Synthesis of Geminal Tristriazoles: Exploration of Unconventional Azide Chemistry

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Supporting information

General. All commercial reagents were used as received. Thin-layer chromatography (TLC) was conducted with precoated glass-backed plates (silica gel 60 F254) and visualized by exposure to UV light (254 nm) or stained with ceric ammonium molybdate (CAM), iodine chamber or by putting the developed chromatographic plates in a chlorine chamber and subsequent staining in a potassium iodide – starch solution. Flash chromatography was performed with silica gel (43-60 μm); the eluent used is reported in parentheses. ^{1}H-NMR spectra were recorded at 400 MHz or 600 MHz spectrometers. ^{13}C-NMR spectra were recorded at 101 MHz or 151 MHz. Chemical shifts are reported in ppm relative to the solvent signal. ^{15}N-NMR spectra were recorded at 61 MHz. Chemical shifts are reported in ppm relative to nitromethane as internal standard. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). IR spectra were recorded using ATR technique. High resolution mass spectra were obtained using ESI ionization methods on a MicroTOF.

General procedure **A** for the CuAAC-reaction with ethyl 2,2-diazido-3-oxobutanoate for the preparation of geminal bistriazoles:

Ethyl 2,2-diazido-3-oxobutanoate was dissolved in a 4:1 mixture of *t*BuOH and Water to yield a 0.1 M solution. Alkyne (2.2 eq.), TBTA (3 mol%), copper(II)sulfate pentahydrate (20 mol%) and sodium ascorbate (42 mol%) were added and the reaction mixture stirred for 16 hours (overnight). The reaction mixture was quenched with a saturated, aqueous solution of EDTA disodium salt, stirred for an additional 20 minutes, and extracted with ethyl acetate. The combined organic phases were washed with brine and dried over sodium sulfate. Evaporation of the solvent *in vacuo* and column chromatography afforded the geminal bistriazoles.

General procedure **B** for the azidation of geminal bistriazoles:

The geminal bistriazole was dissolved in a 2:1 mixture of DMSO and Water to yield a 0.1 M solution. Sodium azide (10.0 eq.) and sodium iodide (20 mol%) were added to the stirred solution followed by IBX-SO_3K (4.0 eq.). The solution was allowed to stir at room temperature until all of the starting material was consumed as indicated by TLC. Saturated, aqueous sodium thiosulfate was added and the reaction mixture diluted with water and extracted with ethyl acetate (3x). The combined organic phases were washed with brine and dried over sodium sulfate. Evaporation of the solvent *in vacuo* and column chromatography afforded the azidomethylenebistriazoles.

High resolution mass analysis data were acquired from the corresponding geminal tristriazoles.

General procedure **C** for the azidation of geminal bistriazoles:

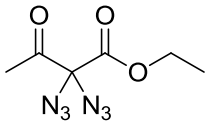
The geminal bistriazole was dissolved in a 2:1 mixture of DMSO and Water to yield a 0.1 M solution. Sodium azide (10.0 eq.) and sodium iodide (20 mol%) were added to the stirred solution followed by IBX-SO_3K (4.0 eq.). The solution was allowed to stir at 60 °C until all of the starting material was consumed as indicated by TLC. Saturated, aqueous sodium thiosulfate was added and the reaction mixture diluted with water and extracted with ethyl acetate (3x). The combined organic phases were washed with brine and dried over sodium sulfate. Evaporation of the solvent *in vacuo* and column chromatography afforded the azidomethylenebistriazoles.

General procedure **D** for the CuAAC-reaction with azidomethylenebistriazoles:

The azidomethylenebistriazole was dissolved in a 4:1 mixture of *t*BuOH and water to yield a 0.01 M solution. Alkyne (3.0 eq.), copper(II)sulfate pentahydrate (40 mol%) and sodium ascorbate (84 mol%) were added and the reaction mixture stirred for 16 hours (overnight). The reaction mixture was quenched with a saturated, aqueous solution of EDTA disodium salt, stirred for an additional 20 minutes, and extracted with ethyl acetate. The combined organic phases were washed with brine and dried over sodium sulfate. Evaporation of the solvent *in vacuo* gave the product upon precipitation by addition of a minimum amount of diethyl ether. The precipitant was collected and washed with a minimum amount of ethyl acetate, water and diethyl ether. Drying under high vacuum afforded the geminal tristriazole.

Experimental data

ethyl 2,2-diazido-3-oxobutanoate (1)

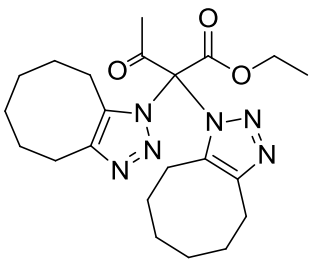


$C_6H_8N_6O_3$
212.17 g/mol

Ethyl acetoacetate (4.0 ml, 31.38 mmol) was dissolved in 200 ml DMSO and 100 ml Water. Sodium azide (20.401 g, 313.81 mmol, 10.0 eq.) and iodine (17.523 g, 69.04 mmol, 2.20 eq.) were added under ice cooling. The ice bath was removed after 5 minutes and the mixture stirred at room temperature for 2 hours. A saturated, aqueous solution of sodium thiosulfate was added and the reaction mixture diluted with water and extracted with diethyl ether (3x). The combined organic phases were washed with water and brine and dried over sodium sulfate. After the solvent was evaporated *in vacuo* the product was obtained as a colorless liquid (5.861 g, 27.62 mmol, 88%) upon purification by column chromatography (PE:Et_2O = 100:0 → 90:10).

TLC: R_f = 0.59 (PE:Et_2O / 9:1, [iodine chamber]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 7.10 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 195.6, 164.3, 83.3, 64.3, 25.1, 14.1; **IR** (ATR): 2985, 2112, 1743, 1359, 1222, 1068, 1008, 942, 853, 747, 582, 544[1].

ethyl 2,2-bis(4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*d*][1,2,3]triazol-1-yl)-3-oxobutanoate

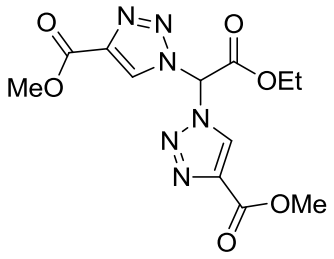


$C_{22}H_{32}N_6O_3$
428.52 g/mol

1 (100 mg, 0.47 mmol) was dissolved in 5 ml and treated with cyclooctyne (112 mg, 1.04 mmol, 2.20 eq.). The solution was stirred for 16 hours at room temperature and directly subjected to column chromatography (PE:EtOAc = 70:30) after evaporation of the solvent *in vacuo*. The product was obtained as viscous oil (129 mg, 0.30 mmol, 64%).

TLC: R_f = 0.45 (PE:EtOAc / 70:30, [UV]); **^{1}H-NMR** (600 MHz, $CDCl_3$): δ [ppm] 4.58-4.46 (m, 2H), 2.92-2.83 (m, 4H), 2.64-2.57 (m, 3H), 2.28-2.13 (m, 4H), 1.80-1.65 (m, 4H), 1.44-1.29 (m, 15H); **^{13}C-NMR** (151 MHz, $CDCl_3$): δ [ppm] 188.9, 161.7, 146.2, 136.6, 86.3, 64.8, 28.9, 27.6, 26.2, 25.7, 25.1, 24.4, 21.9, 13.8; **HRMS** (ESI): [m/z] calculated for [$C_{22}H_{32}N_6O_3Na$] 451.2428, found 451.2408.

dimethyl 1,1'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1*H*-1,2,3-triazole-4-carboxylate) (2a)



$C_{12}H_{14}N_6O_6$
338.28 g/mol

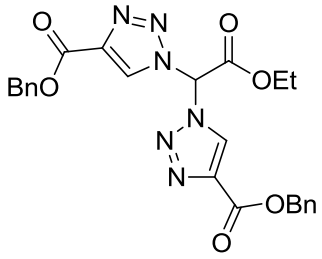
Following the general procedure **A** (1.50 g of **1**, 0.1 M, overnight), dimethyl 1,1'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a viscous oil (1.707 g, 5.05 mmol, 71%) upon purification by column chromatography (PE:EtOAc / 60:40 → 50:50). The resulting viscous oil precipitates the product by addition of a small amount of diethyl ether, thus affording a white solid.

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of a saturated solution in ethyl acetate.

TLC: R_f = 0.24 (PE:EtOAc / 60:40, [CAM]); **^{1}H-NMR** (600 MHz, $CDCl_3$): δ [ppm] 8.60 (s, 2H), 7.78 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 6H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$): δ [ppm] 161.2, 160.3, 141.1, 128.8, 70.7, 66.4, 52.7, 14.0; **^{15}N-NMR** (61 MHz, d_6-DMSO): δ [ppm]

-13.3, -20.3 (d, J = 1.3 Hz), -134.5 (dd, J = 2.0, 4.7 Hz); **IR** (ATR): [cm^{-1}] 3181, 3155, 2962, 1766, 1735, 1534, 1438, 1373, 1268, 1205, 1036 1018, 883, 825, 776, 763, 607, 531, 510; **HRMS** (ESI): [m/z] calculated for [$C_{12}H_{14}N_6O_6Na$] 361.0867, found 361.0867.

dibenzyl 1,1'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1H-1,2,3-triazole-4-carboxylate) (2b)

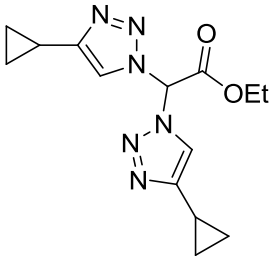


$C_{24}H_{22}N_6O_6$
490.46 g/mol

Following the general procedure **A** (300 mg of **1**, 0.1 M, overnight), dibenzyl 1,1'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1H-1,2,3-triazole-4-carboxylate) was obtained as a white solid (484 mg, 0.99 mmol, 39%) upon purification by column chromatography (PE:EtOAc = 100:0 → 80:20).

TLC: R_f = 0.72 (PE:EtOAc / 80:20, [UV]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.66 (s, 2H), 7.98 (s, 1H), 7.40 (m, 4H), 7.33 (m, 6H), 5.36 (s, 4H), 4.34 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 161.4, 159.7, 140.7, 136.1, 129.1, 128.72, 128.67, 128.6, 70.6, 67.4, 66.1, 13.8; **HRMS** (ESI): [m/z] calculated for [$C_{24}H_{22}N_6O_6Na$] 513.1493, found 513.1485.

ethyl 2,2-bis(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)acetate (2c)

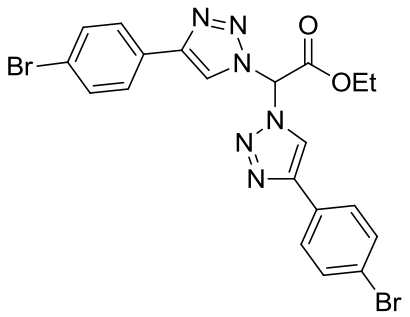


$C_{14}H_{18}N_6O_2$
302.33 g/mol

Following the general procedure **A** (500 mg of **1**, 0.1 M, 3 d), ethyl 2,2-bis(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)acetate was obtained as a white solid (174 mg, 0.58 mmol, 24%) upon purification by column chromatography (PE:EtOAc = 60:40).

TLC: R_f = 0.73 (PE:EtOAc / 80:20, [chlorine chamber / KI-starch stain]); **^{1}H-NMR** (600 MHz, $CDCl_3$): δ [ppm] 7.63 (s, 2H), 7.46 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.94 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.96 (m, 4H), 0.86 (m, 4H); **^{13}C-NMR** (151 MHz, $CDCl_3$): δ [ppm] 162.4, 151.4, 120.4, 70.7, 64.4, 14.0, 8.0, 6.7; **IR** (ATR): [cm^{-1}] 3141, 3108, 3087, 3013, 2960, 1767, 1568, 1433, 1330, 1309, 1233, 1198, 1179, 1146, 1014, 879, 815, 774, 750, 662, 603, 478; **HRMS** (ESI): [m/z] calculated for [$C_{14}H_{18}N_6O_2Na$] 325.1383, found 325.1380.

Ethyl 2,2-bis(4-(4-bromophenyl)-1*H*-1,2,3-triazol-1-yl)acetate (2d)



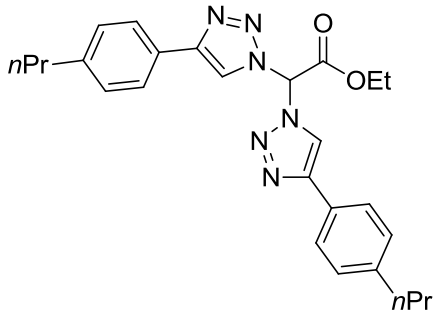
$C_{20}H_{16}Br_2N_6O_2$
532.18 g/mol

Following the general procedure **A** (200 mg of **1**, 0.1 M, overnight), ethyl 2,2-bis(4-(4-bromophenyl)-1*H*-1,2,3-triazol-1-yl)acetate was obtained as a white solid (383 mg, 0.72 mmol, 76%) upon purification by column chromatography (PE:EtOAc = 70:30).

TLC: R_f = 0.63 (PE:EtOAc / 70:30, [UV]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.25 (s, 2H), 7.72 (m, 1H), 7.70 (m, 4H), 7.56 (m, 4H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 162.0, 148.0, 132.3, 128.5, 127.6, 123.1, 120.5, 70.9, 64.88, 14.0; **IR** (ATR): [cm^{-1}] 3132, 3087, 2965, 2938, 1763, 1605, 1552, 1480, 1438, 1398, 1371, 1317, 1296, 1236, 1202,

1065, 1009, 973, 875, 817, 796, 759, 718, 626, 514; **HRMS** (ESI): [m/z] calculated for [$C_{20}H_{17}N_6O_2Br_2$] 530.9774, found 530.9783.

ethyl 2,2-bis(4-(4-propylphenyl)-1*H*-1,2,3-triazol-1-yl)acetate (2e)

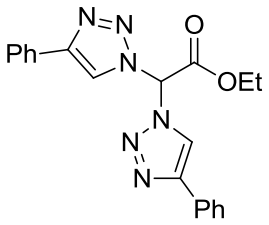


$C_{26}H_{30}N_6O_2$
458.55 g/mol

Following the general procedure **A** (150 mg of **1**, 0.1 M, overnight), ethyl 2,2-bis(4-(4-propylphenyl)-1*H*-1,2,3-triazol-1-yl)acetate was obtained as a white solid (296 mg, 0.65 mmol, 91%) upon purification by column chromatography (PE:EtOAc = 95:5 → 80:20).

TLC: R_f = 0.72 (PE:EtOAc / 80:20, [UV]); **^{1}H-NMR** (600 MHz, $CDCl_3$): δ [ppm] 8.19 (s, 2H), 7.74 (d, *J* = 8.1 Hz, 4H), 7.68 (s, 1H), 7.24 (d, *J* = 8.1 Hz, 4H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 4H), 1.66 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 6H); **^{13}C-NMR** (151 MHz, $CDCl_3$): δ [ppm] 162.2, 149.1, 143.7, 129.2, 127.0, 126.0, 119.9, 71.0, 64.6, 38.0, 24.5, 14.03, 13.9; **IR** (ATR): [cm^{-1}] 3113, 2956, 2930, 2869, 1762, 1497, 1437, 1414, 1368, 1352, 1284, 1238, 1170, 1074, 1015, 879, 818, 797, 771, 592, 529; **HRMS** (ESI): [m/z] calculated for [$C_{26}H_{30}N_6O_2Na$] 481.2322, found 481.2322.

ethyl 2,2-bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetate (2f)

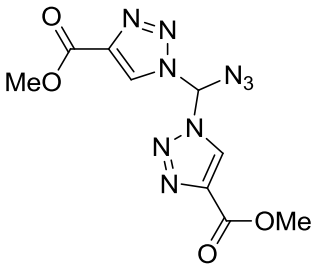


$C_{20}H_{18}N_6O_2$
374.39 g/mol

Following the general procedure **A** (2.0 g of **1**, 0.1 M, overnight), ethyl 2,2-bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetate was obtained as a white solid (2.620 g, 7.00 mmol, 74%) upon purification by column chromatography (PE:EtOAc = 90:10 → 70:30).

TLC: R_f = 0.70 (PE:EtOAc / 70:30, [UV]); **^{1}H-NMR** (600 MHz, $CDCl_3$): δ [ppm] 8.25 (s, 2H), 7.84 (d, *J* = 7.2 Hz, 4H), 7.71 (s, 1H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$): δ [ppm] 162.2, 149.0, 129.6, 129.1, 129.0, 126.1, 120.3, 71.0, 64.7, 14.0; **IR** (ATR): [cm^{-1}] 3130, 3102, 2983, 2961, 1760, 1483, 1457, 1428, 1356, 1282, 1254, 1180, 1072, 1019, 820, 763, 693, 589, 510; **HRMS** (ESI): [m/z] calculated for [$C_{20}H_{18}N_6O_2Na$] 397.1383, found 397.1384.

dimethyl 1,1'-(azidomethylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (3a)

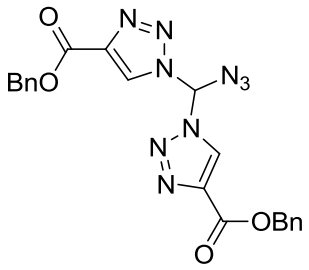


$C_9H_9N_9O_4$
307.22 g/mol

Following the general procedure **B** (1.518 g of **2a**, 0.1 M, overnight), dimethyl 1,1'-(azidomethylene)bis(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a white solid (870 mg, 2.83 mmol, 63%) upon purification by column chromatography (PE:EtOAc = 60:40 → 50:50).

TLC: R_f = 0.22 (PE:EtOAc / 60:40, [CAM]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.77 (s, 1H), 8.64 (s, 2H), 3.94 (s, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 160.3, 140.9, 127.0, 80.7, 52.7; **^{15}N-NMR** (61 MHz, d_6-DMSO): δ [ppm] -17.6, -20.0, -127.2 (d, *J* = 4.4 Hz), 143.0, (d, *J* = 3.6 Hz), 152.8, 293.6; **IR** (ATR): [cm^{-1}] 3147, 3112, 2966, 2264, 2142, 1745, 1718, 1531, 1435, 1371, 1326, 1259, 1218, 1175, 1163, 1117, 1100, 1036, 1008, 989, 953, 871, 846, 823, 779, 692, 650, 636, 616, 550, 530, 498, 456, 432, 413.

dibenzyl 1,1'-(azidomethylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (3b)

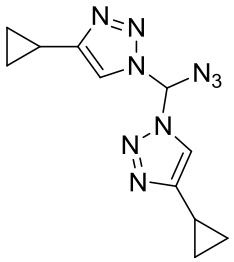


$C_{21}H_{17}N_9O_4$
459.41 g/mol

Following the general procedure **B** (100 mg of **2b**, 0.1 M, 2.0 eq. IBX-SO_3K, overnight), dibenzyl 1,1'-(azidomethylene)bis(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a white solid (174 mg, 0.58 mmol, 24%) upon purification by column chromatography (PE:EtOAc = 90:10 → 80:20).

TLC: R_f = 0.78 (PE:EtOAc / 70:30, [UV]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.56 (s, 1H), 8.53 (s, 2H), 7.42 (m, 4H), 7.35 (m, 6H), 5.38 (s, 4H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 159.6, 141.0, 135.1, 128.82, 128.80, 126.8, 80.7, 67.6; **IR** (ATR): [cm^{-1}] 3135, 2963, 2133, 1725, 1539, 1455, 1389, 1356, 1212, 1168, 1028, 845, 810, 772, 737, 696, 588, 529.

1,1'-(azidomethylene)bis(4-cyclopropyl-1*H*-1,2,3-triazole) (3c)

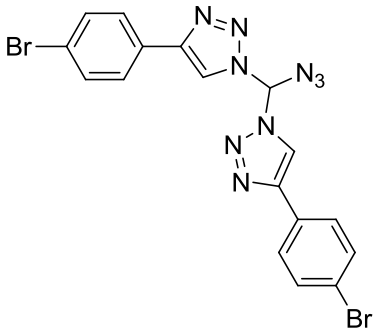


$C_{11}H_{13}N_9$
271.28 g/mol

Following the general procedure **C** (26 mg of **2c**, 0.01 M, overnight), 1,1'-(azidomethylene)bis(4-cyclopropyl-1*H*-1,2,3-triazole) was obtained as a white solid (8 mg, 0.02 mmol, 26%) upon purification by column chromatography (PE:EtOAc = 100:0 → 80:20).

TLC: R_f = 0.75 (PE:EtOAc / 80:20, [chlorine chamber / KI-starch stain]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.06 (s, 1H), 7.56 (s, 2H), 1.95 (m, 2H), 0.99 (m, 4H), 0.89 (m, 4H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 151.7, 118.3, 80.4, 8.1, 6.8; **IR** (ATR): [cm^{-1}] 3099, 3072, 2962, 2116, 1569, 1457, 1318, 1218, 1142, 1034, 934, 798, 704, 551.

1,1'-(azidomethylene)bis(4-(4-bromophenyl)-1*H*-1,2,3-triazole) (3d)

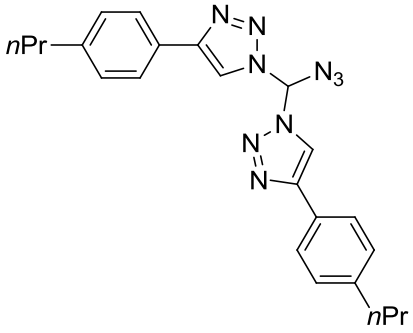


$C_{17}H_{11}Br_2N_9$
501.13 g/mol

Following the general procedure **C** (50 mg of **2d**, 0.01 M, overnight), 1,1'-(azidomethylene)bis(4-(4-bromophenyl)-1*H*-1,2,3-triazole) was obtained as a white solid (21 mg, 0.05 mmol, 19%) upon purification by column chromatography (PE:EtOAc = 90:10 → 70:30).

TLC: R_f = 0.59 (PE:EtOAc / 70:30, [UV]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.28 (s, 1H), 8.13 (s, 2H), 7.72 (m, 4H), 7.58 (m, 4H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 148.3, 132.4, 128.2, 127.7, 123.4, 118.1, 80.8; **IR** (ATR): [cm^{-1}] 2983, 2113, 1744, 1359, 1223, 1068, 1008, 942, 853, 762, 582, 543, 459.

1,1'-(azidomethylene)bis(4-(4-propylphenyl)-1*H*-1,2,3-triazole) (3e)

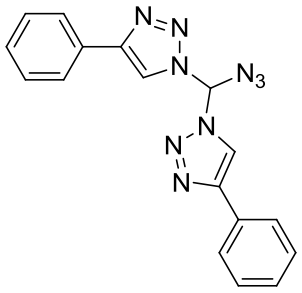


$C_{23}H_{25}N_9$
427.50 g/mol

Following the general procedure **C** (50 mg of **2e**, 0.1 M, overnight), 1,1'-(azidomethylene)bis(4-(4-propylphenyl)-1*H*-1,2,3-triazole) was obtained as a white solid (17 mg, 0.04 mmol, 36%) upon purification by column chromatography (PE:EtOAc = 80:20 → 70:30).

TLC: R_f = 0.74 (PE:EtOAc / 70:30, [UV]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.27 (s, 1H), 8.07 (s, 2H), 7.74 (m, 4H), 7.25 (m, 4H), 2.62 (m, 4H), 1.66 (m, 4H), 0.95 (t, 7.3 Hz, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 149.4, 144.0, 129.3, 126.7, 126.1, 117.6, 80.8, 38.0, 24.5, 13.9; **IR** (ATR): [cm^{-1}] 3130, 2956, 2930, 2869, 2135, 1498, 1434, 1411, 1361, 1259, 1160, 1074, 1014, 936, 801, 781, 526.

1,1'-(azidomethylene)bis(4-phenyl-1*H*-1,2,3-triazole) (3f)

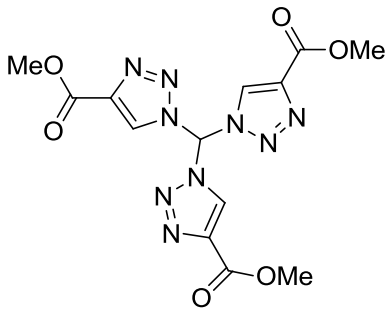


$C_{17}H_{13}N_9$
343.34 g/mol

Following the general procedure **C** (50 mg of **2f**, 0.01 M, overnight), 1,1'-(azidomethylene)bis(4-phenyl-1*H*-1,2,3-triazole) was obtained as a white solid (16 mg, 0.05 mmol, 35%) upon purification by column chromatography (PE:EtOAc = 80:20 → 70:30).

TLC: R_f = 0.68 (PE:EtOAc / 70:30, [UV]); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ [ppm] 8.30 (s, 1H), 8.13 (s, 2H), 7.84 (m, 4H), 7.45 (m, 4 H), 7.38 (m, 2 H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 149.1, 129.1, 129.08, 129.03, 126.0, 117.9, 80.7; **IR** (ATR): [cm^{-1}] 3135, 3105, 3082, 3032, 2984, 2128, 1483, 1423, 1363, 1265, 1161, 1074, 1011, 940, 760, 690.

trimethyl 1,1',1''-methanetriyltris(1*H*-1,2,3-triazole-4-carboxylate) (4a)

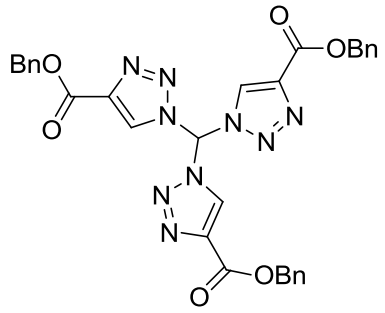


$C_{13}H_{13}N_9O_6$
391.29 g/mol

Following the general procedure **D** (200 mg of **3a**, 0.01 M, overnight), trimethyl 1,1',1''-methanetriyltris(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a white solid (202 mg, 0.52 mmol, 79%) upon precipitation with diethyl ether.

^{1}H-NMR (400 MHz, d_6-DMSO): δ [ppm] 10.34 (s, 1H), 9.33 (s, 3H), 3.87 (s, 9H); **^{13}C-NMR** (101 MHz, d_6-DMSO): δ [ppm] 159.8, 139.8, 130.0, 77.7, 52.2; **^{15}N-NMR** (61 MHz, d_6-DMSO): δ [ppm] -16.4, -19.3, -134.5 (virt. d, *J* = 4.6 Hz); **IR** (ATR): [cm^{-1}] 3169, 3129, 2995, 2957, 1724, 1547, 1435, 1366, 1338, 1275, 1261, 1246, 1205, 1180, 1163, 1147, 1118, 1028, 990, 935, 876, 850, 839, 799, 771, 701, 637, 533, 501, 462, 437; **HRMS** (ESI): [m/z] calculated for [$C_{13}H_{13}N_9O_6Na$] 414.0881, found 414.0882.

tribenzyl 1,1',1''-methanetriyltris(1*H*-1,2,3-triazole-4-carboxylate) (4b)



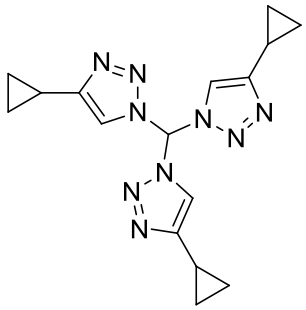
$C_{31}H_{25}N_9O_6$
619.58 g/mol

Following the general procedure **D** (36 mg of **3b**, 0.01M, overnight), tribenzyl 1,1',1''-methanetriyltris(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a white solid (29 mg, 0.05 mmol, 60%) upon precipitation with diethyl ether.

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of a solution in deuterated chloroform.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 9.62 (s, 1H), 8.66 (s, 3H), 7.37 (m, 15H), 5.37 (s, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 159.2, 141.6, 134.9, 128.94, 128.94, 128.90, 128.88, 128.0, 78.2, 67.8; **IR** (ATR): [cm^{-1}] 3134, 3111, 3062, 3034, 2955, 2914, 1722, 1532, 1496, 1438, 1396, 1365, 1285, 1231, 1196, 1153, 1131, 1026, 991, 908, 833, 820, 776, 749, 733, 693, 595, 521; **HRMS** (ESI): [m/z] calculated for [$C_{31}H_{25}N_9O_6Na$] 642.1820, found 642.1821.

tris(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)methane (4c)

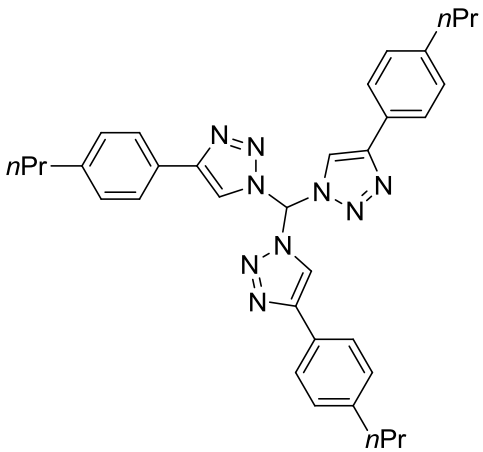


$C_{16}H_{19}N_9$
337.38 g/mol

Following the general procedure **D** (7 mg of **3c**, 0.01M, overnight), tris(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)methane was obtained as a white solid (6 mg, 0.02 mmol, 69%) upon precipitation with diethyl ether.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 9.17 (s, 1H), 7.78 (s, 3H), 1.95 (m, 3H), 0.95 (m, 12H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 151.8, 119.7, 78.3, 8.2, 6.7; **IR** (ATR): [cm^{-1}] 3143, 3093, 2990, 1567, 1437, 1335, 1235, 1153, 1108, 1026, 814; **HRMS** (ESI): [m/z] calculated for [$C_{16}H_{19}N_9Na$] 360.1656, found 360.1657.

tris(4-(4-propylphenyl)-1*H*-1,2,3-triazol-1-yl)methane (4d)

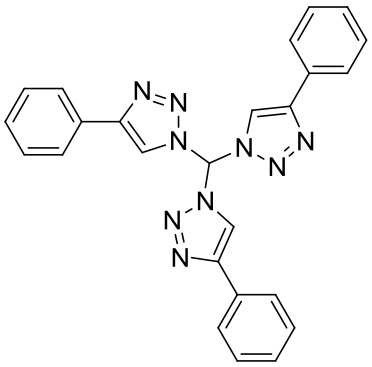


$C_{34}H_{37}N_9$
571.71 g/mol

Following the general procedure **D** (6 mg of **3e**, 0.01M, overnight), tris(4-(4-propylphenyl)-1*H*-1,2,3-triazol-1-yl)methane was obtained as a white solid (6 mg, 0.01 mmol, 75%) upon precipitation with diethyl ether.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 9.54 (s, 1H), 8.38 (s, 3H), 7.75 (m, 6H), 7.25 (m, 6H), 2.62 (m, 6H), 1.66 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 149.6, 144.2, 129.3, 126.5, 126.2, 119.1, 78.8, 38.0, 24.5, 13.9; **IR** (ATR): [cm^{-1}] 3145, 3116, 2958, 2928, 2857, 1499, 1439, 1414, 1365, 1336, 1234, 1176, 1074, 1013, 800, 54; **HRMS** (ESI): [m/z] calculated for [$C_{34}H_{37}N_9Na$] 594.3064, found 594.3059.

tris(4-phenyl-1*H*-1,2,3-triazol-1-yl)methane (4e)

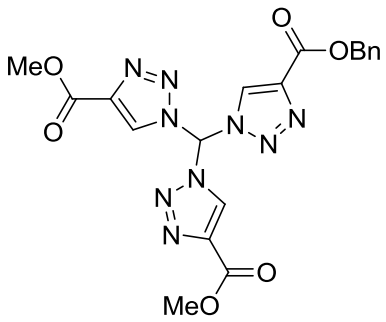


$C_{25}H_{19}N_9$
445.47 g/mol

Following the general procedure **D** (9 mg of **3f**, 0.01M, overnight), tris(4-phenyl-1*H*-1,2,3-triazol-1-yl)methane was obtained as a white solid (9 mg, 0.02 mmol, 77%) upon precipitation with diethyl ether.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 9.52 (s, 1H), 8.41 (s, 3H), 7.85 (m, 6H), 7.46 (m, 6H), 7.39 (m, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 3134, 2953, 1483, 1456, 1418, 1374, 1358, 1237, 1176, 1072, 1013, 843, 800, 758, 691, 511, 454; **IR** (ATR): [cm^{-1}] 3134, 2953, 1483, 1456, 1418, 1374, 1358, 1237, 1176, 1072, 1013, 843, 800, 758, 691, 511, 454; **HRMS** (ESI): [m/z] calculated for [$C_{25}H_{19}N_9Na$] 468.1656, found 468.1648.

dimethyl 1,1'-((4-((benzyloxy)carbonyl)-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (4f)

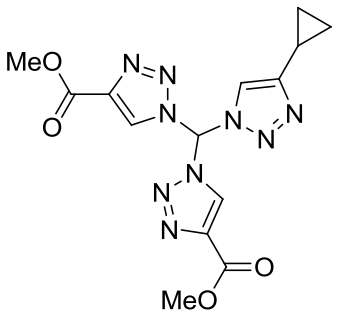


$C_{19}H_{17}N_9O_6$
467.39 g/mol

Following the general procedure **D** (50 mg of **3a**, 0.01M, overnight), dimethyl 1,1'-((4-((benzyloxy)carbonyl)-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a white solid (49 mg, 0.10 mmol, 64%) upon precipitation with diethyl ether.

^{1}H-NMR (400 MHz, d_6-DMSO): δ [ppm] 10.32 (s, 1H), 9.38 (s, 1H), 9.33 (s, 2H), 7.39 (m, 5H), 5.38 (s, 2H), 3.87 (s, 6H); **^{13}C-NMR** (101 MHz, d_6-DMSO): δ [ppm] 159.8, 159.3, 139.8, 139.7, 136.5, 130.3, 130.1, 128.5, 128.30, 128.27, 77.7, 66.4, 52.2; **IR** (ATR): [cm^{-1}] 3095, 3050, 2994, 2951, 1727, 1536, 1433, 1373, 1275, 1212, 1128, 1108, 1029, 813, 779, 750, 690, 596, 520, 415; **HRMS** (ESI): [m/z] calculated for [$C_{19}H_{17}N_9O_6Na$] 490.1194, found 490.1195.

dimethyl 1,1'-((4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (4g)

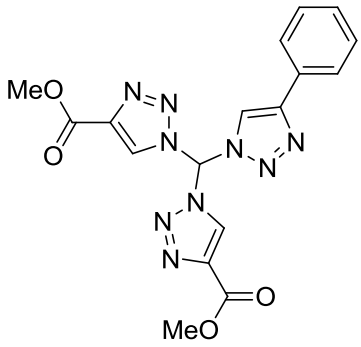


$C_{14}H_{15}N_9O_4$
373.32 g/mol

Following the general procedure **D** (50 mg of **3a**, 0.01M, overnight), dimethyl 1,1'-((4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a white solid (27 mg, 0.07 mmol, 64%) upon precipitation with diethyl ether.

