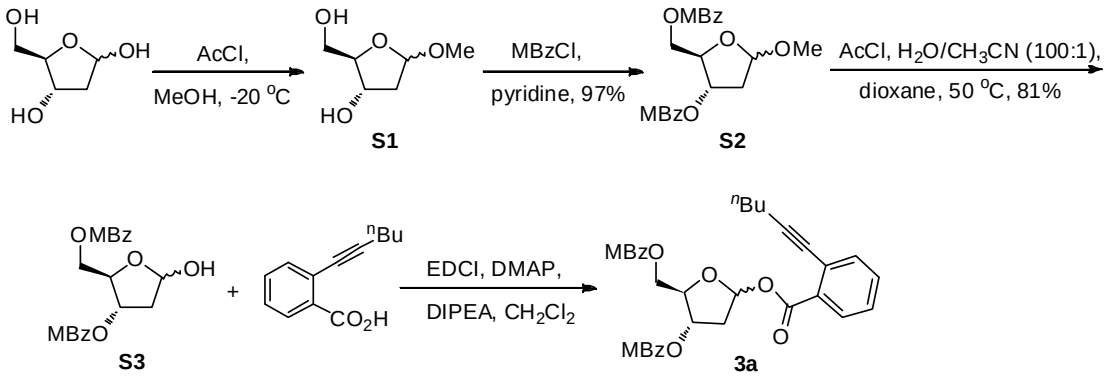
Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Contents

1. Preparation of 2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoates



A general procedure: Into a solution of methyl 2-deoxyribofuranoside **S1**[S1] (2.96 g, 20.0 mmol) and DMAP (0.24 g, 2 mmol) in dry pyridine (30 mL), was added MBzCl (8.53 g, 50 mmol) slowly at 0 °C. The mixture was stirred at room temperature overnight. Methanol (2 mL) was added to consume the excess MBzCl. After the solvent was evaporated under reduced pressure, the residue was dissolved in CH_2Cl_2 (200 mL) and washed with HCl (5%, 200 mL), saturated $NaHCO_3$ (200 mL), and brine (200 mL), successively. The organic phase was dried with Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc 5:1) to afford **S2** (8.1 g, 97%) as a colorless syrup.

Acetyl chloride (6.4 mL, 90.0 mmol) was slowly added to ice-cold water (60 mL, containing 1% of acetonitrile) with stirring. The cooling bath was removed and the mixture was stirred for 30 min at room temperature. The α,β mixture of **S2** (6.0 g, 14.4 mmol) in dioxane (120 mL) was added to this aqueous hydrochloric acid solution and the mixture was stirred at 50 °C overnight. After neutralization with saturated $NaHCO_3$ solution (200 mL), the aqueous phase was extracted with CH_2Cl_2 (3×150 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc 3:1) to afford lactol **S3** (4.71 g, 81%) as a colorless syrup.

A solution of **S3** (2.54 g, 6.31 mmol), *ortho*-hexynylbenzoic acid (1.91 g, 9.46 mmol), DMAP (1.16 g, 9.46 mmol), EDCI (1.82 g, 9.46 mmol), and DIPEA (2.2 mL, 12.6 mmol) in dry CH_2Cl_2 (30 mL) was stirred for 5 h at room temperature, and was then diluted with CH_2Cl_2. The resulting mixture was washed with saturated $NaHCO_3$ and brine, respectively, and was then dried with Na_2SO_4. After the solvent was

removed under reduced pressure, the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 2:1) to provide **3a** as a colorless syrup (3.36 g, 91%; β:α= 1.8:1).

Methyl 3,5-Di-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranoside (S2)

The β isomer: $[\alpha]_D^{29}$ = 4.4 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 6.88-6.95 (m, 2H), 5.59 (brs, 1H), 5.23 (d, *J* = 3.6 Hz, 1H), 4.45–4.55 (m, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.36 (s, 3H), 2.56 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.37–2.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.9, 163.8, 163.6, 131.9, 131.89, 122.6, 122.2, 113.8, 113.76, 105.8, 82.1, 75.5, 65.2, 55.6, 55.5, 55.3, 39.5; HR-ESIMS (m/z) calcd for $C_{22}H_{24}O_8$ $[M+Na]^+$ 439.1363; found 439.1373.

The α isomer: $[\alpha]_D^{29}$ = 125.4 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.6 Hz, 4H), 6.92-6.88 (m, 4H), 5.40 (d, *J* = 7.8 Hz, 1H), 5.19 (d, *J* = 5.0 Hz, 1H), 4.66–4.56 (m, 1H), 4.53–4.51 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.43 (s, 3H), 2.54 (dd, *J* = 13.0, 7.1 Hz, 1H), 2.18 (d, *J* = 14.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.1, 163.8, 163.7, 132.0, 131.9, 122.5, 122.4, 113.8, 113.76, 105.2, 81.1, 74.6, 55.59, 55.56, 55.2, 39.4; HR-ESIMS (m/z) calcd for $C_{22}H_{24}O_8$ $[M+Na]^+$ 439.1363; found 439.1361.

3,5-Di-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate (3a)

The β isomer: $[\alpha]_D^{29}$ = 4.4 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.2 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.41 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.72-6.77 (m, 3H), 5.69-5.73 (m, 1H), 4.65 (dd, *J* = 9.2, 4.8 Hz, 1H), 4.51-4.58 (m, 2H), 3.87 (s, 3H), 3.81(s, 3H), 2.87 (ddd, *J* = 14.4, 7.2, 2.0 Hz, 1H), 2.61 (dt, *J* = 14.4, 5.6 Hz, 1H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.58-1.66 (m, 2H), 1.45-1.51 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.8, 165.5, 163.9, 134.6, 132.0, 131.9, 131.1, 130.5, 127.3, 125.0, 122.1, 121.8, 113.9, 113.7, 99.3, 96.7, 83.1, 79.3, 74.4, 64.3, 55.6, 55.5, 38.9, 30.9, 22.2, 19.6, 13.8; HR-ESIMS (m/z) calcd for $C_{34}H_{34}O_9$ $[M+Na]^+$ 609.2095; found 609.2089.

The α isomer: $[\alpha]_D^{29}$ = 63.6 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-8.00 (m, 4H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H),

7.21 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 4.8 Hz, 1H), 5.58 (d, *J* = 7.2 Hz, 1H), 4.75-4.78 (m, 1H), 4.58 (d, *J* = 4.0 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.69 (ddd, *J* = 14.8, 6.8, 4.8 Hz, 1H), 2.55 (d, *J* = 14.8 Hz, 1H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.53-1.59 (m, 2H), 1.41-1.48 (m ,2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 166.0, 165.3, 163.8, 163.7, 134.6, 132.0, 131.9, 131.5, 130.5, 127.1, 125.2, 122.2, 122.1, 113.9, 113.7, 99.4, 96.8, 84.4, 79.3, 74.4, 64.2, 55.6, 38.9, 30.8, 29.8, 22.2, 19.7,13.8; HR-ESIMS (m/z) calcd for $C_{34}H_{34}O_9$ $[M+Na]^+$ 609.2095; found 609.2100.

3-*O*-Benzyl-5-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate (3b)

The β isomer: $[\alpha]_D^{29}$ = -15.5 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.31–7.14 (m, 6H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 4.4 Hz, 1H), 4.52 (s, 2H), 4.47–4.30 (m, 4H), 3.77 (s, 3H), 2.55 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.47–2.31 (m, 3H), 1.54 (dd, *J* = 14.8, 7.2 Hz, 2H), 1.48–1.34 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.4, 163.5, 137.6, 131.8, 131.7, 131.4, 130.4, 128.6, 128.0, 127.7, 127.2, 124.8, 122.2, 113.6, 99.5, 96.4, 83.1, 79.4, 78.6, 72.2, 64.5, 55.5, 39.0, 30.8, 22.2, 19.6, 13.7; HR-ESIMS (m/z) calcd for $C_{33}H_{34}O_7$ $[M+Na]^+$ 565.2197; found 565.2204.

The α isomer: $[\alpha]_D^{29}$ = 57.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.29–7.17 (m, 5H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 4.0 Hz, 1H), 4.60 (dd, *J* = 8.0, 4.4 Hz, 1H), 4.49 (q, *J* = 11.6 Hz, 2H), 4.43–4.29 (m, 2H), 4.14 (dd, *J* = 6.4, 3.2 Hz, 1H), 3.79 (s, 3H), 2.47–2.30 (m, 4H), 1.62–1.47 (m, 2H), 1.44–1.35 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.3, 163.7, 137.8, 134.5, 131.9, 131.8, 131.5, 130.8, 128.6, 127.9, 127.8, 127.1, 125.1, 122.2, 113.8, 99.4, 96.6, 83.5, 79.3, 78.9, 71.8, 64.2, 55.6, 38.4, 30.8, 22.2, 19.7, 13.8; HR-ESIMS (m/z) calcd for $C_{33}H_{34}O_7$ $[M+Na]^+$ 565.2197; found 565.2197.

3,5-Di-*O*-*p*-methoxybenzoyl-2-deoxy-D-xylofuranosyl *ortho*-hexynylbenzoate (9)

α isomer: $[\alpha]_D^{23}$ = 5.6 (c 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.86 (m, 5H), 7.53 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 – 6.83 (m, 4H), 6.79 (dd, *J* = 5.6, 2.2 Hz, 1H), 5.88 (dt, *J* = 6.6, 4.2 Hz, 1H), 4.78 (dd, *J* = 10.8, 5.2 Hz, 1H), 4.62 (dd, *J* = 5.6, 1.4 Hz, 2H), 3.85 (s, 3H), 3.84

(s, 3H), 2.78 (ddd, *J* = 14.8, 6.8, 2.2 Hz, 1H), 2.62 (ddd, *J* = 14.8, 5.6, 4.0 Hz, 1H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.71 – 1.57 (m, 2H), 1.54 – 1.41 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.6, 163.9, 163.6, 134.7, 132.0, 131.9, 131.9, 131.3, 130.6, 127.3, 124.9, 122.2, 121.8, 113.9, 113.7, 98.2, 96.5, 79.5, 78.9, 72.9, 62.3, 55.6, 55.5, 40.1, 30.9, 22.2, 19.7, 13.8. HR-ESIMS (m/z) calcd for $C_{34}H_{34}O_9$ $[M+Na]^+$: 609.2095; Found: 609.2101.

β isomer: $[\alpha]_D^{23}$ = -42.2 (c 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 4H), 7.86 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87 – 6.75 (m, 4H), 6.69 (d, *J* = 4.8 Hz, 1H), 5.92 – 5.80 (m, 1H), 4.72 (dd, *J* = 8.4, 3.2 Hz, 1H), 4.68 – 4.59 (m, 2H), 3.90 – 3.75 (m, 7H), 2.70 – 2.61 (m, 1H), 2.58 (d, *J* = 14.9 Hz, 1H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.56 (ddd, *J* = 12.2, 7.2, 4.0 Hz, 2H), 1.50 – 1.38 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.1, 165.5, 165.2, 163.8, 163.6, 134.5, 132.0, 131.9, 131.8, 130.4, 127.0, 125.2, 122.3, 122.0, 113.8, 113.7, 98.6, 96.8, 81.3, 79.2, 72.0, 63.4, 55.6, 55.5, 39.7, 30.8, 22.2, 19.6, 13.8. HR-ESIMS (m/z) calcd for $C_{34}H_{34}O_9$ $[M+Na]^+$: 609.2095; Found: 609.2087.

2. General procedure for the *N*-glycosylation of purines

A general procedure: To a solution of 3,5-di-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate **3a** (70 mg, 0.12 mmol) and N2-Boc-6-iodo-2-aminopurine **4a** (36 mg, 0.10 mmol) in dry $ClCH_2CH_2Cl$ (4 mL) was added 4Å MS under argon atmosphere. The resulting mixture was stirred at room temperature for 1 hour and then $Ph_3PAuNTf_2$ (7.4 mg, 0.01 mmol) was added. The stirring was continued at 45 ^{o}C for 6 h (until **4a** was consumed as monitored by TLC). The mixture was filtered. The filtrate was concentrated under reduced pressure to yield a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate 3:2) to provide **5a** (75 mg, 100%, β:α = 2.8:1) as a white foam.

2-*tert*-Butoxycarbonylamino-6-iodo-9-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)purine (5a)

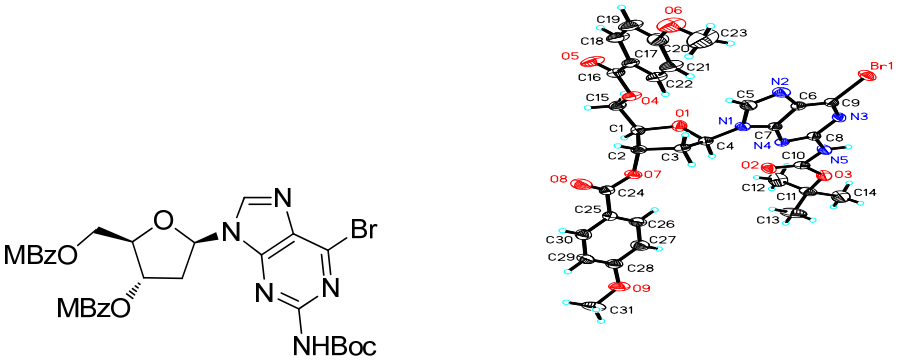
The β isomer: $[\alpha]_D^{29}$ = -36.4 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.59 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.49 (t, *J* = 6.6 Hz, 1H), 5.94–5.77 (m, 1H), 4.82 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 9.5 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 3.18 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.96–2.76 (m, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 164.1, 163.8, 152.1, 150.2, 148.4, 141.8, 135.5, 132.1, 131.7, 122.6, 121.7, 121.6, 113.99, 113.97, 85.2, 83.4, 81.9, 74.9, 83.7, 55.7, 55.6, 37.6, 28.3; HR-ESIMS (m/z) calcd for $C_{31}H_{32}IN_5O_9$ $[M+Na]^+$ 768.1137; found 768.1172.

The α isomer: $[\alpha]_D^{29}$ = -32.2 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.46 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 6.0 Hz, 1H), 5.68 (d, *J* = 6.4 Hz, 1H), 4.89 (brs, 1H), 4.59 (d, *J* = 3.5 Hz, 2H), 4.12 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.29 (d, *J* = 15.2 Hz, 1H), 3.01 (ddd, *J* = 15.2, 6.4 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 164.0, 163.9, 152.0, 150.1, 148.3, 141.8, 135.4, 131.9, 131.6, 122.2, 121.9, 121.2, 114.1, 114.0, 86.6, 84.9, 81.7, 74.8, 63.9, 55.63, 55.63, 38.3, 28.3; HR-ESIMS (m/z) calcd for $C_{31}H_{32}IN_5O_9$ $[M+Na]^+$ 768.1137; found 768.1157.

2-*tert*-Butoxycarbonylamino-6-bromo-9-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)purine (5b)

The β isomer: $[\alpha]_D^{28}$ = -25.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.72 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.52 (t, *J* = 6.8 Hz, 1H), 5.87 (d, *J* = 6.0 Hz, 1H), 4.80 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.73–4.60 (m, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 3.19 (dt, *J* = 14.2, 7.0 Hz, 1H), 2.86 (ddd, *J* = 14.2, 5.9, 2.0 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.6, 164.0, 163.7, 152.3, 150.9, 150.1, 143.5, 142.5, 132.0, 131.7, 131.0, 121.8, 121.6, 113.9, 85.3, 83.3, 81.7, 75.1, 63.9, 55.6, 55.5, 37.7, 28.2; HR-ESIMS (m/z) calcd for $C_{31}H_{32}BrN_5O_9$ $[M+Na]^+$ 720.1276; found 720.1295.

The α isomer: $[\alpha]_D^{28}$ = -42.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.46 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 6.2 Hz, 1H), 5.69 (d, *J* = 6.4 Hz, 1H), 4.90 (s, 1H), 4.59 (d, *J* = 4.0 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.25 (d, *J* = 15.2 Hz, 1H), 3.11–2.89 (m, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 164.1, 163.9, 152.2, 151.0, 150.1, 143.3, 142.3, 131.9, 131.6, 131.0, 121.9, 121.1, 114.1, 114.0, 86.6, 84.9, 81.8, 74.8, 63.9, 55.6, 38.4, 28.3; HR-ESIMS (m/z) calcd for $C_{31}H_{32}BrN_5O_9$ $[M+Na]^+$ 720.1276; found 720.1268.



ORTEP drawing of compound **5bβ** (CCDC 865441)[S2]

2-*tert*-Butoxycarbonylamino-6-chloro-9-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)purine (5c)

The β isomer: $[\alpha]_D^{27}$ = -21.6 (*c* 2.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 6.6 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.52 (t, *J* = 6.8 Hz, 1H), 5.86 (d, *J* = 6.0 Hz, 1H), 4.80 (dd, *J* = 10.8, 3.2 Hz, 1H), 4.71–4.61 (m, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 3.17 (dd, *J* = 14.4, 6.9 Hz, 1H), 2.94–2.76 (m, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.7, 164.0, 163.8, 152.5, 152.2, 151.6, 150.2, 142.6, 132.0, 131.7, 128.5, 121.8, 121.6, 114.0, 113.9, 85.3, 83.3, 81.7, 75.1, 63.9, 55.6, 55.5, 37.7, 28.3; HR-ESIMS (m/z) calcd for $C_{31}H_{32}ClN_5O_9$ $[M+Na]^+$ 676.1781; found 676.1782.

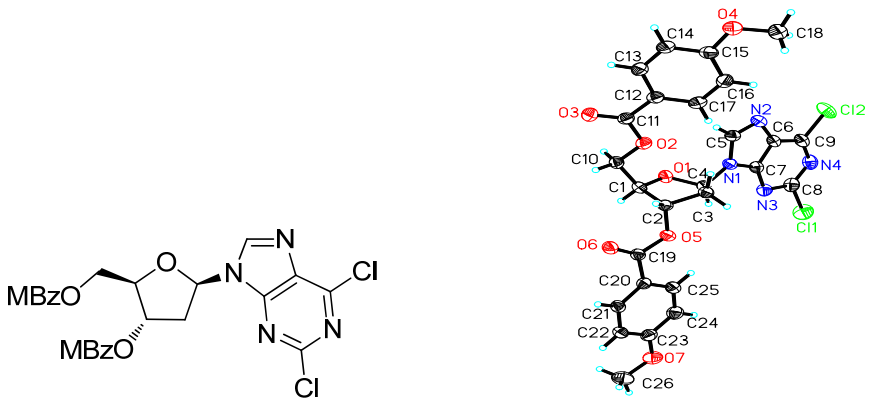
The α isomer: $[\alpha]_D^{27}$ = -55.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.47 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 6.8 Hz, 1H), 5.69 (d, *J* = 6.4 Hz, 1H), 4.90 (s, 1H), 4.59 (d, *J* = 4.0 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 3.23 (d, *J* = 15.3 Hz, 1H), 3.12–2.91 (m, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 164.1, 163.9, 152.4, 152.3, 151.4, 150.1, 142.4, 131.9, 131.6, 128.4, 121.9, 121.1, 114.0, 86.5, 84.9, 81.8, 74.8, 63.9, 55.6, 38.4, 28.3; HR-ESIMS (m/z) calcd for $C_{31}H_{32}ClN_5O_9$ $[M+Na]^+$ 676.1781; found 676.1797.

2,6-Di-chloro-9-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)purine (5d)

The β isomer: $[\alpha]_D^{27}$ = -44.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.55 (t, *J* = 6.8 Hz, 1H), 5.77 (brs, 1H), 4.77 (dt, *J* = 6.6, 3.3 Hz, 1H), 4.69–4.46 (m, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 2.95 (dd, *J* = 6.9, 4.3 Hz, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 164.2, 163.9, 153.2, 152.4, 152.2, 143.8, 132.1, 131.7, 131.4, 121.5, 121.4, 114.0, 85.5, 83.9, 75.0, 63.8, 55.7, 55.6, 38.8; HR-ESIMS (m/z) calcd for $C_{26}H_{22}Cl_2N_4O_7$ $[M+Na]^+$ 595.0758; found 595.0760.

The α isomer: $[\alpha]_D^{27}$ = -54.1 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.62 (dd, *J* = 5.6, 2.0 Hz, 1H), 5.71 (d, *J* = 5.2 Hz, 1H), 4.93 (t, *J* = 3.3 Hz, 1H), 4.61 (d, *J* = 3.8 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.13–2.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 164.2, 164.0, 153.1, 152.3, 151.9, 144.0, 131.9, 131.6, 131.5, 121.7, 120.8, 114.1, 114.07, 87.0, 85.5, 74.8, 63.9, 55.6, 38.8; HR-ESIMS (m/z) calcd for $C_{26}H_{22}Cl_2N_4O_7$ $[M+Na]^+$ 595.0758; found 595.0749.



ORTEP drawing of compound **5dβ** (CCDC 865440)[S2]

6-Chloro-9-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)purine (5e)

The β isomer: $[\alpha]_D^{29}$ = -43.4 (*c* 1.3, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.31 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.58 (dd, *J* = 8.0, 6.0 Hz, 1H), 5.82 (d, *J* = 6.0 Hz, 1H), 4.77 (t, *J* = 7.2 Hz, 1H), 4.72–4.47 (m, 2H), 3.89 (s, 3H), 3.86 (s, 4H), 3.26–3.06 (m, 1H), 2.89 (ddd, *J* = 14.1, 5.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.7, 164.1, 163.9, 152.2, 151.5, 151.3, 143.6, 132.4, 132.0, 131.7, 121.7, 121.5, 113.99, 113.97, 85.5, 83.6, 75.0, 63.8, 55.64, 55.58, 38.1; HR-ESIMS (m/z) calcd for $C_{26}H_{23}ClN_4O_7$ $[M+Na]^+$ 561.1148; found 561.1158.

The α isomer: $[\alpha]_D^{29}$ = -13.3 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.49 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 5.8 Hz, 1H), 5.71 (d, *J* = 6.4 Hz, 1H), 4.92 (s, 1H), 4.67–4.56 (m, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 3.18 (d, *J* = 15.4 Hz, 1H),

3.13–2.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 164.1, 163.9, 152.1, 151.24, 151.16, 143.4, 132.4, 131.9, 131.6, 121.8, 120.9, 114.1, 114.0, 86.8, 85.2, 74.8, 63.9, 55.6, 38.6; HR-ESIMS (m/z) calcd for $C_{26}H_{23}ClN_4O_7$ $[M+Na]^+$ 561.1148; found 561.1149.

2-*tert*-Butoxycarbonylamino-6-iodo-9-(3'-*O*-benzyl-5'-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)purine (8)

The β isomer: $[\alpha]_D^{28}$ = 11.3 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.52 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.31 (t, *J* = 6.4 Hz, 1H), 4.89 (dd, *J* = 10.8, 4.8 Hz, 1H), 4.74–4.65 (m, 2H), 4.63 (dd, *J* = 12.0, 4.2 Hz, 1H), 4.52 (dd, *J* = 12.0, 5.0 Hz, 1H), 4.45 (dd, *J* = 9.2, 4.6 Hz, 1H), 3.87 (s, 3H), 3.15–2.99 (m, 1H), 2.72–2.57 (m, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.7, 152.0, 150.0, 148.1, 142.9, 137.9, 135.7, 131.7, 128.7, 128.1, 128.0, 122.4, 122.1, 113.8, 85.7, 83.3, 81.6, 78.8, 72.3, 64.0, 55.6, 37.4, 28.3; HR-ESIMS (m/z) calcd for $C_{30}H_{32}IN_5O_7$ $[M+Na]^+$ 724.1239; found 724.1247.

The α isomer: $[\alpha]_D^{28}$ = 15.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.52 (s, 1H), 7.30–7.26 (m, 3H), 7.22–7.12 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.62 (dd, *J* = 6.2, 2.6 Hz, 1H), 4.77–4.74 (m, 1H), 4.60–4.47 (m, 2H), 4.41 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.38–4.29 (m, 2H), 3.88 (s, 3H), 2.82–2.78 (m, 2H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.9, 152.0, 150.3, 148.7, 142.9, 136.8, 135.1, 131.9, 128.8, 128.3, 127.7, 121.92, 121.89, 114.0, 85.0, 84.5, 81.7, 79.6, 72.0, 64.2, 55.6, 38.1, 28.3; HR-ESIMS (m/z) calcd for $C_{30}H_{32}IN_5O_7$ $[M+Na]^+$ 724.1239; found 724.1224.

2-*tert*-Butoxycarbonylamino-6-iodo-9-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-xylofuranosyl)purine (10)

The α isomer: $[\alpha]_D^{25}$ = 5.6 (*c* 1.1, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.04 – 7.97 (m, 2H), 7.97 – 7.86 (m, 2H), 7.57 (s, 1H), 7.01 – 6.91 (m, 2H), 6.90 – 6.80 (m, 2H), 6.45 (dd, *J* = 7.0, 6.0 Hz, 1H), 6.17 – 6.09 (m, 1H), 5.27 (dd, *J* = 10.4, 4.4Hz, 1H), 4.69 (dd, *J* = 12.0, 6.4 Hz, 1H), 4.63 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.42 (dt, *J* = 14.8, 6.0 Hz, 1H), 2.85 (ddd, *J* = 14.8, 7.2, 1.6 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.5, 164.0, 163.7, 152.1, 149.9, 148.3, 142.5, 135.9, 131.99, 131.96, 122.6, 122.2, 121.9, 114.0, 113.8, 85.7, 81.8, 81.2, 74.5, 62.5, 55.64, 55.55, 39.1, 28.3; HR-ESIMS (m/z) calcd for $C_{31}H_{32}IN_5O_9$ $[M+Na]^+$ 768.1137; found 768.1123.

The β isomer: $[\alpha]_D^{25}$ = 62.7 (*c* 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.99 – 7.91 (m, 2H), 7.75 – 7.63 (m, 2H), 7.45 (s, 1H), 6.93 – 6.84 (m, 4H), 6.54 (dd, *J* = 7.2, 2.6 Hz, 1H), 5.87 (d, *J* = 3.4 Hz, 1H), 4.75 – 4.60 (m, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.14 – 2.97 (m, 2H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.1, 164.2, 163.8, 152.1, 150.1, 148.5, 141.9, 135.3, 132.0, 131.6, 122.2, 122.0, 121.1, 114.3, 113.9, 84.4, 81.8, 81.5, 72.5, 62.3, 55.7, 55.6, 39.4, 28.4; HR-ESIMS (m/z) calcd for $C_{31}H_{32}IN_5O_9$ $[M+Na]^+$ 768.1137; found 768.1147.

3. General procedure for the *N*-glycosylation of pyrimidine

A general procedure: To a stirred suspension of 3,5-di-*O*-*p*-methoxybenzoyl-2-deoxyribofuranosyl *ortho*-hexynylbenzoate **3a** (59 mg, 0.10 mmol) and uracil **6a** (17 mg, 0.15 mmol) in dry CH_3CN (2 mL) was added BSTFA (80 μL, 0.30 mmol) under argon atmosphere. The mixture was stirred at room temperature for 30 minutes; a clear solution was resulted. Acetonitrile was then evaporated under reduced pressure; $ClCH_2CH_2Cl$ (4 mL) and $Ph_3PAuNTf_2$ (7.4 mg, 0.01 mmol) were added. The stirring was continued at room temperature for 12 h until **3a** was consumed as monitored by TLC. The solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate 2:1) to provide **7a** (50 mg, 100%; β/α = 0.9:1) as a white foam.

1-(3',5'-Di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)uracil (7a)

The β isomer: $[\alpha]_D^{29}$ = -42.0 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.03–6.87 (m, 4H), 6.40 (dd, *J* = 8.2, 5.7 Hz, 1H), 5.61 (dd, *J* = 9.8, 3.8 Hz, 2H), 4.72 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.65 (dd, *J* = 12.2, 3.5 Hz, 1H), 4.53 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.82–2.66 (m, 1H), 2.38–2.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.8, 164.1, 164.06, 162.9, 150.2, 139.0, 132.1, 131.7, 121.7, 121.5, 114.2, 114.0, 103.0, 85.6, 83.2, 74.7, 64.0, 55.7, 38.5; HR-ESIMS (m/z) calcd for $C_{25}H_{24}N_2O_9$ $[M+Na]^+$ 519.1374; found 519.1383.

The α isomer: $[\alpha]_D^{29}$ = -45.4 (*c* 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 6.0 Hz, 1H), 5.73 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.59 (d, *J* = 6.0 Hz, 1H), 4.85 (t, *J* = 4.0 Hz, 1H), 4.55 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.50 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.04–2.88 (m,

1H), 2.53 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.5, 164.3, 164.0, 163.1, 150.1, 139.6, 131.9, 131.8, 121.8, 121.1, 114.13, 114.1, 101.7, 88.1, 85.9, 74.7, 64.0, 55.7, 55.6, 39.1; HR-ESIMS (m/z) calcd for $C_{25}H_{24}N_2O_9$ $[M+Na]^+$ 519.1374; found 519.1386.

1-(3',5'-Di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)thymine (7b)

The β isomer: $[\alpha]_D^{29}$ = -75.9 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (brs, 1H), 8.00 (t, *J* = 9.3 Hz, 4H), 7.29 (s, 1H), 6.95 (d, *J* = 9.2 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.45 (dd, *J* = 8.8, 5.6 Hz, 1H), 5.62 (d, *J* = 6.4 Hz, 1H), 4.77 (dd, *J* = 12.2, 2.8 Hz, 1H), 4.63 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.51 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.69 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.41–2.21 (m, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.89, 165.87, 164.11, 164.07, 163.7, 150.5, 134.7, 132.1, 131.7, 121.7, 121.5, 114.2, 114.0, 111.8, 85.1, 83.0, 74.9, 64.2, 55.66, 55.64, 38.2, 12.3; HR-ESIMS (m/z) calcd for $C_{26}H_{26}N_2O_9$ $[M+Na]^+$ 533.1531; found 533.1524.

The α isomer: $[\alpha]_D^{29}$ = -24.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 1.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 5.6 Hz, 1H), 5.59 (d, *J* = 6.0 Hz, 1H), 4.88 (t, *J* = 4.0 Hz, 1H), 4.55 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.48 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.95 (dt, *J* = 15.2, 6.8 Hz, 1H), 2.47 (d, *J* = 15.6 Hz, 1H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 164.2, 164.0, 163.9, 150.4, 135.5, 131.9, 131.7, 121.8, 121.3, 114.1, 114.0, 110.3, 87.5, 85.5, 74.8, 64.1, 55.7, 55.6, 39.0, 12.8; HR-ESIMS (m/z) calcd for $C_{26}H_{26}N_2O_9$ $[M+Na]^+$ 533.1531; found 533.1529.

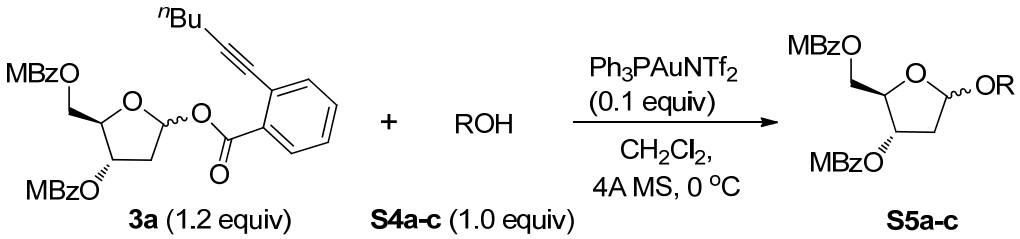
5-Fluoro-1-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-D-ribofuranosyl)uracil (7c)

The β isomer: $[\alpha]_D^{27}$ = -39.5 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.4 Hz, 1H), 8.02–7.96 (m, 4H), 7.66 (d, *J* = 6.0 Hz, 1H), 6.96–6.93 (m, 4H), 6.38 (t, *J* = 6.8 Hz, 1H), 5.58 (d, *J* = 6.8 Hz, 1H), 4.74 (dd, *J* = 12.4, 3.6 Hz, 1H), 4.69 (dd, *J* = 12.4, 3.0 Hz, 1H), 4.54 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.73 (ddd, *J* = 14.4, 5.6, 1.6 Hz, 1H), 2.28–2.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.8, 164.2, 164.1, 156.7, 156.4, 148.7, 142.0, 139.7, 132.1, 131.8, 123.5, 123.2, 121.5, 121.4, 114.2, 114.0, 85.7, 83.5, 74.6, 63.9, 55.7, 38.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -163.8; HR-ESIMS (m/z) calcd for $C_{25}H_{23}FN_2O_9$ $[M+Na]^+$ 537.1280; found 537.1293.

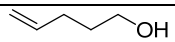
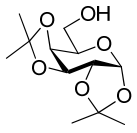
The α isomer: $[\alpha]_D^{27}$ = -54.9 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.4 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 6.4 Hz, 1H), 7.08–6.71 (m, 4H), 6.33 (d, *J* = 7.2 Hz, 1H), 5.62 (d, *J* = 6.0 Hz, 1H), 4.89 (t, *J* = 4.2 Hz, 1H), 4.54 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.47 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.97 (dt, *J* = 15.6, 6.8 Hz, 1H), 2.48 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 164.3, 164.0, 156.9, 156.7, 148.6, 141.6, 139.3, 131.9, 131.7, 124.4, 124.0, 121.7, 121.0, 114.2, 114.1, 87.9, 85.9, 74.6, 64.0, 55.72, 55.66, 39.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -166.0; HR-ESIMS (m/z) calcd for $C_{25}H_{23}FN_2O_9$ $[M+Na]^+$ 537.1280; found 537.1284.

4. General procedure for the glycosylation of alcohols

Scheme S1. Low-concentration-facilitated highly β-selective glycosylation of alcohols (**S4a**-**S4c**) with 2'-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate **3a**.



