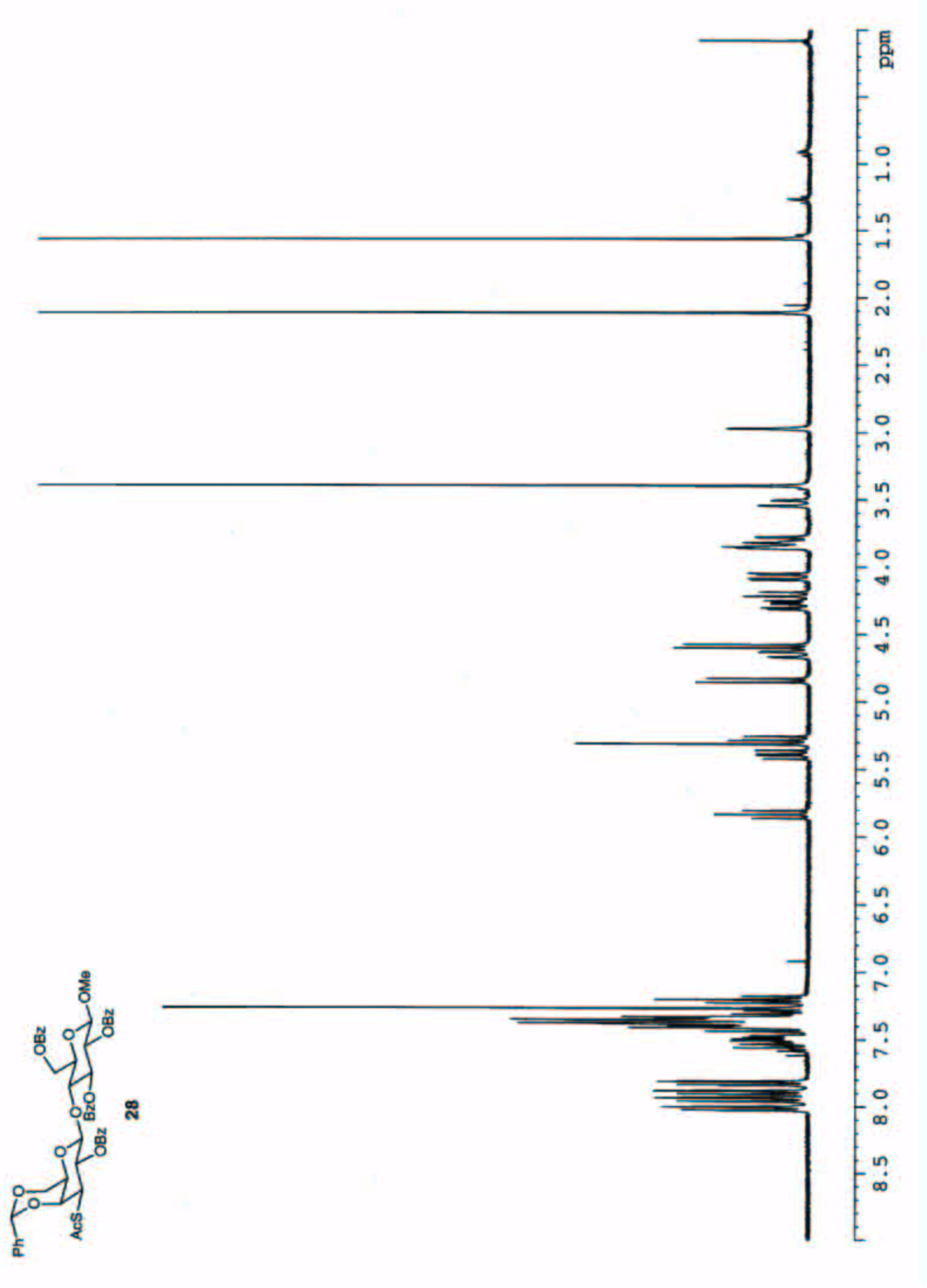
Supporting Information.

^{1}H NMR data for compound **28** (300 MHz, $CDCl_3$): δ 2.11 (3H, s, SAc), 2.98 (1H, s, Gal H-5), 3.40 (3H, s, OMe), 3.53 (1H, dd, $J_{6,6'}$ = 12.4, $J_{6,5}$ = 1.7 Hz, Gal H-6), 3.78-3.86 (3H, m, Glc H-5, Gal H-4, Gal H-6'), 4.08 (1H, dd, $J_{3,2}$ = 11.5, $J_{3,4}$ = 3.3 Hz, Gal H-3), 4.22 (1H, t, $J_{4,3}$ = $J_{4,5}$ = 9.2 Hz, Glc H-4), 4.30 (1H, dd, $J_{6,6'}$ = 12.1, $J_{6,5}$ = 4.2 Hz, Glc H-6), 4.59 (1H, d, $J_{1,2}$ = 7.7 Hz, Glc H-1), 4.65 (1H, dd, $J_{6',6}$ = 12.1, $J_{6',5}$ = 2.0 Hz, Glc H-6'), 4.85 (1H, d, $J_{1,2}$ = 7.7 Hz, Gal H-1), 5.29 (1H, dd, $J_{2,3}$ = 9.2, $J_{2,1}$ = 7.7 Hz, Glc H-2), 5.31 (1H, s, C*H*Ph), 5.40 (1H, dd, $J_{2,3}$ = 11.5, $J_{2,1}$ = 7.7 Hz, Gal H-2), 5.84 (1H, t, $J_{3,2}$ = $J_{3,4}$ = 9.2 Hz, Glc H-3), 7.18-7.61 (17H, m, Ph), 7.82-8.01 (8H, m, Ph).

