to column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain the pure compound **12** respectively.

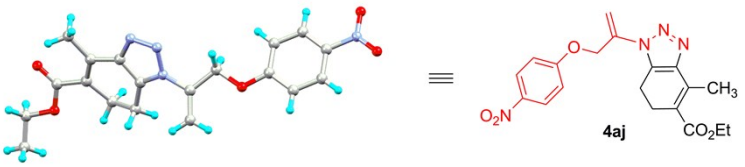


Figure S1. Crystal structure of ethyl 4-methyl-1-(3-(4-nitrophenoxy)prop-1-en-2-yl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate (**4aj**).

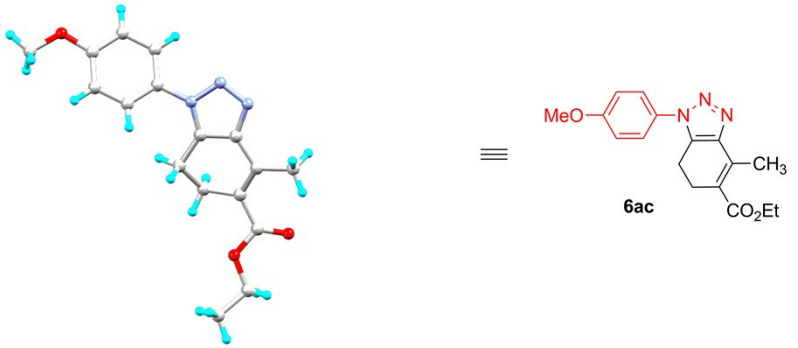


Figure S2. Crystal structure of ethyl 1-(4-methoxyphenyl)-4-methyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate (**6ac**).

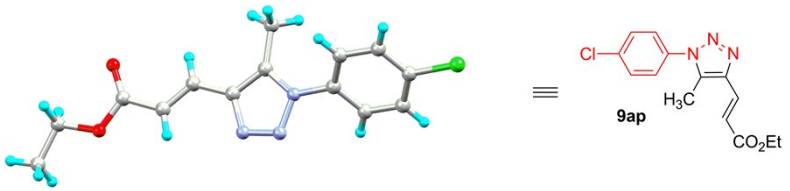
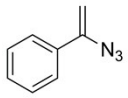
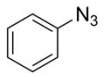
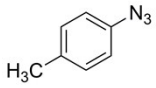
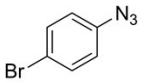
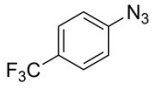
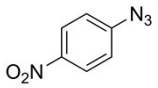
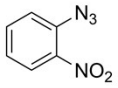


Figure S3. Crystal structure of (*E*)-ethyl 3-(1-(4-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (**9ap**).

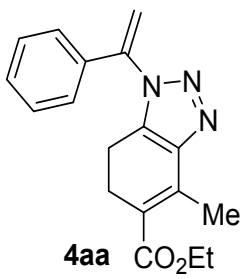
Table S1: Correlation of reactivity of different azides 2 with enone 1a under pyrrolidine-catalysis and DBU-catalysis

Entry	Azide	Pyrrolidine (10 mol%)		DBU (20 mol%)	
		Time (h)	yield (%)	Time (h)	yield (%)
1		24 h	No Reaction	0.5 h	90
2		66 h	50	0.5 h	95
3		40 h	50	0.75 h	88
4		24 h	75	0.5 h	89
5		1.0 h	93	0.5 h	89
6		1.0 h	95	0.3 h	85
7		1.0 h	95	0.5	multiple spots

Reference for pyrrolidine-catalysis, see: D. B. Ramachary and A. B. Shashank, *Chem. Eur. J.* **2013**, *19*, 13175-13181.

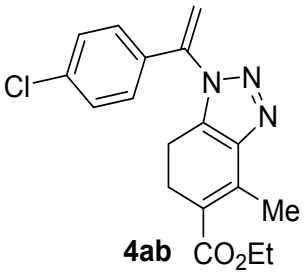
Reference for DBU-catalysis, see: present studies.

Ethyl 4-methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate (4aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 90% (139.5 mg); Mp.: 86-88 °C; IR (Neat): ν_{max} 2979, 2923, 1689, 1603, 1477, 1371, 1274, 1200, 1108, 905, 812, 774, 702, 613 and 524 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (3H, m), 7.25-7.22 (2H, m), 5.78 (1H, d, *J* = 1.2 Hz, olefinic-*H*), 5.64 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 4.24 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.72 (2H, qt, *J* = 8.8, 1.6 Hz), 2.62 (3H, t, *J* = 1.6 Hz, olefinic-CH_3), 2.46 (2H, t, *J* = 9.2 Hz), 1.32 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 145.4 (C), 141.8 (C), 138.2 (C), 134.5 (C), 134.2 (C), 129.7 (CH), 128.7 (2 x CH), 126.1 (2 x CH), 120.8 (C),

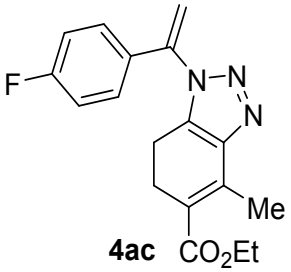


4aa

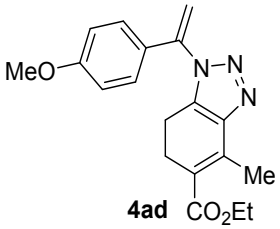
112.3 (CH_2), 60.2 (CH_2, O*C*H_2CH_3), 25.0 (CH_2), 19.2 (CH_2), 15.1 (CH_3), 14.2 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 310.1556 ($M + H^+$), calcd for $C_{18}H_{19}N_3O_2H$ 310.1556.

Ethyl 1-(1-(4-chlorophenyl)vinyl)-4-methyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate (4ab): 

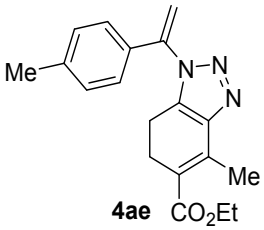
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a light yellow solid; Yield: 84% (144.5 mg); Mp.: 92-94 °C; IR (Neat): ν_{max} 2982, 2925, 1696, 1603, 1562, 1484, 1443, 1278, 1200, 1097, 1055, 839, 782 and 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (2H, td, *J* = 8.4, 2.4 Hz), 7.18 (2H, td, *J* = 8.8, 2.0 Hz), 5.78 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 5.64 (1H, br s, olefinic-*H*), 4.25 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.74 (2H, qt, *J* = 8.8, 1.6 Hz), 2.62 (3H, t, *J* = 1.6 Hz, olefinic-C*H*$_3$), 2.49 (2H, t, *J* = 8.4 Hz), 1.33 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.7 (C), 141.0 (C), 138.3 (C), 136.0 (C), 134.5 (C), 132.8 (C), 129.2 (2 x CH), 127.6 (2 x CH), 121.0 (C), 112.8 (CH_2), 60.4 (CH_2, O*C*H_2CH_3), 25.2 (CH_2), 19.4 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 344.1166 ($M + H^+$), calcd for $C_{18}H_{18}ClN_3O_2H$ 344.1166.

Ethyl 1-(1-(4-fluorophenyl)vinyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ac): 

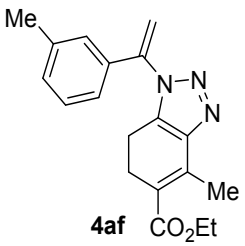
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a light yellow solid; Yield: 85% (139.50 mg); Mp.: 103-105 °C; IR (Neat): ν_{max} 2977, 2920, 2843, 1696, 1603, 1510, 1371, 1205, 1164, 1050, 839, 782, 725 and 673 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (2H, tt, *J* = 8.5, 2.0 Hz), 7.08 (2H, tt, *J* = 8.5, 2.0 Hz), 5.74 (1H, d, *J* = 0.5 Hz, olefinic-*H*), 5.61 (1H, br s, olefinic-*H*), 4.26 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.74 (2H, qt, *J* = 8.5, 1.5 Hz), 2.62 (3H, t, *J* = 1.5 Hz, olefinic-C*H*$_3$), 2.49 (2H, t, *J* = 8.5 Hz), 1.34 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 163.5 (C, d, *J* = 248.7 Hz, *C*-F), 145.6 (C), 141.1 (C), 138.3 (C), 134.5 (C), 130.6 (C, d, *J* = 3.75 Hz), 128.3 (2 x CH, d, *J* = 8.75 Hz), 121.0 (C), 116.0 (2 x CH, d, *J* = 22.5 Hz), 112.2 (CH_2), 60.4 (CH_2, O*C*H_2CH_3), 25.2 (CH_2), 19.3 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 328.1463 ($M + H^+$), calcd for $C_{18}H_{18}FN_3O_2H$ 328.1461.

Ethyl 1-(1-(4-methoxyphenyl)vinyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ad): 

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 81% (137.0 mg); IR (Neat): ν_{max} 2982, 2930, 1701, 1603, 1479, 1438, 1371, 1283, 1205, 1050, 895, 864 and 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (2H, td, *J* = 8.8, 2.4 Hz), 6.89 (2H, td, *J* = 8.8, 2.4 Hz), 5.67 (1H, s, olefinic-*H*), 5.52 (1H, s, olefinic-*H*), 4.25 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.83 (3H, s, OCH_3), 2.71 (2H, br t, *J* = 8.4 Hz), 2.62 (3H, br s, olefinic-CH_3), 2.47 (2H, t, *J* = 8.8 Hz), 1.33 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 160.8 (C), 145.5 (C), 141.6 (C), 138.5 (C), 134.6 (C), 127.7 (2 x CH), 126.8 (C), 120.8 (C), 114.2 (2 x CH), 110.5 (CH_2), 60.3 (CH_2, OCH_2CH_3), 55.3 (CH_3, OCH_3), 25.2 (CH_2), 19.3 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 340.1660 ($M + H^+$), calcd for $C_{19}H_{21}N_3O_3H$ 340.1661.