3a (1.2 equiv) **S4a-c** (1.0 equiv) **S5a-c**

entry	alcohol	conc. (mM)	yield	β/α ratio
1	 **S4a**	25	100%	2.7:1
2	**S4a**	2.5	100%	4.2:1
3	**S4a**	1.0	100%	6.9:1
4	 **S4b**	25	100%	3.2:1
5	**S4b**	2.5	100%	3.8:1
6	**S4b**	1.0	100%	7.5:1
7	 **S4c**	25	100%	3.5:1
8	**S4c**	2.5	93%	5.4:1
9	**S4c**	1.0	88%	11:1

A general procedure: To a solution of 3,5-di-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate **3a** (70 mg, 0.12 mmol) and 5-pentene-1-ol **S4a**

(10 μL, 0.10 mmol) in dry CH_2Cl_2 (4 mL) was added 4Å MS under argon atmosphere. The resulting mixture was stirred at room temperature for 1 hour and then $Ph_3PAuNTf_2$ (7.4 mg, 0.01 mmol) was added. The stirring was continued at 0 ^oC for 5 h. The mixture was filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate 6:1) to provide **S5a** (45 mg, 96%, β:α = 2.7:1) as a colorless syrup.

Pentenyl 3,5-di-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranoside (S5a)

The β isomer: $[\alpha]_D^{28}$ = -3.4 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 6.90 (t, *J* = 8.6 Hz, 4H), 5.86–5.70 (m, 1H), 5.58 (ddd, *J* = 7.2, 4.8, 2.8 Hz, 1H), 5.33 (dd, *J* = 5.4, 2.4 Hz, 1H), 5.06–4.88 (m, 2H), 4.60–4.37 (m, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.75 (dt, *J* = 9.6, 6.8 Hz, 1H), 3.40 (dt, *J* = 9.4, 6.8 Hz, 1H), 2.55 (ddd, *J* = 14.0, 7.2, 2.4 Hz, 1H), 2.34 (dt, *J* = 14.0, 5.2 Hz, 1H), 2.07 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.67–1.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.9, 163.7, 163.6, 138.2, 131.95, 131.88, 122.5, 122.2, 114.9, 113.8, 113.7, 104.8, 81.9, 75.6, 67.7, 65.2, 55.6, 55.5, 39.4, 30.4, 28.8; HR-ESIMS (m/z) calcd for $C_{26}H_{30}O_8$ $[M+Na]^+$ 493.1833; found 493.1836.

The α isomer: $[\alpha]_D^{28}$ = 103.9 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 12.1, 8.9 Hz, 4H), 7.00–6.83 (m, 4H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.41 (dd, *J* = 5.2, 2.4 Hz, 1H), 5.29 (d, *J* = 4.8 Hz, 1H), 5.09–4.89 (m, 2H), 4.59 (dd, *J* = 13.2, 5.6 Hz, 1H), 4.55–4.43 (m, 2H), 3.86 (s, 3H), 3.86 (s, 3H), 3.77 (dt, *J* = 9.4, 6.8 Hz, 1H), 3.46 (dt, *J* = 9.6, 6.4 Hz, 1H), 2.51 (ddd, *J* = 13.6, 8.0, 5.4 Hz, 1H), 2.29–1.95 (m, 3H), 1.86–1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 166.0, 163.6, 163.5, 138.3, 131.8, 131.7, 122.3, 114.8, 113.7, 103.9, 81.0, 74.6, 66.9, 64.3, 55.5, 55.4, 39.3, 30.4, 29.0; HR-ESIMS (m/z) calcd for $C_{26}H_{30}O_8$ $[M+Na]^+$ 493.1833; found 493.1830.

Isopropyl 3,5-di-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranoside (S5b)

The β isomer: $[\alpha]_D^{29}$ = -11.2 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 6.90 (t, *J* = 8.4 Hz, 4H), 5.57 (t, *J* = 4.8 Hz, 1H), 5.48 (dd, *J* = 5.4, 2.8 Hz, 1H), 4.62–4.36 (m, 3H), 3.95 (dt, *J* = 12.4, 6.0 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.49 (ddd, *J* = 14.0, 7.0, 2.8 Hz, 1H), 2.34 (dt, *J* = 14.0, 5.2 Hz, 1H), 1.18 (d, *J* = 6.0 Hz, 2H), 1.14 (d, *J* = 6.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.9, 163.7, 163.5, 132.0, 131.9, 122.5, 122.3, 113.8, 113.7, 102.8,

81.8, 75.9, 69.8, 65.4, 55.6, 55.5, 39.7, 23.6, 21.7; HR-ESIMS (m/z) calcd for $C_{24}H_{28}O_8$ $[M+Na]^+$ 467.1676; found 467.1671.

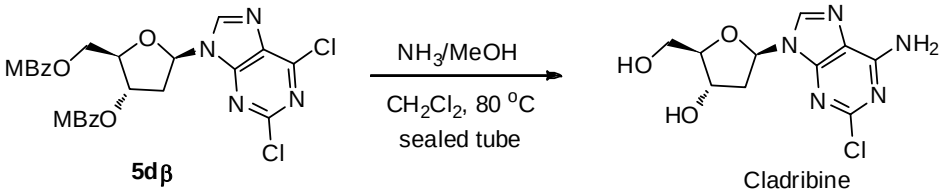
The α isomer: $[\alpha]_D^{29}$ = 118.2 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 6.93–6.88 (m, 4H), 5.47–5.34 (m, 2H), 4.59–4.47 (m, 3H), 3.98 (dt, *J* = 12.4, 6.2 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.51 (ddd, *J* = 13.6, 8.0, 5.4 Hz, 1H), 2.14 (d, *J* = 14.4 Hz, 1H), 1.25 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 163.7, 163.6, 131.9, 131.8, 122.5, 122.4, 113.8, 113.7, 101.8, 80.7, 74.7, 68.9, 64.4, 55.6, 55.5, 39.7, 23.9, 21.7; HR-ESIMS (m/z) calcd for $C_{24}H_{28}O_8$ $[M+Na]^+$ 467.1676; found 467.1677.

3,5-Di-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-D-galactose (S5c)

The β isomer: $[\alpha]_D^{27}$ = -31.8 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 6.92–6.87 (m, 4H), 5.66–5.49 (m, 2H), 5.40 (dd, *J* = 5.2, 1.6 Hz, 1H), 4.56 (dd, *J* = 8.0, 2.2 Hz, 1H), 4.51 (s, 2H), 4.30 (dd, *J* = 4.8, 2.4 Hz, 1H), 4.14 (d, *J* = 9.2 Hz, 1H), 4.02–3.89 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.60 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.71–2.52 (m, 1H), 2.42–2.30 (m, 1H), 1.55 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.9, 163.7, 163.5, 131.92, 131.88, 122.5, 122.2, 113.8, 113.7, 109.4, 108.7, 105.0, 96.4, 82.0, 75.6, 71.2, 70.74, 70.66, 67.3, 67.0, 65.4, 55.6, 55.5, 39.5, 26.2, 26.0, 25.1, 24.4; HR-ESIMS (m/z) calcd for $C_{33}H_{40}O_{13}$ $[M+Na]^+$ 667.2361; found 667.2376.

The α isomer: $[\alpha]_D^{29}$ = 44.6 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.00–6.83 (m, 4H), 5.53 (d, *J* = 5.0 Hz, 1H), 5.48–5.41 (m, 1H), 5.37 (d, *J* = 4.8 Hz, 1H), 4.65–4.39 (m, 4H), 4.32 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.28 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.07 (t, *J* = 6.2 Hz, 1H), 3.91–3.69 (m, 8H), 2.49 (ddd, *J* = 13.2, 7.6, 5.2 Hz, 1H), 2.27 (d, *J* = 14.4 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 163.7, 163.6, 132.0, 131.9, 122.5, 122.4, 113.8, 109.4, 108.7, 104.5, 96.6, 81.6, 74.7, 71.2, 70.85, 70.78, 66.3, 66.1, 64.4, 55.6, 39.4, 26.2, 25.2, 24.7; HR-ESIMS (m/z) calcd for $C_{33}H_{40}O_{13}$ $[M+Na]^+$ 667.2361; found 667.2367.

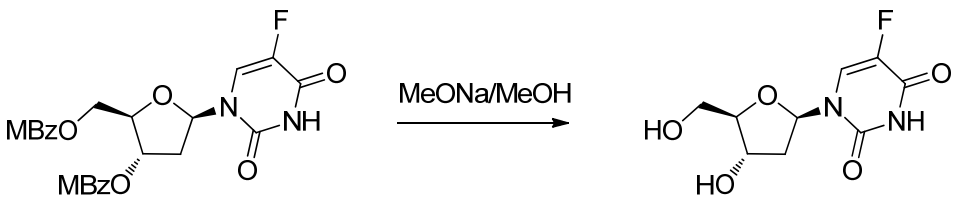
5. Synthesis of cladribine (1)[S3] and floxuridine (2)[S4]



5dβ Cladribine

To a solution of 3,5-tri-*O*-*p*-methoxybenzoyl-2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate **3a** (323 mg, 0.55 mmol) and 2,6-dichloropurine **4d** (95 mg, 0.50 mmol) in dry $ClCH_2CH_2Cl$ (500 mL) was added 4Å MS under argon atmosphere. The resulting mixture was stirred at room temperature for 1 hour and then $Ph_3PAuNTf_2$ (37 mg, 0.05 mmol) was added. The stirring was continued at 45 °C for 6 h (until **4d** was consumed as monitored by TLC). The mixture was filtered, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate 2:1) to provide 2,6-dichloro-9-(3',5'-di-*O*-*p*-methoxybenzoyl-2'-deoxy-β-D-ribofuranosyl)purine **5dβ** (254 mg, 89%) as a white solid and it α anomer **5dα** (23 mg, 8%) as a white foam.

Ice-cold saturated NH_3/MeOH (12 mL) was added into the solution of **5dβ** (115 mg, 0.20 mmol) in CH_2Cl_2 (8 mL) in a sealed tube. The sealed mixture was heated at 80 °C overnight. The solvent was evaporated under reduced pressure. The crude product was dissolved in methanol and silica gel (ca. 200 mg) was added. The solvent was concentrated and the mixture was purified by silica gel column chromatograph (CH_2Cl_2/MeOH 15:1) to afford cladribine **1** (45 mg, 79%) as a white solid: ^{1}H NMR (400 MHz, DMSO) δ 8.35 (s, 1H), 7.81 (s, 2H), 6.26 (t, *J* = 6.8 Hz, 1H), 5.31 (d, *J* = 4.2 Hz, 1H), 4.95 (t, *J* = 5.6 Hz, 1H), 4.39 (brs, 1H), 3.86 (dd, *J* = 7.2, 4.0 Hz, 1H), 3.60 (dt, *J* = 10.0, 4.8 Hz, 1H), 3.56–3.45 (m, 1H), 3.35 (s, 3H), 2.76–2.57 (m, 1H), 2.28 (ddd, *J* = 13.2, 6.0, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 156.8, 153.0, 150.1, 139.9, 118.2, 88.0, 83.6, 70.7, 61.7, 39.4. The data were in agreement with those reported.[S3b]



7cβ Floxuridine

To a stirred suspension of 3,5-di-*O*-*p*-methoxybenzoyl-2-deoxyribofuranosyl

ortho-hexynylbenzoate **3a** (293 mg, 0.50 mmol) and 5-fluorouracil **6c** (130 mg, 0.20 mmol) in dry CH_3CN (10 mL) was added BSTFA (0.5 mL, 2.0 mmol) under argon atmosphere. The mixture was stirred at room temperature for 30 minutes; a clear solution was resulted. Acetonitrile was evaporated under reduced pressure; $ClCH_2CH_2Cl$ (500 mL) and $Ph_3PAuNTf_2$ (37 mg, 0.05 mmol) were added. The stirring was continued at room temperature for 12 h until **3a** was consumed as monitored by TLC. The solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography (CH_2Cl_2/ethyl acetate 5:1) to provide **7cβ** (220 mg, 86%) as a white solid.

The solid **7cβ** (26 mg, 0.05 mmol) was added to a solution of MeONa (20 mg) in MeOH (2 mL). The mixture was stirred at room temperature for 3 h, ion exchange resin (H^+) was then added to neutralize the reaction mixture. The resin was filtered off, the filtrate was concentrated. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH 12:1) to provide floxuridine (**2**) (12 mg, 98%) as a syrup. ^{1}H NMR (400 MHz, DMSO) δ 11.77 (brs, 1H), 8.20 (d, J = 7.2 Hz, 1H), 6.12 (dt, J = 6.4, 1.6 Hz, 1H), 5.22 (brs, 1H), 5.11 (brs, 1H), 4.24 (brd, J = 3.2 Hz), 3.78 (dd, J = 6.8, 3.2 Hz), 3.62 (dd, J = 12.0, 3.2 Hz), 3.57 (dd, J = 12.0, 3.2 Hz), 2.10 (dd, J = 6.4, 4.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ 157.1, 156.9, 149.0, 141.1, 138.8, 124.9, 124.5, 87.5, 84.5, 70.1, 61.0. The data were in agreement with those reported.[S4]

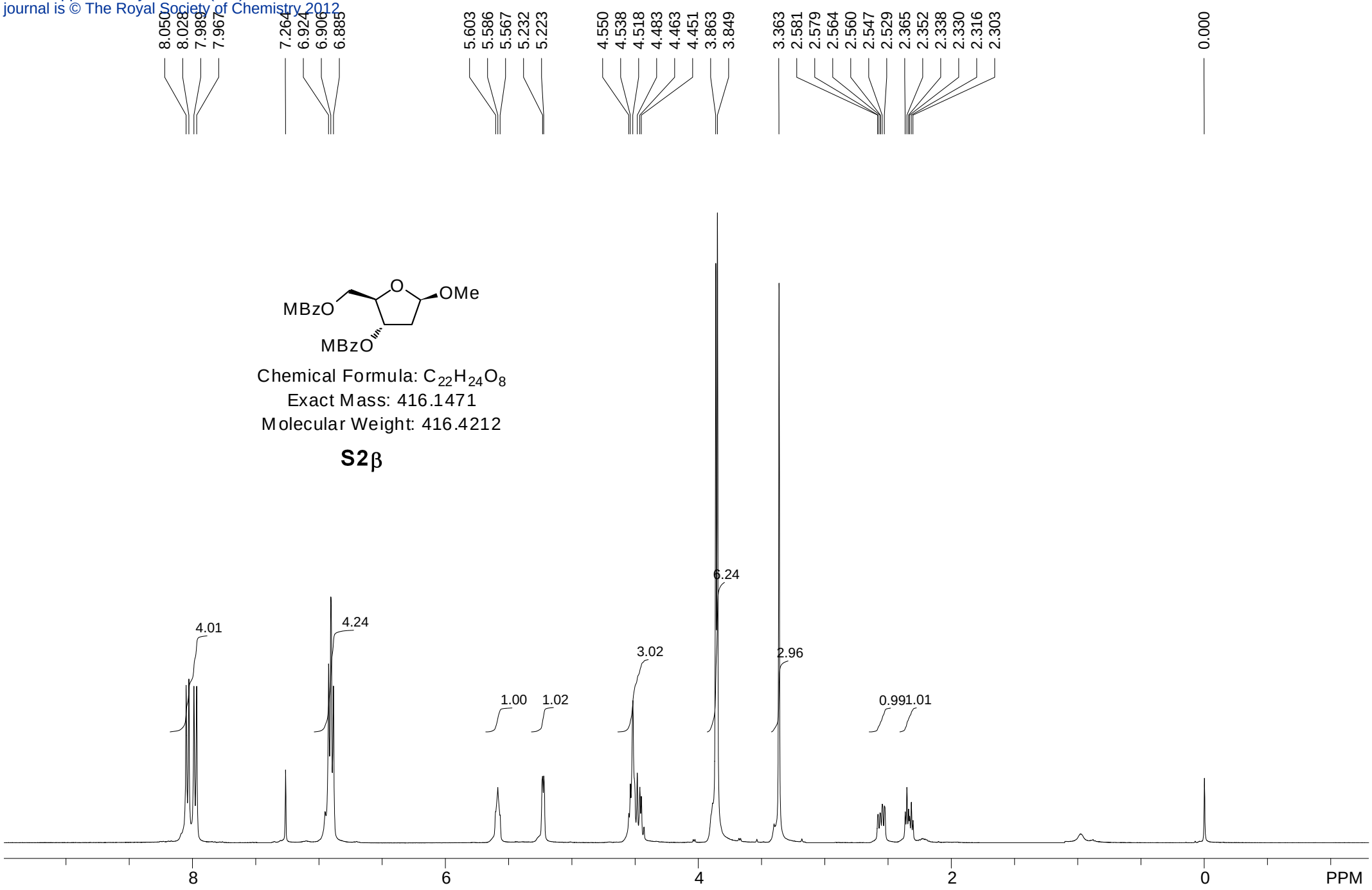
References:

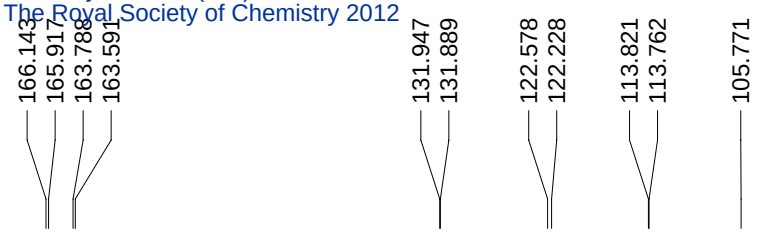
[S1] O. R. Ludek, V. E. Marquez, *Tetrahedron* **2009**, *65*, 8461–8467.

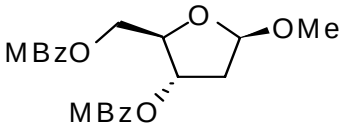
[S2] CCDC 865441 and 865440 contain the supplementary crystallographic data for compounds **5bβ** and **5dβ**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[S3] (a) Z. Janeba, P. Francom, M. J. Robins, *J. Org. Chem.* **2003**, *68*, 989-992. (b) M. Zhong, I. Nowak, J. F. Cannon, M. J. Robins, *J. Org. Chem.* **2006**, *71*, 7773-7779.

[S4] (a) H. Aoyama, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2073–2077. (b) S. Shuto, H. Itoh, S. Ueda, S. Imamura, K. Fukukawa, M. Tsujino, A. Matsuda, T. Ueda, *Chem. Pharm. Bull.* **1988**, *36*, 209-217.

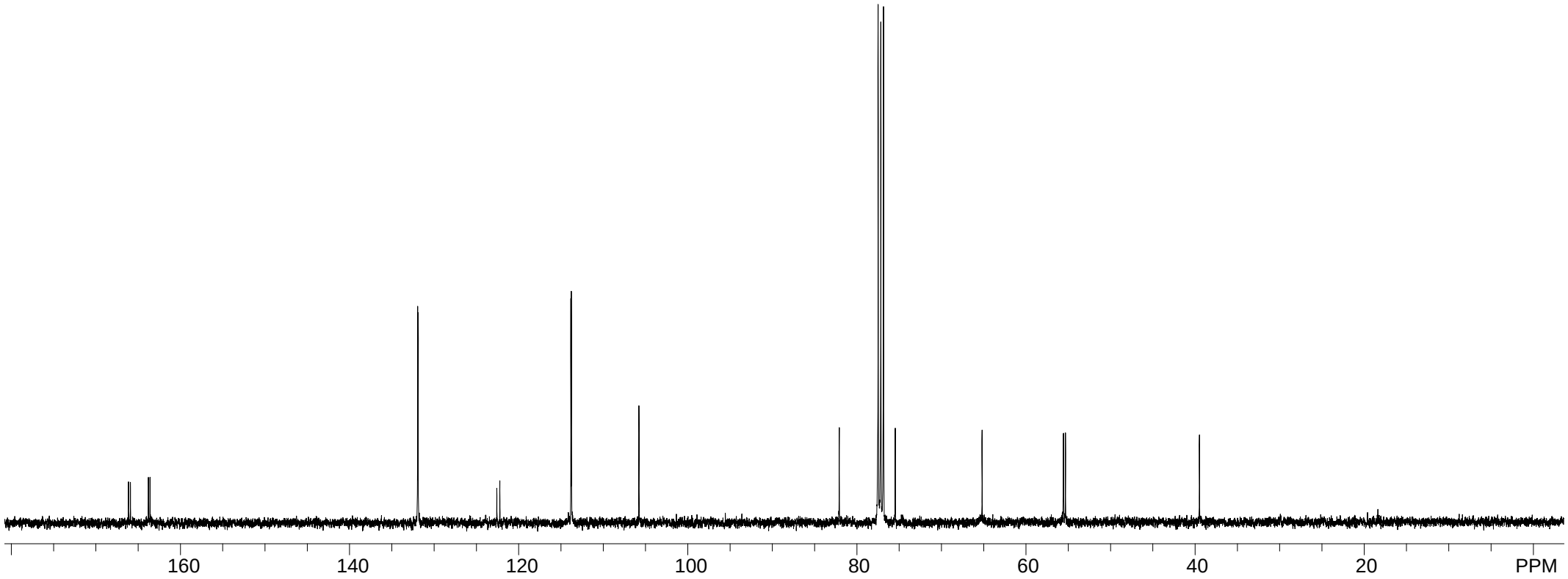


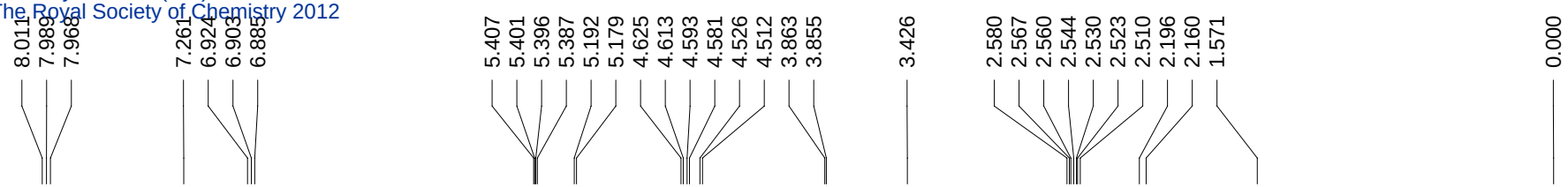


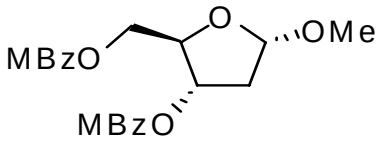


Chemical Formula: $C_{22}H_{24}O_8$
Exact Mass: 416.1471
Molecular Weight: 416.4212

S2β







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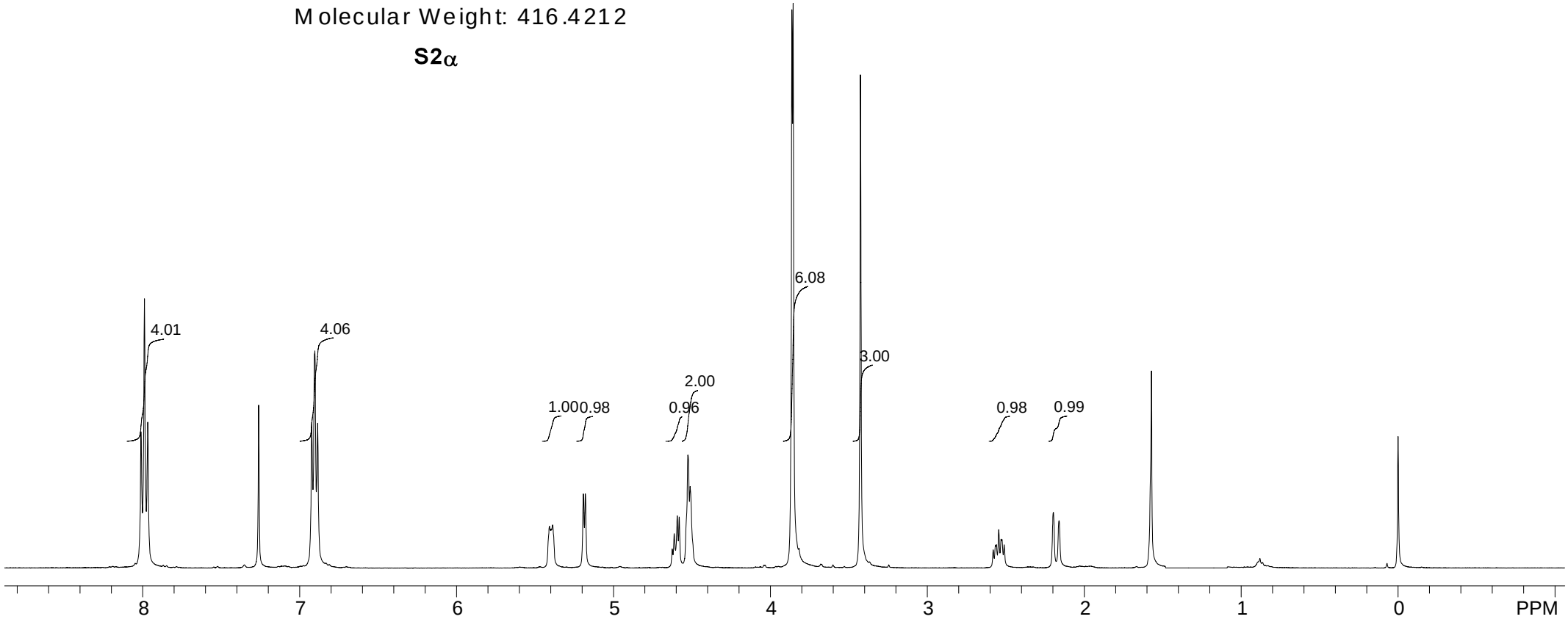
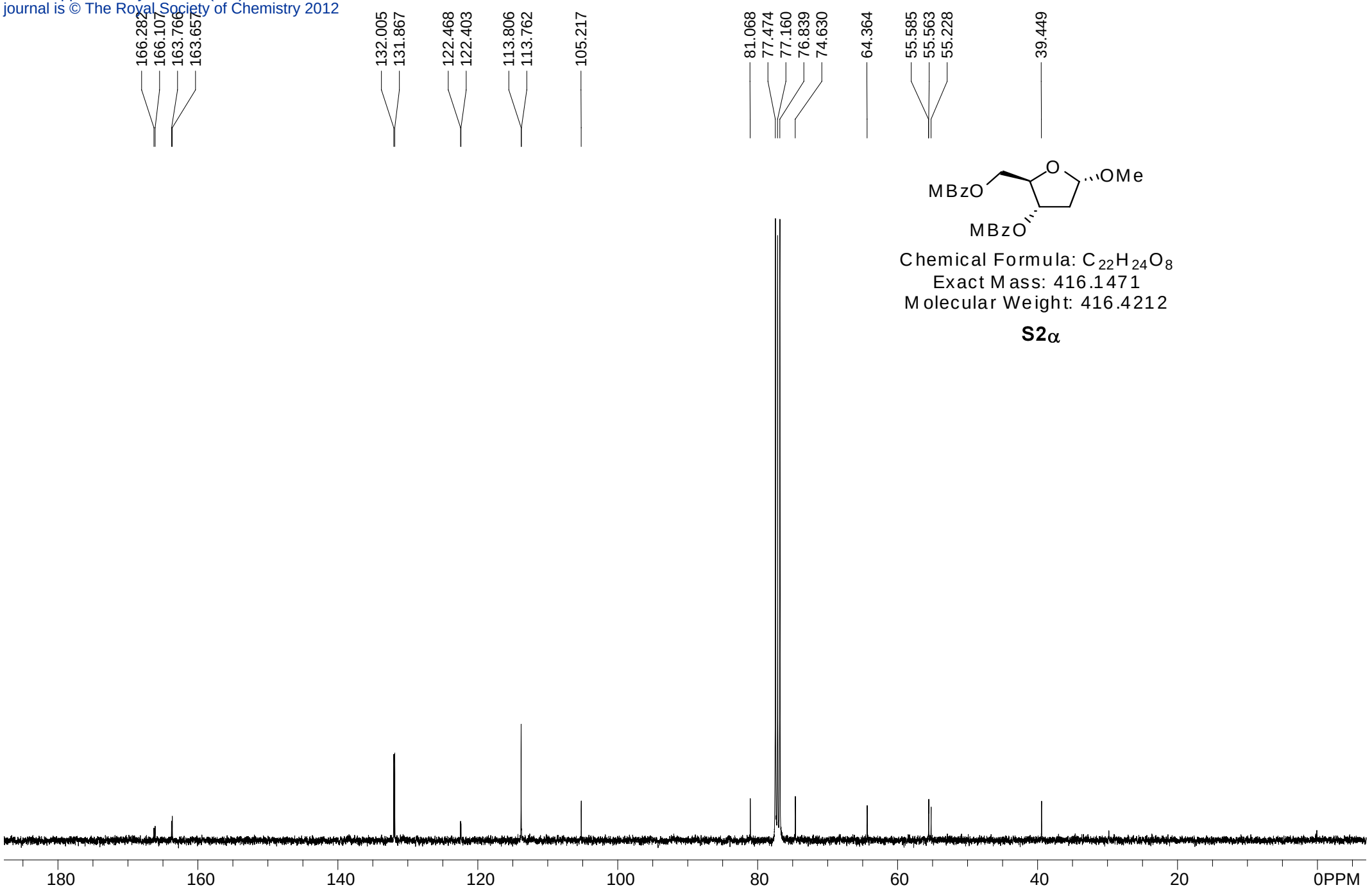
Molecular Weight: 416.4212

S2α





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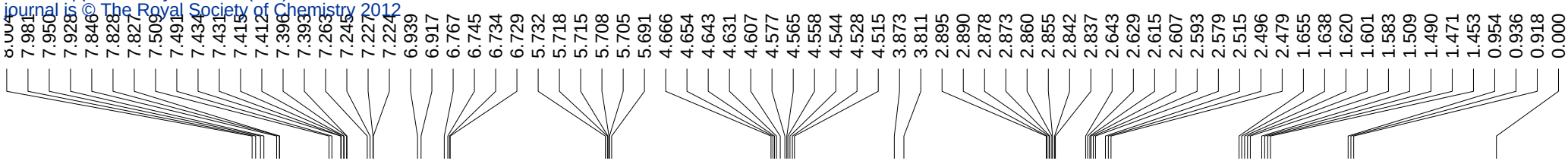
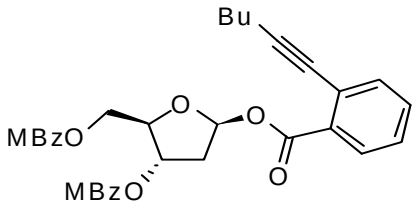
S2α





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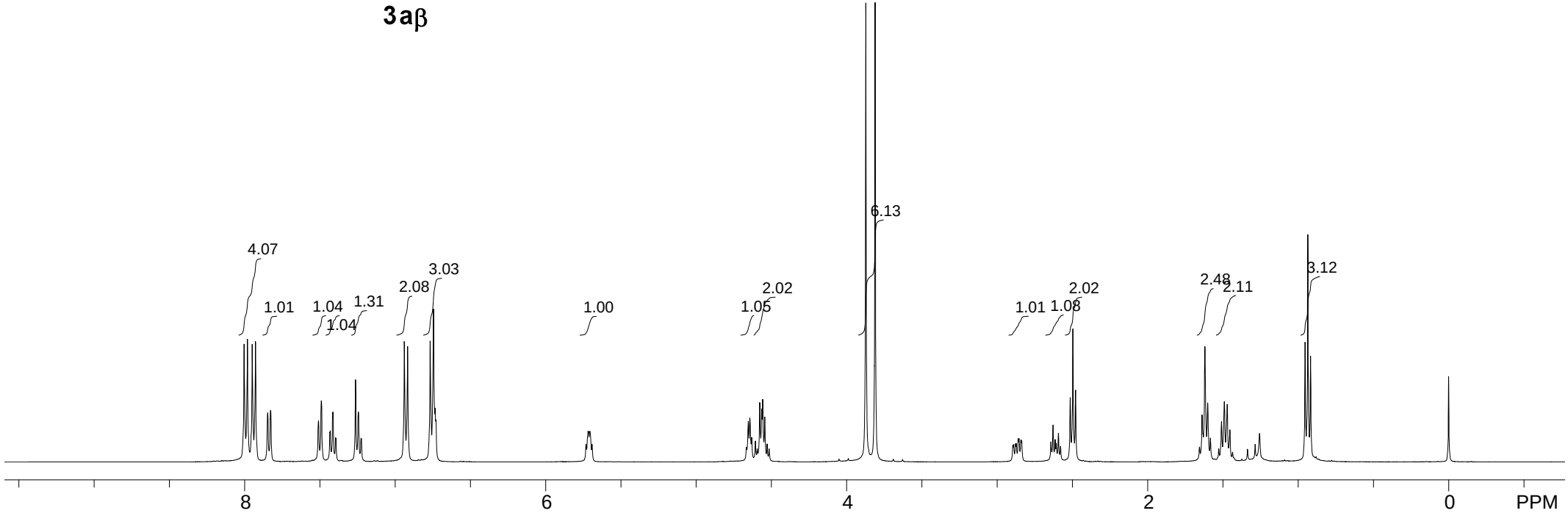
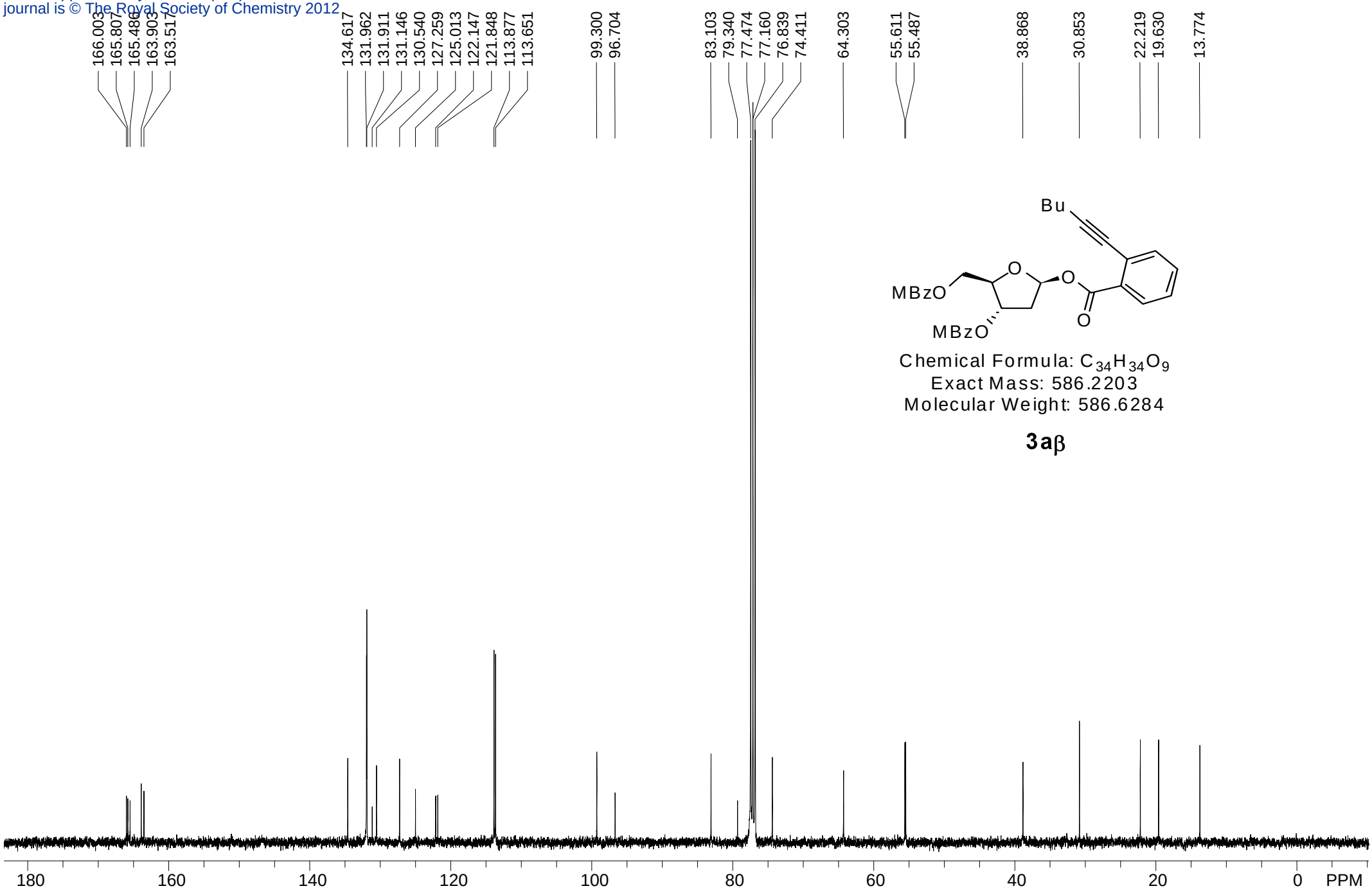
Molecular Weight: 586.6284

