**Supplementary Information**

**P-chiral phosphorus heterocycles: a straightforward synthesis**

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**Experimental**

General Methods: All reactions were carried out under dry high purity nitrogen using standard Schlenk techniques. Experiments including elemental lithium were carried out under dry high purity argon. THF was degassed and freshly distilled from potassium. Other solvents were used without any further purification. The NMR spectra were recorded either with a BRUKER AVANCE DRX 400 spectrometer (\(^1\)H NMR 400.13 MHz, \(^{13}\)C NMR 100.63 MHz, \(^{31}\)P NMR 161.98 MHz) or a BRUKER FOURIER 300 spectrometer (\(^1\)H NMR 300.23 MHz, \(^{13}\)C NMR 75.50 MHz). TMS was used as the internal standard in the \(^1\)H NMR spectra and all other nuclei spectra were referenced to TMS using the \(\Xi\)-scale.\(^{1}\) \(^{13}\)C NMR spectra were recorded as APT spectra. Assignment of the chemical shifts as well as of the configuration of the single stereoisomers was based on COSY, HMQC, HSQC, HMBC and selective NOE experiments. Mass spectra (ESI) were measured with a BRUKER DALTONICS 7T APEX II or a BRUKER DALTONICS ESQUIRE 3000 PLUS spectrometer. IR spectra were recorded with a PERKIN-ELMER SPECTRUM 2000FT-IR spectrometer in the range of 400-4000 cm\(^{-1}\) in KBr. The melting points were determined in glass capillaries sealed under nitrogen using a GALLENKAMP apparatus and are uncorrected. Column chromatography was performed using silica 60 (0.015–0.040 mm) purchased from MERCK. UV light (389 nm), iodine (saturated atmosphere), phosphomolybdic acid (12 g phosphomolybdic acid in 100 ml ethanol) and \(p\)-anisaldehyde (140 ml ethanol, 5 ml sulfuric acid (conc.), 1.5 ml glacial acetic acid, 4 ml \(p\)-anisaldehyde) were used as staining reagent.
The compounds 3,4-dimethyl-1-phenylphosphole,\(^2\) 2-(chloromethyl)pyridine\(^3\), 2,6-pyridinedimethyl ditosylate,\(^4\) and (5\(R\)-(1-methyloxy)-2(5\(H\))-furanone\(^5-7\) were synthesised according to the literature. Other chemicals were commercially and used as received.

**Synthesis of 2a:**

A solution of 3,4-dimethyl-1-phenylphosphole (4.89 g, 26.0 mmol), sulfur (0.880 g, 27.3 mmol) and 3 drops of triethylamine in 20 ml DCM were stirred at room temperature for 3 hours. The crude product was purified by column chromatography (hexanes/diethyl ether = 4:1 to1:2, v/v) to give 2a as a pale yellow solid. Recrystallisation from toluene/hexanes gave the title compound as colourless needles.

Yield: 4.27 g, 82%

R\(_f\) (hexanes/diethyl ether = 2:1, v/v) = 0.45; UV light, iodine
mp: 112–114 °C

\(^1\)H NMR (300.23 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 2.13 (6H, s, 3), 6.13 (2H, d, \(^2J_{H,P} = 30.9\) Hz, 1), 7.37–7.55(3H, m, 5/6, 7), 7.78–7.90 (2H, m, 5/6)

\(^13\)C NMR (75.50 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 17.5 (d, \(^3J_{C,P} = 17.8\) Hz, 3), 125.9 (d, \(^1J_{C,P} = 82.6\) Hz, 1), 127.8 (d, \(^1J_{C,P} = 79.4\) Hz, 4), 128.7 (d, \(J_{C,P} = 12.7\) Hz, 5/6), 130.5 (d, \(J_{C,P} = 11.7\) Hz, 5/6), 132.0 (d, \(^4J_{C,P} = 2.9\) Hz, 7), 153.7 (d, \(^2J_{C,P} = 17.6\) Hz, 2)

\(^31\)P\(^{\{1\}H}\) NMR (161.98 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 46.3

IR (KBr): v [cm\(^{-1}\)] = 3425 m, 3056 w, 2963 w (vC–H), 2343 w, 2343 w, 1814 w, 1765 w, 1608 w, 1541 m, 1480 m, 1436 m, 1380 w, 1307 w, 1262 w, 1182 w, 1138 w, 1101 s, 1026 m, 993 m, 832 w, 821 m, 804 s, 741 m, 732 m, 713 s, 690 m, 662 s, 615 w, 511 s, 479 w, 454 w, 440 w, 428 w, 411 w

MS (ESI): \(m/z\): calc. for C\(_{12}\)H\(_{13}\)PS [M+H]\(^+\): 221.0; found: 221.0
C\(_{12}\)H\(_{13}\)PS (220.27): calc. C 65.43 H 5.95; found C 65.43 H 5.97
Synthesis of 2b:

A mixture of 3,4-dimethyl-1-phenylphosphole (2.64 g, 14.0 mmol) and pieces of lithium (5–10fold excess) in 200 ml THF was stirred at room temperature for 3–4 hours (conversion was monitored by TLC, with phosphomolybdic acid). The deep brown solution was filtered from lithium, tert-butyl chloride (2.00 ml, 18.4 mmol) was added and the mixture was heated to 67 °C for one hour. The orange solution was cooled to −80 °C and benzyl bromide (2.00 ml, 16.8 mmol) was added dropwise. After complete addition, the solution was warmed to room temperature overnight. The reaction was quenched at 0 °C with 100 ml of a saturated NaHCO₃ solution, the mixture was reduced to a volume of ca. 100 ml in vacuum and 200 ml DCM were added. Water was added until both phases were clear. The phases were separated, and the aqueous phase was extracted three times with 20 ml of DCM. The combined organic solutions were filtered over a pad of silica, which was subsequently washed with 200 ml of DCM. Sulfur (0.900 g, 28.1 mmol) and 5 drops of triethylamine were added and the solution was stirred for 20 hour at room temperature.

The crude product was purified by column chromatography (toluene/diethyl ether = 70:1 to 15:1, v/v) to give 2b as a colourless oil, which solidifies to a white solid upon standing at room temperature.

