Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

P-chiral 1-phosphanorbornenes: From asymmetric Phospha-Diels–Alder reactions towards ligand design and functionalisation

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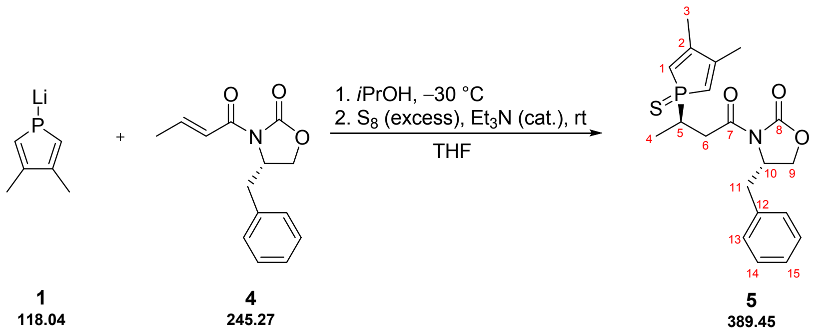
Assignment of NMR spectroscopic data

Compound **5**:

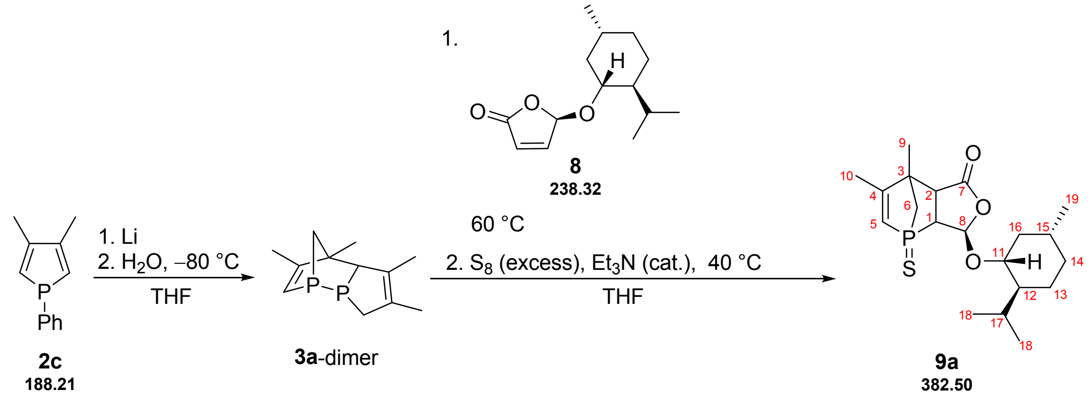


^{1}H NMR (300 MHz): δ= 1.27 (3H, dd, $^3J_{H,P}$ = 18.7 Hz, $^3J_{H,H}$ = 7.1 Hz, *4*), 2.08 (6H, s, *3*), 2.60–2.84 (2H, m, *5*, *11a*), 2.94–3.13 (1H, m, *6a*), 3.24–3.54 (2H, m, *6b*, *11b*), 4.12–4.27 (2H, m, *9*), 4.62–4.75 (1H, m, *10*), 6.03 (2H, d, $^2J_{H,P}$ = 30.4 Hz, *1*), 7.18–7.26 (2H, m, *13*/*14*), 7.26–7.40 (3H, m, *13*/*14*, *15*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ= 15.2 (s, *4*), 17.4 (d, $^3J_{C,P}$ = 3.3 Hz, *3*), 17.6 (d, $^3J_{C,P}$ = 3.3 Hz, *3*) 31.1 (d, $^1J_{C,P}$ = 51.8 Hz, *5*), 37.1 (s, *6*), 37.9 (s, *11*), 55.3 (s, *10*), 66.4 (s, *9*), 122.1–123.5 (m, *1*), 123.1–123.6 (m, *1*), 127.4 (s, *15*), 129.0 (s, *13*/*14*), 129.4 (s, *13*/*14*), 135.1 (s, *12*), 153.3 (s, *8*), 153.8–154.5 (m, *2*), 171.0 (d, $^3J_{C,P}$ = 13.4 Hz, *7*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ= 61.5 ppm

*Compound endo-***9a**:

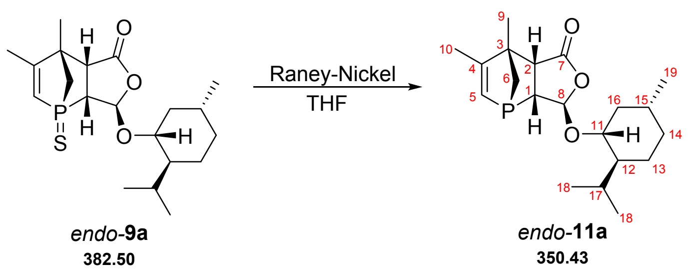


^{1}H NMR (400 MHz): δ = 0.75 (3H, d, $^3J_{H,H}$ = 6.9 Hz, *18a*), 0.81–0.91 (1H, m, *14a*), 0.84 (3H, d, $^3J_{H,H}$ = 7.1 Hz, *18b*), 0.91–1.04 (m, 2H, *13a*, *16a*), 0.93 (3H, d, $^3J_{H,H}$ = 6.5 Hz, *19*), 1.19–1.29 (1H, m, *12*), 1.30–1.40 (1H, m, *15*), 1.63 (3H, s, *9*), 1.61–1.68 (2H, m, *13b*, *14b*), 1.94 (3H, s, *10*), 1.91–1.97 (1H, m, *6a (anti-C=C)*), 2.02–2.08 (2H, m, *6b (syn-C=C)*, *17*), 2.11–2.18 (1H, m, *16b*), 3.13–3.20 (1H, m, *1*), 3.25–3.31 (1H, m, *2*), 3.50 (1H, ddd, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 2.4 Hz, *11*), 5.49 (1H, d, $^3J_{H,P}$ = 13.0 Hz, *8*), 5.90 (1H, d, $^2J_{H,P}$ = 26.3 Hz, *5*) ppm

^{13}C{^{1}H} NMR (101 MHz): δ = 15.7 (s, *18a*), 18.6 (d, $^3J_{C,P}$ = 14.2 Hz, *10*), 19.3 (d, $^3J_{C,P}$ = 16.2 Hz, *9*), 20.9 (s, *18b*), 22.2 (s, *19*), 23.1 (s, *13*), 25.4 (s, *17*), 31.5 (s, *15*), 34.2 (s, *14*), 40.0 (s, *16*), 47.5 (s, *12*), 48.6 (d, $^1J_{C,P}$ = 46.6 Hz, *1*), 50.9 (d, $^2J_{C,P}$ = 21.7 Hz, *3*), 53.5 (s, *2*), 56.5 (d, $^1J_{C,P}$ = 57.6 Hz, *6*), 78.7 (s, *11*), 99.5 (d, $^2J_{C,P}$ = 5.9 Hz, *8*), 121.1 (d, $^1J_{C,P}$ = 69.3 Hz, *5*), 165.5 (d, $^2J_{C,P}$ = 7.2 Hz, *4*), 173.6 (d, $^3J_{C,P}$ = 3.0 Hz, *7*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ = 48.7 ppm

*Compound endo-***11a**:

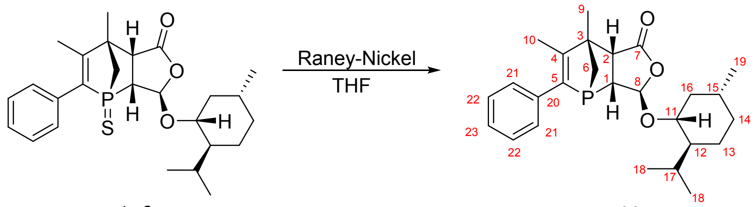


^{1}H NMR (300 MHz): δ = 0.75 (3H, d, $^3J_{H,H}$ = 6.9 Hz, *18a*), 0.87 (3H, d, $^3J_{H,H}$ = 7.1 Hz, *18b*), 0.65–1.13 (3H, m, *13a*, *14a*, *16a*), 0.93 (3H, d, $^3J_{H,H}$ = 6.5 Hz, *19*), 1.15–1.27 (1H, m, *12*), 1.28–1.46 (2H, m, *6a*, *15*), 1.52 (1H, dd, J = 11.5 Hz, J = 8.9 Hz, *6b*), 1.63 (3H, s, *9*), 1.57–1.70 (2H, m, *13b*, *14b*), 1.88 (3H, s, *10*), 1.96–2.16 (2H, m, *16b*, *17*), 2.97–3.07 (2H, m, *1*, *2*), 3.42 (1H, ddd, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 4.2 Hz, *11*), 5.04 (1H, dd, $^3J_{H,P}$ = 8.1 Hz, $^3J_{H,H}$ = 1.4 Hz, *8*), 5.87 (1H, d, $^2J_{H,P}$ = 45.0 Hz, *5*) ppm

$^{13}C\{^1H\}$ NMR (76 MHz): δ = 15.7 (s, *18a*), 18.3 (s, *10*), 19.2 (s, *9*), 20.9 (s, *18b*), 22.2 (s, *19*), 23.2 (s, *13*), 25.4 (s, *17*), 31.4 (s, *15*), 34.3 (s, *14*), 40.0 (s, *16*), 46.3 (d, $^1J_{C,P}$ = 19.6 Hz, *1*), 47.7 (s, *12*), 51.8 (d, $^2J_{C,P}$ = 1.8 Hz, *2*), 53.2 (d, $^1J_{C,P}$ = 4.9 Hz, *6*), 62.9 (d, $^2J_{C,P}$ = 6.1 Hz, *3*), 77.2 (s, *11*), 101.9 (d, $^2J_{C,P}$ = 11.4 Hz, *8*), 124.0 (d, $^1J_{C,P}$ = 24.2 Hz, *5*), 163.8 (d, $^2J_{C,P}$ = 4.3 Hz, *4*), 175.5 (s, *7*) ppm

$^{31}P\{^1H\}$ NMR (162 MHz): δ = −30.0 ppm

Compound endo-**11c**



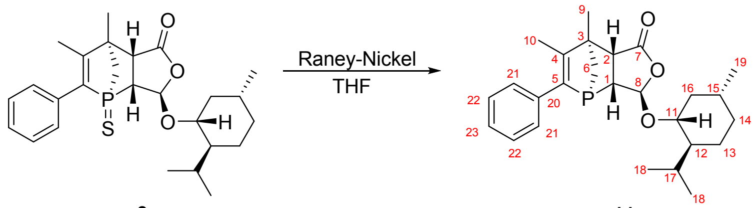
endo-**9c** 458.59 *endo*-**11c** 426.53

^1H NMR (300 MHz): δ = 0.74 (3H, d, $^3J_{H,H}$ = 6.9 Hz, *18a*), 0.64–1.03 (9H, m, *13a*, *14a*, *16a*, *18b*, *19*), 1.06–1.20 (1H, m, *12*), 1.20–1.32 (1H, m, *15*), 1.35–1.49 (1H, m, *6a*), 1.50–1.74 (3H, m, *6b*, *13b*, *14b*), 1.70 (3H, s, *9*), 1.76–1.84 (1H, m, *16b*), 1.94 (3H, s, *10*), 1.99–2.13 (1H, m, *17*), 3.00–3.24 (2H, m, *1*, *2*), 3.36 (1H, ddd, $^3J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 4.1 Hz, *11*), 5.06 (1H, d, $^3J_{H,P}$ = 7.1 Hz, *8*), 7.20–7.41 (5H, m, *21*, *22*, *23*) ppm

$^{13}C\{^1H\}$ NMR (76 MHz): δ = 15.0 (s, *10*), 15.7 (s, *18a*), 20.2 (s, *9*), 20.8 (s, *18b*), 22.1 (s, *19*), 23.1 (s, *13*), 25.4 (s, *17*), 31.3 (s, *15*), 34.2 (s, *14*), 39.8 (s, *16*), 46.8 (d, $^1J_{C,P}$ = 21.3 Hz, *1*), 47.6 (s, *12*), 51.0–51.2 (m, *2*, *6*), 64.5 (d, $^2J_{C,P}$ = 6.3 Hz, *3*), 77.1 (s, *11*), 101.0 (d, $^2J_{C,P}$ = 10.6 Hz, *8*), 127.0 (s, *23*), 128.4 (s, *22*), 129.0 (d, $^3J_{C,P}$ = 6.8 Hz, *21*), 136.8–139.3 (m, *5*, *20*), 153.9 (s, *4*), 175.6 (s, *7*) ppm

$^{31}P\{^1H\}$ NMR (162 MHz): δ = −14.5 ppm

Compound exo-**11c**



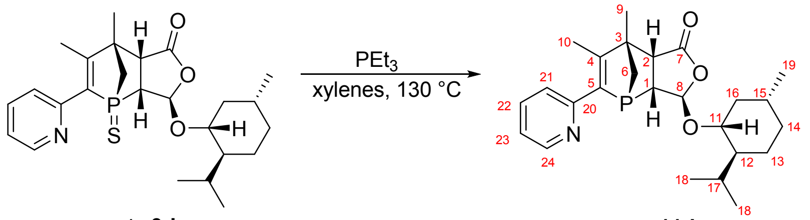
exo-**9c** 458.59 *exo*-**11c** 426.53

^{1}H NMR (300 MHz): δ = 0.80 (3H, d, $^{3}J_{H,H}$ = 6.9 Hz, *18a*), 0.87 (3H, d, $^{3}J_{H,H}$ = 7.0 Hz, *18b*), 0.71–1.08 (3H, m, *13a*, *14a*, *16a*), 0.94 (3H, d, $^{3}J_{H,H}$ = 6.5 Hz, *19*), 1.14–1.42 (3H, m, *6a*, *12*, *15*), 1.51 (1H, dd, J = 12.9 Hz, J = 8.0 Hz, *6b*), 1.60–1.73 (2H, m, *13b*, *14b*), 1.64 (3H, s, *9*), 1.87 (3H, s, *10*), 2.02–2.20 (2H, m, *16b*, *17*), 2.57–2.66 (2H, m, *1*, *2*), 3.55 (1H, ddd, $^{3}J_{H,H}$ = 10.7 Hz, $^{3}J_{H,H}$ = 10.7 Hz, $^{3}J_{H,H}$ = 4.2 Hz, *11*), 5.51 (1H, d, $^{3}J_{H,P}$ = 8.8 Hz, *8*), 7.30–7.15 (3H, m, *21/22, 23*), 7.30–7.38 (2H, m, *21/22,*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ = 13.0 (s, *10*), 15.7 (s, *18a*), 17.8 (s, *9*), 20.9 (s, *18b*), 22.2 (s, *19*), 23.2 (s, *13*), 25.4 (s, *17*), 31.4 (s, *15*), 34.3 (s, *14*), 39.9 (s, *16*), 42.3 (d, $^{1}J_{C,P}$ = 7.1 Hz, *6*), 47.8 (s, *12*), 48.7 (d, $^{2}J_{C,P}$ = 2.4 Hz, *2*), 49.5 (d, $^{1}J_{C,P}$ = 19.0 Hz, *1*), 63.9 (d, $^{2}J_{C,P}$ = 6.4 Hz, *3*), 76.9 (s, *11*), 101.3 (d, $^{2}J_{C,P}$ = 29.2 Hz, *8*), 126.9 (s, *23*), 128.1 (d, $^{3}J_{C,P}$ = 7.3 Hz, *21*), 128.3 (s, *22*), 137.6 (d, $^{2}J_{C,P}$ = 20.5 Hz, *20*), 142.2 (d, $^{1}J_{C,P}$ = 16.5 Hz, *5*), 154.2 (s, *4*), 174.8 (s, *7*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ = −10.1 ppm

