Supporting Information for:

Rotaxane synthesis exploiting the M(I)/M(III) redox couple

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Contents

1. NMR spectra of isolated compounds

1.1 Rhodium [2]rotaxane 1a

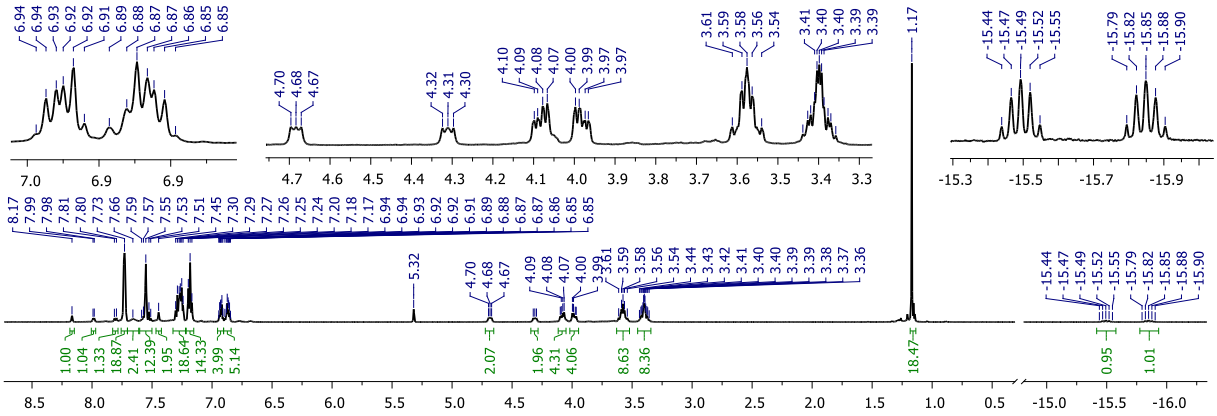

Figure S-1: ^{1}H NMR spectrum of **1a** (CD_2Cl_2, 500 MHz).

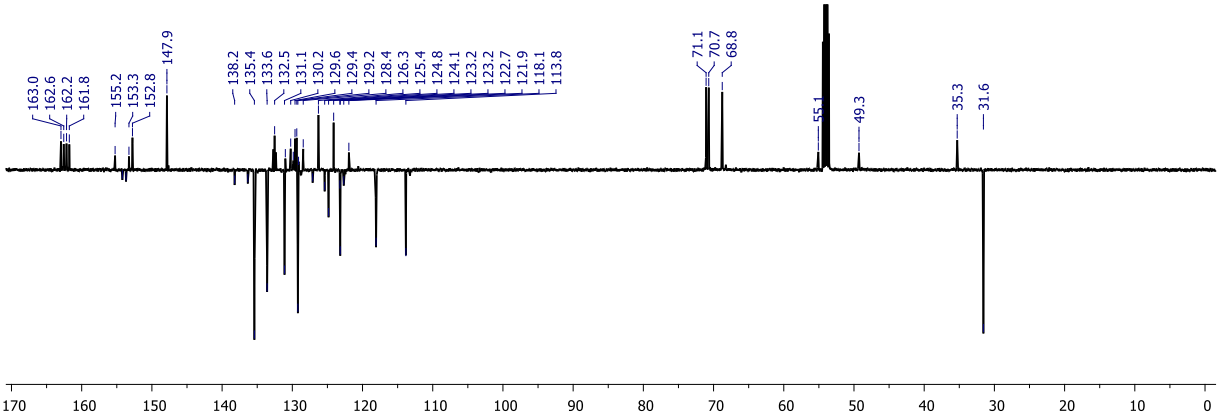

Figure S-2: $^{13}C\{^{1}H\}$ APT NMR spectrum of **1a** (CD_2Cl_2, 126 MHz).

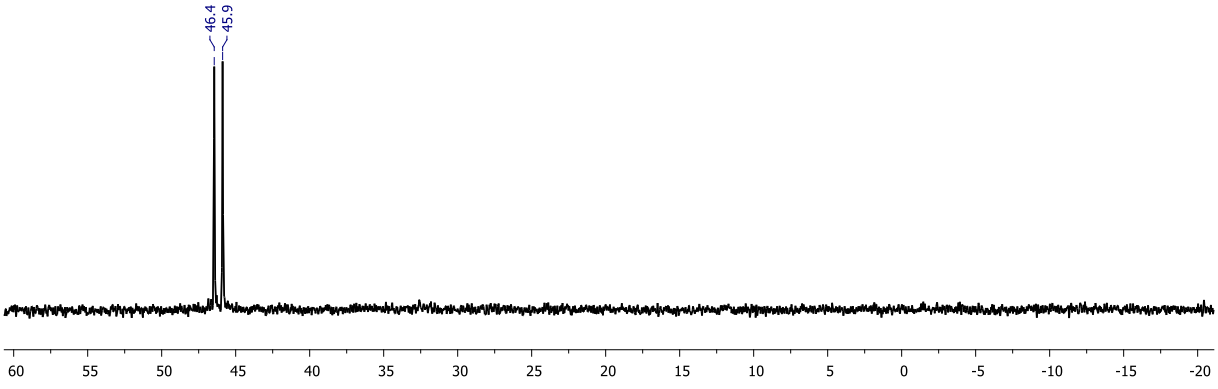

Figure S-3: $^{31}P\{^{1}H\}$ NMR spectrum of **1a** (CD_2Cl_2, 202 MHz).

1.2 Iridium [2]rotaxane 1b

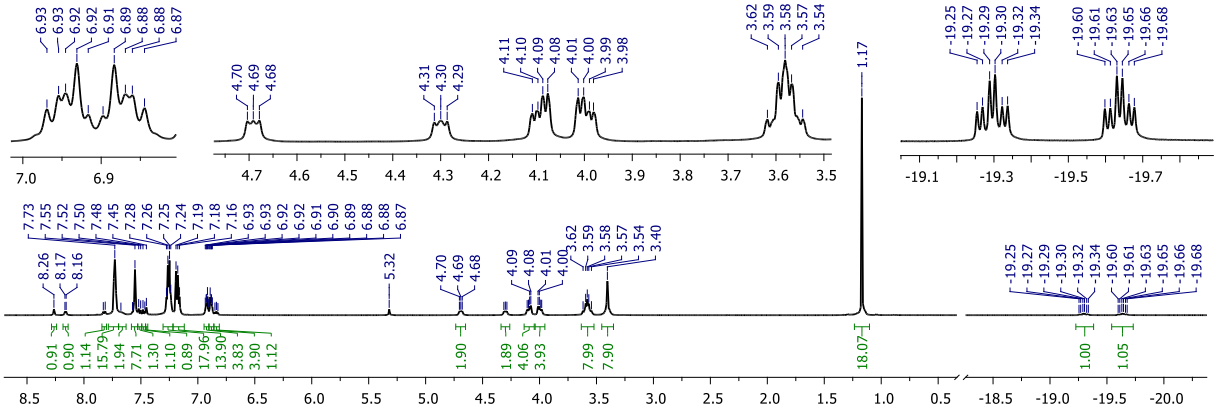

Figure S-4: ^{1}H NMR spectrum of **1b** (CD_2Cl_2, 500 MHz).

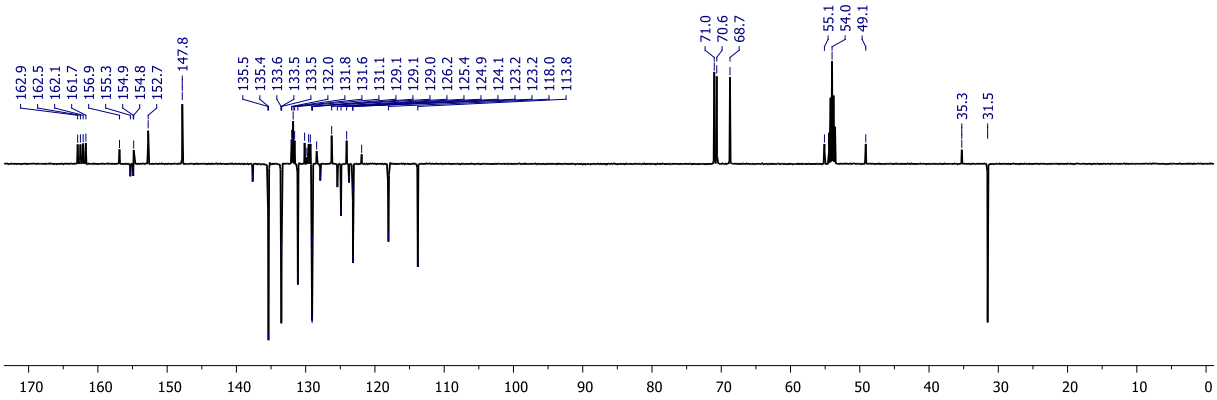

Figure S-5: $^{13}C\{^{1}H\}$ APT NMR spectrum of **1b** (CD_2Cl_2, 126 MHz).

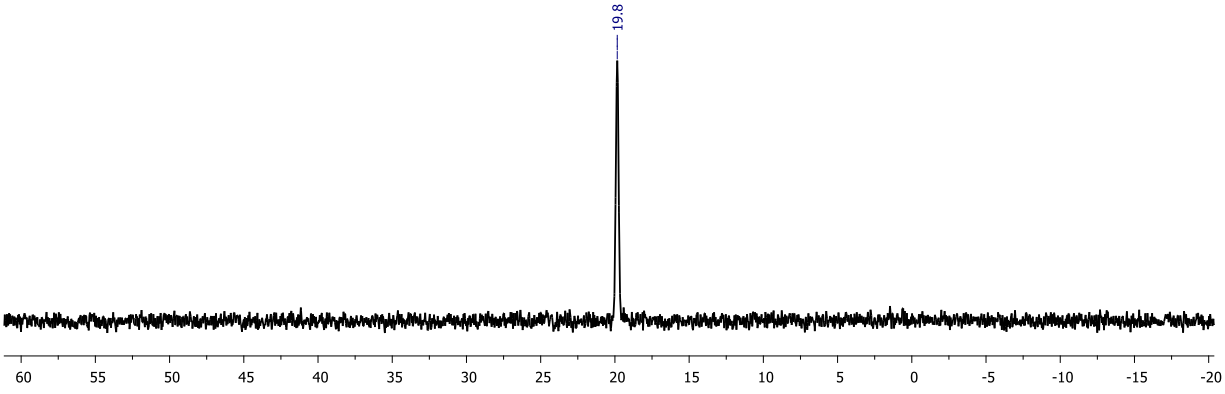

Figure S-6: $^{31}P\{^{1}H\}$ NMR spectrum of **1b** (CD_2Cl_2, 202 MHz).

1.3 [Rh(COD)(PPh$_3$)$_2$][BAr$^F_4$] 2a

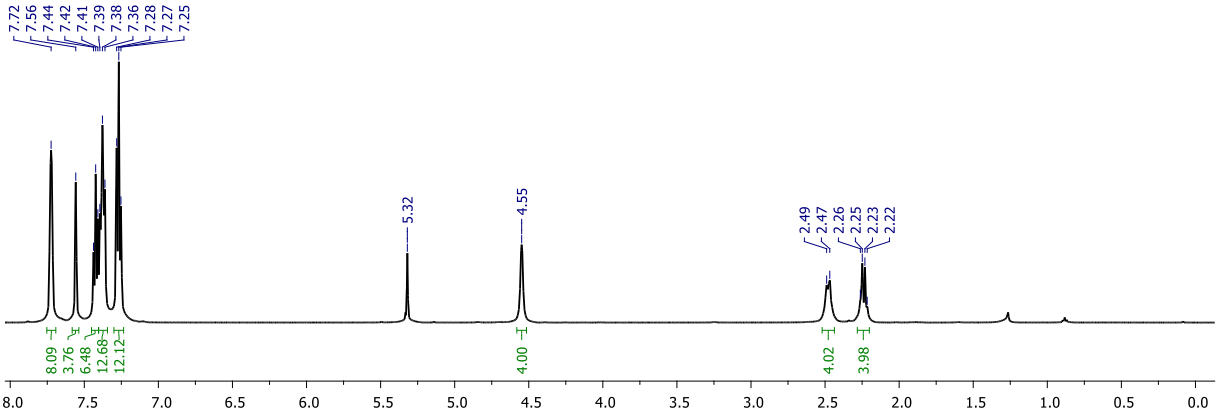

Figure S-7: ^{1}H NMR spectrum of **2a** (CD_2Cl_2, 500 MHz).

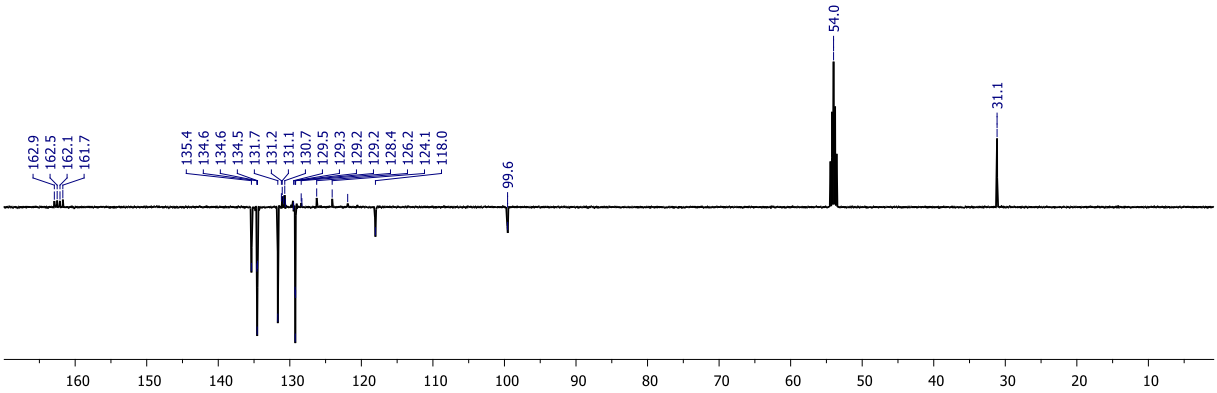

Figure S-8: $^{13}C\{^1H\}$ APT NMR spectrum of **2a** (CD_2Cl_2, 126 MHz).

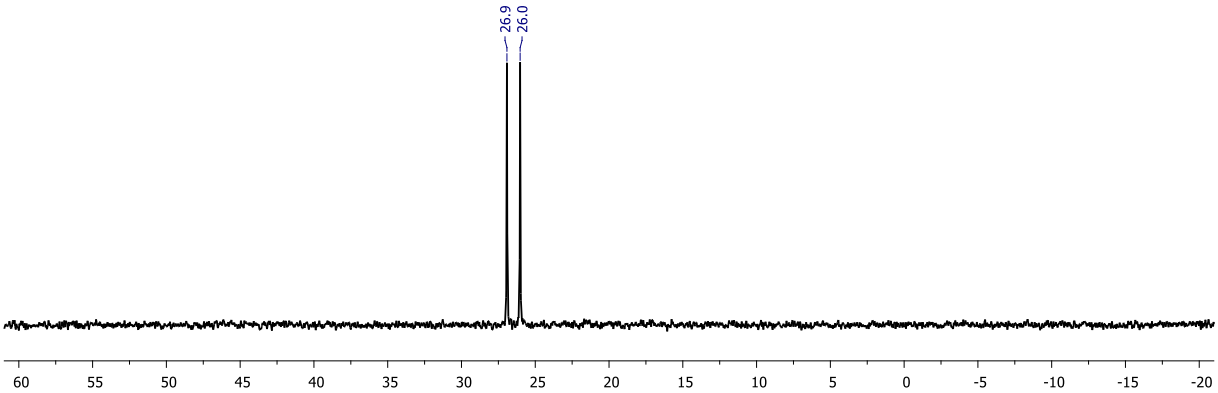

Figure S-9: $^{31}P\{^1H\}$ NMR spectrum of **2a** (CD_2Cl_2, 162 MHz).

1.4 [Ir(COD)(PPh$_3$)$_2$][BAr$^F_4$] 2b

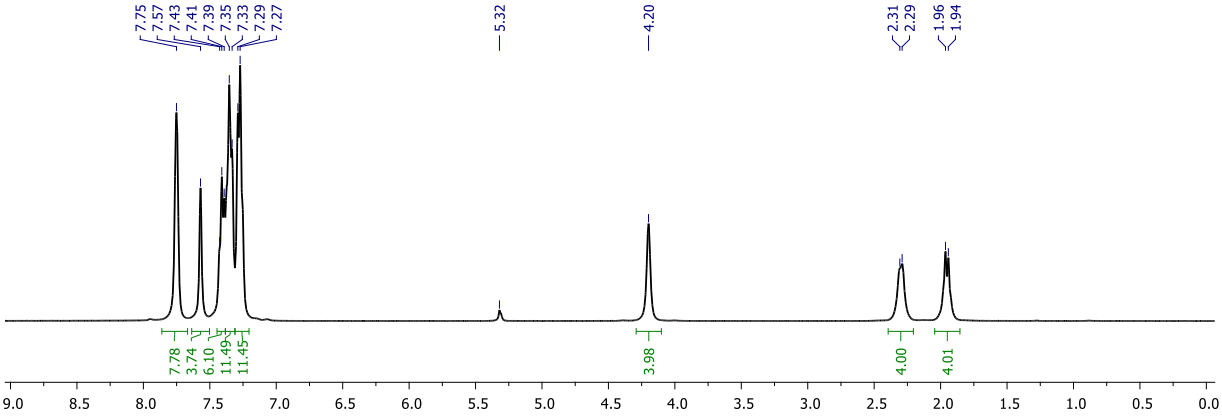

Figure S-10: ^{1}H NMR spectrum of **2b** (CD_2Cl_2, 400 MHz).

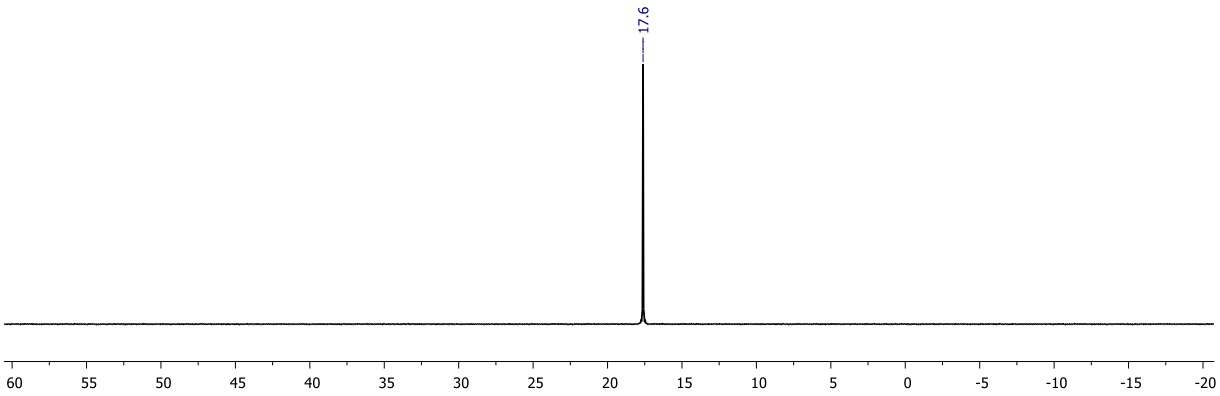

Figure S-11: ^{31}P{^{1}H} NMR spectrum of **2b** (CD_2Cl_2, 162 MHz).

1.5 Ammonium salt 3

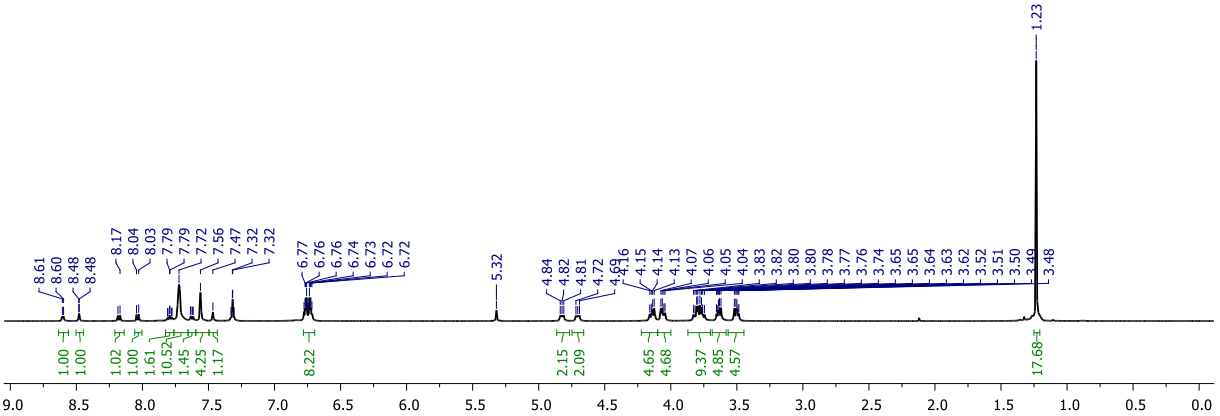

Figure S-12: ^{1}H NMR spectrum of **3** (CD_2Cl_2, 500 MHz).

