Electronic Supplementary Material (ESI) for Dalton Transactions.

Catalytic oxidation of alcohols with novel non-heme N_4-tetradentate manganese(II) complexes

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Supplementary information

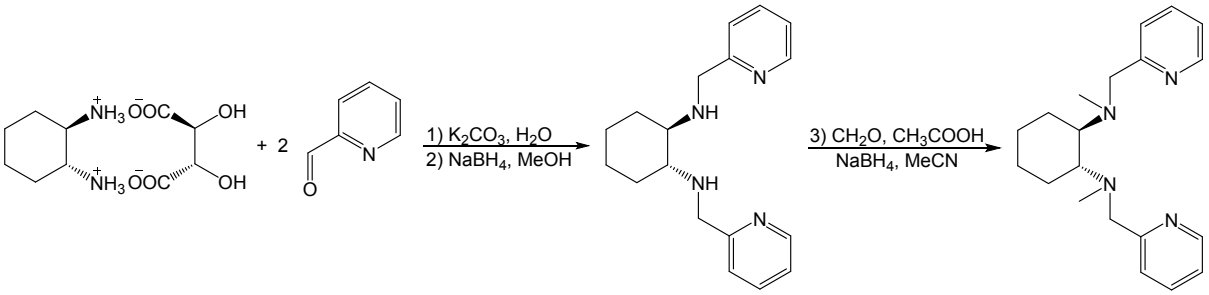
S1 General considerations

All reagents were obtained from commercial sources, i.e. Sigma-Aldrich, Merck and Rochelle Chemicals and used as received. $Mn(OTf)_2$ was stored in a glove box (MBraun) under an Ar atmosphere. Solvents employed in complex synthesis, Et_2O and DCM, were freshly distilled under a N_2 atmosphere using Na/benzophenone and CaH_2, respectively. Catalytic experiments were conducted with 30 % H_2O_2, containing an inhibitor to prevent disproportionation, and stored in a refrigerator when not in use. FT-IR spectra were documented on a BrukerAlpha-P range infrared instrument equipped with an ATR accessory as neat samples in the range of 400 cm^{-1} to 4000 cm^{-1}. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker Ultrashield Plus (600 MHz and 151 MHz, respectively) in 5 mm cylindrical glass tubes. APCI-MS analysis was done on a BrukermicroTOF-Q II mass spectrometer. Magnetic susceptibility measurements were conducted using a Sherwood Scientific MK1 with 4 mm in diameter sample tubes containing 50 mM samples in acetonitrile. Elemental analysis was carried by the University of KwaZulu-Natal (UKZN) Mass Spectrometry Laboratory. Gas chromatographic analysis (GC and GC-MS) were performed on an Agilent 6890 Series GC System with a HP 5 column, 30 m in length, 0.320 mm internal diameter and 0.25 mm film thickness. Rinsing solutions included MeCN (GC) or MeOH and DCM (GC-MS) with N_2 (GC) or He (GC-MS) serving as the carrier gas and biphenyl as an internal standard.

S2 Synthesis of non-heme N_4-tetradentate ligands, *R,R*- and *S,S*-L1 – L4

The resolution of the 1,2-diaminocyclohexane tartrate salt was done according to a previously reported method.[1-2] Chiral ligands, and ***R,R-*** and ***S,S*-L1 - L4** were prepared according to a modified literature procedure.[3]

N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-(*R,R*)-1,2-diaminocyclohexane (*R,R*-BPMCN) (*R,R*-L1)



*Scheme S1: Synthesis of ligand **R,R-BPMCN (R,R-L1)**.*

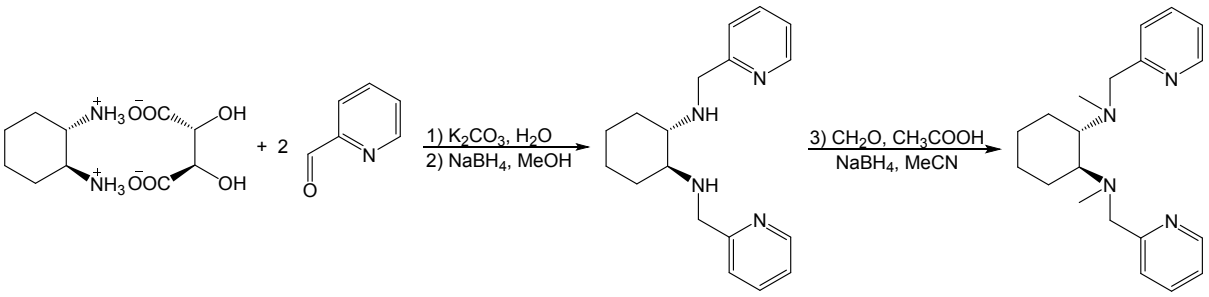
R,R-BPMCN-Imine: In a beaker the *R,R*-DACH salt (346 mg, 1.309 mmol) and K_2CO_3 (360 mg, 2.605 mmol) was dissolved in water (3 ml) which was added to a 100 ml round bottom flask after complete dissolution. Ethanol (5 ml) was added to the solution. The solution was heated almost to reflux during which 2-pyridinecarboxaldehyde (275 mg, 2.567 mmol), dissolved in 5 ml of ethanol, was added to the solution. The reaction mixture was refluxed for 6 hours after which 3 ml of water was added. The solution was then cooled down in an ice bath for 30 min. The water layer was extracted with DCM (3 x 5 ml portions) after which the organic layer was washed with water (2 x 5 ml portions) and saturated NaCl solution (1 x 5 ml portion). The organic layer was dried over Na_2SO_4 and the solvent removed. Diethyl ether (Et_2O) was added until the entire product dissolved. The solvent was reduced to 10 ml and left overnight in the freezer. The product was isolated as a light yellow crystalline solid (226 mg, 60 % yield). FT-IR (ATR) v, cm^{-1}: 3061, 3008, 2928, 2862, 1643, 1567, 1468, 775. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.49 – 8.45 (m, 2H), 8.24 (s, 2H), 7.81 (d, J = 7.9 Hz, 2H), 7.57 (td, J = 7.7, 1.5 Hz, 2H), 7.14 (ddd, J = 7.4, 4.8, 1.1 Hz, 2H), 3.46 (dd, J = 6.4, 3.4 Hz, 2H), 1.78 (ddd, J = 18.9, 11.2, 2.2 Hz, 6H), 1.49 – 1.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 161.45, 154.63, 149.25, 136.45, 124.48, 121.35, 73.57, 32.74, 24.37.

R,R-BPMCN-amine: *R,R*-BPMCN-imine (206 mg, 0.7045 mmol) was dissolved in MeOH (3 ml) and placed in an ice bath for 30 min. 0.136 g (3.595 mmol) $NaBH_4$ (136 mg, 3.595 mmol) was added portion-wise over a period of 5 min whilst stirring the solution. The resulting solution was further stirred for 1 hour at ambient temperature after which it was refluxed for 1 hour. After the allotted time the solution cooled to room temperature, DCM (20 ml) was added and the organic layer washed with water (2 x 5 ml portions) and saturated NaCl solution (1 x 5 ml portion). The organic layer was dried over Na_2SO_4 and the solvent removed to yield a light yellow oil (196 g; 94 %). FT-IR (ATR, v, cm^{-1}): 3450, 3292, 3059, 3008, 2924, 2853, 1590, 1432, 775. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.50 – 8.40 (m, 2H), 7.55 (td, *J* = 7.7, 1.7 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.07 (dd, *J* = 7.0, 5.2 Hz, 2H), 3.96 (d, *J* = 14.1 Hz, 2H), 3.78 (d, *J* = 14.1 Hz, 2H), 2.25 (dd, *J* = 5.4, 3.7 Hz, 2H), 2.07 (dd, *J* = 10.9, 2.6 Hz, 2H), 1.73 – 1.53 (m, 2H), 1.19 – 1.14 (m, 2H), 1.07 – 0.94 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.71, 149.08, 136.41, 122.32, 121.77, 61.38, 52.53, 31.60, 25.02.

R,R-L1: *R,R*-BPMCN-amine (136 mg, 0.4587 mmol) was dissolved in MeCN (5 ml). Whilst stirring, 35 % formaldehyde (436 mg, 5.082 mmol) and glacial acetic acid (0.75 ml) was added to the solution. The solution was stirred for 30 min after which $NaBH_4$ (73 mg, 1.923 mmol) was added portion wise. The reaction mixture was stirred for 72 hours at ambient temperature where after the MeCN was removed in vacuo. KOH (2 M) was added to the oily residue to raise the pH of the solution above 10. The resulting aqueous solution was

extracted with DCM (3 x 10 ml portions), separated and the organic layer washed with H_2O (2 x 10 ml portions) and saturated NaCl solution (1 x 10 ml portion). The organic layer was dried over Na_2SO_4 and the solvent removed in vacuo to obtain a brown oil (114 mg; 77 %). FT-IR (ATR, v, cm^{-1}): 3050, 2930, 2856, 2791, 1591, 1433, 1264, 732. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.51 (d, *J* = 4.8 Hz, 2H), 7.60 (dd, *J* = 6.2, 1.6 Hz, 2H), 7.16 – 7.11 (m, 2H), 3.94 (d, *J* = 14.5 Hz, 2H), 3.82 (d, *J* = 14.6 Hz, 2H), 2.30 (s, 6H), 2.00 (dd, *J* = 10.6, 2.3 Hz, 2H), 1.85 – 1.70 (m, 2H), 1.34 – 1.27 (m, 2H), 1.23 – 1.12 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 161.29, 148.63, 136.32, 122.92, 121.63, 64.53, 60.44, 36.68, 30.96, 25.84, 25.82.

N,N'-dimethyl-N,N'-bis(6-methylpyridyl-2-methyl)-(*S,S*)-1,2-diaminocyclohexane (*S,S*-BPMCN) (*S,S*-L1)



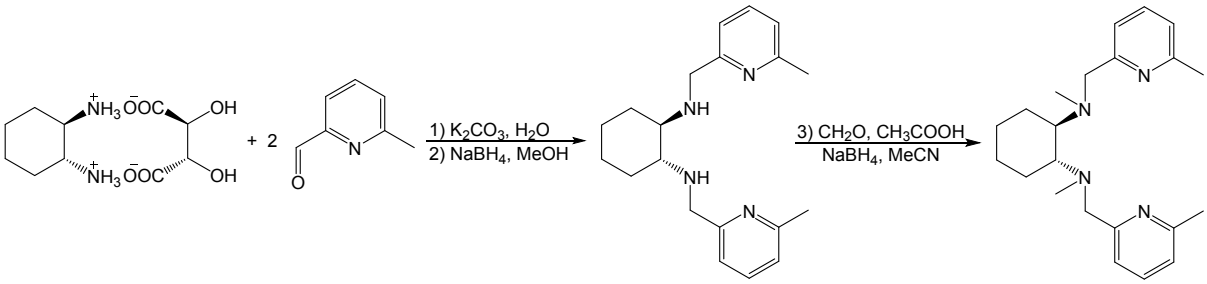
*Scheme S2: Synthesis of ligand **S,S-BPMCN (S,S-L1)**.*

<u>*S,S*-BPMCN-Imine:</u> Prepared according to the same procedure described for *R,R*-BPMCN-Imine. Product isolated as a yellow crystalline solid (228 mg; 59 %). FT-IR (ATR, v, cm^{-1}): 3051, 3009, 2928, 2862, 1643, 1468, 1366, 775. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.56 (d, *J* = 4.7 Hz, 2H), 8.32 (s, 2H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 2H), 7.23 (dd, *J* = 7.3, 5.0 Hz, 2H), 3.58 – 3.52 (m, 2H), 1.92 – 1.81 (m, 6H), 1.52 (t, *J* = 8.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 161.45, 154.62, 149.25, 136.45, 124.48, 121.35, 73.57, 32.74, 24.37.

<u>*S,S*-BPMCN-Amine:</u> Prepared according to the same procedure described for *R,R*-BPMCN-Amine. Product isolated as a yellow oil (187 mg; 88 %). FT-IR (ATR, v, cm^{-1}): 3288, 3063, 3009, 2925, 2853, 1591, 1432, 1119, 753. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.54 (d, *J* = 4.7 Hz, 2H), 7.63 (td, *J* = 7.6, 1.7 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.15 (dd, *J* = 7.1, 5.2 Hz, 2H), 4.04 (d, *J* = 14.1 Hz, 2H), 3.85 (d, *J* = 14.1 Hz, 2H), 2.33 (dd, *J* = 5.4, 3.7 Hz, 2H), 2.16 (dd, *J* = 11.0, 2.5 Hz, 2H), 1.76 – 1.67 (m, 2H), 1.31 – 1.20 (m, 2H), 1.08 (dd, *J* = 9.9, 1.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.67, 149.07, 136.43, 122.34, 121.78, 61.37, 52.51, 31.59, 25.02.

S,S L1: Prepared according to the same procedure described for *R,R*-L1. Product isolated as a dark yellow oil (0.235 g; 68.8 %). FT-IR (ATR, v, cm^{-1}): 3048, 2929, 2855, 2788, 1590, 1433, 1355, 1265, 732. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.51 (d, *J* = 4.8 Hz, 2H), 7.64 – 7.54 (m, 4H), 7.17 – 7.10 (m, 2H), 3.93 (d, *J* = 14.6 Hz, 2H), 3.81 (d, *J* = 14.6 Hz, 2H), 2.67 (dd, *J* = 5.6, 3.2 Hz, 2H), 2.30 (s, 6H), 2.00 (dd, *J* = 10.6, 2.3 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.30 (dd, *J* = 11.1, 2.5 Hz, 2H), 1.22 – 1.12 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 161.41, 148.63, 136.29, 122.89, 121.60, 64.55, 60.51, 36.66, 25.87, 25.84.

N,N'-dimethyl-N,N'-bis(6-methylpyridyl-2-methyl)-(*R,R*)-1,2-diaminocyclohexane (*R,R*-BMPMCN) (*R,R*-L2)



*Scheme S3: Synthesis of ligand **R,R-BMPMCN (R,R-L2)**.*

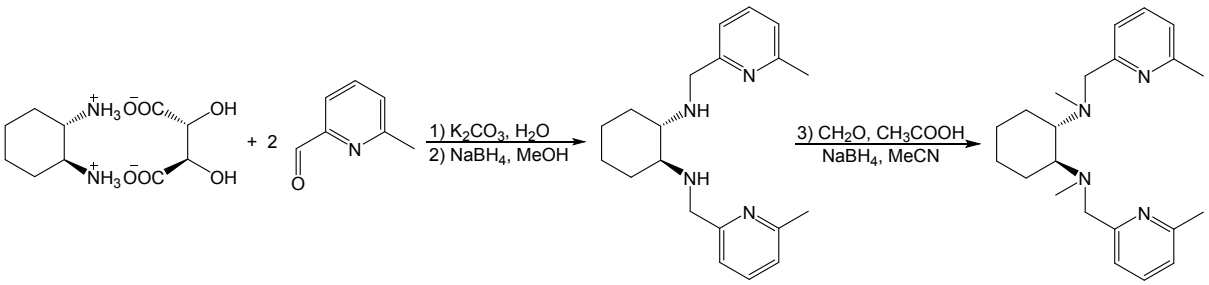
R,R-BMPMCN-Imine: Prepared according to the same procedure described for *R,R*-BPMCN-Imine, employing 6-methyl-2-pyridinecarboxaldehyde as reagent. Product isolated as an orange solid (394 mg; 95 %). FT-IR (ATR, v, cm^{-1}): 3407, 3060, 2927, 2857, 1646, 1572, 1455, 791. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.22 (s, 2H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 3.46 – 3.40 (m, 2H), 2.44 (s, 2H), 1.81 – 1.70 (m, 2H), 1.45 – 1.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 161.72, 157.78, 154.25, 136.63, 124.08, 118.28, 73.63, 32.74, 24.40, 24.30.

R,R-BMPMCN-Amine: Prepared according to the same procedure described for *R,R*-BPMCN-Amine. Product isolated as an orange solid (349 mg; 92 %). FT-IR (ATR, v, cm^{-1}): 3399, 3291, 3061, 2924, 2853, 1577, 1449, 779. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.44 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 3.94 (d, *J* = 14.2 Hz, 2H), 3.73 (d, *J* = 14.2 Hz, 2H), 2.44 (s, 6H), 2.26 (dd, *J* = 5.3, 3.8 Hz, 2H), 2.09 (dd, *J* = 10.9, 2.8 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.16 (dd, *J* = 8.7, 5.3 Hz, 2H), 1.05 – 0.95 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.05, 157.60, 136.62, 121.24, 119.12, 61.42, 52.54, 31.67, 25.04, 24.48.

R,R-L2: Prepared according to the same procedure described for *R,R*-L1. Product isolated as a brown oil (324 mg; 79 %). FT-IR (ATR, v, cm^{-1}): 3370, 3059, 2926, 2854, 2782, 1577,

1452, 1053, 757. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.49 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 3.91 (d, *J* = 14.8 Hz, 2H), 3.77 (d, *J* = 14.8 Hz, 2H), 2.70 – 2.63 (m, 2H), 2.53 (s, 6H), 2.30 (s, 6H), 1.99 (d, *J* = 12.8 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.34 – 1.26 (m, 2H), 1.17 (dd, *J* = 12.4, 6.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.80, 157.10, 136.52, 121.01, 119.63, 64.70, 60.36, 36.70, 30.96, 25.86, 25.69, 24.45.

N,N'-dimethyl-N,N'-bis(6-methylpyridyl-2-methyl)-(*S,S*)-1,2-diaminocyclohexane (*S,S*-BMPMCN) (*S,S*-L2)



*Scheme S4: Synthesis of ligand **S,S-BMPMCN (S,S-L2)**.*

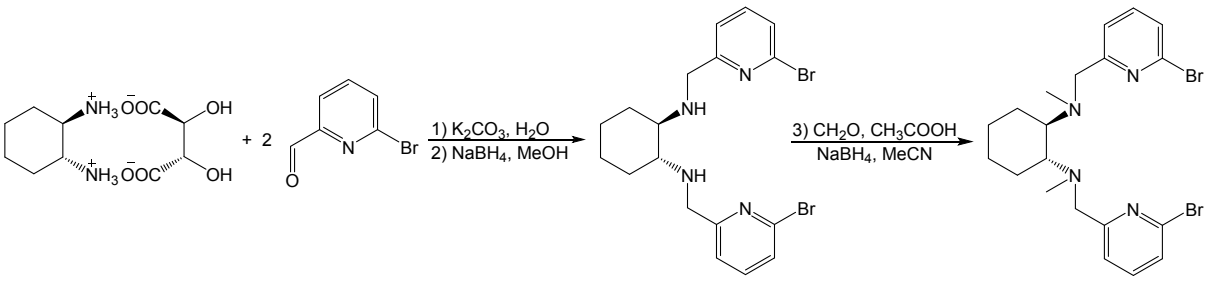
<u>*S,S*-BMPMCN-Imine:</u> Prepared according to the same procedure described for *R,R*-BPMCN-Imine, employing 6-methyl-2-pyridinecarboxaldehyde as reagent. Product isolated as an orange solid (377 mg; 91 %). FT-IR (ATR, v, cm^{-1}): 3402, 3060, 2927, 2857, 1646, 1590, 1455, 791. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.31 (s, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 3.57 – 3.47 (m, 2H), 2.53 (s, 6H), 1.85 (ddd, *J* = 37.7, 15.2, 7.1 Hz, 6H), 1.50 (dd, *J* = 14.3, 5.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 161.72, 157.78, 154.23, 136.63, 124.09, 118.29, 73.63, 32.74, 24.40, 24.30.

<u>*S,S*-BMPMCN-Amine</u>: Prepared according to the same procedure described for *R,R*-BPMCN-Amine. Product isolated as an orange solid (316 mg; 87 %). FT-IR (ATR, v, cm^{-1}): 3563, 3294, 3061, 2924, 2853, 1577, 1449, 778. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.44 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 3.94 (d, *J* = 14.1 Hz, 2H), 3.73 (d, *J* = 14.1 Hz, 2H), 2.44 (s, 6H), 2.25 (dd, *J* = 5.5, 3.6 Hz, 2H), 2.08 (dd, *J* = 10.9, 2.7 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.16 (ddd, *J* = 7.2, 6.0, 2.4 Hz, 2H), 1.05 – 0.94 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.04, 157.61, 136.63, 121.25, 119.14, 61.41, 52.54, 31.66, 25.04, 24.47.

<u>*S,S*-L2:</u> Prepared according to the same procedure described for *R,R*-L1. Product isolated as a brown oil (256 mg; 85 %). FT-IR (ATR, v, cm^{-1}): 3371, 3059, 2926, 2854, 2782, 1577, 1452, 779. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 3.82 (d, *J* = 14.8 Hz, 2H), 3.68 (d, *J* = 14.8 Hz, 2H), 2.58 (dd, *J* = 5.7, 3.2 Hz, 2H), 2.45 (s, 6H), 2.21 (s, 6H), 1.97 – 1.84 (m, 2H), 1.74 – 1.61 (m, 2H), 1.25 –

1.16 (m, 2H), 1.08 (t, *J* = 9.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.83, 157.10, 136.52, 121.00, 119.62, 64.71, 60.38, 36.70, 25.87, 25.69, 24.45.