^{1}H nmr spectrum of compound **28**



General procedure for synthesis of sialylmimetics. A solution of **28** (0.32 mmol) in dry DMF (6 mL) was thoroughly degassed by bubbling N_2 (g) through the solution for 15 mins. 4 Å Sieves and then hydrazine acetate (0.64 mmol) were added and the reaction mixture was left to stir for 1 h under N_2. The α-halo ester coupling partner (1.6 mmol) and then Et_3N (0.40 mmol) were added and the mixture stirred for 2 h at room temperature. The mixture was diluted with EtOAc (30 mL), washed with dil. aq. HCl (0.1M, 15 mL) and H_2O (15 mL), dried (Na_2SO_4) and concentrated under reduced pressure. Column chromatography on silica gel, typically employing a mixture of EtOAc and hexane, afforded the sialylmimetics in high yield.

In this way were prepared:

Compound **29**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (3H, t, J_{vic} = 7.1 Hz, $CO_2CH_2CH_3$), 2.95 (1H, s, Gal H-5), 3.19 (1H, dd, $J_{3,2}$ = 11.2, $J_{3,4}$ = 3.2 Hz, Gal H-3), 3.20 (2H, s, H-2'), 3.41 (3H, s, OMe), 3.58 (1H, d, $J_{6,6'}$ = 12.2 Hz, Gal H-6), 3.76 (1H, d, $J_{6',6}$ = 12.2 Hz, Gal H-6'), 3.83 (1H, ddd, $J_{5,4}$ = 9.4, $J_{5,6}$ = 4.3, $J_{5,6'}$ = 2.1 Hz, Glc H-5), 3.99 (2H, q, J_{vic} = 7.1 Hz, $CO_2CH_2CH_3$), 4.91 (1H, d, $J_{4,3}$ = 3.2 Hz, Gal H-4), 4.19 (1H, t, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, Glc H-4), 4.37 (1H, dd, $J_{6,6'}$ = 12.0, $J_{6,5}$ = 4.3 Hz, Glc H-6), 4.59 (1H, d, $J_{1,2}$ = 7.7 Hz, Glc H-1), 4.61 (1H, dd, $J_{6',6}$ = 12.0, $J_{6',5}$ = 2.1 Hz, Glc H-6'), 4.73 (1H, d, $J_{1,2}$ = 7.8 Hz, Gal H-2), 5.31 (1H, dd, $J_{2,3}$ = 9.4, $J_{2,1}$ = 7.7 Hz, Glc H-2), 5.33 (1H, s, C*H*Ph), 5.47 (1H, dd, $J_{2,3}$ = 11.2, $J_{2,1}$ = 7.8 Hz, Gal H-2), 5.81 (1H, t, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, Glc H-3), 7.25-7.62 (17H, m, Ph), 7.88-8.04 (8H, m, Ph).

Compound **30**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03 (1.32*) (2H, d, J_{vic} = 7.2 Hz, H-3'), 1.05 (1.19*) (3H, t, J_{vic} = 6.9 Hz, $CO_2CH_2CH_3$), 2.90 (2.96*) (1H, s,Gal H-5), 3.25 (3.31*) (1H, dd, $J_{3,2}$ = 11.4, $J_{3,4}$ = 3.2 Hz, Gal H-3), 3.32-3.38 (1H, m, H-2'), 3.41 (3H, s, OMe), 3.55 (3.57*) (1H, dd, $J_{6,6'}$ = 12.3, $J_{6,5}$ = 1.7 Hz, Gal H-6), 3.75 (1H, d, $J_{6',6}$ = 12.3 Hz, Gal H-6'), 3.83 (1H, ddd, $J_{5,4}$ = 9.4, $J_{5,6}$ = 4.2, $J_{5,6'}$ = 1.8 Hz, Glc H-5), 3.90 (4.11*) (2H, q, J_{vic} = 7.2 Hz, $CO_2CH_2CH_3$), 3.94 (3.95*) (1H, d, $J_{4,3}$ = 3.2 Hz, Gal H-4), 4.19 (4.20*) (1H, t, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, Glc H-4), 4.38 (1H, dd, $J_{6,6'}$ = 12.0, $J_{6,5}$ = 4.2 Hz, Glc H-6), 4.58 (4.59*) (1H, d, $J_{1,2}$ = 7.5 Hz, Glc H-1), 4.60 (1H, dd, $J_{6',6}$ = 12.0, $J_{6',5}$ = 1.8 Hz, Glc H-6'), 4.73 (4.75*) (1H, d, $J_{1,2}$ = 7.8 Hz, Gal H-1), 5.28-5.35 (2H, m, Glc H-2, C*H*Ph), 5.36 (5.51*) (1H, dd, $J_{2,3}$ = 11.4, $J_{2,1}$ = 7.8 Hz, Gal H-2), 5.80 (5.83*) (1H, t, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, Glc H-3), 7.19-7.62 (17H, m, Ph), 7.86-7.52 (8H, m, Ph).

**if clearly discernible, the chemical shift for the other diastereomer is indicated in parentheses.*

^{1}H NMR assignments confirmed by ^{1}H-^{1}H COSY NMR.

Compound **31**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.47 (0.77*) (3H, t, J_{vic} = 7.3 Hz, H-4'), 1.21-1.35 (1.45-1.65*) (1H, m, H-3'), 1.45-1.65 (1.74-1.89*) (1H, m, H-3'), 2.94 (2.96*) (1H, s, Gal H-5), 3.09 (3.17*) (1H, dd, J_{vic} = 8.3, 6.6 Hz, H-2'), 3.25 (1H, dd, $J_{3,2}$ = 11.2, $J_{3,4}$ = 3.1 Hz, Gal H-3), 3.41 (3H, s, OMe), 3.55 (3.58*) (1H, dd, $J_{6,6'}$ = 12.2, $J_{6,5}$ = 1.5 Hz, Gal H-6), 3.65 (3H, s, CO$_2$Me), 3.75 (1H, d, $J_{6',6}$ = 12.2 Hz, Gal H-6'), 3.84 (1H, ddd, $J_{5,4}$ = 9.6, $J_{5,6}$ = 4.2, $J_{5,6'}$ = 1.9 Hz, Glc H-5), 3.88 (3.94*) (1H, d, $J_{4,3}$ = 3.1 Hz, Gal H-4), 4.18 (4.20) (1H, t, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, Glc H-4), 4.38 (1H, dd, $J_{6,6'}$ = 12.0, $J_{6,5}$ = 4.2 Hz, Glc H-6), 4.56-4.63 (2H, m, Glc H-1, Glc H-6'), 4.73 (4.74*) (1H, d, $J_{1,2}$ = 7.8 Hz, Gal H-1), 5.28-5.38 (2H, m, Glc H-2, Gal H-2, C*H*Ph), [5.51* (1H, dd, $J_{2,3}$ = 11.2, $J_{2,1}$ = 7.8 Hz, Gal H-2)], 5.80 (5.83*) (1H, t, $J_{3,2}$ = $J_{3,4}$ =9.6 Hz, Glc H-3), 7.15-7.56 (17H, m, Ph), 7.76-8.00 (8H, m, Ph).

