Highly efficient structurally characterised novel precatalysts, di- and mono nuclear heteroleptic Cu(I) dixanthate/xanthate-phosphine complexes for azide-alkyne cycloadditions

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S1: Synthesis of Xanthate Ligands

The potassium salts of dixanthate, **K_2L1**–**K_2L3** and xanthate, **KL4**–**KL5** ligands were synthesised according to the following general procedure. To a stirred 15 mL THF solution of 2,6-pyridinedimethanol (0.139 g, 1mmol), 1,4-benzenedimethanol (0.138 g, 1 mmol), 1,4-cyclohexanediol (0.116 g, 1 mmol), piperonyl alcohol (0.304 g, 2 mmol) and methanol (0.064 g, 2 mmol) was added a pulverized KOH (0.112 g, 2 mmol) and 1.20 mL carbon disulfide (0.152 g, 2 mmol) in each case and the reaction mixture was stirred overnight in an ice bath maintain the temperature around 6 ^{o}C. The solvent was removed on a rotary evaporator to yield cream to light yellow coloured solid which was washed with ethanol followed by diethyl ether.

Characterisation

K_2L1. Yield: (0.249 g, 68%). Anal. Calcd for $C_9H_7N_1K_2O_2S_4$ (367.61): C 29.40, H 1.92, N 3.81; Found: C 29.42, H 1.90, N 3.78. IR (KBr, cm^{-1}): 1122 (ν_{C-O}), 1055 (ν_{C-S}). ^{1}H NMR (500 MHz, DMSO–d_6)δ (ppm): 7.74 –7.16 (m, 3H, –C_5H_3N), 5.40 (s, 4H, –{OCH_2}$_2$–C_5H_3N). ^{13}C{^{1}H} NMR (125 MHz, DMSO–d_6) δ (ppm): 229.62 (–CS_2), 73.04 (–OCH_2), 161.66 – 118.73 (–C_5H_3N). UV-vis (MeOH, λ_{max} (nm), ε (M^{-1} cm^{-1})): 305 (0.36×10^5), 265 (0.21×10^5), 230 (0.25×10^5), 208 (1.98×10^5).

K_2L2. Yield: (0.271 g, 74%). Anal. Calcd for $C_{10}H_8K_2O_2S_4$ (366.63): C 32.76, H 2.20; found: C 32.79, H 2.19. IR (KBr, cm^{-1}): 1098 (ν_{C-O}), 1073 (ν_{C-S}). ^{1}H NMR (500 MHz, DMSO–d_6) δ (ppm): 7.26 –7.21 (m, 4H, Ar–H), 5.29 (s, 4H, –{OCH_2}$_2$–C_6H_4). ^{13}C{^{1}H} NMR (125 MHz, DMSO–d_6) δ (ppm): 230.00 (–CS_2), 72.35 (–OCH_2), 141.36 –126.76 (Ar–C). UV–vis (MeOH, λ_{max} (nm) ε (M^{-1} cm^{-1})): 305 (1.15×10^5), 225 (1.66×10^5), 210 (1.84×10^5).

K_2L3. Yield: (0.244 g, 71%). Anal. Calcd for $C_8H_{10}K_2O_2S_4$ (344.62): C 27.88, H 2.92; Found: C 27.81, H 2.89.IR (KBr, cm^{-1}): 1137 (ν_{C-O}), 1030 (ν_{C-S}). ^{1}H NMR (500 MHz, DMSO–d_6)δ (ppm): 1.92–1.076 (m, 8H, ax/eq {–OCH}$_2$–C_4**H**$_8$–), 5.23-5.15 (m, ax/eq 2H, {–OC**H**}$_2$–C_4H_8). ^{13}C{^{1}H} NMR (125 MHz, DMSO–d_6) δ (ppm): 229.53 (–CS_2), 77.62 ({–O**C**H}$_2$–C_4H_8), 33.16 –27.16 ({–OCH}$_2$–**C**$_4$H$_8$). UV-vis. (MeOH, λ_{max} (nm), ε (M^{-1} cm^{-1})): 305 (1.33×10^5), 230 (1.00×10^5), 210 (0.63×10^5).

KL4. Yield: (0.420 g, 79%). Anal. Calcd for $C_9H_7K_1O_3S_2$ (266.38): C 40.58, H 2.65.Found: C 41.42, H 2.64. IR (KBr, cm^{-1}): 1093 (ν_{C-O}), 1059 (ν_{C-S}).^{1}H NMR (500 MHz, DMSO–d_6)δ (ppm): 6.86 –6.77

(m, 3H, Ar –H), 5.20 (s, 2H, –OCH_2), 5.95 (s, 2H, –O–CH_2–O–). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO–d_6) δ. (ppm): 229.02 (–CS_2), 71.83 (–OCH_2), 99.24 (–O–CH_2–O–). 145.35 –106.91 (Ar –C). UV-vis (MeOH, λ_{max} (nm), ε (M^{-1} cm^{-1})): 303 (0.80 × 10^5), 280 (0.63 × 10^5), 215 (2.24 × 10^5).

KL5. Yield: (0.234 g, 80%). Anal. Calcd for $C_2H_3K_1O_1S_2$ (146.27): C 16.42, H 2.07.Found: C 16.40, H 2.06. IR (KBr, cm^{-1}): 1107 (ν_{C-O}), 1048 (ν_{C-S}).^1H NMR (500 MHz, DMSO–d_6) δ (ppm): 3.67 (s, 3H, –OCH_3) $^{13}C\{^1H\}$ NMR (125 MHz, DMSO–d_6) δ (ppm): 231.00 (–CS_2), 58.13 (–OCH_3). UV-vis (MeOH, λ_{max} (nm), ε (M^{-1} cm^{-1})): 305 (0.41 × 10^5), 225 (0.22 × 10^5), 210 (0.20 × 10^5).

Fig. S1. UV–vis spectra of ligands **1**–**5** in methanol solution

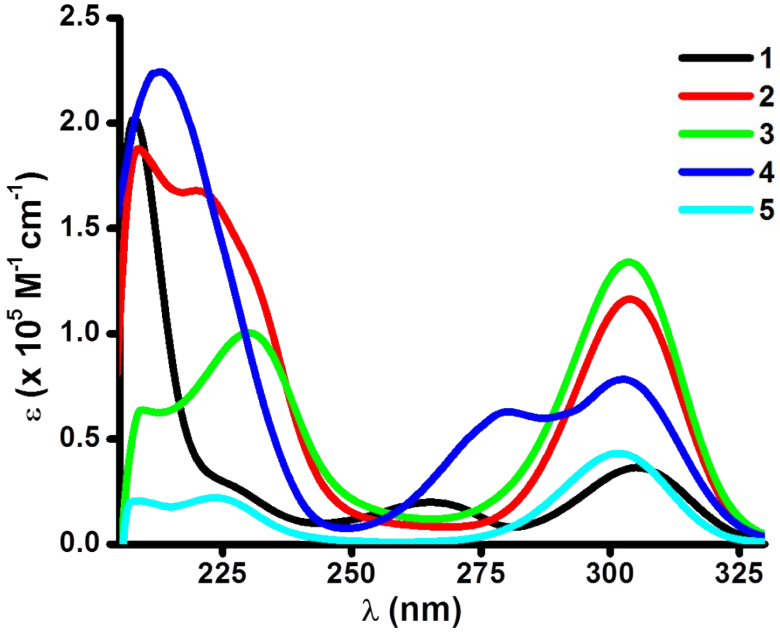


Fig. S2. Non–covalent interactions in **1**–**5**

Fig. S2. 1 Supramolecular structures of **1** sustained by H···H interaction (hydrogen atoms, except those involved in the interactions, are omitted for clarity)

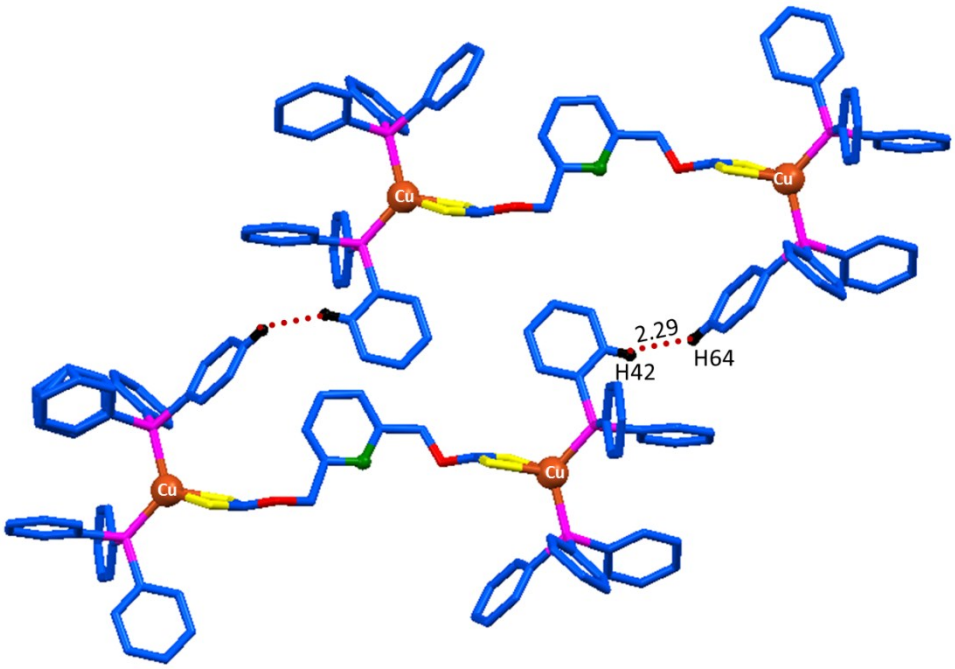
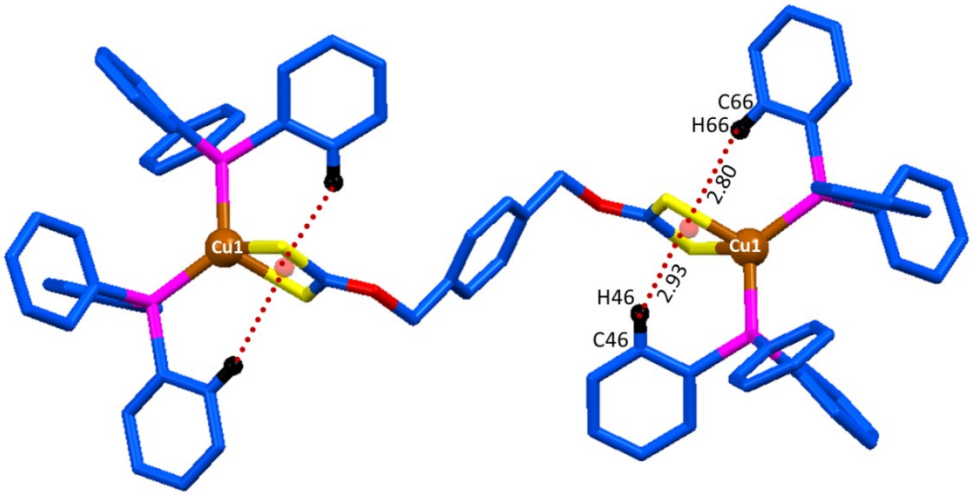


Fig. S2. 2 (a) Intramolecular C–H···π (CuS_2C, chelate) and (b) intermolecular C–H···π interactions in complex **2**



a

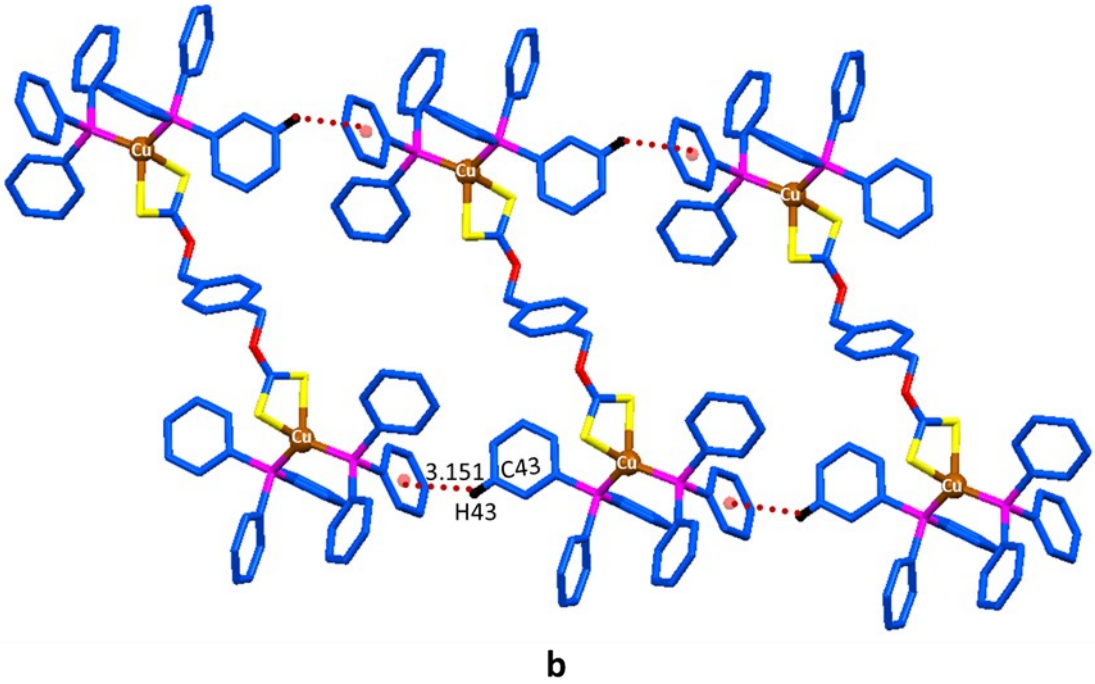
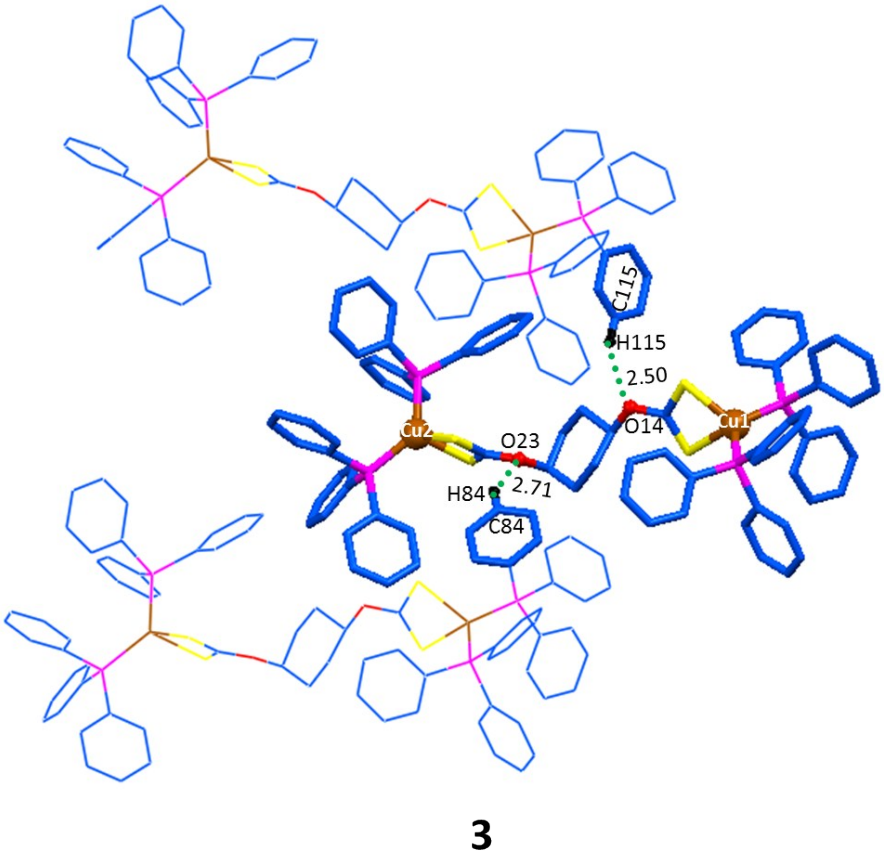
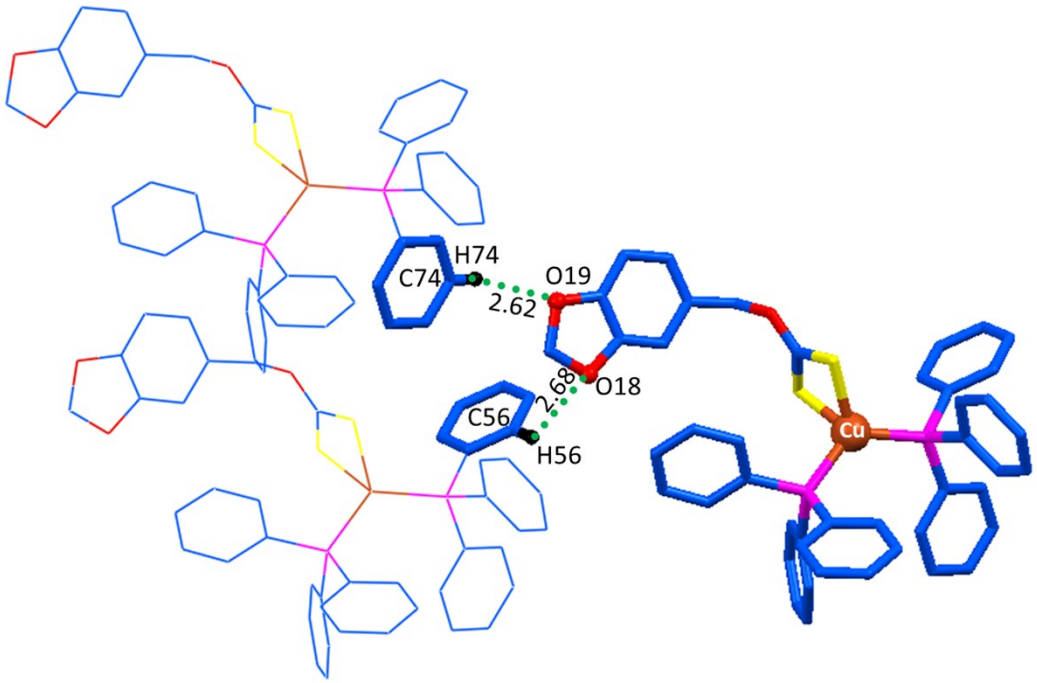


