Design and Synthesis of New Chiral Phosphorus–Olefin Bidentate Ligands and Their Use in the Rhodium-Catalyzed Asymmetric Addition of Organoboroxines to N-Sulfonyl Imines

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Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

THF and dioxane were purified by passing through neutral alumina columns under nitrogen. DMF was distilled over CaH$_2$ under vacuum. CH$_2$Cl$_2$ was distilled over CaH$_2$ under nitrogen. Et$_3$N was distilled over KOH under nitrogen. C$_6$H$_6$ was distilled over benzophenone ketyl under nitrogen. Pentane was distilled over benzophenone ketyl in the presence of triglyme under nitrogen.

2-methyl-2-propenyl bromide (Aldrich), NaH (Kanto Chemical; 60 wt% in mineral oil), Grubbs catalyst (Aldrich; 2nd generation), trifluoroacetic acid (Wako Chemicals), chlorodiphenylphosphine (Wako Chemicals), and methanesulfonyl chloride (Wako Chemicals) were used as received.

(S)-2, (7R)-7, 2-(benzyloxymethyl)-2-propenol, 2-phenyl-2-propenyl bromide, Rh(acac)(C$_2$H$_4$)$_2$, and [RhCl(C$_2$H$_4$)$_2$]$_2$ were synthesized following the literature procedures. Imines 5 and 8 were prepared from the corresponding aldehydes and sulfonamides following the literature procedure. Organoboroxines were prepared by dehydration of the corresponding organoboronic acids following the literature procedure.

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemical and used as received.

II. Synthesis of Ligands and Complexes

(S)-1a

2-Methyl-2-propenyl bromide (726 mg, 5.38 mmol) and NaH (256 mg, 6.40 mmol; 60 wt% in mineral oil) were successively added to a solution of (S)-2 (1.01 g, 4.08 mmol) in DMF (9.0 mL) at 0 °C and the mixture was stirred for 1.5 h at room temperature. The reaction was quenched with H₂O at 0 °C and this was extracted with EtOAc/hexane (1/10). The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford compound (S)-S1 as a colorless oil (1.17 g, 3.88 mmol; 95% yield). [α]35D -55.4 (c 1.02, CHCl₃).

1H NMR (CDCl₃, 50 °C): δ 7.25 (t, 3Jₕₜₜ = 7.5 Hz, 2H), 7.19-7.15 (m, 3H), 6.00 (ddd, 3Jₕₜₜ = 17.0, 10.2, and 6.8 Hz, 1H), 5.06 (d, 3Jₕₜₜ = 10.8 Hz, 1H), 5.04 (d, 3Jₕₜₜ = 18.4 Hz, 1H), 4.77 (s, 1H), 4.73 (s, 1H), 4.34 (bs, 1H), 3.75-3.56 (m, 1H), 3.46 (d, 3Jₕₜₜ = 16.3 Hz, 1H), 3.16-3.04 (m, 1H), 2.91 (dd, 2Jₕₜₜ = 13.6 Hz and 3Jₕₜₜ = 6.8 Hz, 1H), 1.60 (s, 3H), 1.42 (s, 9H).

13C NMR (CDCl₃, 50 °C): δ 155.4, 142.8, 139.0, 137.5, 129.5, 128.4, 126.4, 116.2, 111.6, 79.7, 61.5, 52.2, 39.2, 28.6, 20.1. HRMS (ESI-TOF) calcld for C₁₀H₁₂NO₂Na (M+Na⁺) 324.1934, found 324.1930.

Grubbs catalyst (66.3 mg, 78.1 μmol; 2nd generation) was added to a solution of (S)-S1 (1.16 g, 3.85 mmol) in C₆H₆ (38 mL) and the mixture was stirred for 6 h at 60 °C. The solvent was removed under vacuum, and the residue was chromatographed on silica gel with EtOAc/hexane = 1/20 to afford compound (S)-3a as a colorless oil (1.03 g, 3.77 mmol; 98% yield, ~6/4 mixture of rotamers). [α]35D +177 (c 1.10, CHCl₃).

1H NMR (CDCl₃): δ 7.28-7.22 (m, 2H), 7.22-7.17 (m, 1H), 7.15 (d, 3Jₕₜₜ = 7.5 Hz, 0.8H), 7.12 (d, 3Jₕₜₜ = 7.5 Hz, 1.2H), 5.26 (s, 0.4H), 5.23 (s, 0.6H), 4.73-4.67 (m, 0.4H), 4.61-4.55 (m, 0.6H), 4.02 (d, 3Jₕₜₜ = 15.0 Hz, 0.6H), 3.89 (d, 3Jₕₜₜ = 14.9 Hz, 0.4H), 3.70 (dd, 3Jₕₜₜ = 14.9 Hz and 3Jₕₜₜ = 4.0 Hz, 0.6H), 3.56 (dd, 3Jₕₜₜ = 15.0 Hz and 3Jₕₜₜ = 4.8 Hz, 0.4H), 3.17 (dd, 3Jₕₜₜ = 12.9 Hz and 3Jₕₜₜ = 3.4 Hz, 0.4H), 3.13 (dd, 3Jₕₜₜ = 13.0 Hz and 3Jₕₜₜ = 3.4 Hz, 0.6H), 2.84 (dd, 3Jₕₜₜ = 13.0 Hz and 3Jₕₜₜ = 8.2 Hz, 0.4H), 2.69 (dd, 3Jₕₜₜ = 12.9 Hz and 3Jₕₜₜ = 8.1 Hz, 0.6H), 1.66 (s, 1.8H), 1.63 (s, 1.2H), 1.55 (s, 5.4H), 1.50 (s, 3.6H). 13C NMR (CDCl₃): δ 154.2, 154.0, 138.2, 135.2, 135.1, 129.9, 129.6, 128.2, 127.9, 126.2, 126.0, 123.5, 123.3, 79.5, 79.1, 65.9, 65.6, 56.9, 56.6, 41.3, 39.8, 28.70, 28.66, 14.2, 14.1. HRMS (ESI-TOF) calcld for C₁₀H₁₂NO₂Na (M+Na⁺) 296.1621, found 296.1617.

