

Supporting Information for:

Rapid Determination of Enantiomeric Excess of α -Chiral Cyclohexanones Using Circular Dichroism Spectroscopy

Diana Leung, Eric V. Anslyn*

Department of Chemistry and Biochemistry, The University of Texas at Austin,
1 University Station A1590 NHB, Austin, TX 78712

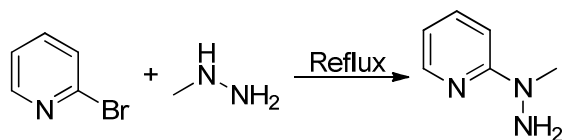
anslyn@austin.utexas.edu

General Experimental Details:

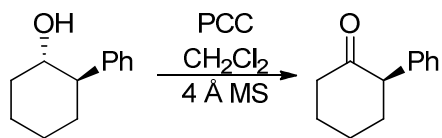
All commercially obtained reagents were used as received. A Varian Mercury 400 MHz, and a Varian Inova 400 MHz spectrometer were used to obtain ^1H and ^{13}C NMR spectra, which were referenced using the solvent residual peak. All LC-MS data were collected on a Surveyor HPLC (autosampler, quaternary pump, and diode array detector) and a Thermo LTQ-XL linear ion trap mass spectrometer with electrospray source. The method of elution used was $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ with 0.1% formic acid, with a flow rate of 0.5 mL/min, where the initial eluent ratio was 5:95 ($\text{CH}_3\text{CN}:\text{H}_2\text{O}$) and the gradient increased to 95:5 ($\text{CH}_3\text{CN}:\text{H}_2\text{O}$) over 4 minutes, followed by 2 minutes at 95:5 ratio ($\text{CH}_3\text{CN}:\text{H}_2\text{O}$). All polarimetry data were collected on an AP-300 Automatic Polarimeter with a 1 dm cell, at the sodium line, at 25°C; where the reported molar optical rotation were averages of three measurements. Circular dichroism spectra were obtained on a CD-Jasco-815 CD spectrophotometer using a temperature controller at 25°C in a Starna 1 mm

quartz cuvette. Synthesis of **3**¹ was conducted according to modified published procedures.

Synthesis:

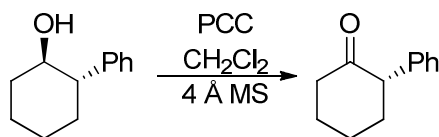


1-methyl-1-(2-pyridyl) hydrazine (3): To a 50 mL 3-neck round bottom flask, 2-bromopyridine (3 mL, 31.5 mmol), and methylhydrazine (25 mL, 475 mmol) were added and refluxed for 3 h under Ar. After cooling, the excess methyl hydrazine was removed *in vacuo*. Then the residue was dissolved with EtOAc (250 mL) and extracted with 10% Na₂CO₃ aqueous (60 mL). The organic layer was then extracted with saturated aqueous NaCl (50 mL x 2). The organic layer was dried over Na₂SO₄ and the solvent was removed *in vacuo* to afford **3** (2.8708 g, 74.0%) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 8.16 (ddd, *J*=5.0, 1.9, 0.9 Hz, 1H), 7.50 – 7.45 (m, 1H), 6.94 – 6.93 (m, 1H), 6.60 (ddd, *J*=7.1, 5.0, 0.9 Hz, 1H), 4.06 (bs, 2H), 3.27 (s, 3H). ¹³C NMR (CDCl₃, 400 MHz): δ 161.2, 147.3, 137.2, 112.9, 107.3, 41.1. HR-MS (CI⁺): 124.0875 (calc. for [M+H⁺] C₆H₁₀N₃⁺: 124.0870).



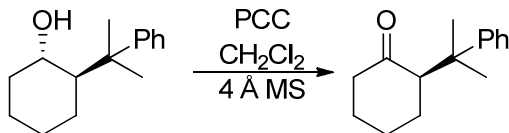
(R)-2-phenylcyclohexanone: In a 250 mL round bottom flask loaded with 4 Å MS, (1*S*,2*R*)-2-phenylcyclohexanol (1.5149 g, 8.595 mmol), pyridinium chlorochromate (PCC, 3.6504 g, 16.93 mmol), and dry CH₂Cl₂ (250 mL) were added and stirred under Ar

for 15 h. The reaction mixture was filtered through 1:1 Celite:silica and washed with diethyl ether (600 mL). The solvent was evaporated away, producing a brown solution with brown particles. Flash chromatography of the residue on silica gel (hexane:ethyl acetate, 8:2) afforded (*R*)-2-phenylcyclohexanone (1.3312 g, 88.9%) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.38 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 7.15 – 7.12 (m, 2H), 3.61 (dd, *J*=12.2, 5.4 Hz, 1H), 2.57 – 2.41 (m, 2H), 2.32 – 2.23 (m, 1H), 2.21 – 2.11 (m, 1H), 2.10 – 1.95 (m, 2H), 1.90 – 1.76 (m, 2H). ¹³C NMR (CDCl₃, 400 MHz): δ 210.3, 138.7, 128.5, 128.3, 126.9, 57.4, 42.2, 35.1, 27.8, 25.3. HR-MS (CI+): 175.1127 (calc. for [M+H⁺] C₁₂H₁₅O⁺ 175.1118). m.p.: 38 – 40°C (lit² m.p. 38 – 39°C). [α]_D²⁴ = +108.2° (lit²: [α]_D²⁴ = +114.7°, [α]_D²⁴ = +108.7°).

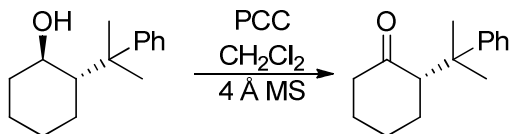


(*S*)-2-phenylcyclohexanone: In a 250 mL round bottom flask loaded with 4 Å MS, (1*R*,2*S*)-2-phenylcyclohexanol (2.1708 g, 12.32 mmol), pyridinium chlorochromate (PCC, 5.2304 g, 24.26 mmol), and dry CH₂Cl₂ (160 mL) were added and stirred under Ar for 15 h. The reaction mixture was filtered through 1:1 Celite:silica and washed with diethyl ether (600 mL). The solvent was evaporated away, producing a brown solution with brown particles. Flash chromatography of the residue on silica gel (hexane:ethyl acetate, 8:2) afforded (*S*)-2-phenylcyclohexanone (1.8083 g, 84.3%) as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.37 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 7.16 – 7.12 (m, 2H), 3.61 (dd, *J*=12.2, 5.4 Hz, 1H), 2.57 – 2.41 (m, 2H), 2.32 – 2.23 (m, 1H), 2.20 – 2.11 (m, 1H), 2.10 – 1.95 (m, 2H), 1.89 – 1.76 (m, 2H). ¹³C NMR (CDCl₃, 400 MHz): δ 210.3, 138.7, 128.5, 128.3, 126.9, 57.4, 42.2, 35.1, 27.8, 25.3. HR-MS (CI+): 175.1125 (calc.

for $[M+H^+]$ $C_{12}H_{15}O^+$: 175.1118). m.p.: 39 – 40°C (lit² m.p. 38 – 39°C). $[\alpha]_D^{24} = -110.8^\circ$ (lit:² $[\alpha]_D^{24} = -114.7^\circ$, $[\alpha]_D^{24} = -109.8^\circ$).

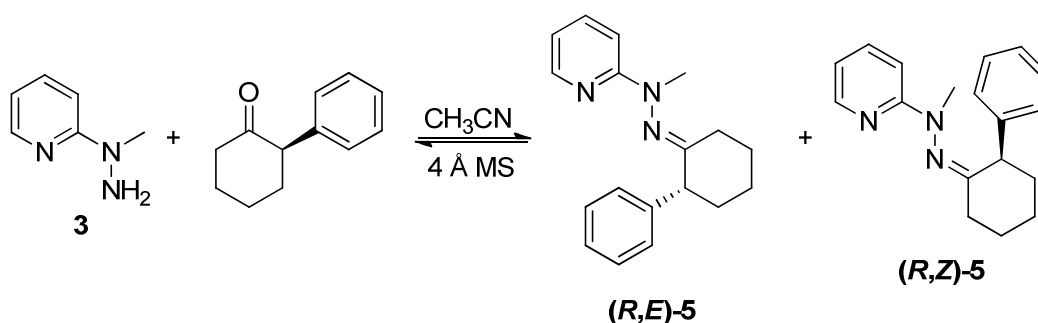


(R)-2-(2-phenylpropan-2-yl)cyclohexanone: In a 250 mL round bottom flask loaded with 4 Å MS, (1*S*,2*R*)-2-(2-phenylpropan-2-yl)cyclohexanol (2.00 g, 9.16 mmol), pyridinium chlorochromate (PCC, 3.8938 g, 18.06 mmol), and dry CH_2Cl_2 (160 mL) were added and stirred under Ar for 15 h. The reaction mixture was filtered through 1:1 Celite:silica and washed with diethyl ether (600 mL). The solvent was evaporated away, producing a brown solution with brown particles. Flash chromatography of the residue on silica gel (hexane:ethyl acetate, 8:2) afforded (*R*)-2-(2-phenylpropan-2-yl)cyclohexanone (1.7064 g, 86.1%) as a clear oil. ¹H NMR ($CDCl_3$, 400 MHz): δ 7.37 – 7.26 (m, 4H), 7.19 – 7.14 (m, 1H), 2.73 (dd, $J=12.2, 4.5$ Hz, 1H), 2.35 – 2.22 (m, 2H), 2.06 – 1.99 (m, 1H), 1.83 – 1.76 (m, 2H), 1.69 – 1.53 (m, 2H), 1.52 – 1.48 (m, 1H), 1.47 (s, 3H), 1.41 (s, 3H). ¹³C NMR ($CDCl_3$, 400 MHz): δ 212.0, 149.8, 127.9, 125.8, 125.5, 60.4, 44.2, 39.2, 30.2, 28.5, 26.6, 26.0, 23.9. HR-MS (CI⁺): 217.1598 (calc. for $[M+H^+]$ $C_{15}H_{21}O^+$: 217.1587). $[\alpha]_D^{24} = 83.7^\circ$.



