Supporting Information

Bismuth(III)-catalyzed Sequential Enamine-Imine Tautomerism/2-Aza-Cope Rearrangement of Stable β-Enaminophosphonates: One-Pot Synthesis of β-Aminophosphonates

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1. General Information

All solvents were treated according to standard procedures prior to use unless otherwise noted. Bi(OTf)₃ (98% purity) was purchased from Energy Chemical. Other reagents were obtained from commercial suppliers and used without further purification. The desired products were purified by column chromatography on silica gel. NMR spectra were recorded on Bruker instrument (400 MHz and 600 MHz) or Varian instrument (300 MHz), using TMS as internal standard. Chemical shifts were given relative to CDCl₃ (7.26 ppm for ¹H NMR, 77.16 ppm for ¹³C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. HRMS was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source.

2. Preparation of starting materials

Method A:

![Chemical Reaction Diagram]

2-bromoethylbenzene (1.1 equiv, 33 mmol) and triisopropyl phosphite (1.0 equiv, 30 mmol) was added to a 100 mL sealed tube equipped with a stirring bar under argon and the tube was then heated in 120 °C oil bath for 24 hours. Product S1 was purified by fast chromatography on silica gel in quantitative yield.

n-BuLi (1.1 equiv, 33 mmol) was added drop by drop to the solution of S1 (30 mmol, 1.0 equiv) in THF at -78 °C under argon and stirred for 2 hours. Then ethyl formate (1.5 equiv, 45 mmol) was added and the resulting mixture was warmed to room temperature slowly overnight. Subsequently, the solvent was evacuated under reduced pressure and dichloromethane/brine was added for extraction. Then the organic phase was separated, dried with sodium sulfate and concentrated to provide 1c as colorless oil (8.50g, 28.5 mmol, 95% yield).

Method B[^1]:

![Chemical Reaction Diagram]
S3 was easily synthesized from 2-bromo-N-methoxy-N-methylacetamide S2 and triisopropyl phosphite with equivalent yield. S3 (3.0 mmol, 1.0 equiv) in 2 mL THF was added the drops to the dispersed solution of NaH (60% in oil, 3.3 mmol, 1.1 equiv) in 10 mL THF at 0 °C under argon flow and stirred for 30 min. Subsequently, 2-iodobenzyl bromide (3.9 mmol, 1.3 equiv) was added and continued to stir for 4 hours. After completion of the reaction as indicated by TLC analysis, the solvent was evacuated under reduced pressure and 20 mL brine was added. Then the resulting mixture was extracted with 3×20 mL dichloromethane and the combined organic phase was dried with sodium sulfate and concentrated to provide the crude S4 for next step.

LiAlH4 (3.3 mmol, 1.1 equiv) was dispersed in 20 mL diethyl ether at -40 °C under argon and S4 in 5 mL diethyl ether was added with drop by drop. After completion of addition, the resulting mixture was allowed to warm to room temperature slowly overnight. Subsequently, the reaction was quenched by addition of KHSO4 solution (2N, 5 mL). Ethyl acetate (10 mL×3) was then added and the organic phase was combined and dried with sodium sulfate. 1d was obtained by column chromatography on silica gel with ethyl acetate/petroleum ether (v/v = 1:1) as the eluent. 1d was achieved as colorless oil (445 mg, 1.05 mmol, 35% yield) and solidifying happens on standing. NMR analysis indicated the product as a mixture of aldehyde and enol and aldehyde is the favorable isomer on standing in CDCl3.

Method C:

S5 was synthesized from bromoacetaldehyde and triisopropyl phosphite with quantitative yield. Then S5 (20 mmol, 1.0 equiv) was added to a solution of 4N HCl at room temperature for 20h. After completion of the reaction as indicated by TLC, 3×20 mL dichloromethane was added for extraction. Then the organic phase was dried with sodium sulfate and concentrated to provide 1i as colorless oil with quantitative yield (4.10 g, 19.7 mmol).

1a-1c, 1j-1k, 1m-1p were synthesized by Method A. 1d-1f and 1h were synthesized by Method B. 1i was synthesized according to Method C. 1g was obtained by removing of TBS protecting group with KHF2 with almost quantitative yield[2]. 1B was synthesized according to literature method[3]. (NMR datas of enol isomers were marked in bold style.)
1a, Colorless oil, R_f = 0.60 (ethyl acetate/petroleum ether = 1:1). ^1H NMR (300 MHz, CDCl_3) δ 7.80 (d, J = 10.2 Hz, 1H), 7.55 (d, J = 7.0 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.39 (dd, J = 8.3, 5.9 Hz, 1H), 4.13 (dt, J = 10.0, 7.0 Hz, 2H), 3.93 (dt, J = 9.9, 7.2 Hz, 2H), 3.77 (d, J = 19.1 Hz, 2H), 1.67 – 1.48 (m, 1H), 1.36 (t, J = 7.1 Hz, 6H). ^13C NMR (75 MHz, CDCl_3) δ 157.6 (d, J = 29.0 Hz), 140.4 (d, J = 1.4 Hz), 128.6 (d, J = 6.9 Hz), 127.8 (s), 125.6 (s), 100.0 (s), 97.4 (s), 61.2 (d, J = 4.7 Hz), 29.2 (d, J = 7.0 Hz), 15.8 (d, J = 7.2 Hz). ^31P NMR (121 MHz, CDCl_3) δ 27.96 (s). HRMS (ESI) m/z: [M+H]^+ calcd for C_{13}H_{20}O_{4}P 271.1094; Found 271.1094.

1b, Colorless oil, Enol/aldehyde = 2.7:1.0, R_f = 0.29 (ethyl acetate/petroleum ether = 1:1). ^1H NMR (300 MHz, CDCl_3) δ 9.66 (s, 0.28H), 7.54 (d, J = 10.2 Hz, 0.72H), 7.05 – 7.32 (m, 5.23H), 4.07 (dd, J = 13.3, 6.6 Hz, 1.18H), 3.88 – 3.56 (m, 3.04H), 3.44 (d, J = 11.9 Hz, 0.72H), 3.35 (m, 0.59H), 3.20 – 3.03 (m, 0.28H), 1.63 (m, 1.46H), 1.52 – 1.16 (m, 8.08H), 0.90 (m, 6.52H). ^13C NMR (75 MHz, CDCl_3) δ 195.4 (d, J = 4.5 Hz), 157.5 (dd, J = 28.2, 11.4 Hz), 140.3, 138.2 (d, J = 6.5 Hz), 128.7, 128.6, 128.5, 127.9, 126.6, 125.6, 98.8 (d, J = 198.8 Hz), 66.5 (dd, J = 7.1, 4.1 Hz), 64.9 (d, J = 5.1 Hz), 54.8 (d, J = 123.8 Hz), 2.3 (d, J = 6.1 Hz), 32.0 (d, J = 71.7 Hz), 29.3 (d, J = 7.0 Hz), 29.1, 18.6, 13.5, 13.4. ^31P NMR (121 MHz, Chloroform-d) δ 27.06 (enol, major), 21.46. HRMS (ESI) m/z: [M+H]^+ calcd for C_{17}H_{22}O_{4}P 327.1720; Found 327.1718.

1c, Colorless oil, R_f = 0.40 (ethyl acetate/petroleum ether = 1:1). ^1H NMR (300 MHz, Chloroform-d) δ 9.74 – 9.60 (m, 1H), 7.29 – 7.13 (m, 5H), 4.76 (ddtt, J = 12.6, 8.8, 6.3, 4.4 Hz, 2H), 3.43 – 3.23 (m, 2H), 3.20 – 2.99 (m, 1H), 1.34 (m, 12H). ^13C NMR (75 MHz, Chloroform-d) δ 195.8 (d, J = 4.7 Hz), 138.6 (d, J = 14.5 Hz), 128.6, 128.4, 126.5, 73.7 – 69.7 (m), 55.7 (d, J = 124.3 Hz), 29.2 (d, J = 4.1 Hz), 25.3 – 22.0 (m). ^31P NMR (121 MHz, Chloroform-d) δ 19.80. HRMS (ESI) m/z: [M+H]^+ calcd for C_{15}H_{22}O_{4}P 299.1407; Found 299.1405.

1d, Colorless oil, Aldehyde/ Enol > 10:1, R_f = 0.50 (ethyl acetate/petroleum ether = 1:1). ^1H NMR (400 MHz, Chloroform-d) δ 9.75 – 9.67 (m, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.26 (dt, J = 14.9, 7.1 Hz, 2H), 6.89 (t, J = 6.8 Hz, 1H), 4.85 – 4.64 (m, 2H), 3.61 – 3.37 (m, 2H), 3.24 – 3.07 (m, 1H), 1.44 – 1.25 (m, 12H). ^13C NMR (101 MHz, Chloroform-d) δ 195.5 (d, J = 4.4 Hz), 140.6 (d, J = 13.4 Hz), 139.5, 131.0, 128.4, 128.1, 100.0, 71.7 (d, J = 6.9 Hz), 53.8 (d, J = 125.1 Hz), 34.4 (d, J = 3.8 Hz), 27.1 – 17.1 (m). ^31P NMR (162 MHz, Chloroform-d) δ 22.64 (enol, minor), 17.97. HRMS (ESI) m/z: [M+H]^+ calcd for C_{13}H_{23}O_{4}P 425.0373; Found 425.0374.
1e, Colorless oil, Aldehyde/ Enol > 10:1, $R_f = 0.50$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.69 (d, $J = 1.5$ Hz, 1H), 7.30 (dd, $J = 8.6, 6.1$ Hz, 1H), 7.08 (td, $J = 8.2, 2.6$ Hz, 1H), 6.89 (td, $J = 8.3, 2.6$ Hz, 1H), 4.89–4.68 (m, 2H), 3.56–3.41 (m, 1H), 3.41–3.32 (m, 1H), 3.23–3.08 (m, 1H), 1.34 (td, $J = 6.5, 4.6$ Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 195.4 (d, $J = 4.3$ Hz), 162.5, 160.0, 134.1 (d, $J = 10.3$ Hz), 132.7 (d, $J = 8.6$ Hz), 131.9 (dd, $J = 13.5, 3.6$ Hz), 116.6 (d, $J = 24.7$ Hz), 113.8 (d, $J = 20.9$ Hz), 71.8 (d, $J = 7.2$ Hz), 53.6 (d, $J = 125.0$ Hz), 26.8 (d, $J = 3.8$ Hz), 25.5–19.4 (m). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 22.42 (enol, minor), 18.03. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{15}$H$_{22}$ClFO$_4$P 351.0923; Found 351.0923.