Ethyl 4-methyl-1-(1-(*p*-tolyl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ae): 

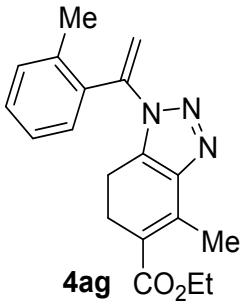
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 83% (134.5 mg); Mp.: 100-102 °C; IR (Neat): ν_{max} 2982, 2920, 1686, 1629, 1603, 1567, 1515, 1365, 1283, 1200, 1159, 1055, 901, 828, 782 and 720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (2H, br d, *J* = 8.5 Hz), 7.11 (2H, br d, *J* = 8.0 Hz), 5.73 (1H, s, olefinic-*H*), 5.59 (1H, s, olefinic-*H*), 4.24 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 2.70 (2H, qt, *J* = 9.0, 1.5 Hz), 2.62 (3H, t, *J* = 1.5 Hz, olefinic-CH_3), 2.44 (2H, t, *J* = 9.0 Hz), 2.37 (3H, s, Ar-CH_3), 1.33 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 145.5 (C), 142.0 (C), 140.0 (C), 138.5 (C), 134.6 (C), 131.5 (C), 129.6 (2 x CH), 126.2 (2 x CH), 120.8 (C), 111.5 (CH_2), 60.3 (CH_2, OCH_2CH_3), 25.2 (CH_2), 21.2 (CH_3), 19.4 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 324.1712 ($M + H^+$), calcd for $C_{19}H_{21}N_3O_2H$ 324.1712.

Ethyl 4-methyl-1-(1-(*m*-tolyl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4af): 

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 82% (132.5 mg); IR (Neat): ν_{max} 2981, 2359, 1734, 1699, 1371, 1239, 1199, 1045, 893, 734, 701 and 608 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (1H, t, *J* = 7.5 Hz), 7.22 (1H, d, *J* = 7.5 Hz), 7.04 (1H, s), 7.02 (1H, d, *J* = 7.5 Hz), 5.76 (1H, s, olefinic-*H*), 5.63 (1H, s,

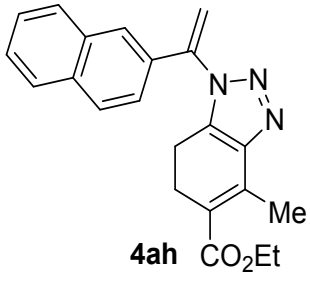
olefinic-*H*), 4.25 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.68 (2H, qt, *J* = 8.5, 1.5 Hz), 2.63 (3H, t, *J* = 1.5 Hz, olefinic-C*H*$_3$), 2.44 (2H, t, *J* = 8.5 Hz), 2.35 (3H, s, Ar-C*H*$_3$), 1.33 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.4 (C), 142.0 (C), 138.6 (C), 138.4 (C), 134.6 (C), 134.2 (C), 130.6 (CH), 128.7 (CH), 126.8 (CH), 123.4 (CH), 120.8 (C), 112.2 (CH$_2$), 60.3 (CH$_2$, O*C*H$_2$CH$_3$), 25.1 (CH$_2$), 21.3 (CH$_3$), 19.3 (CH$_2$), 15.2 (CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 324.1712 (M + H$^+$), calcd for $C_{19}H_{21}N_3O_2H$ 324.1712.

Ethyl 4-methyl-1-(1-(*o*-tolyl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



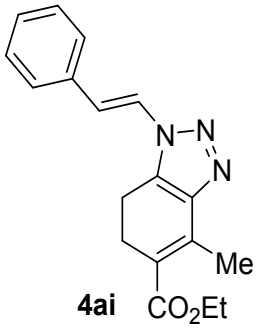
(4ag): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 62% (100.5 mg); IR (Neat): ν$_{max}$ 2983, 1735, 1372, 1233, 1043, 917, 846, 733, 633, 607 and 461 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34 (1H, t, *J* = 8.0 Hz), 7.33 (1H, d, *J* = 8.0 Hz), 7.26 (1H, dt, *J* = 8.0, 0.5 Hz), 7.20 (1H, br d, *J* = 8.0 Hz), 5.96 (1H, s, olefinic-*H*), 5.41 (1H, s, olefinic-*H*), 4.22 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.63 (2H, qt, *J* = 8.5, 2.0 Hz), 2.59 (3H, t, *J* = 2.0 Hz, olefinic-C*H*$_3$), 2.20 (2H, t, *J* = 8.5 Hz), 1.97 (3H, s, Ar-C*H*$_3$), 1.31 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 145.7 (C), 142.1 (C), 138.3 (C), 136.3 (C), 134.0 (C), 133.6 (C), 130.7 (CH), 129.74 (CH), 129.71 (CH), 126.2 (CH), 120.6 (C), 112.3 (CH$_2$), 60.2 (CH$_2$, O*C*H$_2$CH$_3$), 25.0 (CH$_2$), 19.2 (CH$_2$), 19.0 (CH$_3$), 15.1 (CH$_3$), 14.2 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 324.1714 (M + H$^+$), calcd for $C_{19}H_{21}N_3O_2H$ 324.1712.

Ethyl 4-methyl-1-(1-(naphthalen-2-yl)vinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a light yellow solid; Yield: 78% (140.5 mg); Mp.: 98-100 °C; IR (Neat): ν$_{max}$ 2977, 2925, 2837, 1701, 1608, 1515, 1463, 1371, 1298, 1257, 1200, 1055, 1030, 833 and 771 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83-7.81 (2H, m), 7.77 (1H, d, *J* = 7.0 Hz), 7.61 (1H, s), 7.51-7.46 (2H, m), 7.36 (1H, d, *J* = 8.0 Hz), 5.90 (1H, s, olefinic-*H*), 5.71 (1H, s, olefinic-*H*), 4.23 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.67 (2H, br t, *J* = 8.0 Hz), 2.67 (3H, s, Ar-C*H*$_3$), 2.45 (2H, t, *J* = 8.0 Hz), 1.31 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$);



^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 145.3 (C), 141.7 (C), 138.1 (C), 134.5 (C), 133.4 (C), 132.7 (C), 131.3 (C), 128.6 (CH), 128.2 (CH), 127.5 (CH), 127.0 (CH), 126.7 (CH), 125.8 (CH), 123.1 (CH), 120.8 (C), 112.7 (CH_2), 60.1 (CH_2, O*C*H_2CH$_3$), 25.0 (CH_2), 19.1 (CH_2), 15.1 (CH_3), 14.1 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 360.1713 (M + H$^+$), calcd for $C_{22}H_{21}N_3O_2H$ 360.1712.

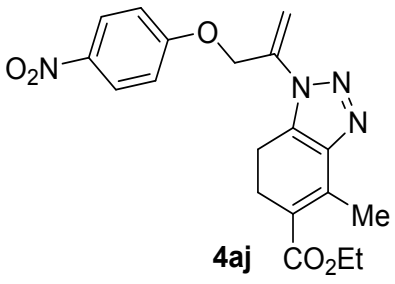
Ethyl (*E*)-4-methyl-1-styryl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ai):



4ai

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (133.5 mg); Mp.: 140-142 °C; IR (Neat): ν_{max} 3049, 2977, 2924, 1679, 1612, 1477, 1448, 1226, 1212, 1024, 751 and 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (1H, d, *J* = 13.6 Hz, olefinic-*H*), 7.49 (2H, br d, *J* = 7.2 Hz), 7.41 (2H, br t, *J* = 7.2 Hz), 7.35 (1H, br t, *J* = 7.2 Hz), 7.32 (1H, d, *J* = 11.6 Hz, olefinic-*H*), 4.27 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 3.01 (2H, t, *J* = 7.6 Hz), 2.89 (2H, qt, *J* = 8.0, 1.2 Hz), 2.60 (3H, t, *J* = 1.2 Hz, olefinic-C*H*$_3$), 1.36 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O-*C*=O), 145.8 (C), 138.3 (C), 133.7 (C), 132.7 (C), 128.9 (2 x CH), 128.8 (CH), 126.7 (2 x CH), 123.6 (CH), 120.9 (CH), 120.8 (C), 60.4 (CH_2, O*C*H_2CH$_3$), 25.1 (CH_2), 18.9 (CH_2), 15.2 (CH_3), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 310.1554 (M + H$^+$), calcd for $C_{18}H_{19}N_3O_2H$ 310.1556.

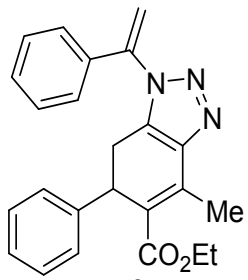
Ethyl 4-methyl-1-(3-(4-nitrophenoxy)prop-1-en-2-yl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4aj): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 82% (158.0 mg); Mp.: 138-140 °C; IR (Neat): ν_{max} 2923, 1749, 1597, 1525, 1506, 1341, 1242, 1042, 854, 748, 689 and 500 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (2H, d, *J* = 8.5 Hz), 7.07 (2H, d, *J* = 9.0 Hz), 5.64 (1H, d, *J* = 0.5 Hz, olefinic-*H*), 5.40 (1H, s, olefinic-*H*), 5.26 (2H, s), 4.27 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.96 (2H, t, *J* = 9.0 Hz), 2.87 (2H, t, *J* = 8.5 Hz), 2.59 (3H, s, olefinic-C*H*$_3$), 1.36 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 162.5 (C), 145.8 (C), 142.1 (C), 137.9 (C), 137.7 (C), 133.8 (C), 125.9 (2 x CH), 121.3 (C), 114.8 (2 x CH), 109.6



4aj

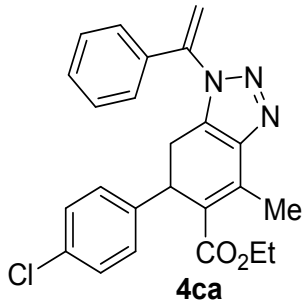
(CH_2), 67.1 (CH_2), 60.4 (CH_2, O*C*H_2CH$_3$), 25.3 (CH_2), 19.7 (CH_2), 15.1 (CH_3), 14.2 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 385.1512 ($M + H^+$), calcd for $C_{19}H_{20}N_4O_5H$ 385.1512.

Ethyl 4-methyl-6-phenyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 80% (155.0 mg); Mp.: 80-82 °C; IR (Neat): ν_{max} 2918, 2849, 1699, 1602, 1491, 1447, 1263, 1209, 1501, 964, 908, 774 and 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (1H, br t, *J* = 8.0 Hz), 7.19–7.17 (3H, m), 7.13 (2H, br t, *J* = 8.0 Hz), 7.01–6.98 (2H, m), 6.94 (2H, td, *J* = 8.0, 0.8 Hz), 5.70 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 5.55 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 4.32 (1H, br d, *J* = 8.0 Hz), 4.11 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 3.03 (1H, dd, *J* = 16.8, 8.8 Hz), 2.77 (3H, d, *J* = 0.8 Hz, olefinic-C*H*$_3$), 2.52 (1H, dd, *J* = 16.8, 2.0 Hz), 1.17 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O-C=O), 145.6 (C), 142.0 (C), 141.7 (C), 139.2 (C), 133.7 (C), 132.8 (C), 129.5 (CH), 128.7 (2 x CH), 128.5 (2 x CH), 126.9 (2 x CH), 126.8 (CH), 126.0 (2 x CH), 124.1 (C), 112.5 (CH_2), 60.4 (CH_2, O*C*H$_2$CH$_3$), 41.0 (CH), 28.3 (CH_2), 15.5 (CH_3), 14.1 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 386.1869 ($M + H^+$), calcd for $C_{24}H_{23}N_3O_2H$ 386.1869.