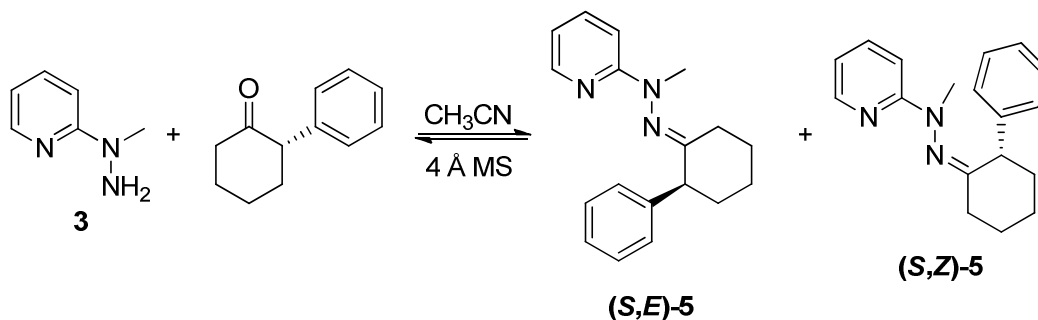
(S)-2-(2-phenylpropan-2-yl)cyclohexanone: In a 250 mL round bottom flask loaded with 4 Å MS, (1*R*,2*S*)-2-(2-phenylpropan-2-yl)cyclohexanol (2.00 g, 9.16 mmol), pyridinium chlorochromate (PCC, 3.8930 g, 18.06 mmol), and dry CH_2Cl_2 (160 mL)

were added and stirred under Ar for 15 h. The reaction mixture was filtered through 1:1 Celite:silica and washed with diethyl ether (600 mL). The solvent was evaporated away, producing a brown solution with brown particles. Flash chromatography of the residue on silica gel (hexane:ethyl acetate, 8:2) afforded (*S*)-2-(2-phenylpropan-2-yl)cyclohexanone (1.9810 g, 100%) as a clear oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.37 – 7.26 (m, 4H), 7.20 – 7.14 (m, 1H), 2.73 (dd, *J*=12.2, 4.4 Hz, 1H), 2.35 – 2.22 (m, 2H), 2.06 – 1.99 (m, 1H), 1.83 – 1.77 (m, 2H), 1.70 – 1.53 (m, 2H), 1.52 – 1.48 (m, 1H), 1.47 (s, 3H), 1.41 (s, 3H). ¹³C NMR (CDCl₃, 400 MHz): δ 212.0, 149.8, 128.0, 125.8, 125.5, 60.4, 44.2, 39.2, 30.2, 28.5, 26.6, 26.0, 23.9. HR-MS (CI⁺): 217.1592 (calc. for [M+H⁺] C₁₅H₂₁O⁺: 217.1587). [α]_D²⁴ = -83.4°.

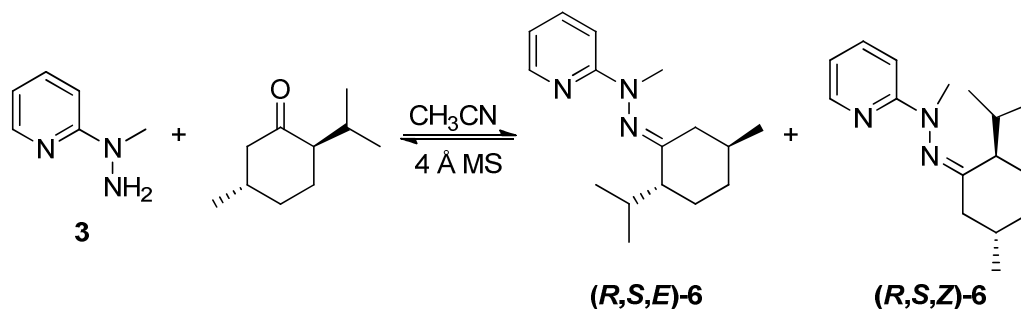


(R)-2-(1-methyl-2-(2-phenylcyclohexylidene)hydrazinyl)pyridine ((R)-5): In a 50 mL round bottom flask, charged with 4 Å MS, 1-methyl-1-(2-pyridyl) hydrazine (**3**, 0.2463 g, 2.00 mmol), (*R*)-2-phenylcyclohexanone (0.3135 g, 1.799 mmol), and dry CH₃CN (18 mL) were added and stirred under Ar for 26 h. The reaction mixture was filtered through Celite and the solvent was removed *in vacuo* to afford a mixture of (*E*)- and (*Z*)-isomers of (*R*)-**5** (0.3789 g, 75.4%) as a yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 8.24 (ddd, *J*=4.9, 1.9, 0.8 Hz, 1H), 8.21 (ddd, *J*=4.9, 1.9, 0.8 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.47 – 7.42 (m, 1H), 7.38 – 7.27 (m, 5H), 7.25 – 7.20 (m, 5H), 6.81 – 6.79 (m, 1H), 6.74 – 6.64 (m, 3H), 4.64 (bs, 1H), 3.86 (dd, *J*=6.7, 5.2 Hz, 1H), 3.23 (s, 3H), 3.19 (s,

3H), 2.68 – 1.60 (m, 16H). ^{13}C NMR (CDCl_3 , 400 MHz): δ 176.6, 160.8, 160.7, 147.5, 147.3, 140.8, 137.0, 136.9, 128.7, 128.4, 127.9, 127.4, 126.4, 126.3, 114.5, 114.1, 109.0, 108.9, 49.2, 41.7, 39.1, 33.2, 32.6, 31.0, 28.6, 28.3, 26.9, 23.2, 21.0. HR-MS (ESI+): 280.1818 (calc. for $[\text{M}+\text{H}^+]$ $\text{C}_{18}\text{H}_{22}\text{N}_3^+$: 280.1809).

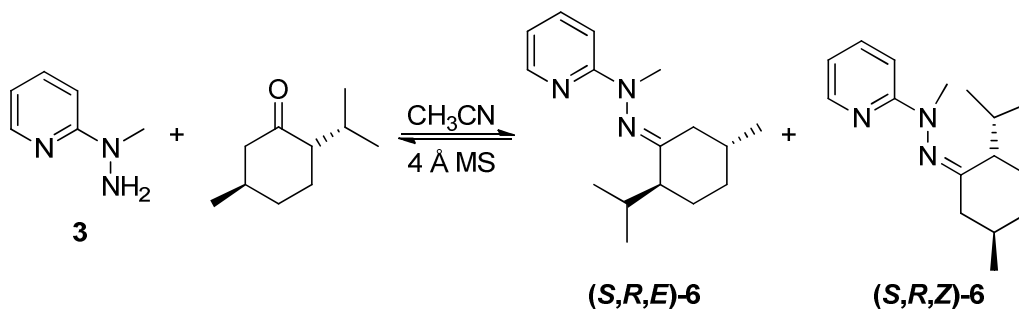


(S)-2-(1-methyl-2-(2-phenylcyclohexylidene)hydrazinyl)pyridine ((S)-5): In a 50 mL round bottom flask, charged with 4 Å MS, 1-methyl-1-(2-pyridyl) hydrazine (**3**, 0.2352 g, 1.91 mmol), (S)-2-phenylcyclohexanone (0.2993 g, 1.718 mmol), and dry CH_3CN (18 mL) were added and stirred under Ar for 26 h. The reaction mixture was filtered through Celite and the solvent was removed *in vacuo* to afford a mixture of (E)- and (Z)-isomers of (S)-**5** (0.4468 g, 93.1%) as a yellow oil. ^1H NMR (CDCl_3 , 400 MHz): δ 8.24 (ddd, $J=4.9, 1.9, 0.8$ Hz, 1H), 8.21 (ddd, $J=4.9, 1.8, 0.8$ Hz, 1H), 7.54 – 7.48 (m, 1H), 7.46 – 7.42 (m, 1H), 7.38 – 7.18 (m, 10H), 6.81 – 6.79 (m, 1H), 6.73 – 6.64 (m, 3H), 4.64 (bs, 1H), 3.86 (dd, $J=6.6, 5.3$ Hz, 1H), 3.23 (s, 3H), 3.19 (s, 3H), 2.69 – 1.58 (m, 16H). ^{13}C NMR (CDCl_3 , 400 MHz): δ 179.1, 176.6, 160.8, 147.5, 147.3, 140.8, 139.4, 136.9, 128.7, 128.3, 127.9, 127.4, 126.4, 126.3, 114.4, 114.1, 109.0, 108.9, 49.2, 41.7, 39.1, 33.2, 32.6, 31.0, 28.6, 28.2, 26.9, 23.2, 21.0. HR-MS (ESI+): 280.1812 (calc. for $[\text{M}+\text{H}^+]$ $\text{C}_{18}\text{H}_{22}\text{N}_3^+$: 280.1809).



((2*R*,5*S*)-2-isopropyl-5-methylcyclohexylidene)-1-methylhydrazinyl)pyridine

((*R,S*)-6): In an oven dried 10 mL round bottom flask, charged with 4Å MS, 1-methyl-1-(2-pyridyl) hydrazine (**3**, 0.3559 g, 2.890 mmol), (*R,S*)-menthone (0.5 mL, 2.89 mmol), and dry CH₃CN (5 mL) were added and refluxed under Ar for 5 h. The reaction mixture was filtered through Celite and the solvent was removed *in vacuo* to afford a mixture of (*E*)- and (*Z*)-isomers of (*R,S*)-**6** (0.0907 g, 12.1%) as a brown oil. ¹H NMR (CDCl₃, 400 MHz): δ 8.23 – 8.21 (m, 2H), 7.48 – 7.42 (m, 2H), 6.72 – 6.63 (m, 4H), 3.18 (s, 3H), 3.18 (s, 3H), 2.91 – 2.85 (m, 1H), 2.43 – 2.34 (m, 2H), 2.13 – 2.08 (m, 2H), 2.06 – 1.97 (m, 2H), 1.94 – 1.71 (m, 6H), 1.53 – 1.49 (m, 1H), 1.31 – 1.21 (m, 4H), 1.03 – 1.02 (m, 6H), 1.01 – 1.00 (m, 6H), 0.95 – 0.93 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz): δ 178.2, 160.7, 147.2, 137.1, 136.9, 114.1, 113.8, 108.9, 108.9, 50.8, 38.7, 36.9, 33.3, 32.3, 29.6, 26.8, 26.5, 21.7, 21.4, 19.3. HR-MS (ESI⁺): 260.2126 (calc. for [M+H⁺] C₁₆H₂₆N₃⁺: 260.2122).



