SUPPORTING INFORMATION

P-Chiral, N-Phosphoryl Sulfonamide Brønsted Acids with an Intramolecular Hydrogen Bond Interaction that Modulates Organocatalysis

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**General Experimental Methods**

All reactions were carried out under anhydrous conditions and under an atmosphere of dry argon unless otherwise indicated. Compounds were purified by normal phase flash column chromatography on silica gel (SDS, 60 Å. C. 40-63 mm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F254), which were visualized by UV when applicable (λ max = 254 nm and/or 366 nm) and/or by staining with vanillin or anisaldehyde in acidic ethanol and/or KMnO₄ in basic water followed by heating. Key compounds were fully characterized by ¹H, ¹³C {¹H} and ³¹P {¹H} NMR and HRMS. Chemical shifts (δ) are reported in ppm relative to the internal deuterated solvent or external H₃PO₄ (δ 0.00 ³¹P), unless indicated otherwise. High-resolution MS spectra were recorded using electrospray ionization (ESI+/-) and Fourier transform ion cyclotron resonance mass analyzer (FTMS).

The reactions were monitored either by TLC or analytical HPLC/MS to confirm completion and homogeneity of the products. Analytical HPLC was performed using a reversed phase C18 5 µm column on a Waters Atlantis T3 instrument and the solvent system indicated below:

Solvent A: H₂O, 0.1% formic acid
Solvent B: CH₃CN, 0.1% formic acid
Mobile phase: linear gradient from 95%A and 5%B to 5%A and 95%B in 13 min, then 2 min at 100% B
Flow rate: 1 mL/min

Compounds 6-bromo-2-methylquinoline (10a), 2-methylquinoline (10b), 2-phenylquinoline (10c) and 4-methylquinoline (10d) were purchased from Sigma Aldrich. The 2-ethylquinoline (10e), ¹ 2-isopropylquinoline (10f), ² 6-nitro-2-methylquinoline (10g) ³ and 6-methoxy-2-methylquinoline (10h) ³ were synthesized according to the literature procedures indicated.

The enantiomeric purity of chiral compounds was determined by chiral HPLC using an Agilent 1100 or Agilent 1260 series instrument and the column and solvent system indicated for each compound. The absolute stereochemistry of all compounds was assigned based on several factors, including the single crystal X-ray of the previously reported key precursor compound 6, ⁴ the single crystal X-ray structures of intermediate phosphinic amide 8d (refer to SI Table 3), the single crystal X-ray structures of catalysts 5a and 5c, the single crystal X-ray structure of compound (S)-2-bromo-6-methyl-3,4-dihydro-2H-1λ²-quinoline (11a), and by analogy with previously reported compounds in the literature.

The names of all compounds were generated using ChemBioDraw Ultra 12.0.
General synthesis of secondary phosphine oxides (SPOs) 7:
We recently reported the synthesis of SPO intermediates 6, 7a, 7c and 7d. The synthesis of analogs 7e and 7f was achieved using the same protocol. The synthesis of SPO analogs 7b was achieved using the previously reported methodology.

(S)-tert-Butyl(2-methoxy-5,6,7,8-tetrahydroanaphthalen-1-yl)phosphine oxide (7e):
Precursor compound 5-bromo-6-methoxy-1,2,3,4-tetrahydroanaphthalene (used to prepare the Grignard reagent) was synthesized according to the method reported by Smith and co-workers.

A three-neck flask under argon was charged with SPO 6 (1 mmol) in 2-MeTHF (3 mL) and cooled to 0 °C. A solution of 2-methoxy-6-phenylnaphthalene-1-yl magnesium bromide (1 M in 2-MeTHF, 4 mmol, 4 mL) was added slowly while keeping the internal temperature <5 °C. The reaction mixture was stirred for 40 min to completion. Saturated and degassed aqueous NH₄Cl solution (5 mL) was added slowly to quench the reaction. The organic layer was collected and the aqueous residue was extracted with DCM (25 mL x3). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel (deactivated with 10% water) using a solvent gradient of hexane/EtOAc (from 50:50 to 0:100, v/v) to obtained the desired product (141 mg) in 53% yield.

1H NMR (400 MHz, CDCl₃): δ 8.28 (s, 0.5 H), 7.17 (d, J = 8.5 Hz, 1H), 7.06 (s, 0.5 H), 6.71 (dd, J = 8.5, 5.1 Hz, 1H), 3.77 (s, 3H), 3.54 – 3.39 (m, 1H), 2.93 (dt, J = 17.0, 5.6 Hz, 1H), 2.72 (t, J = 6.2 Hz, 2H), 1.83 – 1.66 (m, 4H), 1.20 (d, J = 16.6 Hz, 9H).

31P NMR (162 MHz, CDCl₃): δ 36.57.

More detailed characterization and estimation of the enantiomeric purity was performed at the subsequent step, when 7e was converted to the corresponding P-chiral (tert-butyl)-P-arylphosphinic amide 8e.

(S)-tert-Butyl(2-methoxy-6-phenylnaphthalen-1-yl)phosphine oxide (7f):
The precursor 1-bromo-2-methoxy-6-phenylnaphthalene (used to prepare the Grignard reagent) was synthesized according to the method reported by Smith and co-workers.

A three-neck flask under argon was charged with SPO 6 (1 mmol) dissolved in 2-MeTHF (3 mL) and cooled to 0 °C. A solution of 2-methoxy-6-phenylnaphthalen-1-yl
magnesium bromide (1 M in 2-MeTHF, 4 mmol, 4 ml; prepared as previously reported\(^6\)) was added slowly, while keeping the internal temperature <5 °C. The reaction mixture was stirred for 40 min to complete the reaction. Saturated and degassed aqueous NH\(_4\)Cl solution (5 mL) was added slowly to quench the reaction. The organic layer was collected and the aqueous residue was extracted with DCM (25 mL x3). The combined organic extracts were dried over anhydrous Na\(_2\)SO\(_4\) and concentrated. The residue was purified by silica gel chromatography (on deactivated silica with 10% water) eluted with a solvent gradient of hexane/EtOAc gradient (50:50 to 0:100, v/v) to obtained the desired product (189 mg) in 56% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.04 (d, \(J = 9.0\) Hz, 1H), 8.54 (s, 0.5 H), 8.07 (d, \(J = 9.1\) Hz, 1H), 7.98 (s, 1H), 7.81 (dd, \(J = 9.0, 2.1\) Hz, 1H), 7.70 (d, \(J = 7.1\) Hz, 2H), 7.48 (t, \(J = 7.7\) Hz, 2H), 7.37 (t, \(J = 7.4\) Hz, 1H), 7.31 (s, 0.5 H), 7.30 – 7.26 (m, 1H), 3.98 (s, 3H), 1.26 (d, \(J = 16.8\) Hz, 9H).

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 36.19.

More detailed characterization and estimation of the enantiomeric purity was performed at the subsequent step, when 7\(f\) was converted to the corresponding \(P\)-chiral (tert-butyl)-\(P\)-arylphosphinic amide 8\(f\).

**General procedure for the conversion of SPOs 7 to the \(P\)-Chiral (tert-butyl)-\(P\)-arylphosphinic amides 8:**

Chiral SPO 7 (1.0 mmol) was dissolved in 6 mL of degassed acetonitrile and cooled to 0 °C. CCl\(_4\) (1.0 mL), Et\(_3\)N (2.0 mmol) and saturated aqueous solution of NH\(_4\)OH (28% in water, 0.5 mL) were sequentially added dropwise while stirring. The solution was stirred at 0 °C for 30 min and then warmed to RT and allowed to stir for 16 h. Water (5 mL) was added to the reaction mixture and then extracted with EtOAc, the organic layers were combined, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated to give the crude product. The pure product was obtained after first passing the crude through a short silica gel column and then doing a crystallization in DCM/Et\(_2\)O (1:5, v/v) at -20 °C to obtain the phosphoramid products as highly enriched single enantiomers (92-99% ee).
(R)-P-(tert-butyl)-P-phenylphosphinic amide (8a); characterization data consistent with previously reported.\(^7\)

\[
\begin{align*}
\text{Isolated as a white solid in 82\% yield (162 mg) and 96.7\% ee.} \\
\text{\(1^H\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.90–7.84 (m, 2H), 7.57–7.52 (m, 1H), 7.49–7.43 (m, 2H), 2.72 (brs, 2H), 1.16 (d, \(J = 15.3\) Hz, 9H).} \\
\text{\(31^P\) NMR (202 MHz, CDCl\(_3\)): \(\delta\) 41.34.} \\
\text{Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, \(\lambda = 220\) nm; (R)-enantiomer \(t_R\) (major) = 5.88 min, (S)-enantiomer \(t_R\) (minor) = 7.60 min.}
\end{align*}
\]

