***N*-(Phenylthio)- ϵ -caprolactam: A New Promoter for the Activation of Thioglycosides**

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Supporting Material

General Procedures. All reactions were performed in flame-dried modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper or rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. All saccharides and promoters were pre-dried by azeotropic removal of water using toluene. Organic solutions were concentrated by rotary evaporation below 30 °C at ca. 25 Torr. Flash column chromatography was performed employing Silica Gel 60 Sorbent (40-63 μ m, 230-400 mesh). Thin-layer chromatography (analytical and preparative) was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm) and visualized under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate.

Materials. Dichloromethane and Toluene were freshly distilled from calcium hydride at 760 Torr. Trifluoromethanesulfonic anhydride was purchased from Aldrich and distilled from phosphorous pentoxide. Triethylamine was purchased from Aldrich and used without further purification. Tri-*t*-butylpyrimidine was purchased from Lakeview Synthesis and used without further purification. Molecular sieves (MS) (type AW-300) were crushed and freshly flame activated before every use. *N*-(thiophenyl)- ϵ -caprolactam (**1**) was either synthesized or purchased from Aldrich (rare chemical inventory).

Instrumentation. Proton and carbon-13 nuclear magnetic resonance (^1H NMR or ^{13}C NMR) spectra were recorded on a Varian 400, a Bruker DRX-500 (500 MHz) 500, or a Bruker DRX-600 (600 MHz) spectrometer at 20 °C. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to either residual protium in the NMR solvent (CHCl_3 : δ = 7.26 ppm) or to tetramethylsilane (δ = 0 ppm) if the residual protium of the solvent is indistinguishable. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances), integration, coupling constant in Hertz (Hz). Carbon-13 NMR were obtained using the same instruments and were calibrated with CDCl_3 (δ = 77.00 ppm). MALDI high-resolution mass spectrometry was performed on a IonSpec Ultima FTMS.

Methyl-2,3,6-tri-*O*-benzoyl-4-*O*-[2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl]- α -D-glucopyranoside (9): A solution of **3** (50.5 mg, 0.0781 mmol), **8** (37 mg, 0.0731 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (18 mg, 0.0813 mmol), and flame activated AW-300 MS were stirred in dry dichloromethane (2 ml) for 0.5 h at ambient temperature. The reaction mixture was then cooled to $-45\text{ }^{\circ}\text{C}$ (CH_3CN /Dry Ice), stirred for 5 min and then followed by injection of trifluoromethanesulfonic anhydride (16 μL , 0.0945 mmol). The reaction mixture was stirred for 0.5 h at $-45\text{ }^{\circ}\text{C}$, then at ambient temperature for 0.5 h. The solution was quenched with triethylamine (150 μL), filtered and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 5:1) to afford **9** (67 mg, 89 %) as a white foam.

9: ^1H NMR (500 MHz, CDCl_3) δ 8.10-8.05 (m, 2H), 8.00-7.95 (m, 4H), 7.62-7.08 (m, 29H), 6.19 (t, 1H, $J = 9.1\text{ Hz}$), 5.22 (dd, 1H, $J = 10.3, 3.8\text{ Hz}$), 5.16 (d, 1H, $J = 3.6\text{ Hz}$, H'-1), 5.13 (d, 1H, $J = 3.5\text{ Hz}$, H-1), 4.82-4.78 (m, 2H), 4.65-4.59 (m, 3H), 4.42 (d, 1H, $J = 11.4\text{ Hz}$), 4.33-4.21 (m, 4H), 4.15 (d, 1H, $J = 11.7\text{ Hz}$), 4.05 (d, 1H, $J = 12.1\text{ Hz}$), 4.00 (t, 1H, $J = 6.6\text{ Hz}$), 3.91-3.88 (m, 2H), 3.82 (dd, 1H, $J = 9.9, 3.6\text{ Hz}$), 3.47-3.41 (m, 1H), 3.42 (s, 3H), 3.36 (dd, 1H, $J = 8.9, 5.8$); ^{13}C NMR (125 MHz, CDCl_3) 166.1, 166.0, 165.5, 138.4, 138.2, 137.9, 133.3, 133.1, 132.9, 129.9, 129.8, 129.7, 129.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 98.9 (C'-1), 96.7 (C-1),

78.7, 75.3, 74.9, 74.7, 74.5, 73.2, 73.1, 72.9, 72.2, 72.1, 70.6, 68.6, 68.5, 63.4, 55.3;
 HRMS (MALDI-FTMS) m/z : $(M+Na)^+$ calc for $C_{62}H_{60}O_{14}$ 1051.3875, found 1051.3881.

Methyl-2,3,6-tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-galactopyranosyl]- α -D-glucopyranoside (13**):** A solution of **12** (50.4 mg, 0.0909 mmol), **8** (49 mg, 0.0967 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (22.1 mg, 0.0999 mmol), tri-*tert*-butylpyrimidine (TTBP) (96 mg, 0.3871 mmol) and flame activated AW-300 molecular sieves were stirred in dry dichloromethane (2 ml) for 0.5 h at ambient temperature. The reaction mixture was then cooled to $-0\text{ }^{\circ}\text{C}$ (Ice Water), stirred for 5 min and then followed by injection of trifluoromethanesulfonic anhydride (19 μL , 0.1123 mmol). The reaction mixture was stirred for 10 min at $0\text{ }^{\circ}\text{C}$, filtered and then concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 4:1) to afford **13** (81 mg, 95 %) as a white solid/residue.

13: ^1H NMR (500 MHz, CDCl_3) δ 8.12-8.09 (m, 2H), 8.01-7.95 (m, 4H), 7.64-7.11 (m, 24H), 6.22 (t, 1H, $J = 9.4\text{ Hz}$), 5.36 (s, 1H), 5.30 (d, 1H, $J = 3.5\text{ Hz}$, $\text{H}'\text{-1}$), 5.21 (dd, 1H, $J = 10.3, 3.5\text{ Hz}$), 5.16 (d, 1H, $J = 3.8\text{ Hz}$, H-1), 4.82 (dd, 1H, $J = 12.3, 1.9\text{ Hz}$), 4.63 (ABq, 2H, $\nu_A = 4.65$, $\nu_B = 4.61$, $J_{AB} = 12.1\text{ Hz}$), 4.49 (dd, 1H, $J = 12.2, 4.0\text{ Hz}$), 4.33 (d, 1H, $J = 12.1\text{ Hz}$), 4.31 (d, 1H, $J = 9.0\text{ Hz}$), 4.23 (ddd, 1H, $J = 10.1, 3.8, 1.8\text{ Hz}$), 4.19-4.10 (m, 3H), 3.98-3.88 (m, 3H), 3.79 (dd, 1H, $J = 12.8, 1.5\text{ Hz}$), 3.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) 166.2, 166.0, 165.4, 138.6, 138.2, 137.6, 133.4, 133.3, 133.0, 129.9, 129.7, 129.6, 129.5, 129.0, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 128.07, 128.0, 127.7,

127.5, 127.4, 126.2, 100.7, 99.6 (C'-1), 96.8 (C-1), 75.9, 74.3, 74.2, 74.0, 73.3, 72.3, 72.07, 69.2, 68.4, 63.7, 63.2, 55.4, 29.6; HRMS (MALDI-FTMS) m/z : (M+Na)⁺ calc for C₅₅H₅₂O₁₄ 959.3249, found 959.3225.

2-*O*-Benzoyl-3-*O*-allyl-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1-*O*-(2,6-*O*-

dimethoxyphenyl)- β -D-galactopyranoside (15): A solution of **14** (51 mg, 0.0672 mmol), 2,6-dimethoxyphenol (11 mg, 0.0713 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (16 mg, 0.0723 mmol), and flame activated AW-300 molecular sieves were stirred in dry dichloromethane (2 ml) for 0.5 h at ambient temperature. The reaction mixture was then cooled to -45 °C (CH₃CN/dry ice), stirred for 5 min and then followed by injection of trifluoromethanesulfonic anhydride (14 μ L, 0.0832 mmol). The reaction mixture was stirred for 0.5 h at -45 °C, then at ambient temperature for 0.5 h. The solution was quenched with triethylamine, filtered and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 6:1) to afford **15** (45 mg, 85 %) as a white solid/residue.

15: ¹H NMR (500 MHz, CDCl₃) δ 8.20-8.15 (m, 2H), 7.71-7.60 (m, 4H), 7.59-7.53 (m, 1H), 7.49-7.23 (m, 13H), 6.91 (t, 1H, J = 8.5 Hz), 6.40 (d, 2H, J = 8.7 Hz), 6.07-5.90 (m, 1H), 5.66-5.60 (m, 1H), 5.39-5.31 (m, 1H), 5.19-5.14 (m, 1H), 5.12 (d, 1H, J = 11.0 Hz), 4.83 (dd, 1H, J = 8.8, 5.2 Hz), 4.67 (d, 1H, J = 11.1 Hz), 4.43-4.31 (m, 3H), 4.0 (t, 1H, J = 9.2 Hz), 3.83 (br s, 2H), 3.72 (dd, 1H, J = 9.2, 5.4 Hz), 3.36 (s, 6H), 1.12 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) 166.3, 153.4, 138.9, 135.7, 135.6, 135.0, 134.4, 133.4, 133.2,

132.7, 130.7, 129.8, 129.7, 128.2, 128.1, 127.7, 127.2, 125.8, 124.3, 116.5, 104.6 (C-1), 98.7, 76.5, 75.1, 74.9, 71.9, 71.8, 71.5, 61.7, 55.3, 26.9, 19.3; HRMS (MALDI-FTMS) m/z : (M+Na)⁺ calc for C₄₇H₅₂O₉Si 811.3273, found 811.3276.

***p*-Methylphenyl-2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzyl- α -L-fucopyranosyl)-1-thio- β -D-glucopyranoside (**18**):** A solution of **16** (50 mg, 0.0925 mmol), **17** (56 mg, 0.0935 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (22 mg, 0.0994 mmol), and flame activated AW-300 MS were stirred in dry dichloromethane (2 ml) for 1 h at ambient temperature. Trifluoromethanesulfonic anhydride (19 μ L, 0.1129 mmol) was then injected into the solution. The reaction mixture was stirred at ambient temperature until all the starting materials were consumed. The solution was quenched with triethylamine (150 μ L), filtered and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 5:1) to afford **18** (67 mg, 84 %) as a white foam. (higher yields >95 % can be accomplished using procedure for **19**). Spectral data was consistent with published data on **18**.¹

***p*-Methylphenyl-2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzyl- α -D-galactopyranosyl)**

¹ Mong, T. K.-K.; Lee, H.-K.; Durón, S.G.; Wong, C.-H. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 797-802.

-1-thio- β -D-glucopyranoside (19): A solution of **3** (26.1 mg, 0.0404 mmol), **17** (21.3 mg, 0.0356 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (12 mg, 0.0542 mmol), and flame activated AW-300 MS were stirred in dry dichloromethane (2 ml) for 0.5 h at ambient temperature. The reaction mixture was then cooled to $-78\text{ }^{\circ}\text{C}$ (acetone/Dry Ice), stirred for 5 min and then followed by injection of trifluoromethanesulfonic anhydride (13 μL , 0.0773 mmol). The reaction mixture was stirred until the cold bath reached $-10\text{ }^{\circ}\text{C}$ and then was quenched with triethylamine (100 μL), filtered and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 5:1) to afford **19** (37 mg, 93 %) as a white foam.

19: ^1H NMR (500 MHz, CDCl_3) δ 8.04-7.98 (m, 2H), 7.95-7.86 (m, 4H), 7.61 (t, 1H, $J = 7.0\text{ Hz}$), 7.62-7.08 (m, 30H), 6.88 (d, 2H, $J = 8.0\text{ Hz}$), 5.83 (t, 1H, $J = 9.4\text{ Hz}$), 5.33 (t, 1H, $J = 9.9\text{ Hz}$), 4.99 (d, 1H, $J = 3.4\text{ Hz}$, H'-1), 4.92 (dd, 1H, $J = 12.3, 1.8\text{ Hz}$), 4.85 (d, 1H, $J = 9.8\text{ Hz}$, H-1), 4.75 (d, 1H, $J = 12.0\text{ Hz}$), 4.60-4.50 (m, 1H), 4.60 (d, 2H, $J = 2.3\text{ Hz}$), 4.42 (d, 1H, $J = 11.3\text{ Hz}$),), 4.60 (ABq, 2H, $\nu_A = 4.29$, $\nu_B = 4.20$, $J_{AB} = 11.8\text{ Hz}$), 4.26-4.14 (m, 2H), 4.00-3.91 (m, 3H), 3.91-3.80 (m, 1H), 3.85 (dd, 1H, $J = 10.3, 2.6\text{ Hz}$), 3.77 (dd, 1H, $J = 10.0, 3.3\text{ Hz}$), 3.39 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) 165.9, 1.65.5, 1.65.2, 138.7, 138.4, 138.2, 137.9, 133.9, 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.3, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 99.5 (C'-1), 85.7 (C-1), 78.6, 77.4, 75.8, 75.2, 75.0, 74.9, 74.7, 73.3, 73.1, 72.9, 70.7, 70.6, 68.6, 63.4, 21.2; HRMS (MALDI-FTMS) m/z : (M+Na) $^{+}$ calc for $\text{C}_{68}\text{H}_{64}\text{O}_{13}\text{S}$ 1143.396, found 1143.3978.

***p*-Methylphenyl-2-*O*-benzoyl-3-*O*-[2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl]-4-**

***O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio- β -D-galactopyranoside (**20**):** A solution of **3** (25.3 mg, 0.0391 mmol), **23** (25.4 mg, 0.0379 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (9.1 mg, 0.0411 mmol), tri-*tert*-butylpyrimidine (TTBP) (21.4 mg, 0.0857 mmol) and flame activated AW-300 MS were stirred in dry dichloromethane (2 ml) for 0.5 h at ambient temperature. Trifluoromethanesulfonic anhydride (8 μ L, 0.0473 mmol) was then injected into the reaction mixture at ambient temperature and stirred for 5 min. The solution was stirred for 0.5 h at ambient temperature then filtered and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 6:1) to afford **20** (33 mg, 73 %) as a colorless oil.

20: ^1H NMR (500 MHz, CDCl_3) δ 8.20-7.98 (m, 2H), 7.67-7.62 (m, 4H), 7.49-7.21 (m, 29H), 7.14-7.09 (m, 2H), 7.03 (d, 2H, $J = 8.2$ Hz), 5.63 (d, 1H, $J = 3.0$ Hz), 5.51 (t, 1H, $J = 9.8$ Hz), 5.26 (d, 1H, $J = 3.0$ Hz, H'-1), 4.76-4.70 (m, 2H), 4.63 (ABq, 2H, $\nu_A = 4.65$, $\nu_B = 4.60$, $J_{AB} = 11.9$ Hz), 4.61 (d, 1H, $J = 11.8$ Hz, H-1), 4.51 (d, 1H, $J = 11.8$ Hz), 4.35 (dd, 2H, $J = 11.8$, 2.4 Hz), 4.28 (d, 1H, $J = 11.5$ Hz), 4.10 (dd, 1H, $J = 9.7$, 2.8 Hz), 3.91 (dd, 1H, $J = 10.0$, 3.3 Hz), 3.86 (t, 1H, $J = 6.0$ Hz), 3.77 (dd, 1H, $J = 9.5$, 5.6 Hz), 3.67-3.60 (m, 2H), 3.51 (dd, 1H, $J = 9.8$, 2.8 Hz), 3.45 (dd, 1H, $J = 9.5$, 7.0 Hz), 3.17-3.14 (m, 2H), 2.30 (s, 3H), 1.74 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) 170.0, 164.9, 138.8, 138.7, 138.4, 138.3, 137.7, 135.6, 133.2, 133.0, 132.9, 132.4, 129.9, 129.88, 129.84, 129.79, 129.72, 129.6, 128.4, 128.3, 128.2, 128.18, 128.11, 128.0, 127.9,

127.74, 127.71, 127.56, 127.50, 127.4, 127.3, 127.29, 127.21, 93.0 (C'-1), 87.5 (C-1), 78.8, 77.8, 75.7, 74.9, 74.4, 73.3, 73.2, 73.1, 72.8, 69.8, 69.6, 69.3, 64.9, 62.2, 26.8, 21.1, 20.4, 19.1; HRMS (MALDI-FTMS) m/z : (M+Na)⁺ calc for C₇₂H₇₆O₁₂SSi 1215.4719, found 1215.4694.

***p*-Methylphenyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonylamino)-3-*O*-acetyl-4-*O*-[2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl]-6-*O*-*tert*-butyldiphenylsilyl-1-thio- β -D-glucopyranoside (**22**):** A solution of **3** (100 mg, 0.1546 mmol), **21** (111 mg, 0.1498 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (37 mg, 0.1672 mmol), and flame activated AW-300 MS were stirred in dry dichloromethane (2 ml) for 0.5 h at ambient temperature. The reaction mixture was then cooled to -45 °C (CH₃CN/Dry Ice), stirred for 5 min and then followed by injection of trifluoromethanesulfonic anhydride (30 μ L, 0.1783 mmol). The reaction mixture was stirred for 0.5 h at -45 °C, then warmed over 2h to -20 °C. The solution was quenched with triethylamine, filtered and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, 5:1) to afford **22** (138 mg, 71 %) as a pale yellow oil.

22: ¹H NMR (500 MHz, CDCl₃) δ 7.72-7.66 (m, 4H), 7.36-7.23 (m, 26H), 7.13-7.11 (m, 2H), 7.04 (d, 2H, J = 8.0 Hz), 6.0 (d, 1H, J = 8.9 Hz), 5.16 (t, 1H, J = 7.0 Hz), 5.02 (d, 1H, J = 3.2 Hz, H'-1), 4.89 (m, 2H), 4.78 (ABq, 2H, ν_A = 4.81, ν_B = 4.76, J_{AB} = 12.3 Hz), 4.75-4.65 (m, 3H), 4.66 (d, 1H, J = 10.1 Hz, H-1), 4.53 (d, 1H, J = 11.3 Hz), 4.25 (ABq, 2H, ν_A = 4.29, ν_B = 4.21, J_{AB} = 11.7 Hz), 4.10-4.02 (m, 2H), 3.99 (dd, 1H, J = 10.4, 3.5

(Hz), 3.95-3.88 (m, 1H), 3.87-3.77 (m, 3H), 3.74 (dd, 1H, $J = 10.2, 2.5$ Hz), 3.68-3.63 (m, 1H), 3.40 (t, 1H, $J = 7.4$ Hz), 3.32 (dd, 1H, $J = 9.0, 5.8$ Hz), 2.32 (s, 3H), 1.81 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) 170.4, 154.2, 138.6, 138.5, 137.9, 137.8, 137.6, 135.8, 135.7, 133.3, 133.0, 132.2, 130.1, 129.6, 138.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 98.5 (C'-1), 95.5 (C-1), 87.1, 80.4, 78.2, 75.7, 74.7, 74.6, 73.7, 73.6, 73.4, 72.8, 70.3, 68.5, 63.6, 54.8, 29.7, 26.9, 21.1, 20.8, 19.3, 14.2; HRMS (MALDI-FTMS) m/z : $(\text{M}+\text{Na})^+$ calc for $\text{C}_{68}\text{H}_{74}\text{Cl}_3\text{NO}_{12}\text{SSi}$ 1284.3659, found 1284.3562.

Methyl-2,3,6-tri-*O*-benzoyl-4-*O*-[2,3,6-tri-*O*-benzoyl-4-*O*-{2,3,4-tri-*O*-benzyl- α -L-fucopyranosyl}- β -D-glucopyranosyl]- α -D-glucopyranoside (11): A solution of **16** (42 mg, 0.0777 mmol), **17** (46 mg, 0.0768 mmol), *N*-(thiophenyl)- ϵ -caprolactam (**1**) (19 mg, 0.0858 mmol), and flame activated AW-300 MS were stirred in dry dichloromethane (2 ml) for 1 h at ambient temperature. The reaction mixture was then cooled to -45 $^{\circ}\text{C}$ ($\text{CH}_3\text{CN}/\text{Dry Ice}$), stirred for 5 min and then followed by injection of trifluoromethanesulfonic anhydride (15 μL , 0.0892 mmol) and then warmed to ambient temperature. The formation of **18** was monitored by TLC (hexanes:EtOAc 3:1). After the starting materials were consumed, **8** (39 mg, 0.0770 mmol) and *N*-(thiophenyl)- ϵ -caprolactam (**1**) (56 mg, 0.2530 mmol) were added to the reaction mixture and stirred for

30 min. The solution was cooled to $-45\text{ }^{\circ}\text{C}$ and then trifluoromethanesulfonic anhydride (45 μL , 0.2675 mmol) was injected into the mixture, stirred for 0.5h, then stirred at ambient temperature 0.5h (the reaction was stirred overnight, but did not see increase in yield by tlc). The solution was quenched with triethylamine, filtered and concentrated. The crude mixture was directly purified by silica gel flash column chromatography (hexane/EtOAc, gradient eluent 5:1 to 3:1) to afford **11** (39 mg, 36 %) as a colorless oil.

11: ^1H NMR (600 MHz, CDCl_3) δ 8.05-7.09 (m, 45H), 6.02 (t, 1H, $J = 9.1\text{ Hz}$), 5.57 (t, 1H, $J = 9.4\text{ Hz}$), 5.33 (dd, 1H, $J = 9.9, 8.0\text{ Hz}$), 5.12-5.09 (m, 1H), 5.07 (d, 1H, $J = 3.7\text{ Hz}$, H-1), 4.87 (d, 1H, $J = 7.9\text{ Hz}$, H'-1), 4.79-4.66 (m, 5H), 4.62 (d, 1H, $J = 9.2\text{ Hz}$), 4.60 (d, 1H, $J = 5.6\text{ Hz}$, H''-1), 4.58-4.55 (m, 2H), 4.46-4.42 (m, 1H), 4.45 (d, 1H, $J = 11.4\text{ Hz}$), 4.15-4.06 (m, 4H), 3.85-3.77 (m, 2H), 3.66 (ddd, 1H, $J = 10.0, 5.1, 1.9\text{ Hz}$), 3.62 (q, 1H, $J = 6.3\text{ Hz}$), 3.33 (s, 3H), 0.55 (d, 3H, $J = 6.3\text{ Hz}$); ^{13}C NMR (150 MHz, CDCl_3) 165.9, 165.8, 165.7, 165.3, 164.9, 138.7, 138.3, 138.2, 133.3, 133.1, 132.9, 129.9, 129.8, 129.7, 129.5, 129.4, 128.5, 128.4, 128.3, 128.2, 128.0, 127.5, 127.4, 100.5 (C'-1), 100.1 (C''-1), 96.7 (C-1), 79.1, 77.6, 76.4, 75.7, 75.4, 74.7, 74.3, 73.9, 73.9, 72.7, 72.4, 72.2, 70.0, 68.4, 67.5, 62.8, 62.4, 55.4, 29.7, 15.8; HRMS (MALDI-FTMS) m/z : $(\text{M}+\text{Na})^+$ calc for $\text{C}_{82}\text{H}_{76}\text{O}_{21}$ 1419.4771, found 1419.4761.