Synthesis and Application of Quinazoline–Oxazoline-Containing (Quinazox) Ligands

Tomasz Fekner, Helge Müller–Bunz, and Patrick J. Guiry

Supporting Information

Table of Contents

1. Experimental Procedures	S-2
1.1. General Methods	S-2
1.2. Synthesis of Biaryl (22)	S-3
1.3. Synthesis of Quinazoline–Oxazoline-Containing Ligands	S-15
1.4. Asymmetric Allylic Alkylation (AAA) Studies	S-18
2. X-Ray Single-Crystal Data	S-20
2.1. Ligand (<i>S_a,S</i>)-(–)-(24)	S-20
2.2. Ligand (<i>S_a,S</i>)-(–)-(25)	S-40
3. Copies of ¹H, ¹³C, and ³¹P NMR Spectra	S-61

1. Experimental Procedures

1.1. General Methods

All reactions were performed under anhydrous conditions and an inert atmosphere of nitrogen in the oven-dried glassware with magnetic stirring. Yields refer to chromatographically and spectroscopically (^1H NMR) homogenous materials, unless otherwise indicated. Reagents were used as obtained from commercial sources, or purified according to the guidelines of Perrin and Armarego.¹ Evaporation in vacuo refers to the removal of volatiles on a Büchi rotary evaporator attached to a water respirator (~ 20 mm Hg). Flash chromatography was carried out using Merck Kiesegel 60 F₂₅₄ (230–400 mesh) silica gel following the method of Still *et al.*² Only distilled solvents were used as eluents. Thin-layer chromatography (TLC) was performed on Merck DC-Alufolien plates pre-coated with silica gel 60 F₂₅₄. They were visualized either by quenching of ultraviolet fluorescence, or by charring with 5% w/v phosphomolybdic acid in 95% EtOH, 10% w/v ammonium molybdate in 1M H₂SO₄, or 10% KMnO₄ in 1M H₂SO₄. Observed retention factors (R_f) are quoted to the nearest 0.05, unless a higher accuracy was necessary to distinguish close-eluting compounds. All reaction solvents were distilled before use, unless otherwise indicated. Anhydrous CH₂Cl₂ was obtained by refluxing over CaH₂. Anhydrous THF was obtained by distillation, immediately before use, from sodium/benzophenone ketyl under an inert atmosphere of nitrogen. Anhydrous DMF was obtained by distillation under reduced pressure from CaH₂, and stored over 4Å molecular sieves. High-resolution mass spectrometry (HRMS) measurements are valid to ± 5 ppm. Melting points (mp) are quoted to the nearest 0.5 °C.

¹ Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1988.

² Still, W. C.; Hahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

1.2. Synthesis of Biaryl (22)

1-Chloro-3-methylbut-2-ene (11)^{3,4}

Concd HCl (560 mL) and alcohol **9** (165 g, 1.92 mol) were pre-cooled separately in an ice–salt bath to $-5\text{ }^{\circ}\text{C}$. The acid was added to the alcohol and the mixture was stirred vigorously for 90 min while the temperature was maintained between -5 and $0\text{ }^{\circ}\text{C}$. The organic phase was separated, washed with water ($2 \times 50\text{ mL}$) and brine ($2 \times 50\text{ mL}$), and dried (Na_2SO_4) to give a colorless liquid (175.5 g, 85%) that by ^1H NMR analysis proved to be a mixture of allylic chlorides **11** and **12** in a $\sim 7:1$ ratio, respectively. No attempt was made to isolate the desired product **11**, and the foregoing mixture was used in the next step without any further purification. Allyl chloride **11**⁴: ^1H NMR (300 MHz, CDCl_3) 1.73 (s, 3H), 1.77 (s, 3H), 4.08 (d, $J = 8.0\text{ Hz}$, 2H), and 5.44 ($\sim\text{t}$, $J = 8.0\text{ Hz}$, 1H). Allyl chloride **12**⁴: ^1H NMR (300 MHz, CDCl_3) 1.69 (s, 6H), 5.04 (d, $J = 10.6\text{ Hz}$, 1H), 5.23 (d, $J = 17.2\text{ Hz}$, 1H), and 6.10 (dd, $J = 17.2, 10.6\text{ Hz}$, 1H).

2,2-Dimethylbut-3-enoyl chloride (10)

To a vigorously stirred suspension of Mg turnings (80 g, 3.3 mol) in THF (600 mL) was added a solution of allylic chlorides **11** and **12** ($\sim 7:1$, 92 g, 0.88 mol) in THF (150 mL) dropwise over 5 h. The resulting dark mixture was stirred for an additional 20 min and poured into a 2-L beaker filled with freshly made dry ice. After the reaction mixture reached room temperature (~ 2 h), it was treated with 4M HCl (350 mL) and saturated with NaCl. The phases were separated, and the extraction was completed with additional portions of CH_2Cl_2 . The combined organic extracts were dried (MgSO_4), and evaporated in vacuo to give a yellow oil (95 g) that by ^1H NMR analysis

³ Vani, P. V. S. N.; Chida, A. S.; Srinivasan, R.; Chandrasekharam, M.; Singh, A. K. *Synth. Commun.* **2001**, *31*, 219–224.

⁴ Schneider, P.; Cloux, R.; Föti, K.; Kováts, E. *Synthesis*, **1990**, *11*, 1027–1031.

contained acids **8** and **13** in a ~33:1 ratio, respectively, as the main products. Acid **8**^{5,6}: ¹H NMR (300 MHz, CDCl₃) 1.33 (s, 6H), 5.11 (d, *J* = 10.5 Hz, 1H), 5.15 (d, *J* = 17.5 Hz, 1H), 6.05 (dd, *J* = 17.5, 10.5 Hz, 1H), and 11.9 (s, 1H). Acid **13**⁷: ¹H NMR (300 MHz, CDCl₃) 1.65 (s, 3H), 1.76 (s, 3H), 3.09 (d, *J* = 7.0 Hz, 2H), and 5.30 (~t, *J* = 7.0 Hz, 1H).

In two separate, additional runs, 52.6 g (0.50 mol) and 26.3 g (0.25 mol) of allyl chlorides **11** and **12** (~7:1) were reacted as described above. The crude products from the three runs were combined and added dropwise over 6 h to refluxing SOCl₂ (145 mL, 2.0 mol). After the addition was complete, the reaction mixture was refluxed for an additional hour and stirred at room temperature overnight. Fractional distillation under reduced pressure through a Vigreux column (45 × 2 cm) fitted with an efficient condenser gave the title compound **10** (105 g, 48% from a mixture of **11** and **12**) as the fraction boiling at 34.0–34.5 °C/22 mmHg (Lit.⁶ 48.5–50.0 °C/50 mmHg). The ¹H NMR analysis showed the product **10** to be of >99.6% isomeric purity. Acyl chloride **10**⁸: a colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.41 (s, 6H), 5.24 (d, *J* = 17.4 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), and 5.99 (dd, *J* = 17.4, 10.6 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 24.6, 54.6, 115.8, 139.6, and 178.1; IR (neat) ν_{max} 1807, 1778, 951, 930, and 901 cm⁻¹.

2-(1,1-Dimethylallyl)quinazolin-4-ol (**16**)

To a suspension of anthranilamide (**7**) (100 g, 0.735 mol) in CH₂Cl₂ (1.3 L) was added Et₃N (133 mL, 0.96 mol) and the mixture was cooled in an ice bath. During vigorous stirring, a solution of acyl chloride **10** (97.8 g, 0.735 mol) in CH₂Cl₂ (200 mL) was added dropwise over 3 h. After an additional 5 h at room temperature, the reaction mixture was evaporated in vacuo. An analytical sample of amide **15** was prepared by flash chromatography of a small amount of the residue (silica gel, EtOAc) followed by crystallization from EtOAc/pentane. Amide **15**: a white solid; *R_f* = 0.70 (EtOAc); mp 193.5–194.5 °C (EtOAc/pentane); ¹H NMR (400 MHz, *d*₆-DMSO) δ 1.30 (s, 6H),

⁵ Hayashi, Y.; Orikasa, S.; Tanaka, K.; Kanoh, K.; Kiso, Y. *J. Org. Chem.* **2000**, *65*, 8402–8405.

⁶ Russell, R. A. *Aust. J. Chem.* **1975**, *28*, 2535–2538.

⁷ Cane, E. D.; Yang, G.; Coates, R. M.; Pyun, H.-J.; Hohn, T. M. *J. Org. Chem.* **1992**, *57*, 3454–3462.

⁸ Karpf, M. *Helv. Chim. Acta* **1984**, *67*, 73–85.

5.18 (dd, $J = 10.6, 1.0$ Hz, 1H), 5.23 (dd, $J = 17.4, 1.0$ Hz, 1H), 6.06 (dd, $J = 17.4, 10.6$ Hz, 1H), 7.10 (ddd, $J = 7.9, 7.4, 1.1$ Hz, 1H), 7.48 (ddd, $J = 8.4, 7.4, 1.4$ Hz, 1H), 7.74 (br s, 1H), 7.80 (dd, $J = 7.9, 1.4$ Hz, 1H), 8.27 (br s, 1H), 8.53 (dd, $J = 8.4, 1.1$ Hz, 1H), and 11.9 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, d_6 -DMSO) δ 24.3, 46.0, 114.0, 119.2, 119.8, 122.1, 128.4, 132.1, 139.9, 142.5, 170.7, and 174.0; IR (CHCl_3) ν_{max} 1666, 1608, 1579, 1516, 1148, 1377, and 1298 cm^{-1} ; MS (ESI) m/z (rel intensity) 266 (100%, MH^+), 233 (5), and 216 (80); HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2$ (MH^+) 233.1290, found 233.1286. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.20; H, 6.92; N, 12.07.

The foregoing light brown residue containing amide **15** was suspended in EtOH (1.2 L), and the mixture was cooled in an ice bath. 10 M NaOH (220 mL, 2.2 mol) was added dropwise over 15 min, and the reaction was refluxed for 2 h. The resulting clear solution was subsequently re-cooled to 0 °C and neutralized with concd HCl (~190 mL). The reaction mixture was concentrated in vacuo to a thick paste and diluted with water (~2 L). The precipitate formed was filtered, washed with a copious amount of water, and dried to give the title compound **16** (151 g, 96%) as an off-white solid that was used in the next step without any further purification. An analytical sample of quinazolinol **16** was prepared by flash chromatography of a small amount of the crude product (silica gel, EtOAc) followed by crystallization from EtOH/ H_2O . Quinazolinol **16**: a white solid; $R_f = 0.15$ (CH_2Cl_2); mp 136.0–137.0 °C (EtOH/ H_2O); ^1H NMR (300 MHz, d_4 -methanol) δ 1.51 (s, 6H), 5.18–5.24 (m, 2H), 6.14 (dd, $J = 17.5, 10.5$ Hz, 1H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.69–7.78 (m, 2H), and 8.15 (d, $J = 8.0$ Hz, 1H); ^1H NMR (400 MHz, d_6 -DMSO) δ 1.47 (s, 6H), 5.13 (dd, $J = 10.5, 1.0$ Hz, 1H), 5.14 (dd, $J = 17.6, 1.0$ Hz, 1H), 6.22 (dd, $J = 17.6, 10.5$ Hz, 1H), 7.49 (ddd, $J = 7.9, 7.2, 1.2$ Hz, 1H), 7.64 (ddd, $J = 8.2, 1.2, 0.4$ Hz, 1H); 7.79 (ddd, $J = 8.2, 7.2, 1.6$ Hz, 1H), 8.11 (ddd, $J = 7.9, 1.6, 0.4$ Hz, 1H), and 11.8 (br s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, d_6 -DMSO) δ 25.2, 43.1, 113.4, 120.6, 125.5, 126.3, 127.2, 134.2, 143.5, 148.0, 160.5, and 162.1; IR (CHCl_3) ν_{max} 1678, 1606, and 1470 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}$ ($\text{M}-\text{H}^+$) 213.1028, found 213.1022. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.80; H, 6.57; N, 12.98.

4-Chloro-2-(1,1-dimethylallyl)quinazoline (**14**)

A solution of quinazolinol **16** (151 g, 0.71 mol) in PhH (1.2 L) was azeotropically dried under a Dean–Stark trap. The solution was cooled to room temperature and treated with PhNEt₂ (175 mL, 1.10 mol) followed by POCl₃ (40 mL, 0.43 mol). The reaction mixture was then refluxed for 2 h, cooled to room temperature, and diluted with EtOAc (750 mL). The mixture was washed successively with water (3 × 750 mL), 1 M HCl (3 × 750 mL), water (750 mL), satd NaHCO₃ (750 mL), water (750 mL), and brine (750 mL). The organic layer was dried (MgSO₄), and evaporated in vacuo to give an off-white solid. Purification by flash chromatography (silica gel, pentane → pentane/CH₂Cl₂, 3/1) gave the title compound **14** (157.2 g, 96%) as a low-melting white solid: *R*_f = 0.65 (pentane/CH₂Cl₂, 3/1); ¹H NMR (300 MHz, CDCl₃) δ 1.62 (s, 6H), 5.11 (dd, *J* = 10.6, 1.1 Hz, 1H), 5.15 (dd, *J* = 17.5, 1.1 Hz, 1H), 6.43 (dd, *J* = 17.5, 10.6 Hz, 1H), 7.57 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H), 7.83 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.98 (ddd, *J* = 8.5, 1.2, 0.5 Hz, 1H), and 8.13 (ddd, *J* = 8.4, 1.4, 0.5 Hz, 1H); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 26.6, 45.4, 111.6, 121.7, 125.3, 127.8, 128.5, 134.2, 145.8, 151.1, 161.9, and 170.5; IR (CHCl₃) *v*_{max} 1618, 1572, 1556, 1479, 1335, 1327, and 1240 cm⁻¹; HRMS calcd for C₁₃H₁₄N₂Cl (MH⁺) 233.0846, found 233.0834.

2-(1,1-Dimethylallyl)-4-(2-methoxynaphthalen-1-yl)quinazoline (**18**)

To a solution of aryl chloride **14** (70.0 g, 0.30 mol) in DME (385 mL) was added Pd(PPh₃)₄ (5.23 g, 4.50 mmol) followed by 2M Na₂CO₃ (330 mL, 0.66 mol), arylboronic acid **17**⁹ (64.0 g, 0.32 mol), and EtOH (480 mL). The reaction mixture was refluxed for 5 h (TLC), cooled to room temperature, and partitioned between CH₂Cl₂ and water. The phases were separated, and the extraction was completed with additional portions of CH₂Cl₂. The combined organic extracts were dried (MgSO₄), and evaporated in vacuo. Purification by flash chromatography (silica gel, CH₂Cl₂) gave a pink solid that was triturated with pentane (700 mL) for 10 h. The precipitate was filtered, washed with pentane (3 × 50 mL), and dried to give the title compound **18** (104 g, 97%) as a white solid: *R*_f = 0.70 (CH₂Cl₂); mp 146.0–147.0 °C (EtOAc/pentane);¹⁰ ¹H NMR (400 MHz, CDCl₃) δ

⁹ Lim, C. W.; Tissot, O.; Mattison, A.; Hooper, M. W.; Brown, J. M.; Cowley, A. R.; Hulmes, D. I.; Blacker, A. J. *Organic Process Research & Development* **2003**, 7, 379–384.

