

Supplementary Information

Conformational Twisting of a Formate-Bridged Diiridium Complex Enables Catalytic Formic Acid Dehydrogenation

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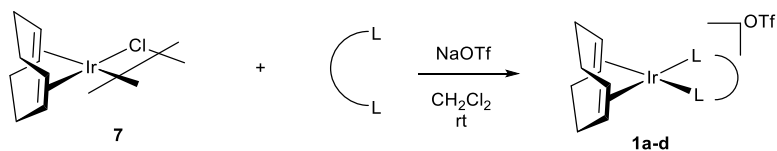
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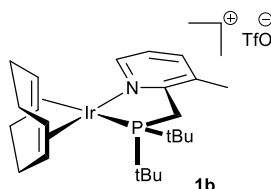
II. ¹H NMR Spectra for Attempted Conversion to 5-type Dimers

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I. Synthesis of Complexes 1b-1d.



Complex 1b



Complex **1b** was synthesized using the procedure for the synthesis of complex **1a** (See main text experimental section). 2-(di-*tert*-Butylphosphino)-6-methylpyridine (31.0 mg, 0.12 mmol), chloro(1,5-cyclooctadiene)iridium(I) dimer (41.4 mg, 0.062 mmol), and sodium trifluoromethanesulfonate (39.0 mg, 0.22 mmol) were used. Pure product was isolated as an orange solid (74.0 mg, 85% yield).

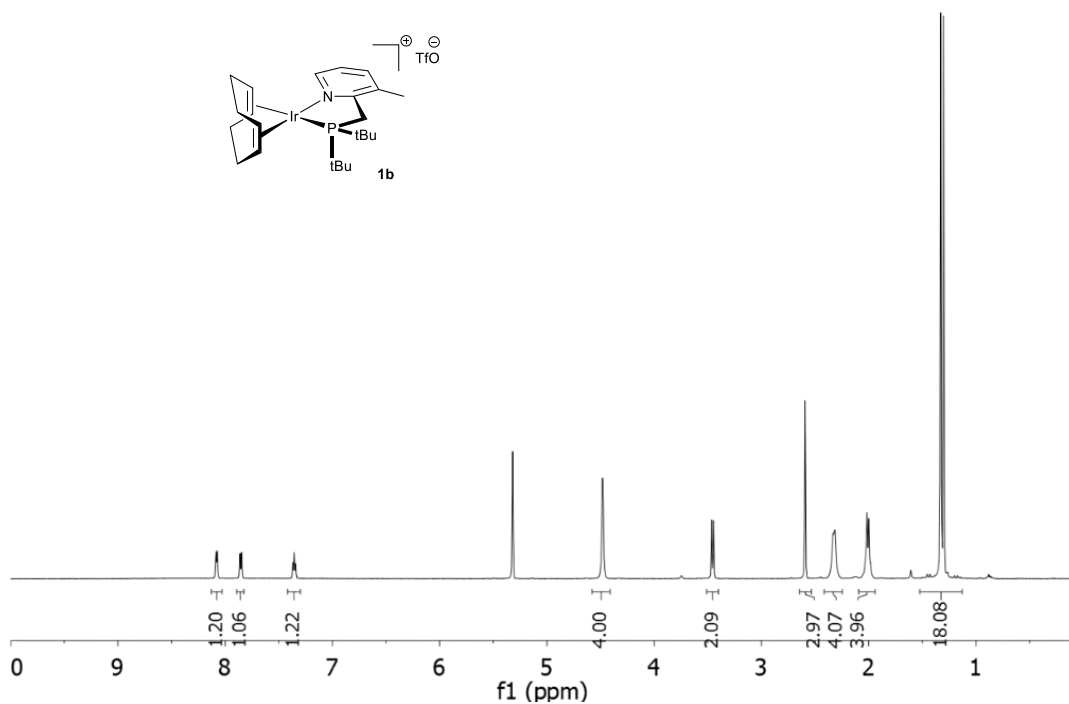
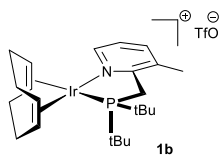
¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 8.08 (d, J = 5.9 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 6.8 Hz, 1H), 4.48 (d, J = 3.9 Hz, 4H) 3.46 (d, J = 8.9 Hz, 2H), 2.59 (s, 3H), 2.32 (d, J = 9.9 Hz, 4H), 1.31 (d, J = 13.6 Hz, 18H)

¹³C NMR (126 MHz, Methylene Chloride- *d*₂) δ 164.83, 146.75, 141.56, 134.09, 134.02, 124.25, 37.29, 37.15, 32.02, 31.83, 29.79, 29.76, 22.04

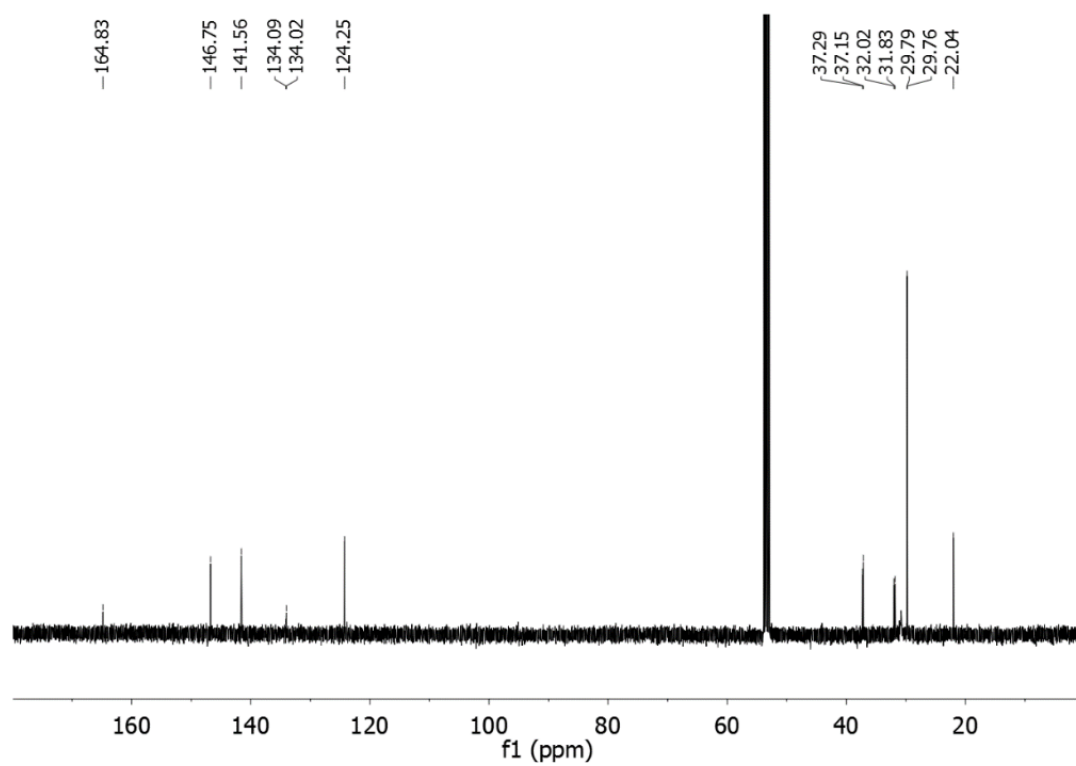
³¹P NMR (202 MHz, Methylene Chloride-*d*₂) δ 54.11

HRMS (ESI/APCI): m/z = 552.2341 g/mol, calc'd for C₂₃H₃₈IrNP⁺ [M]⁺: 552.2366 g/mol.

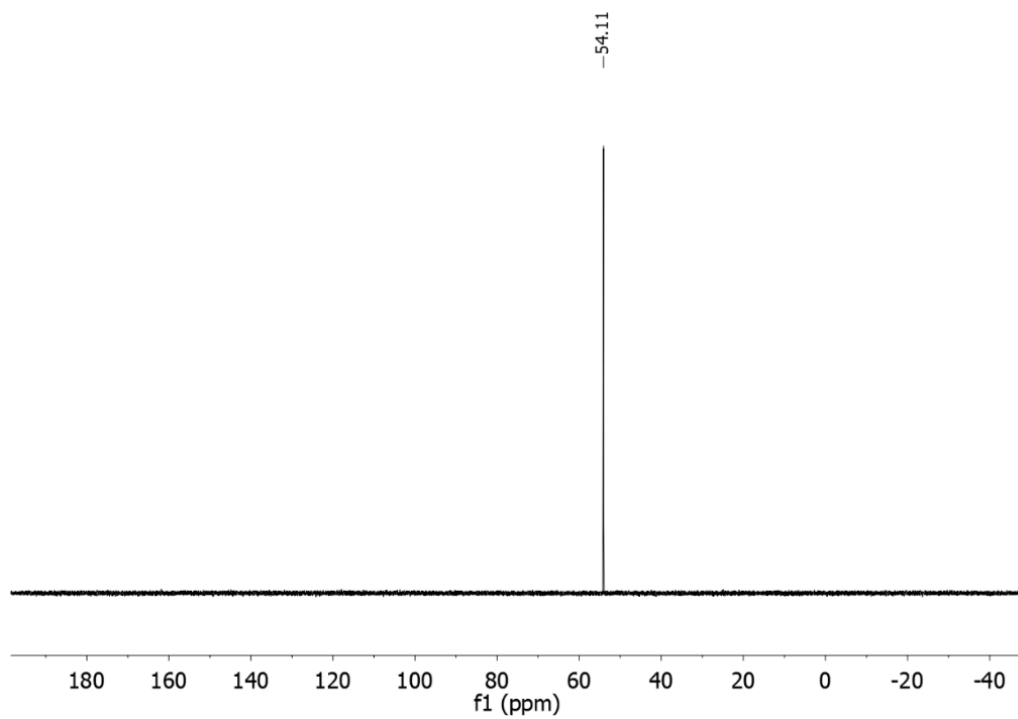
FT-IR (thin film/cm⁻¹) ν = 2947, 2923, 2876, 2834, 2427, 2297, 1733, 1594, 1559, 1540, 1466, 1430, 1391, 1371, 1333, 1269, 1222, 1149, 1113, 1088, 1031, 966, 937, 893, 879, 825, 808



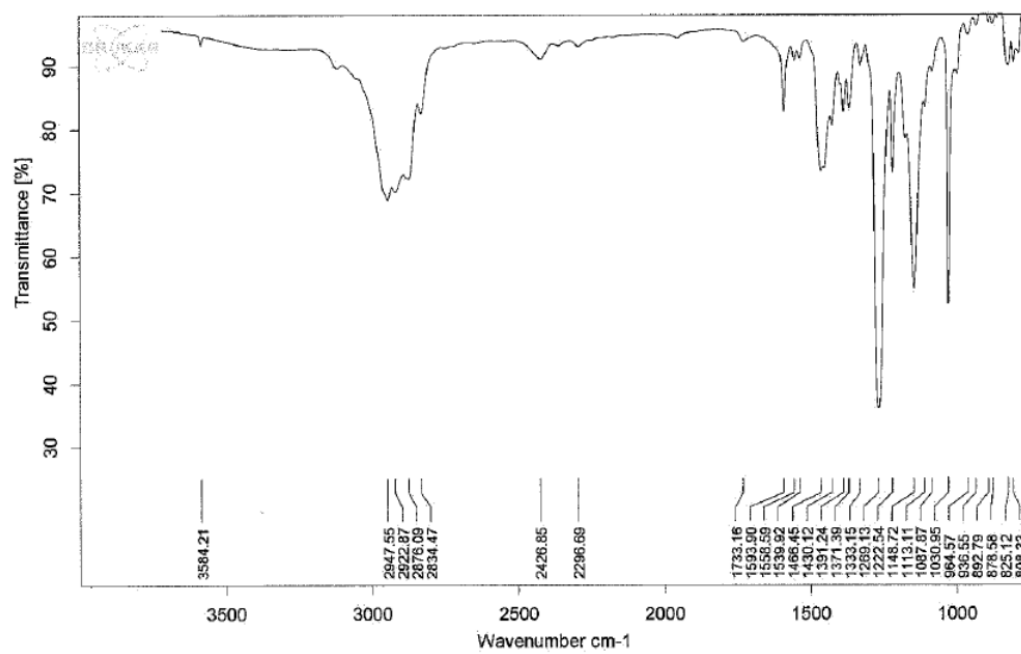
¹H NMR Spectrum of Complex **1b** at 25 °C in CD₂Cl₂



¹³C NMR Spectrum of Complex **1b** at 25 °C in CD₂Cl₂

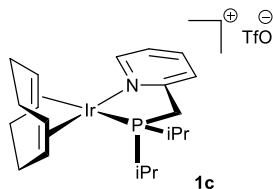


^{31}P NMR Spectrum of Complex **1b** at 25 °C in CD_2Cl_2



IR Spectrum of Complex **1b**.

