Supporting Information for

The First Chiral Diene-Based Metal–Organic Frameworks for Highly Enantioselective Carbon-Carbon Bond Formation Reactions

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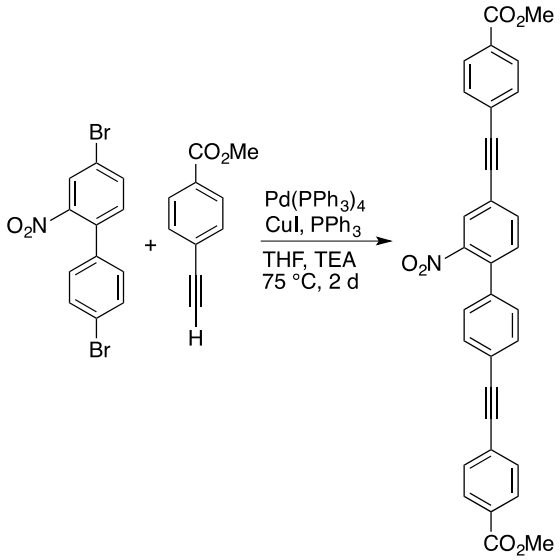
1. General experimental

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or in an inert atmosphere glovebox. ^{1}H NMR spectra were recorded on a Bruker NMR 500 DRX spectrometer at 500 MHz and referenced to the proton resonance resulting from incomplete deuteration of the $CDCl_3$ (δ 7.26) or DMSO-d_6 (δ 2.50). ^{13}C NMR spectra were recorded at 125 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of $CDCl_3$ (δ 77.00) or DMSO-d_6 (δ 39.50). The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad, app: apparent. Mass spectra were obtained with an Agilent 1100 LC-MSD Mass Spectrometer and Agilent 6224 Accurate-Mass TOF-MS. Thermogravimetric analysis (TGA) was performed in air using a Shimadzu TGA-50 equipped with a platinum pan and heated at a rate of 3 °C per minute. Single-crystal X-ray diffraction was performed on a Bruker APEX II CCD-based detector at ChemMatCARS (Sector 15), Advanced Photon Source (APS), Argonne National Laboratory. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Venture, dual microsource (Cu and Mo) diffractometer with a CMOS detector. Cu Kα radiation was used. The PXRD patterns were processed with the APEX 2 package using the PILOT plug-in. ICP-MS data were obtained with an Agilent 7700x ICP-MS and analyzed using ICP-MS MassHunter version B01.03. Samples were diluted in a 2% HNO_3 matrix and analyzed with a 159Tb internal standard against a six-point standard curve over the range from 0.1 ppb to 1000 ppb. The correlation coefficient was > 0.9997 for all analyses of interest. Data collection was performed in Spectrum Mode with five replicates per sample and 100 sweeps per replicate. Nitrogen adsorption experiments were performed on a Quantachrome-1C surface area analyzer at liquid nitrogen temperature. Enantiomeric excess (ee) values were determined by chiral high performance liquid chromatography (HPLC) using a Shimadzu SCL-10A HPLC equipped with a SPD-M10A photodiode array detector and by chiral gas chromatography (GC) using a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector (FID). UV-Vis spectra were obtained using a Shimadzu UV-2401 PC UV-Vis spectrophotometer. 1,4-Dioxane was distilled over Na under N_2. Toluene was purified by passing through a neutral alumina column under N_2. 2-Cyclohexen-1-one, 2-cyclohepten-1-one, 2-cyclopenten-1-one, 4-hexen-3-one were purchased and distilled before use. $[RhCl(C_2H_4)]_2$, $Rh(acac)(C_2H_4)_2$, phenylboronic acid, 4-fluorophenylboronic acid, and 4-methoxyphenylboronic acid were used as received. 4,4'-

Dibromo-2-nitrobiphenyl [CAS: 439797-69-0], methyl 4-ethynylbenzoate [CAS: 3034-86-4], *N*-(4-chlorophenyl)methylidene-4-methylbenzenesulfonamide [CAS: 3157-65-1], *N*-phenylmethylidene-4-methylbenzenesulfonamide [CAS: 51608-60-7], *N*-(4-methoxyphenyl)methylidene-4-methylbenzenesulfonamide [CAS: 135822-88-7], (1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid [CAS: 1252606-18-0] were prepared according to or analogous to the reported procedures.[1-5]

2. Procedures for ligand synthesis

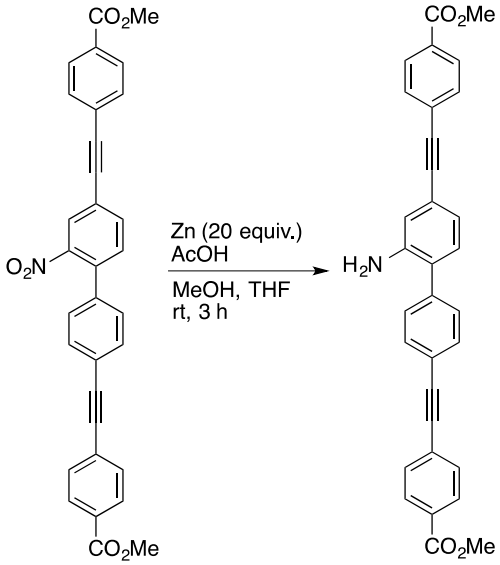
Dimethyl-4-4'-((2-nitro-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-dilyl))dibenzoate



A mixture of tetrakis(triphenylphosphine)palladium(0) (288.9 mg, 0.2500 mmol), triphenylphosphine (78.7 mg, 0.300 mmol), and copper(I) iodide (95.2 mg, 0.500 mmol) was dissolved in THF (6.3 mL) and triethylamine (TEA, 6.3 mL). To the mixture were added 4,4'-dibromo-2-nitrobiphenyl (893 mg, 2.50 mmol) and methyl 4-ethynylbenzoate (1.20 g, 7.49 mmol), and the resulting mixture was stirred under nitrogen at 75 °C for 2 d. The solution was then cooled to room temperature, and the volatiles were removed in vacuo. The residue was extracted with $CHCl_3$ and water, and the combined organic extracts were dried over $MgSO_4$ and filtered. After evaporation of the solvent, the residue was subjected to flash column chromatography on silica gel ($CHCl_3$ as eluent) to afford dimethyl 4,4'-((2-amino-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))dibenzoate (816.5 mg, 1.584 mmol, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.94 (s, 3H), 3.95 (s, 3H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.0

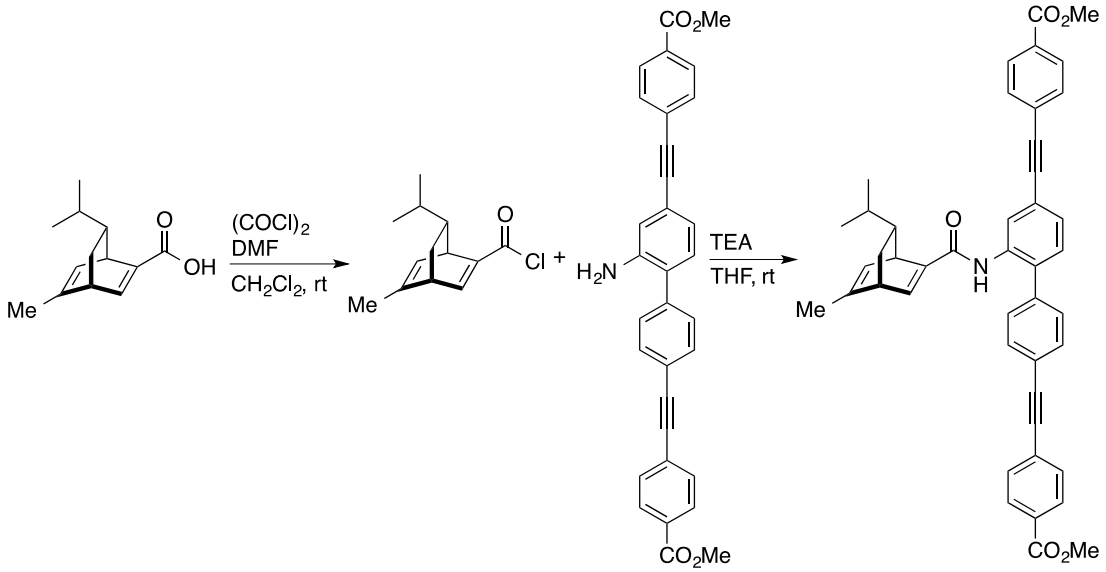
Hz, 1H), 7.58–7.65 (m, 6H), 7.77 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.04 (app d, *J* = 8.0 Hz, 3H), 8.06 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.25, 52.33, 89.26, 89.98, 91.55, 91.62, 123.18, 123.65, 126.74, 127.27, 127.68, 127.96, 129.55, 129.64, 129.69, 130.29, 131.57, 131.71, 131.92, 132.10, 135.09, 135.45, 136.97, 148.97, 166.35, 166.50. ESI-MS: cald for $C_{32}H_{22}NO_6$ $[M+H]^+$ 516.1, found 516.0.

Dimethyl 4,4'-((2-amino-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))dibenzoate



A mixture of dimethyl 4,4'-((2-nitro-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))dibenzoate (1.289 g, 2.500 mmol) and zinc powder (3.269 g, 50.00 mmol) was dissolved in acetic acid (8.3 mL), MeOH (50 mL) and THF (75 mL) under nitrogen. After stirring at rt for 3 h, saturated sodium bicarbonate was added at 0 °C. The solution was extracted with $CHCl_3$, and then the combined organic extracts were dried over Na_2SO_4 and filtered. After evaporation of the solvent, the residue was subjected to flash column chromatography (silica gel, hexane/$CHCl_3$/EtOAc = 10/10/1) to give dimethyl 4,4'-((2-amino-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))dibenzoate (658.4 mg, 1.356 mmol, 54% yield). ^{1}H NMR ($CDCl_3$): δ 3.93 (s, 3H), 3.94 (s, 3H), 6.96 (d, *J* = 1.3 Hz, 1H), 7.03 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.56–7.66 (m, 6H), 8.03 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 52.22, 52.25, 88.52, 89.30, 92.03, 92.44, 118.51, 121.86, 122.30, 122.92, 127.32, 127.86, 128.05, 128.97, 129.51, 129.54, 130.41, 131.51, 131.53, 132.24, 139.27, 143.44, 166.53, 166.57. HRMS(ESI): calcd for $C_{32}H_{24}NO_4$ $[M+H]^+$ 486.1705, found 486.1693.

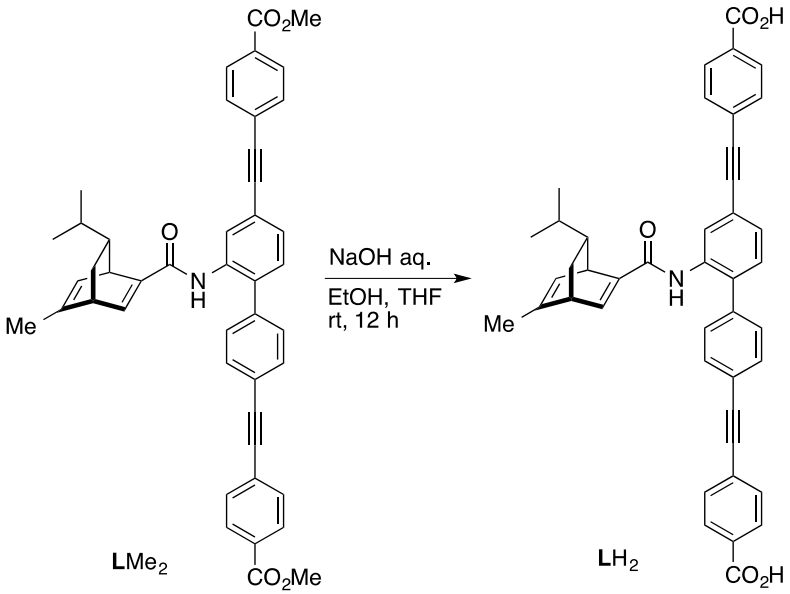
Dimethyl 4,4'-((2-((1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamido)-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))dibenzoate (LMe$_2$)



To a solution of (1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid (84.3 mg, 0.409 mmol) in CH_2Cl_2 was added oxalyl chloride (42 μL, 0.49 mmol) and DMF (3 drops) at 0 °C. The mixture was stirred at room temperature for 3 h, and then the residue was added to a mixture of dimethyl 4,4'-((2-amino-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))dibenzoate (198.4 mg, 0.4086 mmol), TEA (85 μL, 0.61 mmol), and THF (41 mL). After stirring at room temperature for 24 h, saturated NH_4Cl was slowly added at 0 °C. The mixture was extracted with Et_2O, and the combined organic extracts were dried over $MgSO_4$ and filtered. After evaporation of the solvent, the residue was subjected to flash column chromatography (silica gel, hexanes/$CHCl_3$/EtOAc = 20/20/1) to give **L**Me$_2$ (157.1 mg, 0.2332 mmol, 57% yield). ^{1}H NMR ($CDCl_3$): δ 0.80 (d, *J* = 6.5 Hz, 3H), 0.92–0.98 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 1.01–1.12 (m, 1H), 1.12–1.20 (m, 1H), 1.50–1.58 (m, 1H), 1.80 (d, *J* = 1.0 Hz, 3H), 3.30–3.37 (m, 1H), 3.93 (s, 3H), 3.94 (s, 3H), 3.96–4.03 (m, 1H), 5.78 (d, *J* = 6.0 Hz, 1H), 6.65 (dd, *J* = 6.5, 1.5 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.54 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 8.73 (d, *J* = 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 18.85, 21.19, 21.74, 31.61, 33.67, 39.76, 43.74, 47.75, 52.15, 52.22, 89.13, 89.87, 91.50, 92.11, 122.79, 123.23, 123.82, 123.98, 127.02, 127.49, 127.87, 129.30, 129.41,

129.46, 129.54, 129.73, 129.86, 131.15, 131.50, 132.46, 135.03, 137.87, 139.53, 143.70, 144.97, 163.27, 166.40, 166.51. HRMS (ESI): calcd for $C_{45}H_{40}NO_5$ $[M+H]^+$ 674.2906, found 674.2892.

4,4'-((2-((1*R*,4*R*,7*R*)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamido)-[1,1'-biphenyl]-4,4'-diyl)bis(ethyne-2,1-diyl))dibenzoic acid (LH_2)



LMe_2 (223.8 mg, 0.3321 mmol) was dissolved in a mixture of THF (17 mL), EtOH (17 mL), and 1 M NaOH (aq) (17 mL). After stirring at room temperature for 12 h, 1 M HCl (aq) was slowly added at 0 °C. The filtrate was extracted with EtOAc, and the combined organic extracts were concentrated in vacuo. The residue was washed with water, hexanes, MeOH, and EtOAc to give compound **L**H_2 (165.7 mg, 0.2566 mmol, 77% yield). ^{1}H NMR ($CDCl_3$): δ 0.79 (d, *J* = 5.5 Hz, 3H), 0.84–0.93 (m, 1H), 0.89 (d, *J* = 5.5 Hz, 3H), 0.95–1.04 (m, 1H), 1.45–1.55 (m, 1H), 1.78 (s, 3H), 3.91 (d, *J* = 5.5 Hz, 1H), 5.76 (d, *J* = 6.0 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.54 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.712 (d, *J* = 8.0 Hz, 2H), 7.714 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 9.26 (s, 1H), 13.17 (br, 2H). ^{13}C NMR ($CDCl_3$): δ 18.78, 21.18, 21.70, 30.41, 31.33, 33.37, 42.98, 47.37, 89.25, 89.31, 91.31, 91.88, 120.84, 121.46, 123.70, 126.44, 126.55, 128.98, 129.58, 129.59, 130.31, 130.60, 130.67, 131.51, 131.54, 131.61, 135.50, 137.15, 139.15, 139.69, 143.46, 143.68, 163.89, 166.68. ESI-MS: calcd for $C_{43}H_{35}NO_5$ $[M]^-$ 645.3, found 644.9.

3. Synthesis and characterization of $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(L)_6$•143DMF•109$H_2O$ (E_2-MOF)

LH_2 (8.3 mg, 13 µmol), $ZrCl_4$ (3.0 mg, 13 µmol), DMF (1.8 mL), trifluoroacetic acid (10 µL) were charged in a vial. The vial was then heated in a 70 °C oven for 5 days, resulting in colorless crystals (15.4 mg, 5.43 µmol, 42% yield). E_2-MOF has 73% solvent weight based on TGA analysis (Figure S2). Solvent content determined by ^{1}H NMR/TGA: DMF 61.4%, H_2O 11.6%.

Analysis of digested E_2-MOF by ^{1}H NMR: 15.4 mg of E_2-MOF was added to 0.50 mL of DMSO-d_6. To this solution was added 0.50 mL of saturated K_3PO_4 in D_2O. After shaking for 15 minutes, MOF was totally dissolved and the organic phase was analyzed by ^{1}H NMR.

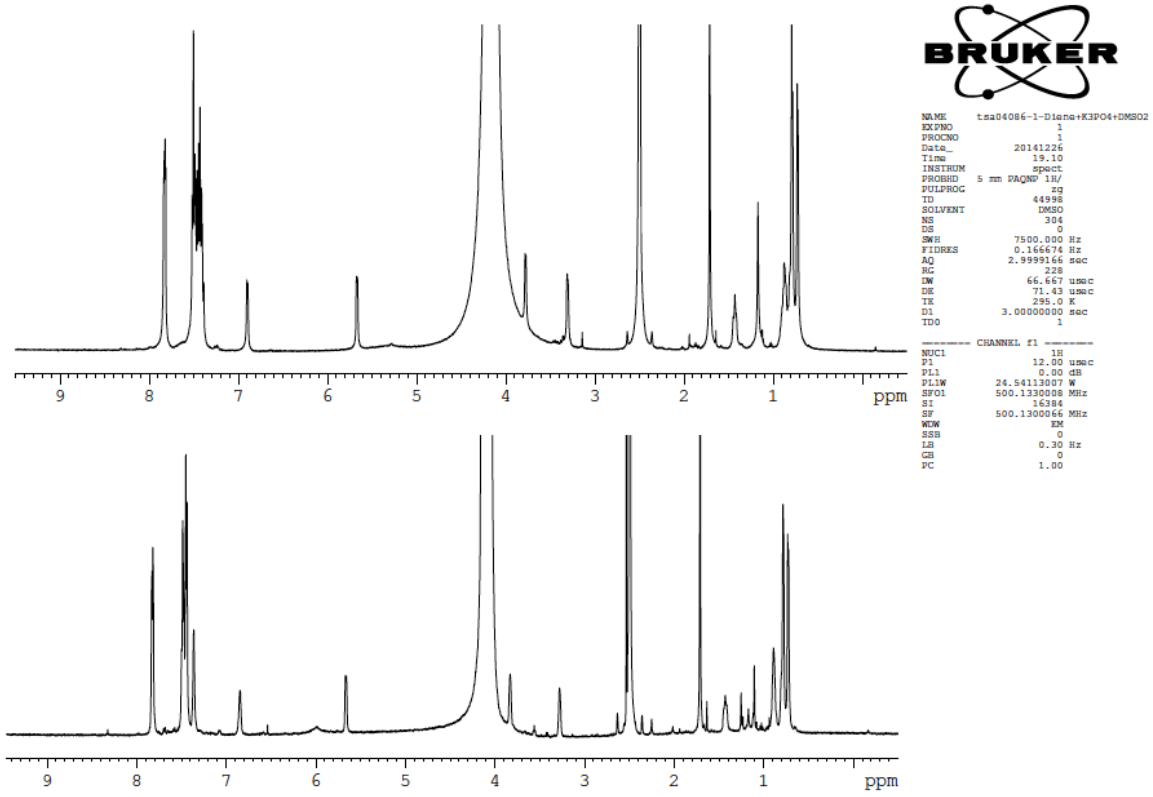


Fig. S1 ^{1}H NMR spectrum of **L**H_2 in K_3PO_4/D_2O/DMSO-d_6 (top). ^{1}H NMR spectrum of E_2-MOF digested in K_3PO_4/D_2O/DMSO-d_6 (bottom).

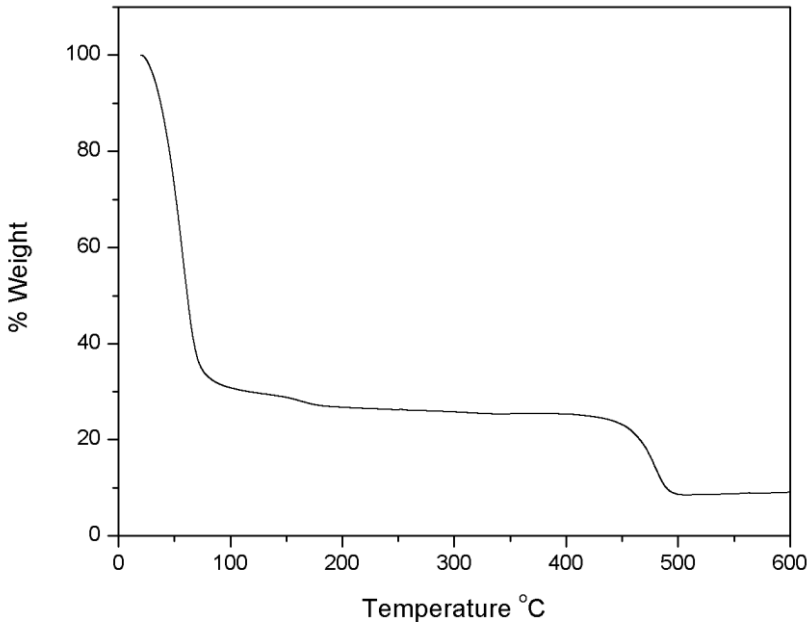


Fig. S2 TGA curve of freshly prepared E_2-MOF. A solvent weight loss of 73% was observed in the room temperature to 200 °C range.

Quantitative determination of the content of solvent molecules:

Freshly prepared E_2-MOF (6.19 mg, 2.18 μmol) was briefly dried on a filter paper and loaded into a vial. After addition of 0.75 mL of CD_3OD and 8.6 μL of mesitylene as an internal standard, the crystals were soaked overnight to ensure thorough solvent exchange from the pores. The content of solvent molecules in E_2-MOF was measured by the supernatant of ^1H NMR. The exact amount of DMF was calculated against the internal standard. Following determination of the total amount of solvent by TGA, the amount of water was calculated.

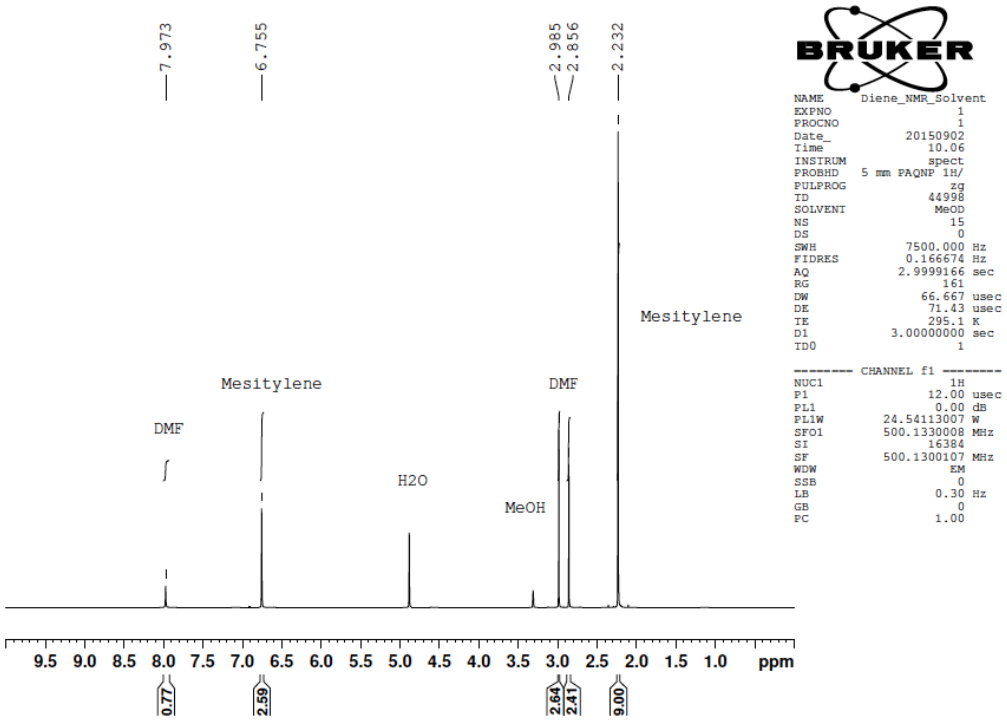


Fig. S3 Quantitative ^{1}H NMR analysis of the solvent contents in E_2-MOF (d_4-methanol).