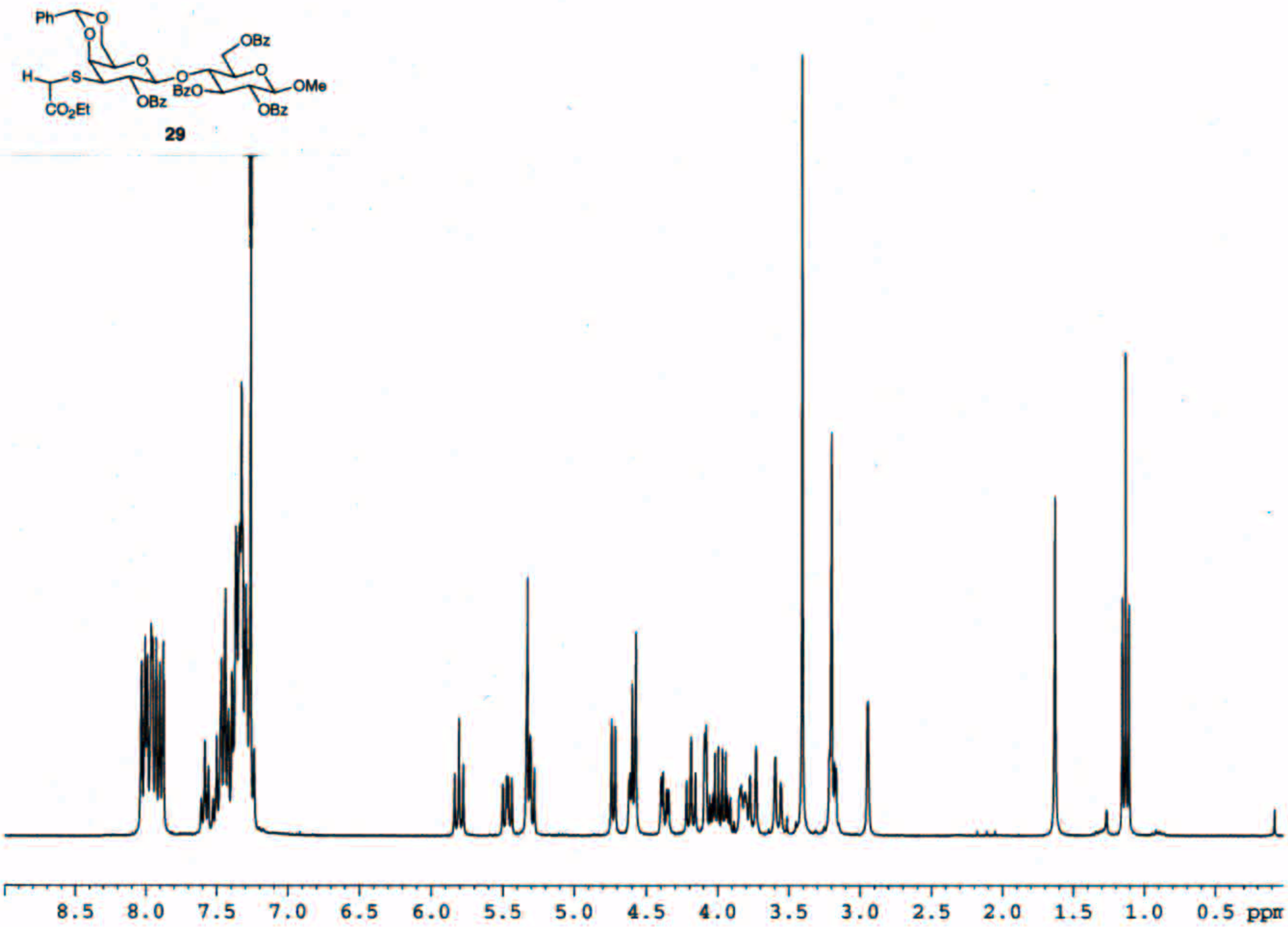
**if clearly discernible, the chemical shift for the other diastereomer is indicated in parentheses.*

^{1}H NMR assignments confirmed by ^{1}H-^{1}H COSY NMR.