Yield: 2.80 g, 85%

Rᵣ (toluene/diethyl ether = 40:1, v/v) = 0.24; UV light, iodine

mp: 99–103 °C

¹H NMR (300.23 MHz, CDCl₃): δ [ppm] = 1.94 (6H, dd, ḳ₄H,P = 1.7 Hz, ḳ₄H,H = 0.8 Hz, 3), 3.41 (2H, d, ḳ₂H,P = 14.5 Hz, 4), 5.96 (2H, dq, ḳ₂H,P = 30.9 Hz, ḳ₄H,H = 0.8 Hz, 1), 7.12–7.19 (2H, m, 7), 7.21–7.31 (3H, m, 6, 8)

¹³C{¹H} NMR (75.50 MHz, CDCl₃): δ [ppm] = 17.3 (d, ḳ₁JC,P = 79.5 Hz, 1), 127.2 (d, ḳJC,P = 3.9 Hz, 8), 128.2 (d, ḳJC,P = 3.3 Hz, 6), 129.7 (d, ḳJC,P = 5.5 Hz, 7), 132.0 (d, ḳJC,P = 8.5 Hz, 5), 153.5 (d, ḳJC,P = 16.8 Hz, 2)

³¹P{¹H} NMR (161.98 MHz, CDCl₃): δ [ppm] = 50.8
IR (KBr): ν [cm\(^{-1}\)] = 3429 s, 2968 m (νC–H), 2348 w, 1631 m, 1539 m, 1496 m, 1397 w, 1312 w, 1262 w, 1142 m, 1024 m, 830 m, 811 m, 779 s, 700 s, 660 w, 634 s, 570 m, 500 m, 480 w, 439 w  

MS (ESI): \( m/z \): calc. for \( \text{C}_{13}\text{H}_{15}\text{PS} [M+Na]^+ \): 257.1; found: 257.1  
\( \text{C}_{13}\text{H}_{15}\text{PS} \) (234.30): calc. C 66.64 H 6.45; found C 66.74 H 6.46  

Synthesis of 2c:  

A mixture of 3,4-dimethyl-1-phenylphosphole (4.53 g, 24.1 mmol) and pieces of lithium (5–10 fold excess) in 200 ml THF was stirred at room temperature for 3–4 hours (conversion was monitored by TLC, with phosphomolybdic acid). The deep brown solution was filtered from lithium, \textit{tert}-butyl chloride (3.40 ml, 31.3 mmol) was added and the mixture was heated to 67 °C for one hour. The orange solution was cooled to −80 °C and 2-(chloromethyl)pyridine (3.38 g, 26.5 mmol) dissolved in 20 ml THF was added dropwise. After complete addition, the solution was warmed to room temperature overnight. The reaction was quenched at 0 °C with 100 ml of a saturated NaHCO\(_3\) solution, the mixture was reduced to a volume of ca. 100 ml in vacuum and 200 ml DCM were added. Water was added until both phases were clear. The phases were separated, and the aqueous phase was extracted three times with 20 ml of DCM. The combined organic solutions were filtered over a pad of silica, which was subsequently washed with 200 ml of diethyl ether. Sulfur (0.900 g, 28.1 mmol) and 5 drops of triethylamine were added, and the solution was stirred for 90 minutes at room temperature. The crude product was purified by column chromatography (toluene/ethyl acetate = 2:1 to 2:3, v/v) to give 2c as a pale yellow solid.  

Yield: 4.30 g, 76%  
\( R_f \) (toluene/ethyl acetate = 2:3, v/v) = 0.31; UV light, iodine  
mp: 86–88 °C  
\(^1\)H NMR (300.23 MHz, CDCl\(_3\)) \( \delta \) [ppm] = 1.92 (6H, d, \(^4\)J\(_{H,H} = 0.8\) Hz, 3), 3.50 (2H, d, \(^2\)J\(_{H,P} = 14.5\) Hz, 4), 5.99 (2H, dq, \(^2\)J\(_{H,P} = 30.9, \(^4\)J\(_{H,H} = 0.8\) Hz), 7.06–7.14(1H, m, 8), 7.21–7.35 (1H, m, 6), 7.45–7.65 (1H, m, 7), 8.30–8.52 (1H, m, 9)
\(^{13}\)C\{\(^{1}\)H\} NMR (75.50 MHz, CDCl\(_3\)): \(\delta [ppm] = 17.4\) (d, \(^3J_{C,P} = 17.6\) Hz, 3), 42.7 (d, \(^1J_{C,P} = 44.9\) Hz, 4), 122.1 (d, \(^5J_{C,P} = 3.2\) Hz, 8), 123.5 (d, \(^1J_{C,P} = 80.0\) Hz, 1), 125.2 (d, \(^3J_{C,P} = 4.7\) Hz, 6), 136.1 (d, \(^4J_{C,P} = 2.6\) Hz, 7), 149.4 (d, \(^4J_{C,P} = 2.7\) Hz, 9), 152.5 (d, \(^2J_{C,P} = 8.8\) Hz, 5), 153.1 (d, \(^2J_{C,P} = 17.8\) Hz, 2)

\(^{31}\)P\{\(^{1}\)H\} NMR (161.98 MHz, CDCl\(_3\)): \(\delta [ppm] = 49.3\)

IR (KBr): \(\nu [cm^{-1}] = 3428\) s, 3063 w, 3003 w, 2952 s (\(\nu C–H\)), 2907 m (\(\nu C–H\)), 1589 s, 1567 m, 1542 m, 1472 s, 1433 s, 1401 w, 1385 w, 1317 w, 1260 s, 1150 w, 1084 s, 1022 m, 993 w, 859 w, 838 m, 828 s, 810 s, 791 s, 753 m, 714 m, 672 s, 587 m, 499 s, 480 w, 438 w, 431 w, 415 w, 404 w

MS (ESI): \(m/z\): calc. for C\(_{12}\)H\(_{14}\)NPS [\(M+Na^+\)]: 258.1; found: 258.0
C\(_{12}\)H\(_{14}\)NPS (235.29): calc. C 61.26 H 6.00; found C 61.15 H 5.83

Synthesis of 2d:

A mixture of 3,4-dimethyl-1-phenylphosphole (4.08 g, 21.7 mmol) and pieces of lithium (5–10 fold excess) in 200 ml THF was stirred at room temperature for 3–4 hours (conversion was monitored by TLC, with phosphomolybdic acid). The deep brown solution was filtered from lithium, tert-butyl chloride (3.07 ml, 28.2 mmol) was added and the mixture was heated to 67 °C for one hour. Subsequently, the orange solution was cooled to −80 °C and 1,2-bis(chloromethyl)benzene (1.90 g, 10.9 mmol) dissolved in 50 ml THF was added dropwise. After complete addition, the solution was warmed to room temperature overnight. The reaction was quenched at 0 °C with 100 ml of a saturated NaHCO\(_3\) solution, the mixture was reduced to a volume of ca. 100 ml in vacuum and 200 ml DCM were added. Water was added until both phases were clear. The phases were separated and the aqueous phase was extracted three times with 20 ml of DCM. The combined organic solutions were filtered over a pad of silica, which was subsequently washed with 200 ml of DCM. Sulfur (1.39 g, 43.4 mmol) and 5 drops of triethylamine were added and the solution was stirred for 90 minutes at room temperature. The crude product was purified by column chromatography (toluene/ethyl acetate = 10:1 to 6:1, v/v) to give 2d as a pale yellow solid.
Crystals suitable for X-ray crystallography were obtained from a mixture of DCM and hexanes at 4 °C.