3aβ





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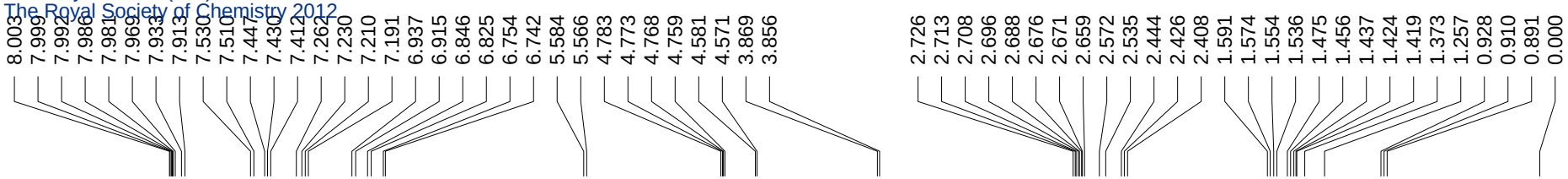
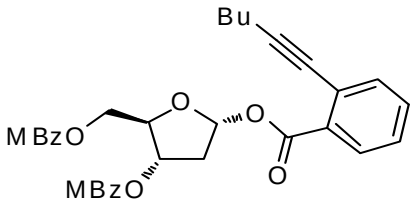
3aβ





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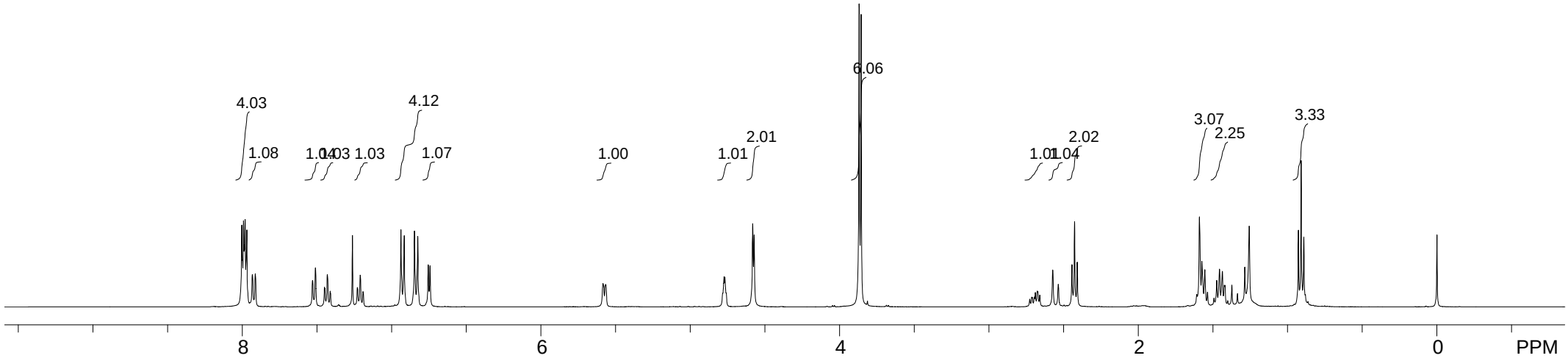
3aα



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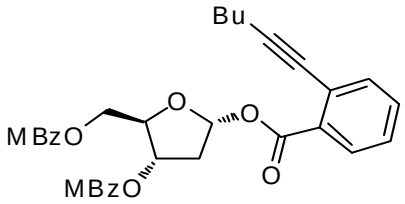

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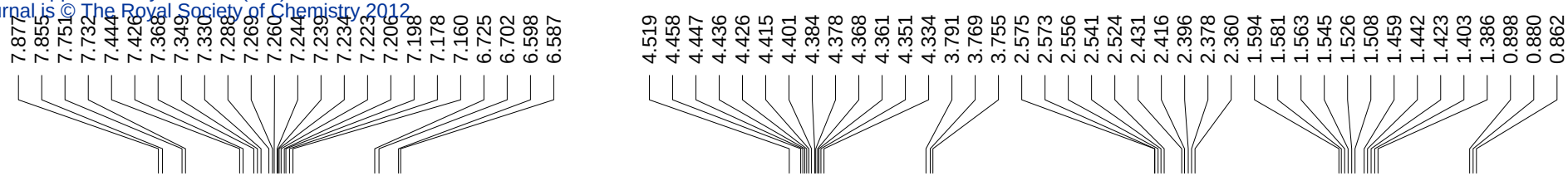
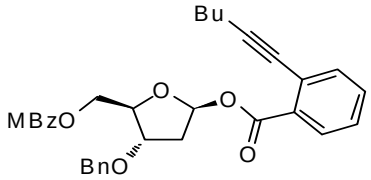
Molecular Weight: 586.6284

3aα





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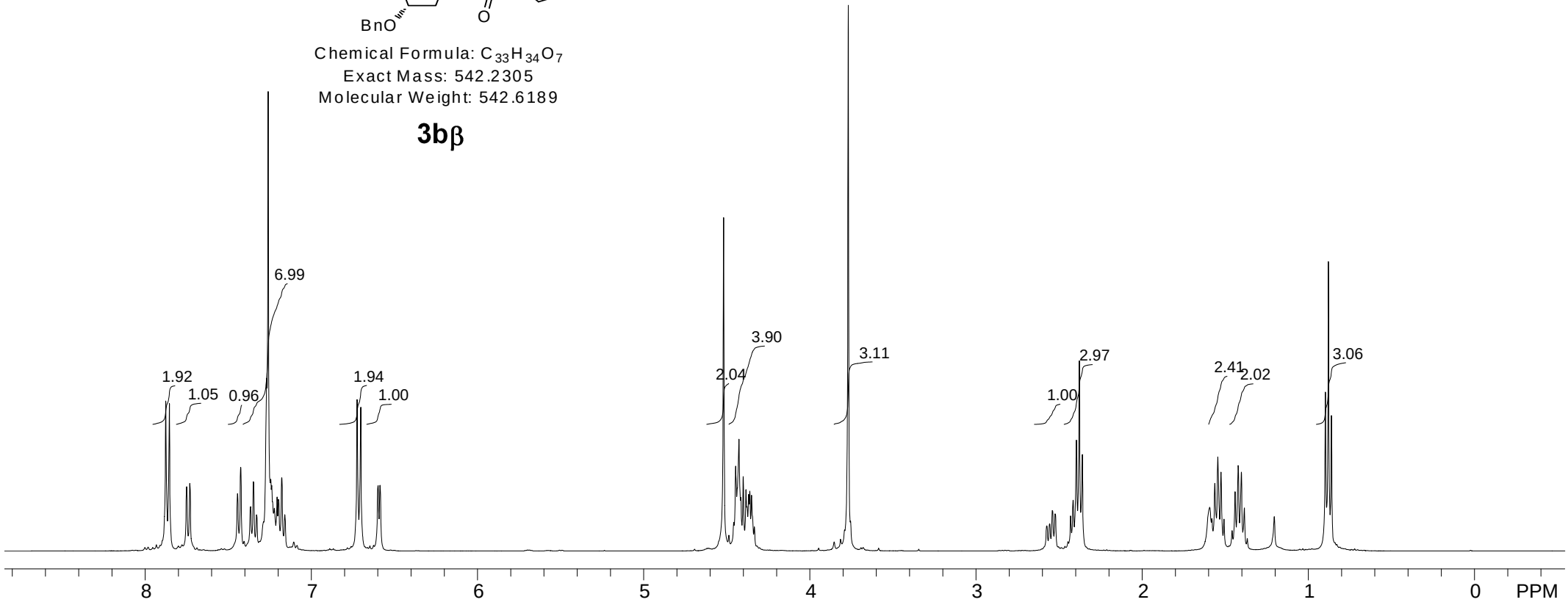
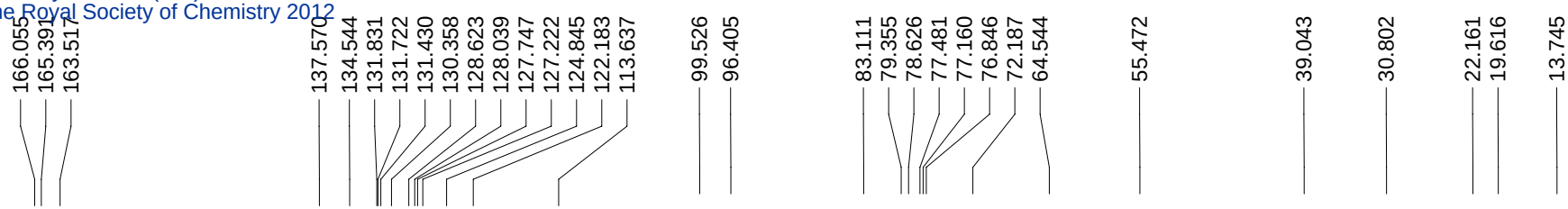
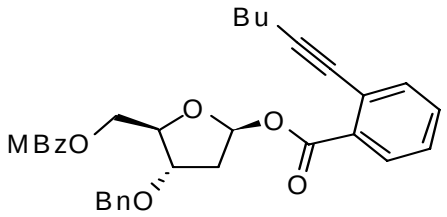
Molecular Weight: 542.6189

3bβ







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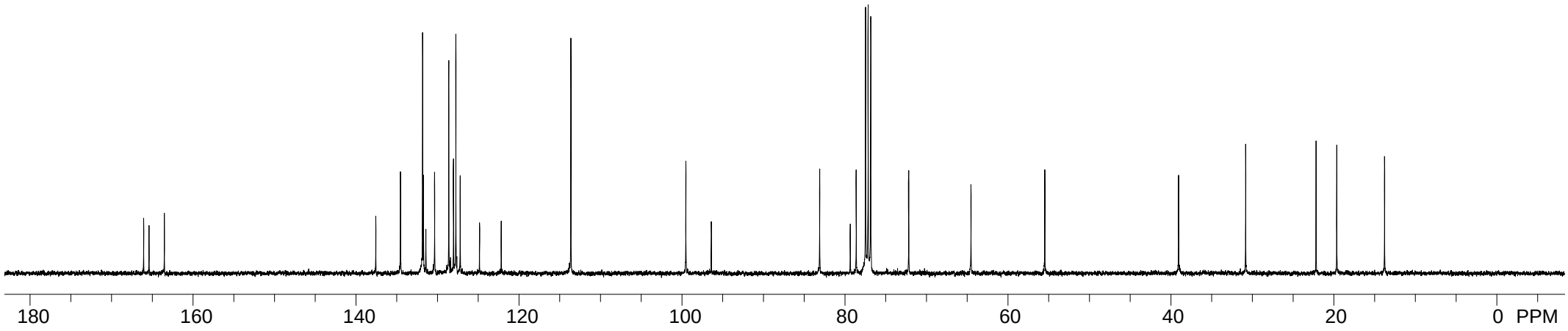
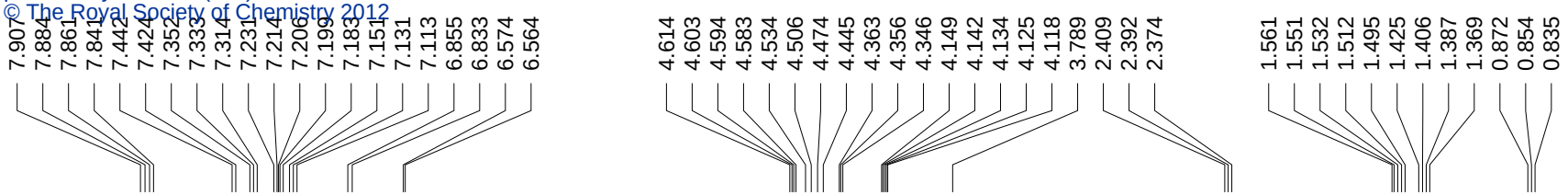
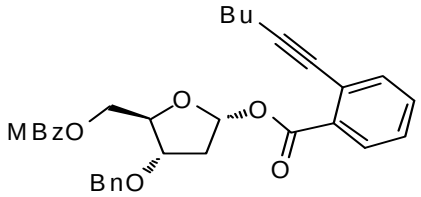
Molecular Weight: 542.6189

3bβ

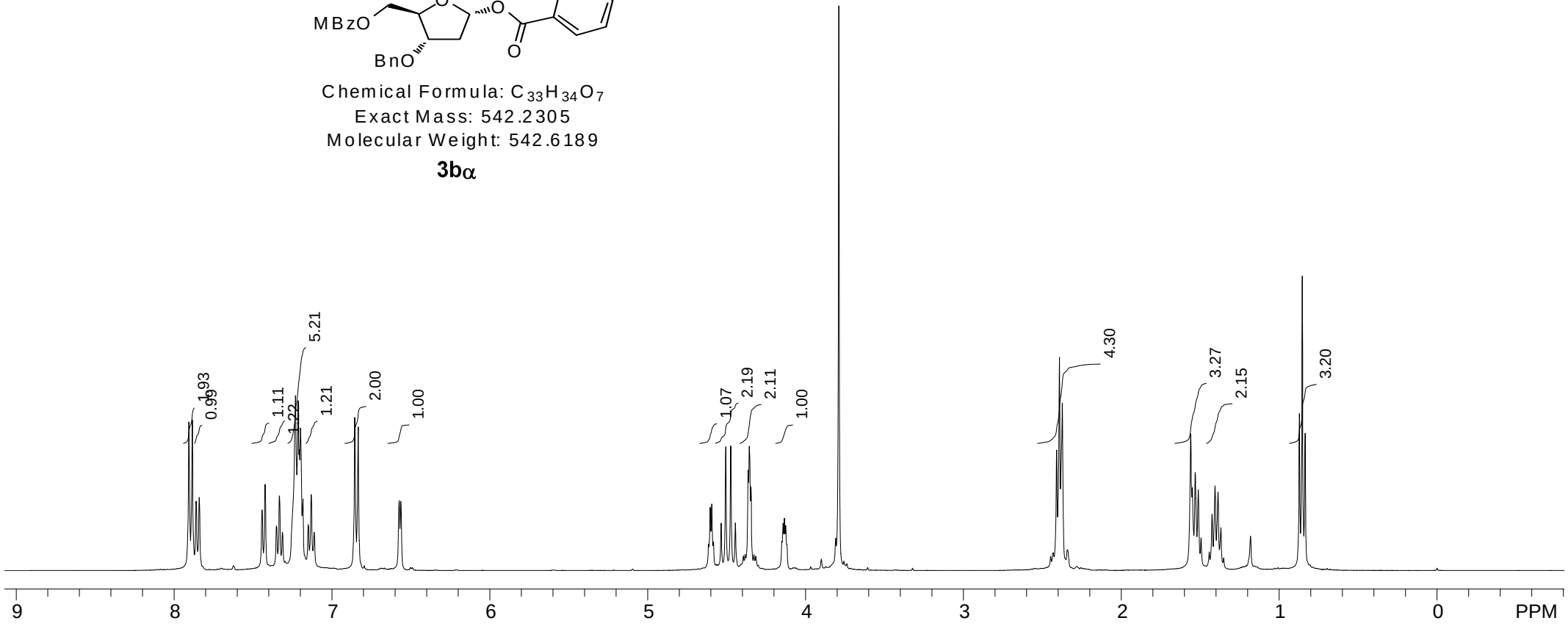


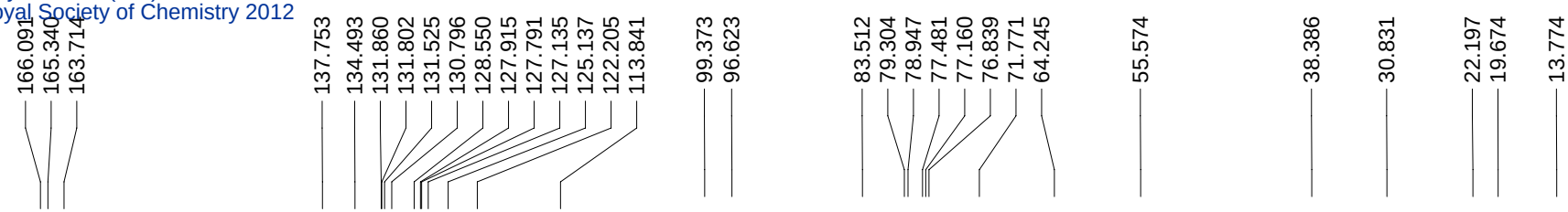


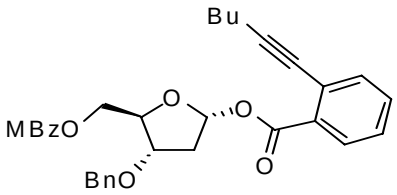


Chemical Formula: $C_{33}H_{34}O_7$
Exact Mass: 542.2305
Molecular Weight: 542.6189

3bα

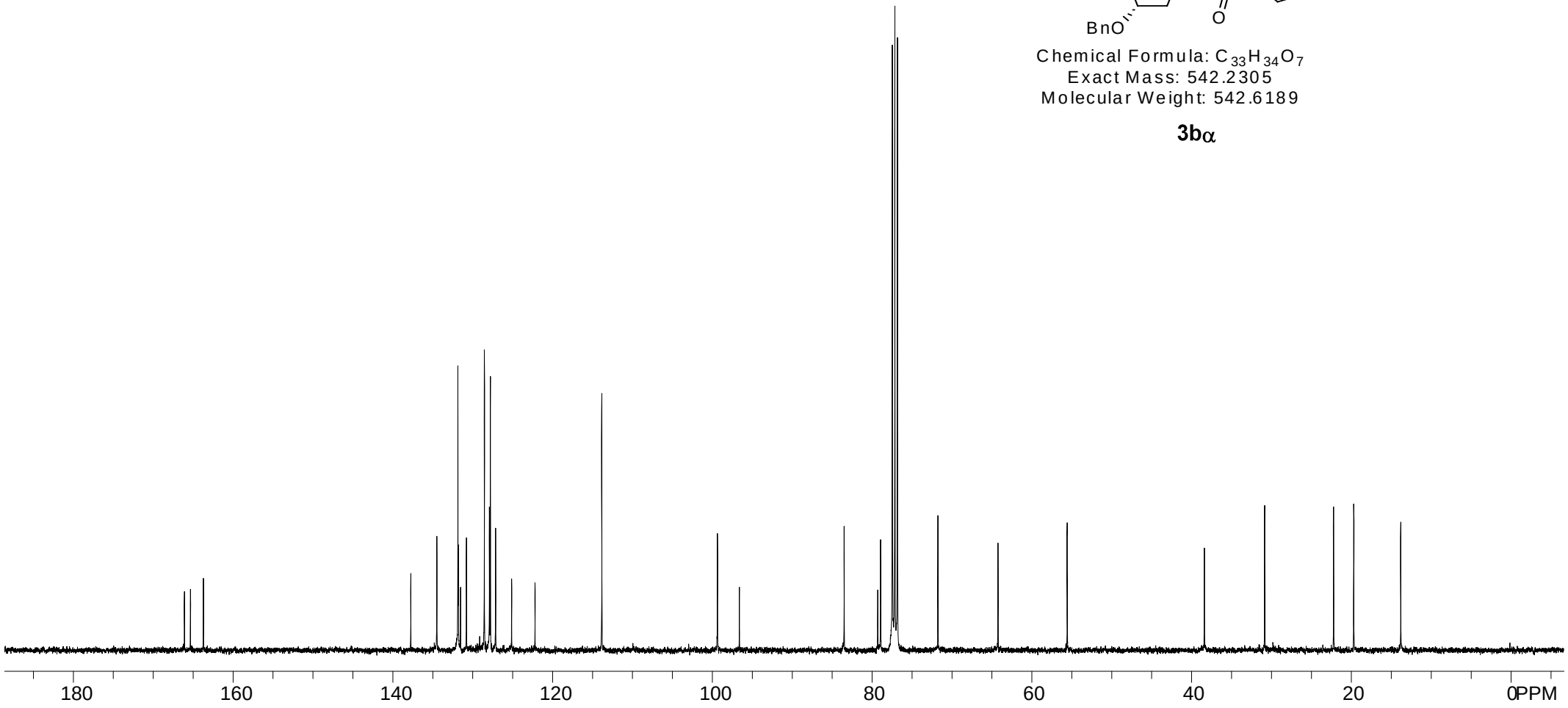


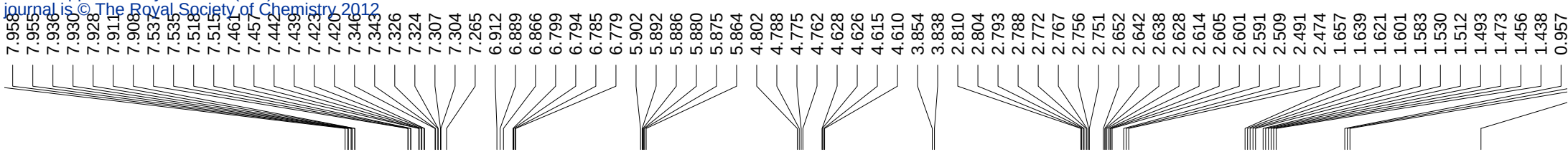


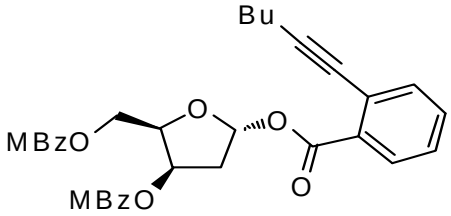


Chemical Formula: $C_{33}H_{34}O_7$
Exact Mass: 542.2305
Molecular Weight: 542.6189

3bα

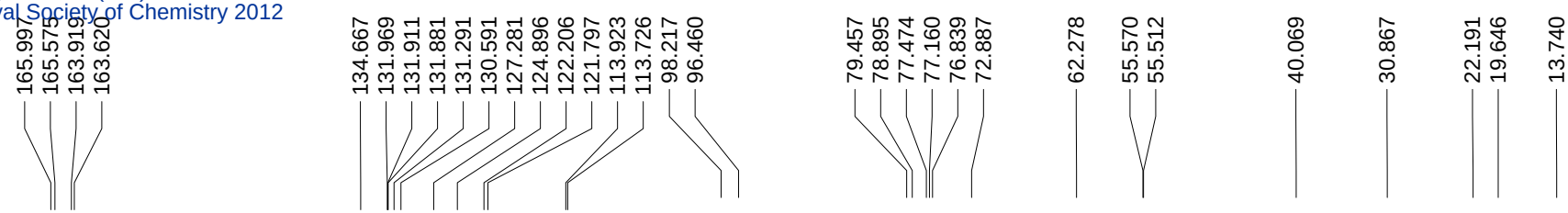


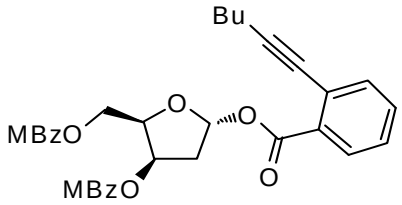




Chemical Formula: $C_{34}H_{34}O_9$
Exact Mass: 586.2203
Molecular Weight: 586.6284

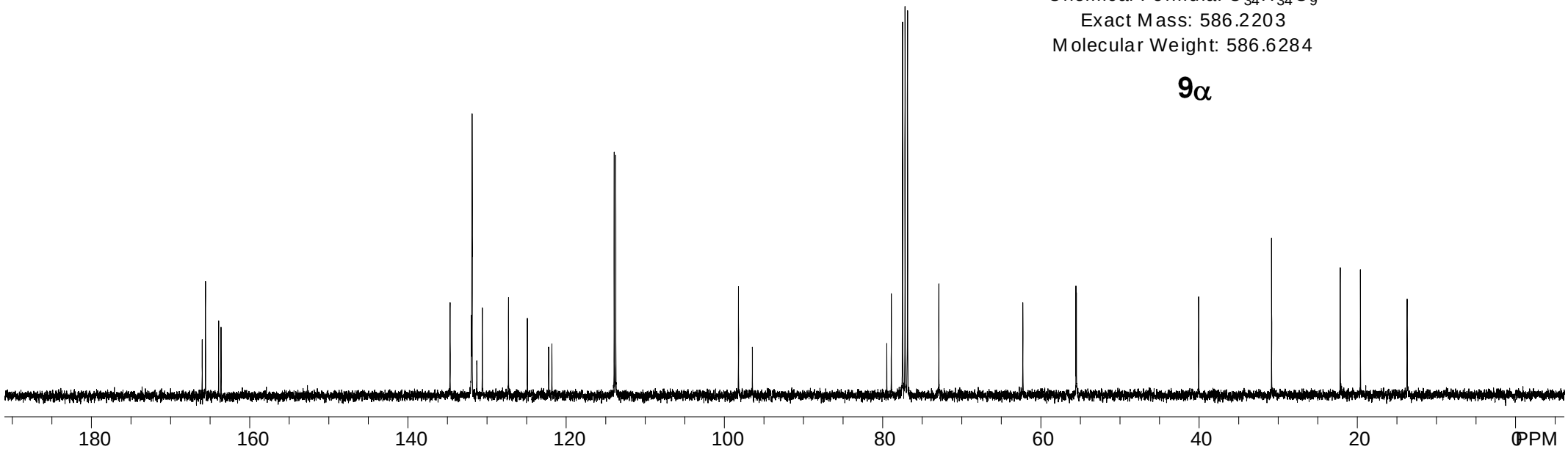
9α

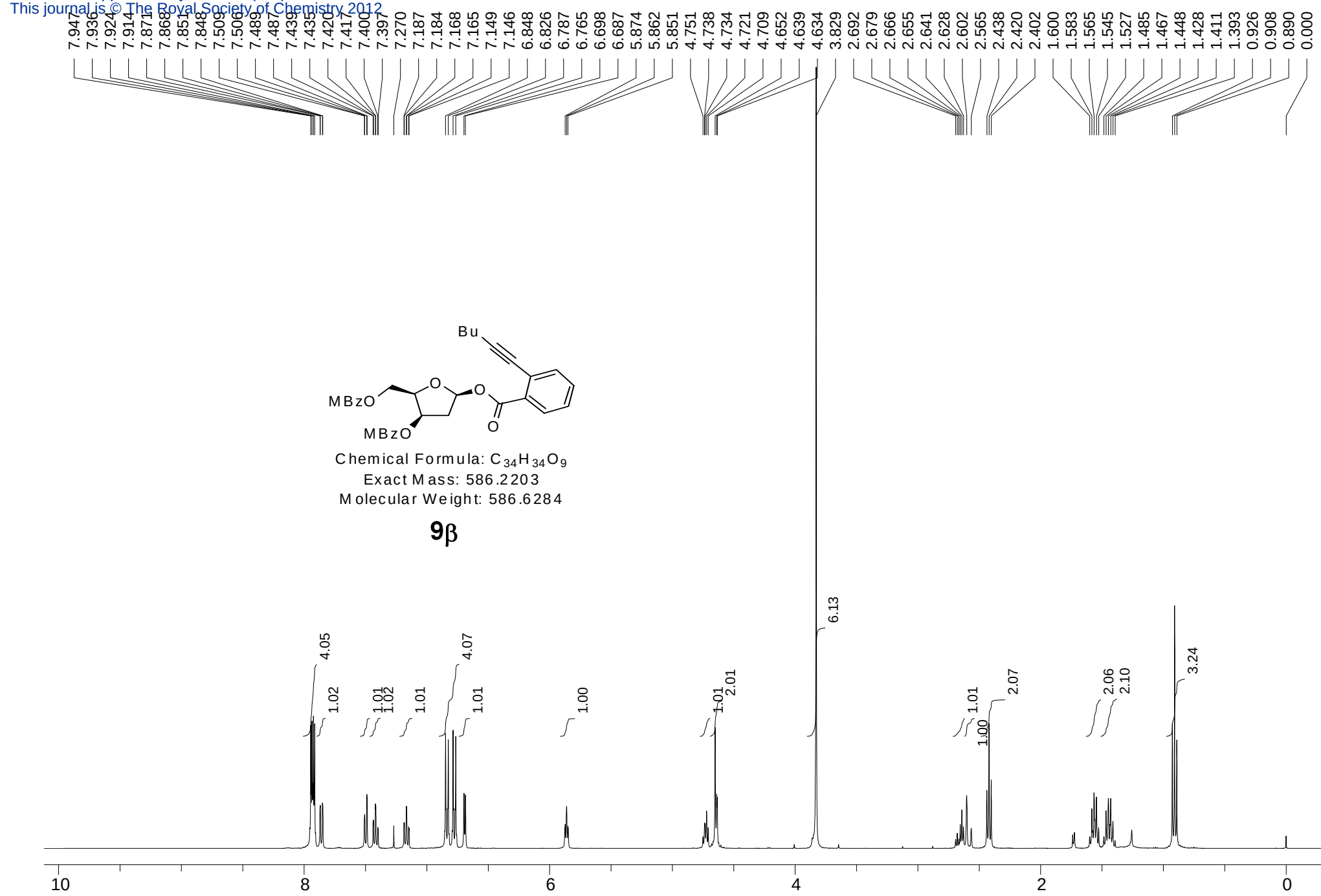


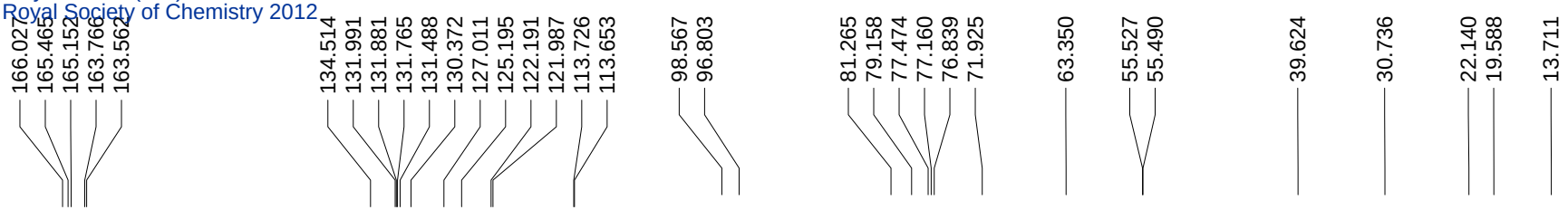


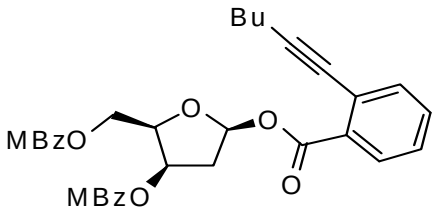
Chemical Formula: $C_{34}H_{34}O_9$
Exact Mass: 586.2203
Molecular Weight: 586.6284

9α



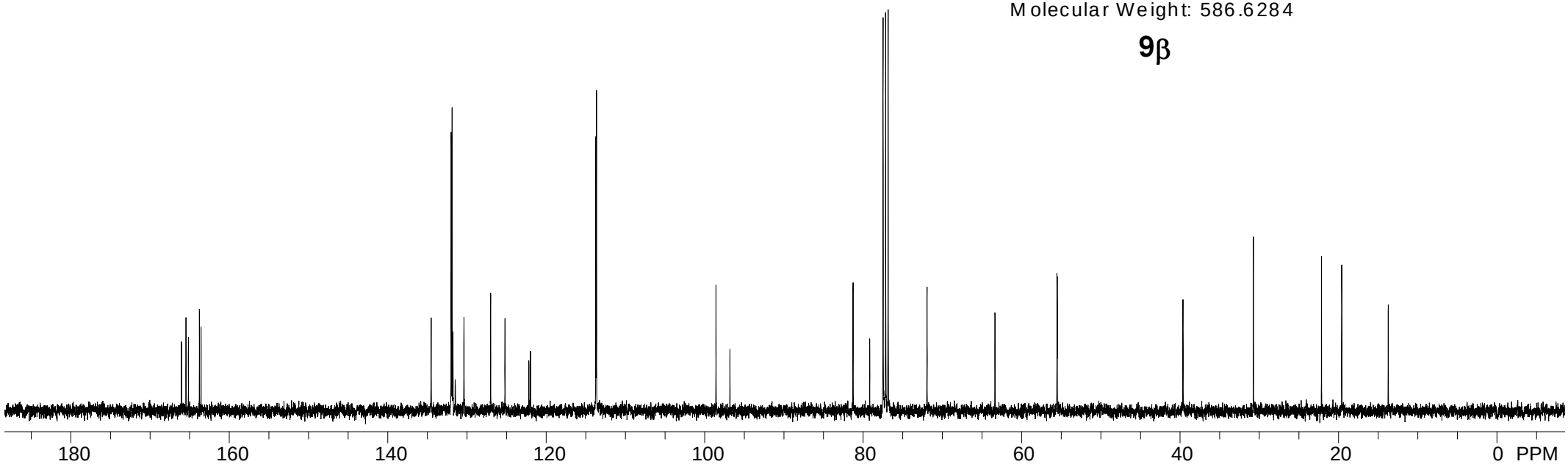


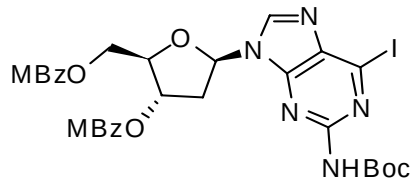




Chemical Formula: $C_{34}H_{34}O_9$
Exact Mass: 586.2203
Molecular Weight: 586.6284

