Supporting Information for:

The natural product Lepidiline A as an *N*-heterocyclic carbene ligand precursor in complexes of the type [Ir(cod)(NHC)PPh_3)]X: synthesis, characterization, and application in hydrogen isotope exchange catalysis

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1. General Remarks

1.1 General Considerations

All reagents were obtained from commercial suppliers (Aldrich, Alfa Aesar or Strem) and used without further purification, unless otherwise stated. Purification was carried out according to standard laboratory methods.[1]

Benzene was dried by heating to reflux over sodium wire, and then distilled under argon. Tetrahydrofuran was dried by heating to reflux over sodium wire, using benzophenone ketyl as an indicator, and then distilled under nitrogen. Diethyl ether and toluene were obtained from a PureSolv SPS-400-5 Solvent Purification System, and deoxygenated by bubbling argon through for a minimum of thirty minutes. Dichloromethane was dried by heating to reflux over calcium hydride, and then distilled under argon. All distilled solvents were stored under an argon atmosphere over molecular sieves (Å).

Triphenylphosphine was purified by recrystallisation from ethanol.

Thin layer chromatography was carried out using Camlab silica plates coated with fluorescent indicator UV_{254}. Plates were analysed using a Mineralight UVGL-25 lamp or developed using vanillin solution.

Flash column chromatography was carried out using Prolabo silica gel (230-400 mesh).

IR spectra were obtained on a Shimadzu IRAffinity-1 Spectrophotometer machine.

^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz (unless otherwise stated), 100 MHz, 128 MHz, 376 MHz, and 162 MHz, respectively. Chemical shifts are reported in ppm. Coupling constants are reported in Hz and refer to $^{3}J_{H\text{-}H}$ couplings, unless otherwise stated.

High resolution mass spectrometry (HRMS) data were acquired at the EPSRC UK National Mass Spectrometry Facility at Swansea University unless stated otherwise. Ionisation methods are stated for each example.

All crystallographic measurements were made at low temperature with graphite monochromated Mo radiation (λ = 0.71073 Å) and an Oxford Diffraction Xcalibur E instrument. Structures were solved using SIR92 and were refined to convergence against F^2 using all independent reflections and the program SHELXL-2014.[2,3] All programs were used within the WinGX GUI.[4]

Crystals of **6d** were found to contain traces of solvent. The solvent sites were highly disordered and partially occupied. The identity solvent could not be modelled or identified using crystallographic means, though the sample was crystallised from CH_2Cl_2 and diethyl ether. The SQUEEZE routine of the program PLATON was thus used to remove the effect of the solvent from the structural analysis.[5] A total of 191 electron equivalents were thus removed from 921.1Å^3 of unit cell space.

Crystals of **6e** were found to be twinned. A hklf 5 formatted reflection file was created for a twin law corresponding to a 180° rotation about reciprocal 0 -1 2. Refinement with this dataset gave an improved model, as compared to the untreated data, and a refined BASF of 0.0560(6).

Additionally, across the structures, several groups were modelled as disordered over multiple sites. These were the solvent and anion in **3.HCl**; the solvent, anion and two phenyl rings of **6b**; one anion and one benzyl group of **6d**; 10 of the CF_3 groups of the anions of the twinned structure of **6e**; one phenyl ring of a benzyl group in **12**; the anion of **14**, and; one anion and the solvent of **15**. In all cases appropriate constraints and restraints were applied to the disordered groups to ensure that the interatomic distances and the displacement ellipsoids of these groups approximated to normal values.

Selected crystallographic data is given in Tables S3 and S4, and full details are available in cif format, CCDC reference numbers 1970326 to 1970331 and 1971355 to 1971359.

For labelling reactions, the level of deuterium incorporation in the substrate was determined by ^{1}H NMR spectroscopy. The integrals were calibrated against a peak corresponding to a position not expected to be labelled. **Equation 1** was then used to calculate the extent of labelling:

$$\%\, Deuteration = 100 - \left[\left(\frac{residual\ integral}{number\ of\ labelling\ sites}\right) x\ 100\right]$$

Equation 1

Compounds which appear in the manuscript are given the same numbers here as they have in the manuscript. Compounds not appearing in the manuscript are numbered **S1**, **S2**, etc.

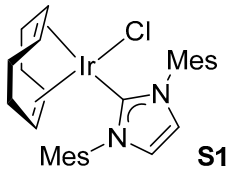
2. Experimental Procedures

2.1 Procedures relating to Manuscript Section 2 and 2.1

*2.1.1 Towards η⁴–cycloocta-1,5-diene(1,3-dimesitylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate **1a***

Preparation of chloro(η⁴–cycloocta-1,5-diene)(1,3-dimesitylimidazol-2-ylidene)iridium(I) S1[6]

To a flame-dried Schlenk tube was added η⁴-cycloocta-1,5-dieneiridium(I) chloride dimer **13** (600 mg, 0.893 mmol) and potassium *t*-butoxide (200 mg, 1.786 mmol). After stirring the solid mixture under high vacuum for 10 min, dry THF (15 mL) was added under an argon atmosphere, and the resultant red-black solution stirred at room temperature for a further 10 min. Subsequently, the 1,3-dimesitylimidazolium chloride (609 mg, 1.786 mmol) was added in one portion, causing a dark red to dark yellow colour change, and the reaction mixture stirred at room temperature for 3 h. The THF was then removed *in vacuo* and the residue purified by flash column chromatography, eluting the yellow fraction with a 1:1 mixture of EtOAc and petroleum ether, to afford product complex **S1** as a yellow microcrystalline solid (1.132 g, 99% yield).



S1

m.p. (°C): > 200 °C (dec.).

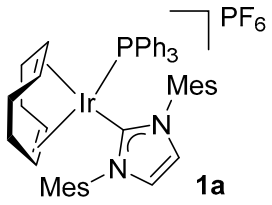
FTIR (neat): 3092, 3009, 2916, 2876, 1609, 1485 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01-6.98 (2 × br s, 4H, ArH), 6.98 (s, 2H, olefinic CH), 4.20-4.14 (m, 2H, COD olefinic CH), 3.01-2.98 (m, 2H, COD olefinic CH), 2.39 (s, 12H, $ArCH_3$), 2.19 (s, 6H, $ArCH_3$), 1.80-1.62 (m, 4H, COD CH_2), 1.41-1.23 (m, 4H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 138.8, 137.6, 136.3, 134.6, 129.7, 128.3, 123.5, 82.8, 51.6, 33.7, 29.2, 21.4, 19.9, 15.5.

Preparation of η⁴–cycloocta-1,5-diene(1,3-dimesitylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 1a[7]

The yellow complex (COD)Ir(IMes)Cl **S1** (700 mg, 1.093 mmol) was dissolved in dry THF (15 mL) in a previously flame-dried round bottom flask, fitted with stopcock sidearm. The mixture was stirred, and after all the solids had dissolved, silver hexafluorophosphate (276 mg, 1.092 mmol) was added, affording a yellow to opaque orange colour change and formation of a precipitate. The reaction mixture was stirred for 15 min at room temperature before filtration through celite under an argon atmosphere, using the necessary flame-dried glassware. Addition of triphenylphosphine (287 mg, 1.094 mmol) to the clear orange solution resulted in the immediate appearance of a bright red colour. After stirring the solution for 1 h at room temperature, the solvent was removed under reduced pressure and the crude product triturated with EtOAc to afford product complex **1a** as a red, microcrystalline solid (885 mg, 80% yield).



1a

FTIR (CH_2Cl_2): 3040, 2995, 2319, 1631, 1495 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.40 (m, 5H, ArH), 7.31-7.25 (m, 6H, ArH), 7.14-7.07 (m, 6H, ArH), 7.00 (s, 2H, ArH), 6.62 (s, 2H, olefinic CH), 4.41-4.33 (m, 2H, COD CH), 3.33-3.26 (m, 2H, COD CH), 2.33 (s, 6H, $ArCH_3$), 2.09 (s, 6H, $ArCH_3$), 1.74 (s, 6H, $ArCH_3$), 1.67-1.45 (m, 6H, COD CH_2), 1.31-1.22 (m, 2H, COD CH_2).

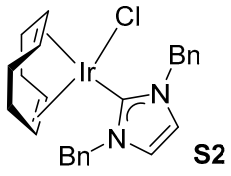
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5 (d, $^2J_{C\text{-}P}$ = 8.0 Hz), 139.2, 135.7, 135.2, 135.1, 134.6, 131.2, 130.7, 130.2, 129.7, 128.5, 126.4, 80.9, 80.0, 77.4, 31.4, 30.4, 21.2, 20.9, 18.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.3 (PPh_3), -144.3 (PF_6).

*2.1.2 Towards η^4–cycloocta-1,5-diene(1,3-dibenzylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate **7***

Preparation of chloro(η^4–cycloocta-1,5-diene)(1,3-dibenzylimidazol-2-ylidene)iridium(I) S2[8,9]

To a previously flame-dried Schlenk tube containing η^4-cycloocta-1,5-dieneiridium(I) chloride dimer **13** (400 mg, 0.596 mmol) dissolved in dry benzene (10 mL), was added a solution of sodium ethoxide (1 M, 1.2 mL, 1.200 mmol), resulting in a red to yellow colour change. The solution was stirred for 10 min at room temperature, and 1,3-dibenzylimidazolium chloride[10] (339 mg, 1.190 mmol) was added in one portion. The solution was stirred for 3 d at 60 °C under an argon atmosphere, resulting in a gradual colour change from yellow to orange. The solvent was subsequently removed *in vacuo*, and the residue purified via flash column chromatography, eluting with DCM. The product-containing fractions were combined and concentrated under reduced pressure to give product **S2** as a yellow solid (553 mg, 80% yield).



S2

mp: > 195 °C (dec.)

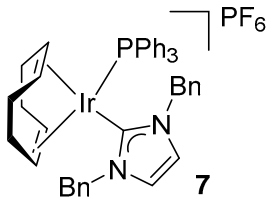
FTIR (neat): 3171, 2951, 1569, 1500 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 10 H, ArH), 6.77 (s, 2H, olefinic CH), 5.78 (d, ^2J = 14.8 Hz, 2H, $ArCH_2$), 5.62 (d, ^2J = 14.8 Hz, 2H, $ArCH_2$), 4.67-4.61 (m, 2H, COD CH), 2.98-2.94 (m, 2H, COD CH), 2.22-2.11 (m, 4H COD CH_2), 1.76-1.71 (m, 2H, COD CH_2), 1.61-1.56 (m, 2H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.5, 135.8, 128.4, 127.7, 127.6, 120.0, 84.6, 53.9, 51.4, 33.1, 29.0.

Preparation of η^4–cycloocta-1,5-diene(1,3-dibenzylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 7

To a stirred solution of complex **S2** (263 mg, 0.450 mmol) in dry THF (5 mL) under an argon atmosphere was added triphenylphosphine (118 mg, 0.450 mmol). Silver hexafluorophosphate (137 mg, 0.542 mmol) was then added, causing the clear yellow solution to turn red. The solution was stirred for 16 h at room temperature, then filtered through celite under an argon atmosphere. The red filtrate was then concentrated under reduced pressure. The crude product was recrystallized from DCM/Et_2O, giving product **7** as a red solid (357 mg, 83% yield).



7

mp: > 190 °C (dec.).

FTIR (neat): 3169, 3140, 2962, 1571, 1482 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.50 (m, 3H, ArH), 7.49-7.43 (m, 6H, ArH), 7.36-7.30 (m, 12H, ArH), 7.00-6.94 (m, 4H, ArH), 6.78 (s, 2H, olefinic CH), 5.51 (d, ^2J = 15.1 Hz, 2H, $ArCH_2$), 4.53 (d, ^2J = 15.1 Hz, 2H, $ArCH_2$), 4.44-4.37 (m, 2H, COD CH), 3.89-3.82 (m, 2H, COD CH), 2.30-2.19 (m, 2H, COD CH_2), 2.16-2.05 (m, 2H, COD CH_2), 2.04-1.92 (m, 4H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 134.5, 134.0, 133.9, 133.8, 131.7, 130.5, 130.0, 129.4, 129.3, 128.9, 127.9, 122.8, 87.0, 86.9, 80.7, 54.5, 31.2, 30.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ 18.2 (s, PPh_3), -144.3 (septet, $^1J_{P\text{-}F}$ = 710 Hz, PF_6).

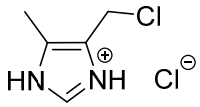
^{19}F NMR (365 MHz, $CDCl_3$): δ -73.44 (d, $^1J_{F\text{-}P}$ = 710 Hz)

HRMS (ESI): m/z calc'd for $C_{43}H_{43}{}^{191}IrN_2P$ [M^+]: 809.2764; found: 809.2764.

2.1.3 The Synthesis of Lepidiline A and Related Salts

Preparation of 5-(chloromethyl)-4-methyl-1H-imidazole hydrochloride 9[11]

A 250 mL round-bottom flask was charged with thionyl chloride (50 mL, 82 g, 690 mmol, excess) and a stirrer bar, and then cooled to 0 °C in an ice bath. Subsequently, (4-methyl-1*H*-imidazol-5-yl)methanol hydrochloride **8** (10.0 g, 67.3 mmol) was added portionwise, taking care in controlling the rate of effervescence. Once all of **8** had been added, cooling was removed and the reaction mixture stirred at room temeperature for 4 h. Following this, chloroform (50 mL) was added to the reaction mixture, the precipitate was collected by filtration and washed with cold chloroform (20 mL). The product was dried in a vacuum oven (0.1 mbar, 40 ^oC) overnight, to yield **9** as a bright white solid (11.13 g, 99%).



9

mp: 274-275 °C (lit.[11] = 277 °C).

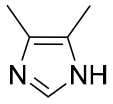
FTIR (neat): 3086, 2988, 2826, 2736, 2646, 1638, 1530, 1481, 1443, 833 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ 14.52 (br s, 1H, CH=N^{+}H), 8.93 (s, 1H, ArH), 5.54 (br s, 1H, NH), 4.46 (s, 2H, $ArCH_2Cl$), 2.25 (s, 3H, $ArCH_3$).

^{13}C NMR (100 MHz, DMSO-d_6): δ 134.0, 128.5, 125.2, 34.3, 9.0.

Preparation of 4,5-Dimethyl-1H-imidazole 10[11]

5-(Chloromethyl)-4-methyl-1*H*-imidazole hydrochloride **9** (8.0 g, 47.9 mmol) was dissolved in ethanol (125 mL) inside a reinforced hydrogenation vessel. Subsequently, palladium on charcoal (0.8 g, 10% w/w) was added, ensuring no dry powder remained on the sides of the vessel. The reaction vessel was sealed and placed under a hydrogen atmosphere (5 atm) in a Cook hydrogenation apparatus. After agitating the reaction mixture overnight, the hydrogen atmosphere was replenished inside the vessel and the reaction mixture agitated for a further 2 d. After removal of the vessel from the hydrogenation apparatus, the reaction mixture was filtered through celite; ensuring ethanol was used to rinse the glassware, and keeping the palladium residues wet. The filtrate was concentrated under reduced pressure then mixed with a solution of saturated aqueous K_2CO_3 (100 mL). **NOTE** – palladium residues on celite were quenched separately by soaking with saturated aqueous K_2CO_3. The basified reaction mixture extracted with diethyl ether (4 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to reveal the desired product **10** as an off-white solid (4.023 g, 87%).



10

mp: 101-102 °C (lit.[11] = 102 °C).

FTIR (neat): 3123, 2918, 1657, 1607, 1449 $cm^{-1.}$

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 1H, ArH), 2.14 (s, 6H, $ArCH_3$).

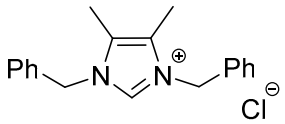
^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4, 126.6, 10.7.

Preparation of *N*,*N*'-dibenzyl-4,5-dimethylimidazolium chloride (Lepidiline A) 3·HCl[12]

To a flame-dried round-bottom flask was added 4,5-dimethylimidazole **10** (2.00 g, 20.8 mmol) and dry THF (20 mL). The mixture was stirred, and once all solids had dissolved, sodium hydride (499 mg, 20.8 mmol) was added portionwise to control the rate of effervescence. Following this, benzyl chloride (5.27 g, 41.6 mmol) was added to the reaction mixture dropwise with stirring. The flask was then fitted with a reflux condenser

and heated to the 80 °C, and the reaction mixture was then stirred at this temperature for 48 h. On cooling, the solvent was removed *in vacuo* and the residue diluted with DCM (20 mL). This DCM mixture was filtered through celite and concentrated under reduced pressure to reveal an off-white solid. The solid was collected by filtration and washed with acetone to give the desired product Lepidiline A **3·HCl** as a bright white solid (4.40 g, 68% yield).

X-ray quality crystals were gown by slow diffusion of diethyl ether into a saturated DCM solution of **3·HCl** at 4 °C overnight.



3·HCl

mp: 245-247 °C.

FTIR (neat): 3375, 3111, 3030, 2956, 1628, 1551, 1497, 1454 $cm^{-1.}$

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.44 (s, 1H, NCHN), 7.46-7.42 (m, 4H, ArH), 7.41-7.37 (m, 2H, ArH), 7.35-7.31 (m, 4H, ArH), 5.46 (s, 4H, CH_2Ar), 2.13 (s, 6H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ 135.4, 134.2, 129.0, 128.4, 127.7, 127.1, 49.6, 8.0.

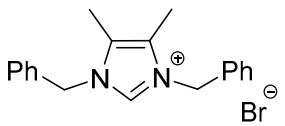
HRMS (positive NSI): m/z calc'd for $C_{19}H_{21}N_2$ $[M]^+$: 277.1699; found: 277.1699.

HRMS (negative NSI): peaks observed at m/z 34.8 and 36.8 in a 3:1 ratio of abundance, consistent with a chloride anion.

X-ray data: See Section 4.

Preparation of *N*,*N*'-Dibenzyl-4,5-dimethylimidazolium bromide 3·HBr

To a flame-dried round-bottom flask was added 4,5-dimethylimidazole **10** (1.00 g, 10.4 mmol) and dry THF (10 mL). The mixture was stirred, and once all solids had dissolved, sodium hydride (250 mg, 10.4 mmol) was added portionwise to control the rate of effervescence. Following this, benzyl bromide (3.74 g, 21.9 mmol) was added to the reaction mixture dropwise with stirring. The flask was then fitted with a reflux condenser and heated to the 80 °C, and the reaction mixture was then stirred at this temperature for 4 h. On cooling, the solvent was removed *in vacuo* and the residue diluted with DCM (20 mL). This DCM mixture was filtered through celite and concentrated under reduced pressure to reveal an off white solid. The solid was collected by filtration and washed with acetone to give the desired product **3·HBr** as a bright white solid (3.46 g, 93% yield).



3·HBr

mp: 240-241 °C.

FTIR (neat): 3028, 2910, 2752, 1761, 1628, 1558, 1495, 1452 $cm^{-1.}$

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.33 (s, 1H, NCHN), 7.47-7.42 (m, 4H, ArH), 7.41-7.36 (, 2H, ArH), 7.34-7.31 (m, 4H, ArH), 5.45 (s, 4H, CH_2Ar), 2.13 (s, 6H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ 135.3, 134.2, 129.0, 128.5, 127.7, 127.1, 49.6, 8.0.

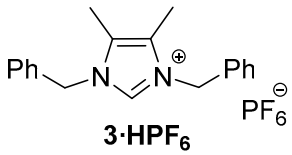
HRMS (positive NSI): m/z calc'd for $C_{19}H_{21}N_2$ $[M]^+$: 277.1699; found: 277.1699.

HRMS (negative NSI): peaks observed at m/z 78.9 and 80.9 in a 1:1 ratio of abundance, consistent with a bromide anion.

Preparation of *N*,*N*'-Dibenzyl-4,5-dimethylimidazolium hexafluorophosphate 3·HPF_6

N,*N*'-Dibenzyl-4,5-dimethylimidazolium bromide **3·HBr** (1.0 g, 2.80 mmol) was dissolved in a methanol/water mixture (5 mL:5 mL) and stirred vigorously, before the addition of ammonium hexafluorophosphate (548 mg, 3.362 mmol) to the reaction vessel in one portion, causing immediate precipitation of a bright white solid. After stirring for 16 h at room temperature, the solid was collected by filtration, washed with diethyl ether then dried in a vacuum oven (0.1 mbar, 40 °C) overnight to give the product **3·HPF_6** as a colourless crystalline solid (1.180 g, 99% yield).

X-ray quality crystals were grown by recrystallisation of **3·HPF_6** from hot chloroform.



3·HPF_6

mp: 139-140 °C.

FTIR (neat): 3159, 3105, 2752, 1973, 1638, 1564, 1497, 1452, 1352, 1213, 1184 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (s, 1H, NCHN), 7.47-7.37 (m, 6H, ArH), 7.33-7.30 (m, 4H, ArH), 5.42 (s, 4H, CH_2Ar), 2.13 (s, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 134.2, 129.0, 128.5, 127.7, 127.2, 49.7, 8.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ -144.2 (septet, $^{1}J_{P\text{-}F}$ = 712 Hz, PF_6).

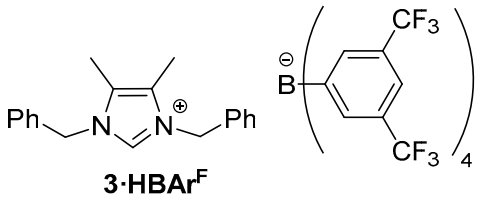
HRMS (positive NSI): m/z calc'd for $C_{19}H_{21}N_2$ $[M]^+$: 277.1699; found: 277.1699.

X-ray data: See Section 4.

Preparation of *N*,*N*'-Dibenzyl-4,5-dimethylimidazolium tetrakis[(3,5-trifluoromethylphenyl)]borate, 3·$HBAr^F$

Following a related procedure for salt metathesis to the corresponding BArF salt,[13] imidazolium bromide **3·HBr** (40 mg, 0.112 mmol) and $NaBAr^F$ (100 mg, 0.113 mmol) were added to a round-bottom flask and dissolved in a 1:1 mixture of DCM and H_2O (5 mL:5 mL). The reaction mixture was stirred for 16 h, ensuring that the organic and aqueous phases stirred without a visual bilayer. The reaction mixture was subsequently transferred to a separating funnel and diluted with DCM (5 mL). The organic phase was separated, and the

aqueous phase was washed with DCM (5 mL). The combined organic phases were washed with water (10 mL) then brine (10 mL). The DCM was phase was dried over sodium sulfate, the solvent was removed *in vacuo* and the residue passed through a short plug of silica, eluting with DCM. Removal of the solvent *in vacuo* once more gave the desired product **3·HBAr^F** as a white solid (118 mg, 92% yield).



3·HBAr^F

mp: 92-94 °C.

FTIR (neat): 2959, 1609, 1562, 1458, 1437, 1352, 1273, 1123 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (br s, 8H, ArH_{BArF}), 7.55 (s, 1H, NCHN), 7.50 (br s, 4H, ArH_{BArF}), 7.43-7.34 (m, 6H, ArH), 7.06-7.02 (m, 4H, ArH), 4.99 (s, 4H, CH_2Ar), 2.12 (s, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 49.5 Hz), 134.9, 131.9, 130.5, 130.3, 130.2, 129.2, 129.0, 128.8, 127.9, 121.9 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 117.6, 51.8, 8.6.

^{11}B NMR (128 MHz, $CDCl_3$): δ -6.62 [BAr^F $B(Ar_4)$].

^{19}F NMR (365 MHz, $CDCl_3$): δ -62.38 (BAr^F CF_3).

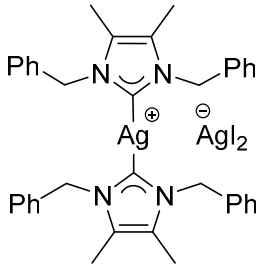
HRMS (positive ESI): m/z calc'd for $C_{19}H_{21}N_2$ $[M]^+$: 277.1699; found: 277.1703.

HRMS (negative ESI): m/z calc'd for $C_{32}H_{12}BF_{24}$ $[BAr^F]^-$: 863.0660; found: 863.0623.

2.2 Procedures relating to Manuscript Section 2.2

Preparation of bis(*N*,*N*'-dibenzyl-4,5-dimethylimidazol-2-ylidene)silver(I) silver diiodide 11

In a modification of published procedures,[14,15] a flame-dried round-bottom flask fitted with a stopcock sidearm was charged with silver(I) oxide (65 mg, 0.280 mmol), sodium iodide (84 mg, 0.560 mmol), and **3·HBr** (200 mg, 0.560 mmol). Dry DCM (5 mL) was added to the solid mixture with stirring, and the resulting black mixture was stirred under an argon atmosphere for 16 h. During the course of the reaction, the black colour of the reaction mixture turned clear, leaving a grey-white precipitate out of solution. The reaction mixture was diluted with DCM and filtered through celite to produce a colourless solution. Addition of hexane (5-10 mL) and removal of half the solvent mixture under reduced pressure led to the precipitation of the product **11** as a bright white solid (252 mg, 88%).



11

mp: > 200 °C (dec.).

FTIR (neat): 3063, 3028, 2999, 2949, 1645, 1494, 1454, 1389 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 12H, ArH), 7.16-7.11 (m, 8H, ArH), 5.34 (s, 8H, CH_2Ar), 1.98 (s, 12H, CH_3).

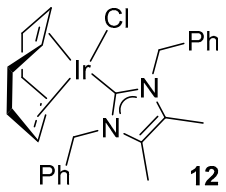
^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 136.4, 129.0, 128.0, 126.9, 126.2, 53.3, 84.

HRMS (positive NSI): m/z calc'd for $C_{38}H_{40}AgN_4$ $[M]^+$: 859.2298; found: 859.2297.

Preparation of chloro(η^4–cycloocta-1,5-diene)(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) iridium(I) 12 from 11

To a flame-dried round bottom flask fitted with a stopcock sidearm was added η^4-(cycloocta-1,5-diene)iridium(I) chloride dimer **13** (131 mg, 0.195 mmol) and dry DCM (20 mL). To this stirred, orange solution was added silver complex **11** (200 mg, 0.195 mmol) in one portion, causing the immediate formation of a bright yellow, opaque reaction mixture. After stirring for 1 h, the mixture was filtered through celite and the filtrate concentrated *in vacuo*. Subsequent dilution of the crude product with diethyl ether and scratching the inside of the glassware with a spatula initiated immediate crystallisation of the product complex **12**. The product was collected by filtration and washed with cold diethyl ether (5 mL) to yield **12** as a yellow, crystalline solid (212 mg, 89% yield).

X-ray quality crystals were grown *via* slow diffusion of diethyl ether into a DCM solution of the product at 4 °C overnight.



12

mp: 224-226 °C

FTIR (neat): 3051, 2951, 2924, 2872, 2826, 1655, 1602, 1497, 1452, 1391 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 4H, ArH), 7.30-7.24 (m, 6H, ArH), 5.84 (d, ^{2}J = 16.1 Hz, 2H, CH_2Ar), 5.72 (d, ^{2}J = 16.1 Hz, 2H, CH_2Ar), 4.56-4.53 (m, 2H, COD CH), 2.87-2.85 (m, 2H, COD CH), 2.12-2.02 (m, 2H, COD CH_2), 1.92-1.83 (overlapping m and s, 8H, COD CH_2, CH_3), 1.64-1.57 (m, 2H, COD CH_2), 1.43-1.36 (m, 2H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.6, 137.5, 128.8, 127.5, 126.8, 125.6, 84.3, 52.5, 52.2, 33.5, 29.4, 9.6

HRMS (positive NSI): m/z calc'd for $C_{27}H_{32}{}^{191}IrN_2$ $[M]^+$: 469.1251; found: 469.1246.

X-ray Data: See Section 4.

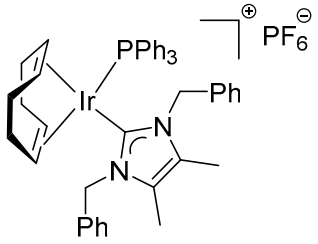
One-pot preparation of chloro(η^4–cycloocta-1,5-diene)(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) iridium(I) 12 from 3·HBr

A flame-dried round-bottom flask fitted with a stopcock sidearm was charged with silver(I) oxide (324 mg, 1.40 mmol), sodium iodide (149 mg, 2.80 mmol), and **3·HBr** (1.0 g, 2.8 mmol). Dry DCM (30 mL) was added to the solid mixture with stirring, and the resulting black mixture was stirred under an argon atmosphere for 16 h. On observing the black to clear colour change (indicating the formation of **11**), η^4-(cycloocta-1,5-diene)iridium(I) chloride dimer **13** (937 mg, 1.40 mmol) was added to the reaction vessel in one portion, causing the same clear to bright yellow colour change as above. After 3 h stirring at room temperature, the mixture was filtered through celite and the filtrate concentrated *in vacuo*. Subsequent dilution of the crude product with diethyl ether and scratching the inside of the glassware with a spatula initiated immediate crystallisation of the desired product. The product was collected by filtration and washed with a minimal amount of cold diethyl ether (5 mL) and petroleum ether (10 mL) to yield complex **12** as a yellow, crystalline solid (1.588 g, 93%. yield).

Preparation of η^4–cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) hexafluorophosphate 6a

To a flame-dried round-bottom flask fitted with stopcock sidearm was added complex **12** (100 mg, 0.163 mmol), triphenylphosphine (43 mg, 0.163 mmol), and dry THF (5 mL). On formation of a homogeneous yellow solution after 5 min stirring, silver hexafluorophosphate (41 mg, 0.163 mmol) was added to the reaction vessel in one portion, causing a yellow to opaque red colour change. After stirring the reaction mixture at room temperature for 16 h, the reaction mixture was directly filtered through celite in air, rinsing the celite with DCM before concentrating the filtrate *in vacuo*. The resulting red solid was precipitated from a solution of diethyl ether by addition of ethanol, to give complex **6a** as a red microcrystalline solid (121 mg, 75% yield).

X-ray quality crystals were grown via slow evaporation of a $CDCl_3$ solution of **6a** at room temperature over 2 weeks.



6a

mp: > 228 °C (dec.).

FTIR (neat): 2959, 2932, 1497, 1477, 1435, 1094 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.42 (m, 15H, ArH), 7.41-7.36 (m, 4H, ArH), 7.33-7.28 (m, 2H, ArH), 7.02-6.97 (m, 4H, ArH), 5.91 (d, ^{2}J = 16.7 Hz, 2H, CH_2Ar), 4.52 (d, ^{2}J = 16.7 Hz, 2H, CH_2Ar), 4.22-4.17 (m, 2H, COD CH), 3.71-3.68 (m, 2H, COD CH), 2.12-2.01 (m, 2H, COD CH_2), 1.86-1.74 (overlapping m and s, 8H, COD CH_2, and CH_3), 1.70-1.59 (m, 4H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0 (d, $^{2}J_{C\text{-}P}$ = 8 Hz), 136.1, 133.9, 133.8, 131.4, 130.7, 130.2, 129.5, 129.0, 128.9, 128.1, 127.9, 125.2, 87.6, 87.5, 79.7, 52.0, 31.0, 30.4, 9.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.0 (s, PPh_3), -144.2 (septet, $^{1}J_{P\text{-}F}$ = 711.2 Hz, PF_6).

HRMS (positive NSI): m/z calc'd for $C_{45}H_{47}{}^{191}IrN_2P$ $[M]^+$: 839.3102; found: 839.3099.

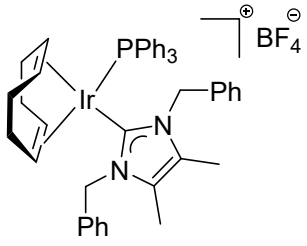
HRMS (positive NSI): m/z calc'd for $[PF_6]^-$: 144.9647; found: 144.9649.

X-ray Data: See Section 4.

Preparation of η^4–cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) tetrafluoroborate 6b

To a flame-dried round-bottom flask fitted with stopcock sidearm was added complex **12** (100 mg, 0.163 mmol), triphenylphosphine (43 mg, 0.163 mmol), and dry THF (5 mL). On formation of a homogeneous yellow solution after 5 min stirring, silver tetrafluoroborate (32 mg, 0.163 mmol) was added to the reaction vessel in one portion, causing a yellow to opaque red colour change. After stirring the reaction mixture at room temperature for 16 h, the reaction mixture was directly filtered through celite in air, rinsing the celite with DCM before concentrating the filtrate *in vacuo*. The resulting red solid was precipitated from a solution of DCM/ethanol by addition of petroleum ether, to give complex **6b** as a red microcrystalline solid (132 mg, 87% yield).

X-ray quality crystals were grown via slow diffusion of diethyl ether into a saturated DCM solution of **6b** at 4 °C over 2 d.



6b

mp: > 221 °C (dec.).

FTIR (neat): 3075, 2957, 2886, 2357, 1609, 1564, 1479, 1435, 1352, 1273 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.43 (m, 15H, ArH), 7.41-7.36 (m, 4H, ArH), 7.34-7.28 (m, 2H, ArH), 7.02-6.98 (m, 4H, ArH), 5.93 (d, ^{2}J = 16.7 Hz, 2H, CH_2Ar), 4.55 (d, ^{2} = 16.7 Hz, 2H, CH_2Ar), 4.23-4.18 (m, 2H, COD CH), 3.72-3.68 (m, 2H, COD CH), 2.11-2.02 (m, 2H, COD CH_2), 1.83-1.74 (overlapping m and s, 8H, COD CH_2, and CH_3), 1.70-1.59 (m, 4H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0 (d, $^{2}J_{C\text{-}P}$ = 8 Hz), 136.2, 134.0, 133.9, 131.4, 130.8, 120.4, 129.1, 129.0, 128.0, 127.9, 125.4, 87.5, 87.4, 79.7, 52.0, 31.0, 30.5, 9.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.0 (s, PPh_3).

^{19}F NMR (376 MHz, $CDCl_3$): δ -153.4 (s, BF_4).

^{11}B NMR (128 MHz, $CDCl_3$): δ -0.72 (s, BF_4).

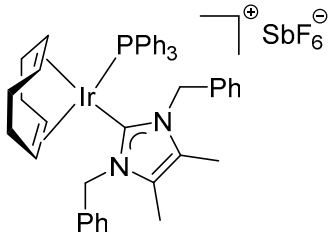
HRMS (positive NSI): m/z calc'd for $C_{45}H_{47}{}^{191}IrN_2P$ $[M]^+$: 839.3102; found: 839.3103.

X-ray Data: See Section 4.

Preparation of η^4–cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) hexafluoroantimonate 6c

To a flame-dried round-bottom flask fitted with stopcock sidearm was added complex **12** (100 mg, 0.163 mmol), triphenylphosphine (43 mg, 0.163 mmol), and dry THF (5 mL). On formation of a homogeneous yellow solution after 5 min stirring, silver hexafluoroantimonate (56 mg, 0.163 mmol) was added to the reaction vessel in one portion, causing a yellow to opaque red colour change. After stirring the reaction mixture at room temperature for 16 h, the reaction mixture was directly filtered through celite in air, rinsing the celite with DCM before concentrating the filtrate *in vacuo*. The resulting crude solid was triturated with petroleum ether, to give complex **6c** as a red microcrystalline solid (142 mg, 81% yield).

X-ray quality crystals were grown by layering diethyl ether on top of a $CDCl_3$ solution of **6c**. The bilayer was allowed to mix for approximately 1 week, and crystals were obtained after this time.



6c

Appearance: red, microcrystalline solid.

mp: > 224 °C (dec.).

FTIR (neat): 3053, 2909, 2878, 1607, 1497, 1433 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.36 (m, 19H, ArH), 7.33-7.28 (m, 2H, ArH), 7.02-6.97 (m, 4H, ArH), 5.91 (d, ^{2}J = 16.6 Hz, 2H, CH_2Ar), 4.51 (d, ^{2}J = 16.7 Hz, 2H, CH_2Ar), 4.23-4.17 (m, 2H, COD CH), 3.72-3.68 (m, 2H, COD

CH), 2.12-2.02 (m, 2H, COD CH_2), 1.83-1.74 (overlapping m and s, 8H, COD CH_2, and CH_3), 1.70-1.59 (m, 4H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 136.1, 133.9, 133.8, 131.4, 130.8, 130.2, 129.4, 129.1, 129.0, 126.1, 127.9, 125.3, 87.6, 87.5, 79.7, 52.0, 31.0, 30.4, 9.2

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.1 (s, PPh_3).

HRMS (positive NSI): m/z calc'd for $C_{45}H_{47}{}^{191}IrN_2P$ $[M]^+$: 839.3102; found: 839.3097.

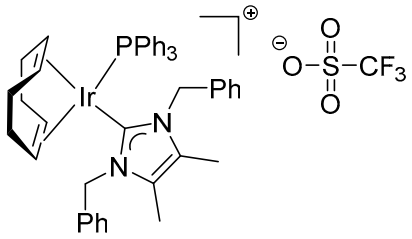
HRMS (positive NSI): m/z calc'd for $^{121}SbF_6$ $[SbF_6]^-$: 234.8948; found: 234.8942.

X-ray Data: See Section 4.

Preparation of η^4–cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) trifluoromethanesulfonate 6d

To a flame-dried round-bottom flask fitted with stopcock sidearm was added complex **12** (100 mg, 0.163 mmol), triphenylphosphine (43 mg, 0.163 mmol), and dry THF (5 mL). On formation of a homogeneous yellow solution after 5 min stirring, silver trifluoromethanesulfonate (42 mg, 0.163 mmol) was added to the reaction vessel in one portion, causing a yellow to opaque red colour change. After stirring the reaction mixture at room temperature for 16 h, the reaction mixture was directly filtered through celite in air, rinsing the celite with DCM before concentrating the filtrate *in vacuo*. The resulting crude solid was triturated with petroleum ether, to give complex **6d** as a red microcrystalline solid (142 mg, 88% yield).

X-ray quality crystals were grown via slow diffusion of diethyl ether into a saturated DCM solution of **6d** at 4 °C overnight.



6d

mp: > 224 °C (dec.).

FTIR (neat): 3061, 2949, 2922, 1657, 1497, 1433, 1395, 1220 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.37 (m, 19H, ArH), 7.35-7.29 (m, 2H, ArH), 7.02-6.97 (m, 4H, ArH), 5.92 (d, ^2J = 16.6 Hz, 2H, CH_2Ar), 4.54 (d, ^2J = 16.6 Hz, 2H, CH_2Ar), 4.24-4.19 (m, 2H, COD CH), 3.73-3.68 (m, 2H, COD CH), 2.11-2.02 (m, 2H, COD CH_2), 1.84-1.75 (overlapping m and s, 8H, COD CH_2, and CH_3), 1.71-1.63 (m, 4H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0 (d, $^2J_{C\text{-}P}$ = 8 Hz), 136.1, 134.0, 133.8, 131.5, 130.8, 130.3, 129.5, 129.1, 129.0, 128.1, 127.9, 125.3, 87.6, 87.5, 79.8, 52.1, 31.0, 30.4, 9.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.15 (s, PPh_3).

^{19}F NMR (376 MHz, $CDCl_3$): δ -77.91 (s, OTf).

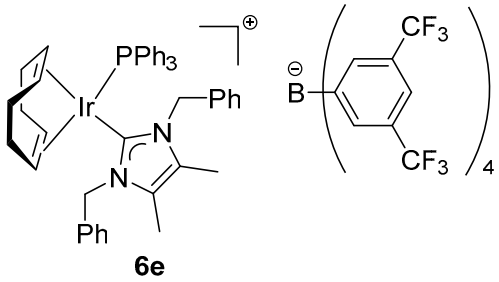
HRMS (positive NSI): m/z calc'd for $C_{45}H_{47}{}^{191}IrN_2P$ $[M]^+$: 839.3102; found: 839.3097.

HRMS (positive NSI): m/z calc'd for $[CF_3SO_3]^-$: 148.9526; found: 148.9528.

X-ray Data: See Section 4.

Preparation of η⁴–cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) tetrakis(3,5-trifluoromethylphenyl)borate 6e

To a flame-dried round-bottom flask fitted with a stopcock sidearm was added η⁴-cycloocta-1,5-dieneiridium(I) chloride dimer **13** (15 mg, 0.022 mmol) and dry THF (5 mL). The mixture was stirred, and, after all solids had dissolved, triphenylphosphine (11.4 mg, 0.044 mmol) was added in one portion, resulting in an orange to yellow colour change. After stirring the reaction mixture at room temperature for a further 5 min, the imidazolium salt **3·HBArF** (50 mg, 0.044 mmol) was added in one portion and allowed to dissolve completely. After a further 5 min stirring, potassium *t*-butoxide (8 mg, 0.066 mmol) was added in one portion, causing an immediate yellow to bright red, then black, colour change. The reaction mixture was stirred for 1 h at room temperature, then the solvent was removed *in vacuo*. The red-black residue was dissolved in DCM and passed through a short plug of silica, eluting the bright red fraction with DCM. The combined fractions were concentrated under reduced pressure to reveal a red, oily solid which was recrystallised by from EtOH/H_2O to give the product **6e** as a red crystalline solid (62 mg, 82% yield).



6e

mp: 158-160 °C.

FTIR (neat): 3080, 2928, 1608, 1499, 1435, 1352 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.70 (m, 8H, ArH_{BArF}), 7.55-7.32 (m, 25H, ArH_{BArF} + ArH), 6.95-6.89 (m, 4H, ArH), 5.92 (d, ^2J = 16.7 Hz, 2H, CH_2Ar), 4.40 (d, ^2J = 16.6 Hz, 2H, CH_2Ar), 4.26-4.21 (m, 2H, COD CH), 3.4-3.70 (m, 2H, COD CH), 2.09-1.99 (m, 2H, COD CH_2), 1.87-1.72 (overlapping m and s, 12H, COD CH_2, and CH_3), 1.71-1.57 (m, 4H, COD CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 161.8 (q, $^1J_{C\text{-}B}$ = 49.5 Hz), 135.4, 134.8, 133.7, 133.6, 131.4, 130.6, 130.1, 129.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.3, 124.6 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 117.4, 87.8, 87.7, 80.1, 52.0, 30.7, 30.3, 9.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.76 (s, PPh_3).

^{11}B NMR (128 MHz, $CDCl_3$): δ -6.59 (BAr^F).

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.43 (s, $ArCF_3$).

HRMS (positive NSI): m/z calc'd for $C_{45}H_{47}{}^{191}IrN_2P$ $[M]^+$: 839.3102; found: 839.3089.

HRMS (positive NSI): m/z calc'd for $[C_{32}H_{12}BF_{24}]^-$: 863.0660; found: 863.0639.

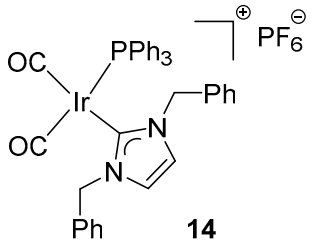
X-ray Data: See Section 4.

2.3 Procedures relating to Manuscript Section 2.3

Preparation of dicarbonyl(1,3-dibenzylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 14

The reaction was carried out in a Radley's carousel. Complex **7** (65 mg, 0.068 mmol) was dissolved in DCM (5 mL) in an oven-dried carousel tube. Under an argon atmosphere, the stirred reaction mixture was cooled to -78 °C, then the tube was evacuated and back-filled with CO gas *via* a balloon. The carousel was transferred to the heating block and stirred at room temperature for 1 h. In this time, a red to yellow/orange colour change was observed. The reaction volume was reduced by half before adding dry Et_2O dropwise (~5 mL) to precipitate the product from DCM, giving complex **14** as a bright yellow solid (30 mg, 49% yield).

X-ray quality crystals were obtained *via* slow diffusion of Et_2O in a saturated DCM solution of the **14** at room temperature.



14

mp: 155-157 °C

FTIR (neat): 3161, 3134, 2922, 2852, 2054, 1973, 1687, 1591, 1552, 1472, 1404, 1379, 1367, 1223, 1165, 1111, 1034, 945, 773 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.60 (m, 3H, ArH), 7.57–7.51 (m, 6H, ArH), 7.40–7.28 (m, 12H, ArH), 7.10–7.03 (overlapping s and m, 6H, NCH=CHN + ArH), 4.97 (d, ^2J = 16.0 Hz,, 2H, $ArCH_2$), 4.49 (d, ^2J = 16.0 Hz, 2H, $ArCH_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 133.9, 133.8, 132.8, 130.0, 129.9, 129.3, 129.0, 128.8, 128.2, 128.0, 124.5, 55.0. Note: carbonyl and carbene carbons not observed.

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.52 (app t, $^3J_{P\text{-}H}$ = 10 Hz, PPh_3), -144.25 (septet, $^1J_{P\text{-}F}$ = 711 Hz, PF_6).

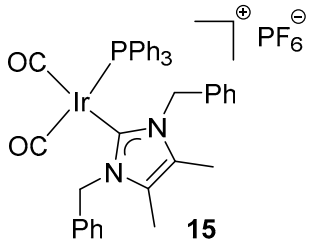
^{19}F NMR (376 MHz, $CDCl_3$): δ -72.90 (d, $^1J_{P\text{-}F}$ = 711 Hz, PF_6).

X-Ray: See Section 4.

Preparation of dicarbonyl(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 15

The reaction was carried out in a Radley's carousel. Complex **6a** (180 mg, 0.183 mmol) was dissolved in DCM (5 mL) in an oven-dried carousel tube. Under an argon atmosphere, the stirred reaction mixture was cooled to -78 °C, then the tube was evacuated and back-filled with CO gas *via* a balloon. The carousel was transferred to the heating block and stirred at room temperature for 1 h. In this time, a red to yellow/orange colour change was observed. The reaction volume was reduced by half before adding dry Et_2O dropwise (~5 mL) to triturate the product from DCM, giving complex **15** as a bright yellow solid (86 mg, 50% yield).

X-ray quality crystals were obtained *via* slow diffusion of Et_2O in a saturated DCM solution of **15** at room temperature.



15

mp: 160-161 °C

FTIR (neat): 2980, 2073, 2014, 1651, 1435, 1097, 883 cm^{-1}.

FTIR (CH_2Cl_2): 3067, 2083, 2025, 1437, 1275, 1256, 1098, 847, 768, 690 cm^{-1-}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.60 (m, 3H, ArH), 7.58–7.53 (m, 6H, ArH), 7.51–7.44 (m, 6H, ArH), 7.40–7.31 (m, 6H, ArH), 7.00–6.95 (m, 4H, ArH), 5.26 (d, ^2J = 16.2 Hz, 2H, $ArCH_2$), 4.53 (d, ^2J = 16.2 Hz, 2H, $ArCH_2$), 1.86 (s, 6H, $ArCH_3$).

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.05 (s, PPh_3), -144.30 (septet, $^1J_{P\text{-}F}$ = 710 Hz, PF_6).

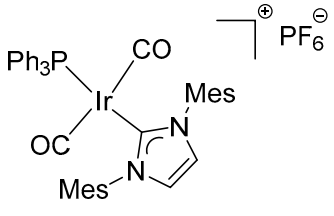
^{19}F NMR (376 MHz, $CDCl_3$): δ -73.2 (d, $^1J_{P\text{-}F}$ = 710 Hz, PF_6).

X-Ray: See Section 4.

Preparation of dicarbonyl(dimesitylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 16

The reaction was carried out in a Radley's carousel. Complex **1a** (200 mg, 0.198 mmol) was dissolved in DCM (5 mL) in an oven-dried carousel tube. Under an argon atmosphere, the stirred reaction mixture was cooled to -78 °C, then the tube was evacuated and back-filled with CO gas *via* a balloon. The carousel was transferred to the heating block and stirred at room temperature for 1 h. In this time, a red to yellow (or orange) colour change was observed. The reaction volume was reduced by half before adding dry Et_2O dropwise (~5 mL) to triturate the product from DCM, giving complex **16** as a bright orange solid (130 mg, 68% yield).

X-ray quality crystals were obtained *via* slow diffusion of Et_2O in a saturated DCM solution of **16** at room temperature.



16

mp: > 195 °C (dec.).

FTIR (CH_2Cl_2): 3169, 3140, 3072, 2924, 2010, 1991, 1609, 1483, 1436, 1234, 847 cm^{-1}.

FTIR (neat): 2980, 2052, 1994, 1981, 1483, 1435, 1030, 833 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.50 (m, 3H, ArH), 7.49 (s, 2H, NCH=CHN), 7.47–7.39 (m, 6H, ArH), 7.16–7.06 (m, 10H, ArH), 2.39 (s, 6H, $ArCH_3$), 2.09 (s, 12H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 133.4, 133.3, 132.7, 130.0, 129.5, 129.3, 126.2, 100.1, 21.3, 18.2.

^{31}P NMR (162 MHz, $CDCl_3$): δ -4.10 (br s), -7.7 (s), -144.3 (septet, $^1J_{P\text{-}F}$ = 711 Hz, PF_6).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.7 (d, $^1J_{P\text{-}F}$ = 711 Hz, PF_6).

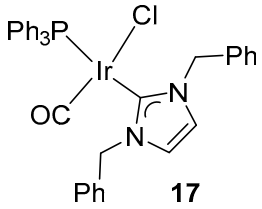
HRMS (positive ESI): m/z calc'd for $C_{40}H_{39}{}^{191}IrN_2OP$ $[M–CO]^+$: 787.2426; found: 787.2423.

HRMS (negative ESI): m/z calc'd for PF_6 $[M]^-$: 144.9647; found: 144. 9649.

X-Ray: See Section 4.

Preparation of chloro(carbonyl)(1,3-dibenzylimidazol-2-ylidene)(triphenylphosphine)iridium(I) 17[14]

Chloro(η^4–cycloocta-1,5-diene)(1,3-dibenzylimidazol-2-ylidene)iridium(I) **S2** (206 mg, 0.353 mmol) was added to a flame-dried Schlenk tube under an argon atmosphere then dissolved in dry DCM (5 mL). At room temperature, the flask was placed under a light vacuum before sealing the system. The argon/vacuum line was replaced by a CO balloon before re-opening the Schlenk flask valve. The mixture was stirred at room temperature for 1 h, after which time the reaction mixture had turned from dark- to light-yellow. After this time, the flask was flushed with argon, and triphenylphosphine (92 mg, 0.351 mmol) was added slowly in one portion. This addition caused some effervescence due to the substitution of a CO ligand by phosphine. After a further 1 h stirring, the volume of DCM was reduced by half before precipitating the product as a yellow solid by the addition of dry Et_2O, to give complex **17** as a yellow solid (114 mg, 42% yield).



17

FTIR (CH_2Cl_2): 3049, 1950, 1497, 1481, 1454, 1435, 1406, 1271, 1260, 1096, 756, 731, 702 cm^{-1}.

FTIR (neat): 3100, 1942, 1604, 1585, 1570, 1495, 1479, 1408, 1207, 1096, 692 cm^{-1}.

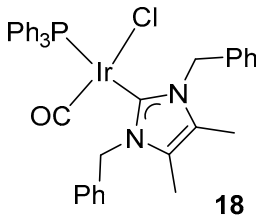
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.70 (m, 6H, ArH), 7.47–7.45 (m, 4H, ArH), 7.40–7.33 (m, 15H, ArH), 6.82 (s, 2H, NCH=CHN), 5.93 (d, ^2J = 14.7 Hz, 2H, $ArCH_2$), 5.67 (d, ^2J = 14.7 Hz, 2H, $ArCH_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6 (d, $^3J_{C\text{-}P}$ = 114.9), 170.5 (d, $^3J_{C\text{-}P}$ = 10.2 Hz), 136.4, 134.8, 134.7, 134.1, 133.6, 129.8, 128.8, 128.6, 128.1, 127.9, 127.8, 120.7, 55.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.3 (PPh_3).

Preparation of chloro(carbonyl)(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene)(triphenylphosphine)iridium(I) 18

Chloro(η^4–cycloocta-1,5-diene)(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) iridium(I) **12** (185 mg, 0.302 mmol) was added to a flame-dried Schlenk tube under an argon atmosphere then dissolved in dry DCM (5 mL). At room temperature, the flask was placed under a light vacuum before sealing the system. The argon/vacuum line was replaced by a CO balloon before re-opening the Schlenk flask valve. The mixture was stirred at room temperature for 1 h, after which time the reaction mixture had turned from dark- to light-yellow. After this time, the flask was flushed with argon, and triphenylphosphine (79 mg, 0.302 mmol) was added slowly in one portion. This addition caused some effervescence due to the substitution of a CO ligand by phosphine. After a further 1 h stirring, the volume of DCM was reduced by half before precipitating the product as a yellow solid by the addition of dry Et_2O, to give complex **18** as a yellow solid (183 mg, 76% yield).



18

mp: 228 °C

FTIR (CH_2Cl_2): 3053, 1948, 1497, 1435, 1096, 746 cm^{-1}.

FTIR (neat): 3055, 1944, 1603, 1587, 1495, 1433, 1394, 1116, 858, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.59 (m, 5H, ArH), 7.42–7.26 (m, 20H, ArH), 6.13 (d, ^2J = 16.0 Hz, 2H, $ArCH_2$), 5.62 (d, ^2J = 16.0 Hz, 2H, $ArCH_2$), 1.91 (s, 6H, $ArCH_3$).

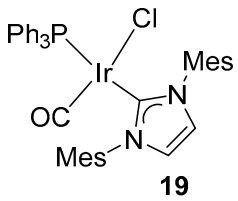
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 137.2, 134.9, 134.8, 134.1, 133.6, 129.9, 128.8, 128.0, 127.9, 127.6, 127.4, 125.7, 52.8, 9.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 24.10 (s, PPh_3).

HRMS (positive ESI): m/z calc'd for $C_{37}H_{35}{}^{191}IrN_2P$ $[M–CO]^+$: 789.2219; found: 789.2215.

Preparation of chloro(carbonyl)(1,3-dimesitylimidazol-2-ylidene)(triphenylphosphine)iridium(I) 19

Chloro(η^4–cycloocta-1,5-diene)(1,3-dimesitylimidazol-2-ylidene)iridium(I) **S1** (200 mg, 0.312 mmol) was added to a flame-dried Schlenk tube under an argon atmosphere, then dissolved in dry DCM (5 mL). At room temperature, the flask was placed under a light vacuum before sealing the system. The argon/vacuum line was replaced by a CO balloon before re-opening the Schlenk flask valve. The mixture was stirred at room temperature for 1 h, after which time the reaction mixture had turned from dark- to light-yellow. After this time, the flask was flushed with argon, and triphenylphosphine (82 mg, 0.312 mmol) was added slowly in one portion. This addition caused some effervescence due to the substitution of a CO ligand by phosphine. After a further 1 h stirring, the volume of DCM was reduced by half before precipitating the product as a yellow solid by the addition of dry Et_2O, to give complex **19** as a yellow solid (120 mg, 47% yield).



19

mp: > 195 °C (dec.)

FTIR (CH_2Cl_2): 3057, 2991, 2920, 1942, 1607, 1481, 1435, 1255, 708 cm^{-1}.

FTIR (neat): 2980, 2907, 1928, 1479, 1433, 1404, 1379, 1332, 1095, 847 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.34 (m, 6H, ArH), 7.31–7.25 (m, 3H, ArH), 7.24–7.18 (m, 6H, ArH), 7.09 (s, 2H, NCH=CHN), 7.01 (s, 4H, ArH), 2.42 (s, 6H, $ArCH_3$), 2.28 (s, 12H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8 (d, $^2J_{C\text{-}P}$ = 12 Hz), 138.4, 136.4, 136.0, 135.1, 135.0, 134.2, 133.7, 129.5, 129.0, 127.6, 127.5, 122.82, 122.76, 21.4, 19.1,

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.6 (s, PPh_3).

HRMS (positive ESI): m/z calc'd for $C_{40}H_{39}{}^{191}IrN_2OP$ $[M\text{-}Cl]^+$: 787.2426; found: 787.2429.

Generation of MeCN-d_3-stabilised Ir(III)-dihydride Complexes *in situ*

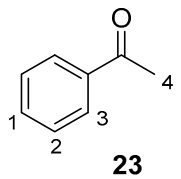
The complex of interest (~10 mg) was dissolved in MeCN-d_3 (0.6 mL) and transferred to an oven-dried NMR tube, which was then sealed with a rubber septum. Hydrogen gas was bubbled through the solution carefully for 30 min, taking care not to force the solution from the tube. After this time, the sample was analysed directly by NMR spectroscopy at 300 K.

2.4 Procedures relating to Manuscript Section 2.4

*Rate Monitoring for the Deuteration of Acetophenone **23** with Catalysts **6a** and **7***

A three-necked round-bottom flask fitted with one stopcock side arm and two Subaseals was flame-dried. To this flask was added the iridium(I) complex, **6a** (21.2 mg, 0.0215 mmol, 1 mol%) or **7** (20.5 mg, 0.0215 mmol, 1 mol%), and acetophenone **23** (0.28 mL, 2.150 mmol). The solvent, DCM (25mL), was added, rinsing the inner walls of the flask, and one Subaseal was replaced with a greased glass stopper. The reaction solution was placed under an atmosphere of argon and stirred whilst being cooled to -78 °C in a dry ice/acetone bath. The flask was twice evacuated and flushed with argon at this temperature. Following a third evacuation, an atmosphere of deuterium gas was introduced to the flask via a balloon. The deuterium balloon was left in place for the duration of the reaction to ensure a continuous supply of deuterium. The cold bath was removed and the flask warmed in oil bath to 25 °C. The reaction mixture was stirred for 2 h. An aliquot (0.2 mL) of the reaction mixture was removed at intervals of 10, 20, 30, 40, 50, 60, and 120 min. Each aliquot was transferred to a vial containing diethyl ether. After removal of solvent *in vacuo*, the residue was analysed by ^{1}H NMR spectroscopy. The extent of labelling was determined using **Equation 1**.

Data for acetophenone **23**:



23

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.5 Hz, 2H, ArH^3), 7.56 (t, *J* = 7.4 Hz, 1H, ArH^1), 7.46 (t, *J* = 7.4 Hz, 2H, ArH^2), 2.60 (s, 3H, CH_3^4).

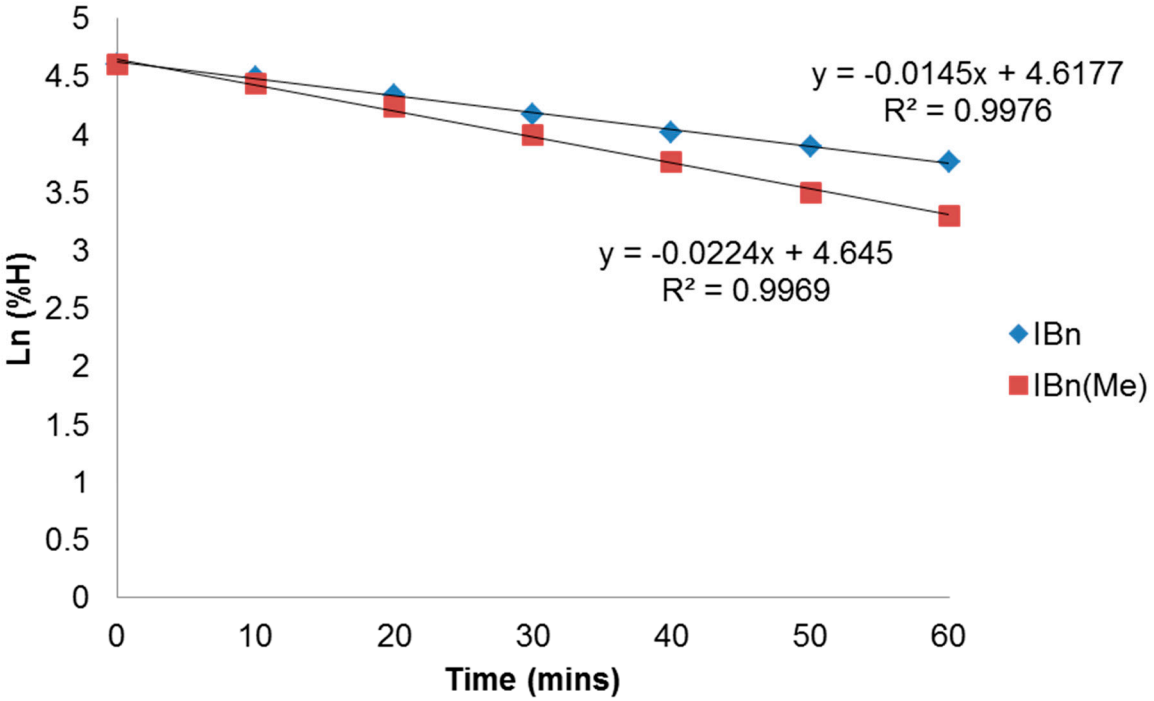
Incorporation expected at δ 7.95. Determined against integral at δ 2.60.

The raw data is detailed below in Table S1:

Table S1. Kinetic data for labelling of **23** using catalysts **6a** and **7**.

Entry[a]	*Time (min)*	*%D (catalyst **7**)*	*%D (catalyst **6a**)*
1	10	10	17
2	20	24	31
3	30	34	45
4	40	44	56
5	50	50	64
6	60	56	70
7	120	70	84

As these reaction were carried out with a vast excess of substrate and D_2 *versus* catalyst, the conditions can be described as pseudo first order in catalyst. Therefore, a plot of *ln*(%H) *versus* time gives a straight line representing first order decay of substrate with a gradient of $-k_{obs}$. The positive value of this gradient is what is quoted in the manuscript. See a graphical illustration below:

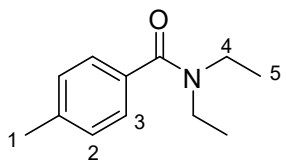


Evaluation of Counter-ion influence in the IBn^{Me}/PPh_3 complexes 6a-6e

All substrates for labelling were commercially available, except for *N*,*N*-diethyl-*p*-toluamide **28**, which was prepared as described below.

Preparation of *N*,*N*-diethyl-*p*-toluamide 28[16]

A solution of p-toluoyl chloride (1.99 g, 12.9 mmol) in DCM (50 mL) was cooled to 0 °C in an ice bath, and diethylamine (3.34 mL, 32.3 mmol) was added dropwise. The solution was stirred at 0 °C for 30 min, then allowed to warm to room temperature and stirred for 16 h. The reaction mixture was then washed with an aqueous solution of HCl (3 M, 3 × 100 mL) and saturated aqueous sodium bicarbonate (100 mL), then dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure delivered amide **28** as a white crystalline solid (2.06 g, 83% yield).



28

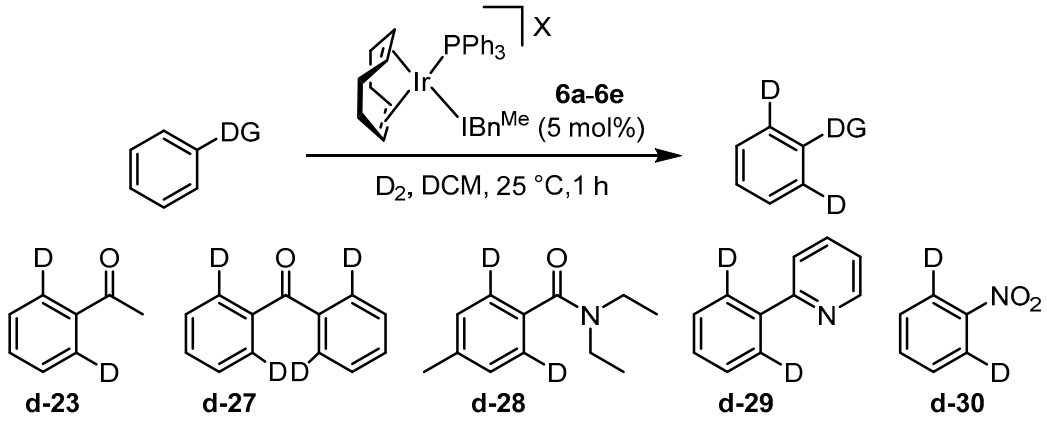
mp: 55-56 °C (lit.[16] 53.5-55.5 °C)

FTIR (CH_2Cl_2): 2972, 2874, 1618, 1429 cm^{-1}.