Trifluoroacetic acid (7.5 mL) was added to a solution of (S)-3a (1.03 g, 3.77 mmol) in CH₂Cl₂ (37 mL) and the mixture was stirred for 1.5 h at room temperature. The solvent was removed under vacuum, and the remaining trifluoroacetic acid was further removed by dissolving the residue in C₆H₆ and concentrated under vacuum for three times, followed by the same sequence with hexane for three times. The residue thus obtained was chromatographed on silica gel with MeOH/CH₂Cl₂ = 1/10 to afford compound (S)-S2 as a purple solid (1.03 g, 3.59 mmol; 95% yield). [α]35D +54.5 (c 0.32, CHCl₃).

1H NMR (CDCl₃): δ 10.30 (bs, 1H), 9.23 (bs, 1H), 7.31 (t, 3Jₕₜₜ = 7.5 Hz, 2H), 7.25 (t, 3Jₕₜₜ = 8.1 Hz, 1H), 7.20 (d, 3Jₕₜₜ = 6.8 Hz, 2H), 5.34 (s, 1H), 4.70-4.62 (m, 1H), 3.84 (d, 3Jₕₜₜ = 4.8 Hz, 0.8H).
= 15.0 Hz, 1H), 3.80 (d, $^2\text{J}_{\text{HH}} = 15.0$ Hz, 1H), 3.15 (dd, $^2\text{J}_{\text{HH}} = 13.6$ Hz and $^3\text{J}_{\text{HH}} = 6.1$ Hz, 1H), 2.95 (dd, $^2\text{J}_{\text{HH}} = 13.6$ Hz and $^3\text{J}_{\text{HH}} = 8.9$ Hz, 1H), 1.78 (s, 3H). $^{13}\text{C}$ NMR (CDCl$_3$): δ 162.8 (q, $^1\text{J}_{\text{CP}} = 35.9$ Hz), 135.8, 135.3, 129.2, 128.8, 127.2, 122.4, 117.0 (q, $^1\text{J}_{\text{CP}} = 293$ Hz), 66.9, 53.9, 39.3, 13.6. HRMS (ESI-TOF) calcd for C$_{12}$H$_{16}$O$_{2}$ (M−CF$_3$CO$_2$) 174.1277, found 174.1278.

1 M NaOHaq (15 mL) was added to a solution of (S)-S2 (1.03 g, 3.59 mmol) in Et$_2$O (5.0 mL) and the mixture was extracted with Et$_2$O. The organic layer was dried over MgSO$_4$, filtered, and concentrated under vacuum. The residue was dissolved in THF (9.0 mL) and Et$_3$N (2.20 mL, 15.8 mmol) and chlorodiphenyolphosphine (710 µL, 3.95 mmol) were successively added to it with additional THF (2.0 mL). The mixture was stirred for 9 h at room temperature, and the volatiles were removed under vacuum. This was chromatographed on silica gel with degassed Et$_3$N/hexane = 1/2 to afford compound (S)-1a as a yellow oil (1.06 g, 2.97 mmol; 83% yield). [α]$^{25}$D +235 (c 1.03, THF).

$^1$H NMR (C$_6$D$_6$): δ 7.58 (t, $^3\text{J} = 7.2$ Hz, 2H), 7.48 (t, $^3\text{J} = 7.4$ Hz, 2H), 7.23-7.19 (m, 2H), 7.18-7.05 (m, 9H), 5.27-5.21 (m, 1H), 4.77-4.68 (m, 1H), 3.60 (bs, 2H), 3.44 (ddd, $^2\text{J}_{\text{HH}} = 12.8$ Hz, $^3\text{J}_{\text{HH}} = 3.9$ Hz, and $^4\text{J}_{\text{HH}} = 2.8$ Hz, 1H), 2.75 (dd, $^2\text{J}_{\text{HH}} = 12.8$ Hz and $^3\text{J}_{\text{HH}} = 9.5$ Hz, 1H), 1.28 (s, 3H). $^{13}\text{C}$ NMR (C$_6$D$_6$): δ 140.2 (d, $^1\text{J}_{\text{CP}} = 7.7$ Hz), 139.5 (d, $^1\text{J}_{\text{CP}} = 18.1$ Hz), 139.4, 137.1, 134.9 (d, $^1\text{J}_{\text{CP}} = 12.9$ Hz), 134.8 (d, $^1\text{J}_{\text{CP}} = 12.9$ Hz), 132.7 (d, $^1\text{J}_{\text{CP}} = 19.6$ Hz), 132.6 (d, $^1\text{J}_{\text{CP}} = 19.6$ Hz), 130.0, 128.61 (d, $^1\text{J}_{\text{CP}} = 5.7$ Hz), 128.59 (d, $^1\text{J}_{\text{CP}} = 4.7$ Hz), 128.5 (d, $^1\text{J}_{\text{CP}} = 4.1$ Hz), 126.3, 125.2 (d, $^1\text{J}_{\text{CP}} = 6.7$ Hz), 73.1 (d, $^1\text{J}_{\text{CP}} = 30.5$ Hz), 57.6 (d, $^1\text{J}_{\text{CP}} = 9.3$ Hz), 45.2 (d, $^1\text{J}_{\text{CP}} = 5.7$ Hz), 14.0. $^{31}$P$^{1}$H NMR (C$_6$D$_6$): δ 43.5 (s). HRMS (ESI-TOF) calcd for C$_{24}$H$_{28}$NP (M+H$^+$) 358.1719, found 358.1717.