(R)-P-(tert-butyl)-P-(2-methoxyphenyl)phosphinic amide (8b):

\[
\begin{align*}
\text{Isolated as a white solid in 73\% yield (166 mg) and 95\% ee.} \\
\text{\(1^H\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.90 (ddd, \(J = 11.9, 7.5, 1.8\) Hz, 1H), 7.49 – 7.40 (m, 1H), 7.10 – 7.02 (m, 1H), 6.93 – 6.87 (m, 1H), 3.83 (s, 3H), 3.17 (s, 2H), 1.08 (d, \(J = 15.9\) Hz, 9H).} \\
\text{\(13^C\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 159.2 (d, \(J = 3.9\) Hz), 135.5 (dd, \(J = 5.5, 3.0\) Hz), 133.3, 121.0 (dd, \(J = 10.6, 2.5\) Hz), 119.4 (d, \(J = 101.4\) Hz), 110.6 (d, \(J = 7.0\) Hz), 55.2, 34.3 (d, \(J = 93.7\) Hz), 24.2.} \\
\text{\(31^P\) NMR (203 MHz, CDCl\(_3\)): \(\delta\) 46.01.} \\
\text{HRMS: calculated for C\(_{11}\)H\(_{18}\)NNaO\(_2\)P\(^+\) [M+H\(^+\)]: 250.0967, found: 250.0967.} \\
\text{Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, \(\lambda = 220\) nm; (S)-enantiomer \(t_R\) (minor) = 7.38 min, (R)-enantiomer \(t_R\) (major) = 10.23 min.}
\end{align*}
\]

(R)-P-(tert-butyl)-P-(4-methoxyphenyl)phosphinic amide (8c)

\[
\begin{align*}
\text{Isolated as a white solid in 48\% yield (109 mg) and >99\% ee.} \\
\text{\(1^H\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.77 – 7.70 (m, 2H), 6.92 (dd, \(J = 8.9, 2.4\) Hz, 2H), 3.83 (s, 3H), 2.84 (s, 2H), 1.11 (d, \(J = 15.2\) Hz, 9H).} \\
\text{\(13^C\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 162.4 (d, \(J = 2.9\) Hz), 135.0 (d, \(J = 9.6\) Hz), 121.4 (d,}
\begin{align*}
J &= 123.0 \text{ Hz), 113.6 (d, } J = 12.5 \text{ Hz), 55.2, 32.3 (d, } J = 93.5 \text{ Hz), 24.8.} \\
^{31}P \text{ NMR (203 MHz, CDCl\textsubscript{3}): } \delta 41.44. \\
\text{HRMS: calculated for C}_{11}H_{18}NNaO_{2}P^{+} [M+H]^{+}: 250.0967, \text{ found: 250.0968.} \\
\text{Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, } \lambda = 220 \text{ nm; (R)-enantiomer } t_R (\text{major}) = 7.08 \text{ min, (S)-enantiomer } t_R (\text{minor}) = 12.49 \text{ min.}
\end{align*}

(R)-P-(tert-butyl)-P-(2-methoxynaphthalen-1-yl)phosphinic amide (8d)

\begin{center}
\includegraphics[width=0.2\textwidth]{8d.png}
\end{center}

Isolated as a white solid in 42% yield (116 mg) and >99% ee.

\begin{align*}
^1H \text{ NMR (400 MHz, CDCl\textsubscript{3}): } &\delta 9.59 \text{ (d, } J = 8.5 \text{ Hz, 1H), 7.99 (d, } J = 9.1 \text{ Hz, 1H), 7.76} \\
&\text{(dt, } J = 8.2, 1.7 \text{ Hz, 1H), 7.54 (dd, } J = 8.6, 6.7, 1.5 \text{ Hz, 1H), 7.38 (dd, } J = 8.0, 6.8, 1.2 \text{ Hz, 1H), 7.31 \text{ – 7.23 (m, 1H), 3.99 (s, 3H), 3.22 (s, 2H), 1.16 (d, } J = 16.0 \text{ Hz, 9H).}
\end{align*}

\begin{align*}
^{13}C \text{ NMR (101 MHz, CDCl\textsubscript{3}): } &\delta 158.7 \text{ (d, } J = 3.2 \text{ Hz), 136.7 (d, } J = 6.7 \text{ Hz), 134.7, 129.4 (d, } J = 9.1 \text{ Hz), 128.0, 127.6 (d, } J = 2.2 \text{ Hz), 127.5, 124.2, 112.8, 111.9, 111.8, 56.0, 35.9 (d, } J = 93.2 \text{ Hz), 24.4.} \\
^{31}P \text{ NMR (162 MHz, CDCl\textsubscript{3}): } &\delta 50.06. \\
\text{HRMS: calculated for C}_{15}H_{20}NNaO_{2}P^{+} [M+H]^{+}: 300.1124, \text{ found: 300.1115.} \\
\text{Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, } \lambda = 220 \text{ nm; (S)-enantiomer } t_R = 8.46 \text{ min, (R)-enantiomer } t_R \text{ (single peak) = 28.96 min.}
\end{align*}

(R)-P-(tert-butyl)-P-(2-methoxy-5,6,7,8-tetrahydronaphthalen-1-yl)phosphinic amide (8e)

\begin{center}
\includegraphics[width=0.2\textwidth]{8e.png}
\end{center}

Isolated as a white solid in 45% yield (126 mg) and >99% ee.

\begin{align*}
^1H \text{ NMR (500 MHz, CDCl\textsubscript{3}): } &\delta 7.15 \text{ (d, } J = 8.5 \text{ Hz, 1H), 6.72 (dd, } J = 8.5, 4.8 \text{ Hz, 1H), 3.79 (s, 3H), 3.65 \text{ – 3.56 (m, 1H), 3.20 (dt, } J = 17.7, 5.7 \text{ Hz, 1H), 3.12 (s, 2H), 2.72 (t, } J = 6.6 \text{ Hz, 2H), 1.86 \text{ – 1.77 (m, 1H), 1.75 \text{ – 1.66 (m, 2H), 1.65 \text{ – 1.55 (m, 1H), 1.13 (d, } J = 15.8 \text{ Hz, 9H).} \\
^{13}C \text{ NMR (126 MHz, CDCl\textsubscript{3}): } &\delta 158.09 \text{ (d, } J = 4.6 \text{ Hz), 145.82 (d, } J = 7.0 \text{ Hz), 133.25 (d, } J = 2.1 \text{ Hz), 131.73 (d, } J = 10.3 \text{ Hz), 117.61 (d, } J = 95.2 \text{ Hz), 108.24 (d, } J = 7.4 \text{ Hz), 55.16, 35.83 (d, } J = 91.8 \text{ Hz), 29.87, 28.51 (d, } J = 2.2 \text{ Hz), 24.41 (d, } J = 0.9 \text{ Hz), 22.39 (d, } J = 84.5 \text{ Hz).} \\
^{31}P \text{ NMR (203 MHz, CDCl\textsubscript{3}): } &\delta 50.18.
\end{align*}
HRMS: calculated for C_{15}H_{24}NNaO_{2}P^{+} [M+H]^{+}: 304.1437, found: 304.1142.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (S)-enantiomer t_{R} = 4.96 min, (R)-enantiomer t_{R} (single peak) = 6.20 min.

(R)-P-(tert-butyl)-P-(2-methoxy-6-phenynaphthalen-1-yl)phosphinic amide (8f)

Isolated as a white solid in 60% yield (212 mg) and >99% ee.

^{1}H NMR (500 MHz, CDCl_{3}): δ 9.64 (d, J = 9.1 Hz, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.94 (s, 1H), 7.80 (dd, J = 9.1, 2.1 Hz, 1H), 7.70 (d, J = 7.0 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.24 (dd, J = 9.0, 4.3 Hz, 1H), 3.95 (s, 3H), 3.31 (brs, 2H), 1.17 (d, J = 16.1 Hz, 9H).

^{13}C NMR (126 MHz, CDCl_{3}): δ 158.7 (d, J = 3.2 Hz), 140.6, 136.5, 135.9 (d, J = 6.7 Hz), 134.9 (d, J = 2.1 Hz), 129.7 (d, J = 9.0 Hz), 128.9, 128.2 (d, J = 2.1 Hz), 127.3, 127.2, 127.0, 125.63, 112.4 (d, J = 93.6 Hz), 112.3 (d, J = 7.7 Hz), 56.0, 35.9 (d, J = 93.2 Hz), 24.4.