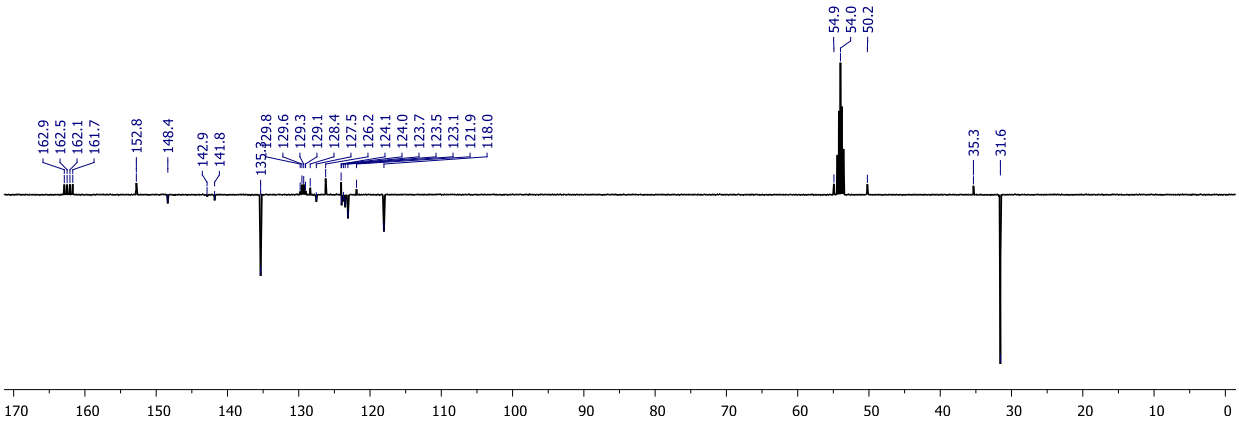

Figure S-13: $^{13}C\{^{1}H\}$ APT NMR spectrum of **3** (CD_2Cl_2, 126 MHz).

1.6 Pseudo[2]rotaxane 3·db24c8

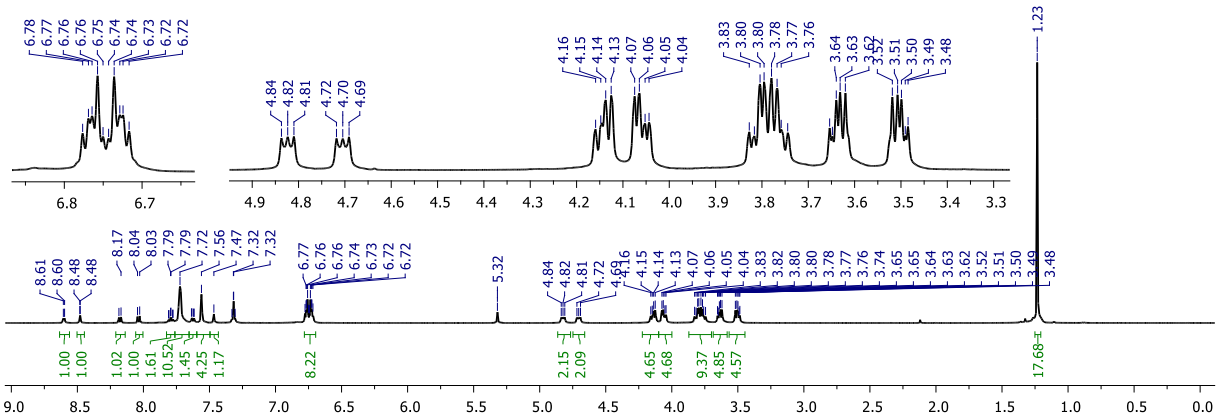

Figure S-14: ^{1}H NMR spectrum of **3**·db24c8 (CD_2Cl_2, 500 MHz).

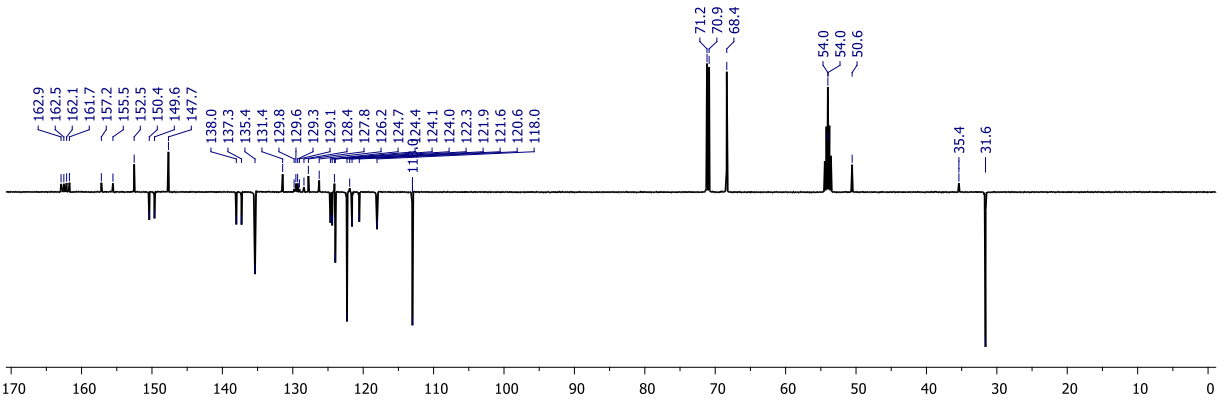

Figure S-15: $^{13}C\{^{1}H\}$ APT NMR spectrum of **3**·db24c8 (CD_2Cl_2, 126 MHz).

1.7 Stack plot of ^{1}H NMR spectra of 1a, 1b, 3·db24c8 and 3

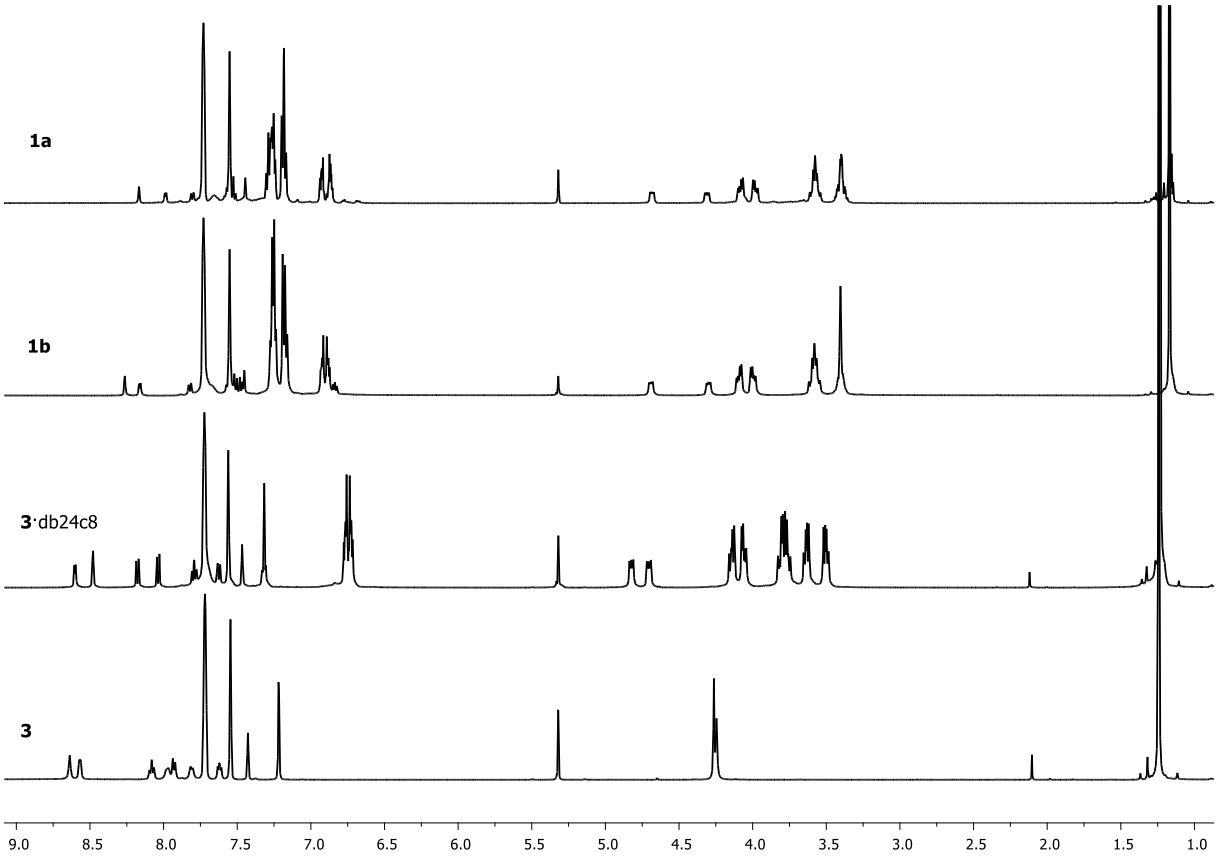

Figure S-16: ^{1}H NMR spectra of **1a**, **1b**, **3**·db24c8 and **3**.

1.8 [Rh(bipy)H$_2$(PPh$_3$)$_2$][BAr$^F_4$] 4a[BAr$^F_4$]

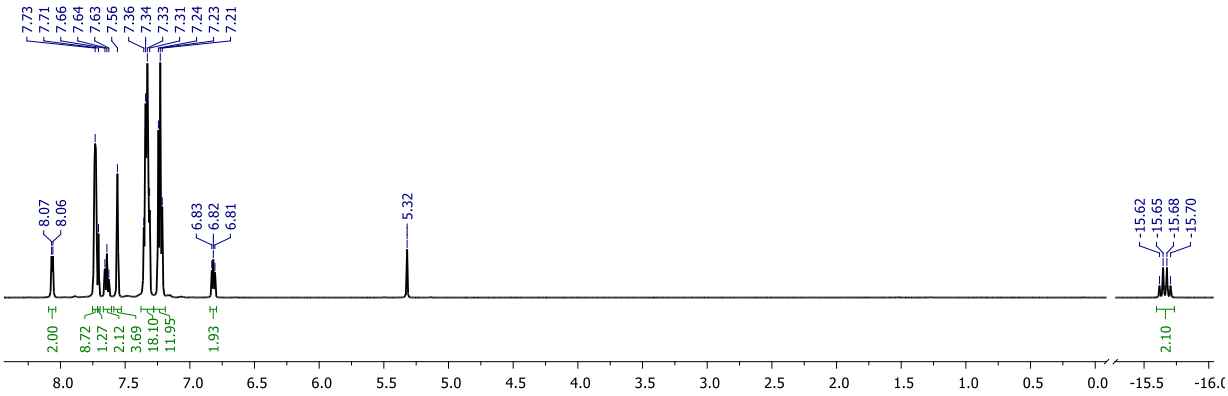

Figure S-17: ^{1}H NMR spectrum of **4a**[BAr$^F_4$] (CD_2Cl_2, 500 MHz).

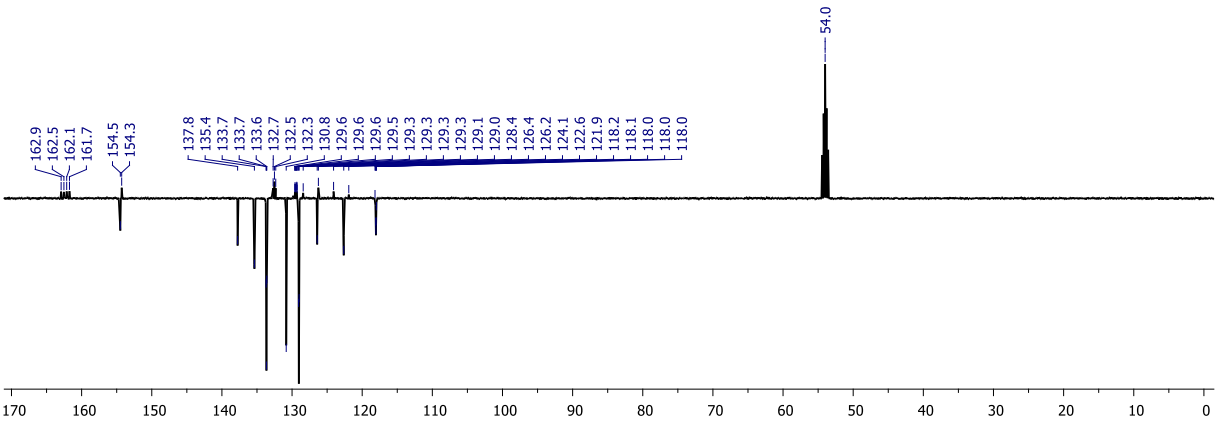

Figure S-18: $^{13}C\{^{1}H\}$ APT NMR spectrum of **4a**[BAr^{F}_{4}] (CD_2Cl_2, 126 MHz).

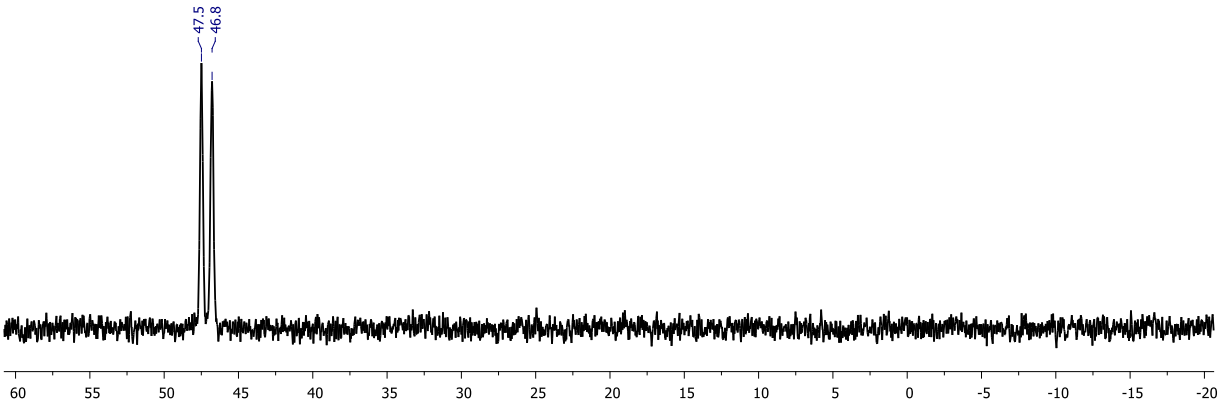

Figure S-19: $^{31}P\{^{1}H\}$ NMR spectrum of **4a**[BAr^{F}_{4}] (CD_2Cl_2, 162 MHz).

1.9 [Ir(bipy)H_2(PPh_3)$_2$][BAr^{F}_{4}] 4b[BAr^{F}_{4}]

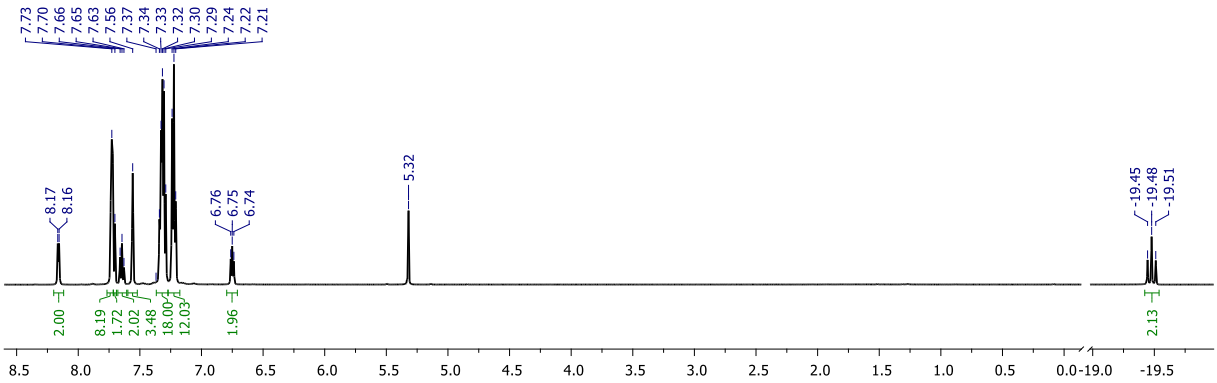

Figure S-20: ^{1}H NMR spectrum of **4b**[BAr^{F}_{4}] (CD_2Cl_2, 500 MHz).

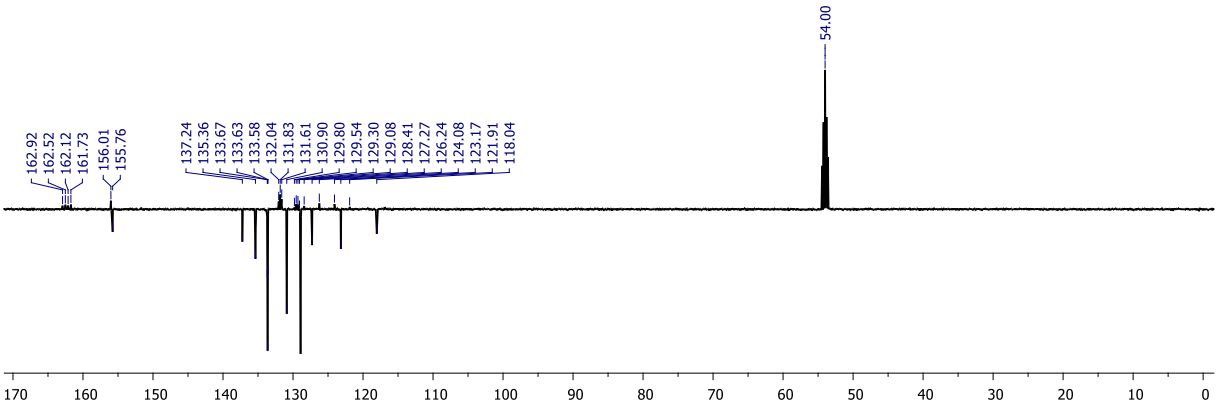

Figure S-21: $^{13}C\{^{1}H\}$ APT NMR spectrum of **4b**[BAr^{F}_{4}] (CD_2Cl_2, 126 MHz).

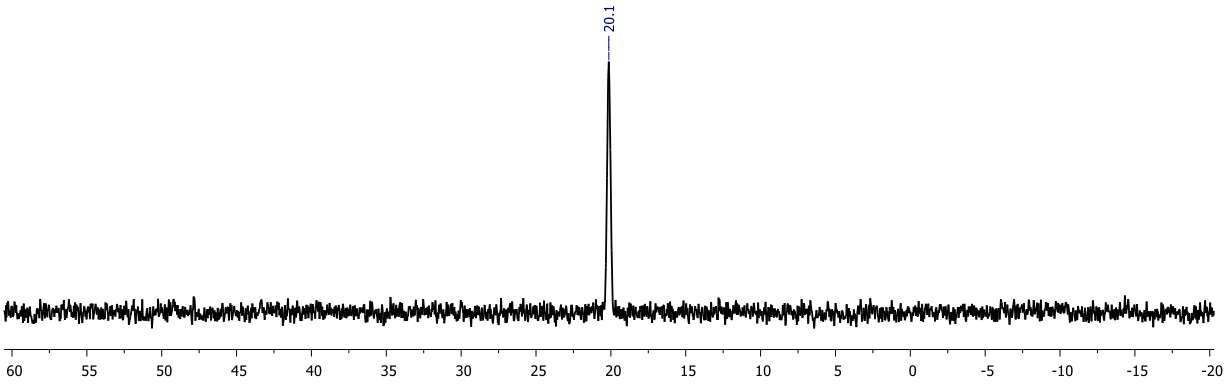

Figure S-22: $^{31}P\{^{1}H\}$ NMR spectrum of **4b**[BAr^{F}_{4}] (CD_2Cl_2, 162 MHz).

1.10 [Rh(bipy)(COD)(PPh_3)][BAr^{F}_{4}] 5a

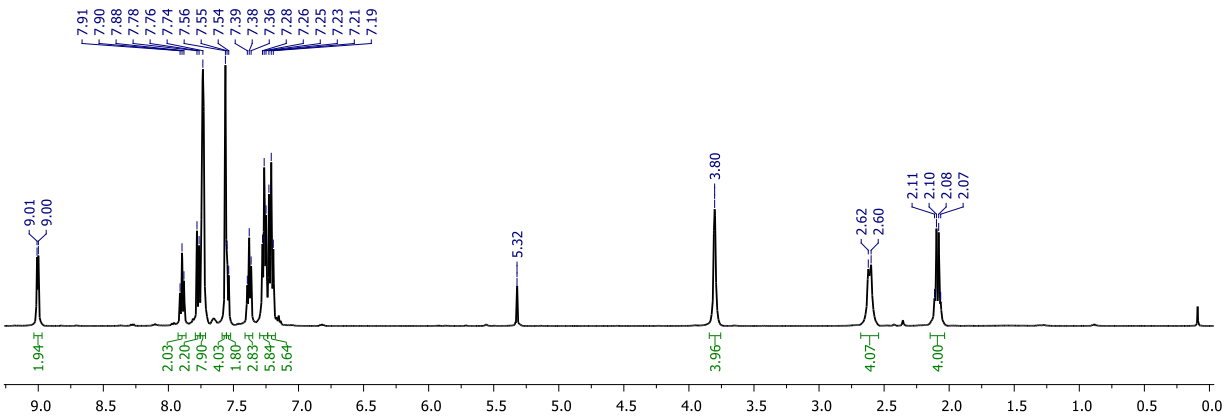

Figure S-23: ^{1}H NMR spectrum of **5a** (CD_2Cl_2, 500 MHz).

