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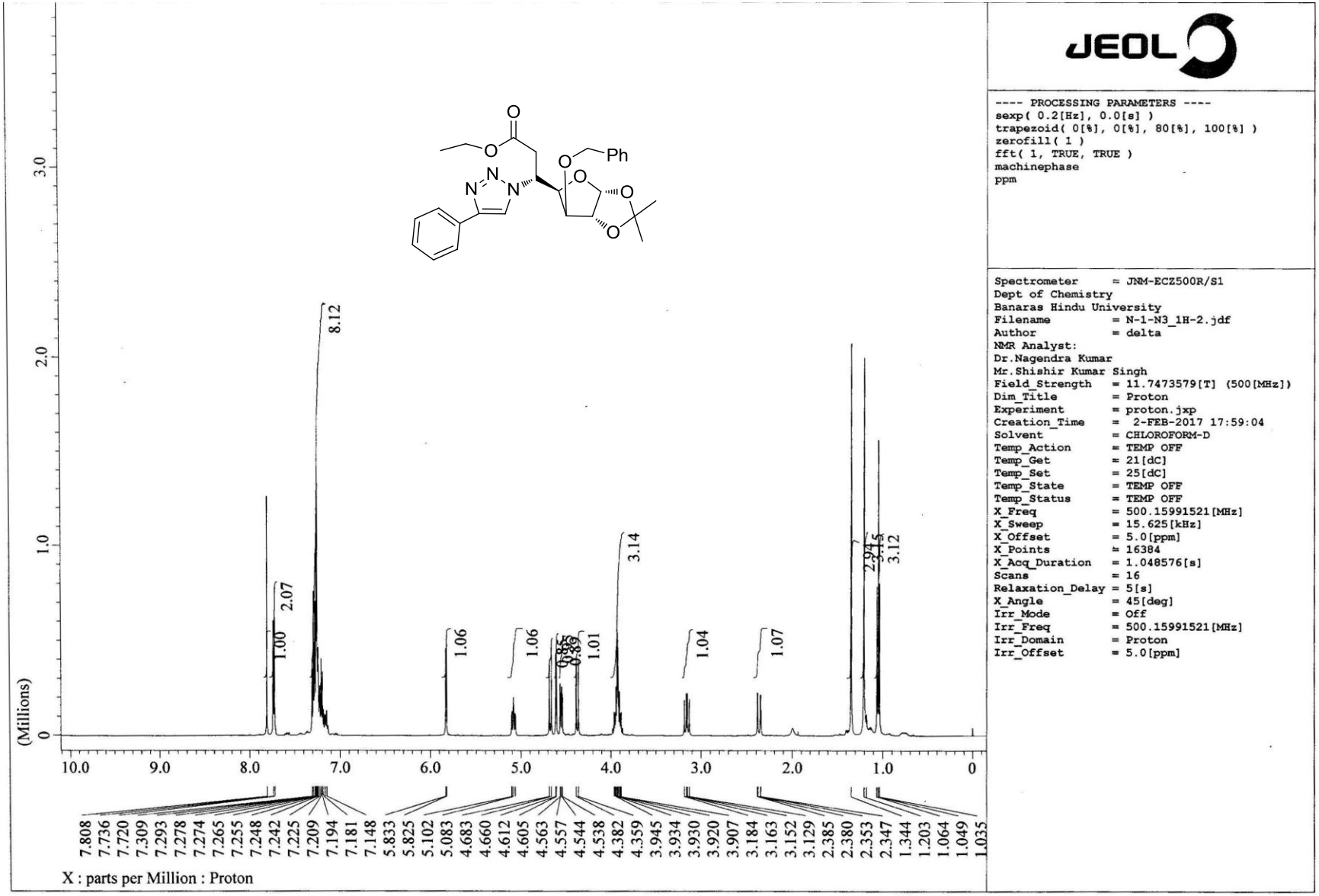
Catalyst loading and optimization study

For this, we first standardized the amount of complex $[(PPh_3)_2Cu(\mu\text{-tda})Cu(PPh_3)_2].6H_2O$ used in a prototype reaction, as shown in **Table S1**. Compound **4a** was formed in excellent yield in 18 hrs at room temperature at a low catalyst loading of 2 mol %. At 1 mol%, the product was isolated in 82 % yield (Table S1, entry 2). Further reducing the catalyst loading to 0.5 mol%, we were still able to achieve the click reaction, however, with somewhat reduced yield of 77% (Table S1, entry 3). Therefore, using 2 mol % as the optimum catalyst concentration, we further optimized the time-period at room temperature (Table S1, entries 5-9). The complex shows superb catalytic activity i.e. 2 mol % of catalyst **1** afforded **4a** in excellent yield (96 %) at room temperature, within 30 minutes (Table S1, entry 9). Interestingly, at the optimal catalyst loading of 2 mol %, our complex was able to catalyse the cycloaddition even in the absence of a base. The reagents were totally converted into product under base-free (Table S2, entry 12) as well as solvent-free conditions (Table S2, entry 13).

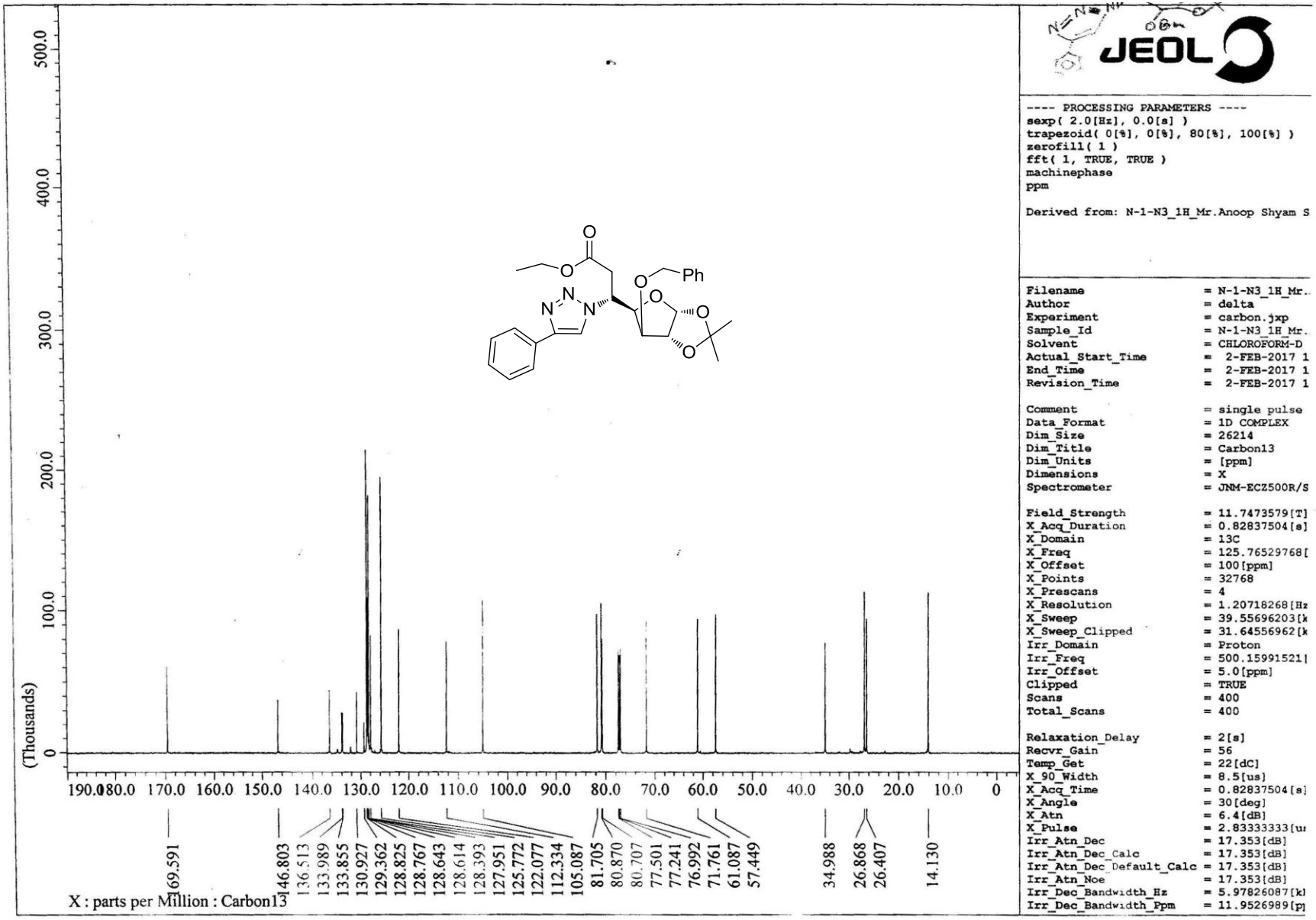
Table S1

Entry[a)]	Catalyst(mol%)	Temp(°C)	Time(h)	Yield(%)[b)]
1	2	r.t.	18	97
2	1	r.t.	18	82
3	0.5	r.t.	18	77
4	0	r.t.	18	Trace
5	2	r.t.	7	97
6	2	r.t.	3	91
7	2	r.t.	2	97
8	2	r.t.	1	95
9	2	r.t.	0.5	96
10	---[c]	r.t.	0.5	93
11	---[d]	r.t.	0.5	89
12[e]	2	r.t.	0.5	97
13[f]	2	r.t.	0.5	96
14[g]	2	r.t.	10 min	93