¹⁰ When a sample of biaryl **18** was placed in a heating block pre-heated to 131 °C, it melted at 132 °C.

1.69 (s, 6H), 3.77 (s, 3H), 5.09 (dd, $J = 10.7, 1.2$ Hz, 1H), 5.15 (dd, $J = 17.5, 1.2$ Hz, 1H), 6.57 (dd, $J = 17.5, 10.7$ Hz, 1H), 7.15 (~d, $J = 8.5$ Hz, 1H), 7.29 (ddd, $J = 8.5, 6.8, 1.4$ Hz, 1H), 7.356 (ddd, $J = 7.9, 6.8, 1.4$ Hz, 1H), 7.359 (ddd, $J = 8.2, 6.8, 1.2$ Hz, 1H), 7.43 (ddd, $J = 8.2, 1.5, 0.5$ Hz, 1H), 7.44 (d, $J = 9.1$ Hz, 1H), 7.81 (ddd, $J = 8.5, 6.8, 1.6$ Hz, 1H), 7.88 (d, $J = 7.9$ Hz, 1H), 8.03 (d, $J = 9.1$ Hz, 1H), and 8.11 (d, $J = 8.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 27.04, 27.06, 45.8, 56.9, 111.1, 113.9, 120.6, 123.3, 123.9, 124.5, 126.6, 126.7, 127.0, 128.0, 128.7, 129.2, 131.0, 133.10, 133.14, 147.0, 150.5, 154.7, 166.6, and 171.2; IR (CHCl_3) ν_{max} 1616, 1595, 1568, 1550, 1514, 1491, 1471, 1346, 1269, and 1252 cm^{-1} ; HRMS calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}$ (MH^+) 355.1810, found 355.1818. Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}$: C, 81.33; H, 6.26; N, 7.90. Found: C, 80.98; H, 6.24; N, 7.78.

Optimization Studies

To a solution of aryl chloride **14** (10.0 g, 43.1 mmol) in DME (55 mL) was added a specified amount of $\text{Pd}(\text{PPh}_3)_4$ (see below), followed by 2M Na_2CO_3 (47 mL, 95 mmol), arylboronic acid **17** (9.14 g, 45.3 mmol), and EtOH (68 mL). The reaction mixture was refluxed until **14** was consumed (TLC). The title product **18** was isolated as described above. The results as summarized in Table S1:

Table S1. Cross-coupling between Aryl Chloride **14** and Arylboronic Acid **17** – Optimization Studies

$\text{Pd}(\text{PPh}_3)_4$ (mol %)	yield ^a	TON
2.0	14.0 g, 92%	46
1.0	13.0 g, 85%	85
0.5	12.8 g, 84%	168
0.25	11.8 g, 77%	308

^aIsolated yield of **18**. TON: turnover number.

Formation of the aryl ethyl ether **29** accounts for the diminished yields of **18** at the lower catalyst loadings. Ether **18**: a pale yellow liquid; $R_f = 0.70$ (CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 1.52 (t, $J = 7.1$ Hz, 3H), 1.64 (s, 6H), 4.67 (q, $J = 7.1$ Hz, 2H), 5.12 (dd, $J = 10.7, 1.3$ Hz, 1H),

5.18 (d, $J = 17.5, 1.3$ Hz, 1H), 6.52 (dd, $J = 17.5, 10.7$ Hz, 1H), 7.44 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.74 (ddd, $J = 8.5, 7.0, 1.5$ Hz, 1H), 7.94 (ddd, $J = 8.5, 1.1, 0.6$ Hz, 1H), and 8.12 (ddd, $J = 8.2, 1.5, 0.6$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 14.3, 26.6, 45.4, 62.4, 101.7, 114.7, 123.1, 125.8, 127.6, 132.7, 146.7, 151.3, 166.1, and 170.5; IR (CHCl_3) ν_{max} 1621, 1579, 1497, 1442, 1381, 1346, 1321, and 1100 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}$ (MH^+) 243.1497, found 243.1486.

3-[4-(2-Methoxynaphthalen-1-yl)quinazolin-2-yl]-3-methylbutane-1,2-diol (**30**)¹¹

To a suspension of alkene **18** (44.3 g, 125 mmol) and 4-methylmorpholine *N*-oxide (NMO) (58.5 g, 0.50 mol) in Me_2CO (550 mL) and water (270 mL) was added OsO_4 (4% in H_2O , 7.7 mL, 1.2 mmol; **CAUTION**: Toxic).¹² The resulting deep-purple suspension was stirred at room temperature for 96 h to give a clear, colorless solution. Na_2SO_3 (100 g, 0.79 mol) was added and the mixture was stirred for an additional 2 h. The reaction mixture was extracted with CH_2Cl_2 , the combined extracts were dried (MgSO_4), and evaporated in vacuo. Purification by flash chromatography (silica gel, $\text{CH}_2\text{Cl}_2 \rightarrow \text{EtOAc}$) gave the title compound **30** (47.1 g, 97%) as a white solid: $R_f = 0.65$ (EtOAc); mp 133.0–134.0 °C (EtOAc/pentane); ^1H NMR (400 MHz, CDCl_3)¹¹ δ 1.56 (s, 3H, **30a**), 1.58 (s, 3H, **30b**), 1.61 (s, 3H, **30a**), 1.62 (s, 3H, **30b**), 2.68 (br s, 1H), 3.48 (dd, $J = 10.9, 8.8$ Hz, 1H, **30b**), 3.57 (dd, $J = 10.9, 9.0$ Hz, 1H, **30a**), 3.79 (s, 3H, **30a**), 3.80 (s, 3H, **30b**), 3.82 (dd, $J = 10.9, 3.4$ Hz, 1H, **30a**), 3.84 (dd, $J = 10.9, 3.3$ Hz, 1H, **30a**), 3.97 (dd, $J = 8.8, 3.3$ Hz, 1H, **30b**), 4.02 (dd, $J = 9.0, 3.4$ Hz, 1H, **30a**), 5.86 (s, 1H), 7.06–7.12 (m, 1H+1H, **30a+30b**), 7.29–7.50 (m, 5H+5H, **30a+30b**), 7.83–7.90 (m, 2H+2H, **30a+30b**), and 8.04–8.10 (m, 1H+1H, **30a+30b**); $^{13}\text{C}\{^1\text{H}\}/^{13}\text{C}$ DEPT-135 NMR (101 MHz, CDCl_3)¹¹ δ 23.11 (CH_3), 23.14 (CH_3), 26.8 (CH_3), 27.3 (CH_3), 44.5 (ipso C), 44.8 (ipso C), 56.5 (CH_3), 56.6 (CH_3), 63.4 (CH_2), 63.6 (CH_2), 78.8 (CH), 79.4 (CH), 113.3 (CH), 113.4 (CH), 119.3 (ipso C), 119.5 (ipso C).

¹¹ Diol **30** comprises two atropdiastereomers, major (**30a**) and minor (**30b**), in a ~1.5:1 ratio, respectively. The DEPT spectrum was recorded at 75 MHz.

¹² OsO_4 is highly toxic and should be handled with care. For further safety information, see: <http://www.hazard.com/msds/>.

C), 123.40 (ipso C), 123.44 (ipso C), 123.93 (CH), 123.96 (CH), 123.99 (CH), 124.1 (CH), 127.02 (CH), 127.04 (CH), 127.12 (CH), 127.14 (CH), 127.25 (CH), 127.30 (CH), 128.13 (CH), 128.15 (CH), 128.4 (CH), 128.5 (CH), 128.8 (ipso C), 128.9 (ipso C), 131.4 (CH), 132.7 (ipso C), 132.8 (ipso C), 134.0 (CH), 150.0 (ipso C), 150.2 (ipso C), 154.6 (ipso C), 154.7 (ipso C), 166.2 (ipso C), 166.7 (ipso C), 170.7 (ipso C), and 170.8 (ipso C) (two carbon signals obscured); IR (CHCl₃) $\nu_{\max}$ 3010, 1616, 1595, 1568, 1554, 1514, 1491, 1473, 1462, 1435, 1340, 1269, 1252, 1215, and 1082 cm⁻¹; HRMS calcd for C₂₄H₂₅N₂O₃ (MH⁺) 389.1865, found 389.1851. Anal. Calcd for C₂₄H₂₄N₂O₃: C, 74.21; H, 6.23; N, 7.21. Found: C, 73.92; H, 6.20; N, 7.08.

2-[4-(2-Methoxynaphthalen-1-yl)-quinazolin-2-yl]-2-methylpropionaldehyde (**19**)

A solution of diol **30** (47.1 g, 121 mmol) in CH₂Cl₂ (500 mL) was cooled in an ice bath. During vigorous stirring, a solution of periodic acid (36.0 g, 158 mmol) in H₂O (500 mL) was added, and the resulting bright yellow biphasic mixture was stirred at 0 °C for 2 h and at room temperature for an additional 1 h (TLC). The reaction mixture was neutralized with concd NaHCO₃, the phases were separated, and the extraction was completed with additional portions of CH₂Cl₂. The combined organic extracts were dried (MgSO₄), and evaporated in vacuo. Purification by flash chromatography (silica gel, CH₂Cl₂ → CH₂Cl₂/EtOAc, 10/1) gave the title compound **19** (42.9 g, 99%) as a white solid: R_f = 0.45 (CH₂Cl₂); mp 126.0–127.0 °C (EtOAc/pentane); ¹H NMR (400 MHz, CDCl₃) δ 1.68 (s, 6H), 3.78 (s, 3H), 7.11 (~dd, J = 8.4, 1.0 Hz, 1H), 7.31 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.37 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.41 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.48 (ddd, J = 8.2, 1.5, 0.7 Hz, 1H), 7.85 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 7.89 (dd, J = 8.4, 1.6 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 8.10 (ddd, J = 8.4, 1.0, 0.7 Hz, 1H), and 10.1 (s, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 21.9, 22.0, 54.5, 56.7, 113.6, 119.8, 123.8, 124.0, 124.2, 127.0, 127.1, 127.2, 128.1, 128.5, 129.0, 131.3, 132.9, 133.7, 150.5, 154.7, 167.5, 167.6, and 202.9; IR (CHCl₃) $\nu_{\max}$ 1726, 1616, 1595, 1549, 1514, 1493, 1470, 1347, 1269, and 1252 cm⁻¹; HRMS calcd for C₂₃H₂₁N₂O₂ (MH⁺) 357.1603, found 357.1599. Anal. Calcd for C₂₃H₂₀N₂O₂: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.52; H, 5.68; N, 7.86.

2-[4-(2-Methoxynaphthalen-1-yl)-quinazolin-2-yl]-2-methylpropionaldehyde oxime (**31**)

A suspension of aldehyde **19** (42.9 g, 121 mmol) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (46.3 g, 0.67 mol) in pyridine (250 mL) and EtOH (250 mL) was refluxed for 2 h. The resulting yellow solution was evaporated in vacuo to give an off-white solid that was suspended in 0.2 M H_2SO_4 (10 L). The mixture was stirred for 10 min and the precipitate was filtered, washed with a copious amount of water, and dried to give the title compound **31** (43.4 g, 97%) as a white solid that was used in the next step without any further purification. An analytical sample of the title compound **31** was prepared by crystallization from EtOAc/pentane. Oxime **31**: a white solid; $R_f = 0.75$ ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 4/1); mp 174.5–175.5 °C (EtOAc/pentane); ^1H NMR (400 MHz, d_6 -DMSO) δ 1.625 (s, 3H), 1.631 (s, 3H), 3.78 (s, 3H), 7.05 (ddd, $J = 8.1, 1.4, 0.6$ Hz, 1H), 7.34 (ddd, $J = 8.2, 6.8, 1.4$ Hz, 1H), 7.40 (ddd, $J = 8.1, 6.8, 1.2$ Hz, 1H), 7.43 (ddd, $J = 8.2, 1.3, 0.5$ Hz, 1H), 7.54 (ddd, $J = 8.1, 6.8, 1.1$ Hz, 1H), 7.68 (d, $J = 9.1$ Hz, 1H), 7.84 (s, 1H), 7.97 (ddd, $J = 8.4, 6.8, 1.3$ Hz, 1H), 8.02 (dd, $J = 8.4, 1.2$ Hz, 1H), 8.09 (ddd, $J = 8.1, 1.1, 0.8$ Hz, 1H), 8.22 (d, $J = 9.1$ Hz, 1H), and 10.6 (s, 1H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 25.6, 25.8, 45.0, 56.3, 113.8, 118.6, 122.7, 123.6, 123.7, 126.3, 127.2, 127.6, 128.07, 128.12, 128.4, 131.2, 132.3, 134.2, 149.7, 154.3, 155.0, 166.7, and 169.1; IR (CHCl_3) ν_{max} 1616, 1595, 1568, 1550, 1514, 1493, 1471, 1348, 1269, and 1254 cm^{-1} ; HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_2$ (MH^+) 372.1712, found 372.1715. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_2$: C, 74.37; H, 5.70; N, 11.31. Found: C, 74.32; H, 5.72; N, 11.30.

2-[4-(2-Methoxynaphthalen-1-yl)-quinazolin-2-yl]-2-methylpropionitrile (**20**)

A suspension of oxime **31** (43.4 g, 117 mmol) in Ac_2O (310 mL) was refluxed for 4 h. The resulting yellow solution was cooled to room temperature and evaporated in vacuo. The residue

was subsequently triturated with Et₂O (250 mL) for 1 h. The precipitate was collected by filtration, washed with Et₂O (3 × 50 mL), and dried to give the title compound **20** (40.4 g, 98%) as a pale yellow solid that was used in the next step without any further purification. An analytical sample of the title compound **20** was prepared by crystallization from CH₂Cl₂/pentane. Biaryl **20**: a white solid; *R*_f = 0.45 (CH₂Cl₂); mp 202.0–203.0 °C (CH₂Cl₂/pentane); ¹H NMR (400 MHz, CDCl₃) δ 1.967 (s, 3H), 1.970 (s, 3H), 3.79 (s, 3H), 7.11 (dddd, *J* = 8.4, 1.6, 0.7, 0.6 Hz, 1H), 7.32 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.37 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.45 (ddd, *J* = 8.4, 6.7, 1.2 Hz, 1H), 7.51 (ddd, *J* = 8.4, 1.6, 0.6 Hz, 1H), 7.89 (ddd, *J* = 8.4, 6.7, 1.6 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.06 (d, *J* = 9.1 Hz, 1H), and 8.18 (ddd, *J* = 8.4, 1.2, 0.7 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 27.18, 27.23, 41.8, 56.7, 113.5, 119.5, 123.9, 124.0, 124.1, 127.0, 127.2, 127.7, 128.1, 128.7, 129.0, 131.4, 132.8, 134.6, 150.5, 154.7, 164.2, and 168.2 (one carbon signal obscured); IR (CHCl₃) ν_{max} 1618, 1595, 1568, 1552, 1514, 1493, 1470, 1348, 1269, and 1252 cm⁻¹; HRMS calcd for C₂₃H₂₀N₃O (MH⁺) 354.1606, found 354.1607. Anal. Calcd for C₂₃H₁₉N₃O: C, 78.16; H, 5.42; N, 11.89. Found: C, 77.91; H, 5.45; N, 11.89.