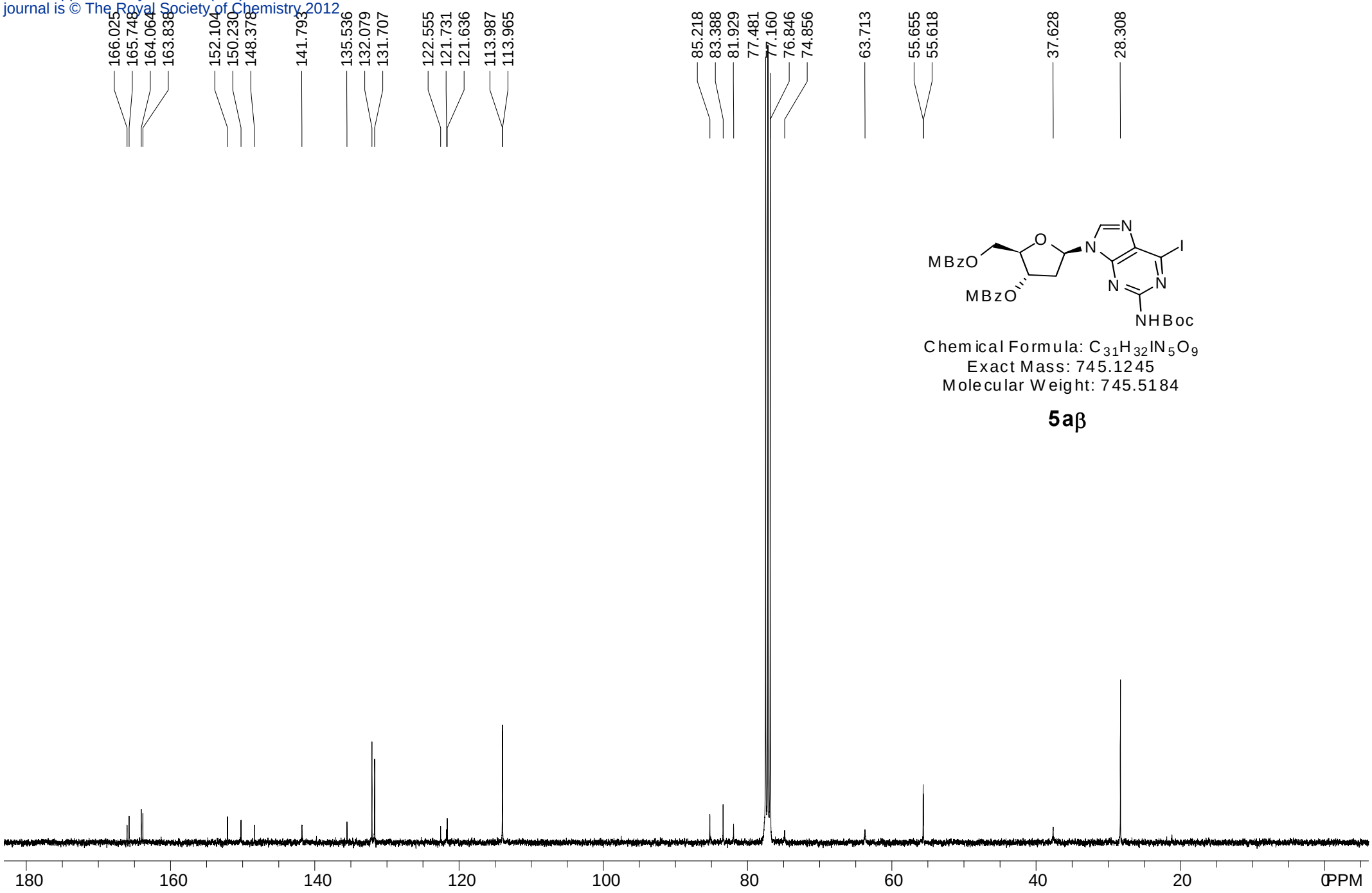
9β





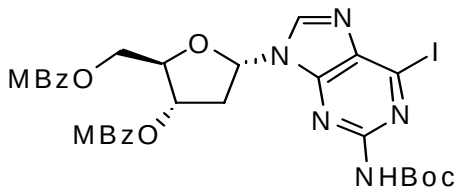
Chemical Formula: $C_{31}H_{32}IN_5O_9$
Exact Mass: 745.1245
Molecular Weight: 745.5184

5aβ



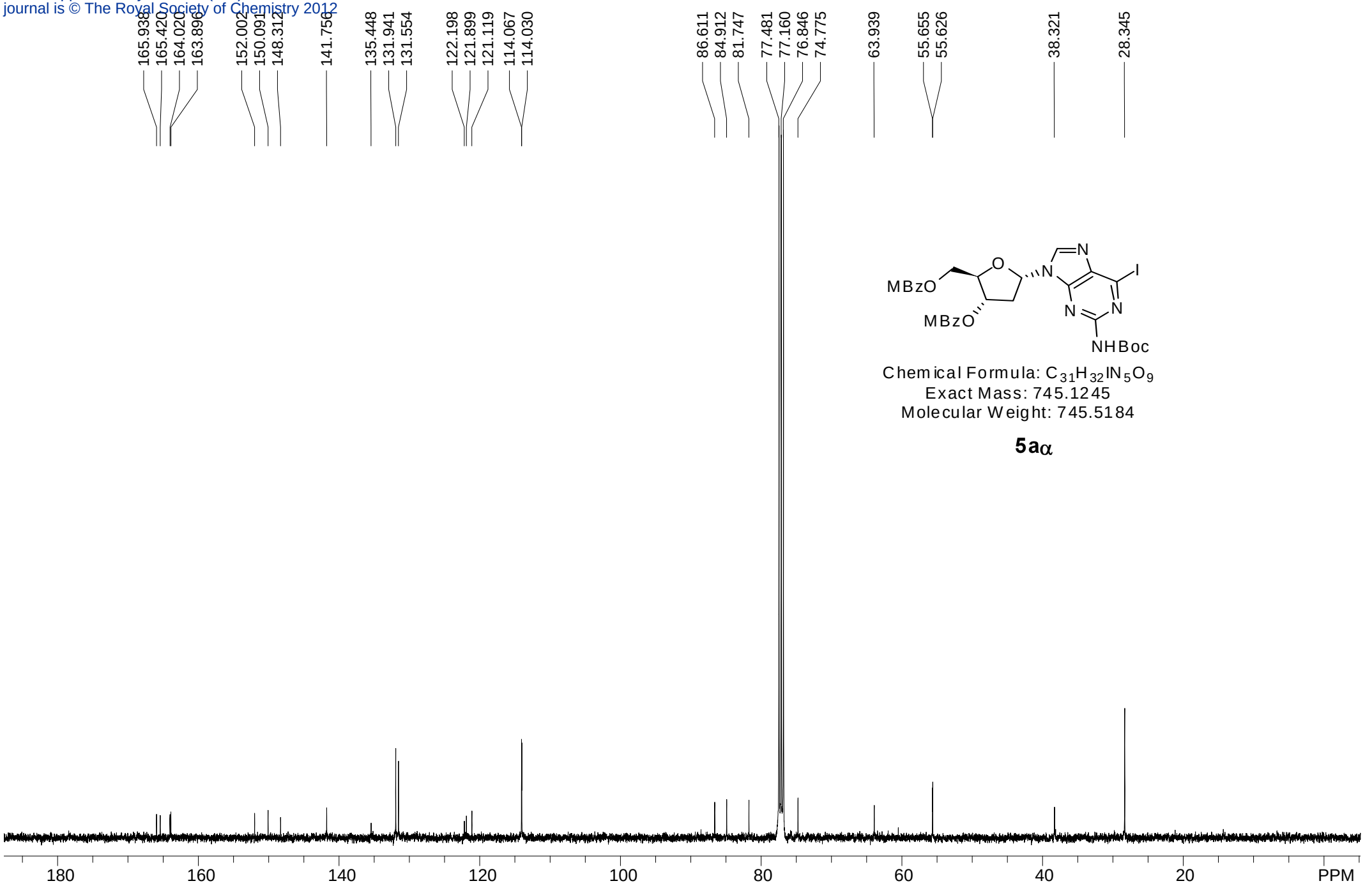
Chemical Formula: $C_{31}H_{32}IN_5O_9$
Exact Mass: 745.1245
Molecular Weight: 745.5184

5aβ



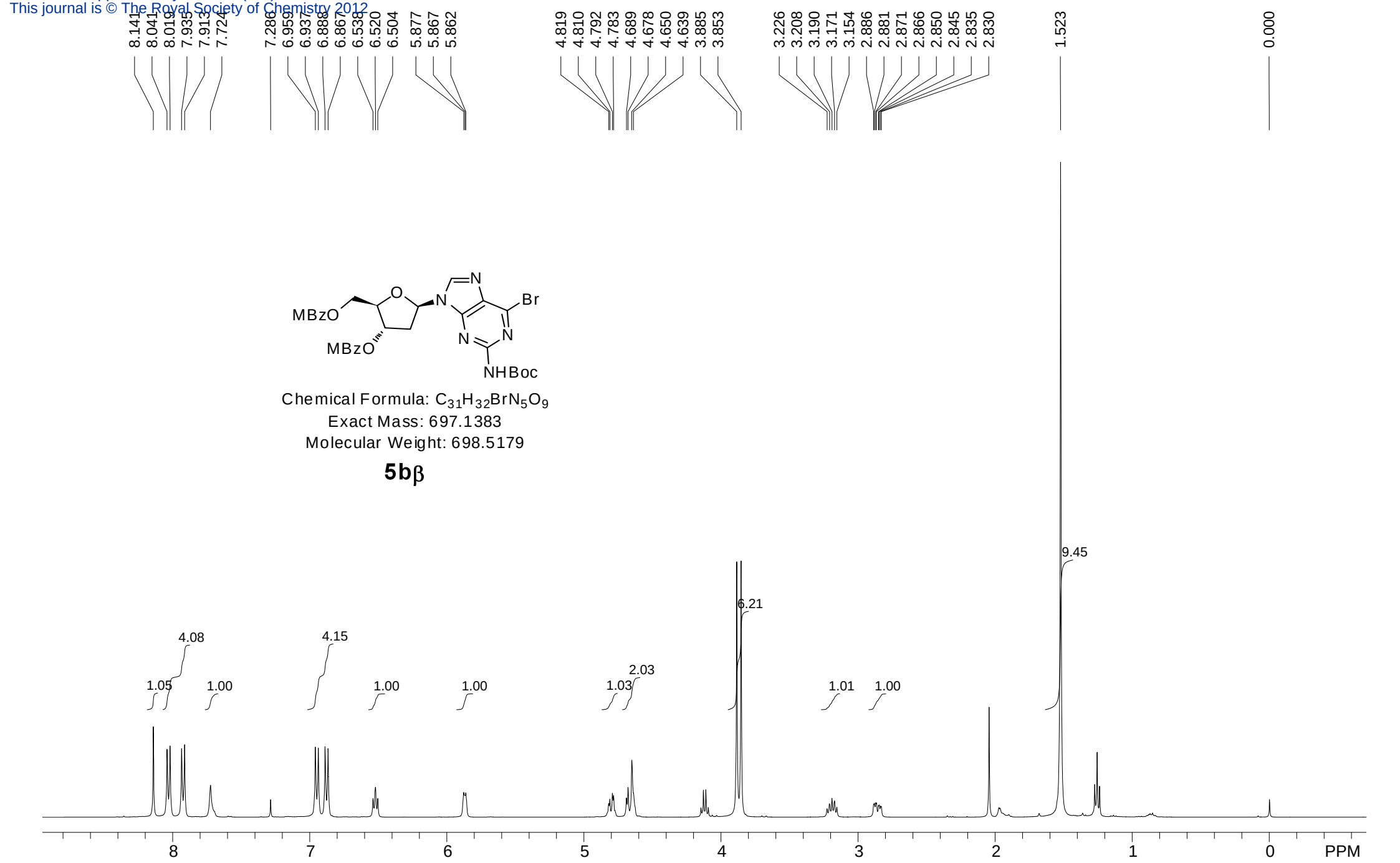
Chemical Formula: $C_{31}H_{32}IN_5O_9$
Exact Mass: 745.1245
Molecular Weight: 745.5184

5aα

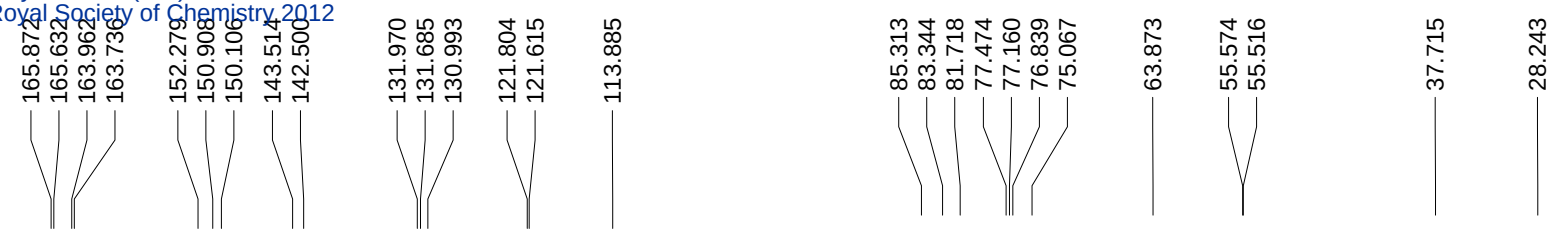


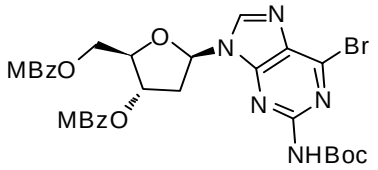
Chemical Formula: $C_{31}H_{32}IN_5O_9$
Exact Mass: 745.1245
Molecular Weight: 745.5184

5aα



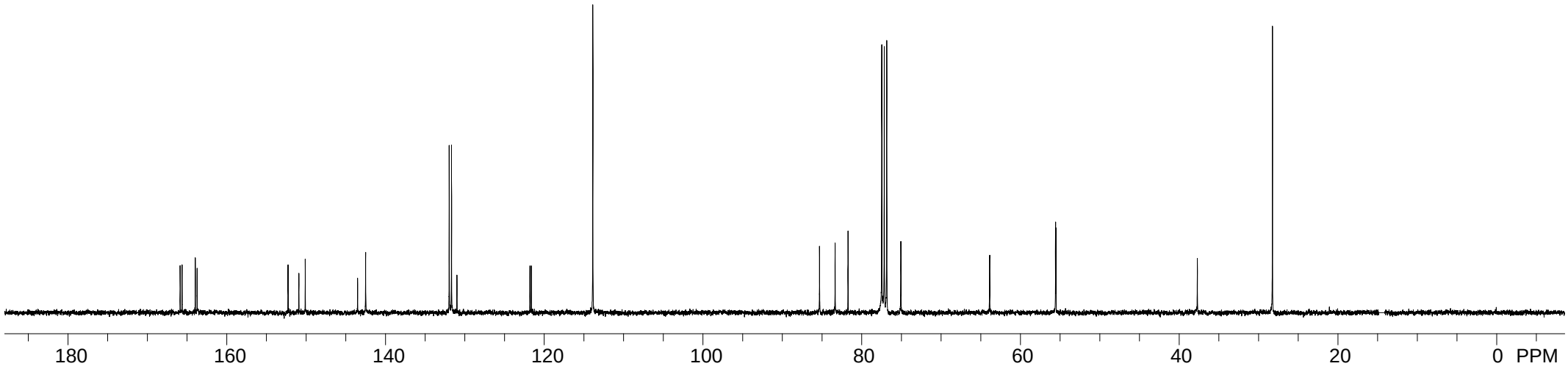
Electronic Supplementary Material (ESI) for Chemical Communications

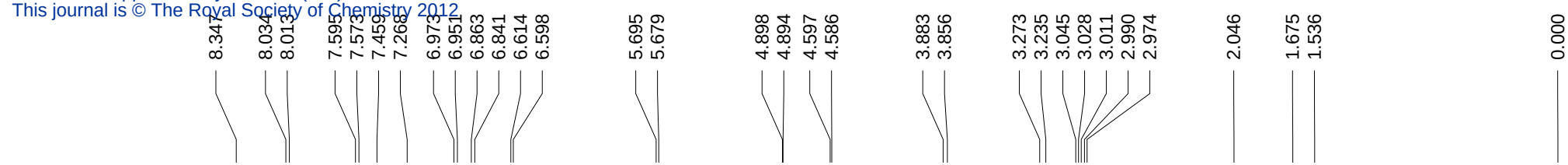


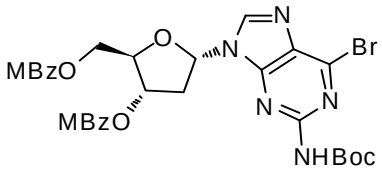


Chemical Formula: $C_{31}H_{32}BrN_5O_9$
Exact Mass: 697.1383
Molecular Weight: 698.5179

5bβ

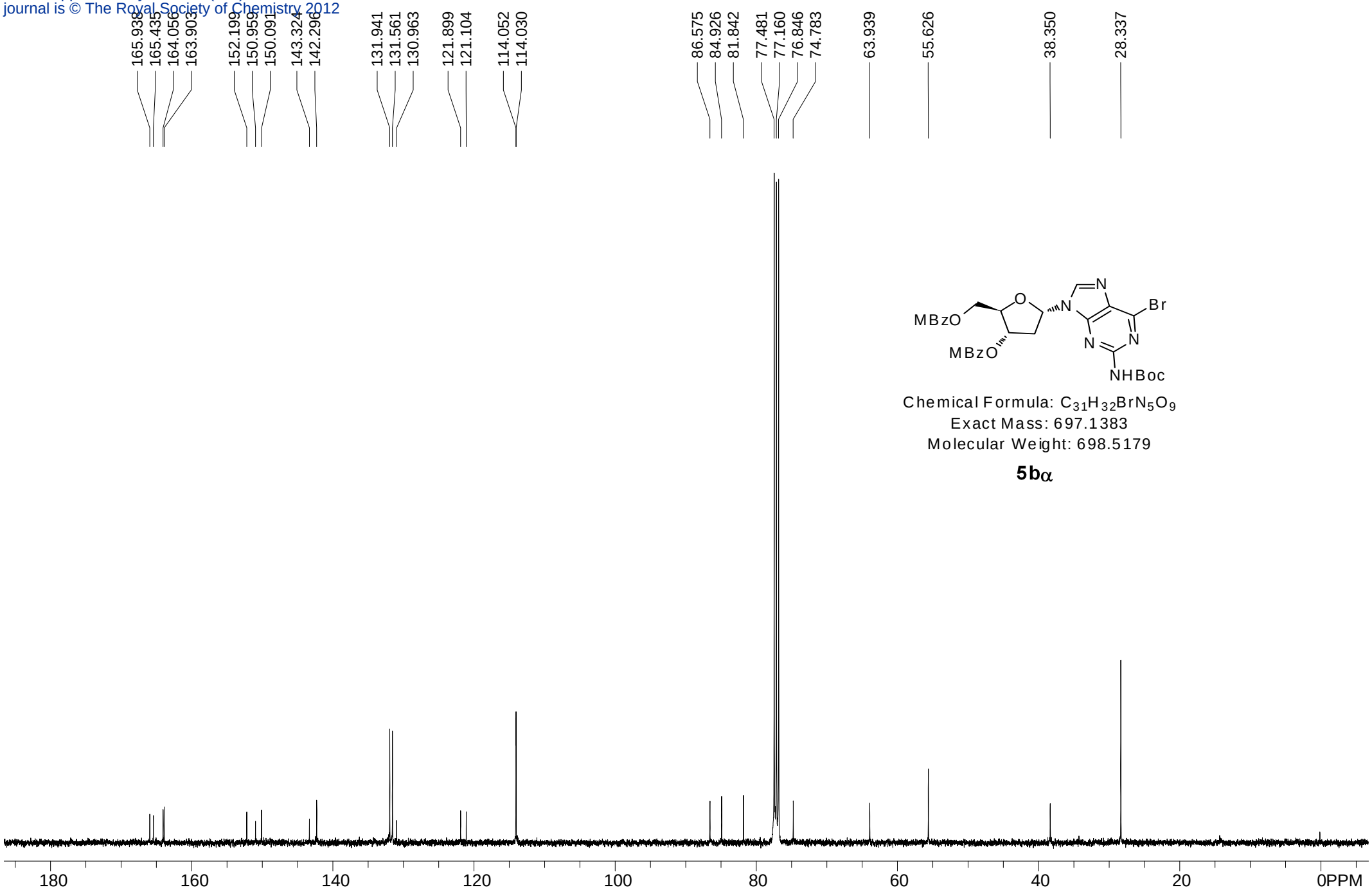






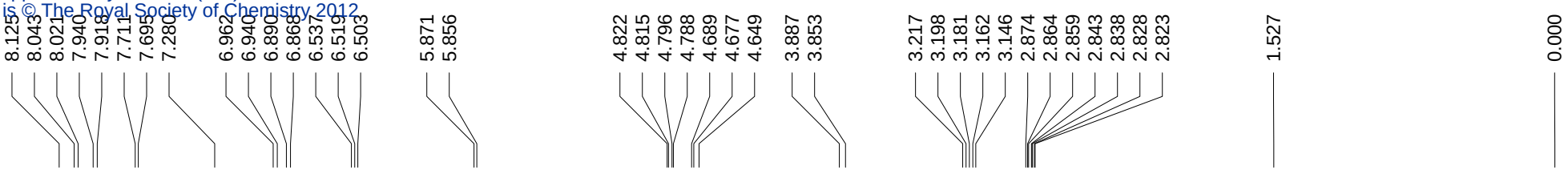
Chemical Formula: $C_{31}H_{32}BrN_5O_9$
Exact Mass: 697.1383
Molecular Weight: 698.5179

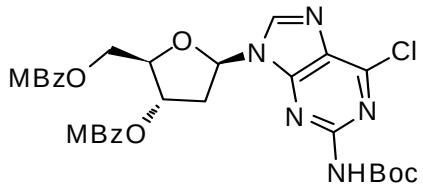
5bα



Chemical Formula: $C_{31}H_{32}BrN_5O_9$
Exact Mass: 697.1383
Molecular Weight: 698.5179

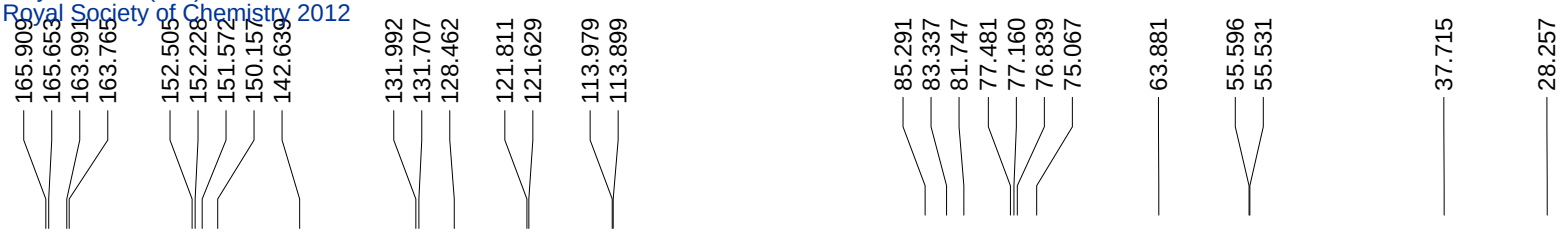
5bα

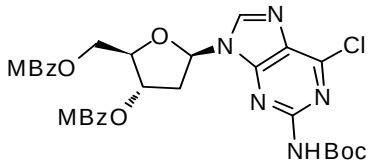




Chemical Formula: $C_{31}H_{32}ClN_5O_9$
Exact Mass: 653.1889
Molecular Weight: 654.0669

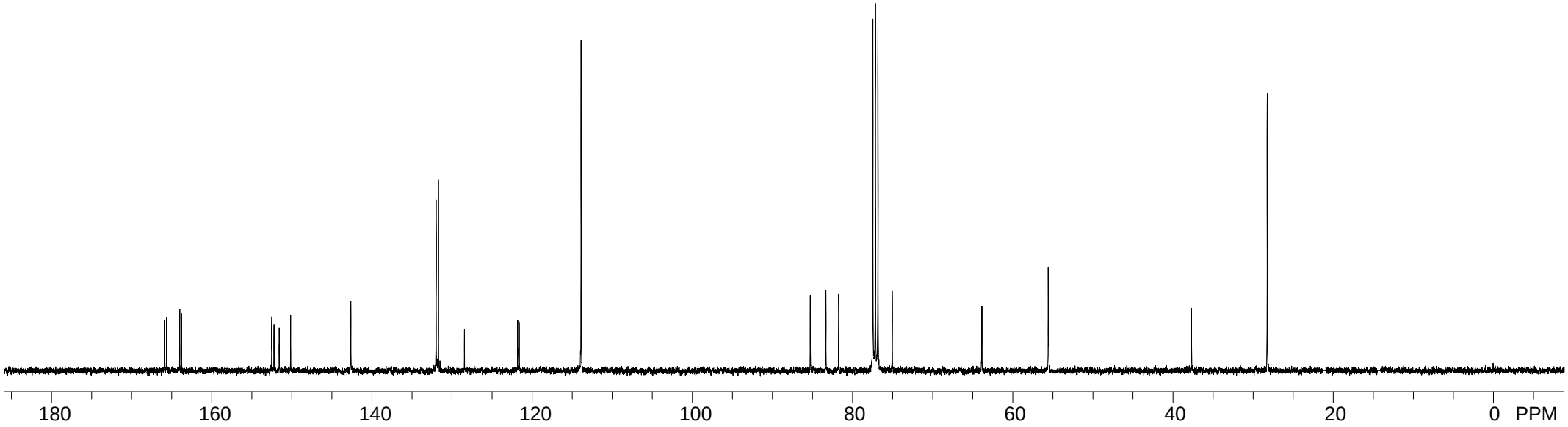
5cβ

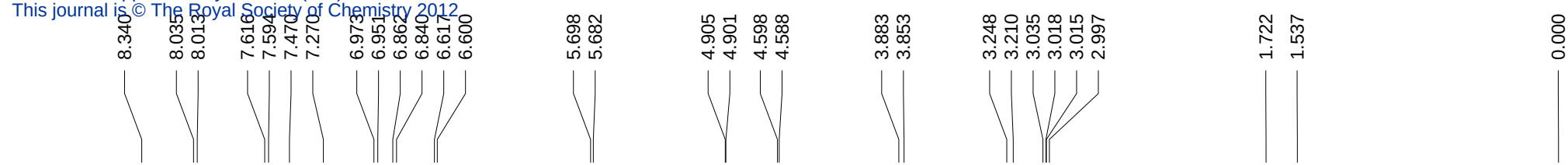


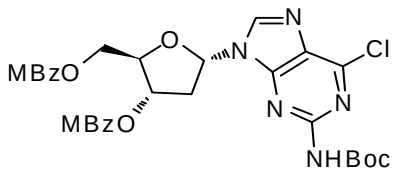


Chemical Formula: $C_{31}H_{32}ClN_5O_9$
Exact Mass: 653.1889
Molecular Weight: 654.0669

5cβ

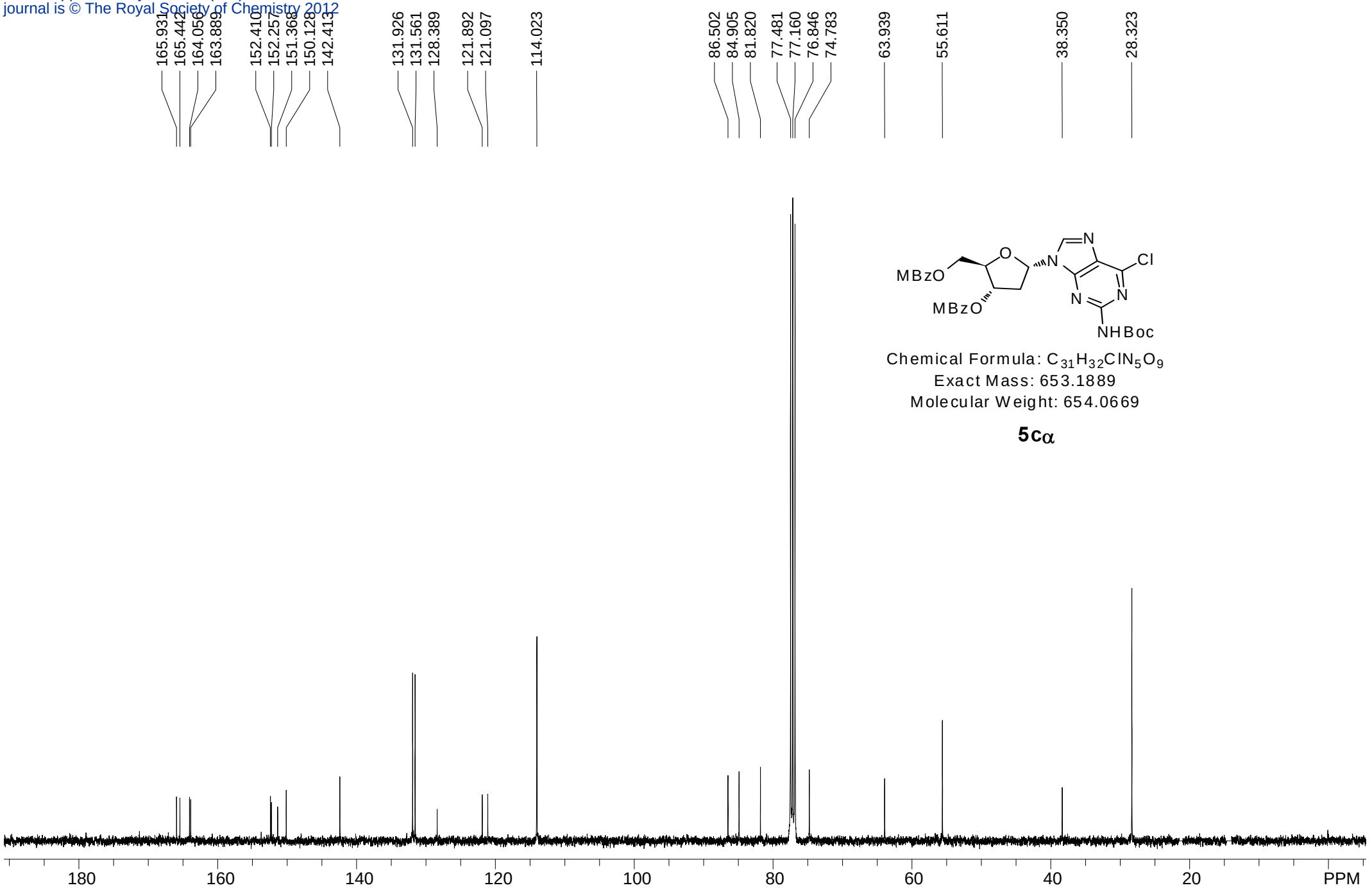






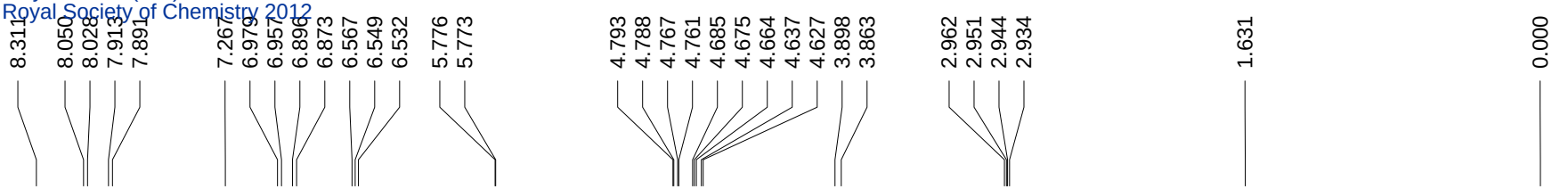
Chemical Formula: $C_{31}H_{32}ClN_5O_9$
Exact Mass: 653.1889
Molecular Weight: 654.0669

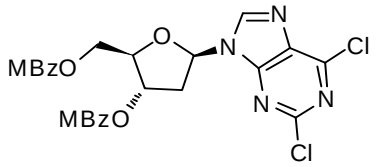
5cα



Chemical Formula: $C_{31}H_{32}ClN_5O_9$
Exact Mass: 653.1889
Molecular Weight: 654.0669

