Ruthenium Catalyzed C–H bond Borylation

José A. Fernández-Salas, Simone Manzini, Lorenzo Piola, Alexandra M. Z. Slawin, and Steven P. Nolan*

EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST (UK).

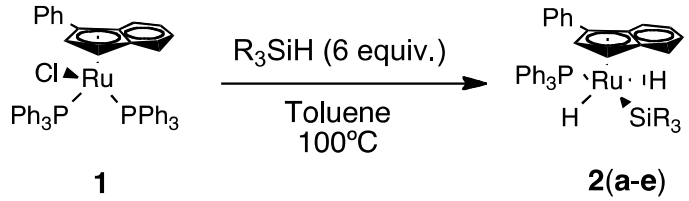
Contents

GENERAL CONSIDERATIONS:

Anhydrous toluene was dispensed from a solvent purification system from Innovative Technology. Anhydrous N,N-dimethylacetamide was distilled from sodium (Na) under argon (Ar) atmosphere. Anhydrous solvents (DMF, NMP and 1,4-dioxane) were used as received. All solvents were degassed and stored in a glovebox. Catalyst syntheses were performed in an MBraun glovebox containing dry argon and less than 1 ppm oxygen or using standard Schlenk techniques. ^{1}H, ^{13}C, ^{31}P and ^{19}F Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 300 or Bruker Avance II 400 Ultrashield NMR spectrometers. Chemical shifts are reported in δ ppm. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre at Swansea University, Grove building, Singleton Park, Swansea, SA2 8PP, Wales, UK. Elemental analyses were performed at the London Metropolitan University. Bis(pinacolato)diboron was purchased from BASF and used as received. Complex **1** was synthesised according to the previously reported procedure.[1] Pyridines **3a-c** were purchased from Sigma Aldrich and used as received. Pyridines **3d,**[2] **3e,**[2] **3f,**[2] **3g,**[3] **3h,**[2] **3i**[4] and **3j**[2] were prepared according to the literature.[5]

EXPERIMENTAL PROCEDURES AND CHARACTERIZATION:

General procedure to the synthesis of complexes 2.



1 **2(a-e)**

In the glovebox, complex **1**[1] (500 mg, 0.58 mmol) was dissolved in toluene (10 ml) in a 25 ml Schlenk flask. Outside the glovebox the desired silane was added (6 equiv.). The reaction was stirred for the determined time at 100°C, then the volatiles were removed *under vacuo*. The resulting residue was washed with pentane three time, yielding **2** in the reported yield.

Complex	Silane	t (h)	Yield
2a	Et_3SiH	16 h	85 %
2b	$(EtO)_3SiH$	3 h	69 %
2c	$PhMe_2SiH$	3 h	60 %
2d	Ph_2MeSiH	16 h	65 %
2e	Ph_3SiH	16 h	70 %

[$RuH_2(PPh_3)(\eta^5$-3-phenylindenyl)($SiEt_3$)] (2a):

^{1}H NMR (400 MHz, C_6D_6): δ 7.570 (m, 2H), 7.46 (m, 1H), 7.19 (m, 7H), 7.01 (m, 4H), 6.89 (m, 10H) 6.64 (m, 1H), 6.52 (m, 1H), 5.47 (m, 1H), 5.02 (m, 1H), 1.16 (t J= 8.3 Hz, 9H), 0.74 (sext. *J* = 7.11 Hz 3H), 0.63 (sext. *J* = 7.11 Hz 3H) -12.89 (bs, 1H), -13.83 (bs, 1H); ^{13}C NMR (101 MHz,

C_6D_6): δ 138.0, 137.5, 137.4, 134.1 (d, *J* = 11.4 Hz), 129.3, 129.1 (d *J* = 1.5 Hz), 128.6, 127.5, 126.1, 125.5, 125.3, 123.4, 121.6, 108.6, 106.5, 93.0, 89.9 (d, *J* = 3.0 Hz), 73.7 (d, J=8.8 Hz), 13.5, 9.8; ^{31}P NMR (162 MHz, C_6D_6): δ 66.2. Anal. Calcd. for $C_{39}H_{43}PRuSi$: C, 69.72%; H, 6.45%. Found: C, 69.62%; H, 6.48%.

[$RuH_2(PPh_3)(\eta^5$-3-phenylindenyl)($SiOEt_3$)] (2b):

^{1}H NMR (400 MHz, C_6D_6): δ 7.56 (m, 2H), 7.48 (m, 1H), 7.15 (m, 7H), 7.01 - 6.83 (m, 13H) 6.66 (m, 1H), 6.42 (m, 1H), 5.69 (m, 1H), 3.89 (m, 6H), 1.26 (t, *J* = 7.9 Hz, 9H) -12.26 (bs, 1H), -13.24 (bs, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 138.0, 137.5, 137.0, 134.0 (d, *J* = 11.4 Hz), 129.6, 129.2, 129.1 (d, *J* = 1.5 Hz), 128.6, 127.6, 127.5, 126.4, 126.3, 125.9, 123.7, 121.6, 110.6, 106.5, 94.0, 89.9 (d, *J* = 4.4 Hz), 73.1 (d, *J* = 8.8 Hz), 57.8, 18.8; ^{31}P NMR (162 MHz, C_6D_6): δ 60.6. Anal. Calcd. for $C_{39}H_{43}PRuSi$: C, 65.16; H, 5.89. Found: C, 65.25; H, 5.95.

[$RuH_2(PPh_3)(\eta^5$-3-phenylindenyl)($SiMe_2Ph$)] (2c):

^{1}H NMR (400 MHz, C_6D_6): δ 7.87 (m, 2H), 7.46 (m, 1H), 7.39 (m, 2H), 7.27 - 7.12 (m, 9H), 6.99 (m, 3H), 6.89 (m, 9H), 6.75 (m, 1H), 6.69 (m, 1H), 6.58 (m, 1H), 5.28 (m, 1H), 4.88 (m, 1H), 0.65 (s, 3H), 0.36 (s, 3H), -13.00 (bs, 2H); ^{13}C NMR (101 MHz, C_6D_6): δ 152.1, 138.1, 137.6, 137.5, 134.5 (d, *J* = 11.4 Hz), 134.4, 129.7 (d, *J* = 4.0Hz), 129.1, 128.5, 128.3, 128.2, 128.1, 127.9, 126.4, 126.7, 126.3, 124.1, 122.0, 109.3, 107.0, 94.1, 91.2 (d, *J* = 4.4 Hz), 76.5 (d, *J* = 8.8 Hz), 10.7, 10.4; ^{31}P NMR (162 MHz, C_6D_6): δ 66.5. Anal. Calcd. for $C_{41}H_{38}PRuSi$: C, 71.28; H, 5.54. Found: C, 71.15; H, 5.65.

[$RuH_2(PPh_3)(\eta^5$-3-phenylindenyl)($SiMePh_2$)] (2d):

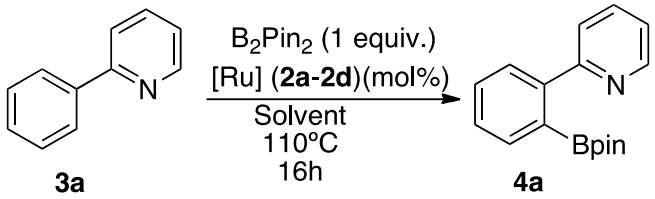
^{1}H NMR (400 MHz, C_6D_6): δ 7.82 (m, 4H), 7.46 (m, 5H), 7.29 (m, 5H), 7.17 (m, 5H) 7.04 (m, 7H), 6.99-6.75 (m, 16H), 6.68 (m, 1H), 6.50 (m, 1H), 4.96 (m, 2H), 0.60 (s, 3H), -11.81 (bs, 1H), -13.20 (bs, 1H); ^{13}C NMR (101MHz, C_6D_6): δ 149.5, 148.1, 137.4, 137.0, 136.9, 135.7, 134.8, 135.2, 134.4, 133.9, 133.8, 130.0, 129.8, 129.2, 128.7, 127.7, 127.5, 126.2, 126.0, 123.8, 121.8, 109.6, 106.7, 93.5, 92.4 (d, *J* = 4.4 Hz), 75.5 (d, *J* = 8.8 Hz), 8.62; ^{31}P NMR (162MHz, C_6D_6): δ 63.3. Anal. Calcd. for $C_{46}H_{40}PRuSi$: C, 73.24; H, 5.35. Found: C, 73.23; H, 5.43.

[$RuH_2(PPh_3)(\eta^5$-3-phenylindenyl)($SiPh_3$)] (2e):

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.66 (m, 1H), 7.49 (m, 8H), 7.28 (m, 6H), 7.13 (m, 18H) 6.86 (m, 9H), 6.58 (m, 7H), 5.89 (m, 1H), 4.76 (m, 1H), 4.10 (m, 1H), 4.22 (m, 1H), -11.55 (d, *J* = 30.0 Hz, 1H), -13.25 (d, J = 30.0 Hz, 1H); ^{13}C NMR (101 MHz, CD_2Cl_2): δ 145.9, 137.3, 136.7, 136.7, 136.3, 136.1, 135.3, 133.8, 133.7, 130.4, 130.2, 129.5, 129.3, 128.6, 128.4, 128.5, 128.2, 127.5, 127.4, 127.3, 126.6, 126.4, 125.9, 124.1, 122.0, 111.1, 107.4, 93.6 (d, *J* = 3.6 Hz), 93.5, 74.1 (d, *J* =

8.8 Hz); ^{31}P (162MHz, CD_2Cl_2) δ 58.7. Anal. Calcd. for $C_{51}H_{42}PRuSi$: C, 75.16; H, 5.19. Found: C, 69.88, H, 5.20.

Optimization of the conditions for the borylation of 2-phenylpyridine.

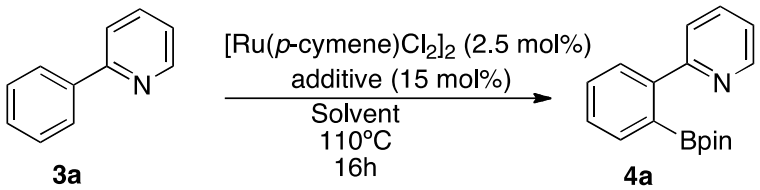


3a **4a**

Entry	[Ru] (mol %)	Solvent	Conv. [a] **2a** (%)
1	**2a** (2.5)	Toluene	20
2	**2a** (2.5)	NMP	-[b]
3	**2a** (2.5)	DMF	-[b]
4	**2a** (2.5)	DMAc	-[b]
5	**2a** (2.5)	1,4-dioxane	>95
6	**2a** (2.5)	1,4-dioxane[c]	-[b]
7	**2a** (2.5)	1,4-dioxane[d]	-[b]
8	**2b** (2.5)	1,4-dioxane	19
9	**2c** (2.5)	1,4-dioxane	10
10	**2d** (2.5)	1,4-dioxane	12
11	**2e** (2.5)	1,4-dioxane	27
12	**2a** (2.0)	1,4-dioxane	>95
13	**2a (1.5)**	**1,4-dioxane**	**>95**
14	**2a** (1.0)	1,4-dioxane	85

[a] Conversion determined by ^1H-NMR spectroscopy. [b] Starting material was recovered unchanged. [c] 60°C. [d] 80°C.

Borylation of 2-phenylpyridine using [Ru(*p*-cymene)Cl_2]$_2$.



3a **4a**

Entry	Additive	Solvent	Conv. [a] **2a** (%)
1	$AdCO_2H$	toluene	60

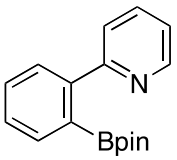
2	$AdCO_2H$	1,4-dioxane	68
3	$AdCO_2H$	NMP	-[b]
4	**KOAc**	**1,4-dioxane**	**76**
5	$MesCO_2H$	1,4-dioxane	23
6	$PhCO_2H$	1,4-dioxane	63
7	PPh_3	1,4-dioxane	-[b]

[a] Conversion determined by ^{1}H-NMR spectroscopy. [b] Starting material was recovered unchanged.

General procedure for the ruthenium-calayzed borylation:

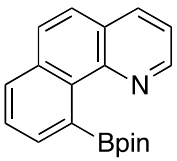
In a vial fitted with a screwcap, in the glovebox, bis(pinacolato)diboron (0.25 mmol), the corresponding pyridine (**3a-3j**) (0.25 mmol) and **2a** (0.00375 mmol, 1.5 mol%) were dissolved in 1,4-dioxane (0.5 mL). Then, outside of the glovebox, the resulting mixture was stirred 16 h at 110^{o}C. Solvent was removed under reduced pressure. The crude material was purified by recrystallization from dichloromethane/hexane.

2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyridine (4a):[6]



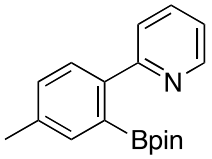
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (d, *J* = 5.5 Hz, 1H), 8.01-7.92 (m, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.41 (td, *J* = 7.4, 1.2 Hz, 1H), 7.36 (ddd, *J* = 7.2, 5.5, 1.2 Hz, 1H), 7.29 (td, *J* = 7.4, 1.2 Hz, 1H), 1.43 (s, 12H).

10-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[h]quinolone (4b):[6]



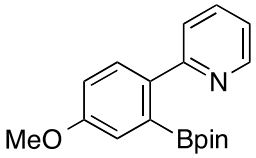
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.19 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 1H), 7.73-7.66 (m, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.52 (dd, *J* = 7.9, 4.5 Hz, 1H), 1.55 (s, 12H).

2-[4-Methyl-2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-pyridine (4c):[7]



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (ddd, *J* = 5.6, 1.5, 1.0 Hz, 1H), 7.92 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.31 (ddd, *J* = 7.4, 5.6, 1.0 Hz, 1H), 7.11 – 7.07 (m, 1H), 2.39 (s, 3H), 1.43 (s, 12H).

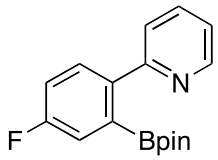
2-[4-Methoxy-2-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-pyridine (4d):



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (d, *J* = 5.7 Hz, 1H), 7.90 (td, *J* = 8.0, 1.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.28-7.23 (m, 2H), 6.81 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.88 (s, 3H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 156.6, 142.9, 141.8, 129.9, 122.8, 121.4, 116.8, 116.4,

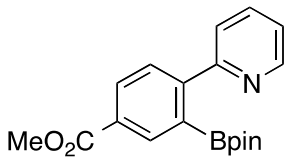
113.8, 80.2, 55.3, 27.1; **MS** (ESI): *m*/*z* 312 ($M+H^+$, 100); **HRMS** (ESI): Calcd. for $C_{18}H_{23}BNO_3$ ($M+H^+$), 312.1766; found 312.1768.

2-[4-Fluoro-2-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-pyridine (4e):



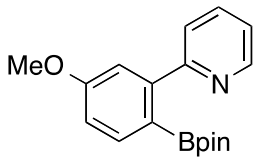
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (d, *J* = 5.9 Hz, 1H), 8.03-791 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.63 (dd, *J* = 8.4, 4.7 Hz, 1H), 7.39-7.33 (m, 2H), 6.96 (td, *J* = 8.7, 2.5 Hz, 1H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6 (d, *J* = 252.4 Hz), 155.6, 143.1, 142.2, 132.9, 123.1 (d, *J* = 8.6 Hz), 122.4, 118.2 (d, *J* = 19.9 Hz), 117.2, 115.0 (d, *J* = 23.8 Hz), 80.3, 27.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ -110.0; **MS** (ESI): *m*/*z* 300 ($M+H^+$, 81); **HRMS** (ESI): Calcd. for $C_{17}H_{19}BFNO_2$ ($M+H^+$), 300.1567; found 300.1566.

