

Supporting Information

A Photoinduced, Benzyne Click Reaction

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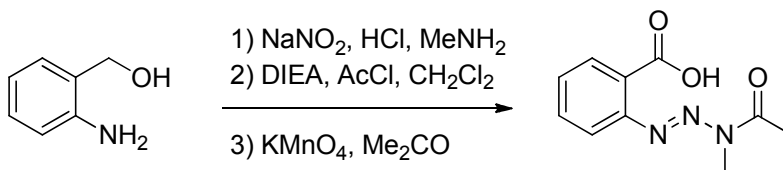
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1. GENERAL

Reagents and solvents for organic synthesis were used as received. Thin-layer chromatography (TLC) was conducted on glassbacked silica plates visualized with either UV illumination, basic permanganate stain, or bromocresol green stain. Flash chromatography was conducted on 60 Å silica gel. NMR spectra were recorded on a Bruker Advance 400, chemical shift values are reported in ppm on the δ scale relative to TMS ($\delta = 0.00$) as an internal standard. Irradiation for photolysis was performed using an LED Engin LZ1-10U600 365 nm LED powered by a DC 12 V, 2 A source through a 700 mA FlexBlock Constant Current Driver.

2. SYNTHETIC PROCEDURES

2-(3-Acetyl-3-methyltriaz-1-en-1-yl)benzoic acid (1)



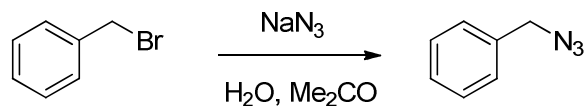
To a stirred suspension of 2-Aminobenzyl alcohol (1.85g, 15.0 mmol, 1.00 eq) in H₂O (12 mL) at 0 °C, was added conc. HCl (7.5 mL, 90 mmol, 6.00 eq). NaNO₂ (1.08g, 15.6 mmol, 1.03 eq) in H₂O (3 mL) was then added dropwise and the solution was allowed to stir for an additional 10 m. The resulting diazonium solution was then added dropwise to a stirred solution of 33% MeNH₂ in EtOH (36 mL, 288 mmol, 19.2 eq) at -25 °C. Immediately after addition, the reaction mixture was extracted with CHCl₃ (2 × 60 mL). The combined organic layers were washed with NaHCO₃ (4 × 60 mL), brine, dried over Na₂SO₄, and concentrated under reduced pressure to afford a red-orange oil that was used without further purification.

To a stirred solution of the red-orange oil in CH₂Cl₂ (100 mL) at 0 °C, was added DIEA (10.5 mL, 60.0 mmol, 4.0 eq) followed by careful addition of AcCl (1.07 mL, 15.0 mmol, 1.0 eq). After stirring for 2 h, the reaction mixture was carefully washed with dilute HCl several times until the aqueous layer achieved a pH of 5. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure to afford a yellow-orange solid that was used without further purification.

To a stirred solution of the yellow-orange solid in acetone (250 mL) was added KMnO₄ (3.34g, 21.1 mmol, 1.41 eq) and the reaction was allowed to stir for an additional 15 h. A saturated solution of Na₂SO₃ was then added until the purple color no longer persisted. The reaction was then diluted with EtOAc (200 mL), and carefully acidified with dilute HCl until the aqueous portion achieved a pH of 5. The organic layer was separated, washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure to afford a brown solid, which was triturated in Et₂O and filtered to give 2-(3-Acetyl-3-methyltriaz-1-en-1-yl)benzoic acid (1.3 g, 5.9 mmol, 39%) as of a pale brown solid. ¹H NMR (400 MHz, CDCl₃) δ : 12.50 (br. s., 1 H), 8.41 (dd, $J = 1.5, 7.8$ Hz, 1 H), 7.85 - 7.78 (m, 1 H), 7.72 - 7.64 (m, 1 H), 7.62 - 7.55 (m, 1 H), 3.56 (s, 3 H), 2.68 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ : 172.41, 165.91,

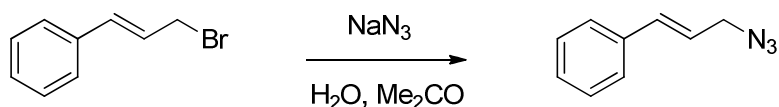
164.34, 133.87, 133.20, 130.04, 125.12, 116.60, 28.51, 22.00. ESI-MS Calculated for C₁₀H₁₁N₃O₃ [M+H]⁺ = 222.09, found = 222.11

(Azidomethyl)benzene (15)



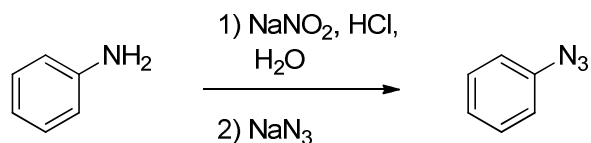
To a stirred solution of Benzyl bromide (0.12 mL, 1.00 mmol, 1.0 eq) in 50 mL of 1:4 H₂O/Me₂CO (v/v) was added NaN₃ (96 mg, 1.50 mmol, 1.5 eq). After 24 h, the reaction was extracted with Et₂O (3 × 20 mL), washed with brine, dried over K₂CO₃, and concentrated under reduced pressure to give (Azidomethyl)benzene in quantitative yield as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ: 7.40 (m, 5 H), 4.37 (s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ: 135.54, 128.91, 128.37, 128.29, 54.85.

(E)-(3-Azidoprop-1-en-1-yl)benzene (16)



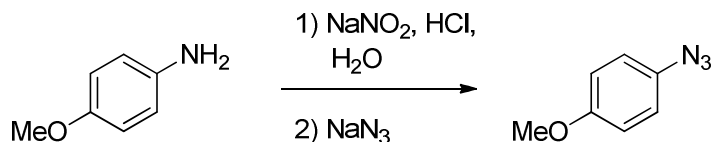
To a stirred solution of NaN₃ (3.25 g, 50.0 mmol, 5.0 eq) in 100 mL of 4:1 Me₂CO/H₂O was added Cinnamyl bromide (1.97 g, 10.0 mmol, 1.0 eq). After stirring for 18 h, the reaction was diluted with EtOAc (50 mL), washed with brine (3 × 100 mL), dried over Na₂SO₄, and concentrated under reduced pressure to give (E)-(3-Azidoprop-1-en-1-yl)benzene (1.51g, 9.49 mmol, 95%) as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ: 7.45 (m, 2 H), 7.38 (m, 2 H), 7.31 (m, 1 H), 6.69 (d, *J* = 15.7 Hz, 1 H), 6.28 (dt, *J* = 15.7, 6.7 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ: 136.13, 134.56, 128.78, 128.29, 126.77, 122.53, 53.07.

Azidobenzene (17)



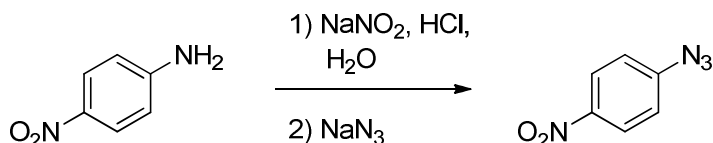
To a stirred solution of Aniline (293 μL, 3.22 mmol, 1.0 eq) in H₂O (2 mL) and conc. HCl (1 mL) at 0 °C was added NaNO₂ (289 mg, 4.19 mmol, 1.3 eq) in H₂O (1 mL). After stirring for 15 m, a solution of NaN₃ (251 mg, 3.87 mmol, 1.2 eq) in H₂O (1 mL) was carefully added (CAUTION: vigorous release of N₂). The reaction was left to stir for 1 h, followed by extraction with Et₂O (3 × 20 mL). The combined organic layers were dried over K₂CO₃, and carefully concentrated under reduced pressure to give Azidobenzene (189 mg, 1.6 mmol, 50%) as an orange oil. ¹H NMR (400 MHz, CDCl₃) δ: 7.38 (m, 2 H), 7.17 (m, 1 H), 7.06 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ: 140.09, 129.79, 124.90, 119.09.

1-Azido-4-methoxybenzene (18)



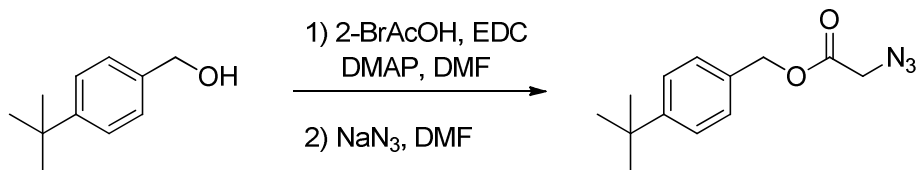
To a stirred solution of p-Anisidine (396 mg, 3.21 mmol, 1.0 eq) in H_2O (2 mL) and conc. HCl (1 mL) at 0 °C was added NaNO_2 (289 mg, 4.19 mmol, 1.3 eq) in H_2O (1 mL). After stirring for 15 m, a solution of NaN_3 (251 mg, 3.87 mmol, 1.2 eq) in H_2O (1 mL) was carefully added (CAUTION: vigorous release of N_2). The reaction was left to stir for 1 h, followed by extraction with Et_2O (3×20 mL). The combined organic layers were dried over K_2CO_3 , and carefully concentrated under reduced pressure to give 1-Azido-4-methoxybenzene (320 mg, 2.15 mmol, 67%) as a dark brown solid. ^1H NMR (400 MHz, CDCl_3) δ : 6.98 (m, 2 H), 6.92 (m, 2 H), 3.82 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 157.05, 132.38, 120.00, 115.16, 55.55.

1-Azido-4-nitrobenzene (19)



To a stirred suspension of p-Nitroaniline (444 mg, 3.21 mmol, 1.0 eq) in H_2O (2 mL), MeOH (1 mL) and conc. HCl (1 mL) at 0 °C was added NaNO_2 (289 mg, 4.19 mmol, 1.3 eq) in H_2O (1 mL). After stirring for 15 m, a solution of NaN_3 (251 mg, 3.87 mmol, 1.2 eq) in H_2O (1 mL) was carefully added (CAUTION: vigorous release of N_2). The reaction was left to stir for 1 h, followed by extraction with Et_2O (3×50 mL). The combined organic layers were dried over K_2CO_3 , and carefully concentrated under reduced pressure to give a solid yellow residue. The residue was purified over silica using flash column chromatography, eluting with 1:1 EtOAc/Hexanes to give 1-Azido-4-nitrobenzene (401 mg, 2.44 mmol, 76%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.27 (m, 2 H), 7.16 (m, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 146.88, 144.65, 125.58, 119.40.

4-(*tert*-Butyl)benzyl 2-azidoacetate (20)

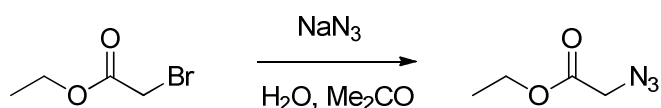


To a stirred solution of 2-Bromoacetic acid (927 mg, 6.67 mmol, 1.33 eq) in DMF (50 mL) was added *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (1.28 g, 6.67 mmol, 1.33 eq) and *N,N*-Dimethylamino pyridine (61 mg, 0.50 mmol, 0.10 eq). After stirring for 30 min, 4-*tert*-Butylbenzyl alcohol (885 μL , 5.00 mmol, 1.0 eq) was added, and the reaction was allowed to stir an

additional 18 h. The reaction mixture was diluted with EtOAc (200 mL) and was washed with 0.1 M HCl (2 × 50 mL), NaHCO₃ (2 × 50 mL), and brine (2 × 50 mL), dried over Na₂SO₄, and concentrated under reduced pressure to give a orange residue.

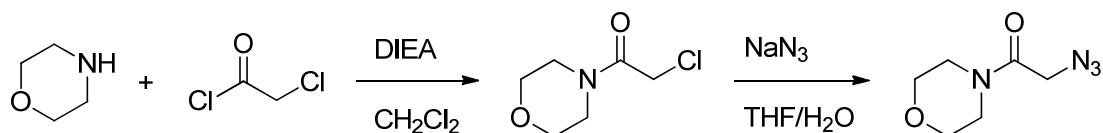
The residue was taken up in DMF (10 mL), NaN₃ (1.30 g, 20.0 mmol, 4.0 eq) was added, and the reaction stirred for 18 h at 80 °C. After cooling to room temperature, the reaction was diluted with EtOAc (50 mL) and was washed with H₂O (5 × 50 mL), dried over Na₂SO₄, and concentrated under reduced pressure to give a dark orange residue that was purified over silica using flash column chromatography, eluting with 70:30 (Hexanes:EtOAc) to give 4-(*tert*-Butyl)benzyl 2-azidoacetate (1.10 g, 4.45 mmol, 89%) as an orange oil. ¹H NMR (400 MHz, CDCl₃) δ: 7.44 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 5.22 (s, 2 H), 4.12 (s, 2 H), 1.35 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃) δ: 168.27, 151.83, 132.11, 128.56, 125.68, 67.38, 50.33, 34.68, 31.34.

Ethyl 2-azidoacetate (21)



To a stirred solution of NaN₃ (3.25 g, 50.0 mmol, 5.0 eq) in 100 mL of 4:1 Me₂CO/H₂O was added Ethyl 2-bromoacetate (1.1 mL, 10.0 mmol, 1.0 eq). After stirring for 18 h, the reaction was diluted with EtOAc (50 mL), washed with brine (3 × 100 mL), dried over Na₂SO₄, and concentrated under reduced pressure to give Ethyl 2-azidoacetate (828 mg, 6.4 mmol, 64%) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ: 4.28 (q, *J* = 7.2 Hz, 2 H), 3.88 (s, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ: 168.23, 61.58, 50.04, 13.81.

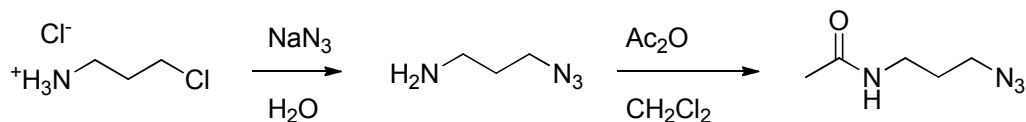
2-Azido-1-morpholinoethanone (22)



To a stirred solution of morpholine (0.88 mL, 10.0 mmol, 1.0 eq) and *N,N*-Diisopropylethylamine (2.1 mL, 12.5 mmol, 1.25 eq) in CH₂Cl₂ (50 mL) at 0 °C, was added chloroacetyl chloride (0.72 mL, 9.0 mmol, 0.9 eq) dropwise. The reaction was allowed to stir at 0 °C for 45 m, and for another 45 m at 25 °C. The reaction mixture was then diluted with EtOAc (250 mL), washed with 0.5 M HCl (4 × 25 mL), NaHCO₃ (4 × 25 mL), and brine. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to yeild 2-chloro-1-morpholinoethanone (979 mg, 5.99 mmol, 60%) as a brown oil that was used without further purification. To a stirring solution of NaN₃ (562 mg, 8.65 mmol, 1.5 eq) in H₂O (1.1 mL) was added a solution of 2-chloro-1-morpholinoethanone (943 mg, 5.76 mmol, 1.0 eq) in THF (223 μL) and was refluxed for 2 h. After cooling to room temperature, the reaction mixture was extracted with EtOAc (3 × 25 mL), washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure to give 2-azido-1-morpholinoethanone (559 mg, 3.28

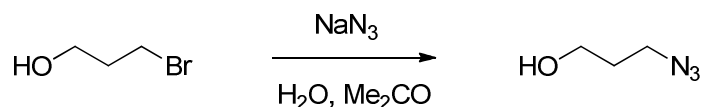
mmol, 57%) as a light brown solid. ^1H NMR (400 MHz, CDCl_3) δ : 3.94 (s, 2 H), 3.74 -3.68 (m, 4 H), 3.68 - 3.63 (m, 2 H), 3.40 (t, $J = 4.8$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 165.78, 66.63, 50.39, 45.37, 42.21.

N-(3-Azidopropyl)acetamide (23)



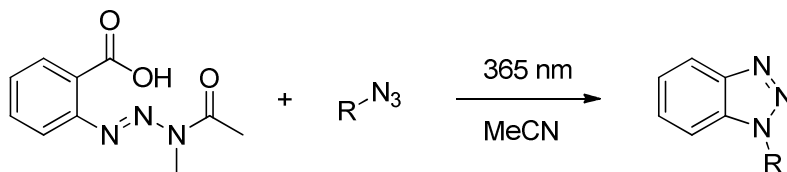
To a stirred solution of 3-chloropropylamine hydrochloride (2.00 g, 15.4 mmol, 1.0 eq), in H_2O (20 mL) was added sodium azide (3.00 g, 46.1 mmol, 3.0 eq), and the mixture heated to 80°C . After 18 h, the reaction was cooled and KOH pellets were added to basify the solution, followed by extraction with Et_2O (5×20 mL). The combined organic layers were dried over K_2CO_3 and carefully concentrated to give 3-azidopropyl amine (1.12 g, 11.2 mmol, 73%) as a colourless oil that was used without further purification. To a stirred solution of 3-azidopropyl amine (1.52 g, 15.2 mmol, 1.0 eq) in CH_2Cl_2 (15 mL) at 25°C was added a solution of acetic anhydride (1.43 mL, 15.2 mmol, 1.0 eq) in CH_2Cl_2 (2.5 mL) dropwise over 5 minutes. After an additional 15 h of stirring, the reaction was washed with NaHCO_3 (2×40 ml), brine, dried over Na_2SO_4 , and concentrated under reduced pressure to afford a yellow oil. Purification over silica using flash column chromatography, eluting with 95:5 (CH_2Cl_2 :MeOH) to give *N*-(3-azidopropyl)acetamide (1.17 g, 8.23 mmol, 54%) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ : 6.08 (br. s, 1 H), 3.34 (m, 4 H), 1.98 (s, 3 H), 1.79 (quin, $J = 6.6$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 170.80, 48.92, 36.66, 28.55, 22.70.

3-Azidopropan-1-ol (24)



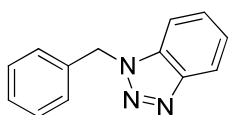
To a stirred solution of 3-bromopropanol (0.44 mL, 5.00 mmol, 1.0 eq) in acetone (16 mL) was added a solution of NaN_3 (1.63g, 25.00 mmol, 5.0 eq) in H_2O (4 mL), followed by a small amount of KI. After 48 h, the reaction was extracted with Et_2O (3×50 mL), the combined organic layers were dried over K_2CO_3 , and concentrated under reduced pressure to give 3-azidopropan-1-ol (481 mg, 4.76 mmol, 95%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ : 3.77 (m, 2 H), 3.47 (t, $J = 6.7$ Hz, 2 H), 1.85 (dt, $J = 12.4, 6.4$ Hz, 2 H), 1.73 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 59.60, 48.38, 31.40.

Synthesis of Benzotriazoles using Photolysis of Compound 1.



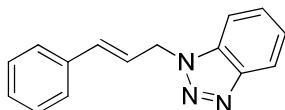
In a 20 mL scintillation vial was added MeCN (2 mL) followed by solutions of a corresponding azido compound (1.5 mL, 50 mM, 1.0 eq) and triazenylbenzoic acid (**1**) (1.5 mL, 50 mM, 1.0 eq) in MeCN. The vial was placed about 1 cm below the light source and irradiated for 15 m until complete consumption of **1** was observed. Reaction was repeated 10 times, samples were combined, and solvent was removed under reduced pressure. The reaction mixture was dissolved in CH₂Cl₂ (30 mL), washed with NaHCO₃, brine, dried over Na₂SO₄, concentrated under reduced pressure, and purified over silica using flash column chromatography to give the corresponding benzotriazole. Spectral data matched those obtained from the Larock method. ESI-MS values of benzotriazole authentic standards obtained from Larock method are reported for comparison.

1-Benzyl-1*H*-benzo[*d*][1,2,3]triazole (**5**)



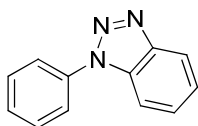
Pale brown solid (107 mg, 0.51 mmol, 68%). ¹H NMR (400 MHz, CDCl₃) δ: 8.08 (td, *J* = 8.1, 1.0 Hz, 1 H), 7.44 - 7.28 (m, 8 H), 5.86 (s, 2 H) ¹³C NMR (100 MHz, CDCl₃) δ: 146.27, 134.74, 132.84, 129.01, 128.48, 127.59, 127.44, 123.97, 120.05, 109.74, 52.30. ESI-MS Calculated for C₁₃H₁₁N₃ [M+H]⁺ = 210.10, found = 210.04, Authentic standard = 210.04.

1-Cinnamyl-1*H*-benzo[*d*][1,2,3]triazole (**6**)



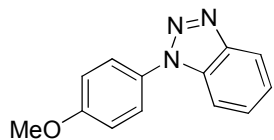
Pale yellow solid (102 mg, 0.43 mmol, 58%). ¹H NMR (400 MHz, CDCl₃) δ: 8.11 (d, *J* = 8.3 Hz, 1 H), 7.59 (d, *J* = 8.3 Hz, 1 H), 7.49 (td, *J* = 7.6, 1.0 Hz, 1 H), 7.44 - 7.26 (m, 6H), 6.71 (d, *J* = 15.9 Hz, 1 H), 6.43 (dt, *J* = 15.9, 6.3 Hz, 1 H), 5.48 (dd, *J* = 6.3, 1.5 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ: 146.30, 135.61, 134.43, 132.94, 128.72, 128.40, 127.41, 126.67, 124.00, 122.23, 120.05, 109.83, 50.57. ESI-MS Calculated for C₁₅H₁₃N₃ [M+H]⁺ = 236.12, found = 236.08, Authentic standard = 236.08.

1-Phenyl-1*H*-benzo[*d*][1,2,3]triazole (**7**)



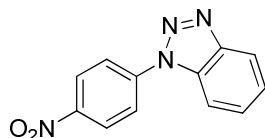
Pale yellow solid (48 mg, 0.25 mmol, 33%). ¹H NMR (400MHz, CDCl₃) δ: 8.16 (dd, *J* = 8.3, 1.0 Hz, 1 H), 7.82 - 7.73 (m, 3 H), 7.66 - 7.59 (m, 2 H), 7.58 - 7.48 (m, 2 H), 7.47 - 7.42 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ = 146.51, 137.01, 132.32, 129.88, 128.69, 128.26, 124.42, 122.88, 120.30, 110.39. ESI-MS Calculated for C₁₂H₉N₃ [M+H]⁺ = 196.09, found = 195.92, Authentic standard = 195.92.

