Supporting Information:

H-Phosphonate Synthesis and Biological Evaluation of an Immunomodulatory Phosphoglycolipid from Thermophilic Bacteria

Chin Heng Gan,a Hadhi Wijaya,a Lan-Hui Li,c,d Chih-Feng Wei,d Yi-Jen Peng,d Shih-Hsiung Wu,c,* Kuo-Feng Hua,b,d,f,* and Yulin Lam,a,*

a Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543
b Department of Biotechnology and Animal Science, National Ilan University, No 1 Sec 1 Shennong Road, Yilan County 260, Taiwan
c Department of Laboratory Medicine, Linsen, Chinese Medicine and Kunming Branch, Taipei City Hospital, No 100, Kunning Street, Taipei 10844, Taiwan
d Department of Pathology, Tri-Service General Hospital, National Defense Medical Center, No 161, Sec 6, Minquan E. Road, Taipei 11490, Taiwan
e Institute of Biological Chemistry, Academia Sinica, 128 Academia Road Sec 2, Nankang, Taipei 115, Taiwan
f Department of Medical Research, China Medical University Hospital, China Medical University, No 91, Hsueh-Shih Road, Taichung 40402, Taiwan

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Synthetic Procedures and Characterization Data of Intermediates and Compounds 1a-1s.

General Procedures. All chemical reagents and solvents were obtained from Sigma Aldrich, Merck, Alfa Aesar, Fluka, or TCI and were used without further purification. Microwave-assisted reactions were performed using the Biotage Initiator microwave synthesizer. TLC were performed on precoated silica plated (Merck silica gel 60, F254) and visualised with UV or stained with phosphomolybdic acid, alkaline potassium permanganate stain. Flash chromatography was performed on silica (Merck, 70-230 mesh). $^1$H, $^{13}$C and $^{31}$P NMR spectra were measured on a Bruker AMX 300, 400 or 500 spectrometer. Chemical shifts were reported in parts per million (δ) relative to the tetramethylsilane standard. Mass spectra were performed on a Finnigan/MAT LCQ mass spectrometer under either electron spray ionisation (ESI) or electron impact (EI) techniques.

Synthesis of 5. To a solution of (S)-(+-)-solketal (722μl, 5.47mmol) in ACN/H$_2$O (1:1, 20ml) was added TEMPO (85mg, 0.547mmol) and BAIB (4.23g, 13.1mmol). The reaction was stirred at room temperature for 4h. The reaction mixture was quenched with solid Na$_2$S$_2$O$_3$ and diluted with water. The aqueous layer was washed with EA 3 times. The organic layers were combined, dried over MgSO$_4$, filtered and concentrated. The crude mixture was passed through a short pad of silica (hexane:EA = 2:1) to yield 5 (494mg, 62%) as an orange liquid. 5 was then used in the subsequent step without further purification.

General procedure for the synthesis of 6. To a solution of 5 (4mmol) in DCM (10ml) was added CDI (713mg, 4.4mmol). The reaction was stirred at room temperature for 1h, after which R$_3$NH$_2$ (4.4mmol) in DCM (10ml) was added and the reaction further stirred at room temperature for 12h. The reaction mixture was then concentrated, and flash chromatography of the crude mixture (hexane:EA = 8:1) yielded 6 as a white solid.
Synthesis of 6a. 6a (852mg, 63%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.40 (dd, $J$ = 7.6, 5.3 Hz, 1H), 4.22 (dd, $J$ = 8.7, 7.7 Hz, 1H), 4.02 (dd, $J$ = 8.8, 5.3 Hz, 1H), 3.25 – 3.16 (m, 2H), 1.50 – 1.40 (m, 6H), 1.33 (s, 3H), 1.21 (d, $J$ = 22.0 Hz, 2H), 1.08 (dd, $J$ = 13.7, 6.6 Hz, 2H), 0.79 (d, $J$ = 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.99, 110.75, 75.05, 67.78, 39.03, 38.91, 29.91, 29.69, 29.66, 29.63, 29.60, 29.53, 29.51, 29.49, 29.21, 27.94, 27.39, 26.81, 26.15, 25.01, 22.63. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{23}$H$_{45}$NNaO$_3$ 406.3297; found 406.3299.

Synthesis of 6b. 6b (570mg, 84%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 6.57 (s, 1H), 4.42 (dd, $J$ = 7.5, 5.3 Hz, 1H), 4.28 – 4.19 (m, 1H), 4.05 (dt, $J$ = 12.7, 4.3 Hz, 1H), 3.31 – 3.13 (m, 2H), 1.48 (dd, $J$ = 13.2, 6.6 Hz, 3H), 1.44 (s, 3H), 1.35 (s, 3H), 1.33 – 1.15 (m, 26H), 1.14 – 1.05 (m, 2H), 0.82 (dd, $J$ = 6.5, 3.0 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.59, 111.35, 75.68, 68.38, 39.66, 39.52, 30.55, 30.32, 30.29, 30.26, 30.23, 30.15, 30.12, 29.84, 28.55, 28.02, 27.44, 26.76, 25.63, 23.25. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{25}$H$_{49}$NNaO$_3$ 434.3610; found 434.3622

Synthesis of 6c. 6c (766mg, 76%) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-d) δ 4.39 (dd, $J$ = 7.6, 5.3 Hz, 1H), 4.21 (dd, $J$ = 8.8, 7.6 Hz, 1H), 4.01 (dd, $J$ = 8.7, 5.3 Hz, 1H), 3.28 – 3.10 (m, 2H), 1.51 – 1.36 (m, 6H), 1.32 (s, 3H), 1.19 (s, 30H), 1.08 (d, $J$ = 6.7 Hz, 2H), 0.79 (d, $J$ = 6.6 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.90, 110.65, 74.98, 67.69, 38.97, 38.83, 29.85, 29.63, 29.60, 29.57, 29.54, 29.47, 29.45, 29.42, 29.14, 27.86, 27.32, 26.74, 26.06, 24.94, 22.55. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{27}$H$_{53}$NNaO$_3$ 462.3918; found 462.3920

General procedure for the synthesis of 3. To a solution of 6 (2mmol) in ACN (15ml) was added 1M HCl (2mL). The reaction was stirred at room temperature for 1h, after which it was
quenched with saturated NaHCO$_3$. The aqueous layer was washed with EA 3 times, and the organic layers were combined, dried over MgSO$_4$, filtered and concentrated to yield 3 as a white solid. 3 was used in subsequent steps without further purification.

**Synthesis of 3a.** 3a (672mg, 88%) was obtained as a white solid. $^1$H NMR (500 MHz, DMSO) δ 7.61 (s, 1H), 5.40 (d, $J = 3.4$ Hz, 1H), 4.60 (s, 1H), 3.84 (s, 1H), 3.57 (s, 1H), 3.42 (d, $J = 4.2$ Hz, 1H), 3.31 (s, 2H), 3.05 (s, 2H), 1.48 (d, $J = 5.6$ Hz, 1H), 1.39 (s, 3H), 1.23 (s, 22H), 1.13 (s, 3H), 0.84 (d, $J = 5.1$ Hz, 6H). $^{13}$C NMR (126 MHz, DMSO) δ 171.76, 72.96, 63.97, 38.44, 38.08, 29.27, 29.15, 29.01, 28.74, 27.34, 26.73, 26.31, 22.43. HRMS (ESI) m/z: [M-H]- calcd. for C$_{20}$H$_{40}$NO$_3$ 342.3014; found 342.3020.

**Synthesis of 3b.** 3b (443mg, 86%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.42 (d, $J = 5.5$ Hz, 1H), 4.62 (t, $J = 5.8$ Hz, 1H), 3.83 (dd, $J = 9.4, 5.8$ Hz, 1H), 3.59 – 3.51 (m, 1H), 3.45 – 3.37 (m, 1H), 3.11 – 2.96 (m, 2H), 1.49 (tt, $J = 13.2, 6.6$ Hz, 1H), 1.43 – 1.33 (m, 2H), 1.21 (d, $J = 26.6$ Hz, 26H), 1.14 – 1.10 (m, 0H), 0.84 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.78, 72.96, 63.99, 40.09, 38.43, 38.10, 29.24, 29.22, 29.14, 29.13, 28.97, 28.94, 28.72, 28.70, 27.34, 27.32, 26.72, 26.69, 26.29, 22.44. HRMS (ESI) m/z: [M+Na]+ calcd. for C$_{22}$H$_{45}$NNaO$_3$ 394.3297; found 394.3305

**Synthesis of 3c.** 3c (564mg, 81%) was obtained as a white solid. $^1$H NMR (400 MHz, Methanol-$d_4$) δ 4.00 (dd, $J = 5.9, 4.0$ Hz, 1H), 3.71 (dd, $J = 11.4, 4.0$ Hz, 1H), 3.62 (dd, $J = 11.4, 5.9$ Hz, 1H), 3.16 (td, $J = 7.1, 5.1$ Hz, 2H), 1.44 (qd, $J = 8.2, 7.4, 4.9$ Hz, 3H), 1.18 (s, 30H), 1.08 (dd, $J = 8.4, 5.0$ Hz, 2H), 0.78 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (101 MHz, MeOD) δ 172.85, 72.38, 64.12, 39.00, 38.99, 29.85, 29.63, 29.60, 29.57, 29.52, 29.46, 29.27, 29.21, 27.88, 27.32, 26.79, 22.46. HRMS (ESI) m/z: [M+Na]+ calcd. for C$_{24}$H$_{49}$NNaO$_3$ 422.3610; found 422.3597
General procedure for the synthesis of 7. To a solution of 3 (567mg, 1mmol) and 6 (1.5mmol) in MTBE (15ml) was added NIS (675mg, 3mmol) and 4Å molecular sieves. The reaction was stirred at room temperature for 1h, after which it was cooled to 0°C and TMSOTf (542µl, 3mmol) in MTBE (4ml) was added dropwise. The reaction was further stirred at room temperature for 1h, after which it was quenched with TEA and Na₂S₂O₃. The reaction mixture was filtered through celite and diluted with Et₂O. The organic layer was washed with NaHCO₃ twice followed by brine. The organic layer was then dried over MgSO₄, filtered and concentrated. Flash chromatography of the crude mixture (hexane:Et₂O = 1:1) yielded 7 as a white solid.

Synthesis of 7a. 7a (519mg, 45%) was obtained as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.04 (m, 15H), 4.89 – 4.67 (m, 4H), 4.53 (d, J = 12.0 Hz, 1H), 4.49 – 4.37 (m, 2H), 4.11 (t, J = 5.0 Hz, 1H), 3.94 – 3.80 (m, 2H), 3.80 – 3.73 (m, 1H), 3.73 – 3.51 (m, 5H), 3.40 (dd, J = 10.2, 3.6 Hz, 1H), 3.28 – 3.08 (m, 2H), 1.43 (td, J = 13.2, 6.7 Hz, 3H), 1.16 (d, J = 7.5 Hz, 22H), 1.10 – 1.04 (m, 2H), 0.79 (d, J = 6.6 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 170.90, 137.76, 137.54, 128.42, 128.36, 127.99, 127.91, 127.76, 127.63, 98.20, 80.40, 78.05, 75.45, 74.92, 73.51, 71.06, 70.66, 70.30, 68.09, 63.63, 39.35, 39.01, 29.89, 29.67, 29.63, 29.60, 29.54, 29.26, 27.91, 27.36, 26.88, 22.61. HRMS (ESI) m/z: [M-H]- calcd. for C₄₇H₆₇N₄O₇ 799.5015; found 799.4983.

Synthesis of 7b. 7b (386mg, 48%) was obtained as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.20 (m, 12H), 7.17 – 7.10 (m, 2H), 4.91 (d, J = 3.5 Hz, 1H), 4.83 (q, J = 10.7 Hz, 2H), 4.77 (d, J = 11.0 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 11.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 4.21 (s, 1H), 3.96 – 3.85 (m, 3H), 3.82 (d, J = 9.9 Hz, 1H), 3.78 – 3.71 (m, 1H), 3.71 – 3.62 (m, 3H), 3.55 – 3.50 (m, 0H), 3.49 – 3.42 (m, 1H), 3.32 – 3.14 (m, 2H), 1.49 (td, J = 13.2, 6.7 Hz, 3H), 1.23 (d, J = 11.2 Hz, 26H), 1.17 – 1.10 (m, 2H), 0.85 (d, J = 6.6 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 177.96, 170.99, 137.74, 137.62, 137.55, 128.37, 128.32, 128.31, 127.95, 127.87, 127.83, 127.73, 127.70, 127.63, 98.07, 80.34, 78.03, 75.37, 74.88, 73.42, 70.98, 70.49,
70.40, 68.07, 63.59, 39.33, 38.97, 29.85, 29.63, 29.60, 29.56, 29.52, 29.48, 29.23, 27.87, 27.32, 26.84, 22.57. HRMS (ESI) m/z: [M-H]- calcd. for C_{49}H_{73}N_4O_8 829.5457; found 829.5506

**Synthesis of 7c.** 7c (375mg, 40%) was obtained as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.14 (m, 9H), 7.08 (dd, \(J = 7.1, 2.2\) Hz, 1H), 4.89 – 4.63 (m, 3H), 4.45 (ddd, \(J = 21.4, 17.4, 8.9\) Hz, 2H), 4.12 (tt, \(J = 15.9, 8.0\) Hz, 2H), 3.95 – 3.79 (m, 2H), 3.79 – 3.71 (m, 1H), 3.71 – 3.50 (m, 3H), 3.40 (dd, \(J = 10.1, 3.3\) Hz, 1H), 3.25 – 3.06 (m, 2H), 1.42 (dt, \(J = 8.6, 6.6\) Hz, 3H), 1.17 (d, \(J = 9.3\) Hz, 30H), 1.07 (dd, \(J = 13.2, 6.6\) Hz, 3H), 0.79 (d, \(J = 6.6\) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.77, 137.62, 129.25, 128.41, 128.36, 127.99, 127.91, 127.76, 127.63, 125.45, 98.21, 80.40, 78.06, 75.45, 74.92, 73.51, 71.07, 70.69, 70.28, 68.10, 63.64, 39.36, 39.01, 29.89, 29.64, 29.26, 27.91, 27.36, 26.88, 22.61. HRMS (ESI) m/z: [M+Na]+ calcd. for C\(_{51}\)H\(_{78}\)N\(_4\)NaO\(_7\) 879.5606, found 879.5623.

**General procedure for the synthesis of 8.** To a solution of 7 (0.1mmol) in DCM (6ml) and pyridine (6ml) was added AcSH (6ml). The reaction was stirred at room temperature for 12h. The reaction mixture was then diluted with DCM and washed with 5M HCl twice and saturated NaHCO\(_3\). The organic layer was concentrated, and flash chromatography of the crude mixture (EA: MeOH = 20:1) yielded 8 as a white solid.

**Synthesis of 8a.** 8a (243mg, 66%) was obtained as a white solid. \(^1\)H NMR (500 MHz, MeOD) \(\delta\) 7.29 – 7.01 (m, 15H), 4.75 (s, 6H), 4.69 – 4.59 (m, 3H), 4.47 (ddd, \(J = 36.1, 26.8, 11.6\) Hz, 4H), 4.13 (t, \(J = 3.0\) Hz, 1H), 4.07 (dd, \(J = 10.5, 3.5\) Hz, 1H), 3.94 (dd, \(J = 10.0, 3.4\) Hz, 1H), 3.64 (ddd, \(J = 19.5, 10.1, 6.0\) Hz, 3H), 3.58 – 3.45 (m, 3H), 3.25 – 3.13 (m, 3H), 3.02 (dt, \(J = 13.2, 7.4\) Hz, 1H), 1.84 (s, 3H), 1.42 (ddd, \(J = 17.0, 10.2, 5.4\) Hz, 3H), 1.17 – 1.06 (m, 22H), 0.79 – 0.75 (m, 6H). \(^{13}\)C NMR (126 MHz, MeOD) \(\delta\) 173.91, 173.22, 140.01, 139.84, 139.44, 129.39, 129.32, 129.25, 129.13, 128.77, 128.72, 128.64, 128.59, 128.56, 98.79, 82.33, 79.62,
Synthesis of 8b. 8b (212mg, 64%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) δ 7.41 – 7.13 (m, 15H), 4.76 (d, $J = 11.2$ Hz, 1H), 4.83 – 4.69 (m, 4H), 4.75 – 4.68 (m, 2H), 4.65 (d, $J = 11.2$ Hz, 1H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.57 (ddd, $J = 36.1$, 26.5, 11.6 Hz, 4H), 4.54 (d, $J = 11.1$ Hz, 1H), 4.49 (d, $J = 12.0$ Hz, 1H), 4.23 (s, 1H), 4.23 (s, 1H), 4.17 (dd, $J = 10.5$, 3.4 Hz, 1H), 4.17 (dd, $J = 10.5$, 3.4 Hz, 1H), 4.05 (dd, $J = 9.9$, 3.2 Hz, 1H), 4.05 (dd, $J = 9.9$, 3.2 Hz, 1H), 3.83 – 3.72 (m, 3H), 3.74 (dt, $J = 14.3$, 10.7 Hz, 3H), 3.72 – 3.53 (m, 4H), 3.68 – 3.57 (m, 3H), 3.21 – 3.05 (m, 1H), 3.18 – 3.05 (m, 1H), 1.94 (s, 3H), 1.94 (s, 3H), 1.72 – 1.42 (m, 4H), 1.58 – 1.46 (m, 3H), 1.42 – 0.99 (m, 33H), 1.38 – 1.11 (m, 33H), 0.87 (d, $J = 6.6$ Hz, 7H), 0.87 (d, $J = 6.6$ Hz, 7H). $^{13}$C NMR (126 MHz, MeOD) δ 173.92, 173.23, 140.02, 139.85, 139.45, 129.39, 129.32, 129.26, 129.14, 128.78, 128.73, 128.65, 128.60, 128.56, 98.81, 82.34, 79.63, 76.38, 75.78, 74.36, 72.33, 72.20, 70.10, 69.67, 54.42, 40.37, 40.24, 31.03, 30.76, 30.46, 29.14, 28.53, 28.13, 23.07, 22.81. HRMS (ESI) m/z: [M+H]+ calcd. for C_{49}H_{73}N_{2}O_{8} 817.5361; found 817.5363.

