

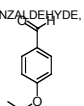
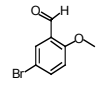
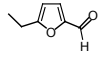
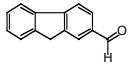
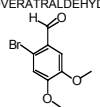
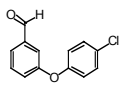
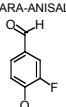
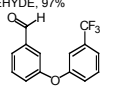
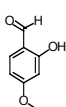
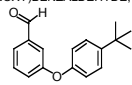
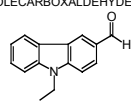
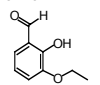
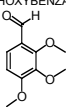
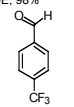
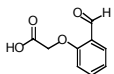
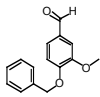
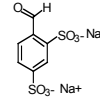
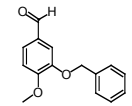
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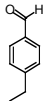
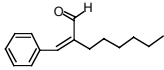
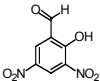
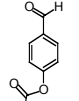
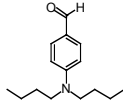
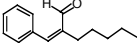
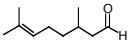
### **Small Molecule Inhibitors of Mucin-Type *O*-Linked Glycosylation from a Uridine-Based Library**

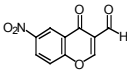
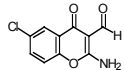
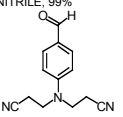
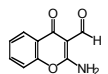
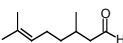
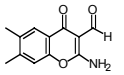
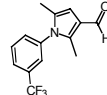
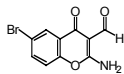
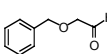
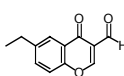
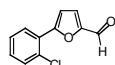
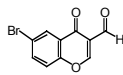
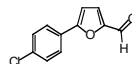
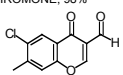
**Howard C. Hang, Chong Yu, Kelly G. Ten Hagen, E Tian, Katharine A. Winans, Lawrence A. Tabak, and Carolyn R. Bertozzi**

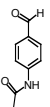
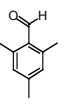
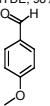
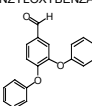
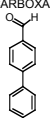
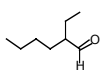
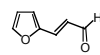
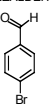
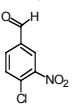
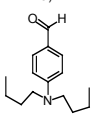
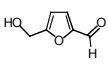
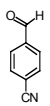
**Supplemental Table S1.** List of Aldehydes Used in the Synthesis of Uridine-Based Library from Aldrich and ChemDiv [1]

| Aldehyde number | Aldrich number | Name/Structure                        | Aldehyde number | Aldrich number | Name/Structure                          | Aldehyde number | Aldrich number | Name/Structure                                   |
|-----------------|----------------|---------------------------------------|-----------------|----------------|-----------------------------------------|-----------------|----------------|--------------------------------------------------|
| 1A              | 10604-6        | 2-CHLORO-6-NITROBENZALDEHYDE, 97%<br> | 11A             | 12809-0        | 3-ETHOXY-4-HYDROXYBENZALDEHYDE, 99%<br> | 21A             | 13871-1        | 2,4,6-TRIMETHOXYBENZALDEHYDE, 98%<br>            |
| 2A              | 10846-4        | CYCLOHEXANECARBOXALDEHYDE, 98%<br>    | 12A             | 12837-6        | 4-FLUOROBENZALDEHYDE, 98%<br>           | 22A             | 13903-3        | 2-CHLORO-5-NITROBENZALDEHYDE, 97%<br>            |
| 3A              | 11009-4        | 2-ETHYLBUTYRALDEHYDE, 92+%<br>        | 13A             | 12944-5        | INDOLE-3-CARBOXALDEHYDE, 97%<br>        | 23A             | 14039-2        | 3,5-DIMETHYL-4-HYDROXYBENZALDEHYDE, 95%<br>      |
| 4A              | 11221-6        | 4-CHLOROBENZALDEHYDE, 97%<br>         | 14A             | 12948-8        | 5-IODOVANILLIN, 97%<br>                 | 24A             | 14041-4        | 3,5-DI-TERT-BUTYL-2-HYDROXYBENZALDEHYDE, 99%<br> |
| 5A              | 11755-2        | ORTHO-TOLUALDEHYDE, 97%<br>           | 15A             | 12965-8        | META-ANISALDEHYDE, 97%<br>              | 25A             | 14124-0        | 2-CHLORO-6-FLUOROBENZALDEHYDE, 95%<br>           |
| 6A              | 12213-0        | 3,5-DIBROMOSALICYLALDEHYDE, 98%<br>   | 16A             | 13060-5        | 5-BROMOVANILLIN, 97%<br>                | 26A             | 14368-5        | 3-HYDROXY-4-METHOXYBENZALDEHYDE, 99%<br>         |
| 7A              | 12325-0        | 4-ANTIPYRINECARBOXALDEHYDE, 97%<br>   | 17A             | 13061-3        | 5-BROMOVERATRALDEHYDE, 98%<br>          | 27A             | 14408-8        | 4-HYDROXYBENZALDEHYDE, 98%<br>                   |
| 8A              | 12371-4        | 4-BENZYLOXYBENZALDEHYDE, 97%<br>      | 18A             | 13215-2        | 2,4,5-TRIMETHOXYBENZALDEHYDE, 98%<br>   | 28A             | 14432-0        | 4-HYDROXY-3-NITROBENZALDEHYDE, 97%<br>           |
| 9A              | 12491-5        | 4-CARBOXYBENZALDEHYDE<br>             | 19A             | 13517-8        | 4-ISOPROPYLBENZALDEHYDE, 98%<br>        | 29A             | 14542-4        | 5-ACETOXYMETHYL-2-FURALDEHYDE, 99%<br>           |
| 10A             | 12497-4        | 2-CHLOROBENZALDEHYDE, 99%<br>         | 20A             | 13728-6        | 5-BROMOSALICYLALDEHYDE, 98%<br>         | 30A             | 14625-0        | 3-CYANOBENZALDEHYDE, 98%<br>                     |