^{1}H NMR (400 MHz, d_6-acetone): δ 7.27-7.21 (m, 4H, ArH^2 + ArH^3), 3.54-3.31 (m, 4H, NCH_2^4), 2.35 (s, 3H, $ArCH_3^1$), 1.13 (br s, 6H, $NCH_2CH_3^5$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 139.0, 134.4, 128.9, 126.3, 43.3, 39.2, 21.3, 14.2, 12.9

Labelling of substrates 23, 27, 28, 29 and 30



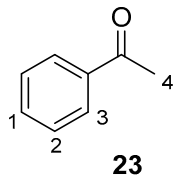
Scheme S1

Scheme S1 represents the assessment of five different catalysts **6a**-**6e** (X = BF_4, PF_6, SbF_6, OTf, and BArF) at 25 °C, applying substrates **23**, **27**, **28**, **29**, and **30**.

All reactions were carried out using a Radley's 12-chamber carousel. The water inlet for the carousel reflux system was turned on prior to any further reaction set up. To a 25 mL oven-dried carousel tube was added the substrate of choice (0.215 mmol, unless otherwise stated) and iridium(I) catalyst (0.01075 mmol, 5 mol%, unless otherwise stated) under air. DCM (2.5 mL, unless otherwise stated) was added, rinsing the inner walls of the tube. The tube was then sealed at the screw cap (with gas inlet left open) and reconnected to the carousel rack. After charging all necessary carousel tubes with reactants, the tubes were cooled to -78 °C and the air in the tubes was replaced with argon. Separately, the carousel heating block was set to 25 °C. The cooled flasks on the carousel rack were twice evacuated and flushed with deuterium *via* a balloon. The carousel tube gas inlets were then closed, creating a sealed atmosphere of deuterium. After sealing the flasks, the rack was transferred to the heating block and the reaction timer was started. The reaction mixture was stirred for 1 h before removing excess deuterium and replacing with air. The solution was then washed with DCM and transferred to a single necked flask before removing the solvent under reduced pressure. The level and regioselectivity of deuterium incorporation in the substrate was determined by ^{1}H NMR spectroscopy. The integrals were calibrated against a peak corresponding to a position not expected to be labelled.

Spectroscopic details of each substrate are given below, and labelling results are summarised in Table S2 immediately following.

Data for acetophenone **23**:

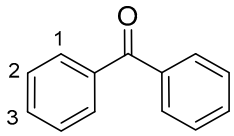


23

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.5 Hz, 2H, ArH^3), 7.56 (t, *J* = 7.4 Hz, 1H, ArH^1), 7.46 (t, *J* = 7.4 Hz, 2H, ArH^2), 2.60 (s, 3H, CH_3^4).

Incorporation expected at δ 7.95. Determined against integral at δ 2.60.

Data for benzophenone **27**:

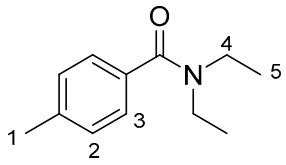


27

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.0 Hz, 4H, ArH^1), 7.59 (t, *J* = 8.0 Hz, 2H, ArH^3), 7.49 (t, *J* = 7.9 Hz, 4H, ArH^2).

Incorporation expected at δ 7.81. Determined against integral at δ 7.59.

Data for *N*,*N*-diethyltoluoylamide **28**:

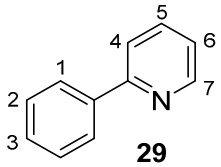


28

^{1}H NMR (400 MHz, d_6-acetone): δ 7.27-7.21 (m, 4H, ArH^2 + ArH^3), 3.54-3.31 (m, 4H, NCH_2^4), 2.35 (s, 3H, $ArCH_3^1$), 1.13 (br s, 6H, $NCH_2CH_3^5$).

Incorporation expected at δ 7.27-7.21, and determined against integral at δ 2.35.

Data for 2-phenylpyridine **29**:

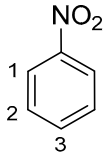


29

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.7 Hz, 1H, ArH^7), 8.00 (d, *J* = 7.1 Hz, 2H, ArH^1), 7.79-7.73 (m, 2H, ArH^5 + ArH^6), 7.52-7.41 (m, 3H, ArH^2 + ArH^3), 7.26-7.23 (m, 1H, ArH^4).

Incorporation expected at δ 8.00. Determined against integral at δ 7.79-7.73.

Data for nitrobenzene **30**:



30

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 7.7 Hz, ^4J = 1.1 Hz, 2H, ArH^1), 7.71 (tt, *J* = 7.4 Hz, ^4J = 1.1 Hz, 1H, ArH^3), 7.56 (t, ^3J = 7.4 Hz, 2H, ArH^2).

Incorporation expected at δ 8.25. Determined against integral at δ 7.71.

Table S2. Labelling of substrates **23**, **27**-**30** using catalysts **6a**-**6e**.

Entry	Substrate	%D				
		6a, X = PF_6[f]	**6b, X = BF_4**[g]	**6c, X = SbF_6**[h]	**6d, X = OTf**[i]	**6e, X = BAr^F**[j]
1	**23**[a]	96	96	96	79	97
2	**27**[b]	91	87	93	29	97
3	**28**[c]	98	87	93	43	99
4	**29**[d]	82	89	90	85	87
5	**30**[e]	5	4	5	4	16

Substrate quantities per reaction: [a] 26.0 mg; [b] 33.0 mg; [c] 39.0 mg; [d] 41.0 mg; [e] 26.0 mg.

Catalyst quantities per reaction: [f]10.6 mg, [g]10.0 mg, [h]11.6 mg, [i]10.6 mg, [j]18.3 mg.

3. Computational Chemistry

3.1 Details of Computational Methods

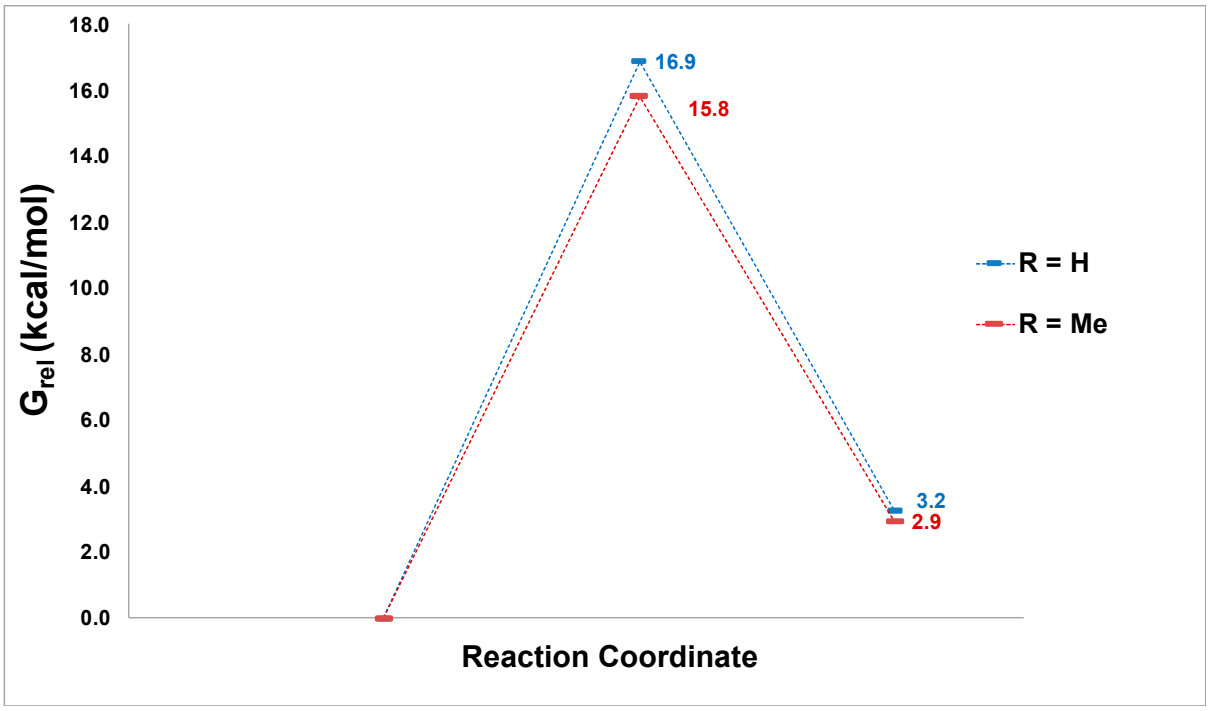
Density functional theory[17,18] (DFT) was employed to calculate the gas-phase electronic structures and energies for all species involved in model C-H activation processes. All structures were optimised with the hybrid meta-GGA exchange correlation functional M06.[19] The M06 density functional was used in conjunction with the 6-31G(*d*)[20] basis set for main group non-metal atoms and the Stuttgart RSC[21] effective core potential along with the associated basis set for Ir. The participating transition states (TS) are located at the same level of theory. Harmonic vibrational frequencies are calculated (ignoring the incorporation of deuterium) at the same level of theory to characterize respective minima (reactants, intermediates, and products with no imaginary frequency) and first order saddle points (TSs with one imaginary frequency). The validity of using the 6-31G(d) basis set has been checked in previous work by comparative single point energy calculations employing the def2-TZVP basis set for all atoms.[22] All calculations using the M06 functional have been performed using Gaussian 09 quantum chemistry program package.[23] All coordinates provided are listed in Cartesian format, with charge and multiplicity of each system given at the top of the coordinate list (i.e. 0 1 = neutral singlet; 1 1 = 1+ charged singlet).

3.2 Calculation of Percent Buried Volume for NHC and Phosphine Ligands in Complexes 14-16

All Percent Buried Volume (%V_{bur}) data were calculated using *SambVca* and *SambVca 2.0* web applications.[24] All structural geometries used as input for these calculations were derived from DFT-optimised structures and not X-ray crystal data. The main input data required to run the *SambVca* online software for each ligand are the coordinates of the ligand itself plus the central metal atom. The metal-ligand bond distance, *d*, is dictated by the result of the DFT geometry optimisation. The ligand atom coordinated to the metal and the metal atom itself were used to define the z-axis (maintaining the default Z-negative option). For NHC ligands, the xz-plane was defined using the two nitrogen atoms flanking the coordinating atom. For phosphines, the xz-plane was defined using the three atoms directly bound to the phosphorus atom. The metal atom was then deleted before proceeding with the remainder of the calculation. Default mesh spacing and sphere radius were kept constant at 0.1 Å and 3.5 Å, respectively. Importantly, the distance of the coordination point to the centre of the sphere was left as 0, as the true ligand-metal bond distance has already been set by the metal atom. Additionally, default atomic radii were described by Bondi radii scaled by 1.17. Hydrogen atoms were not included in the *%V_{bur}* calculations described. The coordinates of the ligand itself were first optimised in *Gaussian 09* as part of a full iridium(III) hydride complex cation of the formula $[(NHC)Ir(PPh_3)(H)_2(DCM)_2]^+$, and the optimised coordinates converted to .pdb format. The .pdb file was then uploaded to the SambVca web application.[24]

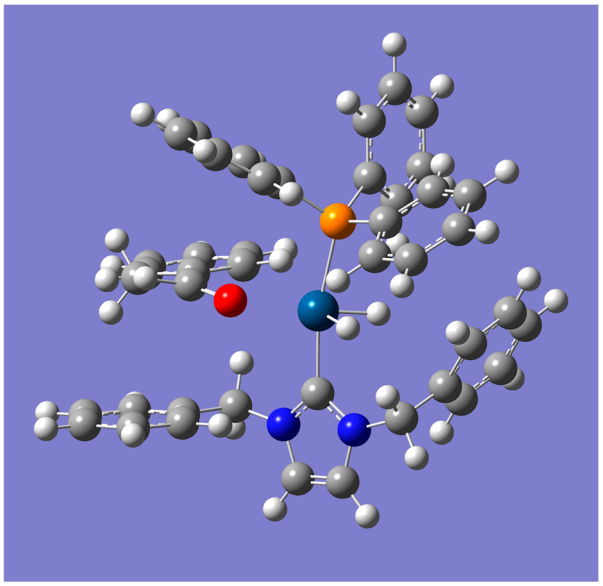
3.3 Calculated Potential Energy Surface for C-H Activation Study

Relating to Manuscript Scheme 5



Cartesian Coordinates for DFT Calculations

IBn_R (**24**, R = H)



Sum of Electronic and Zero-point Energies = -2291.378155 Hartree

Sum of Electronic and Thermal Energies = -2291.334174 Hartree

Sum of Electronic and Thermal Enthalpies = -2291.333230 Hartree

Sum of Electronic and Thermal Free Energies = -2291.459780 Hartree

Dipole Moment = 3.9643 Debye

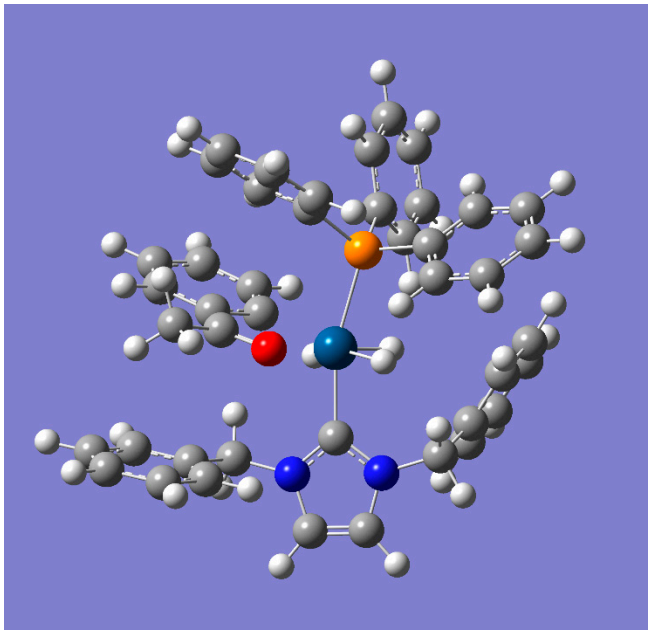
1 1

C	1.36451	-4.57125	-0.38133
C	2.46749	-4.04654	0.19244
N	0.45214	-3.54017	-0.52313
N	2.20151	-2.70432	0.39830
C	-2.00355	-3.62490	-0.09266
C	-3.15882	-2.92634	-0.44091
C	-1.89672	-4.17744	1.18316
C	-4.18792	-2.76430	0.48105
H	-3.24435	-2.47611	-1.43250
C	-2.92211	-4.01140	2.10769
H	-0.99644	-4.72684	1.46362
C	-4.06832	-3.30058	1.75968
H	-5.08085	-2.20850	0.19946
H	-2.82854	-4.44330	3.10254
H	-4.87039	-3.17060	2.48396
C	4.21469	-1.32134	-0.05649
C	4.00540	-1.40290	-1.43231
C	5.38970	-0.73571	0.42052
C	4.95780	-0.90391	-2.31782
H	3.09134	-1.85477	-1.81841
C	6.33842	-0.23220	-0.46195
H	5.55894	-0.67444	1.49744
C	6.12394	-0.31635	-1.83679
H	4.78668	-0.97881	-3.39016
H	7.25465	0.21286	-0.07772
H	6.87057	0.06542	-2.53059
C	3.19656	-1.80111	0.94733

H	2.65763	-0.95547	1.39413
H	3.69582	-2.32156	1.77678
C	-0.88345	-3.76549	-1.08831
H	-0.85723	-4.77998	-1.50968
H	-1.02925	-3.08094	-1.93361
C	0.95936	-2.36182	-0.04823
Ir	-0.04214	-0.54291	-0.08352
H	-1.17609	-1.33390	0.65766
H	-0.79546	-1.16495	-1.27875
P	-1.59496	1.22669	-0.28654
C	-0.87621	2.79367	-0.91565
C	-0.12057	3.58150	-0.03721
C	-0.92632	3.14497	-2.26586
C	0.57087	4.69439	-0.50231
H	-0.08414	3.33583	1.02535
C	-0.23223	4.25954	-2.72987
H	-1.52117	2.55701	-2.96352
C	0.52068	5.03282	-1.85290
H	1.14300	5.30438	0.19546
H	-0.28972	4.52796	-3.78314
H	1.05800	5.90620	-2.21782
C	-2.44720	1.72406	1.25095
C	-2.51905	0.82620	2.32089
C	-3.07737	2.97024	1.35732
C	-3.20659	1.17177	3.48095
H	-2.04167	-0.15136	2.23910
C	-3.76131	3.31205	2.51756
H	-3.03284	3.67515	0.52652
C	-3.82472	2.41372	3.58060
H	-3.25977	0.46621	4.30814
H	-4.24757	4.28277	2.59289
H	-4.36027	2.68426	4.48875
C	-2.93673	0.77397	-1.44943

C	-4.28414	0.88650	-1.10338
C	-2.59632	0.23224	-2.69703
C	-5.27391	0.46553	-1.98916
H	-4.56901	1.29346	-0.13413
C	-3.58593	-0.17311	-3.58438
H	-1.54598	0.12410	-2.97508
C	-4.92864	-0.06252	-3.22769
H	-6.32123	0.55382	-1.70605
H	-3.30926	-0.58232	-4.55439
H	-5.70442	-0.38874	-3.91766
C	1.73846	1.18666	3.19203
C	2.94410	1.64190	3.72332
C	3.95338	2.08722	2.87454
C	3.76449	2.07880	1.49704
C	2.57180	1.59801	0.94485
C	1.56421	1.15810	1.81635
H	0.93158	0.85899	3.84493
H	3.09208	1.65811	4.80125
H	4.89302	2.44778	3.28775
H	4.56763	2.41893	0.84565
H	0.57223	0.86310	1.43741
C	2.41074	1.49328	-0.52553
O	1.57918	0.73487	-1.03295
C	3.29743	2.29259	-1.42456
H	3.40636	3.32650	-1.07619
H	4.29784	1.83274	-1.45902
H	2.88093	2.28165	-2.43574
H	3.41368	-4.49071	0.47232
H	1.13851	-5.58051	-0.69924

IBn_TS (**25**, R = H)



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Sum of Electronic and Thermal Energies = -2291.311350 Hartree

Sum of Electronic and Thermal Enthalpies = -2291.310406 Hartree

Sum of Electronic and Thermal Free Energies = -2291.432887 Hartree

Dipole Moment = 2.5424 Debye

1 1

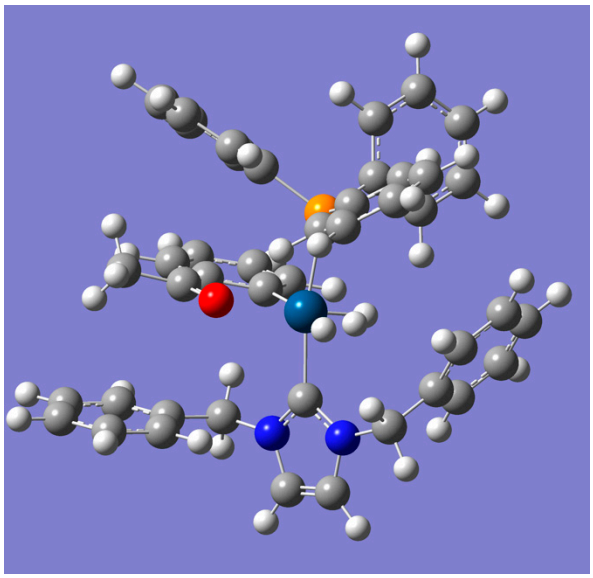
C	1.79428	4.47235	0.37082
C	2.83454	3.88884	-0.26156
N	0.82061	3.50117	0.53128
N	2.47232	2.57121	-0.48345
C	-1.64042	3.71705	0.19220
C	-2.81325	3.06790	0.57857
C	-1.55619	4.27372	-1.08393
C	-3.88317	2.96221	-0.30454
H	-2.88040	2.61181	1.56857
C	-2.62247	4.16285	-1.97035
H	-0.64321	4.78455	-1.39506
C	-3.78715	3.50353	-1.58348

H	-4.78845	2.44288	0.00650
H	-2.54622	4.59863	-2.96494
H	-4.62169	3.41772	-2.27740
C	4.40387	0.99928	-0.28460
C	4.53489	1.27935	1.07357
C	5.29284	0.10412	-0.88647
C	5.54778	0.67831	1.81840
H	3.84049	1.96438	1.56039
C	6.30424	-0.49357	-0.14433
H	5.19117	-0.11891	-1.95050
C	6.43568	-0.20400	1.21319
H	5.64333	0.90739	2.87816
H	6.99856	-1.17892	-0.62744
H	7.23147	-0.66442	1.79544
C	3.35100	1.63059	-1.16114
H	2.72050	0.86022	-1.62150
H	3.82738	2.17719	-1.98781
C	-0.47973	3.79470	1.14823
H	-0.38301	4.80365	1.57188
H	-0.62799	3.10405	1.98718
C	1.23284	2.31227	0.01150
Ir	0.14470	0.53162	-0.02026
H	-1.06458	1.37198	-0.59844
H	-0.43684	1.16768	1.36255
P	-1.55246	-1.11598	0.32935
C	-0.91579	-2.74288	0.88041
C	-0.30622	-3.59070	-0.05391
C	-0.90844	-3.10586	2.23044
C	0.29244	-4.77683	0.35576
H	-0.30925	-3.33136	-1.11282
C	-0.30338	-4.29113	2.63762
H	-1.38925	-2.47033	2.97234
C	0.29937	-5.12765	1.70352

H	0.75284	-5.42846	-0.38574
H	-0.31327	-4.56485	3.69086
H	0.76529	-6.05771	2.02393
C	-2.60483	-1.46599	-1.12084
C	-2.91808	-0.42597	-2.00284
C	-3.21057	-2.71493	-1.29313
C	-3.81513	-0.63523	-3.04427
H	-2.46837	0.55831	-1.86760
C	-4.10042	-2.92292	-2.34192
H	-2.99466	-3.52777	-0.60036
C	-4.40311	-1.88491	-3.21824
H	-4.05467	0.18311	-3.72129
H	-4.56417	-3.89910	-2.46976
H	-5.10258	-2.04942	-4.03571
C	-2.75074	-0.58704	1.61454
C	-4.12835	-0.64368	1.39180
C	-2.27877	-0.09116	2.83728
C	-5.01671	-0.20120	2.36989
H	-4.51903	-1.02271	0.44841
C	-3.16756	0.33153	3.81765
H	-1.20472	-0.02643	3.01933
C	-4.54040	0.28551	3.58105
H	-6.08769	-0.24175	2.18010
H	-2.78792	0.70609	4.76655
H	-5.23675	0.62915	4.34352
C	0.61123	-1.21073	-2.75868
C	1.25010	-2.23355	-3.45407
C	2.30094	-2.94437	-2.87360
C	2.68255	-2.64063	-1.57849
C	2.03817	-1.62052	-0.86120
C	0.99330	-0.85992	-1.45745
H	-0.20359	-0.67295	-3.24408
H	0.92972	-2.47052	-4.46752

H	2.80519	-3.73369	-3.42640
H	3.47601	-3.21440	-1.10012
H	0.39958	0.69895	-1.60281
C	2.32720	-1.39251	0.54846
O	1.68548	-0.51572	1.16204
C	3.31256	-2.21665	1.30362
H	2.99266	-3.26856	1.30866
H	4.30801	-2.16485	0.84160
H	3.37518	-1.85408	2.33287
H	1.65122	5.48573	0.72168
H	3.79700	4.27461	-0.57133

IBn_P (**26,** R = H)



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Sum of Electronic and Thermal Energies = -2291.334714 Hartree

Sum of Electronic and Thermal Enthalpies = -2291.333770 Hartree

Sum of Electronic and Thermal Free Energies = -2291.454612 Hartree

Dipole Moment = 1.8435 Debye

1 1

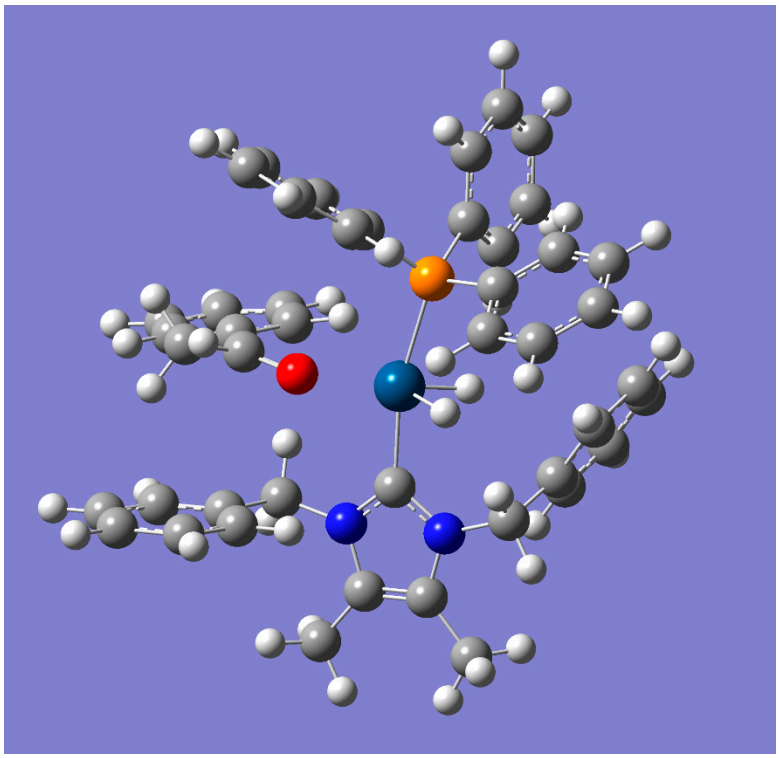
C	-1.97797	-4.43508	0.24774

C	-2.98422	-3.78733	-0.36921
N	-0.98374	-3.50015	0.48472
N	-2.58647	-2.46917	-0.50732
C	1.50478	-3.76906	0.30991
C	2.67726	-3.26903	0.87726
C	1.50897	-4.16670	-1.02690
C	3.83779	-3.15646	0.11689
H	2.68699	-2.95769	1.92489
C	2.66728	-4.05453	-1.78829
H	0.59657	-4.55926	-1.47845
C	3.83391	-3.54879	-1.21785
H	4.74336	-2.75764	0.57061
H	2.66197	-4.37197	-2.82949
H	4.74184	-3.46689	-1.81284
C	-4.39976	-0.79807	-0.11876
C	-4.36040	-1.03318	1.25310
C	-5.32955	0.11347	-0.62812
C	-5.23611	-0.36374	2.10589
H	-3.63914	-1.73862	1.66660
C	-6.20814	0.77511	0.22048
H	-5.36340	0.29887	-1.70360
C	-6.16250	0.53721	1.59388
H	-5.19571	-0.55589	3.17640
H	-6.93654	1.47244	-0.18990
H	-6.85223	1.05116	2.26051
H	-3.94599	-4.13033	-0.72658
H	-1.86753	-5.47153	0.53681
C	-3.49827	-1.49883	-1.10227
H	-2.91146	-0.78099	-1.68099
H	-4.10304	-2.05572	-1.83156
C	0.26183	-3.90447	1.14852
H	0.11075	-4.95554	1.42848
H	0.36145	-3.35865	2.09496

C	-1.34976	-2.25802	0.02891
Ir	-0.12941	-0.53644	0.14759
H	0.97598	-1.43882	1.31493
H	0.38929	-1.15545	1.82094
P	1.55376	1.15801	0.22738
C	0.93567	2.88058	0.31737
C	0.39118	3.44829	-0.84197
C	0.91567	3.61417	1.50682
C	-0.16618	4.72114	-0.80834
H	0.41235	2.89730	-1.78287
C	0.35535	4.88803	1.53748
H	1.35237	3.20189	2.41479
C	-0.18999	5.44185	0.38347
H	-0.58157	5.14905	-1.71948
H	0.35470	5.45230	2.46806
H	-0.62304	6.44016	0.40948
C	2.75462	1.19006	-1.14708
C	3.06426	0.01802	-1.84244
C	3.47010	2.36102	-1.42667
C	4.06277	0.02030	-2.81095
H	2.53096	-0.90660	-1.62086
C	4.46499	2.35975	-2.39713
H	3.25270	3.27784	-0.87913
C	4.76065	1.19020	-3.09246
H	4.29135	-0.89795	-3.34955
H	5.01280	3.27576	-2.60942
H	5.53875	1.19183	-3.85348
C	2.58949	0.91161	1.71908
C	3.97356	0.74551	1.63741
C	1.96009	0.80879	2.96828
C	4.71607	0.48345	2.78698
H	4.47838	0.81204	0.67420
C	2.70610	0.56142	4.11364

H	0.87590	0.92225	3.04352
C	4.08702	0.39387	4.02289
H	5.79416	0.35356	2.71239
H	2.20908	0.49508	5.07976
H	4.67074	0.19282	4.91911
C	-0.77915	0.31348	-2.74054
C	-1.47985	1.08168	-3.66561
C	-2.43389	2.01824	-3.25284
C	-2.66926	2.19334	-1.90041
C	-1.96503	1.42796	-0.95824
C	-1.01205	0.45584	-1.36647
H	-0.04686	-0.41329	-3.09126
H	-1.28441	0.94845	-4.72911
H	-2.97839	2.60664	-3.98805
H	-3.40305	2.92715	-1.56585
H	0.78568	-1.36757	-0.83347
C	-2.15422	1.58262	0.47732
O	-1.52600	0.83288	1.25558
C	-3.04590	2.63035	1.05016
H	-2.73997	3.62528	0.69661
H	-4.08565	2.46331	0.73363
H	-2.99593	2.59880	2.14187

IBnMe_R (**24**, R = Me)



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Sum of Electronic and Thermal Energies = -2369.853363 Hartree

Sum of Electronic and Thermal Enthalpies = -2369.852418 Hartree

Sum of Electronic and Thermal Free Energies = -2369.984221 Hartree

Dipole Moment = 4.0315 Debye

1 1

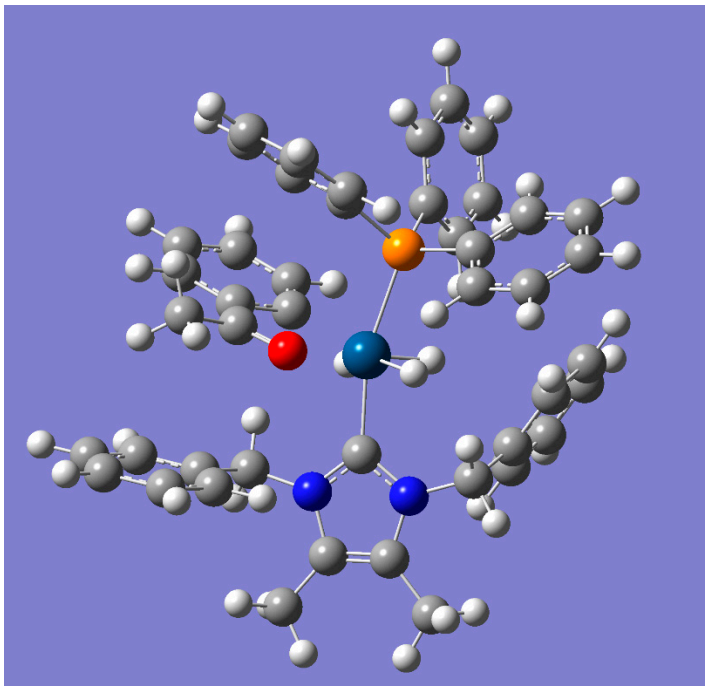
C	-2.14466	4.02867	-0.34785
C	-3.13639	3.28337	0.20299
N	-1.04286	3.18236	-0.48966
N	-2.60597	2.00842	0.39416
C	1.35550	3.72303	-0.05171
C	2.63153	3.28716	-0.40849
C	1.13971	4.22431	1.23106
C	3.67571	3.33647	0.50876
H	2.80340	2.87337	-1.40473
C	2.18294	4.27346	2.15051
H	0.14153	4.55447	1.52433

C	3.45246	3.82653	1.79256
H	4.66264	2.97780	0.22016
H	2.00390	4.66420	3.15077
H	4.26744	3.86277	2.51338
C	-4.25957	0.22493	-0.12195
C	-4.02579	0.34790	-1.49100
C	-5.30218	-0.59347	0.31963
C	-4.81850	-0.34424	-2.40352
H	-3.21553	0.98361	-1.84928
C	-6.09072	-1.28926	-0.58977
H	-5.49306	-0.68572	1.39074
C	-5.84938	-1.16580	-1.95710
H	-4.62963	-0.23697	-3.47013
H	-6.90541	-1.91710	-0.23285
H	-6.47226	-1.69975	-2.67231
C	-3.39544	0.90707	0.90960
H	-2.69646	0.19262	1.36148
H	-4.01685	1.28634	1.73262
C	0.23271	3.63339	-1.05128
H	0.04242	4.61312	-1.50664
H	0.50971	2.96424	-1.87565
C	-1.31724	1.92272	-0.03629
Ir	0.03518	0.34072	-0.06499
H	0.97068	1.36768	0.65841
H	0.62295	1.08330	-1.28332
P	1.93537	-1.04727	-0.27866
C	1.56700	-2.77086	-0.79146
C	1.05370	-3.65536	0.16636
C	1.63156	-3.18141	-2.12444
C	0.61303	-4.92104	-0.20357
H	1.01248	-3.36128	1.21646
C	1.18853	-4.44919	-2.49336
H	2.04201	-2.51642	-2.88314

C	0.67480	-5.31890	-1.53741
H	0.22835	-5.60153	0.55464
H	1.25562	-4.75986	-3.53443
H	0.33394	-6.31090	-1.82806
C	2.97644	-1.24346	1.20985
C	2.94813	-0.26220	2.20593
C	3.86843	-2.31655	1.32859
C	3.79791	-0.35459	3.30452
H	2.26671	0.58450	2.11294
C	4.71149	-2.40777	2.42939
H	3.90629	-3.08127	0.55227
C	4.67648	-1.42702	3.41819
H	3.77220	0.41679	4.07230
H	5.40100	-3.24547	2.51482
H	5.33894	-1.49983	4.27876
C	3.07217	-0.36768	-1.54673
C	4.42474	-0.14302	-1.28437
C	2.54931	0.00210	-2.79411
C	5.24053	0.43878	-2.25251
H	4.84797	-0.41112	-0.31721
C	3.36874	0.56881	-3.76292
H	1.48930	-0.15263	-3.00630
C	4.71702	0.79276	-3.49054
H	6.29269	0.61299	-2.03460
H	2.95330	0.84199	-4.73129
H	5.35759	1.24485	-4.24531
C	-1.37114	-1.59244	3.24438
C	-2.48023	-2.24169	3.78420
C	-3.36899	-2.91148	2.94813
C	-3.15542	-2.93464	1.57437
C	-2.06456	-2.26197	1.01264
C	-1.17583	-1.59709	1.87099
H	-0.65645	-1.08486	3.88943

H	-2.64534	-2.23313	4.85973
H	-4.23215	-3.42325	3.36859
H	-3.86567	-3.45114	0.93095
H	-0.25038	-1.13701	1.48635
C	-1.90596	-2.18830	-0.45966
O	-1.25499	-1.28565	-0.99384
C	-2.58455	-3.19573	-1.33078
H	-2.54986	-4.20512	-0.90563
H	-3.64121	-2.91022	-1.45947
H	-2.10809	-3.18914	-2.31545
C	-4.52912	3.63225	0.57544
H	-4.76358	4.65465	0.26213
H	-5.25711	2.96476	0.09387
H	-4.69455	3.57770	1.66071
C	-2.13489	5.45945	-0.74271
H	-1.34123	6.02414	-0.23378
H	-1.99855	5.59486	-1.82452
H	-3.08766	5.92813	-0.47556

IBnMe_TS (**25**, R = Me)



Sum of Electronic and Zero-point Energies = -2369.877353 Hartree

Sum of Electronic and Thermal Energies = -2369.831091 Hartree

Sum of Electronic and Thermal Enthalpies = -2369.830147 Hartree

Sum of Electronic and Thermal Free Energies = -2369.959034 Hartree

Dipole Moment = 2.5061 Debye

1 1

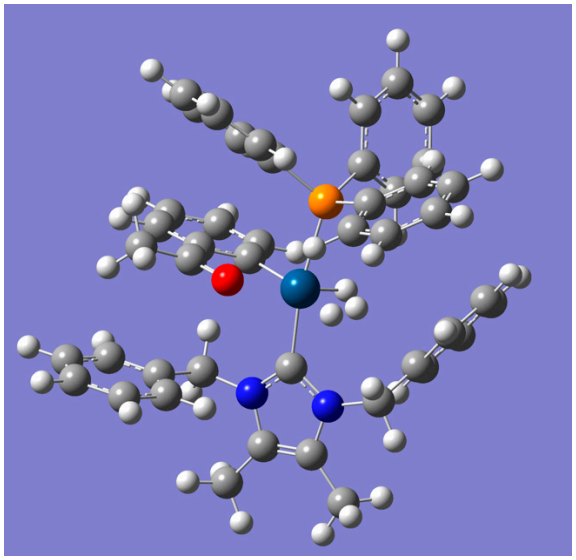
C	2.76077	3.70269	0.31201
C	3.61708	2.85409	-0.31298
N	1.56353	3.00412	0.48746
N	2.91439	1.66505	-0.51256
C	-0.75806	3.84102	0.14041
C	-2.06713	3.55852	0.53199
C	-0.52077	4.33058	-1.14372
C	-3.12420	3.75141	-0.35145
H	-2.25897	3.15098	1.52712
C	-1.57650	4.51980	-2.03007
H	0.50080	4.54325	-1.46438
C	-2.88048	4.22799	-1.63670
H	-4.13909	3.51441	-0.03555
H	-1.38038	4.90020	-3.03103
H	-3.70604	4.37625	-2.33077
C	4.34582	-0.36264	-0.23975
C	4.45670	-0.13669	1.13061
C	5.03803	-1.43324	-0.81289
C	5.25726	-0.96381	1.91550
H	3.91003	0.68599	1.59260
C	5.83491	-2.25992	-0.02971
H	4.95271	-1.61384	-1.88633
C	5.94913	-2.02366	1.33932
H	5.34080	-0.77421	2.98411
H	6.37834	-3.08329	-0.49004

H	6.57991	-2.66364	1.95327
C	3.50531	0.50043	-1.14905
H	2.68843	-0.08661	-1.58544
H	4.11208	0.85583	-1.99375
C	0.37374	3.59760	1.10388
H	0.69948	4.53602	1.56883
H	0.04300	2.93938	1.91632
C	1.65405	1.74460	-0.01556
Ir	0.13649	0.30456	-0.04470
H	-0.81357	1.43183	-0.61870
H	-0.23717	1.05696	1.35208
P	-1.93588	-0.82276	0.34342
C	-1.74361	-2.54809	0.92798
C	-1.39735	-3.54639	0.00786
C	-1.80058	-2.86989	2.28717
C	-1.12049	-4.83871	0.44056
H	-1.35554	-3.31890	-1.05749
C	-1.51741	-4.16272	2.71726
H	-2.08132	-2.11404	3.01891
C	-1.17546	-5.14883	1.79709
H	-0.86298	-5.60454	-0.29000
H	-1.57476	-4.40059	3.77767
H	-0.96195	-6.16107	2.13555
C	-3.06059	-0.91458	-1.09120
C	-3.10268	0.15255	-1.99483
C	-3.97908	-1.96092	-1.22388
C	-4.04385	0.16797	-3.01827
H	-2.40465	0.98384	-1.88851
C	-4.91268	-1.94667	-2.25480
H	-3.97415	-2.78661	-0.51297
C	-4.94632	-0.88350	-3.15230
H	-4.07126	1.00673	-3.71190
H	-5.62171	-2.76658	-2.35171

H	-5.68099	-0.87218	-3.95524
C	-2.94476	0.03185	1.61791
C	-4.28800	0.34164	1.39177
C	-2.35609	0.40830	2.83265
C	-5.02463	1.02347	2.35817
H	-4.76814	0.06314	0.45481
C	-3.09833	1.07148	3.80178
H	-1.30319	0.18940	3.01713
C	-4.43426	1.38838	3.56177
H	-6.06788	1.26643	2.16507
H	-2.63066	1.34944	4.74460
H	-5.01263	1.91942	4.31535
C	0.05783	-1.49168	-2.77800
C	0.37514	-2.65051	-3.48066
C	1.19671	-3.62715	-2.91611
C	1.67029	-3.44410	-1.62905
C	1.34547	-2.28684	-0.90356
C	0.54313	-1.26463	-1.48374
H	-0.58097	-0.74613	-3.25197
H	-0.01485	-2.78671	-4.48830
H	1.45230	-4.52400	-3.47577
H	2.28058	-4.21693	-1.16230
H	0.44711	0.41593	-1.62329
C	1.70904	-2.14945	0.50023
O	1.35379	-1.12518	1.11769
C	2.42931	-3.22067	1.24506
H	1.81881	-4.13532	1.26256
H	3.38895	-3.45932	0.76661
H	2.61166	-2.88961	2.27069
C	2.95867	5.10596	0.75286
H	3.95456	5.45366	0.45972
H	2.22889	5.78962	0.29711
H	2.88350	5.21618	1.84329

C	5.02362	3.03266	-0.74944
H	5.40858	3.99912	-0.40877
H	5.67850	2.25267	-0.33771
H	5.12417	3.00894	-1.84353

IBnMe_P (**26**, R = Me)



Sum of Electronic and Zero-point Energies = -2369.899556 Hartree

Sum of Electronic and Thermal Energies = -2369.853358 Hartree

Sum of Electronic and Thermal Enthalpies = -2369.852414 Hartree

Sum of Electronic and Thermal Free Energies = -2369.979560 Hartree

Dipole Moment = 2.0657 Debye

1 1

C	2.94904	3.59836	0.26903
C	3.75361	2.69068	-0.33397
N	1.72978	2.95448	0.50062
N	3.00188	1.52327	-0.46969
C	-0.59669	3.86341	0.29276
C	-1.87145	3.71802	0.84081
C	-0.46832	4.23694	-1.04483
C	-3.00466	3.93259	0.06187

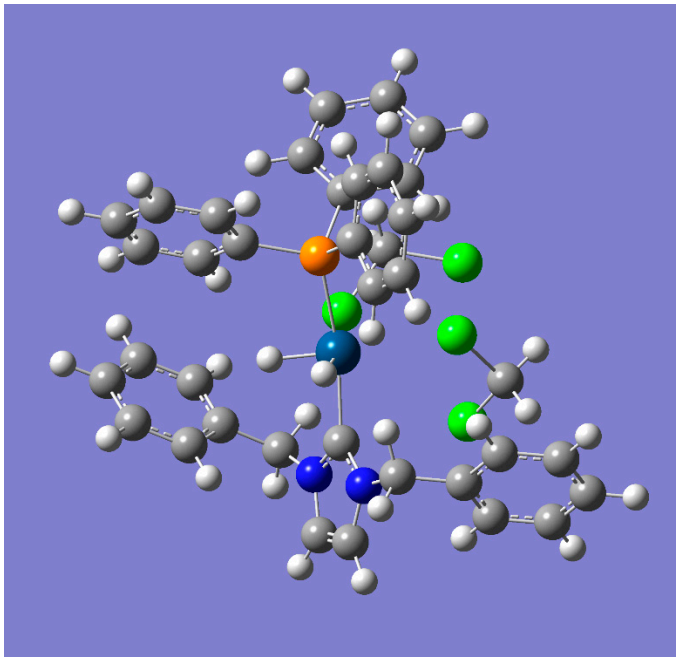
H	-1.98439	3.42666	1.88813
C	-1.59956	4.45327	-1.82474
H	0.52489	4.34387	-1.48435
C	-2.87016	4.30087	-1.27321
H	-3.99272	3.80686	0.50112
H	-1.48873	4.74869	-2.86662
H	-3.75502	4.47445	-1.88310
C	4.28988	-0.57873	-0.08115
C	4.31819	-0.34227	1.29129
C	4.94484	-1.70361	-0.59193
C	4.98630	-1.22082	2.14239
H	3.80974	0.52960	1.70451
C	5.61563	-2.57685	0.25512
H	4.92582	-1.89060	-1.66753
C	5.63679	-2.33674	1.62873
H	5.00090	-1.02543	3.21303
H	6.13104	-3.44302	-0.15652
H	6.16486	-3.01694	2.29415
C	3.58849	0.32911	-1.05907
H	2.80238	-0.20739	-1.59529
H	4.29707	0.66504	-1.82742
C	0.61895	3.64891	1.15540
H	1.01421	4.61825	1.47973
H	0.35761	3.12272	2.08141
C	1.75220	1.65853	0.05382
Ir	0.10681	0.32143	0.16365
H	-0.72580	1.47463	1.33294
H	-0.22762	1.05077	1.83591
P	-1.97598	-0.84439	0.22112
C	-1.85422	-2.66889	0.34578
C	-1.46979	-3.38950	-0.79269
C	-2.04323	-3.35305	1.54971
C	-1.27520	-4.76435	-0.72391

H	-1.33158	-2.87644	-1.74504
C	-1.84474	-4.72913	1.61596
H	-2.36283	-2.81803	2.44218
C	-1.45671	-5.43648	0.48243
H	-0.98112	-5.30965	-1.61951
H	-2.00437	-5.25015	2.55801
H	-1.30735	-6.51338	0.53561
C	-3.10894	-0.56797	-1.18399
C	-3.08616	0.64241	-1.88288
C	-4.10138	-1.51019	-1.48015
C	-4.03225	0.89987	-2.86970
H	-2.33404	1.39646	-1.64883
C	-5.04231	-1.25072	-2.46968
H	-4.14384	-2.44986	-0.92994
C	-5.00764	-0.04636	-3.16729
H	-4.00210	1.84544	-3.40882
H	-5.80741	-1.99128	-2.69432
H	-5.74485	0.15498	-3.94229
C	-2.94699	-0.30108	1.67912
C	-4.23499	0.22376	1.55244
C	-2.34959	-0.34560	2.94733
C	-4.91394	0.69374	2.67466
H	-4.71277	0.27651	0.57486
C	-3.03553	0.11097	4.06576
H	-1.33746	-0.74151	3.06021
C	-4.31940	0.63635	3.92930
H	-5.91642	1.10291	2.56363
H	-2.56609	0.06049	5.04652
H	-4.85414	1.00103	4.80419
C	0.49452	-0.68538	-2.72202
C	0.95862	-1.61797	-3.64470
C	1.62389	-2.77673	-3.22951
C	1.80554	-3.00452	-1.87662

C	1.33663	-2.07410	-0.93655
C	0.68331	-0.87965	-1.34745
H	-0.01334	0.21190	-3.07477
H	0.80470	-1.44022	-4.70853
H	1.98733	-3.49297	-3.96310
H	2.31299	-3.90901	-1.54008
H	-0.54137	1.37228	-0.81752
C	1.48369	-2.26771	0.49922
O	1.08536	-1.37286	1.27522
C	2.06072	-3.51560	1.07506
H	1.46861	-4.38616	0.75798
H	3.09228	-3.66176	0.72504
H	2.05953	-3.45119	2.16644
C	5.16044	2.79999	-0.79324
H	5.58904	3.75652	-0.47775
H	5.78755	2.00390	-0.36915
H	5.24880	2.74859	-1.88734
C	3.21649	5.01347	0.62931
H	2.50885	5.70477	0.15011
H	3.17521	5.18925	1.71300
H	4.21895	5.29920	0.29474

3.4 $\%V_{bur}$ Calculations

$[(H)_2(DCM)_2Ir(IBn)(PPh_3)]^+$ for calculation of $\%V_{bur}$



Sum of Electronic and Zero-point Energies = -3826.035111 Hartree

Sum of Electronic and Thermal Energies = -3825.990924 Hartree

Sum of Electronic and Thermal Enthalpies = -3825.989980 Hartree

Sum of Electronic and Thermal Free Energies = -3826.114797 Hartree

Dipole Moment = 1.3480 Debye

1 1

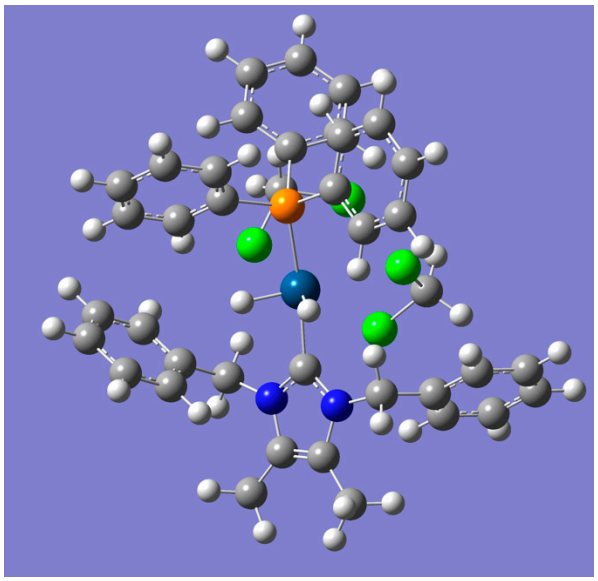
C	2.78755	3.72957	-0.62423
C	3.39146	2.86145	-1.46186
N	1.72253	3.05516	-0.05222
N	2.68424	1.67271	-1.38136
C	-0.54439	4.05283	0.25704
C	-1.63995	4.20850	1.10727
C	-0.70544	4.28187	-1.10964
C	-2.87677	4.59778	0.60285
H	-1.51970	4.03229	2.17733
C	-1.94480	4.65965	-1.61617
H	0.13861	4.15685	-1.78896

C	-3.03103	4.82476	-0.76176
H	-3.72002	4.72687	1.27950
H	-2.05965	4.83377	-2.68429
H	-3.99538	5.13632	-1.15992
C	4.20285	-0.31204	-1.58550
C	5.16938	0.22437	-0.73579
C	4.29829	-1.65588	-1.95743
C	6.21392	-0.57064	-0.26706
H	5.10302	1.26209	-0.41082
C	5.34161	-2.44921	-1.49469
H	3.53816	-2.08568	-2.61303
C	6.30442	-1.90656	-0.64561
H	6.95768	-0.14062	0.40138
H	5.40030	-3.49434	-1.79211
H	7.12216	-2.52466	-0.28042
C	3.06809	0.50173	-2.15896
H	2.17591	-0.12422	-2.26850
H	3.32827	0.86065	-3.16611
C	0.79139	3.70331	0.86196
H	1.29736	4.61208	1.21781
H	0.66900	3.06316	1.74341
C	1.63596	1.77514	-0.51070
Ir	0.11867	0.37719	-0.25151
H	0.25292	0.22997	-1.79796
H	-0.83805	1.51721	-0.71266
Cl	-0.49224	0.96149	2.42082
Cl	1.69255	-1.65011	0.60916
C	3.18397	-1.24558	1.57037
H	3.15320	-1.89897	2.44411
H	4.03677	-1.45352	0.91779
C	-0.82287	-0.26251	3.71039
H	-1.60001	-0.92911	3.33405
H	-1.15636	0.31311	4.57526

Cl	3.26224	0.42916	2.10580
Cl	0.59026	-1.21259	4.16567
P	-1.73066	-1.09130	-0.49120
C	-2.37891	-1.89591	1.03040
C	-1.60817	-2.89842	1.63519
C	-3.58544	-1.51568	1.62404
C	-2.03747	-3.50621	2.80932
H	-0.67014	-3.21999	1.17935
C	-4.01032	-2.12275	2.80473
H	-4.20661	-0.75069	1.15985
C	-3.23869	-3.11639	3.39943
H	-1.43010	-4.28462	3.26746
H	-4.95526	-1.82206	3.25356
H	-3.57499	-3.59262	4.31838
C	-1.42989	-2.54135	-1.57098
C	-0.34772	-2.56459	-2.45480
C	-2.29603	-3.64255	-1.53419
C	-0.13329	-3.66102	-3.28469
H	0.33630	-1.71726	-2.48977
C	-2.08386	-4.73486	-2.36572
H	-3.14379	-3.64568	-0.84861
C	-1.00052	-4.74647	-3.24113
H	0.71620	-3.66606	-3.96552
H	-2.76479	-5.58287	-2.32827
H	-0.83247	-5.60497	-3.88840
C	-3.18989	-0.24614	-1.20267
C	-3.96764	-0.80958	-2.21684
C	-3.54668	1.00558	-0.68413
C	-5.08458	-0.13398	-2.70083
H	-3.70050	-1.77536	-2.64298
C	-4.67145	1.66846	-1.15864
H	-2.94174	1.46716	0.09971
C	-5.44165	1.10032	-2.17017

H	-5.67716	-0.57866	-3.49799
H	-4.93400	2.63999	-0.74270
H	-6.31778	1.62353	-2.54853
H	4.25364	2.96926	-2.10729
H	3.00732	4.76102	-0.38213

$[(H)_2(DCM)_2Ir(IBnMe)(PPh_3)]^+$ for calculation of $\%V_{bur}$



Sum of Electronic and Zero-point Energies = -3904.603324 Hartree

Sum of Electronic and Thermal Energies = -3904.555943 Hartree

Sum of Electronic and Thermal Enthalpies = -3904.554999 Hartree

Sum of Electronic and Thermal Free Energies = -3904.686201 Hartree

Dipole Moment = 6.6682 Debye

1 1

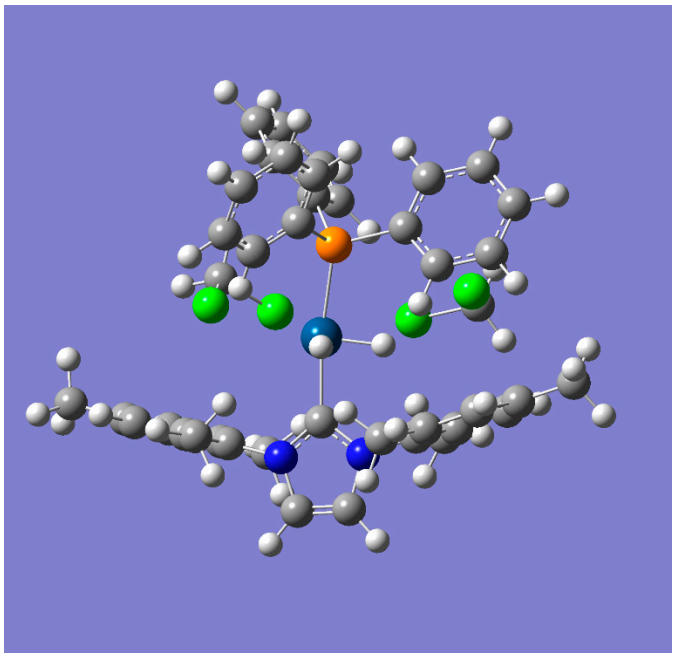
C	3.17966	3.78668	0.61312
C	3.85834	2.80079	-0.02765
N	1.95928	3.23301	1.00464
N	3.03248	1.67411	-0.00266
C	-0.17956	4.47344	0.72333
C	-1.41813	4.82510	1.26395
C	0.02269	4.60133	-0.65117

C	-2.43790	5.29993	0.44472
H	-1.58191	4.73150	2.33872
C	-0.99835	5.07212	-1.47222
H	0.98107	4.31672	-1.08839
C	-2.22951	5.42546	-0.92696
H	-3.39861	5.57151	0.87968
H	-0.82859	5.16578	-2.54334
H	-3.02589	5.79668	-1.57002
C	4.32305	-0.43530	0.37058
C	4.96411	0.08778	1.49229
C	4.50546	-1.78455	0.05344
C	5.77432	-0.72534	2.28476
H	4.81612	1.13155	1.76974
C	5.30921	-2.59666	0.84307
H	3.99680	-2.20245	-0.81762
C	5.94931	-2.06749	1.96383
H	6.26515	-0.30288	3.16014
H	5.43538	-3.64699	0.58691
H	6.57968	-2.70160	2.58438
C	3.44770	0.38933	-0.54149
H	2.54100	-0.17350	-0.79013
H	3.96370	0.57716	-1.49371
C	0.90895	4.00018	1.65408
H	1.38965	4.85801	2.14218
H	0.49123	3.39558	2.46622
C	1.84913	1.93249	0.62355
Ir	0.16184	0.71144	0.63086
H	0.60369	0.41762	-0.83061
H	-0.53621	1.90264	-0.08923
Cl	-1.26283	1.68723	3.05788
Cl	1.38728	-1.42351	1.83634
C	2.34892	-1.04150	3.32898
H	1.84855	-1.55673	4.15052

H	3.35757	-1.42078	3.14656
C	-1.85235	0.63982	4.39812
H	-2.62533	-0.01252	3.98849
H	-2.24398	1.31295	5.16138
Cl	2.43254	0.68005	3.68639
Cl	-0.58316	-0.36079	5.11800
P	-1.77628	-0.56892	0.12460
C	-2.79831	-1.17125	1.52872
C	-2.25150	-2.14924	2.36898
C	-4.07747	-0.67836	1.79910
C	-2.97520	-2.63411	3.45214
H	-1.25484	-2.54473	2.16583
C	-4.79795	-1.15929	2.89126
H	-4.51970	0.08095	1.15500
C	-4.25093	-2.13767	3.71686
H	-2.53969	-3.39611	4.09584
H	-5.79396	-0.76895	3.09146
H	-4.81687	-2.51313	4.56711
C	-1.45315	-2.13463	-0.78013
C	-0.26507	-2.30784	-1.49668
C	-2.39607	-3.17173	-0.77465
C	-0.02236	-3.48926	-2.19226
H	0.48158	-1.51444	-1.51095
C	-2.15434	-4.34962	-1.47172
H	-3.32647	-3.05954	-0.21742
C	-0.96528	-4.51127	-2.17935
H	0.91026	-3.60992	-2.74027
H	-2.89578	-5.14607	-1.45797
H	-0.77401	-5.43693	-2.71889
C	-2.98834	0.34412	-0.90676
C	-3.73606	-0.28318	-1.90747
C	-3.22383	1.69716	-0.62958
C	-4.69924	0.42855	-2.61715

H	-3.56692	-1.33297	-2.14224
C	-4.19511	2.40193	-1.33197
H	-2.64977	2.21048	0.14494
C	-4.93337	1.76913	-2.32859
H	-5.26843	-0.07054	-3.39916
H	-4.36391	3.45308	-1.10215
H	-5.68995	2.32221	-2.88209
C	5.18145	2.81319	-0.69871
H	5.67167	3.78060	-0.55044
H	5.85359	2.03759	-0.30792
H	5.08846	2.65607	-1.78220
C	3.55044	5.19690	0.88447
H	2.82239	5.90315	0.46182
H	3.63032	5.40374	1.96037
H	4.52318	5.42243	0.43581

$[(H)_2(DCM)_2Ir(IMes)(PPh_3)]^+$ for calculation of $\%V_{bur}$



Sum of Electronic and Zero-point Energies = -3983.126865 Hartree

Sum of Electronic and Thermal Energies = -3983.075923 Hartree

Sum of Electronic and Thermal Enthalpies = -3983.074979 Hartree

Sum of Electronic and Thermal Free Energies = -3983.212635 Hartree

Dipole Moment = 2.8831 Debye

1 1

C	-3.40530900	2.45259700	0.26649000
C	-2.50344500	3.44818700	0.12598800
N	-2.69873400	1.26213300	0.19425000
N	-1.26540800	2.84210500	-0.02997500
C	-0.06178500	3.59433400	-0.22925600
C	0.69894300	3.95863100	0.88475900
C	0.27433300	3.97232300	-1.53201700
C	1.84201900	4.72394500	0.66181400
C	1.43531800	4.72422100	-1.70488200
C	2.23123700	5.10395300	-0.62319800
H	2.45301100	5.02121400	1.51606900
H	1.72228700	5.02488700	-2.71450500
C	-3.33841700	-0.01976200	0.27256600
C	-3.53521500	-0.60349700	1.52731600
C	-3.74878200	-0.63233000	-0.91649600
C	-4.14363600	-1.85881300	1.56729000
C	-4.35772400	-1.88089600	-0.82364000
C	-4.55976600	-2.51013900	0.40597200
H	-4.29971000	-2.33824700	2.53558500
H	-4.67750400	-2.38034000	-1.74036700
C	-3.50598800	0.01902800	-2.24263100
H	-3.83660000	1.06660600	-2.25671200
H	-2.43227600	0.02034500	-2.48991400
H	-4.03543400	-0.51205600	-3.04247300
C	-3.09669400	0.08783300	2.78198000
H	-2.01419800	0.28665800	2.77677600
H	-3.59289900	1.06048300	2.90587300
H	-3.32488200	-0.52020800	3.66419600
C	-5.22649800	-3.85151900	0.46692100

H	-4.79972000	-4.54289700	-0.27217500
H	-5.12945000	-4.30706300	1.46020400
H	-6.29971600	-3.77175900	0.24524100
C	3.49971200	5.87164100	-0.84374700
H	3.77354800	6.46348200	0.03777800
H	4.33769100	5.18974500	-1.04943200
H	3.41907200	6.54966000	-1.70210100
C	-0.58629800	3.58699500	-2.69763900
H	-0.73469000	2.49783500	-2.75129600
H	-1.58431000	4.04307700	-2.63334900
H	-0.12946700	3.90733200	-3.64092500
C	0.30849200	3.52011700	2.26401500
H	-0.71346200	3.83158300	2.52163500
H	0.33381000	2.42290700	2.35694400
H	0.98842800	3.93757800	3.01483700
C	-1.36273400	1.48439500	0.00573400
Ir	0.08846300	0.00581800	0.01404900
H	-1.12243900	-0.94689800	-0.12284000
H	-0.27257100	-0.14502900	1.51921500
P	1.42356300	-1.91037900	0.34865600
C	0.47276300	-3.47506900	0.23739700
C	-0.81508500	-3.51859100	0.78562700
C	0.99948300	-4.62705700	-0.35367800
C	-1.56420200	-4.68873200	0.73434500
H	-1.24711500	-2.62923500	1.24930400
C	0.24547500	-5.79605500	-0.40821500
H	2.00155500	-4.61093100	-0.78229400
C	-1.03695400	-5.82827800	0.13131800
H	-2.56657100	-4.70313100	1.16161800
H	0.66380300	-6.68550900	-0.87589800
H	-1.62577000	-6.74250600	0.08395700
C	2.22590600	-2.01781600	1.99231400
C	2.41842900	-0.86013000	2.75268300