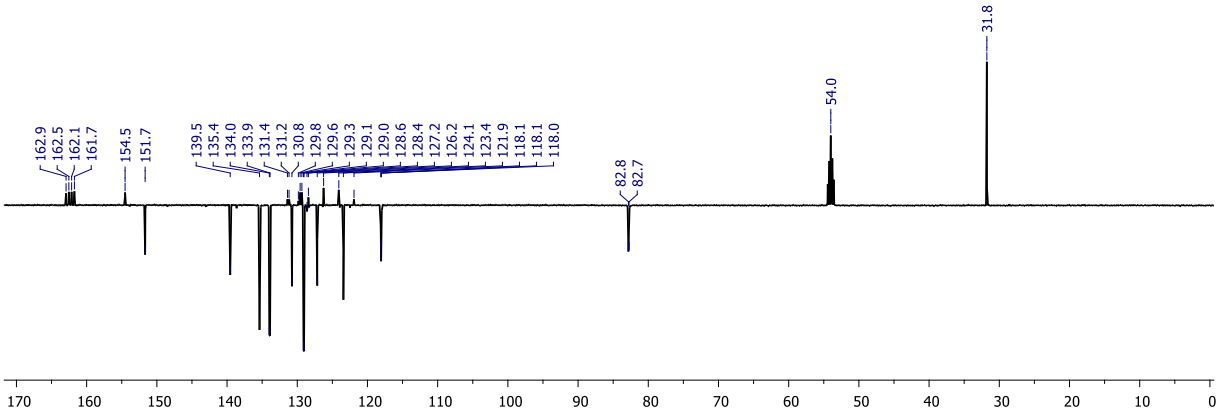

Figure S-24: $^{13}C\{^{1}H\}$ APT NMR spectrum of **5a** (CD_2Cl_2, 126 MHz).

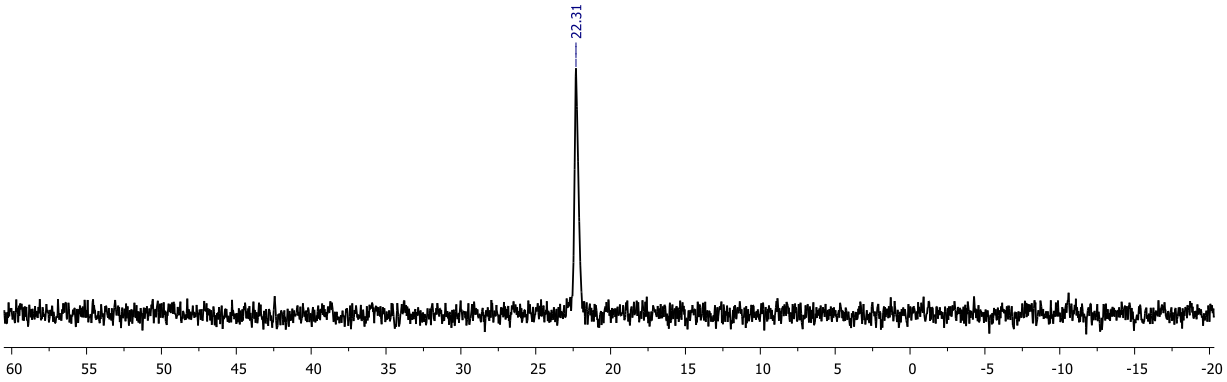

Figure S-25: $^{31}P\{^{1}H\}$ NMR spectrum of **5a** (CD_2Cl_2, 162 MHz).

1.11 [Ir(bipy)(COD)(PPh_3)][BAr^F_4] 5b

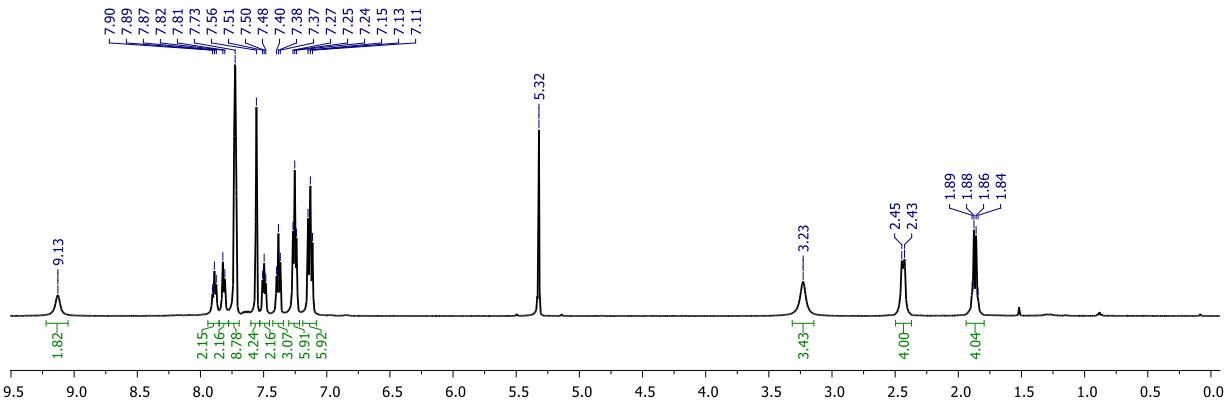

Figure S-26: ^{1}H NMR spectrum of **5b** (CD_2Cl_2, 500 MHz).

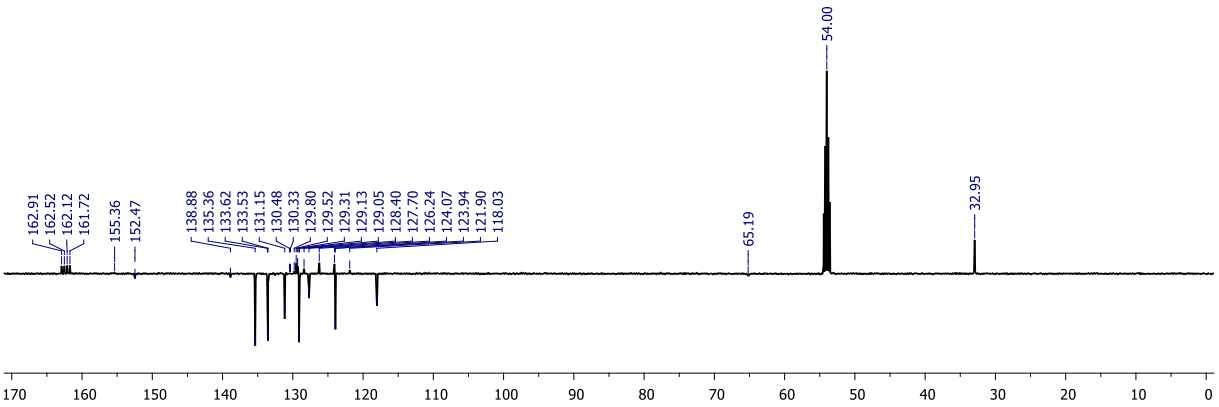

Figure S-27: $^{13}C\{^{1}H\}$ APT NMR spectrum of **5b** (CD_2Cl_2, 126 MHz).

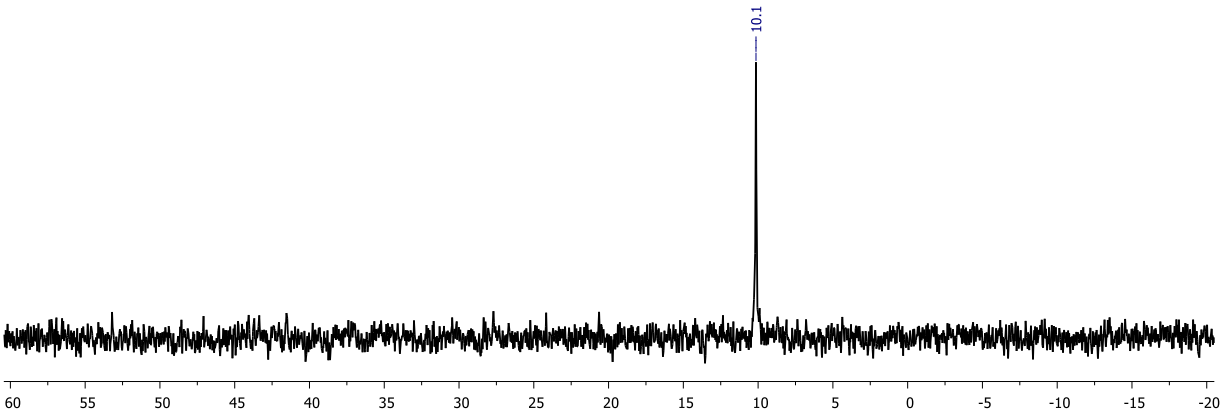

Figure S-28: $^{31}P\{^{1}H\}$ NMR spectrum of **5b** (CD_2Cl_2, 162 MHz).

1.12 [Rh(bipy)(COD)][BAr$^{F}_{4}$] 6a

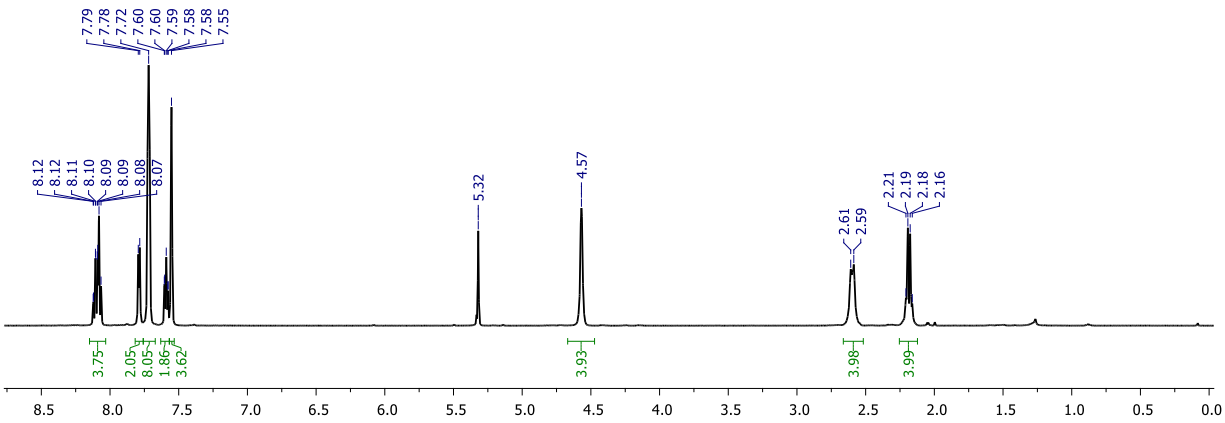

Figure S-29: ^{1}H NMR spectrum of **6a** (CD_2Cl_2, 500 MHz).

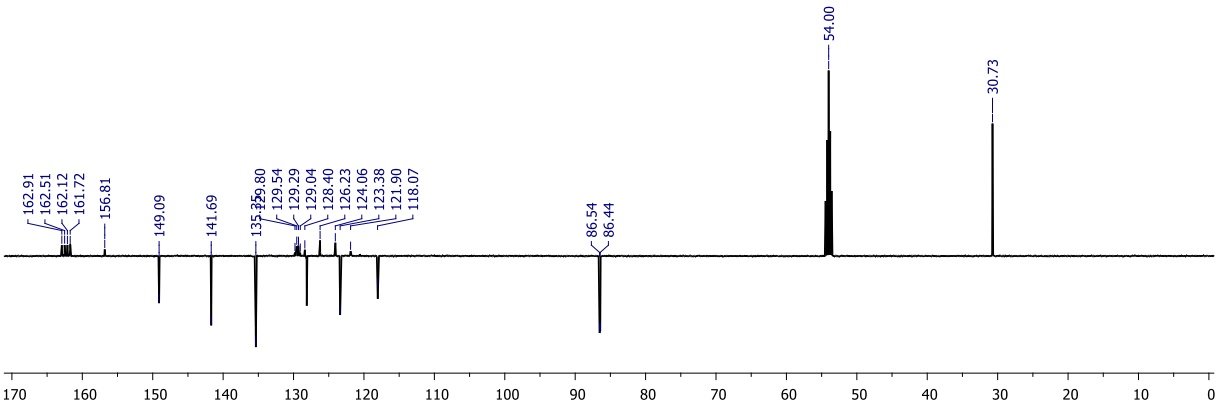

Figure S-30: $^{13}C\{^{1}H\}$ APT NMR spectrum of **6a** (CD_2Cl_2, 126 MHz).

1.13 [Ir(bipy)(COD)][BAr$^{F}_{4}$] 6b

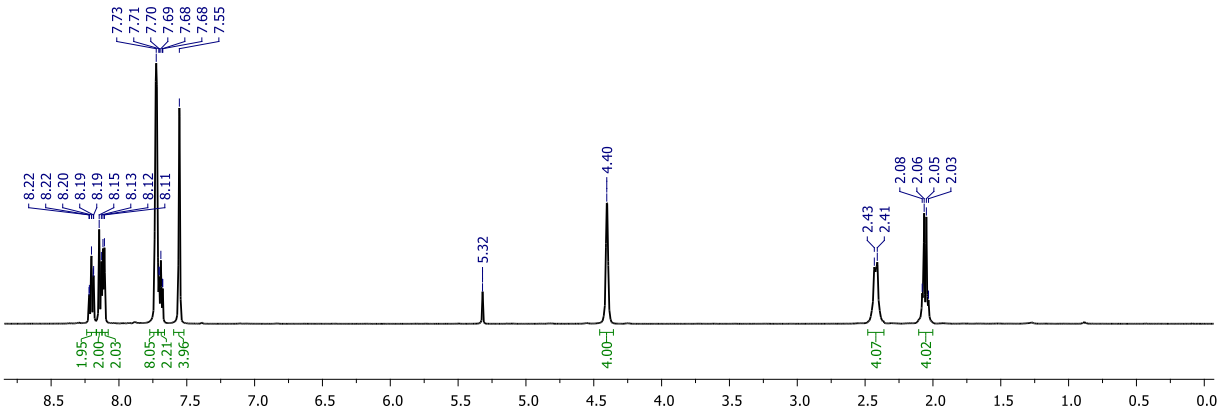

Figure S-31: ^{1}H NMR spectrum of **6b** (CD_2Cl_2, 500 MHz).

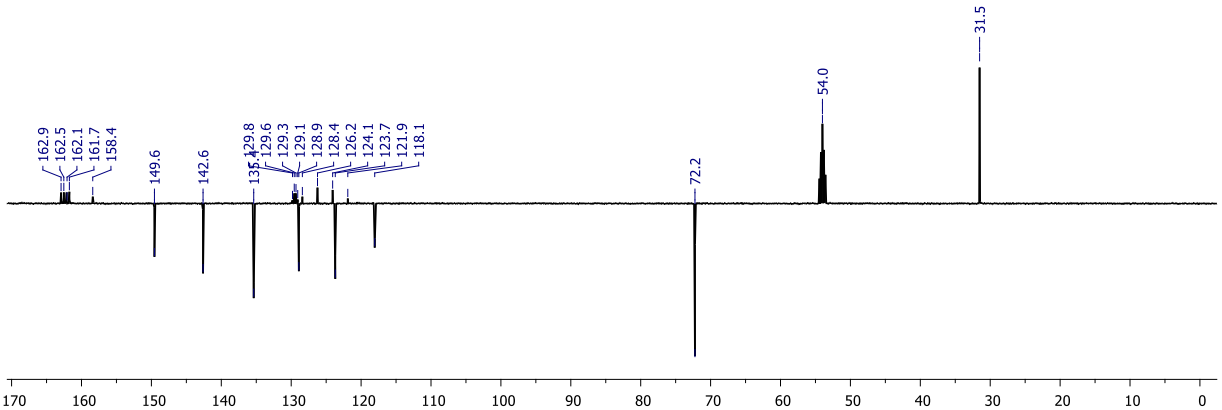

Figure S-32: $^{13}C\{^{1}H\}$ APT NMR spectrum of **6b** (CD_2Cl_2, 126 MHz).

1.14 [Rh(bipy)(PPh$_3$)$_2$][BAr$^F_4$] 7

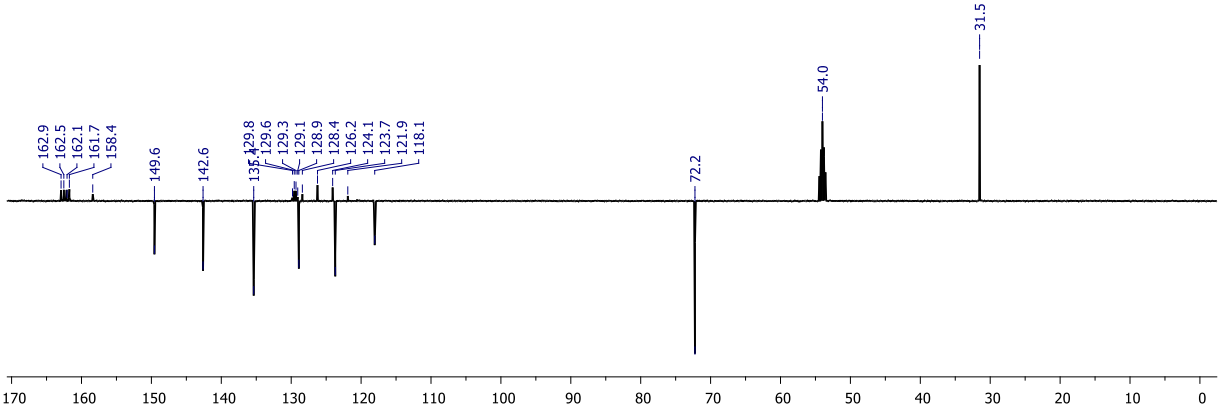

Figure S-33: ^{1}H NMR spectrum of **7** (CD_2Cl_2, 500 MHz).

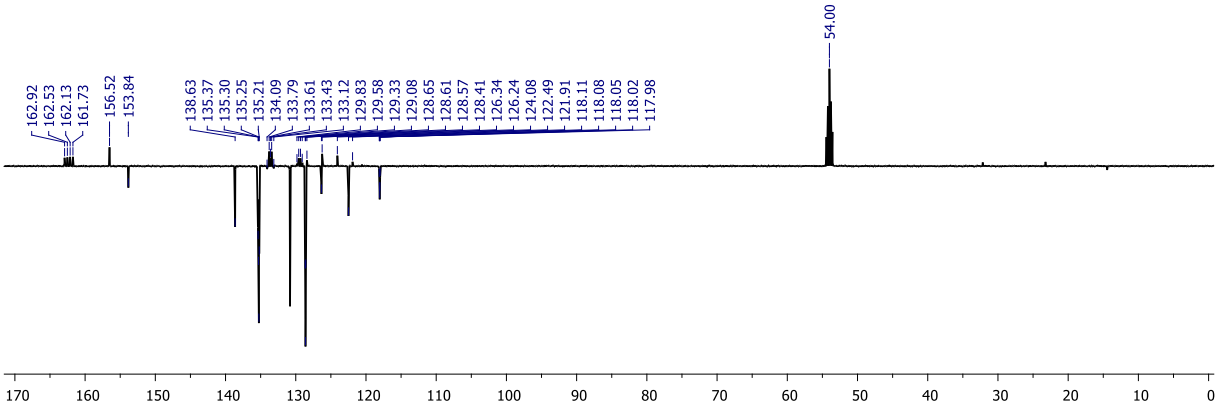

Figure S-34: $^{13}C\{^1H\}$ APT NMR spectrum of **7** (CD_2Cl_2, 126 MHz).

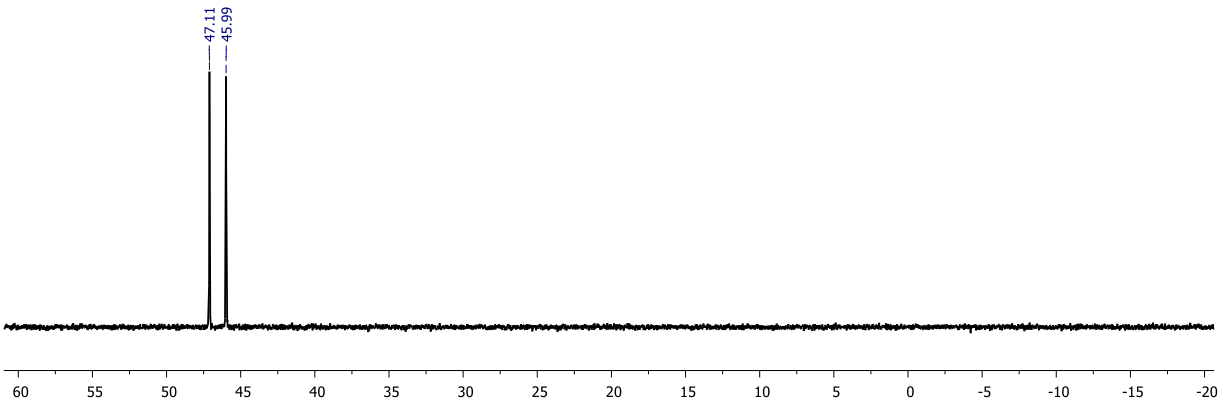

Figure S-35: $^{31}P\{^1H\}$ NMR spectrum of **7** (CD_2Cl_2, 162 MHz).