^{31}P NMR (203 MHz, CDCl_{3}): δ 50.11.
HRMS: calculated for C_{21}H_{25}NO_{2}P^{+} [M+H]^{+}: 354.1617, found: 354.1618.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 80/20, 1.0 mL/min, λ = 220 nm; (S)-enantiomer t_{R} = 10.91 min, (R)-enantiomer (single peak) t_{R} = 15.34 min.

General procedure for the conversion of arylphosphinic amides 8 to Brønsted acids 3b and 4:
A slurry of NaH (3 equiv of 60% NaH in oil) in anhydrous THF (3.0 mL) at 0 °C was added to a solution of phosphinamidate 8 (0.5 mmol, 1 equiv) and the mixture was stirred for 30 min. The arylsulfonyl chloride (1.5 equiv) was added slowly, and the mixture was warmed to RT and monitored by TLC. After complete conversion (~12-15 h), NH_{4}Cl (0.1 g) was added portion-wise, the mixture was diluted with THF and filtered. The filtrate was concentrated and the crude residue was purified by flash column chromatography on silica gel to give the desired product. The product was dissolved in DCM (15 mL) and thoroughly washed with 4 M HCl (2x) to remove any salt impurities and completely protonate the catalyst. The organic layer was separated and concentrated under reduced pressure. The residue was taken up in toluene (5 mL), evaporated to dryness again and dried under high vacuum for 24 h to give the catalyst.

Note: Upon completion of the coupling reaction between intermediate 8 and the sulfonyl chloride, some analogs 4 were used directly in the subsequent demethylation step (without isolation/purification) to get the final catalysts 5.
(R)-N-(tert-butyl(2-methoxyphenyl)phosphoryl)-2,4,6-trisopropylbenzenesulfonamide (3b): This compound was recently reported by Han and coworkers.\(^8\)

Isolated as a yellow solid in 97% yield (240 mg).
\(^1\)H NMR (500 MHz, CD\(_3\)OD): δ 7.74 (ddd, J = 7.0, 1.5 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.11 (s, 2H), 6.91 (dd, J = 7.8, 5.3 Hz, 1H), 6.77 (t, J = 7.0 Hz, 1H), 4.49 - 4.40 (m, 2H), 3.54 (s, 3H), 2.88 (hept, J = 6.9 Hz, 1H), 1.27 – 1.21 (m, 12H), 1.14 – 1.04 (m, 15H).
\(^{31}\)P NMR (202 MHz, CD\(_3\)OD): δ 33.97;
HRMS: calculated for C\(_{26}\)H\(_{40}\)NO\(_4\)PSNa [M+Na]: 516.2308, found: 516.2305.

(R)-N-(tert-butyl(phenyl)phosphoryl)-2,4,6-trisopropylbenzenesulfonamide (4a):

Isolated as a yellow solid in 96% yield (223 mg).
\(^1\)H NMR (500 MHz, CD\(_3\)OD): δ 7.66-7.62 (m, 2H), 7.35 (td, J = 7.5, 1.5 Hz, 1H), 7.22 (td, J = 8.0, 3.0 Hz, 2H), 7.04 (s, 2H), 4.51-4.45 (m, 2H), 2.88-2.82 (m, 1H), 1.23 (d, J = 7.0 Hz, 6H), 1.21 (d, J = 6.5 Hz, 6H), 1.06 (d, J = 7.0 Hz, 6H), 1.01 (d, J = 15.5 Hz, 9H);
\(^{13}\)C NMR (125 MHz, CD\(_3\)OD): δ 150.8, 149.2, 142.7, 134.8 (d, J = 112.0 Hz), 134.5 (d, J = 8.1 Hz), 131.3 (d, J = 1.8 Hz), 128.1 (d, J = 10.9 Hz), 123.6, 35.3, 33.9 (d, J = 103.8 Hz), 30.2, 25.6, 25.2, 25.1, 24.33, 24.30;
\(^{31}\)P NMR (202 MHz, CD\(_3\)OD): δ 31.74;
HRMS: calculated for C\(_{25}\)H\(_{38}\)NO\(_3\)PSNa [M+Na]: 486.2202, found: 486.2194.

(R)-N-(tert-butyl(4-methoxyphenyl)phosphoryl)-2,4,6-trisopropylbenzenesulfonamide (4b):

Upon completion of the coupling reaction with the sulfonyl chloride, compound 4b was used directly in the subsequent demethylation step to get the final catalyst 5b.
(R)-N-(tert-butyl(2-methoxynaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (4c):

Compound was isolated as a white solid in 98% yield (173 mg).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.43 (d, $J = 8.9$ Hz, 1H), 8.02 (d, $J = 9.1$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.56 - 7.43 (m, 2H), 7.37 (t, $J = 8.0$ Hz, 1H), 7.32 - 7.27 (m, 1H), 7.05 (s, 2H), 4.16 (hept, $J = 6.5$ Hz, 2H), 4.10 (s, 3H), 2.81 (hept, $J = 7.0$ Hz, 1H), 1.31 - 1.11 (m, 21H), 1.10 (d, $J = 6.8$ Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 158.42, 152.56, 150.27, 136.80 (d, $J = 7.6$ Hz), 135.92 (d, $J = 2.3$ Hz), 135.43, 129.60 (d, $J = 10.0$ Hz), 128.28, 127.99, 127.57 (d, $J = 2.3$ Hz), 124.64, 123.75, 111.89 (d, $J = 8.2$ Hz), 110.79, 110.03, 56.53, 37.40 (d, $J = 8.2$ Hz), 34.18, 29.91, 24.91 (d, $J = 3.4$ Hz), 24.60, 23.63 (d, $J = 5.8$ Hz).

$^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 43.1.

HRMS: calculated for C$_{30}$H$_{41}$O$_4$NPS: 542.2499, found: 542.2491.

(R)-N-(tert-butyl(2-methoxy-5,6,7,8-tetrahydronaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (4d):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.47 (s, 1H), 7.17 (d, $J = 8.5$ Hz, 1H), 7.08 (s, 2H), 6.74 (dd, $J = 8.5$, 5.2 Hz, 1H), 4.18 (hept, $J = 6.7$ Hz, 2H), 3.89 (s, 3H), 3.40 (dt, $J = 18.0$, 6.2 Hz, 1H), 3.03 (dt, $J = 17.9$, 5.5 Hz, 1H), 2.85 (hept, $J = 6.9$ Hz, 1H), 2.74 - 2.64 (m, 2H), 1.73 - 1.56 (m, 4H), 1.26 (d, $J = 6.7$ Hz, 6H), 1.24 - 1.15 (m, 15H), 1.13 (d, $J = 6.7$ Hz, 6H).

$^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 44.0.

Upon completion of the coupling reaction with the sulfonyl chloride, the crude compound 4d was used directly in the subsequent demethylation step to get the final catalyst 5d.
(R)-N-(tert-butyl(2-methoxy-6-phenylnaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (4e):

![Structural formula of the compound](image)

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.51 (d, $J = 9.2$ Hz, 1H), 8.08 (d, $J = 9.1$ Hz, 1H), 7.95 (t, $J = 2.1$ Hz, 1H), 7.75 (dd, $J = 9.2$, 2.1 Hz, 1H), 7.68 (dd, $J = 8.3$, 1.3 Hz, 2H), 7.52 (d, $J = 6.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.39 – 7.34 (m, 1H), 7.31 (d, $J = 9.1$, 4.7 Hz, 1H), 7.06 (s, 2H), 4.18 (hept, $J = 6.7$ Hz, 2H), 4.11 (s, 3H), 2.81 (hept, $J = 6.8$ Hz, 1H), 1.26 – 1.20 (m, 15H), 1.18 (dd, $J = 6.9$, 2.4 Hz, 6H), 1.12 (d, $J = 6.7$ Hz, 6H).

$^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 43.2.

Upon completing of the coupling reaction with the sulfonyl chloride, compound 4e the crude product was used directly in the subsequent demethylation step to get the final catalyst 5e.

General procedure for the synthesis of Brønsted acids 5:

![Reagents and products diagram](image)

Note: Upon completion of the coupling reaction between intermediate 8 and the sulfonyl chloride, some analogs 4 were used directly in the subsequent demethylation step to get the final catalysts 5.

Demethylation step: A solution of intermediates 3b or 4 in dry DCM (5 mL) was cooled to -78 °C, then BBr$_3$ (1.2 equiv in hexane) was added slowly over a 5 min period. After the addition was finished, the reaction mixture was allowed to warm-up to RT and stirred overnight. The reaction was quenched with water and diluted with DCM. The organic fraction was washed with 1 N HCl, dried over anhydrous MgSO$_4$, concentrated and purified by flash column chromatography on silica gel. The isolated product was re-dissolved in DCM (15 mL) and thoroughly washed with 4 M HCl (15 mL x 2) to remove any metal impurities and completely protonate the catalyst. The organic layer
was separated and concentrated under reduced pressure. The residue was taken up in toluene (5 mL), evaporated to dryness again and allowed to dry under high vacuum for a minimum of 24 h to give (R)-phenolic catalyst.