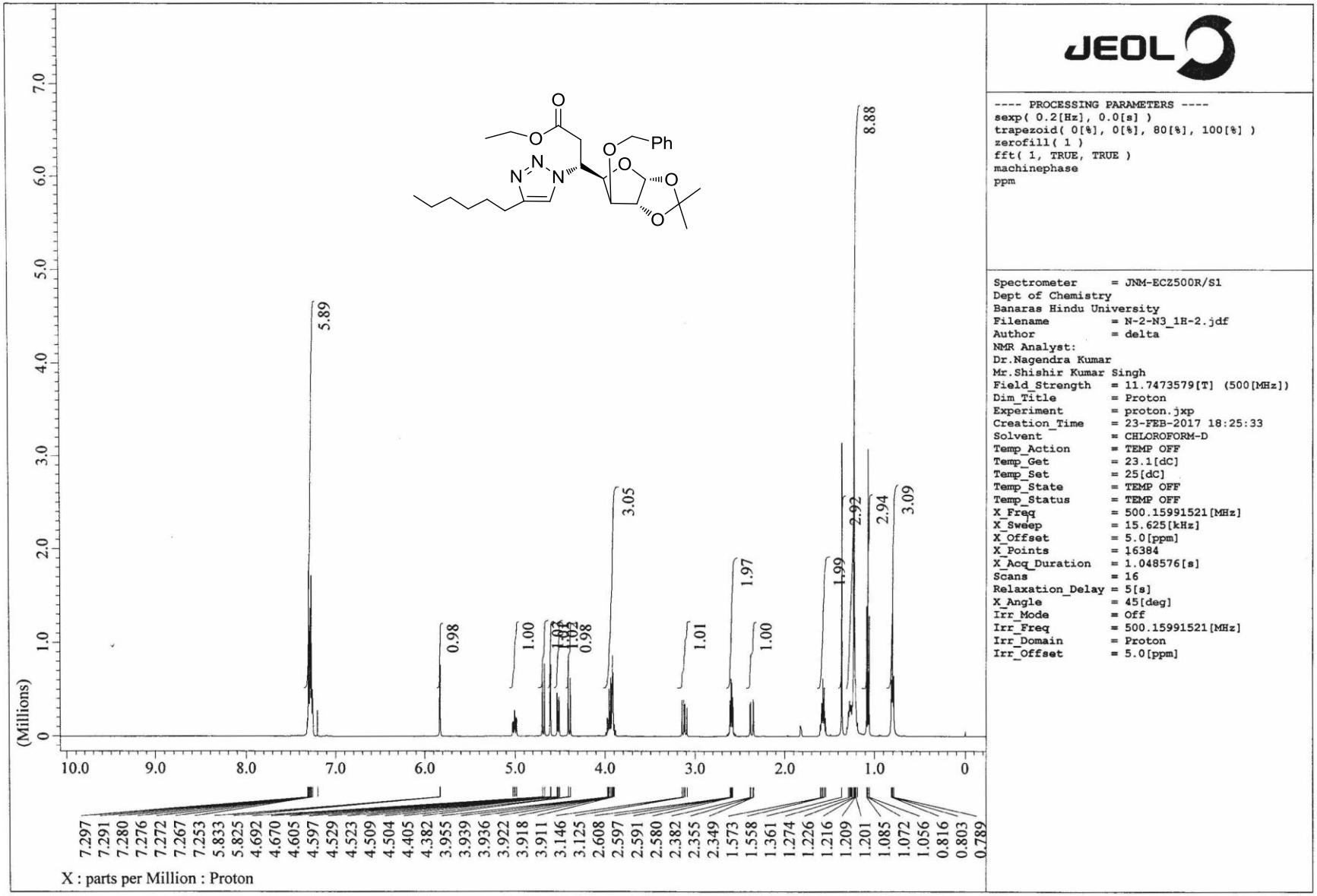
[a)]Molar ratio: 2a (1 equiv.), 3a (1.2 equiv.), DIPEA (0.1 equiv.), DCM (2mL). [b)]Yields reported after purification by column chromatography. [c)]Catalyst recovered from entry 1. [d)]Catalyst recovered from entry 2 [e)]reaction without base. [f)] reaction without solvent. [g)] reaction in neat conditions.



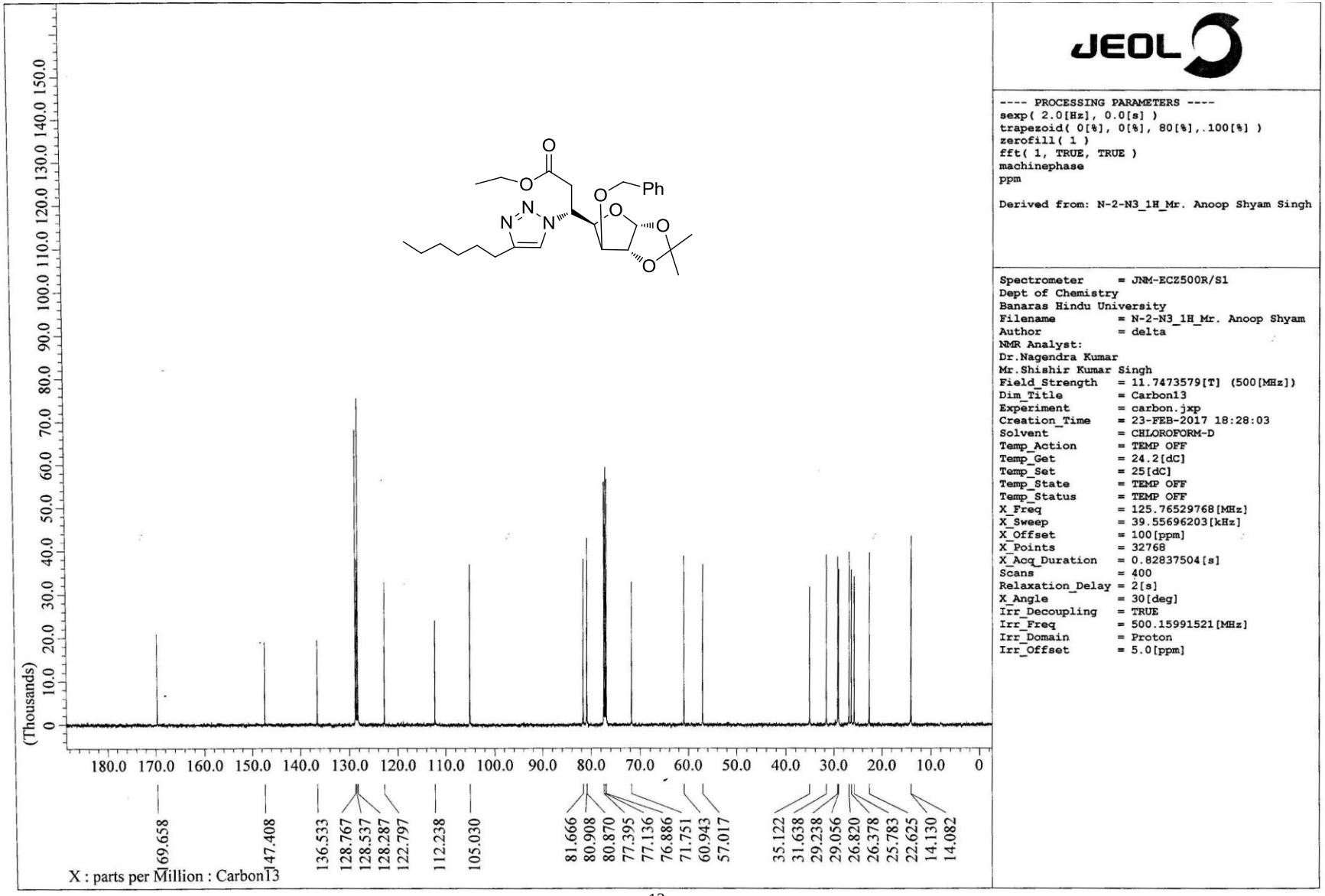
Spectrum 1: 500 MHz ^{1}H NMR of compound **4a**



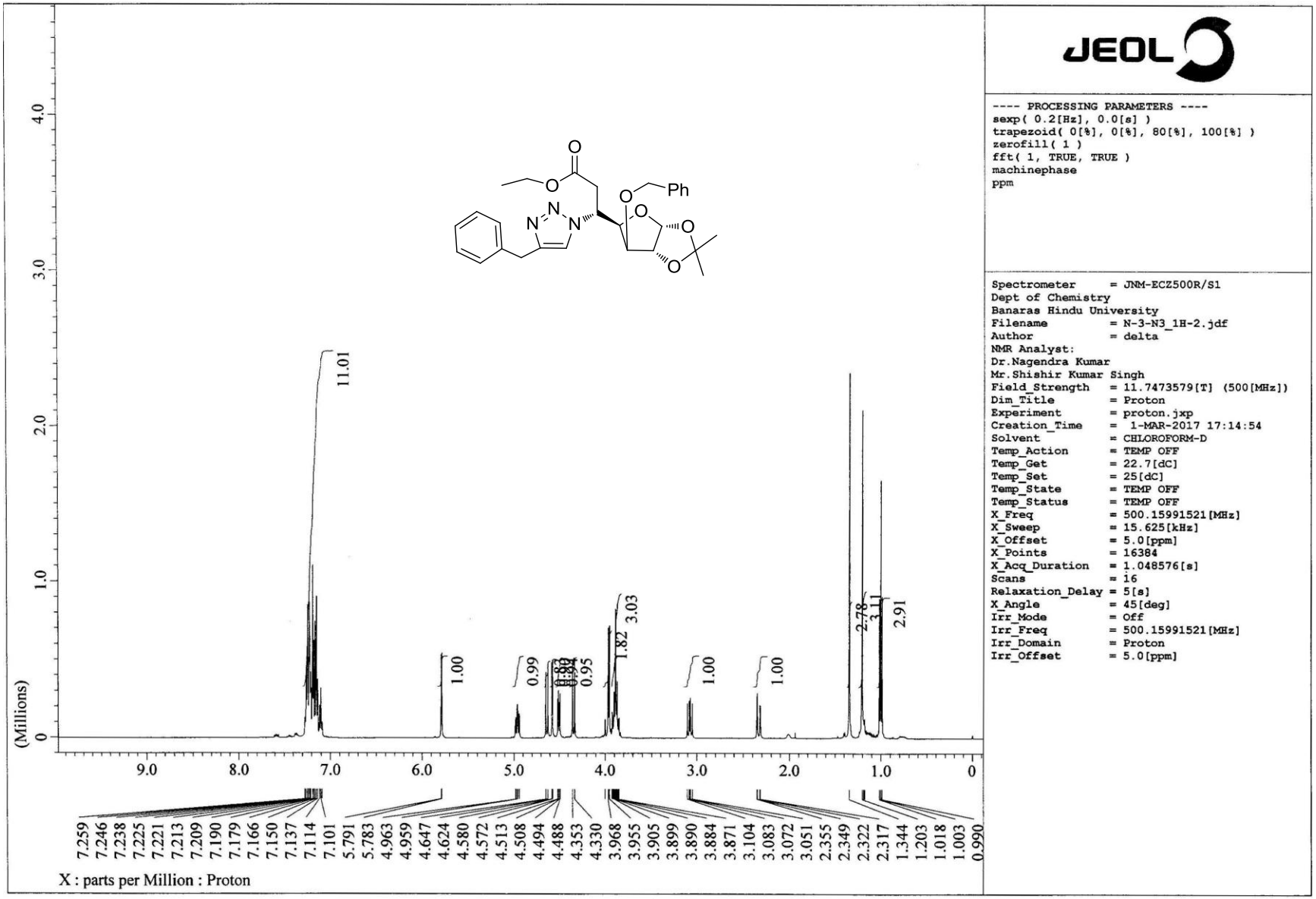
Spectrum 2: 125 MHz ^{13}C NMR of compound **4a**



