Supporting Information

Post-assembly Functionalization of Organoplatinum(II) Metallacycles via Copper-free Click Chemistry

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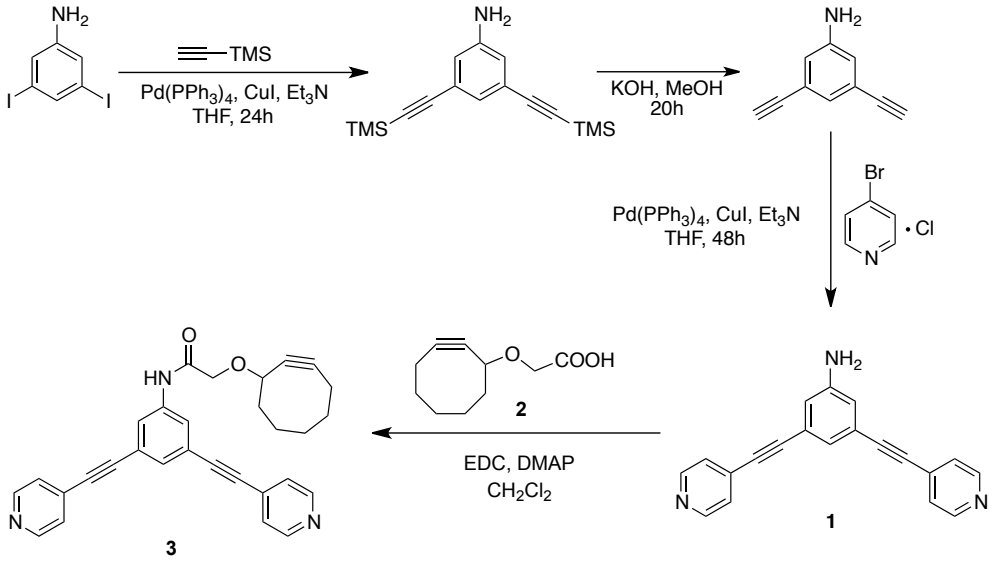
Materials and Methods: All chemicals were purchased from commercial sources and used without further purification. All solvents are dried over standard drying agents.[1] Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Thin layer chromatography (TLC) was performed on precoated silica gel plates (Merck silica gel 60 F_{254}). TLC spots were detected by a UV hand lamp at λ= 254 nm or λ= 366 nm or staining with $KMnO_4$ staining solution (3.0 g $KMnO_4$, 20 g K_2CO_3 in 300 mL 5% aqueous NaOH). 1-cyclooctyn-3-glycolic acid (**2**),[2] 1-(azidomethyl)pyrene[3] and 2-(azidoethyl)biotinamide,[4] 3,6-Bis-[*trans*-Pt$(PEt_3)_2(NO_3)_2$]phenanthrene (**4**)[5] and 4,4′-[*trans*-Pt$(PEt_3)_2(NO_3)_2$]diphenylketone (**5**),[6] were prepared according to the literature procedures.

NMR spectra were recorded on a Varian Unity 300 MHz and 500 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}P\{^1H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Mass spectra for the compounds and metallacycles were recorded on a Micromass Quattro II triple-quadruple mass spectrometer using electrospray ionization with a MassLynx operating system.

Synthesis of 120°-cyclooctyne tethered dipyridyl donor (3)

Synthesis of 120°-cyclooctyne tethered dipyridyl donor (3) is summarized in Scheme S1.



Scheme S1

3,5-diethynylaniline

A 100 mL Schlenk flask was charged with 3,5-diiodoaniline (3.44 g, 10.0 mmol), tetrakis(triphenylphosphine) palladium (1.15 g, 1.0 mmol, 10 mol%) and cuprous iodide (190.5 mg, 1.0 mmol, 10 mol%) under a stream of nitrogen. Freshly distilled THF (25 mL) and dry triethylamine (25 mL) were added to the flask via syringe, and the reaction

mixture was stirred for 24 h at 55 °C. The solvent was then evaporated, and the resulting residue was extracted with ethyl acetate over water. The organic phase was washed with water and dried over anhydrous $MgSO_4$. Purification by silica gel flash chromatography (Hexane : EtOAc 5 : 1; $R_f = 0.35$) yields 3,5-bis(trimethylsilylethynyl)aniline.

The solution of 3,5-bis(trimethylsilylethynyl)aniline in methanol (20 mL) in then cooled to 0 °C in an ice bath. A solution of KOH (2.24 g, 40 mmol in 10 ml Methanol) is then added dropwise. After the addition is complete, the reaction was stirred for 12 h at room temperature. The solvent was then evaporated, and the resulting residue was extracted with dichloromethane over water. Silica gel flash chromatography (Hexane : EtOAc 2 : 1; $R_f = 0.41$) gave brown needles of 3,5-diethynylaniline. Yield (overall): 1.07 g, 76%)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.03 (s, 1H, Ar*H*), 6.79 (d, 2H, Ar*H*), 3.81 (bs, 2H, NH_2), 3.02 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.4, 126.3, 123.3, 119.0, 83.1, 76.8. ESI-MS m/z = 142.06 $[M+H]^+$.

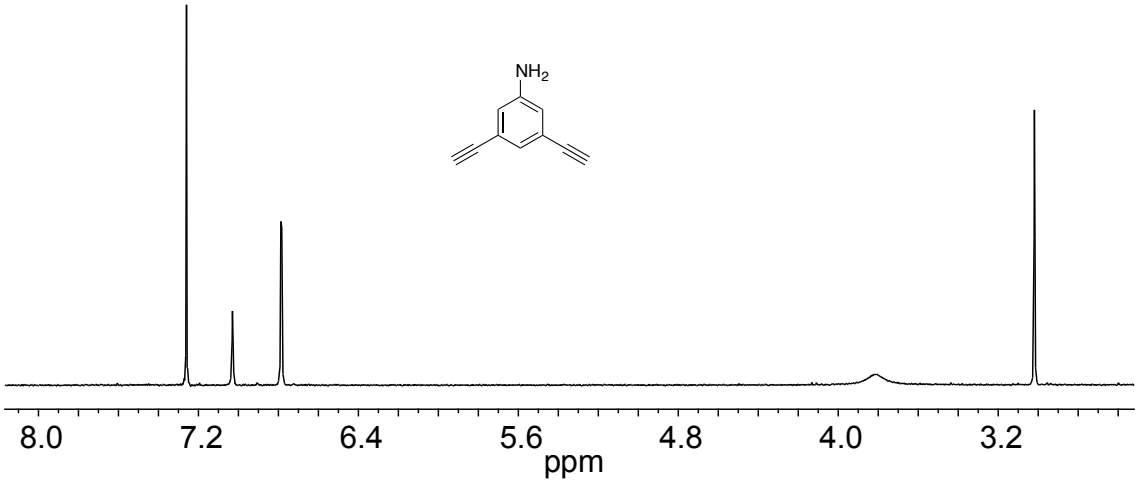


Figure S1. ^{1}H NMR (300 MHz) spectrum of 3,5-diethynylaniline in $CDCl_3$.

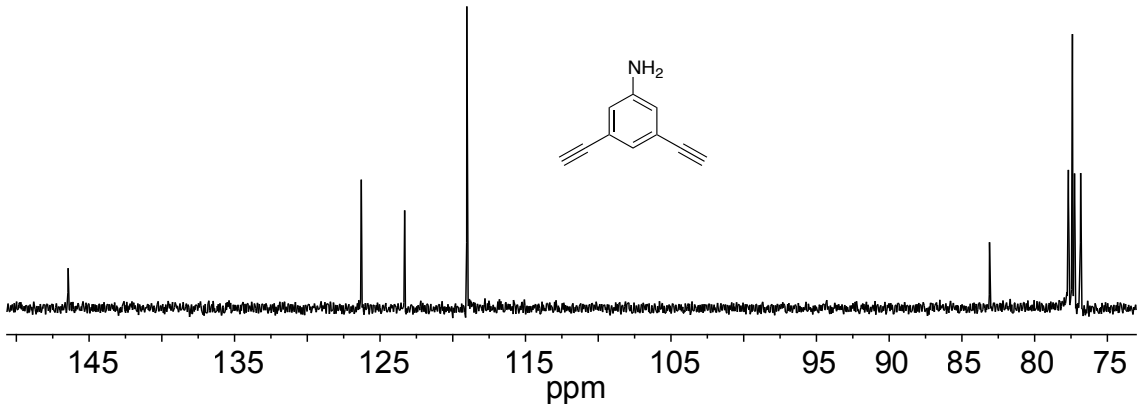


Figure S2. ^{13}C NMR (75 MHz) spectrum of 3,5-diethynylaniline in $CDCl_3$.