| Aldehyde number | Aldrich number | Name/Structure                                                                                                                | Aldehyde number | Aldrich number | Name/Structure                                                                                                                | Aldehyde number | Aldrich number | Name/Structure                                                                                                                                           |
|-----------------|----------------|-------------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|-------------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| 31              | 14645-5        | ISOVALERALDEHYDE, 97%<br>                    | 41A             | 15372-9        | 2-ETHOXYBENZALDEHYDE, 97+%<br>               | 51A             | 17360-6        | 4-ETHOXYBENZALDEHYDE, 99%<br>                                         |
| 32              | 14686-2        | 2-HYDROXY-5-METHOXYBENZALDEHYDE, 98%<br>     | 42A             | 15429-6        | 5-BROMO-ORTHO-ANISALDEHYDE, 99%<br>          | 52A             | 18699-6        | 5-ETHYL-2-FURALDEHYDE, 98%<br>                                        |
| 33              | 15014-2        | 2-FLUORENECARBOXALDEHYDE, 99%<br>            | 43A             | 15557-8        | 6-BROMOVERATRICALDEHYDE, 98%<br>             | 53A             | 19530-8        | 3-(4-CHLOROPHENOXY)BENZALDEHYDE, 97%<br>                              |
| 34              | 15104-1        | 2,4-DIMETHYLBENZALDEHYDE, TECH., 90%<br>     | 44A             | 15558-6        | 3-FLUORO-PARA-ANISALDEHYDE, 99%<br>          | 54A             | 19539-1        | 3-(3-(TRIFLUOROMETHYL)PHENOXY)-BENZALDEHYDE, 97%<br>                  |
| 35              | 15106-8        | 2,5-DIMETHYLBENZALDEHYDE, 99%<br>            | 45A             | 16069-5        | 2-HYDROXY-4-METHOXYBENZALDEHYDE, 98%<br>     | 55A             | 19592-8        | 3-(4-TERT-BUTYLPHENOXY)BENZALDEHYDE, 98%<br>                          |
| 36              | 15148-3        | 9-ETHYL-3-CARBAZOLECARBOXALDEHYDE, 98%<br>  | 46A             | 16098-9        | 3-ETHOXYSALICYLALDEHYDE, 97%<br>             | 56A             | 19687-8        | ALPHA,ALPHA,ALPHA-TRIFLUORO-M-TOLUALDEHYDE, 97%<br>                   |
| 37              | 15209-9        | 2,3,4-TRIMETHOXYBENZALDEHYDE, 99%<br>      | 47A             | 16116-0        | ALPHA-BROMOCINNAMALDEHYDE, 98%<br>         | 57A             | 20770-5        | METHACROLEIN, TECH., 85%<br>                                        |
| 38              | 15211-0        | 10-CHLORO-9-ANTHRALDEHYDE, 97%<br>         | 48A             | 16141-1        | ALPHA-CHLOROCINNAMALDEHYDE, 97%<br>        | 58A             | 22494-4        | ALPHA,ALPHA,ALPHA-TRIFLUORO-P-TOLUALDEHYDE, 98%<br>                 |
| 39              | 15215-3        | 2-FORMYLPHENOXYACETIC ACID, 97%<br>        | 49A             | 16361-9        | 4-BENZYLOXY-3-METHOXYBENZALDEHYDE, 98%<br> | 59A             | 23090-1        | 4-FORMYL-1,3-BENZENEDISULFONIC ACID, DISODIUM SALT HYDRATE, 97%<br> |
| 40              | 15262-5        | 5-BROMO-2-THIOPHENECARBOXALDEHYDE, 95%<br> | 50A             | 16395-3        | 3-BENZYLOXY-4-METHOXYBENZALDEHYDE, 98%<br> | 60A             | 23254-8        | 3-ETHOXYMETHACROLEIN, 96%<br>                                       |
|                 |                |                                                                                                                               |                 |                |                                                                                                                               |                 |                | cis vs trans?                                                                                                                                            |

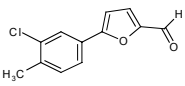
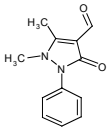
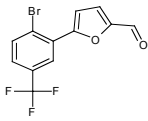
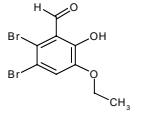
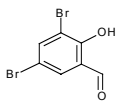
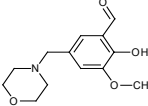
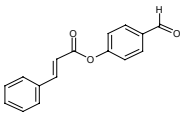
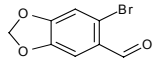
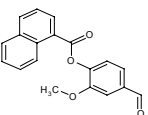
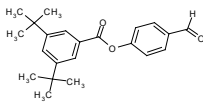
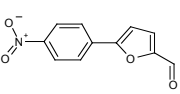
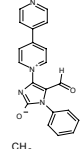
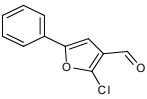
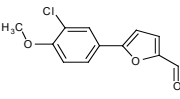
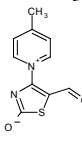
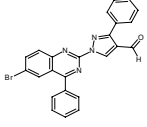
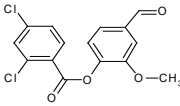
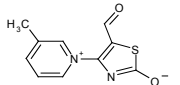
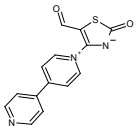
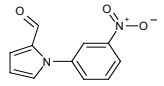
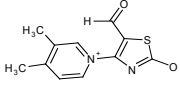
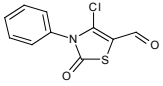
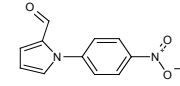
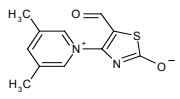
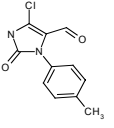
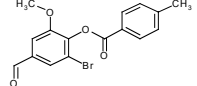
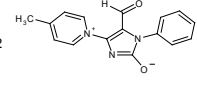
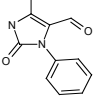
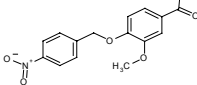
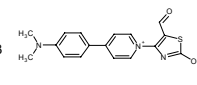
| Aldehyde number | Aldrich number | Name/Structure                                                                                                                       | Aldehyde number | Aldrich number | Name/Structure                                                                                                                                                   | Aldehyde number | Aldrich number | Name/Structure                                                                                                                  |
|-----------------|----------------|--------------------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|---------------------------------------------------------------------------------------------------------------------------------|
| 61A             | 23363-3        | 4-ETHYLBENZALDEHYDE, 98%<br>                        | 71A             | 26467-9        | 2,6,6-TRIMETHYL-1-CYCLOHEXENE-1-ACETALDEHYDE, TECH., 80%<br>                    | 81A             | 29128-5        | ALPHA-HEXYLCINNAMALDEHYDE, TECH., 85%<br>    |
| 62A             | 23808-2        | 4-BUTOXYBENZALDEHYDE, 99%<br>                       | 72A             | 27221-3        | CYCLOPROPANECARBOXALDEHYDE, 98%<br>                                             | 82A             | 29231-1        | 2,3,6-TRICHLOROBENZALDEHYDE, 97%<br>         |
| 63A             | 23996-8        | TRANS-CINNAMALDEHYDE, 99+%<br>                      | 73A             | 27680-4        | 3,5-DINITROSALICYLALDEHYDE, 97%<br>                                             | 83A             | 29251-6        | 5-BROMO-2,4-DIMETHOXYBENZALDEHYDE, 99%<br>   |
| 64A             | 24260-8        | 4-ACETOXYBENZALDEHYDE, 98%<br>                      | 74A             | 27868-8        | 9-ANTHRALDEHYDE, 97%<br>                                                        | 84A             | 30355-0        | 3,5,5-TRIMETHYLHEXANAL, 95%<br>              |
| 65A             | 25069-4        | ALPHA,ALPHA,ALPHA-TRIFLUORO-O-TOLUALDEHYDE, 98%<br> | 75A             | 27886-6        | 3-FURALDEHYDE, 99%<br>                                                          | 85A             | 31991-0        | 2-FURALDEHYDE, 99%, A.C.S. REAGENT<br>       |
| 66A             | 25275-1        | 3-ETHOXY-4-METHOXYBENZALDEHYDE, 99%<br>            | 76A             | 26345-2        | 4-BROMO-2-THIOPHENECARBOXYALDEHYDE, 90%<br>                                    | 86A             | 33851-6        | 4-(DIBUTYLAMINO)BENZALDEHYDE<br>            |
| 67A             | 25614-5        | 2-ETHYLACROLEIN, TECH., 85%<br>                   | 77A             | 28899-3        | ALPHA-AMYL CINNAMALDEHYDE, 97%, MIXTURE OF CIS AND TRANS<br>                  | 87A             | 32620-8        | 2-(DIPHENYLPHOSPHINO)BENZALDEHYDE, 97%<br> |
| 68A             | 26084-3        | 2,3,4-TRIHYDROXYBENZALDEHYDE, 98%<br>             | 78A             | 28901-9        | mix of cis and trans<br>2-METHOXYCINNAMALDEHYDE, 96%, PREDOMINANTLY TRANS<br> | 88A             | 33954-7        | 3-BROMO-4-FLUOROBENZALDEHYDE, 98%<br>      |
| 69A             | 26266-8        | CROTONALDEHYDE, 99+%, PREDOMINANTLY TRANS<br>     | 79A             | 29013-0        | mostly trans<br>3,5-BIS(TRIFLUOROMETHYL)BENZALDEHYDE, 97%<br>                 | 89A             | 34252-1        | 3-FLUORO-2-METHYLBENZALDEHYDE, 98%<br>     |
| 70A             | 26459-8        | 1,4-BENZODIOXAN-6-CARBOXALDEHYDE, 98%<br>         | 80A             | 29097-1        | 2,2-DIMETHYL-4-PENTENAL, TECH., 90%<br>                                       | 90A             | 34364-1        | (R)-(+)-CITRONELLAL, TECH., 90%<br>        |