C	2.68634500	-3.24351800	2.48678600
C	3.06208700	-0.92659700	3.98557400
H	2.05559200	0.09951400	2.38270300
C	3.32862400	-3.30833900	3.71795700
H	2.54231400	-4.15537700	1.90653900
C	3.51688100	-2.14965500	4.46817000
H	3.20381000	-0.01994000	4.57073500
H	3.68192900	-4.26657100	4.09414000
H	4.01678600	-2.20250200	5.43358300
C	2.79628800	-2.13499900	-0.84252000
C	4.13996300	-2.17861000	-0.46254900
C	2.46818900	-2.18279200	-2.20354400
C	5.13828700	-2.27097900	-1.43059400
H	4.41263100	-2.14021800	0.59168800
C	3.46446500	-2.28249100	-3.16717200
H	1.42051200	-2.15012800	-2.50855100
C	4.80384800	-2.32313000	-2.78108000
H	6.18239000	-2.30324400	-1.12515200
H	3.19312000	-2.31644300	-4.22125400
H	5.58612600	-2.39625300	-3.53417000
Cl	1.77316000	1.06051000	-3.06379500
C	3.15188000	1.23071200	-1.95815600
H	3.73923400	0.31041400	-1.99216400
H	3.73394300	2.10516500	-2.25474600
Cl	2.64383000	1.50155200	-0.25738400
Cl	-1.40740400	-2.92705000	-2.66553700
C	-1.52410400	-2.42735200	-4.36968500
H	-2.57130300	-2.23041000	-4.60288400
H	-1.12056800	-3.22428700	-4.99478400
Cl	-0.59161800	-0.94026300	-4.70212800
H	-4.47806100	2.46414000	0.40692800
H	-2.60904700	4.52503800	0.11793300

Percent Buried Volume Output from SambVca (as shown in Manuscript Table 2)

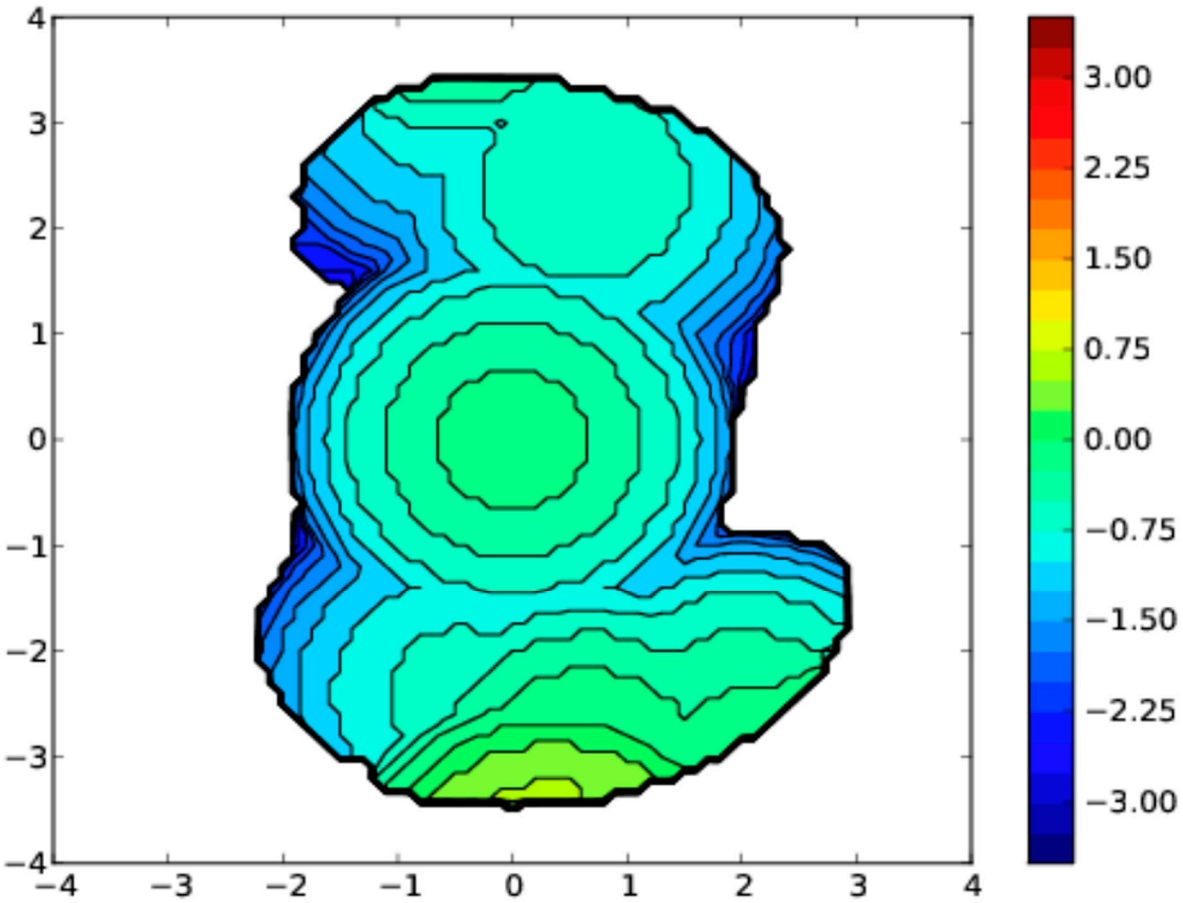
Entry	Complex	*N*-Substituent	R′	$\%V_{bur}(PPh_3)$	$\%V_{bur}$(NHC)	Σ ($\%V_{bur}$)
1	**14**	Bn	H	26.9	28.9	55.8
2	**15**	Bn	Me	27.0	29.2	56.2
3	**16**	Mes	H	27.9	32.6	60.5

*In relation to complex **14** – IBn ligand*

%V Free	**%V Buried**	% V Tot/V Ex
71.1	**28.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	32.2	12.6	44.9	**71.8**	28.2
NW	34.4	10.5	44.9	**76.6**	23.4
NE	32.0	12.9	44.9	**71.3**	28.7
SE	29.0	15.8	44.9	**64.7**	35.3

Steric Map

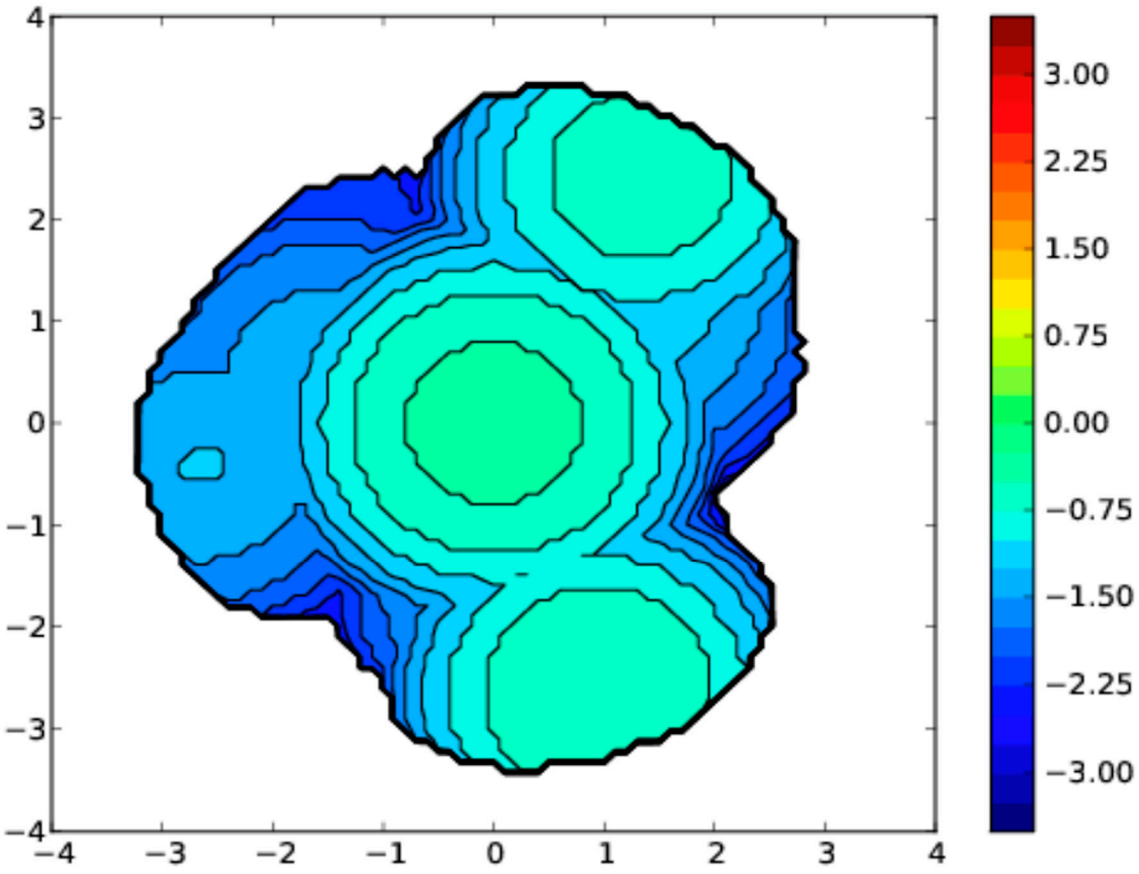


*In relation to complex **14** – PPh_3 ligand*

%V Free	**%V Buried**	% V Tot/V Ex
73.1	**26.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	33.8	11.1	44.9	**75.3**	24.7
NW	34.6	10.3	44.9	**77.0**	23.0
NE	31.1	13.8	44.9	**69.3**	30.7
SE	31.7	13.1	44.9	**70.8**	29.2

Steric Map

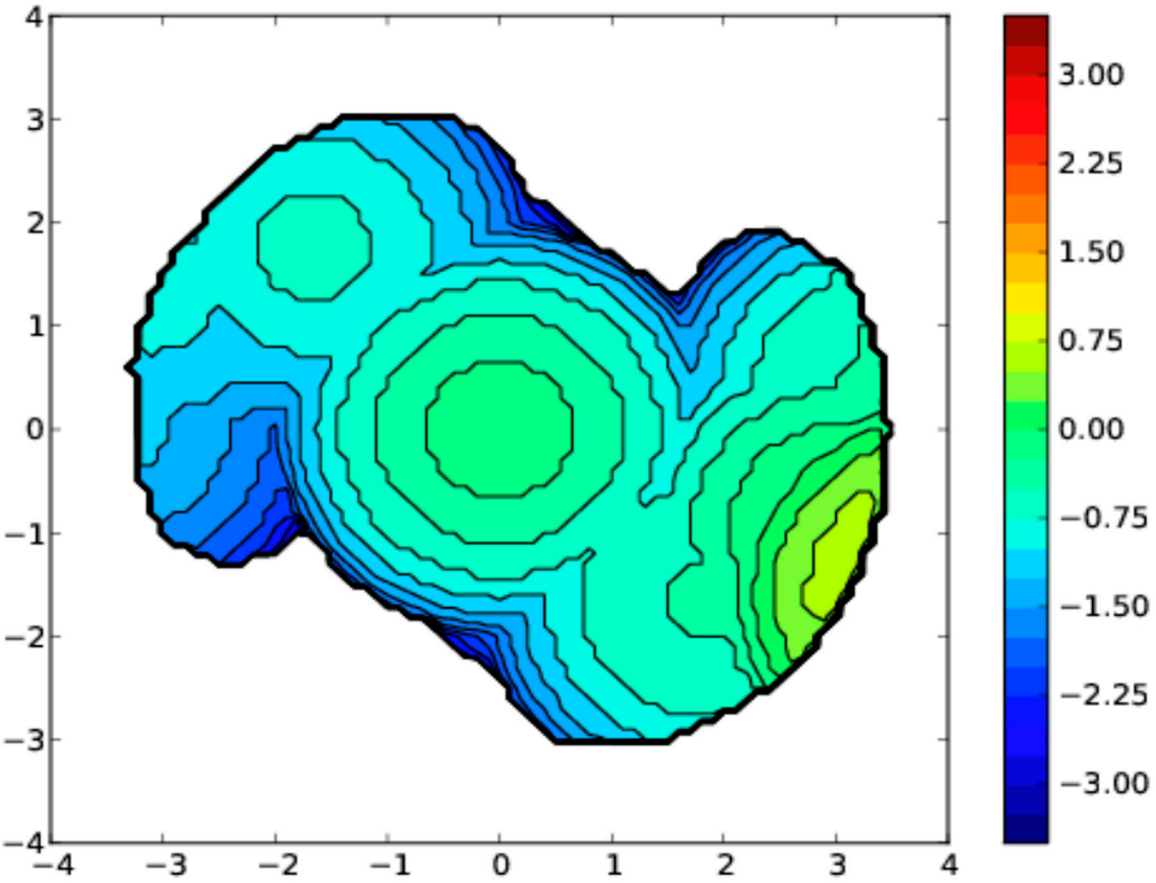


*In relation to complex **15** – IBn^{Me} ligand*

%V Free	**%V Buried**	% V Tot/V Ex
70.8	**29.2**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	36.2	8.6	44.9	**80.8**	19.2
NW	30.5	14.3	44.9	**68.1**	31.9
NE	33.7	11.2	44.9	**75.0**	25.0
SE	26.5	18.3	44.9	**59.2**	40.8

Steric Map

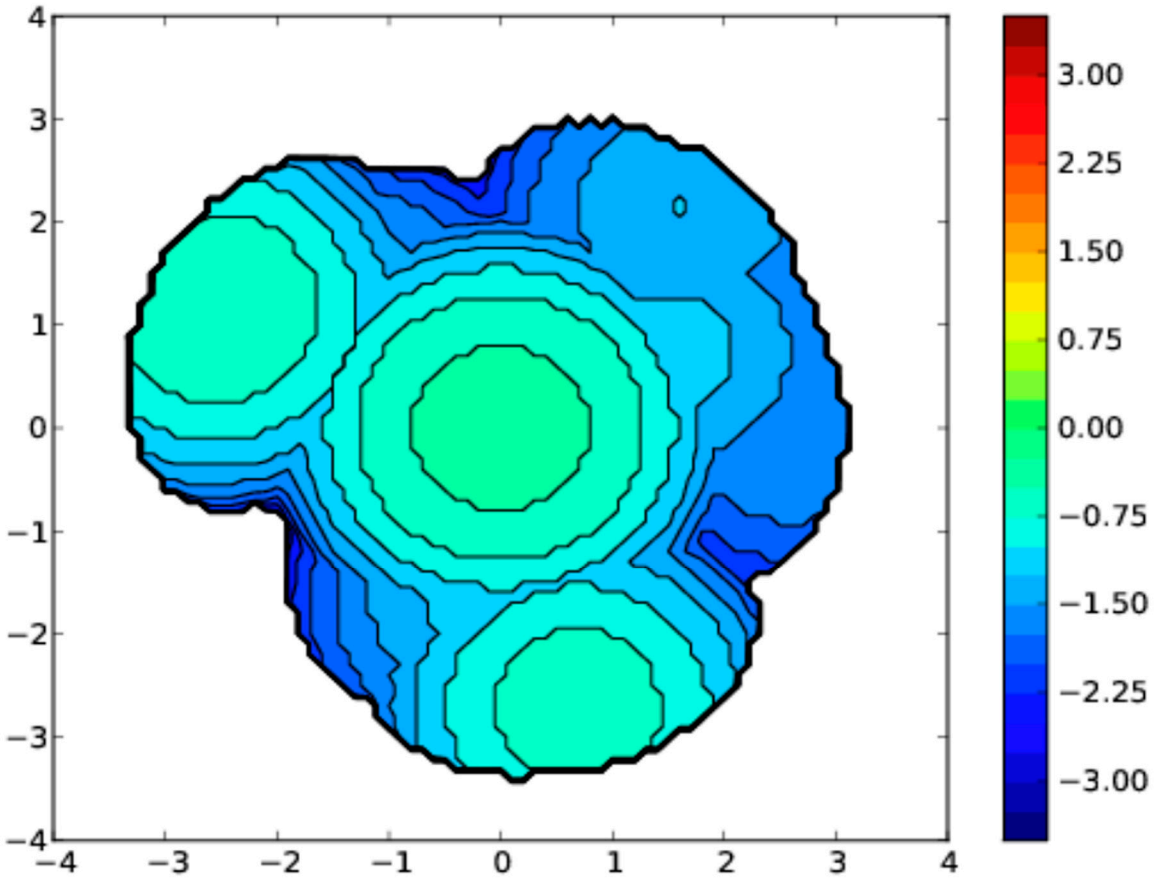


*In relation to complex **15** – PPh_3 ligand*

%V Free	**%V Buried**	% V Tot/V Ex
73.0	**27.0**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	34.2	10.7	44.9	**76.2**	23.8
NW	31.4	13.4	44.9	**70.0**	30.0
NE	33.4	11.4	44.9	**74.5**	25.5
SE	32.0	12.8	44.9	**71.4**	28.6

Steric Map

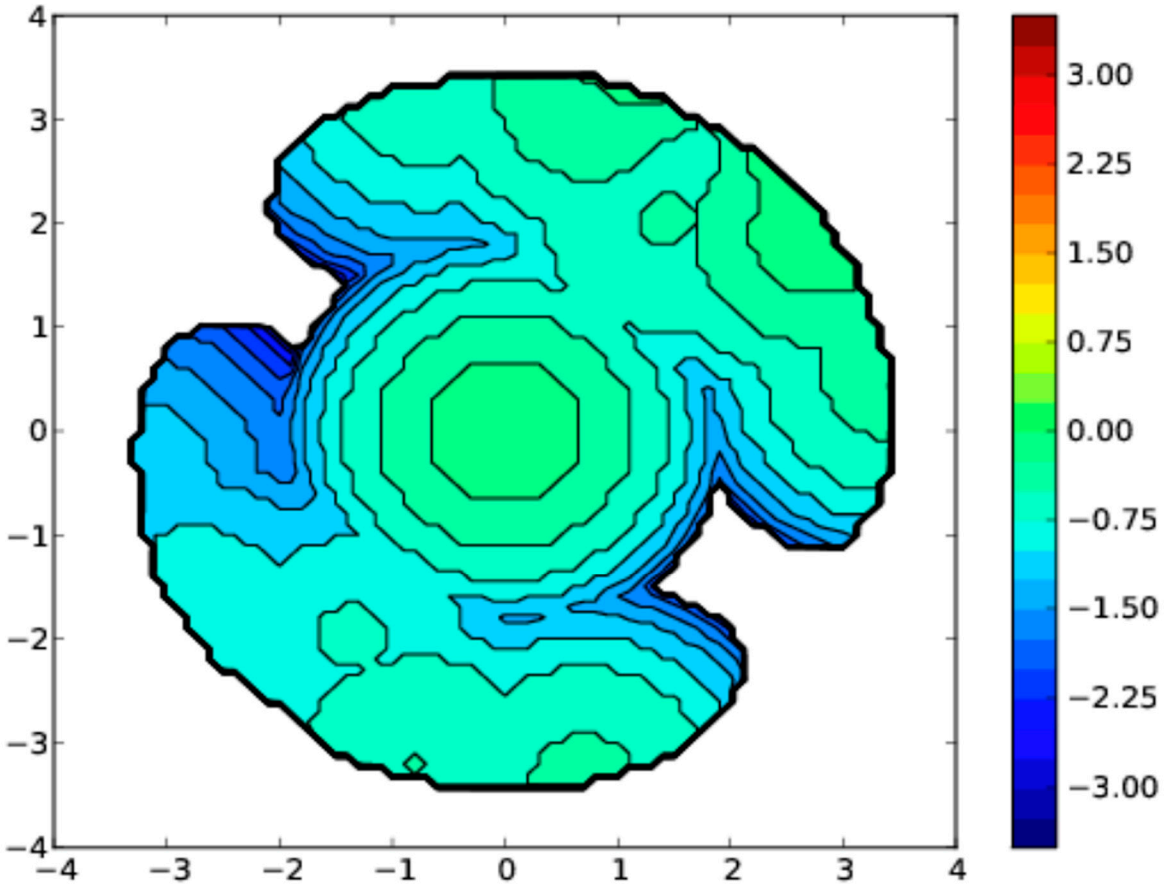


*In relation to complex **16** – IMes ligand*

%V Free	**%V Buried**	% V Tot/V Ex
67.4	**32.6**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	29.5	15.4	44.9	**65.7**	34.3
NW	33.0	11.9	44.9	**73.5**	26.5
NE	26.6	18.2	44.9	**59.3**	40.7
SE	31.9	12.9	44.9	**71.2**	28.8

Steric Map

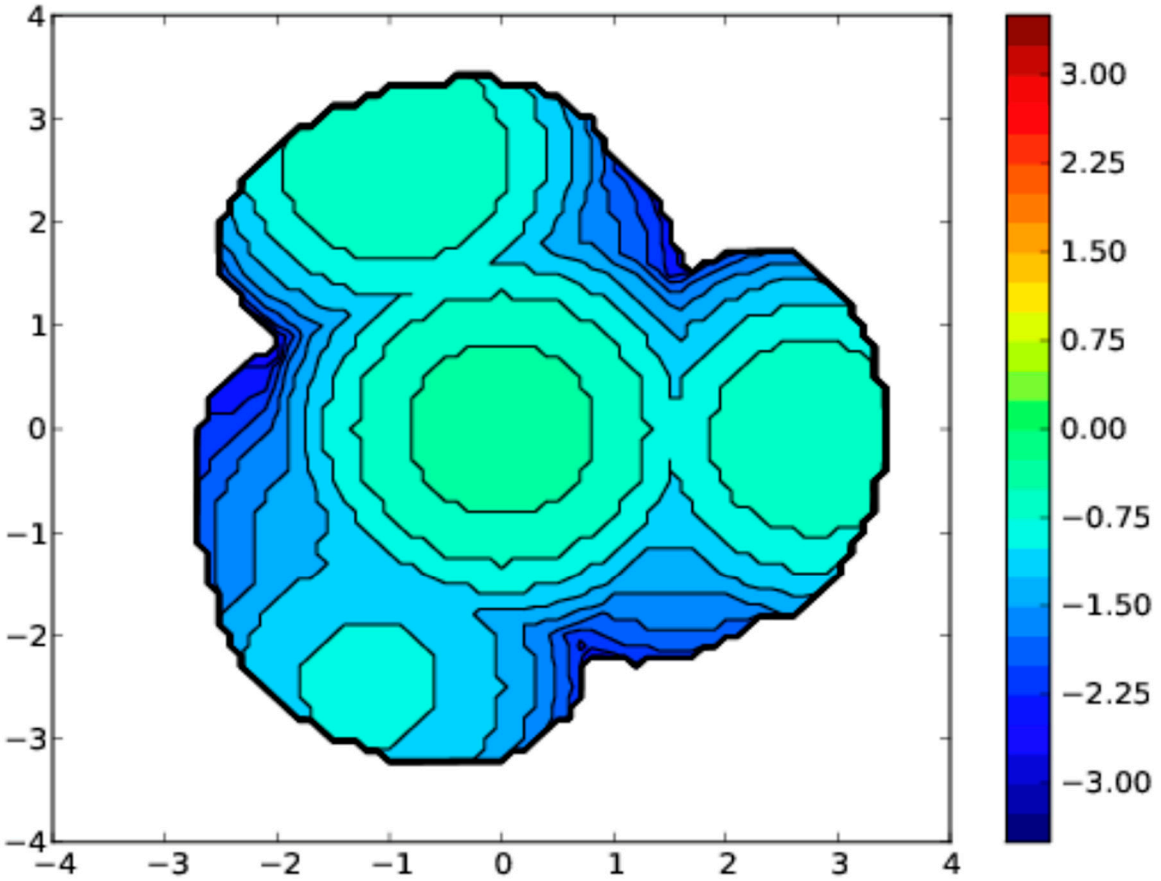


*In relation to complex **16** – PPh_3 ligand*

%V Free	**%V Buried**	% V Tot/V Ex
72.1	**27.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	32.5	12.4	44.9	**72.4**	27.6
NW	31.7	13.2	44.9	**70.6**	29.4
NE	32.6	12.3	44.9	**72.6**	27.4
SE	32.7	12.1	44.9	**72.9**	27.1

Steric Map



4. X-Ray Crystallography

4.1 Tables of X-ray Crystallography data for

Table S3. Selected Crystallographic and Refinement Parameters for Compounds **3·HCl**, **3·PF_6**, **12**, **14** , **15**, and **16**.

Compound	**3·HCl**	**3·HPF_6**	**12**	**14**	**15**	**16**
Included Solvent	**H_2O**	**none**	**none**	**none**	**0.34CH_2Cl_2**	**none**
Formula	$C_{19}H_{23}ClN_2O$	$C_{19}H_{21}F_6N_2P$	$C_{27}H_{32}ClIrN_2$	$C_{37}H_{31}F_6IrN_2O_2P_2$	$C_{39.34}H_{35.68}Cl_{0.68}F_6IrN_2O_2P_2$	$C_{41}H_{39}F_6IrN_2O_2P_2$
Formula Weight	330.84	422.35	612.19	903.78	960.67	959.88
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	Fd2d	P 2_1/n	P 2_1/c	P 2_1/n	P 2_1/c	P 2_1/c
λ Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
***a* Å**	8.9190(5)	13.8684(7)	9.2905(2)	13.3732(2)	29.2129(10)	15.0331(5)
***b* Å**	17.3610(11)	19.9139(12)	17.1452(4)	19.2021(2)	10.9161(3)	14.3859(4)
***c* Å**	45.922(2)	13.9902(6)	15.0134(3)	14.3880(2)	24.0106(8)	18.2315(5)
β°	90	91.357(4)	93.825(2)	109.299(2)	91.503(3)	97.749(3)
Volume $Å^3$	7110.7(7)	3862.6(3)	2386.12(9)	3487.12(9)	7654.1(4)	3906.8(2)
Temp. K	168(2)	123(2)	123(2)	123(2)	150(2)	138(2)
Z	16	8	4	4	8	4
Refls. Collected	9367	18511	19146	17769	54390	29438
2θ max °	54.0	54.0	60.0	59.8	56.0	59.9
Refls. Unique	3517	8284	6493	8795	18161	9714
Refls. Obs.	3108	5002	5024	7377	13544	7730
Rint	0.0367	0.0524	0.0540	0.0253	0.0527	0.0537
Goodness of Fit	1.019	1.034	1.016	1.044	1.044	1.022
R[I>2s(I)],*F*	0.0397	0.0643	0.0376	0.0287	0.0446	0.0343
Rw, F^2	0.0870	0.1147	0.0786	0.0563	0.0898	0.0566
Max/min electron density $eÅ^{-3}$	0.183/-0.201	0.308/-0.342	1.371/-1.143	0.878/-0.804	1.307/-1.223	1.220/-0.741

Table S4. Selected Crystallographic and Refinement Parameters for Salt Forms of Compounds **6a**-**e**.

Compound	**6a**	**6b**	**6c**	**6d**	**6e**
Anion	**PF_6**	**BF_4**	**SbF_6**	**OTf**	**BAr^F**
Included Solvent	**$CHCl_3$**	**CH_2Cl_2**	**none**	**trace solvent***	**$0.2CH_2Cl_2$**
Formula	$C_{46}H_{48}Cl_3F_6IrN_2P_2$	$C_{46}H_{49}BCl_2F_4IrN_2P$	$C_{45}H_{47}F_6IrN_2PSb$	$C_{46}H_{47}F_3IrN_2O_3PS$	$C_{77.2}H_{59.4}Cl_{0.4}F_{24}IrN_2P$
Formula Weight	1103.35	1010.75	1074.76	988.08	1719.22
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space Group	P $2_1/c$	P $2_1/c$	P-1	P $2_1/c$	P-1
λ Å	0.71073	0.71073	0.71073	0.71073	0.71073
***a* Å**	17.8611(2)	18.0569(5)	10.7430(4)	20.2134(8)	13.3736(2)
***b* Å**	12.6708(2)	12.6004(3)	13.3364(5)	21.5269(12)	21.8310(4)
***c* Å**	19.5384(2)	19.0492(5)	15.9041(6)	30.0770(12)	27.1909(3)
α°	90	90	83.205(3)	90	106.248(2)
β°	92.5180(10)	93.797(3)	85.143(3)	94.201(4)	90.655(2)
γ°	90	90	69.422(4)	90	105.460(2)
Volume $Å^3$	4417.55(10)	4324.6(2)	2115.98(15)	13052.3(10)	7314.0(2)
Temp. K	123(2)	123(2)	123(2)	123(2)	123(2)
Z	4	4	2	12	4
Refls. Collected	27842	20364	21703	58905	102041*
2θ max °	59.76	58.17	60.82	55.00	57.94
Refls. Unique	11384	10286	11350	28971	102041*
Refls. Obs.	9416	8271	9520	18564	84458
Rint	0.0315	0.0388	0.0362	0.0517	*
Goodness of Fit	1.031	1.038	1.029	1.049	1.100
R[I>2s(I)],*F*	0.0285	0.0442	0.0351	0.0585	0.0496
Rw, F^2	0.0579	0.1148	0.0731	0.1301	0.1096
Max/min electron density $eÅ^{-3}$	0.941/-0.731	1.826/-2.001	1.452/-1.008	2.068/-1.695	1.642/-1.387

"*See experimental text in Section 1.1.

4.2 X-ray Structure of 3·HCl

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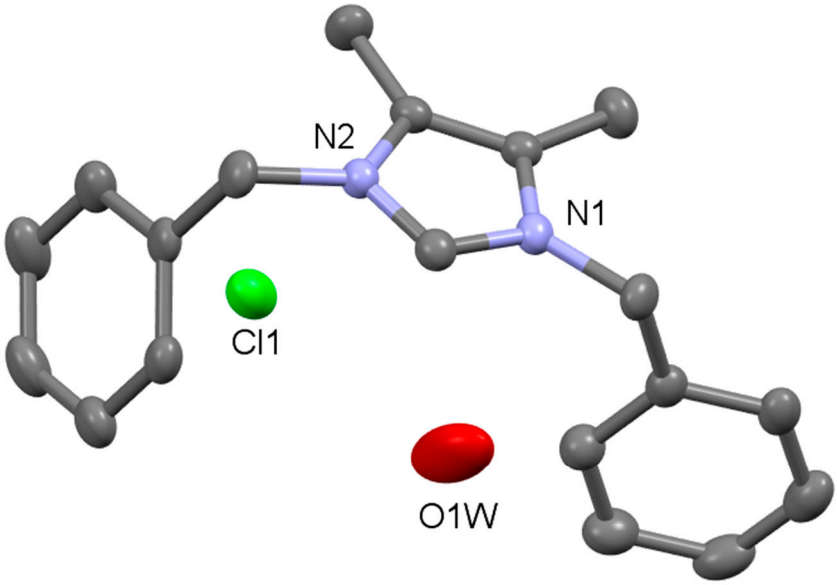
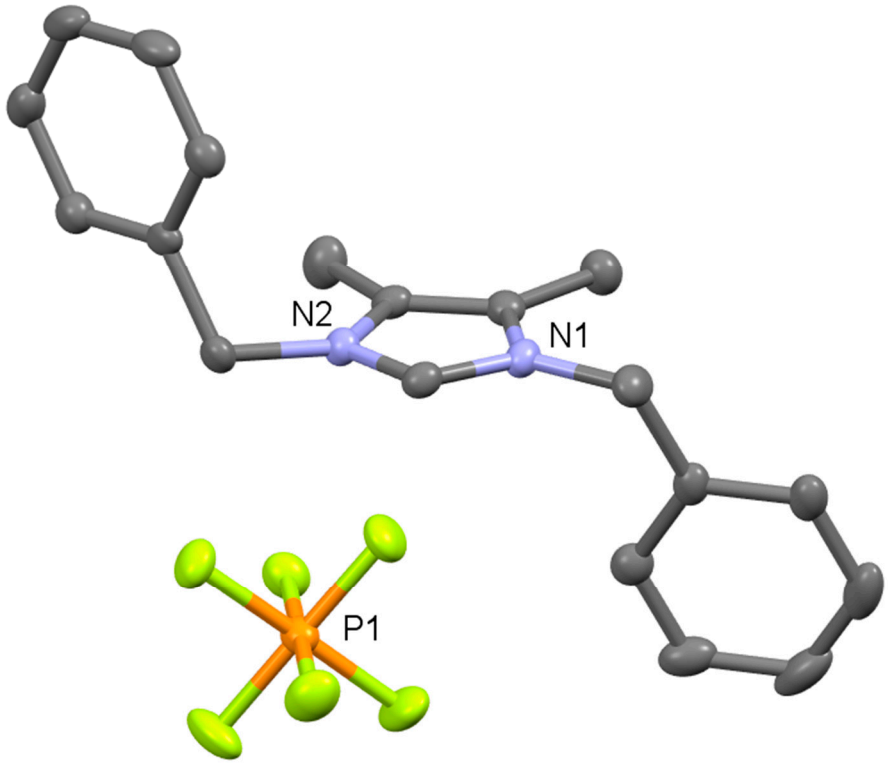


4.3 X-ray Structure of 3·HPF_6

CCDC 1970327



4.4 X-ray Structure of 12

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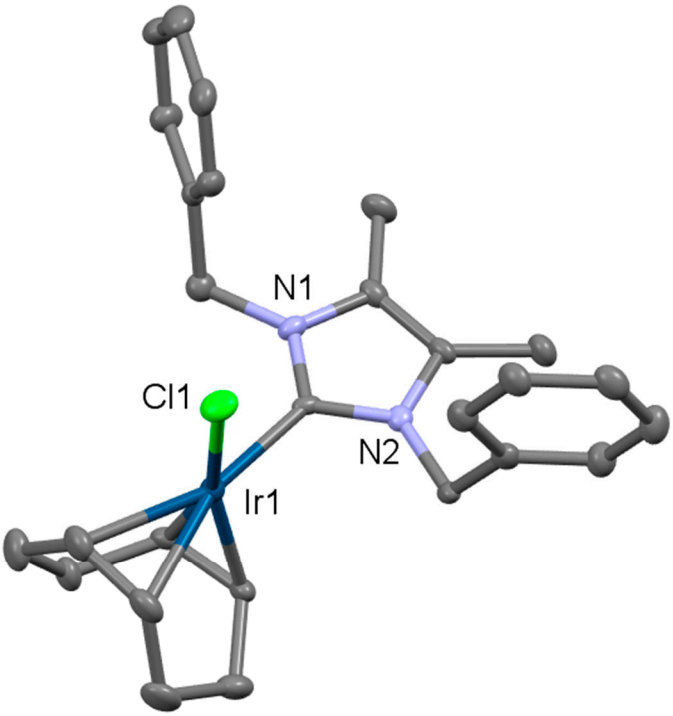

4.5 X-ray Structure of 14

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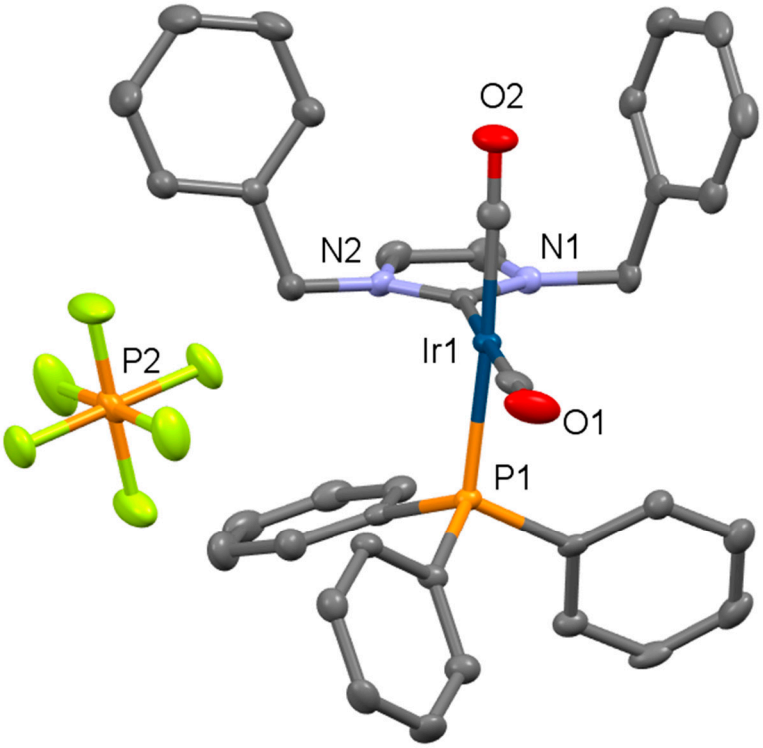
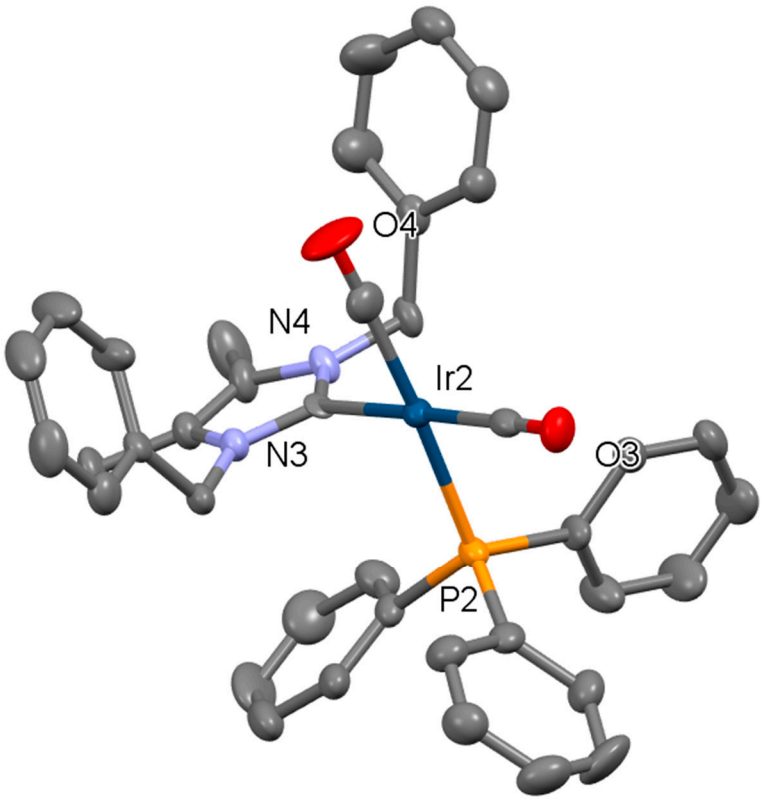


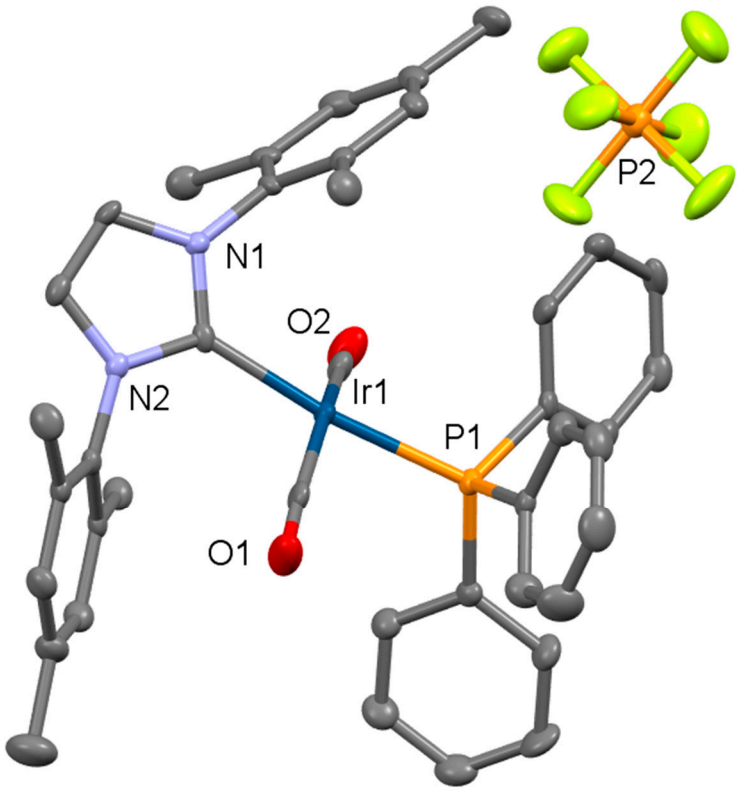
4.6 X-ray Structure of 15

CCDC 1970330



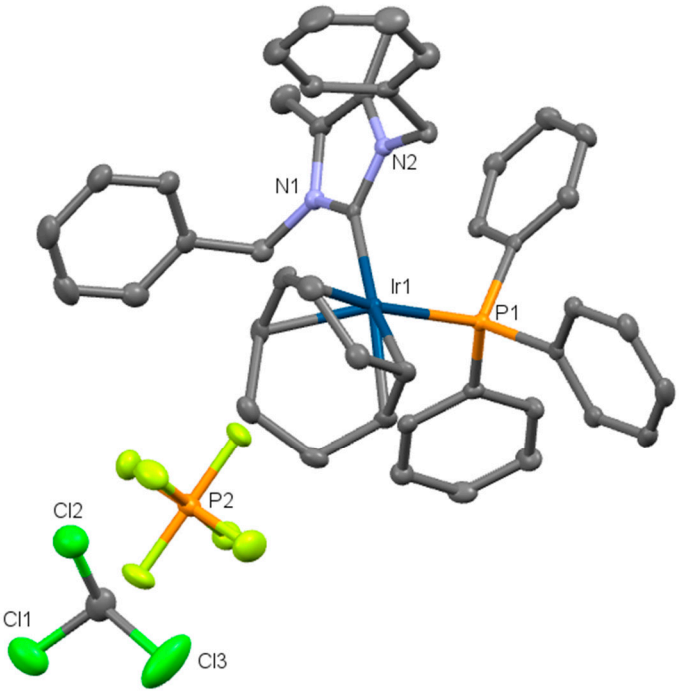
4.7 X-ray Structure of 16

CCDC 1970331



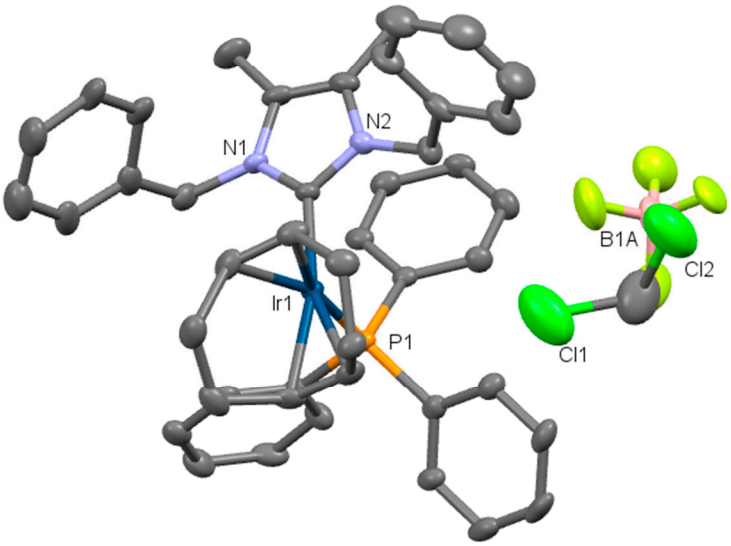
4.8 X-ray Structure of 6a

CCDC 1971355



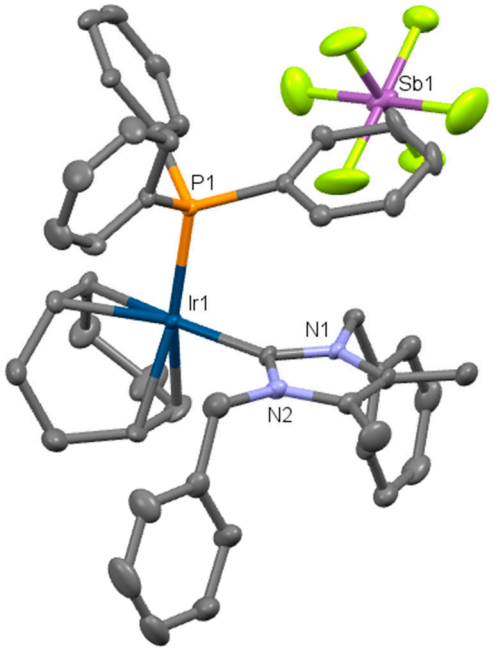
4.9 X-ray Structure of 6b

CCDC 1971356



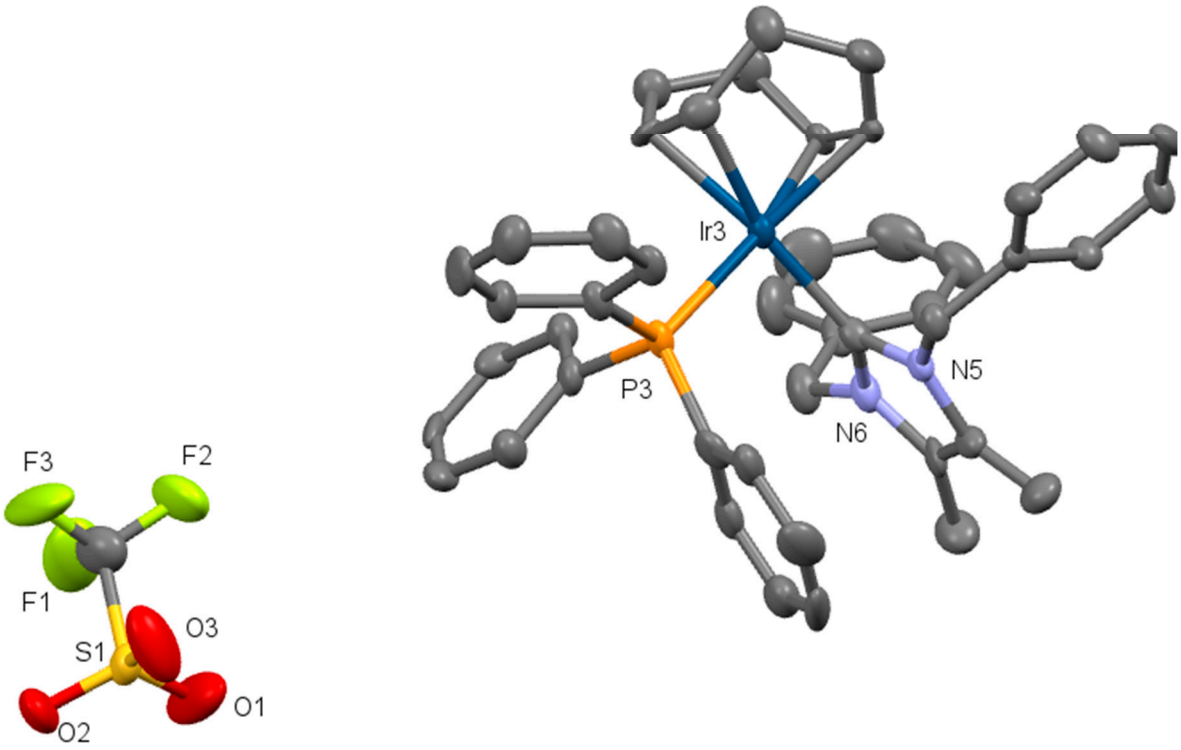
4.10 X-ray Structure of 6c

CCDC 1971357



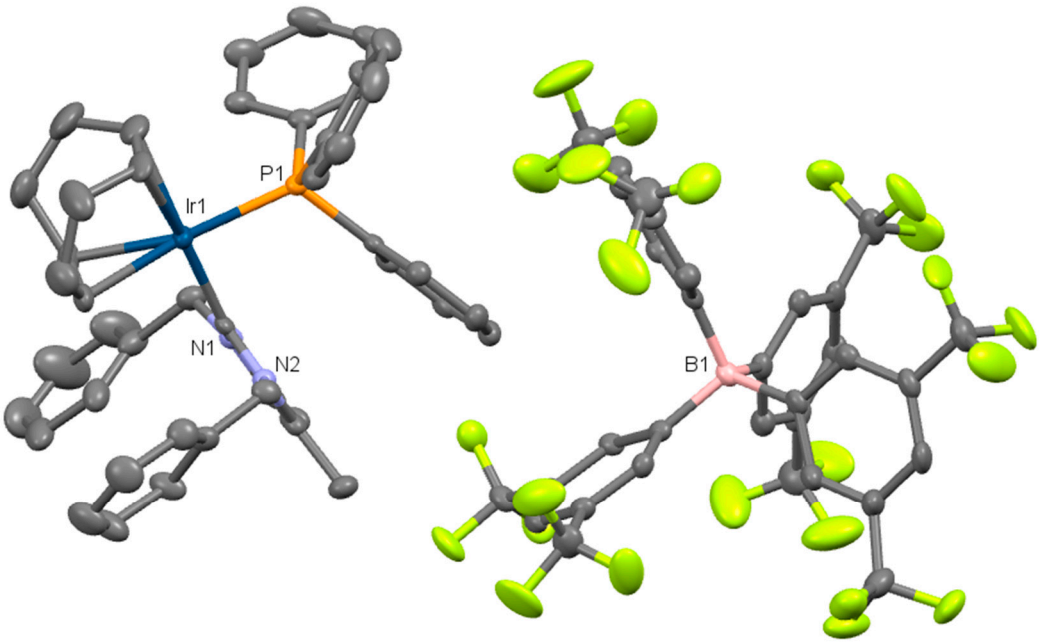
4.11 X-ray Structure of 6d

CCDC 1971358



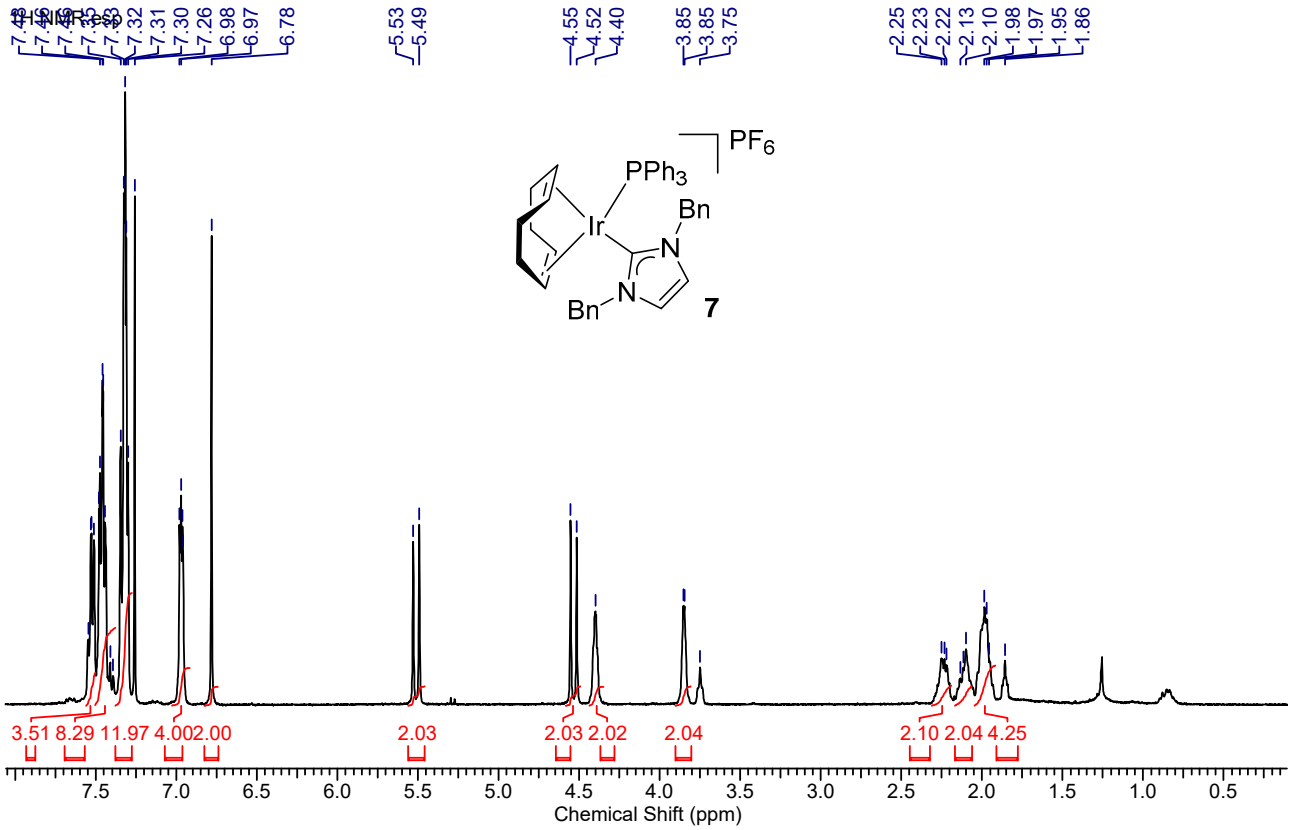
4.12 X-ray Structure of 6e

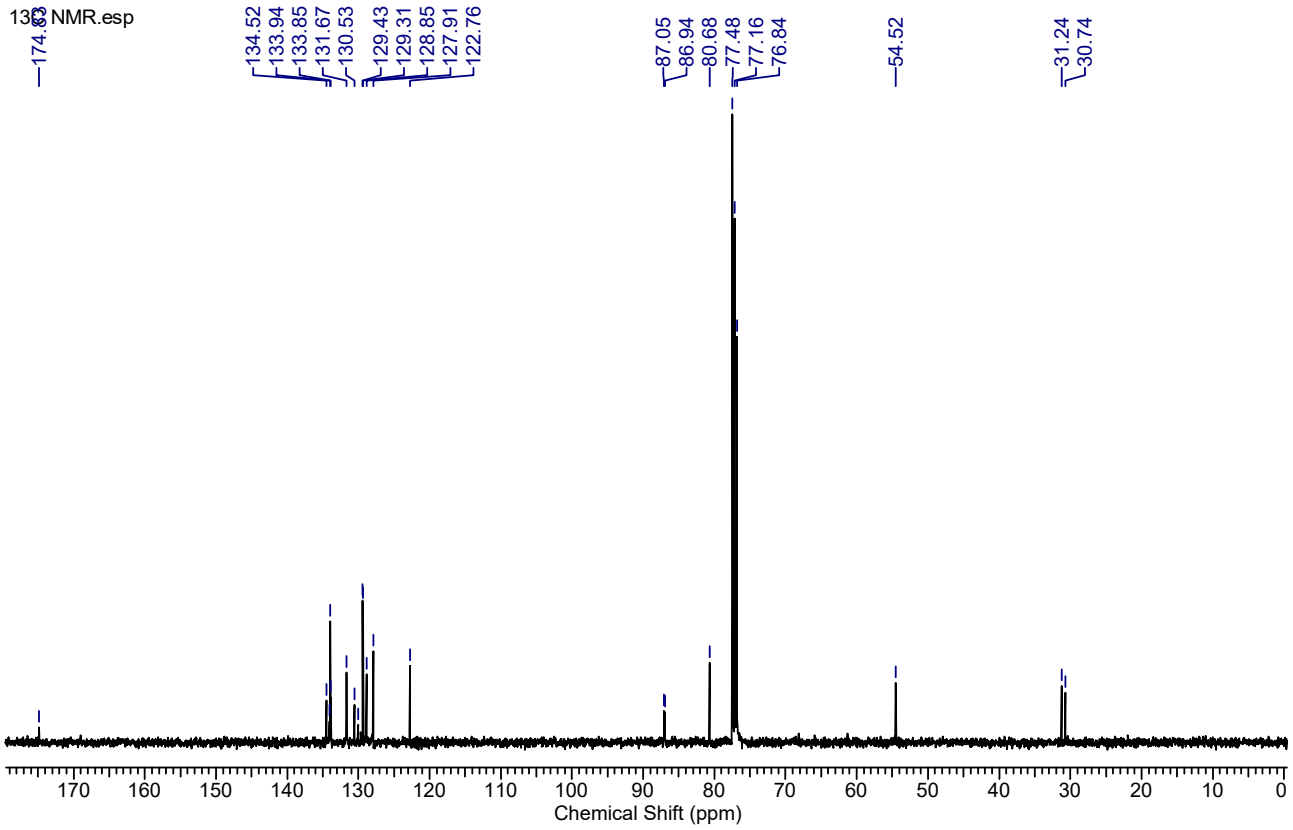
CCDC 1971359



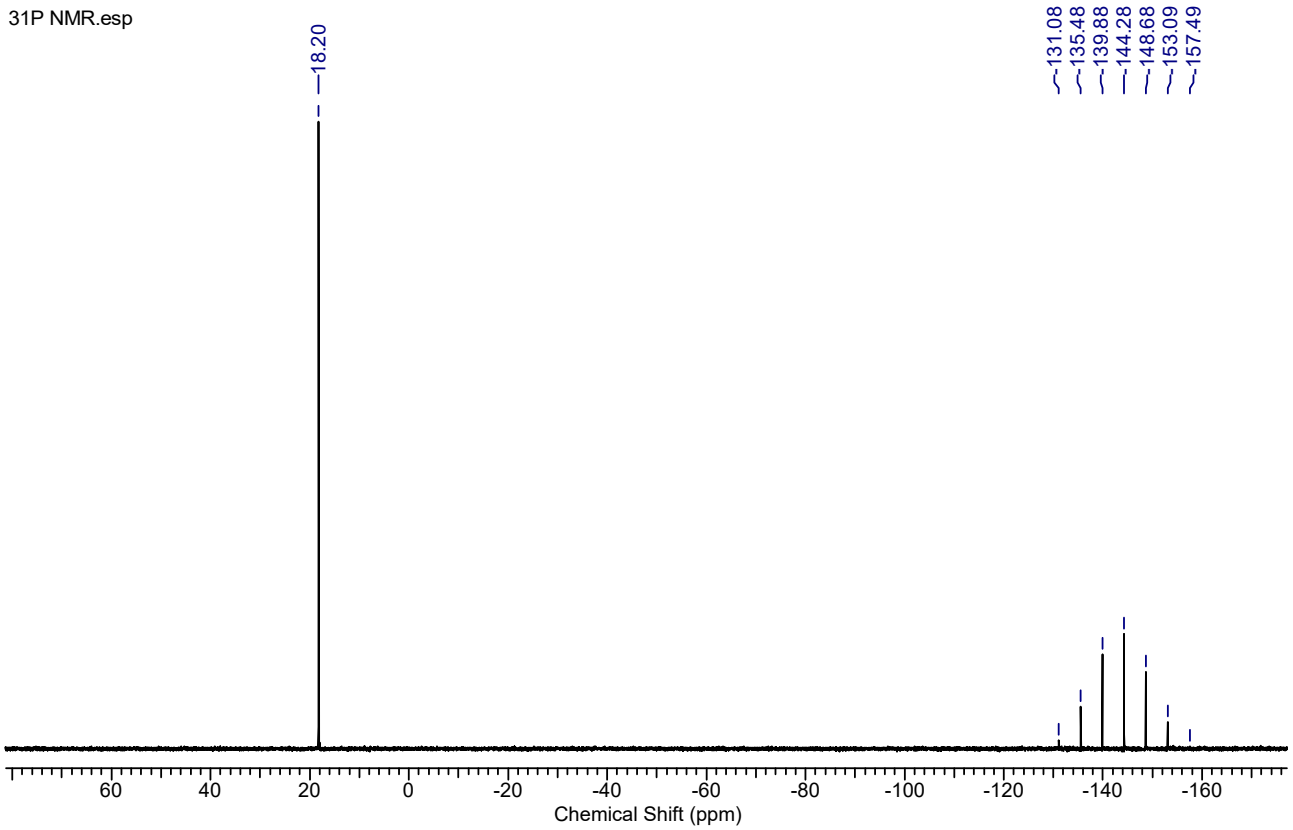
5. NMR Spectra

η^4–Cycloocta-1,5-diene(1,3-dibenzylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 7