^{1}H-NMR (400 MHz, d_6-DMSO): δ [ppm] 10.26 (s, 1H), 9.27 (s, 2H), 8.40 (s, 1H), 3.87 (s, 6H), 2.01 (m, 1H), 0.94 (m, 2H), 0.78 (m, 2H); **^{13}C-NMR** (101 MHz, d_6-DMSO): δ [ppm] 159.8, 150.7, 139.7, 129.7, 121.2, 77.4, 52.2, 7.7, 6.3; **IR** (ATR): [cm^{-1}] 3123, 2995, 2954, 1735, 1626, 1550, 1432, 1376, 1355, 1337, 1267, 1244, 1227, 1215, 1187, 991, 842, 831, 776, 694; **HRMS** (ESI): [m/z] calculated for [$C_{14}H_{15}N_9O_4Na$] 396.1139, found 396.1124.

dimethyl 1,1'-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (4h)

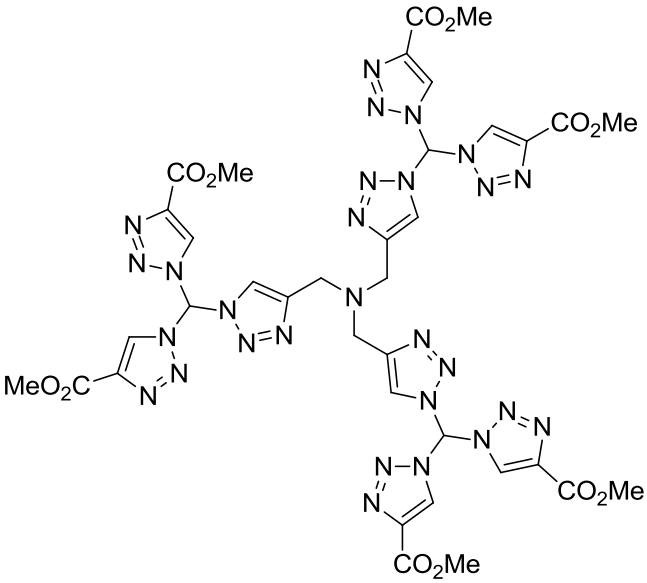


$C_{17}H_{15}N_9O_4$
409.35 g/mol

Following the general procedure **D** (300 mg of **3a**, 0.01M, overnight), dimethyl 1,1'-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) was obtained as a white solid (327 mg, 0.80 mmol, 82%) upon precipitation with diethyl ether.

^{1}H-NMR (600 MHz, d_6-DMSO): δ [ppm] 10.39 (s, 1H), 9.36 (s, 2H), 9.10 (s, 1H), 7.92 (m, 2H), 7.48 (m, 2H), 7.40 (m, 1H), 3.88 (s, 6H); **^{13}C-NMR** (151 MHz, d_6-DMSO): δ [ppm] 159.8, 147.7, 139.7, 129.8, 129.2, 128.9, 128.7, 125.5, 121.6, 77.7, 52.1; **IR** (ATR): [cm^{-1}] 3129, 3087, 2996, 2953, 1756, 1553, 1428, 1210, 1185, 1029, 988, 765, 694, 624, 468, 420; **HRMS** (ESI): [m/z] calculated for [$C_{17}H_{15}N_9O_4Na$] 432.1139, found 432.1139.

hexamethyl 1,1',1'',1''',1'''',1'''''-((4,4',4''-(nitrilotris(methylene))tris(1*H*-1,2,3-triazole-4,1-diyl))tris(methanetriyl))hexakis(1*H*-1,2,3-triazole-4-carboxylate) (5)

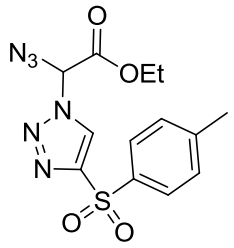


$C_{36}H_{36}N_{28}O_{12}$
1052.85 g/mol

3a (170 mg, 0.55 mmol) was dissolved in 40 ml ^{t}BuOH and 10 ml Water. Tripropargyl amine (16 µL, 0.11 mmol, 0.20 eq.), copper(II)sulfate pentahydrate (55 mg, 0.22 mmol, 40 mol%) and sodium ascorbate (92 mg, 0.46 mmol, 84 mol%) were added and the solution stirred for 16 h at room temperature. The resulting suspension was quenched with a saturated, aqueous solution of EDTA disodium salt and extracted with ethyl acetate (4x). The combined organic phases were washed with brine and **NOT** dried over sodium sulfate. The solvent was removed in vacuo and to the crude product was added a small portion of ethyl acetate. The suspension was filtered off and washed with another portion of ethyl acetate, hot aqueous EDTA disodium salt, water and diethyl ether. The product was obtained as a white solid (90 mg, 0.09 mmol, 81%) upon drying under high vacuum.

^{1}H-NMR (600 MHz, d_6-DMSO): δ [ppm] 10.48 (s, 3H), 9.32 (s, 6H), 8.67 (s, 3H), 3.86 (s, 18 H), 3.75 (s, 6H); **^{13}C-NMR** (151 MHz, d_6-DMSO): δ [ppm] 159.8, 144.6, 139.5, 129.8, 125.0, 77.2, 52.1, 46.5; **IR** (ATR): [cm^{-1}] 3133, 3003, 2955, 1736, 1552, 1436, 1372, 1344, 1261, 1223, 1182, 1123, 1091, 1032, 993, 942, 839, 814, 795, 774, 692, 534, 517, 481, 466, 438; **HRMS** (ESI): [m/z] calculated for [$C_{36}H_{37}N_{28}O_{12}$] 1053.3140, found 1053.3140.

***rac* ethyl 2-azido-2-(4-tosyl-1*H*-1,2,3-triazol-1-yl)acetate (7)**

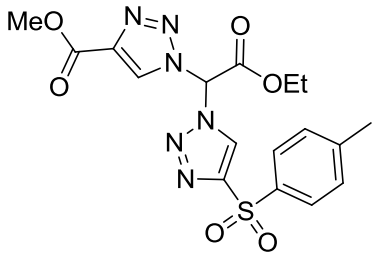


$C_{13}H_{14}N_6O_4S$
350.35 g/mol

1 (500 mg, 2.36 mmol) was dissolved in 50 ml acetonitrile and tosyl acetylene (467 mg, 2.59 mmol, 1.1 eq.) was added to the solution and the reaction mixture stirred at 60 °C for two days. The organic phase was evaporated *in vacuo* and the desired product obtained upon purification with column chromatography (PE:EtOAc = 80:20 → 60:40) as a viscous, colorless oil (268 mg, 0.76 mmol, 32%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 8.41 (s, 1H), 7.97 (m, 2H), 7.35 (m, 2H), 6.34 (s, 1H), 4.36 (m, 2H), 3.58 (s, 1H), 2.43 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 163.2, 150.5, 145.6, 136.8, 130.2, 128.5, 125.5, 72.4, 64.6, 21.8, 14.1; **IR** (ATR): [cm^{-1}] 3134, 2983, 2939, 2121, 1755, 1496 1446, 1305, 1105, 1085, 1016, 813, 645, 600, 570, 535, 494.

***rac* methyl 1-(2-ethoxy-2-oxo-1-(4-tosyl-1*H*-1,2,3-triazol-1-yl)ethyl)-1*H*-1,2,3-triazole-4-carboxylate (8)**



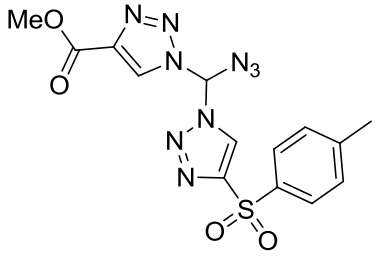
$C_{17}H_{18}N_6O_6S$
434.42 g/mol

7 (132 mg, 0.38 mmol) was dissolved in 4 ml ^{t}BuOH, 1 ml Water and 500 µL acetonitrile. Methyl propiolate (37 µL, 0.41 mmol, 1.1 eq.), TBTA (2.6 mg, 4.97 µmol, 1 mol%), copper(II)sulfate pentahydrate (19 mg, 0.08 mmol, 20 mol%) and sodium ascorbate (31 mg, 0.16 mmol, 42 mol%) were

added to the solution and the reaction mixture stirred 16 h at room temperature. The reaction was quenched with a saturated solution of EDTA disodium salt in water and extracted with ethyl acetate (3x). The combined organic phases were washed with brine and dried over sodium sulfate. The organic phase was evaporated *in vacuo* and the product obtained upon purification by column chromatography (PE:EtOAc = 70:30 → 50:50) as a white solid (38 mg, 0.09 mmol, 23%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 8.70 (s, 1H), 8.62 (s, 1H), 7.94 (m, 2H), 7.89 (s, 1H), 7.33 (m, 2H), 4.37 (m, 2H), 3.93 (s, 3H), 2.40 (s, 3H), 1.25 (m, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ [ppm] 161.1, 160.3, 150.6, 145.8, 140.9, 136.5, 130.3, 130.2, 129.0, 128.5, 128.2, 127.3, 70.7, 66.4, 52.6, 21.8, 13.9; **IR** (ATR): [cm^{-1}] 3157, 2970, 2927, 1726, 1595, 1556, 1434, 1236, 1119, 1025, 842, 766, 672, 603, 535, 492; **HRMS** (ESI): [m/z] calculated for [$C_{17}H_{18}N_6O_6SNa$] 457.0901, found 457.0901.

***rac* methyl 1-(azido(4-tosyl-1*H*-1,2,3-triazol-1-yl)methyl)-1*H*-1,2,3-triazole-4-carboxylate (9)**

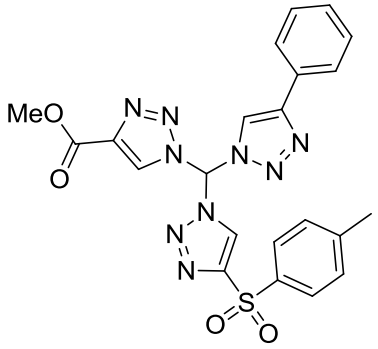


$C_{14}H_{13}N_9O_4S$
403.37 g/mol

8 (38 mg, 0.09 mmol) was dissolved in 3 ml DMSO and 1 ml Water. Sodium azide (57 mg, 0.87 mmol, 10.0 eq.), sodium iodide (3 mg, 0.02 mmol, 20 mol%) and IBX-SO_3K were added to the solution and the resulting yellow reaction mixture was stirred for 16 h at room temperature. The reaction was quenched by addition of a saturated, aqueous solution of sodium thiosulfate and extracted with ethyl acetate (3x). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was evaporated *in vacuo* and the crude product subjected to column chromatography (PE:EtOAc = 70:30 → 50:50) to obtain the product as a white solid (8 mg, 0.02 mmol, 23%).

^{1}H-NMR (400 MHz, d_6-DMSO): δ [ppm] 9.48 (s, 1H), 9.30 (s, 1H), 9.08 (s, 1H), 7.89 (m, 2H), 7.49 (m, 2H), 3.86 (s, 3H), 2.40 (s, 3H); **^{13}C-NMR** (101 MHz, d_6-DMSO): δ [ppm] 160.0, 148.5, 145.4, 139.3, 136.6, 130.3, 128.9, 128.2, 127.6, 80.5, 52.1, 21.1; **IR** (ATR): [cm^{-1}] 3124, 2956, 2924, 2852, 2127, 1739 1595, 1557, 1498, 1369, 1328, 1218, 1185, 1150, 1122, 1102, 771, 673, 602, 492, 446.

***rac* methyl 1-((4-phenyl-1*H*-1,2,3-triazol-1-yl)(4-tosyl-1*H*-1,2,3-triazol-1-yl)methyl)-1*H*-1,2,3-triazole-4-carboxylate (6)**



$C_{22}H_{19}N_9O_4S$
505.50 g/mol

9 (7 mg, 0.02 mmol) was dissolved in 1 ml ^{t}BuOH and 300 µL Water. Phenylacetylene (8 µL, 0.07 mmol, 4.0 eq.), copper(II)sulfate pentahydrate (2 mg, 0.01 mmol, 40 mol%) and sodium ascorbate (3 mg, 0.01 mmol. 84 mol%) were added and the solution stirred for 16 h at room temperature. The reaction was quenched with addition of a saturated, aqueous solution of EDTA disodium salt and extracted with ethyl acetate (3x). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude product subjected to column chromatography (PE:EtOAc = 60:30 → 40:60) to obtain the product as a white solid (4 mg, 0.01 mmol, 46%).

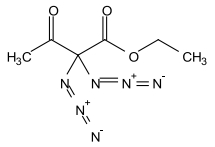
^{1}H-NMR (400 MHz, d_6-DMSO): δ [ppm] 10.32 (s, 1H), 9.51 (s, 1H), 9.37 (s, 1H), 9.12 (s, 1H), 7.90 (m, 4H), 7.48 (m, 4H), 7.40 (m, 1H), 3.87 (s, 3H), 2.40 (s, 3H); **^{13}C-NMR** (101 MHz, d_6-DMSO): δ [ppm] 159.8, 148.9, 147.7, 145.5, 139.7, 136.4, 130.3, 130.1, 129.2, 129.0, 128.7, 127.7, 125.6, 121.8, 77.8, 52.2, 21.1; **IR** (ATR): [cm^{-1}] 3140, 2974, 2955, 2924, 2852, 1743, 1595, 1558, 1507, 1487,

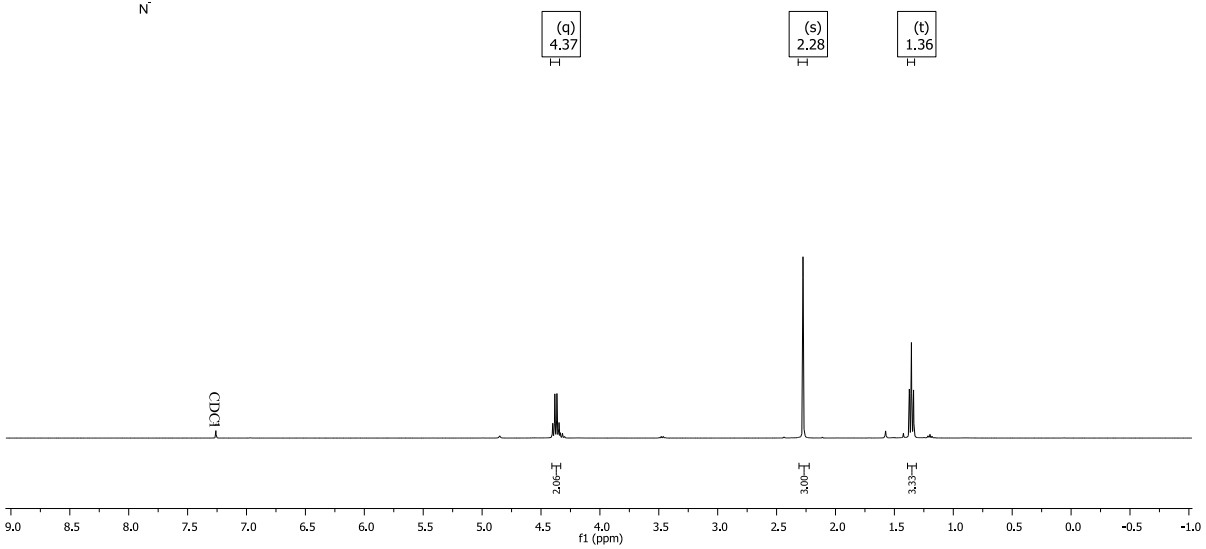
1424, 1324, 1269, 1212, 1154, 1114, 1085, 1026, 1016, 978, 836, 798, 767, 705, 675, 640, 605, 533; **HRMS** (ESI): [m/z] calculated for [$C_{22}H_{19}N_9O_4SNa$] 528.1173, found 528.1163.

Spectra (^{1}H-NMR, ^{13}C-NMR, ^{15}N-NMR, ^{1}H-^{15}N HMBC, IR)

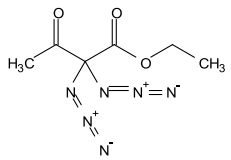
ethyl 2,2-diazido-3-oxobutanoate (1)

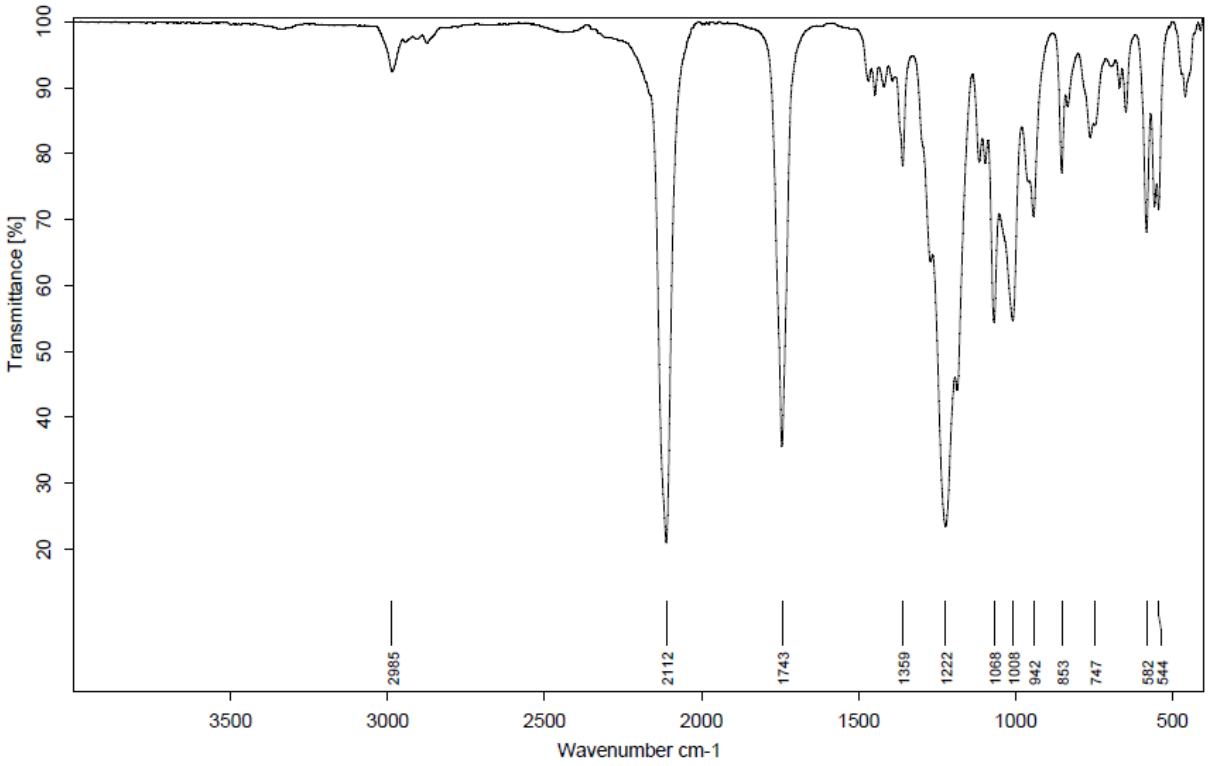
^{1}H NMR(400MHz, CDCl)



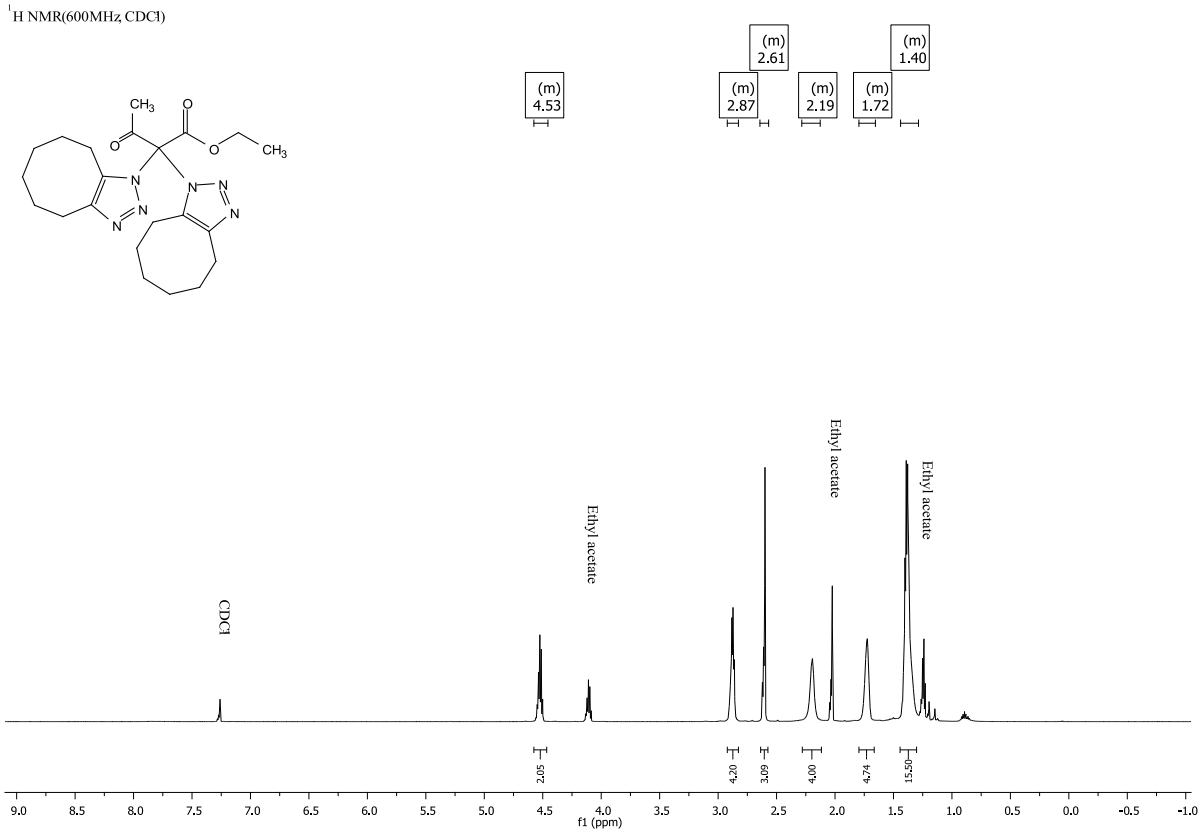


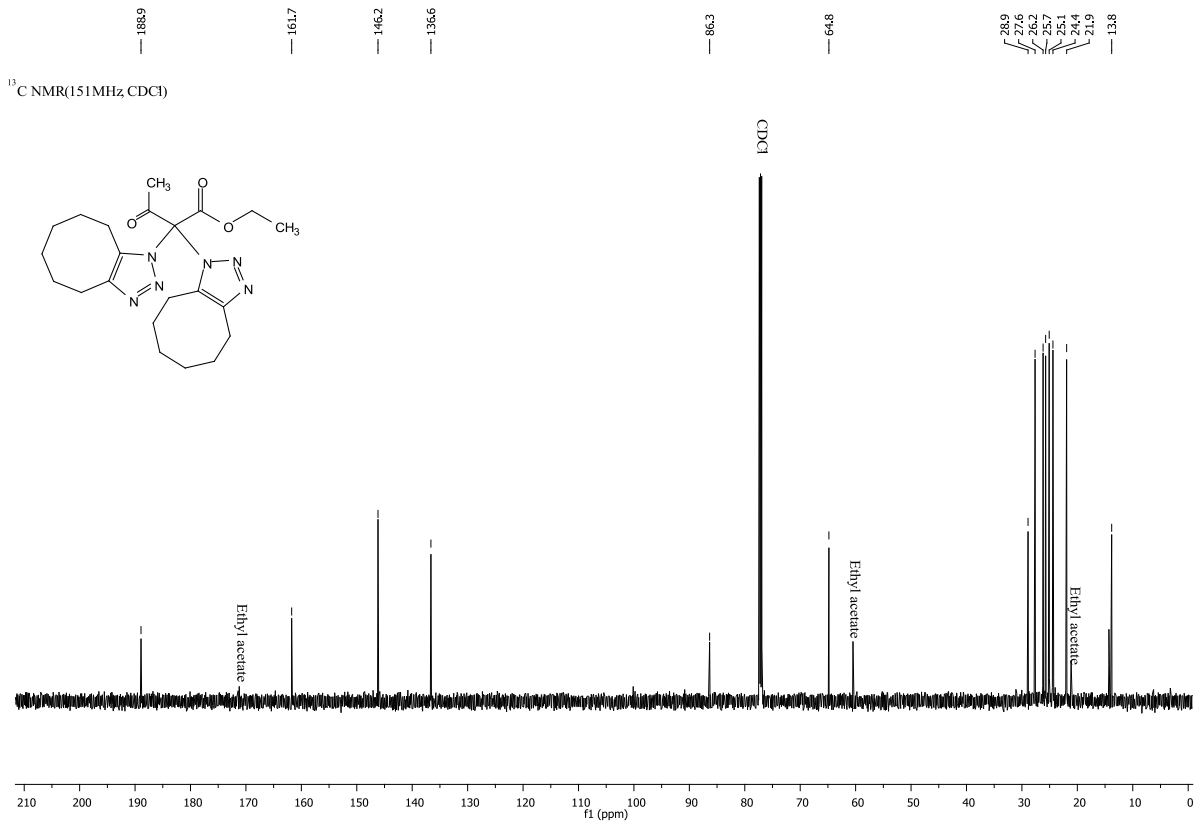
^{13}C NMR(101MHz, CDCl)



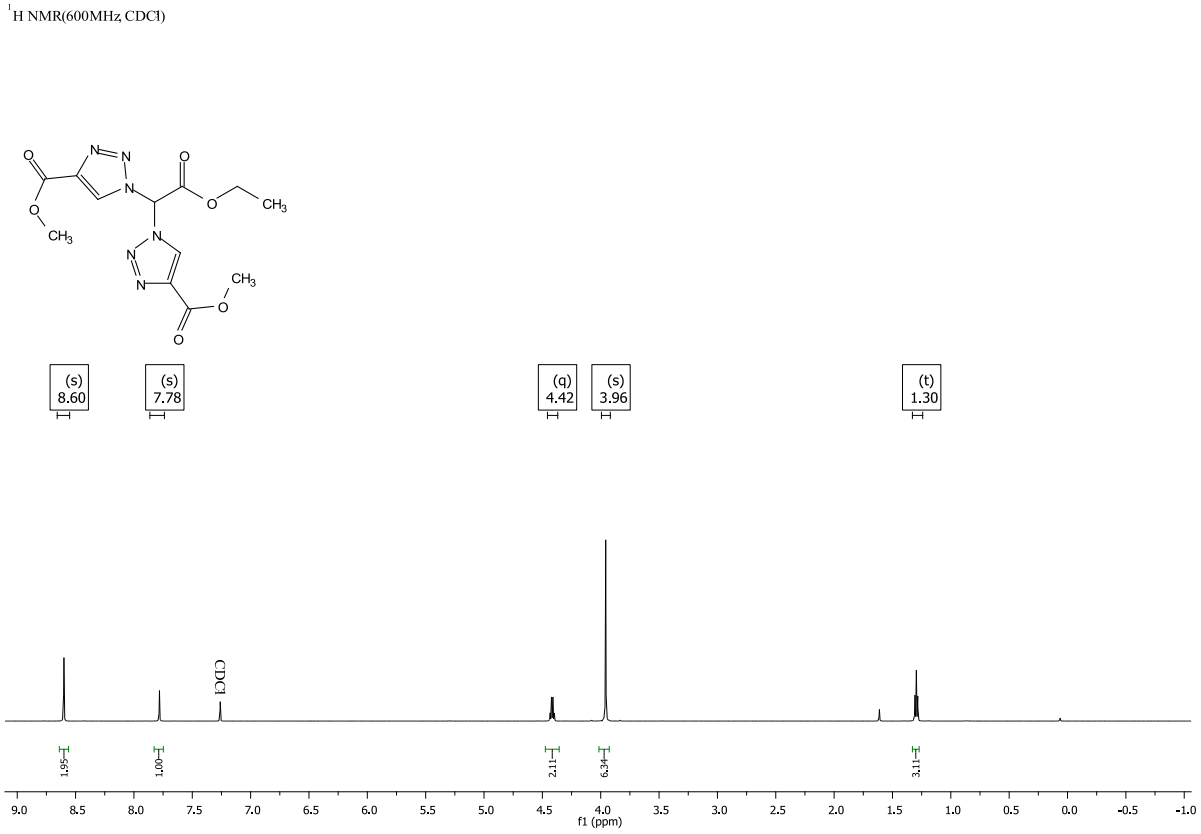


ethyl 2,2-bis(4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*d*][1,2,3]triazol-1-yl)-3-oxobutanoate

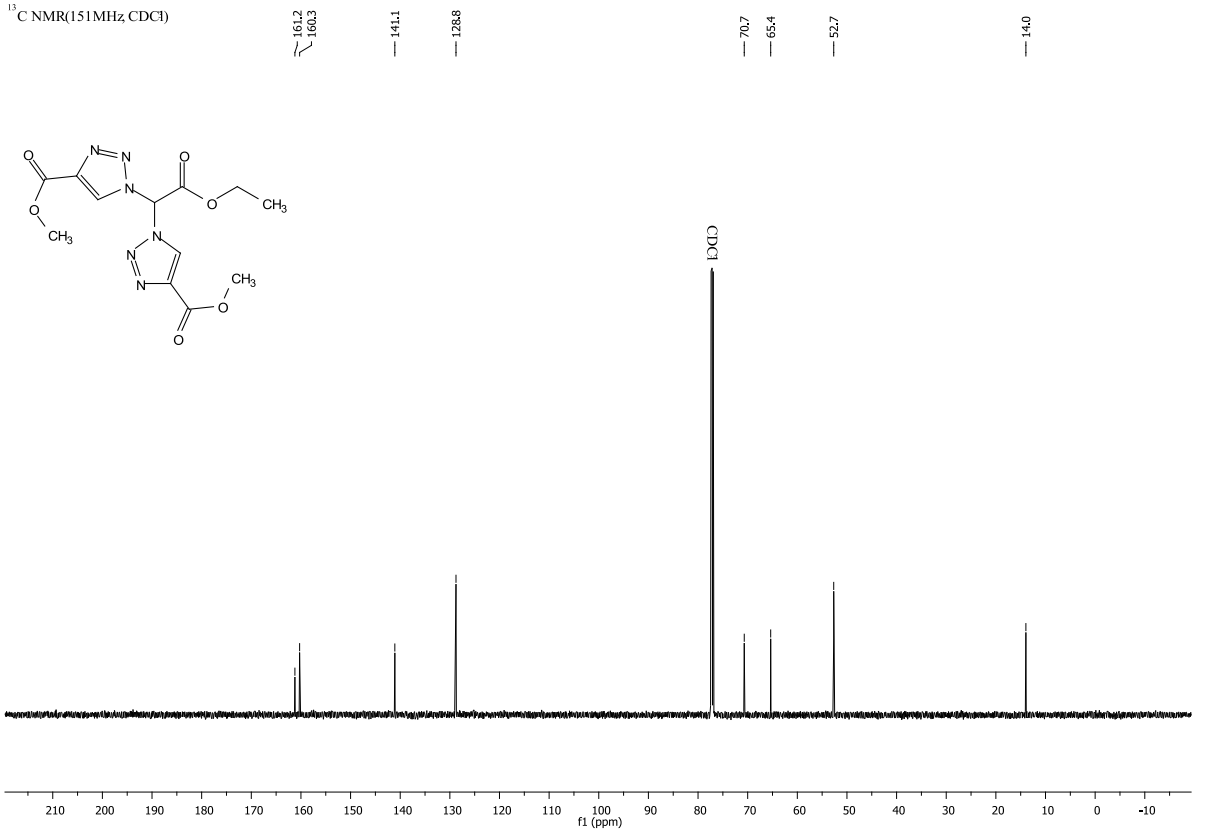




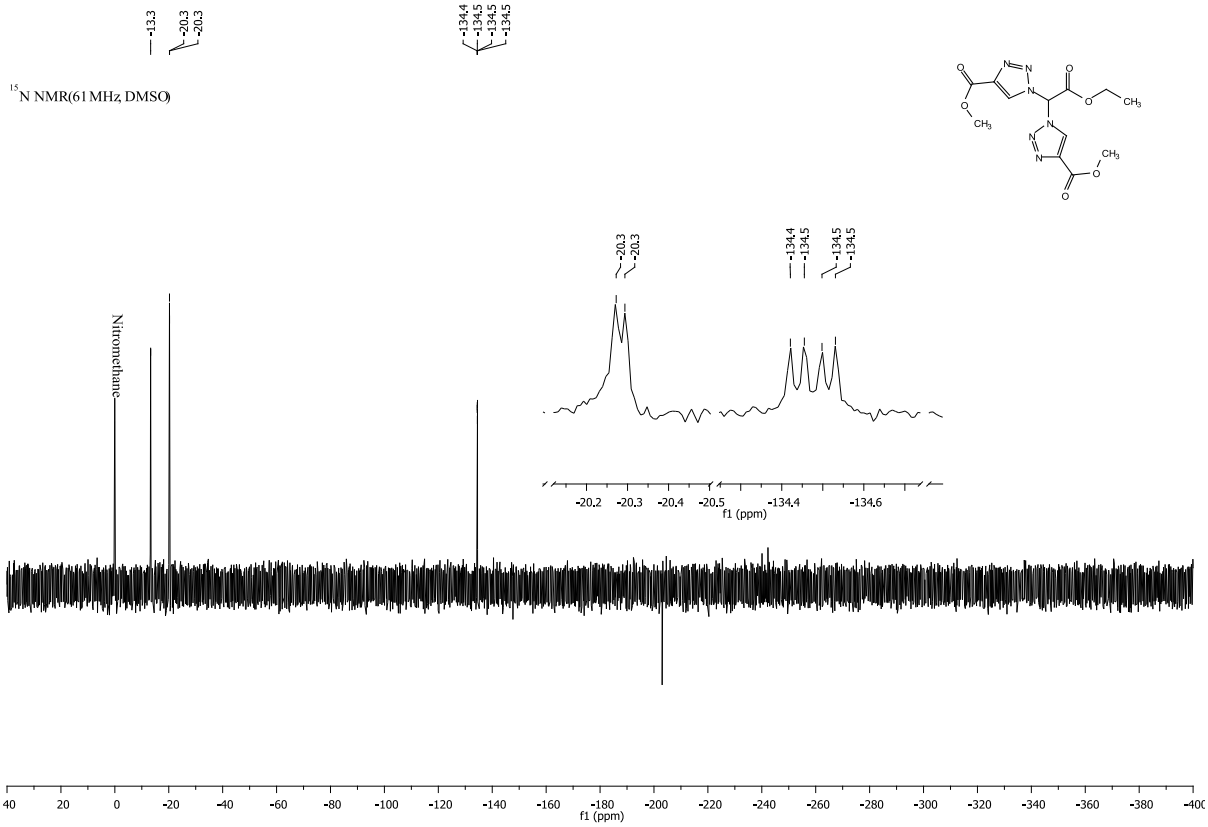
dimethyl 1,1'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1*H*-1,2,3-triazole-4-carboxylate) (2a)