Fig. S2. 3 C–H···O interactions in complex **3** and **4** (hydrogen atoms, except those involved in the interactions, are omitted for clarity)





4

Fig. S2. 4 C–H···π, C–H···O interactions in complex **5** (hydrogen atoms except those involved in the interactions and some carbon skeleton are omitted for clarity)

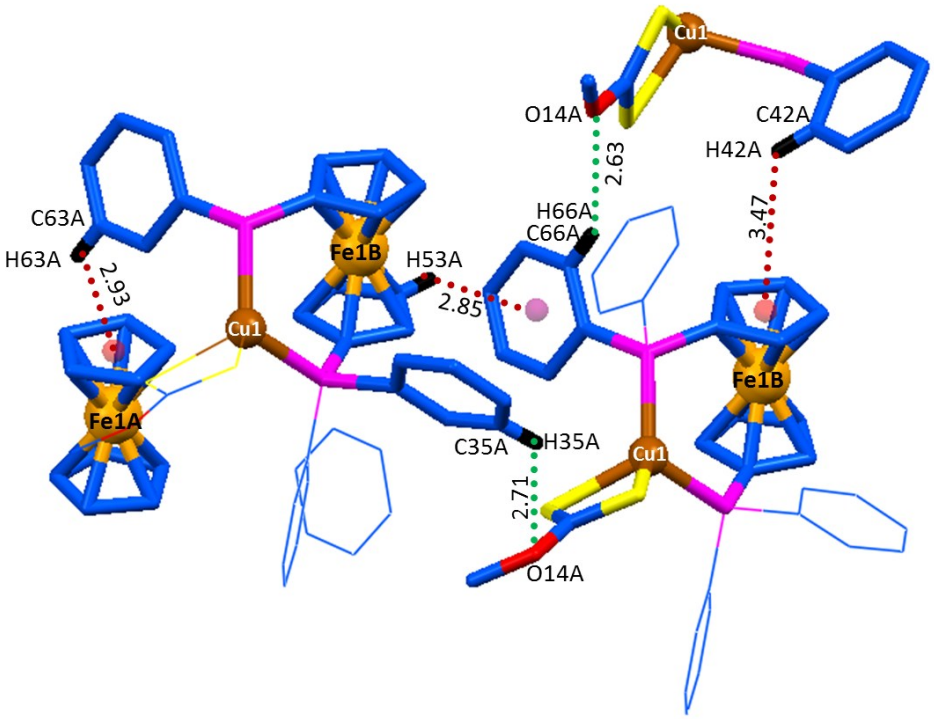


Table S1: Selected bond lengths (Å) and angles (°) for complexes **1–5**

	1	**2**	**3**	**3***	**4**	**5A**	**5B**
Bond lengths							
Cu(1) –P(1)	2.2435(16)	2.2651(9)	2.2549(14)	2.2333(14)	2.2309(6)	2.246(3)	2.242(4)
Cu(1) – P(2)	2.2464(15)	2.2510(9)	2.2430(14)	2.2450(14)	2.2457(6)	2.243(4)	2.262(3)
Cu(1) – S(11)	2.378(2)	2.4428(9)	2.4388(15)	2.3898(15)	2.3881(6)	2.367(4)	2.416(4)
Cu(1) – S(13)	2.4495(17)	2.4122(9)	2.3752(16)	2.4187(16)	2.4235(7)	2.423(4)	2.371(4)
S(11) – C(12)	1.658(8)	1.675(3)	1.677(6)	1.686(6)	1.698(2)	1.690(14)	1.680(13)
S(13) – C(12)	1.685(8)	1.697(3)	1.651(6)	1.677(6)	1.687(2)	1.658(15)	1.672(13)
C(12) – O(14)	1.436(10)	1.344(4)	1.367(6)	1.351(6)	1.333(3)	1.364(14)	1.352(13)
Angles							
P(1)– Cu(1)–P(2)	123.27(6)	122.06(3)	126.57(6)	128.77(6)	125.21(2)	111.82(13)	114.58(12)
P(1)–Cu(1)– S(11)	114.26(7)	113.62(3)	102.76(5)	111.59(5)	117.51(2)	110.66(14)	121.17(13)
P(2)–Cu(1)–S(11)	113.22(8)	111.56(4)	112.66(6)	110.28(6)	104.29(2)	122.22(15)	108.53(13)
P(1)–Cu(1)–S(13)	112.73(7)	105.25(3)	113.91(6)	114.62(6)	112.79(2)	114.80(14)	119.93(14)
P(2)–Cu(1)–S(13)	108.16(6)	120.41(3)	113.25(6)	103.25(5)	110.80(2)	117.75(13)	110.99(12)
S(11)–Cu(1)–S(13)	74.71(7)	74.52(3)	74.64(5)	75.58(5)	75.29(2)	75.09(13)	75.70(13)
C(12)–S(11)–Cu(1)	82.8(2)	81.73(12)	80.1(2)	81.06(18)	81.52(8)	82.3(5)	80.2(4)
C(12)–S(13)–Cu(1)	80.0(2)	82.25(12)	82.59(19)	80.35(19)	82.40(8)	81.2(5)	81.7(4)
S(11)–C(12)–S(13)	122.4(4)	121.4(2)	122.6(3)	122.4(3)	120.48(13)	121.4(8)	122.4(7)

***** this column gives the comparable coordination geometry around Cu(2) in complex **3**

Table S2: Weak secondary interactions and their parameters observed in compounds **1**–**5**

Donor (D)-acceptor (A) hydrogen bonds (Å, °)					
Complex	D–H···A	d(H···A)	d(D···A)	∠D–H···A	Symmetry Element
3	C(115)–H(115)··· O(14)	2.50	3.304(8)	144	1-x,1/2+y,3/2-z
	C(84)–H(84)··· O(23)	2.71	3.525(8)	146	1+x,y,z
4	C(74)–H(74)··· O(19)	2.62	3.252(5)	125	-x, 2-y, -z
	C(56)–H(56)··· O(18)	2.68	3.273(5)	121	x, -1+y,z

5	C(66A)–H(66A)··· O(14A)	2.63	3.375(4)	137	½-x, y,1/2+z
	C(35A)–H(35A)··· O(14A)	2.71	3.322(4)	124	x,1+y,z
H···H and C–H···π interactions in **1-5,** distances in Å					
Complex	H···H		H···H		Symmetry element
1	H(64)···H(42)		2.29		(1+x,-1+y,z)
Complex	C–H···π		C–H···π		Symmetry element
1	C(72)–H(72)··· π (C61–C66)		3.33		1-x,1-y,1-z
2	C(43)–H(43)··· π (C71–C76)		3.15		x,1+y,z
3	C(135)–H(135)··· π(C31–C36)		3.17		x,3/2-y,1/2+z
	C(55)–H(55)··· π(C121–C126)		3.13		x,3/2-y,-1/2+z
4	C(20)–H(20)··· π (C51–C56)		2.70		-x,2-z,1-z
	C(85)–H(85)··· π (C21–C26)		3.32		1+x,y,z
5	C(44A)–H(44A)··· π (C31B–C36B)		3.20		1-x,2-y,-1/2+z
	C(45A)–H(45A)··· π (C41B–C46B)		3.25		x,y,z
	C(46A)–H(46A)··· π (C41B–C46B)		3.32		x,y,z
	C(53A)–H(53A)··· π (C61A–C66A)		2.85		x,1+y,z
	C(42A)–H(42A)··· π (C81A–C85A)		3.48		½-x,y,1/2+z
	C(63A)–H(63A)··· π (C81B–C85B)		2.94		x,y,z
	C(83B)-H(83B)··· π (C81B–C85B)		2.77		x,-1+y,z

Table S3 Reaction time optimisation of catalyst **1** for Click reaction

Entry[a]	Catalyst	mol%	Time (minutes)	Solvent[c]	Yield (%)[g]
1	1	3	**5**	$CDCl_3$	**33**
2	1	3	**15**	$CDCl_3$	**41**
3	1	3	**30**	$CDCl_3$	**50**
4	1	3	**60**	$CDCl_3$	**69**
5	1	3	**90**	$CDCl_3$	**84**
6	1	3	**105**	$CDCl_3$	**91**
7	1	3	**120**	$CDCl_3$	**95**

[a]Entry : sugar azide (1.0 equiv.) and alkyne(1.1 equiv.). [c]Dry solvent. [g]Yields reported after ^{1}H NMR study.

S2: The synthesis of various triazolyl linked glycoconjugates (**8a-i**)

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-phenyl-[1,2,3]-triazole (8a)[1]

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100mg, 0.268 mmol) and phenylacetylene (32.4 μL, 0.295 mmol) were taken in dichloromethane (1.0 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03 μmol) to afford triazole derivative **8a**. Yield (95%), white solid, m.p. 200–202 °C, R_f = 0.5, (45% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.82 (d, *J* = 6.5 Hz, 2H), 7.42–7.39 (m, 2H), 7.34–7.31 (m, 1H), 5.94 (d, *J* = 8.5 Hz, 1H), 5.52 (t, *J* = 9.5 Hz, 1H), 5.45–5.42 (m, 1H),5.26 (t, *J* = 9.5 Hz, 1H), 4.33–4.29 (m, 1H), 4.16–4.13 (m, 1H),4.05–4.02 (m, 1H), 2.06 (s, 6H), 2.02 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 168.9, 148.4, 129.8, 128.7, 128.4, 125.8, 117.7, 85.6, 75.0, 72.6, 70.1, 67.6, 61.5, 20.5, 20.46, 20.43and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-(9-phenanthrene)- [1,2,3]-triazole (8b)

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol) and 9-ethynylphenanthrene (60 mg, 0.295 mmol) were taken in dichloromethane (1 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03 μmol) to afford triazole derivative **8b.** Yield (96%), white solid,m.p.;168–170 °C; R_f = 0.40, (40% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (d, *J* = 7.5 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.16 (s, 1H), 7.99

(s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.68–7.59 (m, 4H), 6.03 (d, *J* = 9.5 Hz, 1H), 5.62 (t, *J* = 9.5 Hz, 1H), 5.50 (t, *J* = 9.5 Hz, 1H), 5.31 (t, *J* = 9.5 Hz, 1H), 4.35–4.32 (m, 1H), 4.20–4.18 (m, 1H), 4.11–4.06 (m, 1H), 2.07-2.03 (m, 9H), 1.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 169.0, 147.3, 131.1, 130.6, 130.4, 129.8, 128.8, 128.6, 127.2, 126.9, 126.8, 126.7, 126.0, 125.8, 122.9, 122.4, 121.2, 85.9, 75.1, 72.5, 70.4, 67.7, 61.5, 20.6, 20.4, and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-(4-bromophenyl)-[1,2,3]-triazole (8c)[1]

2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol), 1-bromo-4-ethynylbenzene (53 mg, 0.293 mmol) were taken in dry dichloromethane (1.0 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03μmol) to afford the corresponding triazole **8c.** Yield (95%). White solid; m.p. = 214–217 °C; R_f = 0.50 (40% ethyl acetate/*n*-hexane); ^{1}H NMR (500.15 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 5.93 (d, *J* = 9.0 Hz, 1H), 5.52–5.42 (m, 2H), 5.28–5.24 (m, 1H), 4.34–4.30 (m, 1H), 4.16–4.13 (m, 1H), 4.05–4.02 (m, 1H), 2.08-2.07 (m, 6H), 2.03 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 169.0, 147.4, 132.0, 128.7, 127.3, 122.5, 117.8, 85.7, 75.1, 72.6, 70.1, 67.6, 61.5, 20.6, 20.5, 20.4, and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-(3-cyclohexenyl)-[1,2,3]-triazole (8d)[1]

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100mg, 0.268 mmol) and 1-Ethynylcyclohexene (34.6 μL, 0.295 mmol) were taken in dichloromethane (1.0 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03 μmol) to afford triazole derivative **8d**. Yield (95%).off white solid, m.p. = 196–198 °C; R_f = 0.5 (40% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (s, 1H), 6.52 (s, 1H), 5.85 (d, *J* = 9.5 Hz, 1H), 5.44–5.36 (m, 2H), 5.22–5.18 (m, 1H), 4.27–4.24 (m, 1H), 4.10–4.07 (m, 1H), 3.99–3.97 (m, 1H), 2.31 (s, 2H), 2.15–2.11 (m, 2H), 2.03–2.02 (m, 6H), 1.98 (s, 3H), 1.83 (s, 3H), 1.71 (d, *J* = 5.5, 2H), 1.62 (d, *J* = 5.0, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 169.7, 169.2, 168.8,149.9, 126.5, 125.8, 116.1, 85.4, 74.8, 72.6, 70.0, 67.6, 61.4, 26.1, 25.1, 22.2, 21.9, 20.5, 20.39, 20.36, and 20.0 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-4-(4-*n*-pentylphenyl)-[1,2,3]-triazole (8e)[1]

2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol), 1-ethynyl-4-pentylbenzene (57.3 μL, 0.321 mmol) were taken in dichloromethane (1.0 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03 μmol) to afford triazole derivative **8e.** Yield (96%).solid; m.p.= 170–176 °C; R_f = 0.5 (35% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.26–7.22 (m, 2H), 5.93 (d, *J* = 9.5 Hz, 1H), 5.54–5.51 (m, 1H), 5.45–5.42 (m, 1H), 5.29–5.25 (m, 1H), 4.34–4.30 (m, 1H), 4.16–4.14 (m, 1H), 4.04–4.02 (m, 1H), 2.63-2.60 (m, 2H), 2.07–2.06 (m, 6H), 2.03 (s, 3H),1.86 (s, 3H), 1.63–1.61 (m, 2H), 1.32–1.24 (m, 4H), 0.89-0.86 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 168.9, 148.5, 143.5, 128.8, 127.1, 125.7, 117.3, 85.6, 75.1, 72.7, 70.1, 67.7, 61.5, 35.6, 31.3, 30.9, 29.6, 22.4, 20.6, 20.5, 20.4, 20.1, and 13.9 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranos-1-yl)-4-(1,2;5,6-*O*-isopropylidene-3-*O*-methyl-*α*-D-glucofuranos-3-yl)-[1,2,3]-triazole (8f)

2,3,4,6-tetra-*O*-acetyl-*β*-D-galactocopyranosyl azide (100 mg, 0.268 mmol), and 1,2,5,6-*O*-isopropylidene-3-*O*-propargyloxy-α-D-glucofuranos-3-yl (87.9 mg, 0.295 mmol) were taken in dichloromethane (1.0 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03 μmol) to afford triazole derivative **8f.** Yield (94%), off white solid; m.p. = 36–40 °C; R_f = 0.5 (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 5.86–5.82 (m, 2H), 5.52–5.47 (m, 2H), 5.25–5.22 (m, 1H), 4.81–4.73 (m, 2H), 4.56 (d, *J* = 3.5 Hz, 1H), 4.29–4.15 (m, 3H), 4.12–4.05 (m, 3H), 4.01–3.95 (m, 2H), 2.17 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.85 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 169.8, 169.6, 168.9, 145.5, 120.9, 111.7, 108.9, 105.2, 86.2, 82.4, 81.6, 81.0, 74.1, 72.4, 70.6, 67.8, 67.2, 66.8, 63.7, 61.0, 26.79, 26.71, 26.1, 25.3, 20.5, 20.3, and 20.1 ppm.