3,5-bis(4-pyridylethynyl)aniline (1)

3,5-diethynylaniline (705.9 mg, 5.0 mmol), tetrakis(triphenylphosphine) palladium (577.5 mg, 0.5 mmol, 10 mol%) and cuprous iodide (95.2 mg, 0.5 mmol, 10 mol%) were taken in 100 mL Schlenk flask under nitrogen. Freshly distilled THF (25 mL) and dry triethylamine (25 mL) were added to the flask via syringe, and the reaction mixture was stirred for 48 h at 55 °C. The solvent was then evaporated, and the resulting residue was extracted with ethyl acetate over water. The organic phase was washed with brine and dried over anhydrous $MgSO_4$. Purification by silica gel flash chromatography with ethyl acetate as eluent yields pale yellow powder of 3,5-bis(4-pyridylethynyl)aniline. Yield: 1.21 (82%).

^1H NMR (CD_2Cl_2, 500 MHz): δ 8.61 (d, 4H, Hα-Py), 7.40 (d, 4H), 7.15 (t, 1H), 6.91 (d, 2H, Hβ-Py), 3.94 (s, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 150.0, 147.3, 131.1, 125.6, 125.2, 123.5, 118.7, 92.9, 86.8. ESI-MS m/z = 296.2 $[M+H]^+$.

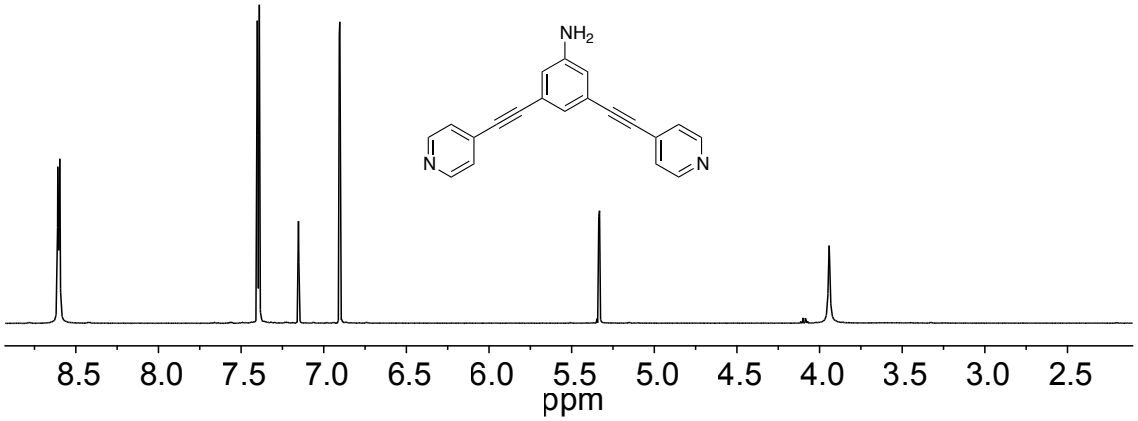


Figure S3. ^{1}H NMR (500 MHz) spectrum of 3,5-bis(4-pyridylethynyl)aniline (**1**) in CD_2Cl_2.

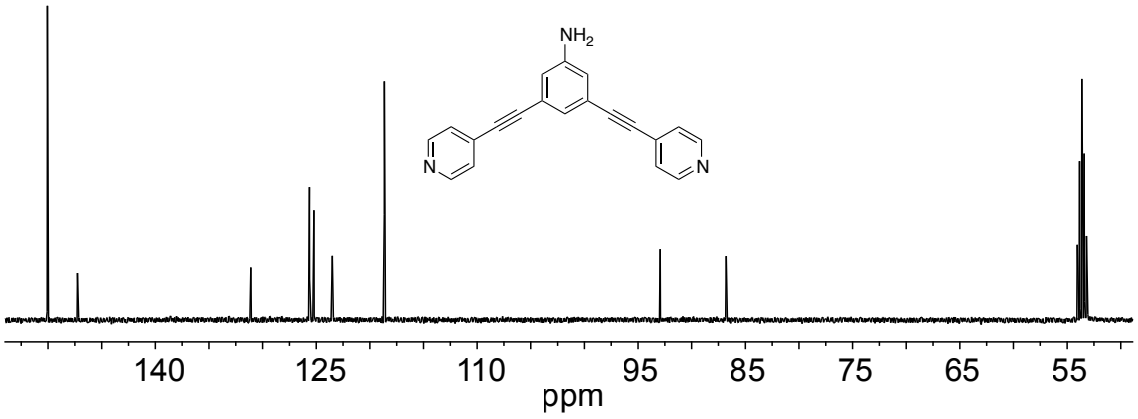


Figure S4. ^{13}C NMR (75 MHz) spectrum of 3,5-bis(4-pyridylethynyl)aniline (**1**) in CD_2Cl_2.

120°-cyclooctyne tethered dipyridyl donor (3)

A 25 mL Schlenk flask was charged with 3,5-bis(4-pyridylethynyl)aniline **1** (177.2 mg, 0.6 mmol), 1-cyclooctyn-3-glycolic acid **2** (91.1 mg, 0.5 mmol), EDC (143.7 mg, 0.75 mmol), DMAP (61.1 mg; 0.5 mmol) under nitrogen and then 10 mL of distilled dichloromethane was added and the reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was then quenched with water and the organic phase was extracted with dichloromethane and dried over $MgSO_4$. Purification by silica gel flash chromatography with eluent (EtOAc : methanol 10 : 1; R_f = 0.68) provided the desired compound **3**. Yield: mg (35%).

^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.62 (d, 4H, Hα-Py), 8.39 (s, 1H, N*H*$_2$), 7.86 (d, 2H, Ar*H*), 7.53 (t, 1H, Ar*H*), 7.42 (d, 4H, Hβ-Py), 4.37 (m, 1H), 4.20 (d, 1H, *J* = 15.3 Hz), 4.05 (d, 1H, *J* = 15.3 Hz), 2.04-2.34 (m, 4H), 1.78-1.98 (m, 3H), 1.67-1.74 (m, 2H), 1.54 (m, 1H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 168.1, 150.1, 138.2, 130.8, 125.7, 123.4, 102.5, 92.2, 91.0, 87.7, 73.8, 68.6, 42.4, 34.5, 29.8, 26.5, 20.8. ESI-MS m/z = 460.2 $[M+H]^+$.

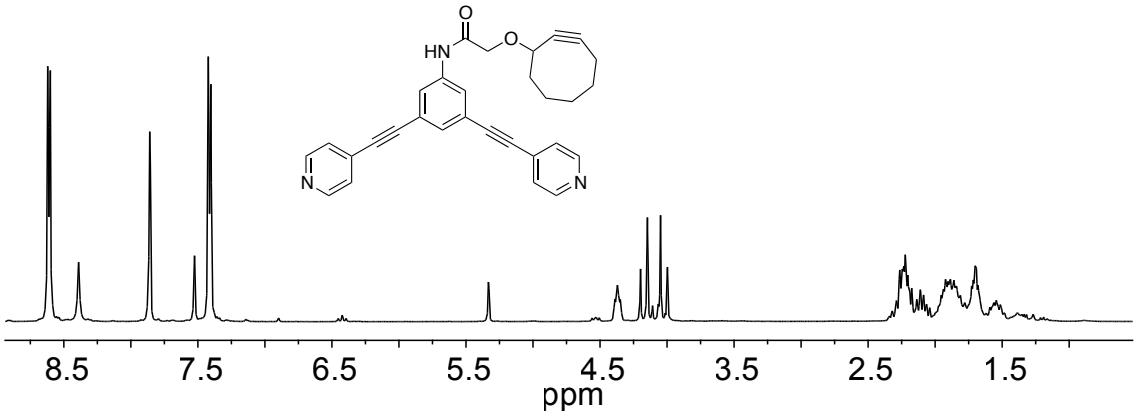


Figure S5. ^{1}H NMR (300 MHz) spectrum of 120°-cyclooctyne tethered dipyridyl donor (**3**) in CD_2Cl_2.