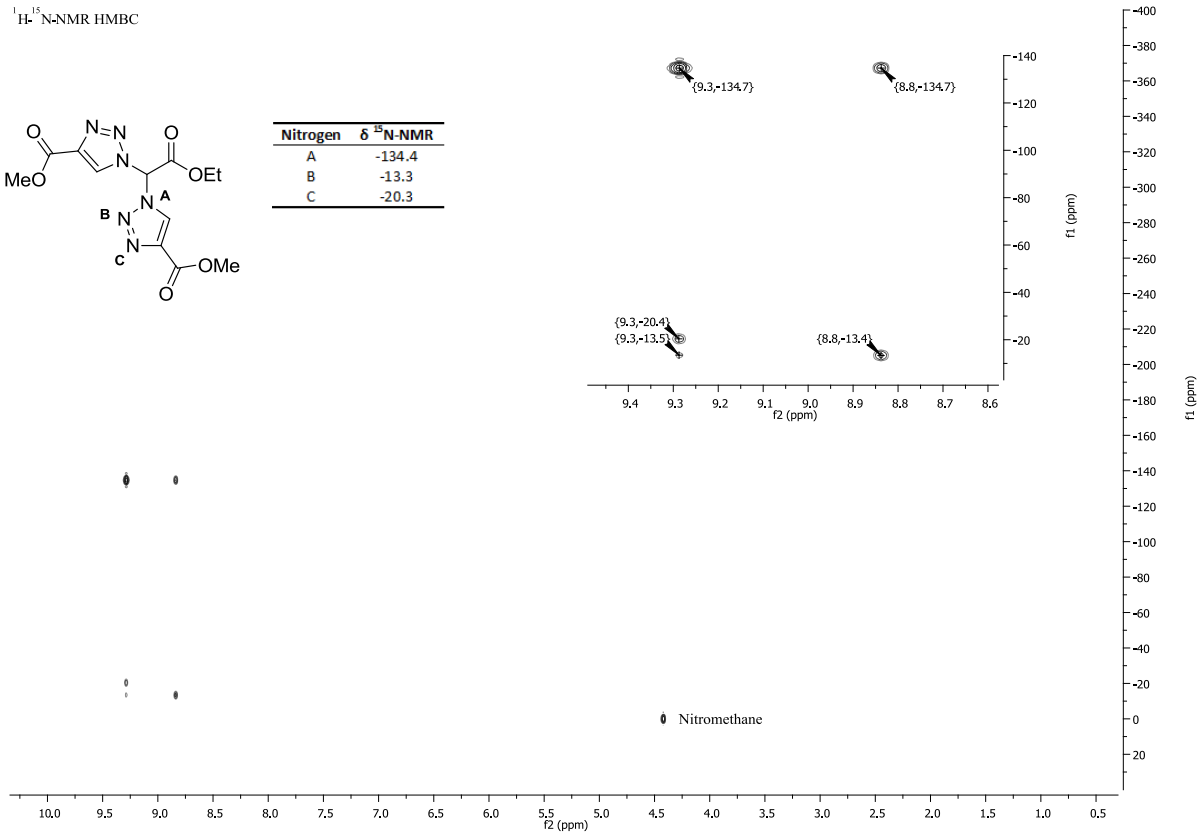


^{13}C NMR(151MHz, CDCl)



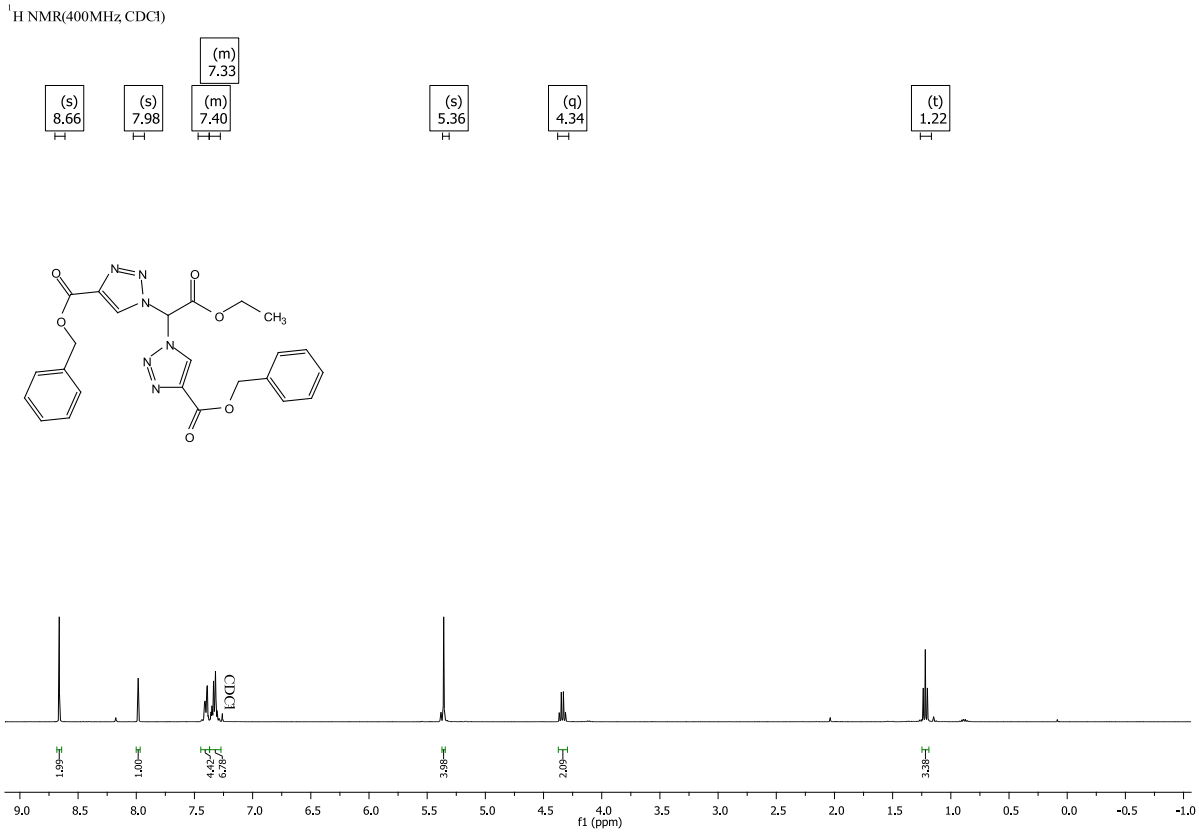
^{15}N NMR(61MHz, DMSO)

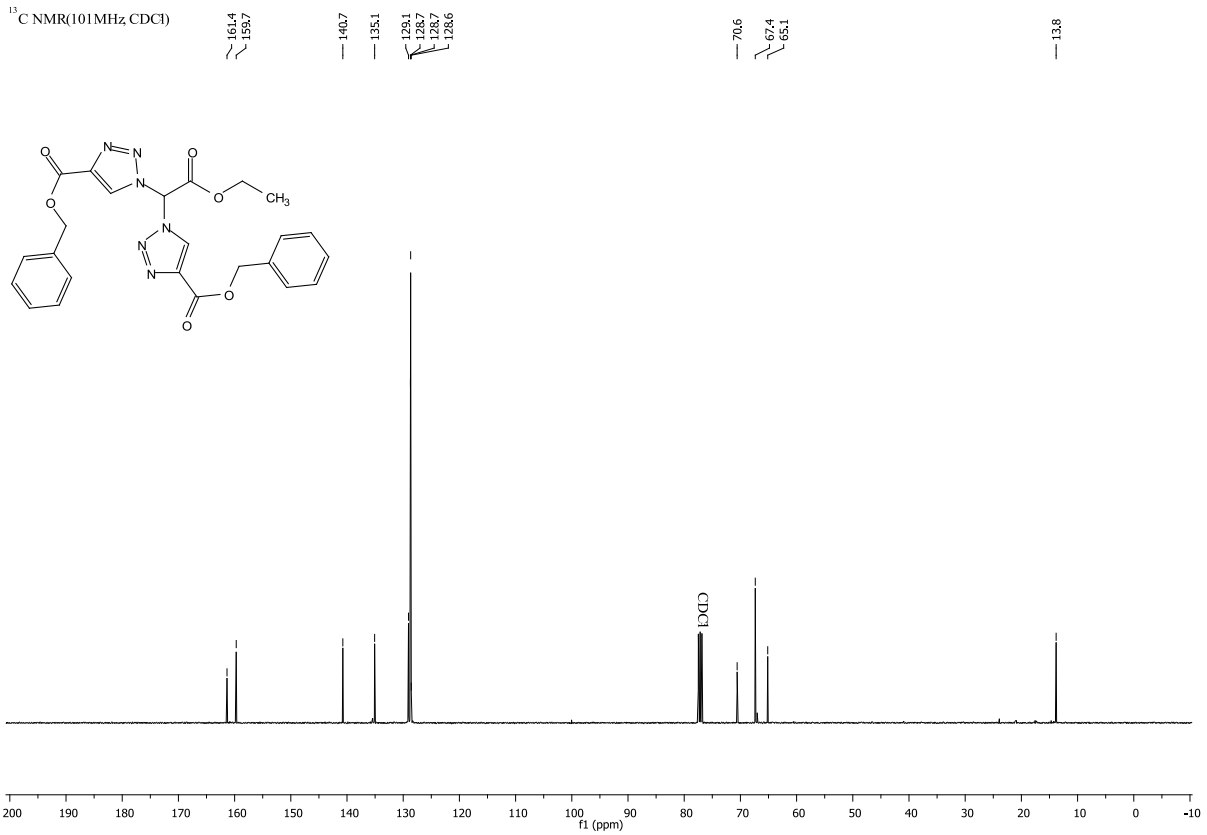




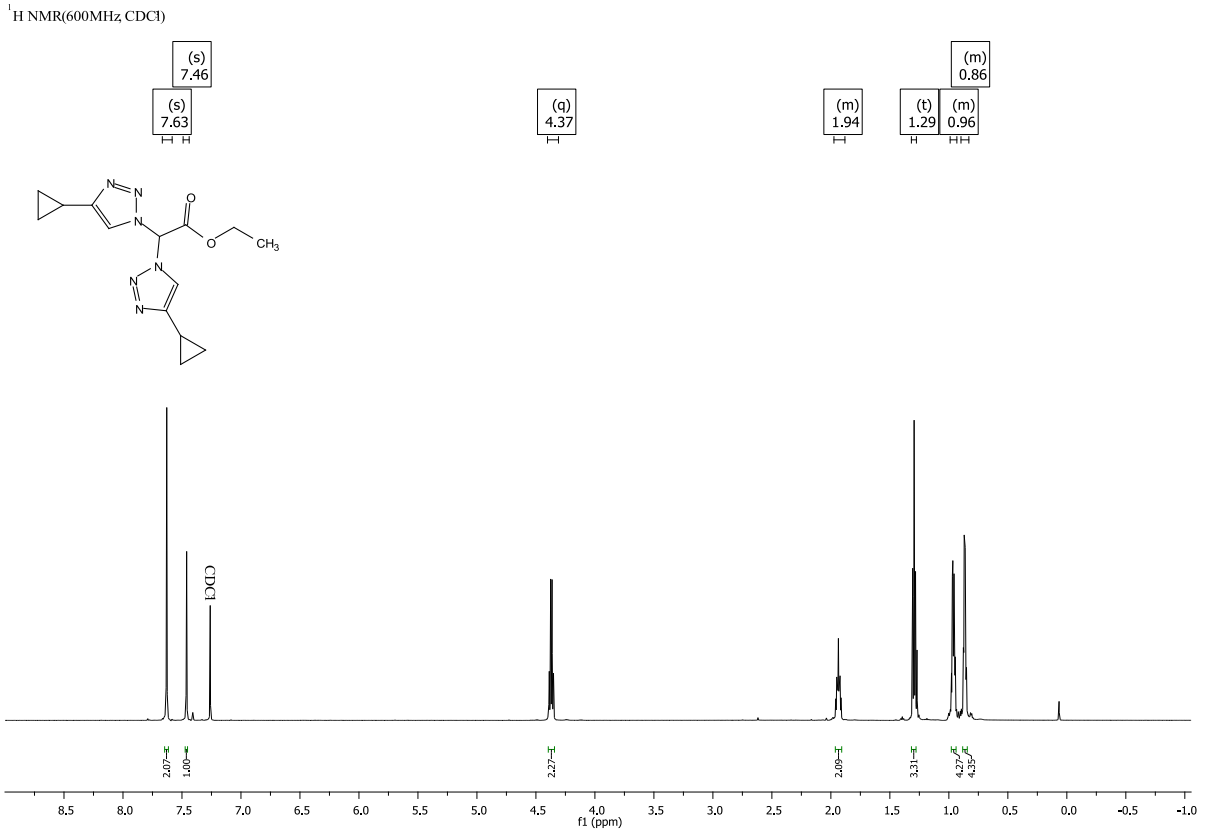
Nitrogen	δ ^{15}N-NMR
A	-134.4
B	-13.3
C	-20.3

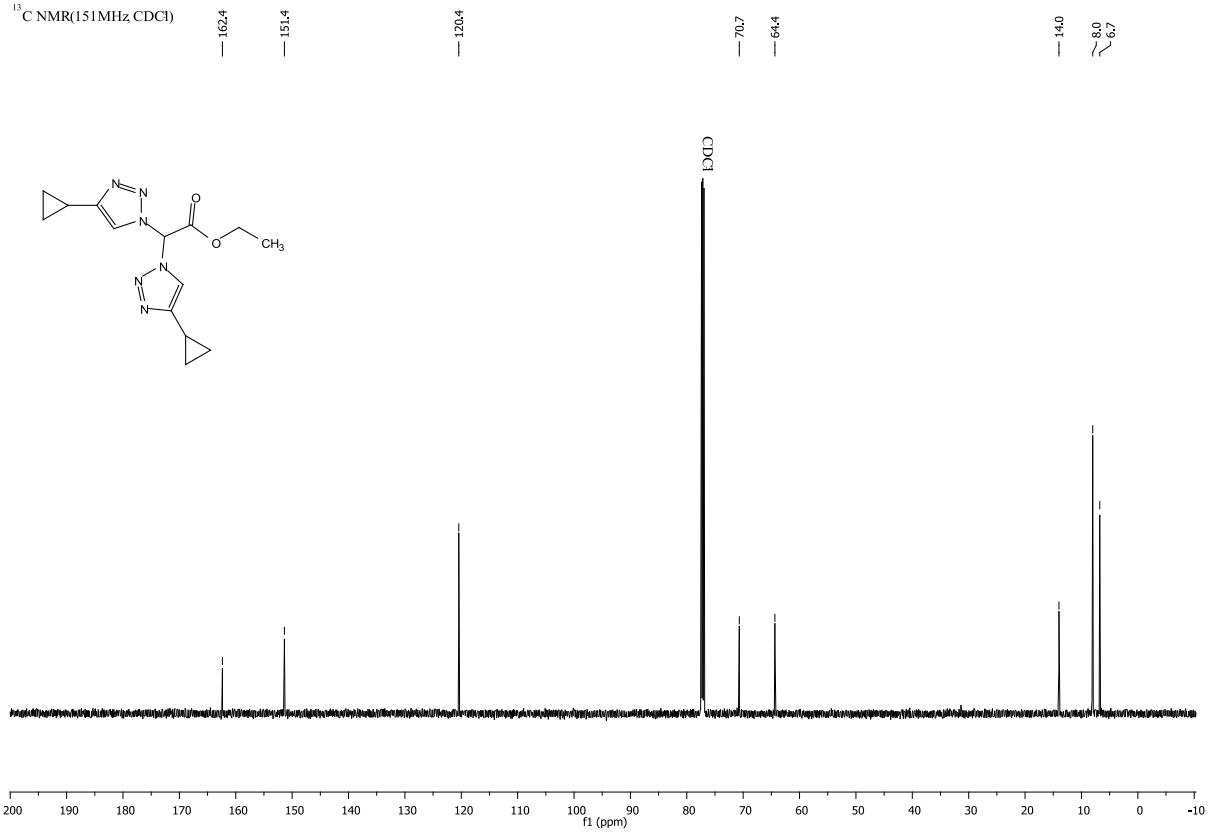
dibenzyl 1,1'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1*H*-1,2,3-triazole-4-carboxylate) (2b)



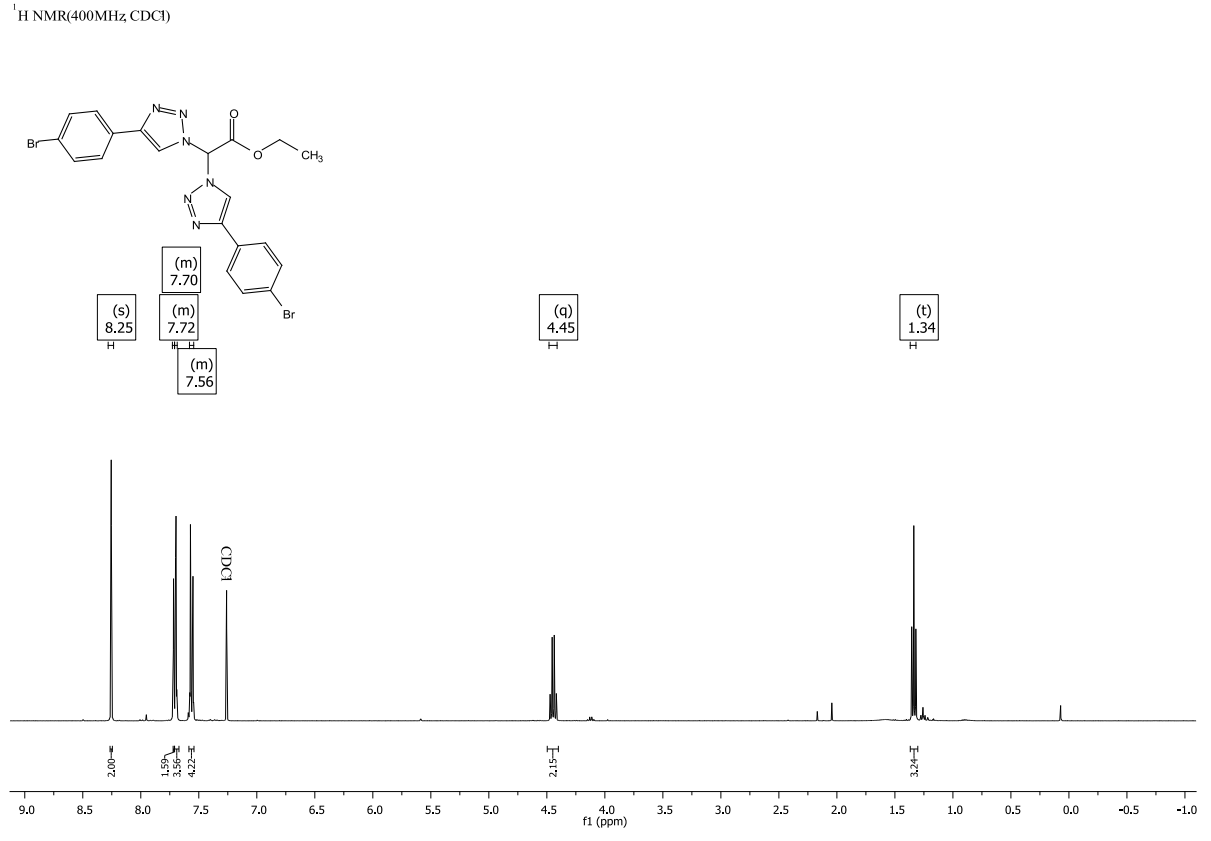


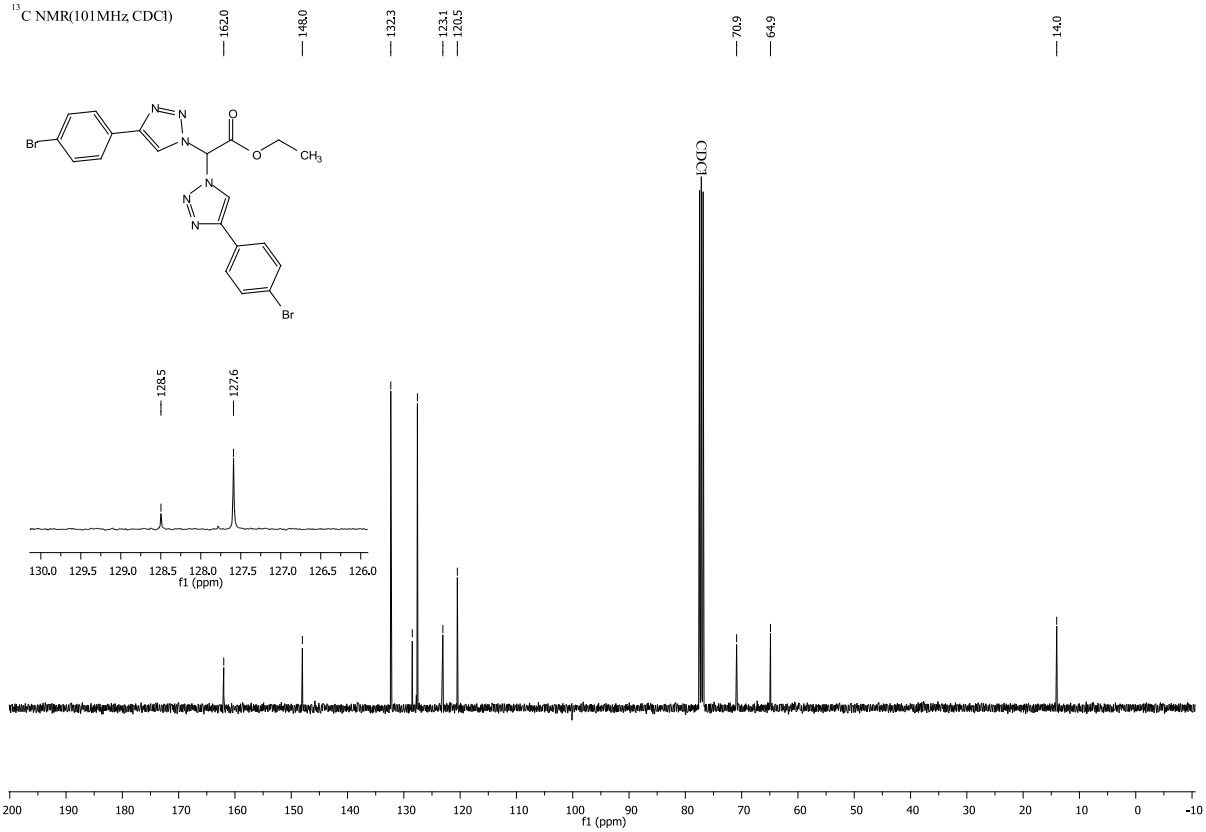
ethyl 2,2-bis(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)acetate (2c)



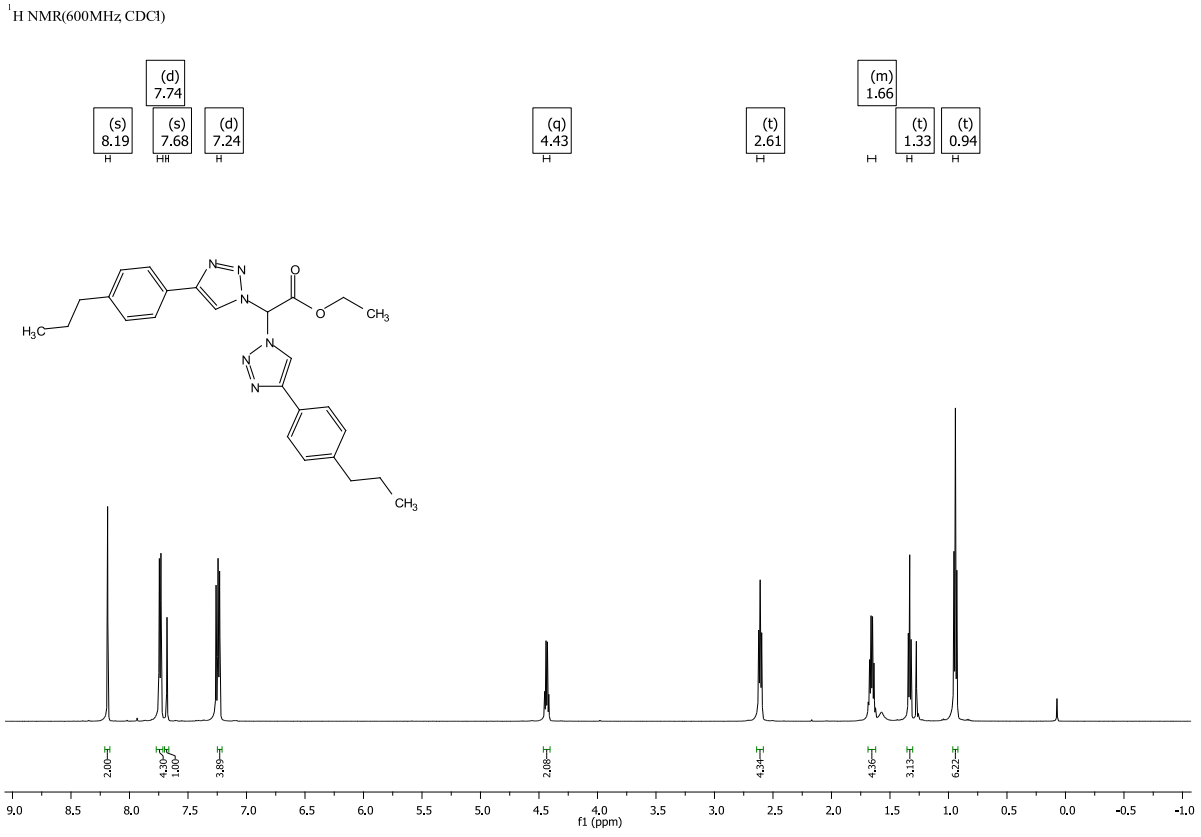


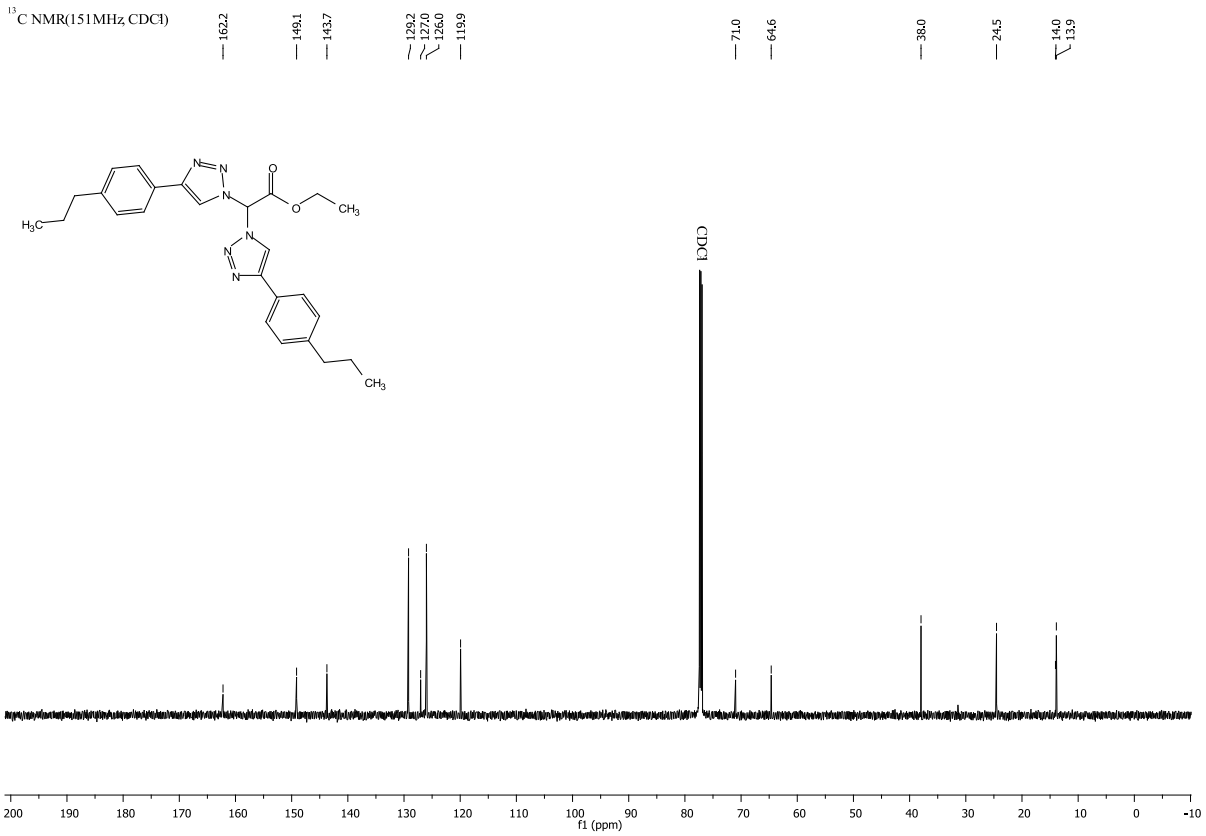
ethyl 2,2-bis(4-(4-bromophenyl)-1*H*-1,2,3-triazol-1-yl)acetate (2d)



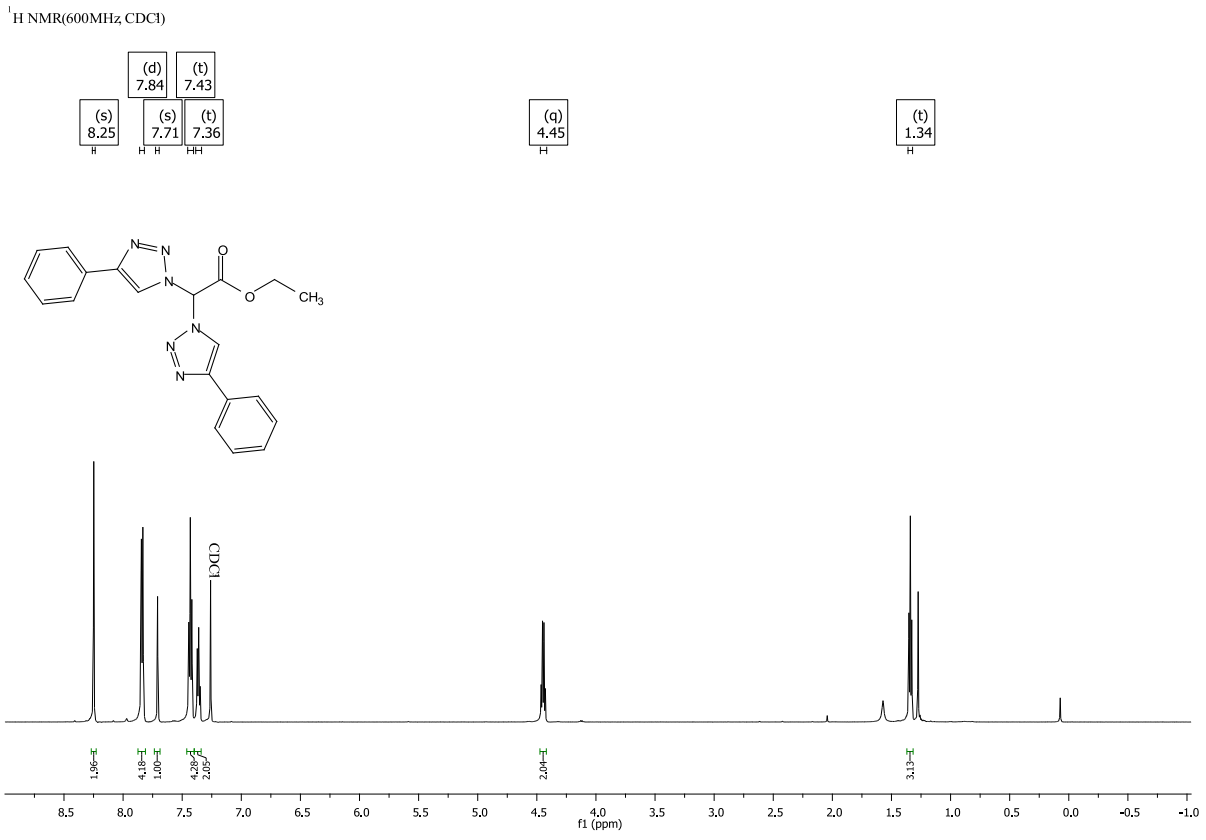


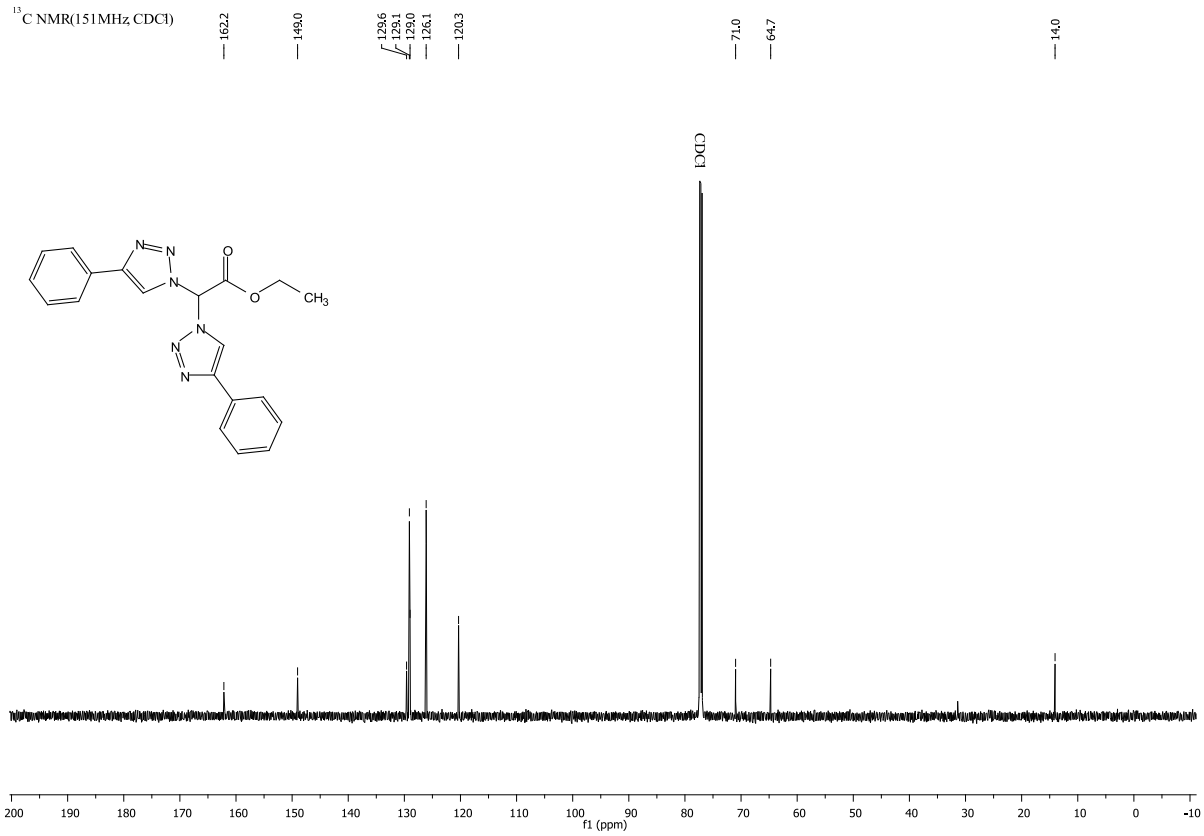
ethyl 2,2-bis(4-(4-propylphenyl)-1*H*-1,2,3-triazol-1-yl)acetate (2e)