1f, Colorless oil, Aldehyde/ Enol = 6.6:1.0, $R_f = 0.37$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-d) 9.69 (s, 1H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 4.77 (dq, $J = 12.7, 6.3$ Hz, 2H), 3.47–3.26 (m, 3H), 3.22–3.04 (m, 1H), 1.45–1.28 (m, 12H); enol: $\delta$ 10.67 (d, $J = 13.0$ Hz, 0.15H, enol), 4.52 (ddt, $J = 19.1, 13.4, 6.3$ Hz, 0.31H, enol), 1.09 (dd, $J = 24.0, 6.2$ Hz, 1.61H, enol). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 195.2 (d, $J = 4.6$ Hz), 142.9 (d, $J = 13.8$ Hz), 129.1, 128.7, 125.3 (d, $J = 3.8$ Hz), 123.6 (d, $J = 188.8$ Hz), 71.6 (t, $J = 7.3$ Hz), 55.5 (d, $J = 125.4$ Hz), 28.8 (d, $J = 3.8$ Hz), 25.7–20.1 (m). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 22.32 (enol, minor), 18.17. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{10}$H$_{12}$F$_3$O$_4$P 367.1281; Found 367.1282.

1g, Colorless oil, $R_f = 0.20$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.62 (d, $J = 2.0$ Hz, 1H), 7.04–6.95 (m, 2H), 6.77 (dd, $J = 9.0, 2.4$ Hz, 2H), 4.75 (dddd, $J = 12.4, 11.0, 5.2, 3.8$ Hz, 2H), 3.33–3.20 (m, 2H), 3.11–2.92 (m, 1H), 1.34 (dd, $J = 6.1, 4.4$ Hz, 12H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 196.1 (d, $J = 4.6$ Hz), 155.5, 129.6, 129.5–128.6 (m), 115.5, 72.1 (dd, $J = 7.0, 5.1$ Hz), 55.8 (d, $J = 124.7$ Hz), 28.5 (d, $J = 4.1$ Hz), 25.9–18.5 (m). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 19.08. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{13}$H$_{23}$O$_5$P 315.1356; Found 315.1356.

1h, Colorless oil, Aldehyde/ Enol > 10:1, $R_f = 0.55$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (300 MHz, Chloroform-d) $\delta$ 9.80–9.37 (m, 1H), 7.00 (d, $J = 8.5$ Hz, 2H), 6.85–6.57 (m, 2H), 4.94–4.54 (m, 2H), 3.41–3.12 (m, 2H), 3.09–2.88 (m, 1H), 1.45–1.20 (m, 12H), 0.93 (s, 9H), 0.13 (s, 6H). $^{13}$C NMR (151 MHz, Chloroform-d) $\delta$ 196.1, 154.2, 131.3 (d, $J = 14.6$ Hz), 120.0, 73.8–66.8 (m), 56.0 (d, $J = 123.8$ Hz), 28.6, 25.6, 24.4–21.6 (m), 18.1, -4.6.
$^{31}$P NMR (121 MHz, Chloroform-$d$) $\delta$ 24.30 (enol, minor), 19.93. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{31}$H$_{38}$O$_4$PSi 429.2221; Found 429.2218.

1i, Colorless oil, $R_f = 0.50$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.92 (t, $J = 3.3$ Hz, 1H), 4.04 (d, $J = 12.4$, 8.0, 6.2 Hz, 2H), 2.37 (dd, $J = 21.9$, 3.3 Hz, 2H), 0.64 (d, $J = 6.3$ Hz, 13H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 192.1 (d, $J = 6.2$ Hz), 70.3 (d, $J = 6.5$ Hz), 43.1 (d, $J = 128.1$ Hz), 27.6–16.7 (m). $^{31}$P NMR (121 MHz, Chloroform-$d$) $\delta$ 17.51. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_8$H$_{18}$O$_4$P 209.0937; Found 209.0937.

1j, Colorless oil, $R_f = 0.57$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 9.55 (d, $J = 2.5$ Hz, 1H), 5.65 (dddd, $J = 22.7$, 16.8, 8.9, 4.9 Hz, 1H), 5.07 – 4.79 (m, 2H), 4.63 (dddd, $J = 16.0$, 9.8, 5.2, 3.1 Hz, 2H), 2.88 (dddt, $J = 26.5$, 9.4, 3.0 Hz, 1H), 2.21 – 1.89 (m, 3H), 1.87 – 1.66 (m, 1H), 1.23 (dd, $J = 6.2$, 1.9 Hz, 12H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 196.4 (d, $J = 4.7$ Hz), 136.6, 116.1, 71.2 (dd, $J = 7.0$, 2.7 Hz), 52.9 (d, $J = 126.8$ Hz), 31.8 (d, $J = 13.7$ Hz), 23.8 (dd, $J = 7.7$, 4.3 Hz), 22.4 (d, $J = 4.3$ Hz). $^{31}$P NMR (121 MHz, Chloroform-$d$) $\delta$ 20.88. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{12}$H$_{32}$O$_4$P 263.1407; Found 263.1404.

1k, Colorless oil, Aldehyde/Enol $> 10:1$, $R_f = 0.43$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.69 (d, $J = 1.9$ Hz, 1H), 7.58 – 6.95 (m, 5H), 6.45 (d, $J = 15.8$ Hz, 1H), 6.31 – 5.93 (m, 1H), 4.76 (dq, $J = 12.7$, 6.3 Hz, 2H), 3.31 – 3.01 (m, 1H), 2.91 (dq, $J = 16.7$, 9.0 Hz, 1H), 2.79 – 2.56 (m, 1H), 1.49 – 1.21 (m, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 195.9 (d, $J = 4.3$ Hz), 136.7, 132.3, 128.3, 127.2, 126.0, 71.6 (t, $J = 6.5$ Hz), 53.8 (d, $J = 126.1$ Hz), 27.0 (d, $J = 4.1$ Hz), 25.4 – 20.0 (m). $^{31}$P NMR (162 MHz, Chloroform-$d$) $\delta$ 23.26 (enol, minor), 19.03. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{17}$H$_{26}$O$_4$P 325.1563; Found 325.1563.

1l, Colorless oil, $R_f = 0.55$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.66 (d, $J = 2.2$ Hz, 1H), 7.28 (t, $J = 7.3$ Hz, 2H), 7.18 (dd, $J = 16.4$, 7.3 Hz, 3H), 4.81 – 4.57 (m, 2H), 2.95 (ddt, $J = 26.7$, 9.8, 3.1 Hz, 1H), 2.74 (dddd, $J = 14.4$, 9.2, 5.5 Hz, 1H), 2.68 – 2.51 (m, 1H), 2.45 – 2.25 (m, 1H), 2.16 – 1.88 (m, 1H), 1.39 – 1.24 (m, 12H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 196.5 (d, $J = 4.6$ Hz), 140.4, 128.4, 126.2, 71.3 (d, $J = 6.9$ Hz), 53.1 (d, $J = 126.6$ Hz), 33.8 (d, $J = 13.5$ Hz), 25.1 (d, $J = 4.2$ Hz), 24.3 – 23.2 (m). $^{31}$P NMR (162 MHz, Chloroform-$d$) $\delta$ 19.59. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{16}$H$_{26}$O$_4$P 313.1563; Found 313.1563.
1m, Colorless oil, $R_f = 0.55$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 9.64 (s, 1H), 5.07 – 4.47 (m, 2H), 1.86 – 1.68 (m, 1H), 1.63 – 1.10 (m, 12H), 0.94 (t, $J = 7.2$ Hz, 2H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 196.3, 70.8, 53.4 (d, $J = 126.6$ Hz), 25.1 (d, $J = 4.7$ Hz), 24.4 – 22.8 (m), 21.1 (d, $J = 14.0$ Hz), 13.3. $^{31}$P NMR (121 MHz, Chloroform-$d$) $\delta$ 20.84. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{11}$H$_{24}$O$_4$P 251.1407; Found 251.1405.

1n, Colorless oil, $R_f = 0.55$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.62 (d, $J = 3.1$ Hz, 1H), 4.92 – 4.55 (m, 2H), 2.99 (ddt, $J = 26.2, 10.4, 3.1$ Hz, 1H), 2.11 – 1.89 (m, 1H), 1.60 (dd, $J = 12.4, 8.6$ Hz), 1.33 (m, 12H), 1.26 (m, 1H), 0.86 – 0.59 (m, 2H), 0.55 – 0.37 (m, 1H), 0.28 – 0.05 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 196.9 (d, $J = 4.9$ Hz), 71.2 (dd, $J = 7.0, 4.0$ Hz), 52.2 (d, $J = 126.3$ Hz), 32.1 (d, $J = 4.9$ Hz), 26.6 (d, $J = 13.3$ Hz), 23.8 (dd, $J = 11.9, 4.4$ Hz), 22.8, 21.2. $^{31}$P NMR (162 MHz, Chloroform-$d$) $\delta$ 20.23. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{12}$H$_{26}$O$_4$P 265.1563; Found 265.1562.

1o, Colorless oil, Aldehyde/ Enol > 10:1, $R_f = 0.59$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 9.70 (dd, $J = 3.1, 2.2$ Hz, 1H), 4.79 (m, 2H), 2.39 – 1.97 (m, 1H), 1.36 (qd, $J = 6.8, 6.3, 2.2$ Hz, 12H), 1.26 (m, 1H), 0.86 – 0.59 (m, 2H), 0.55 – 0.37 (m, 1H), 0.28 – 0.05 (m, 1H). $^{13}$C NMR (75 MHz, Chloroform-$d$) $\delta$ 196.3, 71.3 (d, $J = 5.5$ Hz), 58.3 (d, $J = 130.0$ Hz), 30.5 – 20.7 (m), 5.5 (d, $J = 5.1$ Hz), 4.0 (t, $J = 7.3$ Hz). $^{31}$P NMR (121 MHz, Chloroform-$d$) $\delta$ 24.46 (enol, minor). 19.62. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{11}$H$_{22}$O$_4$P 249.1250; Found 249.1250.

1p, Colorless oil, $R_f = 0.59$ (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.46 (d, $J = 1.0$ Hz, 1H), 4.50 – 3.62 (m, 4H), 1.24 (s, 3H), 1.22 – 1.14 (m, 9H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 199.0 (d, $J = 1.9$ Hz), 62.6 (d, $J = 7.3$ Hz), 48.7 (d, $J = 133.1$ Hz), 16.7 (d, $J = 5.0$ Hz), 16.1 (d, $J = 5.7$ Hz). $^{31}$P NMR (162 MHz, Chloroform-$d$) $\delta$ 26.43. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_8$H$_{18}$O$_4$P 209.0937; Found 209.0937.
Table S1: Screening of catalysts

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*Reaction Conditions: cat. (0.01 mmol), 1a (0.10 mmol), 2a (0.11 mmol), 4Å MS (50 mg), toluene (1.0 mL), under argon for 48 h at 110 °C. ^Isolated yield. ^Reaction with 5 mol% metal catalyst.
4. Reaction Optimization

General Procedure

Under argon, the indicated catalyst, additive, 1a, 2a and 4Å molecular sieve (50 mg) were added to an oven-dried 10 mL glass tube equipped with a stirring bar. The tube was filled with a rubber plug to ensure inert (argon) atmosphere. Solvent was added and the mixture was stirred for 2 minutes at room temperature before moving it to a pre-heated oil bath. After completion of the reaction indicated by thin-layer chromatography analysis, the product was obtained by column chromatography on silica gel. Reaction temperature (entries 1-5 and 37-40), solvent (entries 6-13), antagonistic anion of the bismuth catalyst (entries 14-26), additive (entries 27-32), catalyst loading (entries 33-36) and concentration (entries 41-42) were investigated and the results were summarized in the following table. **The best conditions are Bi(OTf)$_3$ (0.005 mmol), 1a (0.10 mmol), 2a (0.11 mmol), 4Å MS (50 mg), DCE (1.0 mL), under argon for 60 h at 100 °C.**

### Table S2: Reaction Optimization

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<th>Solvent</th>
<th>Temp [°C]</th>
<th>Result [%]</th>
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5. Experimental details and Characterization data

5.1. Relative configuration Analysis of products

Figure 1. $^1$HNMR spectrum of product A
Figure 2. $^{13}$C NMR spectrum of product A

Figure 3. HSQC spectrum of product A
Figure 4. 2D NOE spectrum of product A
(Green lines are NOE signals and red lines are H-H Cosey signals)

Configuration analysis of two diasteromers

Figure 5. Configuration analysis and proposed pathway
The reaction of 1c and 2a gave rise to two diastereomers A and B; product A is the major product and more polar under TLC analysis. With spectrum analysis of the $^1$HNMR (Figure 1), $^{13}$CNMR (Figure 2), HSQC (Figure 3), 2D NOE (Figure 4) of product A and H-H interaction analysis of threo- and erythro-isomers (Figure 5), the relative configuration of A is confirmed to be (±)-threo-3c" and another isomer B is defined as (±)-threo-3c'. In similar to the case of 3c, the configurations of other products are defined as that the more polar one is (±)-threo-isomer and the less polar one is (±)-threo-isomer.