1-(4-Methoxyphenyl)-1H-benzo[d][1,2,3]triazole (8)



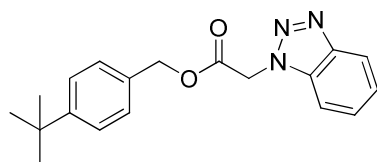
Yellow Solid (67 mg, 0.30 mmol, 40%). ^1H NMR (400MHz, CDCl_3) δ : 8.13 (d, $J = 8.3$ Hz, 1 H), 7.69 - 7.62 (m, 3 H), 7.52 (td, $J = 7.7, 0.8$ Hz, 1 H), 7.45 - 7.38 (m, 1 H), 7.13 - 7.07 (m, 2 H), 3.89 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 159.86, 146.20, 132.64, 129.95, 128.05, 124.57, 124.28, 120.10, 114.98, 110.28, 55.66. ESI-MS Calculated for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 226.10$, found = 226.15, Authentic standard = 226.02.

1-(4-Nitrophenyl)-1H-benzo[d][1,2,3]triazole (9)



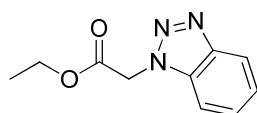
Obtained via Larock procedure; no product could be isolated from photolysis. Yellow Solid (27 mg, 0.11 mmol, 37%). ^1H NMR (400 MHz, d_6 -DMSO) δ : 8.53 (m, 2 H), 8.27 (m, 3 H), 8.12 (dt, $J = 8.4, 0.9$ Hz, 1 H), 7.77 (ddd, $J = 8.3, 7.1, 1.0$ Hz, 1 H), 7.60 (ddd, $J = 8.2, 7.1, 0.9$ Hz, 1 H). ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 147.03, 146.57, 141.71, 131.89, 129.96, 126.11, 125.83, 123.38, 120.57, 111.78. ESI-MS Calculated for $\text{C}_{12}\text{H}_8\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+ = 241.07$, found = 241.05.

4-(tert-Butyl)benzyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)acetate (10)



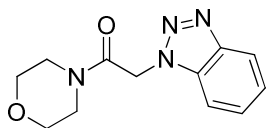
Pale orange solid (87 mg, 0.27 mmol, 36%). ^1H NMR (400 MHz, CDCl_3) δ : 8.12 (dd, $J = 8.3, 0.8$ Hz, 1 H), 7.56 - 7.50 (m, 1 H), 7.49 - 7.38 (m, 4 H), 7.26 (d, $J = 8.1$ Hz, 2 H), 5.48 (s, 2 H), 5.22 (s, 2 H), 1.35 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 166.32, 151.96, 146.07, 133.40, 131.63, 128.46, 127.92, 125.67, 124.14, 120.23, 109.29, 67.82, 49.11, 34.68, 31.30. ESI-MS Calculated for $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+ = 324.17$, found = 324.11, Authentic standard = 324.11.

Ethyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)acetate (11)



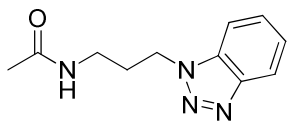
Pale yellow solid (81 mg, 0.39 mmol, 53%). ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (d, $J = 8.3$ Hz, 1 H), 7.52 - 7.43 (m, 2 H), 7.40 - 7.32 (m, 1 H), 5.40 (s, 2 H), 4.21 (q, $J = 7.1$ Hz, 2 H), 1.23 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 166.39, 145.96, 133.38, 127.88, 124.10, 120.06, 109.32, 62.28, 49.05, 14.02. ESI-MS Calculated for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+ = 206.09$, found = 206.00, Authentic standard = 206.00.

2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-morpholinoethanone (12)



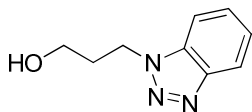
White solid (108 mg, 0.44 mmol, 58%). ^1H NMR (400 MHz, d_6 -DMSO) δ : 8.02 (d, $J = 8.3$ Hz, 1 H), 7.74 (d, $J = 8.3$, 1 H), 7.52 (t, $J = 7.5$ Hz, 1 H), 7.39 (t, $J = 7.5$ Hz, 1 H), 5.83 (s, 2 H), 3.77 - 3.68 (m, 2 H), 3.68 - 3.58 (m, 4 H), 3.53 - 3.43 (m, 2 H). ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 164.87, 145.54, 134.42, 127.58, 124.21, 119.44, 111.48, 66.44, 55.37, 49.24, 45.31, 42.38. ESI-MS Calculated for $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+ = 247.12$, found = 247.10, Authentic standard = 247.20.

N-(3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)propyl)acetamide (13)



Pale yellow solid (51 mg, 0.23 mmol, 31%). ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (d, $J = 8.3$ Hz, 1 H), 7.55 - 7.51 (m, 1 H), 7.50 - 7.44 (m, 1 H), 7.39 - 7.32 (m, 1 H), 6.52 (br. s., 1 H), 4.69 (t, $J = 6.8$ Hz, 2 H), 3.26 (q, $J = 6.3$ Hz, 2 H), 2.22 (quin, $J = 6.7$ Hz, 2 H), 1.92 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 170.74, 145.88, 132.87, 127.57, 124.16, 119.85, 109.39, 45.74, 36.80, 29.09, 23.13. ESI-MS Calculated for $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+ = 219.12$, found = 219.11, Authentic standard = 219.11.

3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)propan-1-ol (14)



Pale yellow oil (35 mg, 0.20 mmol, 26%). ^1H NMR (400 MHz, CDCl_3) δ : 8.02 (d, $J = 8.3$ Hz, 1 H), 7.60 (d, $J = 8.3$ Hz, 1 H), 7.46 (t, $J = 7.7$ Hz, 1 H), 7.35 (m, 1 H), 4.80 (t, $J = 6.8$ Hz, 2 H), 3.67 (t, $J = 5.8$ Hz, 2 H), 3.51 (br. s., 1 H), 2.25 (quin, $J = 6.3$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ : 145.71, 133.17, 127.38, 124.05, 119.75, 109.55, 58.75, 44.69, 32.21. ESI-MS Calculated for $\text{C}_9\text{H}_{11}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 178.10$, found = 178.11, Authentic standard = 178.02.

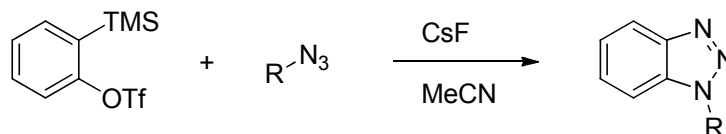
3. SPECTROSCOPIC YIELD DETERMINATION

LC-MS

Separation was performed with a Waters 1525 system. The gradient employed was A = water + 0.1% formic acid, B = acetonitrile + 0.1% formic acid, 5–95% B over 60 min with a Waters XBridge C18 5u column (4.6 × 150 mm). Mass spectra were acquired with a Waters Micromass ZQ mass detector in EI+ mode: Capillary voltage = 3.50 kV, cone voltage = 30 V, extractor = 3 V, RF lens = 0.0 V, source T = 100 °C, desolvation T = 200 °C, desolvation gas = 300 L h⁻¹, desolvation gas = 0.0 L h⁻¹. The system was operated by and spectra were processed using the Waters Empower software suite.

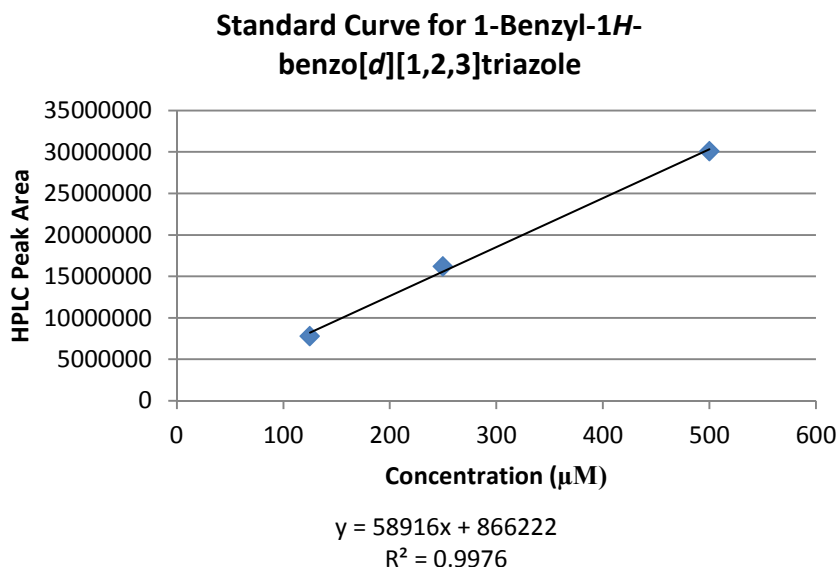
Standard curves were generated using pure benzotriazole prepared via the Larock procedure. Serial dilutions were done to prepare 500, 250, and 125 μM (MeCN) samples for a 3-point curve where peak area via HPLC was plotted against concentration.

General procedure for Benzotriazole Authentic Standard preparation using Larock Method



To a stirred solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (85 μL, 0.35 mmol, 1.2 eq) and the corresponding azido compound (0.30 mmol, 1.0 eq) in MeCN (10 mL) was added CsF (91 mg, 0.60 mmol, 2.0 eq). After stirring for 18 h, the reaction mixture was washed with NaHCO₃, brine, dried over Na₂SO₄, and purified over silica using flash column chromatography to give the corresponding Benzotriazole compound.

Concentration of (5) (μM)	HPLC Peak Area
125	7811334
250	16224101
500	30114326



Percent Conversion to Benzotriazole determined via Spectroscopy

In a 2 mL microcentrifuge tube was added MeCN (27.5 μ L) followed by solutions of a corresponding azido compound (7.5 μ L, 100 mM, 1.0 eq) and triazenylbenzoic acid (**1**) (15 μ L, 50 mM, 1.0 eq) in MeCN. The tube was placed about 2 cm below the light source and irradiated for 3 m. 6.66 μ L of the irradiated solution was diluted to 200 μ L with MeCN and benzotriazole formation was monitored using HPLC-MS. 100% conversion would correlate to a 500 μ M solution of benzotriazole.

1-Benzyl-1*H*-benzo[*d*][1,2,3]triazole (**5**)

	HPLC Peak Area	Percent Conversion
Run 1	24513945	83 %
Run 2	25272854	86 %
Run 3	23510758	80 %
Average		83 %
Standard Dev.		3 %
Run with (1) exposed to ambient light/temp for several months*	19913086	77 %

**A new standard curve had to be prepared due to variations attributed to lamp performance after several weeks. Yield is based on new standard curve.*

1-Cinnamyl-1*H*-benzo[*d*][1,2,3]triazole (**6**)

	HPLC Peak Area	Percent Conversion
Run 1	63090893	66 %
Run 2	63482716	67 %
Run 3	66055382	67 %
Average		67 %
Standard Dev.		1 %

1-Phenyl-1*H*-benzo[*d*][1,2,3]triazole (**7**)

	HPLC Peak Area	Percent Conversion
Run 1	11650744	34 %
Run 2	11047481	32 %
Run 3	10971848	31 %
Average		32 %
Standard Dev.		2 %

1-(4-Methoxyphenyl)-1*H*-benzo[*d*][1,2,3]triazole (8)

	HPLC Peak Area	Percent Conversion
Run 1	11983895	32 %
Run 2	11422097	30 %
Run 3	11840775	31 %
Average		31 %
Standard Dev.		1%

1-(4-Nitrophenyl)-1*H*-benzo[*d*][1,2,3]triazole (9)

	HPLC Peak Area	Percent Conversion
Run 1	1084017	3 %
Run 2	1097162	3 %
Run 3	965984	3 %
Average		3 %
Standard Dev.		0 %

4-(*tert*-Butyl)benzyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)acetate (10)

	HPLC Peak Area	Percent Conversion
Run 1	19635059	75 %
Run 2	18793702	72 %
Run 3	18942658	72 %
Average		73 %
Standard Dev.		2 %

Ethyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)acetate (11)

	HPLC Peak Area	Percent Conversion
Run 1	17649803	61 %
Run 2	16478454	57 %
Run 3	17646220	61 %
Average		60 %
Standard Dev.		2 %

2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-morpholinoethanone (12)

	HPLC Peak Area	Percent Conversion
Run 1	19211436	68 %
Run 2	20086228	71 %
Run 3	21737750	77 %
Average		72 %
Standard Dev.		5 %

***N*-(3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)propyl)acetamide (13)**

	HPLC Peak Area	Percent Conversion
Run 1	20679782	88 %
Run 2	20965516	90 %
Run 3	20479177	87 %
Average		88 %
Standard Dev.		2 %

3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)propan-1-ol (14)

	HPLC Peak Area	Percent Conversion
Run 1	16930310	87 %
Run 2	16516603	85 %
Run 3	16410510	84 %
Average		85 %
Standard Dev.		2 %

Molar Ratio, Irradiation Time, and Solvent Effect Experiments

In a 2 mL microcentrifuge tube was added the appropriate solvent, followed by solutions of (Azidomethyl)benzene (**15**) and triazenylbenzoic acid (**1**) in the appropriate solvent to achieve a 50 μ L solution of 15 mM triazenylbenzoic acid (**1**) and the corresponding concentration of (Azidomethyl)benzene (**15**) based on the appropriate molar ratio. The tube was placed about 2 cm below the light source and irradiated for the appropriate time. 6.66 μ L of the irradiated solution was diluted to 200 μ L with MeCN and benzotriazole formation was monitored using HPLC-MS*. 100% conversion would correlate to a 500 μ M solution of benzotriazole. *A new standard curve had to be prepared due to variations attributed to lamp performance after several weeks. Yield is based on new standard curve.

Entry	Solvent	Irradiation Time	Azide Equivalents	HPLC Peak Area	Percent Conversion
1	THF	3 m	1	740864	3 %
2	THF	3 m	2	896018	3 %
3	THF	3 m	5	3296494	13 %
4	THF	3 m	10	5928268	23 %
5	CHCl ₃	3 m	1	12268574	47 %
6	CHCl ₃	3 m	2	14635806	56 %
7	CHCl ₃	3 m	5	16913386	65 %
8	CHCl ₃	3 m	10	15917112	61 %
9	Dioxane	3 m	1	6500111	25 %
10	Dioxane	3 m	2	7302813	28 %
11	Dioxane	3 m	5	10229420	39 %
12	Dioxane	3 m	10	11928272	46 %
13	MeCN	5 s	1	423307	2 %

14	MeCN	1 m	1	14588945	56 %
15	MeCN	3 m	1	21290649	82 %
16	MeCN	5 m	1	21616422	83 %
17	MeCN	3 m	2	23476480	90 %
18	MeCN	3 m	5	25305365	97 %
19	MeCN	3 m	10	25518267	98 %

Water Tolerance Experiments

In a 2 mL microcentrifuge tube was added MeCN and the appropriate amount of H₂O followed by solutions of 2-Azido-1-morpholinoethanone (**22**) (7.5 μ L, 100 mM, 1.0 eq)* and triazenylbenzoic acid (**1**) (15 μ L, 50 mM, 1.0 eq) in MeCN. The tube was placed about 2 cm below the light source and irradiated for 3 m. 6.66 μ L of the irradiated solution was diluted to 200 μ L with MeCN and benzotriazole formation was monitored using HPLC-MS. 100% conversion would correlate to a 500 μ M solution of benzotriazole. *Concentration was increased to achieve solutions >50% water.

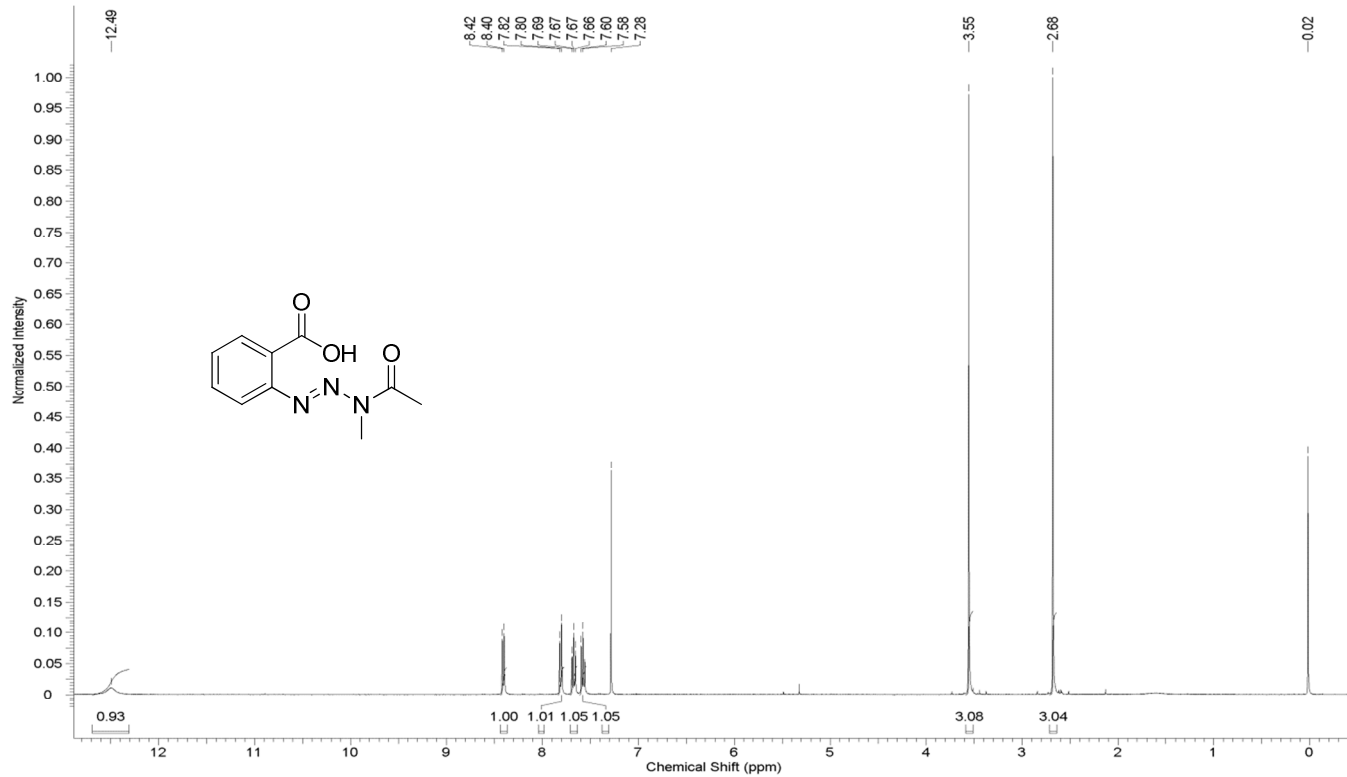
% Water	Run 1		Run 2		Run 3*		Average	Standard Dev.
	Peak Area	Percent Conversion	Peak Area	Percent Conversion	Peak Area	Percent Conversion		
0	20472896	72 %	20533024	72 %	26118215	61 %	68 %	6 %
10	6207479	22 %	14891765	52 %	13190756	31 %	35 %	15 %
20	7349911	26 %	9894391	35 %	9792834	23 %	28 %	6 %
30	3092329	11 %	6562328	23 %	8368868	19 %	18 %	6 %
40	6096025	21 %	5027298	18 %	4940317	11 %	17 %	5 %
50	3535529	12 %	3308907	12 %	4034358	9 %	11 %	2 %
70	1662791	6 %	1474828	5 %	4262409	10 %	7 %	3 %

*A new standard curve had to be prepared due to variations attributed to lamp performance after several weeks. Yield is based on new standard curve.