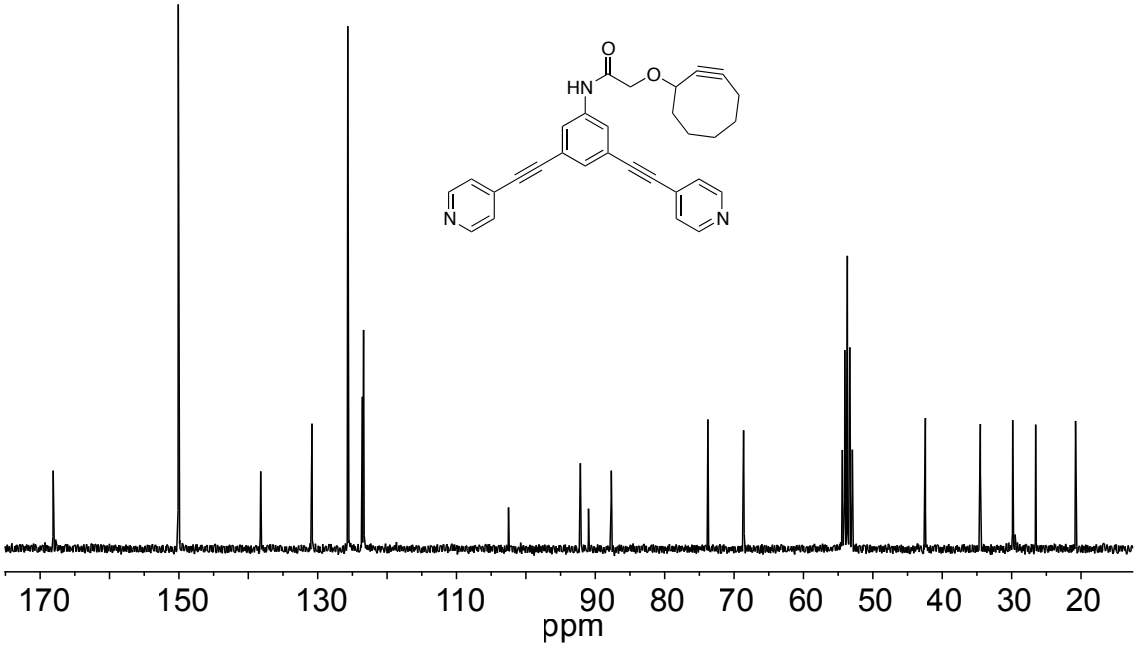


Figure S6. ^{13}C NMR (75 MHz) spectrum of 120°-cyclooctyne tethered dipyridyl donor (**3**) in CD_2Cl_2.

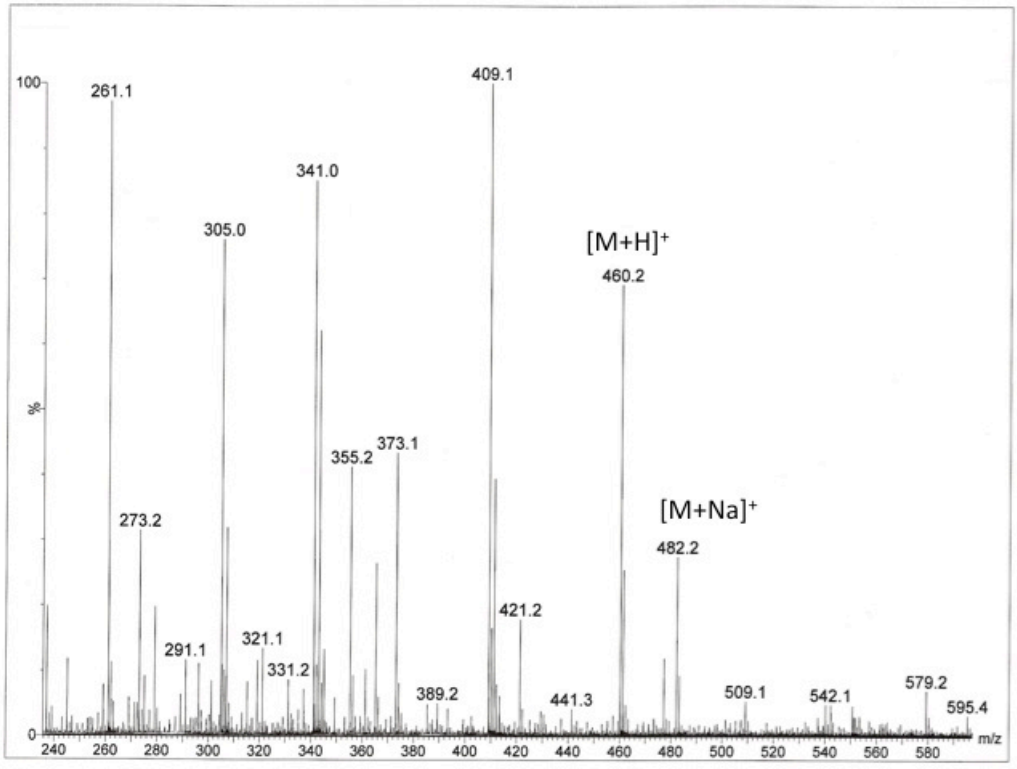


Figure S7. ESI-MS spectrum of 120°-cyclooctyne tethered dipyridyl donor (**3**).

Self-assembly of Rhomboid 6

In a 1: 1 molar ratio, 120°-cyclooctyne tethered dipyridyl donor **3** (1.69 mg, 0.0037 mmol) and 3,6-Bis-[*trans*-Pt(PEt_3)$_2$(NO_3)$_2$]phenanthrene **4** (4.27 mg, 0.0037) were dissolved in 1.0 mL of CD_2Cl_2 in a 2 dram vial. The reaction mixture was allowed to stir for 8 h at room temperature. To the resulting homogeneous solution, diethyl ether was added to precipitate the product, which was then isolated and dried under reduced pressure and re-dissolved in CD_2Cl_2 for characterization.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ 9.40 (d, 4H, Hα'-Py, J = 5.4 Hz), 9.16 (s, 2H, -C(O)N*H*), 8.87 (s, 4H, Phen*H*), 8.68 (d, 4H, Hα''-Py, *J* = 5.4 Hz), 8.16 (s, 4H, Ar*H*), 7.95 (d, 4H, Hβ'-Py, *J* = 5.4 Hz), 7.80 (d, 4H, Hβ''-Py, *J* = 5.4 Hz), 7.75 (s, 2H, Ar*H*), 7.60 (d, 12H, Phen*H*, *J* = 5.1 Hz), 4.43 (m, 2H), 4.27 (d, 2H, *J* = 15.0 Hz), 4.13 (d, 2H, *J* = 15.0 Hz), 2.07-2.34 (m, 8H), 1.80-1.98 (m, 6H), 1.67-1.72 (m, 4H), 1.55 (m, 2H), 1.34 (m, 16H, PC*H*$_2$CH$_3$), 1.13-1.20 (m, 24H, PCH$_2$C*H*$_3$) ppm. ^{31}P {^{1}H} NMR (CD_2Cl_2, 121.4 MHz) δ 12.7 ppm (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2709 Hz). ESI-MS ($C_{136}H_{186}N_{10}O_{16}P_8Pt_4$) m/z [**6** – 2$NO_3$]$^{2+}$ 1560.5; [**6** – 3NO_3]$^{3+}$ 1019.02.

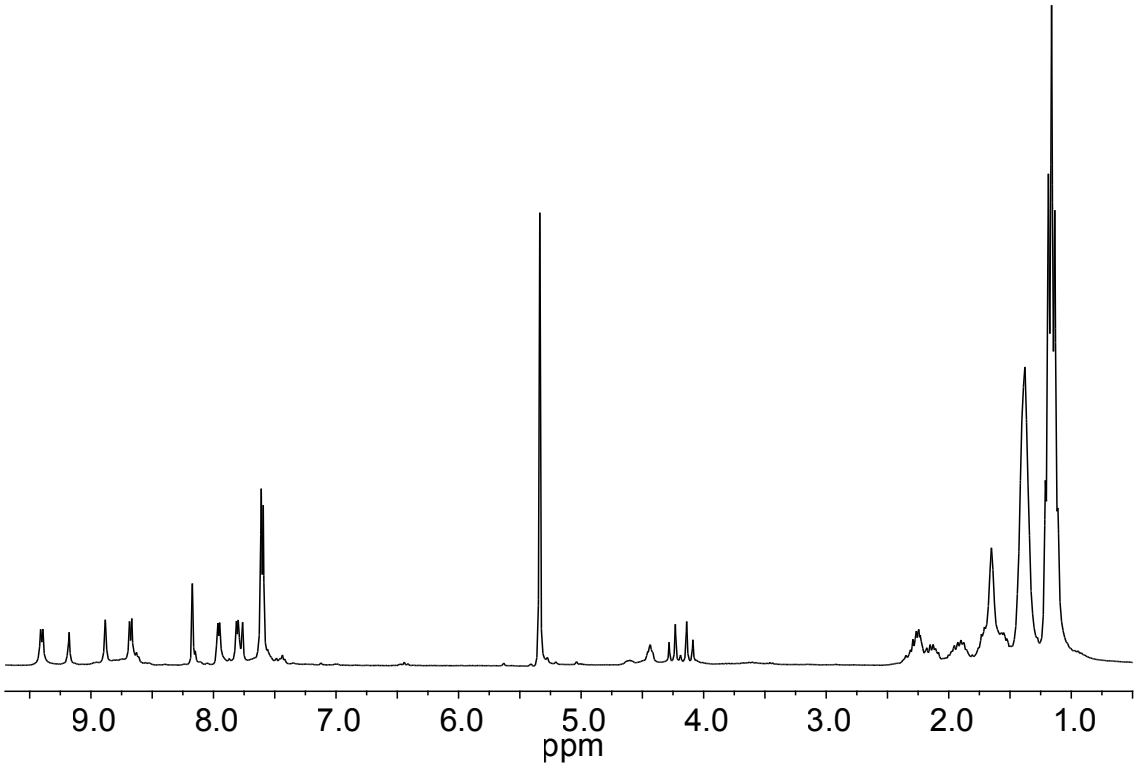


Figure S8. ^{1}H NMR (300 MHz) spectrum of rhomboid **6** in CD_2Cl_2.