2-[4-Methoxycarbonyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyridine (4f):



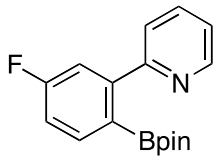
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 (d, *J* = 5.0 Hz, 1H), 8.36 (d, *J* = 1.0 Hz, 1H), 8.06-7.98 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 (ddd, *J* = 7.5, 5.6, 1.0 Hz, 1H), 3.93 (s, 3H), 1.44 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 155.5, 143.9, 142.5, 141.5, 133.0, 132.7, 130.0, 124.1, 121.5, 118.7, 80.9, 52.6, 27.4. **MS** (ESI): *m*/*z* 340 ($M+H^+$, 93); **HRMS** (ESI): Calcd. for $C_{19}H_{23}BNO_4$ ($M+H^+$), 340.1715; found 340.1718.

2-[5-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyridine (4g):[6]



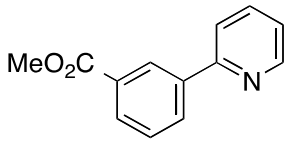
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (ddd, *J* = 5.6, 1.6, 1.0 Hz, 1H), 7.95 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H), 7.75 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.35 (ddd, *J* = 7.5, 5.6, 1.2 Hz, 1H), 7.17 (d, *J* = 2.3 Hz, 1H), 6.98 (dd, *J* = 8.0, 2.3 Hz, 1H), 3.84 (s, 3H), 1.41 (s, 12H).

2-[5-Fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyridine (4h):



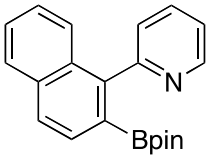
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (d, *J* = 5.7 Hz, 1H), 7.99 (td, *J* = 7.7, 1.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.48-7.37 (m, 1H), 7.30 (dd, *J* = 7.9, 2.7 Hz, 1H), 7.03 (t, *J* = 8.1 Hz, 1H), 1.45 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1 (d, *J* = 245.1 Hz), 155.0, 142.9, 141.9, 140.0 (d, *J* = 12.7 Hz), 130.3 (d, *J* = 7.8 Hz), 123.4, 118.7 (d, *J* = 26.4 Hz), 117.8, 117.5 (d, *J* = 2.9 Hz), 81.0, 27.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ -105; **MS** (ESI): *m*/*z* 300 ($M+H^+$, 100); **HRMS** (ESI): Calcd. for $C_{17}H_{19}BFNO_2$ ($M+H^+$), 300.1567; found 300.1567.

2-[5-Methoxycarbonyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyridine (4i):[6]



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74-8.65 (m, 1H), 8.35-8.33 (m, 1H), 8.12-7.97 (m, 2H), 7.92 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.80 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.44 (ddd, *J* = 7.5, 5.6, 1.3 Hz, 1H), 3.94 (s, 3H), 1.43 (s, 12H).

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-yl)pyridine (4j):

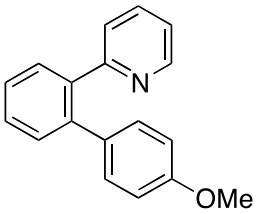


^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (dd, *J* = 5.5, 0.7 Hz, 1H), 8.34-8.26 (m, 2H), 8.01 (ddd, *J* = 8.1, 7.5, 1.6 Hz, 1H), 7.93-7.86 (m, 3H), 7.55 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.47 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.39 (ddd, *J* = 7.5, 5.5, 1.1 Hz, 1H), 1.42 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 144.5, 142.0, 135.1, 133.9, 131.9, 130.0, 130.1, 128.8, 127.4, 125.6, 123.2, 122.2, 122.2, 81.1, 27.5. **MS** (ESI): *m*/*z* 332 ($M+H^+$, 100); **HRMS** (ESI): Calcd. for $C_{21}H_{23}BNO_2$ ($M+H^+$), 300.1816; found 332.1820.

General procedure for the one pot borylation Suzuki-Miyaura coupling.

In a vial fitted with a screwcap, in the glovebox, bis(pinacolato)diboron (0.25 mmol), the 2-phenylpyridine (**3a**) (0.25 mmol) and **2a** (0.00375 mmol, 1.5 mol%) were dissolved in 1,4-dioxane (0.5 mL). Then, outside of the glovebox, the resulting mixture was stirred 16 h at 110°C. Volatiles was removed under reduced pressure. Then Suzuki-Miyaura coupling was carried out following a procedure developed in our laboratory.[8] In the glovebox, KOH (0.375 mmol, 1.5 equiv) was added to the mixture. A solution of the palladium pre-catalyst [Pd(IPr*)(cinnamyl)Cl] in DME (1 mL of DME, 3.0 mol%) and the chloroanisole (0.375 mmol, 1.5 equiv.) were added sequentially. The reaction mixture was then stirred (800 rpm) at room temperature or 60°C during 16 h. Then the solution was cooled, quenched with water (5 mL), and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and the volatiles were evaporated in vaccuo. The crude product was finally purified by flash chromatography on silica gel.

2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine (5):[9]



^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.71-7.62 (m, 1H), 7.47-7.36 (m, 4H), 7.15-7.04 (m, 3H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.82-6.72 (m, 2H), 3.79 (s, 3H).

REFERENCES:

(1) Manzini, S.; Urbina-Blanco, C. A.; Poater, A.; Slawin, A. M. Z.; Cavallo, L.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 1042.

(2) Xu, J.; Cheng, G.; Su, D.; Liu, Y.; Wang, X.; Hu, Y. *Chem. Eur. J.* **2009**, *15*, 13105.

(3) Li, X.; Zou, D.; Leng, F.; Sun, C.; Li, J.; Wu, Y.; Wu, Y. *Chem. Commun.* **2013**, *49*, 312.

(4) Molander, G. A.; Trice, S. L. J.; Kennedy, S. M. *J. Org. Chem.* **2012**, *77*, 8678.

(5) Liu, C.; Yang, W. *Chem. Commun.* **2009**, 6267.

(6) Kawamorita, S.; Miyazaki, T.; Ohmiya, H.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 19310.

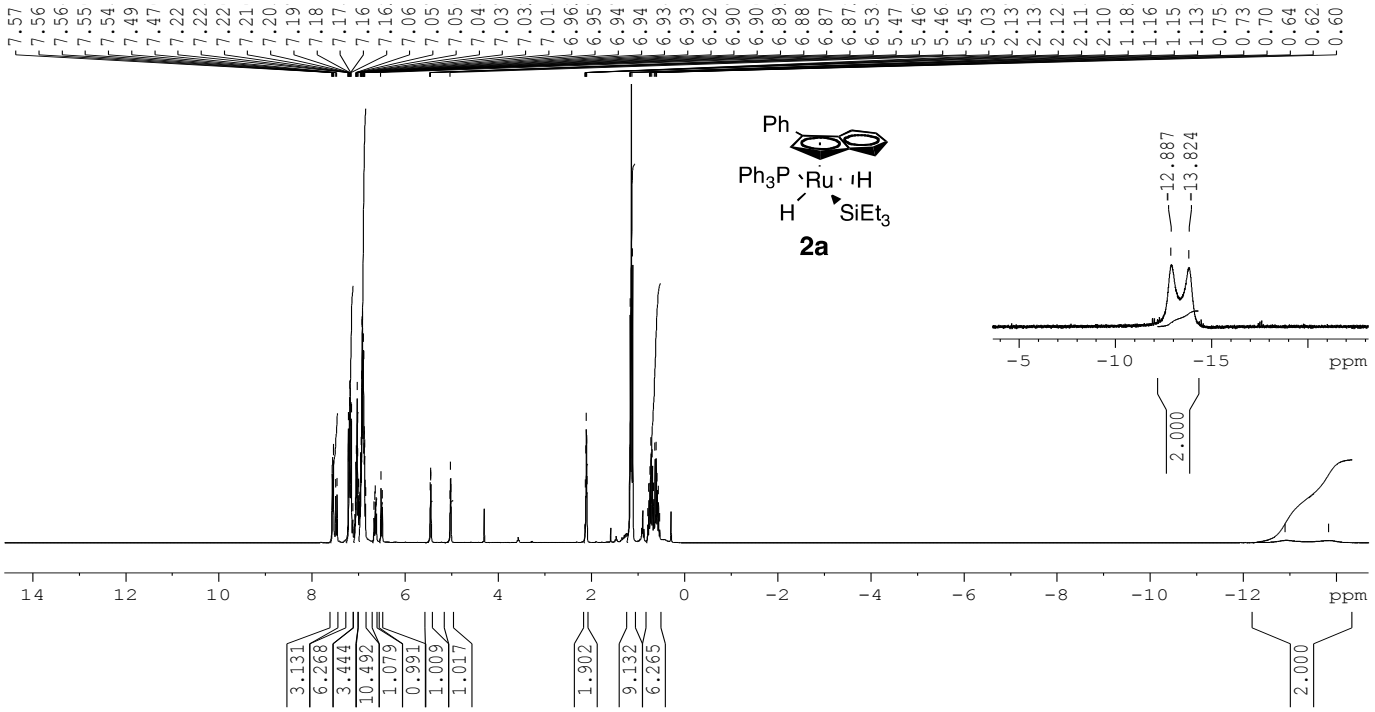
(7) Maity, A.; Anderson, B. L.; Deligonul, N.; Gray, T. G. *Chem. Sci.* **2013**, *4*, 1175.

(8) Chartoire, A.; Lesieur, M.; Falivene, L.; Slawin, A. M. Z.; Cavallo, L.; Cazin, C. S. J.; Nolan, S. P. *Chem. Eur. J.* **2012**, *18*, 4517.

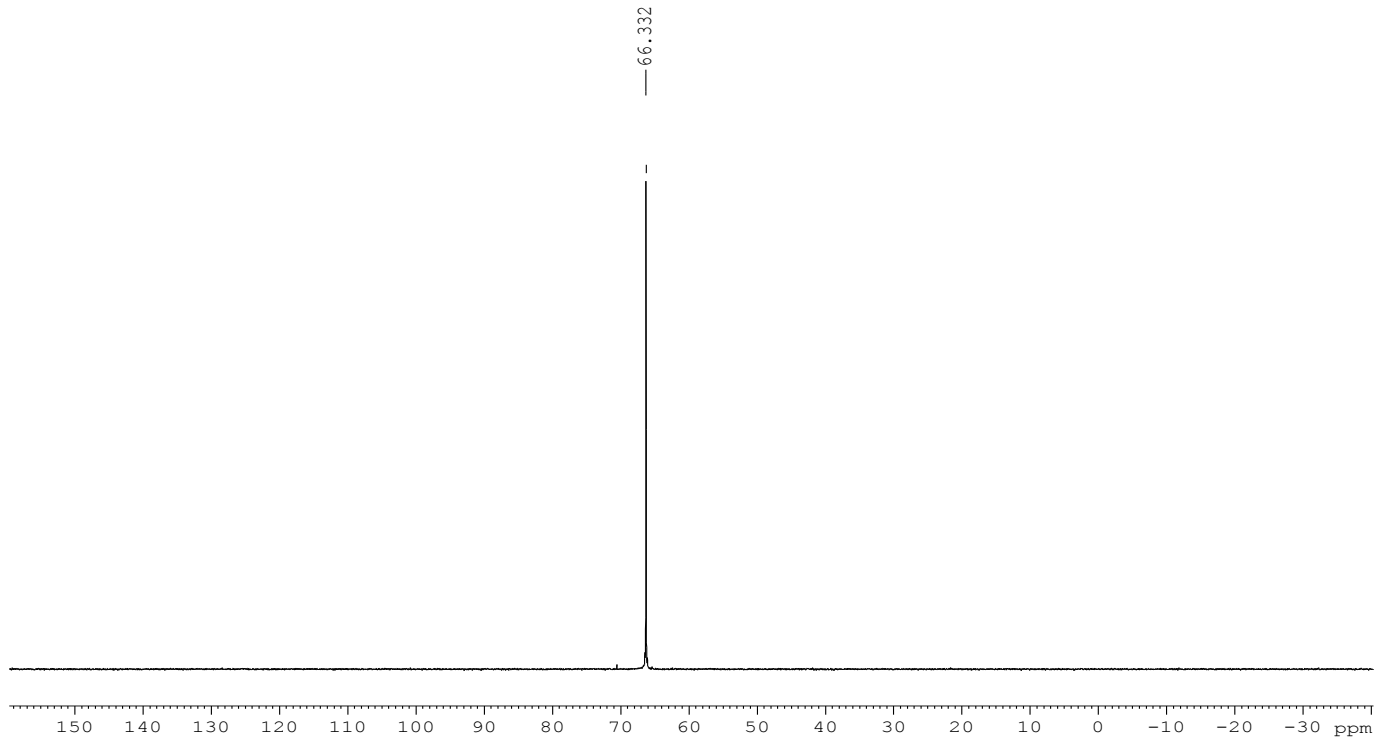
(9) Punji, B.; Song, W.; Shevchenko, G. A.; Ackermann, L. *Chem. Eur. J.* **2013**, *19*, 10605

NMR SPECTRA:

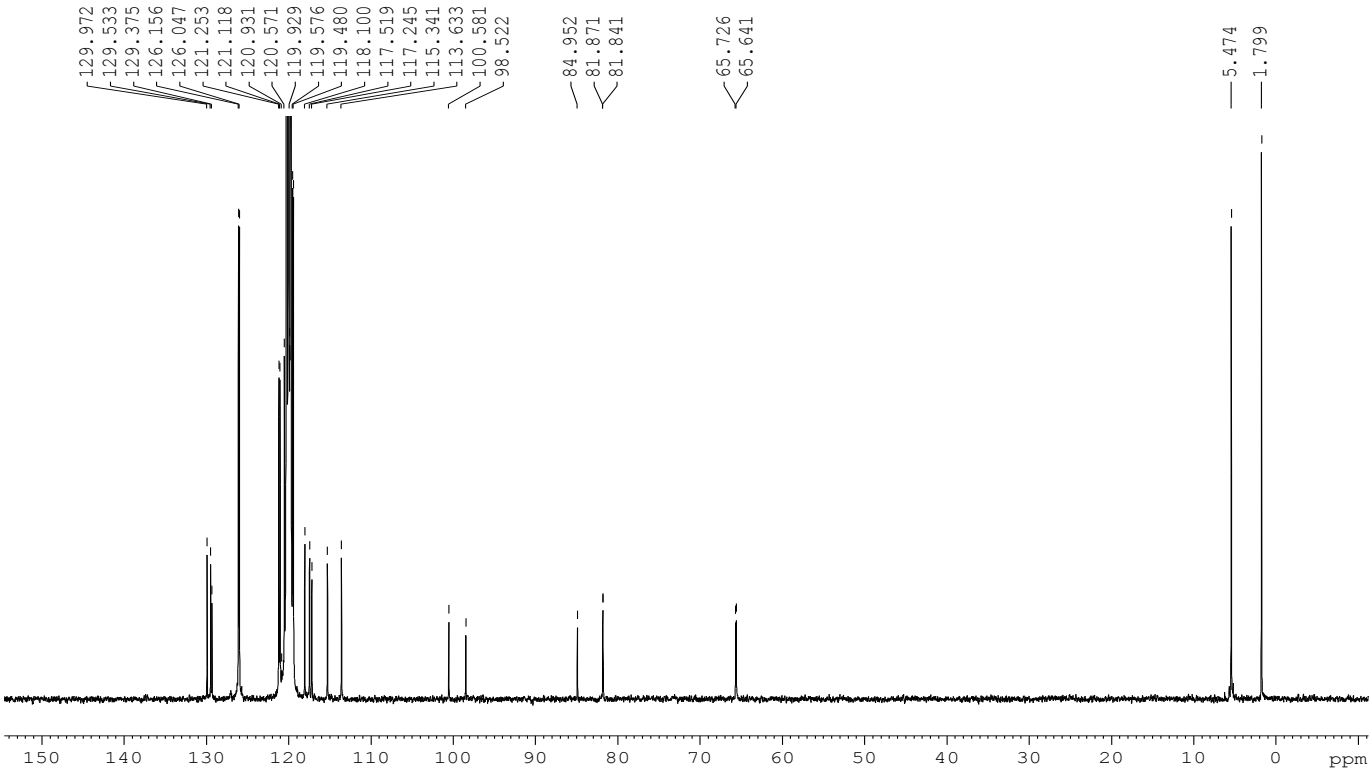
2a: ^{1}H NMR in C_6D_6



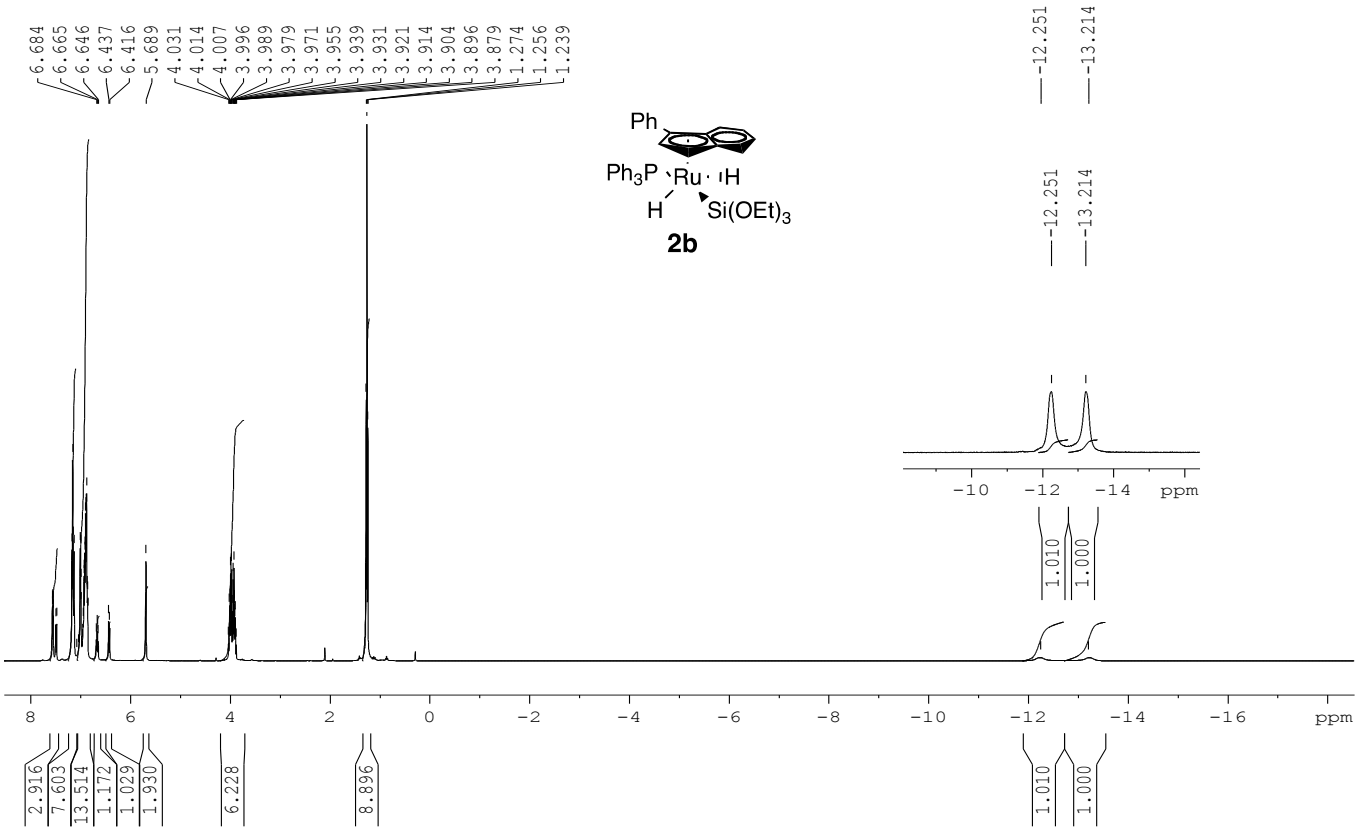
$^{31}P\{^{1}H\}$ NMR C_6D_6



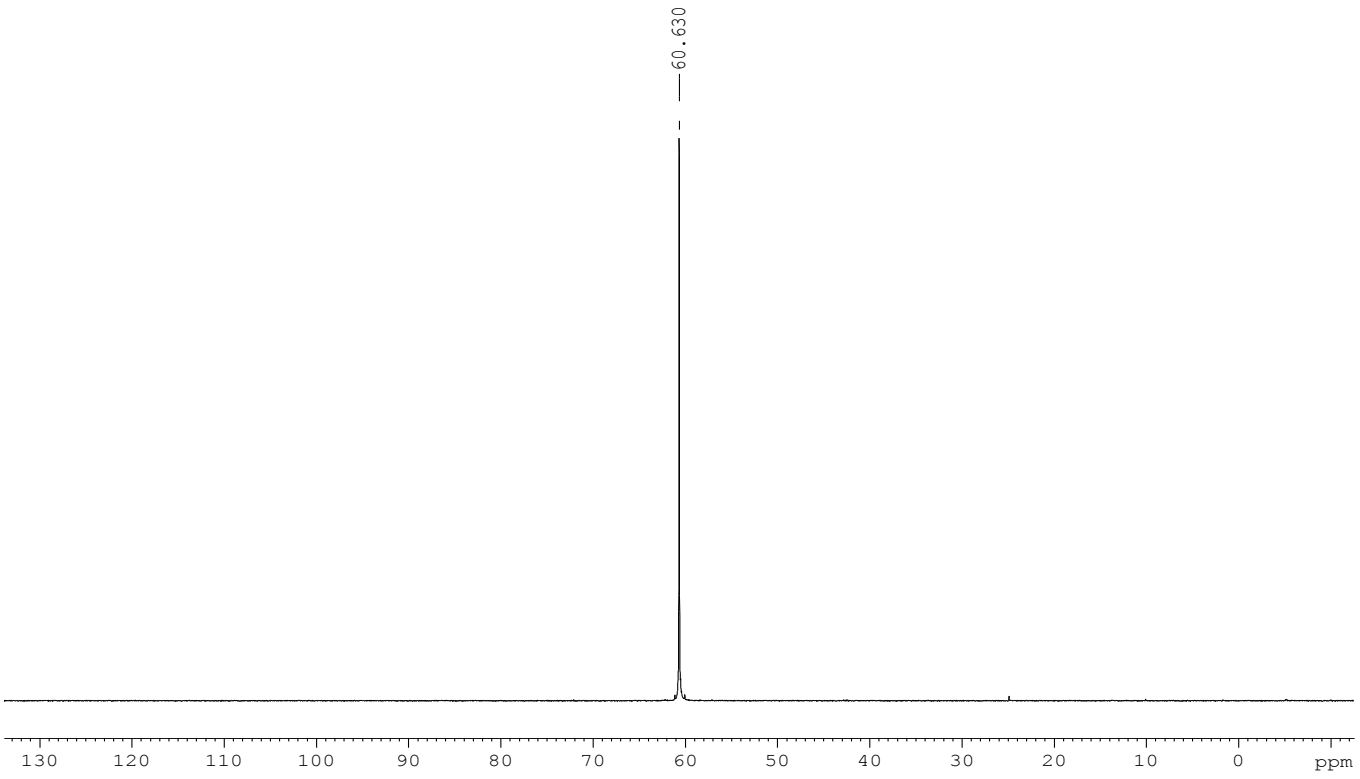
$^{13}C\{^{1}H\}$ NMR C_6D_6



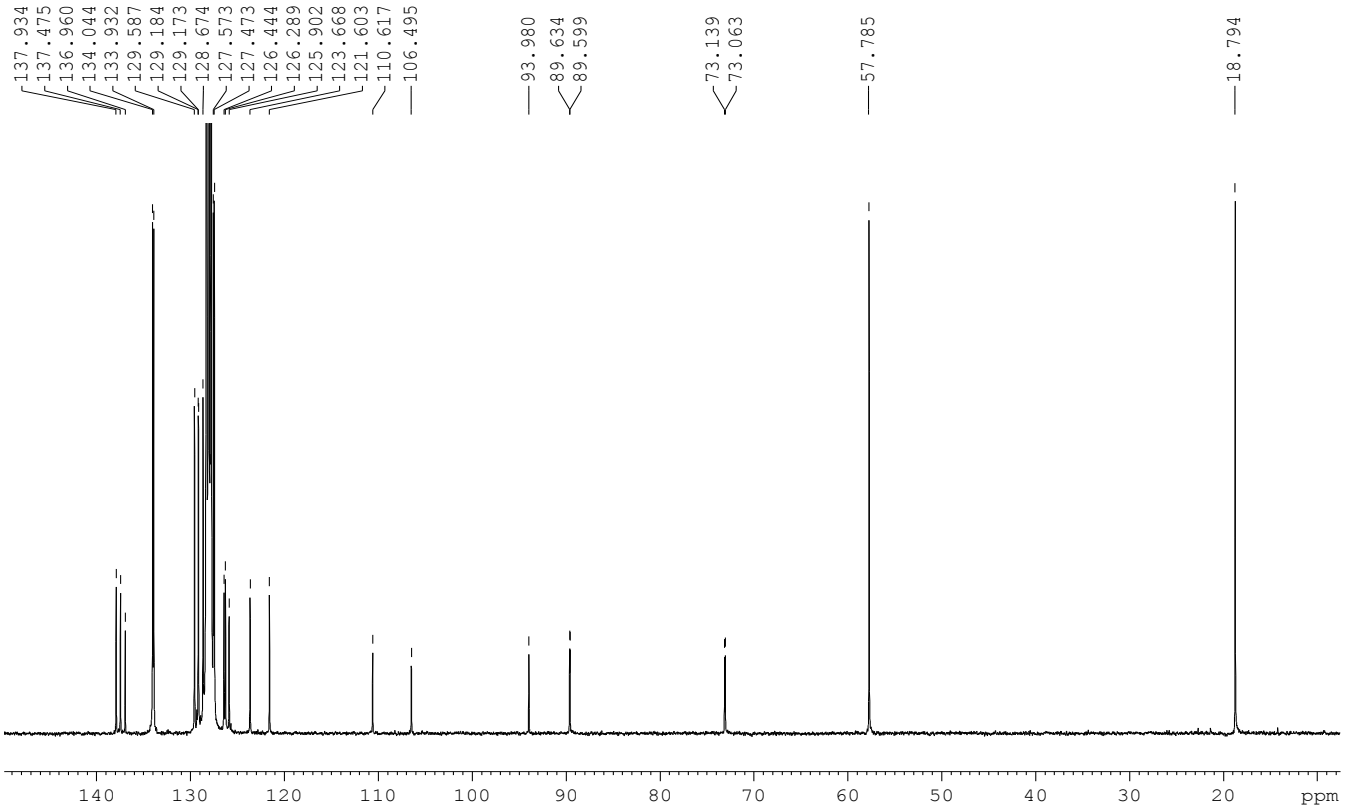
2b: ^{1}H NMR C_6D_6



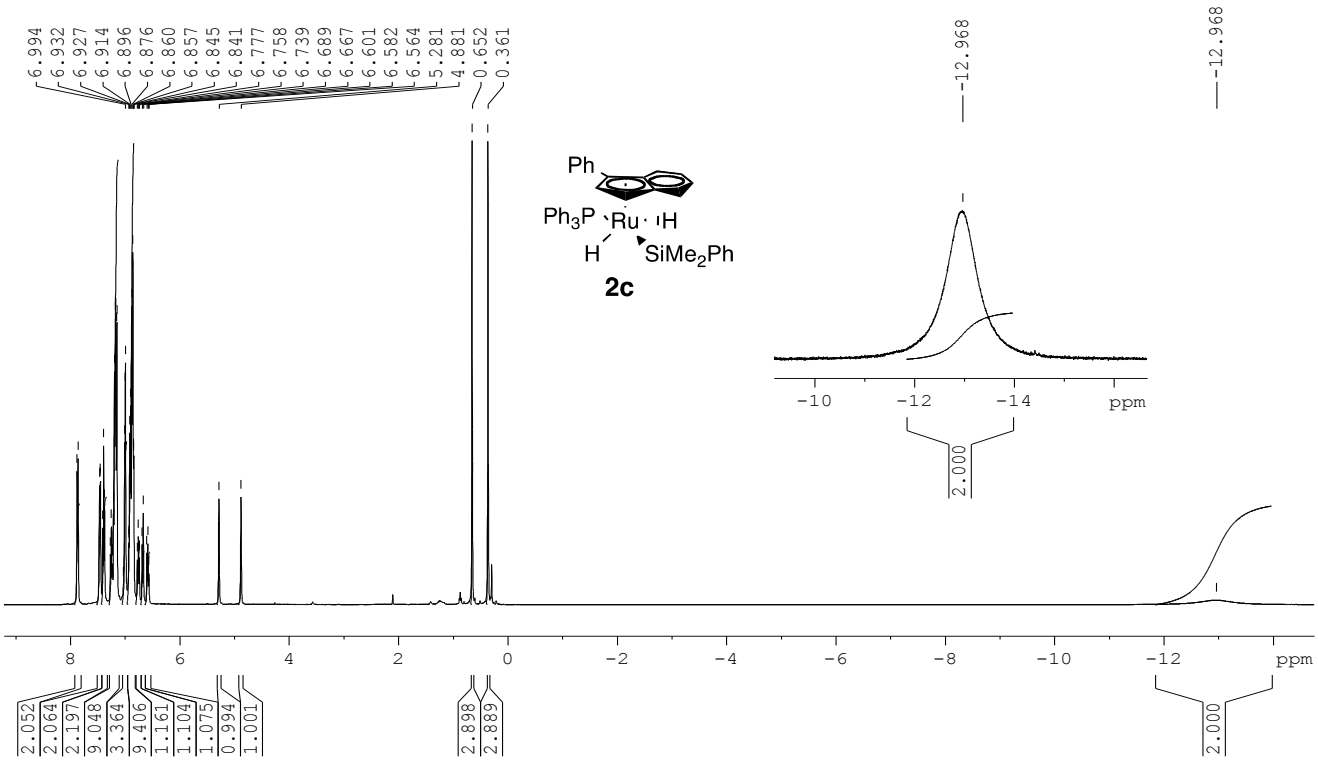
$^{31}P\{^{1}H\}$ NMR in C_6D_6



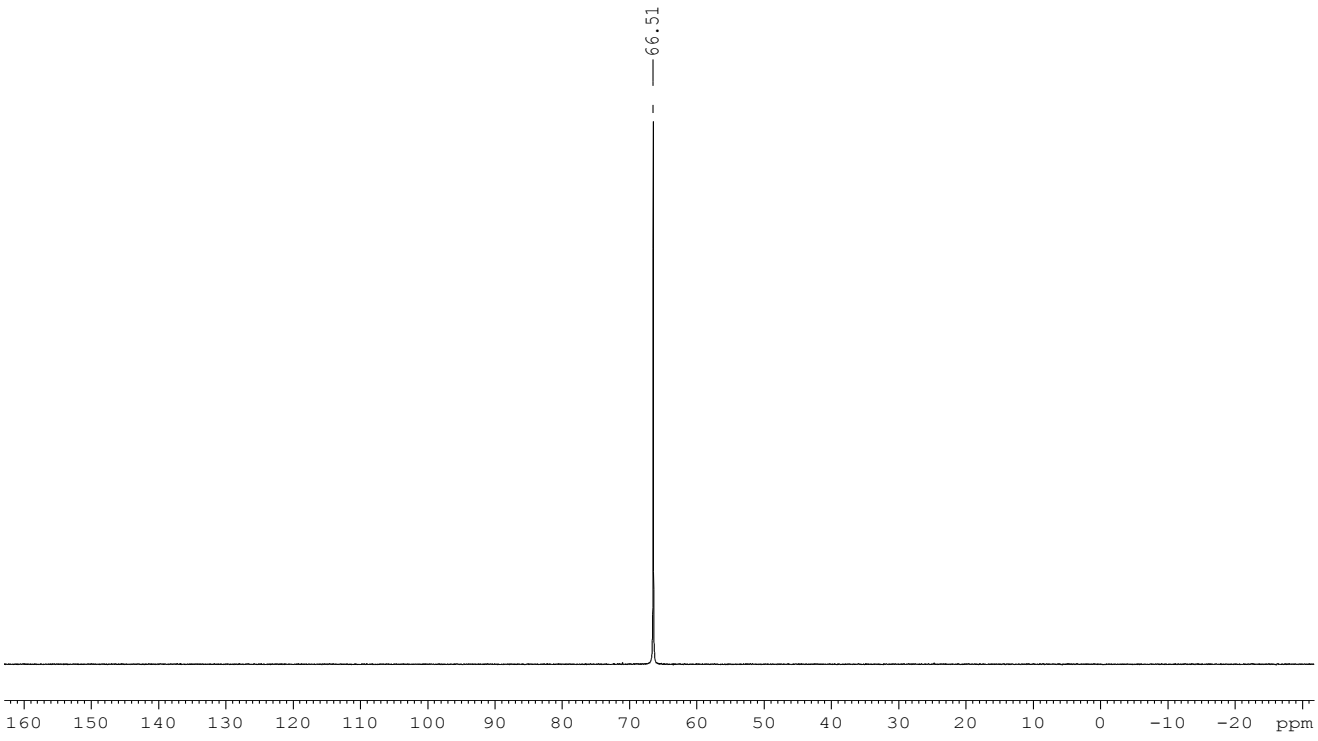
$^{13}C\{^{1}H\}$ NMR in C_6D_6



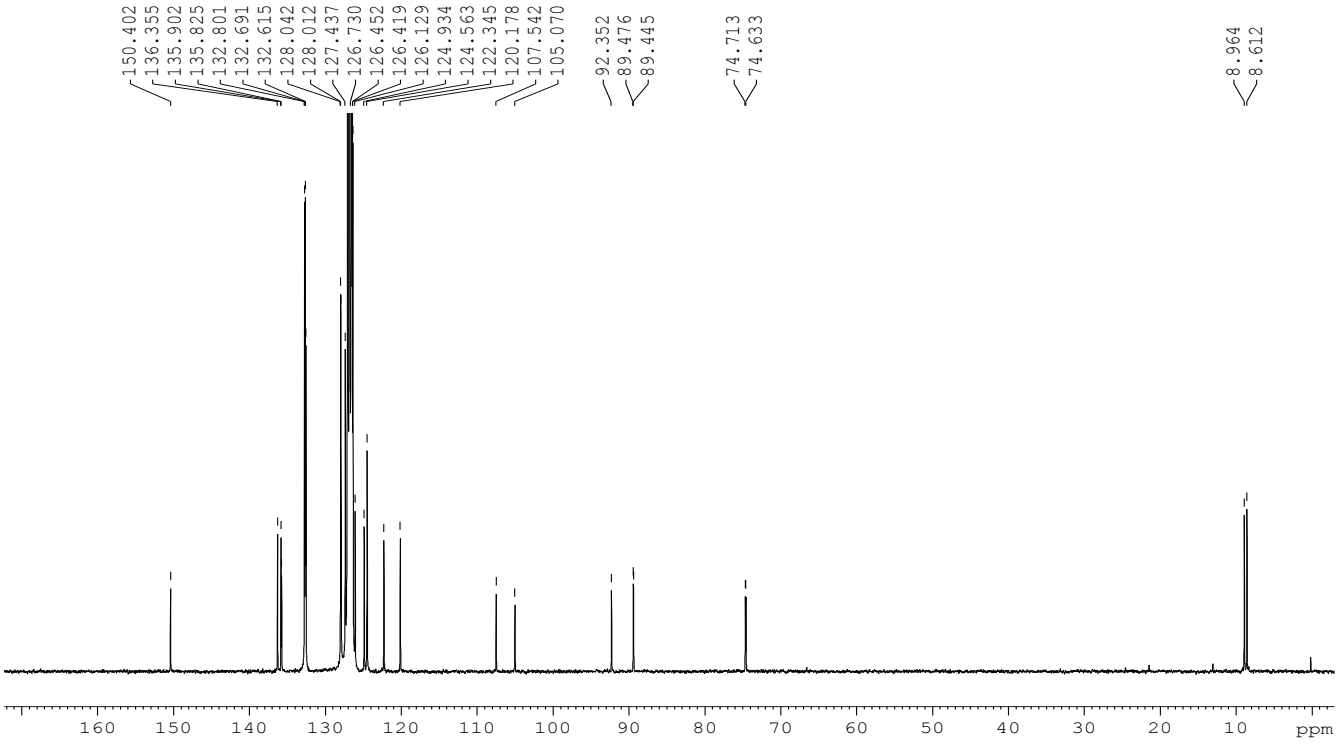
