Inversion of Product Selectivity in an Enzyme-Inspired Metallosupramolecular Tweezer Catalyzed Epoxidation Reaction

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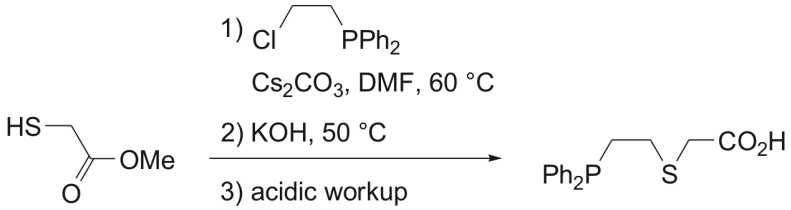
Supporting Information

A) General methods

All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or an inert atmosphere glovebox unless otherwise noted. CH_2Cl_2 was dried and purified through activated alumina columns as described by Grubbs et al. prior to use for reactions that were carried out under an inert atmosphere.[1] All solvents were degassed with nitrogen prior to use except for solvents that were used under ambient conditions. Iodosobenzene (TCI America), 2-acetamidopyridine (**11**, TCI America), Eu^{III} tris[3-(hepta-fluoropropylhydroxymethylene)-*d*-camphorate] (Fluka), [Pt(benzonitrile)$_2$Cl$_2$] (Strem), NaBArF (NaB[3,5-$(CF_3)_2(C_6H_3)]_4$, SynQuest) were obtained from commercial suppliers and used as received except for NaBArF, which was dried *in vacuo* before use (48 h, 100 °C, 50 mTorr). Ligands **1**[2], **3**[3] and 2-chloroethyldiphenylphosphine[4] were prepared according to literature procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. All other chemicals were used as received from Aldrich Chemical Company. ^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 300 MHz, on a Varian Inova 400 MHz FT-NMR spectrometer at 400 MHz or on a Bruker Avance 500 MHz FT-NMR at 500 MHz and referenced to residual proton resonances in deuterated solvents. ^{13}C{^{1}H} NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 75.5 MHz or on a Varian Inova 400 MHz FT-NMR spectrometer at 100.6 MHz. ^{31}P{^{1}H} NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 121.5 MHz or on a Varian Inova 400 MHz FT-NMR spectrometer at 162.0 MHz and referenced relative to an external 85% H_3PO_4 standard. ^{19}F{^{1}H} NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 282.5 MHz or on a Bruker Avance 400 MHz FT-NMR at 376.5 MHz and referenced relative to an external $CFCl_3$ in $CDCl_3$ standard. All chemical

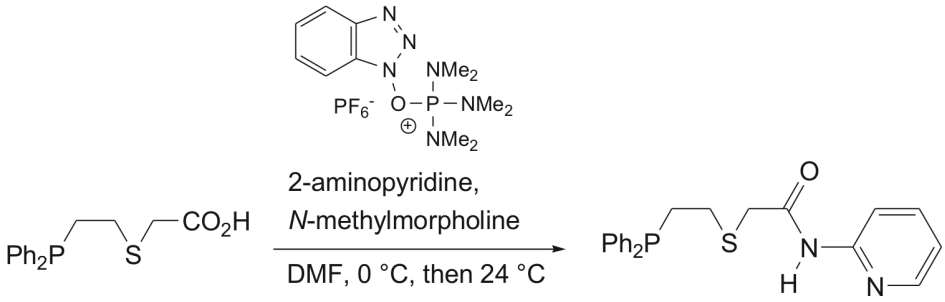
shifts are reported in ppm. FT-IR spectra were recorded using KBr pellets on a Thermo Nicolet Nexus 670 FT-IR spectrometer. UV/Vis spectra were recorded on an Agilent 8453 UV/Vis spectrometer using quartz cuvettes (diameter = 1 cm). High-resolution electrospray ionization (ESI) mass spectra were recorded on an Agilent 6210 TOF LC/MS spectrometer. Low-resolution electrospray ionization (ESI) mass spectra were recorded on an Agilent LC/MS MSD1100 mass spectrometer. High-resolution electron ionization (EI) mass spectra were recorded on a Fisions VG 70-250 SE mass spectrometer. Flash chromatographic purifications were carried out using a Biotage SP4 system. Gas chromatographic (GC) data were obtained on an Agilent 6890 Series GC system equipped with an FID detector. ITC measurements were carried out using a Microcal LLC Isothermal Titration Microcalorimeter^{TM}. Elemental analyses were performed by the Microanalytical Laboratory of the University of Illinois, Urbana-Champaign, IL.

B) Synthetic procedures and characterization



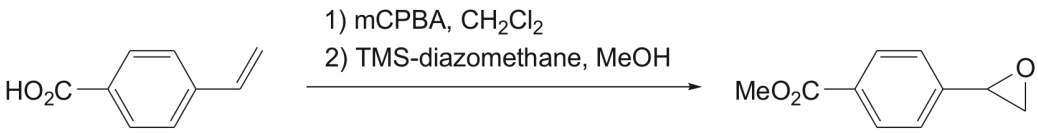
2-Diphenylphosphanylethylsulfanylacetic acid[5]: 2-Chloroethyldiphenylphosphine[4] (1.50 g, 6.03 mmol, 1 equiv) was dissolved in DMF (10 mL, anhydrous), followed by the addition of Cs_2CO_3 (1.96 g, 6.02 mmol, 1 equiv) and methyl thioglycolate (550 μL, 6.04 mmol, 1 equiv). The suspension was stirred at 60 °C for 24 h, followed by the addition of KOH (0.680 g, 12.1 mmol, 2 equiv) and stirring at 50 °C for another 22 h. The reaction mixture was allowed to cool to room temperature, followed by the addition of CH_2Cl_2 (100 mL) and 5% aq. AcOH (100 mL). The water phase was extracted with CH_2Cl_2 (2 x 100 mL), and the combined organic phase was

washed with H_2O (50 mL), dried with $MgSO_4$, filtered and concentrated *in vacuo*. Chromatographic purification (Flash 40+M column, *n*-hexanes/ethyl acetate 8% → 66%, 1320 mL, flowrate 40 mL/min) afforded 2-diphenylphosphanylethylsulfanylacetic acid (1.01 g, 55%) as a white powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.9 (br s, 1 H), 7.8-7.34 (m, 10 H), 3.27 (s, 2 H), 2.79-2.68 (m, 2 H), 2.42-2.33 (m, 2 H); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = 175.4 (s), 137.9 (d, *J*(C,P) = 12.8 Hz), 132.9 (d, *J*(C,P) = 19.0 Hz), 129.1 (s), 128.8 (d, *J*(C,P) = 6.9 Hz), 33.5 (s), 29.4 (d, *J*(C,P) = 24.2 Hz), 28.0 (d, *J*(C,P) = 13.0 Hz); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = –16.4 (s); HRMS (ESI): *m/z*: calcd for $C_{16}H_{18}O_2PS$ $[M + H]^+$: 305.0765; found: 305.0757; elemental analysis calcd (%) for $C_{16}H_{17}O_2PS$: C 63.14, H 5.63; found: C 63.04, H 5.40.



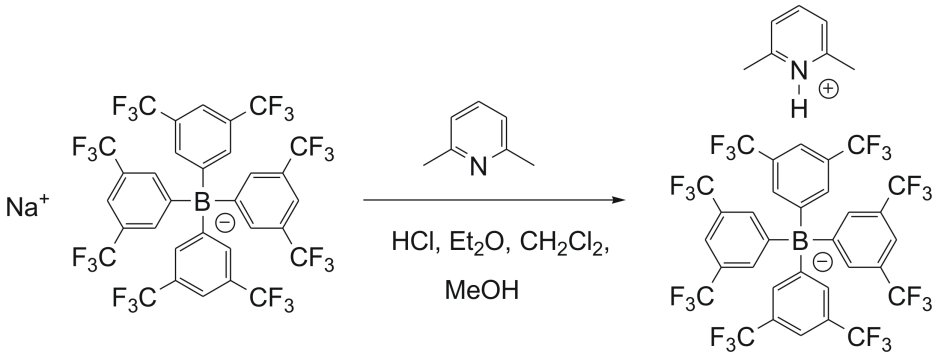
2-(2-Diphenylphosphanylethylsulfanyl)-*N*-pyridin-2-ylacetamide, 2: 2-Diphenylphosphanylethylsulfanylacetic acid (346 mg, 1.14 mmol, 1 equiv) and 2-aminopyridine (161 mg, 1.71 mmol, 1.5 equiv) were weighed out into a Schlenk flask, evacuated and put under an atmosphere of nitrogen. DMF (10 mL, anhydrous) and *N*-methylmorpholine (312 μL, 2.84 mmol, 2.49 equiv) were added to the flask, followed by cooling of the reaction flask to 0 °C. After 20 min, (benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate (BOP, 503 mg, 1.14 mmol, 1 equiv) was added to the reaction mixture under a nitrogen stream. The reaction mixture was stirred for 1.5 h at 0 °C and was then allowed to warm up to 24 °C and was stirred for another 18 h. CH_2Cl_2 (70 mL) and water (100 mL) were subsequently added to

the reaction mixture. The water phase was extracted with CH_2Cl_2 (2 x 70 mL) and the combined organic phase was dried with Na_2SO_4, followed by concentration *in vacuo*. Chromatographic purification (Flash 40+M column, *n*-pentane/ethyl acetate 12% → 100%, 1320 mL, flowrate 40 mL/min) yielded **2** (300 mg, 69%) as a white powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.35 (s, 1 H), 8.30 (d, *J* = 3.0 Hz, 1 H), 8.19 (d, *J* = 8.5 Hz, 1 H), 7.78 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 1 H), 7.42-7.38 (m, 4 H), 7.32-7.3 (m, 6 H), 7.12 (dd, *J* = 7.0, 5.0 Hz, 1 H), 3.41 (s, 2 H), 2.72-2.67 (m, 2 H), 2.41-2.38 (m, 2 H); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = 168.0 (s), 151.5 (s), 147.9 (s), 139.2 (s), 138.3 (d, *J*(C,P) = 12.6 Hz), 133.2 (d, *J*(C,P) = 19.0 Hz), 129.3 (s), 129.1 (d, *J*(C,P) = 6.3 Hz), 120.5 (s), 114.2 (s), 37.7 (s), 30.0 (d, *J*(C,P) = 21.7 Hz), 28.5 (d, *J*(C,P) = 15.5 Hz); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = –17.2 (s); FT-IR (KBr, cm^{-1})[6]: 3286 (N-H), 1678 (C=O), 1581 (N-C=O); HRMS (ESI): *m/z*: calcd for $C_{21}H_{22}N_2OPS$ $[M + H]^+$: 381.1190; found: 381.1183; elemental analysis calcd (%) for $C_{21}H_{21}N_2OPS$: C 66.30, H 5.57, N 7.37; found: C 66.20, H 5.60, N 7.41.