4ba

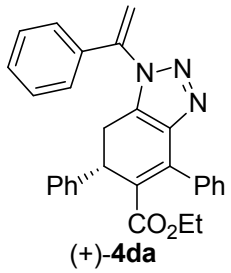
Ethyl 6-(4-chlorophenyl)-4-methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 70% (147.1 mg); Mp.: 96-98 °C; IR (Neat): ν_{max} 2979, 2919, 1699, 1638, 1603, 1488, 1367, 1260, 1208, 1051, 1014, 907, 733 and 720 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (1H, t, *J* = 7.5 Hz), 7.17–7.13 (4H, m), 6.93–6.91 (4H, m), 5.70 (1H, s, olefinic-*H*), 5.57 (1H, s, olefinic-*H*), 4.29 (1H, br d, *J* = 8.0 Hz), 4.12 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 3.02 (1H, dd, *J* = 17.0, 8.5 Hz), 2.78 (3H, br s, olefinic-C*H*$_3$), 2.44 (1H, dd, *J* = 16.5, 2.0 Hz), 1.19 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O-*C*=O), 145.5 (C), 141.7 (C), 140.5 (C), 139.7 (C), 133.8 (C), 132.6 (C), 132.5 (C), 129.7 (CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.4 (2 x CH), 126.0 (2 x CH), 123.6 (C), 112.7 (CH_2), 60.5 (CH_2, O*C*H$_2$CH$_3$), 40.5 (CH),



4ca

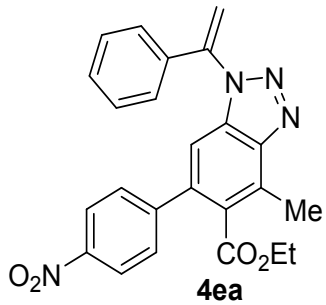
28.2 (CH_2), 15.5 (CH_3), 14.1 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 420.1479 ($M + H^+$), calcd for $C_{24}H_{22}ClN_3O_2H$ 420.1479.

Ethyl (*S*)-4,6-diphenyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4da): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a semi solid; Yield: 67% (149.5 mg); $[\alpha]_D^{25}$ = +24.75 (*C* = 0.20, $CHCl_3$, 89.9% *ee*); IR (Neat): ν_{max} 2922, 2852, 1719, 1593, 1512, 1345, 1287, 1262, 1082, 1502, 854, 691 and 598 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (2H, td, *J* = 6.8, 1.6 Hz), 7.45 (2H, tt, *J* = 6.8, 2.0 Hz), 7.41 (1H, tt, *J* = 6.8, 1.6 Hz), 7.29 (1H, tt, *J* = 7.6, 1.6 Hz), 7.24–7.23 (3H, m), 7.18–7.14 (4H, m), 6.98 (2H, td, *J* = 8.0, 1.2 Hz), 5.72 (1H, d, *J* = 1.2 Hz, olefinic-*H*), 5.57 (1H, d, *J* = 0.8 Hz, olefinic-*H*), 4.36 (1H, dd, *J* = 8.8, 2.8 Hz), 3.85-3.79 (2H, m, OCH_2CH_3), 3.17 (1H, dd, *J* = 16.8, 8.8 Hz), 2.63 (1H, dd, *J* = 16.8, 3.2 Hz), 0.77 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-C=O), 144.4 (C), 141.7 (C), 141.3 (C), 139.6 (C), 136.0 (C), 133.7 (C), 132.9 (C), 129.6 (CH), 128.8 (2 x CH), 128.7 (2 x CH), 128.6 (2 x CH), 128.3 (CH), 128.0 (2 x CH), 127.2 (CH), 127.1 (2 x CH), 126.4 (C), 126.0 (2 x CH), 112.8 (CH_2), 60.5 (CH_2, OCH_2CH_3), 42.0 (CH), 28.4 (CH_2), 13.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 448.2024 ($M + H^+$), calcd for $C_{29}H_{25}N_3O_2H$ 448.2025.



(+)-**4da**

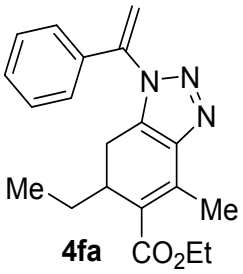
Ethyl 4-methyl-6-(4-nitrophenyl)-1-(1-phenylvinyl)-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ea): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 36% (78.0 mg); Mp.: 128-130 °C; IR (Neat): ν_{max} 3054, 2919, 2856, 1719, 1595, 1513, 1341, 1267, 1046, 778 and 708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (2H, td, *J* = 8.8, 2.0 Hz), 7.46–7.42 (3H, m), 7.39 (2H, tt, *J* = 6.8, 2.8 Hz), 7.28 (2H, td, *J* = 6.8, 1.2 Hz), 6.83 (1H, s, Ar-*H*), 5.86 (1H, d, *J* = 1.2 Hz, olefinic-*H*), 5.81 (1H, d, *J* = 1.2 Hz, olefinic-*H*), 4.10 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.95 (3H, s, Ar-CH_3), 1.03 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.1 (C, O-*C*=O), 147.3 (C), 147.2 (C), 145.5 (C), 142.3 (C), 138.3 (C), 134.1 (C), 132.6 (C), 130.8 (C), 130.0 (CH), 129.3 (2 x CH), 129.2 (C), 128.9 (2 x CH), 126.7 (2 x



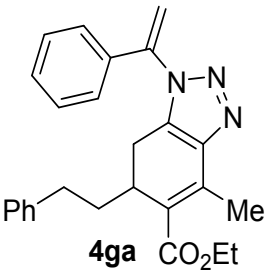
4ea

CH), 123.5 (2 x CH), 111.8 (CH_2), 109.6 (CH), 61.5 (CH_2, O*C*H_2CH_3), 14.4 (CH_3), 13.7 (CH_3); HRMS (ESI-TOF) m/z 429.1563 ($M + H^+$), calcd for $C_{24}H_{20}N_4O_4H$ 429.1563.

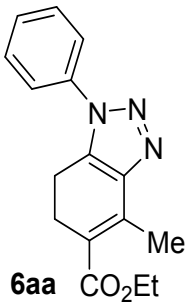
Ethyl 6-ethyl-4-methyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellowish semi solid; Yield: 78% (132.0 mg); IR (Neat): ν_{max} 2961, 2926, 1695, 1601, 1296, 1207, 1051, 907, 773 and 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (3H, m), 7.23 (2H, dd, *J* = 8.0, 2.0 Hz), 5.79 (1H, d, *J* = 0.4 Hz, olefinic-*H*), 5.65 (1H, s, olefinic-*H*), 4.29-4.21 (2H, m, OC*H*$_2$CH$_3$), 2.97-2.91 (1H, m), 2.61 (3H, s, Ar-C*H*$_3$), 2.60 (1H, dd, *J* = 16.8, 7.6 Hz), 2.41 (1H, dd, *J* = 17.2, 1.2 Hz), 1.47-1.38 (1H, m), 1.33 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 1.22–1.15 (1H, m), 0.67 (3H, t, *J* = 7.2 Hz, CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 145.0 (C), 142.0 (C), 137.2 (C), 134.4 (C), 133.8 (C), 129.8 (CH), 128.9 (2 x CH), 126.3 (2 x CH), 126.2 (C), 112.6 (CH_2), 60.3 (CH_2, O*C*H_2CH_3), 36.9 (CH), 25.8 (CH_2), 22.9 (CH_2), 15.5 (CH_3, Ar-*C*H_3), 14.3 (CH_3, OCH$_2$*C*H$_3$), 11.2 (CH_3, CH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 338.1868 ($M + H^+$), calcd for $C_{20}H_{23}N_3O_2H$ 338.1868.



Ethyl 4-methyl-6-phenethyl-1-(1-phenylvinyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (4ga): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 77% (160.1 mg); IR (Neat): ν_{max} 2924, 2853, 1699, 1602, 1451, 1367, 1258, 1207, 1051, 909, 749 and 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.33 (3H, m), 7.24-7.20 (5H, m), 7.00 (2H, d, *J* = 6.0 Hz), 5.78 (1H, s, olefinic-*H*), 5.64 (1H, s, olefinic-*H*), 4.23-4.19 (2H, m, OC*H*$_2$CH$_3$), 3.10-3.05 (1H, m), 2.64-2.58 (1H, m), 2.63 (3H, s, Ar-C*H*$_3$), 2.47-2.40 (2H, m), 2.33-2.27 (1H, m), 1.76-1.69 (1H, m), 1.55–1.47 (1H, m), 1.28 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 144.9 (C), 141.9 (C), 141.3 (C), 137.8 (C), 134.4 (C), 133.6 (C), 129.8 (CH), 128.9 (2 x CH), 128.2 (2 x CH), 128.1 (2 x CH), 126.3 (2 x CH), 125.9 (C), 125.8 (CH), 112.7 (CH_2), 60.3 (CH_2, O*C*H_2CH_3), 35.0 (CH), 34.1 (CH_2), 32.8 (CH_2), 23.2 (CH_2), 15.5 (CH_3), 14.2 (CH_3); HRMS (ESI-TOF) m/z 414.2182 ($M + H^+$), calcd for $C_{26}H_{27}N_3O_2H$ 414.2181.

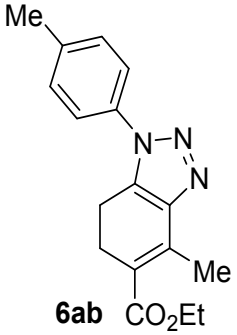


Ethyl 4-methyl-1-phenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6aa):



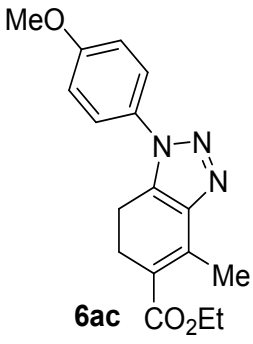
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 95% (135 mg); Mp.: 96-98 °C; IR (Neat): ν_{max} 3066, 2988, 2930, 1699, 1605, 1508, 1449, 1285, 1201, 1054, 918, 761, 693 and 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (4H, br s), 7.50 (1H, br s), 4.28 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.97 (2H, br t, *J* = 8.0 Hz), 2.85 (2H, br t, *J* = 8.0 Hz), 2.64 (3H, br s, olefinic-CH_3), 1.36 (3H, t, *J* = 6.8 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 146.0 (C), 138.7 (C), 136.1 (C), 133.5 (C), 129.6 (2 x CH), 129.1 (CH), 123.0 (2 x CH), 120.9 (C), 60.4 (CH_2, OCH_2CH_3), 25.4 (CH_2), 19.6 (CH_2), 15.3 (CH_3, olefinic-CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 284.1402 ($M + H^+$), calcd for $C_{16}H_{17}N_3O_2H$ 284.1399.