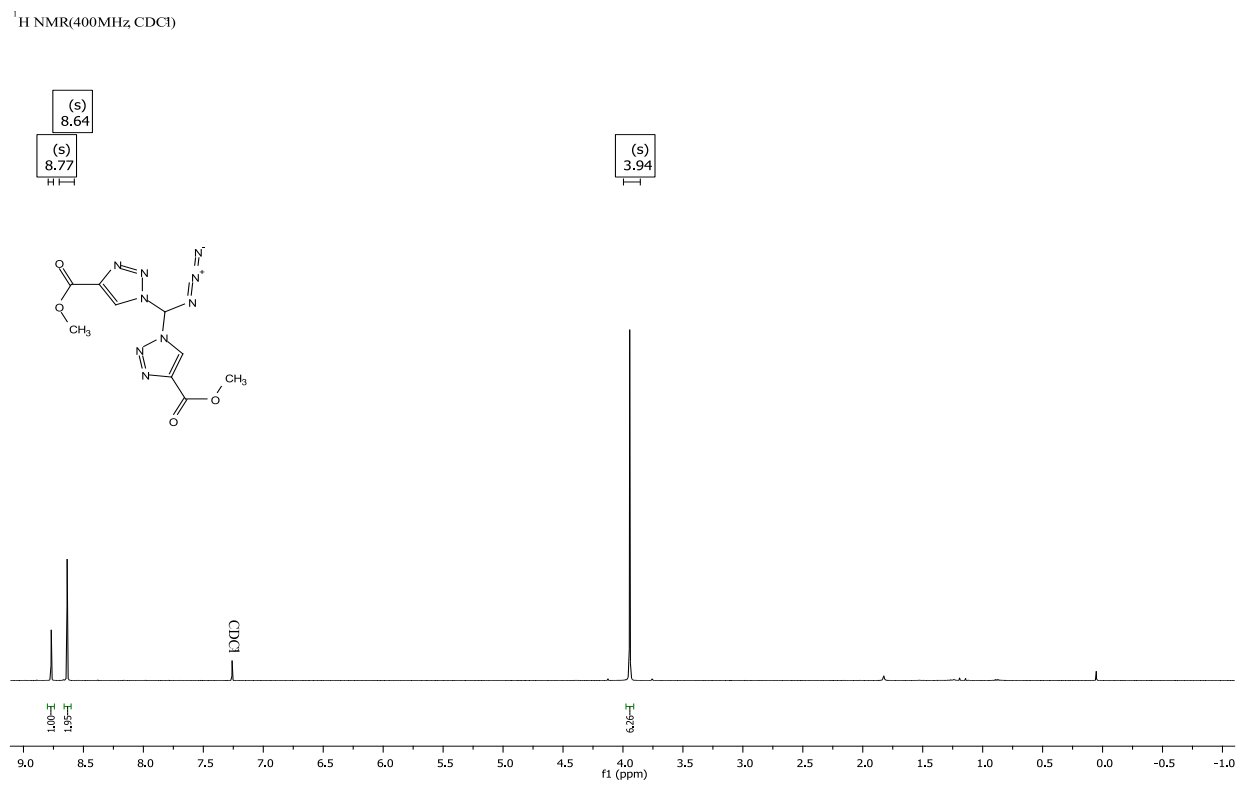


ethyl 2,2-bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetate (2f)

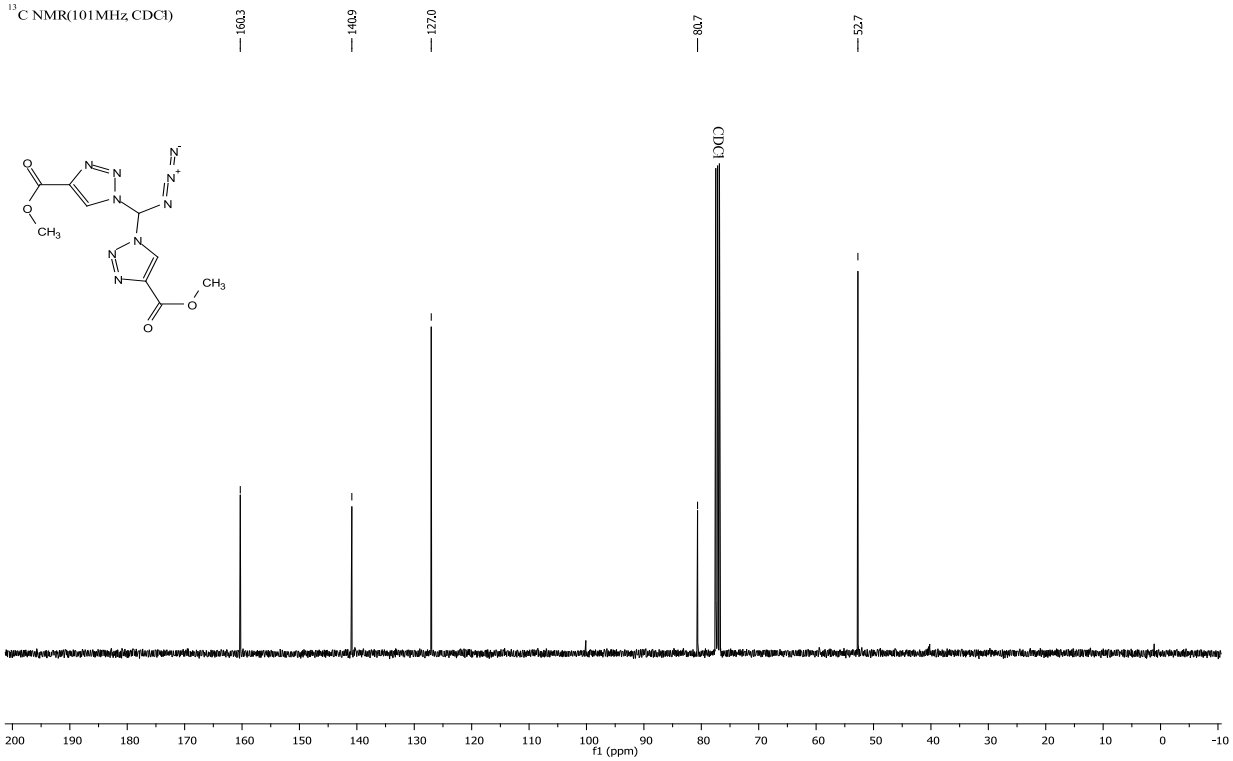




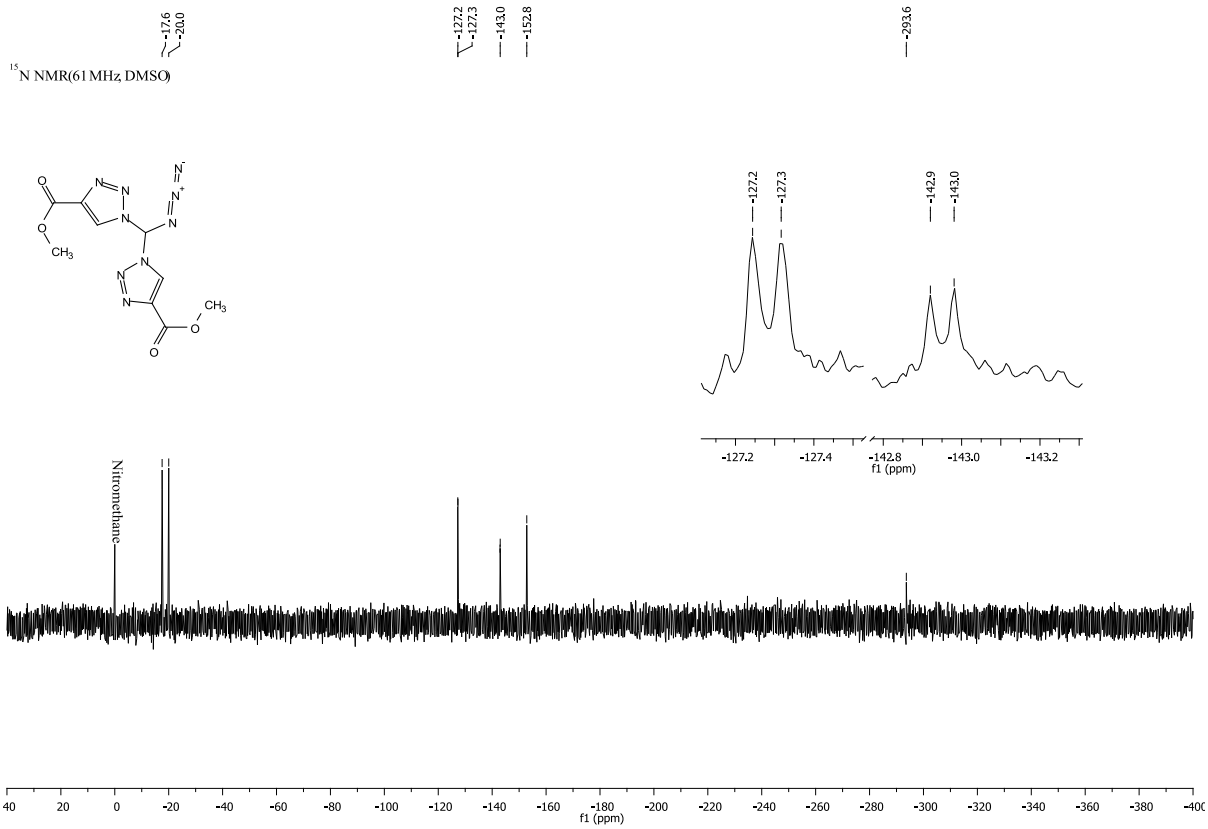
dimethyl 1,1'-(azidomethylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (3a)

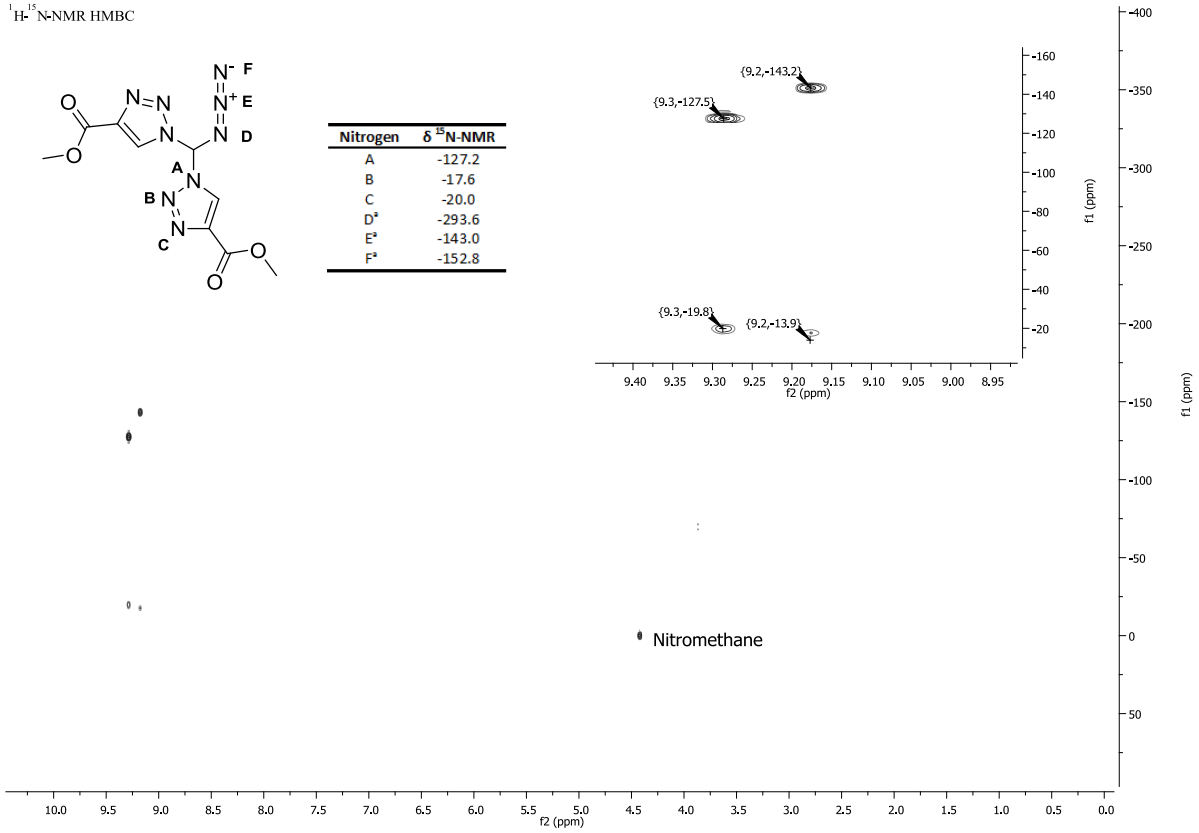


^{13}C NMR(101MHz, CDCl)



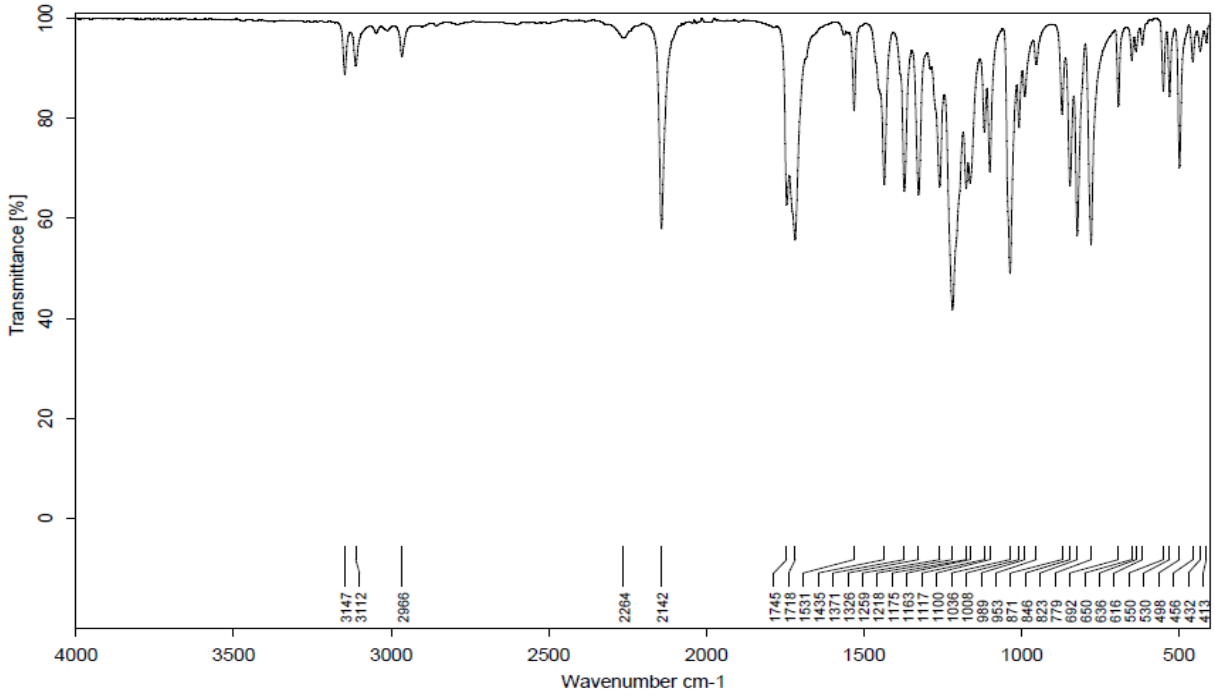
^{15}N NMR(61MHz, DMSO)





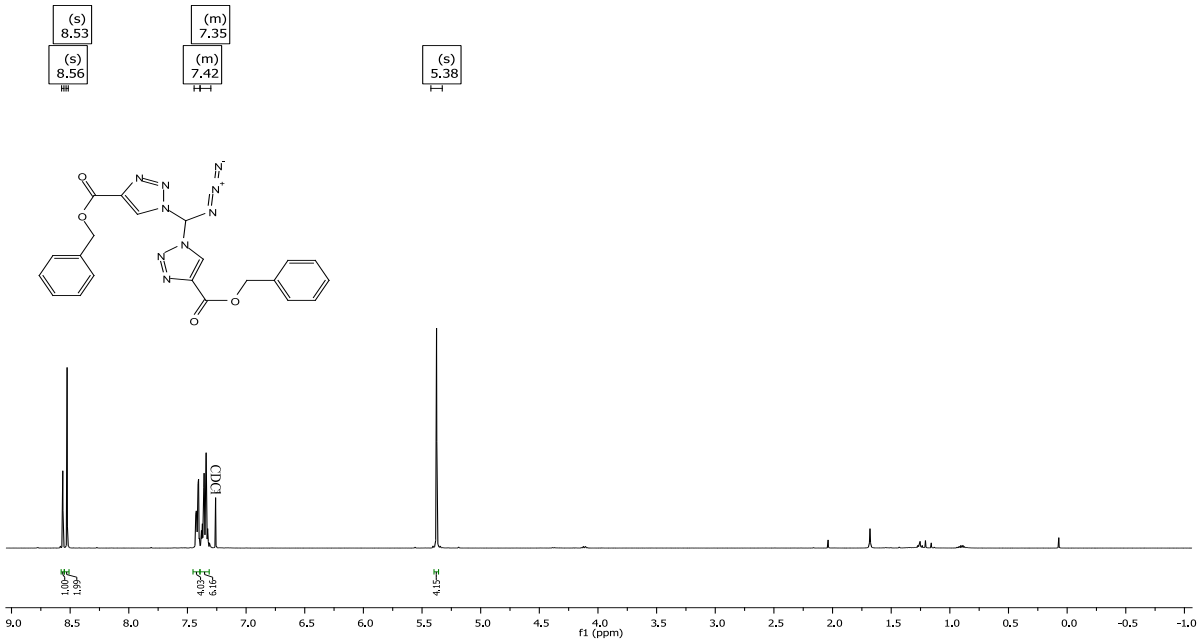
Nitrogen	δ ^{15}N-NMR
A	-127.2
B	-17.6
C	-20.0
D[a]	-293.6
E[a]	-143.0
F[a]	-152.8

[a] On the basis of the ^{15}N and HMBC NMR spectra, an assignment of the chemical shifts for the individual azide nitrogens was not possible with full certainty. The assignment is based on the ^{15}N data collection found in: Berger Stefan; Braun, Siegmar; Kalinowski, Hans-Otto. *NMR-Spektroskopie von Nichtmetallen: ^{15}N-NMR-Spektroskopie*. Stuttgart, New York: Georg Thieme Verlag, 1992. Print.

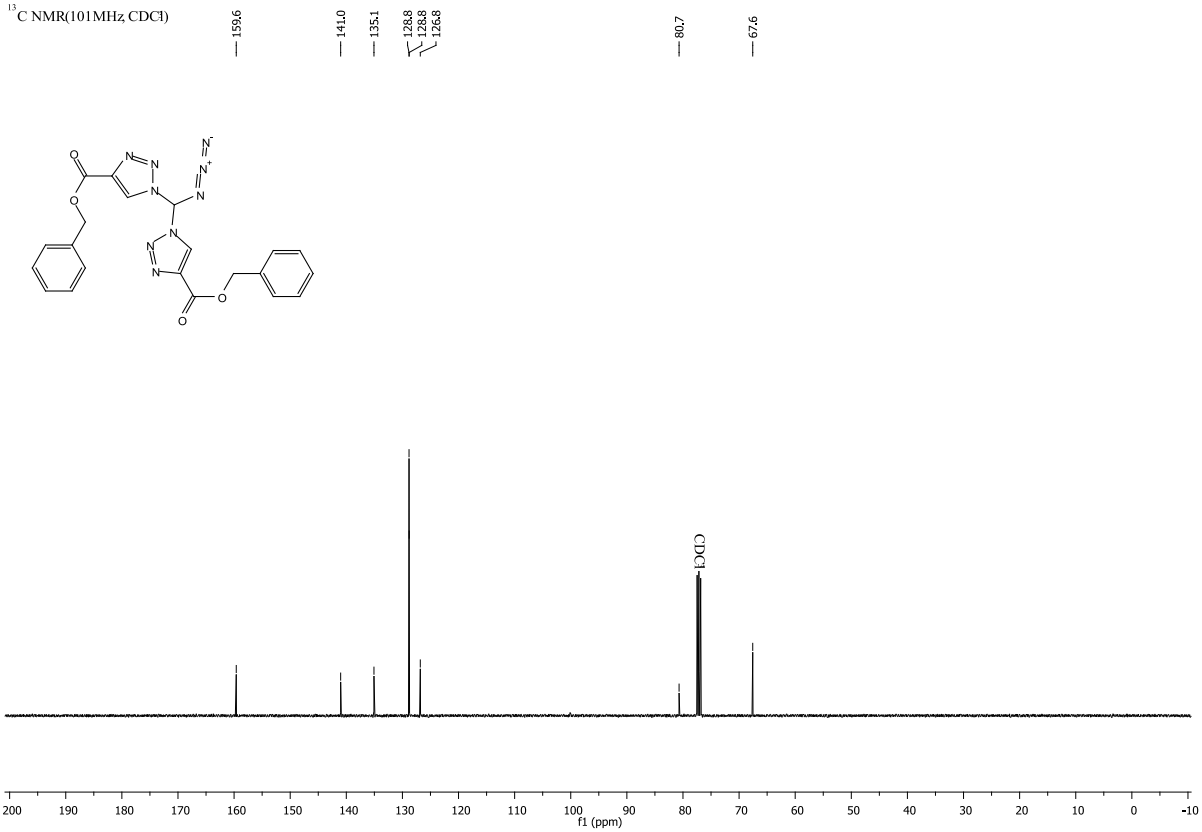


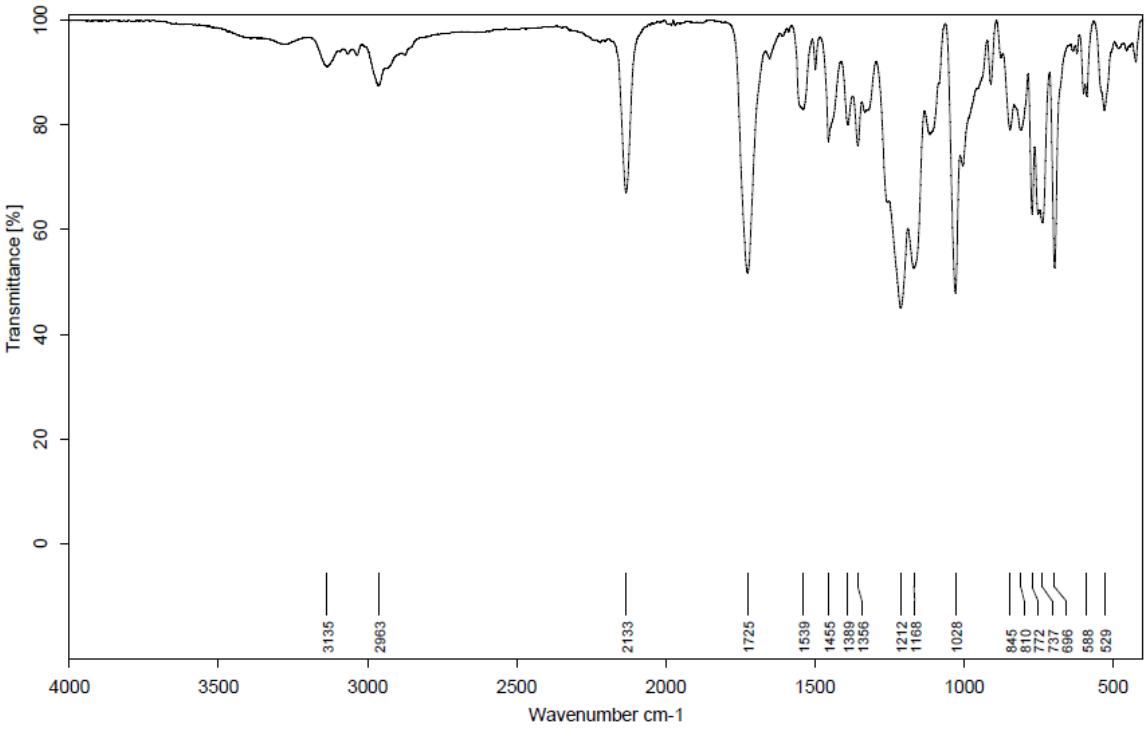
dibenzyl 1,1'-(azidomethylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (3b)

^{1}H NMR(400MHz, CDCl)



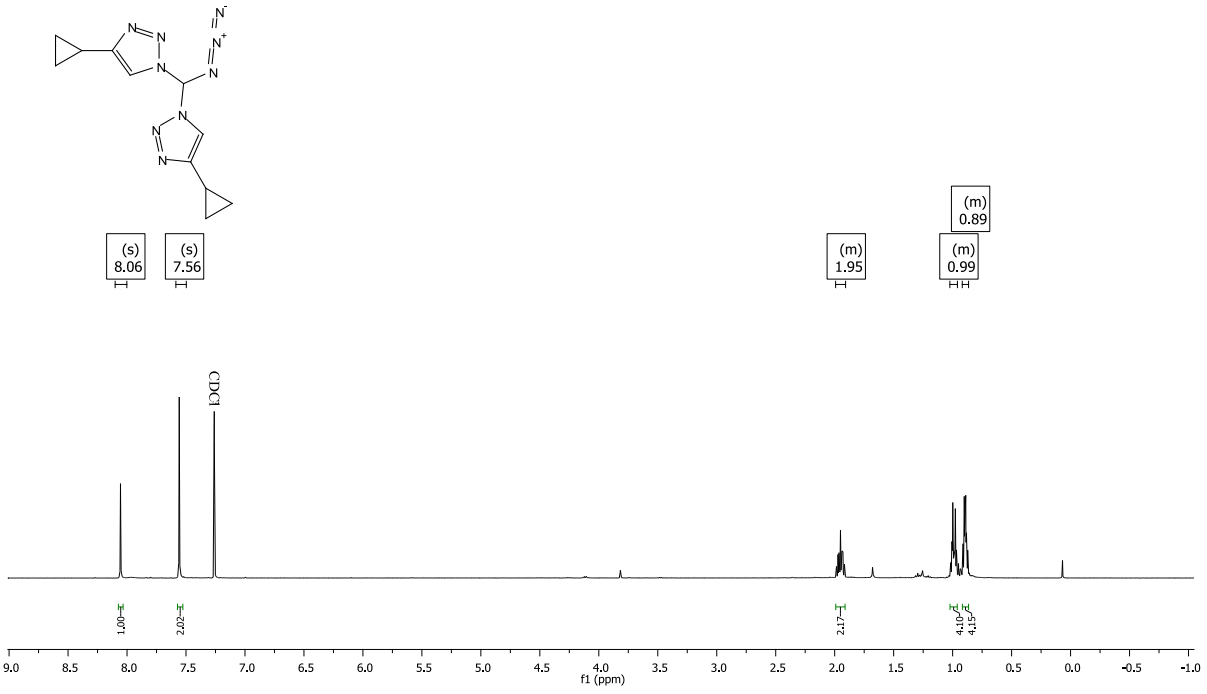
^{13}C NMR(101MHz, CDCl)



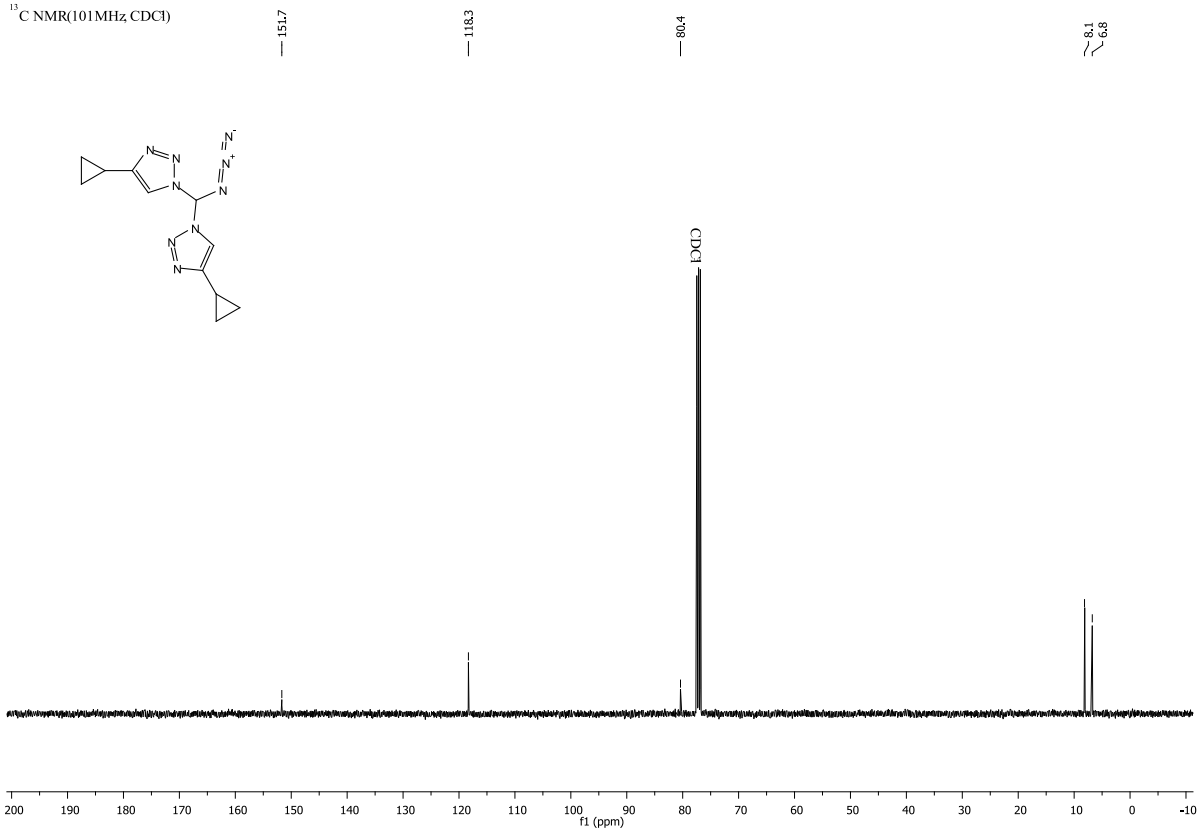


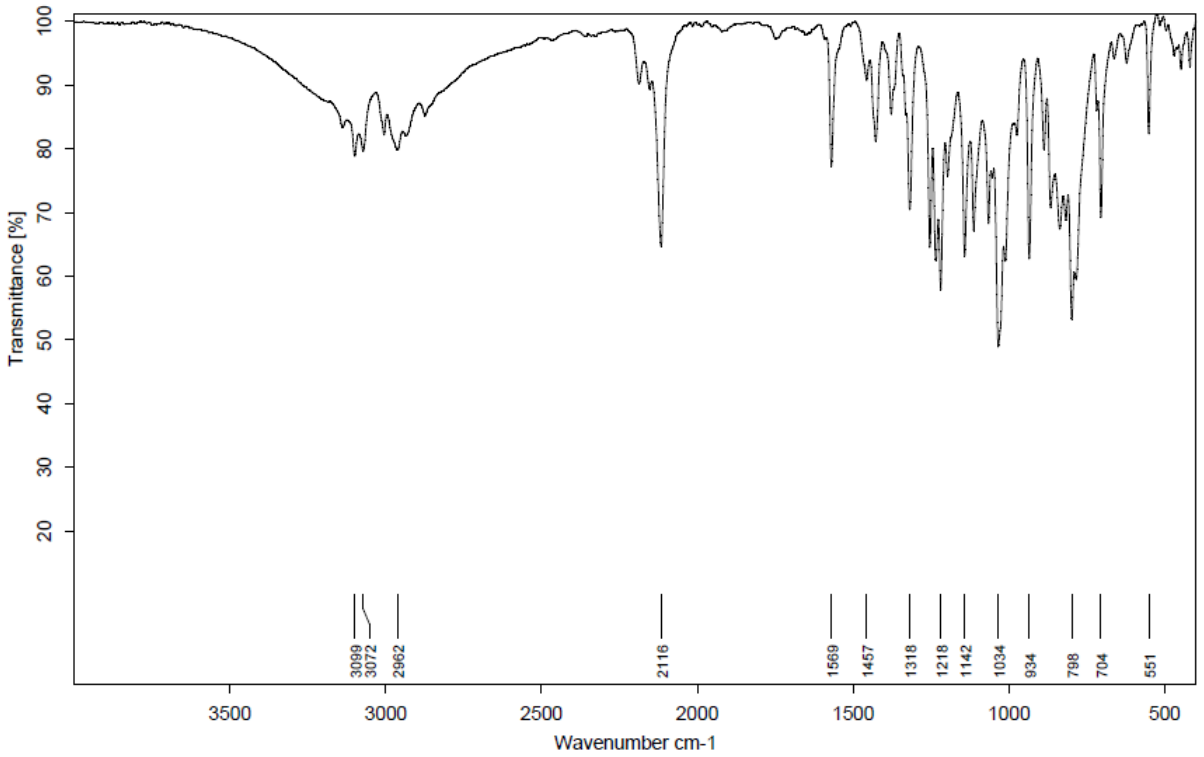
1,1'-(azidomethylene)bis(4-cyclopropyl-1*H*-1,2,3-triazole) (3c)

^{1}H NMR(400MHz, CDCl)



