Supporting Information for:

Fe-Catalyzed Bis-phosphorylation of Amino-2-en-1-ones with Trialkyl phosphites

Shengmei Guo, Kun Jie, Ling Huang, Zhebin Zhang, Yufeng Wang, Zhengjiang Fu, Hu Cai*

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1. General experiment detail and materials

Experimental: All non-aqueous reactions and manipulations were performed in air atmosphere using standard techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen. All reactions were monitored by TLC with silica gel-coated plates.

NMR spectra were recorded on Agilent Technologies 400 and AVANCE III 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants ($J$) are reported in Hz and refer to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Daltonics APEX II 47e Specification (ESI).

2. General Procedure

\[
\text{Cat} + \text{HCHO} + \text{R}_2\text{NH} \rightarrow \text{Cat} + \text{NR}_2\text{R}_2
\]
2-((diethylamino)methyl)-1-phenylprop-2-en-1-one (1a): Ketone 1 (1 mmol) was mixed with silica gel (2.0 g) in a mortar. Then formaldehyde (0.18 g, 3 mmol, 37% in H₂O), and dialkylamine (2 mmol) were added and mixed. The mixture was placed into a flask with a cap, and stirred for 5–7 hours at room temperature. Then diethyl ether (20 ml) was added. After filtration and the removal of the solvent at the reduced pressure, the product was isolated. Further purification of the crude reaction mixture on silica gel column gave the pure product.

General procedure for 3a: To a 50 mL Schlenk tube with a stir bar added allylamine derivatives 1a (81.9 mg, 0.3 mmol), triethyl phosphite (149.5 mg, 3 eq.), Fe(NO₃)₃·9H₂O (20 mol%) and DCE (2 mL), the mixture was stirred at 100 °C for 5h, and monitored by TLC. The solution was then evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (pure EA) to get product 3a.

General procedure for 5a and 5b: To a 50 mL Schlenk tube with a stir bar added allylamine derivatives 1a (81.9 mg, 0.3 mmol), diethyl phosphite (82.8 mg, 2 eq.) and DCE (2 mL), the mixture was stirred at 100°C for 8h. Then, trialkyl phosphite (1.5 eq.), Fe(NO₃)₃·9H₂O (20 mol%), DCE (2 mL) were added. the
mixture was stirred at 100 °C for 5 h, and monitored by TLC. The solution was then evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (pure EA) to get product.

3. Experimental characterization data for products

1. Tetraethyl (2-benzoylpropane-1,3-diyl)bis(phosphonate) (3a)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 95% yield. $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 7.4$ Hz, 2H), 7.58 (t, $J = 7.1$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 2H), 4.34 (ddd, $J = 20.5$, 13.9, 6.6 Hz, 1H), 4.13 – 3.91 (m, 8H), 2.44 – 2.32 (m, 2H), 2.14 – 2.01 (m, 2H), 1.24 (t, $J = 7.0$ Hz, 6H), 1.14 (t, $J = 7.0$ Hz, 6H). $^{13}\text{C}$ NMR (101 MHz, CDCl$_3$) $\delta$ 199.77, 199.68, 199.59, 135.05, 133.61, 128.92, 128.88, 77.32, 77.00, 76.68, 62.56, 62.49, 62.35, 62.29, 34.46, 34.43, 34.41, 28.95, 28.85, 27.53, 27.43, 16.24, 16.18, 16.10, 16.03. $^{31}\text{P}$ NMR (243 MHz, CDCl$_3$) $\delta$ 28.09. HRMS (m/z): calcd for C$_{18}$H$_{31}$O$_7$P$_2$ [M+H]$^+$: 421.1540, found: 421.1541.