N_2 adsorption isotherms of E_2-MOF

E_2-MOF was activated using the freeze-drying protocol. After decanting the mother liquid, freshly prepared crystals of E_2-MOF were washed with DMF, CH_3CN, and then CH_2Cl_2 several times. The resulting crystals were washed with benzene several times and then soaked in benzene overnight before loading into a BET sample cell. About 1 mL of benzene was left in the sample cell, and the sample cell placed in an ice/NaCl bath and evacuated under a dynamic vacuum for 24 h. The ice/NaCl bath was removed and the sample was kept under vacuum at room temperature for another 5 h, and then heated under vacuum at 60 °C for 24 h. The resulting freeze-dried E_2-MOF was used to perform gas uptake measurements.

The observed negligible surface areas was presumably due to framework distortion upon solvent removal. The crystallinity of E_2-MOF was lost after removal of solvent at rt and 60 °C (Fig. S5).

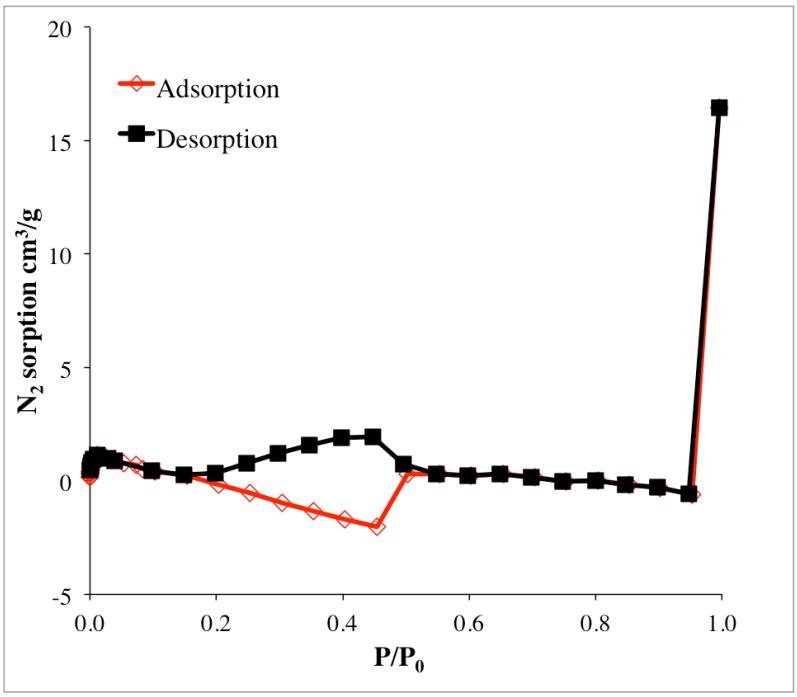


Fig. S4 N_2 sorption isotherms for E_2-MOF at 77 K.

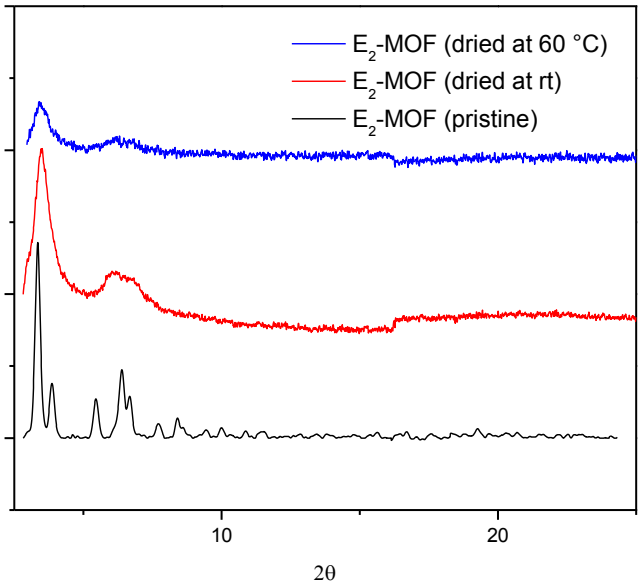


Fig. S5. PXRD spectrum of dried E_2-MOF at rt and 60 °C

Stability of E_2-MOF in different solvents

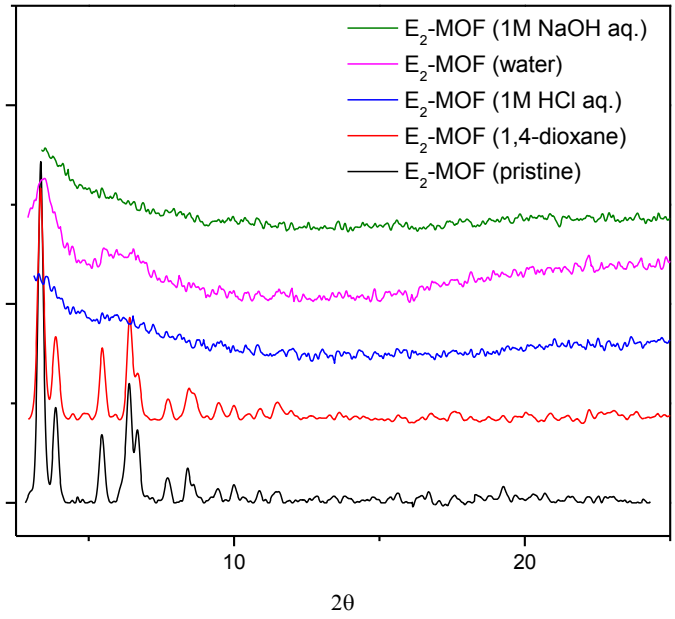


Fig. S6. PXRD spectrum of E_2-MOF soaked in 1,4-dioxane, 1M HCl aq., water, and 1M NaOH aq. for 40 h.

General procedure for dye absorption measurements of E_2-MOF, E_2-MOF•RhCl, and E_2-MOF•Rh(acac)

Freshly prepared E_2-MOF (9.15 mg, 3.23 μmol) was briefly dried on a filter paper, and then soaked in a methanol solution of Brilliant Blue R-250 (24 mM, 0.71 mL) for 12 h. The resulting dark blue crystals were washed with water thoroughly until the washing become colorless. After addition of DMSO (0.5 mL) to the washed sample, the solid was digested by saturated K_3PO_4 in water (0.4 mL). The resultant clear solution of DMSO was diluted to 20 mL and adjusted to a pH of 1.2 by HCl. Absorption experiments were performed on Shimadzu UV-2401 PC UV-Vis spectrophotometer. The concentration of BBR-250 was determined by comparing the UV-Vis absorption with a standard curve. The dye absorption measurements of E_2-MOF, E_2-MOF•Rh(acac), and E_2-MOF•RhCl indicate that the uptake of BBR-250 per unit cell is 5.32 (112 wt%), 4.47 (107 wt%), 2.53 (98 wt%), respectively.

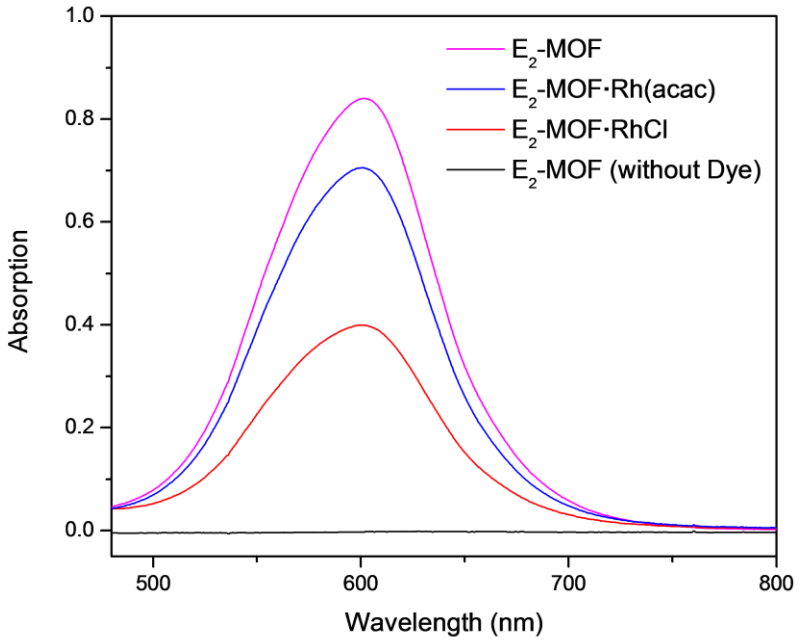


Fig. S7 UV-Vis measurement of released BBR-250 from E_2-MOF, E_2-MOF•Rh(acac), and E_2-MOF•RhCl (normalized).

4. X-ray structure determination

Single crystal X-ray diffraction of E_2-MOF was collected with a Bruker APEX II CCD-based detector at ChemMatCARS (Sector 15), Advanced Photon Source (APS), Argonne National Laboratory. The crystals were mounted inside a capillary tube (0.2 mm ID) with a small amount of mother liquor to prevent solvent loss from the crystal. Data were collected at 296 K. The frames were integrated with the Bruker SAINT© built-in APEX II software package using a narrow-frame integration algorithm which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. Structures were solved by direct methods and refined to convergence by the least squares method on F^2 using the SHELXTL software suite.[6]

Due to the disorder caused by random orientations, the diene moiety cannot be located in the electron density map and are thus modeled in the single crystal structure. The SQUEEZE subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered guest molecules.[7] The resulting new HKL4 files were used to further refine the structures. Due to the relatively weak diffraction and low resolution, which is not uncommon for

this kind of framework with very large solvent accessible void space, restraints (SIMU and DELU) on displacement parameters are applied. All non-hydrogen atoms are refined anisotropically.

Table S1 Crystal data and structure refinements of E_2-MOF.

Empirical formula	$Zr_6(O)_4(OH)_4L_6$	Density (calcd. g/cm^3)	0.225
Formula weight	4541.81	Absorption coeff. (mm^{-1})	0.171
Temperature (K)	296(2)	F(000)	6496
Wavelength (Å)	0.51800	Crystal size (mm)	0.08 × 0.08 × 0.08
Crystal system	Cubic	Crystal color & shape	Colorless block
Space group	$Fm\bar{3}m$	θ range data collection	0.65 – 15.75
Unit cell dimensions	a = 45.887(8) b = 45.887(8) c = 45.887(8) α = 90 β = 90 γ = 90	Limiting indices	-47<=h<=48, -42<=k<=48, -33<=l<=47
		Reflection collected	159296
		Independent reflections	2870
		R(int)	0.1444
		Data/restraints/parameters	2870/85/71
		Goodness-of-fit on F^2	1.119
Volume (Å^3)	96622(28)	Final R indices [I>2σ(I)]	R1 = 0.0523, wR2 = 0.1431
Z	4	R indices (all data)	R1 = 0.0559, wR2 = 0.1472

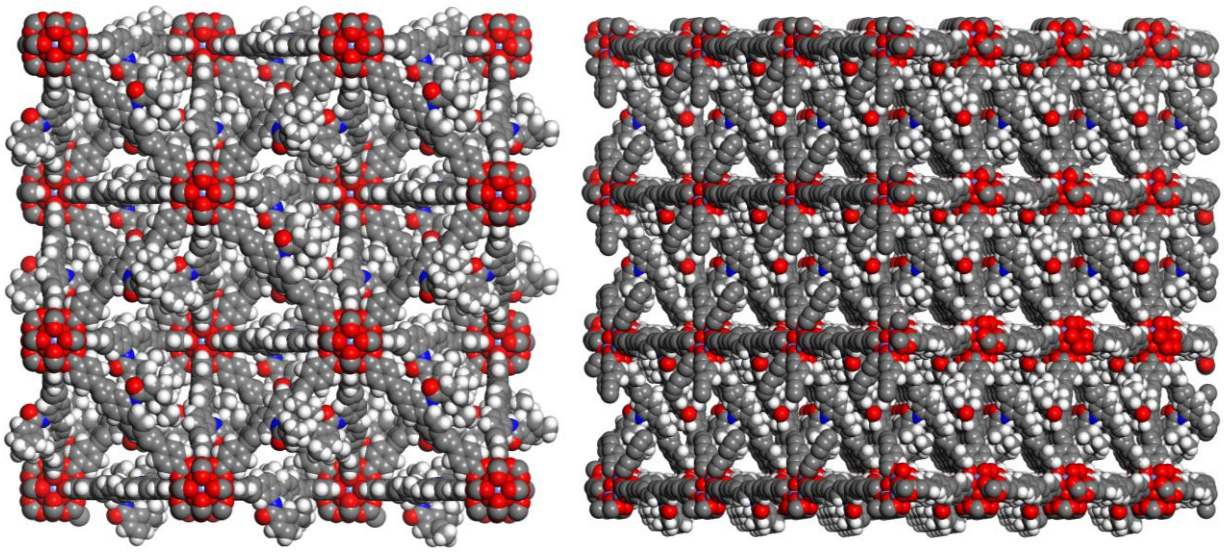


Fig. S8 Space filling model of E_2-MOF along the (100) direction (left) and the (111) direction (right).

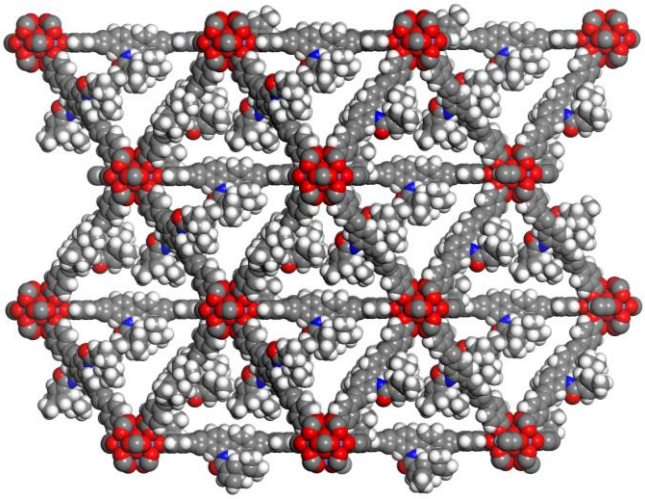


Fig. S9 Space filling model of E_2-MOF along the (110) direction.

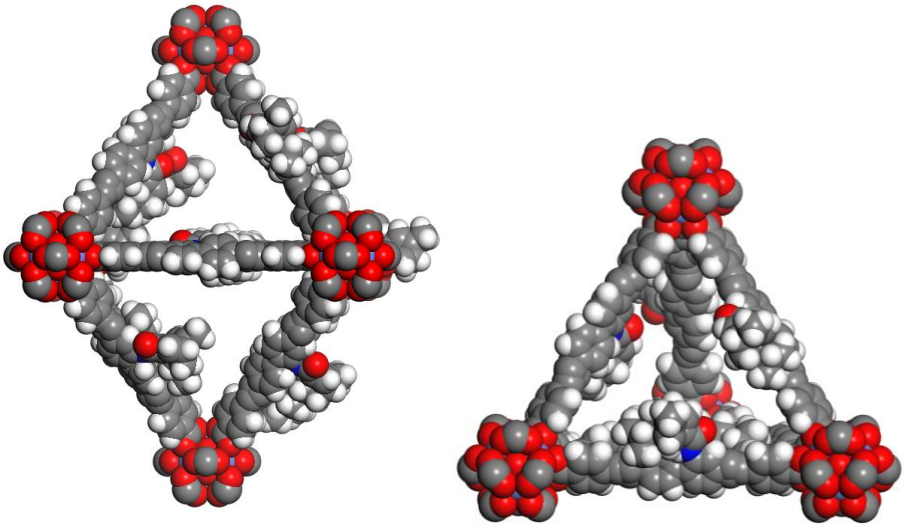


Fig. S10 Octahedral cage (left) and tetrahedral cage (right) of E_2-MOF.

5. X-ray absorption spectroscopy

X-ray absorption data for $[RhCl(nbd)]_2$, RhCl-**L**Me_2, and E_2-MOF•RhCl were collected at Beamline 9-BM-B at the Advanced Photon Source (APS) at Argonne National Laboratory. Spectra were collected at the Rh K-edge (23220 eV) in transmission mode. The X-ray beam was monochromatized by a Si(111) monochromater and detuned by 25% to minimize harmonics. In an inert environment, 11 – 37 mg dry Rh samples (sufficient to achieve 1-2 absorption edges) were ground thoroughly with a mortar and pestle, then blended with polyethylene glycol (PEG)

and pressed into pellets for XAFS analysis. A Rh foil was used as the reference for energy calibration and was measured simultaneously while collecting data for experimental samples. The incident beam intensity (I_0) and transmitted beam intensity (I_t) were measured by ionization chambers with I_0 filled with 40% N_2, 60% He, and I_t filled with air. The beam was masked to 1 mm × 1mm. Data were collected in three regions, with all energies listed relative to the environmental Rh K-edge (23220 eV): a pre-edge region, -150 to -20 eV (5 eV step size, 1.0 s dwell time); XANES region, -10 to 25 eV (0.5 eV step size, 1.0 s dwell time); and EXAFS region, 3.62 $Å^{-1}$ to 13.93 $Å^{-1}$ (0.05 $Å^{-1}$ step size, 1.0 s dwell time). Three spectra were collected at room temperature

X-ray absorption data for Rh(acac)-**L**Me_2, and E_2-MOF•Rh(acac) were collected at Beamline 20-BM-B at the Advanced Photon Source (APS) at Argonne National Laboratory. Spectra were collected at the Rh K-edge (23220 eV) in transmission mode. The X-ray beam was monochromatized by a Si(111) monochromater and detuned by 15% to minimize harmonics. In an inert environment, 11 – 37 mg dry Rh samples (sufficient to achieve 1-2 absorption edges) were ground thoroughly with a mortar and pestle, then blended with polyethylene glycol (PEG) and pressed into pellets for XAFS analysis. A Rh foil was used as the reference for energy calibration and was measured simultaneously while collecting data for experimental samples. The incident beam intensity (I_0) and transmitted beam intensity (I_t) were measured by ionization chambers with filled with 100% Ar. The beam was masked to 1 mm × 1mm. Data were collected in three regions, with all energies listed relative to the environmental Rh K-edge (23220 eV): a pre-edge region, -200 to -30 eV (10 eV step size, 1.0 s dwell time); XANES region, -30 to 30 eV (1.0 eV step size, 1.0 s dwell time); and EXAFS region, 2.80 $Å^{-1}$ to 15.97 $Å^{-1}$ (0.05 $Å^{-1}$ step size, 1.0 s dwell time). Two spectra were collected at room temperature..

Data were processed and analyzed using the Athena and Artemis programs of the IFEFFIT package[8] based on FEFF 6.[9] Prior to averaging, data were aligned to the first and largest peak in the smoothed first derivative of the absorption spectrum for the reference foil, background removed, and spectra processed to obtain a normalized unit edge step. Data were processed and fit with k^2-weighting in R-space. All single-scattering and multiple-scattering paths with relative intensity greater than 10% of the first single scattering path and half-path length (R_{eff}) less than 5Å were used for fitting. $[RhCl(nbd)]_2$ was fit with ΔR = 1.25 - 5 Å, and Δk = 2.0 – 12, yielding 23 independent points. E_2-MOF•RhCl was fit with ΔR = 1 – 5.4 Å, and

$\Delta k = 2.0 – 11.2$, yielding 25 independent points. Rh(acac)-**L**Me_2 was fit with $\Delta R = 1$ - 4 Å, and $\Delta k = 2.0 – 12.75$, yielding 20 independent points. E_2-MOF•Rh(acac) was fit with $\Delta R = 1 – 4$ Å, and $\Delta k = 2.0 – 12.75$, yielding 20 independent points. For all fits, the number of parameters used was less than 2/3 the total number of independent points, as determined by the Nyquist Equation. Fits were performed in R-space. Refinement was performed by optimizing an amplitude factor S_0^2 and energy shift parameter E_0 which are common to all paths, in addition to parameters for bond length (ΔR) and mean squared relative displacement of the scattering atoms (σ^2). $[RhCl(nbd)]_2$ was fit with the corresponding crystal structure ZOWVUC obtained from the Cambridge Crystallographic Database.

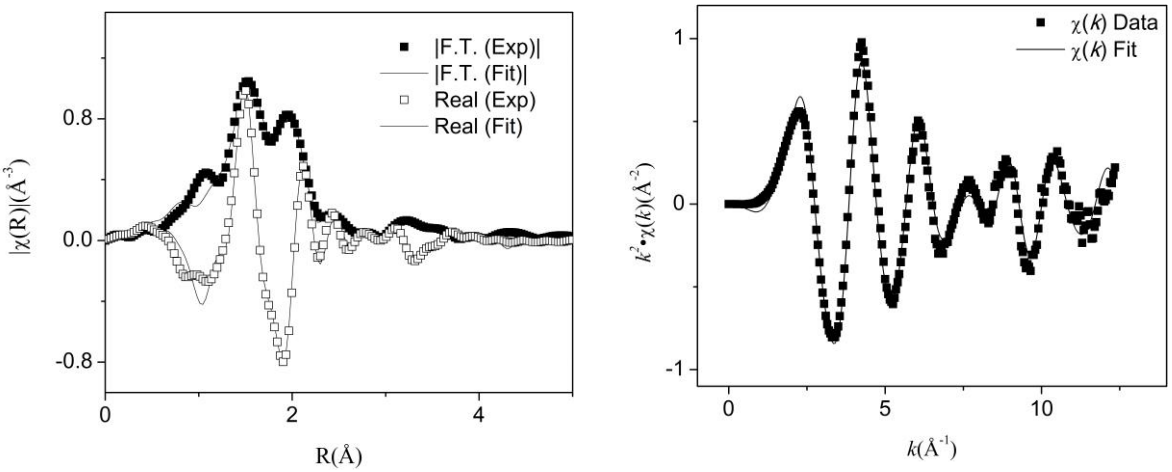


Fig. S11 EXAFS data (squares) and best fits (lines) for $[RhCl(nbd)]_2$ in *R*-space (left) and *k*-space (right). Data are displayed in *R*-space containing both magnitude of Fourier Transform and real components. A final *R*-factor of 0.01 was obtained for $[RhCl(nbd)]_2$ with a reduced χ^2 of 64.32.

Table S2 EXAFS fitting parameters and calculated error for fit of $[RhCl(nbd)]_2$

Parameter	Value	Error
S_0^2	1.0	0.1
E_0	-2.8	0.9
ΔR C_1	0.01	0.01
ΔR C_2	0.014	0.007
ΔR C_3	0.00	-0.04
ΔR C_4	0.3	0.1
ΔR Rh	-0.03	0.04
ΔR C-Cl	0.0	0.1
σ^2 C_1	0.003	0.001
σ^2 C_2	0.004	0.001

σ^2 C_3	0.002	0.0004
σ^2 C_4	0.002	0.0004
σ^2 Rh	0.008	0.003
σ^2 C_{ms}	0.03	0.3
σ^2 C_{long}	0.02	0.01

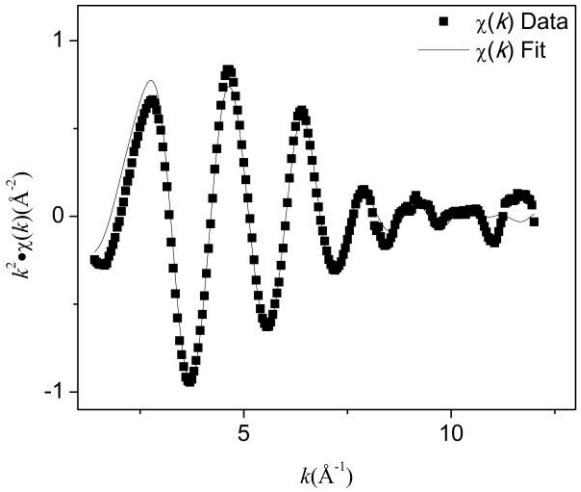


Fig. S12 EXAFS data (squares) and best fits (lines) for E_2-MOF metalated with RhCl(THF) in *k*-space. A final *R*-factor of 0.01 and reduced χ^2 of 342.03 were obtained for the fit.

Table S3 EXAFS fitting parameters and calculated error for fit of E_2-MOF metalated with RhCl(THF)

Parameter	**Value**	**Error**
S_0^2	1.05	0.00
E_0	7	2
ΔR C_1	-0.04	0.03
ΔR O	0.02	0.08
ΔR Cl	0.02	0.02
ΔR C_2	-0.07	0.02
ΔR C_3	0.01	0.02
ΔR C_{long}	0.05	0.07
σ^2 C_1	0.007	0.005
σ^2 O	0.002	0.0009
σ^2 Cl	0.004	0.002
σ^2 C_2	0.002	0.0009
σ^2 Rh	0.002	0.0009
σ^2 C_{long}	0.01	0.01

RhCl-**L**Me_2 was fitted using a combination of monomer and dimer models, the fractional contribution of each being dictated by a variable multiplied directly by the S_0^2 parameter. While

fitted values suggested a distribution of 85% monomer, 15% dimer, this specific method of fitting intrinsically contains a significant amount of error, and the amount of dimer could be less than 5%. Systemic errors in the data for this particular sample are also significant. A reasonable fit could be obtained without inclusion of the dimeric paths, but was rejected due to the *a priori* knowledge obtained by NMR.