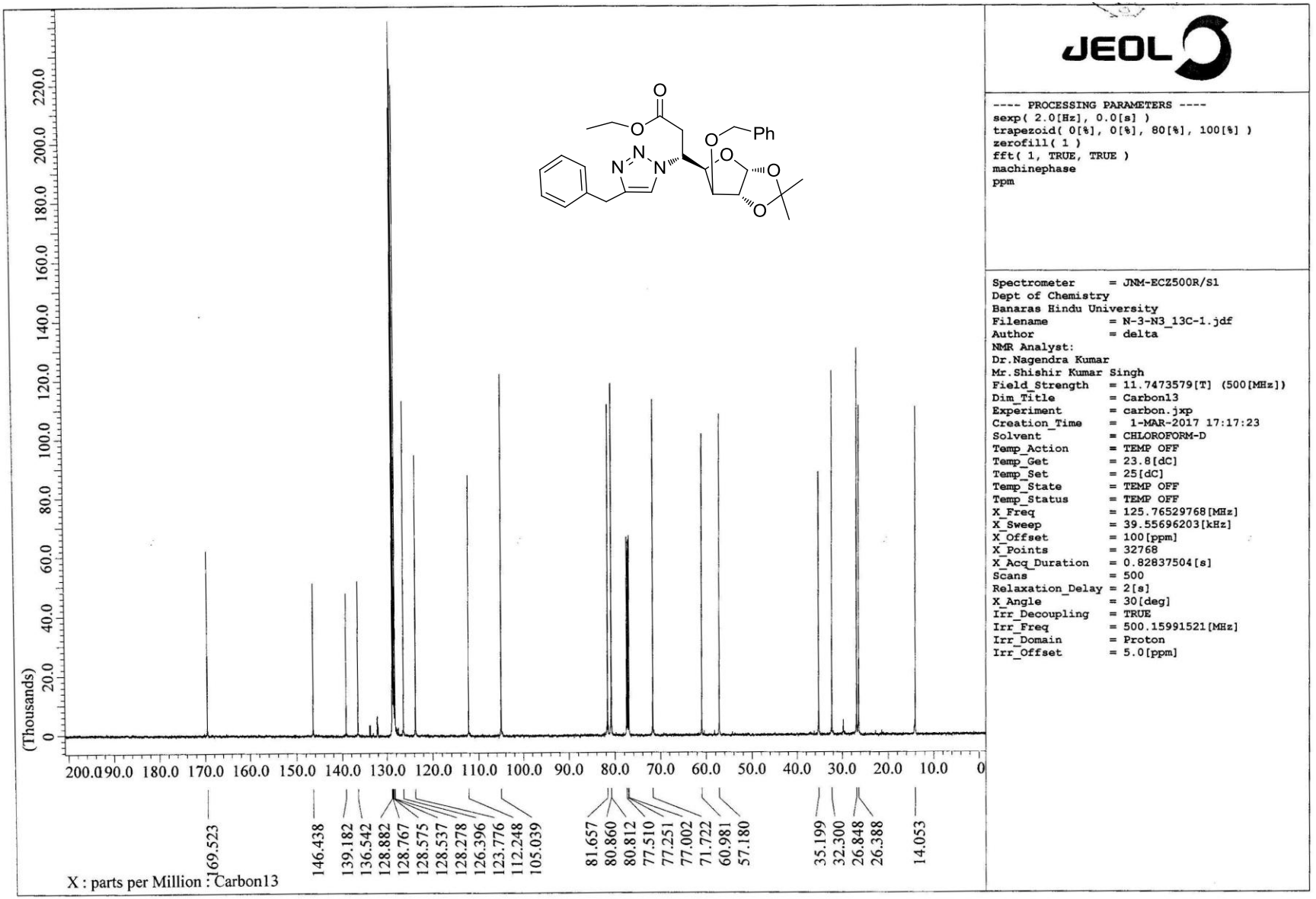
Spectrum 3: 500 MHz ^{1}H NMR of compound **4b**



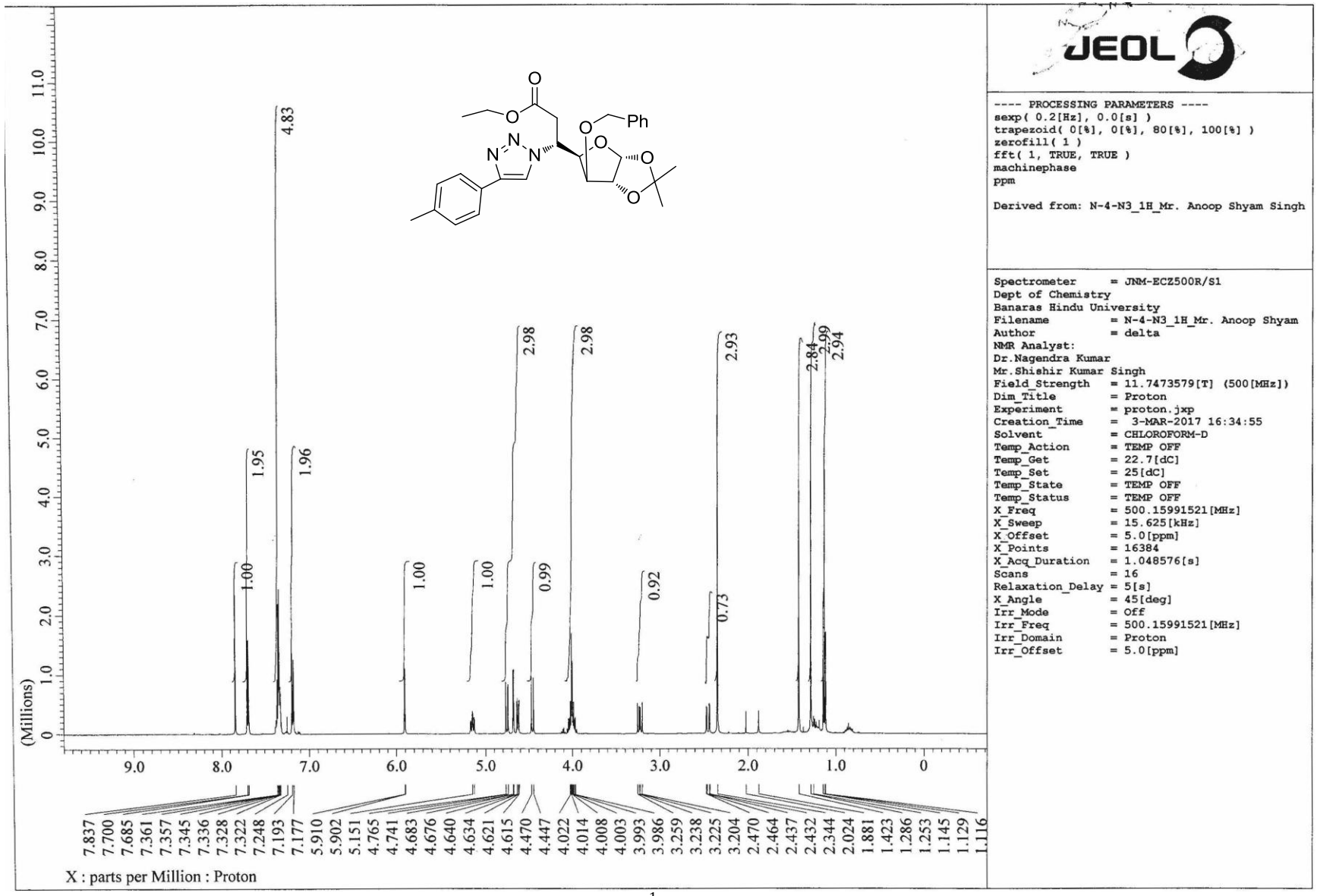
Spectrum 4: 125 MHz ^{13}C NMR of compound **4b**



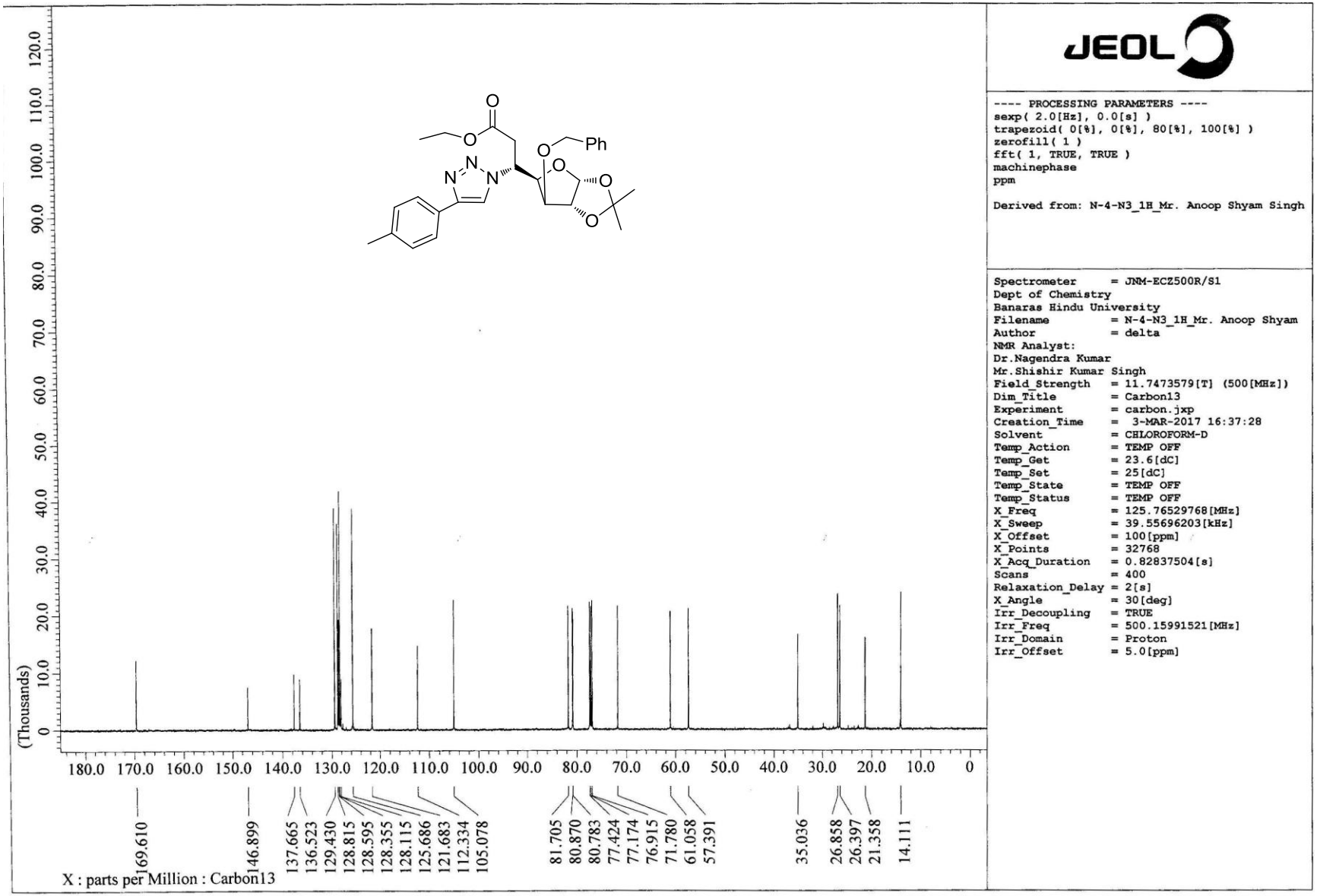
Spectrum 5: 500 MHz ^{1}H NMR of compound **4c**