5.2 General procedure for the reaction

Bi(OTf)$_3$ (3.4 mg, 0.01 mmol, 0.10 equiv), β-formyl phosphonate 1a-1o (0.10 mmol, 1.0 equiv), amine 2a and 4Å molecular sieve (50 mg) were added to an oven-dried 10 mL glass tube equipped with a stirring bar under argon atmosphere. Then the tube was filled with a rubber plug and 1,2-dichlorethane (1.0 mL) was added with a syringe. After stirring at room temperature for 2 minutes, the tube was moved to a pre-heated oil bath and stirring was continued for 60h. Upon completion of the reaction as indicated by TLC analysis, the products 3a′-3o′ and 3a″-3o″ were achieved by column chromatography on silica gel by using EA/PE (v/v = 1:10 to 1:5) as the eluant.

Et$_3$N was added to the eluant (0.5 mL Et$_3$N/200 mL) to prevent the product from hydrolysis on silica gel. For 3a, 3b and 3g, the two diastereomers were not isolated by column chromatography and NMR data of the corresponding erythro-isomers were marked in bold style.

3a, 76% yield, 36 mg, erythro/threo ≈ 1/1.7, colorless oil, $R_f$ = 0.26 (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 – 7.65 (m, 2H), 7.45 – 7.20 (m, 8H), 7.17 – 6.97 (m, 5H), 5.62 – 5.36 (m, 1H), 5.06 – 4.74 (m, 2H), 4.12 – 3.74 (m, 5.06H), 3.45 (ddd, $J = 26.2, 13.7, 6.4$ Hz, 0.37H), 3.32 – 3.18 (m, 0.37H), 3.16 – 3.02 (m, 1.26H), 2.92 – 2.72 (m, 0.63H), 2.49 (ddt, $J = 21.7, 15.5, 7.8$ Hz, 1.26H), 2.35 (ddt, $J = 21.3, 6.6, 2.1$ Hz, 0.64H), 2.29 – 2.19 (m, 0.38H), 1.21 – 0.97 (m, 6.0H), $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.0 (d, $J = 5.5$ Hz), 166.9 (s), 140.9 (s), 140.0 (t, $J = 7.7$ Hz), 139.6 (dd, $J = 18.7, 11.4$ Hz), 136.3 (s), 136.1 (s), 135.3 (s), 134.4 (s), 129.4 (s), 128.7 (s), 128.4 (s), 128.3 (s), 128.1 (s), 127.9 (s), 127.8 (s), 127.7 (s), 127.6 (s), 127.4 (s), 125.4 (s), 117.2 (s), 116.6 (s), 61.0 (d, $J = 6.6$ Hz), 60.7 (dd, $J = 11.0, 6.8$ Hz), 60.4 (d, $J = 6.9$ Hz), 60.2 (s), 59.4 (s), 43.6 (dd, $J = 91.7, 57.2$ Hz), 41.8 (dd, $J = 119.2, 30.9$ Hz), 38.2 (t, $J = 14.6$ Hz).
Hz), 37.3 (d, J = 47.6 Hz), 31.0 (d, J = 24.9 Hz), 30.0 (d, J = 14.5 Hz), 24.6 – 24.0 (m), 15.0 (dt, J = 472.8, 233.7 Hz). $^3$P NMR (162 MHz, CDCl$_3$) δ 32.20 (s, erythro), 30.82 (s, threo). HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{29}$H$_{35}$NO$_3$P 476.2349; Found 476.2347.

3b, 56% yield, 30 mg, erythro/threo ≈ 1/1.3, colorless oil, R$_f$ = 0.39 (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.65 (dd, J = 5.4, 2.9 Hz, 2H), 7.45 – 7.00 (m, 13H), 5.64 – 5.31 (m, 1H), 5.07 – 4.72 (m, 2H), 4.13 – 3.65 (m, 5H), 3.54 – 3.32 (m, 0.43H), 3.31 – 2.99 (m, 1.55H), 2.86 – 2.68 (m, 0.56H), 2.63 – 2.09 (m, 2.63H), 1.61 – 1.09 (m, 8H), 0.97 – 0.69 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.3 (s), 167.2 (d, J = 3.3 Hz), 141.4 (d, J = 8.5 Hz), 140.6 (d, J = 8.6 Hz), 140.1 (d, J = 11.5 Hz), 136.7 (s), 136.5 (s), 135.9 (s), 134.9 (s), 129.8 (s), 129.7 – 129.7 (m), 129.2 (s), 128.9 (s), 128.8 (s), 128.5 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.8 (s), 125.8 (s), 116.8 (d, J = 16.2 Hz), 65.1 (dd, J = 16.0, 7.0 Hz), 64.8 (dd, J = 10.4, 7.1 Hz), 60.6 (s), 59.6 (d, J = 11.7 Hz), 45.6 – 43.4 (m), 43.3 – 41.4 (m), 38.9 – 38.5 (m), 37.8 (d, J = 23.2 Hz), 32.4 (dd, J = 10.9, 6.2 Hz), 31.3 (d, J = 14.3 Hz), 30.4 (d, J = 15.6 Hz), 29.5 (d, J = 14.5 Hz), 19.0 – 18.1 (m), 13.5 (d, J = 4.8 Hz). $^3$P NMR (121 MHz, CDCl$_3$) δ 33.18 (s, erythro), 31.61 (s, threo). HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{33}$H$_{43}$NO$_3$P 532.2975; Found 532.2974.

3c', (+)-erythro-3c, 26% yield, 13 mg, colorless oil, R$_f$ = 0.27 (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.73 – 7.58 (m, 2H), 7.51 – 7.08 (m, 13H), 5.41 (td, J = 16.6, 8.4 Hz, 1H), 4.90 (d, J = 10.0 Hz, 1H), 4.75 (d, J = 17.0 Hz, 1H), 4.65 – 4.45 (m, 2H), 3.55 – 3.33 (m, 1H), 3.19 (td, J = 15.2, 6.5 Hz, 1H), 2.48 – 2.27 (m, 2H), 2.23 – 2.03 (m, 1H), 1.21 (d, J = 6.2 Hz, 3H), 1.10 (d, J = 6.2 Hz, 3H), 1.03 (dd, J = 10.6, 6.2 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 166.9 (s), 141.8 (d, J = 8.9 Hz), 140.3 (s), 136.6 (s), 134.9 (s), 129.7 (s), 129.4 (s), 128.6 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.8 (s), 125.7 (s), 117.6 (s), 69.6 (d, J = 7.2 Hz), 59.7 (d, J = 2.4 Hz), 44.0 (s), 42.2 (s), 39.1 (d, J = 13.2 Hz), 30.5 (d, J = 2.9 Hz), 23.9 (ddd, J = 14.9, 9.0, 4.1 Hz). $^3$P NMR (121 MHz, CDCl$_3$) δ 30.10 (s). HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{31}$H$_{39}$NO$_3$P 504.2662; Found 504.2661.

3c'', (+)-threo-3c, 46% yield, 23 mg, colorless oil, R$_f$ = 0.25 (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.63 (dd, J = 8.2, 1.4 Hz, 1H), 7.49 – 7.23 (m, 6H), 7.22 – 6.99 (m, 7H), 5.64 – 5.38 (m, 1H), 4.95 (t, J = 12.5 Hz, 3H), 4.63 (ddd, J = 25.9, 13.4, 6.1 Hz, 2H), 3.93 – 3.74 (m, 1H), 3.26 – 2.95 (m, 2H), 2.90 – 2.70 (m, 1H), 2.64 – 2.43 (m, 1H), 2.23 (ddd, J = 21.9, 6.5, 4.3 Hz, 1H), 1.21 (d, J = 6.1 Hz, 6H), 1.08 (d, J = 6.2 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.1 (s), 141.0 (d, J = 8.9 Hz), 140.1 (s), 136.9 (s), 136.2 (s), 129.7 (s), 129.0 (s), 128.8 (s), 128.3 (s), 128.2 (s), 128.0 (s), 127.8 (s), 125.7 (s), 116.8 (s), 69.7 (dd, J = 23.2, 7.2 Hz), 60.6 (s), 45.2 (d, J = 138.6 Hz), 37.8 (s), 31.3 (d, J = 2.9 Hz), 24.1 (dd, J = 6.6, 3.5 Hz), 23.8 (dd, J =
11.6, 5.2 Hz). $^{31}$P NMR (121 MHz, CDCl$_3$) δ 29.13 (s). HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{31}$H$_{33}$NO$_3$P 504.2662; Found 504.2661.

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 29.13 (s). HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{31}$H$_{33}$NO$_3$P 504.2662; Found 504.2661.

3d', (±)-erythro-3d, 20% yield, 13 mg, colorless oil, R$_f$ = 0.26 (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (t, $J$ = 7.7 Hz, 1H), 7.66 (d, $J$ = 6.9 Hz, 2H), 7.48 (t, $J$ = 6.8 Hz, 1H), 7.44 – 7.18 (m, 10H), 6.87 (t, $J$ = 7.0 Hz, 1H), 5.45 (dq, $J$ = 10.0, 7.3 Hz, 1H), 4.88 (d, $J$ = 10.1 Hz, 1H), 4.73 (d, $J$ = 17.1 Hz, 1H), 4.67 – 4.48 (m, 2H), 4.05 (ddd, $J$ = 21.0, 7.0, 2.6 Hz, 1H), 2.43 – 2.28 (m, 1H), 2.26 – 2.12 (m, 1H), 1.22 (d, $J$ = 6.1 Hz, 3H), 1.12 – 1.00 (m, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 127.2 (s), 142.8 (d, $J$ = 7.6 Hz), 140.4 (s), 139.4 (s), 137.6 (s), 136.6 (s), 135.3 (s), 132.4 (s), 131.8 (s), 130.0 (s), 129.7 (s), 128.7 (s), 128.3 (s), 128.1 (s), 127.8 (s), 127.6 (s), 127.3 (s), 101.0 (s), 100.6 (s), 69.8 – 69.7 (m), 59.8 (s), 41.2 (d, $J$ = 140.4 Hz), 39.4 (d, $J$ = 12.4 Hz), 35.9 (s), 24.2 – 23.8 (m). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 29.38 (s). HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{31}$H$_{33}$NO$_3$P 630.1629; Found 630.1629.

