Operationally Unsaturated Ruthenium Complex Stabilized by a Phosphine 1-Azaallyl Ligand

Supporting Information

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I – Experimental Procedures

General Experimental Considerations

All reactions were performed under an inert (Ar or N_2) atmosphere using standard Schlenk line techniques or an MBRAUN glovebox, unless otherwise stated. Vials, flasks, and NMR tubes were oven dried (156 °C) and cooled under inert atmosphere before use. Unless otherwise stated, all reaction solvents were dried and degassed, and obtained from an Innovative Technology 400-5 Solvent Purification system and stored over 4 Å molecular sieves prior to use. Pyridine was dried over CaH_2, distilled under reduced pressure and stored over 4 Å molecular sieves under an inert atmosphere. The following materials were prepared using literature procedures **H[L1]**,[1] [RuCl(Cp*)(PPh_3)$_2$].[2] All other reagents were purchased from commercial sources and used without further purification. Deuterated solvents were obtained from commercial sources and were degassed and stored over 4 Å molecular sieves.

All NMR spectra were obtained on a 400/600 MHz Varian or 400/600 MHz Bruker spectrometer at 25 °C unless otherwise stated. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to TMS at 0 ppm using residual solvent (for ^{1}H) or solvent signals (^{13}C) signals as follows: $CDCl_3$ (δ_H = 7.26; δ_c = 77.4), C_6D_6 (δ_H = 7.16; δ_c = 128.1), toluene-d_8 (δ_H = 2.09, δ_c = 20.4). ^{31}P{^{1}H} NMR spectra obtained in protio solvents were externally referenced to a sample of 85% H_3PO_4 at δ_P = 0. *In situ* yields determined from ^{31}P{^{1}H} NMR spectra were done with an internal standard, and spectra were run with an increased delay time of 5 s unless otherwise stated. Multiplicities are described as s (singlet), d (doublet), t (triplet), sept (septet), br (broad), ov (overlapping), and m (multiplet). Signal assignments were made through a combination of 2D NMR experiments (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC). Charge-transfer Matrix Assisted Laser Desorption/Ionization Mass Spectrometry data were collected on an AB Sciex 5800 TOF/TOF mass spectrometer using pyrene as the matrix in a 20:1 molar ratio to complex. Solutions were prepared in benzene and spotted on a sample plate under an inert atmosphere and transferred to the instrument in a closed resealable plastic bag. The instrument was equipped with a 349 nm OptiBeam On-Axis laser. The laser pulse rate was 400 Hz and data were collected in reflectron positive mode. Reflectron mode was externally calibrated at 50 ppm mass tolerance. Each mass spectrum was collected as a sum of 500 shots. HRMS were collected on a Bruker MicrOTOF 11, and samples were prepared in MeCN at a concentration of 1 mg/mL. Infrared spectra were collected on solid samples using a Bruker ALPHA II ATR FTIR spectrometer. UV-visible spectra were collected using an Agilent Technologies Cary 8454 UV-Visible spectrometer, fitted with a Unisoko CoolspeK UV USP-203-A cryostat for low temperature analyses. All UV-vis measurements

were obtained with samples in a 3.5 mL glass cuvette (optical path length 1 cm) sealed with a screw cap fitted with a septum. A background of solvent only (benzene or toluene) was obtained and subtracted from spectra of compounds of interest.

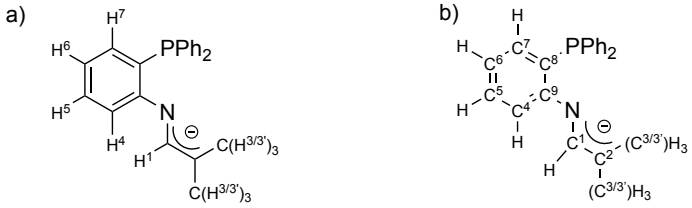

Figure S1. General labelling scheme for: a) proton environments for phosphine 1-azaallyl ligand **L1**, and b) carbon environments for **L1**. This scheme is used consistently for all compounds throughout the experimental. In all complexes with **L1** the carbon and proton environments for $C^3/C^{3'}$ and $H^3/H^{3'}$, respectively, are inequivalent. However, the exact assignment of C^3 vs $C^{3'}$ or H^3 or $H^{3'}$ was not made, so the assignment here is ambiguous.

Synthesis of [RuCl(Cp*)(H[L1])], 1.

A 100 mL Schlenk tube was charged with a suspension of **H[L1]** (192 mg, 0.578 mmol) in acetonitrile (8 mL), a suspension of $RuCl(Cp^*)(PPh_3)_2$ (300 mg, 0.375 mmol) in acetonitrile (5 mL), and a stir bar. The reaction mixture was refluxed under argon at 80 °C for 1 h. The flask was cooled to –15 °C, and dry and degassed hexanes (5 mL) were cannula transferred into the reaction vessel. The reaction was stirred vigorously for 30 seconds, and then the hexanes layer was removed by cannula transfer. This hexanes wash was repeated two more times (2 × 5 mL). The reaction was returned to reflux and the extraction process was repeated twice more for a total of 3 h of reflux. The last hexanes wash was performed at ambient temperature. The acetonitrile was removed under reduced pressure to produce a yellow-green oil. The oil was redissolved in minimal benzene (ca. 1 mL), then cold hexanes (5 mL) was added, and the suspension was stirred for 15 min. The mixture was filtered through a frit to isolate **1** as a fine orange powder. Yield: 75% (169 mg, 0.280 mmol). MALDI-MS (pyrene): *m/z* found: 603.1 Calc: 603.2 ($[RuCl(Cp^*)(\mathbf{L1})]^{\bullet+}$); ESI-MS: *m/z* found: 568.1734 Calc: 568.1707 ($[RuCl(Cp^*)(\mathbf{L1})–Cl]^+$), found: 609.2013 Calc: 609.1973 ($[RuCl(Cp^*)(\mathbf{L1})–Cl+MeCN]^+$); ATR-FTIR ($cm^{-1}$): ν 1463.09 (N=C); UV-Vis: λ_{max} = 723 nm (ε = 126 ± 10 $Lmol^{-1}cm^{-1}$; X-ray quality crystals of ***Z*-1** were grown from a THF/Pentane mixture at –20 ºC.

***Z*-1** (major conformer, 80% relative integration) ^1H NMR (400 MHz, C_6D_6) (note: the signals between 6.80-7.30 ppm are overlapped with ***E*-1** aromatic signals) δ = 8.03-7.97 (m, 2H, $P(C_6H_5)_2$),

7.61 (d, J = 9.3 Hz, 1H, H^1), 7.52 – 7.42 (m, 1H, H^5), 7.29-7.38 (m, 2H P(C_6H_5)$_2$), 7.24-7.18 (m, 3H, P(C_6H_5)$_2$), 7.10-7.04 (m, 1H, P(C_6H_5)$_2$), 7.02-6.96 (m, 4H, P(C_6H_5)$_3$), 6.94-6.89 (m, 2H, H^6 & H^7), 6.73 (dd, J = 7.1, 3.8 Hz, 1H, H^4), 3.82 (d of sept, J = 9.3, 6.5 Hz, 1H, H^2), 1.47 (d, $^3J_{H\text{-}P}$ = 1.7 Hz, 15H, $C_5(CH_3)_5$), 1.37 (d, J = 6.5 Hz, 3H, H^3), 0.98 (d, J = 6.5 Hz, 3H, $H^{3'}$); ***Z*-1** $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ = 183.5 (s, C^1), 163.3 (s, C^9), 134.6 (d, $J_{C\text{-}P}$ = 10.7 Hz, P(C_6H_5)$_2$), 133.4 (d, $J_{C\text{-}P}$ = 2.0 Hz, C^5), 133.1 (d, $J_{C\text{-}P}$ = 9.9 Hz, P(C_6H_5)$_2$), 130.3 (d, $J_{C\text{-}P}$ = 2.1 Hz, C^6/C^7), 128.9 (d, J = 2.2 Hz, P(C_6H_5)$_2$), 128.5 (d, J = 1.5 Hz, P(C_6H_5)$_2$), 126.8 (d, J = 3.7 Hz, P(C_6H_5)$_2$), 82.9 (d, $J_{C\text{-}P}$ = 3.7 Hz, C^8), 37.2 (C^2), 21.9 (C^3), 20.7 ($C^{3'}$), 10.0 (Cp*–CH_3); ***Z*-1** $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ = 55.2 (80 %).

***E*-1** (minor conformer, 20% relative integration) ^1H NMR (400 MHz, C_6D_6) (Diagnostic signals) δ = 8.30 (d, J = 9.6 Hz, 1H, H^1), 2.76 (sept, J = 9.6, 6.5 Hz, 1H, H^2), 1.49 (d, $^3J_{H\text{-}P}$ = 1.6 Hz, 15H, $C_5(CH_3)_5$), 0.80 (d, J = 6.5 Hz, 3H, H^3), 0.65 (d, J = 6.5 Hz, 3H, $H^{3'}$); ***E*-1** $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ = 53.4 (20 %); ***E*-1** $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, Diagnostic signals) δ = 182.4 (C^1), 32.6 (C^2), 20.5 (C^3), 19.8 ($C^{3'}$).

Synthesis of [Ru(Cp*)(L1)(py)], 2.

In a glovebox, Li[HMDS] (33 mg, 0.20 mmol) was dissolved in benzene (1 mL) and added to a solution of **1** (60 mg, 0.10 mmol) dissolved in a 2:1 mixture of benzene (1 mL) and pyridine (0.5 mL). The reaction was left to stir in the glovebox (ca. 26 ˚C) for 1.5 h. The solvent was reduced under vacuum to ca 0.5 mL and both pyridine (3 drops) and hexanes (4 mL) were added. The mixture was stirred for 3 min at room temperature, and then cooled to –20 ˚C for 15 min, during which time an orange solid precipitated. The suspension was filtered through a glass microfibre plug, and the collected orange solids were washed with cold hexanes (2 × 1 mL). The filtrate was collected, and the solvent was reduced under vacuum to ca 0.5 mL. The hexane precipitation was performed twice more using the same filter pipette. After the third filtration, benzene (1 mL) and 1 drop of pyridine were added to the filter pipette to redissolve the orange solids, the orange solution was collected in a 20 mL vial and the solvent was removed to produce **2** as an orange powder. *Note*: prolonged vacuum drying and removal of excess pyridine results in the formation of pyridine-free complex **4**. Since complete drying of **2** is not possible, an accurate yield of **2** cannot be ascertained, and some of the ^1H and $^{13}C\{^1H\}$ NMR aromatic signals are obscured by excess pyridine. ^1H NMR (400 MHz, C_6D_6): δ = 6.41 (s, 1H, H^2) 2.12 (s, 3H, H^3), 1.85 (s, 3H, $H^{3'}$), 1.42 (d, J = 1.6 Hz, 15H, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6) (note: several aromatic signals are obscured by signals for excess pyridine): δ = 165.5 (C^9), 138.9 (C^1), 134.8, 132.5, 132.4, 130.4, 128.3, 127.6, 115.9, 115.2 (C^2), 110.6, 83.8 ($C_5(CH_3)_5$), 22.2 ($C^{3'}$), 18.7 (C^3), 10.3 ($C_5(CH_3)_5$); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ = 65.9 (s); MALDI-MS (pyrene) *m/z* found:

566.7 Calc: 566.7 ([Ru(Cp*)(**L1**)]$^+$); ATR-FTIR (cm^{-1}): 2903 (Csp^3–H), 1322 (Csp^2–N); UV-Vis: λ_{max} = 411 nm (ε = 3530 ± 157 L mol^{-1} cm^{-1}); X-ray quality crystals of **2** were grown by slow evaporation from a hexanes/pyridine mixture of **2** at –20 ˚C.

Synthesis of [Ru(Cp*)(L1)]$_n$, 4 in the Solid-State (n = 2) and 3 in Solution (n = 1).

Rigorously dried **2** was dissolved in benzene or toluene at room temperature, which gave a dark green solution. The solvent was removed under vacuum to give an orange powder; Yield: 41 mg; 84% (0.072 mmol). Redissolution in non-coordinating solvents consistently afforded a dark green solution (compound **3**). Solid-state analysis of **4**: MALDI-MS (pyrene): *m/z* found: 567.1 Calc: 567.2 ([Ru(Cp*)(**L1**)]$^+$); FTR-ATIR (cm^{-1}): 2949 (Csp^3–H), 1321 (Aromatic Csp^2–N). Solution-state analysis of **3**: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.98 (s, 1H, H^7), 7.14–6.97 (m, 10H, P(C_6H_5)$_2$), 6.63 – 6.54 (ov m, 2H, H^5 & H^1), 6.33 (m, 1H, H^6), 6.10 (br, 1H, H^4), 1.94 (s, 3H, H^3), 1.65 (s, 3H, $H^{3\prime}$), 1.30 (d, $J_{H\text{-}P}$ = 1.5 Hz, 15H, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298 K): δ = no observed signal if rigorously dried, a very broad signal at ca. 64 ppm is observed if pyridine removal is incomplete; Diagnostic ^{13}C{^{1}H} NMR signals found through 2D correlation experiments (101 MHz, C_6D_6, 298 K) (note: due to dynamic processes involving **L1**, no other ^{13}C{^{1}H} signals were observed at room temperature): δ = 139.8 (C^1), 118.1 (C^2), 22.6 ($C^{3\prime}$), 18.8 (C^3); UV-Vis: λ_{max} = 630 nm (ε = 551 ± 55 Lmol^{-1}cm^{-1}.

In-Situ Formation of [Ru(Cp*)(L1)]$_2$, 4 at Reduced Temperature

Solid **4** (8 mg, 0.7 × 10^{-3} mmol) obtained by rigorous drying of **2**, was dissolved in toluene-d_8 (ca. 0.7 mL) and added to an NMR tube. Dissolution of solid **4** at room temperature affords monomer **3**. The NMR tube was inserted into an Inova 600 spectrometer, and the instrument was cooled to –70 ˚C. At –50 ˚C a distinct singlet appeared in the ^{31}P{^{1}H} NMR spectrum at δ_P = 66.1, indicating dimerization of **3** to give **4**. ^{1}H NMR (599 MHz, toluene-d_8, 223 K): δ = 7.85 – 7.75 (m, 8H, P(C_6H_5)$_2$), 7.73 (d, J = 5.4 Hz, 2H, H^7), 7.42 (t, J = 8.2 Hz, 8H, P(C_6H_5)$_2$), 6.62 (s, 2H, H^1), 6.43 – 6.32 (m, 2H, H^5), 6.28 (t, J = 7.0 Hz, 4H, P(C_6H_5)$_2$), 5.97-5.94 (m, 4H, H^4 & H^6) 2.22 (s, 6H, H^3), 1.94 (s, 6H, $H^{3\prime}$), 1.42 (s, 30H, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (243 MHz, toluene-d_8, 223 K) δ = 66.1 (s); ^{13}C{^{1}H} NMR signals found through 2D correlation experiments (151 MHz, toluene-d_8, 223 K) (note: **4** reverts to **3**

upon warming, therefore a direct detect $^{13}C\{^1H\}$ spectrum could not be acquired with sufficient signal to noise): 153.6 (*C*^{7}), 138.7 (*C*^{1}), 122.8 (*C*^{4} & *C*^{6}), 115.2 (*C*^{2}), 110.3 (*C*^{5}), 22.5 (*C*$^{3'}$), 20.1 (*C*^{3}).

Synthesis of [Ru(Cp*)(L1)(PPh$_3$)], 5

In a glovebox, PPh_3 (6 mg, 0.023 mmol) was dissolved in benzene (0.5 mL) and added to a solution of complex **3** (19 mg, 0.034 mmol) in benzene (1 mL). An immediate colour change from dark green to red was observed. The PPh_3 vial was rinsed with benzene (2 × 0.5 mL) and the rinses were added to the reaction vial. The reaction was allowed to stir for 5 min at 26 ˚C. The solvent was then removed under reduced pressure to afford **5** as a dark red solid. Yield: 24 mg (86 %). ^1H NMR (600 MHz, C_6D_6): 7.90 – 7.50 (br m, 3H, P(C_6H_5)$_2$), 7.45 – 7.35 (m, 1H, *H*^{7}), 7.31-7.21 (ov, 3H, P(C_6H_5)$_3$), 7.08 – 6.73 (m, 15H, *H*^{5}, P(C_6H_5)$_2$, P(C_6H_5)$_3$), 6.71 – 6.52 (m, 6H, *H*^{6}) 6.46 (s, 1H, *H*^{1}), 6.04 (m, 1H, *H*^{4}), 2.01 (s, 3H, *H*$^{3'}$), 1.75 (s, 3H, *H*^{3}), 1.33 (s, 15H, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ = 165.8 (d, J_{CP} = 24.2 Hz, *C*^{9}), 139.0 (*C*^{1}), 137.1 (br, P(C_6H_5)$_3$), 134.6 (br, P(C_6H_5)$_3$), 134.2 (br, P(C_6H_5)$_3$), 133.8 (*C*^{4}), 133.3 (d, J_{CP} = 9.1 Hz, *C*^{8}), 129.8 (*C*^{5}), 128.4 (P(C_6H_5)$_2$), 127.2 (br, P(C_6H_5)$_3$), 123.5 (P(C_6H_5)$_2$), 119.2 (P(C_6H_5)$_2$), 118.9 (*C*^{6}), 117.0 (d, J_{CP} = 17.6 Hz, P(C_6H_5)$_2$), 115.4 (*C*^{2}), 110.1 (d, J_{CP} = 6.0 Hz, *C*^{7}), 90.1 ($C_5(CH_3)_5$), 22.7 (*C*$^{3'}$), 20.7 (*C*^{3}), 10.4 ($C_5(CH_3)_5$); $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ = 65.8 (d, J_{PP} = 34.0 Hz), 43.8 (d, J_{PP} = 34.0 Hz). MALDI-MS (pyrene) *m/z* found: 567.1 Calc: 567.1 ([**5** – PPh_3]$^+$); found: 804.2 Calc: 804.2 ([**5** + O – C_3H_6]$^+$) FTR-ATIR (cm^{-1}): 2895 (C*sp*^{3}–H), 1318 (Aromatic C*sp*^{2}-N); UV-Vis: λ_{max} = 737 nm (ε = 684 ± 61 L mol^{-1} cm^{-1}.