Compound endo-**11d**



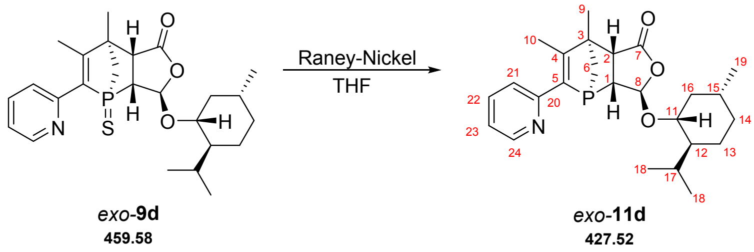
endo-**9d** 459.58 | *endo*-**11d** 427.52

^{1}H NMR (300 MHz): δ = 0.67 (3H, d, $^{3}J_{H,H}$ = 6.9 Hz, *18a*), 0.80 (3H, d, $^{3}J_{H,H}$ = 7.0 Hz, *18b*), 0.59–0.99 (3H, m, *13a*, *14a*, *16a*), 0.88 (3H, d, $^{3}J_{H,H}$ = 6.5 Hz, *19*), 1.10–1.30 (2H, m, *12*, *15*), 1.32–1.44 (1H, m, *6a*), 1.50–1.62 (3H, m, *6b*, *13b*, *14b*), 1.65 (3H, s, *9*), 1.95 (3H, s, *10*), 2.00–2.09 (1H, m, *17*), 2.09–2.18 (1H, m, *16b*), 2.95–3.18 (2H, m, *1*, *2*), 3.31 (1H, ddd, $^{3}J_{H,H}$ = 10.6 Hz, $^{3}J_{H,H}$ = 10.6 Hz, $^{3}J_{H,H}$ = 4.1 Hz, *11*), 5.68 (1H, d, $^{3}J_{H,P}$ = 8.3 Hz, *8*), 7.06–7.12 (1H, m, *23*), 7.16–7.27 (1H, m, *21*), 7.44–7.75 (1H, m, *22*), 8.43–8.60 (1H, m, *24*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ = 15.0 (s, *10*), 15.8 (s, *18a*), 20.1 (s, *9*), 20.9 (s, *18b*), 22.4 (s, *19*), 23.2 (s, *13*), 25.5 (s, *17*), 31.5 (s, *15*), 34.4 (s, *14*), 40.1 (s, *16*), 46.3 (d, $^{1}J_{C,P}$ = 21.8 Hz, *1*), 47.6 (s, *12*), 50.9 (d, $^{1}J_{C,P}$ = 5.6 Hz, *6*), 52.2 (s, *2*), 65.1 (d, $^{2}J_{C,P}$ = 6.7 Hz, *3*), 77.5 (s, *11*), 102.7 (d, $^{2}J_{C,P}$ = 10.0 Hz, *8*), 121.3 (s, *23*), 123.1 (d, $^{3}J_{C,P}$ = 4.1 Hz, *21*), 135.8 (s, *22*), 140.6 (d, $^{1}J_{C,P}$ = 18.1 Hz, *5*), 149.4 (s, *24*), 155.8 (s, *4*), 157.2 (d, $^{2}J_{C,P}$ = 17.3 Hz, *20*), 175.5 (s, *7*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ = −13.6 ppm

Compound exo-**11d**

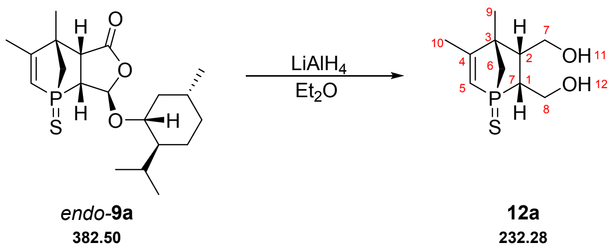


^{1}H NMR (300 MHz): δ = 0.70 (3H, d, $^3J_{H,H}$ = 6.9 Hz, *18a*), 0.77 (3H, d, $^3J_{H,H}$ = 7.0 Hz, *18b*), 0.57–0.99 (3H, m, *13a*, *14a*, *16a*), 0.86 (3H, d, $^3J_{H,H}$ = 6.4 Hz, *19*), 1.01–1.32 (3H, m, *6a*, *12*, *15*), 1.33–1.47 (1H, m, *6b*), 1.48–1.64 (2H, m, *13b*, *14b*), 1.57 (3H, s, *9*), 1.93 (3H, s, *10*), 1.96–2.03 (1H, m, *17*), 2.03–2.11 (1H, m, *16b*), 2.51–2.59 (1H, m, *2*), 2.61–2.73 (1H, m, *1*), 3.46 (1H, ddd, $^3J_{H,H}$ = 10.6 Hz, $^3J_{H,H}$ = 10.6 Hz, $^3J_{H,H}$ = 4.1 Hz, *11*), 5.48 (1H, d, $^3J_{H,P}$ = 9.0 Hz, *8*), 7.04 (1H, dd, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,H}$ = 4.8 Hz, *23*), 7.19 (1H, d, $^3J_{H,H}$ = 7.7 Hz, *21*), 7.57 (1H, dd, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,H}$ = 7.7 Hz, *22*), 8.51 (1H, d, $^3J_{H,H}$ = 4.8 Hz, *24*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ = 13.4 (s, *10*), 15.7 (s, *18a*), 17.7 (s, *9*), 20.8 (s, *18b*), 22.2 (s, *19*), 23.2 (s, *13*), 25.4 (s, *17*), 31.3 (s, *15*), 34.3 (s, *14*), 39.7 (s, *16*), 41.7 (d, $^1J_{C,P}$ = 7.2 Hz, *6*), 47.7 (s, *12*), 48.8 (s, *2*), 49.3 (d, $^1J_{C,P}$ = 19.2 Hz, *1*), 64.3 (d, $^2J_{C,P}$ = 6.6 Hz, *3*), 76.4 (s, *11*), 101.1 (d, $^2J_{C,P}$ = 29.9 Hz, *8*), 121.3 (s, *23*), 122.8 (d, $^3J_{C,P}$ = 6.7 Hz, *21*), 135.9 (s, *22*), 142.8 (d, $^1J_{C,P}$ = 14.8 Hz, *5*), 149.4 (s, *24*), 156.5 (d, $^2J_{C,P}$ = 19.8 Hz, *20*), 157.8 (s, *4*), 174.7 (s, *7*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ = −12.1 ppm