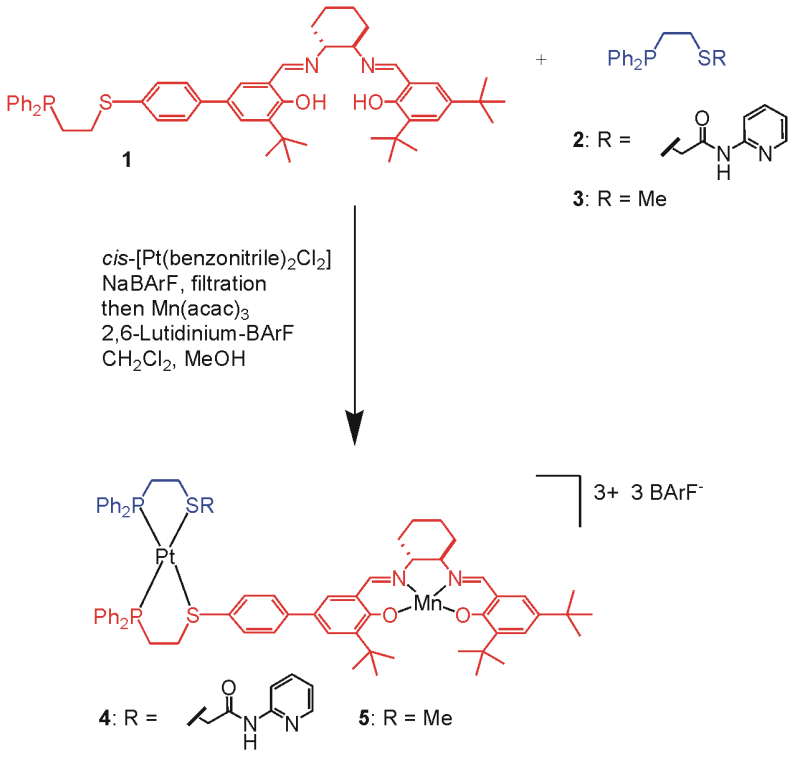


(±)-4-Oxiranyl-benzoic acid methyl ester[7] (standard for GC experiments): Under ambient conditions, 4-vinylbenzoic acid (100 mg, 0.675 mmol, 1 equiv) and 3-chloroperbenzoic acid (277 mg, 77% purity, 1.24 mmol, 1.84 equiv) were dissolved in CH_2Cl_2 (10 mL) and the colorless reaction solution was stirred at 24 °C for 3 h. The reaction was quenched by the slow addition of triphenylphosphine (354 mg, 1.35 mmol, 2 equiv), which resulted in significant gas formation. After 45 min, MeOH (5 mL) was added to the reaction mixture, followed by titration of (trimethylsilyl)diazomethane solution (1.5 mL, 2 M in Et_2O, 3 mmol, 4.4 equiv) into the

reaction solution until the yellow color persisted. Chromatographic purification (Flash 12+M column, 5% → 33% EtOAc/hexanes, 108 mL, flowrate 12 mL/min) afforded (±)-4-oxiranyl-benzoic acid methyl ester (32.8 g, 27%) as a white powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.5 Hz, 2 H), 7.34 (d, J = 8.5 Hz, 2 H), 3.91-3.90 (m, 4 H), 3.19 (dd, J = 5.5, 4.0 Hz, 1 H), 2.79 (dd, J = 5.5, 2.5 Hz, 1 H); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 167.0 (s), 143.1 (s), 130.2 (s), 130.0 (s), 125.6 (s), 52.4 (s), 52.1 (s), 51.7 (s); MS (EI): *m/z*: calcd for $C_{10}H_{10}O_3$ $[M]^+$: 178.0630; found: 178.0625.



[2,6-Lutidinium][tetrakis{(3,5-trifluoromethyl)phenyl}borate] (2,6-Lutidinium-BArF): NaBArF (100 mg, 0.113 mmol, 1 equiv) was dissolved in a mixture of CH_2Cl_2 (5 mL) and MeOH (2 mL). 2,6-Lutidine (20 μL, 0.17 mmol, 1.5 equiv) and HCl (in Et_2O, 1 M, 110 μL, 0.11 mmol, 1 equiv) were added slowly to the reaction mixture, which turned cloudy. After stirring for 2 h at 24 °C, the solution was evacuated, redissolved in CH_2Cl_2 (5 mL), filtered through Celite and evacuated again, resulting in 2,6-Lutidinium-BArF (104 mg, 97%) as a white powder. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 13.75 (s, 1 H), 7.96 (t, J = 9.6 Hz, 1 H), 7.74 (s, 8 H), 7.56 (s, 4 H), 7.38 (d, J = 7.8 Hz, 2 H), 2.57 (s, 6 H); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = 162.3 (q, J(B,C) = 49.9 Hz), 154.9 (s), 144.7 (s), 135.3 (s), 129.4 (q, J(C,F) = 34.4 Hz), 125.2 (s), 125.1 (q, J(C,F) = 272.5 Hz), 118.0 (s), 20.9 (s); ^{19}F{^{1}H} NMR (282.5 MHz, CD_2Cl_2): δ = -63.4 (s); HRMS (ESI): *m/z*: calcd for $C_7H_{10}N$ $[M - BArF]^+$: 108.0813, found: 108.0812.

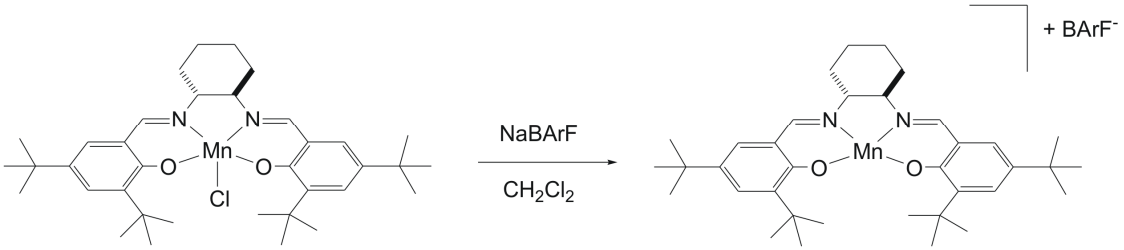


General protocol for the synthesis of complexes 4 and 5: Under ambient conditions, a solution of ligand **1** (15.0 mg in 6 mL CH_2Cl_2, 0.019 mmol, 1 equiv) was added dropwise to a solution of *cis*-[$PtCl_2$(benzonitrile)$_2$] (8.7 mg in 6 mL CH_2Cl_2, 0.019 mmol, 1 equiv), followed by the addition of the solution of ligand **2** (7.0 mg in 6 mL CH_2Cl_2, 0.019 mmol, 1 equiv) or **3** (4.8 mg in 6 mL CH_2Cl_2, 0.019 mmol, 1 equiv). The yellow solution was stirred at 24 °C for 1 h, followed by the addition of NaBArF (34.5 mg, 0.0389 mmol, 2.1 equiv, dissolved in 3 mL CH_2Cl_2) to the reaction mixture. After stirring for 1 h at 24 °C, the mixture was filtered through Celite. $Mn(acac)_3$ (13.0 mg, 0.0370 mmol, 2 equiv) was dissolved in MeOH (2 mL), 2,6-Lutidinium-BArF (126 mg, 0.130 mmol, 7 equiv) was dissolved in CH_2Cl_2 (3 mL) and the two solutions were combined to give a light green solution, which was immediately added to the reaction mixture. Within approx. 15 min, the reaction mixture turned dark brown. The reaction mixture was stirred for 21 h at 24 °C, followed by concentration *in vacuo* and purification via gel

filtration with Sephadex® LH-20 (6 g, mobile phase: MeOH, column diameter: 1.5 cm). The first dark brown band was collected into 6 fractions, which were individually analyzed via low resolution ES-MS. Fractions that contained a peak at *m/z* = 479 (for **4**, $[M - 3\ BArF]^{3+}$) or 439 (for **5**, $[M - 3\ BArF]^{3+}$) and no peak at *m/z* = 253 (predominant peak in the 2nd green band) were recombined, concentrated and dried *in vacuo* for 48 h, resulting in complex **4** (65.5 mg, 88%) or **5** (64.5 mg, 89%) as dark brown solids.

(*R*,*R*)-4: ^{1}H NMR (400 MHz, CD_2Cl_2)[8]: δ = 52 (br s), 19 (br s), 9.4 (s), 8.1-6.9 (m), 4.2-3.9 (m), 3.5-1.9 (m), -30.0 (s), -33.1 (s), -35.7 (s), -38.5 (s); $^{31}P\{^{1}H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 62 (very br s), 47.4 (br s, *J*(Pt,P) = 3217 Hz); $^{19}F\{^{1}H\}$ NMR (376.5 MHz, CD_2Cl_2): δ = -61.7 (s); UV/Vis (25 °C, CH_2Cl_2, nm): 420 (br)[6c]; FT-IR (KBr, cm^{-1})[6]: 3406 (N-H), 1680 (C=O), 1610 (C=N), 1537 (N-C=O); HRMS (ESI): *m/z*: calcd for $C_{105}H_{94}BF_{24}MnN_4O_3P_2PtS_2$ $[M - 2\ BArF]^{2+}$: 1150.7490; found: 1150.7542; elemental analysis calcd (%) for $C_{169}H_{118}B_3F_{72}MnN_4O_3P_2PtS_2$: C 50.38, H 2.95, N 1.39; found: C 50.40, H 3.10, N 1.46.

(*R*,*R*)-5: ^{1}H NMR (400 MHz, CD_2Cl_2)[8]: δ = 56 (br s), 21 (br s), 9.4 (s), 8.0-7.0 (m), 3.2-2.0 (m), -30.3 (s), -33.3 (s), -35.7 (s), -38.7 (s); $^{31}P\{^{1}H\}$ NMR (162.0 MHz, CD_2Cl_2): δ = 55.4 (br s, *J*(Pt-P) = 3037 Hz), 47.9 (br s, *J*(Pt,P) = 3024 Hz); $^{19}F\{^{1}H\}$ NMR (376.5 MHz, CD_2Cl_2): δ = -62.2 (s); UV/Vis (25 °C, CH_2Cl_2, nm)[6c]: 420 (br); FT-IR (KBr, cm^{-1})[6]: 1610 (C=N); HRMS (ESI): *m/z*: calcd for $C_{99}H_{90}BF_{24}MnN_2O_2P_2PtS_2$ $[M - 2\ BArF]^{2+}$: 1090.7329; found: 1090.7354; elemental analysis calcd (%) for $C_{163}H_{114}B_3F_{72}MnN_2O_2P_2PtS_2$: C 50.08, H 2.94, N 0.72; found: C 49.22, H 2.89, N 0.80.