2-[4-(2-Hydroxynaphthalen-1-yl)quinazolin-2-yl]-2-methylpropionitrile (**32**)

A solution of biaryl **20** (353 mg, 1.0 mmol) in CH₂Cl₂ (10 mL) was cooled in an ice bath and treated with AlBr₃ (1.07 g, 4.0 mmol). The resulting brown solution turned green after ~20 min, and after an additional 20 min at 0 °C it was allowed to warm and stir at room temperature for a further 6 h. The reaction mixture was re-cooled to 0 °C and quenched with MeOH to give an orange solution. 1 M HCl (10 mL) was added, and the phases were separated. The extraction was completed with additional portions of CH₂Cl₂. The combined extracts were dried (MgSO₄) and evaporated in vacuo. Purification by flash chromatography (silica gel, CH₂Cl₂ → CH₂Cl₂/EtOAc, 10/1) gave the title compound **32** (320 mg, 94%) as a pale yellow solid: *R*_f = 0.70 (CH₂Cl₂/EtOAc, 10/1); mp 224.5–225.5 °C (EtOAc/pentane); ¹H NMR (400 MHz, *d*₆-DMSO) δ 1.86 (s, 3H), 1.87 (s, 3H), 7.05 (~ddd, *J* = 8.3, 1.2, 0.6 Hz, 1H), 7.30 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.33 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.57 (ddd, *J* = 8.4, 1.4, 0.6 Hz, 1H), 7.63 (ddd, *J* =

8.3, 6.7, 1.2 Hz, 1H), 7.94 (~dd, $J = 8.2, 1.6$ Hz, 1H), 8.04 (d, $J = 8.9$ Hz, 1H), 8.04 (ddd, $J = 8.4, 6.7, 1.6$ Hz, 1H), 8.15 (ddd, $J = 8.4, 1.1, 0.8$ Hz, 1H), and 10.0 (s, 1H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 26.6, 26.8, 41.2, 115.5, 118.1, 123.0, 123.27, 123.32, 123.6, 126.97, 127.02, 127.7, 128.0, 128.1, 128.2, 131.0, 132.8, 134.8, 149.8, 152.7, 163.8, and 168.3; IR (CHCl_3) ν_{max} 1620, 1599, 1564, 1549, 1489, 1460, 1408, 1390, 1352, and 1209 cm^{-1} ; HRMS calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}$ (MH^+) 340.1450, found 340.1463. Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}$: C, 77.86; H, 5.05; N, 12.38. Found: C, 77.64; H, 5.11; N, 12.24.

1-[2-(Cyanodimethylmethyl)quinazolin-4-yl]naphthalen-2-yl trifluoromethanesulfonate (**21**)

First method

To a suspension of phenol **32** (10.0 g, 29.5 mmol) in CH_2Cl_2 (150 mL) was added DMAP (10.8 g, 88.5 mmol), and the mixture was cooled in an ice bath. During vigorous stirring, Tf_2O (5.5 mL, 32 mmol) was added dropwise over 10 min, the reaction mixture was stirred at $0\text{ }^\circ\text{C} \rightarrow$ room temperature for 12 h and washed with 1M HCl and brine. The organic layer was dried (MgSO_4), evaporated in vacuo to give a yellow solid. Purification by flash chromatography (silica gel, CH_2Cl_2 /pentane, 1/1) gave the title compound **21** (11.4 g, 82%) as a white solid, identical (TLC, ^1H NMR) with the product obtained according to the second method.

Second method (preferred)

A suspension of biaryl **20** (23.2 g, 65.7 mmol) in CH_2Cl_2 (400 mL) was cooled in an ice bath. During vigorous stirring, AlBr_3 (70 g, 0.26 mol) and NaI (9.86 g, 65.7 mmol) were added to give a dark-brown mixture that was stirred at room temperature for 6 h. After it was re-cooled to $0\text{ }^\circ\text{C}$, the reaction mixture was quenched with methanol to give an orange solution. 1 M HCl (400

mL) was added, the phases were separated, and the extraction was completed with additional portions of CH₂Cl₂. The combined organic extracts were washed with brine, dried (MgSO₄), and evaporated in vacuo to give a light-brown solid. The crude phenol **20** was suspended in CH₂Cl₂ (300 mL) and treated with DMAP (24.0 g, 197 mmol) to give a clear solution. After the mixture was cooled in an ice-bath, Tf₂O (12.2 mL, 72 mmol) was added dropwise over 5 min, and the stirring was continued at room temperature for 5 h. The reaction mixture was re-cooled to 0 °C, 1 M HCl (300 mL) was added, and the mixture was stirred vigorously for 5 min. The phases were separated and the extraction was completed with additional portions of CH₂Cl₂. The combined organic extracts were washed with brine, dried (MgSO₄), and evaporated in vacuo to give an orange solid. Purification by flash chromatography (silica gel, pentane/CH₂Cl₂, 2/1 → CH₂Cl₂) gave the title compound **21** (26.5 g, 86% or 96% brsm) as a white solid and the recovered starting material **20** (2.4 g, 10%). Biaryl **21**: *R_f* = 0.70 (CH₂Cl₂/EtOAc, 9/1); mp 131.5–132.5 °C (EtOAc/pentane); ¹H NMR (400 MHz, CDCl₃) δ 1.95 (s, 3H), 1.98 (s, 3H), 7.26 (~ddd, *J* = 8.4, 1.6, 0.8 Hz, 1H), 7.43 (ddd, *J* = 8.3, 1.4, 0.6 Hz, 1H), 7.46 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.9, 1.1 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.96 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 8.02 (~d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), and 8.23 (ddd, *J* = 8.5, 1.0, 0.8 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 27.0, 27.3, 41.8, 118.1 (q, *J* = 320 Hz), 119.4, 123.4, 123.7, 125.8, 126.2, 126.8, 127.5, 128.38, 128.44, 129.1, 132.20, 132.24, 132.4, 134.8, 144.4, 150.8, 164.1, and 164.3 (one carbon signal obscured); IR (CHCl₃) *v*_{max} 1566, 1556, 1493, 1425, 1248, 1230, 1219, and 1139 cm⁻¹; HRMS calcd for C₂₃H₁₇N₃O₃F₃S (MH⁺) 472.0943, found 472.0922. Anal. Calcd for C₂₃H₁₆N₃O₃F₃S: C, 58.59; H, 3.42; N, 8.91; S, 6.80. Found: C, 58.49; H, 3.39; N, 8.83; S, 7.10.

2-[4-(2-Diphenylphosphanylnaphthalen-1-yl)quinazolin-2-yl]-2-methylpropionitrile (**22**)

To a solution of NiCl₂(dppe) [1.26 g, 2.38 mmol; dppe: 1,2-bis(diphenylphosphino)ethane] in DMF (70 mL) was added Ph₂PH (2.5 mL, 14.3 mmol), and the mixture was stirred at 100 °C for 30 min. A solution of triflate **21** (11.2 g, 23.8 mmol) and DABCO (10.7 g, 95.2 mmol)

in DMF (80 mL) was added via cannula and the resulting dark brown mixture was stirred at 100 °C for 1 h. An additional portion of Ph₂PH (2.5 mL, 14.3 mmol) was added, and the mixture was stirred at 100 °C for 42 h (TLC). The volatiles were removed in vacuo, the residue was taken up in CH₂Cl₂, and filtered through Celite[®]. The filtrate was washed successively with water and brine, dried (MgSO₄), and concentrated in vacuo to give a gray solid. Purification by flash chromatography (silica gel, CH₂Cl₂/pentane, 1/1 → CH₂Cl₂), followed by re-crystallization (EtOAc/pentane) gave the title compound **22** as a white solid (9.6 g, 80%). The mother liquor was concentrated and chromatographed as described above to give an additional portion of the product **22** (1.0 g, 8%; 10.6 g, 88% overall). Biaryl **22**: *R_f* = 0.60 (CH₂Cl₂); mp 200.0–201.0 °C (EtOAc/pentane); ¹H NMR (400 MHz, CDCl₃) δ 1.56 (s, 3H), 1.65 (s, 3H), 7.06 (~dd, *J* = 8.4, 0.8 Hz, 1H), 7.13–7.38 (m, 12 H), 7.39–7.42 (m, 2 H), 7.53 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.86–7.92 (m, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), and 8.20 (dt, *J* = 8.5, 0.8 Hz, 1H); ¹³C{¹H}/¹³C DEPT-135 NMR (101 MHz, CDCl₃)¹³ δ 26.5 (CH₃), 27.0 (CH₃), 41.7 (ipso C), 123.9 (ipso C), 123.99 (ipso C), 124.02 (ipso C), 125.9 (CH), 126.0 (CH), 126.7 (CH), 127.06 (CH), 127.12 (CH), 127.9 (CH), 128.16 (CH), 128.24 (CH), 128.3 (CH), 128.37 (CH), 128.44 (CH), 128.7 (CH), 128.9 (CH), 129.4 (CH), 129.96 (CH), 129.97 (CH), 131.65 (ipso C), 131.73 (ipso C), 133.1 (CH), 133.3 (CH), 133.4 (ipso C), 133.5 (CH), 133.7 (CH), 134.1 (CH), 134.3 (ipso C), 136.2 (ipso C), 136.3 (ipso C), 136.9 (ipso C), 137.0 (ipso C), 141.4 (ipso C), 141.7 (ipso C), 150.3 (ipso C), 164.0 (ipso C), 170.1 (ipso C), and 170.2 (ipso C); ³¹P{¹H} NMR (162 MHz, CDCl₃) δ –12.6; IR (CHCl₃) *v*_{max} 1614, 1603, 1568, 1554, 1491, 1470, 1435, 1342, 1228, and 1221 cm^{–1}; HRMS calcd for C₃₄H₂₇N₃P (MH⁺) 508.1943, found 508.1960. Anal. Calcd for C₃₄H₂₆N₃P: C, 80.46; H, 5.16; N, 8.28. Found: C, 80.28; H, 5.14; N, 8.24.

¹³ Due to spectrum complexity, C–P couplings were not assigned.

1.3. Synthesis of Quinazoline–Oxazoline-Containing Ligands

(S_a,S)-(–)- and *(R_a,S)*-(+)-4-(2-Diphenylphosphanylnaphthalen-1-yl)-2-[1-(4-isopropyl-4,5-dihydrooxazol-2-yl)-1-methylethyl]quinazoline (**24**)

A high-pressure tube was charged with nitrile **22** (600 mg, 1.18 mmol), *(S)*-(+)-valinol (**23**, R = Prⁱ) (366 mg, 3.55 mol), Cd(OAc)₂·2H₂O (315 mg, 1.18 mmol; **CAUTION**: Carcinogenic),¹⁴ and PhCl (2 mL). The tube was sealed and the mixture was stirred at 140 °C for 68 h. After this time, the reaction mixture was cooled to room temperature, diluted with CH₂Cl₂ (5 mL) and water (2 mL), and stirred for 10 min. The resulting suspension was filtered through a pad of Celite[®], the phases were separated, and the extraction was completed with additional portions of CH₂Cl₂. The combined extracts were dried (MgSO₄) and evaporated in vacuo to give a brown oil. Purification by flash chromatography (silica gel, pentane/EtOAc, 2/1) gave a ~1:1 mixture of the title compounds (*R_a/S_a,S*)-**24** (447 mg, 63%). The two diastereomers were separated by repeated column chromatography (silica gel, pentane/EtOAc/Et₃N, 800/200/1). Ligand *(S_a,S)*-(–)-**24** (first¹⁵ isomer): a white solid; $[\alpha]_D^{20}$ –208 (*c* 0.61, CHCl₃); mp 197.0–198.0 °C (EtOAc/pentane); ¹H NMR (400 MHz, CDCl₃) δ 0.71 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H), 1.55 (s, 3H), 1.67 (s, 3H), 1.74 (dq, *J* = 6.8, 6.8, 4.7 Hz, 1H), 3.78–3.83 (m, 1H), 3.83–3.94 (m, 2H), 7.07 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.14–7.40 (m, 14H), 7.50 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.81 (ddd, *J* = 8.4, 6.4, 1.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), and 8.11 (dt, *J* = 8.5, 0.9 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃)¹³ δ 17.2, 18.5, 25.3, 25.7, 31.9, 45.9, 69.3, 71.4, 123.7, 123.8, 126.35, 126.37, 126.5, 126.6, 126.9, 127.0, 127.9, 128.06, 128.14, 128.2, 128.3, 128.4, 128.5, 128.9, 129.0, 129.92, 129.93, 131.9, 132.0, 132.9, 133.1, 133.3, 133.36, 133.37, 133.5, 133.7, 133.8, 133.9, 136.7, 136.8, 137.3, 137.5, 142.2, 142.6, 150.3, 168.3, 168.95, 169.02, and 171.1; ³¹P{¹H} NMR (162 MHz, CDCl₃) δ –13.14; IR (CHCl₃) ν_{max} 1662, 1554, 1491, 1481, 1323, 1126,

¹⁴ Cd(OAc)₂ is highly carcinogenic and should be handled with care. For further safety information, see: <http://www.hazard.com/msds/>.

¹⁵ Based on the order of elution of the two atropisomers from the silica gel column with the solvent system described in the experimental procedure.

and 1101 cm^{-1} ; HRMS calcd for $\text{C}_{39}\text{H}_{37}\text{N}_3\text{OP}$ (MH^+) 594.2674, found 594.2695. Anal. Calcd for $\text{C}_{39}\text{H}_{36}\text{N}_3\text{OP}$: C, 78.90; H, 6.11; N, 7.08. Found: C, 78.67; H, 6.05; N, 7.03. Crystals of the ligand (*S_a,S*)-(-)-**24** suitable for X-ray diffraction analysis were grown by slow evaporation of an EtOAc/pentane solution. For crystallographic data, see Chapter 2.1 (p. S-20).