Ethyl 4-methyl-1-(*p*-tolyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ab):



Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (130.5 mg); Mp.: 100-102 °C; IR (Neat): ν_{max} 3039, 2982, 2928, 1693, 1520, 1441, 1284, 1202, 1116, 1046, 821 and 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (2H, d, *J* = 8.5 Hz), 7.34 (2H, d, *J* = 8.5 Hz), 4.27 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 2.94 (2H, t, *J* = 8.0 Hz), 2.84 (2H, t, *J* = 8.0 Hz), 2.64 (3H, s, olefinic-CH_3), 2.44 (3H, s, Ar-CH_3), 1.36 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.9 (C), 139.3 (C), 138.8 (C), 133.7 (C), 133.5 (C), 130.1 (2 x CH), 122.9 (2 x CH), 120.8 (C), 60.4 (CH_2, OCH_2CH_3), 25.4 (CH_2), 21.1 (CH_3, Ar-CH_3), 19.6 (CH_2), 15.3 (CH_3, olefinic-CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 298.1559 ($M + H^+$), calcd for $C_{17}H_{19}N_3O_2H$ 298.1556.

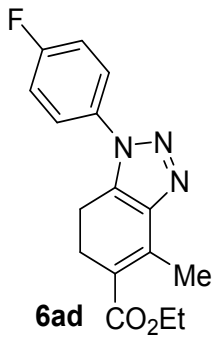
Ethyl 1-(4-methoxyphenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ac):



Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (134.5 mg); Mp.: 120-122 °C; IR (Neat): ν_{max} 2992, 2951, 1768, 1696, 1605, 1518, 1285, 1248, 1205, 1114, 1035, 835 and 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (2H, td, *J* = 8.8, 3.6 Hz), 7.04 (2H, td, *J* = 8.8, 3.6 Hz), 4.27 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.87 (3H, s, OCH_3), 2.94-2.90 (2H, m), 2.86-2.82 (2H,

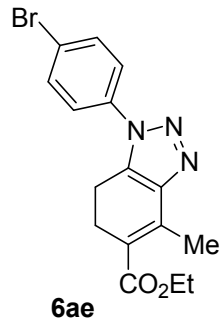
m), 2.63 (3H, s, olefinic-CH_3), 1.35 (3H, t, J = 7.2 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 160.0 (C), 145.7 (C), 138.7 (C), 133.5 (C), 129.1 (C), 124.4 (2 x CH), 120.7 (C), 114.6 (2 x CH), 60.3 (CH_2, O*C*H$_2$CH$_3$), 55.5 (CH_3, O*C*H$_3$), 25.3 (CH_2), 19.4 (CH_2), 15.2 (CH_3, olefinic-*C*H$_3$), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 314.1505 (M + H$^+$), calcd for $C_{17}H_{19}N_3O_3H$ 314.1505.

Ethyl 1-(4-fluorophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ad): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 88% (150.5 mg); IR (Neat): ν_{max} 3078, 2988, 2853, 1700, 1606, 1517, 1445, 1203, 1051, 842, 774, 703 and 603 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.53 (2H, m), 7.27-7.23 (2H, m), 4.27 (2H, q, J = 7.0 Hz, OCH_2CH$_3$), 2.95 (2H, t, J = 8.0 Hz), 2.86 (2H, t, J = 8.0 Hz), 2.62 (3H, s, olefinic-CH_3), 1.36 (3H, t, J = 7.0 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 162.6 (C, d, J = 248.7 Hz, *C*-F), 145.9 (C), 138.4 (C), 133.5 (C), 132.2 (C, d, J = 2.5 Hz), 124.9 (2 x CH, d, J = 8.75 Hz), 121.0 (C), 116.6 (2 x CH, d, J = 23.7 Hz), 60.3 (CH_2, O*C*H$_2$CH$_3$), 25.3 (CH_2), 19.4 (CH_2), 15.2 (CH_3, olefinic-*C*H$_3$), 14.2 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 302.1306 (M + H$^+$), calcd for $C_{16}H_{16}FN_3O_2H$ 302.1305.



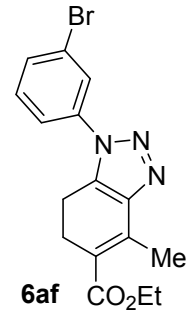
6ad

Ethyl 1-(4-bromophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ae): Prepared following the procedure **A** and purified by column chromatography using (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 89% (160.4 mg); Mp.: 140-142 °C; IR (neat): ν_{max} 3400, 1698, 1608, 1494, 1458, 1283, 1202, 1107, 1040, 823 and 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (2H, td, J = 7.2, 1.6 Hz), 7.44 (2H, td, J = 7.2, 1.6 Hz), 4.27 (2H, q, J = 6.0 Hz, OCH_2CH$_3$), 2.96 (2H, dt, J = 6.8, 1.2 Hz), 2.86 (2H, qt, J = 7.2, 1.2 Hz), 2.62 (3H, t, J = 1.2 Hz, olefinic-CH_3), 1.36 (3H, t, J = 5.6 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 146.2 (C), 138.4 (C), 135.1 (C), 133.3 (C), 132.8 (2 x CH), 124.3 (2 x CH), 122.9 (C), 121.1 (C), 60.4 (CH_2), 25.3 (CH_2), 19.6 (CH_2), 15.2 (CH_3, olefinic-*C*H$_3$), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 362.0504 (M + H$^+$), calcd for $C_{16}H_{16}BrN_3O_2H$ 362.0504.

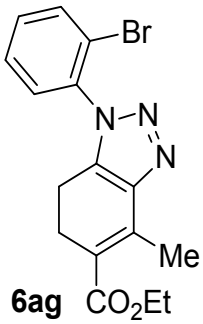


6ae

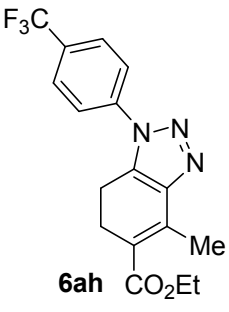
Ethyl 1-(3-bromophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6af): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 80% (144.4 mg); Mp.: 102-104 °C; IR (Neat): ν_{max} 2980, 1699, 1605, 1495, 1441, 1274, 1201, 1095, 1035, 995, 869, 783, 762 and 433 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (1H, t, *J* = 2.0 Hz), 7.63 (1H, ddd, *J* = 8.0, 2.0, 1.0 Hz), 7.49 (1H, ddd, *J* = 8.0, 2.0, 1.0 Hz), 7.43 (1H, t, *J* = 8.0 Hz), 4.28 (2H, q, *J* = 7.5 Hz, OC*H*$_2$CH$_3$), 2.98 (2H, br t, *J* = 8.5 Hz), 2.87 (2H, qt, *J* = 8.0, 1.5 Hz), 2.63 (3H, t, *J* = 1.5 Hz, olefinic-C*H*$_3$), 1.36 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O-*C*=O), 146.2 (C), 138.4 (C), 137.2 (C), 133.4 (C), 132.1 (CH), 130.9 (CH), 126.1 (CH), 123.2 (C), 121.5 (CH), 121.2 (C), 60.4 (CH$_2$, O*C*H$_2$CH$_3$), 25.4 (CH$_2$), 19.7 (CH$_2$), 15.2 (CH$_3$, olefinic-*C*H$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 362.0504 (M + H^+), calcd for $C_{16}H_{16}BrN_3O_2H$ 362.0504.



Ethyl 1-(2-bromophenyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ag): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 64% (115.4 mg); Mp.: 252-254 °C; IR (Neat): ν_{max} 2979, 2925, 2853, 1700, 1608, 1507, 1442, 1369, 1285, 1202, 1052, 764 and 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (1H, m), 7.52-7.45 (3H, m), 4.27 (2H, q, *J* = 6.8 Hz, OC*H*$_2$CH$_3$), 2.85 (2H, t, *J* = 7.6 Hz), 2.76 (2H, t, *J* = 7.6 Hz), 2.65 (3H, s, olefinic-C*H*$_3$), 1.35 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 145.1 (C), 138.5 (C), 136.0 (C), 135.2 (C), 133.7 (CH), 131.8 (CH), 128.9 (CH), 128.5 (CH), 121.0 (C), 120.5 (C), 60.4 (CH$_2$, O*C*H$_2$CH$_3$), 25.2 (CH$_2$), 19.0 (CH$_2$), 15.3 (CH$_3$, olefinic-*C*H$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 362.0504 (M + H^+), calcd for $C_{16}H_{16}BrN_3O_2H$ 362.0504.

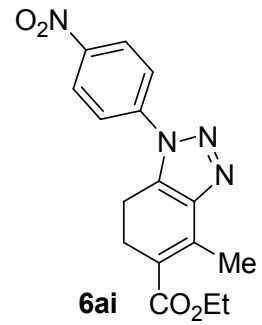


Ethyl 4-methyl-1-(4-(trifluoromethyl)phenyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ah): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 89% (156.5 mg); Mp.: 143-145 °C; IR (Neat): ν_{max} 2989, 2894, 1688, 1614, 1525, 1442, 1417, 1373, 1324, 1261, 1205, 1166, 1118, 843, 777, 738 and 596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (2H, d, *J* = 7.6 Hz), 7.72 (2H, d, *J* = 7.6 Hz), 4.28



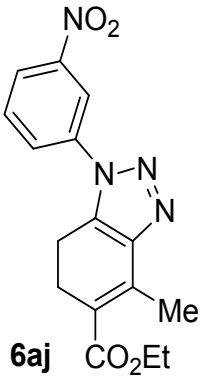
(2H, q, J = 6.8 Hz, OCH_2CH$_3$), 3.02 (2H, t, J = 8.0 Hz), 2.88 (2H, t, J = 8.0 Hz), 2.63 (3H, s, olefinic-CH_3), 1.36 (3H, t, J = 7.2 Hz, OCH$_2$CH_3); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.7 (C, O-*C*=O), 146.5 (C), 138.9 (C), 138.3 (C), 133.5 (C), 131.1 (C, q, J = 26 Hz), 127.0 (2 x CH, q, J = 3.0 Hz), 123.5 (C, q, J = 217.0 Hz, *C*F$_3$), 123.0 (2 x CH), 121.4 (C), 60.5 (CH$_2$, O*C*H$_2$CH$_3$), 25.4 (CH$_2$), 19.8 (CH$_2$), 15.3 (CH$_3$, olefinic-*C*H$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 352.1274 (M + H$^+$), calcd for $C_{17}H_{16}F_3N_3O_2H$ 352.1273.