N,N'-dimethyl-N,N'-bis(6-bromopyridyl-2-methyl)-(*R,R*)-1,2-diaminocyclohexane (*R,R*-BBPMCN) (*R,R*-L3)



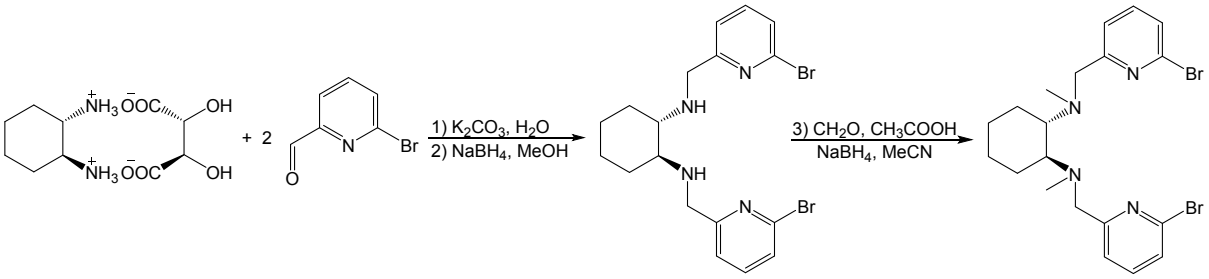
*Scheme S5: Synthesis of ligand **R,R-BBPCN (R,R-L3)**.*

R,R-BBPCN-Imine: Prepared according to the same procedure described for *R,R*-BPMCN-Imine, employing 6-bromo-2-pyridinecarboxaldehyde as reagent. The product was isolated, after recrystallisation in EtOH, as a white crystalline solid (394 mg; 68 %). FT-IR (ATR, v, cm^{-1}): 2930, 2855, 1649, 1546, 1439, 1119, 791. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.15 (s, 2H), 7.82 (dd, *J* = 7.6, 0.5 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 7.8, 0.6 Hz, 2H), 3.45 – 3.35 (m, 2H), 1.83 – 1.66 (m, 6H), 1.42 (dd, *J* = 15.2, 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.09, 155.79, 141.31, 138.84, 128.97, 119.77, 73.52, 32.56, 24.25.

R,R-BBPCN-Amine: Prepared according to the same procedure described for *R,R*-BPMCN-Amine. Product isolated as a white solid (345 mg; 92 %). FT-IR (ATR, v, cm^{-1}): 3291, 3238, 2927, 2855, 1553, 1403, 781. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 3.96 (d, *J* = 14.7 Hz, 2H), 3.74 (d, *J* = 14.7 Hz, 2H), 2.21 (dd, *J* = 5.5, 3.6 Hz, 2H), 2.07 (dd, *J* = 10.9, 2.8 Hz, 2H), 1.68 – 1.62 (m, 2H), 1.17 – 1.14 (m, 2H), 1.01 – 0.93 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 162.55, 141.40, 138.97, 126.09, 121.19, 61.40, 51.88, 31.67, 24.96.

R,R-L3: Prepared according to the same procedure described for *R,R*-L1. Product isolated as a yellow oil (461 mg; 88 %). FT-IR (ATR, v, cm^{-1}): 3047, 2927, 2853, 2784, 1553, 1402, 1115, 782. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.45 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 3.81 (d, *J* = 15.3 Hz, 2H), 3.68 (d, *J* = 15.3 Hz, 2H), 2.65 – 2.47 (m, 2H), 2.20 (s, 6H), 1.88 (d, *J* = 12.8 Hz, 2H), 1.73 – 1.66 (m, 2H), 1.23 – 1.16 (m, 2H), 1.12 – 1.04 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 163.43, 140.94, 138.69, 125.77, 121.38, 64.85, 59.75, 36.80, 25.86, 25.77.

N,N'-dimethyl-N,N'-bis(6-bromopyridyl-2-methyl)-(*S,S*)-1,2-diaminocyclohexane (*S,S*-BBPMCN) (*S,S*-L3)



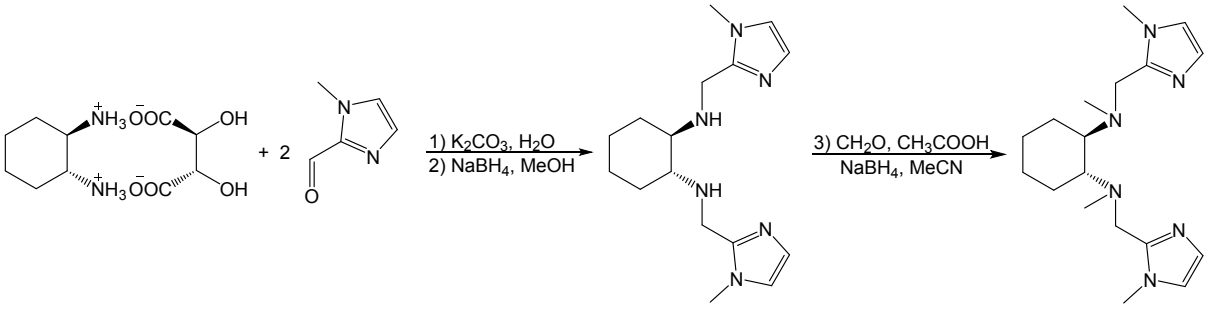
*Scheme S6: Synthesis of ligand **S,S-BBPCN (S,S-L3)**.*

S,S-BBPCN-Imine: Prepared according to the same procedure described for *R,R*-BPMCN-Imine, employing 6-bromo-2-pyridinecarboxaldehyde as reagent. The product was isolated, after recrystallisation in EtOH, as a white crystalline solid (432 mg; 74 %). FT-IR (ATR, v, cm^{-1}): 2982, 2930, 2854, 1649, 1546, 1438, 1119, 791. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.24 (s, 2H), 7.91 (dd, *J* = 7.7, 0.7 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.45 (dd, *J* = 7.8, 0.8 Hz, 2H), 3.55 – 3.44 (m, 2H), 1.97 – 1.86 (m, 2H), 1.85 – 1.75 (m, 4H), 1.56 – 1.45 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 160.09, 155.79, 141.30, 138.84, 128.97, 119.77, 73.52, 32.56, 24.25.

S,S-BBPCN-Amine: Prepared according to the same procedure described for *R,R*-BPMCN-Amine. Product isolated as a white solid (392 mg; 96 %). FT-IR (ATR, v, cm^{-1}): 3278, 3197, 3047, 2932, 2849, 2773, 1552, 1402, 1124, 780. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 3.96 (d, *J* = 14.7 Hz, 2H), 3.74 (d, *J* = 14.7 Hz, 2H), 2.21 (dd, *J* = 5.5, 3.6 Hz, 2H), 2.07 (dd, *J* = 10.9, 2.7 Hz, 2H), 1.72 – 1.57 (m, 2H), 1.16 (ddd, *J* = 11.1, 5.2, 1.7 Hz, 2H), 0.97 (dd, *J* = 9.8, 1.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 162.53, 141.40, 138.97, 126.09, 121.19, 61.40, 51.87, 31.66, 24.96.

S,S-L3: Prepared according to the same procedure described for *R,R*-L1. Product isolated as a yellow oil (492 mg; 85 %). FT-IR (ATR, v, cm^{-1}): 3064, 2927, 2853, 2784, 1553, 1402, 1115, 782. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.45 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 3.81 (d, *J* = 15.3 Hz, 2H), 3.68 (d, *J* = 15.3 Hz, 2H), 2.56 (dd, *J* = 5.7, 3.2 Hz, 2H), 2.20 (s, 6H), 1.89 (d, *J* = 12.8 Hz, 2H), 1.73 – 1.67 (m, 2H), 1.20 (d, *J* = 8.9 Hz, 2H), 1.09 (t, *J* = 9.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 163.40, 140.94, 138.69, 125.78, 121.39, 64.85, 59.74, 36.81, 25.86, 25.76.

N,N'-dimethyl-N,N'-bis(1-methyl-2-imidazolemethyl)-(*R,R*)-1,2-diaminocyclohexane (*R,R*-BMIMCN) (*R,R*-L4)



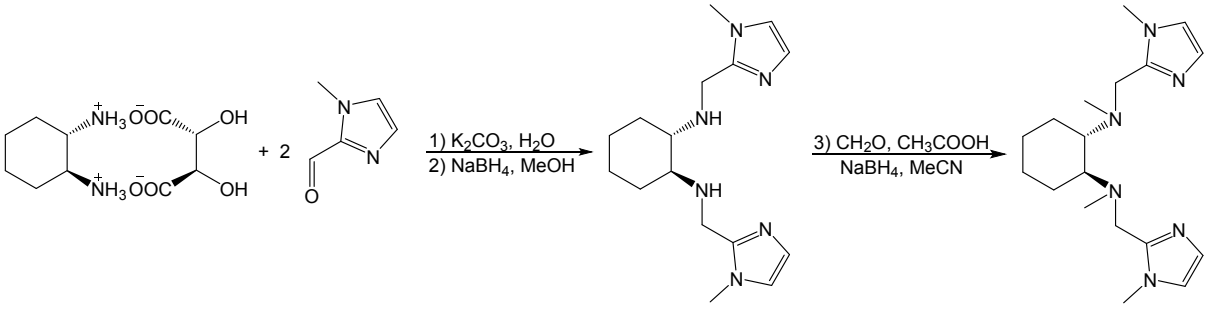
*Scheme S7: Synthesis of ligand **R,R-BMIMCN (R,R-L4)**.*

R,R-BMIMCN-Imine: Prepared according to the same procedure described for *R,R*-BPMCN-Imine, employing 1-methyl-2-imidazolecarboxaldehyde as reagent. Product isolated as a light yellow oil (348 mg; 90 %). FT-IR (ATR, v, cm^{-1}): 3381, 3281, 3106, 2927, 2857, 1464, 1518, 1438, 752. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.15 (s, 2H), 6.96 (d, *J* = 0.8 Hz, 2H), 6.79 (s, 2H), 3.82 (s, 6H), 3.23 – 3.18 (m, 2H), 1.80 – 1.69 (m, 4H), 1.62 (dt, *J* = 9.7, 8.8 Hz, 2H), 1.43 – 1.37 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 152.18, 143.17, 128.88, 124.73, 74.80, 35.51, 32.92, 24.34.

R,R-BMIMCN-Amine: Prepared according to the same procedure described for *R,R*-BPMCN-Amine. Product isolated as a yellow oil (309 mg; 94 %). FT-IR (ATR, v, cm^{-1}): 3288, 3109, 2926, 2854, 1520, 1449, 1109, 731. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 6.82 (d, *J* = 1.2 Hz, 2H), 6.71 (d, *J* = 1.1 Hz, 2H), 3.86 (d, *J* = 13.5 Hz, 2H), 3.63 (d, *J* = 13.5 Hz, 2H), 3.56 (s, 6H), 2.18 (dd, *J* = 5.5, 3.6 Hz, 2H), 2.08 (dd, *J* = 11.0, 2.7 Hz, 2H), 1.68 – 1.63 (m, 2H), 1.17 (dd, *J* = 15.1, 5.5 Hz, 2H), 1.01 – 0.94 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 146.84, 127.00, 121.14, 61.18, 43.07, 32.80, 31.27, 24.90.

R,R-L4: Prepared according to the same procedure described for *R,R*-L1. Product isolated as a yellow oil (250 mg; 78 %). FT-IR (ATR, v, cm^{-1}): 3366, 3105, 2928, 2855, 2788, 1499, 1449, 1115, 731. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 6.91 (d, *J* = 1.2 Hz, 2H), 6.82 (d, *J* = 1.1 Hz, 2H), 3.76 (d, *J* = 13.4 Hz, 2H), 3.71 (d, *J* = 13.3 Hz, 8H), 2.59 (dd, *J* = 5.2, 3.1 Hz, 2H), 2.05 (s, 6H), 1.94 (dd, *J* = 8.0, 4.4 Hz, 2H), 1.76 (dd, *J* = 6.4, 2.5 Hz, 2H), 1.24 – 1.13 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 146.22, 126.89, 121.40, 62.01, 50.94, 35.42, 32.72, 25.64, 24.44.

N,N'-dimethyl-N,N'-bis(1-methyl-2-imidazolemethyl)-(*S,S*)-1,2-diaminocyclohexane (*S,S*-BMIMCN) (*S,S*-L4)



*Scheme S8: Synthesis of ligand **S,S-BMIMCN (S,S-L4)**.*

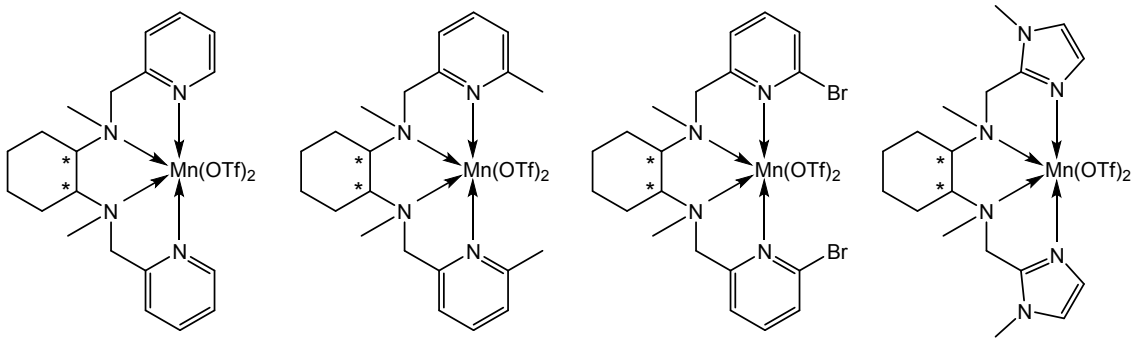
S,S-BMIMCN-Imine: Prepared according to the same procedure described for *R,R*-BPMCN-Imine, employing 1-methyl-2-imidazolecarboxaldehyde as reagent. Product isolated as a yellow oil (348 mg; 90 %). FT-IR (ATR, v, cm^{-1}): 3385, 3284, 3106, 2927, 2857, 1646, 1438, 752. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 8.24 (s, 2H), 7.04 (s, 2H), 6.87 (s, 2H), 3.90 (s, 6H), 3.34 – 3.24 (m, 2H), 1.91 – 1.77 (m, 4H), 1.71 (dd, *J* = 16.5, 13.8 Hz, 2H), 1.53 – 1.43 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 152.17, 143.16, 128.87, 124.73, 74.80, 35.52, 32.92, 24.34.

S,S-BMIMCN-Amine: Prepared according to the same procedure described for *R,R*-BPMCN-Amine. Product isolated as a yellow oil (317 mg; 95 %). FT-IR (ATR) v, cm^{-1}: 3292, 3108, 2926, 2854, 1520, 1449, 1109, 731. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 6.82 (d, *J* = 1.1 Hz, 2H), 6.71 (d, *J* = 1.1 Hz, 2H), 3.86 (d, *J* = 13.5 Hz, 2H), 3.63 (d, *J* = 13.5 Hz, 2H), 3.56 (s, 6H), 2.18 (dd, *J* = 5.4, 3.6 Hz, 2H), 2.11 – 2.05 (m, 2H), 1.70 – 1.63 (m, 2H), 1.18 (dd, *J* = 12.9, 6.3 Hz, 2H), 1.04 – 0.92 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 146.83, 126.99, 121.14, 61.17, 43.05, 32.80, 31.26, 24.89.

S,S-L4: Prepared according to the same procedure described for *R,R*-L1. Product isolated as a yellow oil (233 mg; 70 %). FT-IR (ATR, v, cm^{-1}): 3371, 3106, 2928, 2855, 2790, 1499, 1449, 1115, 731. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 6.83 (d, *J* = 1.2 Hz, 2H), 6.74 (d, *J* = 1.1 Hz, 2H), 3.68 (d, *J* = 13.4 Hz, 2H), 3.62 (d, *J* = 13.1 Hz, 8H), 2.51 (dd, *J* = 5.2, 3.2 Hz, 2H), 1.97 (s, 6H), 1.86 (dd, *J* = 8.2, 4.1 Hz, 2H), 1.68 (dd, *J* = 6.4, 2.5 Hz, 2H), 1.18 – 1.04 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ: 146.21, 126.88, 121.40, 62.00, 50.93, 35.42, 32.72, 25.63, 24.44.

S3 Synthesis of non-heme N_4-tetradentate $Mn(OTf)_2$ complexes: *R,R*- and *S,S*-C1 – C4

The N_4-tetradentate non-heme manganese(II)-triflate complexes were prepared according to a modified literature procedure.[3-4]



C1 **C2** **C3** **C4**

Figure S1: Non-heme N_4-tetradentate $Mn(OTf)_2$ comlexes synthesised in this study. Asterisk denotes R,R/S,S configuration.

[(*R,R*-L1)Mn(OTf)$_2$], *R,R*-C1

To a stirring solution of $Mn(OTf)_2$ (165 mg, 0.443 mmol) in dichloromethane (2 ml) was added ***R,R*-L1** (155 mg, 0.478 mmol) in dichloromethane (2 ml). The reaction mixture was stirred for 1 hour. After the allotted time, the pale yellow solution was filtered to remove metallic manganese, the solvent reduced and Et_2O added. The pale-yellow/beige solid which formed was washed with Et_2O (2 x 20 ml portions), dried *in vacuo* to afford a beige solid (146 mg, 46 %). UV/vis, nm (ε, A/mol dm^{-3}): 210.5 (3463), 263.5 (4082). Anal. Calc. (Found) for $MnC_{22}N_4O_6H_{28}F_6S_2$: C 38.99 (39.45); H 4.17 (3.84); N 8.27 (8.47); S 9.47 (9.14). μ_{eff} = 5.553 BM (297 K, MeCN). APCI-MS (m/z): 528.1214 [M-OTf]$^+$.

[(*S,S*-L1)Mn(OTf)$_2$], *S,S*-C1

Prepared according to the same procedure outlined above employing $Mn(OTf)_2$ (131 mg, 0.352 mmol) and ***S,S*-L1** (120 mg, 0.369 mmol) as reagents. Product isolated as a beige solid (137 mg; 49 %). UV/vis, nm (ε, A/mol dm^{-3}): 214.5 (3634), 265.5 (4141). Anal. Calc. (Found) for $MnC_{22}N_4O_6H_{28}F_6S_2$.0.5MeCN: C 39.57 (39.33); H 4.27 (4.16); N 9.03 (9.15); S 9.19 (9.27). μ_{eff} = 5.909 BM (297 K, MeCN). APCI-MS (m/z): 528.1244 [M-OTf]$^+$.

[(*R,R*-L2)Mn(OTf)$_2$], *R,R*-C2

Prepared according to the same procedure outlined above employing $Mn(OTf)_2$ (222 mg, 0.598 mmol) and ***R,R*-L2** (223 mg, 0.632 mmol) as reagents. Product isolated as a beige solid (235 mg; 56 %). UV/vis, nm (ε, A/mol dm^{-3}): 221.5 (3946), 271 (4598). Anal. Calc. (Found) for $MnC_{24}N_4O_6H_{32}F_6S_2$: C 40.85 (41.15); H 4.58 (4.46); N 7.94 (8.30); S 9.09 (8.98). μ_{eff} = 5.964 BM (297 K, MeCN). APCI-MS (m/z): 556.1512 [M-OTf]$^+$.

[(*S,S*-L2)Mn(OTf)$_2$], *S,S*-C2

Prepared according to the same procedure outlined above employing $Mn(OTf)_2$ (244 mg, 0.655 mmol) and ***S,S*-L2** (243 mg, 0.689 mmol) as reagents. Product isolated as a beige solid (360 mg; 74 %). UV/vis, nm (ε, A/mol dm^{-3}): 219.5 (4215), 269.5 (4627). Anal. Calc. (Found) for $MnC_{24}N_4O_6H_{32}F_6S_2$: C 40.85 (40.66); H 4.58 (4.54); N 7.94 (8.30); S 9.09 (8.83). μ_{eff} = 5.798 BM (297 K, MeCN). APCI-MS (m/z): 556.1548 [M-OTf]$^+$.

[(*R,R*-L3)Mn(OTf)$_2$], *R,R*-C3

Prepared according to the same procedure outlined above employing $Mn(OTf)_2$ (194 mg, 0.523 mmol) and ***R,R*-L3** (267 mg, 0.554 mmol) as reagents. Product isolated as a beige solid (253 mg; 58 %). UV/vis, nm (ε, A/mol dm^{-3}): 220 (4812), 262.5 (4995). Anal. Calc. (Found) for $MnC_{22}N_4O_6H_{28}F_6S_2Br_2$.0.25DCM: C 31.20 (30.78); H 3.36 (3.49); N 6.54 (6.86); S 7.49 (7.89). μ_{eff} = 5.761 BM (297 K, MeCN). APCI-MS (m/z): 685.9374 [M-OTf]$^+$.

[(*S,S*-L3)Mn(OTf)$_2$], *S,S*-C3

Prepared according to the same procedure outlined above employing $Mn(OTf)_2$ (228 mg, 0.615 mmol) and ***S,S*-L3** (310 mg, 0.643 mmol) as reagents. Product isolated as a beige solid (265 mg; 49 %). UV/vis, nm (ε, A/mol dm^{-3}): 234 (4195), 267.5 (4018). Anal. Calc. (Found) for $MnC_{22}N_4O_6H_{28}F_6S_2Br_2.Et_2O$: C 34.34 (34.76); H 3.99 (3.77); N 6.16 (6.92); S 7.05 (7.28). μ_{eff} = 5.775 BM (297 K, MeCN). APCI-MS (m/z): 685.9420 [M-OTf]$^+$.

[(*R,R*-L4)Mn(OTf)$_2$], *R,R*-C4

Prepared according to the same procedure outlined above employing $Mn(OTf)_2$ (212 mg, 0.570 mmol) and ***R,R*-L4** (197 mg, 0.596 mmol) as reagents. Product isolated as a white solid (206 mg; 53 %). UV/vis, nm (ε, A/mol dm^{-3}): 228 (2874), 280 (300). Anal. Calc. (Found) for $MnC_{20}N_4O_6H_{30}F_6S_2$: C 35.14 (35.30); H 4.43 (4.62); N 12.3 (12.20); S 9.38 (9.29). μ_{eff} = 5.713 BM (297 K, MeCN). APCI-MS (m/z): 534.1426 [M-OTf]$^+$.