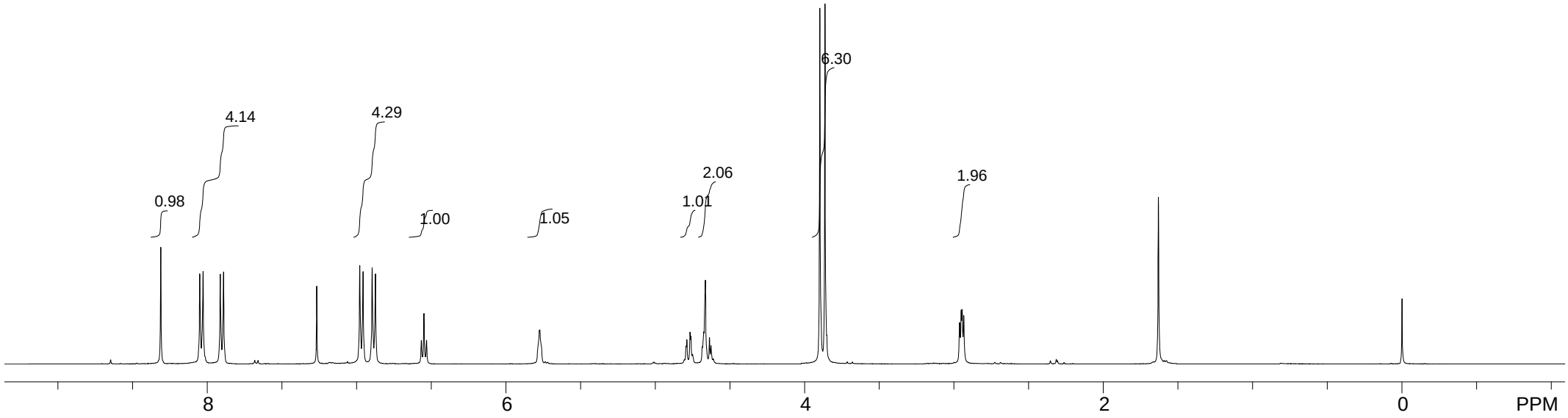
5cα

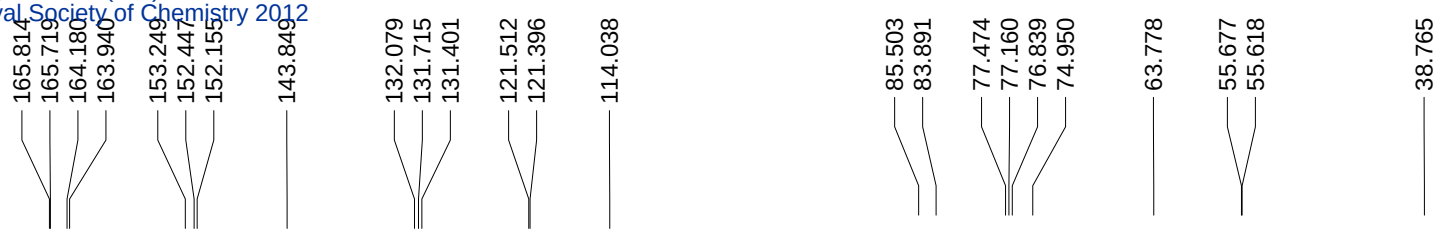


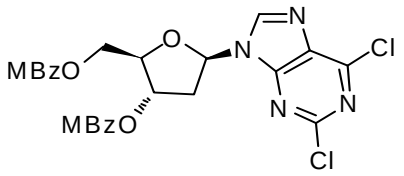


Chemical Formula: $C_{26}H_{22}Cl_2N_4O_7$
Exact Mass: 572.0866
Molecular Weight: 573.3815

5dβ

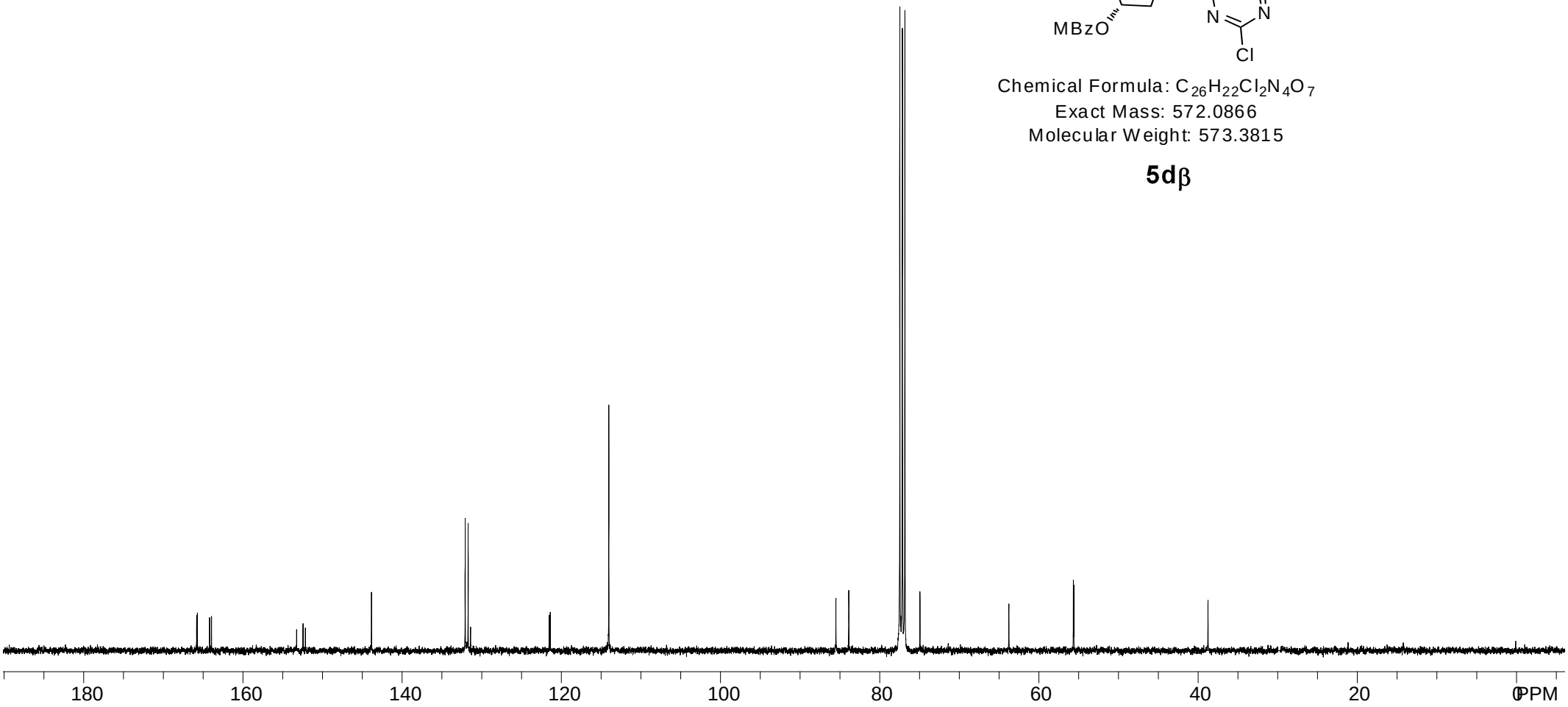


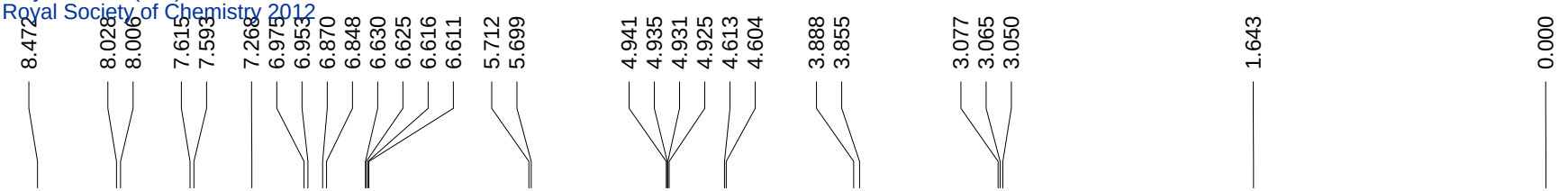


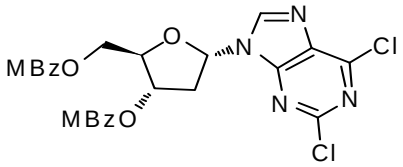


Chemical Formula: $C_{26}H_{22}Cl_2N_4O_7$
Exact Mass: 572.0866
Molecular Weight: 573.3815

5dβ

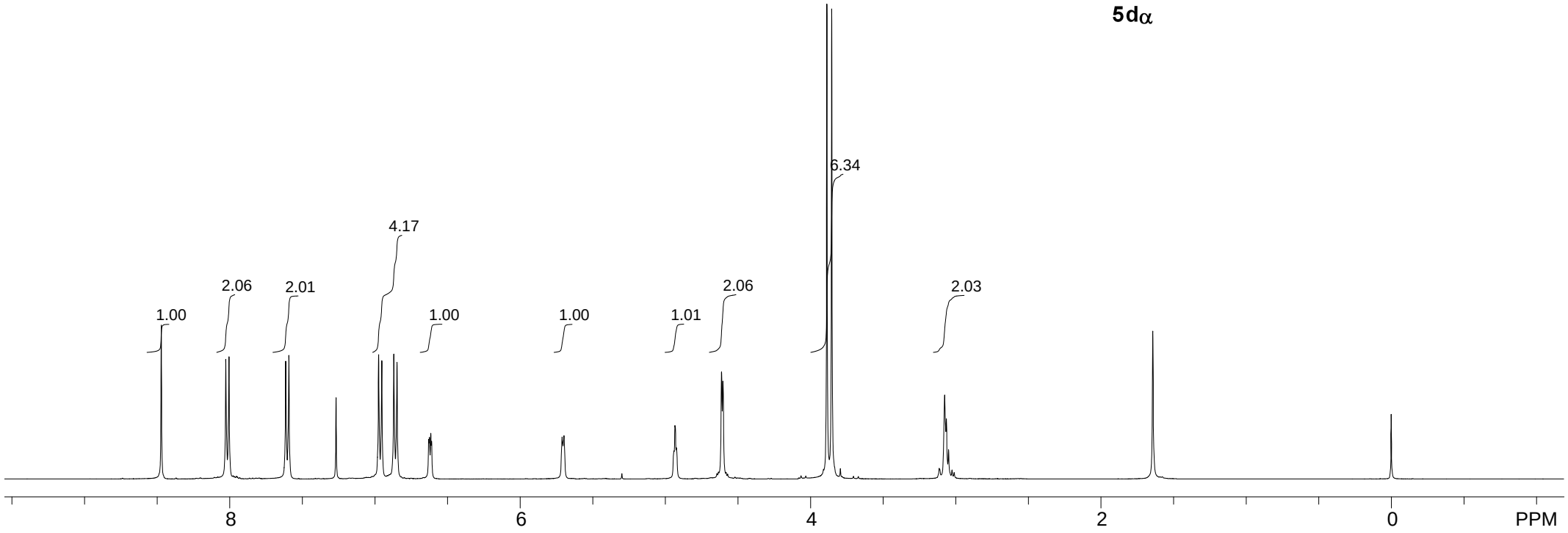


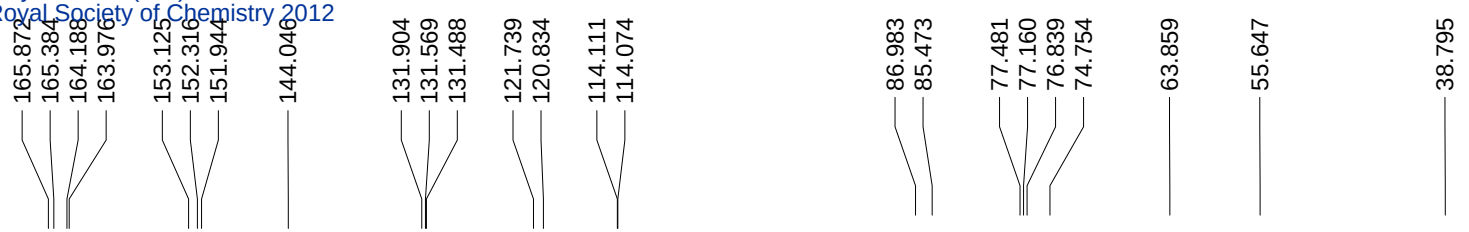


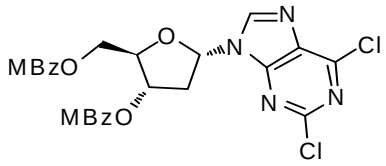


Chemical Formula: $C_{26}H_{22}Cl_2N_4O_7$
Exact Mass: 572.0866
Molecular Weight: 573.3815

5dα

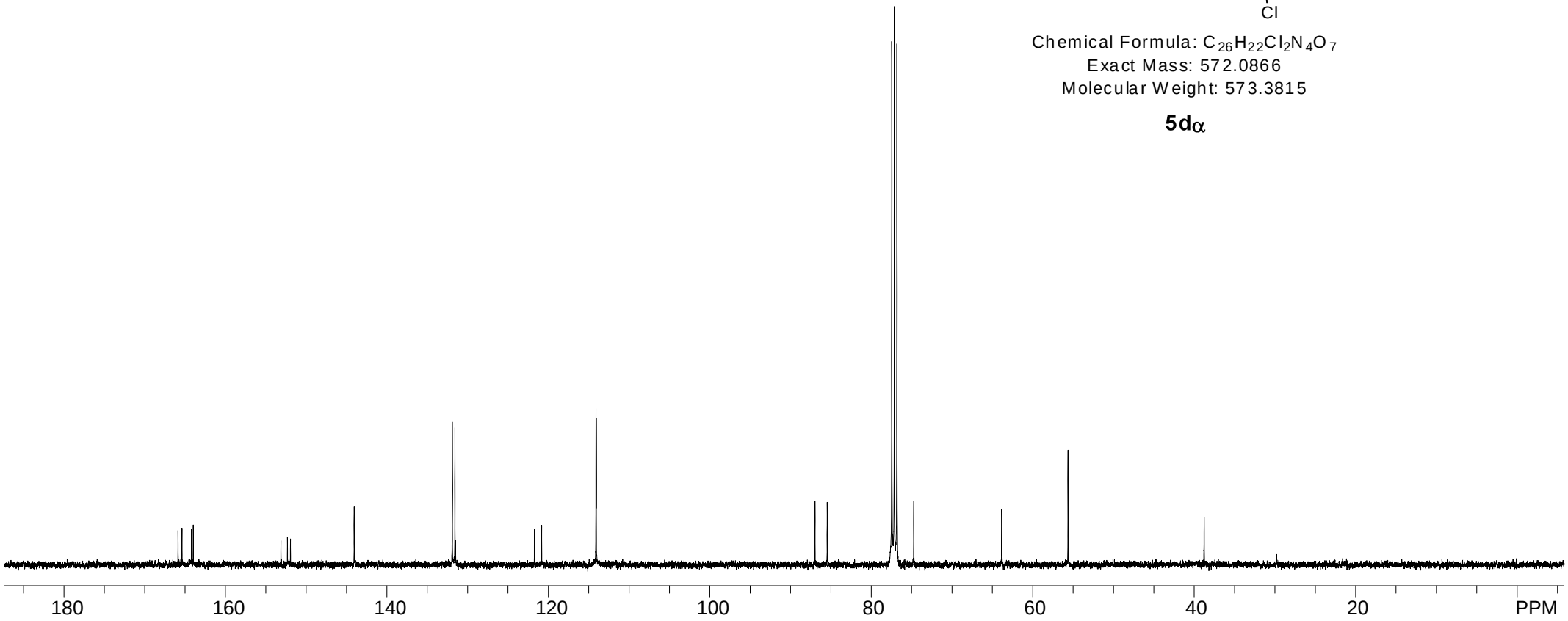


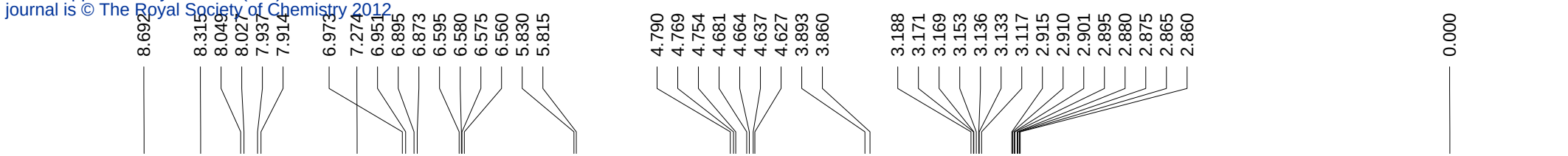


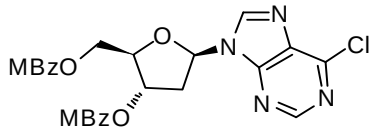


Chemical Formula: $C_{26}H_{22}Cl_2N_4O_7$
Exact Mass: 572.0866
Molecular Weight: 573.3815

5dα

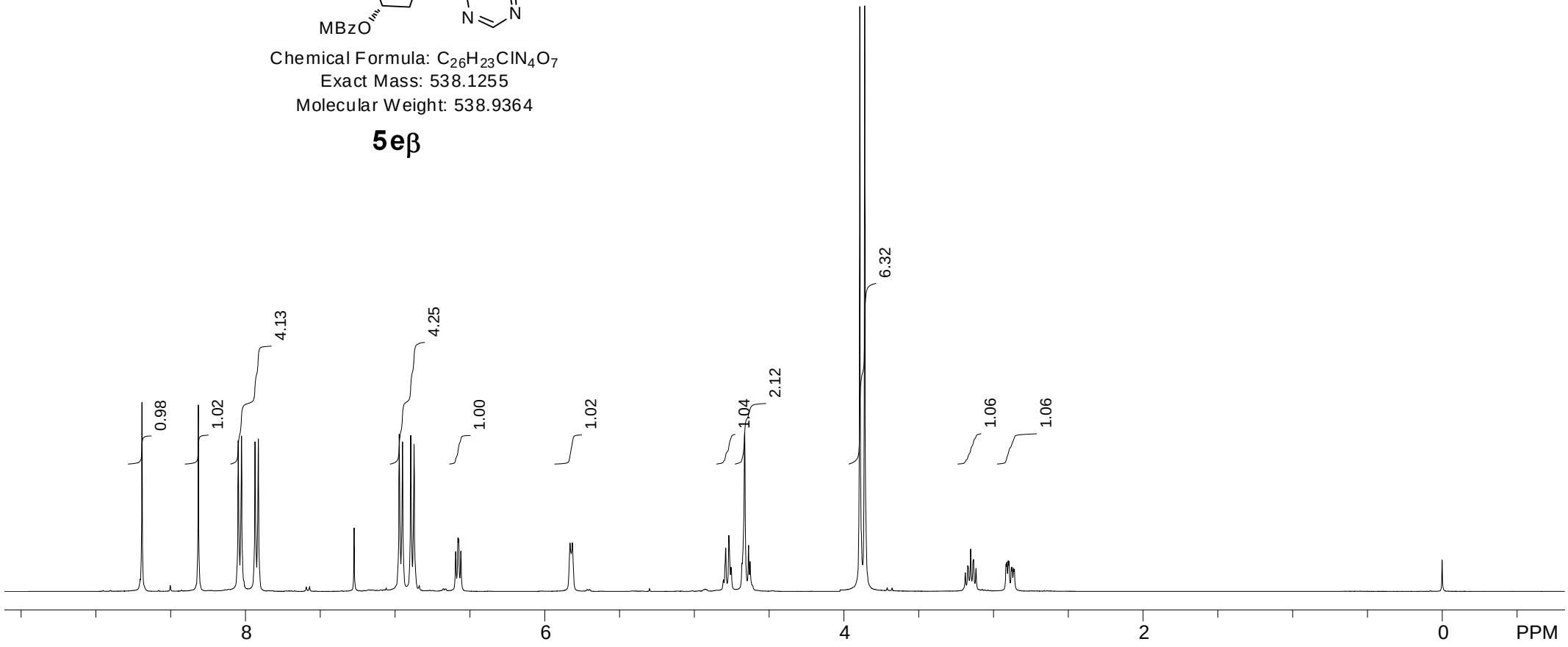


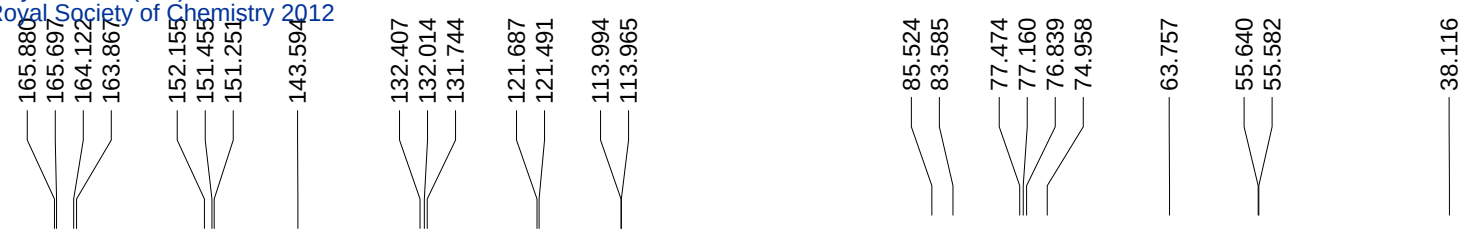


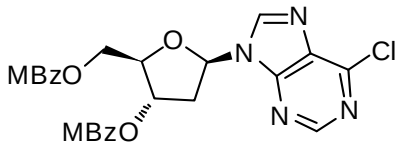


Chemical Formula: $C_{26}H_{23}ClN_4O_7$
Exact Mass: 538.1255
Molecular Weight: 538.9364

5eβ

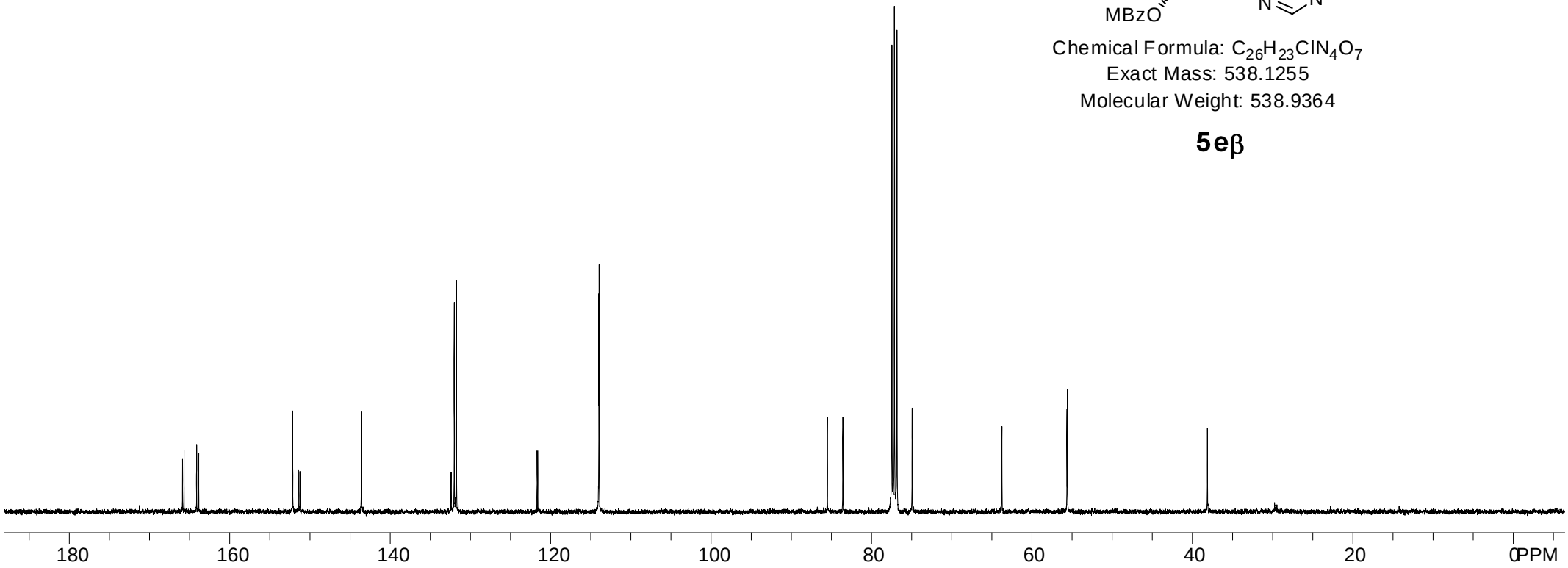


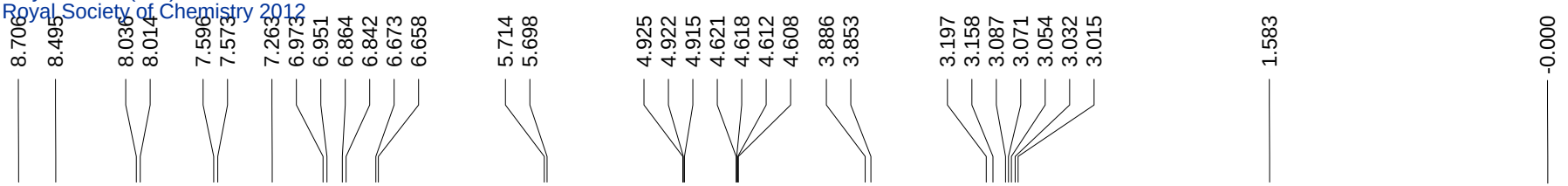


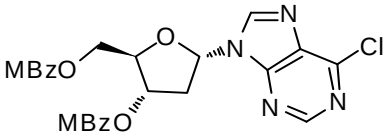


Chemical Formula: $C_{26}H_{23}ClN_4O_7$
Exact Mass: 538.1255
Molecular Weight: 538.9364

5eβ

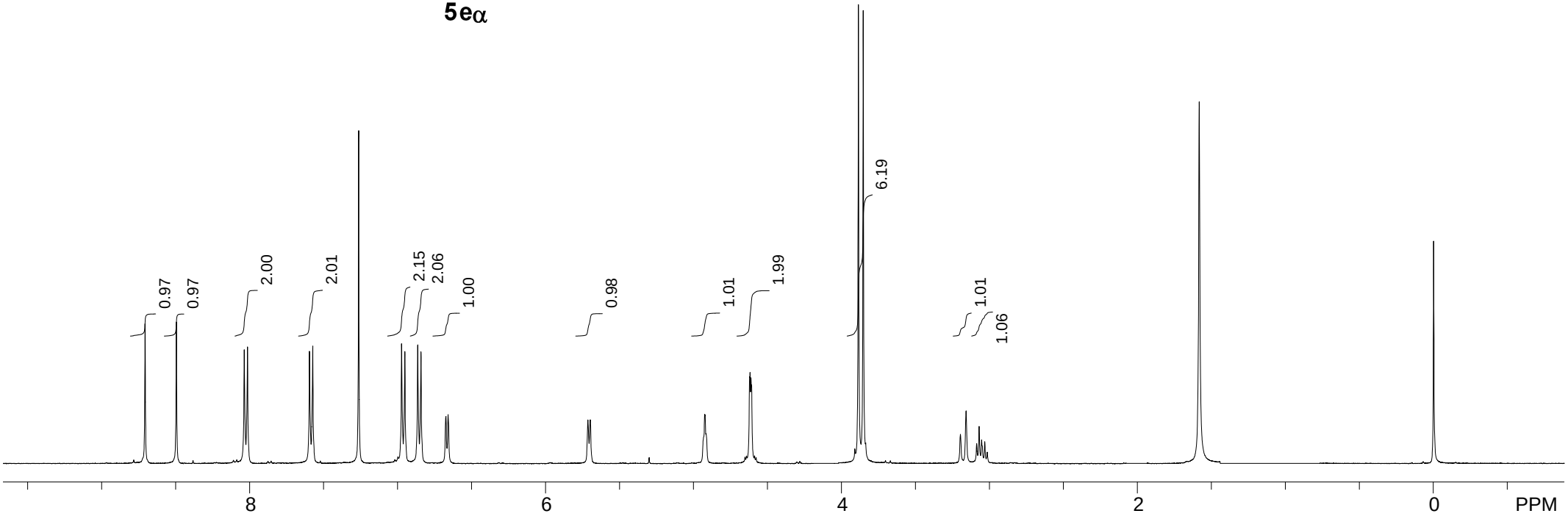


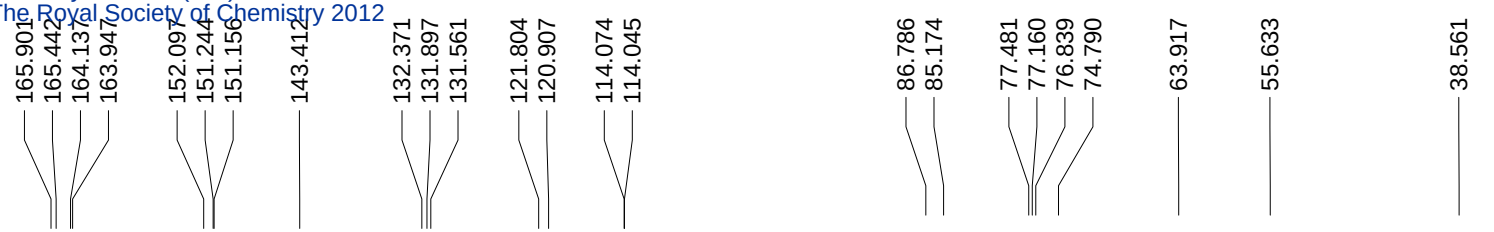


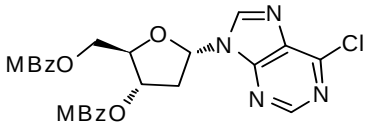


Chemical Formula: $C_{26}H_{23}ClN_4O_7$
Exact Mass: 538.1255
Molecular Weight: 538.9364

5eα

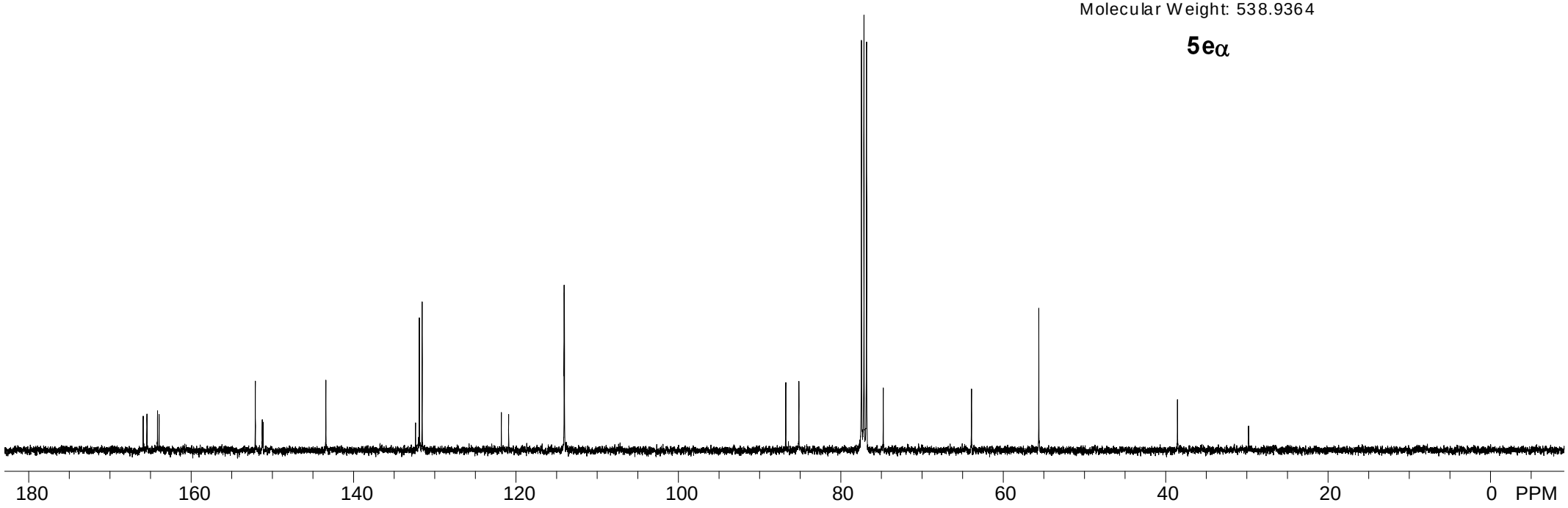


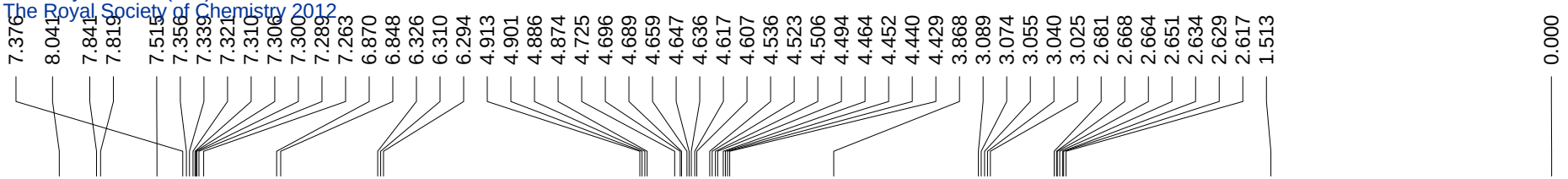


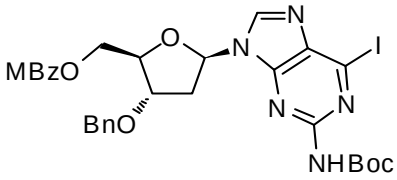


Chemical Formula: $C_{26}H_{23}ClN_4O_7$
Exact Mass: 538.1255
Molecular Weight: 538.9364

