### Supplementary Table 1: Glycan profiles for MUC5AC preparations.

Glycans released from each mucin were permethylated and analyzed by NSI-MS. Table 1 presents details (glycan reference number, structural representation, composition, GlyTouCan accession, theoretical m/z, detected m/z, amount, and relative abundance) for the glycans released from MUC5AC only.

| Glycan # | Representative Structure | Composition | GlyTouCan Accession(s) | Theoretical m/z (M+Na)¹ | Detected m/z (M+Na)¹ | % Total Profile | % Total Profile w/o Peeling |
|----------|-------------------------|-------------|------------------------|--------------------------|---------------------|-----------------|--------------------------|
| 1        | (Hex)(HexNAc)1          | (Hex)1 (HexNAc)1 | G76305TG, G85856KC     | 518.257                  | 518.26              | 91.72           | 16.83                    | 17.01                   |
| 2        | (Hex)(HexNAc)1 (Deoxyhexose)1 | (Hex)1 (HexNAc)1 (Deoxyhexose)1 | G84432QH     | 592.346                  | 592.35              | 73.00           | 13.40                    | 14.26                   |
| 3        | (Hex)(HexNAc)1 (Deoxyhexose)1 | (Hex)2 (HexNAc)1 (Deoxyhexose)1 | G73318SN, G33088KK   | 896.446                  | 896.45              | 10.38           | 1.91                     | 2.03                    |
| 4        | (Hex)(HexNAc)1 (NeuAc)1  | (Hex)1 (HexNAc)1 (NeuAc)1 | G65562ZE     | 879.431                  | 879.44              | 5.99            | 1.15                     | 1.17                    |
| 5        | (HexNAc)1               | (HexNAc)1    | G57321FI               | 314.157                  | 314.16              | 2.50            | 0.46                     | 0.49                    |
| 6        | (Hex)(HexNAc)1 (Deoxyhexose)1 | (Hex)2 (HexNAc)1 (Deoxyhexose)1 | G47180UC     | 1053.520                 | 1053.53             | 1.37            | 0.25                     | 0.27                    |
| 7        | (Hex)(HexNAc)1 (Deoxyhexose)2 | (Hex)2 (HexNAc)1 (Deoxyhexose)2 | G68200GL     | 1070.535                 | 1070.54             | 0.88            | 0.16                     | 0.17                    |
| 8        | (Hex)(HexNAc)2           | (Hex)1 (HexNAc)2 | G90330MR, G81730RY, G58866BR | 763.384                  | 763.39              | 87.06           | 15.98                    | 17.00                   |
| 9        | (Hex)(HexNAc)3 (Deoxyhexose)1 | (Hex)2 (HexNAc)3 (Deoxyhexose)1 | G91435IE, G68724RR, G52132UU | 1386.699                 | 1386.71             | 24.48           | 4.49                     | 4.78                    |
| 10       | (Hex)(HexNAc)4           | (Hex)2 (HexNAc)4 | G24704SK, G12074GQ     | 1457.736                 | 1457.74             | 23.39           | 4.29                     | 4.57                    |
| 11       | (Hex)(HexNAc)2 (Deoxyhexose)1 | (Hex)2 (HexNAc)2 (Deoxyhexose)1 | G94514RB, G61216ZY     | 1141.573                 | 1141.58             | 20.85           | 3.83                     | 4.07                    |
| 12       | (Hex)(HexNAc)3           | (Hex)2 (HexNAc)3 | G85815PP, G13480MW    | 1212.610                 | 1212.62             | 17.99           | 3.28                     | 3.49                    |
| 13       | (Hex)(HexNAc)2           | (Hex)2 (HexNAc)2 | G94973KT               | 987.483                  | 987.49              | 17.03           | 3.13                     | 3.33                    |
| 14       | (Hex)(HexNAc)2 (Deoxyhexose)2 | (Hex)3 (HexNAc)2 (Deoxyhexose)2 | G20310OM, G78177LC     | 1519.762                 | 1519.77             | 12.29           | 2.26                     | 2.40                    |
| 15       | (Hex)(HexNAc)3 (Deoxyhexose)1 | (Hex)3 (HexNAc)3 (Deoxyhexose)1 | G68741QE, G14803LR     | 1590.799                 | 1590.81             | 12.21           | 2.24                     | 2.38                    |
| 16       | (Hex)(HexNAc)4           | (Hex)3 (HexNAc)4 | G94517VF, G57672ST     | 1661.836                 | 1661.84             | 11.04           | 2.03                     | 2.15                    |
| 17       | (Hex)(HexNAc)4 (Deoxyhexose)1 | (Hex)2 (HexNAc)4 (Deoxyhexose)1 | G23700TV       | 1631.825                 | 1631.83             | 10.85           | 1.99                     | 2.12                    |
| 18       | (Hex)(HexNAc)2 (Deoxyhexose)1 | (Hex)1 (HexNAc)2 (Deoxyhexose)1 | G32426JY, G74353PF     | 937.473                  | 937.48              | 10.15           | 1.86                     | 1.98                    |
| 19       | (Hex)(HexNAc)2 (Deoxyhexose)2 | (Hex)2 (HexNAc)2 (Deoxyhexose)2 | G00033MO, G61730RY, G56868BH | 763.384                  | 763.39              | 87.06           | 15.98                    | 17.00                   |
| 20       | (Hex)(HexNAc)3 (Deoxyhexose)1 | (Hex)1 (HexNAc)3 (Deoxyhexose)1 | G68893BQ, G23430M     | 1008.510                 | 1008.51             | 7.48            | 1.27                     | 1.45                    |
| 21       | (Hex)(HexNAc)4 (Deoxyhexose)1 | (Hex)3 (HexNAc)4 (Deoxyhexose)1 | G20330AF, G29956GF | 1835.925                 | 1835.93             | 7.29            | 1.34                     | 1.42                    |
| 22       | (Hex)(HexNAc)4 (Deoxyhexose)2 | (Hex)3 (HexNAc)4 (Deoxyhexose)2 | G803330DF | 1016.552                 | 1016.51             | 5.07            | 0.93                     | 0.99                    |
|   | Description                                      | Accession Numbers               | M1   | M2   | Delta | RSD  |
|---|--------------------------------------------------|---------------------------------|------|------|-------|------|
| 23| (Hex)3 (HexNAc)2 (Deoxyhexose)1                  | G15049KC, G19111LP, G41488NC   | 1345.67 | 1345.68 | 4.93  | 0.30 |
| 24| (Hex)3 (HexNAc)3 (Deoxyhexose)2                  | G20544KC, G71204KR, G90420KY   | 1764.88 | 1764.90 | 4.80  | 0.88 |
| 25| (Hex)3 (HexNAc)3                                  | G85537AD, G65585FG             | 1416.70 | 1416.72 | 3.25  | 0.60 |
| 26| (Hex)3 (HexNAc)5 (Deoxyhexose)1                  | G35949CT, G71094KR, G08426KY   | 1764.88 | 1764.90 | 4.80  | 0.88 |
| 27| (Hex)1 (HexNAc)2 (NeuAc)1                        | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 28| (Hex)1 (HexNAc)4                                  | G59229NY                      | 1253.64 | 1253.65 | 2.25  | 0.41 |
| 29| (Hex)4 (HexNAc)3 (Deoxyhexose)2                  | G68308CM                      | 1968.98 | 1968.99 | 2.02  | 0.37 |
| 30| (Hex)3 (HexNAc)5 (Deoxyhexose)1                  | G86537AD, G89585FG            | 1416.70 | 1416.72 | 3.25  | 0.60 |
| 31| (Hex)1 (HexNAc)3 (Deoxyhexose)1                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 32| (Hex)1 (HexNAc)3                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 33| (Hex)2 (HexNAc)2 (NeuAc)1                        | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 34| (Hex)3 (HexNAc)3 (Deoxyhexose)2                  | G68308CM                      | 1968.98 | 1968.99 | 2.02  | 0.37 |
| 35| (Hex)2 (HexNAc)3 (Deoxyhexose)2                  | G68308CM                      | 1968.98 | 1968.99 | 2.02  | 0.37 |
| 36| (Hex)3 (HexNAc)2 (NeuAc)1                        | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 37| (Hex)1 (HexNAc)3                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 38| (Hex)2 (HexNAc)2                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 39| (Hex)3 (HexNAc)2                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 40| (Hex)2 (HexNAc)3 (Deoxyhexose)1                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 41| (Hex)1 (HexNAc)4                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 42| (Hex)3 (HexNAc)3                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 43| (Hex)2 (HexNAc)3                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 44| (Hex)1 (HexNAc)3 (Deoxyhexose)1                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 45| (Hex)3 (HexNAc)3 (Deoxyhexose)2                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 46| (Hex)4 (HexNAc)4                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| 47| (Hex)3 (HexNAc)4                                  | G85608AG, G64844ET             | 1124.55 | 1124.56 | 2.52  | 0.46 |
| #  | Structure Description                                           | Glycan ID | Exact Mass (m/z) | Experimental (m/z) | monoisotopic mass error (ppm) | isotopic mass error (ppm) |
|----|-----------------------------------------------------------------|-----------|-----------------|-------------------|-------------------------------|--------------------------|
| 48 | (Hex)5 (HexNAc)5 (Deoxyhexose)1                                 | G26557KN  | 1356.120        | 1356.13           | 0.29                         | 0.05                     |
| 49 | (Hex)5 (HexNAc)5 (Deoxyhexose)1                                | G37951JE, G84713HO | 1358.170 | 1358.18          | 0.25                         | 0.05                     |
| 50 | (Hex)6 (HexNAc)7 (Deoxyhexose)2                                | G20852ZHZ | 1690.341        | 1690.36           | 0.25                         | 0.05                     |
| 51 | (Hex)4 (HexNAc)6 (Deoxyhexose)2                                | GB8654S | 1383.870        | 1383.88           | 0.21                         | 0.04                     |
| 52 | (Hex)5 (HexNAc)5 (Deoxyhexose)3                                | GB5292NPZ | 1430.220       | 1430.23           | 0.14                         | 0.03                     |
| 53 | (Hex)6 (HexNAc)5 (Deoxyhexose)2                                | G70999Y1, G30583FY | 1445.215 | 1445.22          | 0.13                         | 0.02                     |
| 54 | (Hex)5 (HexNAc)6 (Deoxyhexose)2                                | GA44672E | 1465.736        | 1465.73           | 0.11                         | 0.02                     |
| 55 | (Hex)3 (HexNAc)5                                                | G20553CFI | 1906.942       | 1906.97           | 2.51                         | 0.46                     |
| 56 | (Hex)2 (HexNAc)5 (Deoxyhexose)1                                | GB3956KG | 849.970         | 849.98            | 0.62                         | 0.11                     |
| 57 | (Hex)3 (HexNAc)1                                                | GB653PT  | 722.357         | 722.36            | 4.80                         | 0.88                     |
| 58 | (Hex)2 (HexNAc) (NeuAc)1                                        | GB51267U | 1083.531       | 1083.54           | 1.84                         | 0.34                     |
| 59 | (Hex)1 (Deoxyhexose)1                                           | GB590850MO | 447.220       | 447.22            | 32.79                        | 6.02                     |

**Note:** Glycan 59 is the expected product of peeling reactions.

| Total w/ Peel | 544.90 |
| Total w/o Peel | 512.11 |

| Total w/ Peel | 100.00 |
| Total w/o Peel | 100.00 |
### Supplementary Table 2: Sulfated glycan profiles for MUC2, MUC5B, and MUC5AC preparations.

Glycans released from each mucin were permethylated and analyzed by NSI-MS. Table 2 presents details (glycan reference number, structural representation, composition, GlyTouCan accession, theoretical m/z, detected m/z, amount, and relative abundance) for the top 5 sulfated glycans detected from each mucin preparation by negative mode NSI-MS.

| Source | Representation Structure | Composition | GlyTouCan Accession(s) | Theoretical m/z (M-H) | Detected m/z (M-H) | Signal Intensity | % of Total sulfated glycans | % of Top 5 sulfated glycans | Detection mass (M-H) | Signal Intensity | % of Total sulfated glycans | % of Top 5 sulfated glycans |
|--------|--------------------------|-------------|------------------------|-----------------------|-------------------|-----------------|--------------------------|--------------------------|------------------------|-----------------|--------------------------|--------------------------|
| S1     | 1-1000                  | S1 (Hex)(HexNAc)1 | 073022112C | 560.202 | 560.201 | 887059 | 8.36 | 21.96 | 560.20 | 560.201 | 887059 | 8.36 | 21.96 |
| S2     | 1-1000                  | S1 (Hex)(HexNAc)(Deoxyhexose)1 | 024667128C | 734.291 | 734.290 | 1025409 | 9.67 | 25.39 | 734.29 | 734.290 | 1025409 | 9.67 | 25.39 |
| S3     | 1-1000                  | S1 (Hex)(HexNAc)2 | 024630960C | 805.328 | 805.330 | 4010391 | 19.68 | 34.30 | 805.33 | 805.330 | 4010391 | 19.68 | 34.30 |
| S4     | 1-1000                  | S1 (Hex)2(HexNAc)1(Deoxyhexose)1 | 024630960C | 938.391 | 938.389 | 1172196 | 11.05 | 29.02 | 938.39 | 938.389 | 1172196 | 11.05 | 29.02 |
| S5     | 1-1000                  | S1 (Hex)(HexNAc)2(Deoxyhexose)1 | 024630960C | 979.417 | 979.410 | 2695001 | 13.22 | 23.05 | 979.42 | 979.410 | 2695001 | 13.22 | 23.05 |
| S6     | 1-1000                  | S1 (Hex)(HexNAc)2(Deoxyhexose)1 | 024630960C | 1183.517 | 1183.515 | 243921 | 4.51 | 11.85 | 1183.52 | 1183.515 | 243921 | 4.51 | 11.85 |
| S7     | 1-1000                  | S1 (Hex)(HexNAc)2(Deoxyhexose)1 | 024630960C | 1224.540 | 1224.540 | 1588826 | 7.80 | 13.59 | 1224.54 | 1224.540 | 1588826 | 7.80 | 13.59 |
| S8     | 1-1000                  | S1 (Hex)(HexNAc)2(Deoxyhexose)1 | 024630960C | 1428.641 | 1428.641 | 476006 | 4.49 | 11.78 | 1428.64 | 1428.641 | 476006 | 4.49 | 11.78 |

Note 1: GlyTouCan Accessions are for the indicated compositions.
Supplementary Table 3: Glycan profiles for MUC2, MUC5B, and MUC5AC preparations

Glycans released from each mucin were permethylated and analyzed by NSI-MS. Table 3 presents details (glycan reference number, structural representation, composition, GlyTouCan accession, theoretical m/z, detected m/z, amount, and relative abundance) for the glycans released from all three mucins for cross-comparison.

| Rank | Representation Structure | GlyTouCan Accession(s) | Theoretical m/z | Detected m/z | % Total Peptide | Tolerance | % Total Peptide | Theoretical m/z | Detected m/z | % Total Peptide | Tolerance | % Total Peptide |
|------|--------------------------|-------------------------|----------------|-------------|----------------|----------|----------------|----------------|-------------|----------------|----------|----------------|
| 1    | (Hex) (Hex) | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK | 365.21FDFK |
(Hex)5 (HexNAc)5 (Deoxyhexose)1

(Hex)3 (HexNAc)4 (Deoxyhexose)4

(Hex)2 (HexNAc)5 (Deoxyhexose)2

(Hex)3 (HexNAc)2 (Deoxyhexose)3

(Hex)3 (HexNAc)3 (Deoxyhexose)1

(Hex)4 (HexNAc)5 (Deoxyhexose)2

(Hex)5 (HexNAc)4 (Deoxyhexose)2

(Hex)3 (HexNAc)5 (Deoxyhexose)1

(Hex)3 (HexNAc)3 (Deoxyhexose)4

(Hex)3 (HexNAc)2 (Deoxyhexose)2

G20310DM, G78177LC

G66741QE, G16458JH

G70999YJ, G02681FY

G84853WN

G21630AC

G98518WL

G68308CM

G90829NZ

G92547QZ

G65612SS

G93333OF

G90965BZ

G08426KY

G99804SJ

G32752FJ

G23700TV

1415.204

1276.633

1256.120

1690.341

1118.552

1103.546

1087.539

1552.772

1016.502

1835.925

1661.836

1631.825

1590.799

1465.730

1430.213

1118.555

1103.549

1582.796

1552.776

1037.018

1805.919

1706.851

1693.856

1661.837

0.32

1.18

0.47

0.49

0.05

0.09

0.04

0.12

0.13

0.22

0.46

0.40

0.06

0.15

0.11

0.31

0.27

0.30

0.51

0.16

0.03

0.09

0.05

0.06

0.15

0.15

0.05
| No. | Hex(1) (HexNAc(1)) (Deoxyhexose(1)) | G28921PH | 1139.065 | 1139.07 | 0.64 | 0.12 | 0.13 |
|-----|----------------------------------|---------|----------|--------|------|------|------|
| 74  | Hex(1) (HexNAc(1)) (Deoxyhexose(1)) | G28052FT | 949.970 | 949.98 | 0.62 | 0.11 | 0.12 |
| 75  | Hex(1) (Deoxyhexose(1)) | G00068MO | 447.220 | 447.221 | 38.66 | 10.40 | na   |
| 76  | Hex(1) (NeuAc(1)) | G30207PZ, G63069TR | 634.305 | 634.306 | 43.37 | 11.67 | na   |