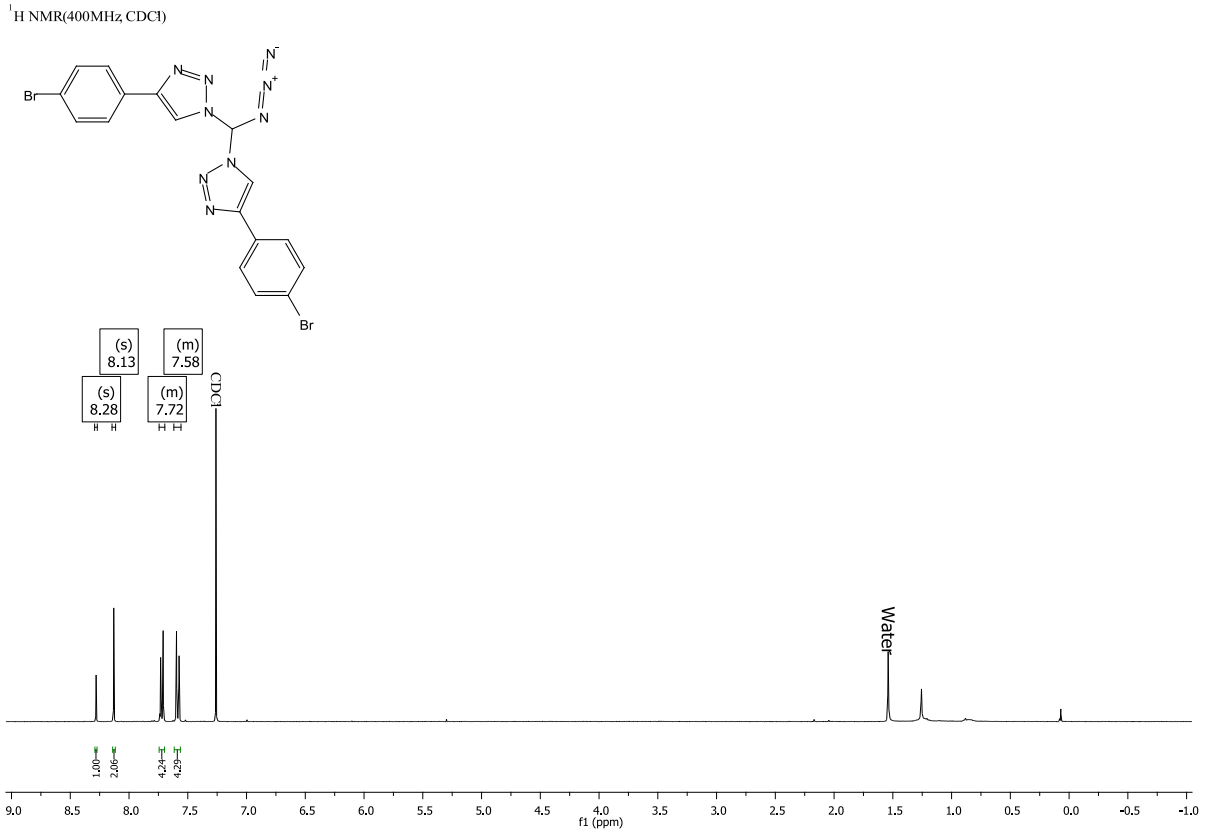
^{13}C NMR(101MHz CDCl)



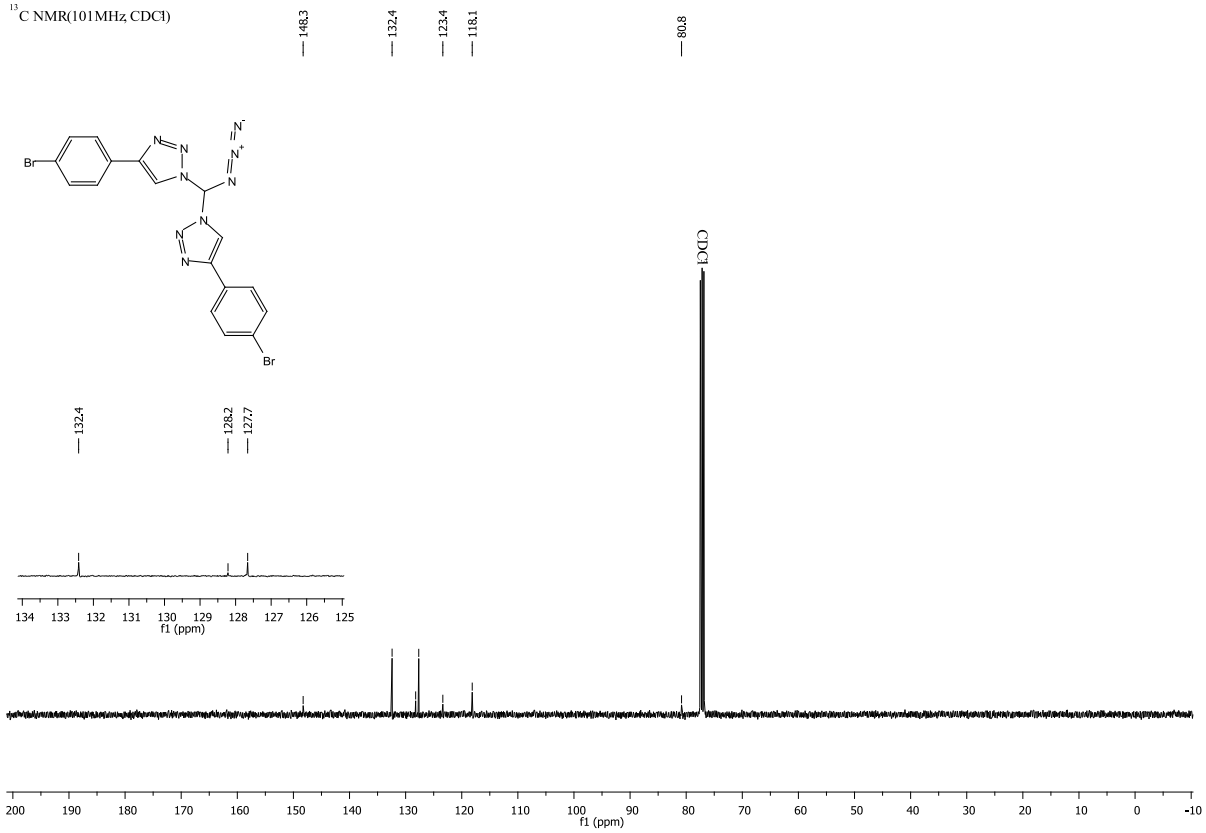


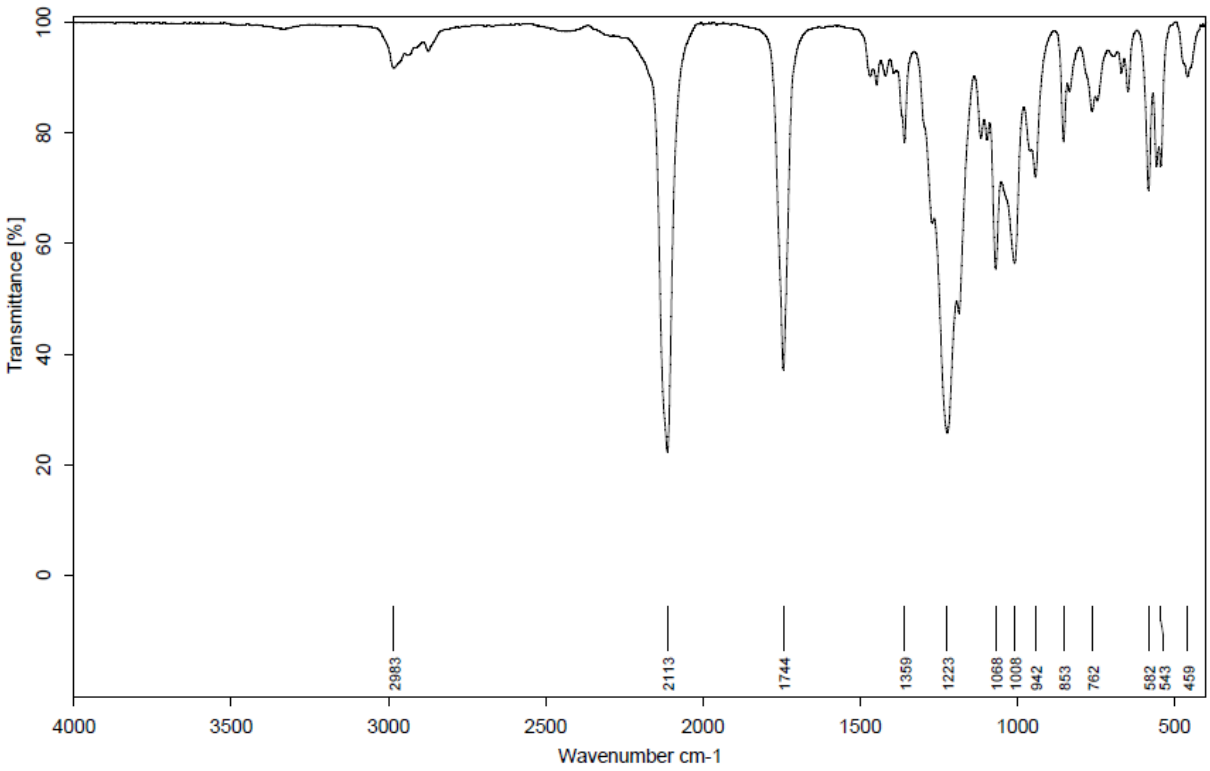
1,1'-(azidomethylene)bis(4-(4-bromophenyl)-1*H*-1,2,3-triazole) (3d)

^{1}H NMR(400MHz, CDCl)

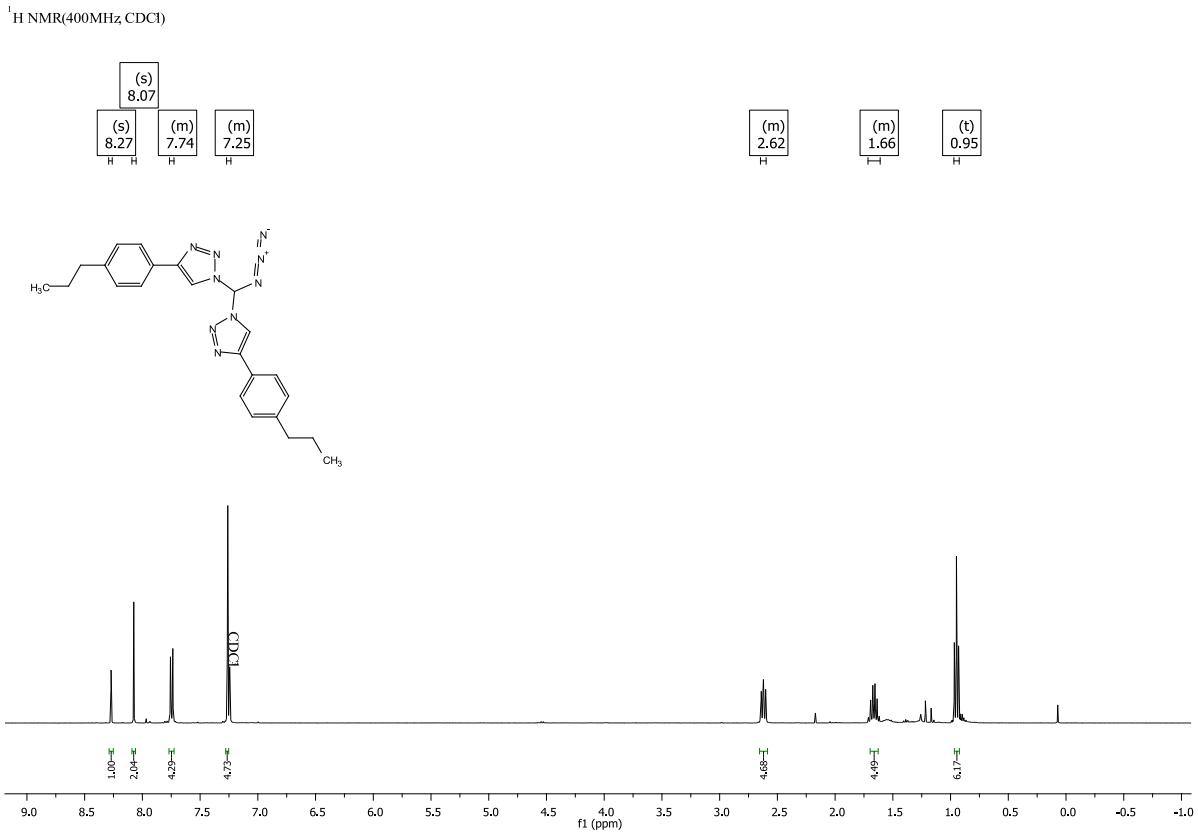


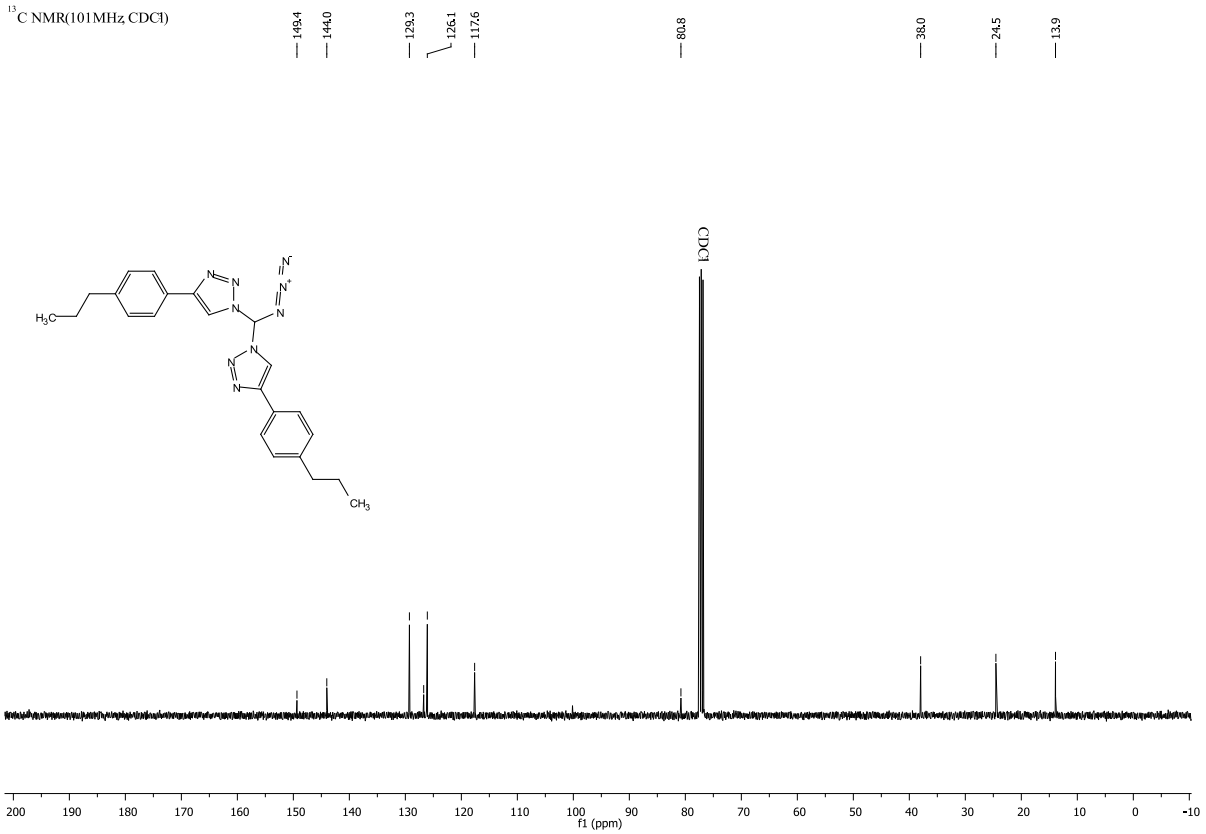
^{13}C NMR(101MHz, CDCl)

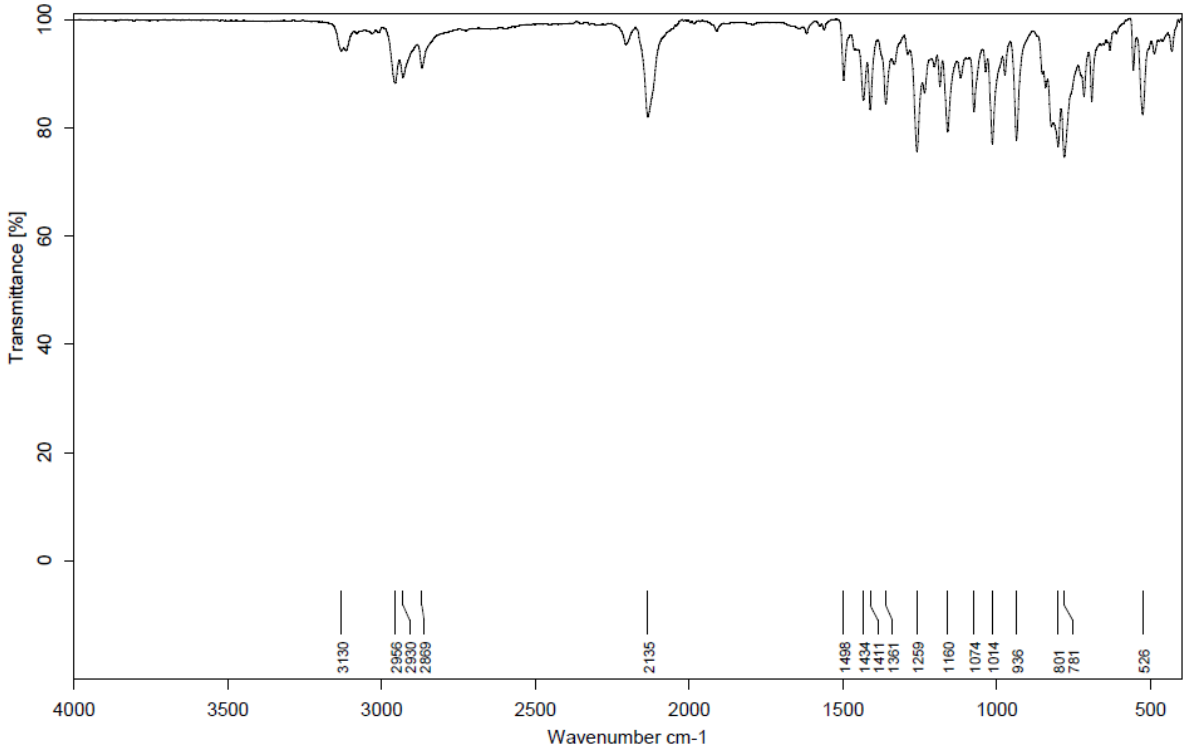




1,1'-(azidomethylene)bis(4-(4-propylphenyl)-1*H*-1,2,3-triazole) (3e)

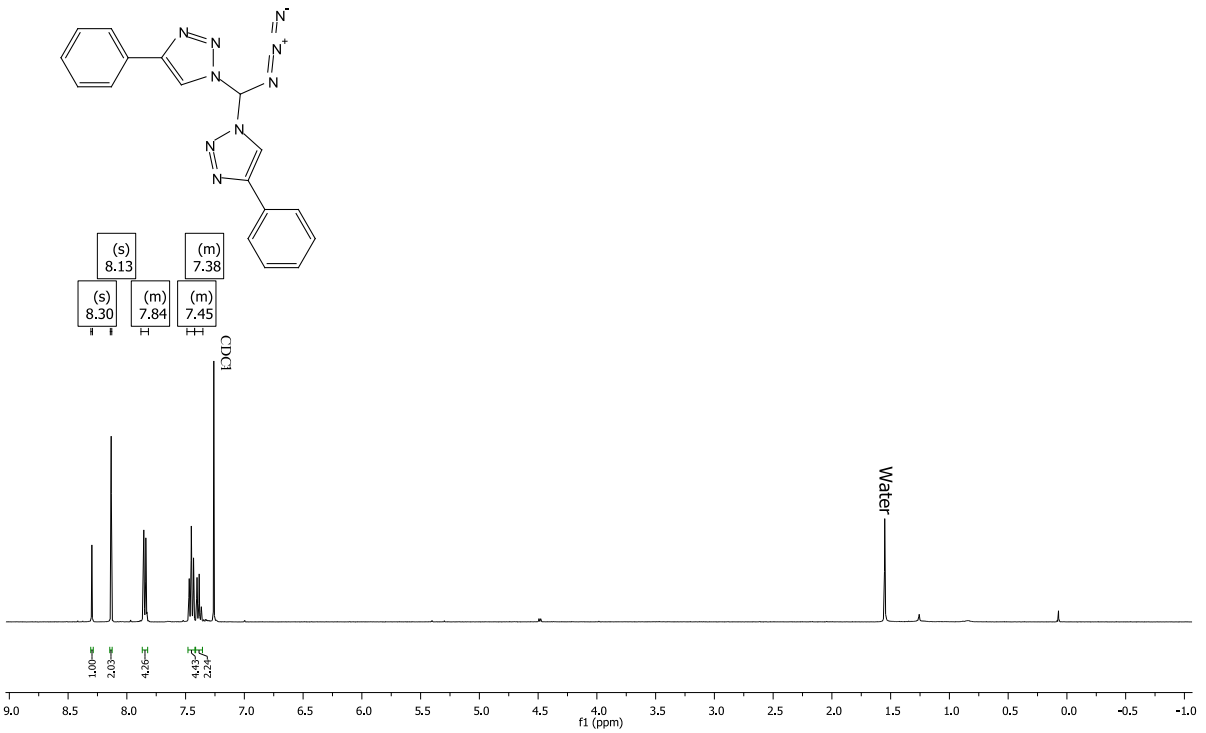



13C NMR(101MHz, CDCl)
149.4
144.0
129.3
126.1
117.6
80.8
38.0
24.5
13.9
CDCl3
f1 (ppm)

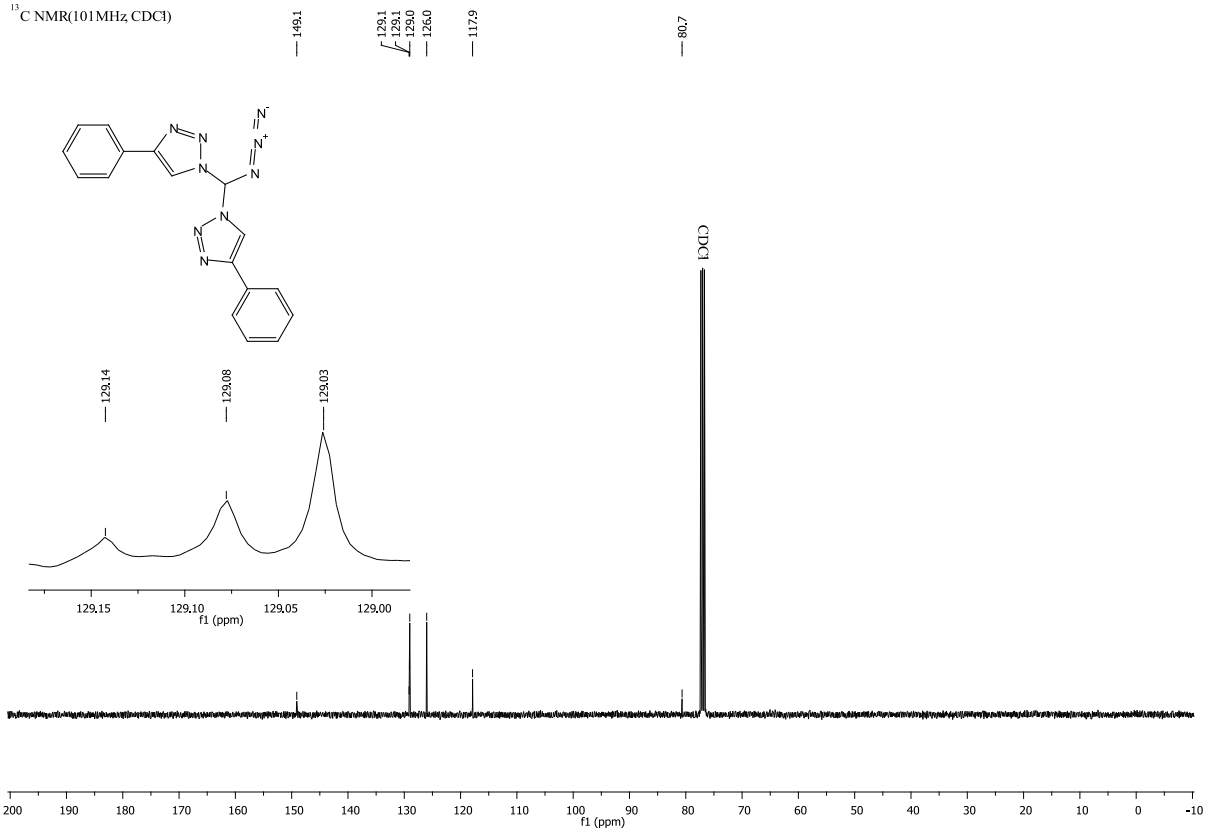

Transmittance [%]
Wavenumber cm-1
3130
2956
2930
2869
2135
1498
1434
1411
1361
1259
1160
1074
1014
936
801
781
526

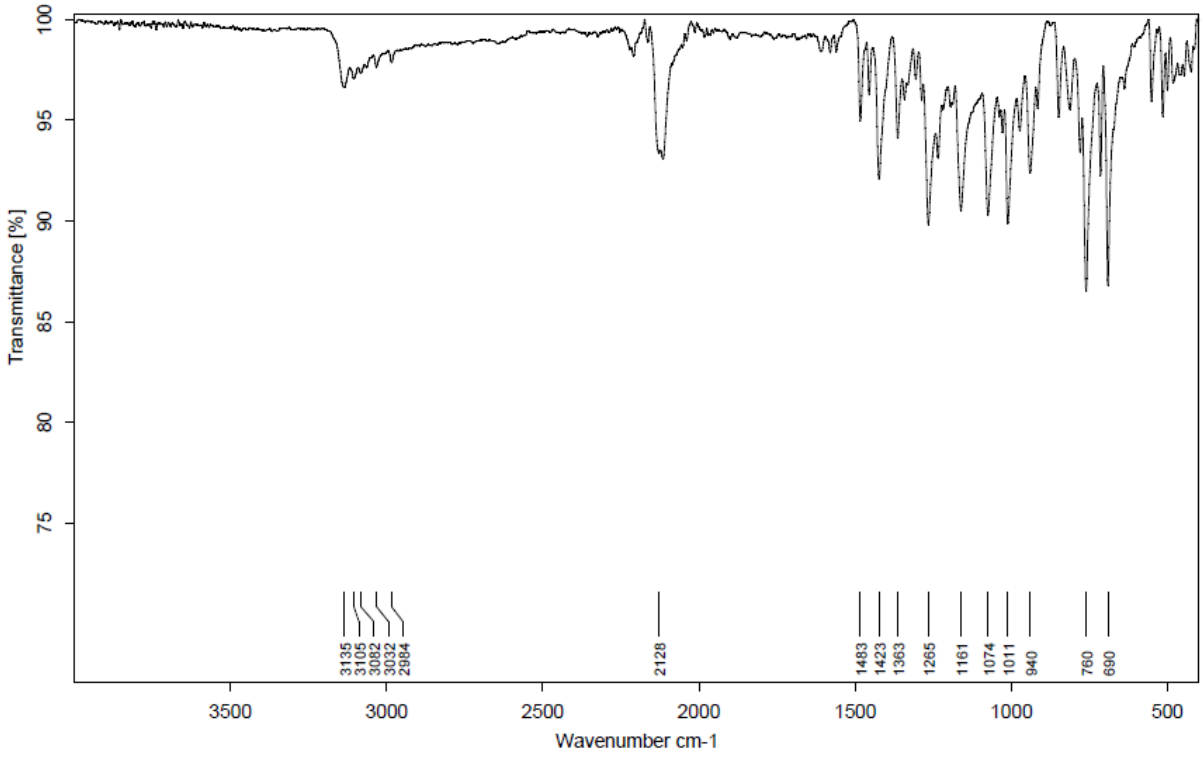
1,1'-(azidomethylene)bis(4-phenyl-1*H*-1,2,3-triazole) (3f)

^{1}H NMR(400MHz, CDCl)



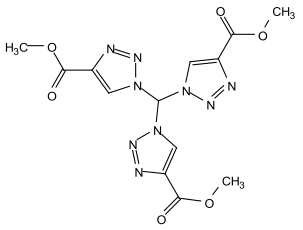
^{13}C NMR(101MHz, CDCl)

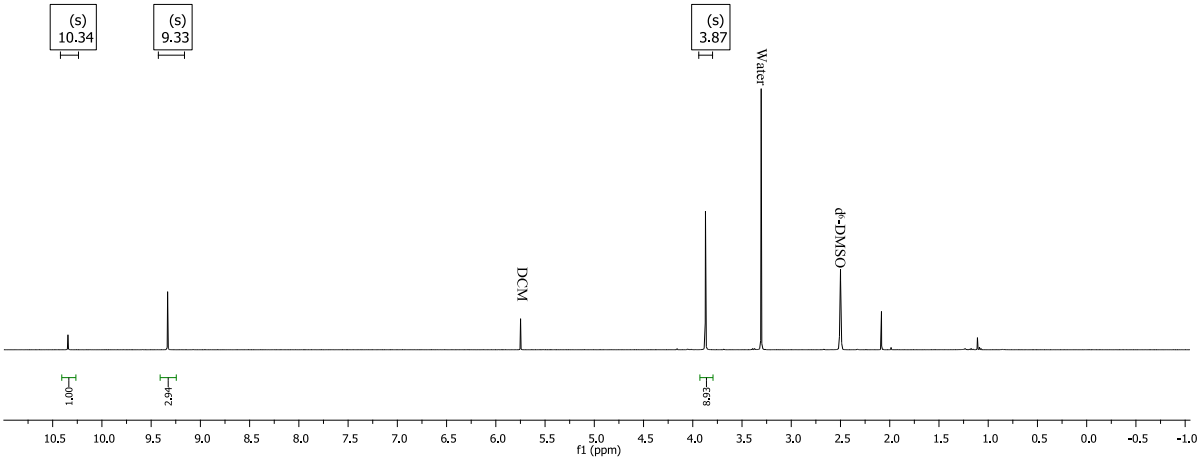




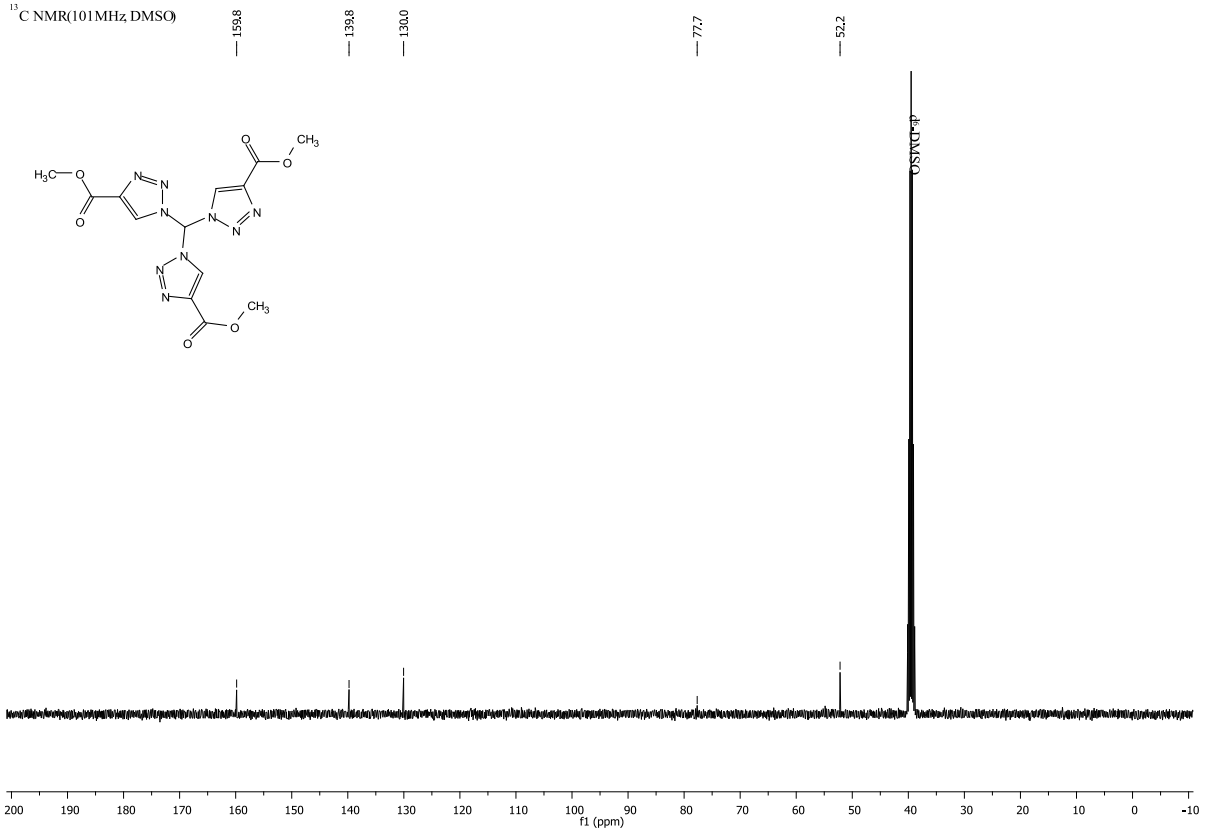
trimethyl 1,1',1''-methanetriyltris(1*H*-1,2,3-triazole-4-carboxylate) (4a)

^{1}H NMR(400MHz, DMSO)