(*R*,*R*)-[(salen)-Mn^{III}][tetrakis{(3,5-trifluoromethyl)phenyl}borate], (*R*,*R*)-[(salen)-Mn^{III}-BArF], 6: In a glovebox, NaBArF (153 mg, 0.173 mmol, 1.1 equiv) was added to (*R*,*R*)-*N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino-manganese(III) chloride (100 mg in 5 mL CH_2Cl_2, 0.157 mmol, 1 equiv), resulting in a dark brown solution. After stirring for 3 h at 24 °C, the solution was filtered through Celite and concentrated *in vacuo*, resulting in (*R*,*R*)-[(salen)-Mn^{III}-BArF] (216 mg, 94%) as a dark brown powder. ^{1}H NMR (400 MHz, CD_2Cl_2)[8]: δ= 19 (br s), 7.7 (s), 7.6 (s), 3.5 (s), 2.4 (s), -33.7 (s), -36.2 (s); ^{19}F{^{1}H} NMR (376.5 MHz, CD_2Cl_2): δ = -63.1 (s); UV/Vis (25 °C, CH_2Cl_2, nm)[6c]: 430; FT-IR (KBr, cm^{-1})[6]: 1605 (C=N); HRMS (ESI): *m/z*: calcd for $C_{36}H_{52}MnN_2O_2$ [M – BArF]$^+$: 599.3409; found: 599.3410; elemental analysis calcd (%) for $C_{68}H_{64}BF_{24}MnN_2O_2$: C 55.83, H 4.41, N 1.91; found: C 55.51, H 4.59, N 1.95.

C) General procedure for catalytic experiments

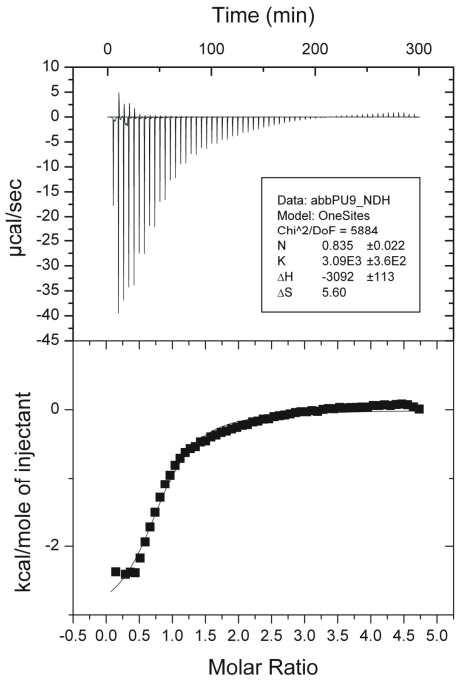
Catalytic reactions were carried out in duplicate or triplicate. Stock solutions were prepared freshly in the glovebox before running catalytic experiments. Solution 1: 29 μL styrene, 37.9 mg 4-vinylbenzoic acid, 38 μL *n*-hexadecane were diluted to 1 mL with CH_2Cl_2; solution 2: 1.7 mg 2-acetamidopyridine **11** was diluted to 1 mL with CH_2Cl_2. In a glovebox, complex **4** (5.2 mg, 1.3 μmol, 5 mol% with respect to total olefin conc.), **5** (5.0 mg, 1.3 μmol, 5 mol% with respect to total olefin conc.) or **6** (1.9 mg, 1.3 μmol, 5 mol% with respect to total olefin conc.) were mixed

with stock solution 1 (50 μL, styrene: 13 μmol, 0.5 equiv; 4-vinylbenzoic acid: 13 μmol, 0.5 equiv; *n*-hexadecane: 6.4 μmol, 0.25 equiv) and CH_2Cl_2 (30 mL). For entries 5 and 7, stock solution 2 (100 μL, 2-acetamidopyridine: 1.3 μmol, 5 mol% with respect to total olefin conc.) was added to the mixture. For entries 2-4, 4-ethylbenzoic acid (entry 2: 1.9 mg, 0.013 mmol, 0.5 equiv; entry 3: 9.6 mg, 0.064 mmol, 2.5 equiv; entry 4: 19.2 mg, 0.128 mmol, 5 equiv) was added to the mixture. The flasks were transferred to a Schlenk line, put under positive N_2 pressure and cooled to 0 °C. PhIO (5.6 mg, 0.026 mmol, 1 equiv) was added to the reaction mixture in a N_2 stream, followed by stirring of the brown solutions at 0 °C for 2 h. Triphenylphosphine (13.4 mg, 0.0512 mmol, 2 equiv) was added to quench the reaction mixture. After 10 min, the reaction mixture was allowed to warm up to room temperature (30 min). Conversion of carboxylic acid groups to the corresponding methyl ester, which facilitates gas chromatographic analysis,[9] was carried out under ambient conditions by the addition of MeOH (20 mL) and (trimethylsilyl)-diazomethane (500 μL, 2 M, 1 mmol, 40 equiv) to the reaction mixture, resulting in a brown-yellow solution. The reaction mixture was concentrated under moderate vacuum (240 mbar/40 °C), followed by analysis via gas chromatography. Chromatographic purification (Flash 12+M column, 3% → 50% Et_2O/pentane, 150 mL, flowrate 12 mL/min) of recombined mixtures of two duplicate catalytic runs gave 4-oxiranyl-benzoic acid methyl ester (methylated form of epoxide **9**), to which the chiral shift reagant Eu^{III} tris[3-(hepta-fluoropropylhydroxymethylene)-*d*-camphorate] was added in increments of 0.5 mg until the *ee* could be determined by ^{1}H NMR integration of the methylene epoxide proton signal at δ = 3.19 (shifted to δ = 3.6-4.2).

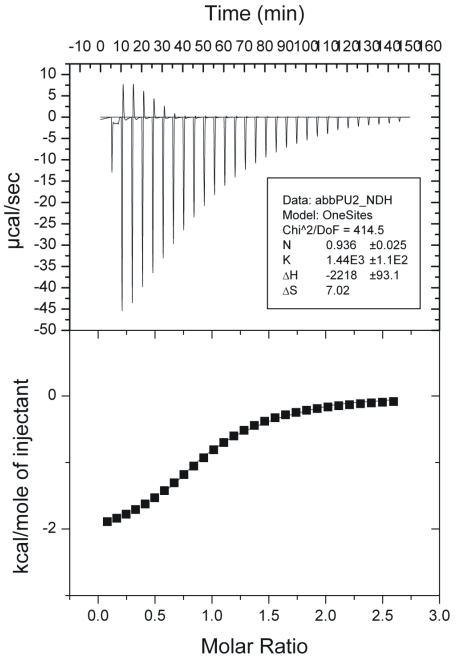
D) Isothermal titration calorimetry (ITC)

General Procedure for Isothermal Titration Calorimetry (ITC). All ITC runs were carried out using a Microcal LLC Isothermal Titration Microcalorimeter^{TM} as follows: solutions (1 - 5 mM) of the amidopyridines in CH_2Cl_2 were prepared in volumetric glassware. A solution (53 mM) of the styrenes in CH_2Cl_2 was also prepared in volumetric glassware. The amidopyridines were added to the cell of the calorimeter and the cell was equilibrated at 298 K. In aliquots of 4-7 μLs, the styrenes were added into the sample cell with 200 s increments between additions of the aliquots to allow for thermal equilibration between injections. Blank runs in which the styrenes were injected to a cell of only CH_2Cl_2 were performed and subtracted from experimental data to account for the $\Delta S_{dilution}$ in each run. Fits to obtain the thermodynamic data (ΔG, ΔH, ΔS, K_a, n) were performed using software provided by Microcal LLC using a single-site binding model. The binding constant (K_a) for the hydrogen bonded complex between carboxylic acid **7** and catalyst **4** was found to be 3090 ± 360 M^{-1} at 25 ^{o}C. This equates to 56 % of catalyst **4** (and 5.6 % of substrate **7**) being bound in the supramolecular H-bonded complex at the concentrations used in the catalytic experiments (0.043 mM for **4** and 0.43 mM for **7**). At 0 ^{o}C the K_a is calculated to be 5006 M^{-1}, which equates to 67 % of **4** (6.7 % of **7**) being bound in the supramolecular H-bonded complex at the same concentrations.

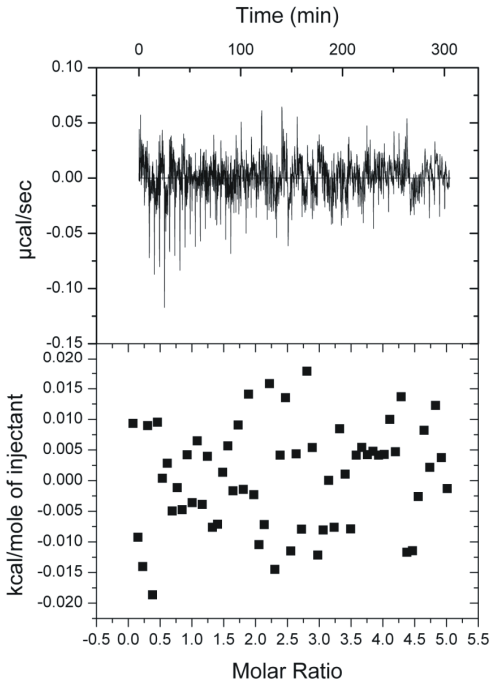
1) Combination of 4-vinylbenzoic acid 7 and complex 4



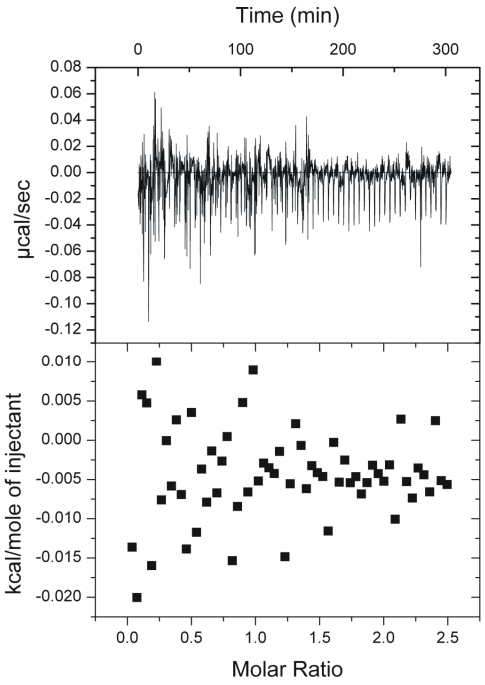
2) Combination of 4-vinylbenzoic acid 7 and 2-acetamidopyridine 11