Yield: 3.05 g, 72%

Rf (toluene/ethyl acetate = 5:1, v/v) = 0.37; UV light, iodine

mp: 148–150 °C

1H NMR (400.13 MHz, CDCl3): $\delta$ [ppm] = 1.91–2.04 (12H, m, 3), 3.66 (4H, d, $^2J_{H,P}$ = 13.2 Hz, 4), 5.99 (4H, d, $^2J_{H,P}$ = 31.0 Hz, 1), 7.05–7.22 (4H, m, 6/7)

13C{1H} NMR (100.63 MHz, CDCl3): $\delta$ [ppm] = 17.0–17.7 (m, 3), 37.4 (d, $^1J_{C,P}$ = 43.8 Hz, 4), 123.5 (d, $^1J_{C,P}$ = 79.0 Hz, 1), 127.2 (s, 6/7), 131.1 (s, 6/7), 131.6–131.9 (m, 5), 153.3 (d, $^2J_{C,P}$ = 17.2 Hz, 2)

31P{1H} NMR (161.98 MHz, CDCl3): $\delta$ [ppm] = 50.5

IR (KBr): $\nu$ [cm$^{-1}$] = 3434 w, 3051 m, 2942 m ($\nu$C–H), 2911 s ($\nu$C–H), 1597 w, 1539 s, 1488 m, 1446 s, 1430 s, 1381 m, 1316 m, 1210 w, 1136 w, 1076 w, 1058 m, 1042 w, 1023 m, 990 w, 869 s, 852 m, 824 s, 811 s, 788 s, 774 s, 718 m, 696 m, 671 m, 563 m, 533 w, 491 s, 462 w, 425 w, 417 w, 406 w

MS (ESI): m/z: calc. for C$_{20}$H$_{24}$P$_2$S$_2$ [M+Na]$^+$:413.1; found: 413.1
C$_{20}$H$_{24}$P$_2$S$_2$ (390.48): calc. C 61.52 H 6.20; found C 61.15 H 6.33

Synthesis of 2e:

A mixture of 3,4-dimethyl-1-phenylphosphole (3.34 g, 17.8 mmol) and pieces of lithium (5–10 fold excess) in 200 ml THF was stirred at room temperature for 3–4 hours (conversion was monitored by TLC, with phosphomolybdic acid). The deep brown solution was filtered from lithium, tert-butyl chloride (2.55 ml, 23.6 mmol) was added and the mixture was heated to 67 °C for one hour. Subsequently, the orange solution was cooled to −80 ºC and 2,6-bis(tosylmethyl)pyridine (3.98 g, 8.88 mmol) dissolved in 50 ml THF was added dropwise. After complete addition, the solution was warmed to room temperature overnight. The reaction was quenched at 0 ºC with 100 ml of a saturated NaHCO$_3$ solution, the mixture was reduced to a volume of ca. 100 ml in vacuum and 200 ml DCM were added. Water was
added until both phases were clear. The phases were separated and the aqueous phase was extracted three times with 20 ml of DCM. The combined organic solutions were filtered over a pad of silica, which was subsequently washed with 200 ml of diethyl ether. Sulfur (1.14 g, 35.2 mmol) and 5 drops of triethylamine were added and the solution was stirred for 90 minutes at room temperature. 

The crude product was purified by column chromatography (toluene/ethyl acetate = 3:1 to 2:1, v/v) to give 2e as a pale yellow solid. Crystals suitable for X-ray crystallography were obtained from a mixture of DCM and hexanes at 4 °C.

Yield: 2.61 g, 75%

Rf (diethylether) = 0.25; UV light, iodine

mp: 191–192 °C

1H NMR (400.13 MHz, CDCl3): \(\delta [ppm] = 2.03 \ (12H, s, 3)\), 3.54 \( (4H, d, ^2J_{H,P} = 14.3 \text{ Hz, 4})\), 6.14 \( (4H, d, ^2J_{H,P} = 30.9 \text{ Hz, 1})\), 7.17 \( (2H, d, ^3J_{H,H} = 7.7 \text{ Hz, 6})\), 7.57 \( (1H, t, ^3J_{H,H} = 7.7 \text{ Hz, 7})\)

13C{1H} NMR (100.63 MHz, CDCl3): \(\delta [ppm] = 17.5 \ (d, ^3J_{C,P} = 17.9 \text{ Hz, 3})\), 42.4 \( (d, ^1J_{C,P} = 45.5 \text{ Hz, 4})\), 123.3–123.5 \( (m, 6)\), 123.7 \( (d, ^1J_{C,P} = 79.8 \text{ Hz, 1})\), 136.4 \( (s \ (br), 7)\), 152.4–152.7 \( (m, 5)\), 153.1 \( (d, ^2J_{C,P} = 18.0 \text{ Hz, 2})\)

31P{1H} NMR (161.98 MHz, CDCl3): \(\delta [ppm] = 49.2\)

IR (KBr): \(\nu [\text{cm}^{-1}] = 3429 \text{ s, 3055 w, 2965 m (vC–H)}, 1588 \text{ m, 1571 m, 1537 m, 1452 s, 1389 w, 1316 w, 1263 m, 1227 w, 1140 m, 1080 m, 1022 w, 993 w, 954 w, 854 s, 834 m, 820 m, 801 m, 786 w, 751 w, 696 m, 634 s, 585 w, 482 w, 452 w, 405 w\)

MS (ESI): \(m/z\): calc. for C19H23NP2S2 [M+Na]+: 414.1; found: 414.1

C20H31O3PS (391.47): calc. C 58.29 H 5.92; found C 57.30 H 5.90
**Synthesis of 7-Phosphanorbornenes:**

**Synthesis of 3a:**

A solution of 2a (1.50 g, 6.82 mmol) and (5R)-(l-menthylxoy)-2(5H)-furanone (0.540 g, 2.27 mmol) in 15 ml of toluene was heated at 110 °C for 72 hours. Morpholine (400 μl, 4.54 mmol) was added to quench the remaining (5R)-(l-menthylxoy)-2(5H)-furanone. After 3 hours at 110 °C, maleic anhydride (1.56 g, 15.9 mmol) was added to quench unreacted 2a, and the solution was left to stir at 110 °C for 3 hours and another 12 hours at room temperature. The crude product was purified by column chromatography (hexanes/diethyl ether = 7:1 to 5:1, v/v) to give 3a as a mixture of diastereomers.