((S,R)-2-isopropyl-5-methylcyclohexylidene)-1-methylhydrazinylpyridine

((S,R)-6): In an oven dried 10 mL round bottom flask, charged with 4 Å MS, 1-methyl-1-(2-pyridyl) hydrazine (**3**, 0.3561 g, 2.891 mmol), (S,R)-menthone (0.5 mL, 2.89 mmol), and dry CH₃CN (5 mL) were added and refluxed under Ar for 5 h. The reaction mixture was filtered through Celite and the solvent was removed *in vacuo* to afford a mixture of (E)- and (Z)-isomers of (S,R)-**6** (0.2387 g, 31.8%) as a brown oil. ¹H NMR (CDCl₃, 400 MHz): δ 8.23 – 8.21 (m, 2H), 7.47 – 7.43 (m, 2H), 6.71 – 6.65 (m, 4H), 3.18 (s, 3H), 3.18 (s, 3H), 2.92 – 2.85 (m, 1H), 2.43 – 2.34 (m, 2H), 2.13 – 2.08 (m, 2H), 2.05 – 1.98 (m, 2H), 1.93 – 1.72 (m, 6H), 1.54 – 1.47 (m, 1H), 1.31 – 1.19 (m, 4H), 1.03 – 1.02 (m, 6H), 1.01 – 1.00 (m, 6H), 0.95 – 0.93 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz): δ 180.2, 178.2, 160.8, 147.3, 137.0, 136.9, 114.1, 113.9, 109.1, 108.9, 50.8, 50.6, 38.7, 36.9, 34.7, 34.5, 33.3, 32.4, 29.4, 28.7, 27.1, 26.9, 26.5, 22.6, 21.8, 21.46, 21.2, 20.7, 19.4. HR-MS (ESI+): 260.2124 (calc. for [M+H⁺] C₁₆H₂₆N₃⁺: 260.2122).

General Experimental Details on Polarimetry Analysis:

(R)-2-phenylcyclohexanone: In a 10 mL volumetric flask, (R)-2-phenylcyclohexanone (1.0509 g, 603.1 mM, 10.5 w/v%) was added and brought to the mark with benzene. Read sample in 1 dm cell three times, $[\alpha]_D^{24} = +108.48^\circ$, $+108.10^\circ$, and $+108.10^\circ$, giving an average of $[\alpha]_D^{24} = +108.2^\circ$.

(S)-2-phenylcyclohexanone: In a 10 mL volumetric flask, (S)-2-phenylcyclohexanone (1.0522 g, 603.9 mM, 10.5 w/v%) was added and brought to the mark with benzene. Read sample in 1 dm cell three times, $[\alpha]_D^{24} = -110.82^\circ$, -110.72° , and -110.82° , giving an average of $[\alpha]_D^{24} = +110.8^\circ$.

(R)-2-(2-phenylpropan-2-yl)cyclohexanone: In a 10 mL volumetric flask, (R)-2-(2-phenylpropan-2-yl)cyclohexanone (1.4124 g, 652.9 mM, 14.1 w/v%) was added and brought to the mark with CH₂Cl₂. Read sample in 1 dm cell three times, $[\alpha]_D^{24} = +84.47^\circ$, $+83.26^\circ$, and $+83.26^\circ$, giving an average of $[\alpha]_D^{24} = +83.7^\circ$.

(S)-2-(2-phenylpropan-2-yl)cyclohexanone: In a 10 mL volumetric flask, (S)-2-(2-phenylpropan-2-yl)cyclohexanone (1.3556 g, 626.7 mM, 13.6 w/v%) was added and brought to the mark with CH₂Cl₂. Read sample in 1 dm cell three times, $[\alpha]_D^{24} = -83.80^\circ$, -83.80° , and -82.62° , giving an average of $[\alpha]_D^{24} = -83.4^\circ$.

General Experimental Details on CD Titrations:

Stock Solutions for CD Titrations of 6. In a 5 mL volumetric flask (S)-BINAP ((S)-**1**, 0.0124 g, 19.9 μmol), and [Cu^I(CH₃CN)₄]PF₆ (0.0074 g, 19.9 μmol) were added and brought to the mark with dry CH₃CN to give a 3.97 mM stock solution of [Cu^I((S)-**1**)(CH₃CN)₂]PF₆. In a 10 mL volumetric flask, (R,S)-**6** (0.0399 g, 154 μmol) was added and brought to the mark with dry CH₃CN to give a 15.4 mM stock solution. In a 10 mL volumetric flask, (S,R)-**6** (0.0496 g, 191 μmol) was added and brought to the mark with dry CH₃CN to give a 19.1 mM stock solution.

CD Titrations of 6. In separate vials, [Cu^I((S)-**1**)(CH₃CN)₂]PF₆ (100 μL, 400 μM), and different equivalents of (R,S)- or (S,R)-**6** (15.4 mM or 19.1 mM, respectively) to [Cu^I((S)-

$1)(\text{CH}_3\text{CN})_2]\text{PF}_6$ were added and brought to 1 mL with dry CH_3CN . CD measurements were taken from 220 – 470 nm, affording the isotherms.

Stock Solutions for CD Titrations of 5. In a 50 mL volumetric flask (*S*)-BINAP ((*S*)-**1**, 0.0336 g, 54.0 μmol), and $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (0.0202 g, 54.2 μmol) were added and brought to the mark with dry CH_3CN to give a 1.08 mM stock solution of $[\text{Cu}^{\text{I}}((\text{S})\text{-1})(\text{CH}_3\text{CN})_2]\text{PF}_6$. In a 50 mL volumetric flask (*R*)-**5** (0.2526 g, 904.1 μmol) was added and brought to the mark with dry CH_3CN to give a 18.1 mM stock solution. In a 50 mL volumetric flask (*S*)-**5** (0.3095 g, 1.108 mmol) was added and brought to the mark with dry CH_3CN to give 22.2 mM stock solution.

CD Titrations of 5. In separate vials, $[\text{Cu}^{\text{I}}((\text{S})\text{-1})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (373 μL , 400 μM), and different equivalents of (*R*)- or (*S*)-**5** (18.1 mM or 22.2 mM, respectively) to $[\text{Cu}^{\text{I}}((\text{S})\text{-1})(\text{CH}_3\text{CN})_2]\text{PF}_6$ were added and brought to 1 mL with dry CH_3CN . CD measurements were taken from 220 – 470 nm, affording the isotherms.

General Experimental Details on Enantiomeric Excess Calibration Curves:

In separate vials, stock solution of $[\text{Cu}^{\text{I}}((\text{S})\text{-1})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (373 μL , 400 μM) were added and different mixtures of (*R*)- and (*S*)-**5** stock solutions (18.1 mM or 22.2 mM, respectively) were added to each vial in order to span the complete *ee* range (-100% to 100% in increments of 10% *ee*), where the total concentration of **5** was 10 mM for each solution. Dry CH_3CN was added to bring the volume to 1 mL. CD measurements were taken from 220 – 470 nm.

General Experimental Details on Analysis of Unknown Samples:

In separate vials, stock solution $[\text{Cu}^{\text{I}}((\text{S})\text{-1})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (373 μL , 400 μM) were added and a mixture of (*R*)- and (*S*)-**5** stock solutions (18.1 mM or 22.2 mM, respectively)

were added to each vial in order to obtain samples with different ee , where the total concentration of **5** was 10 mM for each solution. CD measurements were taken from 220 – 470 nm.

Tables:

Table S-1: Enantiomeric excess determination of unknown samples of **5** using ee calibration curve.

Sample	Actual ee	Experimental ee	Absolute Error
1	72.1%	70.1%	2.0%
2	-52.0%	-57.6%	5.6%
3	80.1%	81.9%	1.8%
4	4.2%	-7.7%	11.9%
5	-75.9%	-87.8%	11.9%

Figures:

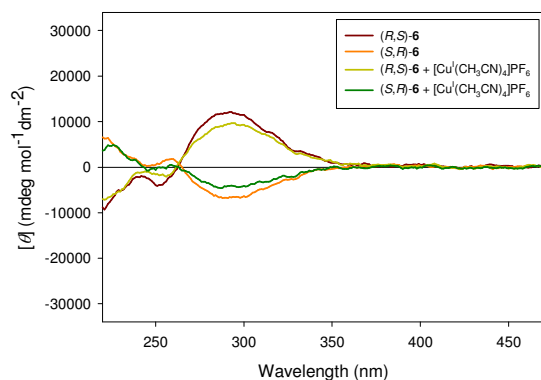


Figure S-1: CD spectra of (*R,S*)-**6** (398 μM), (*S,R*)-**6** (403 μM), (*R,S*)-**6** (398 μM) mixed with $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (401 μM), and (*S,R*)-**6** mixed with $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (401 μM) in CH_3CN .