Compound **12a**

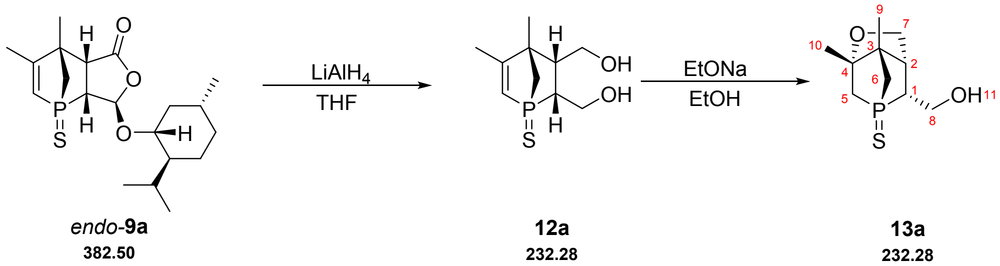


^{1}H NMR (400 MHz): δ = 1.45 (3H, s, *9*), 1.88 (3H, s, *10*), 1.89–2.01 (2H, m, *6*), 2.47–2.70 (1H, m, *2*), 2.72–2.90 (1H, m, *1*), 3.36–3.48 (1H, m, *7a*), 3.59–3.71 (1H, m, *8a*), 3.71–3.81 (1H, m, *7b*), 4.15–4.26 (1H, m, *8b*), 4.81 (2H, s (br), *11*, *12*), 5.76 (1H, d, $^2J_{H,P}$ = 26.3 Hz, *5*) ppm

^{13}C{^{1}H} NMR (101 MHz): δ = 19.1 (d, $^3J_{C,P}$ = 15.0 Hz, *9*), 19.7 (d, $^3J_{C,P}$ = 17.0 Hz, *10*), 44.7 (d, $^1J_{C,P}$ = 42.4 Hz, *1*), 49.6 (d, $^2J_{C,P}$ = 24.2 Hz, *3*), 52.0 (s, *2*), 54.7 (d, $^1J_{C,P}$ = 56.3 Hz, *6*), 59.0 (d, $^2J_{C,P}$ = 6.2 Hz, *8*), 59.5 (d, $^3J_{C,P}$ = 3.4 Hz, *7*), 121.4 (d, $^1J_{C,P}$ = 68.8 Hz, *5*), 163.9 (d, $^2J_{C,P}$ = 7.4 Hz, *4*) ppm

$^{31}P\{^1H\}$ NMR (162 MHz): $\delta = 48.2$ ppm

Compound **13a**

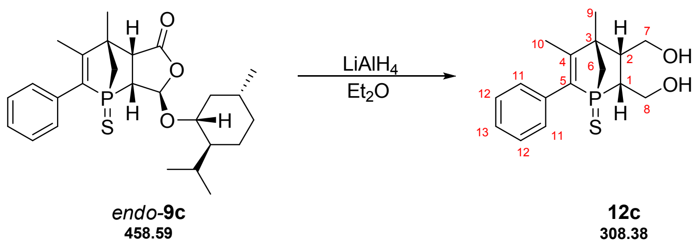


^1H NMR (300 MHz): $\delta = 1.15$ (3H,, *9*/*10*), 1.21 (3H, s, *9*/*10*), 1.79–1.98 (2H, m, *5a*, *6a*), 1.99–2.13 (1H, m, *5b*/*6b*), 2.18–2.34 (1H, m, *5b*/*6b*), 2.39–2.67 (2H, m, *1*, *2*), 3.05 (1H, s (br), *11*), 3.71–4.24 (4H, m, *7*, *8*) ppm

$^{13}C\{^1H\}$ NMR (76 MHz): $\delta = 18.2$ (d, $^3J_{C,P} = 16.0$ Hz, *9*/*10*), 23.9 (d, $^3J_{C,P} = 7.3$ Hz, *9*/*10*), 39.9 (d, $^1J_{C,P} = 51.5$ Hz, *5*/*6*), 41.4 (d, $^1J_{C,P} = 44.8$ Hz, *5*/*6*), 44.0 (d, $^1J_{C,P} = 47.6$ Hz, *1*), 47.2 (d, $^2J_{C,P} = 1.5$ Hz, *2*), 51.6 (d, $^2J_{C,P} = 19.5$ Hz, *3*), 57.9 (d, $J_{C,P} = 1.9$ Hz, *7*/*8*), 66.1 (s, *7*/*8*), 86.2 (s, *4*) ppm

$^{31}P\{^1H\}$ NMR (162 MHz): $\delta = 44.9$ ppm

Compound **12c**

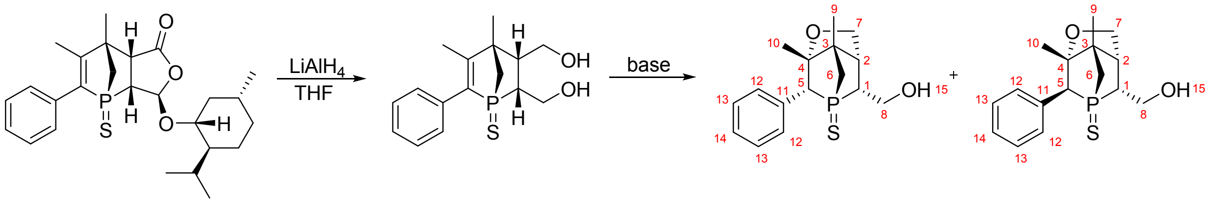


^1H NMR (400 MHz): $\delta = 1.54$ (3H, s, *9*), 1.94 (3H, d, $^4J_{H,P} = 2.7$ Hz, *10*), 2.00–2.10 (2H, m, *6*), 2.61–2.72 (1H, m, *2*), 2.85–2.98 (1H, m, *1*), 3.54–3.63 (1H, m, *7a*), 3.73–3.82 (1H, m, *8a*), 3.83–3.91 (1H, m, *7b*), 4.20–4.31 (1H, m, *8b*), 7.26–7.30 (2H, m, *11*), 7.34 (1H, t, $^3J_{H,H} = 7.4$ Hz, *13*), 7.42 (2H, t, $^3J_{H,H} = 7.4$ Hz, 11, *12*) ppm

$^{13}C\{^1H\}$ NMR (101 MHz): $\delta = 16.0$ (d, $^3J_{C,P} = 11.6$ Hz, *10*), 20.3 (d, $^3J_{C,P} = 16.9$ Hz, *9*), 45.1 (d, $^1J_{C,P} = 41.6$ Hz, *1*), 48.4 (d, $^2J_{C,P} = 22.8$ Hz, *3*), 52.6 (s, *2*), 53.6 (d, $^1J_{C,P} = 56.8$ Hz, *6*), 59.5 (d, $^2J_{C,P} = 6.2$ Hz, *8*), 59.8 (d, $^3J_{C,P} = 3.7$ Hz, *7*), 127.8 (d, $^5J_{C,P} = 1.6$ Hz, *13*), 128.3 (s, *12*), 129.5 (d, $^3J_{C,P} = 5.1$ Hz, *11*), 132.1 (d, $^2J_{C,P} = 9.5$ Hz, *10*), 132.8 (d, $^1J_{C,P} = 64.3$ Hz, *5*) , 154.6 (d, $^2J_{C,P} = 13.7$ Hz, *4*) ppm

$^{31}P\{^1H\}$ NMR (162 MHz): $\delta = 56.4$ ppm

Compound (*R*)-**13b** and (*S*)-**13b**



endo-**9c** 458.59 | **12c** 308.38 | (*R*)-**13c** 308.38 | (*S*)-**13c** 308.38