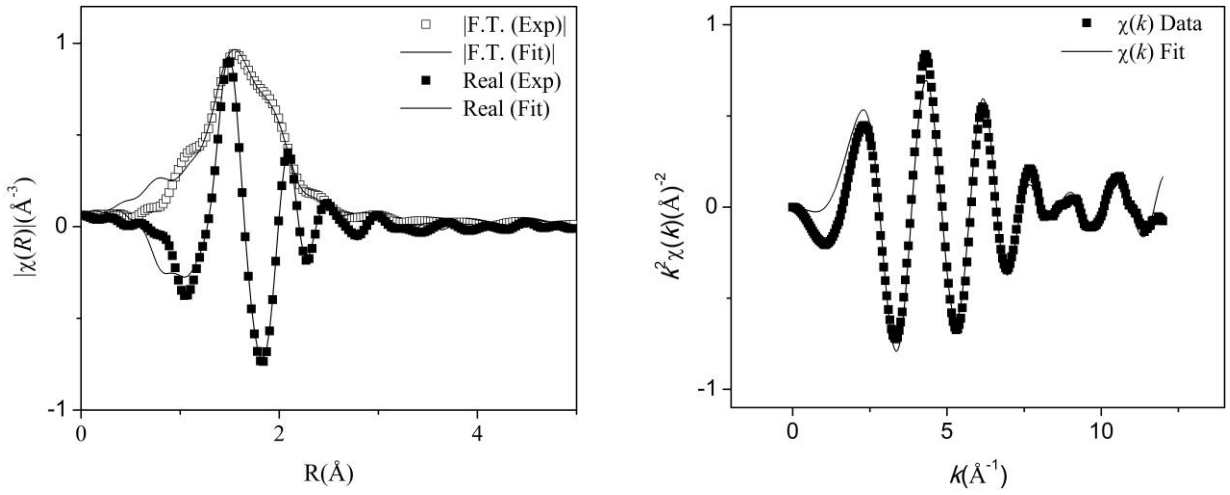


Fig. S13 EXAFS data (squares) and best fits (lines) for RhCl-**L**Me$_2$ in *R*-space (left) and *k*-space (right). Data are displayed in *R*-space containing both magnitude of Fourier Transform and real components. A final *R*-factor of 0.01 was obtained for [RhCl(nbd)]$_2$ with a reduced χ^2 of 1430.

Table S4 EXAFS fitting parameters and calculated error for fit of RhCl-**L**Me$_2$

Parameter	**Value**	**Error**
S_0^2	1.05	0.00
Frac	0.15	0.3
E_0	-1	1
ΔR C_1	0.00	0.02
ΔR Cl	0.03	0.03
ΔR C_2	0.06	0.03
ΔR C_3	-0.06	0.03
ΔR C_{long}	0.04	0.1
ΔR Rh	0.03	0.4
ΔR O	0.03	0.1
σ^2 C_1	0.004	0.006
σ^2 Cl	0.002	0.002
σ^2 C_2	0.002	0.002

σ^2 C_3	0.002	0.002
σ^2 Rh	0.02	0.09
σ^2 C_{long}	0.002	0.002
σ^2 O	0.002	0.002

Rh(acac)-**L**Me$_2$, and E$_2$-MOF•Rh(acac) were fit with the reported crystal structure UGOSAL obtained from the Cambridge Crystallographic Database.[3]

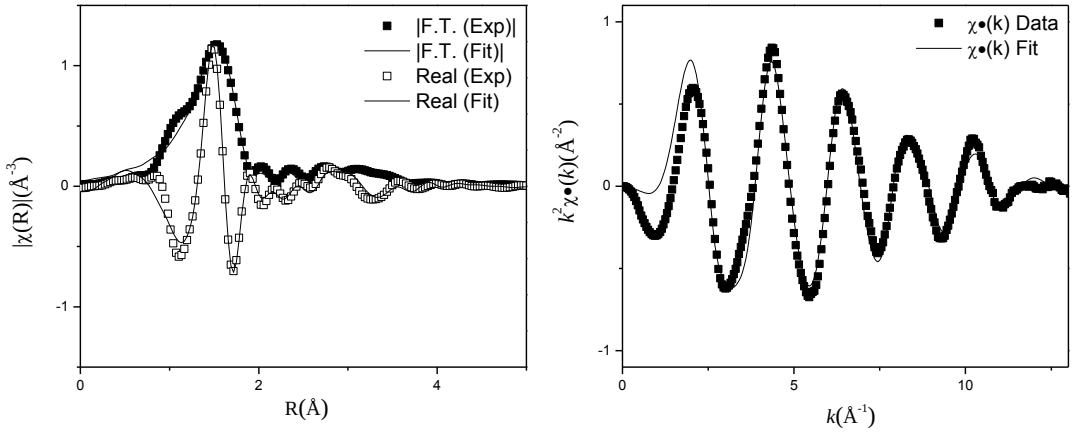


Fig. S14 EXAFS data (squares) and best fits (lines) for Rh(acac)-**L**Me$_2$ in *R*-space (left) and *k*-space (right). Data are displayed in *R*-space containing both magnitude of Fourier Transform and real components. A final *R*-factor of 0.016 was obtained for Rh(acac)-**L**Me$_2$ with a reduced χ^2 of 1587.25.

Table S5 EXAFS fitting parameters and calculated error for fit of Rh(acac)-**L**Me$_2$

Parameter	**Value**	**Error**
S_0^2	0.86	0.12
E_0	-2.86	1.13
ΔR O	-0.03	0.02
ΔR C_8	0.04	0.02
ΔR C_7	0.18	0.09
ΔR C_2	0.07	0.06
ΔR C_1	0.08	0.08
σ^2 O	0.001	0.003

σ^2 C_8	0.002	0.003
σ^2 C_7	0.01	0.01
σ^2 C_2	0.002	0.002
σ^2 C_1	0.002	0.002

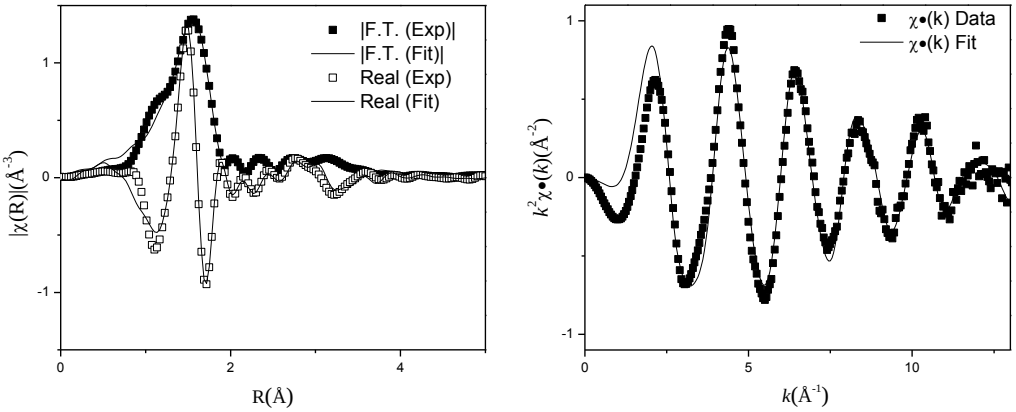


Fig. S15 EXAFS data (squares) and best fits (lines) for E_2-MOF•Rh(acac) in *R*-space (left) and *k*-space (right). Data are displayed in *R*-space containing both magnitude of Fourier Transform and real components. A final *R*-factor of 0.016 was obtained for E_2-MOF•Rh(acac) with a reduced χ^2 of 78.77.

Table S6 EXAFS fitting parameters and calculated error for fit of E_2-MOF•Rh(acac)

Parameter	**Value**	**Error**
S_0^2	0.91	0.16
E_0	-1.77	1.24
ΔR O	-0.02	0.03
ΔR C_8	0.03	0.03
ΔR C_7	0.20	0.12
ΔR C_2	0.07	0.05
ΔR C_1	0.10	0.06
σ^2 O	0.002	0.004

σ^2 C_8	0.002	0.003
σ^2 C_7	0.01	0.02
σ^2 C_2	0.0005	0.004
σ^2 C_1	0.001	0.007

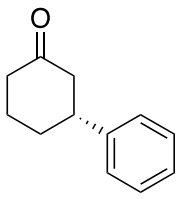
6. Asymmetric 1,4-addion of arylboronic acids to α,β–unsaturated ketones with E_2-MOF •RhCl

Post-synthetic metalation of E_2-MOF with $[RhCl(C_2H_4)_2]_2$.

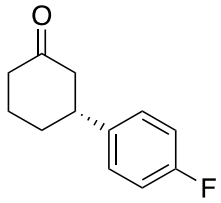
Freshly prepared E_2-MOF was briefly dried on a filter paper and then weighted on a 1 dram vial (1.50 mg, 0.529 μmol). After addition of THF (1.5 mL) and $[RhCl(C_2H_4)_2]_2$ (42 μL, 0.53 μmol, 0.0125 M solution in THF), the mixture was allowed to stand overnight, and then the resulting brown solid was centrifuged out of suspension and washed with 1.5 mL of THF four times. ICP-MS analysis gave 66% Rh-loading of **L**.

A typical procedure for E_2-MOF•RhCl catalyzed asymmetric 1,4-addition reaction (Table 1).

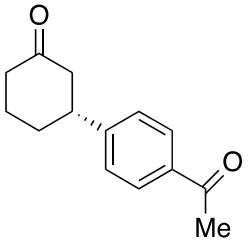
E_2-MOF (1.50 mg, 0.529 μmol) was metalated with $[RhCl(C_2H_4)_2]_2$ (42 μL, 0.53 μmol, 0.0125 M solution in THF) as above. A mixture of 2-cyclohexenone (**1a**) (340 μL, 3.49 mmol), phenylboronic acid (**2a**) (510.6 mg, 4.188 mmol), E_2-MOF•RhCl (0.349 μmol Rh) in toluene (1.2 mL) and H_2O (2.3 mL) was refluxed under nitrogen atmosphere at 100 °C for 40 h. The mixture was extracted with Et_2O. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel (hexanes/$CHCl_3$/ethyl acetate = 20/10/1) to give (*R*)-3-phenylcyclohexanone (588.2 mg, 97% yield, 93% ee).



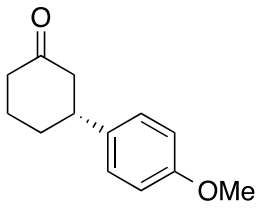
(*R*)-3-Phenylcyclohexanone.[10] ^{1}H NMR ($CDCl_3$): δ 1.73–1.92 (m, 2H), 2.05–2.12 (m, 1H), 2.12–2.20 (m, 1H), 2.38 (td, *J* = 13.3, 5.8 Hz, 1H), 2.43–2.50 (m, 1H), 2.50–2.63 (m, 2H), 3.01 (tt, *J* = 12.0, 3.8 Hz, 1H), 7.20–7.27 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H). The ee was measured by HPLC (Chiralpak AD, 0.6 mL/min, hexanes/2-propanol = 99/1, 210 nm, t_1 = 20.3 min (minor), t_2 = 24.8 min (major)).



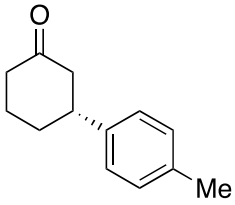
(*R*)-3-(4-Fluorophenyl)cyclohexanone.[10] ^{1}H NMR ($CDCl_3$): δ 1.71–1.87 (m, 2H), 2.03–2.10 (m, 1H), 2.10–2.18 (m, 1H), 2.37 (td, *J* = 13.3 , 6.5 Hz, 1H), 2.42–2.52 (m, 2H), 2.57 (ddt, *J* = 14.0, 4.0, 2.0 Hz, 1H), 2.99 (tt, *J* = 11.8, 3.8 Hz, 1H), 7.01 (app t, $J_{H\text{-}F}$ = 8.9 Hz, $J_{H\text{-}H}$ = 8.9 Hz, 2H), 7.17 (dd, $J_{H\text{-}F}$ = 5.3 Hz, $J_{H\text{-}H}$ = 8.9 Hz, 2H). The ee was measured by HPLC (Chiralpak AD, 0.6 mL/min, hexanes/2-propanol = 95/5, 210 nm, t_1 = 11.9 min (minor), t_2 = 14.4 min (major)).



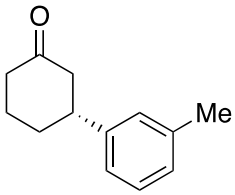
(*R*)-3-(4-Acetylphenyl)cyclohexanone.[11] ^{1}H NMR ($CDCl_3$) δ 1.74–1.94 (m, 2H), 2.05–2.13 (m, 1H), 2.13–2.21 (m, 1H), 2.39 (td, *J* = 13.3, 6.2 Hz, 1H), 2.45–2.52 (m, 1H), 2.52–2.64 (m, 2H), 2.59 (s, 3H), 3.08 (tt, *J* = 11.8, 3.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H). The ee was measured by HPLC (Chiralpak AD, 0.6 mL/min, hexanes/2-propanol = 90/10, 250 nm, t_1 = 27.3 min (major), t_2 = 31.9 min (minor)).



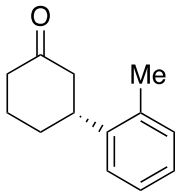
(*R*)-3-(4-Methoxy)cyclohexanone.[10] ^{1}H NMR ($CDCl_3$): δ 1.70–1.87 (m, 2H), 2.02–2.09 (m, 1H), 2.09–2.18 (m, 1H), 2.37 (td, *J* = 13.0, 5.8 Hz, 1H), 2.41–2.53 (m, 2H), 2.57 (ddt, *J* = 14.0 Hz, 4.3, 2.0 Hz, 1H), 2.96 (tt, *J* = 11.8, 3.8 Hz, 1H), 3.80 (s, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H). The ee was measured by HPLC (Chiralcel OD-H, 0.6 mL/min, hexanes/2-propanol = 97/3, 210 nm, t_1 = 22.3 min (major), t_2 = 23.7 min (minor)).



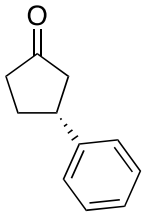
(*R*)-3-(4-Methylphenyl)cyclohexanone.[10] ^{1}H NMR ($CDCl_3$): 1.71–1.89 (m, 2H), 2.03–2.10 (m, 1H), 2.10–2.18 (m, 1H), 2.33 (s, 3H), 2.34–2.42 (m, 1H), 2.42–2.48 (m, 1H), 2.48–2.62 (m, 2H), 2.98 (tt, *J* = 11.8, 3.9 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H). The ee was measured by HPLC (Chiralcel OJ, 0.6 mL/min, hexanes/2-propanol = 95/5, 225 nm, t_1 = 18.2 min (major), t_2 = 19.3 min (minor)).



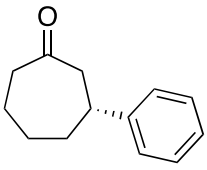
(*R*)-3-(3-Methylphenyl)cyclohexanone.[12] ^{1}H NMR ($CDCl_3$): δ 1.71–1.91 (m, 2H), 2.03–2.20 (m, 1H), 2.11–2.20 (m, 1H), 2.35 (s, 3H), 2.36–2.43 (m, 1H), 2.43–2.49 (m, 1H), 2.49–2.62 (m, 2H), 2.97 (tt, *J* = 11.8, 4.0 Hz, 1H), 6.99–7.05 (m, 1H), 7.04 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H). The ee was measured by HPLC (Chiralcel OD-H, 0.8 mL/min, hexanes/2-propanol = 95/5, 210 nm, t_1 = 13.7 min (minor), t_2 = 15.9 min (major)).



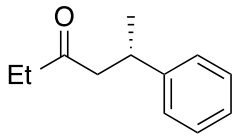
(*R*)-3-(2-Methylphenyl)cyclohexanone.[12] ^{1}H NMR ($CDCl_3$): δ 1.74–1.90 (m, 2H), 1.97–2.05 (m, 1H), 2.14–2.22 (m, 1H), 2.33 (s, 3H), 2.41 (td, *J* = 13.3, 6.0 Hz, 1H), 2.45–2.55 (m, 3H), 3.17–3.26 (m, 1H), 7.11–7.19 (m, 2H), 7.19–7.26 (m, 2H). The ee was measured by HPLC (Chiralpak AD, 0.6 mL/min, hexanes/2-propanol = 97/3, 210 nm, t_1 = 10.6 min (minor), t_2 = 12.5 min (major)).



(*R*)-3-Phenylcyclopentanone.[10] ^{1}H NMR ($CDCl_3$): δ 1.96–2.08 (m, 1H), 2.28–2.42 (m, 2H), 2.43–2.54 (m, 2H), 2.70 (dd, *J* = 18.0, 7.5 Hz, 1H), 3.40–3.50 (m, 1H), 7.25–7.31 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 2H). The ee was measured by GC (γ-dex 225. Inj: 250 °C. Det: 250 °C. Column temp: 80 °C, ramp of 1 °C/min to 200 °C and held for 10 min. Column flow: 1.0 mL/min, t_1 = 67.7 min (minor), t_2 = 68.4 min (major)).



(*R*)-3-Phenylcycloheptanone.[10] ^{1}H NMR ($CDCl_3$): δ 1.44–1.56 (m, 1H), 1.66–1.80 (m, 2H), 1.95–2.15 (m, 3H), 2.59 (dd, *J* = 9.5, 4.2 Hz, 2H), 2.62–2.67 (m, 1H), 2.86–2.93 (m, 1H), 2.94 (t, *J* = 12.5 Hz, 1H), 7.15–7.23 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 2H). The ee was measured by HPLC (Chiralcel OD-H, 0.6 mL/min, hexanes/2-propanol = 95/5, 210 nm, t_1 = 15.0 min (minor), t_2 = 16.3 min (major)).



(*S*)-5-Phenyl-3-hexanone.[13] ^{1}H NMR ($CDCl_3$): δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 3H), 2.29 (dq, *J* = 17.5, 7.3 Hz, 1H), 2.35 (dq, *J* = 17.5, 7.3 Hz, 1H), 2.63 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.73 (dd, *J* = 16.0, 6.5 Hz, 1H), 3.27–3.38 (m, 1H), 7.16–7.21 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H). The ee was measured by HPLC (Chiralpak AD, 0.6 mL/min, hexanes/2-propanol = 99.8/0.2, 210 nm, t_1 = 17.1 min (major), t_2 = 18.4 min (minor)).

A procedure for the synthesis of mixure of RhCl(LMe_2) and [RhCl(LMe_2)]$_2$

A mixture of $[RhCl(C_2H_4)_2]_2$ (3.9 mg, 0.02 mmol Rh), **L**Me_2 (14.2 mg, 0.021 mmol) in THF (0.5 mL) was stirred under nitrogen atmosphere at 60 °C for 30 min. After addition of benzene to the mixture, the precipitated solid was washed with benzene to give a mixture of RhCl(**L**Me_2) and [RhCl(**L**Me_2)]$_2$ (11.0 mg, 68% yield). ^{1}H NMR ($CDCl_3$): compound A. 0.66 (d, *J* = 6.0 Hz, 3H), 0.83 (d, *J* = 6.0 Hz, 3H), 0.80–1.00 (m, 1H), 1.08–1.32 (m, 3H), 1.39 (s, 3H), 3.09 (d, *J* = 4.0 Hz, 1H), 3.33–3.45 (m, 1H), 3.93 (s, 3H), 3.95 (s, 3H), 4.00 (s, 1H), 4.65 (d, *J* = 4.0 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.28–7.41 (m, 3H), 7.59 (d, *J* = 8.2 Hz, 4H), 7.63 (d, *J* = 7.5 Hz, 2H), 8.02 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H), 8.83 (s, 1H). compound B. 0.75 (d, *J* = 6.5 Hz, 1H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.80–1.00 (m, 1H), 1.08–1.32 (m, 3H), 1.47 (s, 3H), 3.18 (d, *J* = 5.5 Hz, 1H), 3.33–3.45 (m, 1H), 3.91 (s, 3H), 3.96 (s, 3H), 4.05 (s, 1H), 4.73 (d, *J* = 5.0 Hz, 1H), 6.76 (s, 1H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.28–7.41 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 8.64 (s, 1H).

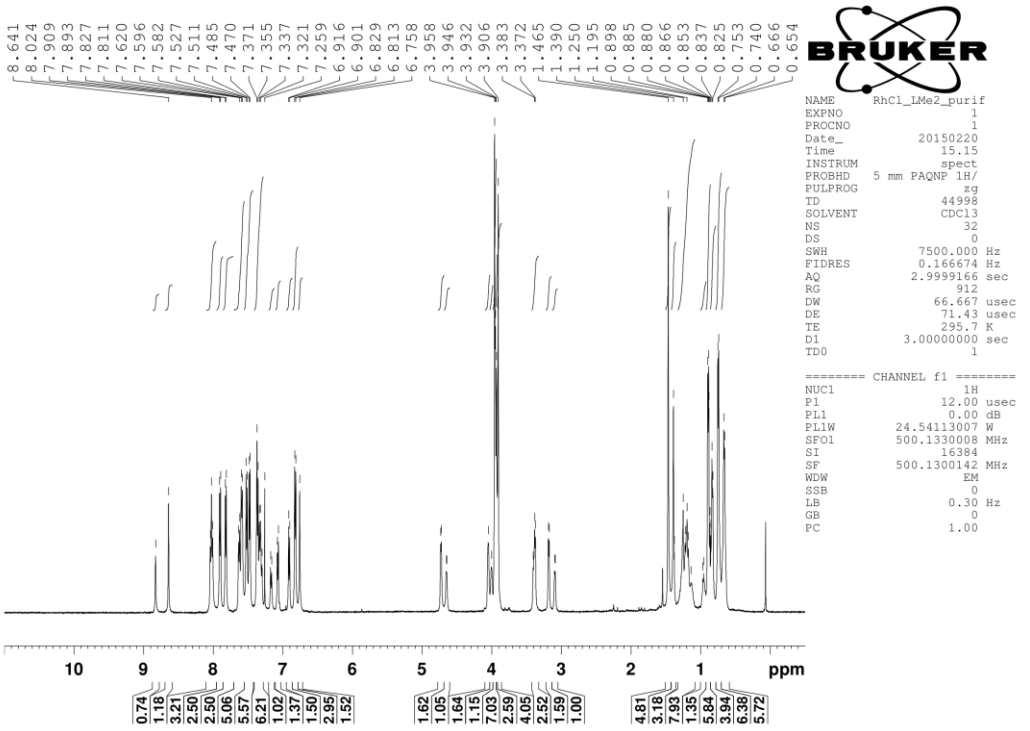
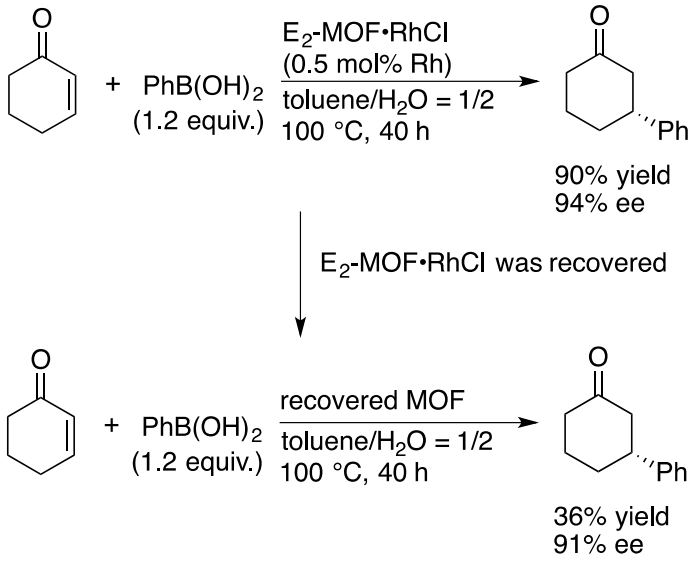


Fig. S16 ^{1}H NMR of a mixture of RhCl(LMe$_2$) and [RhCl(LMe$_2$)]$_2$

Recyclability test for E$_2$-MOF•RhCl catalyzed asymmetric 1,4-addition of α,β-unsaturated ketone



Scheme S1 Recycle of E$_2$-MOF•RhCl for the 1,4-addition reaction.

