Ferrocenium Complex Aided *O*-Glycosylation of Glycosyl Halides

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Supplementary Information

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General experimental procedures

Chemicals (1,2,3,4,6-penta-O-acetyl-D-glucopyranose, 1,2,3,4,6-penta-O-acetyl-D-galactopyranose, diethylamino sulfur trifluoride, thionyl chloride, and *N, N*-dimethyl formamide) were purchased from Carbosynth, TCI, and Sigma Aldrich and were used without any further purification. Dry solvents were obtained by standard distillation procedures.[1] Molecular sieves (4 Å) were crushed and activated for 3 h at 375 ℃ and allowed to cool under *vacuo* prior to use. Reactions were monitored by TLC on Kieselgel F254. Compounds were detected under UV light and by charring with 10% sulfuric acid in methanol. Column chromatography was performed with silica gel 60 (70-230 mesh). The NMR spectra of the products matched those in the literature.[2,3]

^{1}H NMR, and 2D NMR spectra were recorded in $CDCl_3$ using a Bruker instrument (300 MHz) and referenced to a residual solvent signal. Exact masses were obtained on Agilent 6230 ESI TOF LCMS mass spectrometer.

[1] Arnold J. Gordon, Richard A. Ford, The Chemist's Companion - A handbook of practical data, techniques, and references, Wiley-Interscience Publication, John Wiley & Sons, New York, 1972.

[2] S. A. Geringer; A. V. Demchenko, *Org. Biomol. Chem*., 2018, **16**, 9133.

[3] G. H. Posner; S. R. Haines, *Tetrahedron Lett*., 1985, **26**, 5-8.

Synthesis of Glycosyl Halides

2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl chloride (1): To a solution of 2,3,4,5-tetra-*O*-benzyl-α/β-D-galactopyranose (1.0 g, 1.8 mmol) in $ClCH_2CH_2Cl$ (10-15 mL) and *N,N*-dimethyl formamide (0.5 mL), thionyl chloride (0.6 g, 5.5 mmol) was added dropwise and allowed to stir under argon for 1 h at 0 °C. The reaction was monitored by TLC. After the reaction was complete, the reaction mixture was concentrated under *vacuo* and dissolved in a mixture of ethyl acetate and hexanes as eluent (10 mL, 1:1, v/v). Then the reaction mixture was passed through a short pad of silica gel and rinsed with the mixture of ethyl acetate and hexanes (1:1, v/v). Evaporation of the solvents afforded the title compound **1** as a colorless oil (1.0 g, 1.7 mmol, 98% yield). NMR spectral data of **1** matched the literature.[2]

2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl fluoride (2): To a solution of 2,3,4,5-tetra-*O*-benzyl-α/β-D-galactopyranose (0.7 g, 1.3 mmol) in THF (12 mL) under argon at 0 °C, diethylamino sulfur trifluoride (DAST) (0.3 g, 1.6 mmol) was added. The cooling bath was removed and the reaction mixture was allowed to stir at room temperature. The reaction was monitored by TLC and complete after 20 minutes. Methanol (0.3 mL) was added at 0 °C and allowed to stir for 5 min. The reaction mixture was concentrated under *vacuo*, washed with saturated $NaHCO_3$ solution (50 mL) and extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated under *vacuo*. The crude product was purified by silica gel column chromatography using ethyl acetate and hexanes as eluent (1:4, v/v) to afford the title compound **2** as a colorless oil (0.6 g, 1.1 mmol, 86%). NMR spectral data of **2** matched the literature.[3]

2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl fluoride (3): To a solution of 2,3,4,5-tetra-*O*-benzyl-α/β-D-glucopyranose (0.9 g, 1.7 mmol) in THF (15 mL) under argon at 0 °C, DAST (0.3 g, 1.9 mmol) was added. The cooling bath was removed and the reaction mixture was allowed to stir at room temperature. The reaction was monitored by TLC. After 20 min, the reaction was complete. Methanol (0.5 mL) was added at 0 °C and the mixture allowed to stir for 5 min. The reaction mixture was concentrated under *vacuo* and, washed with saturated $NaHCO_3$ solution (50 mL) and extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated under *vacuo*. The crude product was purified by silica gel column chromatography utilizing ethyl acetate and hexanes as eluent (1/4, v/v)

which afforded the title compound **3** as a colorless oil (0.7 g, 1.3 mmol, 81% yield).[3] NMR spectral data of **3** matched the literature.[3]

2,3,4,6-Tetra-*O*-benzoyl-α/β-D-glucopyranosyl fluoride (4): To a solution of 2,3,4,5-tetra-*O*-benzoyl-α/β D-glucopyranose (1.0 g, 1.6 mmol) in THF (15 mL) under argon at 0 °C, DAST (0.324 g, 2 mmol) was added. The cooling bath was removed and the reaction mixture was allowed to stir at room temperature. The reaction was monitored by TLC. After 20 min, the reaction was complete. Methanol (0.5 mL) was added at 0 °C and the mixture was allowed to stir for 5 min. The reaction mixture was concentrated under *vacuo,* washed with saturated $NaHCO_3$ solution (50 mL) and extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated under *vacuo*. Then the crude product was purified by silica gel column chromatography utilizing ethyl acetate and hexanes (1/4, v/v) as eluent which afforded the title compound **4** as a white foam in (0.204 g, 0.34 mmol, 23%). NMR spectral data of **4** matched the literature.[3]

Synthesis of disaccharides

Method A: To a solution of the galactosyl chloride donor (**1**, 0.035 mmol) and the glycosyl acceptor[4] (**5, 6, 7** and **8**, 0.015 mmol) in CH_2Cl_2, 4 Å molecular sieves were added and allowed to stir under argon for 20 min at room temperature. Then the ferrocenium salt ($[FcB(OH)_2]SbF_6$, 0.009 mmol, 60 mol%) was added as a promoter[5] and the reaction mixture allowed to stir for 4-6 h at rt.

Method B: To a solution of glycosyl fluoride donor (**2** and **3**, 0.05 mmol), and glycosyl acceptor[4, 6, 7] (**5, 6, 7, 8** and **9**, 0.06 mmol) in CH_2Cl_2, 4 Å molecular sieves were added and allowed to stir under argon for 20 min at room temperature. Then ferrocenium salt ($FcBF_4$, 0.035 mmol, 70 mol%) was added as a promoter and allowed to stir for 2-16 h at rt.

Method C: To a solution of glycosyl fluoride donor (**4,** 0.05 mmol), and glycosyl acceptor[4] (**5,** 0.04 mmol) in CH_2Cl_2, 4 Å molecular sieves were added and allowed to stir under argon for 20 min at room temperature. Then the ferrocenium salt ($FcBF_4$, 0.016 mmol, 40 mol%) was added as a promoter and the reaction was allowed to stir for 8 h at rt.

Method D: To a solution of glycosyl fluoride donor (**2, 3** & **4,** 0.02 mmol), and cholesterol (**10,** 0.02 mmol) in CH_2Cl_2, 4 Å molecular sieves were added and allowed to stir under argon for 20 min at room temperature. Then ferrocenium salt ($FcBF_4$, 0.008 mmol, 40 mol%) was added as a promoter and allowed to stir for 8-14 h at rt.

Reactions were monitored by TLC. After the reaction was over, the reaction mixture was filtered through a pad of celite and rinsed with CH_2Cl_2. Evaporation of solvent afforded a crude product which was purified by silica gel column chromatography utilizing ethyl acetate and hexanes (gradient elution) to afford the corresponding disaccharides.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (11): The title compound was obtained as colorless oil in 86% (13 mg,

[4] S. C. Ranade, S. Kaeothip and A. V. Demchenko, *Org. Lett.,* 2010, **12**, 5628-5631.

[5] F. S. Kamounah and J. B. Christensen, *J. Chem. Research*, 1997, 150.

[6] Y. Kondo, *Agri. Biol. Chem*., 1975, **39**, 1879–1881.

[7] T. Ogawa and T. Kaburagi, *Carbohydr. Res.,* 1982, **103**, 53–64.

0.012 mmol) yield (α/β=1/1.1) by following method A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (d, *J* = 7.7 Hz, 1H, diastereomer β), 3.34 (s, 3H), 3.31 (s, 3H). NMR spectral data of **11** matched the literature.[2, 8, 9] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.46.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (12): The title compound was obtained as colorless oil in 64% (10 mg, 0.010 mmol) yield (α/β = 1.2/1) by following method A. NMR spectral data of **12** matched the literature.[2, 9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (d, *J* = 3.61 Hz, 1H), 3.36 (d, *J* = 3.82 Hz, 6H). HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (13): The title compound was obtained as colorless oil in 63% (9 mg, 0.0094 mmol) yield (α/β = 1.6/1) by following method A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (d, *J* = 3.1 Hz, 1H, diastereomer α), 3.39 (s, 3H), 3.29 (s, 3H). NMR spectral data of **13** matched the literature.[2, 9] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.46.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (14): The title compound was obtained as colorless oil in 45% (7 mg, 0.0067 mmol) yield (α/β = 1.2/1) by following method A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.91 (d, *J* = 3.8 Hz, 1H, diastereomer α), 3.30 (dd, = 14.6, 7.5 Hz, 6H). NMR spectral data of **14** matched the literature.[2, 8] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.46.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (15): The title compound was obtained as colorless oil in 50% (27 mg, 0.027 mmol) yield (α/β = 1/1.3) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07 (d, *J* = 10.69 Hz, 1H, diastereomer α), 3.21 (S, 6H). NMR spectral data of **15** matched the literature.[2, 9] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (16): The title compound was obtained as colorless oil in 31% (17 mg,

[8] H. D. Premathilake and A. V. Demchenko, *Beilstein. J. Org. Chem*., 2012, **8**, 597–605.

[9] Y. Kobashi and T. Mukaiyama, *Bull. Chem. Soc. Jpn*., 2005, 910–916.

0.017 mmol) yield (α/β = 1/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (d, *J* = 3.5 Hz, 1H, diastereomer α), 3.44 (d, *J* = 10.8 Hz, 6H). NMR spectral data of **16** matched the literature. [2, 9] HR FAB MS $[M+Na]^+$ calcd for

$C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (17): The title compound was obtained as colorless oil in 34% (20 mg, 0.020 mmol) yield (α/β = 2.3/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (d, *J* = 3.0 Hz, 1H, diastereomer α), 3.24 (d, *J* = 13.6 Hz, 6H). NMR spectral data of **17** matched the literature.[2, 9] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.40.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (18): The title compound was obtained as an oil in 32% (18 mg, 0.018 mmol) yield (α/β = 1.6/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.06 (d, *J* = 3.6 Hz, 1H, diastereomer α), 3.48 (d, *J* = 5.9 Hz, 6H). NMR spectral data of **18** matched the literature.[2] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (19): The title compound was obtained as colorless oil in 10% (4 mg, 0.0045 mmol) yield (α/β = 1.8/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (d, *J* = 2.9 Hz, 1H), 3.37 (s, 3H). NMR spectral data of **19** matched the literature.[10] HR FAB MS $[M+Na]^+$ calcd for $C_{55}H_{58}O_{11}Na^+$ 917.39; found 917.38.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (20): The title compound was obtained as colorless oil in 45% (24 mg, 0.024 mmol) yield (α/β = 1/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.94 (d, *J* = 2.8 Hz, 1H), 3.34 (d, *J* = 7.5 Hz, 6H). NMR spectral data of **20** matched the literature.[2, 9] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 2,4,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (21): The title compound was obtained as colorless oil in 52% (25 mg, 0.025 mmol) yield (α/β = 1.5/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.6

[10] T. Kimura, T. Eto, D. Takahashi and K. Toshima, *Org. Lett.*, 2016, **18**, 3190−3193.

(d, J = 3.5 Hz, 1H), 3.42 (d, J = 3.9 Hz, 6H). NMR spectral data of **21** matched the literature.[2, 9] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (22): The title compound was obtained as colorless oil in 48% (28 mg, 0.028 mmol) yield (α/β = 1/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (d, J = 3.3 Hz, 1H), 3.39 (d, J = 5.7 Hz, 6H). NMR spectral data of **22** matched the literature.[2, 9] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (23): The title compound was obtained as colorless oil in 46% (23 mg, 0.023 mmol) yield (α/β = 1/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72 (d, J = 2.8 Hz, 1H), 3.39 (s, 6H). NMR spectral data of **23** matched the literature.[2] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$ 1009.45; found 1009.44.

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (24): The title compound was obtained as colorless oil in 12% (6 mg, 0.0067 mmol) yield (α/β = 1/1) by following method B. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (d, J = 3.4 Hz, 1H), 3.43 (s, 3H). NMR spectral data of **24** matched the literature.[11] HR FAB MS $[M+Na]^+$ calcd for $C_{55}H_{58}O_{11}Na^+$ 917.39; found 918.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (25): The title compound was obtained as colorless oil in 24% (10 mg, 0.0095 mmol) yield (β-only) by following method C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (t, J = 9.5 Hz, 1H), 4.21 (d, J = 11.1 Hz, 1H). NMR spectral data of **25** matched the literature.[2] HR FAB MS $[M+Na]^+$ calcd for $C_{62}H_{58}O_{15}Na^+$ 1065.37; found 1065.36.

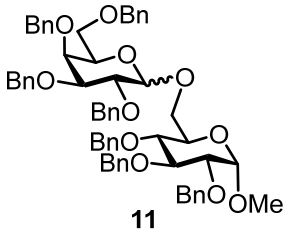
Cholesteryl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside (26): The title compound was obtained as colorless oil in 87% (17 mg, 0.019 mmol) yield (α/β = 1/5) by following method D. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.27 (d, J = 18.3 Hz, 1H), 4.93 (d, J = 12.3 Hz, 2H). NMR spectral data of α/β-glycoside **26** matched the literature.[12] HR FAB MS $[M+Na]^+$ calcd for $C_{61}H_{80}O_6Na^+$ 931.59; found 931.58.

[11] L. Sun, X. Wu, D.-C. Xiong and X.-S. Ye, *Angew. Chem. Int. Ed*., 2016, **55**, 8041–8044.

[12] G. Sun, Y. Wu, A. Liu, S. Qiu, W. Zhang, Z. Wang and J. Zhang, *Synlett*, 2018, 668–672.

Cholesteryl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (27): The title compound was obtained as colorless oil in 55% (12 mg, 0.013 mmol) yield (α/β = 1/1) by following method D. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28 (d, *J* = 18.5 Hz, 1H), 3.42 (d, *J* = 8.7 Hz, 2H), 0.98 (d, *J* = 6.8 Hz, 7H). NMR spectral data of α/β-glycoside **27** matched the literature.[12] HR FAB MS $[M+Na]^+$ calcd for $C_{61}H_{80}O_6Na^+$ 931.59; found 931.58.