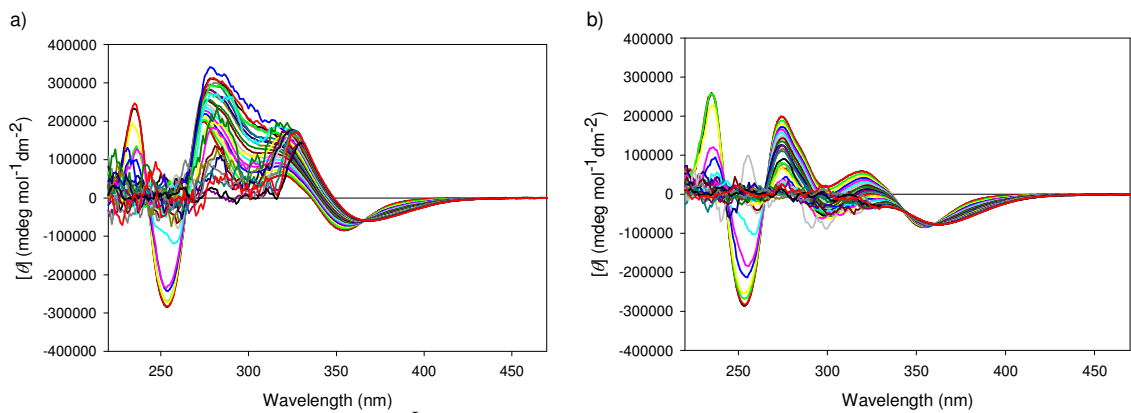


Figure S-2: CD spectra of $[\text{Cu}^{\text{I}}((S)\text{-1})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (398 μM) in CH_3CN upon addition of: a) $(R,S)\text{-6}$ (15.4 mM). b) $(S,R)\text{-6}$ (19.1 mM).

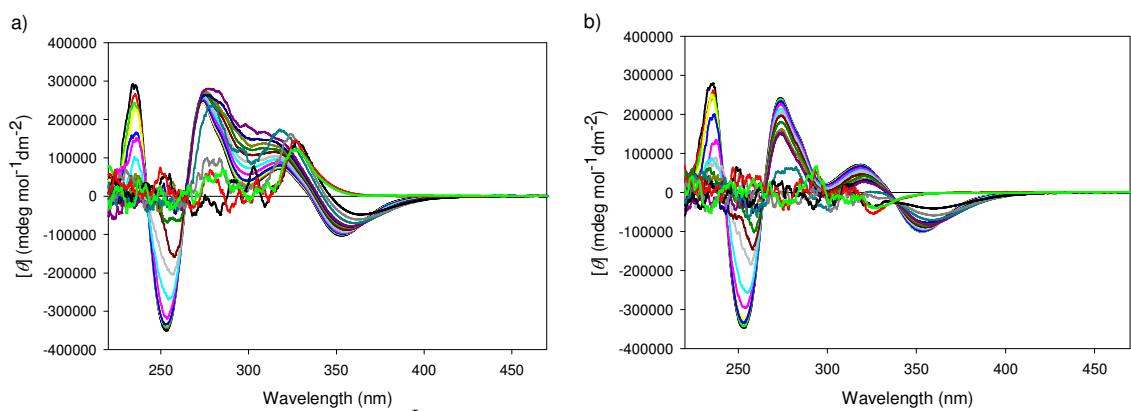


Figure S-3: CD spectra of $[\text{Cu}^{\text{I}}((S)\text{-1})(\text{CH}_3\text{CN})_2]\text{PF}_6$ (398 μM) in CH_3CN upon addition of: a) $(R)\text{-5}$ (18.1 mM). b) $(S)\text{-5}$ (22.2 mM).

NMR Results:

Figure S-4: ^1H NMR of (CDCl_3 , 400 MHz) of compound 3.

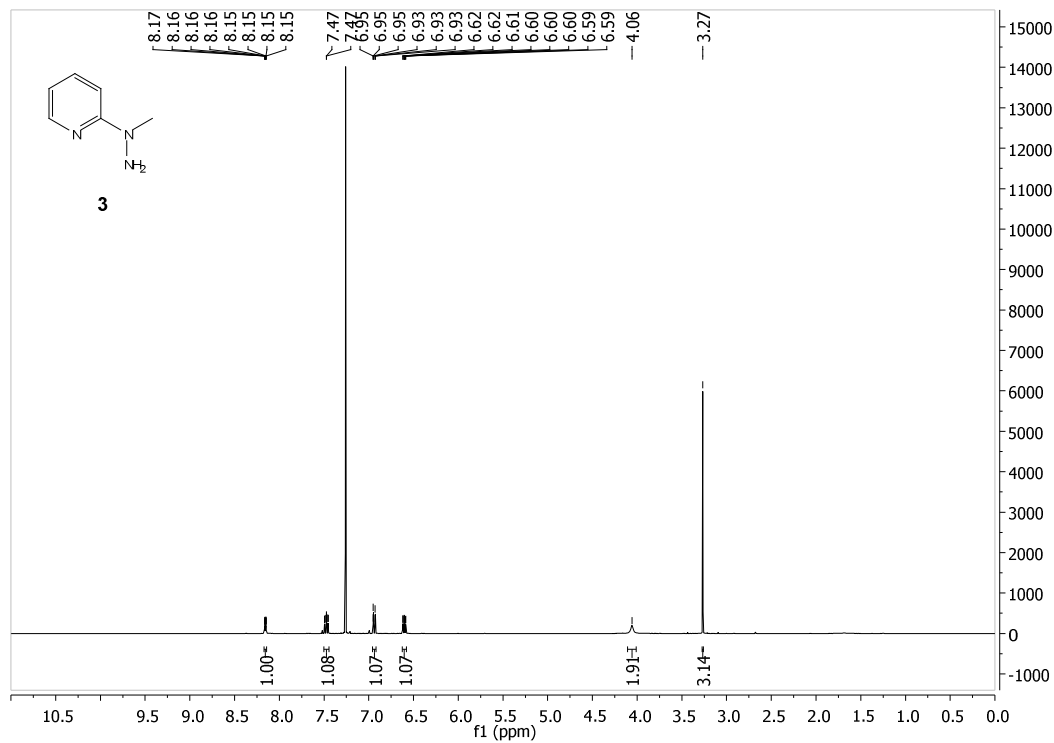


Figure S-5: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound 3.

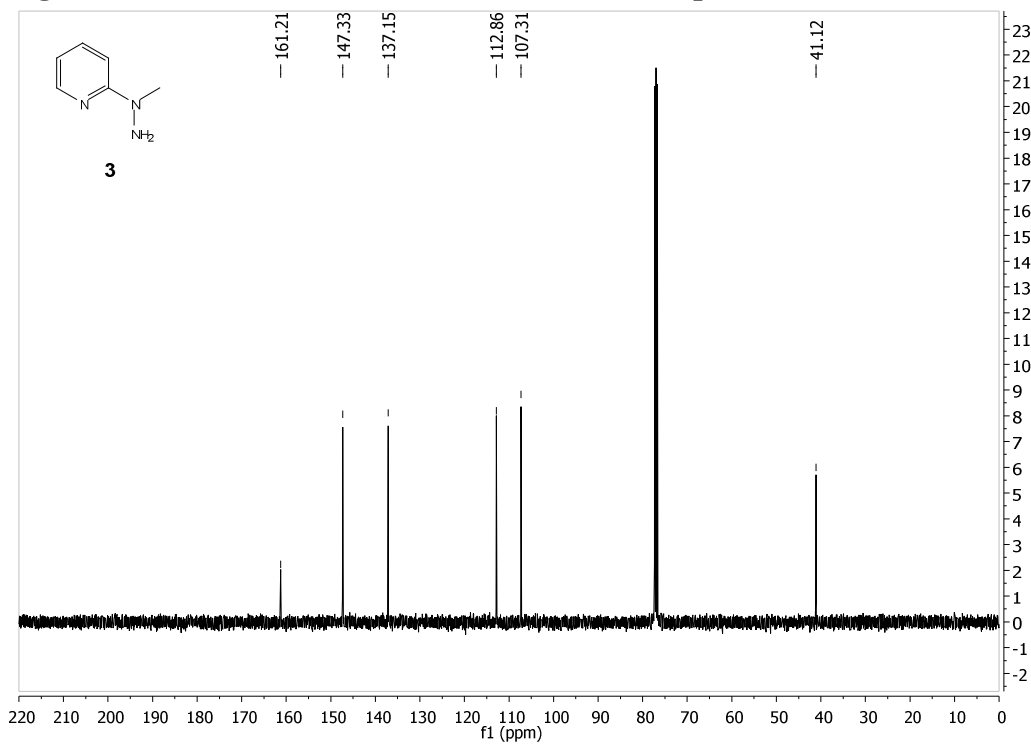


Figure S-6: ^1H NMR of (CDCl_3 , 400 MHz) of compound (*R*)-2-phenylcyclohexanone.

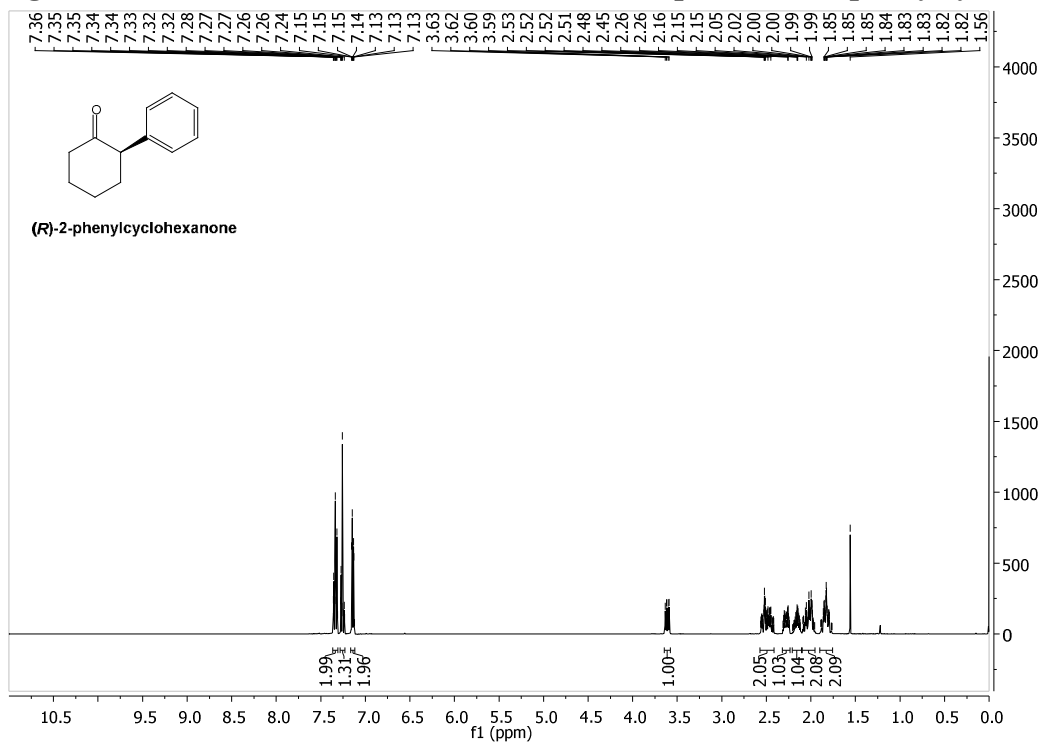


Figure S-7: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (*R*)-2-phenylcyclohexanone.