Ethyl 4-methyl-1-(4-nitrophenyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ai): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 85% (140.0 mg); Mp.: 138-140 °C; IR (neat): ν_{max} 3096, 2976, 2926, 1699, 1598, 1527, 1444, 1347, 1297, 1203, 1114, 1054, 856, 749 and 686 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.45 (2H, td, J = 9.5, 1.5 Hz), 7.82 (2H, td, J = 9.0, 2.0 Hz), 4.29 (2H, q, J = 7.0 Hz, OCH_2CH$_3$), 3.07 (2H, t, J = 8.5 Hz), 2.91 (2H, t, J = 9.0 Hz), 2.63 (3H, s, olefinic-CH_3), 1.37 (3H, t, J = 7.0 Hz, OCH$_2$CH_3); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 147.4 (C), 146.8 (C), 140.9 (C), 138.0 (C), 133.4 (C), 125.3 (2 x CH), 123.0 (2 x CH), 121.6 (C), 60.6 (CH$_2$, O*C*H$_2$CH$_3$), 25.4 (CH$_2$), 20.0 (CH$_2$), 15.2 (CH$_3$, olefinic-*C*H$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 329.1250 (M + H$^+$), calcd for $C_{16}H_{16}N_4O_4H$ 329.1250.



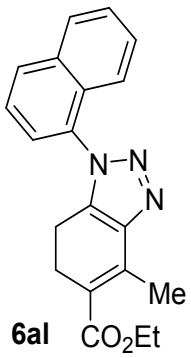
6ai

Ethyl 4-methyl-1-(3-nitrophenyl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6aj): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 60% (99 mg); Mp.: 108-110 °C; IR (Neat): ν_{max} 2982, 1735, 1702, 1537, 1371, 1239, 1201, 1045, 779, 756, 677 and 607 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.44 (1H, t, J = 2.0 Hz), 8.37 (1H, ddd, J = 8.5, 2.0, 1.0 Hz), 8.01 (1H, ddd, J = 8.0, 2.0, 1.0 Hz), 7.80 (1H, t, J = 8.5 Hz), 4.29 (2H, q, J = 7.0 Hz, OCH_2CH$_3$), 3.06 (2H, t, J = 9.0 Hz), 2.91 (2H, qt, J = 9.0, 1.5 Hz), 2.64 (3H, t, J = 2.0 Hz, olefinic-CH_3), 1.37 (3H, t, J = 7.0 Hz, OCH$_2$CH_3); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 148.8 (C), 146.6 (C), 138.0 (C), 137.1 (C), 133.5 (C), 130.9 (CH), 128.4 (CH), 123.6 (CH), 121.6 (C), 117.6 (CH), 60.5 (CH$_2$, O*C*H$_2$CH$_3$), 25.4 (CH$_2$), 19.8 (CH$_2$), 15.2 (CH$_3$, olefinic-*C*H$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 329.1251 (M + H$^+$), calcd for $C_{16}H_{16}N_4O_4H$ 329.1250.



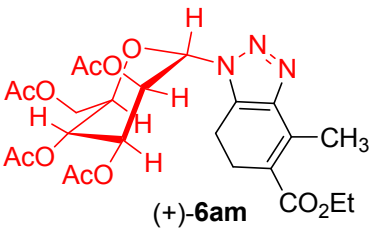
6aj

Ethyl 4-methyl-1-(naphthalen-1-yl)-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6al): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white semisolid; Yield: 87% (145.5 mg); IR (Neat): ν_{max} 2976, 1707, 1593, 1512, 1445, 1350, 1242, 1190, 1128, 824 and 534 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (1H, d, *J* = 8.0 Hz), 7.97 (1H, d, *J* = 8.0 Hz), 7.61-7.56 (2H, m), 7.54-7.50 (2H, m), 7.41 (1H, d, *J* = 8.5 Hz), 4.28 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 2.83 (2H, qt, *J* = 9.0, 1.5 Hz), 2.71 (3H, t, *J* = 1.5 Hz, olefinic-CH_3), 2.66 (2H, t, *J* = 9.0 Hz), 1.35 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.1 (C), 138.5 (C), 136.2 (C), 134.1 (C), 131.9 (C), 130.6 (CH), 128.88 (C), 128.87 (CH), 127.8 (CH), 127.0 (CH), 124.9 (CH), 124.2 (CH), 122.2 (CH), 121.0 (C), 60.3 (CH_2, OCH_2CH_3), 25.2 (CH_2), 18.7 (CH_2), 15.3 (CH_3, olefinic-CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 334.1555 ($M + H^+$), calcd for $C_{20}H_{19}N_3O_2H$ 334.1556.



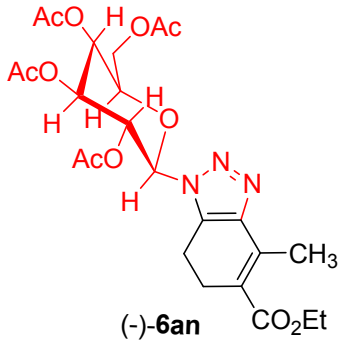
6al

(*2R,3R,4S,5S,6S*)-2-(Acetoxymethyl)-6-(5-(ethoxycarbonyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6am): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 5:5) and was isolated as a semi solid; Yield: 69% (186.5 mg); $[\alpha]_D^{25}$ = +7.63 (*C* = 0.059, $CHCl_3$); IR (Neat): ν_{max} 2981, 2359, 1745, 1699, 1367, 1209, 1048, 982, 903, 775, 599 and 504 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.10-6.07 (1H, m), 5.96-5.93 (2H, m), 5.40 (1H, t, *J* = 10.0 Hz), 4.32 (1H, dd, *J* = 12.5, 5.5 Hz), 4.27 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 4.00 (1H, dd, *J* =12.0, 2.0 Hz), 3.84-3.82 (1H, m), 2.92-2.83 (4H, m), 2.58 (3H, s, olefinic-CH_3), 2.22 (3H, s, $COCH_3$), 2.08 (3H, s, $COCH_3$), 2.06 (3H, s, $COCH_3$), 2.05 (3H, s, $COCH_3$), 1.35 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.2 (C, O-*C*=O), 169.8 (C, O-*C*=O), 169.6 (C, O-*C*=O), 169.1 (C, O-*C*=O), 167.7 (C, O-*C*=O), 145.9 (C), 137.8 (C), 134.7 (C), 121.5 (C), 82.3 (CH), 71.6 (CH), 68.8 (CH), 68.4 (CH), 66.0 (CH), 61.7 (CH_2), 60.4 (CH_2, OCH_2CH_3), 25.0 (CH_2), 20.7 (CH_3, $COCH_3$), 20.59 (CH_3, $COCH_3$), 20.57 (CH_3, $COCH_3$), 20.5 (CH_3, $COCH_3$), 18.3 (CH_2), 15.1 (CH_3, olefinic-CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 538.2037 ($M + H^+$), calcd for $C_{24}H_{31}N_3O_{11}H$ 538.2037.



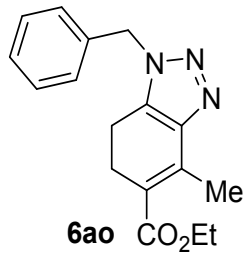
(+)-**6am**

(*2R,3R,4S,5R,6R*)-2-(Acetoxymethyl)-6-(5-(ethoxycarbonyl)-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (6an): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (1:9 to 5:5) and was isolated as a semi solid; Yield: 72% (193.0 mg); $[\alpha]_D^{25}$ = -8.18 (*C* = 0.055, $CHCl_3$); IR (Neat): ν_{max} 2981, 1745, 1699, 1367, 1283, 1207, 1129, 1088, 1046, 982, 775 and 599 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.87 (1H, td, *J* = 7.0, 2.0 Hz), 5.46-5.40 (2H, m), 5.23 (1H, tt, *J* = 7.5, 2.0 Hz), 4.30-4.24 (3H, m), 4.20 (1H, dd, *J* = 12.5, 2.0 Hz), 3.99 (1H, ddd, *J* =10.5, 5.0, 2.5 Hz), 3.10-2.95 (2H, m), 2.86 (2H, m), 2.54 (3H, t, *J* = 1.5 Hz, olefinic-C*H*$_3$), 2.086 (3H, s, COC*H*$_3$), 2.084 (3H, s, COC*H*$_3$), 2.04 (3H, s, COC*H*$_3$), 1.88 (3H, s, COC*H*$_3$), 1.34 (3H, t, *J* = 7.5 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.3 (C, O-*C*=O), 169.8 (C, O-*C*=O), 169.4 (C, O-*C*=O), 168.9 (C, O-*C*=O), 167.8 (C, O-*C*=O), 146.5 (C), 137.7 (C), 134.1 (C), 121.6 (C), 86.0 (CH), 75.1 (CH), 72.4 (CH), 69.4 (CH), 67.8 (CH), 61.5 (CH_2), 60.4 (CH_2, O*C*H$_2$CH$_3$), 24.9 (CH_2), 20.6 (CH_3, CO*C*H$_3$), 20.49 (CH_3, CO*C*H$_3$), 20.46 (CH_3, CO*C*H$_3$), 20.1 (CH_3, CO*C*H$_3$), 19.2 (CH_2), 15.1 (CH_3, olefinic-*C*H$_3$), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 538.2037 ($M + H^+$), calcd for $C_{24}H_{31}N_3O_{11}H$ 538.2037.