2-(Benzzyloxy)methyl)-2-propenyl methanesulfonate

Et$_3$N (5.40 mL, 38.7 mmol) and methanesulfonyl chloride (1.50 mL, 19.4 mmol) were successively added to a solution of 2-(benzzyloxy)methyl)-2-propenol (2.75 g, 15.4 mmol) in CH$_2$Cl$_2$ (25 mL) at 0 °C. The mixture was stirred for 50 min at 0 °C and the reaction was quenched with saturated NaHCO$_3$aq. This was extracted with CH$_2$Cl$_2$ and the organic layer was washed with saturated NaClaq, dried over MgSO$_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/4 to afford 2-(benzzyloxy)methyl)-2-propenyl methanesulfonate as a colorless oil (2.88 g, 11.2 mmol; 73% yield).

$^1$H NMR (CDCl$_3$): δ 7.38-7.28 (m, 5H), 5.40-5.37 (m, 2H), 4.76 (s, 2H), 4.52 (s, 2H), 4.08 (s, 2H), 2.99 (s, 3H). $^{13}$C NMR (CDCl$_3$): δ 139.1, 137.8, 128.5, 127.9, 127.8, 118.2, 72.5, 70.2, 70.1, 37.8. HRMS (ESI-TOF) calcd for C$_{12}$H$_{16}$O$_4$SNa (M+Na$^+$) 279.0662, found 279.0663.

(S)-1b

This was synthesized from (S)-2 and 2-(benzzyloxy)methyl)-2-propenyl methanesulfonate, following the procedure for (S)-1a. Brown oil. 62% overall yield. [α]$^{25}$D +187 (c 0.56, THF).

$^1$H NMR (C$_6$D$_6$): δ 7.57 (t, $^3\text{J} = 7.1$ Hz, 2H), 7.46 (t, $^3\text{J} = 7.6$ Hz, 2H), 7.21-7.11 (m, 13H), 7.09-7.04 (m, 3H), 5.56-5.53 (m, 1H), 4.80-4.73 (m, 1H), 4.15 (d, $^2\text{J}_{\text{HH}} = 12.2$ Hz, 1H), 4.11 (d, $^2\text{J}_{\text{HH}} = 12.1$ Hz, 1H), 3.86-3.76 (m, 2H), 3.68-3.61 (m, 2H), 3.38 (ddd, $^2\text{J}_{\text{HH}} = 12.7$ Hz,
$^3J_{HH} = 4.2$ Hz, and $^4J_{HH} = 2.8$ Hz, 1H), 2.80 (ddd, $^2J_{HH} = 12.8$ Hz, $^3J_{HH} = 9.3$ Hz, and $^4J_{HH} = 0.6$ Hz, 1H). $^{13}$C NMR ($C_6D_6$): δ 139.8 (d, $J_{CP} = 7.2$ Hz), 139.3 (d, $J_{CP} = 18.1$ Hz), 139.2, 139.0, 138.9, 134.9 (d, $J_{CP} = 12.9$ Hz), 134.8 (d, $J_{CP} = 12.9$ Hz), 132.7 (d, $J_{CP} = 20.2$ Hz), 132.6 (d, $J_{CP} = 19.1$ Hz), 130.0, 128.64 (d, $J_{CP} = 6.2$ Hz), 128.59 (d, $J_{CP} = 7.2$ Hz), 128.5 (d, $J_{CP} = 5.2$ Hz), 127.9, 127.7, 127.3 (d, $J_{CP} = 6.7$ Hz), 126.4, 72.9 (d, $J_{CP} = 31.5$ Hz), 72.0, 66.9, 54.6 (d, $J_{CP} = 9.3$ Hz), 44.7 (d, $J_{CP} = 5.2$ Hz). $^{31}$P{$^1$H} NMR ($C_6D_6$): δ 44.8 (s). HRMS (ESI-TOF) calcd for $C_{31}H_{31}NOP$ (M+H$^+$) 464.2138, found 464.2130.

(S)-1c

This was synthesized from (S)-2 and 2-phenyl-2-propenyl bromide, following the procedure for (S)-1a. Pink solid. 85% overall yield. [α]$^{25}_D$ +224 (c 0.53, THF).