1.15 $[Rh(PPh_3)_2]_2[BAr^F_4]_2$ 8

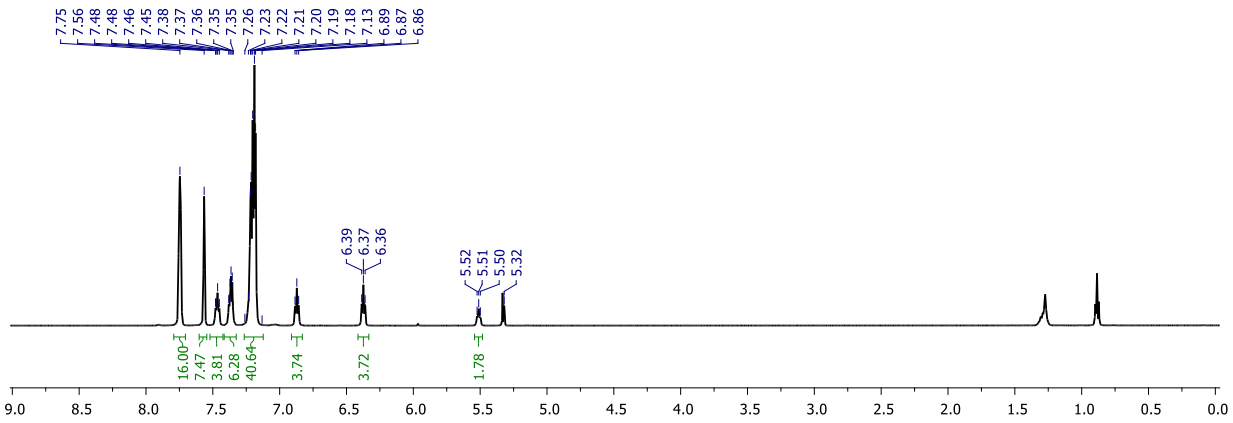

Figure S-36: ^{1}H NMR spectrum of **8** (CD_2Cl_2, 500 MHz).

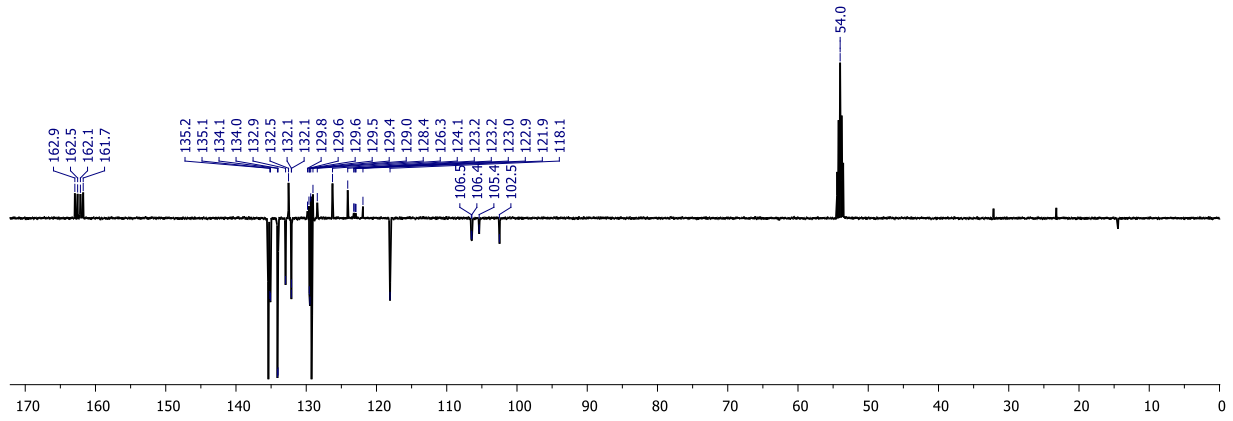

Figure S-37: $^{13}C\{^{1}H\}$ APT NMR spectrum of **8** (CD_2Cl_2, 126 MHz).

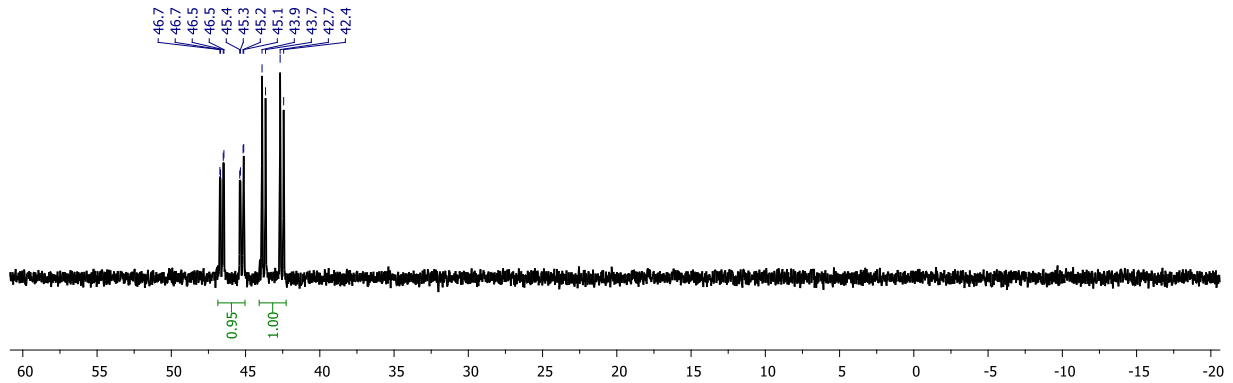

Figure S-38: $^{31}P\{^{1}H\}$ NMR spectrum of **8** (CD_2Cl_2, 162 MHz).

1.16 5-phthalimidomethylbipyridine

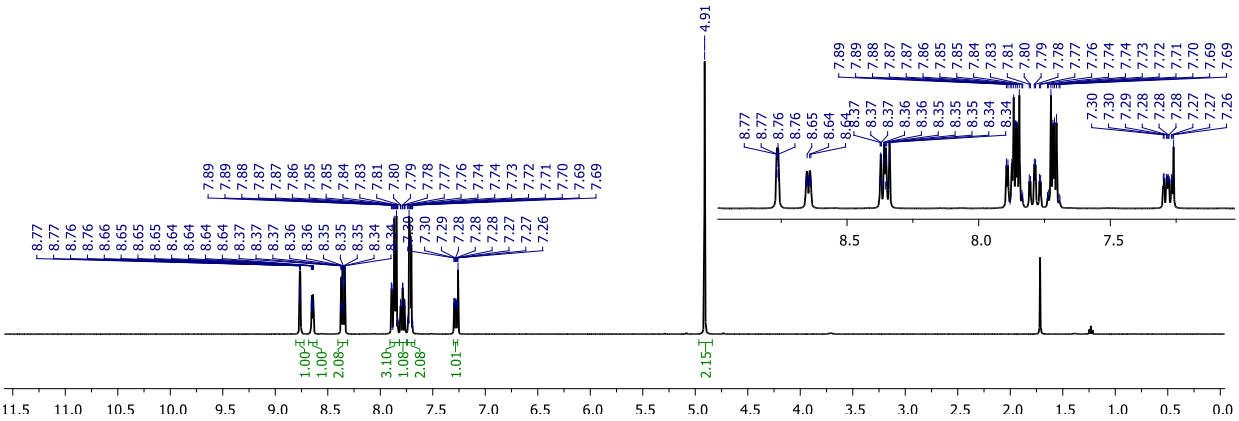

Figure S-39: ^{1}H NMR spectrum of 5-phthalimidomethylbipyridine ($CDCl_3$, 400 MHz).

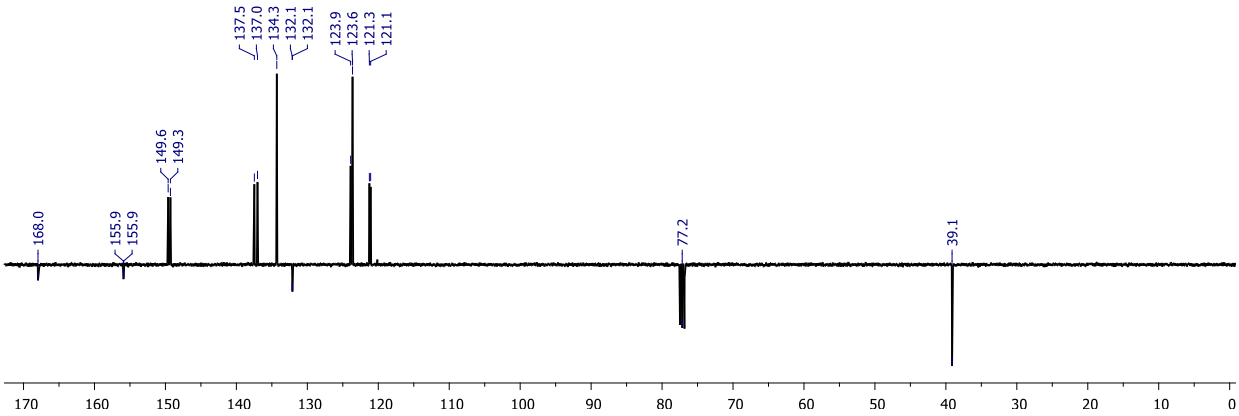

Figure S-40: $^{13}C\{^{1}H\}$ APT NMR spectrum of 5-phthalimidomethylbipyridine ($CDCl_3$, 101 MHz).

1.17 5-aminomethylbipyridine

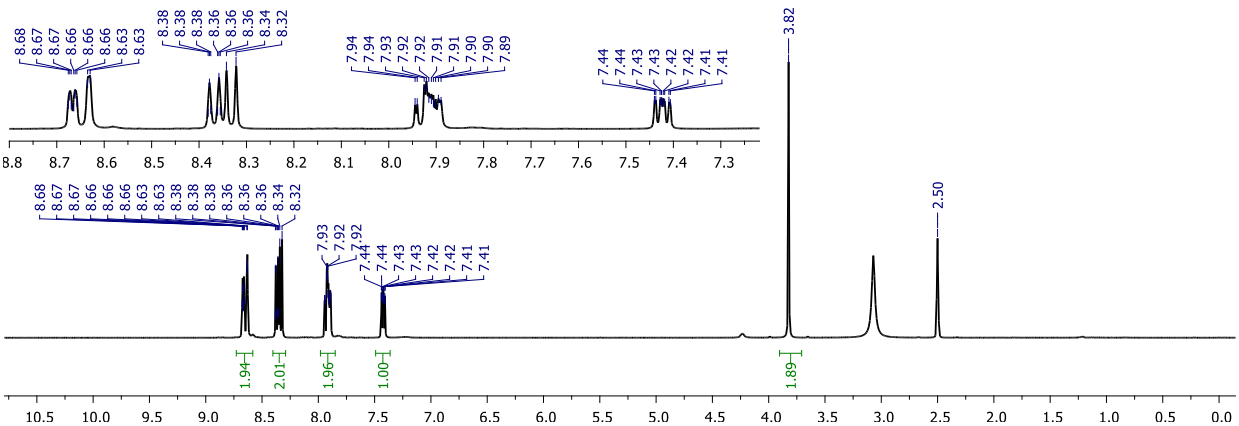

Figure S-41: ^{1}H NMR spectrum of 5-aminomethylbipyridine ($(CD_3)_2SO$, 400 MHz).

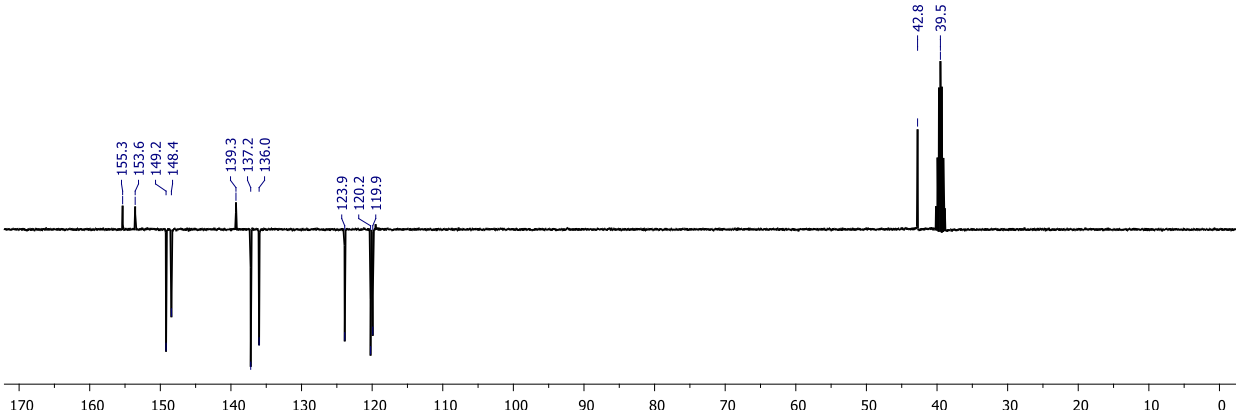

Figure S-42: $^{13}C\{^{1}H\}$ APT NMR spectrum of 5-aminomethylbipyridine ($(CD_3)_2SO$, 101 MHz).

1.18 Amine 10

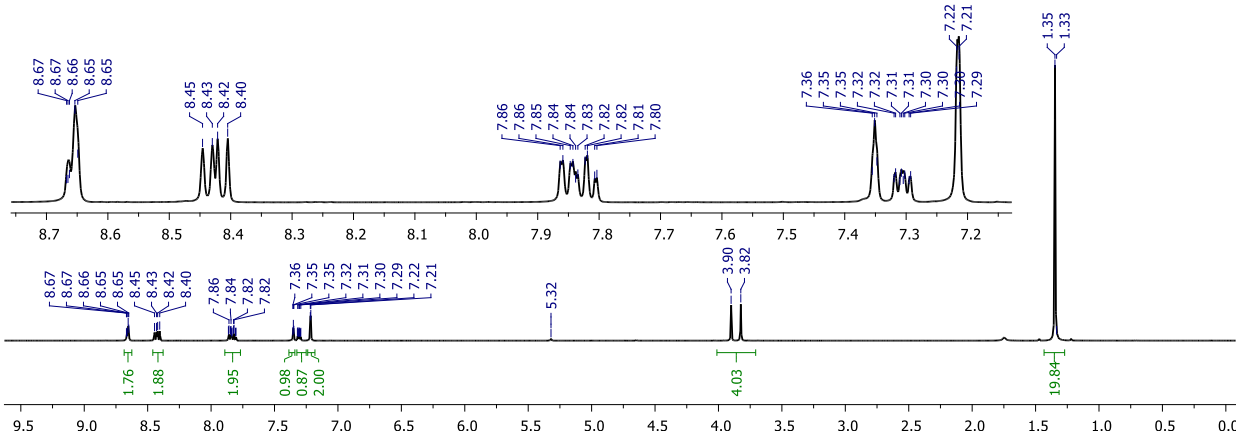

Figure S-43: ^{1}H NMR spectrum of **10** (CD_2Cl_2, 500 MHz).

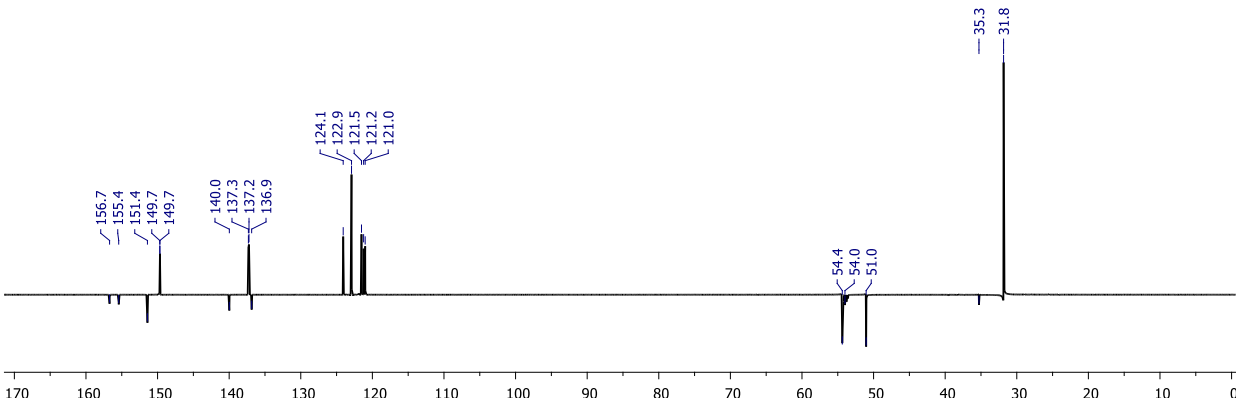

Figure S-44: $^{13}C\{^{1}H\}$ APT NMR spectrum of **10** (CD_2Cl_2, 126 MHz).

2. Selected *in situ* reaction data

2.1 Hydrogenation of 2a+bipy @ 50 °C

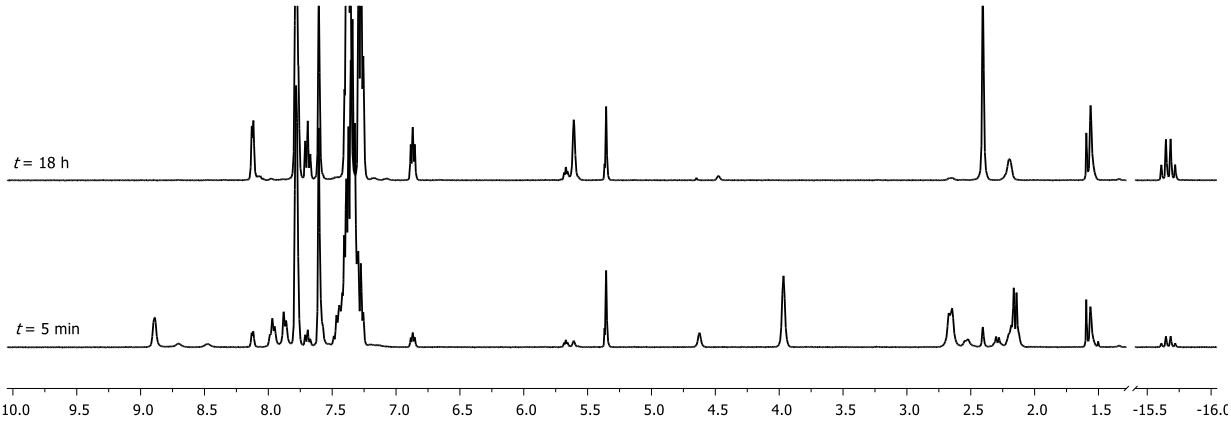

Figure S-45: Selected ^{1}H NMR spectra recorded during the hydrogenation of **2a**+bipy (400 MHz, CD_2Cl_2).

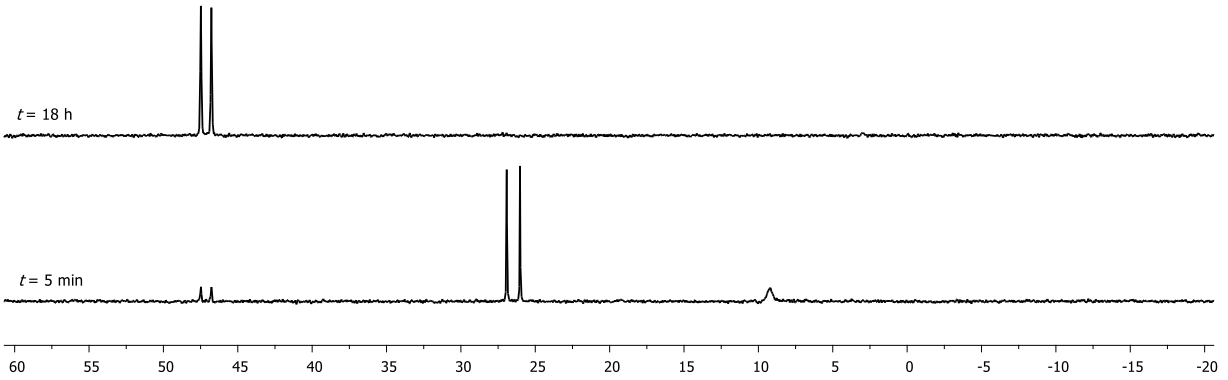

Figure S-46: Selected ^{31}P{^{1}H} NMR spectra recorded during the hydrogenation of **2a**+bipy (400 MHz, CD_2Cl_2).