Crystals, suitable for X-ray crystallography, were obtained from a mixture of acetone/water at room temperature.

diastereomeric ratios crude product:

syn/anti (R1 to C=C) ratio could not be determined, d.r. (all syn) = 68:21:7:4

diastereomeric ratios product:

only syn, d.r. = 97:3:0:0

yield: 0.509 g, 49%

Rf (hexanes/diethyl ether = 1:1, v/v) = 0.45; UV light, p-anisaldehyde

mp: 209–210 °C

\[\alpha\] = −91.1° (c = 0.62 in toluene)

1H NMR (400.13 MHz, CDCl3): \(\delta [ppm] = 0.75–0.79 (3H, m, 18a), 0.89–0.92 (3H, m, 18b), 0.80–1.06 (3H, m, 13a, 14a, 16a), 0.93–0.97 (3H, m, 19), 1.18–1.30 (1H, m, 12), 1.31–1.42 (1H, m, 15), 1.57 (3H, s, 9), 1.64 (3H, s, 10), 1.60–1.74 (2H, m, 13b, 14b), 1.99–2.07 (1H, m, 16b), 2.08–2.20 (1H, m, 17), 3.18–3.26 (1H, m, 6), 3.36–3.43 (1H, m, 3), 3.45–3.55 (1H, m, 11), 3.74–3.94 (1H, m, 1), 4.07–4.16 (1H, m, 2), 5.24 (1H, s, 8), 7.37–7.59 (5H, m, 21, 22, 23).

13C\{1H\} NMR (100.63 MHz, CDCl3): \(\delta [ppm] = 15.4 (d, 3J_{C,P} = 3.2 \text{ Hz}, 9), 15.6 (s, 18a), 16.5 (d, 3J_{C,P} = 3.9 \text{ Hz}, 10), 20.9 (s, 18b), 22.3 (s, 19), 23.0 (s, 13), 25.3 (s, 17), 31.4 (s, 15), 34.2
(s, 14), 39.8 (s, 16), 45.5 (d, $^2J_{C,P} = 18.7$ Hz, 2), 47.0 (d, $^2J_{C,P} = 16.7$ Hz, 1), 47.6 (s, 12), 51.6 (d, $^1J_{C,P} = 8.0$ Hz, 3/6), 52.1 (d, $^1J_{C,P} = 8.9$ Hz, 3/6), 77.2 (s, 11), 101.8 (d, $^3J_{C,P} = 16.7$ Hz, 8), 128.8 (d, $J_{C,P} = 11.9$ Hz, 21/22), 129.8 (d, $J_{C,P} = 9.5$ Hz, 21/22), 131.4 (d, $^1J_{C,P} = 80.2$ Hz, 20), 131.4 (d, $^4J_{C,P} = 2.8$ Hz, 23), 131.9 (d, $^2J_{C,P} = 6.4$ Hz, 4/5), 134.3 (d, $^2J_{C,P} = 7.5$ Hz, 4/5), 175.4 (d, $^3J_{C,P} = 11.9$ Hz, 21/22), 129.8 (d, $J_{C,P} = 9.5$ Hz, 21/22), 131.4 (d, $^1J_{C,P} = 80.2$ Hz, 20), 131.9 (d, $^2J_{C,P} = 6.4$ Hz, 4/5), 134.3 (d, $^2J_{C,P} = 7.5$ Hz, 4/5), 175.4 (d, $^3J_{C,P} = 11.9$ Hz, 21/22), 129.8 (d, $J_{C,P} = 9.5$ Hz, 21/22), 131.4 (d, $^1J_{C,P} = 80.2$ Hz, 20), 131.9 (d, $^2J_{C,P} = 6.4$ Hz, 4/5), 134.3 (d, $^2J_{C,P} = 7.5$ Hz, 4/5), 175.4 (d, $^3J_{C,P} = 11.9$ Hz, 21/22).

$^{31}$P{${}^1$H} NMR (161.98 MHz, CDCl$_3$): $\delta$[ppm] = 108.1

IR (KBr): $\nu$ [cm$^{-1}$] = 3444 s, 2925 m (C–H), 2854 w (C–H), 1746 w (O–C=O), 1634 m, 1456 w, 1384 w, 1261 w, 1102 m, 1022 m, 945 w, 304 w

MS (ESI): $m/z$: calc. for C$_{26}$H$_{35}$O$_3$PS [M+Na]$^+$: 481.2; found: 481.0

C$_{26}$H$_{35}$O$_3$PS (458.59): calc. C 68.09 H 7.69; found C 68.10 H 7.88

Synthesis of 3b:

A solution of 2b (0.492 g, 3.00 mmol) and (5R)-(l-menthyl)oxo-2(5H)-furanone (0.500 g, 2.10 mmol) in 20 ml chlorobenzene was heated at 130 °C for 120 hours. After the solution was cooled to room temperature, maleic anhydride (0.229 g, 2.34 mmol) was added to quench unreacted 2b. After 16 hours, morpholin (184 μl, 2.10 mmol) was added to quench unreacted (5R)-(l-menthyl)oxo-2(5H)-furanone and the solution was left to stir at room temperature for another 10 hours. The crude product was purified by column chromatography (hexanes/diethyl ether = 3:1 to 1:1, v/v) to give 3b as a mixture of diastereomers. Crystals, suitable for X-ray crystallography, were obtained from a mixture of DCM and hexanes at room temperature.

diastereomeric ratios crude product:

syn/anti (R$^1$ to C=C) = 96/4, d.r. (all syn) = 85:7:5:3
diastereomeric ratios product:

only syn, d.r. = 93:5:1:1

yield: 0.514 g, 52%

R$_f$ (hexanes/diethyl ether = 1:1, v/v) = 0.45; UV light, p-anisaldehyde

mp: 167–170 °C
$\alpha_1^3 = -69.2^\circ$ (c = 2.13 in toluene)

$^1$H NMR (300.23 MHz, CDCl$_3$): $\delta$[ppm] = 0.70–0.76 (3H, m, 18a), 0.83–0.90 (3H, m, 18b), 0.61–1.07 (3H, m, 13a, 14a, 16a), 0.89–0.96(3H, m, 19), 1.13–1.27 (1H, m, 12), 1.27–1.41 (1H, m, 15), 1.56–1.71 (2H, m, 13b, 14b), 1.76 (3H, s, 9), 1.82 (3H, s, 10), 1.91–2.02 (1H, m, 16b), 2.00–2.14 (1H, m, 17), 2.75–2.83 (1H,m, 6), 2.95–3.05 (1H, m, 3), 3.36–3.51 (3H, m, 11/20), 3.52–3.76 (1H, m, 1), 3.87–3.99 (1H, m, 2), 5.15 (1H, s, 8), 7.19–7.41(5H, m, 22/23/24).