$^1$H NMR ($C_6D_6$): δ 7.65-7.61 (m, 2H), 7.54-7.50 (m, 2H), 7.25-7.21 (m, 2H), 7.17-7.05 (m, 9H), 6.99-6.95 (m, 5H), 6.00 (dt, $^3J_{HH} = 4.9$ Hz and $^4J_{HH} = 2.2$ Hz, 1H), 4.92-4.85 (m, 1H), 4.24-4.15 (m, 2H), 3.52 (ddd, $^2J_{HH} = 12.8$ Hz, $^3J_{HH} = 4.2$ Hz, and $^4J = 2.8$ Hz, 1H), 2.80 (dd, $^2J_{HH} = 12.8$ Hz and $^3J_{HH} = 9.5$ Hz, 1H). $^{13}$C NMR ($C_6D_6$): δ 139.9 (d, $J_{CP} = 8.3$ Hz), 139.6, 139.14 (d, $J_{CP} = 17.6$ Hz), 139.09, 134.9 (d, $J_{CP} = 12.9$ Hz), 134.8 (d, $J_{CP} = 12.9$ Hz), 134.2, 132.7 (d, $J_{CP} = 20.2$ Hz), 132.5 (d, $J_{CP} = 19.6$ Hz), 130.0, 128.72 (d, $J_{CP} = 6.2$ Hz), 128.68 (d, $J_{CP} = 8.8$ Hz), 128.66 (d, $J_{CP} = 6.2$ Hz), 128.6, 127.8, 126.4, 125.9, 125.5 (d, $J_{CP} = 6.7$ Hz), 73.6 (d, $J_{CP} = 31.0$ Hz), 54.5 (d, $J_{CP} = 9.3$ Hz), 45.1 (d, $J_{CP} = 6.2$ Hz). $^{31}$P{$^1$H} NMR ($C_6D_6$): δ 44.2 (s). HRMS (ESI-TOF) calcd for $C_{29}H_{27}NP$ (M+H$^+$) 420.1876, found 420.1864.

Rh(acac)((S)-1a) (4)

A solution of (S)-1a (318 mg, 0.890 mmol) in $C_6H_6$ (4.0 mL) was added slowly over 25 min to a solution of Rh(acac)($C_2H_4$)$_2$ (214 mg, 0.829 mmol) in $C_6H_6$ (1.0 mL) at 30 °C, and the mixture was stirred for 1 h at 30 °C. The reaction mixture was filtered through PTFE membrane with $C_6H_6$ and the solvent was removed under vacuum. The solid thus obtained was washed with hexane and dried under vacuum to afford complex 4 as a yellow solid (396 mg, 0.708 mmol; 85% yield). [α]$^{25}_D$ -20.5 (c 0.52, THF). Recrystallization of this complex from benzene/pentane afforded single crystals suitable for X-ray crystallographic analysis.

$^1$H NMR ($C_6D_6$): δ 8.25-8.18 (m, 2H), 7.98-7.92 (m, 2H), 7.17-7.07 (m, 3H), 7.06-6.94 (m, 8H), 5.36 (s, 1H), 3.75 (s, 1H), 3.52-3.45 (m, 1H), 2.84 (t, $J_{HH} = 14.0$ Hz, 1H), 2.63 (dd, $^2J_{HH} = 12.8$ Hz and $^3J_{HH} = 8.8$ Hz, 1H), 2.44-2.29 (m, 2H), 1.97 (s, 3H), 1.93 (s, 3H), 1.89 (s, 3H). $^{31}$P{$^1$H} NMR ($C_6D_6$): δ 127.9 (d, $^1J_{PRh} = 202$ Hz). Anal. Calcd for $C_{29}H_{31}NO_2PRh$: C, 62.26; H, 5.59. Found: C, 62.27; H, 5.52.

General Procedure for [RhCl((S)-1)]$_2$

A solution of (S)-1 (1.0 equiv) in $C_6H_6$ (ca. 5.0 mL for 1.0 mmol of (S)-1) was added slowly over 20 min to a solution of [RhCl($C_2H_4$)$_2$]$_2$ (1.1 equiv Rh) in $C_6H_6$ (ca. 2.5 mL for 1.0 mmol of (S)-1) at 30 °C, and the mixture was stirred for 1 h at 30 °C. The reaction mixture was filtered through PTFE membrane with $C_6H_6$ and the solvent was removed under vacuum. The solid thus obtained was washed with hexane and dried under vacuum to afford complex [RhCl((S)-1)]$_2$, which was directly used as a catalyst for the addition reaction.
III. Catalytic Reactions

General Procedure for Table 1.

4 M KOHaq (10 µL, 40 µmol) was added to a solution of [RhCl((S)-1c)]₂ (5.6 mg, 10 µmol Rh), imine 5 (0.200 mmol), and organoboroxine (0.600 mmol B) in dioxane (0.50 mL), and the mixture was stirred for 6 h at 60 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC to afford compound 6.

Entry 1. (CAS 796966-21-7 for (R)-enantiomer) White solid. 90% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 16.8 min [minor enantiomer], 22.0 min [major enantiomer]. 97% ee. [α]20\text{D} +6.1 (c 0.93, CHCl₃). The absolute configuration was determined by comparison of the optical rotation with the literature value.⁹

¹H NMR (CDCl₃): δ 7.55 (d, 3JHH = 8.1 Hz, 2H), 7.24-7.14 (m, 7H), 7.07-7.03 (m, 4H), 5.53 (d, 3JHH = 6.8 Hz, 1H), 5.06 (d, 3JHH = 6.8 Hz, 1H), 2.39 (s, 3H).

¹³C NMR (CDCl₃): δ 143.5, 140.2, 139.2, 137.4, 133.5, 129.5, 128.9, 128.8, 128.7, 127.9, 127.4, 60.9, 21.6.