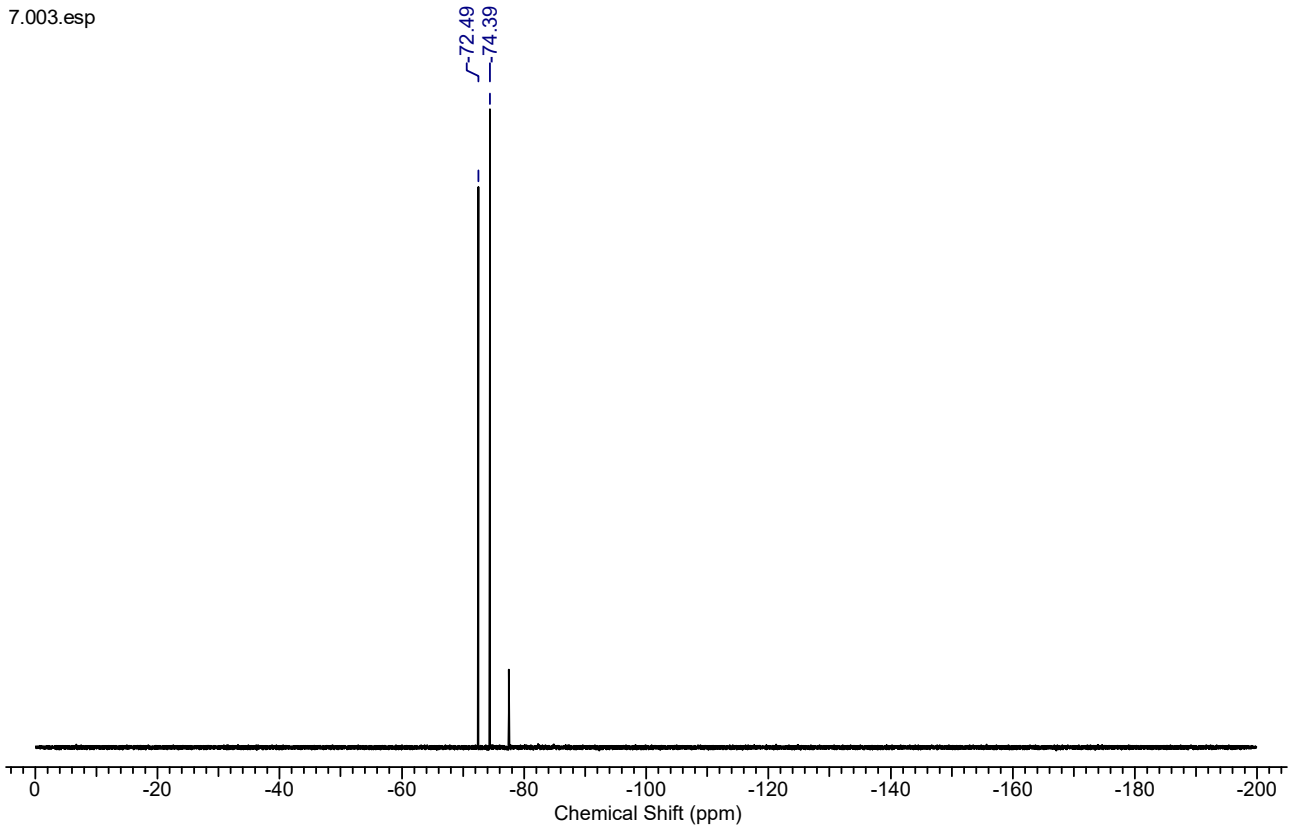




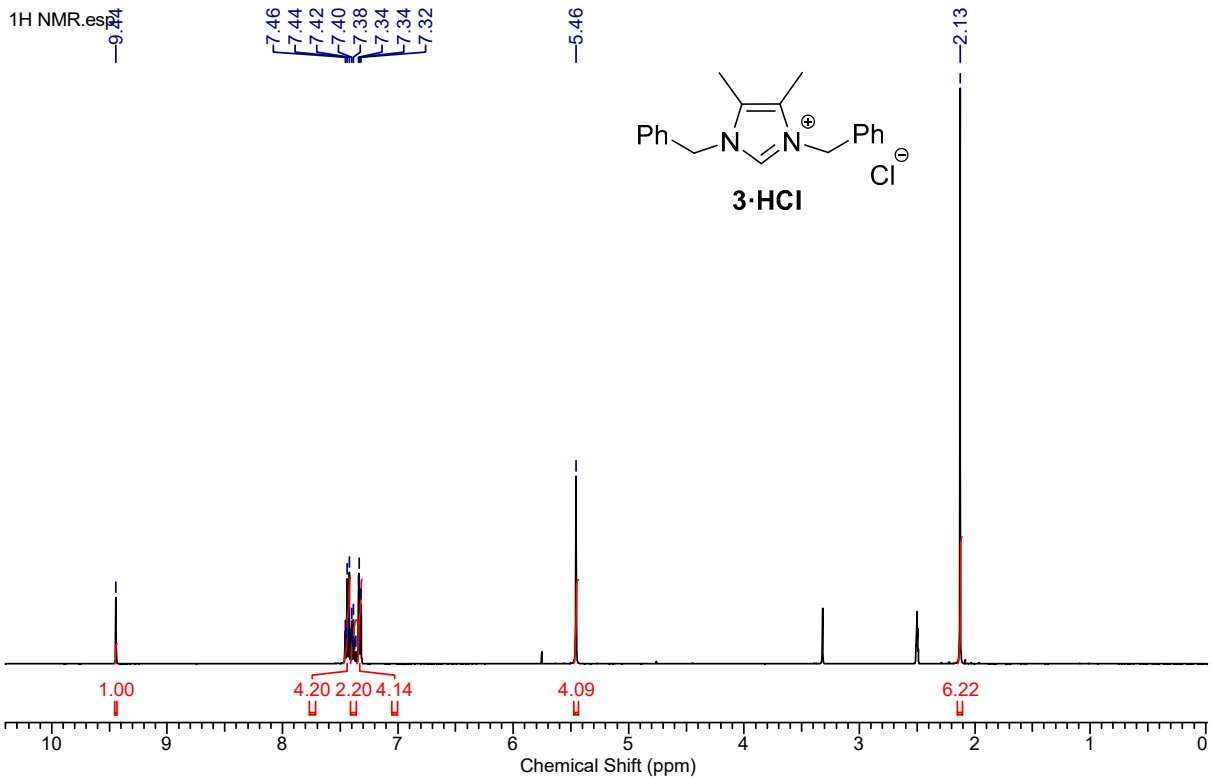
31P NMR.esp

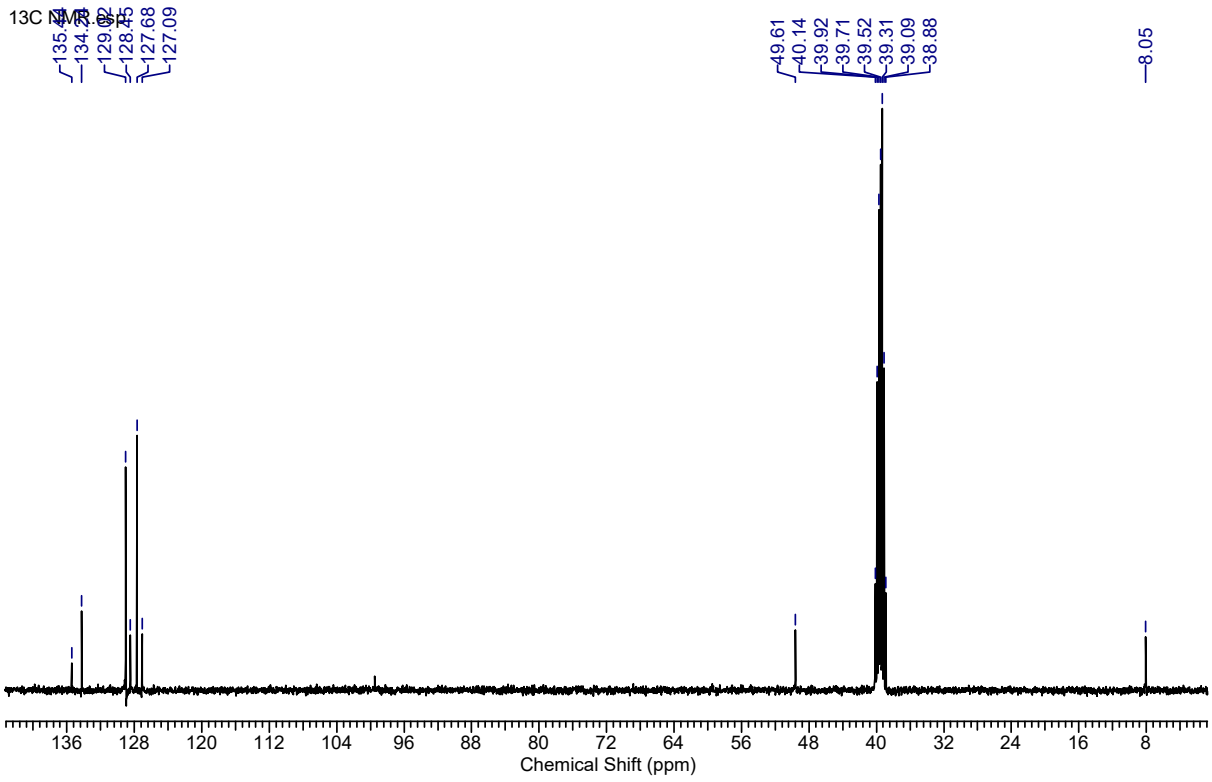


7.003.esp

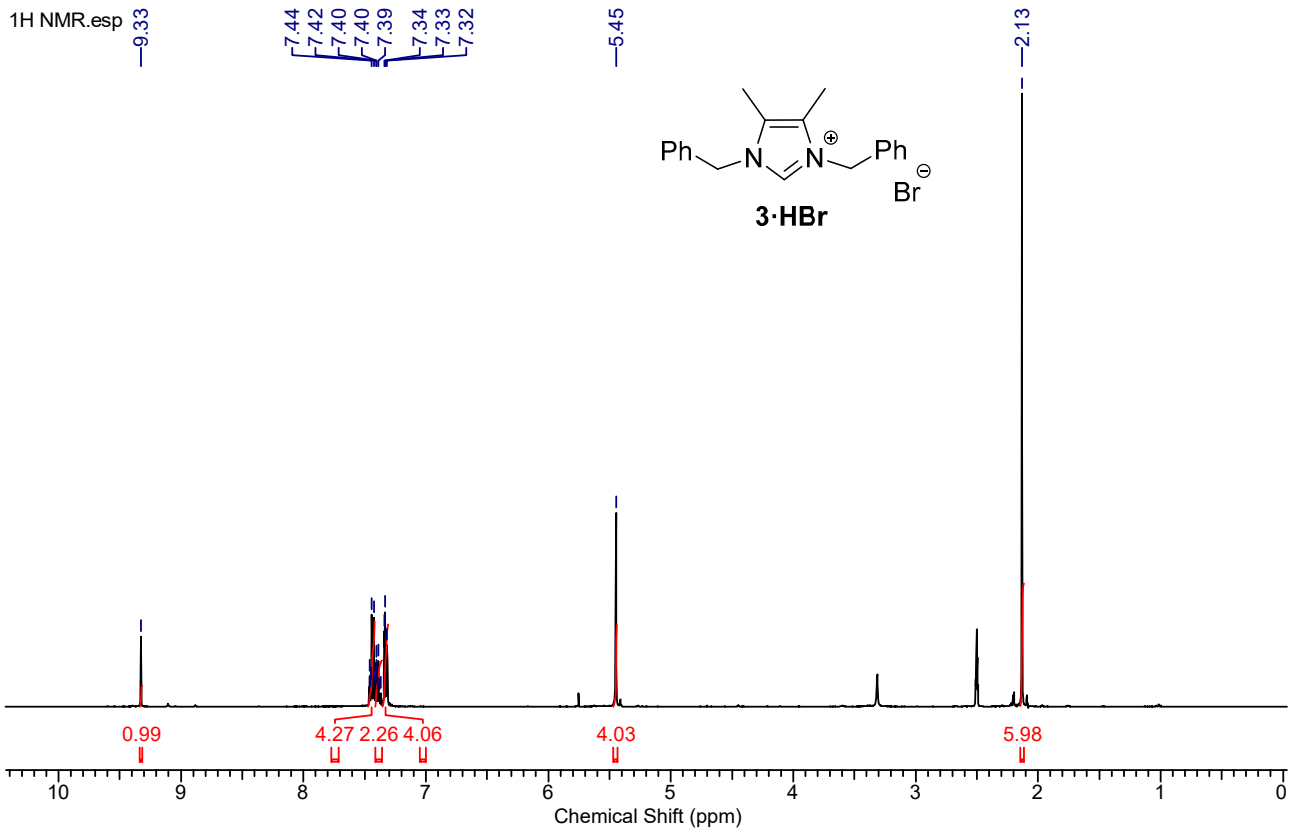


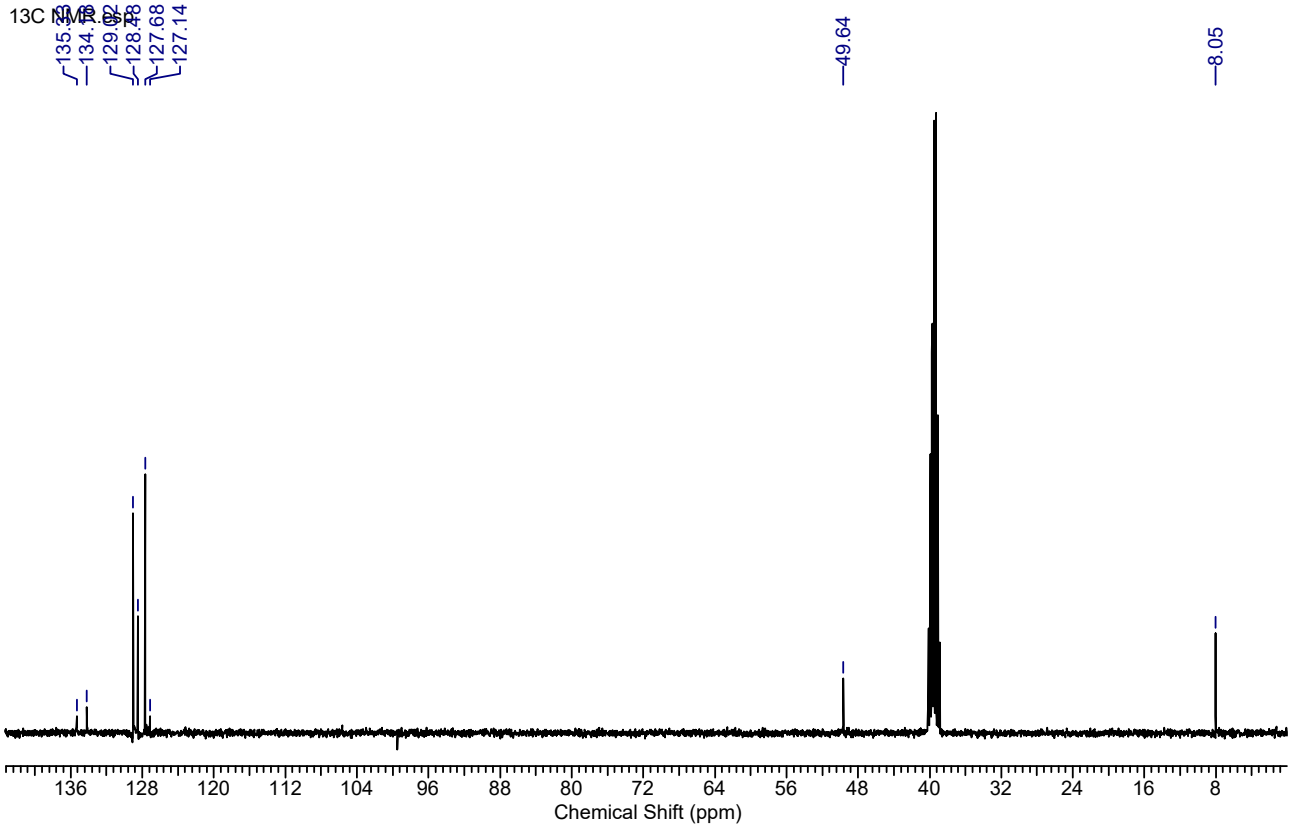
***N,N'*-Dibenzyl-4,5-dimethylimidazolium chloride (Lepidiline A) 3·HCl**



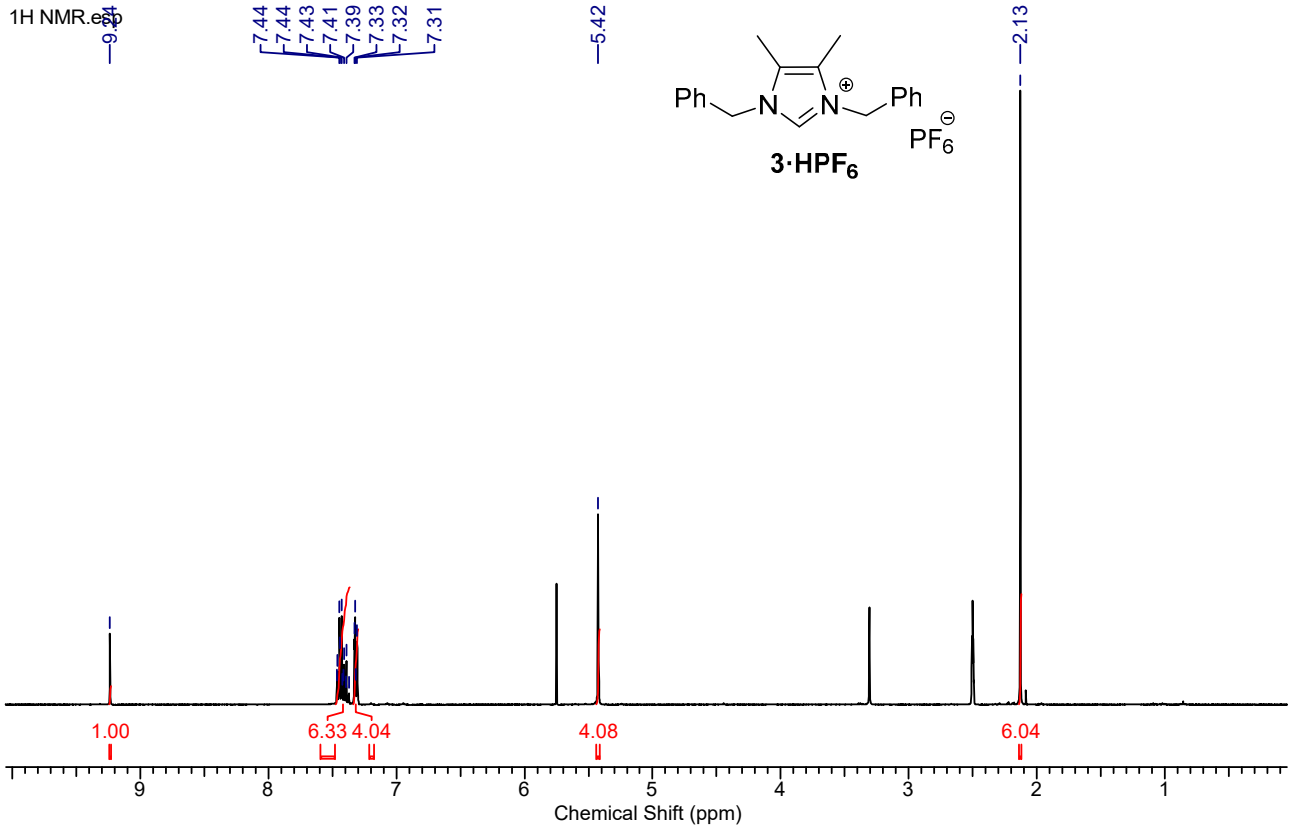


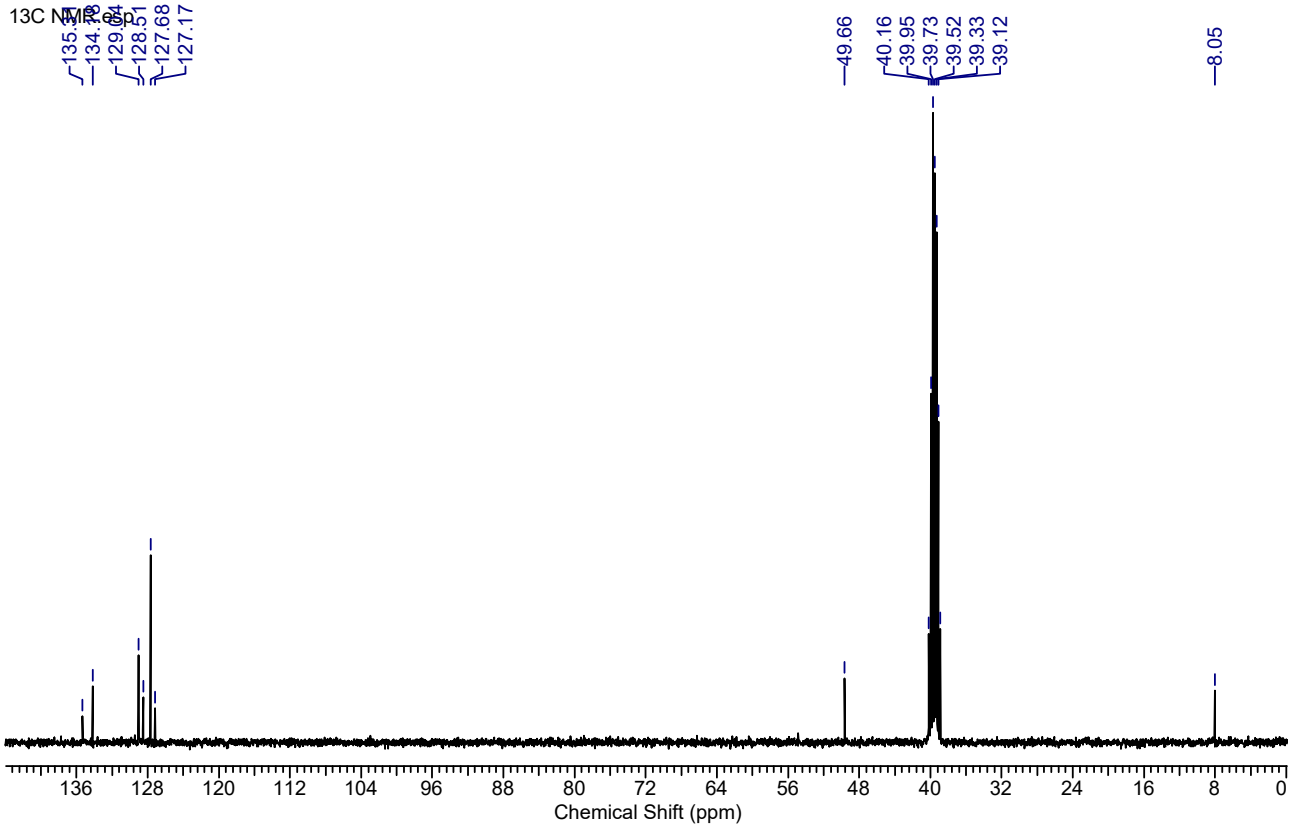
***N,N'*-Dibenzyl-4,5-dimethylimidazolium bromide 3·HBr**

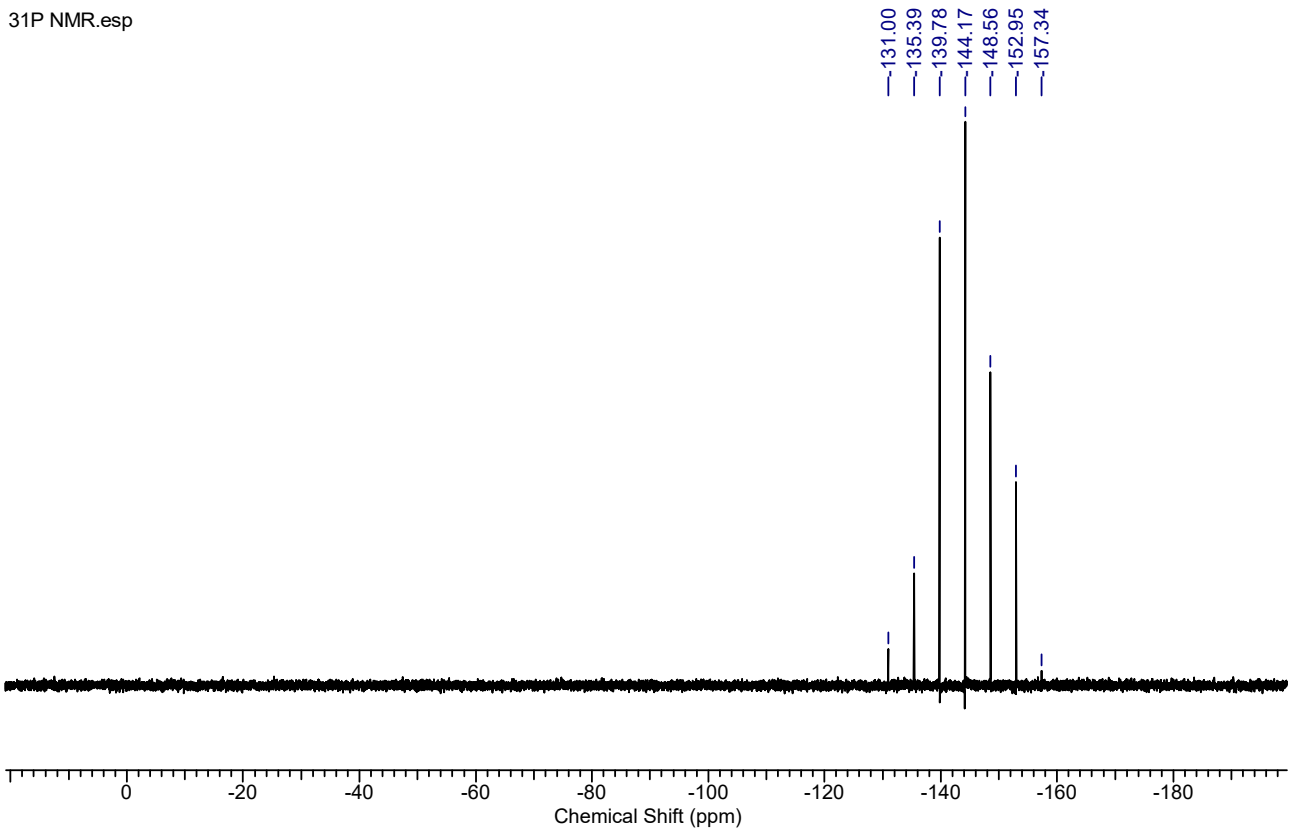




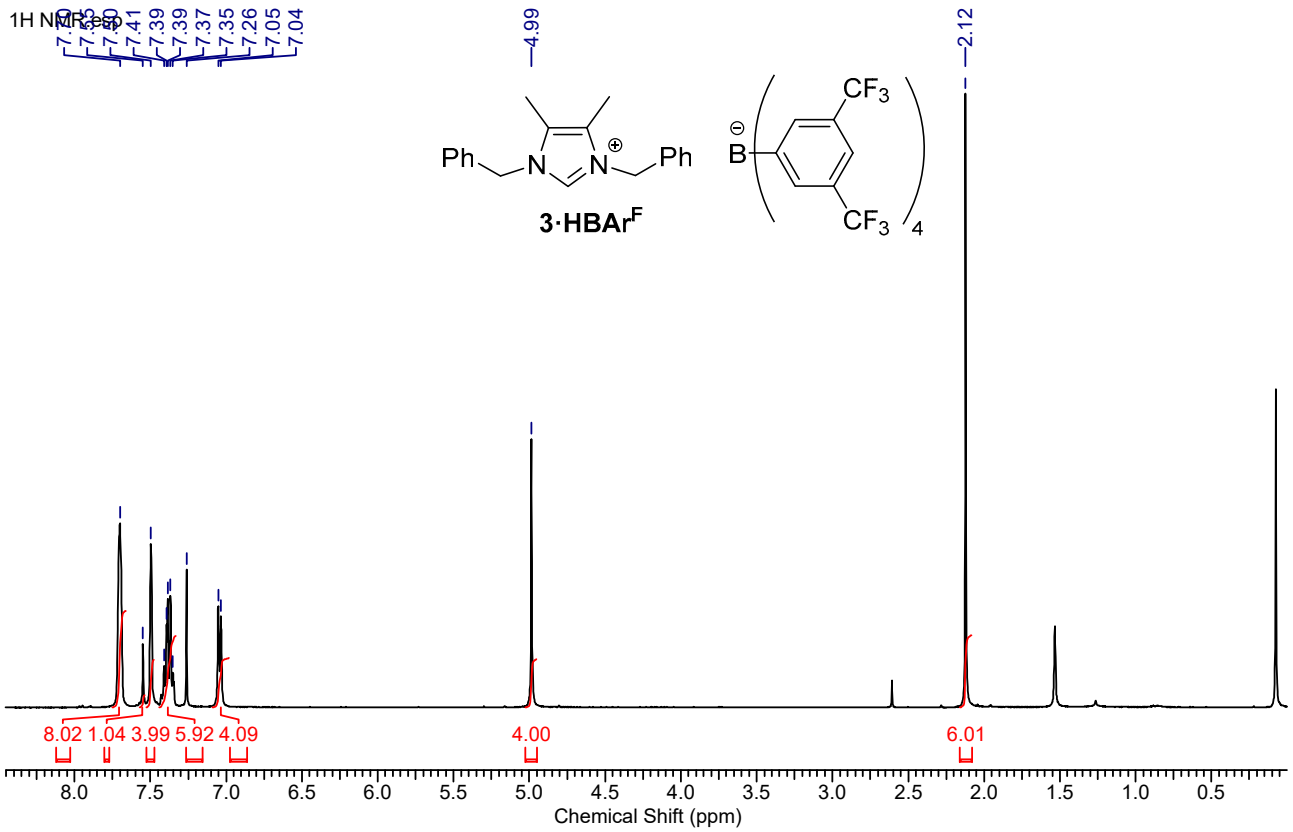
***N,N'*-Dibenzyl-4,5-dimethylimidazolium hexafluorophosphate 3·HPF$_6$**

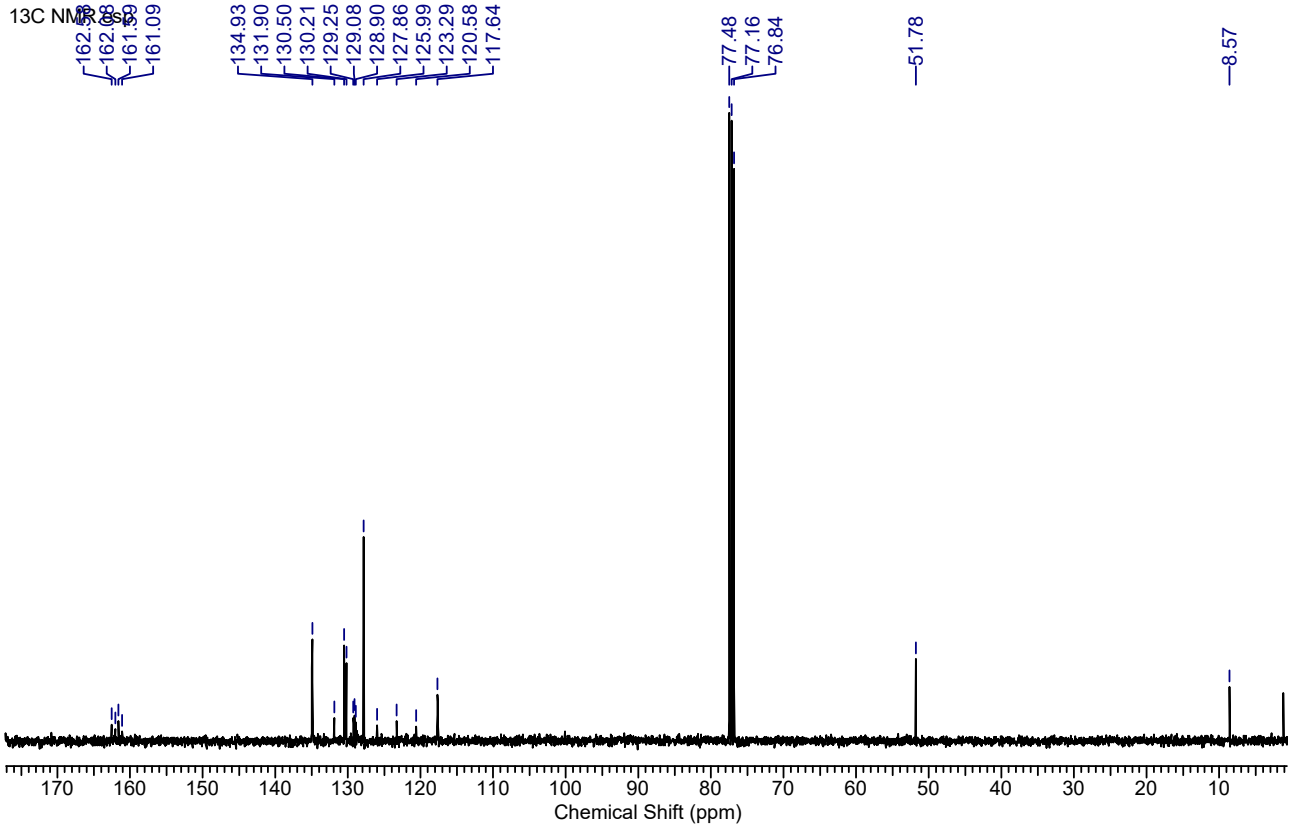


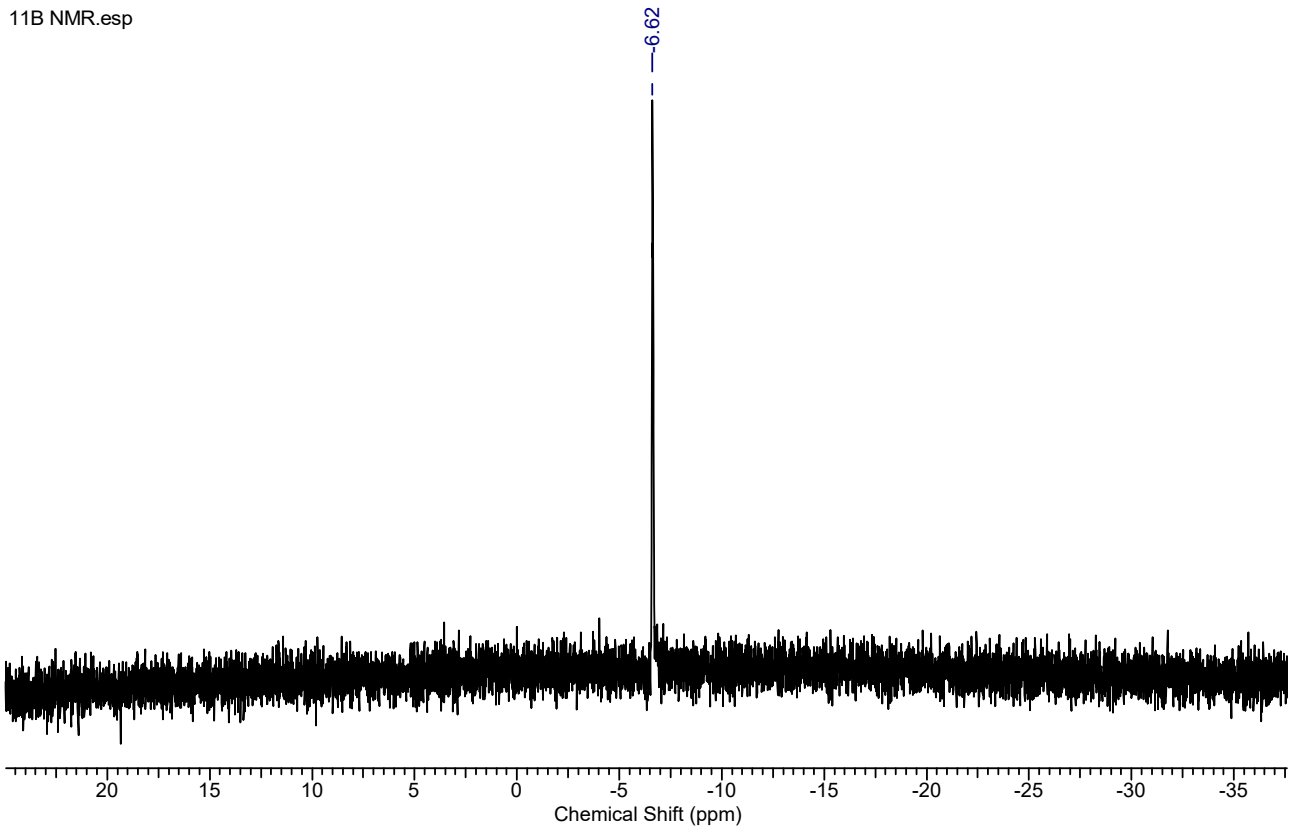


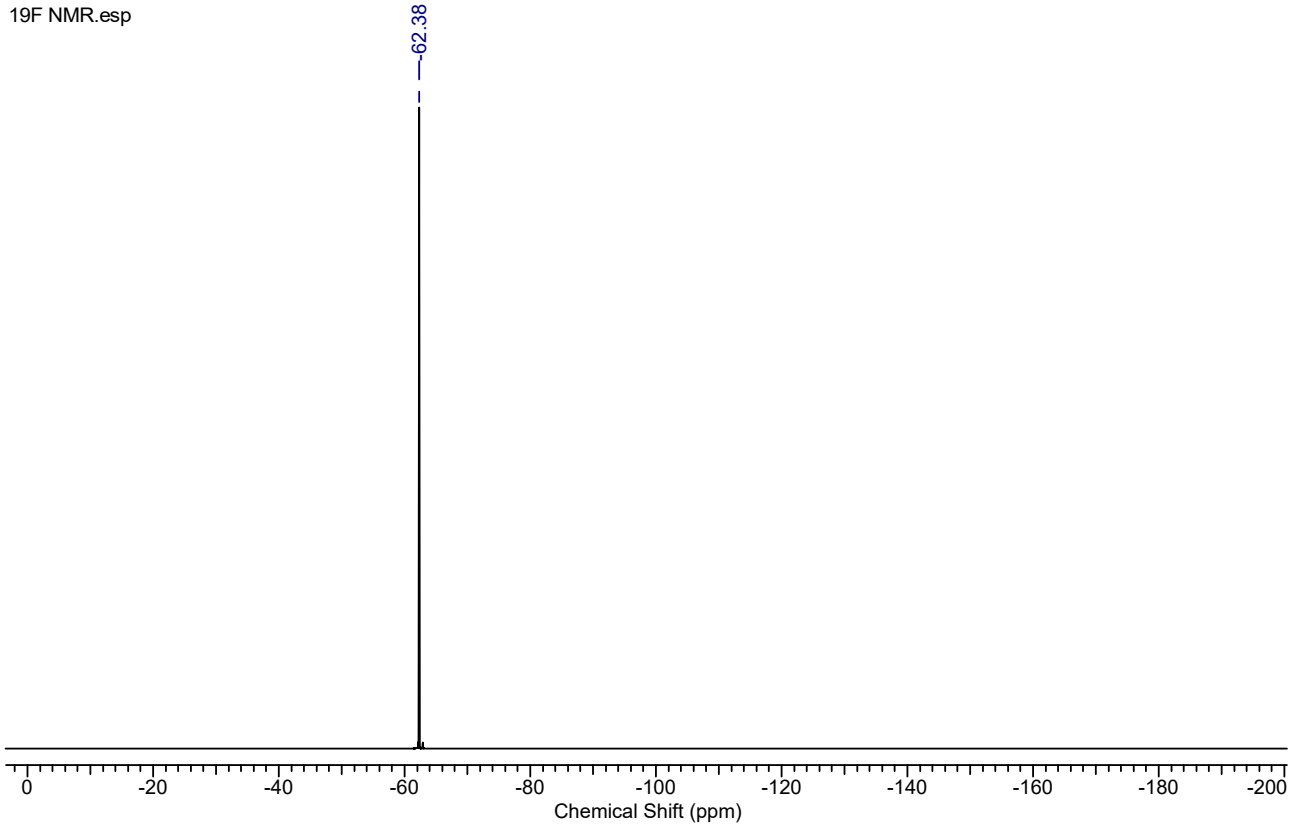

31P NMR.esp
131.00
135.39
139.78
144.17
148.56
152.95
157.34
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Chemical Shift (ppm)

***N,N'*-Dibenzyl-4,5-dimethylimidazolium tetrakis[(3,5-trifluoromethylphenyl)]borate, 3·HBAr^F**

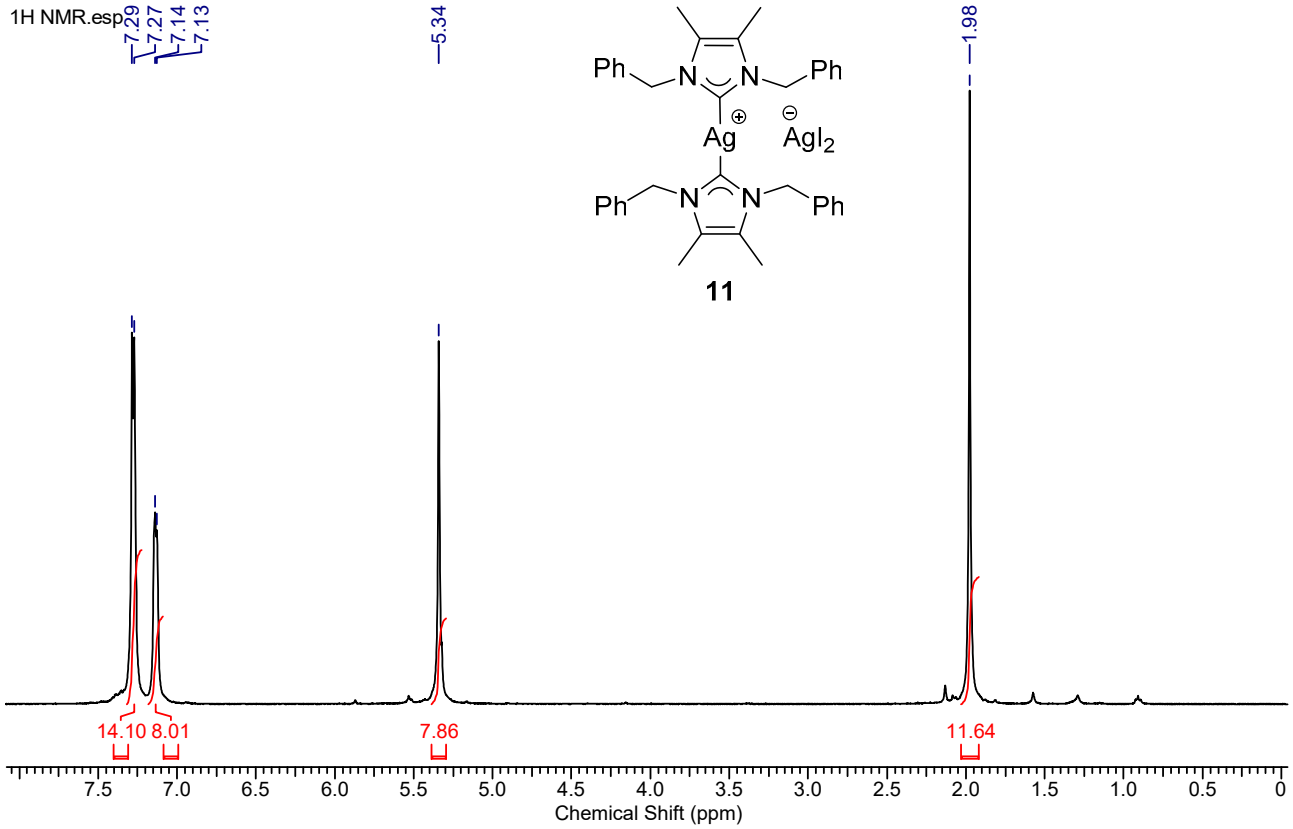


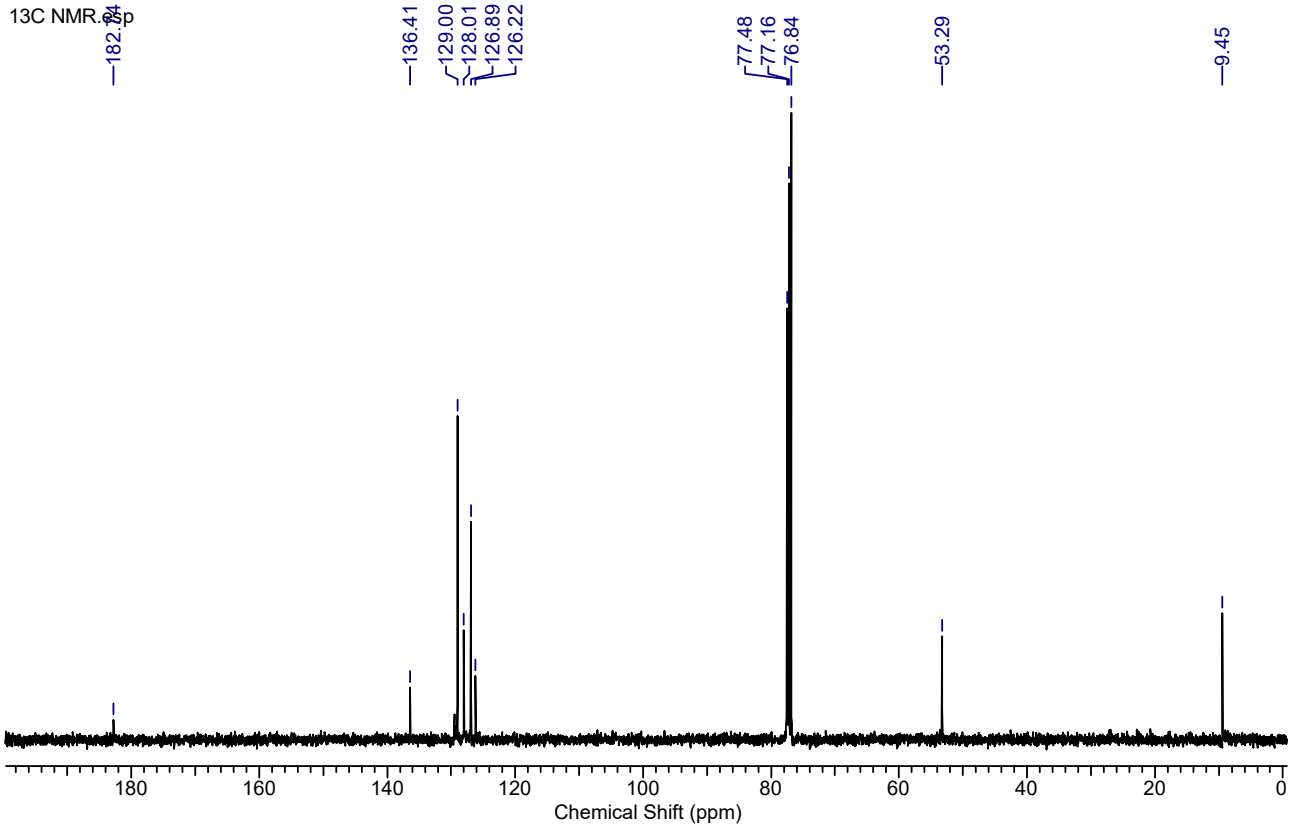



11B NMR.esp
6.62
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
Chemical Shift (ppm)

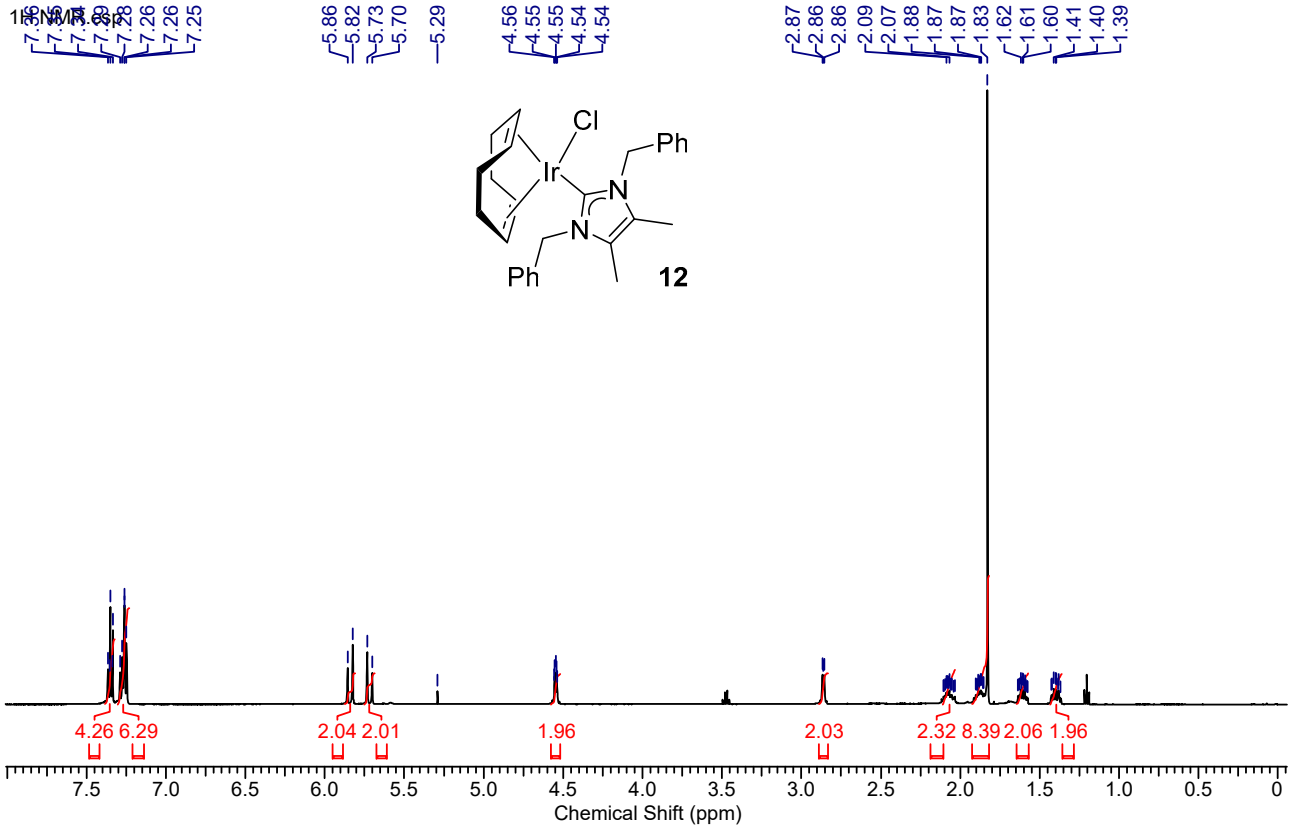

19F NMR.esp
-62.38
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

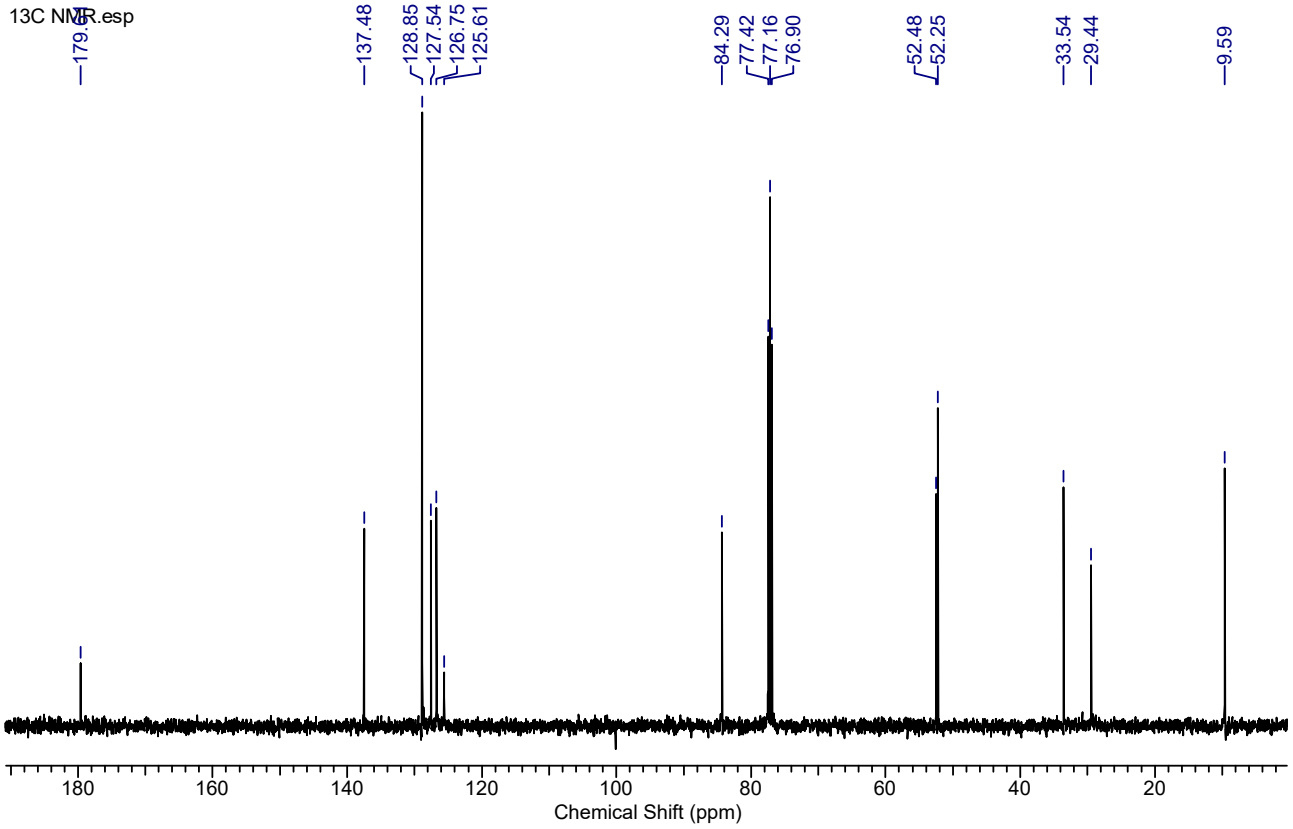
Bis(*N,N'*-dibenzyl-4,5-dimethylimidazol-2-ylidene)silver(I) silver diiodide 11



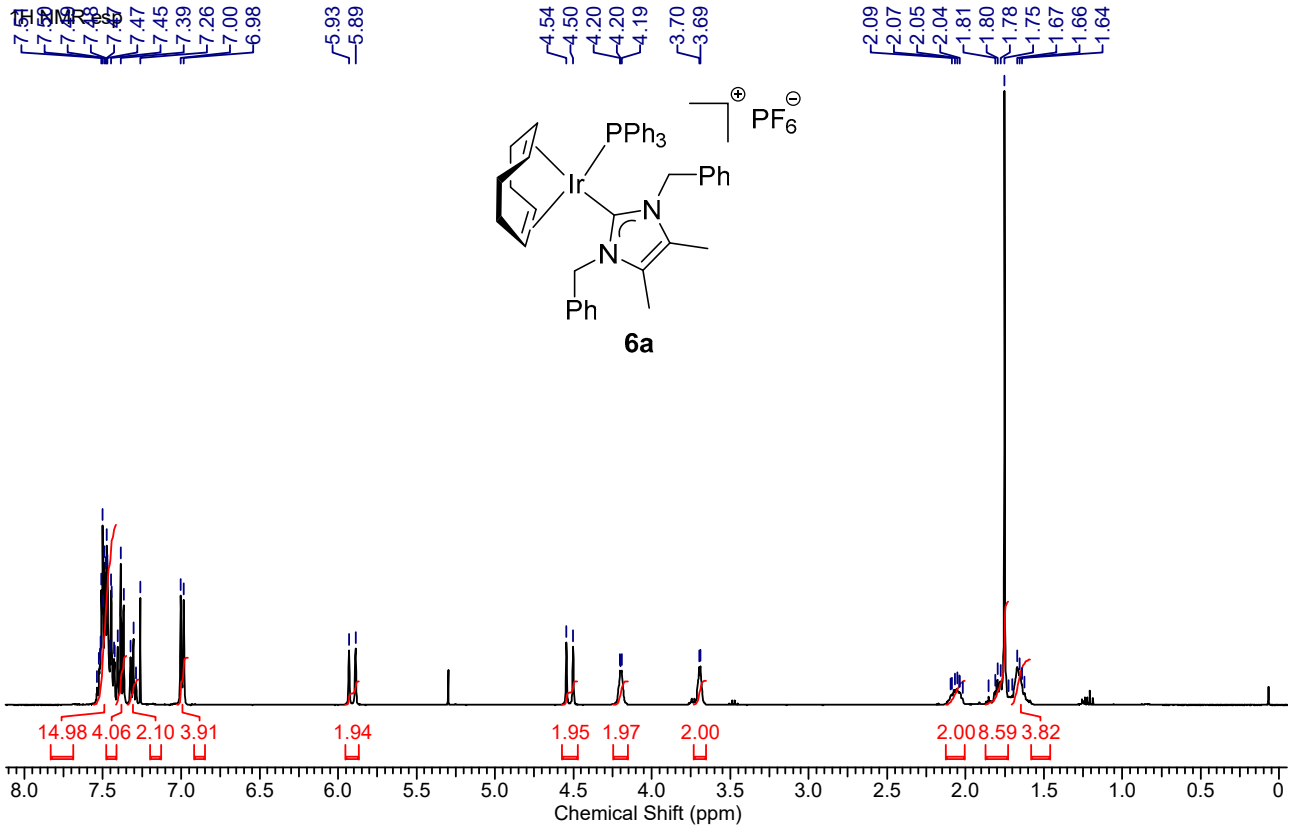


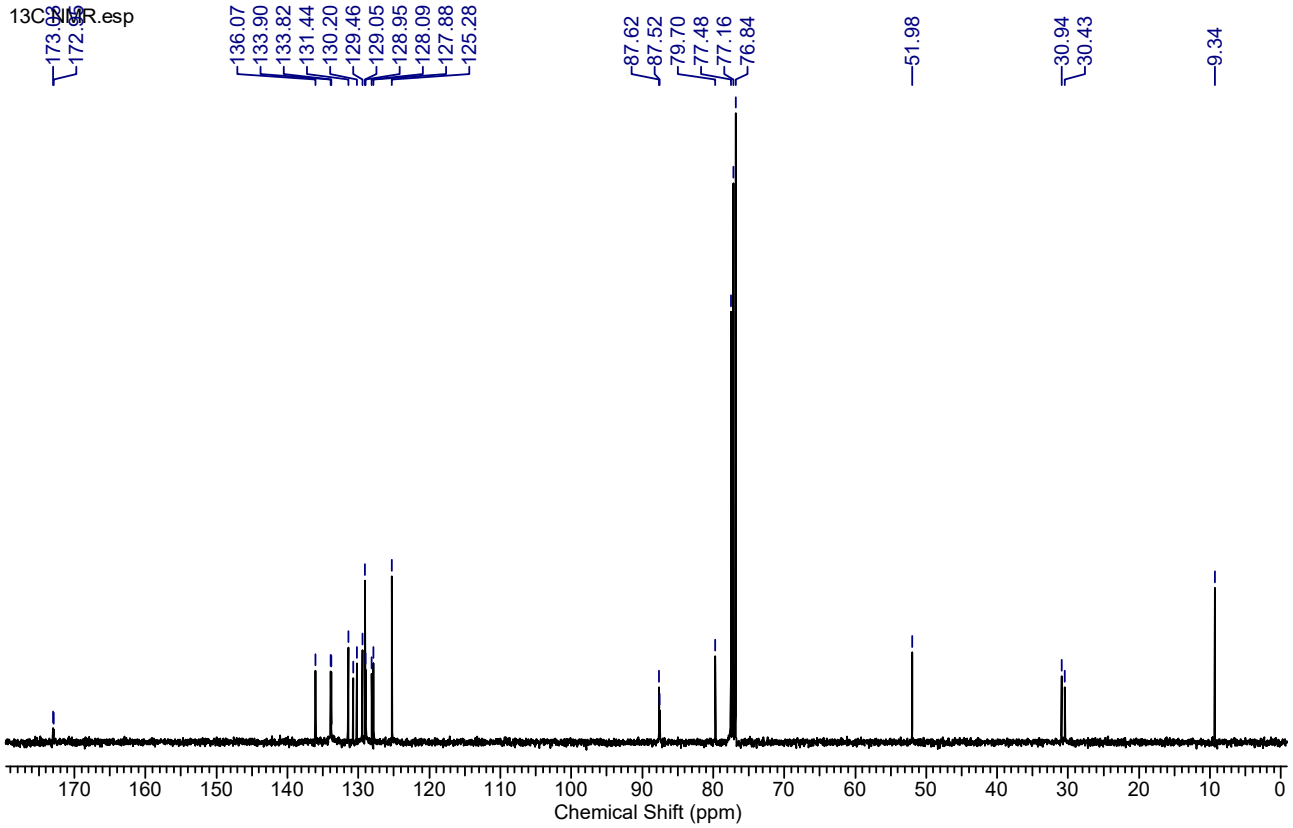
Chloro(η^4–cycloocta-1,5-diene)(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) iridium(I) 12

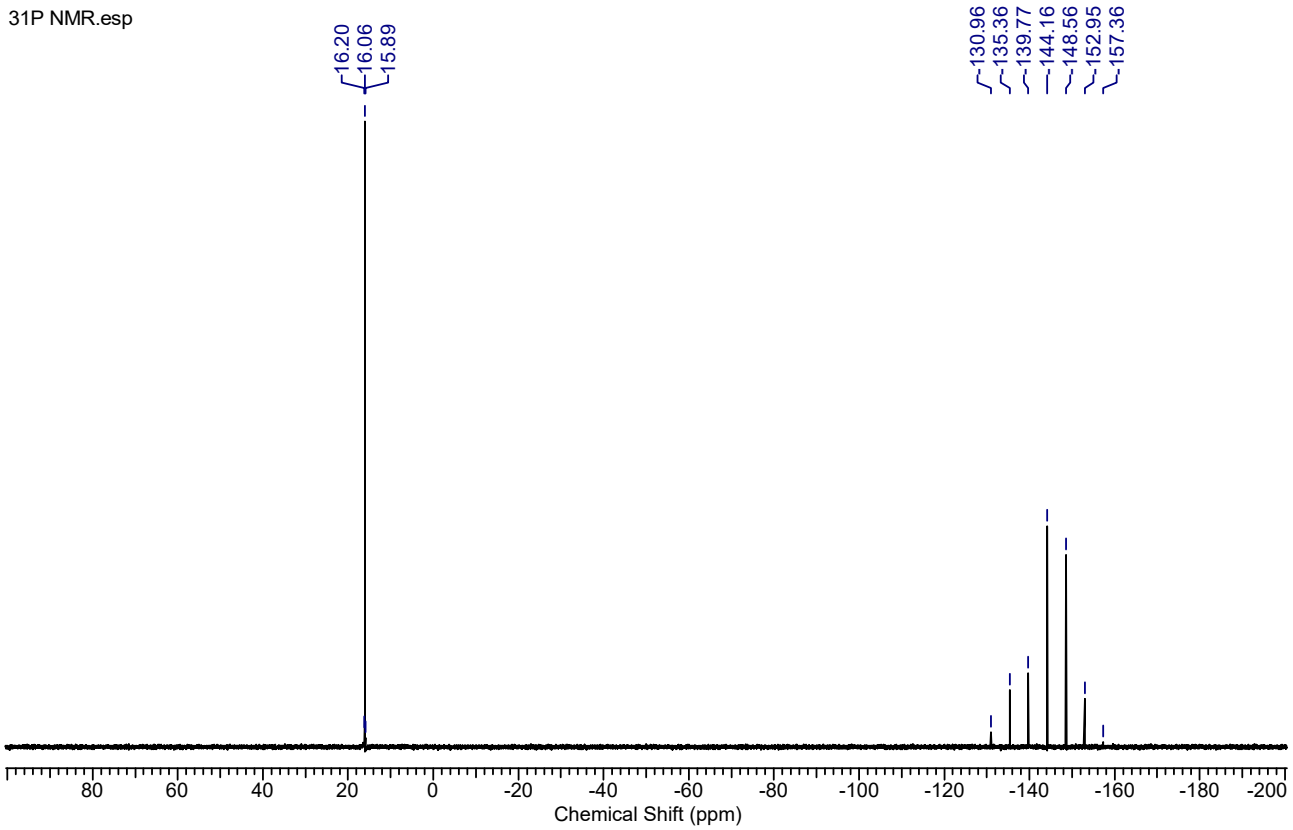




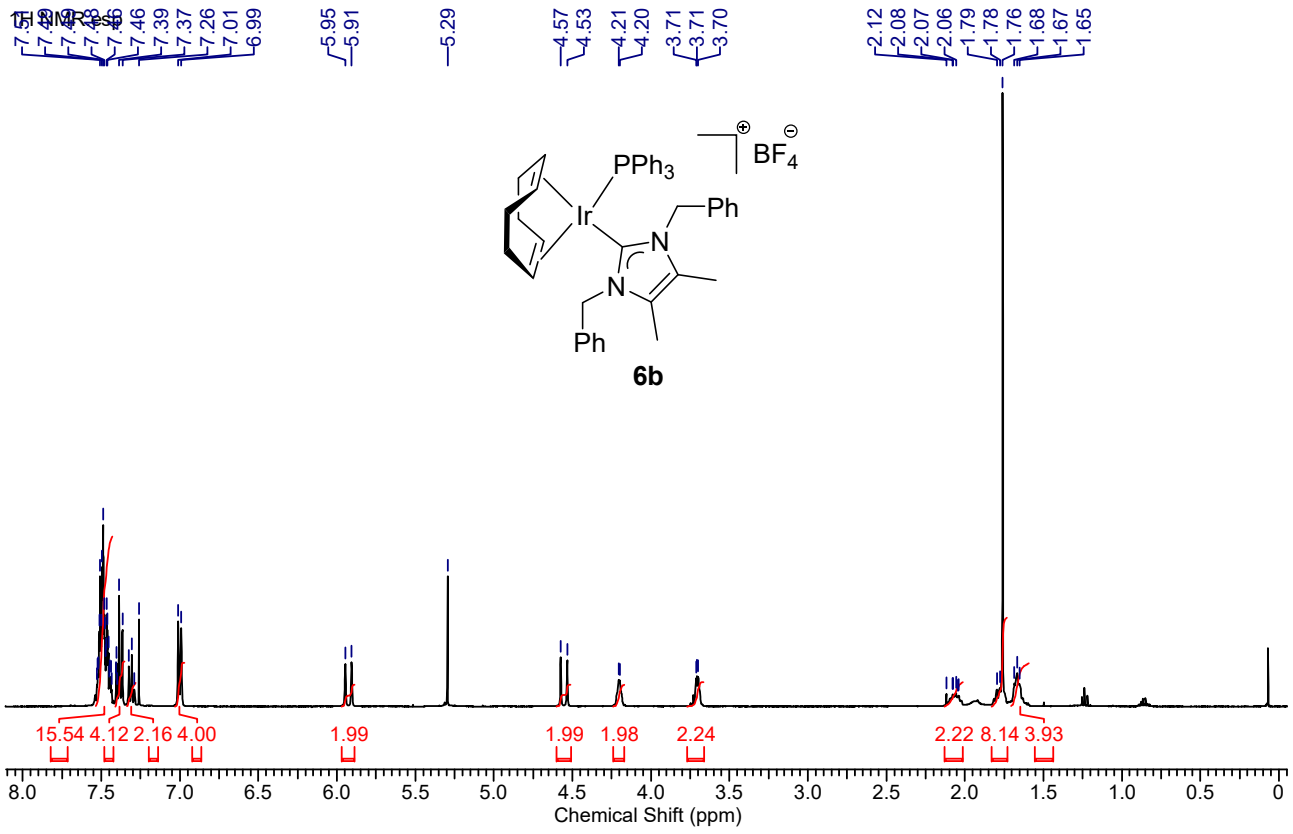
η^4–Cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) hexafluorophosphate 6a