**(R)-N-(tert-butyl(2-hydroxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (5a):**

![Structure of (R)-N-(tert-butyl(2-hydroxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide](image)

Compound was isolated as a yellow solid in 92% yield (221 mg).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.60 (s, 1H), 7.42 (ddt, $J$ = 8.4, 7.1, 1.4 Hz, 1H), 7.31-7.23 (m, 1H), 7.14 (s, 2H), 6.97 – 6.89 (m, 1H), 6.84 – 6.75 (m, 1H), 6.41 (d, $J$ = 8.7 Hz, 1H), 3.91 (hept, $J$ = 6.6 Hz, 2H), 2.90 (hept, $J$ = 6.9 Hz, 1H), 1.30 – 1.14 (m, 27H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 163.6 (d, $J$ = 5.0 Hz), 153.7, 150.3, 135.1 (d, $J$ = 2.1 Hz), 134.2 (s), 133.0 (d, $J$ = 8.4 Hz), 123.9, 118.8 (d, $J$ = 12.5 Hz), 118.0 (d, $J$ = 9.3 Hz), 107.5 (d, $J$ = 117.5 Hz), 34.6 (d, $J$ = 86.2 Hz), 34.2, 30.1, 24.7 (d, $J$ = 47.0 Hz), 23.8, 23.5 (d, $J$ = 4.2 Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 45.42.

HRMS: calculated for C$_{25}$H$_{39}$NO$_4$PS$^+$ [M+H$^+$]: 480.2332, found: 480.2336.

**(R)-N-(tert-butyl(4-hydroxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (5b):**

![Structure of (R)-N-(tert-butyl(4-hydroxyphenyl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide](image)

Isolated as a yellow solid, in 80% yield (193 mg).

$^1$H NMR (500 MHz, MeOD): $\delta$ 7.51–7.44 (m, 2H), 7.17 (s, 2H), 6.77 (dd, $J$ = 8.5, 2.5 Hz, 2H), 4.27–4.14 (m, 2H), 2.96–2.87 (m, 1H), 1.31–1.20 (m, 12H), 1.18–1.03 (m, 15H).

$^{13}$C NMR (126 MHz, MeOD): $\delta$ 161.4, 152.4, 149.6, 136.6, 134.8 (d, $J$ = 11.0 Hz), 123.1, 116.5 (d, $J$ = 125.4 Hz), 114.7 (d, $J$ = 13.8 Hz), 34.0, 33.1 (d, $J$ = 93.4 Hz), 28.9, 23.8 (d, $J$ = 38.7 Hz), 23.0, 22.7 (d, $J$ = 6.2 Hz).

$^{31}$P NMR (203 MHz, MeOD): $\delta$ 41.15.

HRMS: calculated for C$_{25}$H$_{39}$NO$_4$PS$^+$ [M+H$^+$]: 480.2332, found: 480.2335.
(R)-N-(tert-butyl(2-hydroxynaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (5c):

\[
\begin{align*}
\text{Isolated as a yellow solid in 95% yield (252 mg).} \\
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): } \delta 12.55 (s, 1H), 8.15 (m, 1H), 7.88 (d, } J = 8.9 \text{ Hz, 1H), } \\
7.70 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.06 (m, 3H), 6.56 (s, 1H), 3.88 (hept, } J = 6.7 \text{ Hz, 2H), } \\
2.88 (hept, } J = 6.9 \text{ Hz, 1H), } 1.36 – 1.14 (m, 21H), 1.11 (d, } J = 6.7 \text{ Hz, 6H).} \\
\text{\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): } \delta 166.5 (d, } J = 4.8 \text{ Hz), 153.4, 150.1, 136.5 (d, } J = 2.3 \text{ Hz), } \\
134.6, 133.6 (d, } J = 8.6 \text{ Hz), 128.4 (d, } J = 10.2 \text{ Hz), 128.0 (d, } J = 197.2 \text{ Hz), 125.5 (d, } J = 4.2 \text{ Hz), } \\
123.9, 123.2, 120.4 (d, } J = 11.1 \text{ Hz), 36.8 (d, } J = 85.8 \text{ Hz), 34.2, 30.2, } \\
24.8, 24.7 (d, } J = 39.8 \text{ Hz), 23.5 (d, } J = 4.6 \text{ Hz).} \\
\text{\textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}): } \delta 47.72. \\
\text{HRMS: calculated for } C_{29}H_{41}NO_4PS^+[M+H]^+: 530.2488, \text{ found: 530.2496.}
\end{align*}
\]

(R)-N-(tert-butyl(2-hydroxy-5,6,7,8-tetrahydronaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (5d):

\[
\begin{align*}
\text{Isolated as a yellow solid in 93% yield (248 mg).} \\
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): } \delta 11.50 (s, 1H), 7.17 (s, 2H), 7.14 (d, } J = 8.4 \text{ Hz, 1H), } \\
6.75 (dd, } J = 8.4, 5.2 \text{ Hz, 1H), 6.19 (d, } J = 10.9 \text{ Hz, 1H), 3.97 (hept, } J = 6.5 \text{ Hz, 2H), } \\
3.13 (ddd, } J = 15.9, 10.1, 5.4 \text{ Hz, 1H), 2.95 – 2.78 (m, 2H), 2.75 – 2.67 (m, 2H), 1.98 – 1.68 (m, 4H), 1.31 (d, } J = 6.6 \text{ Hz, 6H), } \\
1.27 – 1.22 (m, 12H), 1.18 (d, } J = 16.6 \text{ Hz, 9H).} \\
\text{\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): } \delta 162.9 (d, } J = 5.6 \text{ Hz), 153.3, 150.2, 140.3 (d, } J = 9.1 \text{ Hz), } \\
136.0, 135.0, 128.9 (d, } J = 10.4 \text{ Hz), 124.0, 116.4 (d, } J = 11.0 \text{ Hz), 106.3 (d, } J = 109.8 \text{ Hz), } \\
36.2 (d, } J = 83.9 \text{ Hz), 34.1, 30.3, 29.5, 24.8 (d, } J = 84.6 \text{ Hz), 24.8 (d, } J = 14.8 \text{ Hz), 24.3, 23.6, 22.4, 22.1.} \\
\text{\textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}): } \delta 49.00. \\
\text{HRMS: calculated for } C_{29}H_{45}NO_4PS^+[M+H]^+: 534.2801, \text{ found: 534.2808.}
\end{align*}
\]
(R)-N-(tert-butyl(2-hydroxy-6-phenynaphthalen-1-yl)phosphoryl)-2,4,6-triisopropylbenzenesulfonamide (5e):

Isolated as a yellow solid in 88% yield (267 mg).

$^1$H NMR (500 MHz, CDCl$_3$) δ 12.49 (s, 1H), 8.30 (d, J = 8.9 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.64 (s, 1H), 7.44 – 7.30 (m, 6H), 7.17 (s, 2H), 7.13 (dd, J = 8.9, 4.7 Hz, 1H), 3.98 (hept, J = 6.7 Hz, 2H), 2.89 (hept, J = 6.9 Hz, 1H), 1.35 (d, J = 6.7 Hz, 6H), 1.28 – 1.12 (m, 21H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 166.2 (d, J = 4.3 Hz), 153.6, 150.6, 140.0, 136.8, 135.3, 134.7, 132.9 (d, J = 8.7 Hz), 128.6 (d, J = 10.1 Hz), 128.3, 126.9, 126.6 (d, J = 126.9 Hz), 126.3 (d, J = 4.1 Hz), 124.0, 120.3 (d, J = 10.8 Hz), 98.3 (d, J = 111.8 Hz), 36.9 (d, J = 85.1 Hz), 34.2, 30.3, 25.2, 24.6, 23.5 (d, J = 6.9 Hz).

$^{31}$P NMR (203 MHz, CDCl$_3$): δ 48.88.

HRMS: calculated for C$_{35}$H$_{45}$NO$_4$PS$^+$ [M+H]$^+$: 606.2801, found: 606.2803.