(*S*)-**13c**:

^{1}H NMR (300 MHz): δ= 0.85 (3H, s, *10*), 1,21 (3H, s, *9*), 2,26 (1H, ddd, $^2J_{H,H}$ = 13.4 Hz, $^2J_{H,P}$ = 9.9 Hz, $^4J_{H,H}$ = 2.2 Hz, *6a*), 2.37 (1H, dd, $^2J_{H,H}$ = 13.4 Hz, $^2J_{H,P}$ = 6.5 Hz, *6b*), 2.52–2.67 (2H, m, *2*, *15*), 2.67–2.84 (1H, m, *1*), 3.55 (1H, dd, $^2J_{H,P}$ = 13.9 Hz, $^4J_{H,H}$ = 2.2 Hz, *5*), 3.99–4.19 (3H, m, *7*, *8a*), 4.21–4.37 (1H, m, *8b*), 7.17–7.42 (5H, m, *12*, *13*, *14*) ppm

^{13}C{^{1}H} NMR (76 MHz): 18.8 (d, $^3J_{C,P}$ = 15.1 Hz, *9*), 20.9 (d, $^3J_{C,P}$ = 2.6 Hz, *10*), 40.7 (d, $^1J_{C,P}$ = 47.7 Hz, *6*), 45.1 (d, $^1J_{C,P}$ = 49.7 Hz, *1*), 46.9 (d, $^2J_{C,P}$ = 2.3 Hz, *2*), 51.5 (d, $^2J_{C,P}$ = 17.6 Hz, *3*), 55.1 (d, $^1J_{C,P}$ = 42.1 Hz, *5*), 58.6 (s, *8*), 66.3 (s, *7*), 92.6 (d, $^2J_{C,P}$ = 7.1 Hz, *4*), 127.5 (s (br), *12*/*13*/*14*), 128.6 (s (br), *12*/*13*/*14*), 134.2 (d, $^2J_{C,P}$ = 2.9 Hz, *11*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ= 50.5 ppm

(*R*)-**13c**:

^{1}H NMR (300 MHz): δ= 1.34 (3H, s, *9*), 1.42 (3H, d, $^4J_{H,P}$ = 1.8 Hz, *10*), 1.94 (1H, dd, $^2J_{H,P}$ = 6.9 Hz, $^2J_{H,H}$ = 13.0 Hz, *6a*), 2.14 (1H, dd, $^2J_{H,P}$ = 8.2 Hz, $^2J_{H,H}$ = 13.0 Hz, *6b*), 2,14 (1H, s (br), *15*), 2.57–2.68 (1H, m, *2*), 2.71–2.86 (1H, m, *1*), 3.17 (1H, d, $^2J_{H,P}$ = 19.8 Hz, *5*), 3.79–3.95 (1H, m, *8a*), 3.99–4.13 (3H, m, *7*, *8b*), 7.27–7.38 (3H, m, *13*, *14*), 7.63–7.74 (2H, m, *12*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ= 19.2 (d, $^3J_{C,P}$ = 14.5 Hz, *9*), 24.2 (d, $^3J_{C,P}$ = 8.8 Hz, *10*), 39.5 (d, $^1J_{C,P}$ = 54.3 Hz, *6*), 46.3 (d, $^1J_{C,P}$ = 43.0 Hz, *1*), 47.5 (d, $^2J_{C,P}$ = 2.1 Hz, *2*), 51.8 (d, $^2J_{C,P}$ = 17.9 Hz, *3*), 56.0 (d, $^1J_{C,P}$ = 42.0 MHz, *5*), 58.3 (d, $^2J_{C,P}$ = 3.4 Hz, *7*), 65.8 (s, *8*), 86.7 (d, $^2J_{C,P}$ = 3.2 Hz, *4*), 127.3 (d, $^5J_{C,P}$ = 2.2 Hz, *14*), 128.2 (s, *13*), 130.3 (d, $^3J_{C,P}$ = 6.7 Hz, *12*), 132.2 (d, $^2J_{C,P}$ = 4.5 Hz, *11*) ppm.

^{31}P{^{1}H} NMR (162 MHz): δ= 51.0 ppm

Attempts for the optimisation reactions in ethanol: Sodium ethanolate in ethanol was prepared from sodium metal (5 mg, 0.22 mmol) and 5 ml of ethanol. The diol **12c** (6 mg, 0.02 mmol) was added and the reaction was left to stir at the given temperature for the given time.

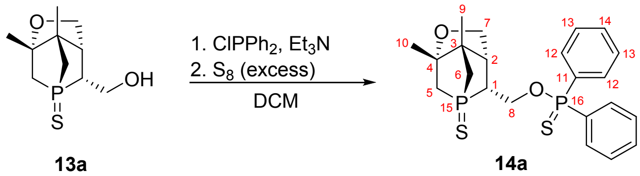
Reactions in isopropanol: The reaction was carried out in the same manner as described for the reaction in ethanol.

Reactions in THF: A solution of diol **12c** (6 mg, 0.02 mmol) and potassium *tert*-butoxide (4 mg, 0.04 mmol) in 2 ml of THF was stirred at the given temperature for the given time.

The reaction mixtures were analysed by $^{31}P\{^1H\}$ NMR spectroscopy (no deuterated solvent).

solvent	**Base**	***T* in °C**	***t* in days**	***ratio*** **12c : (*R*)-13c : (*S*)-13c**
ethanol	NaOEt	−30	5	100 : 0 : 0
		0	7	56 : 26 : 18
		25	0.75	30 : 42 : 32
isopropanol	NaO^{i}Pr	−30	4	100 : 0 : 0
		0	7	47 : 17 : 36
		25	1	48 : 24 : 28
THF	KO^{t}Bu	−30	5	28 : 28 : 44
		25	1.5	< 1 : 48 : 72

Compound **14a**

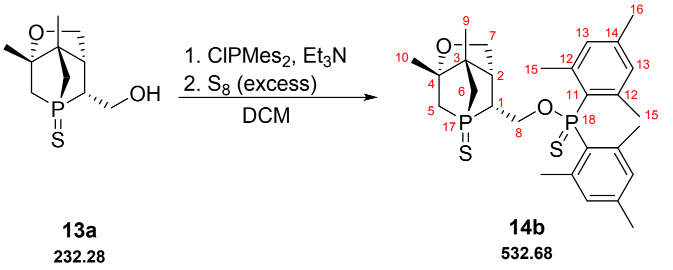


^{1}H NMR (400 MHz): δ = 1.19 (3H, s, *9*), 1.24 (3H, s, *10*), 1.82–1.98 (2H, m, *5a*, *6a*), 2.00–2.12 (1H, m, *6b*), 2.18–2.32 (1H, m, *5b*), 2.45–2.58 (1H, m, *2*), 2.77–2.93 (1H, m, *1*), 3.93 (1H, dd, $^2J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 5.8 Hz, *7a*), 4.19 (1H, d, $^2J_{H,H}$ = 10.2 Hz, *7b*), 4.27–4.40 (1H, m, *8a*), 4.40–4.50 (1H, m, *8b*), 7.38–7.58 (6H, m, *12*, *14*), 7.81–7.99 (4H, m, *13*) ppm