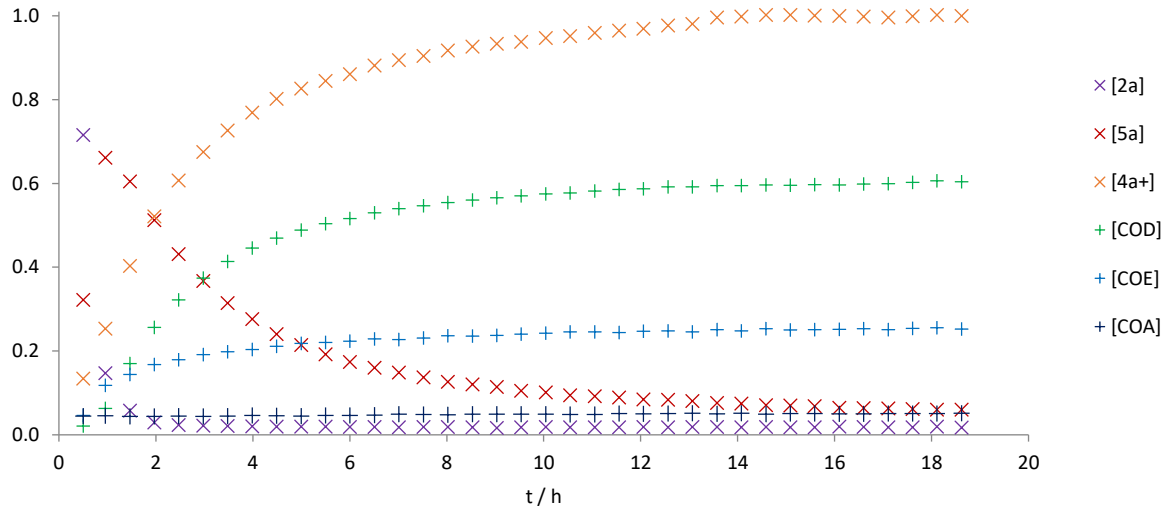

Figure S-47: Relative concentration of species observed during the hydrogenation of **2a**+bipy over 18 h, determined by integration of ^{1}H NMR data.

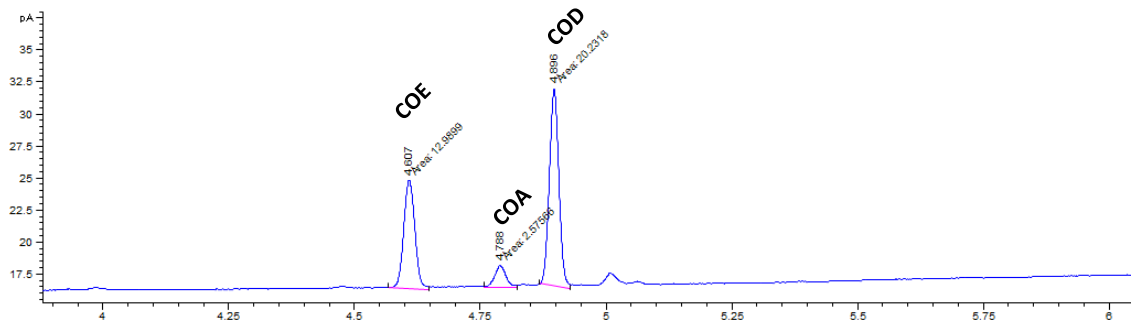

Figure S-48: GC trace obtained following hydrogenation of **2a**+bipy.

2.2 Hydrogenation of 2b+bipy @ RT

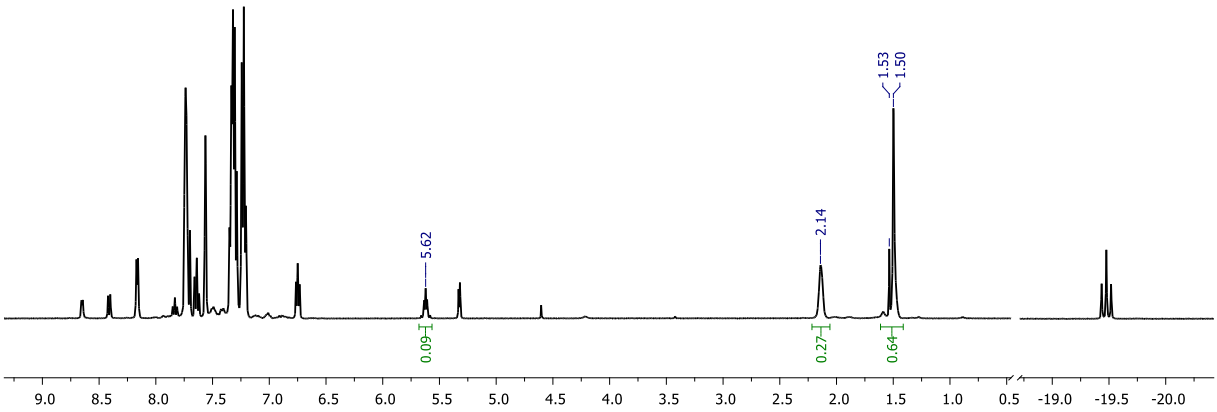

Figure S-49: ^{1}H NMR spectrum obtained following hydrogenation of **2b**+bipy (400 MHz, CD_2Cl_2). Signals belonging to COA and COE integrated.

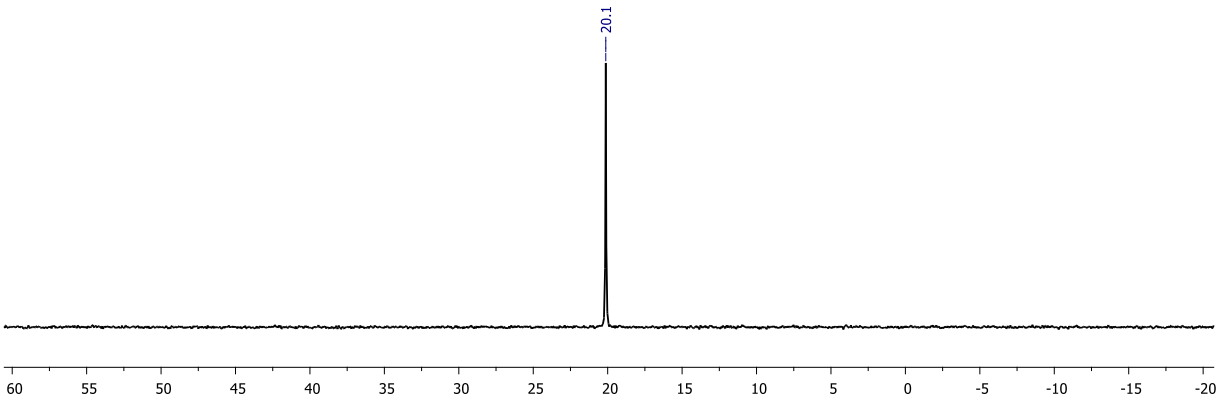

Figure S-50: $^{31}P\{^{1}H\}$ NMR spectrum obtained following hydrogenation of **2b**+bipy (162 MHz, CD_2Cl_2).

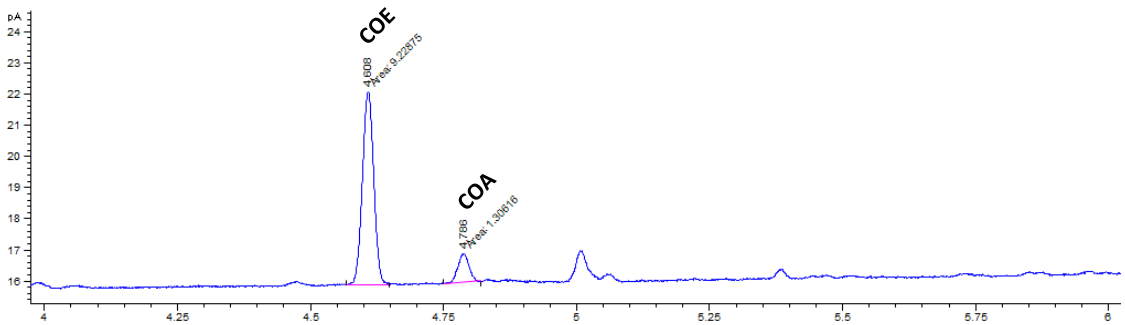

Figure S-51: GC trace obtained following hydrogenation of **2b**+bipy.

2.3 Reaction between 2a and bipy

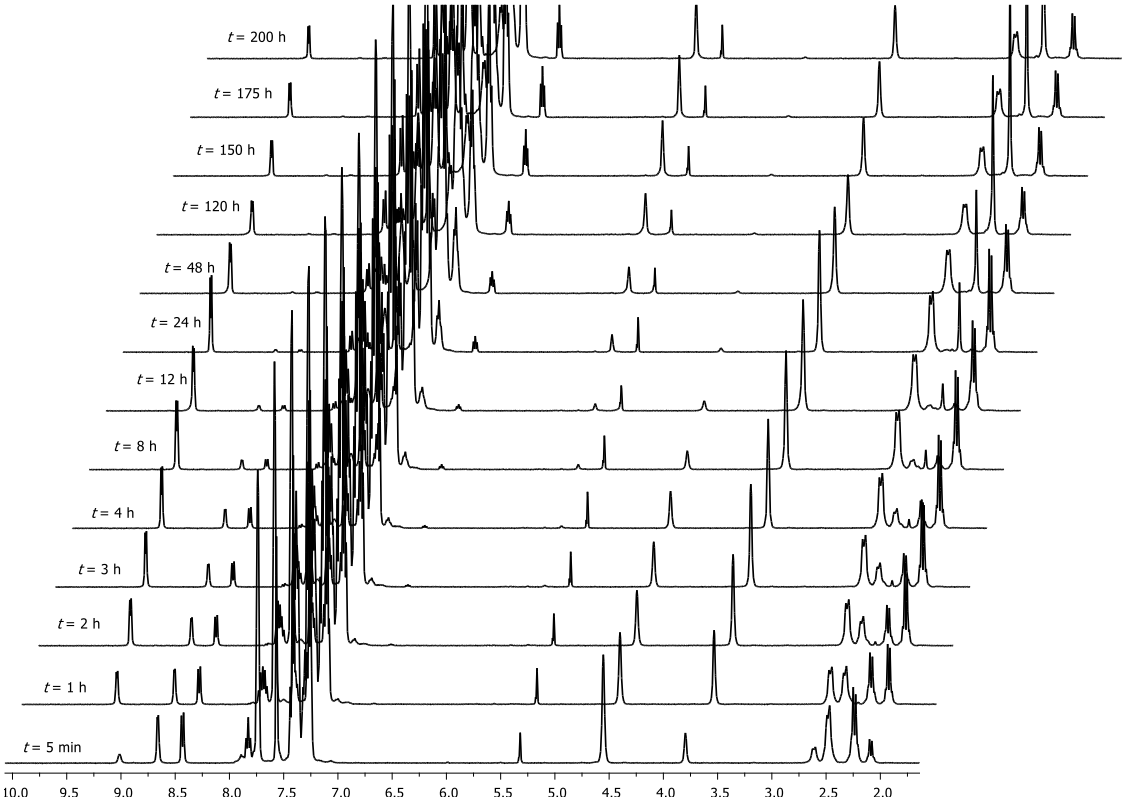

Figure S-52: Selected ^{1}H NMR spectra recorded during the reaction between **2a** with bipy (400 MHz, CD_2Cl_2).

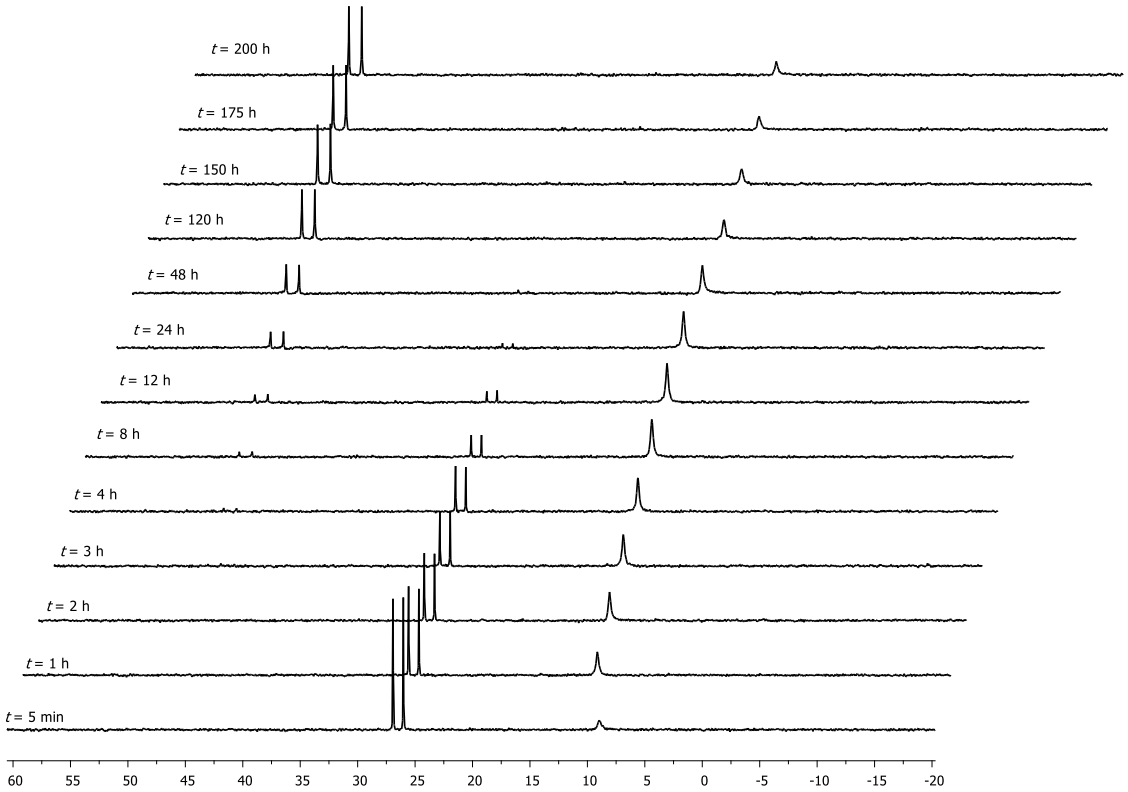

Figure S-53: Selected $^{31}P\{^{1}H\}$ NMR spectra recorded during the reaction between **2a** and bipy (162 MHz, CD_2Cl_2).

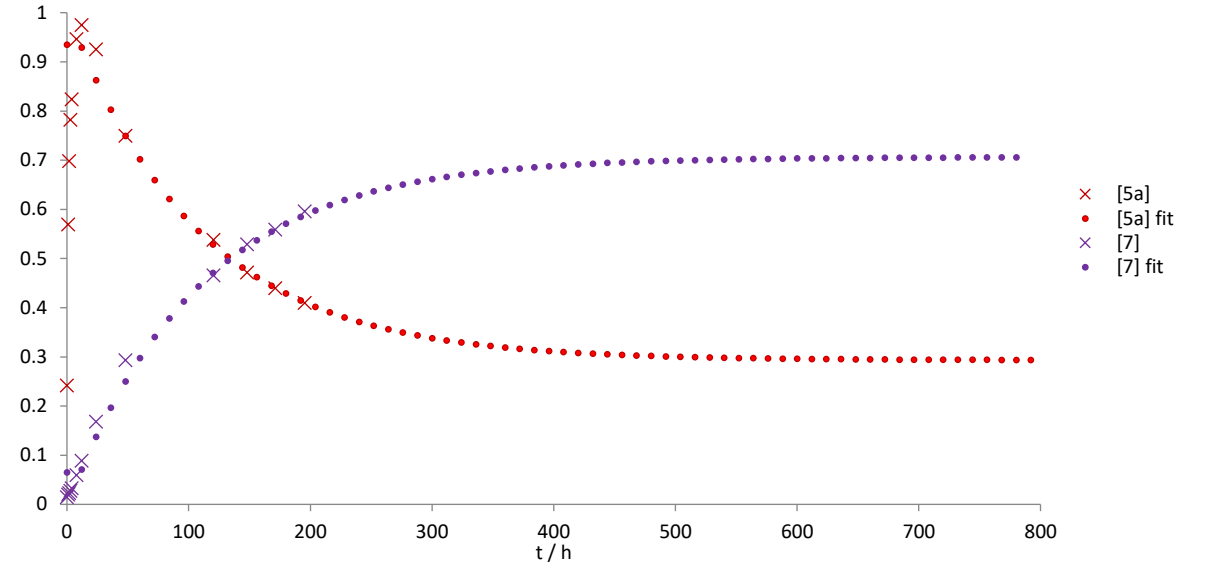

Figure S-54: Relative concentration of species observed during the reaction between **2a** and bipy, determined by integration of ^{1}H NMR data. Approach to equilibrium modelled using rates of formation of **7** and depletion of **5b**.

2.4 Reaction between 2b and bipy

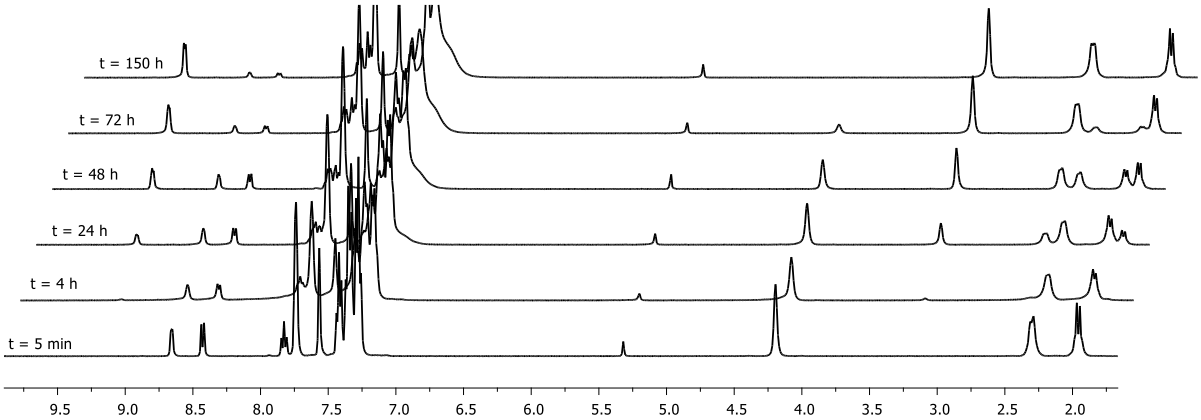

Figure S-55: Selected ^{1}H NMR spectra recorded during the reaction between **2b** and bipy (400 MHz, CD_2Cl_2).

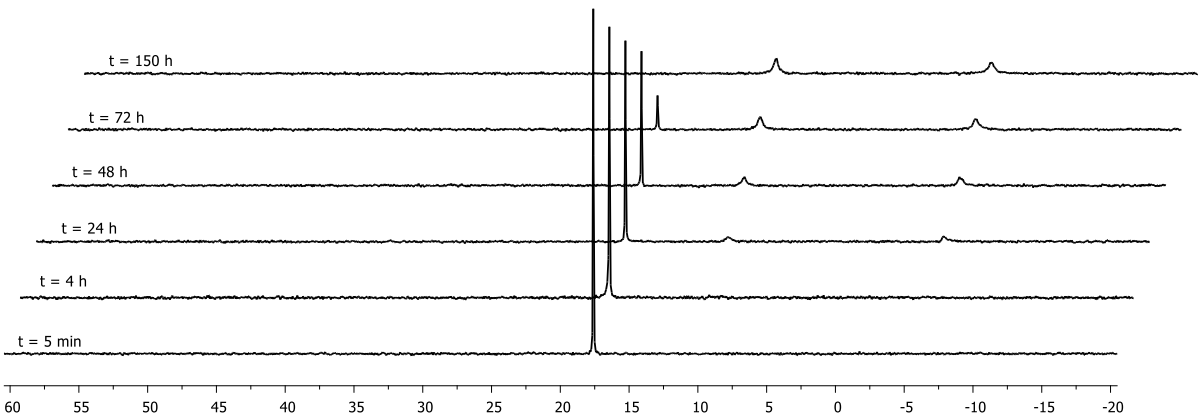

Figure S-56: Selected ^{31}P{^{1}H} NMR spectra recorded during the reaction between **2b** and bipy (162 MHz, CD_2Cl_2).

2.5 Hydrogenation of 2a

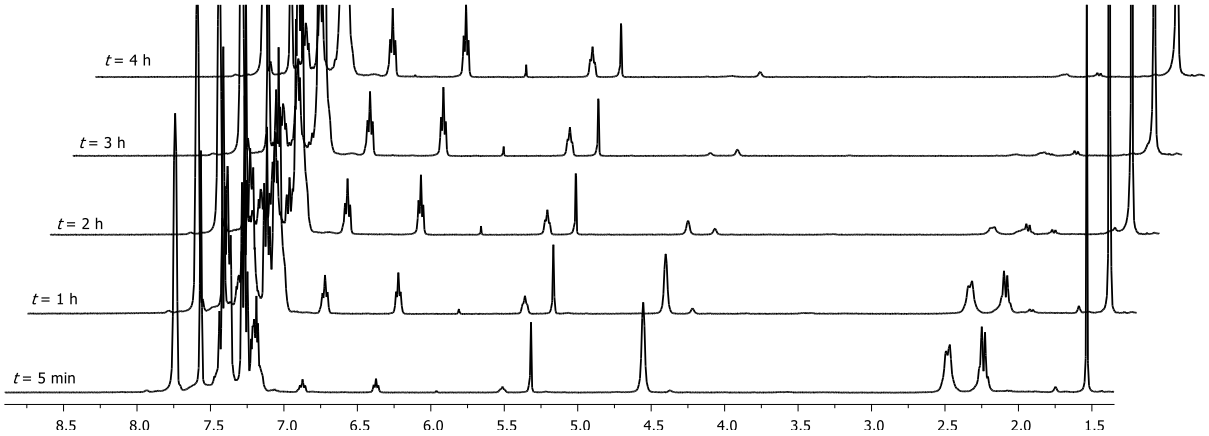

Figure S-57: Selected ^{1}H NMR spectra recorded during the hydrogenation of **2a** (400 MHz, CD_2Cl_2).