2c: ^{1}H NMR in C_6D_6



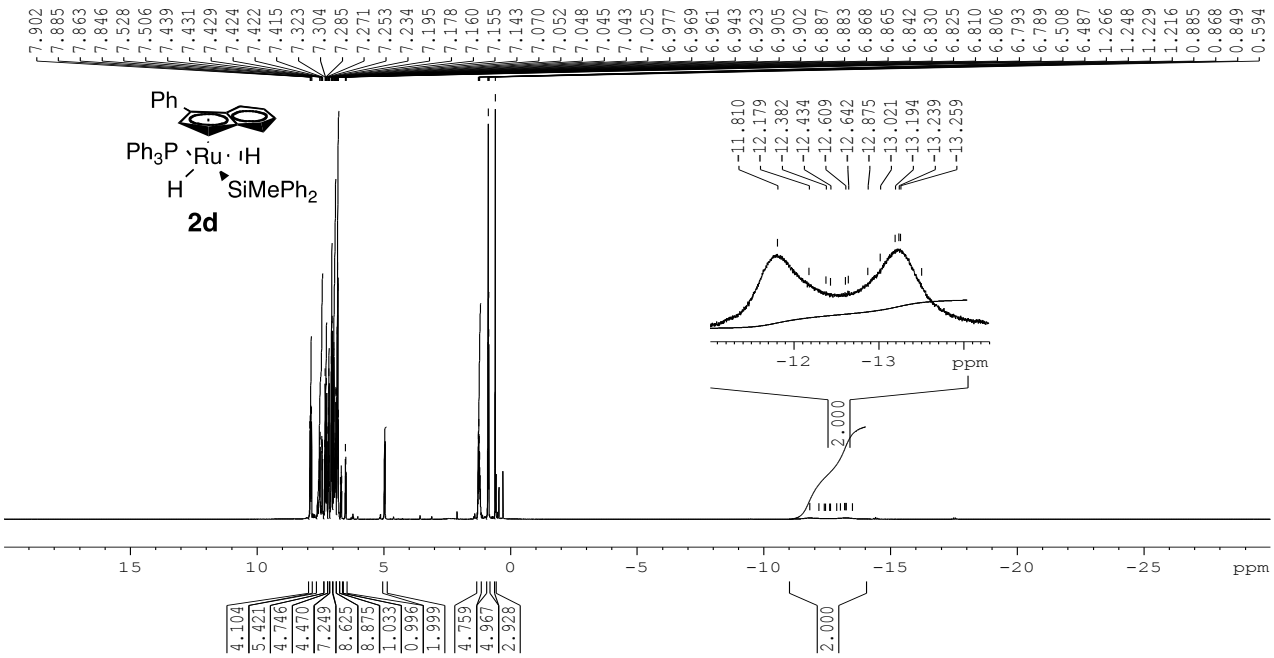
$^{31}P\{^{1}H\}$ NMR in C_6D_6



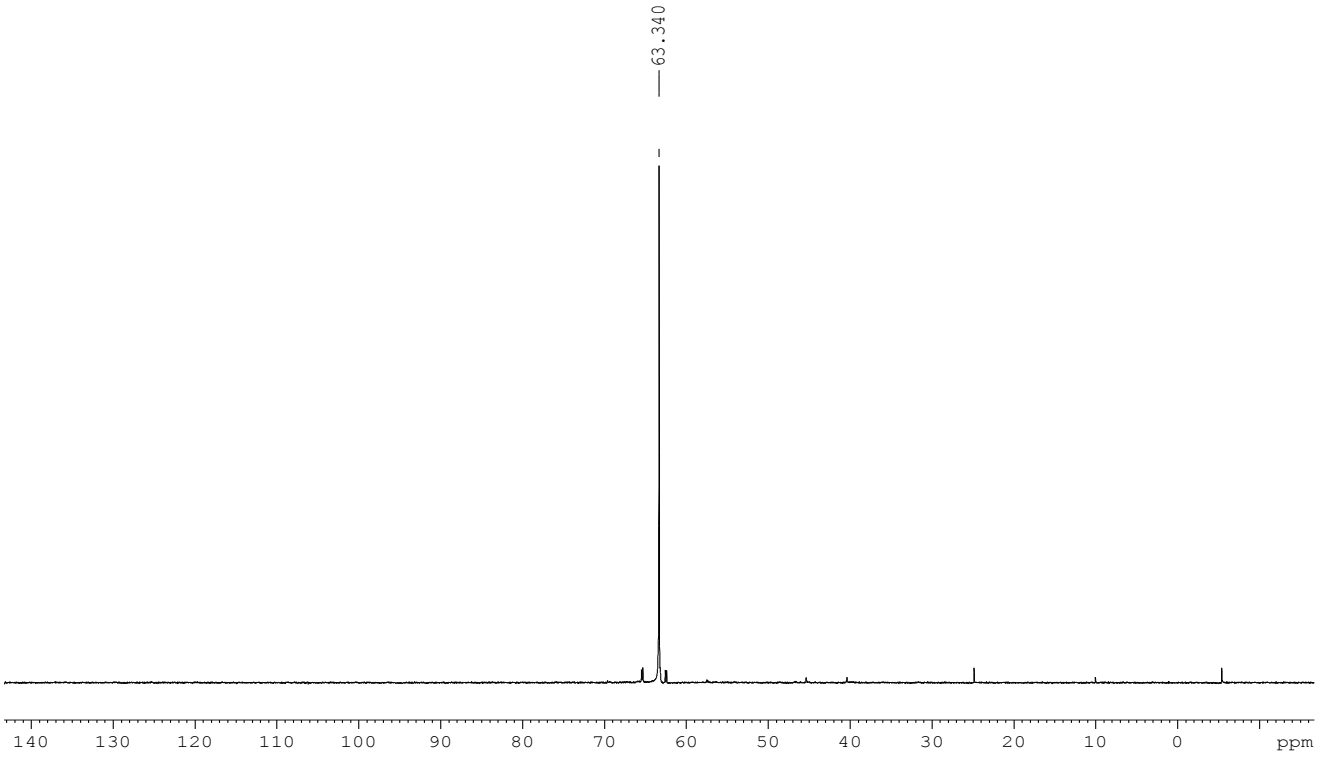
$^{13}C\{^{1}H\}$ NMR in C_6D_6


150.402
136.355
135.902
135.825
132.801
132.691
132.615
128.042
128.012
127.437
126.730
126.452
126.419
126.129
124.934
124.563
122.345
120.178
107.542
105.070
92.352
89.476
89.445
74.713
74.633
8.964
8.612
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