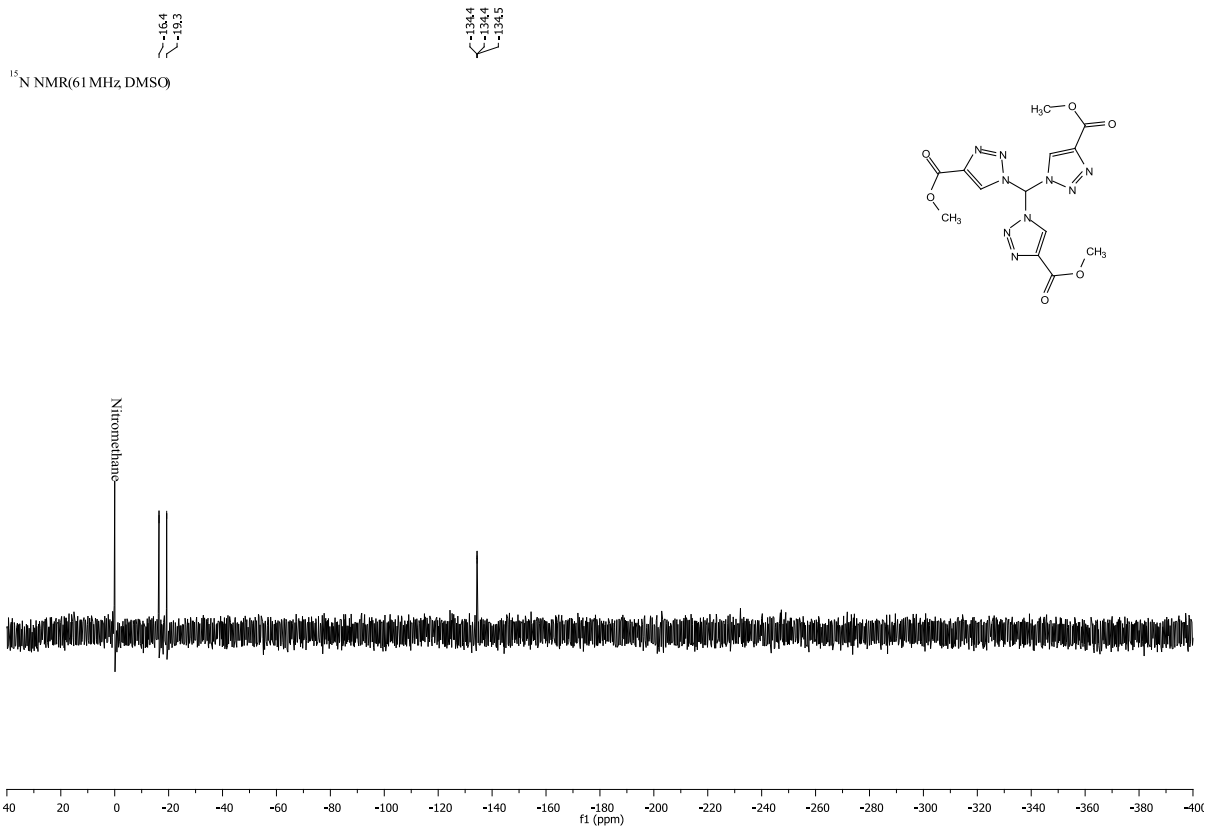




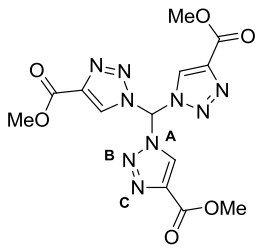
^{13}C NMR(101MHz, DMSO)



^{15}N NMR(61MHz, DMSO)



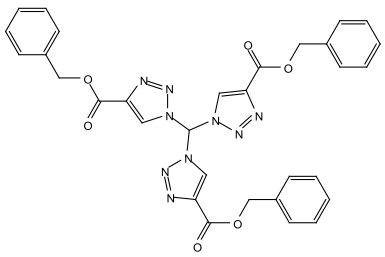
^{1}H-^{15}N-NMR HMBC

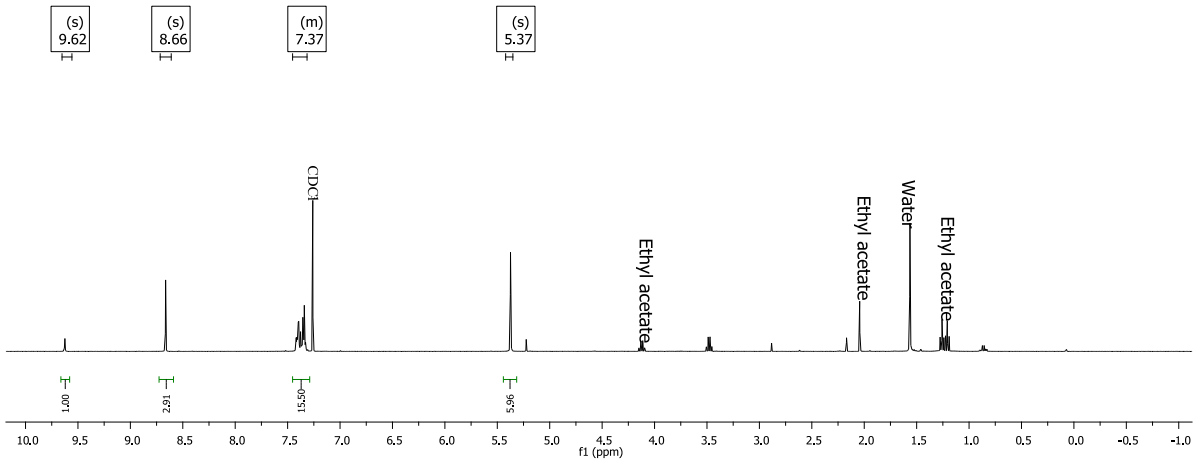


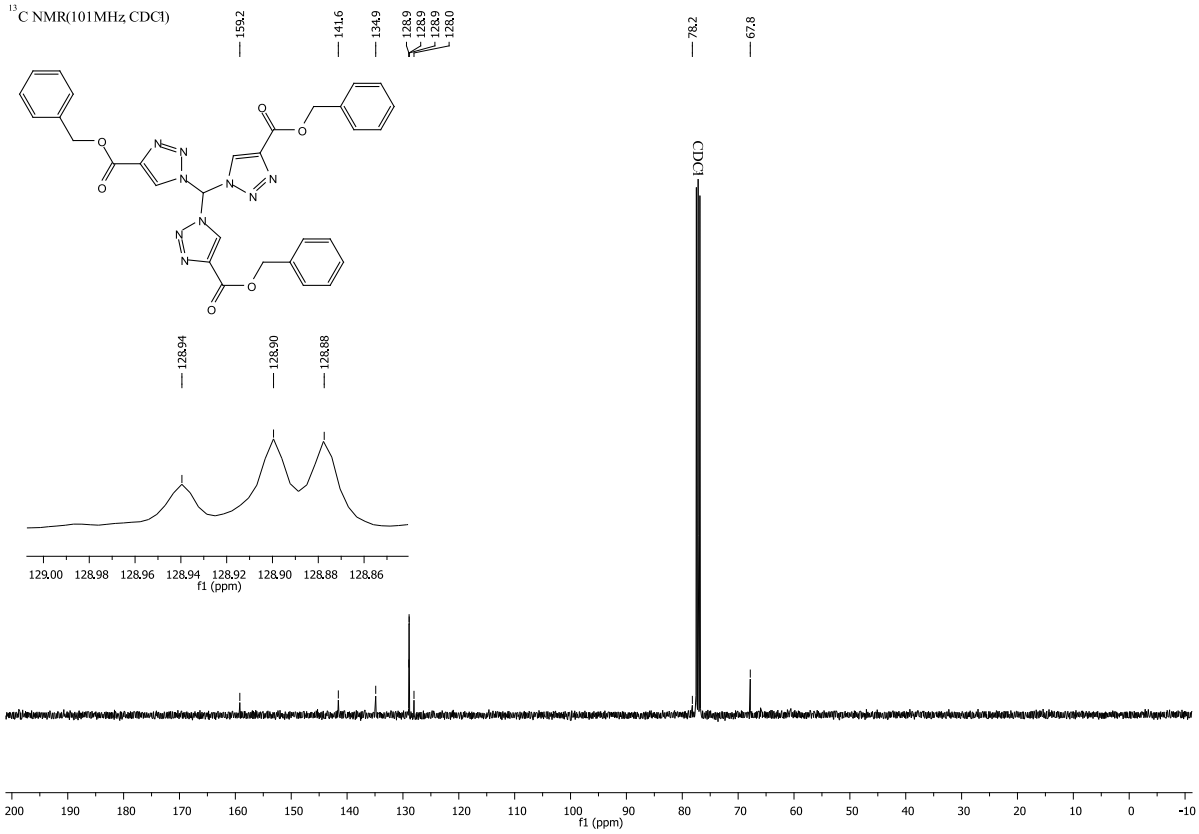
Nitrogen	δ ^{15}N-NMR
A	-134.4
B	-16.4
C	-19.3

tribenzyl 1,1',1''-methanetriyltris(1*H*-1,2,3-triazole-4-carboxylate) (4b)

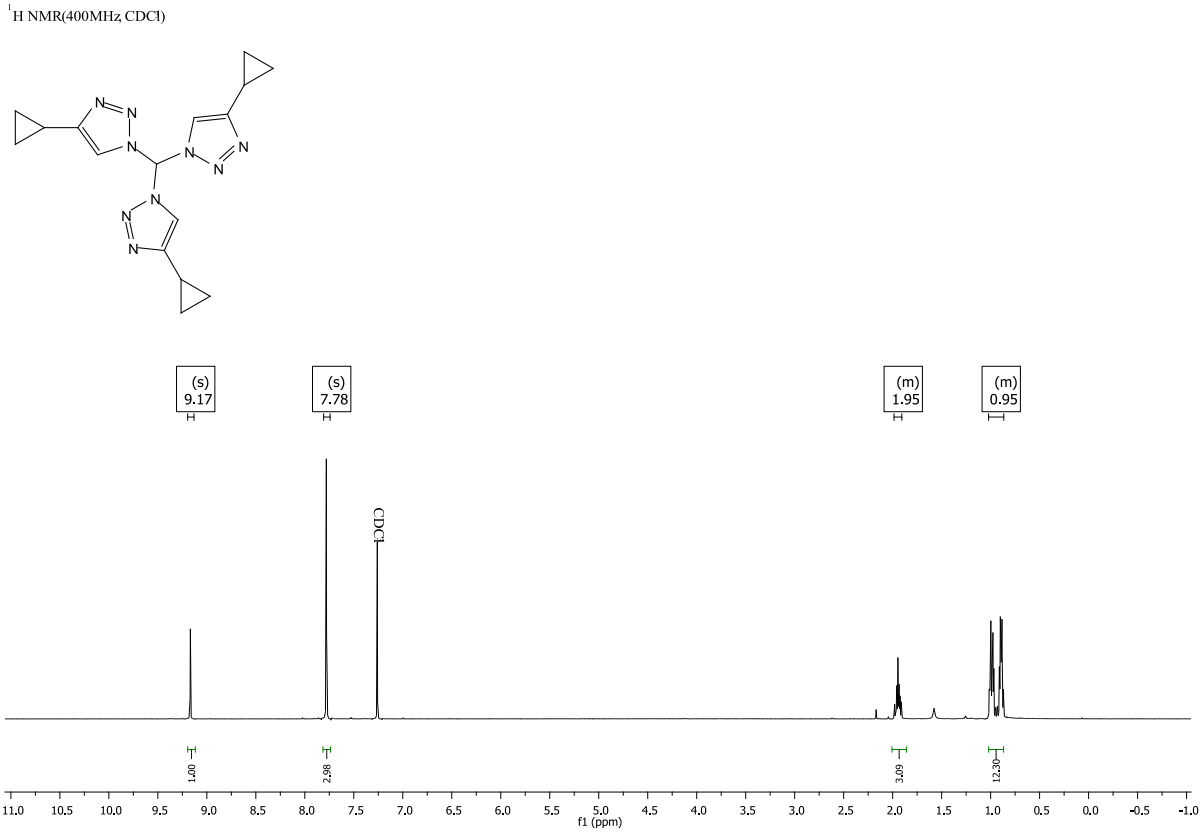
^{1}H NMR(400MHz, CDCl)

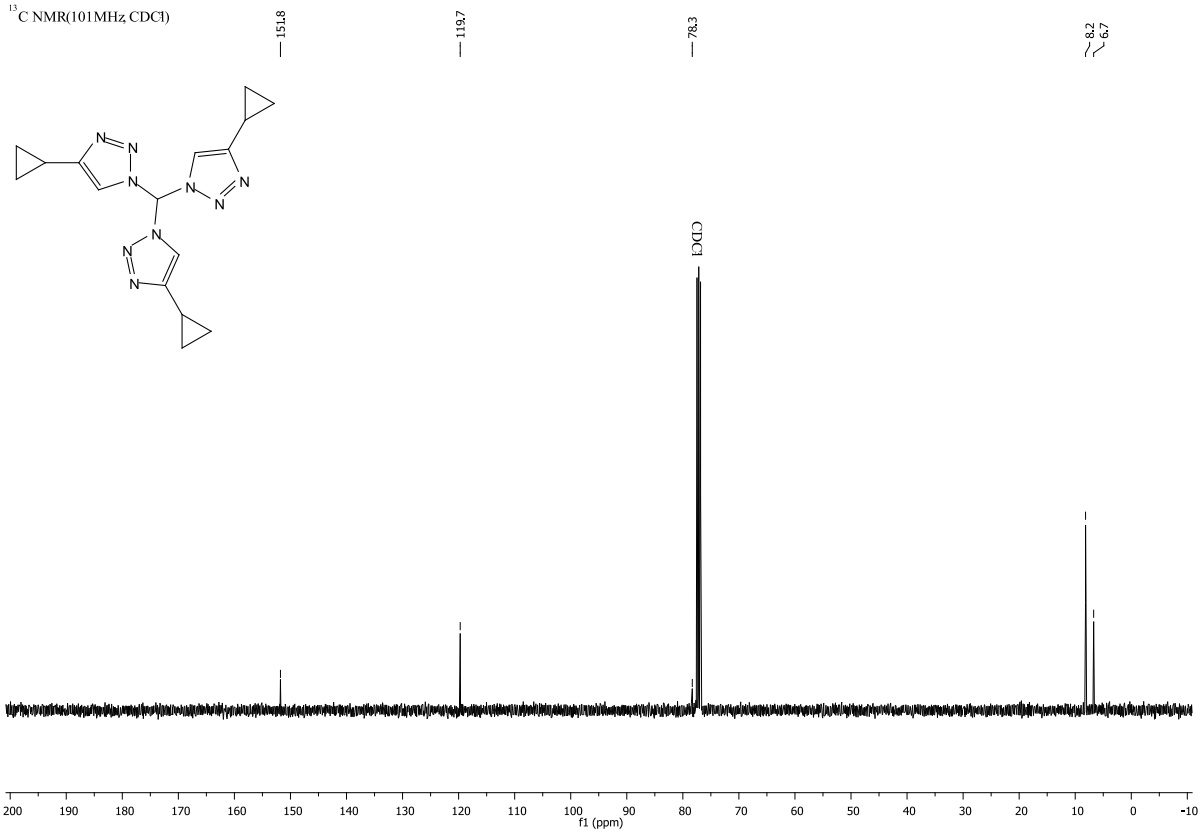




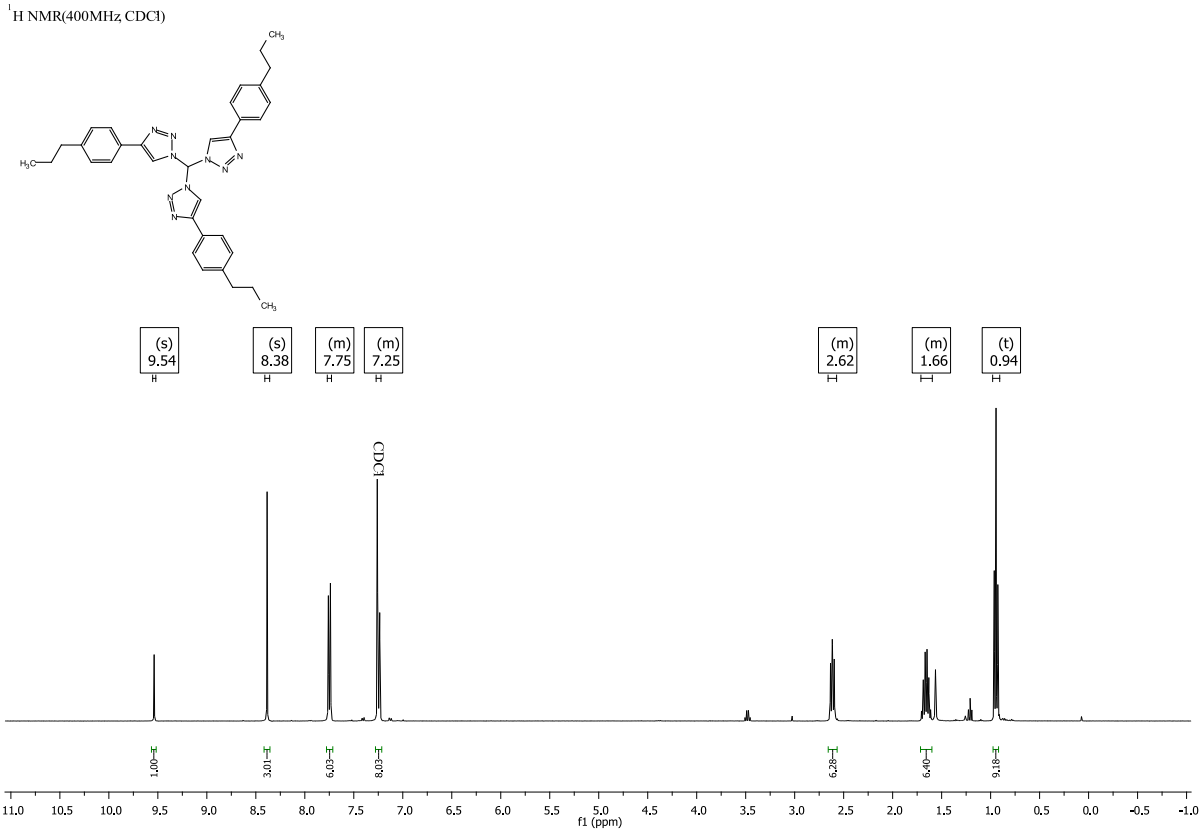


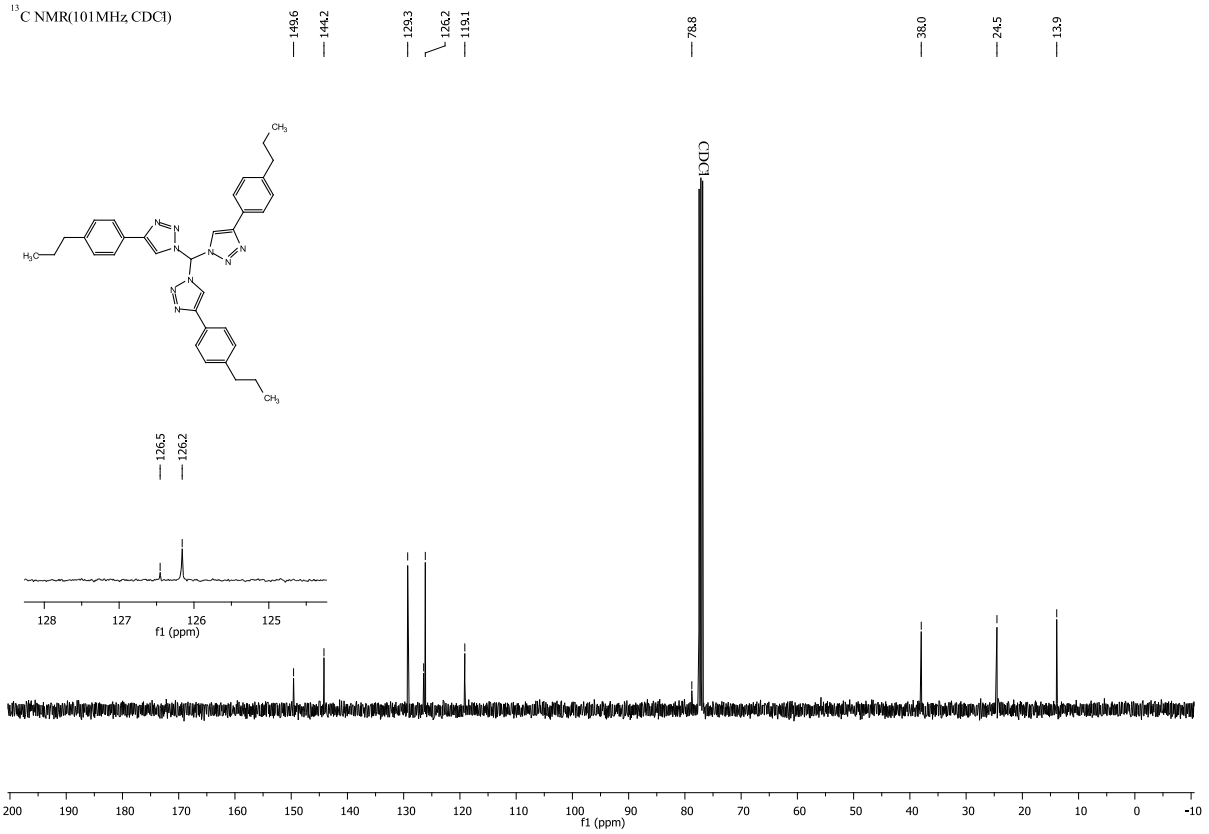
tris(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)methane (4c)



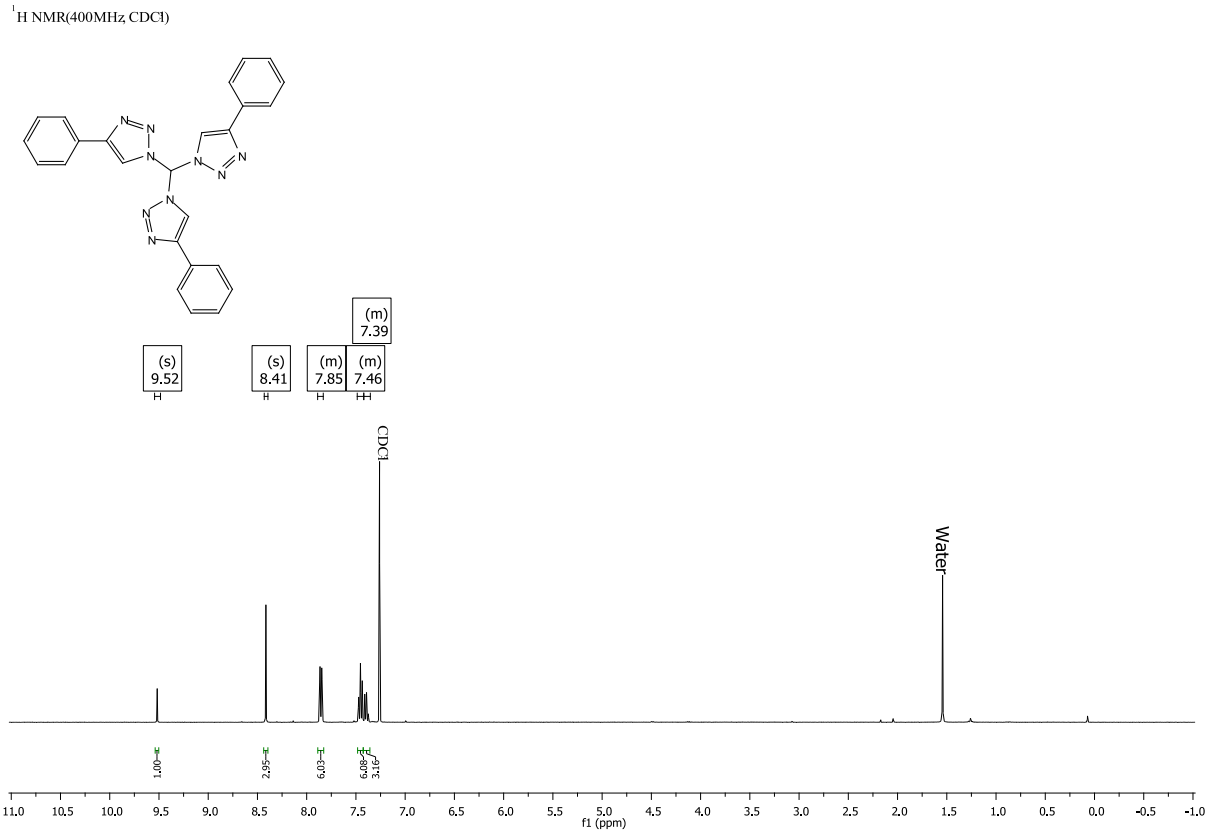


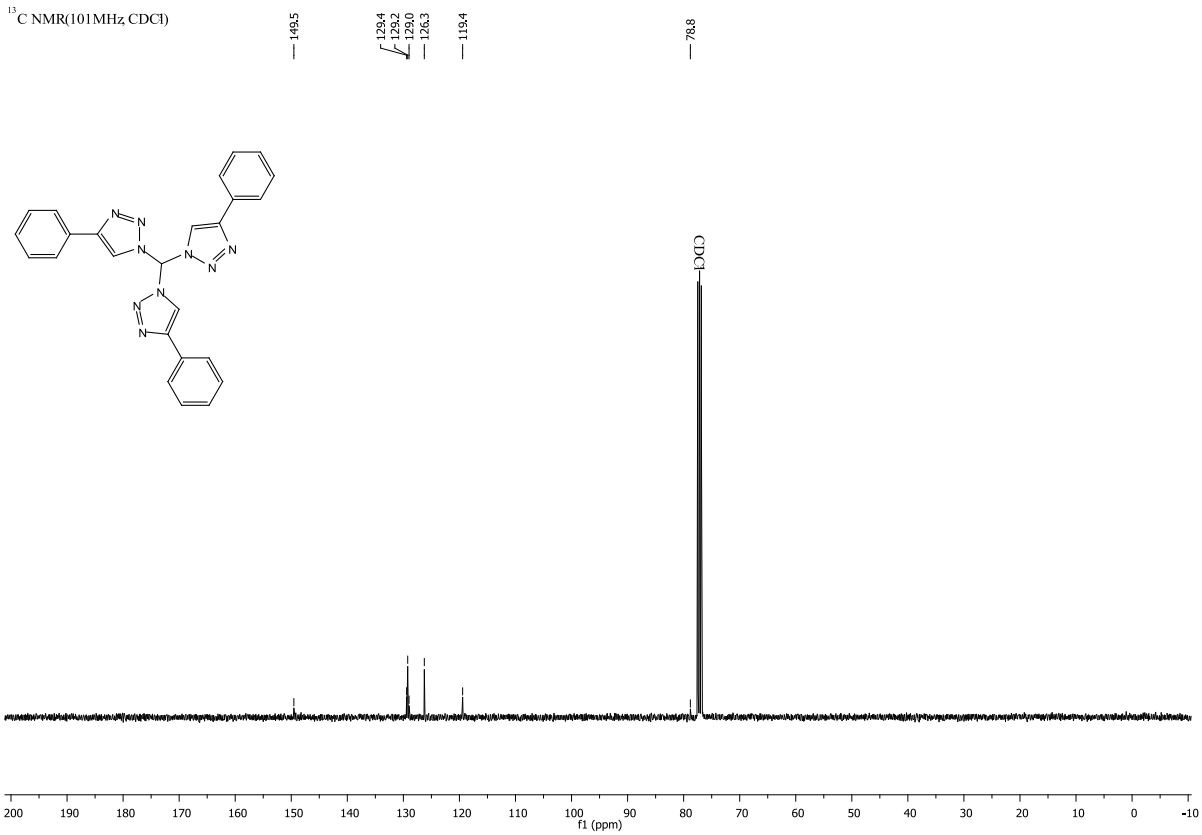
tris(4-(4-propylphenyl)-1*H*-1,2,3-triazol-1-yl)methane (4d)



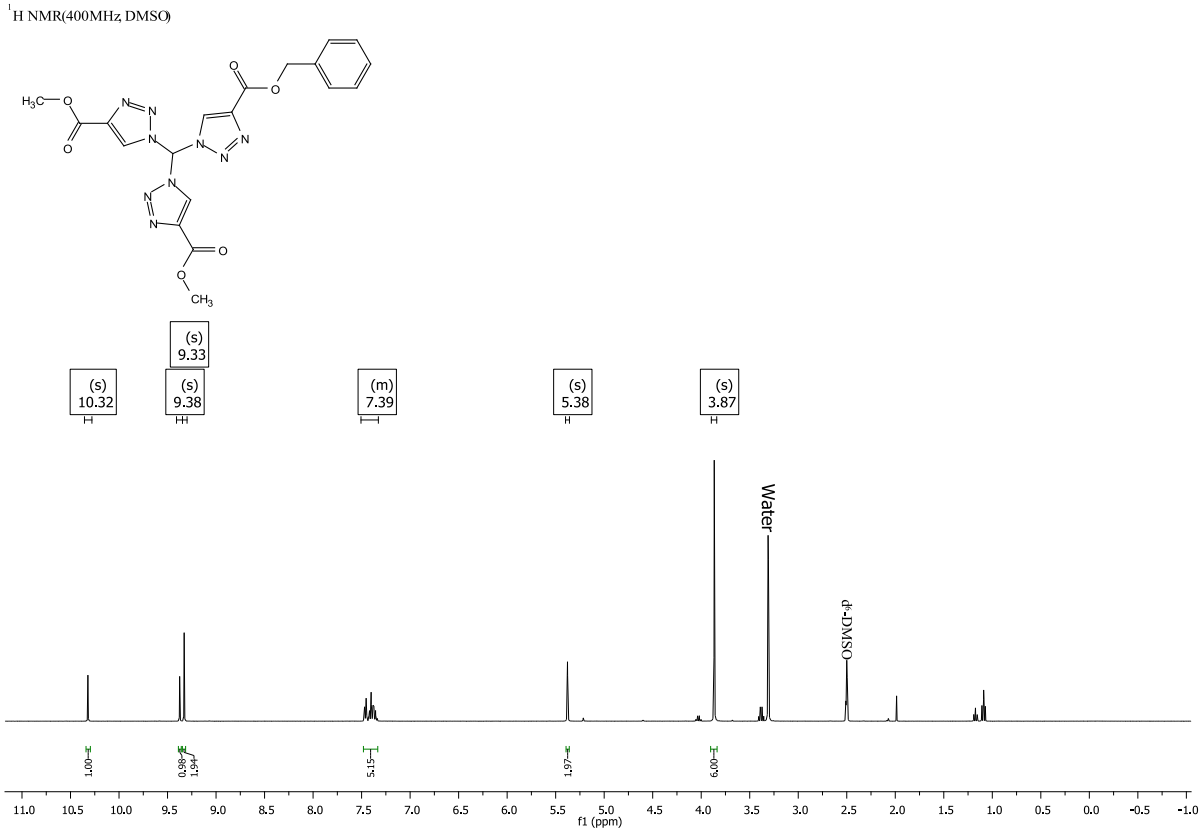


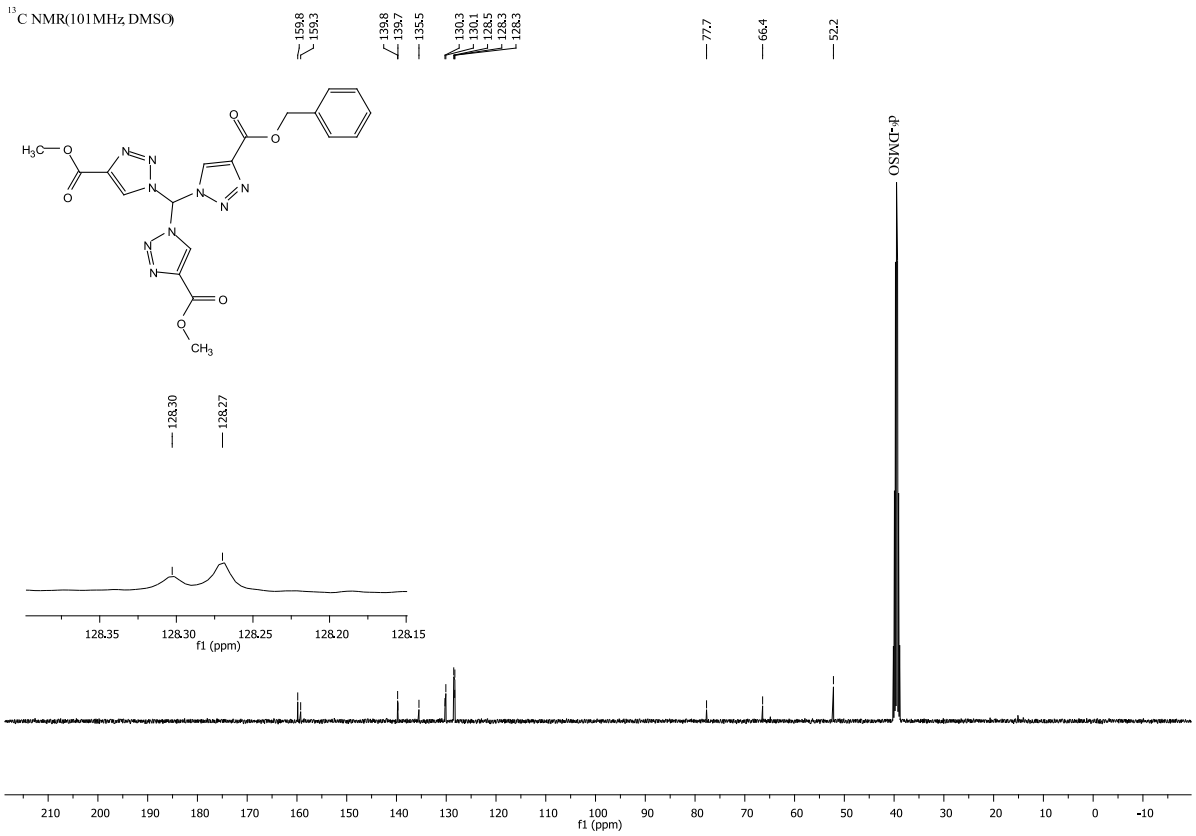
tris(4-phenyl-1*H*-1,2,3-triazol-1-yl)methane (4e)



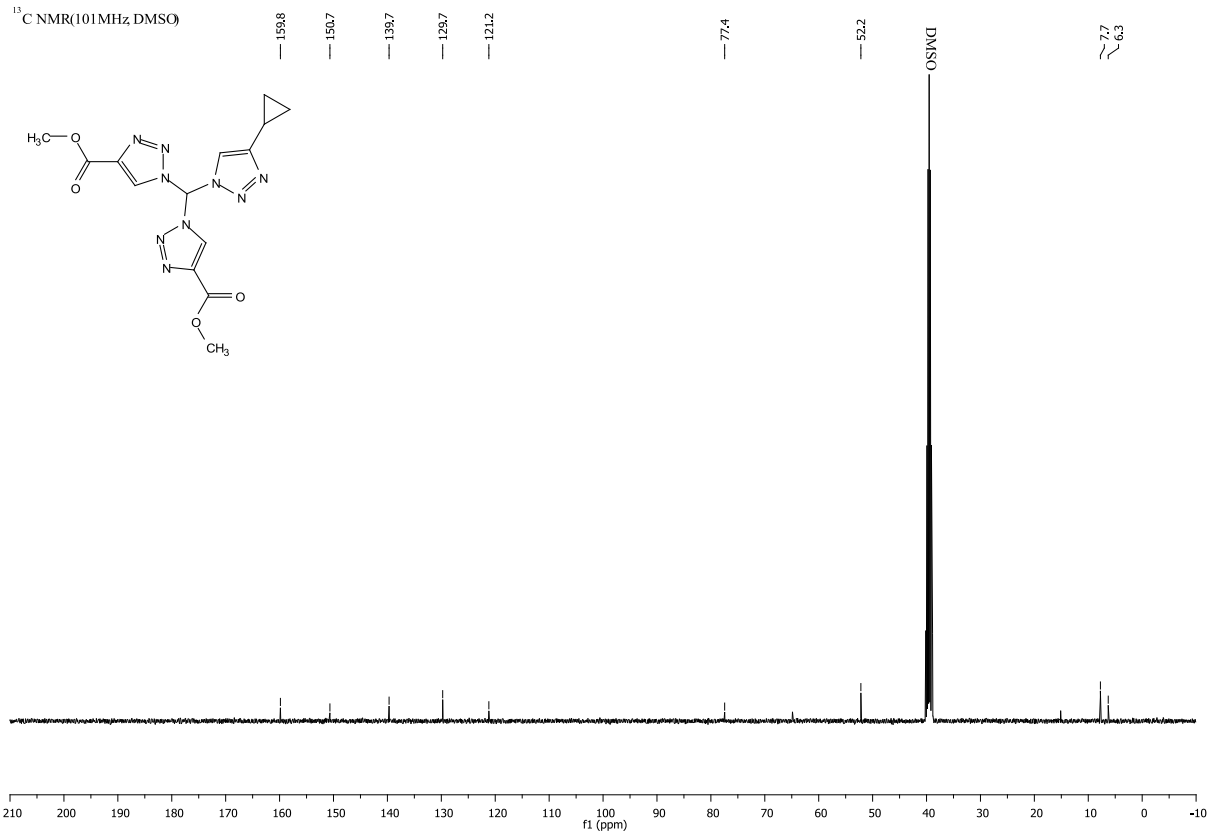


dimethyl 1,1'-((4-((benzyloxy)carbonyl)-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (4f)