Complex 1c



Complex **1c** was synthesized using the procedure used for the synthesis of complex **1a** (see main text experimental section). 2-((Diisopropylphosphino)methyl)pyridine (63.4 mg, 0.28 mmol), chloro(1,5-cyclooctadiene)iridium(I) dimer (95 mg, 0.14 mmol), and sodium trifluoromethanesulfonate (100 mg, 0.58 mmol) were used. Pure product was isolated as an orange solid (99 mg, 70 % yield).

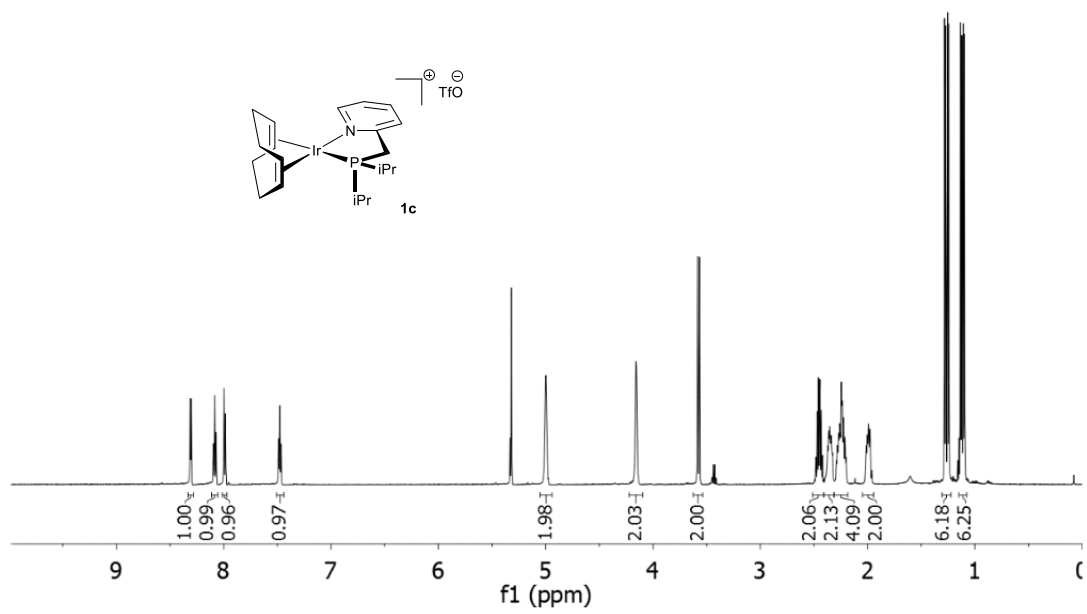
¹H NMR (600 MHz, Methylene Chloride-*d*₂) δ 8.33 – 8.28 (m, 1H), 8.08 (tt, *J* = 7.7, 1.3 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.48 (ddd, *J* = 7.4, 5.9, 1.5 Hz, 1H), 5.00 (tt, *J* = 4.9, 2.1 Hz, 2H), 4.16 (dt, *J* = 5.7, 2.3 Hz, 2H), 3.58 (d, *J* = 10.1 Hz, 2H), 2.45 (dp, *J* = 8.8, 7.1 Hz, 2H), 2.41 – 2.31 (m, 2H), 2.31 – 2.19 (m, 4H), 2.05 – 1.94 (m, 2H), 1.26 (dd, *J* = 16.6, 7.1 Hz, 6H), 1.12 (dd, *J* = 15.2, 6.9 Hz, 6H).

¹³C NMR (151 MHz, Methylene Chloride-*d*₂) δ 166.80, 149.79, 141.46, 125.10, 125.04, 124.44, 93.86, 93.79, 62.10, 33.47, 33.25, 33.06, 28.32, 24.51, 24.32, 18.53, 17.

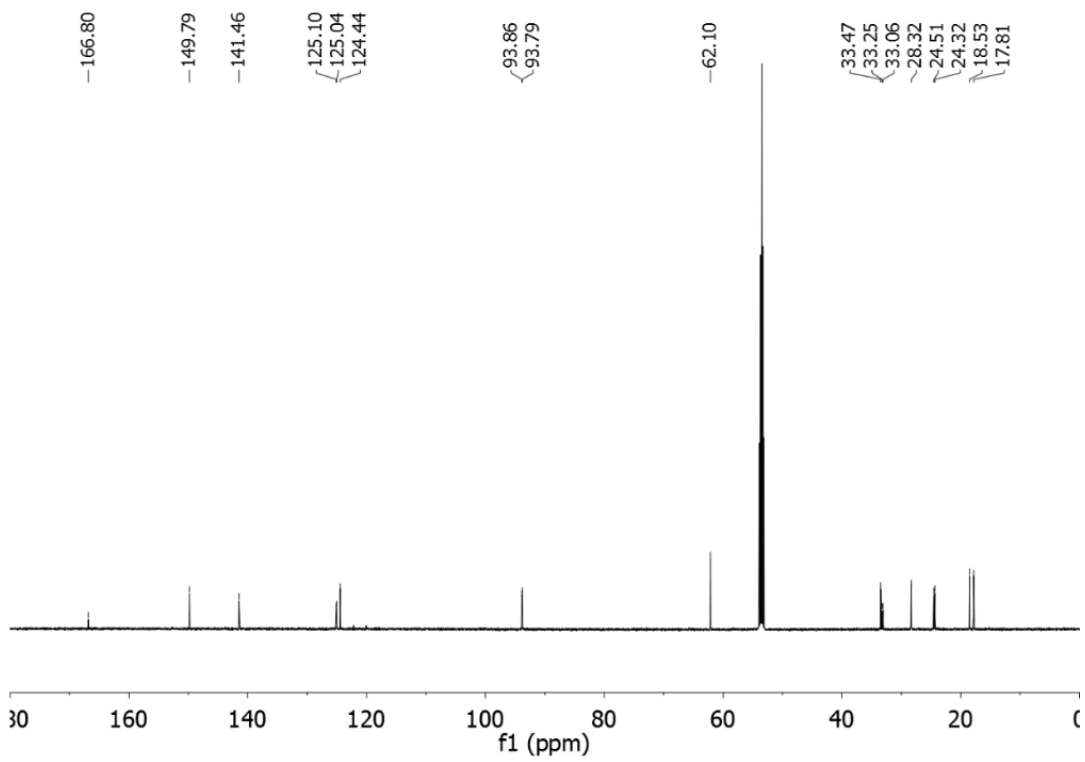
³¹P NMR (202 MHz, Methylene Chloride-*d*₂) δ 47.68

MALDI: *m/z* = 510.2 g/mol, calc'd. for C₂₀H₃₂IrNP⁺ [M]⁺: 509.7 g/mol.

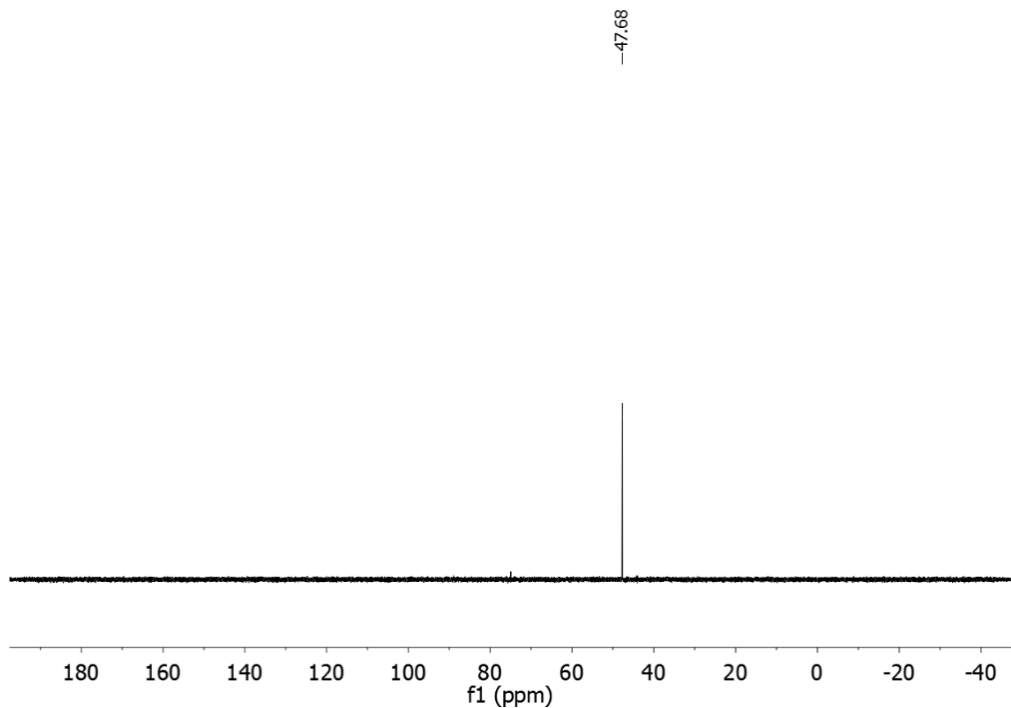
FT-IR (thin film/cm⁻¹) ν = 3126, 3066, 2964, 2925, 2884, 2838, 2430, 2367, 1999, 1720, 1609, 1564, 1542, 1471, 1450, 1390, 1373, 1334, 1270, 1224, 1152, 1109, 1083, 1083, 1069, 1032, 1002, 966, 934, 884, 823.