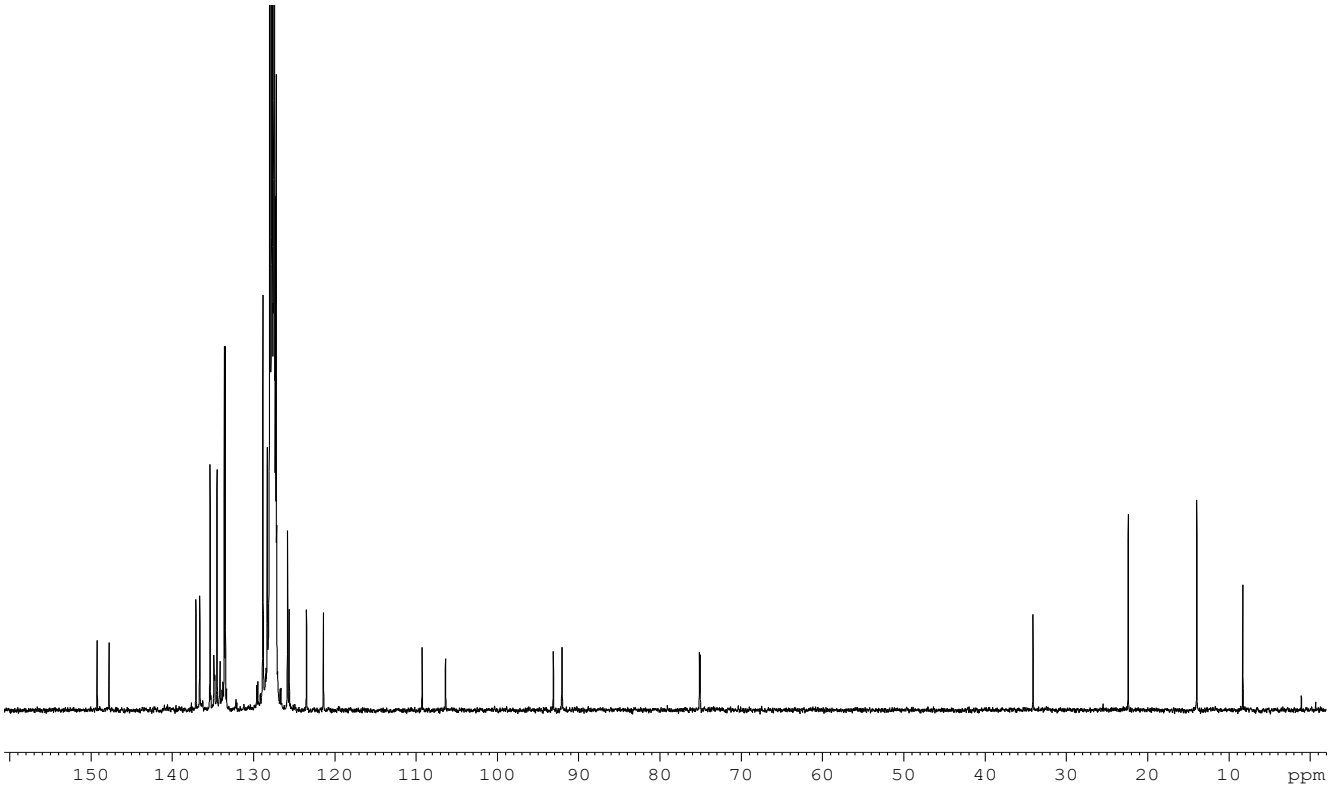
2d. ^{1}H NMR in C_6D_6



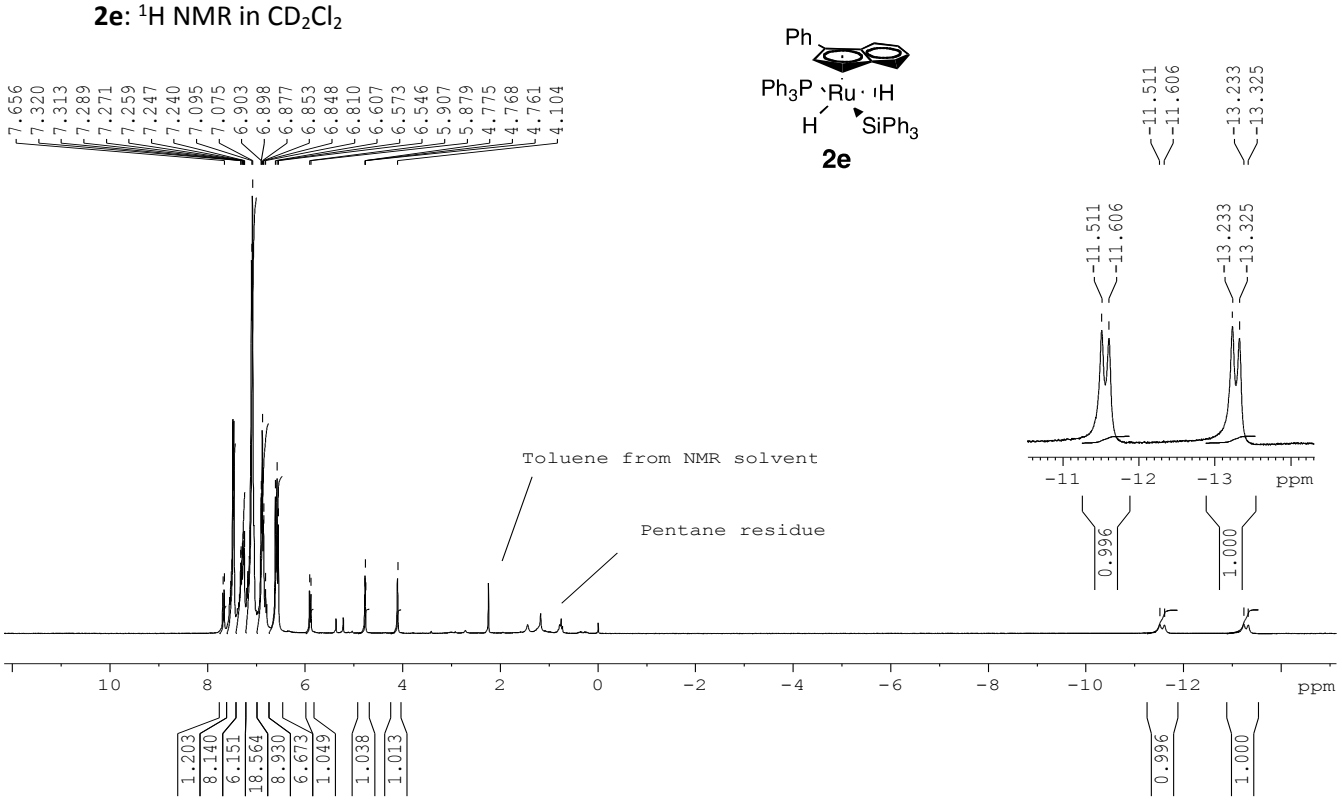
$^{31}P\{^{1}H\}$ NMR in C_6D_6



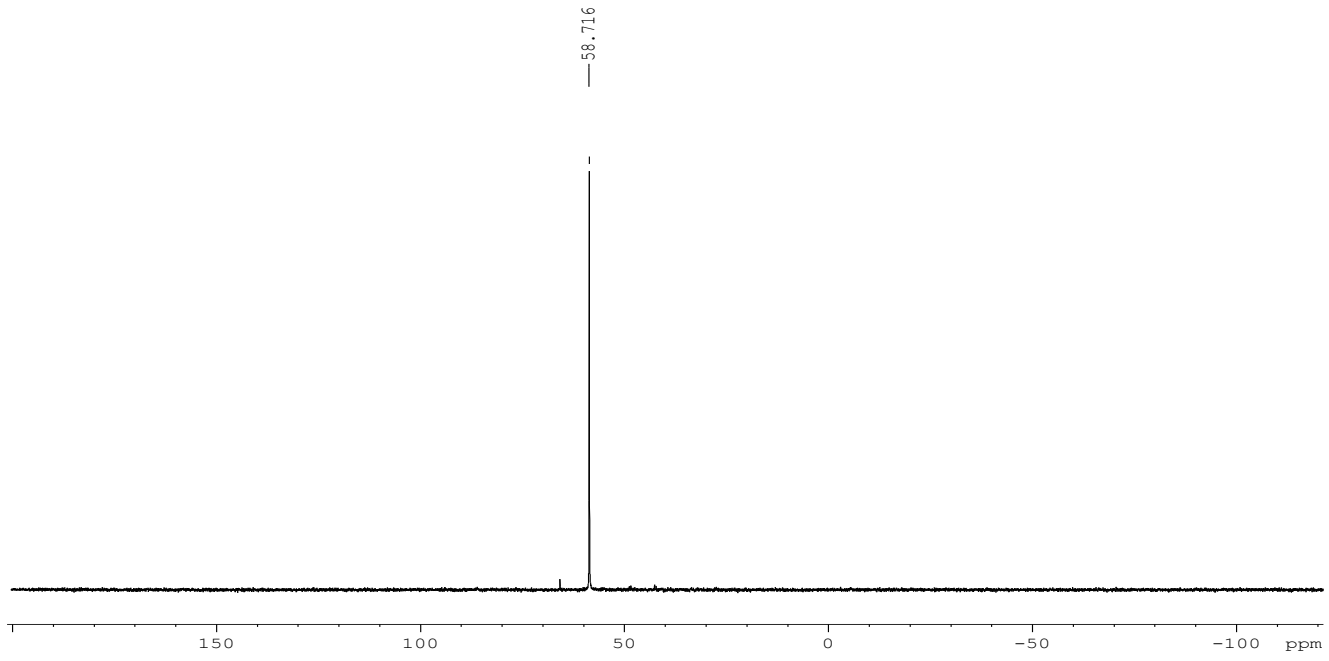
$^{13}C\{^{1}H\}$ NMR in C_6D_6



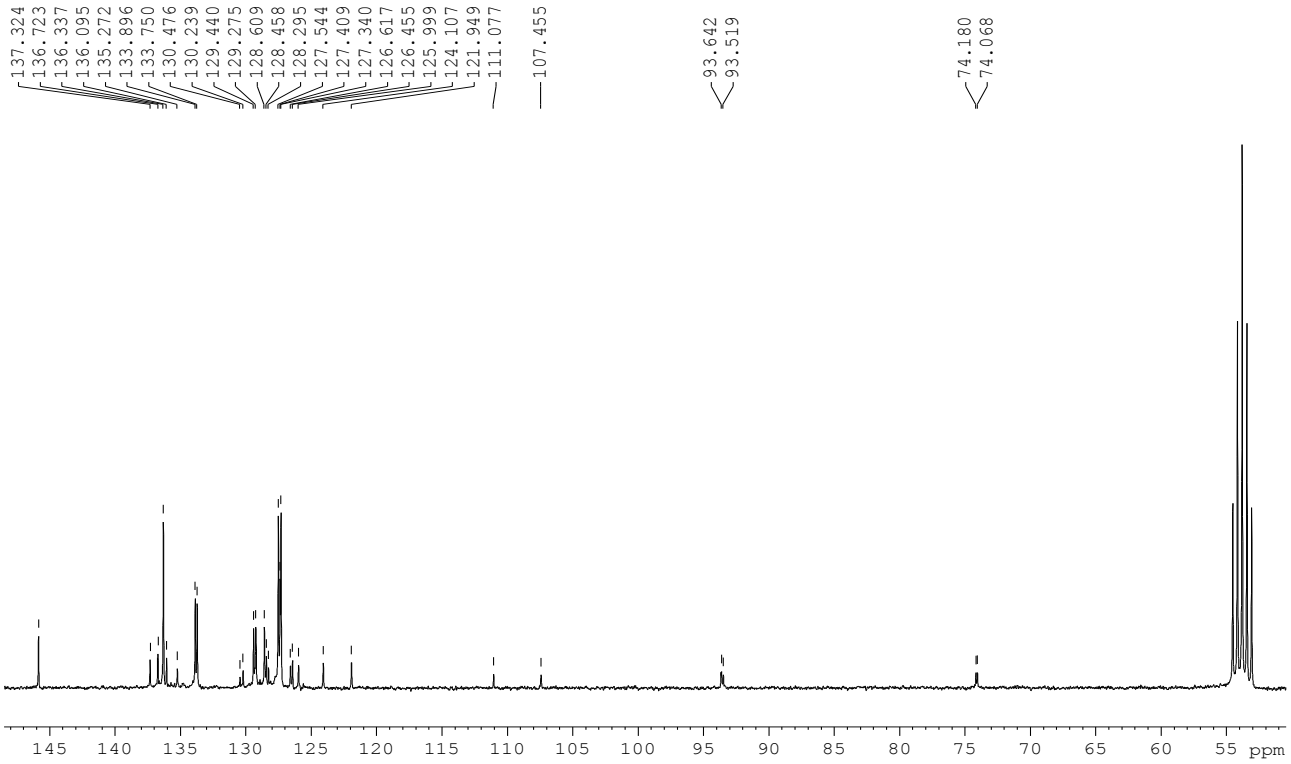
2e: ^{1}H NMR in CD_2Cl_2

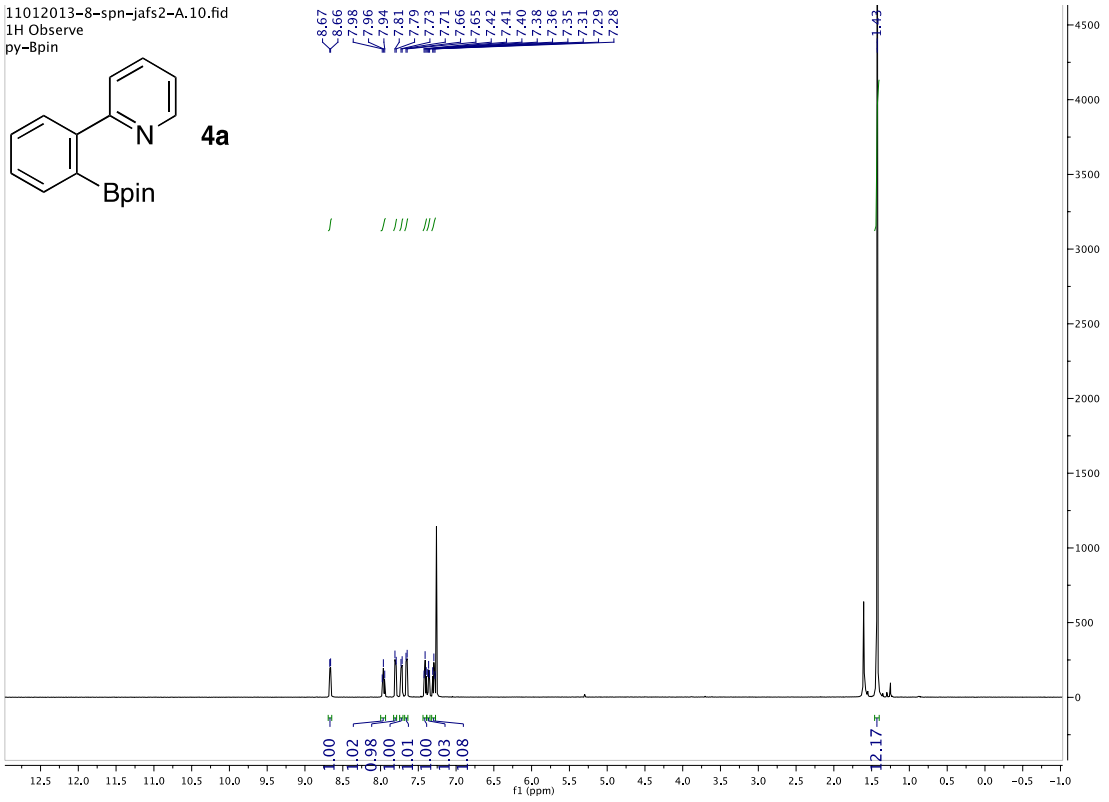


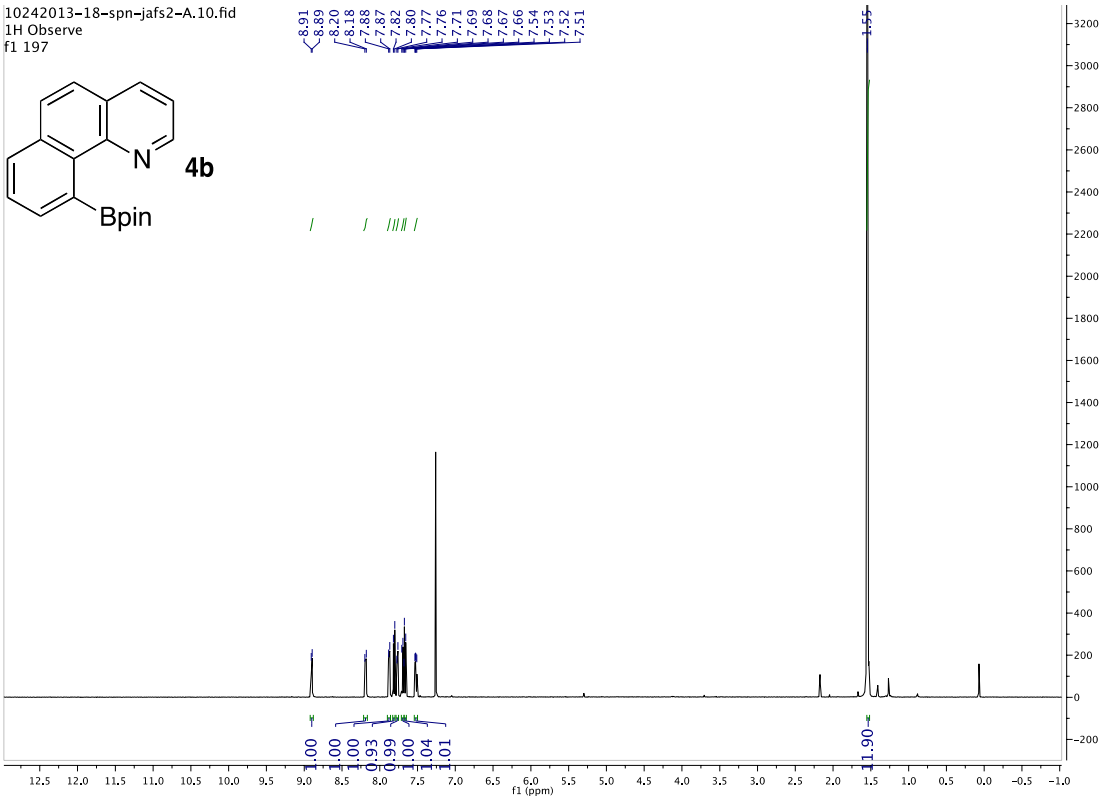
$^{31}P\{^{1}H\}$ NMR in C_2Cl_2

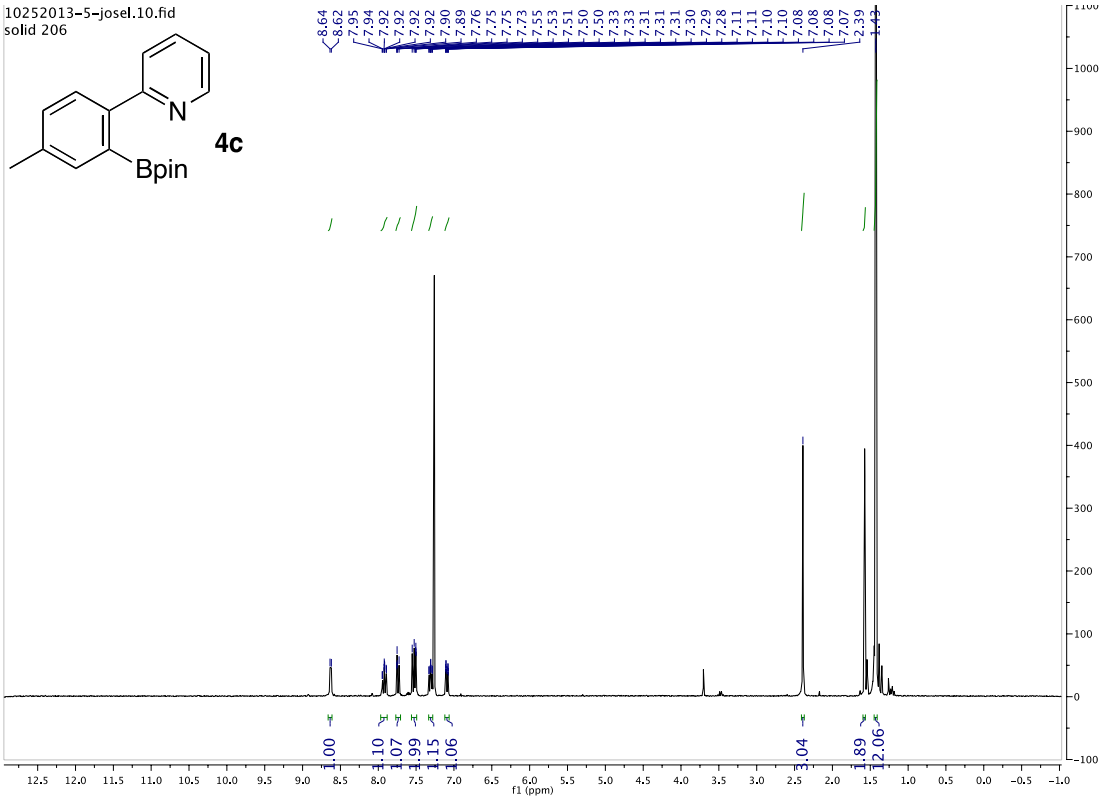


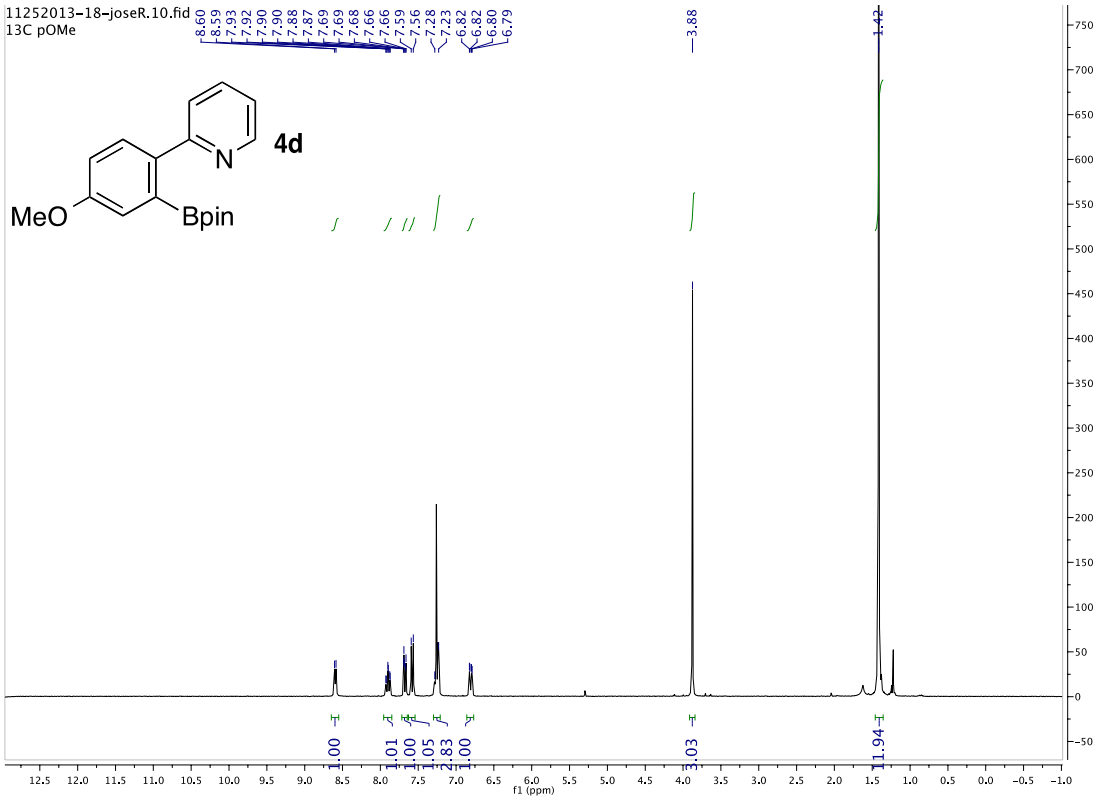
$^{13}C\{^{1}H\}$ NMR in CD_2Cl_2