3d", (±)-threo-3d, 32% yield, 20 mg, colorless oil, R$_f$ = 0.23 (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J$ = 7.7 Hz, 1H), 7.64 (d, $J$ = 7.3 Hz, 2H), 7.43 – 7.22 (m, 8H), 7.16 (dd, $J$ = 8.6, 4.1 Hz, 2H), 6.83 (t, $J$ = 7.6 Hz, 1H), 5.58 (td, $J$ = 17.2, 7.2 Hz, 1H), 4.99 (dd, $J$ = 22.0, 13.7 Hz, 2H), 4.53 (dd, $J$ = 31.8, 12.6, 6.3 Hz, 2H), 3.96 – 3.80 (m, 1H), 3.36 (ddd, $J$ = 26.4, 14.2, 5.7 Hz, 1H), 3.17 (dt, $J$ = 23.3, 11.7 Hz, 1H), 2.89 – 2.74 (m, 1H), 2.70 – 2.56 (m, 1H), 2.55 – 2.42 (m, 1H), 1.14 (dd, $J$ = 10.4, 6.2 Hz, 6H), 1.01 (dd, $J$ = 17.8, 6.2 Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 167.2 (s), 142.9 (d, $J$ = 7.0 Hz), 139.8 (s), 139.4 (s), 137.0 (s), 136.0 (s), 132.4 (s), 131.4 (s), 130.0 (s), 129.7 (s), 128.9 (s), 128.3 (s), 128.1 (s), 127.8 (s), 127.7 (s), 116.7 (s), 100.6 (s), 69.7 (dd, $J$ = 42.2, 6.9 Hz), 60.8 (s), 42.6 (d, $J$ = 142.7 Hz), 36.8 (d, $J$ = 159.5 Hz), 29.4 (s), 23.77 (m). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.23 (s). HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{31}$H$_{33}$NO$_3$P 630.1629; Found 630.1630.

3e', (±)-erythro-3e, 20% yield, 11 mg, colorless oil, R$_f$ = 0.26 (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 – 7.78 (m, 1H), 7.63 (dd, $J$ = 6.7, 5.1 Hz, 2H), 7.52 – 7.24 (m, 8H), 7.06 (dd, $J$ = 8.6, 2.6 Hz, 1H), 6.88 (td, $J$ = 8.3, 2.7 Hz, 1H), 5.59 – 5.37 (m, 1H), 4.91 (d, $J$ = 10.1 Hz, 1H), 4.80 (d, $J$ = 17.1 Hz, 1H), 4.60 – 4.47 (m, 2H), 4.14 – 3.99 (m, 1H), 3.58 – 3.41 (m, 1H), 3.38 – 3.22 (m, 1H), 2.53 (dd, $J$ = 20.8, 7.1, 2.5 Hz, 1H), 2.45 – 2.31 (m, 1H), 2.19 (dd, $J$ = 18.6, 11.8 Hz, 1H), 1.21 (d, $J$ = 6.2 Hz, 3H), 1.12 – 1.07 (d, $J$ = 6.2 Hz, 3H), 1.04 (dd, $J$ = 8.4, 6.2 Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.8 (s), 160.4 (d, $J$ = 249.2 Hz), 140.0 (s), 136.4 (s), 135.0 (s), 134.6 (d, $J$ = 10.2 Hz), 133.4 (d, $J$ = 7.6 Hz), 132.4 (s),
130.0 (s), 129.8 (s), 128.6 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.8 (s), 117.5 (s), 116.4 (d, \( J = 24.2 \) Hz), 113.4 (d, \( J = 15.2 \) Hz), 69.8 (d, \( J = 5.7 \) Hz), 59.8 (s), 41.0 (d, \( J = 151.0 \) Hz), 39.1 (d, \( J = 12.0 \) Hz), 29.0 (d, \( J = 188.8 \) Hz), 23.9 (m). \(^{31}\)P NMR (121 MHz, CDCl\(_3\)) \( \delta \) 29.55 (s). HRMS (ESI) m/z: [M+H]\(^+\) calcd for C\(_{31}\)H\(_{37}\)ClFNO\(_3\)P 556.2178; Found 556.2180.

3e\(^{\prime\prime}\), (±)-threo-3e, 34% yield, 19 mg, colorless oil, \( R_f = 0.23 \) (ethyl acetate/petroleum ether = 1:5). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.59 (t, \( J = 7.2 \) Hz, 2H), 7.45 – 7.24 (m, 6H), 7.18 – 7.09 (m, 3H), 7.01 (dd, \( J = 8.6, 2.5 \) Hz, 1H), 6.80 (td, \( J = 8.3, 2.5 \) Hz, 1H), 6.80 (td, \( J = 8.3, 2.5 \) Hz, 1H), 5.67 – 5.47 (m, 1H), 5.06 – 4.89 (m, 2H), 4.69 – 4.41 (m, 2H), 3.94 – 3.76 (m, 1H), 3.49 – 3.26 (m, 1H), 3.20 – 3.00 (m, 1H), 2.87 – 2.69 (m, 1H), 2.69 – 2.54 (m, 1H), 2.50 – 2.26 (m, 1H), 1.19 – 1.14 (d, \( J = 6.2 \) Hz, 6H), 1.04 (dd, \( J = 11.7, 6.2 \) Hz, 6H). \(^13\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 166.9 (s), 161.0 (d, \( J = 286.0 \) Hz), 139.7 (s), 137.0 (s), 136.0 (s), 134.6 (d, \( J = 10.6 \) Hz), 134.1 (m), 132.9 (d, \( J = 8.5 \) Hz), 130.0 (s), 129.8 (s), 128.7 (s), 128.4 (s), 128.3 (s), 128.2 (s), 127.9 (s), 127.8 (s), 116.8 (s), 116.4 (d, \( J = 24.5 \) Hz), 113.3 (d, \( J = 21.2 \) Hz), 69.8 (dt, \( J = 63.5, 27.1 \) Hz), 60.71 (s), 42.9 (d, \( J = 97.5 \) Hz), 37.0 (s), 28.9 (m), 23.7 (ddd, \( J = 92.8, 55.7, 46.2 \) Hz). \(^3\)P NMR (162 MHz, CDCl\(_3\)) \( \delta \) 27.43 (d, \( J = 122.3 \) Hz). HRMS (ESI) m/z: [M+H]\(^+\) calcd for C\(_{31}\)H\(_{37}\)ClFNO\(_3\)P 556.2178; Found 556.2178.

3f\(^{\prime\prime}\), (±)-erythro-3f, 24% yield, 14 mg, colorless oil, \( R_f = 0.26 \) (ethyl acetate/petroleum ether = 1:5). \(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.64 – 7.58 (m, 2H), 7.51 (d, \( J = 8.1 \) Hz, 2H), 7.46 – 7.25 (m, 10H), 5.46 (m, 1H), 4.95 (d, \( J = 10.0 \) Hz, 1H), 4.82 (d, \( J = 17.1 \) Hz, 1H), 4.54 (m, 2H), 4.05 (m, 1H), 3.43 (ddd, \( J = 20.6, 14.5, 5.7 \) Hz, 1H), 3.24 (td, \( J = 15.0, 7.1 \) Hz, 1H), 2.43 – 2.29 (m, 2H), 2.23 – 2.13 (m, 1H), 1.21 (d, \( J = 6.2 \) Hz, 3H), 1.06 (dd, \( J = 8.5, 6.2 \) Hz, 6H), 1.00 (d, \( J = 6.2 \) Hz, 3H). \(^13\)C NMR (151 MHz, Chloroform-d) \( \delta \) 167.3, 146.0 (d, \( J = 7.5 \) Hz), 140.2, 136.5, 134.9, 129.9, 129.7, 128.6, 128.2, 128.2, 128.1, 127.8, 124.9 (d, \( J = 3.7 \) Hz), 117.7, 69.9, 59.7, 43.2 (d, \( J = 143.5 \) Hz), 39.2 (d, \( J = 12.0 \) Hz), 30.2 (d, \( J = 161.7 \) Hz), 26.4 – 21.8 (m). \(^3\)P NMR (162 MHz, Chloroform-d) \( \delta \) 29.72. HRMS (ESI) m/z: [M+H]\(^+\) calcd for C\(_{32}\)H\(_{38}\)F\(_3\)NO\(_3\)P 572.2536; Found 572.2536.

3f\(^{\prime\prime}\), (±)-threo-3f, 44% yield, 25 mg, colorless oil, \( R_f = 0.23 \) (ethyl acetate/petroleum ether = 1:5). \(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.58 – 7.53 (m, 2H), 7.46 – 7.34 (m, 5H), 7.32 – 7.25 (m, 3H), 7.22 (d, \( J = 8.1 \) Hz, 2H), 7.14 – 7.08 (m, 2H), 5.52 (ddt, \( J = 17.2, 10.0, 7.2 \) Hz, 1H), 5.06 – 4.88 (m, 2H), 4.71 – 4.49 (m, 2H), 3.92 – 3.78 (m, 1H), 3.28 (ddd, \( J = 19.6, 14.4, 6.5 \) Hz, 1H), 3.10 (td, \( J = 14.4, 6.7 \) Hz, 1H), 2.79 (ddd, \( J = 12.3, 7.4, 4.4 \) Hz, 1H), 2.53 (dt, \( J = 14.3, 7.9 \) Hz, 1H), 2.20 (ddd, \( J = 22.2, 6.6, 2.4 \) Hz, 1H), 1.20 (ddd, \( J = 6.2, 1.7 \) Hz, 6H), 1.07

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(dd, \(J = 6.1, 3.9\) Hz, 6H). \(^{13}\)C NMR (151 MHz, Chloroform-d) \(\delta\) 167.2, 145.5 (d, \(J = 7.6\) Hz), 139.8, 136.8, 136.0, 129.9, 129.4, 128.7, 128.4, 128.0, 127.8, 125.0 (d, \(J = 3.7\) Hz), 116.9, 70.0 (dd, \(J = 65.6, 7.2\) Hz), 60.6, 45.3 (d, \(J = 139.3\) Hz), 37.4, 30.3 (d, \(J = 194.6\) Hz), 25.6 – 21.8 (m). \(^{31}\)P NMR (162 MHz, Chloroform-d) \(\delta\) 27.82. HRMS (ESI) m/z: [M+H]+ caleld for C\(_{32}\)H\(_{38}\)F\(_2\)NO\(_3\)P 572.2536; Found 572.2536.