2. Tetraethyl (2-(4-methylbenzoyl)propane-1,3-diyl)bis(phosphonate) (3b)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 83% yield. $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 7.9$ Hz, 1H), 7.05 (d, $J = 12.4$ Hz, 2H), 4.00 (tt, $J = 14.8$, 7.5 Hz, 8H), 2.44 (s, 3H), 2.32 (s, 3H), 2.29 – 2.19 (m, 2H), 2.12 – 1.98 (m, 2H), 1.21 (dt, $J = 19.0$, 6.9 Hz, 12H). $^{13}\text{C}$ NMR (101 MHz, CDCl$_3$) $\delta$ 199.52, 199.45, 199.37, 144.36, 132.94, 129.39, 128.78, 61.88, 61.82, 61.77, 61.70, 34.67, 34.64, 34.61, 29.47, 29.35, 28.06, 27.94, 21.66, 16.29, 16.23, 16.16. $^{31}\text{P}$ NMR (162 MHz, DMSO) $\delta$ 33.23. HRMS (m/z): calcd for C$_{19}$H$_{33}$O$_7$P$_2$ [M+H]$^+$: 435.1696, found: 435.1697.

3. Tetraethyl (2-(2,4-dimethylbenzoyl)propane-1,3-diyl)bis(phosphonate) (3c)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 88% yield. $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 7.9$ Hz, 1H), 7.11 – 7.04 (m, 2H), 4.02 (dt, $J = 21.4$, 7.6 Hz, 8H), 2.47 (s, 3H), 2.35 (s, 3H), 2.31 – 2.21 (m, 2H), 2.13 – 2.03 (m, 2H), 1.24 (dt, $J = 18.3$, 7.0 Hz, 12H). $^{13}\text{C}$ NMR (101 MHz, CDCl$_3$) $\delta$ 202.06 (s), 142.60 (s), 139.96 (s), 133.31 (s), 133.00 (s), 129.56 (s), 126.56 (s), 61.96 (dd, $J = 6.5$, 2.2 Hz), 44.02 (s), 37.68 (t, $J = 3.6$ Hz), 28.96 (d, $J = 11.0$ Hz), 27.56 (d, $J = 10.9$ Hz), 21.58 (d, $J = 10.7$ Hz), 16.43 (t, $J = 6.5$ Hz). $^{31}\text{P}$ NMR (243 MHz, CDCl$_3$) $\delta$ 28.51. HRMS (m/z): calcd for C$_{20}$H$_{35}$O$_7$P$_2$ [M+H]$^+$: 449.1853, found: 449.1853.
4. Tetraethyl (2-(1-naphthoyl)propane-1,3-diyl)bis(phosphonate) (3d)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 80% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J = 8.4$ Hz, 1H), 8.09 (d, $J = 7.0$ Hz, 1H), 8.00 (d, $J = 8.2$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.61 – 7.48 (m, 3H), 4.21 – 4.12 (m, 1H), 4.02 (dt, $J = 14.5$, 7.2 Hz, 7H), 2.37 (td, $J = 17.1$, 7.7 Hz, 2H), 2.23 – 2.11 (m, 2H), 1.20 (dt, $J = 19.4$, 7.0 Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 202.63 (s), 134.45 (s), 133.98 (s), 133.29 (s), 130.91 (s), 128.48 (d, $J = 5.8$ Hz), 128.18 (s), 126.64 (s), 126.51 (s), 125.78 (s), 62.00 (dd, $J = 6.4$, 3.7 Hz), 39.21 (t, $J = 3.4$ Hz), 28.87 (d, $J = 11.0$ Hz), 27.46 (d, $J = 10.9$ Hz), 16.36 (t, $J = 6.3$ Hz). $^{31}$P NMR (162 MHz, DMSO) $\delta$ 33.14. HRMS (m/z): calcd for C$_{22}$H$_{33}$O$_7$P$_2$ [M+H]$^+$: 471.1696, found: 471.1699.