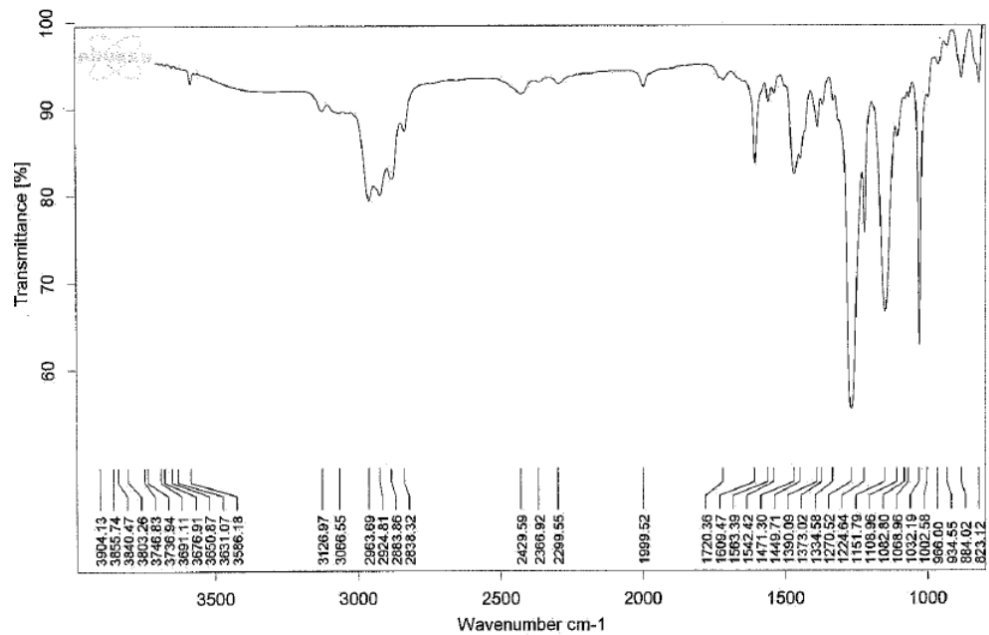
¹H NMR Spectrum of Complex **1c** at 25 °C in CD₂Cl₂



¹³C NMR Spectrum of Complex **1c** at 25 °C in CD₂Cl₂

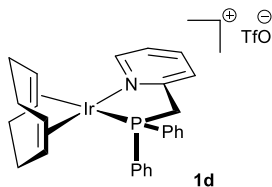


31P NMR Spectrum of Complex **1c** at 25 °C in CD₂Cl₂



IR Spectrum of Complex **1c**

Complex 1d



Complex **1d** was synthesized using the procedure used for the synthesis of complex **1a** (see main text experimental section). 2-((Diphenylphosphino)methyl)pyridine (80.5 mg, 0.29 mmol), chloro(1,5-cyclooctadiene)iridium(I) dimer (97.0 mg, 0.14 mmol), and sodium trifluoromethanesulfonate (39.0 mg, 0.22 mmol) were used. Pure product was isolated as an orange solid (140.0 mg, 67% yield).

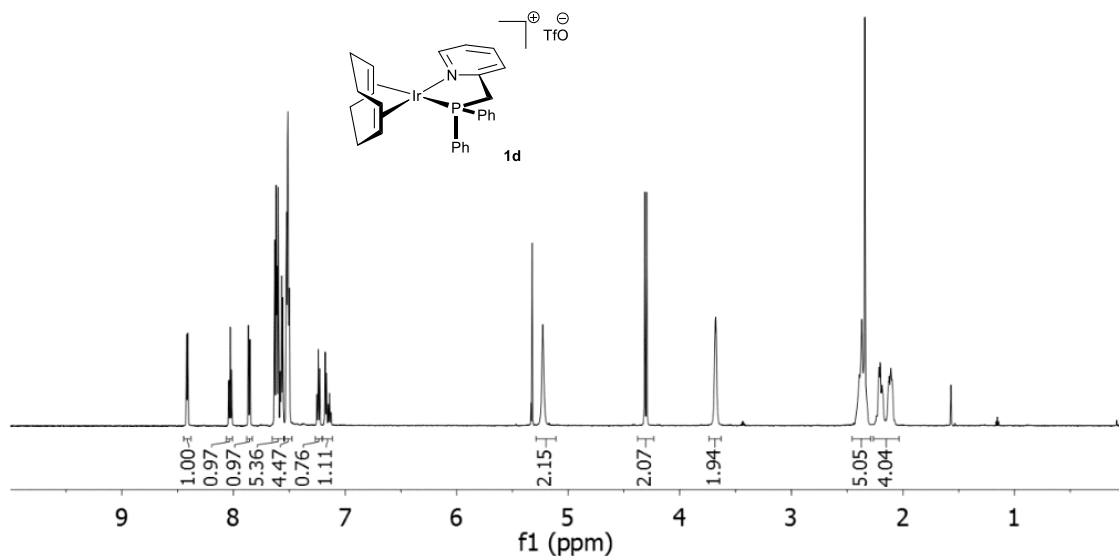
¹H NMR (600 MHz, Methylene Chloride-*d*₂) δ 8.42 (dd, $J = 5.9, 1.5$ Hz, 1H), 8.03 (tt, $J = 7.8, 1.4$ Hz, 1H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.65 – 7.55 (m, 5H), 7.54 – 7.47 (m, 4H), 7.20 – 7.11 (m, 1H), 5.23 (d, $J = 5.7$ Hz, 2H), 4.30 (d, $J = 10.9$ Hz, 2H), 3.68 (d, $J = 4.7$ Hz, 2H), 2.35 (d, $J = 16.9$ Hz, 5H), 2.11 (t, $J = 8.6$ Hz, 4H)

¹³C NMR (126 MHz, Methylene Chloride-*d*₂) δ 163.65, 163.60, 150.44, 141.42, 138.02, 133.30, 133.21, 132.34, 132.32, 129.61, 129.53, 129.01, 128.20, 127.54, 127.11, 125.69, 125.60, 125.28, 124.94, 122.40, 119.84, 95.90, 95.80, 63.75, 41.42, 41.17, 32.91, 28.86, 21.20

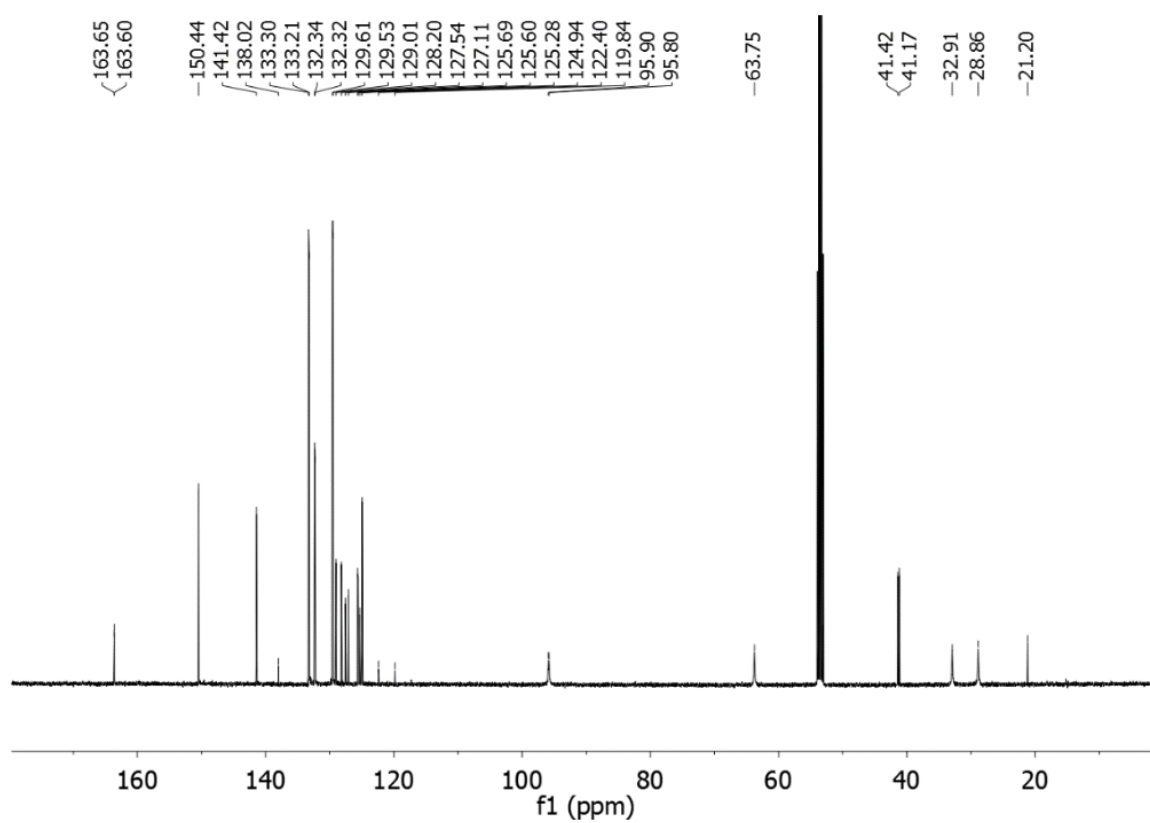
³¹P NMR (202 MHz, Methylene Chloride-*d*₂) δ 34.47

HRMS (ESI/APCI): $m/z = 578.1605$ g/mol, calc'd. for C₂₆H₂₈IrNP⁺ [M]⁺: 578.1583 g/mol.

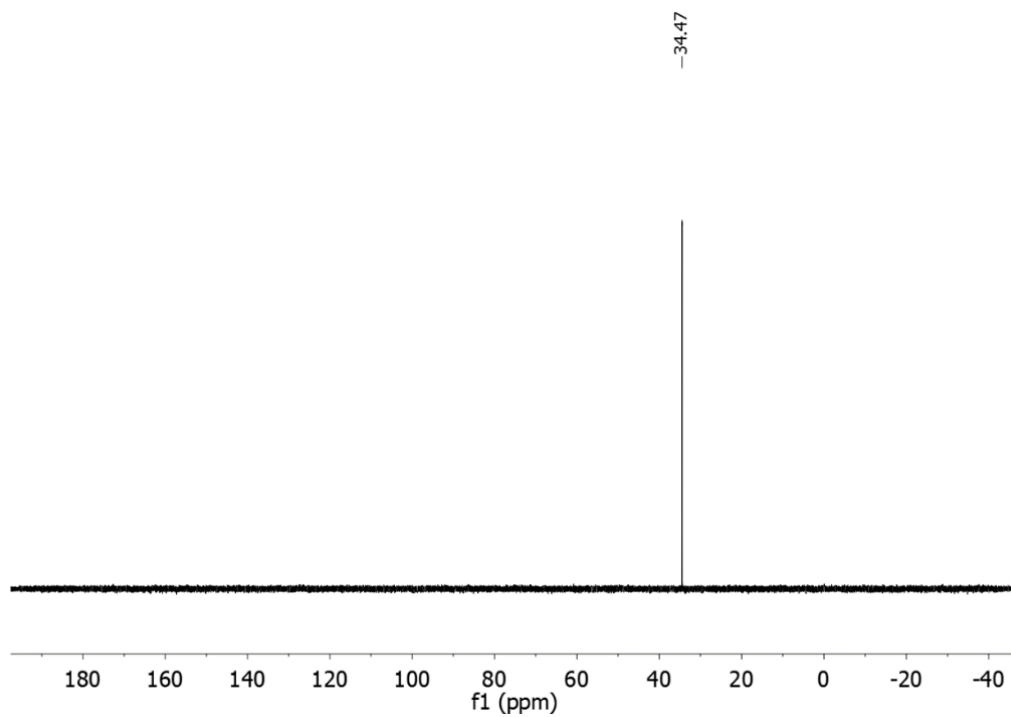
FT-IR (thin film/cm⁻¹) $\nu = 3056, 2963, 2919, 2886, 2836, 1608, 1564, 1475, 1436, 1475, 1436, 1400, 1334, 1310, 1267, 1223, 1152, 1104, 1066, 1030, 999, 966, 895, 842, 817.$