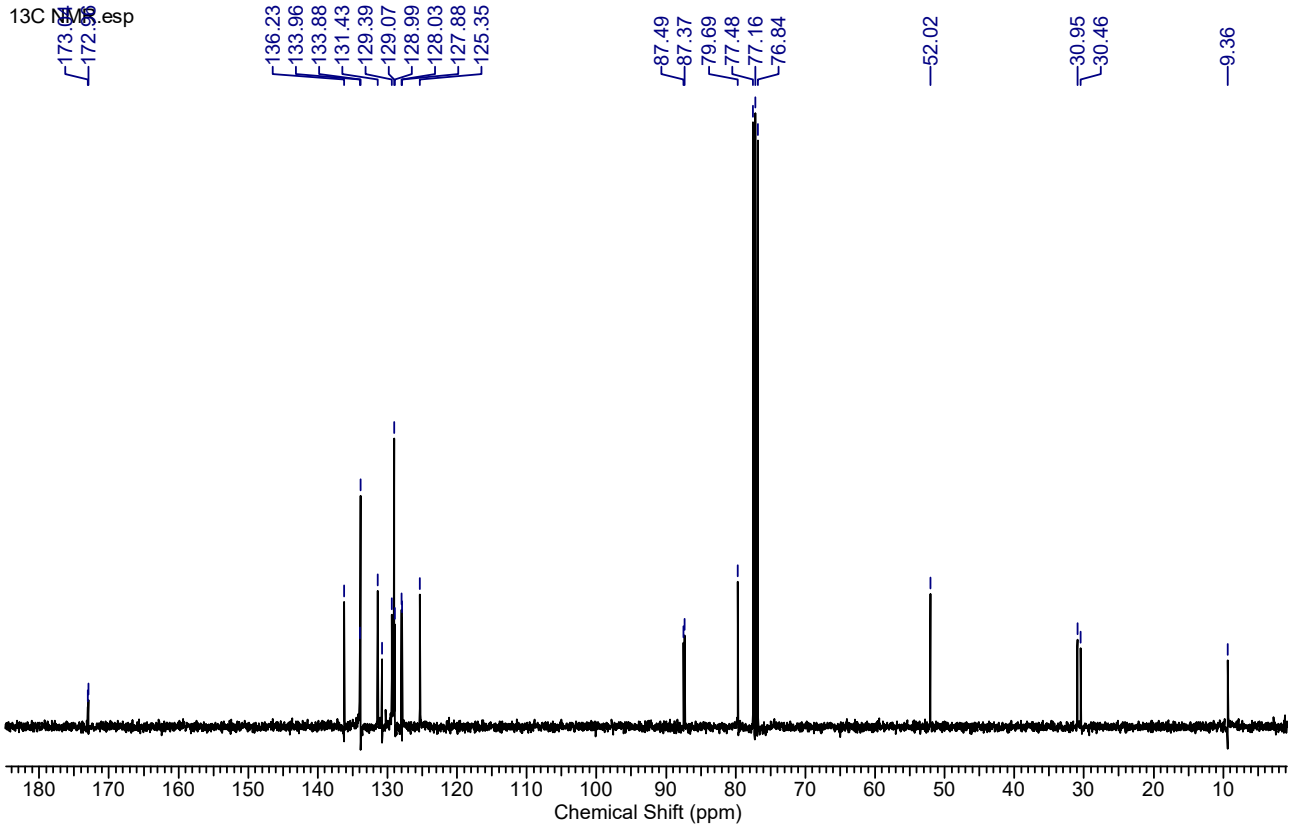




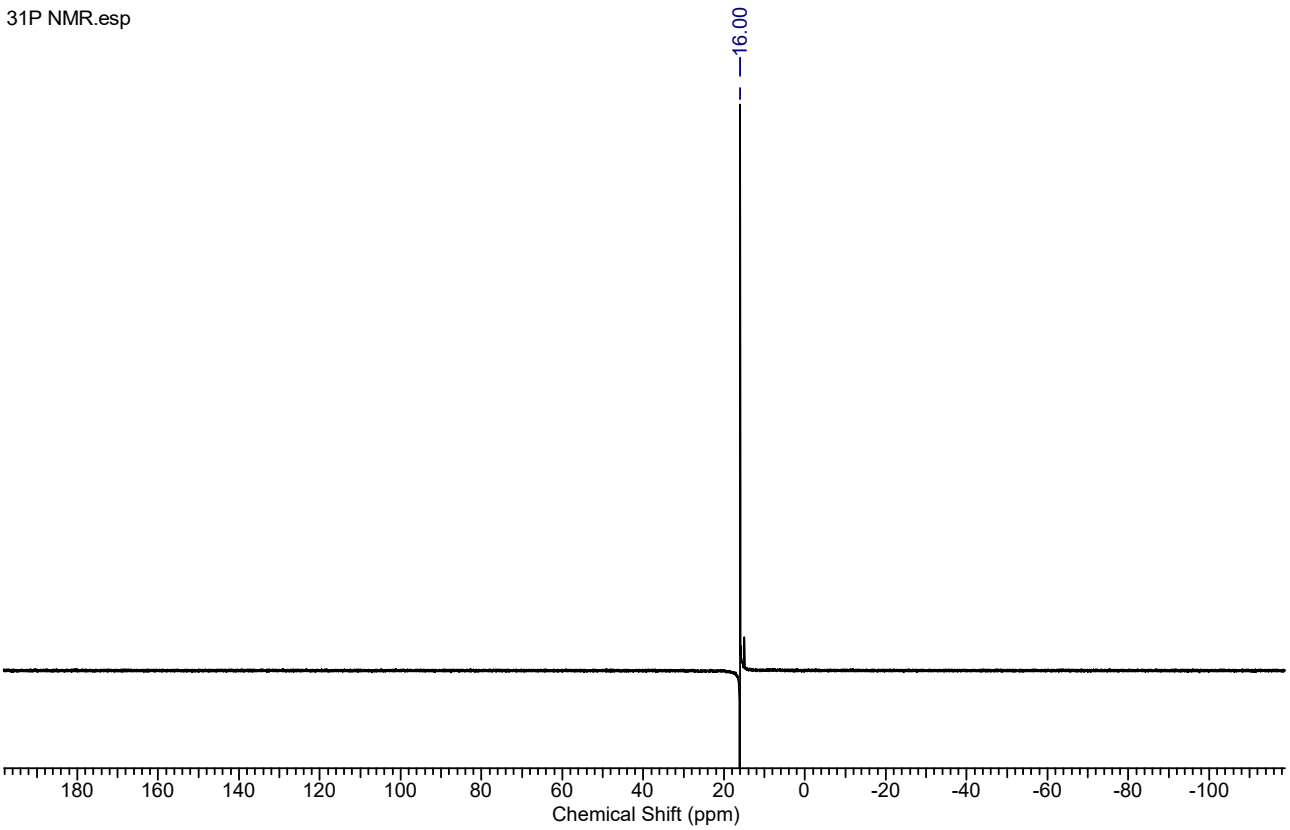

31P NMR.esp
16.20
16.06
15.89
130.96
135.36
139.77
144.16
148.56
152.95
157.36
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

η^4–Cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) tetrafluoroborate 6b

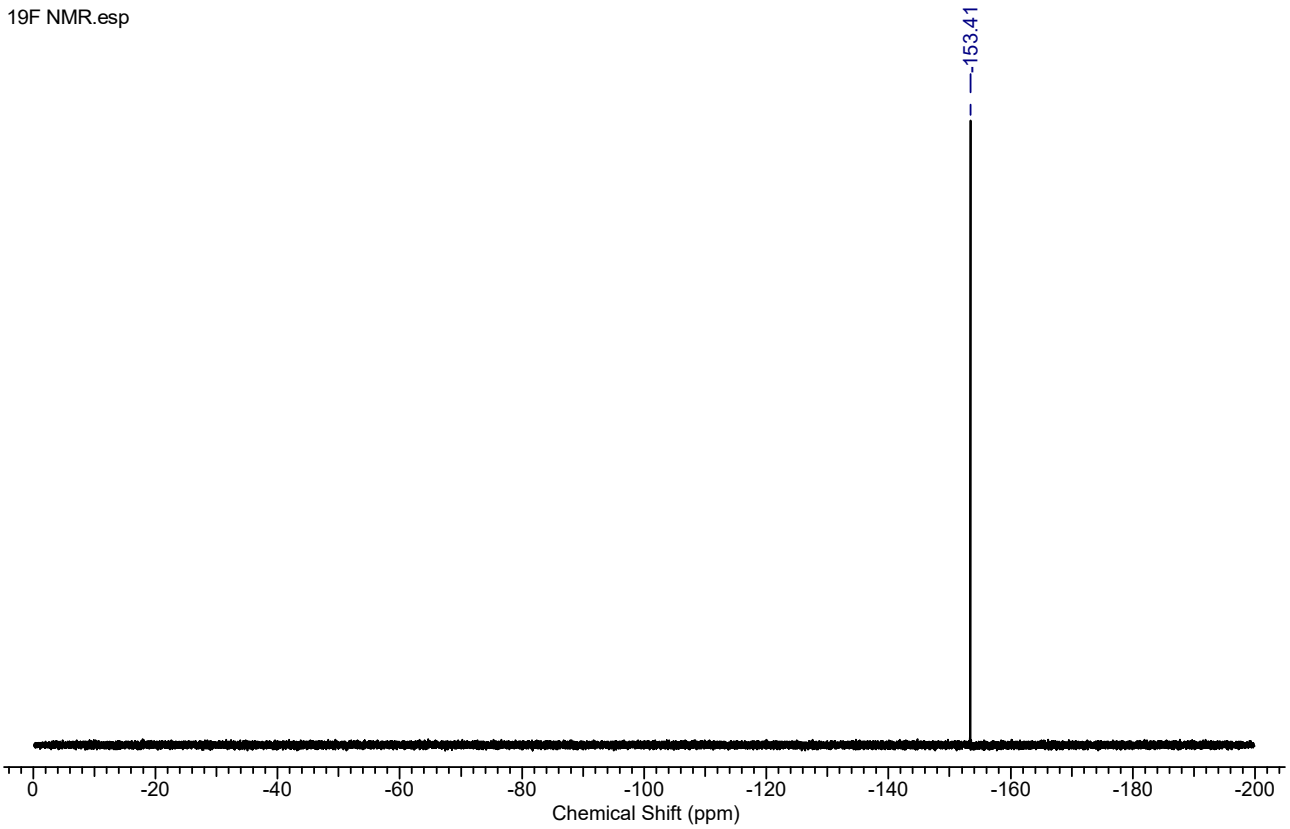


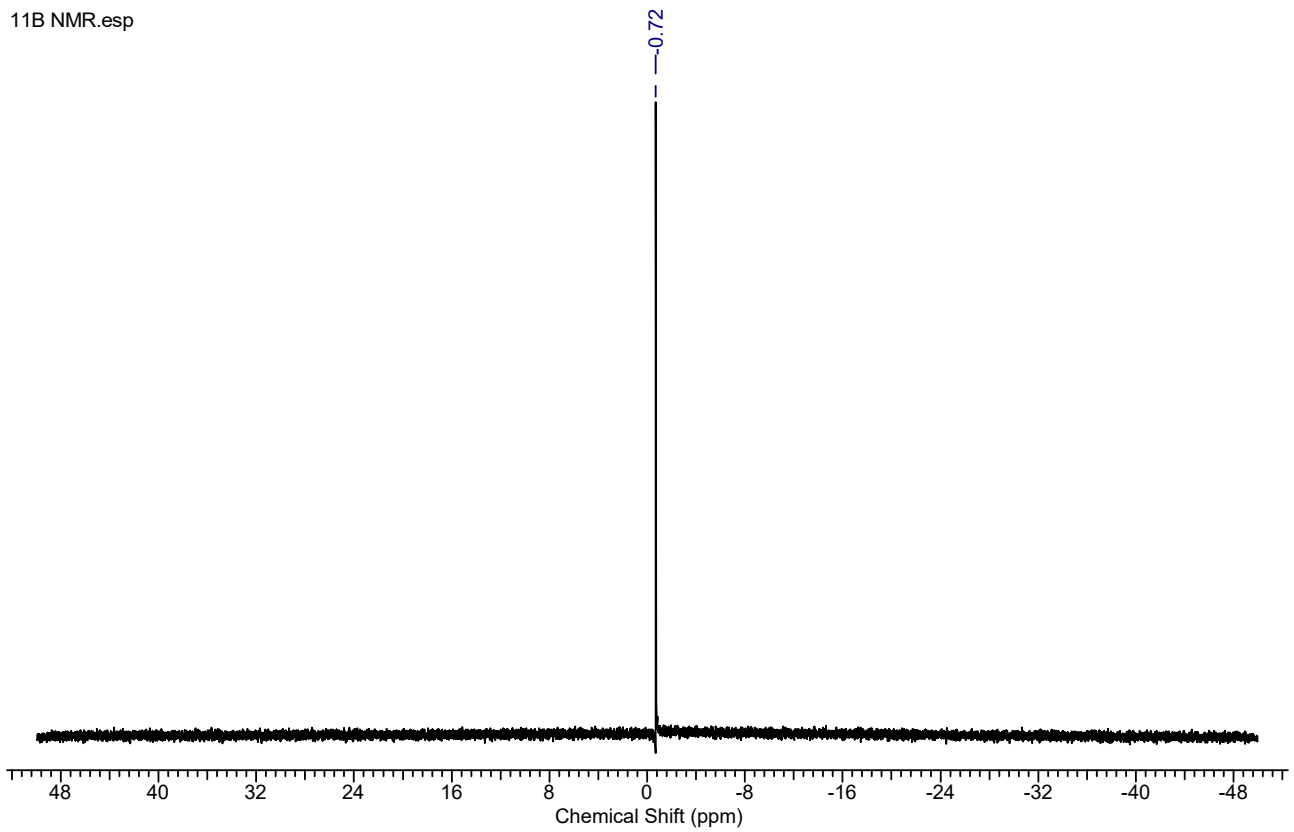


31P NMR.esp

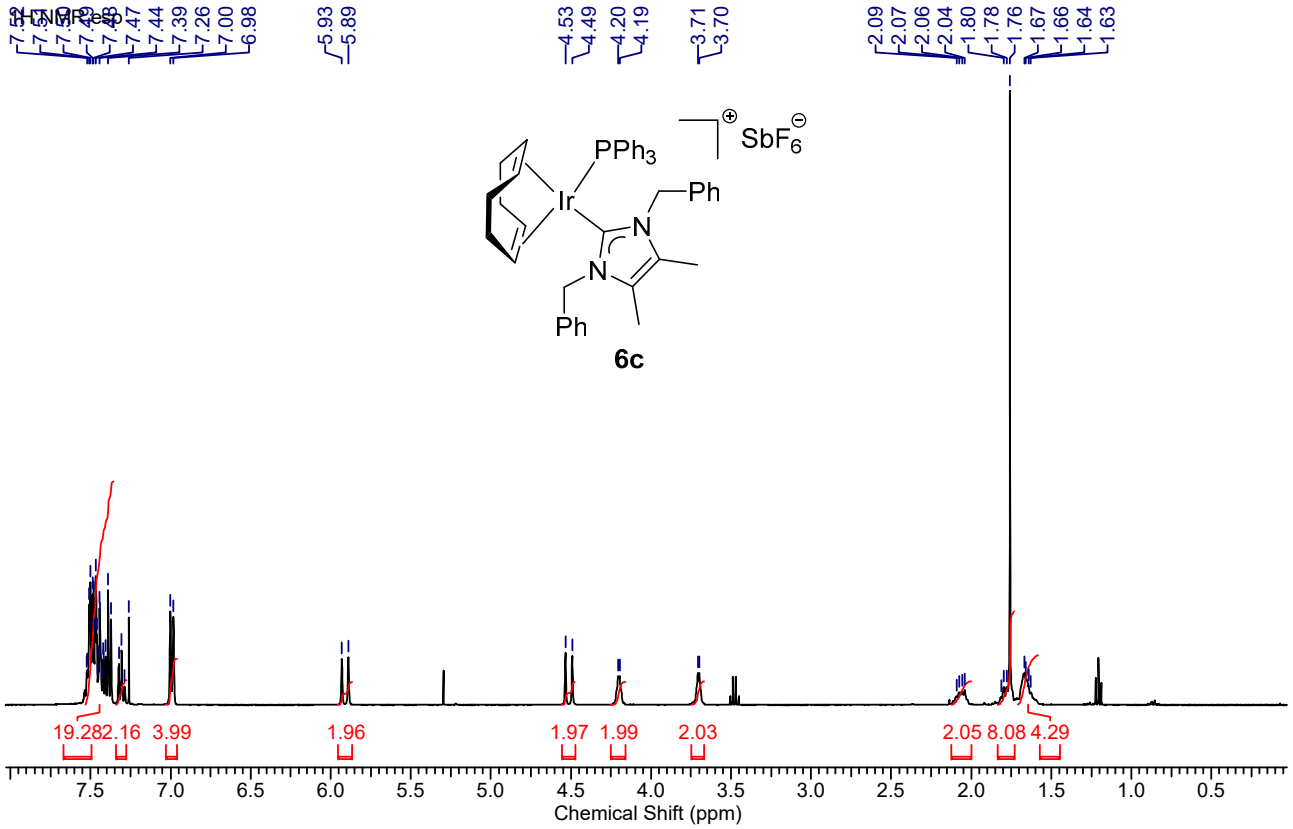


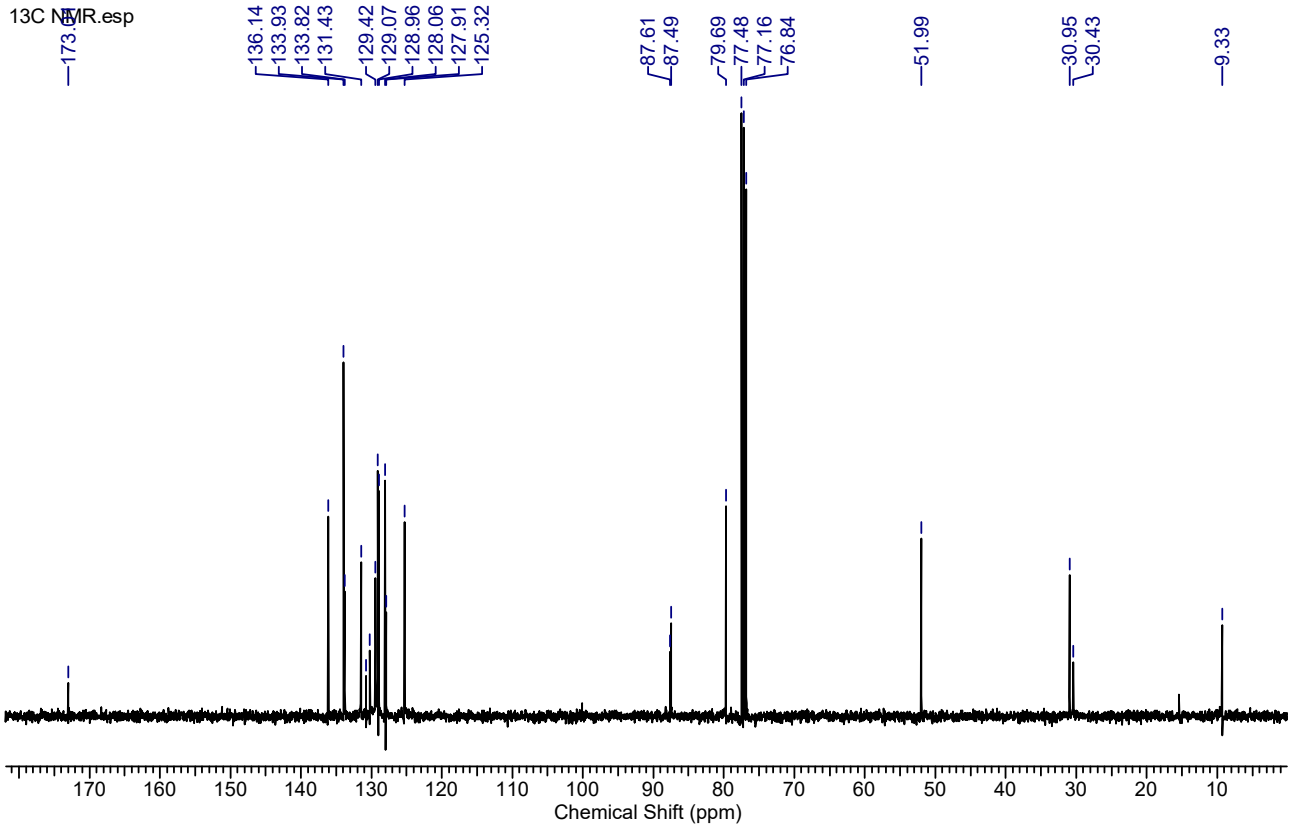
19F NMR.esp

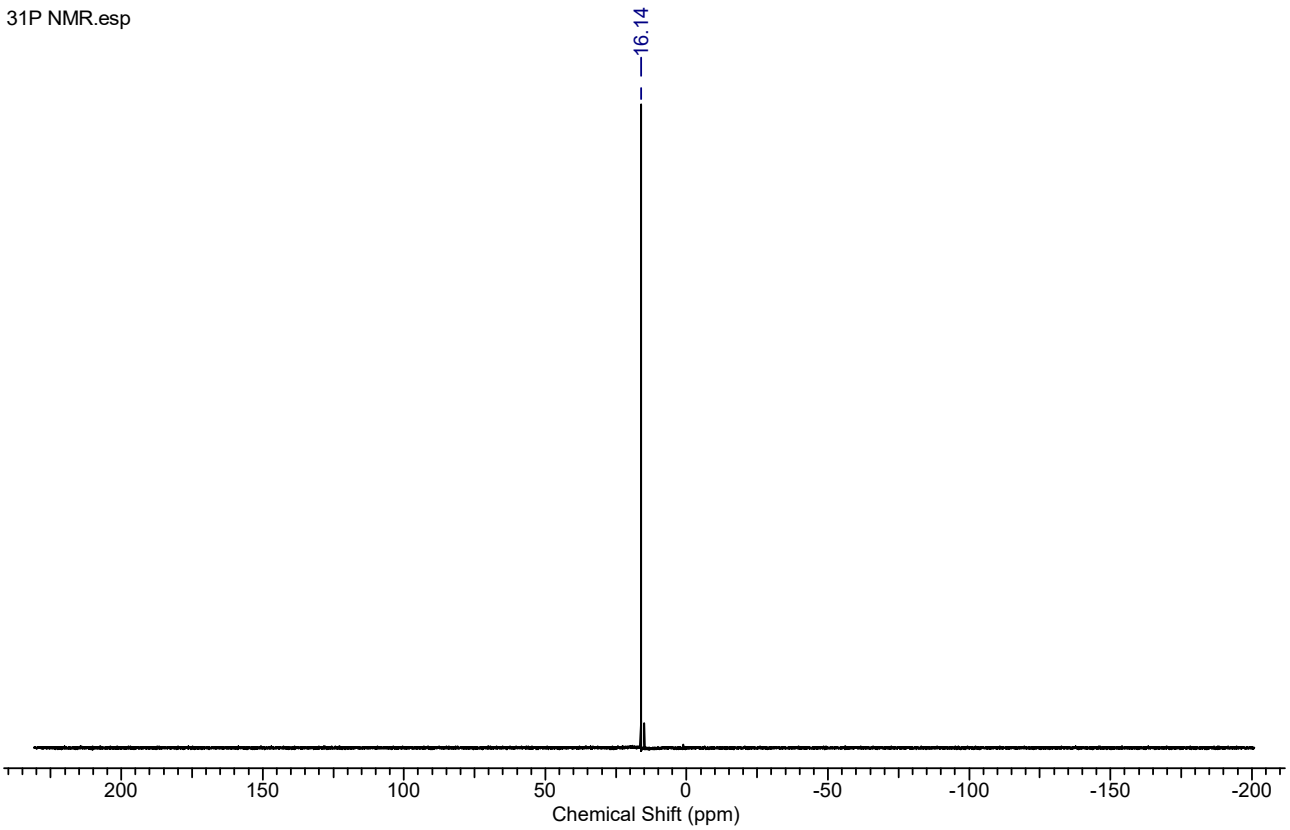



11B NMR.esp
0.72
48
40
32
24
16
8
0
-8
-16
-24
-32
-40
-48
Chemical Shift (ppm)

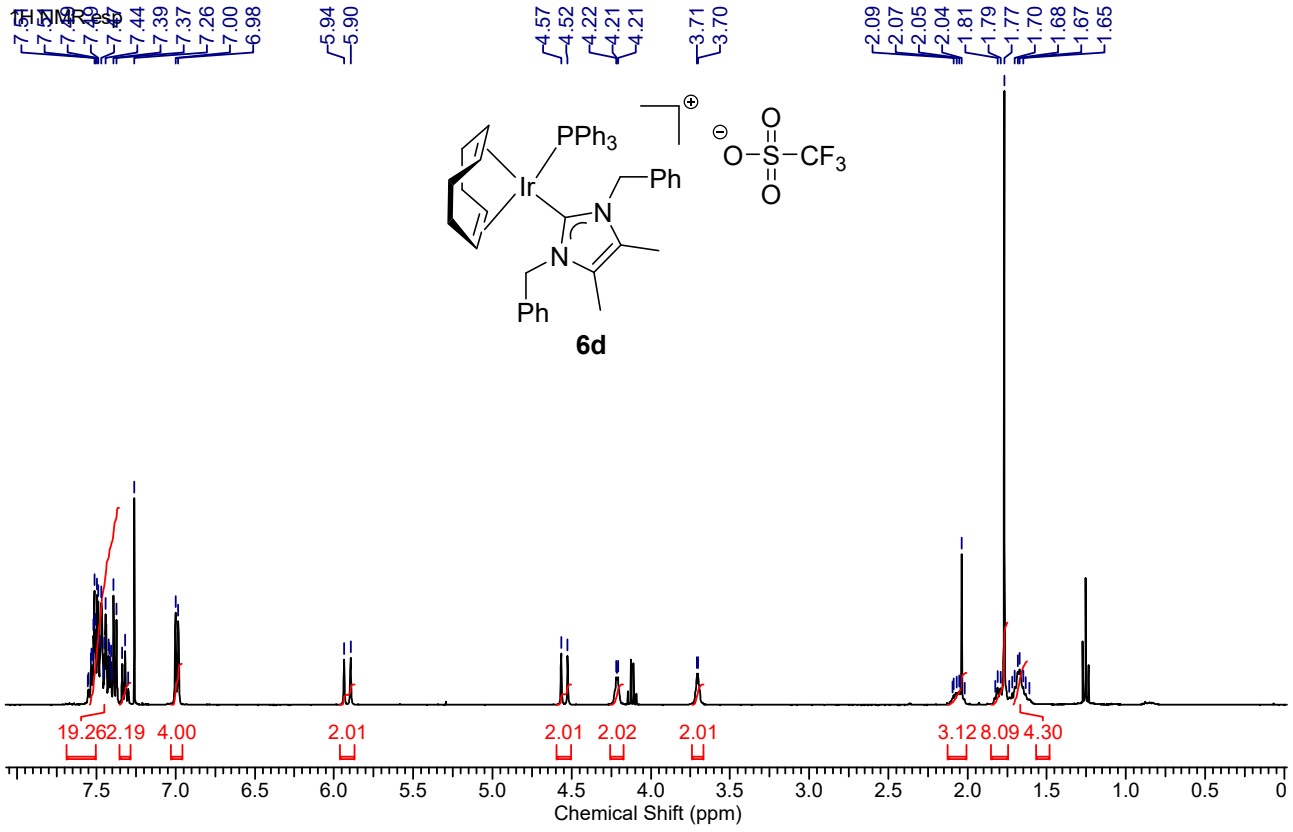
η^4–Cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) hexafluoroantimonate 6c

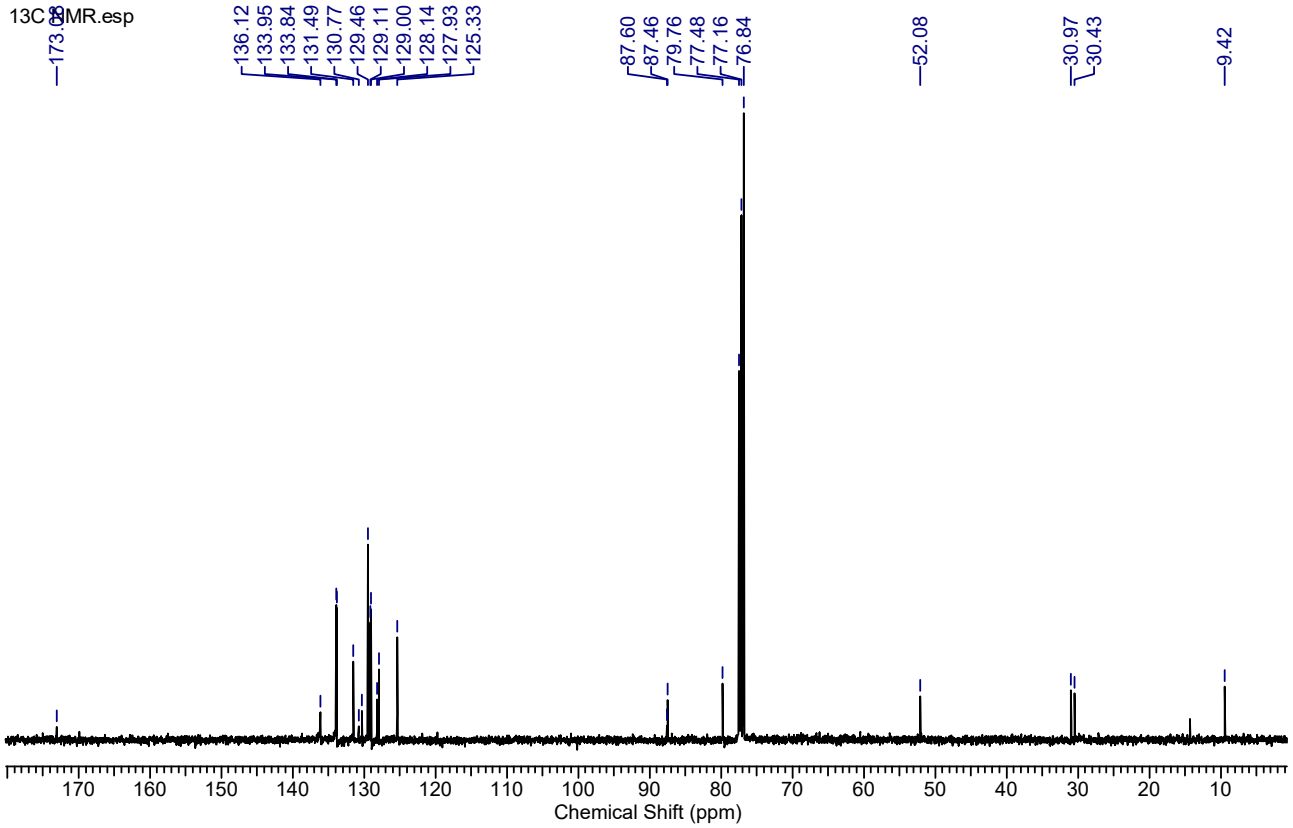


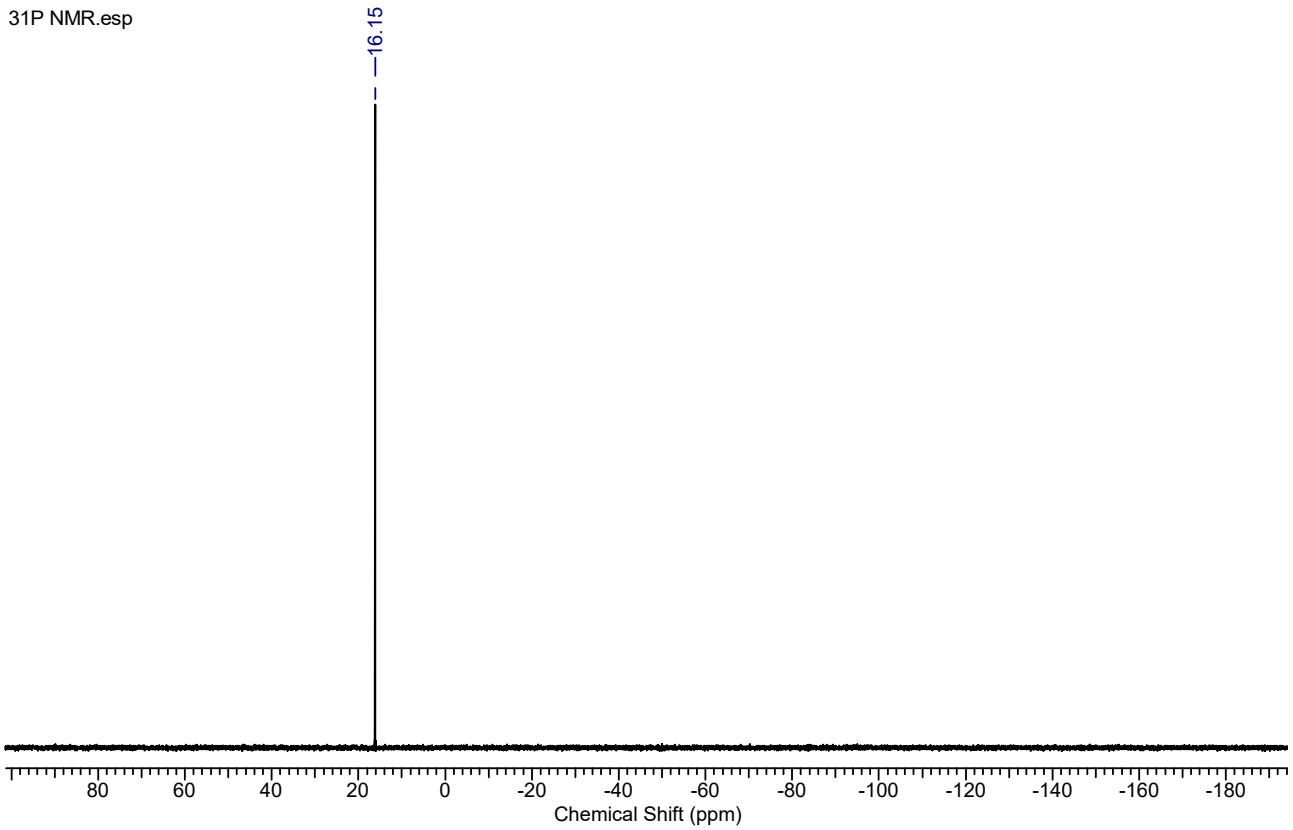


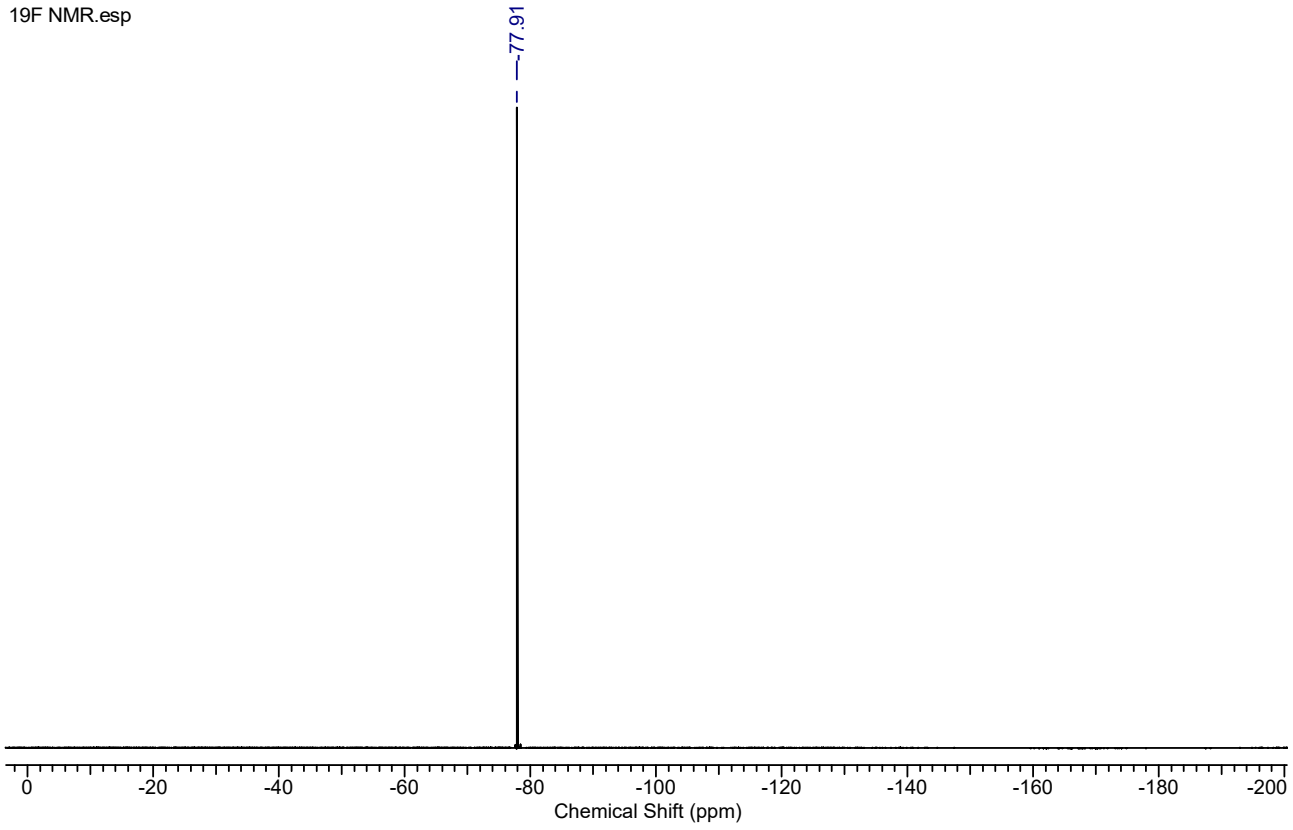

31P NMR.esp
16.14
200
150
100
50
0
-50
-100
-150
-200
Chemical Shift (ppm)

η^4–Cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) trifluoromethanesulfonate 6d

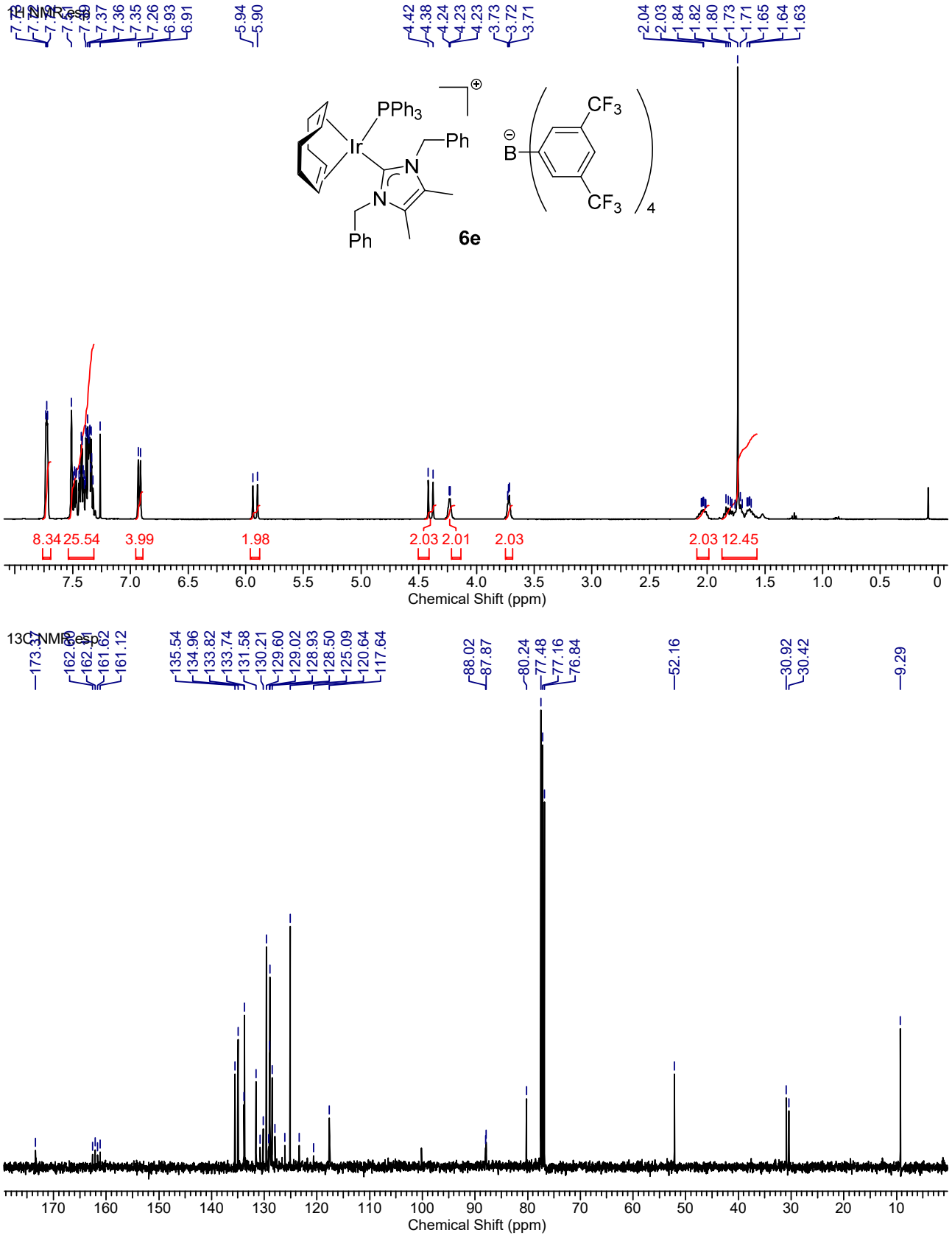


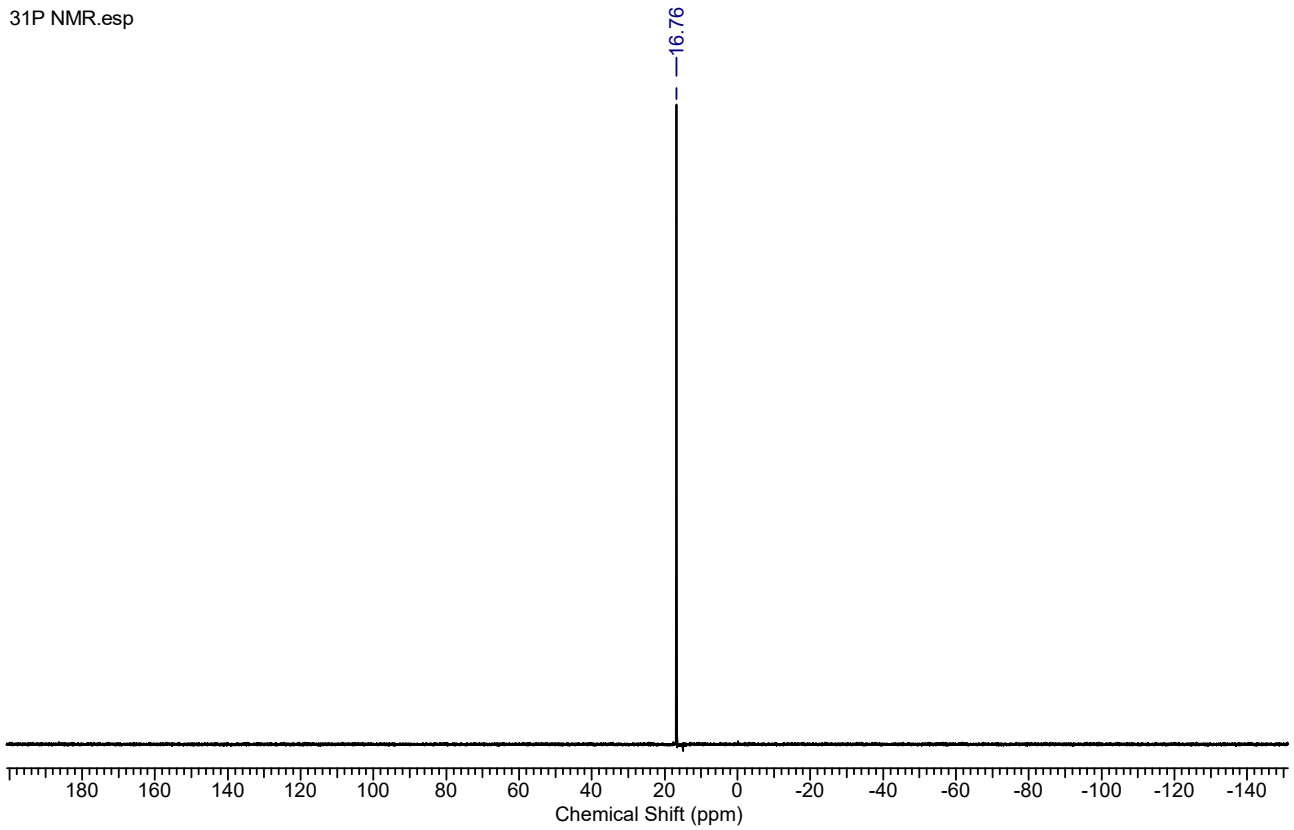


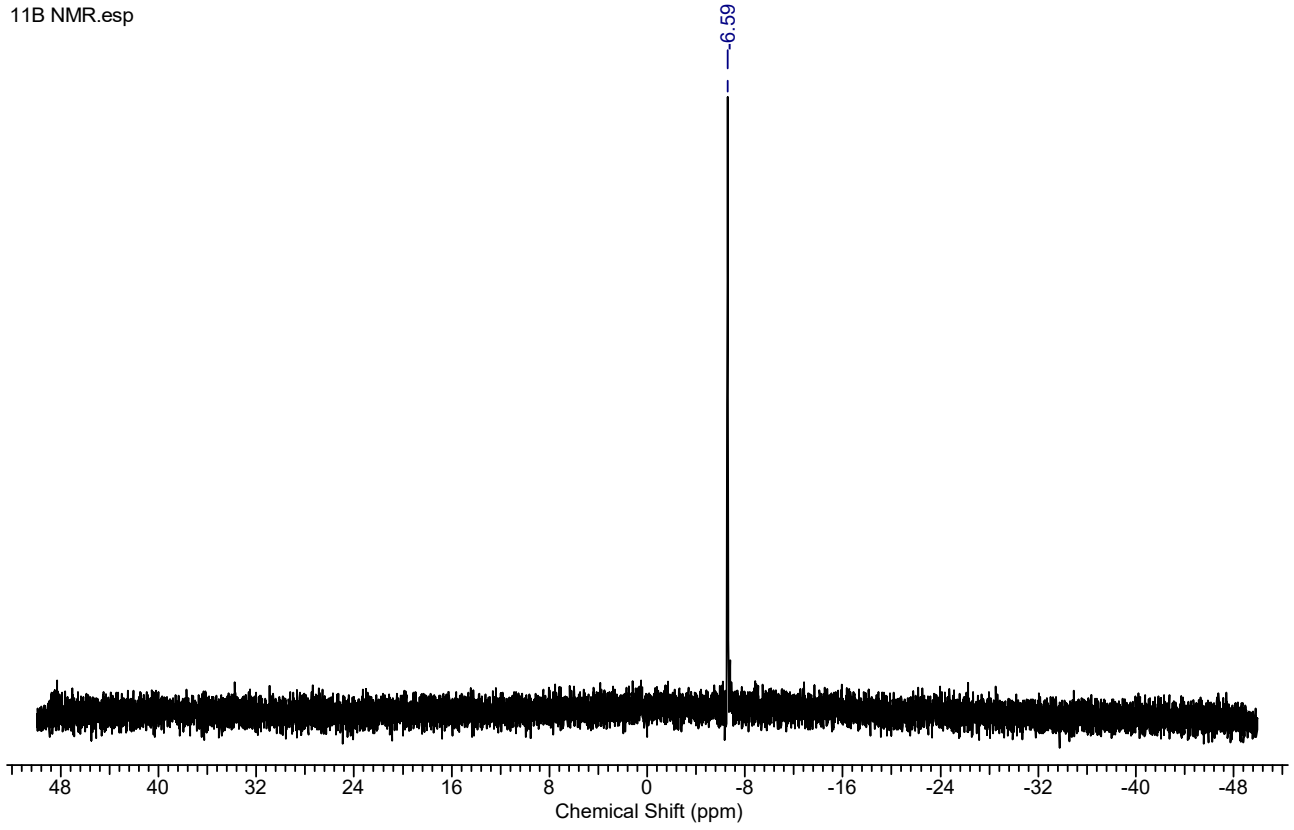

31P NMR.esp
16.15
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Chemical Shift (ppm)

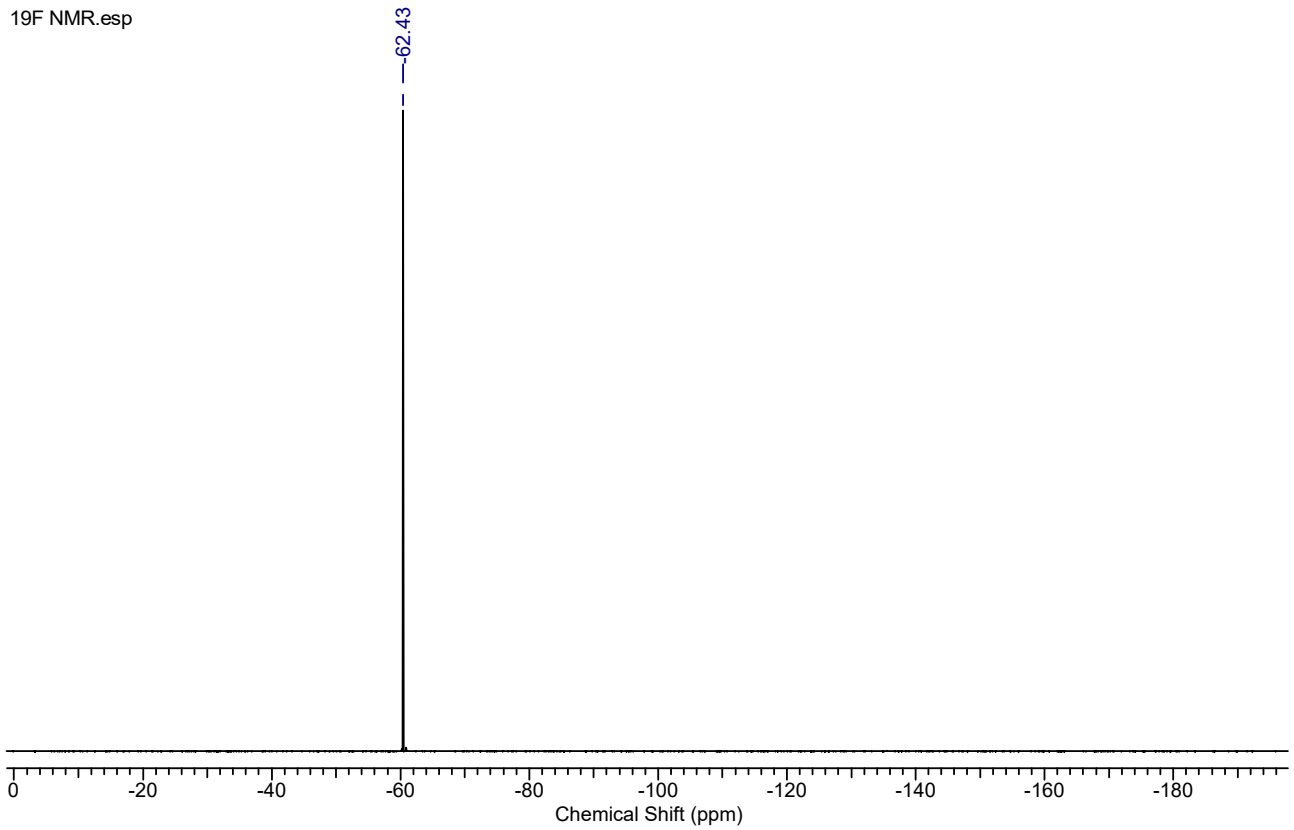

19F NMR.esp
-77.91
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

η^4–Cycloocta-1,5-diene(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene) (triphenylphosphine)iridium(I) tetrakis(3,5-trifluoromethylphenyl)borate 6e

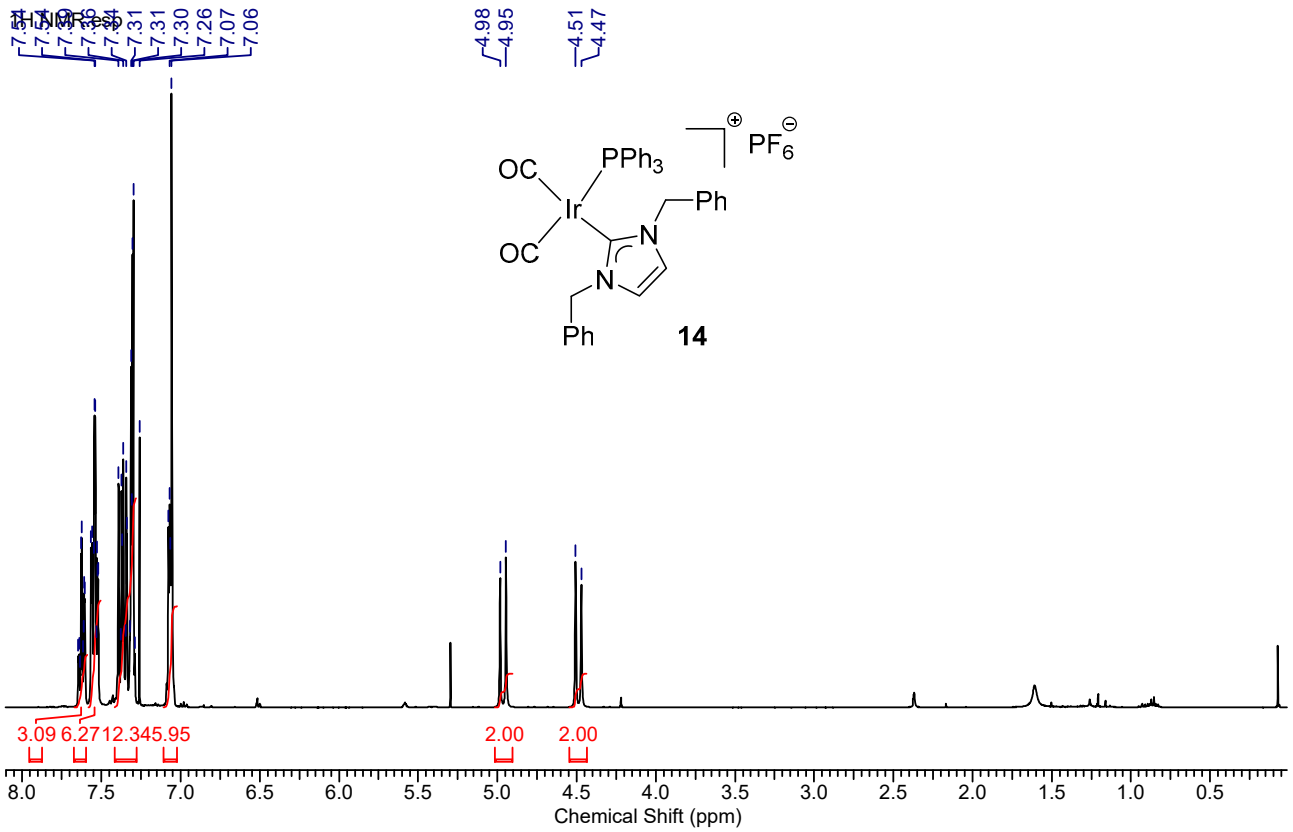


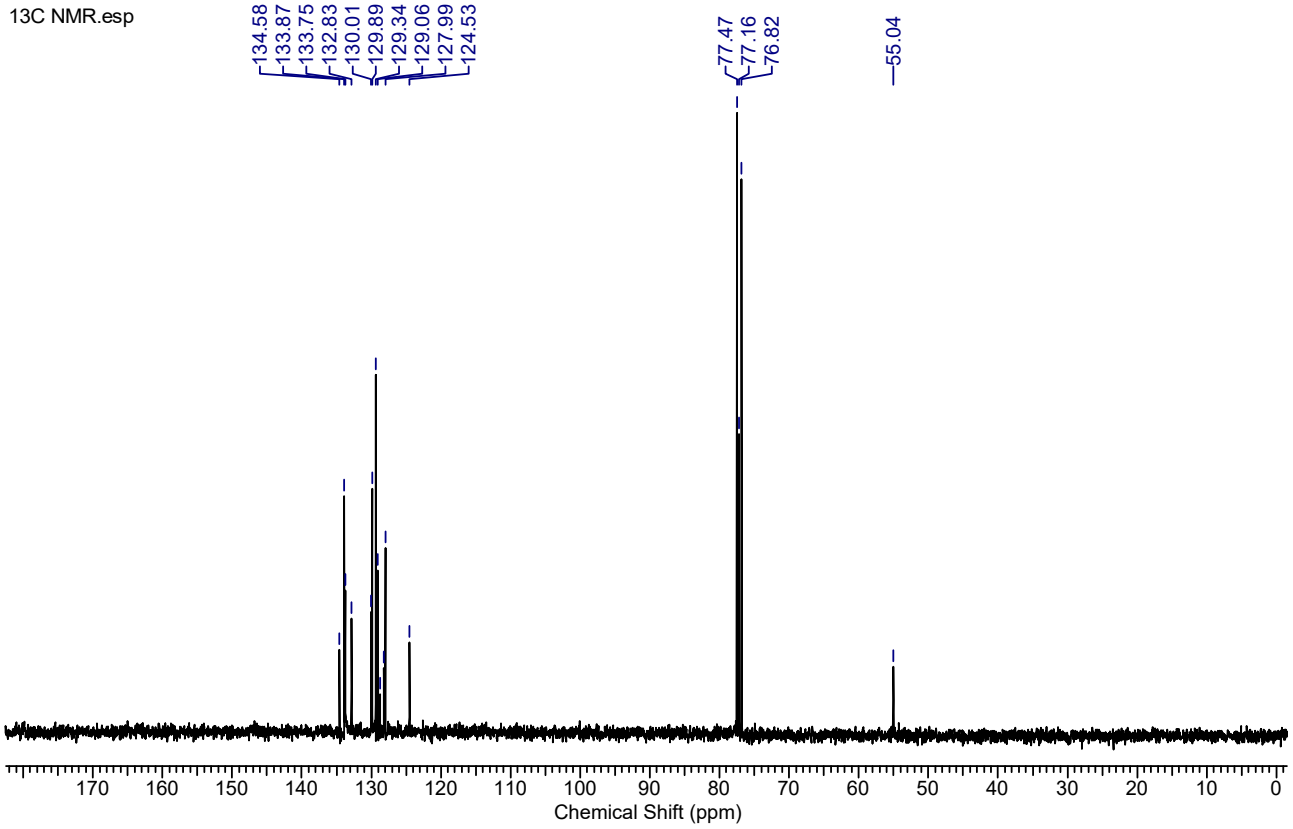

31P NMR.esp
16.76
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)

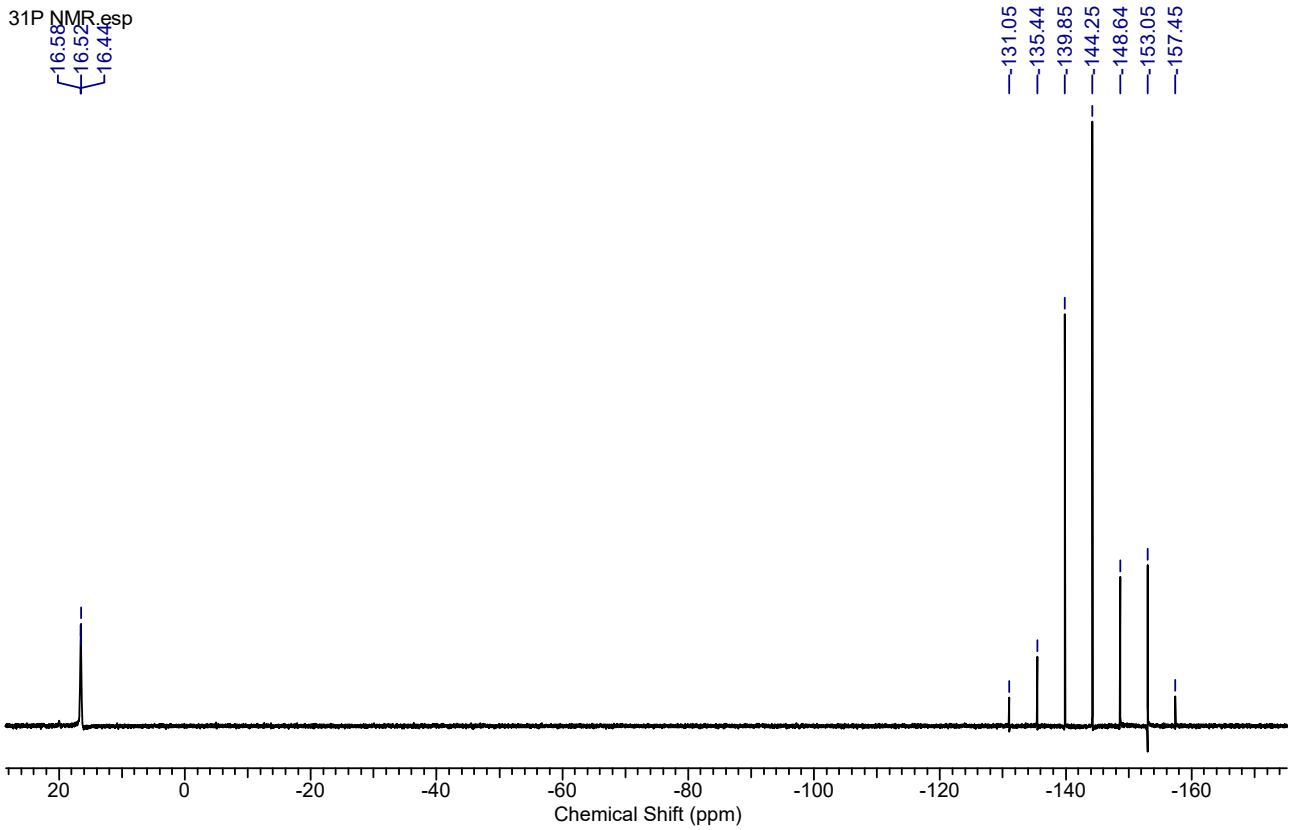

11B NMR.esp
-6.59
48
40
32
24
16
8
0
-8
-16
-24
-32
-40
-48
Chemical Shift (ppm)