General procedure for the transfer hydrogenation of quinolines 10 to the tetrahydroquinolines 11:

General procedure for the synthesis of the racemic tetrahydroquinolines:

An oven dried 2 dram vial equipped with a stir bar was cooled to ambient temperature in a desiccator and subsequently charged with the requisite quinoline (0.200 mmol). 1 mL of DCM, Hantzsch ester (152 mg, 0.600 mmol) and diphenylphosphinic acid (21.8 mg, 0.500 mmol). The vial was capped under air, sealed with parafilm and the mixture was stirred at RT for 2-24 h. Progress of the reaction was monitored by TLC (20% EtOAc and 80% hexanes). The crude product was purified by flash chromatography on silica gel (using EtOAc/hexanes) to afford the desired tetrahydroquinoline.
General procedure for the asymmetric transfer hydrogenation of quinolines 10 to the tetrahydroquinolines 11:

An oven-dried flask was fitted with magnetic stirring bar and charged with the quinoline (reactions were typically carried out at a 0.1-0.2 mmol scale), catalyst (5 mol%), Hantzsch ester (3.0 equiv) and solvent (0.5 mL). The resulting mixture was stirred at RT (~22 °C), unless otherwise indicated and monitored by TLC. When all starting material was consumed, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using the solvent system indicated to isolate the corresponding product.

(S)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (11a):

Reaction time: 5 h using catalyst 5c. Known compound9, purified using a 0-2% EtOAc/hexanes eluent gradient; isolated as white solid in 98% yield (44.2 mg) and 88% ee. The compound was crystallized from DCM/hexanes to afford the tetrahydroquinoline 11e in 93% ee.

1H NMR (500 MHz, CDCl3): δ 7.09 – 7.05 (d, J = 2.4 Hz, 1H), 7.03 (dd, J = 8.4, 2.4 Hz, 1H), 6.34 (d, J = 8.4 Hz, 1H), 3.76 (s, 1H), 3.38 (dqd, J = 9.3, 6.3, 2.9 Hz, 1H), 2.80 (ddd, J = 17.0, 11.5, 5.7 Hz, 1H), 2.75 – 2.64 (dt, 1H), 1.98 – 1.87 (m, 1H), 1.55 (m, 1H), 1.20 (d, J = 6.3 Hz, 3H).

13C NMR (101 MHz, CDCl3): δ 143.9, 131.8, 129.5, 123.3, 115.5, 108.4, 47.2, 29.8, 26.5, 22.6.

Chiral HPLC method: Chiralpak OD-H, hexane/IPA = 98/2, 1.0 mL/min, λ = 254 nm; (R)-enantiomer t_R (minor) = 8.6 min, (S)-enantiomer t_R (major) = 11.2 min.

For the purpose of comparison the product was also analyzed using the same chiral HPLC column and solvent system as previously reported:9 Chiralcel OJ-H, hexane/IPA = 95/5, 0.8 mL/min, λ = 254 nm; (S)-enantiomer t_R (major) = 19.04 min, (R)-enantiomer t_R (minor) = 23.19 min.
(S)-2-methyl-1,2,3,4-tetrahydroquinoline (11b):
NMR and chiral HPLC data consistent with those previously reported.\textsuperscript{10}

\[
\text{\includegraphics[width=0.5\textwidth]{s16.png}}
\]

Compound was purified using a 0-1% EtOAc/hexanes as the eluent; isolated as a pale-yellow oil in 73% yield (21.6 mg) and 88% ee.
\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.02 – 6.90 (m, 2H), 6.60 (td, \(J = 7.3, 1.2\) Hz, 1H), 6.47 (dd, \(J = 8.4, 1.2\) Hz, 1H), 3.70 (broad s, 1H), 3.40 (dqd, \(J = 10.0, 6.3, 2.8\) Hz, 1H), 2.90 – 2.78 (m, 1H), 2.73 (ddd, \(J = 16.3, 5.2, 3.4\) Hz, 1H), 1.93 (dddd, \(J = 12.8, 5.6, 3.4, 2.8\) Hz, 1H), 1.63 – 1.55 (m, 1H), 1.21 (d, \(J = 6.3\) Hz, 3H).
\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) 144.9, 129.4, 126.8, 121.3, 117.1, 114.1, 47.3, 30.3, 26.7, 22.8.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, \(\lambda = 254\) nm; (R)-enantiomer \(t_R\) (minor) = 6.78 min, (S)-enantiomer (major) \(t_R = 7.79\) min.

(R)-2-phenyl-1,2,3,4-tetrahydroquinoline (11c):
NMR and chiral HPLC data consistent with those previously reported.\textsuperscript{10}

\[
\text{\includegraphics[width=0.5\textwidth]{s16.png}}
\]

Compound was purified using a 0-3% EtOAc/hexanes eluent and isolated as a white solid 95% yield (39.9 mg) and 59.3% ee.
\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.45 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.07 – 6.97 (m, 2H), 6.66 (td, \(J = 7.3, 1.2\) Hz, 1H), 6.55 (d, \(J = 7.5\) Hz, 1H), 4.45 (dd, \(J = 9.4, 3.3\) Hz, 1H), 4.05 (s, 1H), 2.93 (ddd, \(J = 16.2, 10.7, 5.5\) Hz, 1H), 2.75 (dt, \(J = 16.3, 4.8\) Hz, 1H), 2.13 (ddddd, \(J = 13.1, 5.4, 4.5, 3.3\) Hz, 1H), 2.00 (ddddd, \(J = 13.0, 10.7, 9.3, 5.1\) Hz, 1H).
\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): \(\delta\) 144.9, 144.9, 129.4, 128.7, 127.6, 127.0, 126.7, 121.0, 117.3, 114.1, 56.4, 31.1, 26.5.
Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, \(\lambda = 254\) nm; (S)-enantiomer \(t_R\) (minor) = 15.13 min, (R)-enantiomer \(t_R\) (major) = 21.39 min (major).

(R)-4-methyl-1,2,3,4-tetrahydroquinoline (11d):
NMR and chiral HPLC data consistent with those previously reported\textsuperscript{11}
Compound purified using a 0-20% Et$_2$O in pentane and isolated a pale-yellow oil in 70% yield and 30% ee. 

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.06 (d, $J$ = 7.6 Hz, 1H), 6.96 (tdd, $J$ = 7.3, 1.7, 0.8 Hz, 1H), 6.63 (td, $J$ = 7.4, 1.2 Hz, 1H), 6.48 (dd, $J$ = 7.9, 1.2 Hz, 1H), 3.91 (s, 1H), 3.39 – 3.23 (m, 2H), 2.92 (h, $J$ = 6.6 Hz, 1H), 2.04 – 1.94 (m, 1H), 1.68 (dddd, $J$ = 13.0, 6.9, 6.1, 3.5 Hz, 1H), 1.29 (d, $J$ = 7.0 Hz, 3H). 

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 144.3, 128.6, 126.9, 126.8, 117.1, 114.3, 39.2, 30.4, 30.0, 22.8.

Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 0.6 mL/min, $\lambda$ = 254 nm; (S)-enantiomer $t_R$ (minor) = 16.41 min, (R)-enantiomer $t_R$ (major) = 17.67 min.

($S$)-2-ethyl-1,2,3,4-tetrahydroquinoline (11e):

NMR and chiral HPLC data consistent with those previously reported.$^{10}$

![Chemical structure](image)

Compound was purified using a 0-2% EtOAc in hexanes and isolated as a pale-yellow oil in 72% yield (23.1 mg) and 75% ee. 

$^1$H NMR (500 MHz, CDCl$_3$): δ 6.96 (ddt, $J$ = 8.2, 7.4, 0.8 Hz, 2H), 6.60 (td, $J$ = 7.4, 1.2 Hz, 1H), 6.48 (dt, $J$ = 7.4, 1.3 Hz, 1H), 3.77 (s, 1H), 3.17 (ddt, $J$ = 9.4, 6.4, 2.9 Hz, 1H), 2.88 – 2.77 (m, 1H), 2.73 (ddd, $J$ = 16.3, 5.4, 4.0 Hz, 1H), 1.98 (dddd, $J$ = 12.7, 5.6, 4.0, 2.9 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.56 – 1.49 (m, 2H), 1.00 (t, $J$ = 7.5 Hz, 3H). 

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 144.9, 129.4, 126.8, 121.5, 117.0, 114.1, 53.2, 29.6, 27.7, 26.6, 10.2.

Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, $\lambda$ = 254 nm; (R)-enantiomer $t_R$ (minor) = 6.56 min, (S)-enantiomer $t_R$ (major) = 7.91 min.

($R$)-2-isopropyl-1,2,3,4-tetrahydroquinoline (11f):

![Chemical structure](image)

NMR and chiral HPLC data consistent with those previously reported,$^{10}$ purified using a 0-2% EtOAc/hexanes eluent; isolated as a pale-yellow oil in 77% yield (27.0 mg) and 66% ee. 