Compound **34**. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.76-1.85 (1.87-1.97*) (1H, m, H-3a'), 2.31-2.44 (2.42-2.55*) (1H, m, H-3b'), 2.93 (2.95*) (1H, s, Gal H-5), 3.38-3.42 (4H, m, OMe, H-2'), [3.40* (3H, s, OMe)], 3.43 (3.67*) (1H, dd, $J_{3,2}$ = 11.5, $J_{3,4}$ = 3.1 Hz, Gal H-3), 3.54 (3.59*) (1H, dd, $J_{6,6'}$ = 12.2, $J_{6,5}$ = 1.5 Hz, Gal H-6), [3.66* (1H, dd, J_{vis} = 8.3, 5.3 Hz, H-2')], 3.76 (3.78) (1H, d, $J_{6',6}$ = 12.2 Hz, Gal H-6'), 3.81 (3.83*) (1H, ddd, $J_{5,4}$ = 9.6, $J_{5,6}$ = 4.2, $J_{5,6'}$ = 2.2 Hz, Glc H-5), 4.02 (1H, d, $J_{4,3}$ = 3.1 Hz, Gal H-4), 4.01-4.24 (4.09-4.29*) (4H, m, Glc H-4, Gal H-4*, H-4'), 4.34 (1H, dd, $J_{6,6'}$ = 12.0, $J_{6,5}$ = 4.2 Hz, Glc H-6), 4.59 (1H, d, $J_{1,2}$ = 7.7 Hz, Glc H-1), 4.62 (1H, dd, $J_{6',6}$ = 12.0, $J_{6',5}$ = 2.2 Hz, Glc H-6'), 4.74 (4.77*) (1H, d, $J_{1,2}$ = 7.7 Hz, Gal H-1), 5.29 (5.30*) (1H, dd, $J_{2,3}$ = 9.3, $J_{2,1}$ = 7.7 Hz, Glc H-2), 5.33 (5.38*) (1H, s, C*H*Ph), 5.36 (5.55*) (1H, dd, $J_{2,3}$ = 11.5, $J_{2,1}$ = 7.7 Hz, Gal H-2), 5.82 (5.83*) (1H, t, $J_{3,2}$ = $J_{3,4}$ = 9.3 Hz, Glc H-3), 7.23-7.62 (17H, m, Ph), 7.81-8.01 (8H, m, Ph).

**if clearly discernible, the chemical shift for the other diastereomer is indicated in parentheses.*

^{1}H NMR assignments confirmed by ^{1}H-^{1}H COSY NMR.



29

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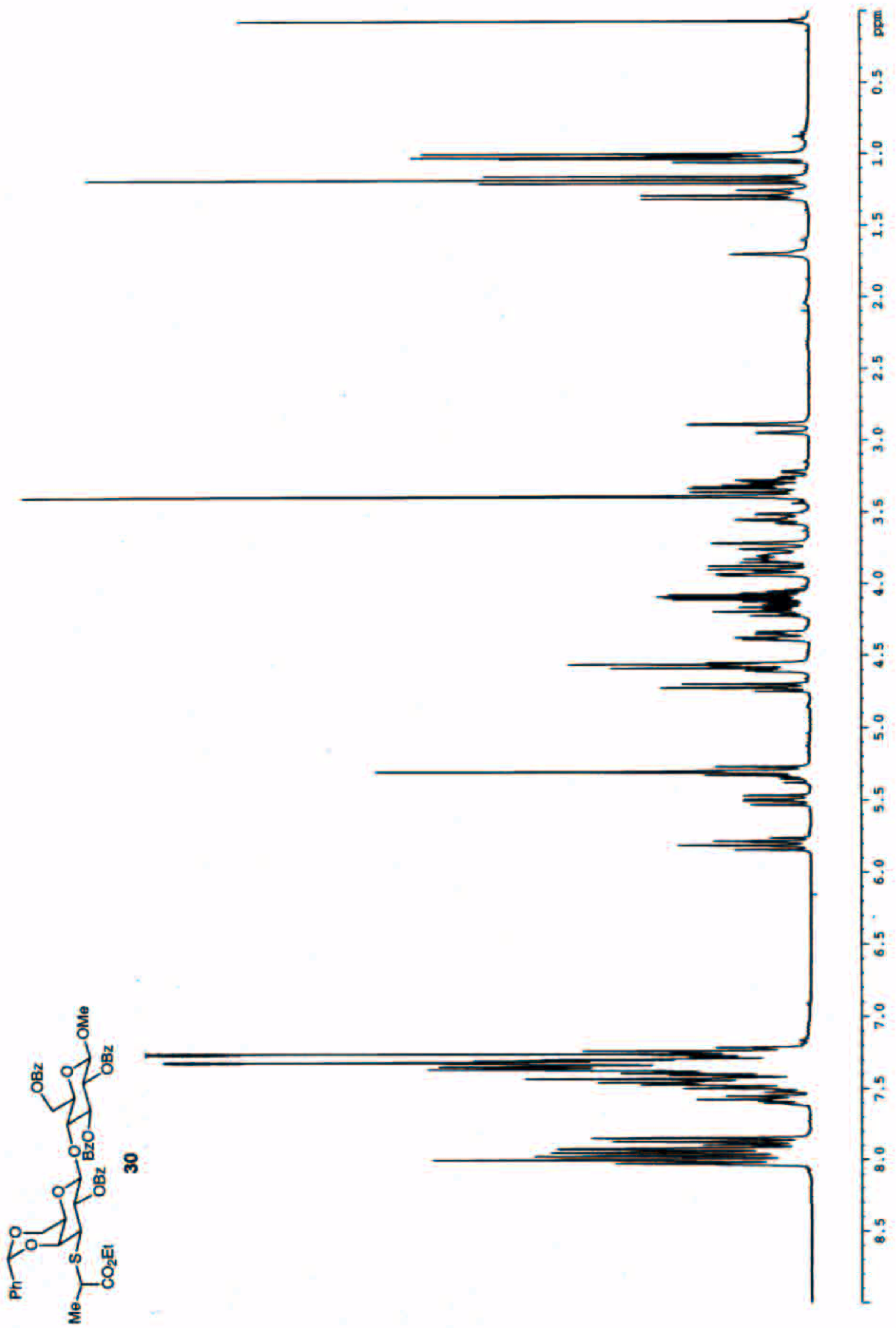