| Aldehyde number | Aldrich number | Name/Structure                                                                                                                       | Aldehyde number | Aldrich number | Name/Structure                                                                                                                           | Aldehyde number | Aldrich number | Name/Structure                                                                                                                                             |
|-----------------|----------------|--------------------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|------------------------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 91A             | 34648-9        | 3-(TRIFLUOROMETHOXY)BENZALDEHYDE, 95%<br>           | 101A            | 39011-9        | 2-CHLORO-3-QUINOLINECARBOXALDEHYDE, 98%<br>             | 111A            | 40219-2        | 3-FORMYL-6-NITROCHROMONE, 99%<br>                                       |
| 92A             | 34649-7        | 2-FLUORO-3-(TRIFLUOROMETHYL)BENZALDEHYDE, 95%<br>   | 102A            | 39319-3        | HYDROCINNAMALDEHYDE, TECH., 90%<br>                     | 112A            | 40235-4        | 2-AMINO-6-CHLORO-3-FORMYLCHROMONE, 97%<br>                              |
| 93A             | 34807-4        | 2-CHLORO-4-FLUOROBENZALDEHYDE, 97%<br>              | 103A            | 39385-1        | 2-HYDROXY-5-METHYL-1,3-BENZENEDICARBOXALDEHYDE, 97%<br> | 113A            | 40278-8        | ACETALDEHYDE, 99.5+%, A.C.S. REAGENT<br>                                |
| 94A             | 34908-9        | 2-CYANOBENZALDEHYDE, 98%<br>                        | 104A            | 39964-7        | 3,3'-(4-FORMYLPHENYLIMINO)DIPROPIONITRILE, 99%<br>      | 114A            | 41047-0        | 5-BROMO-2-HYDROXY-3-METHOXYBENZALDEHYDE, 97%<br>                        |
| 95A             | 35990-4        | 3,3-DIMETHYLBUTYRALDEHYDE, 95%<br>                  | 105A            | 40202-8        | 2-AMINO-3-FORMYLCHROMONE, 97%<br>                       | 115A            | 41201-5        | 3-BROMO-P-ANISALDEHYDE, 99%<br>                                         |
| 96A             | 37375-3        | (S)-(-)-CITRONELLAL, 96%<br>                        | 106A            | 40209-5        | 2-AMINO-3-FORMYL-6,7-DIMETHYLCHROMONE<br>              | 116A            | 41709-2        | 2,5-DIMETHYL-1-(3-(TRIFLUOROMETHYL)PHENYL)PYRROLE-3-CARBOXALDEHYDE<br> |
| 97A             | 37682-5        | 2-CHLORO-5-(TRIFLUOROMETHYL)BENZALDEHYDE, 98%<br> | 107A            | 40210-9        | 2-AMINO-6-BROMO-3-FORMYLCHROMONE, 98%<br>             | 117A            | 41811-0        | ISOBUTYRALDEHYDE, REDISTILLED, 99.5+%<br>                             |
| 98A             | 38218-3        | BENZYLOXYACETALDEHYDE, 97%<br>                    | 108A            | 40213-3        | 6-ETHYL-3-FORMYLCHROMONE, 98%<br>                     | 118A            | 42847-7        | 5-(2-CHLOROPHENYL)FURFURAL, 95%<br>                                   |
| 99A             | 38403-8        | 4-TERT-BUTYLBENZALDEHYDE, 97%<br>                 | 109A            | 40216-8        | 6-BROMO-3-FORMYLCHROMONE, 99%<br>                     | 119A            | 42849-3        | 5-(4-CHLOROPHENYL)FURFURAL, 95%<br>                                   |
| 100A            | 38774-6        | 4-ACETOXY-3,5-DIMETHOXYBENZALDEHYDE, 98%<br>      | 110A            | 40218-4        | 6-CHLORO-3-FORMYL-7-METHYLCHROMONE, 98%<br>           | 120A            | 43398-5        | 5-BROMO-2-FURALDEHYDE, 97%<br>                                        |

| Aldehyde number | Aldrich number | Name/Structure                                                                                                             | Aldehyde number | Aldrich number | Name/Structure                                                                                                            | Aldehyde number | Aldrich number | Name/Structure                                                                                                              |
|-----------------|----------------|----------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|---------------------------------------------------------------------------------------------------------------------------|-----------------|----------------|-----------------------------------------------------------------------------------------------------------------------------|
| 121A            | A180-0         | 4-ACETAMIDOBENZALDEHYDE, TECH.<br>        | 131A            | D20425-0       | DIPHENYLACETALDEHYDE, 97%<br>            | 141A            | M680-8         | MESITALDEHYDE, 98%<br>                   |
| 122A            | A8810-7        | P-ANISALDEHYDE, 98%<br>                   | 132A            | D3600-3        | 3,4-DIBENZYLOXYBENZALDEHYDE, 98%<br>     | 142A            | T1220-3        | 1,2,3,6-TETRAHYDROBENZALDEHYDE, 99%<br>  |
| 123A            | B3468-0        | 4-BIPHENYLCARBOXALDEHYDE, 99%<br>         | 133A            | E2910-9        | 2-ETHYLHEXANAL, 96%<br>                  | 143A            | T3240-9        | 2-THIOPHENECARBOXALDEHYDE, 98%<br>       |
| 124A            | B5700-1        | 2-BROMOBENZALDEHYDE, 98%<br>              | 134A            | F2060-2        | TRANS-3-(2-FURYL)ACROLEIN, 97%<br>       | 144A            | T3550-5        | M-TOLUALDEHYDE, 97%<br>                  |
| 125A            | B5720-6        | 3-BROMOBENZALDEHYDE, 97%<br>              | A135            | F480-7         | 2-FLUOROBENZALDEHYDE, 97%<br>            | 145A            | T3560-2        | P-TOLUALDEHYDE, 97%<br>                  |
| 126A            | B5740-0        | 4-BROMOBENZALDEHYDE, 99%<br>             | 136A            | F500-5         | 3-FLUOROBENZALDEHYDE, 97%<br>            | 146A            | T4800-3        | TRIBROMOACETALDEHYDE, 97%<br>            |
| 127A            | C2340-3        | 3-CHLOROBENZALDEHYDE, 97%<br>           | 137A            | G480-2         | DL-GLYCERALDEHYDE, 95%<br>             | 147A            | T7150-1        | TRIMETHYLACETALDEHYDE, 97%<br>         |
| 128A            | C5870-3        | 4-CHLORO-3-NITROBENZALDEHYDE, 98%<br>   | 138A            | H1980-8        | 3-HYDROXYBENZALDEHYDE, 97%<br>         | 148A            | 33,851-6       | 4-(DIBUTYLAMINO)-BENZALDEHYDE, 98%<br> |
| 129A            | C5880-0        | 5-CHLORO-2-NITROBENZALDEHYDE, TECH.<br> | 139A            | H4080-7        | 5-(HYDROXYMETHYL)FURFURAL, 99%<br>     |                 |                |                                                                                                                             |
| 130A            | C8960-9        | 4-CYANOBENZALDEHYDE, 95%<br>            | 140A            | H4810-7        | 5-HYDROXY-2-NITROBENZALDEHYDE, 98%<br> |                 |                |                                                                                                                             |