$^{13}C\{^1H\}$ NMR (101 MHz): δ = 18.2 (d, $^3J_{C,P}$ = 15.7 Hz, *9*), 23.9 (d, $^3J_{C,P}$ = 7.3 Hz, *10*), 40.3 (d, $^1J_{C,P}$ = 52.2 Hz, *6*), 41.6 (d, $^1J_{C,P}$ = 44.8 Hz, *5*), 43.1 (dd, $^1J_{C,P}$ = 46.5 Hz, $^3J_{C,P}$ = 9.1 Hz, *1*), 47.3 (d, $^2J_{C,P}$ = 2.0 Hz, *2*), 51.5 (d, $^2J_{C,P}$ = 18.7 Hz, *3*), 60.3 (dd, $^2J_{C,P}$ = 5.3 Hz, $^2J_{C,P}$ = 5.3 Hz, *8*), 66.2 (s, *7*), 86.3 (d, $^2J_{C,P}$ = 1.4 Hz, *4*), 128.6 (dd, $^2J_{C,P}$ = 13.5 Hz, $^6J_{C,P}$ = 2.5 Hz, *12*), 131.3 (dd, $^3J_{C,P}$ = 11.6 Hz, $^7J_{C,P}$ 5.7 Hz, *13*), 132.1 (d, $^4J_{C,P}$ = 2.4 Hz, *14*), 133.6 (dd, $^1J_{C,P}$ = 109.8 Hz, $^5J_{C,P}$ = 6.2 Hz, *11*) ppm

$^{31}P\{^1H\}$ NMR (162 MHz): δ = 44.2 (s, *15*), 83.0 (s, *16*) ppm

Compound **14b**

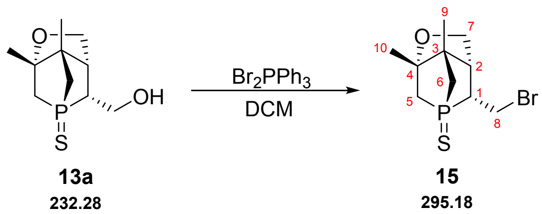


^{1}H NMR (300 MHz): δ= 1.18 (3H, s, *9*), 1.23 (3H, s, *10*), 1.81–1.96 (2H, m, *5a*, *6a*), 1.97–2.25 (2H, m, *5b*, *6b*), 2.25 (6H, s, *16*), 2.18–2.44 (1H, m, *2*), 2.37 (12H, d, $^4J_{H,P}$ = 9.0 Hz, *15*), 2.72–2.95 (1H, m, *1*), 3.82 (1H, dd, $^2J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 5.8 Hz, *7a*), 4.13 (1H, d, $^2J_{H,H}$ = 10.2 Hz, *7b*) 4.13–4.26 (1H, m, *8a*), 4.38–4.50 (1H, m, *8b*), 6.82 (4H, s, *13*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ= 18.3 (d, $^3J_{C,P}$ = 16.1 Hz, *9*), 20.9 (s, *16*), 23.2–23.4 (m, *15*), 23.8 (d, $^3J_{C,P}$ = 7.1 Hz, *10*), 39.7–41.7 (m, *5*, *6*), 43.5 (dd, $^1J_{C,P}$ = 45.5 Hz, $^3J_{C,P}$ = 8.2 Hz, *1*), 47.3 (s, *2*), 51.3 (d, $^2J_{C,P}$ = 18.8 Hz, *3*), 58.8 (dd, $^2J_{C,P}$ = 11.2 Hz, $^2J_{C,P}$ = 4.8 Hz, *8*), 66.0 (s, *7*), 86.3 (s, *4*), 129.1–130.9 (m, *11*), 131.1–132.3 (m, *13*), 140.2–141.4 (m, *12*, *14*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ = 43.5 (s, *17*), 83.0 (s, *18*) ppm

Compound **15**

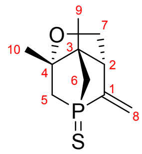


^{1}H NMR (300 MHz): δ= 1.24 (3H, s, *9*), 1.27 (3H, s, *10*), 1.83–2.26 (4H, m, *5*, *6*), 2.44–2.62 (1H, m, *2*), 2.66–2.91 (1H, m, *1*), 3.26–3.56 (1H, m, *8a*), 3.89–4.15 (3H, m, *7*, *8b*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ= 18.3 (d, $^3J_{C,P}$ = 16.2 Hz, *9*), 23.8 (d, $^3J_{C,P}$ = 7.4 Hz, *10*), 27.7 (d, $^2J_{C,P}$ = 6.0 Hz, *8*), 39.3–41.7 (m, *5*, *6*), 45.4 (d, $^1J_{C,P}$ = 41.5 Hz, *1*), 47.1 (d, $^2J_{C,P}$ = 2.4 Hz, *2*), 51.2 (d, $^2J_{C,P}$ = 18.5 Hz, *3*), 65.7 (s, *7*), 86.4 (d, $^2J_{C,P}$ = 1.3 Hz, *4*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ= 46.7 ppm

Side product **16**



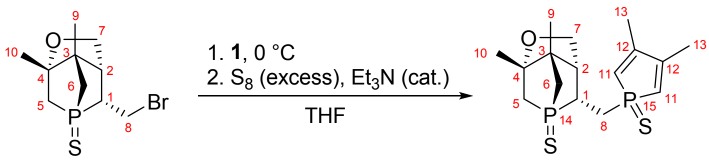
16
214.26

^{1}H NMR (300 MHz): δ = 1.22 (3H, s, *9*), 1.32 (3H,s , *10*), 1.94–2.21 (4H, m, *5*, *6*), 2.82–2.95 (1H, m, *2*), 3.80 (1H, d, $^2J_{H,H}$ = 8.5 Hz, *7a*), 4.20 (1H, dd, $^2J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 5.7 Hz, *7b*), 5.81 (1H, d, $^3J_{H,P}$ = 42.0 Hz, *8a*), 6.03 (1H, d, $^3J_{H,P}$ = 22.0 Hz, *8b*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ = 17.9 (d, $^3J_{C,P}$ = 14.1 Hz, *9*), 24.0 (d, $^3J_{C,P}$ = 7.6 Hz, *10*), 40.5 (d, $^1J_{C,P}$ = 52.9 Hz, *5/6*), 43.4 (d, $^1J_{C,P}$ = 48.3 Hz, *5/6*), 50.5 (d, $^2J_{C,P}$ = 14.6 Hz, *3*), 52.7 (d, $^2J_{C,P}$ = 15.6 Hz, *2*), 73.0 (s, *7*), 86.6 (s, *4*), 124.0 (d, $^2J_{C,P}$ = 8.2 Hz, *8*), 148.5 (d, $^1J_{C,P}$ = 68.1 Hz, *1*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ = 37.8 ppm