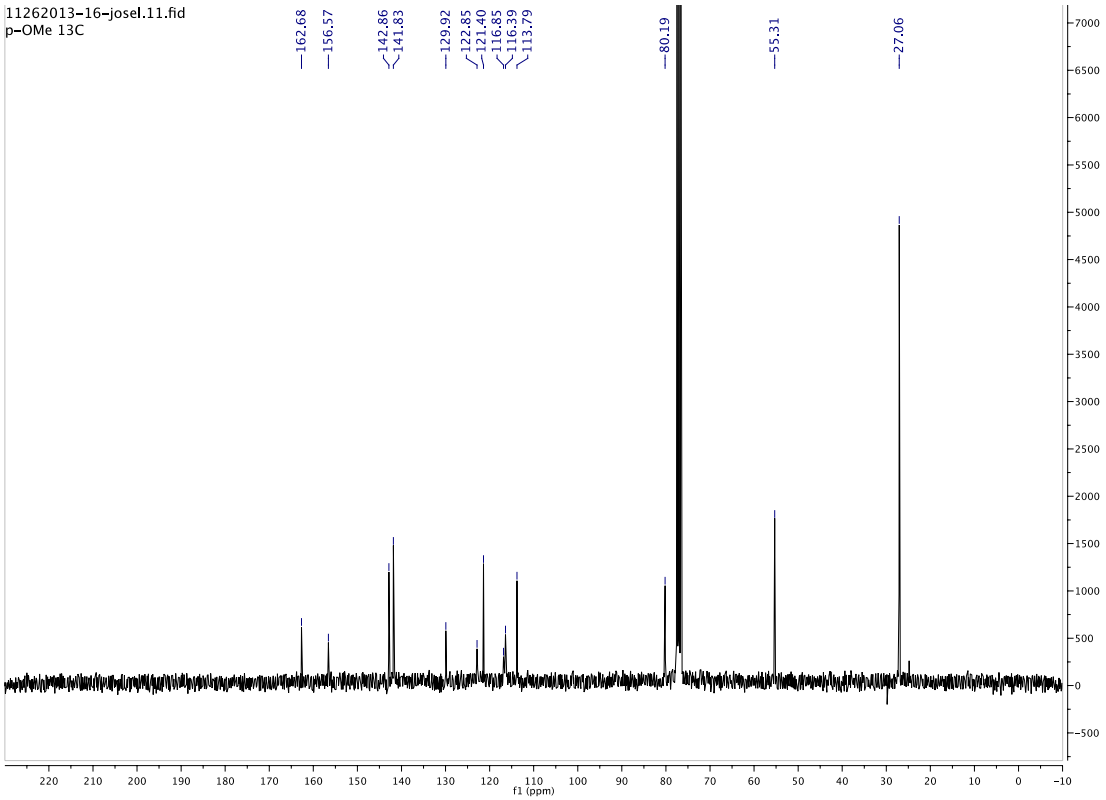


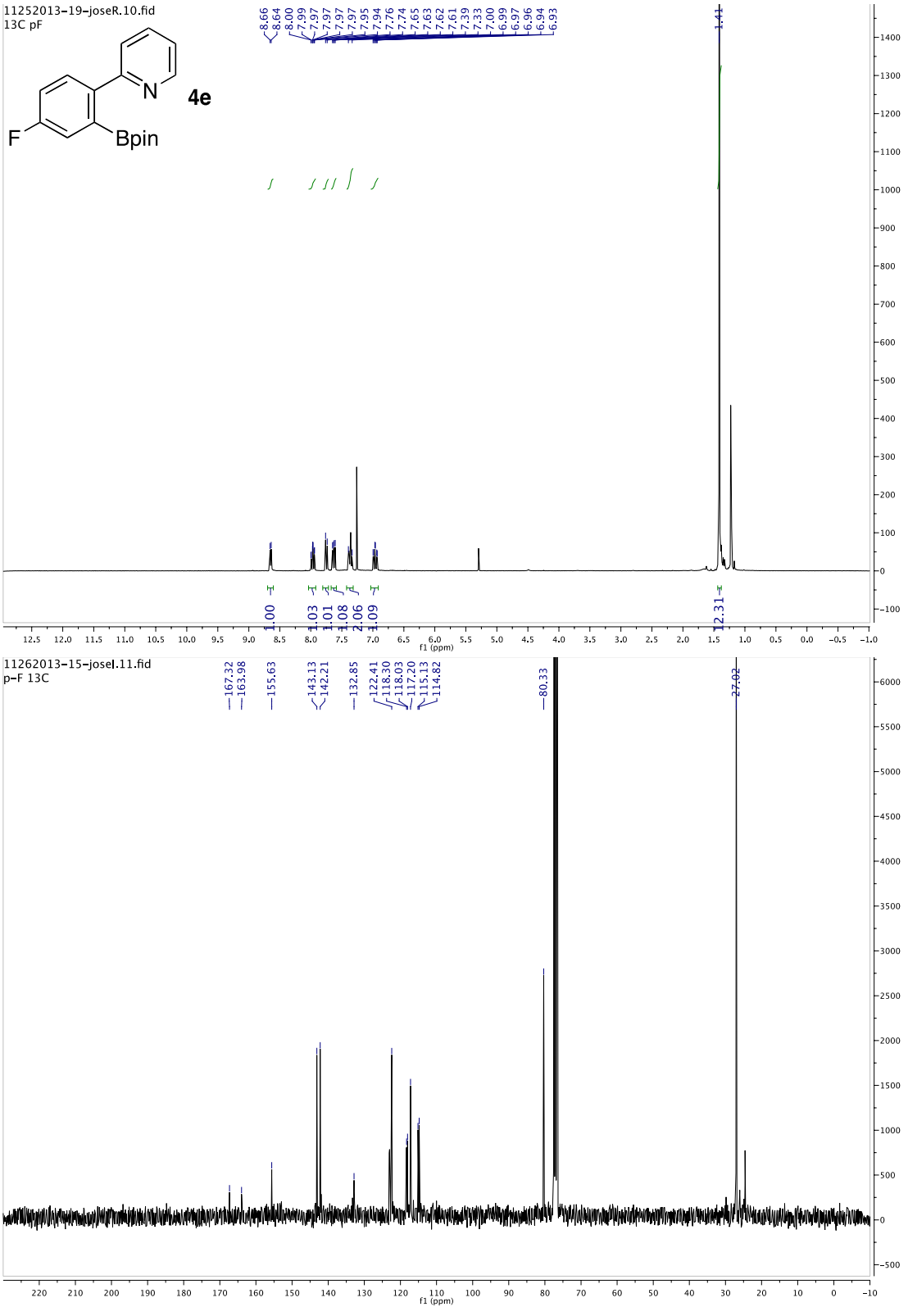

11012013-8-spn-jafs2-A.10.fid
1H Observe
py-Bpin
N
Bpin
4a
8.67
8.66
7.98
7.96
7.94
7.81
7.79
7.73
7.71
7.66
7.65
7.42
7.41
7.40
7.38
7.36
7.35
7.31
7.29
7.28
1.43
1.00
1.02
0.98
1.00
1.01
1.00
1.03
1.08
12.17
f1 (ppm)

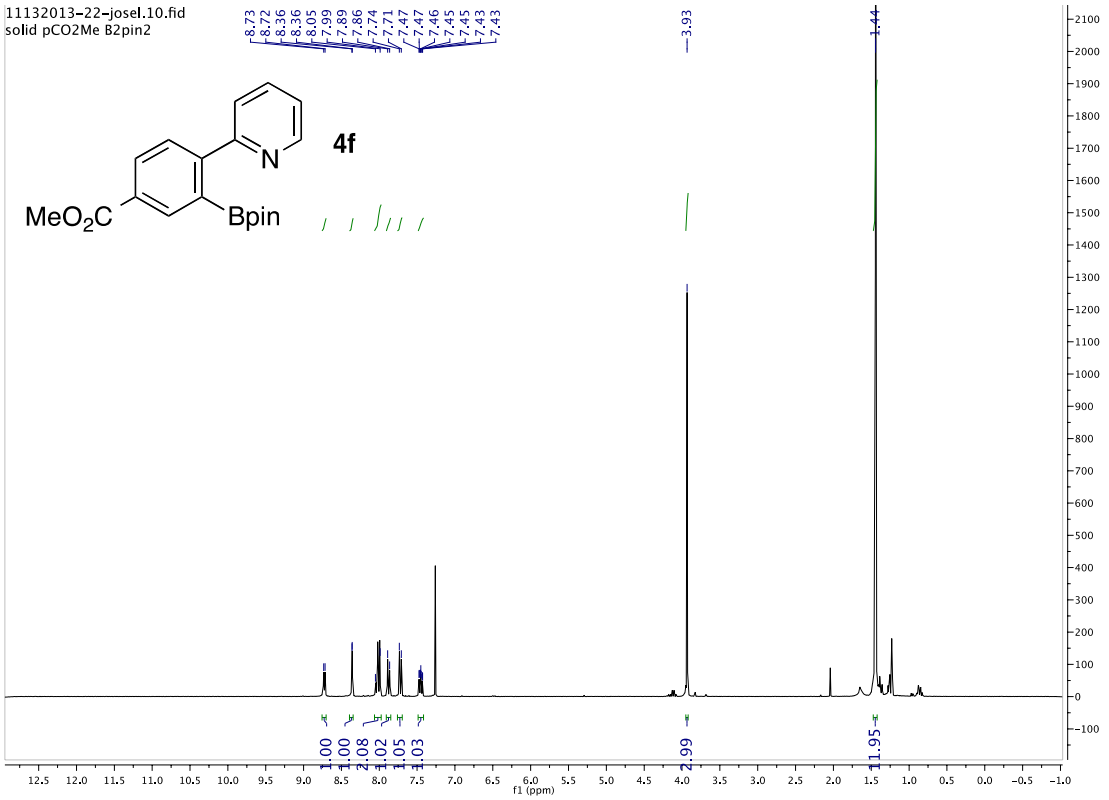

10242013-18-spn-jafs2-A.10.fid
1H Observe
f1 197
4b
Bpin
8.91
8.89
8.20
8.18
7.88
7.87
7.82
7.80
7.77
7.76
7.71
7.69
7.68
7.67
7.66
7.54
7.53
7.52
7.51
1.55
1.00
1.00
1.00
0.93
0.99
1.00
1.04
1.01
11.90
f1 (ppm)