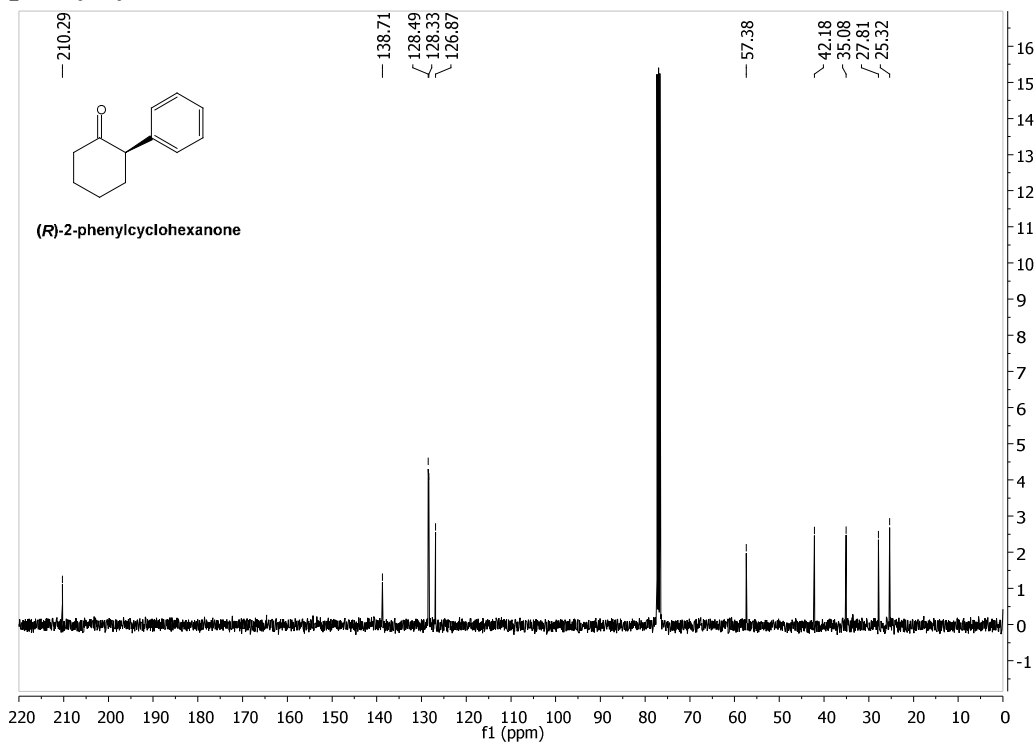


Figure S-8: ^1H NMR of (CDCl_3 , 400 MHz) of compound (*S*)-2-phenylcyclohexanone.

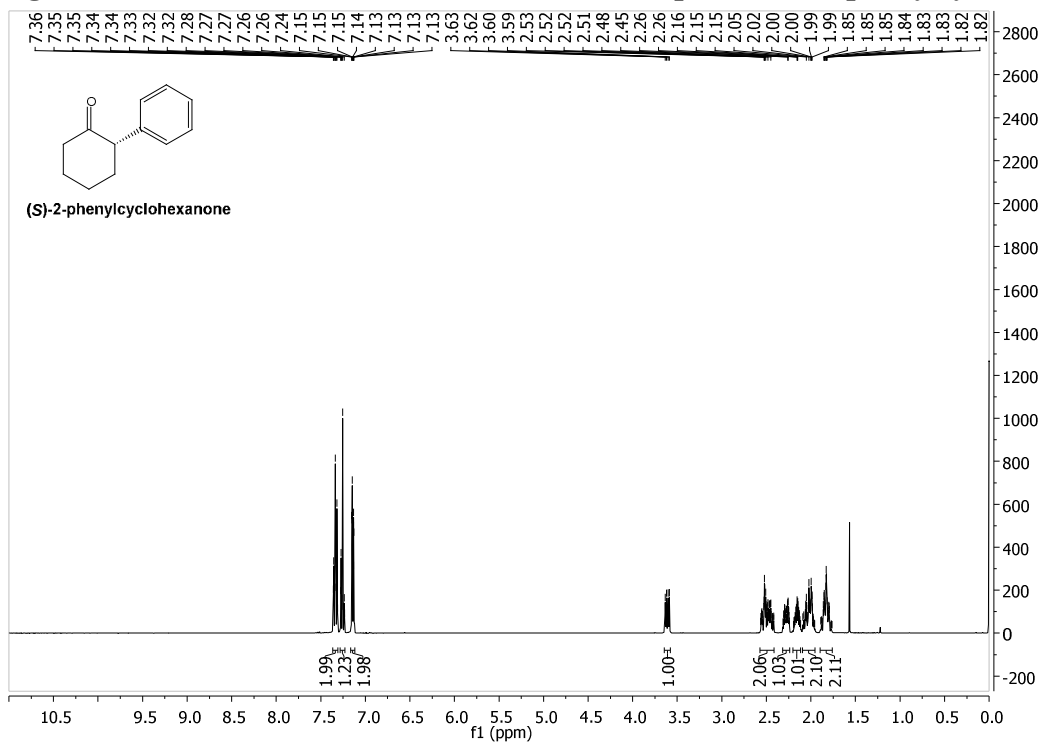


Figure S-9: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (*S*)-2-phenylcyclohexanone.

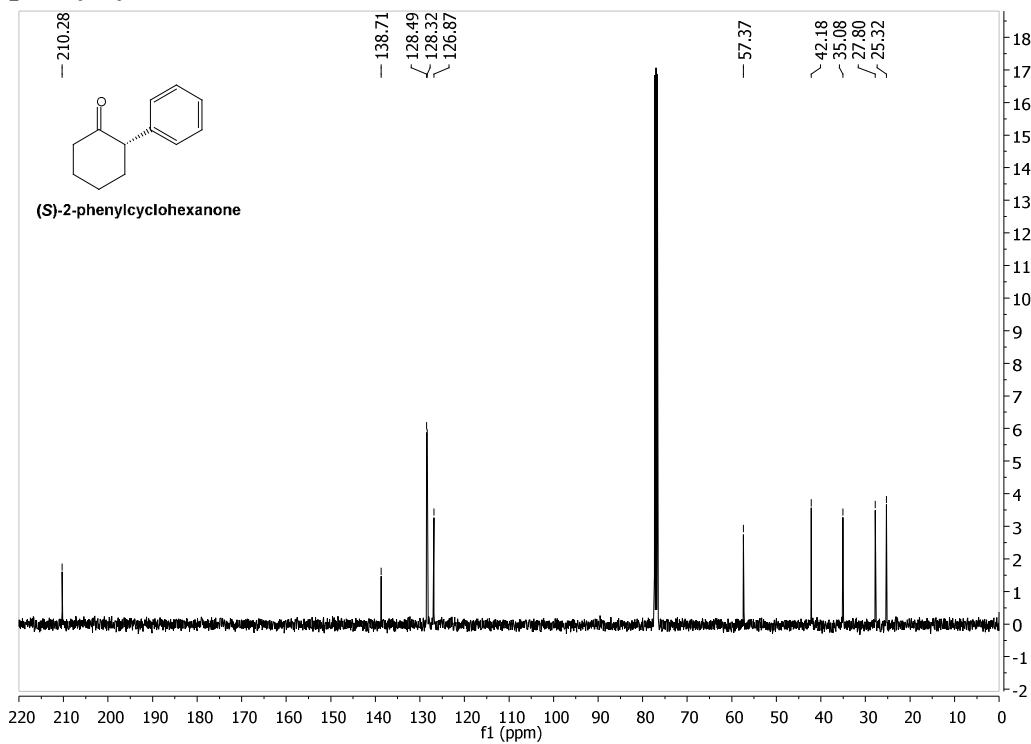


Figure S-10: ^1H NMR of (CDCl_3 , 400 MHz) of compound (*R*)-2-(2-phenylpropan-2-yl)cyclohexanone.