Note 1: Glycans 81, 82, 83 are the expected products of peeling reactions.
Supplementary Table 4: Primer sequences

| Primer  | Sequence                        |
|---------|---------------------------------|
| ECE1_F  | TGCCATTGTTGTCAGAGCTG            |
| ECE1_R  | TAGCTTGTGAACAGTTTCCAGG          |
| HWP1_F  | GCTGGTTCAGAATCATCCATGC          |
| HWP1_R  | AAGGGTCAGTGCCAGGAGGTG           |
| HGC1_F  | GTCAGTTCTCTGCAACCTT CATC        |
| HGC1_R  | AAACAGCAGAGAACCAGCG             |
| NRG1_F  | GGTTGCACGGTTGTCGAAACC           |
| NRG1_R  | TGGTGTGCTGCTGCTGCTGTTG          |
| ACT1_F  | CCCAGGTATTGCTGAACGTA            |
| ACT1_R  | GAACCCACCATCCAGACAGA            |
| YWP1_F  | TGCTAGTACTGCTAAACAAAGTCAC       |
| YWP1_R  | CACCATTAACACCACAGCA             |
| UME6_F  | TCATTCAATCCTACTCGTCCACC         |
| UME6_R  | CCAGATCCATAGCAGTGCCTG           |
| RIP1_F  | TGCTGACAGAGTCAAAGAAACC          |
| RIP1_R  | GAACCAACCACCGAAATCAC            |
| EFG1_F  | CATCACAACCAGGTTCTACAACCAAT      |
| EFG1_R  | CTACTATTAGCAGCACCACCC           |
| 18S_F   | GGATTTACTGAAGACTAACTACTG        |
| 18S_R   | GAACAAACCGATCCCTAGT             |
| ALS3_F  | ACTTCCACAGCTGCTTCCACTTCT        |
| ALS3_R  | TCCACGGAACCGGTGTGTGCT           |
| HYR1_F  | CGGTTCTGGAAGTGTCATAA            |
| HYR1_R  | AGAGTTGAACCTGCGTCTAG            |
| EED1_F  | TGCTCTACCCACCACAAACAG           |
| EED1_R  | TGTCCGGTGTGCTGCTCATA            |
Supplementary Note: Glycan synthesis protocols with NMR spectra and HPLC traces of synthesized glycans

**General methods.** All commercial reagents were used as supplied unless otherwise stated, and solvents were dried and distilled using standard techniques. Thin layer chromatography was performed on silica-coated glass plates (TLC Silica Gel 60 F<sub>254</sub>, Merck) with detection by fluorescence, charring with 5% H<sub>2</sub>SO<sub>4</sub>(aq), or staining with a ceric ammonium molybdate solution. Organic solutions were concentrated and/or evaporated to dry under vacuum in a water bath (<50 °C). Molecular sieves were dried at 400 °C under vacuum for 20-30 minutes prior to use. Amberlite IR-120H resin was washed extensively with MeOH and dried under vacuum prior to use. Medium-pressure liquid chromatography (MPLC) was performed using a CombiFlash Companion equipped with RediSep normal-phase flash columns, and solvent gradients refer to sloped gradients with concentrations reported as % v/v. NMR spectra were recorded on a Bruker Avance DMX-500 (500 MHz) spectrometer, and assignments achieved with the assistance of 2D gCOSY, 2D gTOCSY, 2D gHSQC, and 2D gHMBC; chemical shifts are expressed in ppm and referenced to either Si(CH<sub>3</sub>)<sub>4</sub> (for CDCl<sub>3</sub>), residual CHD<sub>2</sub>OD (for CD<sub>3</sub>OD), or a MeOH internal standard (for D<sub>2</sub>O). Low resolution electron-spray ionization mass spectrometry (ESI-MS) was performed using a Waters micromass ZQ. High resolution mass spectrometry was performed using an Agilent 1100 LC equipped with a photodiode array detector, and a Micromass QTOF I equipped with a 4 GHz digital-time converter. Optical rotation was determined in a 10 cm cell at 20 °C using a Perkin-Elmer Model 341 polarimeter. HPLC analysis was performed using an Agilent 1100 LC equipped with an Atlantis T3 (3 µm, 2.1x100 mm) C18 column and ELSD detection.

![Chemical structures](image)  

(a) Ac<sub>2</sub>O, Pyr, 0 °C → rt, 97%; (b) HCl, MeOH, 60 °C; (c) pMPCH(OMe)<sub>2</sub>, DMF, 69% (2 steps).

**Acetyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranoside (8)**
D-Galactosamine hydrochloride (7; 12.35 g, 57.27 mmol) in anhydrous pyridine (80 mL) was cooled to 0 °C, and then Ac₂O (40 mL) added dropwise over 15 min and the flask slowly warmed to rt. After 16 hours, the reaction mixture was concentrated to a syrup via co-evaporation with toluene (2 x 50 mL), and then the crude material was purified via MPLC on silica gel using 0→60% acetone – CH₂Cl₂ to afford the pure product as a white solid (21.63 g, 55.55 mmol, 97% yield). \( R_f = 0.11 \) (3:7 acetone : CH₂Cl₂). [α]₉⁺: +9.8° (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δH 5.70 (d, 1H, J = 8.8 Hz, H-1), 5.43 (d, 1H, J = 9.5 Hz, NH), 5.38 (dd, 1H, J = 3.3, <1 Hz, H-4), 5.09 (dd, 1H, J = 11.3, 3.3 Hz, H-3), 4.45 (ddd, 1H, J = 11.2, 9.2, 9.2 Hz, H-2), 4.17 (dd, 1H, J = 11.3, 6.6 Hz, H-6a), 4.12 (dd, 1H, J = 11.3, 6.5 Hz, H-6b), 4.02 (dd, 1H, J = 6.5, 6.5, 1.0 Hz, H-5), 2.17 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.94 (s, 3H, NHAc). ¹³C NMR (CDCl₃, 125 MHz): δC 170.97 (C=O), 170.62 (C=O), 170.47 (C=O), 170.39 (C=O), 169.79 (C=O), 93.28 (C-1), 72.11 (C-5), 70.55 (C-3), 66.56 (C-4), 61.52 (C-6), 50.06 (C-2), 23.54 (NHAc), 21.11 (OAc), 20.89 (2x OAc), 20.86 (OAc). LRMS m/z calc’d for C₁₆H₂₃NNaO₁₀ (M+Na)⁺: 412.12; found: 412.10.

Methyl 2-acetamido-2-deoxy-4,6-O-(p-methoxybenzylidene)-α-D-galactopyranoside (9)

The starting material (8; 5.953 g, 15.29 mmol) was dissolved into 2% v/v conc. HCl in MeOH and left heating at 60 °C. After 3 days, the mixture was evaporated to dry to afford the desired methyl α-glycoside crude product: \( R_f = 0.29 \) (1:4 CH₃OH : CH₂Cl₂); LRMS m/z calc’d for C₂₉H₁₇NNaO₆ (M+Na)⁺: 258.10; found: 258.06. The crude material and p-methoxybenzylidene dimethyl acetal (3.2 mL, 19 mmol) were added to anhydrous DMF (35 mL) under Ar (acidity maintained from previous step). After 18 hours of mixing at ambient temperature, the reaction mixture was neutralized with Et₃N (to pH 8), concentrated to a syrup, and then purified via MPLC on silica gel using 0→60% acetone (w/ 0.1% NH₄OH) – CH₂Cl₂ to afford the desired product as a white solid (3.722 g, 10.53 mmol, 69% yield over 2 steps). \( R_f = 0.57 \)
(0.01:10.29:9.96:60 NH₄OH : MeOH : acetone : CH₂Cl₂). [α]D²⁰: +135° (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δH 7.46 – 7.43 (m, 2H, Ar), 6.90 – 6.87 (m, 2H, Ar), 5.91 (d, 1H, J = 8.9 Hz, NH), 5.50 (s, 1H, PhCH), 4.83 (d, 1H, J = 3.5 Hz, H-1), 4.44 (ddd, 1H, J = 10.9, 9.0, 3.5 Hz, H-2), 4.24 (dd, 1H, J = 12.5, 1.4 Hz, H-6), 4.15 (d, 1H, J = 3.4, <1 Hz, H-4), 4.03 (dd, 1H, J = 12.5, 1.6 Hz, H-6), 3.82 – 3.79 (m, 4H, H-3 and ArOCH₃), 3.60 – 3.59 (m, 1H, H-5), 3.38 (s, 3H, OCH₃), 2.94 (d, 1H, J = <1 Hz, 3- OH), 2.02 (s, 3H, Ac). ¹³C NMR (CDCl₃, 125 MHz): δC 171.39 (C=O), 160.30 (Ar), 130.30 (Ar), 127.85 (Ar), 113.70 (Ar), 101.30 (PhCH), 99.49 (C-1), 75.59 (C-4), 69.40 (C-6), 68.97 (C-3), 62.86 (C-5), 55.56 (OCH₃), 55.43 (ArOCH₃), 50.54 (C-2), 23.51 (Ac). LRMS m/z calc’d for C₁₇H₂₃NNaO₇ (M+Na)⁺: 376.14; found: 376.08.

Methyl 2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (11)

The glycosyl acceptor (9; 602 mg, 1.70 mmol), glycosyl donor [ref 1] (10; 2.726 g, 4.255 mmol), and crushed molecular sieves (3 Å, 1.905 mg) in anhydrous CH₂Cl₂ (10 mL) and anhydrous acetonitrile (20 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then N-iodosuccinimide (NIS) was added (777 mg, 3.45 mmol) followed by the drop-wise addition of triflic acid (TfOH) (23 µL, 0.26 mmol). After 5 hours, the mixture was neutralized with Et₃N (to pH 8), warmed to ambient temperature, filtered over Celite, and diluted with CH₂Cl₂ (100 mL). The organic phase was washed with sat’d Na₂S₂O₃(aq) solution (100 mL), sat’d NaCl(aq) solution (100 mL), dried with Na₂SO₄, filtered, and evaporated to dry to afford the crude product: LRMS m/z calc’d for C₅₁H₄₉NNaO₁₆...
The crude mixture was then dissolved into AcOH (16 mL) and H2O (4 mL). After 3 hours at ambient temperature, the mixture was neutralized with excess sat’d NaHCO3(aq) solution and the product extracted with CH2Cl2 (2 x 100 mL). The combined organic phases were washed with sat’d NaHCO3(aq) (3 x 100 mL), dried with Na2SO4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→10% MeOH – CH2Cl2 to afford the pure product as a white solid (1.007 g, 1.237 mmol, 73% yield over 2 steps). Rf = 0.38 (1:19 MeOH : CH2Cl2). [α]D20: +170° (c 1.0, CHCl3).

**1H NMR (CDCl3, 500 MHz):** δ H 8.07 – 8.05 (m, 2H, Ar), 8.04 – 8.02 (m, 2H, Ar), 7.99 – 7.97 (m, 2H, Ar), 7.74 – 7.71 (m, 2H, Ar), 7.61 – 7.55 (m, 2H, Ar), 7.53 – 7.50 (m, 1H, Ar), 7.48 – 7.44 (m, 2H, Ar), 7.44 – 7.38 (m, 5H, Ar), 7.22 – 7.18 (m, 2H, Ar), 5.95 (dd, 1H, J = 3.5, <1 Hz, Gal_H4), 5.84 (dd, 1H, J = 10.4, 8.0 Hz, Gal_H2), 5.64 (dd, 1H, J = 10.4, 3.5 Hz, Gal_H3), 5.45 (d, 1H, J = 8.9 Hz, NH), 5.04 (d, 1H, J = 8.0 Hz, Gal_H1), 4.73 (d, 1H, J = 3.6 Hz, GalN_H1), 4.62 – 4.54 (m, 3H, Gal_H6a, Gal_H6b, and GalN_H2), 4.44 – 4.41 (m, 1H, Gal_H5), 4.21 – 4.19 (m, 1H, GalN_H4), 3.84 (dd, 1H, J = 10.8, 3.0 Hz, GalN_H3), 3.77 (ddd, 1H, J = 11.2, 6.2, 2.7 Hz, GalN_H6a), 3.71 – 3.69 (m, 1H, GalN_H5), 3.54 (ddd, 1H, J = 11.3, 8.9, 4.3 Hz, GalN_H6b), 3.27 (s, 3H, OCH3), 3.10 (d, 1H, J = <1 Hz, 4-OH), 2.44 (dd, 1H, J = 8.8, 3.0 Hz, 6-OH), 1.34 (s, 3H, Ac).

**13C NMR (CDCl3, 125 MHz):** δ C 170.10 (Ac), 166.27 (C=O), 165.81 (C=O), 165.94 (C=O), 133.91 (Ar), 133.77 (Ar), 133.71 (Ar), 133.53 (Ar), 130.18 (Ar), 130.00 (Ar), 129.91 (Ar), 129.90 (Ar), 129.44 (Ar), 129.26 (Ar), 128.85 (Ar), 128.81 (Ar), 128.79 (Ar), 128.71 (Ar), 128.47 (Ar), 102.07 (Gal_C1), 98.82 (GalN_C1), 79.86 (GalN_C3), 72.24 (Gal_C5), 71.62 (Gal_C3), 69.90 (Gal_C2), 69.44 (GalN_C5), 68.87 (GalN_C4), 68.36 (Gal_C4), 62.85 (GalN_C6), 62.83 (Gal_C6), 55.30 (OCH3), 48.05 (GalN_C2), 22.56 (Ac).

LRMS m/z calc’d for C43H43NNaO15 (M+Na)+: 836.25; found: 836.23.

**Methyl β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (1)**

The starting material (11; 83 mg, 0.10 mmol) was dissolved into anhydrous MeOH (1.5 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10) and the mixture heated at 50 °C. After 14 hours, the reaction mixture was cooled to rt, neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and then evaporated to dry. The crude
material was purified via RPLC on C-18 silica gel using 0→40% acetonitrile – H₂O to afford the pure product as a white solid (36 mg, 0.091 mmol, 89% yield); data characterization is in agreement with that previously published [ref 2]. [α]D: +95° (c 1.0, H₂O). ¹H NMR (D₂O, 500 MHz): δH 4.77 – 4.76 (m, 1H, GalN_H1), 4.45 (d, 1H, J = 7.8 Hz, Gal_H1), 4.32 (dd, 1H, J = 11.1, 3.7 Hz, GalN_H2), 4.22 (dd, 1H, J = 2.9, <1 Hz, GalN_H4), 3.99 (dd, 1H, J = 11.1, 3.1 Hz, GalN_H3), 3.95 (ddd, 1H, J = 7.4, 4.9, <1 Hz, GalN_H5), 3.90 (dd, 1H, J = 3.4, <1 Hz, GalH4), 3.77 (dd, 1H, J = 11.7, 7.4 Hz, Gal_H6a), 3.78 – 3.72 (m, 2H, Gal_H6a and GalN_H6b), 3.72 (dd, 1H, J = 11.7, 4.5 Hz, Gal_H6b), 3.64 (ddd, 1H, J = 7.7, 4.5, <1 Hz, Gal_H5), 3.60 (dd, 1H, J = 9.9, 3.4 Hz, Gal_H3), 3.50 (dd, 1H, J = 9.9, 7.8 Hz, Gal_H2), 3.38 (s, 3H, OCH₃), 2.01 (s, 3H, Ac). ¹³C NMR (D₂O, 125 MHz): δC 175.23 (C=O), 105.34 (Gal_C1), 98.95 (GalN_C1), 77.92 (GalN_C3), 75.59 (Gal_C5), 73.17 (Gal_C3), 71.24 (Gal_C2), 71.07 (GalN_C5), 69.38 (GalN_C4), 69.21 (Gal_C4), 61.86 (GalN_C6), 61.59 (Gal_C6), 55.72 (OCH₃), 49.22 (GalN_C2), 22.64 (Ac). ESI-HRMS m/z calc’d for C₁₅H₂₇N₃NaO₁₁ (M+Na)⁺: 420.1482; found: 420.1482. HPLC purity analysis: 99.1%, Rₜ 4.54 minutes, Atlantis T3 C18 column.