5eα

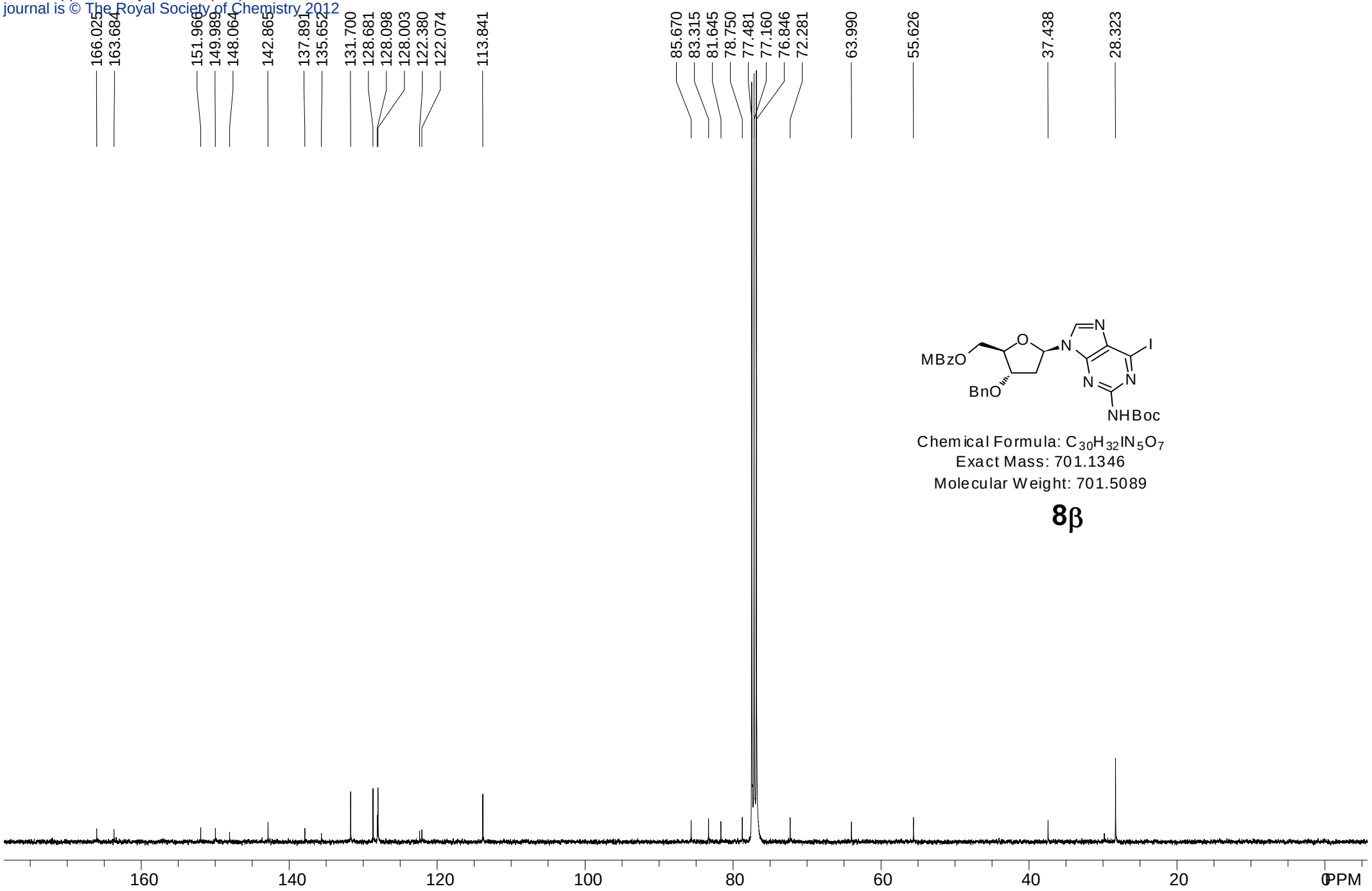






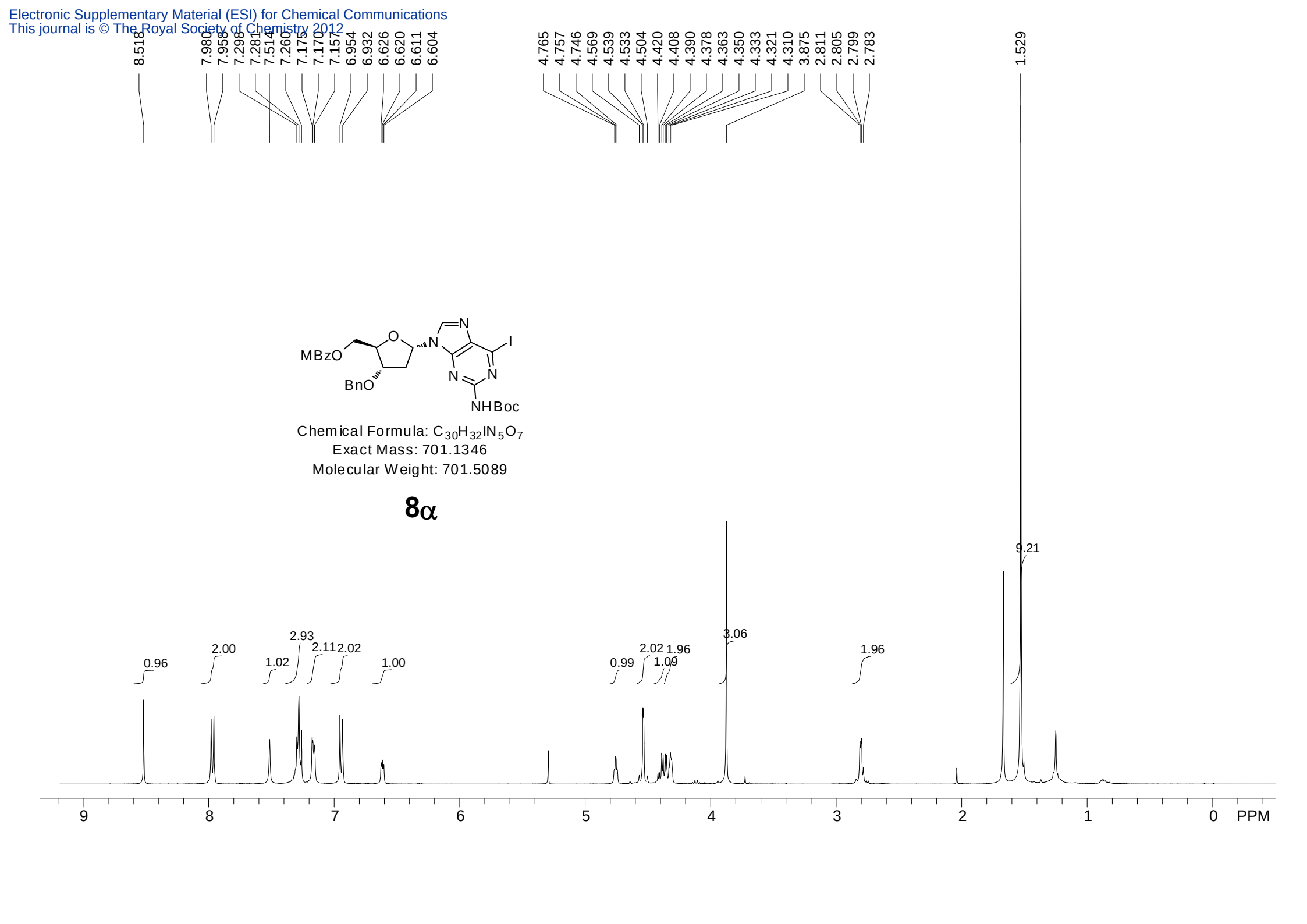
Chemical Formula: $C_{30}H_{32}IN_5O_7$
Exact Mass: 701.1346
Molecular Weight: 701.5089

8β



Chemical Formula: $C_{30}H_{32}IN_5O_7$
Exact Mass: 701.1346
Molecular Weight: 701.5089

8β



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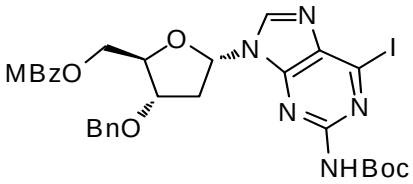
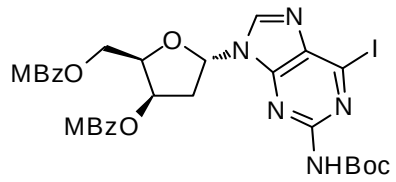


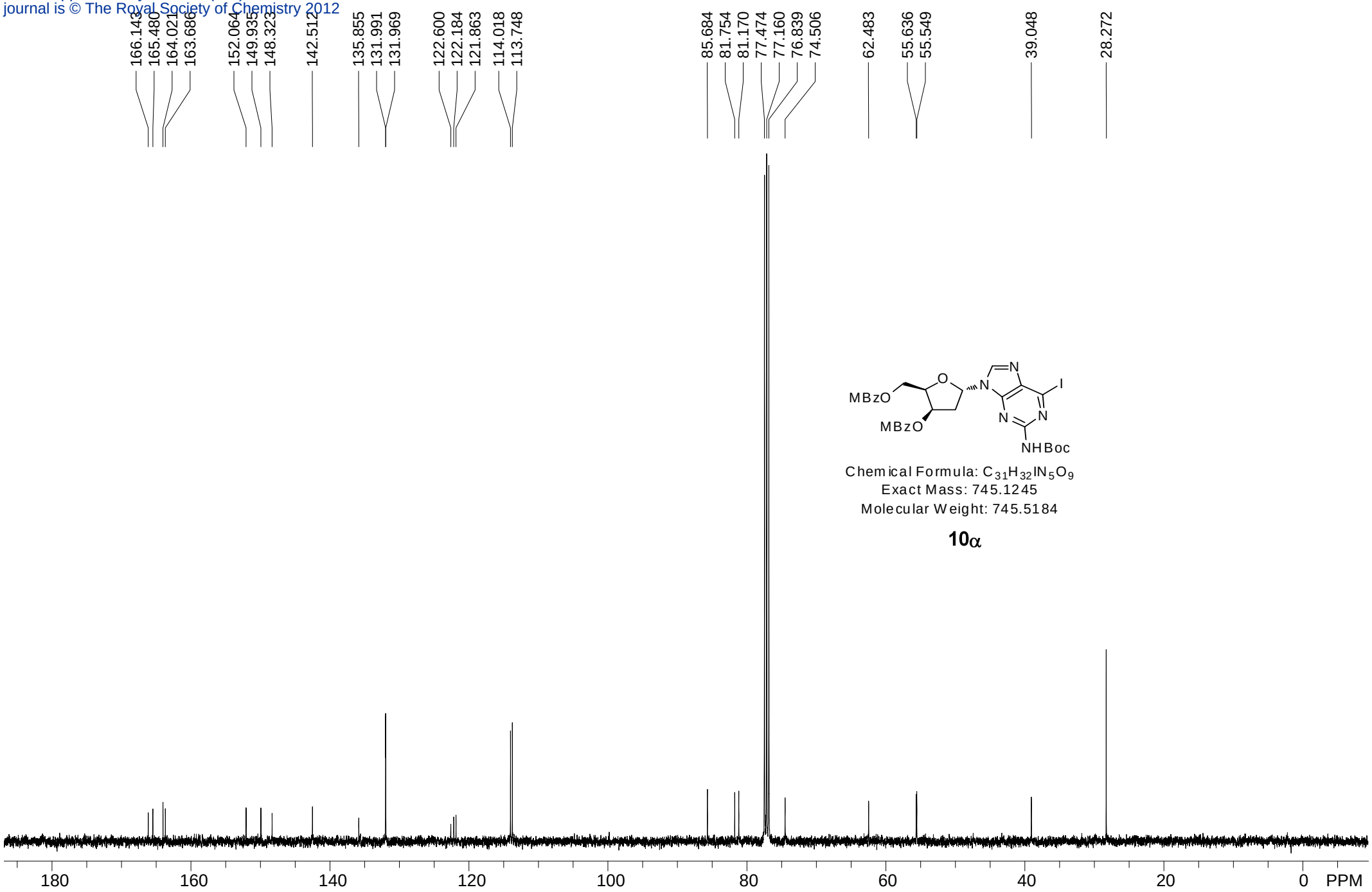
Chemical Formula: $C_{30}H_{32}IN_5O_7$
Exact Mass: 701.1346
Molecular Weight: 701.5089

8α



Chemical Formula: $C_{31}H_{32}IN_5O_9$
Exact Mass: 745.1245
Molecular Weight: 745.5184

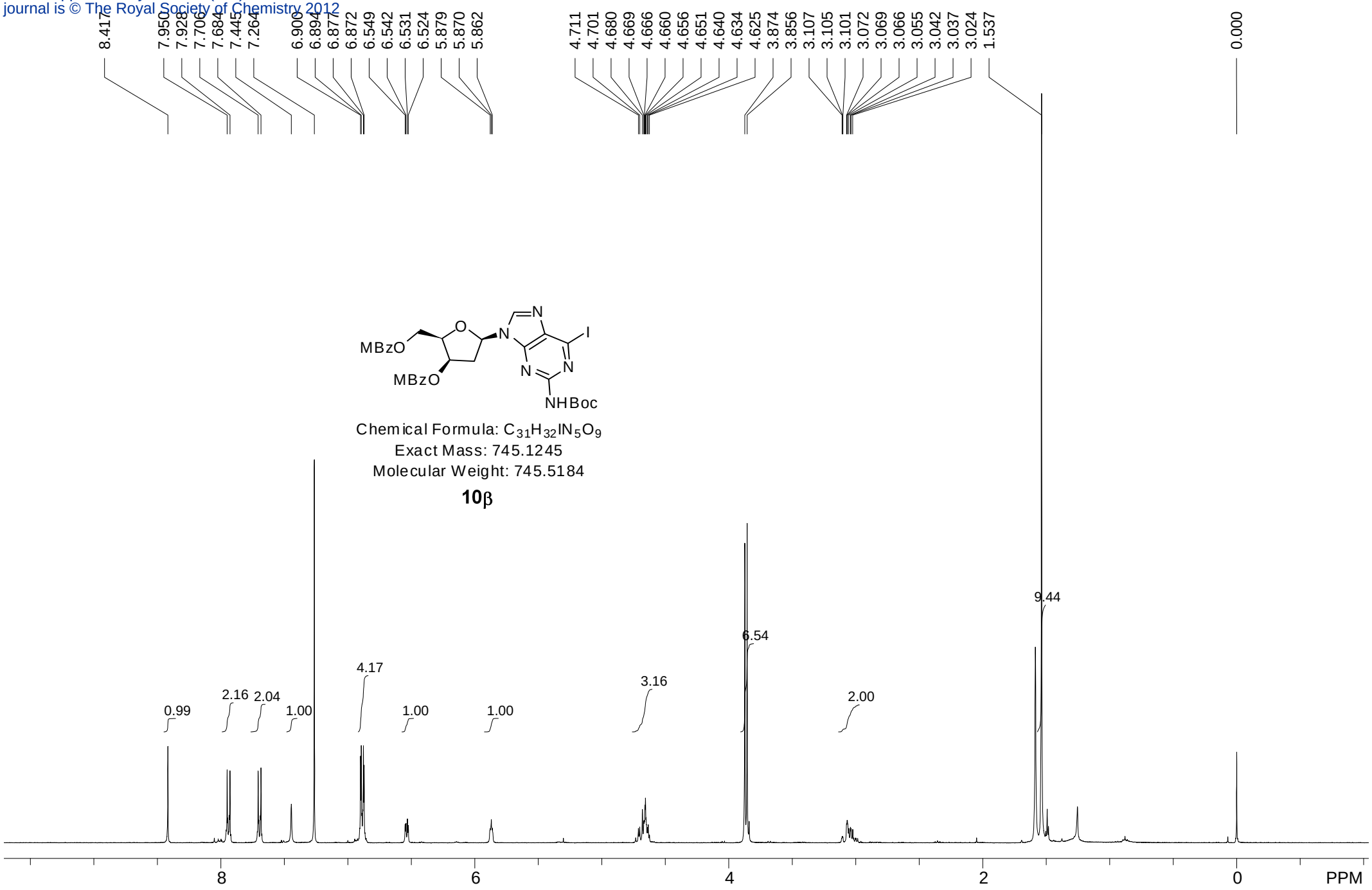
10α

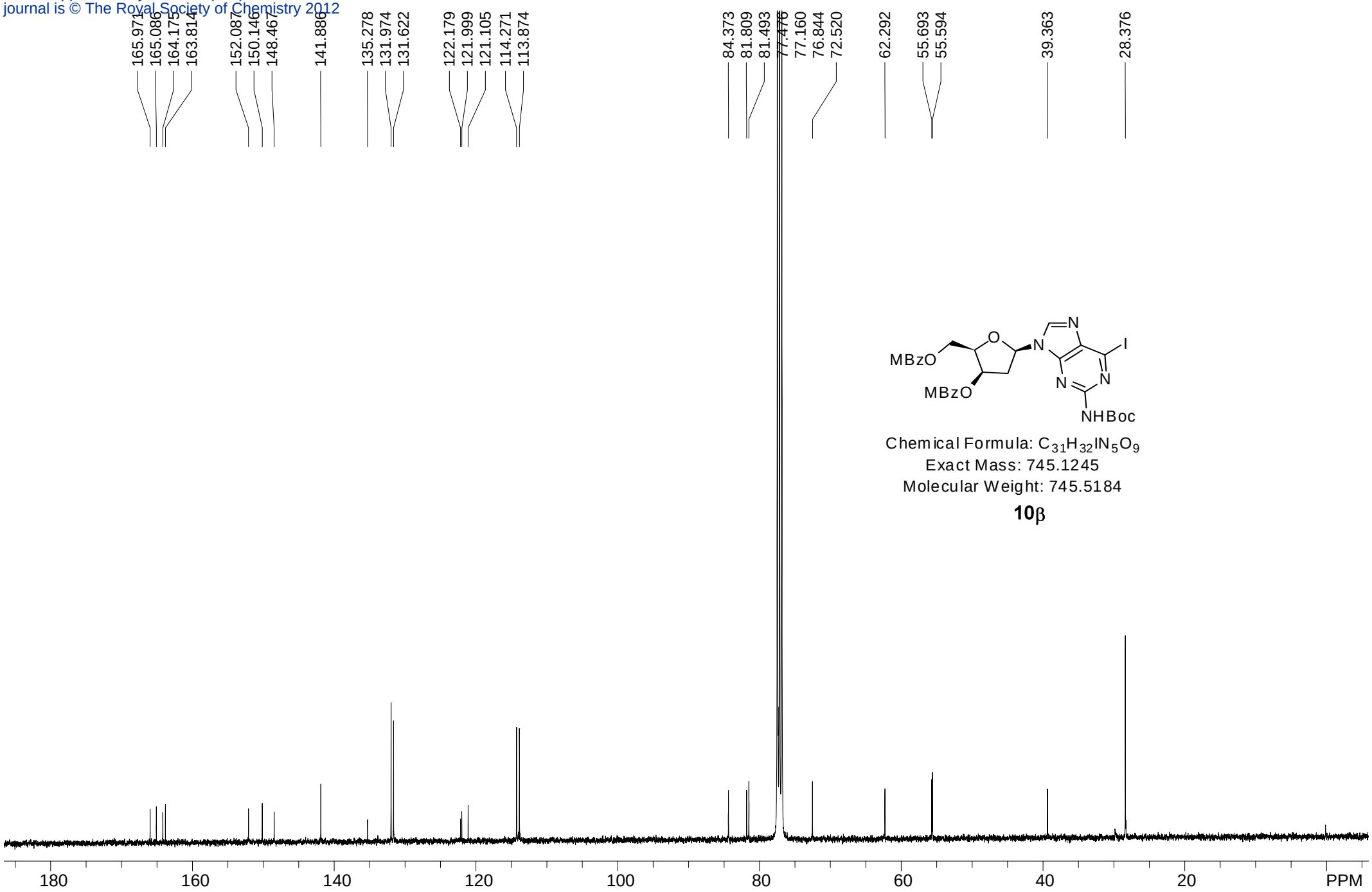


Chemical Formula: $C_{31}H_{32}IN_5O_9$
Exact Mass: 745.1245
Molecular Weight: 745.5184

10α

Electronic Supplementary Material (ESI) for Chemical Communications

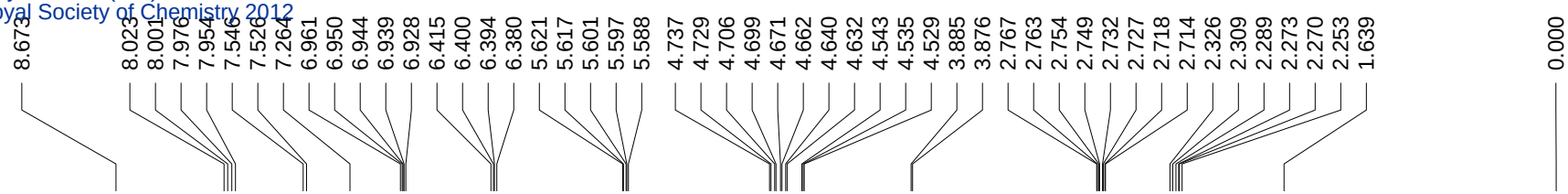


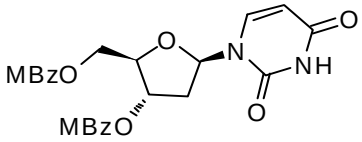


Chemical Formula: $C_{31}H_{32}IN_5O_9$
Exact Mass: 745.1245
Molecular Weight: 745.5184

10β

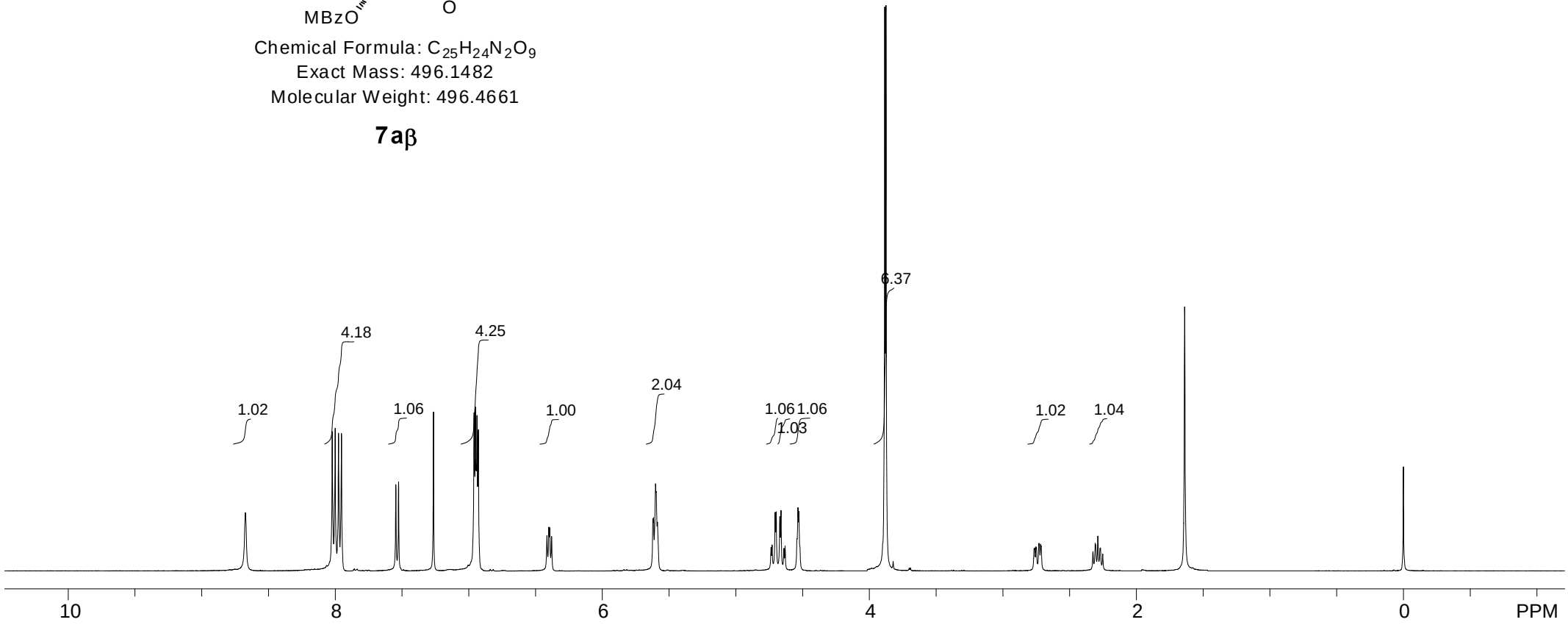
Electronic Supplementary Material (ESI) for Chemical Communications

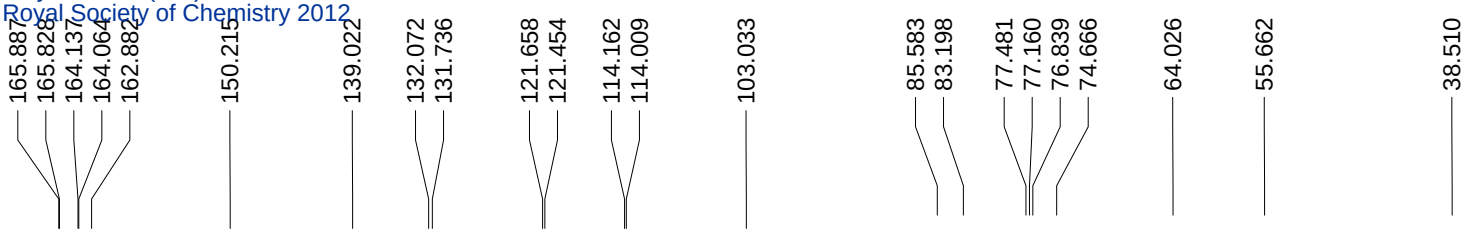


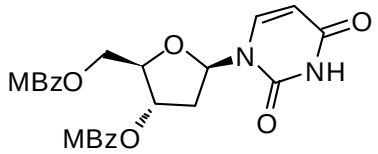


Chemical Formula: $C_{25}H_{24}N_2O_9$
Exact Mass: 496.1482
Molecular Weight: 496.4661

7aβ



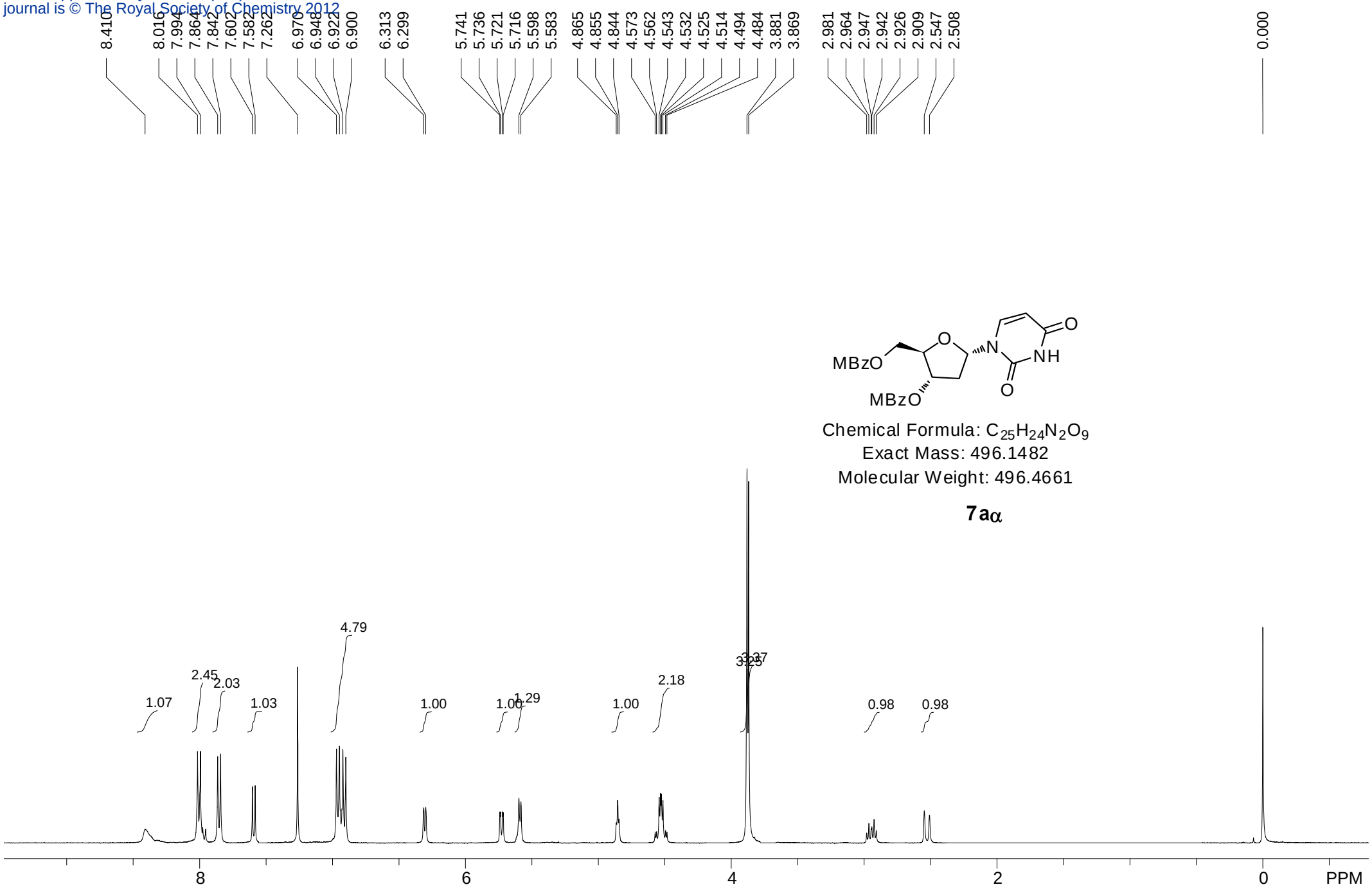


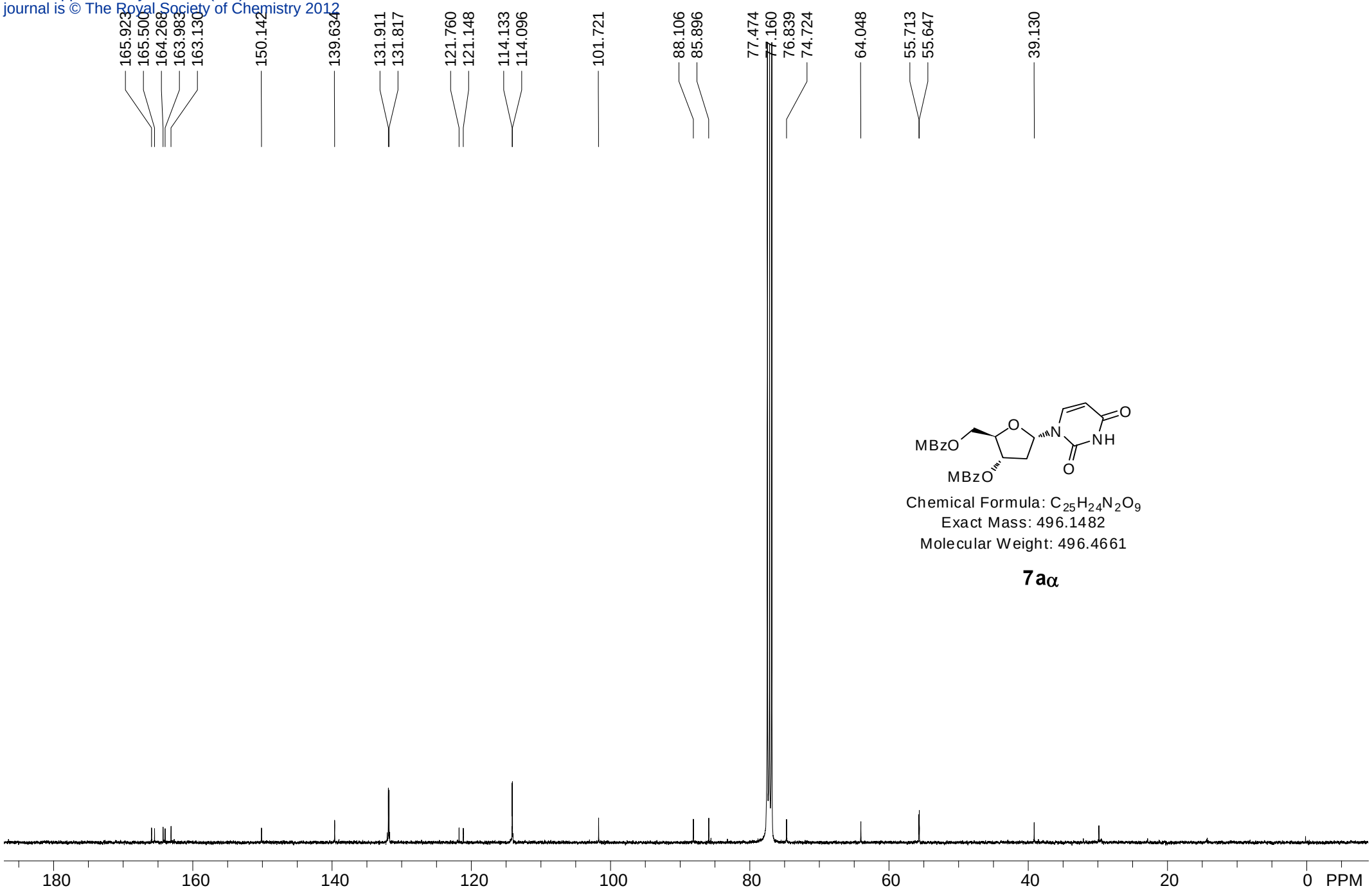


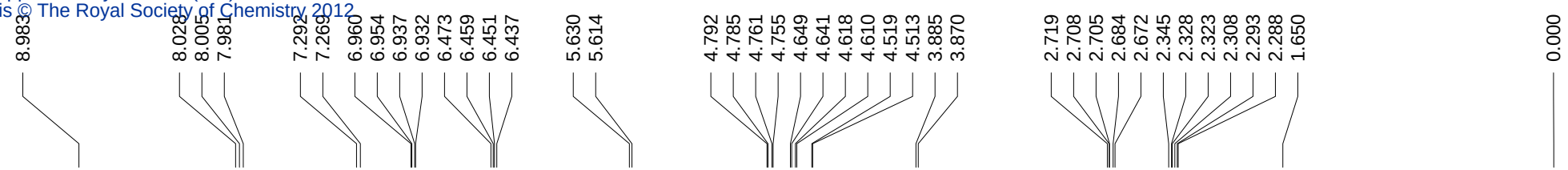
Chemical Formula: $C_{25}H_{24}N_2O_9$
Exact Mass: 496.1482
Molecular Weight: 496.4661