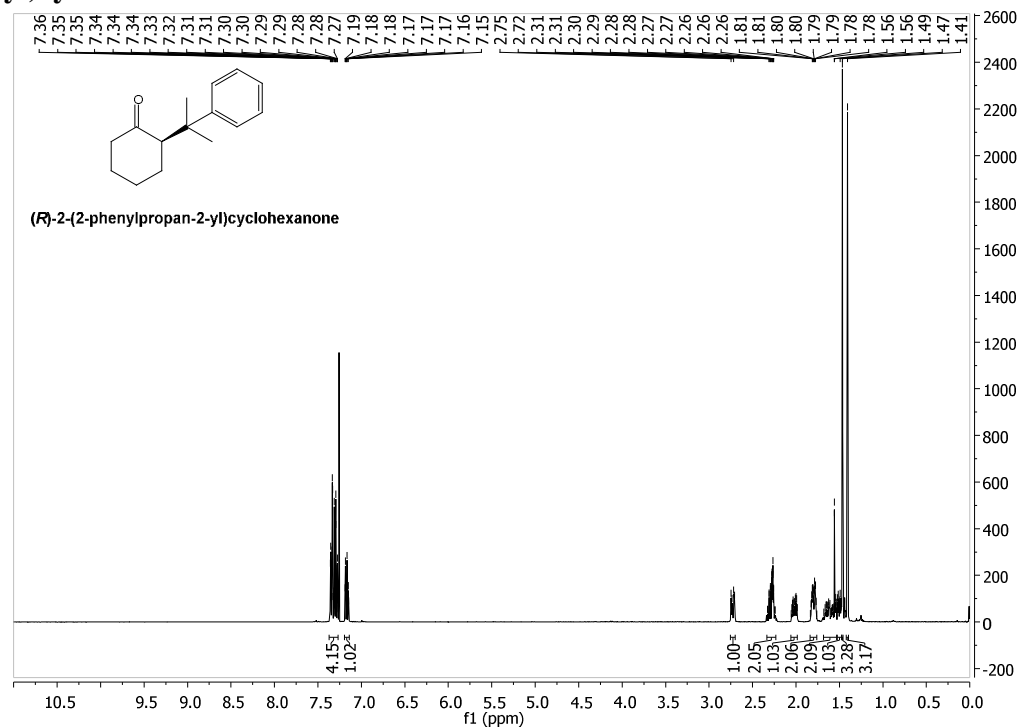


Figure S-11: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (*R*)-2-(2-phenylpropan-2-yl)cyclohexanone.

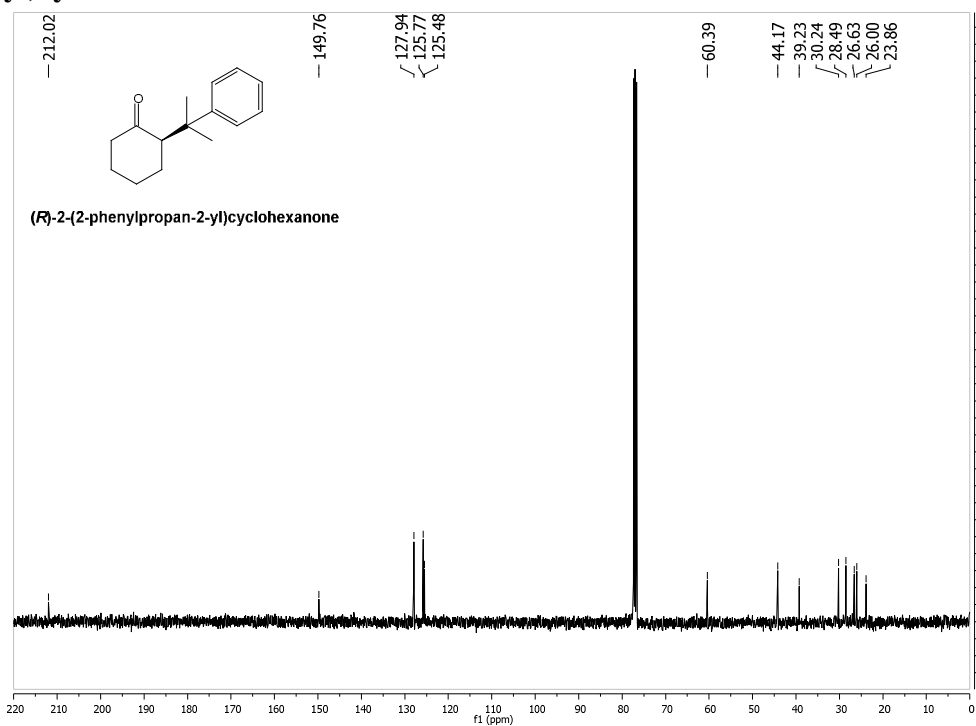


Figure S-12: ^1H NMR of (CDCl_3 , 400 MHz) of compound (*S*)-2-(2-phenylpropan-2-yl)cyclohexanone.

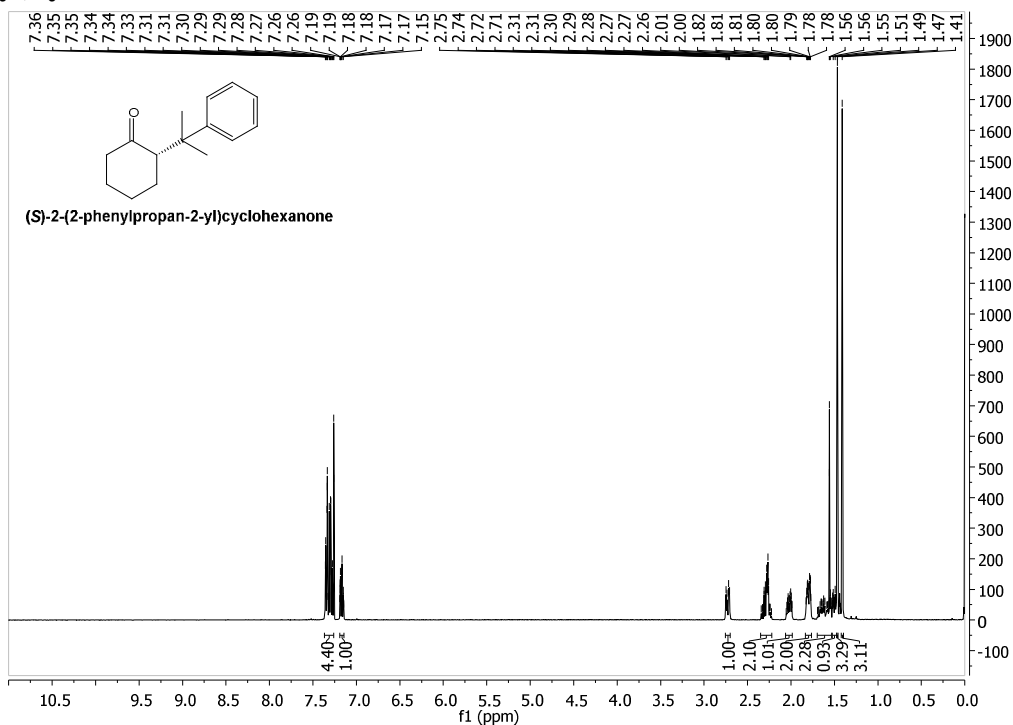


Figure S-13: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (*S*)-2-(2-phenylpropan-2-yl)cyclohexanone.

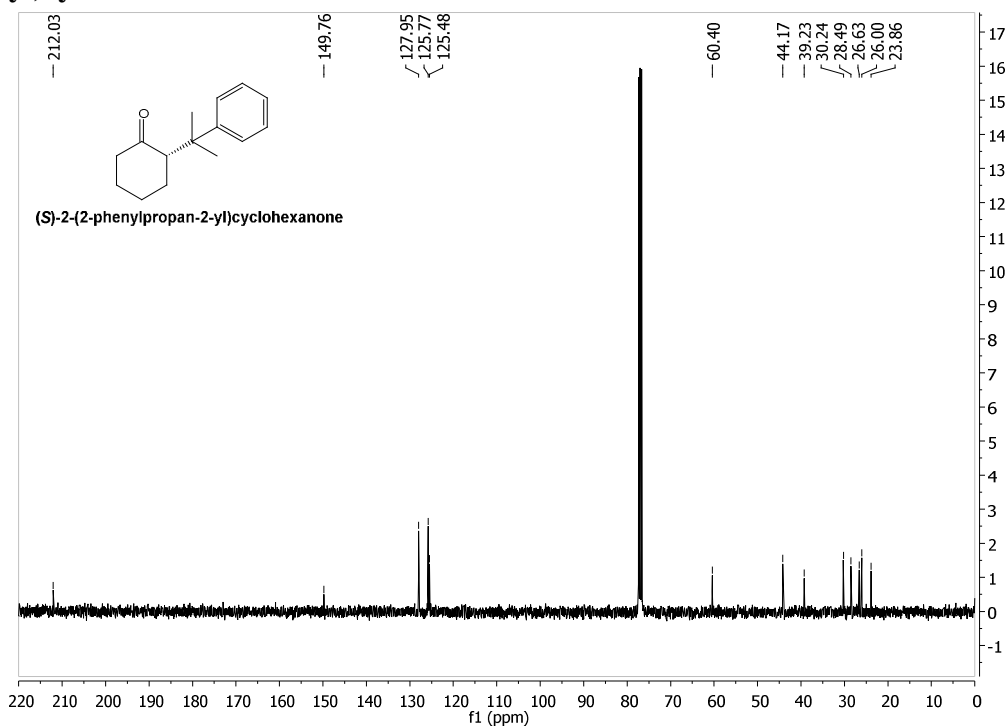


Figure S-14: ^1H NMR of (CDCl_3 , 400 MHz) of compound (*R*)-5.