(a) NIS, TfOH, CH₂Cl₂/CH₃CN, 0 °C, 76%; (b) NH₂NH₂·H₂O, EtOH, 80 °C; then Ac₂O, NaHCO₃, 63%.
Methyl 2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl-(1→3)[3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (13)

The glycosyl acceptor (11; 135 mg, 0.166 mmol), glycosyl donor [ref 6] (12; 87 mg, 0.18 mmol), and crushed molecular sieves (3 Å, 190 mg) in anhydrous CH$_2$Cl$_2$ (1.0 mL) and anhydrous acetonitrile (1.0 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then NIS was added (67 mg, 0.30 mmol) followed by the drop-wise addition of TfOH solution (15% v/v in CH$_2$Cl$_2$; 10 µL, 0.017 mmol). After 3 hours, the mixture was neutralized with Et$_3$N (to pH 8), warmed to ambient temperature, and diluted with CH$_2$Cl$_2$ (60 mL). The organic phase was washed with saturated Na$_2$S$_2$O$_3$(aq) solution (60 mL), saturated NaCl(aq) solution (60 mL), dried with Na$_2$SO$_4$, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→20% acetone (containing 0.05% v/v NH$_4$OH(aq)) – CH$_2$Cl$_2$ to afford the pure product as a white solid (156 mg, 0.127 mmol, 76% yield). $R_f$ = 0.58 (0.01:19.99:80 NH$_4$OH : acetone : CH$_2$Cl$_2$).

$[\alpha]_{D}^{20}: +123^\circ$ (c 1.0, CHCl$_3$).

$^1$H NMR (CDCl$_3$, 500 MHz): δH 8.09 – 8.06 (m, 2H, Ar), 8.02 – 7.99 (m, 2H, Ar), 7.93 – 7.90 (m, 2H, Ar), 7.87 – 7.71 (m, 6H, Ar), 7.65 – 7.59 (m, 2H, Ar), 7.52 – 7.46 (m, 5H, Ar), 7.43 – 7.40 (m, 1H, Ar), 7.39 – 7.35 (m, 2H, Ar), 7.24 – 7.20 (m, 2H, Ar), 5.93 (dd, 1H, $J = 3.2$, <1 Hz, Gal_H4), 5.82 (dd, 1H, $J = 10.7$, 9.1 Hz, GlcN_H3), 5.76 (dd, 1H, $J = 10.4$, 8.0 Hz, Gal_H2), 5.56 (dd, 1H, $J = 10.4$, 3.4 Hz, Gal_H3), 5.33 (d, 1H, $J = 8.4$ Hz, GlcN_H1), 5.18 (dd, 1H, $J = 9.6$, 9.6 Hz, GlcN_H4), 5.06 (d, 1H, $J = 8.9$ Hz, NH), 4.85 (d, 1H, $J = 8.0$ Hz, Gal_H1), 4.53 – 4.50 (m, 2H, Gal_H6$^a$ and Gal_H6$^b$), 4.35 (dd, 1H, $J = 12.2$, 4.2 Hz, GlcN_H6$^a$), 4.35 – 4.29 (m, 2H, GalN_H2 and Gal_H5), 4.29 (dd, 1H, $J = 10.8$, 8.5 Hz, GlcN_H2), 4.22 (d, 1H, $J = 3.5$ Hz, GalN_H1), 4.19 (dd, 1H, $J = 12.2$, 2.0 Hz, GlcN_H6$^b$), 3.96 – 3.95 (m, 1H, GalN_H4), 3.87 (ddd, 1H, $J = 10.1$, 4.3, 2.3 Hz, GlcN_H5), 3.76 (dd, 1H, $J = 10.6$, 2.4 Hz, GalN_H6$^a$), 3.69 (dd, 1H, $J = 10.7$, 8.5 Hz, GalN_H6$^b$), 3.65 – 3.61 (m, 2H, GalN_H3 and GalN_H5), 2.81 (s, 3H, OCH$_3$), 2.76 (d, 1H, $J = <1$ Hz, GalN_4-OH), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.86 (s, 3H, OAc), 1.28 (s, 3H, NHAc). $^{13}$C NMR (CDCl$_3$, 125 MHz): δC 170.91 (C=O), 170.28 (C=O), 169.87 (C=O), 169.77 (C=O), 167.71
(C=O), 166.18 (C=O), 165.79 (C=O), 165.72 (C=O), 164.84 (C=O), 134.52 (Ar), 134.01 (Ar), 133.74 (Ar), 133.71 (Ar), 133.60 (Ar), 131.68 (Ar), 130.27 (Ar), 129.96 (Ar), 129.38 (Ar), 129.26 (Ar), 128.94 (Ar), 128.86 (Ar), 128.76 (Ar), 128.72 (Ar), 128.53 (Ar), 102.02 (Gal_C1), 99.13 (GlcN_C1), 98.23 (Fuc_C1), 79.92 (GalN_C3), 72.19 (Gal_C5), 72.05 (GlcN_C5), 71.61 (Gal_C3), 71.09 (GalN_C6), 70.83 (GalN_C3), 69.82 (Gal_C2), 69.19 (GlcN_C4), 68.54 (GalN_C5), 68.25 (GalN_C4), 68.16 (Gal_C4), 62.57 (Gal_C6), 62.24 (GlcN_C6), 54.89 (GlcN_C2), 54.50 (OCH3), 47.88 (GalN_C2), 22.62 (NHAc), 20.99 (OAc), 20.86 (OAc), 20.67 (OAc). LRMS m/z calc’d for C63H62N2NaO24 (M+Na)+: 1253.36; found: 1253.32.

**Methyl β-d-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-d-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-d-galactopyranoside (2)**

![Methyl β-d-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-d-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-d-galactopyranoside (2)](attachment:image)

The protected trisaccharide (13; 146 mg, 0.119 mmol) and NH₂NH₂·H₂O (47 µL, 0.98 mmol) were added to EtOH (3.0 mL) and left mixing at 80 °C. After 16 hours, the mixture was cooled to ambient temperature and then NaHCO₃ (406 mg, 4.83 mmol) and Ac₂O added (0.23 mL, 2.4 mmol). After another 4 hours, the solution was evaporated to dry and the crude mixture purified via RPLC on C-18 silica gel using 0→30% acetonitrile – H₂O to afford the pure product as a white solid (45 mg, 0.075 mmol, 63% yield over 2 steps). [α]D²⁰: +54° (c 0.3, H₂O). ¹H NMR (D₂O, 500 MHz): δH 4.75 (d, 1H, J = 3.8 Hz, GalN_H1), 4.52 (d, 1H, J = 8.5 Hz, GlcN_H1), 4.44 (d, 1H, J = 7.8 Hz, Gal_H1), 4.31 (dd, 1H, J = 11.1, 3.7 Hz, GalN_H2), 4.20 (dd, 1H, J = 3.0, <1 Hz, GalN_H4), 4.06 (dd, 1H, J = 10.6, 3.0 Hz, GalN_H6a), 4.03 (ddd, 1H, J = 11.0, 2.6, <1 Hz, GalN_H5), 3.99 (dd, 1H, J = 11.1, 3.1 Hz, GalN_H3), 3.93 (dd, 1H, J = 12.3, 1.8 Hz, GlcN_H6a), 3.90 (dd, 1H, J = 3.3, <1 Hz, Gal_H4), 3.77 – 3.70 (m, 4H, Gal_H6a, GlcN_H6a, Gal_H6b, and GalN_H6b), 3.71 (dd, 1H, J = 10.4, 8.5 Hz, GlcN_H2), 3.63 (ddd, 1H, J = 7.6, 4.7, <1 Hz, Gal_H5), 3.60 (dd, 1H, J = 9.9, 3.4 Hz, Gal_H3), 3.53 (dd, 1H, J = 10.3, 8.3 Hz, GlcN_H3), 3.50 (dd, 1H, J = 10.0, 7.9 Hz, Gal_H2), 3.46 – 3.41 (m, 2H, GlcN_H5 and GlcN_H4), 3.35 (s, 3H, OCH₃), 2.00 (s, 6H, 2x Ac). ¹³C NMR (D₂O, 125 MHz): δC 175.25 (C=O), 175.09 (C=O), 105.34 (Gal_C1), 102.27 (GlcN_C1), 98.82 (GalN_C1), 77.73
(GalN\_C3), 76.49 (GlcN\_C5), 75.61 (Gal\_C5), 74.43 (GlcN\_C3), 73.17 (Gal\_C3), 71.25 (Gal\_C2), 70.67 (GalN\_C6), 70.59 (GlcN\_C4), 69.93 (GalN\_C5), 69.62 (GalN\_C4), 69.22 (Gal\_C4), 61.60 (Gal\_C6), 61.36 (GlcN\_C6), 56.15 (GlcN\_C2), 55.51 (OCH\_3), 49.17 (Gal\_C2), 22.81 (Ac), 22.65 (Ac). ESI-HRMS m/z calc’d for C\textsubscript{23}H\textsubscript{40}N\textsubscript{2}Na\textsubscript{16}(M+Na): 623.2276; found: 623.2276. HPLC purity analysis: >99.5%, R\textsubscript{t} 5.39 minutes, Atlantis T3 C18 column.

(a) NaH, DMF/THF; then NiCl\textsubscript{2}; then BnBr, 57%; (b) BzCl, Py, CH\textsubscript{2}Cl\textsubscript{2}, 86%.

Ethyl 3-\textit{O}-benzyl-4,6-\textit{O}-benzylidene-1-thio-\textit{\beta}-\textit{D}-galactopyranoside (15)

The starting material [ref 3] (14; 506 mg, 1.62 mmol) and NaH (60% oil dispersion; 138 mg, 3.45 mmol) were added to anhydrous THF (20 mL) and anhydrous DMF (2 mL) and left mixing at ambient temperature for 1 hour. Anhydrous NiCl\textsubscript{2} was added [ref 4] (209 mg, 1.6 mmol), and after another hour benzyl bromide was added drop-wise over 5 min (212 µL, 1.78 mmol). After 20 hours the reaction was quenched via the slow addition of MeOH (2 mL), 3 drops of AcOH were added, and then the mixture evaporated to dry. The crude material was redissolved into CH\textsubscript{2}Cl\textsubscript{2} (120 mL) and then washed with sat’d NaCl\textsubscript{(aq)} solution (2 x 120 mL), dried with Na\textsubscript{2}SO\textsubscript{4}, filtered, and then evaporated to dry. The crude material was purified via MPLC using 0\textendash;30% EtOAc – toluene to afford the pure product as a white solid (374 mg, 0.929 mmol, 57% yield). R\textsubscript{f} = 0.53 (1:4 acetone : toluene). [\textalpha]\textsubscript{D}\textsuperscript{20}: +6.7° (c 1.0, CHCl\textsubscript{3}). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): δH 7.52 – 7.48 (m, 2H, Ar), 7.41 – 7.27 (m, 8H, Ar), 5.44 (s, 1H, PhCH\textsubscript{2}), 4.79 (d, 1H, J = 12.3 Hz, PhCH\textsubscript{2}H\textsuperscript{\text{b}}), 4.76 (d, 1H, J = 12.3 Hz, PhCH\textsubscript{2}H\textsuperscript{\text{b}}), 4.35 (d, 1H, J = 9.6 Hz, H-
Ethyl 2-O-benzyloxy-3-O-benzyl-4,6-O-benzylidene-1-thio-β-D-galactopyranoside (16)

The starting material (15; 1.112 g, 2.763 mmol) and benzoyl chloride (0.42 mL, 3.6 mmol) were added to anhydrous pyridine (2.0 mL) and anhydrous CH₂Cl₂ (8.0 mL). After 3 hours, the mixture was quenched via the dropwise addition of MeOH (1 mL), evaporated to dry, and then purified via MPLC using 0→10% EtOAc – toluene to afford the pure product as a white solid (1.207 g, 2.382 mmol, 86% yield). Rᵣ = 0.47 (1:9 acetone : toluene). [α]ᵢD²⁰: +25° (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δH 8.05 – 8.02 (m, 2H, Ar), 7.60 – 7.53 (m, 3H, Ar), 7.47 – 7.44 (m, 2H, Ar), 7.40 – 7.34 (m, 3H, Ar), 7.24 – 7.16 (m, 5H, Ar), 5.73 (dd, 1H, J = 9.7, 9.7 Hz, H-2), 5.51 (s, 1H, PhCH₂), 4.68 (d, 1H, J = 12.8 Hz, PhCH₃H), 4.61 (d, 1H, J = 12.8 Hz, PhCH₃H), 4.53 (d, 1H, J = 9.8 Hz, H-1), 4.35 (dd, 1H, J = 12.3, 1.5 Hz, H-6a), 4.27 (dd, 1H, J = 3.4, <1 Hz, H-4), 4.01 (dd, 1H, J = 12.3, 1.7 Hz, H-6b), 3.74 (dd, 1H, J = 9.6, 3.4 Hz, H-3), 3.46 – 3.45 (m, 1H, H-5), 2.91 (dq, 1H, J = 12.3, 7.5 Hz, SCH₂H₂CH₃), 2.76 (dq, 1H, J = 12.3, 7.5 Hz, SCH₂H₂CH₃), 1.27 (dd, 3H, J = 7.5, 7.5 Hz, SCH₂CH₃). ¹³C NMR (CDCl₃, 125 MHz): δC 165.46 (C=O), 138.01 (Ar), 137.94 (Ar), 133.21 (Ar), 130.33 (Ar), 130.07 (Ar), 129.25 (Ar), 128.53 (Ar), 128.51 (Ar), 128.41 (Ar), 127.92 (Ar), 127.88 (Ar), 126.68 (Ar), 101.56 (PhCH), 83.09 (C-1), 78.32 (C-3), 73.63 (C-4), 71.20 (PhCH₂), 70.34 (C-5), 69.58 (C-6), 68.95 (C-2), 22.92 (SCH₂CH₃), 15.05 (SCH₂CH₃). LRMS m/z calc’d for C₂₂H₂₈NaO₅S (M+Na)⁺: 529.17; found: 529.22.
Methyl 3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-(p-methoxybenzylidene)-α-D-galactopyranoside (17)

The glycosyl acceptor (9; 209 mg, 0.591 mmol), glycosyl donor (16; 359 mg, 0.709 mmol), and molecular sieves (3 Å; 343 mg) in anhydrous CH₂Cl₂ (4.0 mL) and anhydrous acetonitrile (2.0 mL) were left mixing at rt under Ar. After 1 hour, the mixture was cooled to -40 °C and then N-iodosuccinimide (239 mg, 1.06 mmol) and dropwise triflic acid (7 µL, 0.08 mmol) were added. Three equivalent batches were prepared in parallel (2.527 mmol glycosyl donor combined), and after 4 hours, the mixture was neutralized with Et₃N, warmed to ambient temperature, filtered over Celite, combined and diluted with CH₂Cl₂ (250 mL). The organic
phase was washed with sat’d Na$_2$S$_2$O$_3$(aq) solution (250 mL), sat’d NaCl(aq) solution (250 mL), dried with Na$_2$SO$_4$, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH$_4$OH) – CH$_2$Cl$_2$ to afford the semi-pure product: $R_f = 0.28$ (1:4 acetone w/ 0.1% NH$_4$OH : CH$_2$Cl$_2$). LRMS m/z calc’d for C$_{44}$H$_{47}$NNaO$_{13}$ (M+Na)$^+$: 820.29; found: 820.15. The mixture was then added to anhydrous MeOH (5.0 mL), and NaOMe solution added (1.5 M NaOMe in MeOH; to pH 10). After 14 hours at 50 °C, the mixture was neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH$_4$OH – CH$_2$Cl$_2$) to afford the pure product as a white solid (989 mg, 1.43 mmol, 56% yield over 2 steps). $R_f = 0.13$ (1:4 acetone w/ 0.1% NH$_4$OH : CH$_2$Cl$_2$).