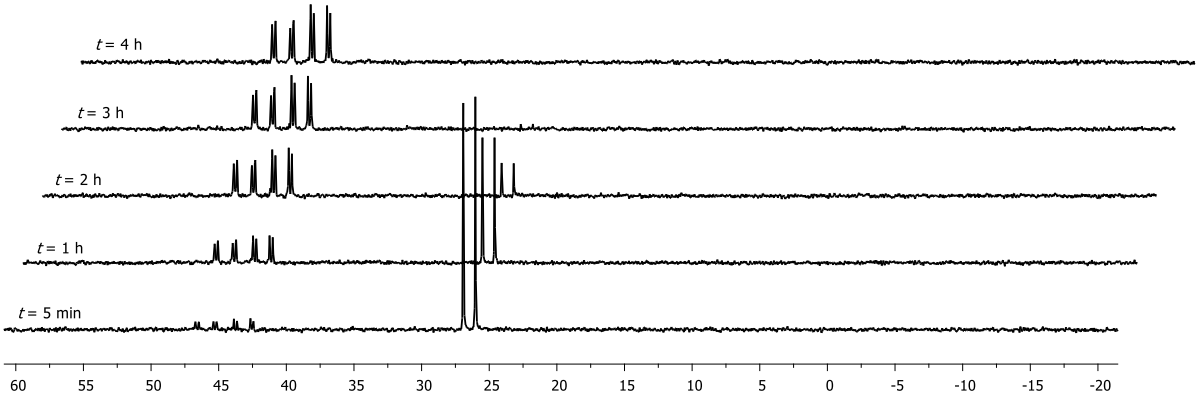

Figure S-58: Selected $^{31}P\{^{1}H\}$ NMR spectra recorded during the hydrogenation of **2a** (162 MHz, CD_2Cl_2).

2.6 Hydrogenation of 2b

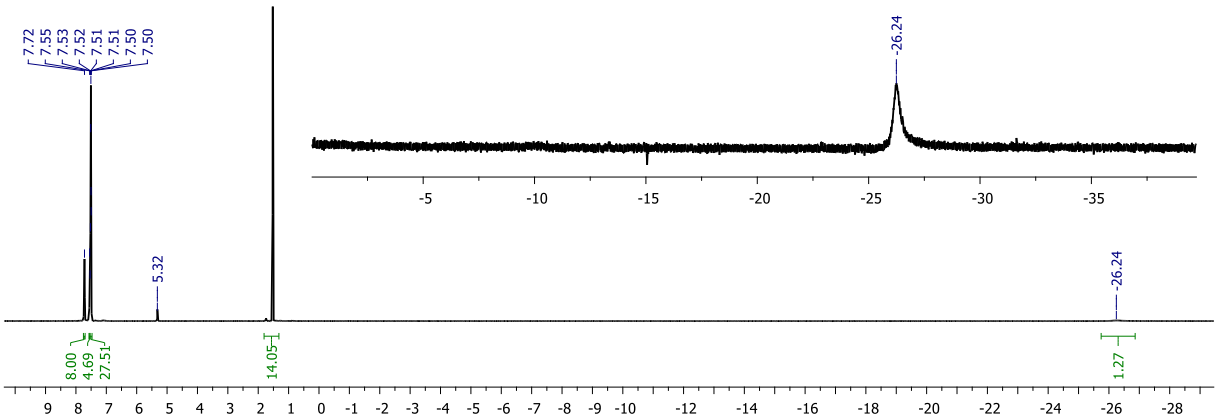

Figure S-59: ^{1}H NMR spectrum of *in situ* generated **9** at 298 K (500 MHz, CD_2Cl_2).

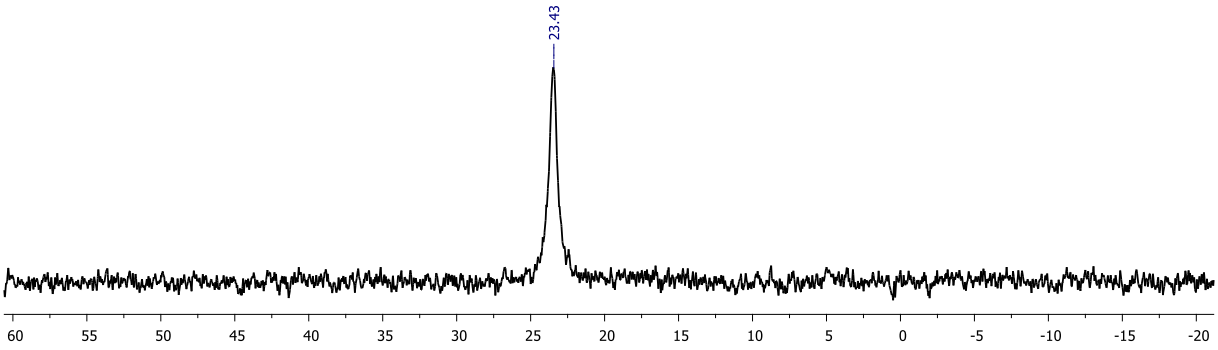

Figure S-60: $^{31}P\{^{1}H\}$ NMR spectrum of *in situ* generated **9** at 298 K (202 MHz, CD_2Cl_2).

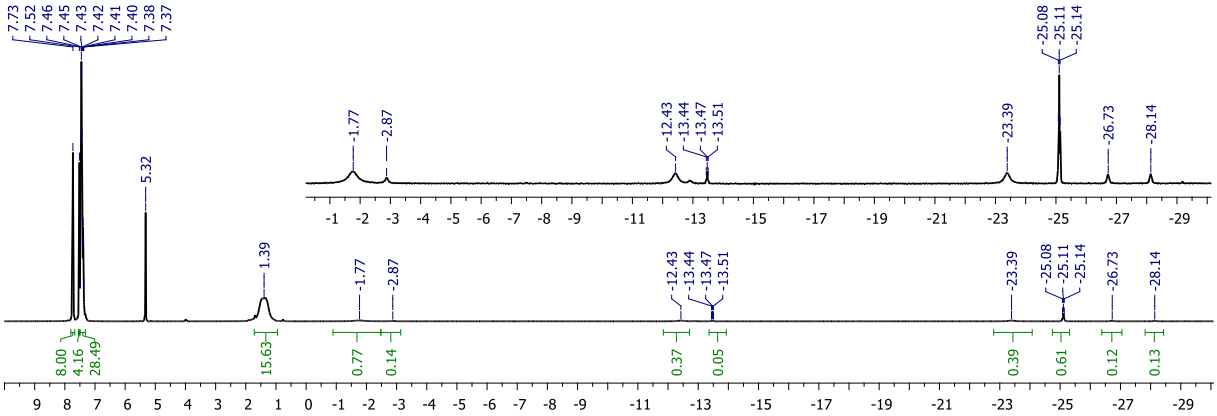

Figure S-61: ^{1}H NMR spectrum of *in situ* generated **9** at 185 K (500 MHz, CD_2Cl_2).

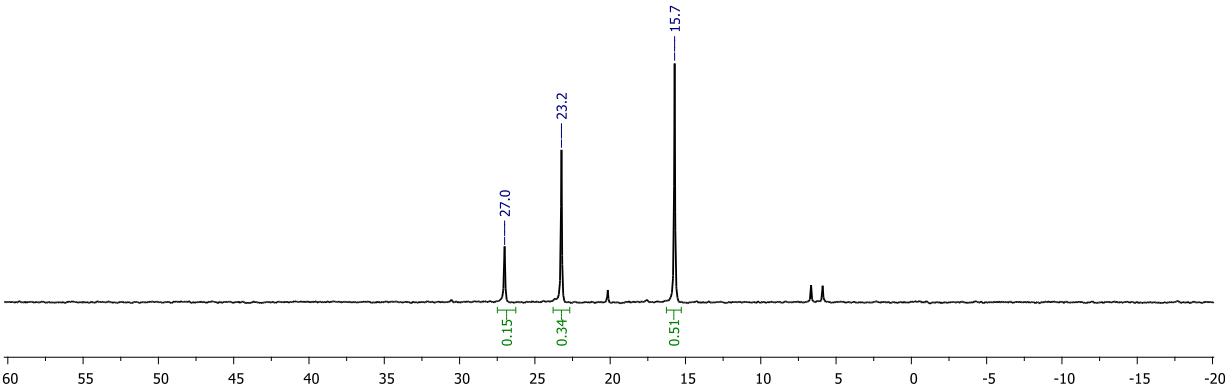

Figure S-62: $^{31}P\{^{1}H\}$ NMR spectrum of *in situ* generated **9** at 185 K (202 MHz, CD_2Cl_2).

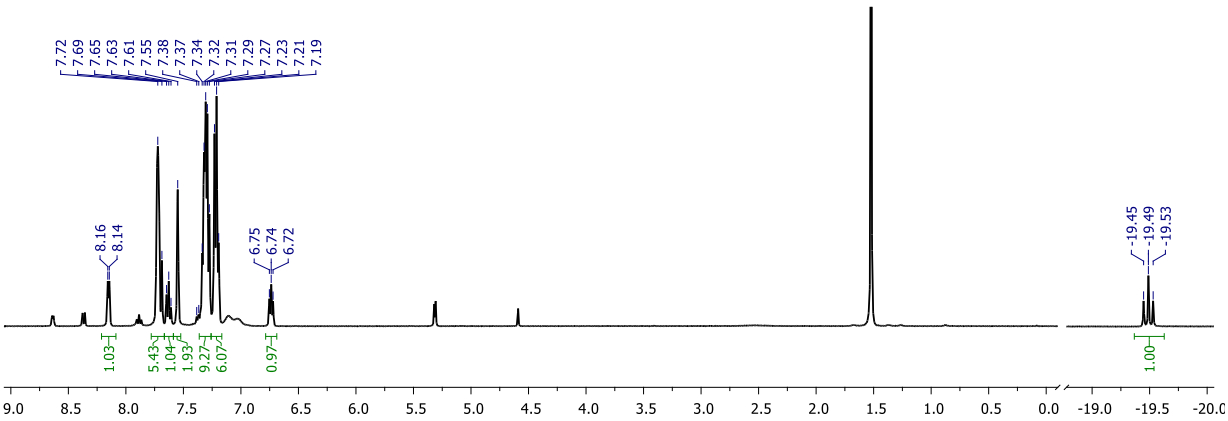

Figure S-63: ^{1}H NMR spectrum obtained following reaction between **9** and bipy (400 MHz, CD_2Cl_2).

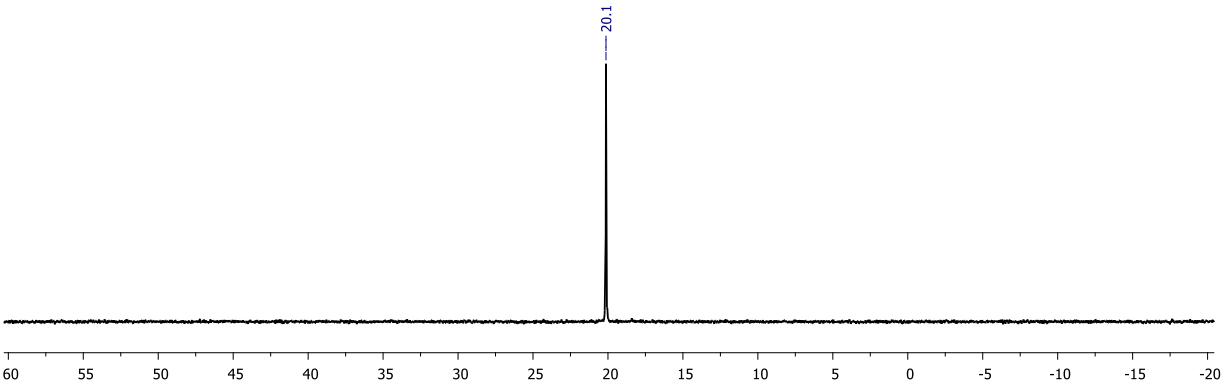

Figure S-64: $^{31}P\{^{1}H\}$ spectrum obtained following reaction between **9** and bipy (162 MHz, CD_2Cl_2).

2.7 Reaction between 3 and db24c8

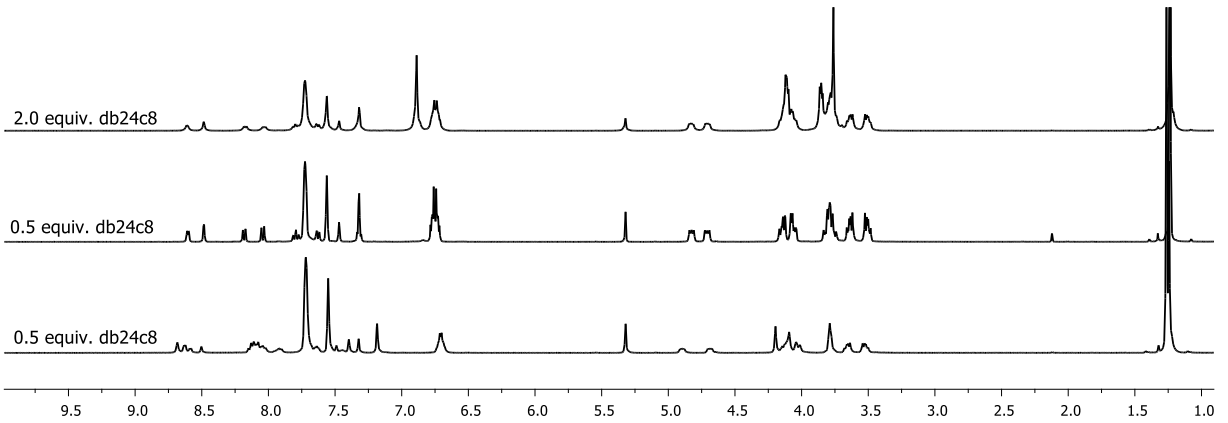

Figure S-65: ^{1}H NMR spectra following reaction between **3** and db24c8 (400 MHz, CD_2Cl_2).

2.8 Attempted hydrogenation of COD mediated by 4a[BAr^F_4]

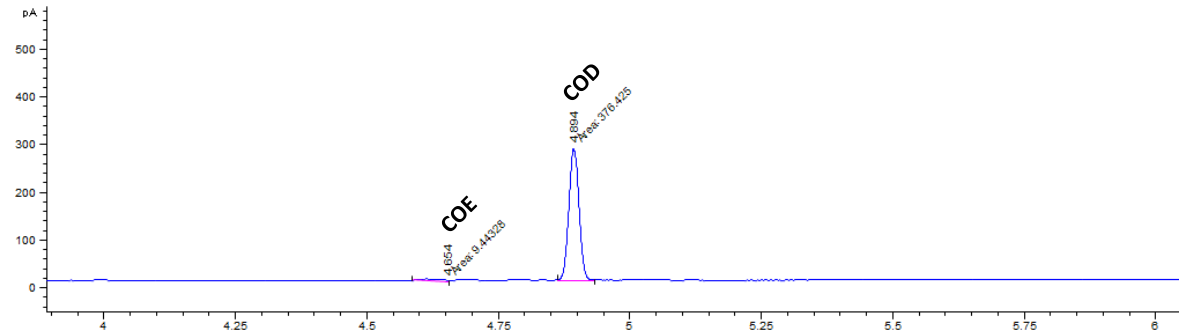

Figure S-66: GC trace obtained following the reaction of **4a**+COD under dihydrogen.

2.9 Reaction between 5a and PPh_3

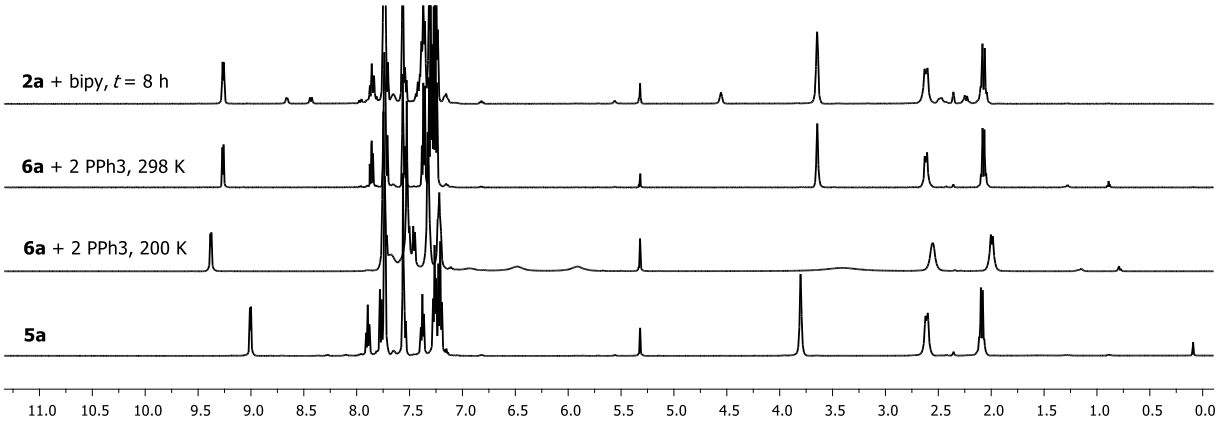

Figure S-67: ^{1}H NMR spectra demonstrating reaction between **5a** and PPh_3 in CD_2Cl_2: **2a**+bipy (400 MHz), **6a**+2PPh_3 (500 MHz) and, for comparison, isolated **5a** (500 MHz).

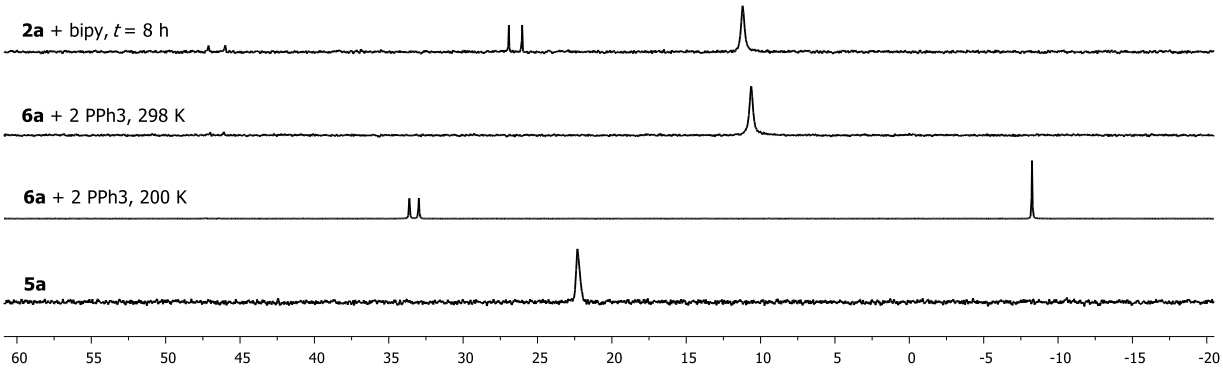

Figure S-68: $^{31}P\{^1H\}$ NMR spectra demonstrating the reaction between **5a** and PPh_3 in CD_2Cl_2: from **2a**+bipy (162 MHz), **6a**+2PPh_3 (202 MHz) and, for comparison, isolated **5a** (202 MHz).

2.10 Hydrogenation of 7

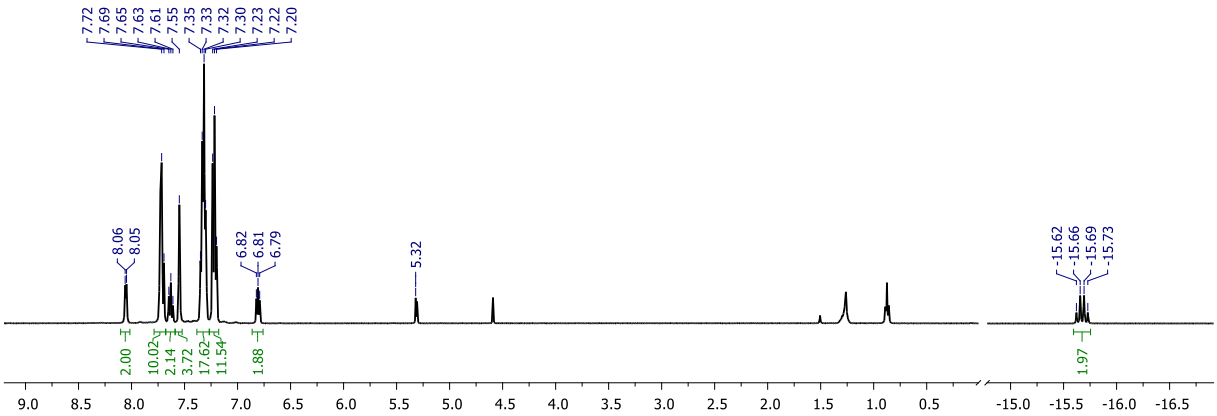

Figure S-69: ^{1}H NMR spectrum obtained following hydrogenation of **7** (400 MHz, CD_2Cl_2).