Representative Procedure for Determination of Molar Absorptivity (ε) of 1, 2, 3, and 5.

A solution of **1**, **2**, **3**, or **5** (4 mM, 3.0 mL) was prepared in benzene (in the case of **2,** a 1:1 benzene/pyridine mix was used) and placed into a 3.5 mL cuvette at room temperature. The sample was diluted to concentrations of 4 to 1 mM in 0.5 mM intervals by adding C_6H_6 through the septum cap using a gas tight syringe, or by returning the solution to the glovebox to add additional solvent. Solutions were mixed well (~30-60 s) before acquiring a UV-Vis spectrum. The data is depicted in Figure S21 and S22.

Titration of 3 with Pyridine and Analysis by UV-vis Spectroscopy.

A solution of **3** in benzene (1.5 mM, 3.0 mL) was added to a cuvette at room temperature. A separate solution of pyridine (10 mg, 0.12 mmol) in benzene (4 mL) was prepared in a 4 mL screw cap vial with a septum cap. An initial UV-vis spectrum of **3** was recorded. Pyridine was added in 0.25

equivalent portions using a 250 μL gas tight syringe, up to 2 equivalents total. Then pyridine was added in 0.5 equivalent portions up to 5 equivalents total. The solution was mixed well (30 s) after each addition and before a spectrum was recorded. The data is depicted in Figure 3 of the manuscript.

Variable Temperature UV-Vis Spectroscopy of 3.

A solution of **3** in toluene at 1.5 mM or 0.75 mM (3.0 mL) was added to a cuvette, and a UV-vis spectrum was recorded at room temperature. The solution was cooled in the UV-Vis spectrometer sample holder to 0, –25, and –50 ºC, and a spectrum was collected at each temperature. A colour change from green to orange was observed. A fresh solution (0.75 mM) was also heated from 25 to 30, 40, and 50 ºC. UV-Vis spectra were recorded at the desired temperatures. The data is depicted in Figure 5 and S24.

Low Temperature Addition of PPh_3 to 2 and 3.

Two separate solutions were prepared, (A) **4** was dissolved in toluene to give **3** (1.5 mM, 3.0 mL), or (B) **4** was dissolved in toluene with 5.0 equiv of pyridine to generate **2** (1.5 mM, 3.0 mL). These solutions were added to a cuvette fitted with a septum cap. A room temperature UV-Vis spectrum was then acquired, and the UV-Vis instrument was cooled to 0 ˚C. Another UV-Vis spectrum was acquired at 0 ˚C. With a microliter syringe, PPh_3 (10 equiv) in toluene (105 mM) was added in one injection. Scans were acquired immediately and every 0.5 s over 10 min with complex **3**. Scans were acquired every 5 s over 100 min with **2**. The data is depicted in Figures S25 and S26.

II – NMR Spectra

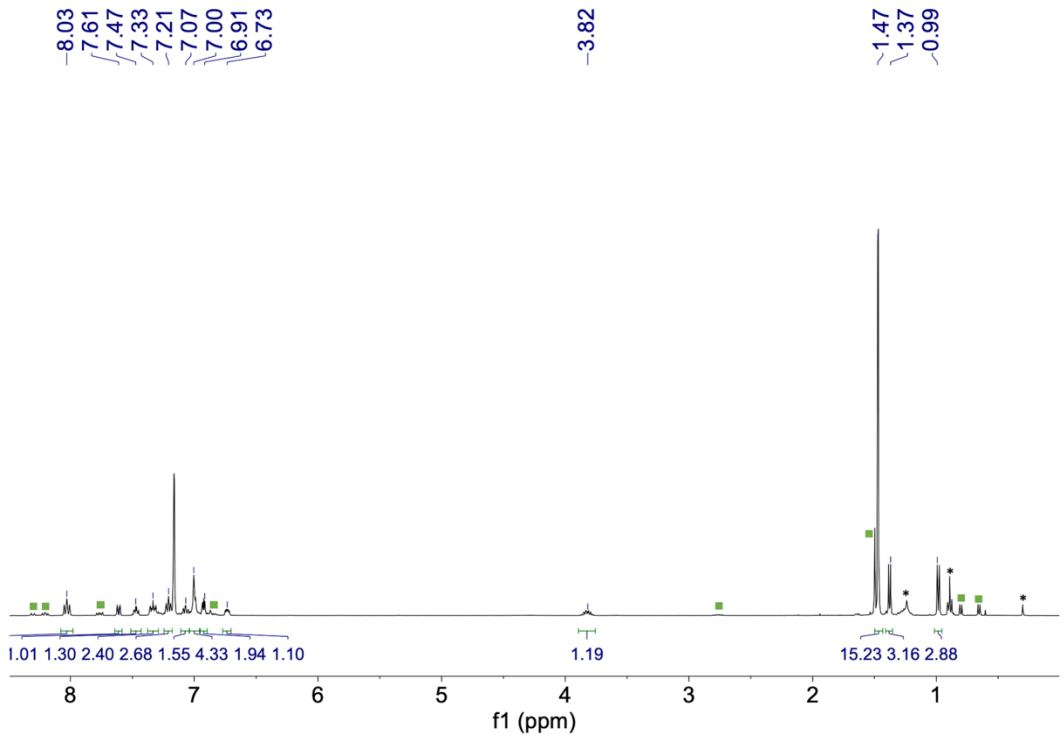

Figure S2. ^{1}H NMR spectrum of **1** (400 MHz, C_6D_6). Major peaks correspond to the ***Z*-1** isomer, and the minor ***E*-1** isomer is identified with a green square (■). Minor solvent and grease impurities are noted (*).

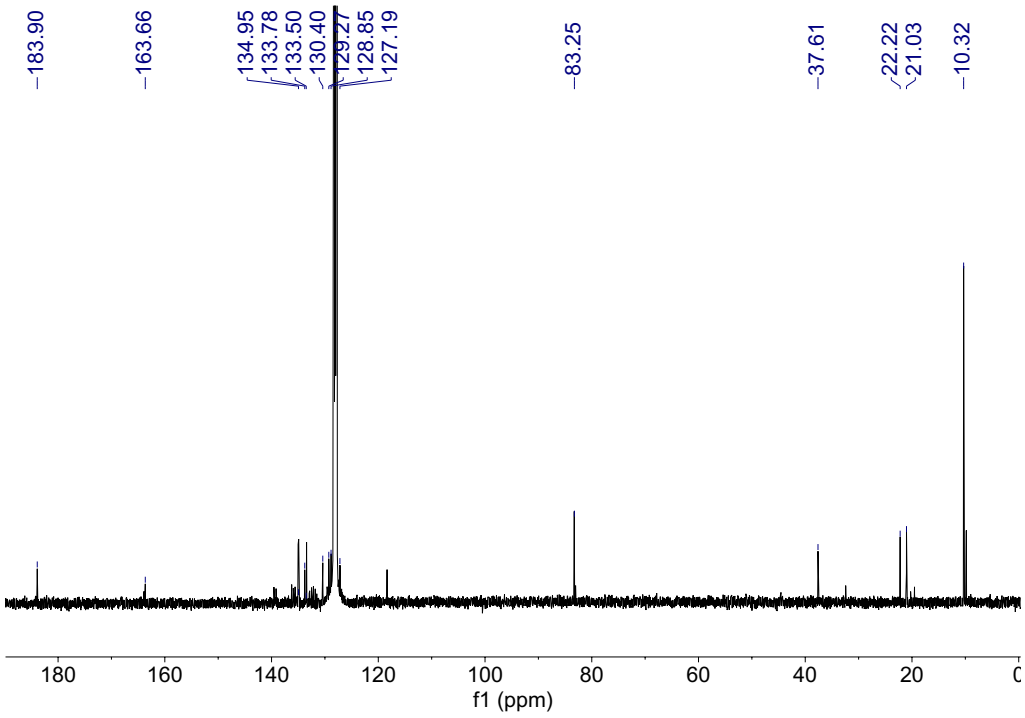

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (101 MHz, C_6D_6).

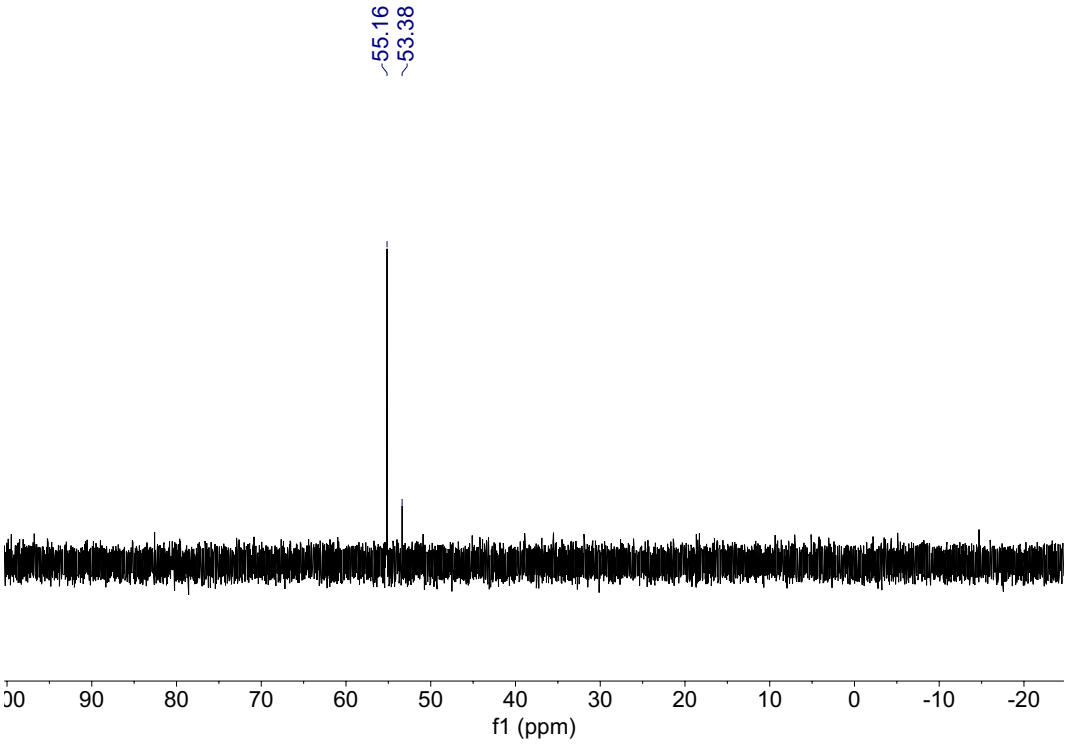

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **1** (162 MHz, C_6D_6). The signals at 55.2 and 53.4 ppm are assigned to the *Z* and *E* isomers, respectively, which are observed here in 5:1 ratio.

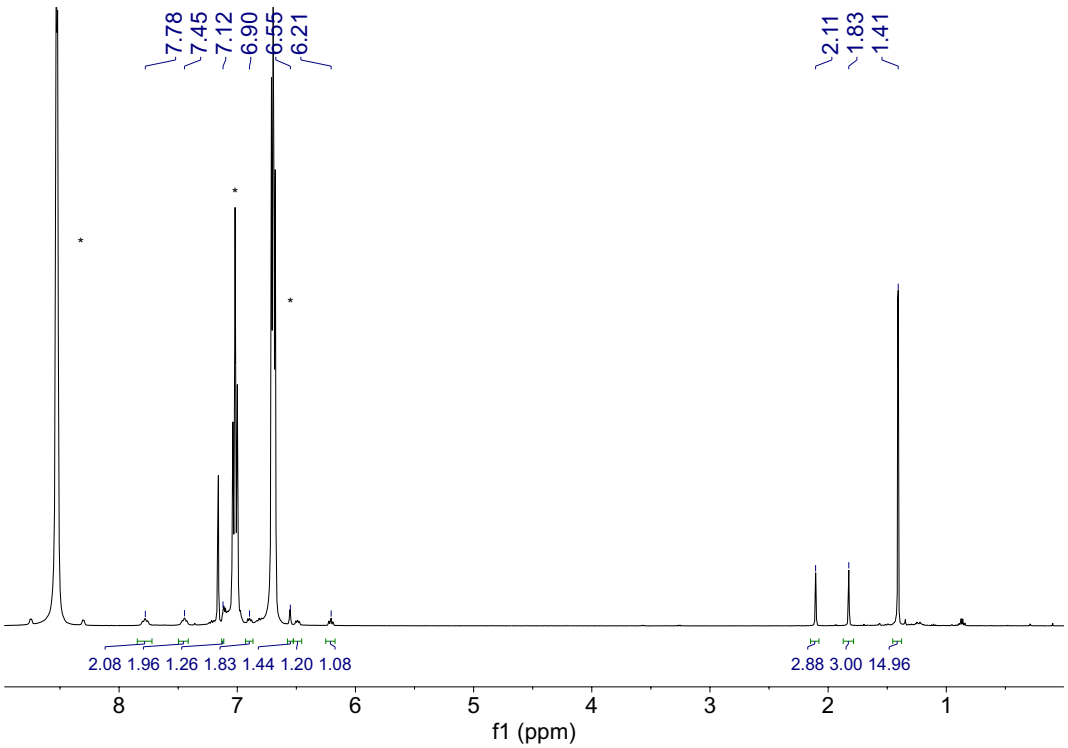

Figure S5. ^{1}H NMR spectrum of **2** (400 MHz, C_6D_6). '*' denotes excess pyridine, some aromatic signals are obscured by the excess pyridine.

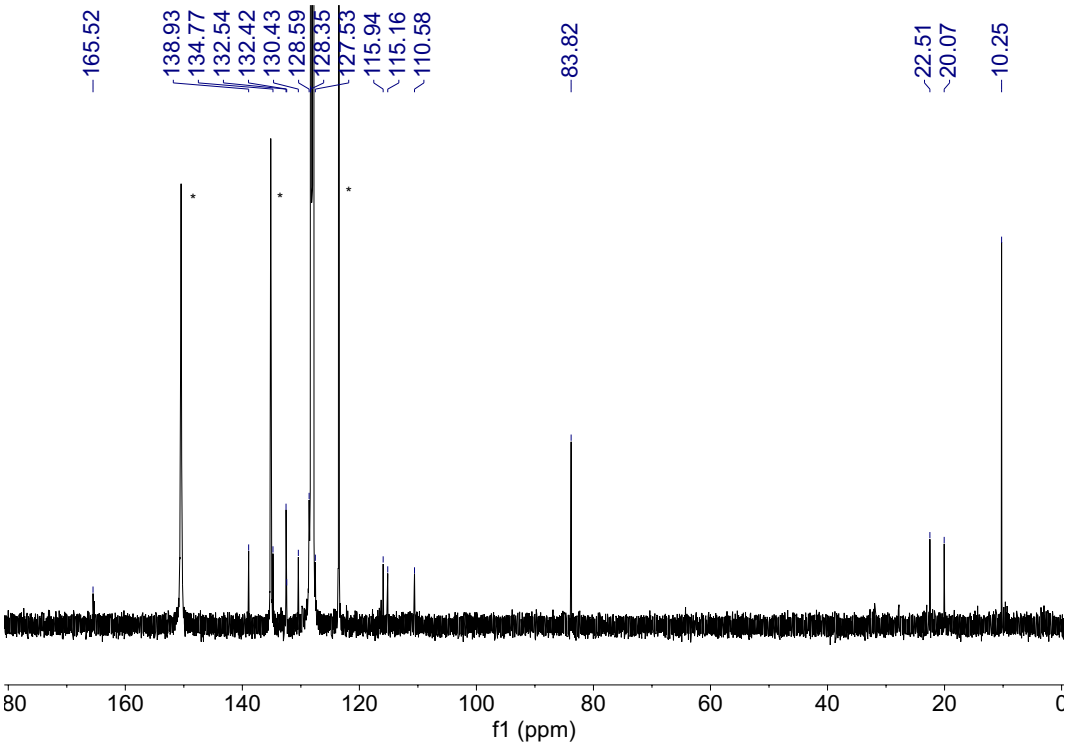

Figure S6. $^{13}C\{^{1}H\}$NMR spectrum of **2** (151 MHz, C_6D_6). '*' denotes excess pyridine, some aromatic signals are obscured by the excess pyridine.

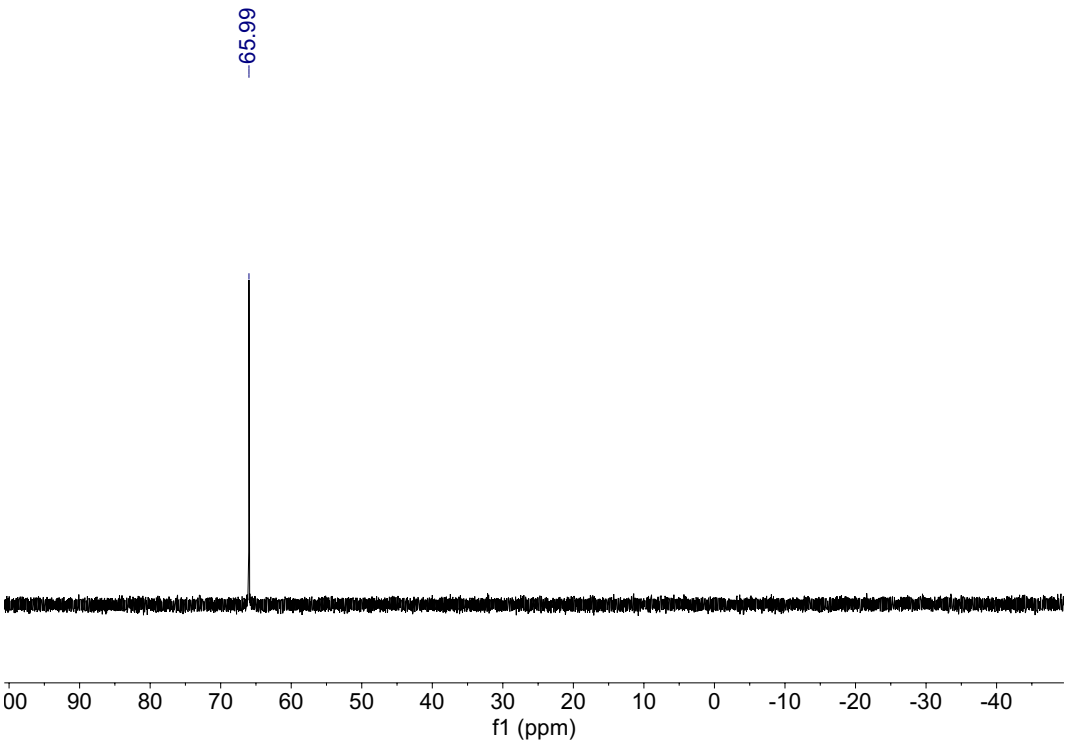

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (162 MHz, C_6D_6).