$[\alpha]_D^{20}$: +127° (c 0.67, CHCl$_3$).

$^1$H NMR (CDCl$_3$, 500 MHz): δH 7.52 – 7.46 (m, 4H, Ar), 7.39 – 7.37 (m, 2H, Ar), 6.88 – 6.85 (m, 2H, Ar), 5.87 (d, 1H, $J = 8.4$ Hz, NH), 5.56 (s, 1H, pMPC$\text{H}$), 5.45 (s, 1H, PhC$\text{H}$), 4.95 (d, 1H, $J = 3.6$ Hz, GalNAc$\text{H}_1$), 4.81 (d, 1H, $J = 12.4$ Hz, PhC$\text{H}_3^b$), 4.77 (d, 1H, $J = 12.4$ Hz, PhC$\text{H}_2^b$), 4.67 (ddd, 1H, $J = 11.0, 8.5, 3.6$ Hz, GalNAc$\text{H}_2$), 4.39 (d, 1H, $J = 7.7$ Hz, Gal$\text{H}_1$), 4.38 – 4.37 (m, 1H, GalNAc$\text{H}_4$), 4.25 (dd, 1H, $J = 12.3, 1.5$ Hz, Gal$\text{H}_6^a$), 4.23 (dd, 1H, $J = 12.4, 1.5$ Hz, GalNAc$\text{H}_6^a$), 4.09 – 4.08 (m, 1H, Gal$\text{H}_4$), 4.06 (ddd, 1H, $J = 9.7, 7.8, 1.6$ Hz, Gal$\text{H}_2$), 4.02 (dd, 1H, $J = 12.3, 1.7$ Hz, Gal$\text{H}_6^b$), 4.02 (dd, 1H, $J = 12.4, 1.5$ Hz, GalNAc$\text{H}_6^b$), 3.94 (dd, 1H, $J = 11.0, 3.2$ Hz, GalNAc$\text{H}_3$), 3.80 (s, 3H, OCH$_3$), 3.62 – 3.61 (m, 1H, GalNAc$\text{H}_5$), 3.43 (dd, 1H, $J = 9.8, 3.5$ Hz, Gal$\text{H}_3$), 3.41 (s, 3H, OCH$_3$), 3.34 – 3.33 (m, 1H, Gal$\text{H}_5$), 2.85 (d, 1H, $J = 1.7$ Hz, 2-OH), 2.00 (s, 3H, Ac). $^{13}$C NMR (CDCl$_3$, 125 MHz): δC 171.13 (C=O), 160.23 (Ar), 138.61 (Ar), 137.99 (Ar), 130.64 (Ar), 129.27 (Ar), 128.56 (Ar), 128.45 (Ar), 128.11 (Ar), 128.07 (Ar), 127.90 (Ar), 126.33 (Ar), 113.73 (Ar), 105.05 (Gal$\text{C}_1$), 101.47 (PhCH), 101.20 (pMPC$\text{H}$), 99.65 (GalNAc$\text{C}_1$), 78.68 (Gal$\text{C}_3$), 76.13 (GalNAc$\text{C}_4$), 75.67 (GalNAc$\text{C}_3$), 73.96 (Gal$\text{C}_4$), 71.88 (PhCH$_2$), 69.63 (Gal$\text{C}_2$), 69.50, 69.38 (Gal$\text{C}_6$ and GalNAc$\text{C}_6$), 67.03 (Gal$\text{C}_5$), 63.31 (GalNAc$\text{C}_5$), 55.64 (OCH$_3$), 55.53 (OCH$_3$), 48.73 (GalNAc$\text{C}_2$), 23.87 (Ac). LRMS m/z calc’d for C$_{37}$H$_{43}$NNaO$_{12}$ (M+Na)$^+$: 716.27; found: 716.26.
Methyl 2,3,4-tri-O-benzyl-α-L-fucopyranosyl-(1→2)-3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-(p-methoxybenzylidene)-α-D-galactopyranoside (19)

The glycosyl acceptor (17; 198 mg, 0.285 mmol), glycosyl donor [ref 5] (18; 212 mg, 0.366 mmol), and molecular sieves (3 Å; 246 mg) in anhydrous CH₂Cl₂ (5.0 mL) were left mixing at rt under Ar. After 1 hour, the mixture was cooled to -78 °C and then trimethylsilyl triflate was added dropwise (7.5 μL, 0.041 mmol). Three equivalent batches were prepared in parallel (0.836 mmol glycosyl donor combined), and after 3 hours the mixtures were neutralized with Et₃N, filtered over Celite, combined and then diluted with CH₂Cl₂ (500 mL). The organic phase was washed with sat’d NaHCO₃(aq) solution (500 mL), sat’d NaCl(aq) solution (500 mL), dried with Na₂SO₄, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH₄OH) – CH₂Cl₂ to afford the pure product as a white solid (670 mg, 0.603 mmol, 72% yield). Rf = 0.45 (1:4 acetone w/ 0.1% NH₄OH : CH₂Cl₂). [α]D₂⁰: +34° (c 1.0, CHCl₃). 

¹H NMR (CDCl₃, 500 MHz): δH 7.54 – 7.50 (m, 2H, Ar), 7.48 – 7.45 (m, 2H, Ar), 7.35 – 7.32 (m, 5H, Ar), 7.29 – 7.20 (m, 13H, Ar), 7.19 – 7.12 (m, 5H, Ar), 6.78 – 6.75 (m, 2H, Ar), 6.11 (d, 1H, J = 8.3 Hz, NH), 5.50 (s, 1H, pMPC H), 5.48 (d, 1H, J = 3.8 Hz, Fuc_H1), 5.43 (s, 1H, PhCH), 4.89 (d, 1H, J = 11.4 Hz, PhCHF²H), 4.89 (d, 1H, J = 3.5 Hz, GalNAc_H1), 4.81 (d, 1H, J = 11.9 Hz, PhCHF²H), 4.76 (d, 1H, J = 11.9 Hz, PhCHF²H, and Gal_H1), 4.54 (d, 1H, J = 11.4 Hz, PhCHF²H), 4.53 (d, 1H, J = 12.1 Hz, PhCHF²H), 4.39 (dd, 1H, J = 3.0, <1 Hz, GalNAc_H4), 4.25 – 4.18 (m, 4H, Gal_H6, GalNAc_H6, Gal_H2, and Fuc_H5), 4.12 (dd, 1H, J = 3.6, <1 Hz, Gal_H4), 4.04 – 3.96 (m, 3H, Gal_H6, GalNAc_H6, and GalNAc_H3), 3.94 (dd, 1H, J = 10.1, 3.8 Hz, Fuc_H2), 3.89 (dd, 1H, J = 10.2, 2.6 Hz, Fuc_H3), 3.74 (s, 3H, OCH₃), 3.73 – 3.72 (m, 1H, Fuc_H4), 3.66 (dd, 1H, J = 9.5, 3.7 Hz, Gal_H3), 3.58 – 3.57 (m, 1H, GalNAc_H5), 3.37 (s, 3H, OCH₃), 3.34 – 3.32 (m, 1H, Gal_H5), 1.87 (s, 3H, Ac), 0.92 (d, 3H, J = 6.4 Hz, Fuc_H6). 

¹³C NMR (CDCl₃, 125 MHz): δC 170.03 (C=O), 160.09 (Ar), 139.51 (Ar), 139.41 (Ar), 138.86 (Ar), 138.73 (Ar),
Methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (3)

The starting material (19; 37 mg, 0.033 mmol) and Pd(OH)$_2$ (20% w/w on carbon, 13 mg) in MeOH (0.8 mL) and H$_2$O (0.8 mL) were left mixing under H$_2$ at atmospheric pressure. After 48 hours, the solid catalyst was removed via filtration and the solution evaporated to dry. The crude material was purified via RPLC on C-18 silica gel using 0→60% acetonitrile – H$_2$O to afford the pure product as a white solid (14 mg, 0.026 mmol, 78% yield); data characterization is in agreement with that previously published [ref 2]. $[\alpha]_D^{20}$: +42° (c 0.5, H$_2$O). $^1$H NMR (D$_2$O, 500 MHz): δH 5.22 (d, 1H, Fuc_H1), 4.75 (m, 1H, GalN_H1), 4.62 (d, 1H, J = 7.7 Hz, Gal_H1), 4.21 (dq, 1H, J = 6.6, <1 Hz, Fuc_H5), 4.13 – 4.09 (m, 2H, GalN_H2 and GalN_H4), 4.11 (dd, 1H, J = 11.2, 2.9 Hz, GalN_H3), 3.96 (ddd, 1H, J = 6.2, 6.2, <1 Hz, GalN_H5), 3.89 (dd, 1H, J = 3.4, <1 Hz, Gal_H4), 3.82 (dd, 1H, J = 9.7, 3.4 Hz, Gal_H3), 3.79 – 3.71 (m, 5H, GalN_H6a, Fuc_H2, GalN_H6b, Gal_H6a, and Gal_H6b), 3.67 – 3.60 (m, 4H, Fuc_H4, Fuc_H3, Gal_H5, and Gal_H2), 3.35 (s, 3H, OCH$_3$), 2.03 (s, 3H, Ac), 1.18 (d, 3H, J = 6.6 Hz, Fuc_H6). $^{13}$C NMR (D$_2$O, 125 MHz): δC 174.31 (C=O), 102.63 (Gal_C1), 99.94 (Fuc_C1), 98.53 (GalN_C1), 76.93 (Gal_C2), 75.66 (Gal_C5), 74.14 (GalN_C3), 74.21 (Gal_C3), 74.11 (Fuc_C4), 71.06 (GalN_C5), 70.21 (Fuc_C3), 69.71 (Gal_C4 and GalN_C4),
68.72 (Fuc_C2), 67.44 (Fuc_C5), 61.88 (GalN_C6), 61.56 (Gal_C6), 55.74 (OCH₃), 50.06 (GalN_C2), 22.59 (Ac), 16.00 (Fuc_C6). ESI-HRMS m/z calc’d for C_{21}H_{37}N_{15}O_{15} (M+Na)^+: 566.2061; found: 566.2061. HPLC purity analysis: >99.5%, Rₜ 5.55 minutes, Atlantis T3 C18 column.

(a) Ac₂O, Py, 96%; (b) 9, NIS, TfOH, CH₂Cl₂/ACN, 0 °C, 73%; (c) NaOMe, MeOH, 98%; (d) NIS, TfOH, -40 °C, 47%; (e) AcOH, H₂O, 70 °C; (f) Ac₂O, Py, 71% (2 steps); (g) NaOMe, MeOH/H₂O, 66%.
Ethyl 2,3-di-O-acetyl-4,6-O-benzylidene-1-thio-β-D-galactopyranoside (20)

The starting material (14; 1.071 g, 3.429 mmol) was dissolved into anhydrous pyridine (6.0 mL) and Ac₂O (6.0 mL), and left mixing at rt. After 3 hours, the reaction mixture was evaporated to dry via co-evaporation with toluene (3 x 10 mL), and then the crude material was purified via MPLC on silica gel using 0→40% acetone–toluene to afford the pure product as a white solid (1.306 g, 3.294 mmol, 96% yield). \( R_f = 0.64 \) (1:4 acetone : toluene). \([\alpha]_{D}^{20}: +28^\circ\) (c 1.0, CHCl₃).

\(^1\)H NMR (CDCl₃, 500 MHz): \( \delta H \) 7.51 – 7.46 (m, 2H, Ar), 7.40 – 7.34 (m, 3H, Ar), 5.48 (s, 1H, PhCH), 5.46 (dd, 1H, \( J = 9.9, 9.9 \) Hz, H-2), 4.98 (dd, 1H, \( J = 10.0, 3.5 \) Hz, H-3), 4.45 (d, 1H, \( J = 9.8 \) Hz, H-1), 4.39 (dd, 1H, \( J = 3.5, <1 \) Hz, H-4), 4.31 (dd, 1H, \( J = 12.5, 1.5 \) Hz, H-6\( ^a \)), 3.99 (dd, 1H, \( J = 12.5, 1.6 \) Hz, H-6\( ^b \)), 3.53 – 3.52 (m, 1H, H-5), 2.87 (dq, 1H, \( J = 12.3, 7.5 \) Hz, SCH\( ^bCH\)\( _3 \)), 2.72 (dq, 1H, \( J = 12.3, 7.5 \) Hz, SCH\( ^aPH\)\( _3 CH\)\( _3 \)), 2.05 (s, 3H, Ac), 1.28 (dd, 3H, \( J = 7.5, 7.5 \) Hz, SCH\( _2CH\)\( _3 \)). \(^{13}\)C NMR (CDCl₃, 125 MHz): \( \delta C \) 170.69 (C=O), 169.53 (C=O), 137.72 (Ar), 129.21 (Ar), 128.30 (Ar), 126.46 (Ar), 101.20 (PhCH), 82.86 (C-1), 73.71 (C-4), 73.10 (C-3), 69.80 (C-5), 69.18 (C-6), 66.70 (C-2), 22.90 (SCH\( _2CH\)\( _3 \)), 20.96 (Ac), 20.95 (Ac), 14.88 (SCH\( _2CH\)\( _3 \)). LRMS \( m/z \) calc’d for C\( _{19}H_{24}NaO_{7}S \) (M+Na\(^+\)): 419.11; found: 419.11.

Methyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-(p-methoxybenzylidene)-α-D-galactopyranoside (21)

The glycosyl acceptor (9; 504 mg, 1.43 mmol), glycosyl donor (20; 1.119 g, 2.823 mmol), and crushed molecular sieves (3 Å, 1.476 g) in anhydrous CH\( _2\)Cl\( _2 \) (10 mL) and anhydrous acetonitrile (5 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then NIS added (641 mg, 2.85 mmol) followed by the drop-wise
addition of TfOH (12 µL, 0.14 mmol). After 5 hours, the mixture was neutralized with Et₃N (to pH 8), warmed to ambient temperature, diluted with CH₂Cl₂ (100 mL), and filtered over Celite. The organic phase was washed with saturated Na₂S₂O₃(aq) solution (100 mL), saturated NaCl(aq) solution (100 mL), dried with Na₂SO₄, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0 → 40% acetone (containing 0.05% v/v conc’d NH₄OH : CH₂Cl₂) – CH₂Cl₂ to afford the mostly pure intermediate as a white solid (722 mg, 1.05 mmol, 73% yield). $R_f = 0.39 \text{ (3:7 acetone w/ 0.1% NH}_4\text{OH : CH}_2\text{Cl}_2)$. $[\alpha]_{D}^{20} = +122^\circ$ (c 1.0, CH₃OH).

$1^H$ NMR (CD₃OD, 500 MHz): $\delta$H 7.53 – 7.49 (m, 2H, Ar), 7.46 – 7.43 (m, 2H, Ar), 7.36 – 7.33 (m, 3H, Ar), 6.85 – 6.82 (m, 2H, Ar), 5.59 (s, 1H, PhCH), 5.57 (s, 1H, pMPC), 5.27 (dd, 1H, $J = 10.4, 8.0$ Hz, Gal_H2), 5.05 (dd, 1H, $J = 10.4, 3.7$ Hz, Gal_H3), 4.88 (d, 1H, $J = 8.0$ Hz, Gal_H1), 4.72 (d, 1H, $J = 3.5$ Hz, GalNAc_H1), 4.56 (dd, 1H, $J = 11.2, 3.5$ Hz, GalNAc_H2), 4.49 (dd, 1H, $J = 3.3, <1$ Hz, GalNAc_H3), 4.42 (dd, 1H, $J = 3.7, 0.7$ Hz, Gal_H4), 4.25 (dd, 1H, $J = 12.4, 1.5$ Hz, Gal_H4a), 4.17 (dd, 1H, $J = 12.5, 1.6$ Hz, Gal_H6b), 4.16 – 4.13 (m, 1H, GalNAc_H6b), 4.12 – 4.09 (m, 2H, GalNAc_H6b and GalNAc_H3), 3.77 (s, 3H, ArOCH₃), 3.71 – 3.70 (m, 1H, GalNAc_H5), 3.67 – 3.66 (m, 1H, Gal_H5), 3.42 (s, 3H, OAc), 2.01 (s, 3H, NHAc), 2.00 (s, 3H, OAc). $^{13}$C NMR (CD₃OD, 125 MHz): $\delta$C 173.24 (C=O), 172.03 (C=O), 171.69 (C=O), 161.52 (Ar), 139.58 (Ar), 132.31 (Ar), 130.16 (Ar), 129.25 (Ar), 128.96 (Ar), 127.71 (Ar), 114.40 (Ar), 102.94 (Gal_C1), 102.32 (ArCH), 102.05 (ArCH), 101.12 (GalNAc_C1), 77.34 (GalNAc_C4), 75.49 (GalNAc_C3), 75.09 (Gal_C4), 73.39 (Gal_C3), 70.51 (Gal_C2), 70.38 (GalNAc_C6), 70.12 (Gal_C6), 67.95 (Gal_C5), 64.62 (GalNAc_C5), 55.98 (OCH₃), 55.83 (ArOCH₃), 50.05 (GalNAc_C2), 23.09 (NHAc), 21.08 (OAc), 20.73 (OAc). LRMS m/z calc’d for C₃₄H₄₁NNaO₁₄ (M+Na)⁺: 710.24; found: 710.21.