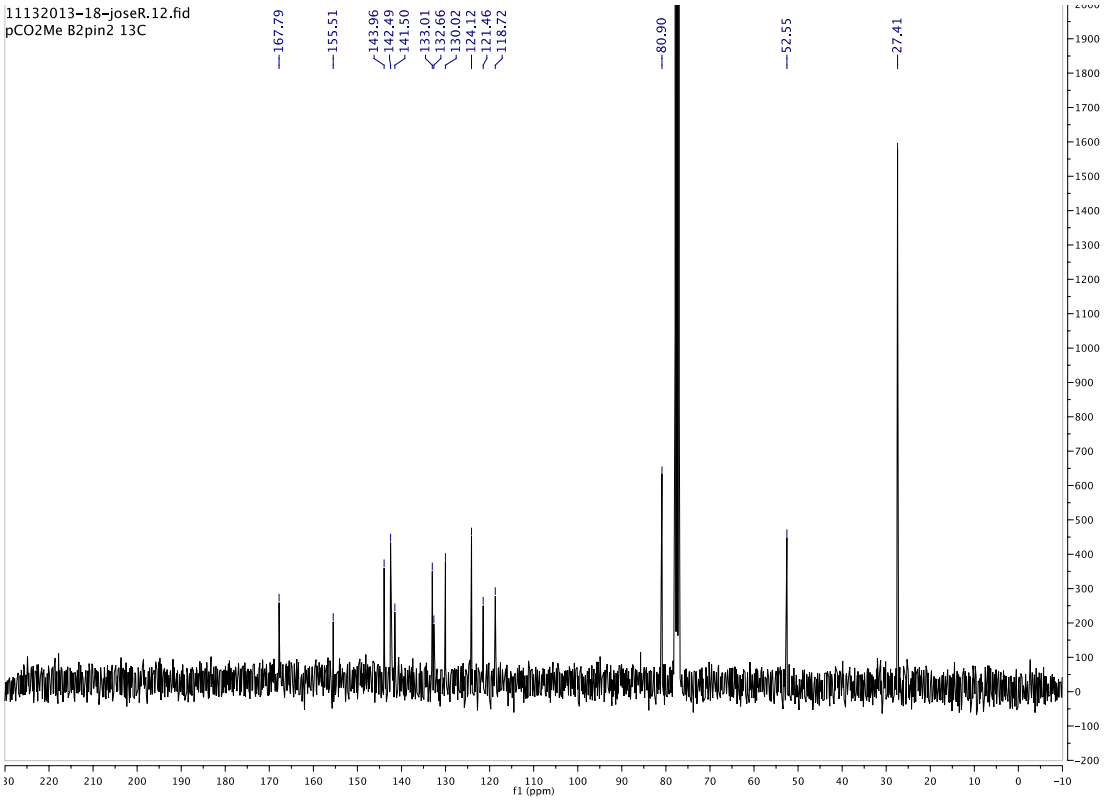

10252013-5-josel.10.fid
solid 206
N
Bpin
4c
8.64
8.62
7.95
7.94
7.92
7.92
7.92
7.92
7.90
7.89
7.76
7.75
7.75
7.73
7.55
7.53
7.51
7.50
7.50
7.33
7.33
7.31
7.31
7.31
7.30
7.29
7.28
7.11
7.11
7.10
7.10
7.08
7.08
7.08
7.07
2.39
1.43
1.00
1.10
1.07
1.99
1.15
1.06
3.04
1.89
12.06
f1 (ppm)

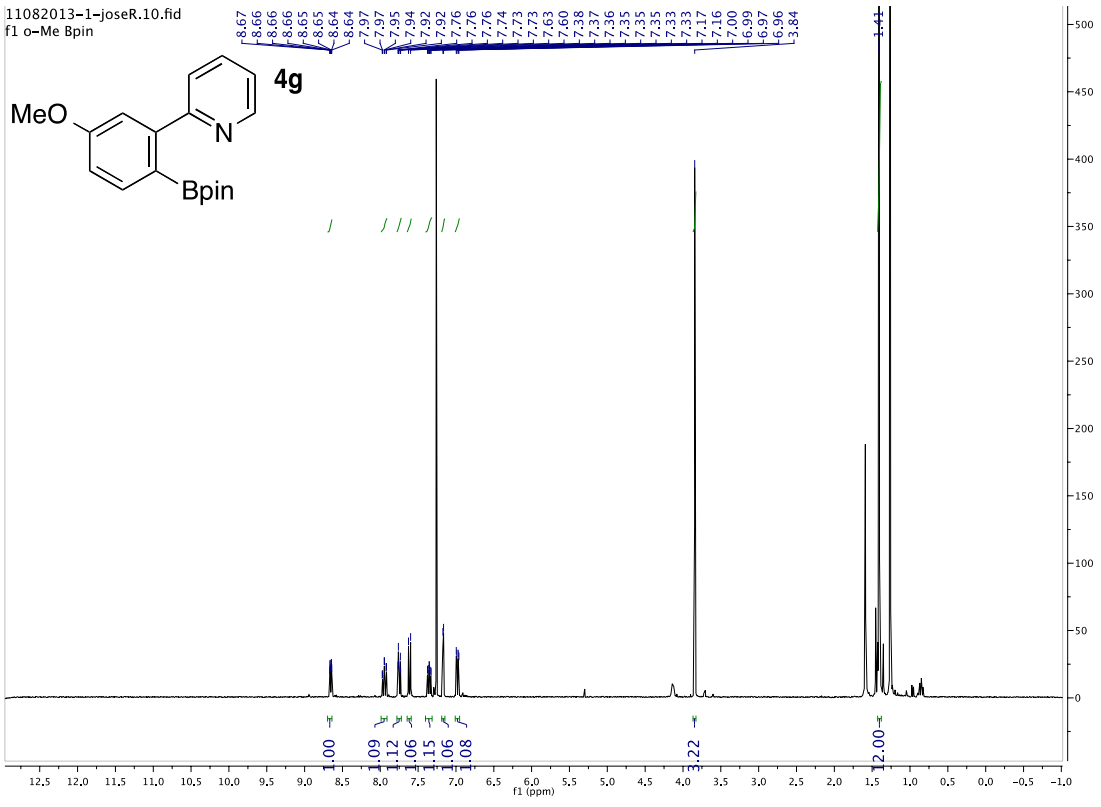

11252013-18-joseR.10.fid
13C pOMe
8.60
8.59
7.93
7.92
7.90
7.90
7.88
7.87
7.69
7.69
7.68
7.66
7.66
7.59
7.56
7.28
7.23
6.82
6.82
6.80
6.79
3.88
1.42
4d
N
MeO
Bpin
1.00
1.01
1.00
1.05
2.83
1.00
3.03
11.94
f1 (ppm)

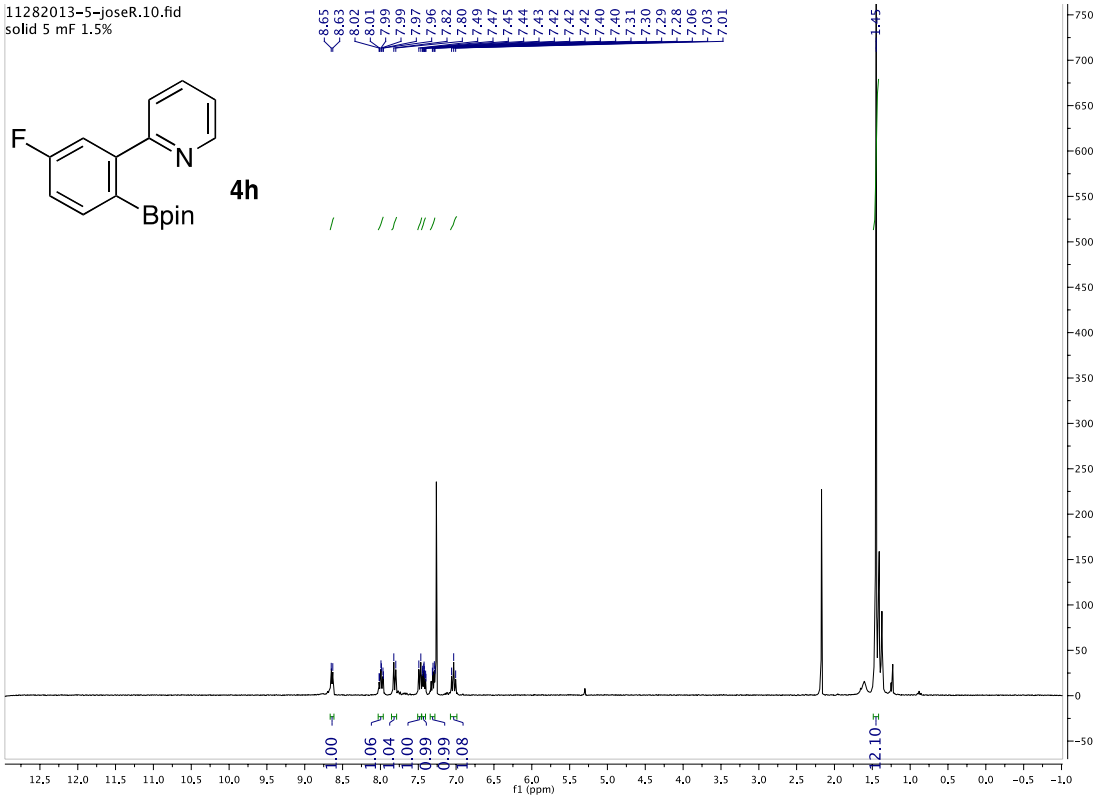

11262013-16-josel.11.fid
p-OMe 13C
162.68
156.57
142.86
141.83
129.92
122.85
121.40
116.85
116.39
113.79
80.19
55.31
27.06
f1 (ppm)

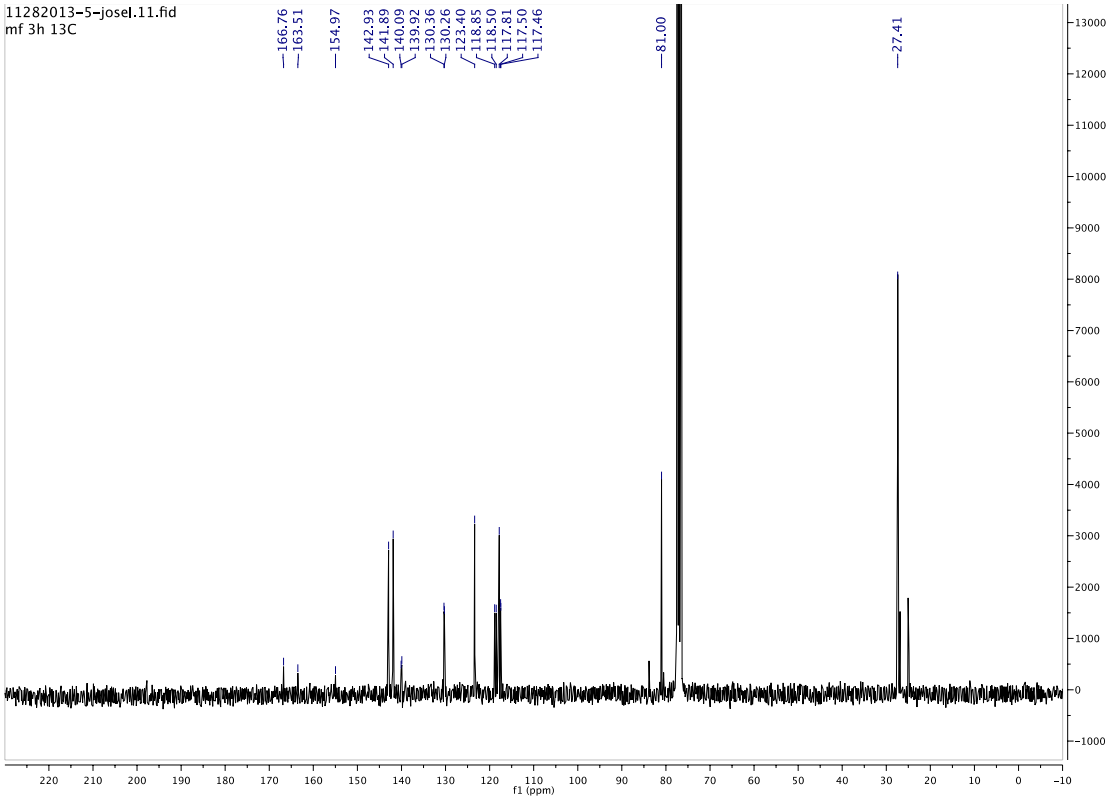

11252013-19-joseR.10.fid
13C pF
4e
F
Bpin
N
8.66
8.64
8.00
7.99
7.97
7.97
7.97
7.97
7.95
7.94
7.76
7.74
7.65
7.63
7.62
7.61
7.39
7.33
7.00
6.99
6.97
6.96
6.94
6.93
1.41
1.00
1.03
1.01
1.08
2.06
1.09
12.31
f1 (ppm)
11262013-15-josel.11.fid
p-F 13C
167.32
163.98
155.63
143.13
142.21
132.85
122.41
118.30
118.03
117.20
115.13
114.82
80.33
27.02
f1 (ppm)