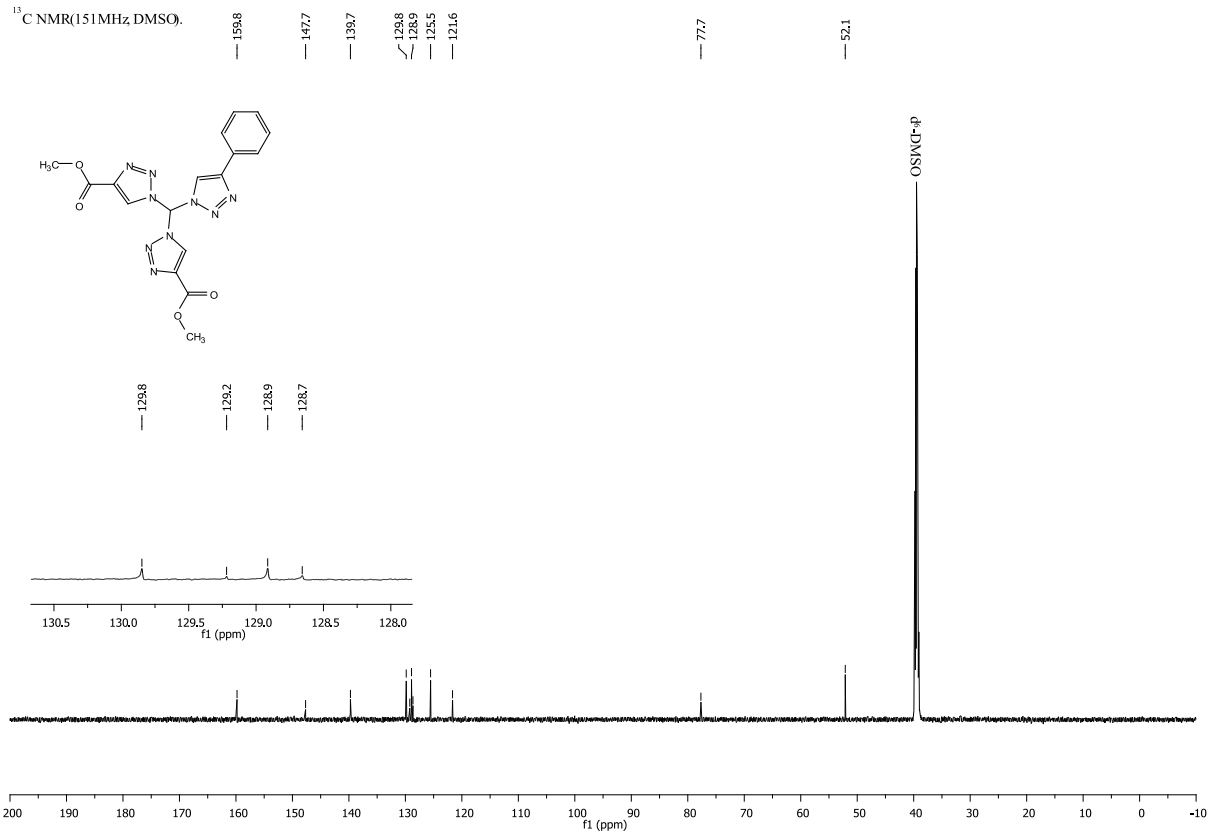




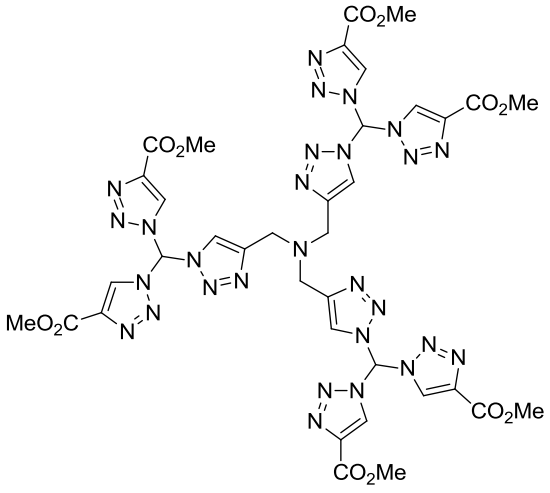
dimethyl 1,1'-((4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (4g)



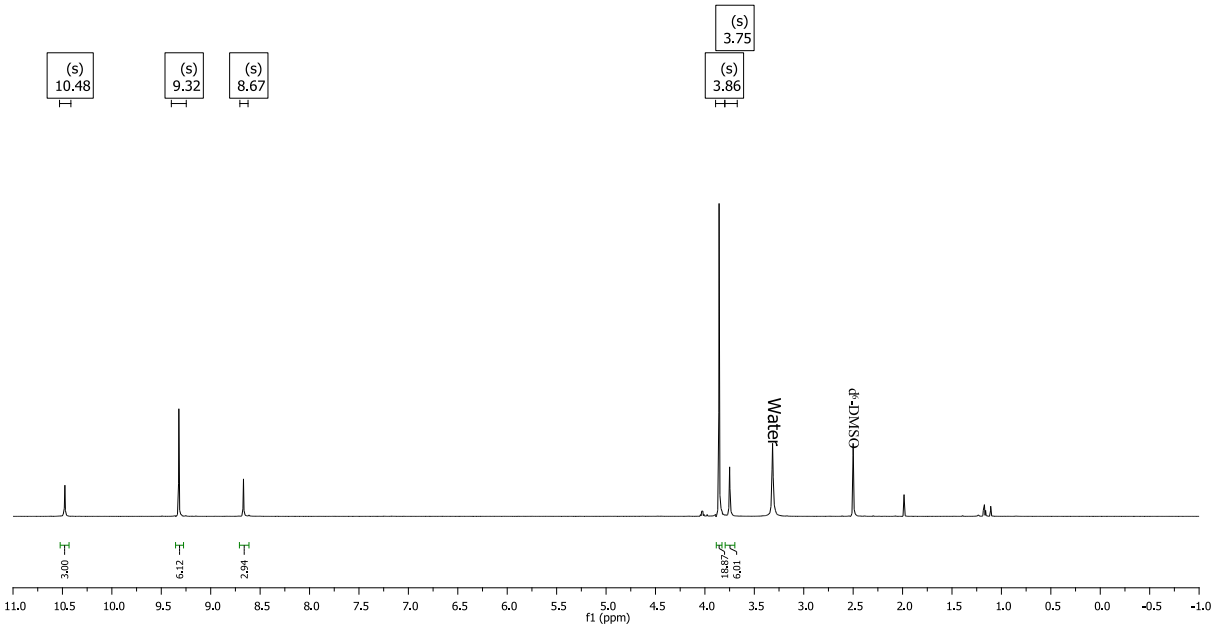
dimethyl 1,1'-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methylene)bis(1*H*-1,2,3-triazole-4-carboxylate) (4h)



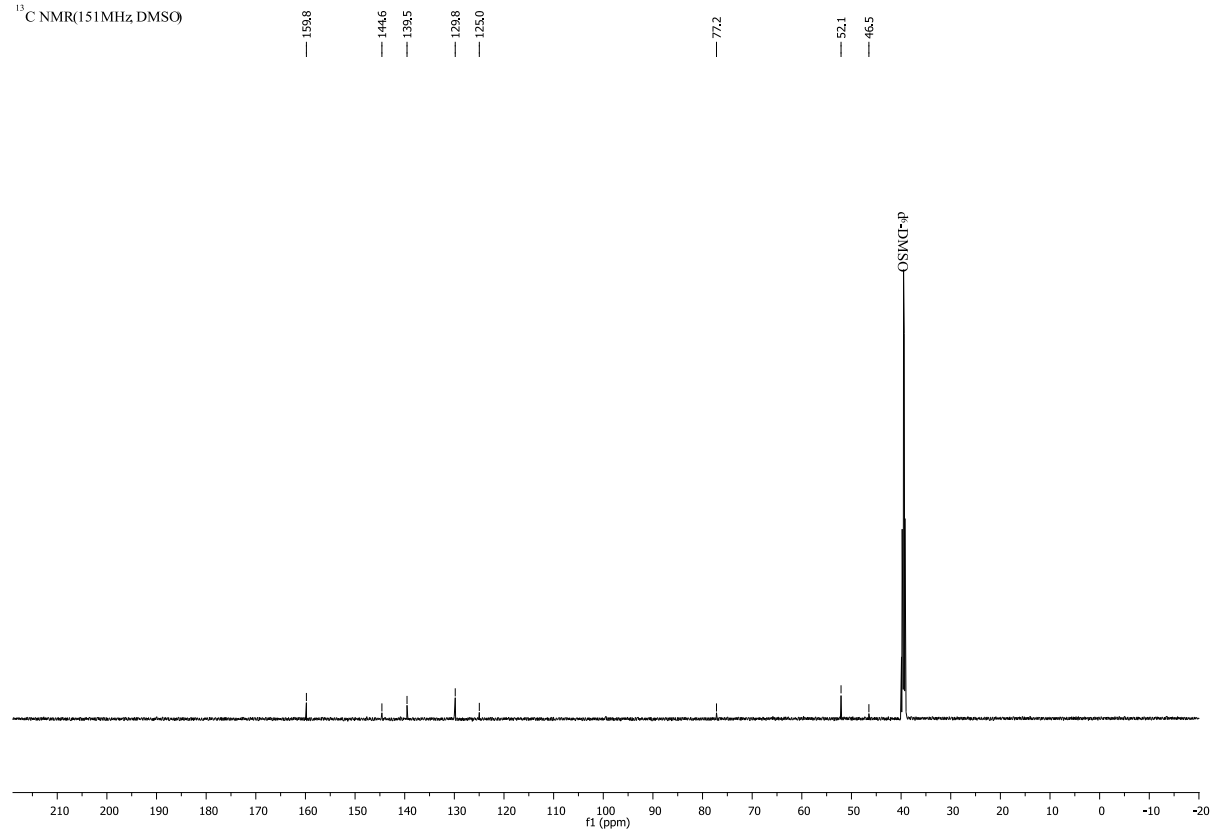
hexamethyl 1,1',1'',1''',1'''',1'''''-((4,4',4''-(nitrilotris(methylene))tris(1*H*-1,2,3-triazole-4,1-diyl))tris(methanetriyl))hexakis(1*H*-1,2,3-triazole-4-carboxylate) (5)



^{1}H NMR(600MHz, DMSO)

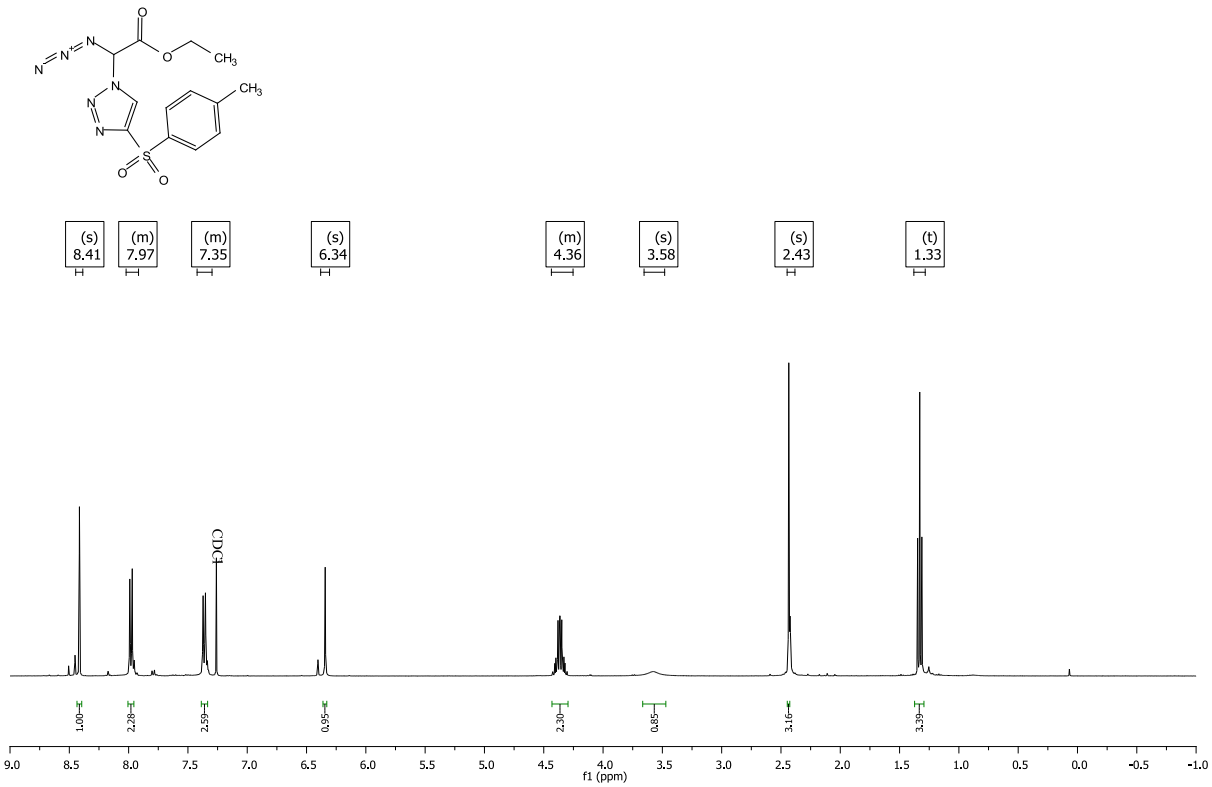


^{13}C NMR(151MHz, DMSO)

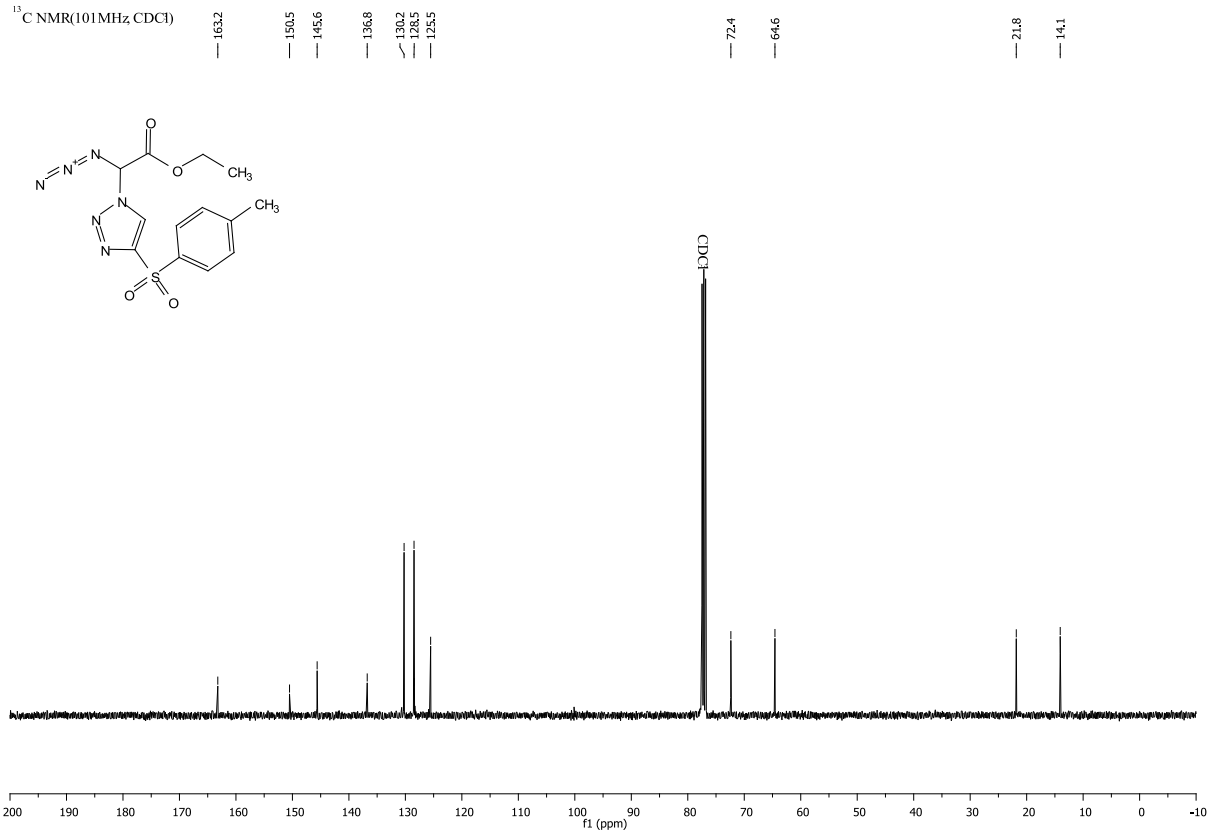


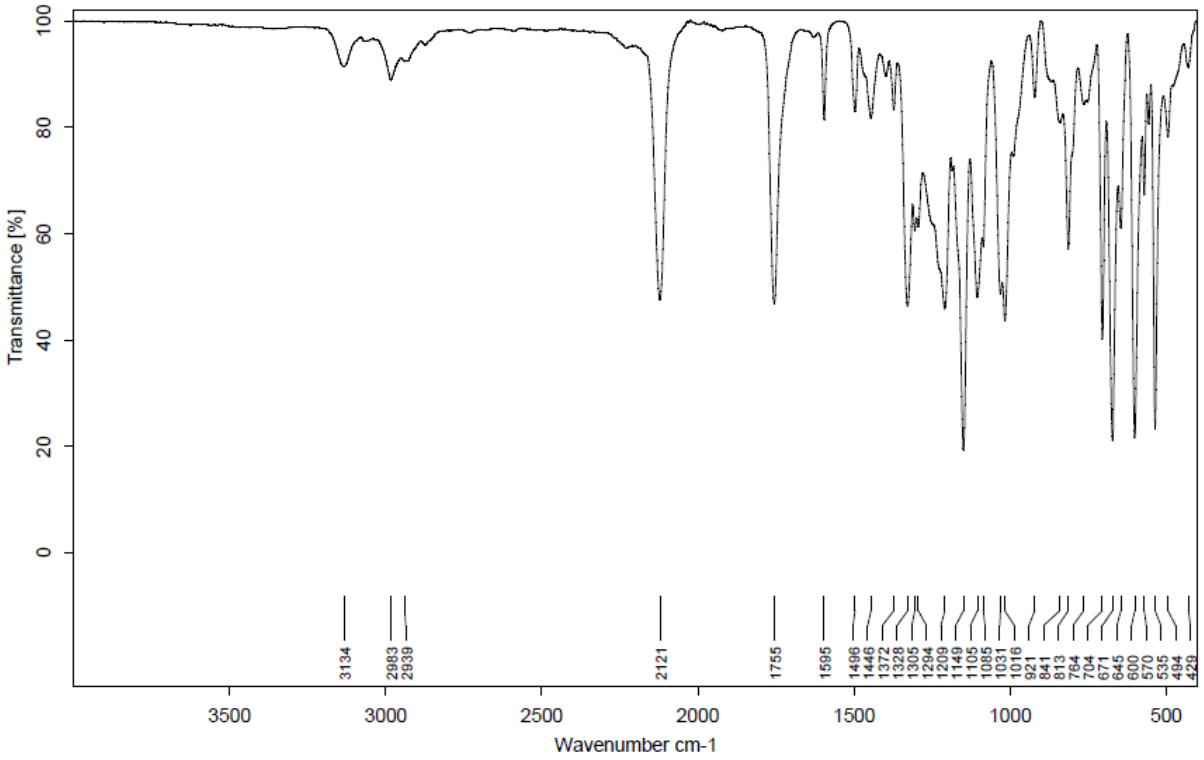
rac ethyl 2-azido-2-(4-tosyl-1*H*-1,2,3-triazol-1-yl)acetate (7)

^{1}H NMR(400MHz, CDCl)

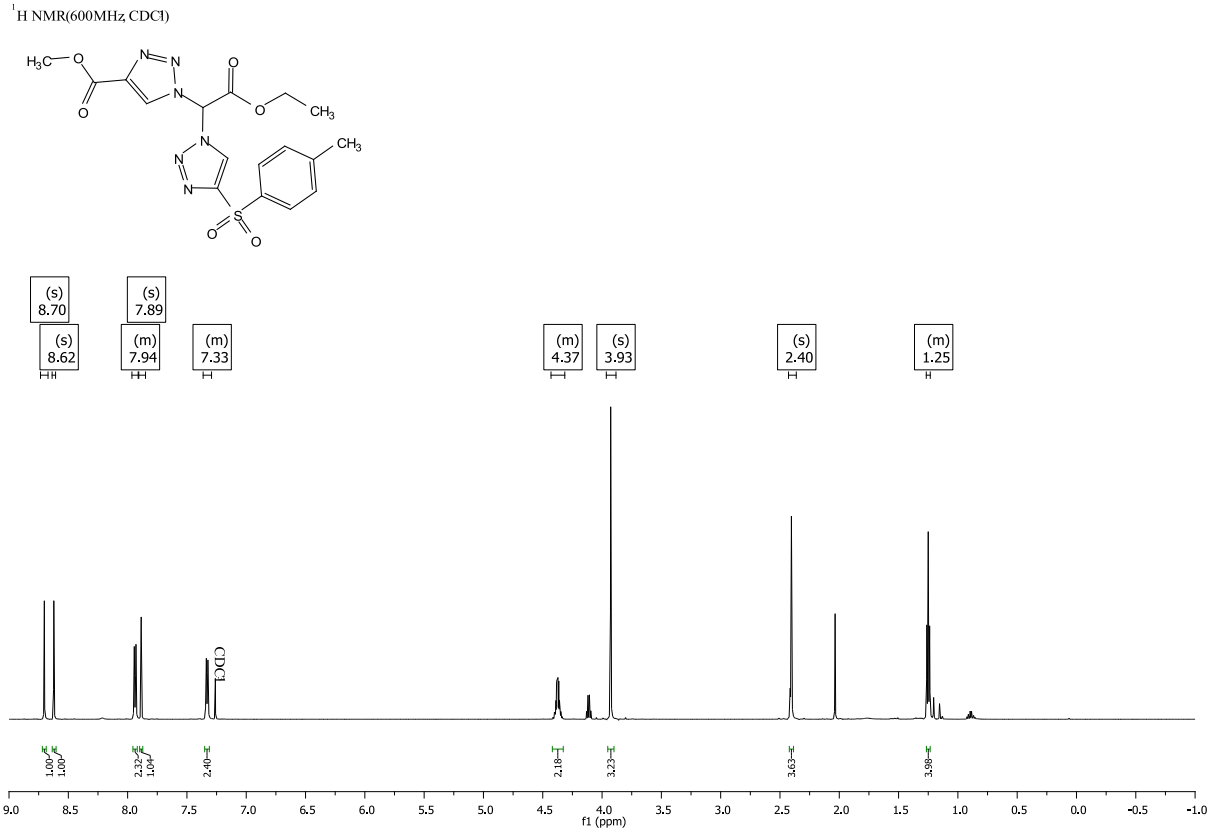


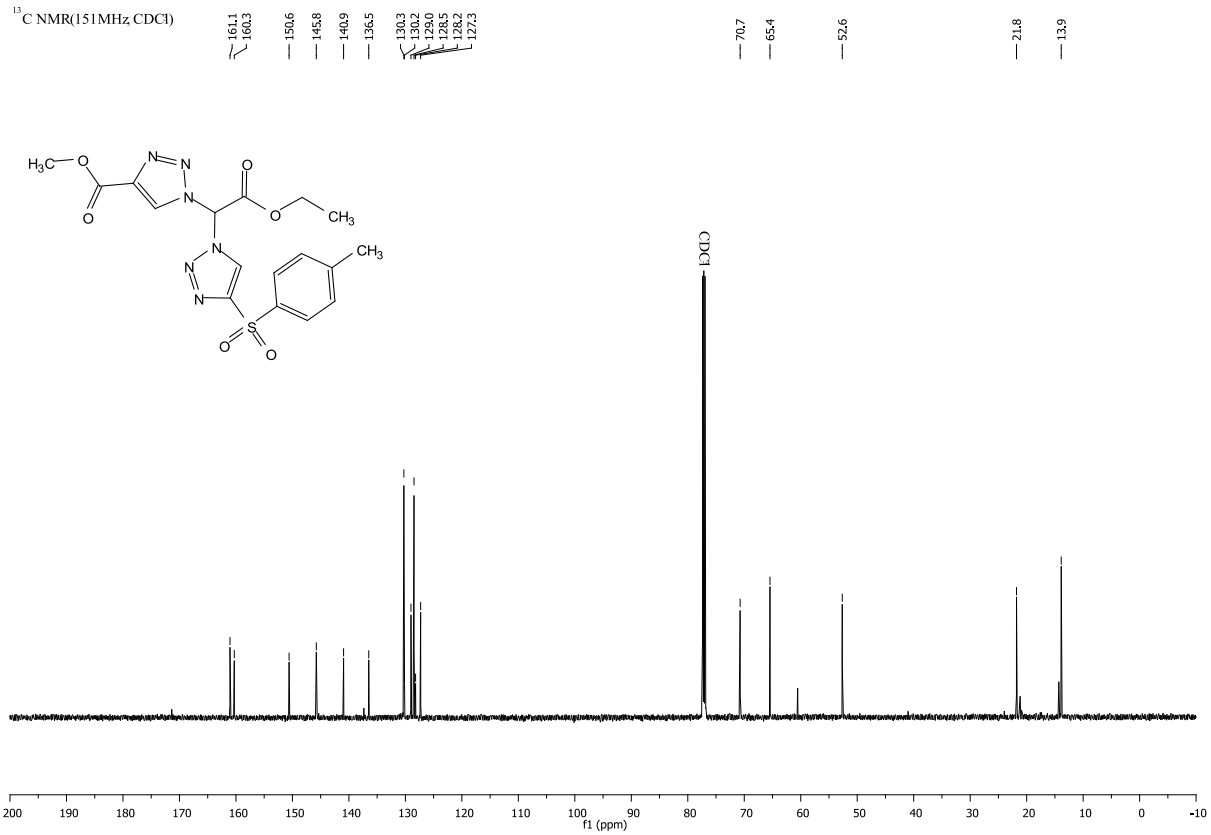
^{13}C NMR(101MHz, CDCl)



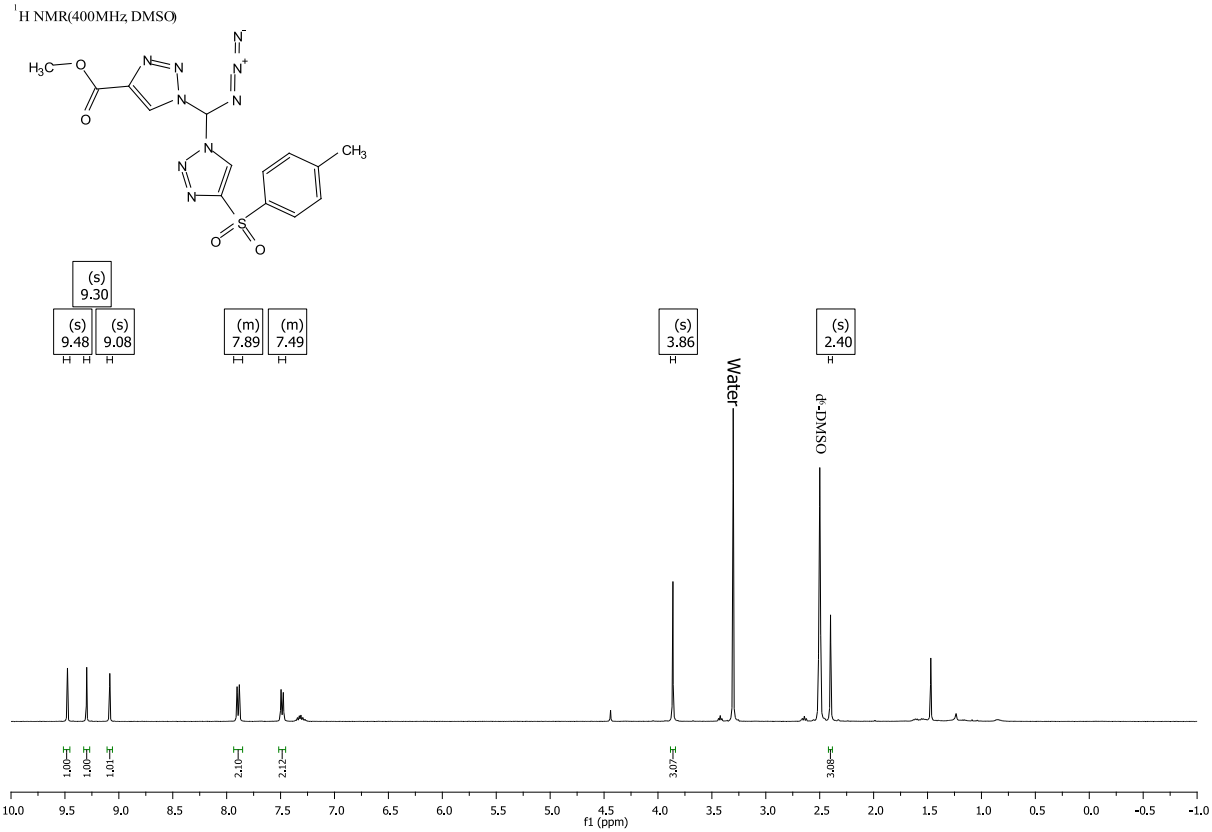


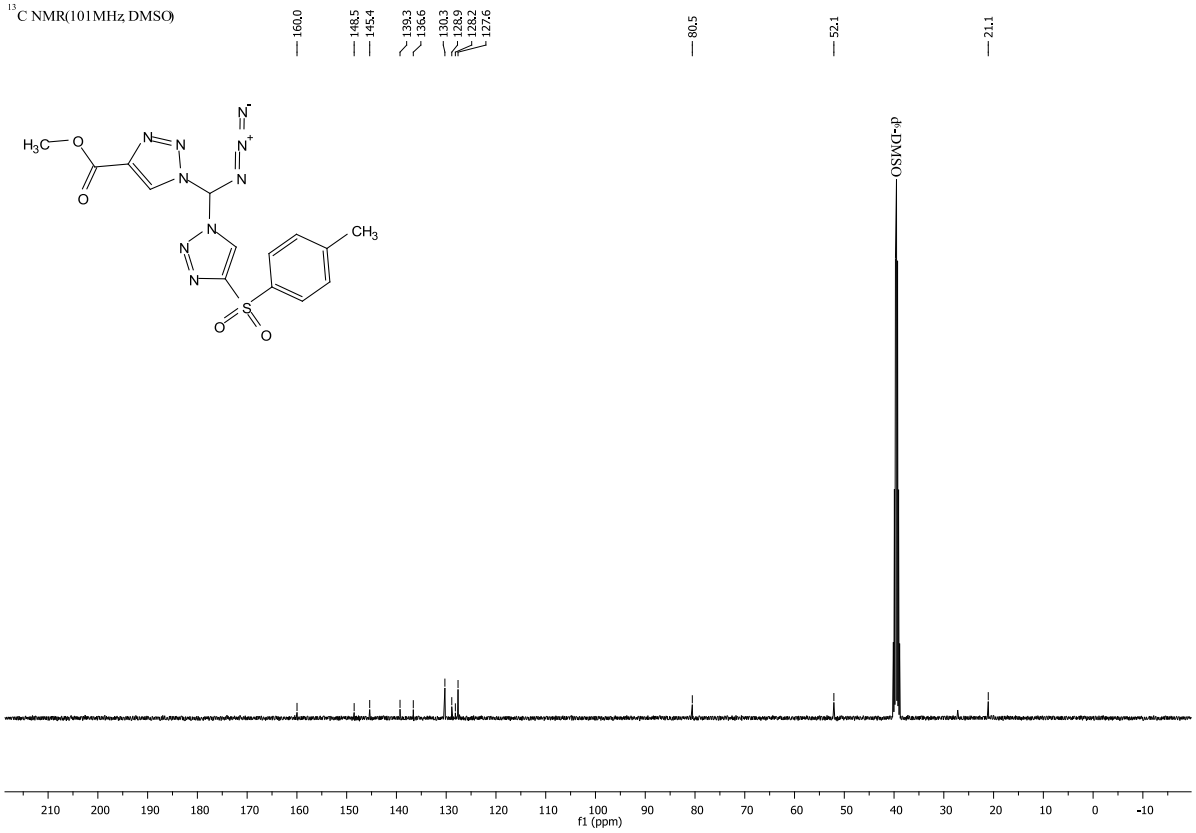
***rac* methyl 1-(2-ethoxy-2-oxo-1-(4-tosyl-1*H*-1,2,3-triazol-1-yl)ethyl)-1*H*-1,2,3-triazole-4-carboxylate (8)**