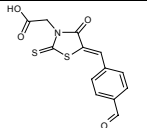
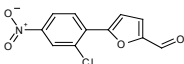
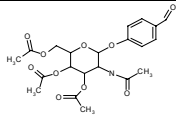
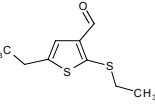
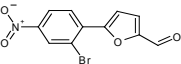
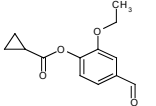
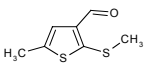
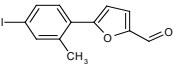
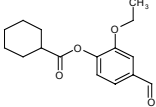
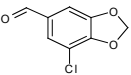
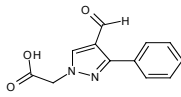
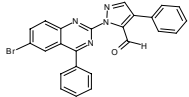
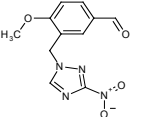
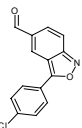
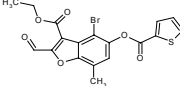
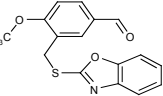
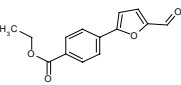
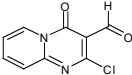
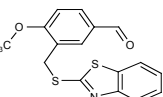
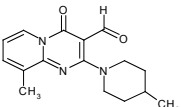
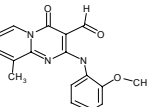
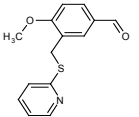
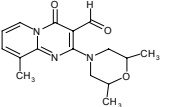
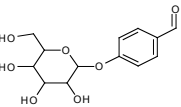
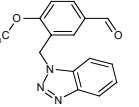
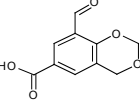
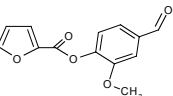
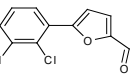
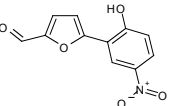
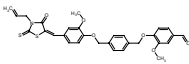
| Aldehyde Number | ChemDiv ID Number | Structure | Aldehyde Number | ChemDiv ID Number | Structure | Aldehyde Number | ChemDiv ID Number | Structure |
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| 1               | 000L-0595         |           | 11              | 0133-0078         |           | 21              | 0310-0468         |           |
| 2               | 0053-0040         |           | 12              | 0156-0048         |           | 22              | 0312-0012         |           |
| 3               | 0073-0005         |           | 13              | 0167-0097         |           | 23              | 0350-0061         |           |
| 4               | 0073-0068         |           | 14              | 0199-0121         |           | 24              | 0415-0003         |           |
| 5               | 0077-0017         |           | 15              | 0199-0141         |           | 25              | 0422-0033         |           |
| 6               | 0080-0044         |           | 16              | 0238-0022         |           | 26              | 0423-0159         |           |
| 7               | 0083-0037         |           | 17              | 0238-0026         |           | 27              | 0496-0020         |           |
| 8               | 0083-0038         |           | 18              | 0257-0041         |           | 28              | 0496-0023         |           |
| 9               | 0087-0033         |           | 19              | 0257-0048         |           | 29              | 0529-0026         |           |
| 10              | 0133-0059         |           | 20              | 0273-0001         |           | 30              | 0606-3992         |           |