E_2-MOF (3.73 mg, 1.32 μmol) was metalated with $[RhCl(C_2H_4)_2]_2$ (105 μL, 1.32 μmol, 0.0125 M solution in THF) as described above. A mixture of 2-cyclohexenone (**1a**) (168 μL, 1.73 mmol), phenyboronic acid (**2a**) (254 mg, 2.08 mmol), E_2-MOF•RhCl (0.867 μmol Rh) in toluene (0.58 mL) and water (1.2 mL) was refluxed under nitrogen atmosphere at 100 °C for 40 h. After extraction, the solid catalyst was separated via centrifugation. The supernatant was concentrated on a rotary evaporator and subjected to flash column chromatography (silica gel, hexanes/$CHCl_3$/EtOAc = 20/10/1) to give **3a** (272.0 mg, 1.561 mmol, 90% yield, 94% ee). The solid catalyst was added to a solution of 2-cyclohexenone (**1a**) (168 μL, 1.73 mmol), phenylboronic acid (**2a**) (254 mg, 2.08 mmol). After stirring at 100 °C for 40 h, the mixture was worked up and subjected to flash column chromatography (silica gel, hexanes/$CHCl_3$/EtOAc = 20/10/1) to give **3a** (108.5 mg, 0.6227 mmol, 36% yield, 91% ee).

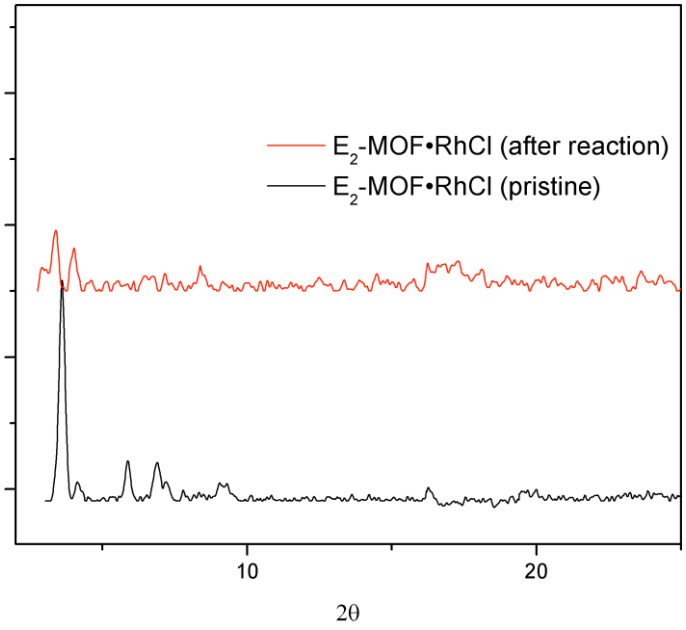


Fig. S17 PXRD spectrum after 1,4-addition reaction with E_2-MOF•RhCl

7. Asymmetric 1,2-addition of arylboronic acids to aldimines with E_2-MOF•Rh(acac)

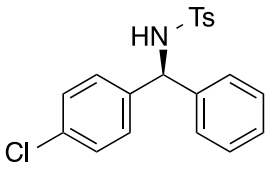
Post-synthetic metalation of E_2-MOF with $Rh(acac)(C_2H_4)_2$.

Freshly prepared E_2-MOF was briefly dried on a filter paper and then weighted with a 1 dram vial (6.0 mg, 2.12 μmol). After addition of THF (1.5 mL) and $Rh(acac)(C_2H_4)_2$ (169 μL, 2.12 μmol, 0.0125 M solution in THF), the mixture was allowed to stand overnight, and then the

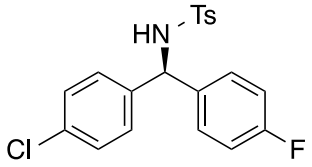
resulting orange solid was centrifuged out of suspension and washed with 1.5 mL of THF four times. ICP-MS analysis gave 13% Rh-loading of **L**.

A typical procedure for E_2-MOF•Rh(acac) catalyzed asymmetric addition reactions of aldimines (Table 3).

E_2-MOF (6.0 mg, 2.12 μmol) was metalated with Rh(acac)$(C_2H_4)_2$ (169 μL, 2.12 μmol, 0.0125 M solution in THF) as above. A mixture of *N*-(4-chlorophenyl)methylidene-4-methylbenzenesulfonamide (**4a**) (2.8 mg, 9.5 μmol), phenylboronic acid (**2a**) (2.3 mg, 19 mmol), E_2-MOF•Rh(acac) (0.29 μmol Rh) in 1,4-dioxane (0.24 mL) was stirred under nitrogen atmosphere at 100 °C for 20 h. After centrifugation, MeOH was added to the supernatant and the mixture was stirred for 30 min. After evaporation of the solvent, the residue was subjected to preparative TLC (silica gel, hexane/ethyl acetate = 3/1) to give (*S*)-*N*-[(4-chlorophenyl)phenylmethyl]-4-methylbenzenesulfonamide (99% NMR yield, 98% ee).

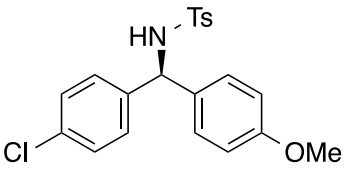


(*S*)-*N*-[(4-chlorophenyl)phenylmethyl]-4-methylbenzenesulfonamide.[14] ^{1}H NMR ($CDCl_3$): 2.39 (s, 3H), 5.11 (d, J = 7.0 Hz, 1H), 5.53 (d, J = 7.0 Hz, 1H), 7.02–7.08 (m, 4H), 7.13–7.20 (m, 4H), 7.20–7.24 (m, 3H), 7.55 (d, J = 8.5 Hz, 2H). The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexanes/2-propanol = 80/20, 230 nm, t_1 = 15.8 min (major), t_2 = 20.7 min (minor)).

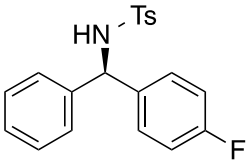


(*S*)-*N*-[(4-Chlorophenyl)(4-fuluorophenyl)methyl]-4-methylbenzenesulfonamide. ^{1}H NMR ($CDCl_3$): 2.40 (s, 3H), 5.42 (d, J = 7.5 Hz, 1H), 5.52 (d, J = 7.5 Hz, 1H), 6.89 (app t, $J_{H\text{-}H}$ = 8.8 Hz, $J_{H\text{-}F}$ = 8.8 Hz, 2H), 6.98–7.05 (m, 4H), 7.14 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.5 Hz,

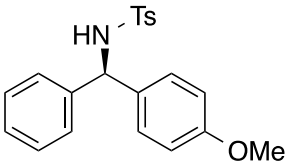
2H), 7.53 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): 21.4, 60.0, 115.5 ($J_{C\text{-}F}$ = 21.6 Hz), 127.1, 128.6, 128.7, 129.0 ($J_{C\text{-}F}$ = 8.3 Hz), 129.4, 133.6, 135.8 ($J_{C\text{-}F}$ = 3.3 Hz), 137.0, 138.7, 143.5, 162.1 ($J_{C\text{-}F}$ = 247.2 Hz). HRMS (ESI) calcd for [M+Na] $C_{20}H_{17}ClFNO_2SNa$ 412.0550, found 412.0550. The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexanes/2-propanol = 80/20, 230 nm, t_1 = 18.7 min (major), t_2 = 20.9 min (minor)).



(*S*)-*N*-[(4-Chlorophenyl)(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide.[14] ^{1}H NMR ($CDCl_3$): 2.39 (s, 3H), 3.74 (s, 3H), 5.31–5.38 (br, 1H), 5.48 (d, J = 7.5 Hz, 1H), 6.72 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 7.15 (app t, J = 8.5 Hz, 4H), 7.54 (d, J = 8.3 Hz, 2H). The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexanes/2-propanol = 80/20, 230 nm, t_1 = 26.1 min (minor), t_2 = 35.1 min (major)).

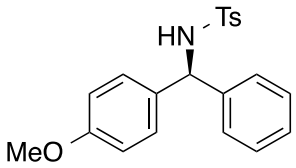


(*R*)-*N*-[(4-Fuluorophenyl)phenylmethyl]-4-methylbenzenesulfonamide.[15] ^{1}H NMR ($CDCl_3$): 2.38 (s, 3H), 5.12–5.31 (br, 1H), 5.55 (d, J = 7.0 Hz, 1H), 6.89 (app t, $J_{H\text{-}H}$ = 8.8 Hz, $J_{H\text{-}F}$ = 8.8 Hz, 2H), 7.03–7.12 (m, 4H), 7.14 (d, J = 8.3 Hz, 2H), 7.18–7.25 (m, 3H), 7.55 (d, J = 8.3 Hz, 2H). The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexanes/2-propanol = 80/20, 235 nm, t_1 = 15.4 min (minor), t_2 = 18.2 min (major)).

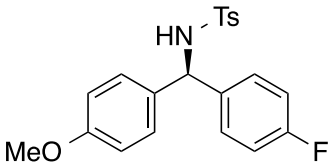


(*R*)-*N*-[(4-Methoxyphenyl)phenylmethyl]-4-methylbenzenesulfonamide.[14] ^{1}H NMR ($CDCl_3$): 2.38 (s, 3H), 3.75 (s, 3H), 5.08 (d, J = 7.0 Hz, 1H), 5.52 (d, J = 7.0 Hz, 1H), 6.73 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.08–7.12 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.16–7.23

(m, 3H), 7.55 (d, J = 8.0 Hz, 2H). The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexanes/2-propanol = 80/20, 210 nm, t_1 = 19.7 min (minor), t_2 = 30.0 min (major)).



(*S*)-*N*-[(4-Methoxyphenyl)phenylmethyl]-4-methylbenzenesulfonamide.[14] The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexanes/2-propanol = 80/20, 210 nm, t_1 = 19.3 min (major), t_2 = 30.5 min (minor)).



(*R*)-*N*-[(4-Fuluorophenyl)(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide.[16] ^{1}H NMR ($CDCl_3$): 2.38 (s, 3H), 3.75 (s, 3H), 5.10–5.28 (br, 1H), 5.49 (d, J = 7.0 Hz, 1H), 6.72 (d, J = 8.5 Hz, 2H), 6.85–6.91 (m, 2H), 6.95 (d, J = 8.5 Hz, 2H), 7.08 (dd, $J_{H\text{-}H}$ = 8.5, $J_{H\text{-}F}$ = 5.0 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H). The ee was measured by HPLC (Chiralcel OD-H, 0.5 mL/min, hexanes/2-propanol = 80/20, 210 nm, t_1 = 21.8 min (major), t_2 = 31.8 min (minor)).

A procedure for the synthesis of Rh(acac)-LMe_2

A mixture of Rh(acac)$(C_2H_4)_2$ (7.7 mg, 0.03 mmol), **L**Me_2 (22.2 mg, 0.033 mmol) in THF (0.6 mL) was stirred under nitrogen atmosphere at 60 °C for 30 min. After evaporation of solvent, the Rh(acac)-LMe_2 was obtained.

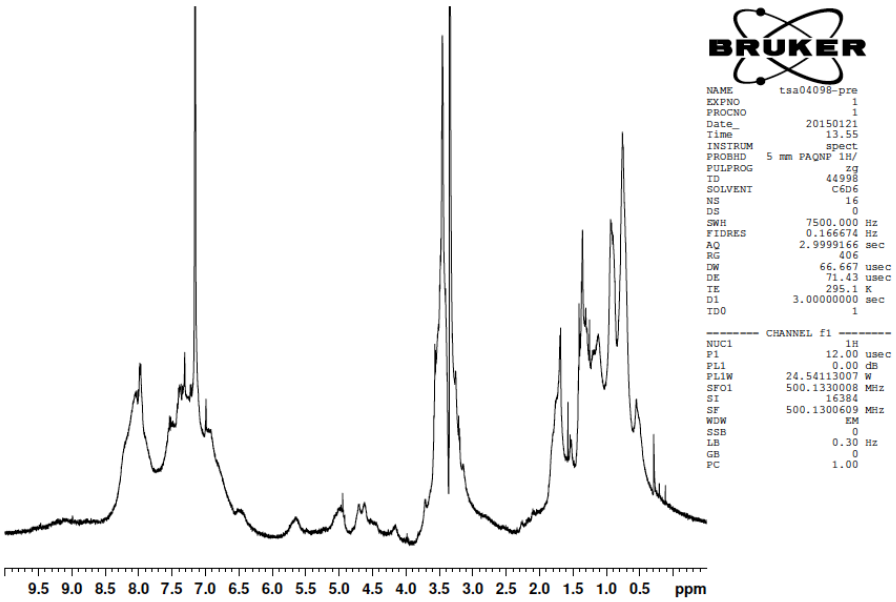
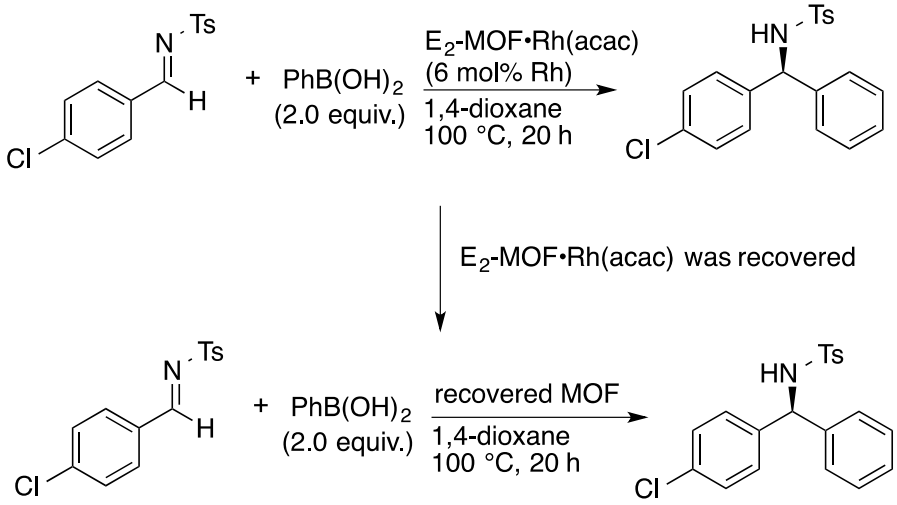


Fig. S18 ^{1}H NMR of Rh(acac)/LMe$_2$

Recyclability test for E$_2$-MOF•Rh(acac) catalyzed asymmetric 1,2-addition of aldimine

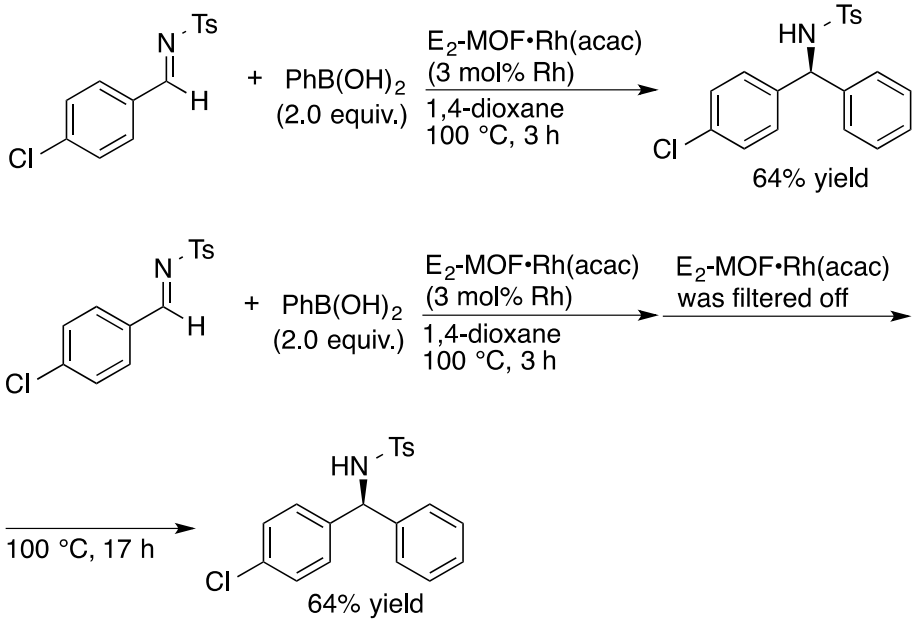


Scheme S2 Recycle of E$_2$-MOF•Rh(acac) for the 1,2-addition reaction.

E$_2$-MOF (21.7 mg, 7.66 μmol) was metalated with Rh(acac)(C$_2$H$_4$)$_2$ (612 μL, 7.66 μmol, 0.0125 M solution in THF) as described above. A mixture of aldimine **4a** (5.0 mg, 17.2 μmol), phenyboronic acid (**2a**) (4.2 mg, 34.4 mmol), E$_2$-MOF•Rh(acac) (1.03 μmol Rh) in 1,4-dioxane (0.86 mL) was stirred under nitrogen atmosphere at 100 °C for 20 h. The solid catalyst was

separated via centrifugation, and then the supernatant was concentrated on a rotary evaporator and subjected to preparative TLC (silica gel, hexanes/ethyl acetate = 3/1) to give **5a**. The recovered solid catalyst was used for subsequent reactions.

Test of "heterogeneity" of E_2-MOF•Rh(acac)



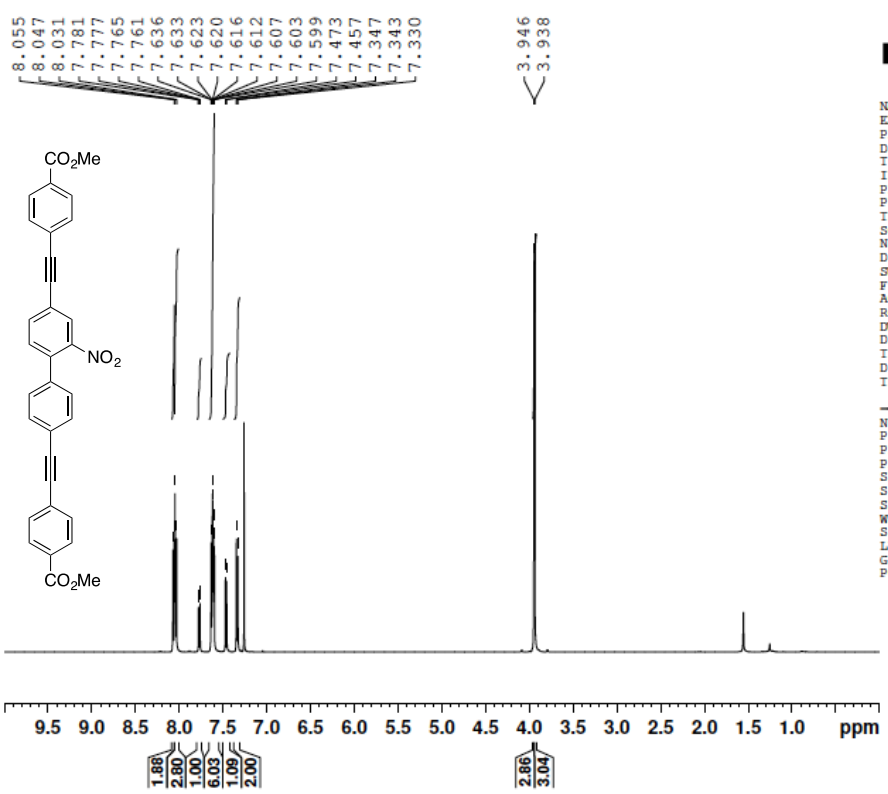
Scheme S3 The asymmetric addition reaction stopped after removal of E_2-MOF•Rh(acac) from the reaction mixture, demonstrating the "heterogeneous" nature of MOF catalysis.

E_2-MOF (7.98 mg, 2.82 μmol) was metalated with Rh(acac)$(C_2H_4)_2$ (225 μL, 2.82 μmol, 0.0125 M solution in THF). A mixture of aldimine **4a** (3.7 mg, 12.6 μmol), phenylboronic acid (**2a**) (3.1 mg, 25.2 μmol), E_2-MOF•Rh(acac) (0.379 μmol Rh), 1,4-dioxane (1.7 mL) was stirred under nitrogen atmosphere at 100 °C for 3 h. After the solid catalyst was separated via centrifugation, the supernatant was concentrated on a rotary evaporator. The residue was subjected to preparative TLC (silica gel, hexanes/EtOAc = 3/1) to give **5a** (64% NMR yield, 98% ee).

E_2-MOF (7.98 mg, 2.82 μmol) was metalated with Rh(acac)$(C_2H_4)_2$ (225 μL, 2.82 μmol, 0.0125 M solution in THF). A mixture of aldimine **4a** (3.7 mg, 12.6 μmol), phenylboronic acid (**2a**) (3.1 mg, 25.2 μmol), E_2-MOF•Rh(acac) (0.379 μmol Rh), 1,4-dioxane (1.7 mL) was stirred under nitrogen atmosphere at 100 °C for 3 h. After the mixture was centrifuged, the resulting supernatant was filtered through a celite, and then the filtrate was allowed to react for an

additional 17 h. After evaporation of the solvent, the residue was subjected to preparative TLC (silica gel, hexanes/EtOAc = 3/1) to give **5a** (64% NMR yield, 98% ee). These two reactions afforded the same yields and enantioselectivity.

8. ^{1}H and ^{13}C NMR spectra, and chiral HPLC charts



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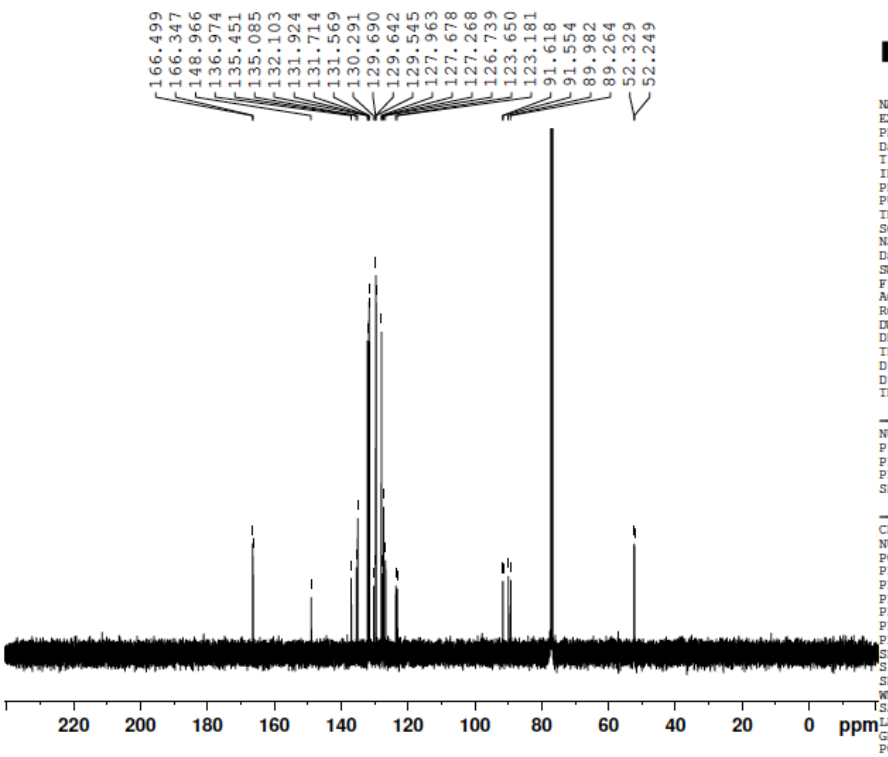

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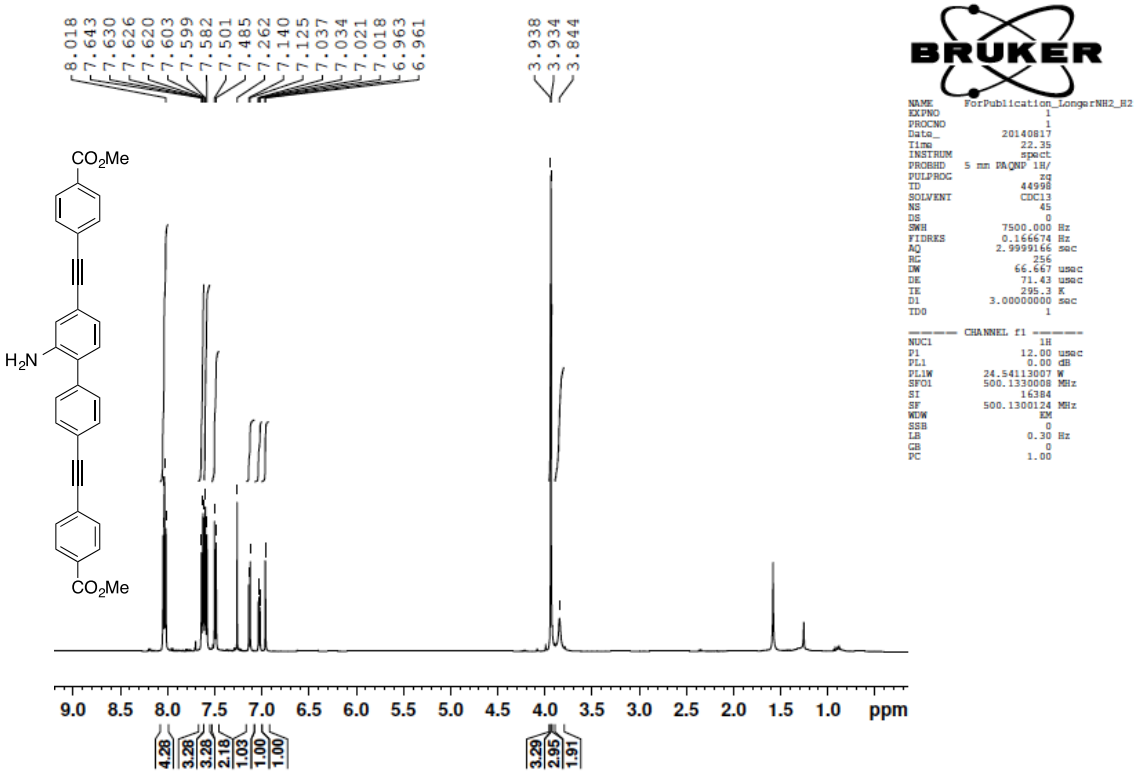