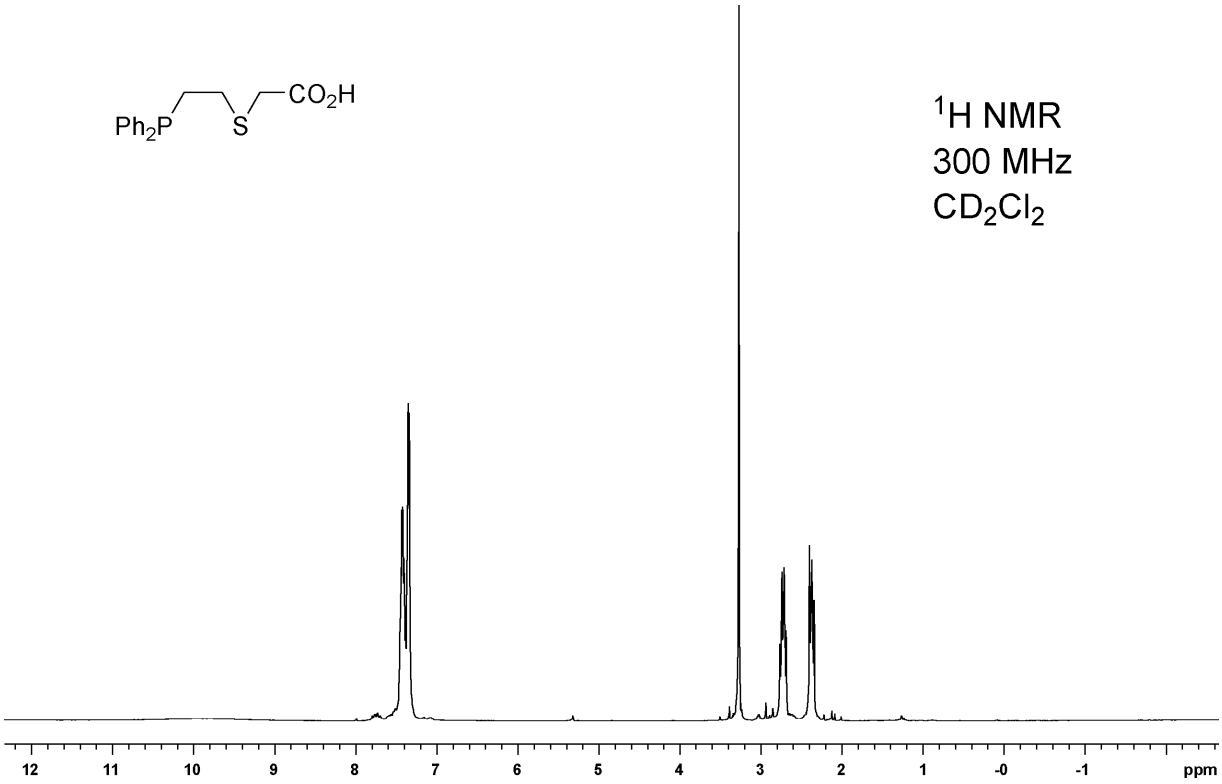
3) Combination of 4-vinylbenzoic acid 7 and complex 5

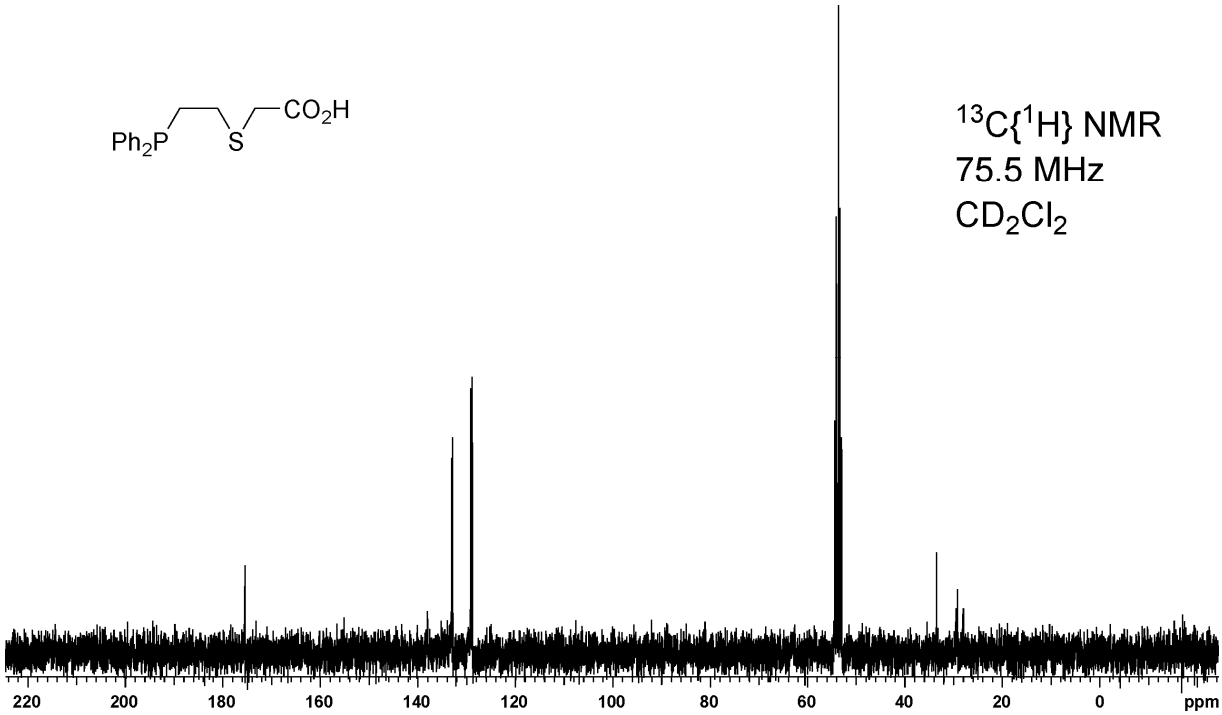


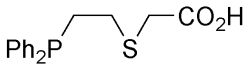
4) Combination of styrene 8 and and 2-acetamidopyridine 11



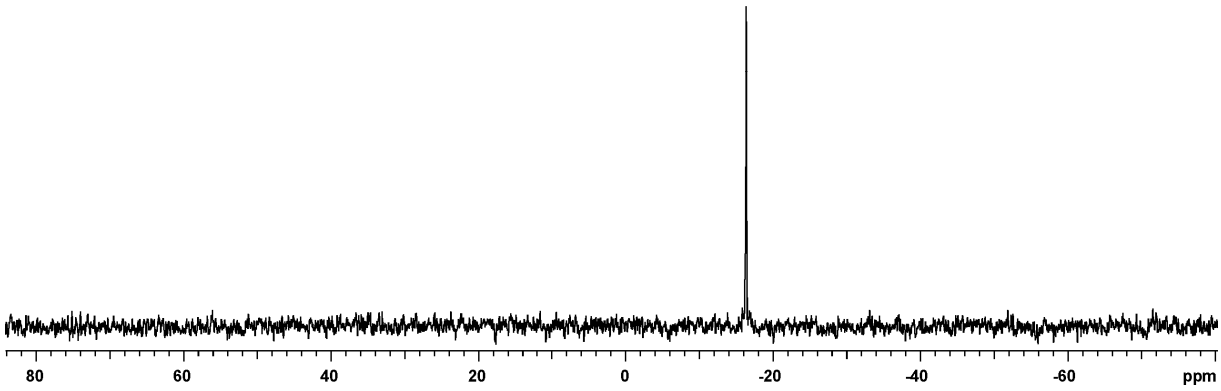
E) ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR Spectra