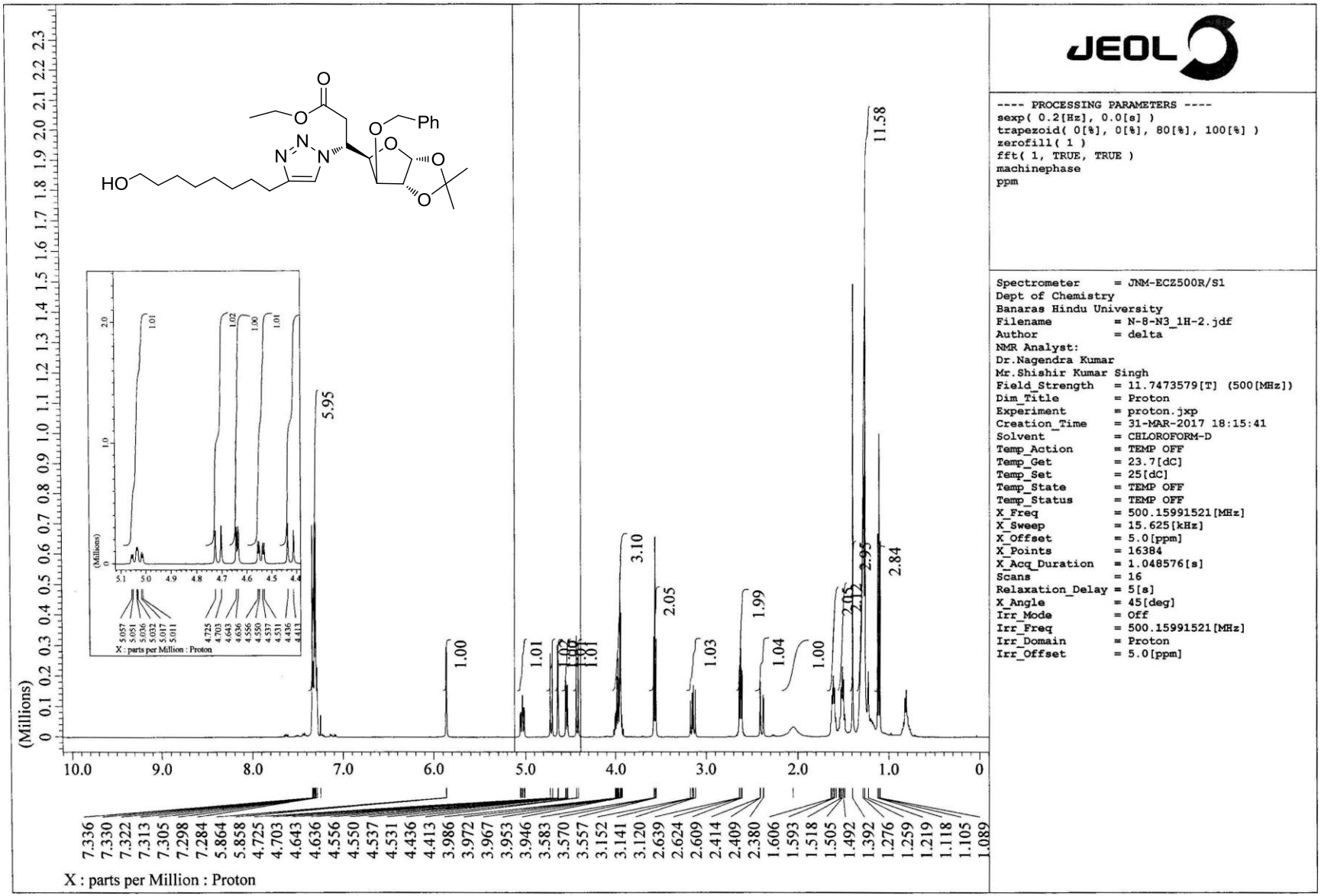
Spectrum 6: 125 MHz ^{13}C NMR of compound **4c**



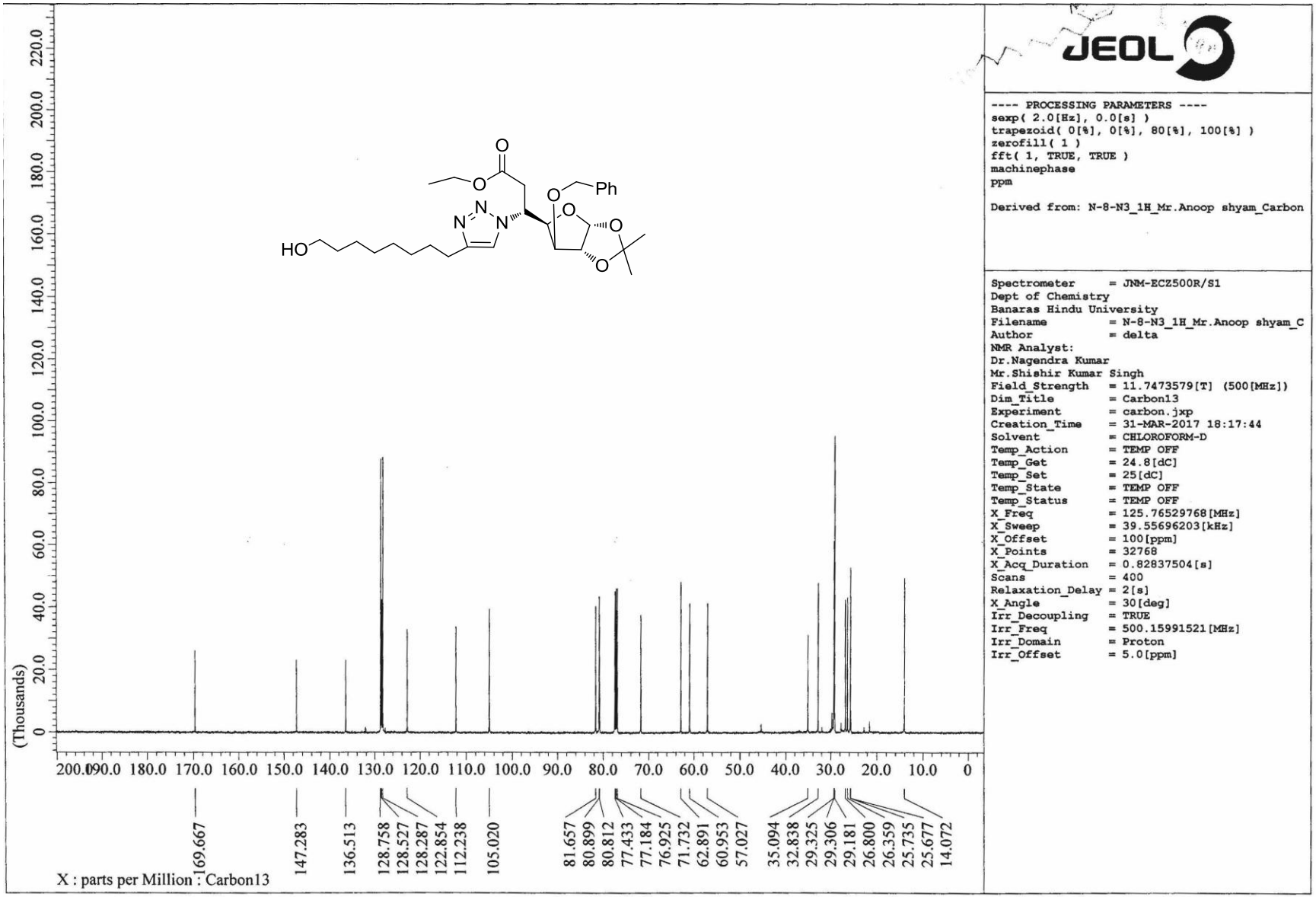
Spectrum 7: 500 MHz ^{1}H NMR of compound **4d**