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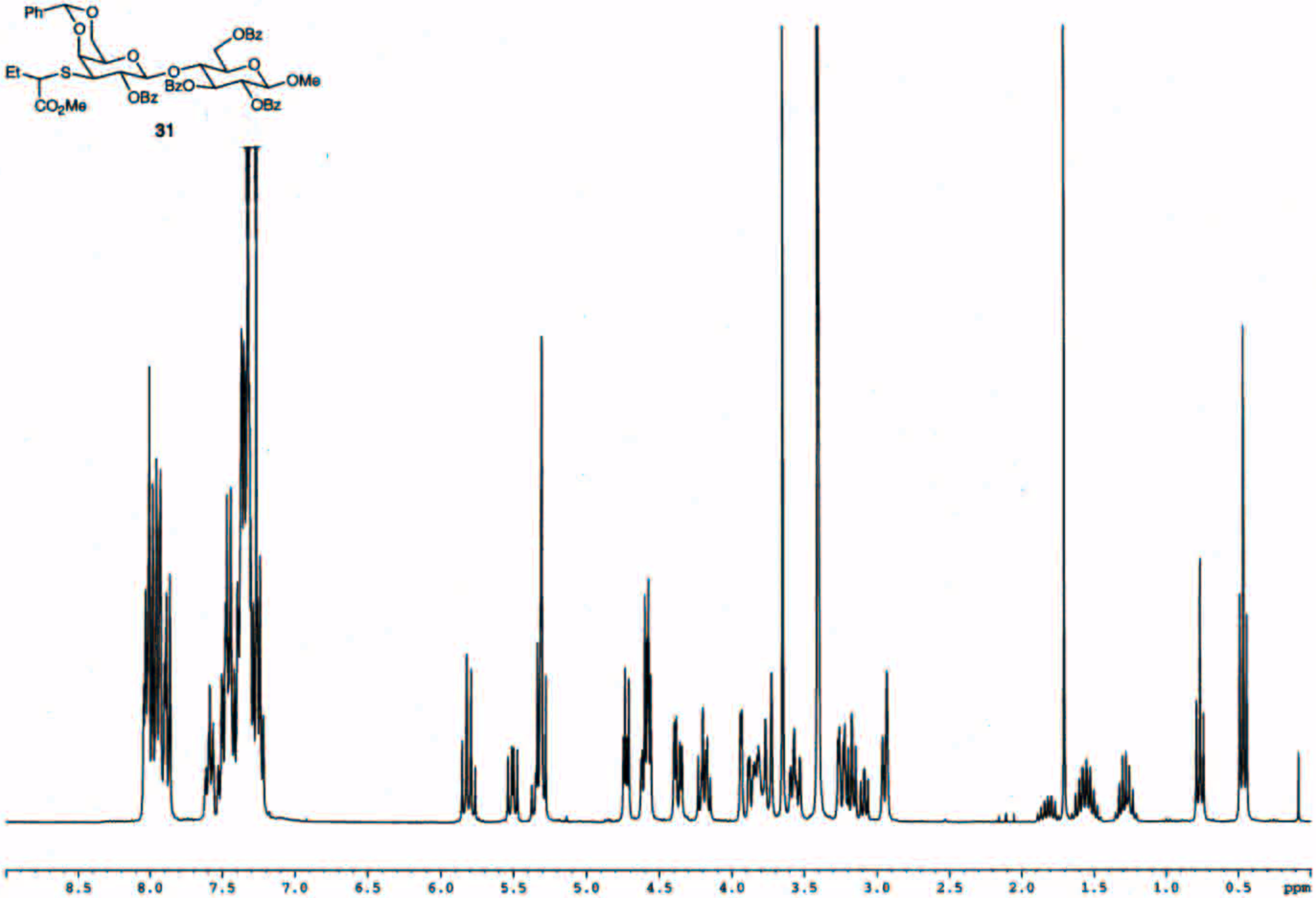
31