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.00 – 6.91 (m, 2H), 6.59 (td, $J$ = 7.3, 1.2 Hz, 1H), 6.52 – 6.45 (m, 1H), 3.76 (s, 1H), 3.04 (dd, $J$ = 10.0, 5.9, 2.9 Hz, 1H), 2.81 (ddd, $J$ = 16.5, 11.3, 5.5 Hz, 1H), 2.77 – 2.70 (m, 1H), 1.92 (dddd, $J$ = 12.5, 5.5, 3.9, 2.9 Hz, 1H), 1.77 – 1.60 (m, 2H), 1.00 (d, $J$ = 6.8 Hz, 3H), 0.98 (d, $J$ = 6.8 Hz, 3H).
$^{13}$C NMR (126 MHz, CDCl$_3$): δ 145.2, 129.3, 126.8, 121.6, 116.9, 114.1, 57.4, 32.7, 26.8, 24.7, 18.7, 18.4.

Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1.0 mL/min, λ = 254 nm; (S)-enantiomer $t_R$ (minor) = 5.90 min, (R)-enantiomer $t_R$ (major) = 8.53 min.

$(S)$-2-methyl-6-nitro-1,2,3,4-tetrahydroquinoline (11g):

NMR and chiral HPLC data consistent with those previously reported; compound was purified by flash column chromatography on silica gel (silica gel was deactivated with a 1% Et$_3$N in hexanes solution) using a 0-15% EtOAc/hexanes eluent gradient; isolated an orange solid in 83% yield (44.2 mg) and 86% ee. The compound was recrystallized from DCM/hexanes to afford the tetrahydroquinoline in 96% ee.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.95−7.86 (m, 2H), 6.42−6.32 (m, 1H), 4.53 (s, 1H), 3.55 (dqd, $J$ = 9.7, 6.4, 3.4 Hz, 1H), 2.90−2.74 (m, 2H), 2.00 (dtd, $J$ = 12.9, 4.8, 3.4 Hz, 1H), 1.58 (dtd, $J$ = 13.0, 9.8, 6.2 Hz, 1H), 1.28 (d, $J$ = 6.4 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 150.4, 137.5, 125.9, 124.4, 119.8, 112.2, 47.6, 29.0, 26.3, 22.4.

Chiral HPLC method: Chiralcel OJ-H, hexane/IPA = 95/5, 1 mL/min, λ = 254 nm; (R)-enantiomer $t_R$ (minor) = 19.35 min, (S)-enantiomer $t_R$ (major) = 20.67 min (major).

$(R)$-3-methyl-1,2,3,4-tetrahydroquinoline (11h):

NMR and chiral HPLC data consistent with those previously reported. Compound was purified by flash column chromatography on silica gel using a 0-10% pentane/Et$_2$O eluent; isolated as a pale-yellow oil in 71% yield (20.9 mg) and 14% ee.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.01-6.91 (m, 2H), 6.61 (td, $J$ = 7.4, 1.2 Hz, 1H), 6.49 (dd, $J$ = 7.9, 1.2 Hz, 1H), 3.89 (s, 1H), 3.27 (ddd, $J$ = 11.0, 3.7, 2.0 Hz, 1H), 2.90 (dd, $J$ = 11.0, 9.6 Hz, 1H), 2.78 (ddd, $J$ = 16.0, 5.0, 2.0 Hz, 1H), 2.43 (dd, $J$ = 16.0, 10.2 Hz, 1H), 2.14−1.99 (m, 1H), 1.05 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 144.4, 129.7, 126.8, 121.3, 117.1, 114.0, 49.0, 35.6, 27.3, 19.2.

Chiral HPLC method: Chiralcel OJ-H, hexane/IPA = 90/10, 0.5 mL/min, λ = 210 nm; (R)-enantiomer $t_R$ = 30.77 min (major), (S)-enantiomer $t_R$ = 37.77 min (minor).
(R)-3-phenyl-1,2,3,4-tetrahydroquinoline (11i):
The precursor 3-phenylquinoline was synthesized according to literature procedure.\textsuperscript{14} NMR and chiral HPLC data consistent with those previously reported.\textsuperscript{15} Compound was purified by flash column chromatography on silica gel using 0-6\% EtOAc/hexanes as the eluent; isolated as a pale-yellow solid in 51\% yield (10.5 mg; yield based on recovered starting material) and 4\% ee.

\textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.30 (m, 2H), 7.30 – 7.22 (m, 3H), 7.02 (d, $J$ = 7.4 Hz, 2H), 6.66 (td, $J$ = 7.4, 1.2 Hz, 1H), 6.57 (dd, $J$ = 8.4, 1.3 Hz, 1H), 4.15 (s, 1H), 3.47 (ddd, $J$ = 11.2, 3.7, 1.9 Hz, 1H), 3.35 (t, $J$ = 10.7 Hz, 1H), 3.16 (tdd, $J$ = 10.2, 5.8, 3.7 Hz, 1H), 3.09 – 2.93 (m, 2H).

\textsuperscript{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 144.1, 144.0, 129.7, 128.8, 127.4, 127.1, 126.8, 121.6, 117.3, 114.3, 48.5, 38.8, 34.8.

Chiral HPLC method: Chiralcel OD, hexane/IPA = 98/2, 1 mL/min, $\lambda$ = 254 nm; (R)-enantiomer $t_R$ = 18.81 min (major), (S)- 10.5 mg $t_R$ = 24.04 min (minor).

Methyl (R)-1,2,3,4-tetrahydroquinoline-2-carboxylate (11j)

Reaction time: 4 h at 50 °C using catalyst 5c. NMR and chiral HPLC data consistent with those previously reported.\textsuperscript{16} purified using a 0-8\% Et$_2$O/hexanes eluent; isolated as a colourless oil in 71\% yield (27.2 mg) and 30\% ee.

\textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.05 – 6.96 (m, 1H), 6.96 (d, $J$ = 7.5 Hz, 1H), 6.65 (td, $J$ = 7.3, 1.2 Hz, 1H), 6.59 (dd, $J$ = 8.0, 1.2 Hz, 1H), 4.40 (s, 1H), 4.05 (dd, $J$ = 8.8, 3.8 Hz, 1H), 3.78 (s, 3H), 2.90 – 2.71 (m, 2H), 2.29 (dt, $J$ = 13.0, 5.6, 3.8 Hz, 1H), 2.01 (ddt, $J$ = 13.0, 9.1, 5.3 Hz, 1H).

\textsuperscript{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 173.8, 143.1, 129.3, 127.2, 120.7, 117.8, 114.7, 54.1, 52.5, 26.0, 24.8.

Chiral HPLC method: Chiralpak AD, hexane/IPA = 80/20, 1 mL/min, $\lambda$ = 254 nm; (R)-$t_R$ = 7.62 min (major), (S)-$t_R$ = 9.04 min (minor).
**Table 1: Solvent Screening and Optimization of Reaction Conditions**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
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<td>99</td>
<td>80</td>
</tr>
<tr>
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<td>1.5</td>
<td>99</td>
<td>75</td>
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<tr>
<td>3</td>
<td>CHCl₃</td>
<td>0.5</td>
<td>99</td>
<td>80</td>
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<tr>
<td>4</td>
<td>CCl₄</td>
<td>1.5</td>
<td>99</td>
<td>86</td>
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<tr>
<td>5</td>
<td>DCE</td>
<td>1.5</td>
<td>99</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>cyclohexane</td>
<td>5</td>
<td>99</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>n-hexane</td>
<td>5</td>
<td>99</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>Et₂O</td>
<td>3</td>
<td>99</td>
<td>85</td>
</tr>
<tr>
<td>9</td>
<td>t-BuOMe</td>
<td>3</td>
<td>99</td>
<td>85</td>
</tr>
<tr>
<td>10</td>
<td>EtOAc</td>
<td>2</td>
<td>99</td>
<td>84</td>
</tr>
</tbody>
</table>

**Table 2: Optimization of Hantzsh Ester**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>5</td>
<td>99</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>5</td>
<td>99</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>t-Bu</td>
<td>3</td>
<td>99</td>
<td>85</td>
</tr>
</tbody>
</table>
$^{1}H$, $^{13}C$, $^{31}P$ NMR spectra and chiral HPLC chromatograms