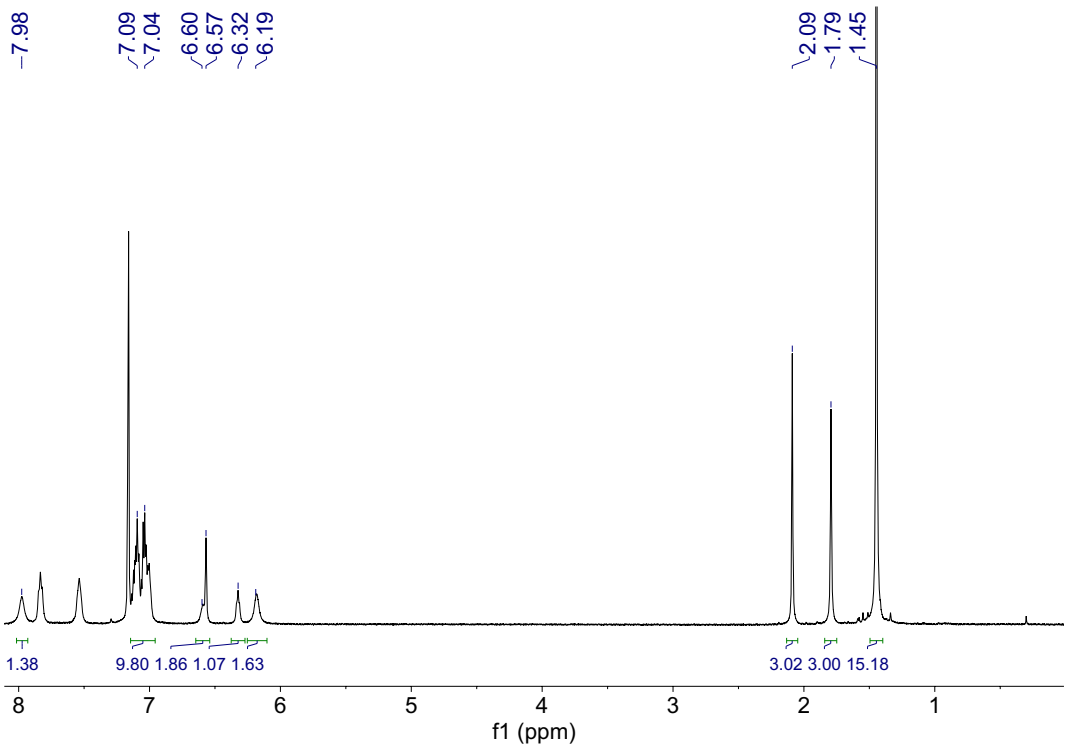

Figure S8. ^{1}H NMR spectrum of **3** (600 MHz, C_6D_6).

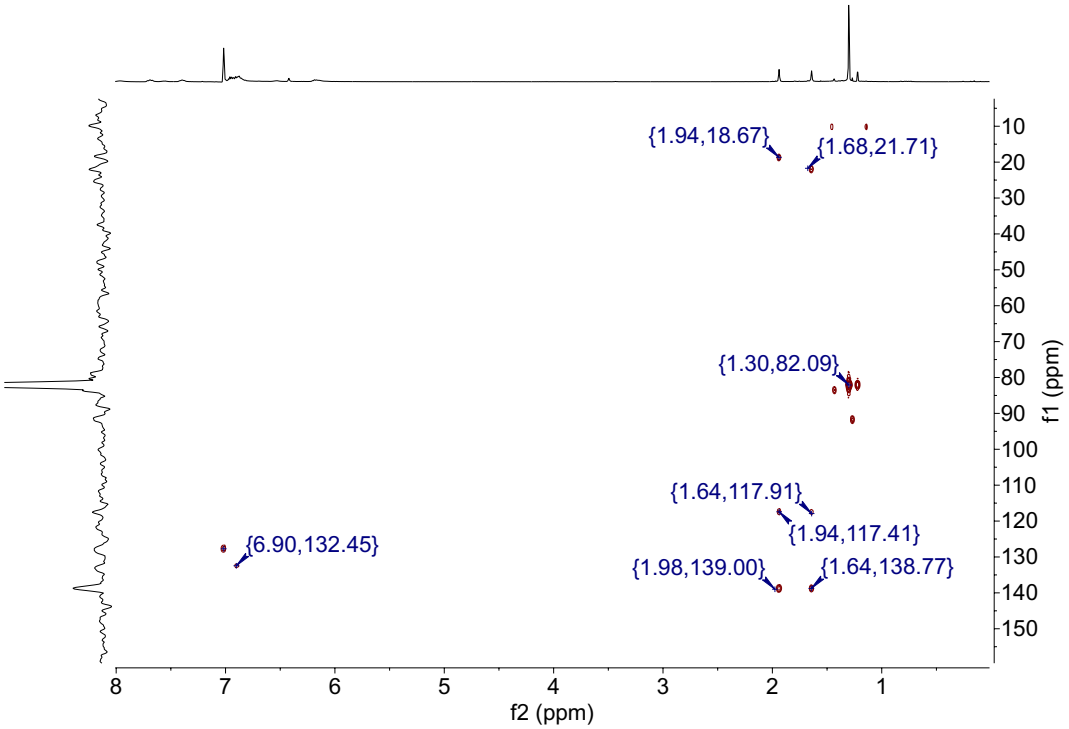

Figure S9. ^{1}H-^{13}C HMBC NMR spectrum of **3** (600 MHz, C_6D_6, 298 K).

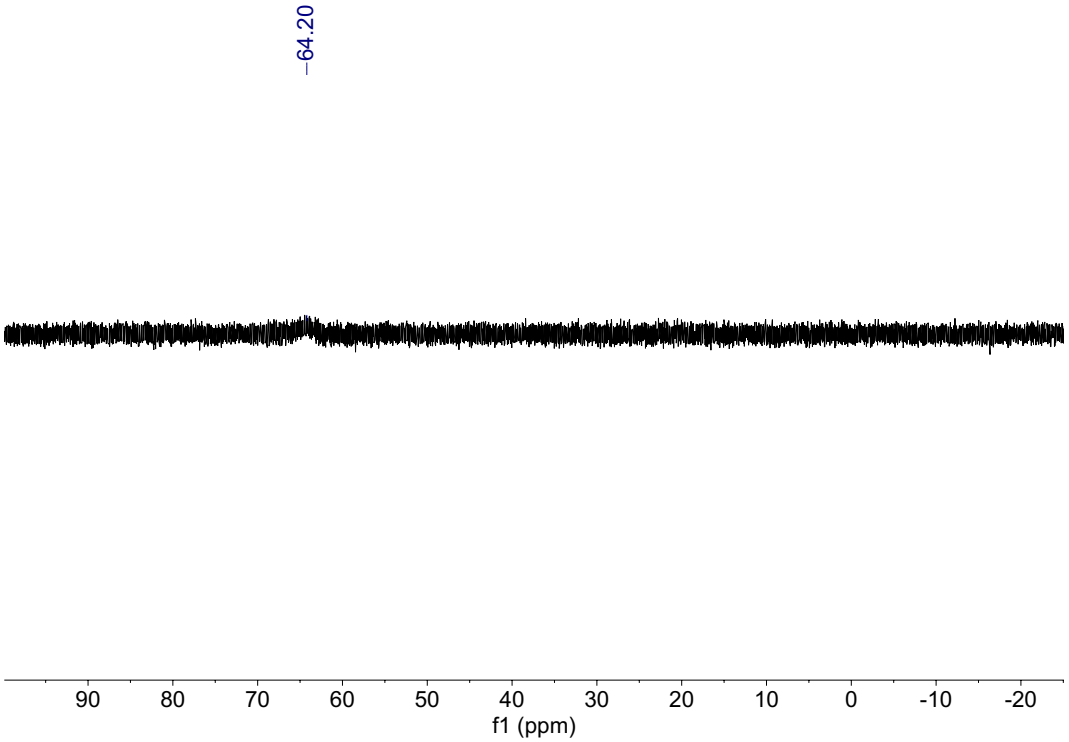

Figure S10. Representative $^{31}P\{^{1}H\}$ NMR spectrum of **3** (243 MHz, C_6D_6, 298K). Note: a broad signal is observed if even minor amounts of pyridine remain in the sample.

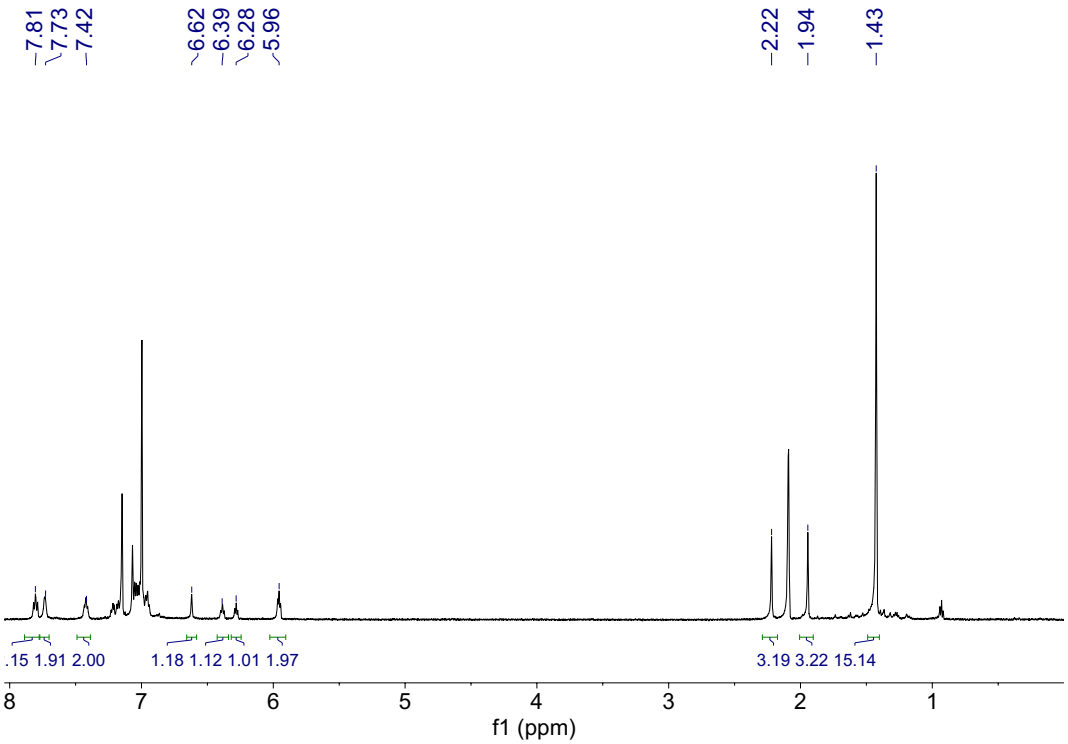

Figure S11. ^{1}H NMR spectrum of **4** (599 MHz, toluene-d_8, 233 K).

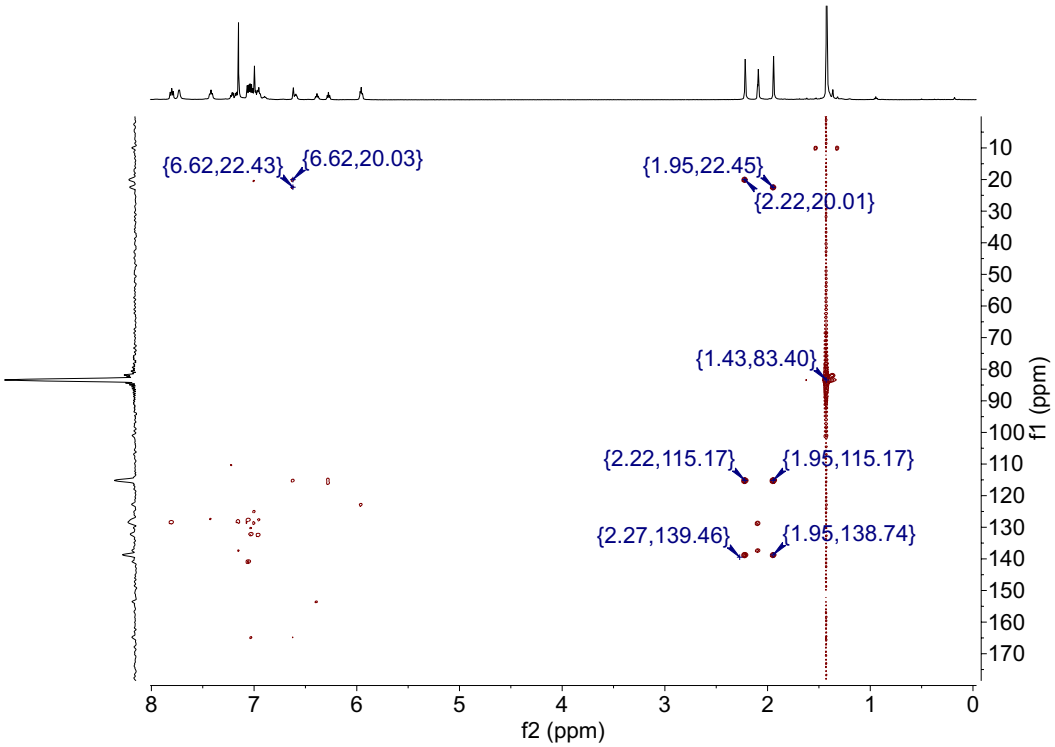

Figure S12. ^{1}H-^{13}C HMBC NMR spectrum of **4** (599 MHz, toluene-d_8, 233 K).

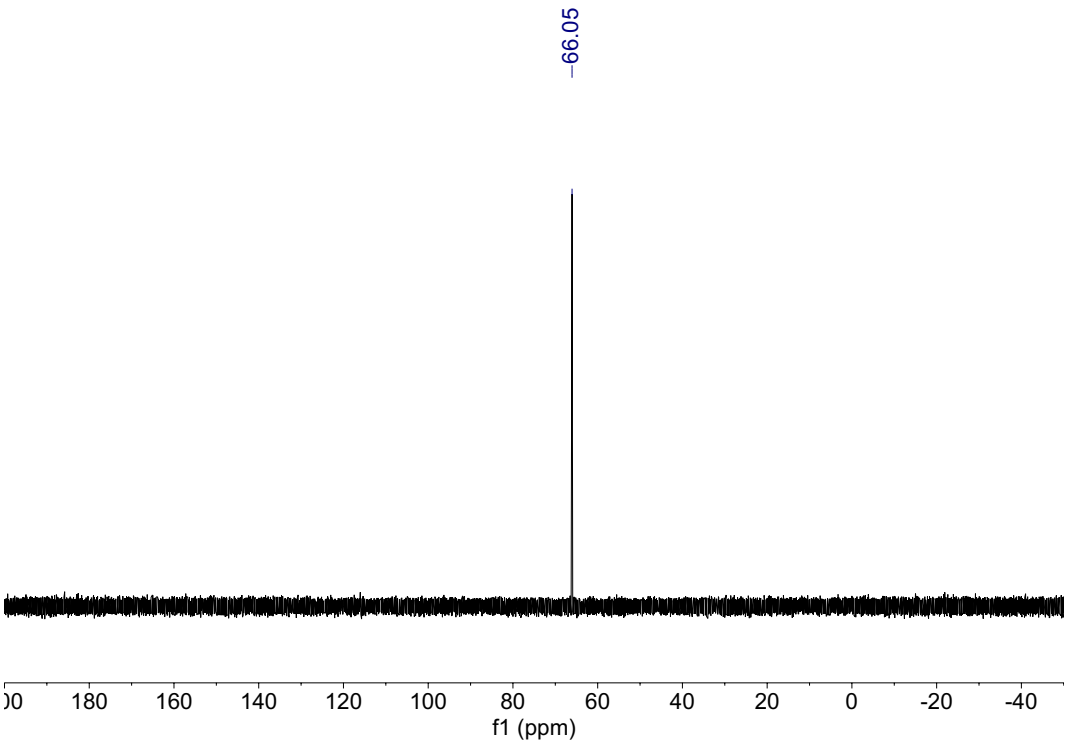

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **4** (243 MHz, toluene-d_8, 233 K).