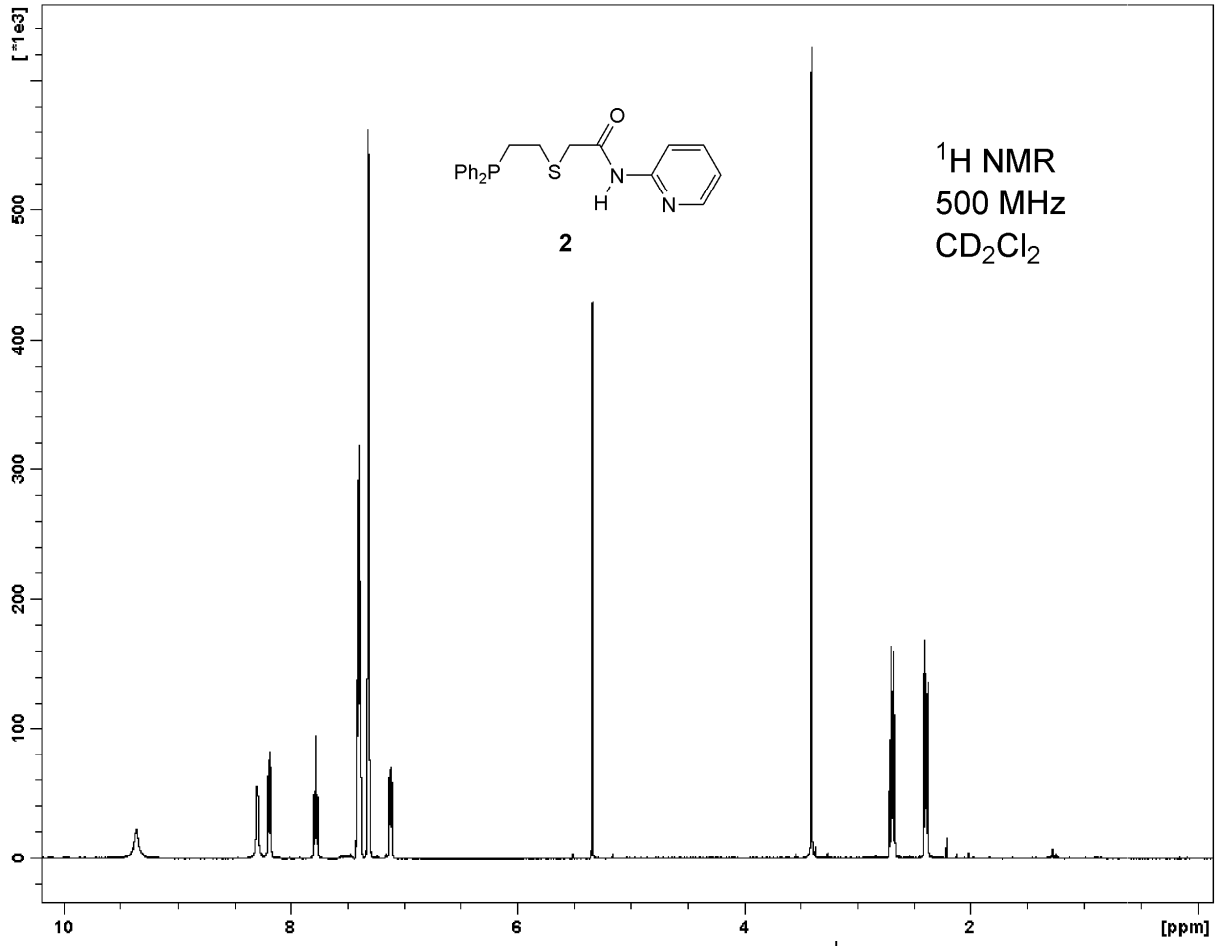






$^{31}P\{^{1}H\}$ NMR
121.5 MHz
CD_2Cl_2

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[ppm]
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S
O
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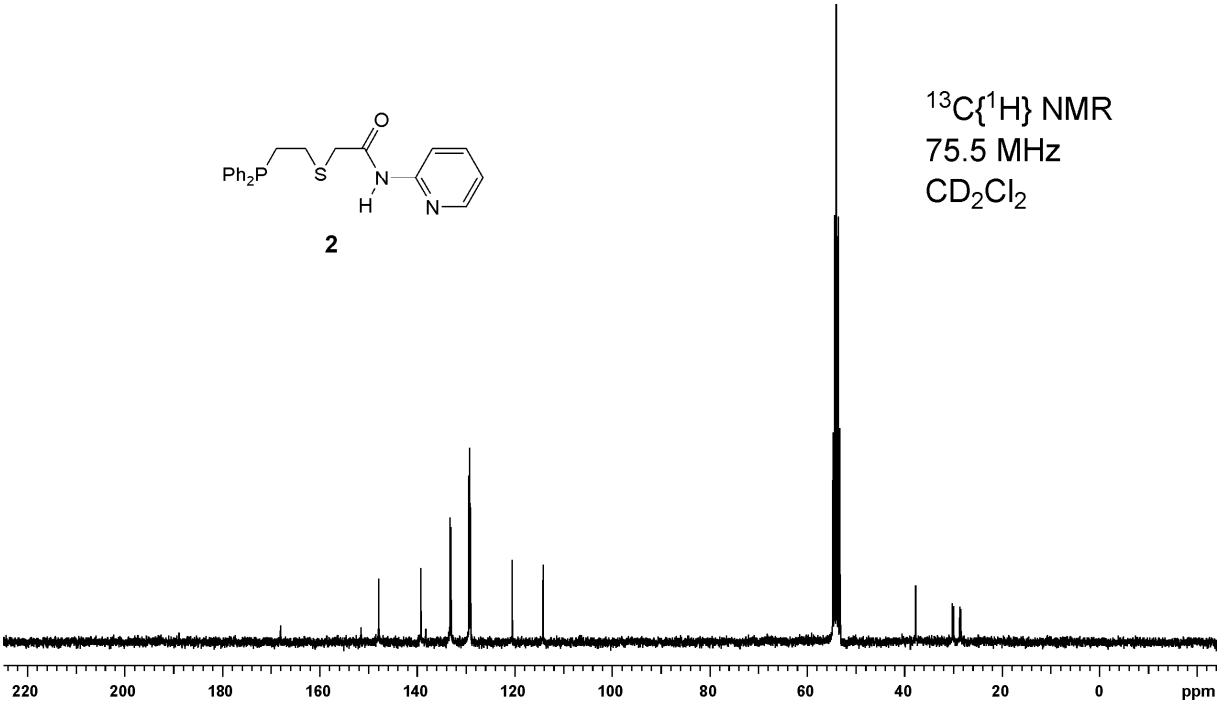
H
N
2
1H NMR
500 MHz
CD2Cl2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H
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2
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75.5 MHz
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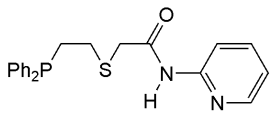

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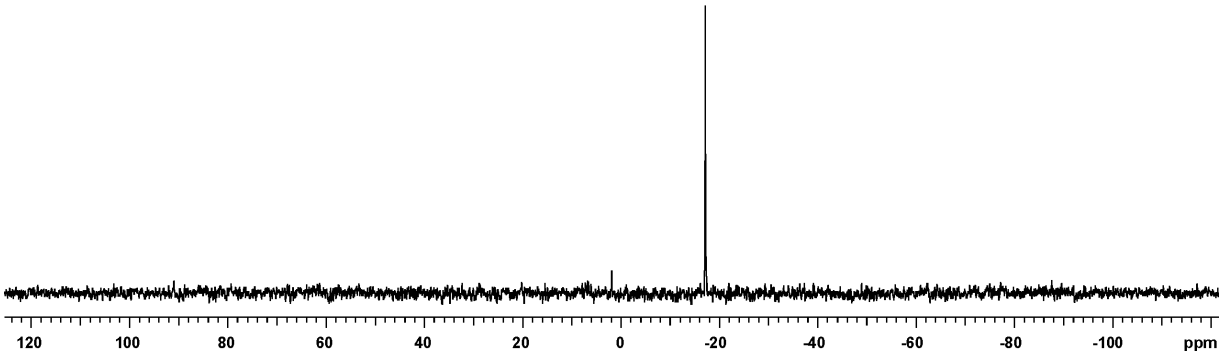

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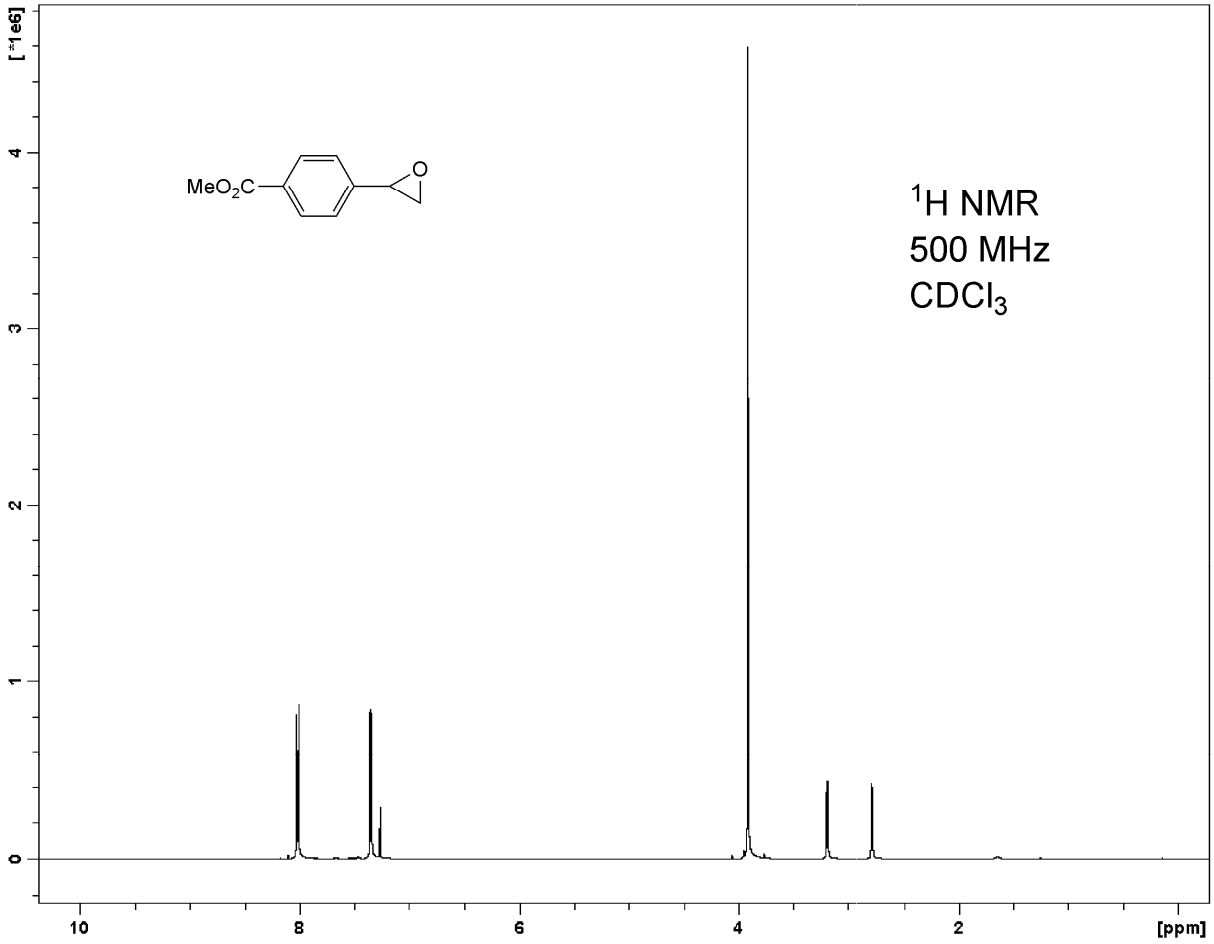
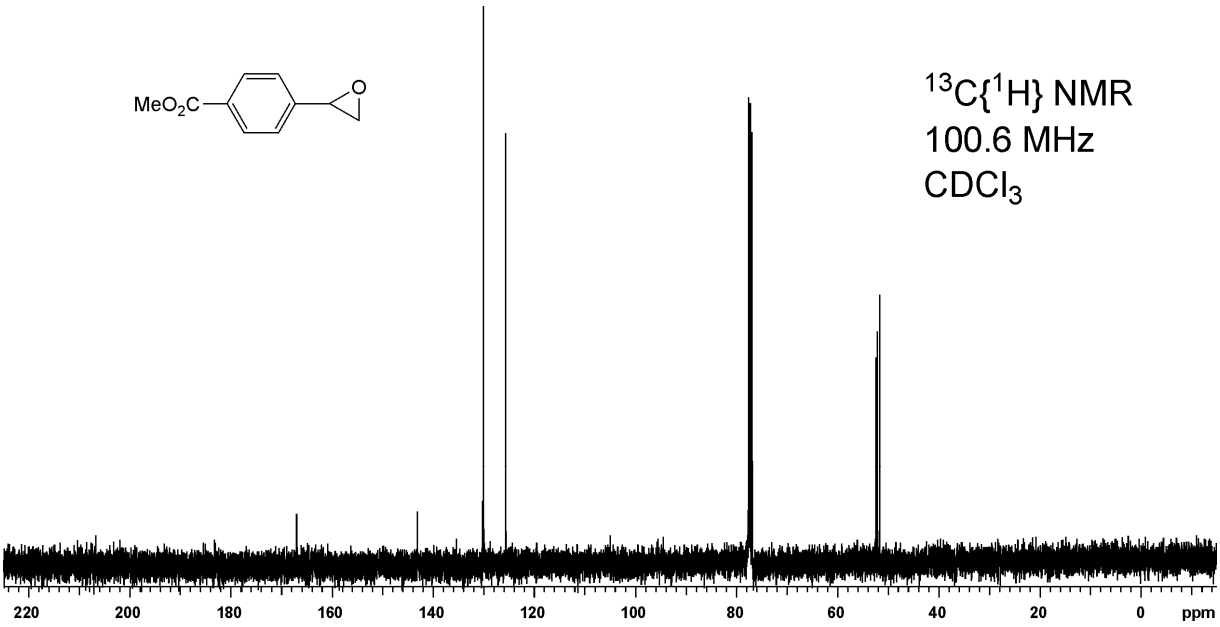
500 MHz
$CDCl_3$