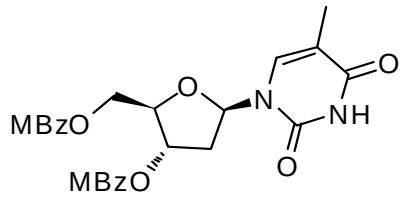
7aβ

Electronic Supplementary Material (ESI) for Chemical Communications



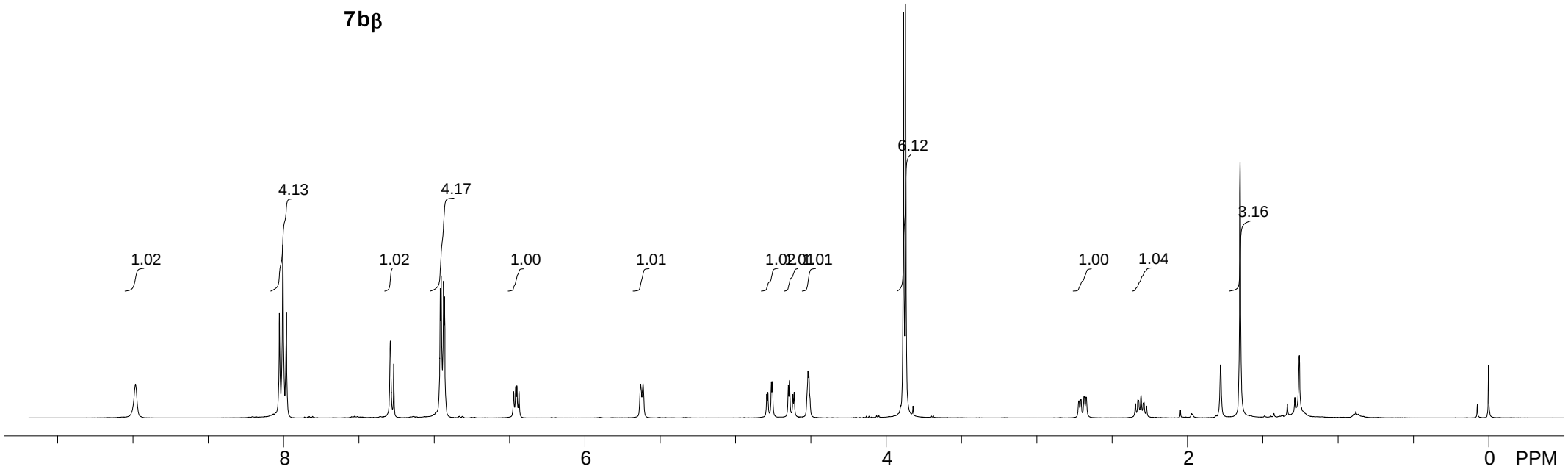


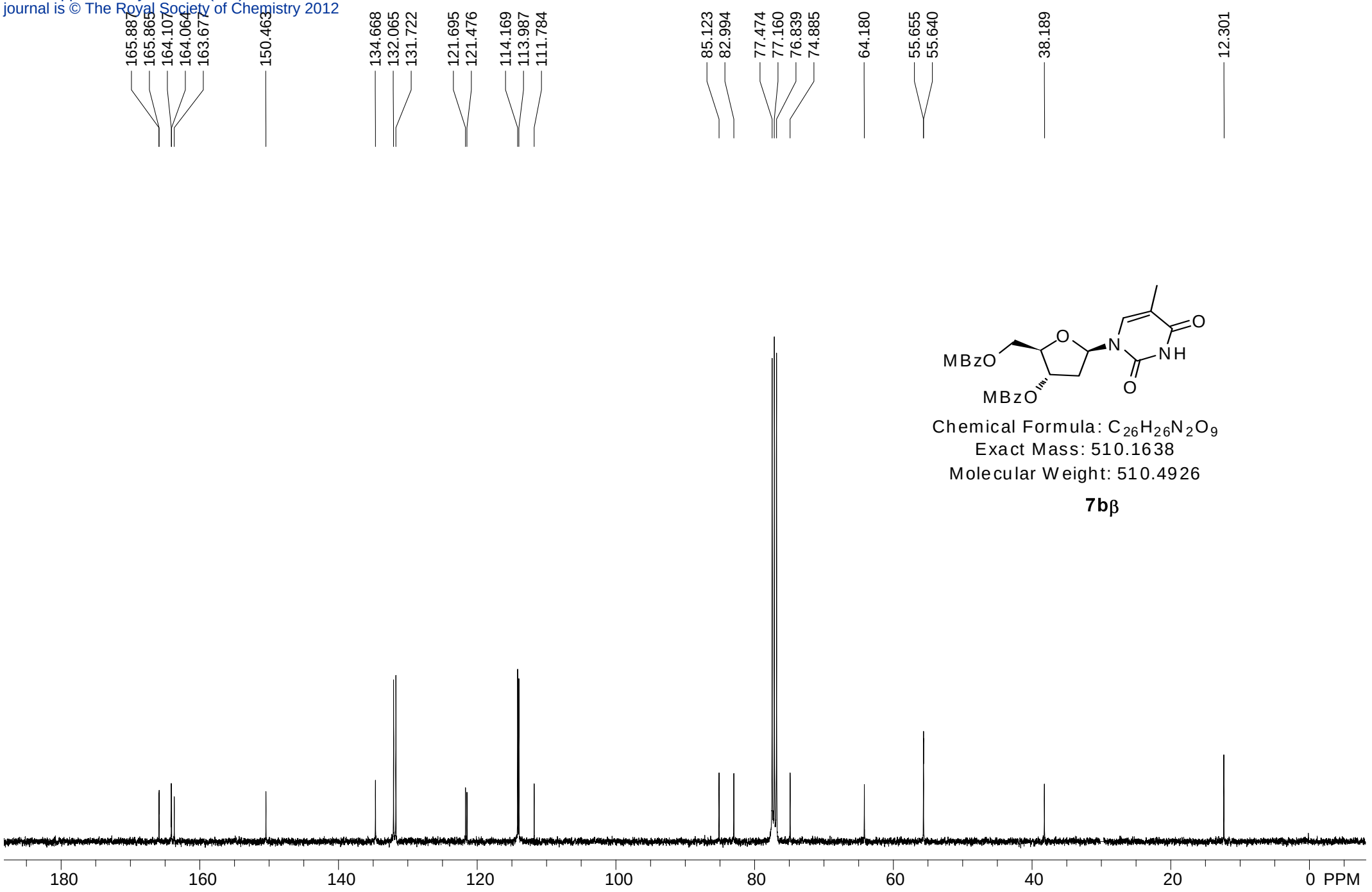


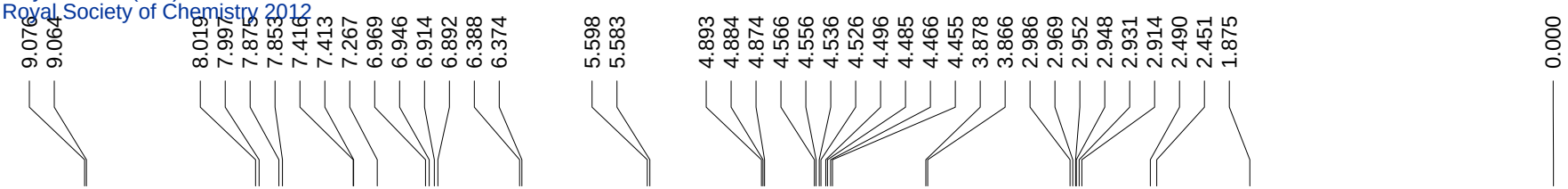


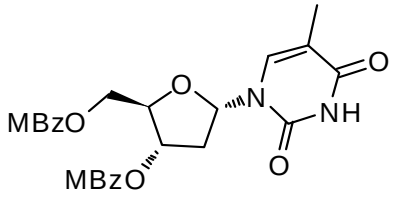
Chemical Formula: $C_{26}H_{26}N_2O_9$
Exact Mass: 510.1638
Molecular Weight: 510.4926

7bβ



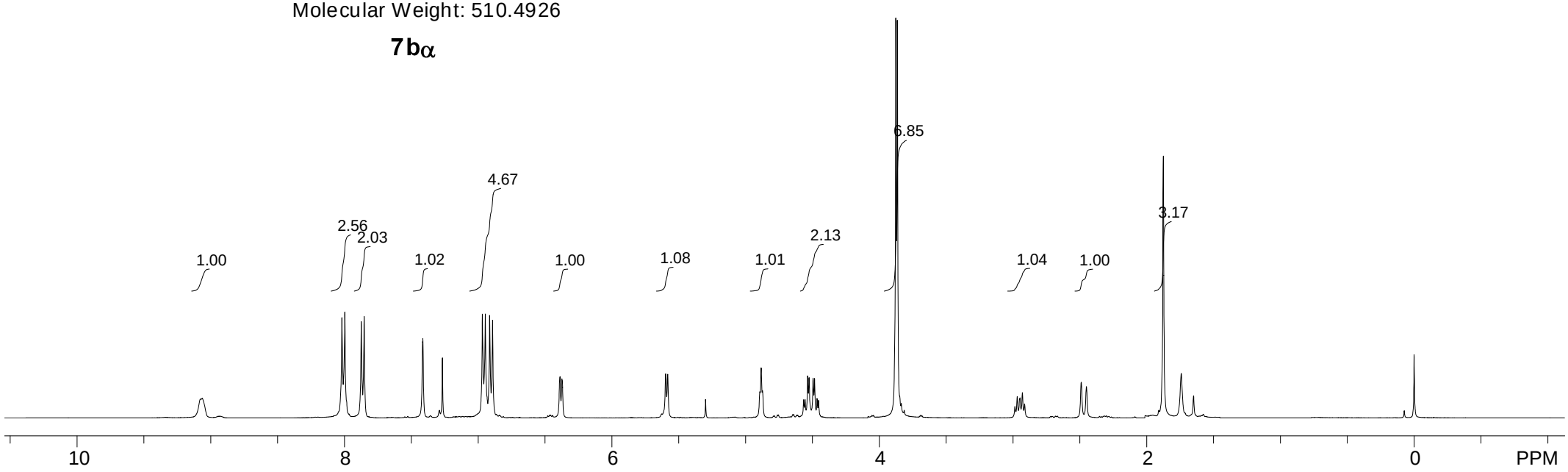


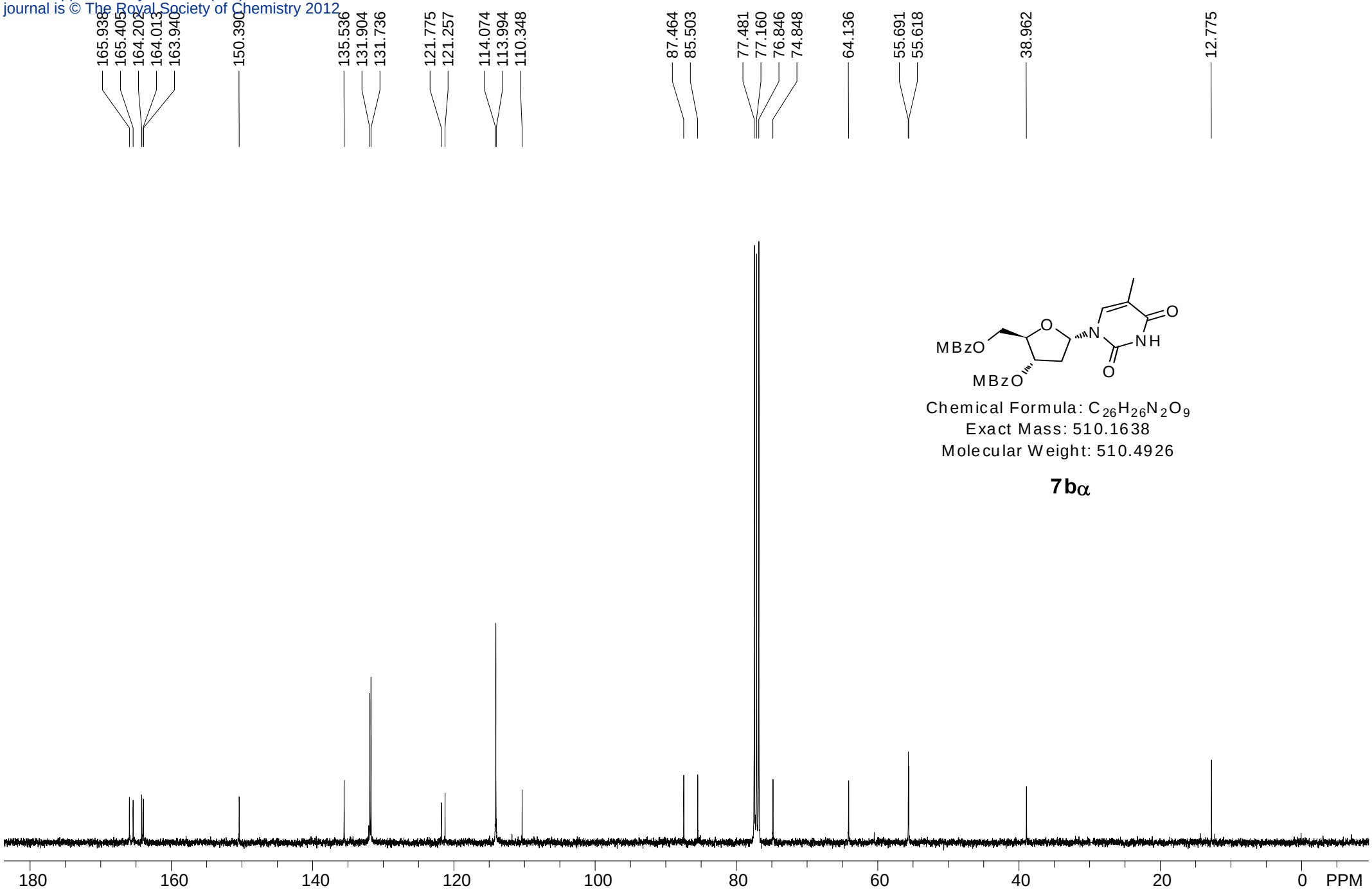


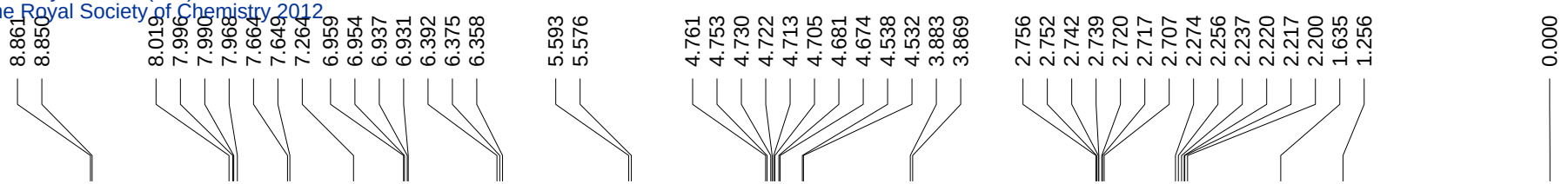


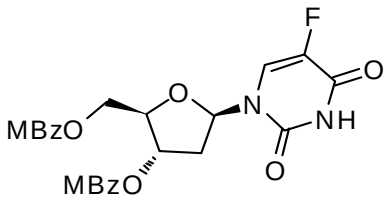
Chemical Formula: $C_{26}H_{26}N_2O_9$
Exact Mass: 510.1638
Molecular Weight: 510.4926

7bα



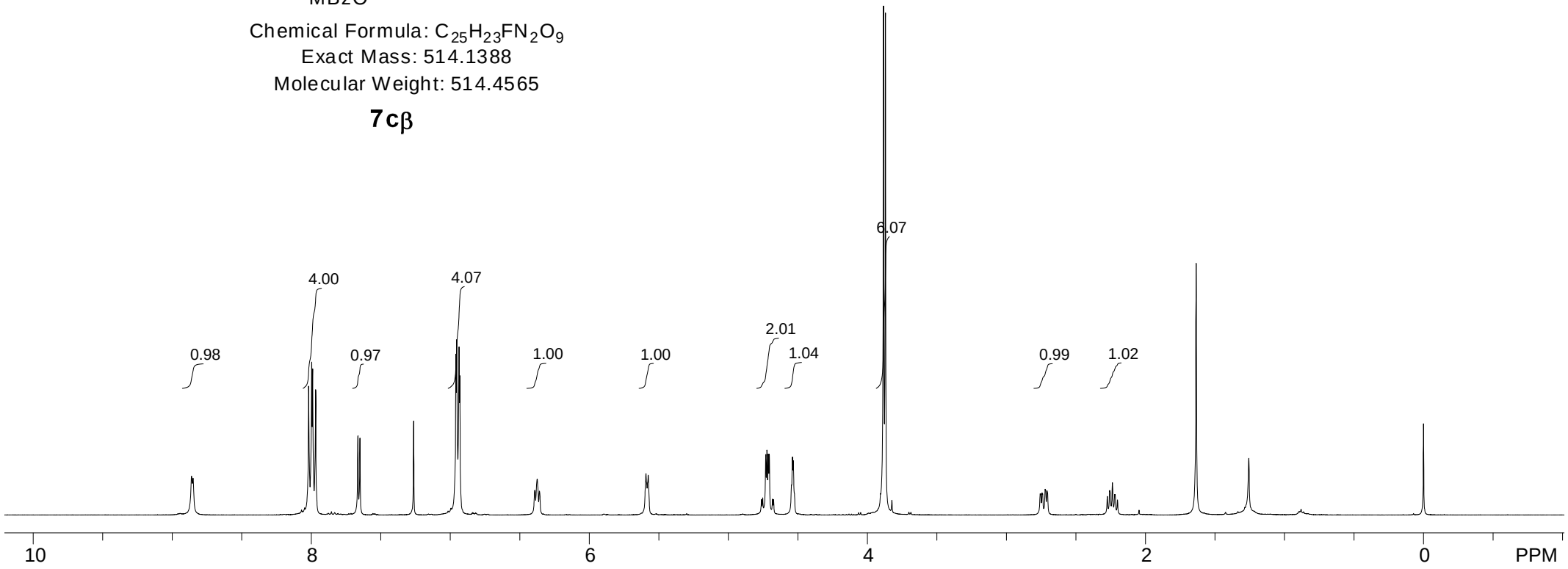


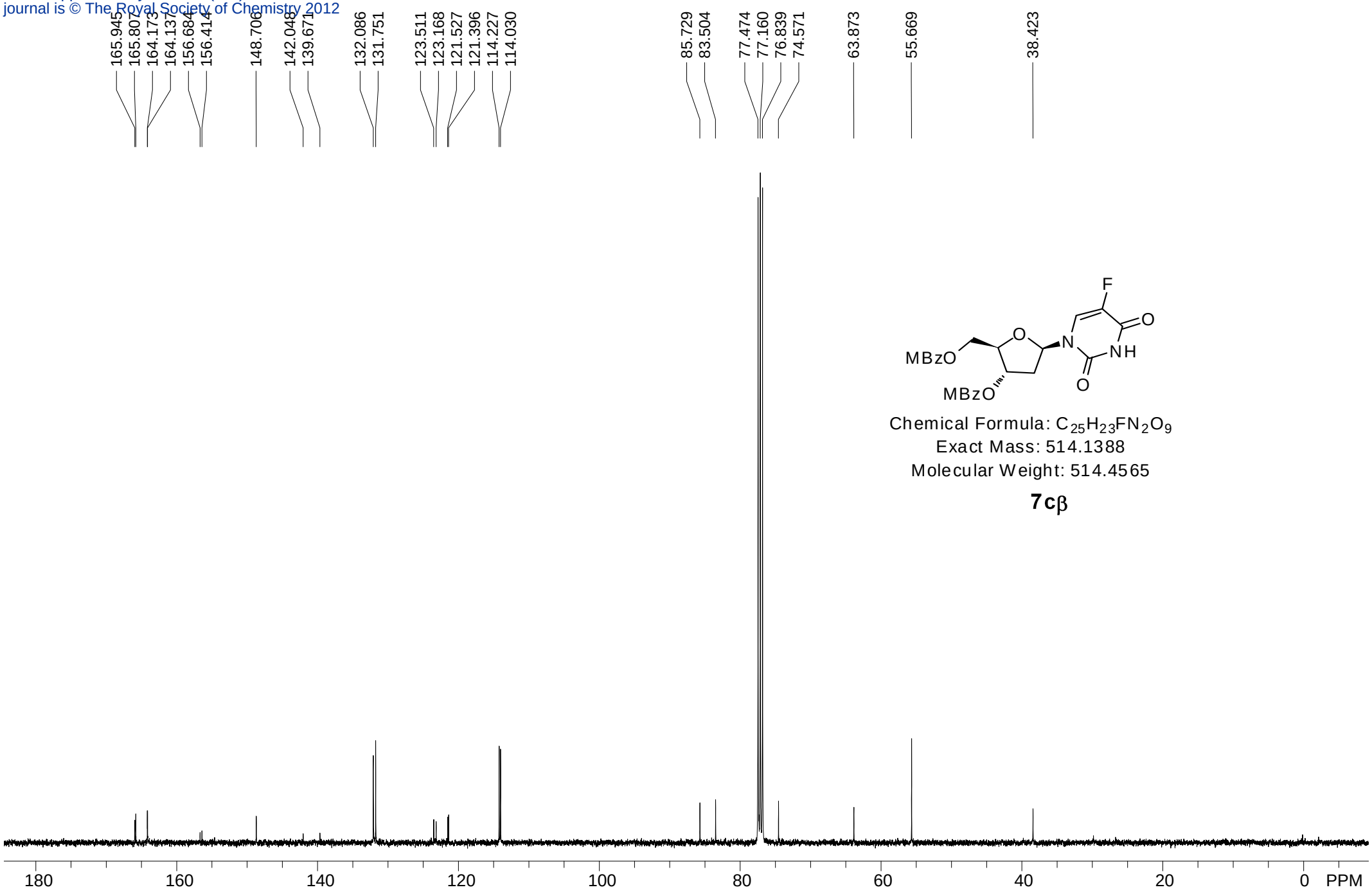




Chemical Formula: $C_{25}H_{23}FN_2O_9$
Exact Mass: 514.1388
Molecular Weight: 514.4565

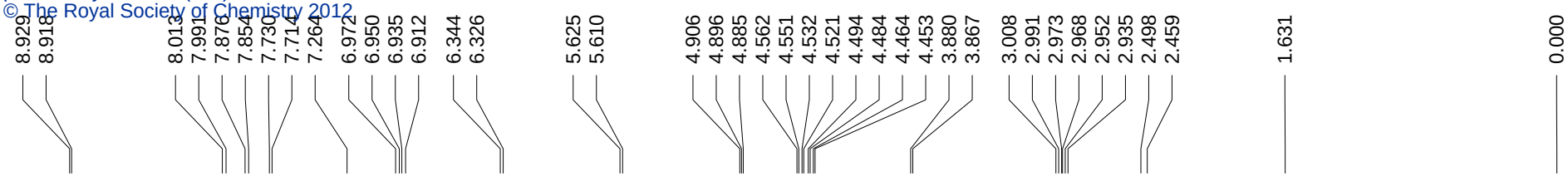
7cβ

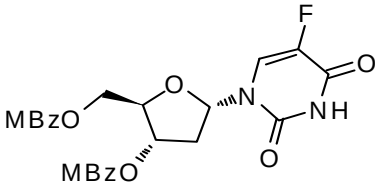




Chemical Formula: $C_{25}H_{23}FN_2O_9$
Exact Mass: 514.1388
Molecular Weight: 514.4565

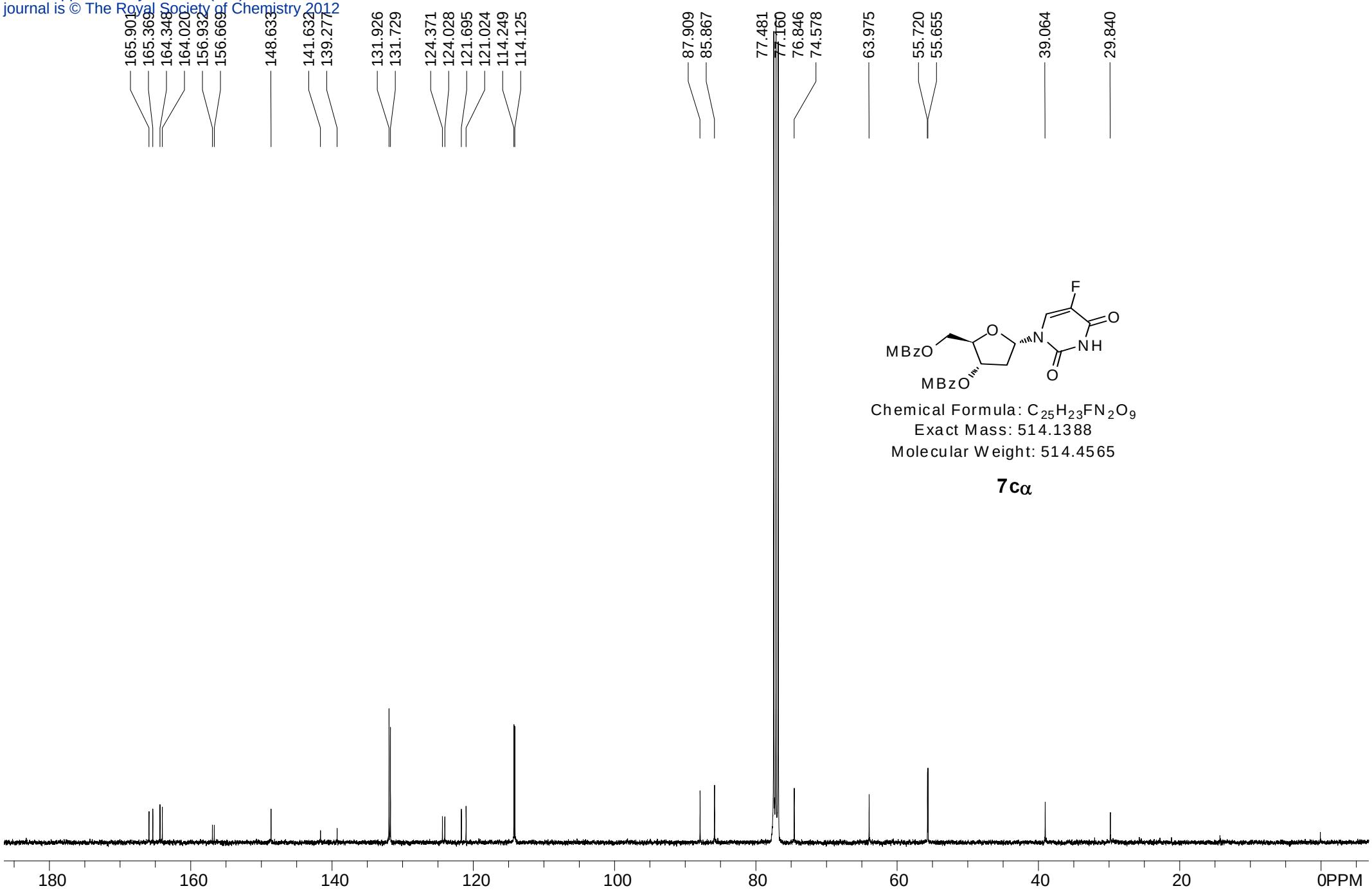
7cβ





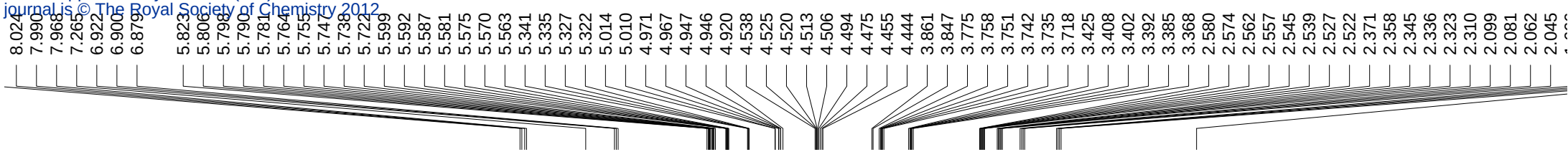
Chemical Formula: $C_{25}H_{23}FN_2O_9$
Exact Mass: 514.1388
Molecular Weight: 514.4565

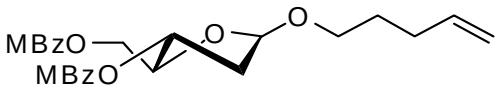
7cα



Chemical Formula: $C_{25}H_{23}FN_2O_9$
Exact Mass: 514.1388
Molecular Weight: 514.4565

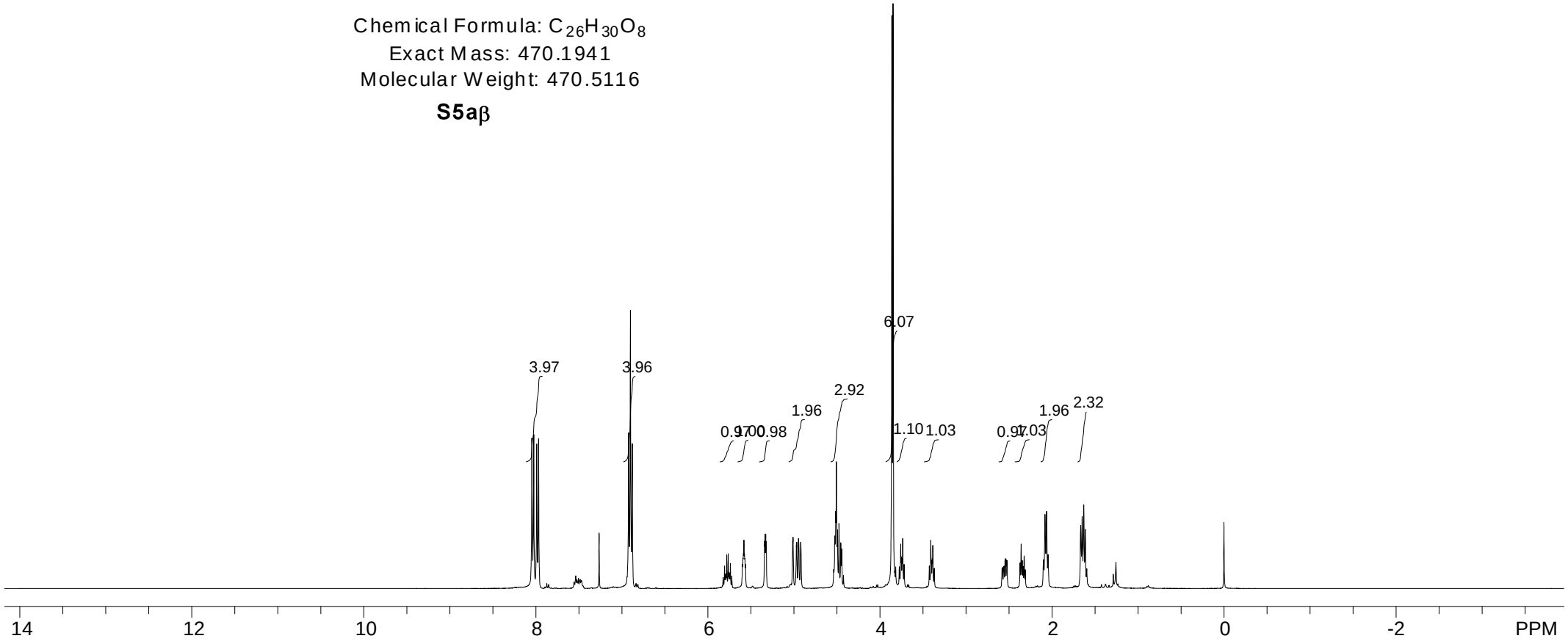
7cα

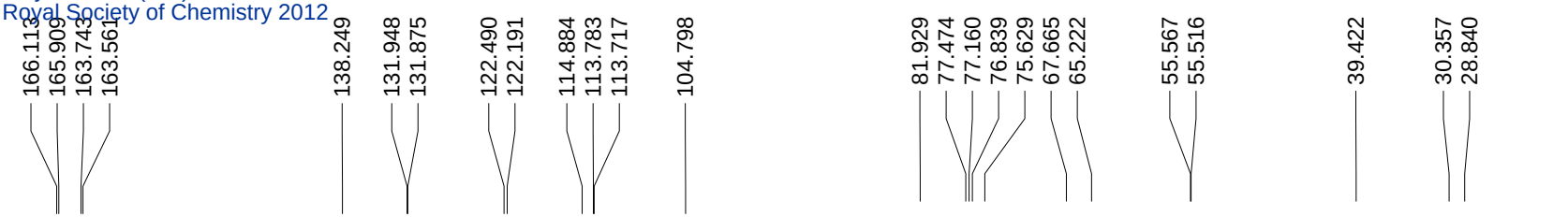


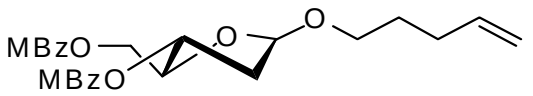


Chemical Formula: $C_{26}H_{30}O_8$
Exact Mass: 470.1941
Molecular Weight: 470.5116