NMR spectra data



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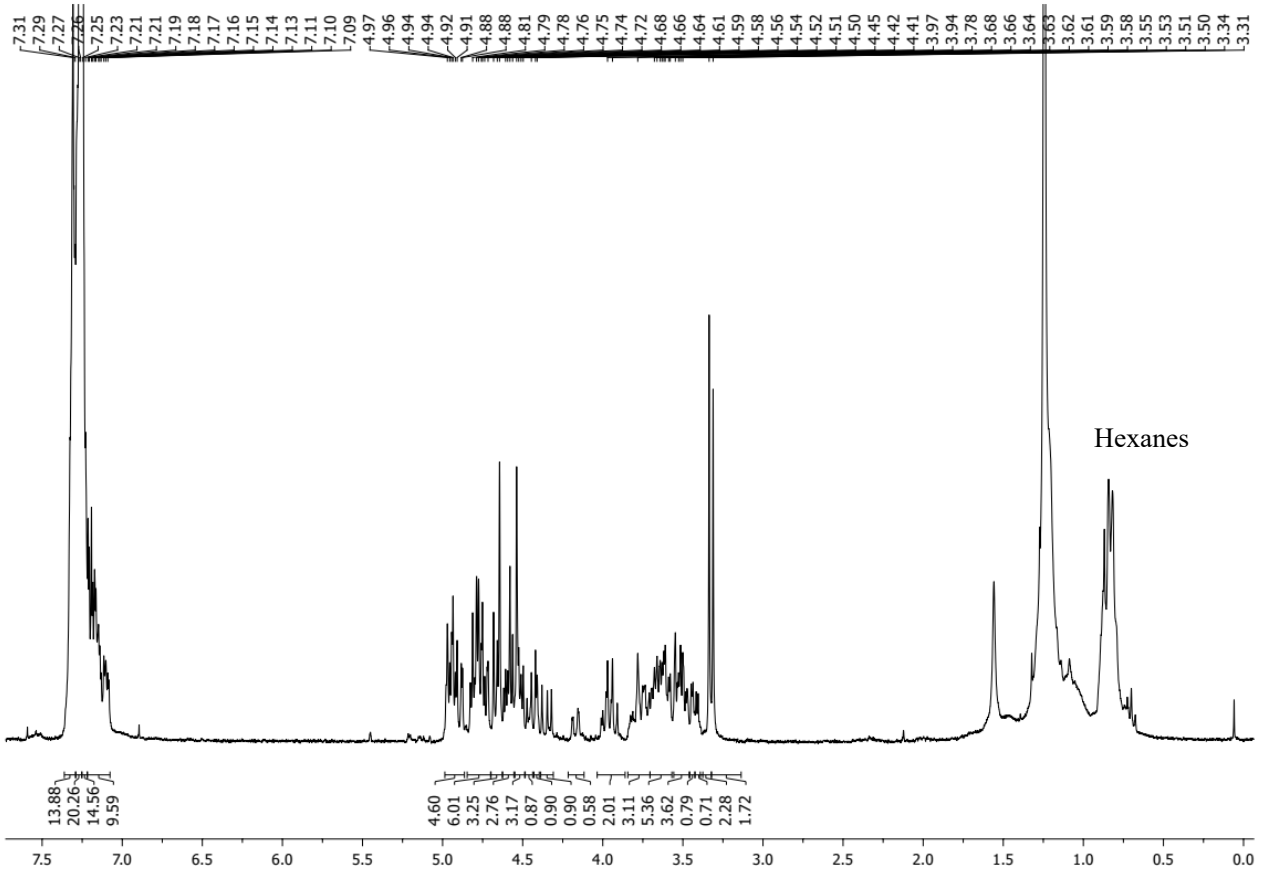

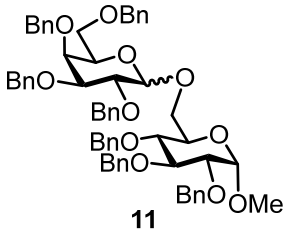
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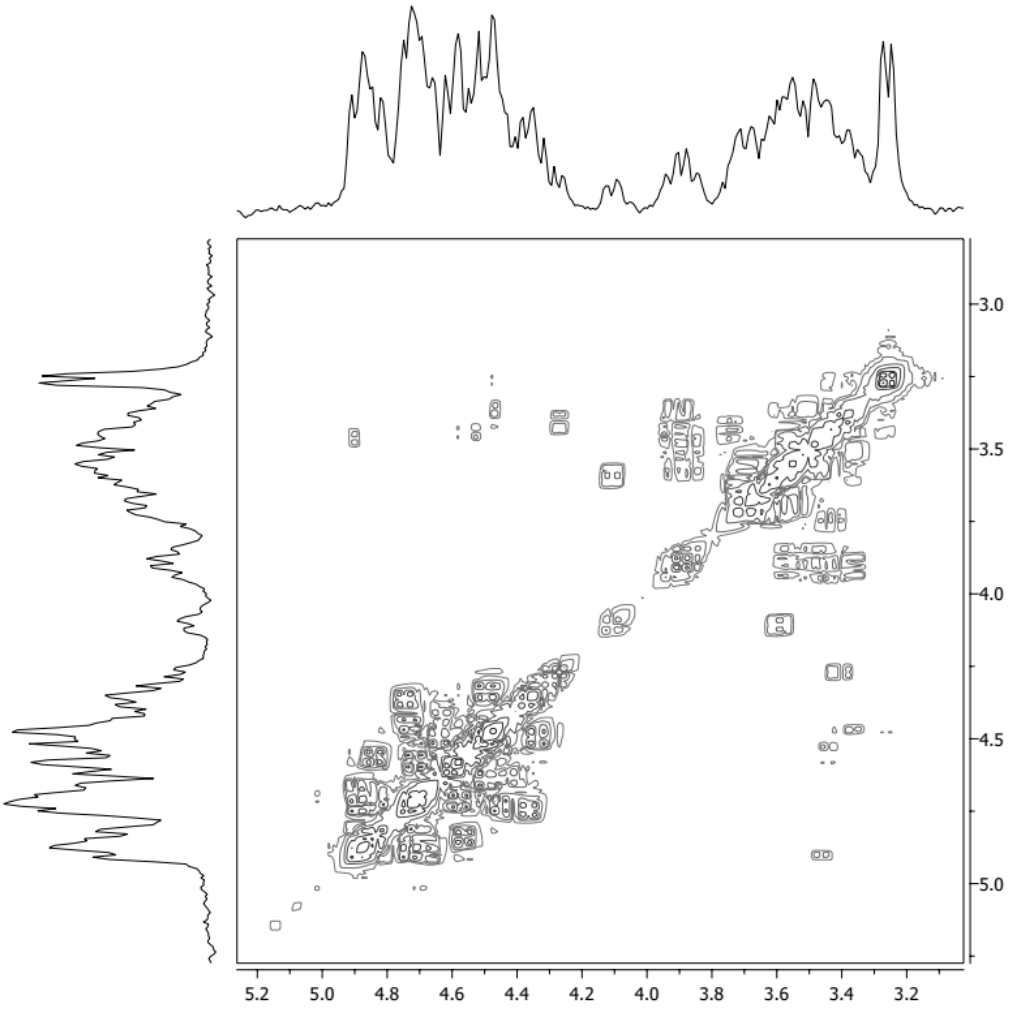
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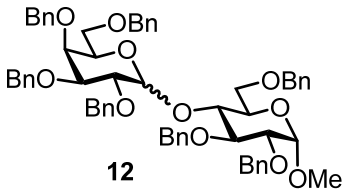

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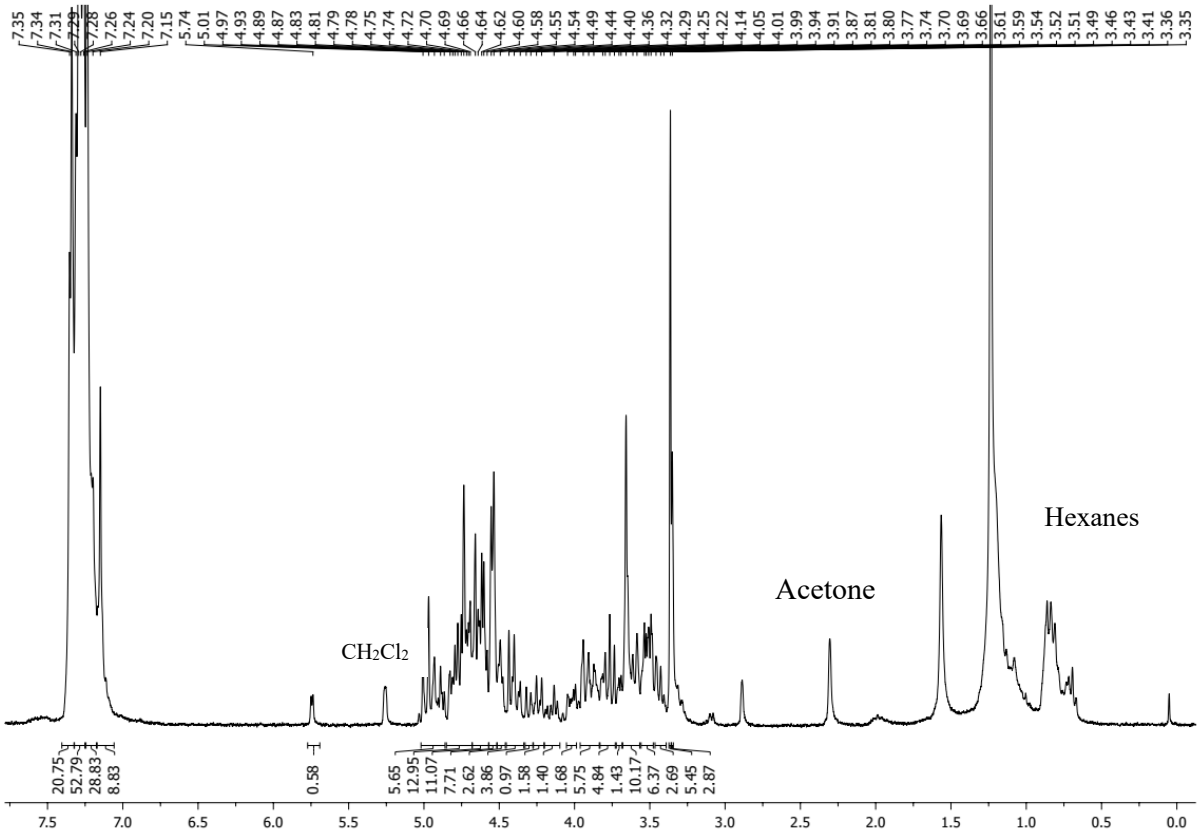

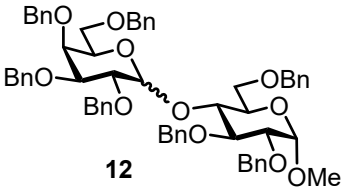
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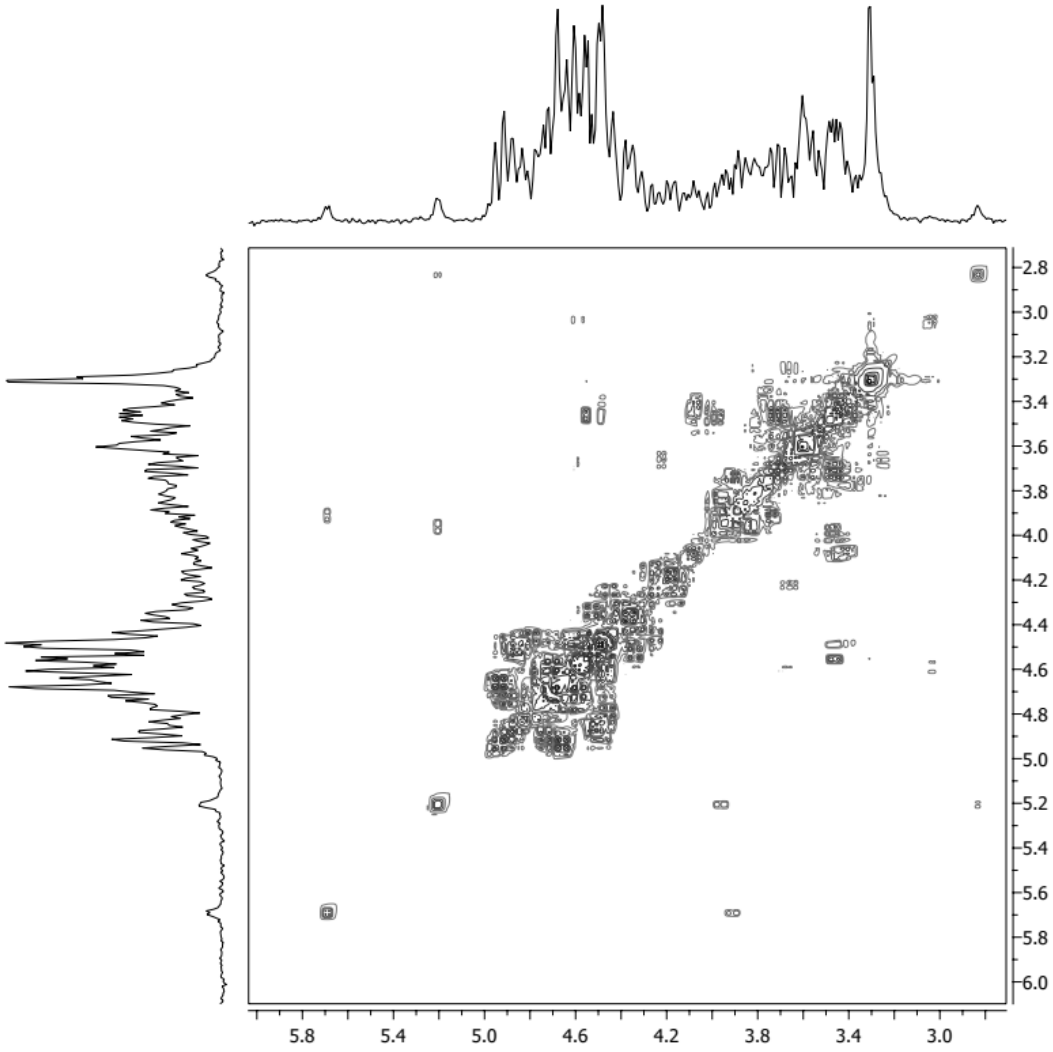
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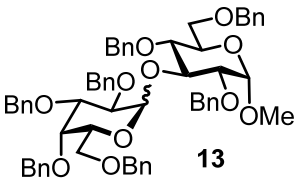

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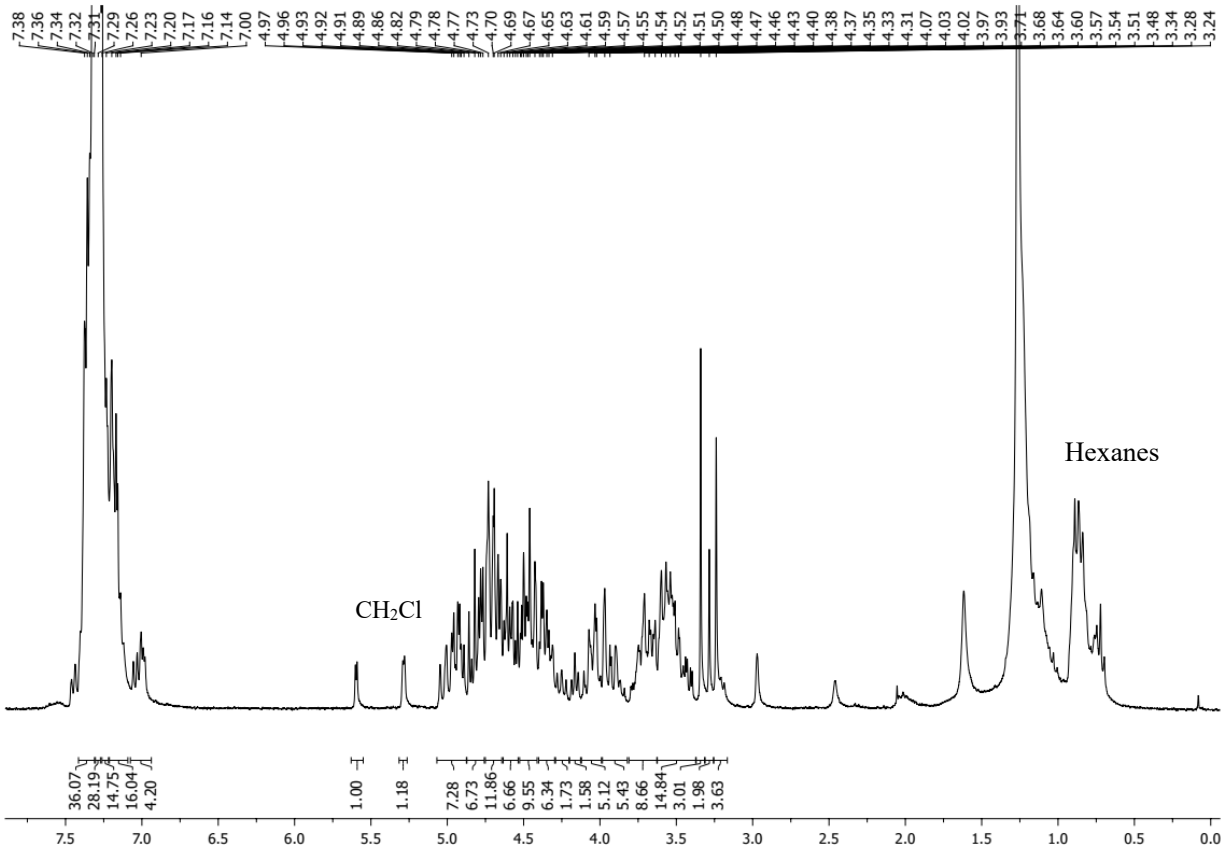