Compounds Listed in Numerical Order

$^{1}H$ NMR of 3b

$^{31}P$ NMR of 3b

3b, R = 2,4,6-(i-Pr)$_3$C$_6$H$_2$
$^{13}$C NMR of 3b

![Carbon-13 NMR spectrum of 3b](image)
$^1$H NMR of 4a

$^{31}$P NMR of 4a
$^{13}$C NMR of 4a
Chiral HPLC Chromatograms of 4a

Method: HPLC instrument: Agilent 1260 HPLC; λ = 220 nm
Column: Phenomenex Lux Cellulose-2, 4.6x100 mm
Solvent A: 0.1% (v/v) HClO₄ in water, Solvent B: CH₃CN; 50-90% solvent B in 15 min at a flow rate of 1.2 mL/min
Top panel, racemic (in red) superimposed with (R)-enantiomer (in blue); bottom panel (R)-4a; (R)-enantiomer t_R = 11.44 min (major), (S)- enantiomer t_R = 12.36 min (minor).
$^1$HNMR of 4c

$^{31}$P NMR of 4c
$^{13}$C NMR of 4c
$^1$HNMR of 4d

$^{31}$P NMR of 4d
$^1$H NMR of 4e

$^{31}$P NMR of 4e
$^1$H NMR of 5a

$^{31}$P NMR of 5a
\(^{13}\text{C} \text{ NMR of } 5a\)
\( ^1\)H NMR of 5b

\[
\text{O} \quad \text{OS} \quad \text{NH} \quad \text{5b}
\]

\( ^31\)P NMR of 5b
$^{13}$C NMR of 5b
$^1$H NMR of 5c

$^{31}$P NMR of 5c
$^{13}$C NMR of 5c
$^1$H NMR of 5d

$^{31}$P NMR of 5d
$^{13}$C NMR of 5d
$^1$H NMR of 5e

$^{31}$P NMR of 5e
\textsuperscript{13}C NMR of 5e
$^{1}$H-NMR of 7e

$^{31}$P-NMR of 7e
$^1$H-NMR, $^{13}$C and $^{31}$P NMR spectra of compound 8a were consistent with those previously reported.\(^7\)

![Chemical structure of 8a](image)

Chiral HPLC chromatograms of 8a

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area [mAU*min^2]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>BB</td>
<td>0.2069</td>
<td>5673.06494</td>
<td>411.40399</td>
<td>98.3002</td>
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<td>BB</td>
<td>0.2540</td>
<td>98.09958</td>
<td>5.90015</td>
<td>1.6998</td>
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</table>
$^1$H NMR of 8b

$^{31}$P NMR of 8b
$^{13}$C NMR of $8b$

Chiral HPLC chromatograms of $8b$
$^1$H NMR of 8c

$^{31}$P NMR of 8c
$^{13}$C NMR of 8e

Chiral HPLC chromatograms of 8e

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.080</td>
<td>VV</td>
<td>0.3243</td>
<td>8036.97559</td>
<td>371.68729</td>
<td>100.0000</td>
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</table>
$^1$H NMR of 8d

$^{31}$P NMR of 8d
$^{13}$C NMR of 8d

Chiral HPLC chromatograms of 8d

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime (min)</th>
<th>Type</th>
<th>Width (min)</th>
<th>Area (mAU*s)</th>
<th>Height (mAU)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.963</td>
<td>BB</td>
<td>1.0990</td>
<td>1.57264e4</td>
<td>216.10506</td>
<td>100.000</td>
</tr>
</tbody>
</table>
$^1$H NMR of 8e

\[ \text{O} \]
\[ \text{NH}_2 \]
\[ \text{OCH}_3 \]

8e

$^{31}$P NMR of 8e
$^{13}$C NMR of 8e

Chiral HPLC chromatograms of 8e

| Peak RetTime Type Width Area Height Area |
|----------------------------------------|----------------|---|---|---|---|
| 1 6.197 BV 0.2148 6538.37207 457.20520 100.0000 |
$^1$H NMR of 8f

$^{31}$P NMR of 8f
$^{13}$C NMR of 8f

Chiral HPLC chromatograms of 8f

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BV</td>
<td>0.9039</td>
<td>3.62257e4</td>
<td>614.41528</td>
<td>100.000</td>
</tr>
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</table>
(S)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (11a)

$^1$H NMR of 11a
$^{13}$C NMR of 11a

Chiral HPLC Chromatograms of 11a

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.575</td>
<td>BB</td>
<td>0.477</td>
<td>492.90408</td>
<td>16.00656</td>
<td>5.2228</td>
</tr>
<tr>
<td>2</td>
<td>11.171</td>
<td>BB</td>
<td>0.448</td>
<td>8944.63574</td>
<td>316.22061</td>
<td>94.7772</td>
</tr>
</tbody>
</table>
For comparison compound 11a was also analyzed using a chiracel OJ-H column in comparison with the literature.⁹

Chiral HPLC Chromatograms of 11a

![Chiral HPLC Chromatogram of 11a](image)

<table>
<thead>
<tr>
<th>Peak RetTime Type Width Area Height Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 19.035 MM 0.5867 1.50542e4 427.68332 93.9108</td>
<td></td>
</tr>
<tr>
<td>2 23.192 MM 0.6424 976.11206 25.32313 6.0892</td>
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</tr>
</tbody>
</table>

Chiral HPLC Chromatogram of crystallized product 11a

![Chiral HPLC Chromatogram of crystallized 11a](image)

<table>
<thead>
<tr>
<th>Peak RetTime Type Width Area Height Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 18.989 MM 0.5980 2.30864e4 643.44177 96.5849</td>
<td></td>
</tr>
<tr>
<td>2 23.121 MM 0.7581 816.29865 17.94708 3.4151</td>
<td></td>
</tr>
</tbody>
</table>
(S)-2-methyl-1,2,3,4-tetrahydroquinoline (11b)

$^1$H NMR of 11b
$^{13}$C NMR of 11b

Chiral HPLC Chromatograms of 11b

---

<table>
<thead>
<tr>
<th>Peak RetTime Type Width</th>
<th>Area [mAU]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1 6.777 MM 0.1708</td>
<td>2120.12207</td>
<td>206.83456</td>
<td>5.7703</td>
</tr>
<tr>
<td>2 7.786 MM 0.2332</td>
<td>3.46218e4</td>
<td>2474.55640</td>
<td>94.2297</td>
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</tbody>
</table>
(R)-2-phenyl-1,2,3,4-tetrahydroquinoline (11c)

$^1$H NMR of 11c
$^{13}$C NMR of 11c

Chiral HPLC Chromatograms of 11c
(R)-4-methyl-1,2,3,4-tetrahydroquinoline (11d)

$^1$H NMR of 11d

$^{13}$C NMR of 11d
Chiral HPLC Chromatograms of 11d

![Chiral HPLC Chromatograms of 11d](image)

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.412</td>
<td>MM</td>
<td>0.5150</td>
<td>1.74665e4</td>
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<tr>
<td>2</td>
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<td>0.5373</td>
<td>3.21006e4</td>
<td>995.67267</td>
<td>64.7618</td>
</tr>
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</table>
(S)-2-ethyl-1,2,3,4-tetrahydroquinoline (11e)

$^1$H NMR of 11e
$^{13}$C NMR of 11e

Chiral HPLC Chromatograms of 11e

| Peak RetTime Type Width Area Height Area % |
|------------------------------------------|------------------------------------------|
| 1 6.562 MM 0.1823 2201.67993 201.33543 12.6316 |
| 2 7.910 MM 0.2248 1.52283e4 1129.25708 87.3684 |
(R)-2-isopropyl-1,2,3,4-tetrahydroquinoline (11f)

$^1$H NMR of 11f
$^{13}$C NMR of 11f

Chiral HPLC Chromatograms of 11f

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>5.896</td>
<td>0.1692</td>
<td>1.3659e4</td>
<td>1345.61450</td>
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<tr>
<td>2</td>
<td>8.525</td>
<td>0.3666</td>
<td>6.5869e4</td>
<td>2994.45923</td>
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</tbody>
</table>
(S)-2-methyl-6-nitro-1,2,3,4-tetrahydroquinoline (11g)

$^1$H NMR of 11g
$^{13}$C NMR of 11g

Chiral HPLC Chromatogram of 11g

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.126</td>
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<td>0.6119</td>
<td>256.38251</td>
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<td>7.1706</td>
</tr>
<tr>
<td>2</td>
<td>20.442</td>
<td>MM</td>
<td>0.9745</td>
<td>3319.06494</td>
<td>56.76318</td>
<td>92.8294</td>
</tr>
</tbody>
</table>
Chiral HPLC Chromatogram of crystallized product 11g

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.352</td>
<td>MM</td>
<td>0.6727</td>
<td>41.21978</td>
<td>1.02125</td>
<td>2.0388</td>
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<tr>
<td>2</td>
<td>20.673</td>
<td>MM</td>
<td>0.9551</td>
<td>1980.56396</td>
<td>34.56263</td>
<td>97.9612</td>
</tr>
</tbody>
</table>
$^1$H NMR of 11h
$^{13}$C NMR of 11h