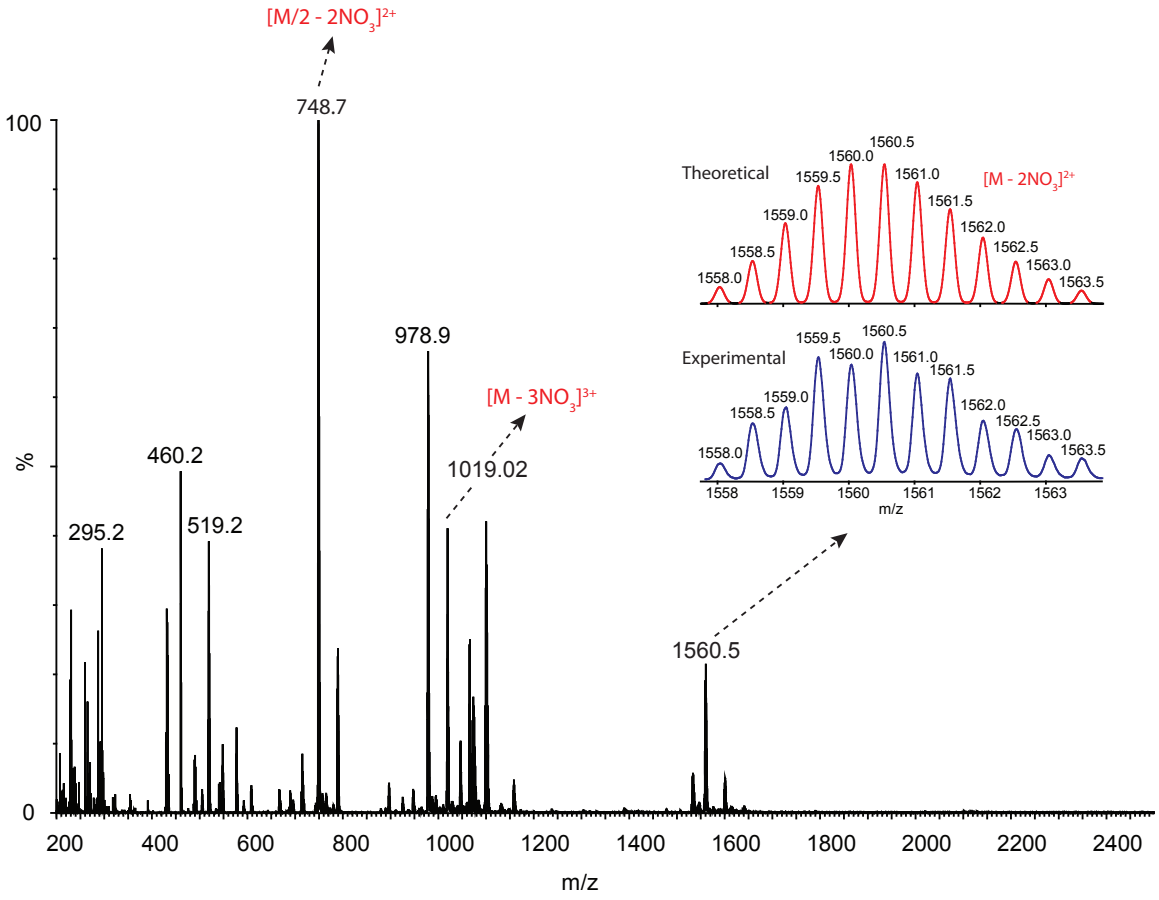


Figure S9. ESI-MS spectrum of rhomboid **6**.

Self-assembly of Hexagon 7

120°-cyclooctyne tethered dipyridyl donor **3** (1.09 mg, 0.0024 mmol) and 4,4′-[*trans*-Pt(PEt$_3$)$_2$(NO$_3$)$_2$]diphenylketone **5** (2.77 mg, 0.0024) were dissolved in 1.0 mL of CD_3OD in a 2 dram vial and the reaction mixture was stirred for 8 h at room temperature. The product was precipitated out with diethyl ether, isolated and dried under reduced pressure and re-dissolved in CD_3OD for characterization.

^{1}H NMR (CD_3OD, 300 MHz): δ 8.90 (d, 12H, Hα-Py, J = 5.7 Hz), 8.07 (s, 6H, Ar*H*), 7.87 (d, 12H, Hβ-Py, *J* = 5.7 Hz), 7.69 (d, 12H, Ar*H*, *J* = 8.1 Hz), 7.54 (s, 3H, Ar*H*), 7.51 (d, 12H, Ar*H*, *J* = 8.0 Hz), 4.43 (m, 3H), 4.23 (d, 3H, *J* = 12.0 Hz), 4.14 (d, 3H, *J* = 15.0 Hz), 2.07-2.32 (m, 12H), 1.80-1.98 (m, 9H), 1.68-1.76 (m, 6H), 1.55 (m, 3H), 1.43 (m, 24H, PC*H*$_2$CH$_3$), 1.13-1.24 (m, 36H, PCH$_2$C*H*$_3$) ppm. ^{31}P {^{1}H} NMR (CD_3OD, 121.4 MHz) δ 14.1 ppm (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2634 Hz). ESI-MS ($C_{201}H_{279}N_{15}O_{27}P_{12}Pt_6$) m/z [{2(**3**) + 2(**4**)} – 3NO$_3$]$^{3+}$ 1021.2, [{2(**3**) + 1(**4**)} – 2NO$_3$]$^{2+}$ 980.5; [M/2 – 2NO$_3$]$^{2+}$ 750.8.

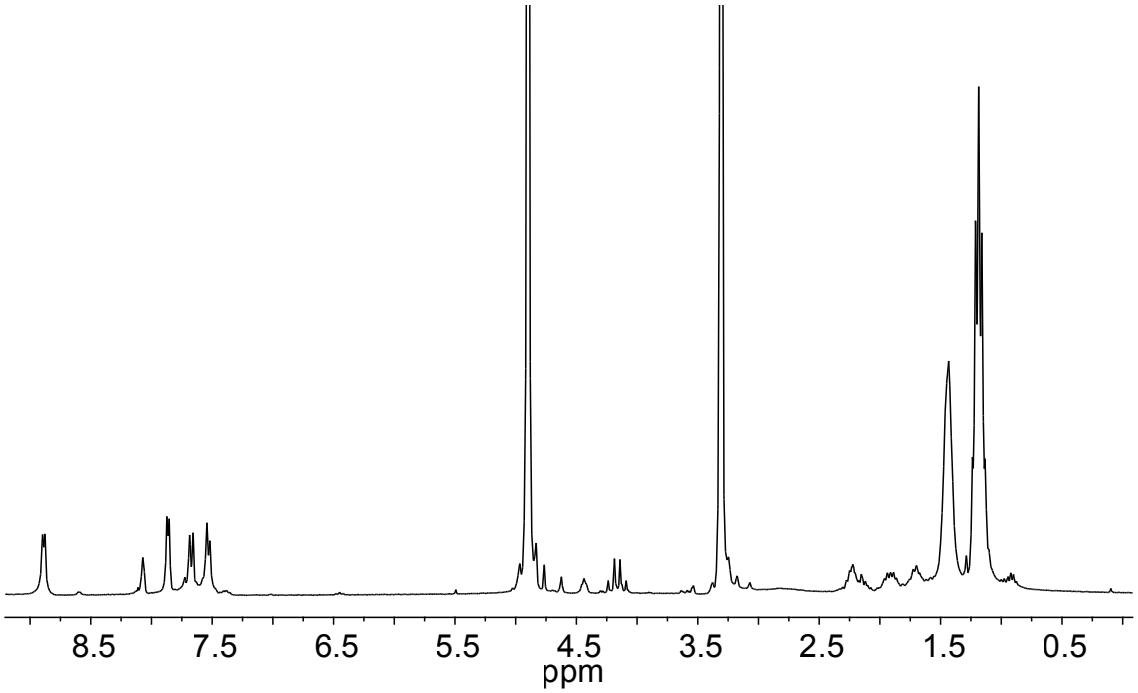


Figure S10. ^{1}H NMR (300 MHz) spectrum of hexagon **7** in CD_3OD.