3g, 40% yield, 21 mg, erytrol/threo \(\approx 1/2.5\), colorless oil, \(R_f = 0.09\) (ethyl acetate/petroleum ether = 1:5), the product was obtained by twice column chromatography on silica gel. \(^{1}H\) NMR (400 MHz, Chloroform-d) \(\delta\) 7.82 (s, 1H), 7.73 – 7.57 (m, 2H), 7.46 – 7.18 (m, 7H), 7.13 (dd, \(J = 7.6, 1.5\) Hz, 2H), 6.85 (d, \(J = 8.4\) Hz, 1H), 6.68 (dd, \(J = 27.8, 8.5\) Hz, 2H), 5.59 – 5.34 (m, 1H), 5.02 – 4.74 (m, 2H), 4.74 – 4.48 (m, 2H), 4.05 – 3.91 (m, 0.28H), 3.89 – 3.72 (m, 0.72H), 3.39 (ddd, \(J = 20.3, 14.9, 5.7\) Hz, 0.29H), 3.18 – 3.01 (m, 1H), 2.94 (td, \(J = 14.5, 7.0\) Hz, 0.72H), 2.72 (dt, \(J = 12.9, 6.2\) Hz, 0.72H), 2.47 (ddd, \(J = 28.1, 14.4, 7.9\) Hz, 1H), 2.37 – 2.25 (m, 0.28H), 2.20 (ddd, \(J = 21.9, 6.6, 2.3\) Hz, 0.72H), 1.26 – 0.97 (m, 12H). major isomer: \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 167.3, 155.1, 140.0, 136.8, 136.1, 131.3 (d, \(J = 8.1\) Hz), 129.8, 128.8, 128.3, 128.1, 128. 0, 127.8, 116.9, 115.2, 70.0 (d, \(J = 7.3\) Hz), 60.6, 45.5 (d, \(J = 137.6\) Hz), 37.7, 29.9 (d, \(J = 88.4\) Hz), 23.9 – 23.5 (m). minor isomer: \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 166.9, 155.1, 140.3, 136.6, 134.8, 132.3 (d, \(J = 8.4\) Hz), 130.1, 128.6, 128.2, 128.1, 128. 0, 127.8, 117.8, 115.2, 70.3 (d, \(J = 7.3\) Hz), 60.0, 43.3 (d, \(J = 139.3\) Hz), 39.1, 29.9 (d, \(J = 88.4\) Hz), 24.1 (dd, \(J = 12.4, 3.4\) Hz). \(^{31}\)P NMR (162 MHz, Chloroform-d) \(\delta\) 28.78 (threo), 30.65(erythro). HRMS (ESI) m/z: [M+H]+ caleld for C\(_{31}\)H\(_{39}\)NO\(_3\)P 520.2611; Found 520.2610.

3h’, (±)-erythro-3h, 20% yield, 13mg, colorless oil, \(R_f = 0.34\) (ethyl acetate/petroleum ether = 1:5). \(^{1}H\) NMR (600 MHz, Chloroform-d) \(\delta\) 7.65 (d, \(J = 7.2\) Hz), 7.43 – 7.34 (m, 4H), 7.32 (t, 2H), 7.27 (t, 2H), 7.19 (d, \(J = 8.3\) Hz, 2H), 6.73 (d, \(J = 8.5\) Hz, 2H), 5.42 – 5.35 (m, 1H), 4.87 (d, \(J = 10.2\) Hz, 1H), 4.72 (d, \(J = 17.1\) Hz, 1H), 4.56 – 4.51 (m, 2H), 4.03 – 3.98 (m, 1H), 3.42 – 3.35 (m, 1H), 3.1 (dd, \(J = 15.0, 6.1\) Hz, 1H), 2.35 – 2.27 (m, 2H), 2.10 – 2.07 (m, 1H), 1.21 (d, \(J = 6.2\) Hz, 3H), 1.12 (d, \(J = 6.2\) Hz, 3H), 1.04 (d, \(J = 6.2\) Hz, 3H), 1.02 (d, \(J = 6.2\) Hz, 3H), 0.98 (s, 9H), 0.18 (s, 6H). \(^{13}\)C NMR (151 MHz, Chloroform-d) \(\delta\) 166.9, 153.7, 140.4, 136.7, 135.0, 134.6 (d, \(J = 9.0\) Hz), 130.3, 129.7, 128.6, 128.2, 128.1, 127.8, 119.7, 117.6, 69.6 (dd, \(J = 11.3, 4.4\) Hz), 59.8 (d, \(J = 2.2\) Hz), 43.2 (d, \(J = 139.0\) Hz), 39.1 (d, \(J = 13.6\) Hz), 29.6 (d, \(J = 2.2\) Hz), 25.7, 24.0 (m), 18.2, –4.4. \(^{31}\)P NMR (162 MHz, Chloroform-d) \(\delta\) 30.73. HRMS (ESI) m/z: [M+H]+ caleld for C\(_{37}\)H\(_{39}\)NO\(_3\)PSi 634.3476; Found 634.3476.

3h”, (±)-threo-3h, 30% yield, 19 mg, colorless oil, \(R_f = 0.31\) (ethyl acetate/petroleum ether = 1:5). \(^{1}H\) NMR (600 MHz, Chloroform-d) \(\delta\) 7.67 (d, \(J = 7.2\) Hz), 7.42 – 7.29 (m, 6H), 7.18 – 7.09 (m, 2H), 6.86 (d, \(J = 8.4\) Hz, 2H), 6.62 (d, \(J = 8.4\) Hz, 2H), 5.52 – 5.42 (m, 1H), 4.95 (d,
J = 17.2, 1H), 4.91 (d, J = 10.2, 1H), 4.71 – 4.65 (m, 1H), 4.64 – 4.58 (m, 1H), 3.86 – 3.74 (m, 1H), 3.05 – 2.92 (m, 1H), 2.85 – 2.74 (m, 1H), 2.53 – 2.43 (m, 1H), 2.23 – 2.13 (m, 1H), 1.22 (d, J = 6.2, 1.4 Hz, 6H), 1.10 (dd, J = 11.2, 6.2 Hz), 0.96 (s, 9H), 0.14 (s, 6H). $^{13}$C NMR (151 MHz, Chloroform-d) $\delta$ 167.1, 153.6, 140.1, 136.9, 136.1, 129.8, 129.7, 128.8, 128.3, 128.2, 128.1, 127.8, 119.6, 116.8, 69.6 (dd, J = 59.0, 6.9 Hz), 69.4 (d, J = 7.9 Hz), 60.6, 45.3 (d, J = 138.0 Hz), 38.0, 30.6 (d, J = 2.3 Hz), 25.7, 23.9 (m), 18.2, -4.5 (d, J = 2.2 Hz). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 28.86. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_3$H$_{15}$NO$_3$PSi 634.3476; Found 634.3476.

![Image of 3i](image)

3i, 51% yield, 21 mg, colorless oil, R$_f$ = 0.33 (ethyl acetate/petroleum ether = 1:5).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.61 – 7.56 (m, 2H), 7.47 – 7.39 (m, 34H), 7.36 – 7.23 (m, 5H), 5.63 (dt, J = 17.3, 10.1, 7.2 Hz, 1H), 5.08 – 4.96 (m, 2H), 4.62 (ddd, J = 12.3, 10.8, 6.2, 3.0 Hz, 2H), 3.91 – 3.78 (m, 1H), 2.44 (dt, J = 12.7, 6.7 Hz, 1H), 2.32 (dt, J = 13.7, 6.7 Hz, 1H), 2.10 (ddd, J = 18.1, 6.3, 4.1 Hz, 2H), 1.24 (d, J = 7.5 Hz, 6H), 1.17 (d, J = 6.2 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-d) $\delta$ 167.1, 140.1, 136.8, 135.0, 129.7, 128.5, 128.2, 128.1, 127.8, 117.4, 69.9 (dd, J = 12.3, 6.6 Hz), 56.6, 41.8 (d, J = 11.6 Hz), 33.5 (d, J = 141.1 Hz), 23.9 (dd, J = 11.2, 4.3 Hz). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 27.74. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{28}$H$_{33}$NO$_3$P 414.2193; Found 414.2190.

3j', (±)-erythro-3j, 29% yield, 14 mg, colorless oil, R$_f$ = 0.31 (ethyl acetate/petroleum ether = 1:5).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.63 – 7.57 (m, 2H), 7.46 – 7.38 (m, 32H), 7.35 – 7.24 (m, 5H), 5.92 – 5.79 (m, 1H), 5.62 – 5.49 (m, 1H), 5.09 – 4.94 (m, 4H), 4.69 – 4.49 (m, 2H), 4.01 – 3.85 (m, 1H), 2.51 (dt, J = 14.9, 7.8 Hz, 1H), 2.38 (dq, J = 14.6, 6.5 Hz, 1H), 2.25 (dq, J = 14.1, 7.8, 6.8 Hz, 2H), 2.12 – 1.84 (m, 3H), 1.20 (dd, J = 6.1, 4.4 Hz, 6H), 1.16 (d, J = 6.2 Hz, 3H), 1.05 (d, J = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 166.7, 140.3, 138.9, 136.7, 135.2, 129.6, 128.6, 128.3, 128.1, 127.8, 117.5, 114.7, 69.5 (dd, J = 7.0, 2.9 Hz), 60.0, 40.6 (d, J = 139.4 Hz), 39.5 (d, J = 11.8 Hz), 33.4 (d, J = 5.6 Hz), 24.6 – 23.9 (m), 23.8 (d, J = 5.1 Hz). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 31.15. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{28}$H$_{36}$NO$_3$P 468.2662; Found 468.2661.

3j'', (±)-threo-3j, 42% yield, 20 mg, colorless oil, R$_f$ = 0.26 (ethyl acetate/petroleum ether = 1:5).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.64 (d, J = 7.2 Hz, 2H), 7.42 (q, J = 8.5, 7.4 Hz, 3H), 7.32 (dt, J = 14.5, 6.9 Hz, 3H), 7.17 – 7.12 (m, 2H), 5.75 (ddt, J = 16.9, 10.3, 6.6 Hz, 1H), 5.66 – 5.50 (m, 1H), 5.08 – 4.87 (m, 4H), 4.67 (dp, J = 12.3, 6.1 Hz, 2H), 3.92 – 3.68 (m, 1H), 2.72 (ddd, J = 12.2, 7.1, 4.3 Hz, 1H), 2.53 (dt, J = 14.5, 8.0 Hz, 1H), 2.14 (q,
$J = 6.9 \text{ Hz, 2H}$), 1.99 – 1.73 (m, 3H), 1.25 (t, $J = 6.0 \text{ Hz, 6H}$), 1.15 (t, $J = 5.6 \text{ Hz, 6H}$). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 166.9, 140.0, 138.3, 137.0, 136.5, 129.7, 128.6, 128.3, 128.1, 128.0, 127.8, 116.7, 114.9, 69.6 (dd, $J = 21.3, 7.1 \text{ Hz}$), 60.7, 42.2 (d, $J = 137.7 \text{ Hz}$), 37.4, 32.9 (d, $J = 9.3 \text{ Hz}$), 24.2, 24.1 – 23.7 (m). $^{31}$P NMR (121 MHz, Chloroform-d) $\delta$ 30.69. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{33}$H$_{39}$NO$_5$P 468.2662; Found 468.2660.