S5aβ

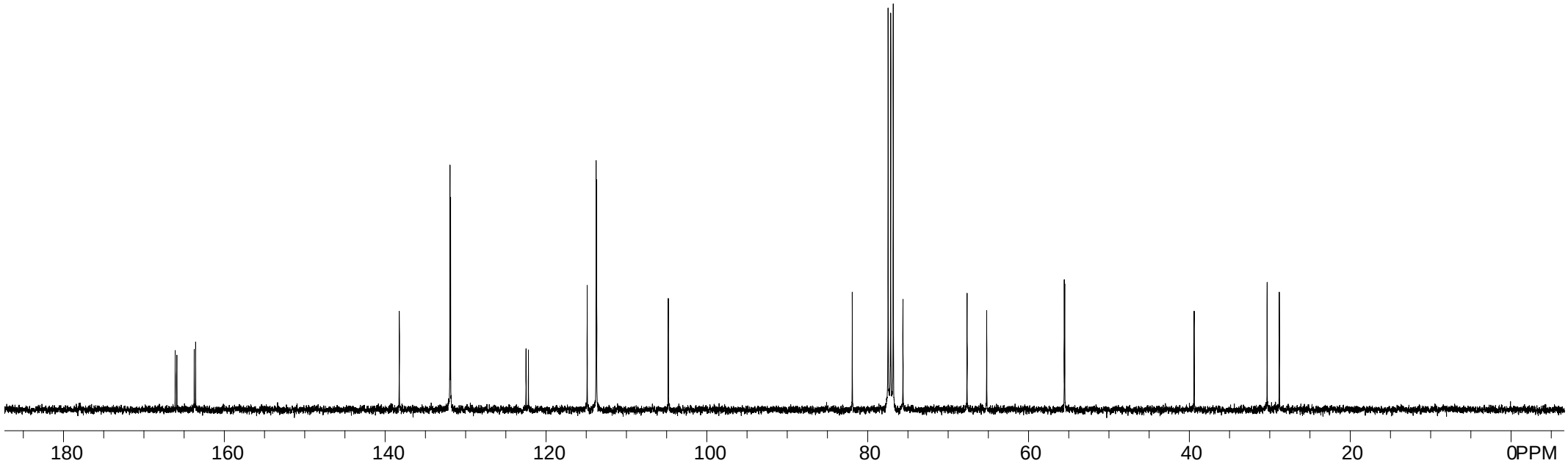


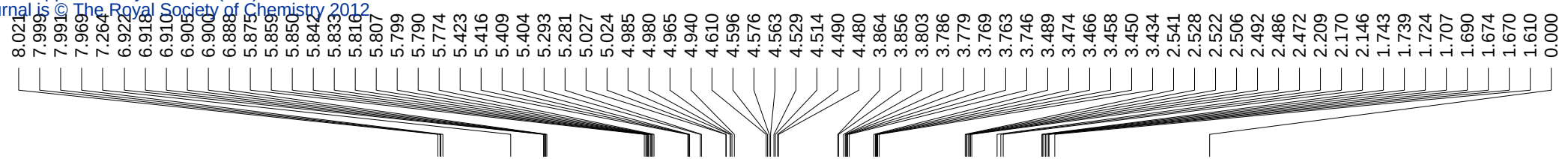




Chemical Formula: $C_{26}H_{30}O_8$
Exact Mass: 470.1941
Molecular Weight: 470.5116

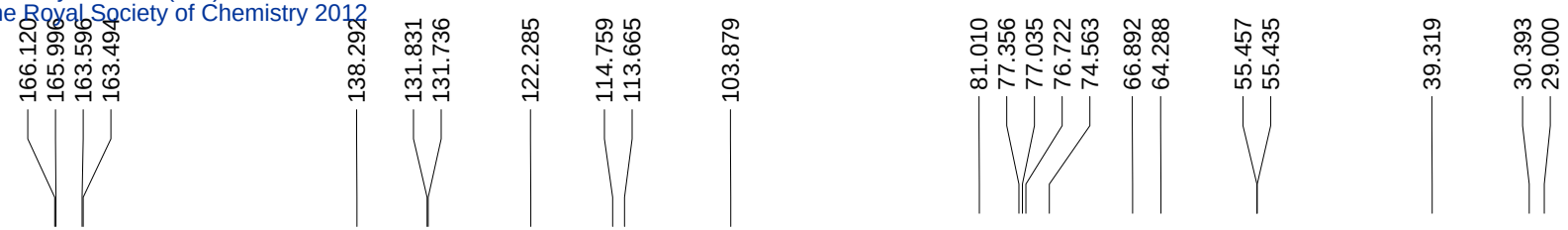
S5aβ





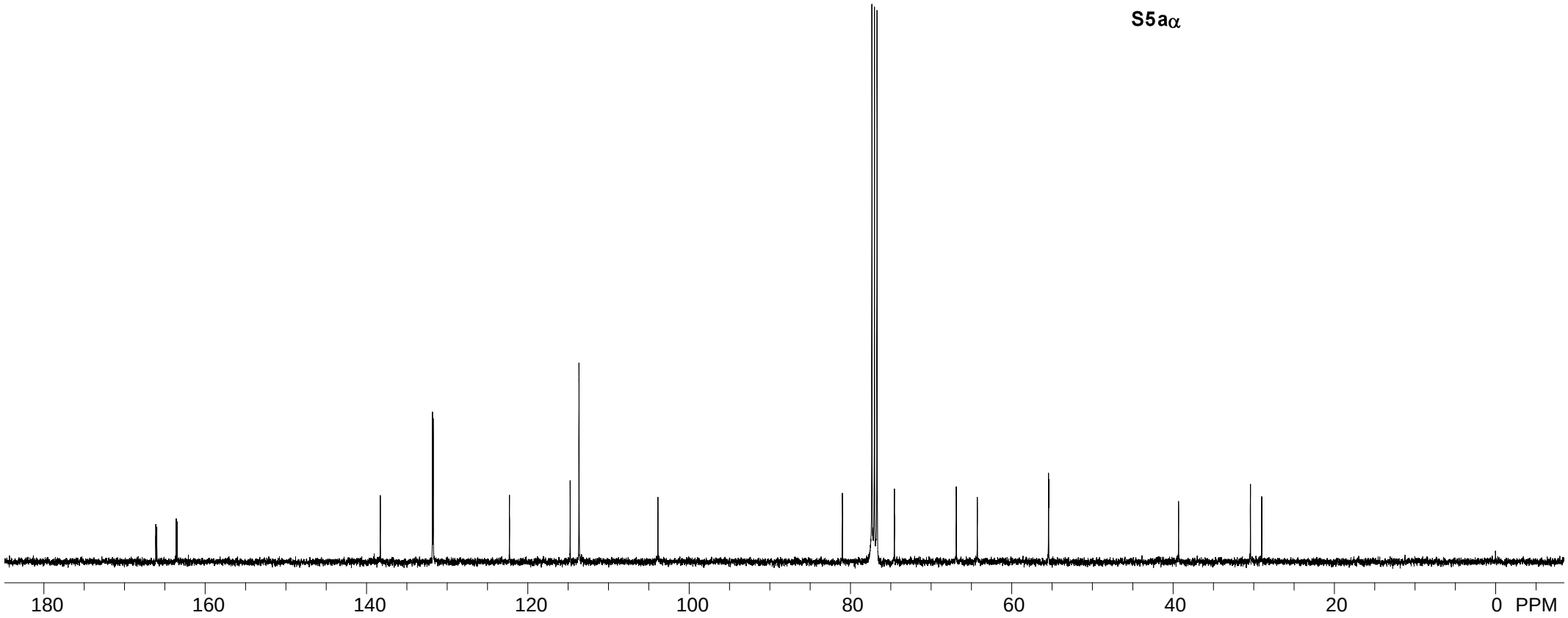
Chemical Formula: $C_{26}H_{30}O_8$
Exact Mass: 470.1941
Molecular Weight: 470.5116

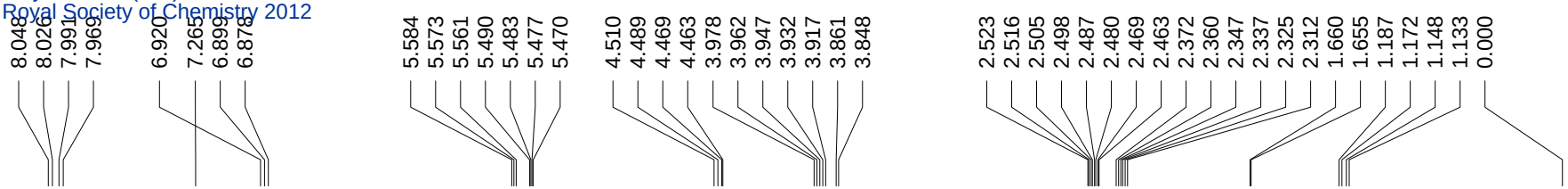
S5aα

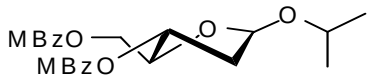


Chemical Formula: $C_{26}H_{30}O_8$
Exact Mass: 470.1941
Molecular Weight: 470.5116

S5aα

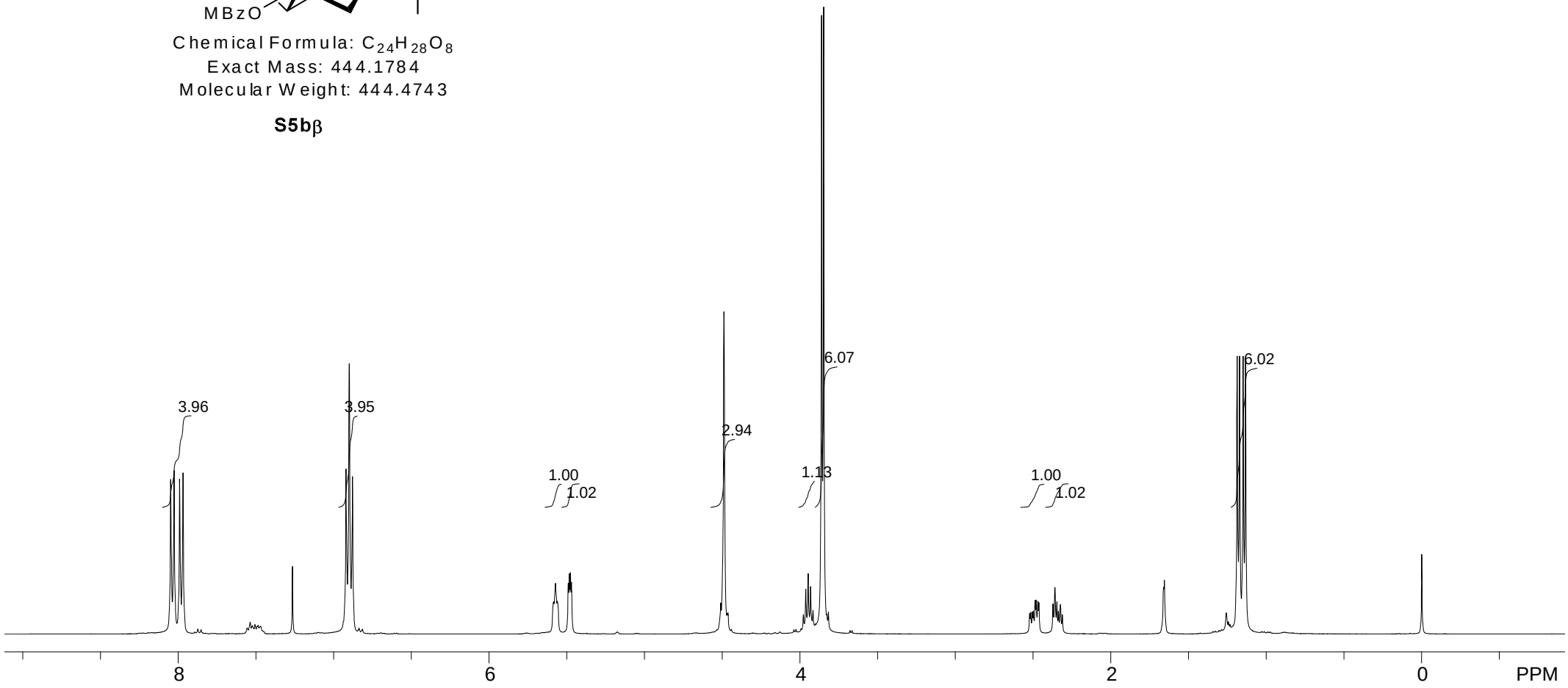






Chemical Formula: $C_{24}H_{28}O_8$
Exact Mass: 444.1784
Molecular Weight: 444.4743

S5bβ



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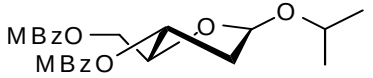
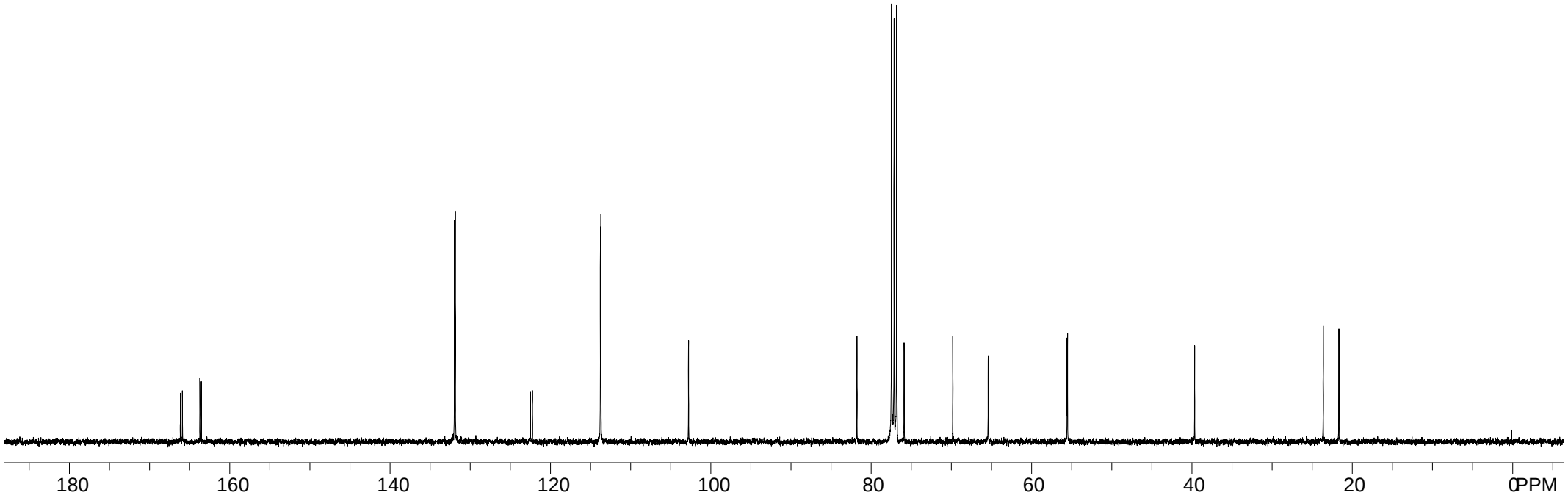
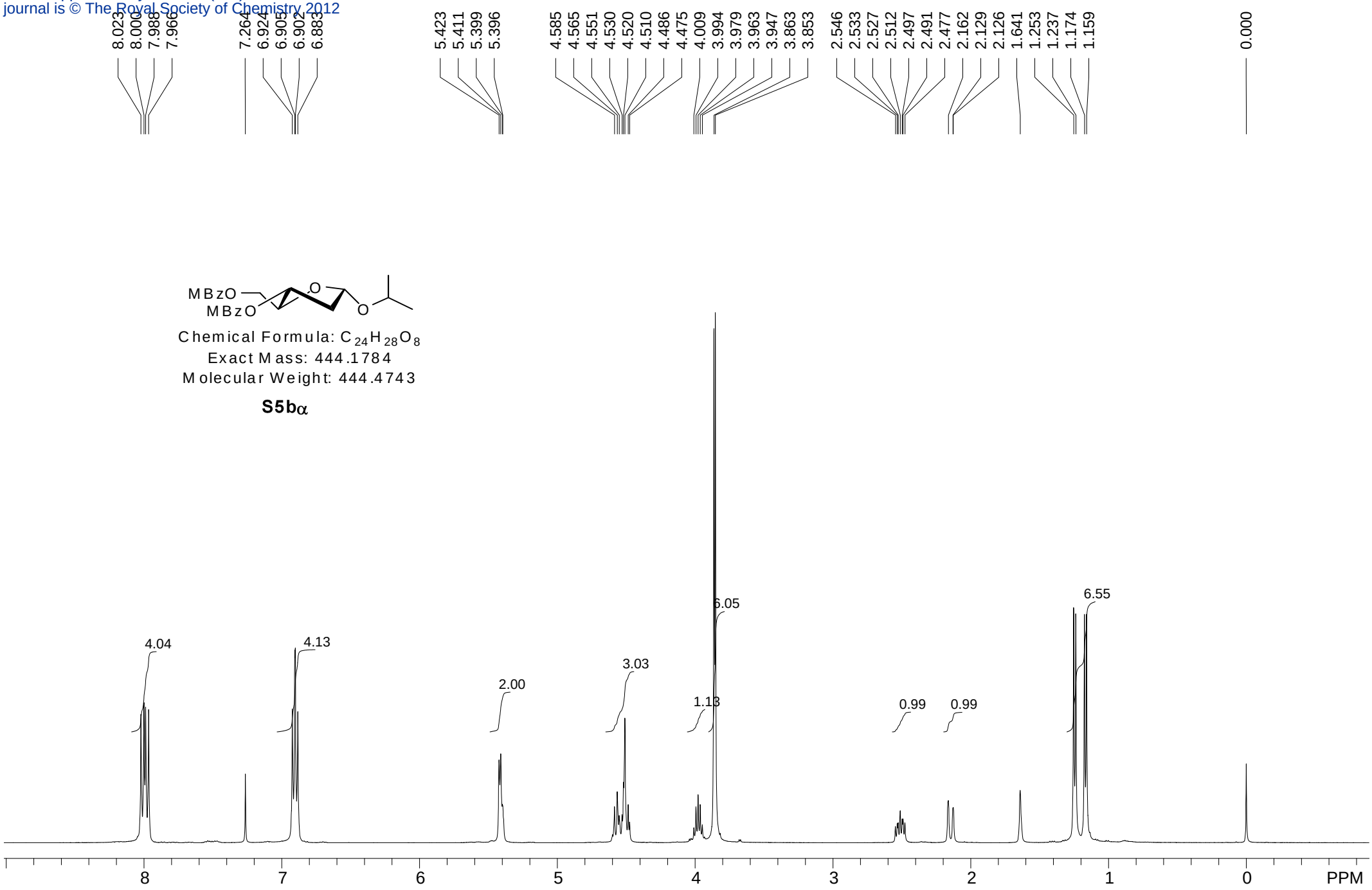
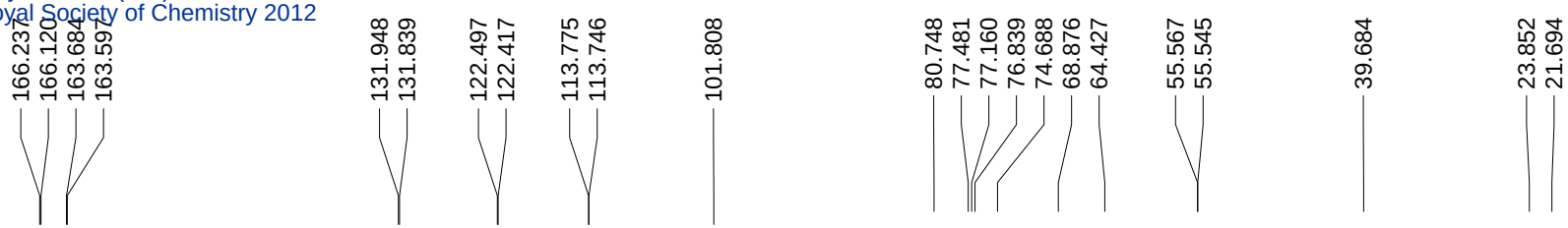


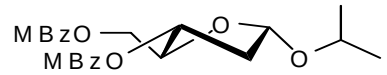
Chemical Formula: $C_{24}H_{28}O_8$
Exact Mass: 444.1784
Molecular Weight: 444.4743

S5bβ



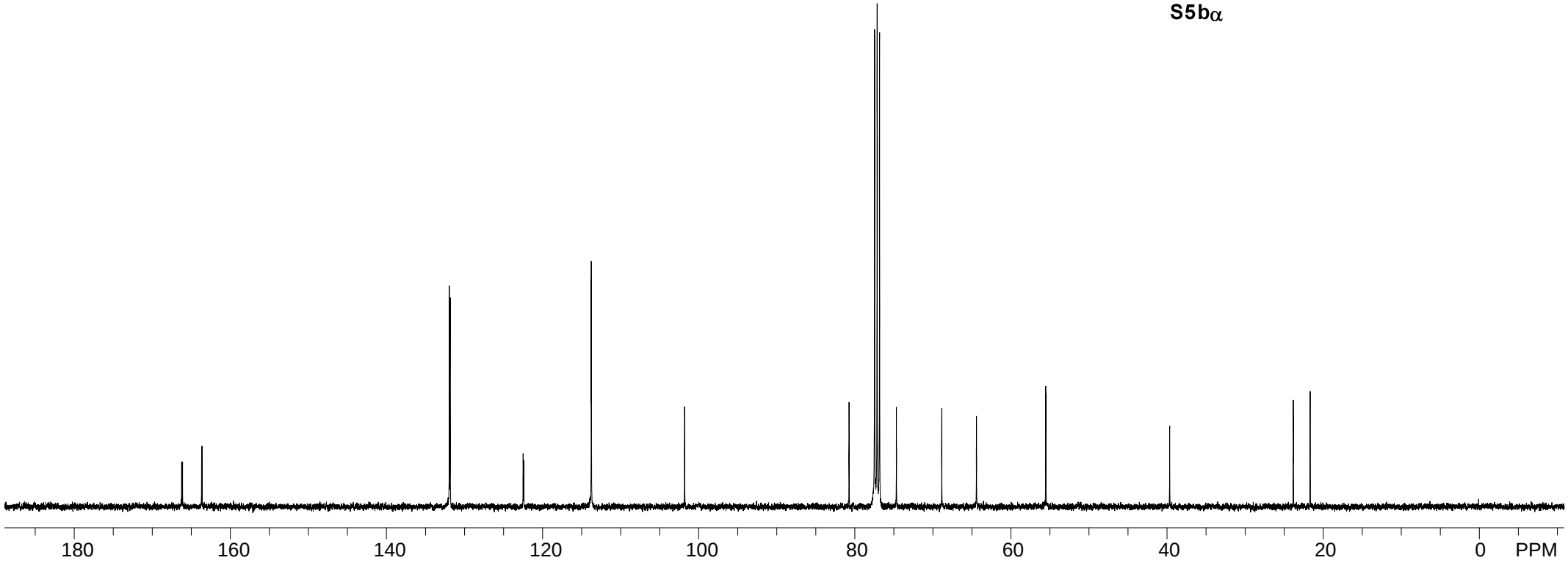


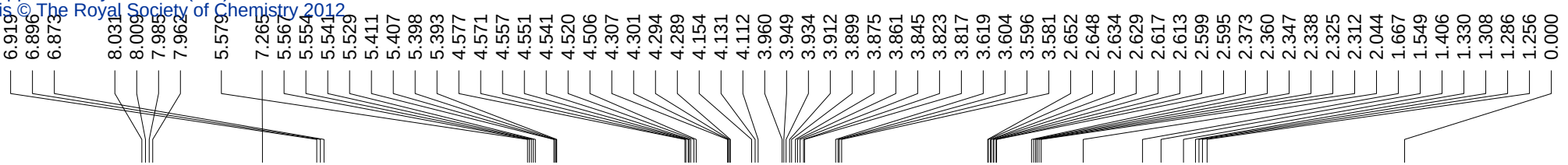


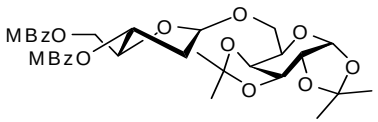


Chemical Formula: $C_{24}H_{28}O_8$
Exact Mass: 444.1784
Molecular Weight: 444.4743

S5bα

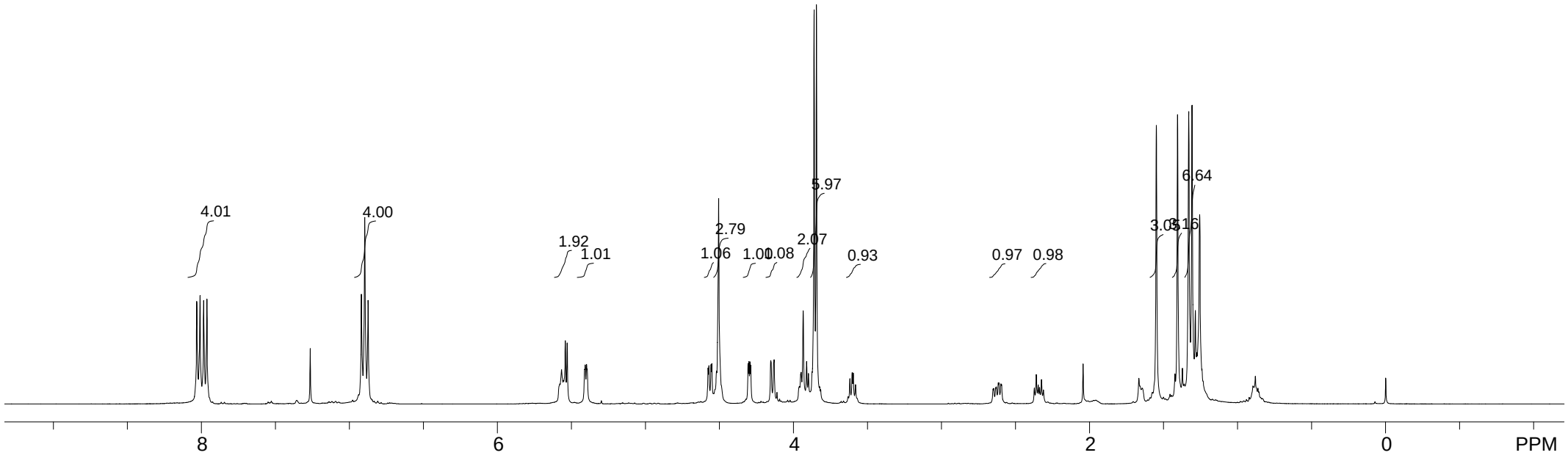


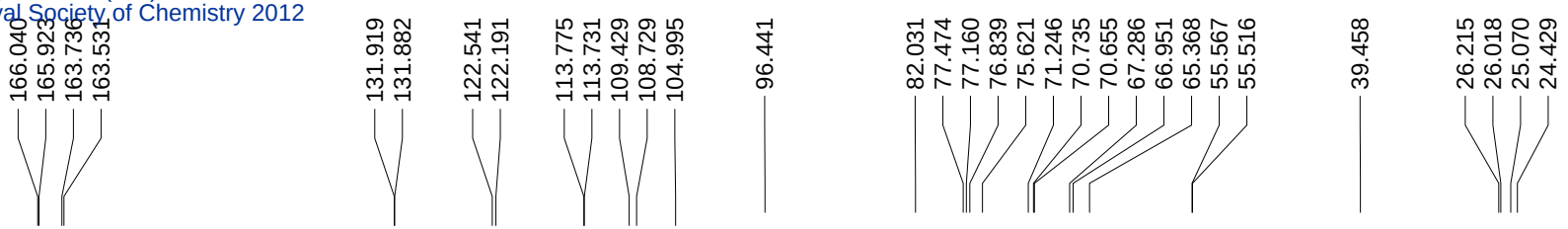


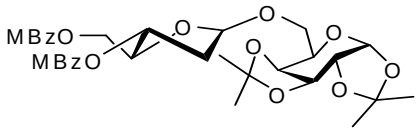


Chemical Formula: $C_{33}H_{40}O_{13}$
Exact Mass: 644.2469
Molecular Weight: 644.6629

S5cβ

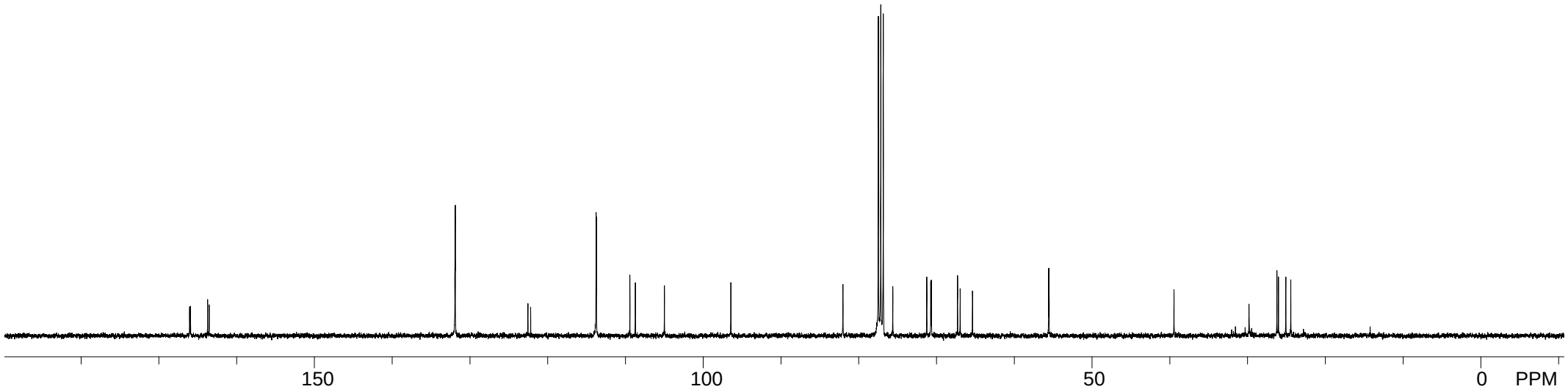


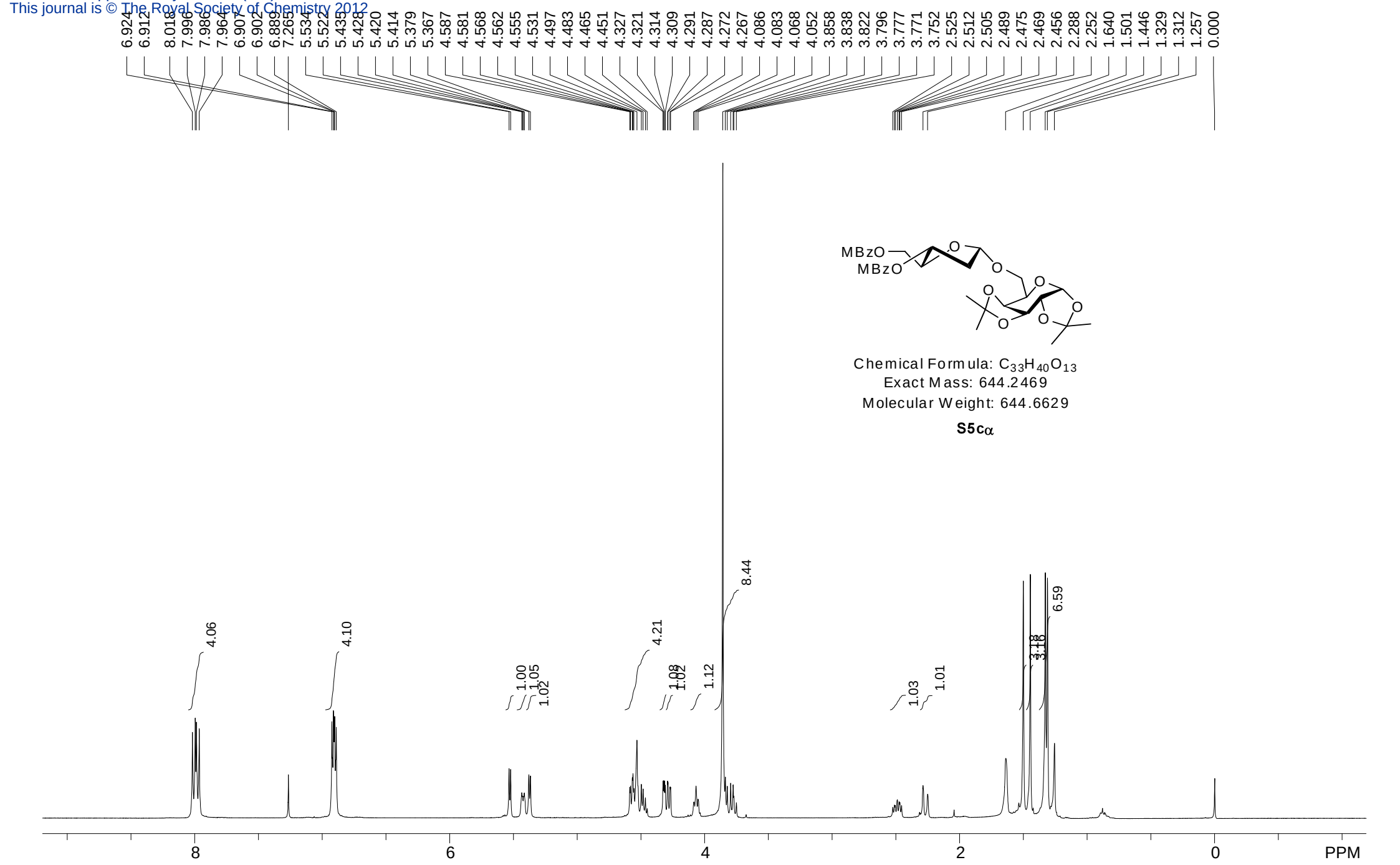


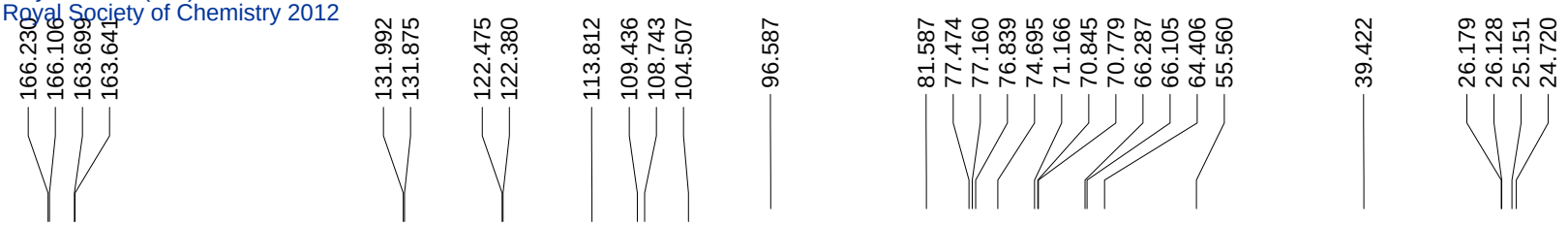


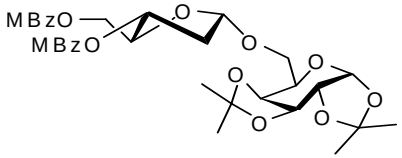
Chemical Formula: $C_{33}H_{40}O_{13}$
Exact Mass: 644.2469
Molecular Weight: 644.6629

S5cβ









Chemical Formula: $C_{33}H_{40}O_{13}$
Exact Mass: 644.2469
Molecular Weight: 644.6629

S5cα