| Aldehyde Number | ChemDiv ID Number | Structure | Aldehyde Number | ChemDiv ID Number | Structure | Aldehyde Number | ChemDiv ID Number | Structure |
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| 32              | 0646-0012         |           | 42              | 0682-0039         |           | 52              | 0780-1101         |           |
| 33              | 0646-0013         |           | 43              | 0682-0041         |           | 53              | 0781-2375         |           |
| 34              | 0646-0014         |           | 44              | 0682-0043         |           | 54              | 0781-2381         |           |
| 35              | 0646-0015         |           | 45              | 0682-0046         |           | 55              | 0781-2388         |           |
| 36              | 0647-0093         |           | 46              | 0683-0056         |           | 56              | 0781-2393         |           |
| 37              | 0647-0094         |           | 47              | 0729-0011         |           | 57              | 0781-2394         |           |
| 38              | 0647-0095         |           | 48              | 0739-0160         |           | 58              | 0781-2500         |           |
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| Aldehyde Number | ChemDiv ID Number | Structure                                                                           | Aldehyde Number | ChemDiv ID Number | Structure                                                                           | Aldehyde Number | ChemDiv ID Number | Structure                                                                             |
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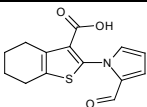
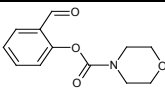
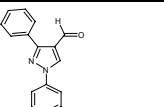
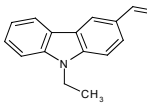
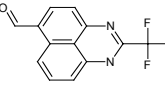
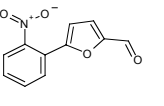
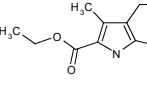
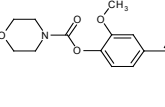
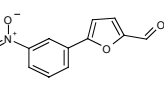
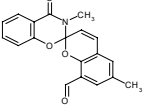
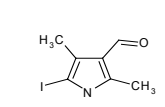
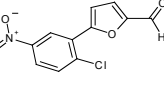
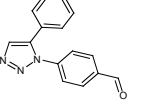
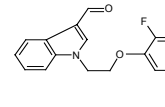
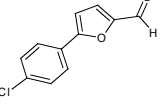
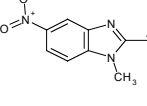
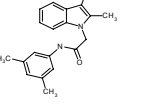
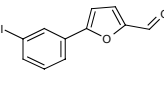
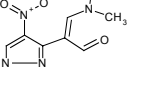
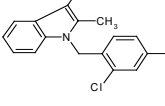
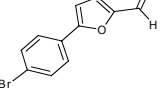
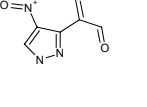
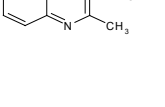
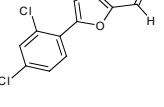
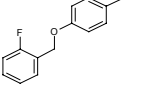
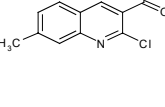
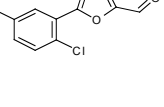
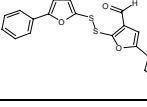
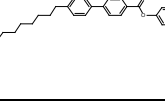
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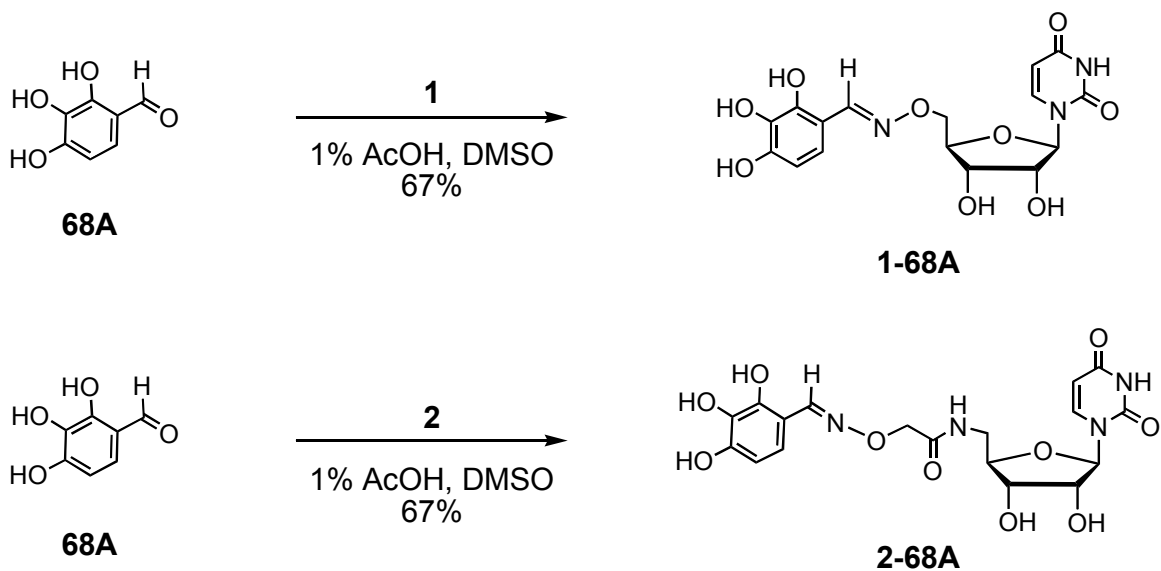
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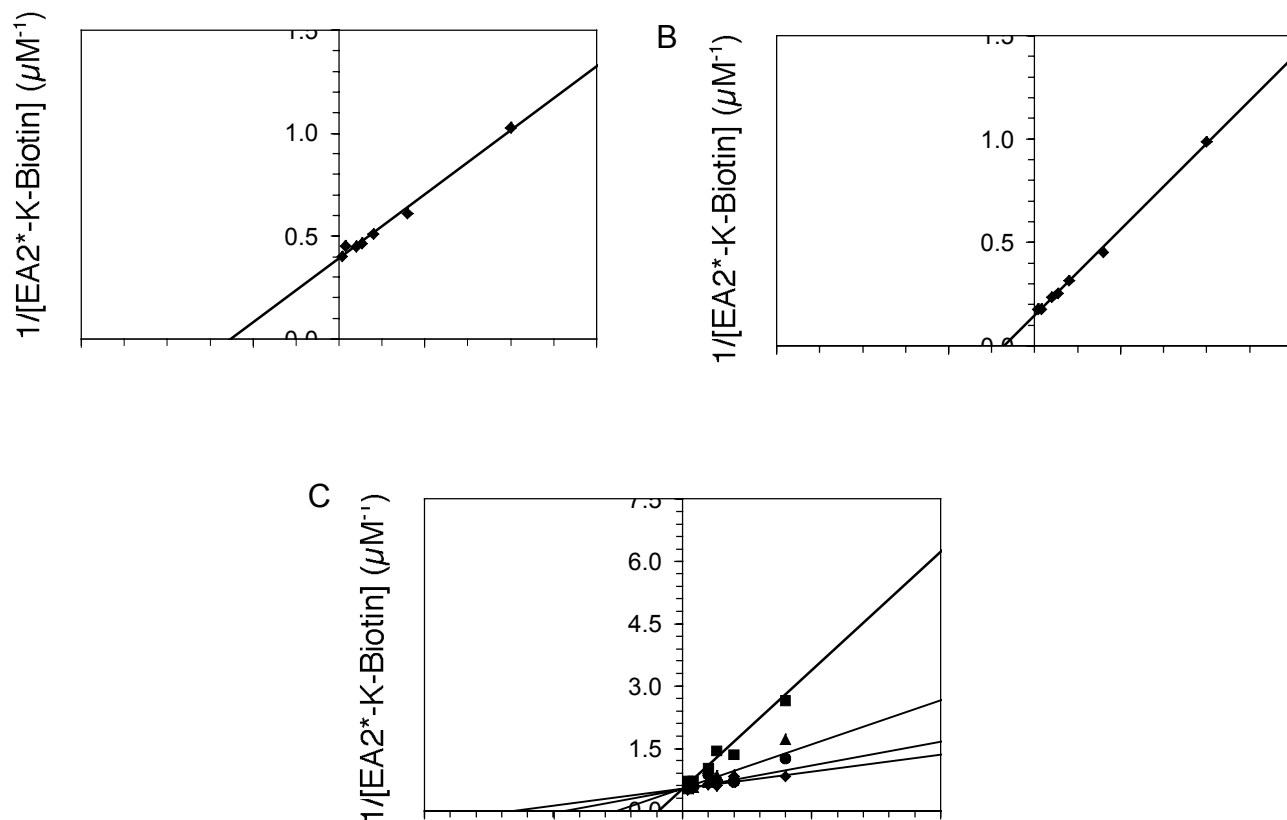
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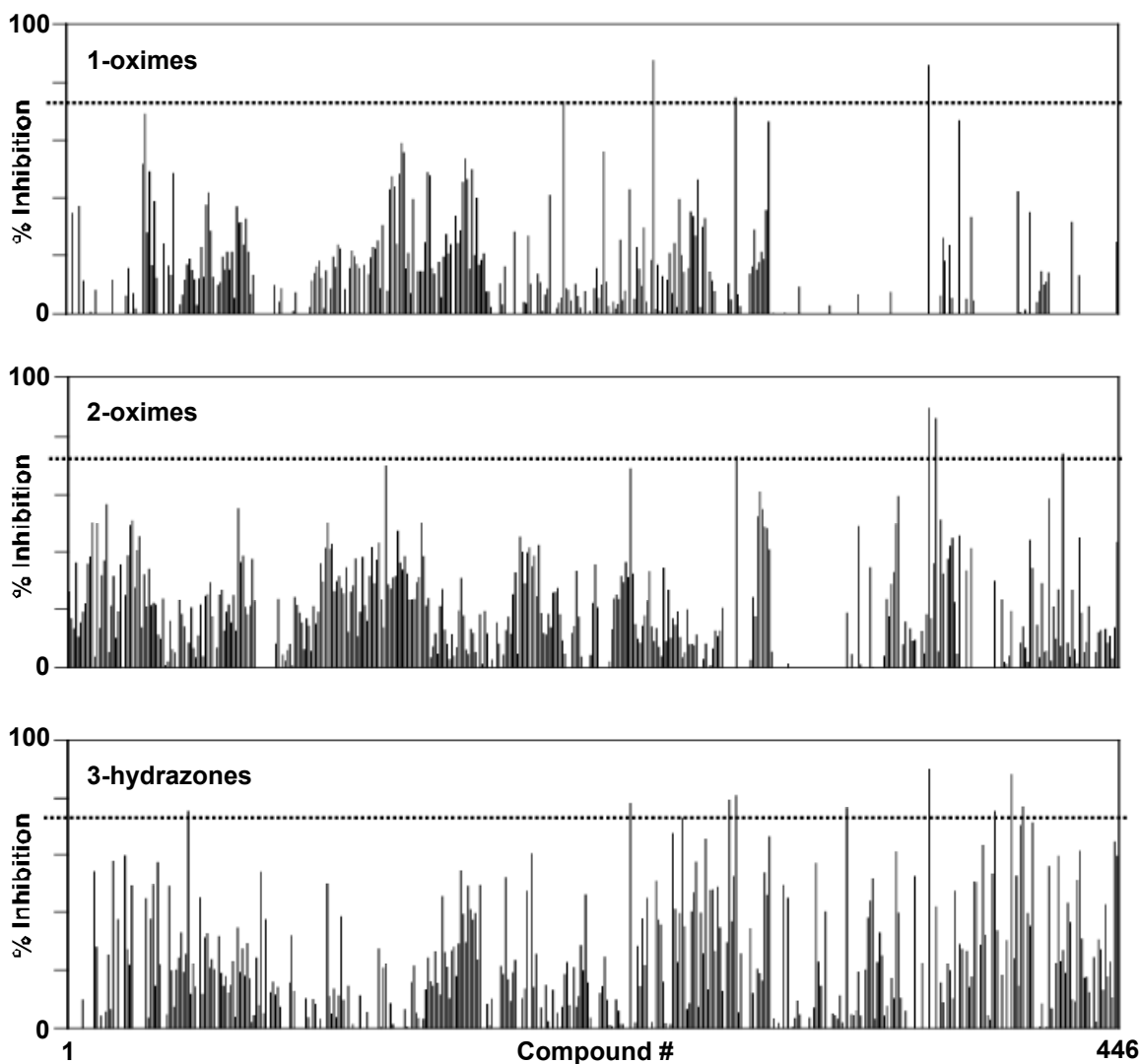
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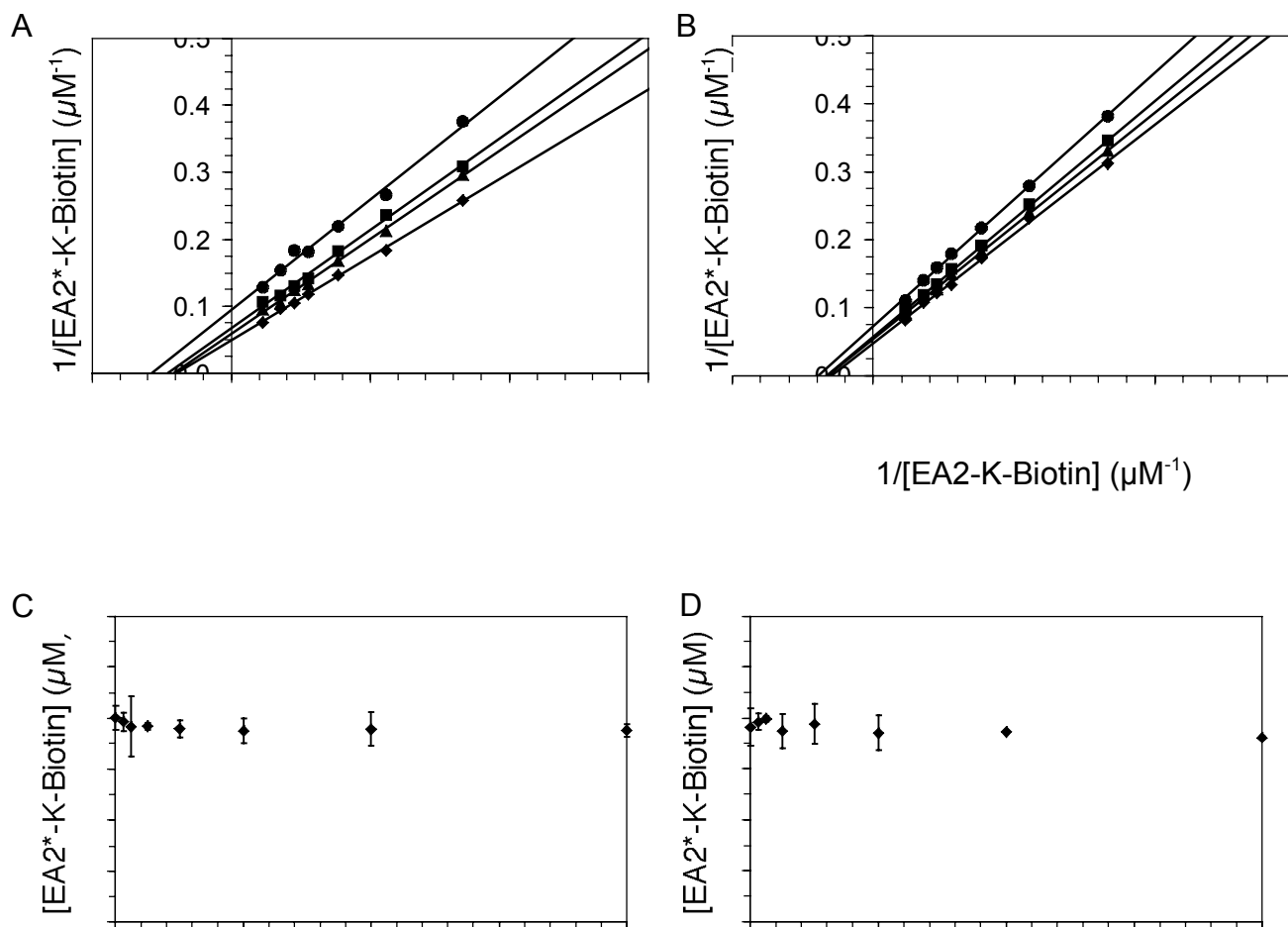
**Supplemental Scheme S1.** Compounds **1-68A** and **2-68A** were identified from secondary screen and resynthesized. For each compound, the aldehyde was reacted with the corresponding uridine-linker in DMSO with 1% AcOH, which afforded compounds **1-68A** and **2-68A** in 65-67% yield as primarily the *E*-isomer (determined by  $^1\text{H}$  NMR analysis). A complete list of aldehydes used in the synthesis of the uridine-based library is provided in Table S1.