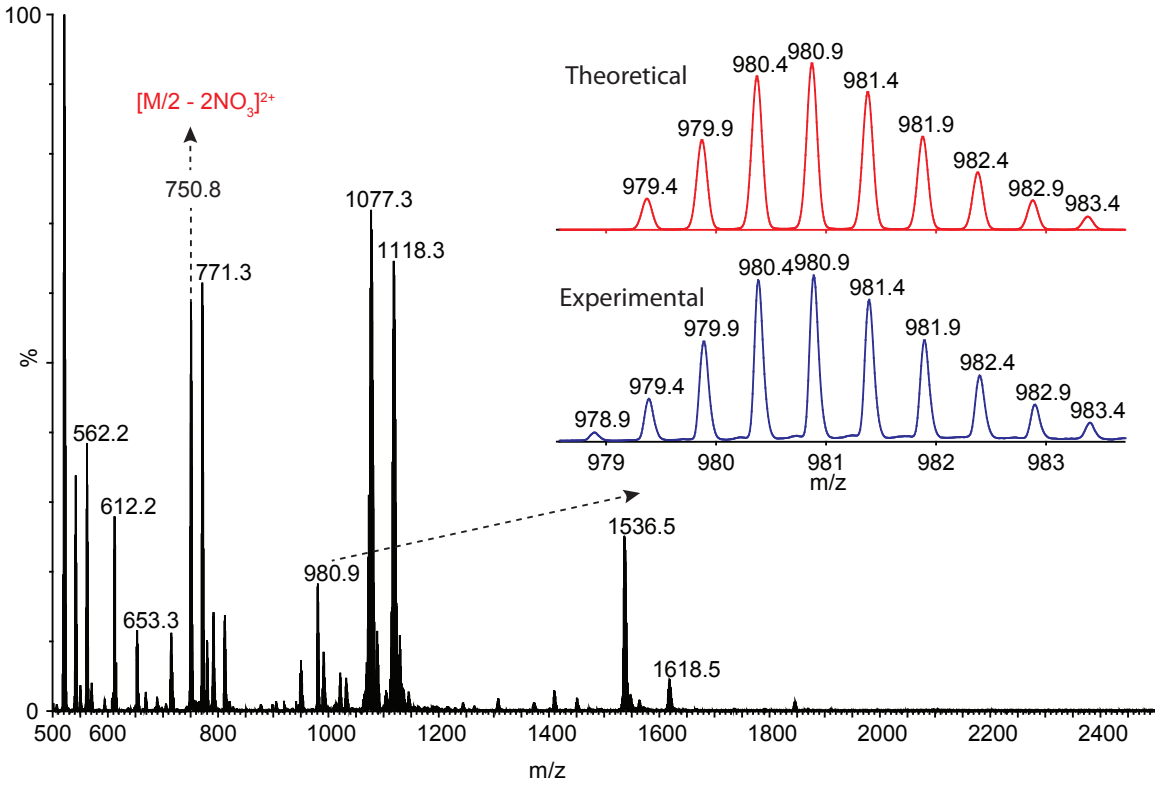


Figure S11. ESI-MS spectrum of hexagon **7**.

General procedure for the post-assembly modification of rhomboid 6 via with different azides via copper-free click chemistry

In a 1:1 stoichiometric fashion, rhomboid **6** and azide (benzyl azide for **8a**, 1-(azidomethyl)pyrene for **8b**, 2-(azidoethyl)biotinamide for **8c**) were dissolved in CD_2Cl_2 in a 2 dram vial. The reaction mixture is stirred at room temperature for 2 h. The product was precipitated out by addition of diethyl ether to the homogeneous reaction mixture. Isolated product was dried under reduced pressure and re-dissolved in CD_2Cl_2.

8a: ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.70 (s, 2H, C(O)N*H*), 9.43 (d, 4H, Hα'-Py, J = 5.7 Hz), 8.88 (s, 4H, Phen*H*), 8.68 (d, 4H, Hα''-Py, J = 5.4 Hz), 8.31 (s, 4H, Ar*H*), 7.99 (d, 4H, Hβ'-Py, J = 5.4 Hz), 7.80 (d, 4H, Hβ''-Py, J = 5.4 Hz), 7.78 (s, 2H, Ar*H*), 7.61 (d, 12H, Phen*H*, J = 4.5 Hz), 7.35-7.45 (m, 8H), 7.23 (d, 2H, Ar*H*, J = 6.0 Hz), 5.61 (s, 4H, CH_2-benzyl), 4.49 (m, 2H), 4.37 (d, 2H, J = 15.9 Hz), 4.22 (d, 2H, J = 15.9 Hz), 2.07-2.34 (m, 8H), 1.80-1.98 (m, 6H), 1.67-1.72 (m, 4H), 1.55 (m, 2H), 1.38 (m, 16H, PCH_2CH$_3$), 1.13-1.19 (m, 24H, PCH$_2$CH_3) ppm. ^{31}P {^{1}H} NMR (CD_2Cl_2, 121.4 MHz) δ 12.7 ppm (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2709 Hz). ESI-MS ($C_{136}H_{186}N_{10}O_{16}P_8Pt_4$) m/z [**6** – 2$NO_3$]$^{2+}$ 1560.5; [**6** – 3NO_3]$^{3+}$ 1019.02.

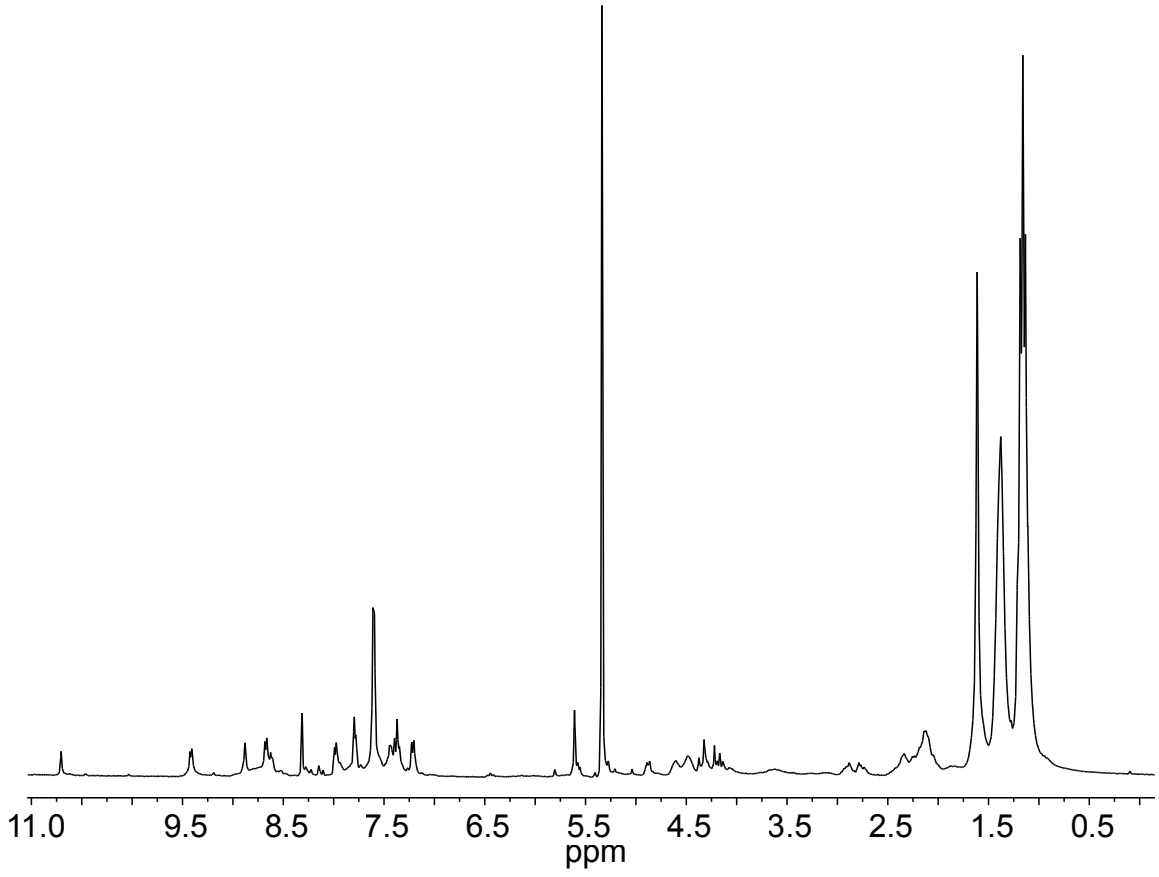


Figure S12. ^{1}H NMR (300 MHz) spectrum of rhomboid **8a** in CD_2Cl_2.