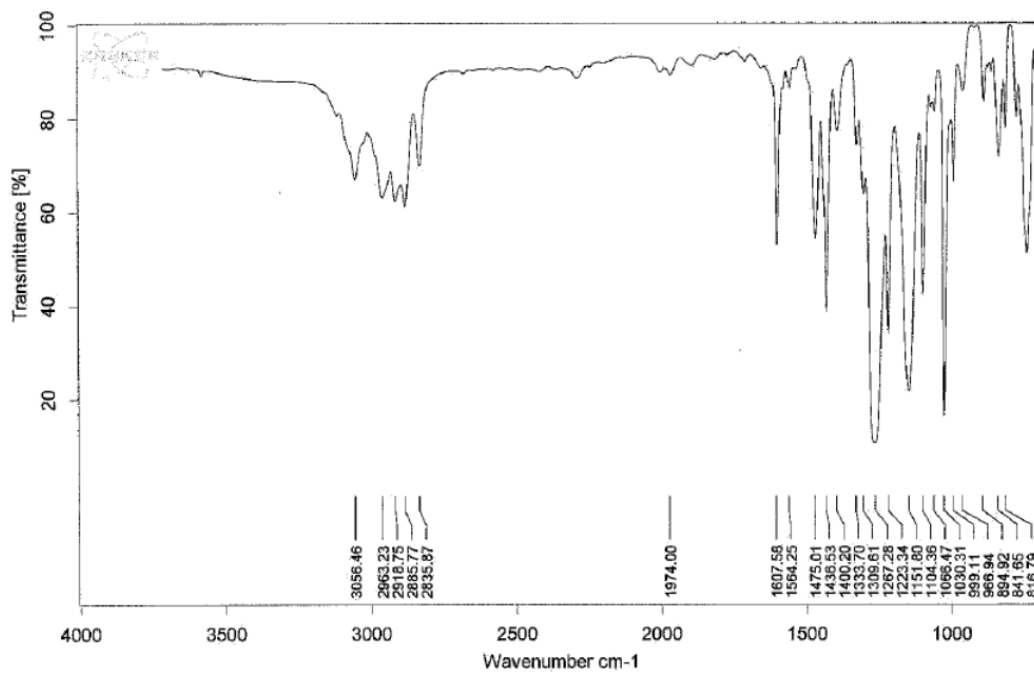
¹H NMR Spectrum of Complex **1d** at 25 °C in CD₂Cl₂



¹³C NMR Spectrum of Complex **1d** at 25 °C in CD₂Cl₂

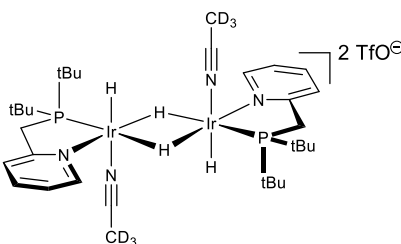


^{31}P NMR Spectrum of Complex **1d** at 25 °C in CD_2Cl_2



IR spectrum of complex **1d**

Complex 4a (solv = MeCN)

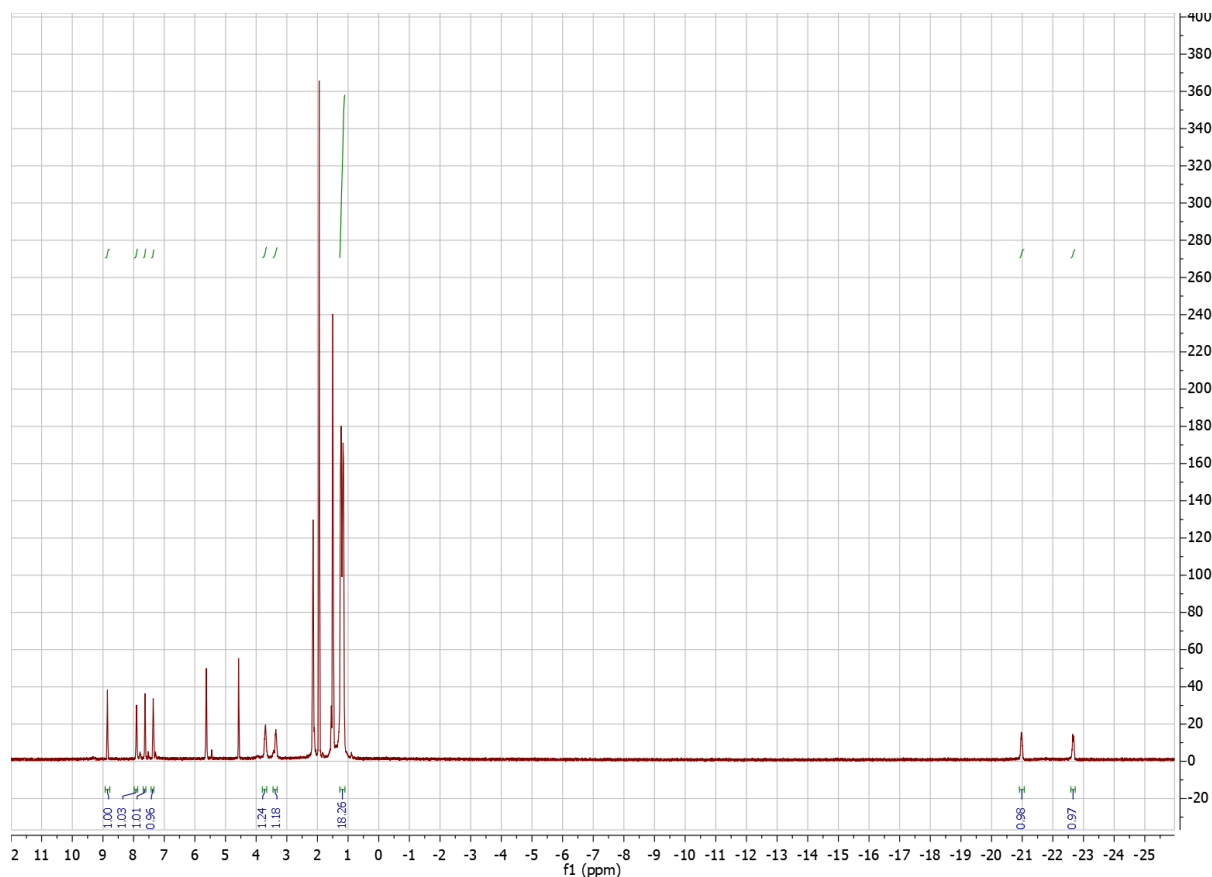


The synthesis of **4a** is described in the main text. We find that the best characterization data for this species can be obtained when the synthesis is run in acetonitrile solvent. These data follow. The crude NMR includes cyclooctene side product.

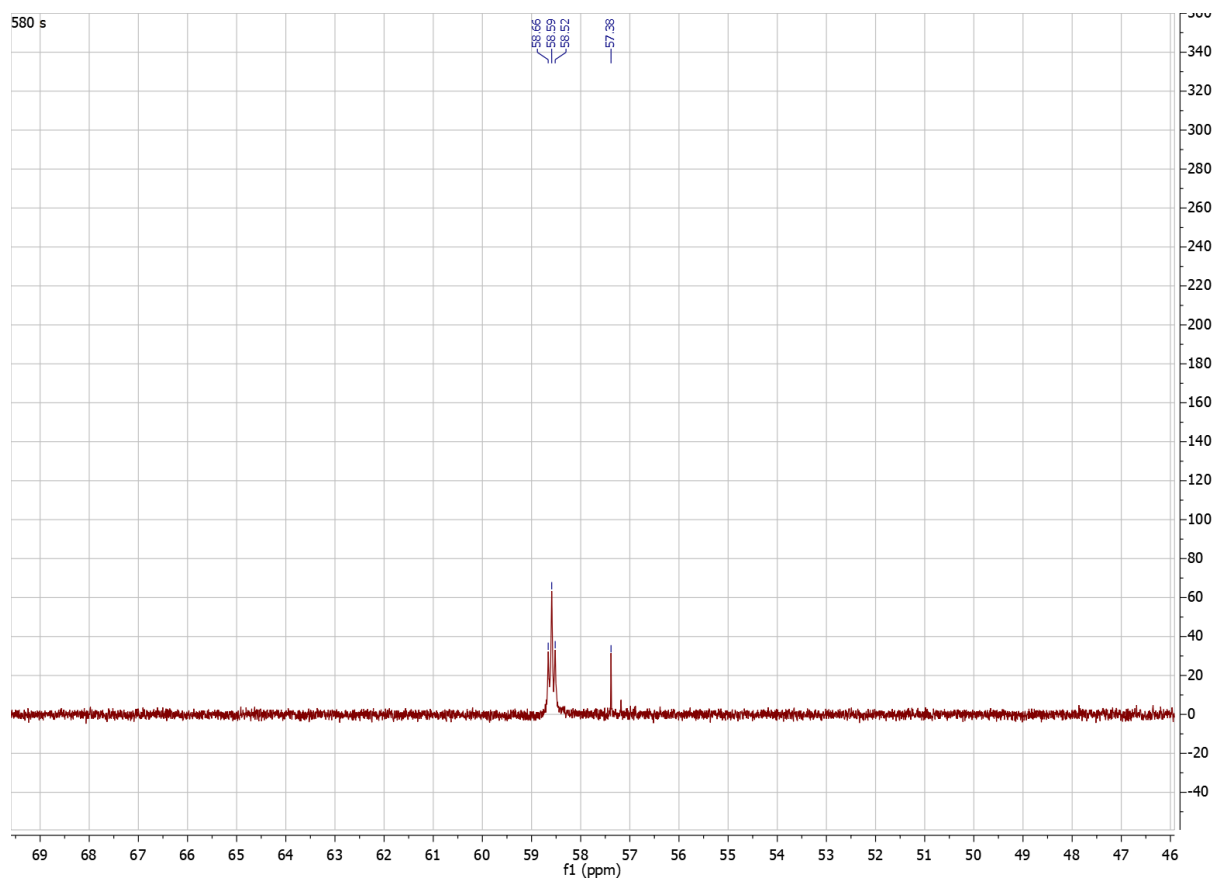
¹H NMR (600 MHz, Methylene Chloride-*d*₂) δ 8.92 – 8.80 (m, 1H), 7.95 – 7.87 (m, 1H), 7.63 (d, $J = 7.9$ Hz, 1H), 7.36 (m, 1H), 3.70 (m, 1H), 3.44 (m, 1H), 1.27 – 1.10 (m, 18H), -20.97 (s, 1H), -22.66 (d, $J = 21.5$ Hz, 1H).