3k', (±)-erythro-3k, 28% yield, 15 mg, colorless oil, $R_f = 0.19$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.66 – 7.60 (m, 2H), 7.44 – 7.25 (m, 12H), 7.18 (t, $J = 7.1 \text{ Hz, 2H}$), 6.44 (d, $J = 2.6 \text{ Hz, 2H}$), 5.57 (dq, $J = 17.7, 8.1 \text{ Hz, 1H}$), 5.09 – 4.89 (m, 2H), 4.60 (m, 2H), 4.11 – 3.91 (m, 1H), 3.02 – 2.71 (m, 2H), 2.58 (dt, $J = 15.3, 7.9 \text{ Hz, 1H}$), 2.39 – 2.08 (m, 2H), 1.21 (dd, $J = 8.8, 6.2 \text{ Hz, 6H}$), 1.14 (d, $J = 6.2 \text{ Hz, 3H}$), 1.06 (d, $J = 6.2 \text{ Hz, 3H}$). $^{13}$C NMR (151 MHz, Chloroform-d) $\delta$ 166.9, 140.3, 137.9, 136.7, 135.1, 130.5, 130.0, 129.7, 128.6, 128.3, 128.1, 127.8, 126.8, 126.1, 117.7, 69.7, 59.7, 41.9 (d, $J = 136.0 \text{ Hz}$), 39.4, 28.9, 24.2. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 30.31. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{33}$H$_{41}$NO$_5$P 530.2819; Found 530.2822.

3k'', (±)-threo-3k, 47% yield, 25 mg, colorless oil, $R_f = 0.18$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.66 (d, $J = 7.4 \text{ Hz, 2H}$), 7.44 – 7.23 (m, 11H), 7.20 – 7.14 (m, 2H), 6.33 – 6.22 (m, 2H), 5.68 – 5.45 (m, 1H), 5.09 – 4.89 (m, 2H), 4.68 (tt, $J = 12.5, 6.2 \text{ Hz, 2H}$), 3.89 (ddt, $J = 16.0, 7.0, 4.1 \text{ Hz, 1H}$), 2.84 – 2.44 (m, 4H), 2.10 – 1.94 (m, 1H), 1.26 (d, $J = 6.1 \text{ Hz, 6H}$), 1.16 (dd, $J = 6.1, 2.4 \text{ Hz, 6H}$). $^{13}$C NMR (151 MHz, Chloroform-d) $\delta$ 167.0, 140.1, 137.7, 136.9, 136.3, 130.6, 130.0, 129.8, 128.7, 128.3, 128.2, 128.1, 127.8, 126.8, 126.0, 116.8, 69.8 (dd, $J = 31.9, 7.1 \text{ Hz}$), 60.7, 43.9 (d, $J = 138.2 \text{ Hz}$), 37.5, 29.4 (d, $J = 91.2 \text{ Hz}$), 25.5 – 20.4 (m). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 28.57. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{33}$H$_{41}$NO$_5$P 530.2819; Found 530.2819.

3l', (±)-erythro-3l, 20% yield, 10 mg, colorless oil, $R_f = 0.30$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (300 MHz, Chloroform-d) $\delta$ 7.59 (d, $J = 6.7 \text{ Hz, 2H}$), 7.41 – 7.39 (m, 3H), 7.35 – 7.15 (m, 10H), 5.57 – 5.34 (m, 1H), 5.00 – 4.79 (m, 2H), 4.74 – 4.47 (m, 2H), 3.95 (s, 1H), 3.09 – 2.89 (m, 1H), 2.87 – 2.74 (d, $J = 7.1 \text{ Hz, 1H}$), 2.54 – 2.36 (m, 1H), 2.31 – 2.12 (m, 3H), 2.05 (d, $J = 21.0 \text{ Hz, 1H}$), 1.29 – 1.11 (m, 9H), 1.05 (d, $J = 4.4 \text{ Hz, 3H}$). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 166.8, 142.8, 140.2, 136.7, 135.0, 129.7, 128.7, 128.6, 128.3, 128.1, 127.8, 125.7, 117.5, 69.6 (d, $J = 7.2 \text{ Hz}$), 60.0, 40.6 (d, $J = 139.4 \text{ Hz}$), 39.4 (d, $J = 12.0 \text{ Hz}$), 35.5, 27.2, 25.7 – 21.5 (m). $^{31}$P NMR (121 MHz, Chloroform-d) $\delta$ 32.65. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{33}$H$_{41}$NO$_5$P 518.2819; Found 518.2818.
$3l^\prime$, (±)-threo-3l, 34% yield, 18 mg, colorless oil, $R_f = 0.23$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (300 MHz, Chloroform-d) $\delta$ 7.63 (d, $J = 7.3$ Hz, 2H), 7.45 – 7.26 (m, 6H), 7.23 – 7.10 (m, 5H), 7.10 – 7.01 (m, 2H), 5.69 – 5.46 (m, 1H), 5.08 – 4.85 (m, 2H), 4.65 (m, 3H), 3.92 – 3.69 (m, 1H), 2.74 (t, $J = 7.7$ Hz, 3H), 2.63 – 2.45 (m, 1H), 2.37 – 2.12 (m, 1H), 2.05 (dq, $J = 14.1$, 7.5, 6.9 Hz, 1H), 1.95 – 1.72 (m, 1H), 1.24 (dd, $J = 6.2$, 3.2 Hz, 6H), 1.12 (dd, $J = 11.8$, 6.2 Hz, 6H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 166.9, 141.9, 139.9, 137.0, 136.5, 129.7, 128.6, 128.3, 128.4, 128.1, 127.6, 127.8, 125.7, 116.6, 69.6 (dd, $J = 19.6$, 7.3 Hz), 60.6, 42.3 (d, $J = 137.5$ Hz), 37.2, 34.9 (d, $J = 8.3$ Hz), 26.2, 25.3 – 21.9 (m). $^{31}$P NMR (121 MHz, Chloroform-d) $\delta$ 30.77. HRMS (ESI) m/z: [M+H]$^+$ caleld for C$_{32}$H$_{41}$NO$_3$P 518.2819; Found 518.2816.

$3m'$, (±)-erythro-3m, 26% yield, 12 mg, colorless oil, $R_f = 0.47$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.63 – 7.57 (m, 2H), 7.46 – 7.37 (m, 3H), 7.37 – 7.24 (m, 5H), 5.66 – 5.46 (m, 1H), 5.07 – 4.92 (m, 2H), 4.59 (ddq, $J = 26.1$, 12.5, 6.2 Hz, 2H), 3.92 (ddt, $J = 11.3$, 7.6, 3.3 Hz, 1H), 2.52 (dt, $J = 15.0$, 7.9 Hz, 1H), 2.25 (dt, $J = 12.4$, 5.9 Hz, 1H), 2.04 – 1.74 (m, 3H), 1.61 (m, 1H), 1.49 (m, 1H), 1.20 (dd, $J = 6.1$, 3.7 Hz, 6H), 1.16 (d, $J = 6.2$ Hz, 3H), 1.05 (d, $J = 6.2$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 166.6, 140.4, 136.8, 135.4, 129.6, 128.6, 128.3, 128.0, 127.8, 117.4, 69.4 (d, $J = 6.9$ Hz), 60.0, 41.1 (d, $J = 139.2$ Hz), 39.5 (d, $J = 12.0$ Hz), 27.2, 24.9 – 23.4 (m), 22.6 (d, $J = 5.7$ Hz), 14.50. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 31.54. HRMS (ESI) m/z: [M+H]$^+$ caleld for C$_{27}$H$_{39}$NO$_3$P 456.2662; Found 456.2661.

$3m''$, (±)-threo-3m, 44% yield, 20 mg, colorless oil, $R_f = 0.27$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (300 MHz, Chloroform-d) $\delta$ 7.68 – 7.61 (m, 2H), 7.41 (q, $J = 6.6$ Hz, 3H), 7.36 – 7.27 (m, 3H), 7.18 – 7.12 (m, 2H), 5.69 – 5.48 (m, 1H), 5.09 – 4.89 (m, 2H), 4.66 (m, 2H), 3.88 – 3.70 (m, 1H), 2.83 – 2.63 (m, 1H), 2.62 – 2.44 (m, 1H), 1.93 – 1.58 (m, 3H), 1.35 (m, 2H), 1.29 – 1.21 (m, 6H), 1.15 (t, $J = 6.3$ Hz, 6H), 0.87 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 166.8, 140.1, 137.1, 136.6, 129.7, 128.6, 128.2, 128.0, 128.0, 127.8, 116.6, 69.5 (dd, $J = 13.8$, 7.1 Hz), 60.8, 42.8 (d, $J = 137.5$ Hz), 37.5, 28.4 (d, $J = 184.1$ Hz), 24.9 – 23.0 (m), 22.1 (d, $J = 9.4$ Hz), 14.1. $^{31}$P NMR (121 MHz, Chloroform-d) $\delta$ 30.96. HRMS (ESI) m/z: [M+H]$^+$ caleld for C$_{27}$H$_{39}$NO$_3$P 456.2662; Found 456.2661.

$3n'$, (±)-erythro-3n, 28% yield, 13 mg, colorless oil, $R_f = 0.36$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.56 (m, 2H), 7.46 – 7.37 (m, 3H), 7.36 – 7.25 (m, 5H), 5.64 – 5.46 (m, 1H), 5.07 – 4.90 (m, 2H), 4.58 (ddq, $J = 25.9$, 12.5, 6.2 Hz, 2H), 3.94 (qd, $J$
= 9.2, 3.4 Hz, 1H), 2.51 (dt, J = 15.1, 7.8 Hz, 1H), 2.32 – 2.16 (m, 1H), 2.13 – 1.89 (m, 2H), 1.87 – 1.59 (m, 2H), 1.23 – 1.13 (m, 9H), 1.05 (d, J = 6.2 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H), 0.90 (d, J = 6.5 Hz, 3H). 13C NMR (101 MHz, Chloroform-d) δ 166.6, 140.4, 136.8, 135.3, 129.6, 128.6, 128.3, 128.1, 127.8, 117.3, 69.4 (t, J = 6.9 Hz), 60.1, 39.6 (d, J = 40.5 Hz), 38.8 (d, J = 87.0 Hz), 34.2, 26.7 (d, J = 5.3 Hz), 24.8 – 23.6 (m), 23.4, 22.3. 31P NMR (162 MHz, Chloroform-d) δ 31.57. HRMS (ESI) m/z: [M+H]+ calcd for C28H41NO3P 470.2819; Found 470.2819.