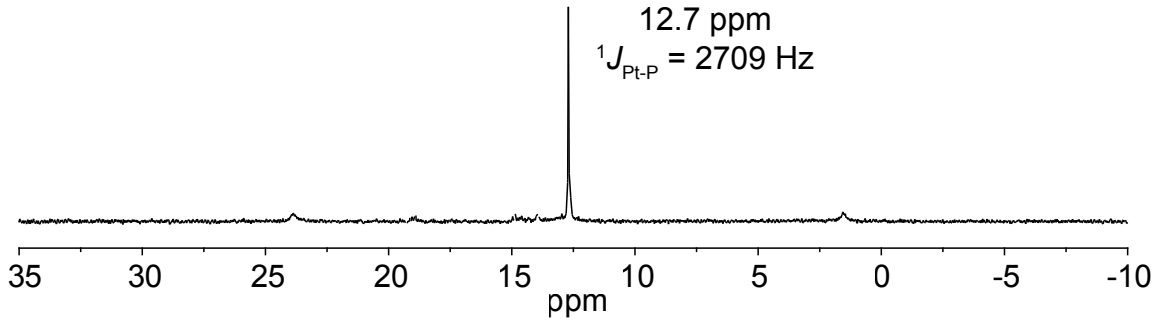


Figure S13. $^{31}P\{^{1}H\}$ NMR (121.4 MHz) spectrum of rhomboid **8a** in CD_2Cl_2.

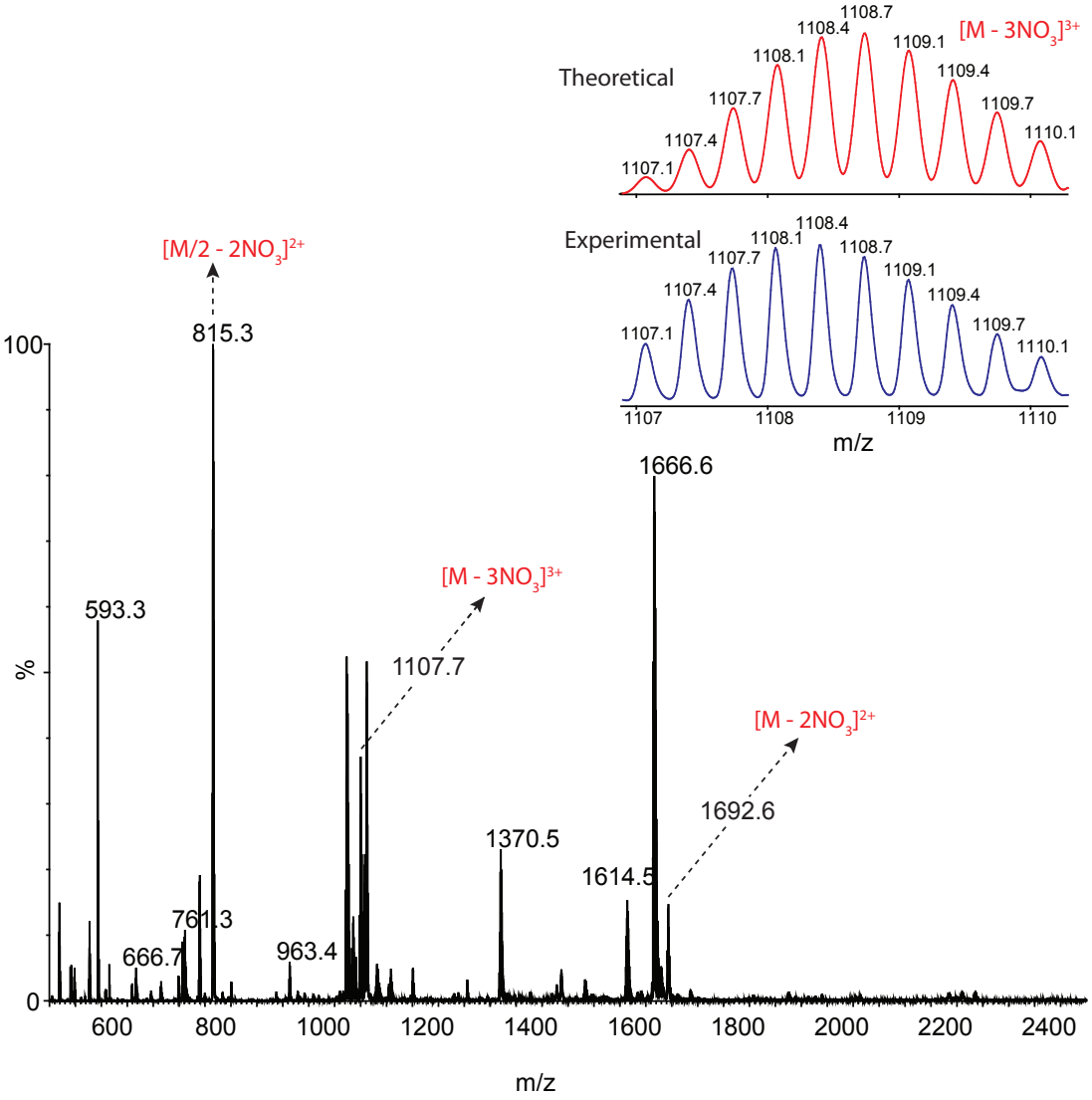


Figure S14. ESI-MS NMR spectrum of rhomboid **8a**.

8b: ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.74 (s, 2H, C(O)N*H*), 9.42 (d, 4H, Hα'-Py, J = 5.4 Hz), 8.87 (s, 4H, Phen*H*), 8.63 (d, 4H, Hα''-Py, J = 6.0 Hz), 8.50 (d, 2H, Ar*H*, J = 9.3 Hz) 8.34 (s, 4H, Ar*H*), 8.06-8.31 (m, 20H, pyreneH), 7.99 (d, 4H, Hβ'-Py, J = 5.4 Hz), 7.80 (s, 2H, Ar*H*), 7.77 (d, 4H, Hβ''-Py, J = 5.4 Hz), 7.59 (d, 12H, Phen*H*, J = 5.1 Hz), 6.30 (s, 4H, CH_2-benzyl), 4.43 (m, 2H), 4.41 (d, 2H, J = 15.9 Hz), 4.24 (d, 2H, J = 16.2 Hz), 2.07-2.34 (m, 8H), 1.80-1.98 (m, 6H), 1.67-1.72 (m, 4H), 1.55 (m, 2H), 1.36 (m, 16H, PCH_2CH$_3$), 1.13-1.20 (m, 24H, PCH$_2$CH_3) ppm. ^{31}P {^{1}H} NMR (CD_2Cl_2, 121.4 MHz) δ 12.7 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$ = 2697 Hz). ESI-MS ($C_{170}H_{208}N_{16}O_{16}P_8Pt_4$) m/z [**8b** – 2$NO_3$]$^{2+}$ 1817.6; [**8b** – 3NO_3]$^{3+}$ 1191.4.