Ligand (*R_a,S*)-(+)-**24** (second¹⁵ isomer): a white solid; $[\alpha]_{\text{D}}^{20} +99.4$ (*c* 0.84, CHCl_3); mp 168.5–170.0 °C (Et_2O); ^1H NMR (400 MHz, CDCl_3) δ 0.74 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 1.48 (s, 3H), 1.53 (s, 3H), 1.72 (dq, *J* = 6.8, 6.8, 4.9 Hz, 1H), 3.78–3.87 (m, 2H), 3.95–4.03 (m, 1H), 7.01 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.03–7.22 (m, 13H), 7.28 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.39 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.4, 2.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), and 7.98 (~dt, *J* = 8.4, 1.0 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}/^{13}\text{C}$ DEPT-135 NMR (101 MHz, CDCl_3) δ 17.3 (CH_3), 18.9 (CH_3), 25.70 (CH_3), 25.72 (CH_3), 32.1 (CH), 45.9 (ipso C), 69.4 (CH_2), 71.5 (CH), 123.7 (ipso C), 123.8 (ipso C), 126.35 (CH), 126.37 (CH), 126.5 (CH), 126.7 (CH), 126.9 (CH), 127.0 (CH), 127.9 (CH), 128.15 (CH), 128.17 (CH), 128.21 (CH), 128.25 (CH), 128.32 (CH), 128.5 (CH), 128.9 (CH), 129.0 (CH), 129.97 (CH), 129.98 (CH), 131.9 (ipso C), 132.0 (ipso C), 133.1 (CH), 133.2 (CH), 133.3 (CH), 133.38 (ipso C), 133.40 (CH), 133.6 (CH), 133.9 (ipso C), 134.1 (ipso C), 136.6 (ipso C), 136.7 (ipso C), 137.3 (ipso C), 137.4 (ipso C), 142.2 (ipso C), 142.6 (ipso C), 150.3 (ipso C), 168.3 (ipso C), 168.86 (ipso C), 168.93 (ipso C), and 171.4 (ipso C); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -13.19; IR (CHCl_3) ν_{max} 1660, 1552, 1491, 1481, 1435, 1126, 1099, and 910 cm^{-1} ; HRMS calcd for $\text{C}_{39}\text{H}_{37}\text{N}_3\text{OP}$ (MH^+) 594.2674, found 594.2688. Anal. Calcd for $\text{C}_{39}\text{H}_{36}\text{N}_3\text{OP}$: C, 78.90; H, 6.11; N, 7.08. Found: C, 78.60; H, 5.95; N, 7.00.

(*S_a,S*)-(-)- and (*R_a,S*)-(+)-2-[1-(4-*tert*-butyl-4,5-dihydrooxazol-2-yl)-1-methylethyl]-4-(2-diphenylphosphanylnaphthalen-1-yl)quinazoline (25**)**

As described for the preparation of **24**, biaryl **22** (600 mg, 1.18 mmol), (*S*)-(+)-*tert*-leucinol (**23**, R = Bu^t) (415 mg, 3.55 mmol), $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (315 mg, 1.18 mmol; **CAUTION**: Carcinogenic),¹⁴ and PhCl (2 mL) were reacted at 140 °C for 71 h. Purification by flash

chromatography (silica gel, pentane/EtOAc, 2/1) gave the recovered starting material **22** (124 mg, 21%) and a ~1:1 mixture the title compounds ($R_a/S_a,S$)-**25** (307 mg, 43%). The two diastereomers were separated by repeated column chromatography (silica gel, pentane/EtOAc, 860/140/1). Ligand (S_a,S)-(-)-**25** (first¹⁵ isomer): a white solid; $[\alpha]_D^{20}$ -203 (c 0.71, CHCl₃); R_f = 0.41 (pentane/EtOAc, 6/1) or 0.23 (pentane/EtOAc/Et₃N, 800/200/1); mp 217.0–218.0 °C (EtOAc/pentane); ¹H NMR (400 MHz, CDCl₃) δ 0.73 (s, 9H), 1.51 (s, 3H), 1.71 (s, 3H), 3.74 (dd, J = 9.6, 7.5 Hz, 1H), 3.84–3.91 (m, 2 H), 7.07 (dd, J = 8.4, 0.5 Hz, 1H), 7.14–7.42 (m, 14H), 7.50 (ddd, J = 8.1, 6.8, 1.1 Hz, 1H), 7.82 (ddd, J = 8.4, 6.7, 1.7 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), and 8.13 (~dt, J = 8.4, 0.9 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃)¹³ δ 25.1, 25.6, 25.7, 33.8, 45.9, 68.6, 75.3, 123.69, 123.71, 126.35, 126.37, 126.5, 126.6, 126.9, 127.0, 127.9, 128.05, 128.13, 128.2, 128.3, 128.4, 128.5, 128.9, 129.0, 129.89, 129.90, 131.9, 132.0, 132.9, 133.1, 133.27, 133.32, 133.4, 133.61, 133.63, 133.8, 136.6, 136.7, 137.4, 137.5, 142.2, 142.6, 150.3, 168.3, 168.9, 169.0, and 170.9; ³¹P{¹H} NMR (162 MHz, CDCl₃) δ -13.14; IR (CHCl₃) $\nu_{\max}$ 1664, 1554, 1479, 1435, 1323, 1252, and 1130 cm⁻¹; HRMS calcd for C₄₀H₃₉N₃OP (MH⁺) 608.2831, found 608.2833. Anal. Calcd for C₄₀H₃₈N₃OP: C, 79.05; H, 6.30; N, 6.91. Found: C, 78.77; H, 6.33; N, 6.91. Crystals of the ligand (S_a,S)-(-)-**25** suitable for X-ray diffraction analysis were grown by slow evaporation of an EtOAc/pentane solution. For crystallographic data, see Chapter 2.2 (p. S-40).

Ligand (R_a,S)-(+)-**25** (second¹⁵ isomer): a white solid; $[\alpha]_D^{20}$ +113 (c 0.76, CHCl₃); R_f = 0.38 (pentane/EtOAc, 6/1) or 0.20 (pentane/EtOAc/Et₃N, 800/200/1); mp 182.0–183.0 °C (EtOAc/pentane); ¹H NMR (400 MHz, CDCl₃) δ 0.89 (s, 9H), 1.59 (s, 3H), 1.63 (s, 3H), 3.84 (dd, J = 9.8, 7.0 Hz, 1H), 4.04–4.12 (m, 2 H), 7.13 (dd, J = 8.5, 0.6 Hz, 1H), 7.15–7.32 (m, 13H), 7.40 (dd, J = 8.5, 3.1 Hz, 1H), 7.51 (ddd, J = 8.1, 6.8, 1.1 Hz, 1H), 7.79 (ddd, J = 8.4, 6.5, 1.8 Hz, 1H), 7.90 (br d, J = 8.2 Hz, 1H), 7.92 (br d, J = 8.4 Hz, 1H), and 8.20 (~dt, J = 8.4, 0.9 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃)¹³ δ 25.76, 25.81, 25.9, 33.9, 46.0, 68.7, 75.3, 123.72, 123.74, 126.42, 126.44, 126.5, 126.7, 126.9, 127.0, 127.9, 128.16, 128.18, 128.2, 128.27, 128.33, 128.5, 128.9, 129.0, 130.00, 130.02, 131.9, 132.0, 133.1, 133.2, 133.3, 133.38, 133.39, 133.42, 133.6, 133.9, 134.1, 136.6, 136.7, 137.3, 137.5, 142.3, 142.6, 150.3, 168.4, 168.8, 168.9, and 171.2; ³¹P{¹H} NMR (162 MHz, CDCl₃) δ -13.13; IR (CHCl₃) $\nu_{\max}$ 1662, 1614, 1552, 1479, 1435, 1325, and 1130 cm⁻¹; HRMS calcd for C₄₀H₃₉N₃OP (MH⁺) 608.2831, found 608.2816. Anal. Calcd for C₄₀H₃₈N₃OP: C, 79.05; H, 6.30; N, 6.91. Found: C, 79.01; H, 6.26; N, 6.78.

1.4. Asymmetric Allylic Alkylation (AAA) Studies

Table S2. Asymmetric Allylic Alkylation of ($\pm$)-**27** with **26a,b**

entry	ligand	base	solvent	R	$T/^\circ\text{C}$	yield (%) ^a	ee (%) ^b
1	(<i>S</i> _a , <i>S</i>)-(-)- 25	KOAc	CH ₂ Cl ₂	Me	rt	>95	55 (<i>R</i>)
2	(<i>S</i> _a , <i>S</i>)-(-)- 25	KOAc	THF	Me	rt	24	22 (<i>S</i>)
3	(<i>S</i> _a , <i>S</i>)-(-)- 25	KOAc	PhMe	Me	rt	<5	18 (<i>S</i>)
4	(<i>S</i> _a , <i>S</i>)-(-)- 25	LiOAc	CH ₂ Cl ₂	Me	rt	81	39 (<i>S</i>)
5	(<i>R</i> _a , <i>S</i>)-(+)- 25	KOAc	CH ₂ Cl ₂	Me	rt	>95	7 (<i>S</i>)
6	(<i>R</i> _a , <i>S</i>)-(+)- 25	LiOAc	CH ₂ Cl ₂	Me	rt	>95	60 (<i>R</i>)
7	(<i>R</i> _a , <i>S</i>)-(+)- 25	LiOAc	CH ₂ Cl ₂	Me	-15	0	N/A
8 ^c	(<i>R</i> _a , <i>S</i>)-(+)- 25	LiOAc	CH ₂ Cl ₂	Me	5	<5	26 (<i>R</i>)
9	(<i>S</i> _a , <i>S</i>)-(-)- 24	KOAc	CH ₂ Cl ₂	Me	rt	>95	15 (<i>S</i>)
10	(<i>S</i> _a , <i>S</i>)-(-)- 24	LiOAc	CH ₂ Cl ₂	Me	rt	>95	58 (<i>S</i>)
11	(<i>R</i> _a , <i>S</i>)-(+)- 24	KOAc	CH ₂ Cl ₂	Me	rt	>95	55 (<i>R</i>)
12	(<i>R</i> _a , <i>S</i>)-(+)- 24	LiOAc	CH ₂ Cl ₂	Me	rt	>95	81 (<i>R</i>)
13 ^d	(<i>S</i> _a / <i>R</i> _a , <i>S</i>)- 24	KOAc	CH ₂ Cl ₂	Me	rt	>95	21 (<i>R</i>)
14	(<i>R</i> _a , <i>S</i>)-(+)- 25	LiOAc	CH ₂ Cl ₂	Et	rt	>95	59 (<i>R</i>)

^aIsolated yield of **28**. ^bDetermined by CSP HPLC. ^cCarried out for 70 h. ^dA ~1:1 mixture of the diastereomeric ligands (*S*_a,*S*)-(-)-**24** and (*R*_a,*S*)-(+)-**24** was used.

General procedure (Table S2, entry 1): A solution of $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ (1.4 mg, 3.8 μmol , 2.5 mol %) and ligand (*S*_a,*S*)-(-)-**25** (5.5 mg, 9.1 μmol , 6.0 mol %) in CH₂Cl₂ (0.9 mL) was stirred at room temperature for 30 min. The resulting pale yellow solution was added to ($\pm$)-(*E*)-1,3-diphenyl-2-propenyl acetate (**27**) (37.8 mg, 0.15 mmol) and stirred for an additional 5 min. Dimethyl malonate (**26a**) (51 μL , 0.45 mmol), N,O-bis(trimethylsilyl)acetamide (BSA, 111 μL , 0.45 mmol), and a pinch of KOAc (~1 mg) were added. The resulting yellow mixture was stirred at room temperature for 24 h, quenched with satd NH₄Cl, and extracted with CH₂Cl₂. The combined organic extracts were dried (MgSO₄), and evaporated in vacuo to give a clear oil (75 mg). The level of conversion of ($\pm$)-(**27**) and the yield of **28a** were estimated by ¹H NMR (300 MHz, CDCl₃) analysis. Alternatively, purification by flash chromatography (silica gel, pentane/EtOAc, 97/3) gave the title compound **28a** (48 mg, 99%) as a clear oil. Its enantiomeric

composition was established by CSP HPLC (Daicel's Chiralpak[®] AD, 1 cm × 25 cm; hexanes/2-propanol, 95/5; 4.5 mL min⁻¹; 25 °C; 254 nm; t_{R1} = 13.7 min for (*R*)-**28a** and t_{R2} = 19.4 min for (*S*)-**28a**), and its optical rotation was compared with the literature data¹⁶ to assign the absolute configuration as *R*.

¹⁶ (a) Sprintz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, 34, 1769–1772. (b) Mino, T.; Saito, A.; Tanaka, Y.; Hasegawa, S.; Sato, Y.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2005**, 70, 1937–1940.

2. X-Ray Single-Crystal Data

2.1. Ligand (*S_a*,*S*)-(–)-(24)

Table S3. Crystal Data and Structure Refinement for Ligand (*S_a*,*S*)-(–)-(24)

Empirical formula	C ₃₉ H ₃₆ N ₃ OP	
Formula weight	593.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	<i>a</i> = 10.6365(12) Å	$\alpha = 90^\circ$
	<i>b</i> = 16.1655(19) Å	$\beta = 90^\circ$
	<i>c</i> = 18.138(2) Å	$\gamma = 90^\circ$
Volume	3118.7(6) Å ³	
<i>Z</i>	4	
Density (calculated)	1.264 Mg/m ³	
Absorption coefficient	0.125 mm ⁻¹	
<i>F</i> (000)	1256	
Crystal size	0.40 × 0.30 × 0.20 mm	
Theta range for data collection	1.69 to 26.00°	
Index ranges	–13 ≤ <i>h</i> ≤ 13, –19 ≤ <i>k</i> ≤ 19, –22 ≤ <i>l</i> ≤ 22	
Reflections collected	24106	
Independent reflections	6061 [<i>R</i> (int) = 0.0300]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9755 and 0.8299	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	6061 / 0 / 541	
Goodness-of-fit on <i>F</i> ²	1.070	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0378, <i>wR</i> ₂ = 0.0908	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0403, <i>wR</i> ₂ = 0.0924	
Absolute structure parameter	–0.04(8)	
Largest diff. peak and hole	0.612 and –0.165 e/Å ³

Figure S1. ORTEP drawing (50% probability thermal ellipsoids) of the molecular structure of ligand (*S_a*,*S*)-(-)-**24**.