Entry 3. (CAS 831225-96-8 for (R)-enantiomer) White solid. 71% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 16.1 min [minor enantiomer], 25.0 min [major enantiomer]. 95% ee. [α]20\text{D} –8.7 (c 1.00, CHCl₃). The absolute configuration was determined by comparison of the optical rotation with the literature value.⁹

¹H NMR (CDCl₃): δ 7.54 (d, 3JHH = 8.3 Hz, 2H), 7.45 (d, 3JHH = 8.2 Hz, 2H), 7.28-7.22 (m, 5H), 7.13 (d, 3JHH = 7.9 Hz, 2H), 7.07-7.03 (m, 2H), 5.62 (d, 3JHH = 7.2 Hz, 1H), 5.18 (d, 3JHH = 6.8 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (CDCl₃): δ 144.4, 143.7, 139.9, 137.2, 129.8 (q, 2JCF = 31.6 Hz), 129.6, 129.0, 128.2, 127.9, 127.4, 127.3, 125.5, 124.1 (q, 1JCF = 272 Hz), 61.1, 21.5.

Entry 4. (CAS 796966-22-8 for (R)-enantiomer) Pale yellow solid. 90% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 20.3 min [minor enantiomer], 32.1 min [major enantiomer]. 97% ee. $[\alpha]^{20}_D +20.4$ (c 1.00, CHCl$_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.$^9$

$^1$H NMR (CDCl$_3$): $\delta$ 7.55 (d, $^3$J$_{HH}$ = 8.2 Hz, 2H), 7.23-7.16 (m, 3H), 7.13 (d, $^3$J$_{HH}$ = 8.4 Hz, 2H), 7.12-7.07 (m, 2H), 6.99 (d, $^3$J$_{HH}$ = 8.8 Hz, 2H), 6.72 (d, $^3$J$_{HH}$ = 8.5 Hz, 2H), 5.52 (d, $^3$J$_{HH}$ = 7.1 Hz, 1H), 5.15 (d, $^3$J$_{HH}$ = 7.1 Hz, 1H), 3.74 (s, 3H), 2.37 (s, 3H).

$^{13}$C NMR (CDCl$_3$): $\delta$ 159.1, 143.2, 140.9, 137.6, 132.9, 129.4, 128.7, 128.6, 127.6, 127.4, 127.3, 114.0, 60.9, 55.4, 21.6.

Entry 5. (CAS 898269-04-0 for (R)-enantiomer) White solid. 95% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 15.0 min [major enantiomer], 17.6 min [minor enantiomer]. 94% ee. $[\alpha]^{20}_D +27.5$ (c 1.01, CHCl$_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.$^9$

$^1$H NMR (CDCl$_3$): $\delta$ 7.51 (d, $^3$J$_{HH}$ = 8.2 Hz, 2H), 7.24-7.14 (m, 6H), 7.05 (d, $^3$J$_{HH}$ = 8.1 Hz, 2H), 6.97 (dd, $^3$J$_{HH}$ = 7.5 Hz and $^4$J$_{HH}$ = 1.4 Hz, 1H), 6.78 (td, $^3$J$_{HH}$ = 7.5 Hz and $^4$J$_{HH}$ = 1.4 Hz, 1H), 6.68 (d, $^3$J$_{HH}$ = 8.1 Hz, 1H), 5.76 (d, $^3$J$_{HH}$ = 9.5 Hz, 1H), 5.65 (d, $^3$J$_{HH}$ = 9.6 Hz, 1H), 3.59 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 156.5, 142.9, 140.7, 137.6, 129.7, 129.2, 129.1, 128.2, 127.8, 127.2, 127.1, 126.9, 120.8, 111.2, 59.1, 55.4, 21.5.
Entry 6. (CAS 158568-79-7 for (R)-enantiomer) Gray solid. 83% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.5 mL/min. Retention times: 24.6 min [minor enantiomer], 26.6 min [major enantiomer]. 96% ee. [α]^{20}_{D} +14.8 (c 1.02, CHCl₃). The absolute configuration was determined by comparison of the optical rotation with the literature value.⁹

¹H NMR (CDCl₃): δ 7.58 (d, 3J_{HH} = 8.1 Hz, 2H), 7.26-7.23 (m, 4H), 7.20-7.17 (m, 2H), 7.16 (d, 3J_{HH} = 8.5 Hz, 2H), 6.19 (dd, 3J_{HH} = 3.3 and 1.8 Hz, 1H), 5.99 (d, 3J_{HH} = 3.2 Hz, 1H), 5.62 (d, 3J_{HH} = 7.7 Hz, 1H), 5.12 (d, 3J_{HH} = 7.3 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (CDCl₃): δ 152.4, 143.3, 142.7, 138.4, 137.5, 129.5, 128.7, 128.1, 127.4, 127.2, 110.4, 108.5, 55.6, 21.6.

Entry 7. The reaction was conducted for 24 h using 0.4 equiv of KOH. White solid. 73% yield.

The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 98/2, flow = 0.5 mL/min. Retention times: 72.4 min [major enantiomer], 87.2 min [minor enantiomer]. 97% ee. [α]^{20}_{D} −11.8 (c 1.01, CHCl₃). The absolute configuration was assigned by analogy with entry 1.

¹H NMR (CDCl₃): δ 7.63 (d, 3J_{HH} = 8.3 Hz, 2H), 7.23-7.16 (m, 5H), 7.14-7.10 (m, 2H), 5.57-5.53 (m, 1H), 4.86 (d, 3J_{HH} = 7.9 Hz, 1H), 4.83 (d, 3J_{HH} = 7.9 Hz, 1H), 2.39 (s, 3H), 1.98-1.82 (m, 2H), 1.74-1.58 (m, 2H), 1.50-1.32 (m, 4H). ¹³C NMR (CDCl₃): δ 143.2, 139.6, 137.9, 135.7, 129.4, 128.5, 127.5, 127.0, 125.9, 63.4, 25.2, 25.0, 22.4, 22.1, 21.6. Anal. Caled for C₂₀H₂₃NO₂S: C, 70.35; H, 6.79. Found: C, 70.27; H, 6.57.
Entry 8. (CAS 1112116-79-6 for (S)-enantiomer) The reaction was conducted in dioxane/H$_2$O (100/1). White solid. 73% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 9.6 min [minor enantiomer], 15.3 min [major enantiomer]. 96% ee. [$\alpha$]$^\circ_{D}$ –27.0 (c 0.64, CHCl$_3$). The absolute configuration was assigned by analogy with entry 1.