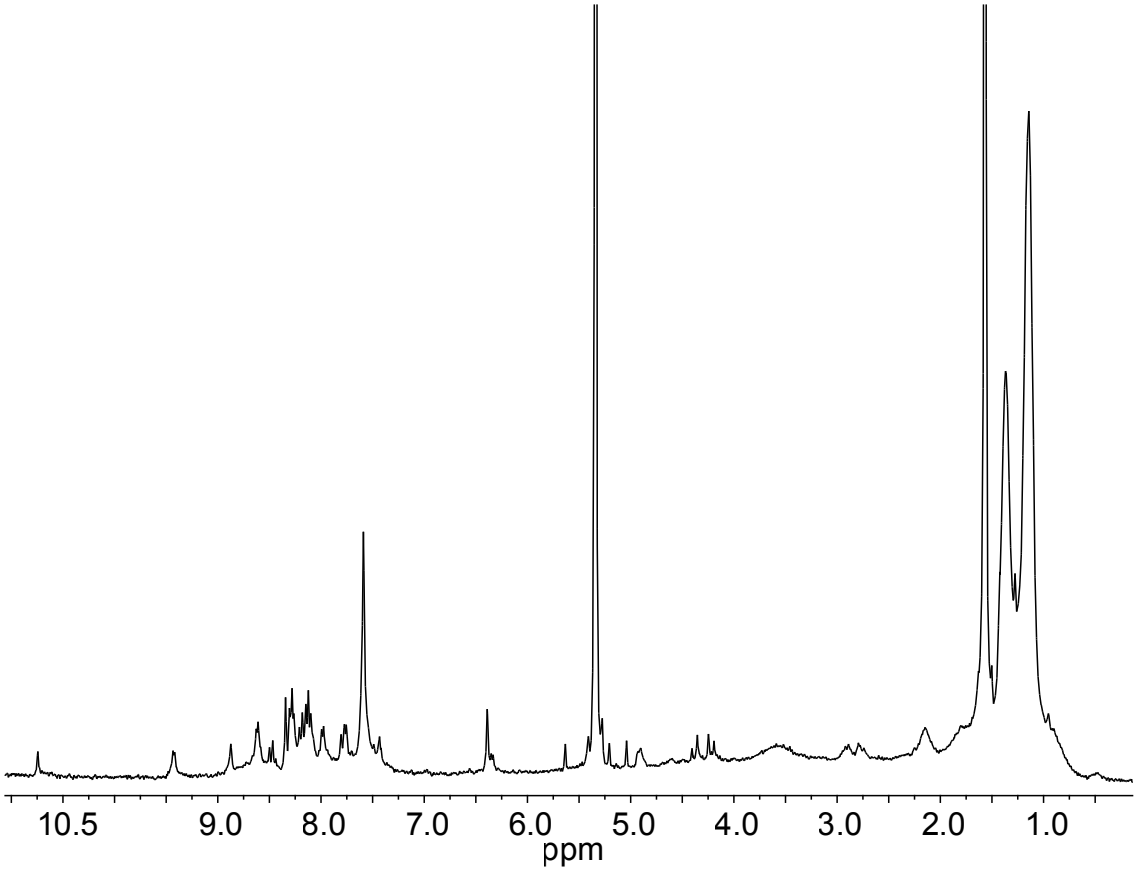


Figure S15. ^{1}H NMR (300 MHz) spectrum of rhomboid **8b** in CD_2Cl_2.

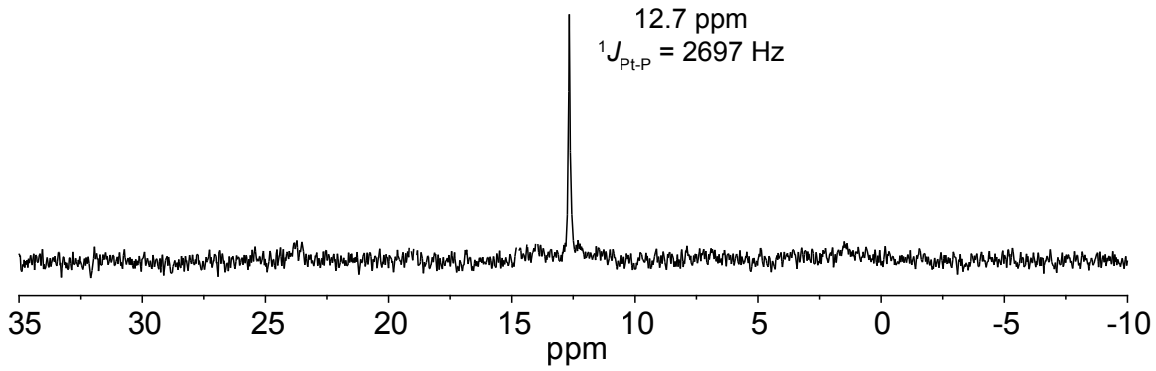


Figure S16. ^{31}P $\{^1H\}$ NMR (121.4 MHz) spectrum of rhomboid **8b** in CD_2Cl_2.

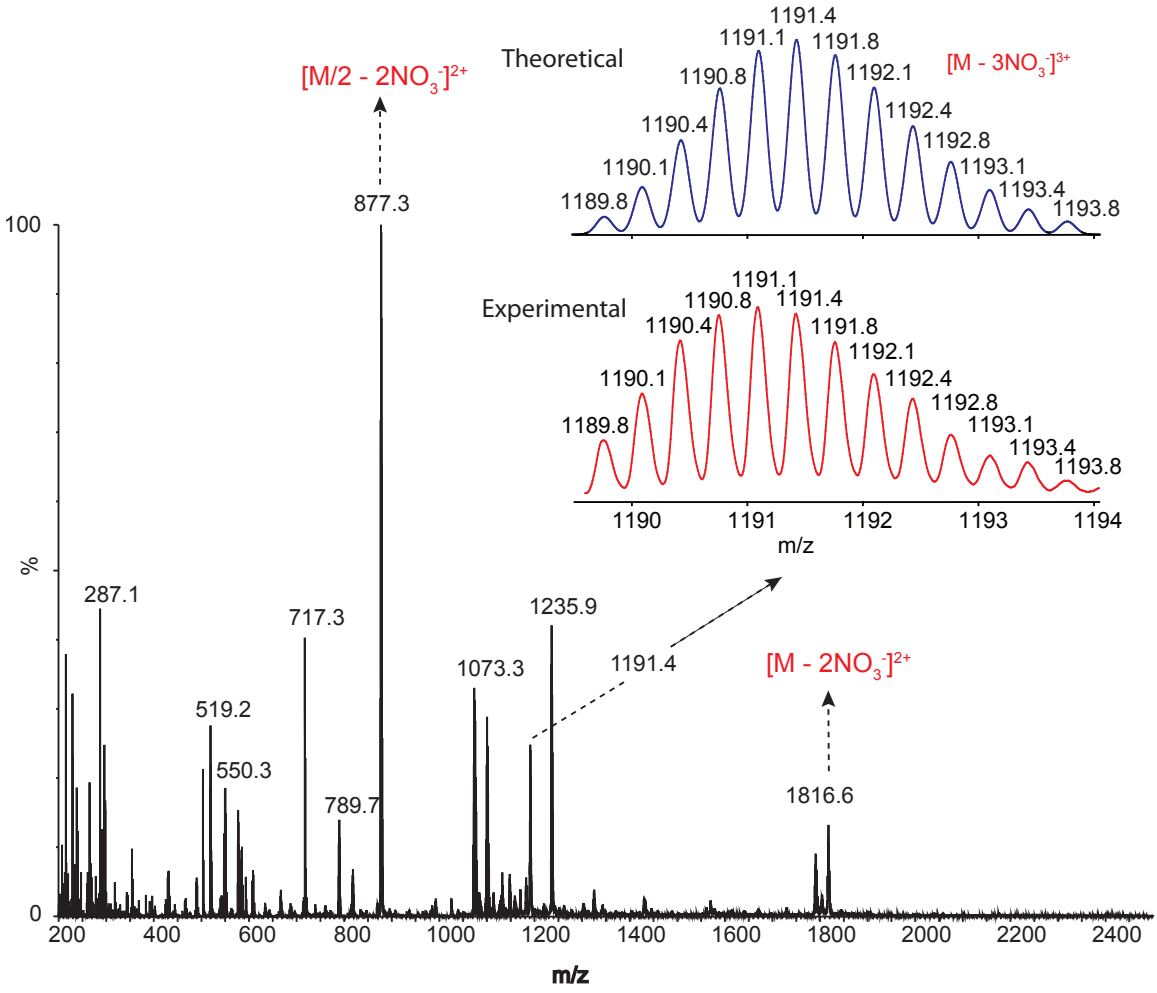


Figure S17. ESI-MS spectrum of rhomboid **8b**.

8c: ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.73 (s, 2H, C(O)N*H*), 9.40 (d, 4H, Hα'-Py, J = 5.4 Hz), 9.10 (s, 2H, C(O)N*H*), 8.86 (s, 4H, Phen*H*), 8.63 (d, 4H, Hα''-Py, *J* = 6.0 Hz), 8.16 (s, 4H, Ar*H*), 7.96 (d, 4H, Hβ'-Py, *J* = 5.4 Hz), 7.78 (d, 4H, Hβ''-Py, *J* = 5.4 Hz), 7.76 (s, 2H, Ar*H*), 7.61 (d, 12H, Phen*H*, *J* = 5.1 Hz), 4.59 (m, 4H, CH_2-benzyl), 4.51 (m, 4H, CH_2-benzyl), 4.43 (m, 2H), 4.30 (d, 2H, *J* = 15.9 Hz), 4.13 (d, 2H, *J* = 16.2 Hz), 3.43 (m, 4H), 3.21 (m, 2H), 2.97 (dd, 2H, *J* = 4.8, 17.7 Hz), 2.74 (d, 1H, *J* = 11 Hz), 2.07-2.34 (m, 8H), 1.80-1.98 (m, 6H), 1.67-1.72 (m, 4H), 1.55 (m, 2H), 1.36 (m, 16H, PCH_2CH$_3$), 1.13-1.20 (m, 24H, PCH$_2$CH_3) ppm. ^{31}P {^{1}H} NMR (CD_2Cl_2, 121.4 MHz) δ 12.7 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$ = 2719 Hz). ESI-MS ($C_{160}H_{226}N_{22}O_{20}P_8Pt_4S_2$) m/z [**8c** – 3$NO_3$]$^{3+}$ 1227.8.