Table S4. Atomic Coordinates $[(x, y, z), \times 10^4]$ and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Ligand (S_a,S)-(-)-**24**

	x	y	z	U(eq) ¹⁷
P	7662(1)	5511(1)	1283(1)	20(1)
C(1)	7566(2)	4704(1)	570(1)	18(1)
C(2)	6510(2)	4606(1)	100(1)	21(1)
C(3)	6461(2)	3986(1)	-407(1)	20(1)
C(4)	7472(2)	3420(1)	-485(1)	18(1)
C(5)	7454(2)	2780(1)	-1020(1)	21(1)
C(6)	8451(2)	2252(1)	-1091(1)	25(1)
C(7)	9508(2)	2338(1)	-634(1)	25(1)
C(8)	9563(2)	2949(1)	-110(1)	21(1)
C(9)	8546(2)	3510(1)	-28(1)	17(1)
C(10)	8561(2)	4164(1)	506(1)	16(1)
C(11)	9689(2)	4231(1)	1001(1)	16(1)
N(1)	9627(2)	3855(1)	1641(1)	17(1)
C(12)	10793(2)	4654(1)	768(1)	16(1)
C(13)	10898(2)	5085(1)	93(1)	22(1)
C(14)	11997(2)	5473(1)	-85(1)	25(1)
C(15)	13034(2)	5440(1)	397(1)	23(1)
C(16)	12960(2)	5020(1)	1050(1)	20(1)
C(17)	11827(2)	4626(1)	1257(1)	17(1)
N(2)	11752(2)	4222(1)	1921(1)	17(1)
C(18)	10680(2)	3871(1)	2075(1)	17(1)
C(19)	10510(2)	3459(1)	2834(1)	22(1)
C(20)	11785(2)	3244(2)	3181(1)	30(1)
C(21)	9782(3)	4076(1)	3320(1)	30(1)
C(22)	9741(2)	2679(1)	2741(1)	19(1)
O	10356(1)	2060(1)	2375(1)	24(1)

¹⁷ U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

C(23)	9546(2)	1341(1)	2449(1)	26(1)
C(24)	8298(2)	1698(1)	2713(1)	23(1)
C(25)	7264(2)	1736(1)	2119(1)	26(1)
C(26)	7696(3)	2186(2)	1427(1)	36(1)
C(27)	6785(2)	875(2)	1931(1)	34(1)
N(3)	8640(2)	2541(1)	2970(1)	24(1)
C(28)	6803(2)	5029(1)	2047(1)	20(1)
C(29)	6087(2)	4314(1)	1975(1)	24(1)
C(30)	5507(2)	3957(1)	2580(1)	28(1)
C(31)	5640(2)	4310(1)	3268(1)	25(1)
C(32)	6348(2)	5018(1)	3351(1)	28(1)
C(33)	6933(2)	5374(1)	2745(1)	25(1)
C(34)	6559(2)	6286(1)	927(1)	21(1)
C(35)	6823(2)	6629(1)	238(1)	27(1)
C(36)	6096(2)	7262(1)	−49(1)	31(1)
C(37)	5082(2)	7559(1)	354(1)	31(1)
C(38)	4806(2)	7228(1)	1039(1)	30(1)
C(39)	5542(2)	6595(1)	1325(1)	24(1)

Table S5. Bond Lengths [Å] and Angles [°] for Ligand (*S_a*,*S*)-(-)-**24**

P–C(28)	1.834(2)
P–C(34)	1.834(2)
P–C(1)	1.8393(18)
C(1)–C(10)	1.377(3)
C(1)–C(2)	1.420(3)
C(2)–C(3)	1.360(3)
C(2)–H(2)	0.95(2)
C(3)–C(4)	1.420(3)
C(3)–H(3)	0.90(2)
C(4)–C(5)	1.417(3)
C(4)–C(9)	1.418(3)
C(5)–C(6)	1.368(3)
C(5)–H(5)	0.91(2)
C(6)–C(7)	1.404(3)
C(6)–H(6)	0.96(2)
C(7)–C(8)	1.371(3)
C(7)–H(7)	0.95(3)
C(8)–C(9)	1.419(3)
C(8)–H(8)	0.94(2)
C(9)–C(10)	1.434(3)
C(10)–C(11)	1.503(3)
C(11)–N(1)	1.312(2)
C(11)–C(12)	1.424(3)
N(1)–C(18)	1.369(2)
C(12)–C(13)	1.412(3)
C(12)–C(17)	1.414(3)
C(13)–C(14)	1.366(3)
C(13)–H(13)	0.99(3)
C(14)–C(15)	1.408(3)

C(14)–H(14)	0.97(2)
C(15)–C(16)	1.367(3)
C(15)–H(15)	0.93(2)
C(16)–C(17)	1.413(3)
C(16)–H(16)	1.00(3)
C(17)–N(2)	1.372(2)
N(2)–C(18)	1.305(3)
C(18)–C(19)	1.539(3)
C(19)–C(22)	1.513(3)
C(19)–C(20)	1.535(3)
C(19)–C(21)	1.540(3)
C(20)–H(20A)	0.97(3)
C(20)–H(20B)	0.95(3)
C(20)–H(20C)	1.05(3)
C(21)–H(21A)	1.02(2)
C(21)–H(21B)	1.00(3)
C(21)–H(21C)	1.00(3)
C(22)–N(3)	1.262(3)
C(22)–O	1.368(2)
O–C(23)	1.452(2)
C(23)–C(24)	1.525(3)
C(23)–H(23A)	0.93(2)
C(23)–H(23B)	1.04(2)
C(24)–N(3)	1.486(3)
C(24)–C(25)	1.541(3)
C(24)–H(24)	1.00(2)
C(25)–C(27)	1.521(3)
C(25)–C(26)	1.522(3)
C(25)–H(25)	0.90(3)
C(26)–H(26A)	0.93(3)
C(26)–H(26B)	1.00(3)

C(26)–H(26C)	0.94(3)
C(27)–H(27A)	1.00(3)
C(27)–H(27B)	0.99(3)
C(27)–H(27C)	0.98(3)
C(28)–C(29)	1.390(3)
C(28)–C(33)	1.391(3)
C(29)–C(30)	1.384(3)
C(29)–H(29)	0.95(2)
C(30)–C(31)	1.379(3)
C(30)–H(30)	0.97(3)
C(31)–C(32)	1.378(3)
C(31)–H(31)	0.97(2)
C(32)–C(33)	1.388(3)
C(32)–H(32)	0.95(3)
C(33)–H(33)	0.91(2)
C(34)–C(39)	1.393(3)
C(34)–C(35)	1.396(3)
C(35)–C(36)	1.385(3)
C(35)–H(35)	0.94(2)
C(36)–C(37)	1.389(3)
C(36)–H(36)	0.91(2)
C(37)–C(38)	1.383(3)
C(37)–H(37)	0.93(3)
C(38)–C(39)	1.390(3)
C(38)–H(38)	0.96(3)
C(39)–H(39)	0.96(3)
C(28)–P–C(34)	103.73(9)
C(28)–P–C(1)	101.67(9)
C(34)–P–C(1)	101.61(9)
C(10)–C(1)–C(2)	119.05(16)

C(10)–C(1)–P	117.82(14)
C(2)–C(1)–P	123.12(14)
C(3)–C(2)–C(1)	121.28(18)
C(3)–C(2)–H(2)	121.1(13)
C(1)–C(2)–H(2)	117.6(13)
C(2)–C(3)–C(4)	120.89(18)
C(2)–C(3)–H(3)	121.0(14)
C(4)–C(3)–H(3)	118.1(14)
C(5)–C(4)–C(9)	119.04(18)
C(5)–C(4)–C(3)	121.92(18)
C(9)–C(4)–C(3)	119.02(17)
C(6)–C(5)–C(4)	120.64(19)
C(6)–C(5)–H(5)	119.6(14)
C(4)–C(5)–H(5)	119.7(14)
C(5)–C(6)–C(7)	120.17(19)
C(5)–C(6)–H(6)	117.4(14)
C(7)–C(6)–H(6)	122.4(14)
C(8)–C(7)–C(6)	121.0(2)
C(8)–C(7)–H(7)	120.4(17)
C(6)–C(7)–H(7)	118.6(17)
C(7)–C(8)–C(9)	120.02(19)
C(7)–C(8)–H(8)	122.0(14)
C(9)–C(8)–H(8)	118.0(13)
C(4)–C(9)–C(8)	119.13(17)
C(4)–C(9)–C(10)	118.67(17)
C(8)–C(9)–C(10)	122.20(17)
C(1)–C(10)–C(9)	121.08(17)
C(1)–C(10)–C(11)	121.09(16)
C(9)–C(10)–C(11)	117.82(16)
N(1)–C(11)–C(12)	121.89(17)
N(1)–C(11)–C(10)	117.06(16)

C(12)–C(11)–C(10)	120.99(16)
C(11)–N(1)–C(18)	117.25(16)
C(13)–C(12)–C(17)	119.89(17)
C(13)–C(12)–C(11)	124.06(17)
C(17)–C(12)–C(11)	116.05(16)
C(14)–C(13)–C(12)	119.90(19)
C(14)–C(13)–H(13)	121.3(14)
C(12)–C(13)–H(13)	118.7(14)
C(13)–C(14)–C(15)	120.41(19)
C(13)–C(14)–H(14)	119.3(14)
C(15)–C(14)–H(14)	120.2(14)
C(16)–C(15)–C(14)	120.78(18)
C(16)–C(15)–H(15)	120.4(14)
C(14)–C(15)–H(15)	118.8(14)
C(15)–C(16)–C(17)	120.16(18)
C(15)–C(16)–H(16)	122.1(14)
C(17)–C(16)–H(16)	117.8(14)
N(2)–C(17)–C(16)	119.78(17)
N(2)–C(17)–C(12)	121.39(17)
C(16)–C(17)–C(12)	118.83(17)
C(18)–N(2)–C(17)	116.49(16)
N(2)–C(18)–N(1)	126.91(17)
N(2)–C(18)–C(19)	118.82(17)
N(1)–C(18)–C(19)	114.19(17)
C(22)–C(19)–C(20)	109.55(17)
C(22)–C(19)–C(18)	108.91(15)
C(20)–C(19)–C(18)	111.22(17)
C(22)–C(19)–C(21)	109.36(18)
C(20)–C(19)–C(21)	110.84(18)
C(18)–C(19)–C(21)	106.90(16)
C(19)–C(20)–H(20A)	106.6(15)

C(19)–C(20)–H(20B)	109.9(15)
H(20A)–C(20)–H(20B)	111(2)
C(19)–C(20)–H(20C)	110.1(14)
H(20A)–C(20)–H(20C)	110(2)
H(20B)–C(20)–H(20C)	109(2)
C(19)–C(21)–H(21A)	107.3(12)
C(19)–C(21)–H(21B)	110.0(15)
H(21A)–C(21)–H(21B)	112(2)
C(19)–C(21)–H(21C)	106.2(15)
H(21A)–C(21)–H(21C)	111(2)
H(21B)–C(21)–H(21C)	110(2)
N(3)–C(22)–O	118.34(17)
N(3)–C(22)–C(19)	127.76(18)
O–C(22)–C(19)	113.89(16)
C(22)–O–C(23)	104.85(15)
O–C(23)–C(24)	104.07(16)
O–C(23)–H(23A)	108.6(14)
C(24)–C(23)–H(23A)	112.6(15)
O–C(23)–H(23B)	106.3(13)
C(24)–C(23)–H(23B)	110.9(13)
H(23A)–C(23)–H(23B)	113.7(19)
N(3)–C(24)–C(23)	103.44(16)
N(3)–C(24)–C(25)	110.99(17)
C(23)–C(24)–C(25)	114.67(18)
N(3)–C(24)–H(24)	105.0(13)
C(23)–C(24)–H(24)	111.4(14)
C(25)–C(24)–H(24)	110.6(14)
C(27)–C(25)–C(26)	110.69(19)
C(27)–C(25)–C(24)	111.06(18)
C(26)–C(25)–C(24)	112.36(18)
C(27)–C(25)–H(25)	111.9(17)

C(26)–C(25)–H(25)	105.5(17)
C(24)–C(25)–H(25)	105.1(17)
C(25)–C(26)–H(26A)	110.6(16)
C(25)–C(26)–H(26B)	108.8(17)
H(26A)–C(26)–H(26B)	114(2)
C(25)–C(26)–H(26C)	111.4(19)
H(26A)–C(26)–H(26C)	103(2)
H(26B)–C(26)–H(26C)	109(2)
C(25)–C(27)–H(27A)	108.5(15)
C(25)–C(27)–H(27B)	112.7(16)
H(27A)–C(27)–H(27B)	104(2)
C(25)–C(27)–H(27C)	113.6(16)
H(27A)–C(27)–H(27C)	105(2)
H(27B)–C(27)–H(27C)	112(2)
C(22)–N(3)–C(24)	106.58(17)
C(29)–C(28)–C(33)	118.26(19)
C(29)–C(28)–P	123.78(15)
C(33)–C(28)–P	117.86(15)
C(30)–C(29)–C(28)	121.10(19)
C(30)–C(29)–H(29)	121.5(13)
C(28)–C(29)–H(29)	117.4(13)
C(31)–C(30)–C(29)	119.9(2)
C(31)–C(30)–H(30)	119.8(15)
C(29)–C(30)–H(30)	120.3(15)
C(32)–C(31)–C(30)	119.9(2)
C(32)–C(31)–H(31)	119.8(13)
C(30)–C(31)–H(31)	120.2(13)
C(31)–C(32)–C(33)	120.18(19)
C(31)–C(32)–H(32)	120.1(16)
C(33)–C(32)–H(32)	119.6(16)
C(32)–C(33)–C(28)	120.64(19)

C(32)–C(33)–H(33)	123.2(14)
C(28)–C(33)–H(33)	116.2(14)
C(39)–C(34)–C(35)	118.60(19)
C(39)–C(34)–P	123.98(16)
C(35)–C(34)–P	117.23(16)
C(36)–C(35)–C(34)	121.2(2)
C(36)–C(35)–H(35)	117.5(14)
C(34)–C(35)–H(35)	121.3(14)
C(35)–C(36)–C(37)	119.4(2)
C(35)–C(36)–H(36)	121.7(15)
C(37)–C(36)–H(36)	118.9(15)
C(38)–C(37)–C(36)	120.2(2)
C(38)–C(37)–H(37)	121.2(15)
C(36)–C(37)–H(37)	118.6(16)
C(37)–C(38)–C(39)	120.1(2)
C(37)–C(38)–H(38)	117.7(17)
C(39)–C(38)–H(38)	122.2(17)
C(38)–C(39)–C(34)	120.5(2)
C(38)–C(39)–H(39)	120.2(15)
C(34)–C(39)–H(39)	119.3(15)

Table S6. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Ligand (S_a,S)-(-)-**24**¹⁸

	U11	U22	U33	U23	U13	U12
P	17(1)	20(1)	21(1)	-5(1)	1(1)	-2(1)
C(1)	17(1)	20(1)	17(1)	-2(1)	2(1)	-4(1)
C(2)	15(1)	24(1)	24(1)	0(1)	1(1)	0(1)
C(3)	16(1)	26(1)	19(1)	0(1)	-4(1)	-4(1)
C(4)	18(1)	19(1)	17(1)	4(1)	2(1)	-5(1)
C(5)	23(1)	23(1)	18(1)	-2(1)	-1(1)	-7(1)
C(6)	30(1)	21(1)	23(1)	-6(1)	1(1)	-5(1)
C(7)	25(1)	23(1)	28(1)	-2(1)	3(1)	4(1)
C(8)	21(1)	21(1)	21(1)	1(1)	-2(1)	1(1)
C(9)	18(1)	20(1)	13(1)	3(1)	0(1)	-3(1)
C(10)	17(1)	18(1)	14(1)	3(1)	2(1)	-4(1)
C(11)	16(1)	13(1)	17(1)	-3(1)	-1(1)	1(1)
N(1)	17(1)	18(1)	17(1)	-1(1)	-1(1)	-1(1)
C(12)	16(1)	16(1)	18(1)	-2(1)	1(1)	2(1)
C(13)	20(1)	26(1)	21(1)	5(1)	-2(1)	0(1)
C(14)	25(1)	29(1)	21(1)	6(1)	4(1)	-4(1)
C(15)	18(1)	22(1)	30(1)	-1(1)	5(1)	-4(1)
C(16)	16(1)	20(1)	24(1)	-4(1)	-2(1)	0(1)
C(17)	18(1)	13(1)	18(1)	-4(1)	1(1)	3(1)
N(2)	18(1)	17(1)	17(1)	-1(1)	-2(1)	1(1)
C(18)	22(1)	13(1)	16(1)	-2(1)	-2(1)	2(1)
C(19)	29(1)	20(1)	17(1)	2(1)	-2(1)	-2(1)
C(20)	37(1)	29(1)	23(1)	8(1)	-13(1)	-11(1)
C(21)	49(2)	22(1)	18(1)	-2(1)	7(1)	-7(1)
C(22)	25(1)	20(1)	11(1)	3(1)	-1(1)	0(1)
O	21(1)	19(1)	32(1)	-2(1)	2(1)	-1(1)

¹⁸ The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U11 + \dots + 2 h k a^* b^* U12]$.