[(*S,S*-L4)Mn(OTf)$_2$], *S,S*-C4

Prepared according to the same procedure outlined above employing $Mn(OTf)_2$ (220 mg, 0.593 mmol) and ***S,S*-L4** (206 mg, 0.623 mmol) as reagents. Product isolated as a white solid (224 g; 52 %). UV/vis, nm (ε, A/mol dm^{-3}): 214.5 (3412), 274 (579). Anal. Calc. (Found) for $MnC_{20}N_4O_6H_{30}F_6S_2$: C 35.14 (35.10); H 4.43 (4.50); N 12.3 (12.44); S 9.38 (9.29). μ_{eff} = 5.650 BM (297 K, MeCN). APCI-MS (m/z): 534.1429 $[M\text{-}OTf]^+$.

S4 Screening of non-heme N_4-tetradentate Mn(II) complexes

Complex ***R,R-*** or ***S,S*-C1** - **C4** (2 µmol) was dissolved in MeCN (1.225 ml) along with BnOH (2 mmol, 0.205 ml) and AcOH (10 equivalents, 1.140 ml). 30 % H_2O_2 (4 equivalents, 0.620 ml) was slowly added by syringe pump over a period of 30 min, where after the reaction was stirred for another 5 min. Final concentrations: complex (0.620 mM), BnOH (620 mM), AcOH (6.2 M) and H_2O_2 (2.5 M). The mixture was filtered through a silica plug and analysed by GC against an internal standard (biphenyl). All runs were done in duplicate.

S5 Optimisation of catalytic alcohol oxidation reaction parameters

S5.1 Optimisation of catalyst concentration

Varying amounts of complex ***S,S*-C4** (0.1 mol % - 1 mol %) was dissolved in MeCN (1.225 ml) along with BnOH (2 mmol, 0.205 ml) and AcOH (10 equivalents, 1.140 ml). 30 % H_2O_2 (4 equivalents, 0.620 ml) was slowly added by syringe pump over a period of 30 min, where after the reaction was stirred for another 5 min. Final concentrations: ***S,S*-C4** (0.25 - 2.5 mM), BnOH (620 mM), AcOH (6.2 M) and H_2O_2 (2.5 M). The mixture was filtered through a silica plug and analysed by GC against an internal standard (biphenyl). All runs were done in duplicate.

S5.2 Optimisation of oxidant concentration

Complex ***S,S*-C4** (4 µmol) was dissolved in MeCN (1.225 ml) along with BnOH (0.8 mmol, 0.085 ml) and AcOH (10 equivalents, 0.460 ml). Varying amounts of 30 % H_2O_2 (0.5 - 8 equivalents) was slowly added by syringe pump over a period of 30 min. where after the reaction was stirred for another 5 min. Final concentrations: ***S,S*-C4** (0.125 mM), BnOH (0.25 mM), AcOH (2.5 M) and H_2O_2 (0.12 - 2 M). The mixture was filtered through a silica plug and analysed against an internal standard (biphenyl) by GC. All runs were done in duplicate.

S5.3 Optimisation of co-catalyst concentration

Complex ***S,S*-C4** (4 µmol) was dissolved in MeCN (1.225 ml) along with BnOH (0.8 mmol, 0.085 ml) and varying amounts of AcOH (0 - 15 equivalents, 0 - 0.690 ml). 30 % H_2O_2 (4 equivalents, 0.250 ml) was slowly added by syringe pump over a period of 30 min. where after the reaction was stirred for another 5 min. Final concentrations: ***S,S*-C4** (0.125 mM), BnOH (0.25 mM), AcOH (0 - 3.8 M) and H_2O_2 (1.0 M). The mixture was filtered through a silica plug and analysed against an internal standard (biphenyl) by GC. All runs were done in duplicate.

S5.4 Optimisation of other parameters: time, temperature, catalyst

Table S1: Effect of variation of reaction time, temperature and change of catalyst on the percentage conversion.

Entry	Catalyst mol %	H_2O_2 (eq.)	AcOH (eq.)	Temp. (°C)	Time (min.)	Conv. (%)
1	0.1 (***R,R*-C1**)	1.2	10	25	35	18.6
2	0.1 (***R,R*-C2**)	1.2	10	25	35	8.3
3	0.1 (***R,R*-C2**)	1.2	10	- 5	35	11.5
4	0.1 (***R,R*-C2**)	1.2	14	25	35	12.4
5	0.1 (***R,R*-C2**)	3	10	25	35	9.6
6	0.1 (***R,R*-C2**)	3	10	25	60	9.3
7	0.1 (***R,R*-C1**)	1.2	10	25	190	17.4

Reaction conditions: Complex ***R,R*-C1** or ***R,R*-C2** (2 µmol) was dissolved in acetonitrile with benzyl alcohol (2 mmol) and AcOH (0 or 1.140 ml). H_2O_2 (0.19 or 0.620 ml) was added by syringe pump over 30 min. at temperature indicated (total volume = 3.19 ml) and stirred for an additional 5 min. [a] Conversions were determined by GC against an internal standard (biphenyl).

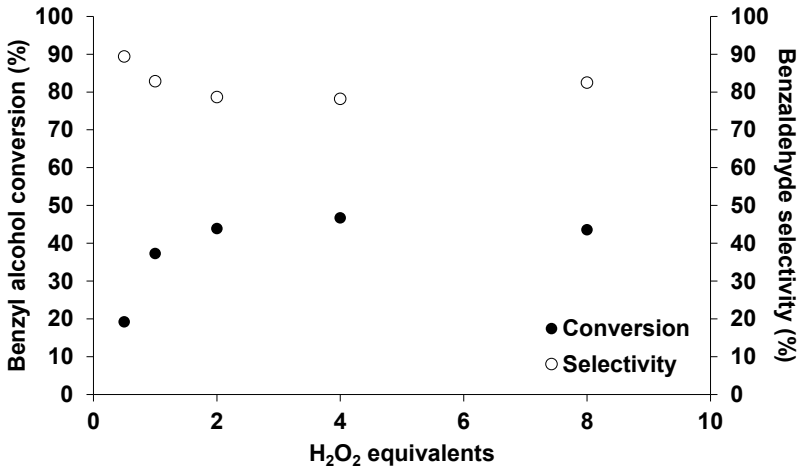


Figure S2: Optimisation of H_2O_2 concentration. Reaction conditions: Complex S,S-C8 (0.5 mol %) in acetonitrile with BnOH (0.8 mmol), AcOH (8 mmol) and H_2O_2 (0.4 - 6.6 mmol) at 298 K for 35 min. All values are the average of a duplicate set of runs.

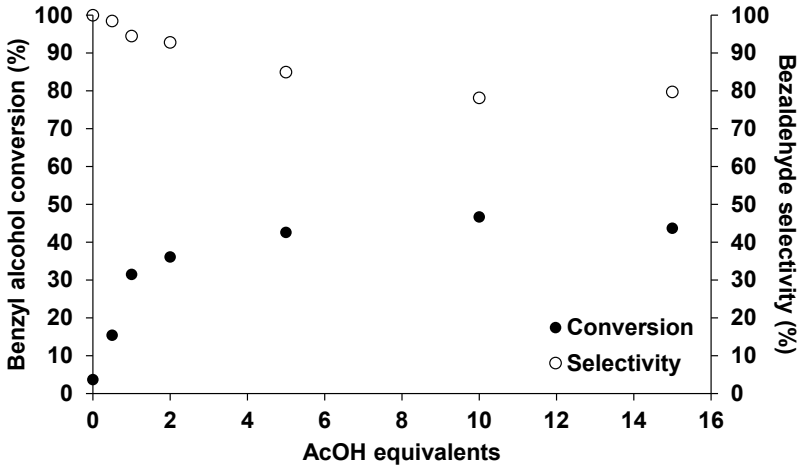


Figure S3: Optimisation of AcOH concentration. Reaction conditions: Complex S,S-C8 (0.5 mol %) in acetonitrile with BnOH (0.8 mmol), AcOH (0 - 12 mmol) and H_2O_2 (3.2 mmol) at 298 K for 35 min. All values are the average of a duplicate set of runs.

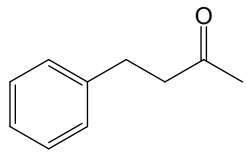
S6 Evaluating primary and secondary alcohol oxidation with *R,R*- and *S,S*-C4

Complex ***R,R*-** or ***S,S*-C4** (0.5 mol %) was dissolved in MeCN (2.395 ml) using an alcohol substrate (0.8 mmol) and AcOH (10 equivalents, 0.460 ml). After everything was thoroughly mixed, 30 % H_2O_2 (4 equivalents, 0.250 ml) was slowly added via syringe pump over a period of 30 minutes after which the mixture was stirred for an additional 5 minutes. Final concentrations = complex (0.125 mM), alcohol (0.25 M), AcOH (2.5 M) and H_2O_2 (1.0 M).

After filtering through a silica plug, the mixture was analysed by GC and GC-MS. All runs were performed in duplicate.

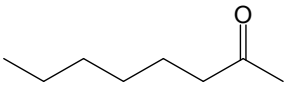
To obtain the isolated products after the oxidation reaction, a saturated sodium hydrogen carbonate ($NaHCO_3$) solution (3 ml) was slowly added to the reaction mixture until the bubbling ceased. DCM (10 ml) was added and separation of the aqueous and organic layers was done. Extraction of the remaining aqueous layer with DCM (2 x 10 ml) was performed where after all the organic layers were combined and dried over Na_2SO_4. After filtration the solvent was allowed to dry in open air.

S6.1 4-Phenyl-2-butanone



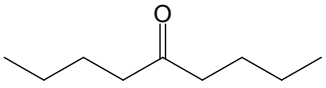
Isolated as a yellow oil (79.5 mg; 63.9 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.37 (t, J = 7.5 Hz, 2H), 7.30 – 7.25 (m, 3H), 2.80 (dddd, J = 15.9, 13.8, 7.6, 4.9 Hz, 2H), 1.94 – 1.78 (m, 2H), 1.31 (d, J = 6.2 Hz, 3H). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 208.13, 142.07, 128.53, 128.43, 126.15, 32.17, 29.76, 23.65. FT-IR (ATR) v, cm^{-1}: 1711 (C=O). Spectral data is consistent with that previously reported in literature.[5]

S6.2 2-Octanone



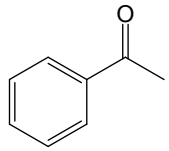
Isolated as a colourless oil (53.2 mg; 50.9 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.42 (ddd, J = 17.8, 14.9, 7.3 Hz, 4H), 2.09 (d, J = 28.9 Hz, 5H), 1.54 (t, J = 4.9 Hz, 2H), 1.31 – 1.20 (m, 2H), 1.08 – 0.77 (m, 3H). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 208.94, 43.43, 31.60, 29.94, 28.85, 23.16, 22.50, 14.04. FT-IR (ATR) v, cm^{-1}: 1708 (C=O). Spectral data is consistent with that previously reported in literature.[6]

S6.3 5-Nonanone



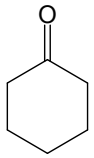
Isolated as a colourless oil (77.8 mg; 67.4 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.41 (dt, J = 35.6, 7.5 Hz, 5H), 1.53 (dt, J = 15.2, 7.6 Hz, 5H), 0.89 (t, J = 7.4 Hz, 8H). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 212.09, 42.66, 22.50, 22.42, 13.99. FT-IR (ATR) v, cm^{-1}: 1711 (C=O). Spectral data is consistent with that previously reported in literature.[7]

S6.4 Acetophenone



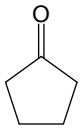
Isolated as a colourless oil (82.1 mg; 84.2 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.96 (dd, J = 8.3, 1.1 Hz, 2H), 7.59 – 7.53 (m, 1H,), 7.46 (t, J = 7.8 Hz, 2H), 2.60 (s, 3H). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 198.36, 137.19, 133.24, 128.68, 128.42, 26.74. FT-IR (ATR) v, cm^{-1}: 1680 (C=O). Spectral data is consistent with that previously reported in literature.[6]

S6.5 Cyclohexanone



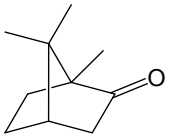
Isolated as a colourless oil (7.5 mg; 9.9 %). Due to the high water solubility and volatility[7] of the compound resulting in a low yield, no usable NMR data could be obtained. FT-IR (ATR) v, cm^{-1}: 1702 (C=O).

S6.6 Cyclopentanone



Isolated as a colourless oil (4.6 mg; 6.6 %). Due to the high water solubility and volatility[7] of the compound resulting in a low yield, no usable NMR data could be obtained. FT-IR (ATR) v, cm^{-1}: 1692 (C=O).

S6.7 Camphor



Isolated as a white solid (105.5 mg; 86.2 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.39 – 2.30 (m, 1H), 2.08 (t, J = 4.5 Hz, 1H), 1.94 (ddd, J = 15.8, 7.9, 3.8 Hz, 1H), 1.83 (d, J = 18.2 Hz, 1H), 1.67 (dd, J = 25.0, 3.7 Hz, 1H), 1.44 – 1.28 (m, 2H), 0.95 (s, 3H), 0.90 (s, 3H), 0.82 (s, 3H). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm): 220.01, 57.86, 46.94, 43.44, 43.17, 30.04, 27.18, 19.92, 19.28, 9.39. FT-IR (ATR) v, cm^{-1}: 1738 (C=O). Spectral data is consistent with that previously reported in literature.[6]

S7 Crystallographic data for complexes *R,R*- and *S,S*-C4

Suitable crystals of ***R,R*-C4** and ***S,S*-C4** were grown by slow diffusion of diethyl ether into concentrated acetonitrile solutions of the complexes.

Table S2: Crystallographic data and structure refinement parameters for Mn(II)-triflate complexes, **R,R-*C4*** *and* **S,S-*C4***.

Parameter	Complex	
	***R,R*-C4**	***S,S*-C4**
Empirical formula	$C_{20}H_{30}F_6MnN_6O_6S_2$	$C_{20}H_{30}F_6MnN_6O_6S_2$
Mr (g/mol)	683.56	683.56
Crystal system	Tetragonal	Tetragonal
Space group	P4(1)2(1)2	P4(3)2(1)2
***a* (Å)**	9.3461(3)	9.3476(4)
***b* (Å)**	9.3461(3)	9.348
***c* (Å)**	32.8191(12)	32.8311(15)
***α* (deg)**	90.00	90.00
***β* (deg)**	90.00	90.00
***γ* (deg)**	90.00	90.00
Crystal dimension (mm)	0.17 x 0.21 x 0.29	0.087 x 0.180 x 0.314
Volume (Å^3)	2866.7(2)	2868.7(2)
Z	4	4
D_{calc} (g/cm^3)	1.584	1.583
F(000)	1404	1404
λ (MoK_a) (Å)	0.71073	0.71073
Temperature (K)	173(2)	200(2)
2*θ* max (deg)	25.541	25.038
absorption corrections applied (mm^{-1})	0.691	0.691
Goodness-of-fit on F^2	1.078	1.056
Final R_1 indices [$I>2\sigma(I)$]	0.0561	0.0555
***wR*$_2$ (all reflections)**	0.1523	0.1380
Flack x parameter	-0.007(9)	0.0003(14)

Table S3: Selected bond lengths (Å), bond angles (°) and torsion angle (°) as determined for Mn(II)-triflate complexes, **R,R-*C4*** *and* **S,S-*C4***.

	Complex	
	***R,R*-C4**	***S,S*-C4**
Bond lengths[a]		
Mn-N1	2.143(6)	2.143(7)
Mn-N3	2.372(5)	2.373(6)
Mn-O1	2.212(6)	2.209(7)
Bond angles		
N1-Mn-N1′	178.9(3)	179.0(4)
N1-Mn-O1	96.3(3)	96.3(3)
N1-Mn-O1′	84.4(2)	84.3(3)
N1-Mn-N3	75.3(2)	75.3(2)
N1-Mn-N3′	103.7(4)	103.9(3)
O1-Mn-O1′	103.7(4)	103.5(4)
O1-Mn-N3	93.8(2)	93.9(3)
O1-Mn-N3′	154.6(2)	154.6(3)
N3-Mn-N3′	76.8(3)	76.7(3)

[a] Symmetry-generated atoms have equivalent bond lengths. Symmetry operator to generate equivalent atoms for ***R,R*-C4** and ***S,S*-C4**: y, x, -z.