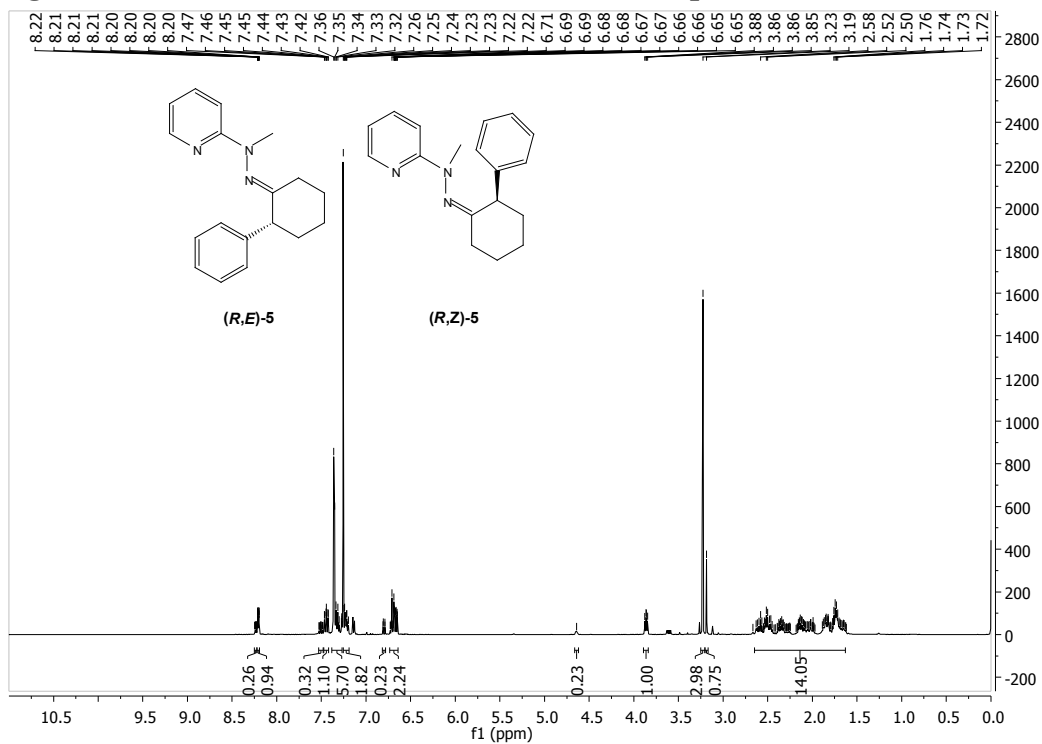


Figure S-15: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (*R*)-5.

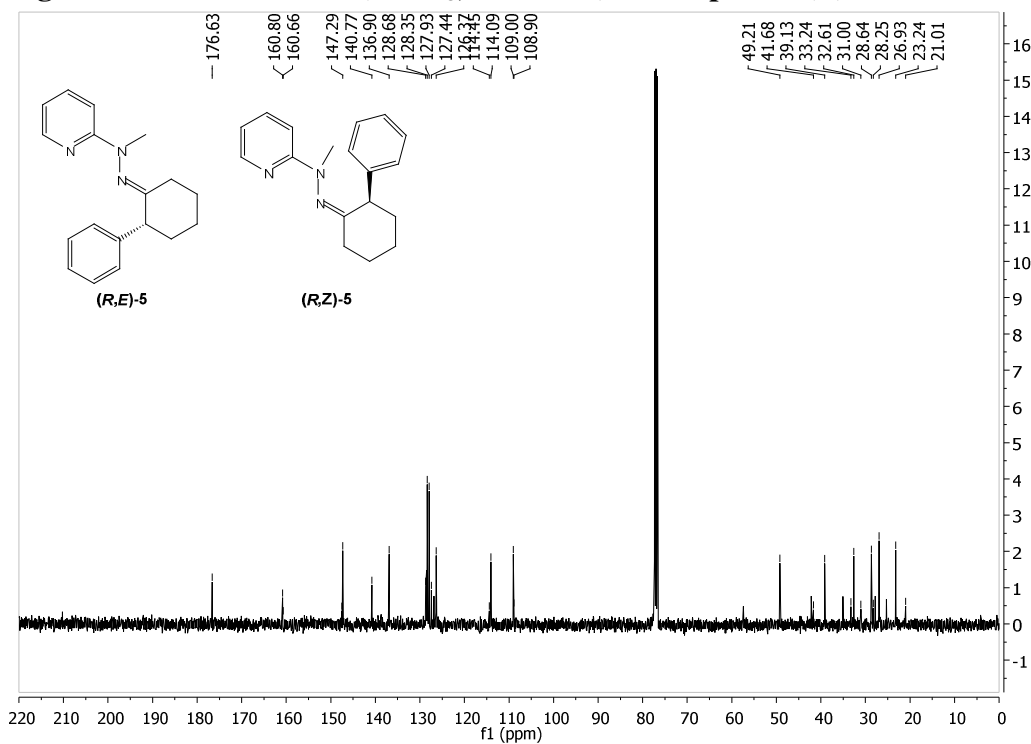


Figure S-16: ^1H NMR of (CDCl_3 , 400 MHz) of compound (S)-5.

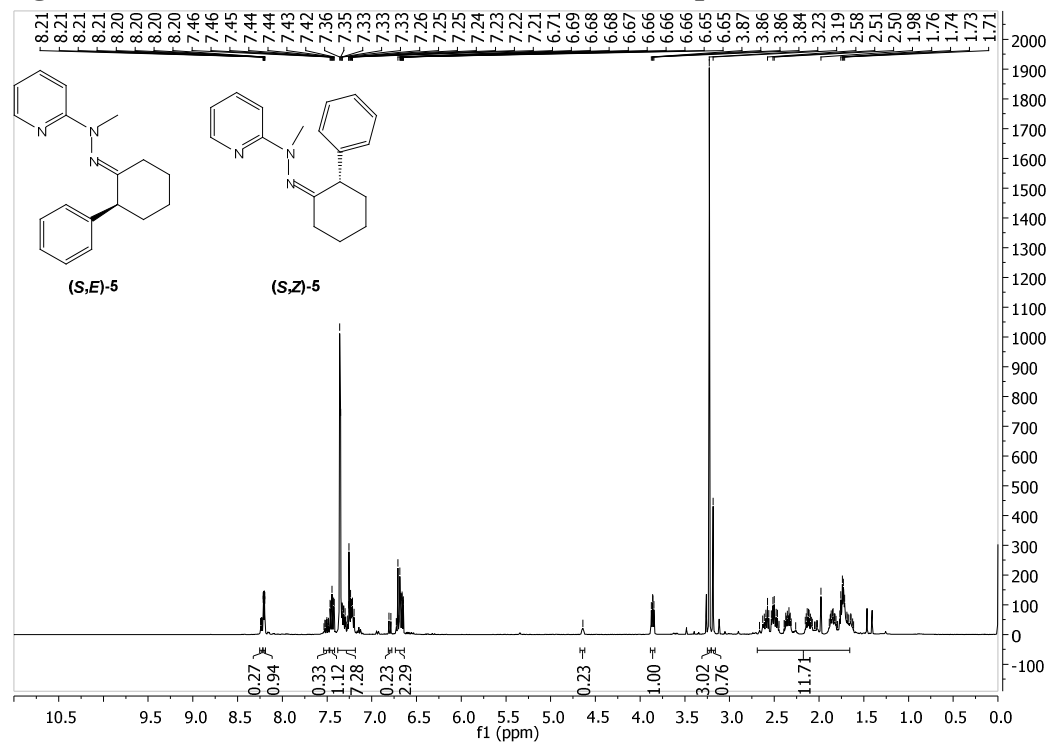


Figure S-17: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (S)-5.

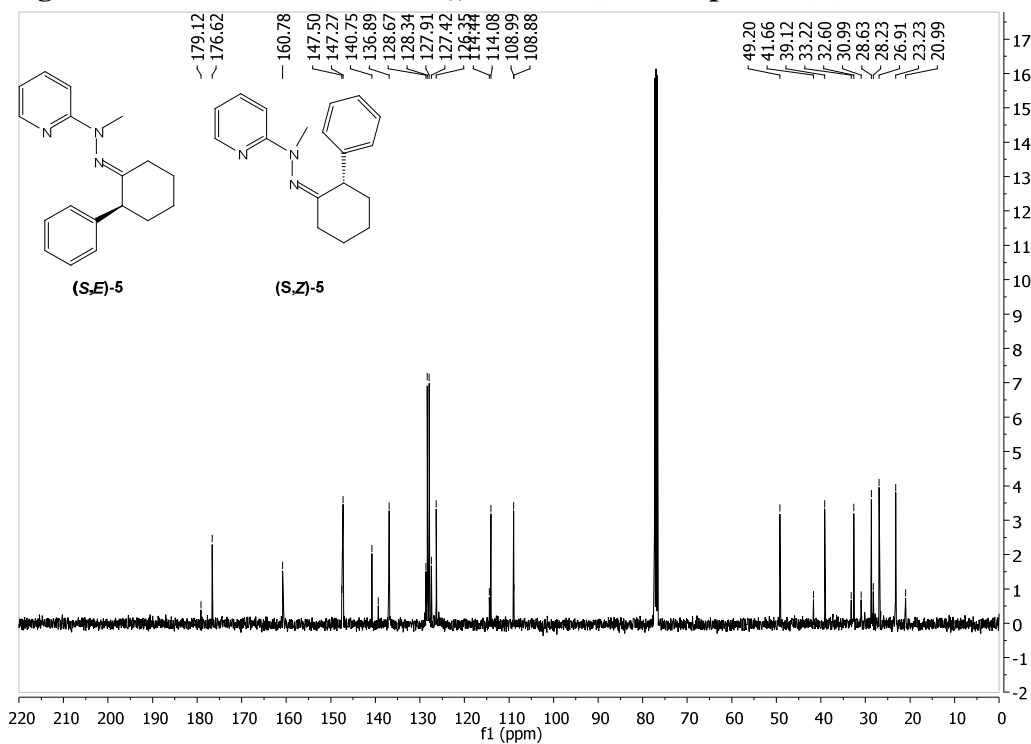


Figure S-18: ^1H NMR of (CDCl_3 , 400 MHz) of compound (*R,S*)-6.