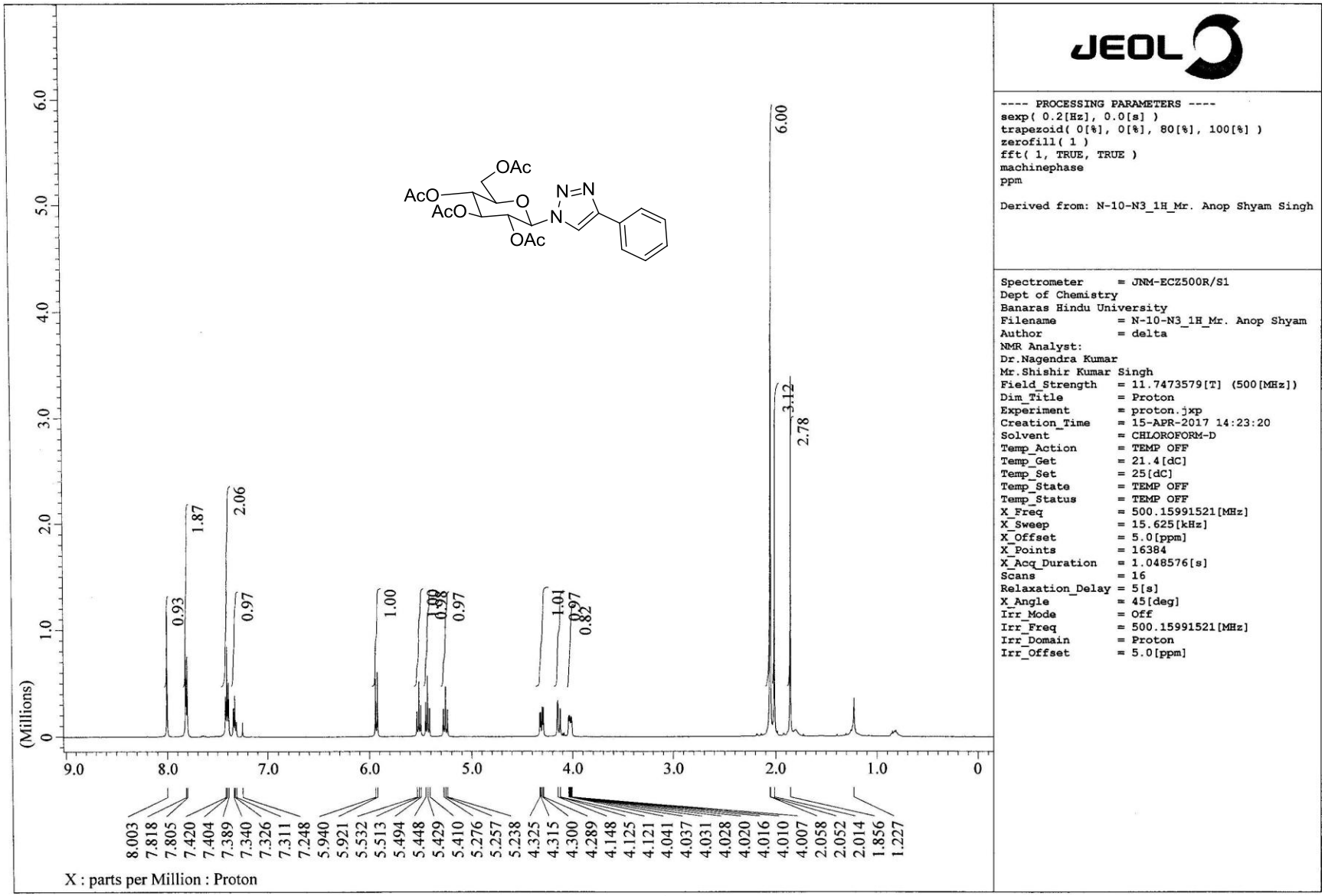
Spectrum 8: 125 MHz ^{13}C NMR of compound **4d**



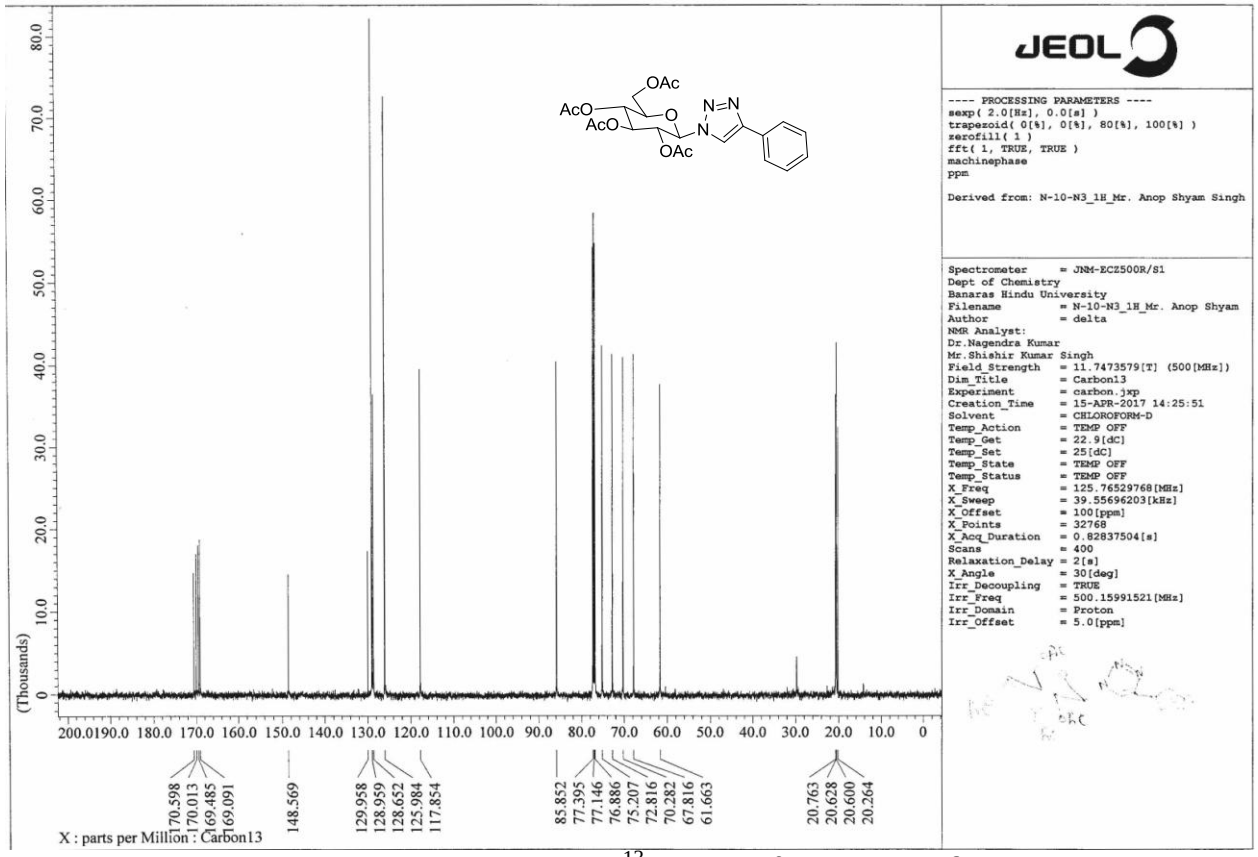
Spectrum 9: 500 MHz ^{1}H NMR of compound **4e**



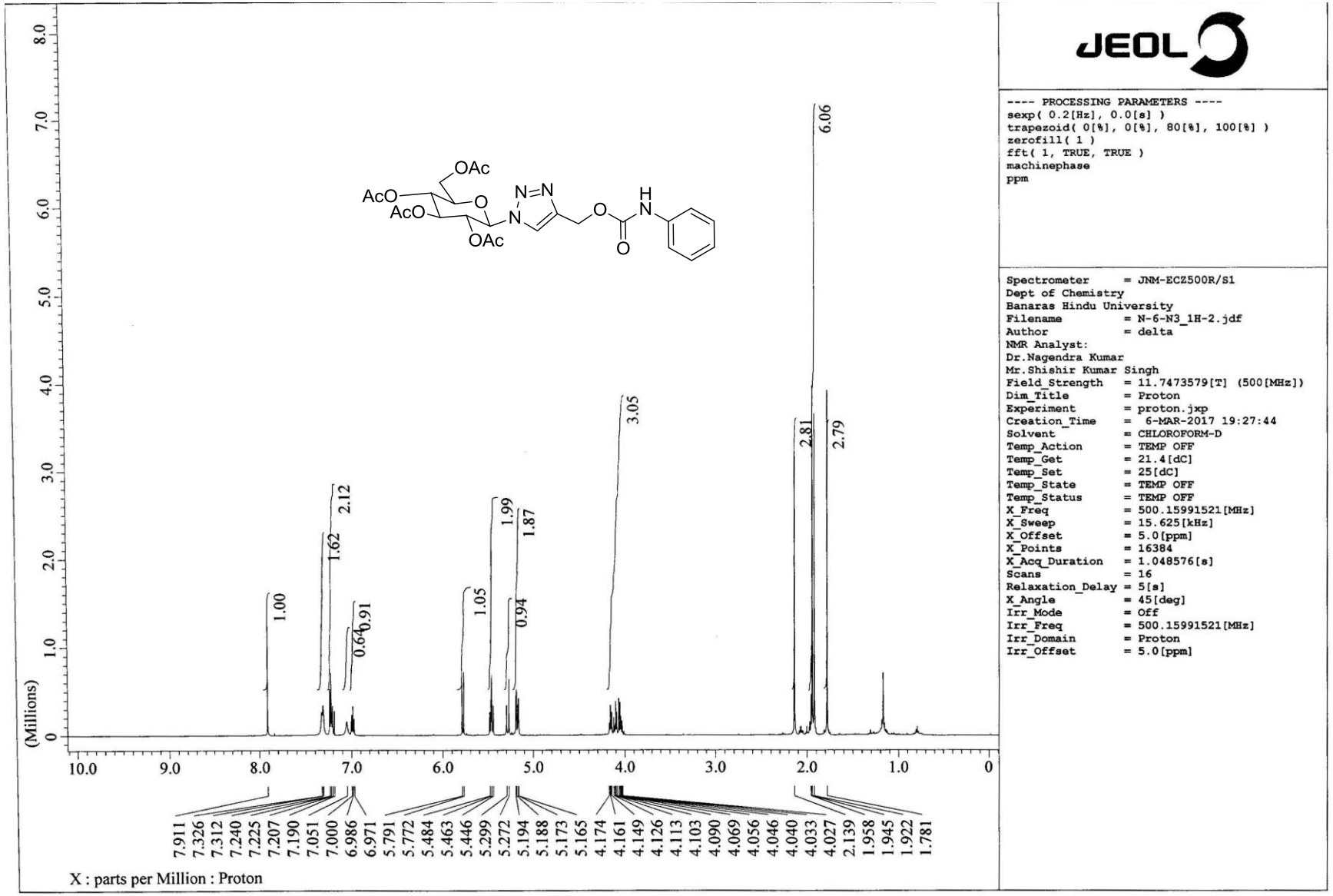
Spectrum 10: 125 MHz ^{13}C NMR of compound **4e**