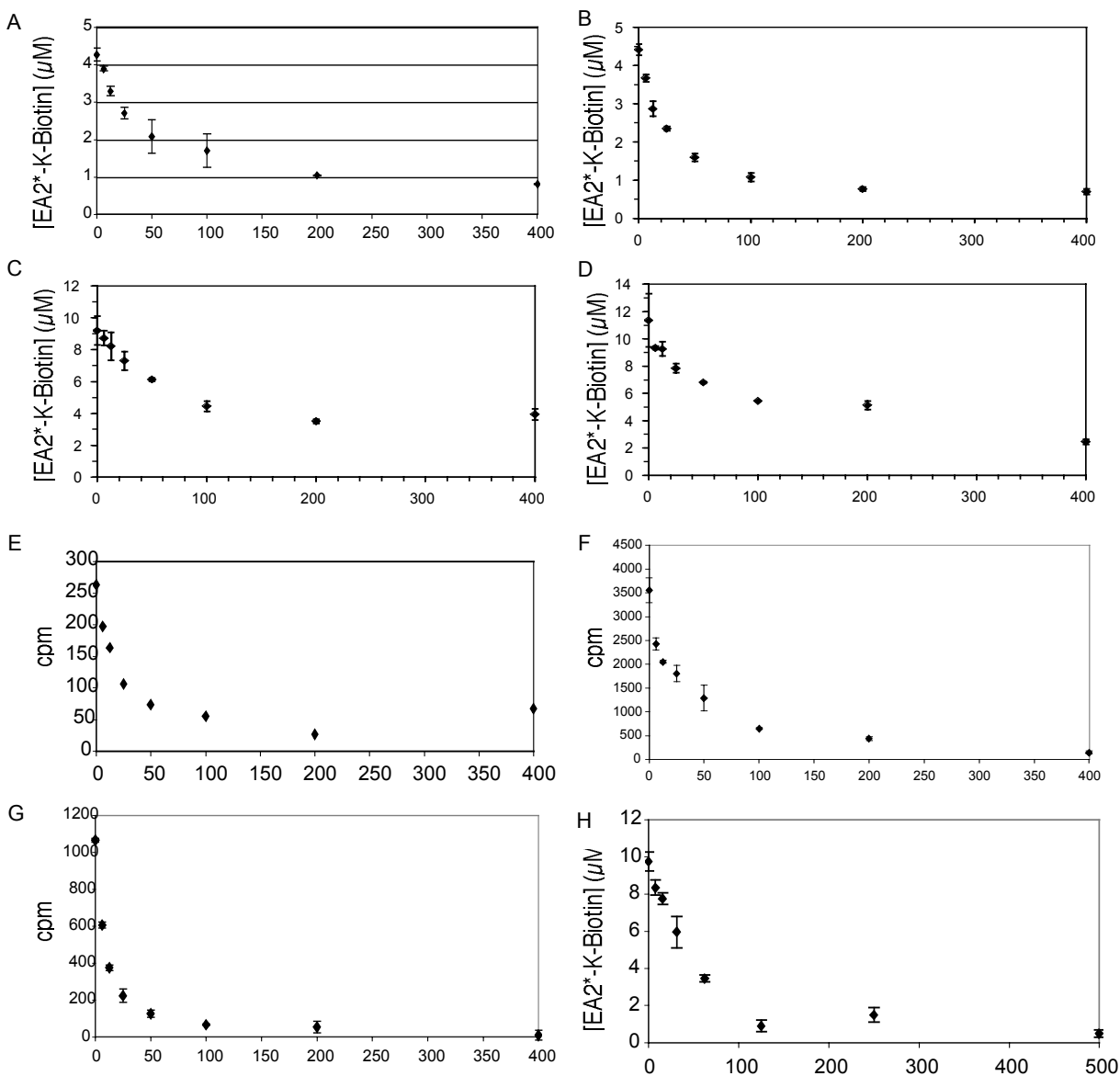
**Supplemental Figure S1.** Validation of ELLA by determination of kinetic parameters for mppGalNAcT-1. (A) The  $K_M$  value for UDP-GalNAc was measured by varying the concentration of UDP-GalNAc from 10 to 500  $\mu\text{M}$ , while maintaining the concentration of EA2-K-Biotin at 250  $\mu\text{M}$ . (B) The  $K_M$  value for EA2-K-Biotin was determined by varying the concentration of EA2-K-Biotin from 10 to 500  $\mu\text{M}$ , while maintaining UDP-GalNAc concentration constant at 250  $\mu\text{M}$ . (C) The  $K_I$  value for UDP was determined by Lineweaver-Burk analysis. Varying concentrations of UDP are represented by  $\diamond = 0$  mM,  $\bullet = 0.10$  mM,  $\blacktriangle = 0.40$  mM,  $\blacksquare = 1.50$  mM. The concentration of UDP-GalNAc was varied from 10 to 500  $\mu\text{M}$  with concentration of EA2-K-Biotin at 50  $\mu\text{M}$ . Each point on the graph represents the average of duplicates.