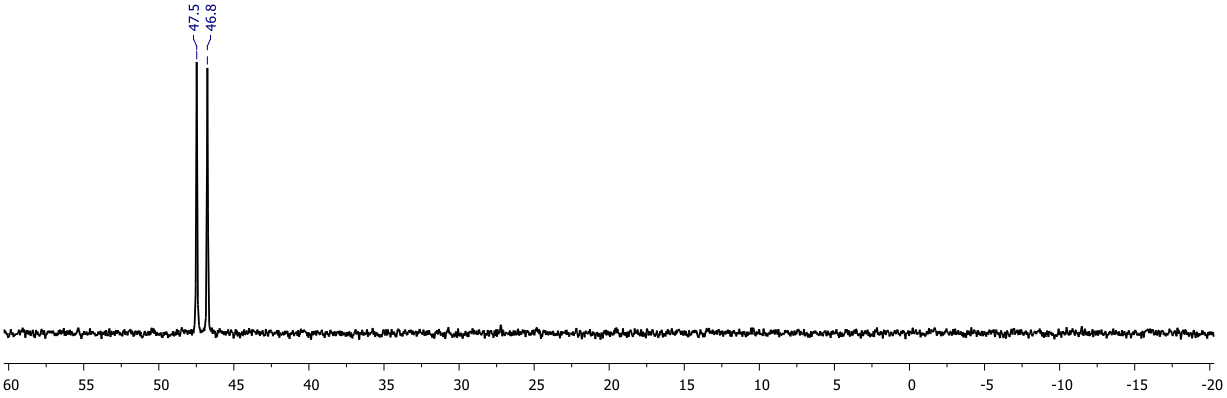

Figure S-70: $^{31}P\{^{1}H\}$ spectrum obtained following hydrogenation of **7** (162 MHz, CD_2Cl_2).

2.11 Reaction between 8 and bipy

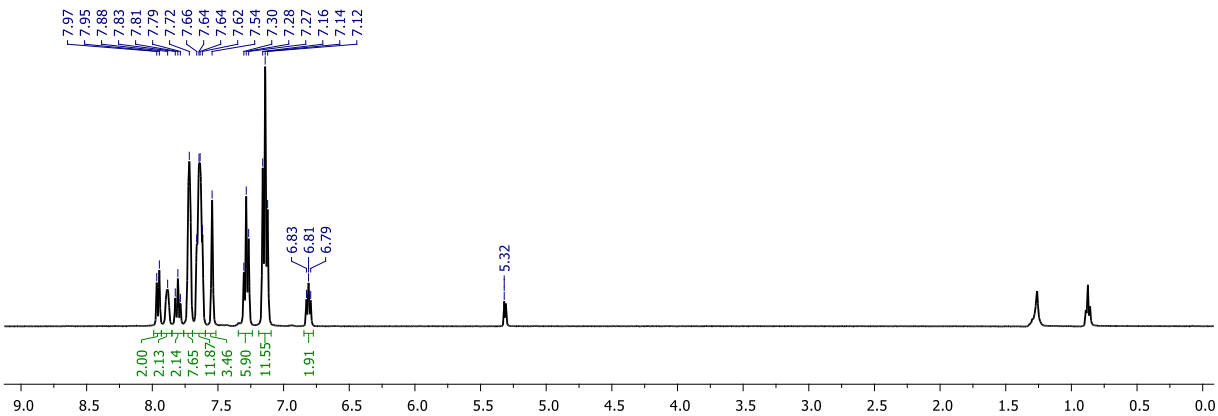

Figure S-71: ^{1}H NMR spectrum obtained following reaction between **8** and bipy (400 MHz, CD_2Cl_2).

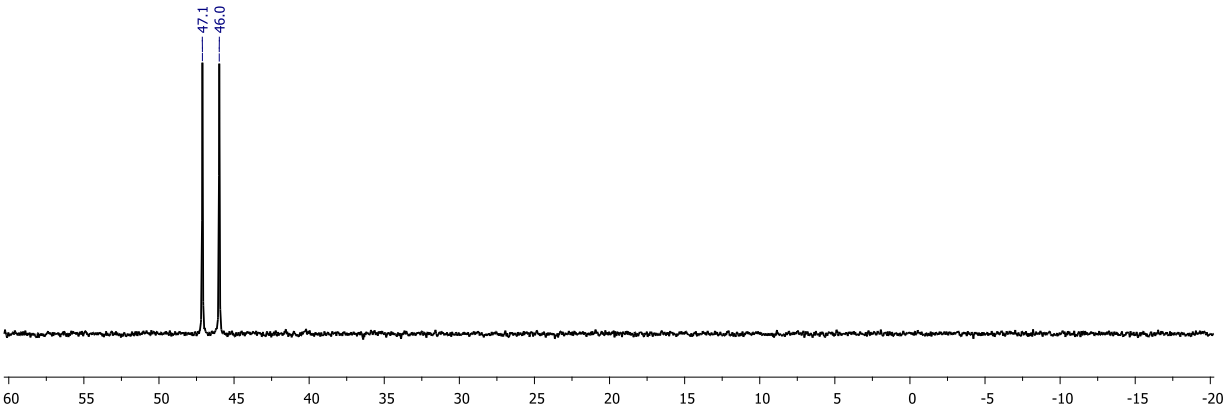

Figure S-72: $^{31}P\{^{1}H\}$ spectrum obtained following reaction between **8** and bipy (162 MHz, CD_2Cl_2).

3. HR ESI-MS spectra of new compounds

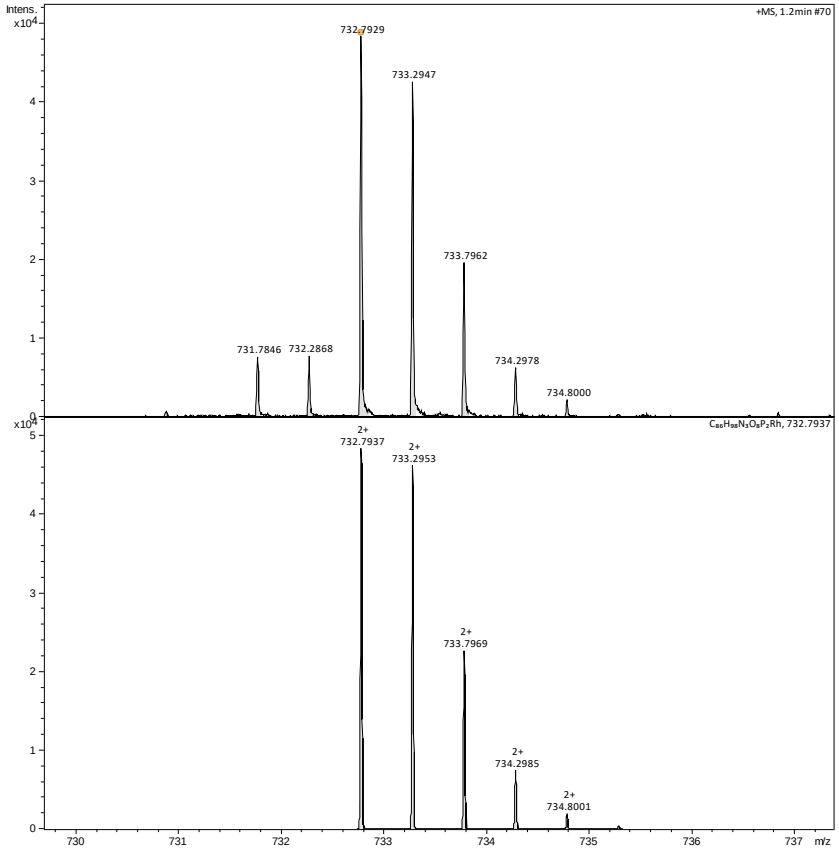

Figure S-73: HR ESI-MS spectrum of **1a** (positive ion, 4 kV).

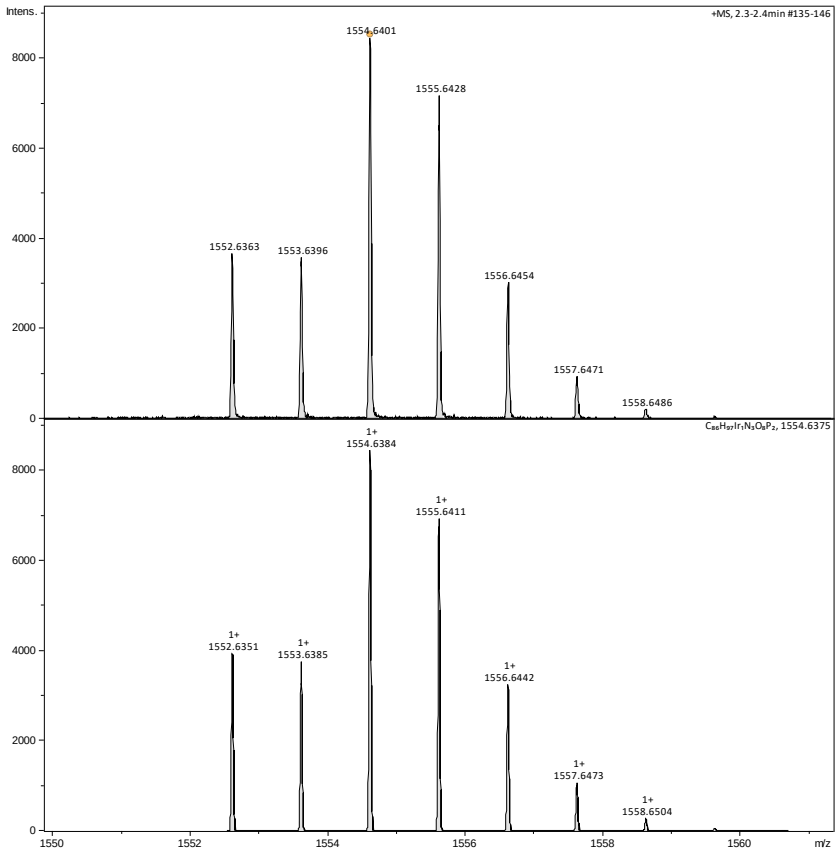

Figure S-74: HR ESI-MS spectrum of **1b**, $[M-H]^+$ (positive ion, 4 kV).

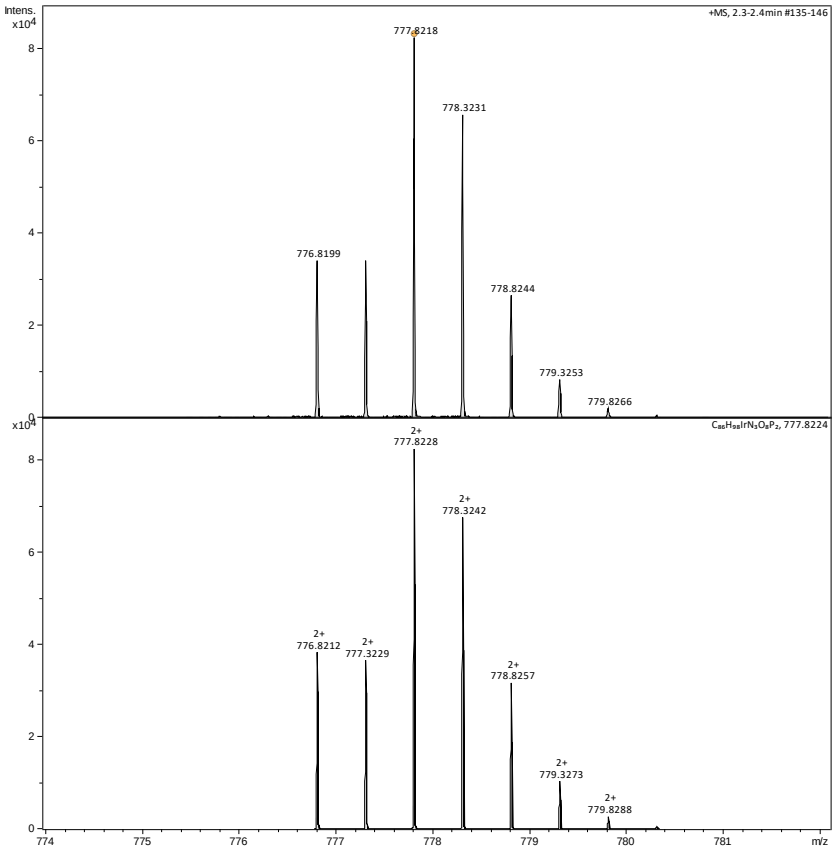

Figure S-75: HR ESI-MS spectrum of **1b**, $[M]^{2+}$ (positive ion, 4 kV).

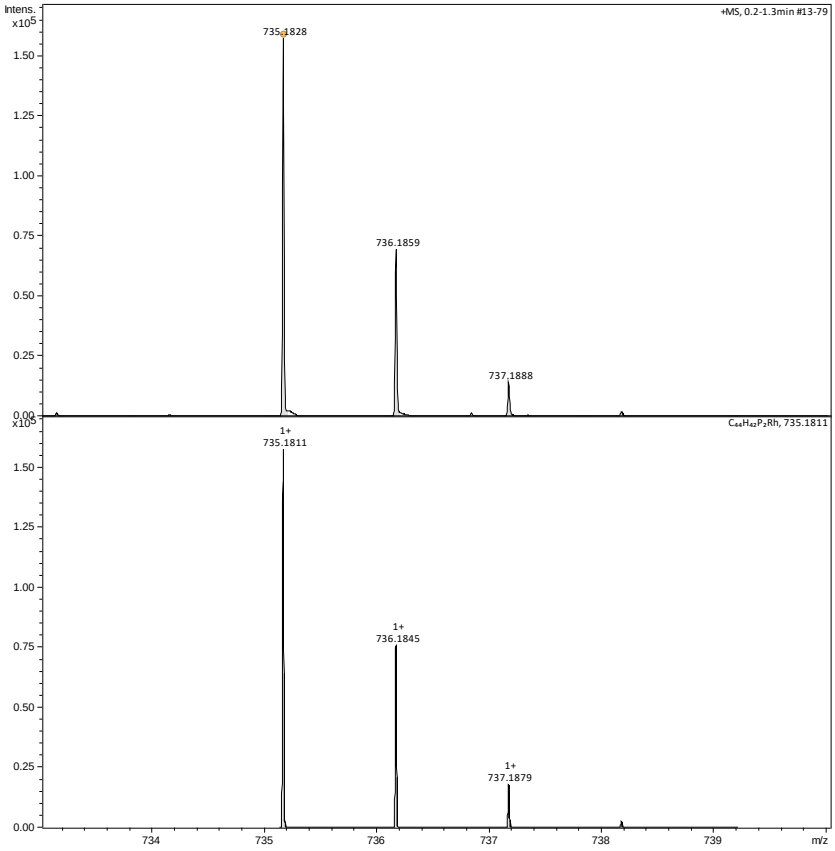

Figure S-76: HR ESI-MS spectrum of **2a** (positive ion, 4 kV).

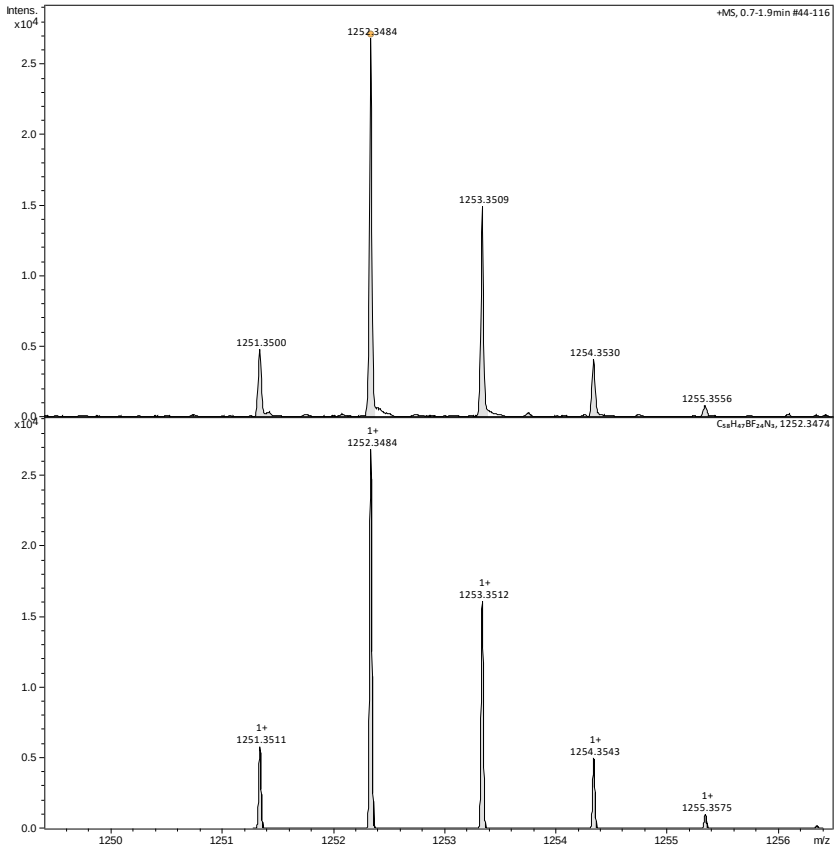

Figure S-77: HR ESI-MS spectrum of **3** (positive ion, 4 kV).

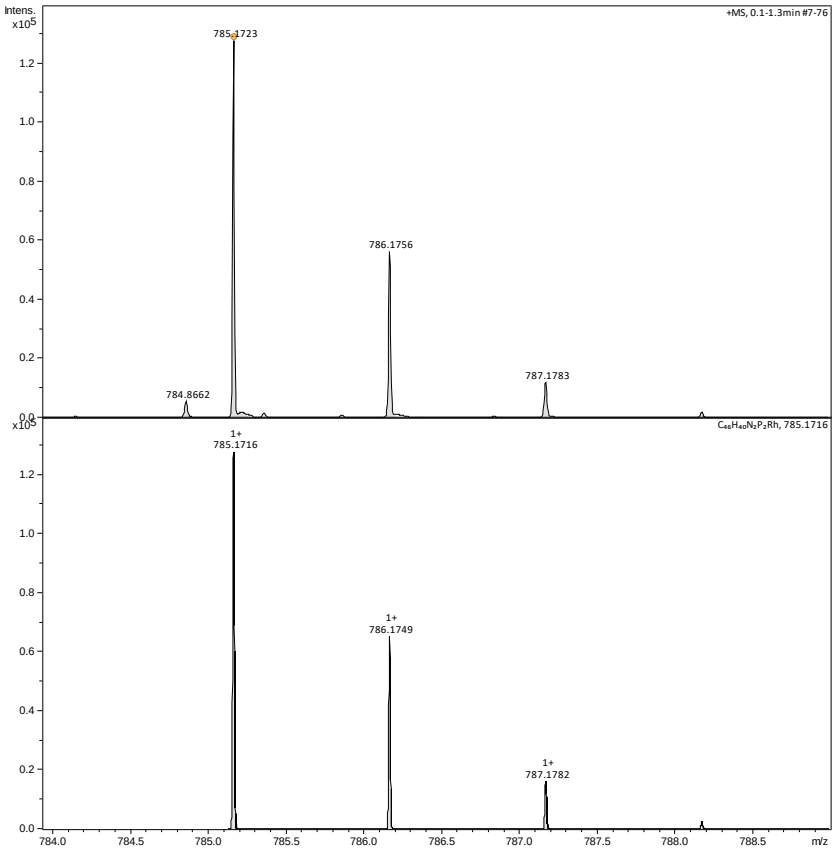

Figure S-78: HR ESI-MS spectrum of **4a** (positive ion, 4 kV).

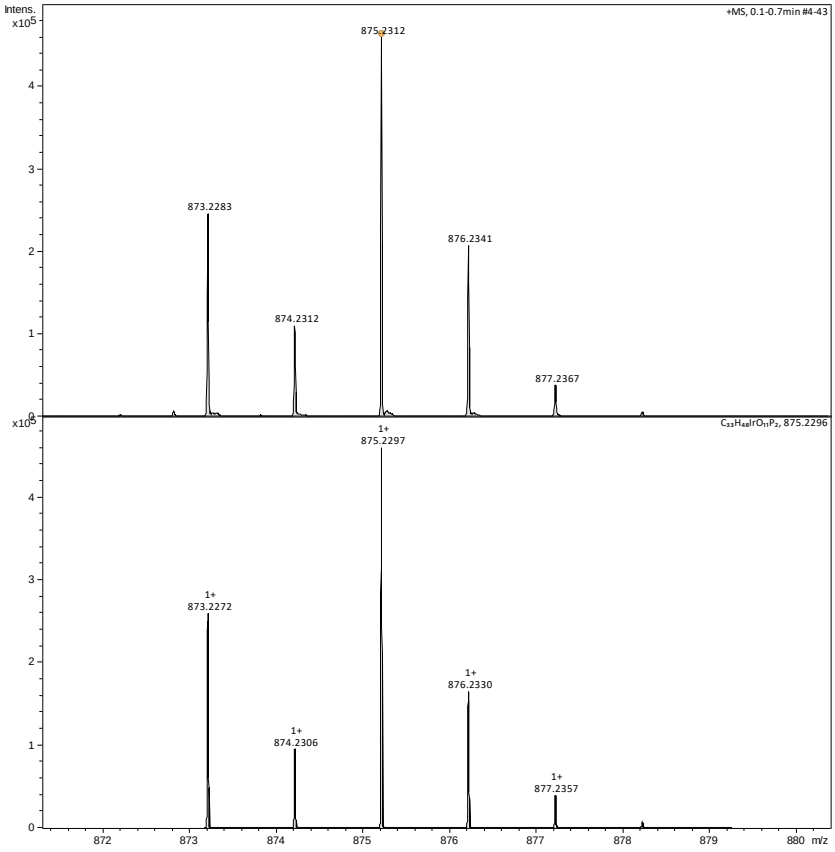

Figure S-79: HR ESI-MS spectrum of **4b** (positive ion, 4 kV).