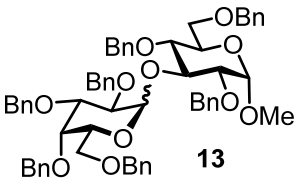
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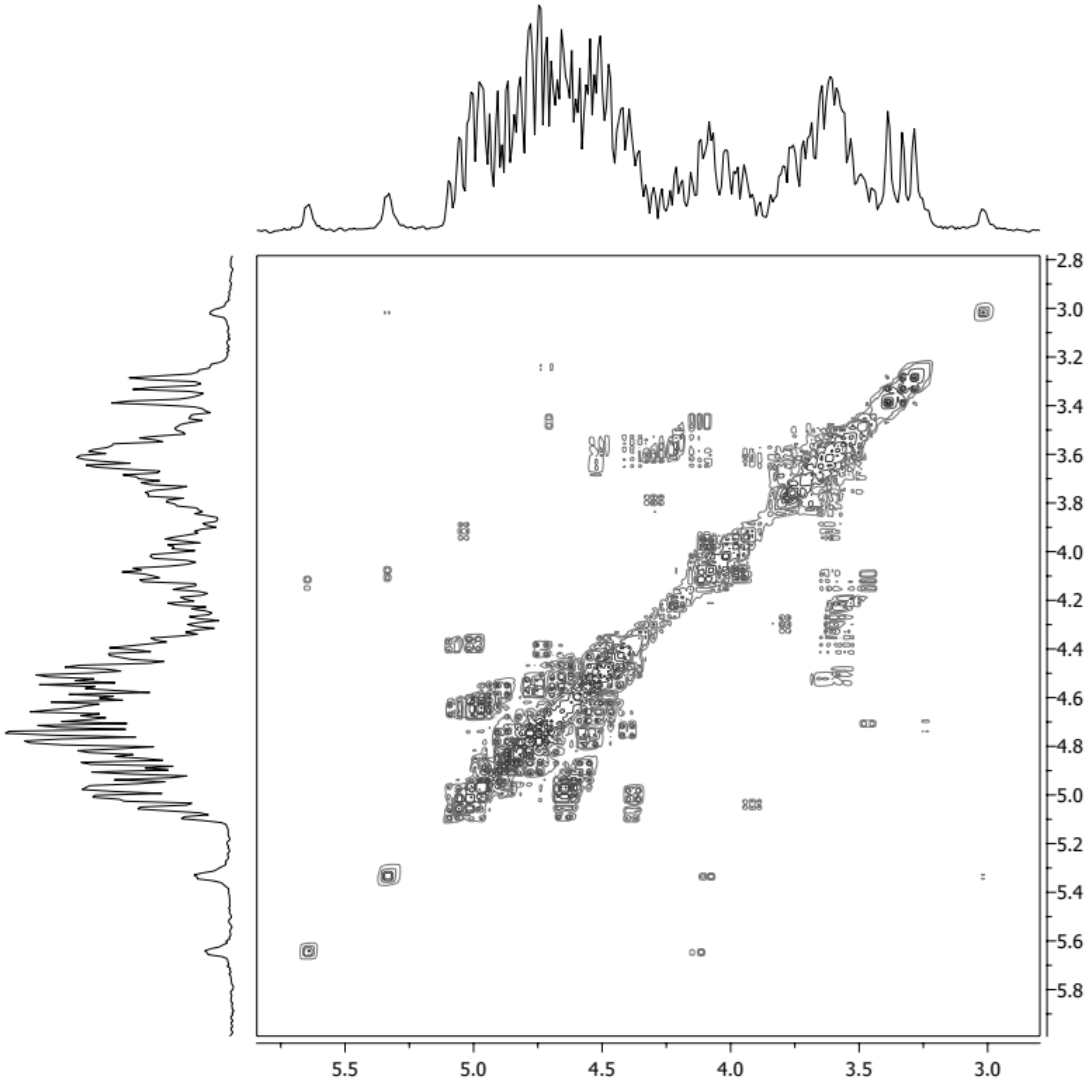
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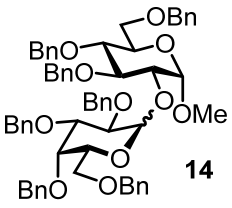

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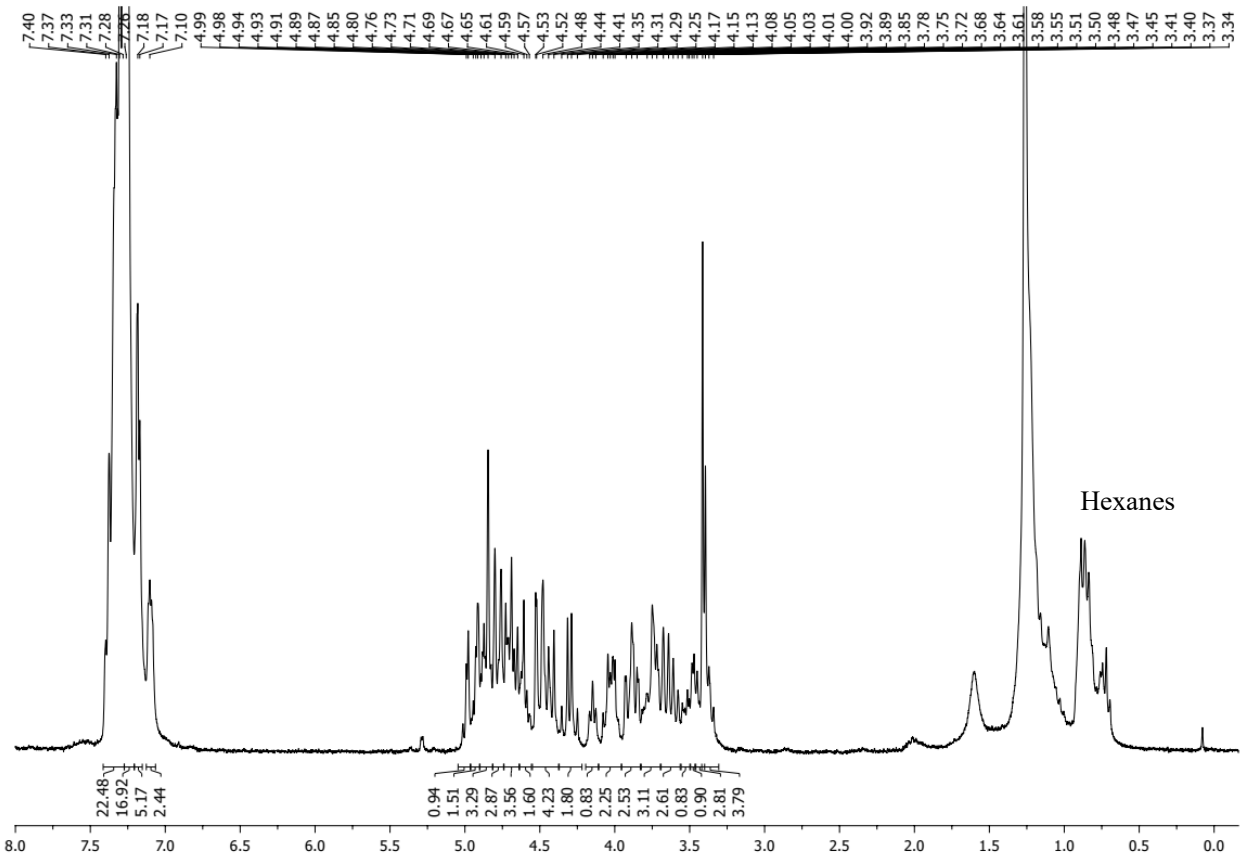

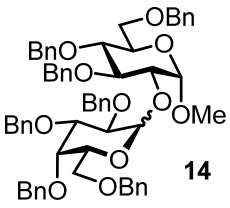
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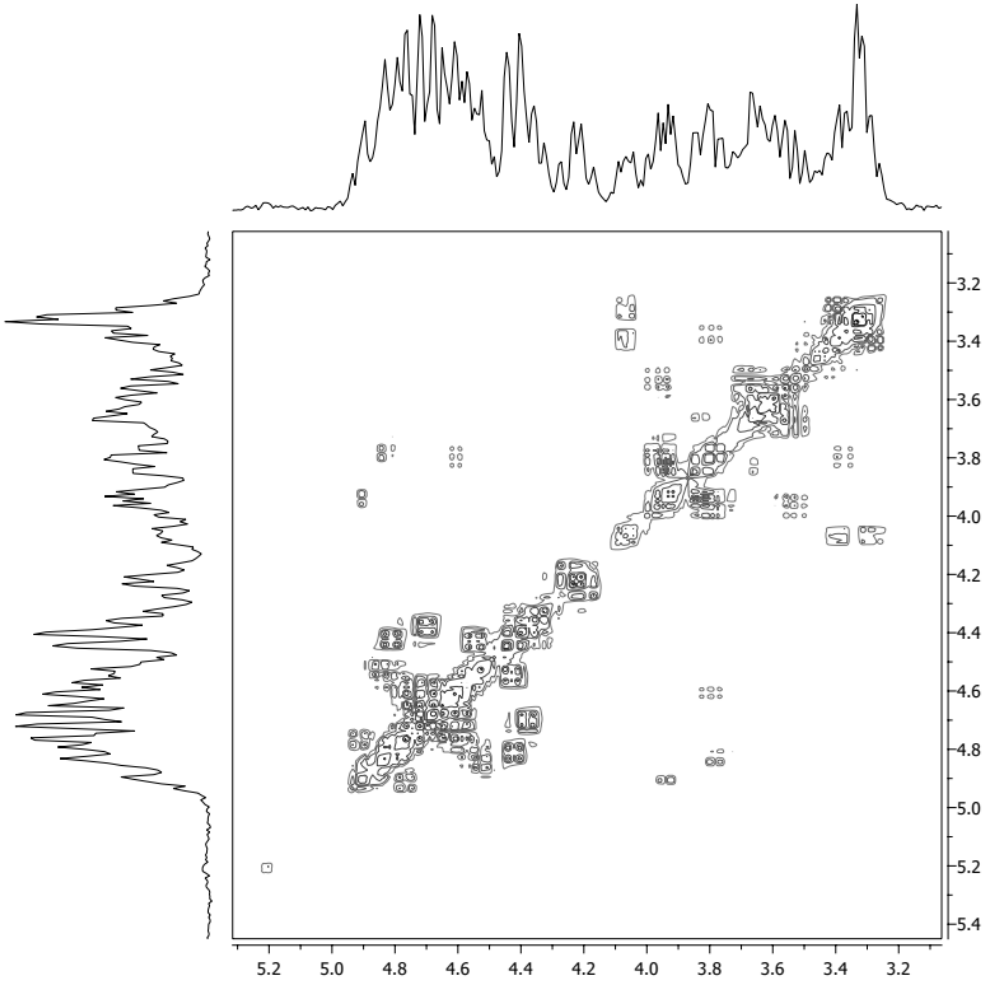
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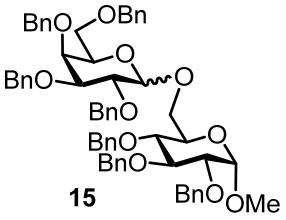

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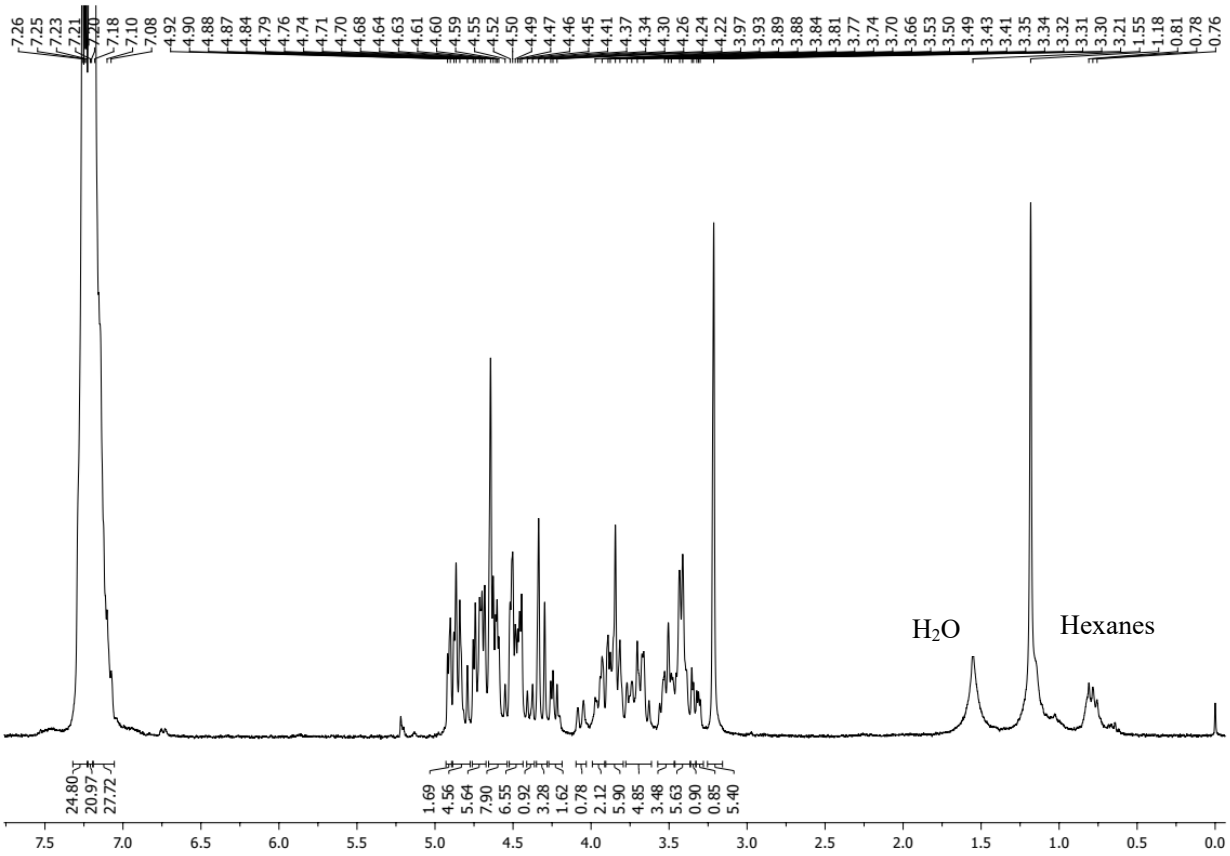

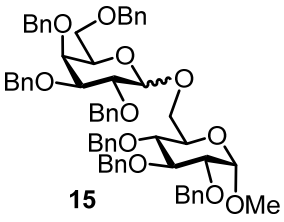
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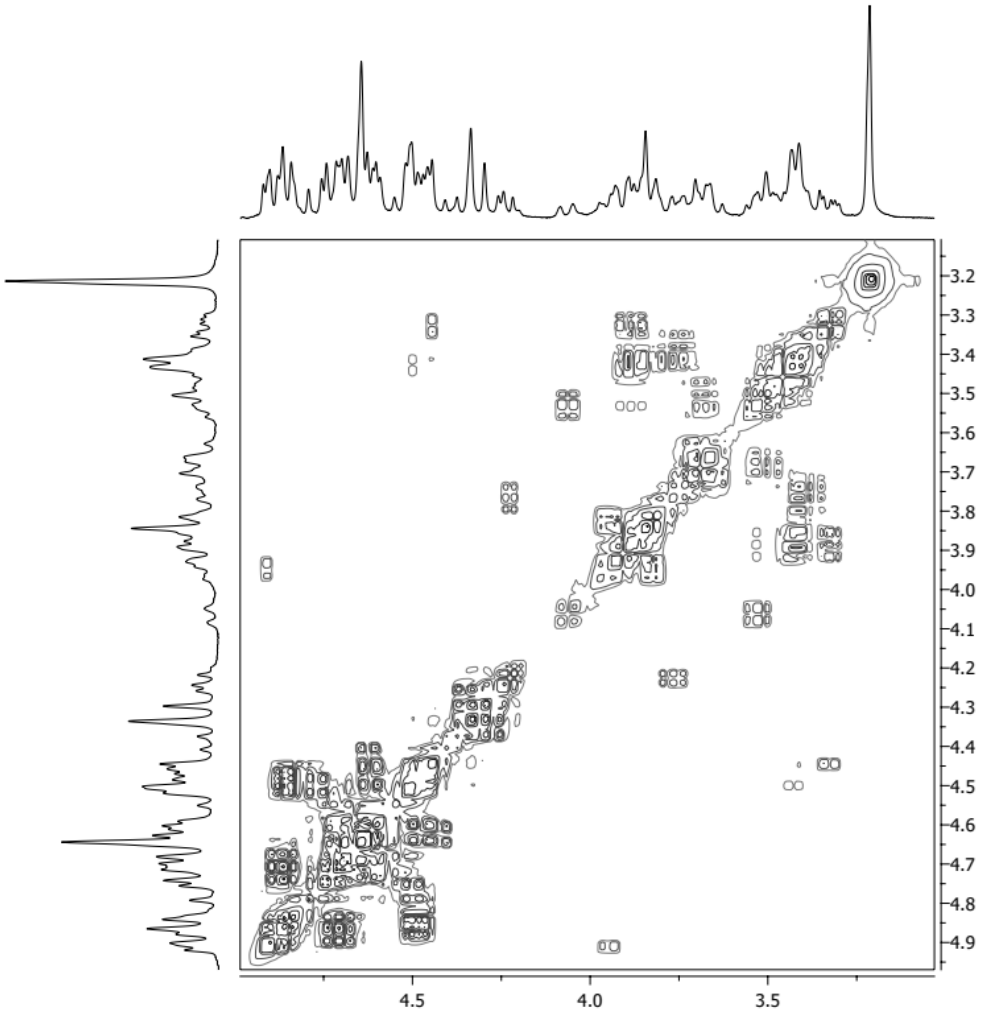
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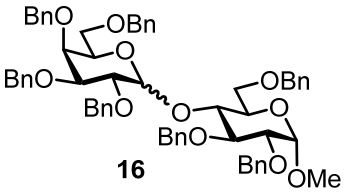