Methyl 4,6-O-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-(p-methoxybenzylidene)-α-D-galactopyranoside (22)

The starting material (21; 548 mg, 0.797 mmol) was dissolved into anhydrous MeOH (6.0 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10). After 2
hours at ambient temperature, the reaction mixture was neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and then evaporated to dry. The crude material was purified via MPLC on silica gel using 0→100% acetone (w/ 0.1% NH₄OH) – CH₂Cl₂ to afford the pure product as a white solid (470 mg, 0.779 mmol, 98% yield). \( R_f = 0.07 \) (1:1 acetone w/ 0.1% NH₄OH).

\( \text{[α]} \text{D}_{20} = +104^\circ \) (c 1.0, CH₃OH).

\( \text{1H NMR (CD}_3\text{OD, 500 MHz): δH 7.59 – 7.55 (m, 2H, Ar), 7.49 – 7.46 (m, 2H, Ar), 7.39 – 7.33 (m, 3H, Ar), 6.90 – 6.86 (m, 2H, Ar), 5.65 (s, 1H, PhC} \text{H}, 5.61 (s, 1H, pMPCH), 4.82 (d, 1H, \( J = 3.4 \) Hz, GalNAc_H1), 4.62 (dd, 1H, \( J = 11.2, 3.4 \) Hz, GalNAc_H2), 4.55 (dd, 1H, \( J = 3.2, <1 \) Hz, GalNAc_H4), 4.52 (d, 1H, \( J = 7.4 \) Hz, Gal_H1), 4.19 (dd, 1H, \( J = 12.4, 1.7 \) Hz, Gal_H6b), 4.17 (dd, 1H, \( J = 12.5, 1.4 \) Hz, GalNAc_H6b), 4.15 – 4.11 (m, 2H, GalNAc_H6b and GalNAc_H3), 3.81 (s, 3H, ArOCH₃), 3.75 – 3.74 (m, 1H, GalNAc_H5), 3.67 (dd, 1H, \( J = 9.9, 7.4 \) Hz, Gal_H2), 3.61 (dd, 1H, \( J = 9.9, 3.5 \) Hz, Gal_H3), 3.58 – 3.57 (m, 1H, Gal_H5), 3.46 (s, 3H, OCH₃), 3.46 (s, 3H, OCH₃), 3.38 (s, 3H, OCH₃), 3.20 (s, 3H, NHAc). \( ^{13} \text{C NMR (CD}_3\text{OD, 125 MHz): δC 174.61 (C=O), 162.06 (Ar), 140.19 (Ar), 132.69 (Ar), 129.50 (Ar), 129.49 (Ar), 128.10 (Ar), 114.78 (Ar), 106.75 (Gal_C1), 102.83, 102.76 (PhCH and pMPCH), 101.50 (GalNAc_C1), 78.01 (GalNAc_C4), 77.92 (Gal_C4), 76.14 (GalNAc_C3), 74.01 (Gal_C3), 72.23 (Gal_C2), 70.83 (Gal_C6), 70.80 (GalNAc_C6), 68.64 (Gal_C5), 64.99 (GalNAc_C5), 56.35 (OCH₃), 56.20 (ArOCH₃), 50.74 (GalNAc_C2), 23.33 (NHAc). LRMS \text{m/z calc’d for } C_{30}H_{37}N_{12}O_{12} (M+Na)^+: 626.22; found: 626.18.

Methyl 4,6-O-benzylidene-3-O-(methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero-\( \alpha \)-D-galacto-2-nonulopyranosylonate)-\( \beta \)-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-(p-methoxybenzylidene)-\( \alpha \)-D-galactopyranoside (24)

The glycosyl acceptor (22; 399 mg, 0.661 mmol), glycosyl donor (23; 601 mg, 1.01 mmol), and crushed molecular sieves (3 Å, 866 mg) in anhydrous CH₂Cl₂ (5.0 mL) and anhydrous acetonitrile (5.0 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to -40 °C, and then NIS (298 mg, 1.32 mmol) and TfOH (9 µL, 0.10 mmol)
were added. After 24 hours, the mixture was neutralized with Et$_3$N (to pH 8), warmed to ambient temperature, filtered over Celite, and evaporated to dry. The crude material was redissolved into CH$_2$Cl$_2$ (30 mL), washed with saturated NaHCO$_3$ solution (2x 30 mL), saturated NaCl solution (30 mL), dried with Na$_2$SO$_4$, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0 → 30% acetone (w/ 0.1% NH$_4$OH) – CH$_2$Cl$_2$ to afford the pure product as a white solid (333 mg, 0.309 mmol, 47% yield).

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.49 – 7.46 (m, 4H, Ar), 7.34 – 7.31 (m, 3H, Ar), 6.85 – 6.82 (m, 2H, Ar), 6.50 (d, 1H, $J = 7.8$ Hz, GalNAc_NH), 5.55 (s, 1H, ArC$_H$), 5.51 (ddd, 1H, $J = 9.7$, 7.1, 2.5 Hz, Neu5Ac_H8), 5.40 – 5.37 (m, 2H, Neu5Ac_NH and ArCH), 5.24 (dd, 1H, $J = 9.4$, 1.3 Hz, Neu5Ac_H7), 5.04 (d, 1H, $J = 3.3$ Hz, GalNAc_H1), 4.87 (ddd, 1H, $J = 12.2$, 9.8, 4.5 Hz, Neu5Ac_H4), 4.64 (ddd, 1H, $J = 11.1$, 7.8, 3.3 Hz, GalNAc_H2), 4.55 (d, 1H, $J = 7.7$ Hz, Gal_H1), 4.41 (dd, 1H, $J = 2.8$, <1 Hz, GalNAc_H4), 4.38 (dd, 1H, $J = 12.2$, 2.4 Hz, Neu5Ac_H9a), 4.25 – 4.20 (m, 3H, GalNAc_H6a, Gal_H6a, and Gal_H3), 4.11 (dd, 1H, $J = 12.4$, <2 Hz, Gal_H6b), 4.07 – 4.01 (m, 4H, Neu5Ac_H5, GalNAc_H3, GalNAc_H6b, and Neu5Ac_H6), 3.95 – 3.89 (m, 3H, Neu5Ac_H9b, Gal_H4, and Gal_H2), 3.78 (s, 3H, OCH$_3$), 3.64 – 3.62 (s, 4H, GalNAc_H5 and OCH$_3$), 3.50 – 3.49 (m, 1H, Gal_H5), 3.40 (s, 3H, OCH$_3$), 2.91 – 2.89 (broad s, 1H, Gal_2-OH), 2.71 (dd, 1H, $J = 12.9$, 4.5 Hz, Neu5Ac_H3$_{eq}$), 2.19 (s, 3H, OAc), 2.15 (s, 3H, OAc), 2.05 – 2.00 (m, 10H, OAc, NHAc, Neu5Ac_H3$_{ax}$, and OAc), 1.88 (s, 3H, NHAc). LRMS $m/z$ calc’d for C$_{50}$H$_{64}$N$_2$NaO$_{24}$ (M+Na)$^+$: 1099.37; found: 1099.27.

**Methyl 2,4,6-tri-O-acetyl-3-O-(methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-O-acetyl-2-deoxy-α-D-galactopyranoside (25)**

The starting material (24; 96 mg, 0.089 mmol) was dissolved into AcOH (1.2 mL) and H$_2$O (0.3 mL) and left mixing at 70 °C. After 7 hours, the mixture was evaporated to dry via co-evaporation with toluene (3 x 2 mL), and then redissolved into pyridine (1.0 mL) and Ac$_2$O (1.0 mL). After 18 hours, the reaction mixture was concentrated to a syrup via co-evaporation with toluene (3 x 2 mL), and then the crude material was purified via MPLC on silica gel using 0 → 15% MeOH – CH$_2$Cl$_2$ to afford the pure product as a white solid (68 mg, 0.063 mmol, 71%
yield over 2 steps. $^1$H NMR (CDCl$_3$, 500 MHz): δH 6.40 (d, 1H, $J = 8.1$ Hz, GalNAc$_N$NH),
5.70 (ddd, 1H, $J = 9.3$, 7.7, 2.6 Hz, Neu5Ac$_H$8), 5.42 (dd, 1H, $J = 2.8$, <1 Hz, GalNAc$_H$4),
5.31 (dd, 1H, $J = 9.4$, 2.7 Hz, Neu5Ac$_H$7), 5.23 (d, 1H, $J = 10.2$ Hz, Neu5Ac$_N$NH), 5.00 (dd, 1H, $J = 10.1$, 8.1 Hz, Gal$_H$2), 4.91 (d, 1H, $J = 3.5$ Hz, GalNAc$_H$1), 4.89 – 4.83 (m, 2H, Gal$_H$2 and Neu5Ac$_H$4), 4.68 (d, 1H, $J = 8.1$ Hz, Gal$_H$2), 4.50 – 4.45 (m, 2H, GalNAc$_H$3 and Neu5Ac$_H$2a), 4.39 (dd, 1H, $J = 12.1$, 2.6 Hz, Neu5Ac$_H$9a), 4.21 (dd, 1H, $J = 11.4$, 4.6 Hz, GalNAc$_H$6a), 4.11 – 4.04 (m, 3H, Neu5Ac$_H$5, GalNAc$_H$5, and Gal$_H$6), 4.01 (dd, 1H, $J = 12.4$, 12.4 Hz, Neu5Ac$_H$3ax).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δC 171.50 (Ac), 171.11 (Ac), 171.03 (Ac), 170.81 (Ac), 170.51 (Ac), 170.49 (Ac), 170.47 (Ac), 170.26 (Ac), 170.24 (Ac), 170.07 (Ac), 168.12 (Neu5Ac$_C$1), 101.63 (Gal$_C$1), 98.66 (GalNAc$_C$1), 96.93 (Neu5Ac$_C$2), 74.42 (GalNAc$_C$3), 72.07 (Neu5Ac$_C$6), 71.51 (Gal$_C$3), 70.95 (Gal$_C$5), 69.58 (GalNAc$_C$4), 69.41 (Neu5Ac$_C$4), 69.02 (Gal$_C$2), 67.75 (Gal$_C$4), 67.61 (Neu5Ac$_C$7), 67.49 (GalNAc$_C$5), 67.40 (Neu5Ac$_C$8), 63.47 (Neu5Ac$_C$9), 63.24 (GalNAc$_C$6), 62.03 (Gal$_C$6), 55.38 (OCH$_3$), 53.35 (OCH$_3$), 49.35 (GalNAc$_C$2), 49.15 (Neu5Ac$_C$5), 37.59 (Neu5Ac$_C$3), 23.30 (NHAc), 23.28 (NHAc), 21.62 (OAc), 21.25 (OAc), 21.02 (2x OAc), 20.93 (4x OAc), 20.85 (OAc). LRMS $m/z$ calc’d for C$_{45}$H$_{64}$N$_2$NaO$_{28}$ (M+Na)$^+$: 1103.35; found: 1103.29.

**Methyl 3-O-(sodium 5-acetamido-3,5-dideoxy-d-glycero-α-d-galacto-2-nonulopyranosylonylate)-β-d-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-d-galactopyranoside (4)**

The starting material (25; 55 mg, 0.051 mmol) was dissolved into 50% aqueous MeOH (1.0 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10). After 14 hours, the reaction mixture was neutralized with acidic resin (Amberlite IR-120H; to
pH 8), filtered, and evaporated to dry. The crude material was purified via RPLC on C-18 silica gel using 0→20% acetonitrile – H₂O to afford the pure product as a white solid (24 mg, 0.034 mmol, 66% yield). [α]D 20°: +32° (c 1.0, H₂O). ¹H NMR (D₂O, 500 MHz): δH 4.79 (d, 1H, J = 3.7 Hz, GalNAc_H1), 4.52 (d, 1H, J = 7.9 Hz, Gal_H1), 4.31 (dd, 1H, J = 11.1, 3.7 Hz, GalNAc_H2), 4.22 (dd, 1H, J = 2.7, <1 Hz, GalNAc_H4), 4.06 (dd, 1H, J = 9.8, 3.2 Hz, Gal_H3), 4.00 (dd, 1H, J = 11.1, 3.0 Hz, GalNAc_H3), 3.96 – 3.92 (m, 2H, GalNAc_H5 and Gal_H4), 3.87 (ddd, 1H, J = 8.9, 6.3, 2.5 Hz, NeuNAc_H8), 3.86 – 3.81 (m, 2H, NeuNAc_H9a and NeuNAc_H5), 3.79 – 3.60 (m, 8H, GalNAc_H6a, GalNAc_H6b, Gal_H6a, Gal_H6b, NeuNAc_H4, NeuNAc_H9b, Gal_H5, and NeuNAc_H6), 3.58 (dd, 1H, J = 8.9, 1.7 Hz, NeuNAc_H7), 3.53 (dd, 1H, J = 9.8, 7.9 Hz, Gal_H2), 3.38 (s, 3H, OCH₃), 2.75 (dd, 1H, J = 12.4, 4.6 Hz, NeuNAc_H3eq), 2.02 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.77 (dd, 1H, J = 12.2, 12.2 Hz, NeuNAc_H3ax). ¹³C NMR (D₂O, 125 MHz): δC 175.64 (C=O), 175.26 (C=O), 174.55 (NeuNAc_C1), 105.12 (Gal_C1), 100.33 (NeuNAc_C2), 98.93 (GalNAc_C1), 78.07 (GalNAc_C3), 76.30 (Gal_C3), 75.41 (Gal_C5), 73.44 (NeuNAc_C6), 72.48 (NeuNAc_C8), 71.09 (GalNAc_C5), 69.68 (Gal_C2), 69.23 (GalNAc_C4), 69.02 (NeuNAc_C4), 68.72 (NeuNAc_C7), 68.00 (Gal_C4), 63.16 (NeuNAc_C9), 61.90 (GalNAc_C6), 61.60 (Gal_C6), 55.73 (OCH₃), 52.30 (NeuNAc_C5), 49.22 (GalNAc_C2), 40.39 (NeuNAc_C3), 22.71 (Ac), 22.68 (Ac). ESI-HRMS m/z calc’d for C₂₆H₄₃N₂NaO₁₉ (M+Na)⁺: 733.2255; found: 733.2250. HPLC purity analysis: 98.2%, R, 5.40 minutes, Atlantis T3 C18 column.
Methyl 2,3,4-tri-O-benzyl-α-L-fucopyranosyl-(1→2)-3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (26)

The starting material (19; 440 mg, 0.396 mmol) was dissolved into AcOH (3.2 mL) and H₂O (0.8 mL) and left mixing at ambient temperature. After 3 hours, the mixture was diluted with CH₂Cl₂ (50 mL) and sat’d NaHCO₃(aq) solution (50 mL), and then solid NaHCO₃ added until gas evolution subsided. The aqueous layer was removed and re-extracted with CH₂Cl₂ (2 x 20 mL), and then the combined organic layers washed with sat’d NaHCO₃(aq) solution (50 mL), dried with Na₂SO₄, filtered, and evaporated to dry. The crude material was purified via MPLC
on silica gel using 0→100% acetone – CH₂Cl₂ to afford the pure product as a white solid (280 mg, 0.282 mmol, 71% yield). \( R_f = 0.49 \) (1:1 acetone : CH₂Cl₂). \([\alpha]_D^{20} = +20^\circ \) (c 1.0, CHCl₃).