C(23)	26(1)	19(1)	34(1)	-1(1)	-5(1)	-3(1)
C(24)	27(1)	20(1)	21(1)	2(1)	2(1)	-5(1)
C(25)	17(1)	26(1)	34(1)	2(1)	2(1)	-3(1)
C(26)	34(1)	37(1)	37(1)	12(1)	-16(1)	-13(1)
C(27)	34(1)	34(1)	33(1)	5(1)	-7(1)	-12(1)
N(3)	29(1)	23(1)	18(1)	-1(1)	4(1)	-4(1)
C(28)	16(1)	22(1)	22(1)	-2(1)	-1(1)	4(1)
C(29)	29(1)	26(1)	18(1)	-5(1)	-1(1)	-2(1)
C(30)	33(1)	23(1)	28(1)	-3(1)	-1(1)	-4(1)
C(31)	27(1)	27(1)	21(1)	-1(1)	2(1)	5(1)
C(32)	29(1)	36(1)	20(1)	-10(1)	0(1)	1(1)
C(33)	23(1)	26(1)	27(1)	-10(1)	0(1)	-4(1)
C(34)	21(1)	15(1)	27(1)	-5(1)	-3(1)	0(1)
C(35)	26(1)	25(1)	28(1)	-4(1)	4(1)	-3(1)
C(36)	43(1)	25(1)	25(1)	1(1)	-4(1)	-8(1)
C(37)	33(1)	23(1)	38(1)	-2(1)	-9(1)	3(1)
C(38)	27(1)	25(1)	39(1)	-6(1)	-1(1)	3(1)
C(39)	22(1)	21(1)	28(1)	-2(1)	0(1)	-3(1)

Table S7. Calculated Hydrogen Coordinates [(x, y, z), $\times 10^4$] and Isotropic Displacement Parameters U(eq) ($\text{\AA}^2 \times 10^3$) for Ligand (*S_a*,*S*)-(-)-**24**

	x	y	z	U(eq)
H(2)	5830(20)	4985(13)	155(12)	19(5)
H(3)	5790(20)	3924(14)	-701(12)	18(5)
H(5)	6790(20)	2732(13)	-1329(13)	22(6)
H(6)	8380(20)	1815(14)	-1444(12)	23(6)
H(7)	10180(30)	1954(18)	-686(15)	43(8)
H(8)	10250(20)	3006(13)	208(12)	18(5)
H(13)	10170(20)	5079(14)	-253(14)	30(6)
H(14)	12070(20)	5753(14)	-556(13)	24(6)
H(15)	13770(20)	5710(14)	265(12)	21(6)
H(16)	13690(20)	4977(15)	1393(14)	36(7)
H(20A)	11610(20)	3003(16)	3661(14)	34(6)
H(20B)	12280(20)	3730(16)	3232(13)	30(6)
H(20C)	12270(30)	2815(17)	2849(14)	40(7)
H(21A)	9640(20)	3801(14)	3816(13)	22(5)
H(21B)	10270(30)	4604(17)	3368(14)	39(7)
H(21C)	8960(30)	4179(16)	3063(14)	37(7)
H(23A)	9480(20)	1082(14)	1991(13)	21(5)
H(23B)	9950(20)	971(15)	2854(14)	30(6)
H(24)	7990(20)	1406(14)	3161(13)	24(6)
H(25)	6650(30)	2056(17)	2314(15)	42(7)
H(26A)	7990(30)	2714(17)	1543(14)	35(7)
H(26B)	7000(30)	2183(18)	1062(16)	51(8)
H(26C)	8400(30)	1928(19)	1216(17)	54(9)
H(27A)	7500(30)	548(17)	1720(15)	41(7)
H(27B)	6530(30)	558(17)	2372(15)	43(7)
H(27C)	6140(30)	871(16)	1544(15)	42(7)
H(29)	6038(19)	4069(13)	1499(12)	15(5)

H(30)	5010(20)	3460(16)	2522(14)	30(6)
H(31)	5270(20)	4047(13)	3696(12)	15(5)
H(32)	6480(30)	5245(15)	3826(15)	37(7)
H(33)	7410(20)	5843(15)	2774(12)	25(6)
H(35)	7480(20)	6428(14)	−54(13)	25(6)
H(36)	6260(20)	7485(14)	−499(13)	22(6)
H(37)	4590(20)	7974(16)	149(13)	30(6)
H(38)	4090(30)	7442(17)	1294(16)	44(7)
H(39)	5340(20)	6353(15)	1796(14)	27(6)

Table S8. Torsion Angles [°] for Ligand (*S_aS*)-(-)-**24**

C(28)–P–C(1)–C(10)	–95.50(15)
C(34)–P–C(1)–C(10)	157.65(15)
C(28)–P–C(1)–C(2)	83.09(17)
C(34)–P–C(1)–C(2)	–23.77(17)
C(10)–C(1)–C(2)–C(3)	0.5(3)
P–C(1)–C(2)–C(3)	–178.08(15)
C(1)–C(2)–C(3)–C(4)	–0.5(3)
C(2)–C(3)–C(4)–C(5)	–178.63(18)
C(2)–C(3)–C(4)–C(9)	–0.3(3)
C(9)–C(4)–C(5)–C(6)	0.5(3)
C(3)–C(4)–C(5)–C(6)	178.88(18)
C(4)–C(5)–C(6)–C(7)	0.1(3)
C(5)–C(6)–C(7)–C(8)	–0.1(3)
C(6)–C(7)–C(8)–C(9)	–0.4(3)
C(5)–C(4)–C(9)–C(8)	–1.0(3)
C(3)–C(4)–C(9)–C(8)	–179.44(17)
C(5)–C(4)–C(9)–C(10)	179.41(17)
C(3)–C(4)–C(9)–C(10)	1.0(3)
C(7)–C(8)–C(9)–C(4)	1.0(3)
C(7)–C(8)–C(9)–C(10)	–179.46(18)
C(2)–C(1)–C(10)–C(9)	0.3(3)
P–C(1)–C(10)–C(9)	178.92(14)
C(2)–C(1)–C(10)–C(11)	–178.72(16)
P–C(1)–C(10)–C(11)	–0.1(2)
C(4)–C(9)–C(10)–C(1)	–1.0(3)
C(8)–C(9)–C(10)–C(1)	179.44(18)
C(4)–C(9)–C(10)–C(11)	178.02(16)
C(8)–C(9)–C(10)–C(11)	–1.5(3)
C(1)–C(10)–C(11)–N(1)	85.9(2)

C(9)–C(10)–C(11)–N(1)	–93.1(2)
C(1)–C(10)–C(11)–C(12)	–96.9(2)
C(9)–C(10)–C(11)–C(12)	84.1(2)
C(12)–C(11)–N(1)–C(18)	–1.1(3)
C(10)–C(11)–N(1)–C(18)	176.03(16)
N(1)–C(11)–C(12)–C(13)	–178.46(18)
C(10)–C(11)–C(12)–C(13)	4.5(3)
N(1)–C(11)–C(12)–C(17)	1.6(3)
C(10)–C(11)–C(12)–C(17)	–175.47(16)
C(17)–C(12)–C(13)–C(14)	–0.1(3)
C(11)–C(12)–C(13)–C(14)	179.98(19)
C(12)–C(13)–C(14)–C(15)	0.7(3)
C(13)–C(14)–C(15)–C(16)	0.0(3)
C(14)–C(15)–C(16)–C(17)	–1.3(3)
C(15)–C(16)–C(17)–N(2)	–178.49(17)
C(15)–C(16)–C(17)–C(12)	1.9(3)
C(13)–C(12)–C(17)–N(2)	179.20(17)
C(11)–C(12)–C(17)–N(2)	–0.8(3)
C(13)–C(12)–C(17)–C(16)	–1.2(3)
C(11)–C(12)–C(17)–C(16)	178.74(16)
C(16)–C(17)–N(2)–C(18)	–179.86(17)
C(12)–C(17)–N(2)–C(18)	–0.3(2)
C(17)–N(2)–C(18)–N(1)	0.8(3)
C(17)–N(2)–C(18)–C(19)	–175.88(16)
C(11)–N(1)–C(18)–N(2)	–0.1(3)
C(11)–N(1)–C(18)–C(19)	176.71(16)
N(2)–C(18)–C(19)–C(22)	–142.29(18)
N(1)–C(18)–C(19)–C(22)	40.6(2)
N(2)–C(18)–C(19)–C(20)	–21.5(2)
N(1)–C(18)–C(19)–C(20)	161.41(17)
N(2)–C(18)–C(19)–C(21)	99.7(2)

N(1)–C(18)–C(19)–C(21)	–77.5(2)
C(20)–C(19)–C(22)–N(3)	126.1(2)
C(18)–C(19)–C(22)–N(3)	–112.1(2)
C(21)–C(19)–C(22)–N(3)	4.4(3)
C(20)–C(19)–C(22)–O	–52.5(2)
C(18)–C(19)–C(22)–O	69.4(2)
C(21)–C(19)–C(22)–O	–174.14(17)
N(3)–C(22)–O–C(23)	–7.5(2)
C(19)–C(22)–O–C(23)	171.22(16)
C(22)–O–C(23)–C(24)	14.4(2)
O–C(23)–C(24)–N(3)	–16.2(2)
O–C(23)–C(24)–C(25)	104.80(19)
N(3)–C(24)–C(25)–C(27)	–172.18(18)
C(23)–C(24)–C(25)–C(27)	71.1(2)
N(3)–C(24)–C(25)–C(26)	63.2(2)
C(23)–C(24)–C(25)–C(26)	–53.5(2)
O–C(22)–N(3)–C(24)	–3.5(2)
C(19)–C(22)–N(3)–C(24)	177.98(18)
C(23)–C(24)–N(3)–C(22)	12.4(2)
C(25)–C(24)–N(3)–C(22)	–111.10(19)
C(34)–P–C(28)–C(29)	93.78(18)
C(1)–P–C(28)–C(29)	–11.42(19)
C(34)–P–C(28)–C(33)	–89.92(17)
C(1)–P–C(28)–C(33)	164.89(16)
C(33)–C(28)–C(29)–C(30)	0.6(3)
P–C(28)–C(29)–C(30)	176.94(17)
C(28)–C(29)–C(30)–C(31)	–0.3(3)
C(29)–C(30)–C(31)–C(32)	0.2(3)
C(30)–C(31)–C(32)–C(33)	–0.3(3)
C(31)–C(32)–C(33)–C(28)	0.7(3)
C(29)–C(28)–C(33)–C(32)	–0.8(3)

P–C(28)–C(33)–C(32)	–177.33(16)
C(28)–P–C(34)–C(39)	19.46(19)
C(1)–P–C(34)–C(39)	124.70(17)
C(28)–P–C(34)–C(35)	–165.66(15)
C(1)–P–C(34)–C(35)	–60.43(17)
C(39)–C(34)–C(35)–C(36)	0.1(3)
P–C(34)–C(35)–C(36)	–175.10(17)
C(34)–C(35)–C(36)–C(37)	–0.3(3)
C(35)–C(36)–C(37)–C(38)	0.4(3)
C(36)–C(37)–C(38)–C(39)	–0.2(3)
C(37)–C(38)–C(39)–C(34)	–0.1(3)
C(35)–C(34)–C(39)–C(38)	0.2(3)
P–C(34)–C(39)–C(38)	174.96(16)

2.2. Ligand (*S_a*,*S*)-(–)-(25)

Table S9. Crystal Data and Structure Refinement for Ligand (*S_a*,*S*)-(–)-(25)

Empirical formula	C ₄₀ H ₃₈ N ₃ OP	
Formula weight	607.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	<i>a</i> = 10.9951(15) Å	$\alpha = 90^\circ$
	<i>b</i> = 16.296(2) Å	$\beta = 90^\circ$
	<i>c</i> = 18.095(3) Å	$\gamma = 90^\circ$
Volume	3242.1(8) Å ³	
<i>Z</i>	4	
Density (calculated)	1.245 Mg/m ³	
Absorption coefficient	0.122 mm ⁻¹	
<i>F</i> (000)	1288	
Crystal size	0.80 × 0.60 × 0.20 mm	
Theta range for data collection	2.17 to 26.00°	
Index ranges	–13 ≤ <i>h</i> ≤ 13, –20 ≤ <i>k</i> ≤ 20, –22 ≤ <i>l</i> ≤ 22	
Reflections collected	25065	
Independent reflections	6375 [<i>R</i> (int) = 0.0264]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9761 and 0.7361	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	6375 / 0 / 558	
Goodness-of-fit on <i>F</i> ²	1.020	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0752	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0331, <i>wR</i> ₂ = 0.0767	
Absolute structure parameter	–0.02(6)	

Largest diff. peak and hole

0.316 and $-0.142 \text{ e}/\text{\AA}^3$

Figure S2. ORTEP drawing (50% probability thermal ellipsoids) of the molecular structure of ligand (*S_a*,*S*)-(-)-**25**.