³¹P NMR (202 MHz, Methylene Chloride-*d*₂) δ 58.59 (t, $J = 17.3$ Hz).

HRMS (ESI/APCI): $m/z = 476.1886$ g/mol, calc'd. for C₃₂H₅₂D₆Ir₂N₄P₂²⁺ [M]²⁺: 476.1879 g/mol.



¹H NMR Spectrum of Complex 4 at 25 °C in CD₃CN



^{31}P NMR Spectrum of Complex **4** at 25 °C in CD_3CN

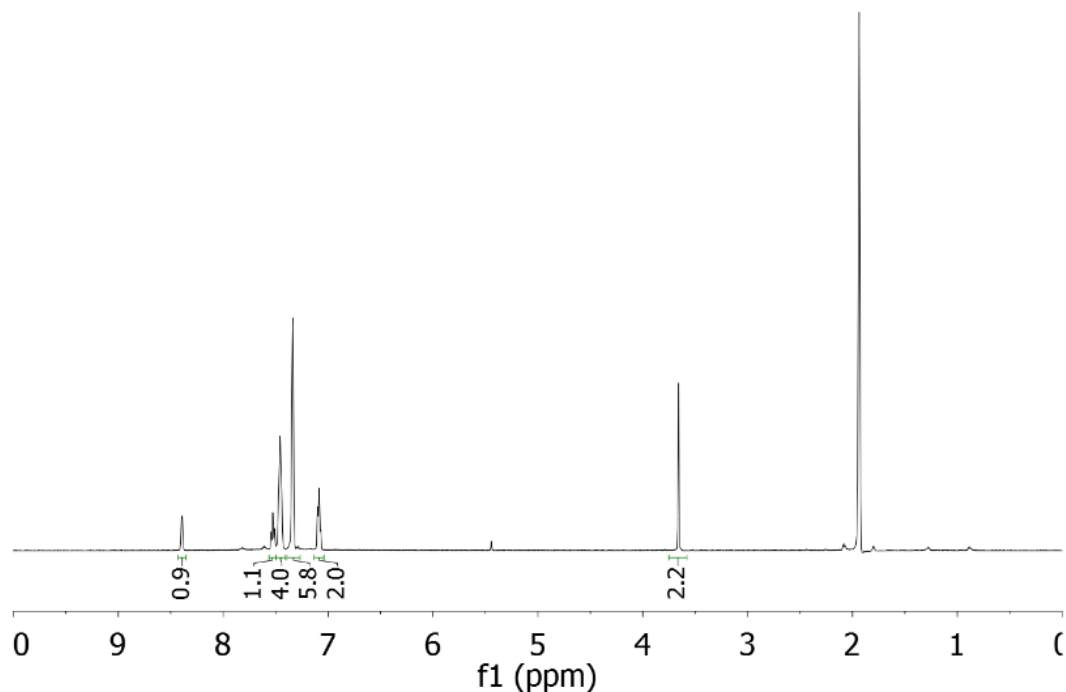
2-((Diphenylphosphino)methyl)pyridine Ligand

All reactions were kept strictly air-free using Schlenk and drybox techniques. The ligand was synthesized using a modified literature procedure as stated in the main text. A solution of 2-picoline (270 μ L, 2.69 mmol) in 18 mL THF was cooled to -78 $^{\circ}$ C. *n*-BuLi (1.7 mL of a 1.56 M solution in hexanes, 2.69 mmol) was added dropwise over 15 minutes and the solution turns orange. The solution was allowed to warm to room temperature and stirred for 1 hour. A solution of diphenylchlorophosphine (0.5 mL, 2.56 mmol) in 20 mL THF was cooled to -94 $^{\circ}$ C in an acetone/liquid nitrogen slush bath. The orange pyridine-2-ylmethanide solution was added slowly dropwise over 75 minutes while the slush bath was kept cold throughout. The resulting light yellow solution was allowed to warm slowly and stirred overnight. The solvent was evaporated in vacuo. The product was extracted with dichloromethane. The dichloromethane was evaporated in vacuo resulting in a mixture of yellow liquid and solid. The product was extracted with hexanes. After evaporation of the hexanes in vacuo, the product was obtained as white solid (260 mg, 35% yield).

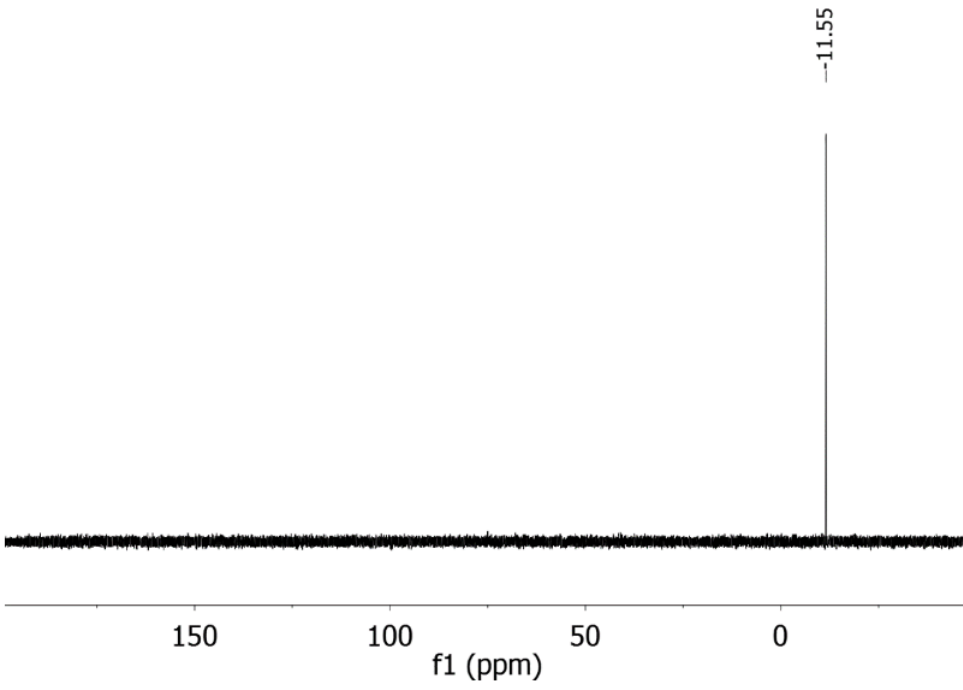
$^1\text{H NMR}$ (600 MHz, Acetonitrile- d_3) δ 8.39 (d, $J = 2.6$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.50 – 7.41 (m, 4H), 7.34 (s, 6H), 7.09 (d, $J = 7.8$ Hz, 2H), 3.66 (s, 2H).

$^{31}\text{P NMR}$ (202 MHz, Acetonitrile- d_3) δ -11.55

Further efforts to characterize this material were inhibited by its high air sensitivity. The white solid was typically taken on through the reactions that follow with no further purification.



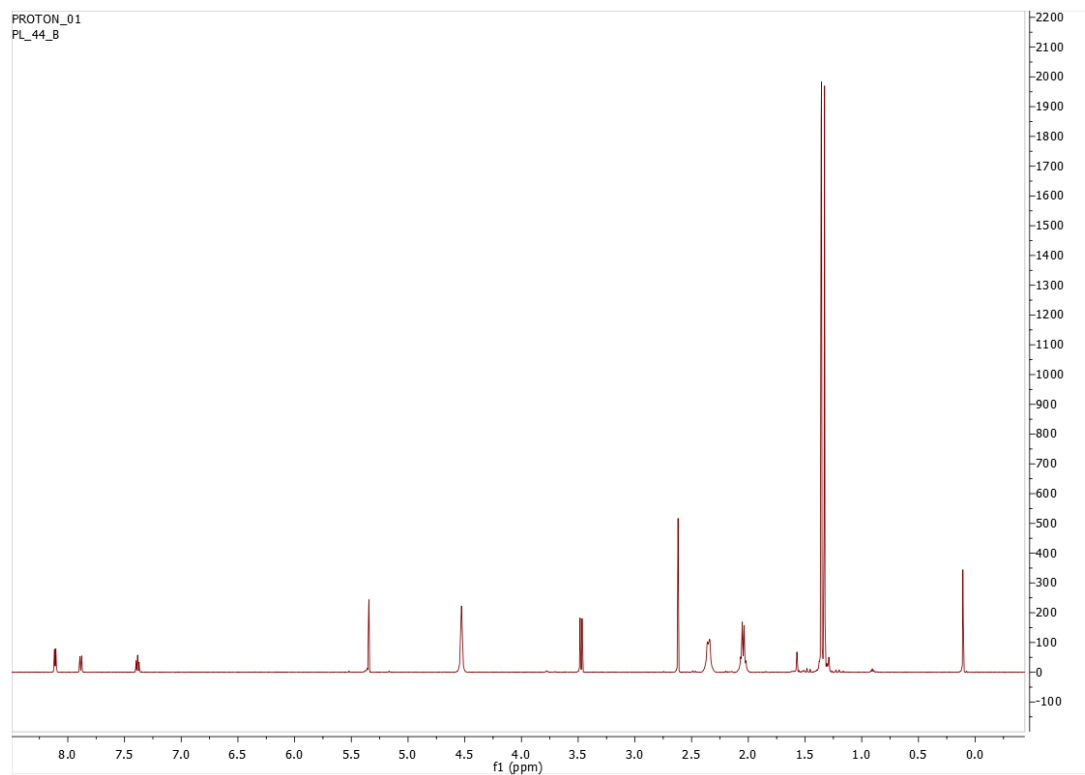
$^1\text{H NMR}$ spectrum of 2-((Diphenylphosphino)methyl)pyridine at 25 $^{\circ}$ C in CD_3CN



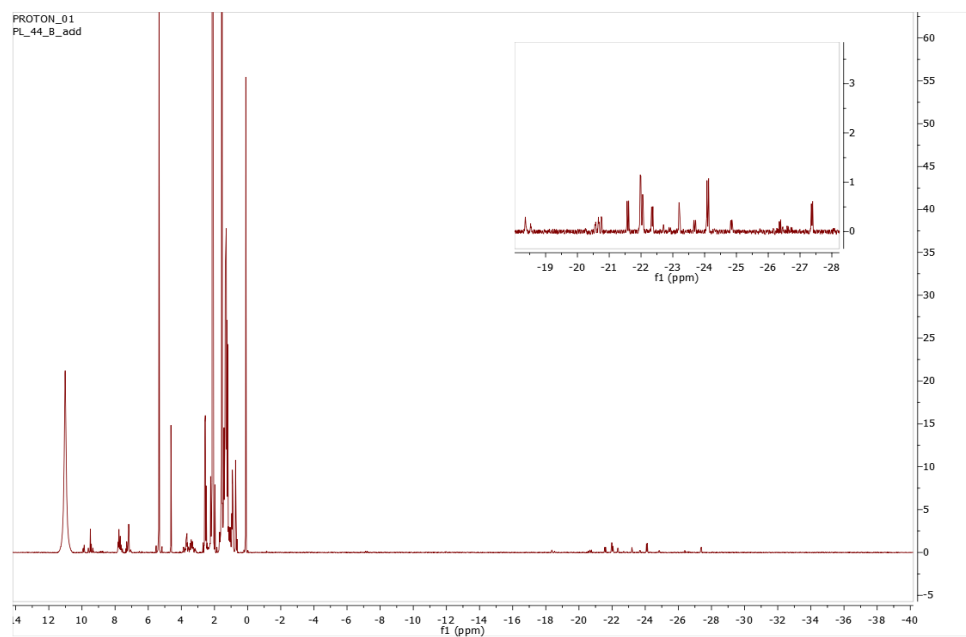
^{31}P spectrum of 2-((Diphenylphosphino)methyl)pyridine at 25 °C in CD_3CN