S8 Spectral data of ligands, complexes and isolated ketone products

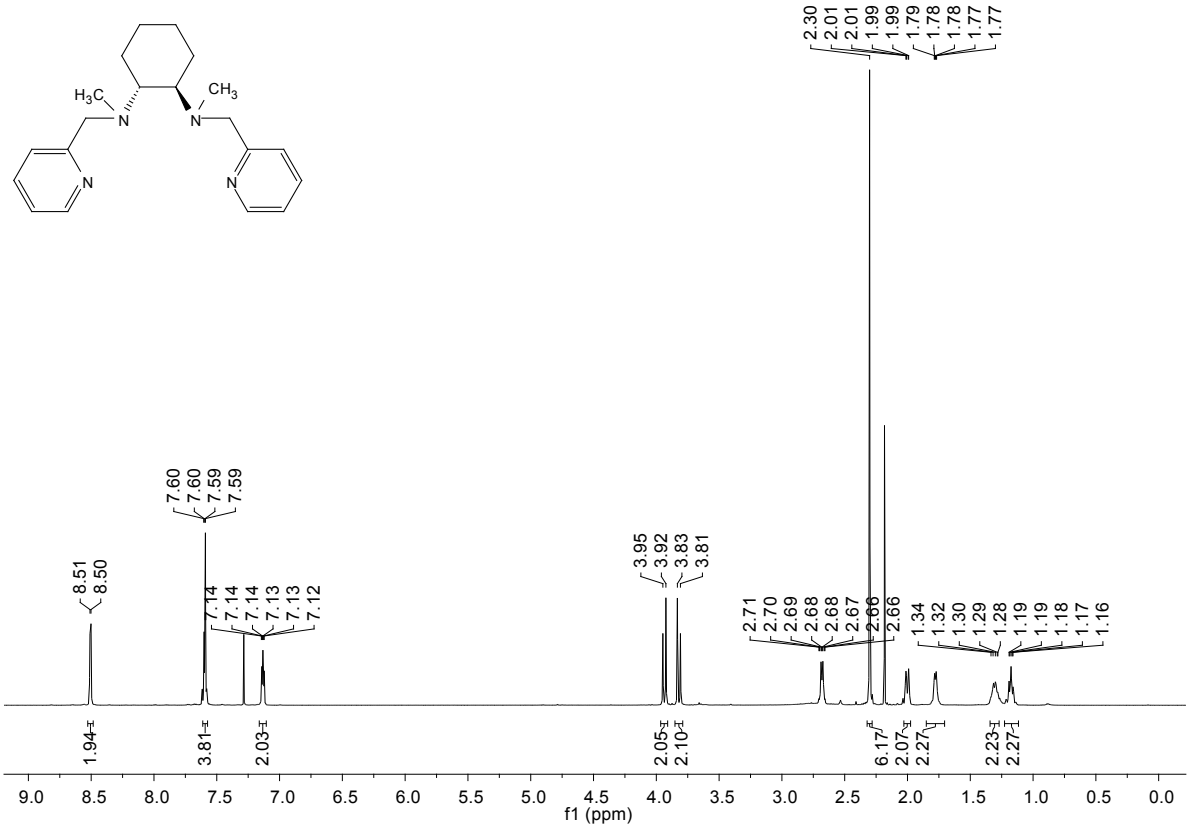


*Figure S4: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **R,R-L1**.*

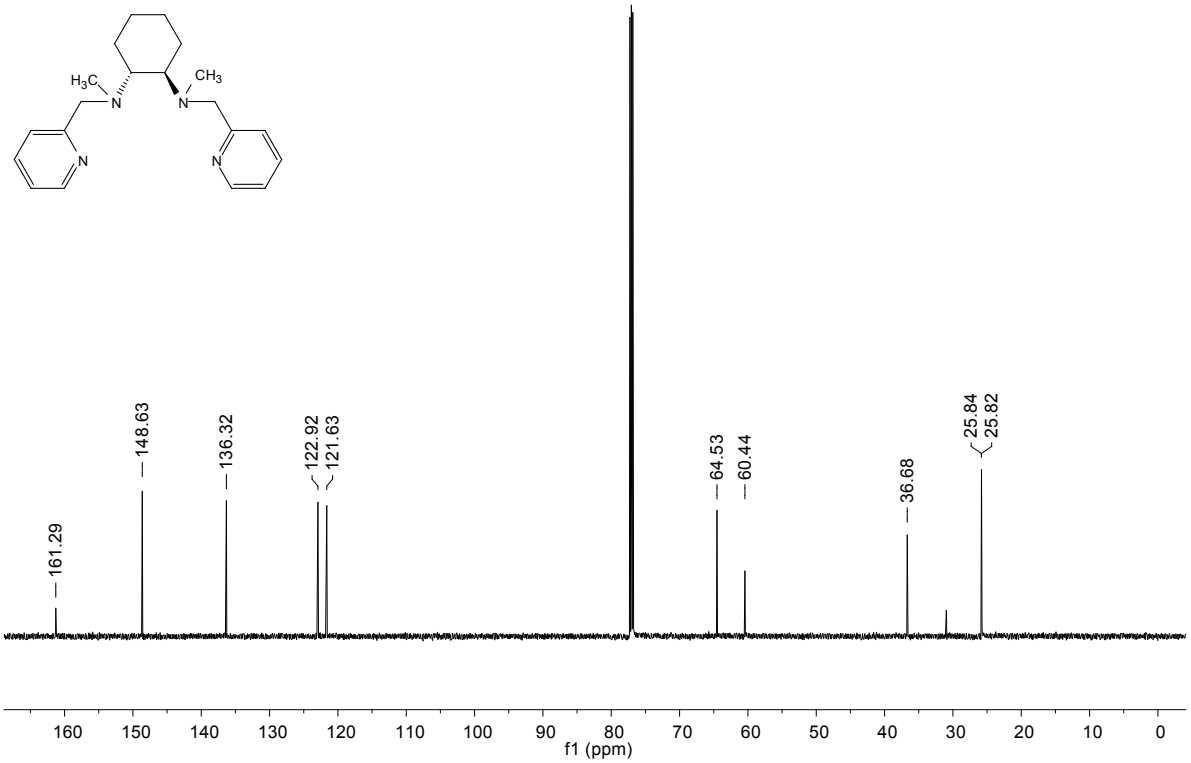


*Figure S5: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **R,R-L1**.*

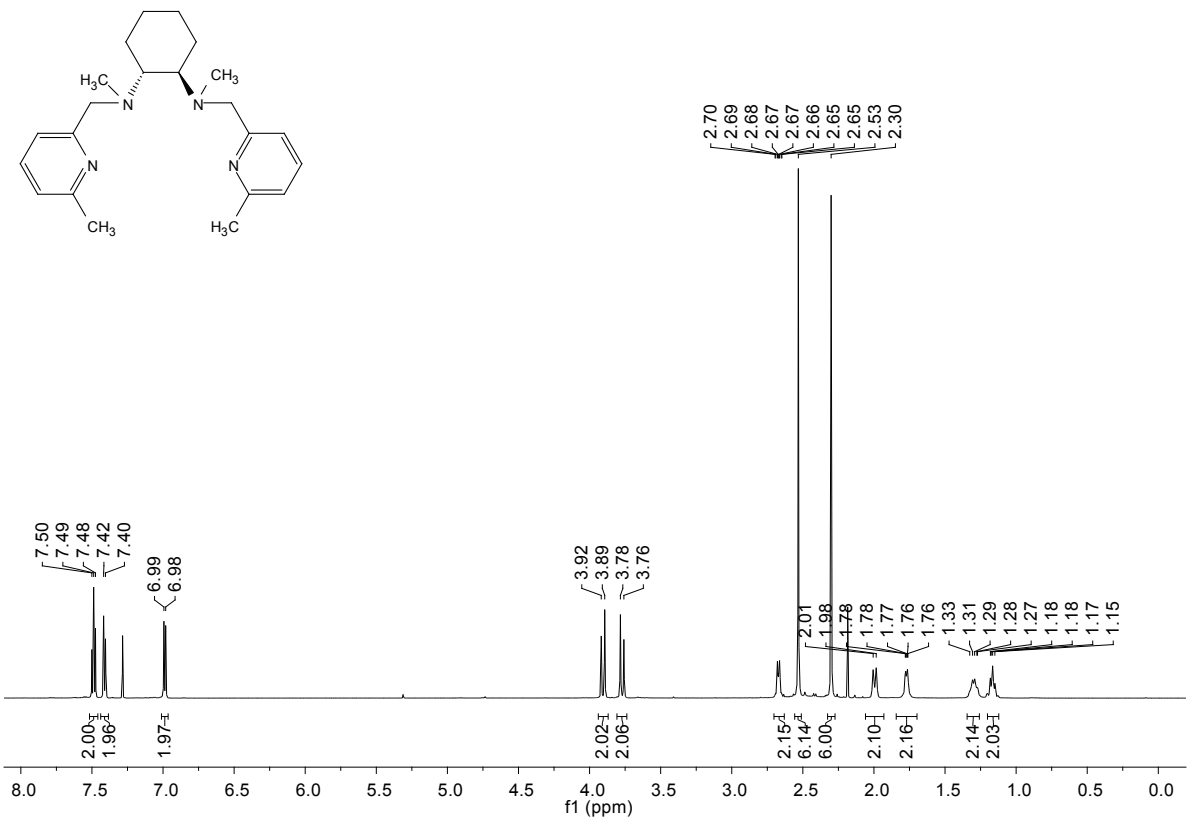


*Figure S6: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **R,R-L2**.*

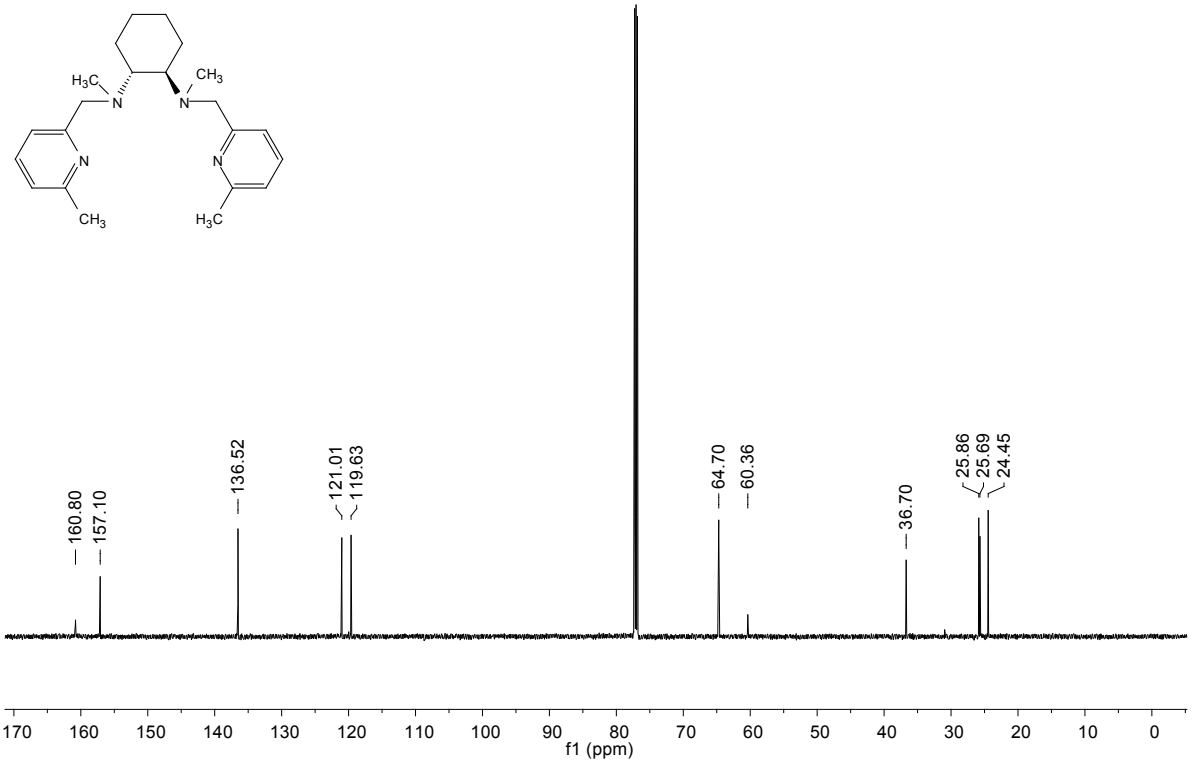


*Figure S7: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **R,R-L2**.*

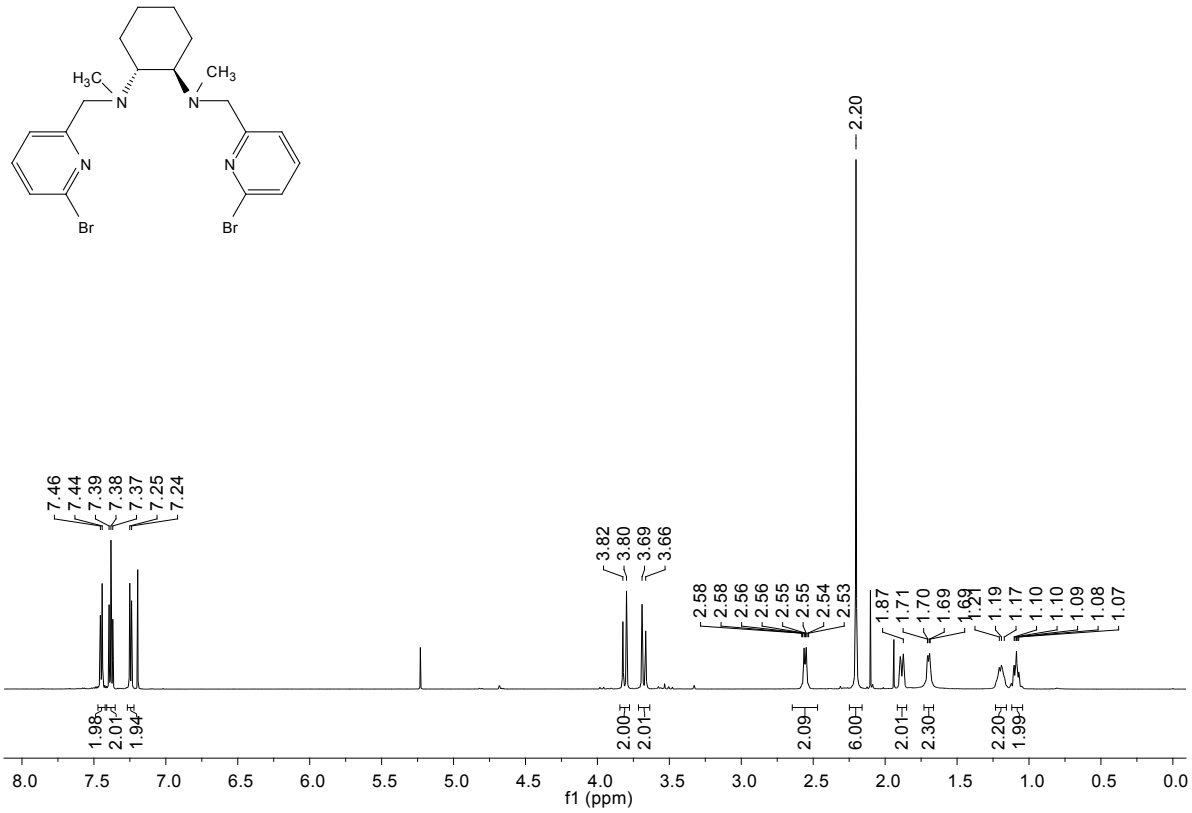


*Figure S8: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **R,R-L3**.*

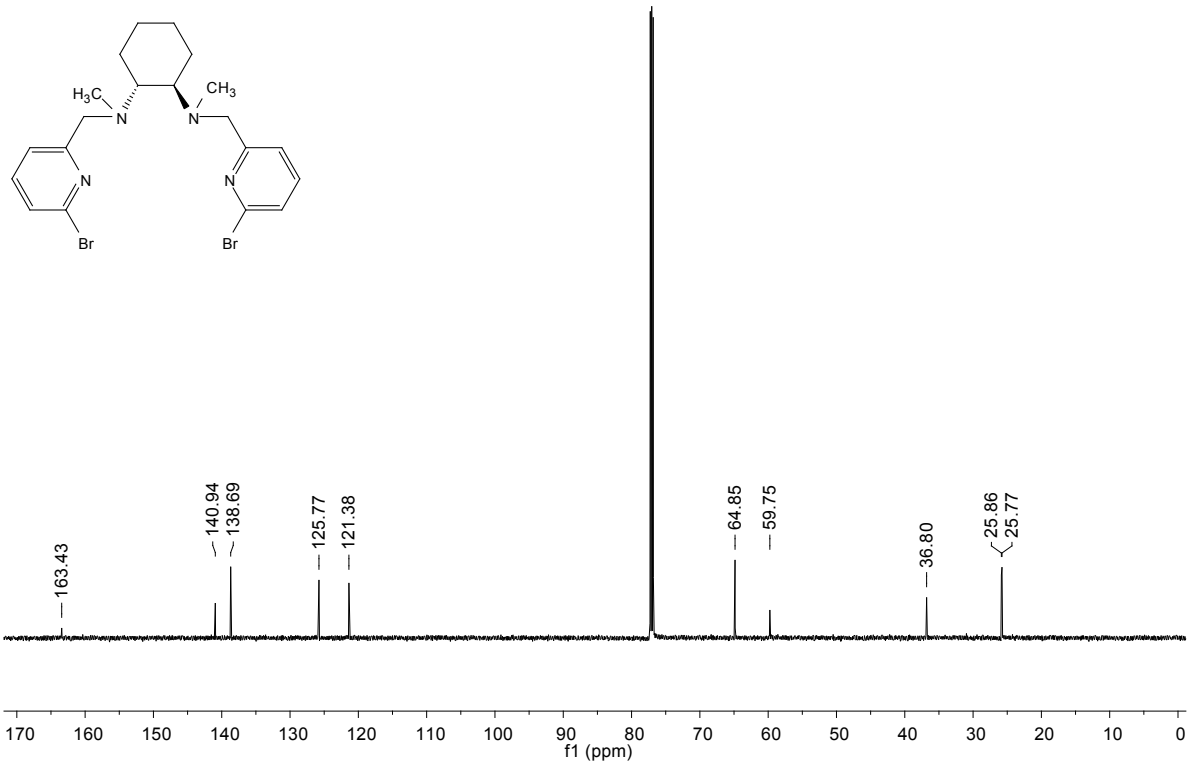


*Figure S9: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **R,R-L3**.*

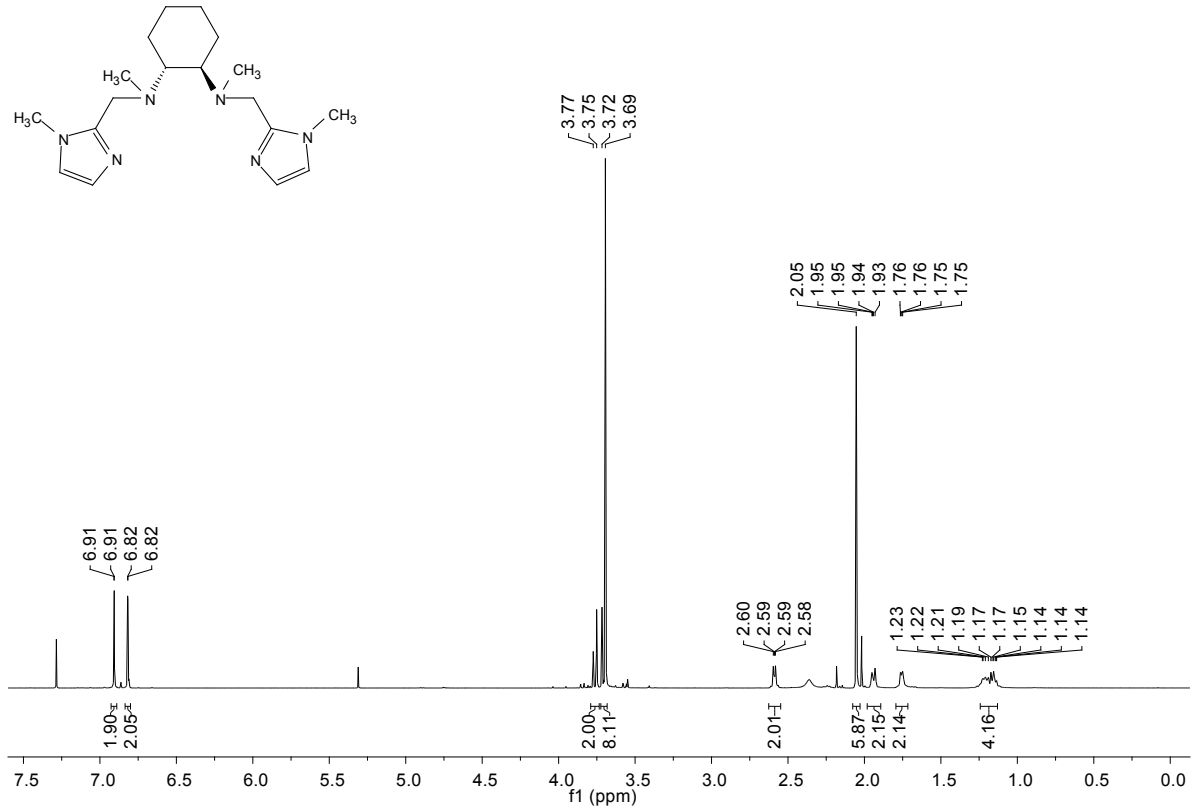


*Figure S10: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **R,R-L4**.*

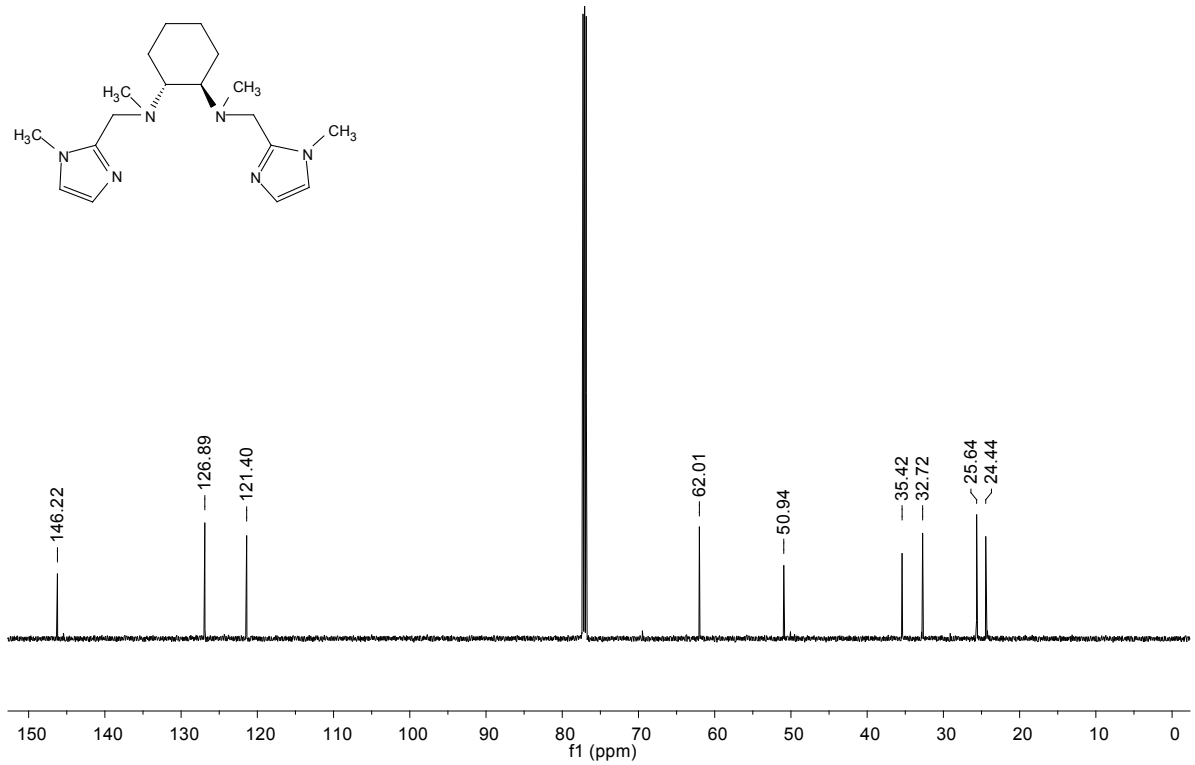