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O
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CDCl3
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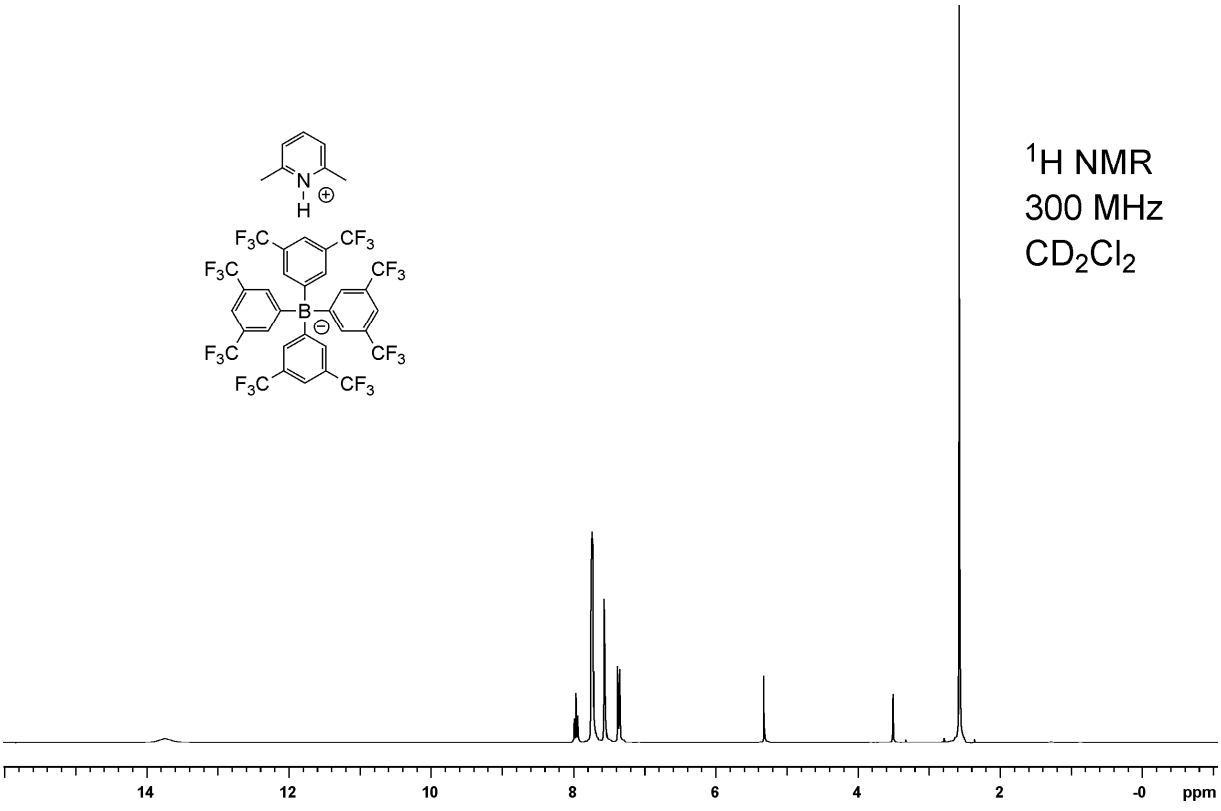
ppm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F3C
CF3
B
1H NMR
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CD2Cl2
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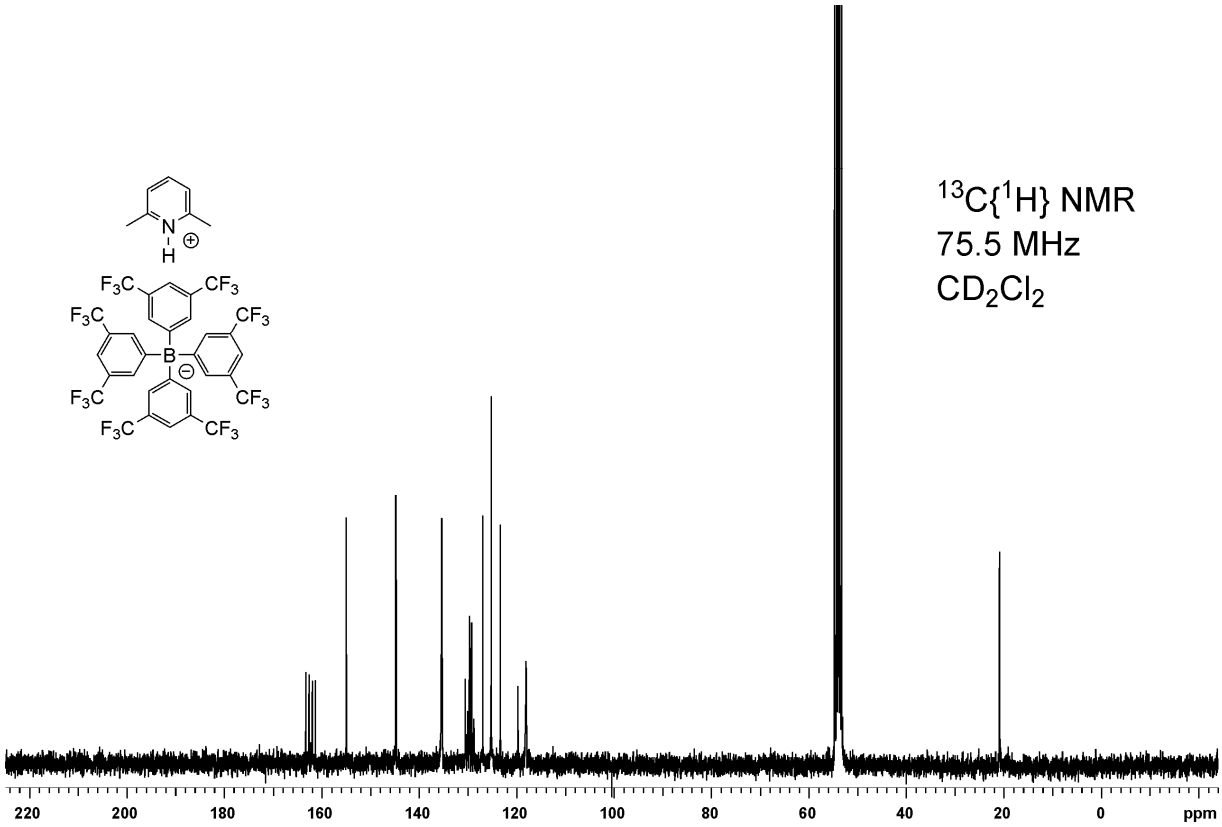
12
10
8
6
4
2
-0
ppm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CD_2Cl_2
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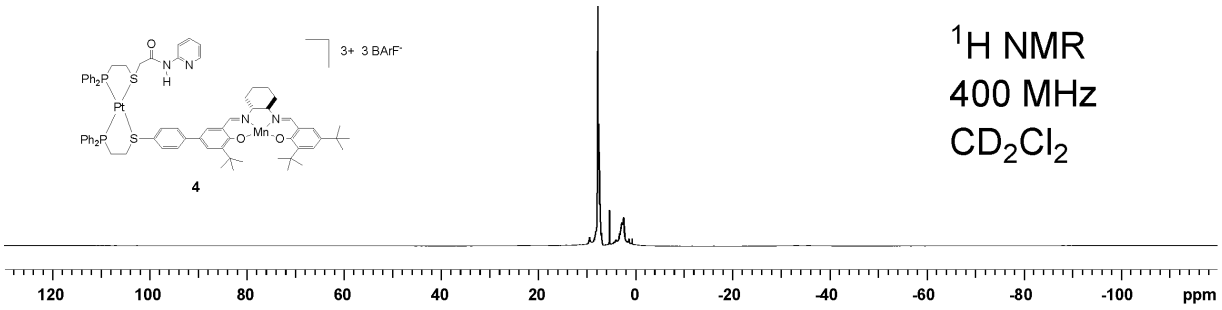
3+ 3 BArF-
4
^{1}H NMR
400 MHz
CD_2Cl_2
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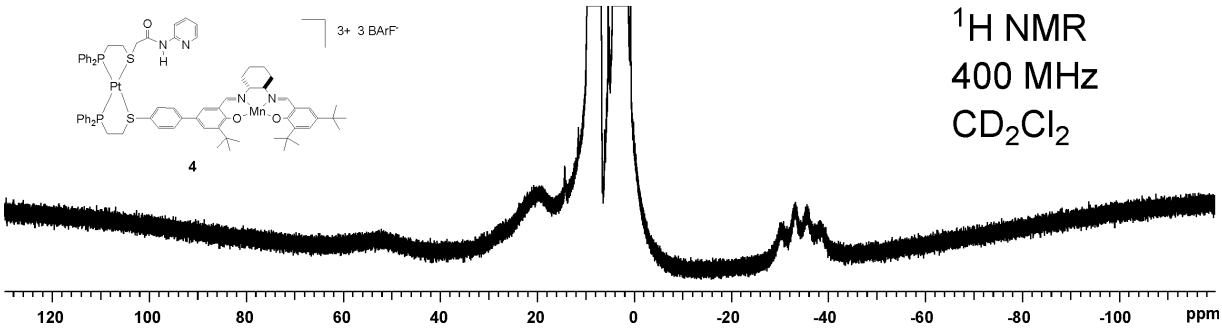
3+ 3 BArF-
4
^{1}H NMR
400 MHz
CD_2Cl_2
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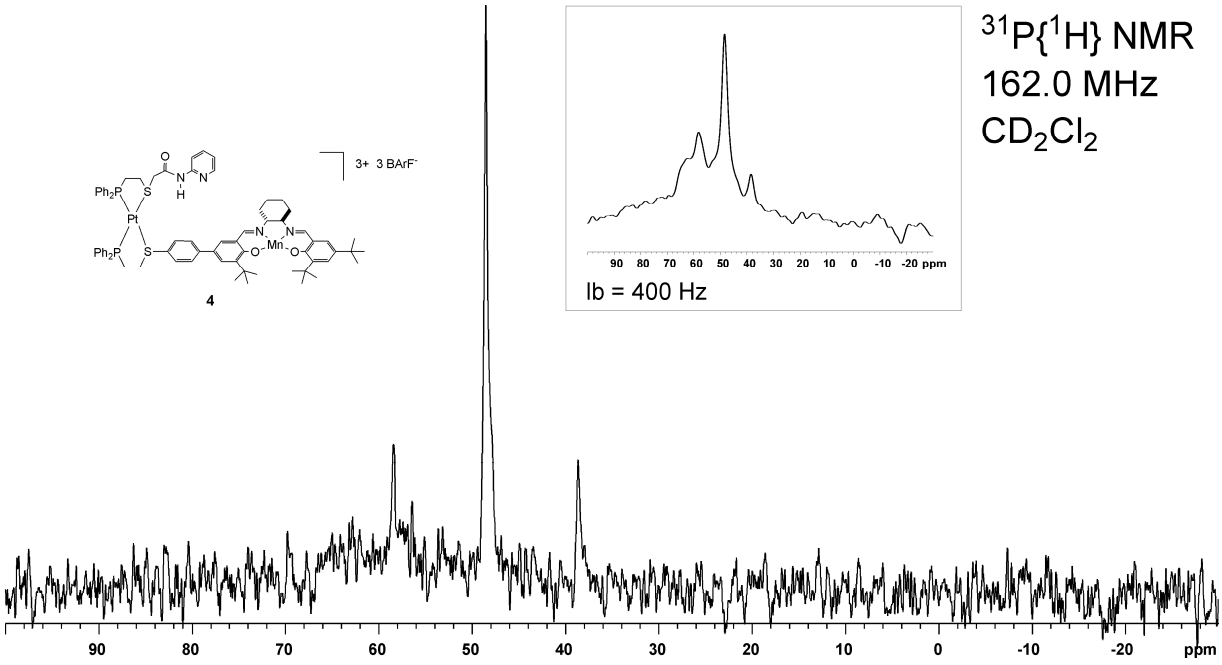
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4
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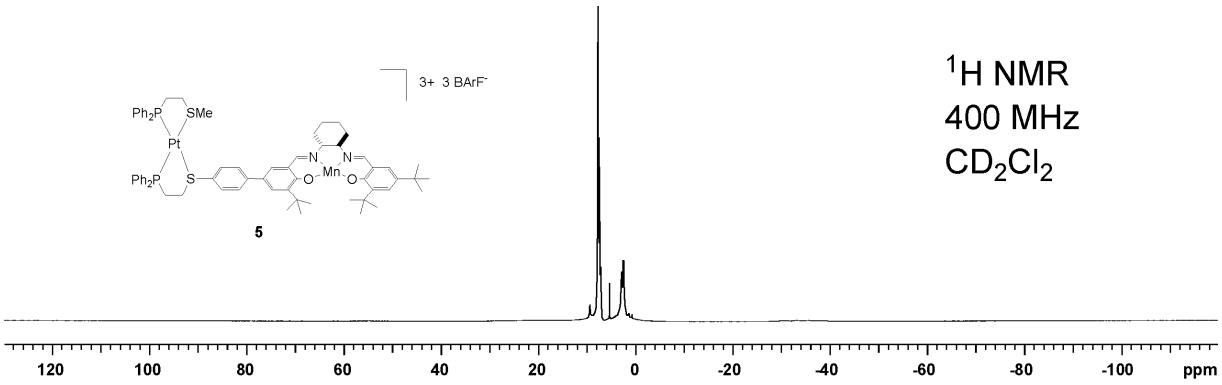
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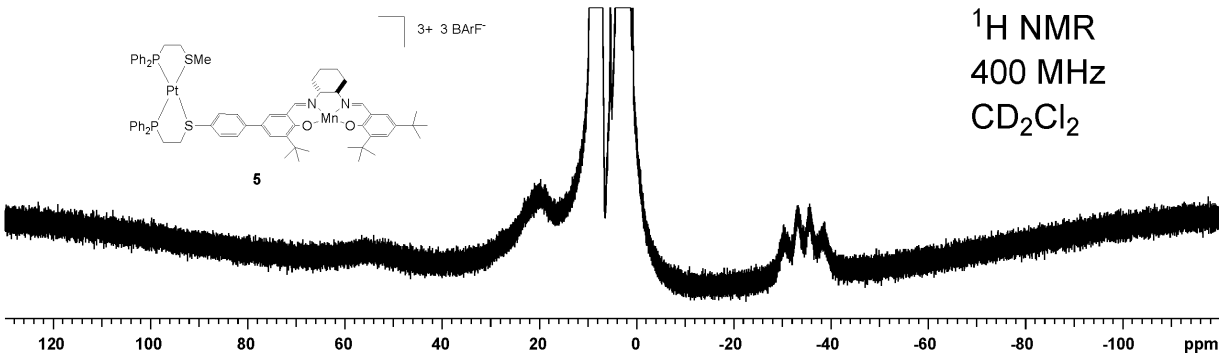
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5
1H NMR
400 MHz
CD2Cl2
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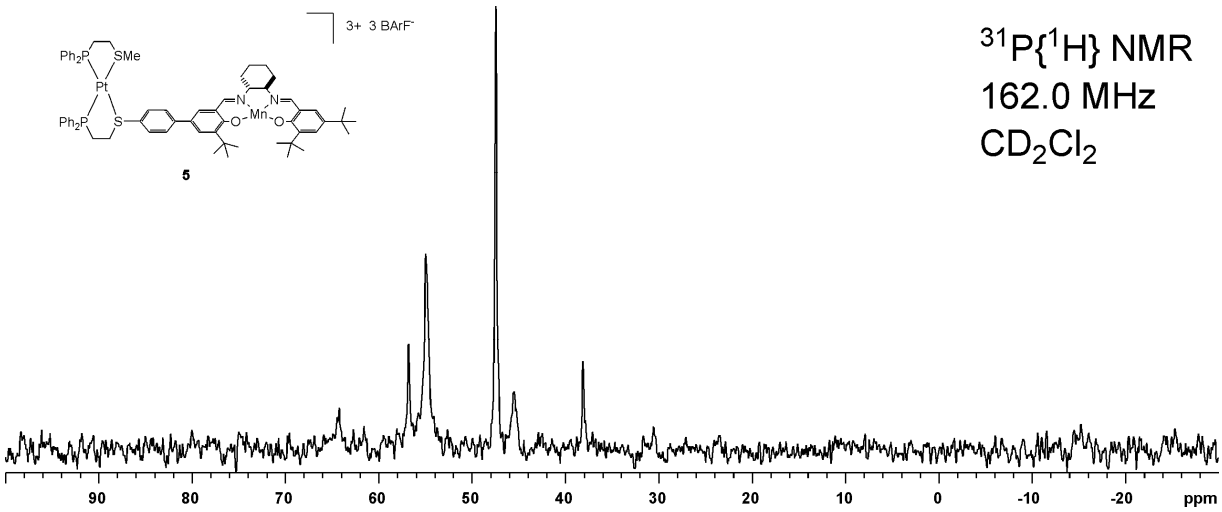
3+ 3 BArF-
Ph2P
SMe
Pt
Ph2P
S
N
Mn
N
O
O
5
31P{1H} NMR
162.0 MHz
CD2Cl2
90
80
70
60
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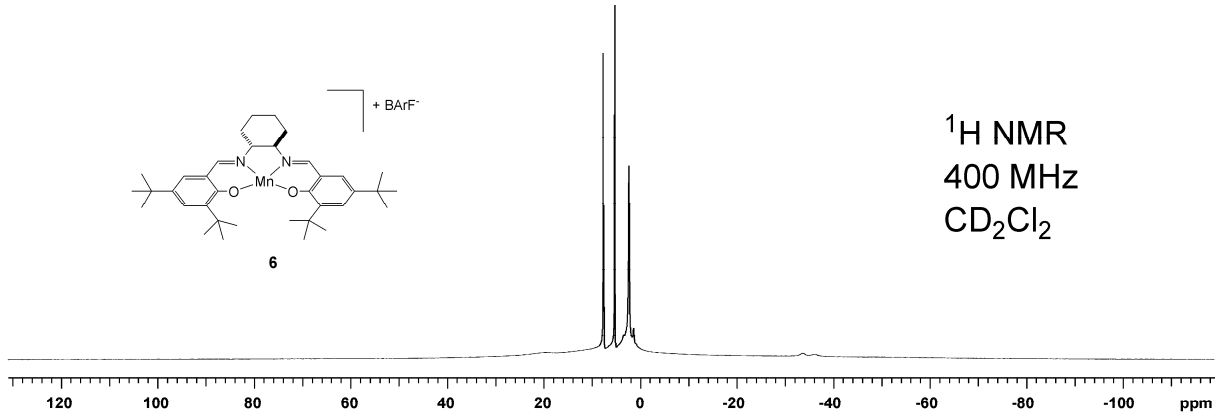
40
30
20
10
0
-10
-20
ppm