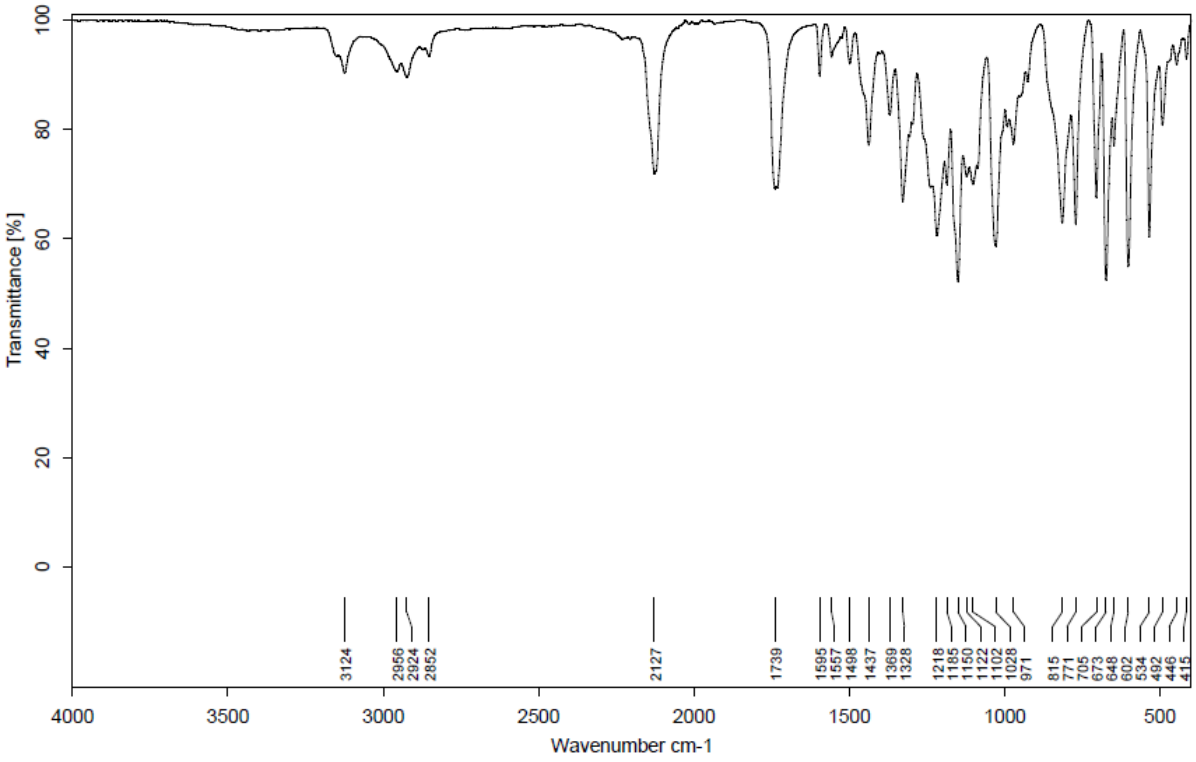




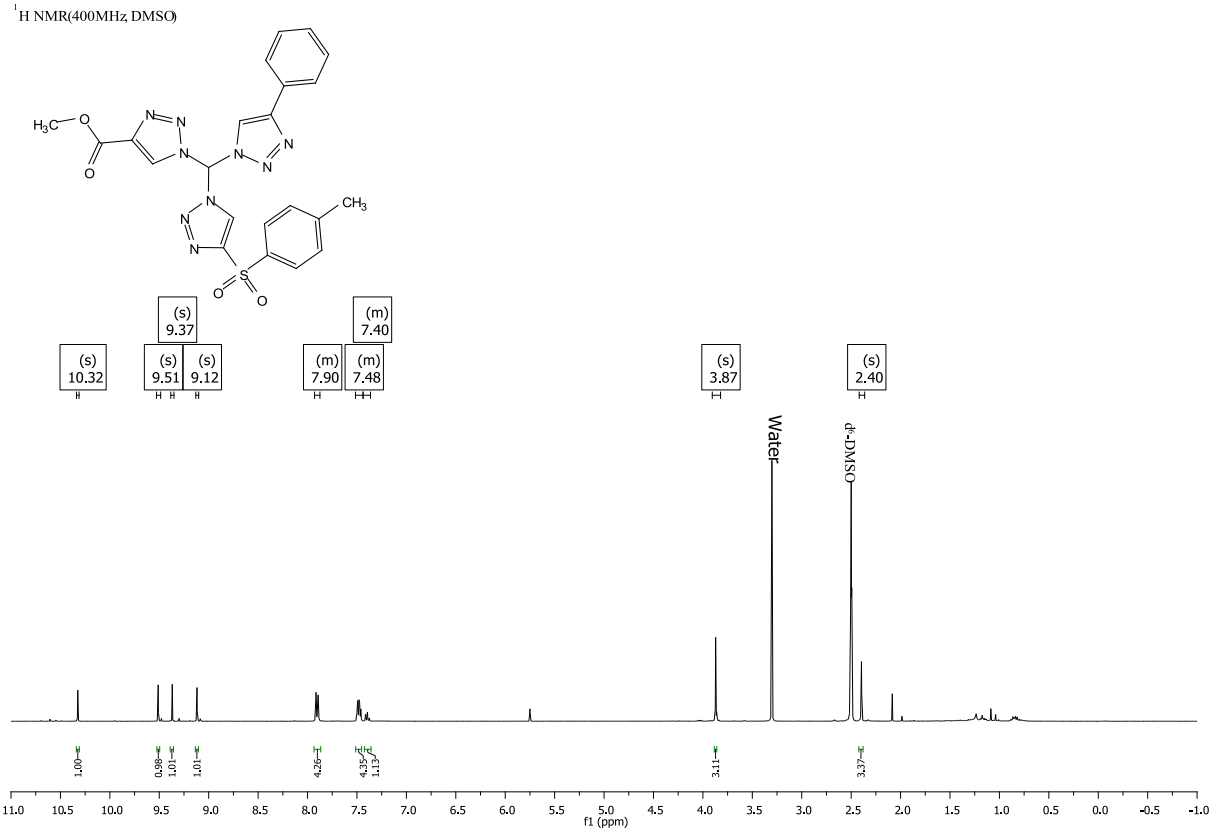
***rac* methyl 1-(azido(4-tosyl-1*H*-1,2,3-triazol-1-yl)methyl)-1*H*-1,2,3-triazole-4-carboxylate (9)**

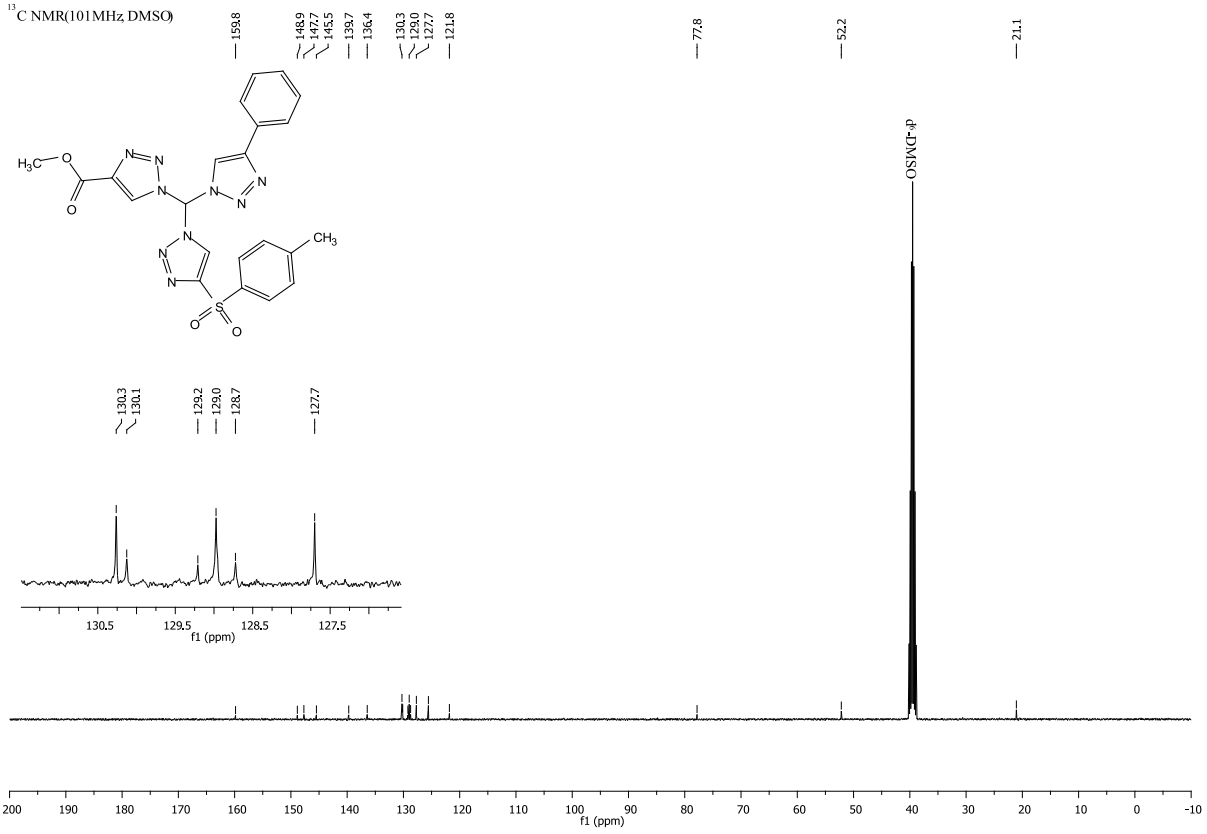



13C NMR(101MHz, DMSO)
160.0
148.5
145.4
139.3
136.6
130.3
128.9
128.2
127.6
80.5
52.1
21.1
d6-DMSO
f1 (ppm)


Transmittance [%]
Wavenumber cm-1
3124
2956
2924
2852
2127
1739
1595
1557
1498
1437
1369
1328
1218
1185
1150
1122
1102
1028
971
815
771
705
673
648
602
534
492
446
415

***rac* methyl 1-((4-phenyl-1*H*-1,2,3-triazol-1-yl)(4-tosyl-1*H*-1,2,3-triazol-1-yl)methyl)-1*H*-1,2,3-triazole-4-carboxylate (6)**





Crystallographic data

Crystallographic data for 2a

R_1 = **4.45%**

Table 1: Crystal data and structure refinement for **2a**.

Empirical formula	$C_{12}H_{14}N_6O_6$
Formula weight	338.29
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.22642(18)
b/Å	9.71725(18)
c/Å	18.0546(4)
α/°	90.00
β/°	101.6053(19)
γ/°	90.00
Volume/Å^3	1585.60(5)
Z	4
ρ_{calc}mg/mm^3	1.417
μ/mm^{-1}	0.116
F(000)	704.0
Crystal size/mm^3	0.12 × 0.09 × 0.08
2Θ range for data collection	4.6 to 65.86°
Index ranges	$-6 \leq h \leq 13$, $-10 \leq k \leq 14$, $-26 \leq l \leq 23$
Reflections collected	12718
Independent reflections	5307[R(int) = 0.0231]
Data/restraints/parameters	5307/0/224
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1101
Final R indexes [all data]	R_1 = 0.0579, wR_2 = 0.1201
Largest diff. peak/hole / e Å^{-3}	0.54/-0.37

Table 2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	4750.2(9)	3022.8(9)	1259.9(5)	24.35(18)
O1	4055.1(11)	5184.6(10)	881.5(5)	31.6(2)
C6	3222.5(12)	4178.6(11)	1919.3(6)	18.04(19)
C5	3309.3(11)	3258.5(11)	2500.8(6)	17.40(19)
N2	1666.7(11)	4911.9(10)	2585.8(6)	23.0(2)
N4	2516.3(10)	3972.1(10)	4240.1(5)	19.82(18)
N6	3625.0(11)	4206.0(12)	5394.2(6)	27.0(2)
C1	1906.5(12)	3182.9(11)	3571.0(6)	18.4(2)
N5	3224.1(11)	3288.9(11)	4869.0(6)	25.2(2)
O3	4242.3(11)	6738.7(11)	6210.2(5)	35.7(2)
N1	2338.2(10)	3748.4(9)	2903.2(5)	17.61(18)
O6	-292.2(10)	2456.5(10)	2800.5(5)	29.8(2)
C10	3186.7(12)	5475.4(13)	5108.8(6)	22.9(2)
O4	3168.5(11)	7859.9(10)	5152.2(5)	33.8(2)
C7	4038.4(12)	4212.2(12)	1295.4(6)	20.8(2)
O5	-487.6(10)	3522.7(11)	3890.0(5)	33.0(2)
C2	208.2(13)	3095.1(11)	3447.6(6)	21.1(2)
N3	2217.5(11)	5176.8(10)	1990.1(6)	23.3(2)
C9	2468.3(13)	5333.8(12)	4371.0(6)	22.9(2)
C8	5542.8(15)	2896.7(16)	644.5(8)	33.3(3)
C11	3590.6(13)	6730.7(14)	5561.2(7)	26.9(2)
C3	-1894.0(16)	2277.2(16)	2554.5(10)	39.7(3)
C12	3617(2)	9144.1(17)	5537.8(10)	51.0(4)
C4	-2216.6(19)	808.3(16)	2389.5(11)	47.0(4)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **2a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	28.0(4)	27.3(4)	20.9(4)	-0.5(3)	12.6(3)	1.0(3)
O1	50.6(6)	24.8(4)	23.8(4)	2.5(3)	17.8(4)	-5.6(4)
C6	23.2(5)	16.5(4)	15.3(4)	-1.3(3)	6.0(4)	-2.5(4)
C5	19.7(5)	16.7(5)	16.9(5)	-1.2(3)	6.3(4)	-0.6(4)
N2	30.6(5)	18.0(4)	22.8(5)	4.3(3)	11.0(4)	5.4(4)
N4	22.7(4)	22.3(4)	15.4(4)	1.6(3)	6.1(3)	3.7(3)
N6	24.6(5)	37.0(6)	19.2(4)	2.2(4)	3.9(4)	0.9(4)
C1	23.8(5)	17.1(5)	16.0(5)	1.2(4)	8.3(4)	1.7(4)
N5	26.0(5)	31.3(5)	18.8(4)	6.7(4)	5.8(4)	3.7(4)
O3	30.8(5)	51.2(6)	22.4(4)	-8.5(4)	-0.8(3)	-4.0(4)
N1	22.7(4)	15.9(4)	15.6(4)	1.2(3)	7.1(3)	1.5(3)
O6	27.3(4)	29.4(5)	32.6(5)	-9.8(4)	5.6(4)	-4.4(3)
C10	17.9(5)	32.5(6)	18.7(5)	-2.8(4)	4.5(4)	1.7(4)
O4	35.5(5)	33.0(5)	29.0(5)	-10.0(4)	-2.7(4)	3.0(4)
C7	26.2(5)	21.8(5)	15.3(5)	-2.4(4)	6.4(4)	-5.2(4)
O5	27.5(4)	45.4(6)	29.0(5)	-3.2(4)	12.8(4)	2.5(4)
C2	24.9(5)	17.6(5)	22.2(5)	3.1(4)	7.9(4)	-0.6(4)
N3	32.0(5)	18.6(4)	21.3(4)	4.1(3)	10.4(4)	2.8(4)
C9	25.6(5)	22.7(5)	20.1(5)	-2.7(4)	4.4(4)	4.4(4)
C8	35.2(7)	43.5(8)	26.8(6)	-4.9(5)	19.3(5)	-1.5(5)
C11	19.4(5)	38.3(7)	22.9(5)	-8.1(5)	4.3(4)	0.5(5)
C3	27.5(6)	35.3(7)	53.0(9)	-9.4(6)	-0.2(6)	-3.3(5)
C12	63.8(11)	36.6(8)	45.8(9)	-16.7(7)	-5.4(8)	0.1(7)
C4	39.7(8)	33.3(8)	64.8(11)	-13.2(7)	2.7(7)	-6.9(6)

Table 4: Bond Lengths for **2a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C7	1.3373(14)	N6	C10	1.3663(17)
O2	C8	1.4530(14)	C1	N1	1.4517(13)
O1	C7	1.2067(14)	C1	C2	1.5400(16)
C6	C5	1.3690(14)	O3	C11	1.2048(15)
C6	C7	1.4757(14)	O6	C2	1.3213(14)
C6	N3	1.3656(14)	O6	C3	1.4655(16)
C5	N1	1.3488(13)	C10	C9	1.3702(16)
N2	N1	1.3593(13)	C10	C11	1.4736(17)
N2	N3	1.3042(13)	O4	C11	1.3360(17)
N4	C1	1.4459(14)	O4	C12	1.4482(18)
N4	N5	1.3631(13)	O5	C2	1.1955(14)
N4	C9	1.3465(15)	C3	C4	1.476(2)
N6	N5	1.2997(15)			

Table 5: Bond Angles for **2a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O2	C8	115.92(10)	C2	O6	C3	118.39(10)
C5	C6	C7	129.77(10)	N6	C10	C9	108.94(11)
N3	C6	C5	109.16(9)	N6	C10	C11	121.04(10)
N3	C6	C7	121.07(10)	C9	C10	C11	129.86(12)
N1	C5	C6	103.88(9)	C11	O4	C12	114.76(11)
N3	N2	N1	106.96(9)	O2	C7	C6	110.38(9)
N5	N4	C1	118.58(9)	O1	C7	O2	125.42(10)
C9	N4	C1	130.30(10)	O1	C7	C6	124.20(11)
C9	N4	N5	111.08(9)	O6	C2	C1	108.56(9)
N5	N6	C10	108.95(10)	O5	C2	C1	123.48(11)
N4	C1	N1	111.56(9)	O5	C2	O6	127.94(11)
N4	C1	C2	111.34(9)	N2	N3	C6	108.76(9)
N1	C1	C2	110.00(9)	N4	C9	C10	104.05(10)
N6	N5	N4	106.98(10)	O3	C11	C10	124.44(13)
C5	N1	N2	111.24(9)	O3	C11	O4	124.42(12)
C5	N1	C1	129.55(9)	O4	C11	C10	111.13(10)
N2	N1	C1	119.15(9)	O6	C3	C4	109.04(12)

Table 6: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2a**.

Atom	***x***	***y***	***z***	**U(eq)**
H5	3913	2461	2598	21
H9	2036	6035	4030	27
H8A	4873	3109	164	50
H8B	5914	1954	629	50
H8C	6376	3542	725	50
H3A	-2258	2835	2096	48
H3B	-2404	2591	2957	48
H12A	3328	9913	5188	77
H12B	4693	9149	5715	77
H12C	3133	9239	5971	77
H4A	-1681	496	2003	70
H4B	-3282	687	2204	70
H4C	-1900	267	2852	70
H1	2286(15)	2271(15)	3636(8)	18(3)

Crystal structure determination of **2a**:

Crystal Data for $C_{12}H_{14}N_6O_6$ (M =338.29): monoclinic, space group $P2_1/n$ (no. 14), a = 9.22642(18) Å, b = 9.71725(18) Å, c = 18.0546(4) Å, β = 101.6053(19)°, V = 1585.60(5) Å^3, Z = 4, T = 150 K, μ(Mo Kα) = 0.116 mm^{-1}, *Dcalc* = 1.417 g/mm^3, 12718 reflections measured ($4.6 \leq 2\Theta \leq 65.86$), 5307 unique ($R_{int}$ = 0.0231) which were used in all calculations. The final R_1 was 0.0445 (>2sigma(I)) andwR_2 was 0.1201.

Crystallographic data for 4a

R_1 = **4.80%**

Table 1: Crystal data and structure refinement for **4a**.

Empirical formula	$C_{31}H_{25}N_9O_6$
Formula weight	619.60
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.6712(4)
b/Å	12.4890(8)
c/Å	17.0137(11)
α/°	90.00
β/°	106.677(4)
γ/°	90.00
Volume/Å^3	2986.3(3)
Z	4
ρ_{calc}mg/mm^3	1.378
μ/mm^{-1}	0.100
F(000)	1288.0
Crystal size/mm^3	0.15 × 0.11 × 0.07
2Θ range for data collection	4.1 to 59.06°
Index ranges	$-12 \leq h \leq 20$, $-15 \leq k \leq 16$, $-23 \leq l \leq 18$
Reflections collected	16696
Independent reflections	6959[R(int) = 0.0177]
Data/restraints/parameters	6959/0/415
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1126
Final R indexes [all data]	R_1 = 0.0778, wR_2 = 0.1298
Largest diff. peak/hole / e Å^{-3}	0.40/-0.29

Table 2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O4	2172.5(9)	1755.4(10)	185.7(7)	49.9(3)
N7	2150.1(9)	4270.4(11)	1764.3(8)	35.5(3)
N4	2246.1(9)	6082.6(10)	1361.3(8)	35.3(3)
N1	829.5(9)	5460.5(11)	1628.2(8)	35.5(3)
O2	-2245.6(8)	6081.5(11)	979.6(8)	50.9(3)
N8	2744.9(11)	3796.0(12)	2439.9(8)	47.6(4)
C13	2629.1(12)	6983.5(13)	440.6(11)	39.9(4)
O5	3182.4(10)	8228.9(11)	-378.2(9)	63.3(4)
C12	1972.8(12)	6281.2(13)	553.3(10)	38.6(4)
C22	2014.0(12)	3634.2(13)	1102(1)	37.8(4)
O6	2072.2(11)	6999.0(11)	-961.6(8)	58.4(4)
N3	-588.7(10)	5257.1(14)	858.4(9)	52.8(4)
N6	3280.4(11)	7177.3(13)	1177.9(10)	53.7(4)
C24	2637.9(12)	1735.7(14)	979.9(10)	40.0(4)
O3	3094.6(11)	988.7(10)	1334.7(8)	61.0(4)
N9	2961.6(11)	2866.5(12)	2207.8(9)	49.5(4)
N2	281.4(11)	4951.8(15)	953.3(10)	55.8(4)
C26	1415.2(14)	140.8(16)	-526.7(12)	51.4(5)
C3	-606.1(11)	5960.3(13)	1461.9(9)	36.3(4)
C23	2523.4(11)	2739.3(13)	1391.2(9)	35.9(4)
C1	1858.8(11)	5362.2(12)	1851.6(9)	34.9(4)
N5	3056.5(10)	6629.0(13)	1740.9(10)	50.4(4)
C14	2678.9(13)	7490.7(14)	-329.3(12)	46.8(4)
C6	-3844.2(12)	6353.8(15)	169.5(11)	45.4(4)
C11	-4397.3(14)	7206.3(18)	-208.5(14)	61.4(5)
C2	297.3(12)	6098.0(13)	1953.4(10)	39.5(4)
C25	2284.7(15)	823.8(17)	-302.9(12)	58.2(5)
C5	-3173.7(13)	6474.2(19)	1010.7(12)	56.3(5)
C7	-3929.8(14)	5396.5(18)	-241.6(14)	59.7(5)
O1	-1502.9(10)	7110.2(12)	2051.9(9)	63.3(4)
C4	-1490.8(12)	6452.3(14)	1542.3(10)	40.9(4)
C29	-155(3)	-1134(3)	-1061(3)	118.7(15)
C31	769.7(18)	283(2)	-1292.1(15)	80.4(7)
C16	1456.5(15)	6658.4(15)	-2397.3(11)	49.1(5)
C30	-9(2)	-352(4)	-1554(2)	117.1(13)
C15	1982.6(18)	7448.9(18)	-1768.9(12)	67.1(6)
C28	454(3)	-1290(2)	-279(3)	113.3(13)
C27	1260.3(19)	-626.1(18)	-13.7(18)	74.8(7)
C17	1939.2(16)	5842.3(17)	-2650.3(14)	60.8(5)
C21	494.3(18)	6735.3(18)	-2755.9(16)	73.0(7)
C20	25(2)	6027(2)	-3353.0(19)	92.9(9)
C18	1464(2)	5129.7(18)	-3247.7(16)	74.8(7)

C19	509(2)	5236(2)	-3595.8(16)	83.9(8)
C8	-4541.2(17)	5298(2)	-1025.9(16)	78.0(7)
C10	-5006.9(17)	7107(2)	-987.4(15)	77.4(7)
C9	-5073.2(16)	6166(3)	-1391.7(15)	81.1(8)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	59.5(8)	46.5(7)	38.8(7)	-5.9(5)	6.3(6)	6.4(6)
N7	36.0(7)	37.8(7)	29.2(7)	0.2(5)	3.8(5)	0.8(6)
N4	31.1(7)	36.2(7)	35.6(7)	-5.5(6)	4.7(5)	-4.3(5)
N1	32.1(7)	42.3(7)	29.6(7)	-6.1(6)	4.9(5)	-3.0(6)
O2	32.6(6)	67.1(8)	49.2(7)	-12.5(6)	5.6(5)	5.6(6)
N8	54.8(9)	50.2(9)	30.4(7)	3.0(6)	0.4(6)	8.0(7)
C13	38.4(9)	33.9(8)	47.8(10)	-1.9(7)	13.0(7)	-1.6(7)
O5	66.3(9)	53.1(8)	76.5(10)	4.3(7)	29.9(8)	-18.2(7)
C12	38.3(9)	38.4(9)	35.8(9)	-3.2(7)	5.1(7)	-4.6(7)
C22	40.4(9)	40.1(9)	29.1(8)	-2.4(7)	4.2(7)	1.1(7)
O6	76.8(10)	55.2(8)	46.0(7)	2.3(6)	22.2(7)	-20.7(7)
N3	32.6(8)	77.1(11)	46.2(9)	-23.0(8)	7.3(7)	-3.9(7)
N6	43.9(9)	54.4(9)	59.3(10)	-3.0(8)	9.3(8)	-16.3(7)
C24	40.0(9)	40.8(9)	38.6(9)	3.7(7)	10.1(7)	1.5(7)
O3	80(1)	47.8(8)	48.9(8)	4.4(6)	8.6(7)	20.2(7)
N9	60(1)	46.1(9)	36.3(8)	3.1(7)	4.1(7)	10.8(7)
N2	34.1(8)	81.9(12)	47.5(9)	-31.8(8)	5.7(7)	-4.1(8)
C26	54.4(12)	47.4(10)	53.5(11)	-14.6(9)	17.1(9)	7.4(9)
C3	37.2(9)	40.1(8)	30.8(8)	-1.7(7)	8.7(7)	-2.3(7)
C23	36.0(9)	38.6(8)	31.9(8)	3.5(7)	8.0(7)	-0.4(7)
C1	32.5(8)	39.6(9)	29.5(8)	-4.6(7)	4.1(6)	-1.3(7)
N5	38.5(8)	55.5(9)	49.9(9)	-6.3(7)	0.8(7)	-14.7(7)
C14	48.2(10)	38.5(9)	59.0(11)	-1.7(8)	23.8(9)	-0.8(8)
C6	30.3(9)	56.7(11)	50.7(10)	-3.2(9)	14.0(8)	4.2(8)
C11	49.7(12)	58.2(12)	72.7(14)	-3.2(11)	11.6(10)	7.5(10)
C2	39.3(9)	41.5(9)	35.6(8)	-8.4(7)	7.4(7)	0.4(7)
C25	65.5(13)	62.4(12)	48.6(11)	-16.2(10)	19.6(10)	2.1(10)
C5	36.1(10)	79.8(14)	53.8(12)	-7.8(10)	14.0(8)	9.9(9)
C7	46.2(11)	62.6(13)	69.1(14)	-8.6(10)	14.4(10)	10.2(9)
O1	50.6(8)	74.8(10)	60.5(9)	-25.8(8)	9.7(7)	9.0(7)
C4	38.6(9)	45.6(9)	37.1(9)	0.6(8)	8.6(7)	0.4(7)
C29	76(2)	106(3)	192(4)	-71(3)	69(3)	-31(2)
C31	70.0(16)	107(2)	58.6(14)	-19.0(13)	9.4(12)	-1.5(14)
C16	62.5(12)	46(1)	43.4(10)	10.2(8)	22.3(9)	1.8(9)
C30	71(2)	165(4)	111(3)	-64(3)	19.0(18)	-19(2)

C15	94.8(17)	59.2(13)	52.5(12)	9.4(10)	29.5(12)	-16.6(12)
C28	124(3)	55.7(16)	199(4)	-6(2)	108(3)	7.7(18)
C27	81.8(17)	50.6(13)	104.7(19)	3.3(13)	47.4(15)	15.2(12)
C17	60.5(13)	58.8(13)	70.8(14)	16.1(11)	31.0(11)	10.3(10)
C21	70.5(16)	56.1(13)	92.3(18)	-1.9(12)	23.3(13)	18.7(11)
C20	74.3(18)	67.9(16)	111(2)	0.2(15)	-13.6(15)	12.2(13)
C18	115(2)	47.1(12)	78.6(16)	5.1(12)	54.2(16)	14.5(13)
C19	119(2)	53.7(14)	64.8(15)	2.8(11)	3.9(15)	-0.5(14)
C8	55.1(14)	97.7(19)	79.0(16)	-38.8(15)	15.9(12)	-1.9(13)
C10	57.6(14)	94.1(19)	70.9(16)	12.9(14)	3.2(12)	23.0(13)
C9	47.3(13)	131(2)	56.6(14)	-13.4(15)	1.3(10)	10.0(14)

Table 4: Bond Lengths for **4a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C24	1.328(2)	N9	C23	1.362(2)
O4	C25	1.466(2)	C26	C25	1.490(3)
N7	N8	1.3632(18)	C26	C31	1.384(3)
N7	C22	1.346(2)	C26	C27	1.358(3)
N7	C1	1.449(2)	C3	C2	1.360(2)
N4	C12	1.340(2)	C3	C4	1.477(2)
N4	C1	1.449(2)	C6	C11	1.381(3)
N4	N5	1.3623(18)	C6	C5	1.494(3)
N1	N2	1.3560(18)	C6	C7	1.373(3)
N1	C1	1.453(2)	C11	C10	1.375(3)
N1	C2	1.341(2)	C7	C8	1.383(3)
O2	C5	1.462(2)	O1	C4	1.198(2)
O2	C4	1.323(2)	C29	C30	1.344(5)
N8	N9	1.295(2)	C29	C28	1.388(5)
C13	C12	1.356(2)	C31	C30	1.356(4)
C13	N6	1.363(2)	C16	C15	1.497(3)
C13	C14	1.476(3)	C16	C17	1.379(3)
O5	C14	1.199(2)	C16	C21	1.371(3)
C22	C23	1.356(2)	C28	C27	1.409(4)
O6	C14	1.333(2)	C17	C18	1.380(3)
O6	C15	1.455(2)	C21	C20	1.374(4)
N3	N2	1.297(2)	C20	C19	1.349(4)
N3	C3	1.357(2)	C18	C19	1.362(4)
N6	N5	1.294(2)	C8	C9	1.376(4)
C24	O3	1.205(2)	C10	C9	1.351(4)
C24	C23	1.468(2)			

Table 5: Bond Angles for **4a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C24	O4	C25	116.97(14)	N4	C1	N7	110.44(13)
N8	N7	C1	117.31(12)	N4	C1	N1	110.29(12)
C22	N7	N8	110.77(13)	N6	N5	N4	106.66(14)
C22	N7	C1	131.60(13)	O5	C14	C13	125.46(18)
C12	N4	C1	130.85(13)	O5	C14	O6	125.46(18)
C12	N4	N5	110.91(14)	O6	C14	C13	109.08(15)
N5	N4	C1	118.11(13)	C11	C6	C5	120.41(18)
N2	N1	C1	120.08(13)	C7	C6	C11	118.61(18)
C2	N1	N2	110.71(13)	C7	C6	C5	120.98(18)
C2	N1	C1	128.82(13)	C10	C11	C6	120.8(2)
C4	O2	C5	116.82(14)	N1	C2	C3	104.56(14)
N9	N8	N7	106.63(13)	O4	C25	C26	111.83(16)
C12	C13	N6	108.87(15)	O2	C5	C6	107.20(15)
C12	C13	C14	128.40(16)	C6	C7	C8	120.5(2)
N6	C13	C14	122.73(15)	O2	C4	C3	111.26(14)
N4	C12	C13	104.43(14)	O1	C4	O2	125.50(16)
N7	C22	C23	104.41(14)	O1	C4	C3	123.23(16)
C14	O6	C15	116.27(15)	C30	C29	C28	121.8(3)
N2	N3	C3	109.12(14)	C30	C31	C26	121.2(3)
N5	N6	C13	109.11(14)	C17	C16	C15	120.3(2)
O4	C24	C23	111.93(14)	C21	C16	C15	121.7(2)
O3	C24	O4	125.01(16)	C21	C16	C17	117.9(2)
O3	C24	C23	123.05(16)	C29	C30	C31	119.3(4)
N8	N9	C23	109.29(13)	O6	C15	C16	107.94(16)
N3	N2	N1	106.91(14)	C29	C28	C27	118.3(3)
C31	C26	C25	118.1(2)	C26	C27	C28	119.3(3)
C27	C26	C25	121.9(2)	C16	C17	C18	120.7(2)
C27	C26	C31	120.0(2)	C16	C21	C20	121.2(2)
N3	C3	C2	108.69(15)	C19	C20	C21	120.1(3)
N3	C3	C4	123.17(14)	C19	C18	C17	119.8(2)
C2	C3	C4	128.13(15)	C20	C19	C18	120.3(2)
C22	C23	C24	131.08(15)	C9	C8	C7	119.5(2)
C22	C23	N9	108.87(14)	C9	C10	C11	120.1(2)
N9	C23	C24	120.03(14)	C10	C9	C8	120.4(2)
N7	C1	N1	111.57(12)				

Table 6: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4a**.

Atom	***x***	***y***	***z***	**U(eq)**
H12	1451	6001	159	46
H22	1652	3776	567	45
H1	2115	5569	2429	42
H11	-4357	7856	67	74
H2	500	6536	2412	47
H25A	2822	401	7	70
H25B	2419	1067	-800	70
H5A	-3129	7220	1177	68
H5B	-3396	6062	1403	68
H7	-3574	4809	9	72
H29	-678	-1583	-1250	142
H31	872	824	-1633	97
H30	-437	-247	-2070	141
H15A	2608	7585	-1835	81
H15B	1637	8121	-1834	81
H28	333	-1821	62	136
H27	1682	-712	507	90
H17	2592	5771	-2416	73
H21	153	7277	-2592	88
H20	-628	6093	-3590	111
H18	1795	4579	-3412	90
H19	189	4760	-4002	101
H8	-4592	4650	-1304	94
H10	-5374	7688	-1236	93
H9	-5481	6104	-1921	97

Crystal structure determination of **4a**:

Crystal Data for $C_{31}H_{25}N_9O_6$ (*M* =619.60): monoclinic, space group $P2_1/n$ (no. 14), *a* = 14.6712(4) Å, *b* = 12.4890(8) Å, *c* = 17.0137(11) Å, *β* = 106.677(4)°, *V* = 2986.3(3) Å^3, *Z* = 4, *T* = 293 K, μ(Mo Kα) = 0.100 mm^{-1}, *Dcalc* = 1.378 g/mm^3, 16696 reflections measured ($4.1 \leq 2\Theta \leq 59.06$), 6959 unique ($R_{int}$ = 0.0177) which were used in all calculations. The final R_1 was 0.0480 (>2sigma(I)) and wR_2 was 0.1298.

Experimental:

The crystal was kept at 150 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimization.

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42, 339.

[2] SHELXS, G.M. Sheldrick, *Acta Cryst.* **2008**, A64, 112.

[3] SHELXL, G.M. Sheldrick, *Acta Cryst.* **2008**, A64, 112.