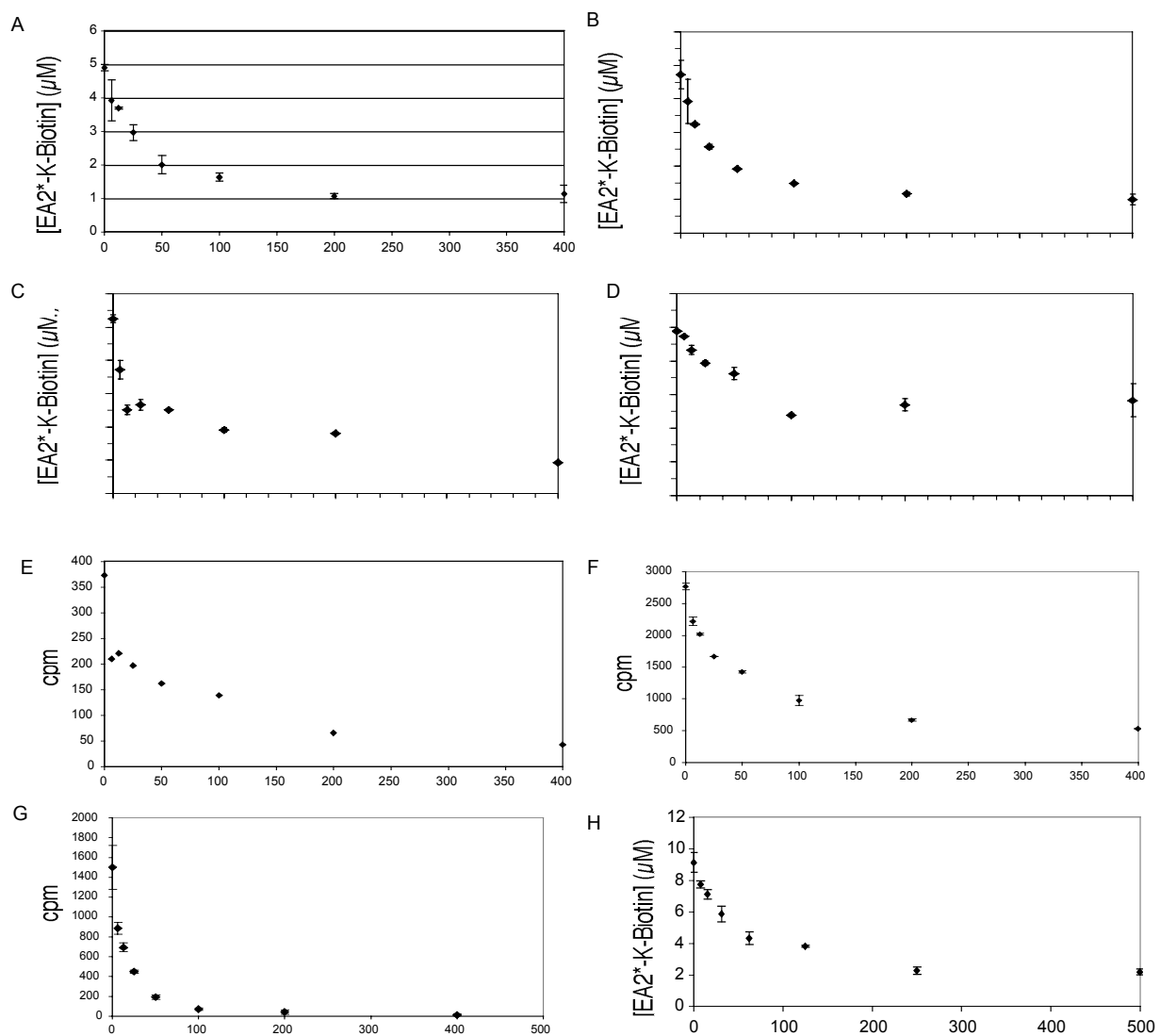
**Supplemental Figure S2.** Preliminary screen of uridine-based library at 40  $\mu\text{M}$  against mppGalNAcT-1. UDP-GalNAc and EA2 peptide **4** concentrations were at their respective  $K_M$  values. Each bar on the graph represents the average of duplicates; error bars represent the high and low values. Dotted lines represent 70% inhibition.