*Figure S11: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **R,R-L4**.*

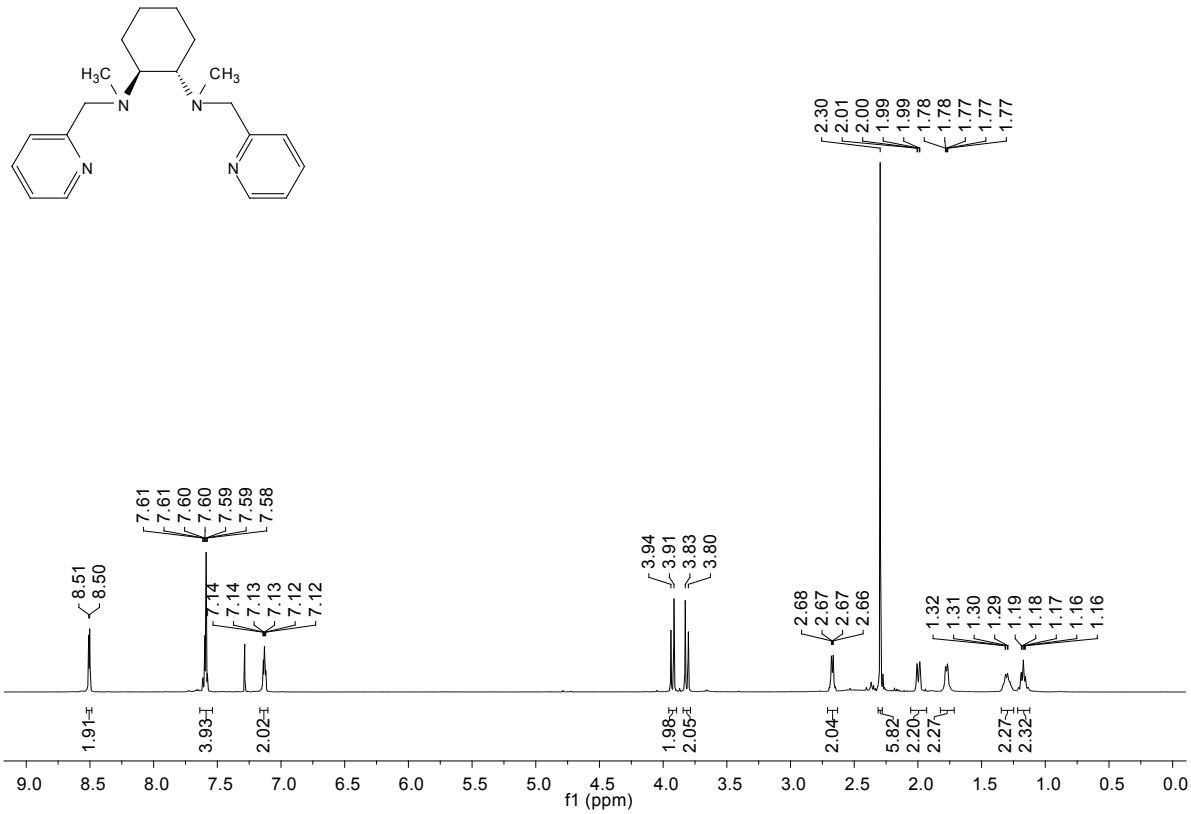


*Figure S12: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **S,S-L1**.*

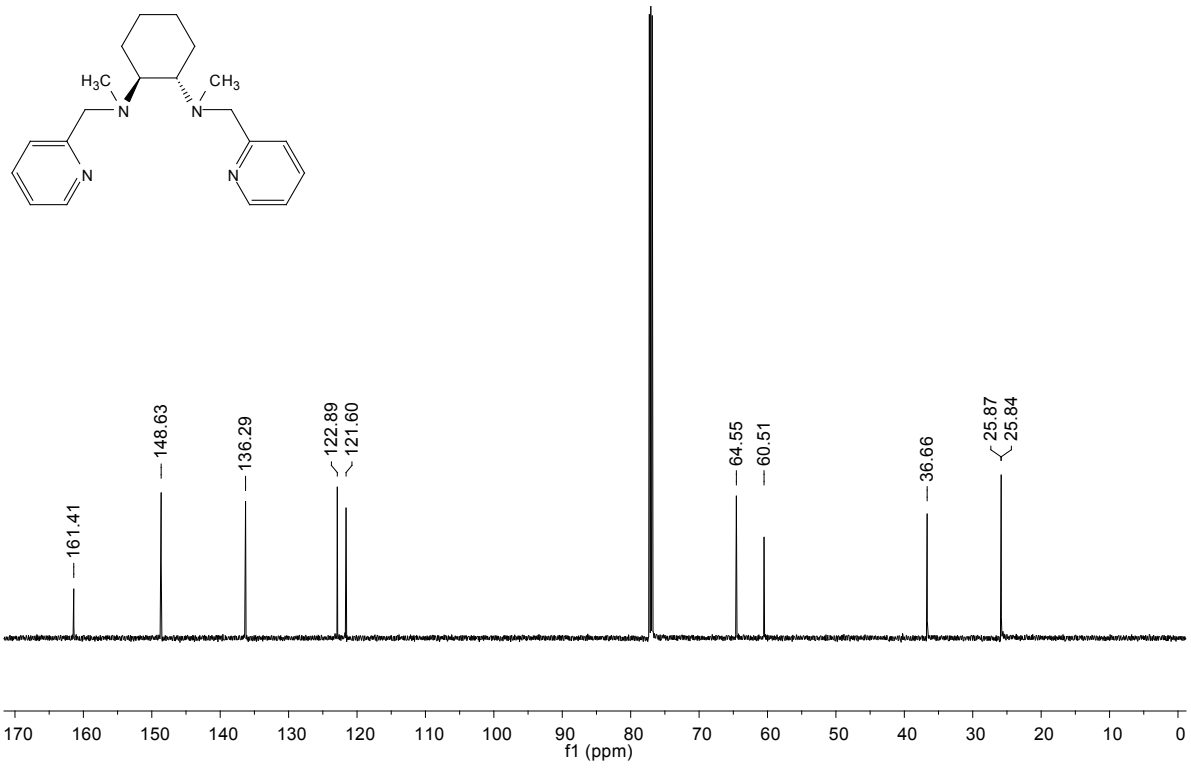


*Figure S13: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **S,S-L1**.*

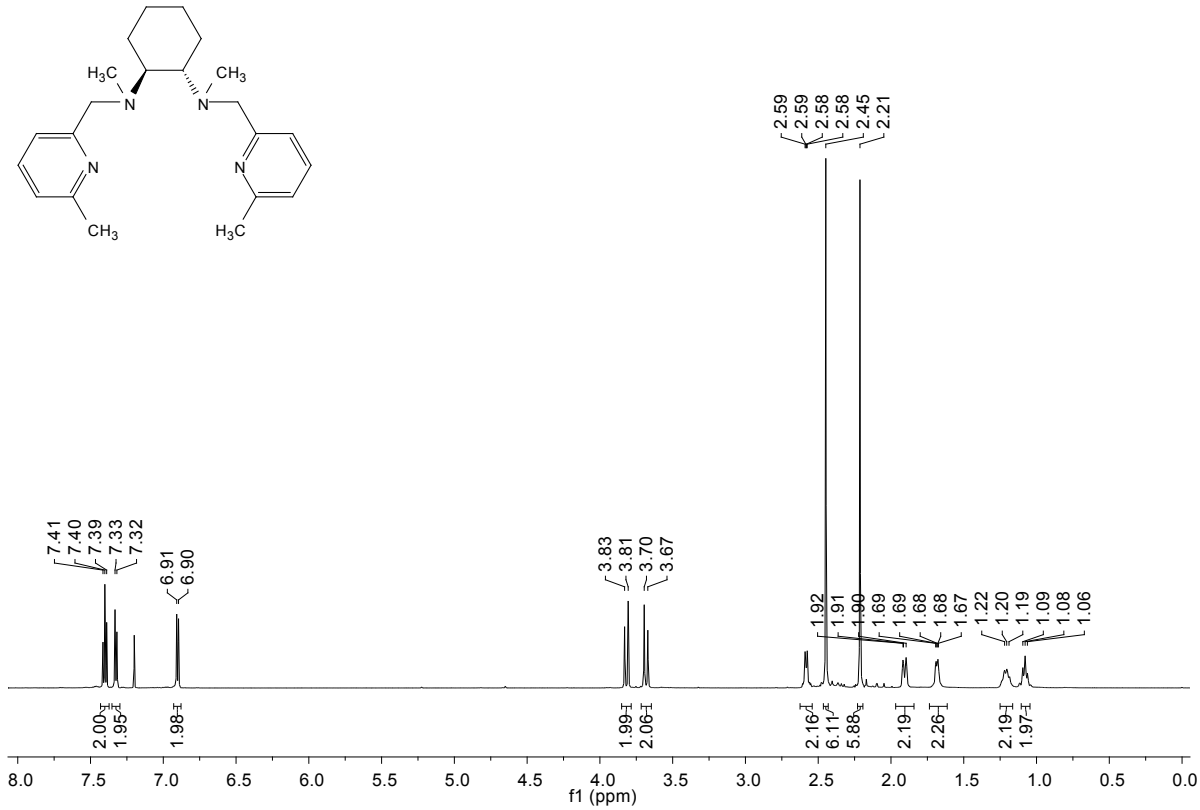


*Figure S14: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **S,S-L2**.*

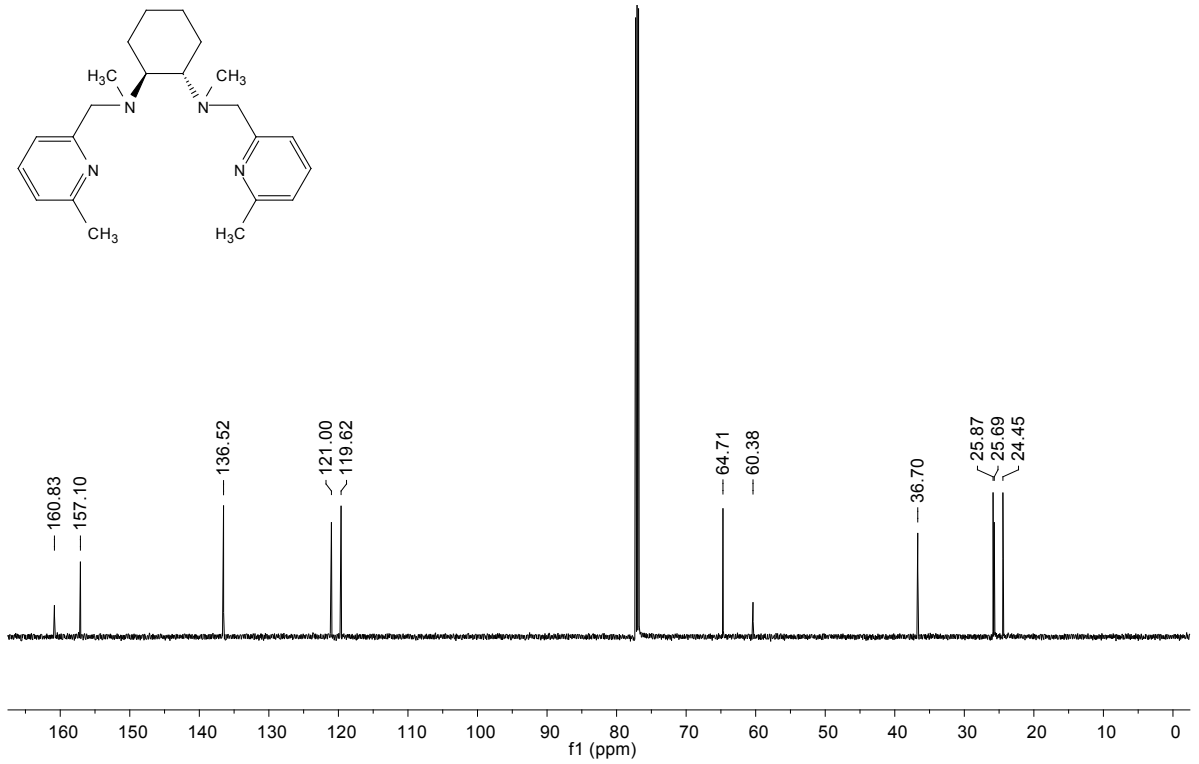


*Figure S15: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **S,S-L2**.*

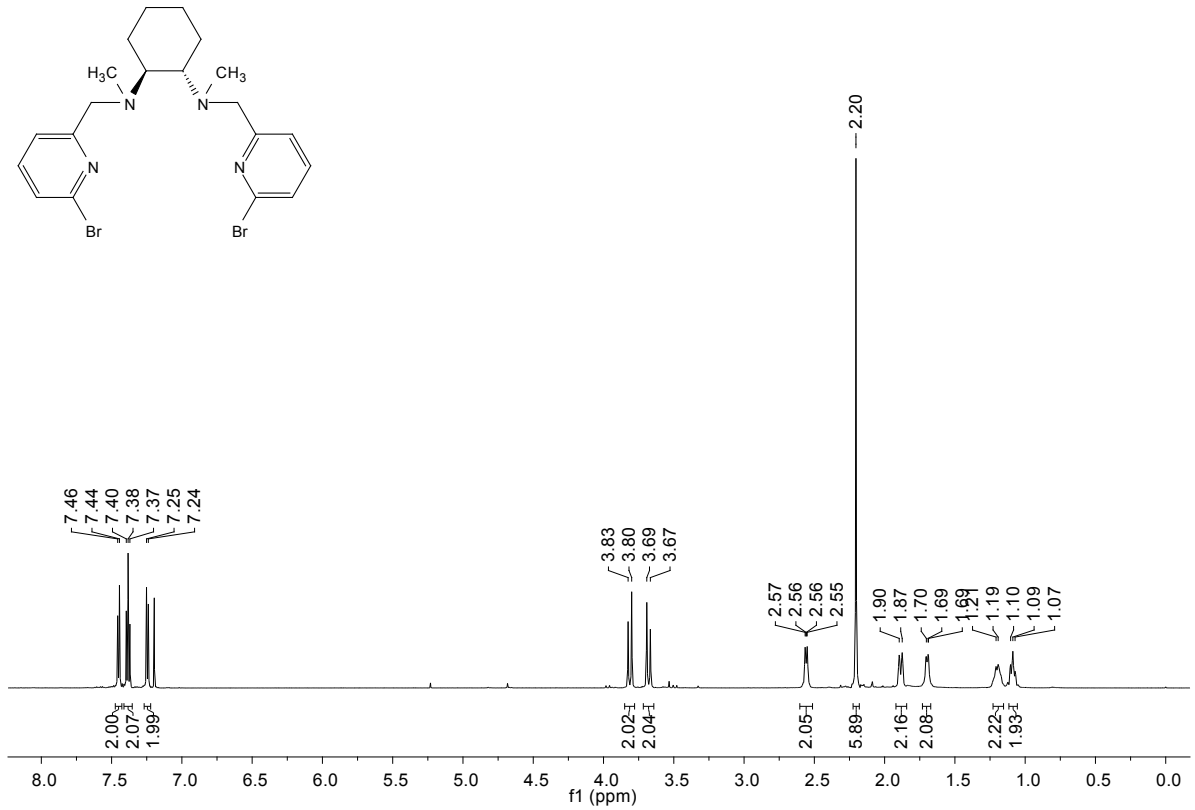


*Figure S16: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **S,S-L3**.*

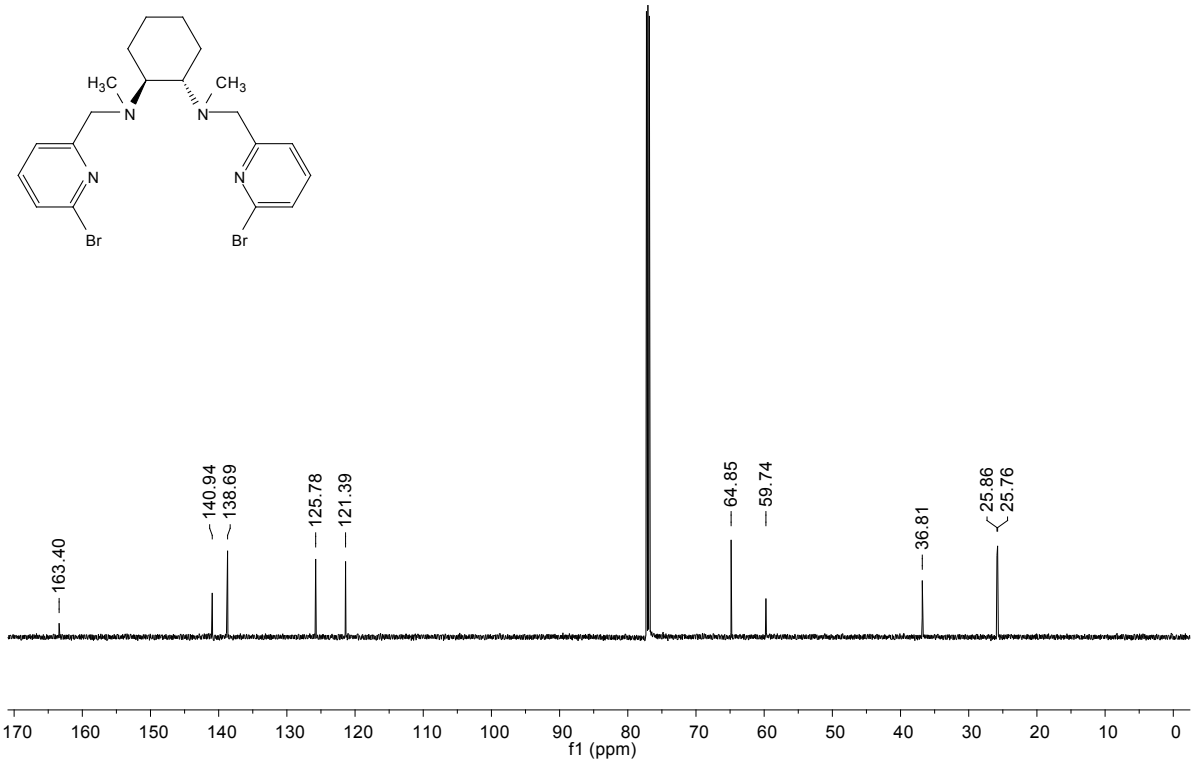


*Figure S17: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **S,S-L3**.*

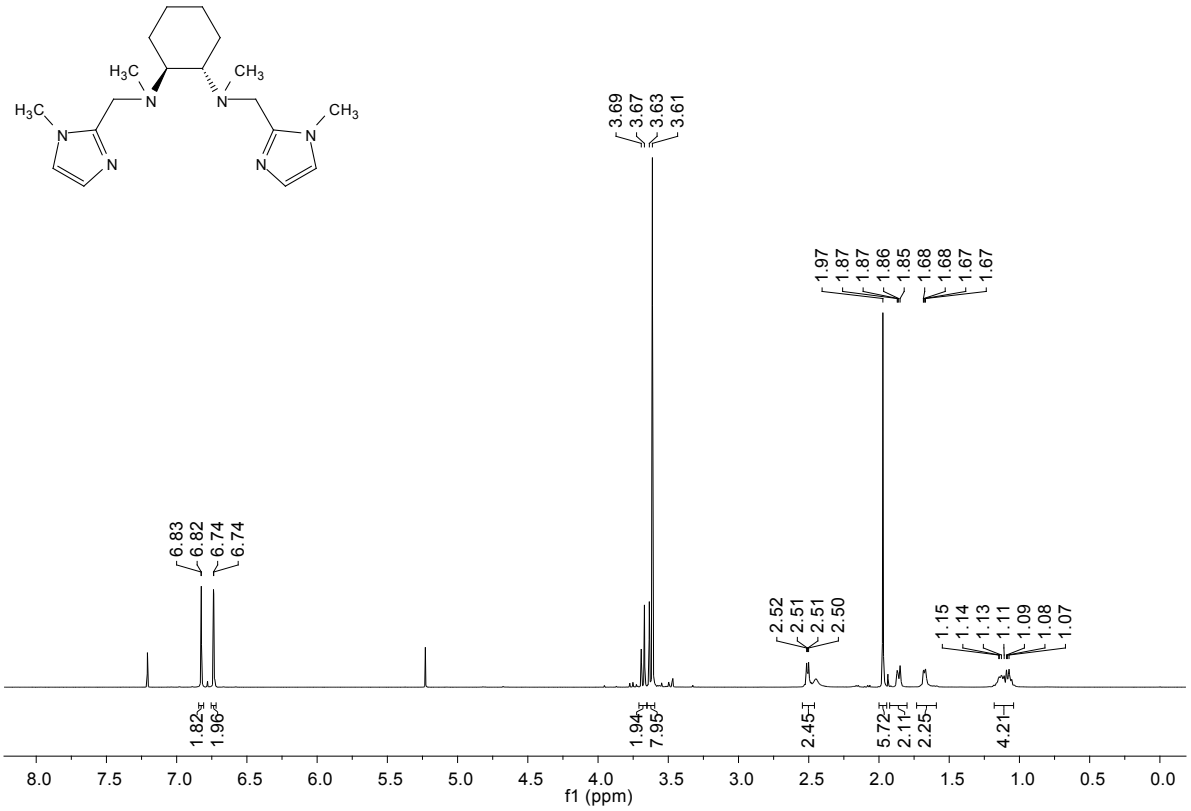


*Figure S18: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ligand **S,S-L4**.*