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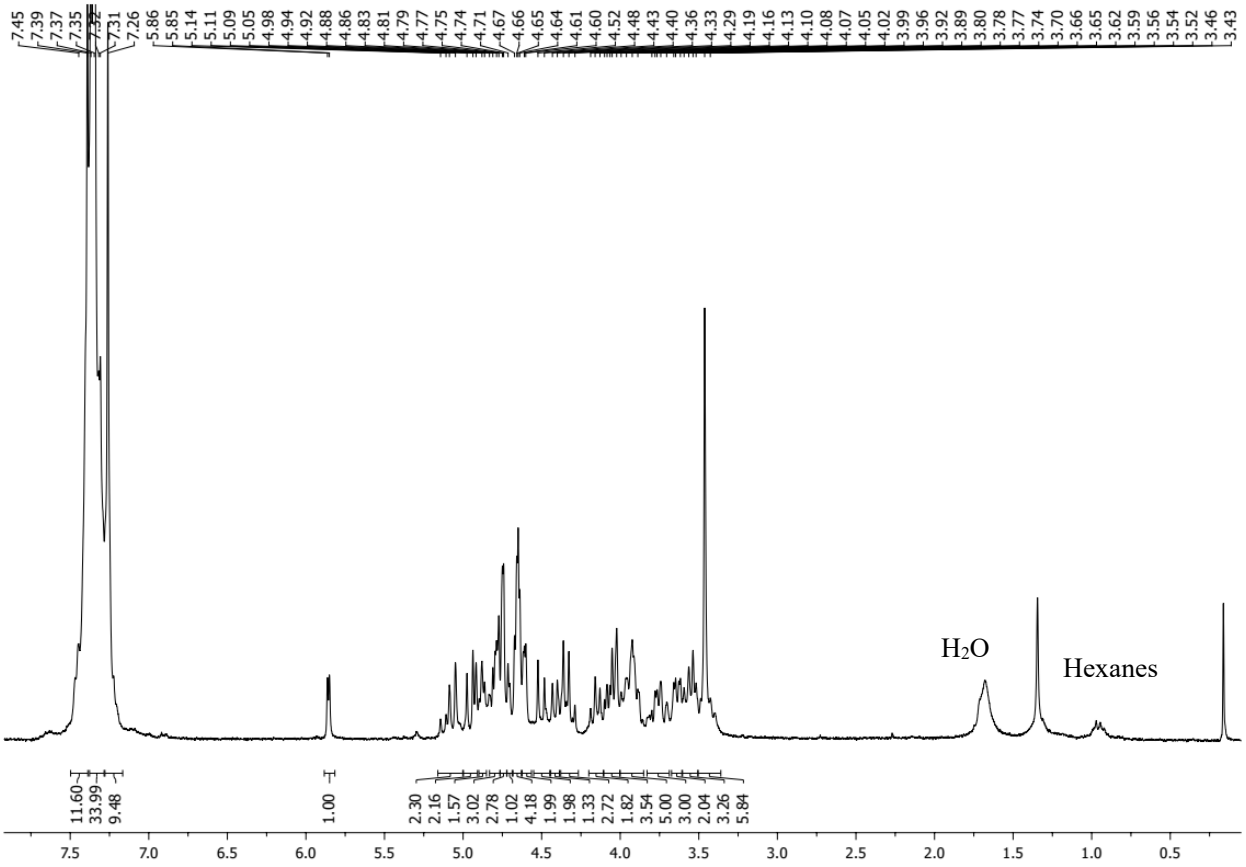

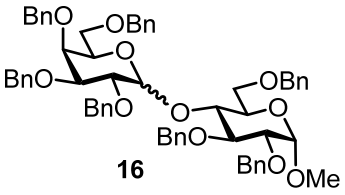
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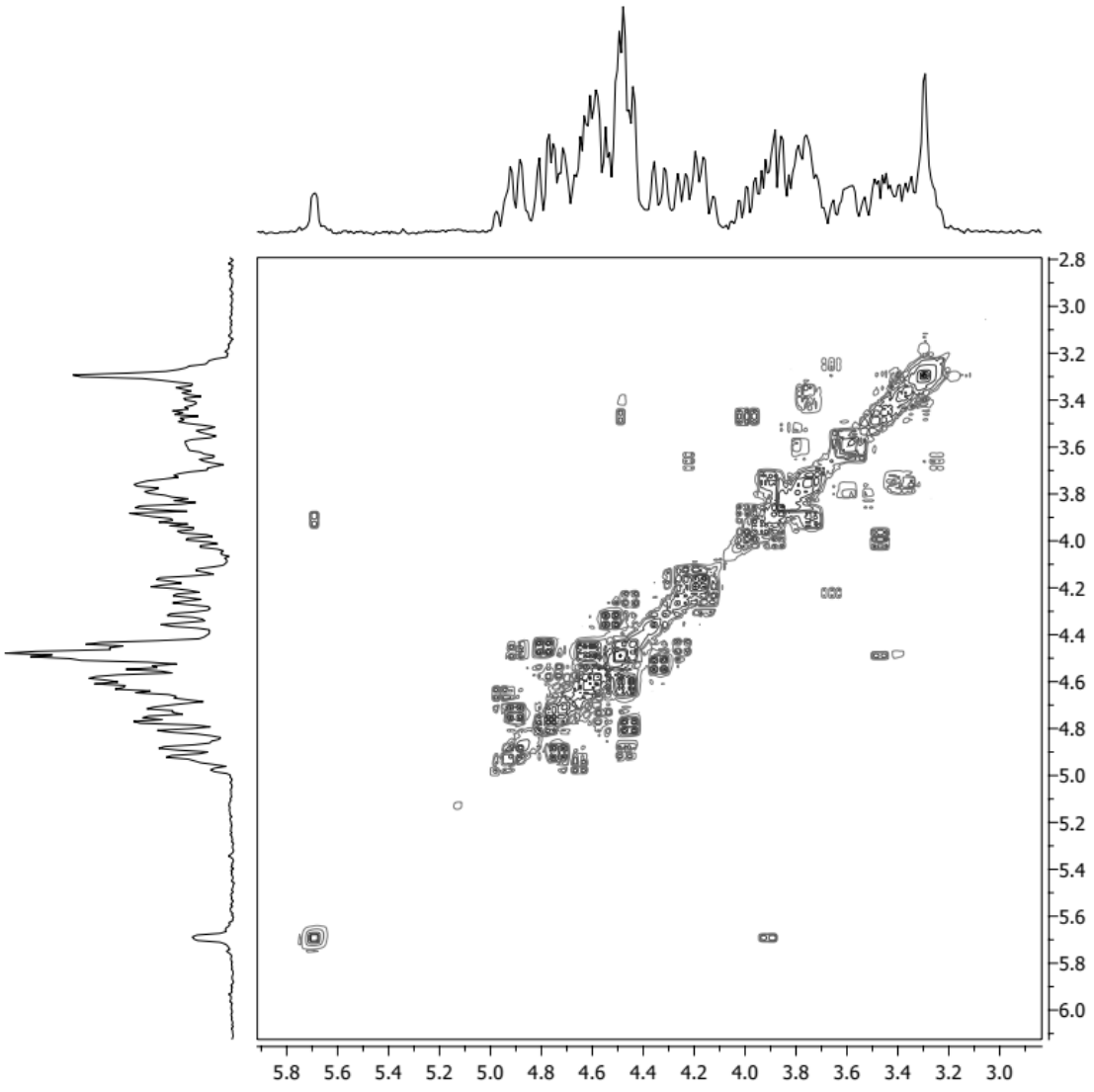
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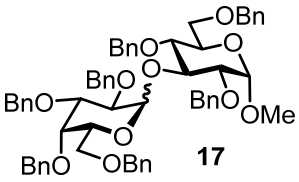

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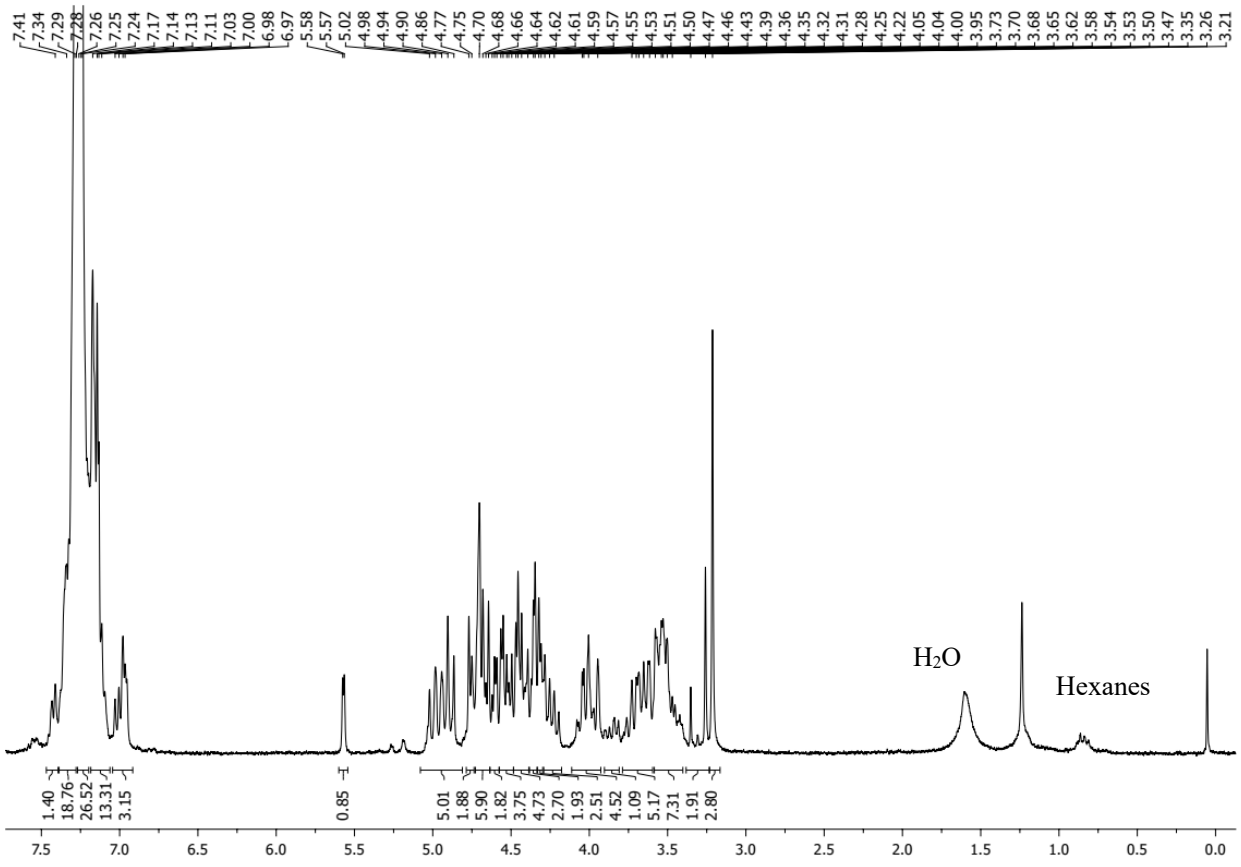

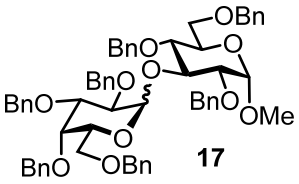
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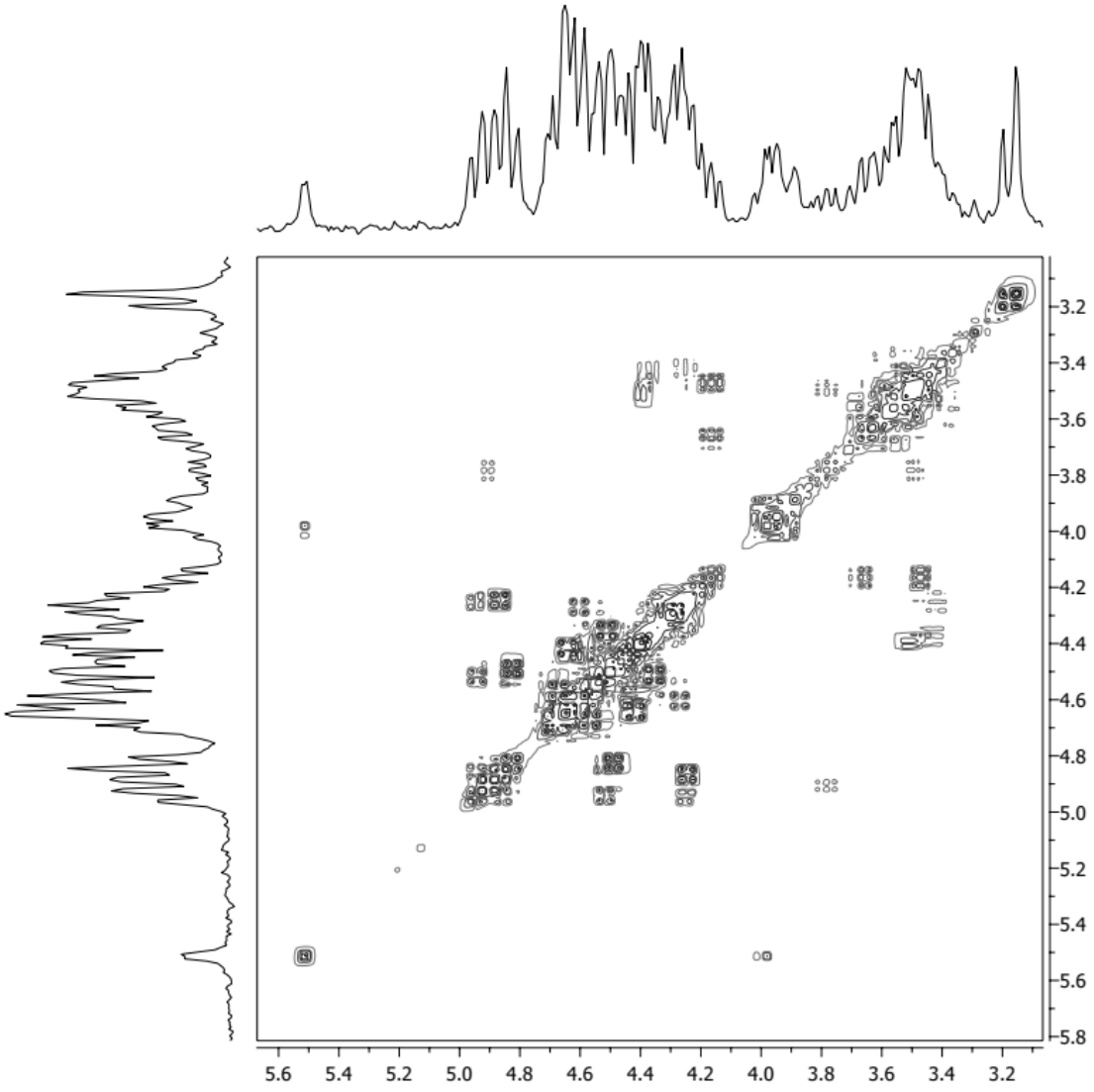
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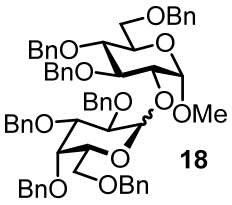

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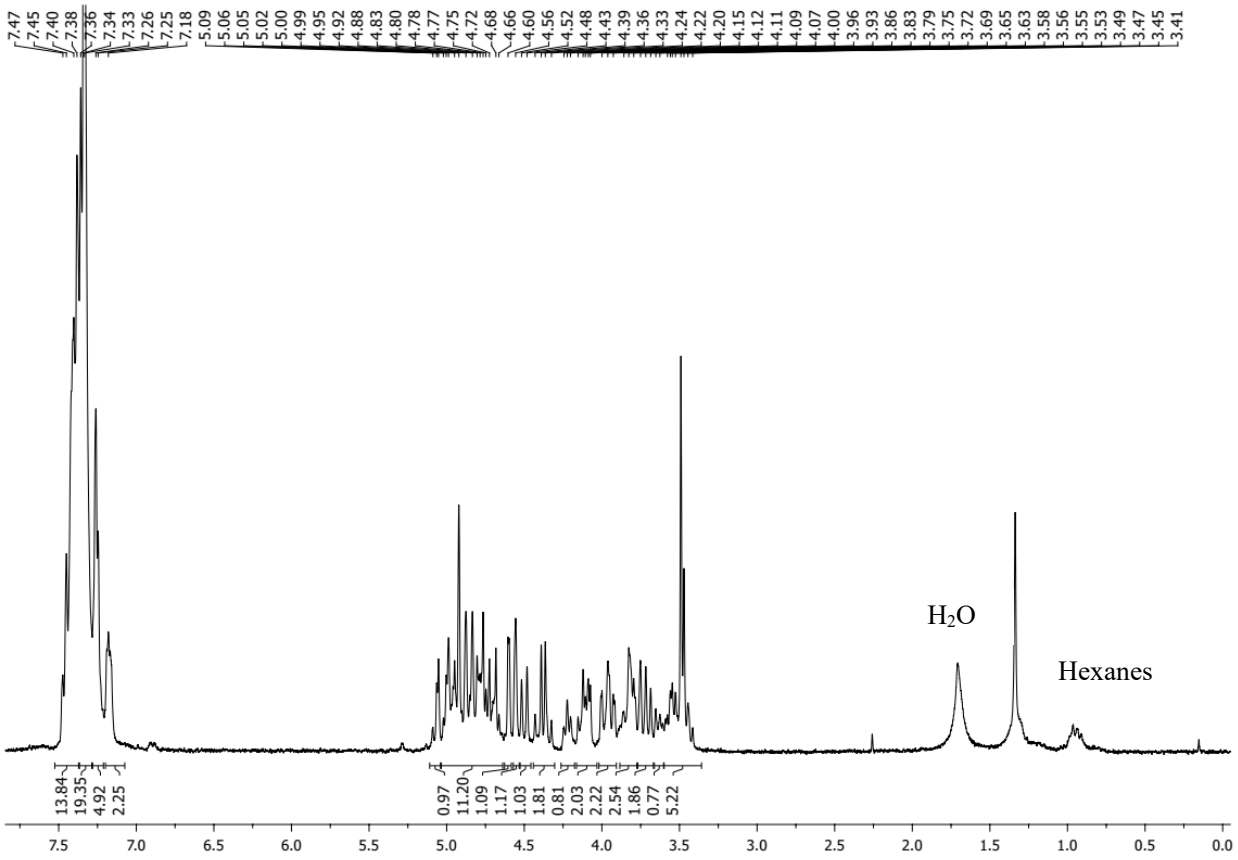