1-(2,3,4,6-Tri-*O*-acetyl-4-*O*(2',3',4',6'-tetra-*O*-acetyl-*β*-D-galacopyranosyl)-*β*-D-glucopyranos-1-yl)4-(*n*-hexane)-[1,2,3]-triazole (8g)[2]

2,3,4,6-Tri-*O*-acetyl-4-*O*(2',3',4',6'-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-*β*-D-glucopyranosyl azide (100 mg, 0.151 mmol), 1-octyne (24.7 μL, 0.179 mmol) were taken in dichloromethane (1 mL) in presence of Cu-catalyst **1** (6.7 mg, 4.5 μmol) to afford triazole derivative **8g**. Yield (96%); white solid; m.p. = 98-100 °C; R_f = 0.45, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500MHz, $CDCl_3$):δ 7.41 (s, 1H), 5.79–5.77 (m, 1H), 5.38–5.35 (m, 3H), 5.1–5.09 (m, 2H), 4.97–4.95 (m, 1H), 4.52–4.45 (m, 2H), 4.15–4.01 (m, 3H), 3.93–3.87 (m, 3H), 2.68 (t, *J* = 7.5

Hz, 2H), 2.14 (s, 3H), 2.08–2.04 (m, 12H), 1.95 (s, 3H), 1.84 (s, 3H),1.64–1.61 (m, 2H), 1.32–1.28 (m, 2H), 0.87–0.84 (m, 3H); ^{13}C NMR (125MHz, $CDCl_3$): δ 170.3, 170.1, 170.06, 170.01, 169.4, 169.1, 169.0, 149.0, 118.7, 101.0, 85.3, 75.8, 75.6, 72.6, 70.8, 70.7, 70.3, 69.0, 66.5, 61.7, 60.7, 31.4, 29.0, 28.7, 25.5, 22.4, 20.7, 20.6, 20.59, 20.56, 20.4, 20.1 and 13.9 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranos-1-yl)-4-(2,3;5,6-di-*O*-isopropylidene-1-*O*-methyl-*β*-D-mannofuranos-1-yl)-[1,2,3]-triazole (8h)

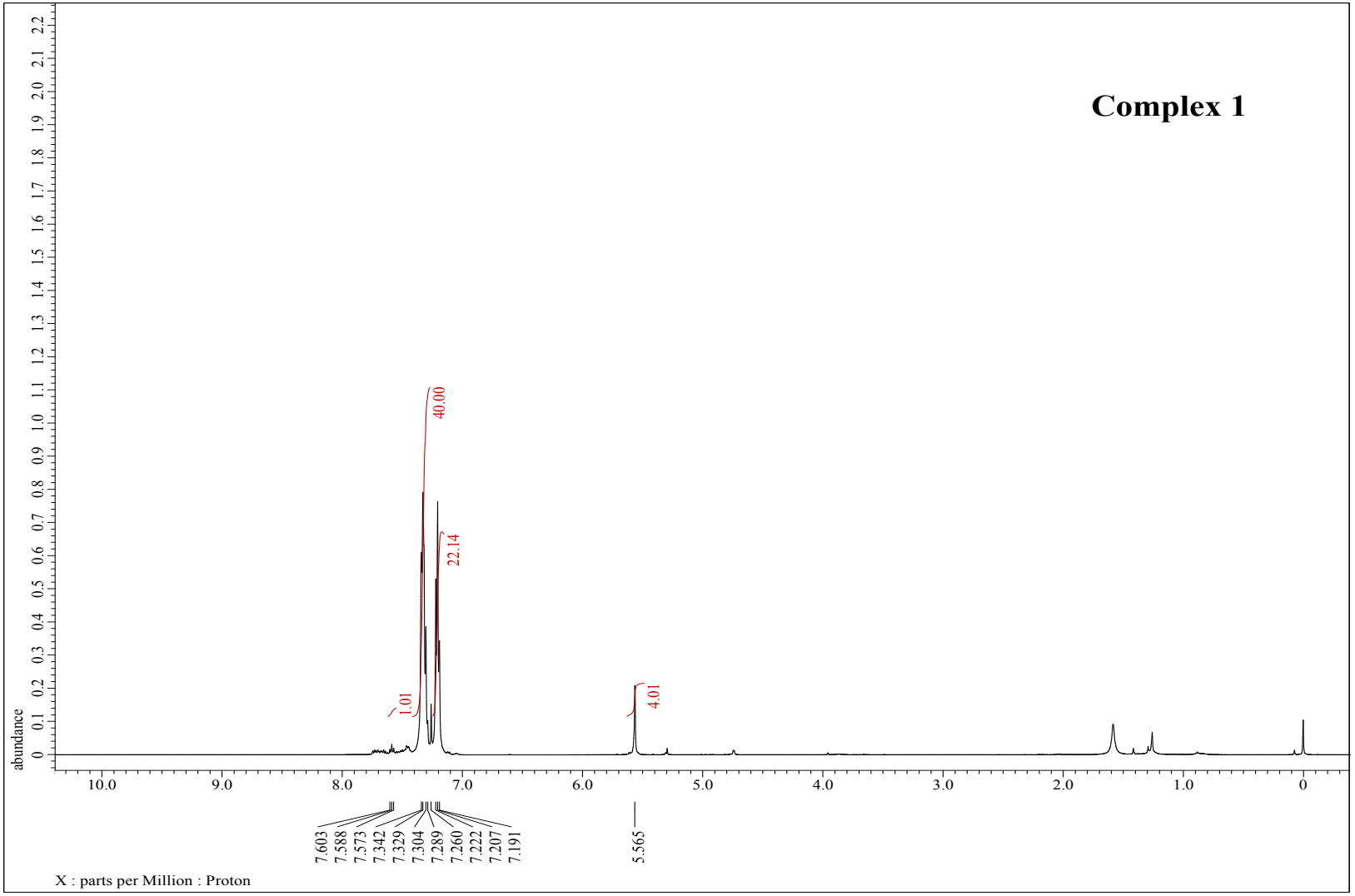
2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl azide (100mg, 0.268 mmol), 2,3;5,6-di-*O*-isopropylidene-1-*O*-propargyloxy-*β*-D-mannofuranos-1-yl (87.9 mg, 0.295 mmol) were taken in dichloromethane (1 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03 μmol) to afford triazole derivative **8h**. Yield (93%); m.p. = 106 °C; R_f = 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 1H), 5.82 (d, *J* = 9.5 Hz, 1H), 5.54–5.50 (m, 2H), 5.24–5.21 (m, 1H), 5.04 (s, 1H), 4.77–4.74 (m, 2H), 4.61–4.58 (m, 2H), 4.39–4.37 (m, 1H), 4.21–4.08 (m, 4H), 4.04-3.96 (m, 2H), 2.20 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.86 (s, 3H), 1.43 (s, 6H), 1.35 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 170.2, 169.8, 169.7, 169.0, 144.8, 121.0, 112.6, 109.1, 105.4, 86.1, 84.9, 80.5, 79.4, 73.9, 73.0, 70.7, 67.8, 66.84, 66.82, 61.1, 60.0, 26.7, 25.8, 25.1, 24.4, 20.5, 20.3 and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-(2,3;5,6-di-*O*-isopropylidene-1-*O*-methyl-*β*-D-mannofuranos-1-yl)-[1,2,3]-triazole (8i)

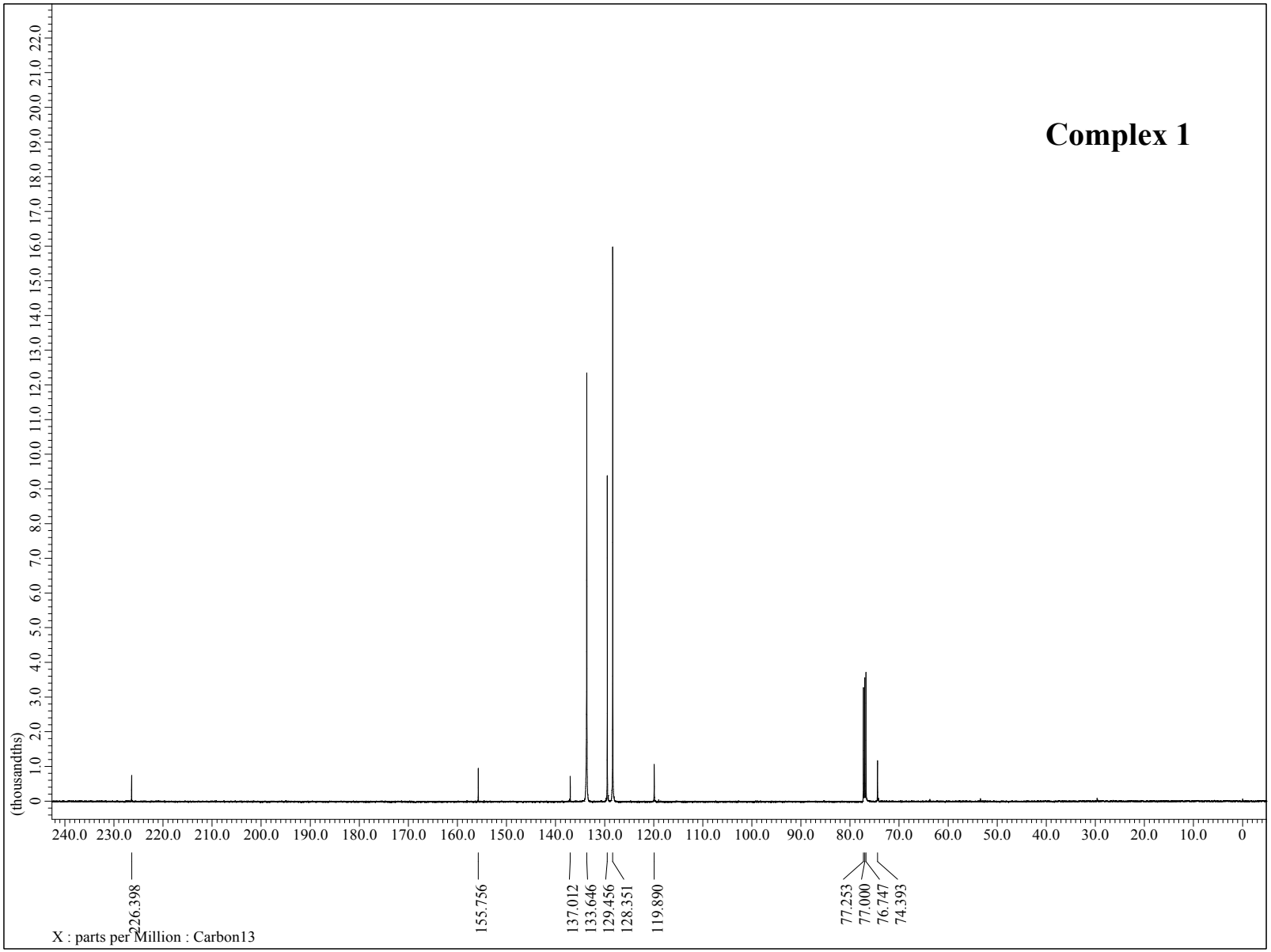
2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol) and 2,3;5,6-di-*O*-isopropylidene-1-*O*-propargyloxy-*β*-D-mannofuranos-1-yl (87.9 mg, 0.295mmol) were taken in dichloromethane (1.0 mL) in presence of Cu-catalyst **1** (11.8 mg, 8.03 μmol) to afford triazole derivative **8i.** Yield (94%); solid, m.p. = 108 °C, R_f = 0.5 (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500.15 MHz, $CDCl_3$): δ 7.80 (s, 1H), 5.86 (d, *J* = 9.5 Hz, 1H), 5.47–5.37 (m, 2H), 5.28-5.21 (m, 1H), 5.069–5.065 (m, 1H), 4.77–4.72 (m, 2H), 4.65–4.60 (m, 2H), 4.41–4.40 (m, 1H), 4.31–4.27 (m, 1H), 4.13–3.97 (m, 5H), 2.06–2.04 (m, 6H), 2.01 (s, 3H), 1.86 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 168.8, 145.2, 121.1, 112.6, 109.1, 105.9, 85.7, 84.9, 80.3, 79.4, 75.0, 73.1, 72.6, 70.3, 67.6, 66.6, 61.5, 60.5, 26.8, 25.8, 25.1, 24.4, 20.6, 20.47, 20.44, and 20.1 ppm.

S3: ^{1}H, ^{13}C and time dependent ^{31}P NMR spectra of complex **1** and **4**

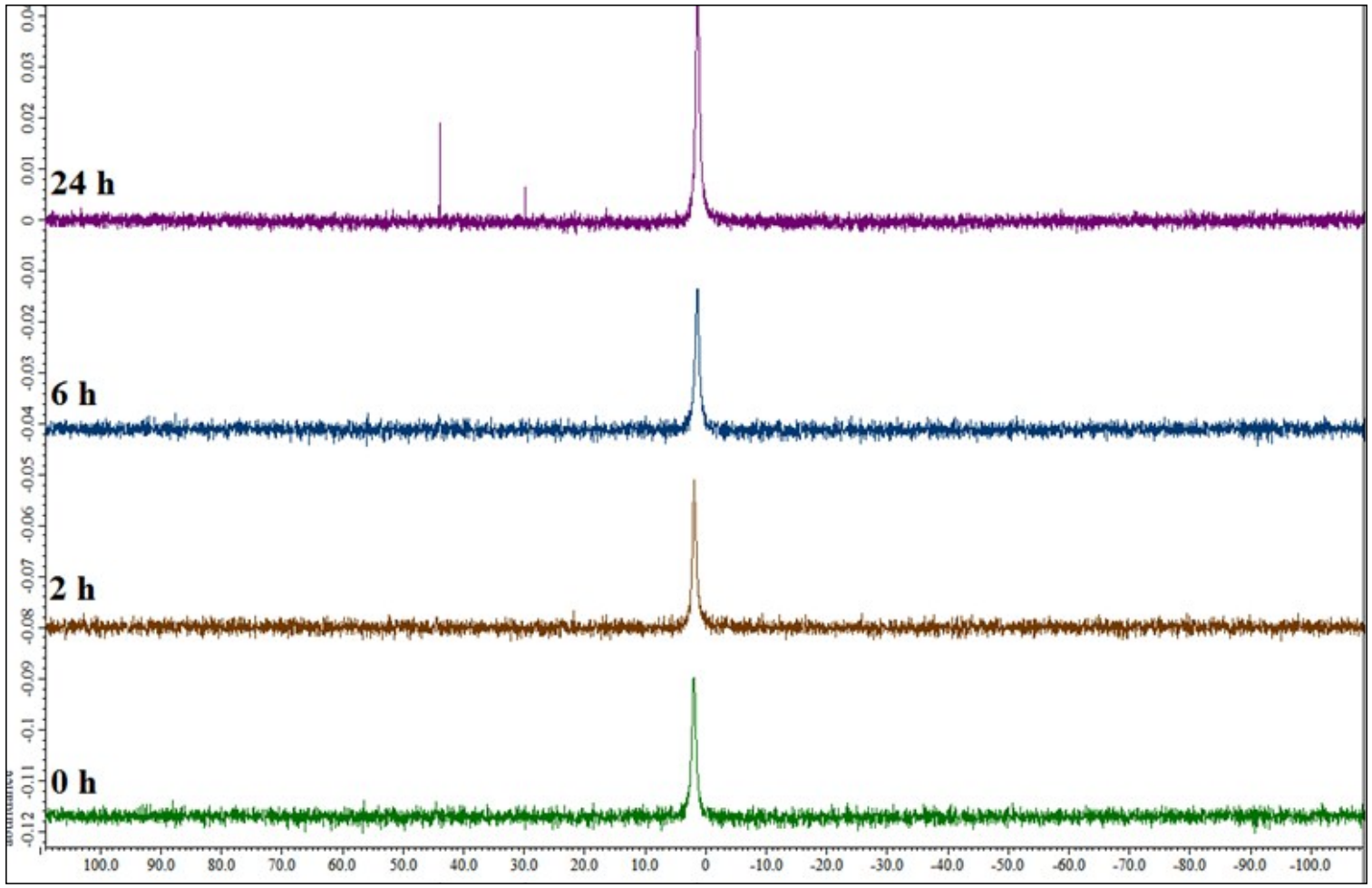
S4: ^{1}H and ^{13}C spectra of triazolyl glycoconjugates (**8a-i**)



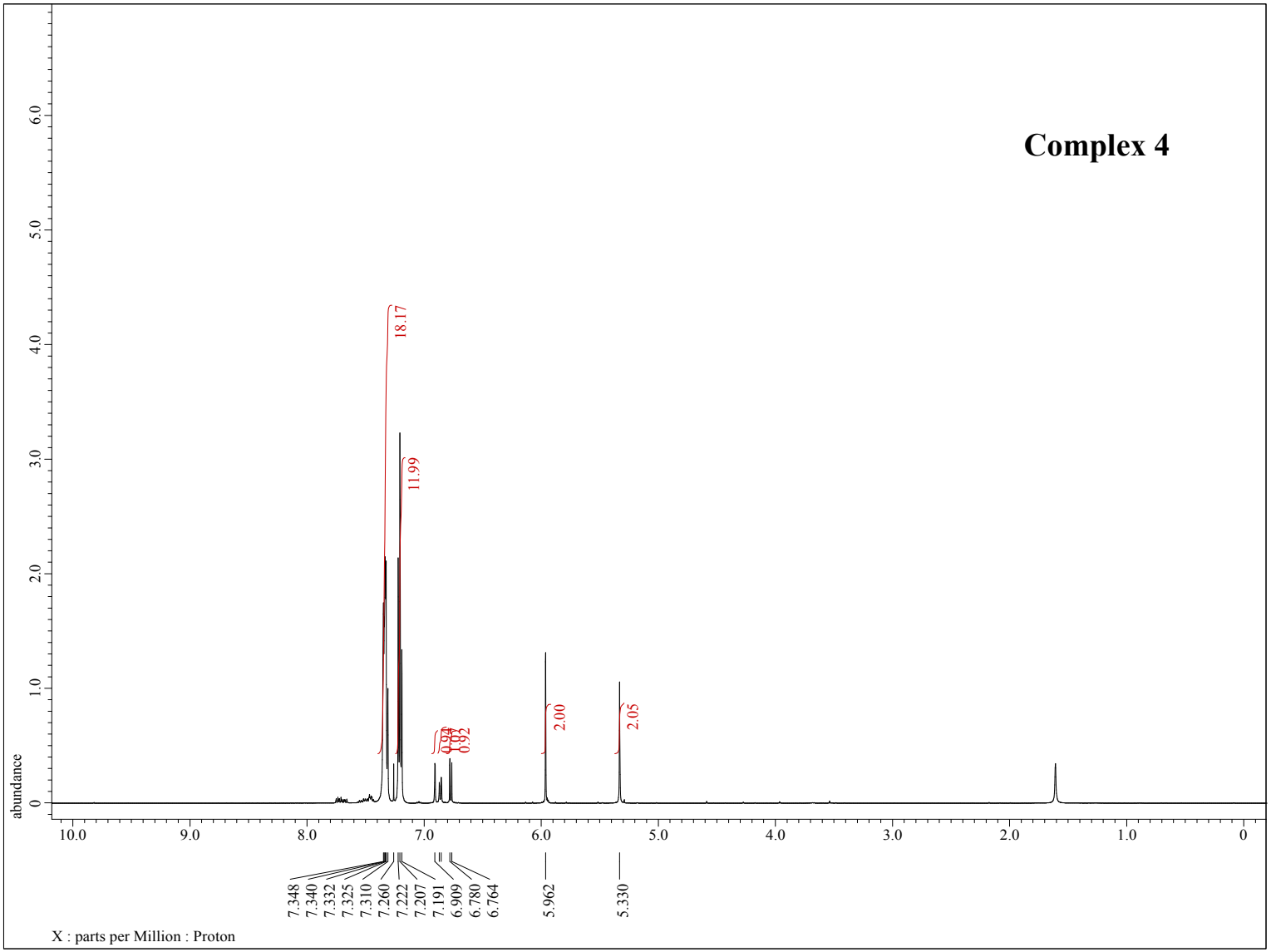
Spectrum 1a: ^{1}H NMR (500 MHz, $CDCl_3$) of complex **1**



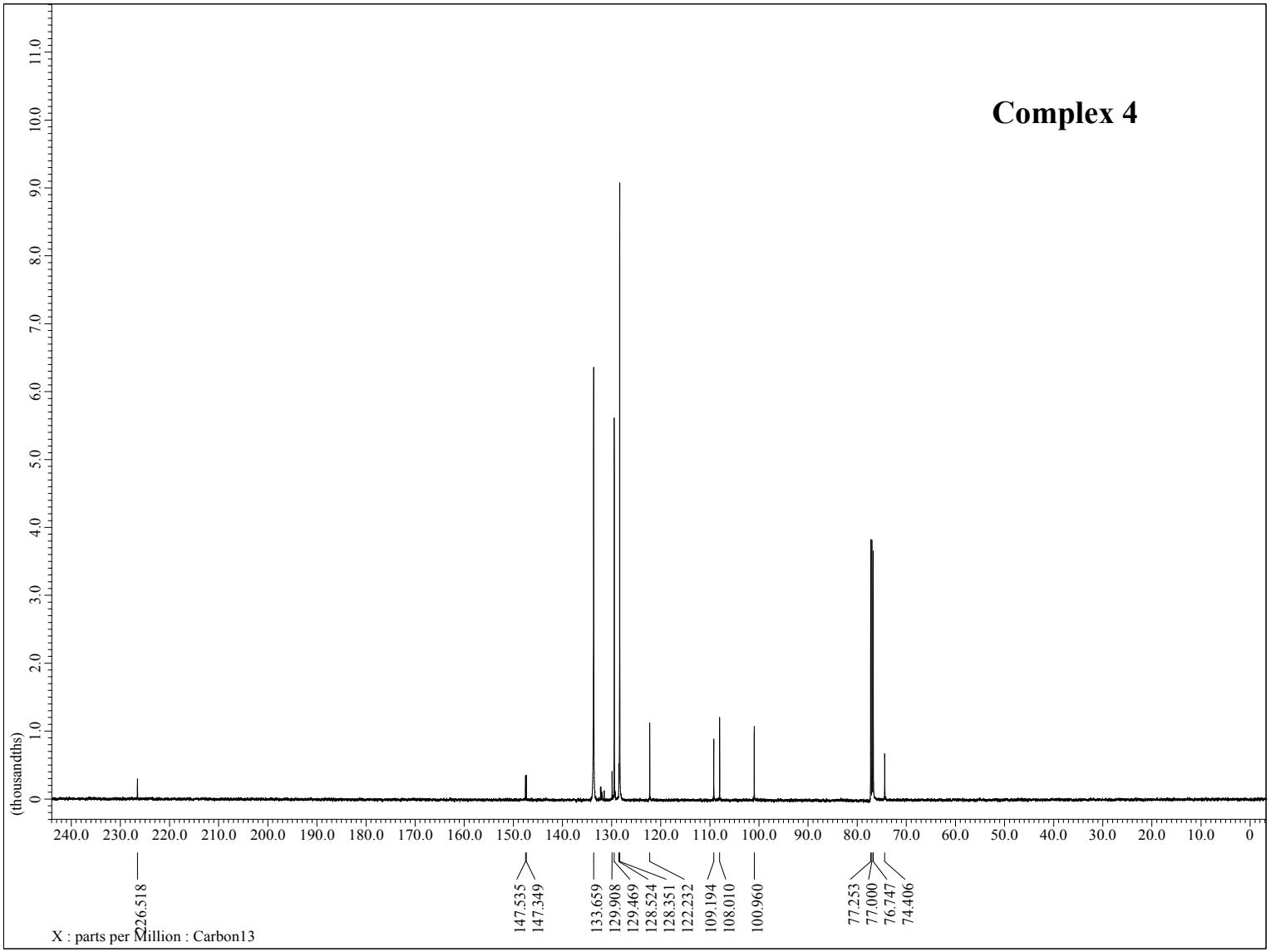
Spectrum 1b: ^{13}C NMR (500 MHz, $CDCl_3$) of complex **1**



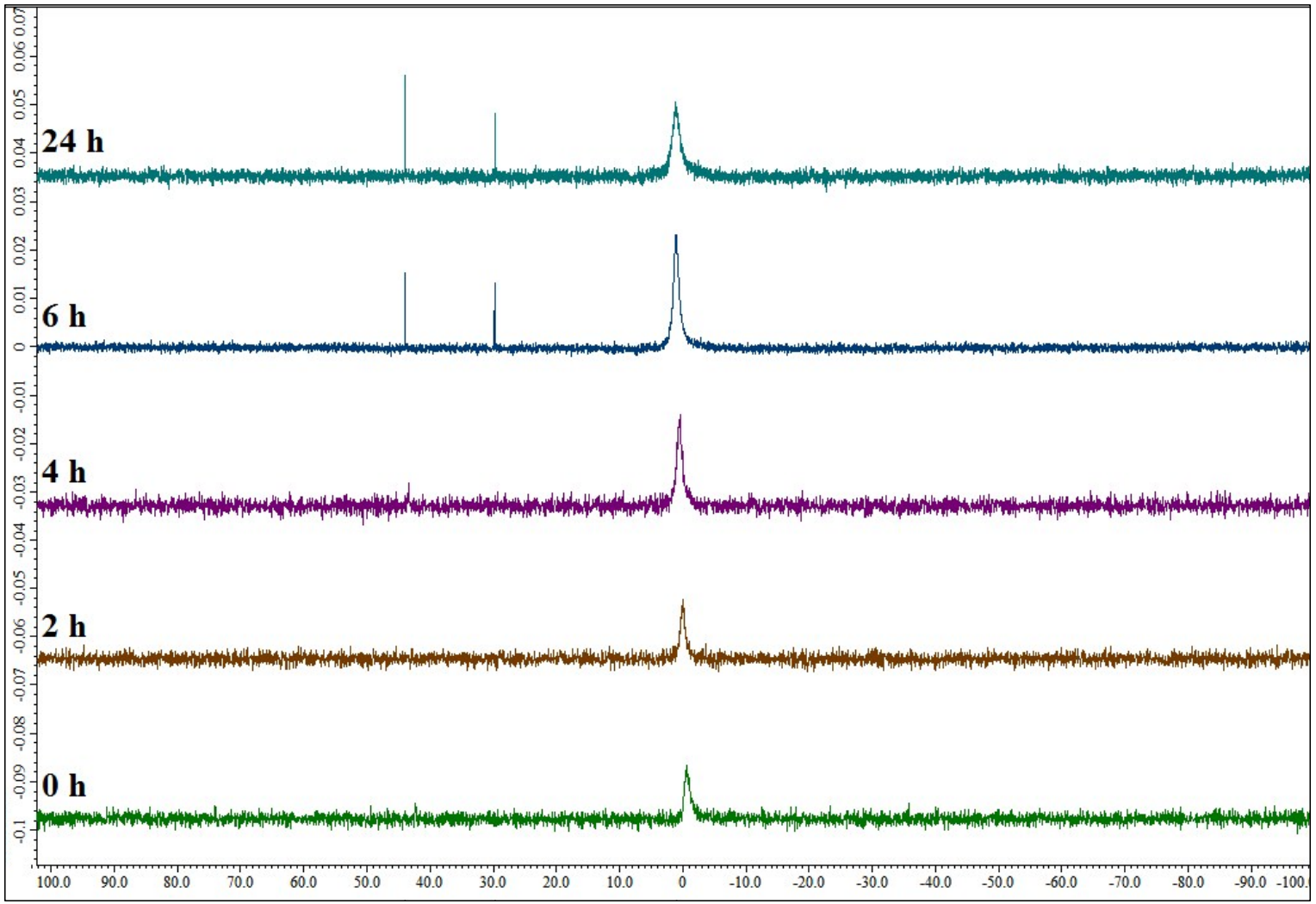
Spectrum 1c: Time dependent ^{31}P NMR (500 MHz, $CDCl_3$) spectra of complex **1**



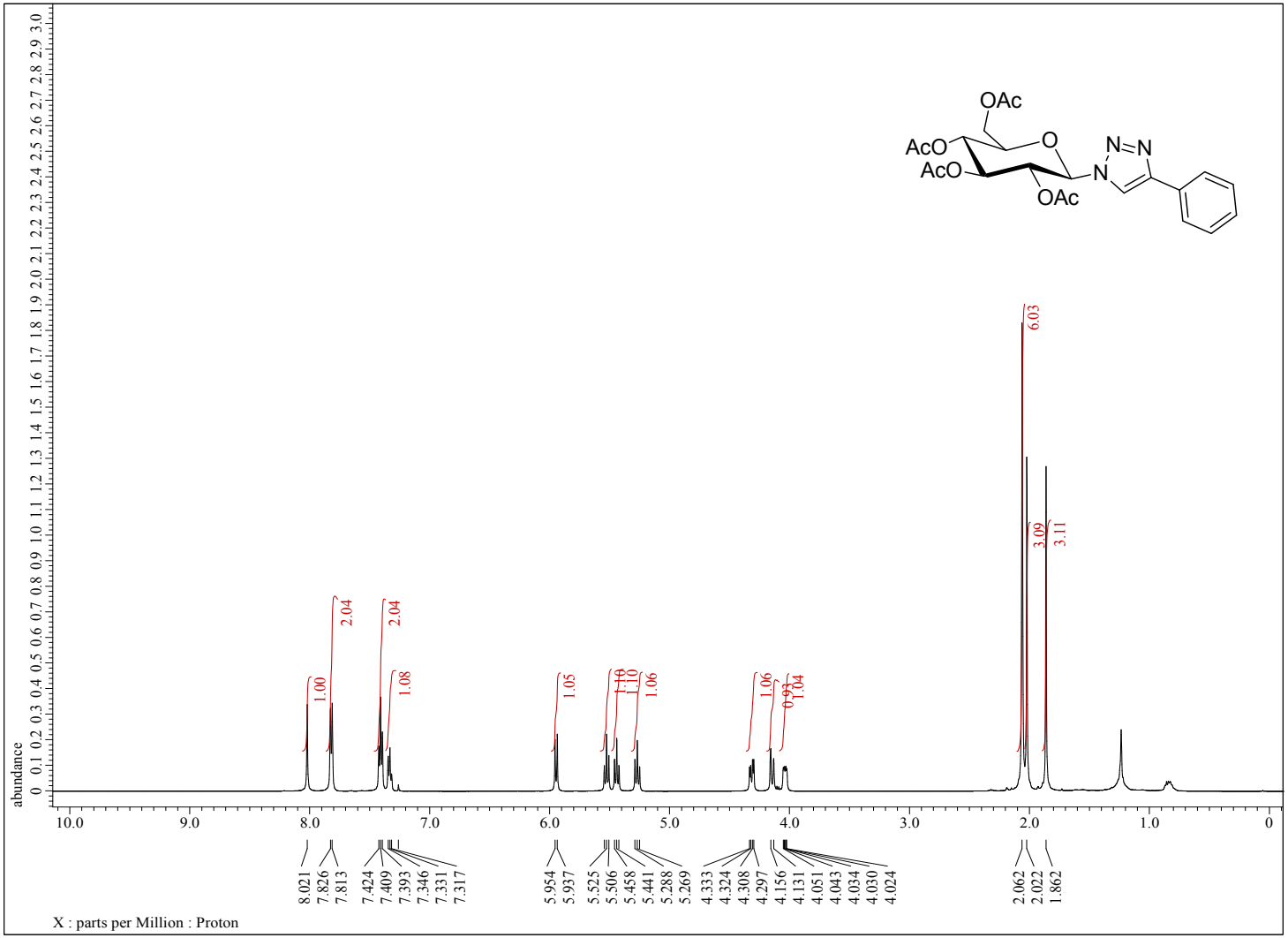
Spectrum 2a: ^{1}H NMR (500 MHz, $CDCl_3$) of complex **4**



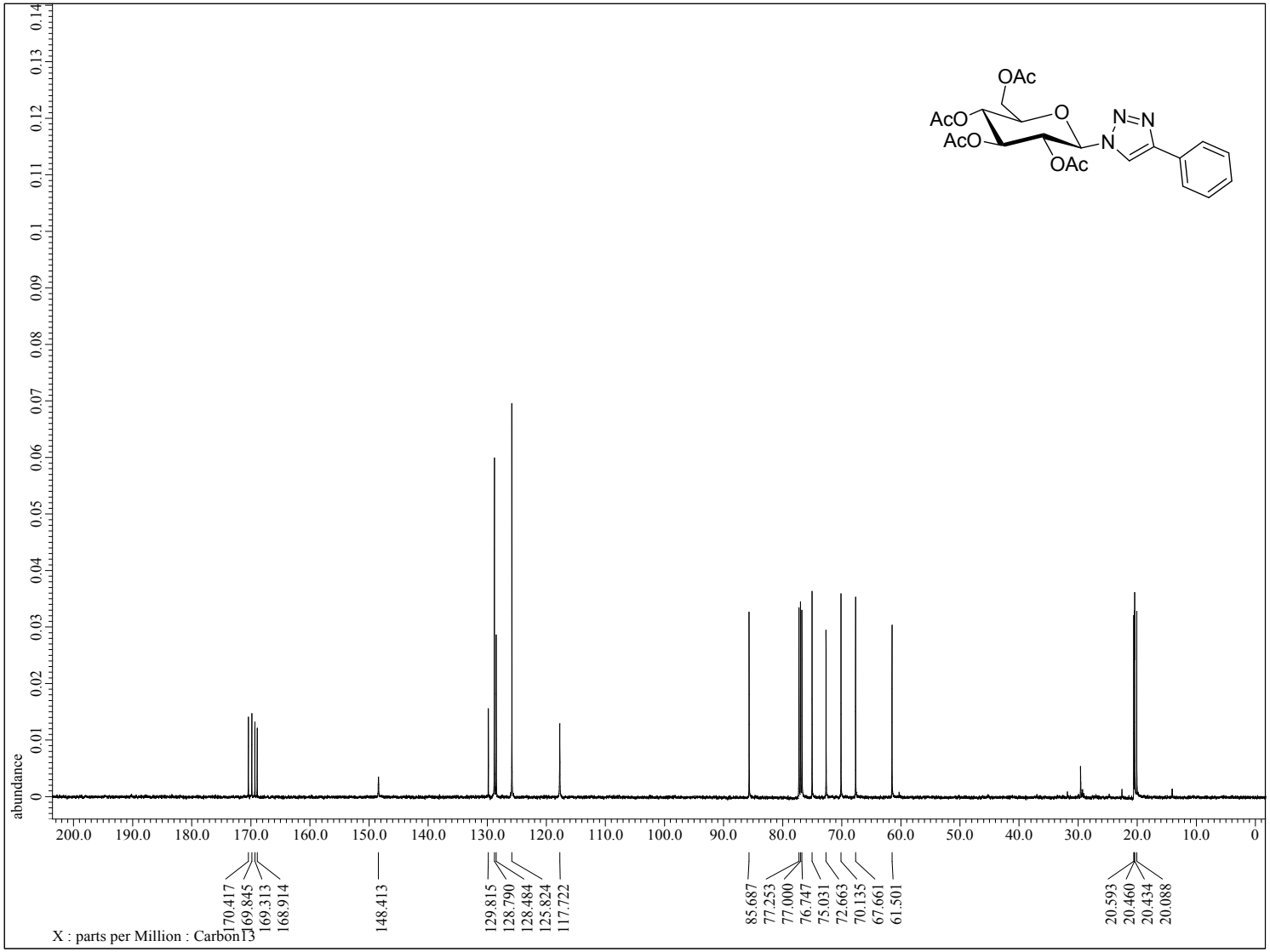
Spectrum 2b: ^{13}C NMR (500 MHz, $CDCl_3$) of complex **4**



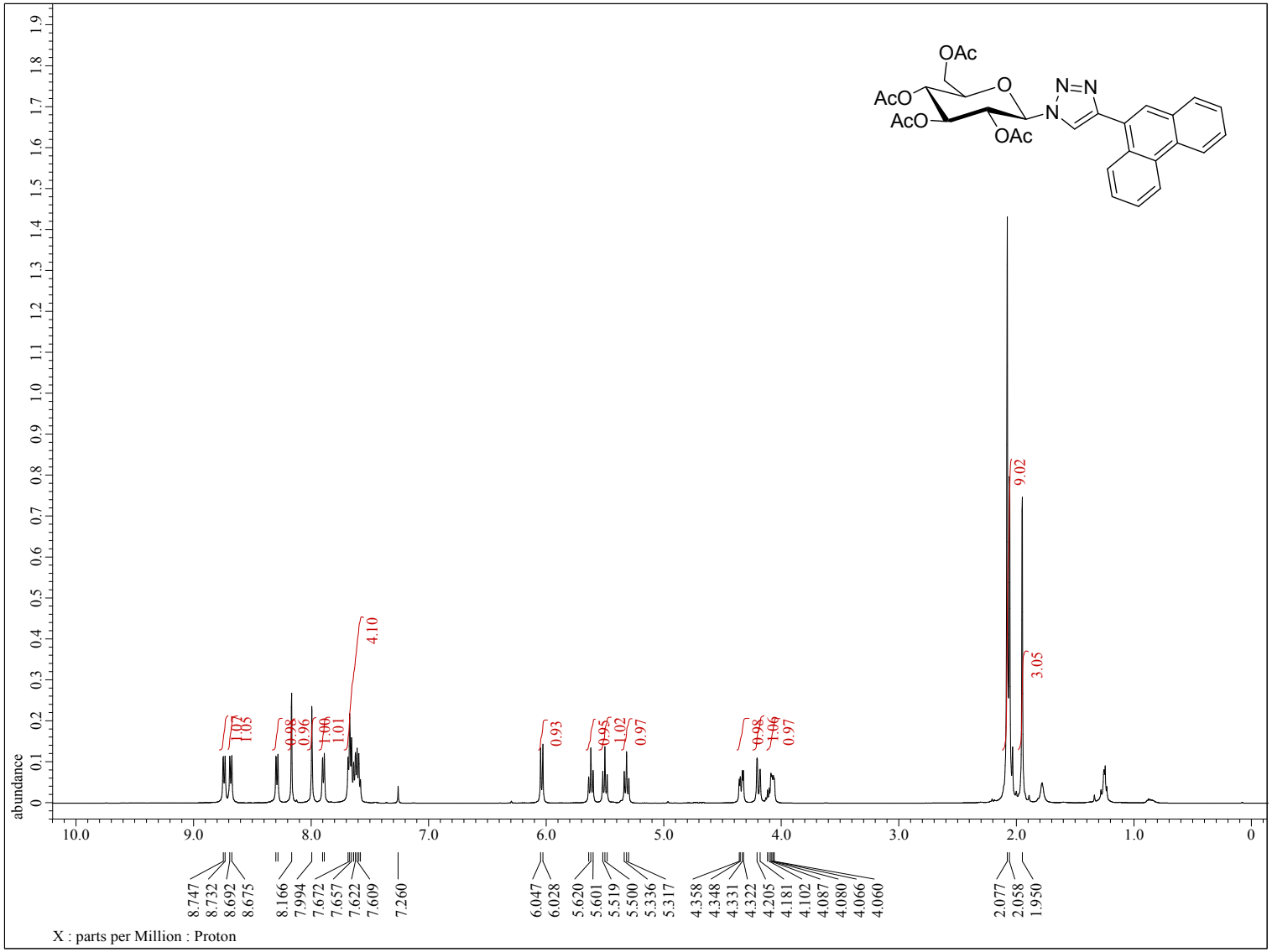
Spectrum 2c : Time dependent ^{31}P NMR (500 MHz, $CDCl_3$) spectra of complex **4**



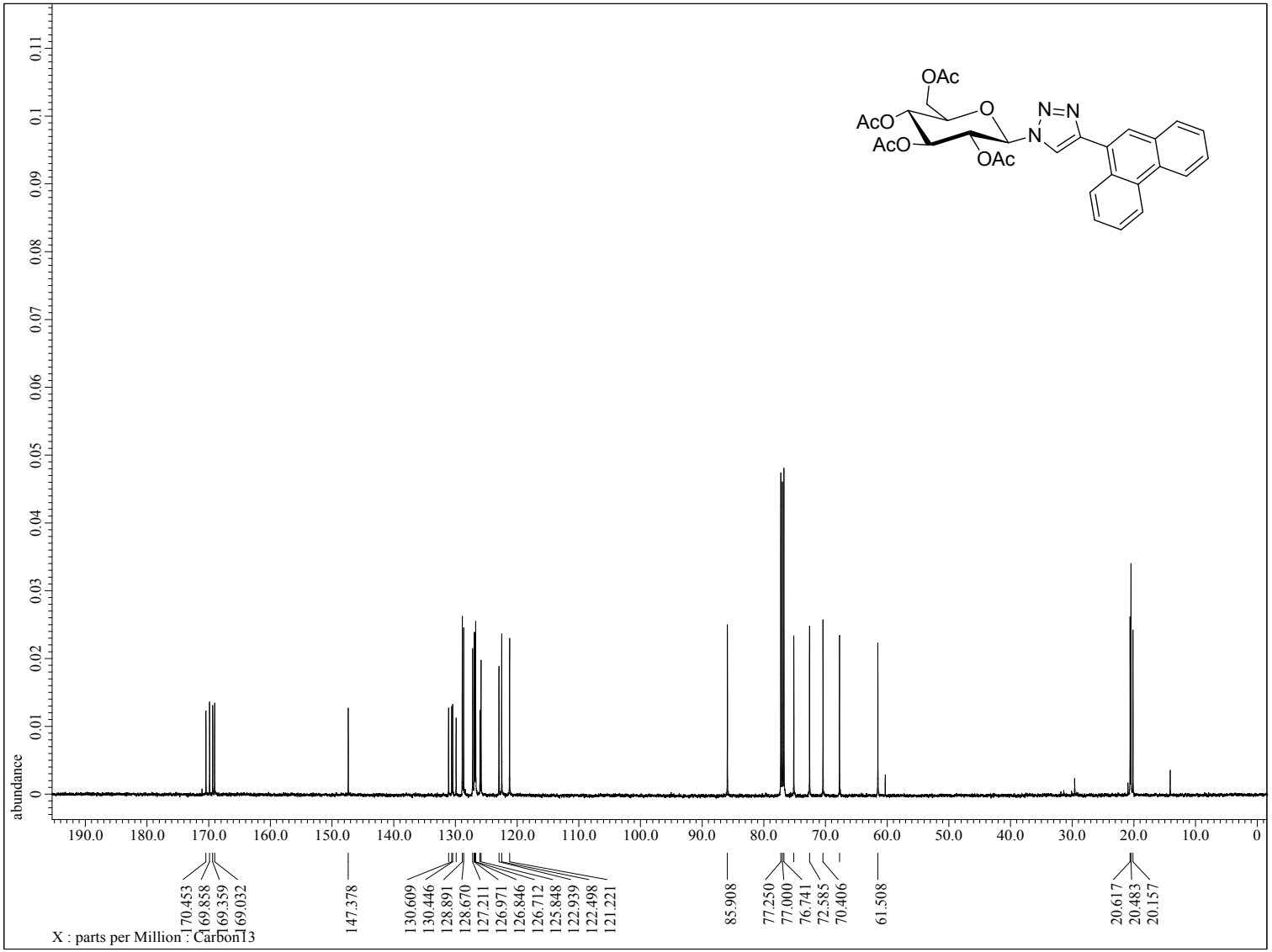
Spectrum 1: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8a**



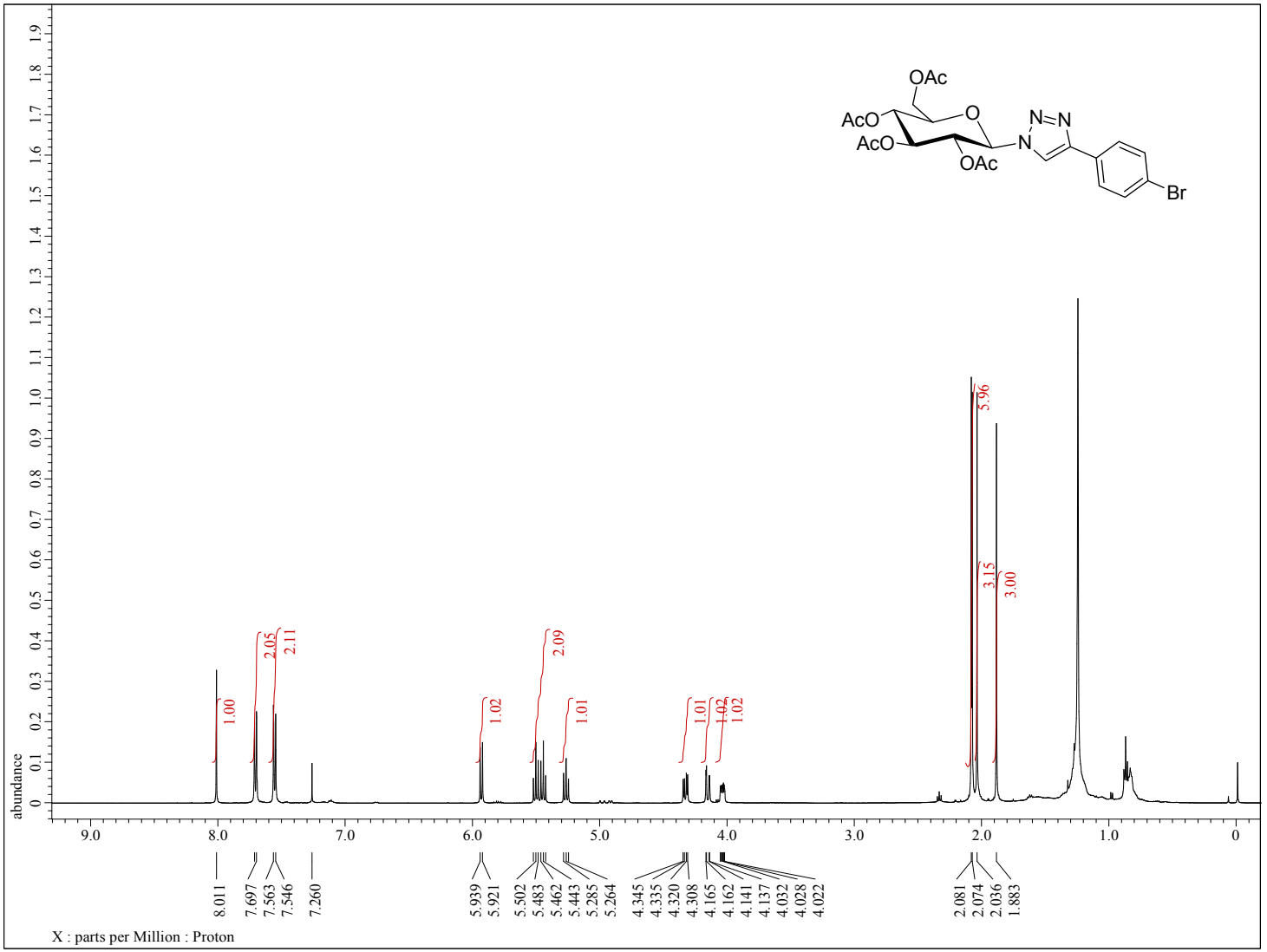
Spectrum 2: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8a**



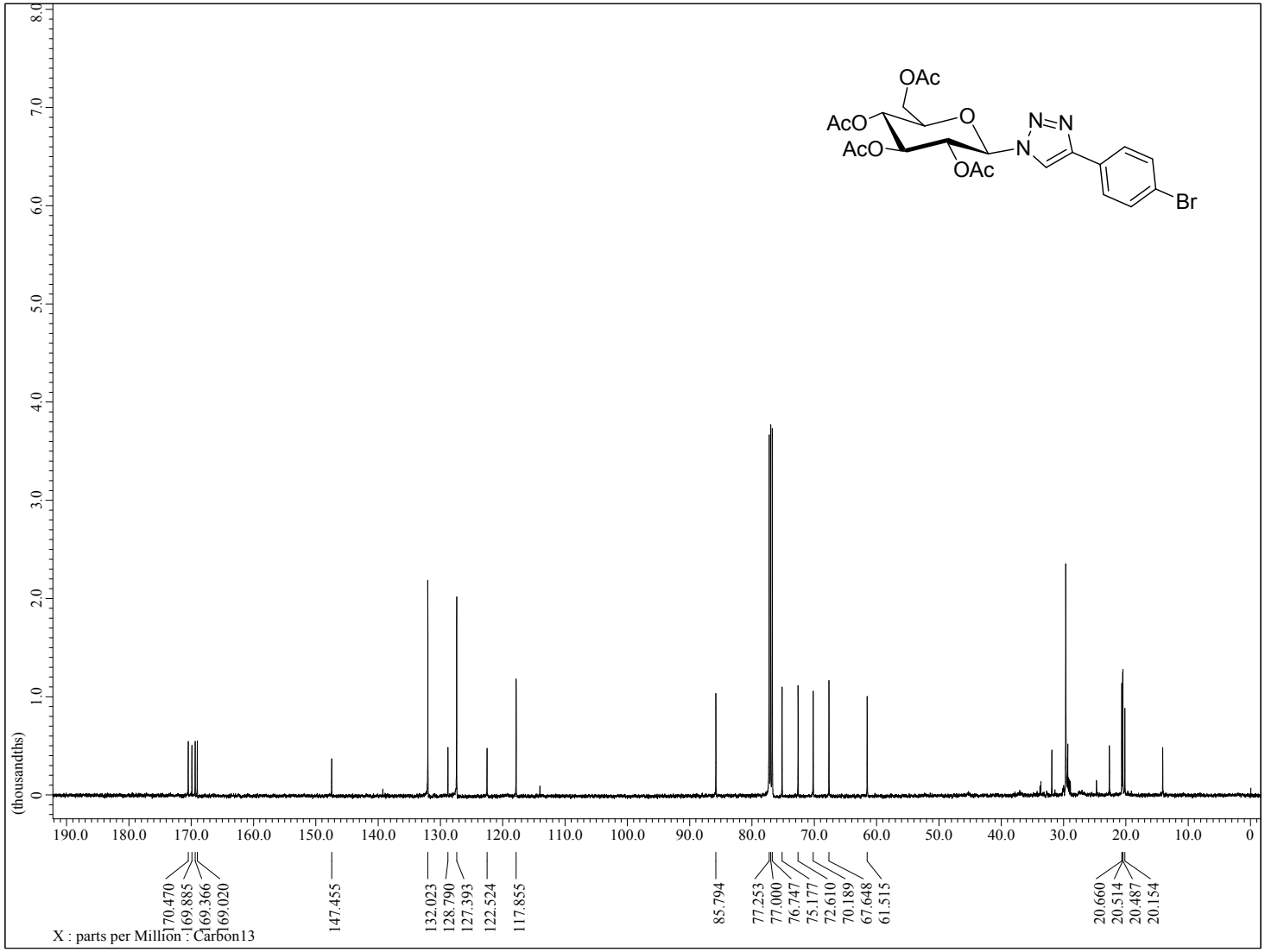
Spectrum 3: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8b**



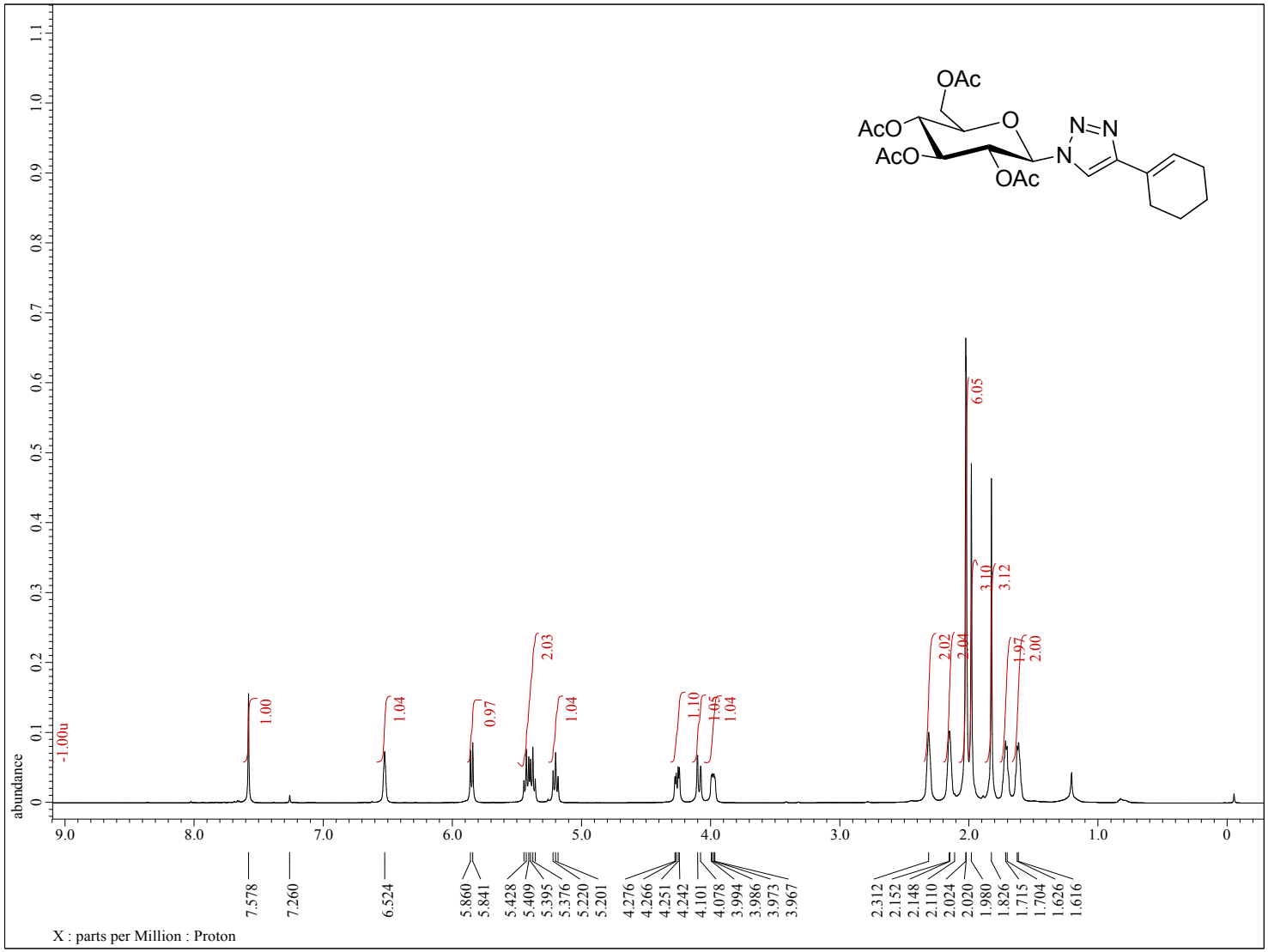
Spectrum 4: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8b**



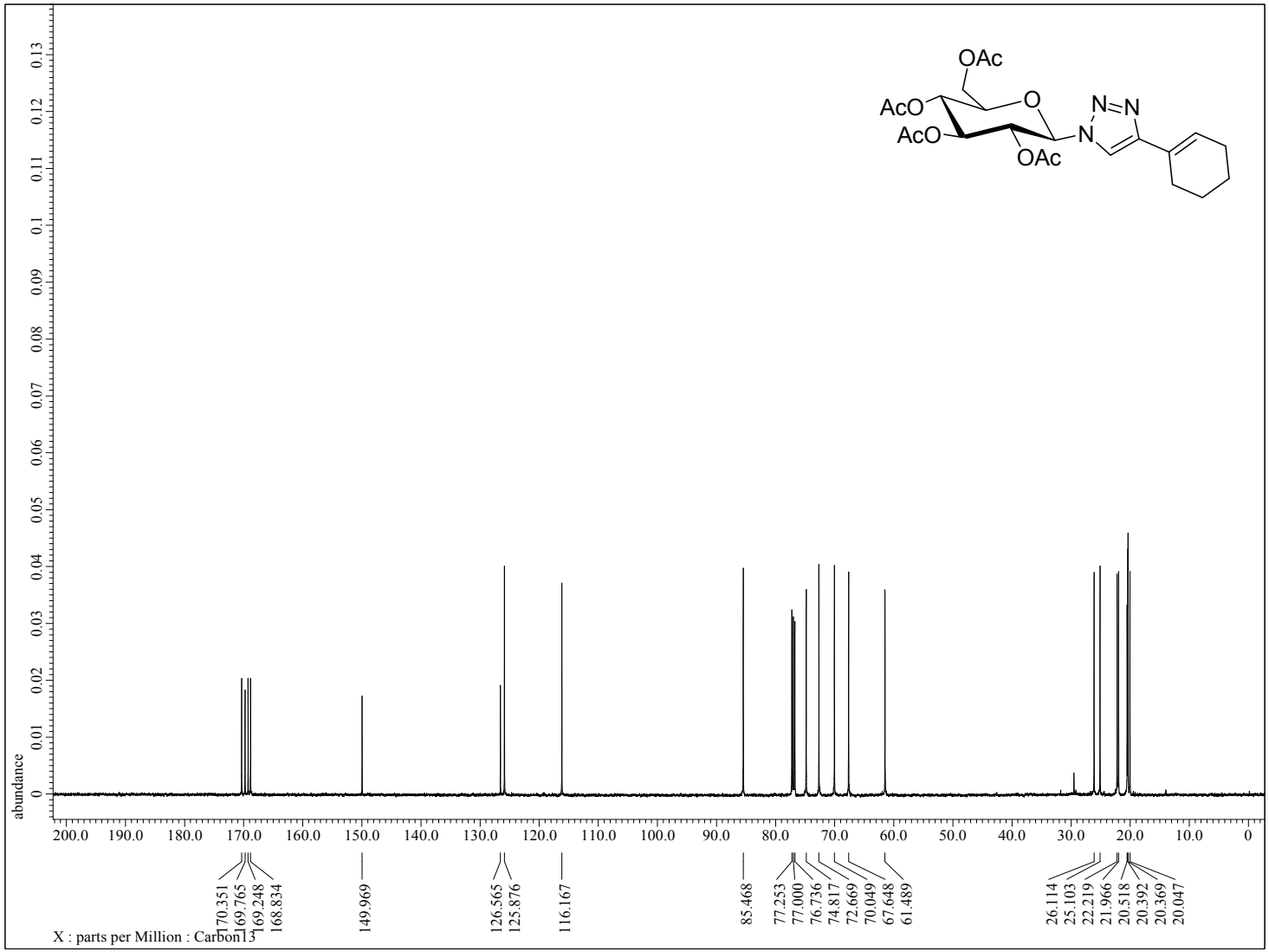
Spectrum 5: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8c**



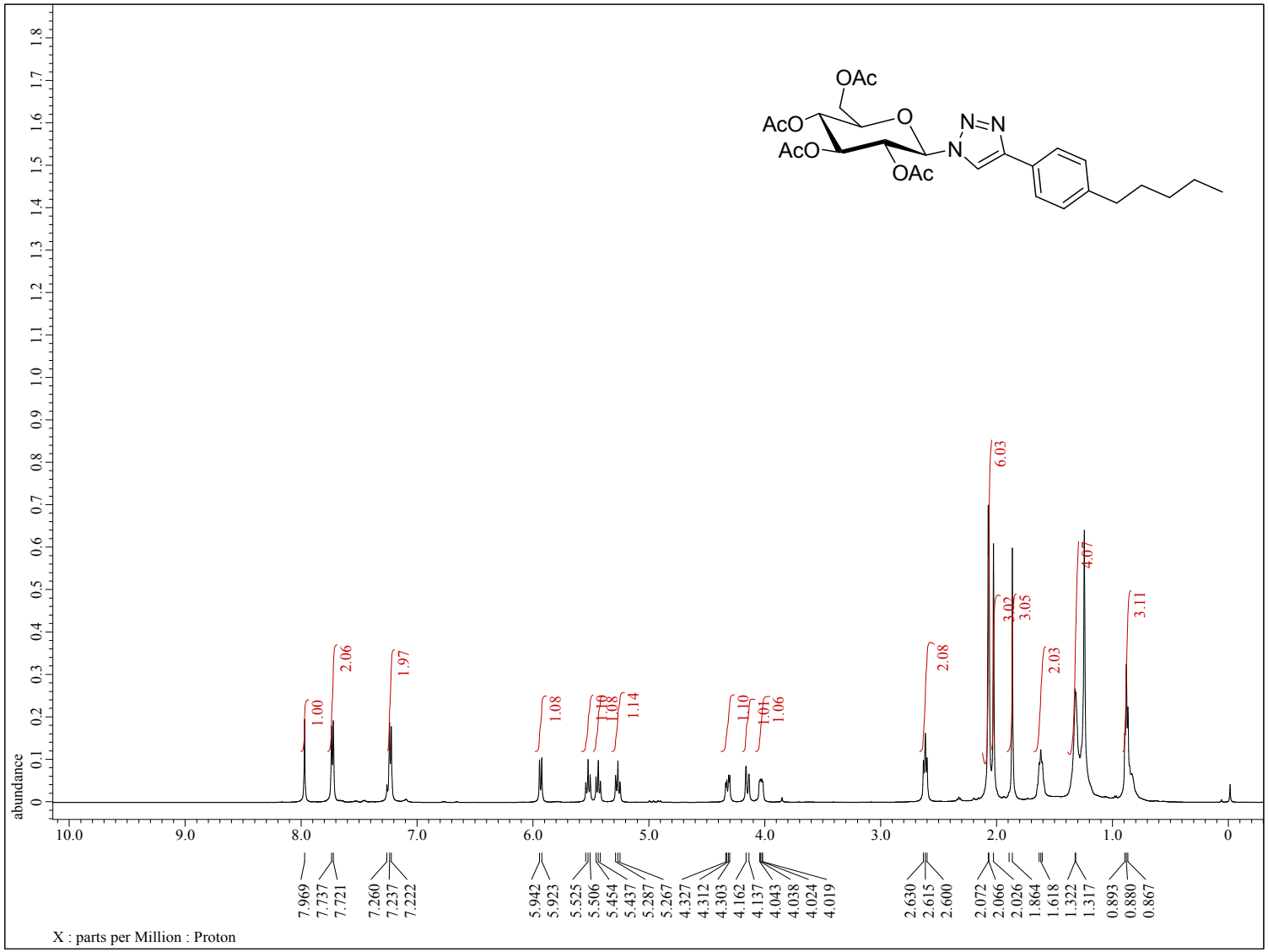
Spectrum 6: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8c**



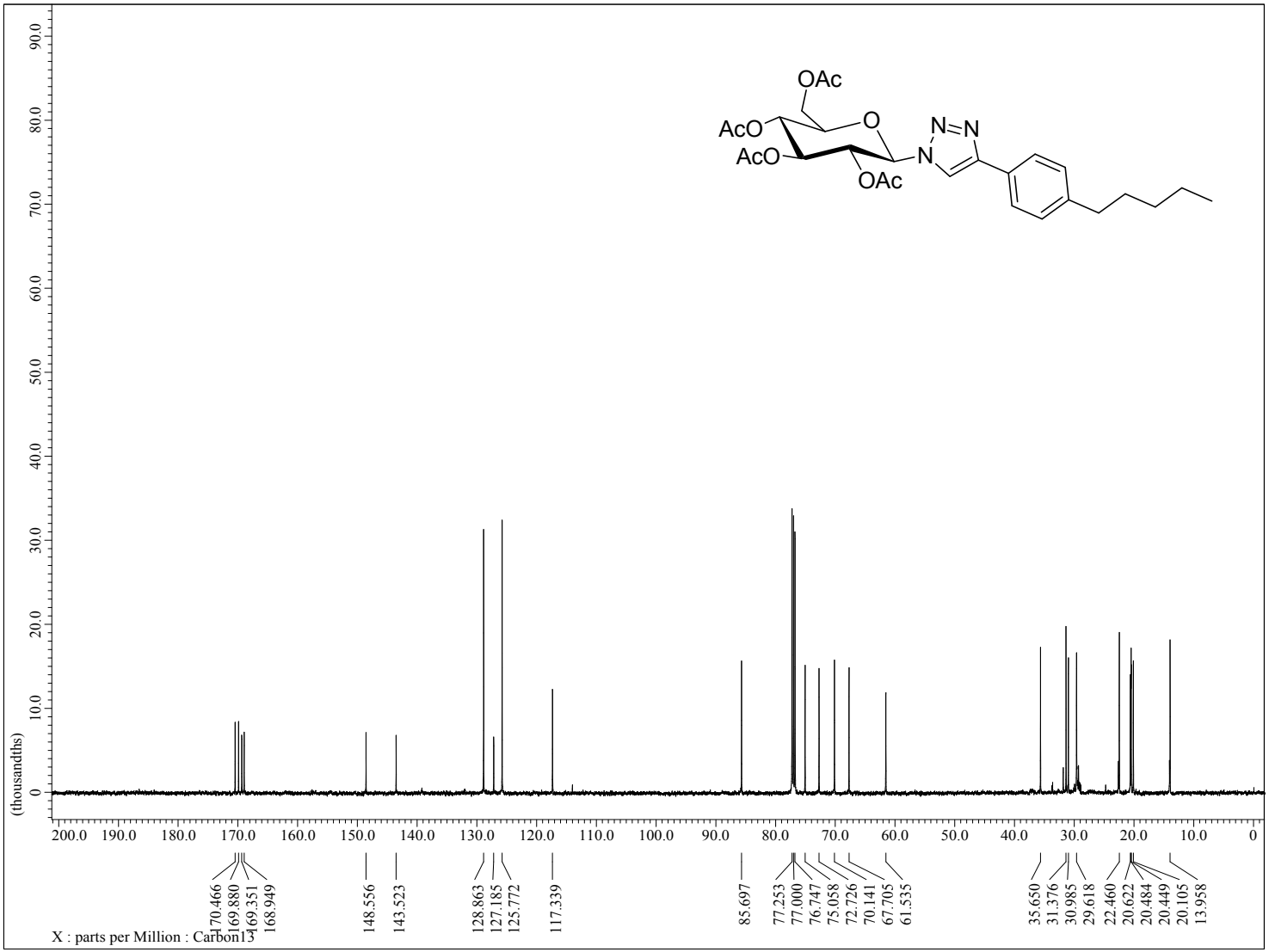
Spectrum 7: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8d**



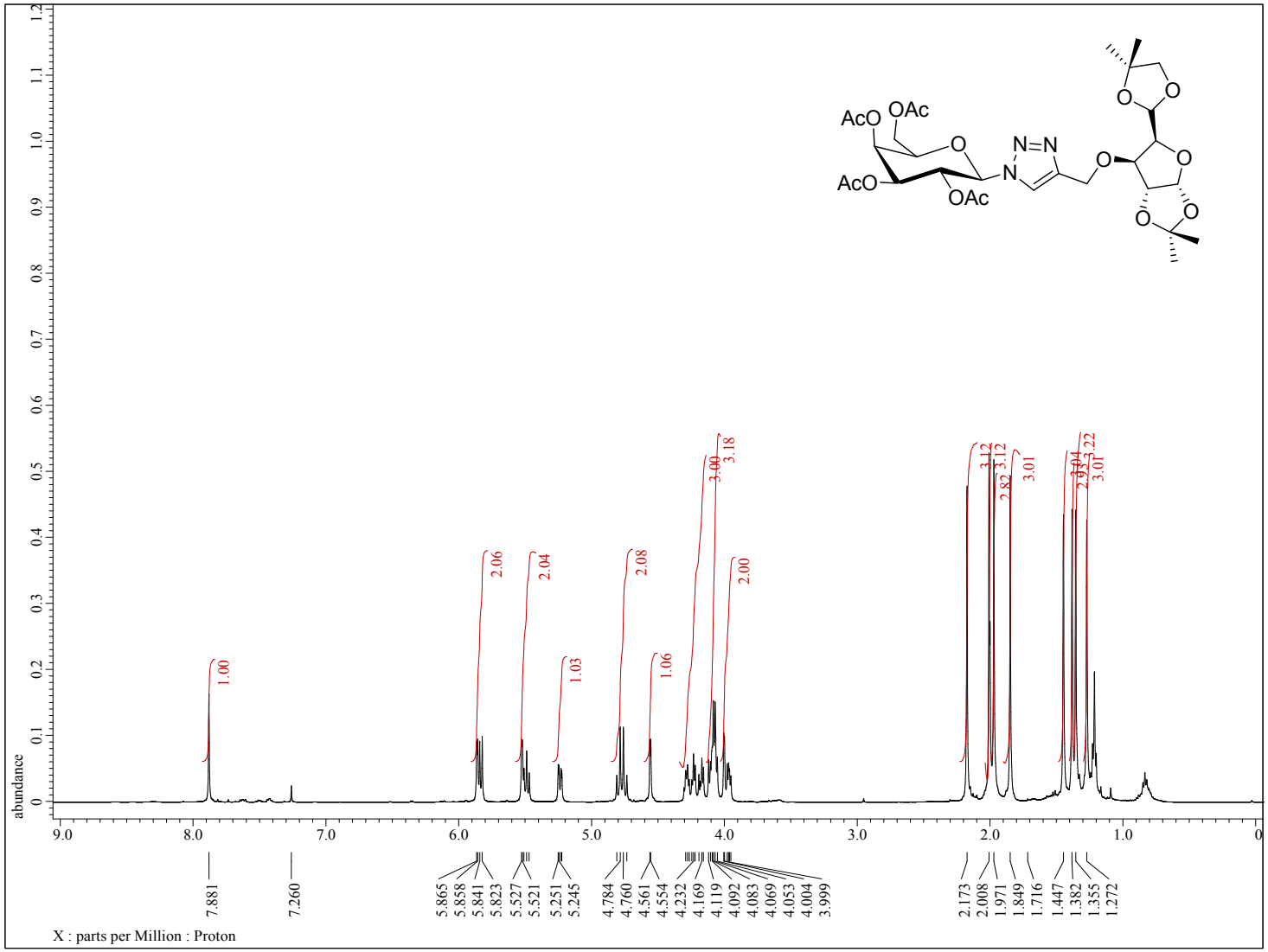
Spectrum 8: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8d**



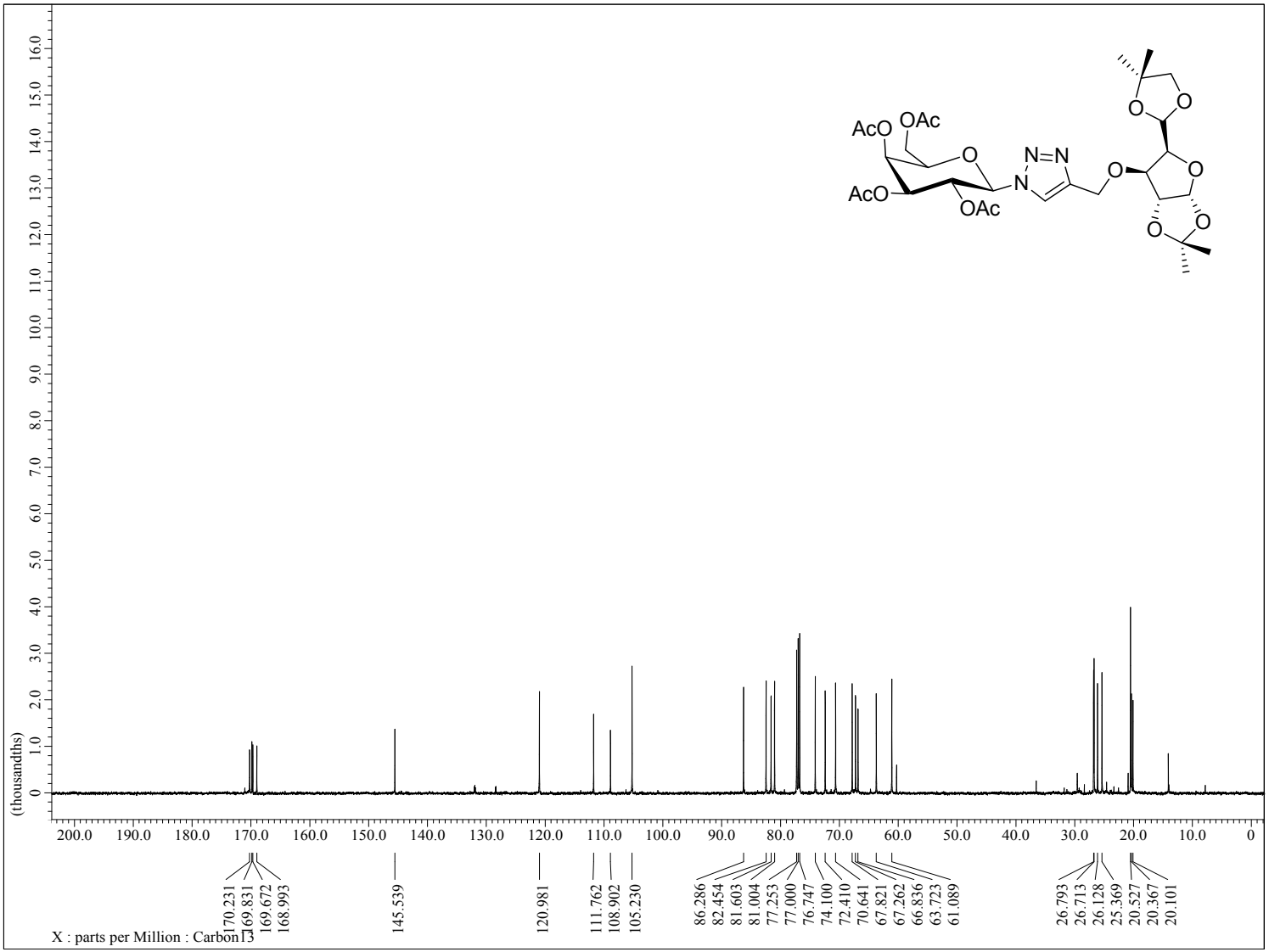
Spectrum 9: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8e**



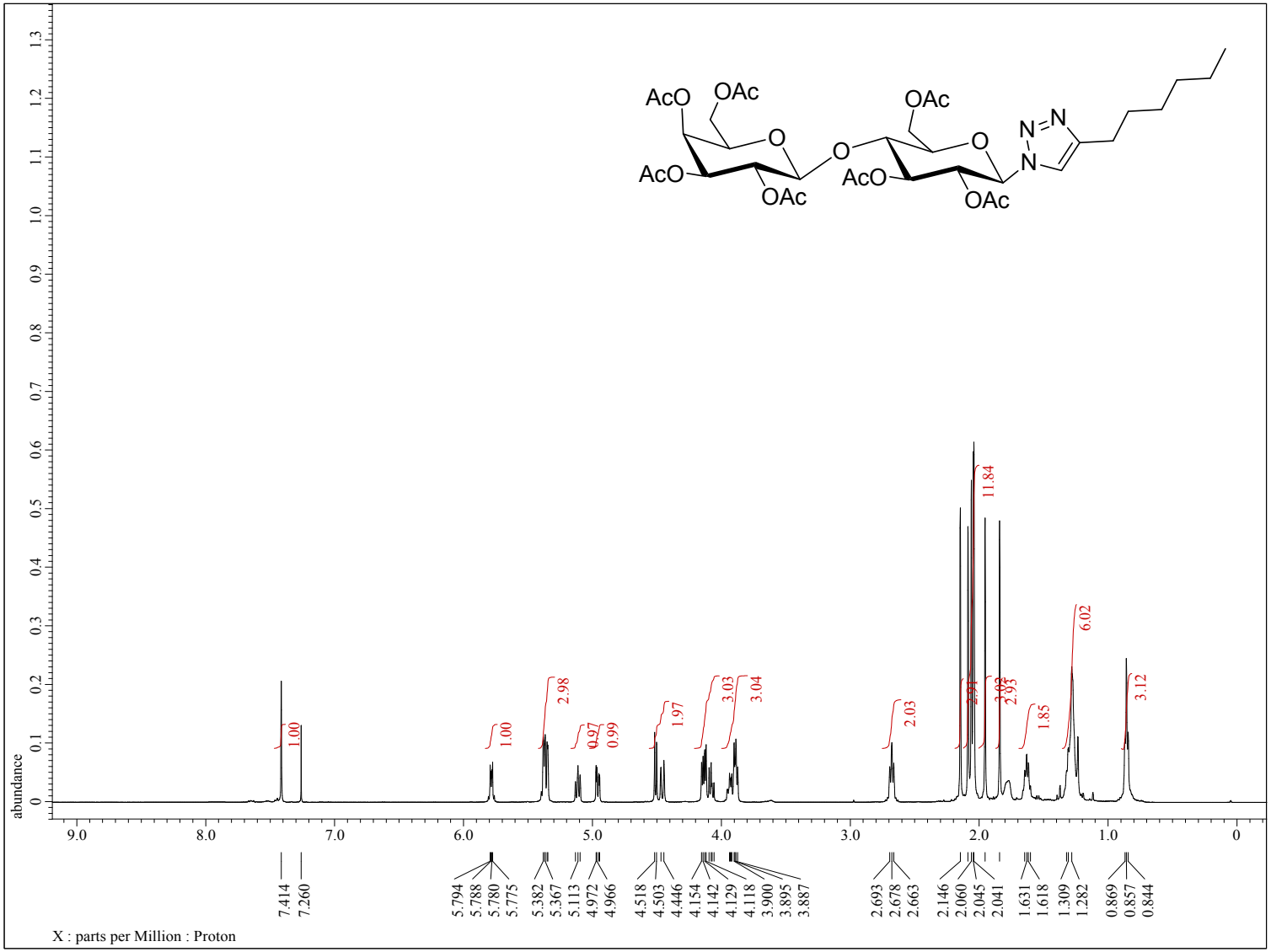
Spectrum 10: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8e**



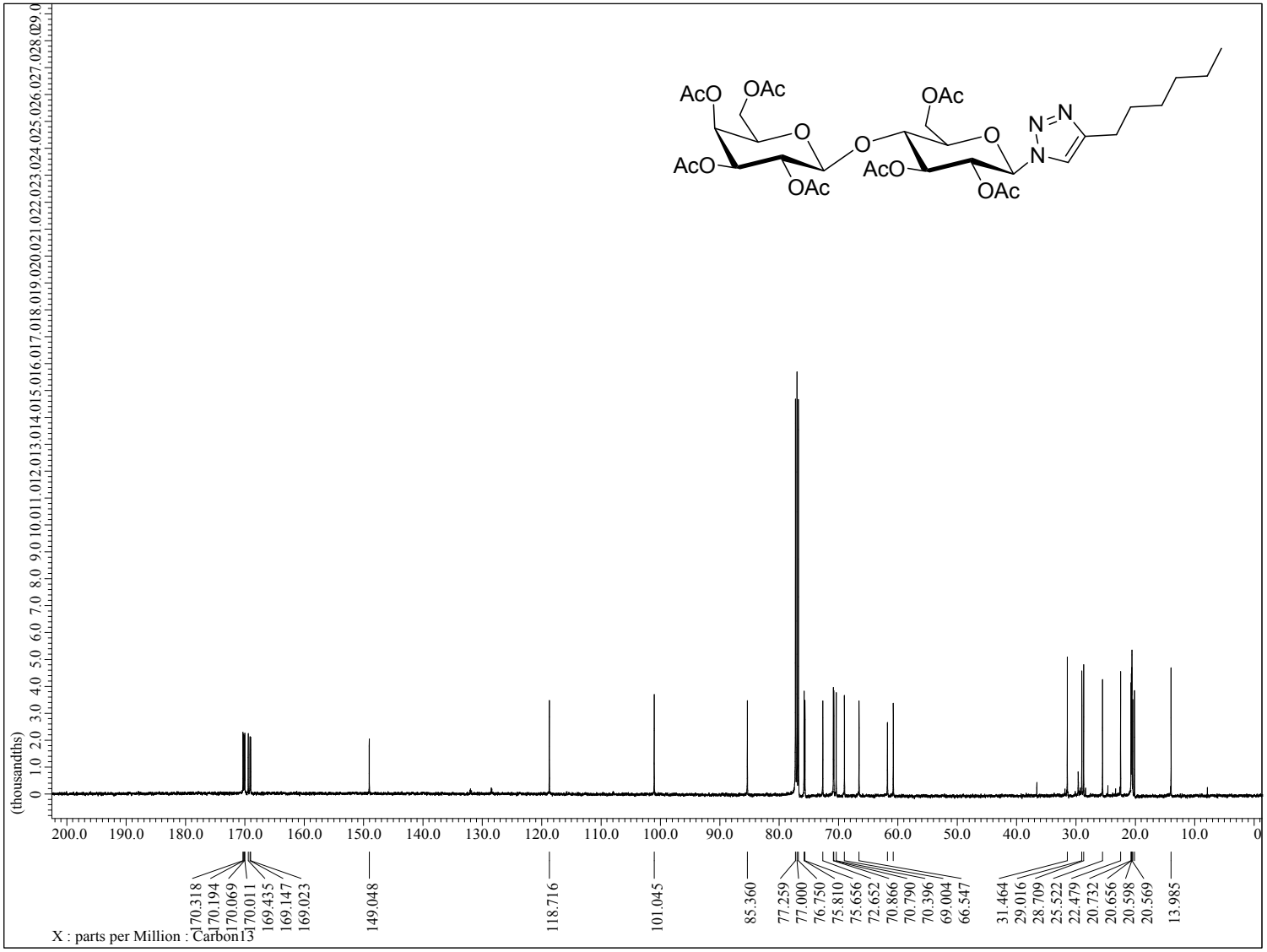
Spectrum 11: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8f**



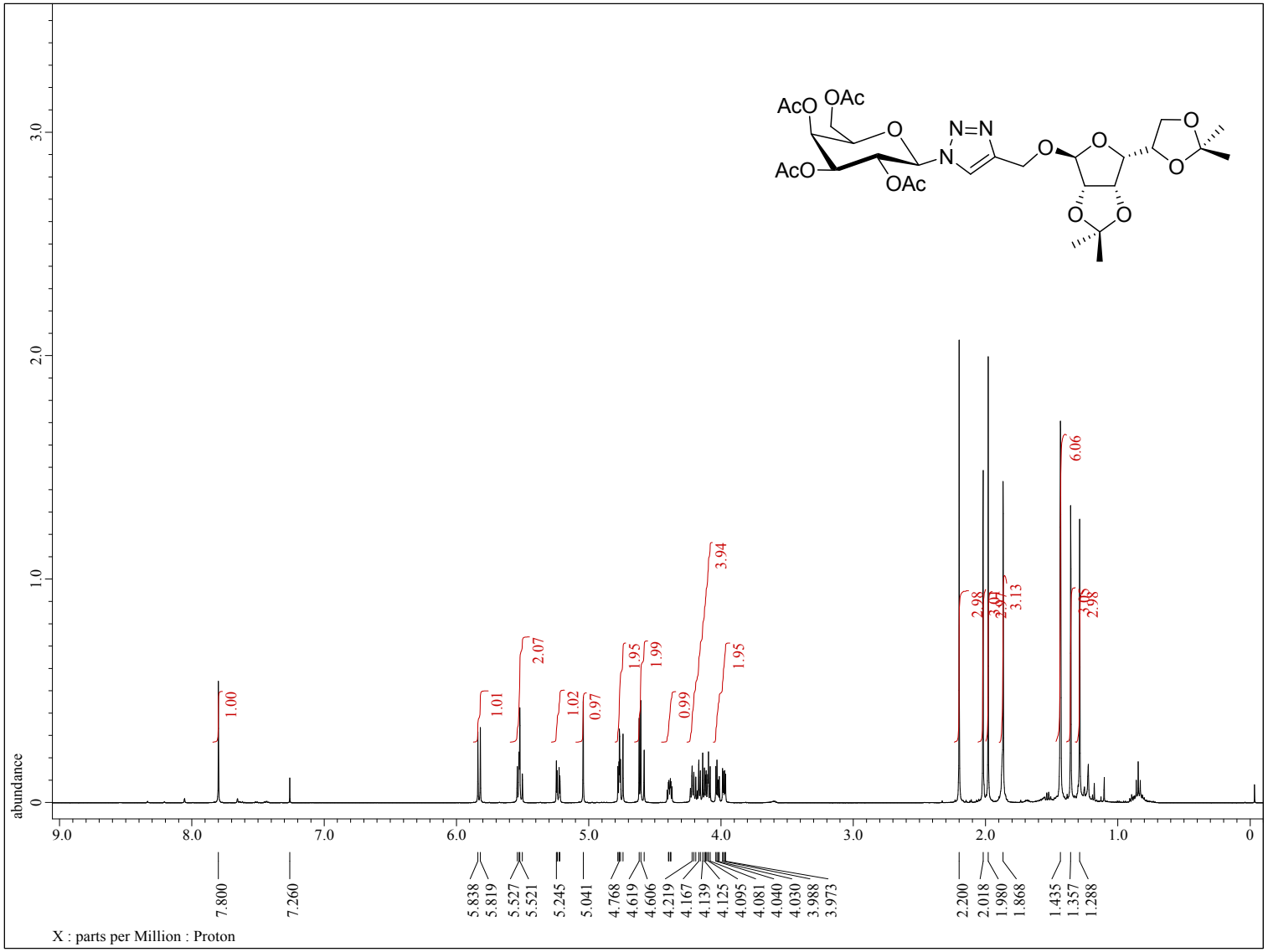
Spectrum 12: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8f**



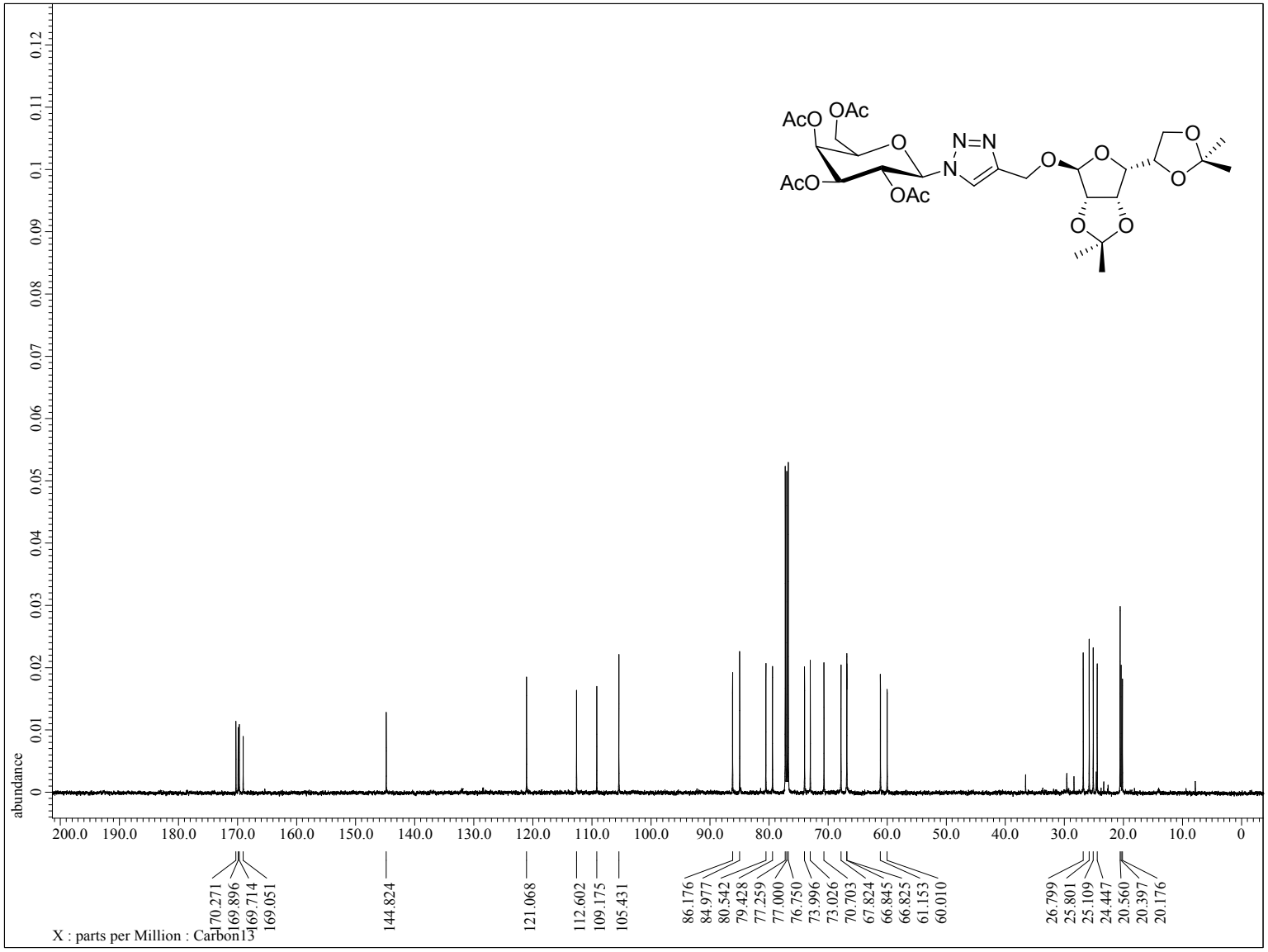
Spectrum 13: ^{1}H NMR (500MHz, $CDCl_3$) of compound **8g**



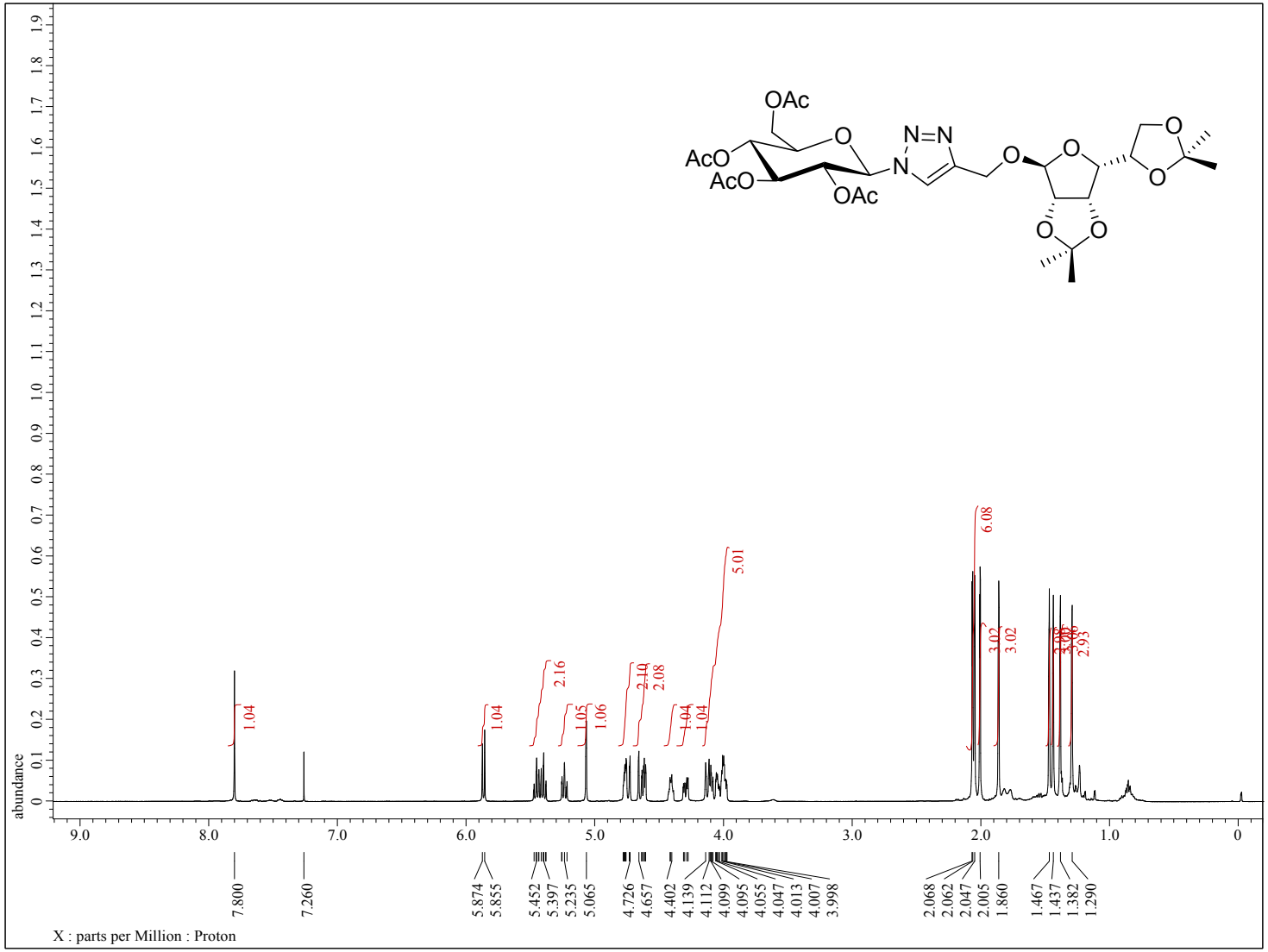
Spectrum 14: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8g**



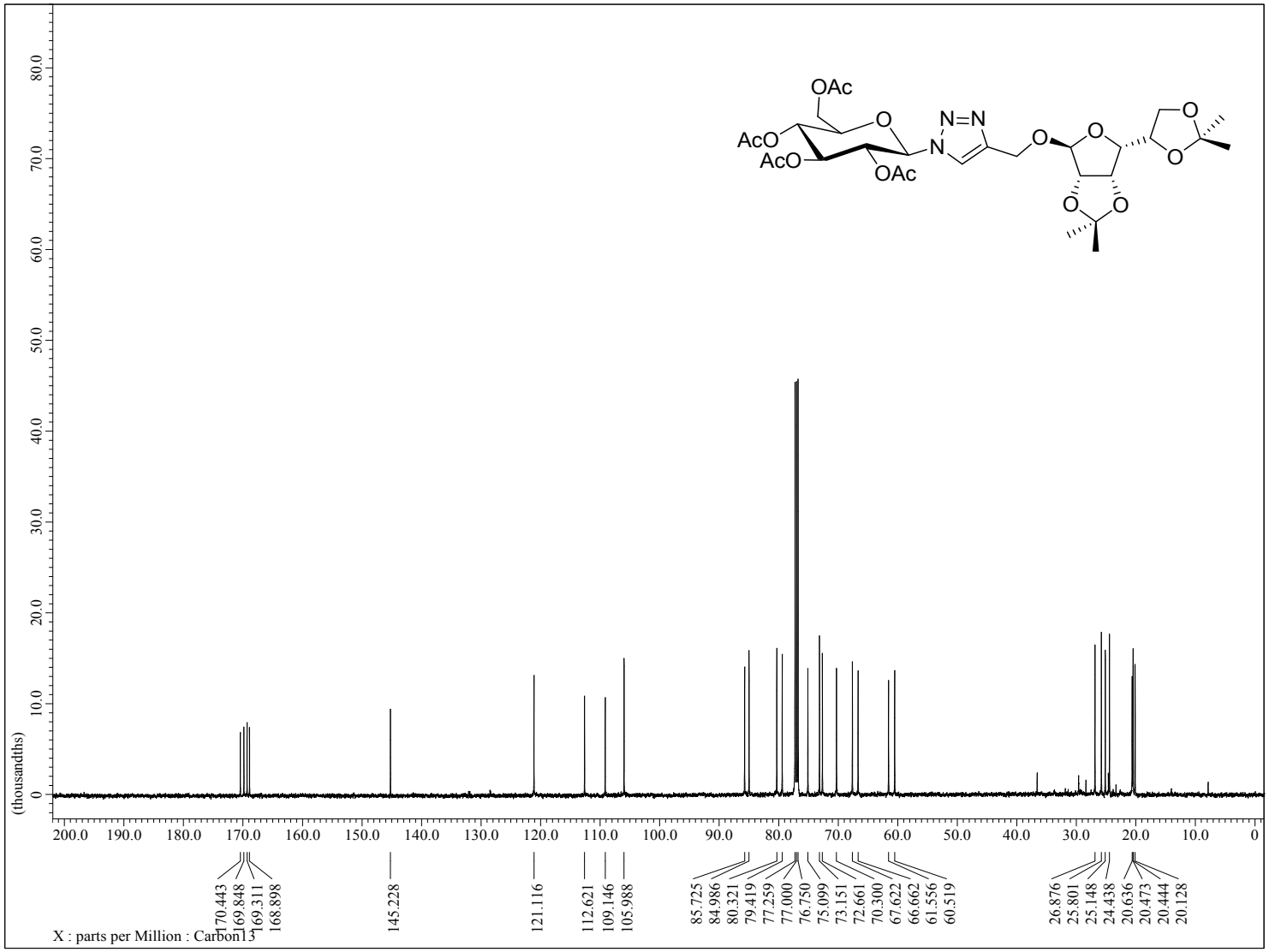
Spectrum 15: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8h**



Spectrum 16: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8h**



Spectrum 17: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8i**



Spectrum 18: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8i**

S5: References

1. K. Kumari, A. S. Singh, K. K. Manar, C. L. Yadav, V. K. Tiwari, M. G. B. Drew and N. Singh, *New J. Chem*., 2019, **43**, 1166.

2. I. S. Okafor and G. Wang *Carbohydr. Res.,* .DOI: 10.1016/j.carres.2017.09.008.