$^1$H NMR (CDCl$_3$): δ 7.45 (d, $^3$J$_{HH} = 8.3$ Hz, 2H), 7.11-7.07 (m, 3H), 7.03 (d, $^3$J$_{HH} = 8.0$ Hz, 2H), 6.93-6.87 (m, 2H), 4.98 (d, $^3$J$_{HH} = 8.2$ Hz, 1H), 4.03 (t, $^3$J$_{HH} = 8.1$ Hz, 1H), 2.31 (s, 3H), 1.97-1.91 (m, 1H), 1.77-1.70 (m, 1H), 1.65-1.51 (m, 3H), 1.32-1.25 (m, 1H), 1.20-1.02 (m, 3H), 0.98-0.80 (m, 2H). $^{13}$C NMR (CDCl$_3$): δ 142.7, 140.1, 137.9, 129.2, 128.1, 127.14, 127.12, 126.9, 63.6, 43.9, 29.9, 29.6, 26.3, 26.0, 21.5.

Entry 9. (CAS 796966-17-1 for (S)-enantomer) White solid. 83% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 17.1 min [major enantiomer], 22.9 min [minor enantiomer]. 96% ee. [$\alpha$]$^\circ_{D}$ –4.7 (c 0.99, CHCl$_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.$^9$
Entry 10. (CAS 796966-18-2 for (S)-enantiomer) Pale brown solid. 87% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 19.9 min [major enantiomer], 31.3 min [minor enantiomer]. 96% ee. $\text{[\ensuremath{\alpha}]^{20}_{D} \text{ –19.1 (c 1.00, CHCl}_3}$]. The absolute configuration was determined by comparison of the optical rotation with the literature value.\(^9\)

\[
\begin{align*}
\text{H} & \text{N} \\
\text{Ts} & \text{Ph} \\
\text{(S)-6c} & \text{OMe}
\end{align*}
\]

Entry 11. (CAS 738626-20-5 for (S)-enantiomer) The reaction was conducted for 24 h using 0.4 equiv of KOH. Pale yellow solid. 70% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 12.9 min [minor enantiomer], 15.6 min [major enantiomer]. 96% ee. $\text{[\ensuremath{\alpha}]^{20}_{D} +10.3 (c 0.99, CHCl}_3}$]. The absolute configuration was determined by comparison of the optical rotation with the literature value.\(^9\)

\[
\begin{align*}
\text{H} & \text{N} \\
\text{Ts} & \text{Me} \\
\text{Ph} & \text{Me} \\
\text{(S)-6h}
\end{align*}
\]

Entry 12. (CAS 1171048-75-1 for racemate) White solid. 93% yield.

The ee was determined on two Daicel Chiralpak AD-H columns with hexane/2-propanol = 80/20, flow = 0.3 mL/min. Retention times: 94.7 min [minor enantiomer], 103.1 min [major enantiomer]. 98% ee. $\text{[\ensuremath{\alpha}]^{20}_{D} \text{ –14.9 (c 0.99, CHCl}_3}$]. The absolute configuration was assigned by analogy with entry 1.

\[
\begin{align*}
\text{H} & \text{N} \\
\text{Ts} & \text{Ph}
\end{align*}
\]

(S)-6i
H NMR (CDCl$_3$): δ 7.78-7.73 (m, 1H), 7.67 (d, $^3$J$_{HH}$ = 8.6 Hz, 1H), 7.66-7.64 (m, 1H), 7.55 (d, $^3$J$_{HH}$ = 8.3 Hz, 2H), 7.50 (s, 1H), 7.47-7.43 (m, 2H), 7.25-7.20 (m, 3H), 7.18-7.14 (m, 3H), 7.03 (d, $^3$J$_{HH}$ = 8.0 Hz, 2H), 5.74 (d, $^3$J$_{HH}$ = 7.4 Hz, 1H), 5.29 (bs, 1H), 2.27 (s, 3H).

13C NMR (CDCl$_3$): δ 143.3, 140.5, 137.7, 137.5, 133.1, 132.7, 129.4, 128.7, 128.6, 128.1, 127.7, 127.64, 127.59, 127.3, 126.5, 126.3, 126.2, 125.3, 61.6, 21.5.

**Entry 13.** (CAS 1032583-00-8 for racemate) Pale brown solid. 88% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 15.1 min [major enantiomer], 19.8 min [minor enantiomer]. 96% ee. [α]$^{20}$D +3.3 (c 1.02, CHCl$_3$). The absolute configuration was assigned by analogy with entry 1.

$^1$H NMR (CDCl$_3$): δ 7.56 (d, $^3$J$_{HH}$ = 8.0 Hz, 2H), 7.23-7.17 (m, 4H), 7.14 (d, $^3$J$_{HH}$ = 8.1 Hz, 2H), 7.13-7.09 (m, 2H), 6.89-6.86 (m, 1H), 6.77 (d, $^3$J$_{HH}$ = 5.0 Hz, 1H), 5.62 (d, $^3$J$_{HH}$ = 7.6 Hz, 1H), 5.03 (d, $^3$J$_{HH}$ = 7.3 Hz, 1H), 2.38 (s, 3H).