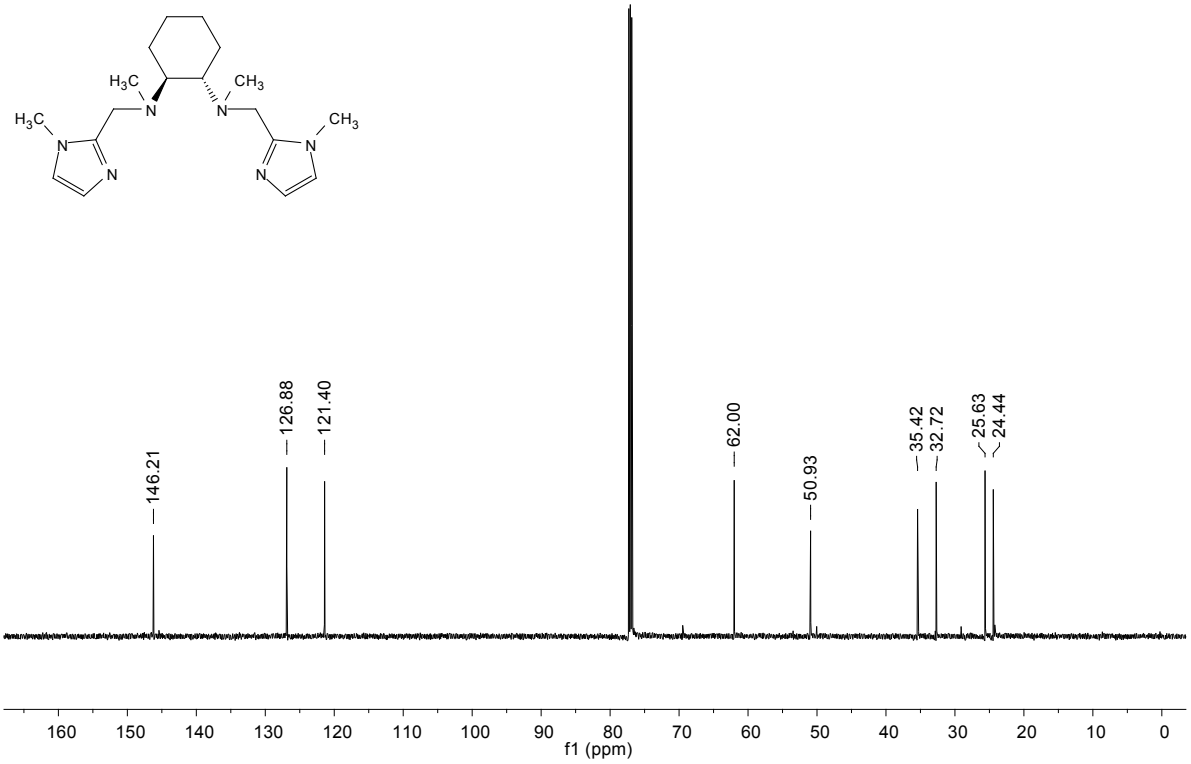


*Figure S19: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **S,S-L4**.*

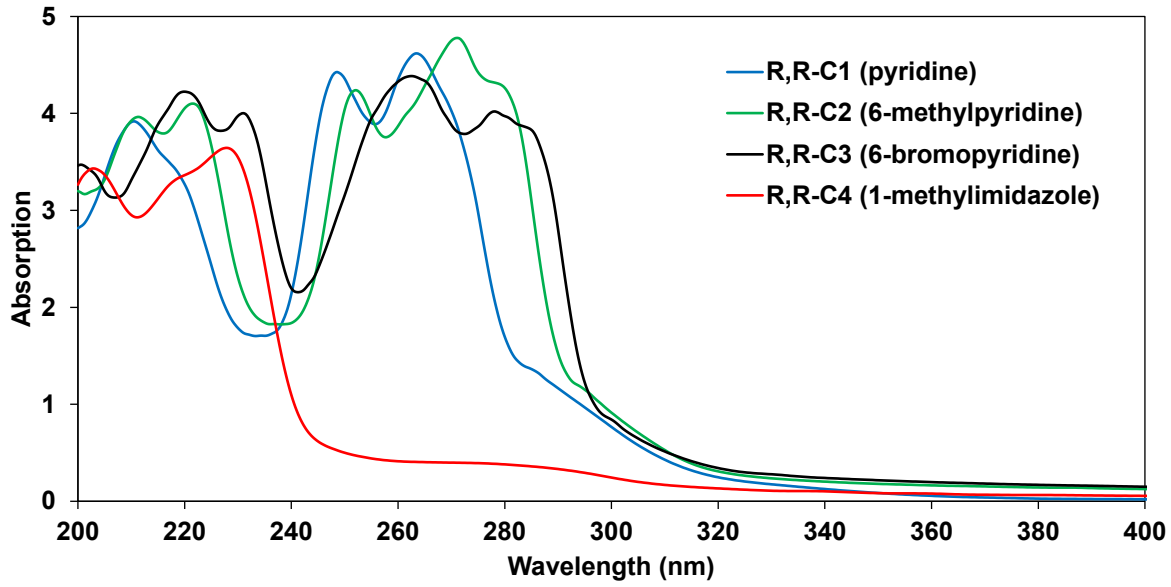


*Figure S20: UV-visible spectrum of complexes **R,R-C1 - C4**.*

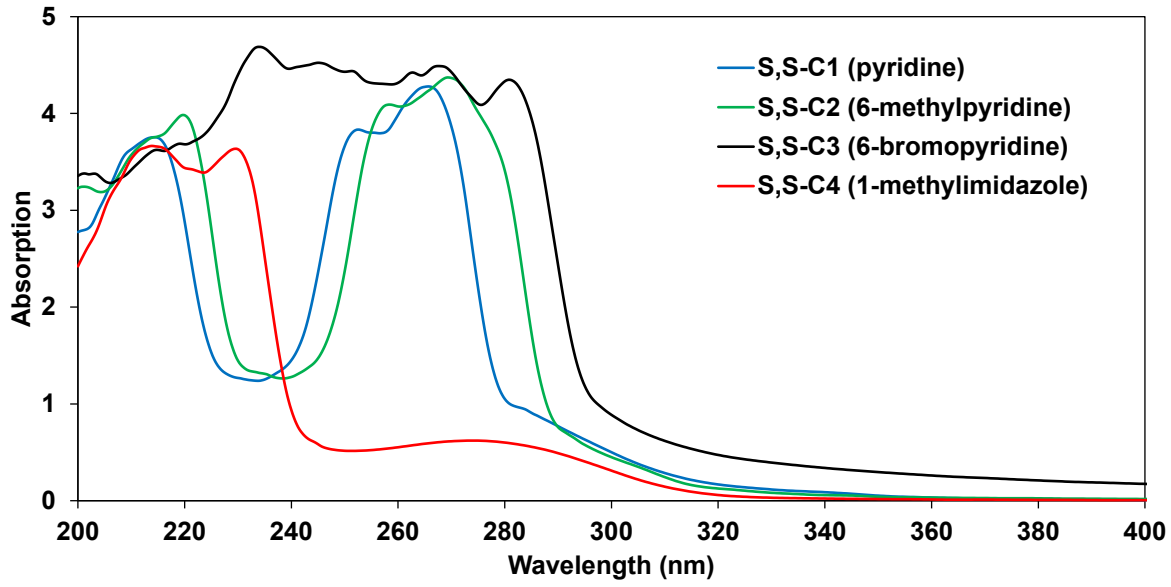


*Figure S21: UV-visible spectrum of complexes **S,S-C1 - C4**.*

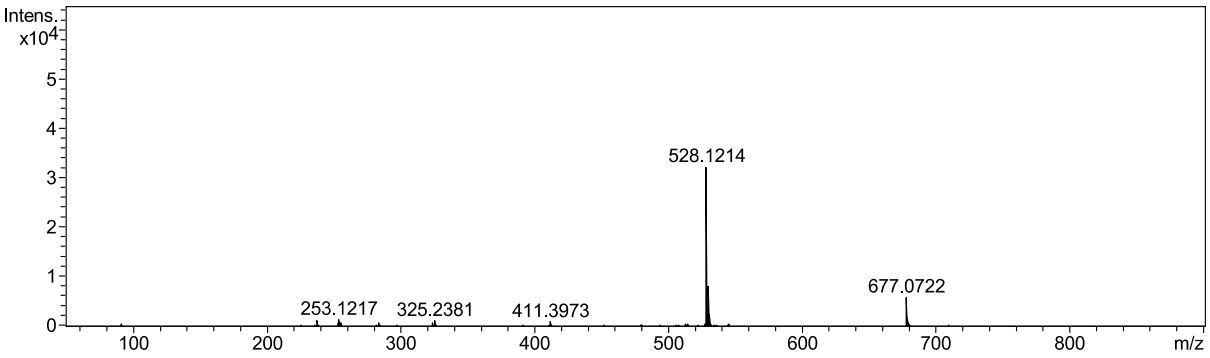


*Figure S22: APCI-MS spectrum of **R,R-C1** recorded in positive ion mode. Isotope clusters found at m/z of 528.12 and 677.07 correspond to the $[M - OTf]^+$ and $[M]^+$ ions, respectively.*

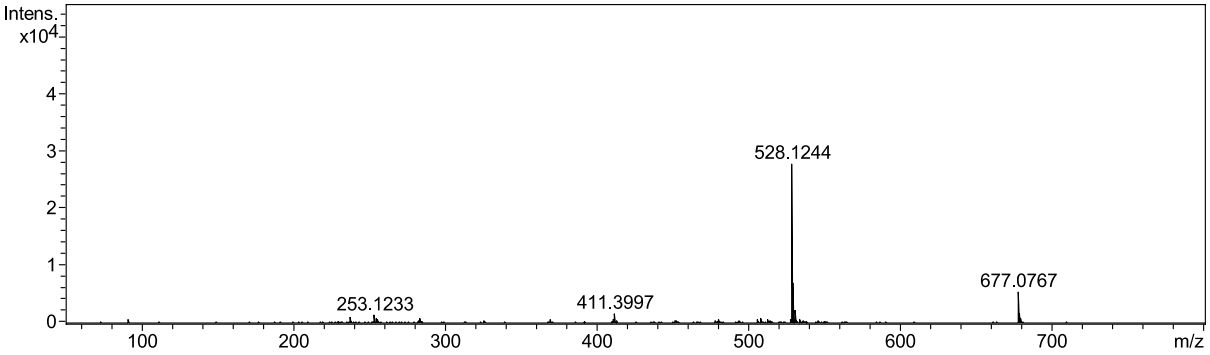


*Figure S23: APCI-MS spectrum of **S,S-C1** recorded in positive ion mode. Isotope clusters found at m/z of 528.12 and 677.08 correspond to the $[M - OTf]^+$ and $[M]^+$ ions, respectively.*

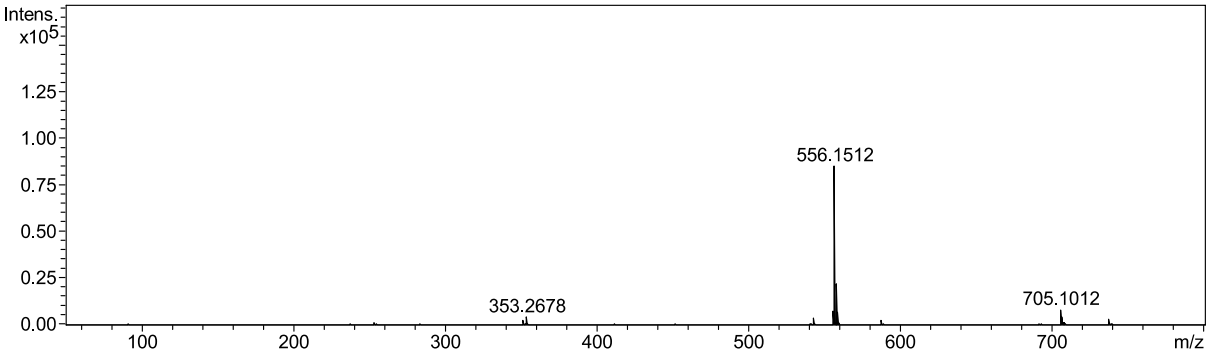


*Figure S24: APCI-MS spectrum of **R,R-C2** recorded in positive ion mode. Isotope clusters found at m/z of 556.15 and 705.10 correspond to the $[M - OTf]^+$ and $[M]^+$ ions, respectively.*

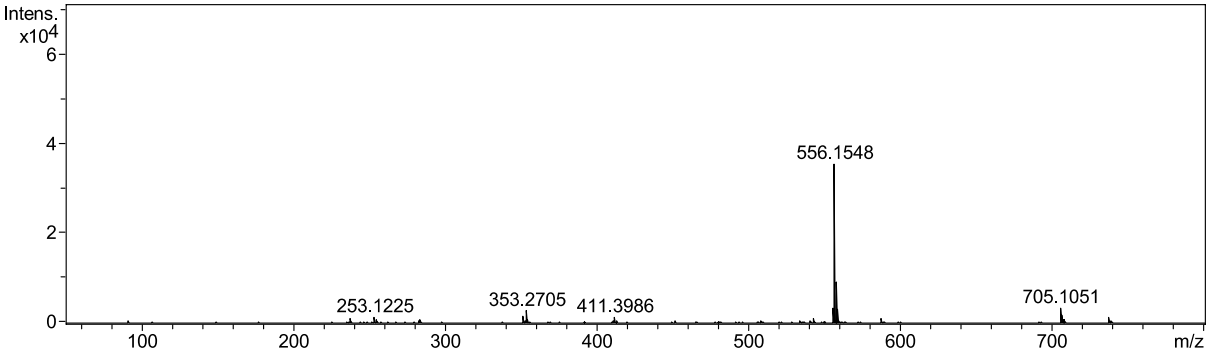


*Figure S25: APCI-MS spectrum of **S,S-C2** recorded in positive ion mode. Isotope clusters found at m/z of 556.15 and 705.11 correspond to the [M - OTf]⁺ and [M]⁺ ions, respectively.*

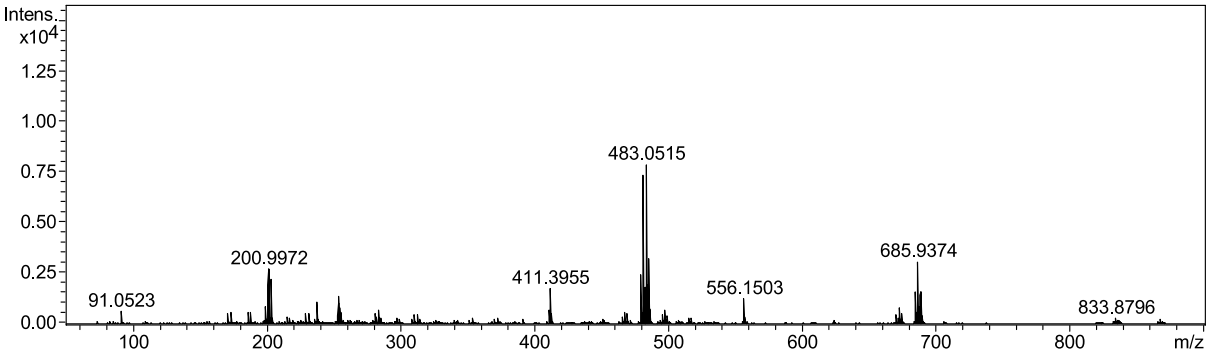


*Figure S26: APCI-MS spectrum of **R,R-C3** recorded in positive ion mode. Isotope clusters found at m/z of 483.05, 685.94 and 833.88 correspond to the [Ligand - H], [M - OTf]⁺ and [M - H]⁺ ions, respectively.*

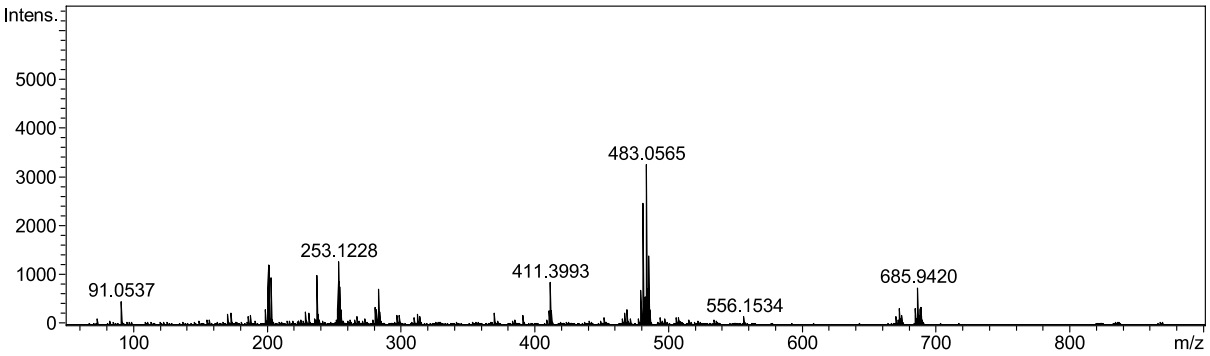


*Figure S27: APCI-MS spectrum of **S,S-C3** recorded in positive ion mode. Isotope clusters found at m/z of 483.06 and 685.94 correspond to the [Ligand - H] and [M - OTf]⁺ ions, respectively.*

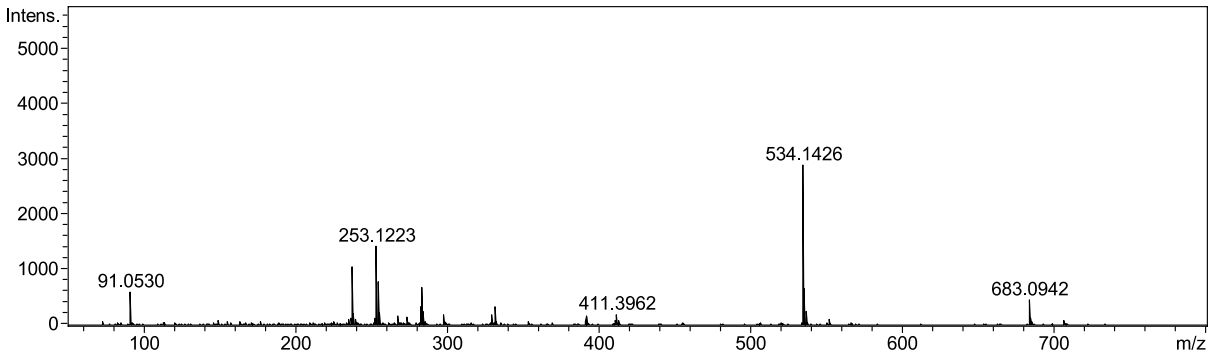


*Figure S28: APCI-MS spectrum of **R,R-C4** recorded in positive ion mode. Isotope clusters found at m/z of 534.14 and 683.09 correspond to the $[M - OTf]^+$ and $[M]^+$ ions, respectively.*

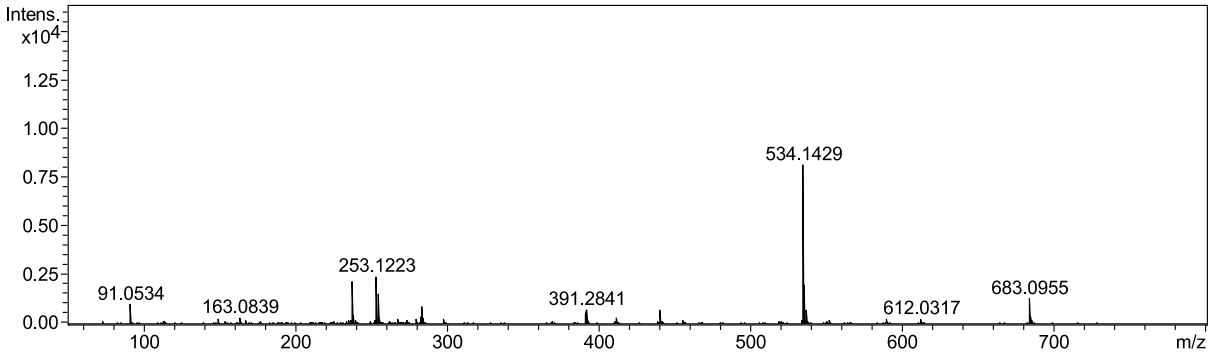


*Figure S29: APCI-MS spectrum of **S,S-C4** recorded in positive ion mode. Isotope clusters found at m/z of 534.14 and 683.10 correspond to the $[M - OTf]^+$ and $[M]^+$ ions, respectively.*

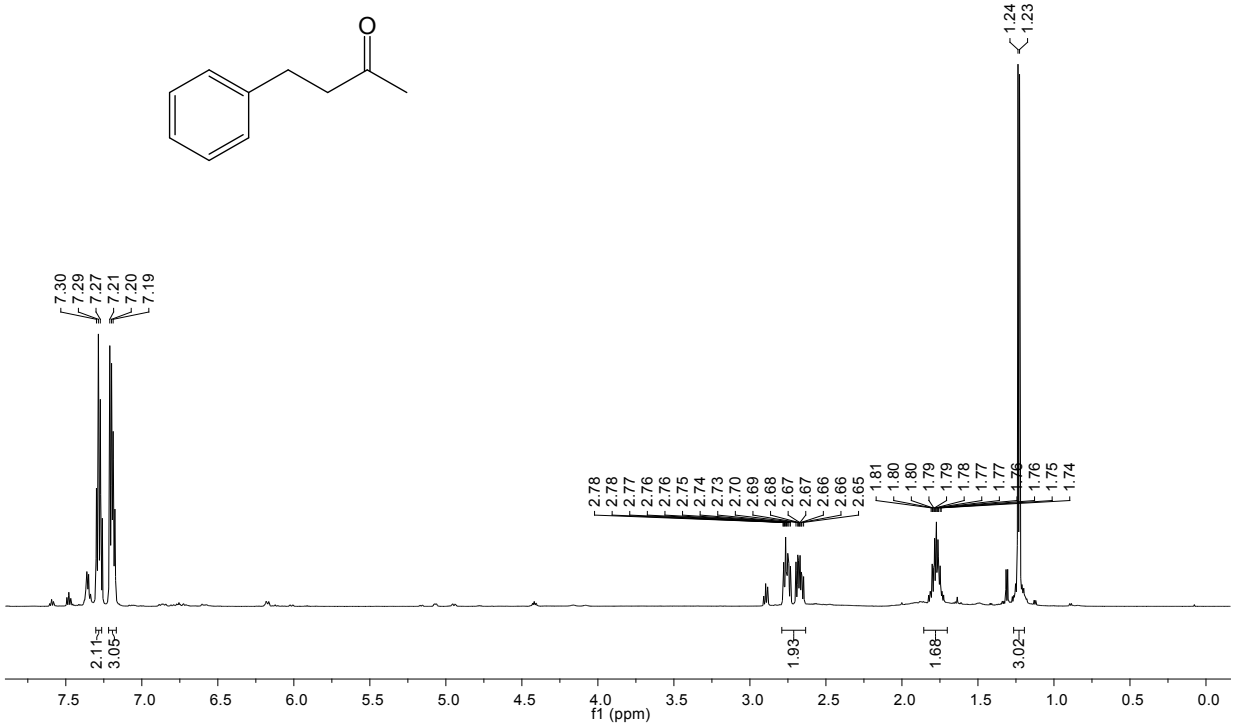


Figure S30: ^1H NMR (600 MHz, $CDCl_3$) spectrum of 4-phenyl-2-butanone.

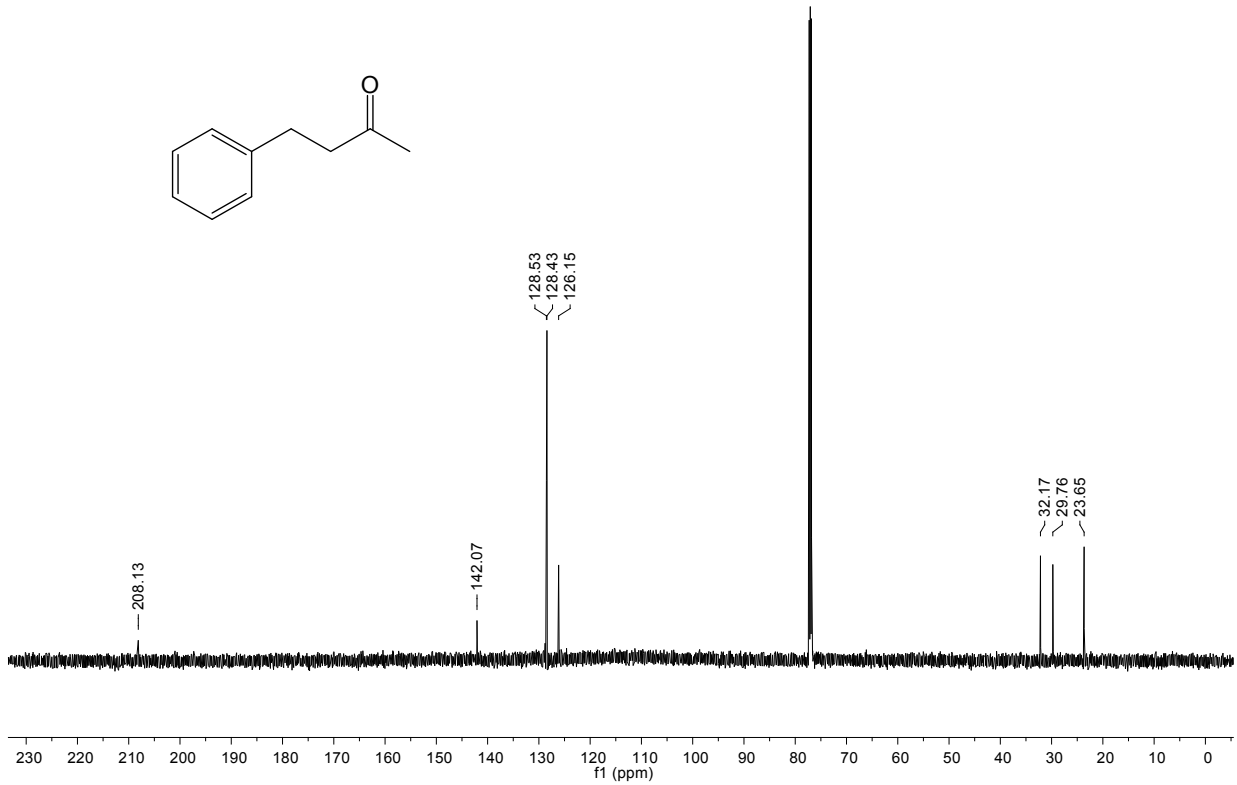


Figure S31: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of 4-phenyl-2-butanone.