\(^1\)H NMR (CDCl₃, 500 MHz): δH 7.53 – 7.50 (m, 2H, Ar), 7.38 – 7.20 (m, 20H, Ar), 7.19 – 7.14 (m, 3H, Ar), 6.95 (d, 1H, \( J = 7.6 \) Hz, NH), 5.45 (s, 1H, PhCH\(_2\)), 5.29 (d, 1H, \( J = 3.8 \) Hz, Fuc_H1), 5.00 (d, 1H, \( J = 12.0 \) Hz, PhCH\(_2\)\(^b\)), 4.85 (d, 1H, \( J = 3.4 \) Hz, GalNAc_H1), 4.82 (d, 1H, \( J = 12.1 \) Hz, PhCH\(_2\)\(^b\)), 4.78 (d, 1H, \( J = 12.2 \) Hz, PhCH\(_2\)\(^b\)), 4.73 (d, 1H, \( J = 11.9 \) Hz, PhCH\(_2\)\(^b\)), 4.60 (d, 1H, \( J = 11.4 \) Hz, PhCH\(_2\)\(^b\)), 4.54 (d, 1H, \( J = 7.3 \) Hz, Gal_H1), 4.40 (dd, 1H, \( J = 10.2, 3.8 \) Hz, Fuc_H2), 3.99 (dd, 1H, \( J = 12.4, 3.8 \) Hz, Fuc_H2), 3.87 (dd, 1H, \( J = 10.2, 3.8 \) Hz, Fuc_H2), 3.79 – 3.73 (m, 3H, Fuc_H4, GalNAc_H5, and GalNAc_H6\(^b\)), 3.60 (dd, 1H, \( J = 9.5, 3.4 \) Hz, Gal_H3), 3.38 – 3.37 (m, 1H, Gal_H5), 3.28 (s, 3H, OCH₃), 3.26 – 3.25 (m, 1H, 4-OH), 2.87 – 2.84 (m, 1H, 6-OH), 1.80 (s, 3H, Ac), 1.24 (d, 3H, \( J = 6.5 \) Hz, Fuc_H6). \(^{13}\)C NMR (CDCl₃, 125 MHz): δC 170.45 (C=O), 139.10 (Ar), 139.05 (Ar), 138.75 (Ar), 138.48 (Ar), 137.77 (Ar), 129.18 (Ar), 128.44 (Ar), 128.36 (Ar), 128.26 (Ar), 128.12 (Ar), 127.93 (Ar), 127.63 (Ar), 127.60 (Ar), 127.58 (Ar), 127.54 (Ar), 127.50 (Ar), 127.35 (Ar), 126.47 (Ar), 103.24 (Gal_C1), 101.08 (PhCH), 98.61, 98.53 (GalNAc_C1 and Fuc_C1), 78.89 (Fuc_C3), 78.51 (Gal_C3), 78.22 (Fuc_C4), 78.16 (Gal_C2), 77.07 (GalNAc_C3), 76.32 (Fuc_C2), 75.05 (PhCH₂), 73.89 (Gal_C4), 73.15 (PhCH₂), 72.94 (PhCH₂), 72.25 (PhCH₂), 69.34 (GalNAc_C5), 69.30 (Gal_C6), 69.20 (GalNAc_C4), 67.92 (Fuc_C5), 66.74 (Gal_C5), 63.03 (GalNAc_C6), 55.42 (OCH₃), 48.99 (GalNAc_C2), 23.06 (Ac), 16.78 (Fuc_C6). LRMS \( m/z \) calc’d for C₅₆H₆₅NNaO₁₅ (M+Na): 1014.43; found: 1014.54.
Methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (5)

The glycosyl acceptor (26; 188 mg, 0.189 mmol), glycosyl donor [ref 6] (12; 118 mg, 0.246 mmol), and crushed molecular sieves (3 Å, 171 mg) in anhydrous CH₂Cl₂ (1.5 mL) and anhydrous acetonitrile (1.5 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then NIS was added (78 mg, 0.35 mmol) followed by the drop-wise addition of TfOH (10 µL, 0.02 mmol). After 2 hours, the mixture was neutralized with Et₃N (to pH 8), warmed to ambient temperature, and diluted with CH₂Cl₂ (60 mL). The organic phase was washed with saturated Na₂S₂O₃(aq) solution (60 mL), saturated NaCl(aq) solution (60 mL), dried with Na₂SO₄, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→40% acetone (containing 0.1% v/v NH₄OH(aq)) – CH₂Cl₂ to afford a mostly pure product (containing a small amount of a lower Rf by-product): Rf = 0.75 (0.01:19.99:80 NH₄OH : acetone : CH₂Cl₂). LRMS m/z calc’d for C₇₆H₈₄N₂NaO₂₄(M+Na)⁺: 1431.53; found: 1431.54. The product and NH₂NH₂·H₂O (112 µL, 2.34 mmol) were then added to EtOH (4.0 mL) and left mixing at 80 °C. After 20 hours, the mixture was evaporated to dry, redissolved into MeOH (4.0 mL), and then NaHCO₃ (788 mg, 9.38 mmol) and Ac₂O added (0.44 mL, 4.7 mmol). After another 4 hours, the solution was evaporated to dry and the crude mixture purified via MPLC on silica gel using 0→30% MeOH – CH₂Cl₂ to afford the partially deprotected product: Rf = 0.07 (3:7 acetone : CH₂Cl₂). LRMS m/z calc’d for C₅₇H₇₂N₂NaO₂₀(M+Na)⁺: 1127.46; found: 1127.28. The starting material and Pd(OH)₂ (20% w/w on carbon; 40 mg) were added to 50% aqueous MeOH (2.0 mL), the atmosphere evacuated, and the flask flushed with H₂(g) (via balloon). After 24 hours, the catalyst was removed via filtration, the mixture evaporated to dry, and the crude material purified via RPLC on C-18 silica gel using 0→60% acetonitrile – H₂O to afford the pure product as a white solid (92 mg, 0.12 mmol, 63% yield over 4 steps). [α]D₂⁰: +5.4° (c 0.5, H₂O).

¹H NMR (D₂O, 500 MHz): δH 5.21 (d, 1H, J = 4.0 Hz, Fuc_H1), 4.73 (d, 1H, J = 3.4 Hz,
GalN_H1), 4.61 (d, 1H, J = 7.7 Hz, Gal_H1), 4.53 (d, 1H, J = 8.5 Hz, GlcN_H1), 4.20 (dq, 1H, J = 6.6, <1 Hz, Fuc_H5), 4.16 (dd, 1H, J = 11.0, 3.4 Hz, GalN_H2), 4.14 (dd, 1H, J = 2.8, <1 Hz, GalN_H4), 4.11 (dd, 1H, J = 11.1, 2.9 Hz, GalN_H3), 4.08 – 4.03 (m, 2H, GalN_H6a and GalN_H5), 3.93 (dd, 1H, J = 12.5, 1.6 Hz, GlcN_H6a), 3.88 (dd, 1H, J = 3.4, <1 Hz, GlcN_H2), 3.82 (dd, 1H, J = 9.7, 3.4 Hz, Gal_H3), 3.78 – 3.71 (m, 5H, Fuc_H2, Gal_H6a, GlcN_H6b, Gal_H6b, and GalN_H6b), 3.71 (dd, 1H, J = 10.2, 8.5 Hz, GlcN_H2), 3.67 – 3.61 (m, 3H, Fuc_H4, Fuc_H3, and Gal_H5), 3.61 (dd, 1H, J = 10.3, 8.2 Hz, GlcN_H3), 3.48 – 3.41 (m, 2H, GlcN_H5 and GlcN_H4), 3.32 (s, 3H, OCH3), 2.03 (s, 3H, Ac), 2.00 (s, 3H, Ac), 1.18 (d, 3H, J = 6.6 Hz, Fuc_H6).

13C NMR (D2O, 125 MHz): δC 175.11 (C=O), 174.31 (C=O), 102.60 (Gal_C1), 102.29 (GlcN_C1), 99.93 (Fuc_C1), 98.37 (GalN_C1), 76.94 (Gal_C2), 76.49 (GlcN_C5), 75.67 (Gal_C5), 74.45 (GlcN_C3), 74.21 (GalN_C3 and Gal_C3), 72.50 (Fuc_C4), 70.82 (GalN_C6), 70.58 (GlcN_C4), 70.20 (Fuc_C3), 69.98, 69.93 (Gal_C4 and GalN_C5), 69.72 (Gal_C4), 68.72 (Fuc_C2), 67.43 (Fuc_C5), 61.57 (Gal_C6), 61.35 (GlcN_C6), 56.15 (GlcN_C2), 55.48 (OCH3), 49.97 (GalN_C2), 22.81 (Ac), 22.58 (Ac), 15.99 (Fuc_C6). ESI-HRMS m/z calc’d for C29H50N2NaO20 (M+Na)+: 769.2855; found: 769.2853. HPLC purity analysis: >99.5%, Rf 5.49 minutes, Atlantis T3 C18 column.

\[ \text{Ethyl 2-deoxy-2-phthalimido-1-thio-\(\beta\)-D-glucopyranoside (27)} \]
The starting material (12; 6.98 g, 14.6 mmol) was dissolved into anhydrous MeOH (50 mL) and anhydrous CH₂Cl₂ (20 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10). After 4 hours at ambient temperature, the reaction mixture was neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and then evaporated to dry to afford the pure product as a white solid (4.97 g, 14.1 mmol, 97% yield). Rᵣ = 0.21 (2:3 acetone : toluene). [α]D²⁰: +8.8° (c 1.0, CH₃OH). ¹H NMR (CD₃OD, 500 MHz): δH 7.90 – 7.81 (m, 4H, Ar), 5.32 (d, 1H, J = 10.5 Hz, H-1), 4.27 (dd, 1H, J = 10.2, 8.4 Hz, H-3), 4.05 (dd, 1H, J = 10.3, 10.3 Hz, H-5, 5.54 (s, 1H, PhCH₃), 3.76 (ddd, 1H, J = 9.6, 9.6, 5.6 Hz, H-6⁶), 3.45 (ddd, 1H, J = 12.0, 5.5, 2.0 Hz, H-5), 3.40 (dd, 1H, J = 9.8, 8.4 Hz, H-4), 2.73 (dq, 1H, J = 12.7, 7.5 Hz, SCC₆H₅CH₃), 2.63 (dq, 1H, J = 12.7, 7.5 Hz, CH₃CH₂), 1.17 (dd, 3H, J = 7.4, 7.4 Hz, SCH₂CH₃). ¹³C NMR (CD₃OD, 125 MHz): δC 169.86 (C=O), 169.58 (C=O), 135.77 (Ar), 135.69 (Ar), 133.36 (Ar), 133.09 (Ar), 124.57 (Ar), 124.24 (Ar), 82.73 (C-5), 82.62 (C-1), 73.87 (C-3), 72.61 (C-4), 63.09 (C-6), 57.88 (C-2), 25.00 (SCH₂CH₃), 15.44 (SCH₂CH₃). LRMS m/z calc’d for C₁₆H₁₉NNaO₆S (M+Na)^+: 376.08; found: 376.01.

**Ethyl 4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (28)**

![Chemical Structure](image)

The starting material (27; 4.974 g, 14.08 mmol), benzylidene dimethyl acetal (2.6 mL, 17 mmol), and camphorsulfonic acid (to pH 3) were added to anhydrous DMF (40 mL) under Ar. After 16 hours of mixing at ambient temperature, the reaction mixture was neutralized with Et₃N (to pH 8), evaporated to dry, and then purified via MPLC on silica gel using 0→70% acetone – toluene to afford the desired product as a white solid (4.977 g, 11.27 mmol, 80% yield). Rᵣ = 0.56 (1:4 acetone : toluene). [α]D²⁰: −4.2° (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δH 7.83 – 7.79 (m, 2H, Ar), 7.69 – 7.64 (m, 2H, Ar), 7.50 – 7.46 (m, 2H, Ar), 7.36 – 7.32 (m, 3H, Ar), 5.54 (s, 1H, PhCH), 5.36 (d, 1H, J = 10.6 Hz, H-1), 4.60 (dd, 1H, J = 9.6, 3.8 Hz, H-3), 4.35 (dd, 1H, J = 10.4, 4.9 Hz, H-6⁶), 4.27 (dd, 1H, J = 10.3, 10.3 Hz, H-2), 3.76 (dd, 1H, J = 10.2, 10.2 Hz, H-6⁶), 3.62 (ddd, 1H, J = 9.6, 9.6, 4.9 Hz, H-5), 3.54 (dd, 1H, J = 9.2, 9.2 Hz, H-4), 3.05 (d, 1H, J = 3.8 Hz, 3-OH), 2.68 (dq, 1H, J = 12.5, 7.4 Hz, SCH₆H₅CH₃), 2.63 (dq, 1H, J = 12.5, 7.4 Hz, SCH₆H₅CH₃), 1.17 (dd, 3H, J = 7.4, 7.4 Hz, SCH₂CH₃). ¹³C NMR (CDCl₃, 125 MHz): δC 168.35 (C=O), 167.82 (C=O), 137.10 (Ar), 134.29 (Ar), 131.74 (Ar), 131.60 (Ar), 129.41 (Ar), 128.43 (Ar), 126.44 (Ar), 123.93 (Ar), 82.62 (C-1), 73.87 (C-3), 72.61 (C-4), 63.09 (C-6), 57.88 (C-2), 25.00 (SCH₂CH₃), 15.44 (SCH₂CH₃).
123.41 (Ar), 101.93 (PhCH), 82.14 (C-4), 81.94 (C-1), 70.46 (C-5), 69.53 (C-3), 68.67 (C-6), 55.69 (C-2), 24.27 (SCH₂CH₃), 14.98 (SCH₂CH₃). LRMS m/z calc’d for C₂₂H₂₃NNaO₆S (M+Na)⁺: 464.11; found: 464.11.

**Ethyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalamido-1-thio-β-D-glucopyranoside (29)**

![Chemical Structure](image)

The starting material (28; 3.001 g, 6.797 mmol) and benzyl bromide (1.1 mL, 9.3 mmol) were added to anhydrous DMF (30 mL), and then NaH added portion-wise (60% oil dispersion; 385 mg, 9.62 mmol). After 1 hour, the reaction was quenched via the drop-wise addition of H₂O and the mixture diluted with EtOAc (200 mL) and saturated NaCl(aq) solution (500 mL). The aqueous layer was removed and then re-extracted with EtOAc (200 mL). The combined organic phases were washed with sat’d NaCl(aq) solution (2 x 500 mL), dried with Na₂SO₄, filtered, and then evaporated to dry. The crude material was purified via MPLC using 0→10% EtOAc – toluene to afford the pure product as a white solid (2.604 g, 4.899 mmol, 72% yield). Rₚ = 0.71 (1:4 EtOAc : toluene). [α]D²⁰: +54° (c 1.0, CHCl₃).

**¹H NMR (CDCl₃, 500 MHz):**

δH 7.85 – 7.82 (m, 1H, Ar), 7.73 – 7.63 (m, 3H, Ar), 7.54 – 7.51 (m, 2H, Ar), 7.42 – 7.35 (m, 3H, Ar), 7.01 – 6.98 (m, 2H, Ar), 6.94 – 6.86 (m, 3H, Ar), 5.63 (s, 1H, PhCH₂), 5.35 (d, 1H, J = 10.6 Hz, H-1), 4.80 (d, 1H, J = 12.3 Hz, PhCH₂PHb), 4.51 (d, 1H, J = 12.3 Hz, PhCH₂PHb), 4.46 (dd, 1H, J = 9.9, 9.0 Hz, H-3), 4.41 (dd, 1H, J = 10.4, 4.9 Hz, H-6b), 4.30 (dd, 1H, J = 10.5, 10.0 Hz, H-2), 3.83 (dd, 1H, J = 10.2, 10.2 Hz, H-6b), 3.82 (dd, 1H, J = 9.2, 9.2 Hz, H-4), 3.70 (ddd, 1H, J = 9.6, 9.6, 4.9 Hz, H-5), 2.68 (dq, 1H, J = 12.5, 7.4 Hz, SCH₂²CH₃), 2.62 (dq, 1H, J = 12.5, 7.4 Hz, SCH₂²CH₃), 1.16 (dd, 3H, J = 7.4, 7.4 Hz, SCH₂CH₃). **¹³C NMR (CDCl₃, 125 MHz):**

δC 167.90 (C=O), 167.58 (C=O), 137.99 (Ar), 137.49 (Ar), 134.13 (Ar), 134.01 (Ar), 131.80 (Ar), 131.74 (Ar), 129.20 (Ar), 128.46 (Ar), 128.27 (Ar), 128.21 (Ar), 127.59 (Ar), 126.23 (Ar), 123.72 (Ar), 123.49 (Ar), 101.48 (PhCH), 83.22 (C-4), 81.96 (C-1), 75.60 (C-3), 74.37 (PhCH₂), 70.63 (C-5), 68.90 (C-6), 54.85 (C-2), 24.24 (SCH₂CH₃), 15.03 (SCH₂CH₃). LRMS m/z calc’d for C₃₀H₂₉NNaO₆S (M+Na)⁺: 554.16; found: 554.09.
Ethyl 3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (30)

A solution of the starting material (29; 2.726 g, 5.128 mmol) in anhydrous CH₂Cl₂ (25 mL) was cooled to 0 °C under Ar, and then Et₃SiH (4.1 mL, 26 mmol) and BF₃·Et₂O (1.3 mL, 10 mmol) were slowly added. After 5 hours, the reaction mixture was neutralized with Et₃N (to pH 8), warmed back to ambient temperature, and then quenched via the slow addition of MeOH (10 mL). The crude mixture was evaporated to dry, and then purified via MPLC on silica gel using 0→30% EtOAc – toluene to afford the pure product as a white solid (2.430 g, 4.554 mmol, 89% yield). Rf = 0.43 (1:4 EtOAc : toluene).