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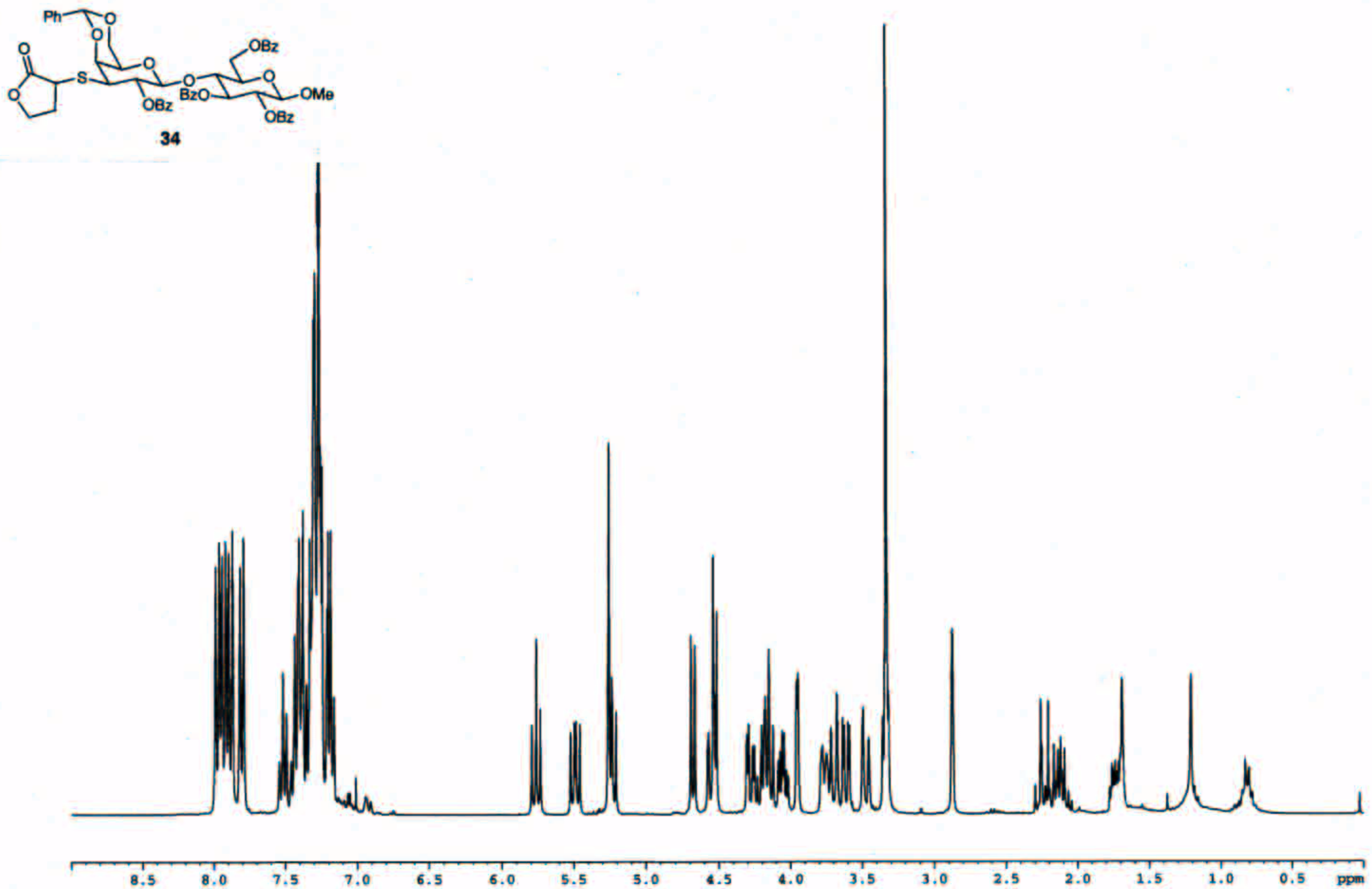
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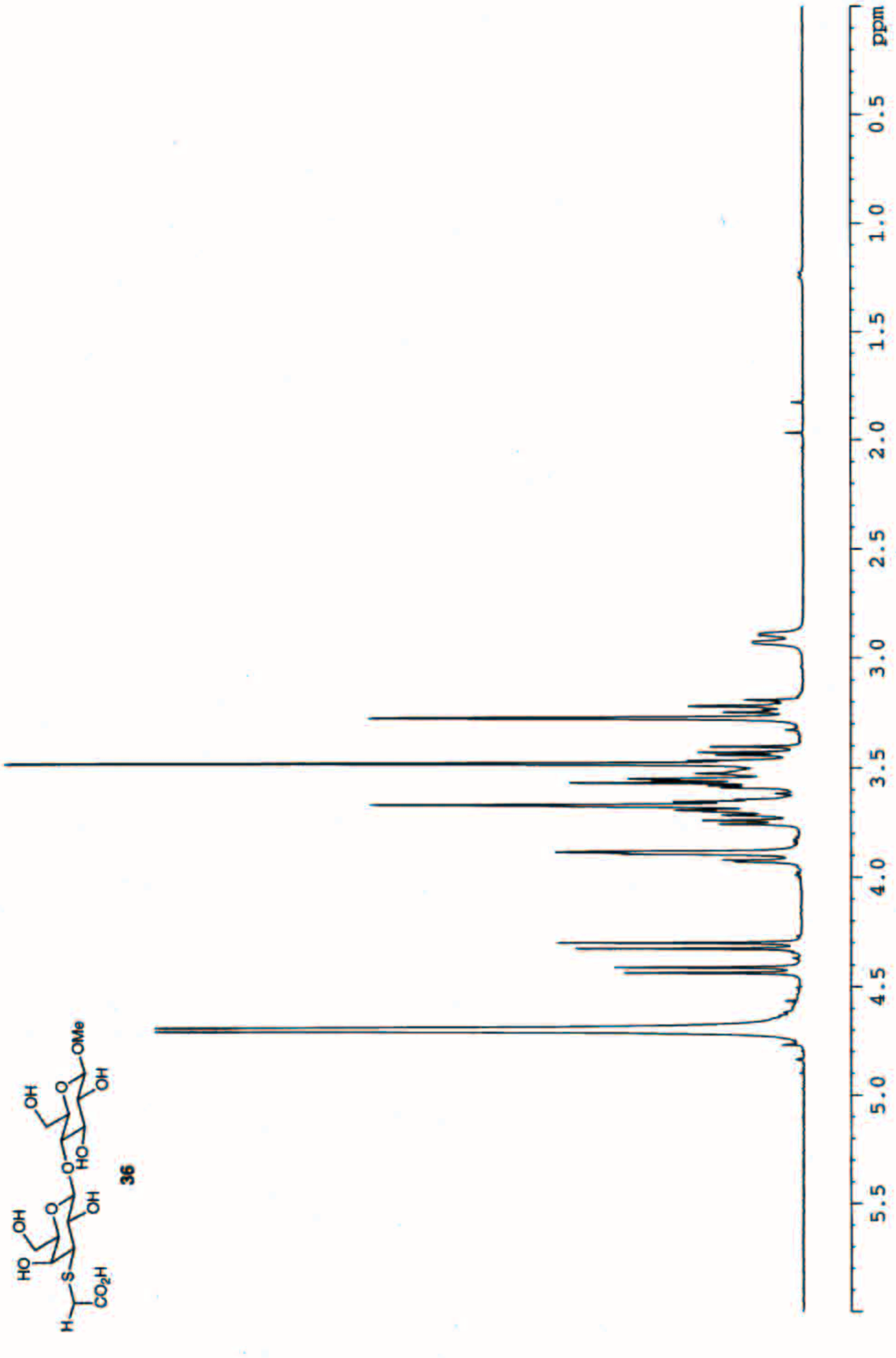
1.0
0.5
ppm

General procedure for de-esterification of fully protected sialylmimetics. To a stirred suspension of the sialylmimetics **29** to **35** (~0.3 mmol) in MeOH (15 mL) was added dropwise NaOH (1M, ~1 mL) until a pH of ~13 was attained. The reaction mixture was left to stir for 18 h before being neutralised with Amberlyte IR-120 (H^+) resin, the resin filtered off and washed with aqueous MeOH (several times), and then concentrated under reduced pressure to give the de-esterified sialylmimetics (generally quantitative yield) as colourless amorphous material.

General procedure for de-*O*-benzylidenation of de-esterified sialylmimetics. A solution of the de-esterified sialylmimetics (~0.3mmol) in 10% aq. TFA (8 mL) was stirred at 0 °C for 8 h before being concentrated *in vacuo* (oil pump, no heat applied). The residue was dissolved in H_2O and the pH adjusted to ~7.3 with NaOH (1M) before being concentrated under reduced pressure. The crude product was purified using chromatography (G10 Sephadex column, H_2O as eluant) and then HPLC (reverse phase C_{18} column, typically around 5% CH_3CN in H_2O as the mobile phase) to give the deprotected sialylmimetics after freeze-drying as a colourless amorphous material.