Synthesis of 8c. 8c (191mg, 70%) was obtained as a white solid. $^1$H NMR (400 MHz, MeOD) δ 7.31 – 6.97 (m, 12H), 4.70 – 4.58 (m, 3H), 4.58 – 4.48 (m, 1H), 4.48 – 4.30 (m, 2H), 4.19 – 3.99 (m, 2H), 3.99 – 3.88 (m, 1H), 3.70 – 3.56 (m, 3H), 3.56 – 3.43 (m, 3H), 3.07 – 2.91 (m, 1H), 1.52 – 1.32 (m, 3H), 1.13 (dd, $J = 36.1$, 7.3 Hz, 30H), 0.77 (dd, $J = 6.6$, 1.8 Hz, 6H). $^{13}$C NMR (101 MHz, MeOD) δ 164.40, 163.70, 130.51, 130.33, 129.93, 119.88, 119.81, 119.75, 119.62, 119.27, 119.21, 119.14, 119.08, 119.05, 89.29, 72.83, 70.12, 66.87, 66.28, 64.85, 62.82, 62.69, 60.60, 60.16, 55.86, 44.90, 30.87, 30.74, 21.54, 21.27, 20.96, 19.63, 19.03, 18.63, 13.59, 13.32. HRMS (ESI) m/z: [M+Na]+ calcd. for C_{53}H_{80}NaN_{2}O_{8} 895.5807; found 895.5788.
Synthesis of 9. To a solution of (S)-(+)solketal (1ml, 8.1mmol) in DMF (15ml) was added BnBr (1.25ml, 10.54mmol) and NaH (422mg, 10.54mmol). The reaction was then stirred at room temperature for 2h. The reaction mixture was quenched with Et₂O and the organic layer washed with water 3 times, followed by brine. The organic layer was then dried with MgSO₄, filtered and concentrate. To a solution of the crude product (8.1mmol) in ACN (15ml) was added 5M HCl (4ml). The reaction was stirred at room temperature for 1h. The reaction mixture was then diluted with EA, and washed with saturated Na₂CO₃ twice, followed by brine. The organic layer was then dried over MgSO₄, filtered and concentrated. Flash chromatography of the crude mixture (hexane:EA = 1:1) yielded 9 (1.06g, 90% over 2 steps) as a colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.20 (m, 5H), 4.46 (s, 2H), 3.81 (dq, J = 5.9, 4.0 Hz, 1H), 3.60 (dd, J = 13.8, 3.8 Hz, 1H), 3.52 (dd, J = 11.4, 5.7 Hz, 1H), 3.46 (qd, J = 9.7, 5.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 137.62, 128.46, 127.86, 127.76, 73.52, 71.69, 70.65, 63.98. HRMS (ESI) m/z: [M+Na]+ calcd. for C₁0H₁₄NaO₃ 205.0835 ; found 205.0837.

General procedure for the synthesis of 10. To a solution of 9 (1mmol) in DMF (10ml) was added fatty acid R¹COOH (1.1 mmol), TBTU (1.6mmol) and NMM (3.2mmol). The reaction mixture was stirred at room temperature for 12h, after which diluted with Et₂O and washed three times with H₂O. The organic layer was then dried and concentrated, following which flash chromatography of the crude mixture (hexane:EA = 8:1) yielded ester 10 as a colorless liquid.

Synthesis of 10a. 10a (417mg, 79%) was obtained as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.18 (m, 5H), 4.48 (s, 2H), 4.09 (qd, J = 11.5, 5.3 Hz, 2H), 4.01 – 3.89 (m, 1H), 3.45 (ddd, J = 13.7, 9.6, 5.3 Hz, 2H), 2.24 (t, J = 7.6 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.44 (dp, J = 13.2, 6.6 Hz, 1H), 1.20 (d, J = 11.8 Hz, 14H), 1.12 – 1.02 (m, 2H), 0.79 (d, J = 6.6 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 173.93, 137.64, 128.44, 127.84, 127.72, 73.47, 70.85, 68.88, 65.31, 39.01,
Synthesis of 10b. 10b (315mg, 81%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.23 – 7.12 (m, 5H), 4.42 (s, 2H), 4.06 (qd, $J = 11.4$, 5.3 Hz, 2H), 3.98 – 3.86 (m, 1H), 3.41 (ddd, $J = 15.6$, 9.7, 5.3 Hz, 2H), 2.19 (t, $J = 7.5$ Hz, 2H), 1.54 – 1.47 (m, 2H), 1.16 (s, 20H), 0.78 (t, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.54, 169.77, 137.53, 132.65, 132.22, 128.08, 127.44, 127.37, 126.39, 115.73, 115.17, 73.12, 70.78, 68.50, 65.10, 34.70, 33.83, 31.65, 29.42, 29.39, 29.35, 29.33, 29.21, 29.17, 29.09, 29.00, 28.86, 28.77, 24.62, 23.85, 22.41, 13.83. HRMS (ESI) m/z: [M+Na]+ calcd. for C$_{24}$H$_{40}$NaO$_4$ 415.2819; found 415.2826.

Synthesis of 10c. 10c (464mg, 77%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.21 (m, 5H), 4.49 (s, 2H), 4.09 (qd, $J = 11.5$, 5.3 Hz, 2H), 4.02 – 3.91 (m, 1H), 3.46 (ddd, $J = 15.7$, 9.6, 5.2 Hz, 2H), 2.25 (t, $J = 7.6$ Hz, 2H), 1.59 – 1.50 (m, 2H), 1.44 (tt, $J = 13.1$, 6.7 Hz, 1H), 1.18 (s, 16H), 1.11 – 1.02 (m, 2H), 0.79 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.95, 137.68, 128.48, 127.88, 127.74, 73.52, 70.88, 68.96, 65.35, 39.05, 34.15, 29.92, 29.68, 29.63, 29.59, 29.44, 29.24, 29.12, 27.96, 27.39, 24.90, 22.64. HRMS (ESI) m/z: [M+Na]+ calcd. for C$_{25}$H$_{42}$NaO$_4$ 429.2975; found 429.2977.

Synthesis of 10d. 10d (391mg, 85%) was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.21 (m, 4H), 4.58 (s, 1H), 4.22 – 4.10 (m, 1H), 4.09 – 3.97 (m, 1H), 3.54 (ddd, $J = 15.7$, 9.6, 5.2 Hz, 2H), 2.34 (t, $J = 7.6$ Hz, 2H), 1.66 – 1.57 (m, 2H), 1.29 (s, 24H), 0.91 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.84, 137.61, 128.37, 127.76, 127.66, 73.41, 70.85, 68.80, 65.26, 34.06, 31.85, 29.62, 29.60, 29.57, 29.53, 29.39, 29.28, 29.18, 29.05, 24.82, 22.61, 14.02. HRMS (ESI) m/z: [M+Na]+ calcd. for C$_{25}$H$_{42}$NaO$_4$ 429.2975, found 429.2986.
Synthesis of 10e. 10e (499mg, 82%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.20 (m, 5H), 4.48 (s, 2H), 4.09 (qd, $J = 11.5$, 5.2 Hz, 2H), 4.02 – 3.90 (m, 1H), 3.45 (ddd, $J = 15.7$, 9.6, 5.2 Hz, 2H), 2.24 (t, $J = 7.6$ Hz, 2H), 1.58 – 1.49 (m, 2H), 1.44 (dp, $J = 13.2$, 6.6 Hz, 1H), 1.18 (s, 18H), 1.12 – 1.02 (m, 2H), 0.79 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.93, 137.63, 128.44, 127.84, 127.71, 73.47, 70.85, 68.89, 65.30, 39.02, 34.11, 29.90, 29.68, 29.63, 29.61, 29.56, 29.42, 29.21, 29.09, 27.92, 27.37, 24.87, 22.62. HRMS (ESI) m/z: [M+Na$^+$]+ calcd. for C$_{26}$H$_{44}$NaO$_4$ 443.3132; found 443.3124.

Synthesis of 10f. 10f (316mg, 77%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 6.91 (m, 5H), 4.43 (s, 2H), 4.11 – 3.96 (m, 2H), 3.96 – 3.82 (m, 1H), 3.40 (ddd, $J = 15.7$, 9.7, 5.3 Hz, 2H), 2.20 (t, $J = 7.6$ Hz, 2H), 1.56 – 1.44 (m, 2H), 1.18 (s, 24H), 0.79 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.56, 137.60, 128.18, 127.54, 127.47, 73.22, 70.84, 68.58, 65.14, 33.90, 31.71, 29.48, 29.44, 29.40, 29.26, 29.14, 29.05, 28.92, 24.68, 22.46, 13.86. HRMS (ESI) m/z: [M+Na$^+$]+ calcd. for C$_{26}$H$_{44}$NaO$_4$ 443.3132; found 443.3129.

Synthesis of 10g. 10g (474mg, 73%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.27 – 7.11 (m, 5H), 4.43 (s, 2H), 4.04 (qd, $J = 11.4$, 5.3 Hz, 2H), 3.90 (s, 1H), 3.40 (ddd, $J = 15.6$, 9.6, 5.3 Hz, 2H), 2.20 (t, $J = 7.5$ Hz, 2H), 1.49 (dd, $J = 14.2$, 7.1 Hz, 2H), 1.42 (td, $J = 13.3$, 6.6 Hz, 1H), 1.17 (s, 20H), 1.10 – 1.01 (m, 2H), 0.78 (d, $J = 6.7$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.60, 137.56, 128.18, 127.54, 127.48, 73.21, 70.83, 68.54, 65.12, 38.86, 33.89, 29.74, 29.52, 29.49, 29.48, 29.45, 29.41, 29.26, 29.06, 28.92, 27.74, 27.21, 24.67, 22.44. HRMS (ESI) m/z: [M+Na$^+$]+ calcd. for C$_{27}$H$_{46}$NaO$_4$ 457.3288; found 457.3292.

General procedure for the synthesis of 11. To a solution of 10 (1mmol) in DCM (10ml) was added fatty acid R$^2$COOH (1.2mmol), DCC (330mg, 1.6mmol) and DMAP (12mg, 0.1mmol). The reaction mixture was stirred at room temperature for 12h, after which it was concentrated.
Flash chromatography of the crude mixture (hexane:EA = 50:1 to hexane:EA = 20:1) yielded 11 as a white solid.

**Synthesis of 11a.** 11a (205mg, 71%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 – 7.13 (m, 5H), 5.22 – 5.09 (m, 1H), 4.45 (q, $J = 12.1$ Hz, 2H), 4.27 (dd, $J = 11.9$, 3.7 Hz, 1H), 4.11 (dd, $J = 11.9$, 6.4 Hz, 1H), 3.50 (d, $J = 5.1$ Hz, 2H), 2.23 (t, $J = 7.5$ Hz, 2H), 2.19 (t, $J = 7.5$ Hz, 2H), 1.57 – 1.47 (m, 4H), 1.43 (td, $J = 13.2$, 6.6 Hz, 2H), 1.18 (s, 32H), 1.10 – 1.04 (m, 4H), 0.78 (d, $J = 6.7$ Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 204.79, 173.16, 172.88, 137.63, 128.28, 127.63, 127.49, 73.18, 69.91, 68.16, 62.53, 38.97, 34.20, 33.99, 29.86, 29.63, 29.58, 29.54, 29.39, 29.20, 29.02, 28.99, 27.87, 27.33, 24.85, 24.78, 22.56. HRMS (ESI) m/z: [M+Na]+ calcd. for C$_{40}$H$_{70}$NaO$_5$ 653.5115; found 653.5119.

**Synthesis of 11b.** 11b (197mg, 87%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 – 7.14 (m, 5H), 5.21 – 5.13 (m, 1H), 4.45 (q, $J = 12.1$ Hz, 2H), 4.27 (dd, $J = 11.9$, 3.8 Hz, 1H), 4.11 (dd, $J = 11.9$, 6.4 Hz, 1H), 3.50 (dd, $J = 5.2$, 1.4 Hz, 2H), 1.57 – 1.47 (m, 4H), 1.43 (td, $J = 13.3$, 6.6 Hz, 2H), 1.19 (d, $J = 13.5$ Hz, 28H), 1.07 (d, $J = 6.9$ Hz, 4H), 0.78 (d, $J = 6.7$ Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.29, 173.00, 137.75, 128.40, 127.75, 127.60, 73.30, 70.03, 68.28, 62.65, 39.08, 34.32, 34.10, 29.95, 29.71, 29.65, 29.50, 29.30, 29.13, 29.10, 27.97, 27.43, 24.96, 24.89, 22.66. HRMS (ESI) m/z: [M+Na]+ calcd. for C$_{38}$H$_{66}$NaO$_5$ 625.4802; found 625.4809.

**Synthesis of 11c.** 11c (223mg, 90%) was obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.30 – 7.11 (m, 5H), 5.21 – 5.10 (m, 1H), 4.51 – 4.37 (m, 2H), 4.27 (dd, $J = 11.9$, 3.8 Hz, 1H), 4.10 (dd, $J = 11.9$, 6.4 Hz, 1H), 3.50 (d, $J = 5.2$ Hz, 2H), 2.20 (dt, $J = 11.8$, 7.5 Hz, 4H), 1.52 (dd, $J = 14.4$, 7.3 Hz, 4H), 1.47 – 1.36 (m, 1H), 1.18 (s, 36H), 1.07 (dd, $J = 12.6$, 6.4 Hz, 2H), 0.79 (t, $J = 7.2$ Hz, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 173.08, 172.80, 137.67, 128.25, 127.60,
127.46, 73.18, 69.94, 68.20, 62.52, 38.96, 34.18, 33.97, 31.82, 29.83, 29.58, 29.55, 29.52, 29.37, 29.25, 29.17, 28.98, 27.85, 27.31, 24.84, 24.77, 22.56, 22.52, 13.96.