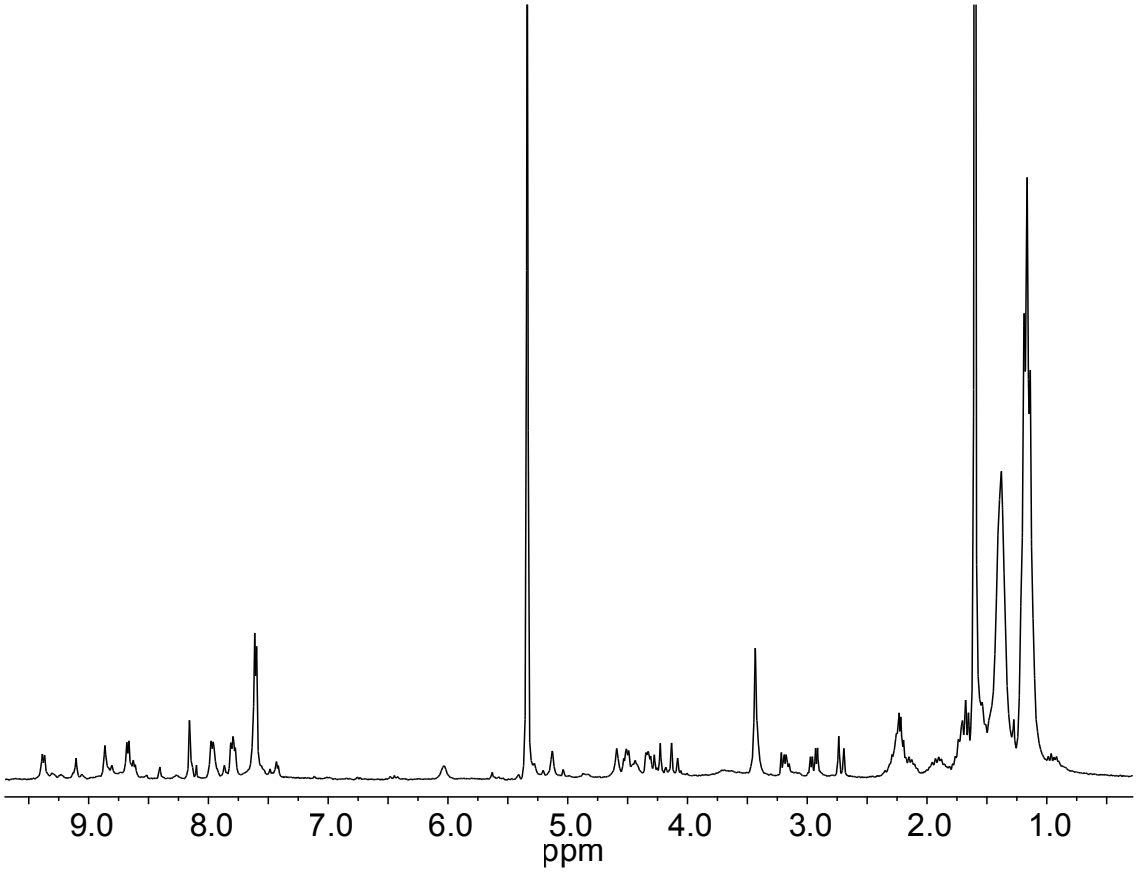


Figure S18. ^{1}H NMR (300 MHz) spectrum of rhomboid **8c** in CD_2Cl_2.

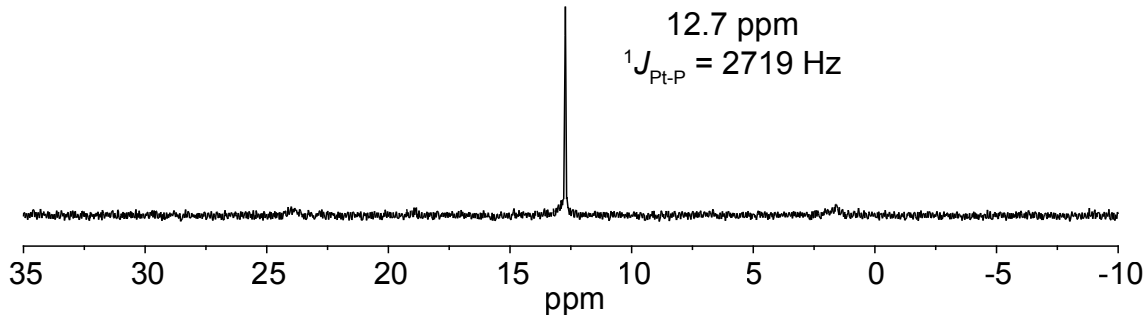


Figure S19. ^{31}P {^1H} NMR (121.4 MHz) spectrum of rhomboid **8c** in CD_2Cl_2.

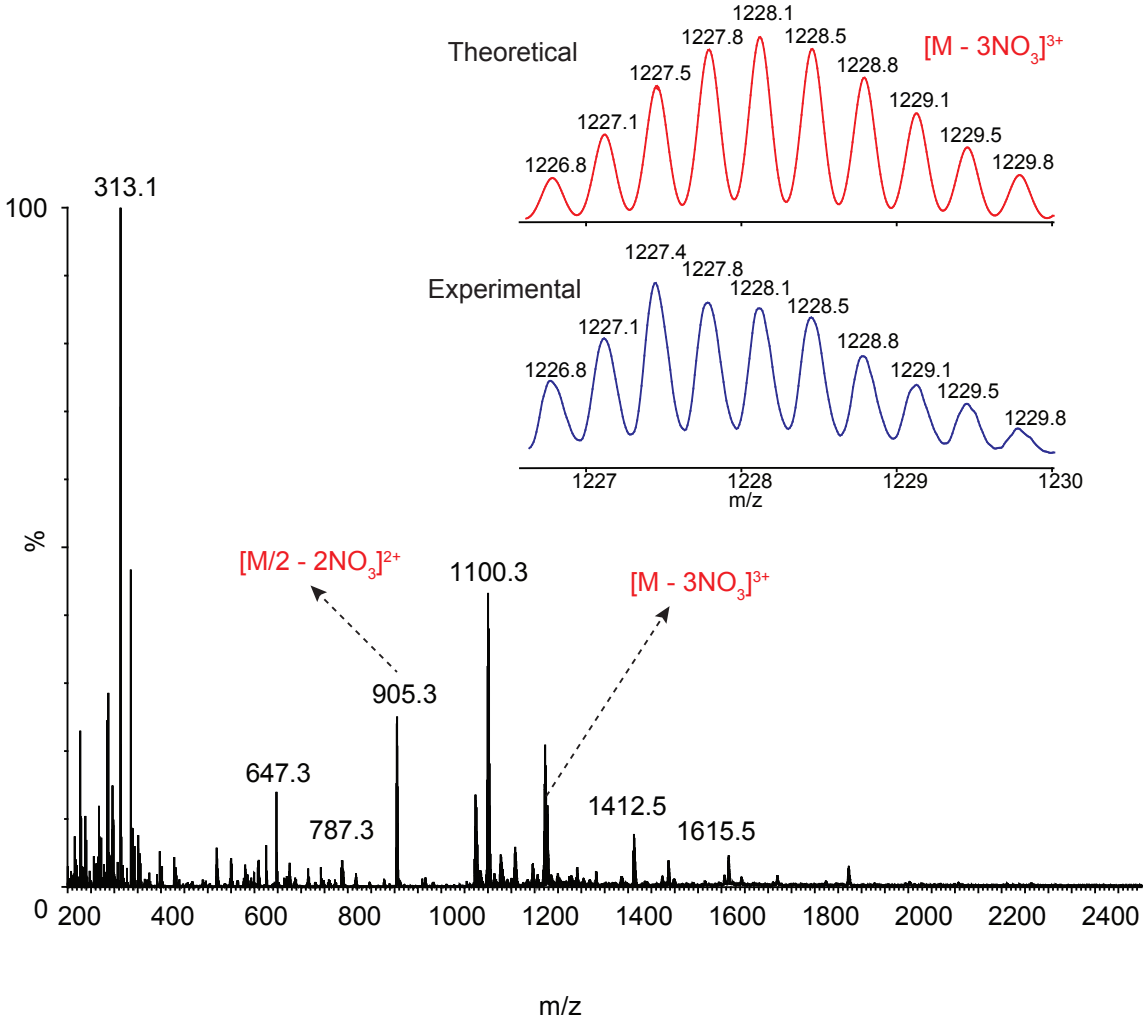


Figure S20. ESI-MS spectrum of rhomboid **8c**.

DFT Calculations

All calculations were performed using the Gaussian09 (G09) program package revision B.01,[7] with the Becke three-parameter hybrid exchange and the Lee−Yang−Parr correlation functionals (B3LYP). The 6-31G** basis set was used for H, C, N, and P atoms, while the Los Alamos National Laboratories (LANL2DZ) basis set and pseudopotential was used for Pt. All geometry optimizations were performed without a solvent field in C_1 symmetry; the results are in the gas phase. To minimize computational cost, the PEt_3 ligands on platinum were modeled as PH_3 ligands.

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