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TD0                                1

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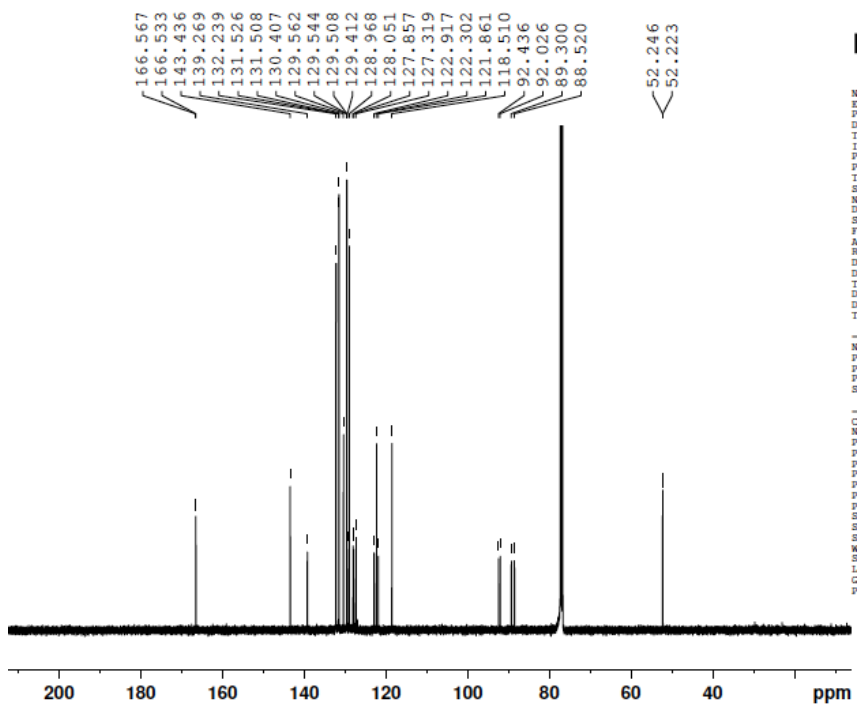


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TE                            296.5 K
D1                        10.00000000 sec
D11                        0.03000000 sec
TD0                                1

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======== CHANNEL f2 ========
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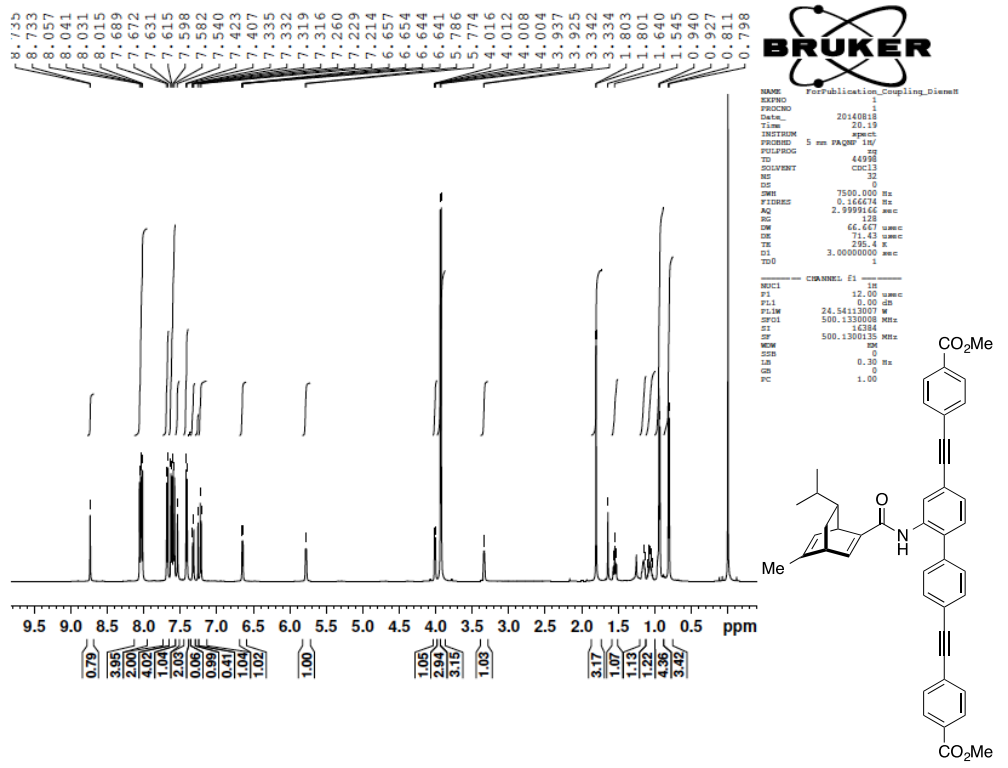
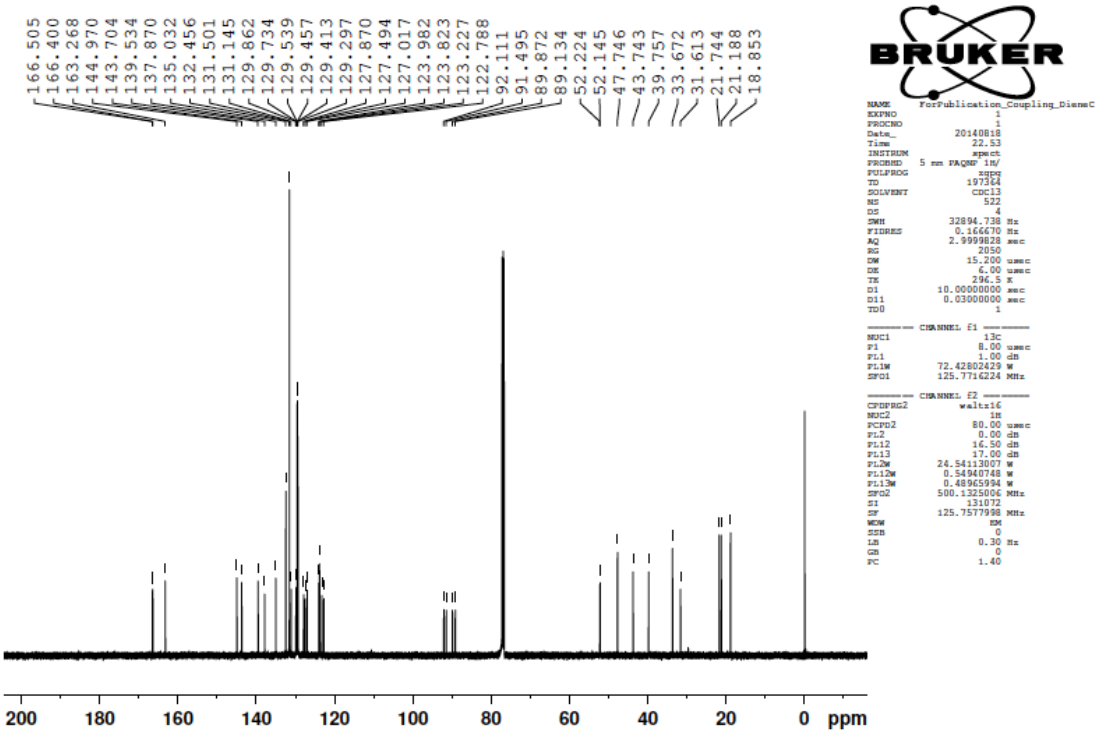
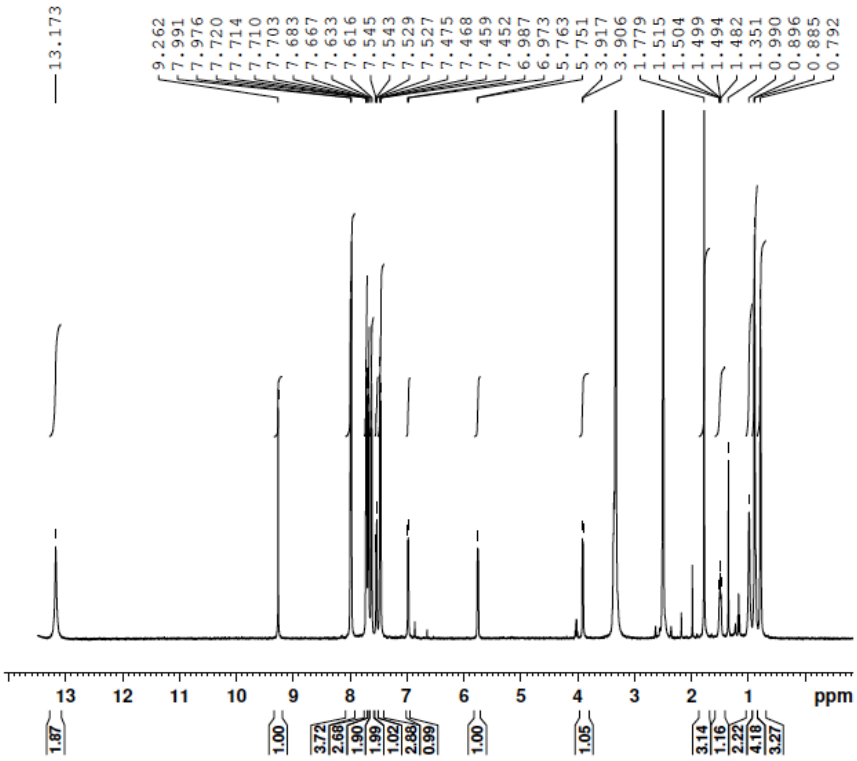
PCPD2                         80.00 usec
PL2                            0.00 dB
PL12                          16.50 dB
PL13                          17.00 dB
PL2W                    24.54113007 W
PL12W                    0.54940748 W
PL13W                    0.48965994 W
SFO2                    500.1325006 MHz
SI                               131072
SF                      125.7577925 MHz
WDW                              EM
SSB                               0
LB                             0.30 Hz
GB                                0
PC                             1.40
```

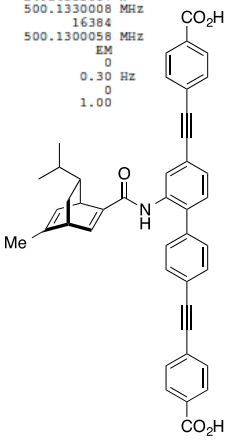

8.735
8.733
8.057
8.041
8.031
8.015
7.689
7.672
7.631
7.615
7.598
7.582
7.540
7.423
7.407
7.335
7.332
7.319
7.316
7.260
7.229
7.214
6.657
6.654
6.644
6.641
5.786
5.774
4.016
4.012
4.008
4.004
3.937
3.925
3.342
3.334
1.803
1.801
1.640
1.545
0.940
0.927
0.811
0.798
BRUKER
NAME ForPublication_Coupling_DieneH
EXPNO 1
PROCNO 1
Date_ 20140818
Time 20.19
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 32
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 128
DW 66.667 usec
DE 71.43 usec
TE 295.4 K
D1 3.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1330008 MHz
SI 16384
SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.79 3.95 2.00 4.02 1.04 2.03 0.06 0.99 0.41 1.04 1.02 1.00 1.05 2.94 3.15 1.03 3.17 1.07 1.13 1.22 4.36 3.42
CO2Me
O
N
H
Me
CO2Me

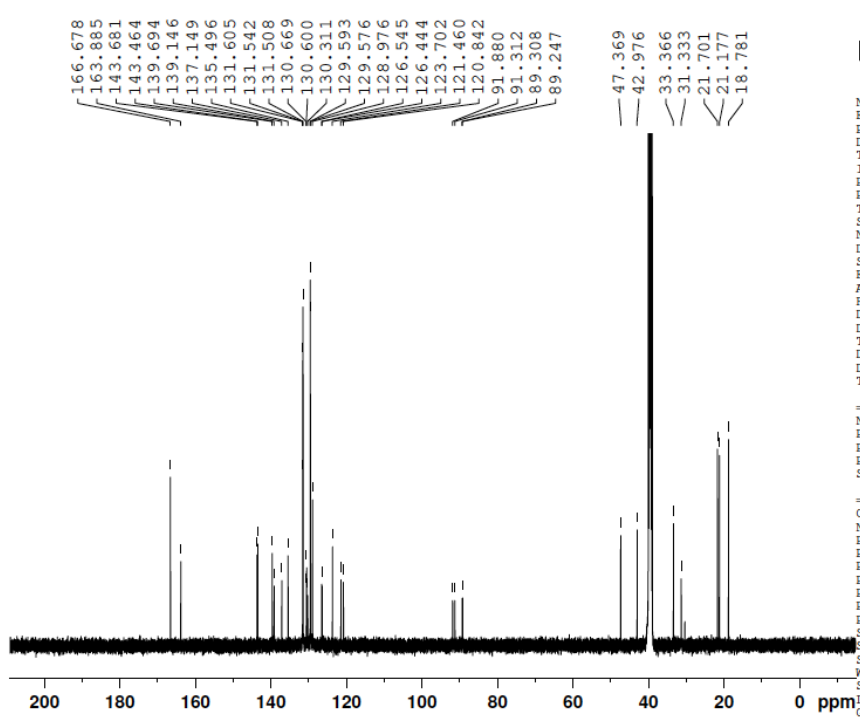

166.505
166.400
163.268
144.970
143.704
139.534
137.870
135.032
132.456
131.501
131.145
129.862
129.734
129.539
129.457
129.413
129.297
127.870
127.494
127.017
123.982
123.823
123.227
122.788
92.111
91.495
89.872
89.134
52.224
52.145
47.746
43.743
39.757
33.672
31.613
21.744
21.188
18.853
BRUKER
NAME ForPublication_Coupling_DieneC
EXPNO 1
PROCNO 1
Date_ 20140818
Time 22.53
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197344
SOLVENT CDCl3
NS 522
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.5 K
D1 10.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577998 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm




```
NAME            DieneLigand
EXPNO                     1
PROCNO                    1
Date_              20140826
Time                  11.53
INSTRUM               spect
PROBHD   5 mm PAQNP 1H/
PULPROG                 zg
TD                   44998
SOLVENT               DMSO
NS                       8
DS                       0
SWH           7500.000 Hz
FIDRES        0.166674 Hz
AQ            2.9999166 sec
RG                     575
DW               66.667 usec
DE               71.43 usec
TE               295.3 K
D1            3.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1              12.00 usec
PL1              0.00 dB
PL1W        24.54113007 W
SFO1        500.1330008 MHz
SI                 16384
SF          500.1300058 MHz
WDW                   EM
SSB                    0
LB               0.30 Hz
GB                     0
PC                  1.00
```

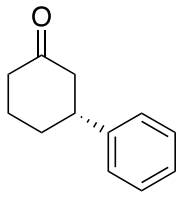


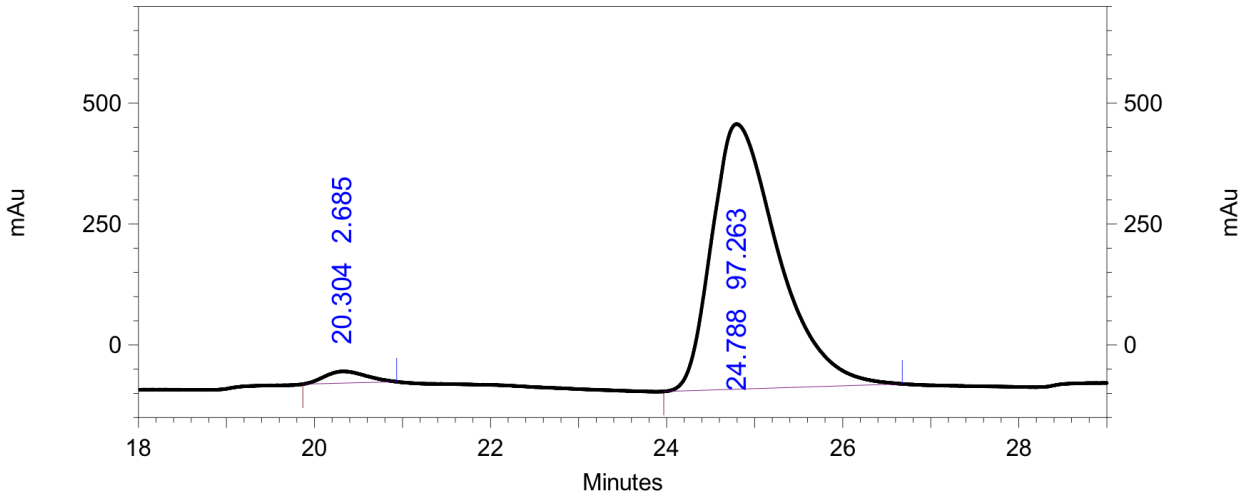


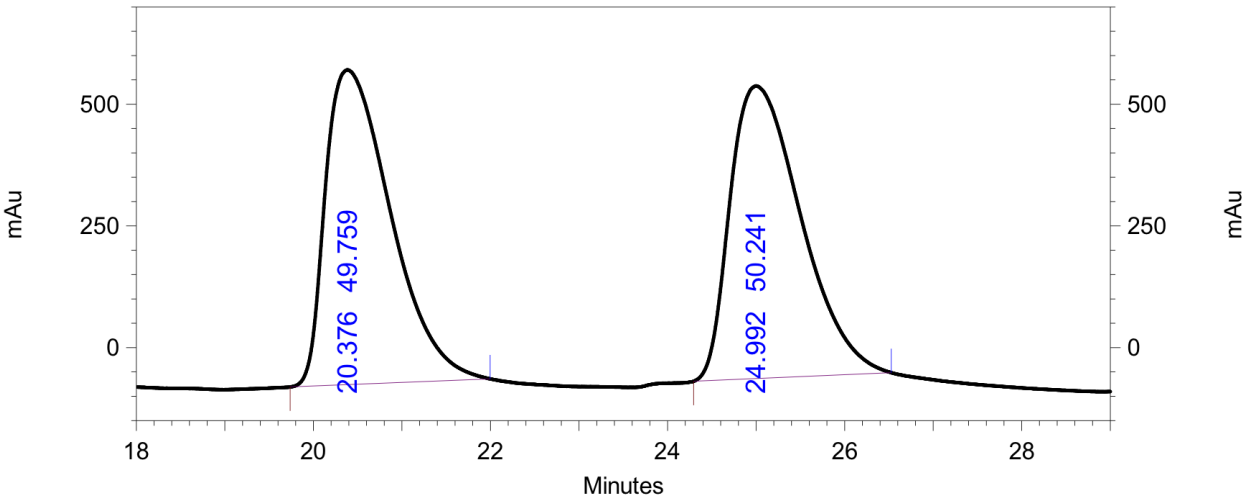

```
NAME            Diene_TM_C
EXPNO                     1
PROCNO                    1
Date_              20140828
Time                   8.54
INSTRUM               spect
PROBHD   5 mm PAQNP 1H/
PULPROG              zgpg
TD                 197364
SOLVENT               DMSO
NS                    1631
DS                       4
SWH          32894.738 Hz
FIDRES        0.166670 Hz
AQ            2.9999828 sec
RG                    2050
DW               15.200 usec
DE                6.00 usec
TE                296.5 K
D1           10.00000000 sec
D11           0.03000000 sec
TD0                      1

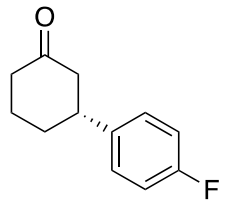
======== CHANNEL f1 ========
NUC1                  13C
P1               8.00 usec
PL1              1.00 dB
PL1W        72.42802429 W
SFO1        125.7716224 MHz