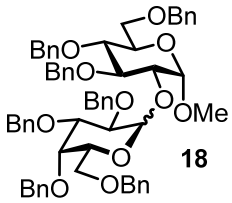
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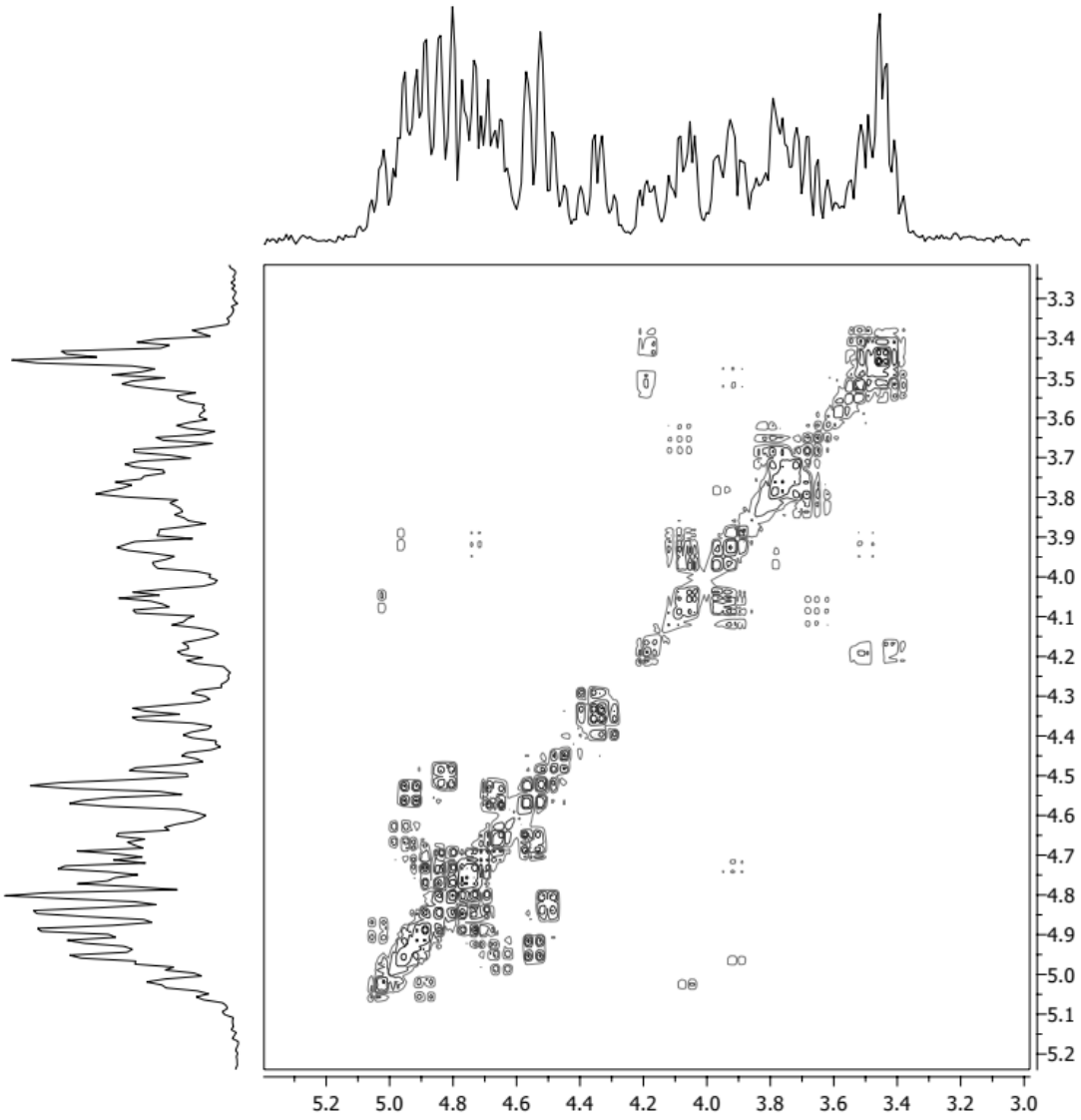
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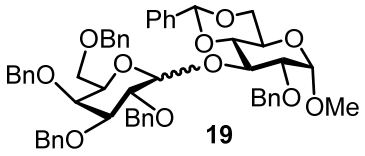

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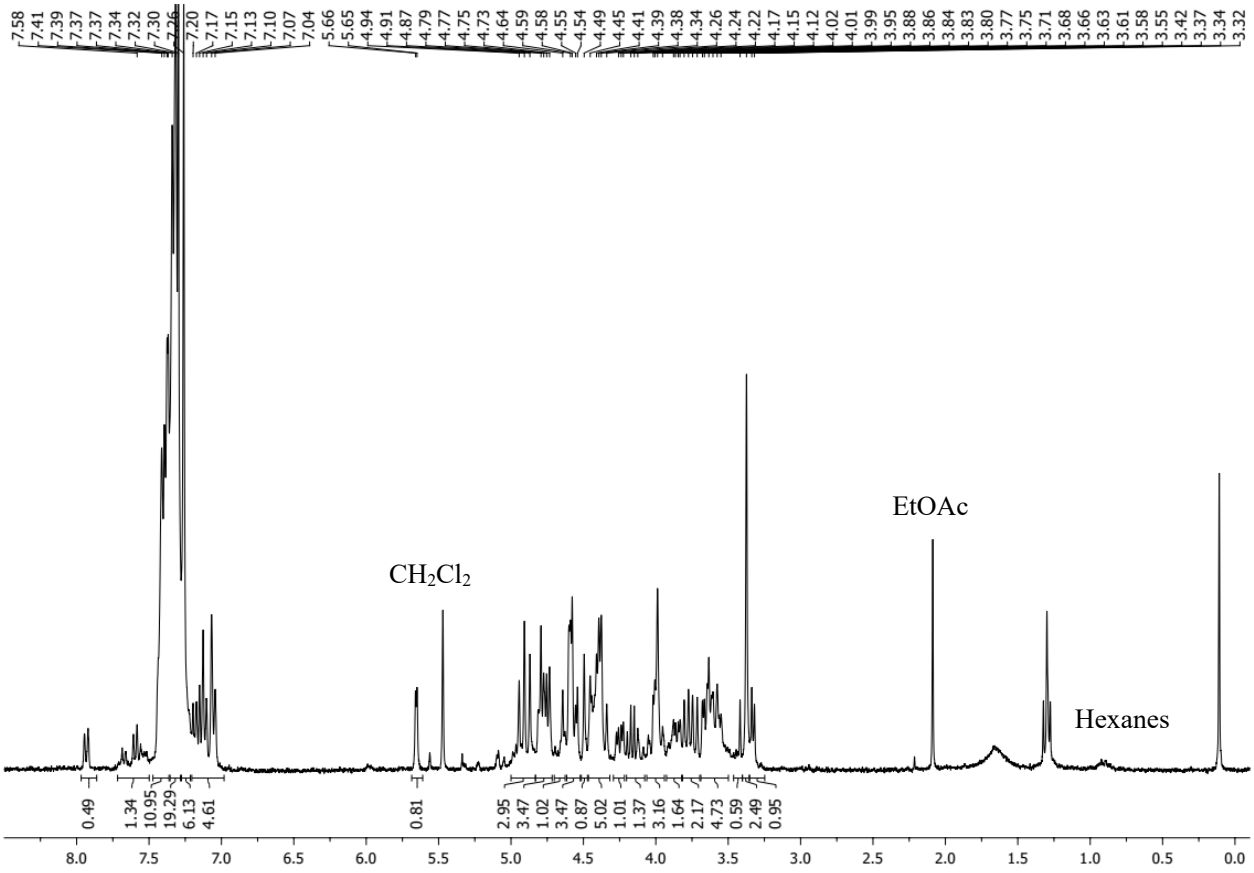

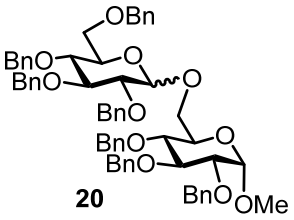

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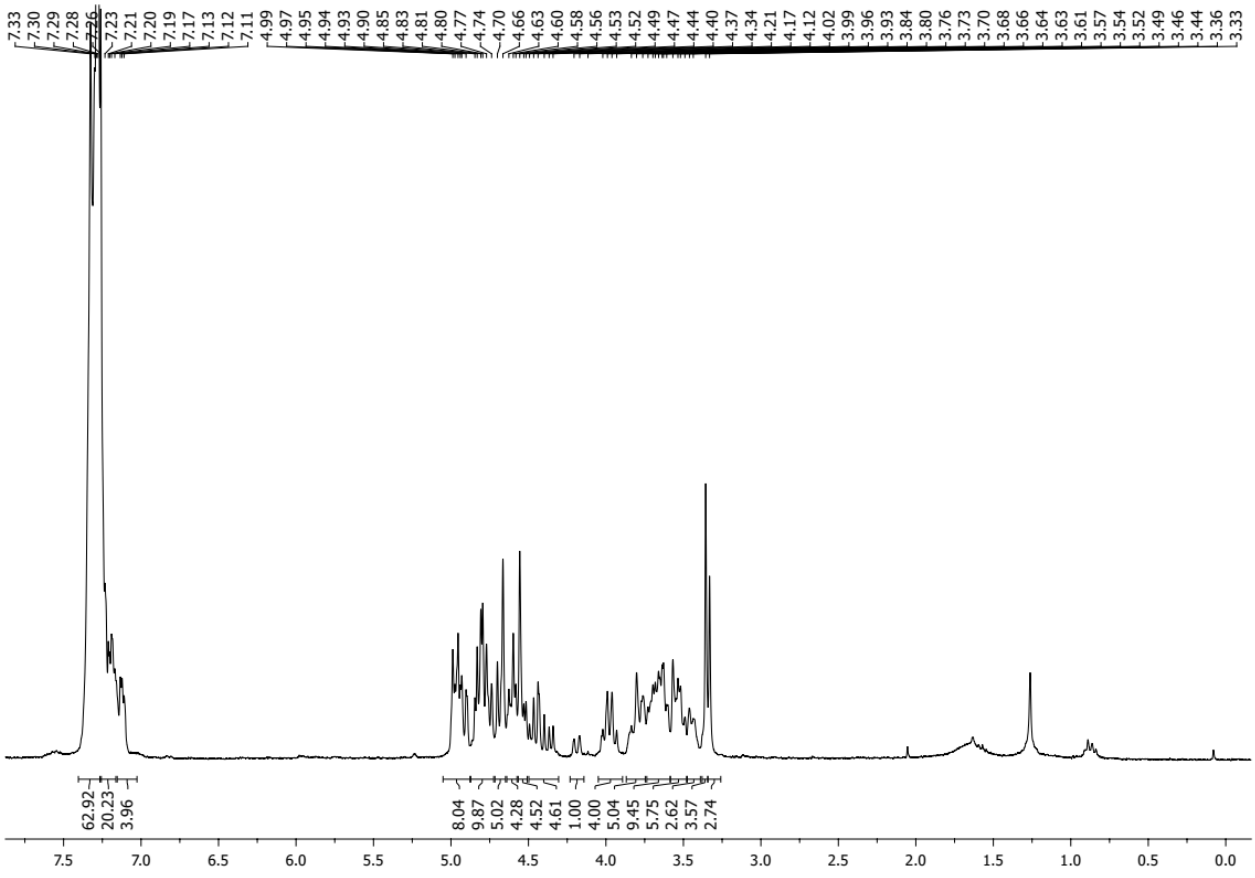

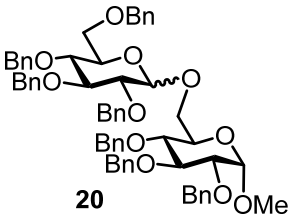
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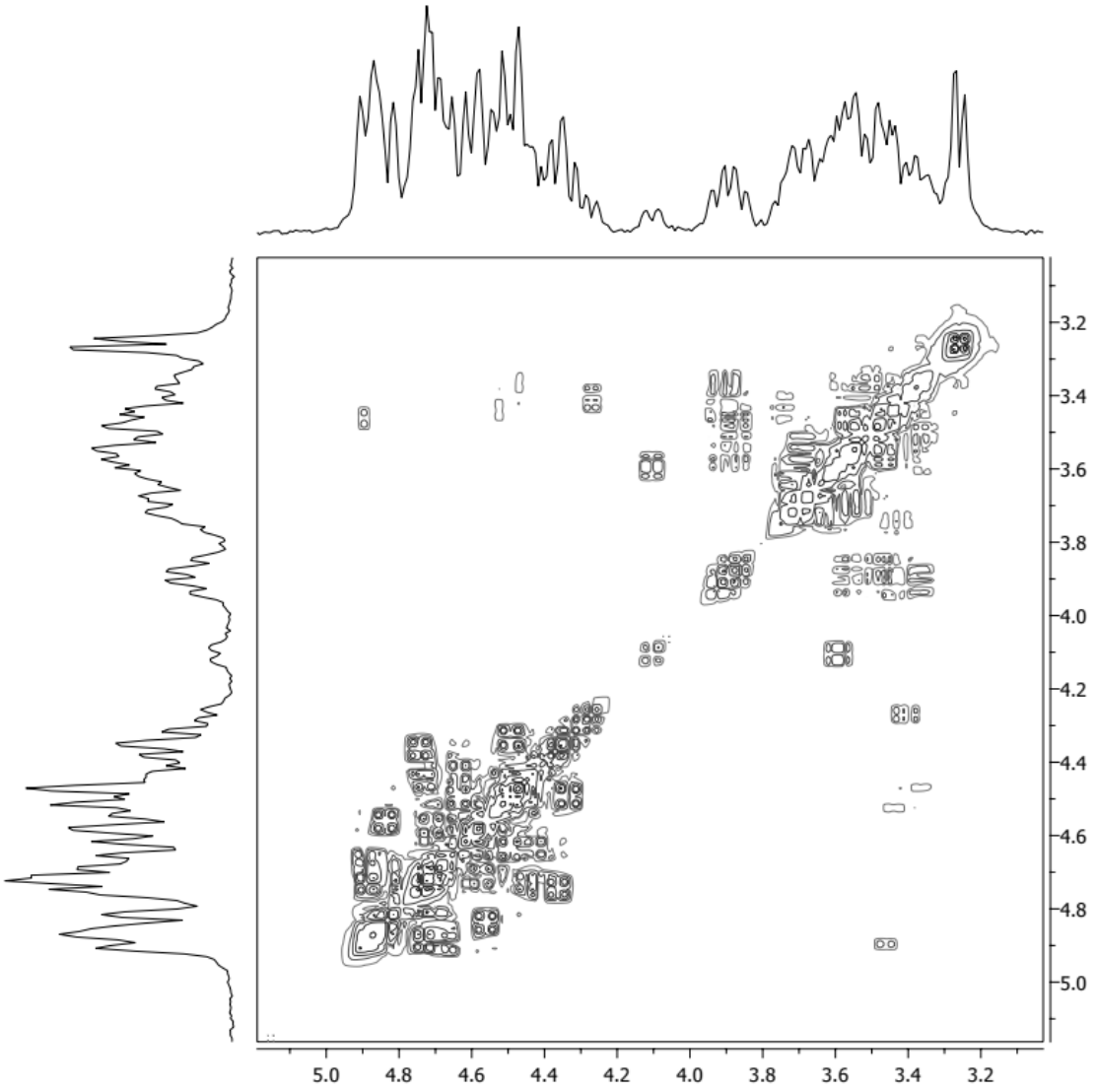
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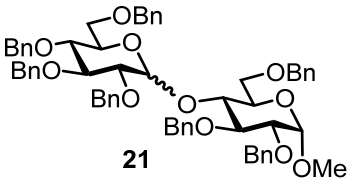