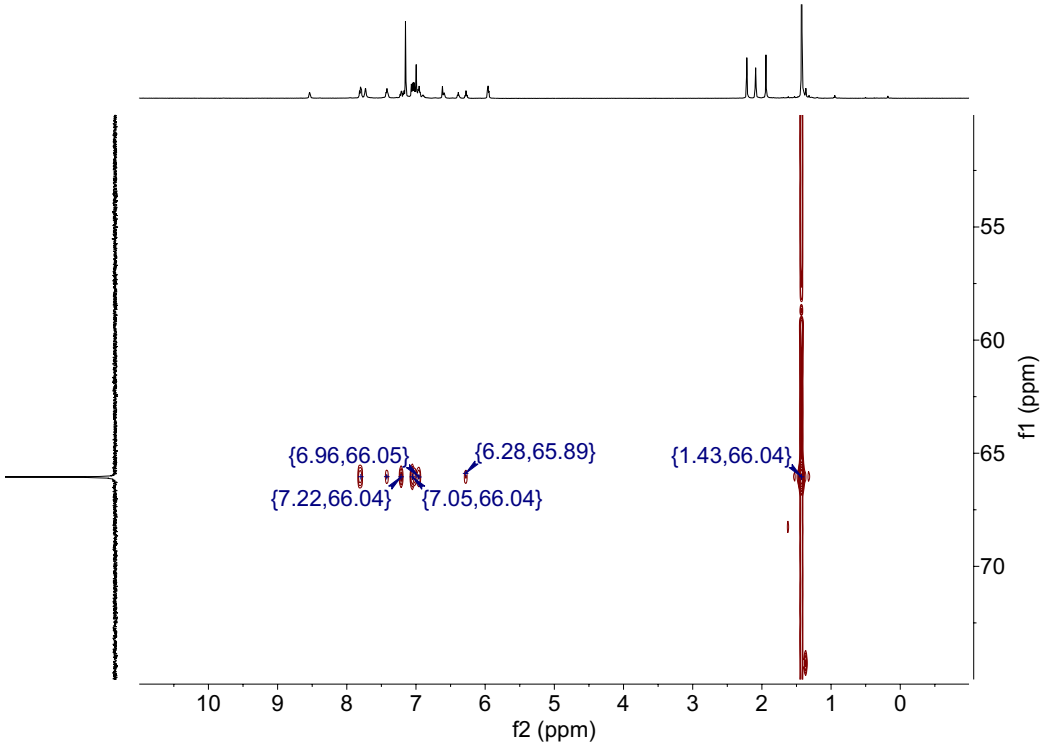

Figure S14. ^{1}H-^{31}P HMBC NMR spectrum of **4** (599 MHz, toluene-d_8, 233 K).

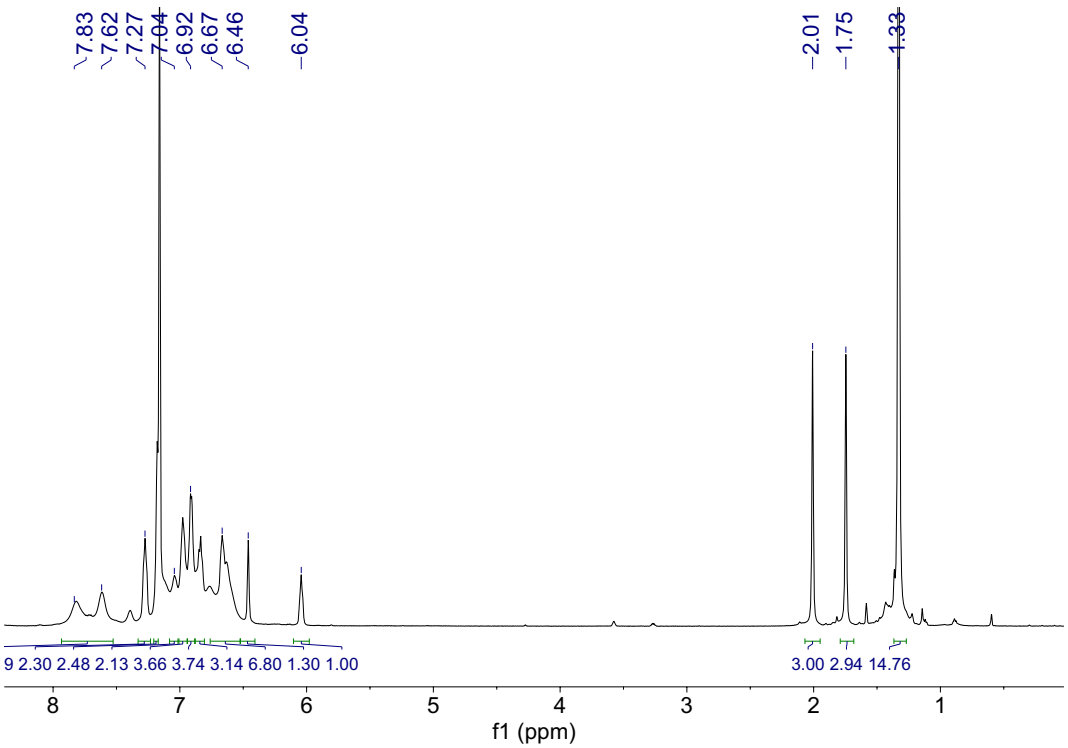

Figure S15. ^{1}H NMR spectrum of **5** (599 MHz, C_6D_6).

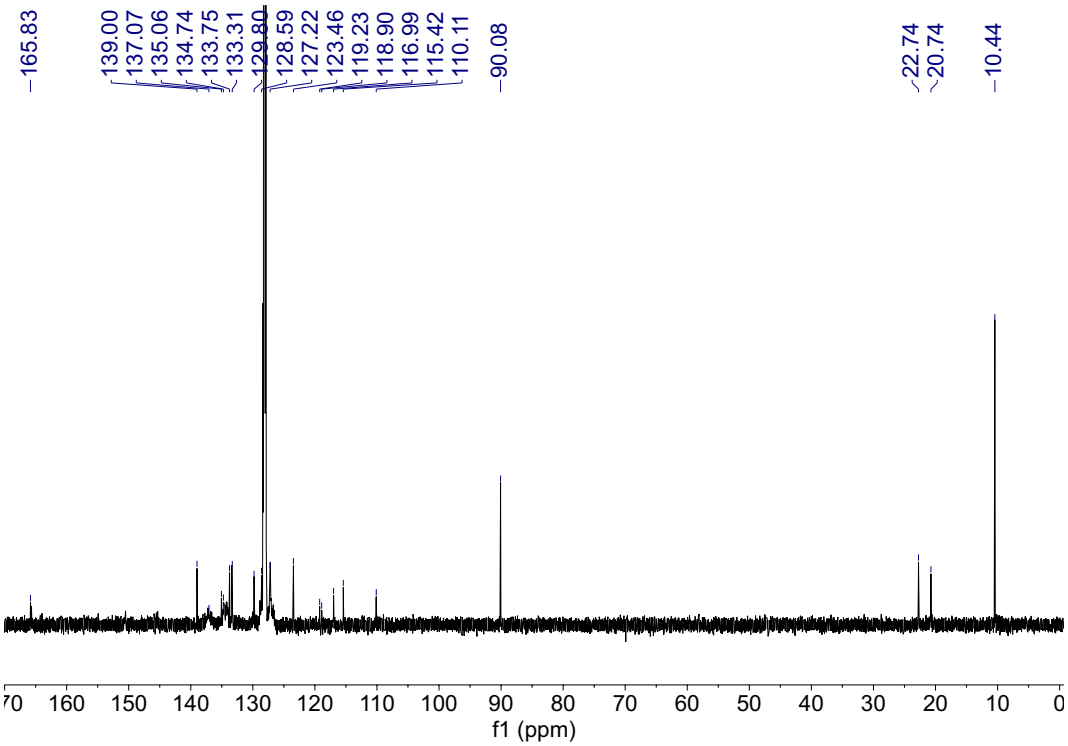

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **5** (151 MHz, C_6D_6).

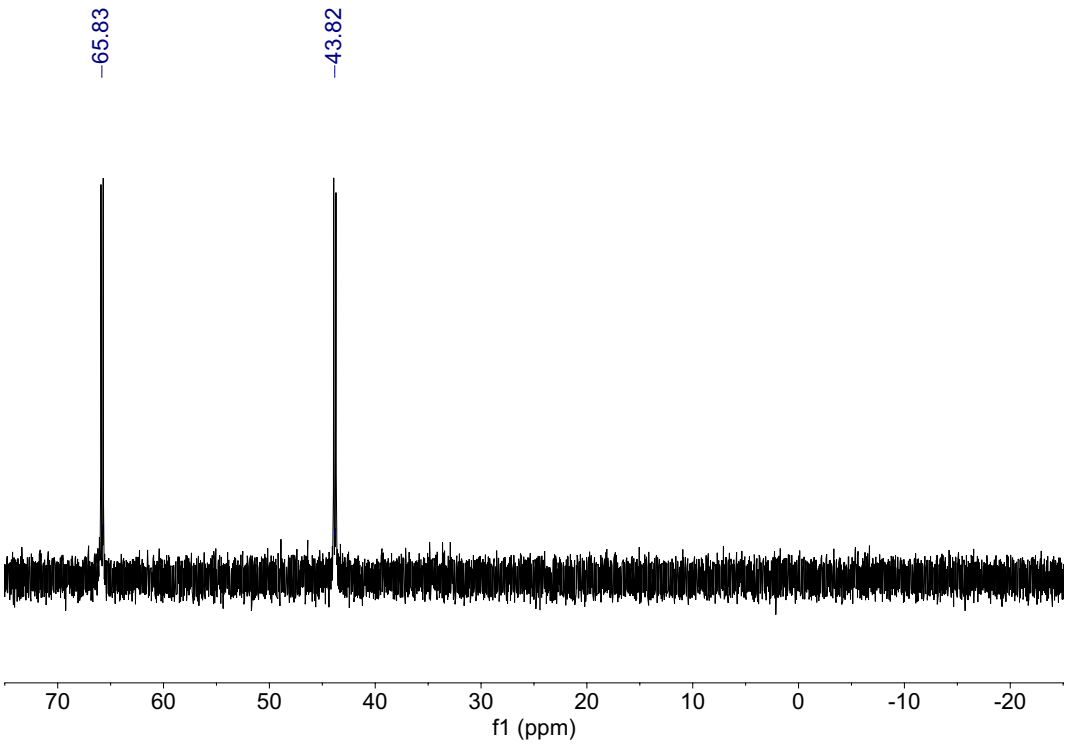

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of **5** (243 MHz, C_6D_6).

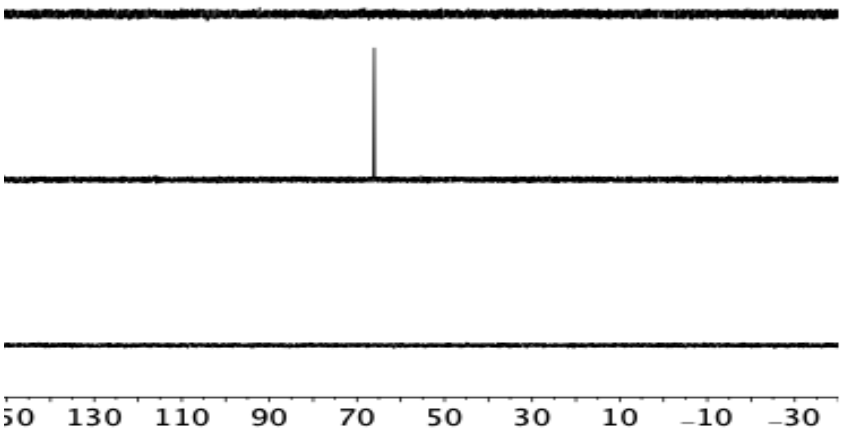

Figure S18. $^{31}P\{^{1}H\}$ VT NMR analysis (243 MHz, toluene-d_8) of complex **3** at 25 ˚C (top), dimer **4** after cooling a solution of **3** to – 50 ˚C (middle), and re-warming to 25 ˚C (bottom).

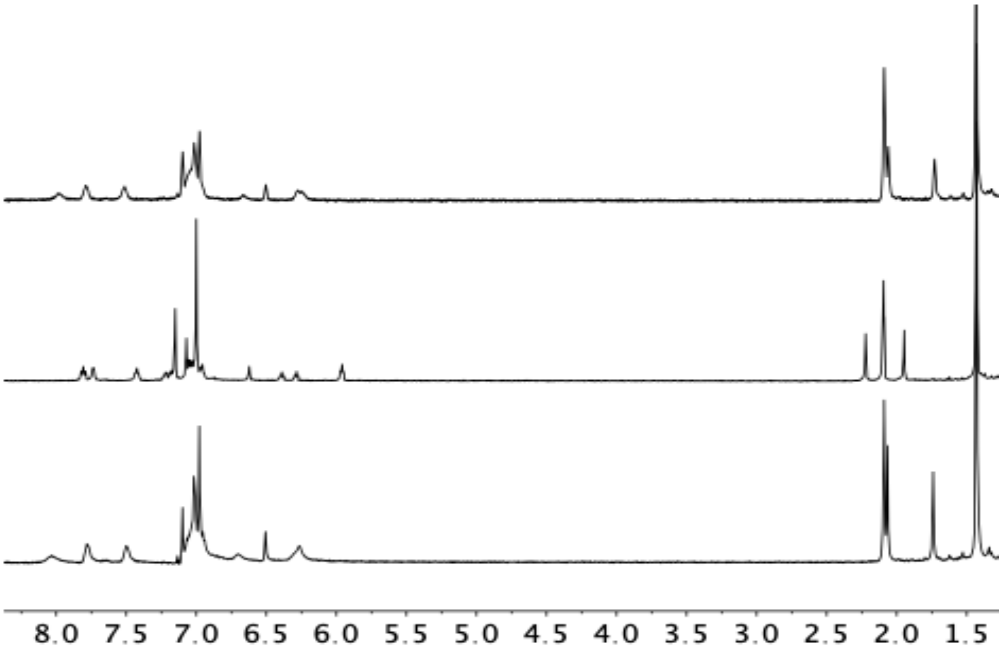

Figure S19. ^{1}H VT NMR analysis (243 MHz, toluene-d_8) of complex **3** at 25 ˚C (top), dimer **4** after cooling a solution of **3** to – 50 ˚C (middle), and re-warming to 25 ˚C (bottom).

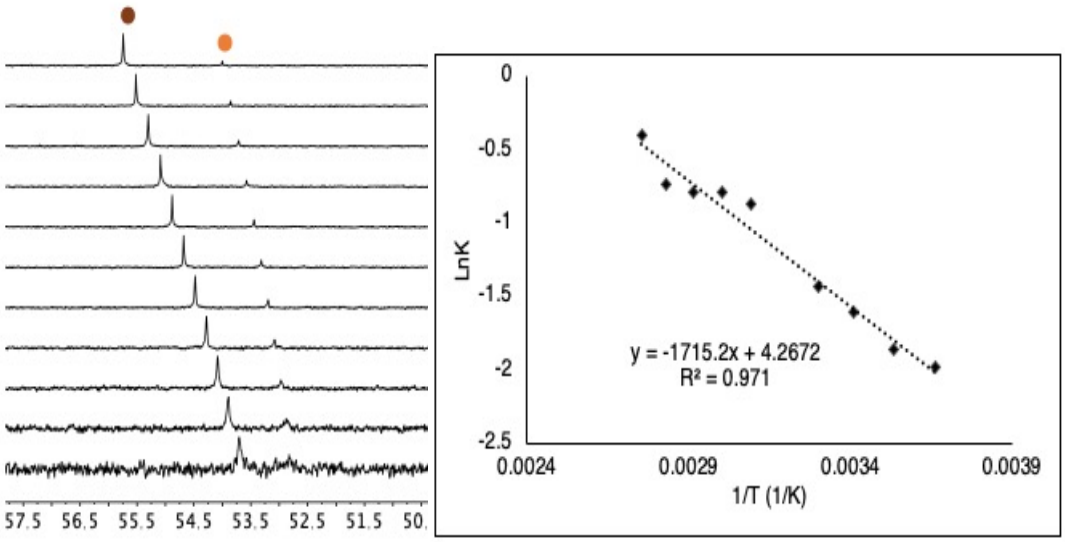

Figure S20. ^{31}P{^{1}H} NMR (243 MHz, toluene-d_8) spectral stack plot of ***Z*-1** (•); ***E*-1** (•) from 0 (top) to 100 ºC (bottom) in 10 ºC intervals (left). Van't Hoff plot derived from ^{31}P{^{1}H} NMR integration values between major and minor signals (right).

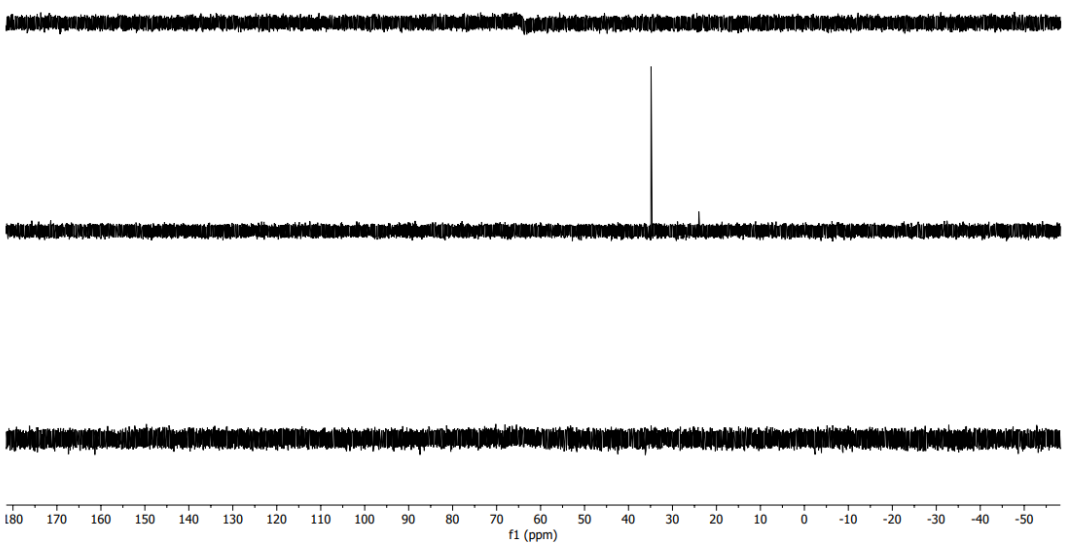

Figure S21. $^{31}P\{^{1}H\}$ NMR of spectra (600 MHz, C_6D_6) of: **3** (top); **3** after bubbled (ca. 15 min) with argon in Schlenk flask (middle); and **3** after three freeze(–78 ˚C)/pump/thaw cycles, and refilled with argon (flow 15 minutes) in an NMR tube (bottom). Observed peak at 35 ppm is an unknown species.