$^{13}$C{$^1$H} NMR (75.50 MHz, CDCl$_3$): $\delta$[ppm] = 15.5 (d, $^3$J$_{C,P}$ = 3.9 Hz, 9), 15.6 (s, 18a), 16.5 (d, $^3$J$_{C,P}$ = 4.6 Hz, 10), 20.9 (s, 18b), 22.2 (s, 19), 23.0 (s, 13), 25.3 (s, 17), 31.4 (s, 15), 32.8–36.0 (m, 14, 20), 39.7 (s, 16), 45.5 (d, $^2$J$_{C,P}$ = 17.0 Hz, 2), 46.9 (d, $^2$J$_{C,P}$ = 15.4 Hz, 1), 47.6 (s, 12), 51.4 (d, $^1$J$_{C,P}$ = 19.1 Hz, 6), 52.0 (d, $^1$J$_{C,P}$ = 19.5 Hz, 3), 77.1 (s, 11), 101.6 (d, $^3$J$_{C,P}$ = 16.0 Hz, 8), 127.5 (d, $^2$J$_{C,P}$ = 3.1 Hz, 22/23/24), 128.8 (d, $^2$J$_{C,P}$ = 2.5 Hz, 22/23/24), 129.4 (d, $^2$J$_{C,P}$ = 5.6 Hz, 22/23/24), 131.4 (d, $^2$J$_{C,P}$ = 6.1 Hz, 4), 132.2 (d, $^2$J$_{C,P}$ = 8.4 Hz, 21), 133.8 (d, $^2$J$_{C,P}$ = 7.3 Hz, 5), 175.4 (d, $^2$J$_{C,P}$ = 13.5 Hz, 7).

$^{31}$P{$^1$H} NMR (161.98 MHz, CDCl$_3$): $\delta$[ppm] = 112.9

IR (KBr): $\nu$[cm$^{-1}$] = 3424 s, 2996 s (vC–H), 2925 s (vC–H), 2869 m (vC–H), 2345 w, 1771 s (vO–C=O), 1631w, 1496 w, 1454 m, 1352 m, 1292 w, 1262 w, 1239 m, 1175 s, 1118 s, 1013 w, 948 s, 888 w, 846 w, 829 w, 810 w, 766 w, 699 m, 648 m, 637 m, 572 w, 505 w, 482 m, 443 m, 412 w, 406 w

MS (ESI): m/z: calc. for C$_{27}$H$_{37}$O$_3$PS [M$+$Na]$^+$: 495.2; found: 495.3
C$_{27}$H$_{37}$O$_3$PS (472.62): calc. C 68.82 H 7.89; found C 68.77 H 7.78

Synthesis of 3c:

A solution of 2c (0.100 g, 0.425 mmol) and (5R)-(1-methyloxy)-2(5H)-furanone (0.102 g, 0.428 mmol) in 8 ml chlorobenzene was heated at 130 °C for 120 hours. The crude product was purified by column chromatography (hexanes/diethyl ether = 1:1, v/v) to give separately the $\text{s}ic$-C products endo-3c and exo-3c as white solids.

Crystals of endo-3c, suitable for X-ray crystallography, were obtained from a mixture of DCM and hexanes at room temperature.
diastereomeric ratios crude product:
syn/anti (R1 to C=C) = 98:2, d.r. (all syn) = 93 (endo, siC=C) : 5 (exo, siC=C) : 2

**endo-3c:**
yield: 0.141 g, 70%
Rf (hexanes/diethyl ether = 1:3, v/v) = 0.30; UV light, p-anisaldehyde
mp: 200–202 °C
$\alpha^2 = -62.6^\circ$ (c = 2.02 in toluene)

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$[ppm] = 0.61–0.70 (3H, m, 18a), 0.75–0.82 (3H, m, 18b), 0.70–0.98 (3H, m, 13a, 14a, 16a), 0.83–0.91 (3H, m, 19), 1.07–1.20 (1H, m, 12), 1.20–1.35 (1H, m, 15), 1.49–1.62 (2H, m, 13b, 14b), 1.74 (3H, s, 9), 1.83 (3H, s, 10), 1.88–1.98 (1H, m, 16b), 1.96–2.08 (1H, m, 17), 2.82–2.94 (1H, m, 6), 3.00–3.10 (1H, m, 3), 3.33–3.44 (1H, m, 11), 3.44–3.62 (3H, m, 1, 20), 3.80–3.91 (1H, m, 2), 5.12 (1H, d, $^3$J$_{H,H} = 7.7$ Hz, $^3$J$_{H,H} = 4.3$ Hz, 24), 7.27 (1H, d, $^3$J$_{H,H} = 7.7$ Hz, 22), 7.56 (1H, dd, $^3$J$_{H,H} = 7.7$ Hz, $^3$J$_{H,H} = 7.7$ Hz, 23), 8.45 (1H, d, $^3$J$_{H,H} = 4.3$ Hz, 25).