5. Tetraethyl (2-(4-methoxybenzoyl)propane-1,3-diyl)bis(phosphonate) (3e)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 78% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 4.17 – 4.04 (m, 1H), 3.96 (p, $J = 7.2$ Hz, 8H), 3.82 (s, 3H), 2.27 (td, $J = 16.8$, 7.7 Hz, 2H), 2.04 (td, $J = 17.6$, 5.5 Hz, 2H), 1.17 (dt, $J = 10.5$, 7.1 Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.41 (s), 163.88 (s), 131.50 (s), 128.57 (s), 113.92 (s), 61.82 (dd, $J = 11.0$, 6.5 Hz), 55.53 (s), 34.45 (t, $J = 3.4$ Hz), 29.64 (d, $J = 12.1$ Hz), 28.24 (d, $J = 12.1$ Hz), 16.28 (t, $J = 6.1$ Hz). $^{31}$P NMR (162 MHz, DMSO) $\delta$ 32.94. HRMS (m/z): calcd for C$_{19}$H$_{33}$O$_8$P$_2$ [M+H]$^+$: 451.1645, found: 451.1648.

6. Tetraethyl (2-(3-methoxybenzoyl)propane-1,3-diyl)bis(phosphonate) (3f)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 95% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.0$ Hz, 1H), 7.46 (s, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 7.04 (d, $J = 7.7$ Hz, 1H), 4.12 – 4.02 (m, 1H), 3.99 – 3.86 (m, 8H), 3.76 (s, 3H), 2.24 (td, $J = 17.5$, 7.4 Hz, 2H), 2.02 (td, $J = 17.6$, 5.3 Hz, 2H), 1.14 (dt, $J = 13.4$, 6.8 Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 199.56, 199.49, 199.41, 159.84, 136.73, 129.61, 121.10, 119.96, 112.80, 77.43, 77.11, 76.79, 61.84, 61.77, 61.75, 61.68, 55.34, 34.99, 34.95, 34.92, 29.38, 29.26, 27.97, 27.86, 16.21, 16.15, 16.09. $^{31}$P NMR (162 MHz, DMSO) $\delta$ 32.44. HRMS (m/z): calcd for C$_{19}$H$_{33}$O$_8$P$_2$ [M+H]$^+$: 451.1645, found: 451.1648.

7. Tetraethyl (2-(4-ethoxybenzoyl)propane-1,3-diyl)bis(phosphonate) (3g)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 70% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 4.15 –
4.10 (m, 1H), 4.09 – 4.04 (m, 2H), 3.98 (p, \( J = 7.0 \) Hz, 8H), 2.29 (td, \( J = 16.7, 7.7 \) Hz, 2H), 2.14 – 2.00 (m, 2H), 1.42 (t, \( J = 6.9 \) Hz, 3H), 1.19 (dt, \( J = 9.9, 7.1 \) Hz, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 198.42, 198.34, 198.27, 163.25, 131.00, 128.30, 114.28, 77.33, 77.01, 76.69, 63.76, 61.85, 61.79, 61.74, 61.67, 34.39, 34.35, 34.32, 29.65, 29.53, 28.24, 28.12, 16.28, 16.22, 14.61. \(^{31}\)P NMR (162 MHz, DMSO) \( \delta \) 27.72.


8. Tetraethyl (2-([1,1’-biphenyl]-4-carbonyl)propane-1,3-diyl)bis(phosphonate) (3h)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 84% yield. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.09 (d, \( J = 8.2 \) Hz, 2H), 7.68 (d, \( J = 8.2 \) Hz, 2H), 7.60 (d, \( J = 7.1 \) Hz, 2H), 7.44 (t, \( J = 7.3 \) Hz, 2H), 7.40 – 7.32 (m, 1H), 4.20 (ddd, \( J = 17.8, 12.0, 5.7 \) Hz, 1H), 4.12 – 3.89 (m, 8H), 2.33 (td, \( J = 16.6, 7.7 \) Hz, 2H), 2.11 (td, \( J = 17.7, 5.4 \) Hz, 2H), 1.20 (dt, \( J = 14.2, 7.0 \) Hz, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 199.55, 199.47, 199.39, 146.04, 139.69, 134.26, 129.25, 128.92, 128.27, 127.27, 127.19, 77.36, 77.05, 76.73, 61.88, 61.82, 61.78, 61.71, 34.90, 34.87, 34.84, 29.63, 29.51, 28.22, 28.11, 16.28, 16.22, 16.17. \(^{31}\)P NMR (243 MHz, CDCl\(_3\)) \( \delta \) 28.05. HRMS (m/z): calcd for C\(_{24}\)H\(_{35}\)O\(_7\)P\(_2\) [M+H]+: 497.1853, found: 497.1850.