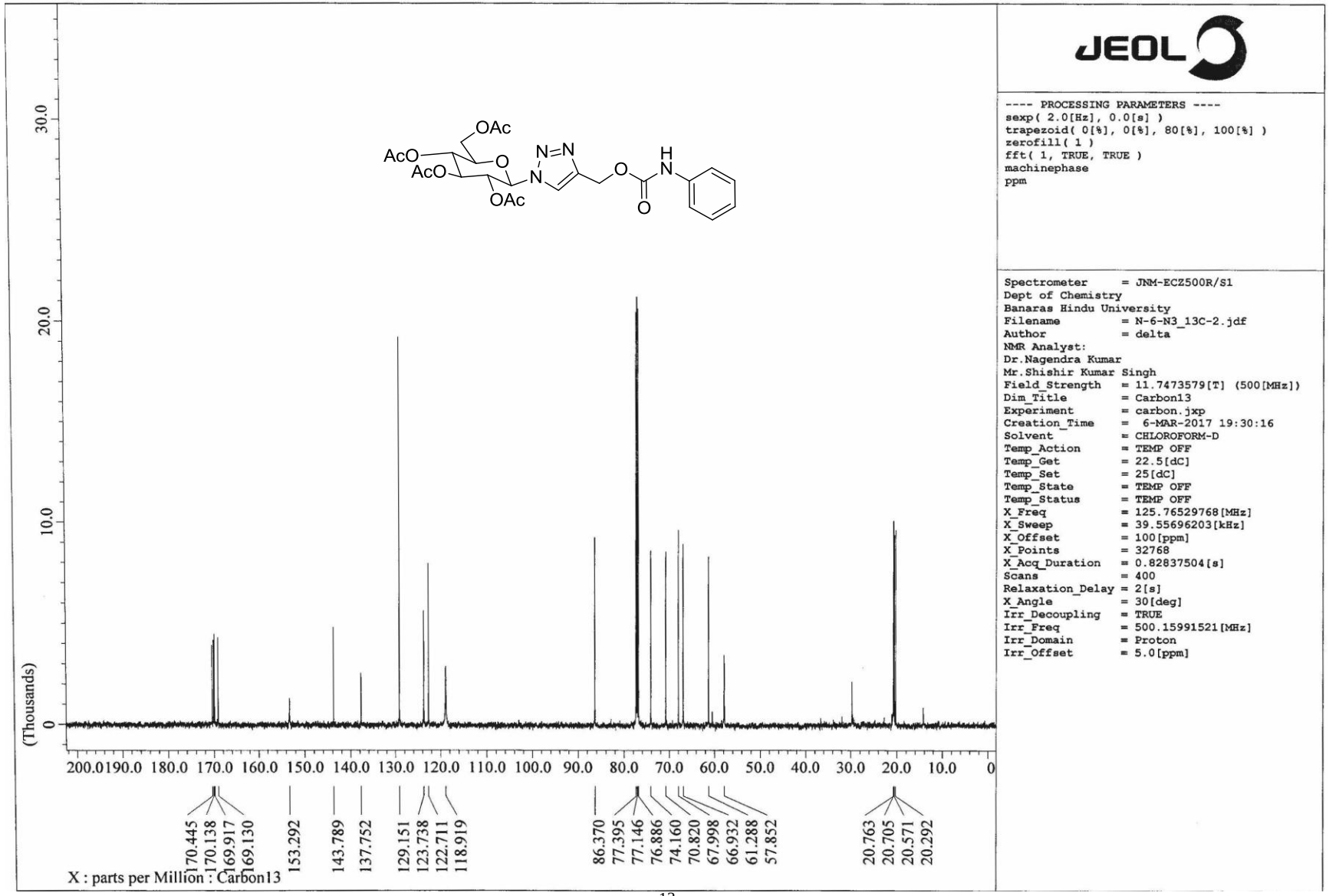
Spectrum 11: 500 MHz ^{1}H NMR of compound **4f**



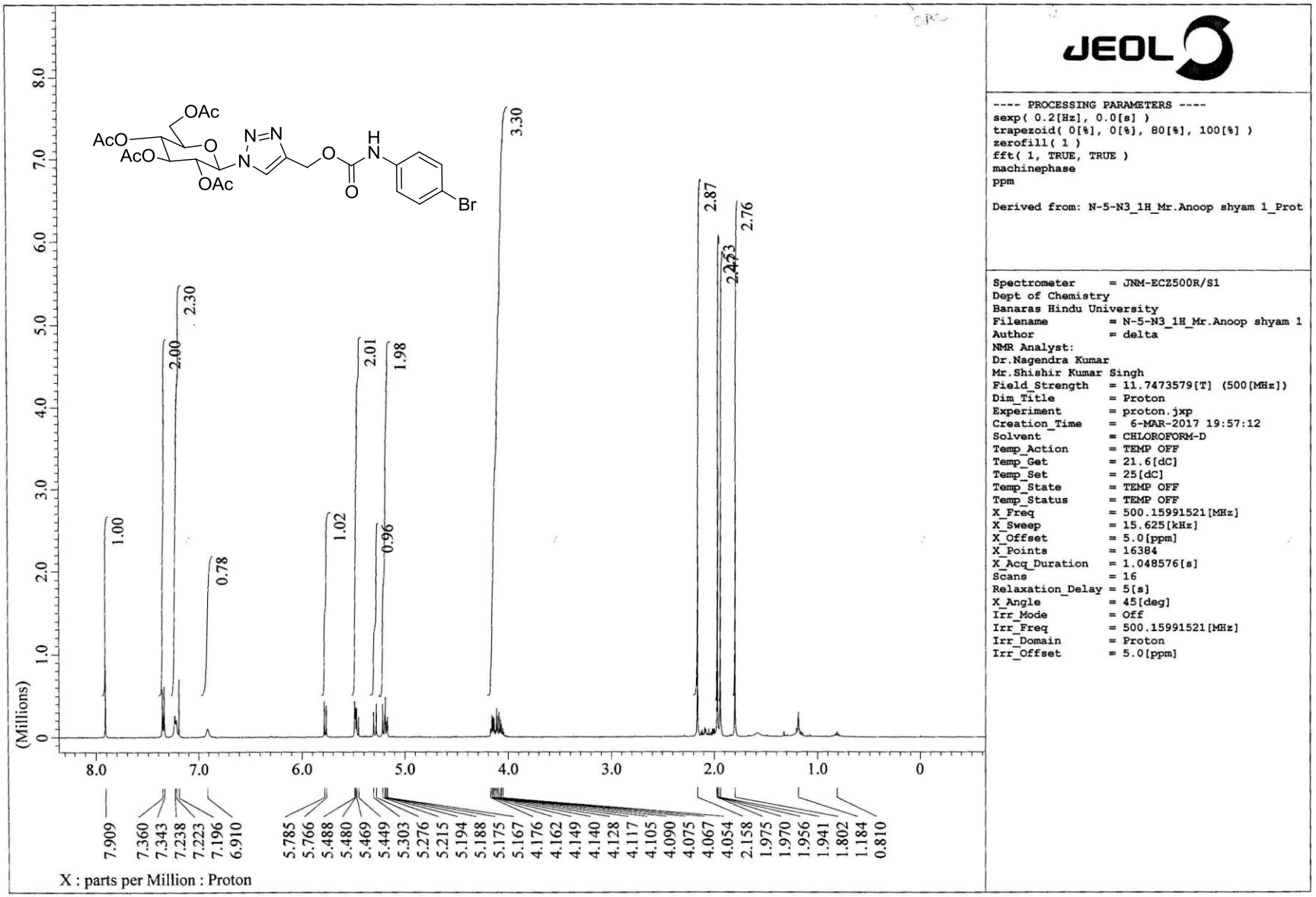
Spectrum 12: 125 MHz ^{13}C NMR of compound **4f**



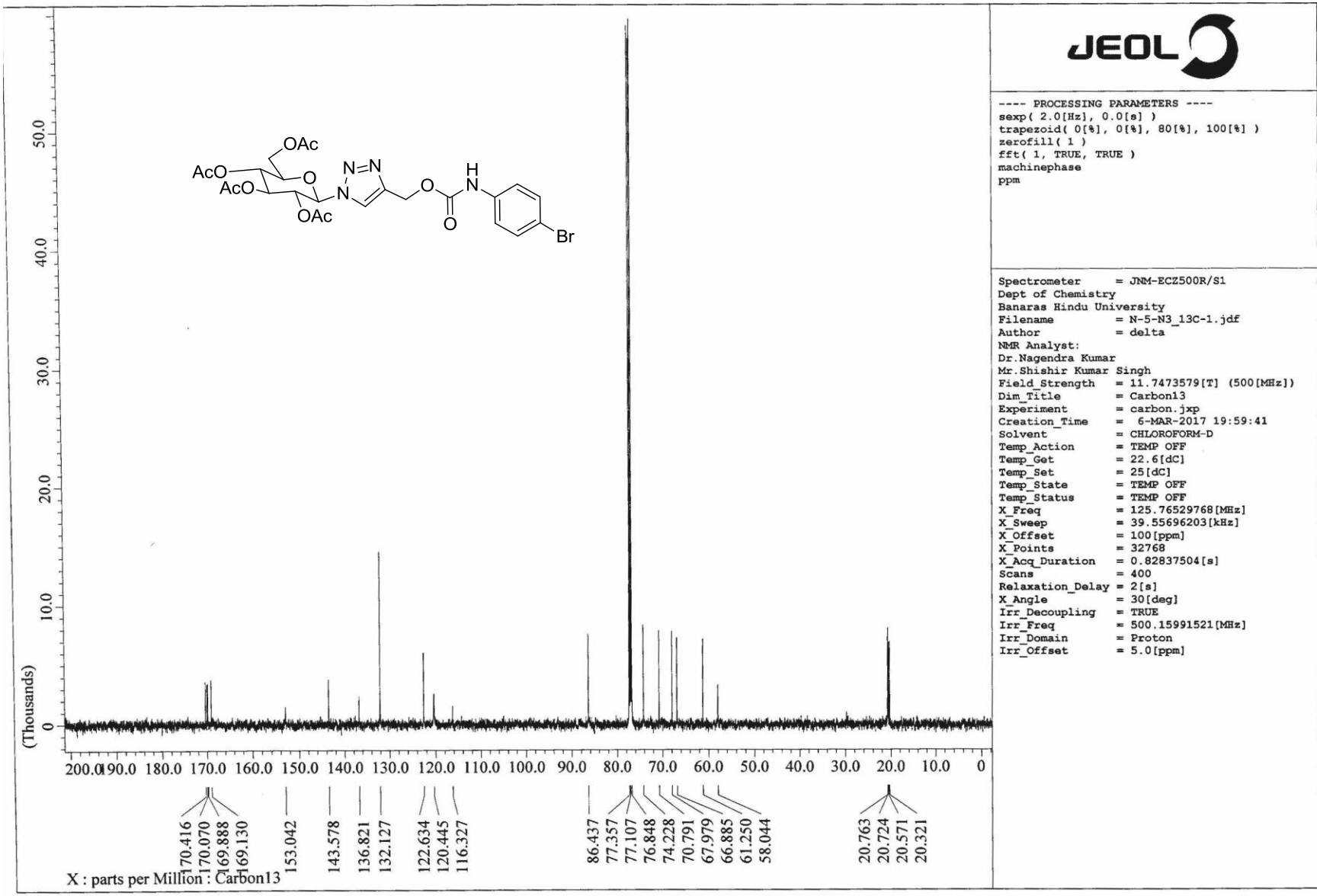
Spectrum 13: 500 MHz ^{1}H NMR of compound **4g**