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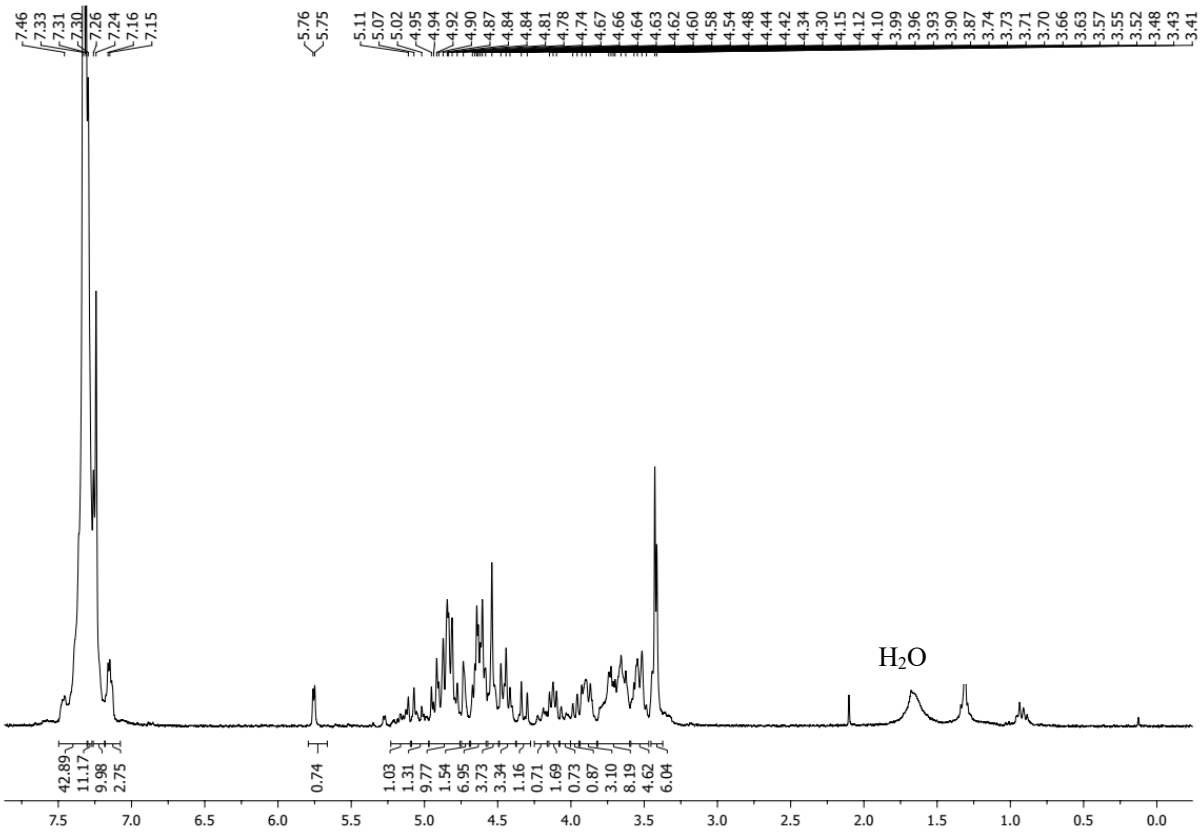

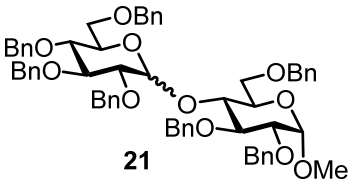
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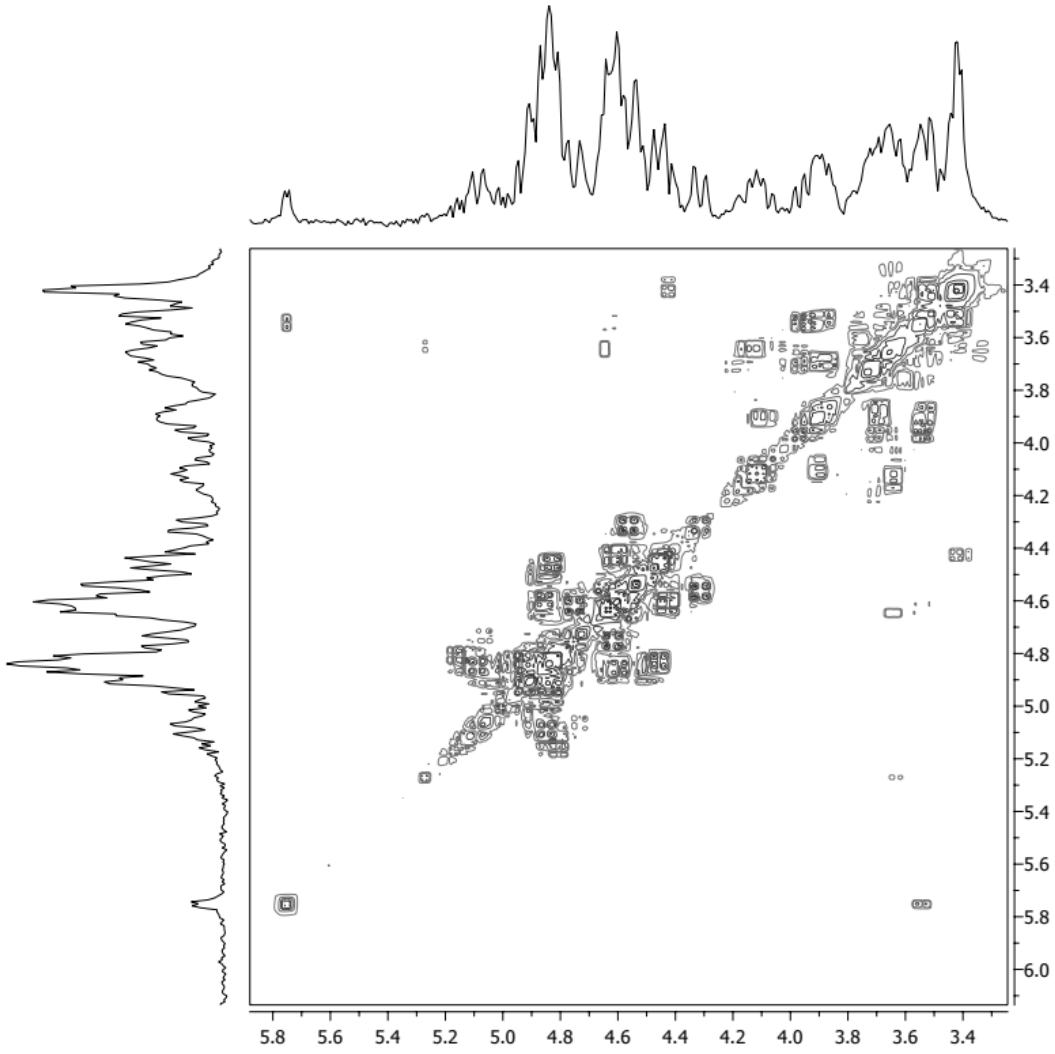
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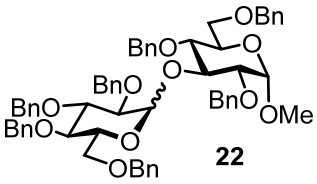

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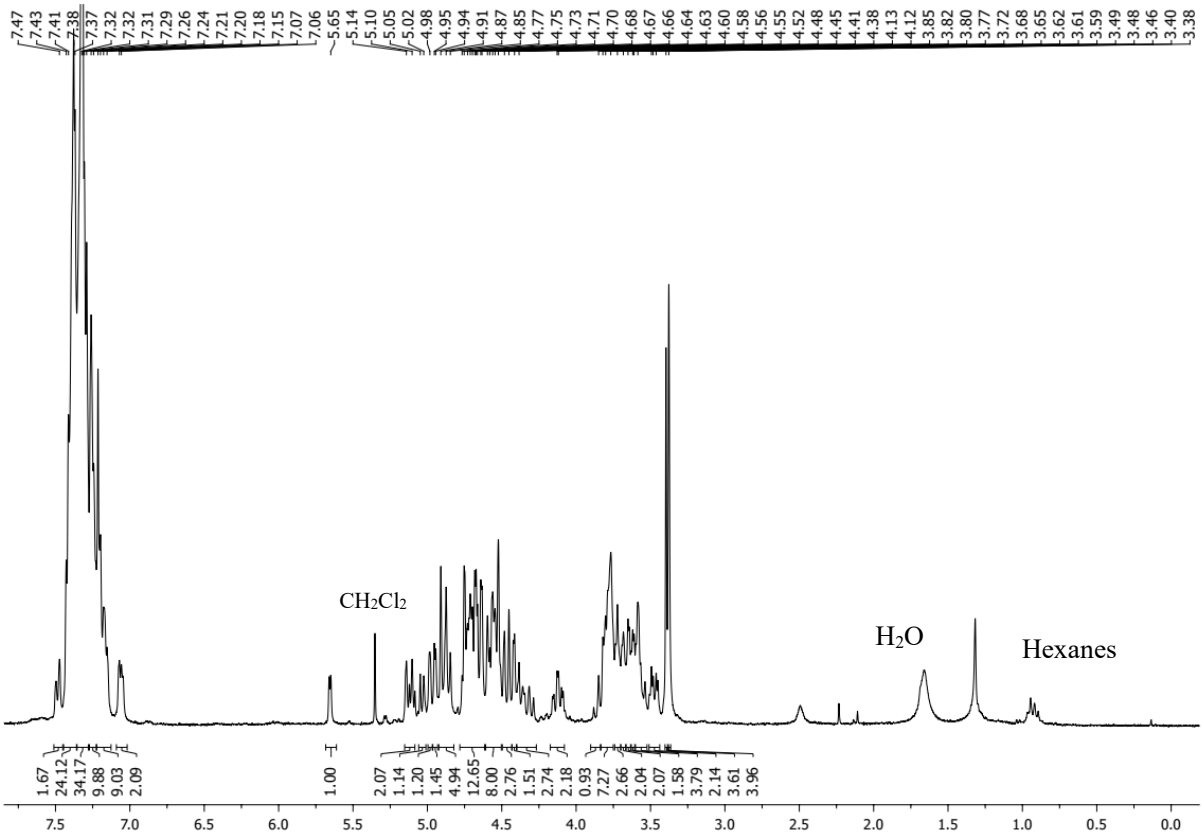

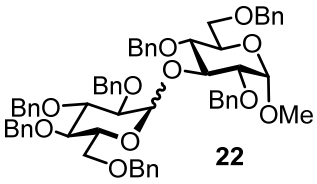
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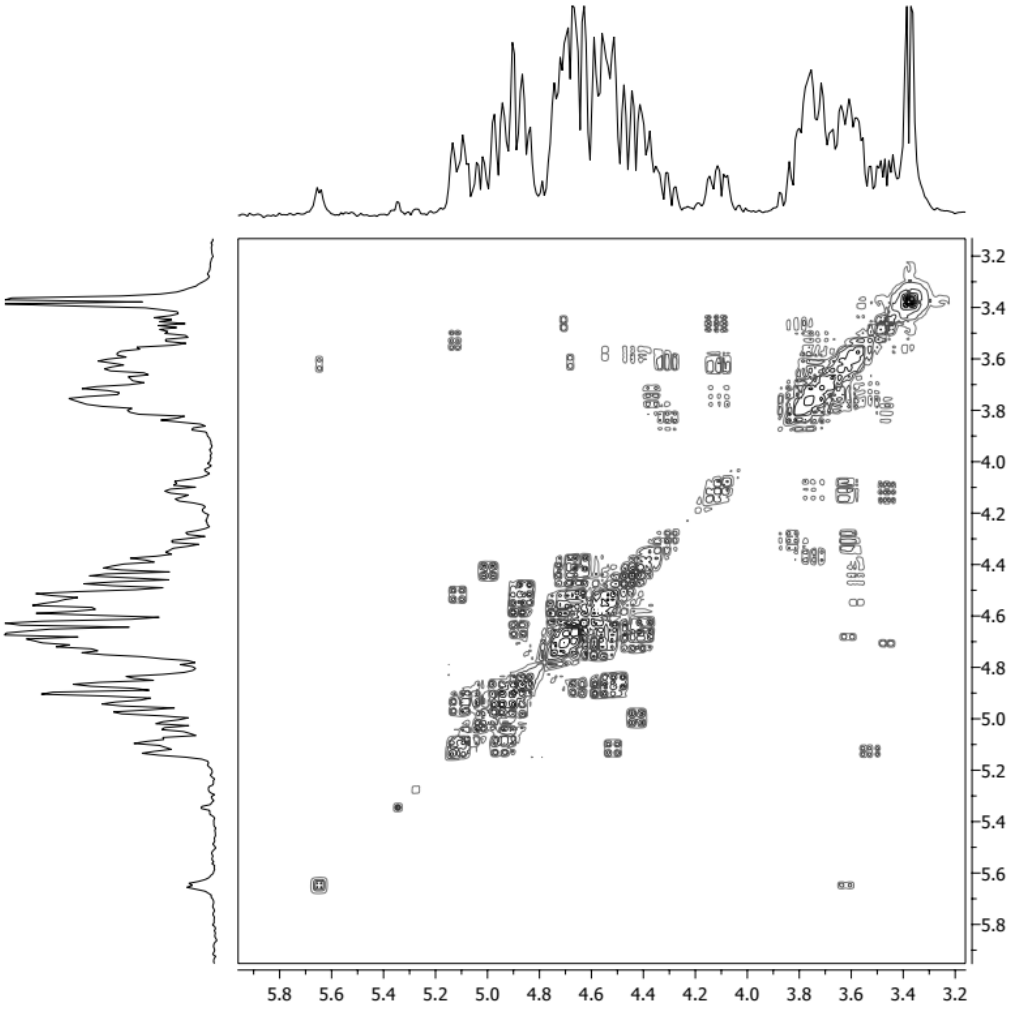
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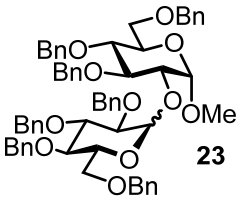

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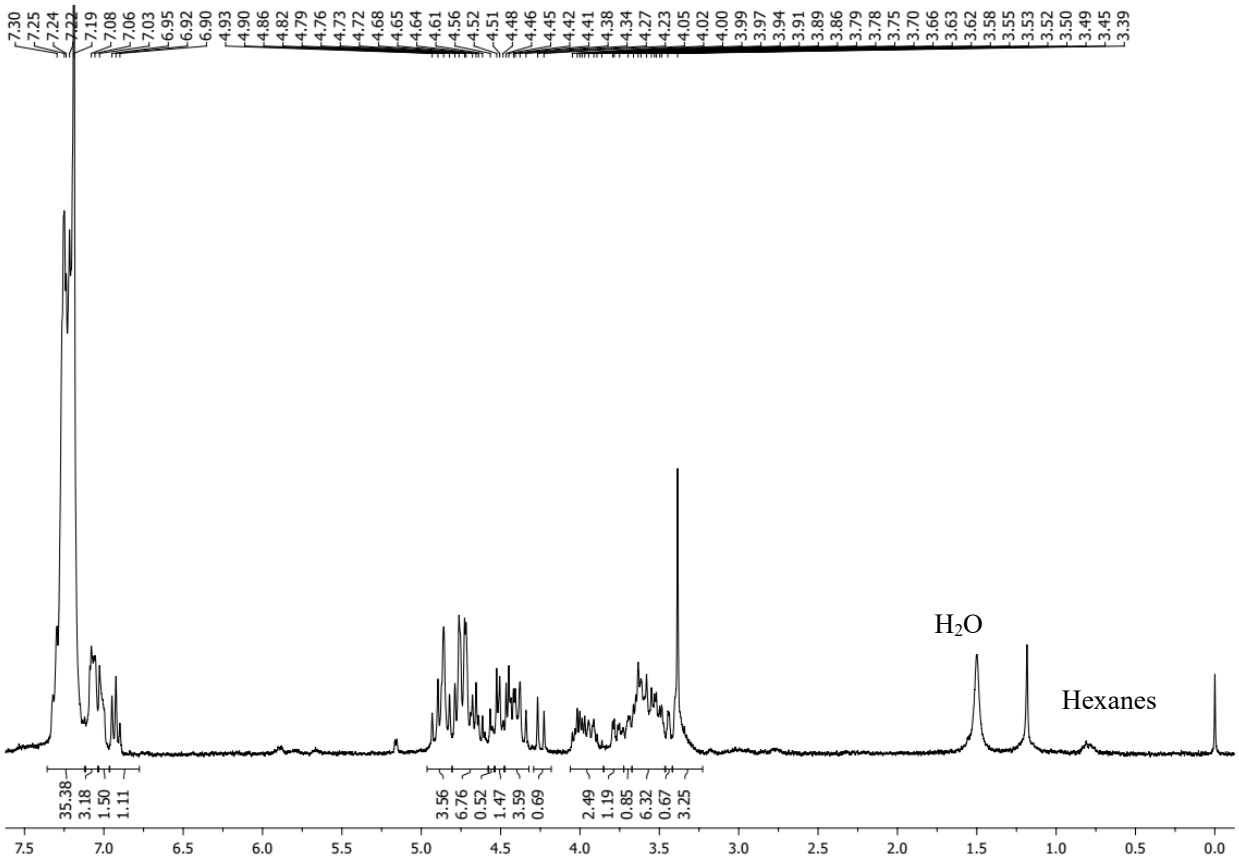