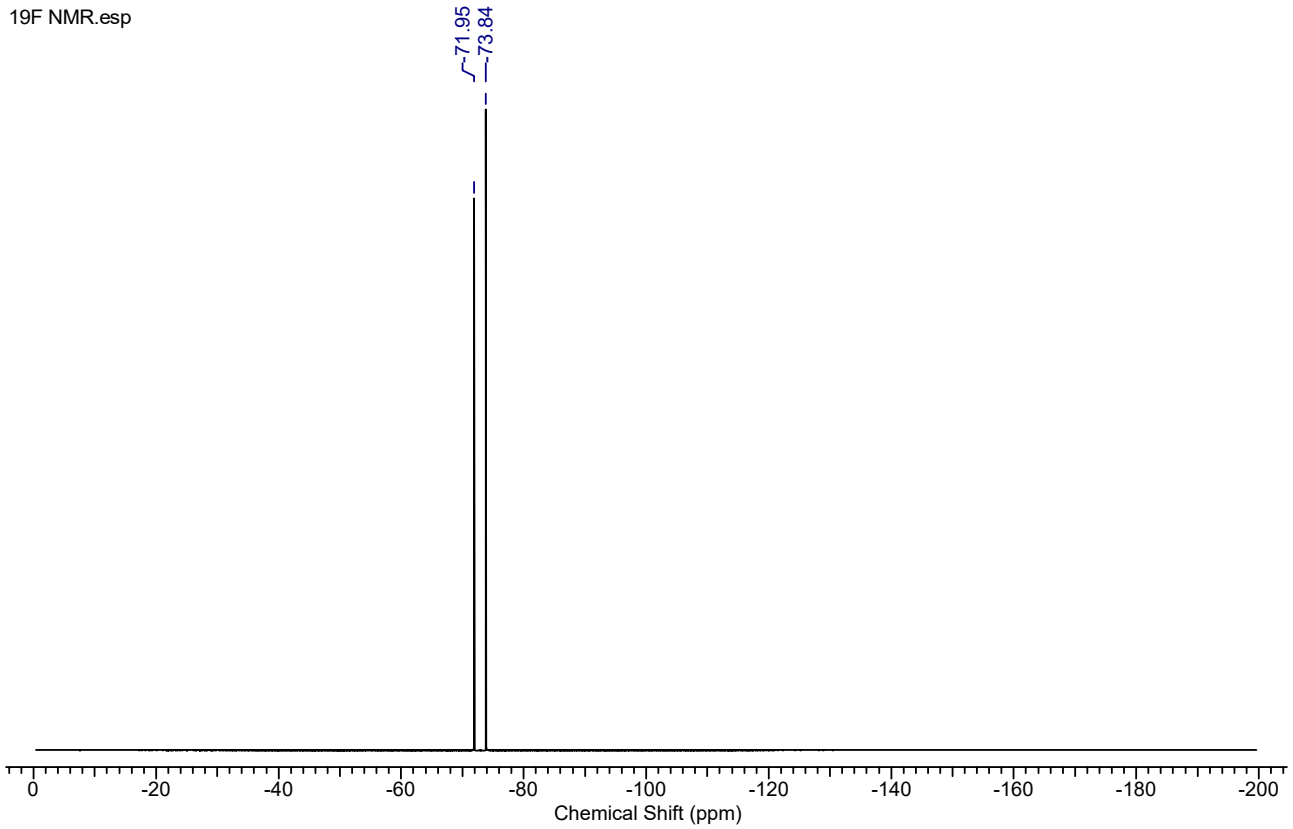

19F NMR.esp
-62.43
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
Chemical Shift (ppm)

dicarbonyl(1,3-dibenzylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 14

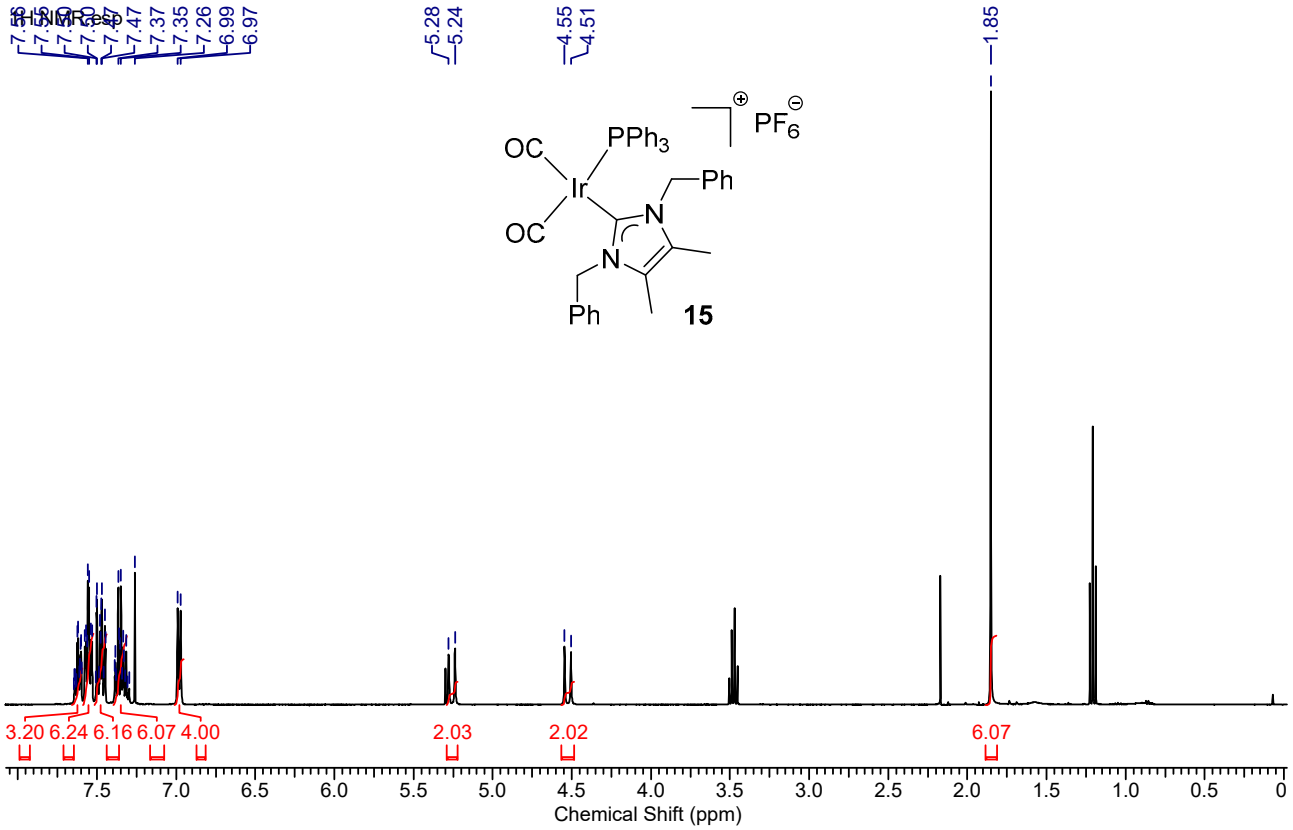


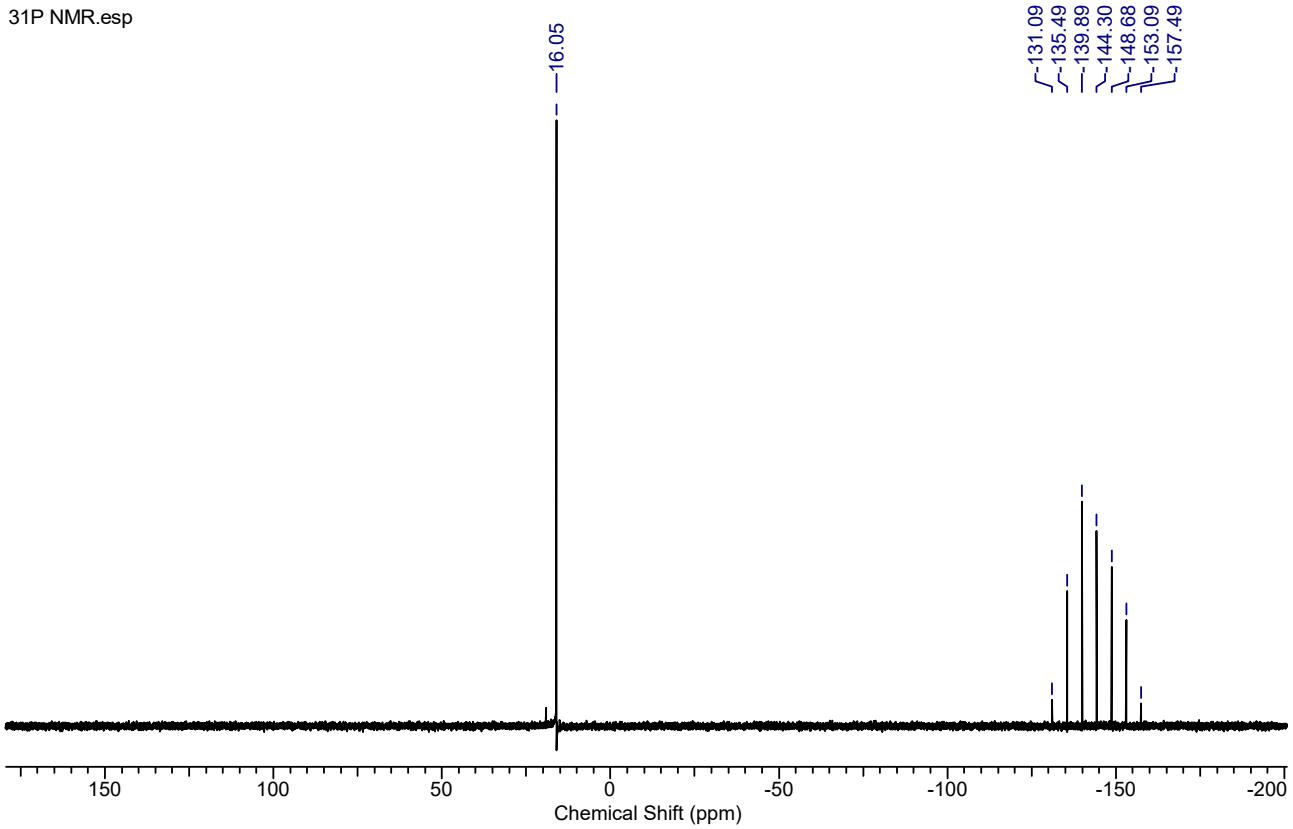


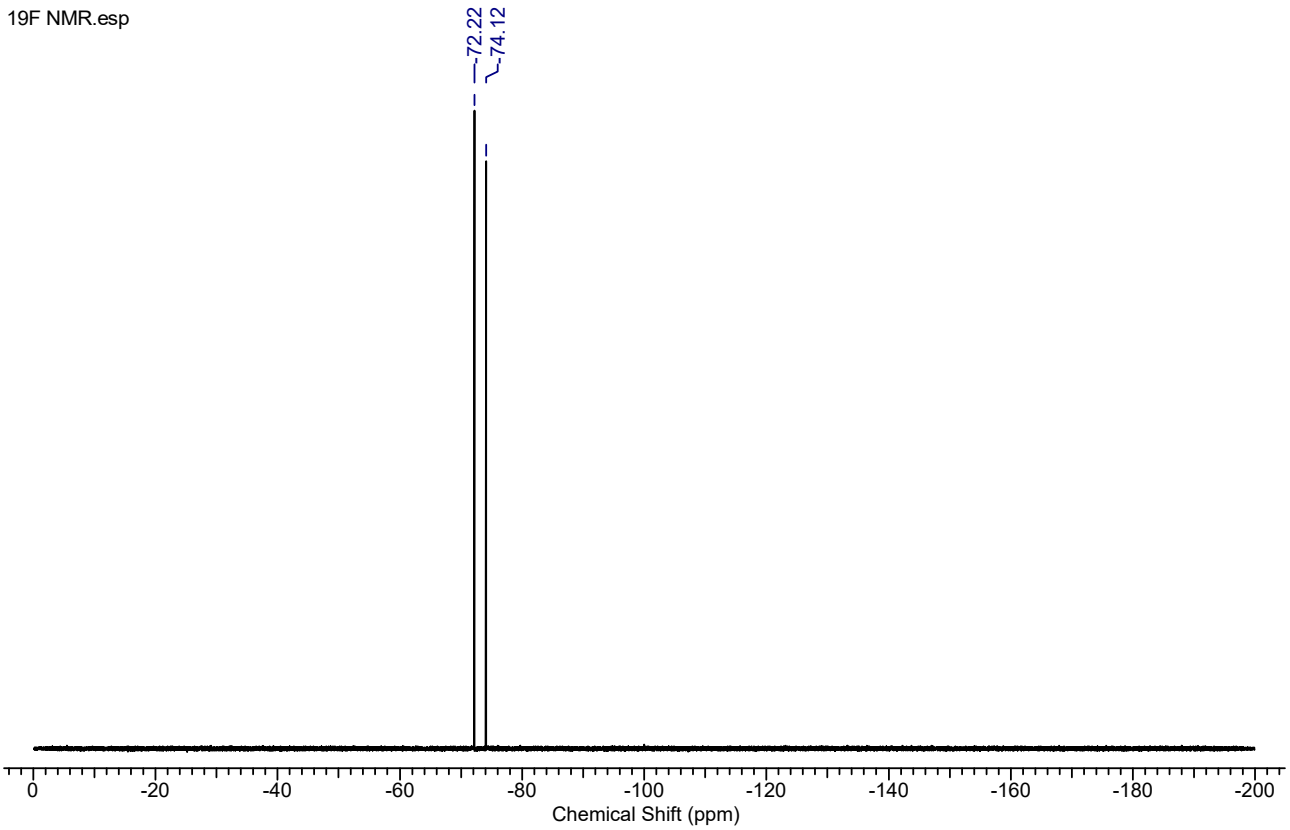

31P NMR.esp
16.58
16.52
16.44
131.05
135.44
139.85
144.25
148.64
153.05
157.45
20
0
-20
-40
-60
-80
-100
-120
-140
-160
Chemical Shift (ppm)


19F NMR.esp
71.95
73.84
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

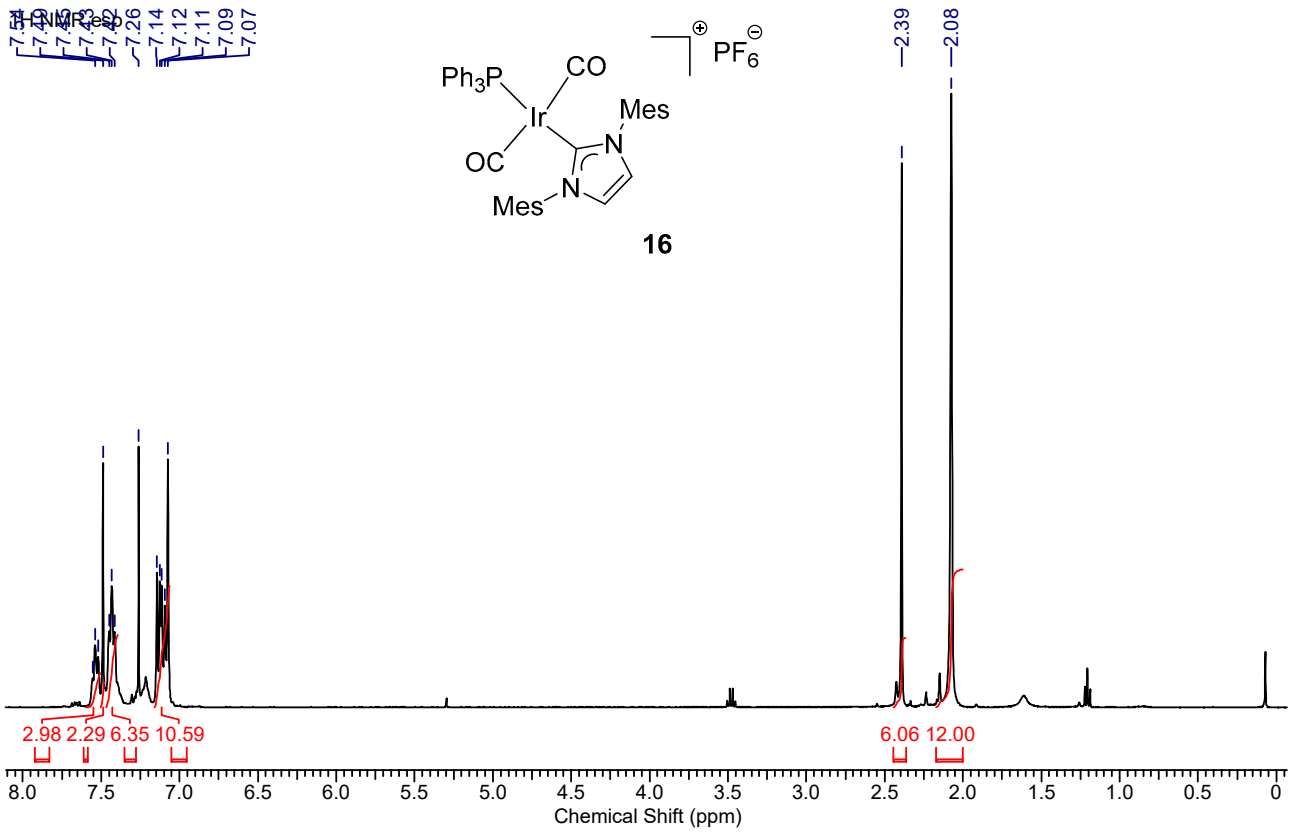
Dicarbonyl(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 15

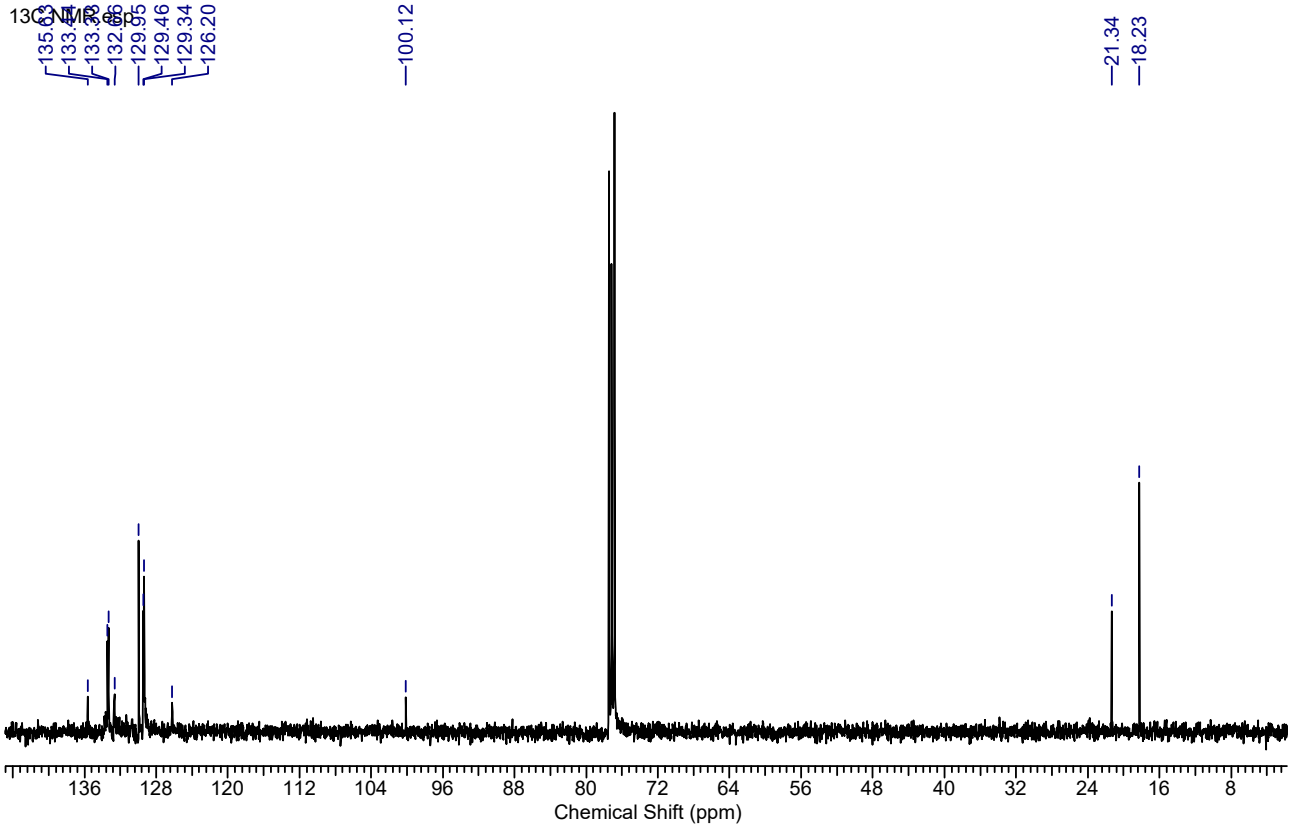




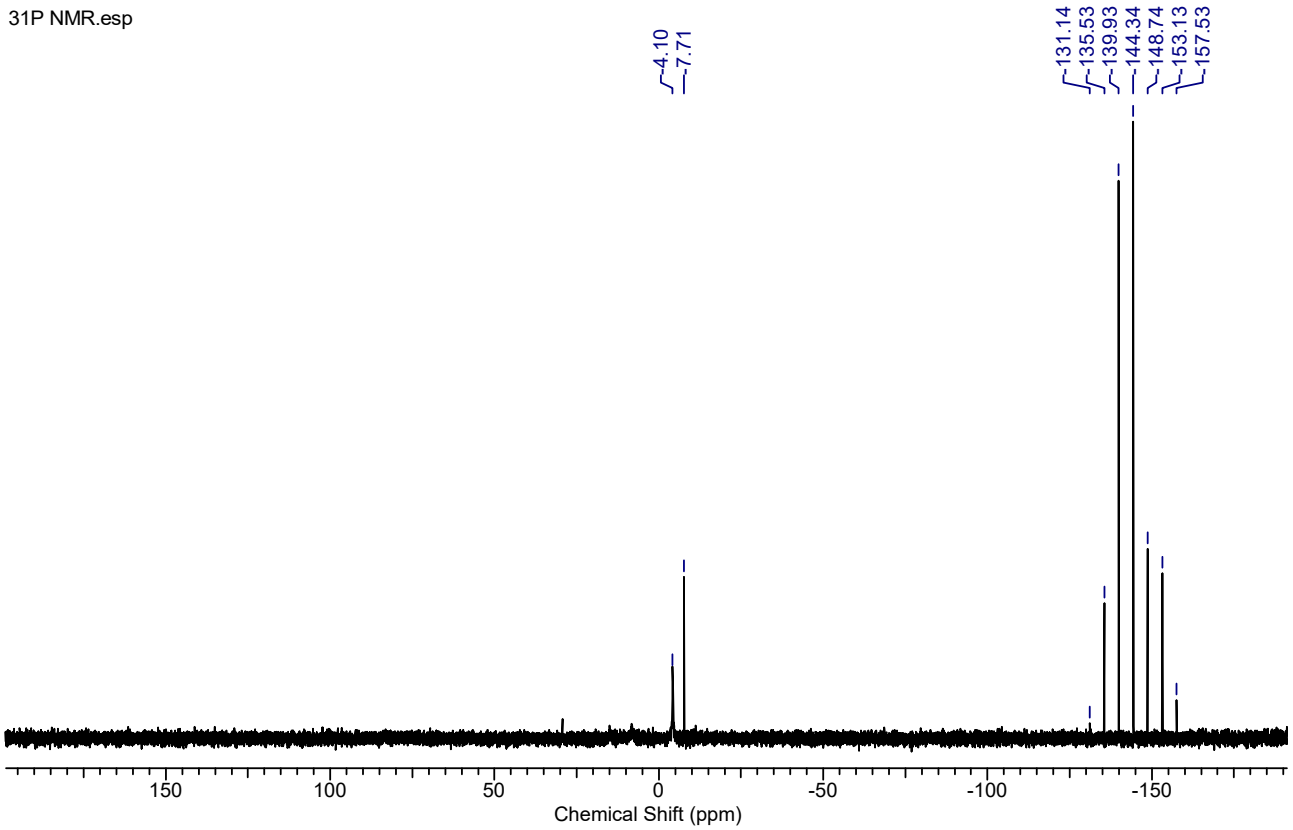

19F NMR.esp
-72.22
-74.12
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

Dicarbonyl(dimesitylimidazol-2-ylidene)(triphenylphosphine)iridium(I) hexafluorophosphate 16

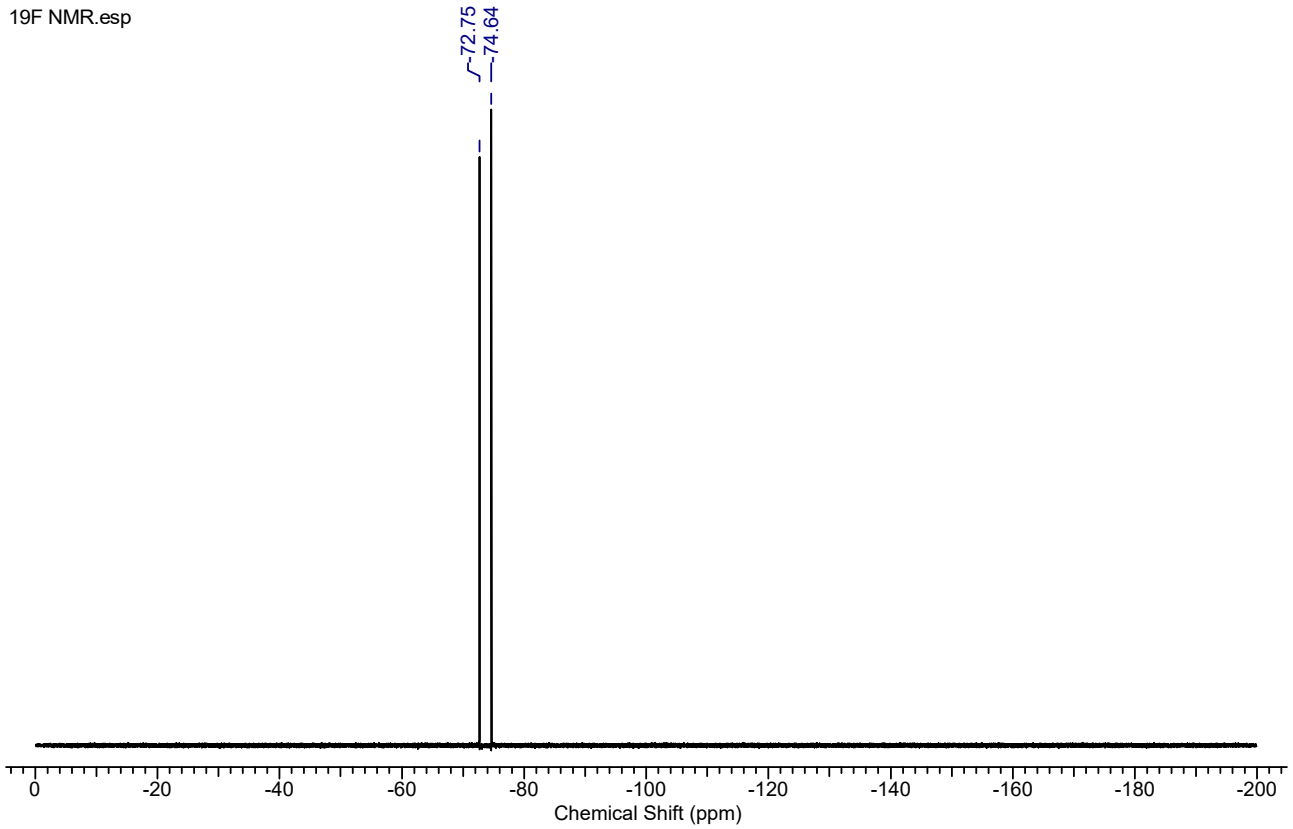




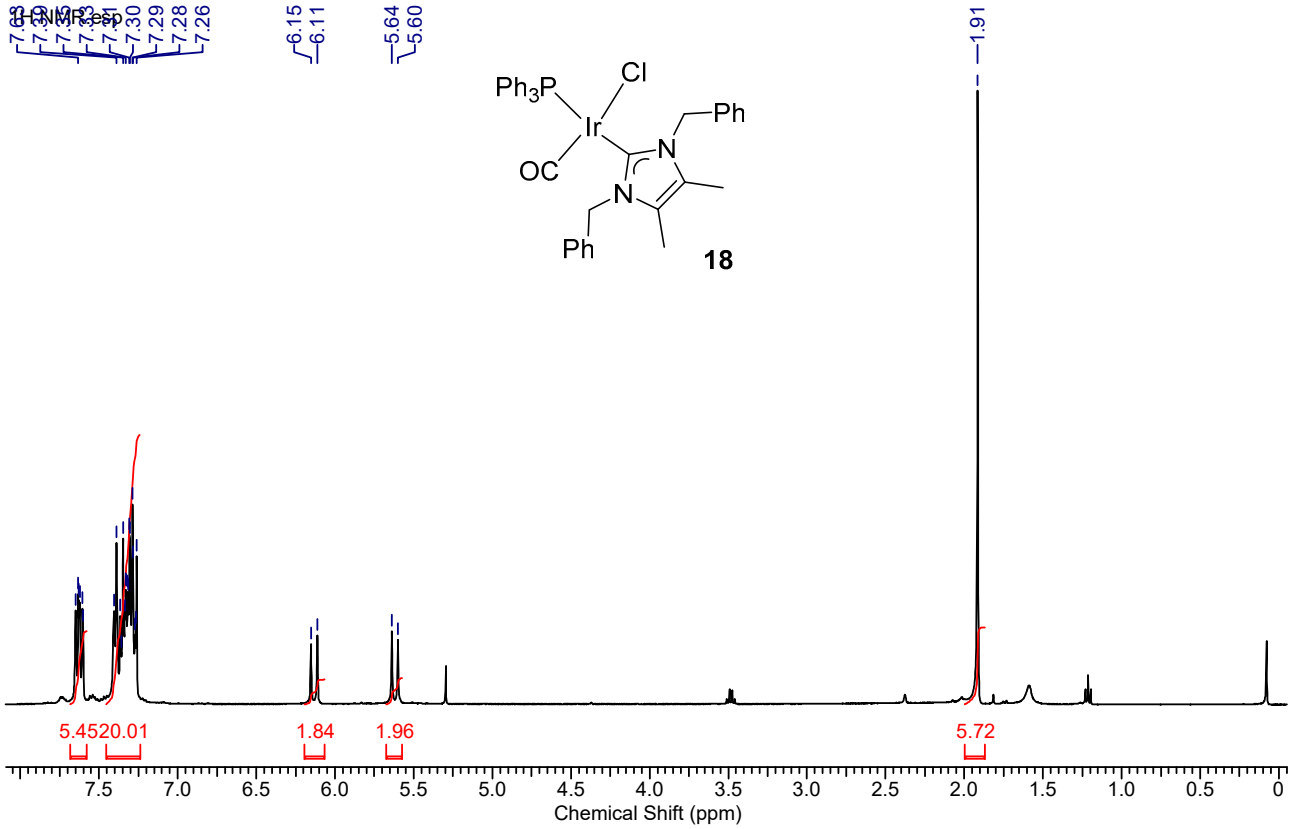
31P NMR.esp

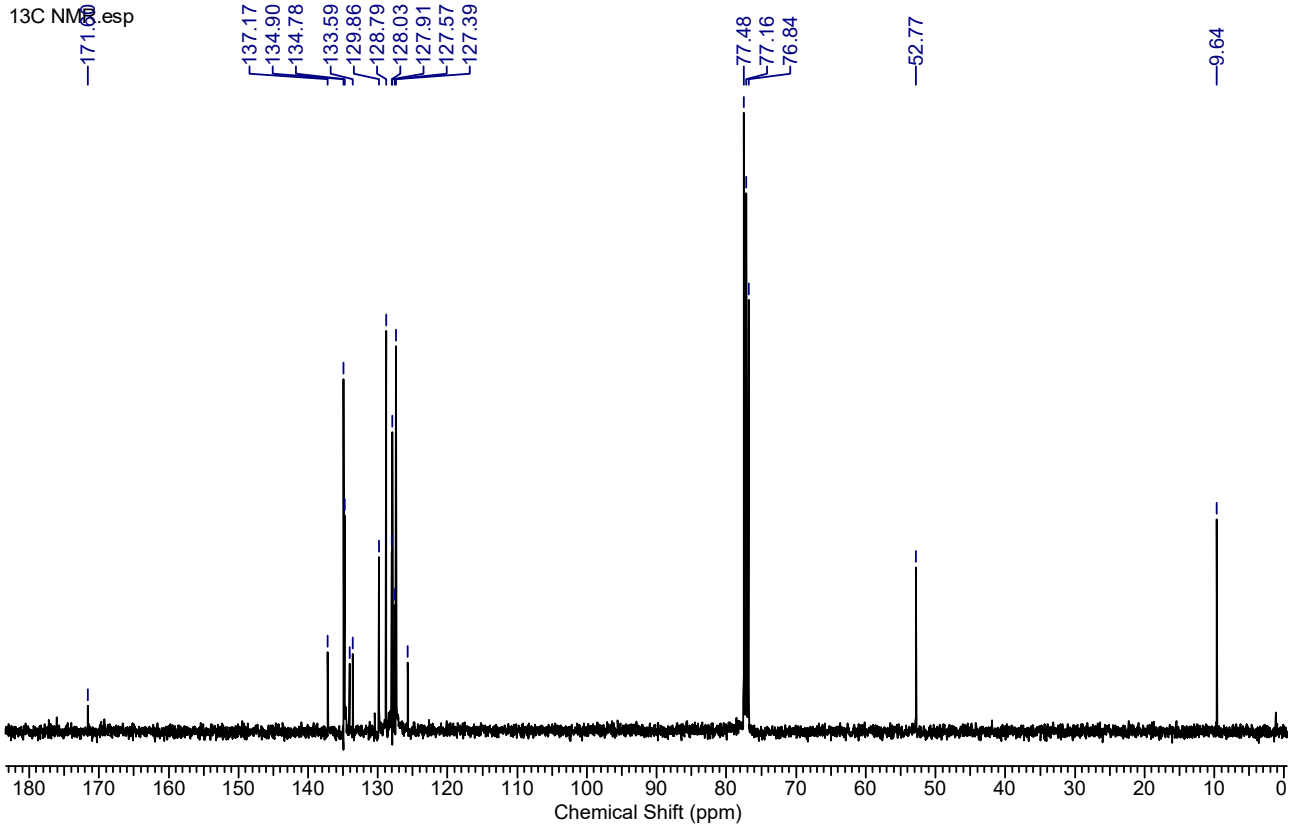


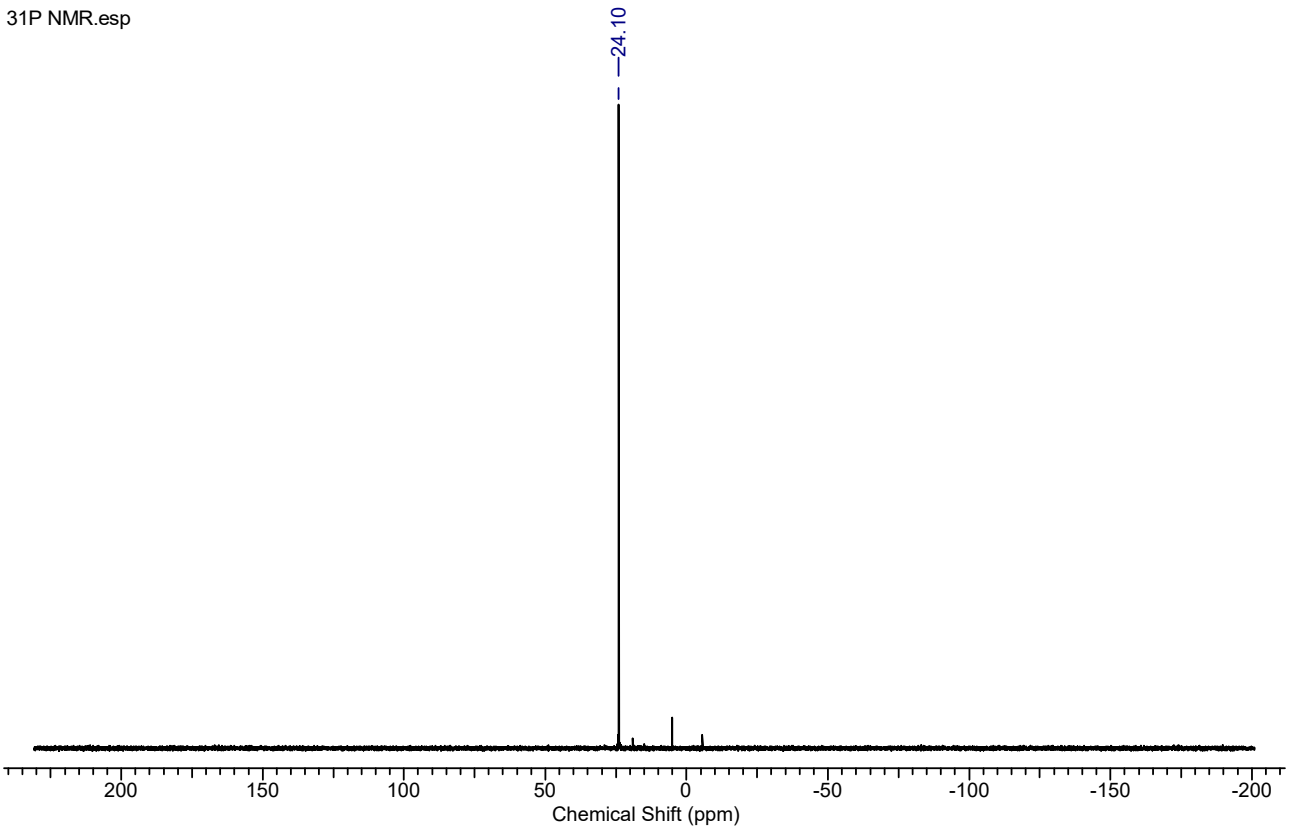
19F NMR.esp



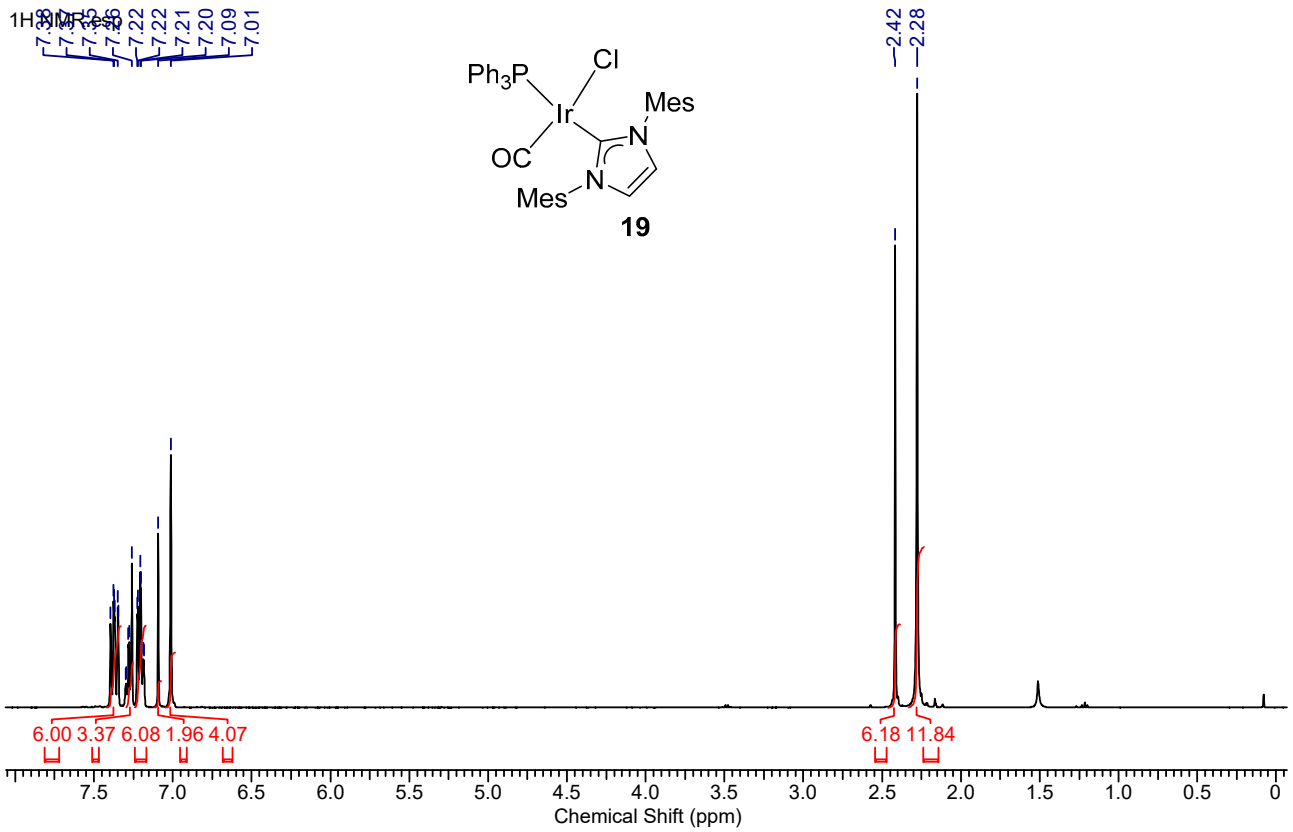
Chloro(carbonyl)(1,3-dibenzyl-4,5-dimethylimidazol-2-ylidene)(triphenylphosphine)iridium(I) 18

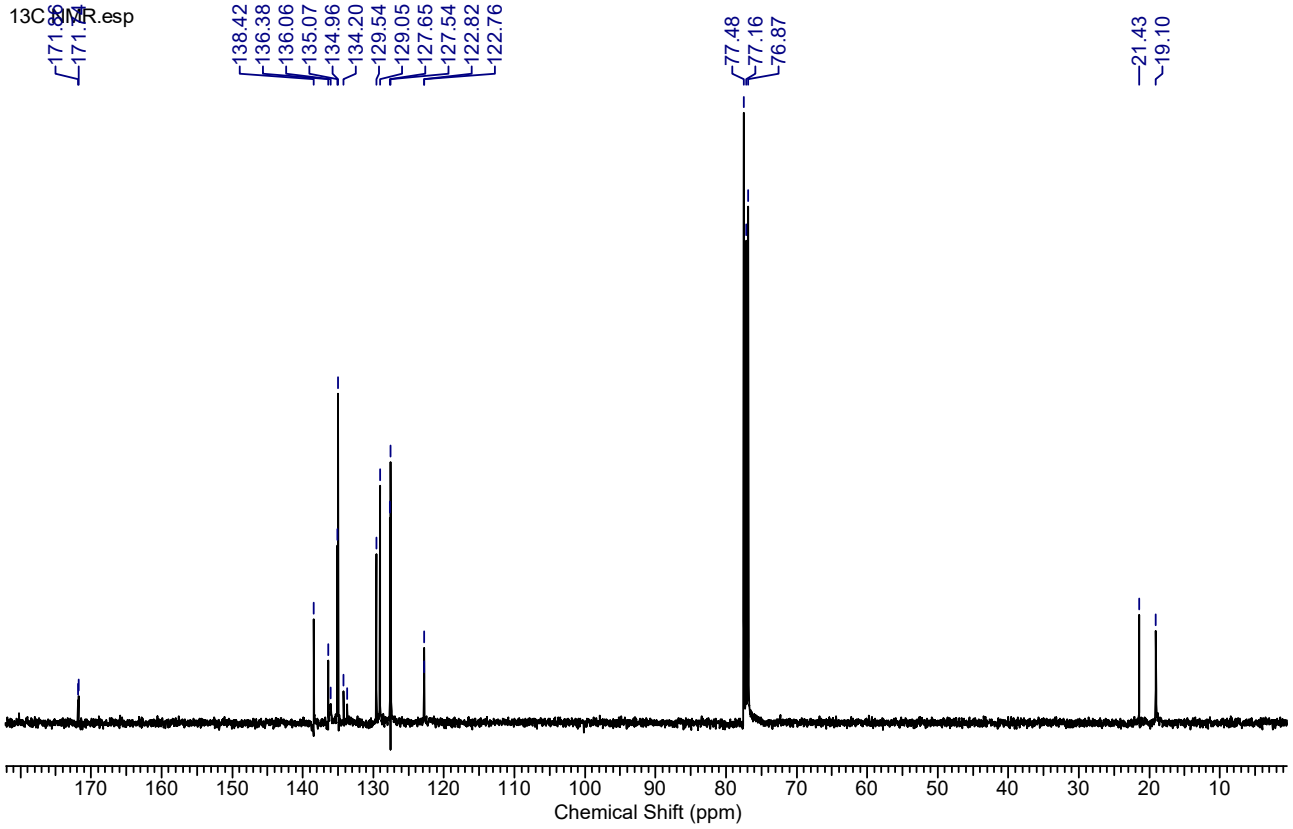


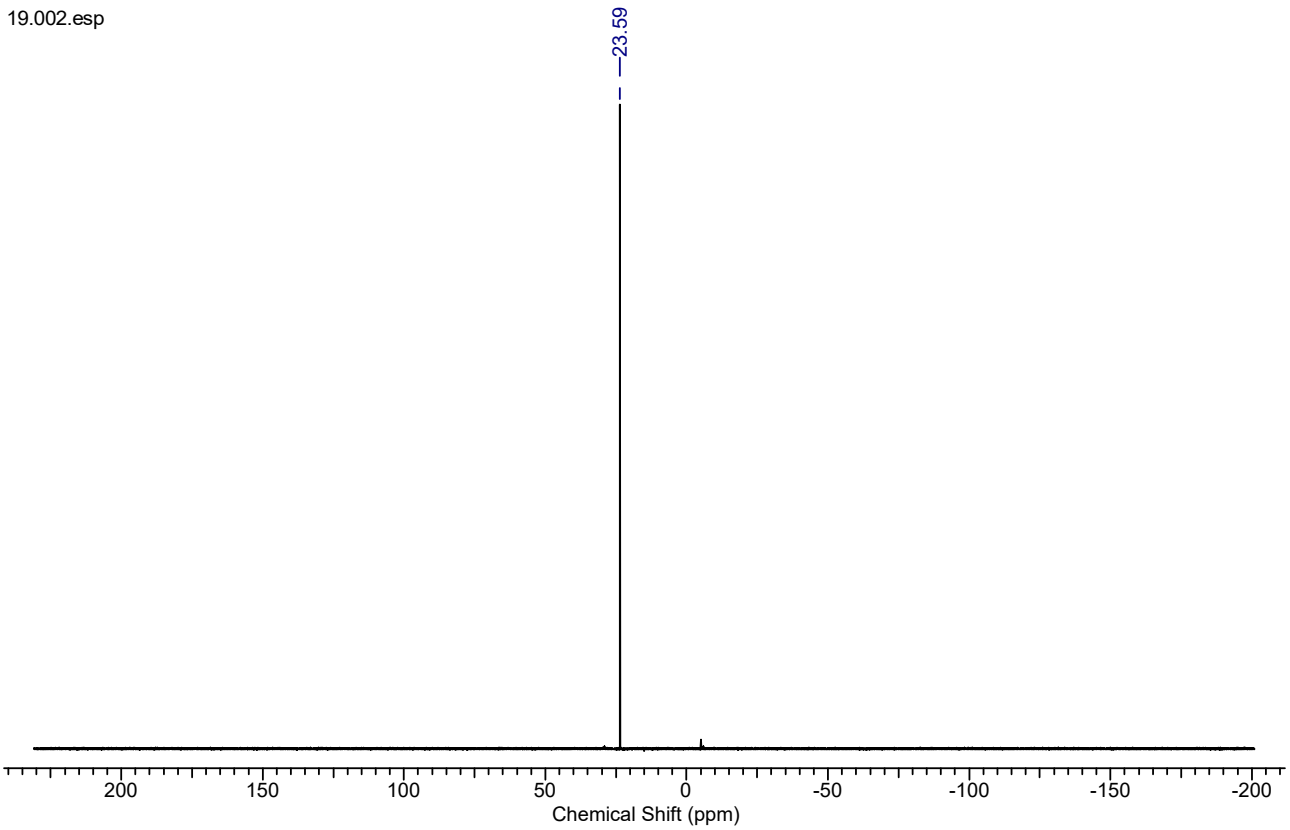



31P NMR.esp
24.10
200
150
100
50
0
-50
-100
-150
-200
Chemical Shift (ppm)

Chloro(carbonyl)(1,3-dimesitylimidazol-2-ylidene)(triphenylphosphine)iridium(I) 19

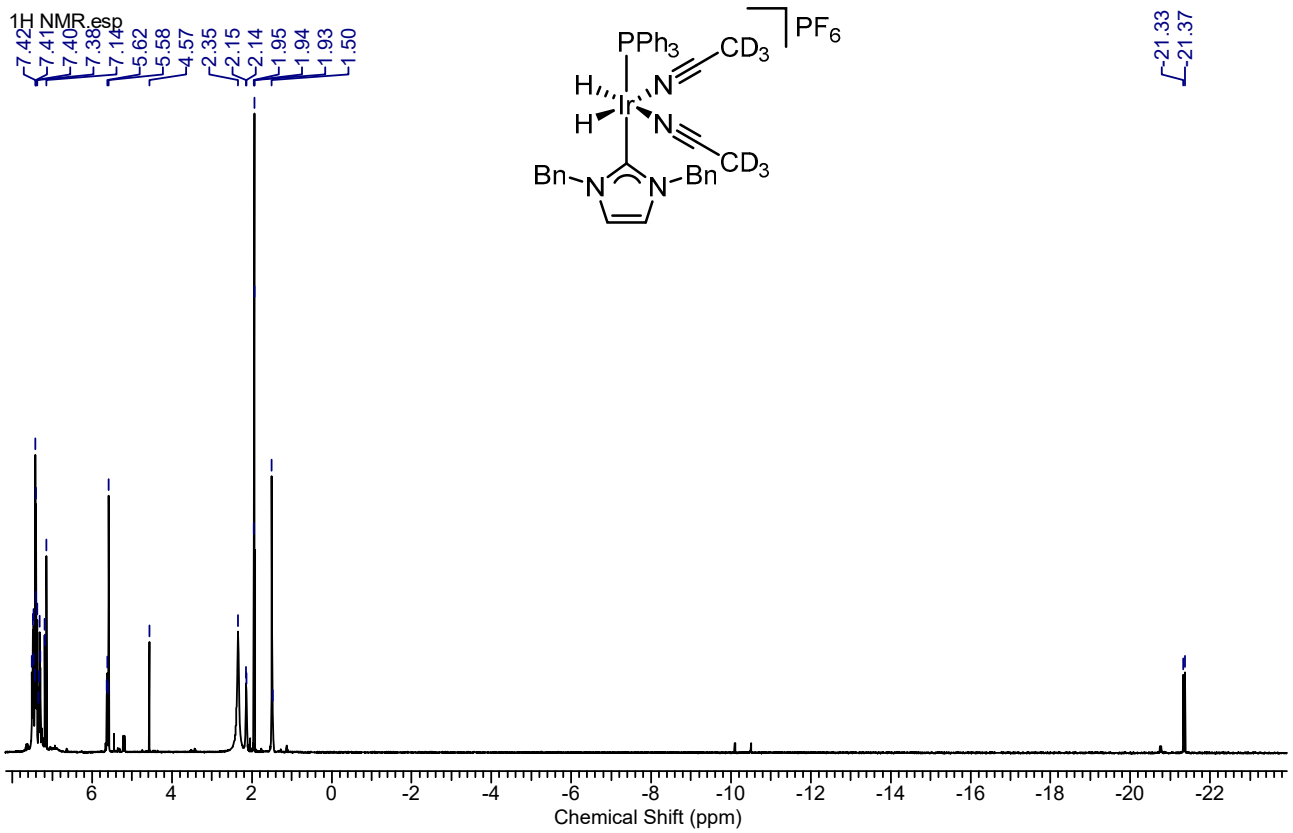


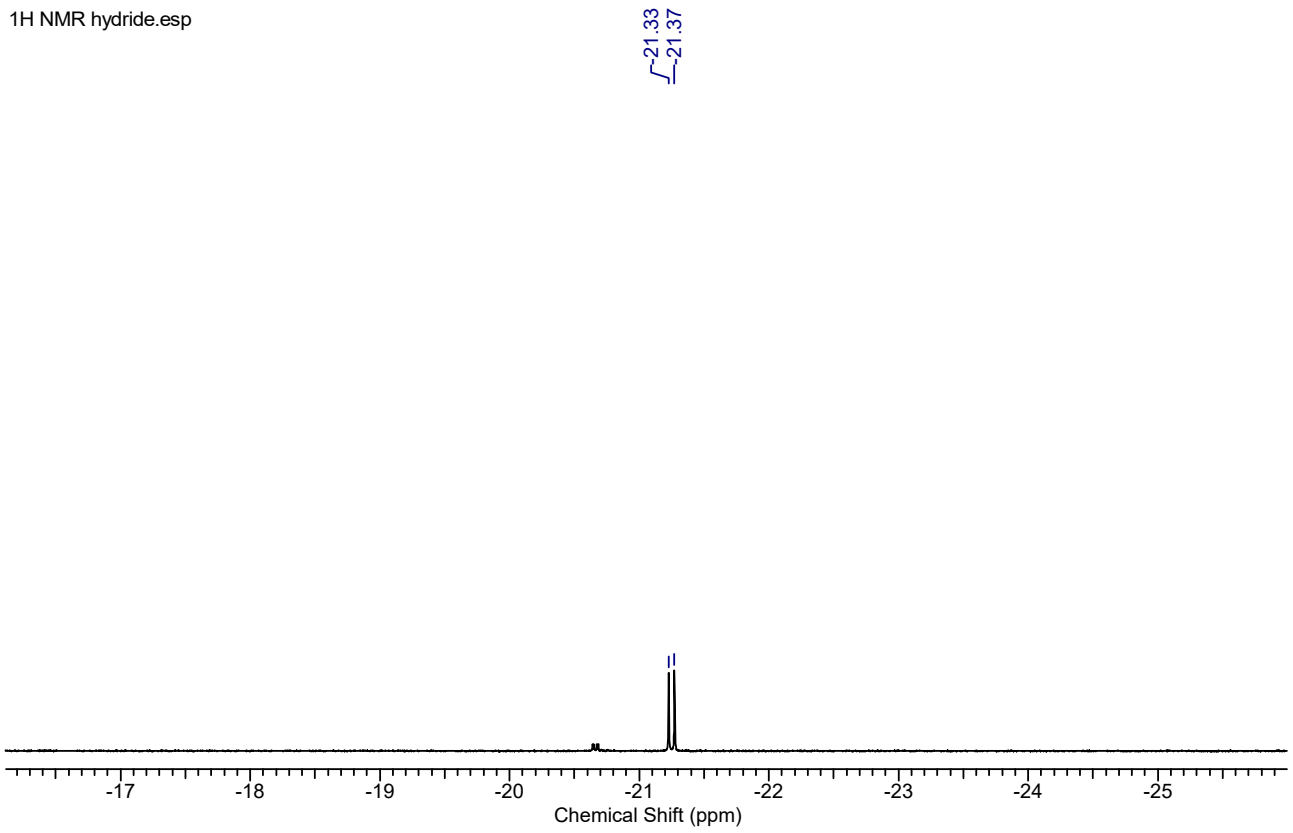



19.002.esp
23.59
200
150
100
50
0
-50
-100
-150
-200
Chemical Shift (ppm)

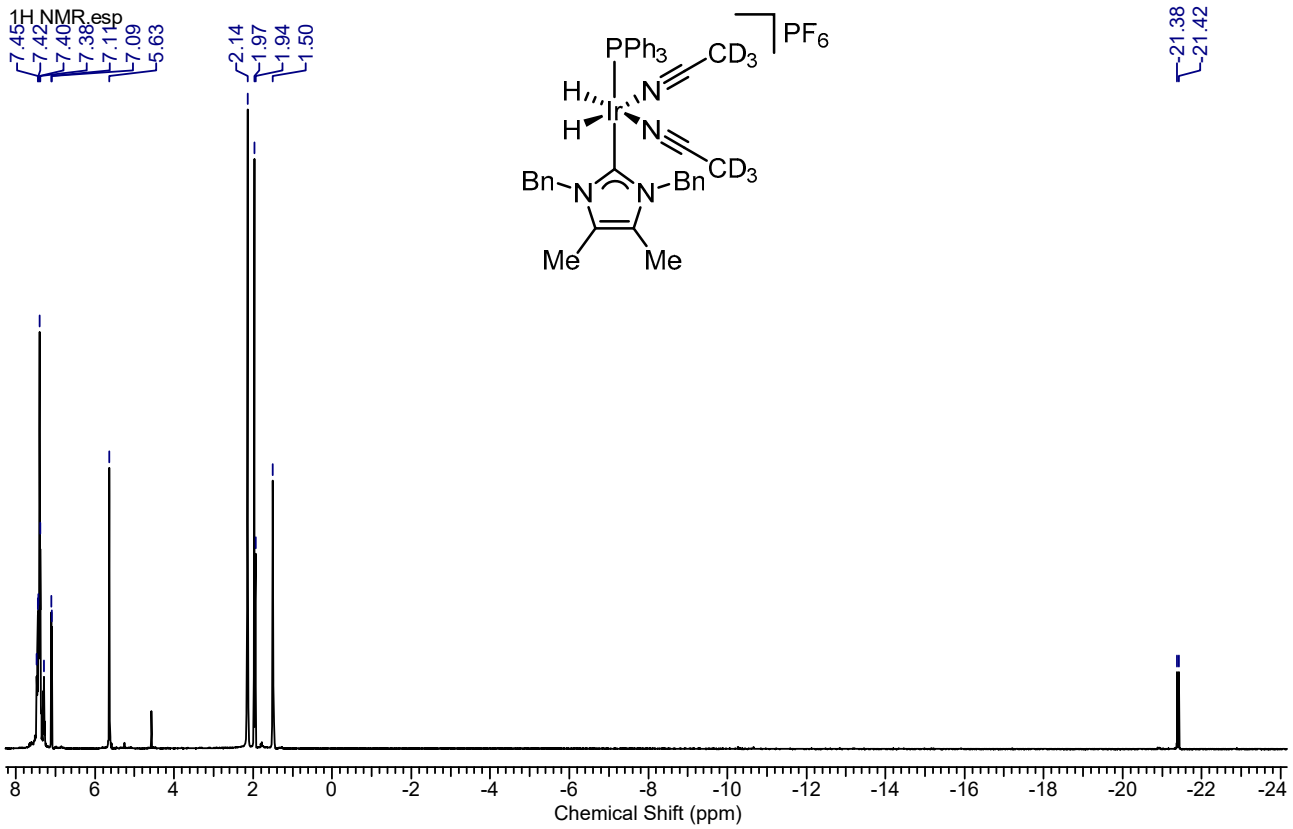
MeCN-d_3-stabilised Ir(III)-dihydride Complexes