$^{13}$C{$^1$H} NMR (100.63 MHz, CDCl$_3$): $\delta$[ppm] = 15.4 (d, $^3$J$_{C,P}$ = 3.4 Hz, 9), 15.5 (s, 18a), 16.5 (d, $^3$J$_{C,P}$ = 4.2 Hz, 10), 20.9 (s, 18b), 22.2 (s, 19), 22.9 (s, 13), 25.2 (s, 17), 31.3 (s, 15), 34.2 (s, 14), 36.2 (d, $^1$J$_{C,P}$ = 45.7 Hz, 20), 39.7 (s, 16), 45.2 (d, $^2$J$_{C,P}$ = 18.0 Hz, 2), 46.6 (d, $^2$J$_{C,P}$ = 16.0 Hz, 1), 47.5 (s, 12), 50.6–53.6 (m, 3, 6), 77.1 (s, 11), 101.7 (d, $^3$J$_{C,P}$ = 16.4 Hz, 8), 122.2 (d, $^5$J$_{C,P}$ = 2.5 Hz, 24), 124.9 (d, $^3$J$_{C,P}$ = 5.3 Hz, 22), 131.6 (d, $^2$J$_{C,P}$ = 6.1 Hz, 4/5), 133.8 (d, $^2$J$_{C,P}$ = 7.4 Hz, 4/5), 136.5 (d, $^4$J$_{C,P}$ = 1.5 Hz, 23), 149.6 (d, $^4$J$_{C,P}$ = 2.1 Hz, 25), 153.0 (d, $^2$J$_{C,P}$ = 8.3 Hz, 21), 175.4 (d, $^3$J$_{C,P}$ = 13.9 Hz, 7).

$^{31}$P{$^1$H} NMR (161.98 MHz, CDCl$_3$): $\delta$[ppm] = 111.7

IR (KBr): $\nu$ [cm$^{-1}$] = 3433 s, 2957 s (vC–H), 2924 s (vC–H), 2868 m (vC–H), 1771 s (vO–C=O), 1635 w, 1593 m, 1469 m, 1436 m, 1888 w, 1352 s, 1308 w, 1290 m, 1239 m, 1176 s, 1156 m, 1117 s, 1078 w, 1051 w, 1013 w, 994 w, 972 w, 947 s, 888 w, 848 m, 839 w, 814 w, 793 w, 775 w, 750 w, 710 w, 683 w, 650 m, 638 m,

MS (ESI): $m/z$: calc. for C$_{26}$H$_{36}$NO$_3$PS $[M+Na]^+$: 496.2; found: 496.2
C$_{26}$H$_{36}$NO$_3$PS (472.62): calc. C 65.94 H 7.66; found C 66.03 H 7.55
exo-3c:
yield: 0.003 g, 2%

R_f (hexanes/diethyl ether = 1:3, v/v) = 0.42; UV light, p-anisaldehyde

1H NMR (300.23 MHz, CDCl_3): δ[ppm] = 0.77–0.81 (3H, m, 3H, 18a), 0.89–0.93 (3H, m, 18b), 0.70–1.11 (3H, m, 13a, 14a, 16a), 0.93–0.97 (3H, m, 19), 1.19–1.48 (2H, m, 12, 15), 1.56–1.74 (2H, m, 13b, 14b), 1.85 (3H, s, 9/10), 1.91 (3H, s, 9/10), 1.95–2.03 (1H, m, 16b), 2.02–2.17 (1H, m, 17), 2.83–2.95 (1H, m, 6), 3.07–3.16 (1H, m, 3), 3.39–3.52 (1H, m, 11), 3.55–3.69 (2H, m, 20), 3.83–3.96 (1H, m, 2), 3.99–4.13 (1H, m, 1), 5.77–5.81 (1H, m, 8), 7.21 (1H, dd, 3_J_H,H = 7.8 Hz, 3_J_H,H = 4.2 Hz, 24), 7.39 (1H, d, 3_J_H,H = 7.8 Hz, 22), 7.67 (1H, dd, 3_J_H,H = 7.8 Hz, 3_J_H,H = 4.2 Hz, 25).

13C{1H} NMR (75.50 MHz, CDCl_3): δ[ppm] = 15.4–15.6 (m, 9/10, 18a), 15.8 (d, 3_J_C,P = 4.0 Hz, 9/10), 21.1 (s, 18b), 22.2 (s, 19), 22.6 (s, 13), 24.9 (s, 17), 31.5 (s, 15), 34.1 (s, 14), 36.0 (d, 1_J_C,P = 45.9 Hz, 20), 41.5 (s, 16), 44.5 (d, 2_J_C,P = 19.4 Hz, 1), 47.2 (d, 2_J_C,P = 17.9 Hz, 2), 47.5 (s, 12), 50.9–52.5 (m, 3, 6), 81.1 (s, 11), 103.2 (d, 3_J_C,P = 12.0 Hz, 8), 122.2 (s, 24), 124.9 (d, 3_J_C,P = 5.3 Hz, 22), 132.5 (d, 2_J_C,P = 7.9 Hz, 4/5), 134.5 (d, 2_J_C,P = 5.1 Hz, 4/5), 136.5 (s, 23), 149.7 (s, 25), 153.2 (d, 2_J_C,P = 8.1 Hz, 21), 174.3 (d, 3_J_C,P = 12.8 Hz, 7).

31P{1H} NMR (161.98 MHz, CDCl_3): δ[ppm] = 113.2

Synthesis of 3d:

A solution of 2d (0.195 g, 0.050 mmol) and (5R)-(1-methylxyloxy)-2(5H)-furanone (0.250 g, 1.049 mmol) in 15 ml chlorobenzene was heated at 130 °C for 120 hours. The crude product was purified by column chromatography (hexanes/diethyl ether = 3:1 to 1:2, v/v) to give endo-3d as a white solid.
The other stereoisomers could not be isolated and assigned. Hence, it was not possible to determine the diastereomeric ratios.

Yield: 0.218 g, 50%

R$_f$ (hexanes/diethyl ether = 2:3, v/v) = 0.37, UV light, p-anisaldehyde

mp: 135–138 °C

$[\alpha]_D^{5} = -76.9^\circ$ (c = 2.06 in toluene)

$^1$H NMR (400.13 MHz, CDCl$_3$): $\delta$[ppm] = 0.70–0.77 (6H, m, 18a), 0.84–0.89 (6H, m, 18b), 0.80–1.02 (6H, m, 13a, 14a, 16a), 0.91–0.95 (6H, m, 19), 1.13–1.24 (2H, m, 12), 1.29–1.42 (2H, m, 15), 1.57–1.72 (4H, m, 13b, 14b), 1.77 (6H, s, 9), 1.87 (6H, s, 10), 1.94–2.02 (2H, m, 16b), 2.02–2.13 (2H, m, 17), 2.85–2.95 (2H, s, 6), 3.01–3.11 (2H, s, 3), 3.35–3.51 (2H, m, 11), 3.59–3.70 (2H, m, 1), 3.78–3.95 (6H, m, 2, 20), 5.17 (2H, s, 8), 7.00–7.10 (2H, m, 22), 7.19–7.26 (2H, m, 23).