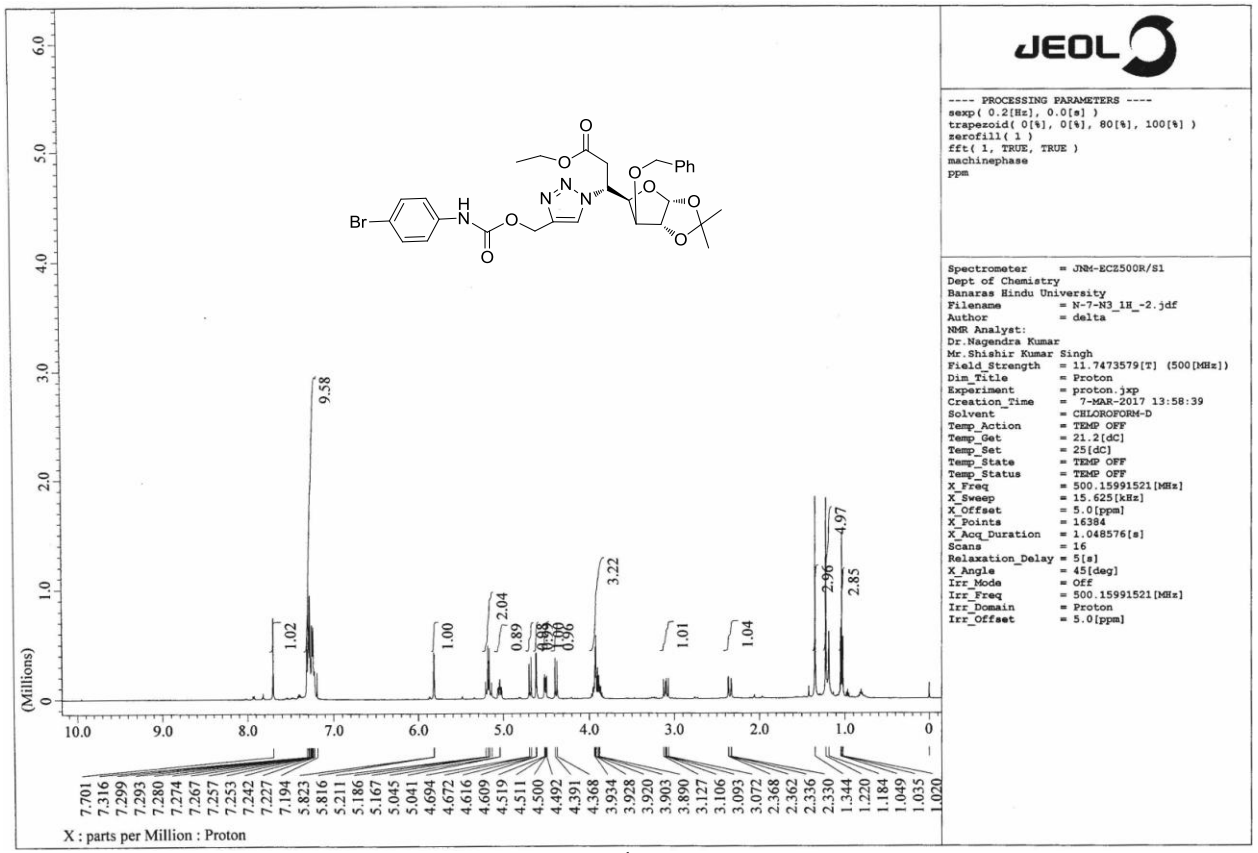
Spectrum 14: 125 MHz ^{13}C NMR of compound **4g**



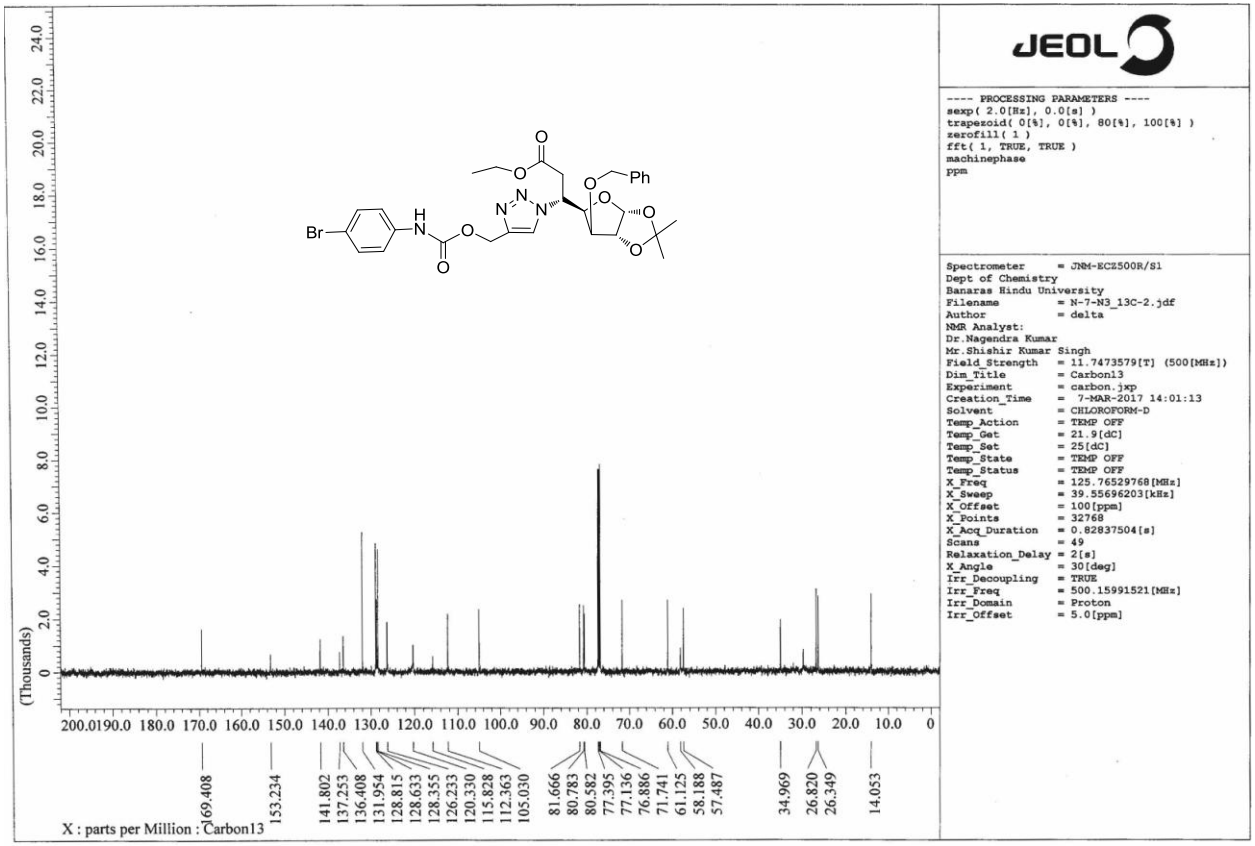
Spectrum 15: 500 MHz ^{1}H NMR of compound **4h**



Spectrum 16: 125 MHz ^{13}C NMR of compound **4h**



Spectrum 17: 500 MHz ^{1}H NMR of compound **4i**



Spectrum 18: 125 MHz ^{13}C NMR of compound **4i**

1-(Ethyl-[3'-*O*-benzyl-5',6'-dideoxy-1',2'-*O*-isopropylidine]-β-L-ido-heptofuranurn-ate-5-yl)-4-(phenyl-1''-yl)-1H-[1,2,3]-triazole (4a)

A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (100mg, 0.253 mmol), phenylacetylene (33µl, 0.306 mmol) and Cu-catalyst 1 (7mg, 5µmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The reaction monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain the crude product. It was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative (97%). White solid ; R_f = 0.4 (35% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.30-7.14 (m, 8H), 5.83 (s, 1H), 5.10-5.56 (m, 1H), 4.67 (d, J = 11.5 Hz, 1H), 4.61 (d, J = 3.5 Hz, 1H), 4.56-4.53 (m, 1H), 4.37 (d, J = 11.5 Hz, 1H), 3.94-3.12 (m, 3H), 3.18-3.12 (m, 1H), 2.38-2.34 (m, 1H), 2.34 (s,3H), 1.20 (s,3H), 1.04 (t, J = 7.5 Hz, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 146.8, 136.5, 133.9, 133.8, 130.9, 129.3, 128.8, 128.7, 128.64, 128.61, 127.9, 125.7, 122.0, 112.3, 105.0, 81.7, 80.8, 80.7, 71.7, 61.0, 57.4, 34.9, 26.8, 26.4,14.1 ppm.

1-(Ethyl-[3'-*O*-benzyl-5',6'-dideoxy-1',2'-*O*-isopropylidine]-*β*-L-ido-heptofuranurn-ate-5-yl)-4-(hexan-1''-yl)-1*H*-[1,2,3]-triazole (4b)

A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (100mg, 0.253 mmol), 1-octyne (45µl, .306 mmol) in presence of Cu-catalyst 1 (7mg, 5µmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The reaction monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain the crude product. It was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative (98%). White solid ; R_f = 0.4 (35% ethyl acetate/*n*-hexane); ^{1}H NMR

(500 MHz, $CDCl_3$): δ 7.29-7.25 (m, 6H), 5.83 (d, J = 3.5 Hz, 1H), 5.21-4.91(m, 1H), 4.68 (d, J = 11.0 Hz, 1H), 4.60-4.50 (m, 1H), 4.39 (d, J = 11.5 Hz, 1H), 3.95-3.91 (m, 3H), 3.14-3.07 (m, 1H), 2.60-2.38 (m, 2H), 2.38-2.34 (m, 1H), 1.57 (m, 2H), 1.36 (m, 3H), 1.27-1.20 (m, 10H), 1.08-1.05 (m,3H), 0.81-0.78 (m,3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 147.4, 136.5, 128.7, 128.5, 128.64, 128.2, 122.7, 112.2, 105.0, 81.6, 80.9, 80.8, 71.7, 60.9, 57.0, 35.1, 31.6, 29.2, 29.0, 26.8, 26.3, 25.7, 22.6, 14.1, 14.0 ppm.