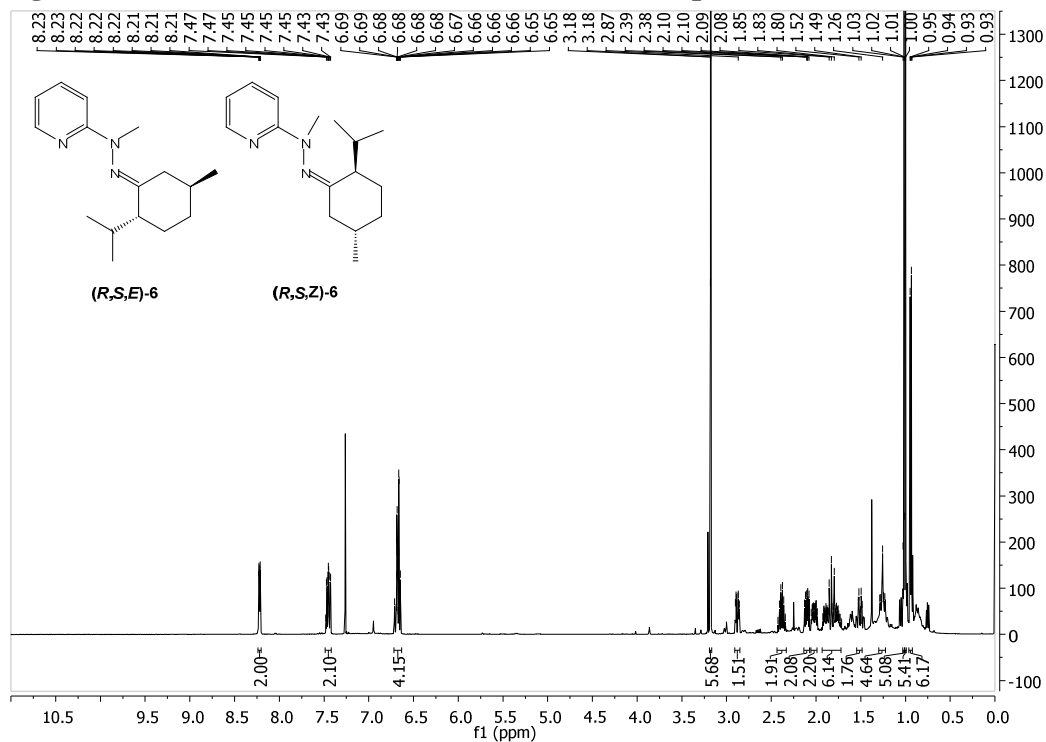


Figure S-19: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (*R,S*)-6.

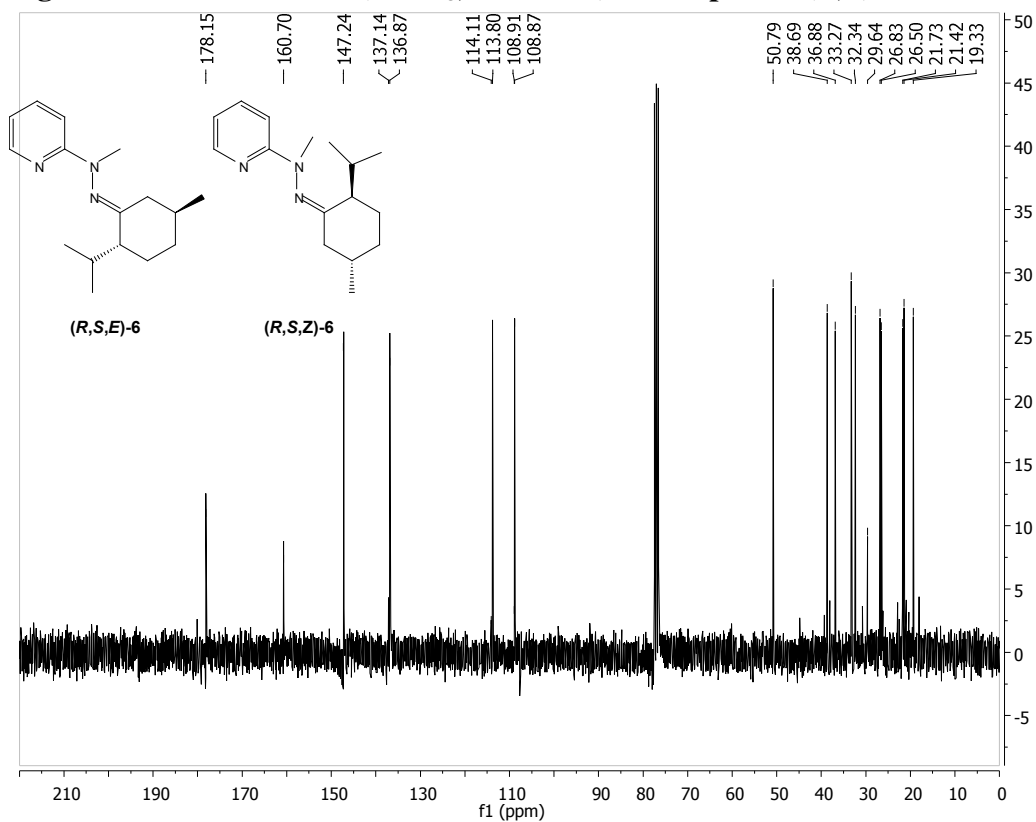


Figure S-20: ^1H NMR of (CDCl_3 , 400 MHz) of compound (*S,R*)-6.

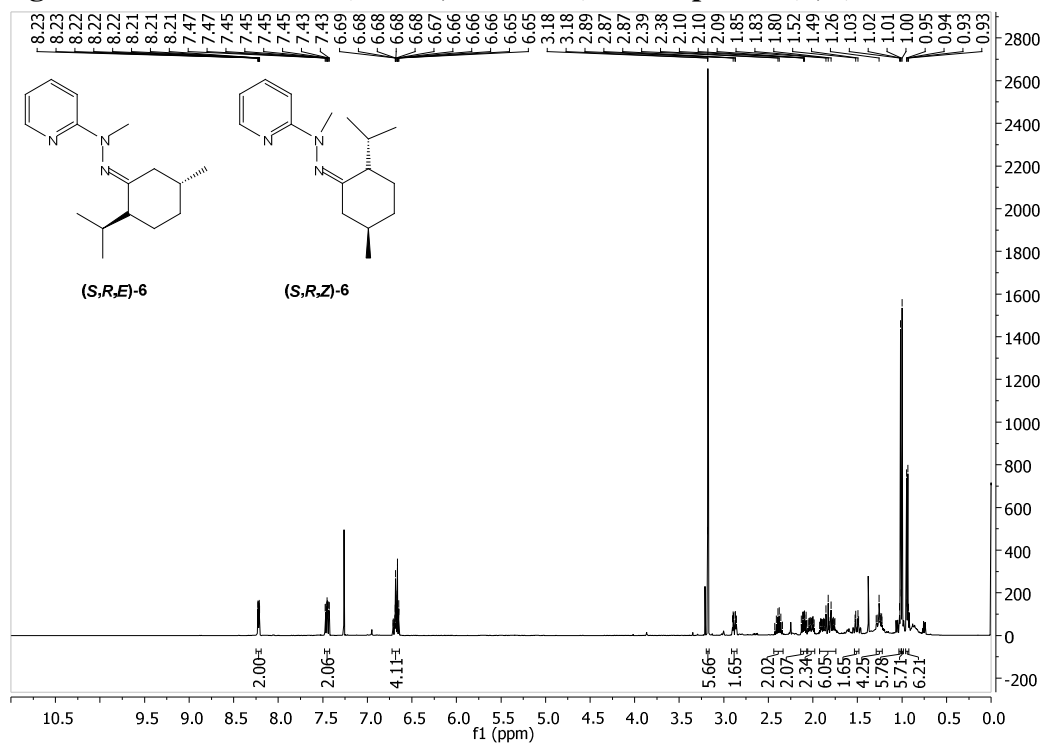
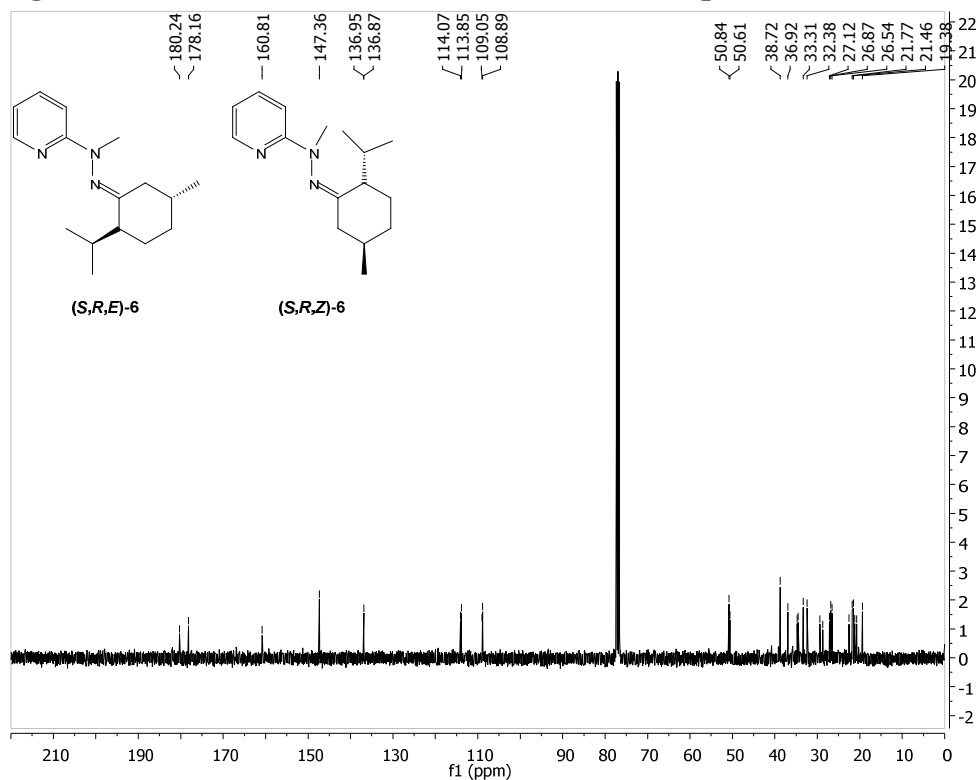


Figure S-21: ^{13}C NMR of (CDCl_3 , 400 MHz) of compound (*S,R*)-6.



References:

- (1) Baldo, M. A.; Chessa, G.; Marangoni, G.; Pitteri, B. *Synthesis* **1987**, 720.
- (2) Johnson, C. R.; Zeller, J. R. *Tetrahedron* **1984**, *40*, 1225.