Chiral HPLC Chromatograms of 11h
$^1$H NMR of 11i
$^{13}$C NMR of 11i

Chiral HPLC Chromatograms of 11i

Signal 6: DAD1 F, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>18.810</td>
<td>MM</td>
<td>0.5948</td>
<td>2835.94873</td>
<td>79.46480</td>
<td>51.8408</td>
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<tr>
<td>2</td>
<td>24.040</td>
<td>MM</td>
<td>0.7355</td>
<td>2634.54956</td>
<td>59.70087</td>
<td>48.1592</td>
</tr>
</tbody>
</table>

Totals: 5470.49829 139.16567
\[^1\]H NMR of 11j

\[^{13}\]C NMR of 11j
Chiral HPLC Chromatograms of 11j

Signal 6: DAD1 F, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.620</td>
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<td>0.4169</td>
<td>2.45852e4</td>
<td>982.85883</td>
<td>65.2355</td>
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<tr>
<td>2</td>
<td>9.041</td>
<td>MM</td>
<td>0.4524</td>
<td>1.31016e4</td>
<td>482.72311</td>
<td>34.7645</td>
</tr>
</tbody>
</table>

Totals: 3.76868e4 1465.50194
X-Ray Data Collection and Structural Refinement Statistics

The X-ray data were collected on a Bruker D8 Venture dual-source diffractometer equipped with a PHOTON II detector and an Oxford Cryostream 800 cooling system, using mirror-monochromatized CuKα radiation (λ = 1.54184 Å) from a microfocus source, in a series of φ- and ω-scans.APEX3 software was used for data collection, integration and reduction. Semi-empirical absorption correction was applied using SADABS-2016/2.

The structures were solved using SHELXT-2014/5 (5a_123K, 11a_253K) or SHELXT-2018/2 (5c_253K, 8d_253K) and refined by full-matrix least-squares using SHELXL-2018/3 within Olex2 and WinGX packages. All non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 (or 1.5 in case of methyl groups) times larger than the respective parent atoms. Nitrogen- and oxygen-bound hydrogen atoms were found in the difference electron density map and were modelled as constrained, with isotropic displacement parameters 1.2 (for nitrogen-bound) or 1.5 (for oxygen-bound) times larger than those of the respective parent atoms. In case of 11a_253K, the amino group was instead allowed to refine as a rigid body to allow for the partial sp³ character of the nitrogen, i.e. the out-of-plane position of the attached hydrogen atom. For disordered moieties, 1,2- and 1,3-interatomic distances were restrained to be equal and the anisotropic displacement parameters of the atoms were restrained to be equal for bonded and spatially close atoms. In case of 5c_253K, the minor disorder component of the 2,4,6-trisopropylbenzenesulfonyl group was partially refined as a rigid body including the benzene ring with the attached secondary carbon atoms of isopropyl groups and the sulfonyl (–SO₂–) group. The occupancies of the disordered moieties were either allowed to refine freely (5c_253K) or were fixed to 0.5 as required by the proximity of a two-fold rotation axis (8d_253K).

CCDC 1935842–1935846 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.
Table 3. Crystallographic data

<table>
<thead>
<tr>
<th>Complex</th>
<th>5a_123K</th>
<th>5c_253K</th>
<th>8d_253K</th>
<th>11a_253K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC Number</td>
<td>1935843</td>
<td>1935844</td>
<td>1935845</td>
<td>1935846</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{25}H_{16}NO_{3}PS</td>
<td>C_{10}H_{15}NO_{3}PS</td>
<td>C_{19}H_{23}Cl_{2}N_{2}O_{6}P_{2}</td>
<td>C_{10}H_{15}BrN</td>
</tr>
<tr>
<td>Formula weight</td>
<td>479.59</td>
<td>561.69</td>
<td>639.50</td>
<td>226.12</td>
</tr>
<tr>
<td>T/K</td>
<td>123.0(1)</td>
<td>253.0(1)</td>
<td>253.0(1)</td>
<td>253.0(1)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1</td>
<td>P2_12_12</td>
<td>P4_2_2</td>
<td>P2_12_12</td>
</tr>
<tr>
<td>a/Å</td>
<td>10.6790(7)</td>
<td>10.5840(6)</td>
<td>10.7127(2)</td>
<td>16.0321(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.0178(8)</td>
<td>15.7917(8)</td>
<td>10.7127(2)</td>
<td>6.1532(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>11.2241(7)</td>
<td>18.4493(10)</td>
<td>27.9476(6)</td>
<td>9.7828(3)</td>
</tr>
<tr>
<td>(\alpha^{\circ})</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta^{\circ})</td>
<td>112.3257(14)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\gamma^{\circ})</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V/Å³</td>
<td>1332.50(15)</td>
<td>3083.6(3)</td>
<td>3207.32(14)</td>
<td>965.06(5)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{calc}/g \text{ cm}^{-3})</td>
<td>1.195</td>
<td>1.210</td>
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<td>1.556</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>1.878</td>
<td>1.721</td>
<td>3.070</td>
<td>5.338</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7543 and 0.5780</td>
<td>0.7536 and 0.6107</td>
<td>0.7536 and 0.6332</td>
<td>0.7543 and 0.5764</td>
</tr>
<tr>
<td>F(000)</td>
<td>516.0</td>
<td>1208.0</td>
<td>1352.0</td>
<td>456.0</td>
</tr>
<tr>
<td>Crystal color and shape</td>
<td>colorless, prism</td>
<td>yellow, lath</td>
<td>colorless, prism</td>
<td>colorless, block</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.655×0.634×0.502</td>
<td>0.644×0.628×0.384</td>
<td>0.314×0.283×0.221</td>
<td>0.337×0.312×0.294</td>
</tr>
<tr>
<td>2(\theta) range for data collection (^\circ)</td>
<td>8.952 to 161.056</td>
<td>7.368 to 145.612</td>
<td>8.84 to 144.914</td>
<td>10.594 to 161.068</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-13 \leq h \leq 13), (-13 \leq k \leq 13), (-13 \leq l \leq 13)</td>
<td>(-13 \leq h \leq 13), (-19 \leq k \leq 19), (-13 \leq l \leq 13)</td>
<td>(-20 \leq h \leq 20), (-7 \leq k \leq 7), (-7 \leq l \leq 7)</td>
<td>(-20 \leq h \leq 20), (-7 \leq k \leq 7), (-7 \leq l \leq 7)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>31499</td>
<td>60068</td>
<td>45989</td>
<td>25154</td>
</tr>
<tr>
<td>Reflections ([R_{int}])</td>
<td>5643 [0.0313]</td>
<td>6006 [0.0411]</td>
<td>3167 [0.0835]</td>
<td>2073 [0.0457]</td>
</tr>
<tr>
<td>Data completeness (%)</td>
<td>99.5 to 2(\theta) = 135.50°</td>
<td>97.6 to 2(\theta) = 135.358°</td>
<td>99.2 to 2(\theta) = 135.50°</td>
<td>97.6 to 2(\theta) = 135.358°</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>5643/1/300</td>
<td>6006/981/483</td>
<td>3167/20/208</td>
<td>2073/0/114</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.034</td>
<td>1.137</td>
<td>1.054</td>
<td>1.145</td>
</tr>
<tr>
<td>Final R indices ([I &gt; 2\sigma(I)])</td>
<td>R1 = 0.0271, wR2 = 0.0709</td>
<td>R1 = 0.0437, wR2 = 0.1133</td>
<td>R1 = 0.0278, wR2 = 0.0744</td>
<td>R1 = 0.0656, wR2 = 0.1579</td>
</tr>
<tr>
<td>Final R indices [all data]</td>
<td>R1 = 0.0273, wR2 = 0.0711</td>
<td>R1 = 0.0440, wR2 = 0.1137</td>
<td>R1 = 0.0280, wR2 = 0.0744</td>
<td>R1 = 0.0662, wR2 = 0.1581</td>
</tr>
<tr>
<td>Largest diff. peak/hole ((e \text{ Å}^{-3}))</td>
<td>0.346/−0.258</td>
<td>0.477/−0.282</td>
<td>0.253/−0.190</td>
<td>0.475/−0.632</td>
</tr>
<tr>
<td>Flack parameter (x)</td>
<td>0.014(9)</td>
<td>0.029(4)</td>
<td>−0.007(5)</td>
<td>0.050(18)</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0090(10)</td>
<td>0.0130(15)</td>
<td>-</td>
<td>0.014(2)</td>
</tr>
</tbody>
</table>
References