II. 1d ^1H NMR Spectra for Attempted Conversion to 5-type Dimers

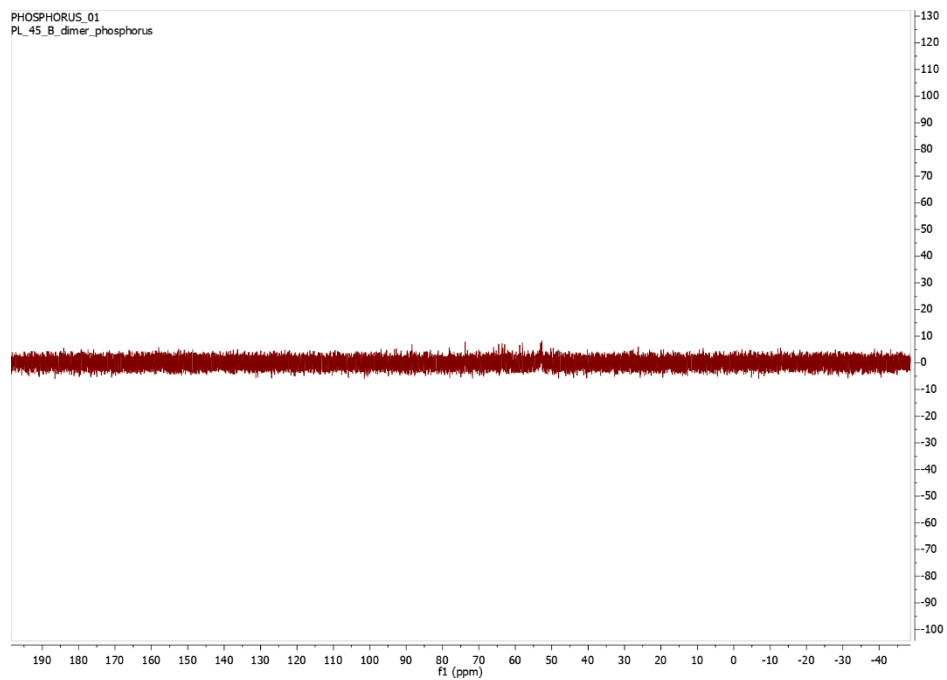
Complex 1b



^1H NMR Spectrum of Complex 1b at 25 °C in CD_2Cl_2

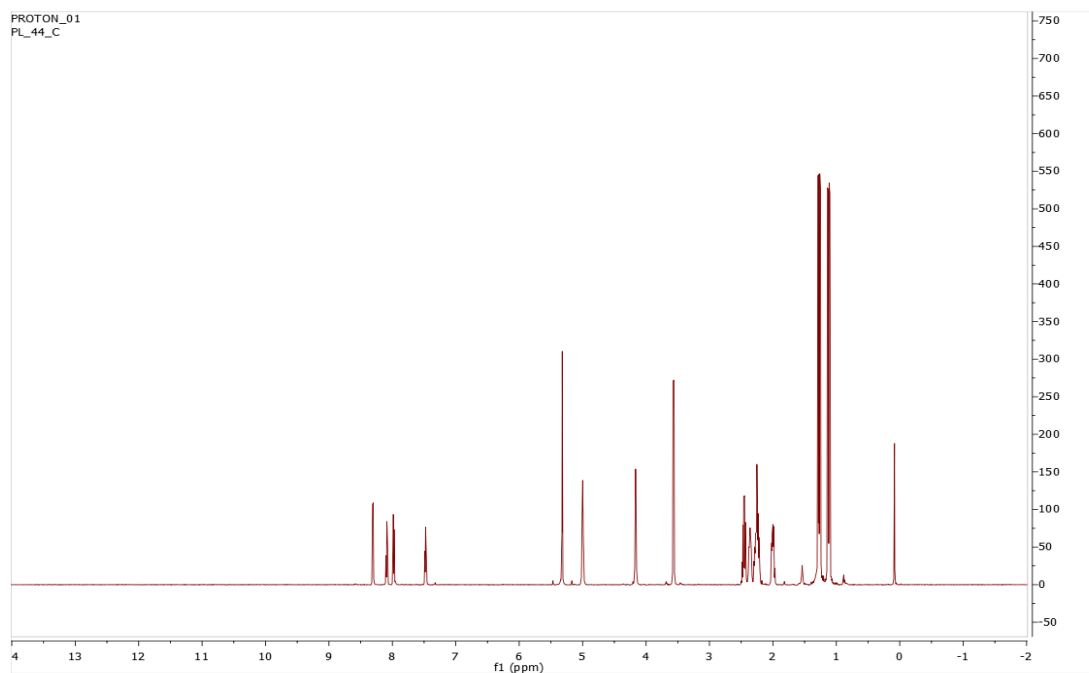


^1H NMR Spectrum of Complex 1b after addition of hydrogen and acetic acid at 25 °C in CD_2Cl_2

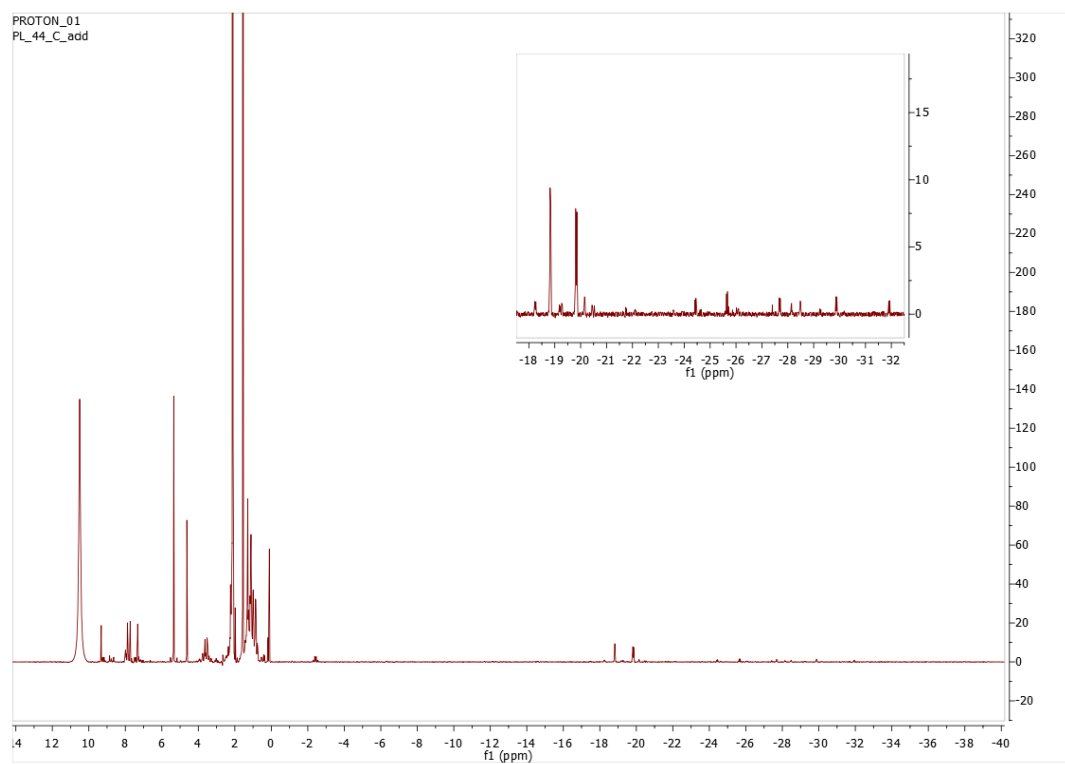


^{31}P NMR Spectrum of Complex **1b** after addition of hydrogen and acetic acid at 25 °C in CD_2Cl_2