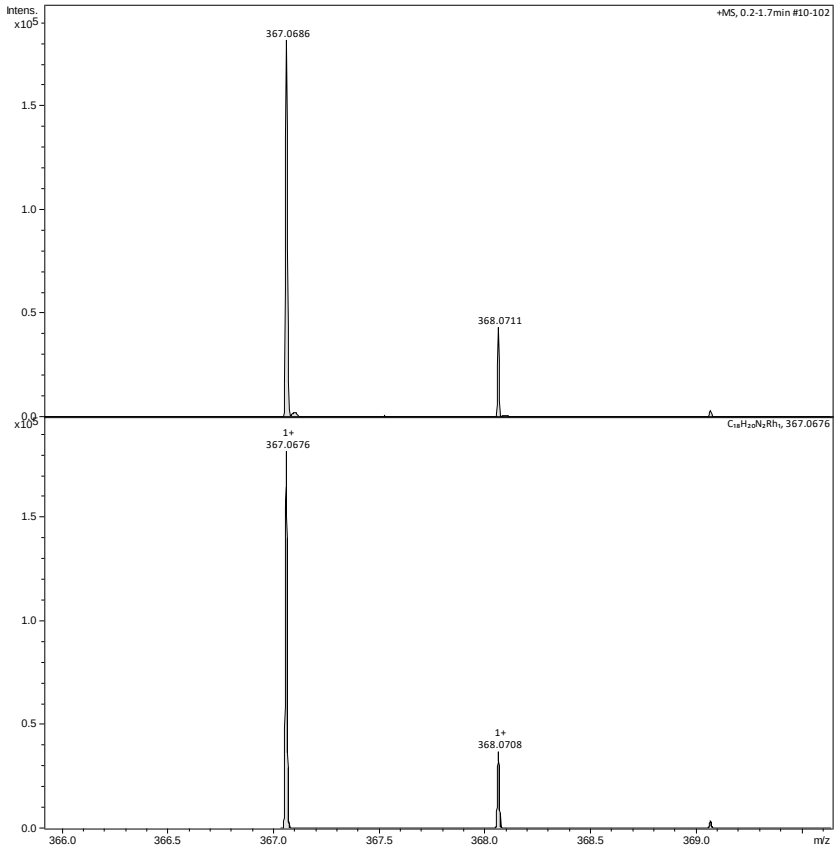

Figure S-80: HR ESI-MS spectrum of **5a** (positive ion, 4 kV).

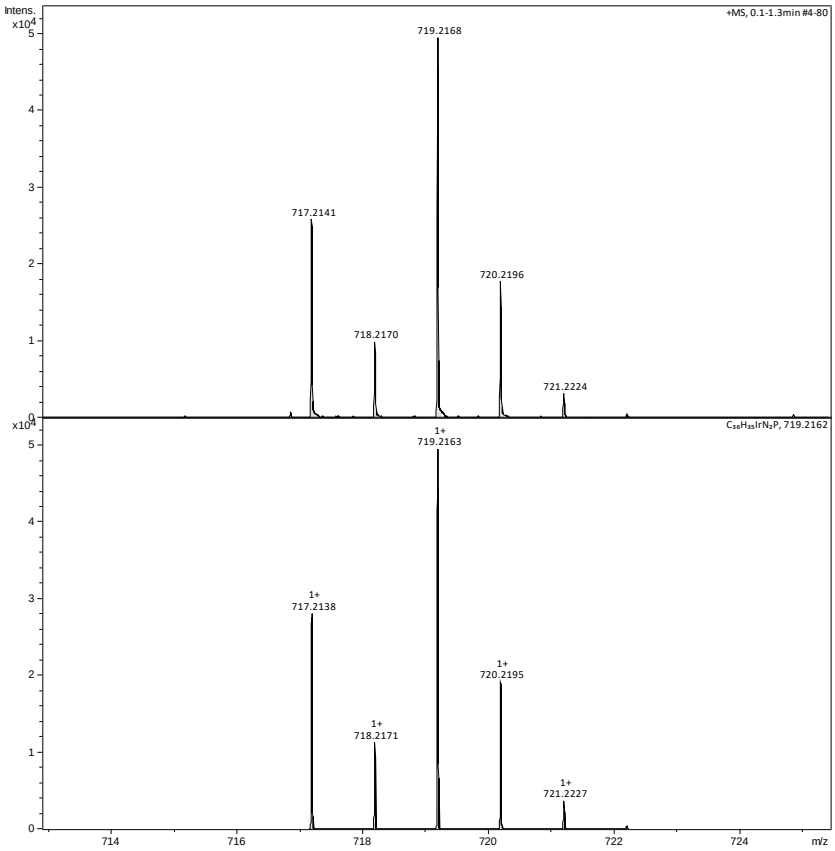

Figure S-81: HR ESI-MS spectrum of **5b** (positive ion, 4 kV).

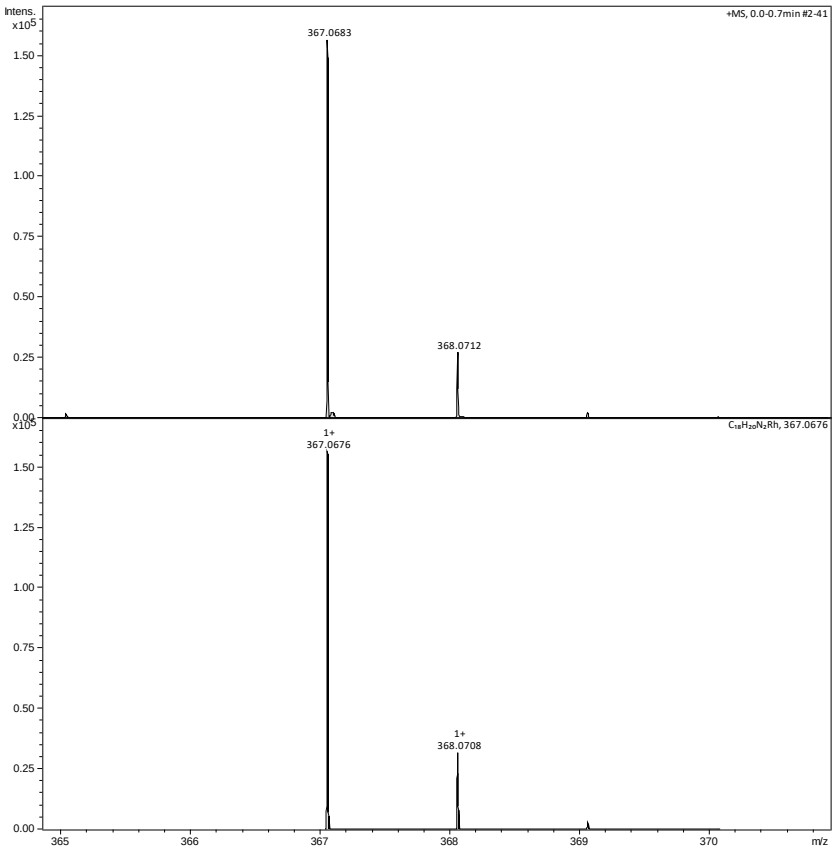

Figure S-82: HR ESI-MS spectrum of **6a** (positive ion, 4 kV).

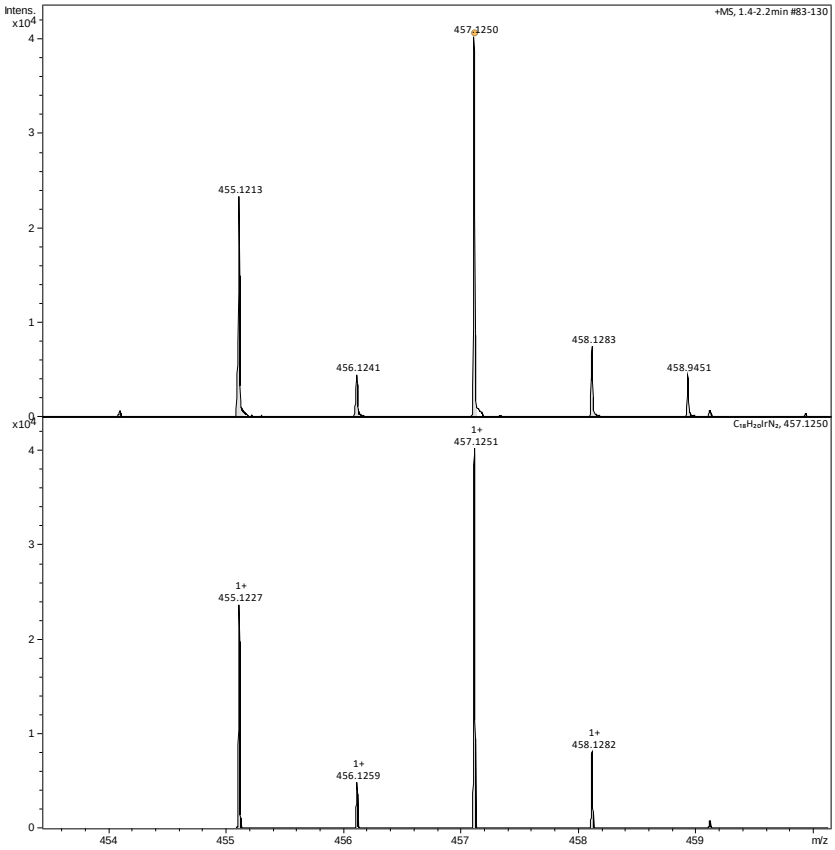

Figure S-83: HR ESI-MS spectrum of **6b** (positive ion, 4 kV).

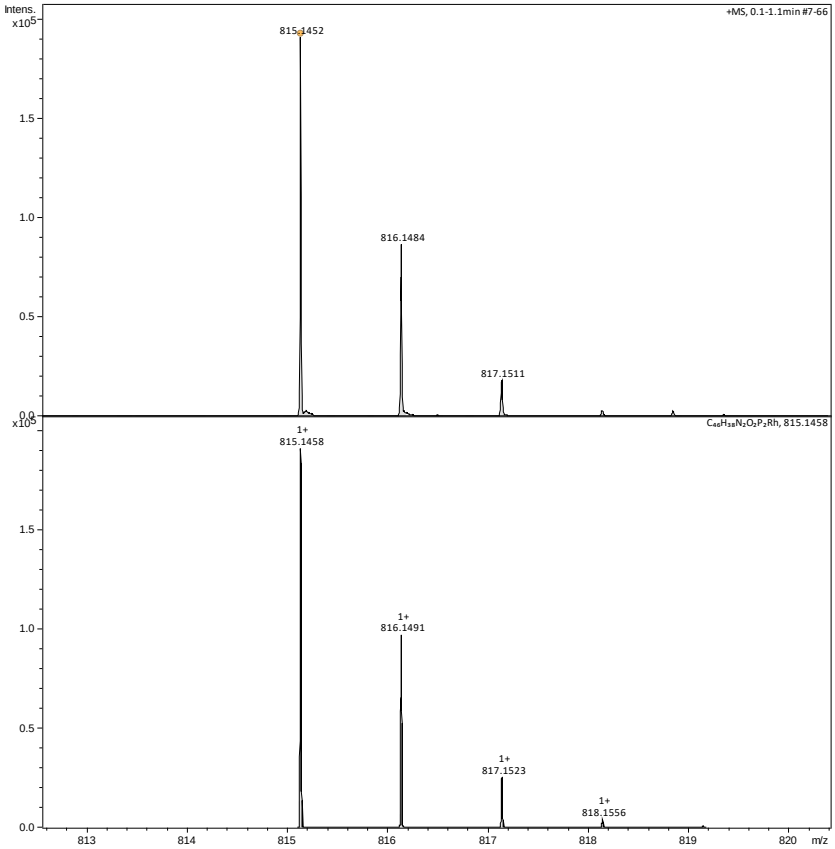

Figure S-84: HR ESI-MS spectrum of **7** (positive ion, 4 kV).

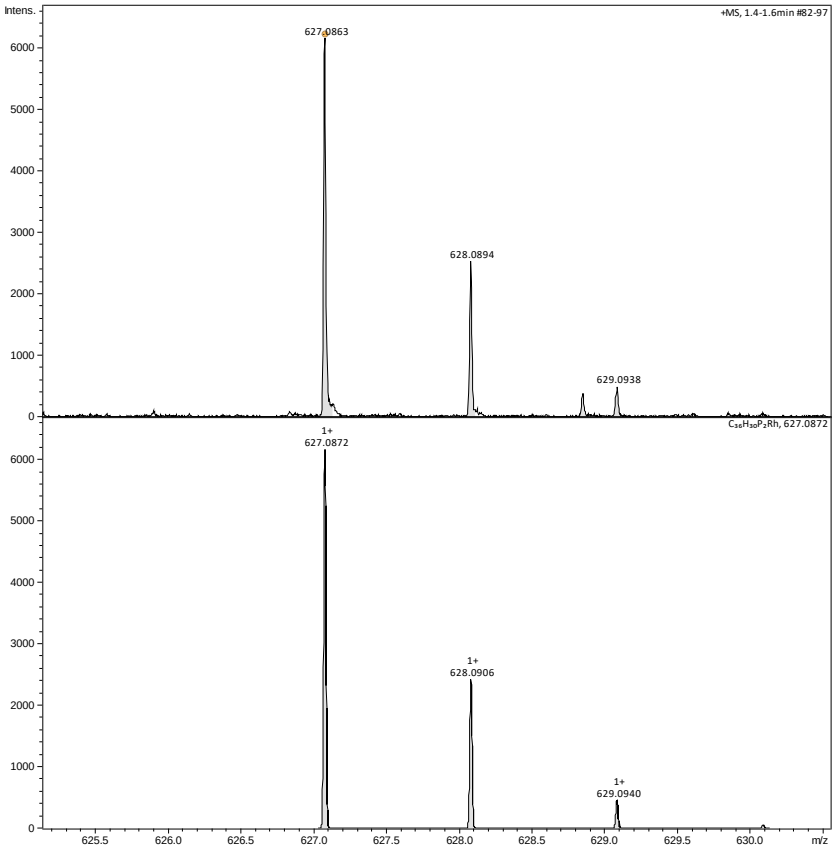

Figure S-85: HR ESI-MS spectrum of **8** (positive ion, 4 kV).

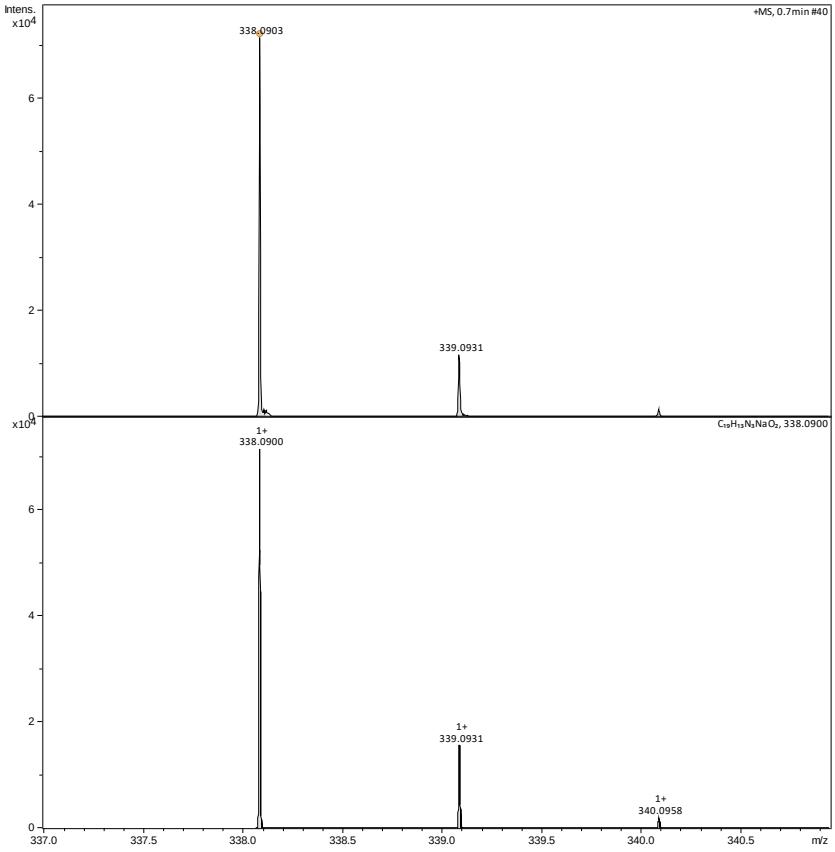

Figure S-86: HR ESI-MS spectrum of 5-phthalimidomethylbipyridine (positive ion, 4 kV).

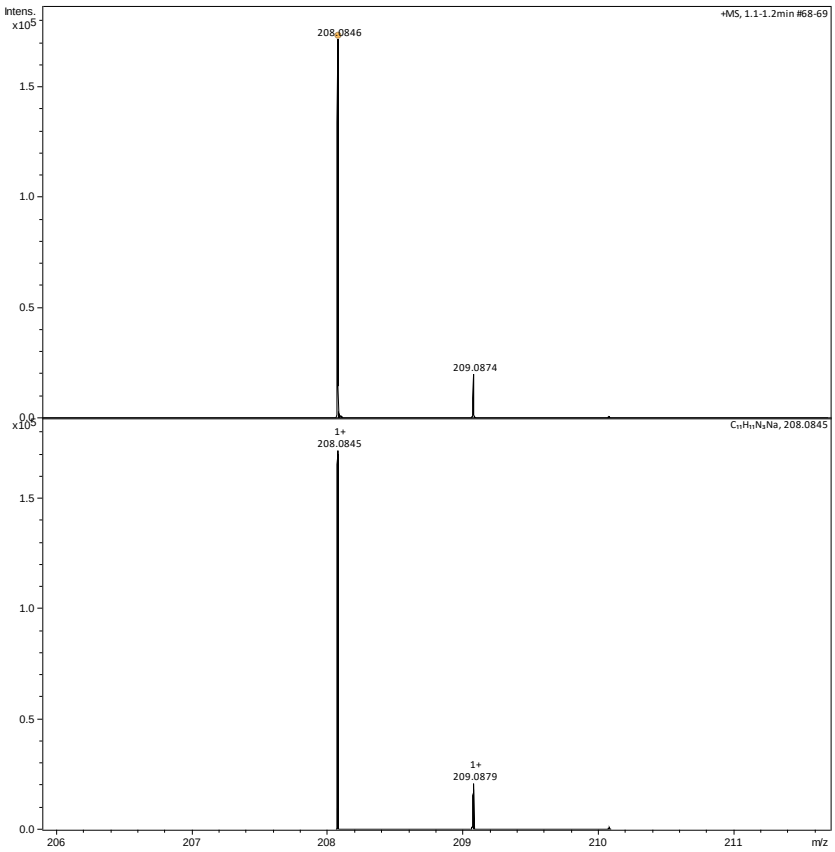

Figure S-87: HR ESI-MS spectrum of 5-aminomethylbipyridine (positive ion, 4 kV).

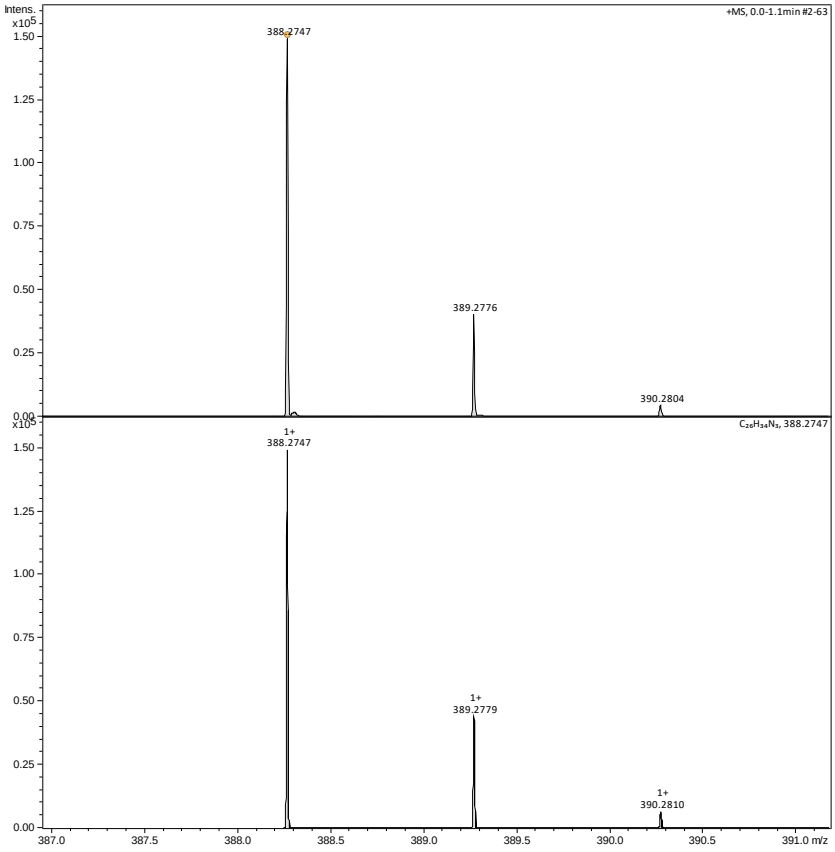

Figure S-88: HR ESI-MS spectrum of **10** (positive ion, 4 kV).