Representative ^1H *NMR spectra follow:*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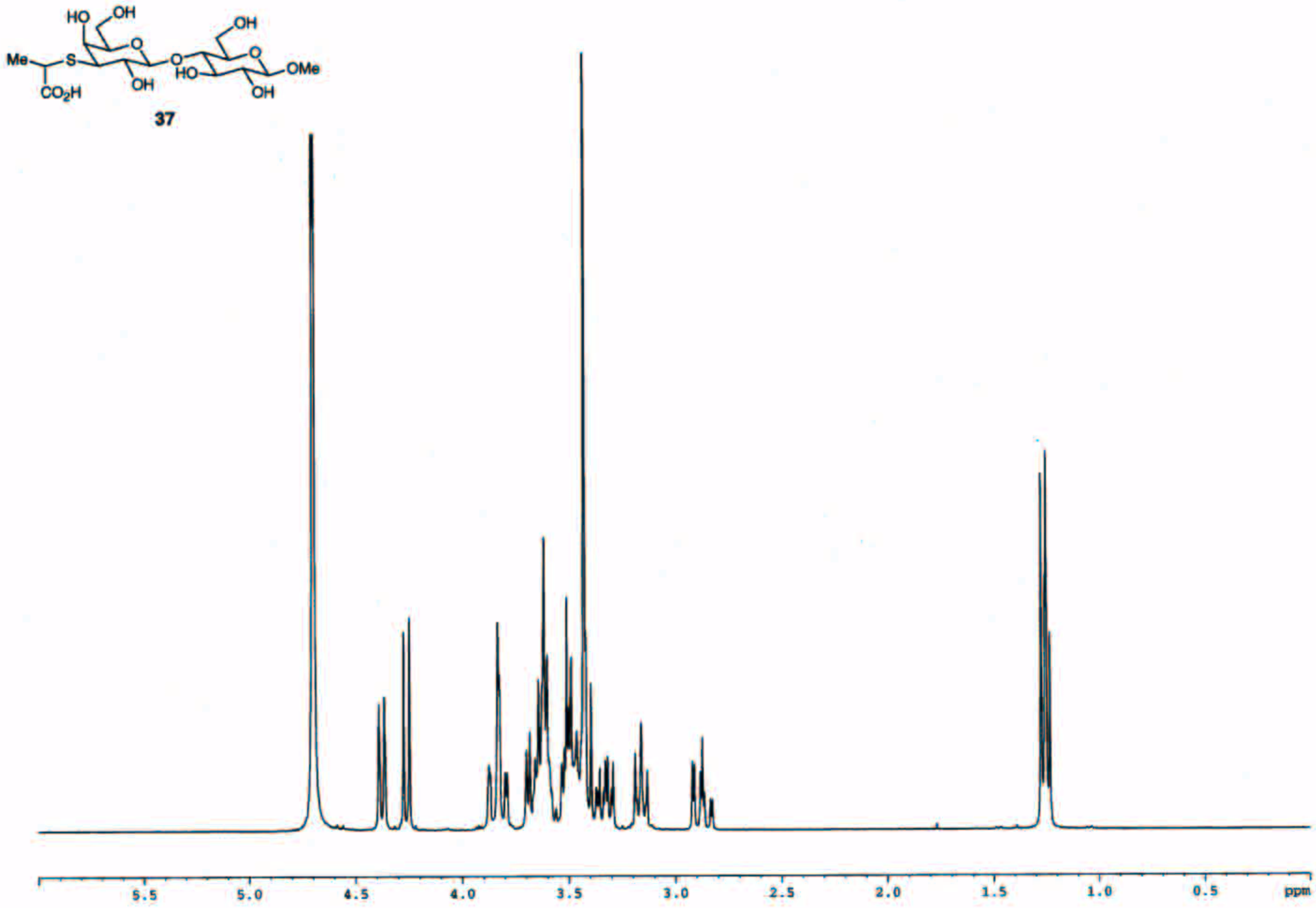
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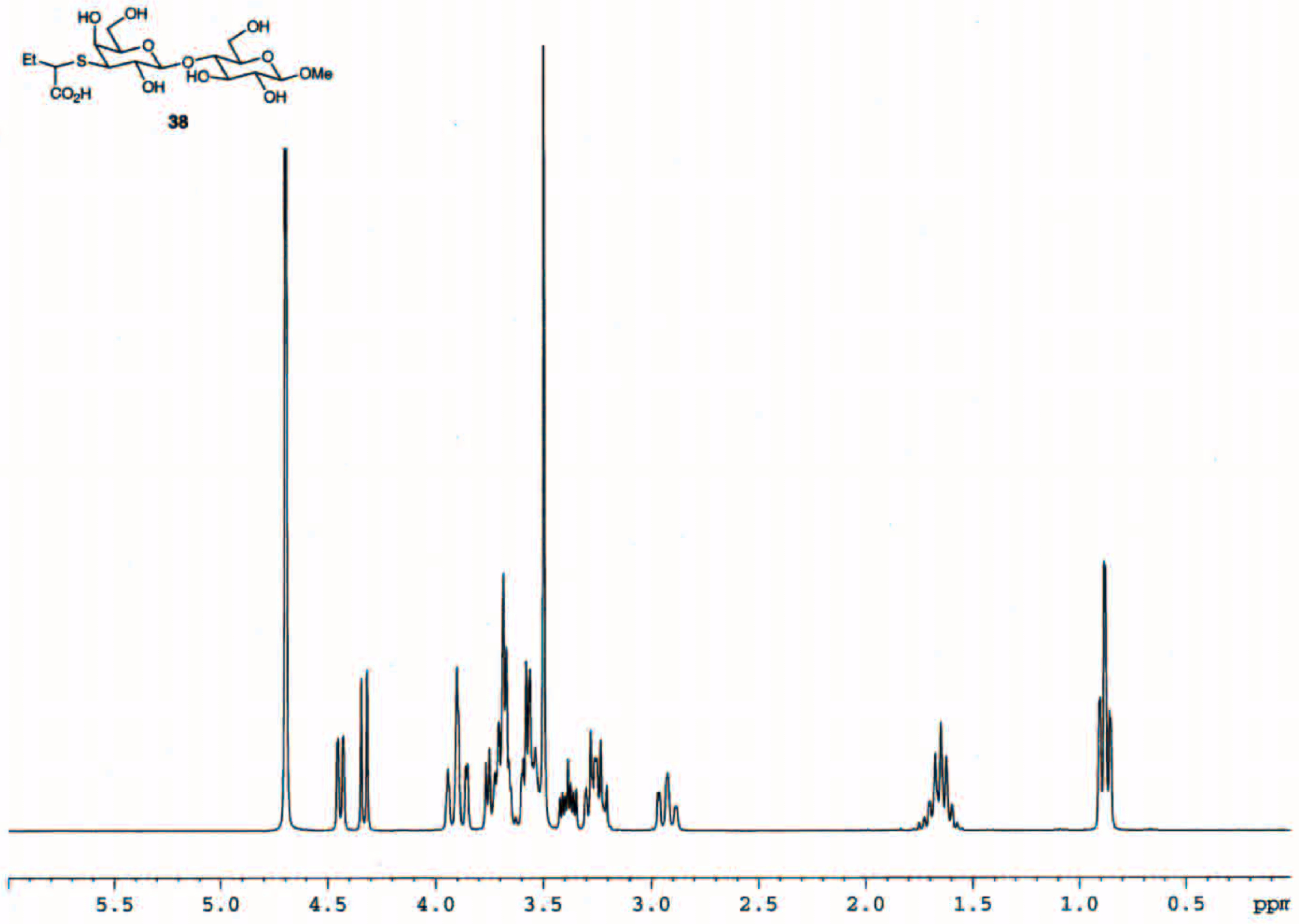
ppm