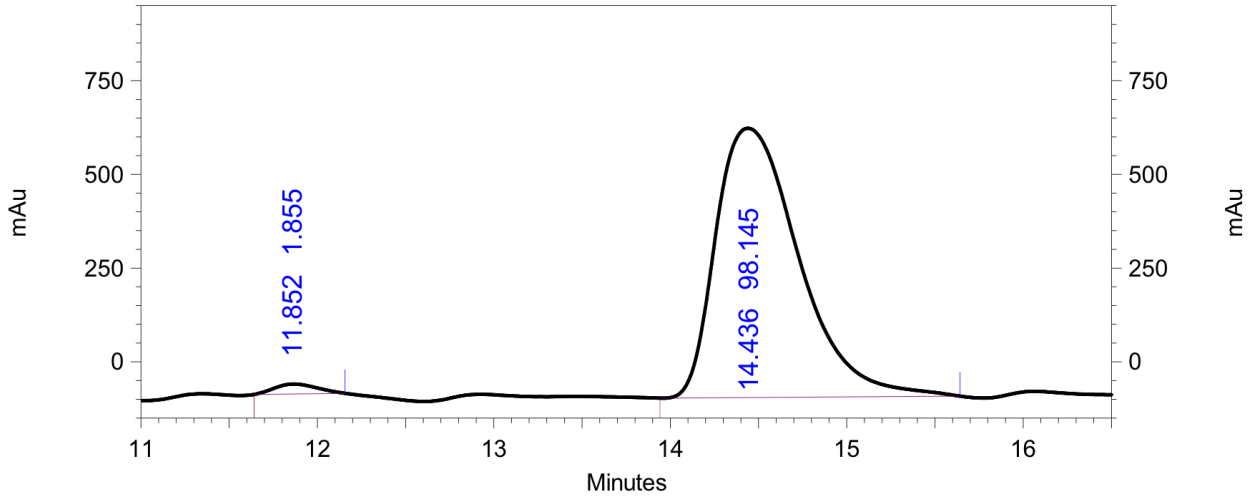
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             16.50 dB
PL13             17.00 dB
PL2W        24.54113007 W
PL12W        0.54940748 W
PL13W        0.48965994 W
SFO2        500.1325006 MHz
SI                131072
SF          125.7578497 MHz
WDW                   EM
SSB                    0
LB               0.30 Hz
GB                     0
PC                  1.40
```

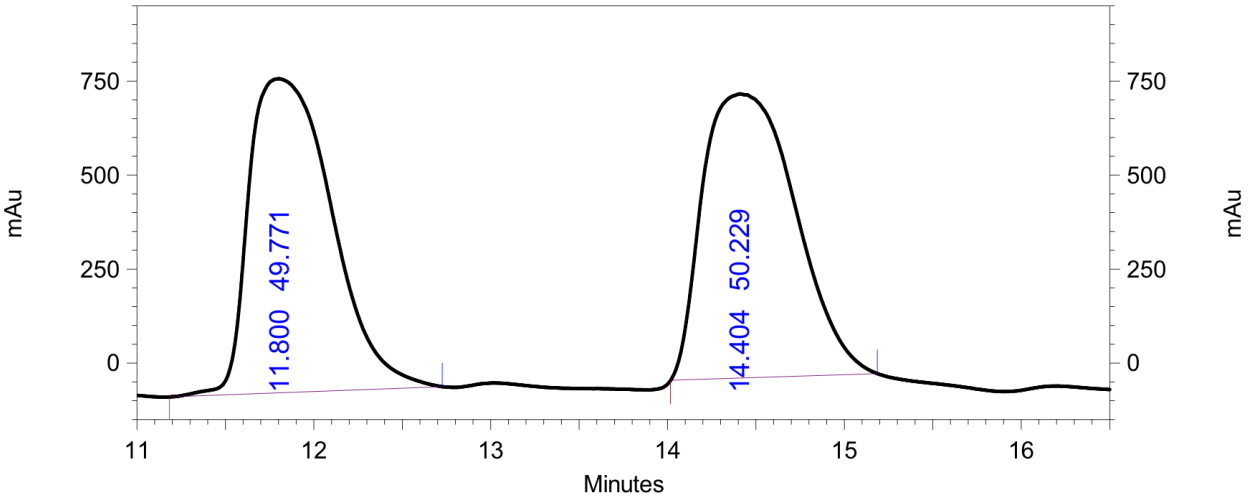


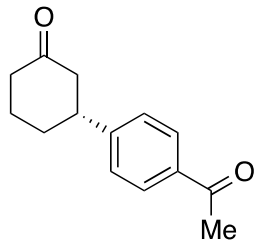

mAu
500
250
0
20.304 2.685
24.788 97.263
18
20
22
24
26
28
Minutes

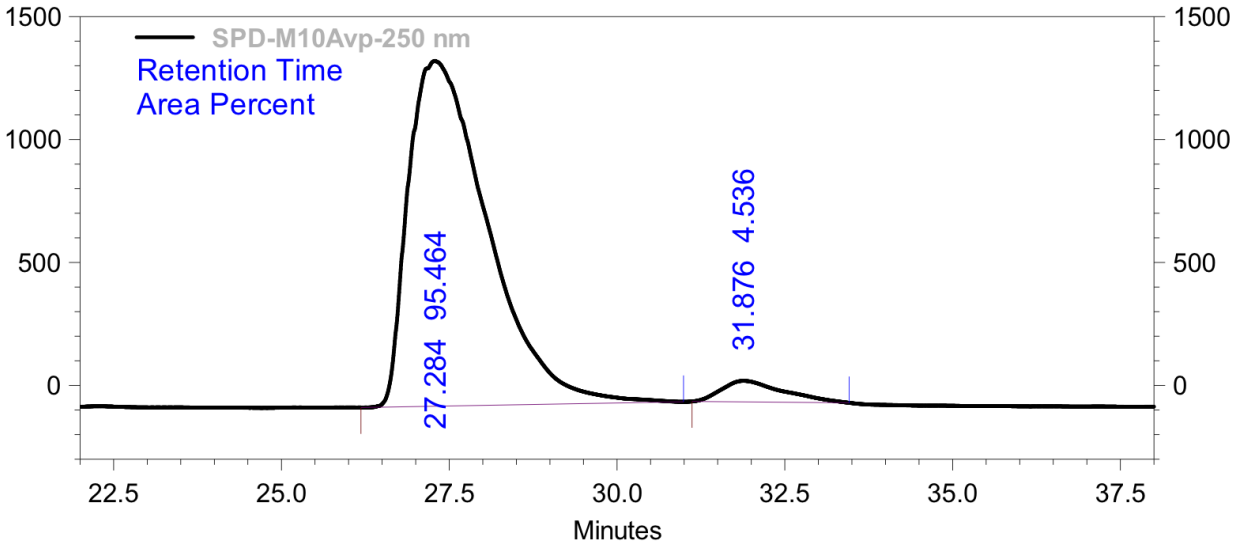

mAu
500
250
0
20.376 49.759
24.992 50.241
18
20
22
24
26
28
Minutes

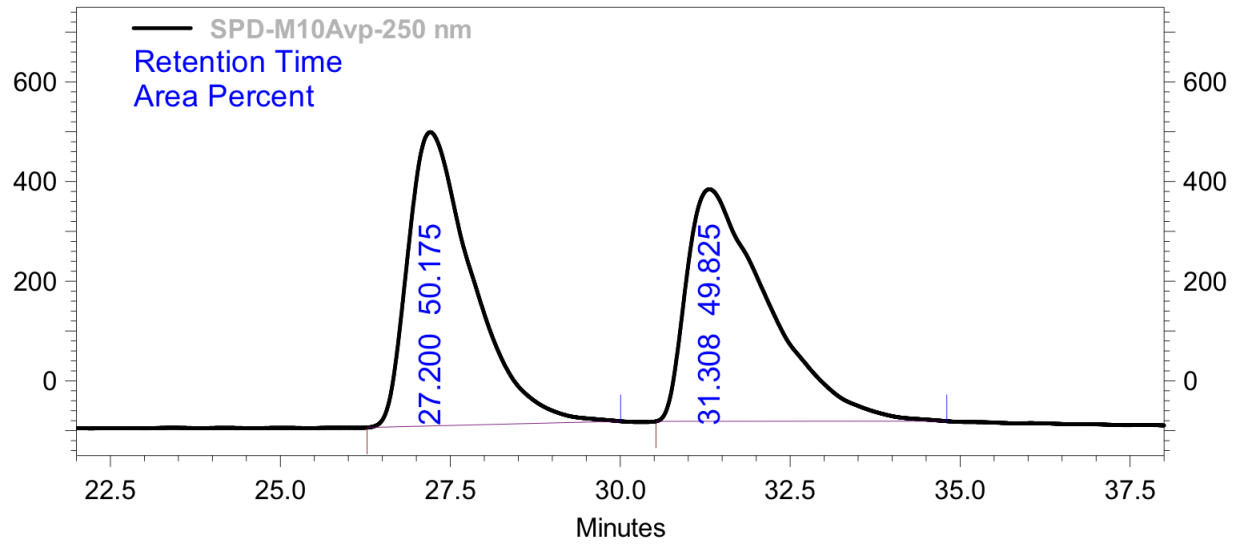

O
F

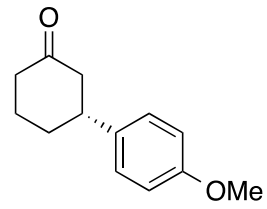

mAu
750
500
250
0
11.852 1.855
14.436 98.145
11
12
13
14
15
16
Minutes

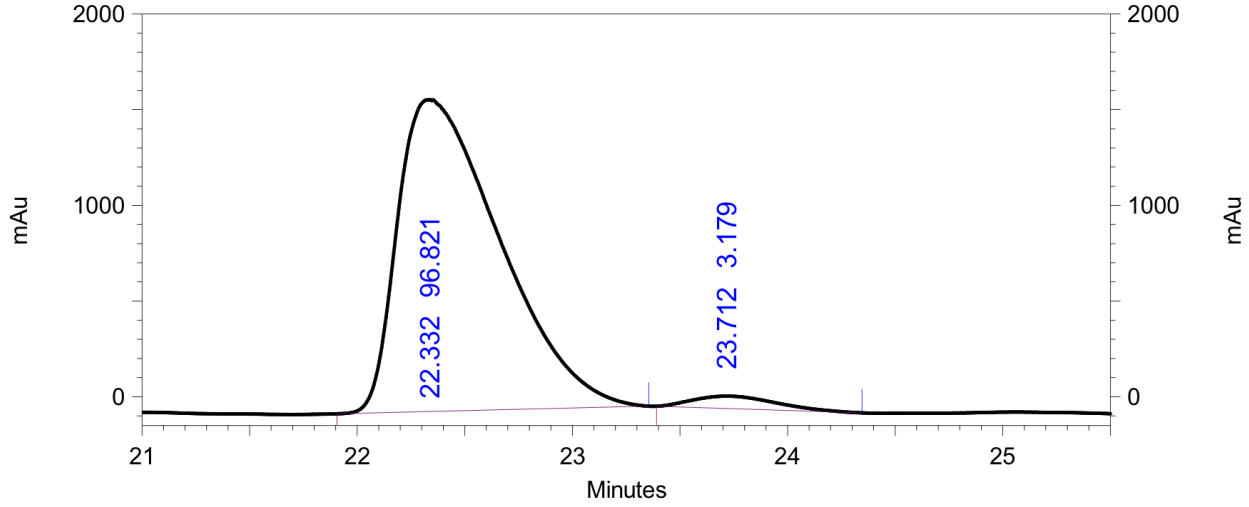

mAu
750
500
250
0
11.800 49.771
14.404 50.229
11
12
13
14
15
16
Minutes

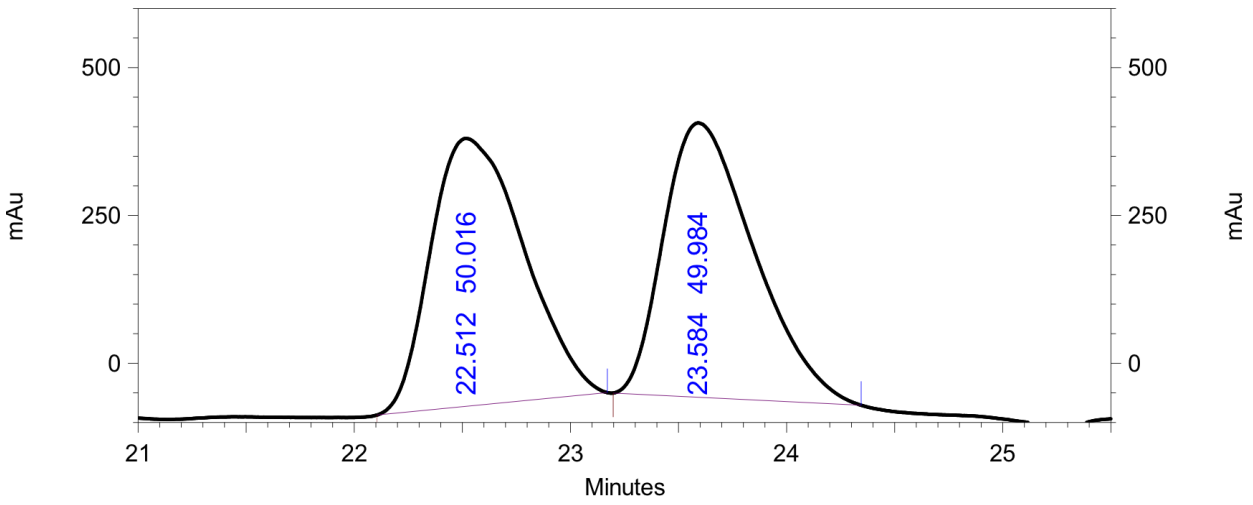

O
O
Me

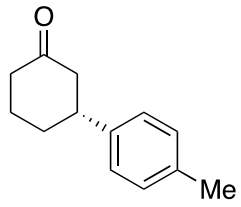

SPD-M10Avp-250 nm
Retention Time
Area Percent
27.284 95.464
31.876 4.536
1500
1000
500
0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
Minutes

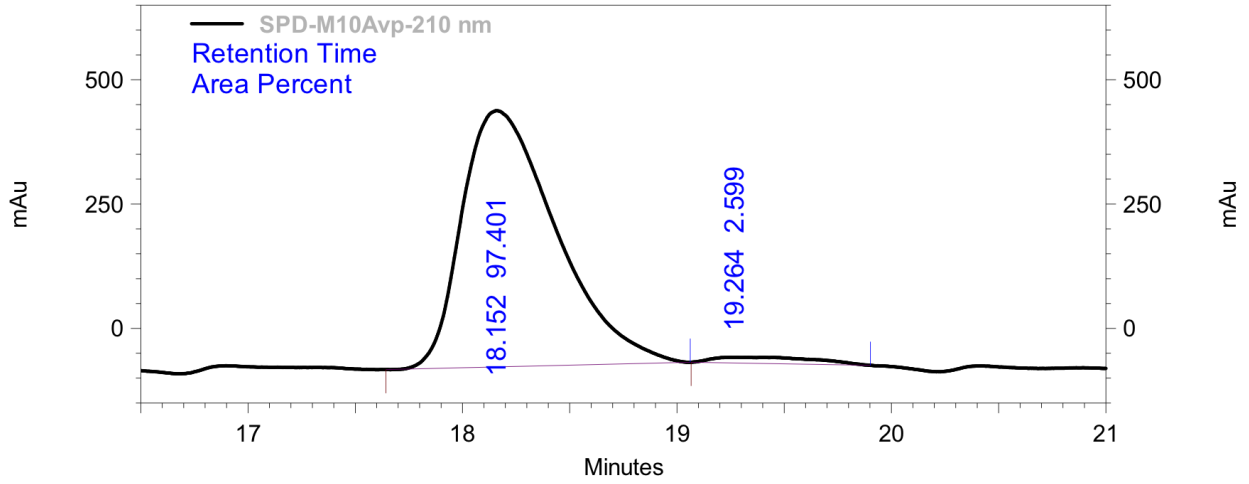

SPD-M10Avp-250 nm
Retention Time
Area Percent
27.200 50.175
31.308 49.825
600
400
200
0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
Minutes

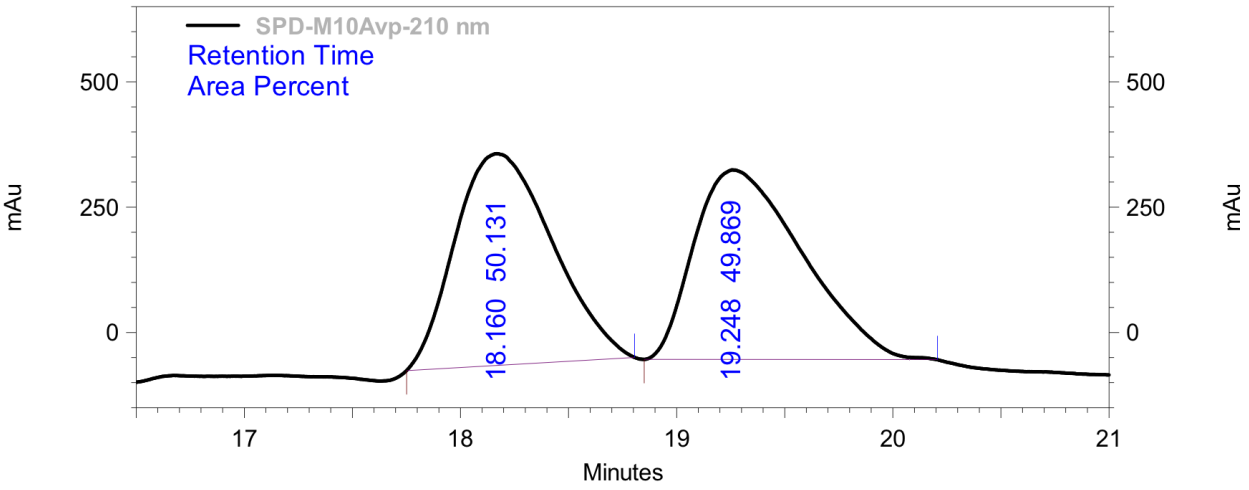

O
OMe

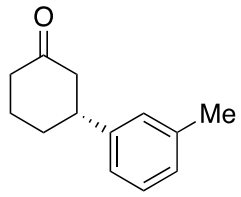

2000
1000
0
mAu
22.332 96.821
23.712 3.179
21
22
23
24
25
Minutes

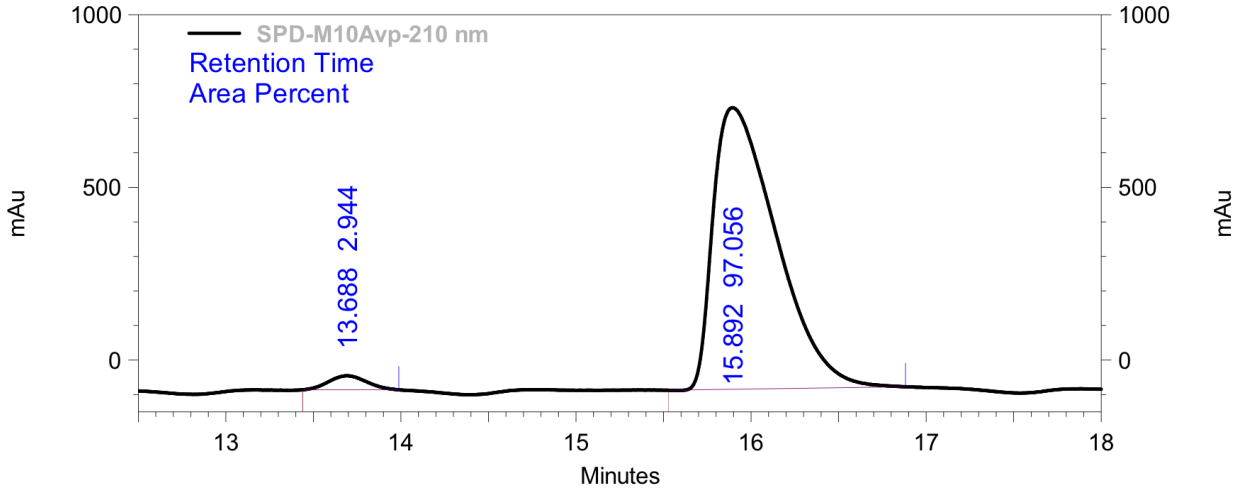

500
250
0
mAu
22.512 50.016
23.584 49.984
21
22
23
24
25
Minutes

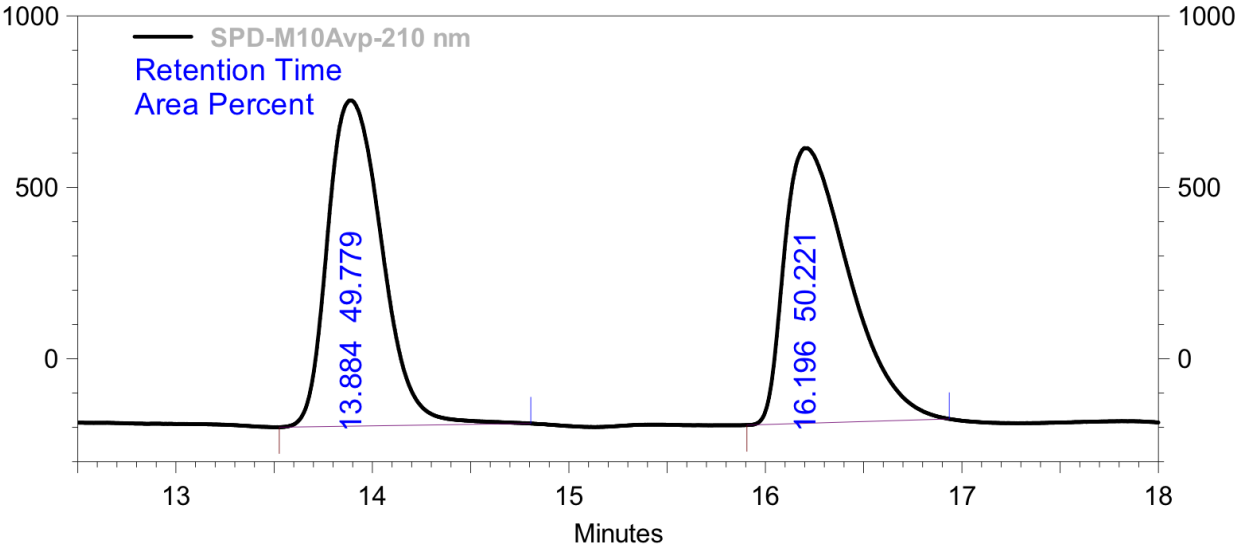

O
Me

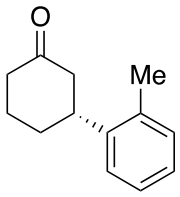

SPD-M10Avp-210 nm
Retention Time
Area Percent
mAu
500
250
0
18.152 97.401
19.264 2.599
17
18
19
20
21
Minutes

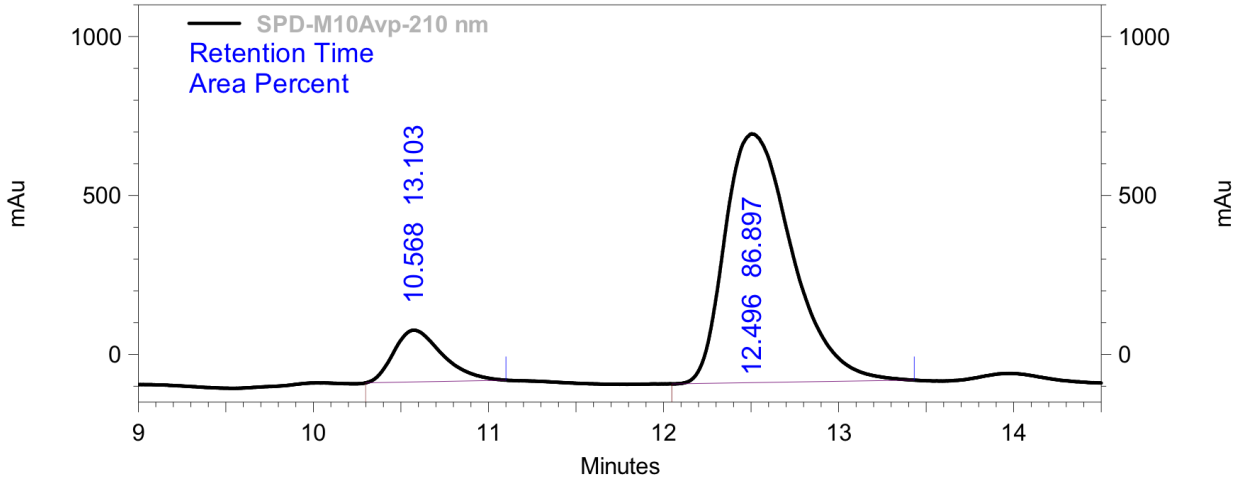