[α]D²⁰: +38° (c 1.0, CHCl₃).

1H NMR (CDCl₃, 500 MHz): δH 7.82 – 7.80 (m, 1H, Ar), 7.72 – 7.66 (m, 3H, Ar), 7.38 – 7.29 (m, 5H, Ar), 7.06 – 7.02 (m, 2H, Ar), 6.98 – 6.92 (m, 3H, Ar), 5.27 (d, 1H, J = 10.0 Hz, H-1), 4.75 (d, 1H, J = 12.2 Hz, PhCH₂Hₐ), 4.63 (d, 1H, J = 11.9 Hz, PhCH₂Hₐ), 4.58 (d, 1H, J = 11.9 Hz, PhCH₂Hₐ), 4.54 (d, 1H, J = 12.2 Hz, PhCH₂Hₐ), 4.38 (dd, 1H, J = 10.2, 7.9 Hz, H-6a), 3.85 – 3.81 (m, 1H, H-4), 3.77 (dd, 1H, J = 10.1, 5.2 Hz, H-6b), 3.68 (ddd, 1H, J = 9.6, 5.0, 5.0 Hz, H-5), 2.97 (d, 1H, J = 2.5 Hz, 4-OH), 2.66 (dq, 1H, J = 12.5, 7.4 Hz, Sch₂H₃), 2.59 (dq, 1H, J = 12.5, 7.4 Hz, Sch₂H₃), 1.16 (dd, 3H, J = 7.4, 7.4 Hz, Sch₂H₃).

13C NMR (CDCl₃, 125 MHz): δC 168.28 (C=O), 167.72 (C=O), 138.33 (Ar), 137.79 (Ar), 134.12 (Ar), 134.02 (Ar), 131.86 (Ar), 128.72 (Ar), 128.36 (Ar), 128.12 (Ar), 128.10 (Ar), 128.02 (Ar), 127.65 (Ar), 123.74 (Ar), 123.48 (Ar), 81.38 (C-1), 79.78 (C-3), 77.77 (C-5), 74.77 (C-4), 74.67 (PhCH₂), 74.00 (PhCH₂), 71.13 (C-6), 54.60 (C-2), 24.17 (Sch₂CH₃), 15.11 (Sch₂CH₃). LRMS m/z calc’d for C₃₀H₃₁NNaO₆S (M+Na)⁺: 556.18; found: 556.11.

(a) TMSOTf, CH₂Cl₂, 0 °C, 58%.
Ethyl 2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (32)

The glycosyl acceptor (30; 621 mg, 1.16 mmol), glycosyl donor [ref 7] (31; 1.715 g, 2.315 mmol), and crushed molecular sieves (3 Å, 1.006 mg) in anhydrous CH₂Cl₂ (25 mL) were left mixing at ambient temperature under Ar. After 1 hour, the reaction flask was cooled to 0 °C, and then trimethylsilyl triflate (32 µL, 0.18 mmol) was added dropwise. The flask was slowly warmed to rt, and after 6 hours was neutralized with Et₃N (to pH 8), filtered over Celite, and diluted with CH₂Cl₂ (250 mL). The organic phase was washed with saturated NaHCO₃ solution (250 mL), saturated NaCl(aq) solution (250 mL), dried with Na₂SO₄, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→10% EtOAc – toluene to afford the pure product as a white solid (747 mg, 0.672 mmol, 58% yield). Rₚ = 0.58 (1:4 EtOAc : toluene). [α]₀^20: +51° (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δH 8.06 – 8.03 (m, 2H, Ar), 7.95 – 7.91 (m, 4H, Ar), 7.81 – 7.76 (m, 4H, Ar), 7.70 – 7.34 (m, 15H, Ar), 7.32 – 7.28 (m, 2H, Ar), 7.25 – 7.21 (m, 2H, Ar), 7.10 – 7.06 (m, 2H, Ar), 6.85 – 6.82 (m, 3H, Ar), 5.88 (dd, 1H, J = 3.4, <1 Hz, Gal_H4), 5.79 (dd, 1H, J = 10.4, 8.0 Hz, Gal_H2), 5.43 (dd, 1H, J = 10.4, 3.5 Hz, Gal_H3), 5.16 (d, 1H, J = 10.5 Hz, GlcN_H1), 5.02 (d, 1H, J = 12.2 Hz, PhCH²H), 4.97 (d, 1H, J = 8.0 Hz, Gal_H1), 4.76 (d, 1H, J = 12.1 Hz, PhCH²H), 4.69 (d, 1H, J = 12.3 Hz, PhCH²H), 4.41 (d, 1H, J = 12.2 Hz, PhCH²H), 4.40 (dd, 1H, J = 11.3, 6.7 Hz, Gal_H6b), 4.37 (dd, 1H, J = 10.2, 8.6 Hz, GlcN_H3), 4.30 (dd, 1H, J = 11.3, 6.9 Hz, Gal_H6b), 4.26 (dd, 1H, J = 10.4, 10.4 Hz, GlcN_H2), 4.24 (dd, 1H, J = 9.8, 8.7 Hz, GlcN_H4), 4.03 (ddd, 1H, J = 6.8, 6.8, <1 Hz, Gal_H5), 3.73 (dd, 1H, J = 11.2, 3.1 Hz, GlcN_H6a), 3.60 (dd, 1H, J = 11.2, 1.4 Hz, GlcN_H6b), 3.43 (ddd, 1H, J = 9.9, 2.8, 1.4 Hz, GlcN_H5), 2.63 (dq, 1H, J = 12.5, 7.4 Hz, SCH²CH₃), 2.55 (dq, 1H, J = 12.5, 7.5 Hz, SCH²CH₃), 2.14 (dd, 3H, J = 7.4, 7.4 Hz, SCH₂CH₃). ¹³C NMR (CDCl₃, 125 MHz): δC 168.12 (C=O), 167.65 (C=O), 166.20 (C=O), 165.67 (C=O), 165.53 (C=O), 165.23 (C=O), 138.74 (Ar), 138.27 (Ar), 134.02 (Ar), 133.88 (Ar), 133.64 (Ar), 133.45 (Ar), 131.87 (Ar), 129.71 (Ar), 129.28 (Ar), 129.27 (Ar), 129.01 (Ar), 128.89 (Ar), 128.76 (Ar), 128.74 (Ar), 128.48 (Ar), 128.38 (Ar), 128.30 (Ar), 128.11 (Ar), 128.01 (Ar), 127.28 (Ar), 123.67 (Ar), 123.44 (Ar), 100.64 (Gal_C1), 81.28 (GlcN_C1), 79.02 (GlcN_C5), 77.96 (GlcN_C4), 77.72 (GlcN_C3), 74.76 (PhH₂), 73.74 (PhH₂), 71.96 (Gal_C3), 71.27 (Gal_C5), 70.55 (Gal_C2), 68.24 (Gal_C4), 67.91
(GlcN-C6), 61.78 (Gal-C6), 54.95 (GlcN-C2), 24.09 (SCH2CH3), 15.09 (SCH2CH3). LRMS m/z calc’d for C64H57N15O15S (M+Na)+: 1134.33; found: 1134.27.

Methyl 2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranoside (33)
The glycosyl acceptor (11; 132 mg, 0.162 mmol), glycosyl donor (32; 203 mg, 0.183 mmol), and crushed molecular sieves (3 Å, 273 mg) in anhydrous CH₂Cl₂ (2.0 mL) and anhydrous acetonitrile (2.0 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then N-iodosuccinimide was added (67 mg, 0.30 mmol) followed by the drop-wise addition of triflic acid (3 µL, 0.017 mmol; in 20 µL CH₂Cl₂). After 6 hours, the mixture was neutralized with Et₃N (to pH 8), warmed to ambient temperature, filtered over Celite, and diluted further with CH₂Cl₂ (60 mL). The organic phase was washed with sat’d Na₂S₂O₃(aq) solution (60 mL), sat’d NaCl(aq) solution (2 x 60 mL), dried with Na₂SO₄, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH₄OH) – CH₂Cl₂ to afford the pure product as a white solid (224 mg, 0.120 mmol, 74% yield). Rₜ = 0.21 (1:9 acetone w/ 0.1% NH₄OH : CH₂Cl₂). [α]D²⁰: +110° (c 1.0, CHCl₃). 

\[ \text{H NMR (CDCl}_3, 500 MHz): \delta H 8.08 - 8.03 (m, 4H, Ar), 7.96 - 7.89 (m, 8H, Ar), 7.79 - 7.76 (m, 2H, Ar), 7.74 - 7.72 (m, 2H, Ar), 7.68 - 7.64 (m, 2H, Ar), 7.64 - 7.60 (m, 1H, Ar), 7.58 - 7.54 (m, 2H, Ar), 7.53 - 7.30 (m, 24H, Ar), 7.26 - 7.20 (m, 4H, Ar), 7.10 - 7.06 (m, 2H, Ar), 6.84 - 6.81 (m, 3H, Ar), 5.92 (dd, 1H, J = 3.5, <1 Hz, Gal_H4’), 5.87 (dd, 1H, J = 3.5, <1 Hz, Gal_H4’), 5.78 (dd, 1H, J = 10.4, 8.0 Hz, Gal_H2'), 5.75 (dd, 1H, J = 10.4, 8.0 Hz, Gal_H2'), 5.53 (dd, 1H, J = 10.4, 3.5 Hz, Gal_H3'), 5.41 (dd, 1H, J = 10.4, 3.5 Hz, Gal_H3'), 5.04 - 5.00 (m, 2H, NH and PhCH=), 4.99 (d, 1H, J = 8.5 Hz, GlcN_H1'), 4.90 (d, 1H, J = 8.0 Hz, Gal_H1'), 4.79 - 4.76 (m, 2H, Gal_H1’ and PhCH=H), 4.68 (d, 1H, J = 12.3 Hz, PhCH=H), 4.51 (dd, 1H, J = 11.7, 5.0 Hz, Gal_H6a'), 4.45 (dd, 1H, J = 11.7, 7.7 Hz, Gal_H6b'), 4.39 (dd, 1H, J = 11.2, 6.7 Hz, Gal_H6a'), 4.38 (d, 1H, J = 12.2 Hz, PhCH=H), 4.37 (dd, 1H, J = 10.7, 8.9 Hz, GlcN_H3), 4.34 - 4.28 (m, 2H, GalNAc_H2 and Gal_H6b'), 4.26 - 4.22 (m, 2H, Gal_H5’ and GlcN_H4), 4.21 (d, 1H, J = 3.6 Hz, GalNAc_H1), 4.15 (dd, 1H, J = 10.8, 8.5 Hz, GlcN_H2), 4.02 (dddd, 1H, J = 6.8, 6.8, <1 Hz, Gal_H5), 3.91 - 3.89 (m, 1H, GalNAc_H4), 3.75 (dd, 1H, J = 10.8, 2.8 Hz, GlcN_H6a'), 3.71 - 3.69 (m, 1H, GalNAc_H6b'), 3.59 - 3.49 (m, 4H, GalNAc_H3, GalNAc_H5, GalNAc_H6b, and GlcN_H6b), 3.38 - 3.35 (m, 1H, GlcN_H5), 2.77 - 2.74 (m, 4H, OCH₃ and GalNAc_4-OH), 1.28 (s, 3H, Ac). 

\[ \text{13C NMR (CDCl}_3, 125 MHz): \delta C 169.85 (C=O, Ac), 167.98 (C=O, Phth), 167.75 (C=O, Phth), 166.22 (C=O, Bz), 166.20 (C=O, Bz), 165.78 (C=O, Bz), 165.73 (C=O, Bz), 165.67 (C=O, Bz), 165.52 (C=O, Bz), 165.18 (C=O, Bz), 164.82 (C=O, Bz), 138.84 (Ar), 138.11 (Ar), 133.98 (Ar), 133.88 (Ar), 133.70 (Ar), 133.66 (Ar), 133.59 (Ar), 133.45 (Ar), 131.95 (Ar), 130.27 (Ar), 130.05 (Ar), 129.95 (Ar), 129.90 (Ar), 129.71 (Ar), 129.28 (Ar), 129.26 (Ar), 129.01 (Ar), 128.97 (Ar), 128.92 (Ar), 128.87 (Ar), 128.85 (Ar), 128.78 (Ar), 128.76 (Ar), 128.73 (Ar),
Methyl β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl-(1→6)-[β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranoside (34)

The starting material (33; 124 mg, 0.0665 mmol) and NH₂NH₂-H₂O (48 µL, 1.0 mmol) in EtOH (1.5 mL) were left heating at 80 ºC. After 24 hours, additional NH₂NH₂-H₂O was added (16 µL, 0.33 mmol), and after another 24 hours the mixture was evaporated to dry to afford the crude product: LRMS m/z calc’d for C_{41}H_{61}N_{2}O_{20} (M+H)^+: 901.38; found: 901.44. The mixture was redissolved into MeOH (2.0 mL) and Ac₂O added (157 µL, 1.66 mmol), and after 4 hours the mixture was evaporated to dry and purified via RPLC on C-18 silica gel using 0→100% acetonitrile – H₂O to afford the pure product as a white solid (45 mg, 0.048 mmol, 72% yield over 2 steps) [α]_D^{20}: +35° (c 1.0, H₂O). ¹H NMR (D₂O, 500 MHz): δH 7.49 – 7.35 (m, 10H, Ar), 4.91 (d, 1H, J = 11.4 Hz, PhCH₆P), 4.73 (d, 1H, J = 4.0 Hz, GalNAc_H1), 4.72 (d, 1H, J = 11.8 Hz, PhCH₆P), 4.64 (d, 1H, J = 11.4 Hz, PhCH₆P), 4.55 (d, 1H, J = 11.9 Hz, PhCH₆P), 4.50 (d, 1H, J = 8.4 Hz, GlcNAc_H1), 4.42 (d, 1H, J = 7.8 Hz, Gal_H1'), 4.30 (dd, 1H, J = 11.0, 3.7 Hz, GalNAc_H2), 4.20 – 4.17 (m, 2H, Gal_H1 and GalNAc_H4), 4.03 – 4.00
(m, 2H, GalNAc_H5 and GalNAc_H6a), 3.97 – 3.91 (m, 4H, GalNAc_H3, GlcNAc_H6a, GlcNAc_H6b, and GlcNAc_H4), 3.89 (dd, 1H, J = 3.4, <1 Hz, Gal_H4’), 3.84 (dd, 1H, J = 3.5, <1 Hz, Gal_H4), 3.77 (dd, 1H, J = 10.5, 8.5 Hz, GlcNAc_H2), 3.76 – 3.58 (m, 9H, Gal_H6a’, Gal_H6b’, GalNAc_H6b, Gal_H6a, GlcNAc_H3, GlcNAc_H5, Gal_H6b, Gal_H5’, and Gal_H3’), 3.51 (dd, 1H, J = 7.8, 7.8 Hz, Gal_H2), 3.50 (dd, 1H, J = 7.8, 7.8 Hz, Gal_H2’), 3.39 – 3.35 (m, 2H, Gal_H3 and Gal_H5), 3.31 (s, 3H, OCH3), 2.00 (s, 3H, Ac), 1.83 (s, 3H, Ac). 13C NMR (D2O, 125 MHz): δC 175.23 (C=O), 174.53 (C=O), 138.23 (Ar), 137.92 (Ar), 129.50 (Ar), 129.39 (Ar), 129.29 (Ar), 129.23 (Ar), 129.03 (Ar), 128.89 (Ar), 105.33 (Gal_C1’), 103.17 (GalNAc_C1), 102.25 (GalNAc_C1), 98.77 (GalNAc_C1), 80.56 (GlcNAc_C3), 77.79 (GalNAc_C3), 76.57 (GlcNAc_C4), 75.96 (Gal_C5), 75.58 (Gal_C5’), 75.14 (PhCH2), 74.58 (GlcNAc_C5), 73.62 (PhCH2), 73.16 (Gal_C3’), 73.08 (Gal_C3), 71.71 (Gal_C2), 71.24 (Gal_C2’), 70.92 (GalNAc_C6), 69.92 (GalNAc_C5), 69.61 (GalNAc_C4), 69.31 (Gal_C4), 69.18 (Gal_C4’), 68.23 (GlcNAc_C6), 61.84 (Gal_C6), 61.55 (Gal_C6’), 55.45 (OCH3), 54.98 (GlcNAc_C2), 49.14 (GalNAc_C2), 22.78 (Ac), 22.64 (Ac). LRMS m/z calc’d for C43H62N2NaO21 (M+Na)+: 965.37; found: 965.40.

Methyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-[β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranoside (6)

The starting material (34; 36 mg, 0.038 mmol) and Pd(OH)2 (20% w/w on carbon, 9 mg) in H2O (1.5 mL) were left mixing under H2 at atmospheric pressure. After 24 hours, the solid catalyst was removed via filtration and the solution evaporated to dry. The crude material was purified via RPLC on C-18 silica gel using 0→60% acetonitrile – H2O to afford the pure product as a white solid (27 mg, 0.035 mmol, 93% yield). [α]D20: +29° (c 0.7, H2O). 1H NMR (D2O, 500 MHz): δH 4.74 (d, 1H, J = 3.8 Hz, GalNAc_H1), 4.54 (d, 1H, J = 8.2 Hz, GlcNAc_H1), 4.46 (d, 1H, J = 7.8 Hz, Gal_H1), 4.43 (d, 1H, J = 7.8 Hz, Gal_H1’), 4.31 (dd,
1H, J = 11.0, 3.7 Hz, GalNAc_H2), 4.19 (dd, 1H, J = 3.2, <1 Hz, GalNAc_H4), 4.07 – 3.97 (m, 4H, GalNAc_H6a, GalNAc_H5, GalNAc_H3, and GlcNAc_H6b), 3.91 (dd, 1H, J = 3.4, <1 Hz, Gal_H4), 3.79 – 3.69 (m, 9H, GlcNAc_H2, Gal_H6a, Gal_H6b, Gal_H6b', GalNAc_H6b, Gal_H5, GlcNAc_H4, and GlcNAc_H3), 3.65 (dd, 1H, J = 10.0, 3.4 Hz, Gal_H3), 3.65 – 3.58 (m, 3H, Gal_H5', Gal_H3', and Gal_H6b'), 3.53 (dd, 1H, J = 9.9, 7.8 Hz, Gal_H2'), 3.49 (dd, 1H, J = 9.9, 7.8 Hz, Gal_H2'), 3.34 (s, 3H, OCH3), 2.00 (s, 3H, Ac), 2.00 (s, 3H, Ac). 13C NMR (D2O, 125 MHz): δC 175.25 (C=O), 175.05 (C=O), 105.35 (Gal_C1'), 103.55 (Gal_C1), 102.17 (GlcNAc_C1), 98.83 (GalNAc_C1), 79.15 (GlcNAc_C4), 77.72 (GalNAc_C3), 76.01 (Gal_C5), 75.62 (Gal_C5'), 75.38 (GlcNAc_C5), 73.17, 73.16 (Gal_C3 and Gal_C3'), 73.04 (GlcNAc_C3), 71.61 (Gal_C2), 71.26 (Gal_C2'), 70.68 (GalNAc_C6), 69.93 (GalNAc_C5), 69.63 (GalNAc_C4), 69.23, 69.20 (Gal_C4 and Gal_C4'), 61.67, 61.61 (Gal_C6 and Gal_C6'), 60.69 (GlcNAc_C6), 55.67 (GlcNAc_C2), 55.53 (OCH3), 49.17 (GalNAc_C2), 22.83 (Ac), 22.66 (Ac). ESI-HRMS m/z calc’d for C29H50N2NaO21 (M+Na)+: 785.2804; found: 785.2806. HPLC purity analysis: >99.5%, Rt 5.34 minutes, Atlantis T3 C18 column.

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$^1\text{H NMR in CDCl}_3$ (500 MHz)
13C NMR (APT) in CDCl3 (125 MHz)
$^1H\_^1H\ gCOSY$ in CDCl$_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1\text{H}_-^1\text{H}$ gCOSY in CDCl$_3$
$^1$H-$^{13}$C gHSQC in CDCl$_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)

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RH.549

| f1 (ppm) | Value |
|----------|-------|
| 0        | 0     |
| 10       | 128.47|
| 20       | 128.71|
| 30       | 128.81|
| 40       | 128.85|
| 50       | 129.26|
| 60       | 129.44|
| 70       | 129.90|
| 80       | 130.00|
| 90       | 133.77|
| 100      | 133.71|
| 110      | 133.53|
| 120      | 165.70|
| 130      | 165.81|
| 140      | 166.27|
| 150      | 170.10|
| 160      | 72.24  |
| 170      | 69.44  |
| 180      | 69.90  |
| 190      | 68.36  |
| 200      | 68.87  |
| 210      | 62.83  |
| 220      | 55.30  |
| 230      | 48.05  |
| 240      | 45.76  |

BzO

AcHN

OMe

HO

BzO

BzO

O

11
$^1$H-$^1$H gCOSY in CDCl$_3$
$^{1}H_{-}^{13}C$ gHSQC in CDCl$_3$
$^1$H NMR in D$_2$O (500 MHz)
$^{13}$C NMR (APT) in D$_2$O (125 MHz)
$^1$H–$^1$H gCOSY in D$_2$O
$^{1}H_{-^{13}C}$ gHSQC in $D_{2}O$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1\text{H-}^1\text{H gCOSY in CDCl}_3$
$^1$H-$^{13}$C gHSQC in CDCl$_3$
$^1$H NMR in D$_2$O (500 MHz)
\textbf{\textsuperscript{13}C NMR (APT) in D\textsubscript{2}O (125 MHz)}

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RH 56.7

\includegraphics[width=\textwidth]{13C_NMR_APT.png}

\begin{align*}
\text{f1 (ppm)} & \hspace{1cm} 0 & 10 & 20 & 30 & 40 & 50 & 60 & 70 & 80 & 90 & 100 & 110 & 120 & 130 & 140 & 150 & 160 & 170 & 180 & 190 \\
\end{align*}
$^1$H$_-^1$H gCOSY in CDCl$_3$
$^{1}H_{-}^{13}C$ gHSQC in D$_2$O
\(^1\)H NMR in CDCl\(_3\) (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)

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RH.604

$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)

138.29
138.05
129.21
128.68
128.38
128.08
126.60
-101.48
-85.52
-80.54
-73.75
-71.76
-70.36
-69.65
-68.24
-23.15
-15.50
$^1$H-$^1$H gCOSY in CDCl$_3$
$^{1}H^{13}C$ gHSQC in CDCl$_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)

[Diagram of molecular structure and NMR spectrum]

- Chemical shifts: 165.46, 168.93, 138.01, 138.27, 137.94, 137.53, 130.33, 130.07, 129.25, 128.31, 128.92, 127.86, 127.82, 127.43, 127.04, 126.68, 126.25, 121.97, 111.51
- J couplings: 83.09, 78.32, 73.63, 70.34, 69.58, 68.95, 22.92, 15.05

- Peaks at f1 (ppm): 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0, -10
$^1$H-$^1$H gCOSY in CDCl$_3$
$^{1}H_{-}^{13}C$ gHSQC in CDCl$_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1H_{-}^1H$ gCOSY in CDCl$_3$
$^{1}H^{13}C$ gHSQC in CDCl$_3$
¹H NMR in CDCl₃ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1$H-$^1$H gCOSY in CDCl$_3$
$^1$H-$^{13}$C gHSQC in CDCl$_3$
$^1$H NMR in D$_2$O (500 MHz)
$^{13}$C NMR (APT) in D$_2$O (125 MHz)
$^{1}H_{-}^{1}H$ gCOSY in $D_{2}O$
$^1H_ {13}C$ gHSQC in $D_2O$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)

[Image of the NMR spectrum]

Jan29-2020.13.fid
RH.559

[Chemical structure diagram]
$^1$H-$^1$H gCOSY in CDCl$_3$
$^1$H-13C gHSQC in CDCl$_3$
$^1$H NMR in CD$_3$OD (500 MHz)
$^{13}$C NMR (APT) in CD$_3$OD (125 MHz)

Jul26-2021.24.fid
RH.561

$\begin{array}{cccccc}
172.03 & 17.69 & -161.52 & 139.58 & 129.92 & 77.34 \\
172.03 & -161.52 & 130.16 & 128.71 & 75.49 & 73.99 \\
& & & & & 70.38 \\
& & & & & 64.95 \\
& & & & & 55.98 \\
& & & & & 50.05 \\
21 & & & & & 23.09 \\
& & & & & 21.08 \\
& & & & & 20.73 \\
\end{array}$
$^1H_-^1H$ gCOSY in CD$_3$OD
$^{1}H_{-}^{13}C$ gHSQC in CD$_3$OD
$^1$H NMR in CD$_3$OD (500 MHz)
$^{13}$C NMR (APT) in CD$_3$OD (125 MHz)
$^1H$-$^1H$ gCOSY in CD$_3$OD
$^1\text{H-}^{13}\text{C gHSQC in CD}_3\text{OD}$
$^{1}H$ NMR in CDCl$_3$ (500 MHz)

Feb03-2020.10.fid
RH.565
$^1$H–$^1$H gCOSY in CDCl$_3$
$^{1}H\text{--}^{13}C$ gHSQC in CDCl$_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1H_\text{g}^1H$ gCOSY in CDCl$_3$
$^1$H NMR in D$_2$O (500 MHz)

Feb 20-2020.10.fid
RH.574
$^{13}$C NMR (APT) in D$_2$O (125 MHz)
$^1$H$_{\text{g}}$$^1$H gCOSY in D$_2$O
$^{1}H_{-}^{13}C$ gHSQC in D$_{2}$O
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1H \text{-} ^1H$ gCOSY in CDCl$_3$
$^{1}H_{-}^{13}C$ gHSQC in CDCl$_3$
\[ ^1H \text{NMR in } D_2O (500 MHz) \]
$^{13}$C NMR (APT) in D$_2$O (125 MHz)
$^1$H - $^1$H gCOSY in D$_2$O
$^1$H-$^{13}$C gHSQC in D$_2$O
$^1$H NMR in CD$_3$OD (500 MHz)
$^{13}$C NMR (APT) in CD$_3$OD (125 MHz)

Jan20-2020.43.fid
RH.551
$^1H\_^1H$ gCOSY in CD$_3$OD
$^1H_{-}^{13}C$ gHSQC in CD$_3$OD
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1H$-$^1H$ gCOSY in CDCl$_3$
$^{1}H\,{}^{13}C$ gHSQC in CDCl$_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$^1$H-$^1$H gCOSY in CDCl$_3$
$^{1}H\text{-}^{13}C$ gHSQC in CDCl$_3$
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)

Jan27–2020.13.fid
RH.556

- 167.72
- 168.28
- 138.33
- 134.12
- 137.79
- 131.86
- 134.02
- 128.36
- 128.72
- 128.12
- 128.02
- 127.65
- 123.74
- 123.48
- 81.38
- 79.78
- 77.77
- 74.67
- 74.00
- 71.13
- 54.60
- 24.17
- 15.11

f1 (ppm):
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
$^1$H-$^1$H gCOSY in CDCl$_3$
$^{1}H_{-}{^{13}}C$ gHSQC in CDCl$_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}\text{C NMR (APT) in CDCl}_3$ (125 MHz)
$^1$H-$^1$H gCOSY in CDCl$_3$
$^1\text{H} - ^{13}\text{C} \text{ gHSQC in CDCl}_3$
$^1$H NMR in CDCl$_3$ (500 MHz)
$^{13}$C NMR (APT) in CDCl$_3$ (125 MHz)
$\textsuperscript{1}H\textsubscript{-}\textsuperscript{1}H \text{ gCOSY in CDCl}_3$
$^{1}H\,^{13}C$ gHSQC in CDCl$_3$
$^1$H NMR in D$_2$O (500 MHz)
$^{13}$C NMR (APT) in D$_2$O (125 MHz)
$^1H_\text{-}^1H$ gCOSY in D$_2$O
$^{1}H_{-}^{13}C$ gHSQC in D$_2$O
$^1$H NMR in D$_2$O (500 MHz)
$^{13}$C NMR (APT) in D$_2$O (125 MHz)
$^{1}H_{-1}H$ gCOSY in $D_{2}O$
$^1$H-$^{13}$C gHSQC in D$_2$O
HPLC Purity Analysis

**Sample 1:** ADC1 A, ADC1 (RACHEL\RH-567-4.D)
Area: 3.9407
99.1%

**Sample 2:** ADC1 A, ADC1 (RACHEL\RH-572-5.D)
Area: 455.555
>99.5%

**Sample 3:** ADC1 A, ADC1 (RACHEL\RH-564-2.D)
Area: 455.555
>99.5%
HPLC Purity Analysis

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**ADC1 A, ADC1 (RACHEL\RH-574\_C18.D)**

- **Signal 1:** ADC1 A, ADC1
- **Use Multiplier & Dilution Factor with ISTDs**
- **Sample Amount:** 5.00000 [ng/ul] (not used in calc.)
- **Dilution:** 1.0000
- **Multiplier:** 1.0000
- **Sorted By:** Signal

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**ADC1 A, ADC1 (RACHEL\RH-573.D)**

- **Signal 1:** ADC1 A, ADC1
- **Use Multiplier & Dilution Factor with ISTDs**
- **Sample Amount:** 5.00000 [ng/ul] (not used in calc.)
- **Dilution:** 1.0000
- **Multiplier:** 1.0000
- **Sorted By:** Signal

---

**ADC1 A, ADC1 (RACHEL\RH-615.D)**

- **Signal 1:** ADC1 A, ADC1
- **Use Multiplier & Dilution Factor with ISTDs**
- **Sample Amount:** 5.00000 [ng/ul] (not used in calc.)
- **Dilution:** 1.0000
- **Multiplier:** 1.0000
- **Sorted By:** Signal

---

**Analysis Method:** D:\PHYSCHEM\METHODS\RH_ELSD_5-95.M

**Injection Date:** 19.08.2020 12:58:29

**Acq. Instrument:** PhysChem

**Acq. Operator:** Rachel

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**Analysis Method:** D:\PHYSCHEM\METHODS\RH_ELSD_5-95.M

**Injection Date:** 24.02.2020 04:05:09

**Acq. Instrument:** PhysChem

**Acq. Operator:** Rachel

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**Analysis Method:** D:\PHYSCHEM\METHODS\RH_ELSD_5-95.M

**Injection Date:** 06.02.2020 12:16:39

**Acq. Instrument:** PhysChem

**Acq. Operator:** Rachel

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**Area Percent Report**

**Last changed:** 06.02.2020 07:03:33 by Rachel

**Last changed:** 19.08.2020 12:57:12 by Rachel

**Acq. Operator:** Rachel

---

**Column:** VWD1 A, Wavelength=254 nm

**VWD1 A, Wavelength=254 nm (RACHEL\RH-574\_C18.D)**

**VWD1 A, Wavelength=254 nm (RACHEL\RH-573.D)**

**ADC1 A, ADC1 (RACHEL\RH-573.D)**

**ADC1 A, ADC1 (RACHEL\RH-615.D)**

**Peak RetTime Type  Width  Area  Height  Area**

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**Totals:**

1. **98.2%**
2. **>99.5%**
3. **>99.5%**