Table S10. Atomic Coordinates $[(x, y, z), \times 10^4]$ and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Ligand (S_a,S)-(-)-**25**

	x	y	z	U(eq) ¹⁹
P	7021(1)	5517(1)	8750(1)	21(1)
C(1)	7100(1)	4698(1)	9444(1)	20(1)
C(2)	8113(1)	4608(1)	9923(1)	25(1)
C(3)	8171(2)	3972(1)	10413(1)	24(1)
C(4)	7217(1)	3394(1)	10466(1)	21(1)
C(5)	7253(2)	2739(1)	10980(1)	25(1)
C(6)	6305(2)	2202(1)	11035(1)	28(1)
C(7)	5290(2)	2285(1)	10577(1)	27(1)
C(8)	5221(1)	2909(1)	10070(1)	23(1)
C(9)	6183(1)	3482(1)	10004(1)	19(1)
C(10)	6153(1)	4145(1)	9486(1)	18(1)
C(11)	5086(1)	4202(1)	8979(1)	17(1)
N(1)	5175(1)	3818(1)	8345(1)	19(1)
C(12)	4003(1)	4623(1)	9190(1)	18(1)
C(13)	3872(2)	5068(1)	9856(1)	24(1)
C(14)	2797(2)	5455(1)	10006(1)	28(1)
C(15)	1820(2)	5406(1)	9509(1)	28(1)
C(16)	1920(1)	4975(1)	8865(1)	24(1)
C(17)	3028(1)	4580(1)	8689(1)	19(1)
N(2)	3125(1)	4162(1)	8034(1)	20(1)
C(18)	4174(1)	3820(1)	7898(1)	20(1)
C(19)	4370(2)	3395(1)	7153(1)	25(1)
C(20)	3158(2)	3216(1)	6768(1)	35(1)
C(21)	5179(2)	3957(1)	6682(1)	33(1)
C(22)	5029(2)	2592(1)	7297(1)	21(1)
O	4382(1)	2057(1)	7728(1)	25(1)

¹⁹ U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(23)	5125(2)	1322(1)	7765(1)	24(1)
C(24)	6325(1)	1566(1)	7395(1)	21(1)
C(25)	7433(1)	1606(1)	7915(1)	24(1)
C(26)	7666(2)	755(1)	8243(1)	29(1)
C(27)	7217(2)	2221(1)	8538(1)	29(1)
C(28)	8536(2)	1867(1)	7462(1)	36(1)
N(3)	6061(1)	2380(1)	7068(1)	24(1)
C(29)	8054(1)	5120(1)	8038(1)	21(1)
C(30)	8664(2)	4373(1)	8092(1)	26(1)
C(31)	9395(2)	4092(1)	7524(1)	29(1)
C(32)	9531(2)	4551(1)	6890(1)	31(1)
C(33)	8928(2)	5293(1)	6826(1)	35(1)
C(34)	8184(2)	5571(1)	7387(1)	29(1)
C(35)	7927(1)	6312(1)	9212(1)	22(1)
C(36)	8984(2)	6648(1)	8928(1)	27(1)
C(37)	9589(2)	7272(1)	9309(1)	33(1)
C(38)	9149(2)	7552(1)	9973(1)	33(1)
C(39)	8087(2)	7227(1)	10257(1)	32(1)
C(40)	7479(2)	6618(1)	9881(1)	27(1)

Table S11. Bond Lengths [Å] and Angles [°] for Ligand (*S_a*,*S*)-(-)-**25**

P–C(29)	1.8342(16)
P–C(35)	1.8353(16)
P–C(1)	1.8353(15)
C(1)–C(10)	1.379(2)
C(1)–C(2)	1.418(2)
C(2)–C(3)	1.367(2)
C(2)–H(2)	0.961(18)
C(3)–C(4)	1.413(2)
C(3)–H(3)	0.942(19)
C(4)–C(5)	1.417(2)
C(4)–C(9)	1.417(2)
C(5)–C(6)	1.365(3)
C(5)–H(5)	0.964(19)
C(6)–C(7)	1.396(2)
C(6)–H(6)	0.958(18)
C(7)–C(8)	1.372(2)
C(7)–H(7)	0.957(19)
C(8)–C(9)	1.416(2)
C(8)–H(8)	0.987(18)
C(9)–C(10)	1.431(2)
C(10)–C(11)	1.492(2)
C(11)–N(1)	1.3117(18)
C(11)–C(12)	1.426(2)
N(1)–C(18)	1.3648(19)
C(12)–C(17)	1.406(2)
C(12)–C(13)	1.414(2)
C(13)–C(14)	1.366(2)
C(13)–H(13)	0.94(2)
C(14)–C(15)	1.404(2)

C(14)–H(14)	1.00(2)
C(15)–C(16)	1.366(2)
C(15)–H(15)	0.965(19)
C(16)–C(17)	1.413(2)
C(16)–H(16)	0.957(19)
C(17)–N(2)	1.3722(19)
N(2)–C(18)	1.305(2)
C(18)–C(19)	1.530(2)
C(19)–C(22)	1.518(2)
C(19)–C(20)	1.532(2)
C(19)–C(21)	1.535(2)
C(20)–H(20A)	0.95(2)
C(20)–H(20B)	0.96(2)
C(20)–H(20C)	1.03(2)
C(21)–H(21A)	0.98(2)
C(21)–H(21B)	0.95(2)
C(21)–H(21C)	1.00(2)
C(22)–N(3)	1.256(2)
C(22)–O	1.3697(19)
O–C(23)	1.4518(18)
C(23)–C(24)	1.532(2)
C(23)–H(23A)	0.964(17)
C(23)–H(23B)	1.017(18)
C(24)–N(3)	1.4805(19)
C(24)–C(25)	1.542(2)
C(24)–H(24)	0.936(16)
C(25)–C(28)	1.525(2)
C(25)–C(27)	1.527(2)
C(25)–C(26)	1.531(2)
C(26)–H(26A)	0.96(2)
C(26)–H(26B)	0.982(19)

C(26)–H(26C)	1.009(19)
C(27)–H(27A)	0.96(2)
C(27)–H(27B)	0.980(19)
C(27)–H(27C)	1.07(2)
C(28)–H(28A)	0.99(2)
C(28)–H(28B)	0.95(2)
C(28)–H(28C)	1.01(2)
C(29)–C(30)	1.395(2)
C(29)–C(34)	1.396(2)
C(30)–C(31)	1.382(2)
C(30)–H(30)	0.922(17)
C(31)–C(32)	1.378(2)
C(31)–H(31)	0.96(2)
C(32)–C(33)	1.383(3)
C(32)–H(32)	0.95(2)
C(33)–C(34)	1.380(3)
C(33)–H(33)	0.96(2)
C(34)–H(34)	0.957(18)
C(35)–C(36)	1.382(2)
C(35)–C(40)	1.399(2)
C(36)–C(37)	1.398(2)
C(36)–H(36)	0.964(18)
C(37)–C(38)	1.373(3)
C(37)–H(37)	0.94(2)
C(38)–C(39)	1.382(3)
C(38)–H(38)	0.91(2)
C(39)–C(40)	1.376(3)
C(39)–H(39)	1.02(2)
C(40)–H(40)	0.957(19)
C(29)–P–C(35)	103.41(7)

C(29)–P–C(1)	101.24(7)
C(35)–P–C(1)	100.10(7)
C(10)–C(1)–C(2)	119.48(13)
C(10)–C(1)–P	118.47(11)
C(2)–C(1)–P	122.03(11)
C(3)–C(2)–C(1)	120.77(14)
C(3)–C(2)–H(2)	120.6(10)
C(1)–C(2)–H(2)	118.6(10)
C(2)–C(3)–C(4)	120.95(14)
C(2)–C(3)–H(3)	121.4(11)
C(4)–C(3)–H(3)	117.7(11)
C(3)–C(4)–C(5)	121.66(14)
C(3)–C(4)–C(9)	119.24(13)
C(5)–C(4)–C(9)	119.08(14)
C(6)–C(5)–C(4)	120.62(15)
C(6)–C(5)–H(5)	120.5(11)
C(4)–C(5)–H(5)	118.8(11)
C(5)–C(6)–C(7)	120.32(15)
C(5)–C(6)–H(6)	118.6(11)
C(7)–C(6)–H(6)	121.1(11)
C(8)–C(7)–C(6)	120.86(15)
C(8)–C(7)–H(7)	120.5(11)
C(6)–C(7)–H(7)	118.6(11)
C(7)–C(8)–C(9)	120.28(15)
C(7)–C(8)–H(8)	121.2(11)
C(9)–C(8)–H(8)	118.5(11)
C(8)–C(9)–C(4)	118.84(13)
C(8)–C(9)–C(10)	122.39(13)
C(4)–C(9)–C(10)	118.77(13)
C(1)–C(10)–C(9)	120.76(13)
C(1)–C(10)–C(11)	121.29(13)

C(9)–C(10)–C(11)	117.92(13)
N(1)–C(11)–C(12)	121.75(13)
N(1)–C(11)–C(10)	116.74(13)
C(12)–C(11)–C(10)	121.45(12)
C(11)–N(1)–C(18)	117.20(13)
C(17)–C(12)–C(13)	119.77(14)
C(17)–C(12)–C(11)	116.14(13)
C(13)–C(12)–C(11)	124.09(14)
C(14)–C(13)–C(12)	119.64(15)
C(14)–C(13)–H(13)	122.1(11)
C(12)–C(13)–H(13)	118.2(11)
C(13)–C(14)–C(15)	120.59(15)
C(13)–C(14)–H(14)	120.8(11)
C(15)–C(14)–H(14)	118.6(11)
C(16)–C(15)–C(14)	120.93(15)
C(16)–C(15)–H(15)	119.2(11)
C(14)–C(15)–H(15)	119.8(11)
C(15)–C(16)–C(17)	119.71(15)
C(15)–C(16)–H(16)	121.0(11)
C(17)–C(16)–H(16)	119.3(11)
N(2)–C(17)–C(12)	121.48(13)
N(2)–C(17)–C(16)	119.16(14)
C(12)–C(17)–C(16)	119.35(13)
C(18)–N(2)–C(17)	116.35(12)
N(2)–C(18)–N(1)	127.04(13)
N(2)–C(18)–C(19)	118.91(13)
N(1)–C(18)–C(19)	114.01(13)
C(22)–C(19)–C(18)	107.85(12)
C(22)–C(19)–C(20)	109.24(13)
C(18)–C(19)–C(20)	111.40(14)
C(22)–C(19)–C(21)	109.38(14)

C(18)–C(19)–C(21)	107.49(13)
C(20)–C(19)–C(21)	111.40(15)
C(19)–C(20)–H(20A)	106.4(13)
C(19)–C(20)–H(20B)	109.2(12)
H(20A)–C(20)–H(20B)	110.7(18)
C(19)–C(20)–H(20C)	112.5(11)
H(20A)–C(20)–H(20C)	114.0(17)
H(20B)–C(20)–H(20C)	104.0(16)
C(19)–C(21)–H(21A)	105.8(12)
C(19)–C(21)–H(21B)	110.4(13)
H(21A)–C(21)–H(21B)	109.1(17)
C(19)–C(21)–H(21C)	109.7(11)
H(21A)–C(21)–H(21C)	112.7(16)
H(21B)–C(21)–H(21C)	109.1(17)
N(3)–C(22)–O	118.74(13)
N(3)–C(22)–C(19)	127.79(14)
O–C(22)–C(19)	113.46(13)
C(22)–O–C(23)	105.07(12)
O–C(23)–C(24)	104.47(12)
O–C(23)–H(23A)	106.3(10)
C(24)–C(23)–H(23A)	114.7(10)
O–C(23)–H(23B)	107.1(10)
C(24)–C(23)–H(23B)	114.7(10)
H(23A)–C(23)–H(23B)	108.9(14)
N(3)–C(24)–C(23)	103.82(12)
N(3)–C(24)–C(25)	111.13(12)
C(23)–C(24)–C(25)	115.10(13)
N(3)–C(24)–H(24)	104.3(9)
C(23)–C(24)–H(24)	111.0(10)
C(25)–C(24)–H(24)	110.8(9)
C(28)–C(25)–C(27)	109.76(14)

C(28)–C(25)–C(26)	109.21(14)
C(27)–C(25)–C(26)	109.55(14)
C(28)–C(25)–C(24)	108.20(14)
C(27)–C(25)–C(24)	110.82(13)
C(26)–C(25)–C(24)	109.27(13)
C(25)–C(26)–H(26A)	111.4(12)
C(25)–C(26)–H(26B)	110.9(11)
H(26A)–C(26)–H(26B)	104.8(15)
C(25)–C(26)–H(26C)	112.6(10)
H(26A)–C(26)–H(26C)	108.0(16)
H(26B)–C(26)–H(26C)	108.8(15)
C(25)–C(27)–H(27A)	109.6(11)
C(25)–C(27)–H(27B)	108.2(11)
H(27A)–C(27)–H(27B)	109.6(16)
C(25)–C(27)–H(27C)	108.9(10)
H(27A)–C(27)–H(27C)	109.7(14)
H(27B)–C(27)–H(27C)	110.7(15)
C(25)–C(28)–H(28A)	110.2(13)
C(25)–C(28)–H(28B)	108.7(13)
H(28A)–C(28)–H(28B)	108.9(18)
C(25)–C(28)–H(28C)	111.2(12)
H(28A)–C(28)–H(28C)	109.5(18)
H(28B)–C(28)–H(28C)	108.2(17)
C(22)–N(3)–C(24)	107.01(13)
C(30)–C(29)–C(34)	117.96(15)
C(30)–C(29)–P	123.86(12)
C(34)–C(29)–P	118.09(12)
C(31)–C(30)–C(29)	121.12(15)
C(31)–C(30)–H(30)	120.9(11)
C(29)–C(30)–H(30)	117.9(11)
C(32)–C(31)–C(30)	120.20(16)

C(32)–C(31)–H(31)	119.7(11)
C(30)–C(31)–H(31)	120.1(11)
C(31)–C(32)–C(33)	119.43(17)
C(31)–C(32)–H(32)	121.6(13)
C(33)–C(32)–H(32)	118.9(13)
C(34)–C(33)–C(32)	120.64(16)
C(34)–C(33)–H(33)	120.4(12)
C(32)–C(33)–H(33)	118.9(12)
C(33)–C(34)–C(29)	120.62(16)
C(33)–C(34)–H(34)	120.5(10)
C(29)–C(34)–H(34)	118.9(10)
C(36)–C(35)–C(40)	118.37(15)
C(36)–C(35)–P	124.52(13)
C(40)–C(35)–P	117.04(12)
C(35)–C(36)–C(37)	120.37(16)
C(35)–C(36)–H(36)	118.9(11)
C(37)–C(36)–H(36)	120.7(11)
C(38)–C(37)–C(36)	120.37(17)
C(38)–C(37)–H(37)	123.2(14)
C(36)–C(37)–H(37)	116.4(14)
C(37)–C(38)–C(39)	119.74(17)
C(37)–C(38)–H(38)	119.5(13)
C(39)–C(38)–H(38)	120.8(13)
C(40)–C(39)–C(38)	120.15(17)
C(40)–C(39)–H(39)	119.2(11)
C(38)–C(39)–H(39)	120.6(11)
C(39)–C(40)–C(35)	120.98(16)
C(39)–C(40)–H(40)	120.4(11)
C(35)–C(40)–H(40)	118.5(11)