SPD-M10Avp-210 nm
Retention Time
Area Percent
mAu
500
250
0
18.160 50.131
19.248 49.869
17
18
19
20
21
Minutes

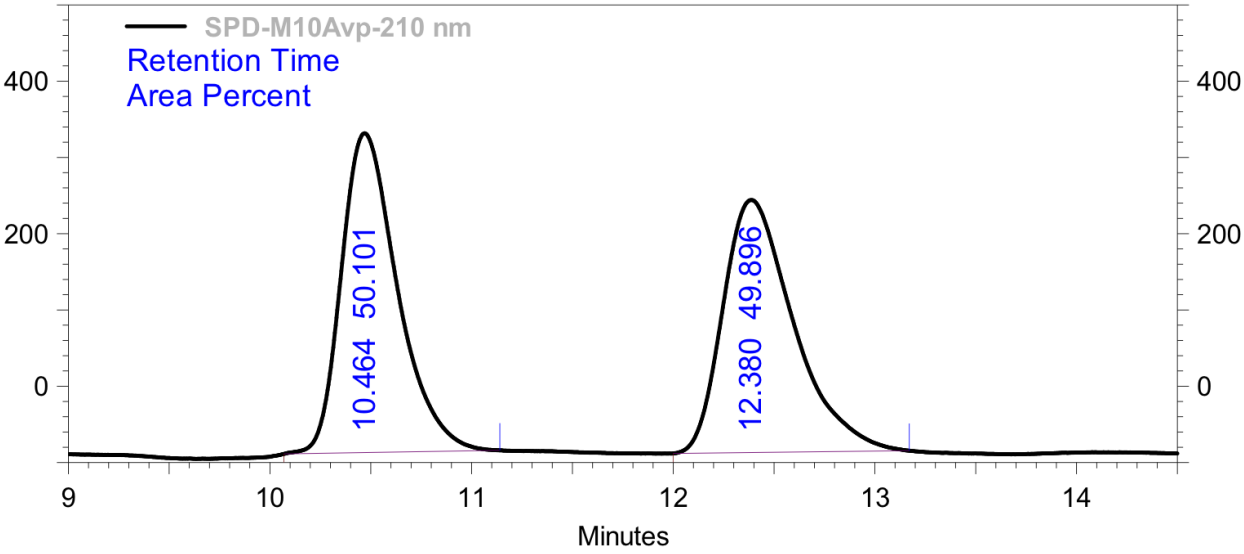

O
Me

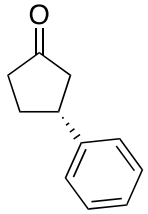

SPD-M10Avp-210 nm
Retention Time
Area Percent
13.688 2.944
15.892 97.056
mAu
1000
500
0
13
14
15
16
17
18
Minutes

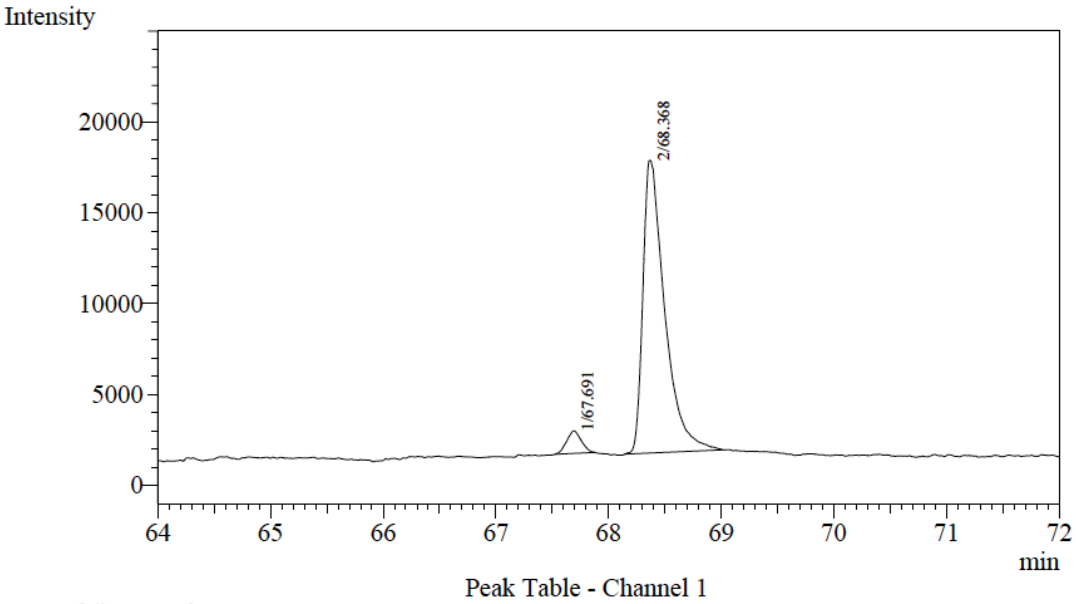

SPD-M10Avp-210 nm
Retention Time
Area Percent
13.884 49.779
16.196 50.221
1000
500
0
13
14
15
16
17
18
Minutes


O
Me


SPD-M10Avp-210 nm
Retention Time
Area Percent
10.568 13.103
12.496 86.897
mAu
1000
500
0
9
10
11
12
13
14
Minutes

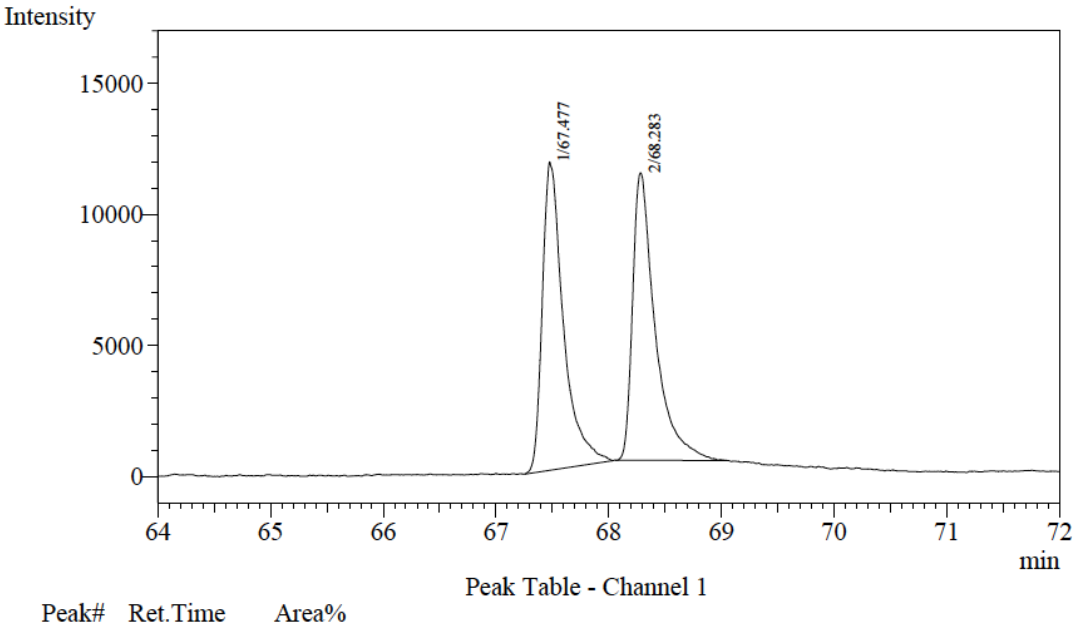

SPD-M10Avp-210 nm
Retention Time
Area Percent
10.464 50.101
12.380 49.896
400
200
0
9
10
11
12
13
14
Minutes





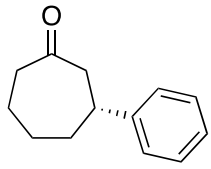
Peak Table - Channel 1

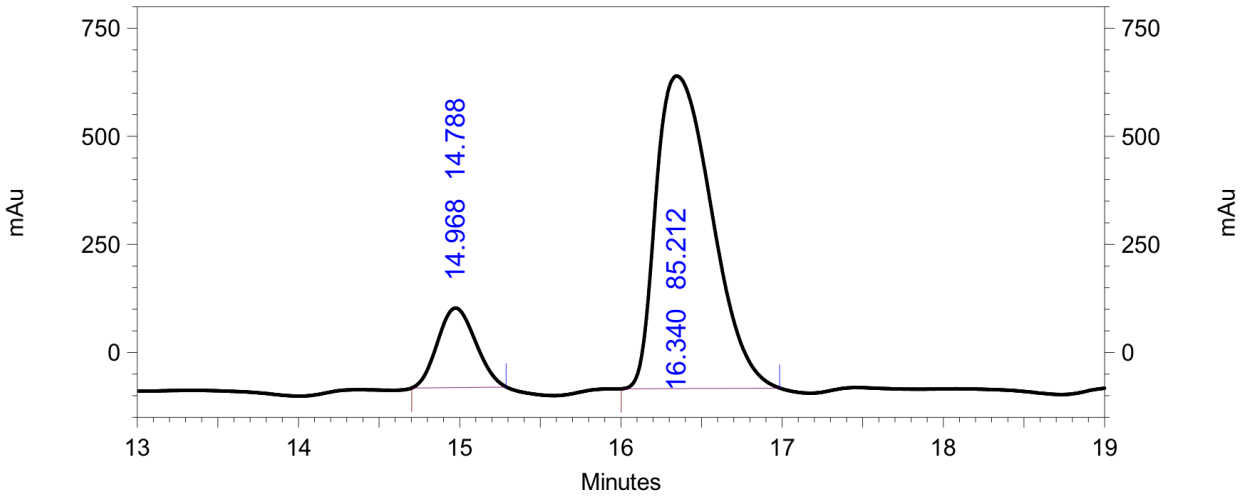
Peak#	Ret.Time	Area%
1	67.691	4.8960
2	68.368	95.1040
Total		100.0000

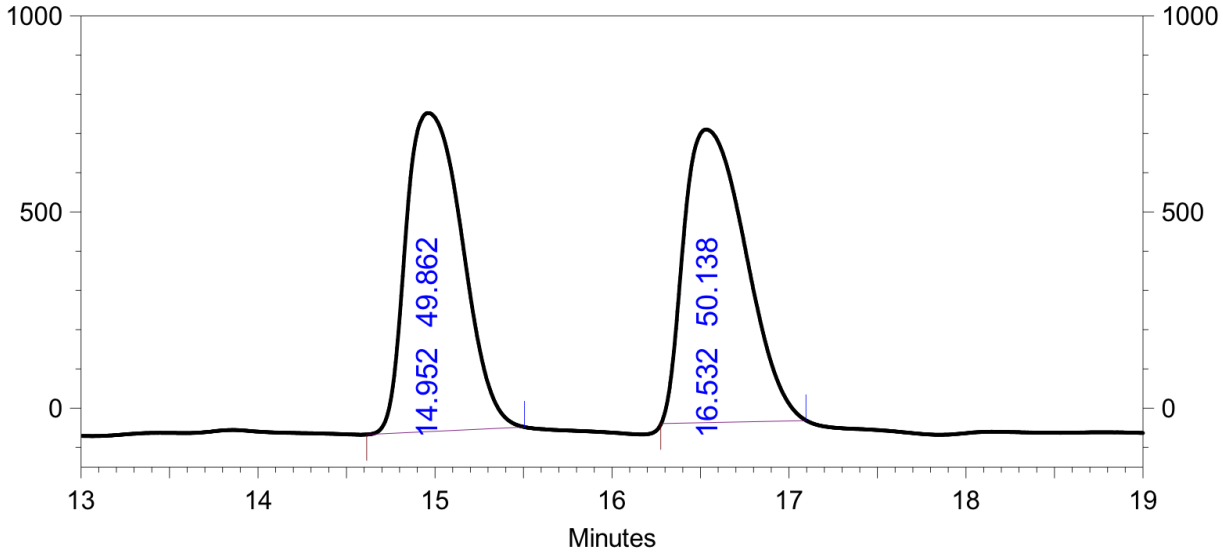


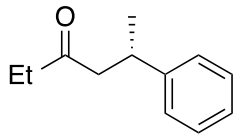
Peak Table - Channel 1

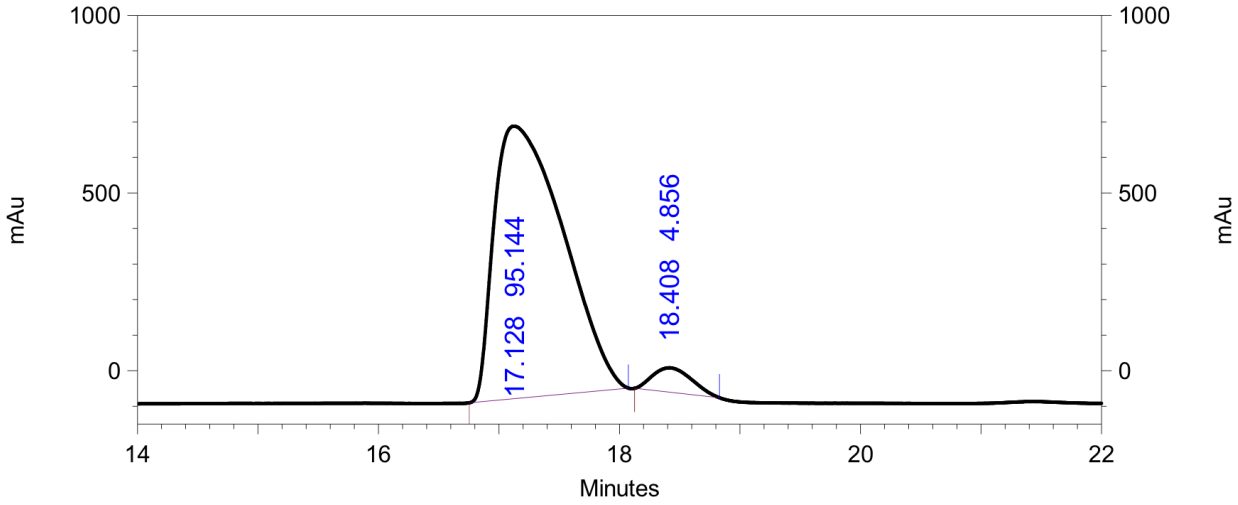
Peak#	Ret.Time	Area%
1	67.477	50.1613
2	68.283	49.8387
Total		100.0000

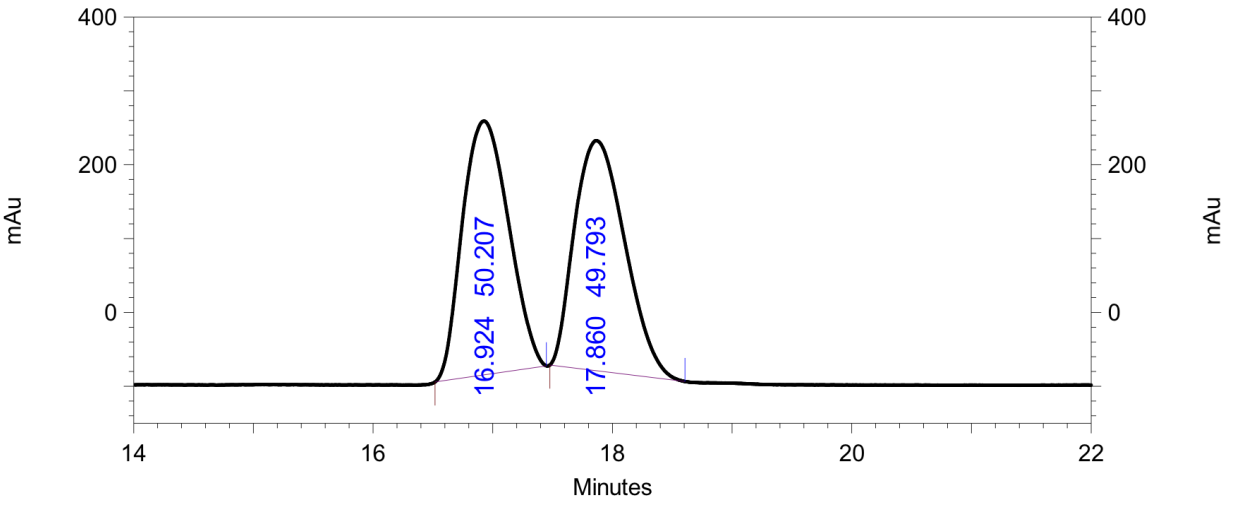

O

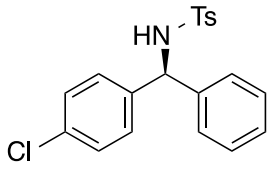

750
500
250
0
mAu
14.968 14.788
16.340 85.212
13
14
15
16
17
18
19
Minutes

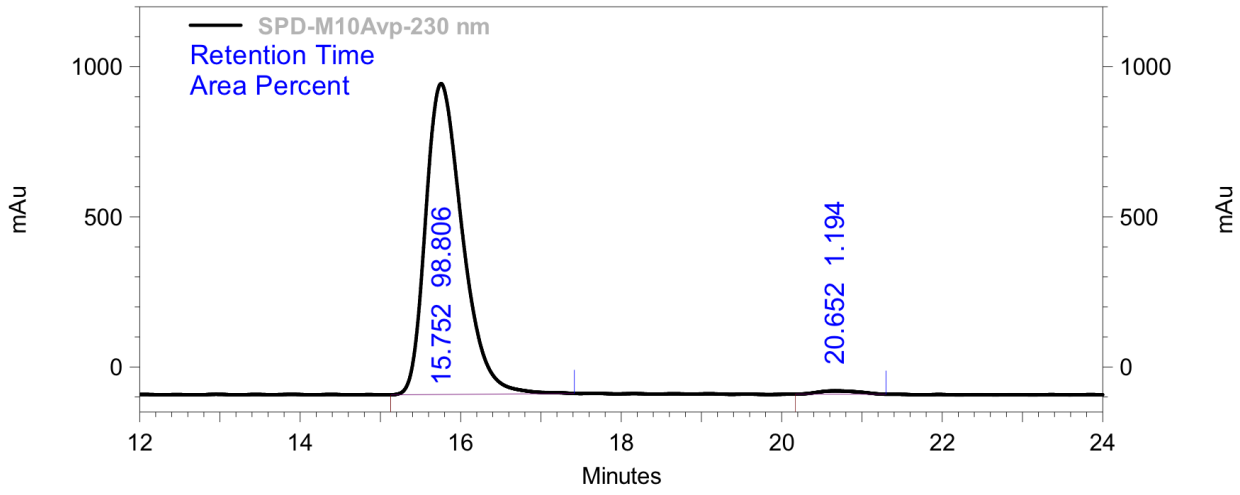

1000
500
0
14.952 49.862
16.532 50.138
13
14
15
16
17
18
19
Minutes

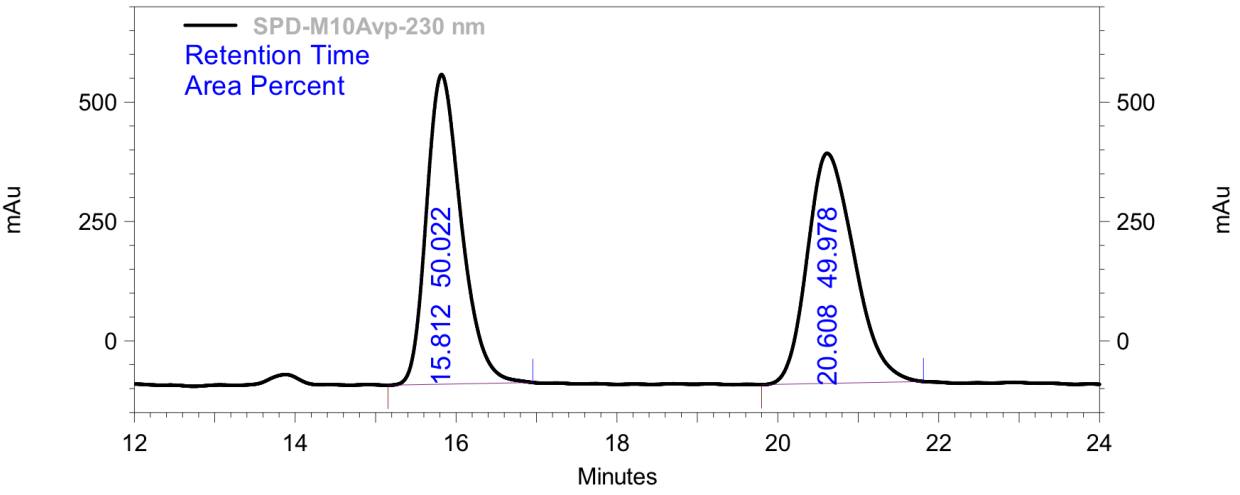

O
Et

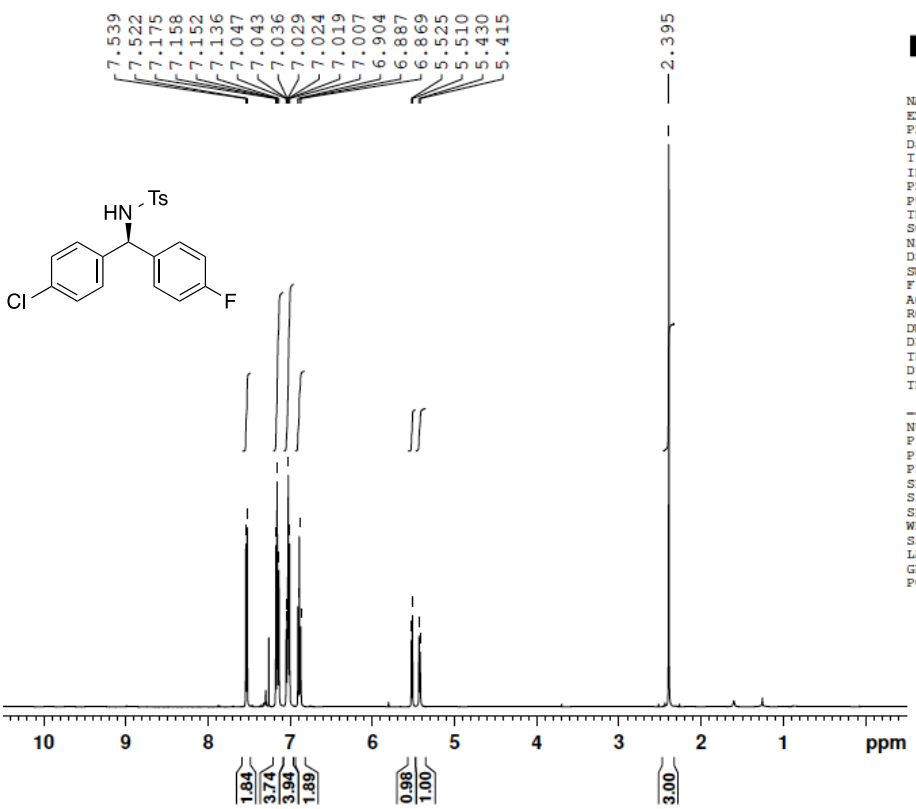

1000
500
0
mAu
17.128 95.144
18.408 4.856
14
16
18
20
22
Minutes


400
200
0
mAu
16.924 50.207
17.860 49.793
14
16
18
20
22
Minutes


HN
Ts
Cl


SPD-M10Avp-230 nm
Retention Time
Area Percent
15.752 98.806
20.652 1.194
mAu
Minutes

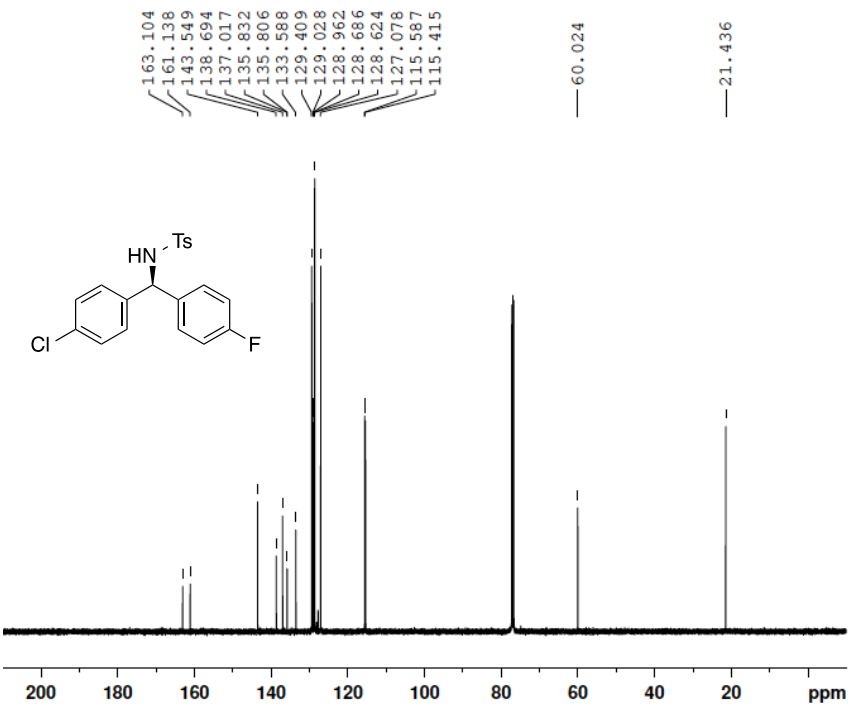

SPD-M10Avp-230 nm
Retention Time
Area Percent
15.812 50.022
20.608 49.978
mAu
Minutes



BRUKER