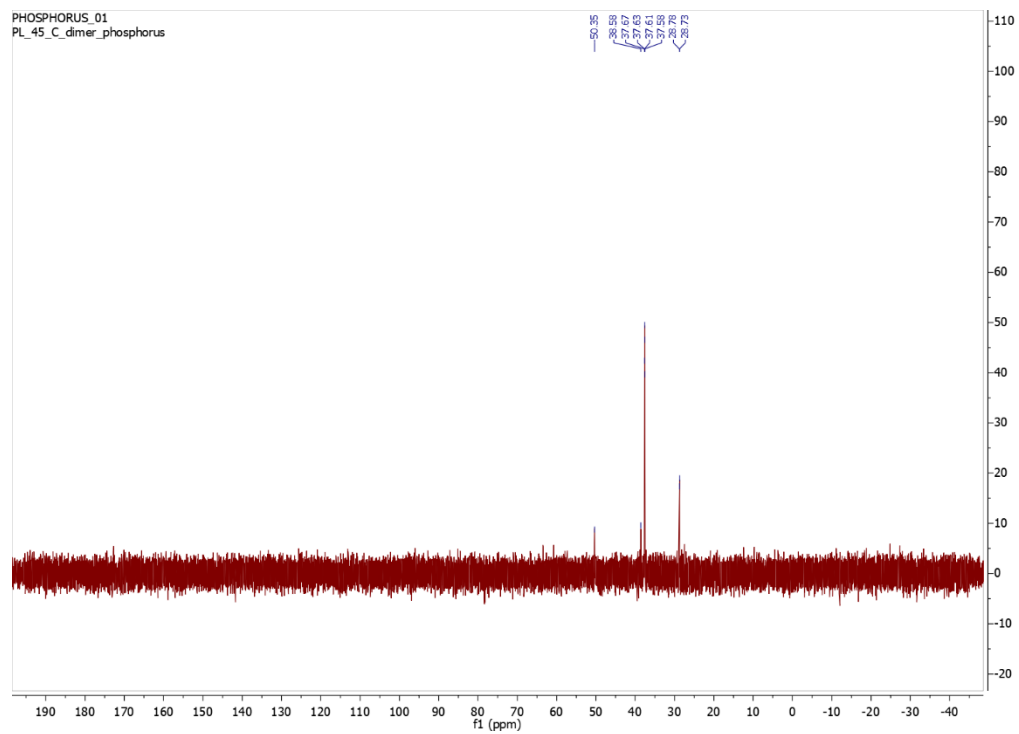
Complex 1c



^1H NMR Spectrum of Complex **1c** at 25 °C in CD_2Cl_2

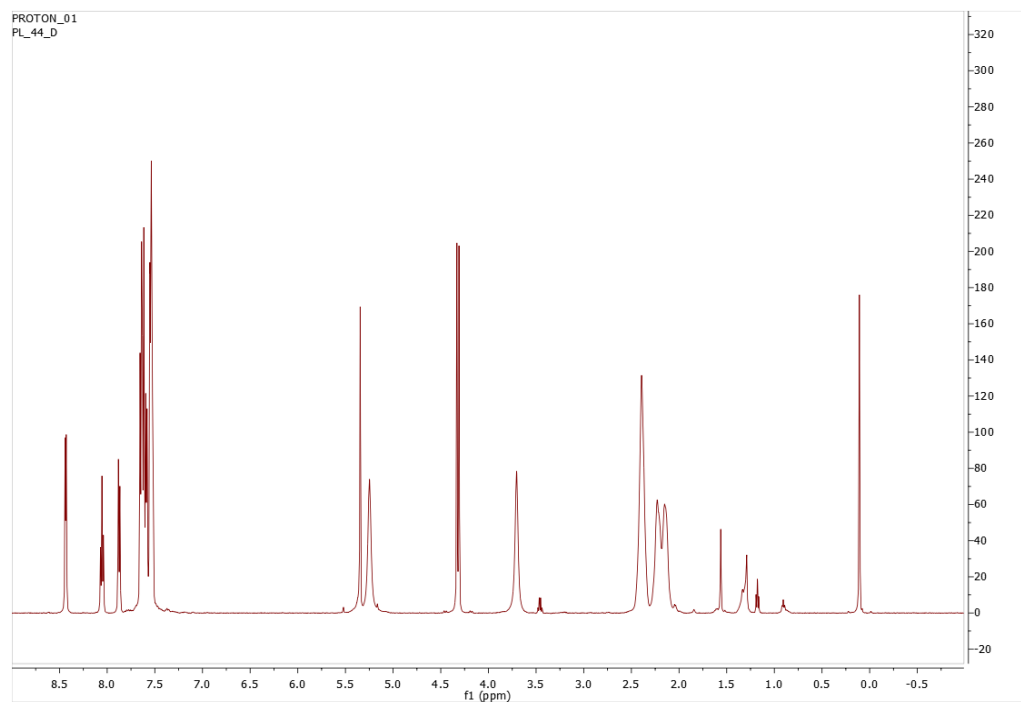


^1H NMR Spectrum of Complex **1c** after addition of hydrogen and acetic acid at 25 °C in CD_2Cl_2

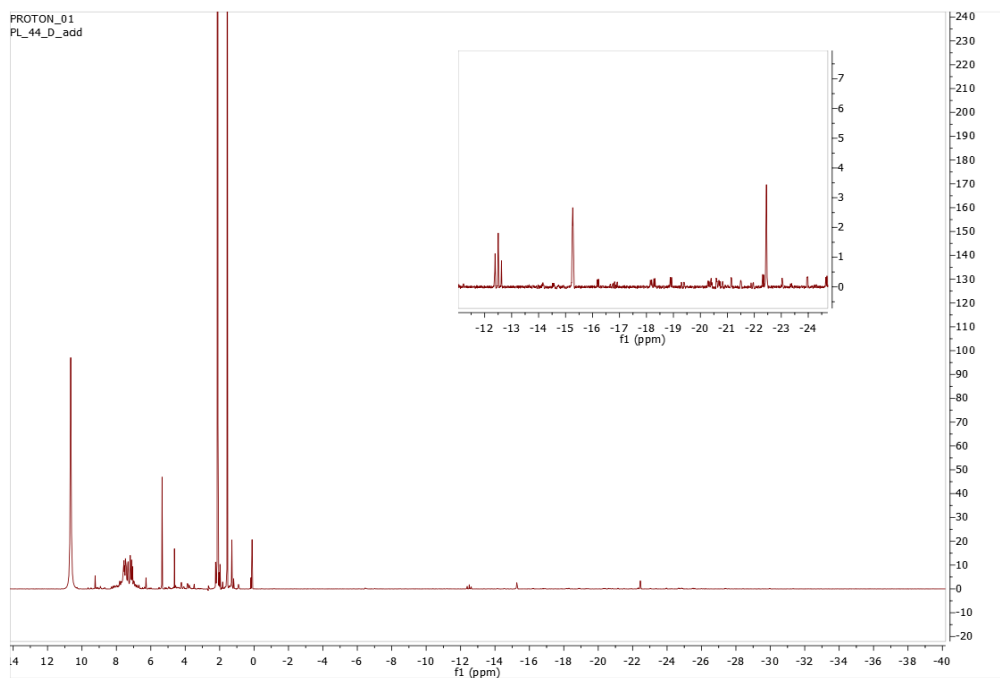


^{31}P NMR Spectrum of Complex **1c** after addition of hydrogen and acetic acid at 25 °C in CD_2Cl_2

Complex 1d

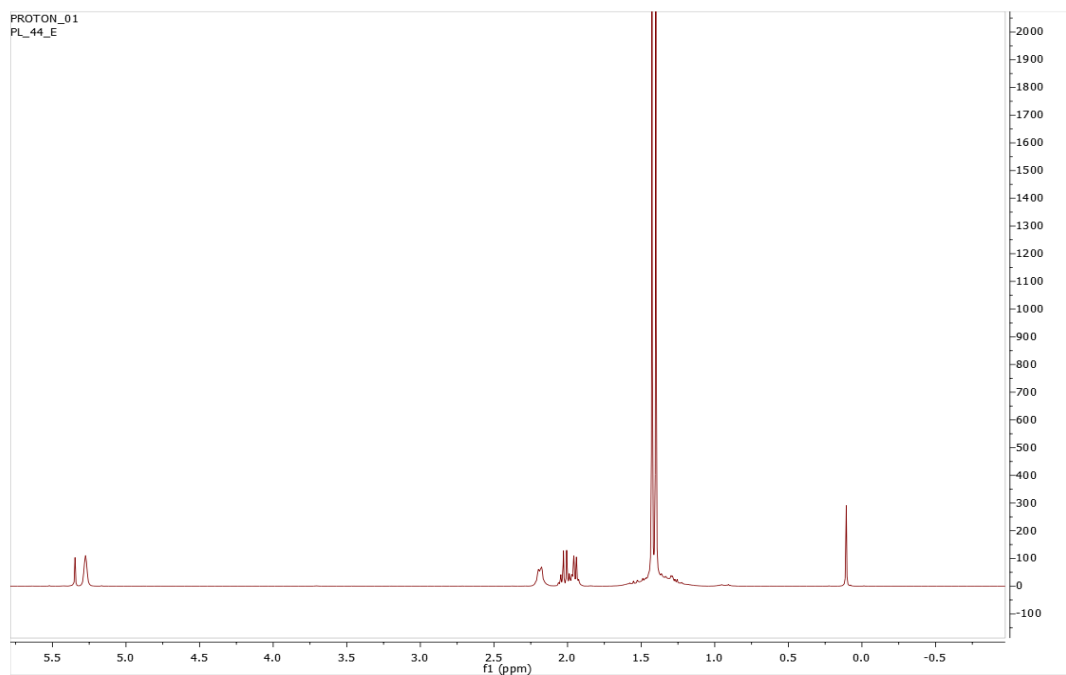


^1H NMR Spectrum of Complex **1d** at 25 °C in CD_2Cl_2

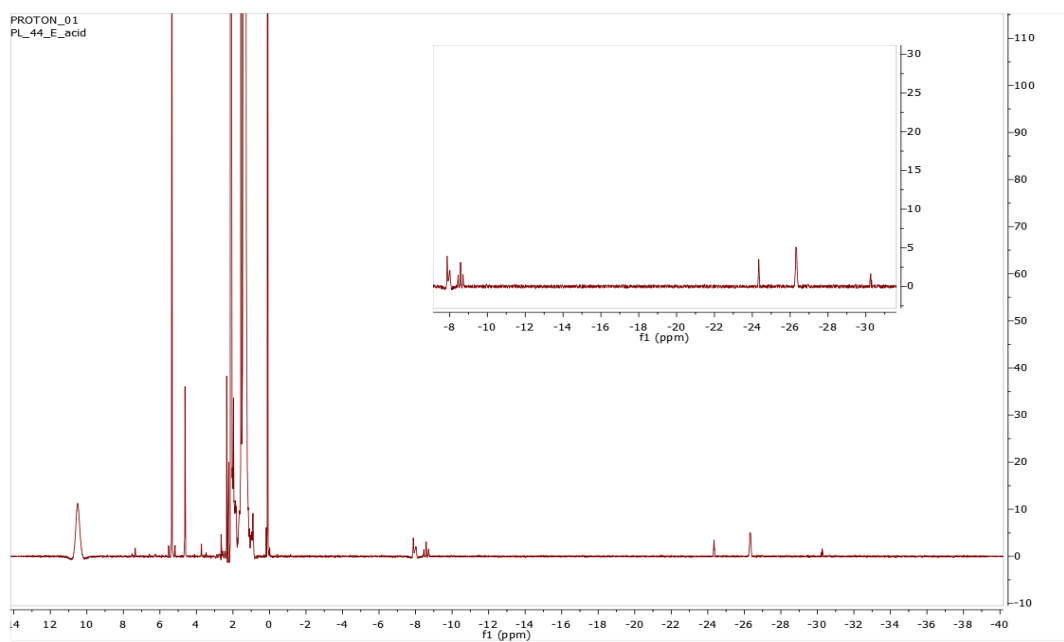


^1H NMR Spectrum of Complex **1d** after addition of hydrogen and acetic acid at 25 °C in CD_2Cl_2