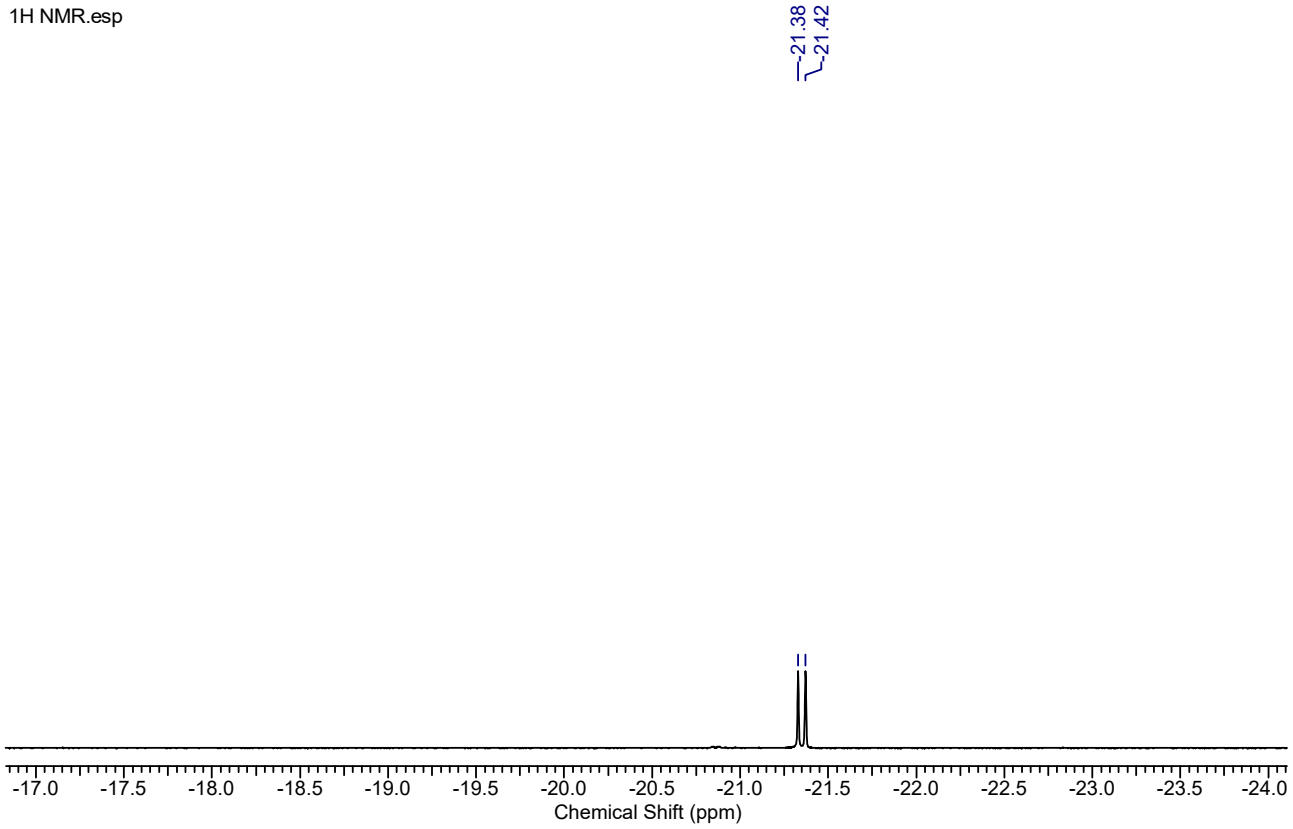
Dihydride Complex 20



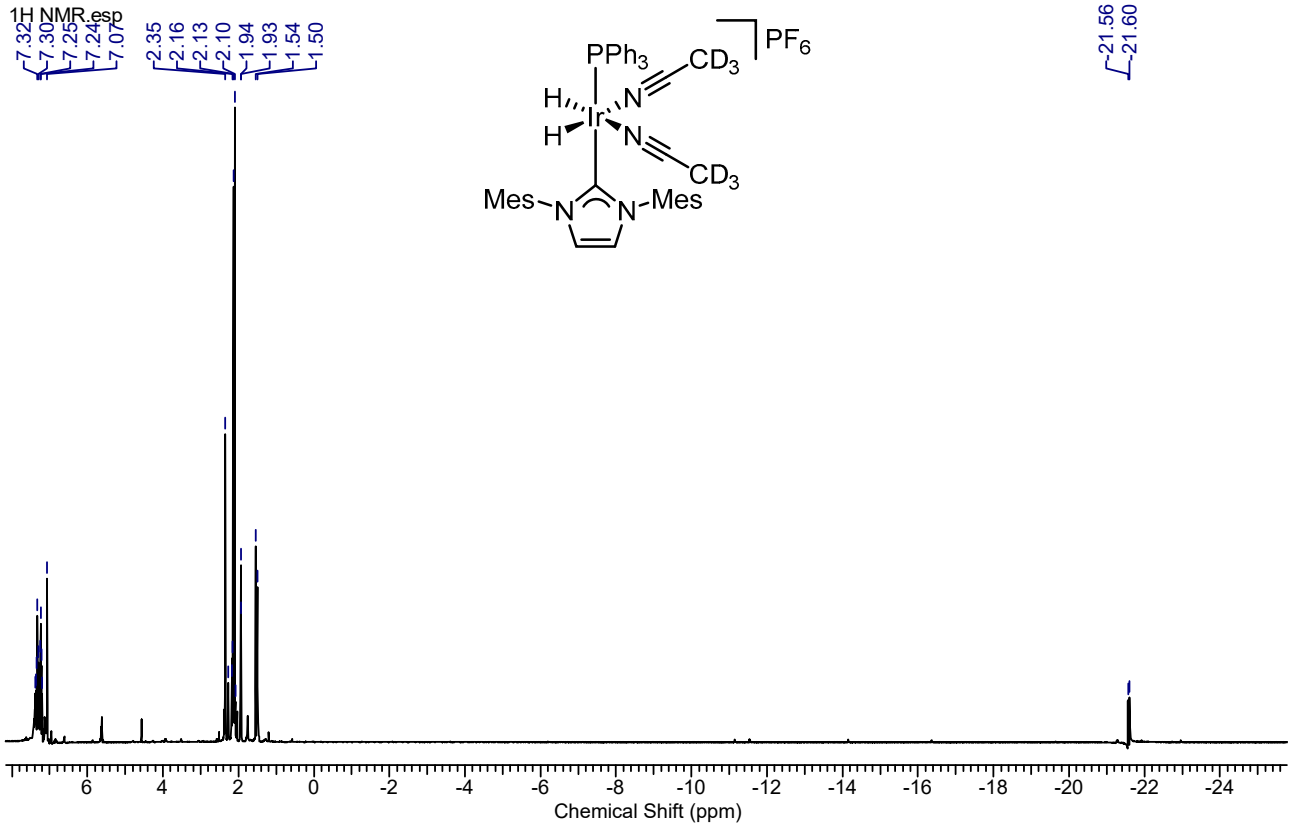


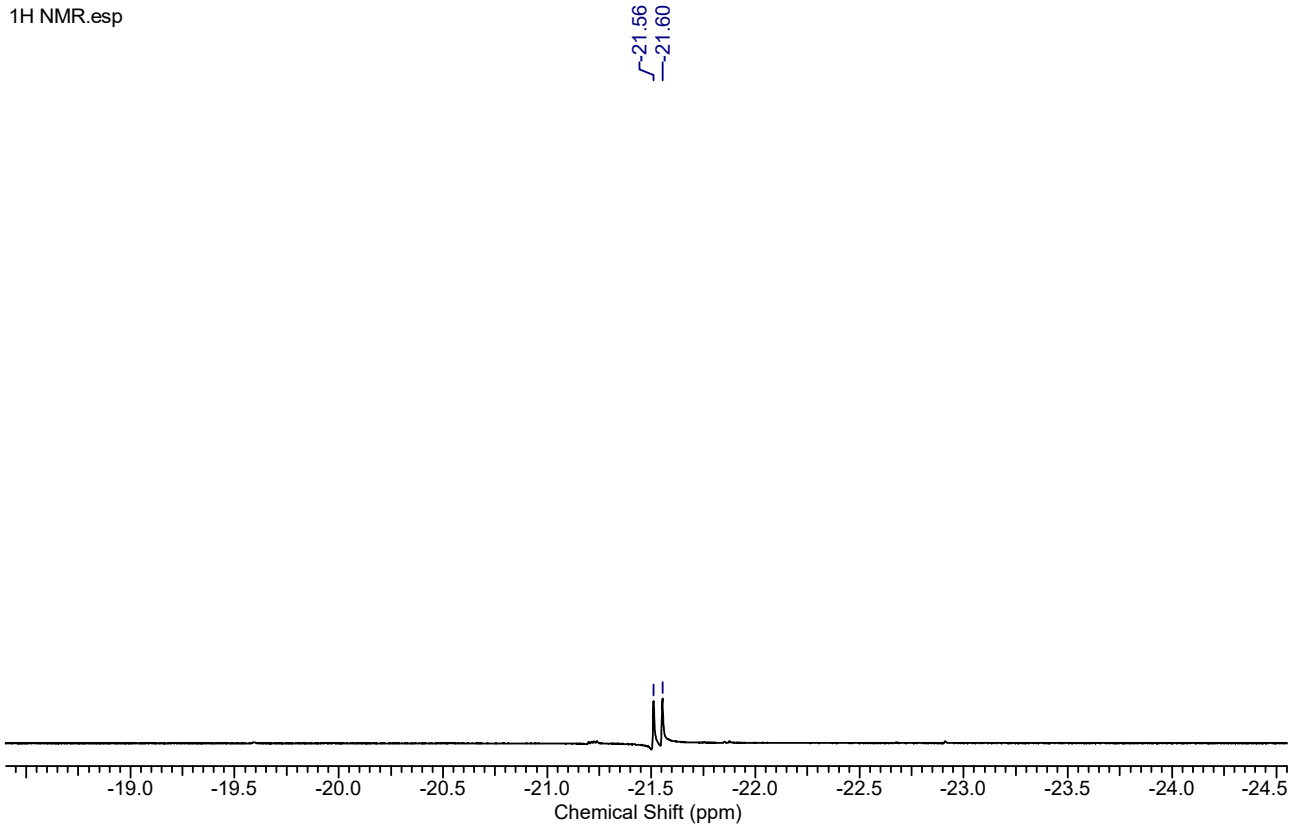
Dihydride Complex 21





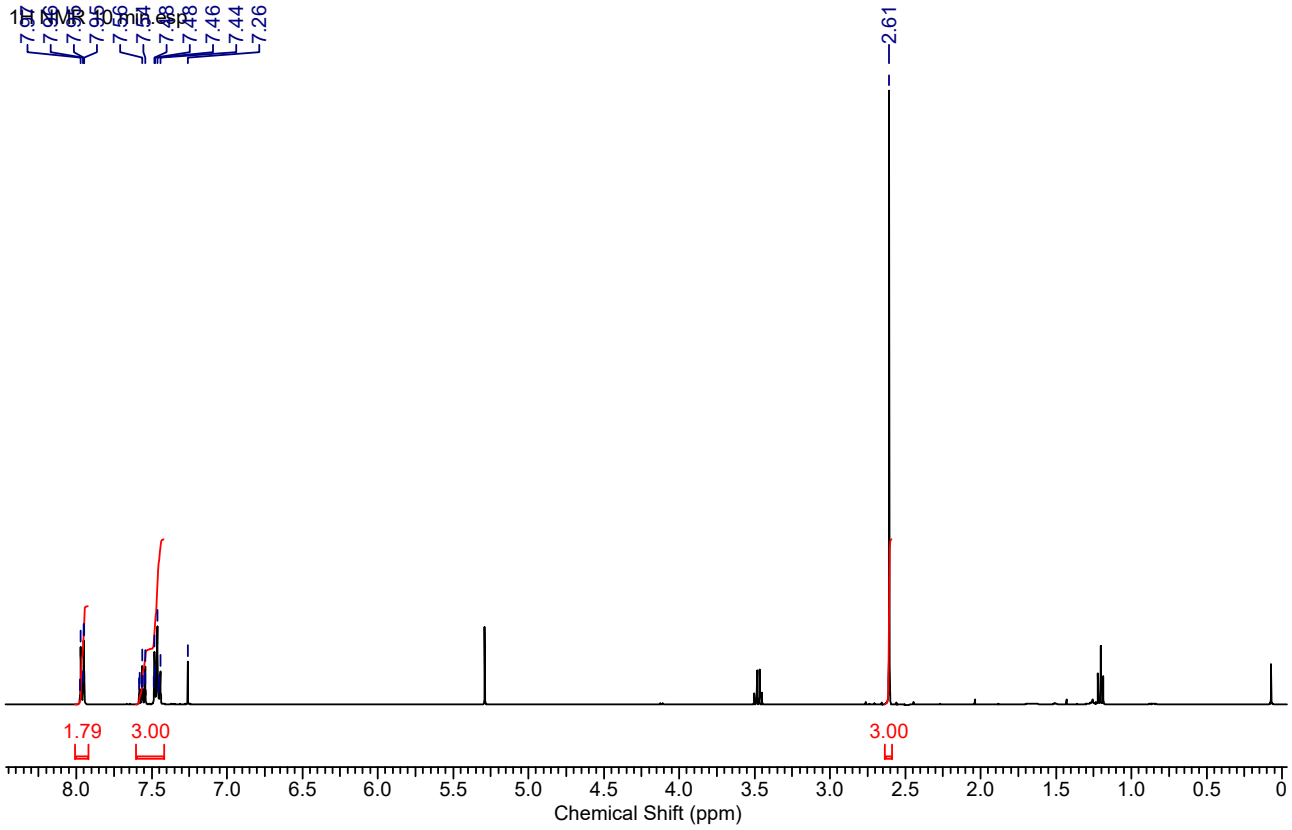
Dihydride Complex 22



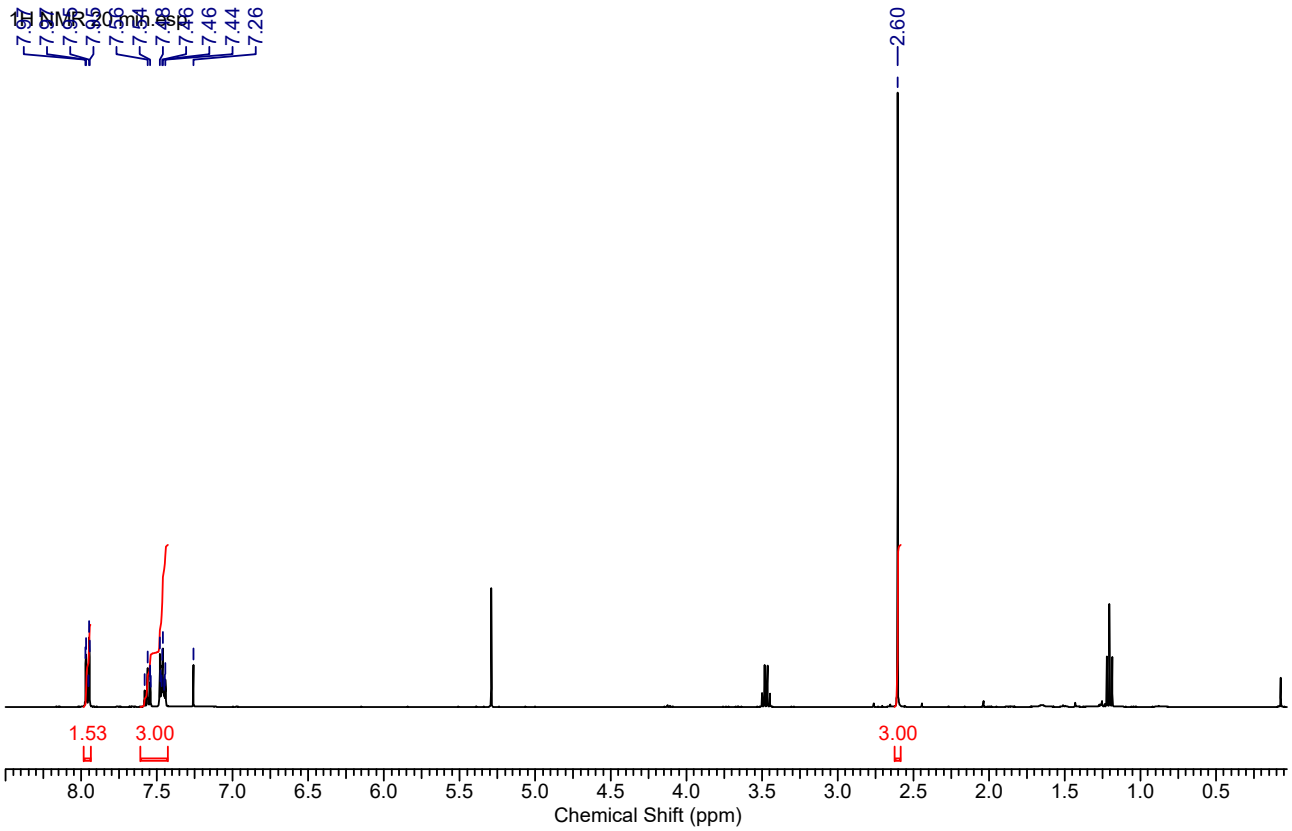


*Rate Monitoring for the Deuteration of Acetophenone **23** with Catalyst **7***

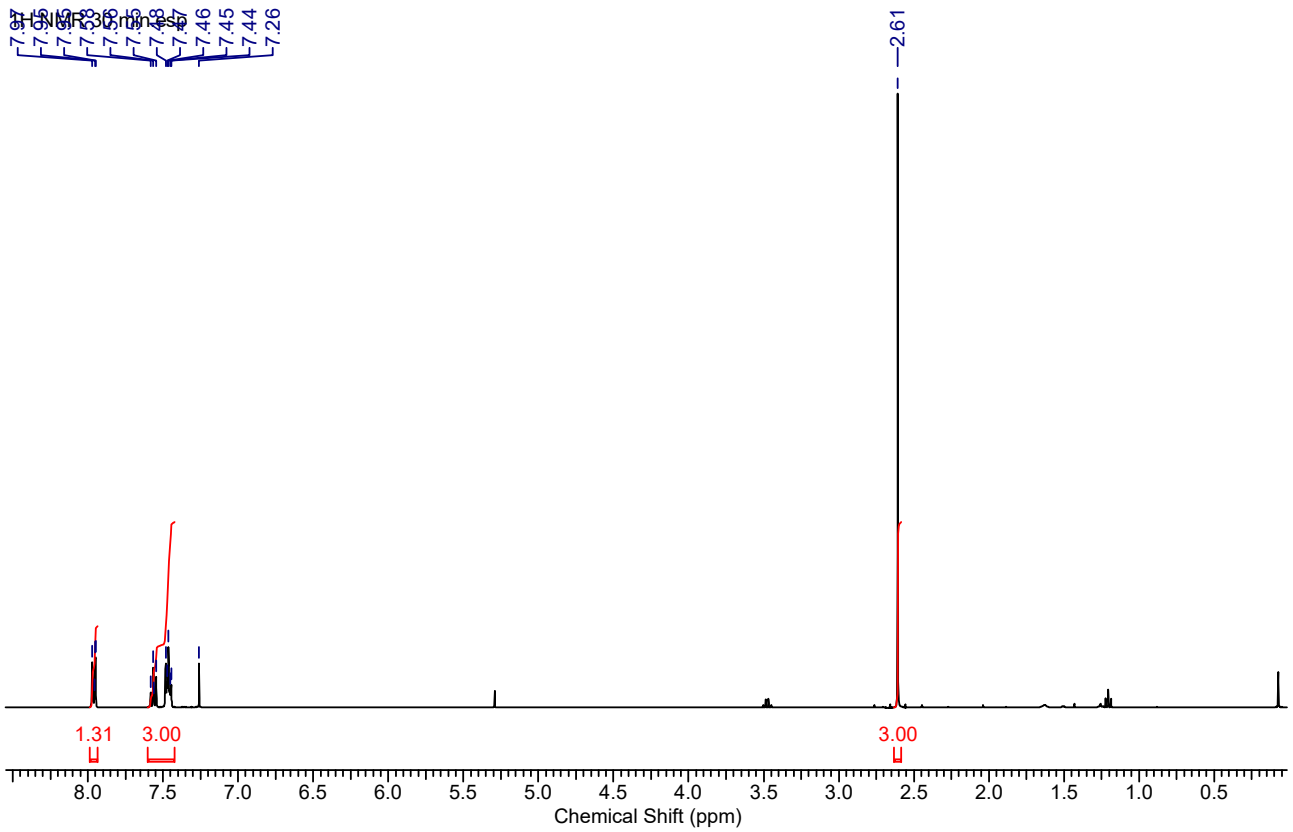
10 min, 10%D



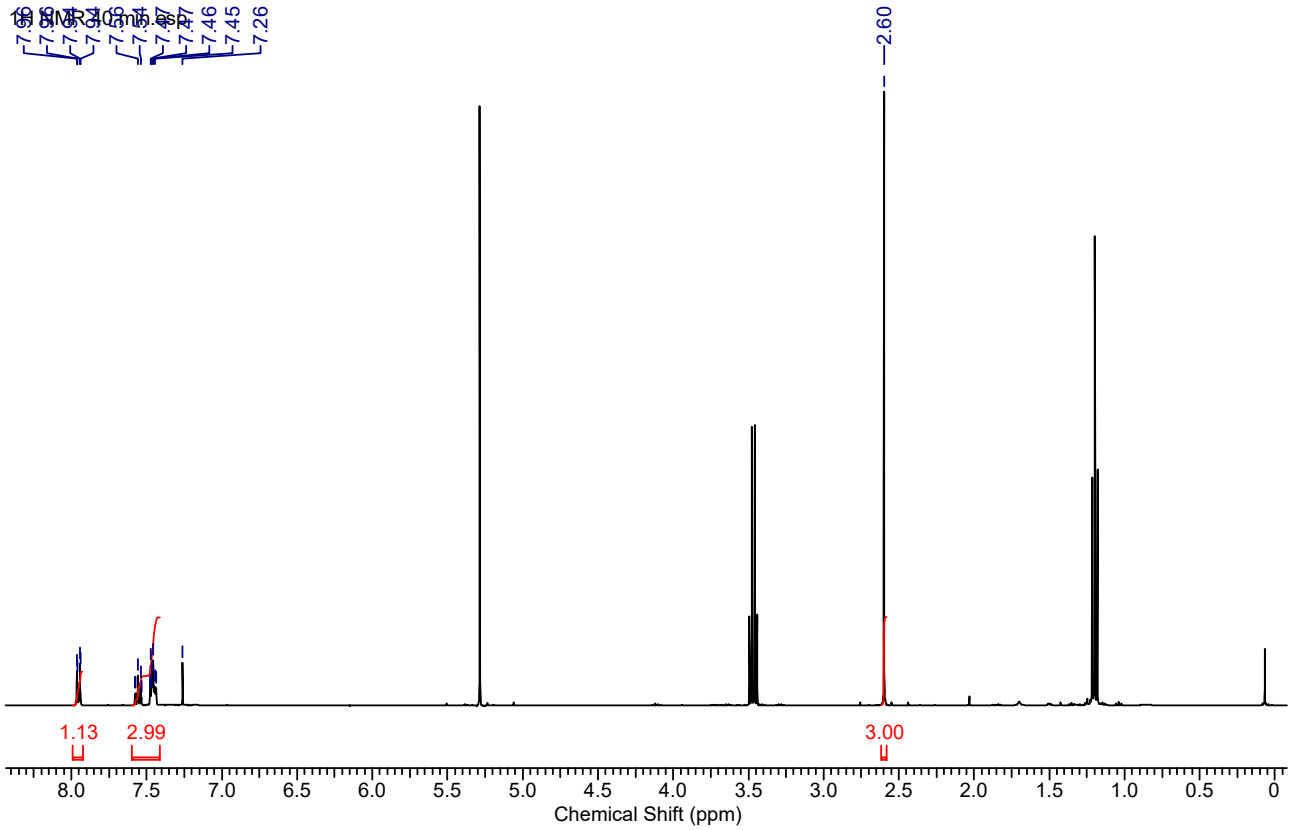
20 min, 24%D



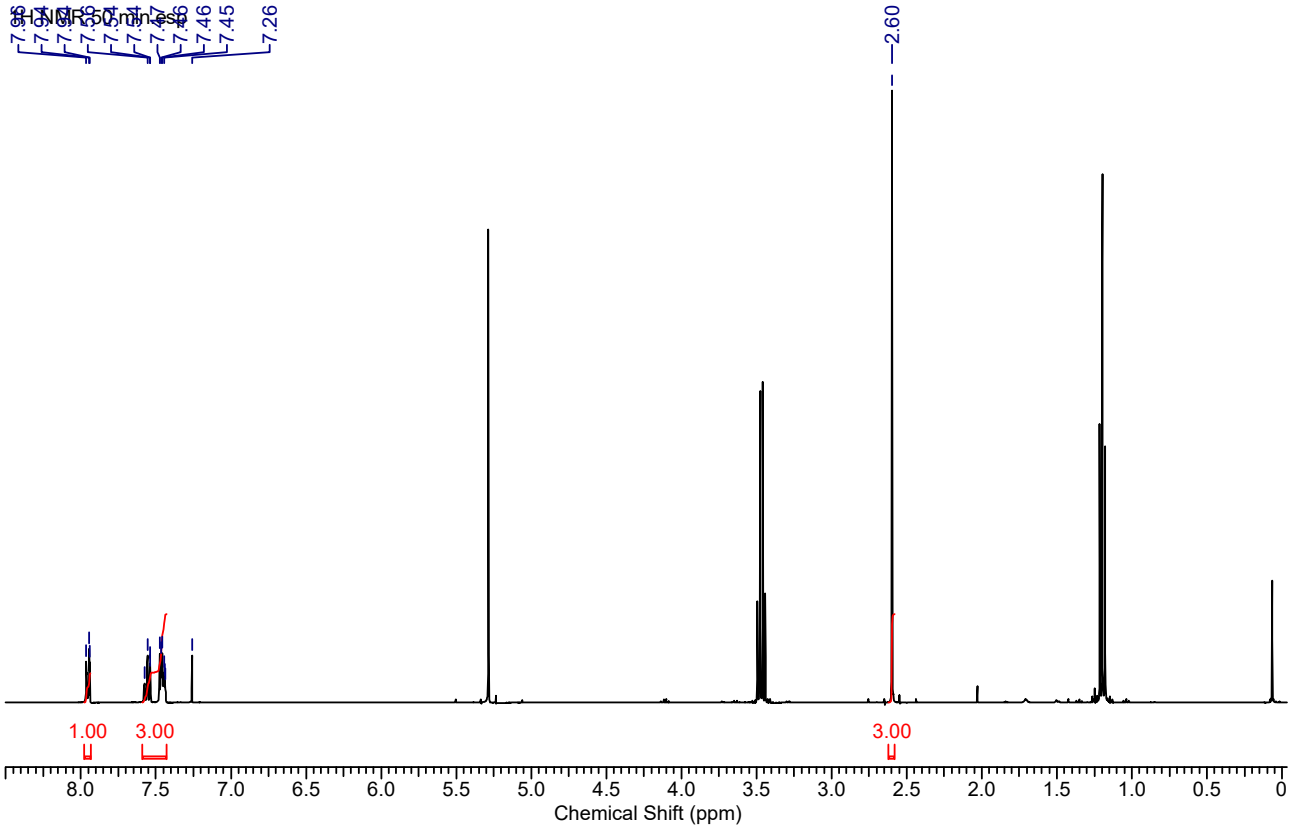
30 min, 34%D



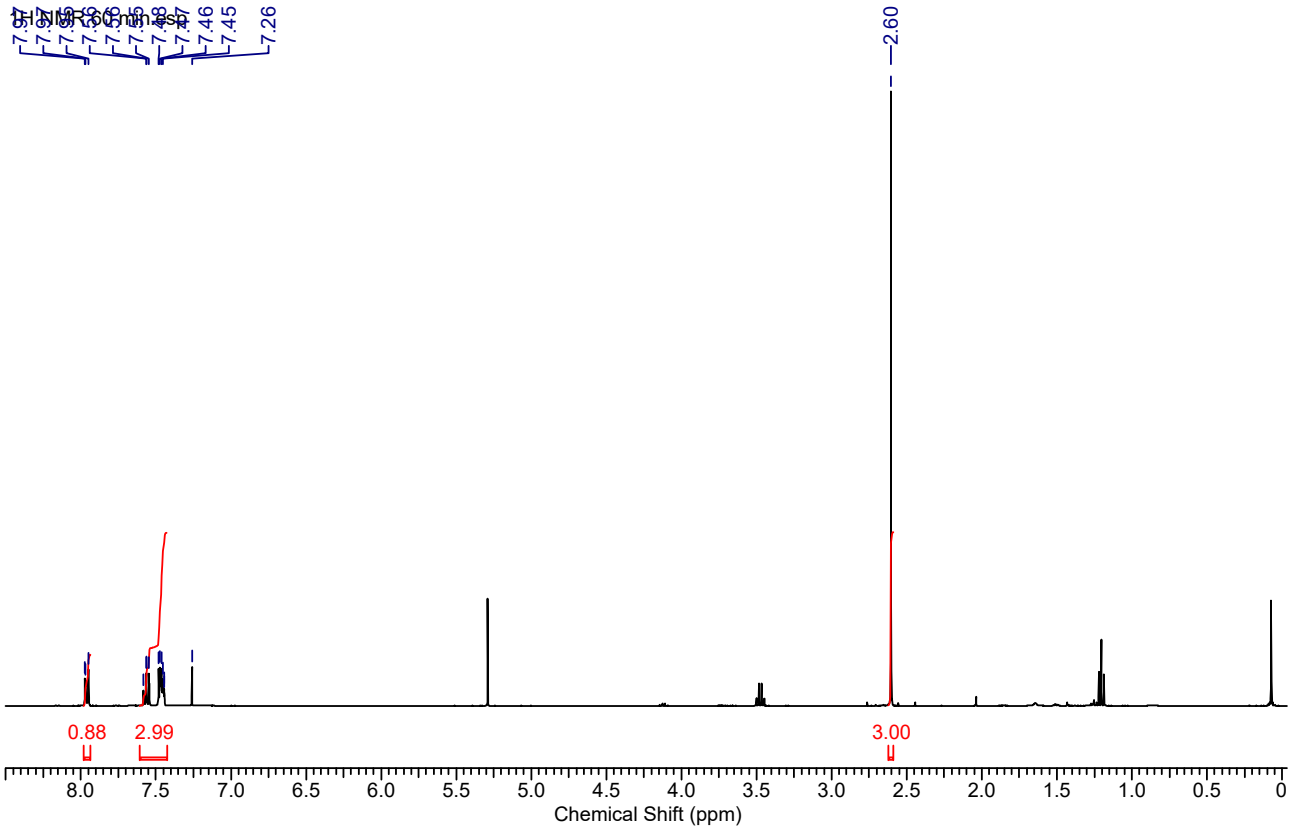
40 min, 44%D



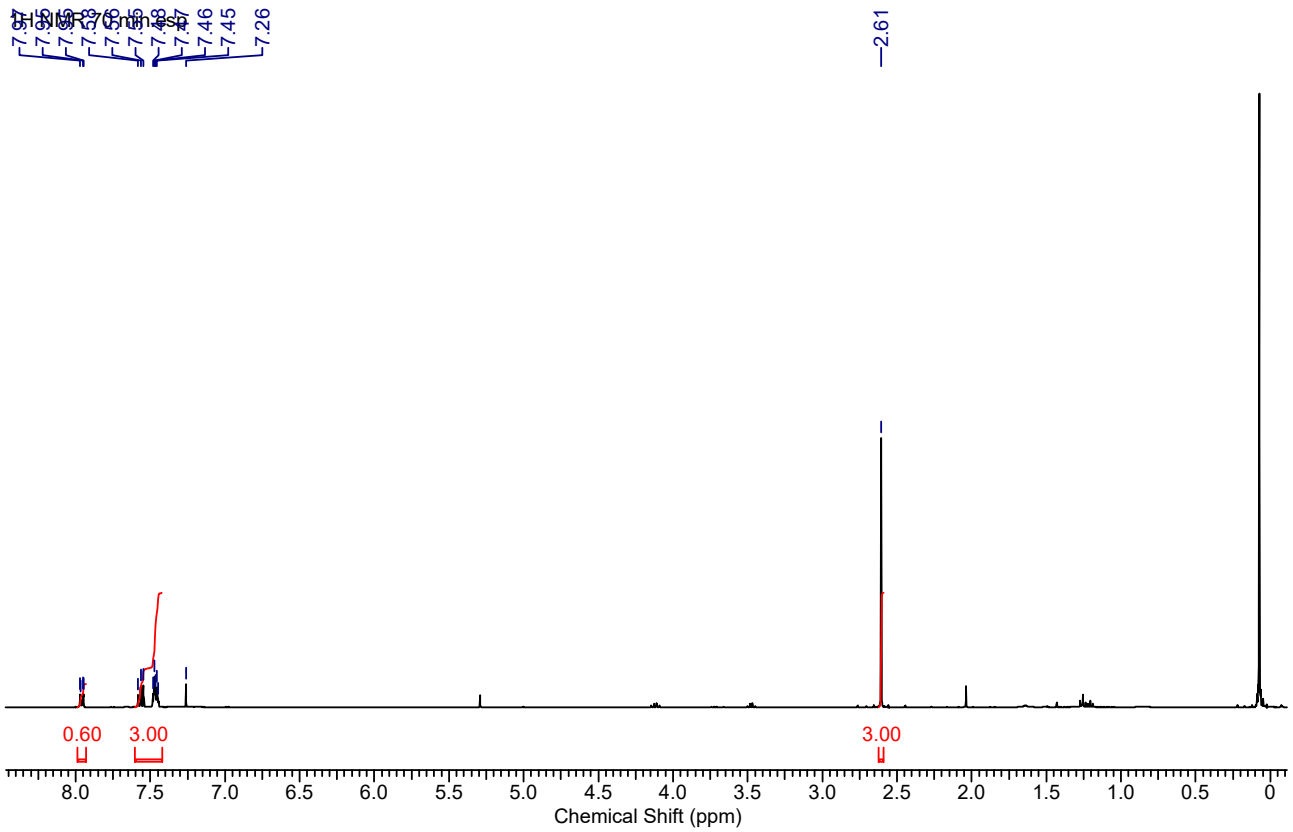
50 min, 50%D



60 min, 56%D

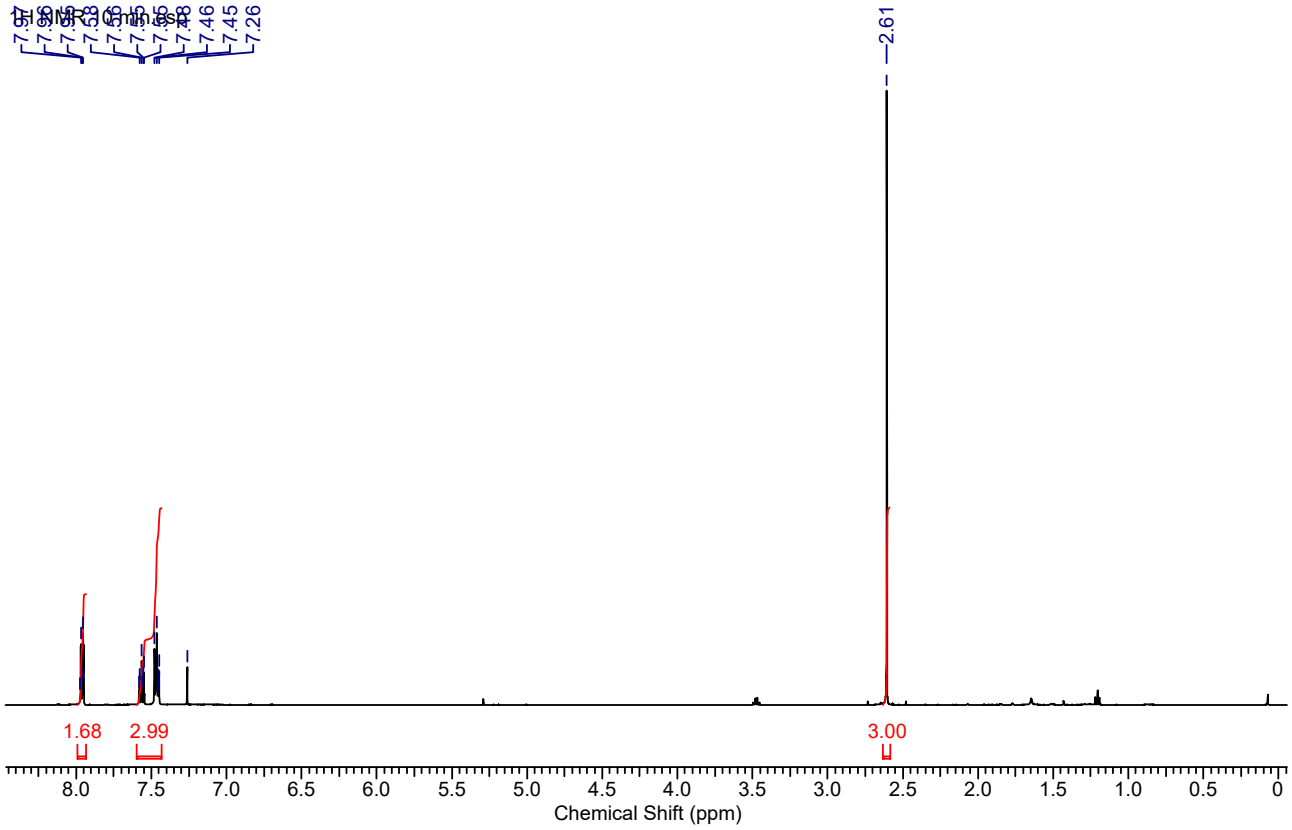


120 min, 70%D

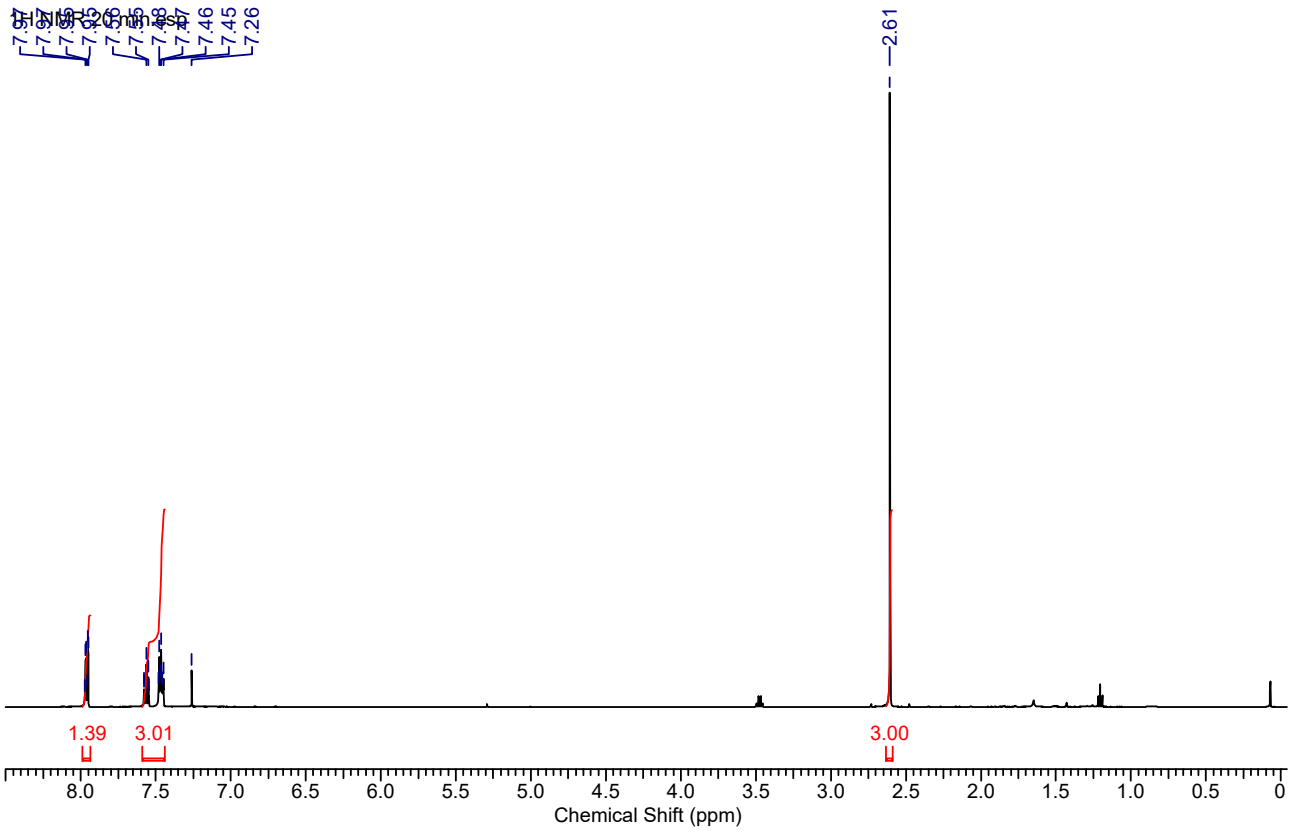

7.47
7.46
7.45
7.26
2.61
0.60
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

*Rate Monitoring for the Deuteration of Acetophenone **23** with Catalyst **6a***

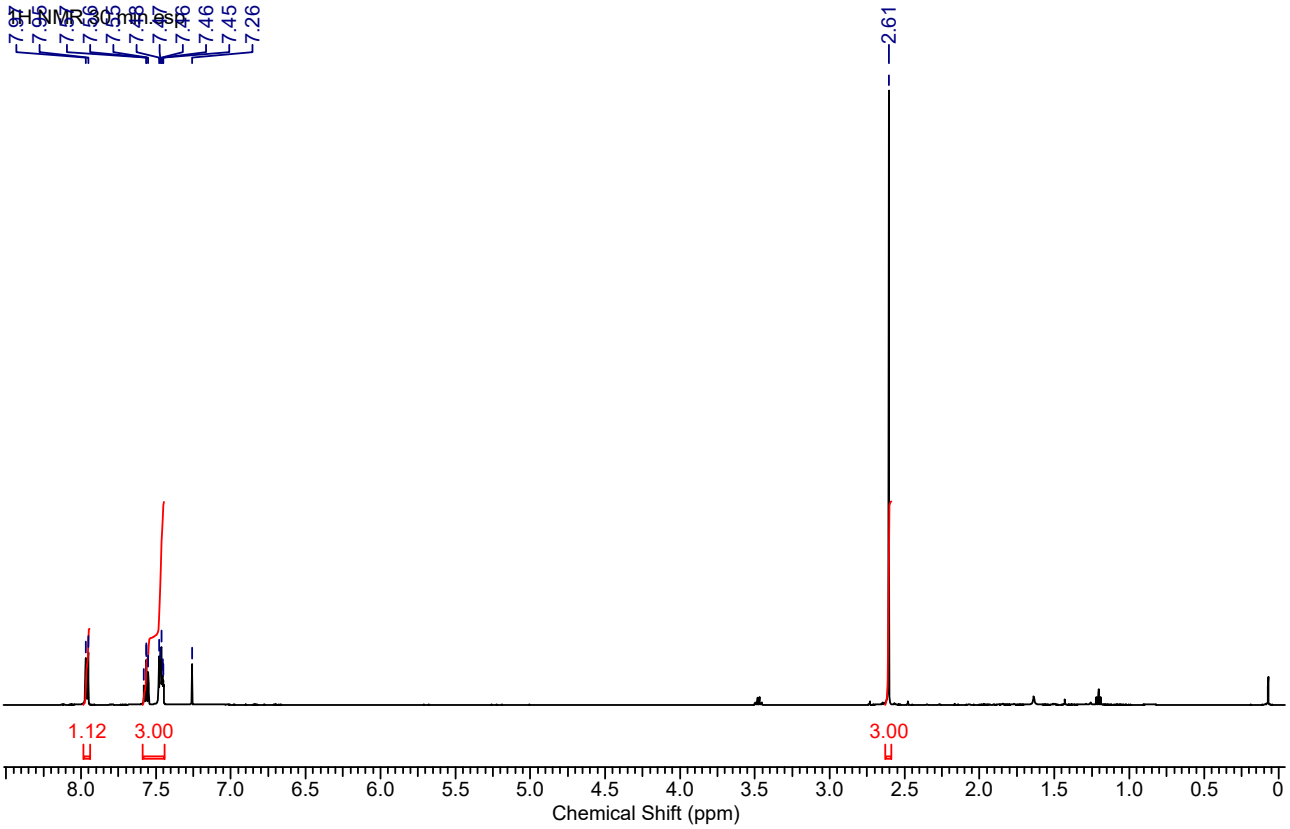
10 min, 17%D



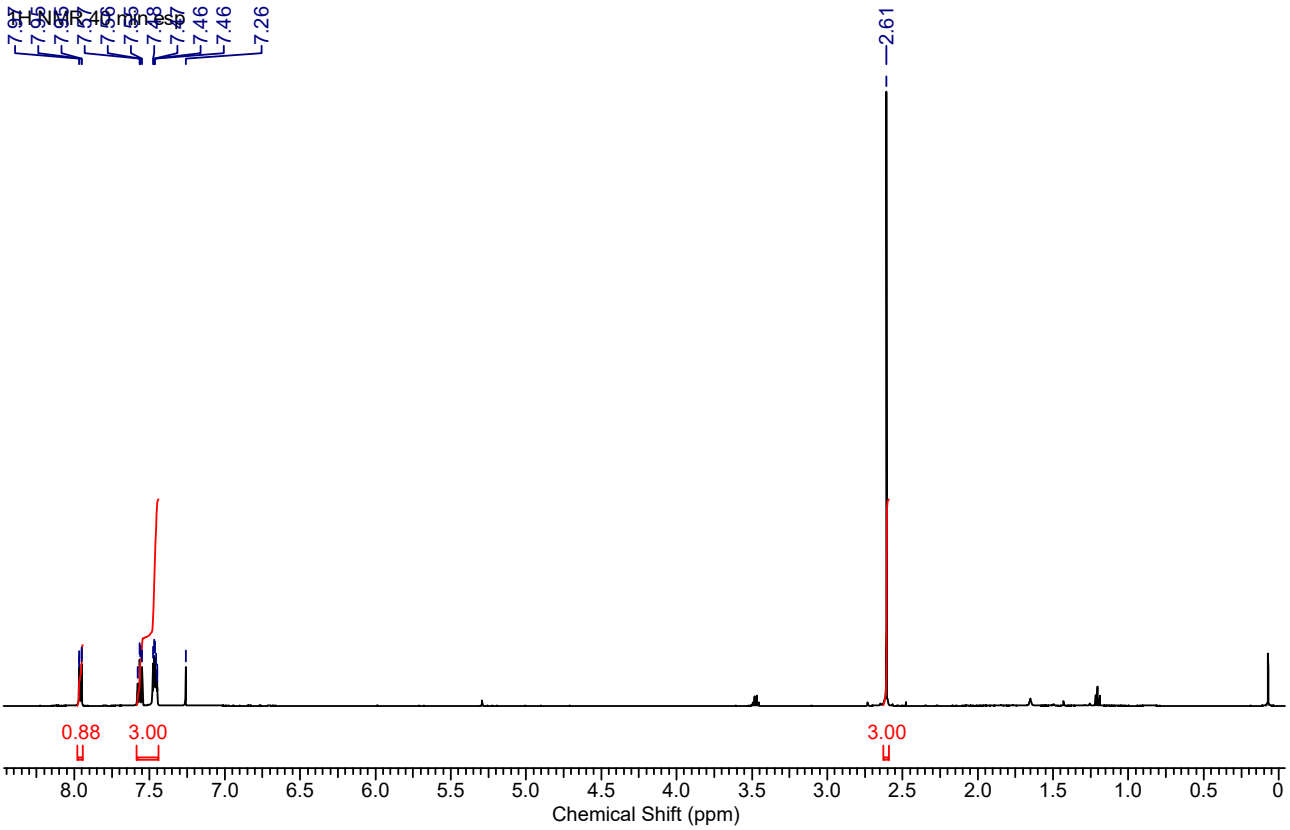
20 min, 31%D



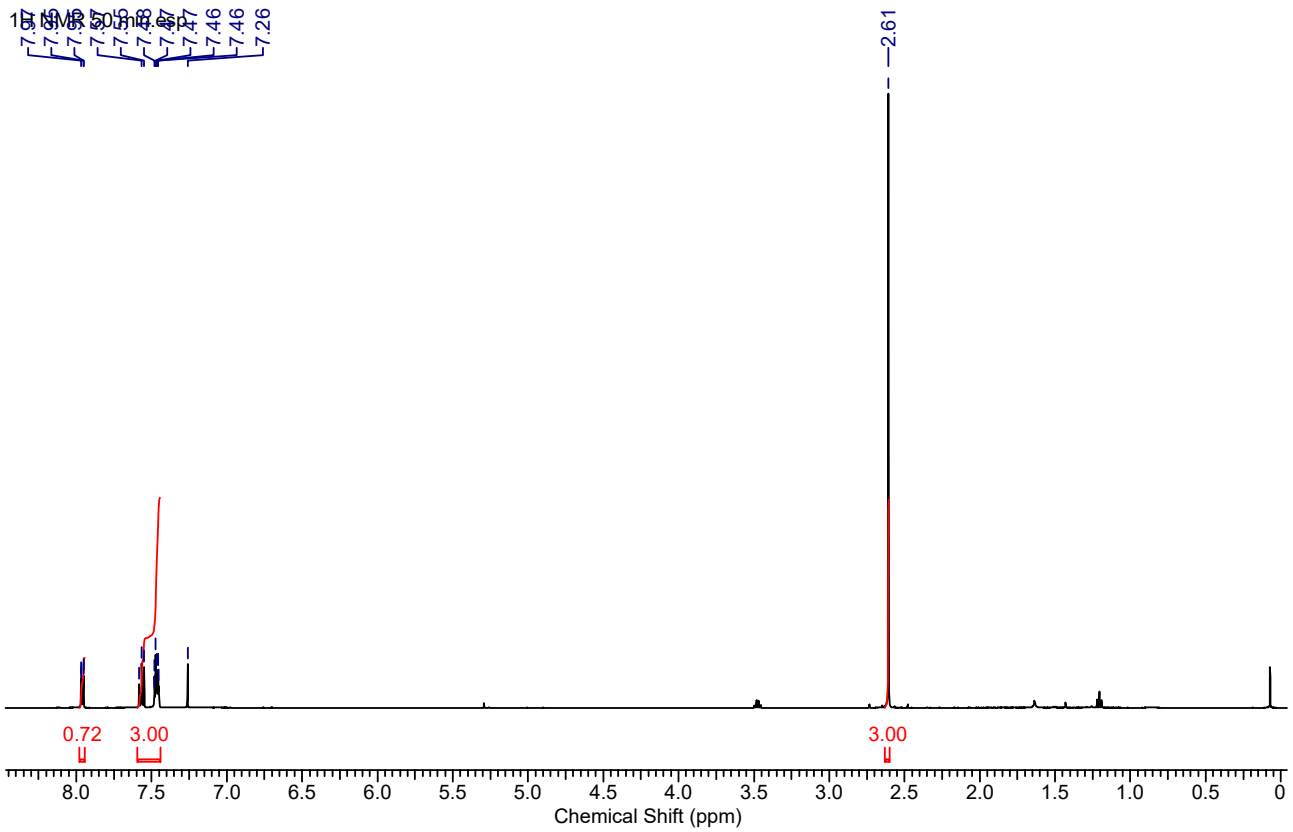
30 min, 45%D



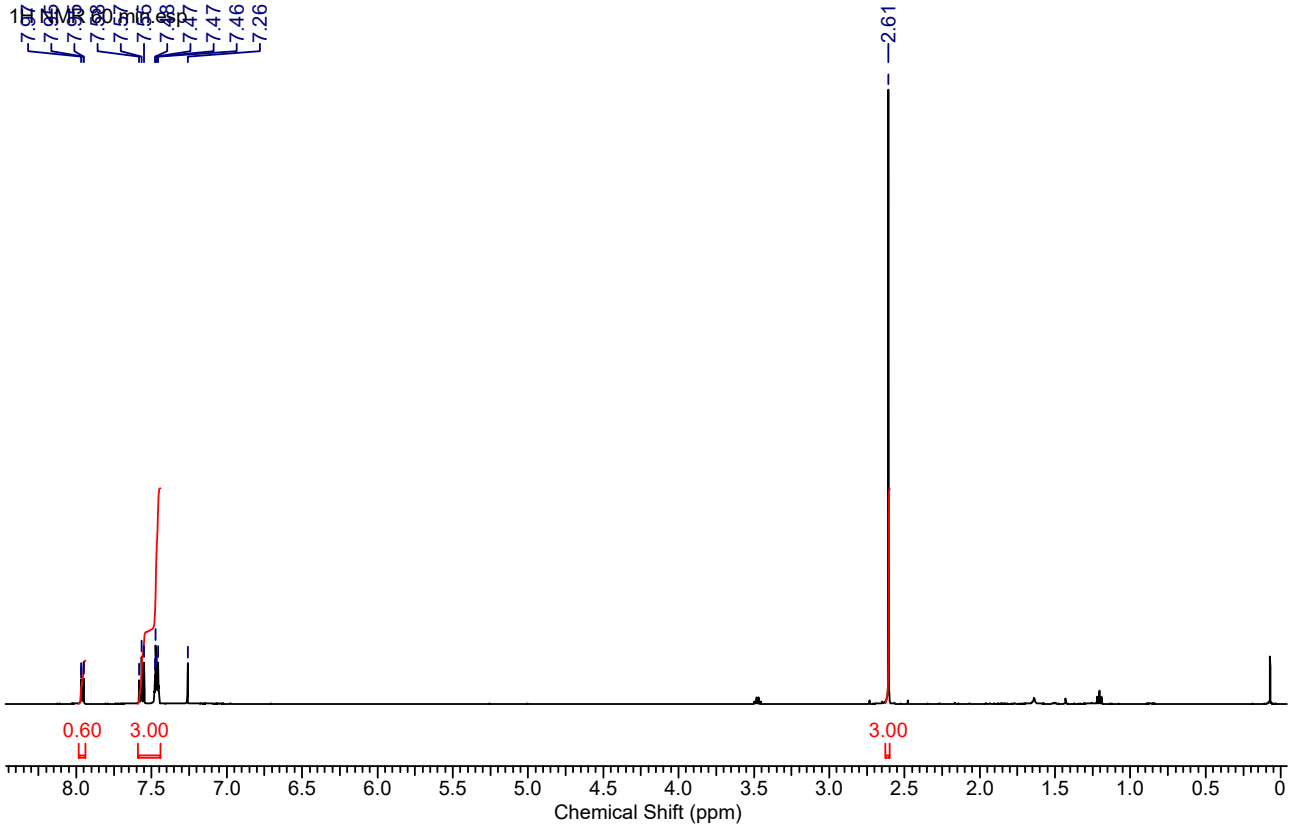
40 min, 56%D



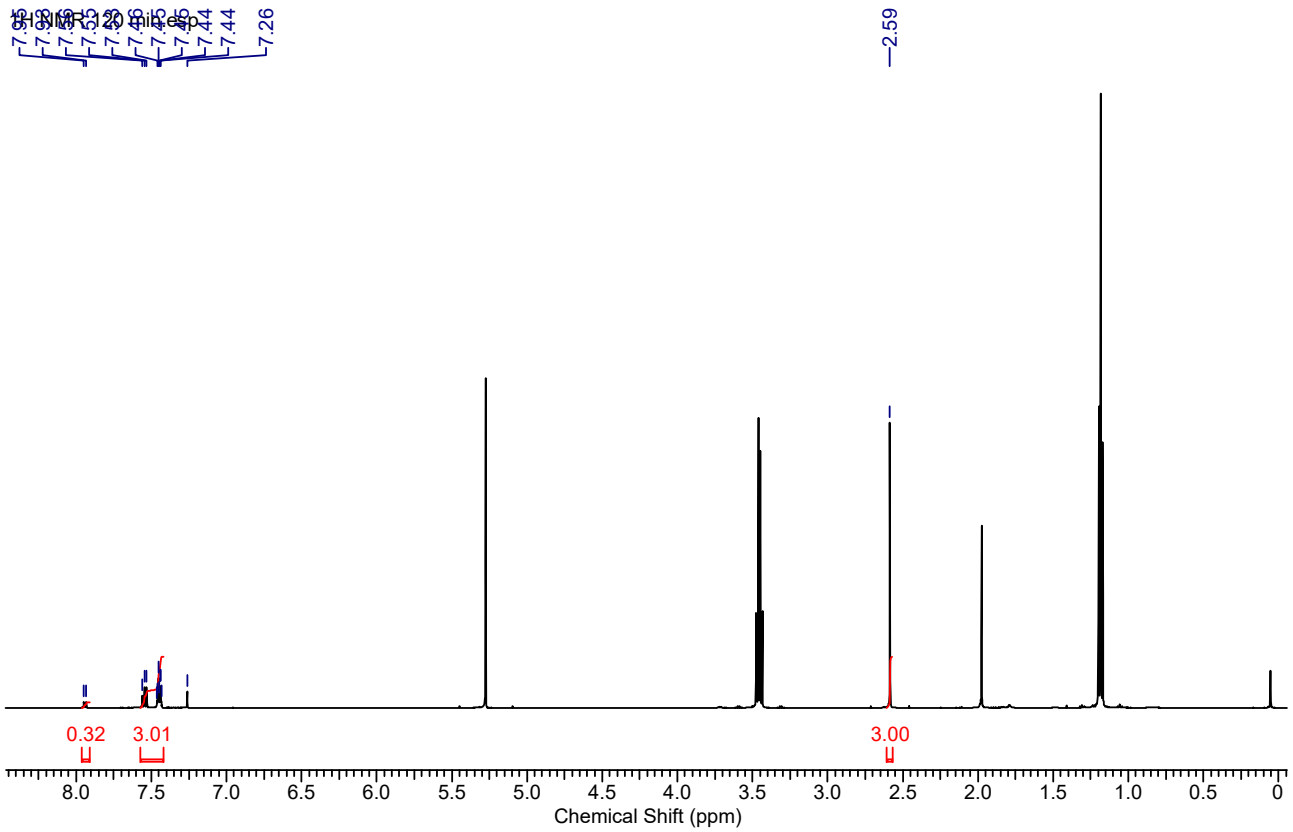
50 min, 64%D



60 min, 70%D

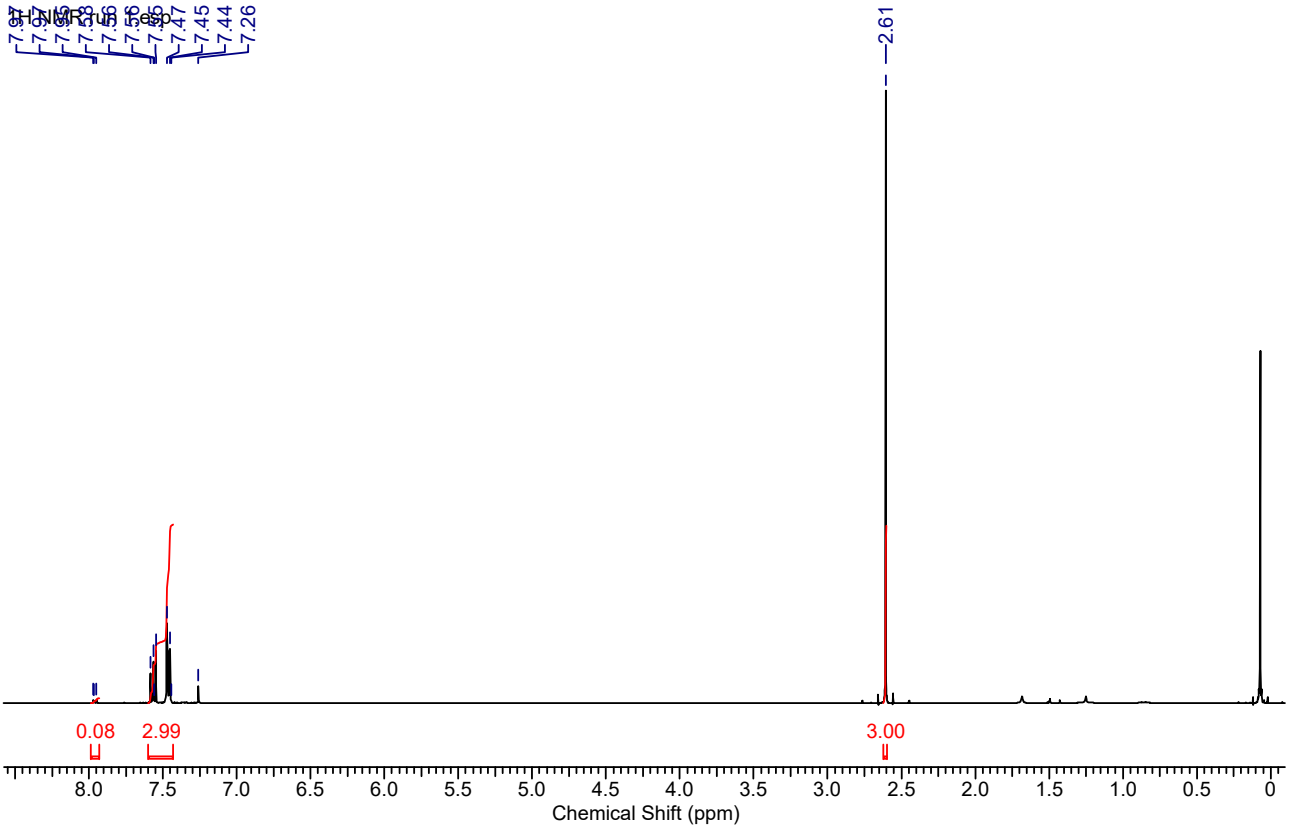


120 min, 84%D

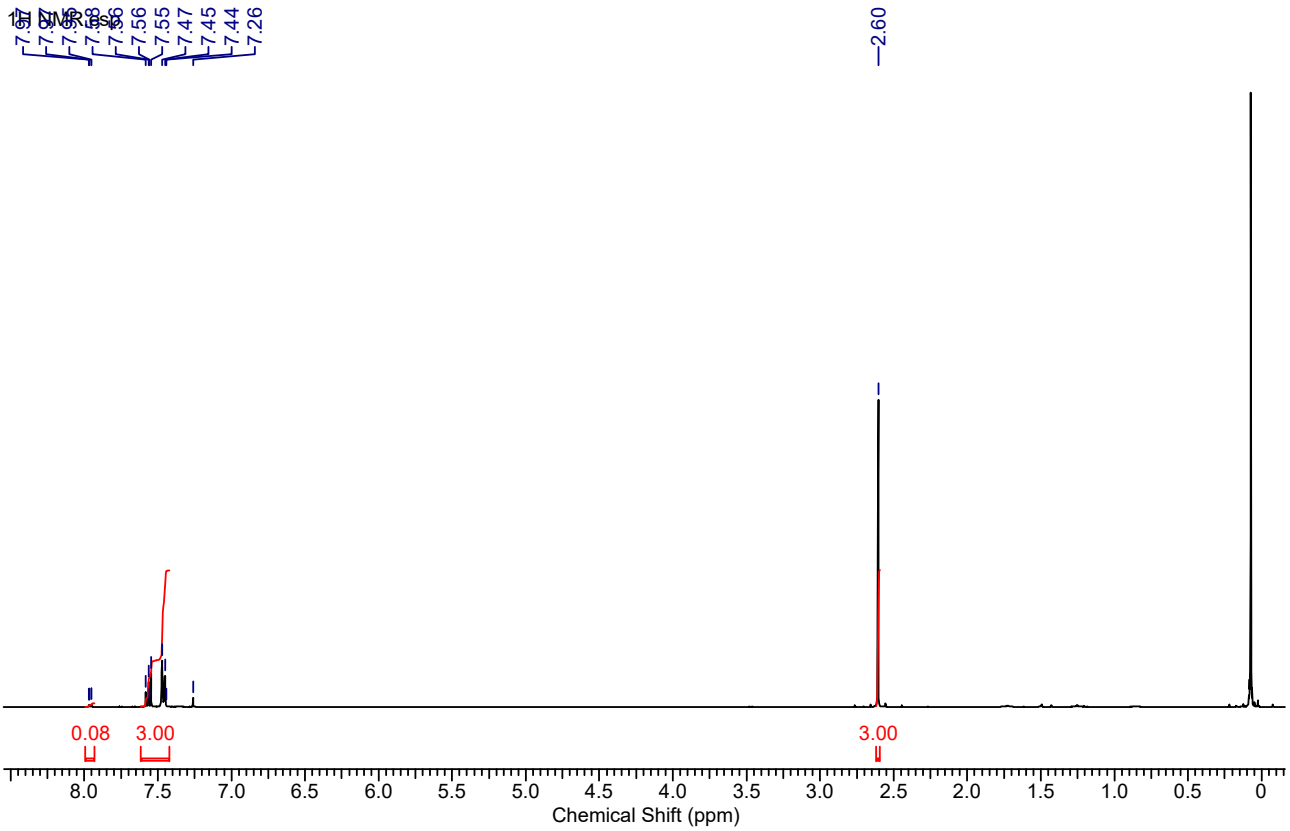

7.45
7.44
7.44
7.26
2.59
0.32
3.01
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