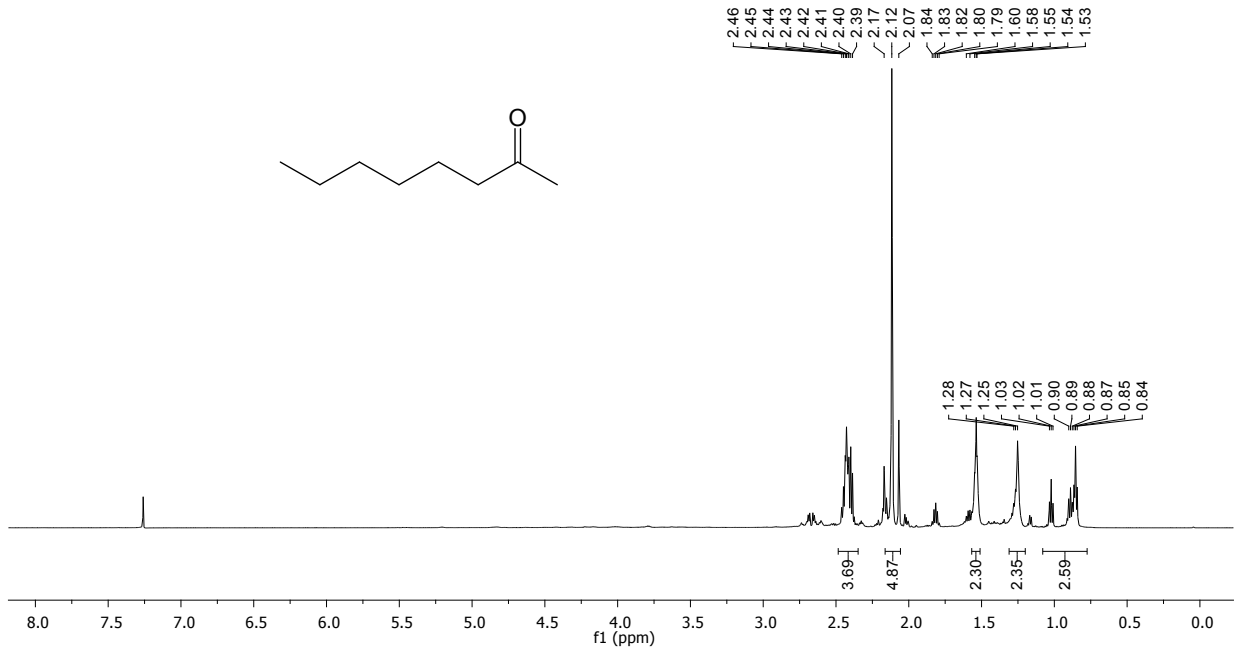


Figure S32: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 2-octanone.

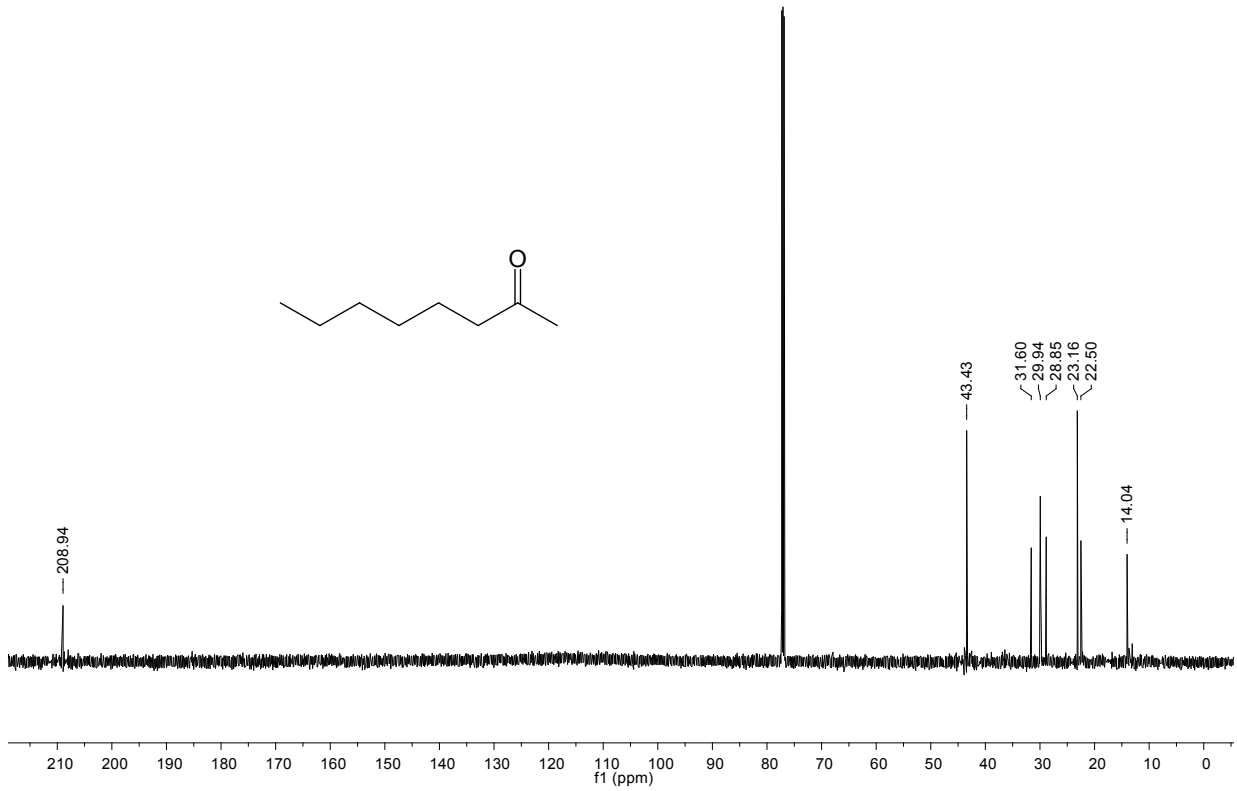


Figure S33: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of 2-octanone.

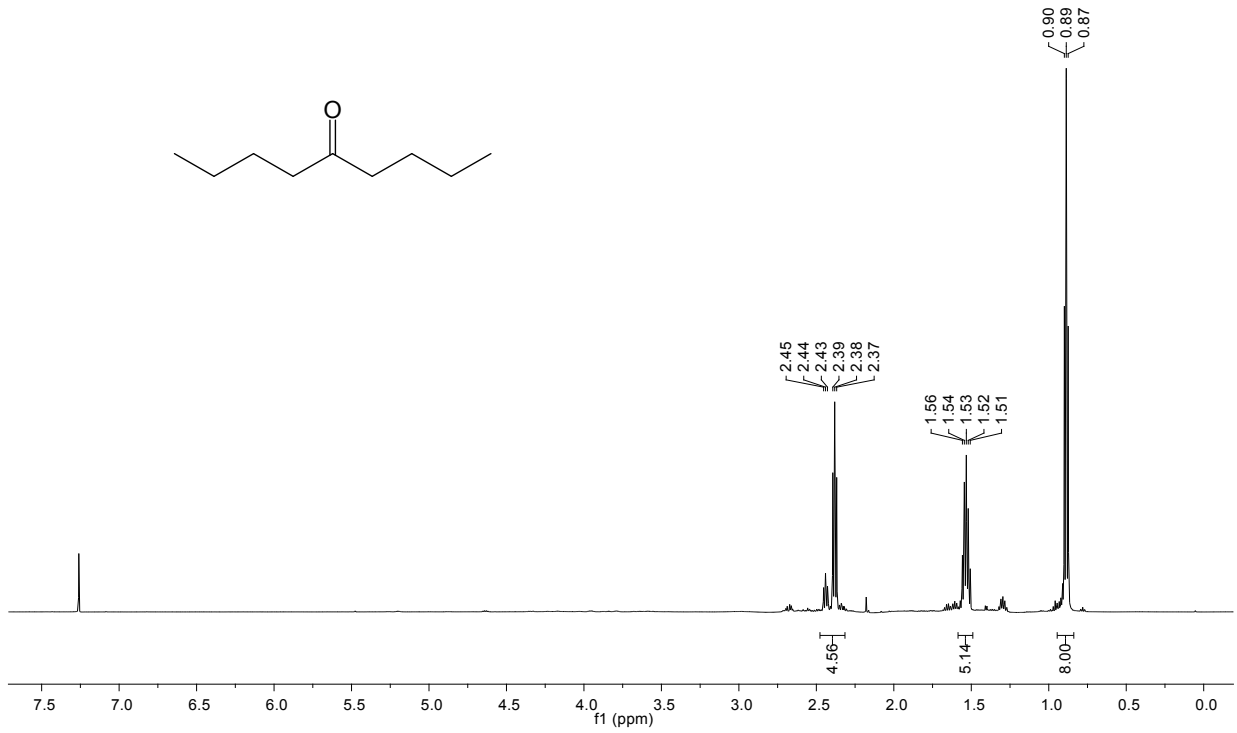


Figure S34: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5-nonanone.

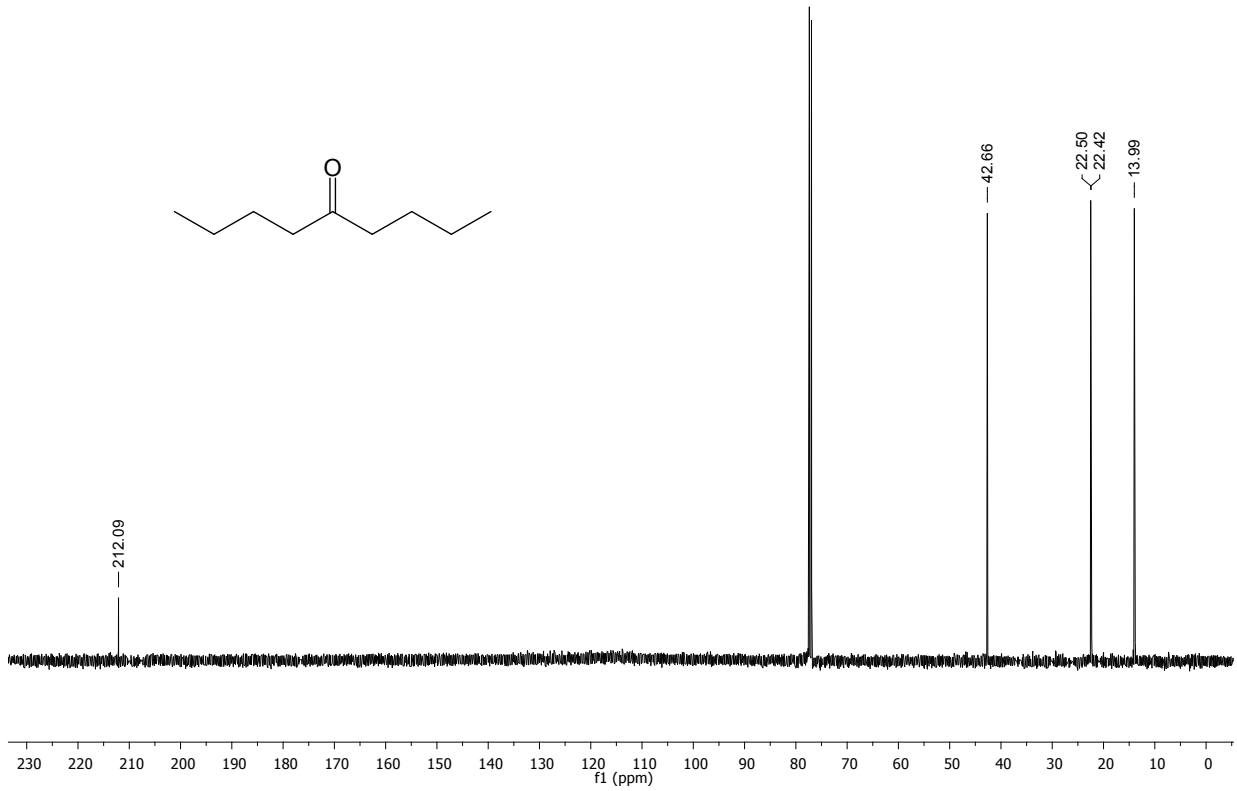


Figure S35: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of 5-nonanone.

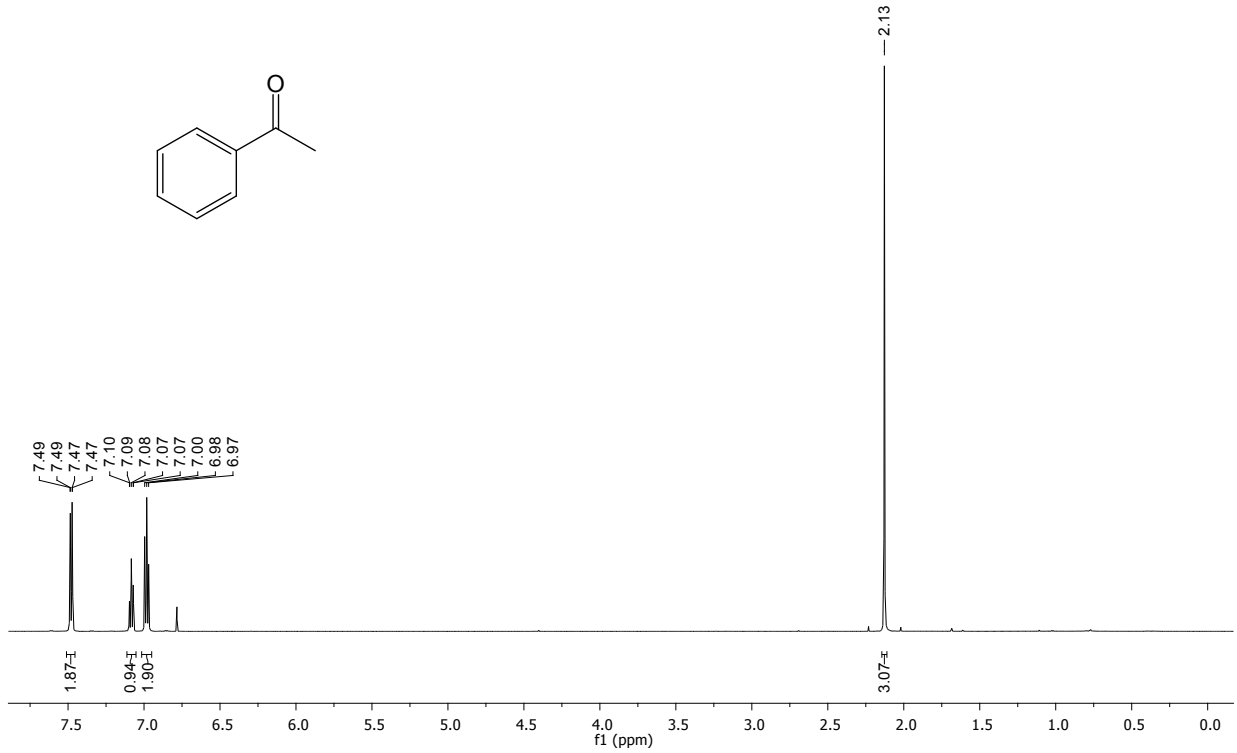


Figure S36: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of acetophenone.

Figure S37: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of acetophenone.

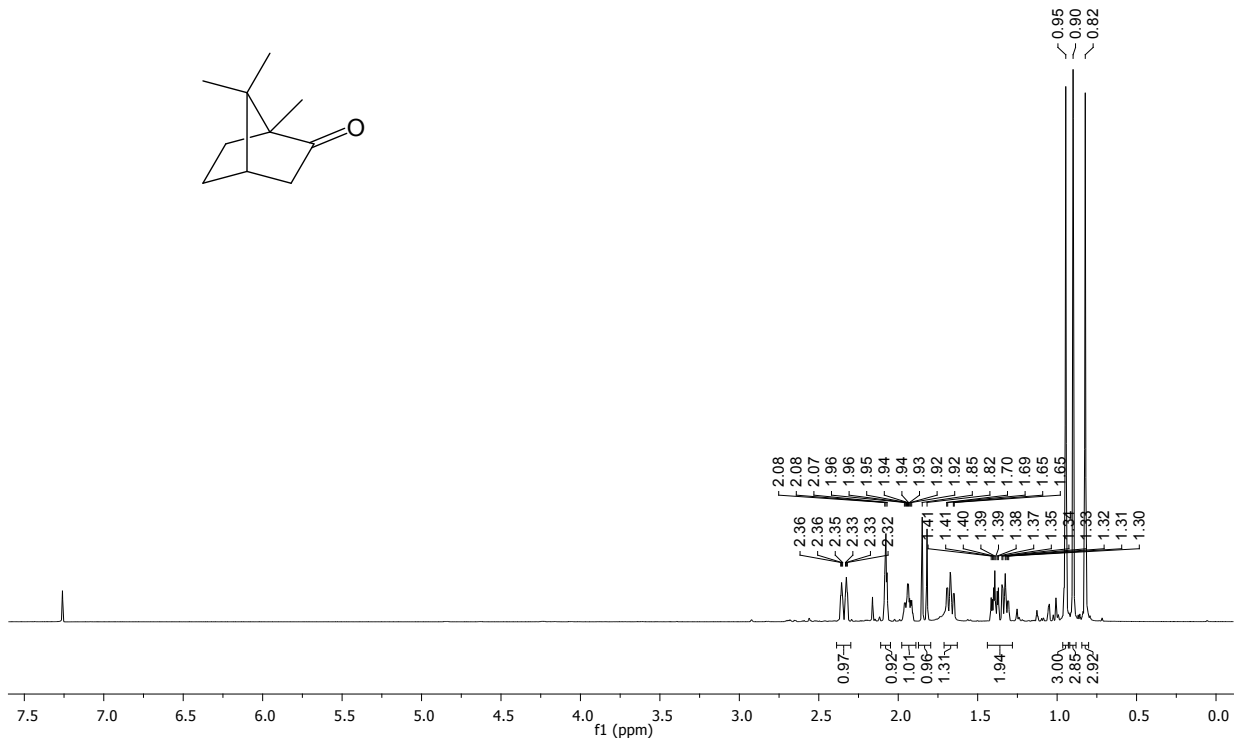


Figure S38: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of camphor.

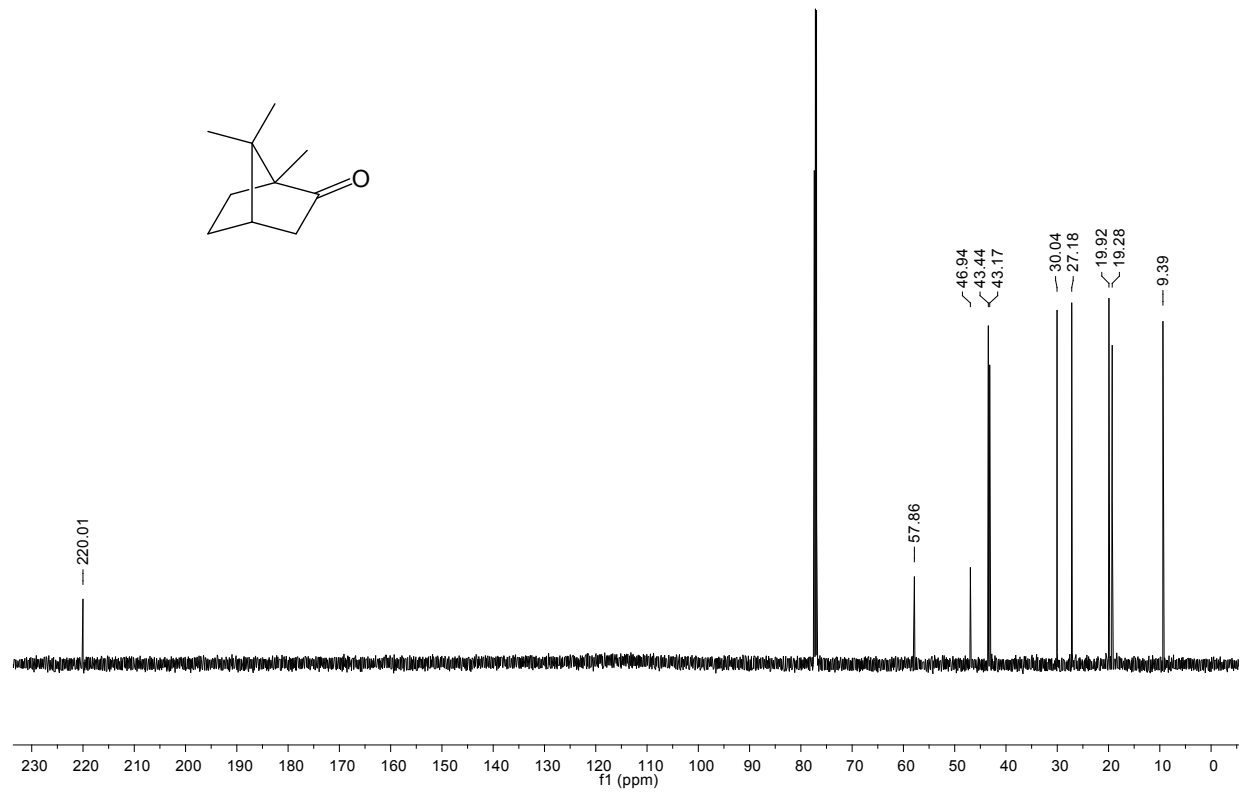


Figure S39: ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of camphor.