9. Tetraethyl (2-((1,3-dihydroisobenzofuran-5-carbonyl)propane-1,3-diyl)bis(phosphonate) (3i)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 79% yield. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.61 (d, \( J = 8.1 \) Hz, 1H), 7.43 (s, 1H), 6.81 (d, \( J = 8.2 \) Hz, 1H), 5.99 (s, 2H), 4.04 – 3.90 (m, 8H), 2.24 (td, \( J = 16.5, 7.6 \) Hz, 2H), 2.03 (td, \( J = 17.5, 5.6 \) Hz, 2H), 1.18 (dt, \( J = 14.2, 7.0 \) Hz, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 197.92 (s), 152.16 (s), 148.36 (s), 130.34 (s), 125.07 (s), 108.36 (s), 107.99 (s), 101.95 (s), 61.80 (dd, \( J = 9.2, 7.0 \) Hz), 34.72 (t, \( J = 3.4 \) Hz), 29.63 (d, \( J = 12.0 \) Hz), 28.23 (d, \( J = 12.0 \) Hz), 16.29 (t, \( J = 6.5 \) Hz). \(^{31}\)P NMR (243 MHz, Acetone) \( \delta \) 27.20. HRMS (m/z): calcd for C\(_{19}\)H\(_{31}\)O\(_9\)P\(_2\) [M+H]+: 465.1438, found: 465.1438.

10. Tetraethyl (2-(4-nitrobenzoyl)propane-1,3-diyl)bis(phosphonate) (3j)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 55% yield. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.29 (d, \( J = 8.8 \) Hz, 2H), 8.18 (d, \( J = 8.8 \) Hz, 2H), 4.21 – 4.09 (m, 1H), 4.03 – 3.87 (m, 8H), 2.34 – 2.22 (m, 2H), 2.07 (ddd, \( J = 7.0, 5.5 \) Hz, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 199.06, 198.99, 198.99, 150.39, 140.45, 129.70, 123.79, 77.36, 77.04, 76.72, 62.05, 61.98, 61.92, 61.86, 35.52, 35.48, 35.45, 30.01.
11. Tetraethyl (2-(2-bromobenzoyl)propane-1,3-diyl)bis(phosphonate) (3k)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 55% yield.

\[ \text{^1H NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.73 (d, \( J \) = 7.4 Hz, 1H), 7.60 (d, \( J \) = 7.3 Hz, 1H), 7.38 (t, \( J \) = 7.0 Hz, 1H), 7.29 (t, \( J \) = 7.0 Hz, 1H), 4.10 – 3.97 (m, 8H), 3.91 (td, \( J \) = 13.8, 6.8 Hz, 1H), 2.31 (td, \( J \) = 17.1, 4.9 Hz, 2H), 2.17 – 2.03 (m, 2H), 1.24 (q, \( J \) = 7.2 Hz, 12H).

\[ \text{^13C NMR (101 MHz, CDCl}_3 \] \( \delta \) 201.10, 201.00, 200.90, 139.16, 139.13, 132.20, 129.78, 127.43, 120.05, 77.35, 77.03, 76.71, 62.03, 61.97, 39.83, 39.80, 39.76, 27.43, 27.34, 26.02, 25.93, 16.32, 16.28, 16.26, 16.22.

\[ \text{^31P NMR (162 MHz, DMSO) \( \delta \) 32.03. HRMS (m/z): calecd for C\textsubscript{18}H\textsubscript{30}NO\textsubscript{9}P\textsubscript{2} [M+H\textsuperscript{+}]\textsuperscript{+}: 466.1390, found: 466.1390.} \]

12. Tetraethyl (2-(3-bromobenzoyl)propane-1,3-diyl)bis(phosphonate) (3l)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 75% yield.