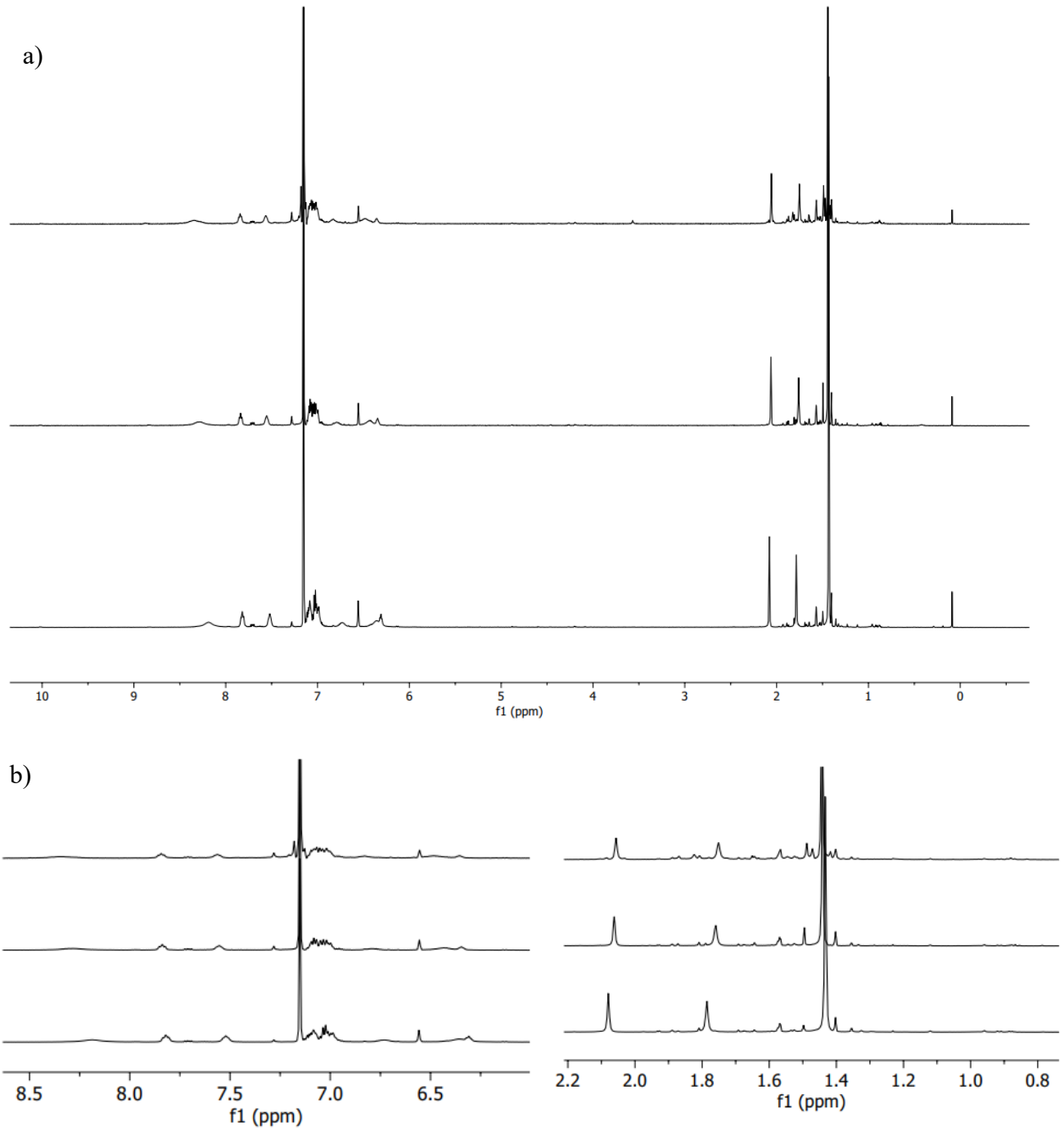

Figure S22. a) Full, and b) expanded ^{1}H NMR of spectra (600 MHz, C_6D_6) of: **3** (top); **3** after bubbled (ca. 15 min) with argon in Schlenk flask (middle); and **3** after three freeze (–78 ˚C)/pump/thaw cycles and refilled with argon (flow 15 minutes) in an NMR tube (bottom).

III – UV-Vis Spectra

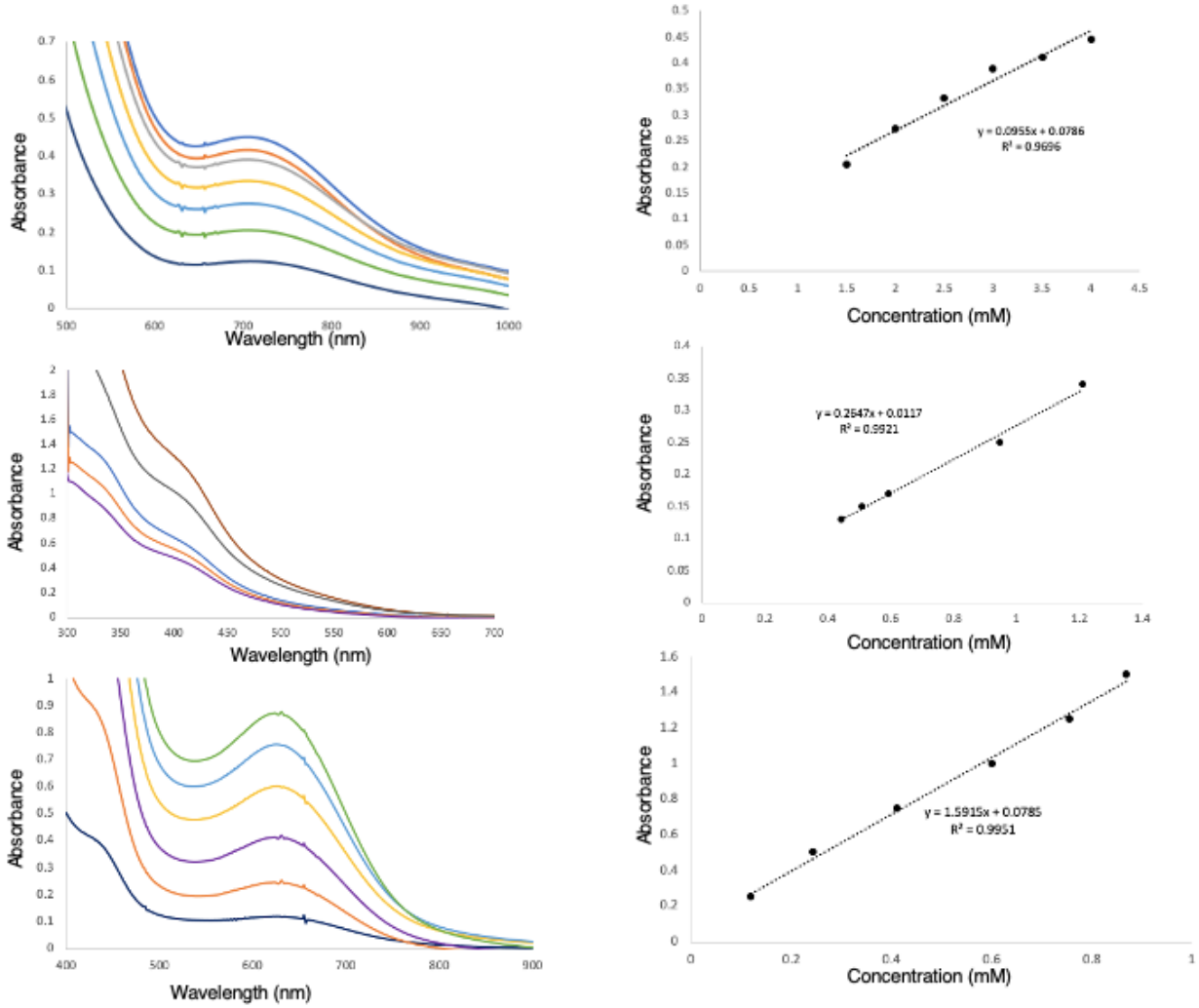

Figure S21. UV-Vis spectra (left) of **1** (top), **2** (middle), **3** (bottom) at various concentrations and corresponding Beer-Lambert plots (right).

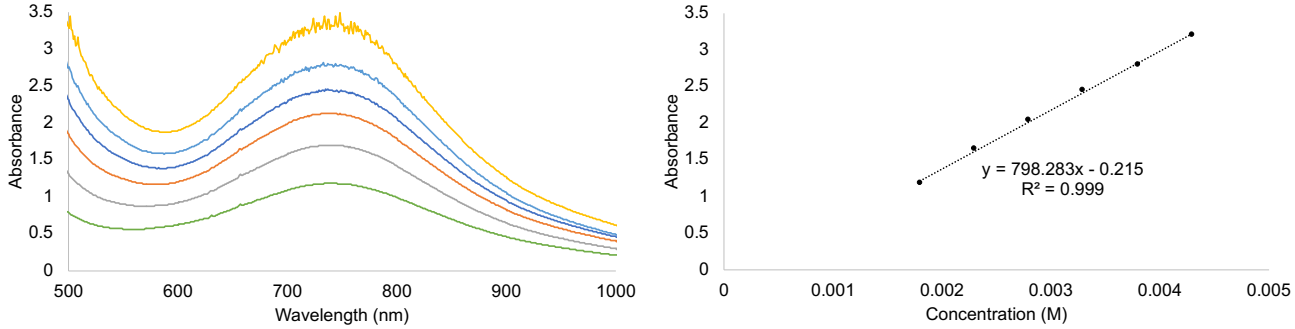

Figure S22. UV-Vis spectra (left) of **5** at various concentrations and the corresponding Beer-Lambert plot (right).

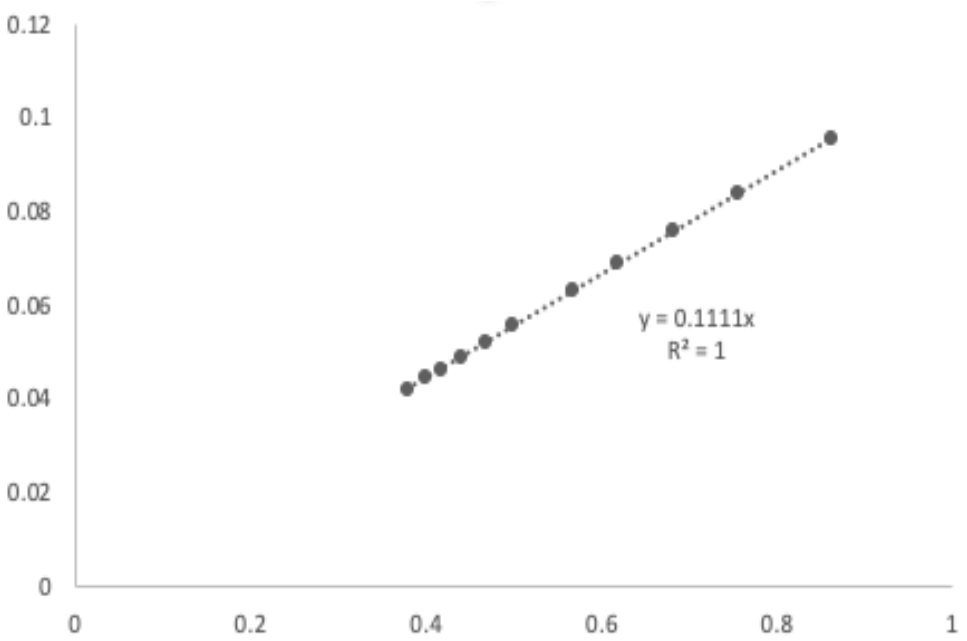

Figure S23. Plot used to calculate K_{eq} of the reaction of **3** with five equivalents of pyridine (**py**) to synthesize **2**. The y-axis was defined by y = (A)/([**3**]$_{initial}$ *[**py**]$_{initial}$) and x = ((A)*([**3**]$_{initial}$ + [**py**]$_{initial}$))/([**3**]$_{initial}$ *[**py**]$_{initial}$).[3] Where: A is the absorbance at various equivalents of pyridine used from acquired UV-vis titration data; [**3**]$_{initial}$ = 1.5 mM; [**py**] = 7.5 mM.

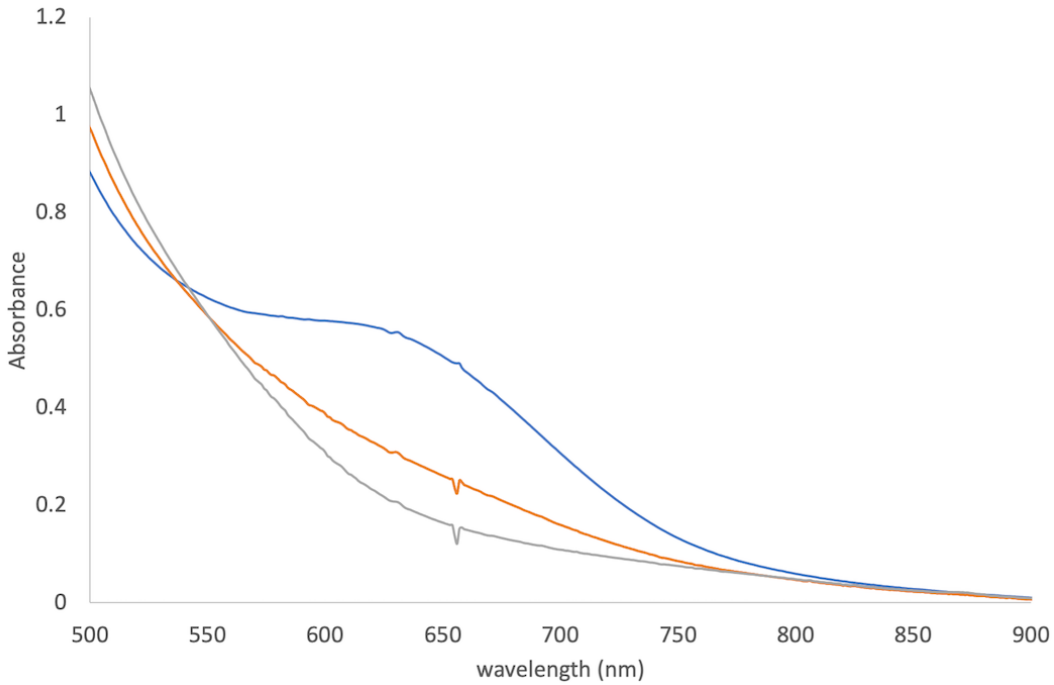

Figure S24. VT UV-vis of **3** (1.5 mM) from 25 to –50 ˚C. Traces correspond to temperatures of 25 (blue), –25 (orange) and –50 ˚C (grey).

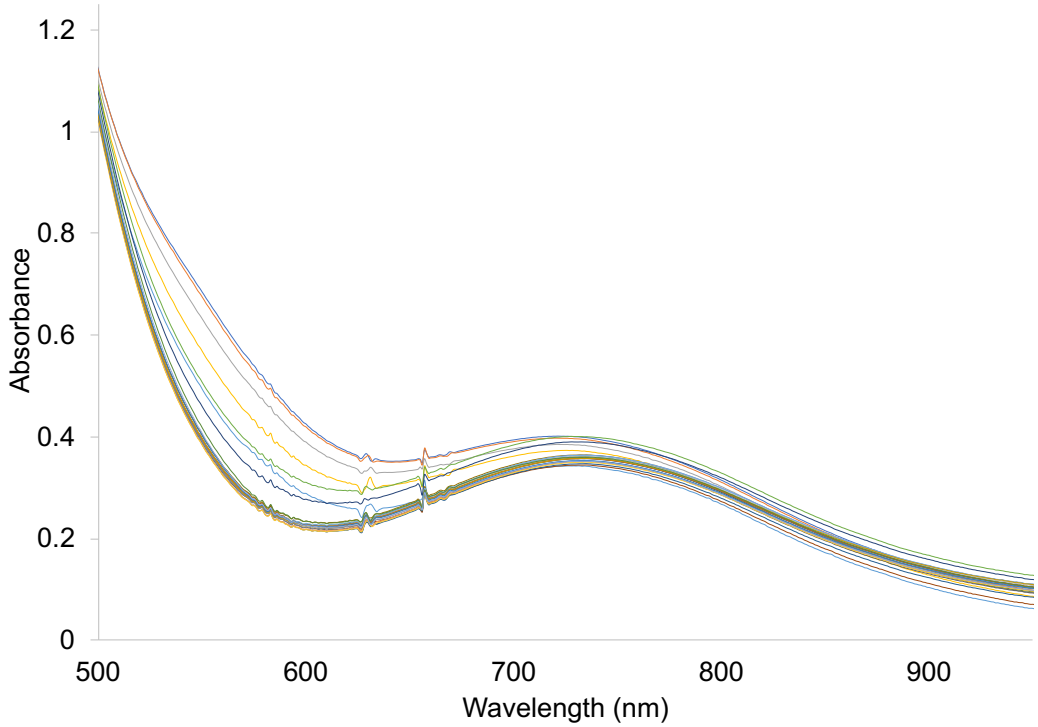

Figure S25. UV-Vis spectrum acquired from the addition of PPh_3 (10 equiv) to complex **2** at 0 ˚C. Scans were acquired every 5 s for 30 mins. For clarity 5s intervals are shown for the first 65s, after which time 100 s intervals are shown.