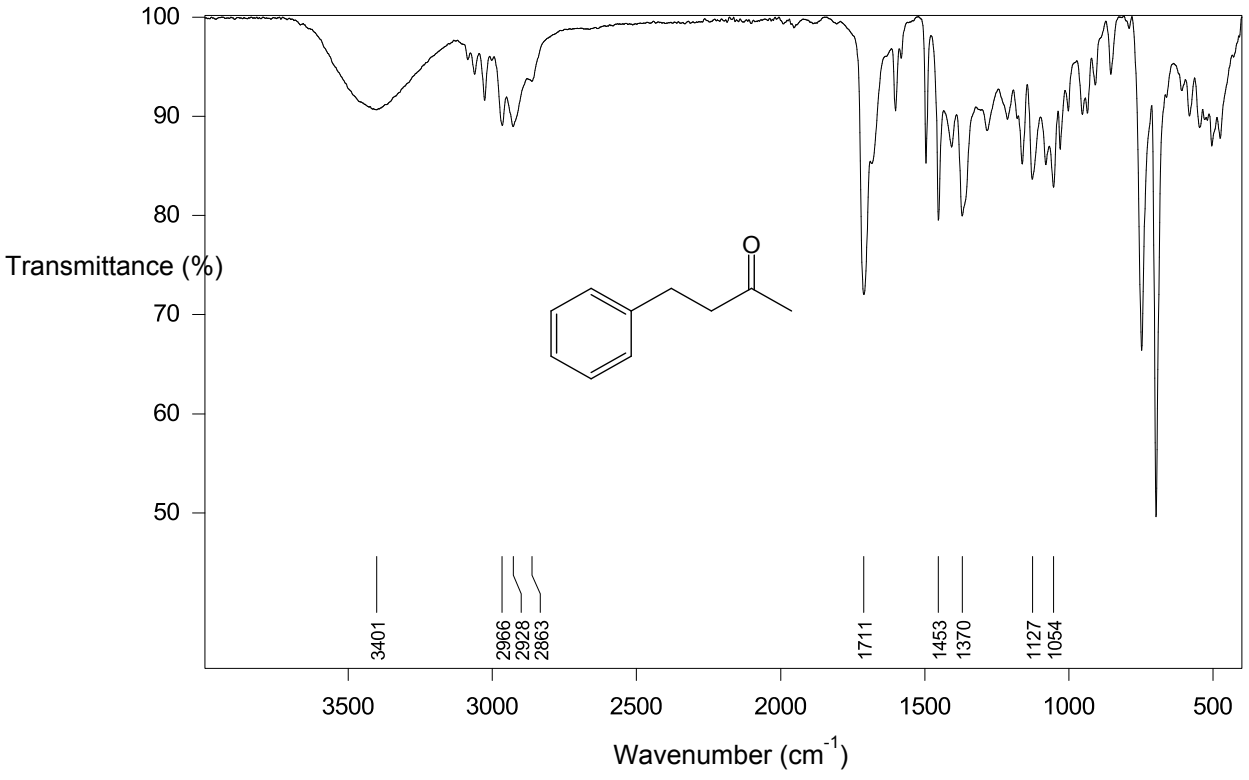


*Figure S40: FT-IR spectrum of isolated **4-phenyl-2-butanone**.*

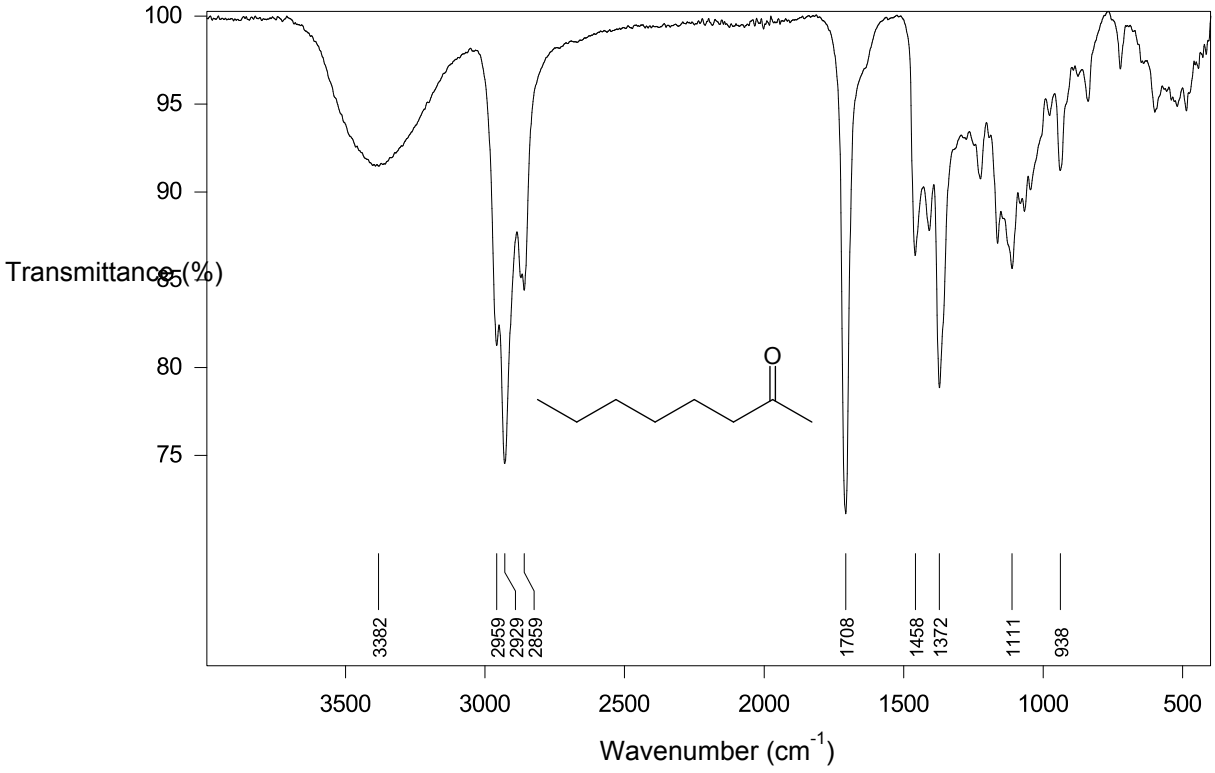


Figure S41: FT-IR spectrum of isolated ***2-octanone****.*

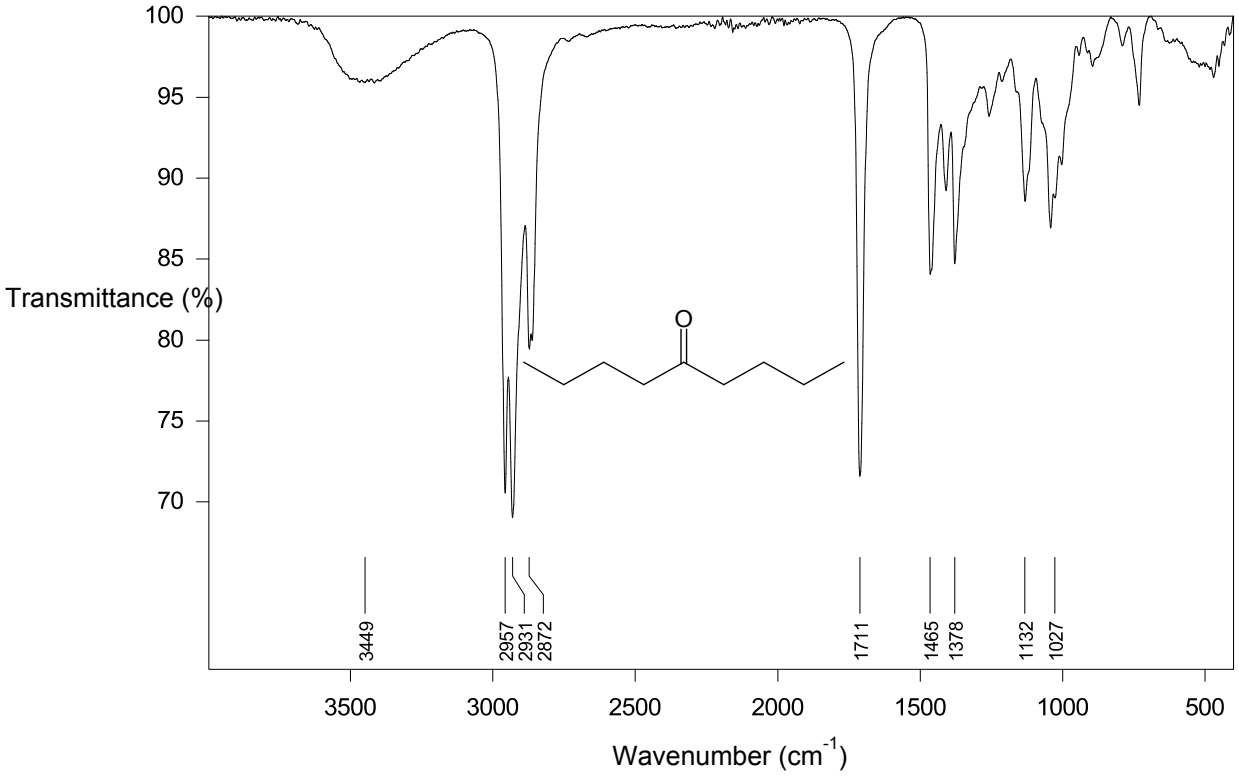


Figure S42: FT-IR spectrum of isolated ***5-nonanone****.*

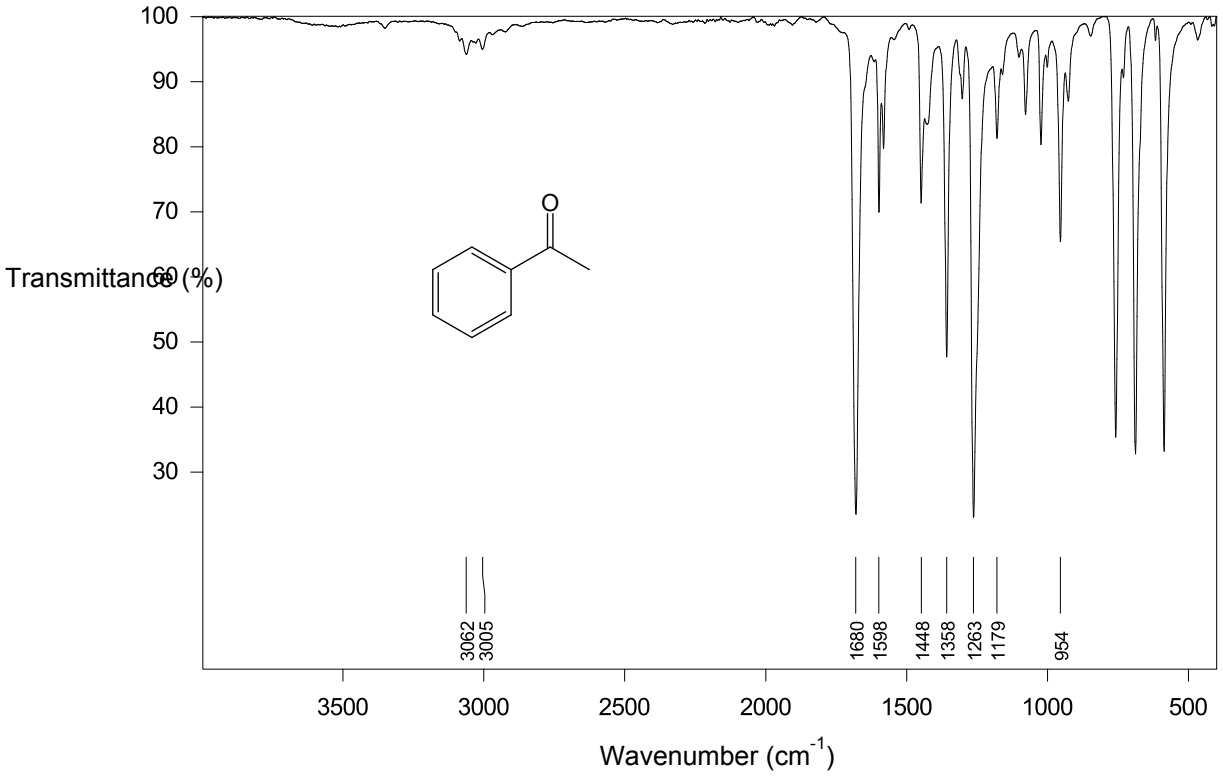


*Figure S43: FT-IR spectrum of isolated **acetophenone**.*

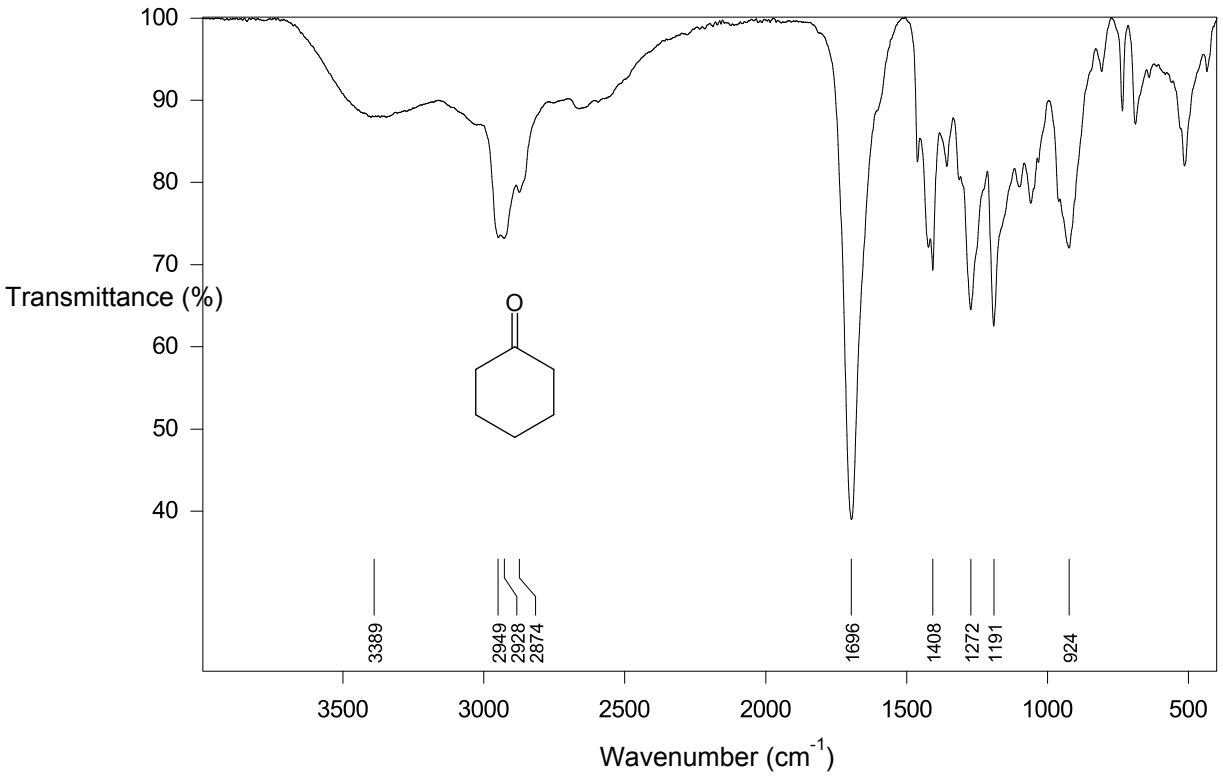


*Figure S44: FT-IR spectrum of isolated **cyclohexanone**.*

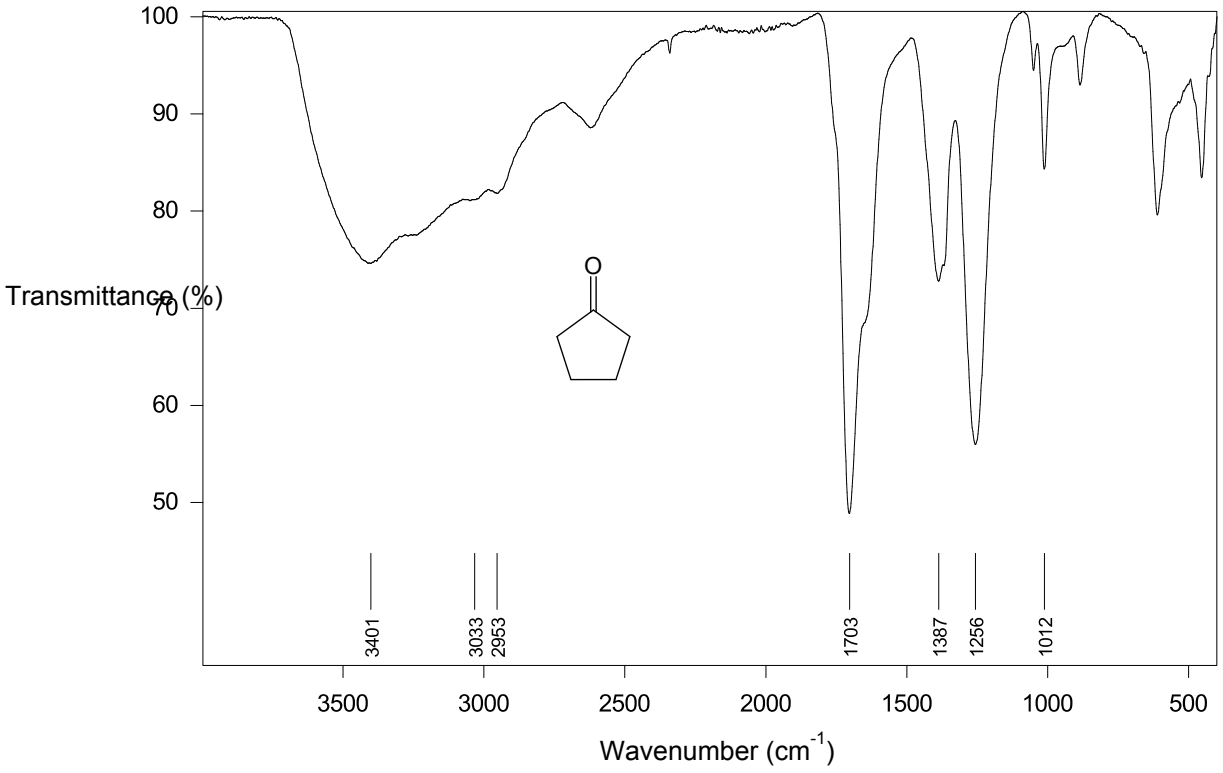


*Figure S45: FT-IR spectrum of isolated **cyclopentanone**.*

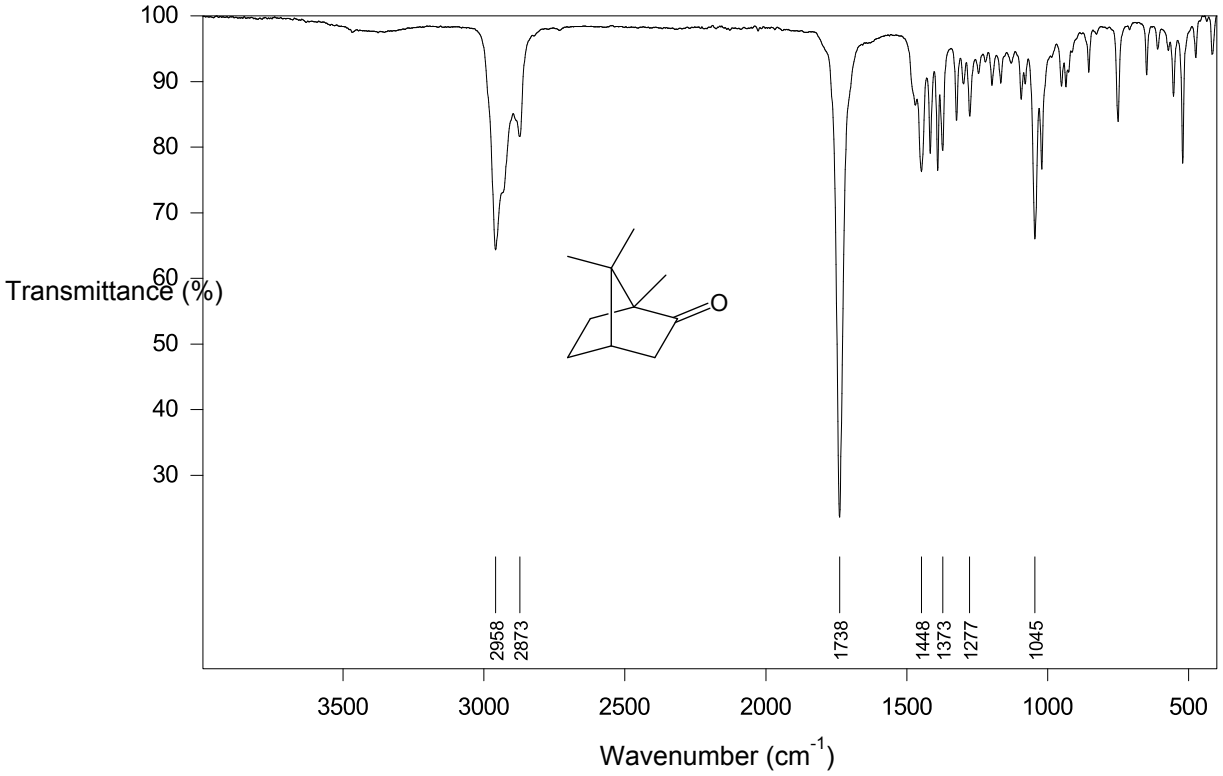


*Figure S46: FT-IR spectrum of isolated **camphor**.*

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