+ BArF-
N
Mn
N
O
O
6
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120
100
80
60
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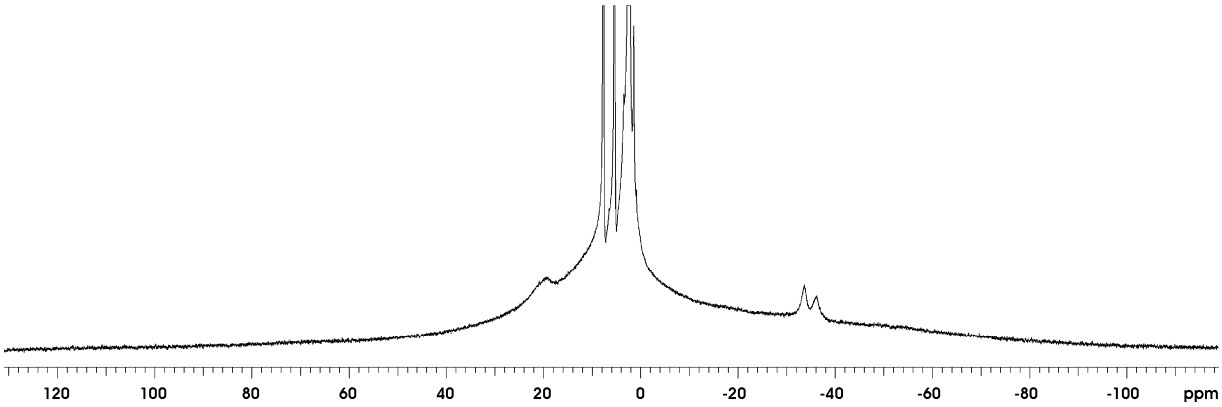
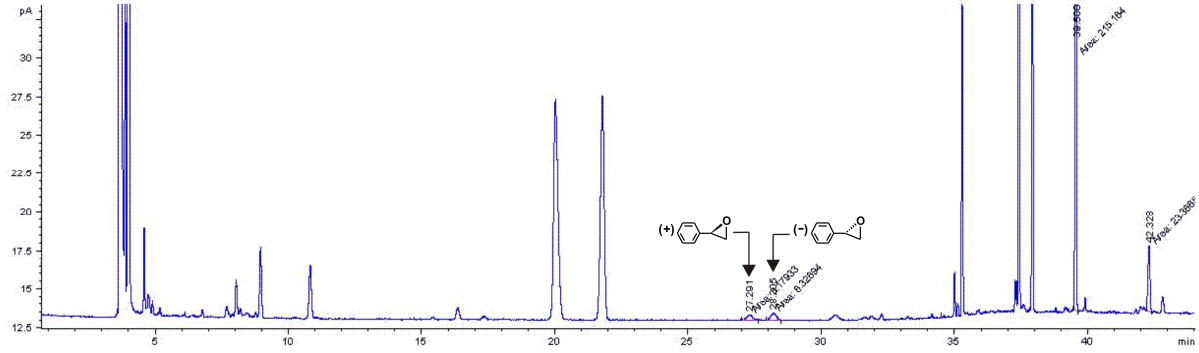
-40
-60
-80
-100
ppm


120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

F) Details of gas chromatographic analysis

A chiral J&W Scientific Cyclodex B column (30 m x 0.250 mm x 0.25 μm) was used with a H_2 flow of 1.1 mL/min. Temperature program: start at 75 °C, ramp to 97 °C, rate 20 °C/min, holdtime at 97 °C: 30 min, ramp to 200 °C, rate 20 °C/min. (+)-Styrene oxide (27.3 min, enantiopure commercial standard), (-)-styrene oxide (28.2 min, racemic commercial standard), *n*-hexadecane (39.6 min, commercial standard), 4-oxiranyl-benzoic acid methyl ester (42.3 min, see above for synthesis and characterization of standard). Correction factors: (±)-Styrene oxide/4-oxiranyl-benzoic acid methyl ester/*n*-hexadecane: 1: 1.18: 2.38.