1-(Ethyl-[3'-*O*-benzyl-5',6'-dideoxy-1',2'-*O*-isopropylidine]-*β*-L-ido-heptofuranurn-ate-5-yl)-4-(1''-phenyl-methan-1''-yl)-1*H*-[1,2,3]-triazole (4c)

A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (100mg, 0.253 mmol), prop-2-yn-1-ylbenzene (43µl, 0.306 mmol) in presence of Cu-catalyst 1 (7mg, 5µmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The reaction monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain the crude product. The crude reaction mixture was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative (94%). White solid; R_f = 0.4 (35% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25-7.10 (m, 11H), 5.78 (d, J = 4.5 Hz, 1H), 4.96-4.94 (m, 1H), 4.63 (d, J = 11.5 Hz, 1H), 4.58 (d, J = 4.0 Hz, 1H), 4.50-4.48 (m, 1H), 4.34 (d, J = 11.5 Hz, 1H), 3.96-3.87 (m, 3H), 3.10-3.05 (m, 1H), 2.35-2.31 (m, 1H), 2.31 (s, 3H), 1.20 (s, 3H), 1.0 (t, J = 6.5 Hz, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 146.4, 139.1, 136.5, 133.9, 128.8, 128.7, 128.6, 128.5, 128.2, 126.3, 123.7, 112.2, 105.0, 81.6, 80.86, 80.81, 71.7, 60.9, 57.1, 35.1, 32.3, 26.8, 26.3, 14.0 ppm.

1-(Ethyl-[3'-*O*-benzyl-5',6'-dideoxy-1',2'-*O*-isopropylidine]-*β*-L-ido-heptofuranurnate-5-yl)-4-(toluene-1''-yl)-1*H*-[1,2,3]-triazole (4d)

A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (100mg, 0.253 mmol) and 1-ethynyl-4-methylbenzene (38µl, 0.306 mmol) in presence Cu-catalyst 1 (7mg, 5µmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The reaction was monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain crude. The crude reaction mixture was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative (99%). oil ; R_f = 0.4 (35% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.69 (d, J = 7.5 Hz, 2H), 7.36-7.32 (m, 5H), 7.18(d, J = 7.5 Hz, 2H), 5.91 (d, J = 4.0 Hz, 1H), 5.15- 4.97 (m, 1H), 4.76-4.61 (m, 3H), 4.43 (d, J = 11.5 Hz, 1H), 4.02-3.98 (m, 3H), 3.25-3.20 (m, 1H), 2.47-2.34 (m, 1H), 2.34 (s, 3H), 1.42 (s, 3H), 1.25 (s, 3H), 1.13 (t, J = 7.5 Hz, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 146.8, 137.6, 136.5, 129.4, 128.8, 128.5, 128.3, 128.1, 125.6, 121.6, 112.3, 105.0, 81.7, 80.8, 80.7, 71.7, 61.0, 57.3, 35.0, 26.8, 26.3, 21.3, 14.1 ppm.

1-(Ethyl-[3'-*O*-benzyl-5',6'-dideoxy-1',2'-*O*-isopropylidine]-*β*-L-ido-heptofuranurn-ate-5-yl)-4-(octan-1''-ol-8''-yl)-1*H*-[1,2,3]-triazole (4e)

A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (100mg, 0.253 mmol), dec-9-yne-1-ol (54µl, 0.306 mmol) in presence of Cu-catalyst 1 (7mg, 5µmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The was reaction monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain the crude product. It was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative 98%, White solid; R_f = 0.4 (35% ethyl acetate/*n*-hexane); ^{1}H

NMR (500 MHz, $CDCl_3$): δ 7.33-7.28 (m, 6H), 5.86 (s, 1H), 5.05-5.01 (m, 1H), 4.71 (d, *J* = 11.0 Hz, 1H), 4.64 (d, *J* = 3.5 Hz, 1H), 4.56-4.53 (dd, *J* = 6.5,3.00 Hz, 1H), 4.32 (d, *J* = 11.5 Hz, 1H), 3.98-3.94 (m, 3H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.15-3.12 (m, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.41-2.40 (m, 1H), 2.08 (bs, 1H), 1.60-1.59 (m,2H), 1.51-1.48 (m,2H), 1.39 (s,3H), 1.27-1.21(m,13H), 1.18-1.08 (m, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 147.2, 136.5, 128.7, 128.5, 128.2, 122.8, 112.2, 105.0, 81.6, 80.9, 80.8, 71.7, 62.8, 60.9, 57.0, 35.0, 32.8, 29.3, 2.18, 26.8, 26.4, 25.7, 25.6, 14.0 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-4-phenyl- [1,2,3]-triazole (4f)

A solution of 2,3,4,6-Tetra-*O*-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol), phenylacetylene (33 µl, 0.322 mmol) in presence of Cu-catalyst 1 (7mg, 5µmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The reaction was monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain crude product. It was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative yield (99%); oil, R_f = 0.5, (50% ethyl acetate/*n*-hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.81 (d, *J* = 6.5 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.38-7.31 (m, 1H), 5.93 (d, *J* = 10 Hz, 1H), 5.51 (t, *J* = 9.5 Hz, 1H), 5.42 (t, *J* = 9.5 Hz, 1H), 5.25 (t, *J* = 9.5Hz, 1H), 4.32-4.28 (m, 1H), 4.14-4.12 (m, 1H), 4.04-4.00(m, 1H), 2.05 (d, *J* = 6.5 Hz, 6H), 2.01 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.0, 169.4, 169.1, 148.5, 129.9, 128.9, 128.6, 125.9, 117.8, 85.8, 75.2, 72.8, 70.2, 67.8, 61.6, 20.7, 20.62, 20.60 and 20.3 ppm.

1'-(4-(((Phenylcarbamoyl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)-2,3,4,6-tetra-*O*-acetyl-α-d-glucopyranose (4g)

A solution of 2,3,4,6-Tetra-*O*-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol), Prop-2-yn-1-yl phenylcarbamate (56mg, 0.322 mmol) in presence of Cu-catalyst 1 (7mg, 5μmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. of The reaction was monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain crude product. This was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative (92%). Oil, R_f = 0.5, (60% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.32 (d, *J* = 7.0 Hz, 2H), 7.24-7.19 (m, 2H), 7.05 (bs, 1H), 7.00-6.97 (m, 1H) 5.78 (d, *J* = 9.5Hz, 1H), 5.46 (m, 2H), 5.29-5.16 (m, 3H), 4.17- 4.02 (m, 3H), 2.13 (s, 3H), 2.00-1.92 (m, 6H), 1.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 170.1, 169.9, 169.1, 153.2, 143.7, 137.7, 129.1, 123.7, 122.7, 118.9, 86.3, 74.1, 70.8, 67.9, 66.9, 61.2, 57.8, 20.8, 20.7, 20.5 and 20.2 ppm.

1'-(4-((((4-bromophenyl)carbamoyl)oxy)methyl)-1H-1,2,3-triazol-1-yl)-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (4h)

A solution of 2,3,4,6-Tetra-*O*-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol), Prop-2-yn-1-yl (4-bromophenyl)carbamate (82mg, 0.322 mmol) in presence of Cu-catalyst 1 (7mg, 5μmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The reaction monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain crude product. It was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative yield (94%); oil, R_f = 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.23-7.22 (m, 2H), 6.91 (bs, 1H), 5.77 (d, *J* = 9.5 Hz, 1H), 5.48-5.44 (m, 2H), 5.29 (d, *J* = 13.5Hz, 1H), 5.21-5.16 (m, 2H), 4.17-4.05 (m, 3H), 2.15 (s,

3H), 1.97-1.94 (m, 6H), 1.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 170.0, 169.8, 169.1, 153.0, 143.5, 136.8, 132.1, 122.6, 120.4, 116.3, 86.4, 74.2, 70.7, 67.9, 66.8, 61.2, 58.0, 20.8, 20.7, 20.5 and 20.3 ppm.

Ethyl 1',2'-isopropylidine-3'-*O*-benzyl-5'-(4-((((4-bromophenyl)carbamoyl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)-5'-deoxy-α-D-*xylo*-heptofuranuronoate (4i)

A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (100mg, 0.253 mmol), Prop-2-yn-1-yl (4-bromophenyl)carbamate (77mg, 0.306 mmol) in presence of Cu-catalyst 1(7mg, 5μmol, 3.5g/L) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min. The reaction monitored by TLC. Upon completion, solvent was removed under reduced pressure to obtain the crude product. It was purified by flash chromatography (ethyl acetate: hexane) to afford triazole derivative 93%, Oil, R_f = 0.5, (60% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.31-7.19 (m, 10H), 5.82 (d, *J* = 3.5 Hz, 1H), 5.21-5.16 (m, 2H), 5.04-5.03 (m, 1H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.68 (d, *J* = 3.5 Hz, 1H), 4.51-4.49 (m, 1H), 4.38 (d, *J* = 11.5 Hz 1H), 3.93-3.89 (m, 3H), 3.12-3.07 (m, 1H), 2.35 (dd, *J* = 13.0, 3.0 Hz, 1H), 1.34 (s, 3H), 1.22-1.18 (s, 5H), 1.03 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 153.2, 141.8, 137.2, 136.4, 131.9, 128.8, 128.6, 128.3, 126.2, 120.3, 115.8, 112.3, 105.0, 81.6, 80.7, 80.5, 71.7, 61.1, 58.1, 57.4, 34.9, 26.8, 26.3 and 14.0 ppm.

Click reaction catalysed by CuOAc

At 2 mol % loading, the cycloaddition reached completion in 8 hrs. The experimental details are as follows:

The reaction was carried out under Argon atmosphere and in dry DCM. A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (500 mg, 1.265 mmol), phenylacetylene (1.65µl, 1.53 mmol) and CuOAc (3mg, 25µmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature. The reaction was monitored by TLC . We found complete conversion in about 8 hrs.

Click reaction in presence of Acetic acid

We also carried out our optimization reaction with Cu-catalyst **1** (2 mol%) and acetic acid (2 equiv.) in dry CH_2Cl_2 (2 mL). It was found that addition of acetic acid slows down the reaction and complete conversion occurs after 6 hours. The experimental details are as follows:

A solution of ethyl-[5-(*S*)-azido-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-*β*-L-ido-heptofuranurnate (100mg, 0.253 mmol), phenylacetylene (33µl, 0.306 mmol), Cu-catalyst **1** (7mg, 5µmol) and acetic acid (29µl, 2equiv.) in dry CH_2Cl_2 (2 mL) was stirred at room temperature and reaction monitored by TLC . We found that complete disappearance of starting material took about 6 hours.