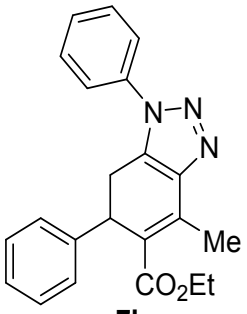
(-)-**6an**

Ethyl 1-benzyl-4-methyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (6ao): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 70% (104.5 mg); IR (Neat): ν_{max}, 2979, 1693, 1607, 1441, 1368, 1284, 1204, 1054, 906, 727 and 459 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (3H, m), 7.20-7.19 (2H, m), 5.49 (2H, s, PhC*H*$_2$N), 4.29 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.75 (2H, t, *J* = 8.5 Hz), 2.61 (2H, t, *J* = 8.5 Hz), 2.57 (3H, br s, olefinic-C*H*$_3$), 1.32 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-*C*=O), 146.0 (C), 138.6 (C), 134.4 (C), 133.8 (C), 129.1 (2 x CH), 128.5 (CH), 127.5 (2 x CH), 120.5 (C), 60.3 (CH_2, O*C*H$_2$CH$_3$), 52.1 (CH_2, PhC*H*$_2$N), 25.1 (CH_2), 18.5 (CH_2), 15.1 (CH_3, olefinic-*C*H$_3$), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 298.1557 ($M + H^+$), calcd for $C_{17}H_{19}N_3O_2H$ 298.1556.



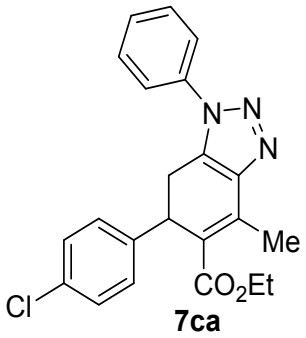
6ao

Ethyl 4-methyl-1,6-diphenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (7ba): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 80% (143.5 mg); Mp.: 104-106 °C; IR (Neat): ν_{max} 2917, 2849, 1684, 1596, 1503, 1364, 1225, 1203, 1079, 1031, 752, 700 and 602 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.41 (5H, m), 7.21-7.15 (3H, m), 7.11 (2H, td, *J* = 6.4, 2.0 Hz), 4.50 (1H, br dd, *J* = 9.2, 1.2 Hz), 4.12 (2H, br q, *J* = 7.2 Hz, OCH_2CH_3), 3.50 (1H, dd, *J* = 16.8, 8.8 Hz), 3.11 (1H, dd, *J* = 16.8, 2.8 Hz), 2.77 (3H, d, *J* = 0.8 Hz, olefinic-CH_3), 1.18 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.3 (C, O-*C*=O), 145.8 (C), 142.6 (C), 138.8 (C), 135.9 (C), 131.6 (C), 129.6 (2 x CH), 129.1 (CH), 128.6 (2 x CH), 126.95 (2 x CH), 126.91 (CH), 124.4 (C), 122.9 (2 x CH), 60.4 (CH_2, OCH_2CH_3), 41.4 (CH), 28.6 (CH_2), 15.5 (CH_3, olefinic-CH_3), 14.0 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 360.1712 ($M + H^+$), calcd for $C_{22}H_{21}N_3O_2H$ 360.1712.



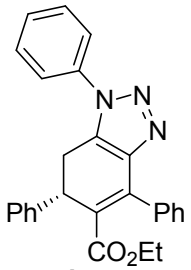
7ba

Ethyl 6-(4-chlorophenyl)-4-methyl-1-phenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (7ca): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 77% (151.1 mg); Mp.: 96-98 °C; IR (Neat): ν_{max} 2983, 2919, 2852, 1699, 1508, 1484, 1284, 1191, 1084, 1033, 1011, 961, 763 and 724 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51–7.49 (2H, m), 7.48–7.44 (1H, m), 7.43–7.41 (2H, m), 7.15 (2H, td, *J* = 7.0, 2.5 Hz), 7.03 (2H, td, *J* = 8.5, 2.0 Hz), 4.48 (1H, br d, *J* = 8.0 Hz), 4.14 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.50 (1H, dd, *J* = 17.0, 9.0 Hz), 3.06 (1H, dd, *J* = 16.5, 2.5 Hz), 2.77 (3H, s, olefinic-CH_3), 1.21 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O-C=O), 145.8 (C), 141.1 (C), 139.4 (C), 135.9 (C), 132.7 (C), 131.4 (C), 129.6 (2 x CH), 129.2 (CH), 128.8 (2 x CH), 128.4 (2 x CH), 123.9 (C), 122.9 (2 x CH), 60.5 (CH_2, OCH_2CH_3), 40.8 (CH), 28.6 (CH_2), 15.5 (CH_3, olefinic-CH_3), 14.1 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 394.1323 ($M + H^+$), calcd for $C_{22}H_{20}ClN_3O_2H$ 394.1322.



7ca

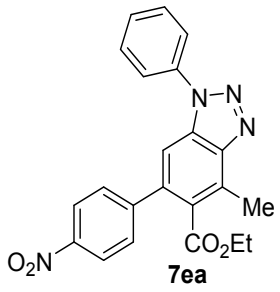
Ethyl (*R*)-1,4,6-triphenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate (7da):



(+)-**7da**

Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 65% (136.5 mg); $[\alpha]_D^{25}$ = +85.0 (*C* = 0.140, $CHCl_3$, 89.63% *ee*); IR (Neat): ν_{max} 3059, 2922, 2851, 1699, 1597, 1507, 1451, 1309, 1228, 1175, 1077, 762 and 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (3H, m), 7.48–7.39 (7H, m), 7.28–7.26 (4H, m), 7.24–7.19 (1H, m), 4.54 (1H, dd, *J* = 8.8, 4.0 Hz), 3.86-3.78 (2H, m, OCH_2CH_3), 3.62 (1H, dd, *J* = 16.8, 8.8 Hz), 3.22 (1H, dd, *J* = 16.8, 4.0 Hz), 0.77 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.0 (C, O-C=O), 144.7 (C), 141.8 (C), 139.2 (C), 135.95 (C), 135.91 (C), 131.8 (C), 129.6 (2 x CH), 129.2 (CH), 128.8 (2 x CH), 128.6 (2 x CH), 128.2 (CH), 128.0 (2 x CH), 127.3 (CH), 127.1 (2 x CH), 126.8 (C), 123.1 (2 x CH), 60.5 (CH_2, OCH_2CH_3), 42.5 (CH), 28.8 (CH_2), 13.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 422.1869 ($M + H^+$), calcd for $C_{27}H_{23}N_3O_2H$ 422.1869.

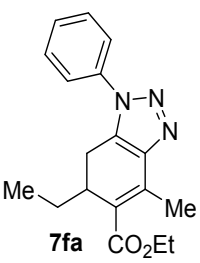
Ethyl 4-methyl-6-(4-nitrophenyl)-1-phenyl-1*H*-benzo[d][1,2,3]triazole-5-carboxylate



7ea

(7ea): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a yellow solid; Yield: 37% (74 mg); Mp.: 118-120 °C; IR (Neat): ν_{max} 2922, 1720, 1513, 1435, 1302, 1083, 1053, 994 and 854 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (2H, d, *J* = 8.5 Hz), 7.77 (2H, td, *J* = 7.5, 1.5 Hz), 7.63 (2H, t, *J* = 7.5 Hz), 7.59 (2H, td, *J* = 8.5, 2.0 Hz), 7.55-7.53 (2H, m), 4.12 (2H, q, *J* = 7.5 Hz, OCH_2CH_3), 2.96 (3H, s, Ar-CH_3), 1.04 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.1 (C, O-*C*=O), 147.4 (2 x C), 145.9 (C), 138.9 (C), 136.5 (C), 132.0 (C), 131.1 (C), 130.0 (2 x CH), 129.5 (2 x CH), 129.4 (C), 129.1 (CH), 123.5 (2 x CH), 123.0 (2 x CH), 108.8 (CH), 61.5 (CH_2, OCH_2CH_3), 14.5 (CH_3), 13.8 (CH_3); HRMS (ESI-TOF) m/z 403.1406 ($M + H^+$), calcd for $C_{22}H_{18}N_4O_4H$ 403.1406.

Ethyl 6-ethyl-4-methyl-1-phenyl-6,7-dihydro-1*H*-benzo[d][1,2,3]triazole-5-carboxylate

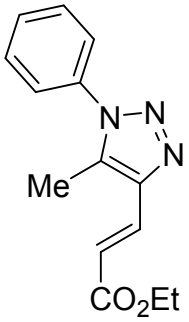


7fa

(7fa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 82% (128 mg); IR (Neat): ν_{max} 2961, 2926, 1693, 1599, 1508, 1454, 1367, 1249, 1191, 1131, 1050, 761 and 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (4H, m), 7.52-7.48 (1H, m), 4.32-4.24

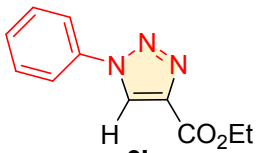
(2H, m, OCH_2CH$_3$), 3.17-3.05 (2H, m), 2.94 (1H, dd, J = 16.4, 1.2 Hz), 2.64 (3H, s, olefinic-CH_3), 1.55-1.45 (1H, m), 1.36 (3H, t, J = 7.2 Hz, OCH$_2$CH_3), 1.31–1.26 (1H, m), 0.80 (3H, t, J = 7.6 Hz, CH$_2$CH_3); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 145.4 (C), 137.4 (C), 136.0 (C), 132.5 (C), 129.6 (2 x CH), 129.0 (CH), 126.2 (C), 122.9 (2 x CH), 60.3 (CH$_2$, O*C*H$_2$CH$_3$), 37.0 (CH), 26.1 (CH$_2$), 23.5 (CH$_2$), 15.5 (CH$_3$, olefinic-C*H*$_3$), 14.2 (CH$_3$, OCH$_2$*C*H$_3$), 11.3 (CH$_3$, CH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 312.1713 (M + H$^+$), calcd for $C_{18}H_{21}N_3O_2H$ 312.1712.

Ethyl (*E*)-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)acrylate (9aa): Prepared following



9aa

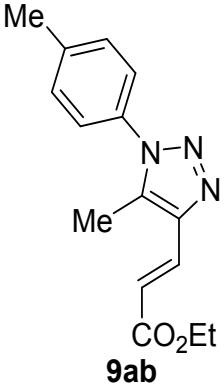
the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 83% (107 mg); Mp.: 108-110 °C; IR (Neat): ν_{max} 2978, 2924, 1705, 1650, 1595, 1501, 1292, 1166, 1131, 1024, 979, 766, 722, 690 and 577 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (1H, d, J = 16.0 Hz, olefinic-*H*), 7.59-7.54 (3H, m), 7.47-7.45 (2H, m), 6.81 (1H, d, J = 16.0 Hz, olefinic-*H*), 4.28 (2H, q, J = 7.0 Hz, OCH_2CH$_3$), 2.42 (3H, s), 1.35 (3H, t, J = 7.0 Hz, OCH$_2$CH_3); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.0 (C, O-*C*=O), 140.8 (C), 135.9 (C), 133.3 (C), 131.7 (CH), 129.7 (CH), 129.6 (2 x CH), 125.0 (2 x CH), 119.2 (CH), 60.5 (CH$_2$, O*C*H$_2$CH$_3$), 14.3 (CH$_3$, OCH$_2$*C*H$_3$), 9.2 (CH$_3$); HRMS (ESI-TOF) m/z 258.1243 (M + H$^+$), calcd for $C_{14}H_{15}N_3O_2H$ 258.1243.