3n″, (±)-threo-3n, 43% yield, 20 mg, colorless oil, Rf = 0.26 (ethyl acetate/petroleum ether = 1:5). 1H NMR (300 MHz, Chloroform-d) δ 7.65 (d, J = 7.9 Hz, 2H), 7.41 (q, J = 7.1, 6.0 Hz, 3H), 7.36 – 7.25 (m, 3H), 7.18 – 7.10 (m, 2H), 5.59 (td, J = 17.0, 7.4 Hz, 1H), 4.99 (dd, J = 17.7, 14.4 Hz, 2H), 4.67 (dp, J = 12.4, 6.0 Hz, 2H), 3.76 (d, J = 18.4 Hz, 0H), 2.77 (dt, J = 12.7, 6.3 Hz, 1H), 2.51 (dt, J = 14.0, 7.6 Hz, 1H), 2.03 – 1.81 (m, 1H), 1.77 – 1.59 (m, 2H), 1.49 (dq, J = 12.6, 6.8, 6.4 Hz, 1H), 1.25 (t, J = 5.4 Hz, 7H), 1.20 – 1.10 (m, 6H), 0.89 – 0.78 (m, 6H). 13C NMR (75 MHz, Chloroform-d) δ 166.7, 140.0, 137.1, 136.6, 129.7, 128.6, 128.3, 128.1, 127.9, 127.8, 116.7, 69.4 (dd, J = 18.9, 7.3 Hz), 60.9, 40.5 (d, J = 138.4 Hz), 37.5, 34.0, 26.1 (d, J = 9.7 Hz), 24.0 (d, J = 22.1 Hz), 22.7, 22.1. 31P NMR (121 MHz, Chloroform-d) δ 31.46. HRMS (ESI) m/z: [M+H]+ calcd for C28H41NO3P 470.2819; Found 470.2818.

3o′, (±)-erythro-3o, 18% yield, 8 mg, colorless oil, Rf = 0.22 (ethyl acetate/petroleum ether = 1:5). 1H NMR (600 MHz, Chloroform-d) δ 7.62 (d, J = 7.2 Hz), 7.46 – 7.27 (m, 8H), 5.67 – 5.44 (m, 1H), 5.02 – 4.92 (m, 2H), 4.70 – 4.53 (m, 2H), 4.12 – 4.00 (m, 1H), 2.86 – 2.75 (m, 1H), 2.35 – 2.25 (m, 1H), 1.44 – 1.37 (m, 1H), 1.36 – 1.29 (m, 1H), 1.25 – 1.17 (m, 9H), 1.0 (d, J = 6.2 Hz, 3H), 0.74 – 0.67 (m, 1H), 0.65 – 0.58 (m, 1H), 0.58 – 0.52 (m, 1H), 0.35 – 0.27 (m, 1H). 13C NMR (151 MHz, Chloroform-d) δ 166.6, 140.5, 136.8, 135.6, 129.6, 128.7, 128.4, 128.1, 128.1, 127.8, 117.3, 69.4 (dd, J = 30.6, 7.8 Hz), 61.3, 46.4 (d, J = 140.8 Hz), 39.0 (d, J = 12.0 Hz), 24.2 (t, J = 3.4 Hz), 24.0 (dd, J = 46.8, 5.4 Hz), 6.8 (m), 3.5. 31P NMR (121 MHz, Chloroform-d) δ 30.50. HRMS (ESI) m/z: [M+H]+ calcd for C27H37NO3P 454.2506; Found 454.2506.

3o″, (±)-threo-3o, 51% yield, 23 mg, colorless oil, Rf = 0.18 (ethyl acetate/petroleum ether = 1:5). 1H NMR (600 MHz, Chloroform-d) δ 7.65 (d, J = 7.4 Hz), 7.43 – 7.27 (m, 6H), 7.15 (d, J = 6.8 Hz), 5.63 – 5.52 (m, 1H), δ 5.01 (d, J = 17.2 Hz), δ 4.94 (d, J = 10.2 Hz), 4.79 – 4.67 (m, 2H), 3.94 – 3.80 (m, 1H), 2.87 – 2.73 (m, 1H), 2.71 – 2.58 (m, 1H), 1.27 (dd, J = 6.2, 2.2 Hz, 6H), 1.18 (d, J = 6.2 Hz, 3H), 1.13 (d, J = 6.2 Hz, 3H), 1.17 – 1.09 (m, 1H), 1.02 – 0.94 (m, 1H), 0.67 – 0.60 (m, 1H), 0.60 – 0.52 (m, 1H), 0.46 – 0.39 (m, 1H), 0.27 – 0.19 (m, 1H),
$^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 166.6, 140.2, 137.0, 136.6, 129.6, 128.6, 128.0, 127.8, 116.7, 69.6 (dd, $J = 17.4, 7.6$ Hz), 62.9, 48.7 (d, $J = 138.8$ Hz), 38.1, 24.3 (m), 23.9 (t, $J = 5.4$ Hz), 8.5 (d, $J = 3.0$ Hz), 5.9 (d, $J = 16.2$ Hz), 5.8. $^{31}$P NMR (121 MHz, Chloroform-$d$) $\delta$ 30.34. HRMS (ESI) m/z: [M+H]$^+$ calcd for $C_{27}H_{37}NO_3P$ 454.2506; Found 454.2506.

$3p$, 44% yield, 18 mg, colorless oil, $R_f = 0.18$ (ethyl acetate/petroleum ether = 1:5). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.62 (dt, $J = 6.8, 1.5$ Hz, 2H), 7.43 – 7.27 (m, 6H), 7.23 – 7.18 (m, 2H), 5.63 – 5.48 (m, 1H), 5.03 – 4.88 (m, 2H), 4.11 – 3.90 (m, 4H), 3.68 (td, $J = 9.7, 2.6$ Hz, 1H), 2.82 (dd, $J = 13.4, 6.4$ Hz, 1H), 2.48 (dt, $J = 13.8, 8.9$ Hz, 1H), 1.36 (d, $J = 17.2$ Hz, 3H), 1.20 (t, $J = 7.1$ Hz, 3H), 1.16 – 1.10 (m, 6H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 166.8, 140.3, 137.3, 136.8, 129.7, 128.8, 128.5, 128.0, 127.9, 127.8, 116.5, 63.8 (d, $J = 3.3$ Hz), 61.6 (dd, $J = 21.5, 7.3$ Hz), 40.1 (d, $J = 139.2$ Hz), 36.9, 21.8 (d, $J = 4.0$ Hz), 17.8 (d, $J = 3.0$ Hz), 16.4 (t, $J = 5.4$ Hz). $^{31}$P NMR (162 MHz, Chloroform-$d$) $\delta$ 28.86. HRMS (ESI) m/z: [M+H]$^+$ calcd for $C_{24}H_{33}NO_3P$ 414.2193; Found 414.2193.

### 5.3 Synthetic Applications

#### 5.3.1 Removing of protecting groups in 3h’’

To a 10 mL vial equipped with a stirring bar, 3h’’ (28 mg, 0.044 mmol, 1.0 equiv) and 6N HCl/THF mixed solvents (v/v = 0.5 mL/1.0 mL) were added. Then the resulting solution was stirred at room temperature for 18h. After completion of the reaction, 3N NaOH (aq) was added to adjust the mixture to strong alkaline solution and stirring was continued for 15 minutes. Then 5mL x 3 ethyl acetate was added for extraction and the organic phase was collected and concentrated under reduced pressure. The product 4h (15 mg, 96% yield) was obtained with column chromatography on silica gel with DCM/MeOH (v/v = 25:1) as the eluant.

4h, 96% yield, 15 mg at 0.044 mmol scale, pale oil, $R_f = 0.85$ (DCM/MeOH = 10:1). $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.02 (d, $J = 7.7$ Hz, 2H), 6.69 (d, $J = 7.6$ Hz, 2H), 5.67-5.4 (m, 1H), 5.05 (d, $J = 12.1$ Hz, 2H), 5.02-4.77 (brs, 3H), 4.79-4.70 (m, 2H), 3.20-2.97 (m, 2H), 2.91-2.74 (m, 1H), 2.58-2.49 (m, 1H), 2.36-2.21 (m, 2H), 1.37-
1.28 (m, 12H). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 155.6, 135.1, 129.8, 129.7, 118.2, 115.8, 70.8 (dd, $J = 16.3$ Hz, 7.6 Hz), 49.9, 43.7 (d, $J = 136.1$ Hz), 39.5, 31.0, 29.7, 24.0 (m). $^{31}$P NMR (121 MHz, Chloroform-$d$) $\delta$ 28.74 (s).

**5.3.2 Procedure for the transformations of product 3i**

As mentioned previously, $\beta$-formyl phosphonate 1i was easily synthesized from simple materials with quantitative yield. Under argon, Bi(O'Tf)$_3$ (68 mg, 0.20 mmol, 0.10 equiv), 1i (416 mg, 2.0 mmol, 1.0 equiv), 2a (490 mg, 2.2 mmol, 1.1 equiv) and 4Å molecular sieve (1.0 g) were added to a 10 mL round-bottomed flask equipped with a stirring bar. Then the flask was moved to a pre-heated 100 $^\circ$C oil bath and stirring was continued for 70 h. Product 3i was not isolated and the mixture was cooled to room temperature and concentrated under reduced pressure. Subsequently, 10 mL THF and 3 mL 4N hydrochloric acid were added to the flask and the resulting mixture was stirred at 60 $^\circ$C overnight. After completion of the reaction as indicated by TLC analysis, 10 mL saturated NaHCO$_3$ (aq) and Boc$_2$O (0.55 mL, 2.4 mmol, 1.2 equiv) was added to the flask and stirring was continued for 16h. The mixture was extracted with 25 mL x 3 ethyl acetate and the organic phase was concentrated under reduced pressure. 4i was obtained by column chromatography on silica gel with 46% yield (321 mg, 0.92 mmol) as colorless oil.

4i (63 mg, 0.18 mmol) was dissolved in CH$_3$CN/H$_2$O/CCl$_4$ (v/v/v = 3 mL : 2mL : 3mL) mixed-solvents. RuCl$_3$ (1.9 mg, 0.0090 mmol, 0.05 equiv) was added and then the mixture was stirred at room temperature for 16 h$^{[4]}$. After completion, 1 mL saturated KH$_2$PO$_4$ and 3 mL brine was added and the resulting mixture was extracted with 4 x 25 mL dichloromethane. The organic phase was concentrated under reduced pressure and submitted to column chromatography under air pressure ($V_{DCM}/V_{MeOH} = 10:1$). 5i was achieved as colorless oil with 80% yield (53 mg, 0.144 mmol).

4i, 46% yield, 321 mg at 2 mmol scale, colorless oil, $R_f$ = 0.49 (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 5.76 (m, 1H), 5.20 (s, 1H), 5.10 (dd, $J = 20.4$, 11.4 Hz, 2H), 4.85 – 4.59 (m, 2H),
3.93 (m, 1H), 2.40 (t, J = 6.1 Hz, 2H), 2.03 – 1.86 (m, 2H), 1.43 (s, 9H), 1.36 – 1.29 (m, 12H). 13C NMR (101 MHz, Chloroform-d) δ 153.9, 133.6, 117.3, 78.7, 70.0 (dd, J = 16.2, 7.1 Hz), 45.7, 39.4 (d, J = 8.1 Hz), 31.0 (d, J = 141.4 Hz), 28.3 (s), 23.9 (m). 31P NMR (121 MHz, Chloroform-d) δ 26.68 (s).

HRMS (ESI) m/z: [M+H]+ calcd for C16H33NO5P 350.2091; Found 350.2094.