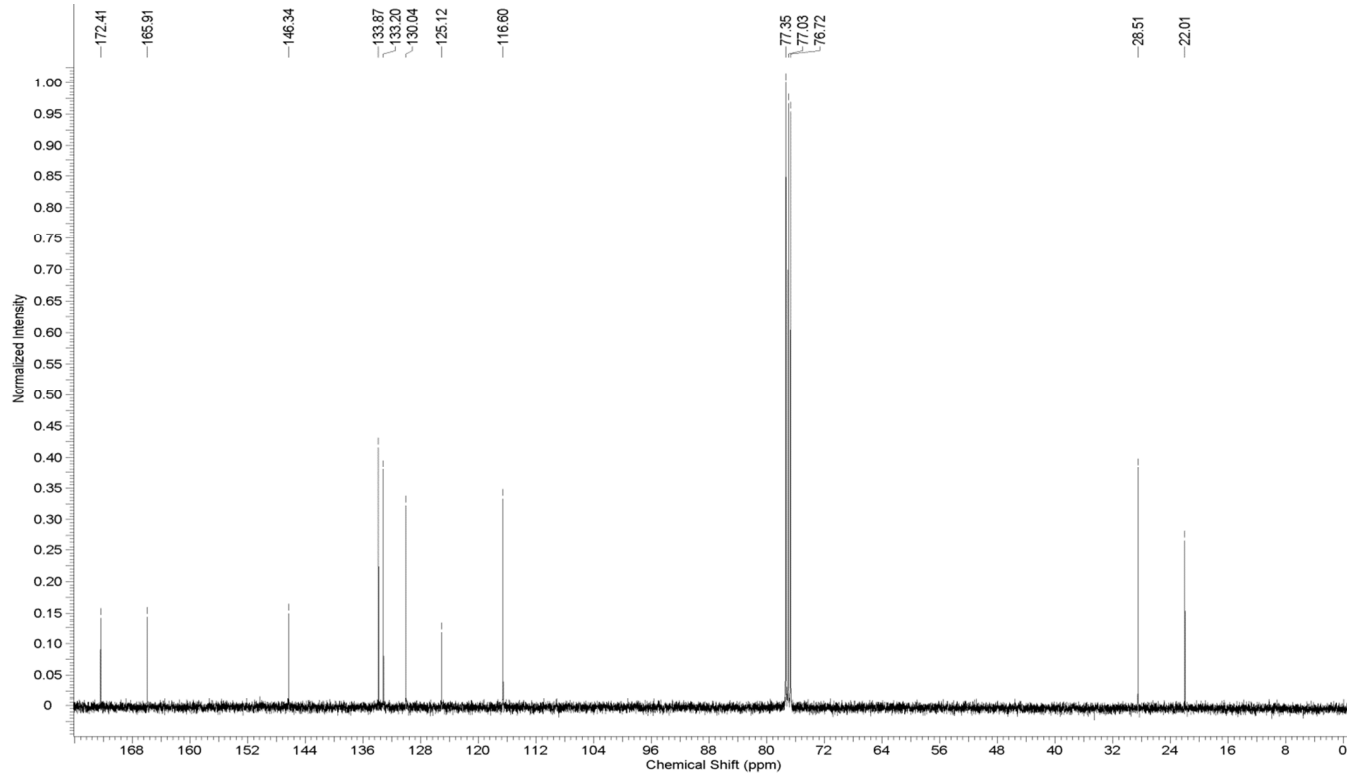
4. NMR SPECTRA

2-(3-Acetyl-3-methyltriaz-1-en-1-yl)benzoic acid (1)

^1H NMR:

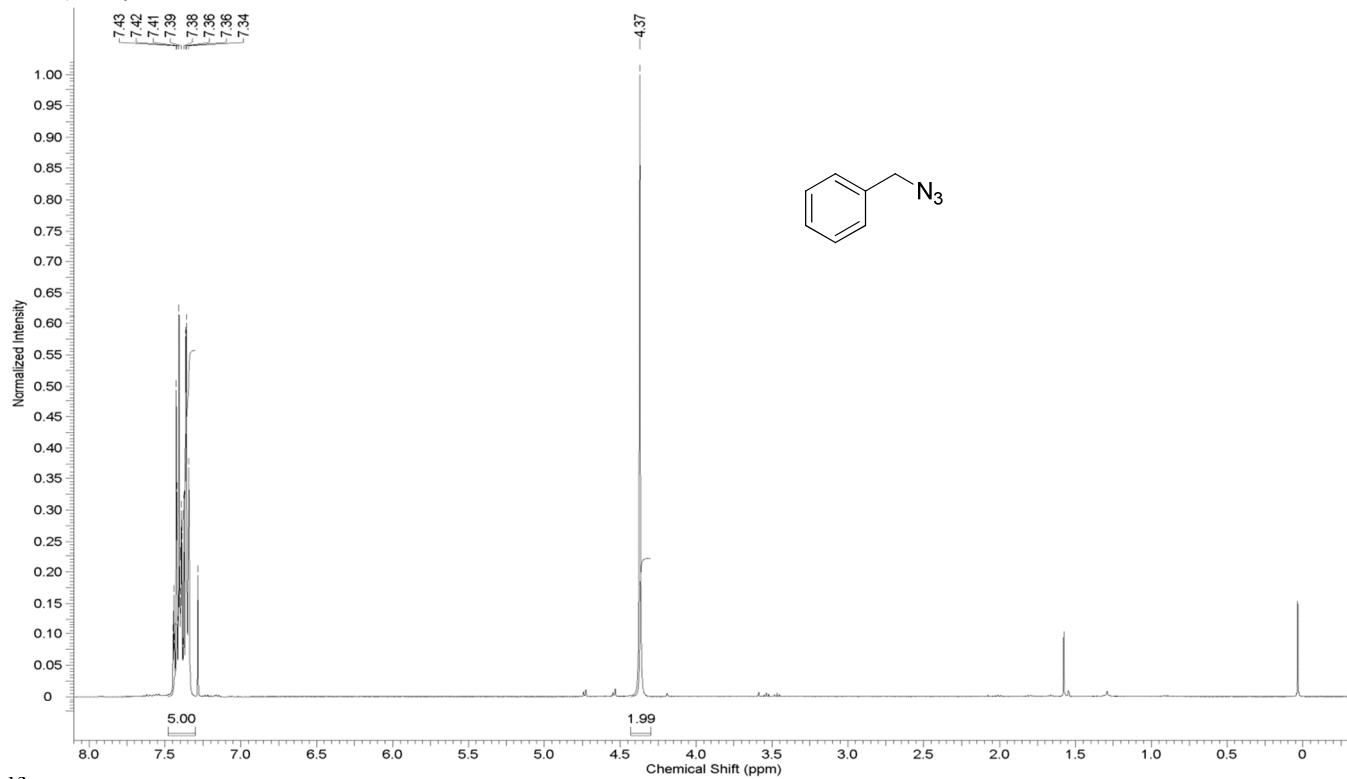


^{13}C NMR:

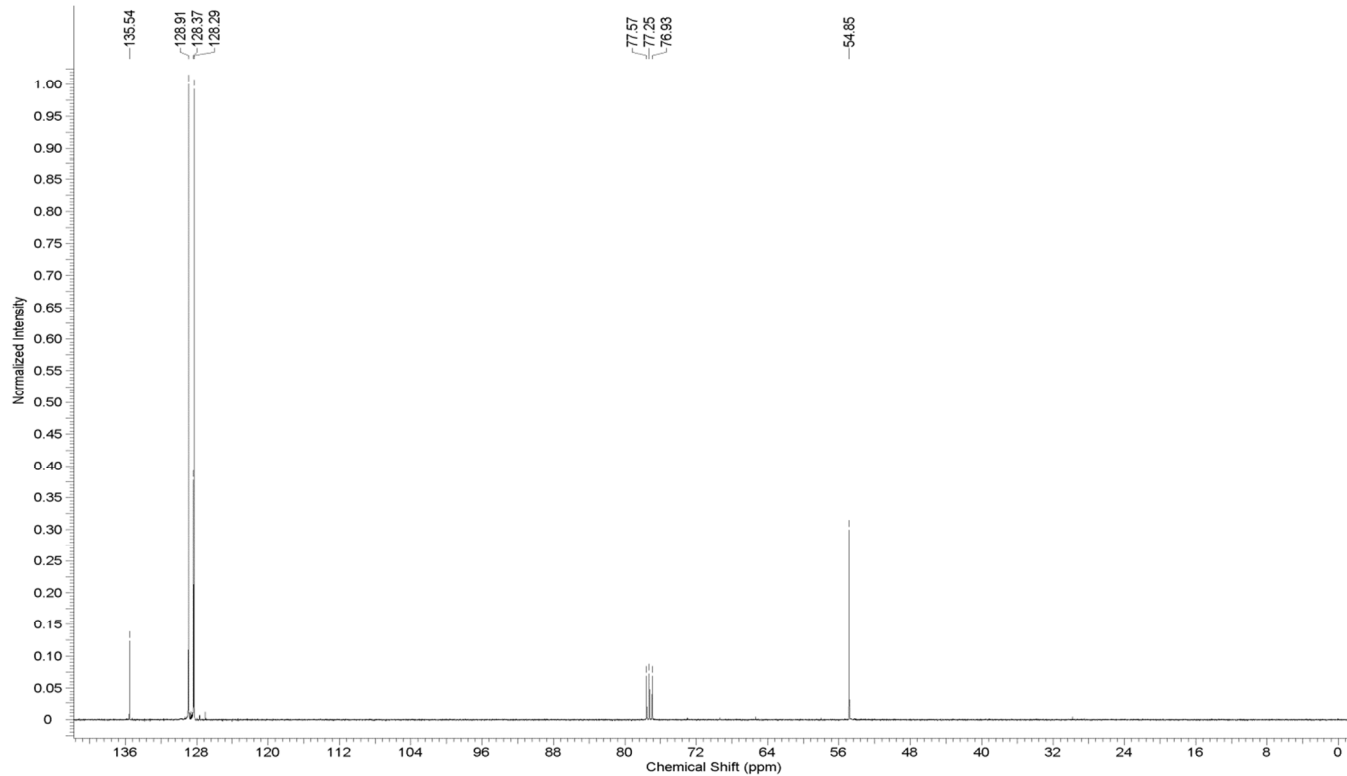


(Azidomethyl)benzene (15)

^1H NMR:

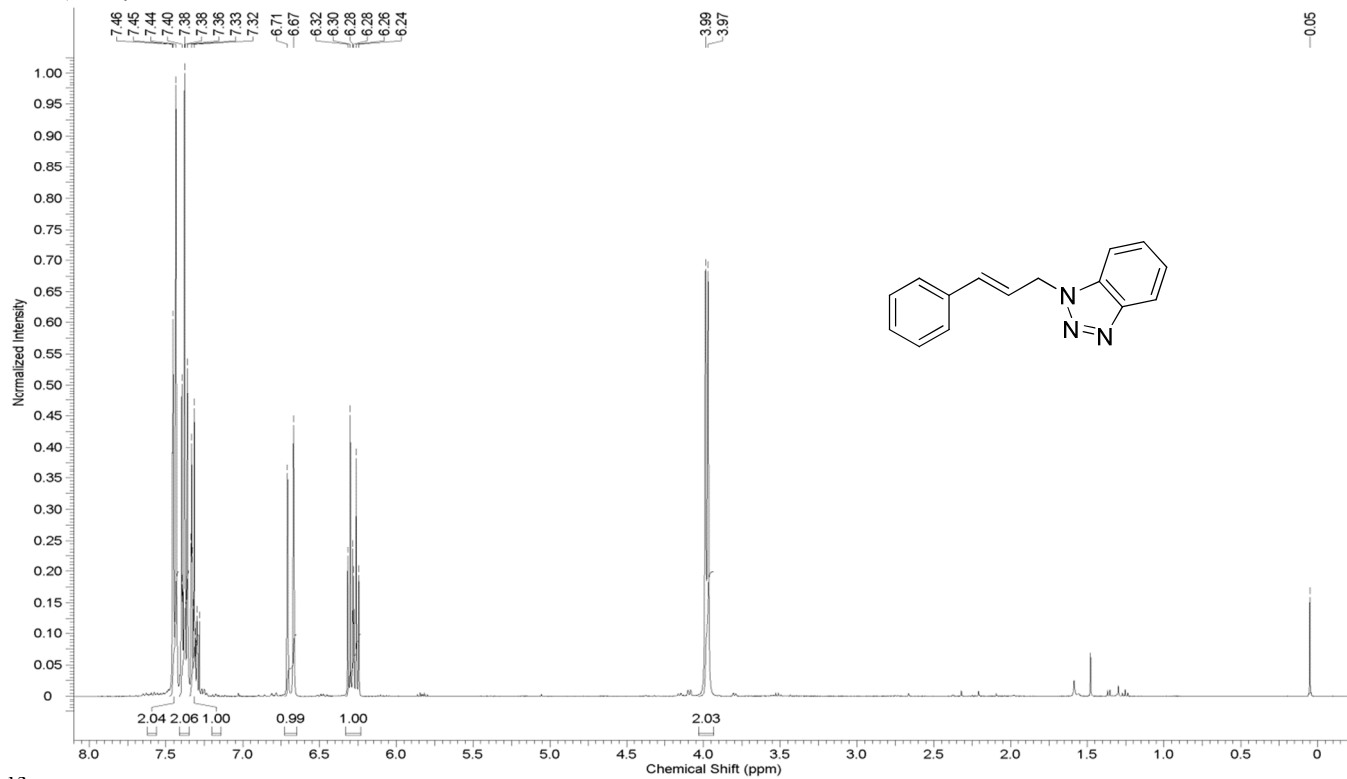


^{13}C NMR:

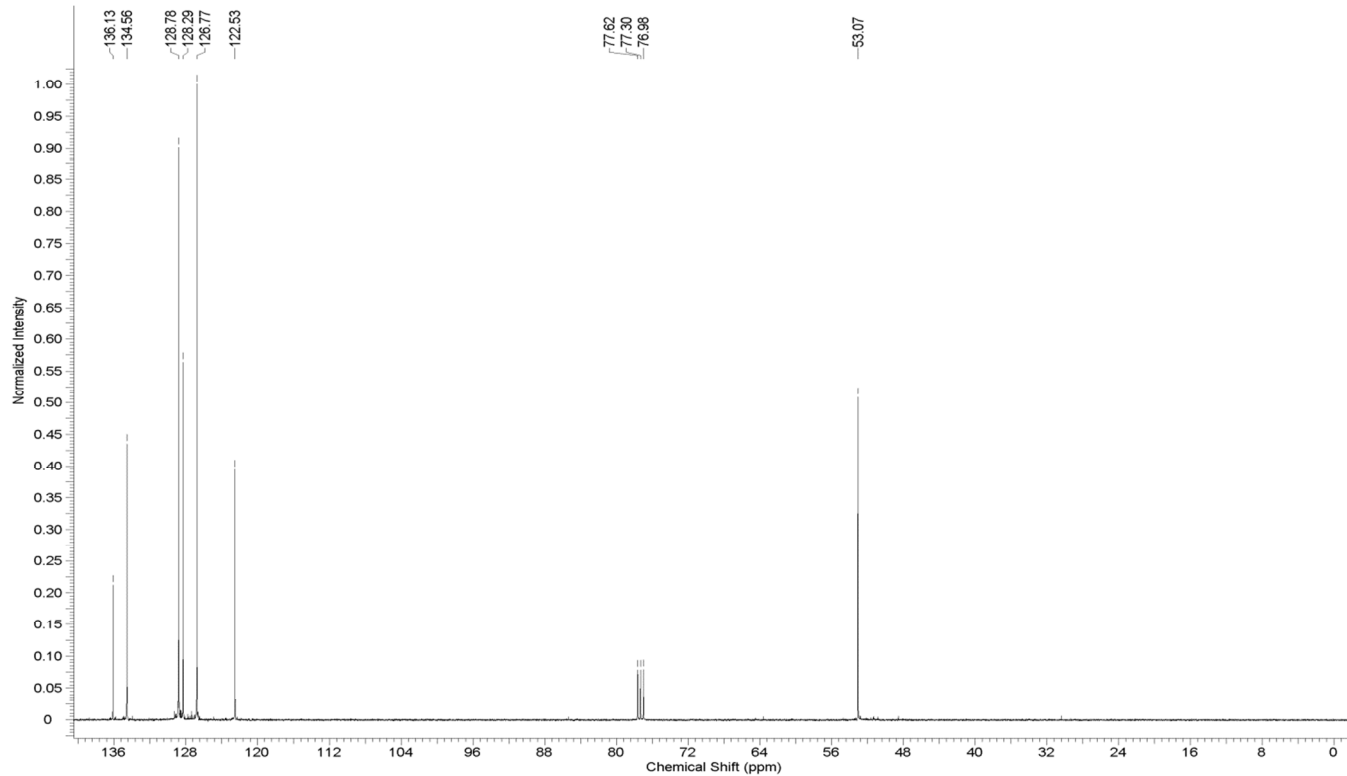


(E)-(3-Azidoprop-1-en-1-yl)benzene (16)

¹H NMR:

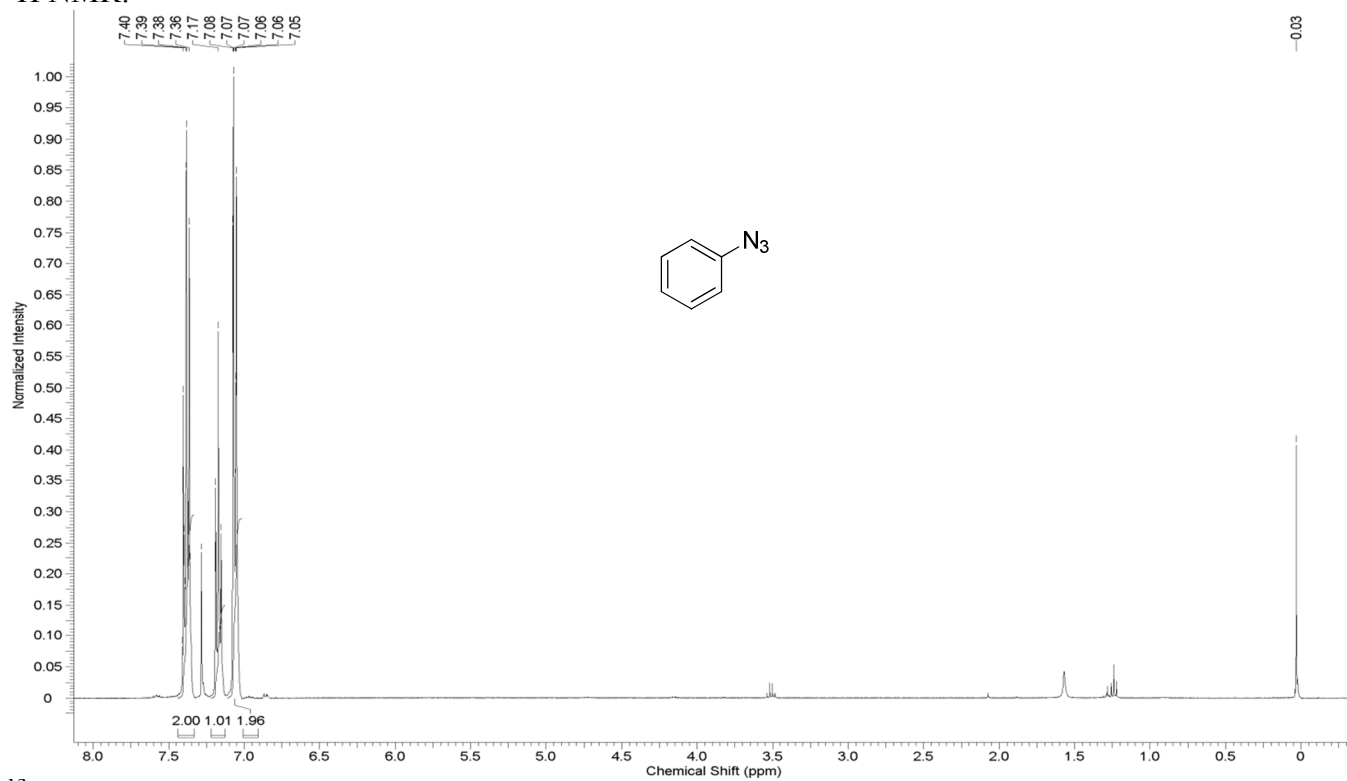


¹³C NMR:

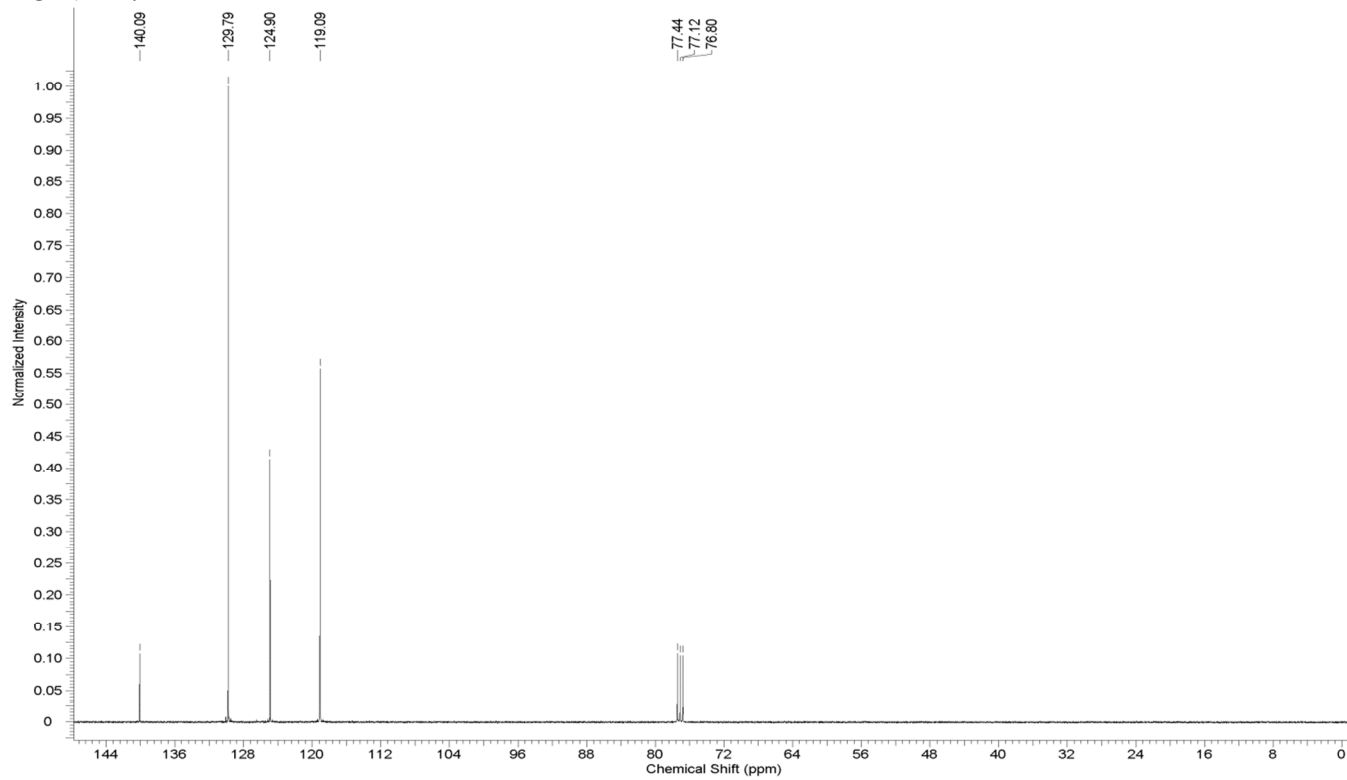


Azidobenzene (17)

^1H NMR:

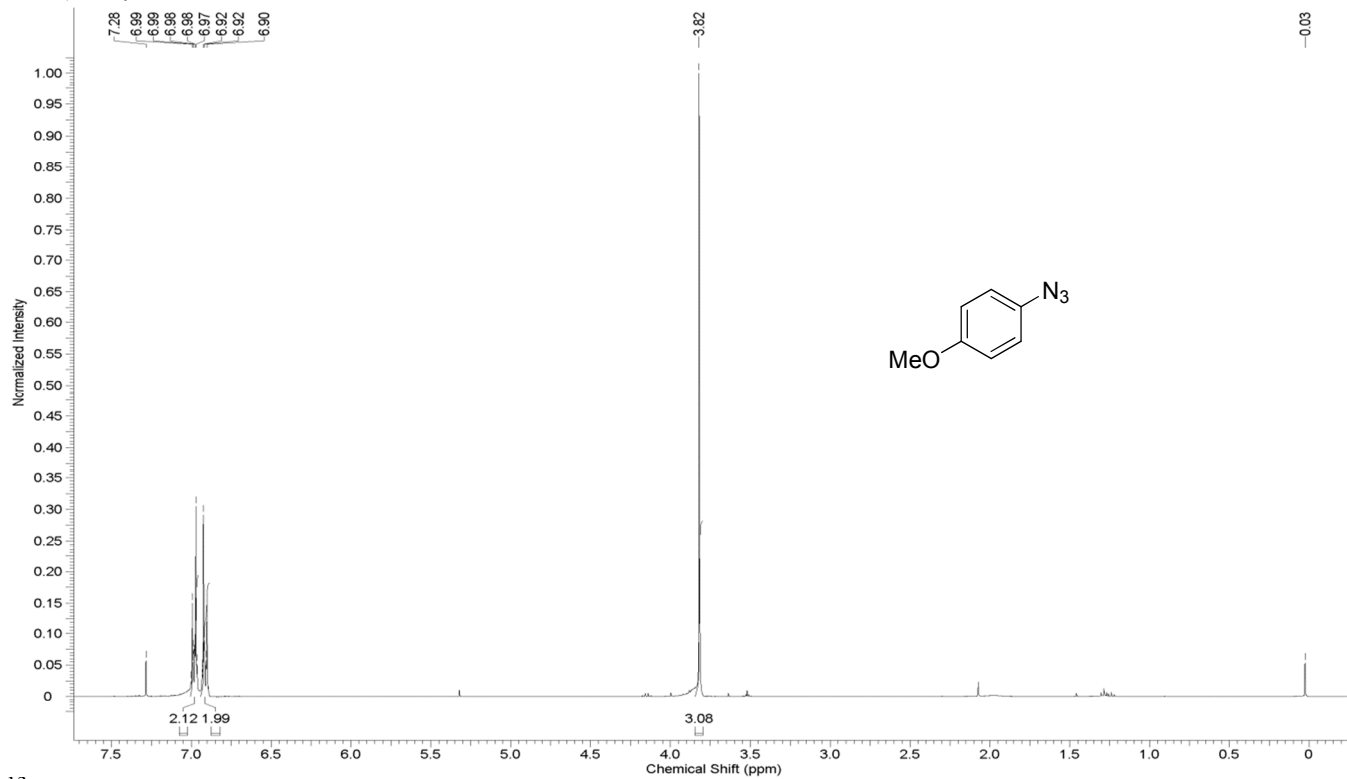


^{13}C NMR:

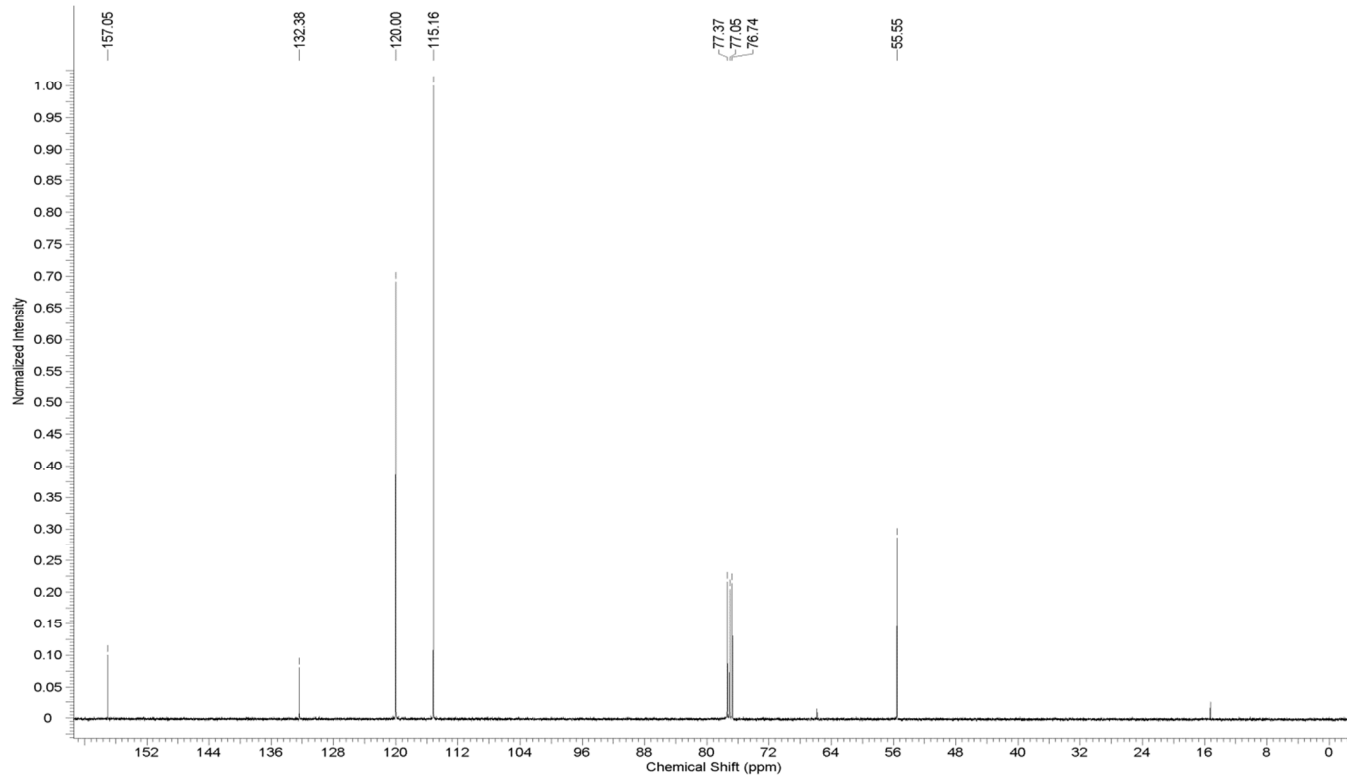


1-Azido-4-methoxybenzene (18)

^1H NMR:

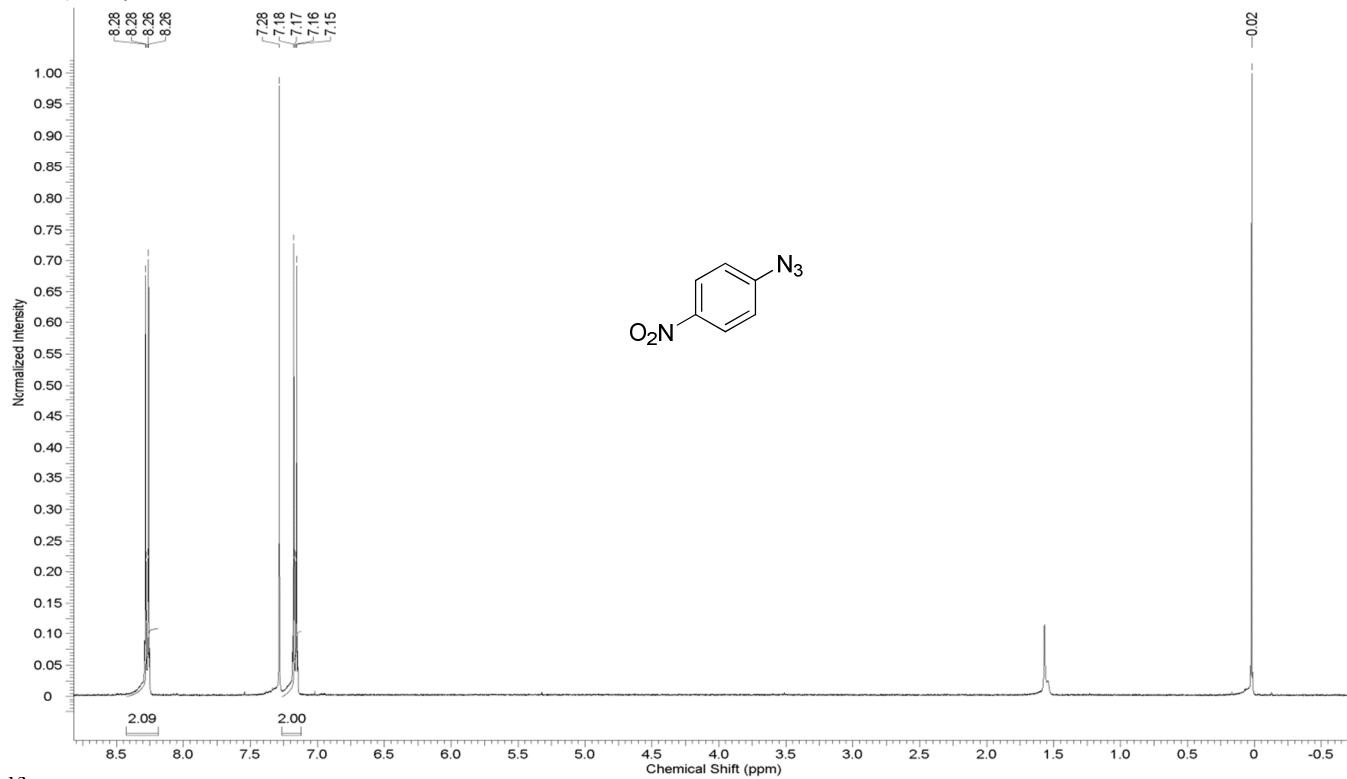


^{13}C NMR:

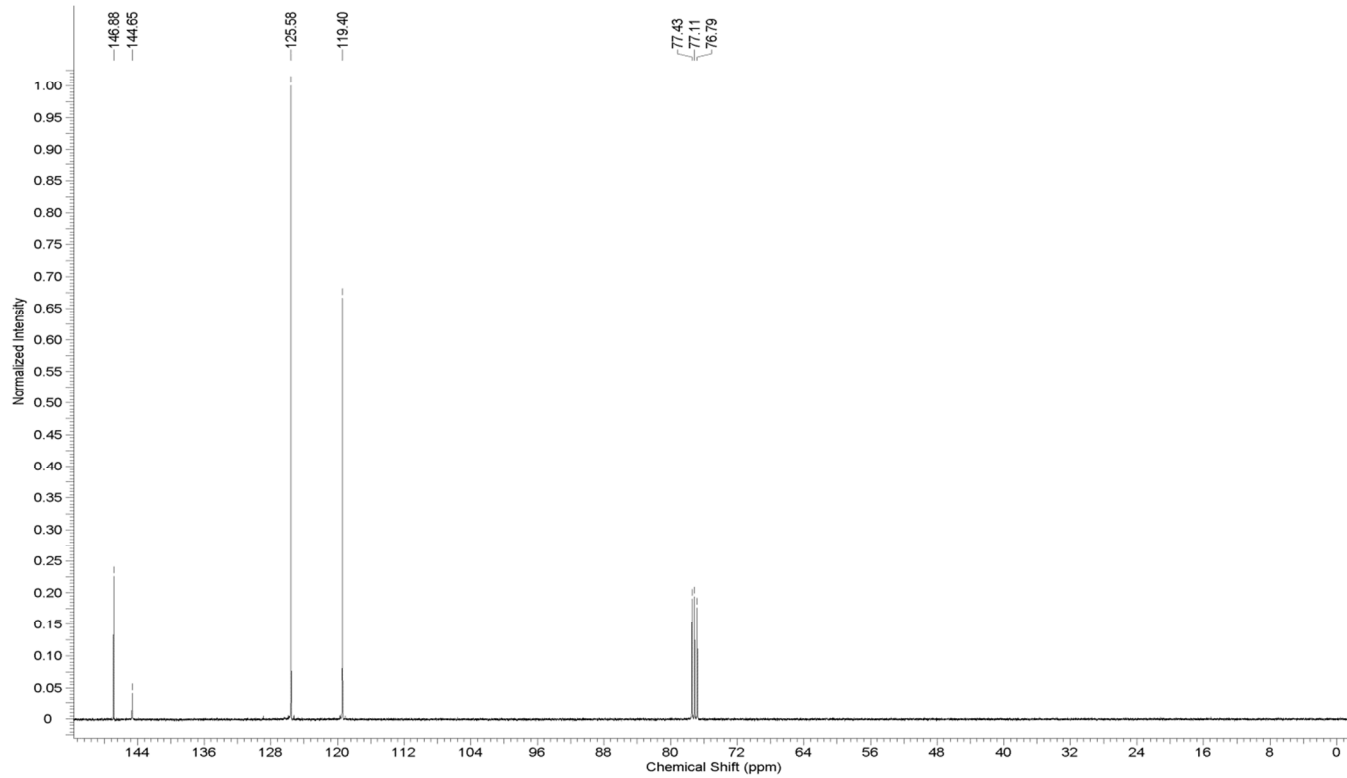


1-Azido-4-nitrobenzene (19)

^1H NMR:

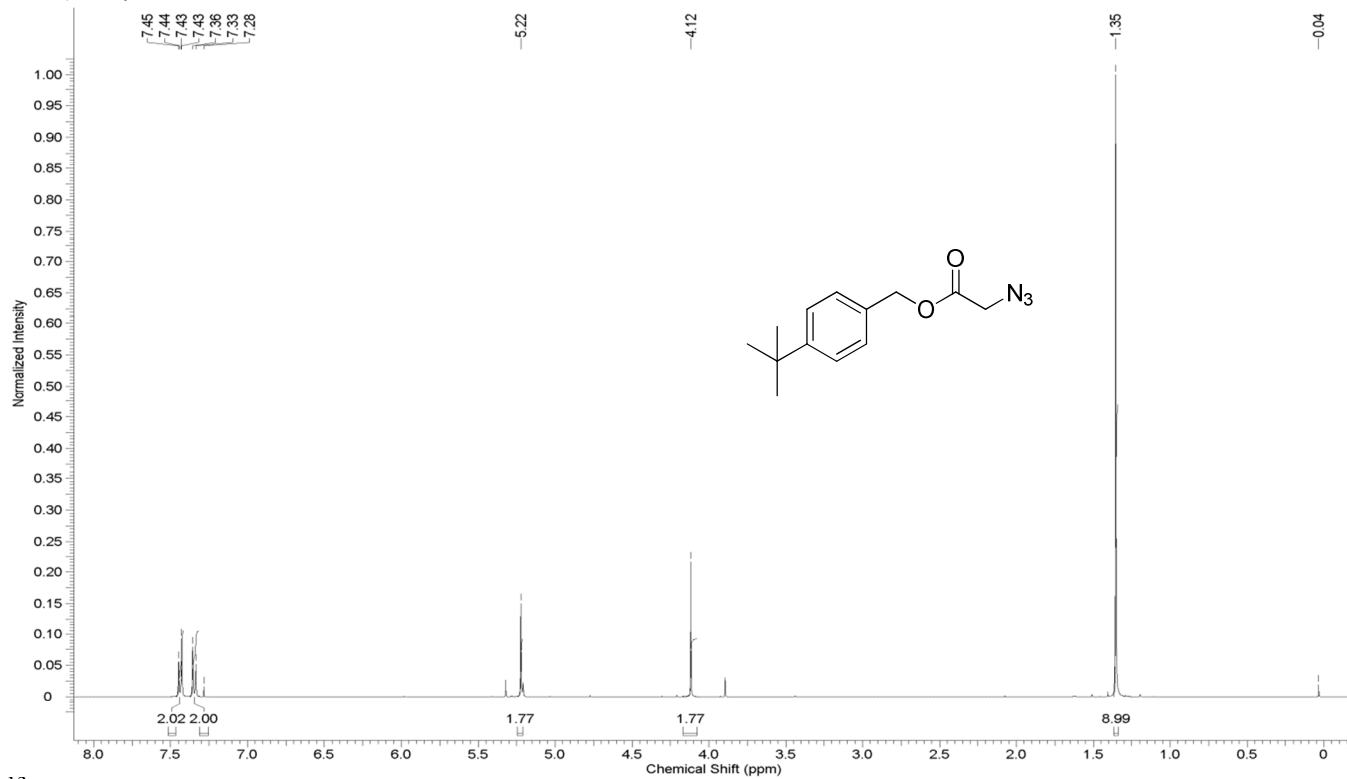


^{13}C NMR:

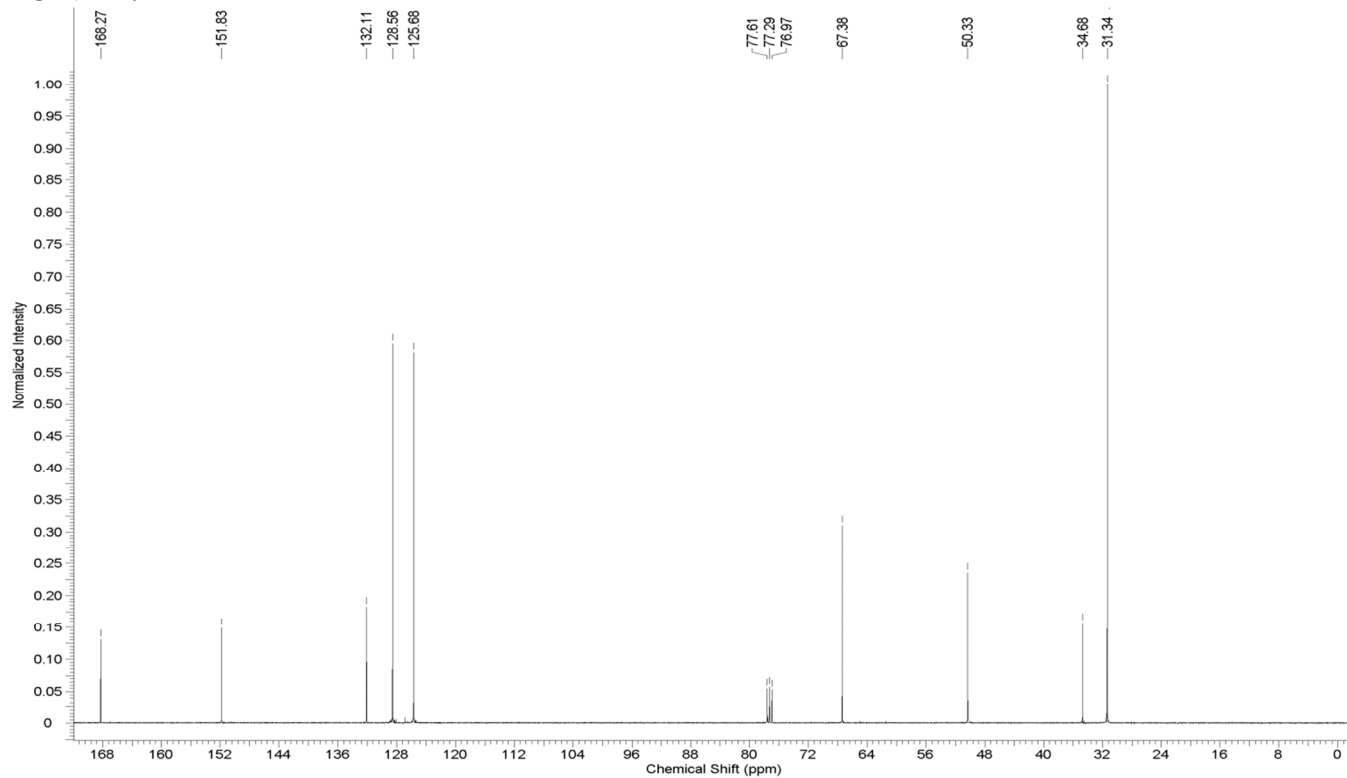


4-(*tert*-Butyl)benzyl 2-azidoacetate (20)

^1H NMR:

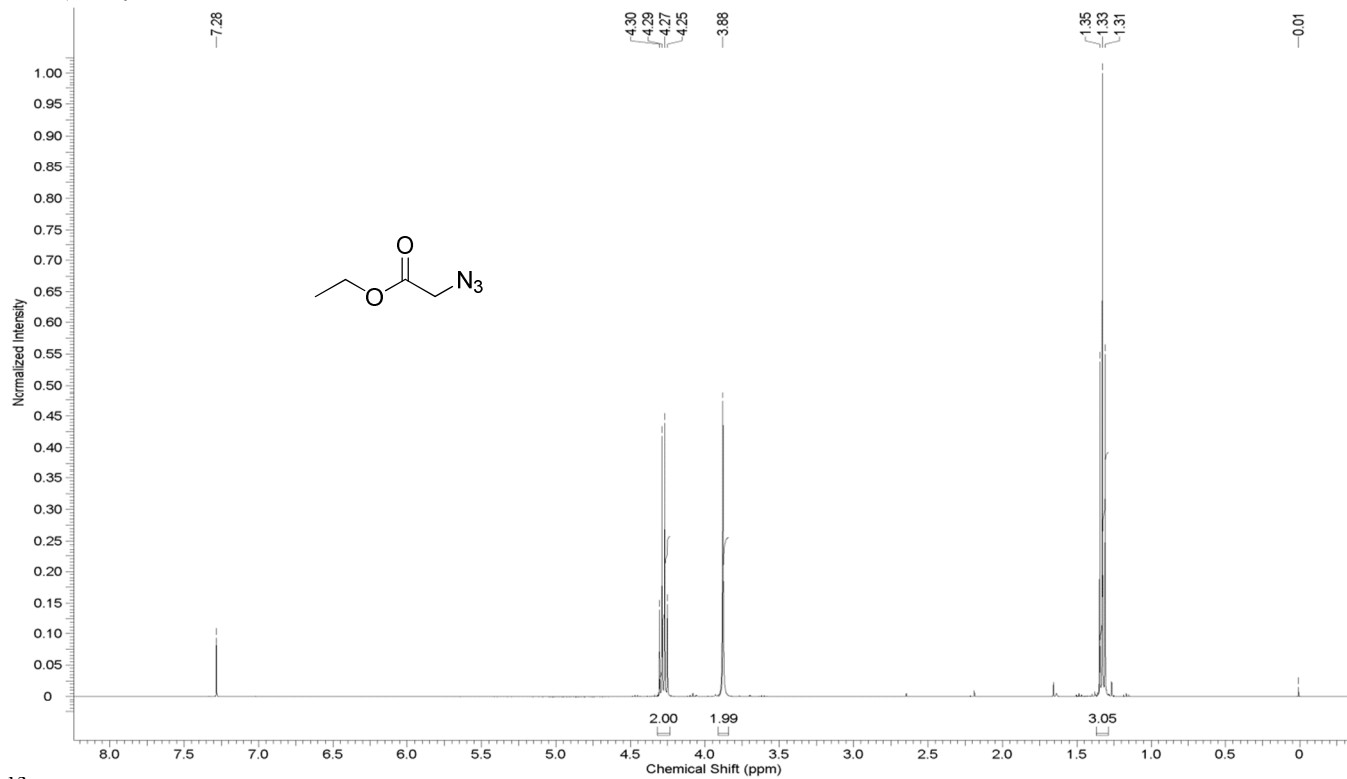


^{13}C NMR:

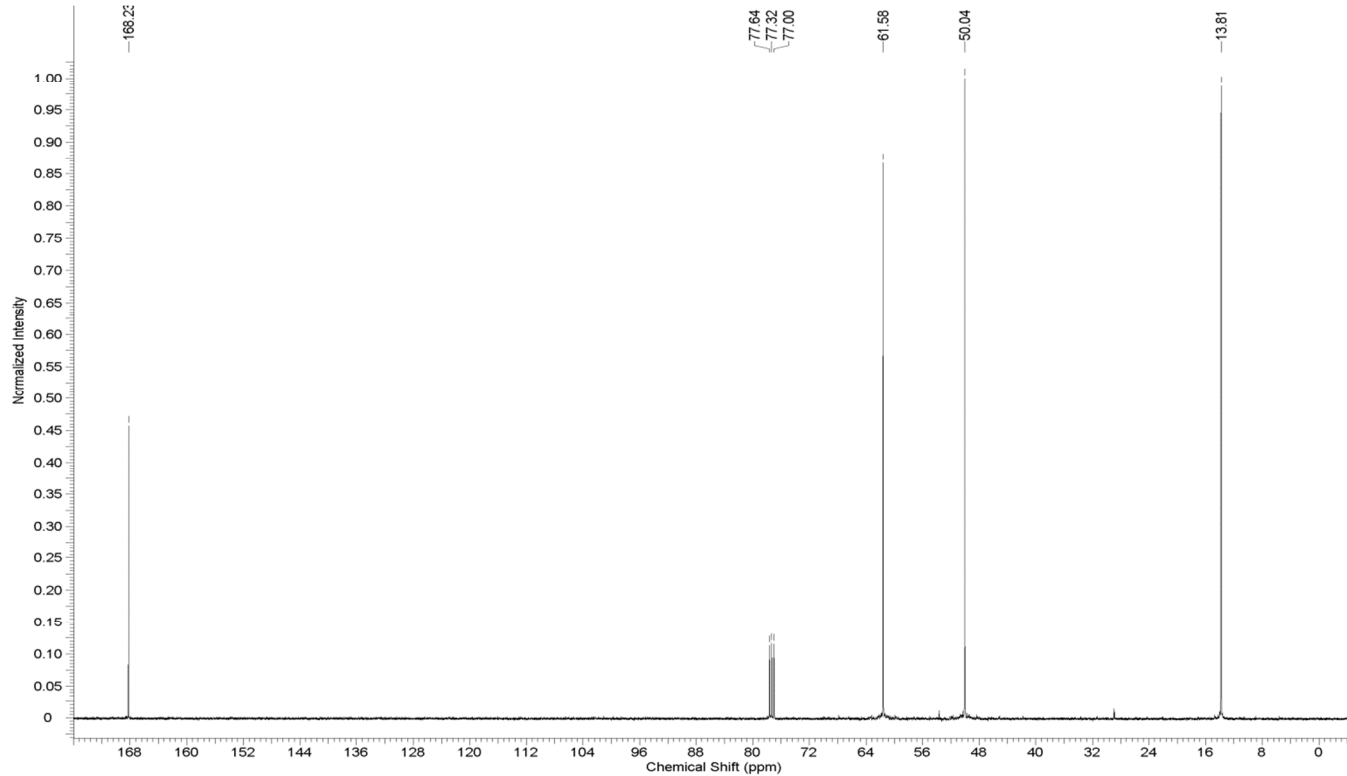


Ethyl 2-azidoacetate (21)

^1H NMR:

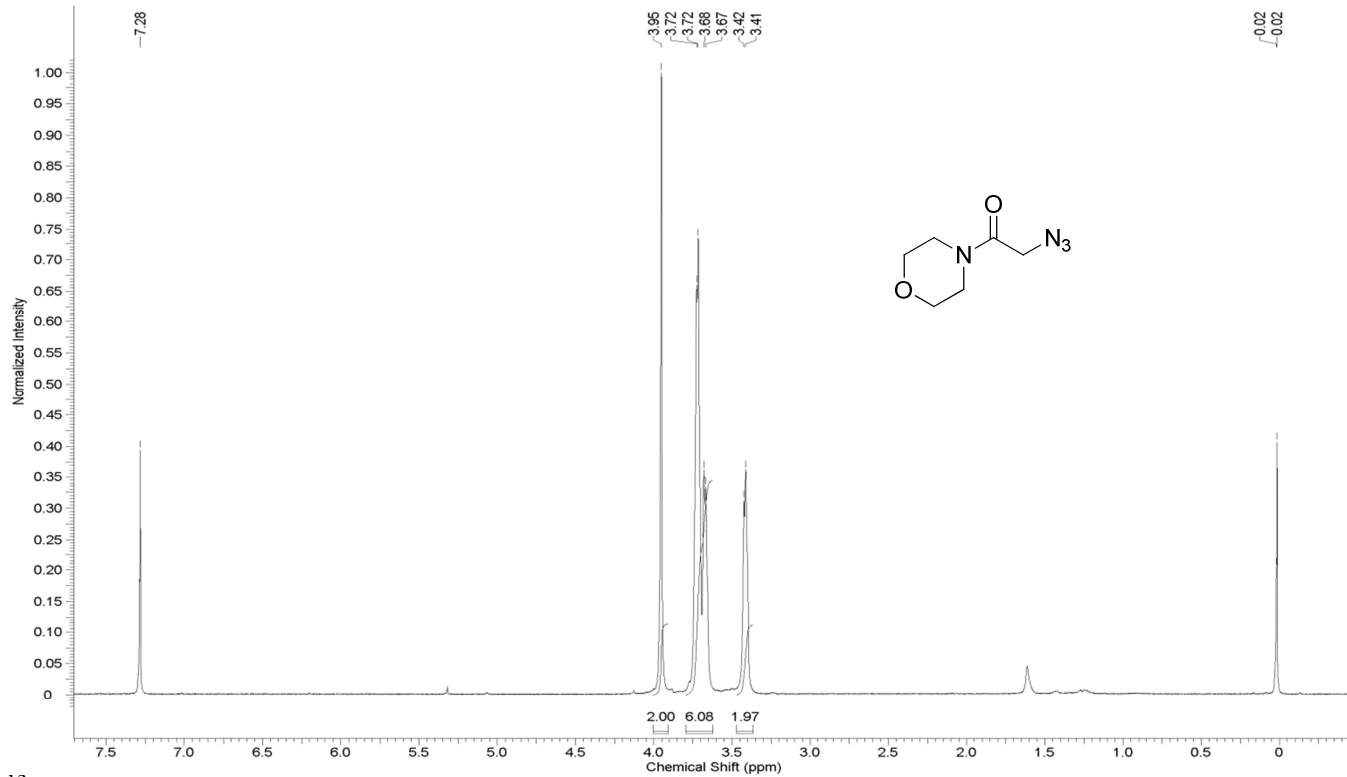


^{13}C NMR:

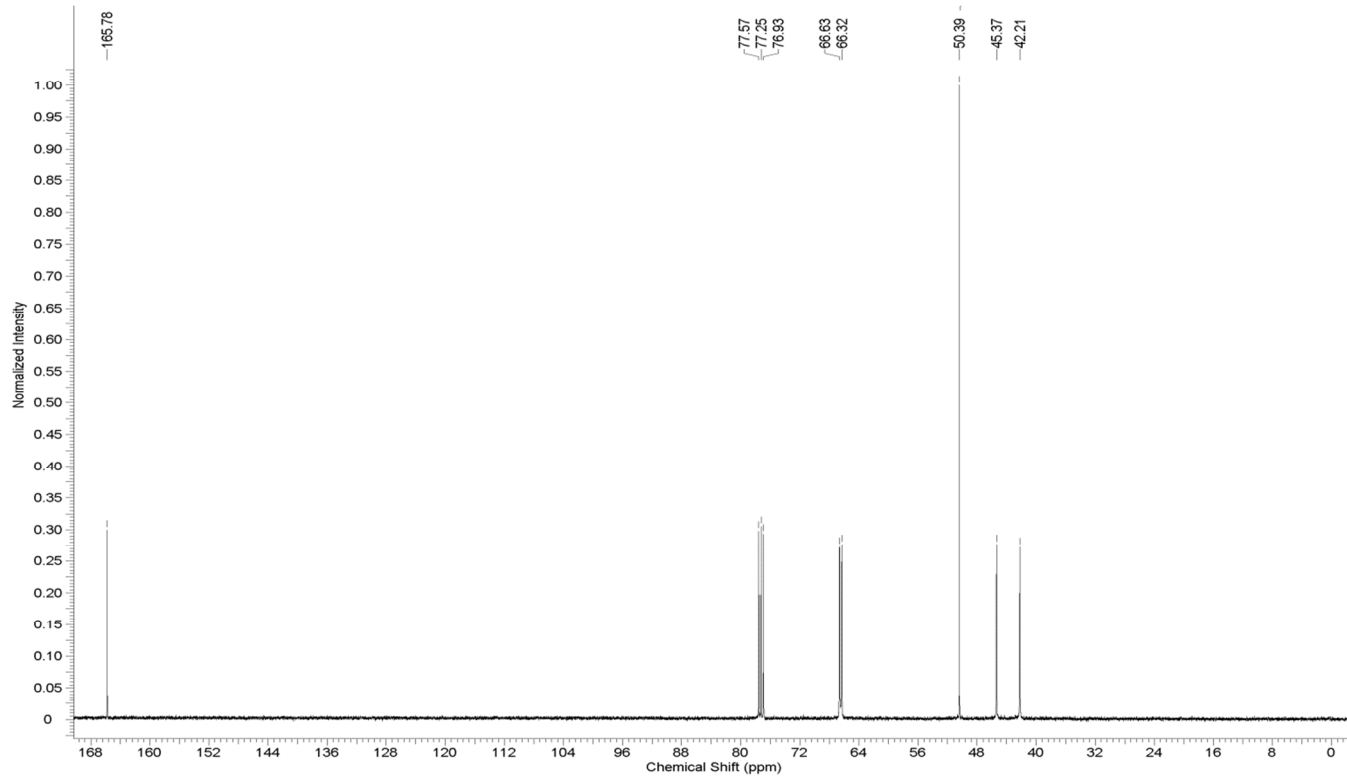


2-Azido-1-morpholinoethanone (22)

^1H NMR:

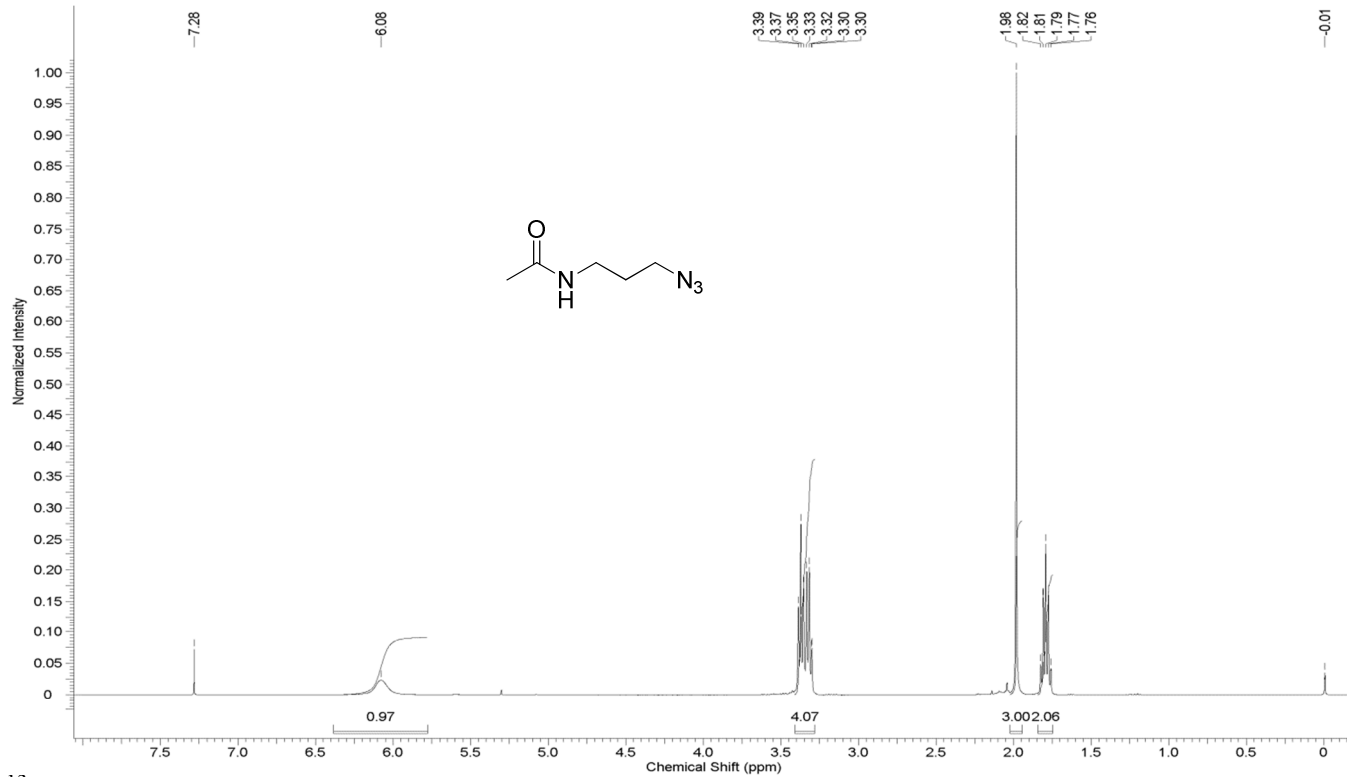


^{13}C NMR:

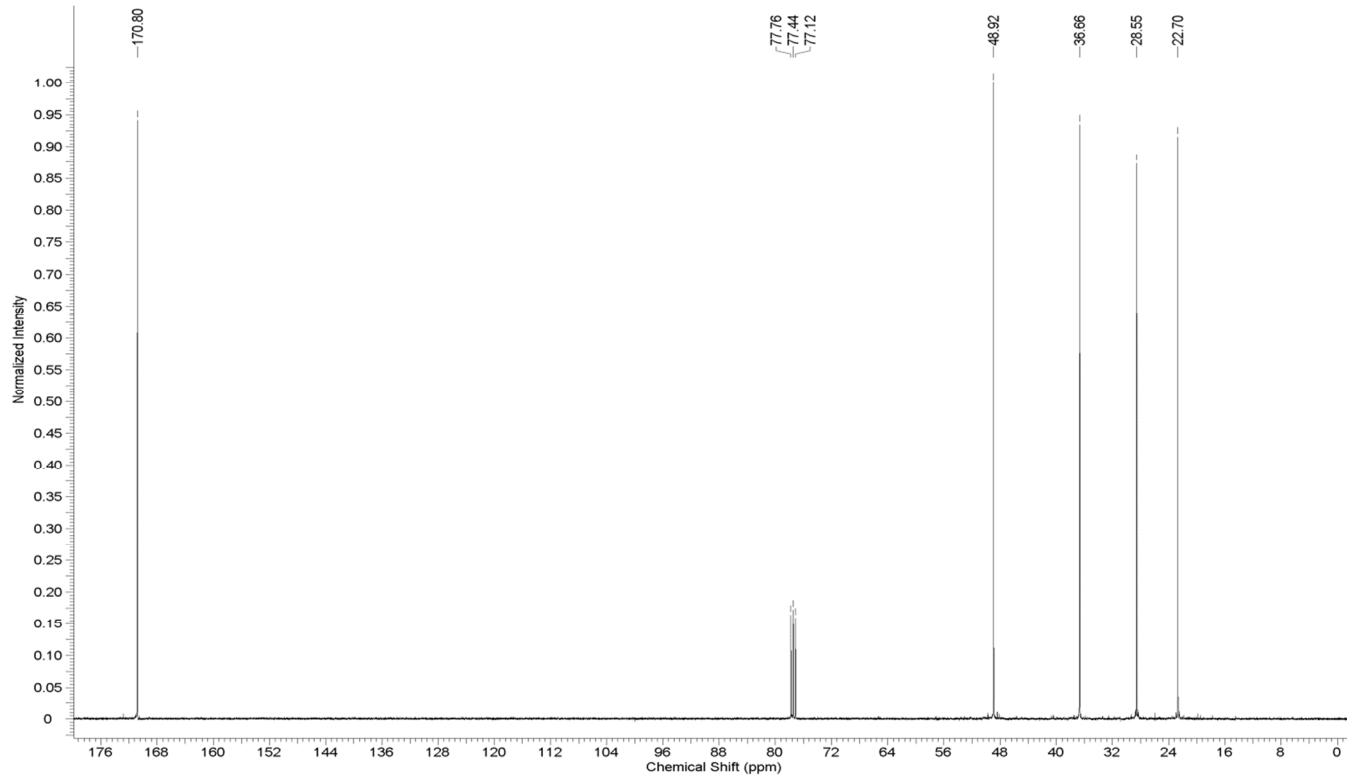


N-(3-Azidopropyl)acetamide (23)

^1H NMR:

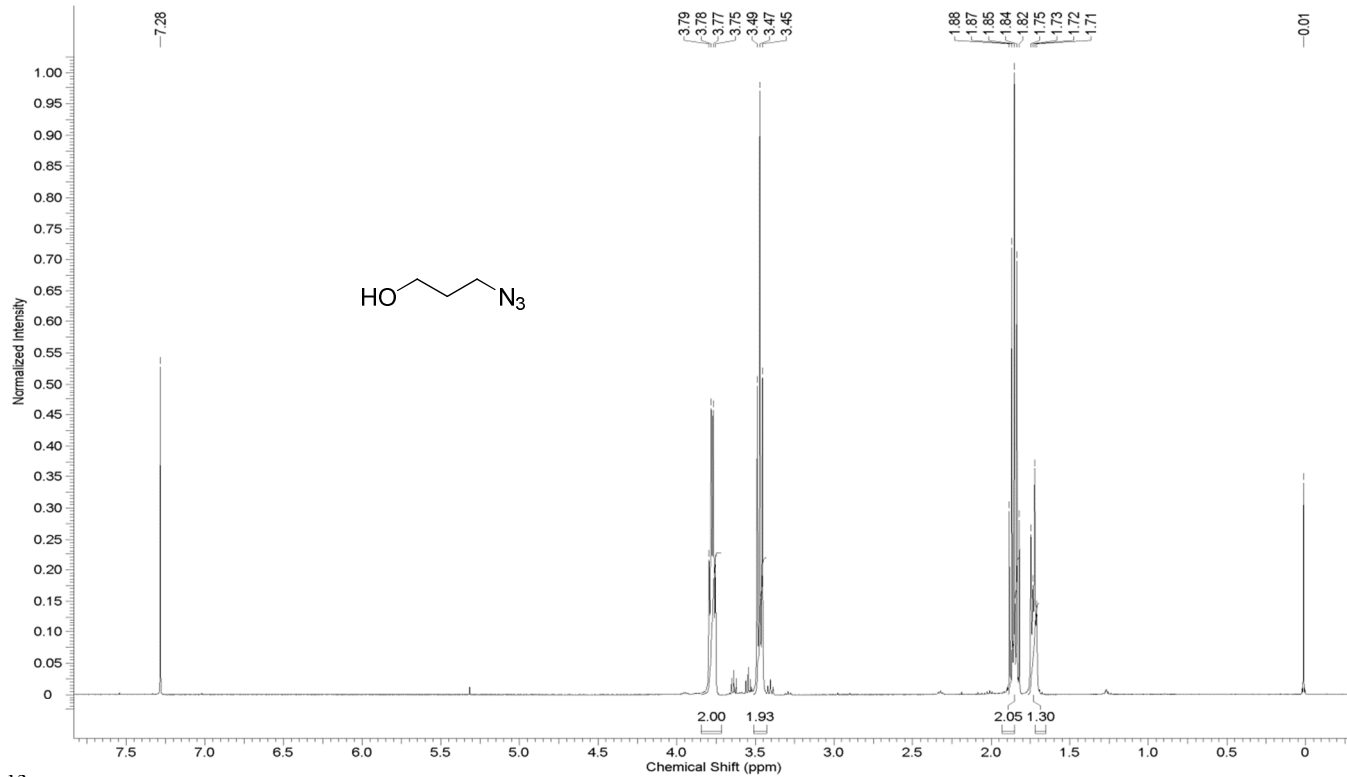


^{13}C NMR:

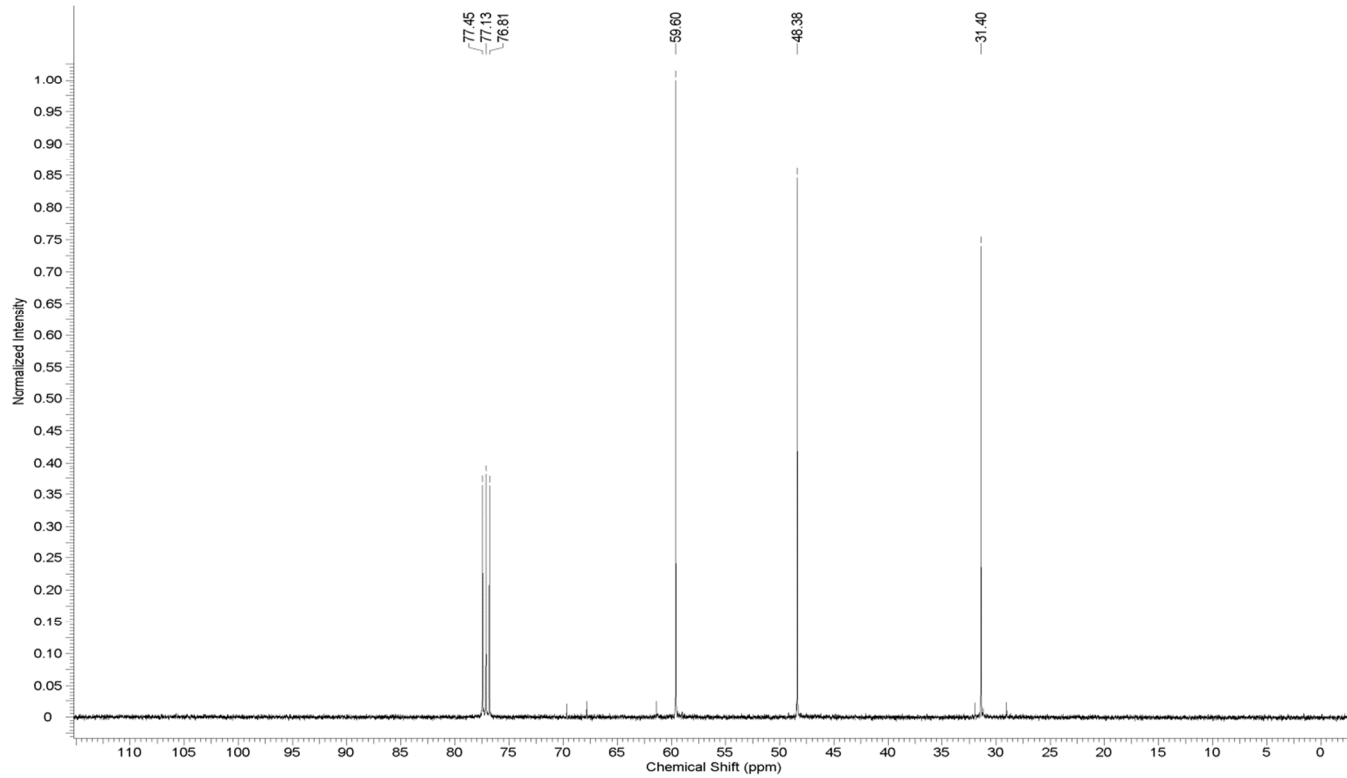


3-Azidopropan-1-ol (24)

^1H NMR:

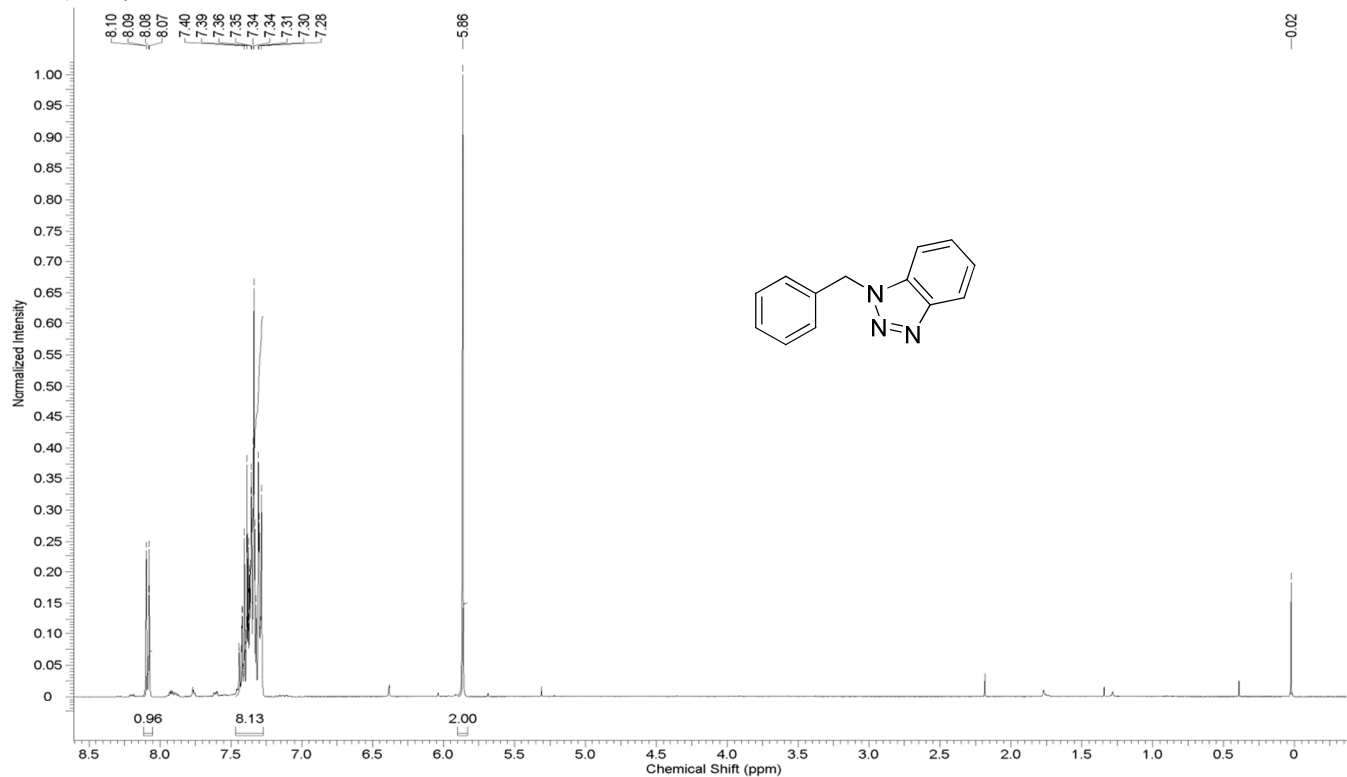


^{13}C NMR:

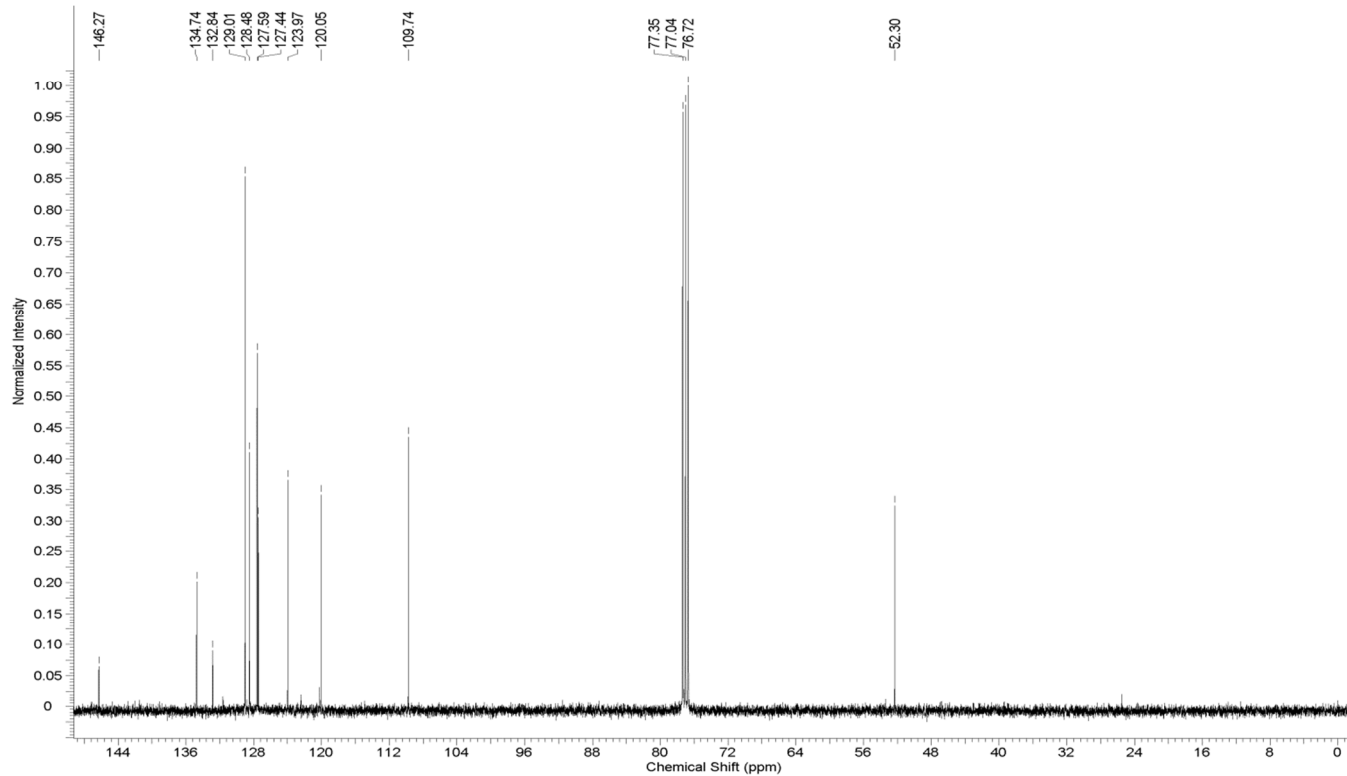


1-Benzyl-1H-benzo[d][1,2,3]triazole (5)

^1H NMR:

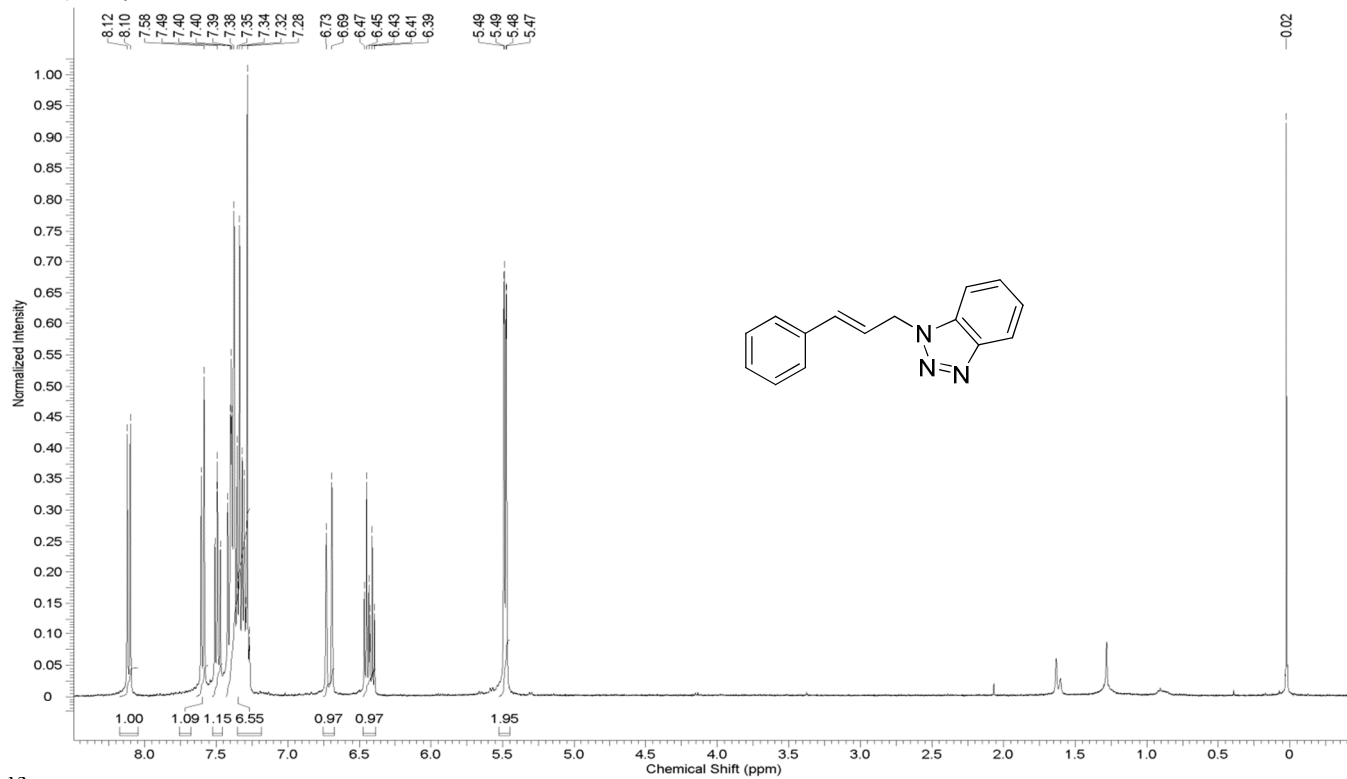


^{13}C NMR:

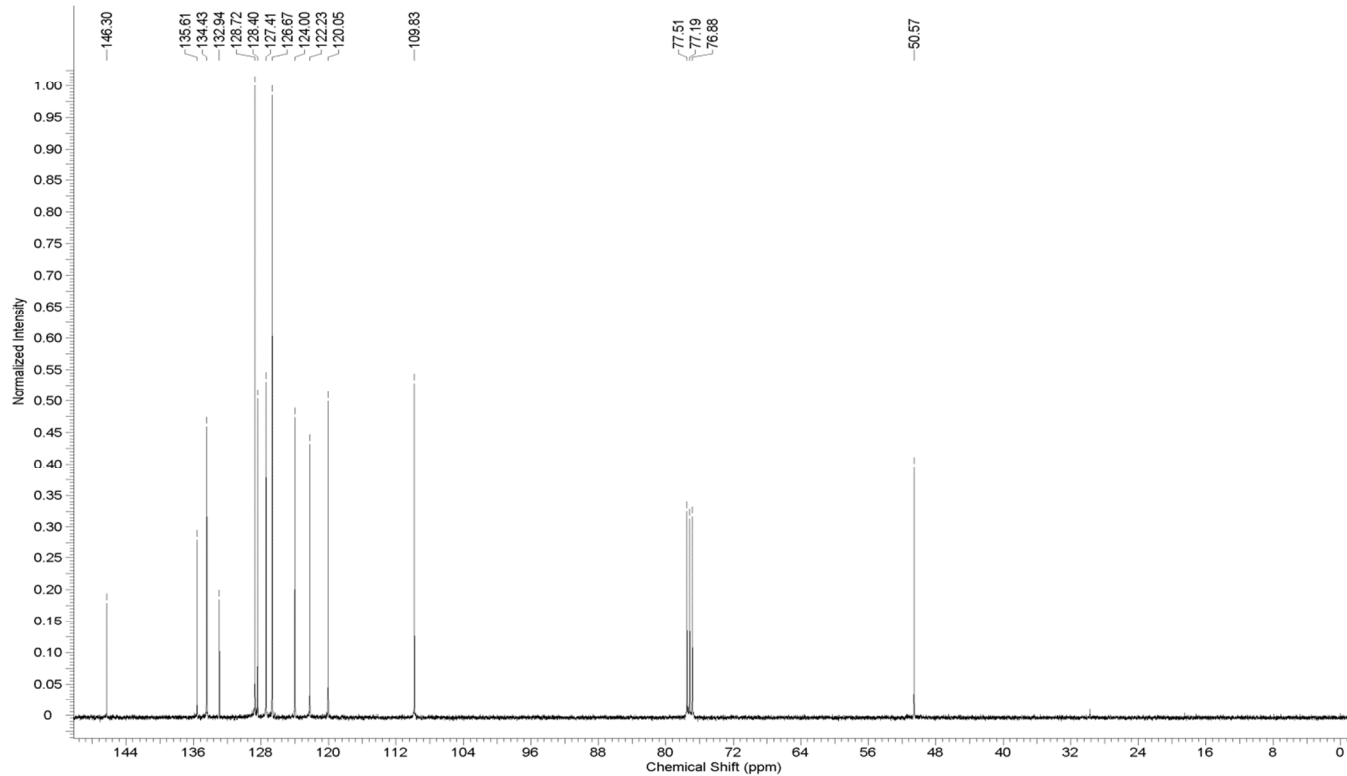


1-Cinnamyl-1H-benzo[d][1,2,3]triazole (6)

^1H NMR:

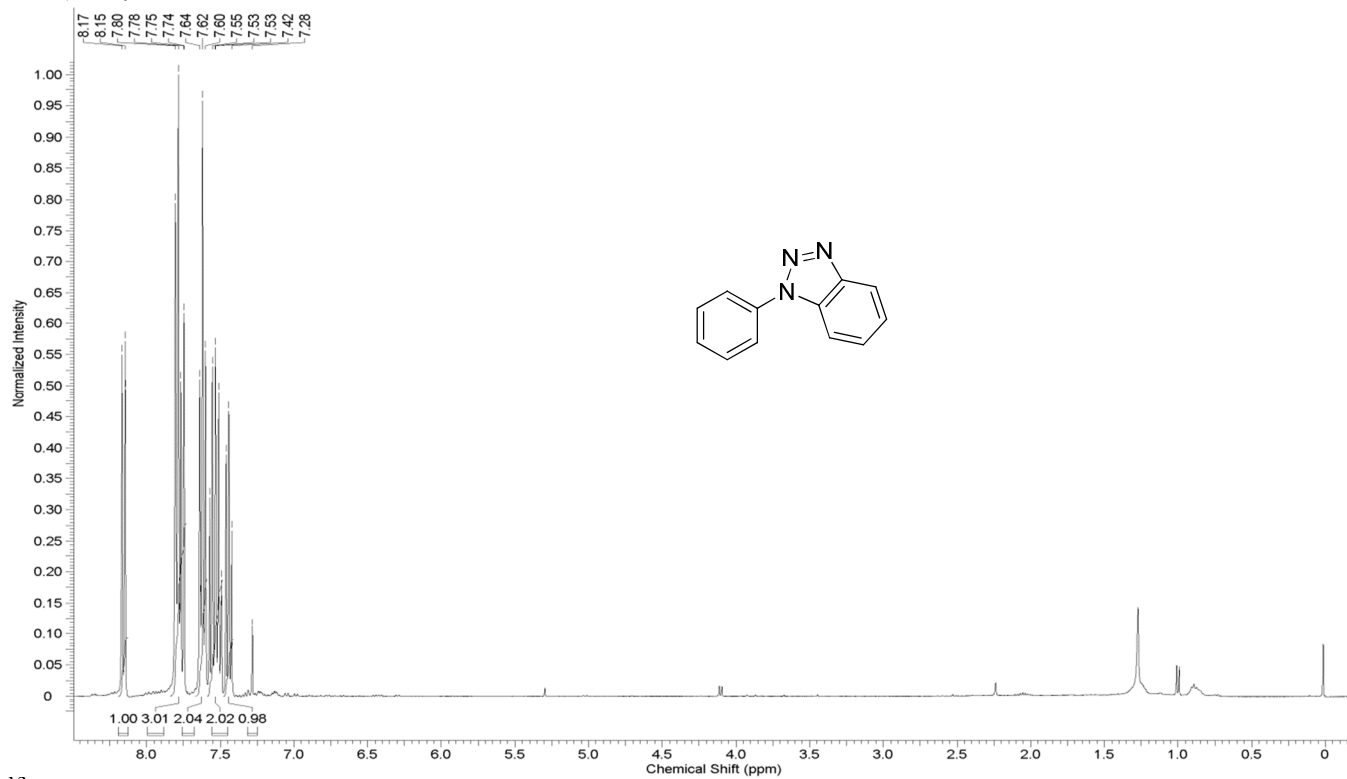


^{13}C NMR:

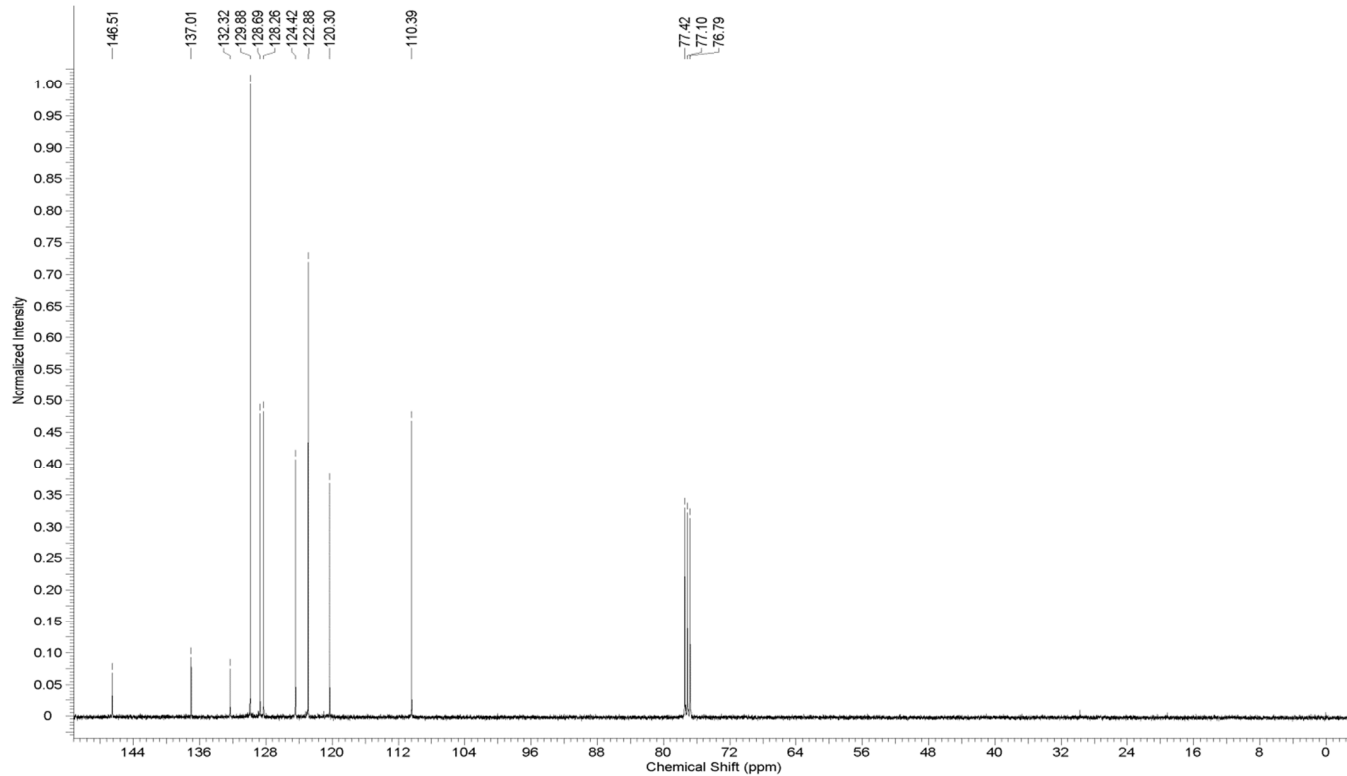


1-Phenyl-1H-benzo[d][1,2,3]triazole (7)