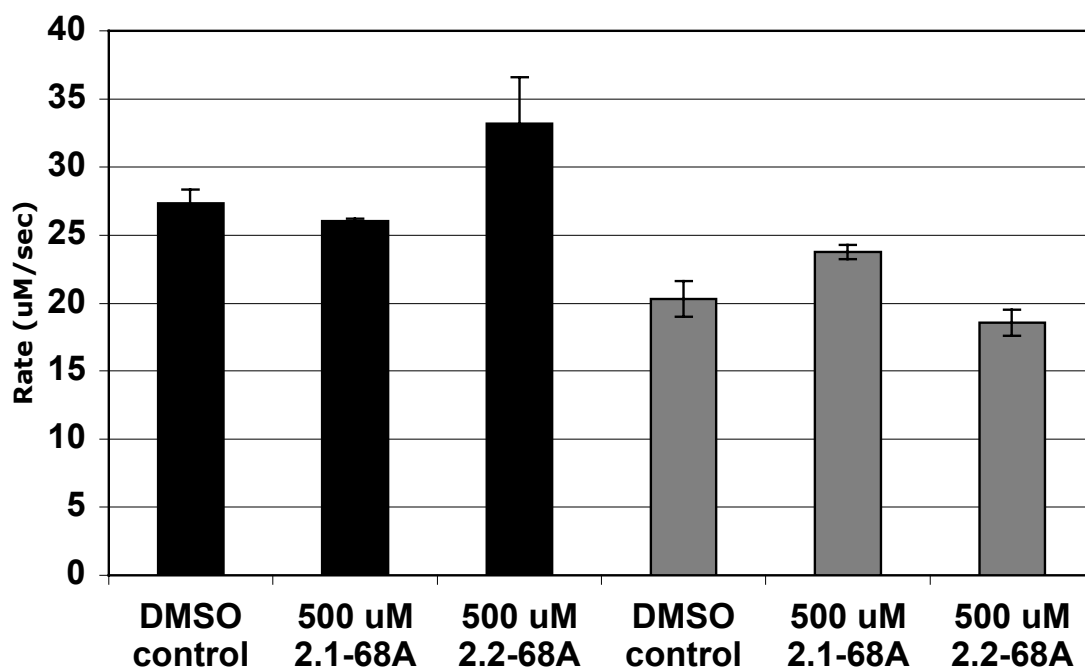
**Supplemental Figure S3.**  $K_I$  measurements for (A) **1-68A** and (B) **2-68A** with respect to EA2-K-Biotin, against mppGalNAcT-1. Inhibitor concentrations were varied from 3 to 24  $\mu M$ , while UDP-GalNAc concentration was held at 20  $\mu M$  with varying EA2-K-Biotin concentration from 25 to 220  $\mu M$ . Varying concentrations of inhibitor are represented by  $\blacklozenge = 0 \mu M$ ,  $\blacktriangle = 6 \mu M$ ,  $\blacksquare = 12 \mu M$  and  $\bullet = 24 \mu M$ . Each data point represents the average of duplicates.  $IC_{50}$  measurements for uridine linkers (C) **1** and (D) **2**. Each data point represents the average of duplicates.



**Supplemental Figure S4.** IC<sub>50</sub> value measurements for **1-68A** against (A-H) ppGalNAcT-1 to -5, 7, 10 and 11, respectively. Inhibitor concentrations were varied from 6.25 to 400 μM or 7.81 to 500 μM. The UDP-GalNAc and EA2-K-Biotin concentrations were adjusted to their respective  $K_M$  values for each isoform, as reported by Ten Hagen *et al* [2]. For ppGalNAcT-7 and -10 the concentration of UDP-GalNAc was at 20 μM and 10 μM, respectively, the concentration of MUC5AC\*\* glycopeptide substrate was at 50 μM for both. Time course experiments were performed for each to determine the initial rates of reaction prior to IC<sub>50</sub> value measurements. Cpm = counts per minute. IC<sub>50</sub> values were determined by curve fitting with KaleidaGraph 3.6.



**Supplemental Figure S5.**  $\text{IC}_{50}$  value measurements for **2-68A** against (A-H) ppGalNAcT-1 to -5, 7, 10 and 11, respectively. Inhibitor concentrations were varied from 6.25 to 400  $\mu\text{M}$  or 7.81 to 500  $\mu\text{M}$ . The UDP-GalNAc and EA2-K-Biotin concentrations were adjusted to their respective  $K_M$  values for each isoform, as reported by Ten Hagen *et al* [2]. For ppGalNAcT-7 and -10 the concentration of UDP-GalNAc was at 20  $\mu\text{M}$  and 10  $\mu\text{M}$ , respectively, the concentration of MUC5AC\*\* glycopeptide substrate was at 50  $\mu\text{M}$  for both. Time course experiments were performed for each to determine the initial rates of reaction prior to the  $\text{IC}_{50}$  value measurements. Cpm = counts per minute.  $\text{IC}_{50}$  values were determined by curve fitting with KaleidaGraph 3.6.



**Supplemental Figure S6.** Evaluation of **1-68A** and **2-68A** with  $\beta$ 1-4GalT (black bars) [3, 4] and with  $\alpha$ 1-3GalT (grey bars) [5].

#### Supplemental References

1. Winans, K.A., and Bertozzi, C.R. (2002). An inhibitor of the human UDP-GlcNAc 4-epimerase identified from a uridine-based library: A strategy to inhibit *O*-linked glycosylation. *Chem. Biol.* 9, 113-129.
2. Ten Hagen, K.G., Hagen, F.K., Balys, M.M., Beres, T.M., Van Wuyckhuysse, B., and Tabak, L.A. (1998). Cloning and expression of a novel, tissue specifically expressed member of the UDP-GalNAc:polypeptide N-acetylgalactosaminyltransferase family. *Journal of Biological Chemistry* 273, 27749-27754.
3. Schanbacher, F.L., and Ebner, K.E. (1970). Galactosyltransferase acceptor specificity of the lactose synthetase A protein. *J. Biol. Chem.* 245, 5057-5061.
4. Fitzgerald, D.K., Colvin, B., Mawal, R., and Ebner, K.E. (1970). Enzymic assay for galactosyl transferase activity of lactose synthetase and  $\alpha$ -lactalbumin in purified and crude systems. *Anal. Biochem.* 36, 43-61.
5. Sharma, A., Okabe, J., Birch, P., McClellan, S.B., Martin, M.J., Platt, J.L., and Logan, J.S. (1996). Reduction in the level of Gal( $\alpha$ 1,3)Gal in transgenic mice and pigs by the expression of an  $\alpha$ (1,2)fucosyltransferase. *Proc. Natl. Acad. Sci. U.S.A.* 93, 7190-7195.