**HRMS (ESI) m/z:** [M+Na]+ calcd. for C_{39}H_{68}NaO_{5} 639.4959; found 639.4963

**Synthesis of 11d.** 11d (214mg, 91%) was obtained as a white solid. ^1H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.41 – 7.23 (m, 5H), 5.33 – 5.21 (m, 1H), 4.63 – 4.48 (m, 2H), 4.38 (dd, \(J = 11.9, 3.8\) Hz, 1H), 4.21 (dd, \(J = 11.9, 6.4\) Hz, 1H), 3.61 (dd, \(J = 5.1, 1.1\) Hz, 2H), 2.32 (dt, \(J = 16.7, 7.5\) Hz, 4H), 1.72 – 1.59 (m, 4H), 1.54 (dq, \(J = 13.2, 6.6\) Hz, 2H), 1.30 (d, \(J = 5.0\) Hz, 34H), 1.18 (d, \(J = 6.8\) Hz, 4H), 0.89 (d, \(J = 6.7\) Hz, 12H). ^13C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 173.22, 172.94, 137.74, 128.38, 127.73, 127.59, 73.28, 70.02, 68.27, 62.64, 39.09, 34.31, 34.09, 29.98, 29.76, 29.74, 29.72, 29.70, 29.66, 29.51, 29.31, 29.14, 29.10, 27.98, 27.45, 24.97, 24.90, 22.67. HRMS (ESI) m/z: [M+Na]+ calcd. for C_{41}H_{72}NaO_{5} 667.5272; found 667.5280

**Synthesis of 11e.** 11e (206mg, 90%) was obtained as a white solid. ^1H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.24 (m, 5H), 5.27 (dd, \(J = 5.7, 4.3\) Hz, 1H), 4.55 (q, \(J = 12.1\) Hz, 2H), 4.38 (dd, \(J = 11.9, 3.7\) Hz, 1H), 4.21 (dd, \(J = 11.9, 6.4\) Hz, 1H), 3.67 – 3.56 (m, 2H), 2.36 – 2.29 (m, 4H), 1.64 (dd, \(J = 13.4, 6.5\) Hz, 4H), 1.54 (td, \(J = 13.2, 6.6\) Hz, 2H), 1.30 (d, \(J = 12.2\) Hz, 34H), 1.18 (d, \(J = 6.7\) Hz, 4H), 0.89 (d, \(J = 6.6\) Hz, 12H). ^13C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 173.22, 172.94, 137.77, 128.37, 127.72, 127.58, 73.29, 70.04, 68.30, 62.63, 39.08, 34.30, 34.09, 29.96, 29.72, 29.69, 29.67, 29.63, 29.48, 29.29, 29.12, 29.09, 27.96, 27.42, 24.96, 24.88, 22.64. HRMS (ESI) m/z: [M+Na]+ calcd. for C_{41}H_{72}NaO_{5} 667.5272; found 667.5287

**Synthesis of 11f.** 11f (234mg, 79%) was obtained as a white solid. ^1H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.21 (m, 5H), 5.32 – 5.18 (m, 1H), 4.54 (q, \(J = 12.1\) Hz, 2H), 4.37 (dd, \(J = 11.9, 3.7\) Hz, 1H), 4.20 (dd, \(J = 11.9, 6.4\) Hz, 1H), 3.60 (dd, \(J = 5.1, 1.1\) Hz, 2H), 2.32 (t, \(J = 7.5\) Hz, 2H), 2.28 (t, \(J = 7.5\) Hz, 2H), 1.62 (tt, \(J = 14.0, 7.1\) Hz, 4H), 1.53 (td, \(J = 13.3, 6.6\) Hz, 2H), 1.29 (s, 36H), S12
1.22 – 1.15 (m, 4H), 0.89 (d, J = 6.7 Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.11, 172.83, 137.76, 128.35, 127.69, 127.56, 73.24, 70.00, 68.25, 62.60, 39.09, 34.27, 34.05, 29.99, 29.77, 29.73, 29.71, 29.66, 29.52, 29.32, 29.13, 29.10, 29.77, 27.46, 24.96, 24.88, 22.67. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{42}$H$_{74}$NaO$_5$ 681.5428; found 681.5432

**Synthesis of 11g.** 11g (194mg, 89%) was obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.31 – 7.11 (m, 5H), 5.22 – 5.09 (m, 1H), 4.53 – 4.37 (m, 2H), 4.27 (dd, J = 11.9, 3.8 Hz, 1H), 4.11 (dd, J = 11.9, 6.4 Hz, 1H), 3.51 (d, J = 5.2 Hz, 2H), 2.21 (dt, J = 12.1, 7.5 Hz, 4H), 1.53 (dd, J = 14.8, 7.5 Hz, 4H), 1.47 – 1.35 (m, 1H), 1.18 (s, 40H), 1.12 – 1.05 (m, 2H), 0.80 (dd, J = 8.3, 6.5 Hz, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 173.33, 173.03, 137.73, 128.37, 127.72, 127.58, 73.30, 70.03, 68.29, 62.63, 39.04, 34.30, 34.09, 31.89, 29.92, 29.66, 29.63, 29.59, 29.45, 29.32, 29.25, 29.10, 29.06, 27.93, 27.38, 24.93, 24.86, 22.64, 22.60, 14.04. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{41}$H$_{72}$NaO$_5$ 667.5272; found 667.5279

**Synthesis of 11h.** 11h (221mg, 84%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.29 – 7.13 (m, 5H), 5.16 (dt, J = 10.2, 5.1 Hz, 1H), 4.45 (q, J = 12.1 Hz, 2H), 4.27 (dd, J = 11.9, 3.7 Hz, 1H), 4.11 (dt, J = 11.9, 6.5 Hz, 1H), 3.53 – 3.47 (m, 2H), 2.23 (t, J = 7.5 Hz, 2H), 2.19 (t, J = 7.5 Hz, 2H), 1.57 – 1.45 (m, 5H), 1.19 (d, J = 12.8 Hz, 48H), 0.80 (t, J = 6.9 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.17, 172.89, 137.65, 128.29, 127.64, 127.50, 73.20, 69.93, 68.18, 62.55, 34.21, 34.00, 31.85, 29.63, 29.59, 29.55, 29.41, 29.29, 29.21, 29.04, 29.00, 24.87, 24.79, 22.60, 14.00. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{42}$H$_{74}$NaO$_5$ 681.5428; found 681.5440

**Synthesis of 11i.** 11i (180mg, 78%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.27 – 7.07 (m, 5H), 5.21 – 5.08 (m, 1H), 4.47 – 4.35 (m, 2H), 4.26 (dd, J = 11.9, 3.7 Hz, 1H), 4.08 (dd, J = 11.9, 6.4 Hz, 1H), 3.47 (d, J = 5.2 Hz, 2H), 2.20 (t, J = 7.5 Hz, 2H), 2.16 (t, J = 7.5 Hz, 4H), 2.14 (t, J = 7.5 Hz, 4H), 2.12 (t, J = 7.5 Hz, 4H), 2.10 (t, J = 7.5 Hz, 4H).
Hz, 2H), 1.57 – 1.44 (m, 4H), 1.18 (s, 50H), 0.79 (t, \( J = 6.9 \) Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 172.68, 172.41, 137.56, 128.06, 127.38, 127.26, 72.96, 69.76, 68.02, 62.33, 33.98, 33.76, 31.73, 29.53, 29.48, 29.45, 29.30, 29.18, 29.10, 28.90, 28.86, 24.71, 24.64, 22.47, 13.84.

HRMS (ESI) m/z: [M+Na]+ calcd. for C\(_{43}\)H\(_{76}\)NaO\(_5\) 695.5585; found 695.5595

**Synthesis of 11j.** 11j (199mg, 72%) was obtained as a white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.41 – 7.25 (m, 4H), 5.33 – 5.22 (m, 1H), 4.56 (d, \( J = 6.4 \) Hz, 2H), 4.38 (d, \( J = 3.7 \) Hz, 1H), 4.23 (d, \( J = 6.4 \) Hz, 1H), 3.62 (d, \( J = 4.4 \) Hz, 2H), 2.34 (t, \( J = 7.5 \) Hz, 2H), 2.30 (t, \( J = 7.5 \) Hz, 2H), 1.71 – 1.60 (m, 4H), 1.55 (s, 1H), 1.39 – 1.24 (m, 42H), 1.19 (d, \( J = 6.4 \) Hz, 3H), 0.91 (dd, \( J = 11.6, 6.6 \) Hz, 9H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 173.16, 172.88, 137.79, 128.36, 127.70, 127.57, 73.29, 70.05, 68.32, 62.63, 39.09, 34.29, 34.08, 31.93, 29.97, 29.74, 29.70, 29.67, 29.64, 29.49, 29.36, 29.29, 29.13, 29.09, 27.97, 27.43, 24.96, 24.89, 22.68, 22.64, 14.07. HRMS (ESI) m/z: [M+Na]+ calcd. for C\(_{41}\)H\(_{72}\)NaO\(_5\) 667.5272; found 667.5285

**Synthesis of 11k.** 11k (211mg, 88%) was obtained as a white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.31 – 7.11 (m, 5H), 5.22 – 5.08 (m, 1H), 4.44 (q, \( J = 12.1 \) Hz, 2H), 4.27 (dd, \( J = 11.9, 3.7 \) Hz, 1H), 4.10 (dd, \( J = 11.9, 6.4 \) Hz, 1H), 3.50 (d, \( J = 5.3 \) Hz, 2H), 2.22 (t, \( J = 7.5 \) Hz, 2H), 2.18 (t, \( J = 7.5 \) Hz, 2H), 1.57 – 1.48 (m, 4H), 1.48 – 1.39 (m, 2H), 1.18 (s, 36H), 1.11 – 1.04 (m, 4H), 0.78 (d, \( J = 6.7 \) Hz, 12H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 173.07, 172.79, 137.62, 128.24, 127.59, 127.45, 73.15, 69.89, 68.14, 62.50, 38.96, 34.16, 33.95, 29.85, 29.62, 29.61, 29.60, 29.59, 29.56, 29.52, 29.37, 29.18, 29.00, 28.97, 27.84, 27.32, 24.83, 24.76, 22.53. HRMS (ESI) m/z: [M+Na]+ calcd. for C\(_{42}\)H\(_{74}\)NaO\(_5\) 684.5428; found 681.5437

**Synthesis of 11l.** 11l (254mg, 82%) was obtained as a white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.31 – 7.13 (m, 4H), 5.22 – 5.11 (m, 1H), 4.45 (q, \( J = 12.1 \) Hz, 2H), 4.27 (dd, \( J = 11.9, 3.8 \) Hz, 1H), 4.11 (dd, \( J = 11.9, 6.4 \) Hz, 1H), 3.57 – 3.44 (m, 2H), 2.21 (dt, \( J = 20.8, 7.5 \) Hz, 4H), 1.52
(tt, J = 14.3, 7.3 Hz, 4H), 1.44 (dt, J = 13.2, 6.7 Hz, 2H), 1.27 – 1.14 (m, 42H), 1.07 (d, J = 7.6 Hz, 3H), 0.80 (dd, J = 12.1, 6.7 Hz, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.23, 172.94, 137.65, 128.31, 127.67, 127.52, 73.22, 69.94, 68.19, 62.56, 38.99, 34.85, 34.24, 34.02, 31.85, 29.88, 29.66, 29.63, 29.62, 29.59, 29.56, 29.41, 29.29, 29.21, 29.05, 29.01, 27.89, 27.35, 25.39, 24.88, 24.80, 24.60, 22.61, 22.57, 14.02. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{42}$H$_{74}$NaO$_5$ 681.5428; found 681.5414

Synthesis of 11m. 11m (198mg, 80%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.11 (m, 5H), 5.20 – 5.10 (m, 1H), 4.44 (q, J = 12.1 Hz, 2H), 4.27 (d, J = 11.9, 3.8 Hz, 1H), 4.10 (dd, J = 11.9, 6.4 Hz, 1H), 3.50 (dd, J = 5.2, 1.3 Hz, 2H), 2.23 (t, J = 7.5 Hz, 2H), 2.19 (t, J = 7.5 Hz, 2H), 1.52 (tt, J = 15.4, 7.9 Hz, 4H), 1.43 (td, J = 13.3, 6.6 Hz, 2H), 1.18 (s, 40H), 1.11 – 1.04 (m, 4H), 0.78 (d, J = 6.7 Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.13, 172.84, 137.62, 128.27, 127.62, 127.48, 73.17, 69.90, 68.15, 62.52, 38.97, 34.19, 33.97, 29.87, 29.64, 29.62, 29.60, 29.57, 29.54, 29.39, 29.20, 29.02, 28.98, 27.86, 27.34, 24.85, 24.77, 22.55. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{44}$H$_{78}$NaO$_5$ 709.5741; found 709.5746

Synthesis of 11n. 11n (216mg, 70%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 – 7.07 (m, 5H), 5.26 – 5.10 (m, 1H), 4.44 (q, J = 12.1 Hz, 2H), 4.27 (d, J = 11.9, 3.7 Hz, 1H), 4.10 (dd, J = 11.9, 6.4 Hz, 1H), 3.58 – 3.35 (m, 2H), 2.20 (dt, J = 20.1, 7.5 Hz, 4H), 1.51 (dt, J = 20.4, 7.3 Hz, 4H), 1.44 (dt, J = 13.2, 6.6 Hz, 1H), 1.18 (s, 46H), 1.08 (d, J = 6.5 Hz, 2H), 0.80 (dd, J = 11.6, 6.6 Hz, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.10, 172.81, 137.67, 128.27, 127.62, 127.48, 73.20, 69.95, 68.21, 62.54, 38.99, 34.20, 33.99, 31.84, 29.87, 29.64, 29.62, 29.58, 29.54, 29.40, 29.27, 29.20, 29.03, 29.00, 27.87, 27.34, 24.86, 24.79, 22.59, 22.55, 13.98. HRMS (ESI) m/z: [M+Na]$^+$ calcd. for C$_{44}$H$_{78}$NaO$_5$ 709.5741; found 709.5746

General procedure for the synthesis of 4. To a solution of 11 (0.5mmol) in EtOH/ACOH (15:1,
16ml) was added 10% Pd/C (10% by weight of 11). The reaction was stirred under a hydrogen atmosphere at room temperature for 12h. The reaction mixture was filtered through celite, and the AcOH stripped off by co-evaporation with hexane. Final concentration of the reaction mixture yielded 4 as a white solid. 4 was used in the subsequent step without further purification.

**General procedure for the synthesis of 12.** To a solution of imidazole (1.56g, 23mmol) in toluene (15ml) at 0°C was added PCl₃ (435µl, 5mmol) in toluene (4.5ml) and TEA (1.81ml, 13mmol). The reaction was stirred for 0.5h, after which 8 (1mmol) in toluene/DCM (3:1, 15ml) was added. The reaction was further stirred for 1h at 0°C, after which TEA (12ml) and H₂O (3ml) was added. The reaction mixture was then diluted further with water and the aqueous layer washed with DCM 3 times. The organic layers were combined, dried over MgSO₄, filtered and concentrated. Flash chromatography of the crude mixture over deactivated silica gel (DCM:MeOH = 20:1 with 1% TEA) gave 12 as a white waxy solid.

**Synthesis of 12a.** 12a (137mg, 80%) was obtained as a translucent gum. ¹H NMR (500 MHz, CDCl₃) δ 5.06 – 4.95 (m, 1H), 4.17 (dd, J = 11.9, 3.6 Hz, 1H), 3.96 (dd, J = 11.9, 6.4 Hz, 1H), 3.79 (dd, J = 7.9, 5.3 Hz, 2H), 2.88 (q, J = 7.3 Hz, 6H), 2.09 (dd, J = 15.4, 7.8 Hz, 4H), 1.38 (dt, J = 18.4, 9.2 Hz, 4H), 1.30 (td, J = 13.3, 6.6 Hz, 2H), 1.14 (t, J = 7.3 Hz, 9H), 1.05 (s, 32H), 0.99 – 0.88 (m, 4H), 0.65 (d, J = 6.7 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 173.05, 172.66, 70.16, 70.10, 62.21, 61.69, 61.66, 45.32, 38.77, 34.01, 33.80, 29.65, 29.42, 29.37, 29.35, 29.20, 29.01, 29.00, 28.84, 28.81, 27.66, 27.12, 24.61, 24.59, 22.37, 8.28. ³¹P NMR (202 MHz, CDCl₃) δ 4.78. HRMS (ESI) m/z: [M-H]- calcd. for C₃₃H₆₄O₇P 603.4395; found 603.4403

**Synthesis of 12b.** 12b (191mg, 65%) was obtained as a translucent gum. ¹H NMR (500 MHz, CDCl₃) δ 5.21 – 5.11 (m, 1H), 4.30 (dd, J = 11.9, 3.3 Hz, 1H), 4.10 (dd, J = 11.9, 6.5 Hz, 1H), 3.95 – 3.88 (m, 2H), 3.01 (q, J = 7.3 Hz, 6H), 2.22 (dd, J = 14.8, 7.4 Hz, 4H), 1.47 (ddd, J =
19.9, 18.3, 5.3 Hz, 6H), 1.24 (dd, J = 27.0, 19.7 Hz, 37H), 1.14 – 1.03 (m, 4H), 0.79 (d, J = 6.6 Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.09, 172.72, 133.56, 119.48, 70.18, 70.13, 62.21, 61.69, 61.66, 45.45, 38.76, 34.01, 33.81, 29.64, 29.40, 29.35, 29.20, 29.01, 29.00, 28.84, 28.82, 27.66, 27.12, 24.62, 24.59, 22.38, 8.33. $^{31}$P NMR (202 MHz, CDCl$_3$) δ 4.35. HRMS (ESI) m/z: [M-H]- calcd. for C$_{31}$H$_{60}$O$_7$P 575.4082; found 575.4080.

**Synthesis of 12c.** 12c (160mg, 83%) was obtained as a translucent gum. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.12 (d, J = 3.2 Hz, 1H), 4.30 (dd, J = 11.9, 3.2 Hz, 1H), 4.08 (dd, J = 11.9, 6.6 Hz, 1H), 3.93 – 3.79 (m, 2H), 3.02 (dd, J = 14.3, 7.1 Hz, 6H), 2.21 (dd, J = 12.3, 7.3 Hz, 4H), 1.47 – 1.36 (m, 4H), 1.31 – 1.22 (m, 9H), 1.18 (s, 36H), 1.09 (s, 3H), 0.78 (d, J = 6.6 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 172.97, 172.60, 70.17, 70.08, 62.18, 61.57, 61.52, 45.39, 38.68, 33.92, 33.72, 31.53, 29.55, 29.30, 29.26, 29.11, 28.96, 28.92, 28.91, 28.75, 28.73, 27.57, 27.02, 24.50, 22.27, 13.70, 8.22. $^{31}$P NMR (121 MHz, CDCl$_3$) δ 4.50. HRMS (ESI) m/z: [M-H]- calcd. for C$_{32}$H$_{62}$O$_7$P 589.4239; found 589.4235

**Synthesis of 12d.** 12d (171mg, 75%) was obtained as a translucent gum. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.20 – 5.06 (m, 1H), 4.30 (dd, J = 11.9, 3.2 Hz, 1H), 4.09 (dd, J = 11.8, 6.5 Hz, 1H), 3.96 – 3.85 (m, 2H), 3.02 (q, J = 7.2 Hz, 6H), 2.22 (q, J = 7.2 Hz, 4H), 1.63 – 1.42 (m, 6H), 1.25 (dd, J = 22.5, 15.1 Hz, 43H), 1.08 (d, J = 6.0 Hz, 4H), 0.79 (d, J = 6.6 Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.60, 172.23, 69.89, 69.82, 61.89, 61.36, 61.32, 53.01, 45.07, 38.48, 33.68, 33.47, 29.36, 29.13, 29.08, 29.05, 28.91, 28.72, 28.71, 28.54, 28.51, 27.36, 26.83, 24.32, 24.29, 22.07, 8.00. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 3.67. HRMS (ESI) m/z: [M-H]- calcd. for C$_{34}$H$_{66}$O$_7$P 617.4552; found 617.4544

**Synthesis of 12e.** 12e (149mg, 75%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.19 (dt, J = 10.0, 5.2 Hz, 1H), 4.35 (dd, J = 11.9, 3.7 Hz, 1H), 4.15 (dd, J = 11.9, 6.4
Hz, 1H), 4.01 (dd, J = 8.1, 5.3 Hz, 2H), 3.56 (q, J = 7.3 Hz, 2H), 3.14 – 3.03 (m, 6H), 2.28 (dd, J = 17.0, 7.8 Hz, 4H), 1.58 (dd, J = 12.6, 6.4 Hz, 4H), 1.51 (td, J = 13.3, 6.7 Hz, 2H), 1.36 (t, J = 7.3 Hz, 10H), 1.25 (d, J = 10.0 Hz, 34H), 1.13 (d, J = 6.8 Hz, 4H), 0.85 (d, J = 6.6 Hz, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.25, 70.16, 62.10, 52.82, 45.70, 34.18, 33.99, 29.84, 29.61, 29.57, 29.54, 29.39, 29.19, 29.04, 29.02, 27.86, 27.31, 24.78, 22.54, 8.50, 7.82. $^{31}$P NMR (202 MHz, CDCl$_3$) δ 4.89. HRMS (ESI) m/z: [M-H]$^-$ calcd. for C$_{34}$H$_{66}$O$_7$P 617.4552; found 617.4554

**Synthesis of 12f.** 12f (153mg, 75%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.04 (s, 1H), 4.26 – 4.15 (m, 1H), 3.99 (dd, J = 11.7, 6.5 Hz, 1H), 3.88 – 3.77 (m, 2H), 2.95 (dd, J = 13.8, 6.7 Hz, 7H), 2.13 (dd, J = 15.4, 7.7 Hz, 4H), 1.43 (d, J = 5.4 Hz, 4H), 1.34 (dt, J = 19.4, 6.4 Hz, 2H), 1.18 (t, J = 7.2 Hz, 11H), 1.09 (s, 36H), 0.98 (d, J = 5.5 Hz, 4H), 0.69 (d, J = 6.6 Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.11, 172.74, 70.24, 70.18, 62.29, 61.83, 45.64, 38.88, 34.10, 33.90, 33.53, 29.77, 29.55, 29.51, 29.49, 29.46, 29.32, 29.12, 28.95, 28.93, 27.77, 27.24, 24.73, 24.70, 22.49, 8.47. $^{31}$P NMR (202 MHz, CDCl$_3$) δ 4.37. HRMS (ESI) m/z: [M-H]$^-$ calcd. for C$_{35}$H$_{68}$O$_7$P 631.4708; found 631.4720

**Synthesis of 12g.** 12g (144mg, 66%) was obtained as a translucent gum. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.66 (s, 1H), 5.15 (d, J = 3.7 Hz, 1H), 4.29 (s, 1H), 4.12 (d, J = 6.2 Hz, 1H), 3.99 (d, J = 5.2 Hz, 2H), 3.05 (d, J = 4.1 Hz, 4H), 2.23 (dd, J = 13.2, 7.0 Hz, 4H), 1.54 (s, 4H), 1.48 – 1.41 (m, 1H), 1.37 – 1.27 (m, 7H), 1.22 (t, J = 8.7 Hz, 40H), 1.12 (s, 2H), 0.80 (dd, J = 8.4, 4.2 Hz, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 172.97, 172.59, 69.95, 69.86, 62.03, 45.62, 38.82, 33.99, 33.81, 31.66, 29.69, 29.42, 29.24, 29.08, 29.05, 28.88, 27.70, 27.15, 24.63, 22.40, 13.82, 8.36. $^{31}$P NMR (121 MHz, CDCl$_3$) δ 4.62. HRMS (ESI) m/z: [M-H]$^-$ calcd. for C$_{35}$H$_{66}$O$_7$P 617.4552; found 617.4554
**Synthesis of 12h.** 12h (142mg, 64%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.17 – 5.11 (m, 1H), 4.30 (dd, $J$ = 11.9, 3.5 Hz, 1H), 4.09 (dd, $J$ = 11.9, 6.5 Hz, 1H), 3.90 (dd, $J$ = 8.0, 5.4 Hz, 2H), 3.06 (q, $J$ = 7.3 Hz, 13H), 2.22 (dd, $J$ = 15.0, 7.4 Hz, 4H), 1.52 (dd, $J$ = 12.1, 6.6 Hz, 4H), 1.31 (t, $J$ = 7.3 Hz, 19H), 1.27 – 1.13 (m, 48H), 0.81 (t, $J$ = 6.9 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.90, 172.52, 70.03, 69.98, 62.06, 61.45, 61.42, 45.44, 33.84, 33.63, 31.44, 29.22, 29.18, 29.02, 28.88, 28.83, 28.82, 28.65, 28.63, 24.44, 24.41, 22.20, 13.64, 8.24. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 4.28. HRMS (ESI) m/z: [M-H] - calcd. for C$_{35}$H$_{68}$O$_7$P 631.4708; found 631.4723.

**Synthesis of 12i.** 12i (147mg, 73%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.15 (dd, $J$ = 5.2, 3.9 Hz, 1H), 4.30 (dd, $J$ = 11.9, 3.2 Hz, 1H), 4.10 (dd, $J$ = 11.9, 6.5 Hz, 1H), 3.92 (dd, $J$ = 7.5, 5.6 Hz, 2H), 2.99 (q, $J$ = 7.2 Hz, 9H), 2.22 (dd, $J$ = 14.8, 7.4 Hz, 4H), 1.56 – 1.46 (m, 5H), 1.26 (t, $J$ = 7.3 Hz, 16H), 1.18 (s, 50H), 0.80 (t, $J$ = 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.29, 172.91, 70.38, 70.32, 62.42, 61.86, 61.38, 45.67, 34.20, 33.99, 31.82, 29.59, 29.55, 29.39, 29.25, 29.21, 29.03, 29.00, 24.81, 24.78, 22.58, 14.01, 8.60. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 4.26. HRMS (ESI) m/z: [M-H] - calcd. for C$_{35}$H$_{68}$O$_7$P 631.4708; found 631.4723.

**Synthesis of 12j.** 12j (148mg, 79%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.14 (dd, $J$ = 5.6, 3.9 Hz, 1H), 4.31 (dd, $J$ = 11.9, 3.5 Hz, 1H), 4.10 (dd, $J$ = 11.9, 6.4 Hz, 1H), 3.93 (dd, $J$ = 7.8, 5.3 Hz, 2H), 3.02 (q, $J$ = 7.2 Hz, 7H), 2.23 (dd, $J$ = 15.4, 7.7 Hz, 4H), 1.53 (d, $J$ = 5.8 Hz, 4H), 1.44 (td, $J$ = 13.2, 6.6 Hz, 1H), 1.28 (t, $J$ = 7.3 Hz, 10H), 1.19 (s, 40H), 1.08 (d, $J$ = 6.5 Hz, 3H), 0.80 (dd, $J$ = 12.5, 6.6 Hz, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.09, 172.70, 70.19, 70.13, 62.24, 61.70, 45.39, 38.79, 34.03, 33.82, 31.64, 29.67, 29.45, 29.42, 29.39, 29.36, 29.22, 29.08, 29.02, 28.86, 28.83, 27.68, 27.14, 24.63, 24.61, 22.39, 13.84, 8.32. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 4.82. HRMS (ESI) m/z: [M-H] - calcd. for C$_{34}$H$_{66}$O$_7$P 617.4552; found 617.4552.
Synthesis of 12k. 12k (161mg, 66%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.14 (dt, $J = 10.2$, 5.2 Hz, 1H), 4.30 (dd, $J = 11.9$, 3.6 Hz, 1H), 4.10 (dd, $J = 11.9$, 6.4 Hz, 1H), 3.94 (dd, $J = 7.9$, 5.4 Hz, 2H), 3.02 (q, $J = 7.1$ Hz, 6H), 2.23 (dd, $J = 15.8$, 8.0 Hz, 4H), 1.51 (dd, $J = 15.1$, 8.9 Hz, 4H), 1.44 (td, $J = 13.3$, 6.7 Hz, 2H), 1.28 (t, $J = 7.3$ Hz, 9H), 1.19 (s, 36H), 1.11 – 1.05 (m, 4H), 0.79 (d, $J = 6.6$ Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.07, 172.68, 70.12, 70.06, 62.19, 61.80, 45.45, 38.81, 34.04, 33.84, 29.70, 29.47, 29.44, 29.42, 29.39, 29.24, 29.06, 28.89, 28.86, 27.70, 27.17, 24.65, 24.63, 22.41, 8.34. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 4.76. HRMS (ESI) m/z: [M-H]- calcd. for C$_{36}$H$_{70}$O$_7$P 645.4865; found 645.4867

Synthesis of 12l. 12l (205mg, 73%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.21 – 5.08 (m, 1H), 4.31 (dd, $J = 11.9$, 3.5 Hz, 1H), 4.10 (dd, $J = 11.9$, 6.5 Hz, 1H), 3.92 (dd, $J = 7.8$, 5.4 Hz, 2H), 3.01 (q, $J = 7.2$ Hz, 8H), 2.24 – 2.19 (m, 4H), 1.54 – 1.50 (m, 4H), 1.44 (dt, $J = 13.2$, 6.6 Hz, 1H), 1.26 (t, $J = 7.3$ Hz, 15H), 1.19 (s, 42H), 1.08 (d, $J = 6.9$ Hz, 2H), 0.80 (dd, $J = 12.1$, 6.6 Hz, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.99, 172.61, 70.16, 70.11, 62.20, 61.58, 61.55, 45.25, 38.72, 33.96, 33.75, 31.58, 29.61, 29.38, 29.35, 29.32, 29.15, 29.01, 28.95, 28.79, 28.77, 27.61, 27.08, 24.57, 24.54, 22.32, 13.76, 8.22. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 4.68. HRMS (ESI) m/z: [M-H]- calcd. for C$_{35}$H$_{68}$O$_7$P 631.4708; found 631.4723

Synthesis of 12m. 12m (168mg, 64%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.14 (dt, $J = 10.6$, 5.2 Hz, 1H), 4.31 (dd, $J = 11.9$, 3.4 Hz, 1H), 4.10 (dd, $J = 11.9$, 6.5 Hz, 1H), 3.93 (dd, $J = 7.7$, 5.4 Hz, 2H), 3.02 (q, $J = 7.2$ Hz, 5H), 2.22 (dd, $J = 15.7$, 7.9 Hz, 4H), 1.51 (t, $J = 11.7$ Hz, 4H), 1.43 (dq, $J = 19.4$, 6.5 Hz, 2H), 1.27 (t, $J = 7.3$ Hz, 11H), 1.19 (s, 40H), 1.08 (d, $J = 6.5$ Hz, 4H), 0.79 (d, $J = 6.6$ Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.99, 172.61, 70.11, 70.06, 62.17, 61.65, 45.32, 38.75, 33.97, 33.77, 29.63, 29.41, 29.38, 29.35, 29.33,
29.18, 28.99, 28.98, 28.82, 28.79, 27.64, 27.10, 24.58, 24.56, 22.34, 8.25.  

$^3$P NMR (202 MHz CDCl$_3$) $\delta$ 4.70. HRMS (ESI) m/z: [M-H]- calcd. for C$_{37}$H$_{72}$O$_7$P 659.5021; found 659.5027

**Synthesis of 12n.** 12n (143mg, 71%) was obtained as a translucent gum. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.14 (dd, $J = 6.0, 3.8$ Hz, 1H), 4.31 (dd, $J = 11.9, 3.6$ Hz, 1H), 4.10 (dd, $J = 11.9, 6.5$ Hz, 1H), 3.92 (dd, $J = 8.0, 5.4$ Hz, 2H), 3.02 (q, $J = 7.3$ Hz, 7H), 2.22 (dd, $J = 15.3, 7.7$ Hz, 4H), 1.53 (dd, $J = 12.2, 6.5$ Hz, 4H), 1.44 (td, $J = 13.5, 6.8$ Hz, 1H), 1.28 (t, $J = 7.3$ Hz, 11H), 1.19 (s, 46H), 1.08 (d, $J = 7.1$ Hz, 2H), 0.80 (dd, $J = 12.0, 6.6$ Hz, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.06, 172.68, 70.25, 70.19, 62.28, 61.68, 61.65, 45.42, 38.80, 34.04, 33.84, 31.64, 29.67, 29.42, 29.39, 29.21, 29.07, 29.01, 28.86, 28.84, 27.68, 27.14, 24.64, 24.62, 22.38, 13.81, 8.31. $^3$P NMR (202 MHz, CDCl$_3$) $\delta$ 4.73. HRMS (ESI) m/z: [M-H]- calcd. for C$_{37}$H$_{72}$O$_7$P 659.5021; found 659.4992

**General procedure for the synthesis of 13.** To a solution of 12 (0.3mmol) in CCl$_3$CN (0.3ml) and pyridine (0.3ml) was added 8 (0.03mmol). The reaction stirred under microwave irradiation at 90°C for 75min, after which I$_2$ (254mg, 1mmol), pyridine (0.3ml) and water (0.03ml) was added. The reaction was further stirred at room temperature for 12h, after which it was diluted with water and washed with DCM 3 times. The organic layers were combined and washed with 1M CuSO$_4$ 3 times. The organic layer was dried over MgSO$_4$, filtered and concentrated. Flash chromatography of the crude mixture over deactivated silica gel (DCM:MeOH = 20:1 with 1% TEA) gave 13 as a TEAH$^+$ salt. The salt was dissolved in MeOH (10ml) and amberlyst-15 resin added. The reaction was hand swirled for 5min, after which it was filtered and concentrated. Flash chromatography of the crude mixture (DCM:MeOH = 15:1) gave 13 as a white solid.

**Synthesis of 13a.** 13a (16.0mg, 78%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27 – 6.99 (m, 13H), 5.12 (s, 1H), 4.80 (d, $J = 3.2$ Hz, 1H), 4.71 (d, $J = 11.2$ Hz, 1H), 4.68 (d,
$J = 11.1$ Hz, 1H), 4.64 – 4.54 (m, 2H), 4.52 (dd, $J = 11.9$, 4.1 Hz, 1H), 4.43 (d, $J = 11.2$ Hz, 1H), 4.39 (d, $J = 12.0$ Hz, 1H), 4.31 – 4.23 (m, 1H), 4.10 (d, $J = 10.2$ Hz, 1H), 4.03 (dd, $J = 12.1$, 6.9 Hz, 1H), 3.89 (s, 3H), 3.68 (d, $J = 14.1$ Hz, 1H), 3.66 – 3.59 (m, 3H), 3.56 (d, $J = 9.9$ Hz, 1H), 3.23 – 3.13 (m, 1H), 3.13 – 3.03 (m, 1H), 2.20 (dd, $J = 15.7$, 8.0 Hz, 4H), 1.89 (s, 2H), 1.55 – 1.43 (m, 6H), 1.42 (s, 1H), 1.18 (s, 76H), 1.07 (d, $J = 6.6$ Hz, 2H), 0.84 – 0.70 (m, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.74, 173.67, 173.38, 171.84, 138.23, 137.86, 137.80, 128.27, 128.18, 127.80, 127.62, 127.52, 127.48, 94.55, 82.56, 81.96, 81.72, 80.63, 78.06, 76.08, 75.00, 74.72, 73.33, 70.85, 63.84, 62.47, 60.57, 38.99, 34.10, 33.97, 31.84, 29.97, 29.86, 29.62, 29.58, 29.48, 29.46, 29.27, 29.09, 29.07, 27.87, 27.33, 27.03, 24.84, 24.78, 24.77, 22.57, 22.45. $^{31}$P NMR (202 MHz, MeOD) $\delta$ -2.24. HRMS (ESI) m/z: [M-H] - calcd. for C$_{87}$H$_{144}$N$_2$O$_{15}$P 1488.0310; found 1488.0311.

**Synthesis of 13b.** 13b (13.3mg, 75%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) $\delta$ 7.27 – 7.03 (m, 13H), 5.13 (s, 1H), 4.81 (s, 1H), 4.79 – 4.74 (m, 0H), 4.71 (d, $J = 11.2$ Hz, 1H), 4.70 – 4.65 (m, 1H), 4.63 – 4.55 (m, 1H), 4.52 (dd, $J = 12.0$, 4.3 Hz, 1H), 4.44 (dd, $J = 13.7$, 9.2 Hz, 0H), 4.42 – 4.37 (m, 0H), 4.28 (d, $J = 11.5$ Hz, 1H), 4.10 (d, $J = 8.7$ Hz, 1H), 4.07 – 4.01 (m, 1H), 3.90 (s, 2H), 3.72 – 3.65 (m, 2H), 3.65 – 3.60 (m, 2H), 3.57 (d, $J = 9.8$ Hz, 2H), 3.18 (dd, $J = 13.5$, 7.0 Hz, 0H), 3.11 (d, $J = 7.6$ Hz, 0H), 2.20 (dd, $J = 16.1$, 8.1 Hz, 3H), 1.89 (s, 2H), 1.58 – 1.45 (m, 7H), 1.41 (dd, $J = 13.2$, 6.6 Hz, 2H), 1.18 (s, 62H), 1.10 – 1.04 (m, 6H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.57, 173.24, 171.98, 169.69, 138.14, 137.87, 137.43, 128.05, 128.03, 127.94, 127.62, 127.43, 127.38, 127.31, 127.26, 97.28, 80.36, 77.75, 74.81, 74.59, 74.49, 73.07, 70.52, 70.04, 68.04, 67.58, 63.56, 62.27, 48.91, 48.74, 48.57, 48.39, 48.22, 48.05, 38.74, 33.85, 33.72, 29.62, 29.39, 29.23, 29.20, 29.05, 29.01, 28.84, 28.81, 27.62, 27.09, 26.80, 24.59, 24.51, 22.20. $^{31}$P NMR (202 MHz, MeOD) $\delta$ -2.25. HRMS (ESI) m/z: [M-H] - calcd. for C$_{86}$H$_{142}$N$_2$O$_{15}$P 1474.0153; found 1474.0150.
Synthesis of 13c. 13c (16.0mg, 80%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.00 (m, 10H), 5.14 (s, 1H), 4.78 (s, 0H), 4.71 (d, $J = 11.2$ Hz, 1H), 4.68 (d, $J = 11.1$ Hz, 1H), 4.60 (d, $J = 11.1$ Hz, 1H), 4.58 – 4.49 (m, 1H), 4.43 (d, $J = 11.3$ Hz, 1H), 4.39 (d, $J = 12.1$ Hz, 1H), 4.29 (dd, $J = 11.8, 9.1$ Hz, 1H), 4.12 (d, $J = 10.5$ Hz, 1H), 3.89 (s, 3H), 3.69 (d, $J = 11.5$ Hz, 1H), 3.65 (d, $J = 9.7$ Hz, 1H), 3.61 (d, $J = 8.7$ Hz, 1H), 3.57 (d, $J = 10.1$ Hz, 1H), 3.18 (dd, $J = 13.3, 7.0$ Hz, 1H), 3.15 – 3.05 (m, 1H), 2.21 (dt, $J = 17.4, 7.4$ Hz, 0H), 1.90 (s, 3H), 1.59 – 1.46 (m, 6H), 1.43 (dd, $J = 13.2, 6.6$ Hz, 3H), 1.18 (s, 66H), 1.07 (d, $J = 6.3$ Hz, 6H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.46, 173.12, 171.97, 138.16, 137.89, 137.349, 128.12, 128.00, 127.91, 127.68, 127.55, 127.37, 127.34, 127.27, 127.20, 97.25, 80.26, 77.79, 74.75, 74.46, 73.06, 70.55, 69.94, 38.07, 67.54, 63.54, 62.20, 38.71, 33.82, 33.68, 31.56, 29.58, 29.35, 29.21, 29.18, 29.05, 29.03, 28.99, 28.81, 28.79, 27.60, 27.06, 26.77, 24.57, 24.50, 22.29, 22.15, 13.57. $^{31}$P NMR (202 MHz, CDCl$_3$) δ -1.58. HRMS (ESI) m/z: [M-H]- calcd. for C$_{88}$H$_{146}$N$_2$O$_{15}$P 1502.0466 found 1502.0439

Synthesis of 13d. 13d (33.3mg, 77%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42 – 7.07 (m, 13H), 5.26 – 5.15 (m, 1H), 4.87 (d, $J = 3.4$ Hz, 1H), 4.78 (dd, $J = 11.1, 7.1$ Hz, 1H), 4.73 (d, $J = 11.1$ Hz, 1H), 4.66 (d, $J = 11.3$ Hz, 1H), 4.63 (d, $J = 9.0$ Hz, 1H), 4.58 (dd, $J = 12.0, 3.6$ Hz, 1H), 4.51 (t, $J = 11.8$ Hz, 1H), 4.45 (dd, $J = 12.0, 7.6$ Hz, 1H), 4.39 – 4.30 (m, 1H), 4.15 (dd, $J = 10.5, 3.5$ Hz, 1H), 3.97 (dd, $J = 11.3, 3.5$ Hz, 3H), 3.74 (dd, $J = 9.4, 6.3$ Hz, 2H), 3.69 (dd, $J = 10.2, 6.9$ Hz, 2H), 3.66 – 3.59 (m, 1H), 3.25 (dt, $J = 15.2, 6.1$ Hz, 1H), 3.20 – 3.08 (m, 2H), 2.32 – 2.19 (m, 4H), 1.95 (s, 3H), 1.54 (dd, $J = 13.6, 6.0$ Hz, 6H), 1.51 – 1.44 (m, 3H), 1.24 (s, 62H), 1.13 (dd, $J = 13.2, 6.4$ Hz, 6H), 0.85 (dd, $J = 12.5, 6.7$ Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.49, 173.44, 173.16, 172.01, 169.70, 169.66, 138.23, 137.95, 137.57, 128.17, 128.13, 128.06, 127.97, 127.72, 127.58, 127.40, 127.35, 127.32, 127.28, 97.30, 80.27, 77.87, 75.80, 74.75, 74.52, 73.32, 73.13, 71.11, 70.62, 70.06, 70.00, 68.18, 67.62, 63.65, 62.26, 52.93, 39.30, 38.77, 33.89, 33.75, 31.62, 29.65, 29.40, 29.36, 29.26, 29.23, 29.10, 29.05, 28.87, 28.84, S23
27.66, 27.11, 26.82, 24.62, 24.55, 22.35, 22.23, 13.65. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -2.66. HRMS (ESI) m/z: [M-H]- calcd. for C$_{84}$H$_{138}$N$_2$O$_{15}$P 1445.9840; found 1445.9834

**Synthesis of 13e.** 13e (16.9mg, 59%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.34 – 7.05 (m, 15H), 5.17 (d, $J = 3.4$ Hz, 1H), 4.83 (d, $J = 3.4$ Hz, 1H), 4.75 (d, $J = 11.2$ Hz, 2H), 4.71 (d, $J = 11.0$ Hz, 1H), 4.64 (d, $J = 11.3$ Hz, 1H), 4.62 (s, 2H), 4.58 – 4.53 (m, 1H), 4.47 (d, $J = 11.2$ Hz, 1H), 4.43 (d, $J = 12.0$ Hz, 1H), 4.31 (dd, $J = 12.0$, 3.1 Hz, 1H), 4.07 (dd, $J = 12.0$, 6.9 Hz, 1H), 3.98 – 3.92 (m, 1H), 3.66 (ddd, $J = 39.8$, 22.8, 10.5 Hz, 3H). 13C NMR (126 MHz, CDCl$_3$) $\delta$ 173.47, 173.12, 171.93, 138.19, 137.91, 137.51, 128.10, 128.02, 127.93, 127.56, 127.36, 127.32, 127.28, 127.21, 97.27, 80.32, 77.78, 74.76, 74.47, 73.08, 70.57, 69.93, 68.08, 63.60, 62.19, 52.84, 39.25, 38.73, 33.84, 33.70, 31.58, 29.60, 29.37, 29.32, 29.22, 29.19, 29.06, 29.03, 29.01, 28.99, 28.82, 28.80, 27.62, 27.08, 26.77, 24.58, 24.51, 22.31. $^{31}$P NMR (202 MHz, MeOD) $\delta$ -2.33. HRMS (ESI) m/z: [M-H]- calcd. for C$_{84}$H$_{138}$N$_2$O$_{15}$P 1445.9840; found 1445.9860.

**Synthesis of 13f.** 13f (18.3mg, 69%) was obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.35 – 7.03 (m, 15H), 5.19 (s, 1H), 4.84 (d, $J = 3.4$ Hz, 1H), 4.77 (d, $J = 11.2$ Hz, 1H), 4.69 (d, $J = 10.6$ Hz, 1H), 4.62 (d, $J = 11.2$ Hz, 1H), 4.56 (s, 1H), 4.50 (s, 1H), 4.44 (d, $J = 12.2$ Hz, 1H), 4.36 – 4.28 (m, 1H), 4.11 (dd, $J = 12.0$, 6.9 Hz, 1H), 3.95 (s, 3H), 3.66 (dd, $J = 23.7$, 9.6 Hz, 6H), 3.30 – 3.07 (m, 2H), 2.26 (td, $J = 7.5$, 4.4 Hz, 4H), 1.95 (s, 3H), 1.50 (dt, $J = 19.7$, 6.5 Hz, 9H), 1.23 (s, 58H), 1.12 (d, $J = 6.3$ Hz, 6H), 0.83 (d, $J = 6.6$ Hz, 18H). 13C NMR (126 MHz, CDCl$_3$) $\delta$ 173.49, 173.15, 138.21, 137.93, 137.54, 128.17, 128.12, 128.06, 127.97, 127.58, 127.39, 127.32, 127.25, 97.27, 80.24, 77.83, 74.76, 74.51, 73.37, 73.11, 70.62, 70.02, 63.59, 62.22, 52.91, 38.76, 33.87, 33.73, 31.61, 29.63, 29.39, 29.35, 29.25, 29.22, 29.04, 28.86, 27.64, 27.10, 26.81, 24.61, 24.54, 22.35, 22.21, 13.64. $^{31}$P NMR (121 MHz, MeOD) $\delta$ -1.87. HRMS
Synthesis of 13g. 13g (14.2mg, 66%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.02 (m, 11H), 5.14 (s, 1H), 4.74 (d, $J = 18.0$ Hz, 1H), 4.71 – 4.66 (m, 1H), 4.60 (d, $J = 11.2$ Hz, 1H), 4.52 (d, $J = 12.1$ Hz, 1H), 4.43 (d, $J = 11.1$ Hz, 1H), 4.39 (d, $J = 12.1$ Hz, 1H), 4.28 (d, $J = 11.8$ Hz, 1H), 4.05 – 4.00 (m, 2H), 3.91 (s, 3H), 3.68 (s, 2H), 3.66 (s, 2H), 3.58 (s, 2H), 3.18 (s, 1H), 3.08 (d, $J = 21.7$ Hz, 1H), 2.20 (dd, $J = 17.6$, 7.7 Hz, 3H), 1.90 (s, 2H), 1.49 (s, 5H), 1.46 – 1.39 (m, 2H), 1.18 (s, 58H), 1.08 (s, 6H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.56, 173.22, 171.91, 138.26, 137.97, 137.59, 129.74, 129.46, 128.10, 128.01, 127.63, 127.46, 127.36, 127.31, 97.36, 80.38, 77.84, 74.80, 74.56, 73.16, 70.63, 69.99, 68.16, 63.69, 62.24, 52.86, 39.31, 38.80, 35.46, 33.92, 33.78, 31.64, 29.68, 29.46, 29.44, 29.42, 29.28, 29.26, 29.23, 29.10, 29.06, 29.02, 28.97, 28.94, 28.87, 27.69, 27.15, 26.92, 26.89, 26.84, 25.36, 24.64, 24.58, 22.38, 22.28, 13.70. $^{31}$P NMR (202 MHz, MeOD) δ -1.80. HRMS (ESI) m/z: [M-H]- calcd. for C$_{84}$H$_{138}$N$_2$O$_{15}$P 1445.9840; found 1445.9856.

Synthesis of 13h. 13h (21.5mg, 71%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.17 (ddt, $J = 59.2$, 7.5, 4.7 Hz, 14H), 5.14 (s, 1H), 4.76 (d, $J = 3.1$ Hz, 1H), 4.69 (s, 1H), 4.66 (s, 1H), 4.60 (d, $J = 11.3$ Hz, 1H), 4.58 – 4.55 (m, 1H), 4.51 (s, 1H), 4.42 (d, $J = 11.0$ Hz, 1H), 4.40 (s, 1H), 4.28 (dd, $J = 11.9$, 2.9 Hz, 1H), 4.14 (dd, $J = 10.4$, 3.1 Hz, 1H), 4.03 (dd, $J = 12.0$, 6.8 Hz, 1H), 3.70 – 3.66 (m, 1H), 3.64 (d, $J = 4.4$ Hz, 3H), 3.57 (d, $J = 9.8$ Hz, 1H), 3.17 (ddd, $J = 21.2$, 14.3, 7.1 Hz, 1H), 3.09 (dd, $J = 13.9$, 6.4 Hz, 1H), 2.20 (dd, $J = 7.5$, 2.7 Hz, 4H), 1.89 (s, 3H), 1.47 (dd, $J = 14.9$, 6.9 Hz, 6H), 1.43 (s, 2H), 1.20 (d, $J = 21.3$ Hz, 74H), 1.07 (d, $J = 6.8$ Hz, 2H), 0.79 (dd, $J = 12.7$, 6.6 Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.02, 173.49, 173.13, 137.96, 137.55, 128.03, 1278.93, 127.57, 127.38, 127.26, 127.22, 77.77, 74.79, 74.47, 73.09, 70.58, 64.64, 62.19, 62.28, 52.79, 39.38, 38.74, 33.96, 33.85, 33.78, 33.71, 31.59, 29.61, 29.37, 29.33, 29.23, 29.20, 29.02, 28.96, 28.92, 28.81, 27.63, 27.09, 26.78, 24.58, 24.54, 22.95, 22.33.
$^{31}$P NMR (202 MHz, MeOD) $\delta$ -0.97. HRMS (ESI) m/z: [M-H]- calcd. for C$_{86}$H$_{142}$N$_2$O$_{15}$P 1474.0153; found 1474.0145

**Synthesis of 13i. 13i** (46.3mg, 64%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.35 – 7.08 (m, 15H), 5.19 (s, 1H), 4.83 (d, $J$ = 2.9 Hz, 1H), 4.77 (d, $J$ = 11.2 Hz, 1H), 4.74 (d, $J$ = 11.0 Hz, 1H), 4.66 (d, $J$ = 11.2 Hz, 2H), 4.58 (d, $J$ = 12.0 Hz, 1H), 4.49 (d, $J$ = 11.2 Hz, 1H), 4.47 – 4.43 (m, 1H), 4.34 (dd, $J$ = 18.7, 6.6 Hz, 1H), 3.98 (s, 4H), 3.69 (ddd, $J$ = 32.3, 22.5, 11.4 Hz, 7H), 3.29 – 3.20 (m, 1H), 3.20 – 3.10 (m, 1H), 2.29 – 2.25 (m, 4H), 1.95 (s, 3H), 1.57 (dd, $J$ = 12.3, 5.8 Hz, 4H), 1.50 (dd, $J$ = 13.3, 6.6 Hz, 4H), 1.24 (s, 66H), 1.14 (s, 4H), 0.84 (d, $J$ = 6.6 Hz, 15H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.46, 137.57, 128.03, 127.96, 127.57, 127.44, 127.24, 97.45, 80.40, 77.81, 74.77, 73.12, 70.66, 68.16, 63.84, 62.09, 52.81, 38.75, 33.85, 33.72, 31.60, 29.62, 29.37, 29.22, 29.03, 29.00, 28.84, 28.81, 27.63, 27.08, 26.76, 24.59, 24.53, 22.33, 22.19, 13.61. $^{31}$P NMR (202 MHz, CDCl$_3$) δ -1.92. HRMS (ESI) m/z: [M-H]- calcd. for C$_{85}$H$_{140}$N$_2$O$_{15}$P 1459.9997; found 1460.0003

**Synthesis of 13j. 13j** (28.7mg, 69%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42 – 7.07 (m, 12H), 5.26 – 5.15 (m, 1H), 4.87 (d, $J$ = 3.4 Hz, 1H), 4.78 (dd, $J$ = 11.1, 7.1 Hz, 1H), 4.73 (d, $J$ = 11.1 Hz, 1H), 4.66 (d, $J$ = 11.3 Hz, 1H), 4.63 (d, $J$ = 9.0 Hz, 1H), 4.58 (dd, $J$ = 12.0, 3.6 Hz, 1H), 4.51 (t, $J$ = 11.8 Hz, 1H), 4.45 (dd, $J$ = 12.0, 7.6 Hz, 1H), 4.39 – 4.30 (m, 1H), 4.15 (dd, $J$ = 10.5, 3.5 Hz, 1H), 3.97 (dd, $J$ = 11.3, 3.5 Hz, 3H), 3.74 (dd, $J$ = 9.4, 6.3 Hz, 2H), 3.69 (dd, $J$ = 10.2, 6.9 Hz, 2H), 3.66 – 3.59 (m, 1H), 3.25 (dt, $J$ = 15.2, 6.1 Hz, 1H), 3.20 – 3.08 (m, 1H), 2.32 – 2.19 (m, 4H), 1.95 (s, 2H), 1.54 (dd, $J$ = 13.6, 6.0 Hz, 5H), 1.51 – 1.44 (m, 3H), 1.24 (s, 64H), 1.13 (dd, $J$ = 13.2, 6.4 Hz, 4H), 0.85 (dd, $J$ = 12.5, 6.7 Hz, 15H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.49, 173.44, 173.44, 173.16, 172.01, 169.70, 169.66, 138.23, 137.95, 137.57, 128.17, 128.13, 128.06, 127.97, 127.72, 127.58, 127.40, 127.35, 127.32, 127.28, 97.30, 80.27, 77.87, 75.80, 74.75, 74.52, 73.32, 73.13, 71.11, 70.62, 70.06, 70.00, 68.18, 67.62, 63.65, 62.26, 52.93,

$^31$P NMR (202 MHz, CDCl$_3$) $\delta$ -2.66.

HRMS (ESI) m/z: [M-H]- calcd. for C$_{84}$H$_{138}$N$_2$O$_{15}$P 1445.9840; found 1445.9834

**Synthesis of 13k.** 13k (28.5mg, 85%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.29 – 7.01 (m, 15H), 5.14 (s, 1H), 4.78 (s, 1H), 4.71 (d, $J$ = 11.2 Hz, 1H), 4.68 (d, $J$ = 11.0 Hz, 1H), 4.61 (d, $J$ = 11.2 Hz, 2H), 4.52 (d, $J$ = 12.1 Hz, 1H), 4.43 (d, $J$ = 11.0 Hz, 1H), 4.39 (d, $J$ = 12.1 Hz, 1H), 4.27 (d, $J$ = 12.0 Hz, 1H), 3.92 (s, 3H), 3.63 (ddd, $J$ = 32.9, 25.1, 11.9 Hz, 6H), 3.18 (dt, $J$ = 15.1, 7.5 Hz, 1H), 3.15 – 3.03 (m, 1H), 2.21 (dd, $J$ = 17.2, 7.8 Hz, 4H), 1.89 (s, 3H), 1.50 (d, $J$ = 5.0 Hz, 4H), 1.43 (dd, $J$ = 13.3, 6.6 Hz, 4H), 1.18 (s, 72H), 1.07 (d, $J$ = 6.5 Hz, 4H), 0.79 (t, $J$ = 6.3 Hz, 15H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.48, 173.14, 138.20, 137.86, 137.52, 128.05, 128.04, 127.97, 127.59, 127.46, 127.41, 127.34, 127.25, 97.42, 80.35, 77.80, 74.76, 74.55, 73.12, 70.63, 68.14, 62.07, 52.79, 39.28, 38.75, 33.85, 33.72, 31.59, 29.62, 29.38, 29.33, 29.20, 29.02, 28.84, 28.81, 27.63, 27.09, 26.75, 24.58, 24.52, 22.33, 22.20, 13.63. $^31$P NMR (202 MHz, CDCl$_3$) $\delta$ -2.05. HRMS (ESI) m/z: [M-H]- calcd. for C$_{88}$H$_{146}$N$_2$O$_{15}$P 1502.0466; found 1502.0470

**Synthesis of 13l.** 13l (13.2mg, 73%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 – 7.08 (m, 15H), 5.19 (s, 1H), 4.83 (d, $J$ = 2.9 Hz, 1H), 4.77 (d, $J$ = 11.2 Hz, 1H), 4.74 (d, $J$ = 11.0 Hz, 1H), 4.66 (d, $J$ = 11.2 Hz, 2H), 4.58 (d, $J$ = 12.0 Hz, 1H), 4.49 (d, $J$ = 11.2 Hz, 1H), 4.47 – 4.43 (m, 1H), 4.34 (dd, $J$ = 18.7, 6.6 Hz, 1H), 3.98 (s, 4H), 3.69 (ddd, $J$ = 32.3, 22.5, 11.4 Hz, 7H), 3.29 – 3.20 (m, 1H), 3.20 – 3.10 (m, 1H), 2.29 – 2.25 (m, 4H), 1.95 (s, 3H), 1.57 (dd, $J$ = 12.3, 5.8 Hz, 4H), 1.50 (dd, $J$ = 13.3, 6.6 Hz, 4H), 1.24 (s, 66H), 1.14 (s, 4H), 0.84 (d, $J$ = 6.6 Hz, 15H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.46, 137.57, 128.03, 127.96, 127.57, 127.44, 127.24, 97.45, 80.40, 77.81, 74.77, 73.12, 70.66, 68.16, 63.84, 62.09, 52.81, 38.75, 33.85, 33.72, 31.60, 29.62, 29.37, 29.22, 29.03, 29.00, 28.84, 28.81, 27.63, 27.08, 26.76, 24.59, 24.53, 22.33,
22.19, 13.61. $^{31}$P NMR (202 MHz, CDCl$_3$) δ -1.92 HRMS (ESI) m/z: [M-H]- calcd. for C$_{83}$H$_{146}$N$_2$O$_{15}$P 1431.9684; found 1431.9652

**Synthesis of 13m.** 13m (49.69mg, 66%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.47 – 6.98 (m, 13H), 5.14 (s, 1H), 4.78 (d, $J$ = 3.3 Hz, 1H), 4.71 (d, $J$ = 11.2 Hz, 1H), 4.67 (d, $J$ = 11.0 Hz, 1H), 4.61 (d, $J$ = 11.3 Hz, 1H), 4.52 (d, $J$ = 12.0 Hz, 1H), 4.42 (d, $J$ = 11.1 Hz, 1H), 4.39 (d, $J$ = 12.0 Hz, 1H), 4.28 (dd, $J$ = 12.1, 3.0 Hz, 1H), 4.03 (dd, $J$ = 12.1, 7.0 Hz, 1H), 3.98 – 3.14 (m, 3H), 3.68 (dd, $J$ = 13.0, 7.6 Hz, 2H), 3.65 – 3.60 (m, 2H), 3.60 – 3.55 (m, 1H), 3.23 – 3.14 (m, 1H), 3.14 – 3.05 (m, 1H), 2.28 – 2.16 (m, 4H), 1.90 (s, 2H), 1.50 (d, $J$ = 5.3 Hz, 5H), 1.47 – 1.39 (m, 3H), 1.18 (s, 70H), 1.10 – 1.03 (m, 2H), 0.79 (dd, $J$ = 12.4, 6.6 Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.54, 173.21, 138.13, 137.42, 128.04, 128.02, 127.95, 127.72, 127.61, 127.54, 127.42, 127.31, 127.25, 97.35, 80.34, 77.76, 74.80, 74.52, 73.10, 70.56, 69.87, 68.06, 67.62, 63.77, 62.13, 52.75, 39.26, 38.72, 33.83, 33.70, 31.57, 29.60, 29.34, 29.30, 29.20, 29.17, 29.00, 28.81, 28.78, 27.61, 27.07, 26.74, 24.56, 24.50, 22.30, 22.16, 22.12, 13.59.

$^{31}$P NMR (202 MHz, CDCl$_3$) δ -2.01. HRMS (ESI) m/z: [M-H]- calcd. for C$_{84}$H$_{138}$N$_2$O$_{15}$P 1445.9840; found 1445.9842

**Synthesis of 13n.** 13n (25.9mg, 68%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.27 – 6.99 (m, 15H), 5.14 (s, 1H), 4.79 – 4.72 (m, 1H), 4.71 – 4.64 (m, 2H), 4.61 (d, $J$ = 10.9 Hz, 2H), 4.41 (dd, $J$ = 22.3, 11.6 Hz, 2H), 4.29 (dd, $J$ = 12.0, 3.0 Hz, 1H), 4.14 – 3.97 (m, 3H), 3.92 (d, $J$ = 3.4 Hz, 3H), 3.68 (dd, $J$ = 18.5, 8.0 Hz, 4H), 3.61 – 3.52 (m, 2H), 3.21 – 3.04 (m, 2H), 2.24 – 2.17 (m, 4H), 1.91 (s, 3H), 1.52 – 1.41 (m, 9H), 1.18 (s, 60H), 1.07 (d, $J$ = 5.9 Hz, 6H), 0.77 (d, $J$ = 6.6 Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.53, 173.20, 138.16, 137.87, 137.47, 128.05, 127.96, 127.60, 127.43, 127.38, 127.33, 127.26, 97.24, 77.81, 74.80, 74.50, 73.11, 70.55, 62.24, 52.88, 48.96, 48.79, 48.62, 48.45, 48.28, 48.11, 47.94, 46.36, 39.40, 38.74, 33.86, 33.72, 31.58, 29.62, 29.37, 29.33, 29.23, 29.04, 29.00, 28.84, 27.63, 27.09, 26.78, 24.59, S28
24.52, 22.32, 22.19. $^{31}$P NMR (202 MHz, MeOD) $\delta$ -2.31. HRMS (ESI) m/z: [M-H]- calcd. for C$_{85}$H$_{140}$N$_{2}$O$_{15}$P calculated 1459.9997, found 1459.9989.

**Synthesis of 13o.** 13o (50.0mg, 74%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) $\delta$ 7.30 – 7.01 (m, 15H), 5.14 (s, 1H), 4.79 (d, $J = 3.0$ Hz, 1H), 4.71 (d, $J = 11.2$ Hz, 1H), 4.68 (d, $J = 11.1$ Hz, 1H), 4.60 (d, $J = 11.2$ Hz, 1H), 4.57 (s, 1H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.43 (d, $J = 11.2$ Hz, 1H), 4.41 – 4.36 (m, 1H), 4.28 (d, $J = 11.5$ Hz, 2H), 3.91 (d, $J = 10.9$ Hz, 4H), 3.68 (d, $J = 13.9$ Hz, 1H), 3.67 – 3.61 (m, 3H), 3.61 – 3.53 (m, 2H), 3.24 – 3.13 (m, 1H), 3.13 – 3.01 (m, 1H), 2.24 – 2.19 (m, 6H), 1.90 (s, 3H), 1.50 – 1.41 (m, 8H), 1.18 (s, 70H), 1.07 (m, 4H), 0.79 (m, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.50, 173.16, 171.95, 169.66, 138.22, 137.94, 137.55, 129.40, 128.12, 128.05, 127.96, 127.72, 127.59, 127.39, 127.30, 127.25, 97.32, 80.35, 77.82, 77.26, 77.00, 76.75, 74.77, 74.50, 73.11, 70.60, 70.02, 68.13, 67.63, 62.22, 52.86, 39.28, 38.76, 33.87, 33.73, 31.60, 29.64, 29.38, 29.35, 29.24, 29.22, 29.08, 29.03, 28.85, 28.83, 27.64, 27.11, 26.80, 24.60, 24.54, 22.34, 22.21, 13.63. $^{31}$P NMR (202 MHz, MeOD) $\delta$ -2.05 HRMS (ESI) m/z: [M-H]- calcd. for C$_{83}$H$_{136}$N$_{2}$O$_{15}$P 1431.9684; found 1431.9676

**Synthesis of 13p.** 13p (34.8mg, 56%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.19 (ddd, $J = 58.5$, 33.6, 29.5 Hz, 11H), 5.14 (s, 1H), 4.81 (s, 1H), 4.70 (dd, $J = 20.3$, 11.1 Hz, 2H), 4.66 – 4.49 (m, 3H), 4.41 (dd, $J = 22.8$, 11.6 Hz, 2H), 4.28 (d, $J = 11.8$ Hz, 2H), 4.03 (dd, $J = 12.1$, 7.0 Hz, 2H), 3.91 (d, $J = 11.0$ Hz, 3H), 3.63 (ddd, $J = 32.9$, 22.9, 11.4 Hz, 4H), 3.24 – 3.04 (m, 2H), 2.20 (dd, $J = 16.1$, 8.3 Hz, 4H), 1.90 (s, 2H), 1.49 (s, 6H), 1.47 – 1.38 (m, 5H), 1.18 (s, 52H), 1.08 (s, 13H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.59, 173.26, 138.22, 137.93, 137.52, 128.12, 128.02, 127.79, 127.67, 127.49, 127.46, 127.38, 127.33, 97.29, 80.34, 77.82, 77.25, 77.00, 76.74, 74.82, 74.56, 73.16, 70.59, 68.13, 62.28, 52.84, 49.13, 48.96, 48.79, 48.62, 48.45, 48.28, 48.11, 39.33, 38.80, 33.96, 33.92, 33.78, 31.65, 29.68, 29.46, 29.44, 29.40, 29.29, 29.27, 29.14, 29.10, 29.06, 28.90, 27.69, 27.16, 26.85, 24.64, 24.57,
22.39, 22.29, 13.72. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -2.61. HRMS (ESI) m/z: [M-H]- calcd. for C$_{82}$H$_{134}$N$_2$O$_{15}$P 1417.9527; found 1417.9536

**Synthesis of 13q.** 13q (26.2mg, 67%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 – 7.03 (m, 15H), 5.13 (s, 1H), 4.80 (s, 1H), 4.70 (dd, $J = 19.6$, 11.1 Hz, 2H), 4.60 (d, $J = 11.2$ Hz, 1H), 4.58 – 4.47 (m, 2H), 4.41 (dd, $J = 20.5$, 11.7 Hz, 2H), 4.28 (d, $J = 12.1$ Hz, 1H), 3.91 (d, $J = 11.2$ Hz, 3H), 3.73 – 3.53 (m, 6H), 3.23 – 3.04 (m, 2H), 2.20 (dd, $J = 15.4$, 7.9 Hz, 4H), 1.90 (s, 3H), 1.51 – 1.41 (m, 9H), 1.18 (s, 60H), 1.07 (d, $J = 6.8$ Hz, 6H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{13}$C NMR (126 MHz, MeOD) $\delta$ 173.51, 173.17, 138.19, 137.90, 137.50, 128.05, 127.96, 127.73, 127.60, 127.42, 127.39, 127.31, 127.24, 97.28, 80.31, 77.79, 74.78, 74.50, 73.10, 70.57, 68.08, 62.21, 52.83, 48.97, 48.80, 48.63, 48.46, 48.29, 48.12, 47.95, 39.28, 38.75, 33.86, 33.72, 31.56, 29.63, 29.40, 29.34, 29.24, 29.21, 29.06, 29.01, 28.85, 28.82, 27.64, 27.10, 26.79, 24.60, 24.53, 22.21. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -2.43. HRMS (ESI) m/z: [M-H]- calcd. for C$_{85}$H$_{140}$N$_2$O$_{15}$P calculated 1459.9997, found 1459.9993.

**Synthesis of 13r.** 13r (34.6mg, 76%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) $\delta$ 7.28 – 7.00 (m, 15H), 5.13 (s, 1H), 4.79 (d, $J = 3.2$ Hz, 1H), 4.69 (dd, $J = 19.4$, 11.1 Hz, 1H), 4.63 – 4.48 (m, 2H), 4.41 (dd, $J = 19.7$, 11.5 Hz, 1H), 4.28 (dd, $J = 12.0$, 2.9 Hz, 2H), 3.90 (d, $J = 11.7$ Hz, 3H), 3.73 – 3.49 (m, 4H), 3.23 – 3.05 (m, 2H), 2.20 (dd, $J = 15.8$, 8.1 Hz, 4H), 1.90 (s, 9H), 1.54 – 1.41 (m, 9H), 1.17 (s, 62H), 1.07 (d, $J = 6.8$ Hz, 6H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.52, 173.18, 138.21, 137.92, 137.52, 128.07, 127.98, 127.75, 127.61, 127.41, 127.33, 127.27, 97.28, 80.32, 77.80, 74.79, 74.52, 73.12, 70.59, 70.01, 68.11, 62.22, 52.85, 49.03, 48.86, 48.69, 48.52, 48.35, 48.18, 48.01, 39.29, 38.77, 33.88, 33.74, 29.65, 29.43, 29.40, 29.26, 29.23, 29.10, 29.07, 29.03, 28.87, 28.84, 27.66, 27.12, 26.81, 24.62, 24.54, 22.24. $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -2.32. HRMS (ESI) m/z: [M-H]- calcd. for C$_{86}$H$_{142}$N$_2$O$_{15}$P 1474.0153; found 1474.0159
**Synthesis of 13s.** 13s (38.9mg, 72%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) δ 7.27 – 6.99 (m, 15H), 5.13 (s, 1H), 4.80 (s, 1H), 4.76 – 4.65 (m, 2H), 4.65 – 4.47 (m, 1H), 4.47 – 4.33 (m, 2H), 4.33 – 4.24 (m, 2H), 4.09 (dd, $J = 14.6, 7.7$ Hz, 1H), 3.89 (s, 2H), 3.72 – 3.50 (m, 4H), 3.22 – 3.03 (m, 2H), 2.27 – 2.10 (m, 4H), 1.90 (s, 9H), 1.45 (dd, $J = 19.9, 13.2, 5.8$ Hz, 9H), 1.17 (s, 54H), 1.07 (d, $J = 6.6$ Hz, 6H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.53, 173.20, 138.23, 137.95, 137.55, 128.16, 128.10, 128.01, 127.77, 127.63, 127.44, 127.36, 127.30, 97.29, 80.31, 77.83, 74.80, 74.55, 73.15, 70.61, 70.04, 68.13, 62.25, 52.88, 49.11, 48.94, 48.77, 48.60, 48.43, 48.26, 48.09, 39.32, 38.80, 33.91, 33.77, 29.68, 29.46, 29.42, 29.40, 29.29, 29.26, 29.10, 29.06, 28.90, 28.87, 27.69, 27.15, 26.84, 24.64, 24.57, 22.28. $^{31}$P NMR (202 MHz, CDCl$_3$) δ -2.36. $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.56, 173.22, 171.91, 138.26, 137.97, 137.59, 129.74, 129.46, 128.10, 128.01, 127.63, 127.46, 127.36, 127.31, 97.36, 80.38, 77.84, 74.80, 74.56, 73.16, 70.63, 69.99, 68.16, 63.69, 62.24, 52.86, 39.31, 38.80, 35.46, 33.92, 33.78, 31.64, 29.68, 29.46, 29.44, 29.42, 29.28, 29.26, 29.23, 29.10, 29.06, 29.02, 28.97, 28.94, 28.87, 27.69, 27.15, 26.92, 26.89, 26.84, 25.36, 24.64, 24.58, 22.38, 22.28, 13.70. HRMS (ESI) m/z: [M-H]- calcd. for C$_{82}$H$_{134}$N$_2$O$_{15}$P 1417.9527; found 1417.9532

**General procedure for the synthesis of 1.** To a solution of 13 (30mg) in DCM/MeOH (1:4, 10ml) was added 10% Pd/C (90mg). The reaction was stirred under a hydrogen atmosphere at room temperature for 12h, after which it was filtered through celite. The mixture was then concentrated and flash chromatography of the crude mixture (DCM:MeOH = 10:1) yielded 1 as a white solid.

**Synthesis of 1a.** 1a (8.0mg, 91%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 5.16 (s, 1H), 4.83 (s, 1H), 4.68 (s, 1H), 4.29 (d, $J = 12.0$ Hz, 1H), 3.98 (s, 2H), 3.83 (s, 2H), 3.74 (d, $J = 9.1$ Hz, 2H), 3.67 (s, 1H), 3.61 – 3.49 (m, 2H), 3.34 (dd, $J = 17.0, 7.8$ Hz, 1H), 3.24 –
3.08 (m, 2H), 2.24 (dd, J = 17.8, 7.7 Hz, 5H), 1.97 (s, 3H), 1.59 – 1.40 (m, 8H), 1.20 (d, J = 19.7 Hz, 76H), 1.06 (s, 2H), 0.79 (dd, J = 13.0, 6.7 Hz, 12H). $^{31}$P NMR (202 MHz, MeOD) δ -2.30. HRMS (ESI) m/z: [M-H]- calcd. for C$_{66}$H$_{126}$N$_{2}$O$_{15}$P 1217.8901; found 1217.8872

**Synthesis of 1b.** 1b (6.5mg, 90%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) δ 5.21 (s, 1H), 4.90 (d, J = 3.0 Hz, 1H), 4.71 (s, 1H), 4.35 (dd, J = 11.9, 3.2 Hz, 2H), 4.12 (dd, J = 12.0, 6.8 Hz, 1H), 4.01 (s, 2H), 3.88 (ddd, J = 24.8, 12.5, 4.7 Hz, 3H), 3.80 (d, J = 12.1 Hz, 2H), 3.73 (dd, J = 9.8, 6.7 Hz, 2H), 3.65 (dd, J = 22.3, 12.4 Hz, 3H), 3.39 (dd, J = 16.1, 6.8 Hz, 1H), 3.25 – 3.14 (m, 2H), 2.30 (dd, J = 16.9, 7.9 Hz, 4H), 2.03 (s, 3H), 1.60 – 1.47 (m, 9H), 1.26 (d, J = 19.1 Hz, 62H), 1.13 (d, J = 6.9 Hz, 6H), 0.84 (d, J = 6.6 Hz, 18H). $^{31}$P NMR (202 MHz, MeOD) δ -2.33 HRMS (ESI) m/z: [M-H]- calcd. for C$_{65}$H$_{120}$N$_{2}$O$_{15}$P calculated 1203.8745, found 1203.8730

**Synthesis of 1c.** 1c (7.5mg, 87%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) δ 5.14 (s, 1H), 4.90 (s, 1H), 4.63 (s, 1H), 4.29 (d, J = 11.6 Hz, 1H), 3.92 (s, 2H), 3.81 (s, 3H), 3.70 (dd, J = 31.4, 17.9 Hz, 3H), 3.64 – 3.49 (m, 2H), 3.37 (d, J = 9.3 Hz, 1H), 3.24 – 3.03 (m, 2H), 2.23 (dd, J = 15.5, 8.0 Hz, 4H), 1.98 (s, 3H), 1.55 – 1.42 (m, 9H), 1.18 (s, 66H), 1.07 (d, J = 6.7 Hz, 6H), 0.79 (t, J = 6.1 Hz, 18H). $^{31}$P NMR (202 MHz, MeOD) δ -3.10. HRMS (ESI) m/z: [M-H]- calcd. for C$_{67}$H$_{128}$N$_{2}$O$_{15}$P 1231.9058; found 1231.9048

**Synthesis of 1d.** 1d (12.5mg, 76%) was obtained as a white solid. $^1$H NMR (500 MHz, CDC1$_3$) δ 5.18 (s, 2H), 4.90 (s, 1H), 4.67 (s, 2H), 4.34 (d, J = 8.8 Hz, 2H), 3.95 (s, 3H), 3.88 – 3.74 (m, 5H), 3.67 (dd, J = 22.5, 13.0 Hz, 5H), 3.38 (dd, J = 21.1, 11.9 Hz, 2H), 3.20 (dd, J = 16.4, 8.4 Hz, 3H), 2.27 (dd, J = 15.6, 8.1 Hz, 5H), 2.00 (d, J = 8.8 Hz, 4H), 1.62 – 1.40 (m, 11H), 1.22 (s, 64H), 1.11 (d, J = 6.9 Hz, 7H), 0.82 (d, J = 6.6 Hz, 18H). $^{31}$P NMR (202 MHz, MeOD) δ -2.44. HRMS (ESI) m/z: [M-H]- calcd. for C$_{65}$H$_{124}$N$_{2}$O$_{15}$P 1203.8745; found 1203.8768
Synthesis of 1e. 1e (7.0 mg, 81%) was obtained as a white solid. $^1$H NMR (500 MHz, MeOD) $\delta$ 5.21 (d, $J = 3.4$ Hz, 1H), 4.90 (d, $J = 3.4$ Hz, 1H), 4.38 (dd, $J = 12.0$, 3.1 Hz, 1H), 4.13 (dd, $J = 12.0$, 6.9 Hz, 1H), 3.99 (t, $J = 5.5$ Hz, 2H), 3.92 – 3.83 (m, 2H), 3.83 – 3.77 (m, 2H), 3.74 – 3.69 (m, 1H), 3.67 (dd, $J = 15.4$, 6.2 Hz, 1H), 3.64 – 3.57 (m, 1H), 3.35 (t, $J = 9.4$ Hz, 1H), 3.27 – 3.15 (m, 2H), 2.30 (dd, $J = 16.7$, 7.8 Hz, 4H), 2.03 (s, 3H), 1.53 (ddd, $J = 19.9$, 19.5, 6.6 Hz, 9H), 1.25 (s, 58H), 1.16 – 1.10 (m, 6H), 0.84 (d, $J = 6.6$ Hz, 18H). $^{31}$P NMR (202 MHz, MeOD) $\delta$ -2.22. HRMS (ESI) m/z: [M-H]- calcd. for C$_{63}$H$_{120}$N$_2$O$_{15}$P 1175.8432; found 1175.8429

Synthesis of 1f. 1f (7.6 mg, 77%) was obtained as a white solid. $^1$H NMR (300 MHz, MeOD) $\delta$ 5.20 (s, 1H), 4.89 (s, 1H), 4.39 (dd, $J = 12.0$, 3.0 Hz, 1H), 4.15 (dd, $J = 12.1$, 6.9 Hz, 1H), 3.98 (s, 2H), 3.88 (d, $J = 7.4$ Hz, 2H), 3.80 (d, $J = 11.3$ Hz, 2H), 3.72 (d, $J = 5.0$ Hz, 1H), 3.69 – 3.62 (m, 1H), 3.59 (s, 1H), 3.37 (d, $J = 10.1$ Hz, 1H), 3.27 – 3.12 (m, 2H), 2.30 (td, $J = 7.4$, 5.1 Hz, 4H), 2.03 (s, 3H), 1.52 (ddd, $J = 19.8$, 13.2, 6.6 Hz, 9H), 1.25 (s, 58H), 1.13 (d, $J = 6.4$ Hz, 6H), 0.84 (d, $J = 6.6$ Hz, 18H). $^{31}$P NMR (121 MHz, MeOD) $\delta$ -1.95. HRMS (ESI) m/z: [M-H]- calcd. for C$_{65}$H$_{120}$N$_2$O$_{15}$P 1203.8745; found 1203.8742

Synthesis of 1g. 1g (7.4 mg, 94%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.14 (s, 1H), 4.88 (s, 1H), 4.63 (s, 1H), 4.29 (d, $J = 8.8$ Hz, 1H), 4.07 – 4.01 (m, 1H), 3.92 (s, 2H), 3.86 – 3.64 (m, 5H), 3.59 (dd, $J = 21.7$, 12.1 Hz, 2H), 3.35 (t, $J = 9.1$ Hz, 1H), 3.16 (d, $J = 24.0$ Hz, 2H), 2.23 (dd, $J = 15.6$, 8.0 Hz, 4H), 2.16 – 2.05 (m, 1H), 1.97 (s, 4H), 1.52 (s, 6H), 1.45 – 1.39 (m, 4H), 1.18 (s, 58H), 1.07 (d, $J = 6.6$ Hz, 6H), 0.78 (t, $J = 6.1$ Hz, 18H). $^{31}$P NMR (202 MHz, MeOD) $\delta$ -2.93. HRMS (ESI) m/z: [M-H]- calcd. for C$_{63}$H$_{120}$N$_2$O$_{15}$P 1175.8432; found 1175.8433

Synthesis of 1h. 1h (8.2 mg, 79%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$
5.15 (s, 1H), 4.32 (s, 2H), 4.07 (s, 2H), 3.94 (s, 2H), 3.84 (s, 2H), 3.73 (s, 3H), 3.58 (s, 2H), 3.10 (d, \( J = 7.0 \text{ Hz}, 2\text{H} \)), 2.28 – 2.19 (m, 4H), 1.93 (s, 3H), 1.44 (dd, \( J = 13.0, 6.5 \text{ Hz}, 7\text{H} \)), 1.18 (s, 74H), 1.08 (s, 6H), 0.81 – 0.77 (m, 18H). \(^{31}\text{P NMR (202 MHz, CDCl}_3\) \( \delta -1.32.\) HRMS (ESI) m/z: [M-H] - calcd. for C\(_{65}\)H\(_{124}\)N\(_2\)O\(_{15}\)P 1203.8745; found 1203.8740

**Synthesis of 1i.** 1i (20.0mg, 83%) was obtained as a white solid. \(^1\text{H NMR (500 MHz, CDCl}_3\) \( \delta 5.20 (s, 1\text{H}), 4.91 (s, 1\text{H}), 4.70 (s, 1\text{H}), 4.35 (dd, \( J = 12.0, 3.2 \text{ Hz}, 1\text{H} \)), 4.13 – 4.06 (m, 1H), 3.99 (s, 2H), 3.92 – 3.84 (m, 2H), 3.84 – 3.76 (m, 2H), 3.72 (d, \( J = 11.7 \text{ Hz}, 1\text{H} \)), 3.65 (dd, \( J = 21.6, 11.4 \text{ Hz}, 2\text{H} \)), 3.40 (t, \( J = 9.4 \text{ Hz}, 1\text{H} \)), 3.28 – 3.13 (m, 2H), 2.29 (dd, \( J = 16.3, 8.2 \text{ Hz}, 4\text{H} \)), 2.03 (s, 3H), 1.60 – 1.45 (m, 8H), 1.24 (s, 66H), 1.13 (d, \( J = 7.1 \text{ Hz}, 4\text{H} \)), 0.85 (dd, \( J = 13.3, 6.6 \text{ Hz}, 15\text{H} \)). \(^{31}\text{P NMR (202 MHz, CDCl}_3\) \( \delta -2.64.\) HRMS (ESI) m/z: [M-H] - calcd. for C\(_{64}\)H\(_{122}\)N\(_2\)O\(_{15}\)P 1189.8588; found 1189.8602

**Synthesis of 1j.** 1j (9.1mg, 69%) was obtained as a white solid. \(^1\text{H NMR (500 MHz, CDCl}_3\) \( \delta 5.15 (s, 1\text{H}), 4.89 (s, 1\text{H}), 4.64 (s, 1\text{H}), 4.29 (dd, \( J = 11.9, 3.1 \text{ Hz}, 2\text{H} \)), 4.06 (d, \( J = 5.1 \text{ Hz}, 1\text{H} \)), 3.95 (s, 2H), 3.82 (t, \( J = 8.6 \text{ Hz}, 2\text{H} \)), 3.78 – 3.72 (m, 2H), 3.72 – 3.63 (m, 2H), 3.63 – 3.52 (m, 2H), 3.37 – 3.31 (m, 2H), 3.16 (dd, \( J = 20.7, 13.3, 5.9 \text{ Hz}, 3\text{H} \)), 2.24 (dd, \( J = 15.9, 8.2 \text{ Hz}, 4\text{H} \)), 1.97 (s, 3H), 1.56 – 1.41 (m, 8H), 1.18 (s, 64H), 1.07 (d, \( J = 6.9 \text{ Hz}, 4\text{H} \)), 0.79 (dd, \( J = 12.9, 6.7 \text{ Hz}, 15\text{H} \)). \(^{31}\text{P NMR (202 MHz, CDCl}_3\) \( \delta -2.84.\) HRMS (ESI) m/z: [M-H] - calcd. for C\(_{63}\)H\(_{120}\)N\(_2\)O\(_{15}\)P 1175.8432; found 1175.8394

**Synthesis of 1k.** 1k (13.1mg, 86%) was obtained as a white solid. \(^1\text{H NMR (500 MHz, CDCl}_3\) \( \delta 5.15 (s, 1\text{H}), 4.83 (d, \( J = 2.9 \text{ Hz}, 1\text{H} \)), 4.64 (s, 1H), 4.30 (dd, \( J = 12.0, 3.1 \text{ Hz}, 1\text{H} \)), 4.07 – 4.03 (m, 1H), 3.91 (t, \( J = 5.5 \text{ Hz}, 2\text{H} \)), 3.87 – 3.79 (m, 1H), 3.79 – 3.70 (m, 3H), 3.70 – 3.54 (m, 3H), 3.34 (t, \( J = 9.3 \text{ Hz}, 1\text{H} \)), 3.14 (qd, \( J = 13.3, 7.6 \text{ Hz}, 2\text{H} \)), 2.23 (dd, \( J = 15.9, 8.1 \text{ Hz}, 4\text{H} \)), 1.97 (s, 3H), 1.47 (dd, \( J = 23.9, 17.2 \text{ Hz}, 8\text{H} \)), 1.18 (s, 72H), 1.06 (s, 4H), 0.77 (s, 15H). \(^{31}\text{P NMR (202 MHz, CDCl}_3\) \( \delta -0.84.\) HRMS (ESI) m/z: [M-H] - calcd. for C\(_{63}\)H\(_{120}\)N\(_2\)O\(_{15}\)P 1175.8432; found 1175.8394
MHz, CDCl₃) δ -2.15. HRMS (ESI) m/z: [M-H]- calcd. for C₆₂H₁₂₈N₂O₁₅P 1231.9058; found 1231.9055

**Synthesis of 1l. 1l** (6.2mg, 88%) was obtained as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 5.14 (s, 1H), 4.85 (d, J = 3.2 Hz, 1H), 4.66 (d, J = 14.9 Hz, 1H), 4.31 (dd, J = 11.9, 3.0 Hz, 1H), 4.06 (dd, J = 12.0, 6.9 Hz, 1H), 3.92 (s, 2H), 3.87 – 3.78 (m, 2H), 3.74 (d, J = 11.7 Hz, 2H), 3.68 – 3.48 (m, 3H), 3.21 – 3.08 (m, 2H), 2.24 (dd, J = 16.4, 7.9 Hz, 4H), 1.97 (s, 3H), 1.58 – 1.39 (m, 8H), 1.25 – 1.16 (m, 62H), 1.07 (d, J = 6.9 Hz, 4H), 0.78 (t, J = 6.9 Hz, 15H). ³¹P NMR (202 MHz, CDCl₃) δ -2.4319. HRMS (ESI) m/z: [M-H]- calcd. for C₆₂H₁₁₈N₂O₁₅P 1161.8275; found 1161.8295

**Synthesis of 1m. 1m** (19.9mg, 79%) was obtained as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 5.14 (s, 1H), 4.79 (s, 1H), 4.31 (d, J = 11.9 Hz, 1H), 4.07 (dd, J = 11.8, 7.0 Hz, 1H), 3.92 (s, 2H), 3.82 (d, J = 10.2 Hz, 2H), 3.72 (t, J = 11.4 Hz, 2H), 3.68 – 3.60 (m, 2H), 3.57 (d, J = 21.4 Hz, 1H), 3.30 (t, J = 9.4 Hz, 1H), 3.19 (dd, J = 13.3, 7.2 Hz, 1H), 3.12 (dd, J = 13.4, 6.5 Hz, 1H), 2.24 (dd, J = 17.4, 7.8 Hz, 4H), 1.96 (s, 3H), 1.54 – 1.43 (m, 7H), 1.18 (s, 70H), 1.07 (s, 2H), 0.79 (dd, J = 12.4, 6.0 Hz, 12H). ³¹P NMR (202 MHz, CDCl₃) δ -1.94. HRMS (ESI) m/z: [M-H]- calcd. for C₆₃H₁₂₀N₂O₁₅P 1175.8432; found 1175.8440

**Synthesis of 1n. 1n** (15.6mg, 94%) was obtained as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 5.16 (s, 1H), 4.80 (d, J = 3.3 Hz, 1H), 4.68 – 4.62 (m, 2H), 4.31 (dd, J = 12.0, 3.5 Hz, 1H), 4.11 – 4.02 (m, 1H), 3.99 (d, J = 5.7 Hz, 2H), 3.82 (dt, J = 27.0, 15.1 Hz, 3H), 3.73 (dd, J = 8.7, 3.1 Hz, 2H), 3.60 (ddd, J = 43.3, 23.3, 14.6 Hz, 5H), 3.35 – 3.28 (m, 1H), 3.20 – 3.10 (m, 2H), 2.28 – 2.21 (m, 4H), 1.97 (s, 3H), 1.49 (d, J = 32.5 Hz, 9H), 1.19 (s, 60H), 1.07 (d, J = 6.7 Hz, 6H), 0.78 (s, 18H). ³¹P NMR (202 MHz, CDCl₃) δ -1.86. HRMS (ESI) m/z: [M-H]- calcd. for C₆₄H₁₂₂N₂O₁₅P 1189.8588; found 1189.8580
Synthesis of 1o. 1o (30mg, 94%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.15 (dd, $J = 6.7$, 3.1 Hz, 1H), 4.82 (d, $J = 3.4$ Hz, 1H), 4.62 (dd, $J = 11.7$, 6.1 Hz, 2H), 4.32 (dd, $J = 12.0$, 3.1 Hz, 1H), 4.07 (dd, $J = 12.0$, 6.9 Hz, 1H), 3.92 (t, $J = 5.9$ Hz, 2H), 3.85 – 3.77 (m, 3H), 3.77 – 3.69 (m, 3H), 3.69 – 3.60 (m, 2H), 3.60 – 3.50 (m, 2H), 3.29 (t, $J = 9.4$ Hz, 1H), 3.25 (dt, $J = 3.2$, 1.6 Hz, 2H), 3.16 (ddd, $J = 20.6$, 13.2, 6.7 Hz, 2H), 2.24 (dt, $J = 9.8$, 7.7 Hz, 4H), 1.97 (s, 3H), 1.52 – 1.44 (m, 8H), 1.18 (s, 62H), 1.07 (m, 4H), 0.80 – 0.77 (m, 15H). $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -2.17. HRMS (ESI) m/z: [M-H]- calcd. for C$_{62}$H$_{118}$N$_2$O$_{15}$P 1181.8275; found 1181.8276

Synthesis of 1p. 1p (15.2mg, 84%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.15 (s, 1H), 4.79 (s, 1H), 4.32 (d, $J = 11.7$ Hz, 1H), 4.07 (s, 1H), 3.93 (s, 1H), 3.82 (s, 1H), 3.73 (s, 1H), 3.64 (s, 1H), 3.58 (s, 1H), 3.19 – 3.06 (m, 1H), 2.24 (dd, $J = 16.2$, 8.6 Hz, 3H), 2.16 – 2.08 (m, 1H), 2.03 – 1.87 (m, 3H), 1.46 – 1.35 (m, 9H), 1.28 – 1.14 (m, 60H), 1.07 (d, $J = 6.5$ Hz, 6H), 0.81 – 0.77 (m, 18H). $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -1.86. HRMS (ESI) m/z: [M-H]- calcd. for C$_{61}$H$_{116}$N$_2$O$_{15}$P 1147.8119; found 1147.8116

Synthesis of 1q. 1q (9.4mg, 74%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.14 (d, $J = 3.6$ Hz, 1H), 4.79 (d, $J = 3.4$ Hz, 1H), 4.63 (s, 2H), 4.32 (dd, $J = 12.0$, 3.2 Hz, 2H), 4.07 (dd, $J = 12.0$, 6.9 Hz, 1H), 3.92 (t, $J = 5.8$ Hz, 2H), 3.87 – 3.77 (m, 2H), 3.73 (dd, $J = 14.7$, 5.4 Hz, 2H), 3.68 – 3.41 (m, 5H), 3.20 – 3.08 (m, 2H), 2.23 (dt, $J = 10.0$, 7.6 Hz, 4H), 1.96 (s, 3H), 1.46 (ddd, $J = 21.4$, 19.9, 6.4 Hz, 9H), 1.24 – 1.17 (m, 60H), 1.07 (d, $J = 6.9$ Hz, 6H), 0.78 (d, $J = 6.6$ Hz, 18H). $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -1.73. HRMS (ESI) m/z: [M-H]- calcd. for C$_{60}$H$_{122}$N$_2$O$_{15}$P 1189.8588; found 1189.8592

Synthesis of 1r. 1r (13.0mg, 76%) was obtained as a white solid. $^1$H NMR (500 MHz, CDCl$_3$)
δ 5.15 (d, J = 3.6 Hz, 1H), 4.85 (d, J = 3.4 Hz, 1H), 4.31 (dd, J = 12.0, 3.1 Hz, 1H), 4.07 (dd, J = 12.0, 7.0 Hz, 1H), 3.92 (t, J = 5.7 Hz, 2H), 3.87 – 3.78 (m, 2H), 3.78 – 3.69 (m, 2H), 3.69 – 3.51 (m, 3H), 3.34 – 3.28 (m, 1H), 3.22 – 3.06 (m, 2H), 2.24 (dd, J = 16.4, 7.7 Hz, 4H), 1.97 (s, 3H), 1.56 – 1.40 (m, 9H), 1.24 – 1.17 (m, 62H), 1.10 – 1.03 (m, 6H), 0.78 (d, J = 6.6 Hz, 18H).

31P NMR (202 MHz, CDCl3) δ -2.44. HRMS (ESI) m/z: [M-H]- calcd. for C_{65}H_{124}N_{2}O_{15}P 1203.8745; found 1203.8742

Synthesis of 1s. 1s (14.2mg, 75%) was obtained as a white solid. 1H NMR (500 MHz, CDCl3) δ 5.14 (d, J = 3.5 Hz, 1H), 4.82 (d, J = 3.4 Hz, 1H), 4.31 (dd, J = 12.0, 3.1 Hz, 1H), 4.07 (dd, J = 12.0, 6.9 Hz, 1H), 3.92 (t, J = 5.8 Hz, 2H), 3.87 – 3.78 (m, 2H), 3.78 – 3.67 (m, 2H), 3.67 – 3.48 (m, 3H), 3.29 (dd, J = 11.5, 7.1 Hz, 1H), 3.14 (ddd, J = 20.5, 12.8, 6.3 Hz, 2H), 2.30 – 2.16 (m, 4H), 1.97 (s, 3H), 1.54 – 1.39 (m, 9H), 1.24 – 1.17 (m, 54H), 1.07 (d, J = 7.0 Hz, 6H), 0.78 (t, J = 6.0 Hz, 18H). 31P NMR (202 MHz, CDCl3) δ -2.15. HRMS (ESI) m/z: [M-H]- calcd. for C_{61}H_{116}N_{2}O_{13}P 1147.8119; found 1147.8113

Biological Experiments.

Evaluation of the effects of compound 1 on IL-6 and TNF-α production in LPS-activated macrophages. Mouse macrophages J774A.1 cells were incubated for 0.5 h with 30 µg/ml PGL or vehicle (0.1% DMSO) followed by incubation for 6 h with 1 µg/ml LPS. The levels of IL-6 (a) and TNF-α (b) in the supernatants were measured by ELISA. The data were expressed as mean ± SD; n = 3.

Evaluation of the effects of compound 1 on the proliferation of J774A.1 macrophages.
J774A.1 macrophages were cultured for 24 h in 96 wells plate containing media which comprise PGL 1b, 1e and 1g (30 ~ 90 µg/ml) or vehicle (0.1% DMSO). Thereafter, 10 µL AlamarBlue® reagent (AbD Serotec, Oxford, U.K.) was added into each well and the cells were further incubated at 37°C for 6 h. The cell viability was determined by the fluorescence intensity detected at 570 nm and 600 nm. The data were expressed as mean ± SD; n = 3.

**Evaluation of the dose-dependent effect of compound 1e on IL-6 and TNF-α production in LPS-activated macrophages.** J774A.1 macrophages were incubated for 0.5 h with 1e (7.5-60 µg/ml) or vehicle (0.1% DMSO) followed by incubation for 6 h with 1 µg/ml LPS. The levels of IL-6 (a) and TNF-α (b) in the supernatants were measured by ELISA. The data were expressed as mean ± SD; n = 3.

**Evaluation of the dose-dependent effect of compound 1e on NF-κB activation in LPS-activated macrophages.** NF-κB reporter cells (J-Blue cells) are derived from J774A.1 macrophages stably transfected with the NF-κB-inducible reporter plasmid (pNiFty2-SEAP). J-Blue cells were incubated with 1e (7.5-30 µg/ml) or vehicle (0.1% DMSO) for 0.5 h and then treated with 1 µg/ml LPS for 24 h. The supernatants were harvested, and NF-κB transcriptional activity was assayed using QUANTI-Blue assay (purchased from InvivoGen, San Diego, CA).

**Evaluation of the effect of compound 1e on the phosphorylation levels of mitogen-activated protein kinases in LPS-activated macrophages.** J774A.1 macrophages were incubated for 0.5 h with 30 µg/ml 1e or vehicle (0.1% DMSO) followed by incubation for 10-30 min with 1 µg/ml LPS. The phosphorylation levels of ERK1/2, JNK1/2 and p38 in the cell lysates were measured by Western blot.

**Evaluation of the effect of compound 1e on the autophagy induction in macrophages.**
J774A.1 macrophages were incubated for 2-6 h with 15 µg/ml 1e or vehicle (0.1% DMSO). The expression levels of LC3, p62 and ATG5 in the cell lysates were measured by Western blot.

**Evaluation of the effect of compound 1e on the IL-6 mRNA expression LPS-activated macrophages.** J774A.1 macrophages were incubated for 0.5 h with 15 µg/ml 1e or vehicle (0.1% DMSO) followed by incubation for 2 and 4 h with 1 µg/ml LPS. The IL-6 mRNA expression was measured by RT-qPCR.

**Additional Biological Data (Figures S1-S3)**

![Graph](image-url)

Figure S1. Effect of compounds 1 on the proliferation of J774A.1 macrophages.
Figure S2. Effect of compound 1e on the phosphorylation levels of mitogen-activated protein kinases in LPS-activated macrophages.

Figure S3. Effect of compound 1e on the autophagy induction in macrophages.
Spectra of Compounds.

$^1$H NMR of 6a

BRUKER
C NMR of 6a
H NMR of 6b
H NMR of 3a

Bruker

1H NMR 500 MHz in CDCl₃
$^1$H NMR of 3b
C NMR of 8a

[Graph of 13C NMR spectrum with assigned peaks and chemical structure of 8a]
H NMR of 8b
$^{13}$C NMR of 8b
$^1$H NMR of 8c
H NMR of 10a
13C NMR of 10a

Current data parameters:

10
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<th>Value</th>
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</table>

**13C NMR of 10c**

![13C NMR Spectrum](image-url)
H NMR of 10d

\[
\begin{align*}
\text{Chemical Shift:} & \quad 14.00 \\
& \quad 8.39 \\
& \quad 7.98 \\
& \quad 7.86 \\
& \quad 7.58 \\
& \quad 7.46 \\
& \quad 7.22 \\
& \quad 7.03 \\
& \quad 6.82 \\
& \quad 6.67 \\
& \quad 5.80 \\
& \quad 5.16 \\
& \quad 4.61 \\
& \quad 4.33 \\
& \quad 3.91 \\
& \quad 3.04 \\
& \quad 2.86 \\
& \quad 2.73 \\
& \quad 2.58 \\
& \quad 2.32 \\
& \quad 1.91 \\
& \quad 1.57 \\
& \quad 1.29 \\
& \quad 1.09 \\
\end{align*}
\]
H NMR of 10f
$^{13}$C NMR of 10f
H NMR of 10g
\textsuperscript{1}H NMR of 11d
$^{13}$C NMR of 11d
H NMR of 11H
$^1$H NMR of 11h
H NMR of 11i
$^1$H NMR of 11j
$^1$H NMR of 11k
$^1$H NMR of 11m
$^{13}$C NMR of 11m
C NMR of 11n
HNMR of 12a
$^{31}$P NMR of 12a
H NMR of 12b
$^{13}$C NMR of 12b
31P NMR of 12d

[Diagram of molecular structure]

BRUKER

S120
C NMR of 12e

\[ \text{C NMR of 12e} \]
$^{1}H$ NMR of 12f
H NMR of 12h
$^{31}$P NMR of 12k
H NMR of 12m
H NMR of 12n
$^{31}P$ NMR of 12n

![Chemical Structure](image)
H NMR of 13a
$^{13}$C NMR of 13a
$^{31}$P NMR of 13a
H NMR of 13b
$^{13}$C NMR of 13c

![NMR Spectrum](image)
H NMR of 13e

Bruker

Current Data Parameters:

1H AX500 HET-13E2 ambient 1H CH3-MeOD = 3:1
$^{31}$P NMR of 13e

[Image: A nuclear magnetic resonance (NMR) spectrum showing a peak at a particular ppm value.]

**Figure Caption:**
$^{31}$P NMR spectrum of compound 13e, demonstrating a peak at a specific ppm value, indicative of its molecular structure.
$^{13}$C NMR of 13f
$^{31}$P NMR of 13f
H NMR of 13g

Current Data Parameters:

- 1H Anx500
- 15.51 Hz Range (3)
$^{13}$C NMR of 13h
$^{31}$P NMR of 13l
$^1$H NMR of 13j
1H NMR of 13l
$^3$P NMR of 13m
H NMR of 13o
13C NMR of 13o
$^{13}$C NMR of 13p
H NMR of 13g
$^1$H NMR of 13s
H NMR of 1a
$^3$P NMR of 1a
$^1$H NMR of 1b
31P NMR of 1b
H NMR of 1c
$^{31}$P NMR of 1c
H NMR of 1d
$^1$H NMR of 1h
H NMR of 1i
$^3$P NMR of Ti

Current Data Parameters:

1. PROC
2. NAME
3. P

Bruker

3p NMR of Ti

477 m/z 13.19 anologue

3jp AX500
H NMR of 1j
H NMR of 11

Current Data Parameters

Bruker
$^{1}H$ NMR of 1m
$^{31}$P NMR of 1n
\(^{1}H\) NMR of \(1p\)
$^{31}$P NMR of $1r$