37



38

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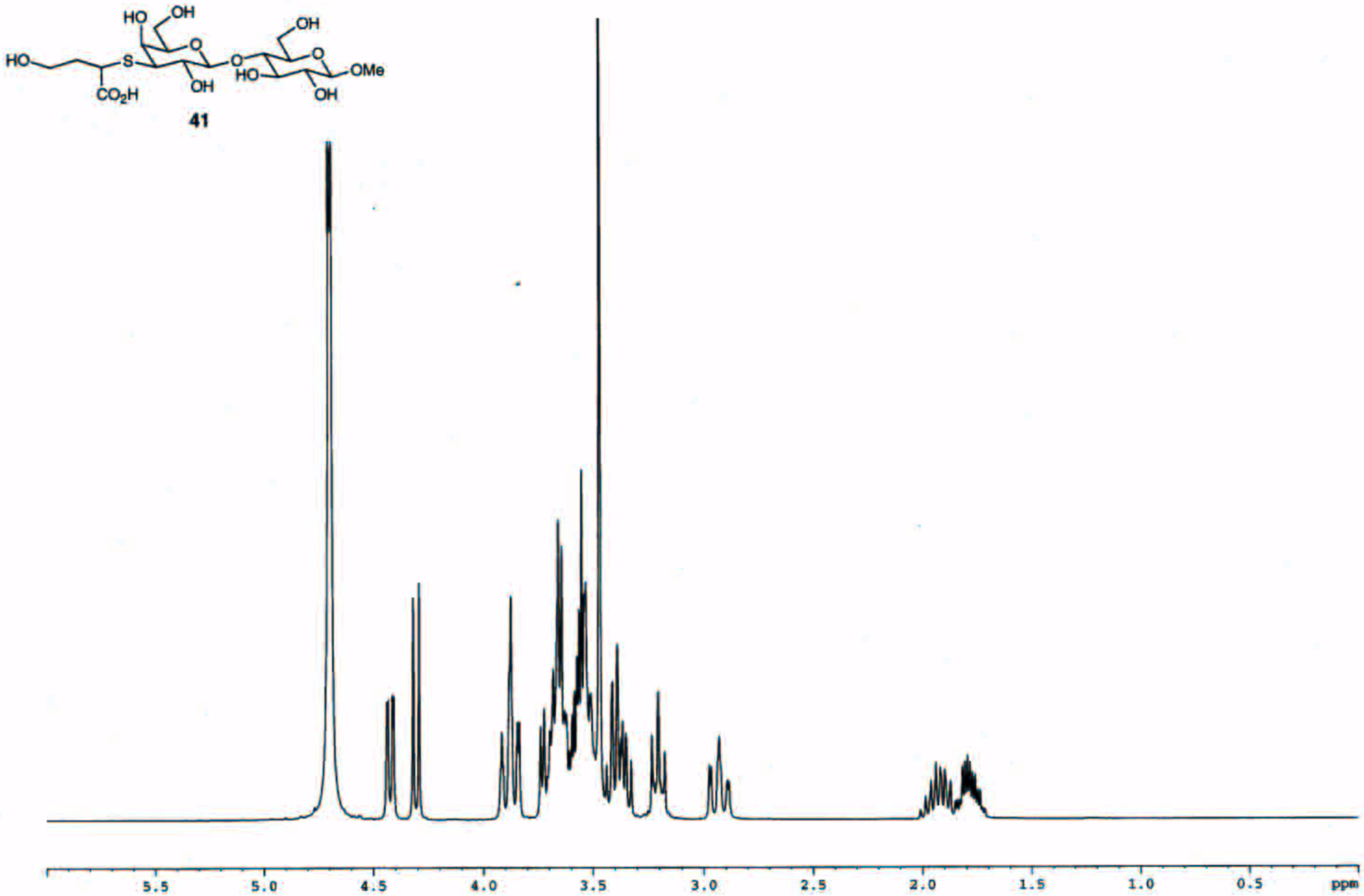

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ppm