Compound **17**

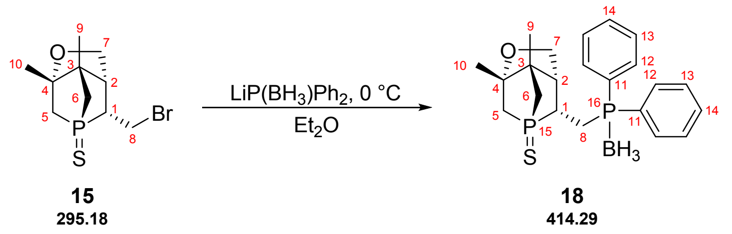


^{1}H NMR (300 MHz): δ = 1.20–1.28 (6H, m, *9*, *10*), 1.79–2.31 (5H, m, *5*, *6*, *8a*), 2.08 (6H, s, *13*), 2.62–2.75 (3H, m, *1*, *2*, *8b*), 3.87–4.12 (2H, m, *7*), 5.95 (1H, d, $^2J_{H,P}$ = 31.0 Hz, *11a*), 6.09 (1H, d, $^2J_{H,P}$ = 30.6 Hz, *11b*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ = 17.2–17.7 (m, *13*), 18.5 (dd, $^3J_{C,P}$ = 12.3 Hz, $^6J_{C,P}$ = 3.4 Hz, *9*), 23.7 (d, $^3J_{C,P}$ = 5.5 Hz, *10*), 23.9–25.7 (m, *8*), 37.0–39.3 (m, *1*), 38.1–42.1 (m, *5*, *6*), 47.2 (s, *2*), 51.5 (dd, $^2J_{C,P}$ = 15.2 Hz, $^5J_{C,P}$ = 4.1 Hz, *3*), 66.5 (s, *7*), 86.3 (s, *4*), 122.7–125.6 (m, *11*), 153.4–154.1 (m, *12*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ = 50.5–51.6 (m, *14*, *15*) ppm

Compound **18**

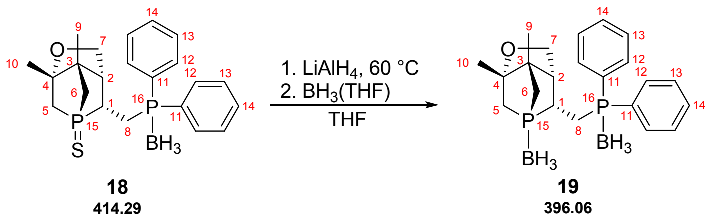


^{1}H NMR (400 MHz): δ = 1.19 (3H, s, *9*), 1.23 (3H, s, *10*),0.30–1.50 (3H, m, *B–**H***),1.79–2.01 (3H, m, *5/6*), 2.06–2.42 (3H, m, *1*, *5/6*, *8*),2.56–2.68 (1H, m, *2*),3.11–3.26 (1H, m, *8*), 3.94 (1H, dd, $^2J_{H,H}$ = 10.8 Hz, $^3J_{H,H}$ = 5.4 Hz, *7a*),4.10 (1H, d, $^2J_{H,H}$ = 10.8 Hz, *7b*), 7.37–7.58 (6H, m, *12/13/14*), 7.60–7.72 (2H, m, *12/13/14*),7.86–7.98(2H, m, *12/13/14*) ppm

^{13}C{^{1}H} NMR (76 MHz): δ = 18.6 (d, $^3J_{C,P}$ = 18.9 Hz, *9*), 19.0 (d, $^2J_{C,P}$ = 35.3 Hz, *8*),23.9 (d, $^3J_{C,P}$= 7.5 Hz, *10*), 37.2 (d, $^1J_{C,P}$ = 46.9 Hz, *1*), 38.8 (d, $^1J_{C,P}$ = 51.0 Hz, *5/6*), 41.0 (d,$^1J_{C,P}$ = 44.2 Hz, *5/6*), 47.8 (d, $^2J_{C,P}$ = 2.4 Hz, *2*), 51.5 (d, $^2J_{C,P}$ = 19.9 Hz, *3*),67.0 (s, *7*), 86.2 (d, $^2J_{C,P}$ = 2.0 Hz, *4*), 126.5 (d, $^1J_{C,P}$ = 55.5 Hz, *11/11'*), 128.6–129.7 (m, *12/13/14*), 130.3 (d, $^1J_{C,P}$ = 55.6 Hz, *11/11'*),131.3–132.3 (m, *12/13/14*), 133.0 (d, *J* = 9.2 Hz, *12/13/14*) ppm

^{31}P{^{1}H} NMR (162 MHz): δ=15.1–16.8 (m (br), *16*),51.8 (d, $^3J_{P,P}$ = 47.3 Hz, *15*) ppm

Compound **19**

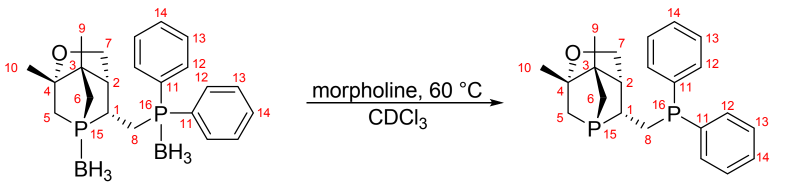


^{1}H NMR (300 MHz): δ=1.19 (3H, s, *9*), 1.24 (3H, s, *10*), 0.00–2.10 (6H, m, *B-**H***),1.55–1.79 (3H, m, *5/6*),1.83–1.97 (1H, m, *5/6*),2.10–2.42 (2H, m, *1/8*), 2.48–2.62 (1H, m, *2*), 2.80–3.00 (1H, m, *8*), 3.89 (1H, dd, $^2J_{H,H}$ = 10.8 Hz, $^3J_{H,H}$ = 5.0 Hz, *7a*), 4.01 (1H, d, $^2J_{H,H}$ = 10.8 Hz, *7b*), 7.37–7.68 (8H, m, *12/13/14*), 7.81–7. 91 (2H, m, *12/13/14*) ppm.

^{13}C{^{1}H} NMR (76 MHz): δ = 18.6 (d, $^3J_{C,P}$ = 10.0 Hz, *9*), 20.3 (d, $^1J_{C,P}$ = 35.4 Hz, *8*), 24.3 (d, $^3J_{C,P}$ = 4.3 Hz, *10*), 32.7 (d, $^1J_{C,P}$ = 28.8 Hz, *1*), 34.1 (d, $^1J_{C,P}$ = 33.2 Hz, *5/6*), 35.4 (d, $^1J_{C,P}$ = 27.2 Hz, *5/6*), 47.9 (d, $^2J_{C,P}$ = 3.6 Hz, *2*), 56.9 (d, $^2J_{C,P}$ = 4.5 Hz, *3*), 66.1 (s, *7*), 86.6 (d, $^2J_{C,P}$ = 4.2 Hz, *4*),126.5 (d, $^1J_{C,P}$ = 56.6 Hz, *11/11'*), 129.0–129.5 (m, *12/13/14*), 130.2 (d, $^1J_{C,P}$ = 55.5 Hz, *11/11'*), 131.7 (d, *J* = 9.4 Hz, *12/13/14*), 133.0 (d, *J* = 9.3 Hz, *12/13/14*)ppm

^{31}P{^{1}H} NMR (162 MHz): δ = 15.7–17.8 (m (br), *16*), 28.8–30.0 (m (br), *15*) ppm

In situ deboranation of **19***, compound* **20**



19 396.06 **20**

$^{31}P\{^{1}H\}$ NMR (162 MHz): $\delta = -36.9$ (d, $^{1}J_{P,P} = 45.6$ Hz); -18.3 (d, $^{1}J_{P,P} = 45.6$ Hz) ppm.

Crystallographic data

CCDC 990595 (*endo*-**9d**), 989748 (**12a**), 989750 (**12b**), 989749 (**13a**), 989751 ((*R*)-**13b**), 989752 ((*S*)-**13b**, 989753 (**14a**), 989754 (**14b**) and 989755 (**18**) 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.