```
NAME                JPF-I-22
EXPNO                      1
PROCNO                     1
Date_               20141218
Time                   14.46
INSTRUM                spect
PROBHD    5 mm PAQNP 1H/
PULPROG                   zg
TD                     44998
SOLVENT                CDCl3
NS                        16
DS                         0
SWH                7500.000 Hz
FIDRES             0.166674 Hz
AQ                 2.9999166 sec
RG                       181
DW                    66.667 usec
DE                    71.43 usec
TE                    295.2 K
D1                 3.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.00 usec
PL1                     0.00 dB
PL1W              24.54113007 W
SFO1              500.1330008 MHz
SI                       16384
SF                500.1300135 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

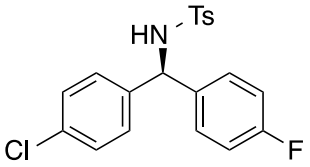


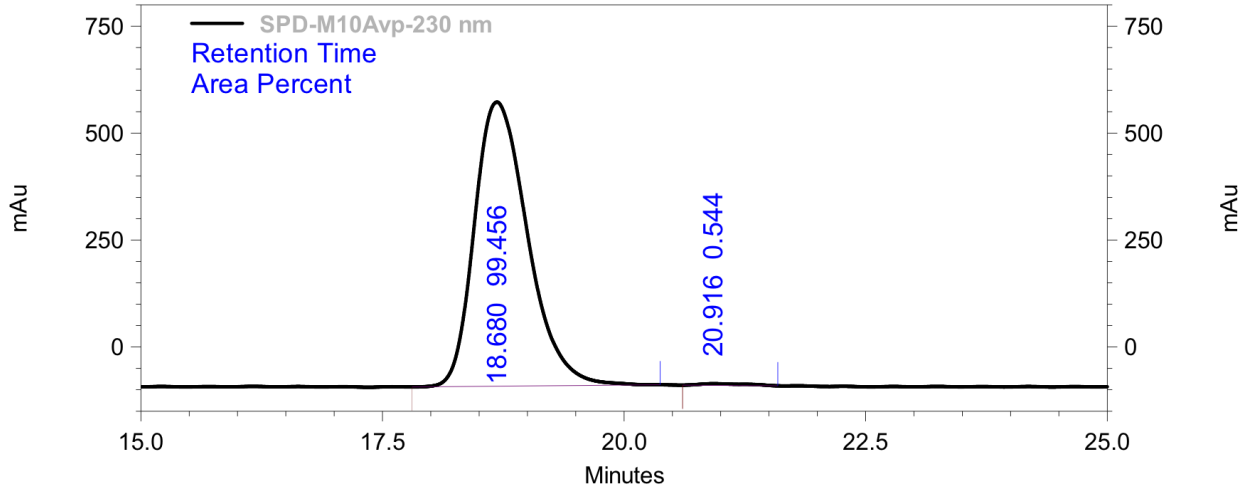
BRUKER

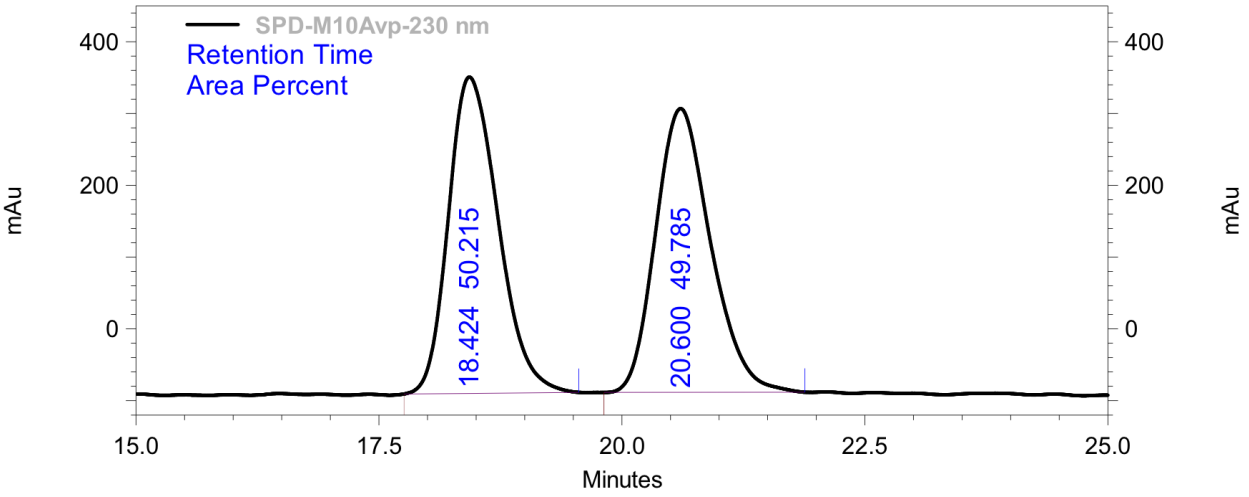
```
NAME           JPF-1-22-13C
EXPNO                     1
PROCNO                    1
Date_              20141218
Time                  22.29
INSTRUM               spect
PROBHD   5 mm PAQNP 1H/
PULPROG                zgpg
TD                   197364
SOLVENT               CDCl3
NS                      318
DS                        4
SWH               32894.738 Hz
FIDRES             0.166670 Hz
AQ                 2.9999828 sec
RG                     2050
DW                   15.200 usec
DE                     6.00 usec
TE                    296.1 K
D1                10.00000000 sec
D11                0.03000000 sec
TD0                       1

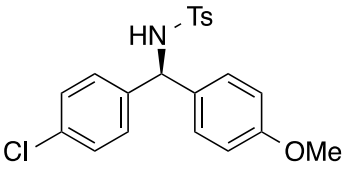
======== CHANNEL f1 ========
NUC1                     13C
P1                      8.00 usec
PL1                     1.00 dB
PL1W              72.42802429 W
SFO1             125.7716224 MHz

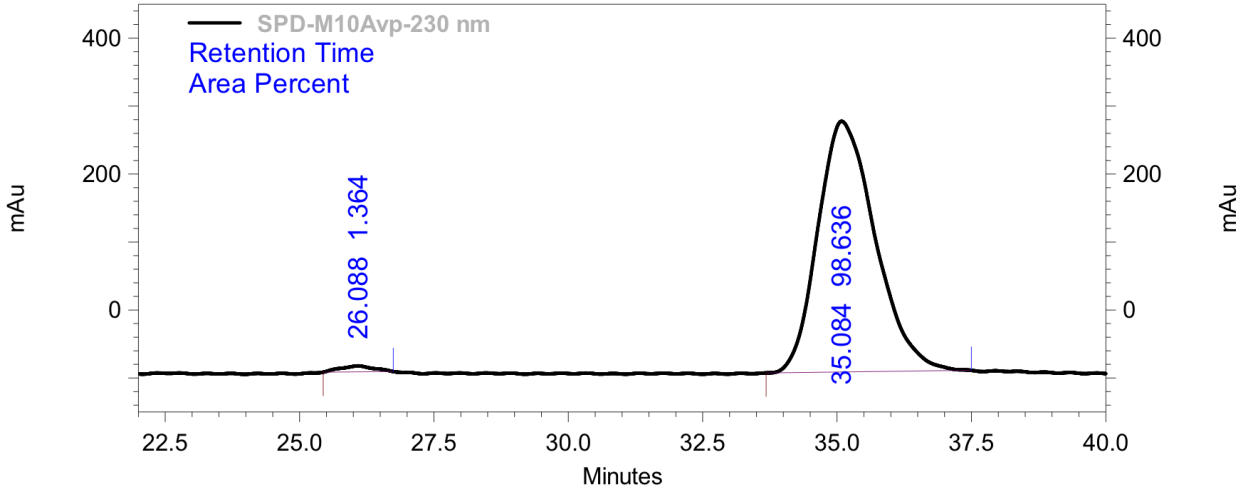
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   16.50 dB
PL13                   17.00 dB
PL2W              24.54113007 W
PL12W              0.54940748 W
PL13W              0.48965994 W
SFO2              500.1325006 MHz
SI                      131072
SF               125.7577982 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.40
```

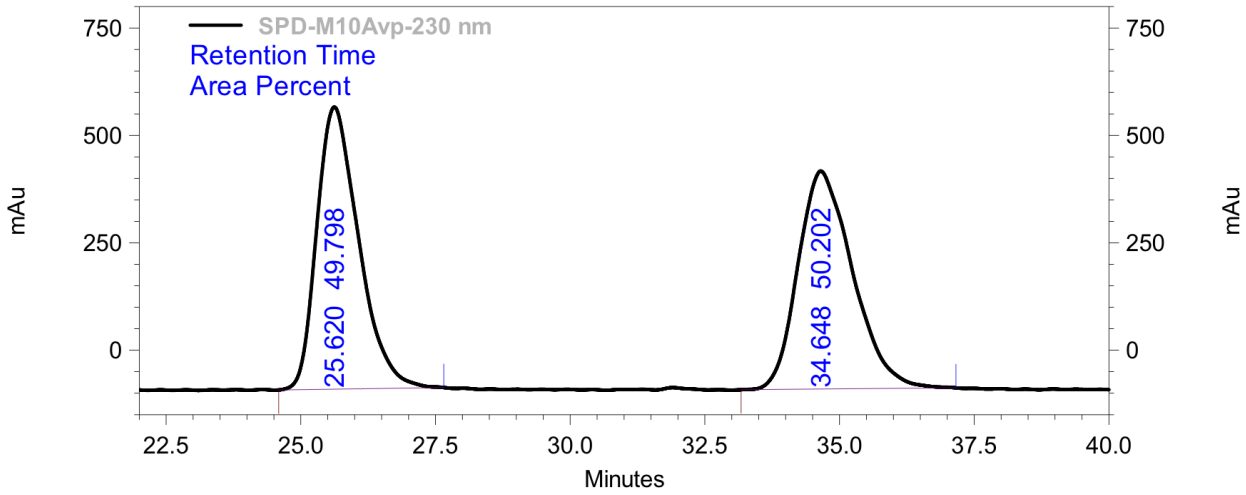

HN
Ts
Cl
F

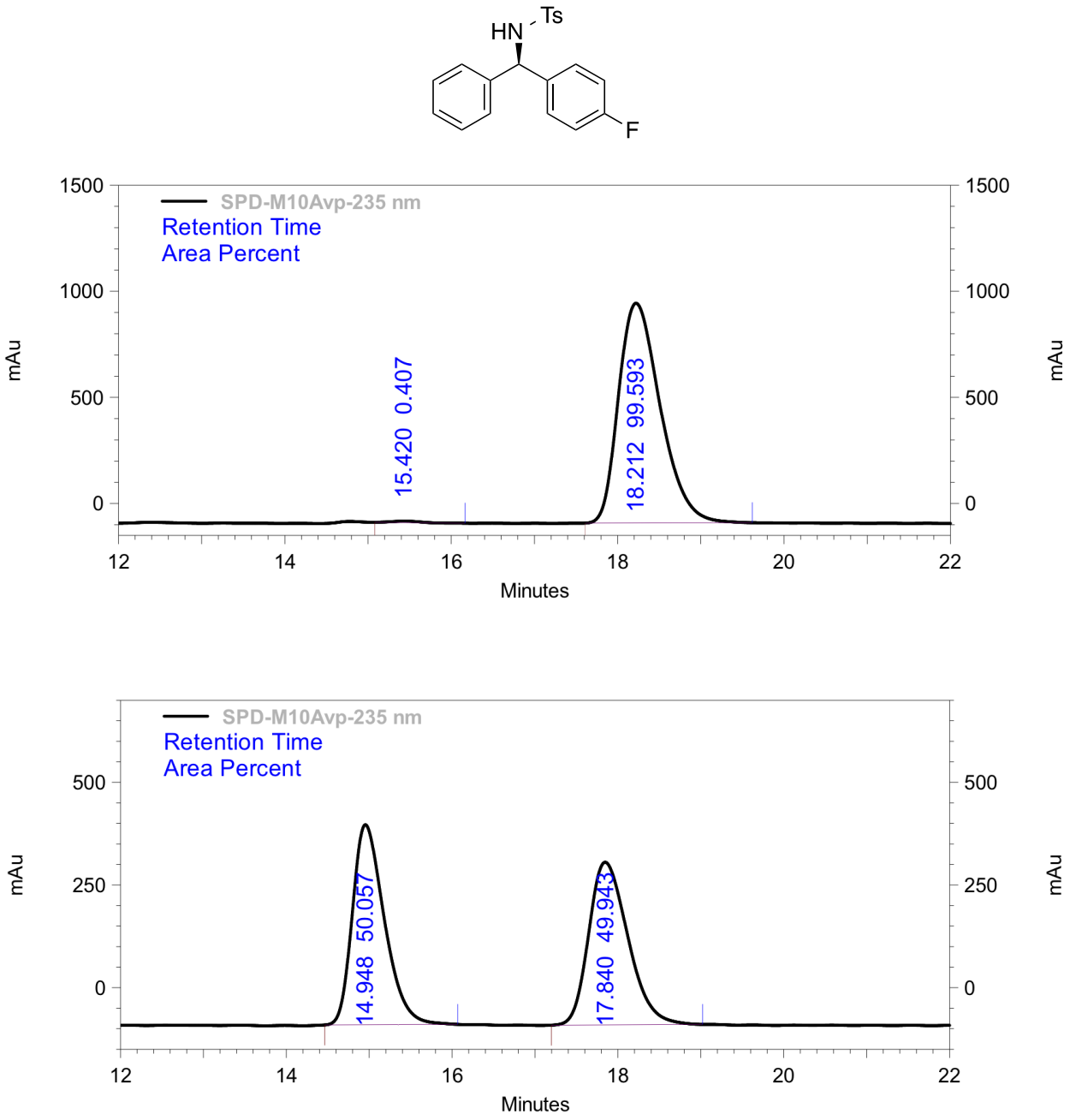

SPD-M10Avp-230 nm
Retention Time
Area Percent
18.680 99.456
20.916 0.544
mAu
Minutes
750
500
250
0
15.0
17.5
20.0
22.5
25.0

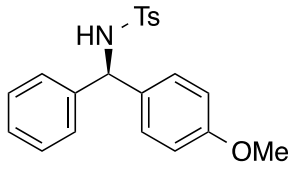

SPD-M10Avp-230 nm
Retention Time
Area Percent
18.424 50.215
20.600 49.785
mAu
Minutes
400
200
0
15.0
17.5
20.0
22.5
25.0

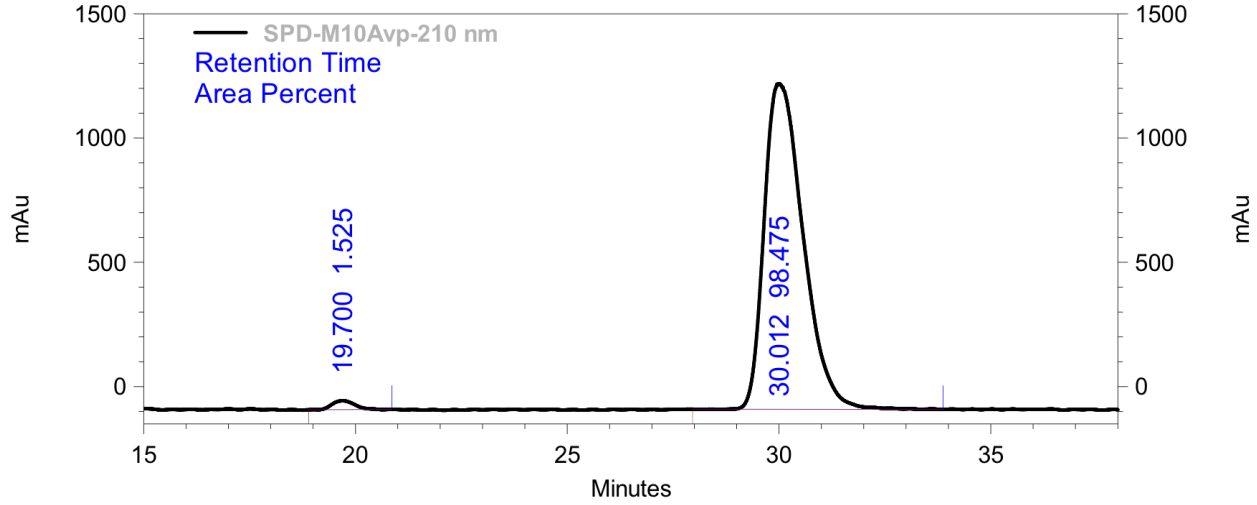

HN
Ts
Cl
OMe

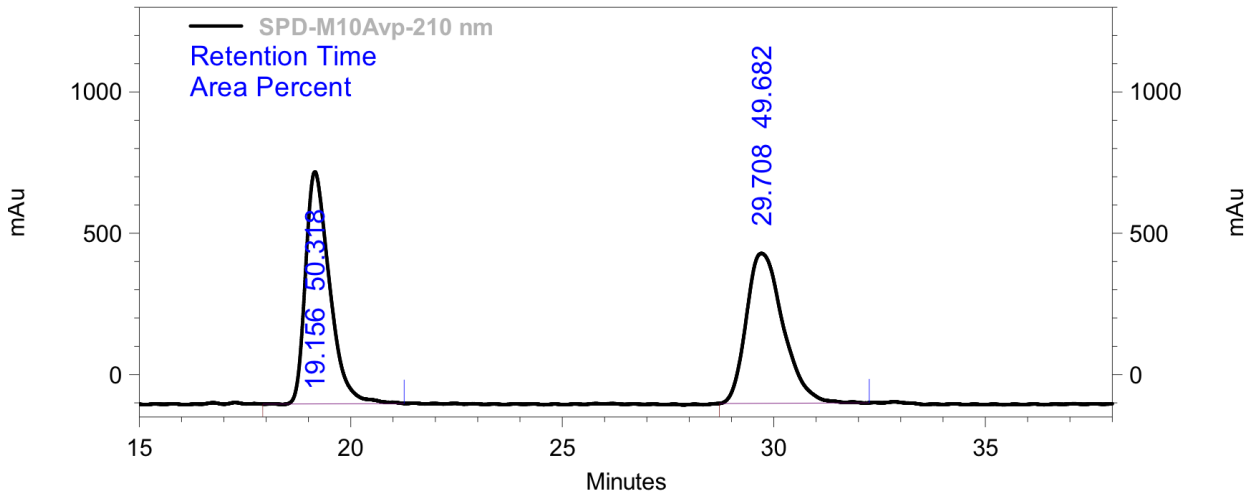

SPD-M10Avp-230 nm
Retention Time
Area Percent
26.088 1.364
35.084 98.636
mAu
Minutes
400
200
0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0

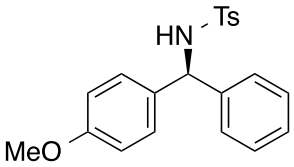

SPD-M10Avp-230 nm
Retention Time
Area Percent
25.620 49.798
34.648 50.202
mAu
Minutes
750
500
250
0
22.5
25.0
27.5
30.0
32.5
35.0
37.5
40.0

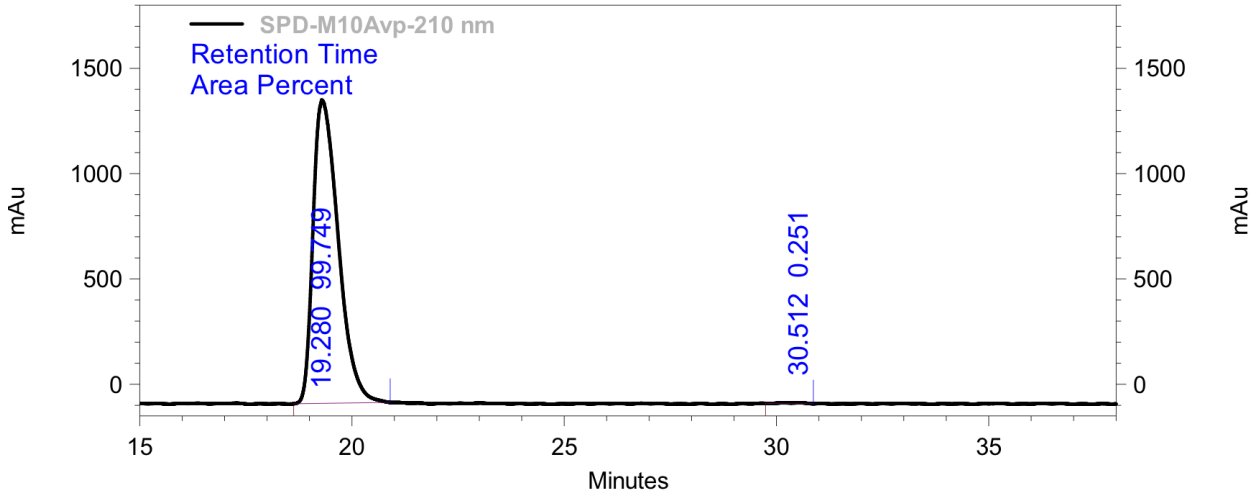

HN
Ts
F
SPD-M10Avp-235 nm
Retention Time
Area Percent
15.420 0.407
18.212 99.593
mAu
Minutes
SPD-M10Avp-235 nm
Retention Time
Area Percent
14.948 50.057
17.840 49.943
mAu
Minutes

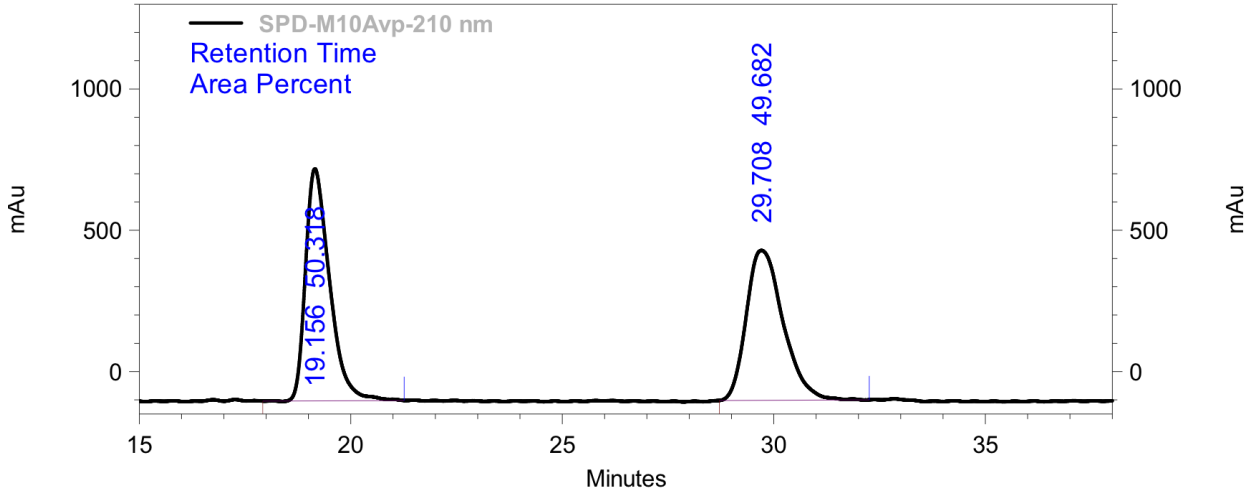

HN
Ts
OMe

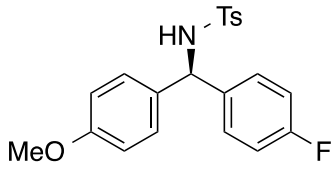

SPD-M10Avp-210 nm
Retention Time
Area Percent
19.700 1.525
30.012 98.475
mAu
Minutes
1500
1000
500
0
15
20
25
30
35

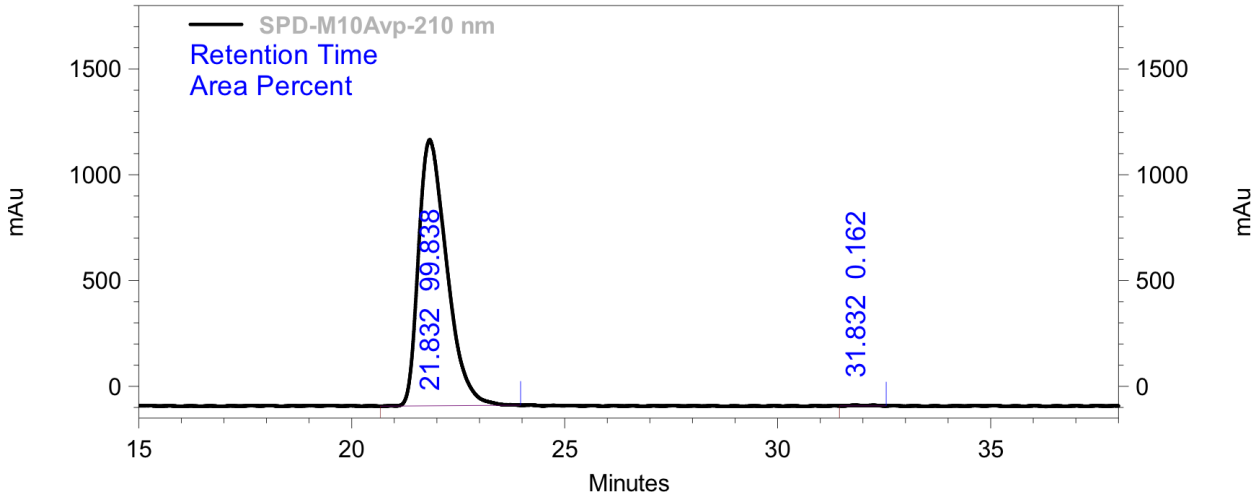

SPD-M10Avp-210 nm
Retention Time
Area Percent
19.156 50.318
29.708 49.682
mAu
Minutes
1000
500
0
15
20
25
30
35

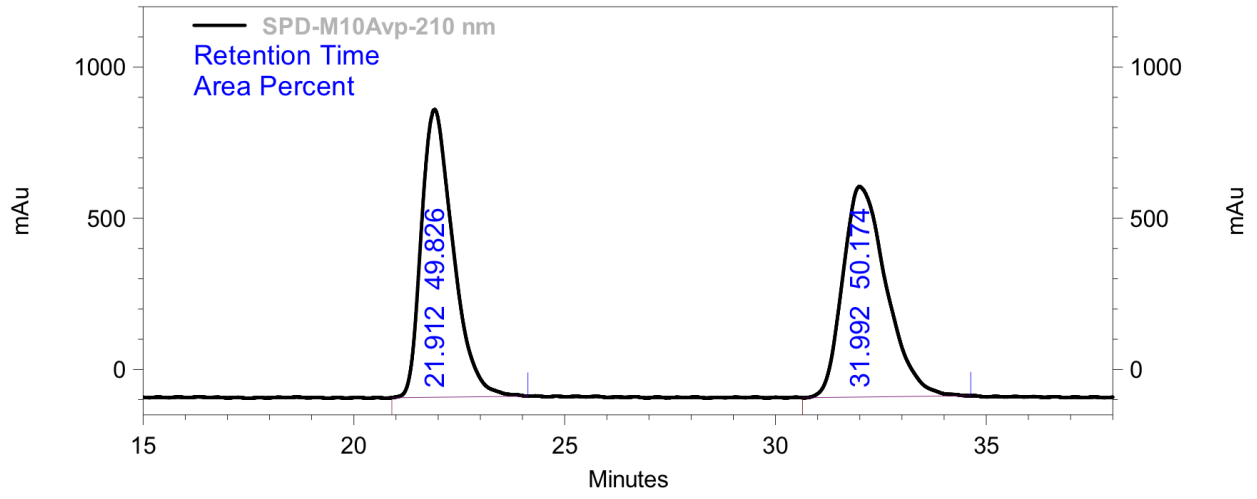

HN
Ts
MeO


SPD-M10Avp-210 nm
Retention Time
Area Percent
19.280 99.749
30.512 0.251
mAu
Minutes


SPD-M10Avp-210 nm
Retention Time
Area Percent
19.156 50.318
29.708 49.682
mAu
Minutes


HN
Ts
MeO
F


SPD-M10Avp-210 nm
Retention Time
Area Percent
21.832 99.838
31.832 0.162
mAu
Minutes


SPD-M10Avp-210 nm
Retention Time
Area Percent
21.912 49.826
31.992 50.174
mAu
Minutes

9. References

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