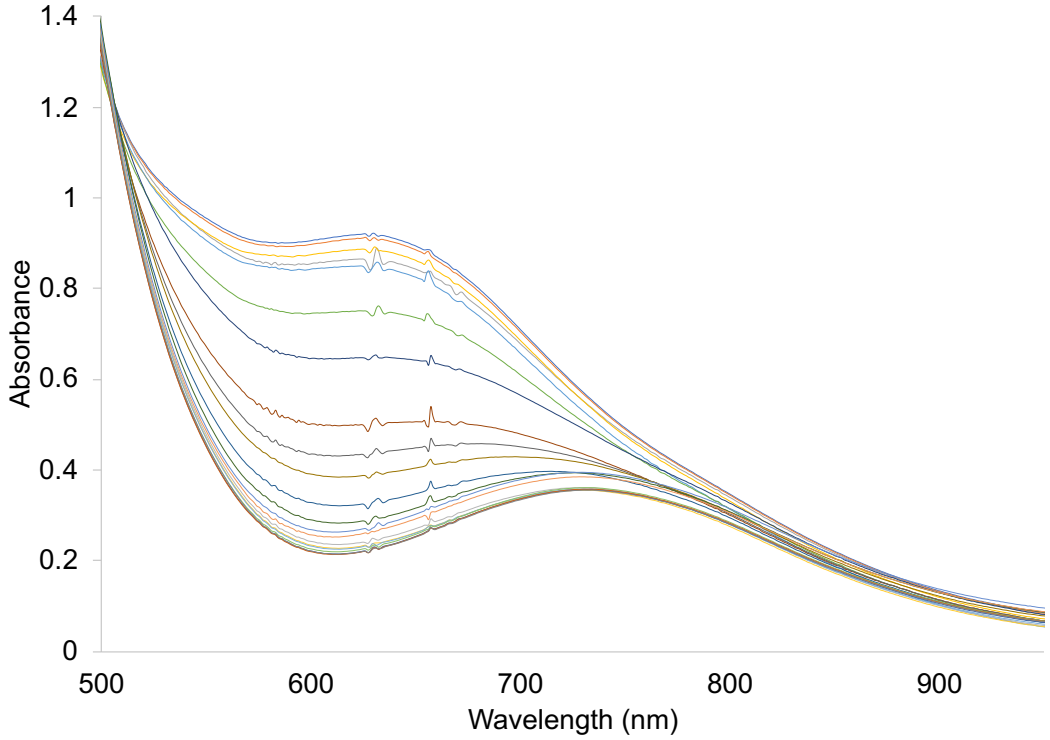

Figure S26. UV-Vis spectrum acquired from the addition of PPh_3 (10 equiv) to complex **3** at 0 ˚C. Scans acquired every 0.5 s for 1 min. For clarity, 5s scanning intervals are shown.

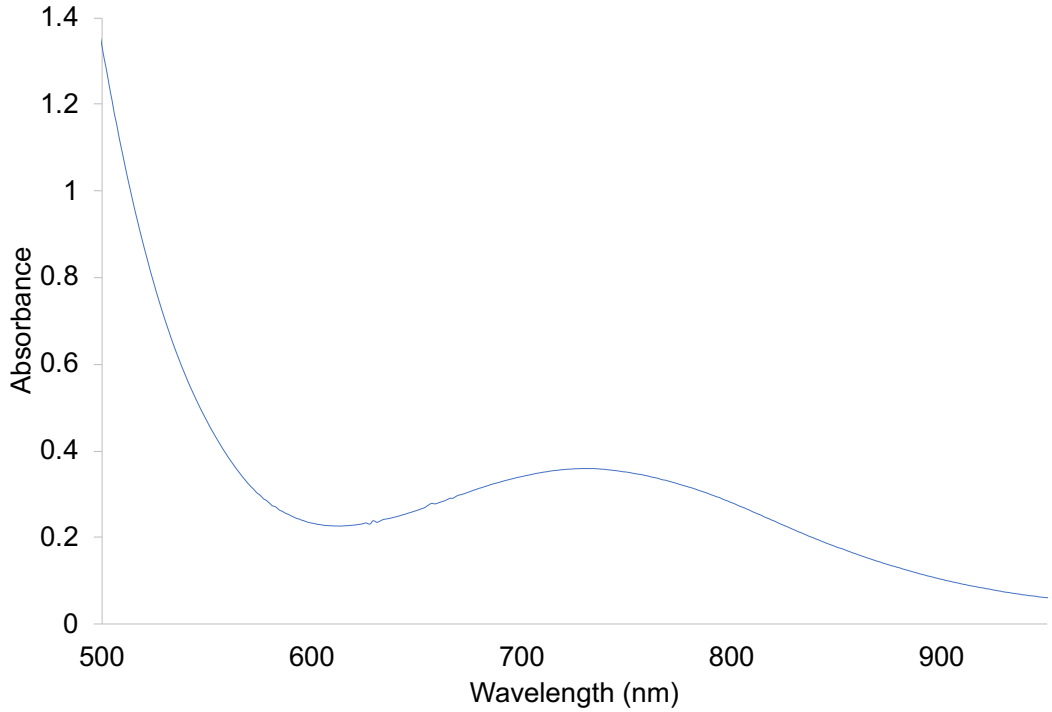

Figure S27. UV-vis spectrum of authentic **5**. Spectrum acquired at 25 ˚C.

IV – IR Spectra

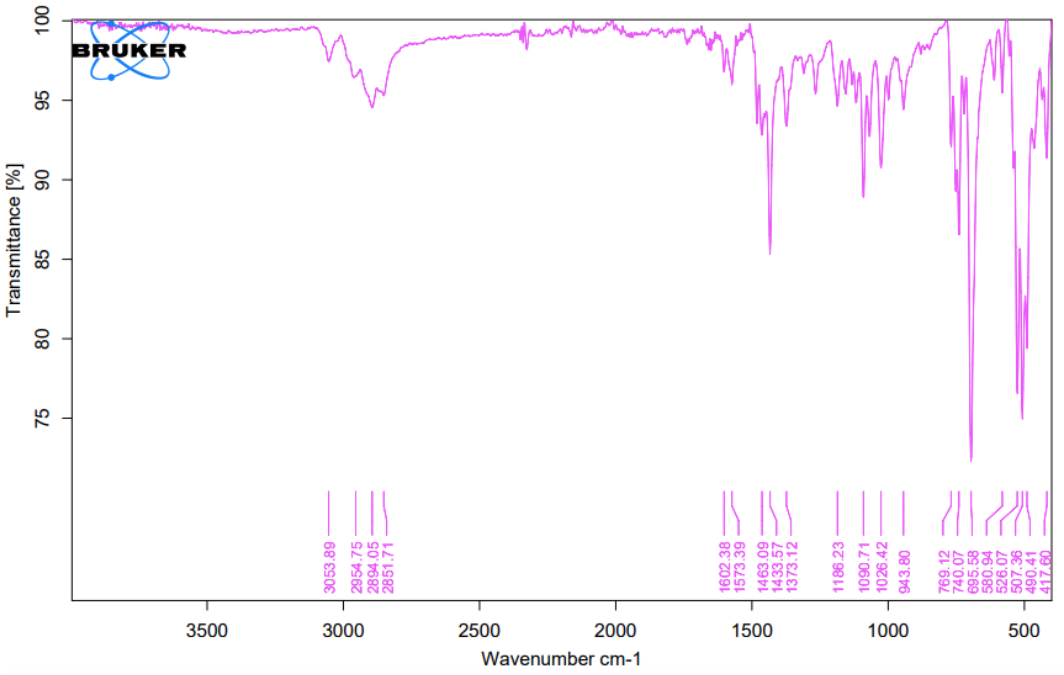

Figure S28. ATR-FTIR spectrum of solid **1**. Data acquired on a Bruker Apex II ATR-FTIR and plotted using OPUS software.

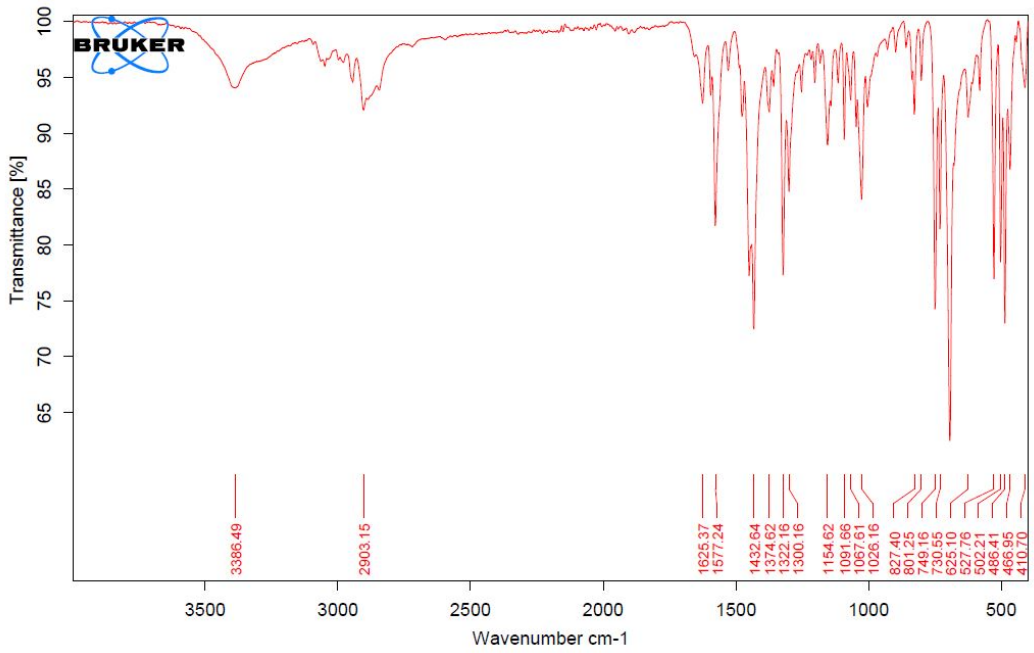

Figure S29. ATR-FTIR spectrum of solid **2**. Data acquired on a Bruker Apex II ATR-FTIR and plotted using OPUS software.

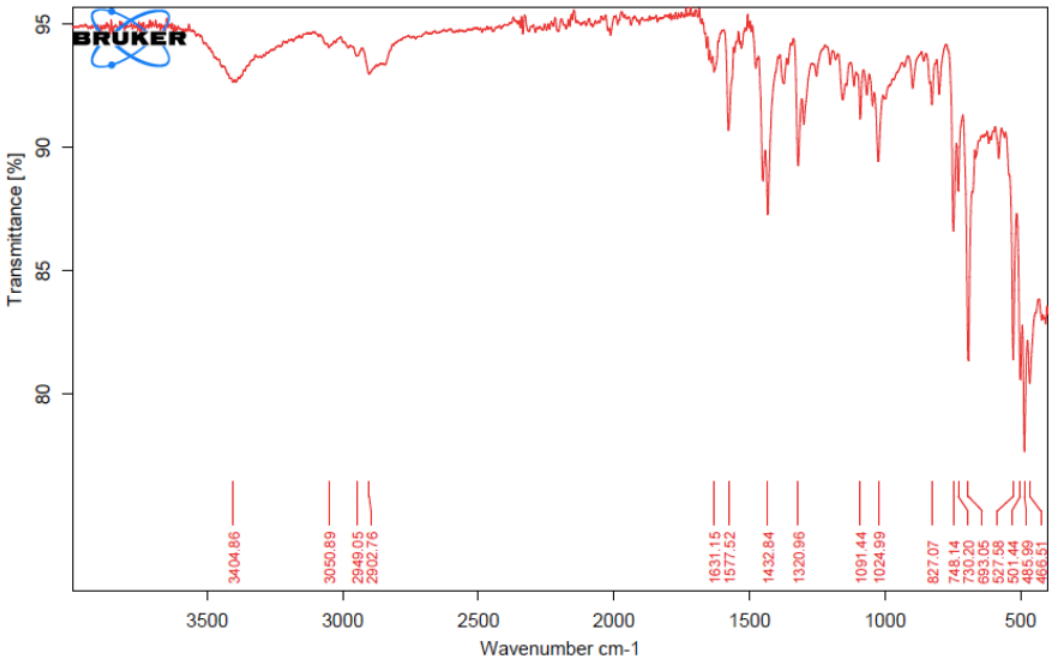

Figure S30. ATR-FTIR spectrum of solid **3**. Data acquired on a Bruker Apex II ATR-FTIR and plotted using OPUS software.

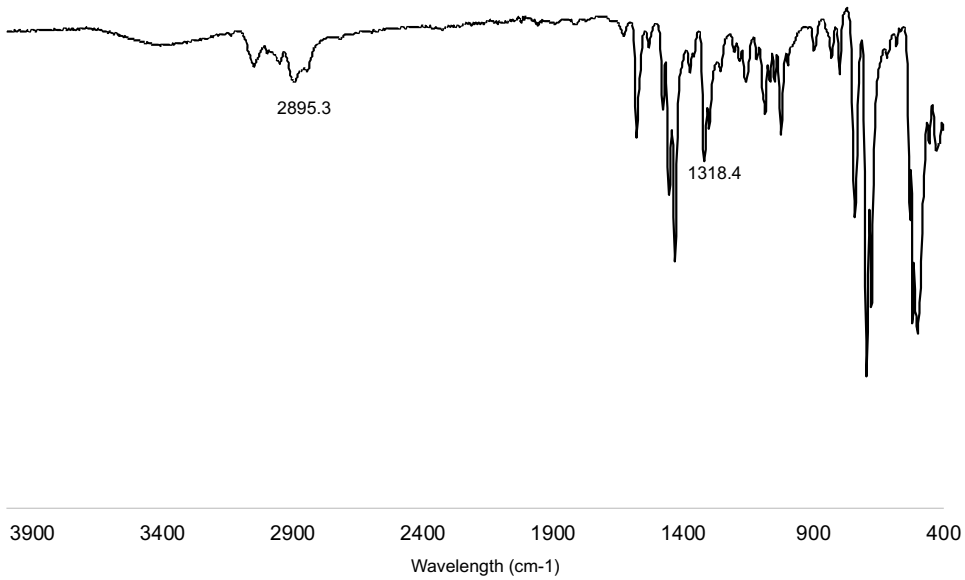

Figure S31. ATR-FTIR spectrum of solid **5**. Data acquired on a Bruker Apex II ATR-FTIR and plotted using Microsoft excel.

V – MALDI Mass Spectra

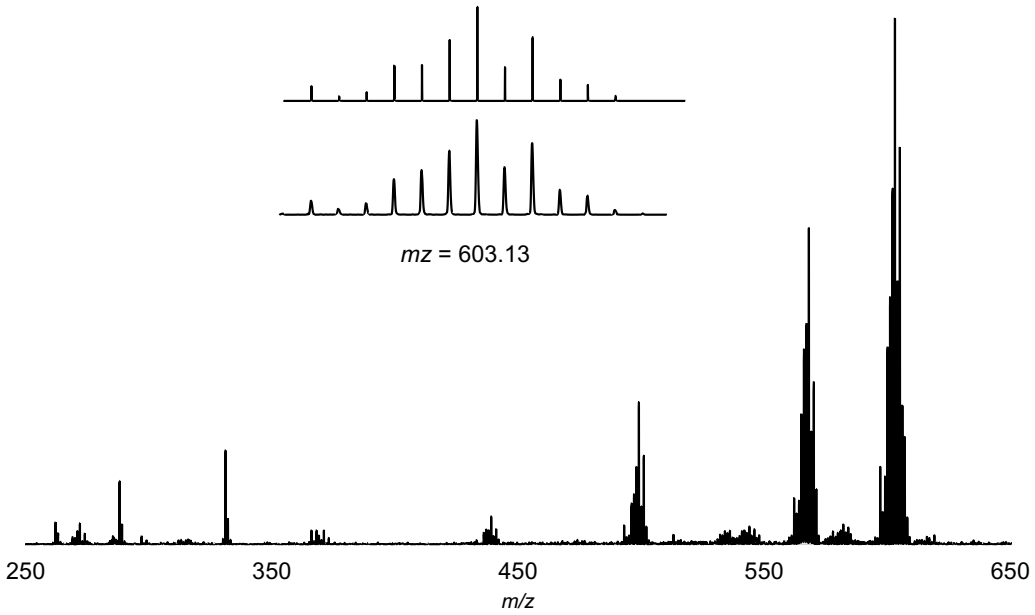

Figure S32. MALDI-TOF mass spectrum of RuCl(Cp*)(**HL1**) (**1**) with pyrene as the matrix. Inset simulation[4] of fragment [Ru(Cp*)(**HL1**)]$^+$ (top) and observed signal (bottom) for *m/z* = 603.1.

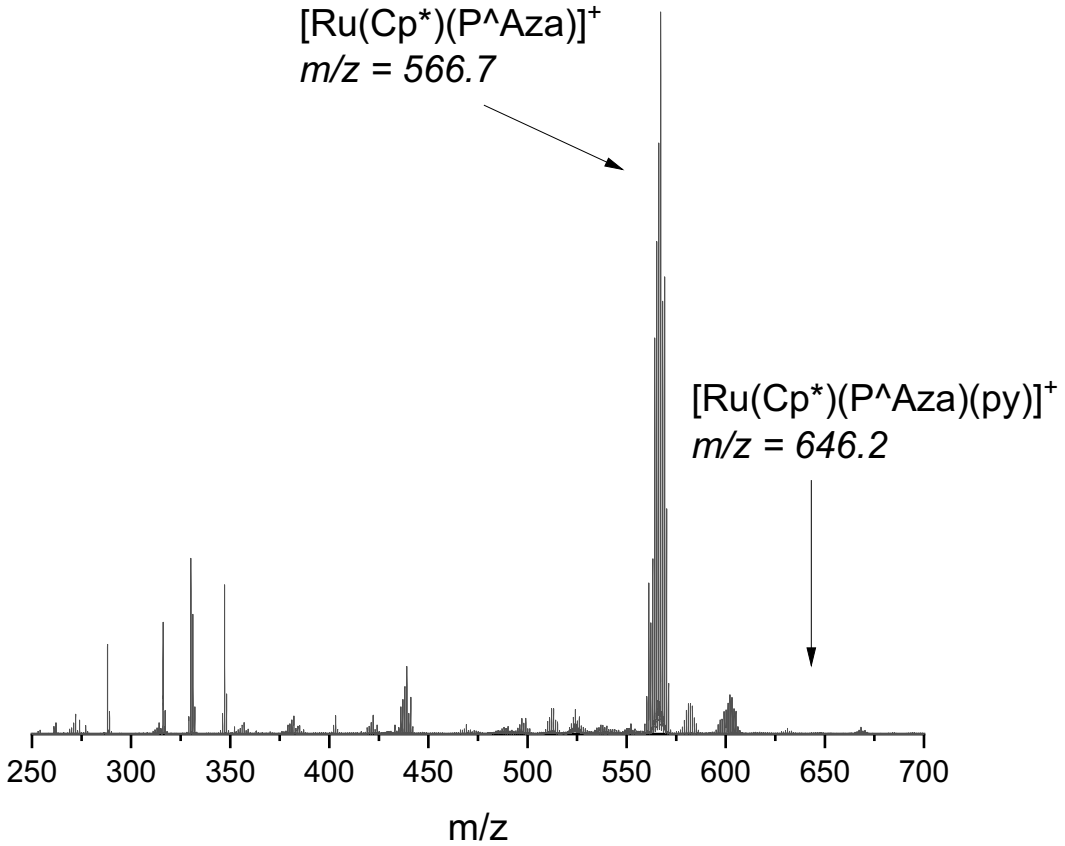

Figure S33. MALDI-TOF mass spectrum of Ru(Cp***)(L1)(**py) (**2**) with pyrene as the matrix. Signal at *m/z* = 566.7 represents [Ru(Cp*)(**L1**)]$^+$. Note: P^Aza = **L1**.