9'aa

Ethyl 1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (9'aa):[3,4] Obtained as byproduct along with product **9aa** in 2-3%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.52 (1H, s), 7.76 (2H, br d, J = 7.6 Hz), 7.60-7.50 (3H, m), 4.47 (2H, q, J = 7.0 Hz, OCH_2CH$_3$), 1.44 (3H, t, J = 7.0 Hz, OCH$_2$CH_3).

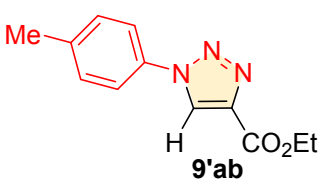
Ethyl (*E*)-3-(5-methyl-1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)acrylate (9ab): Prepared following



9ab

the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white semi solid; Yield: 81% (110 mg); IR (Neat): ν_{max} 2980, 2925, 1706, 1647, 1517, 1297, 1222, 1208, 1164, 1035, 1008, 870, 820, 733, 703, 564 and 509 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (1H, d, J = 16.0 Hz, olefinic-*H*), 7.36-7.32 (4H, m), 6.79 (1H, d, J = 15.5 Hz, olefinic-*H*), 4.28 (2H, q, J = 7.0 Hz, OCH_2CH$_3$), 2.45 (3H, s, Ar-CH_3), 2.40 (3H, s), 1.34 (3H, t, J = 7.0 Hz, OCH$_2$CH_3); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.0 (C, O-

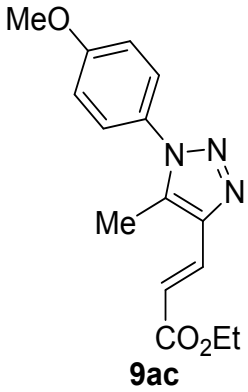
C=O), 140.6 (C), 139.9 (2 x C), 133.3 (C), 131.8 (CH), 130.1 (2 x CH), 124.8 (2 x CH), 118.9 (CH), 60.4 (CH_2, O*C*H_2CH$_3$), 21.1 (CH_3, Ar-*C*H_3), 14.2 (CH_3, OCH$_2$*C*H_3), 9.1 (CH_3); HRMS (ESI-TOF) m/z 272.1399 (M + H^+), calcd for $C_{15}H_{17}N_3O_2H$ 272.1399.



9'ab

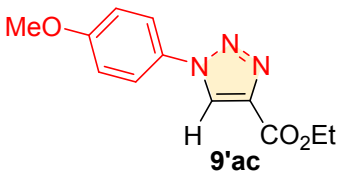
Ethyl 1-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (9'ab):[3,4] Obtained as byproduct along with product **9ab** in 3-5%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (1H, s), 7.63 (2H, m), 7.35 (2H, m), 4.45 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.43 (3H, s, Ar-C*H*$_3$), 1.43 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.6 (C, O-*C*=O), 140.6 (C), 139.7 (C), 134.0 (C), 130.3 (2 x CH), 125.4 (CH), 120.6 (2 x CH), 61.2 (CH_2, O*C*H$_2$CH$_3$), 21.0 (CH_3, Ar-*C*H$_3$), 14.2 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 254.0904 (M + Na^+), calcd for $C_{12}H_{13}N_3O_2Na$ 254.0905.

Ethyl (*E*)-3-(1-(4-methoxyphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (9ac):



9ac

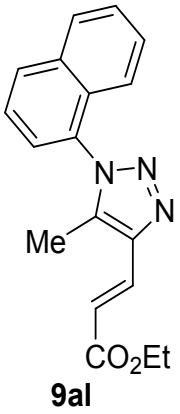
Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a orange solid; Yield: 71% (102); Mp.: 80-82 °C; IR (Neat): ν_{max} 2923, 2851, 1708, 1648, 1517, 1300, 1253, 1174, 1035, 977, 836 and 735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (1H, d, *J* = 16.0 Hz, olefinic-*H*), 7.36 (2H, td, *J* = 9.0, 3.5 Hz), 7.05 (2H, td, *J* = 9.0, 3.5 Hz), 6.79 (1H, d, *J* = 16.0 Hz, olefinic-*H*), 4.28 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 3.89 (3H, s, OC*H*$_3$), 2.38 (3H, s), 1.35 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.1 (C, O-*C*=O), 160.5 (C), 140.5 (C), 133.5 (C), 131.9 (CH), 128.7 (C), 126.4 (2 x CH), 118.9 (CH), 114.7 (2 x CH), 60.5 (CH_2, O*C*H$_2$CH$_3$), 55.6 (CH_3, O*C*H$_3$), 14.3 (CH_3, OCH$_2$*C*H$_3$), 9.1 (CH_3); HRMS (ESI-TOF) m/z 288.1347 (M + H^+), calcd for $C_{15}H_{17}N_3O_3H$ 288.1348.



9'ac

Ethyl 1-(4-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (9'ac):[3,4] Obtained as byproduct along with product **9ac** in 2-3%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (1H, s), 7.63 (2H, m), 7.05 (2H, m), 4.45 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 3.87 (3H, s, Ar-O*C*H$_3$), 1.43 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.7 (C, O-*C*=O), 160.4 (C), 140.6 (C), 129.7 (C), 125.6 (CH), 122.5 (2 x CH), 114.9 (2 x CH), 61.2 (CH_2, O*C*H$_2$CH$_3$), 55.6 (CH_3, Ar-O*C*H$_3$), 14.3 (CH_3, OCH$_2$*C*H$_3$); HRMS (ESI-TOF) m/z 248.1032 (M + H^+), calcd for $C_{12}H_{13}N_3O_2H$ 248.1035.

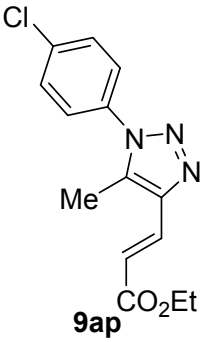
Ethyl (*E*)-3-(5-methyl-1-(naphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)acrylate (9al): Prepared



9al

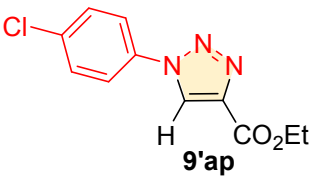
following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 78% (120 mg); IR (Neat): ν_{max} 3059, 2979, 2926, 1705, 1647, 1597, 1440, 1296, 1230, 1188, 1161, 1034, 975, 803 and 773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (1H, d, *J* = 8.4 Hz), 7.98 (1H, d, *J* = 8.4 Hz), 7.73 (1H, d, *J* = 16.0 Hz, olefinic-*H*), 7.64-7.56 (2H, m), 7.51 (2H, t, *J* = 8.8 Hz), 7.19 (1H, d, *J* = 8.4 Hz), 6.87 (1H, d, *J* = 15.6 Hz, olefinic-*H*), 4.50 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.22 (3H, s), 1.46 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-*C*=O), 140.1 (C), 135.4 (C), 134.1 (C), 131.82 (C), 131.76 (CH), 130.9 (CH), 129.4 (C), 128.3 (CH), 128.0 (CH), 127.1 (CH), 125.05 (CH), 125.0 (CH), 121.9 (CH), 119.1 (CH), 60.5 (CH_2, OCH_2CH_3), 14.2 (CH_3, OCH_2CH_3), 8.5 (CH_3); HRMS (ESI-TOF) m/z 308.1399 ($M + H^+$), calcd for $C_{18}H_{17}N_3O_2H$ 308.1399.

Ethyl (*E*)-3-(1-(4-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (9ap): Prepared



9ap

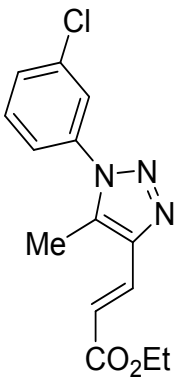
following the procedure **A** and purified by column chromatography using (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 88% (128.5 mg); Mp.: 106-108 °C; IR (neat): ν_{max} 2993, 1717, 1651, 1497, 1300, 1169, 1109, 1005, 832, 748 and 518 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, d, *J* = 15.6 Hz, olefinic-*H*), 7.55 (2H, td, *J* = 8.8, 2.8 Hz), 7.42 (2H, td, *J* = 8.8, 2.0 Hz), 6.81 (1H, d, *J* = 15.6 Hz, olefinic-*H*), 4.28 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.42 (3H, s), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-*C*=O), 141.0 (C), 135.8 (C), 134.3 (C), 133.2 (C), 131.4 (CH), 129.9 (2 x CH), 126.2 (2 x CH), 119.4 (CH), 60.6 (CH_2, OCH_2CH_3), 14.3 (CH_3, OCH_2CH_3), 9.2 (CH_3); HRMS (ESI-TOF) m/z 292.0853 ($M + H^+$), calcd for $C_{14}H_{14}ClN_3O_2H$ 292.0853.



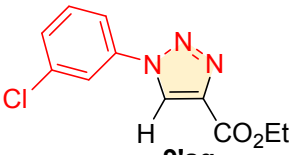
9'ap

Ethyl 1-(4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (9'ap):[3,4] Obtained as byproduct along with product **9ap** in 2-3%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (1H, s), 7.72 (2H, td, *J* = 8.8, 2.8 Hz), 7.53 (2H, td, *J* = 8.8, 2.8 Hz), 4.45 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 1.42 (3H, t, *J* = 7.0 Hz, OCH_2CH_3).

Ethyl (*E*)-3-(1-(3-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (9aq): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (124.5 mg); Mp.: 90-92 °C; IR (Neat): ν_{max} 2980, 1706, 1648, 1549, 1298, 1252, 1221, 1172, 1034, 976, 835, 786 and 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (1H, d, *J* = 16.0 Hz, olefinic-*H*), 7.53-7.51 (3H, m), 7.39-7.37 (1H, m), 6.80 (1H, d, *J* = 15.5 Hz, olefinic-*H*), 4.28 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 2.44 (3H, s), 1.35 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.8 (C, O-*C*=O), 141.0 (C), 136.7 (C), 135.4 (C), 133.2 (C), 131.2 (CH), 130.6 (CH), 129.9 (CH), 125.2 (CH), 123.0 (CH), 119.5 (CH), 60.5 (CH_2, OCH_2CH_3), 14.2 (CH_3, OCH_2CH_3), 9.2 (CH_3); HRMS (ESI-TOF) m/z 292.0855 (M + H^+), calcd for $C_{14}H_{14}ClN_3O_2H$ 292.0853.



