

Exponential Signal Amplification via Dendritic Chain Reaction: The dendritic effect of Self- Immolative Amplifier Component

Supporting Information

Naama Karton-Lifshin and Doron Shabat

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-
Aviv University, Tel Aviv 69978 Israel

Synthetic Schemes and Experimental Procedures

S2-S12

Additional Graphical Data

S13

General methods. All reactions requiring anhydrous conditions were performed under an Argon atmosphere. All reactions were carried out at room temperature unless stated otherwise. Chemicals and solvents were either A.R. grade or purified by standard techniques. Thin layer chromatography (TLC): silica gel plates Merck 60 F₂₅₄: compounds were visualized by irradiation with UV light. Flash chromatography (FC): silica gel Merck 60 (particle size 0.040-0.063 mm), eluent given in parentheses. High pressure liquid chromatography (HPLC): C18 5u, 250x4.6mm, eluent given in parentheses. Preparative HPLC: C18 5u, 250x21mm, eluent given in parentheses. ¹H-NMR spectra were measured using Bruker Avance operated at 400MHz as mentioned. ¹³C-NMR spectra were measured using Bruker Avance operated at 100 MHz as mentioned. The chemical shifts are expressed in δ relative to TMS ($\delta = 0$ ppm) and coupling constants J in Hz. The spectra were recorded in CDCl₃ as solvent at room temperature unless stated otherwise. All general reagents, including salts and solvents, were purchased from Sigma-Aldrich.

Abbreviations. ACN- Acetonitrile, DBTL- Dibutyltin dilaurate, DCM- Dichloromethane, CAM- cerium ammonium molybdate, DMF- N,N-Dimethylformamide, Et₂O- Diethyl ether, EtOAc- Ethylacetate, Hex- n-Hexanes, MeOH- Methanol, *p*-TsOH- *p*-Toluene sulfonic acid, TMS-Cl- Chloro trimethylsilane. AcOH- Acetic acid, NHS- N-Hydroxysuccineimide, EDC- 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide.

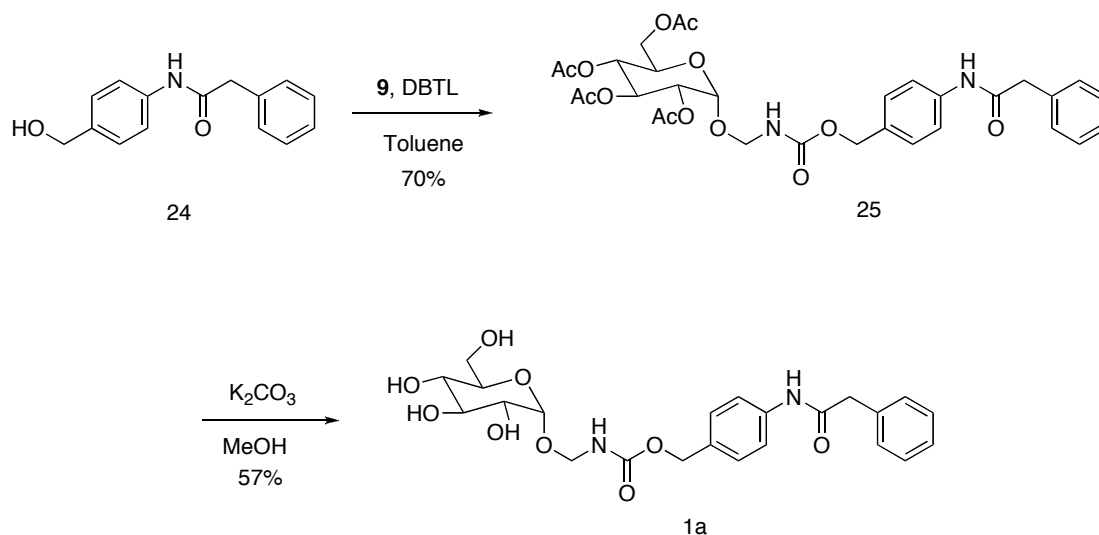
Compound 8

Compound 7¹ (2.67 g, 6.57 mmol) was dissolved in 20 mL of dry DMF. NHS (0.93 g, 8.12 mmol) was added, and then EDC (1.56 g, 8.12 mmol) was added. The reaction mixture was stirred for 12 h at room temperature under an Ar atmosphere and monitored by TLC using CAM solution (EtOAc/Hex 70:30). After completion, the reaction mixture diluted with EtOAc, and was washed with brine. The organic layer was separated, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 60:40) to give compound 2 (2.2 g, 66%) as a colorless viscous liquid.

^1H NMR (200MHz, CDCl_3): δ = 7.43-7.12(9H, m), 5.23 (1H, d, J = 3.8 Hz), 5.08 (1H, t, J = 9.8 Hz), 4.90 (1H, dd, J = 3.8 Hz, J = 10.3 Hz), 4.57 (AB system, 2H, δ_a = 4.50, δ_b = 4.60, J = 17.1 Hz), 4.26 (1H, dd, J = 4.1 Hz, J = 12.2 Hz), 4.06-4.15 (2H, m), 2.85 (4H, s), 2.09 (3H, s), 2.07 (3H, s), 2.02 (3H, s), 2.01 (3H, s). ^{13}C NMR (400MHz, CDCl_3): δ = 171.4, 171.0, 170.7, 170.3, 169.1, 165.6, 97.0, 70.9, 70.3, 69.9, 69.0, 68.8, 66.4, 63.5, 63.2, 62.3, 61.6, 26.3, 21.4, 21.3. MS (ESI): m/z calc. for $\text{C}_{20}\text{H}_{25}\text{NO}_{14}$: 503.4 ; found: 526.1 $[\text{M}+\text{Na}]^+$.

Compound 9

Compound **3** (2.2 g, 4.37 mmol) was dissolved in 20 mL of dry DMF. NaN_3 (426 mg, 7.51 mmol) was added and the solution stirred at room temperature for 30 min under an Ar atmosphere, and monitored by TLC using CAM solution (EtOAc/Hex 70:30). After completion, the reaction mixture diluted with EtOAc, and was washed with brine. The organic layer was separated, dried over MgSO_4 , and evaporated under reduced pressure. The crude product (1.40 g, 77%) was immediately reacted with no further purification.



Compound 25

Compound **24**² (26 mg, 0.11 mmol) was dissolved in 700 μL of dry Toluene. Compound **9** (70 mg, 0.16 mmol) was added, followed by catalytic amount of DBTL.

The reaction mixture was heated to 80°C, stirred for 30 min under an Ar atmosphere, and monitored by TLC (EtOAc/Hex 50:50). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 50:50) to give Compound **25** (50 mg, 70%) as a white solid. The product contained traces of free glucose units, which are further purified in the next step.

¹H NMR (200MHz, CDCl₃) δ = 7.43-7.25 (9H, m), 5.72 (1H, brs), 5.44 (1H, t, *J* = 4.9 Hz), 5.26 (1H, m), 5.06-5.01 (3H, m), 4.89-4.83 (1H, m), 4.76-4.74 (1H, m), 4.16-4.03 (3H, m), 3.74 (2H, s), 2.05-1.97 (12H, m). ¹³C NMR (200MHz, CDCl₃): δ = 170.60, 170.00, 169.51, 169.27, 155.86, 139.15, 137.82, 134.35, 131.69, 129.31, 128.99, 127.44, 125.82, 124.10, 123.86, 119.84, 94.36, 70.92, 70.39, 69.90, 68.28, 67.54, 66.71, 61.75, 60.31, 44.53, 33.71, 20.56, 20.47 MS (ESI): *m/z* calc. for C₃₁H₃₆N₂O₁₃: 644.62 ; found: 667.6 [M+Na]⁺.

Compound **1a**

Compound **25** (50 mg, 0.07 mmol) was dissolved in 5 mL of MeOH. K₂CO₃ (21 mg, 0.14 mmol) was added to the suspension and the reaction mixture stirred at room temperature for 60 min, and monitored by RP-HPLC (grad. 10% to 90% ACN in water, 20 min). After completion, the reaction mixture diluted with MeOH, water and 0.5 mL of AcOH. The crude product mixture was purified by preparative RP-HPLC (grad., 10% to 90% ACN in water, 40 min) to give compound **1a** (20 mg, 57%) as a white solid.

¹H NMR (200MHz, MeOD): δ = 7.56 (2H, d, *J* = 8.4 Hz), 7.36-7.29 (7H, m), 5.07 (2H, s), 4.98 (1H, d, *J* = 3.6 Hz), 4.80-4.69 (3H, m), 3.82-3.58 (6H, m), 3.40 (1H, d, *J* = 3.6 Hz). ¹³C NMR (200MHz, MeOD): δ = 170.84, 157.35, 138.27, 135.26, 132.21, 128.63, 128.23, 128.09, 126.45, 119.66, 96.84, 76.44, 73.51, 72.50, 71.84, 70.15, 69.48, 65.94, 61.07, 43.17. MS (ESI): *m/z* calc. for C₂₃H₂₈N₂O₉: 476.18 ; found: 499.2 [M+Na]⁺. RP-HPLC (grad., 10% to 90% ACN in water, 20 min) 11.44 min, λ=250 nm.

Compound 11

Compound **10**³ (80 mg, 0.18 mmol) was dissolved in 4 mL of dry Toluene. Compound **9** (312 mg, 0.72 mmol) was added, followed by catalytic amount of DBTL. The reaction mixture was heated to 80°C, stirred for 30 min under an Ar atmosphere, and monitored by TLC (EtOAc/Hex 50:50). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 60:40) to give Compound **11** (100 mg, 44%) as a white solid. The product contained traces of free glucose units that were further purified in the next step.

¹H NMR (400MHz, CDCl₃): δ = 8.07 (2H, s), 7.82 (2H, d, *J* = 7.8 Hz), 7.40 (2H, d, *J* = 7.8 Hz), 5.9 (1H, brs), 7.39 (2H, d, *J* = 8.0 Hz), 5.89 (1H, brs), 5.45 (1H, t, *J* = 7.7 Hz), 5.27-5.20 (6H, m), 5.06-4.74 (11H, m), 4.36 (2H, q, *J* = 6.4 Hz), 4.25-4.03 (6H, m) 2.10-2.00 (26H, m), 1.35 (12H, s). ¹³C NMR (400MHz, CDCl₃): δ = 171.40, 170.78, 170.34, 170.15, 166.24, 160.05, 16.36, 156.36, 139.70, 135.86, 132.82, 130.97, 127.86, 127.60, 95.42, 84.63, 77.97, 71.98, 71.73, 71.20, 70.72, 69.11, 68.39, 63.13, 62.62, 61.96, 25.58, 21.36, 21.28, 15.06. MS (ESI): *m/z* calc. for C₅₆H₇₃BN₂O₂₉: 1248.4 ; found: 1271.3 [M+Na]⁺.

Compound 3

Compound **11** (44 mg, 0.03 mmol) was dissolved in 10 mL of MeOH. K₂CO₃ (8 mg, 0.06mmol) was added to the suspension and the reaction mixture stirred at room temperature for 60 min, and monitored by RP-HPLC (grad. 10% to 90% ACN in water, 20 min). After completion, the reaction mixture diluted with MeOH, water and 1 mL of AcOH. The crude product mixture was purified by preparative RP-HPLC (grad., 10% to 90% ACN in water, 40 min) to give compound **3** (10 mg, 34%) as a white solid.

¹³C NMR (400MHz, MeOD): δ = 166.96, 157.93, 136.29, 136.10, 133.11, 132.71, 129.19, 127.93, 98.54, 75.20, 74.84, 73.66, 72.10, 70.93, 62.91, 62.79, 62.61, 50.59, 16.20. MS (ESI): *m/z* calc. for C₃₄H₄₇BN₂O₂₁: 830.28 ; found: 853.3 [M+Na]⁺. RP-HPLC (grad., 10% to 90% ACN in water, 20 min) 11.25 min, λ =250 nm.

Compound 13

Compound **12**⁴ (400 mg, 0.63 mmol) was dissolved in 4 mL of MeOH. Catalytic amount of *p*-TsOH was added to the suspension and the reaction mixture stirred at room temperature for 20 min, and monitored by TLC (EtOAc/Hex 90:10). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc) to give Compound **13** (132 mg, 52%) as a white solid. The product contained traces of free glucose units, which are further purified in the next step.

¹H NMR (400MHz, CDCl₃): δ = 7.75 (2H, d, *J* = 7.9 Hz), 7.31 (2H, d, *J* = 7.9 Hz), 7.14 (2H, s), 7.43 (2H, s), 4.71 (2H, s), 4.50 (4H, s), 4.34 (2H, s), 1.31 (12H, s). ¹³C NMR (400MHz, CDCl₃): δ = 153.8, 140.6, 137.9, 135.8, 134.9, 127.9, 127.7, 91.2, 84.7, 77.1, 64.8, 60.5, 51.2, 30.4, 25.5. MS (ESI): *m/z* calc. for C₂₂H₂₉BO₆: 400.3 ; found: 399.2 [M-H]⁻.

Compound 14

Compound **13** (100 mg, 0.25 mmol) was dissolved in 4 mL of dry Toluene. Compound **9** (650 mg, 1.50 mmol) was added, followed by catalytic amount of DBTL. The reaction mixture was heated to 80°C, stirred for 30 min under an Ar atmosphere, and monitored by TLC (EtOAc/Hex 70:30). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 60:40) to give Compound **14** (300 mg, 74%) as a white solid. The product contained traces of free glucose units that were further purified in the next step.

¹H NMR (400MHz, CDCl₃): δ = 7.82 (2H, d, *J* = 7.9 Hz), 7.43 (4H, m), 7.43 (2H, s), 6.01 (1H, brs), 5.46 (3H, t, *J* = 7.0 Hz), 5.30 (6H, m), 5.21 (5H, m), 5.07 (7H, m), 4.96 (3H, m), 4.84-4.79 (10H, m), 4.21 (5H, m), 4.12 (9H, m), 2.07-2.00 (51H, m). 1.35 (12H, s). ¹³C NMR (400MHz, CDCl₃): δ = 171.52, 170.87, 170.79, 170.33, 170.13, 156.52, 140.10, 135.84, 133.22, 131.00, 127.76, 95.08, 4.61, 77.94, 71.70, 1.27, 70.73, 69.10, 68.38, 62.60, 30.41, 25.60, 21.39, 21.30. MS (ESI): *m/z* calc. for C₇₀H₉₂BN₃O₃₉: 1610.3 ; found: 1653.40 [M+Na]⁺.

Compound 4

Compound **14** (20 mg, 0.02 mmol) was dissolved in 300 μ L of MeOH. K_2CO_3 catalytic amount was added to the suspension and the reaction mixture stirred at room temperature for 60 min, and monitored by RP-HPLC (grad., 10% to 90% ACN in water, 20 min). After completion, the reaction mixture diluted with MeOH, water and 50 μ L of AcOH. The crude product mixture was purified by semi preparative RP-HPLC (grad., 10% to 90% ACN in water, 40 min) to give compound **4** (2 mg, 41%) as a white solid.

^{13}C NMR (400MHz, MeOD): δ =158.08, 136.60, 132.40, 131.84, 131.36, 129.25, 116.93, 98.53, 85.72, 75.52, 75.20, 74.85, 73.66, 72.13, 67.20, 62.82. MS (ESI): m/z calc. for $C_{40}H_{58}BN_3O_{27}$: 1023.70 ; found: 1046.3 $[M+Na]^+$. RP-HPLC (grad., 10% to 90% ACN in water, 20 min) 7.77 min, λ =220 nm.

Compound 15

Compound **10** (300 mg, 0.68 mmol) was dissolved in 10 mL of ACN and cooled to 0°C. NaI (615 mg, 4.10 mmol) was added, and then TMS-Cl (520 μ L, 4.10 mmol) was added dropwise. The reaction mixture stirred for 30 min at room temperature and monitored by TLC (EtOAc/Hex 10:90). After completion, the reaction mixture diluted with EtOAc, and was washed with saturated solution of $Na_2S_2O_3$. The organic layer was separated and was washed with water, then brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 10:90) to give compound **15** (268 mg, 60%) as a white solid.

1H NMR (400MHz, $CDCl_3$): δ = 8.00 (2H, d), 7.89 (2H, d, J = 8.0 Hz), 7.54 (2H, d, J = 8.0 Hz), 5.29 (2H, s), 4.43 (4H, s), 4.37 (2H, q, J = 7.0 Hz), 1.39 (3H, t, 7.0 Hz. ^{13}C NMR (400MHz, $CDCl_3$): δ = 165.9, 158.6, 139.9, 135.9, 134.9, 133.4, 128.3, 127.5, 84.7, 74.6, 62.0, 37.4, 30.4, 25.6, 15.1, -0.93. MS (ESI): m/z calc. for $C_{24}H_{29}BI_2O_5$: 662.6 ; found: 662.6 $[M]^+$.

Compound 17

Compound **15**³ (368 mg, 0.80 mmol) was dissolved in 3 mL of dry DMF and cooled to 0°C. K₂CO₃ (135 mg, 0.97 mmol) was added and the solution stirred at 0°C for 10 min, before compound **16**³ (268 mg, 0.40 mmol) was added. The reaction mixture stirred for 12 h at room temperature and monitored by TLC (EtOAc/Hex 15:85). After completion, the reaction mixture diluted with Et₂O, and was washed with saturated solution of NH₄Cl. The organic layer was separated and was washed with brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 15:85) to give compound **17** (296 mg, 60%) as yellow oil.

¹H NMR (200MHz, CDCl₃): δ = 8.30 (2H, s), 8.13 (4H, s), 7.78 (2H, d, *J* = 7.8 Hz), 7.28 (2H, d, *J* = 7.8 Hz), 5.02 (4H, s), 4.95 (2H, s), 4.72 (8H, s), 4.37 (6H, q, *J* = 7.8 Hz), 1.43 (12H, m), 1.34 (12H, s), 0.91 (36H, s), 0.09 (24H, s). ¹³C NMR (200MHz, CDCl₃): δ = 166.42, 156.91, 135.05, 134.28, 131.47, 130.92, 130.62, 129.75, 128.84, 126.49, 115.56, 83.74, 70.60, 61.01, 60.69, 60.06, 30.81, 29.57, 25.77, 24.73, 24.45, 18.20, 14.13, -0.13, -5.44

Compound 18

Compound **17** (290 mg, 0.23 mmol) was dissolved in 4 mL MeOH. Catalytic amount of *p*-TsOH was added to the suspension and the reaction mixture stirred at room temperature for 20 min, and monitored by TLC (EtOAc/Hex 70:30). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 70:30) to give Compound **18** (84 mg, 47%) as a white solid.

¹H NMR (400MHz, CDCl₃): δ = 8.30 (2H, s), 8.09 (4H, s), 7.70 (2H, d, *J* = 7.9 Hz), 7.17 (2H, d, *J* = 7.9 Hz), 5.02 (4H, s), 4.96 (2H, s), 4.65 (8H, s), 4.38 (6H, m), 1.41 (9H, m), 1.35 (12H, s). ¹³C NMR (200MHz, CDCl₃): δ = 158.82, 157.85, 135.05, 134.28, 131.47, 130.92, 130.62, 129.75, 128.84, 126.49, 106.85, 89.37, 71.64, 65.08, 61.36, 60.49, 25.58, 24.76, 14.26 MS (ESI): *m/z* calc. for C₄₆H₅₅BO₁₅: 858.73 ; found: 881.8 [M+Na]⁺.

Compound 19

Compound **18** (85 mg, 0.09 mmol) was dissolved in 4 mL of dry Toluene. Compound **9** (342 mg, 0.79 mmol) was added, followed by catalytic amount of DBTL. The reaction mixture was heated to 80°C, stirred for 30 min under an Ar atmosphere, and monitored by TLC (EtOAc/Hex 60:40). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 70:30) to give Compound **19** (180 mg, 63%) as a white solid. The product contained traces of free glucose units, which were further purified in the next step.

¹H NMR (400MHz, CDCl₃): δ = 8.34 (2H, brs), 8.11 (4H,s), (2H, d, *J* = 7.8 Hz), 7.30 (2H, d, *J* = 7.8 Hz), 7.30 (2H, d, *J* = 7.8 Hz), 6.01 (4H, brs), 5.44 (4H, t, *J* = 9.7 Hz), 5.26 (4H, brs), 5.27 (10H, brs), 5.17-5.05 (12H, m), 4.87-4.73 (14H, m), 4.42 (7H, m), 4.20 (4H, m), 4.04 (10H, m), 2.07-1.96 (56H, m), 1.45-1.42 (12H, m), 1.34 (12H, s). ¹³C NMR (400MHz, CDCl₃): δ = 171.45, 171.38, 170.75, 170.31, 166.14, 164.22, 158.58, 156.43, 148.48, 139.87, 135.82, 135.16, 133.39, 132.14, 131.95, 130.83, 127.89, 127.77, 127.55, 99.78, 95.05, 77.79, 73.62, 72.53, 71.60, 71.21, 70.75, 70.42, 68.07, 68.37, 62.74, 62.51, 62.25, 61.98, 30.40, 25.57, 23.40, 21.37, 21.29, 15.07. MS (ESI): *m/z* calc. for C₄₀H₁₃₉BN₄O₅₉: 2472.1 ; found: 2494.9 [M+Na]⁺.

Compound 5

Compound **19** (46 mg, 0.01 mmol) was dissolved in 4 mL of MeOH. K₂CO₃ (8 mg, 0.06 mmol) was added to the suspension and the reaction mixture stirred at room temperature for 60 min, and monitored by RP-HPLC (grad. 10% to 90% ACN in water, 20 min). After completion, the reaction mixture diluted with MeOH, water and 1 mL of AcOH. The crude product mixture was purified by preparative RP-HPLC (grad., 10% to 90% ACN in water, 40 min) to give compound **5** (11 mg, 33%) as a white solid.

¹³C NMR (400MHz, MeOD): δ = 167.10, 157.86, 136.17, 133.54, 133.33, 133.07, 132.74, 132.54, 128.59, 98.83, 98.75, 98.54, 75.20, 74.81, 73.65, 72.07, 70.94, 62.95, 62.76, 62.62, 62.46, 16.20. MS (ESI): *m/z* calc. for C₇₂H₉₇BN₄O₄₃: 1717.35 ; found:

1740.2 [M+Na]⁺. RP-HPLC (grad., 10% to 90% ACN in water, 20 min) 10.25 min, λ =245 nm.

Compound 21

Compound **20**⁴ (452 mg, 1.10 mmol) was dissolved in 3 mL of dry DMF and cooled to 0°C. K₂CO₃ (182 mg, 1.31 mmol) was added and the solution stirred at 0°C for 10 min, before compound **15** (363 mg, 0.55 mmol) was added. The reaction mixture stirred for 12 h at room temperature and monitored by TLC (EtOAc/Hex 15:85). After completion, the reaction mixture diluted with Et₂O, and was washed with saturated solution of NH₄Cl. The organic layer was separated and was washed with brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/Hex 15:85) to give compound **21** (200 mg, 28%) as colorless oil.

¹H NMR (200MHz, CDCl₃): δ = 8.31 (2H, s), 7.71 (2H, d, J = 8.0 Hz), 7.39 (4H, s), 7.26 (2H, d, J = 8.0 Hz), 4.96 (4H, s), 4.91 (2H, s), 4.71 (8H, s), 4.67 (4H, s), 4.12 (2H, q, J = 8.6 Hz), 1.43-1.33 (15H, m), 0.91 (36H, s), 0.07 (24H, s). ¹³C NMR (200MHz, CDCl₃): δ = 165.71, 157.79, 152.67, 139.04, 136.92, 134.98, 134.17, 131.62, 130.66, 126.93, 126.37, 125.94, 83.78, 76.75, 70.63, 65.26, 60.96, 60.22, 29.58, 25.85, 24.73, 18.28, 14.32, -5.40. MS (ESI): m/z calc. for C₆₆H₁₀₇BO₁₃Si₄: 1231.7 ; found: 1253.7 [M+Na]⁺.

Compound 22

Compound **21** (190 mg, 0.14 mmol) was dissolved in 4 mL of MeOH. Catalytic amount of *p*-TsOH was added to the suspension and the reaction mixture stirred at room temperature for 20 min, and monitored by TLC (MeOH/DCM 10:90). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (MeOH/DCM 10:90) to give Compound **22** (53 mg, 44%) as a white solid.

¹H NMR (400MHz, MeOD): δ = 8.32 (2H, s), 7.68 (6H, d, J = 7.7 Hz), 7.39 (4H, s), 7.34 (2H, d, J = 7.7 Hz), 5.03 (4H, s), 5.01 (2H, s), 4.62 (8H, s), 4.60 (4H, s), 4.38

(2H, q, $J = 6.9$ Hz), 1.40 (3H, t, $J = 6.9$ Hz), 1.32 (12H, s). ^{13}C NMR (200MHz, MeOD): $\delta = 166.03, 158.02, 153.41, 139.54, 137.43, 134.43, 134.06, 131.85, 130.32, 126.50, 83.67, 76.60, 71.02, 63.49, 60.83, 58.79, 31.57, 30.32, 29.26, 29.00, 23.71, 22.23, 13.15$. MS (ESI): m/z calc. for $\text{C}_{42}\text{H}_{51}\text{BO}_{13}$: 774.66 ; found: 797.3 $[\text{M}+\text{Na}]^+$.

Compound 23

Compound **22** (70 mg, 0.09 mmol) was dissolved in 4 mL of dry Toluene. Compound **9** (468 mg, 1.08 mmol) was added, followed by catalytic amount of DBTL. The reaction mixture was heated to 80°C, stirred for 30 min under an Ar atmosphere, and monitored by TLC (EtOAc). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc) to give Compound **23** (115 mg, 40%) as a white solid. The product contained traces of free glucose units, which were further purified in the next step.

^1H NMR (400MHz, CDCl_3): $\delta = 8.32$ (2H, s), 7.71 (2H, d, $J = 7.1$ Hz), 7.41 (4H, s), 7.27 (2H, d, $J = 7.1$ Hz), 6.37 (2H, brs), 6.20 (3H, brs), 6.10 (2H, t, $J = 7.1$ Hz), 5.44-5.40 (8H, m), 5.29-5.25 (8H, m), 5.13-5.00 (26H, m), 4.86-4.81 (24H, m), 4.40 (2H, q, $J = 7.1$ Hz), 4.25-4.05 (24H, m), 2.15-1.90 (100H, m), 1.39 (3H, t, $J = 7.6$ Hz), 1.32 (12H, s). ^{13}C NMR (400MHz, CDCl_3): $\delta = 171.68, 171.51, 170.95, 170.79, 170.31, 156.60, 135.76, 133.36, 131.70, 130.88, 127.35, 94.89, 94.51, 84.67, 77.90, 73.51, 72.52, 72.29, 71.85, 71.53, 71.30, 71.24, 70.71, 69.42, 69.05, 68.32, 68.23, 62.77, 35.35, 32.60, 30.36, 29.73, 25.96, 23.32, 21.34, 21.27, 14.79$. MS (ESI): m/z calc. for $\text{C}_{138}\text{H}_{177}\text{BN}_6\text{O}_{79}$: 3194.69 ; found: 3217.7 $[\text{M}+\text{Na}]^+$.

Compound 6

Compound **23** (30 mg, 0.01 mmol) was dissolved in 3 mL of MeOH. K_2CO_3 (8 mg, 0.06 mmol) was added to the suspension and the reaction mixture stirred at room temperature for 60 min, and monitored by RP-HPLC (grad. 10% to 90% ACN in water, 20 min). After completion, the reaction mixture diluted with MeOH, water and 1 mL of AcOH. The crude product mixture was purified by preparative RP-HPLC

(grad., 10% to 90% ACN in water, 40 min) to give compound **6** (10 mg, 50%) as a white solid.

^{13}C NMR (400MHz, MeOD): δ = 157.92, 157.76, 134.32, 132.29, 132.16, 131.59, 130.71, 130.13, 127.91, 1012.10, 101.86, 97.81, 77.77, 74.40, 73.71, 72.79, 72.50, 71.18, 70.36, 66.40, 62.03, 30.20, 14.67 .MS (ESI): m/z calc. for $\text{C}_{84}\text{H}_{117}\text{D}_2\text{BN}_6\text{O}_{55}$: 2105.7 ; found: 2106.6 $[\text{M}+\text{H}]^+$. RP-HPLC (grad., 10% to 90% ACN in water, 20 min) 8.71 min, λ =245 nm.

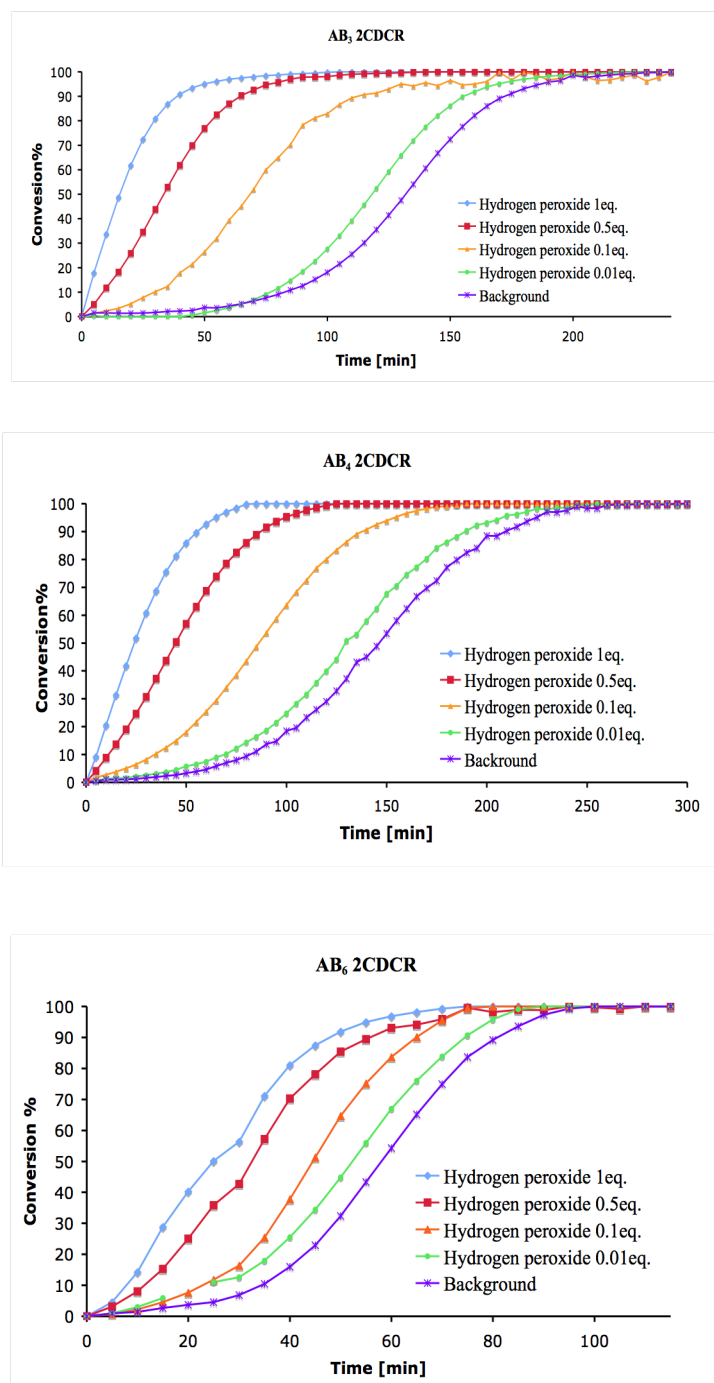


Figure 1: Release of 5-amino-2-nitrobenzoic acid from probe **2** (500 μM) in the presence of the corresponding dendrons (1000 μM) and GOX (0.1 mg/mL) in PBS (pH 8.3) upon addition of buffer only (background) or the indicated equivalents of H_2O_2 . The reaction progress was monitored at 405 nm for the indicated period.

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