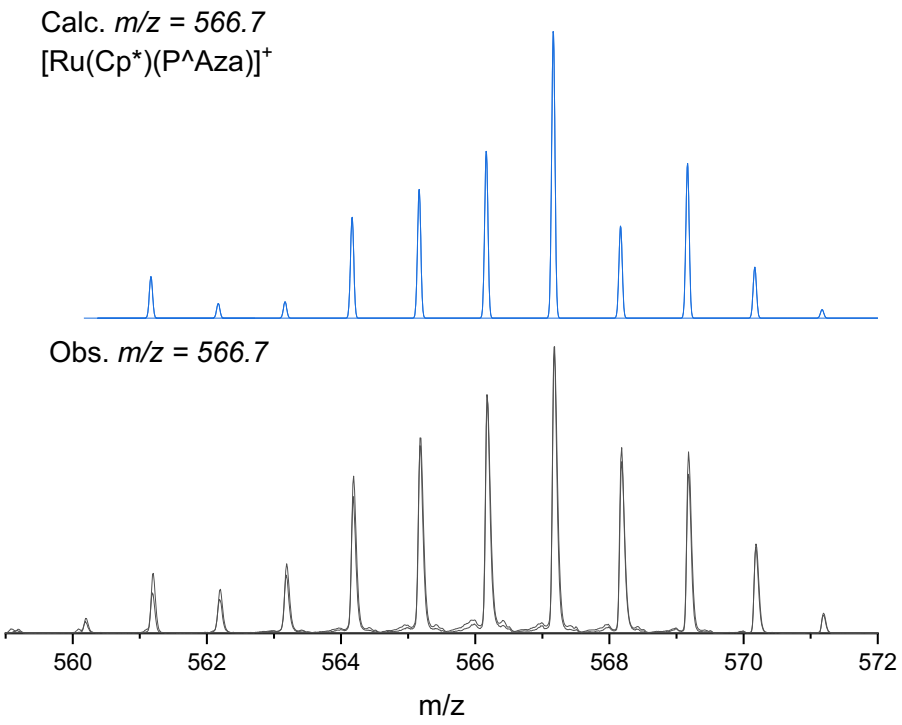

Figure S34. Zoom-in of the observed MALDI-TOF MS signal from Figure S33 (bottom) with *m/z* = 566.7 of **2**; and the simulation[4] (top) of the isotope pattern for the fragment cation [Ru(Cp*)(**L1**)]$^+$ with *m/z* = 566.7.

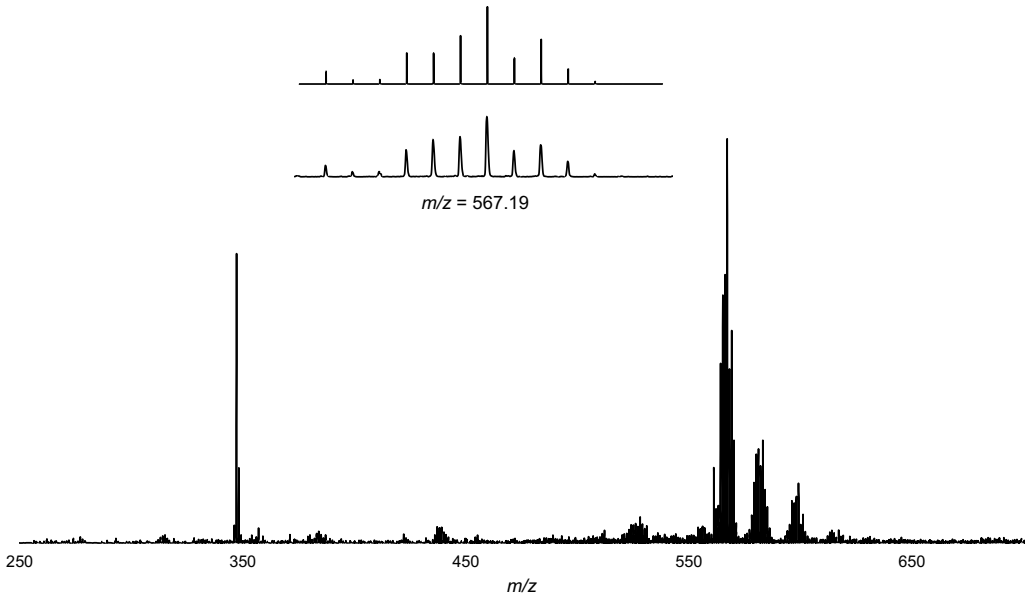

Figure S35. MALDI-TOF mass spectrum of [Ru(Cp*)(**L1**)] (**3**) with pyrene as the matrix. Inset simulation[4] (top) and observed (bottom) for [Ru(Cp*)(**L1**)]$^+$ *m/z* = 567.2.

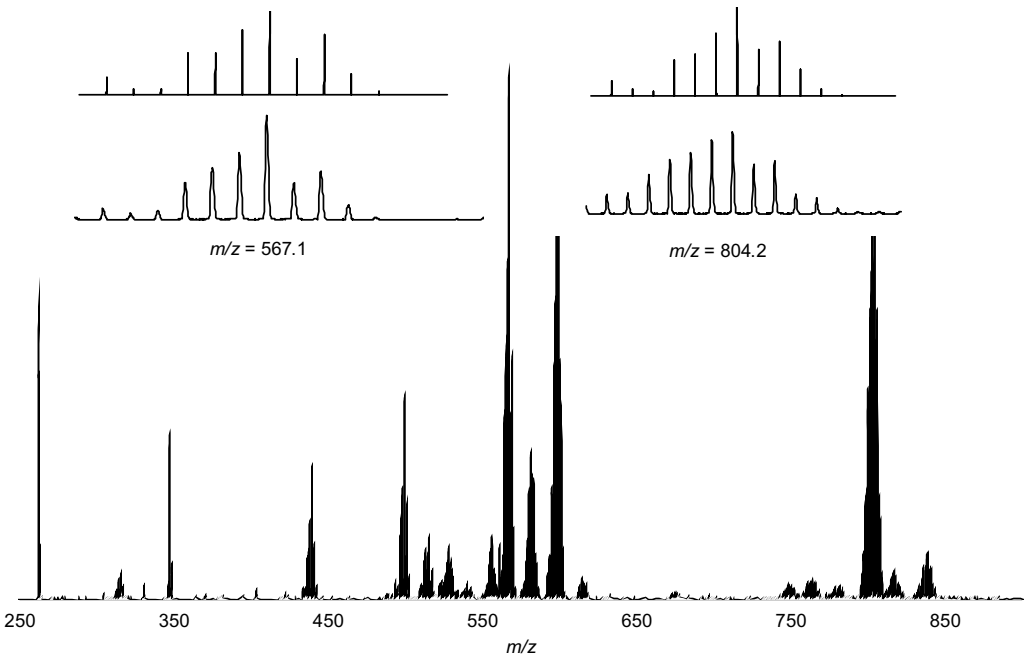

Figure S36. MALDI-TOF mass spectrum of Ru(Cp*)(**L1**)(PPh_3) (**5**) with pyrene as the matrix. Left: inset: simulation[4] for [Ru(Cp*)(**L1**)]$^+$ (top) and observed (bottom) for *m/z* = 567.2. Right inset: simulation[4] for [Ru(Cp*)(O=PPh_3)(**L1**-C_3H_6)]$^+$ (top) and observed (bottom) for *m/z* = 804.2.

VI – Crystallographic Details

Data Collection and Processing. The samples were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of: 9964 reflections with $4.84° < 2\theta < 64.56°$ for **1**; and 9939 reflections with $4.98° < 2\theta < 55.56°$ for **2**. The data collection strategy was a number of ω and φ scans which collected data up to 2θ: 65.39° for **1** and 57.506° for **2**. The frame integration was performed using SAINT.[5] The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[6]

Structure Solution and Refinement. The structures were solved by using a dual space methodology using the SHELXT program.[7] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL program from the SHELX suite of crystallographic software.[8] Graphic plots were produced using the Mercury program.[9]

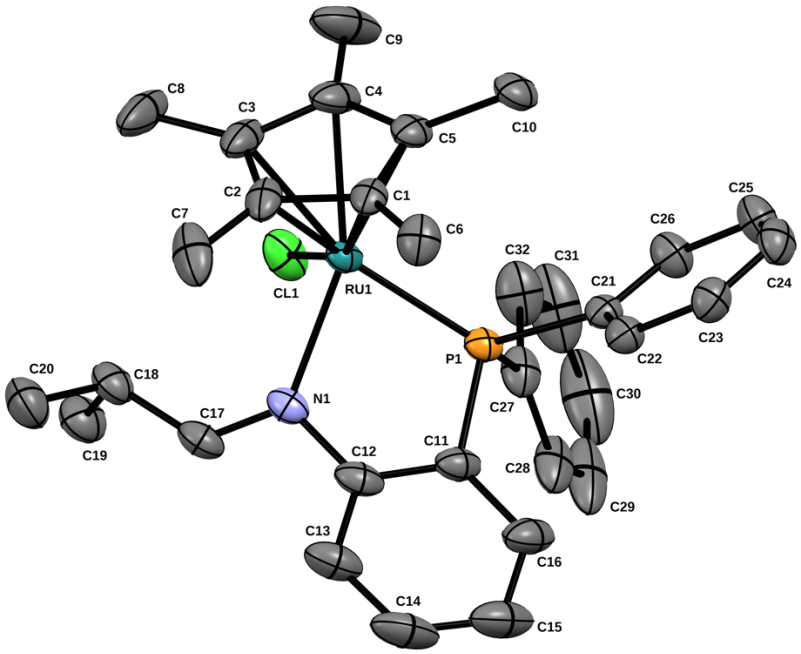

Figure S37. ORTEP drawing of **1** showing naming and numbering scheme. Ellipsoids are at the 50% probability level. Hydrogen atoms were omitted for clarity.

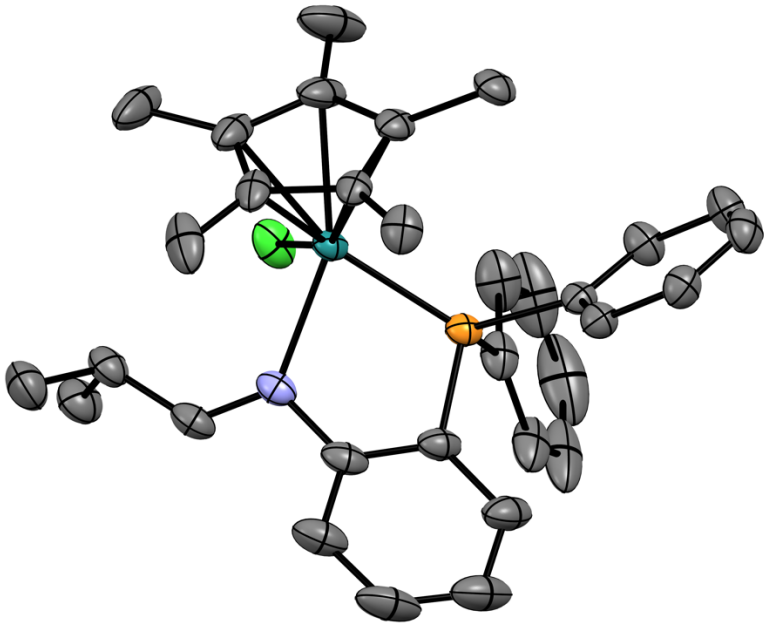

Figure S38. ORTEP drawing of **1.** Ellipsoids are at the 50% probability level and hydrogen atoms were omitted for clarity.

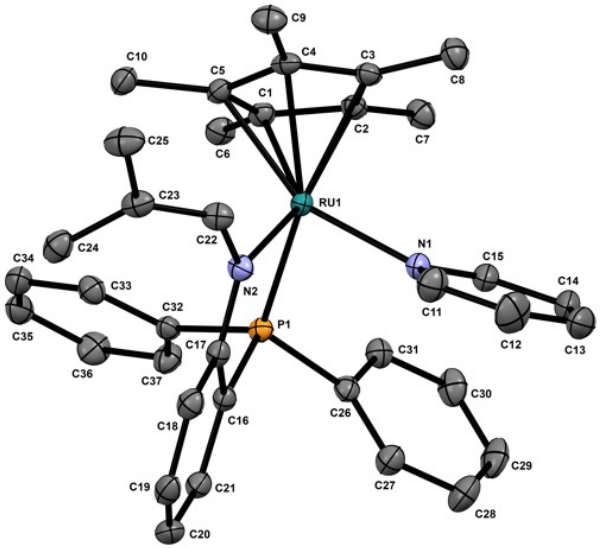

Figure S39. ORTEP drawing of **2** showing naming and numbering scheme. Ellipsoids are at the 50% probability level and hydrogen atoms were omitted for clarity.

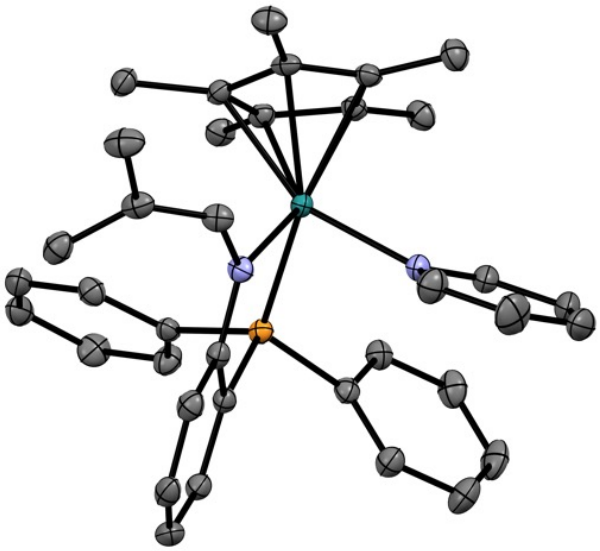

Figure S40. ORTEP drawing of **2**. Ellipsoids are at the 50% probability level and hydrogen atoms were omitted for clarity.

Table S1: Summary of Crystal Data for **1** and **2**.

Compound # (CCDC)	**1 (2206532)**	**2 (2206533)**
Formula	$C_{32}H_{37}ClNPRu$	$C_{37}H_{41}N_2PRu$
Formula Weight (*g/mol*)	603.11	645.76
Crystal Dimensions (*mm*)	0.148 × 0.086 × 0.081	0.149 × 0.108 × 0.049
Crystal Color and Habit	orange prism	red prism
Crystal System	monoclinic	monoclinic
Space Group	P 2_1/c	P 2_1/n
Temperature, K	110	110
a, Å	16.261(3)	10.509(4)
b, Å	11.225(3)	14.918(6)
c, Å	16.025(3)	19.744(7)
α,°	90	90
β,°	103.873(10)	98.065(11)
γ,°	90	90
V, $Å^3$	2839.8(11)	3064.8(19)
Number of reflections to determine final unit cell	9964	9939
Min and Max 2θ for cell determination, °	4.84, 64.56	4.98, 55.56
Z	4	4
F(000)	1248	1344
ρ (*g/cm*)	1.411	1.400

λ, Å, (MoKα)	0.71073	0.71073
μ, (cm^{-1})	0.724	0.593
Diffractometer Type	Bruker Kappa Axis Apex2	Bruker Kappa Axis Apex2
Scan Type(s)	φ and ω scans	φ and ω scans
Max 2θ for data collection, °	65.39	57.506
Measured fraction of data	0.998	0.999
Number of reflections measured	95988	129417
Unique reflections measured	10400	7935
R_{merge}	0.0800	0.1092
Number of reflections included in refinement	10400	7935
Cut off Threshold Expression	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Structure refined using	full matrix least-squares using F^2	full matrix least-squares using F^2
Weighting Scheme	$w=1/[\sigma^2(Fo^2)+(0.0382P)^2+0.9731P]$ where $P=(Fo^2+2Fc^2)/3$	$w=1/[\sigma^2(Fo^2)+(0.0273P)^2+3.0323P]$ where $P=(Fo^2+2Fc^2)/3$
Number of parameters in least-squares	332	377
R_1	0.0394	0.0331
wR_2	0.0835	0.0697
R_1 (all data)	0.0616	0.0525
wR_2 (all data)	0.0918	0.0777
GOF	1.036	1.015
Maximum shift/error	0.001	0.001
Min & Max peak heights on final DF Map (e^-/Å)	-0.869, 0.660	-0.623, 0.894
Where: $R_1 = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / S F_o$ $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]^{½}$ GOF = $[\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{½}$		

VII. Computational Data

Calculations are reported for the following structures: **3-in**, **3-out**, **3-open**, **4** (dimer).