Structure parameters for **9d**: $C_{25}H_{34}NO_3PS$, M = 459.56. T = 130(2) K, orthorhombic space group $P2_1$, a = 1201.55(1) pm, b = 1226.58(1) pm, c = 1671.28(2) pm, V = 2.46313(4) nm^3, ρ_{calc} = 1.239 Mg·m^{-3}, Z = 4, μ = 0.222 mm^{-1}, crystal size 0.40 x 0.40 x 0.40 mm^3, Θ(max) = 30.51°, reflections collected 55234, independent reflections 7533 (R(int) = 0.0285), completeness to Θ = 30.51°: 99.9%, 416 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): $R1$ = 0.0272, $wR2$ = 0.0657, final R indices [I>2σ(I)]: $R1$ = 0.0252, $wR2$ = 0.0644, residual electron density 0.382 e·Å^{-3}.

Structure parameters for **12a**: $C_{10}H_{17}O_2PS$, M = 232.27, T = 130(2) K, orthorhombic space group $P2_1$, a = 876.82(1) pm, b = 909.48(1) pm, c = 1447.18(2) pm, V = 1.15405(2) nm^3, ρ_{calc} = 1.337 Mg·m^{-3}, Z = 4, μ = 0.393 mm^{-1}, crystal size 0.20 x 0.20 x 0.15 mm^3, Θ(max) = 30.51°, reflections collected 29094, independent reflections 3519 (R(int) = 0.0286), completeness to Θ = 30.51°: 99.9%, 195 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): $R1$ = 0.0240, $wR2$ = 0.0594, final R indices [I>2σ(I)]: $R1$ = 0.0227, $wR2$ = 0.0588, residual electron density 0.247 e·Å^{-3}.

Structure parameters for **12c**: $C_{16}H_{21}O_2PS$, M = 308.36, T = 130(2) K, monoclinic space group $P2_1$, a = 819.6(5) pm, b = 833.4(5) pm, c = 1114.4(5) pm, β = 92.054(5)°, V = 0.7607(7) nm^3, ρ_{calc} = 1.346 Mg·m^{-3}, Z = 2, μ = 0.317 mm^{-1}, crystal size 0.20 x 0.15 x 0.10 mm^3, Θ(max) =

30.50°, reflections collected 13043, independent reflections 4636 (R(int) = 0.0279), completeness to Θ = 30.50°: 100.0%, 265 parameters, 1 restraint. 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* = 0.0307, *wR2* = 0.0640, final R indices [I>2σ(I)]: *R1* = 0.0273, *wR2* = 0.0624, residual electron density 0.282 e·Å^{-3}.

Structure parameters for **13a**: $C_{10}H_{17}O_2PS$, *M* = 232.27, *T* = 130(2) K, monoclinic space group *C*2, a = 1499.10(2) pm, b = 739.94(1) pm, c = 1052.96(2) pm, β = 93.746(1)°, *V* = 1.16549(3) nm^3, ρ_{calc} = 1.324 Mg·m^{-3}, *Z* = 4, μ = 0.389 mm^{-1}, crystal size 0.30 x 0.30 x 0.15 mm^3, Θ(max) = 30.51°, reflections collected 20098, independent reflections 3539 (R(int) = 0.0231), completeness to Θ = 30.50°: 99.9%, 195 parameters, 1 restraint. 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* = 0.0221, *wR2* = 0.0566, final R indices [I>2σ(I)]: *R1* = 0.0214, *wR2* = 0.0561, residual electron density 0.278 e·Å^{-3}.

Structure parameters for (*R*)-**13c**: $C_{16}H_{21}O_2PS$, *M* = 308.36, *T* = 130(2) K, orthorhombic space group *P*2$_1$, a = 841.0(5) pm, b = 1295.3(5) pm, c = 1379.9(5) pm, *V* = 1.503(1) nm^3, ρ_{calc} = 1.363 Mg·m^{-3}, *Z* = 4, μ = 0.320 mm^{-1}, crystal size 0.40 x 0.40 x 0.20 mm^3, Θ(max) = 30.50°, reflections collected 18990, independent reflections 4571 (R(int) = 0.0326), completeness to Θ = 30.50°: 99.9%, 265 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* = 0.0348, *wR2* = 0.0755, final R indices [I>2σ(I)]: *R1* = 0.0305, *wR2* = 0.0733, residual electron density 0.281 e·Å^{-3}.

Structure parameters for (*S*)-**13c**: $C_{16}H_{21}O_2PS$, *M* = 308.36, *T* = 130(2) K, orthorhombic space group *P*2$_1$, a = 912.3(5) pm, b = 1168.1(5) pm, c = 1435.5(5) pm, *V* = 1.530(1) nm^3, ρ_{calc} = 1.339 Mg·m^{-3}, *Z* = 4, μ = 0.315 mm^{-1}, crystal size 0.40 x 0.30 x 0.20 mm^3, Θ(max) = 30.51°, reflections collected 20682, independent reflections 4660 (R(int) = 0.0294), completeness to Θ = 30.51°: 99.9%, 265 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* = 0.0302, *wR2* = 0.0657, final R indices [I>2σ(I)]: *R1* = 0.0274, *wR2* = 0.0643, residual electron density 0.287 e·Å^{-3}.

Structure parameters for **14a**: $C_{22}H_{26}O_2P_2S_2$, *M* = 448.49, *T* = 130(2) K, monoclinic space group *C*2, a = 2919.9 (1) pm, b = 912.11(2) pm, c = 1803.09(5) pm, β = 112.228(3)°, *V* = 4.4453(2) nm^3, ρ_{calc} = 1.340 Mg·m^{-3}, *Z* = 8, μ = 0.399 mm^{-1}, crystal size 0.30 x 0.30 x

0.05 mm^3, Θ(max) = 28.28°, reflections collected 36663, independent reflections 11014 (R(int) = 0.0339), completeness to Θ = 28.28°: 99.8%, 713 parameters, 1 restraint. 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* = 0.0359, *wR2* = 0.0657, final R indices [I>2σ(I)]: *R1* = 0.0304, *wR2* = 0.0633, residual electron density 0.295 e·Å^{-3}.

Structure parameters for **14b**: $C_{28}H_{38}O_2P_2S_2$, *M* = 532.64, *T* = 130(2) K, orthorhombic space group *P*2$_1$, a = 845.97(2) pm, b = 1441.32(2) pm, c = 2343.46(4) pm, *V* = 2.85741(9) nm^3, ρ_{calc} = 1.238 Mg·m^{-3}, *Z* = 4, μ = 0.321 mm^{-1}, crystal size 0.40 x 0.30 x 0.10 mm^3, Θ(max) = 28.28°, reflections collected 54563, independent reflections 7094 (R(int) = 0.0413), completeness to Θ = 28.28°: 99.9%, 369 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* = 0.0287, *wR2* = 0.0666, final R indices [I>2σ(I)]: *R1* = 0.0268, *wR2* = 0.0657, residual electron density 0.303 e·Å^{-3}.

Structure parameters for **18**: $C_{22}H_{29}BOP_2S$, *M* = 414.26, *T* = 130(2) K, orthorhombic space group *P*2$_1$, a = 906.43(3) pm, b = 910.50(2) pm, c = 2566.53(9) pm, *V* = 2.1182(1) nm^3, ρ_{calc} = 1.299 Mg·m^{-3}, *Z* = 4, μ = 0.314 mm^{-1}, crystal size 0.20 x 0.15 x 0.10 mm^3, Θ(max) = 26.37°, reflections collected 12042, independent reflections 4316 (R(int) = 0.0570), completeness to Θ = 26.37°: 99.7%, 258 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* = 0.0657, *wR2* = 0.0979, final R indices [I>2σ(I)]: *R1* = 0.0440, *wR2* = 0.0872, residual electron density 0.332 e·Å^{-3}.