**Entry 14.** White solid. 86% yield.

The ee was determined on a Daicel Chiralcel OJ-H column with hexane/2-propanol = 98/2, flow = 0.5 mL/min. Retention times: 72.7 min [minor enantiomer], 82.6 min [major enantiomer]. 89% ee. [α]$^{20}$D +11.2 (c 1.00, CHCl$_3$). The absolute configuration was assigned by analogy with entry 1.
Entry 15. (CAS 796966-23-9 for (R)-enantiomer) Pale yellow solid. 91% yield.

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 26.1 min [major enantiomer], 35.1 min [minor enantiomer]. 95% ee. \([\alpha]^{20}_{D} -13.7\) (c 1.03, CHCl₃). The absolute configuration was determined by comparison of the optical rotation with the literature value.⁹

¹H NMR (CDCl₃): δ 7.55 (d, ³JₗHH = 8.3 Hz, 2H), 7.19-7.14 (m, 4H), 7.06 (d, ³JₗHH = 8.8 Hz, 2H), 6.94 (d, ³JₗHH = 8.8 Hz, 2H), 6.73 (d, ³JₗHH = 8.8 Hz, 2H), 5.49 (d, ³JₗHH = 6.8 Hz, 1H), 5.02 (d, ³JₗHH = 6.6 Hz, 1H), 3.75 (s, 3H), 2.40 (s, 3H).

¹³C NMR (CDCl₃): δ 159.2, 143.4, 139.4, 137.4, 133.4, 132.4, 129.5, 128.8, 128.6, 127.3, 114.1, 60.4, 55.4, 21.6.

Procedure for Equation 3.

4 M KOHₐq (10 μL, 40 μmol) was added to a solution of [RhCl((S)-1c)]₂ (5.6 mg, 10 μmol Rh), imine 8 (64.9 mg, 0.200 mmol), and phenylboroxine (62.3 mg, 0.600 mmol B) in dioxane (0.50 mL), and the mixture was stirred for 6 h at 60 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane/MeOH = 3/16/2 and then with CH₂Cl₂/hexane/MeOH = 100/20/1 to afford compound 9 (CAS 840529-66-0) as a white solid (61.3 mg, 0.152 mmol; 76% yield).

The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 27.5 min [minor enantiomer], 50.6 min [major enantiomer]. 94% ee. \([\alpha]^{20}_{D} +1.2\) (c 1.00, CHCl₃). The absolute configuration was determined by comparison of the optical rotation with the literature value.¹⁰

¹H NMR (CDCl₃): δ 8.14 (d, ³JₗHH = 8.5 Hz, 2H), 7.78 (d, ³JₗHH = 8.6 Hz, 2H), 7.24-7.19 (m, 5H), 7.09 (d, ³JₗHH = 8.7 Hz, 2H), 7.06-7.03 (m, 2H), 5.69 (d, ³JₗHH = 7.2 Hz, 1H), 5.28 (d, ³JₗHH = 7.3 Hz, 1H). ¹³C NMR (CDCl₃): δ 149.9, 146.2, 139.1, 138.3, 134.2, 129.1, 129.0, 128.9, 128.44, 128.42, 127.4, 124.1, 61.2.

---

IV. X-ray Crystal Structure of Rh(acac)((S)-1a)

Data Collection
A yellow C_6H_6 solution of Rh(acac)((S)-1a) was prepared. Crystals suitable for X-ray analysis were obtained by diffusion of pentane at room temperature.

A yellow prism crystal of C_{29}H_{31}NO_2PRh having approximate dimensions of 0.20 x 0.10 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 3 oscillations that were exposed for 90 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

\[
\begin{align*}
a &= 8.270(3) \text{ Å} \\
b &= 11.652(5) \text{ Å} \\
c &= 26.490(8) \text{ Å} \\
V &= 2552.7(15) \text{ Å}^3
\end{align*}
\]

For \( Z = 4 \) and F.W. = 559.45, the calculated density is 1.456 g/cm³. The systematic absences of:

- h00: h ± 2n
- 0k0: k ± 2n
- 00l: l ± 2n

uniquely determine the space group to be:

\[ \text{P2}_1\text{2}_1\text{2}_1 \ (\#19) \]

The data were collected at a temperature of \(-150 ± 1 \) °C to a maximum 2θ value of 55.0°. A total of 42 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at \( \chi = 45.0° \) and \( \phi = 0.0° \). The exposure rate was 500.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at \( \chi = 45.0° \).
and $\phi = 180.0^\circ$. The exposure rate was 500.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

**Data Reduction**

Of the 22742 reflections that were collected, 5782 were unique ($R_{\text{int}} = 0.102$).

The linear absorption coefficient, $\mu$, for Mo-K$\alpha$ radiation is 7.565 cm$^{-1}$. The data were corrected for Lorentz and polarization effects.

**Structure Solution and Refinement**

The structure was solved by direct methods$^{11}$ and expanded using Fourier techniques.$^{12}$ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement$^{13}$ on $F$ was based on 18345 observed reflections ($I > 2.00\sigma(I)$) and 339 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum \frac{|F_o| - |F_c|}{|F_o|} = 0.0594$$

$$R_w = \frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2}^{1/2} = 0.0818$$

The standard deviation of an observation of unit weight$^{14}$ was 1.00. A Chebychev polynomial weighting scheme was used.$^{15}$ Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 3.06 and $-3.34 \text{ e/Å}^3$, respectively. The absolute structure was deduced based on Flack parameter, 0.04(3), refined using 2473 Friedel pairs.$^{16}$

Neutral atom scattering factors were taken from Cromer and Waber.$^{17}$ Anomalous dispersion effects were included in $F_{\text{calc}}$; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.$^{18}$ The values for the mass attenuation coefficients are those of Creagh and


13 Least Squares function minimized:

$$\Sigma w(|F_o| - |F_c|)^2$$

where $w = \text{Least Squares weights}$.