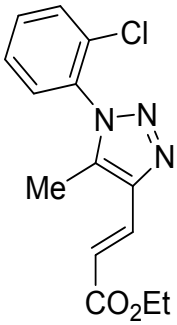
9aq



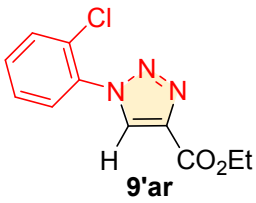
9'aq

Ethyl 1-(3-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (9'aq):[3,4] Obtained as byproduct along with product **9aq** in 2-3%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (1H, s), 7.83 (1H, t, *J* = 8.8 Hz), 7.68 (1H, m), 7.53-7.46 (2H, m), 4.47 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 1.45 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ four quaternary carbons are not appeared, 131.0 (CH), 129.5 (CH), 125.3 (CH), 121.0 (CH), 118.7 (CH), 61.6 (CH_2, OCH_2CH_3), 14.2 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 252.0548 (M + H^+), calcd for $C_{11}H_{10}ClN_3O_2H$ 252.0540.

Ethyl (*E*)-3-(1-(2-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (9ar): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 40% (58 mg); IR (Neat): ν_{max} 2925, 1709, 1650, 1497, 1301, 1264, 1177, 1034, 977 and 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (1H, d, *J* = 15.6 Hz, olefinic-*H*), 7.63-7.60 (1H, m), 7.55 (1H, dt, *J* = 8.0, 2.0 Hz), 7.52-7.48 (1H, m), 7.45 (1H, dt, *J* = 8.0, 2.0 Hz), 6.81 (1H, d, *J* = 16.0 Hz, olefinic-*H*), 4.29 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.29 (3H, s), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O-*C*=O), 140.2 (C), 135.2 (C), 133.5 (C), 131.9 (CH), 131.7 (C), 131.6 (CH), 130.6 (CH), 129.2 (CH), 128.0 (CH), 119.3 (CH), 60.6 (CH_2, OCH_2CH_3), 14.3 (CH_3, OCH_2CH_3), 8.5 (CH_3); HRMS (ESI-TOF) m/z 292.0856 (M + H^+), calcd for $C_{14}H_{14}ClN_3O_2H$ 292.0853.



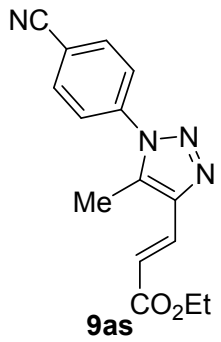
9ar



9'ar

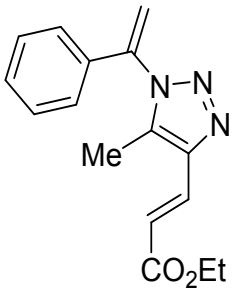
Ethyl 1-(2-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (9'ar):[3,4] Obtained as byproduct along with product **9ar** in 2-3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (1H, s), 7.66-7.61 (2H, m), 7.54-7.47 (2H, m), 4.47 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 1.45 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ four quaternary carbons are not appeared, 131.4 (CH), 130.9 (CH), 129.5 (CH), 128.1 (CH), 127.7 (CH), 61.6 (CH$_2$, OC*H*$_2$CH$_3$), 14.3 (CH$_3$, OCH$_2$C*H*$_3$); HRMS (ESI-TOF) m/z 274.0364 (M + Na$^+$), calcd for $C_{11}H_{10}ClN_3O_2Na$ 274.0359.

Ethyl (*E*)-3-(1-(4-cyanophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)acrylate (9as): Prepared following the procedure **A** and purified by column chromatography using (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 86% (121.5 mg); Mp.: 158-160 °C; IR (neat): ν_{max} 2982, 2923, 2230, 1708, 1649, 1606, 1512, 1300, 1273, 1221, 1172, 1305, 977, 750 and 577 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (2H, dd, *J* = 8.5, 1.5 Hz), 7.70 (2H, d, *J* = 8.5 Hz), 7.61 (1H, br d, *J* = 16.0 Hz, olefinic-*H*), 6.80 (1H, br d, *J* = 15.5 Hz, olefinic-*H*), 4.28 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.50 (3H, s), 1.35 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.6 (C, O-*C*=O), 141.3 (C), 139.0 (C), 133.5 (2 x CH), 133.0 (C), 130.8 (CH), 125.0 (2 x CH), 119.7 (CH), 117.4 (C), 113.3 (C), 60.5 (CH$_2$, OC*H*$_2$CH$_3$), 14.1 (CH$_3$, OCH$_2$C*H*$_3$), 9.2 (CH$_3$); HRMS (ESI-TOF) m/z 283.1191 (M + H$^+$), calcd for $C_{15}H_{14}N_4O_2H$ 283.1191.



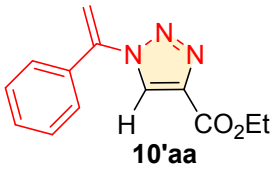
9as

Ethyl (*E*)-3-(5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)acrylate (10aa): Prepared following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 86% (118.5 mg); IR (Neat): ν_{max} 2980, 2359, 1709, 1646, 1370, 1298, 1261, 1184, 1094, 914, 755, 722, 697 and 524 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (1H, d, *J* = 15.5 Hz, olefinic-*H*), 7.40-7.35 (3H, m), 7.18-7.16 (2H, m), 6.80 (1H, d, *J* = 16.0 Hz, olefinic-*H*), 5.98 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.60 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 4.27 (2H, q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$), 2.15 (3H, s), 1.34 (3H, t, *J* = 7.0 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-*C*=O), 142.0 (C), 140.4 (C), 134.3 (C), 133.9 (C), 131.5 (CH), 129.8 (CH), 129.0 (2 x CH), 125.6 (2 x CH), 119.1 (CH), 114.5 (CH$_2$), 60.5 (CH$_2$, OC*H*$_2$CH$_3$), 14.2



10aa

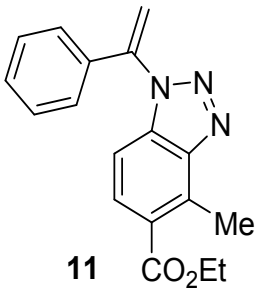
(CH_3, OCH_2CH_3), 8.7 (CH_3); HRMS (ESI-TOF) m/z 306.1218 ($M + Na^+$), calcd for $C_{16}H_{17}N_3O_2Na$ 306.1218.



10'aa

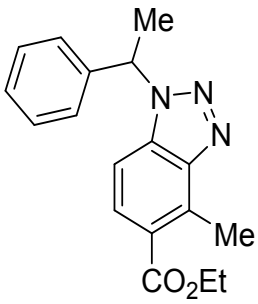
Ethyl 1-(1-phenylvinyl)-1*H*-1,2,3-triazole-4-carboxylate (10'aa): Obtained as byproduct along with product **10aa** in 2-3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.1 (1H, s), 7.50-7.30 (5H, m), 5.9 (1H, s, olefinic-H), 5.61 (1H, s, olefinic-H), 4.43 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 1.42 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.4 (C, O-*C*=O), 142.4 (C), 140.3 (C), 134.3 (C), 131.4 (2 x CH), 127.5 (CH), 127.2 (2 x CH), 125.6 (CH), 110.1 (CH_2), 61.3 (CH_2, OCH_2CH_3), 14.2 (CH_3, OCH_2CH_3).

Ethyl 4-methyl-1-(1-phenylvinyl)-1*H*-benzo[*d*][1,2,3]triazole-5-carboxylate-carboxylate (11): Prepared following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a white solid; Yield: 68% (104 mg); Mp.: 110-112 °C; IR (Neat): ν_{max} 2920, 2851, 1698, 1629, 1477, 1377, 1262, 1224, 1040, 899, 770, 594, 595, 696 and 595 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (1H, d, *J* = 9.0 Hz), 7.43 (1H, tt, *J* = 7.0, 2.0 Hz), 7.38 (2H, tt, *J* = 7.0, 2.0 Hz), 7.28 (2H, td, *J* = 7.0, 2.0 Hz), 6.85 (1H, dd, *J* = 9.0, 0.5 Hz), 5.83 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 5.80 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 4.41 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.16 (3H, s, Ar-CH_3), 1.42 (3H, t, *J* = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O-*C*=O), 147.0 (C), 142.4 (C), 135.6 (C), 134.3 (C), 134.0 (C), 129.9 (CH), 129.8 (CH), 128.8 (2 x CH), 126.8 (2 x CH), 125.0 (C), 111.4 (CH_2), 108.0 (CH), 61.0 (CH_2, OCH_2CH_3), 15.3 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 308.1396 ($M + H^+$), calcd for $C_{18}H_{17}N_3O_2H$ 308.1399.



11

Ethyl 4-methyl-1-(1-phenylethyl)-*1H*-benzo[*d*][1,2,3]triazole-5-carboxylate (12): Prepared following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.5:9.5 to 2:8) and was isolated as a colourless liquid; Yield: 72% (112 mg); IR (Neat): ν_{max} 2925, 1709, 1600, 1494, 1449, 1376, 1288, 1264, 1233, 1185, 1130, 1051, 730, 699 and 532 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (1H, d, *J* = 8.5 Hz), 7.34-7.26 (5H, m), 7.05 (1H, d, *J* = 9.0 Hz), 6.04 (1H, q, *J* = 7.0 Hz), 4.38 (2H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.11 (3H, s, OCH_2CH_3),



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2.17 (3H, d, J = 7.0 Hz), 1.40 (3H, t, J = 7.0 Hz, $CH_2CH_2C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O-*C*=O), 147.4 (C), 139.9 (C), 135.5 (C), 133.5 (C), 129.2 (CH), 128.9 (2 x CH), 128.3 (CH), 126.2 (2 x CH), 124.7 (C), 106.9 (CH), 60.9 (CH_2, OCH_2CH_3), 59.2 (CH), 21.0 (CH_3), 15.2 (CH_3), 14.3 (CH_3, OCH_2CH_3); HRMS (ESI-TOF) m/z 332.1375 ($M + Na^+$), calcd for $C_{18}H_{19}N_3O_2Na$ 332.1375.

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