$^{13}$C{$^1$H} NMR (100.63 MHz, CDCl$_3$): $\delta$[ppm] = 15.1–16.0 (m, 18a, 9), 16.2–17.3 (m, 10), 20.9 (s, 18b), 22.3 (s, 19), 23.0 (s, 13), 25.2 (s, 17), 31.2 (d, $^1$J$_{C,P}$ = 42.4 Hz, 20), 31.4 (s, 15), 34.2 (s, 14), 39.7 (s, 16), 45.1–45.4 (m, 2), 46.7–47.0 (m, 1), 47.6 (s, 12), 51.6 (d, $^1$J$_{C,P}$ = 10.4 Hz, 3/6), 52.1 (d, $^1$J$_{C,P}$ = 11.2 Hz, 3/6), 77.1 (s, 11), 101.3–101.7 (m, 8), 127.9 (s (br), 23), 130.6 (s (br), 22), 131.0–132.3 (m, 4/5), 132.5–133.2 (m, 21), 133.3–135.4 (m, 4/5), 175.1–175.4 (m, 7).

$^{31}$P{$^1$H} NMR (161.98 MHz, CDCl$_3$): $\delta$[ppm] = 112.1

IR (KBr): $\nu$ [cm$^{-1}$] = 3426 s, 2959 s (vC–H), 2926 s (vC–H), 2870 m (vC–H), 2345 w, 1774 s (vO–C=O), 1631 m, 1456 w, 1352 w, 1263 m, 1234 w, 1164 m, 1110 s, 1018 m, 943 m, 803 m, 698 w, 637 w, 598 w, 465 w, 438 w, 416 w, 406 w

MS (ESI): m/z: calc. for C$_{48}$H$_{68}$O$_6$P$_2$S$_2$ [M+Na]$^+$: 889.4; found: 889.5

C$_{48}$H$_{68}$O$_6$P$_2$S$_2$ (867.13): calc. C 66.49 H 7.90; found C 66.41 H 8.03
Synthesis of 3e:

A solution of 2e (0.411 g, 1.05 mmol) and (5R)-(L-methylthio)-2(5H)-furanone (0.500 g, 2.10 mmol) in 20 ml chlorobenzene was heated at 130 °C for 120 hours. The crude product was purified by column chromatography (hexanes/diethyl ether = 1:1 to 1:6, v/v) to give endo-3e as a white solid.

The other stereoisomers could not be isolated and assigned. Hence, it was not possible to determine the diastereomeric ratios.

Yield: 0.464 g, 51%

R<sub>f</sub> (hexanes/diethyl ether = 1:6, v/v) = 0.27; UV light, p-anisaldehyde

mp: 110–112 °C

$\left[\alpha\right]_D^\circ = +16.3^\circ$ (c = 2.03 in toluene)

1H NMR (400.13 MHz, CDCl<sub>3</sub>): δ[ppm] = 0.69–0.79 (6H, m, 18a), 0.84–0.90 (6H, m, 18b), 0.61–1.15 (6H, m, 13a, 14a, 16a), 0.91–0.99 (6H, m, 19), 1.17–1.30 (2H, m, 12), 1.30–1.43 (2H, m, 15), 1.57–1.75 (4H, m, 13b, 14b), 1.71 (6H, s, 10), 1.77 (6H, s, 9), 1.97–2.20 (4H, m, 16b, 17), 3.07–3.16 (2H, m, 3), 3.34–3.55 (6H, m, 6, 11, 20a), 3.57–3.66 (2H, m, 1), 3.66–3.77 (2H, m, 20b), 3.86–3.96 (2H, m, 2), 5.16 (2H, s, 8), 7.09 (2H, d, $^3$J<sub>H,H</sub> = 7.5 Hz, 22), 7.62 (2H, t, $^3$J<sub>H,H</sub> = 7.5 Hz, 23).

13C{1H} NMR (100.63 MHz, CDCl<sub>3</sub>): δ[ppm] = 15.4 (d, $^3$J<sub>C,P</sub> = 3.3 Hz, 9), 15.6 (s, 18a), 16.4 (d, $^3$J<sub>C,P</sub> = 4.6 Hz, 10), 20.9 (s, 18b), 22.3 (s, 19), 23.0 (s, 13), 25.3 (s, 17), 31.4 (s, 15), 34.2 (s, 14), 36.9 (d, $^1$J<sub>C,P</sub> = 46.8 Hz, 20), 40.4 (s, 16), 45.4 (d, $^2$J<sub>C,P</sub> = 17.9 Hz, 2), 46.5 (d, $^2$J<sub>C,P</sub> = 16.5 Hz, 1), 47.6 (s, 12), 51.0 (d, $^1$J<sub>C,P</sub> = 48.3 Hz, 6), 52.4 (d, $^1$J<sub>C,P</sub> = 47.8 Hz, 3), 78.7 (s, 11), 102.9 (d, $^3$J<sub>C,P</sub> = 17.4 Hz, 8), 123.0 (s, 22), 132.3 (d, $^2$J<sub>C,P</sub> = 5.9 Hz, 4/5), 133.5 (d, $^2$J<sub>C,P</sub> = 7.6 Hz, 4/5), 137.5 (s, 23), 154.2 (d, $^2$J<sub>C,P</sub> = 8.4 Hz, 21), 175.6 (d, $^3$J<sub>C,P</sub> = 13.5 Hz, 7).

31P{1H} NMR (161.98 MHz, CDCl<sub>3</sub>): δ[ppm] = 111.1

IR (KBr): ν [cm<sup>−1</sup>] = 3452 s, 2924 s (νC–H), 1774 s (νO–C=O), 1630 s, 1456 m, 1350 w, 1262 w, 1115 m, 1019 w, 944 m, 853 w, 802 w, 684 w, 660 w, 597 w, 555 w, 502 w, 440 w, 431 w, 417 w

MS (ESI): m/z: calc. for C<sub>47</sub>H<sub>67</sub>NO<sub>6</sub>P<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: 890.4; found: 890.4
A solution of 3, nickelocene (3 equivalents per 7-phosphanorbornene unit) and allyl iodide (1.5 equivalents per 7-phosphanorbornene unit) was heated to 50 °C for 3 hours during which the reaction mixture changed colour from dark green to dark red (cloudy). The mixture was filtered through a pad of silica, which was subsequently washed with THF until the dark red band was eluted. The solution containing the nickel complex of syn-4 was treated with 1-methylimidazole (20 equivalents per 7-phosphanorbornene unit), stirred for 20 minutes and filtered through a pad of silica, which was washed with diethyl ether (twice the volume of the silica) to give a yellow solution of syn-4. Upon standing at room temperature for two days, 4b,d,e isomerise to the anti isomer.