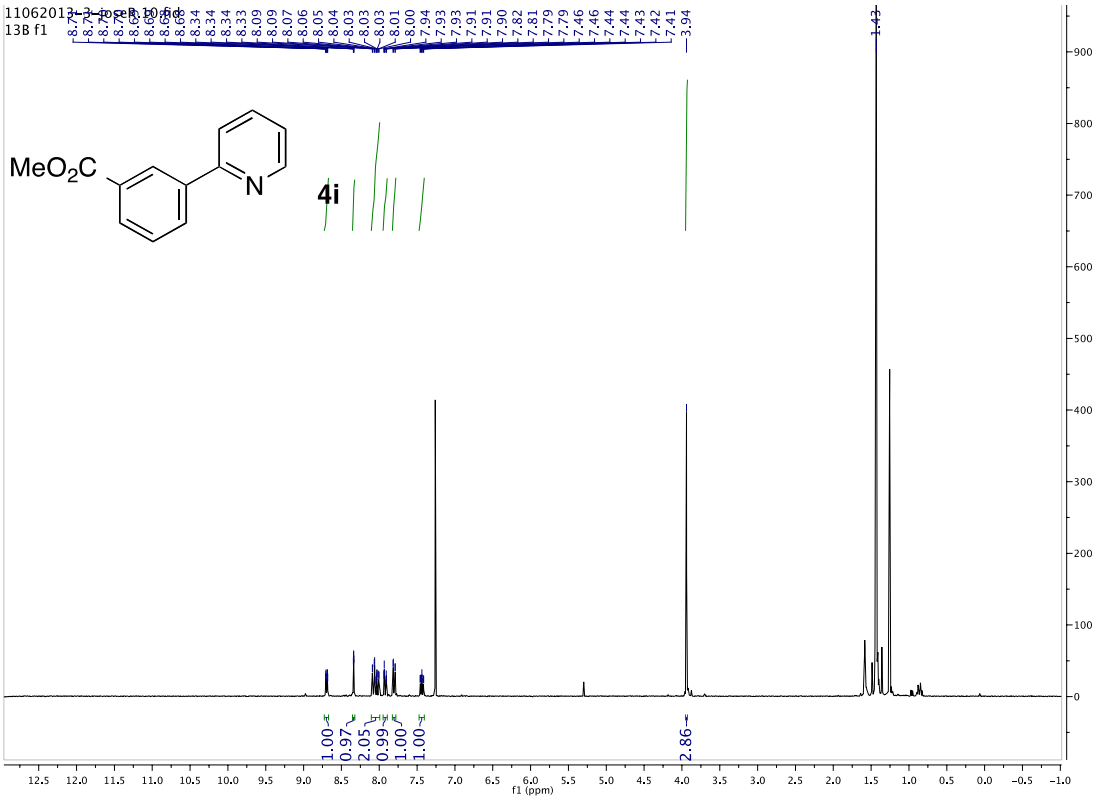

11132013-22-josel.10.fid
solid pCO2Me B2pin2
8.73
8.72
8.36
8.36
8.05
7.99
7.89
7.86
7.74
7.71
7.47
7.47
7.46
7.45
7.45
7.43
7.43
3.93
1.44
4f
N
MeO2C
Bpin
1.00
1.00
2.08
1.02
1.05
1.03
2.99
11.95
f1 (ppm)

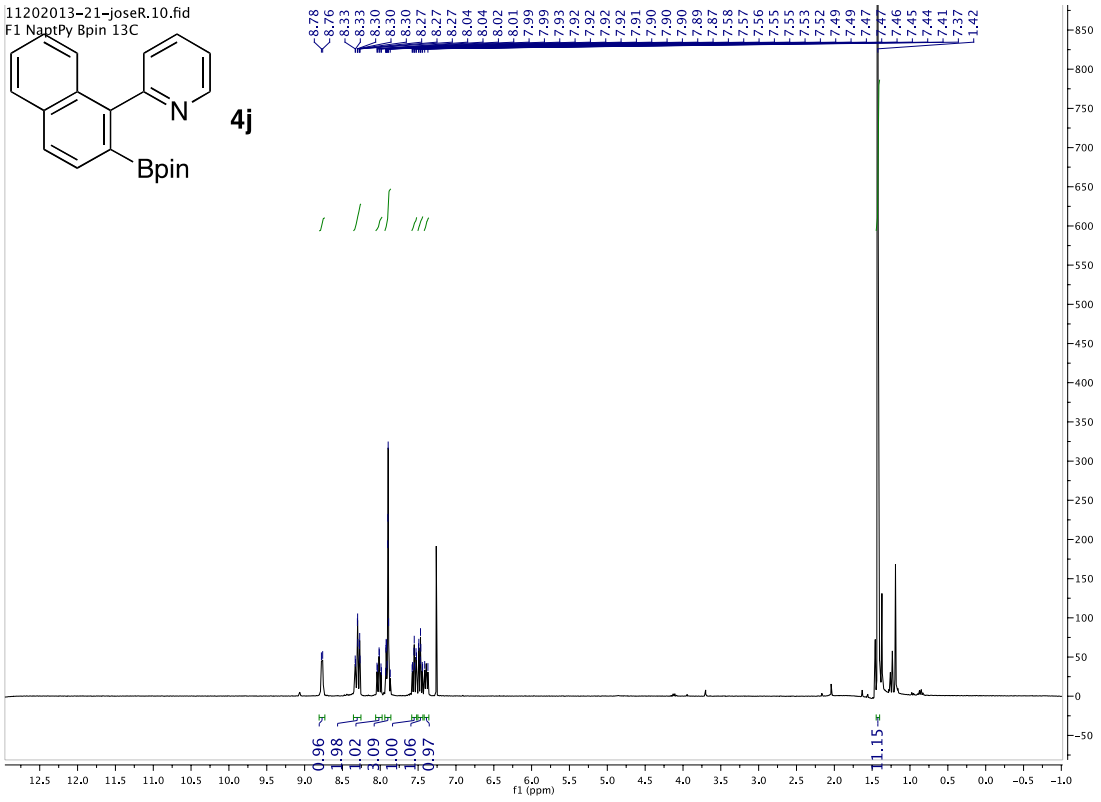

11132013-18-joseR.12.fid
pCO2Me B2pin2 13C
167.79
155.51
143.96
142.49
141.50
133.01
132.66
130.02
124.12
121.46
118.72
80.90
52.55
27.41
f1 (ppm)

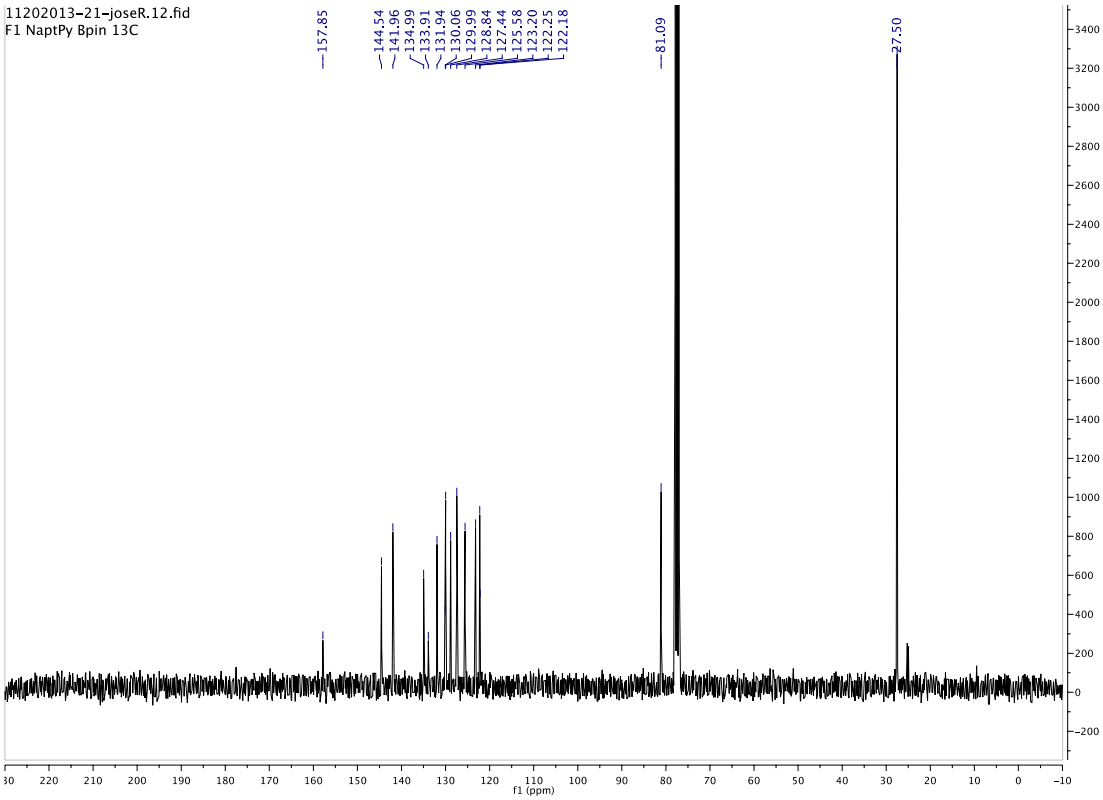

11082013-1-joseR.10.fid
f1 o-Me Bpin
4g
MeO
N
Bpin
8.67 8.66 8.66 8.66 8.65 8.65 8.64 8.64 7.97 7.97 7.95 7.94 7.92 7.92 7.76 7.76 7.76 7.74 7.73 7.73 7.63 7.60 7.38 7.37 7.36 7.35 7.35 7.35 7.33 7.33 7.17 7.16 7.00 6.99 6.97 6.96 3.84 1.41
1.00 1.09 1.12 1.06 1.15 1.06 1.08 3.22 12.00
f1 (ppm)

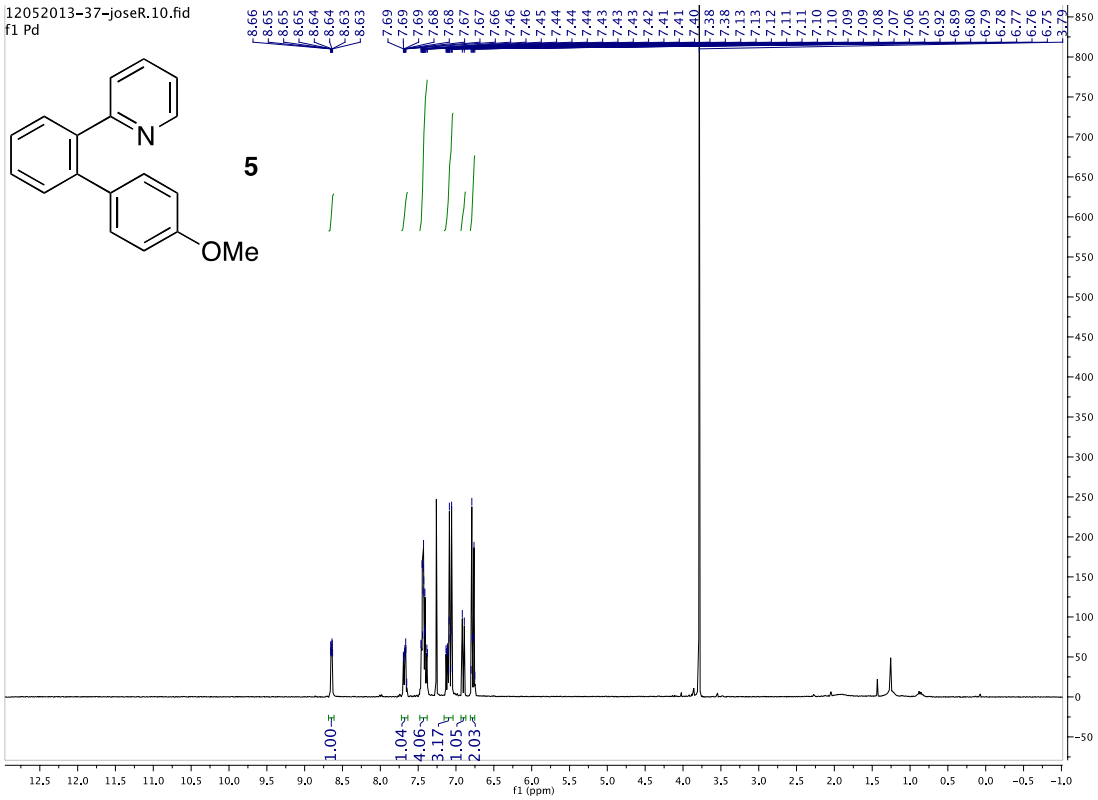

11282013-5-joseR.10.fid
solid 5 mF 1.5%
F
N
Bpin
4h
8.65
8.63
8.02
8.01
7.99
7.99
7.97
7.96
7.82
7.80
7.49
7.47
7.45
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.31
7.30
7.29
7.28
7.06
7.03
7.01
1.45
1.00
1.06
1.04
1.00
0.99
0.99
1.08
12.10
f1 (ppm)


11282013-5-josel.11.fid
mf 3h 13C
166.76
163.51
154.97
142.93
141.89
140.09
139.92
130.36
130.26
123.40
118.85
118.50
117.81
117.50
117.46
81.00
27.41
f1 (ppm)

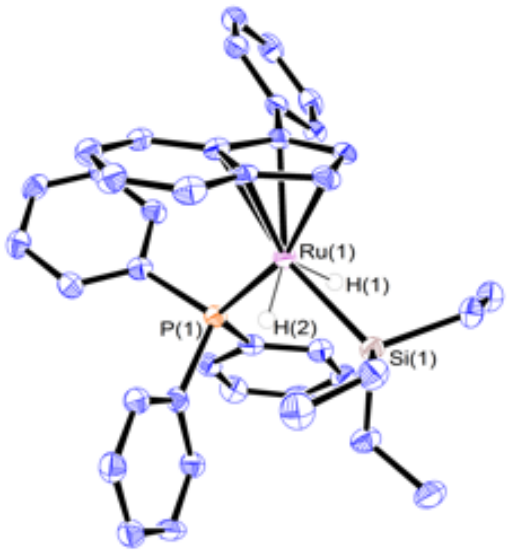

11062013-3-jose-B-10-6d
13B f1
MeO2C
N
4i
1.00
0.97
2.05
0.99
1.00
1.00
2.86
f1 (ppm)


11202013-21-joseR.10.fid
F1 NaptPy Bpin 13C
N
Bpin
4j
8.78
8.76
8.33
8.33
8.30
8.30
8.30
8.27
8.27
8.27
8.04
8.04
8.02
8.01
7.99
7.99
7.93
7.92
7.92
7.92
7.92
7.91
7.90
7.90
7.90
7.89
7.87
7.58
7.57
7.56
7.55
7.55
7.53
7.52
7.49
7.49
7.47
7.47
7.46
7.45
7.44
7.41
7.37
1.42
0.96
1.98
1.02
3.09
1.00
1.06
0.97
11.15
f1 (ppm)


11202013-21-joseR.12.fid
F1 NaptPy Bpin 13C
157.85
144.54
141.96
134.99
133.91
131.94
130.06
129.99
128.84
127.44
125.58
123.20
122.25
122.18
81.09
27.50
f1 (ppm)


12052013-37-joseR.10.fid
f1 Pd
N
OMe
5
1.00
1.04
4.06
3.17
1.05
2.03
f1 (ppm)

ORTEP of the molecular structure of 2a: Thermal ellipsoids drawn at 50% probability and most hydrogen atoms omitted for clarity.



Selected bond distances (Å) and angles (deg): Ru(1)-P(1) = 2.2876(13), Ru(1)-Si(1) = 2.2997 (12), Ru(1)-H(1) = 1.380(13), Ru(1)-H(2) = 1.370(13); P-Ru-Si = 105.35(4), P-Ru-H(1) = 78.9(17), P-Ru-H(2) = 80.1(15), Si-Ru-H(1) = 63.1(17), Si-Ru-H(2) = 54.3(14), H(1)-Ru-H(2) 104(2).