Software package:	*Gaussian Development Version I.13*[10]
Density functional:	**M06**
Basis set:	**DGDZVP** (all-electron for Ru)
Dispersion correction:	**EmpiricalDispersion=GD3**
Implicit solvation method:	**SCRF(CPCM,Solvent=Benzene)**

Table S2: Calculated four lowest excitation energies of three isomers of complex **3** in benzene solution: Method: `TD M06/DGDZVP EmpiricalDispersion=GD3 Int(Grid=SuperFine) SCRF(CPCM,Solvent=Benzene).` Geometries: See **Table S4**.

Structure	λ_{abs}, nm	Oscillator Strength *f*
3-in	438	0.0021
	425	0.0031
	400	0.0012
	374	0.0019
3-out	526	0.0086
	502	0.0067
	454	0.0105
	425	0.0213
3-open	755	0.0117
	685	0.0161
	605	0.0003
	441	0.0876

Table S3. `M06/DGDZVP EmpiricalDispersion=GD3 Int(Grid=SuperFine) SCRF(CPCM,Solvent=Benzene)` energies (in a.u.) at the optimized geometries of **Table S4**.

Structure	SCF Energy	$G°_0$	$G°_{298}$
3-in	-6078.932594	-6078.342173	-6078.407059
3-out	-6078.928764	-6078.338409	-6078.403600
3-open	-6078.930905	-6078.342521	-6078.412295
dimer	-12157.885698	-12156.699900	-12156.800211

Table S4: Optimized `M06/DGDZVP EmpiricalDispersion=GD3 Int(Grid=SuperFine) SCRF(CPCM,Solvent=Benzene)` molecular geometries of **3-in**, **3-out**, **3-open**, and **4** (dimer). The last three columns contain Cartersian coordinates of the nuclei in Å.

Optimized structure: 3-in (minimum)

0,1

C	-1.737688	2.143033	-0.236043
C	-2.797746	1.431964	-0.870832
C	-3.446848	0.615890	0.108811
C	-2.784152	0.820283	1.368316
C	-1.725800	1.747831	1.156814
Ru	-1.289023	-0.055471	-0.099880
P	1.052759	-0.013399	-0.036532
C	1.948062	1.541902	-0.423249
C	2.453577	2.376626	0.579349
C	3.036784	3.599511	0.254242
C	3.125529	4.000749	-1.077495
C	2.627360	3.173007	-2.083020
C	2.037731	1.955299	-1.757143
C	-1.719021	-1.926923	-1.023361
N	-0.884304	-1.255214	-1.881432
C	0.437401	-1.689128	-2.075527
C	1.532950	-1.110008	-1.414825
C	2.838502	-1.490674	-1.745547
C	3.069212	-2.481175	-2.690767
C	1.977443	-3.099648	-3.311655
C	0.681270	-2.702666	-3.018837
C	-1.354837	-2.396602	0.271138
C	-2.499576	-2.868559	1.136872
C	-0.115423	-3.206275	0.588622
C	1.938601	-0.573494	1.477948
C	1.161460	-0.879874	2.597897
C	1.756907	-1.284584	3.790842
C	3.142975	-1.389895	3.873498
C	3.929885	-1.077645	2.764597
C	3.332022	-0.664311	1.578128
H	3.685129	-1.011360	-1.256867
H	4.084815	-2.774341	-2.941162
H	2.145388	-3.886188	-4.043380
H	-0.170839	-3.158566	-3.519318
H	0.074932	-0.806649	2.512389
H	1.137505	-1.519503	4.652551
H	3.612242	-1.708379	4.800606
H	5.012592	-1.148376	2.826756
H	3.963763	-0.390008	0.735492
H	2.400442	2.070503	1.623794
H	3.425822	4.236883	1.043978
H	3.584069	4.952738	-1.331214

H	2.694173	3.478071	-3.124002
H	1.637584	1.319344	-2.546852
H	-2.616262	-3.961454	1.075502
H	-2.310863	-2.632457	2.193017
H	-3.455648	-2.414824	0.856325
H	-0.315411	-4.263856	0.355422
H	0.790692	-2.927299	0.050539
H	0.108843	-3.161223	1.661486
H	-2.780335	-1.924107	-1.295867
C	-3.183476	1.522681	-2.309501
C	-4.710056	-0.148756	-0.118919
C	-3.202993	0.263176	2.688281
C	-0.872034	2.351778	2.224243
C	-0.951378	3.257618	-0.843070
H	-3.925556	0.925115	3.182351
H	-3.675623	-0.718735	2.586210
H	-2.349563	0.147058	3.364662
H	-5.565768	0.534238	-0.188321
H	-4.685176	-0.724923	-1.050967
H	-4.920236	-0.846058	0.697696
H	-3.983683	2.257401	-2.463347
H	-2.331755	1.817585	-2.930053
H	-3.541124	0.558414	-2.685881
H	-1.508125	4.201448	-0.779279
H	0.007965	3.408539	-0.337242
H	-0.734521	3.073321	-1.900766
H	-1.386042	3.195044	2.702944
H	-0.623576	1.629018	3.008838
H	0.070052	2.735019	1.817849

Optimized structure: 3-out (minimum)

0,1

C	0.433644	-0.156476	2.685648
C	1.534237	-0.160125	1.801205
C	2.797631	-0.543599	2.255929
C	2.985606	-0.940355	3.577374
C	1.891915	-0.970158	4.444470
C	0.630369	-0.582524	4.004696
P	1.105975	0.140593	0.041652
C	1.936381	1.696774	-0.469993
C	3.032487	2.251412	0.196104
C	3.603016	3.439184	-0.258078
C	3.091918	4.075950	-1.387589
C	1.999106	3.528340	-2.058344
C	1.419445	2.350688	-1.593928
N	-0.847207	0.269191	2.277560
C	-0.795999	1.474337	1.627544
C	-1.925312	2.037421	1.021758

C	-3.267662	1.866626	1.684097
Ru	-1.261458	0.017910	0.039408
C	-1.962260	-2.036489	-0.498097
C	-3.122637	-1.286835	-0.079529
C	-3.310063	-0.217979	-0.995979
C	-2.241023	-0.243710	-1.953057
C	-1.447814	-1.408003	-1.672513
C	2.137419	-1.132333	-0.786087
C	2.106409	-2.441738	-0.288560
C	2.807238	-3.458588	-0.926503
C	3.542723	-3.183341	-2.080707
C	3.582311	-1.884251	-2.579453
C	2.886243	-0.862431	-1.933379
C	-1.758416	3.325694	0.263916
H	0.542644	1.935566	-2.094518
H	1.589472	4.024603	-2.934102
H	3.539382	5.001644	-1.739458
H	4.448085	3.868637	0.273481
H	3.435982	1.766535	1.083285
H	-0.227116	-0.591574	4.673880
H	2.025342	-1.298078	5.472506
H	3.969574	-1.248853	3.919525
H	3.636680	-0.579775	1.560557
H	2.930383	0.149926	-2.332526
H	4.159162	-1.660274	-3.472882
H	4.087241	-3.978111	-2.583387
H	2.776652	-4.468181	-0.524983
H	1.532298	-2.665548	0.610839
C	-4.483642	0.694417	-1.112981
C	-2.156665	0.614559	-3.173312
C	-0.405074	-1.938106	-2.598428
C	-3.988072	-1.665870	1.076194
C	-1.506030	-3.312758	0.131234
H	-4.098996	2.008952	0.988850
H	-3.367351	0.894484	2.172438
H	-3.374511	2.642385	2.457843
H	-2.395172	3.342617	-0.630842
H	-2.055839	4.188582	0.878641
H	-0.723221	3.476970	-0.064477
H	0.153903	2.024635	1.562406
H	-1.149369	0.603222	-3.602364
H	-2.848677	0.274210	-3.956667
H	-2.404750	1.658407	-2.949239
H	-4.184933	1.743850	-1.220670
H	-5.055401	0.432968	-2.012464
H	-5.163937	0.617562	-0.261096
H	-3.390513	-1.815636	1.982965
H	-4.735393	-0.897949	1.296898
H	-4.523088	-2.602973	0.876706
H	-0.531422	-3.625033	-0.257928

```
H    -1.410590   -3.210237    1.219183
H    -2.214243   -4.129412   -0.061208
H     0.239550   -2.685441   -2.127104
H    -0.892864   -2.413992   -3.458381
H     0.241420   -1.144354   -2.989251
```

Optimized structure: 3-open (minimum)

```
0,1
Ru   -0.882200   -0.701353   -0.261962
P     1.246949    0.308713   -0.055105
C     0.898922    2.030756   -0.528146
C    -0.457888    2.264659   -0.866328
N    -1.362056    1.209978   -0.816003
C    -2.728351    1.479425   -1.046807
C    -3.576674    2.031550   -0.162319
C    -5.026223    2.213061   -0.493342
H    -5.317787    3.270456   -0.444878
H    -5.263918    1.841439   -1.495595
H    -5.664549    1.683578    0.228372
C    -3.139152    2.490620    1.193958
H    -3.070019    3.586143    1.240810
H    -2.158323    2.080743    1.461816
H    -3.865185    2.187043    1.959976
H    -3.120040    1.149775   -2.016155
C    -0.807475    3.579727   -1.240612
C     0.148496    4.587837   -1.280503
C     1.483470    4.342191   -0.950877
C     1.844736    3.050116   -0.576502
H     2.879379    2.831841   -0.309241
H     2.221953    5.137835   -0.984173
H    -0.156566    5.589128   -1.577074
H    -1.839579    3.801029   -1.502132
C     2.673950   -0.179408   -1.090326
C     3.997756    0.164331   -0.793664
C     5.025351   -0.187826   -1.664310
C     4.740999   -0.879991   -2.840984
C     3.424693   -1.220436   -3.146140
C     2.397364   -0.874593   -2.272074
H     1.363901   -1.140317   -2.500777
H     3.197664   -1.759262   -4.062171
H     5.545670   -1.154685   -3.517739
H     6.050810    0.080030   -1.423878
H     4.232092    0.702399    0.123854
C     1.893558    0.387892    1.651697
C     1.400567    1.357977    2.531622
C     1.744319    1.325152    3.880291
C     2.582423    0.322587    4.366822
C     3.076710   -0.647576    3.496413
```

C	2.729674	-0.619347	2.147881
H	3.118426	-1.385865	1.477861
H	3.732431	-1.431162	3.866917
H	2.850952	0.298901	5.419466
H	1.356350	2.085462	4.552954
H	0.741673	2.141672	2.157771
C	-2.539521	-2.144249	-0.623664
C	-3.641161	-1.975117	-1.615842
H	-4.331580	-1.180293	-1.313067
H	-3.248202	-1.710312	-2.604039
H	-4.223639	-2.898174	-1.730055
C	-2.556892	-1.761504	0.740116
C	-3.683641	-1.092087	1.450428
H	-4.177337	-0.356090	0.804493
H	-3.335510	-0.564973	2.344101
H	-4.438718	-1.821404	1.768441
C	-1.281494	-2.127459	1.328552
C	-0.513381	-2.806430	0.327317
C	-1.254574	-2.764008	-0.891792
C	-0.851477	-3.363767	-2.197336
H	-1.143519	-2.723697	-3.037320
H	0.231546	-3.512951	-2.253112
H	-1.327684	-4.341424	-2.347529
C	0.824947	-3.442906	0.518430
H	1.480116	-3.282081	-0.345566
H	1.335967	-3.036774	1.397905
H	0.731589	-4.525832	0.666531
C	-0.893248	-1.923435	2.755889
H	-1.323741	-0.997680	3.154099
H	0.194807	-1.840966	2.865503
H	-1.233157	-2.751004	3.391494

Optimized structure: 4 (C_2 symmetry, minimum)

0,1

Ru	-1.683933	1.120807	-0.584904
P	-2.304905	-1.129091	-0.140499
C	-4.025347	-1.459309	0.483068
C	-4.369635	-0.855755	1.697019
C	-5.607840	-1.072197	2.287981
C	-6.547391	-1.887158	1.656461
C	-6.223943	-2.486805	0.442370
C	-4.969240	-2.284821	-0.134897
H	-4.735128	-2.790017	-1.069989
H	-6.944446	-3.128885	-0.057941
H	-7.521263	-2.055587	2.108538
H	-5.841470	-0.591274	3.235545
H	-3.654527	-0.194506	2.180814
C	-2.171196	-2.546843	-1.314103

C	-1.591304	-3.779333	-1.009408
C	-1.670995	-4.846860	-1.903204
C	-2.344145	-4.702595	-3.113082
C	-2.909425	-3.470140	-3.438777
C	-2.806037	-2.403239	-2.553290
H	-3.233091	-1.439184	-2.826107
H	-3.421754	-3.335184	-4.388042
H	-2.418404	-5.539499	-3.802462
H	-1.207421	-5.795981	-1.644827
H	-1.074302	-3.919598	-0.063464
C	-1.390257	-1.578059	1.368617
C	-0.596892	-0.564480	1.923999
C	0.074064	-0.840252	3.130558
C	-0.112879	-2.032536	3.801366
C	-0.973689	-3.009166	3.285784
C	-1.599493	-2.775007	2.073443
H	-2.299413	-3.512370	1.682121
H	-1.144651	-3.938087	3.823451
H	0.404208	-2.205237	4.742806
H	0.716140	-0.070232	3.553059
N	-0.513749	0.727398	1.336854
C	-0.915414	1.759246	2.210209
C	-1.620806	1.811296	3.369538
C	-2.280264	0.719883	4.166424
H	-1.776213	0.584311	5.136424
H	-2.314292	-0.258751	3.689178
H	-3.315746	1.015220	4.399272
C	-1.780217	3.142842	4.057698
H	-1.326999	3.971566	3.505065
H	-1.318138	3.121574	5.057201
H	-2.840434	3.391625	4.220307
H	-0.606753	2.725546	1.816887
C	-3.701353	2.145222	-0.351038
C	-2.746213	3.197700	-0.233237
C	-2.001714	3.281623	-1.428171
C	-2.506782	2.274727	-2.336108
C	-3.579582	1.608607	-1.682719
C	-4.600268	0.731702	-2.330510
H	-4.244635	0.311221	-3.276171
H	-4.926677	-0.092463	-1.686799
H	-5.493806	1.326576	-2.561728
C	-2.134378	2.158207	-3.777923
H	-1.047188	2.192232	-3.921340
H	-2.496498	1.220818	-4.214365
H	-2.570798	2.979899	-4.361538
C	-1.127557	4.436851	-1.791506
H	-0.633437	4.289330	-2.755567
H	-0.351861	4.633622	-1.041246
H	-1.728629	5.352014	-1.874352
C	-2.723079	4.177558	0.884534

H	-1.769433	4.710509	0.958127
H	-2.921801	3.694131	1.844836
H	-3.507042	4.930831	0.726259
C	-4.878929	1.995701	0.555834
H	-4.590375	1.981437	1.614463
H	-5.444897	1.081334	0.354580
H	-5.566164	2.842991	0.420162
Ru	1.683502	1.119748	0.585855
C	3.704382	2.138880	0.357758
C	2.751560	3.192331	0.232390
C	2.001750	3.281367	1.424012
C	2.502078	2.277072	2.337409
C	3.575901	1.606567	1.690641
C	4.591918	0.729630	2.345636
H	4.230042	0.310006	3.289314
H	4.921699	-0.095184	1.704499
H	5.484485	1.323978	2.581942
C	2.124422	2.166023	3.778271
H	1.036800	2.199788	3.917965
H	2.485811	1.230786	4.219849
H	2.558341	2.990490	4.359823
C	1.128865	4.439674	1.780473
H	0.622569	4.292258	2.738207
H	0.363479	4.642156	1.021254
H	1.733203	5.351781	1.873168
C	2.734653	4.167922	-0.889189
H	1.783528	4.704888	-0.966406
H	2.932520	3.679792	-1.847355
H	3.521729	4.918267	-0.732594
C	4.885530	1.983578	-0.543417
H	4.601940	1.968665	-1.603283
H	5.447223	1.067402	-0.338277
H	5.575255	2.828526	-0.405773
N	0.513368	0.727561	-1.336820
C	0.913909	1.760051	-2.209964
C	1.617248	1.813378	-3.370506
C	2.276067	0.723153	-4.169515
H	1.771975	0.589683	-5.139790
H	2.309482	-0.256401	-3.694192
H	3.311704	1.018393	-4.401734
C	1.775080	3.145719	-4.057558
H	1.326858	3.974472	-3.500995
H	1.307275	3.126899	-5.054469
H	2.834794	3.392692	-4.225817
H	0.606270	2.726052	-1.815204
C	0.596914	-0.563924	-1.924875
C	-0.074895	-0.839465	-3.131018
C	0.112642	-2.030945	-3.803084
C	0.974964	-3.007101	-3.289182
C	1.601418	-2.773421	-2.077087

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C     1.391518   -1.577329   -1.370975
P     2.305163   -1.129985    0.139135
C     4.026623   -1.457323   -0.483058
C     4.368973   -0.860164   -1.700782
C     5.609178   -1.073476   -2.288684
C     6.552807   -1.878289   -1.650295
C     6.231381   -2.471260   -0.432397
C     4.974718   -2.272738    0.141809
H     4.742339   -2.773058    1.079946
H     6.955003   -3.105533    0.073340
H     7.528226   -2.044098   -2.099995
H     5.841150   -0.597888   -3.239323
H     3.650809   -0.206405   -2.190193
C     2.171081   -2.550007    1.310256
C     1.592743   -3.782610    1.002773
C     1.671644   -4.851384    1.895110
C     2.342489   -4.708438    3.106432
C     2.906002   -3.475993    3.435011
C     2.803208   -2.407789    2.550976
H     3.228348   -1.443658    2.826398
H     3.416311   -3.341905    4.385491
H     2.416191   -5.546321    3.794681
H     1.209263   -5.800457    1.634441
H     1.077418   -3.922006    0.055803
H     2.302408   -3.510383   -1.686968
H     1.146500   -3.935333   -3.827855
H    -0.405171   -2.203316   -4.744184
H    -0.718068   -0.069764   -3.552322

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