Table S12. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Ligand (S_a,S)-(-)-**25**²⁰

	U11	U22	U33	U23	U13	U12
P	18(1)	21(1)	23(1)	5(1)	-3(1)	-2(1)
C(1)	22(1)	20(1)	18(1)	3(1)	0(1)	0(1)
C(2)	21(1)	25(1)	28(1)	4(1)	-4(1)	-3(1)
C(3)	22(1)	26(1)	22(1)	2(1)	-8(1)	1(1)
C(4)	25(1)	21(1)	18(1)	-2(1)	2(1)	5(1)
C(5)	30(1)	23(1)	21(1)	2(1)	-1(1)	9(1)
C(6)	37(1)	22(1)	25(1)	7(1)	6(1)	7(1)
C(7)	29(1)	20(1)	32(1)	3(1)	7(1)	-2(1)
C(8)	24(1)	22(1)	23(1)	0(1)	2(1)	2(1)
C(9)	22(1)	18(1)	17(1)	-2(1)	2(1)	3(1)
C(10)	19(1)	19(1)	15(1)	-2(1)	2(1)	3(1)
C(11)	20(1)	14(1)	17(1)	2(1)	1(1)	-3(1)
N(1)	21(1)	17(1)	18(1)	1(1)	0(1)	1(1)
C(12)	20(1)	15(1)	19(1)	2(1)	2(1)	-1(1)
C(13)	28(1)	24(1)	21(1)	-1(1)	-1(1)	0(1)
C(14)	34(1)	26(1)	25(1)	-4(1)	7(1)	4(1)
C(15)	24(1)	26(1)	33(1)	3(1)	8(1)	6(1)
C(16)	20(1)	22(1)	30(1)	5(1)	-1(1)	2(1)
C(17)	23(1)	14(1)	21(1)	4(1)	2(1)	-2(1)
N(2)	23(1)	16(1)	21(1)	1(1)	-3(1)	0(1)
C(18)	26(1)	13(1)	20(1)	2(1)	-2(1)	-1(1)
C(19)	36(1)	20(1)	18(1)	-2(1)	-5(1)	4(1)
C(20)	49(1)	28(1)	28(1)	-9(1)	-18(1)	12(1)
C(21)	57(1)	21(1)	21(1)	1(1)	7(1)	8(1)
C(22)	31(1)	19(1)	14(1)	-3(1)	-3(1)	0(1)
O	24(1)	19(1)	32(1)	2(1)	2(1)	2(1)

²⁰ The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$.

C(23)	24(1)	19(1)	29(1)	1(1)	−3(1)	1(1)
C(24)	27(1)	17(1)	20(1)	−3(1)	2(1)	1(1)
C(25)	22(1)	20(1)	30(1)	−3(1)	2(1)	2(1)
C(26)	28(1)	27(1)	34(1)	−1(1)	−3(1)	5(1)
C(27)	28(1)	28(1)	32(1)	−8(1)	−9(1)	5(1)
C(28)	27(1)	30(1)	52(1)	−4(1)	9(1)	−2(1)
N(3)	34(1)	19(1)	18(1)	−1(1)	1(1)	2(1)
C(29)	19(1)	23(1)	22(1)	2(1)	−6(1)	−6(1)
C(30)	30(1)	23(1)	24(1)	4(1)	−3(1)	−4(1)
C(31)	31(1)	24(1)	33(1)	−1(1)	−5(1)	−1(1)
C(32)	29(1)	38(1)	26(1)	−1(1)	1(1)	−2(1)
C(33)	34(1)	43(1)	27(1)	13(1)	1(1)	−1(1)
C(34)	27(1)	30(1)	30(1)	10(1)	−2(1)	1(1)
C(35)	21(1)	17(1)	27(1)	5(1)	−5(1)	2(1)
C(36)	23(1)	25(1)	32(1)	−1(1)	0(1)	−1(1)
C(37)	25(1)	27(1)	46(1)	−1(1)	1(1)	−4(1)
C(38)	34(1)	22(1)	41(1)	−5(1)	−11(1)	1(1)
C(39)	35(1)	32(1)	29(1)	−3(1)	−5(1)	6(1)
C(40)	26(1)	28(1)	28(1)	2(1)	0(1)	0(1)

Table S13. Calculated Hydrogen Coordinates [(x, y, z), $\times 10^4$] and Isotropic Displacement Parameters U(eq) ($\text{\AA}^2 \times 10^3$) for Ligand (S_a,S)-(-)-**25**

	x	y	z	U(eq)
H(2)	8766(16)	4998(11)	9889(9)	21(4)
H(3)	8842(17)	3905(11)	10731(10)	28(5)
H(5)	7969(17)	2670(11)	11282(10)	25(4)
H(6)	6350(16)	1772(11)	11395(9)	23(4)
H(7)	4643(17)	1895(12)	10622(10)	27(5)
H(8)	4509(17)	2969(11)	9742(10)	24(4)
H(13)	4516(17)	5055(11)	10198(10)	29(5)
H(14)	2685(17)	5767(12)	10476(11)	37(5)
H(15)	1076(17)	5700(12)	9612(10)	33(5)
H(16)	1252(17)	4937(11)	8528(10)	26(5)
H(20A)	3354(19)	2986(13)	6303(12)	42(6)
H(20B)	2715(19)	3721(14)	6708(11)	39(5)
H(20C)	2592(18)	2858(12)	7083(10)	31(5)
H(21A)	4709(18)	4464(13)	6607(10)	36(5)
H(21B)	5335(19)	3712(13)	6217(12)	44(6)
H(21C)	5966(18)	4054(11)	6941(11)	30(5)
H(23A)	5193(14)	1185(10)	8282(9)	16(4)
H(23B)	4659(16)	869(11)	7503(10)	24(4)
H(24)	6488(14)	1230(10)	6987(9)	13(4)
H(26A)	7001(19)	583(13)	8555(11)	36(5)
H(26B)	8379(17)	761(11)	8569(10)	26(5)
H(26C)	7788(16)	322(11)	7851(10)	29(5)
H(27A)	7920(18)	2243(11)	8852(10)	29(5)
H(27B)	7077(18)	2762(12)	8317(10)	29(5)
H(27C)	6443(18)	2030(12)	8851(10)	31(5)
H(28A)	9270(20)	1885(13)	7776(12)	45(6)
H(28B)	8660(20)	1479(14)	7079(12)	44(6)

H(28C)	8405(19)	2420(14)	7228(12)	42(6)
H(30)	8594(16)	4082(10)	8527(10)	20(4)
H(31)	9821(17)	3578(12)	7573(10)	30(5)
H(32)	10011(18)	4365(13)	6489(11)	37(5)
H(33)	9043(18)	5616(13)	6387(11)	38(5)
H(34)	7747(16)	6076(11)	7335(9)	23(4)
H(36)	9301(17)	6438(11)	8469(10)	26(5)
H(37)	10280(20)	7489(14)	9080(13)	54(7)
H(38)	9552(19)	7956(13)	10215(11)	41(6)
H(39)	7771(18)	7409(12)	10762(11)	33(5)
H(40)	6758(17)	6379(11)	10083(10)	27(5)

Table S14. Torsion Angles [°] for Ligand (*S_aS*)-(-)-**25**

C(29)–P–C(1)–C(10)	–102.22(12)
C(35)–P–C(1)–C(10)	151.78(12)
C(29)–P–C(1)–C(2)	76.26(14)
C(35)–P–C(1)–C(2)	–29.73(14)
C(10)–C(1)–C(2)–C(3)	1.3(2)
P–C(1)–C(2)–C(3)	–177.17(12)
C(1)–C(2)–C(3)–C(4)	–1.0(2)
C(2)–C(3)–C(4)–C(5)	–178.87(15)
C(2)–C(3)–C(4)–C(9)	–0.4(2)
C(3)–C(4)–C(5)–C(6)	178.15(15)
C(9)–C(4)–C(5)–C(6)	–0.4(2)
C(4)–C(5)–C(6)–C(7)	0.8(2)
C(5)–C(6)–C(7)–C(8)	–0.6(2)
C(6)–C(7)–C(8)–C(9)	–0.1(2)
C(7)–C(8)–C(9)–C(4)	0.5(2)
C(7)–C(8)–C(9)–C(10)	–179.80(14)
C(3)–C(4)–C(9)–C(8)	–178.82(14)
C(5)–C(4)–C(9)–C(8)	–0.3(2)
C(3)–C(4)–C(9)–C(10)	1.5(2)
C(5)–C(4)–C(9)–C(10)	–179.99(13)
C(2)–C(1)–C(10)–C(9)	–0.2(2)
P–C(1)–C(10)–C(9)	178.36(11)
C(2)–C(1)–C(10)–C(11)	–178.25(13)
P–C(1)–C(10)–C(11)	0.27(19)
C(8)–C(9)–C(10)–C(1)	179.10(14)
C(4)–C(9)–C(10)–C(1)	–1.2(2)
C(8)–C(9)–C(10)–C(11)	–2.8(2)
C(4)–C(9)–C(10)–C(11)	176.95(12)
C(1)–C(10)–C(11)–N(1)	88.11(17)

C(9)–C(10)–C(11)–N(1)	–90.03(16)
C(1)–C(10)–C(11)–C(12)	–94.72(17)
C(9)–C(10)–C(11)–C(12)	87.14(17)
C(12)–C(11)–N(1)–C(18)	–1.40(19)
C(10)–C(11)–N(1)–C(18)	175.76(12)
N(1)–C(11)–C(12)–C(17)	1.8(2)
C(10)–C(11)–C(12)–C(17)	–175.21(12)
N(1)–C(11)–C(12)–C(13)	–177.96(14)
C(10)–C(11)–C(12)–C(13)	5.0(2)
C(17)–C(12)–C(13)–C(14)	–0.2(2)
C(11)–C(12)–C(13)–C(14)	179.60(15)
C(12)–C(13)–C(14)–C(15)	0.7(2)
C(13)–C(14)–C(15)–C(16)	–0.2(2)
C(14)–C(15)–C(16)–C(17)	–0.9(2)
C(13)–C(12)–C(17)–N(2)	179.32(13)
C(11)–C(12)–C(17)–N(2)	–0.5(2)
C(13)–C(12)–C(17)–C(16)	–0.9(2)
C(11)–C(12)–C(17)–C(16)	179.32(13)
C(15)–C(16)–C(17)–N(2)	–178.77(13)
C(15)–C(16)–C(17)–C(12)	1.4(2)
C(12)–C(17)–N(2)–C(18)	–1.18(19)
C(16)–C(17)–N(2)–C(18)	179.03(13)
C(17)–N(2)–C(18)–N(1)	1.8(2)
C(17)–N(2)–C(18)–C(19)	–175.83(12)
C(11)–N(1)–C(18)–N(2)	–0.5(2)
C(11)–N(1)–C(18)–C(19)	177.21(13)
N(2)–C(18)–C(19)–C(22)	–137.00(14)
N(1)–C(18)–C(19)–C(22)	45.11(18)
N(2)–C(18)–C(19)–C(20)	–17.1(2)
N(1)–C(18)–C(19)–C(20)	164.97(14)
N(2)–C(18)–C(19)–C(21)	105.17(17)

N(1)–C(18)–C(19)–C(21)	–72.73(16)
C(18)–C(19)–C(22)–N(3)	–118.08(17)
C(20)–C(19)–C(22)–N(3)	120.70(18)
C(21)–C(19)–C(22)–N(3)	–1.5(2)
C(18)–C(19)–C(22)–O	62.16(16)
C(20)–C(19)–C(22)–O	–59.06(17)
C(21)–C(19)–C(22)–O	178.77(13)
N(3)–C(22)–O–C(23)	–2.88(18)
C(19)–C(22)–O–C(23)	176.91(12)
C(22)–O–C(23)–C(24)	7.58(15)
O–C(23)–C(24)–N(3)	–9.38(15)
O–C(23)–C(24)–C(25)	112.30(13)
N(3)–C(24)–C(25)–C(28)	–61.59(16)
C(23)–C(24)–C(25)–C(28)	–179.22(13)
N(3)–C(24)–C(25)–C(27)	58.80(17)
C(23)–C(24)–C(25)–C(27)	–58.84(17)
N(3)–C(24)–C(25)–C(26)	179.61(13)
C(23)–C(24)–C(25)–C(26)	61.98(17)
O–C(22)–N(3)–C(24)	–3.54(18)
C(19)–C(22)–N(3)–C(24)	176.71(14)
C(23)–C(24)–N(3)–C(22)	7.97(16)
C(25)–C(24)–N(3)–C(22)	–116.32(14)
C(35)–P–C(29)–C(30)	103.88(14)
C(1)–P–C(29)–C(30)	0.52(15)
C(35)–P–C(29)–C(34)	–79.81(13)
C(1)–P–C(29)–C(34)	176.82(12)
C(34)–C(29)–C(30)–C(31)	1.2(2)
P–C(29)–C(30)–C(31)	177.46(13)
C(29)–C(30)–C(31)–C(32)	–0.1(3)
C(30)–C(31)–C(32)–C(33)	–0.2(3)
C(31)–C(32)–C(33)–C(34)	–0.7(3)

C(32)–C(33)–C(34)–C(29)	1.8(3)
C(30)–C(29)–C(34)–C(33)	–2.0(2)
P–C(29)–C(34)–C(33)	–178.53(13)
C(29)–P–C(35)–C(36)	15.53(15)
C(1)–P–C(35)–C(36)	119.77(14)
C(29)–P–C(35)–C(40)	–167.41(12)
C(1)–P–C(35)–C(40)	–63.17(13)
C(40)–C(35)–C(36)–C(37)	0.7(2)
P–C(35)–C(36)–C(37)	177.69(13)
C(35)–C(36)–C(37)–C(38)	0.7(3)
C(36)–C(37)–C(38)–C(39)	–1.4(3)
C(37)–C(38)–C(39)–C(40)	0.6(3)
C(38)–C(39)–C(40)–C(35)	0.8(3)
C(36)–C(35)–C(40)–C(39)	–1.4(2)
P–C(35)–C(40)–C(39)	–178.68(13)

3. Copies of ^1H , ^{13}C , and ^{31}P NMR Spectra

¹H NMR (300 MHz, CDCl₃)

^{31}P NMR (162 MHz, CDCl_3)

S-83

S-87

³¹P NMR (162 MHz, CDCl₃)

³¹P NMR (162 MHz, CDCl₃)

S-95

³¹P NMR (162 MHz, CDCl₃)

S-98