\[ \text{^1H NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.12 (s, 1H), 7.95 (d, \( J \) = 7.6 Hz, 1H), 7.68 (d, \( J \) = 7.9 Hz, 1H), 7.35 (t, \( J \) = 7.8 Hz, 1H), 4.17 – 4.05 (m, 1H), 4.05 – 3.86 (m, 8H), 2.34 – 2.22 (m, 2H), 2.14 – 1.98 (m, 2H), 1.31 – 1.12 (m, 12H).

\[ \text{^13C NMR (101 MHz, CDCl}_3 \] \( \delta \) 198.85, 198.78, 198.70, 137.48, 136.21, 131.65, 130.27, 127.18, 122.99, 77.33, 77.01, 61.98, 61.92, 61.87, 61.80, 35.13, 35.09, 35.06, 29.72, 29.60, 28.32, 28.19, 16.28, 16.22, 16.15.

\[ \text{^31P NMR (162 MHz, DMSO) \( \delta \) 31.98. HRMS (m/z): calecd for C\textsubscript{18}H\textsubscript{30}BrO\textsubscript{7}P\textsubscript{2} [M+H\textsuperscript{+}]\textsuperscript{+}: 499.0645, found: 499.0640.} \]

13. Tetraethyl (2-(4-fluorobenzoyl)propane-1,3-diyl)bis(phosphonate) (3m)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 88% yield.

\[ \text{^1H NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.08 – 7.99 (m, 2H), 7.12 (t, \( J \) = 8.0 Hz, 2H), 4.11 (ddt, \( J \) = 17.9, 12.1, 6.2 Hz, 1H), 4.04 – 3.90 (m, 8H), 2.27 (td, \( J \) = 16.8, 7.9 Hz, 2H), 2.14 – 1.98 (m, 2H), 1.18 (q, \( J \) = 7.1 Hz, 12H).

\[ \text{^13C NMR (101 MHz, CDCl}_3 \] \( \delta \) 198.50, 198.43, 198.38, 167.18, 164.64, 132.06, 132.04, 131.37, 131.28, 115.87, 115.65, 77.38, 77.05, 76.73, 61.88, 61.82, 61.76, 61.70, 34.73, 29.73, 29.61, 28.32, 28.20, 16.22, 16.12.

\[ \text{^31P NMR (162 MHz, DMSO) \( \delta \) 32.62. HRMS (m/z): calecd for C\textsubscript{18}H\textsubscript{30}FO\textsubscript{7}P\textsubscript{2} [M+H\textsuperscript{+}]\textsuperscript{+}: 439.1445, found: 439.1449.} \]

14. Tetraethyl (2-(3,4-dichlorobenzoyl)propane-1,3-diyl)bis(phosphonate) (3n)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 51% yield.

\[ \text{^1H NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.09 (d, \( J \) = 1.3 Hz, 1H), 8.05 – 7.95 (m, 2H), 7.12 (t, \( J \) = 8.0 Hz, 2H), 4.11 (ddt, \( J \) = 17.9, 12.1, 6.2 Hz, 1H), 4.04 – 3.90 (m, 8H), 2.27 (td, \( J \) = 16.8, 7.9 Hz, 2H), 2.14 – 1.98 (m, 2H), 1.18 (q, \( J \) = 7.1 Hz, 12H).

\[ \text{^13C NMR (101 MHz, CDCl}_3 \] \( \delta \) 198.50, 198.43, 198.38, 167.18, 164.64, 132.06, 132.04, 131.37, 131.28, 115.87, 115.65, 77.38, 77.05, 76.73, 61.88, 61.82, 61.76, 61.70, 34.73, 29.73, 29.61, 28.32, 28.20, 16.22, 16.17, 16.12.