Representative GC chromatogram



G) Computational details

The structure of the supramolecular complex between **4** and **7** was investigated using empirical parameters. The force field parameters related to Mn(III) are adapted from the literature. Manchanda et al. developed MM2 force field parameters to obtain an energy minimized structure of di-μ-oxo manganese dimers.[10] More recently, Beagley et al. reported the MM2 force field parameters for the simulation of salen-type manganese complexes.[11] They obtained the structures of manganese complexes with reasonable accuracy compared to X-ray crystal structures. We developed MM2 force field parameters for the Pt(II) complex based on the crystal structure.[3] The

parameters we developed are listed in Tables S1, S2 and S3. The torsion parameters related to platinum (00-Pt-00-00) are set to 0.0. The geometry optimized structure of the Pt(II) complex with our MM2 force field parameters is shown in Figure S1. The crystal structure is superimposed with the structure from the MM2 force field for comparison. The root mean square deviation (RMSD) between the crystal structure and the geometry-optimized structure for the MM2 force field is 1.08 Å. All simulations were performed with Macromodel 6.0.[12]

Table S1. Lennard-Jones parameters.[13]

atom	radius (Å)	ε (kcal/mol)
Pt	2.713	0.2

Table S2. Bond parameters.

bond	equilibrium distance (Å)	binding constant (mdyn/Å)
Pt-S	2.36	2.00
Pt-P	2.27	2.00

Table S3. Angle parameters.

angle	equilibrium angle (°)	angle constant (mdyn/rad^2)
S-Pt-S	90.85	1.00
P-Pt-P	97.65	1.00

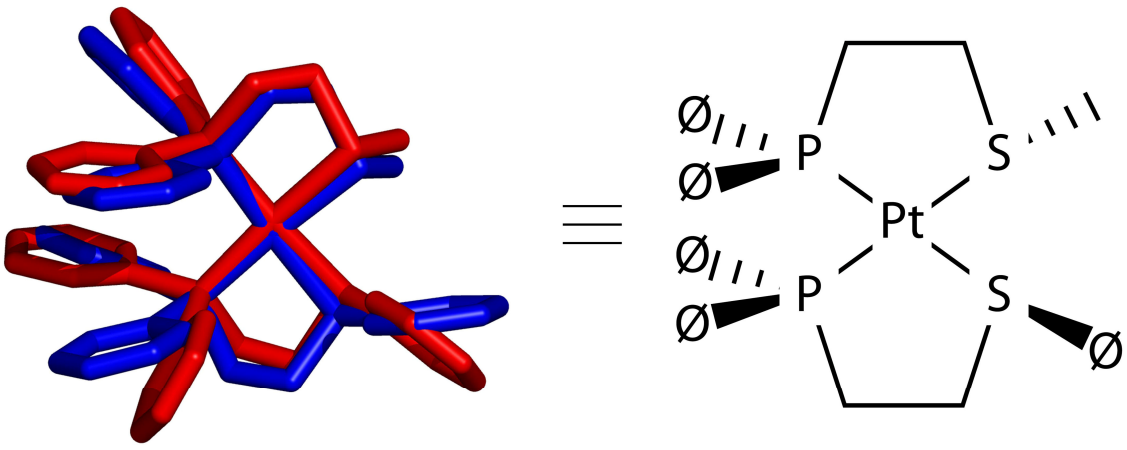


Figure S1. Superimposed structures of the crystal structure (red) and the geometry-optimized structure using the MM2 forcefield (blue). RMSD between the two structures is 1.08 Å.

As shown in Figure S1, the methyl and phenyl groups attached to the sulfur atom have an anti conformation in the crystal structure. The structure from the geometry-optimization with the MM2 force field also adapts an anti conformation. For comparison, we also obtained a geometry optimized-structure for the syn conformer. In our optimized structure, the anti conformer has a lower energy, and the energy difference between syn and anti conformers is 1.5 kcal/mol.

Conformation search

Before simulating the supramolecular complex between catalyst **4** and substrate **7**, we scrutinized the structure of **4** (Figure S2) with a Monte Carlo (MC) conformational search and molecular mechanics calculations. The number of structures examined in the conformational search was 1,000. Energy minimization with a conjugate gradient algorithm was performed on every sampled structure to a gradient norm of less than 0.001 $kJ \cdot mol^{-1} \cdot Å^{-1}$. The selected geometries of the global minimum structure are shown in Tables S4, S5, and S6. The experimental values are also listed for comparison.[3]

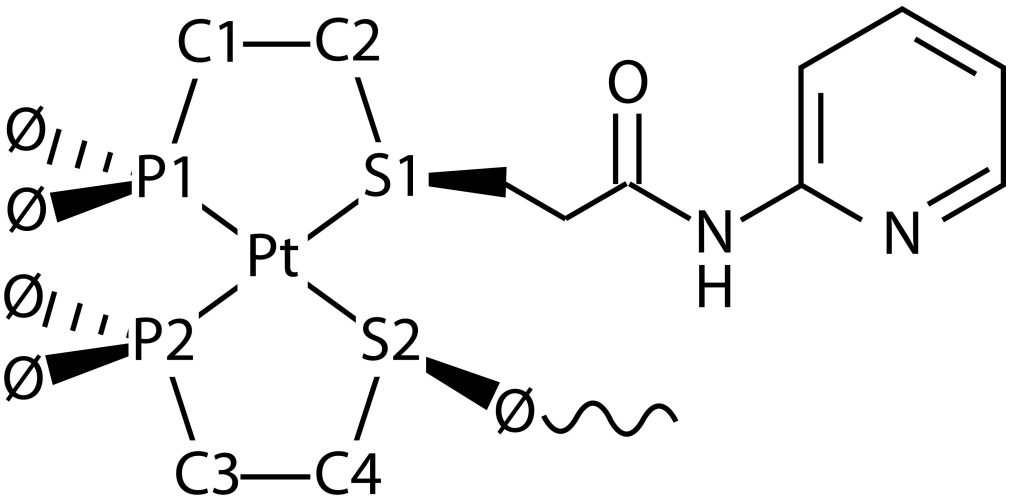


Figure S2. Name for selected atoms of **4** for comparison of structures.

Table S4. Comparison of selected bond lengths obtained from the MM2 simulation and the crystal structure.

bond	MM2 (Å)	crystal structure (Å)
Pt-P1	2.213	2.273
Pt-P2	2.217	2.267
Pt-S1	2.371	2.354
Pt-S2	2.355	2.360

Table S5. Comparison of selected bond angles obtained from the MM2 simulation and the crystal structure.

angle	MM2 (°)	crystal structure (°)
P1-Pt-P2	98.0	97.7
S1-Pt-S2	89.3	90.9
P1-Pt-S1	87.1	86.1
P2-Pt-S2	85.5	80.6

Table S6. Comparison of selected torsion angles obtained from the MM2 simulation and the crystal structure.

torsion	MM2 (°)	crystal structure (°)
P1-C1-C2-S1	-55.5	-58.7
P2-C3-C4-S2	-60.1	-51.7

A Monte Carlo conformational search and molecular mechanics calculation of the supramolecular complex between **4** and **7** was performed to obtain minimum energy structures in the gas phase. The number of structures considered in the conformational search was 1,000, and energy minimization with the conjugate gradient algorithm was then performed on every sampled structure to a gradient norm of less than 0.001 $kJ \cdot mol^{-1} \cdot Å^{-1}$. The global minimum structure found from the Monte Carlo simulation is shown in Figure S3. As expected, molecules **4** and **7** are connected through 2-point hydrogen bonding (Table S7). For the criteria of hydrogen bonding, the rules suggested by McDonald et al. are used.[14] The rules are (1) D-A < 3.9 Å. (2) H-A < 2.5 Å, (3) D-H-A > 90°, (4) AA-A-D > 90° and (5) AA-A-H > 90°, where D is donor, A is acceptor, H is hydrogen and AA is acceptor antecedent. In the analysis of the hydrogen bonding of ~ 50 protein crystal structures, they found that only 9.5% and 5.1% of buried main chain

nitrogen and oxygen atoms fail to hydrogen bond under their rules. In addition, the supramolecular complex between **4** and **7** is stabilized by a π–π interaction. The distance between the centers of the aryl groups is 3.7 Å. This is consistent with the distance between the centers of a benzene dimer (3.7 Å) in the stacked conformer. According to a study of the Kollman group, the stacked conformer of the benzene dimer stabilizes the complex by ~1.3 kcal/mol.[15]

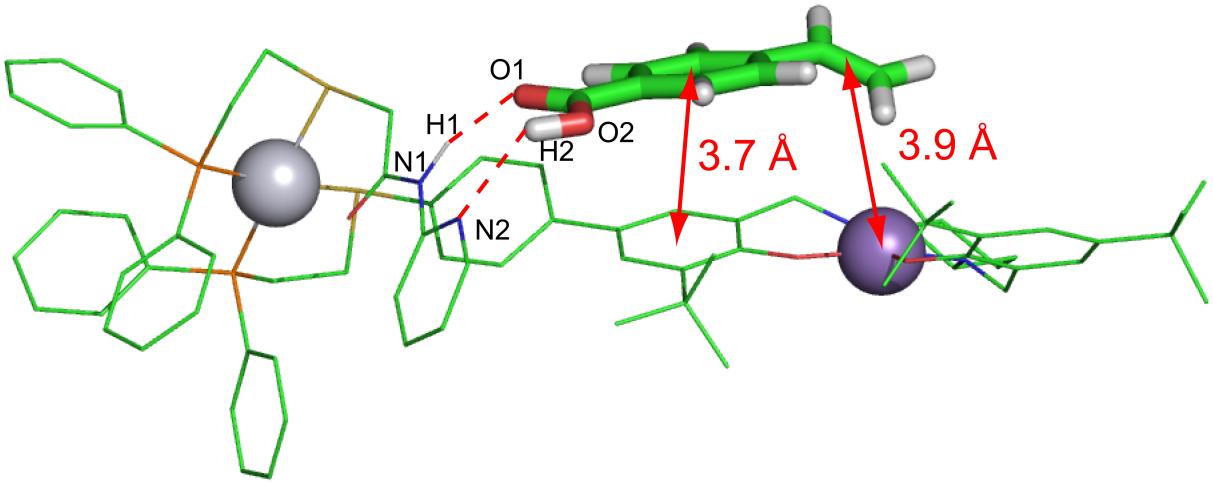


Figure S3. Global minimum structure obtained from a conformation search simulation. Molecule **4** is depicted in line format whereas molecule **7** is depicted in stick format. The Pt atom is shown as a gray sphere and the Mn atom is shown as a purple sphere. The hydrogen bonds between molecules **4** and **7** are drawn with dotted lines. The distance between the Mn atom and the center of the double bond of **7** is 3.85 Å. The phenyl group of the guest molecule **7** has a π–π interaction with the phenyl group of **4**, with a distance between the centers of the phenyl groups of 3.68 Å. The hydrogen atoms of **4** are omitted for clarity.

Table S7. Geometry of hydrogen bonds between molecules **4** and **7**.

	length (Å)		angle (°)
H1-O1	1.85 Å	N1-H1···O1	151.3
H2-N2	2.43 Å	N2···H2-O2	133.4

H) References

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