14 Standard deviation of an observation of unit weight:

$$[\Sigma w(|F_o| - |F_c|)^2/(N_O - N_V)]^{1/2}$$

where: $N_O = \text{number of observations}, N_V = \text{number of variables}$


Hubbell.\textsuperscript{20} All calculations were performed using the CrystalStructure\textsuperscript{21,22} crystallographic software package.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 819417). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.


Experimental Details

A. Crystal Data

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<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
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<tr>
<td>Formula Weight</td>
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<tr>
<td>Crystal Color, Habit</td>
<td>yellow, prism</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>0.20 X 0.10 X 0.10 mm</td>
</tr>
<tr>
<td>Crystal System</td>
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<tr>
<td>Lattice Type</td>
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<tr>
<td>Indexing Images</td>
<td>3 oscillations @ 90.0 seconds</td>
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<td>Detector Position</td>
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<tr>
<td>Lattice Parameters</td>
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<td></td>
<td>b = 11.652(5) Å</td>
</tr>
<tr>
<td></td>
<td>c = 26.490(8) Å</td>
</tr>
<tr>
<td></td>
<td>V = 2552.7(15) Å³</td>
</tr>
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<tr>
<td>F000</td>
<td>1152.00</td>
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<td>(\mu) (MoK(\alpha))</td>
<td>7.565 cm(^{-1})</td>
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### B. Intensity Measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value or Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diffractometer</strong></td>
<td>Rigaku RAXIS-RAPID</td>
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<tr>
<td><strong>Radiation</strong></td>
<td>MoKα ($\lambda = 0.71075 \text{ Å}$)</td>
</tr>
<tr>
<td></td>
<td>graphite monochromated</td>
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<tr>
<td><strong>Detector Aperture</strong></td>
<td>280 mm x 256 mm</td>
</tr>
<tr>
<td><strong>Data Images</strong></td>
<td>42 exposures</td>
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<tr>
<td><strong>$\omega$ oscillation Range (χ=45.0, $\phi=0.0$)</strong></td>
<td>130.0 - 190.0°</td>
</tr>
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<td><strong>Exposure Rate</strong></td>
<td>500.0 sec/°</td>
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<tr>
<td><strong>$\omega$ oscillation Range (χ=45.0, $\phi=180.0$)</strong></td>
<td>0.0 - 160.0°</td>
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<tr>
<td><strong>Exposure Rate</strong></td>
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<td><strong>Detector Position</strong></td>
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<td><strong>$\theta_{\text{max}}$</strong></td>
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<tr>
<td><strong>No. of Reflections Measured</strong></td>
<td>Total: 22742</td>
</tr>
<tr>
<td></td>
<td>Unique: 5782 ($R_{\text{int}} = 0.102$)</td>
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<td>Friedel pairs: 2473</td>
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<td><strong>Corrections</strong></td>
<td>Lorentz-polarization</td>
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## C. Structure Solution and Refinement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td><strong>Structure Solution</strong></td>
<td>Direct Methods (SIR92)</td>
</tr>
<tr>
<td><strong>Refinement</strong></td>
<td>Full-matrix least-squares on F</td>
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<td><strong>Function Minimized</strong></td>
<td>$\sum w (</td>
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<tr>
<td><strong>Least Squares Weights</strong></td>
<td>Chebychev polynomial with 3 parameters</td>
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<td></td>
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<td><strong>$2\theta_{max}$ cutoff</strong></td>
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<td><strong>Anomalous Dispersion</strong></td>
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<td><strong>No. Observations ($I&gt;2.00\sigma(I)$)</strong></td>
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<td><strong>No. Variables</strong></td>
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<td><strong>Reflection/Parameter Ratio</strong></td>
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<td><strong>Residuals: $R$ ($I&gt;2.00\sigma(I)$)</strong></td>
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<td><strong>Residuals: $R_w$ ($I&gt;2.00\sigma(I)$)</strong></td>
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<tr>
<td><strong>Flack parameter</strong></td>
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<tr>
<td><strong>Max Shift/Error in Final Cycle</strong></td>
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<tr>
<td><strong>Maximum peak in Final Diff. Map</strong></td>
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<tr>
<td><strong>Minimum peak in Final Diff. Map</strong></td>
<td>$-3.34 \text{ e}^{-/\text{Å}^3}$</td>
</tr>
</tbody>
</table>
V. $^1$H and $^{13}$C NMR Spectra
compound 1c
compound 1c
compound 6e

\[ \text{MeO} \quad \text{HN} \quad \text{Ts} \]

- 159.0759
- 143.2091
- 140.8766
- 137.5554
- 132.9000
- 129.4445
- 128.7246
- 128.5902
- 127.5535
- 127.3903
- 127.3231
- 114.0001

- 77.3712
- 77.1600
- 76.9392

- 60.9381
- 55.3612
- 21.5831
compound 6d
compound 6e
compound 6e
compound 6h
compound 6i
compound 6i
compound 6j
compound 6j
compound 6k

(500 MHz in CDCl₃)
compound 6k