**nickel complex of syn-4b:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 158.8

**nickel complex of syn-4d:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 156.4

**nickel complex of syn-4e:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = not detectable, probably due to paramagnetism of the complex

**syn-4b:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 120.7

**syn-4d:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 116.7

**syn-4e:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 119.6

**anti-4b:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 85.1

**anti-4d:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 86.0

**anti-4e:** $^{31}$P$\{^1$H$\}$ NMR (161.98 MHz, no lock): $\delta$[ppm] = 84.5
Crystallographic data:

Structure parameters for 2d: C_{20}H_{24}P_{2}S_{2}, M = 390.45, T = 130(2) K, monoclinic space group P2_1/c, a = 1130.23(3) pm, b = 1372.89(3) pm, c = 1341.85(4) pm, β = 105.031(3)°, V = 2.01089(9) nm^3, ρ_{calc} = 1.290 Mg·m^{-3}, Z = 4, μ = 0.423 mm^{-1}, crystal size 0.30 x 0.30 x 0.20 mm^3, 2θ_{max} = 30.51°, reflections collected 22953, independent reflections 6143 (R(int) = 0.0270), completeness to θ = 30.51°: 99.9%, 313 parameters, 0 restraints. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically, R indices (all data): R1 = 0.0409, wR2 = 0.0819, final R indices [I>2σ(I)]: R1 = 0.0318, wR2 = 0.0771, residual electron density 0.381 e Å^{-3}.

Structure parameters for 2e: C_{19}H_{23}NP_{2}S_{2}, M = 391.44, T = 130(2) K, triclinic space group P-1, a = 763.02(2) pm, b = 877.19(3) pm, c = 1564.26(6) pm, α = 102.400(3)°, β = 94.431(3)°, γ = 104.341(3)°, V = 0.98123(6) nm^3, ρ_{calc} = 1.325 Mg·m^{-3}, Z = 2, μ = 0.435 mm^{-1}, crystal size 0.25 x 0.20 x 0.10 mm^3, 2θ_{max} = 26.37°, reflections collected 14414, independent reflections 4010 (R(int) = 0.0307), completeness to θ = 26.37°: 99.9%, 309 parameters, 0 restraints. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically, R indices (all data): R1 = 0.0409, wR2 = 0.0819, final R indices [I>2σ(I)]: R1 = 0.0331, wR2 = 0.0797, residual electron density 0.356 e Å^{-3}.

Structure parameters for 3a: C_{26}H_{35}O_{3}PS, M = 458.57, T = 130(2) K, orthorhombic space group P2_1_2_1_2_1, a = 754.33(2) pm, b = 1404.57(3) pm, c = 2438.17(4) pm, V = 2.5833(1) nm^3, ρ_{calc} = 1.179 Mg·m^{-3}, Z = 4, μ = 0.211 mm^{-1}, crystal size 0.40 x 0.10 x 0.05 mm^3, 2θ_{max} = 26.37°, reflections collected 23054, independent reflections 5288 (R(int) = 0.0528), completeness to θ = 26.37°: 99.9%, 420 parameters, 0 restraints. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically, the H atoms were refined isotropically, R indices (all data): R1 = 0.0435, wR2 = 0.0789, final R indices [I>2σ(I)]: R1 = 0.0363, wR2 = 0.0789, residual electron density 0.280 e Å^{-3}, absolute structure parameter 0.06(6).

Structure parameters for 3b: C_{27}H_{37}O_{3}PS, M = 472.60, T = 130(2) K, orthorhombic space group P2_1_2_1_2_1, a = 989.9(5) pm, b = 1328.0(5) pm, c = 1956.7(5) pm, V = 2.572(2) nm^3, ρ_{calc} = 1.220 Mg·m^{-3}, Z = 4, μ = 0.214 mm^{-1}, crystal size 0.20 x 0.20 x 0.20 mm^3, 2θ_{max} = 30.51°, reflections collected 57680, independent reflections 7832 (R(int) = 0.0345), completeness to θ = 30.51°: 99.9%, 437 parameters, 0 restraints. The structure was solved by direct methods and
all non-hydrogen atoms were refined anisotropically, R indices (all data): \( R1 = 0.0305, \) \( wR2 = 0.0662, \) final R indices \([I>2\sigma(I)]: R1 = 0.0263, \) \( wR2 = 0.0645, \) residual electron density \( 0.236 \text{ eÅ}^{-3}, \) absolute structure parameter \(-0.01(4).\)

Structure parameters for \( 3c: \) \( C_{26}H_{36}NO_3PS, \) \( M = 473.29, \) \( T = 130(2) \text{ K}, \) orthorhombic space group \( P2_12_12_1, \) \( a = 999.28(2) \text{ pm}, \) \( b = 1331.60(2) \text{ pm}, \) \( c = 1917.69(3) \text{ pm}, \) \( V = 2.55176(8) \text{ nm}^3, \) \( \rho_{\text{calc}} = 1.233 \text{ Mg·m}^{-3}, \) \( Z = 4, \) \( \mu = 0.216 \text{ mm}^{-1}, \) crystal size \( 0.20 \times 0.20 \times 0.15 \text{ mm}^3, \) \( 2\theta_{\text{max}} = 30.51^\circ, \) reflections collected 51223, independent reflections 7775 \( (R(\text{int}) = 0.0530), \) completeness to \( \theta = 30.51^\circ: 99.9\%, \) 433 parameters, 0 restraints. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically, R indices (all data): \( R1 = 0.0440, \) \( wR2 = 0.0743, \) final R indices \([I>2\sigma(I)]: R1 = 0.0356, \) \( wR2 = 0.0711, \) residual electron density \( 0.244 \text{ eÅ}^{-3}, \) absolute structure parameter \(-0.01(5).\)

The data were collected on a Gemini diffractometer (Agilent Technologies) using Mo-K\(\alpha\) radiation \( (\lambda = 71.073 \text{ pm}), \) \( \omega\)-scan rotation. Data reduction was performed with the CrysAlisPro (CrysAlisPro: Data collection and data reduction software package, Agilent Technologies) including the program SCALE3 ABSPACK (SCALE3 ABSPACK: Empirical absorption correction using spherical harmonics) for empirical absorption correction. The structures were solved by direct methods with SIR92.\(^8\) The refinement of all non-hydrogen atoms was performed with SHELXL-97.\(^9\) The structure figure was generated with Diamond.\(^{10}\) CCDC 981039 (2d), 981040 (2e), 981041 (3a), 981042 (3b) and 981043 (3c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.