5i, 80% yield, 53 mg at 0.18 mmol scale, colorless oil, Rf = (CH2Cl2/MeOH = 25:1). 1H NMR (400 MHz, Chloroform-d) δ 10.29 (s, 1H), 5.67 (d, J = 8.2 Hz, 1H), 4.71 (m, 2H), 4.21 (s, 1H), 2.98 – 2.55 (m, 2H), 2.23 (dd, J = 18.1, 7.1 Hz, 2H), 1.43 (s, 6H), 1.32 (dd, J = 6.2, 2.5 Hz, 12H). 13C NMR (101 MHz, Chloroform-d) δ 173.9, 154.9, 79.3, 71.4 – 70.6 (m), 43.1, 38.3(CH2), 30.8 (d, CH2, J = 137.6 Hz), 28.3, 23.9 (m). 31P NMR (121 MHz, Chloroform-d) δ 27.61. HRMS (ESI) m/z: [M+H]+ calcd for C15H31NO7P 368.1833; Found 368.1834.

5.3.3 Bismuth-catalyzed hydrogen transfer with Hantzsch ester

Bi(OTf)3 (6.8 mg, 0.010 mmol, 5 mol %), 1B (52 mg, 0.2 mmol, 1.0 equiv), 4-methoxyaniline (28 mg, 0.22 mmol, 1.1 equiv), Hantzsch ester (102 mg, 0.4 mmol, 2.0 equiv) and 4Å molecular sieve (100 mg) were added to a 15 mL sealed tube under argon and then 2.0 mL CHCl3 was added. The tube was moved to a 100 °C oil bath and stirred for 34h. Subsequently, the resulting mixture was concentrated under reduced pressure and submitted to column chromatography for purification. 3B was obtained as pale oil with 94% yield (69 mg, 0.189 mmol). 3B, 94% yield, 69 mg at 0.2 mmol scale, pale oil, Rf = 0.11 (ethyl acetate/petroleum ether = 1:1). 1H NMR (300 MHz, Chloroform-d) δ 8.09 – 7.63 (m, 4H), 7.63 – 7.32 (m, 6H), 6.73 (d, J = 6.6 Hz, 2H), 6.41 (d, J = 6.7 Hz, 2H), 3.73 (s, 3H), 3.49 (td, J = 6.0, 3.0 Hz, 1H), 3.25 (m, 1H), 2.76 (m, 1H), 1.23 (dd, J = 16.2, 7.2 Hz, 3H). 13C NMR (75 MHz, Chloroform-d) δ 152.1, 141.5, 132.7, 132.2, 131.7, 130.8 (dd, J = 13.7, 8.9 Hz), 128.7 (dd, J = 11.4, 4.1 Hz), 114.8, 114.1, 55.8, 45.0 (CH2), 31.5 (d, J = 70.7 Hz), 11.8 (d, J = 2.25 Hz). 31P NMR (121 MHz, Chloroform-d) δ 37.14 (s). HRMS (ESI) m/z: [M+H]+ calcd for C22H25NO5P 366.1617; Found 366.1617.
5.4 Deuterium labeling experiment

Enamine C was synthesized from the condensation of the corresponding aldehyde 1o and amine 2a under 70 °C in the presence of molecular sieve. Enamine C (45 mg, 0.1 mmol) was added to a 10 mL oven-dried tube and 1.0 mL DCE and D$_2$O (1.0 mmol, 10 equiv) were added. Under argon, the resulting mixture was stirred at room temperature for 20 min. Subsequently Bi(OTf)$_3$ (3.4 mg, 0.005 mmol, 0.005 equiv) and 4A MS (100 mg) were added. Then the tube was sealed with a rubber plug and moved to a 100 °C oil bath for 60 h. After completion of the reaction, the mixture was purified by column chromatography on silica gel. Erythro-isomers (4 mg, 8.8% yield) and threo-isomers (12 mg, 26.5% yields) were obtained and analyzed by NMR and HRMS.

Enamine C, yellow oil, R$_f$ = 0.42 (ethyl acetate/petroleum ether = 1:1). $^1$H NMR (300 MHz, Chloroform-d) δ 7.48-7.10 (m, 10H), 6.79-6.63 (m, 1H), 5.64 (d, $J$ = 13.4 Hz, NH), 5.52 – 5.38 (m, 1H), 5.32 – 5.19 (m, 1H), 5.14 (dd, $J$ = 10.0, 2.2 Hz, 1H), 4.47 (ddt, $J$ = 12.4, 8.1, 6.2 Hz, 2H), 3.13 (d, $J$ = 6.9 Hz, 2H), 1.35 – 1.31 (m, 3H), 1.25 (t, $J$ = 10.2 Hz, 6H), 0.70 (dd, $J$ = 7.6, 2.6 Hz, 1H), 0.67 – 0.64 (m, 1H). $^{13}$C NMR (75 MHz, Chloroform-d) δ 147.1 (d, $J$ = 25.3 Hz), 144.0, 132.9, 128.1, 127.2, 126.9, 119.7 (CH$_2$), 93.4 (d, $J$ = 210.8 Hz), 68.7 (d, $J$ = 5.7 Hz), 64.9, 46.6 (CH$_2$), 23.8 (d, $J$ = 3.9 Hz), 23.5 (d, $J$ = 4.8 Hz), 5.7 (d, $J$ = 10.9 Hz), 4.8 (d, $J$ = 5.1 Hz, CH$_3$). $^{31}$P NMR (162 MHz, Chloroform-d) δ 24.07. HRMS (ESI) m/z: [M+H]$^+$ calcd for C$_{22}$H$_{37}$NO$_3$P 454.2506; Found 454.2508.
Figure 6. $^1$HNMR spectrum of erythro-isomers

Figure 7. $^{13}$CNMR spectrum of erythro-isomers
Figure 8. $^1$HNMR spectrum of threo-isomers

Figure 9. $^{13}$CNMR spectrum of threo-isomers
The structures of products were confirmed by NMR analysis (Figures 6-9), the deuteration ratio was confirmed by HRMS analysis (Figure 10-11) with consideration of the isotopic abundance of hydrogen atom. The ratio of [D]-3o/([H]-3o+[D]-3o) for erythro- and threo-isomers were 42.7% and 42.5% respectively.

References:
6. NMR Spectrum

$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1a

- [300 MHz, CDCl$_3$]
- [121 MHz, CDCl$_3$]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1b
[121 MHz, CDCl₃]

[75 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1c
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1d

[400 MHz, CDCl$_3$]
[162 MHz, CDCl₃]

[101 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1e
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1f

[101 MHz, CDCl$_3$]

[400 MHz, CDCl$_3$]
[162 MHz, CDCl₃]

[101 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of $1g$
$^{1}$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1h
[121 MHz, CDCl₃]

Etynylindane standard test sample
Recorded on 400-MR with OneHR probe and PFT tuning

[151 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of $1i$
$^{1}$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1j
[121 MHz, CDCl₃]

[75 MHz, CDCl₃]
$\text{HNMR, } ^{13}\text{CNMR and } ^{31}\text{PNMR spectra of } 1k$
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 11
[101 MHz, CDCl₃]

[162 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1m
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1n
[162 MHz, CDCl₃]

[101 MHz, CDCl₃]
$^{1}\text{HNMR}, ~^{13}\text{CNMR} \text{ and } ^{31}\text{PNMR}$ spectra of $1o$.
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 1p

[400 MHz, CDCl$_3$]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3a

[400 MHz, CDCl$_3$]

[162 MHz, CDCl$_3$]
$^{1}$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3b
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3c'
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3c$''$
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3d'

[400 MHz, CDCl$_3$]

[162 MHz, CDCl$_3$]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3d$''$

[151 MHz, CDCl$_3$]

[400 MHz, CDCl$_3$]
[162 MHz, CDCl₃]

Ethylindene standard test sample
Recorded on 400-MR with OneNMR probe and P2T tuning

[151 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3e′

[400 MHz, CDCl$_3$]

[121 MHz, CDCl$_3$]
Ethylindrical standard test sample
Recorded on 400-MR with OneNMR probe and P2T tuning

$[151 \text{ MHz, CDCl}_3]$ [151 MHz, CDCl$_3$]

$[400 \text{ MHz, CDCl}_3]$ [400 MHz, CDCl$_3$]

$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3e$''$
Ethylindanone standard test sample
Recorded on 400-MR with OneHN probe and PST tuning

[162 MHz, CDCl$_3$]

[151 MHz, CDCl$_3$]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3f

[400 MHz, CDCl$_3$]

[162 MHz, CDCl$_3$]
$^{1}$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3f"
[162 MHz, CDCl₃]

[151 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3g
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3h′
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3h$''$
[162 MHz, CDCl₃]

[151 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3i
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3j'
[162 MHz, CDCl₃]

[101 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3j$''$

[400 MHz, CDCl$_3$]

[121 MHz, CDCl$_3$]
\( ^1\text{HNMR}, \ ^{13}\text{CNMR} \text{ and } ^{31}\text{PNMR} \text{ spectra of } 3k' \)
[162 MHz, CDCl₃]

[151 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3k$''$

[600 MHz, CDCl$_3$]

[162 MHz, CDCl$_3$]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3l'}
1H NMR

[121 MHz, CDCl₃]

13C NMR

[75 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 31$''$
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3m'}
[162 MHz, CDCl₃]

[101 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3m
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3n′
\(^1\)HNMR, \(^{13}\)CNMR and \(^{31}\)PNMR spectra of 3n"
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3o’
[121 MHz, CDCl₃]

[151 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 30$''$ 

[600 MHz, CDCl$_3$] 

P–31 STANDARD PARAMETERS 
PHOSPHATE REGION 

[121 MHz, CDCl$_3$]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3p
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 4h

[600 MHz, CDCl$_3$]

[121 MHz, CDCl$_3$]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 4i
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of $5i$
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of 3B

[300 MHz, CDCl₃]

[121 MHz, CDCl₃]
$^1$HNMR, $^{13}$CNMR and $^{31}$PNMR spectra of enamine C

[300 MHz, CDCl$_3$]

1. Enamine in CDCl$_3$

2. Enamine + D$_2$O in CDCl$_3$
[162 MHz, CDCl₃]

[^13]C NMR (162 MHz, CDCl₃): 141.38 (d, J = 25.3 Hz), 141.29 (q), 123.55 (q), 123.14 (q), 120.03 (q), 118.72 (q), 93.99 (d), 76.74 (d, J = 4.5 Hz), 49.29 (s), 45.93 (d, J = 21.0 Hz), 23.89 (d, J = 5.3 Hz).

[75 MHz, CDCl₃]

[^13]C NMR (75 MHz, CDCl₃): 147.36 (d, J = 25.3 Hz), 111.14 (q), 123.55 (q), 123.14 (q), 120.03 (q), 118.72 (q), 93.99 (d), 76.74 (d, J = 4.5 Hz), 49.29 (s), 45.93 (d, J = 21.0 Hz), 23.89 (d, J = 5.3 Hz), 23.42 (d, J = 4.5 Hz), 3.80 (d, J = 3.6 Hz), 4.78 (d, J = 2.4 Hz).