\[ \text{^31P NMR (162 MHz, DMSO) \( \delta \) 32.62. HRMS (m/z): calecd for C\textsubscript{18}H\textsubscript{30}FO\textsubscript{7}P\textsubscript{2} [M+H\textsuperscript{+}]\textsuperscript{+}: 439.1445, found: 439.1449.} \]
7.86 (dd, $J = 8.3, 1.5$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 3.98 (dd, $J = 14.2, 7.1$ Hz, 8H), 2.27 (td, $J = 16.4, 8.1$ Hz, 2H), 2.13 – 2.00 (m, 2H), $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.21 (s), 138.14 (s), 135.51 (s), 133.49 (s), 130.93 (s), 130.73 (s), 127.81 (s), 62.07 (dd, $J = 11.5, 6.4$ Hz), 35.18 (t, $J = 3.3$ Hz), 29.92 (d, $J = 12.5$ Hz), 28.52 (d, $J = 12.5$ Hz), 16.70 – 16.01 (m). $^{31}$P NMR (162 MHz, DMSO) $\delta$ 31.80. HRMS (m/z): calcd for C$_{18}$H$_{29}$Cl$_2$O$_7$P$_2$ [M+H]$^+$: 489.0760, found: 489.0756.

**15. Tetraethyl (2-(thiophene-2-carbonyl)propane-1,3-diyl)bis(phosphonate) (3o)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 96% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 3.5$ Hz, 1H), 7.65 (d, $J = 4.7$ Hz, 1H), 7.11 (t, $J = 4.3$ Hz, 1H), 4.02 – 3.90 (m, 8H), 2.28 (td, $J = 16.4, 8.0$ Hz, 2H), 2.15 – 1.98 (m, 2H), $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.78 (s), 143.20 (s), 134.91 (s), 133.05 (s), 128.38 (s), 62.17 – 61.63 (m), 36.75 (t, $J = 3.4$ Hz), 29.85 (d, $J = 12.4$ Hz), 28.45 (d, $J = 12.4$ Hz), 16.25 (t, $J = 6.1$ Hz). $^{31}$P NMR (162 MHz, DMSO) $\delta$ 27.14. HRMS (m/z): calcd for C$_{16}$H$_{29}$O$_7$P$_2$S [M+H]$^+$: 427.1104, found: 427.1106.

**16. Tetramethyl (2-benzoylpropane-1,3-diyl)bis(phosphonate) (3p)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 73% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 7.5$ Hz, 2H), 7.59 (t, $J = 10.7$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 2H), 4.22 – 4.10 (m, 1H), 3.64 (d, $J = 10.9$ Hz, 11H), 2.42 – 2.28 (m, 2H), 2.18 – 2.05 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 199.94 (s), 135.50 (s), 133.63 (s), 128.91 (s), 128.65 (s), 52.72 – 52.30 (m), 34.95 (t, $J = 3.4$ Hz), 28.54 (d, $J = 11.8$ Hz), 27.14 (d, $J = 11.8$ Hz). $^{31}$P NMR (162 MHz, D$_2$O) $\delta$ 35.

HRMS (m/z): calcd for C$_{14}$H$_{23}$O$_7$P$_2$ [M+H]$^+$: 365.0914, found: 365.0915.

**17. Tetraisopropyl (2-benzoylpropane-1,3-diyl)bis(phosphonate) (3q)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 95% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 7.3$ Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 2H), 4.62 (dq, $J = 12.5, 6.2$ Hz, 4H), 4.24 – 4.10 (m, 1H), 2.32 – 2.18 (m, 2H), 2.14 – 2.01 (m, 2H), 1.32 – 1.13 (m, 24H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 200.13 (s), 135.87 (s), 133.27 (s), 128.83 (s), 128.54 (s), 70.46 (dd, $J = 19.1, 6.9$ Hz), 34.93 (t, $J = 3.6$ Hz), 31.03 (d, $J = 12.0$ Hz), 29.61 (d, $J = 11.9$ Hz), 24.11 – 23.41 (m). $^{31}$P NMR (162 MHz, D$_2$O) $\delta$ 26.84. HRMS (m/z): calcd for C$_{22}$H$_{39}$O$_7$P$_2$ [M+H]$^+$: 477.2166, found: 477.2169.