¹H NMR:

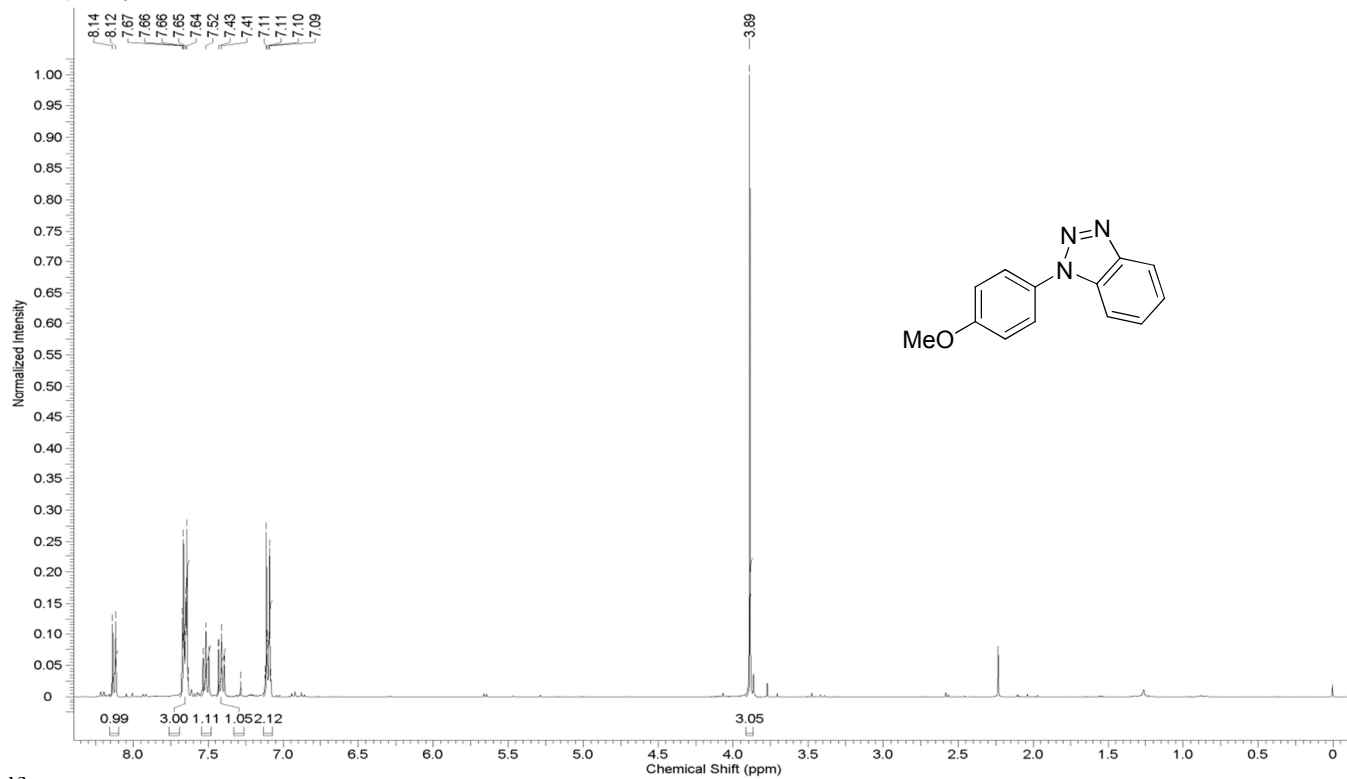


¹³C NMR:

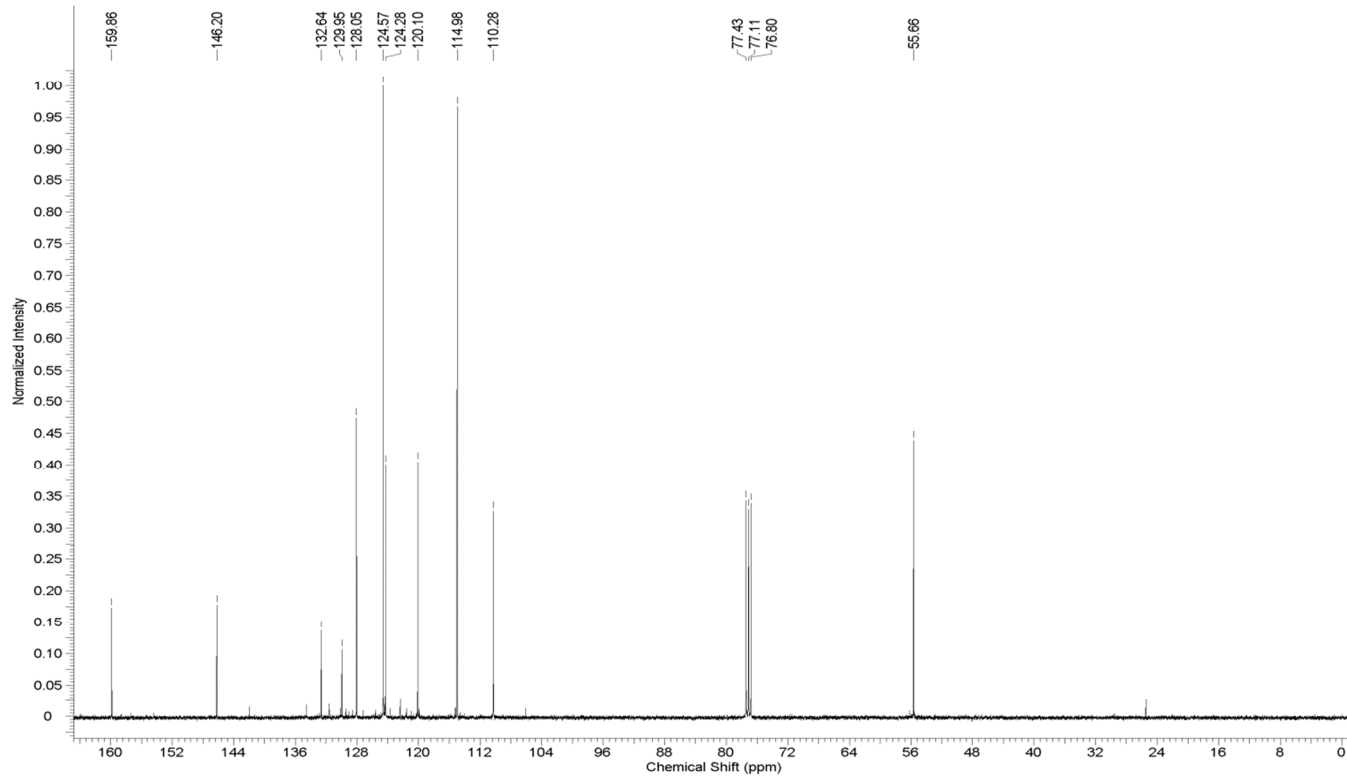


1-(4-Methoxyphenyl)-1H-benzo[d][1,2,3]triazole (8)

¹H NMR:

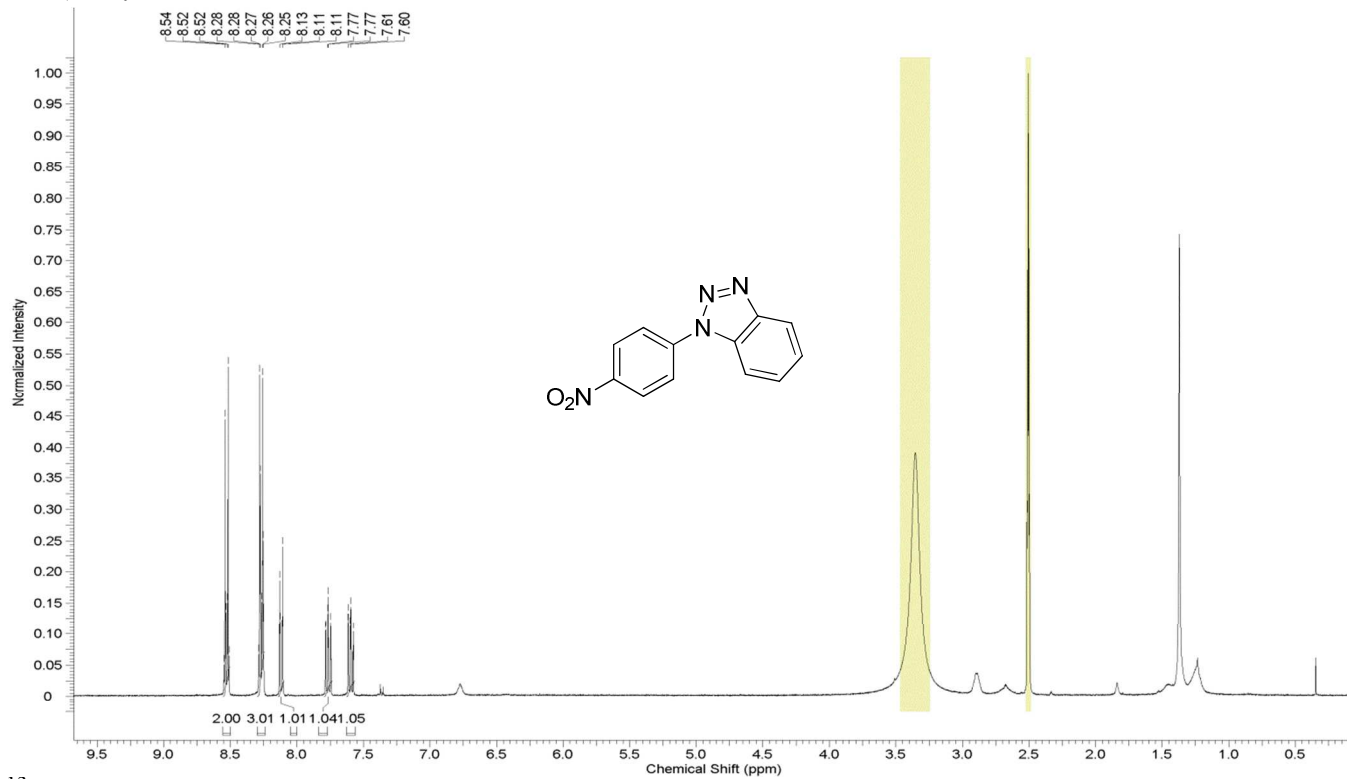


¹³C NMR:

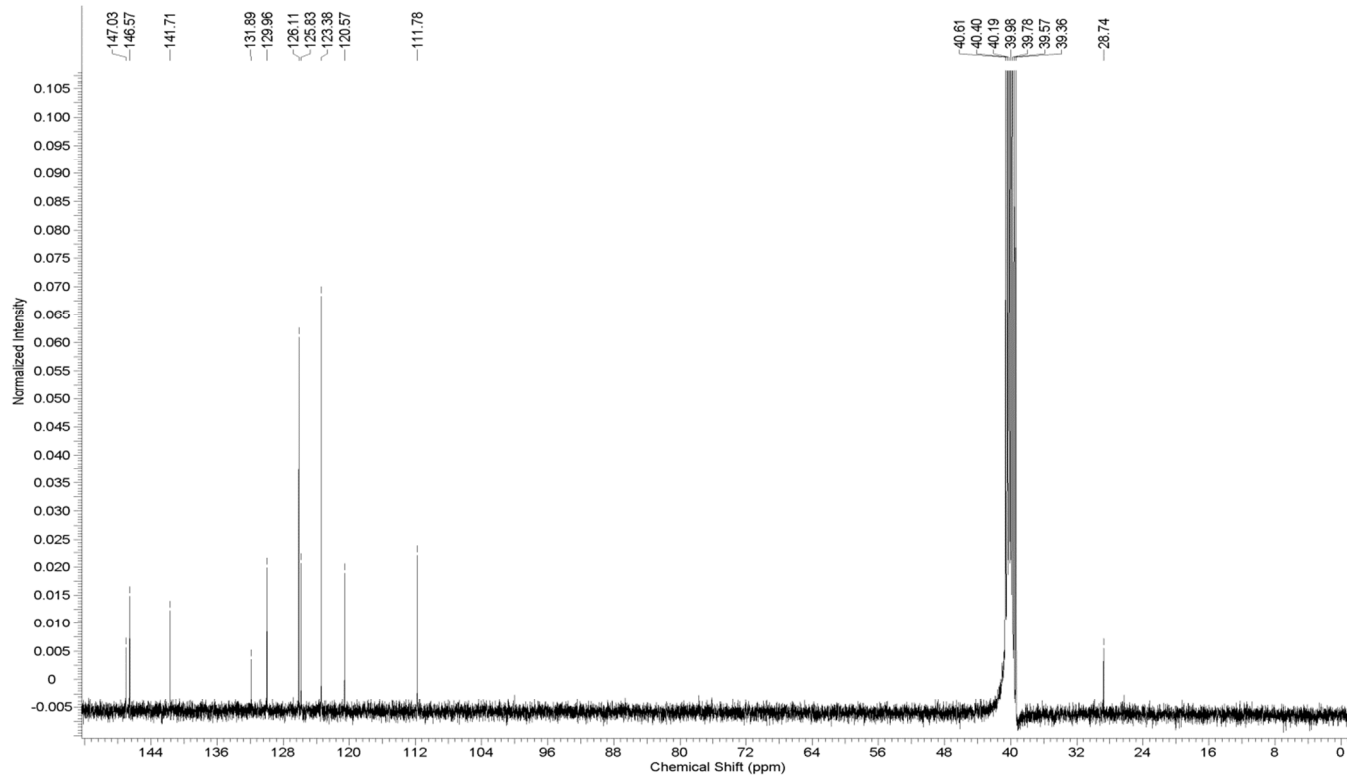


1-(4-Nitrophenyl)-1H-benzo[d][1,2,3]triazole (9)

^1H NMR:

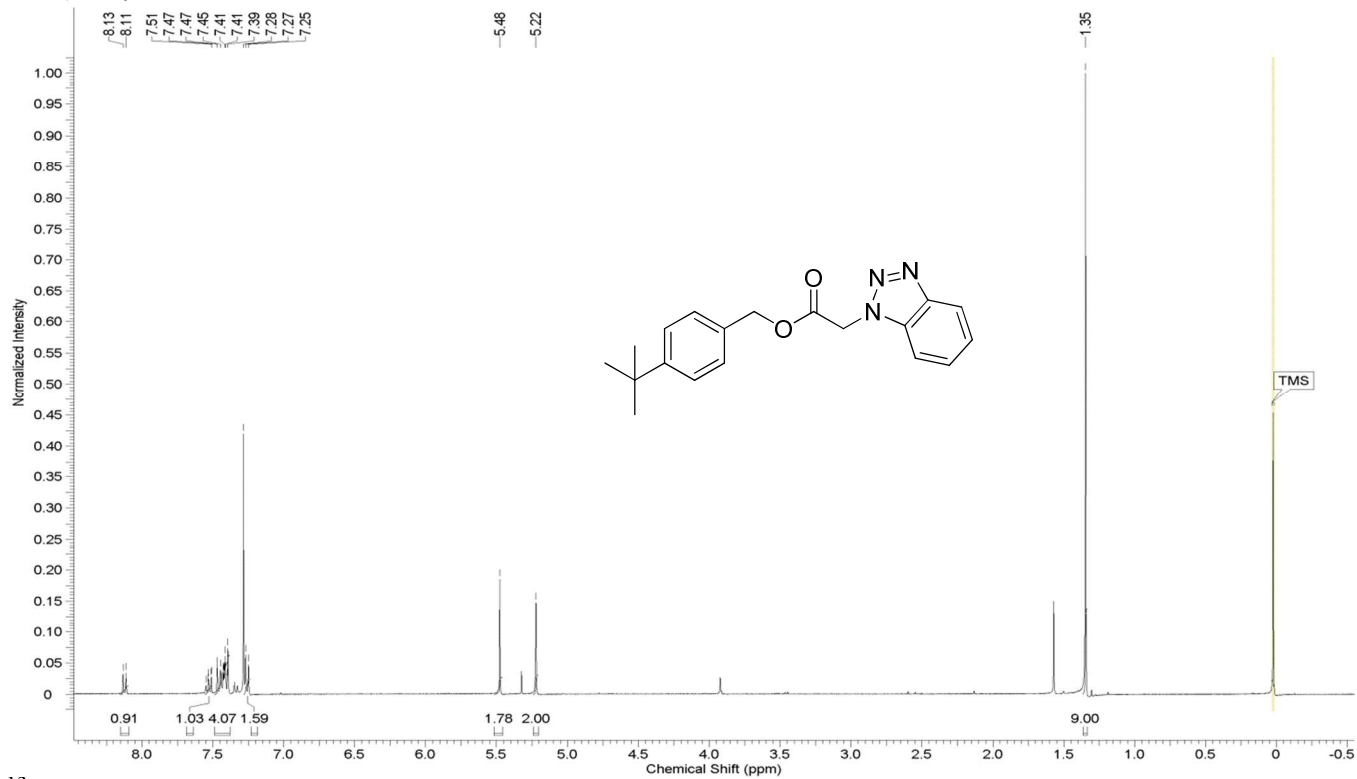


^{13}C NMR:

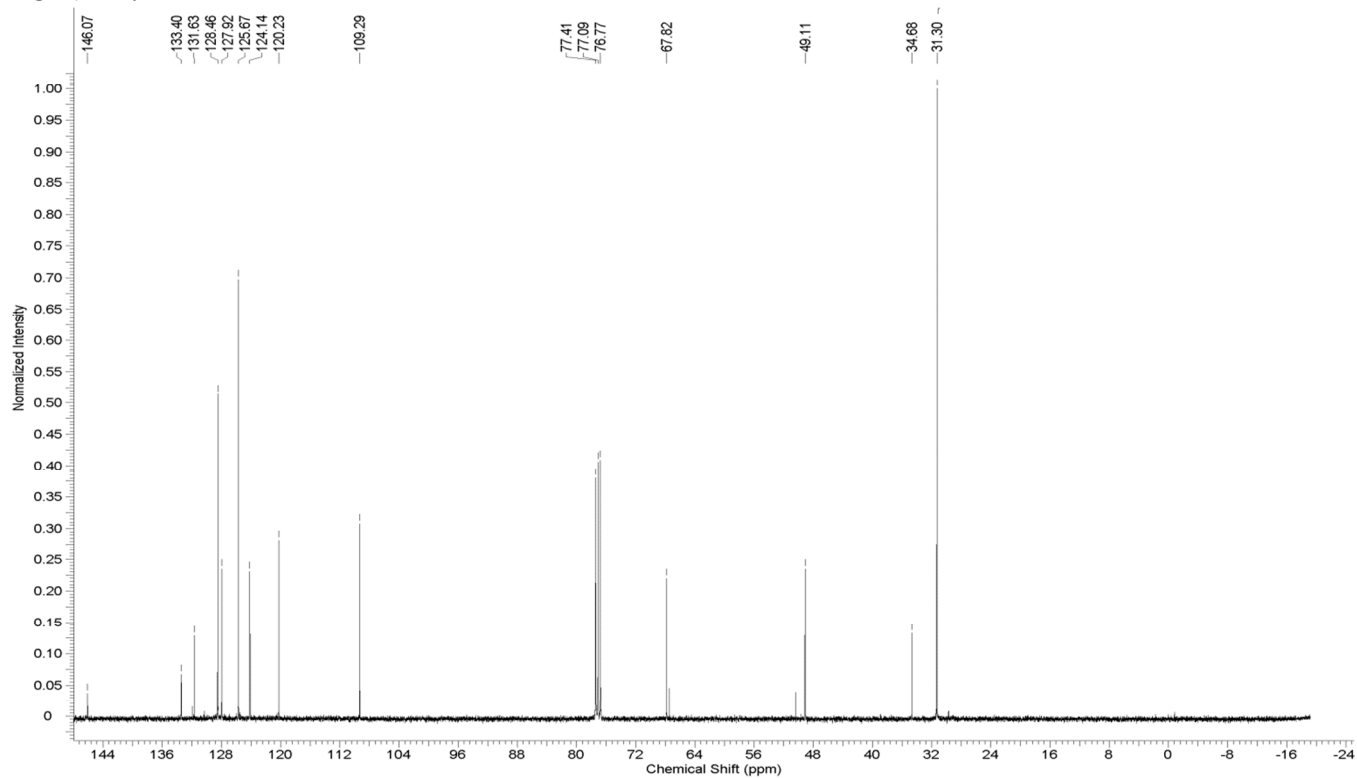


4-(tert-Butyl)benzyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)acetate (10)

¹H NMR:

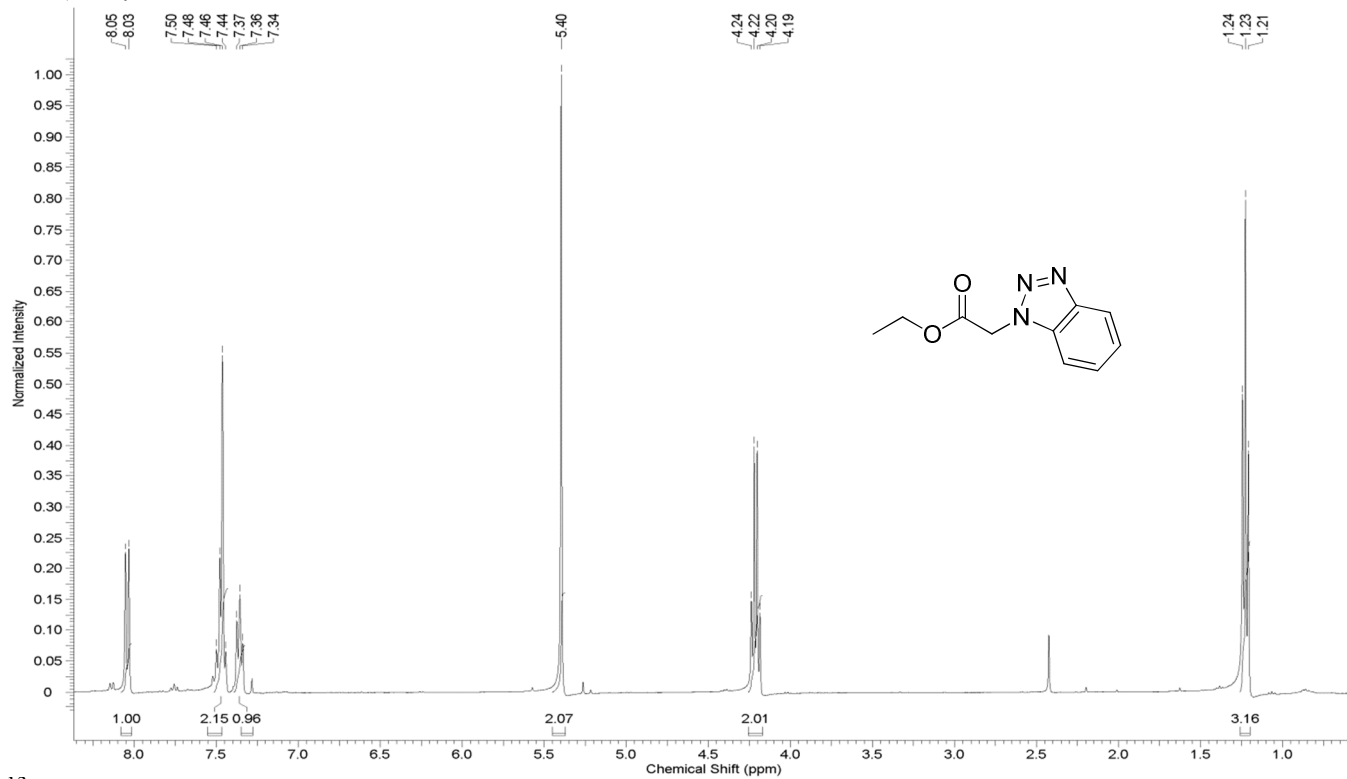


¹³C NMR:

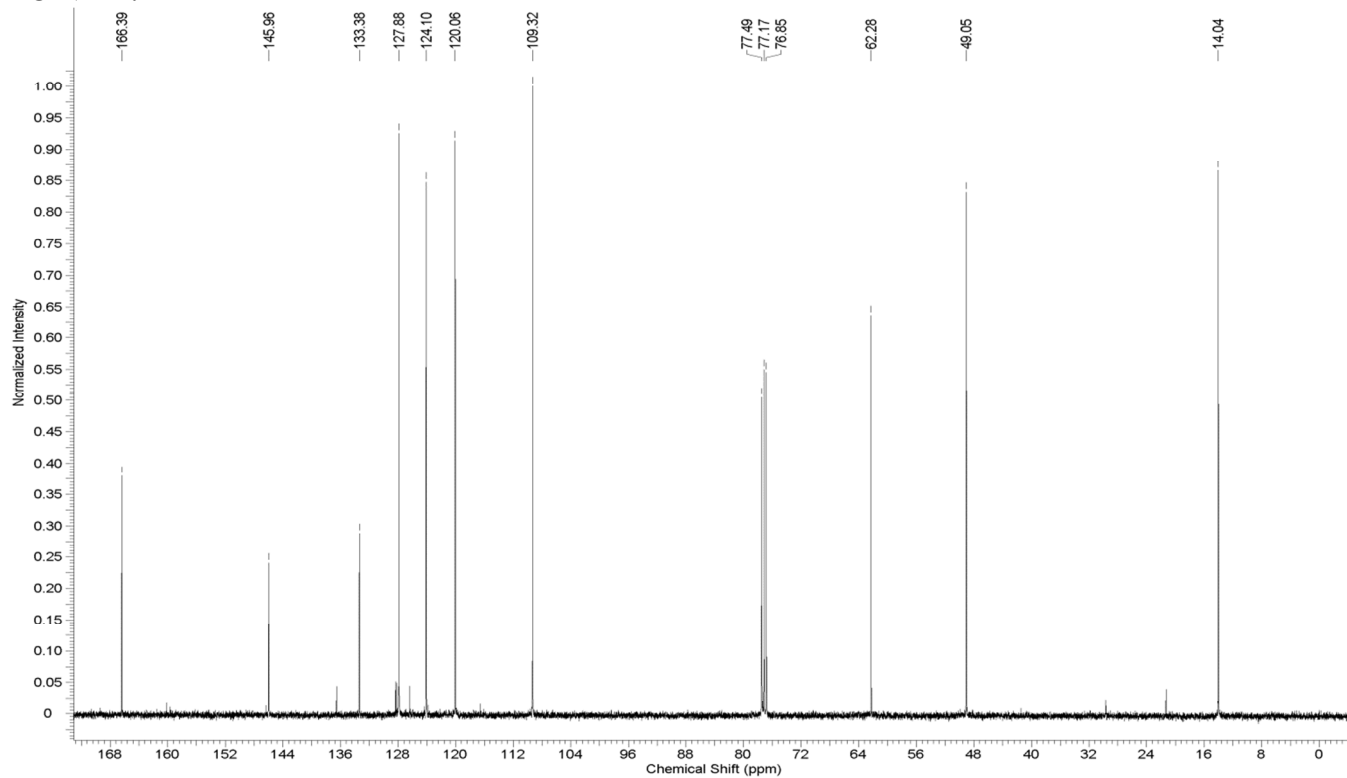


Ethyl 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)acetate (11)

¹H NMR:

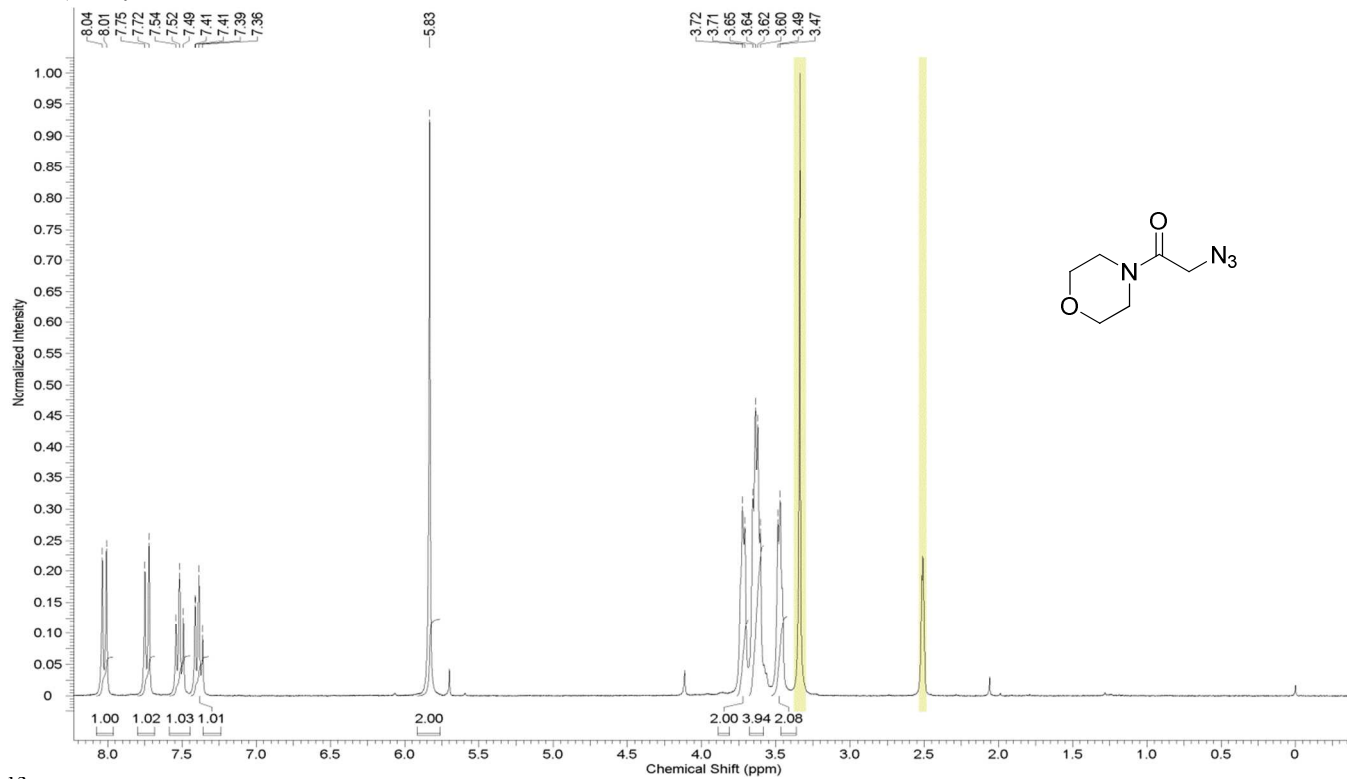


¹³C NMR:

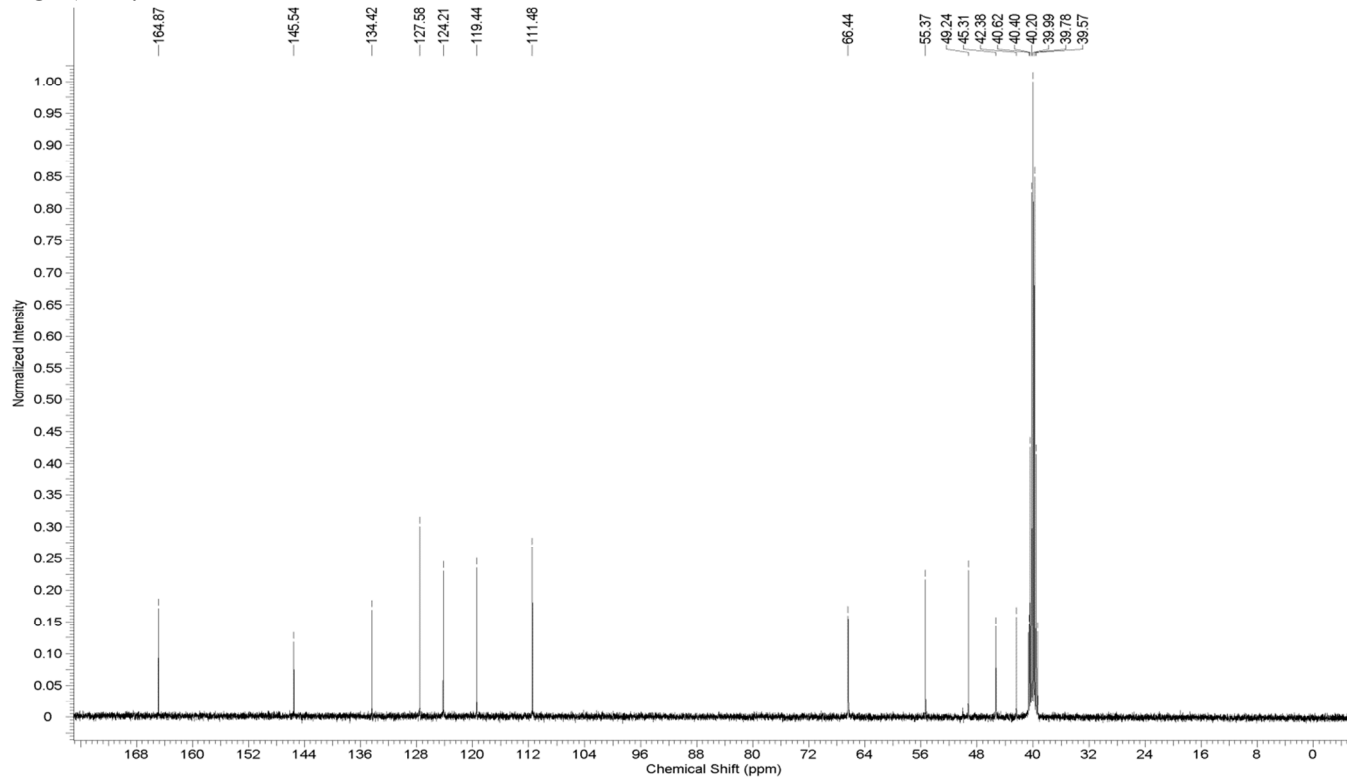


2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-morpholinoethanone (12)

¹H NMR:

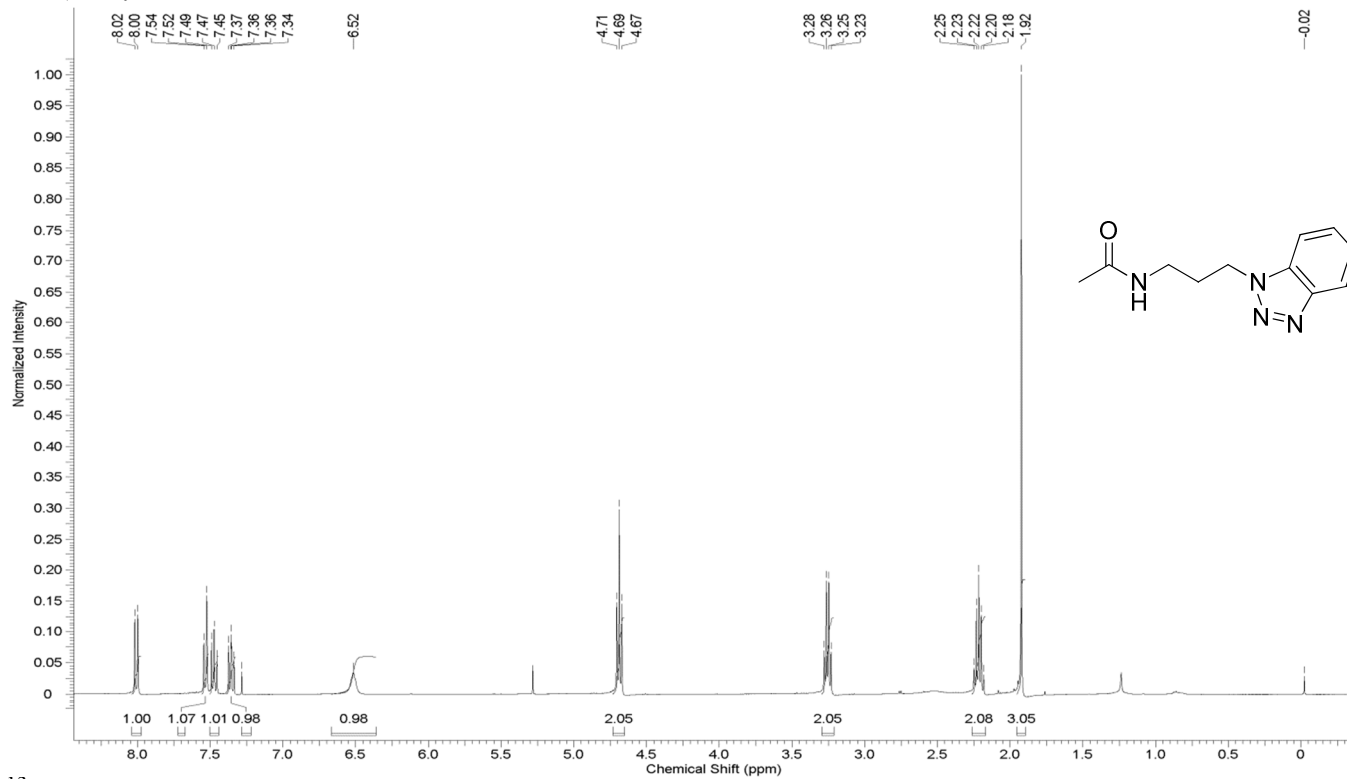


¹³C NMR:

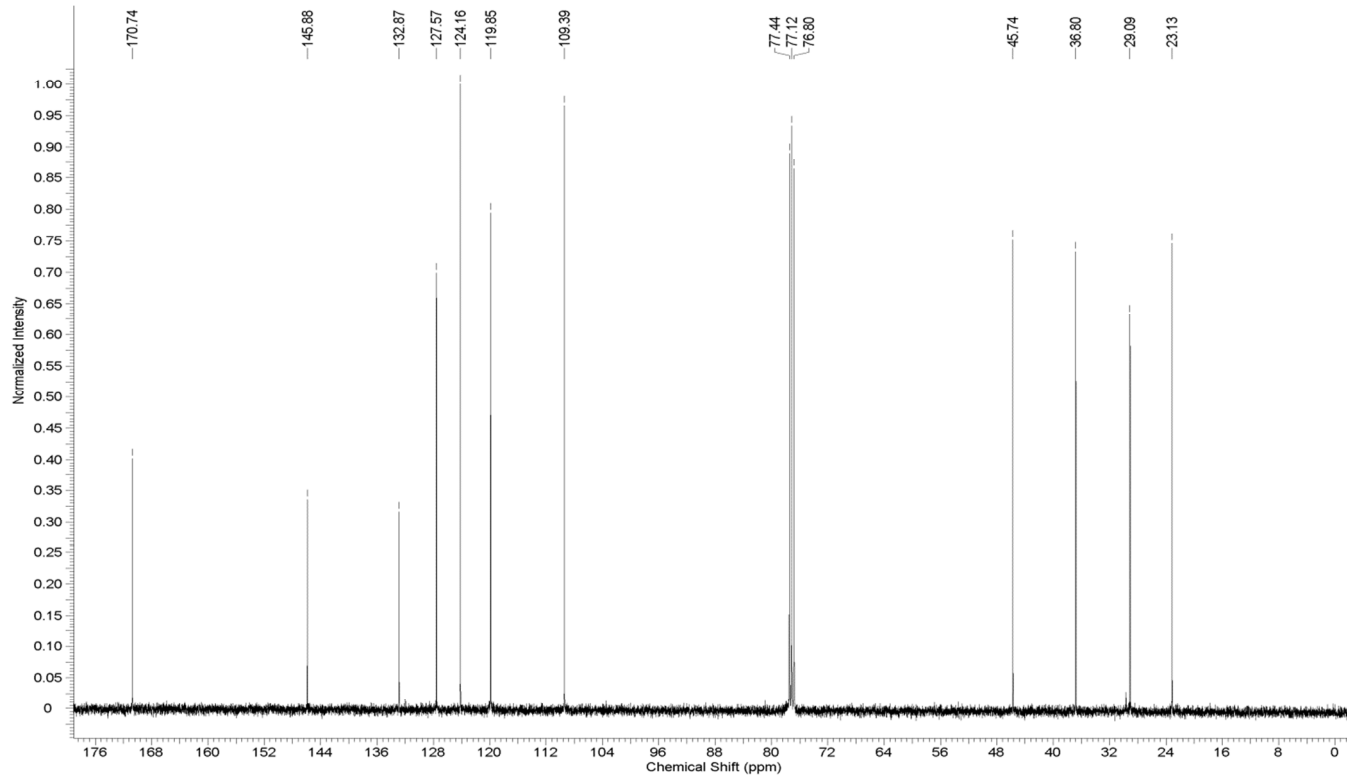


N-(3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)propyl)acetamide (13)

¹H NMR:

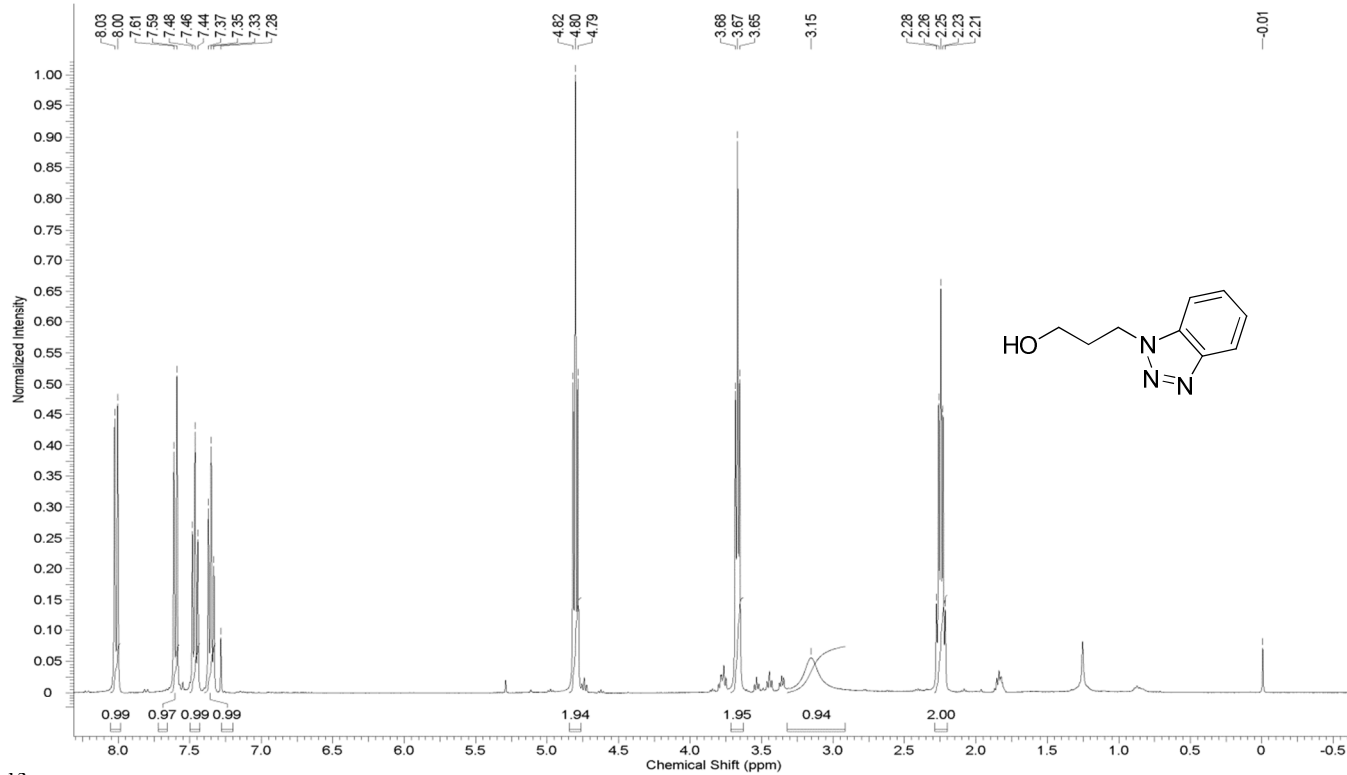


¹³C NMR:



3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)propan-1-ol (14)

¹H NMR:



¹³C NMR:

