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# SUPPORTING INFORMATION

## Activation of 1, 3-dioxolane by protic ionic liquid in aqueous media: A green strategy for the selective cleavage of acetals and ketals

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### Experimental section

Carbohydrate derived substrates **4 – 8**[1], **9**[2], **12**[3], **13**[4], **14**[5] **and 15**[6] are well known and prepared as procedure described in literature. Purity was checked by IR, $^{1}$H NMR and in some cases $^{13}$C NMR spectra of the substrates. Two substrates namely **10** and **11** are new and they were synthesised as follows:

**3-*O*-(carbo-*tert*-butyloxy methyl) 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (10):** To a stirred suspension of NaH (prewashed with hexanes, 162mg, 6.75 mmol) in THF (10 ml), a solution of 1,2: 5,6-di-*O*-isipropylidene-α-D-glucofuranose (1.172g, 4.5 mmol) in THF (10 ml) was added and refluxed for 30 min in an oil bath. *Tert*-butyl bromoacetate (1.3 g, 6.66mmol) was added and the mixture was continued to reflux for 20 hrs. After cooling, cold saturated solution of ammonium chloride was added to destroy excess NaH. THF was removed under vacuum and the reaction mixture was extracted with dichloromethane (3x 10 ml). The combined organic layer was washed with water (3 x 10 ml), dried over anhydrous sodium sulphate and concentrate under vacuo. Purification by column chromatography over silica gel (60-120 mesh) using ethyl acetate-petroleum ether, the elution of (9:1) ethyl acetate-petroleum ether yielded **10** as white needles (1.01g, 60%), m. p 92-94$^{o}$C ($CHCl_3$- petroleum ether); IR (neat) ν 2988, 1741, 1561, 1371, 1381, 1211, 1230, 1162, 1132, 1100, 1079 $cm^{-1}$; $^{1}$H NMR ($CDCl_3$, 300 MHz) δ 5.88 (d, *J*= 3.6 Hz, 1H), 4.71 (d, *J* = 3.6 Hz, 1H), 4.35-4.29 (m, 1H), 4.16- 4.01 (m, 4H), 3.99-3.92(m, 2H), 1.47 (s, 12H), 1.41 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H); $^{13}$CNMR (75MHz, $CDCl_3$) δ 169.39, 111.79, 108.94, 105.17, 83.44, 83.26, 81.93, 81.06, 72.63, 68.86, 67.14, 28.07, 26.80, 26.76, 26.20, 25.36; HRMS for $C_{18}H_{30}O_8$: calcd 374.19407, found 374.19370

**3-*O*-(2-allyloxycarbonyl)benzoyl) 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (11):** A mixture of 1,2:5,6-di-*O*-isipropylidene-α-D-glucofuranose (2.6 g, 10 mmol), phthalic anhydride (1.62g, 11 mmol) in DMF (10 ml) and one drop of pyridine was heated in oil bath at 100$^{o}$C. After completion of reaction (as revealed by TLC) the mixture was diluted with water (100 ml) and extracted with ethyl acetate (3 x 10 ml). The combined organic layer was washed with water, dried, concentrated under reduced pressure, dried under vacuum and used for next step without further purification. The half ester of phthalic acid was dissolved in DMF (20 ml) and then anhydrous $K_2CO_3$ (1.65g, 12 mmol) and allyl bromide (1.5 ml, 18 mmol) was added to it. The mixture was heated at 60$^{o}$C for 3 hr. After dilution of mixture with cold

water, the mixture was extracted with ethyl acetate (3 x 10 ml).The combined organic layer was washed with water, dried over $Na_2SO_4$ and concentrate under reduced pressure. The crude product was purified by column chromatography over silica gel (60-120 mesh). The elution of 5:1 ethyl acetate-petroleum ether afforded **11** as a light yellow syrup (2.73g, 61%); IR (neat) ν 2980, 2940, 1725, 1592, 1450, 1275 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.4 Hz, 1H), 7.70 (bs, 1H), 7.56 (bs, 2H), 6.06 – 5.96 (m, 1H), 5.9 (bs, 1H), 5.42 (bs, 2H), 5.30 (d, *J* = 9.6 Hz, 1H), 4.81 (bs, 3H), 4.27-4.23 (m, 2H), 4.02 (bs, 2H), 1.49 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H); $^{13}$CNMR (75 MHz, $CDCl_3$) δ 166.7, 166.4, 131.9, 131.7, 131.5, 131.4, 131.3, 127.1, 129.0, 118.8, 112.2, 109.3, 105.2, 82.7, 79.7, 77.5, 72.4, 67.2, 66.4, 26.9, 26.8, 26.3, 25.3; EI MS 448, 433 ($M^+$-15), 391, 375, 347, 289, 207, 189, 149, 113, 101; HRMS calcd $C_{23}H_{28}O_9$ 448.1733 found: 448.1790. Non carbohydrate precursors **27-33** are known and prepared as literature procedure.[1,8,9] Identity and purity was checked by $^1H$ NMR spectral analysis.

**General procedure for hydrolytic cleavage of 1,3-dioxolanes:**

A mixture of 1,3-dioxolane (1 mmol) and protic ionic liquid (100 mlo% or 10 mol%) was heated in an oil bath at 70 $^oC$ for 5 min. To this mixture, deionised water (2 mL for carbohydrate compounds) or water-methanol (1:1, v/v, 2 mL for non-carbohydrate substrates) was added and heating was continued until the disappearance of the starting materials (monitored by thin layer chromatography). After cooling, the mixture was extracted with ethyl acetate (3x5 ml) for carbohydrate compounds and diethyl ether (3x5 mL) for non-carbohydrate compounds. The combined organic layer was washed with water, dried over anhydrous sodium sulphate and concentrated at ambient temperature in a rotary evaporator under reduced pressure. The aqueous phase was recycled. In most of the cases the compounds were essentially pure. For collection of analytical data, products were purified by passing through short pad silica gel (60-120 mesh)

column which afforded analytically pure compounds. Diols **3**[1], **16**[2], **17-19**[1], **20**[2], **24**[7], and **25**[5] are known. Analytical data of **21-23** and **26** are given below.

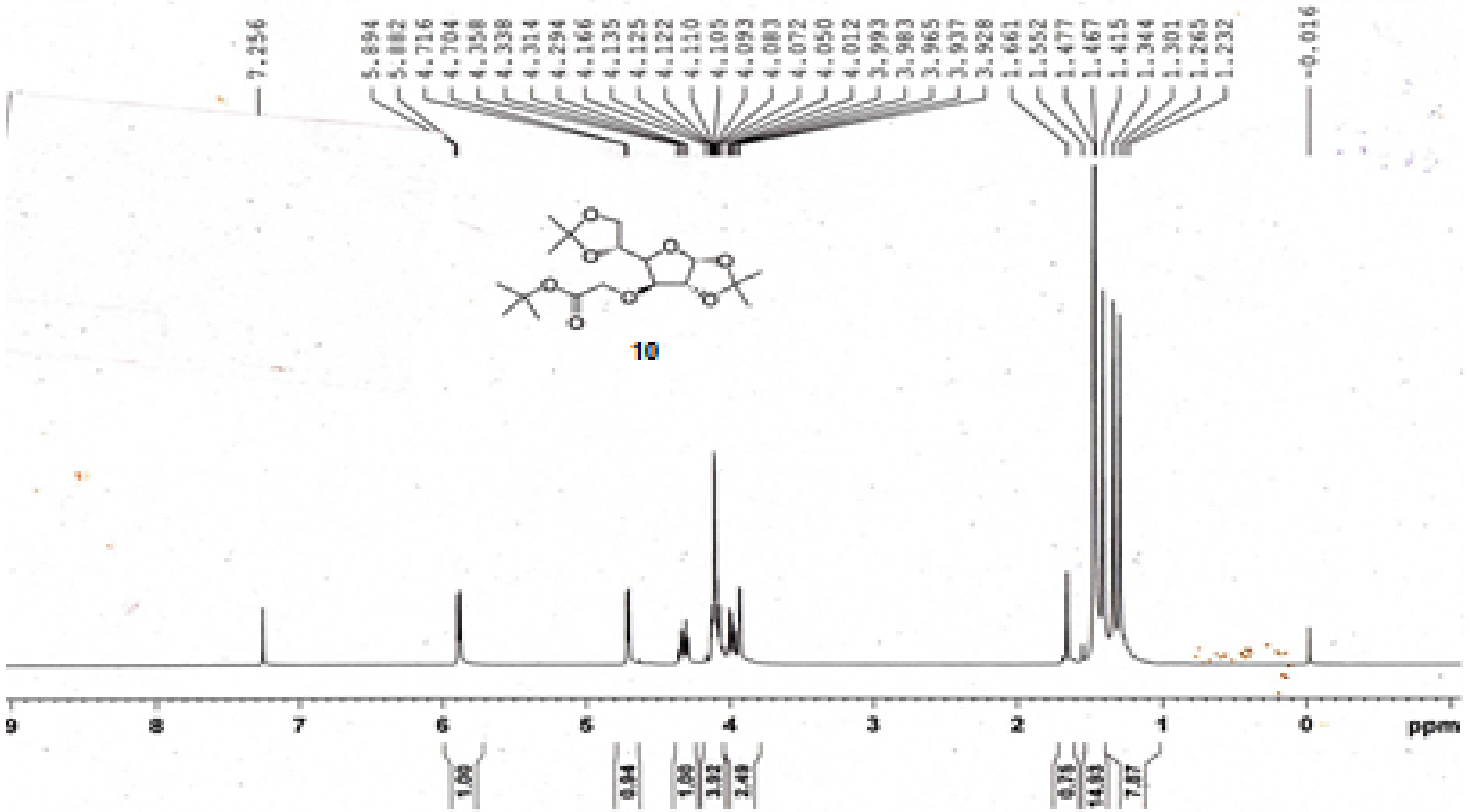
**3-*O*-(carbo-*tert*-butyloxy methyl) 1,2-*O*-isopropylidene-α-D-glucofuranose (21):** Yield: 0.336g, 90%; clear thick syrup; IR (neat) ν 3445, 2981, 2937, 1728, 1458, 1372, 1384, 1250, 1131, 1087 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 5.91 ( d, *J* = 3.9 Hz, 1H), 5.11 (d, *J* = 2.4 Hz, 1H), 4.47 ( d, *J* = 3.6 Hz, 1H), 4.17 – 4.12 (m, 2H), 4.04-3.93 ( m, 2H), 3.85 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.67 ( dd, *J* = 11.1, 6.0 Hz, 1H), 1.49 (s, 12H), 1.29 (s, 3H); $^{13}$NMR (75 MHz, $CDCl_3$) δ 171.35, 111.97, 105.58, 83.73, 82.90, 81.91, 81.77, 68.62, 65.87, 64.37, 27.99, 26.68, 26.24; HRMS for $C_{15}H_{26}O_8$: calcd 334.16277, found 334.16263.

**3-*O*-(2-allyloxycarbonyl) benzoyl 1,2-*O*-isopropylidene-*a*-D-glucofuranose (22):** Yield: 0.313g, 70% , colourless syrup, IR (neat) ν 3507, 2988, 2938, 1727, 1376, 1074 $cm^{-1}$; $^1$HNMR (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 1H), 7.65 – 7.54 (m, 3H), 6.06 -5.96 (m, 1H), 5.91 (d, *J* = 3.9 Hz, 1H), 5.50 (d, *J* = 2.7 Hz, 1H), 5.42 (d, *J* = 17.1Hz, 1h), 5.32 (d, *J* = 11.1 Hz, 1H), 4.83 (d, *J* = 5.4Hz, 2H), 4.70 (d, *J* = 3.6 Hz, 1H), 4.29 (dd, *J* = 8.7 Hz, 2.4Hz, 1H), 3.86-3.77 (m, 2H), 3.72-3.66 (m, 1H), 1,54 (s, 3H), 1.34 (s, 3H); $^{13}$ CNMR (75MHz, $CDCl_3$ ) δ 167.2, 166.7, 132.1, 131.8, 131.3, 131.0, 130.2, 129.2, 128.7, 118.9, 112.1, 104.9, 82.5, 78.7, 77.4, 68.0, 66.4, 63.9, 26.4, 26.0; HRMS calcd for $C_{20}H_{24}O_9$ 408.1420, found: 408.1421.

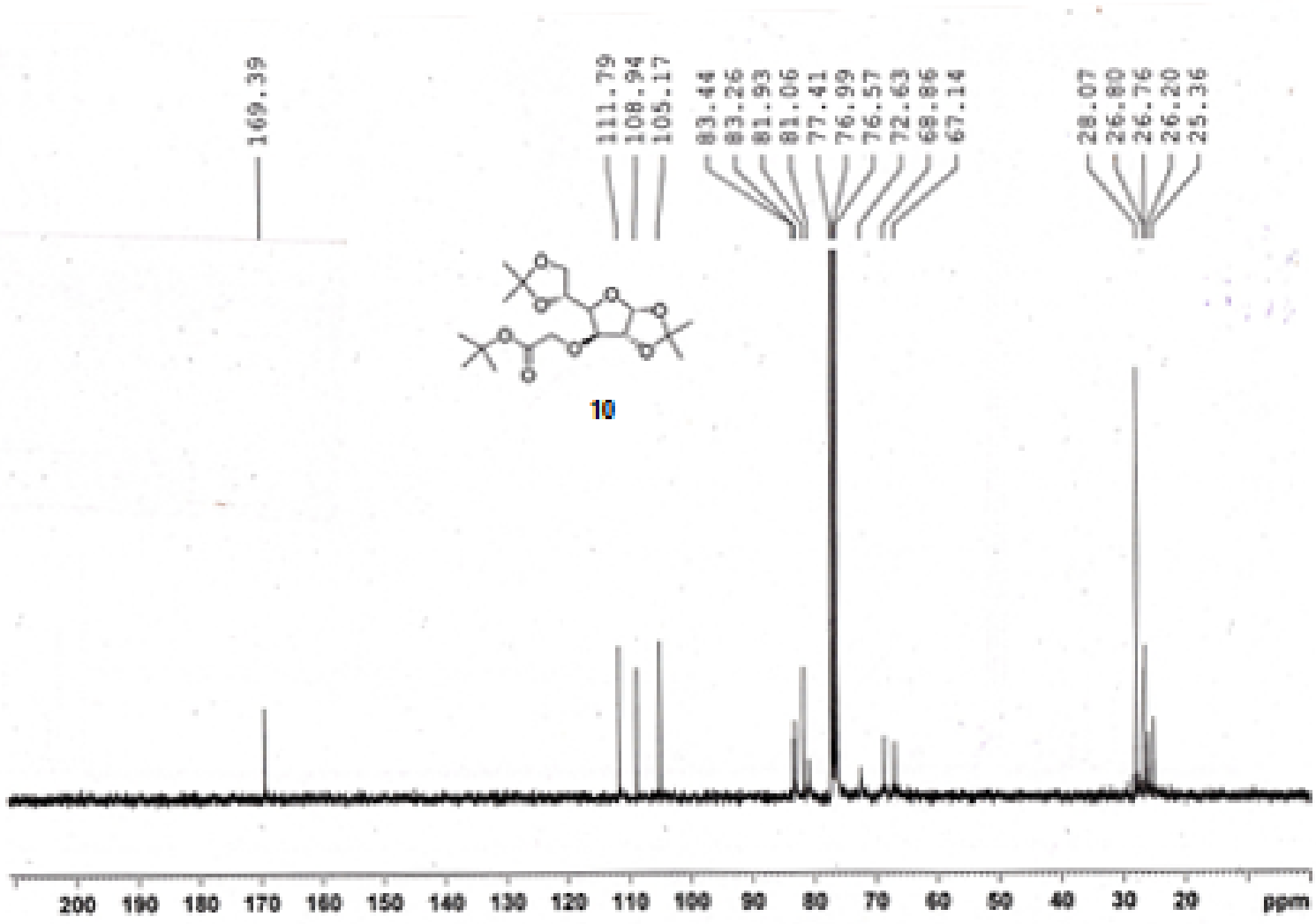
**3-Deoxy-3-*tert*-butyloxyamido 1,2:5,6-di-*O*-isopropylidene α-D-glucofuranose (23):** Yield 0.273g, 75%, colourless thick liquid; IR (neat) ν 3351, 2980, 1688, 1533, 1456, 1368, 1216 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 5.85 (d, *J* = 3.6 Hz, 1H), 5.25 (broad S, 1H, *NH*), 4.53 (d, *J* = 3.6 Hz, 1H), 4.20-4.17 (m, 1H), 4.11-4.07 (m, 1H), 3.83-3.72 (m, 3H), 1.51 (s, 3H), 1.46 (s, 9H), 1.30 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 156.76, 113.18, 112.16, 104.28, 84.09, 81.10, 79.40, 69.29, 64.07, 28.25, 26.44, 26.10; HRMS calcd for $C_{14}H_{25}NO_7$ 319.1631, found 319.1640

**Methyl-2,3-di-*O*-allyl-α-D-glucopyranose (26)**: Yield 0.246g, 90%, colourless syrup, IR (neat) 3434, 3081, 2927, 1647, 1458, 1351 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 5.96-5.85 (m, 2H), 4.35 (dd, *J* = 12.9, 5.7 Hz, 1H), 4.20 (dd, *J* = 11.1, 5.1 Hz, 1H), 4.12-4.04 (m, 2H), 3.76 (d, *J* = 3.0 Hz, 2H), 3.62-3.45 (m, 5H), 3.35-3.30 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 135.16, 134.67, 117.54, 116.95, 98.22, 80.89, 79.47, 74.14, 72.22, 71.02, 69.93, 61.82, 55.12; HRMS calcd for $C_{13}H_{22}O_6$ 274.1416, found 274.1411.

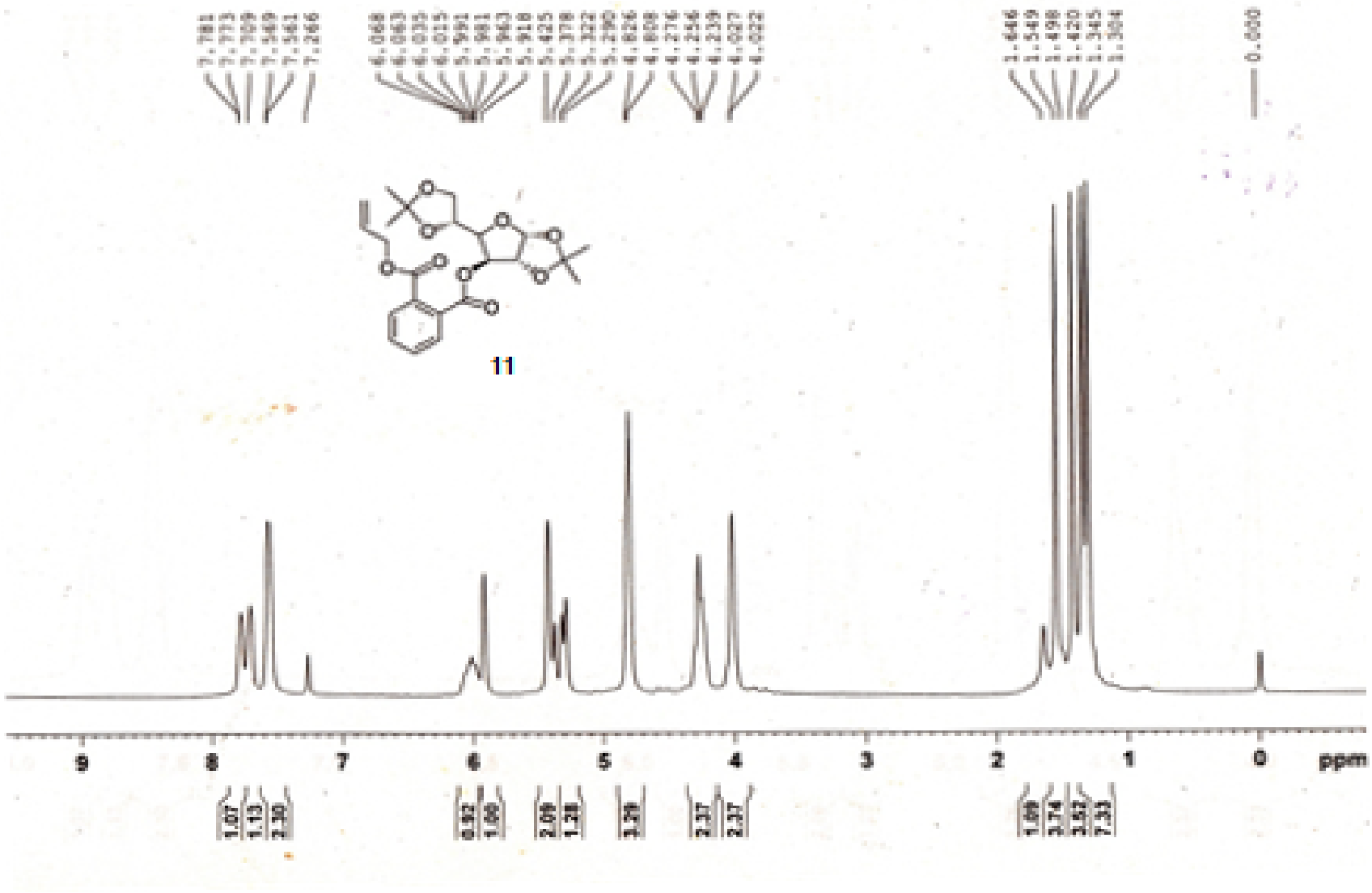
# $^1$H NMR spectra of **10** in $CDCl_3$, 300 MHz



$^{13}$ C NMR spectra of **10** in $CDCl_3$, 75 MHz



$^{1}$H NMR spectra of **11** in $CDCl_3$, 300 MHz



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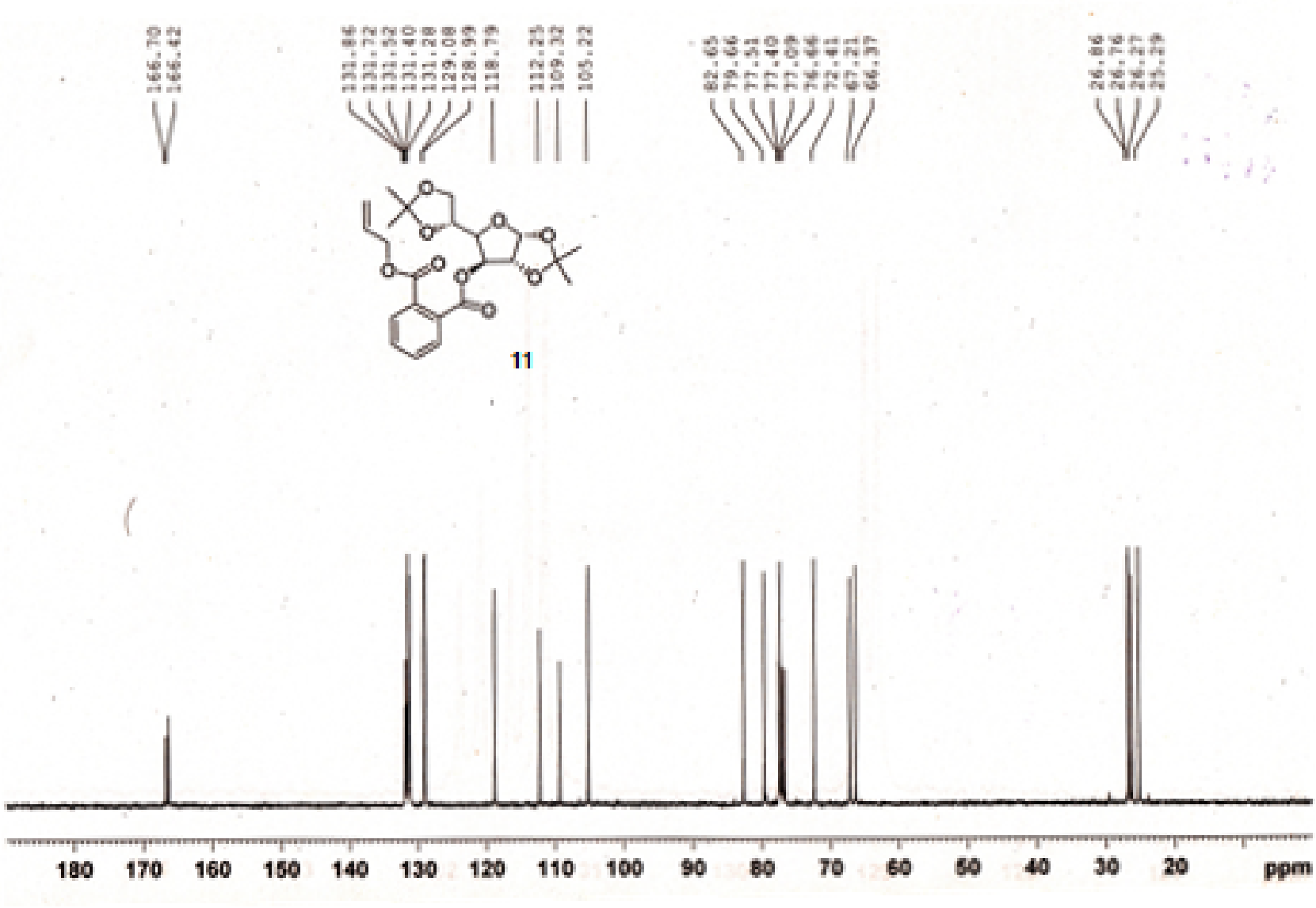

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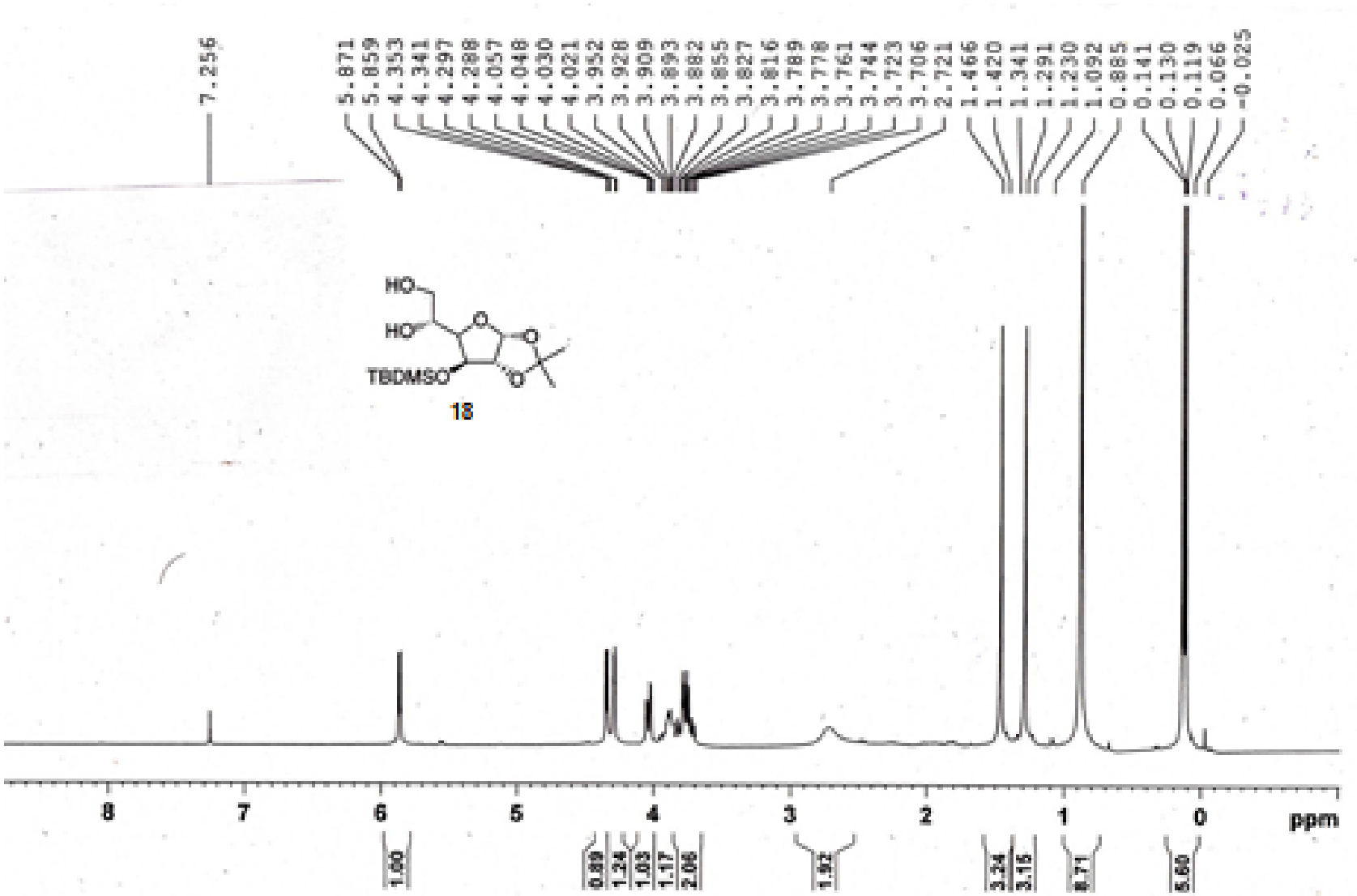

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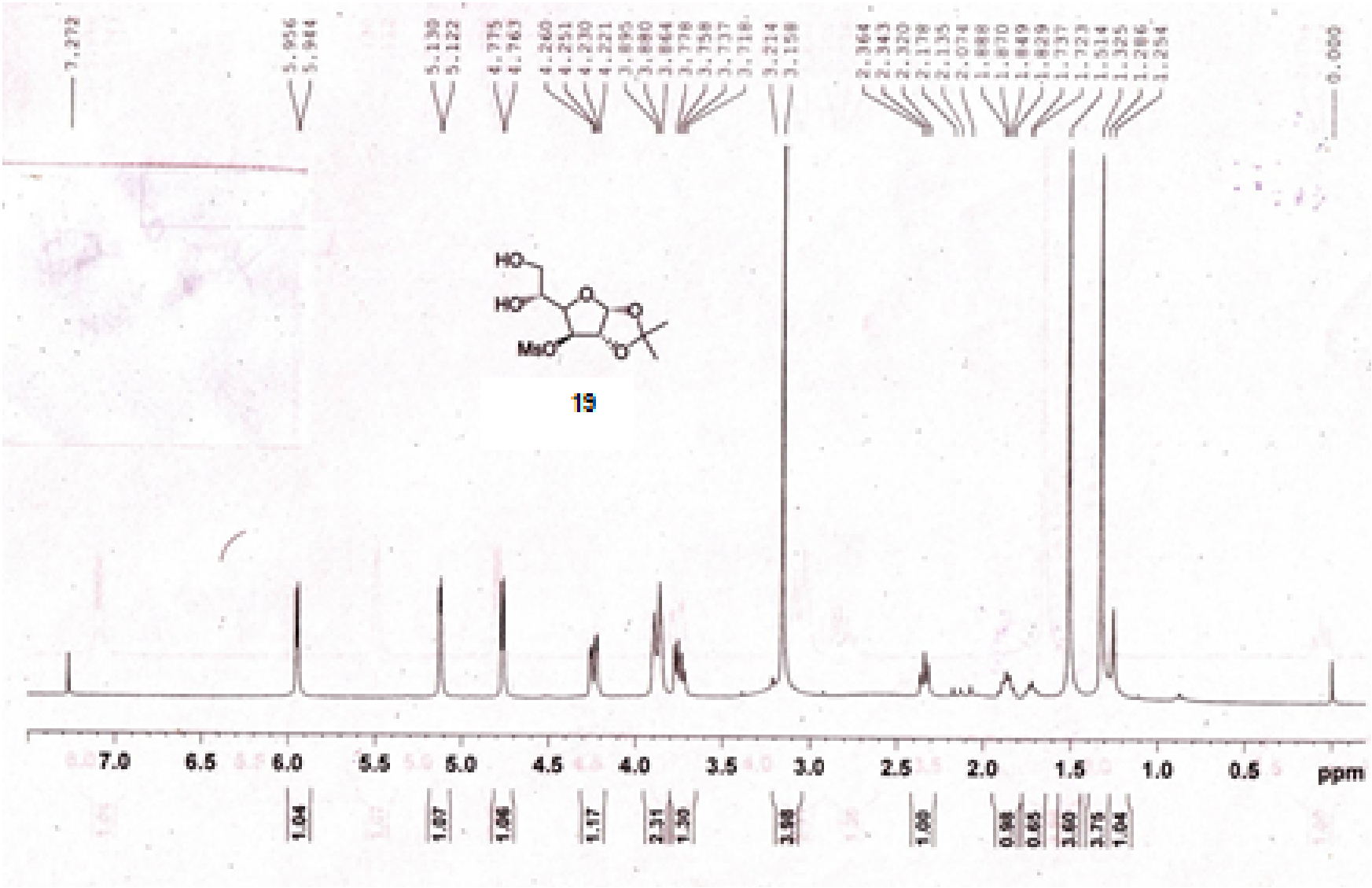
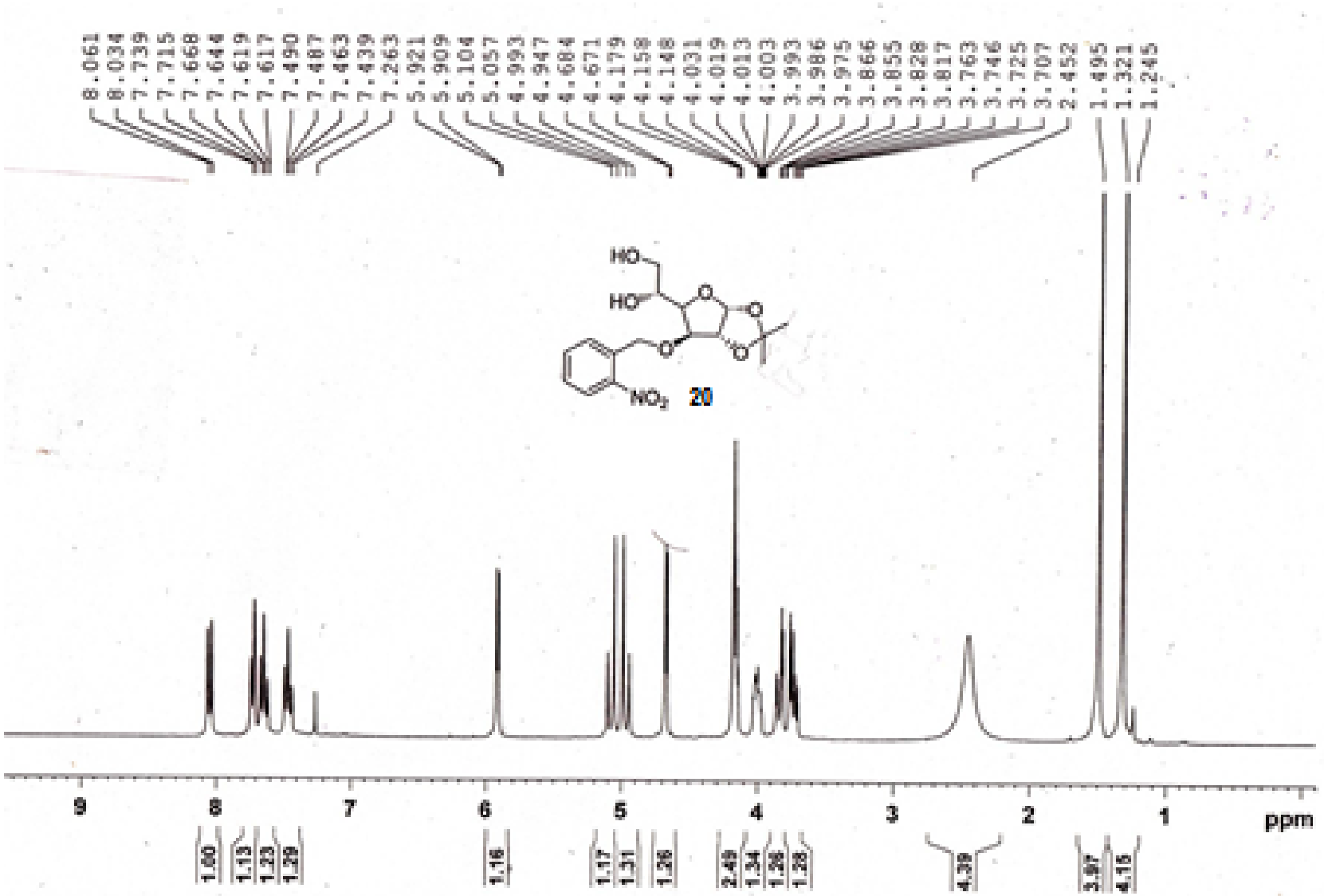


$^1$H NMR spectra of **20** in $CDCl_3$, 300 MHz



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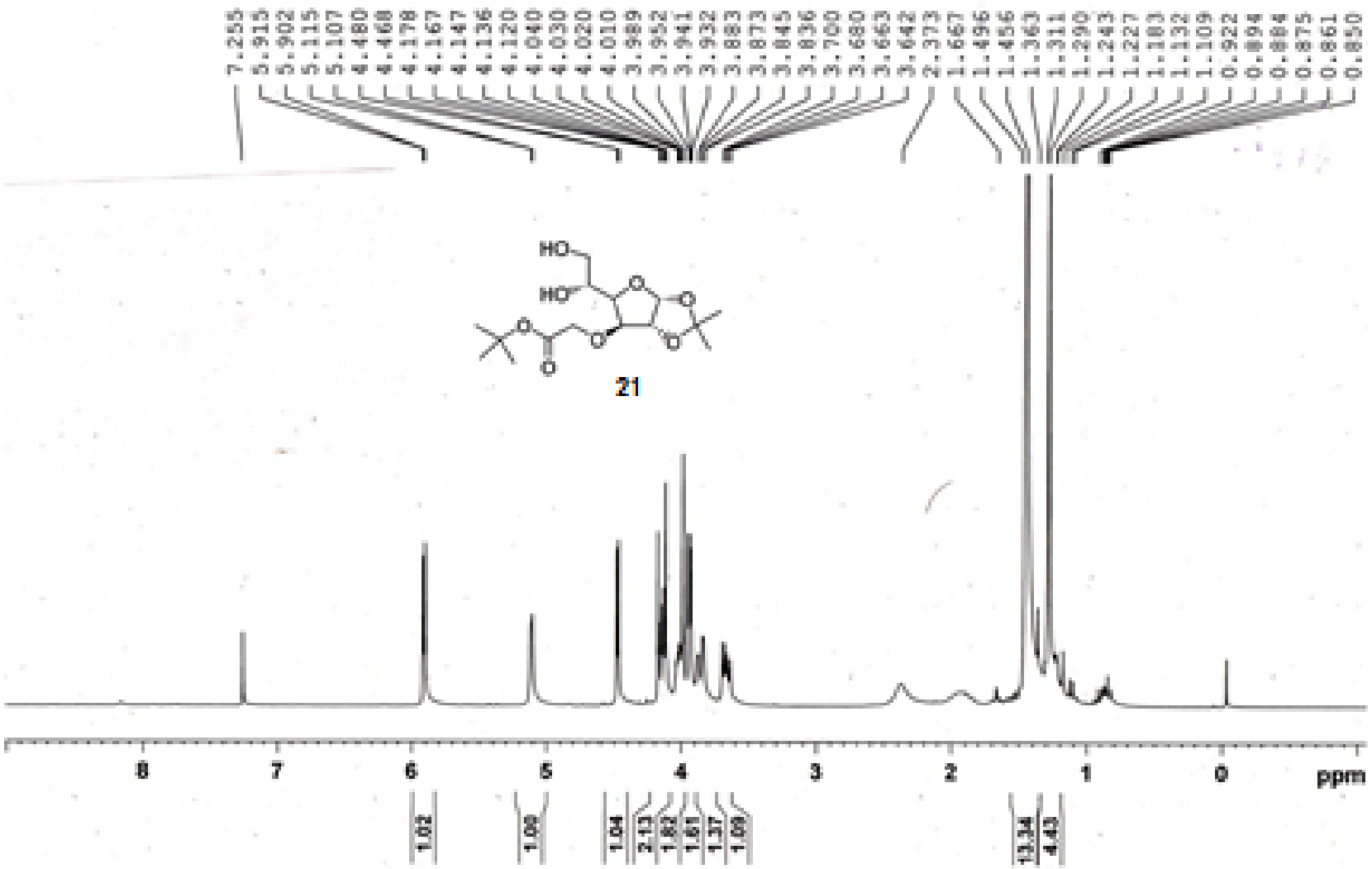
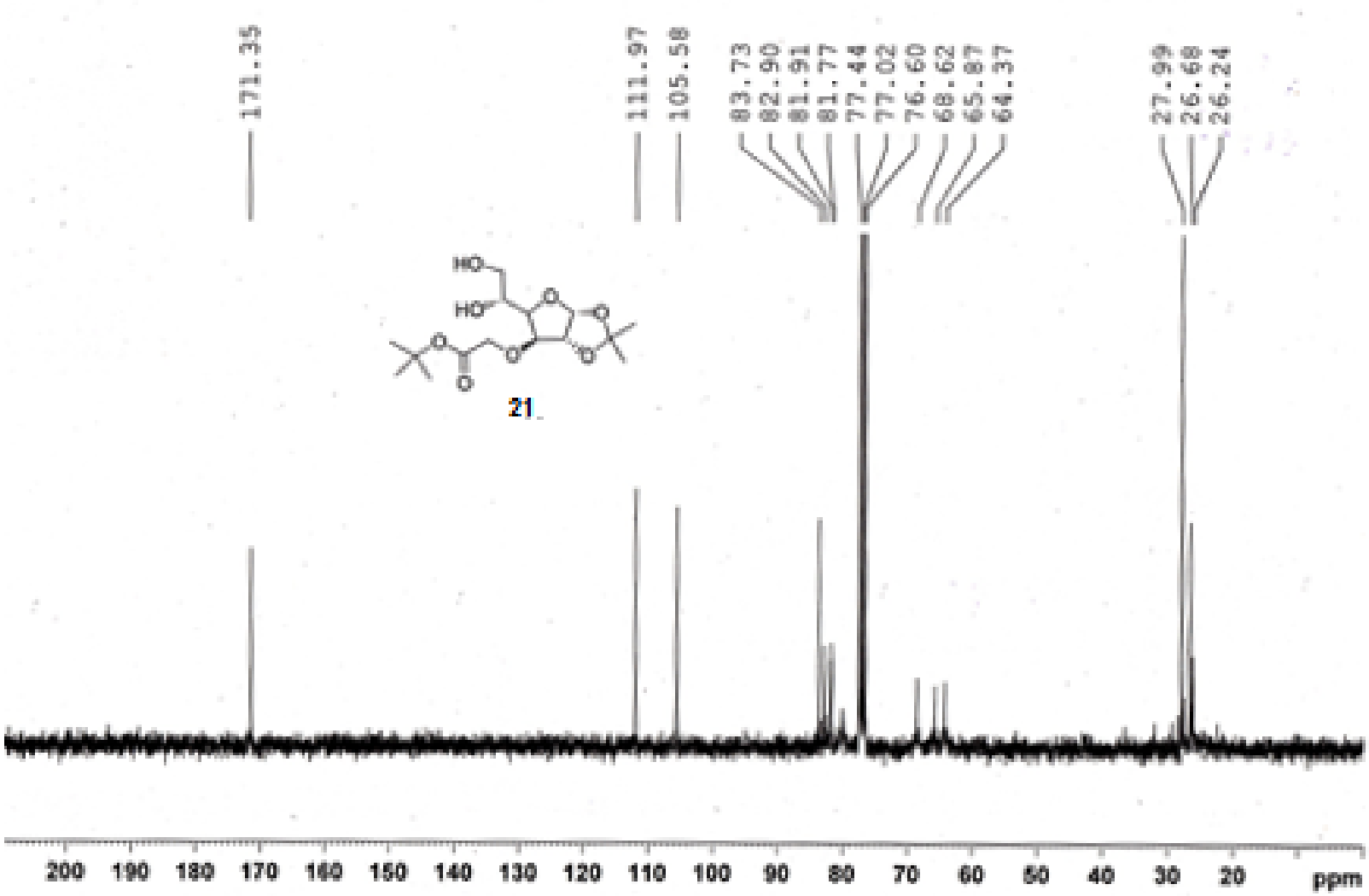


$^{13}C$ NMR spectra of **21** in $CDCl_3$, 75 MHz



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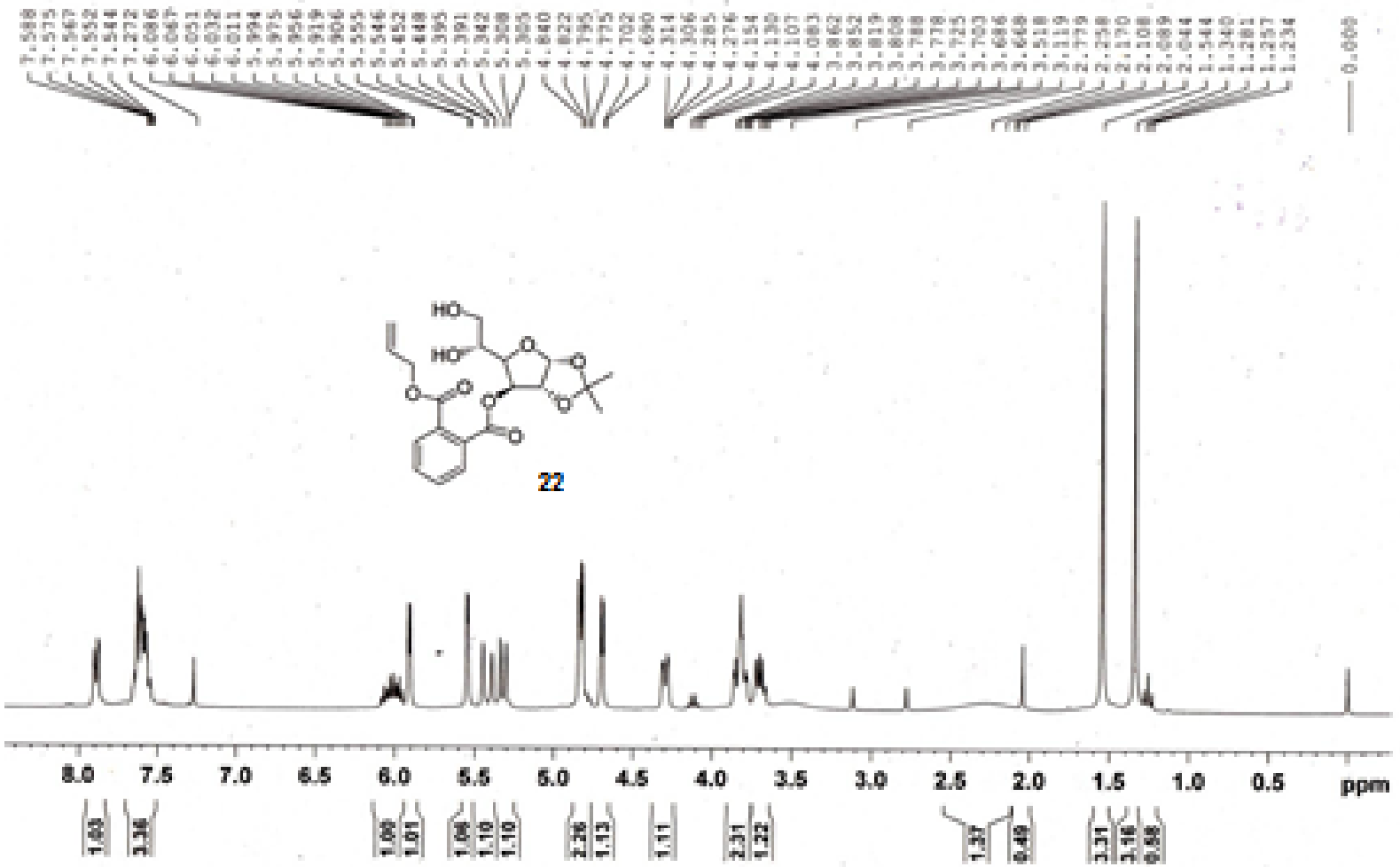

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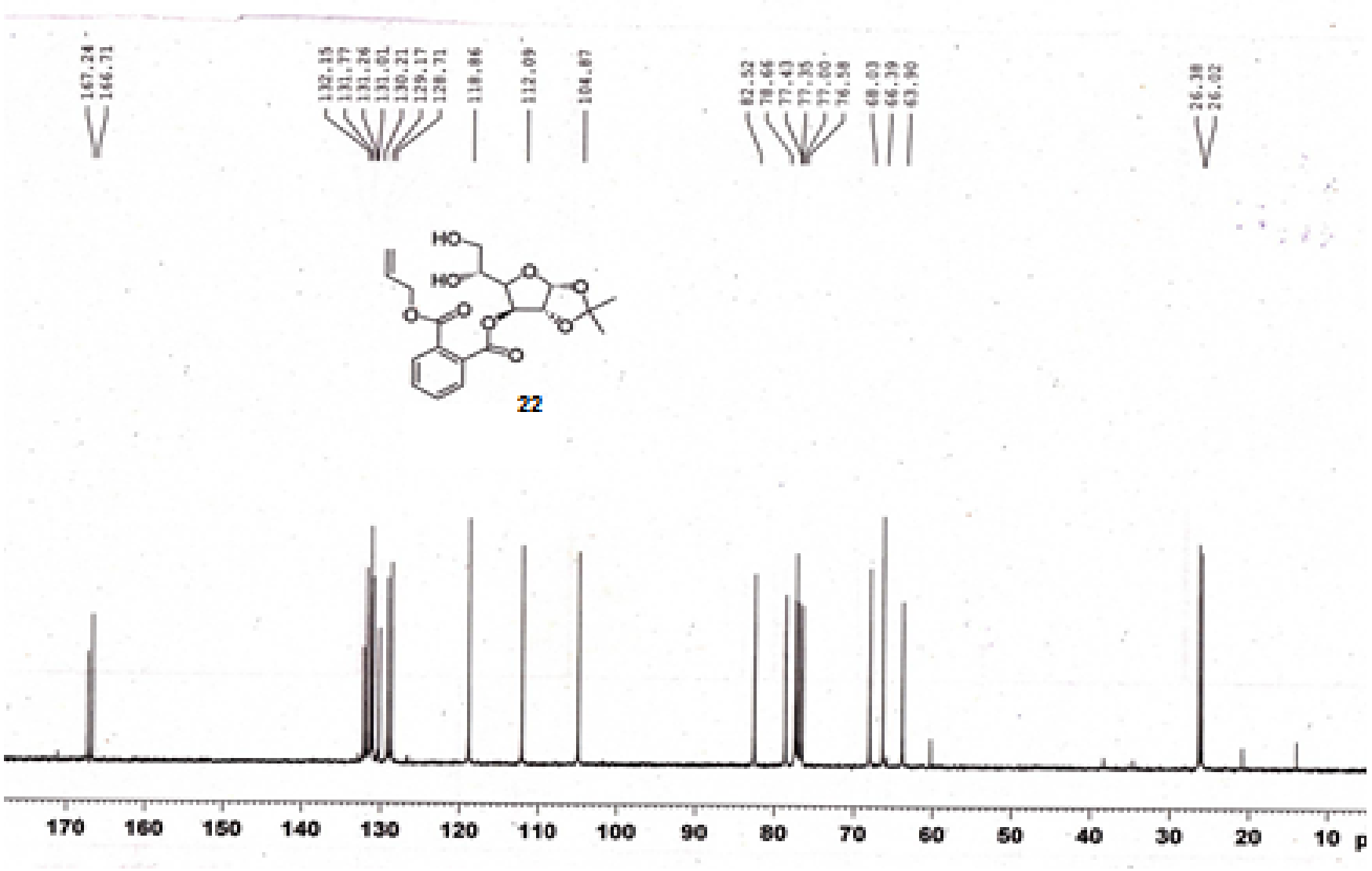

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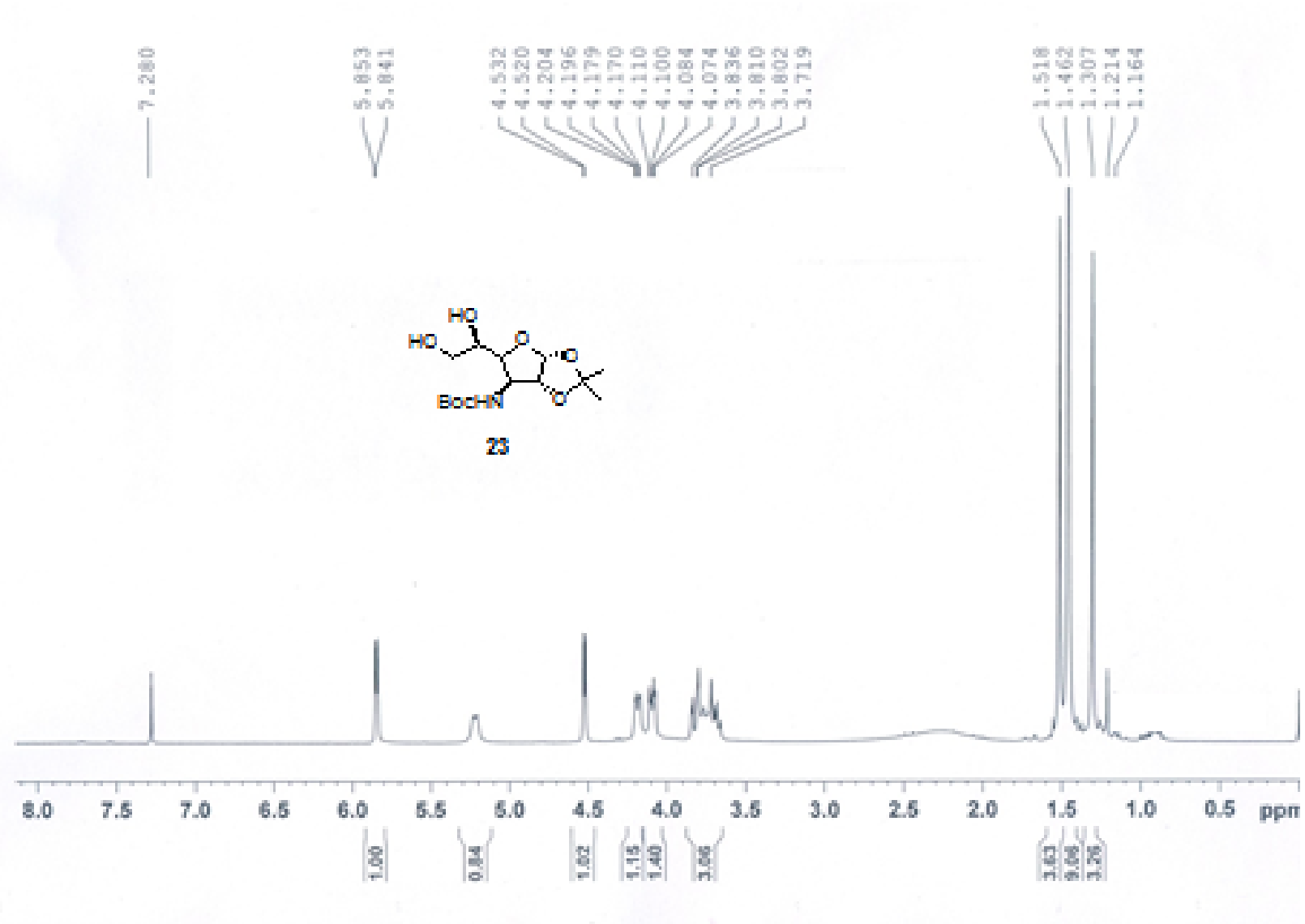
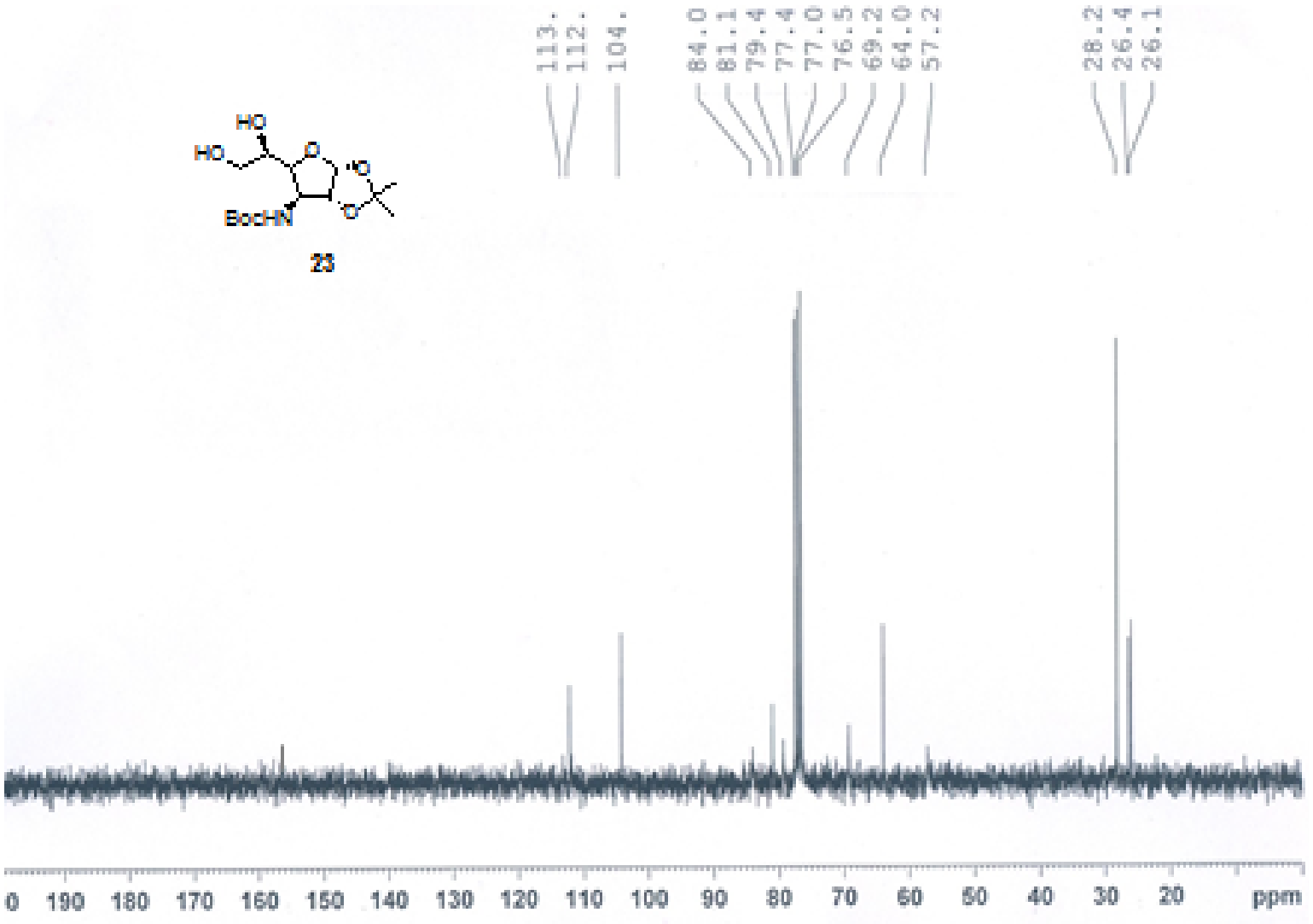


$^{13}C$ NMR spectra of **23** in $CDCl_3$, 75 MHz



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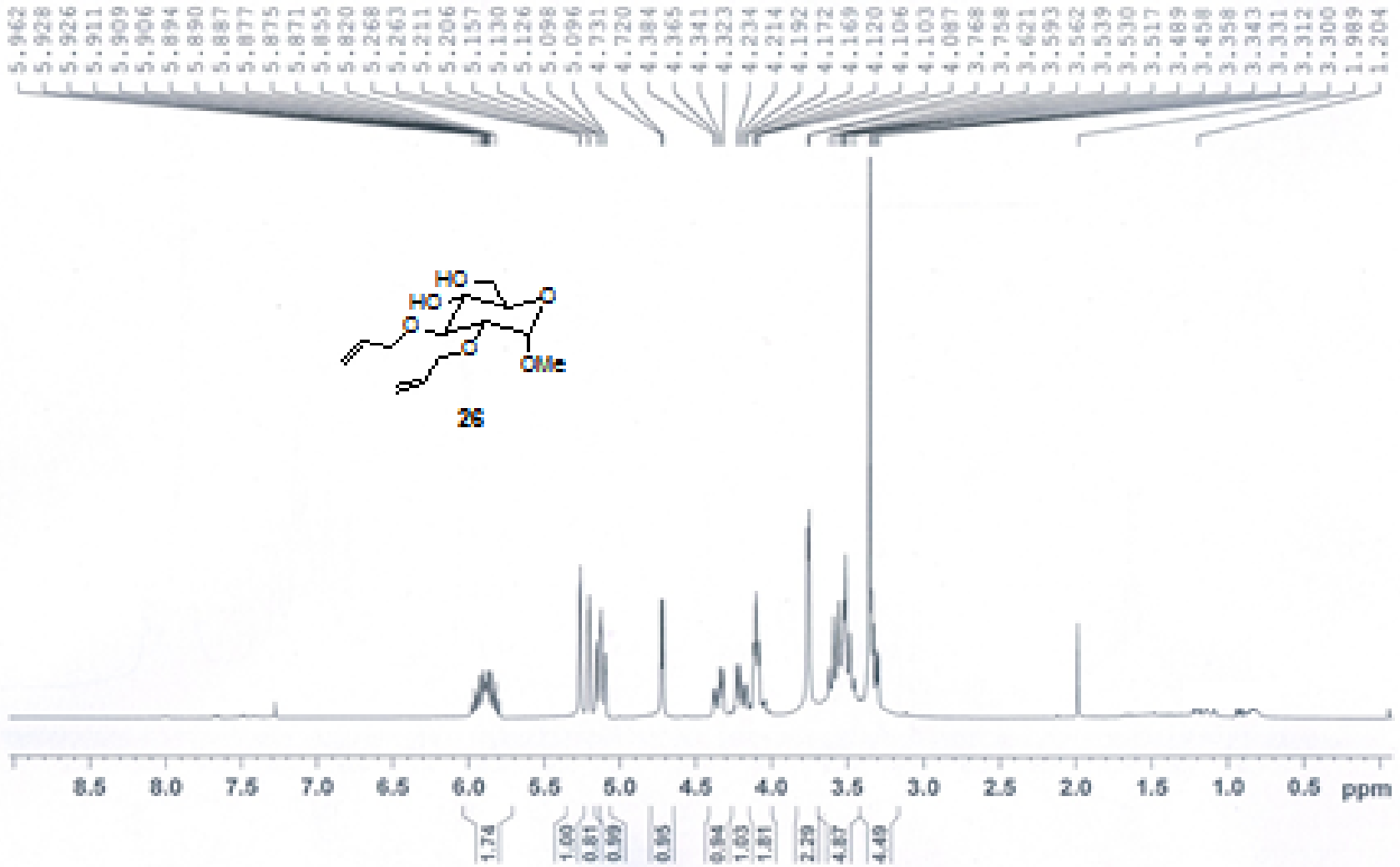

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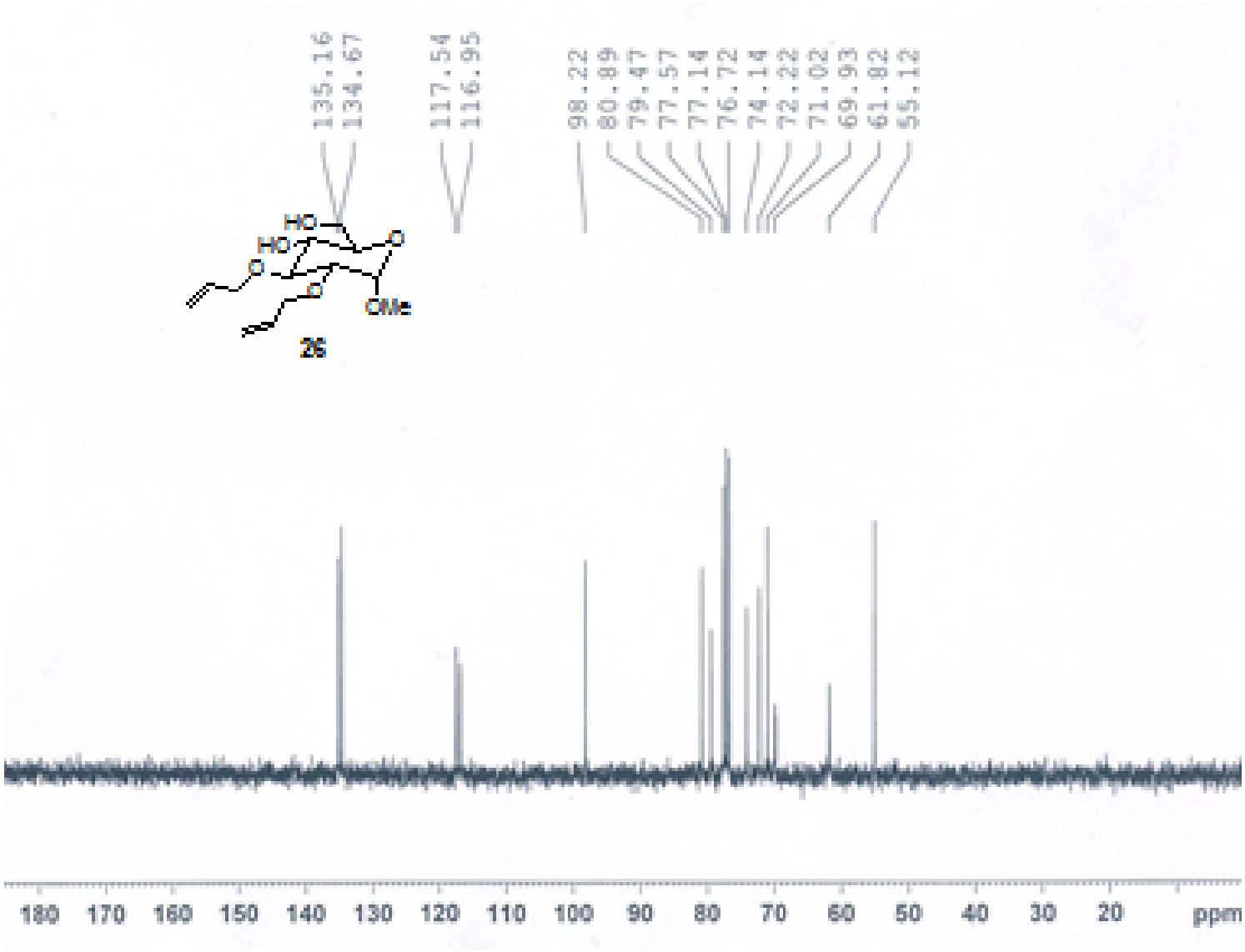

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