Complex 1e

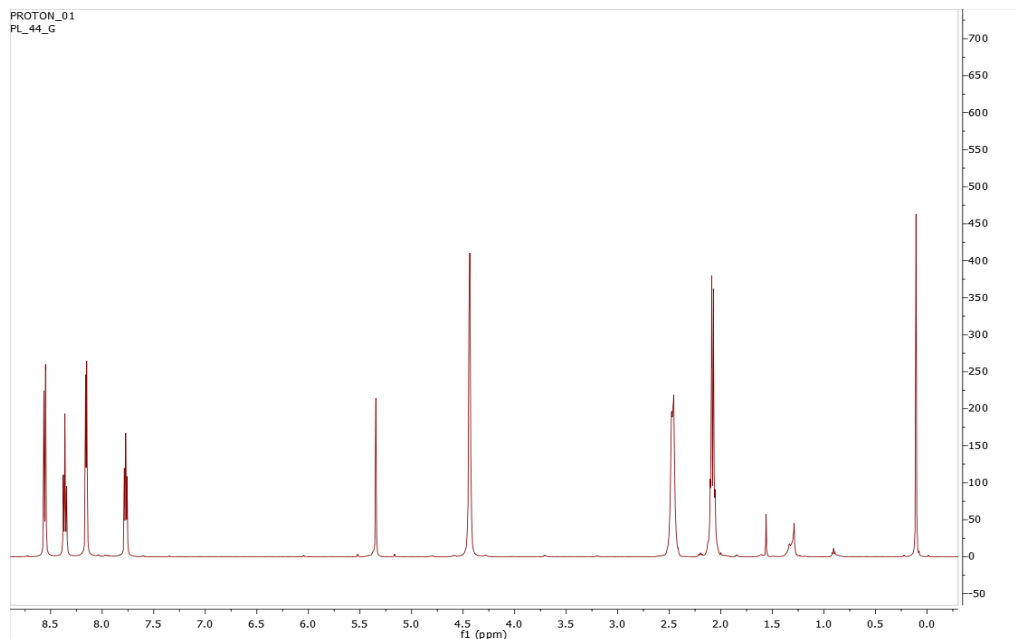


^1H NMR Spectrum of Complex **1e** at 25 °C in CD_2Cl_2

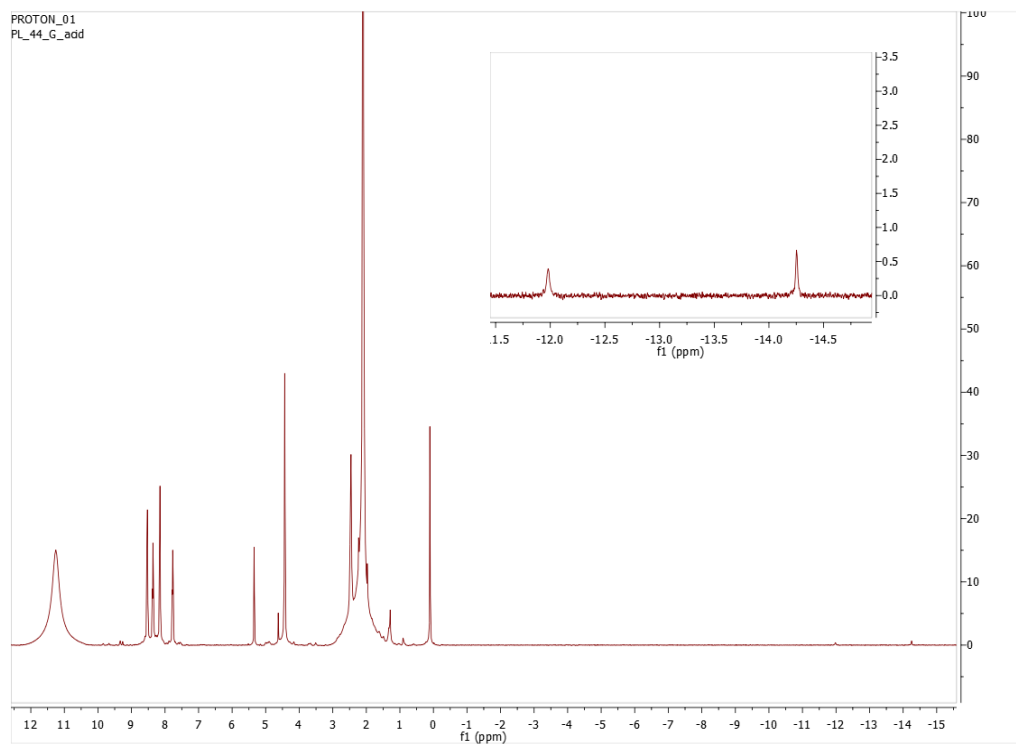


^1H NMR Spectrum of Complex **1e** after addition of hydrogen and acetic acid at 25 °C in CD_2Cl_2

Complex 1g

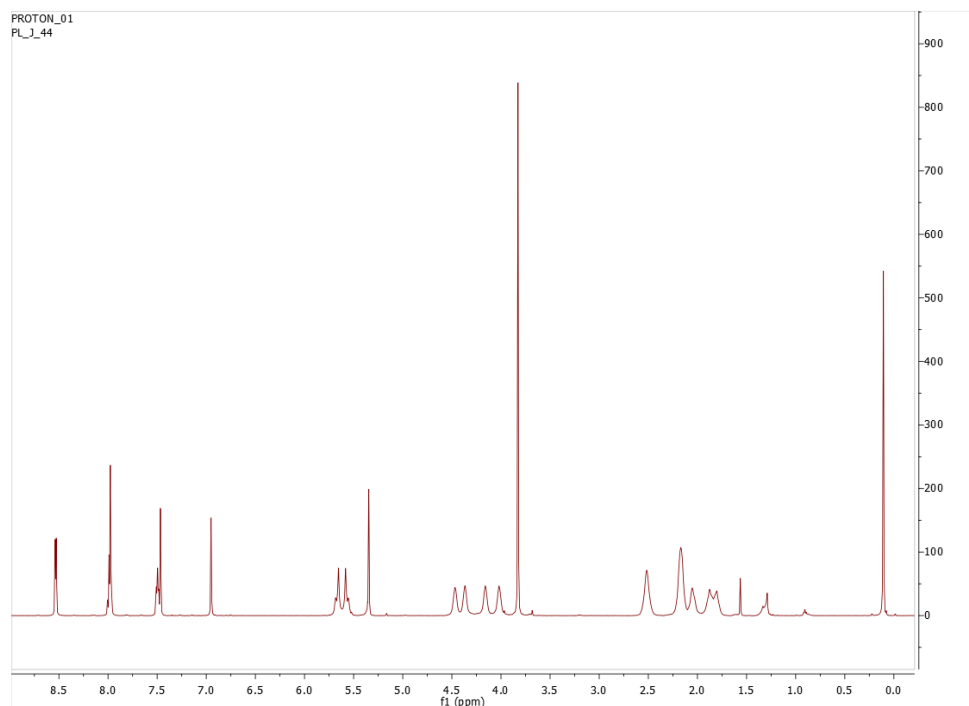


¹H NMR Spectrum of Complex 1g at 25 °C in CD₂Cl₂

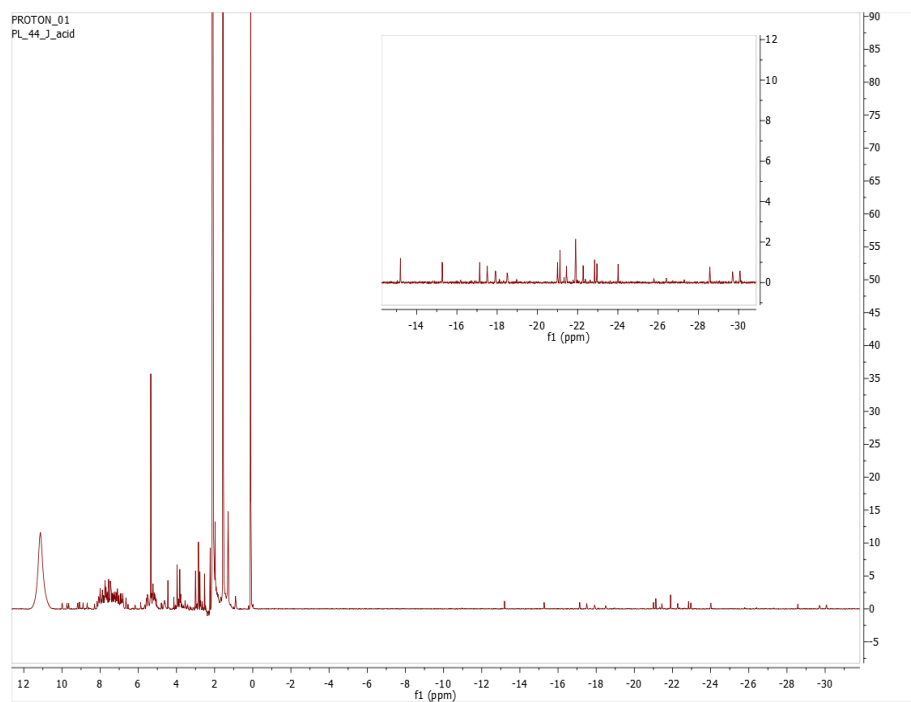


¹H NMR Spectrum of Complex 1g after addition of hydrogen and acetic acid at 25 °C in CD₂Cl₂

Complex 1h

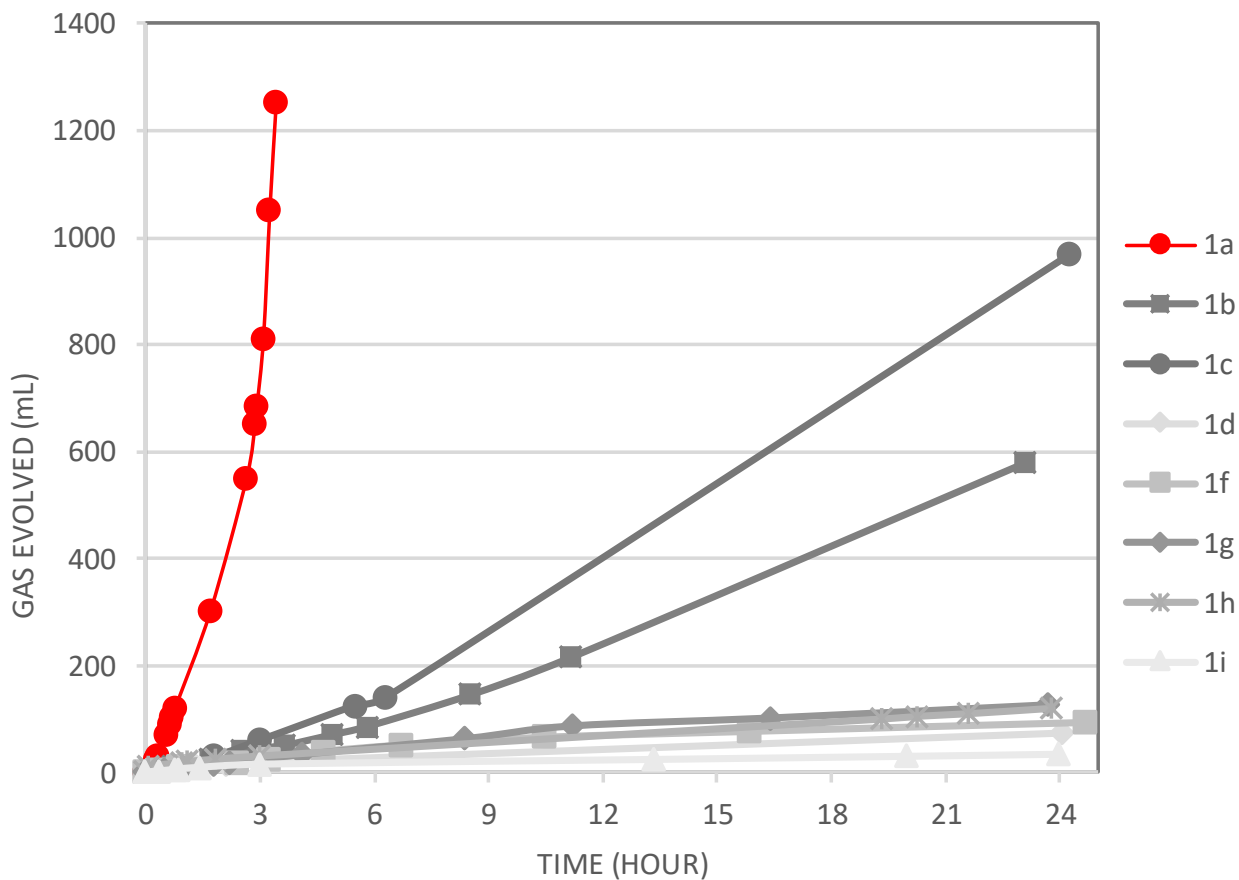


¹H NMR Spectrum of Complex **1h** at 25 °C in CD₂Cl₂



¹H NMR Spectrum of Complex **1h** after addition of hydrogen and acetic acid at 25 °C in CD₂Cl₂

III. Complete Kinetics Graph for Formic Acid Dehydrogenation



Comparison of pre-catalysts 1 in the dehydrogenation of formic acid