**18. Tetrabutyl (2-benzoylpropane-1,3-diyl)bis(phosphonate) (3r)**

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 89% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 7.4$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 4.24 – 4.10 (m, 1H), 2.39 – 2.24 (m, 1H).
2H), 2.18 – 2.01 (m, 2H), 1.60 – 1.43 (m, 8H), 1.29 (tq, 
J = 14.6, 7.3 Hz, 8H), 0.86 (dd, J = 16.4, 7.4 Hz, 
12H). 13C NMR (101 MHz, CDCl3) δ 200.02 (s), 135.71 (s), 133.53 (s), 128.80 (d, J = 8.1 Hz), 
65.85 – 65.38 (m), 34.94 (t, J = 3.4 Hz), 32.52 (dd, 
J = 6.4, 4.2 Hz), 29.64 (d, J = 12.1 Hz), 28.24 (d, J 
= 12.0 Hz), 18.79 (d, J = 4.0 Hz), 13.68 (d, J = 2.2 Hz). 31P NMR (162 MHz, DMSO) δ 32.57. HRMS 

19. Dimethyl (2-((diethoxyphosphoryl)methyl)-3-oxo-3-phenylpropyl)phosphonate (5a)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 76% yield. 1H NMR (400 MHz, CDCl3) δ 8.01 (d, 
J = 7.4 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 
4.21 – 4.06 (m, 1H), 4.00 (p, J = 7.3 Hz, 4H), 3.62 (d, J = 10.9 Hz, 6H), 2.43 – 2.23 (m, 2H), 2.17 – 2.02 (m, 2H), 1.24 – 1.16 (m, 6H). 13C NMR (101 MHz, CDCl3) δ 
199.91 (s), 135.59 (s), 133.51 (s), 128.73 (d, J = 13.8 Hz), 61.91 (t, J = 6.9 Hz), 52.39 (t, J = 6.5 Hz), 
34.96 (t, J = 3.3 Hz), 29.65 (d, J = 12.6 Hz), 28.35 (dd, J = 20.7, 11.8 Hz), 27.05 (d, J = 11.1 Hz), 16.27 (t, J = 5.8 Hz). 31P NMR (243 MHz, CDCl3) δ 30.78, 27.87. HRMS (m/z): calcd for C16H27O7P2 [M+H]+: 393.1227, found: 393.1227.

20. Dibutyl (2-((diethoxyphosphoryl)methyl)-3-oxo-3-phenylpropyl)phosphonate (5b)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 73% yield. 1H NMR (400 MHz, CDCl3) δ 
8.03 (d, J = 7.4 Hz, 2H), 7.56 (s, 1H), 7.48 (t, J = 7.5 Hz, 2H), 
4.22 – 4.13 (m, 1H), 4.05 – 3.86 (m, 8H), 2.40 – 2.28 (m, 2H), 
2.15 – 2.05 (m, 2H), 1.56 – 1.48 (m, 4H), 1.24 (ddd, J = 28.9, 14.8, 7.3 Hz, 10H), 0.87 (q, J = 7.5 Hz, 6H). 13C NMR (101 MHz, CDCl3) δ 200.07 (s), 135.75 (s), 133.51 (s), 128.73 (d, J = 13.8 Hz), 61.91 (t, J = 6.9 Hz), 52.39 (t, J = 6.5 Hz), 34.96 (t, J = 3.3 Hz), 29.65 (d, J = 12.6 Hz), 28.35 (dd, J = 20.7, 11.8 Hz), 27.05 (d, J = 11.1 Hz), 16.27 (t, J = 5.8 Hz). 31P NMR (243 MHz, CDCl3) δ 28.05, 26.71. HRMS (m/z): calcd for C22H39O7P2 [M+H]+: 477.2166, found: 477.2161.
4. Copies of product $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR
\begin{align*}
\text{OP(OEt)\textsubscript{2}}
\end{align*}
O
P(O\textsuperscript{\textcircled{\textit{Bu}}}\textsubscript{2})
\textsuperscript{\textcircled{\textit{Bu}}}
P(OEt\textsubscript{2})
\textsuperscript{\textcircled{\textit{Bu}}}

\begin{center}
\includegraphics[width=\textwidth]{chemicalstructures.png}
\end{center}