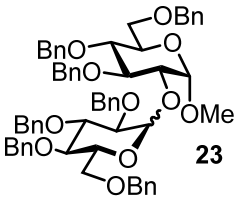
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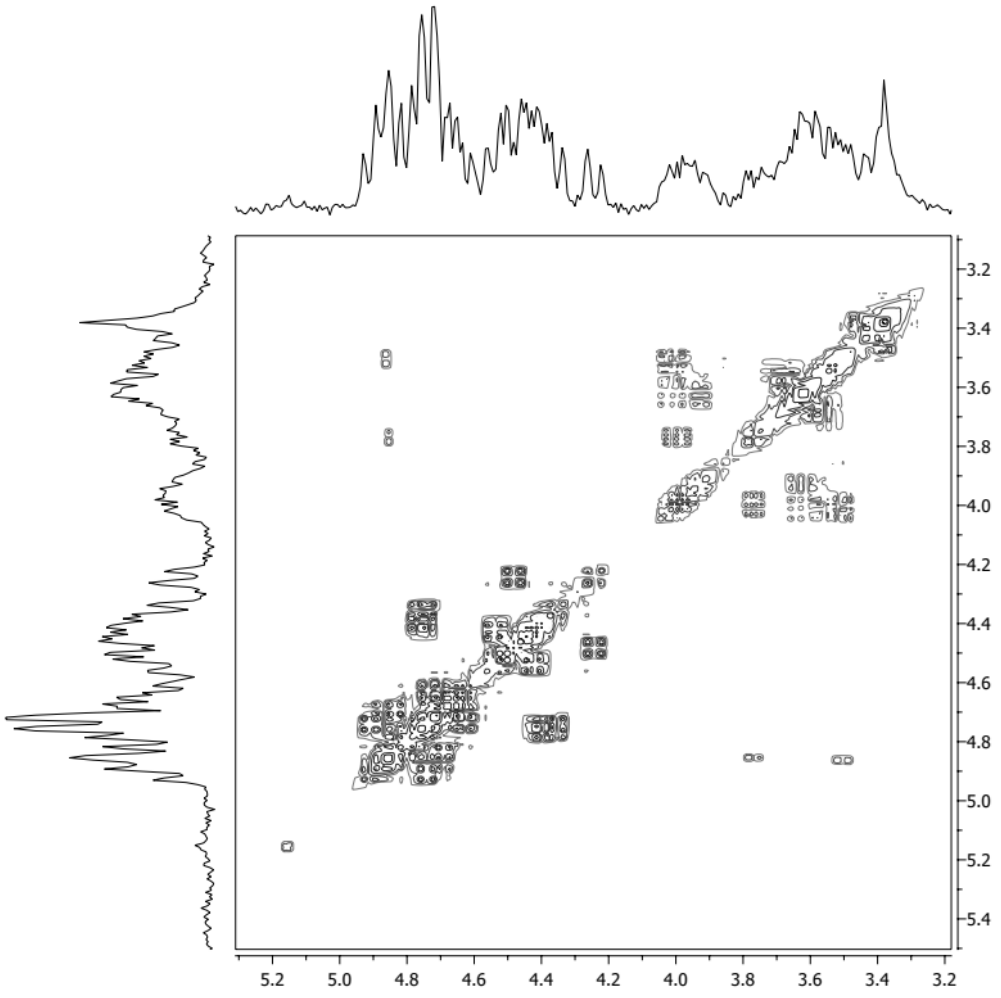
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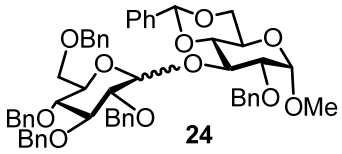

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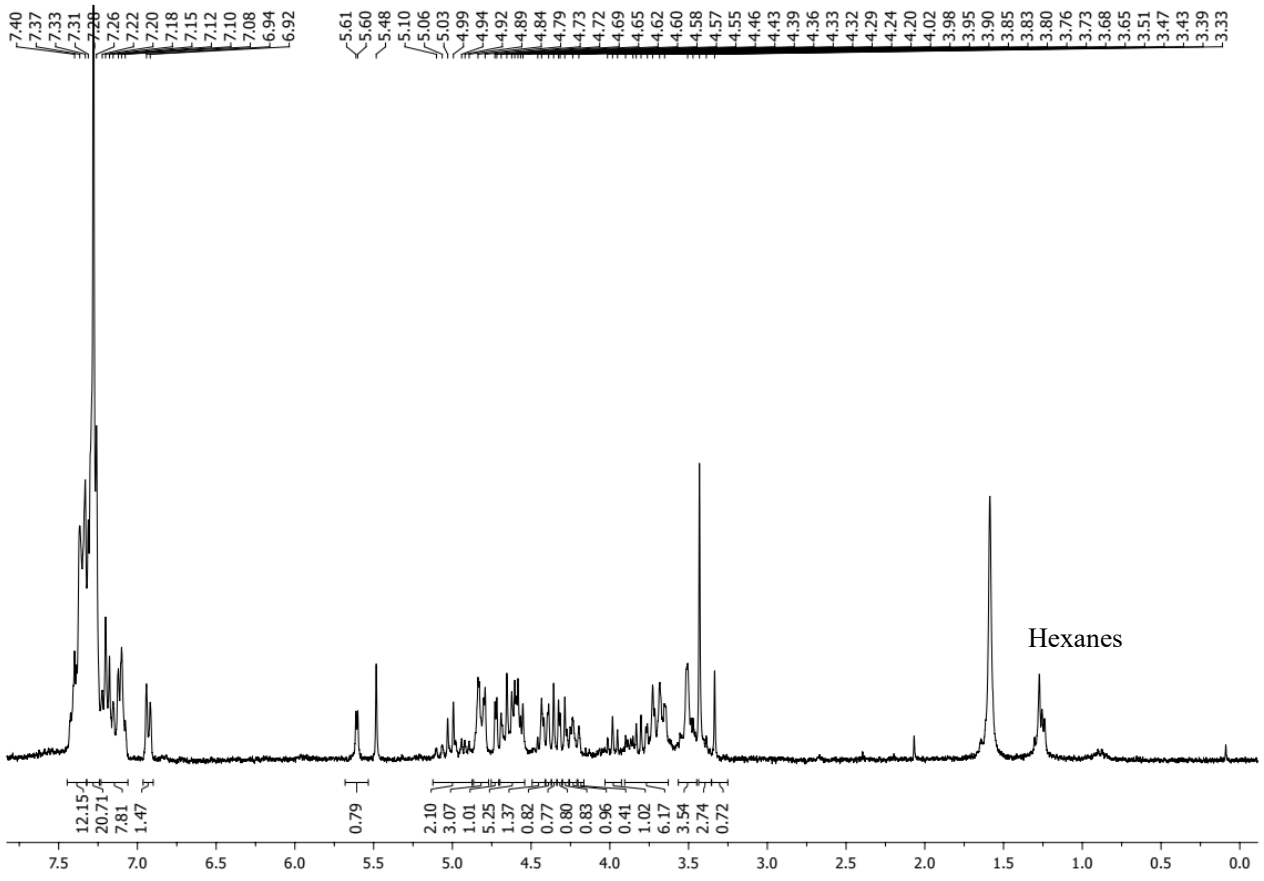

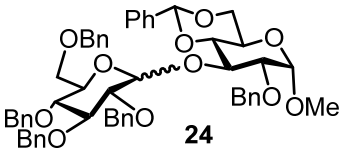
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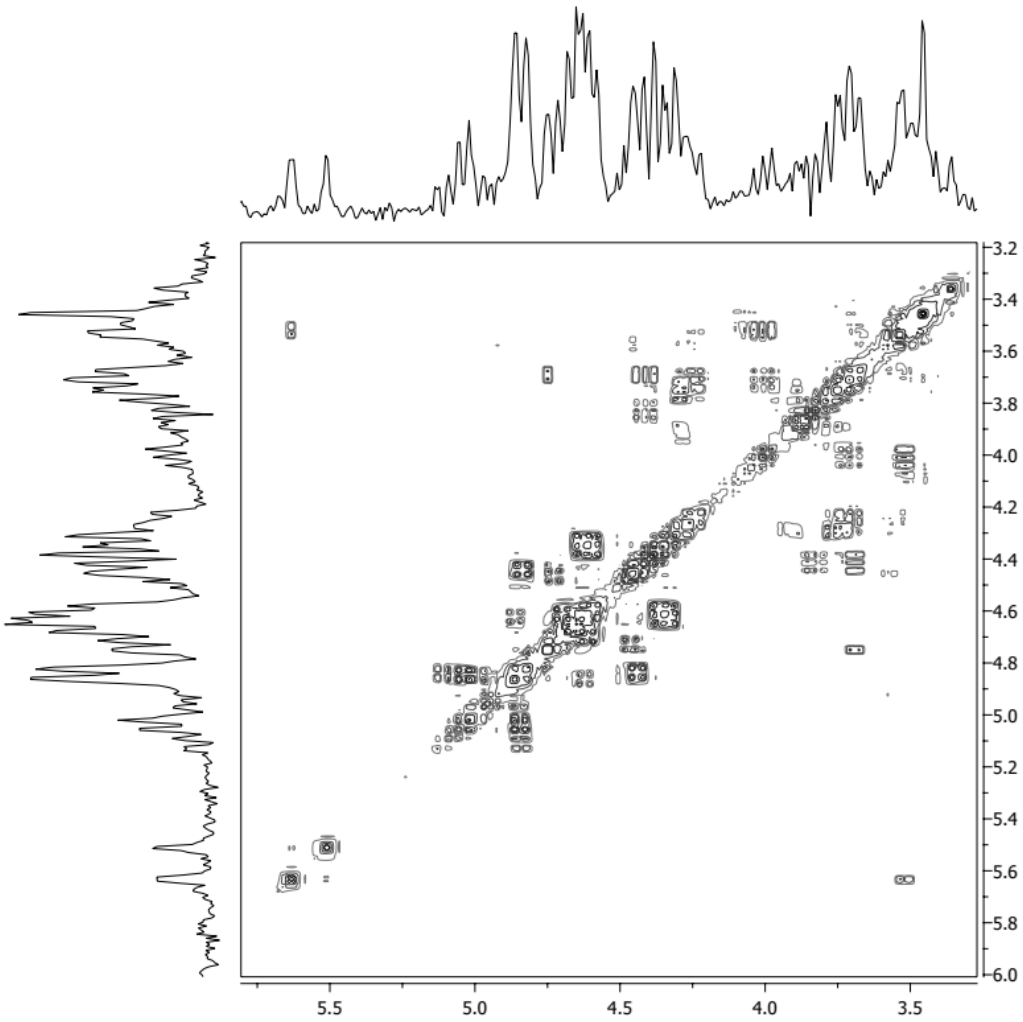
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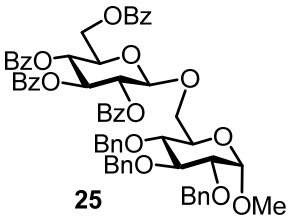

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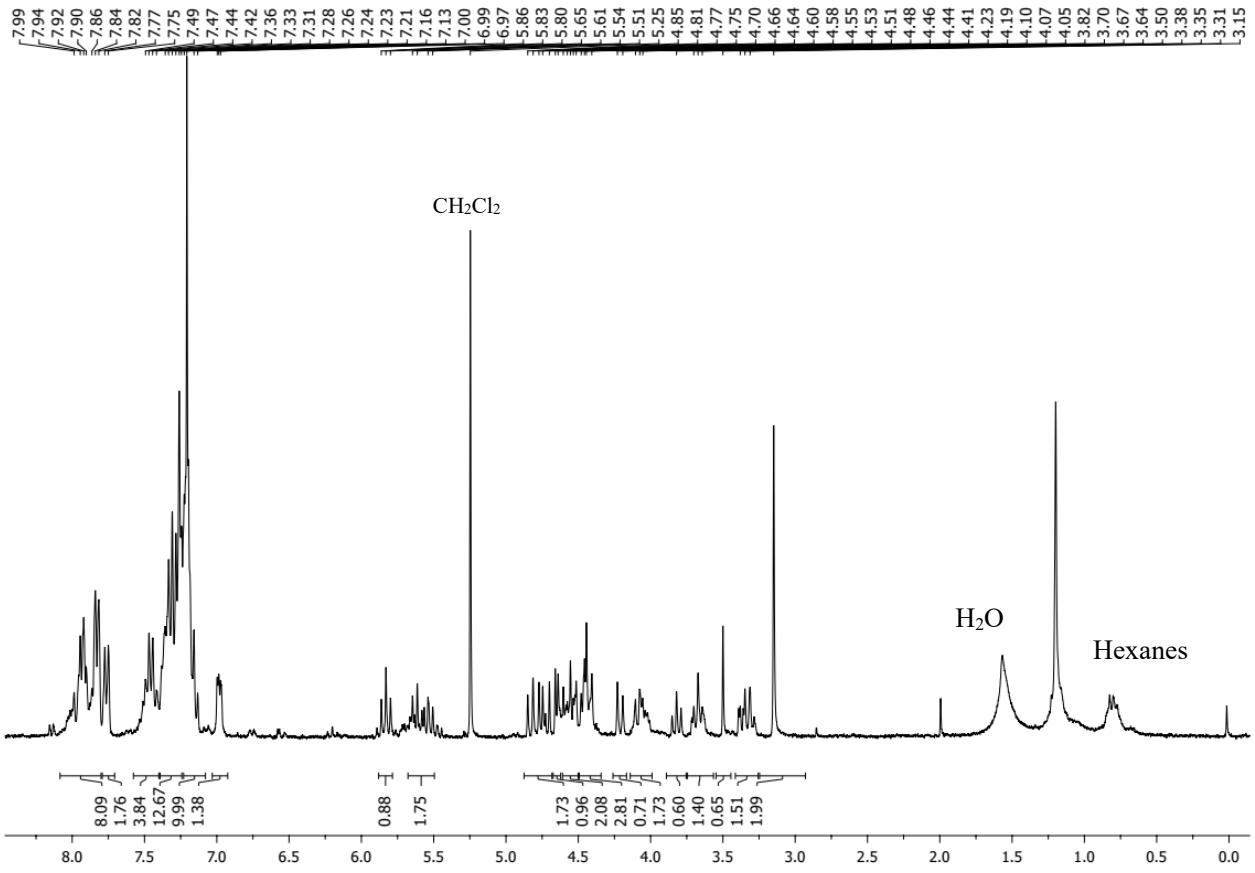

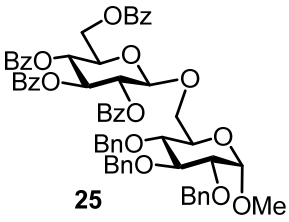
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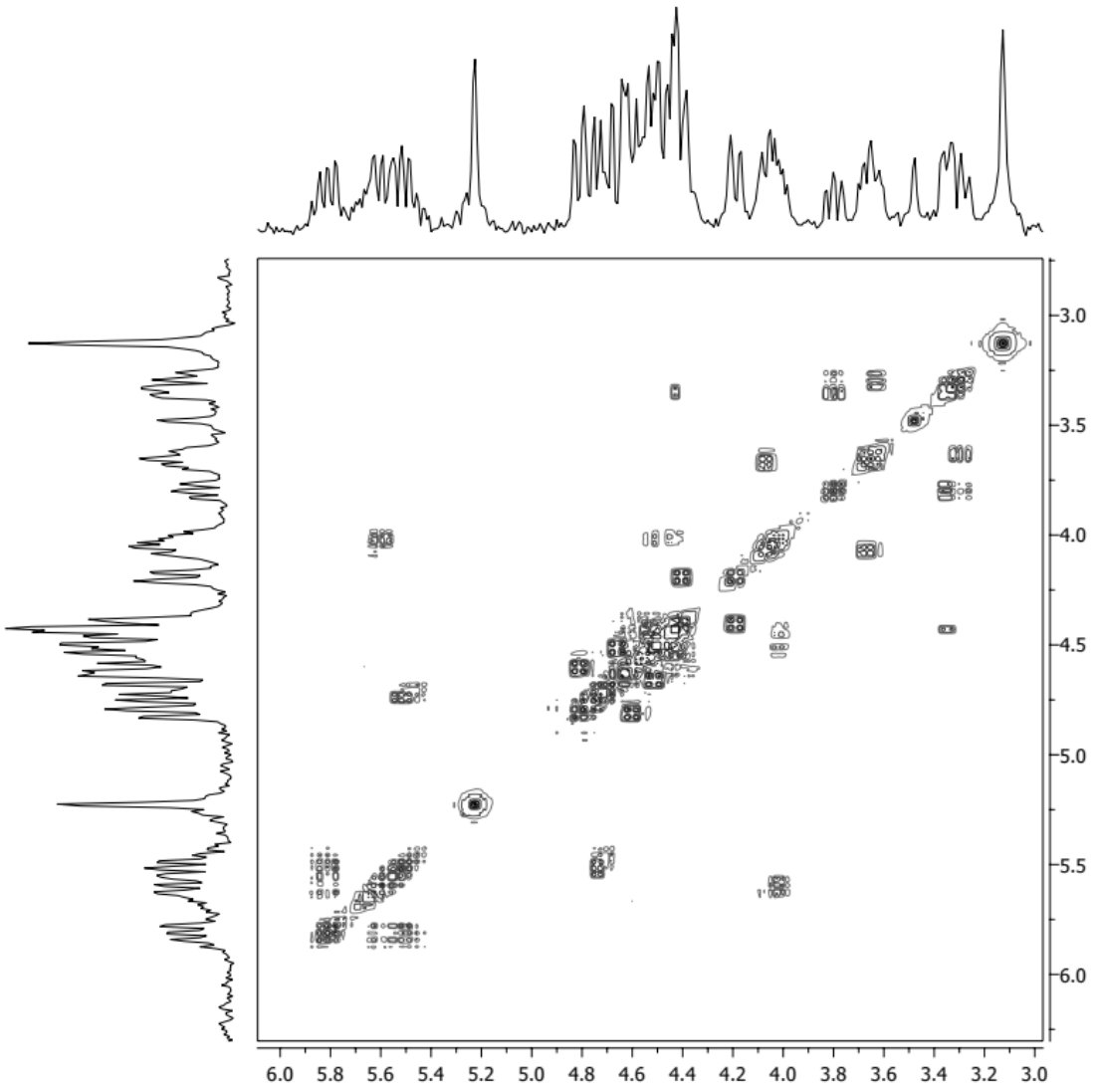
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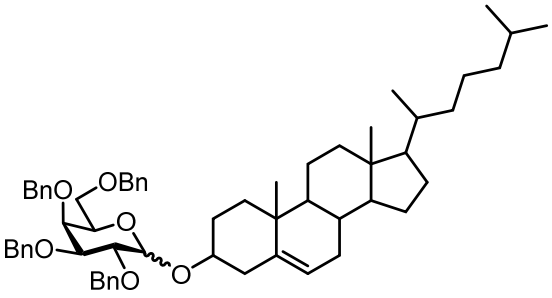

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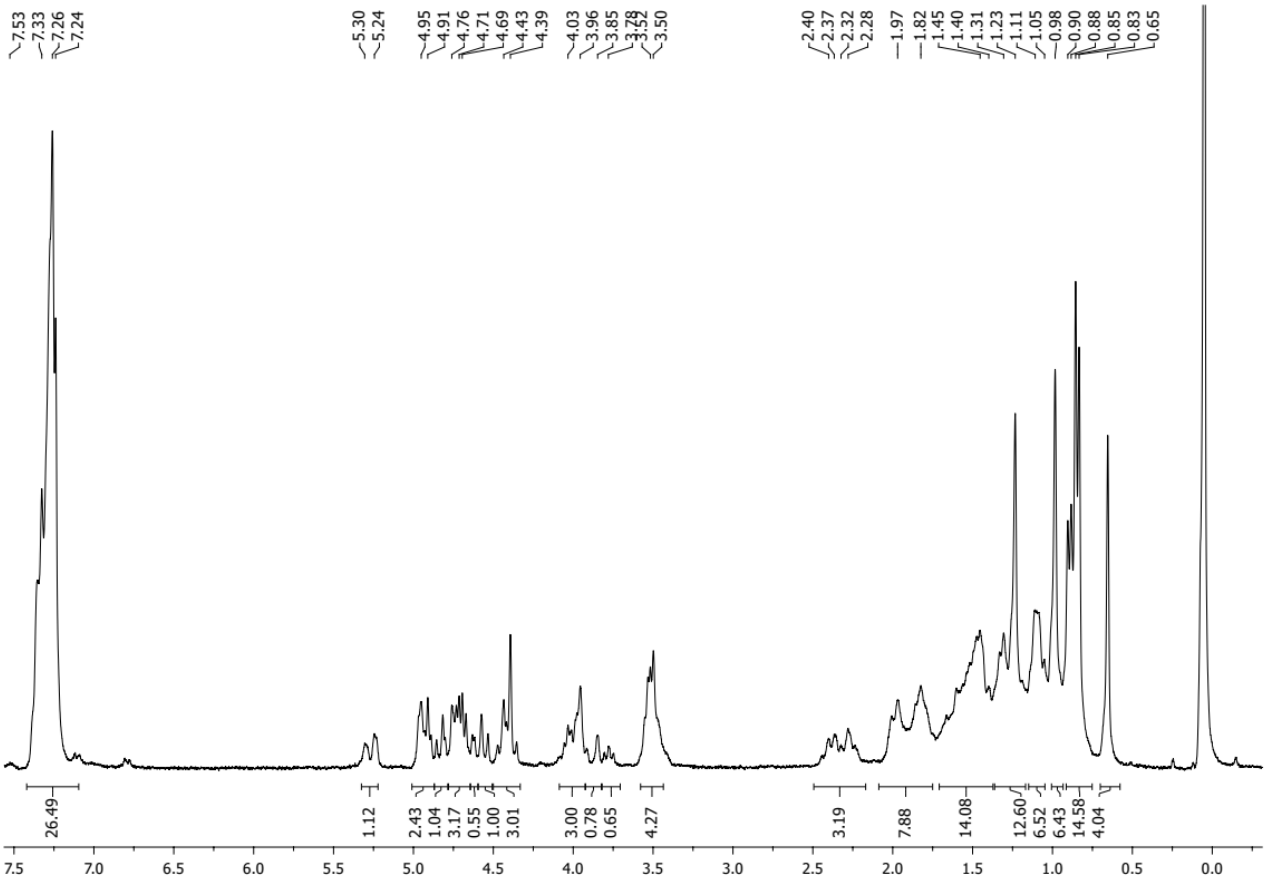

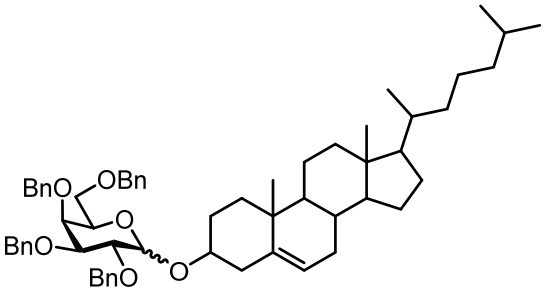
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OBn
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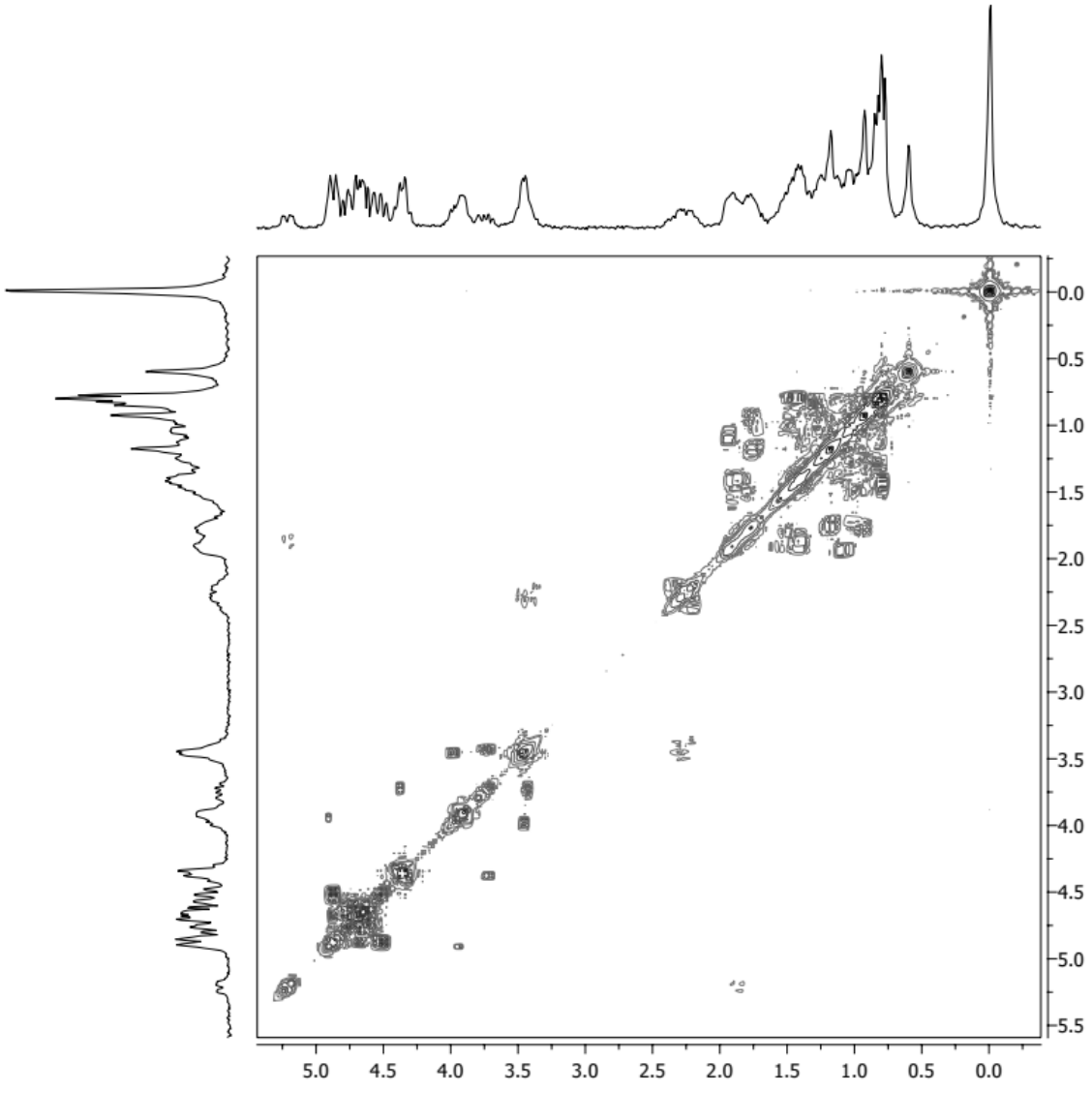
BnO
BnO
O

26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3.5
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4.5
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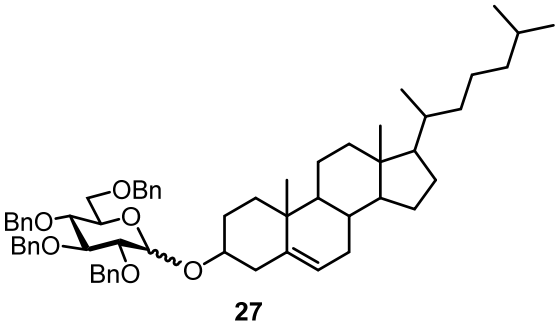
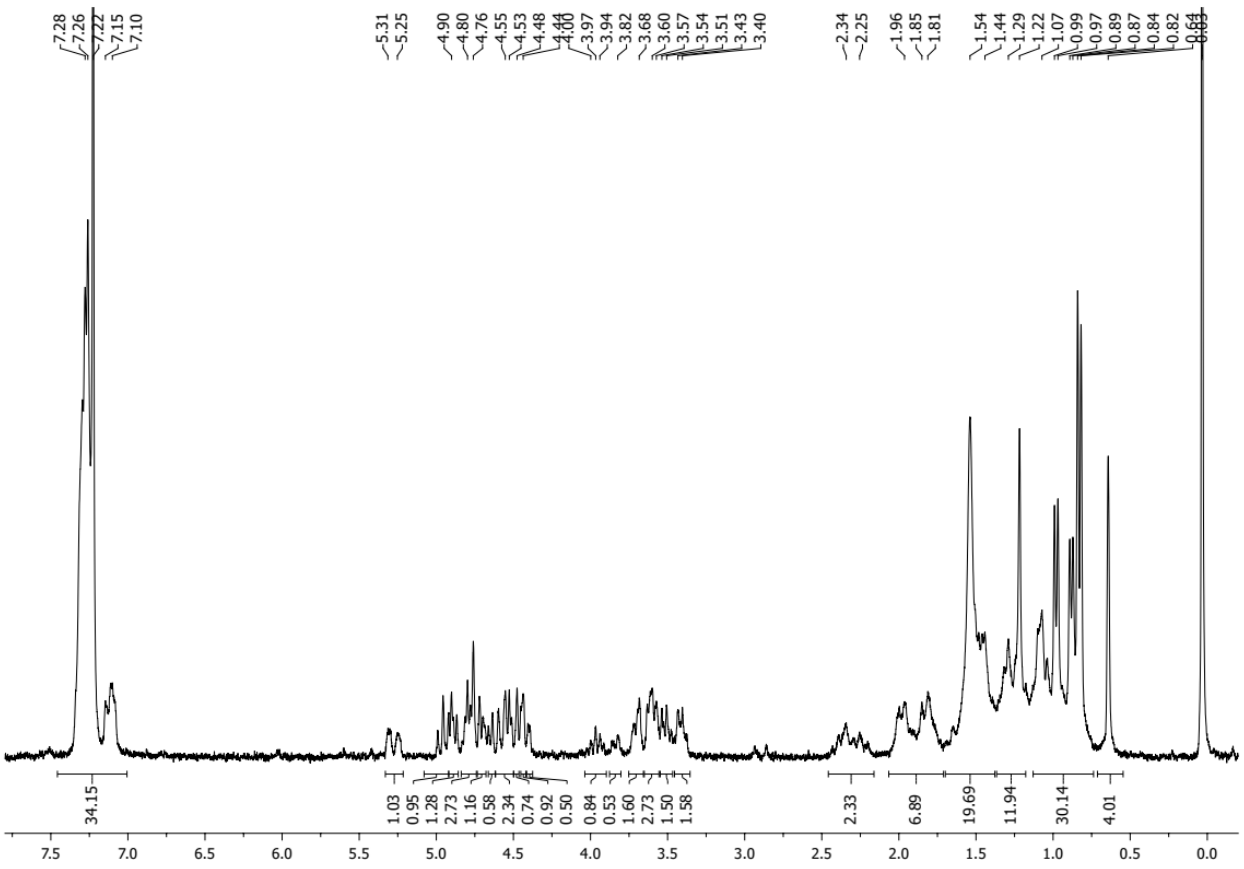
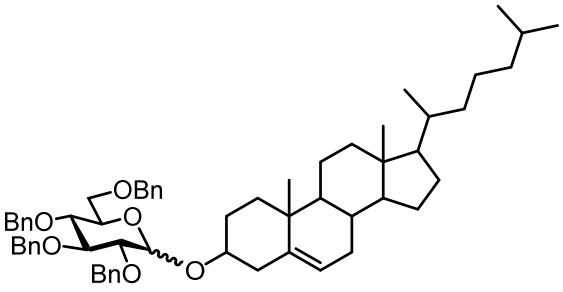
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



27

Table 1, entry 18




OBn
BnO
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BnO
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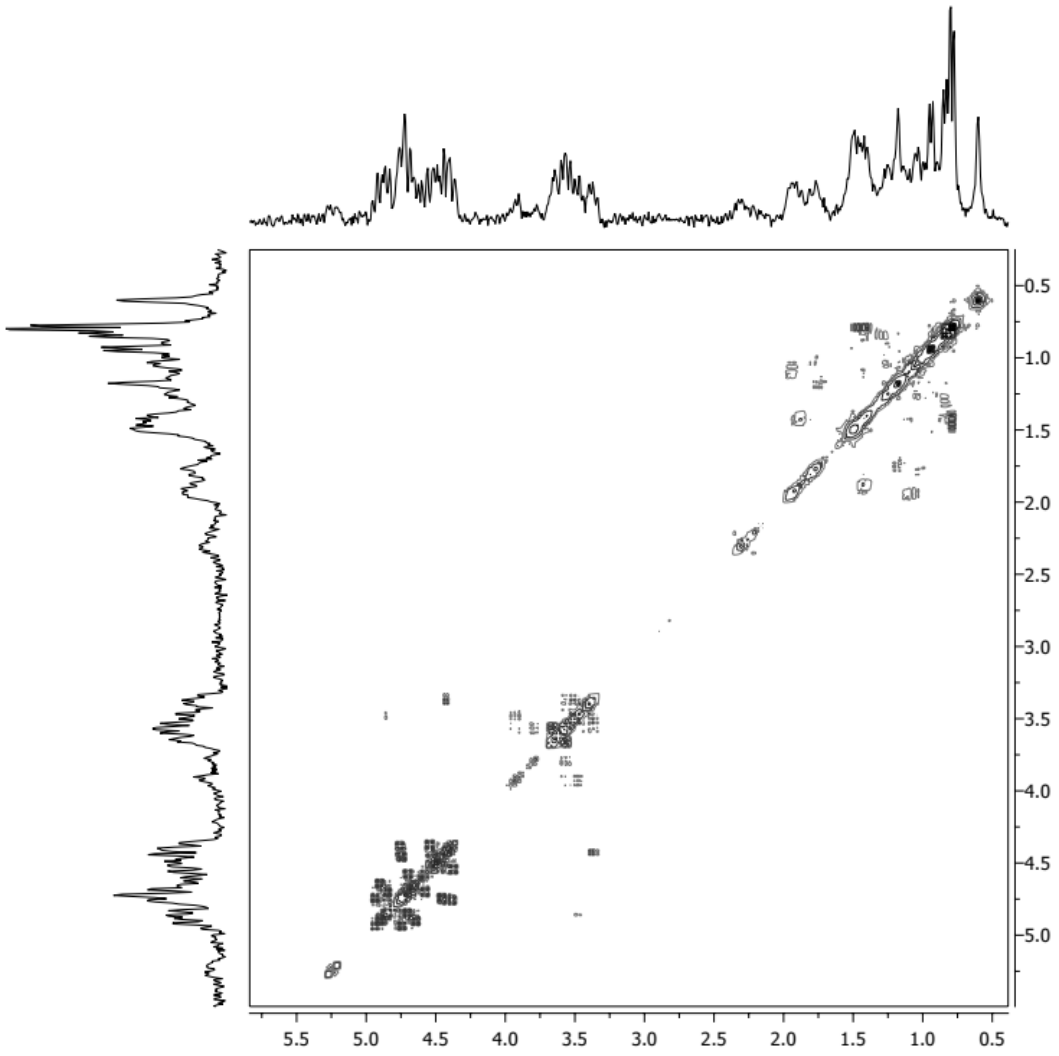
O

27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