Labelling of Acetophenone 23

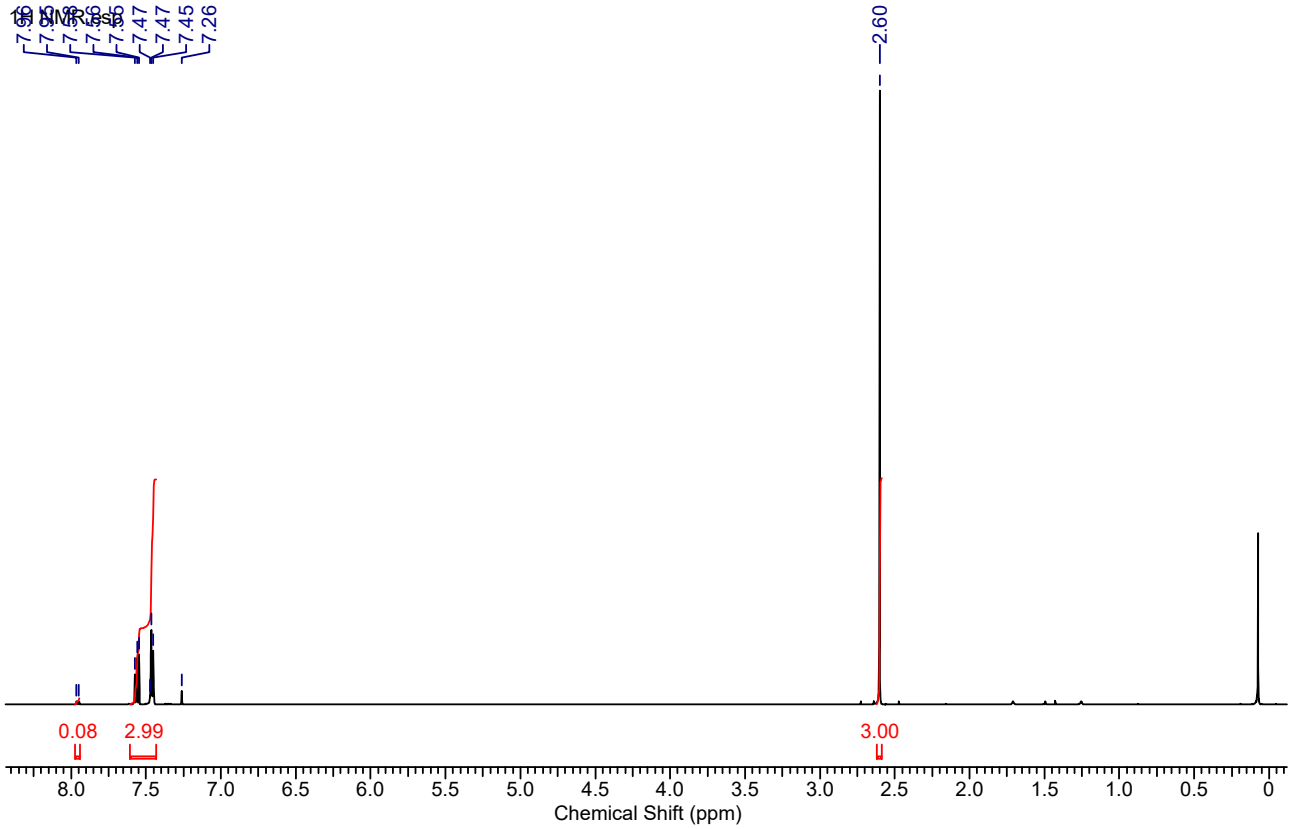
With Catalyst **6a**, 96%D



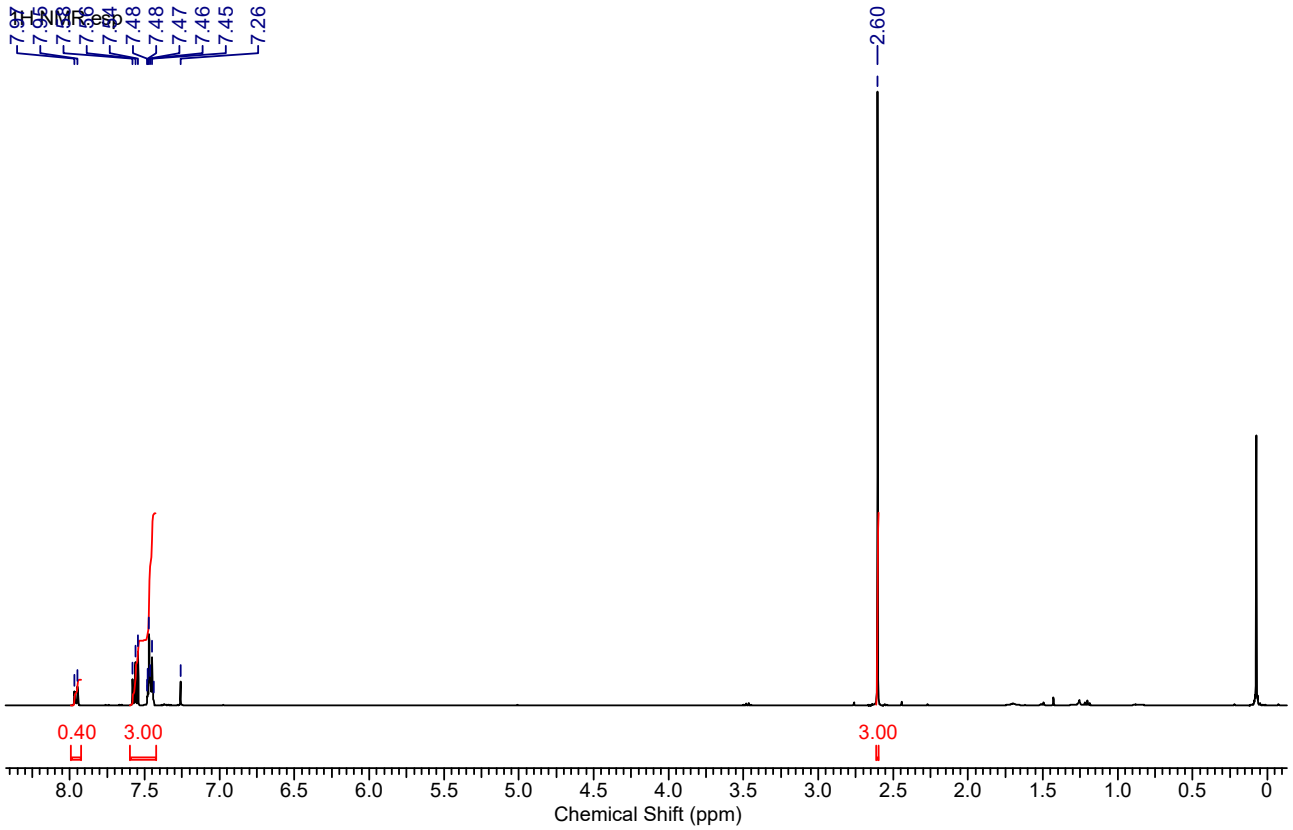
With Catalyst **6b**, 96%D



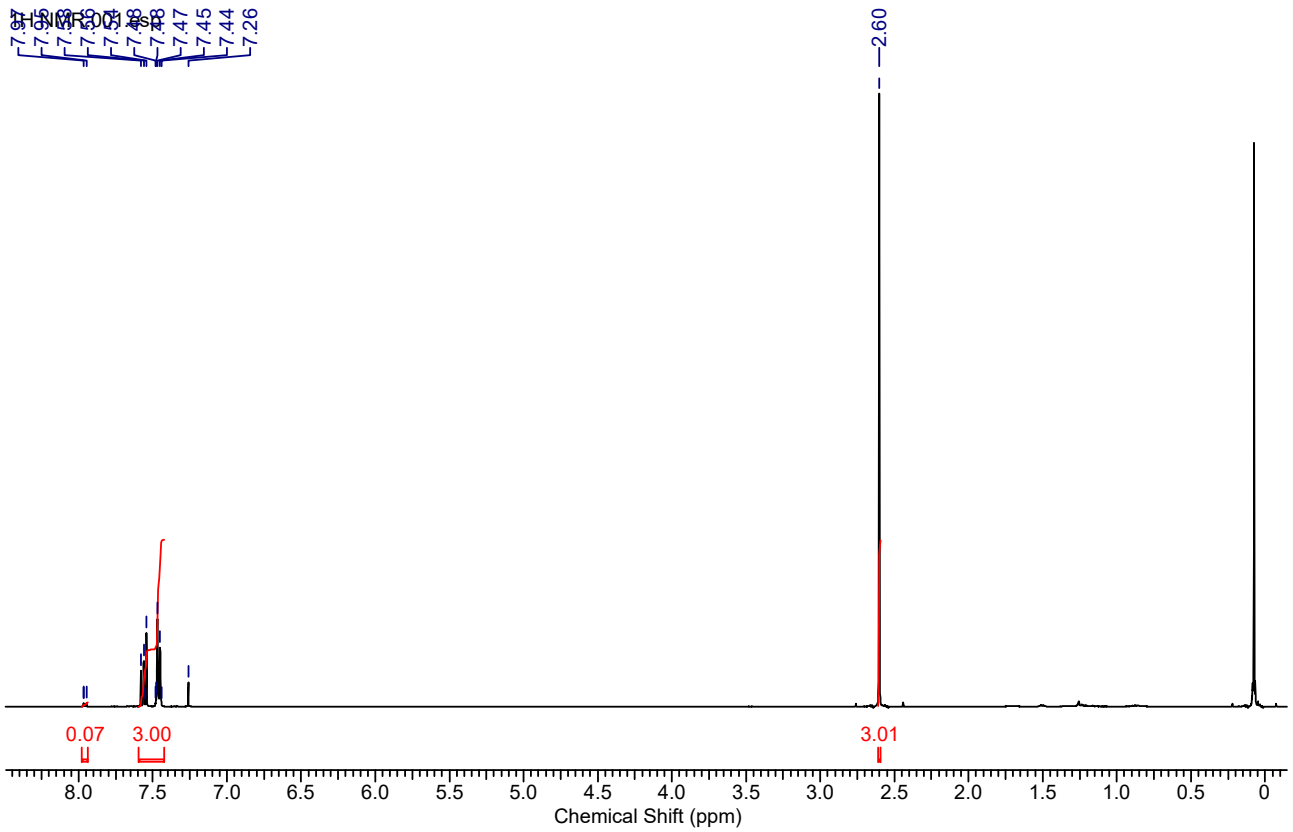
With Catalyst **6c**, 96%D



With Catalyst **6d**, 79%D

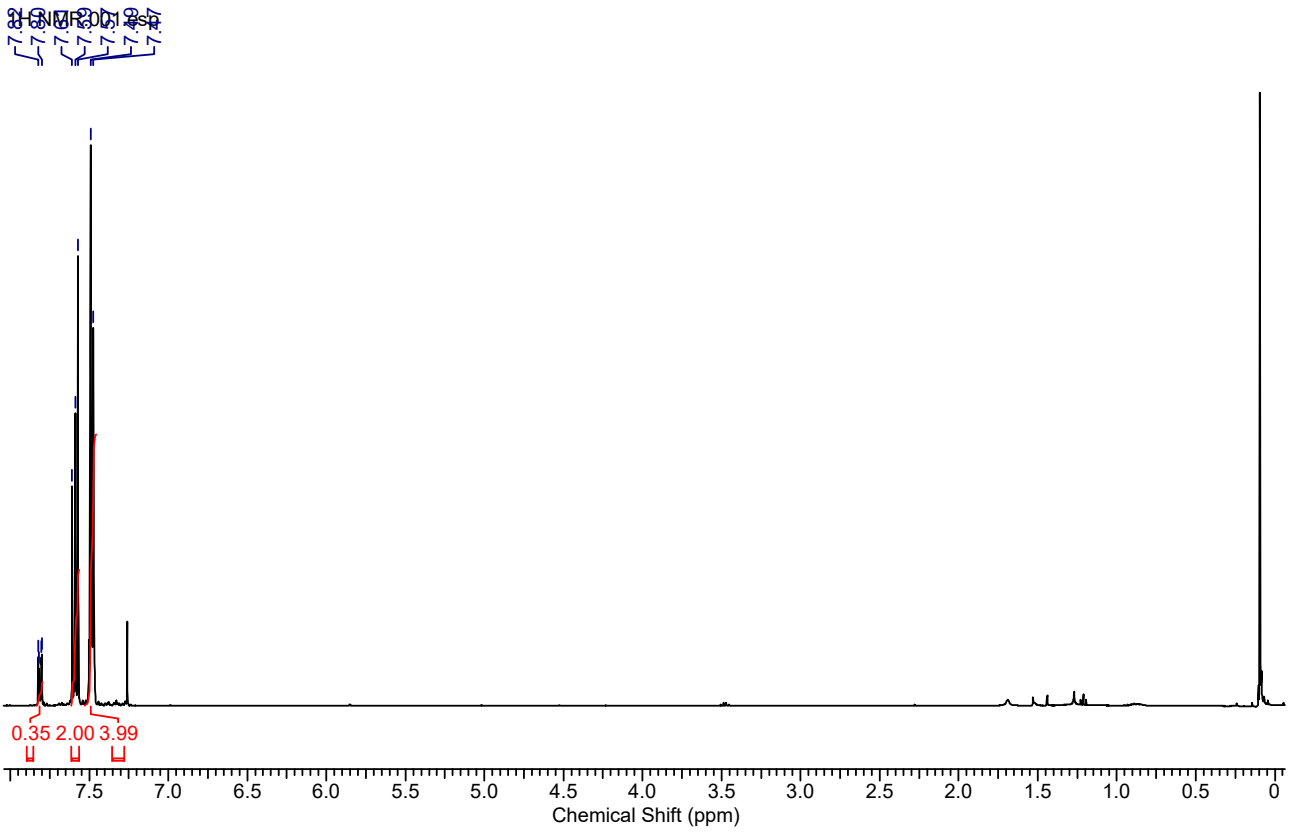


With Catalyst **6e**, 97%D

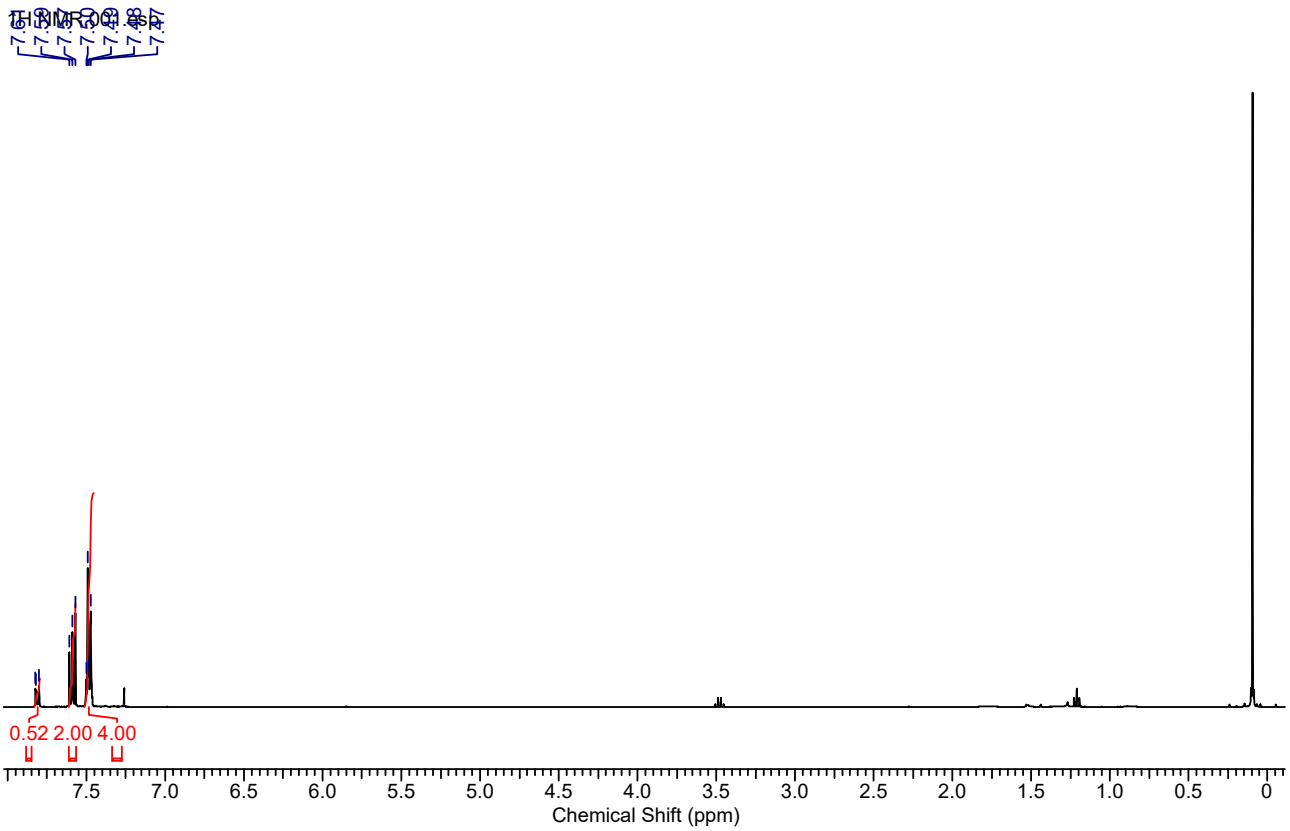


Labelling of Benzophenone 27

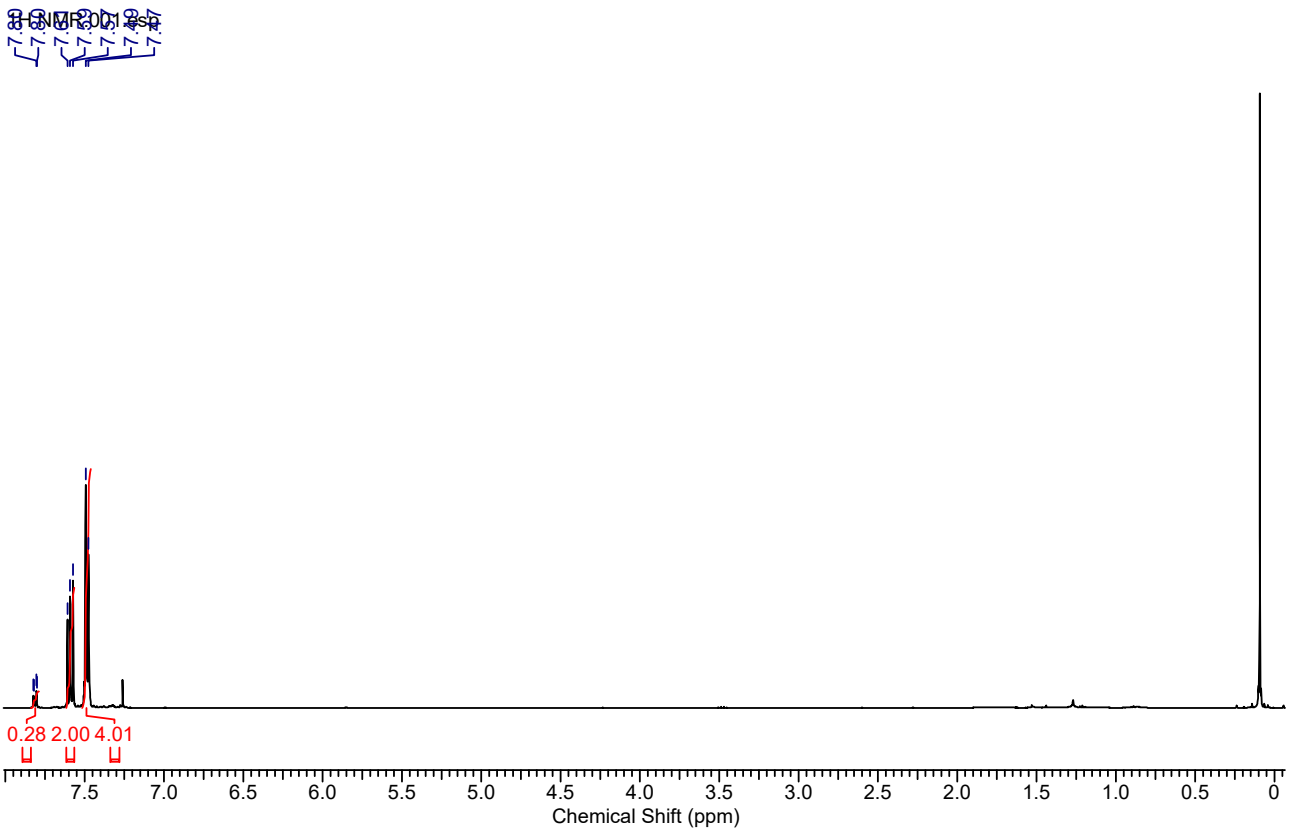
With Catalyst **6a**, 91%D



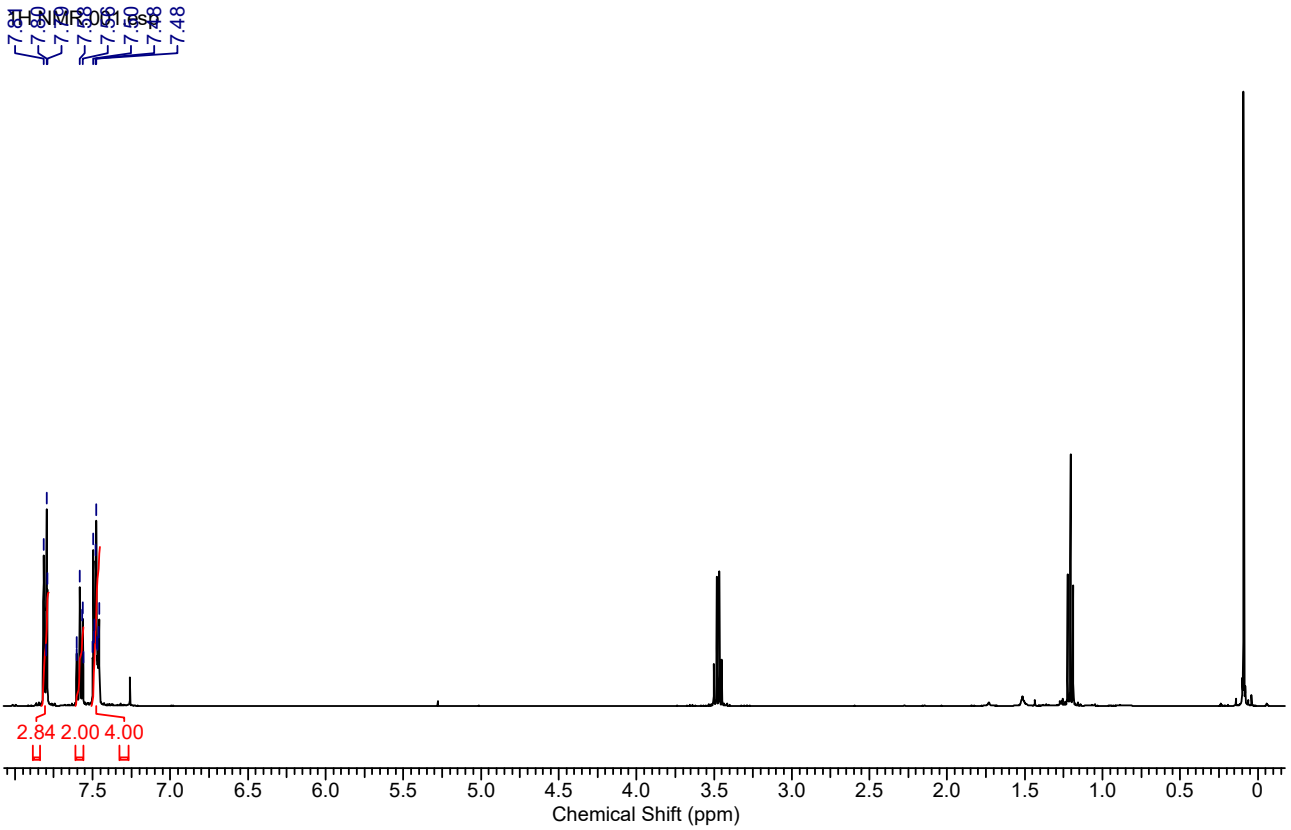
With Catalyst **6b**, 87%D



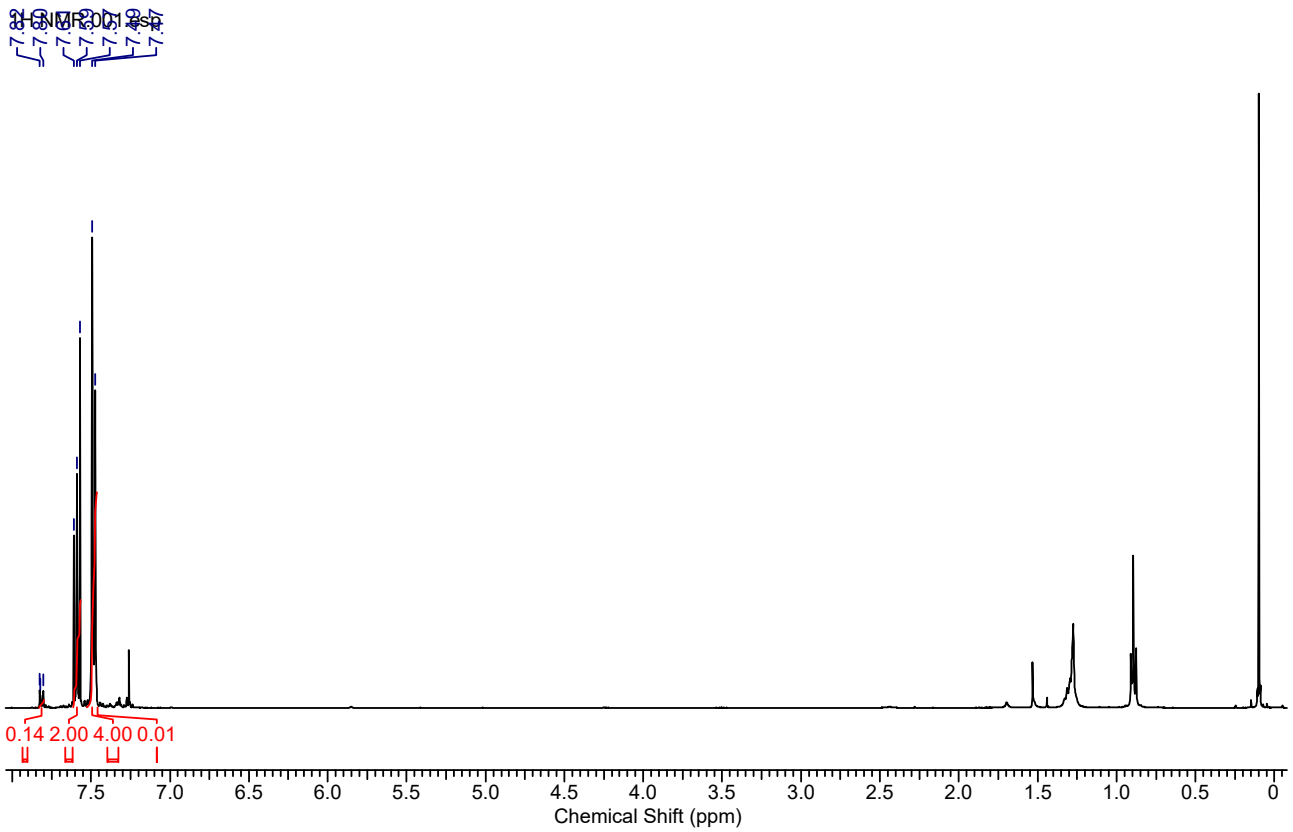
With Catalyst **6c**, 93%D



With Catalyst **6d**, 29%D

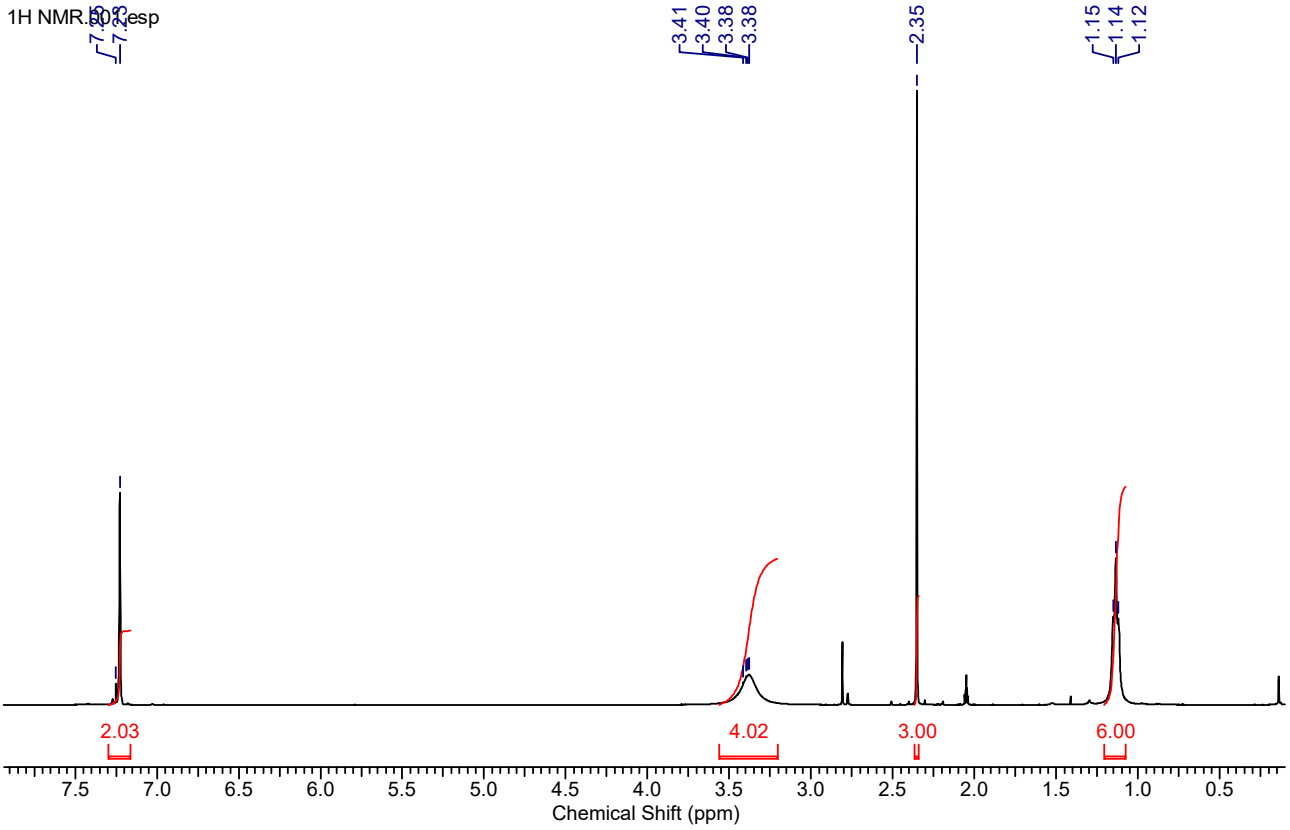


With Catalyst **6e**, 97%D

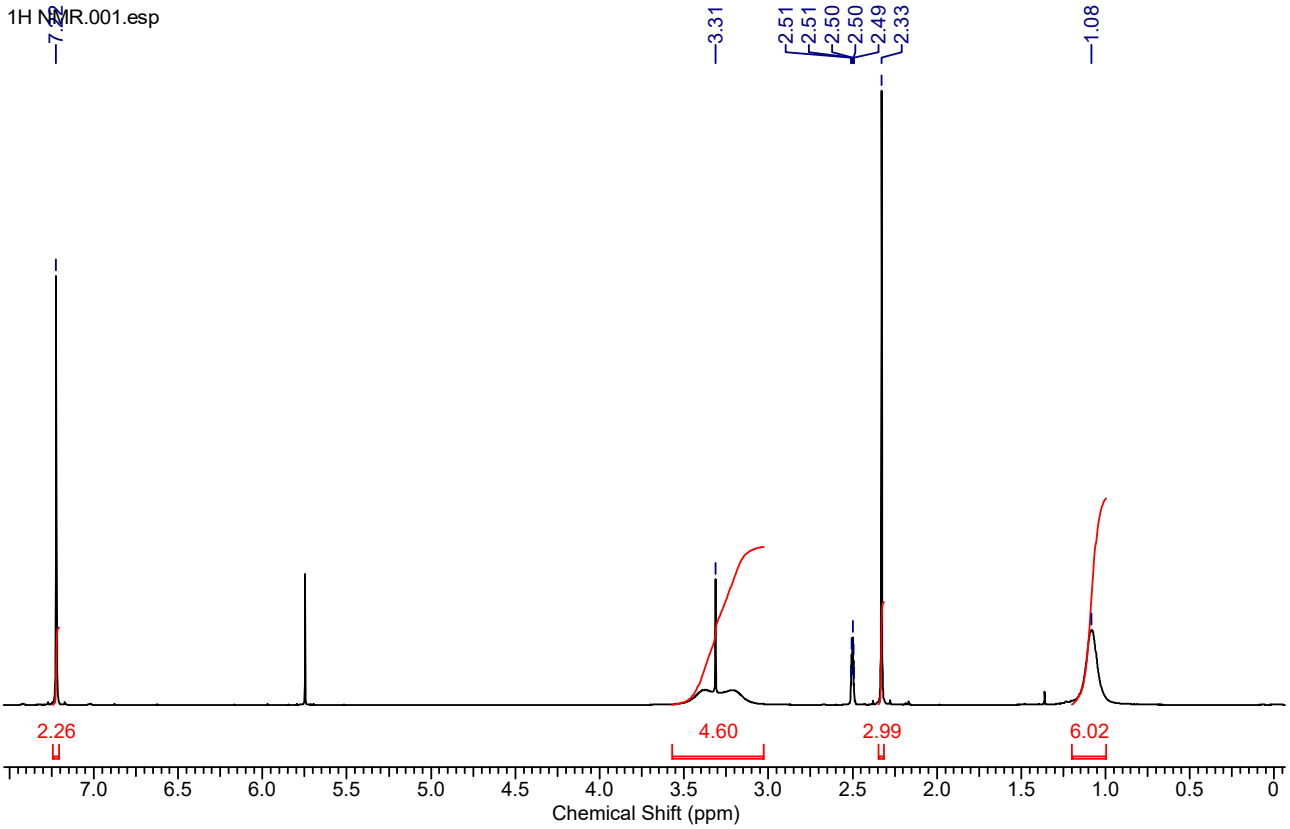


Labelling of *N,N*-Diethyl p-Toluamide 28

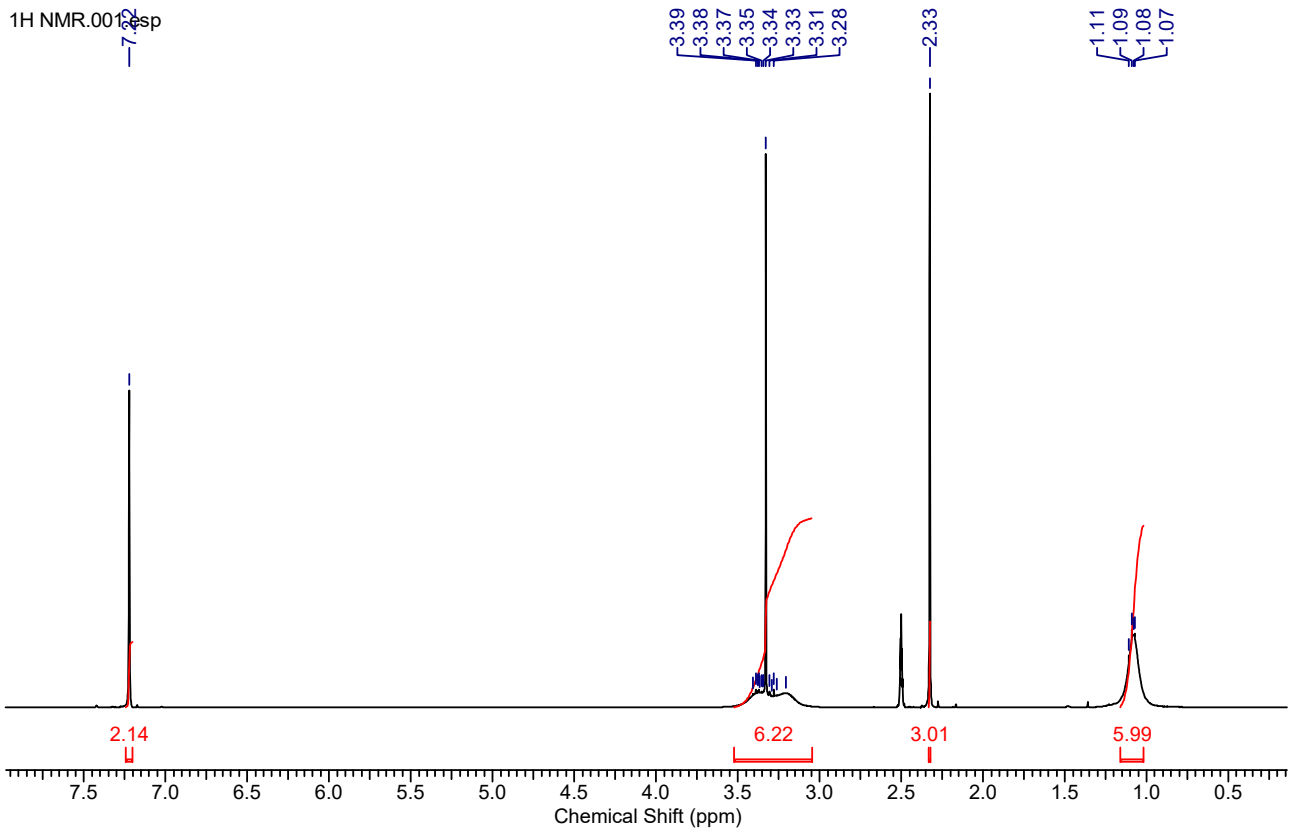
With Catalyst **6a**, 98%D



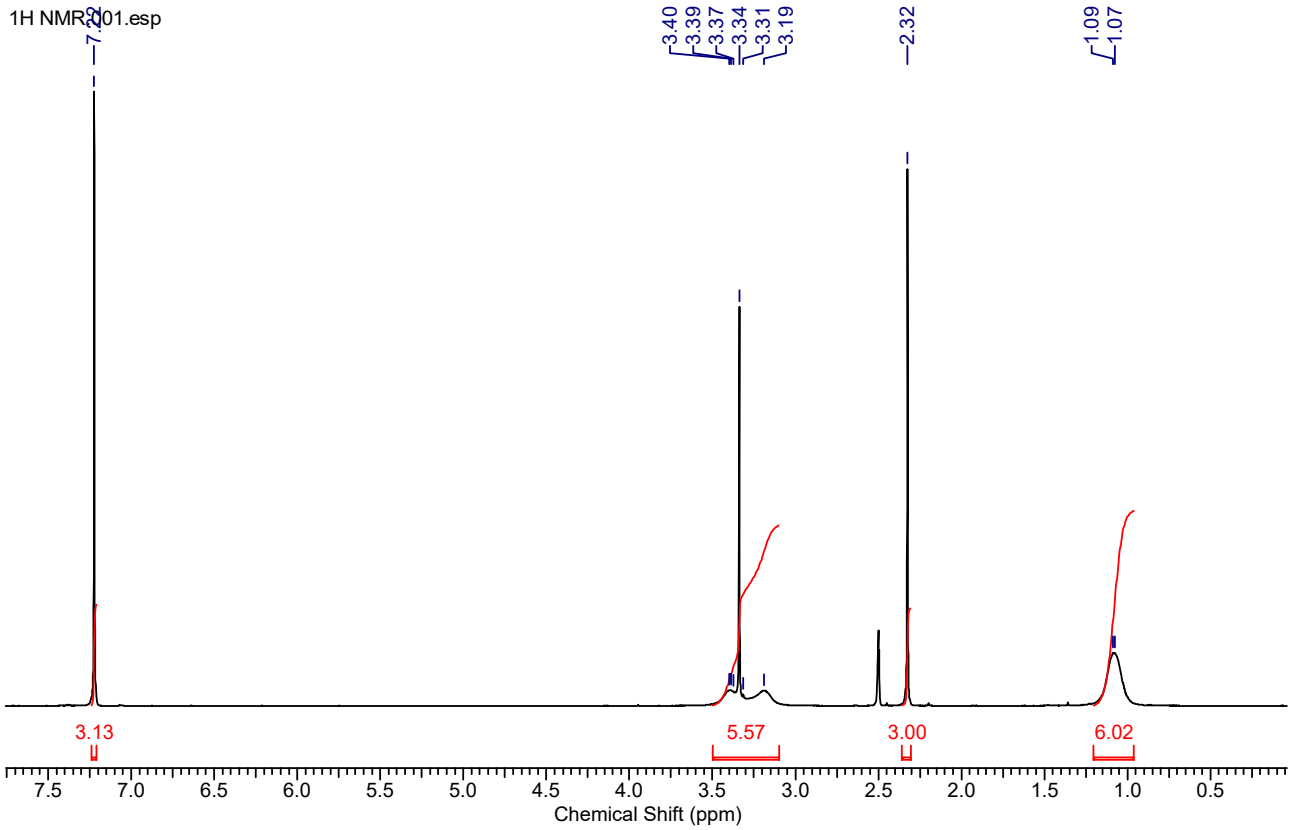
With Catalyst **6b**, 87%D



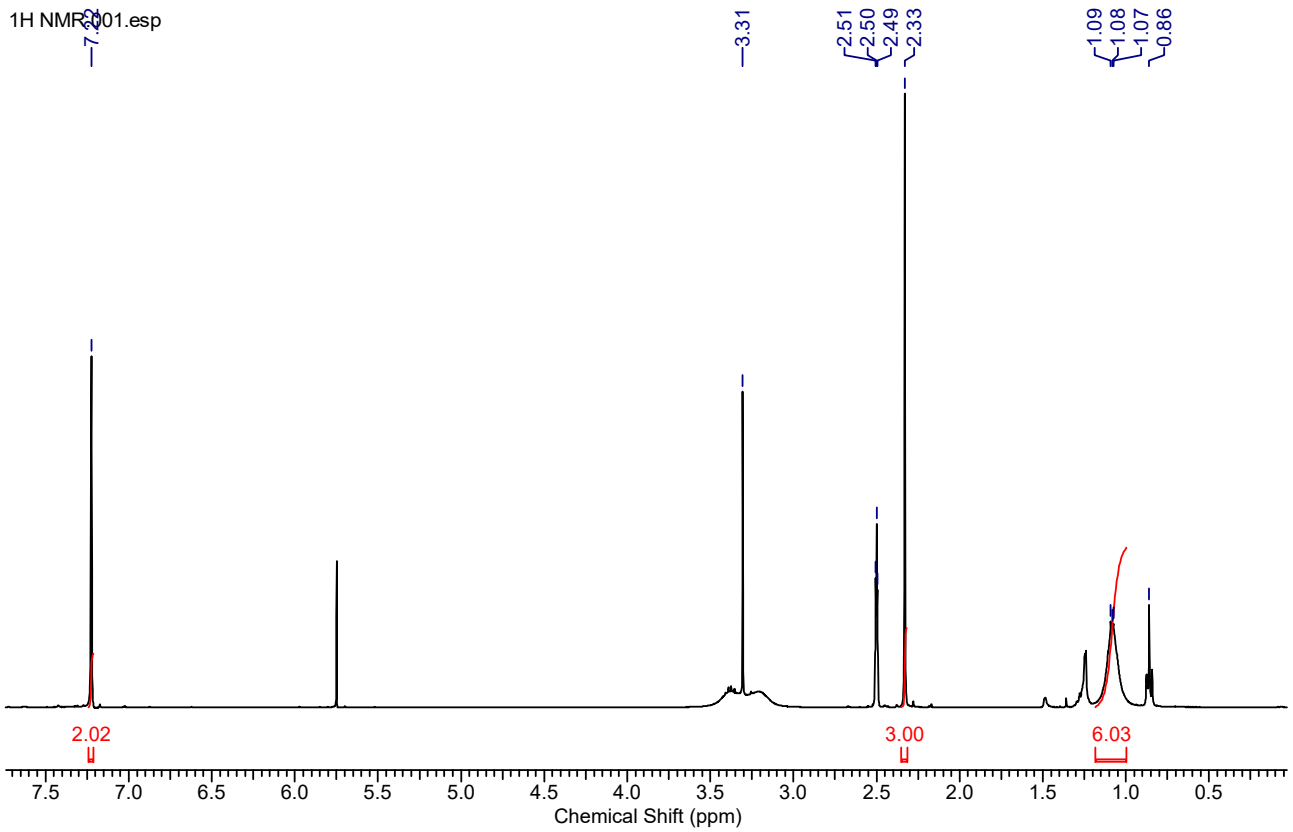
With Catalyst **6c**, 93%D



With Catalyst **6d**, 43%D

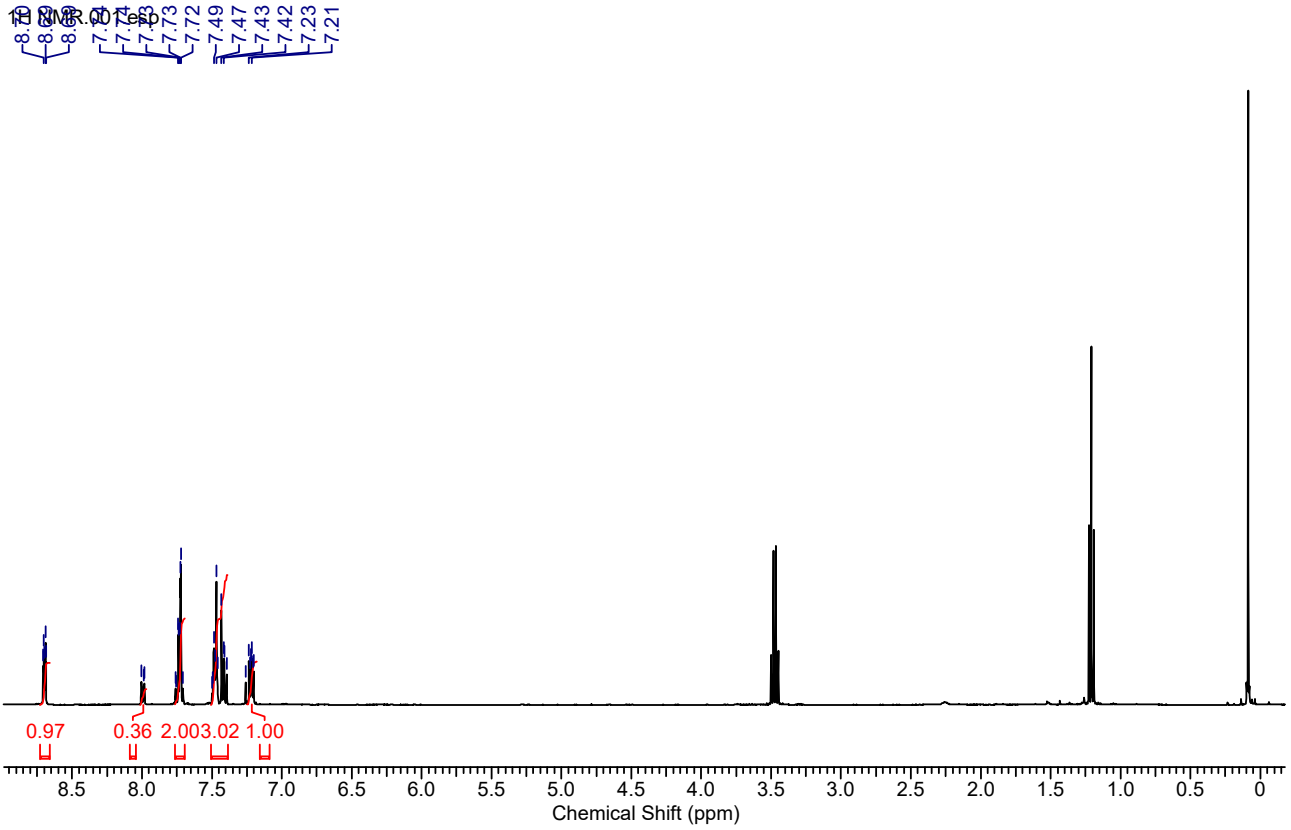


With Catalyst **6e**, 99%D

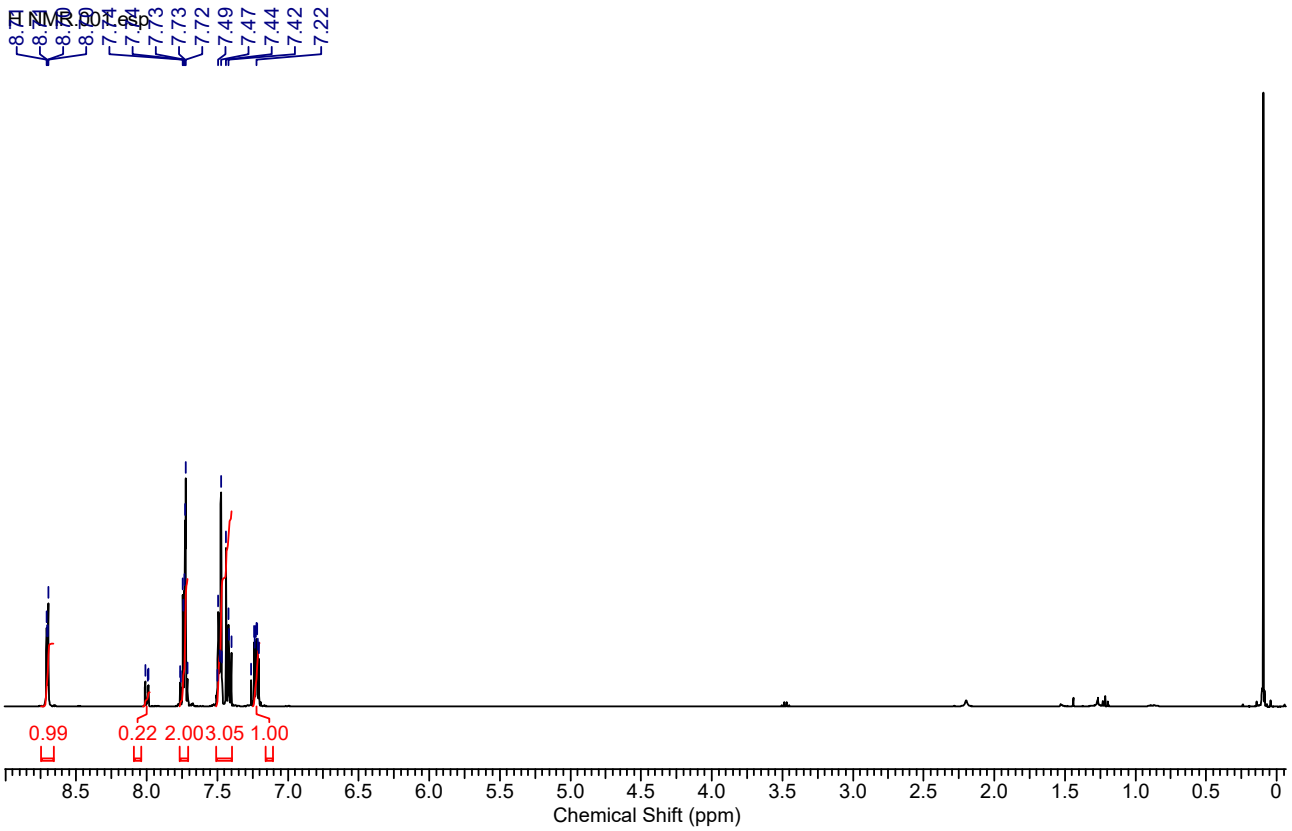


Labelling of 2-Phenylpyridine 29

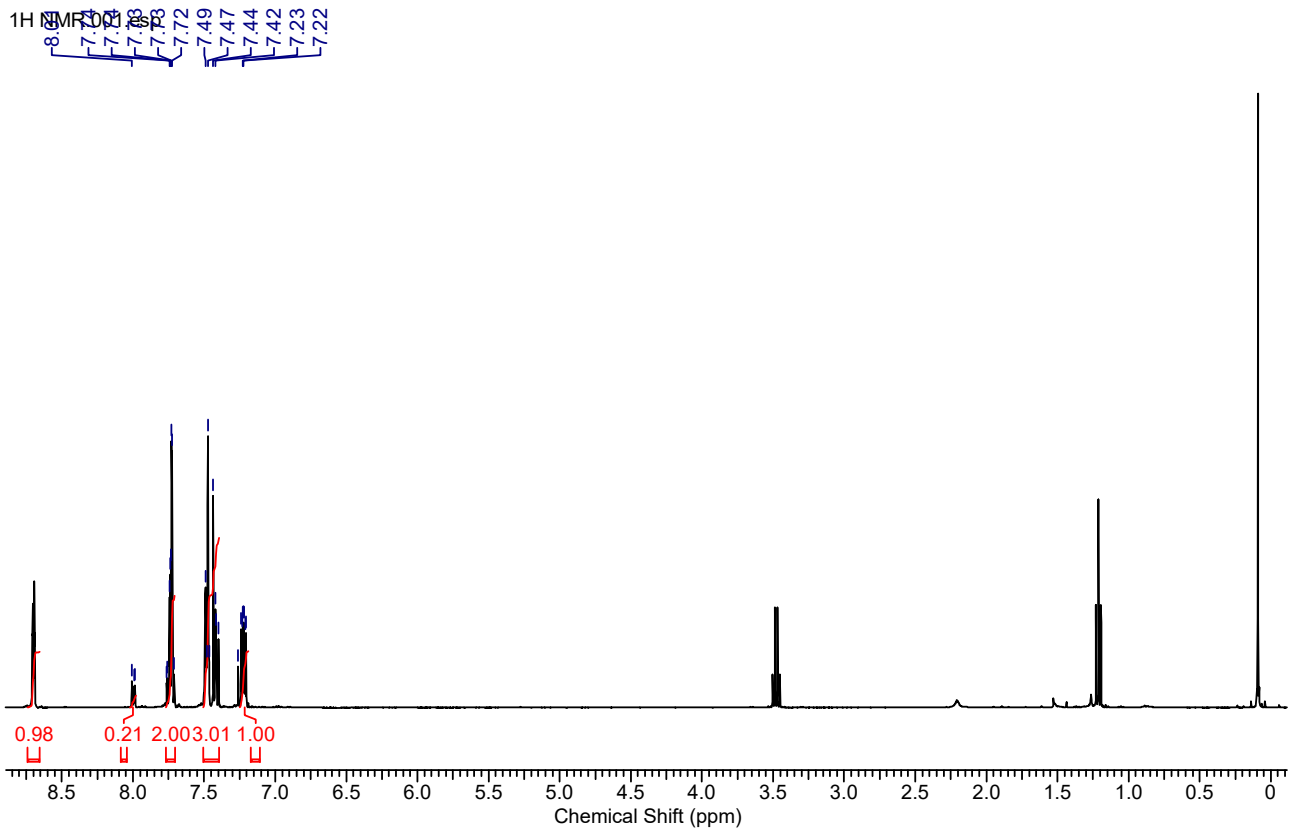
With Catalyst **6a**, 82%D



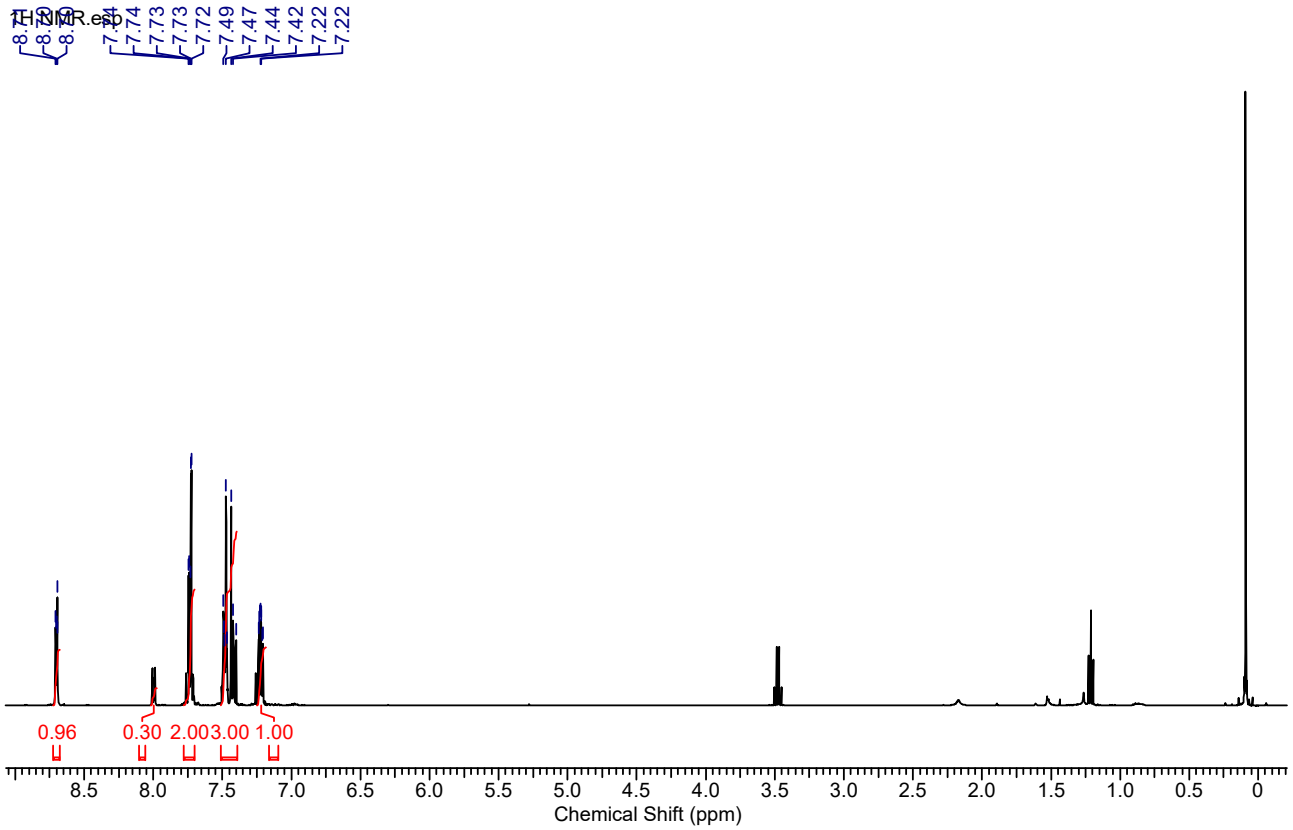
With Catalyst **6b**, 89%D



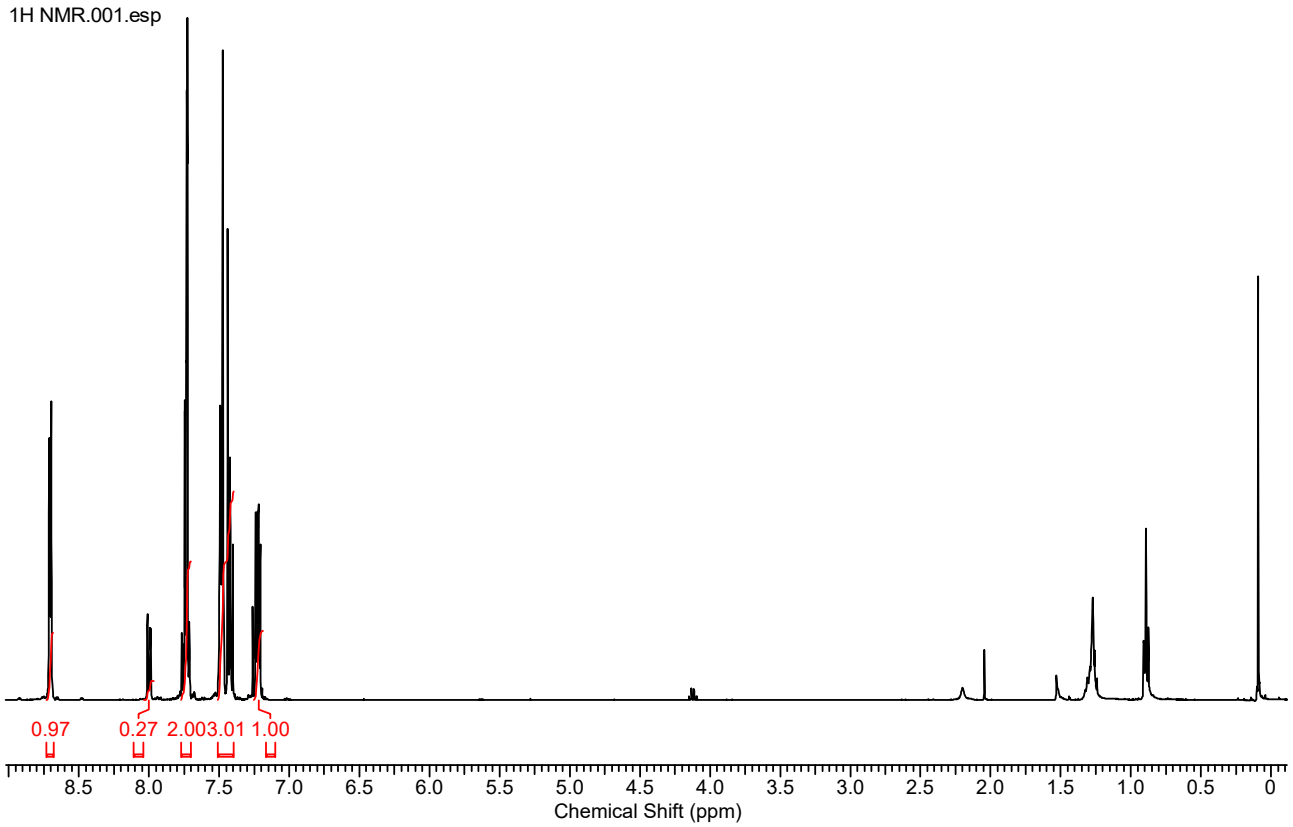
With Catalyst **6c**, 90%D



With Catalyst **6d**, 85%D

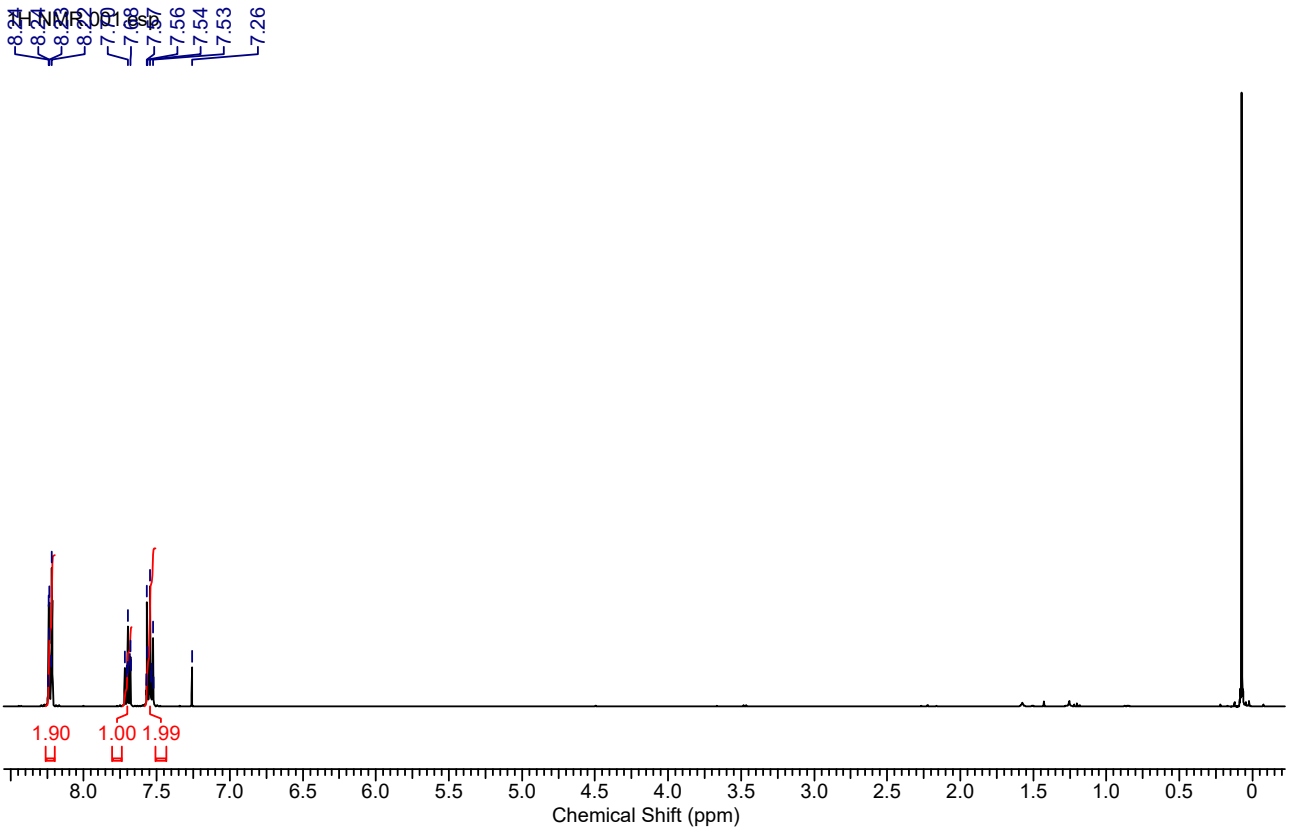


With Catalyst **6e**, 87%D

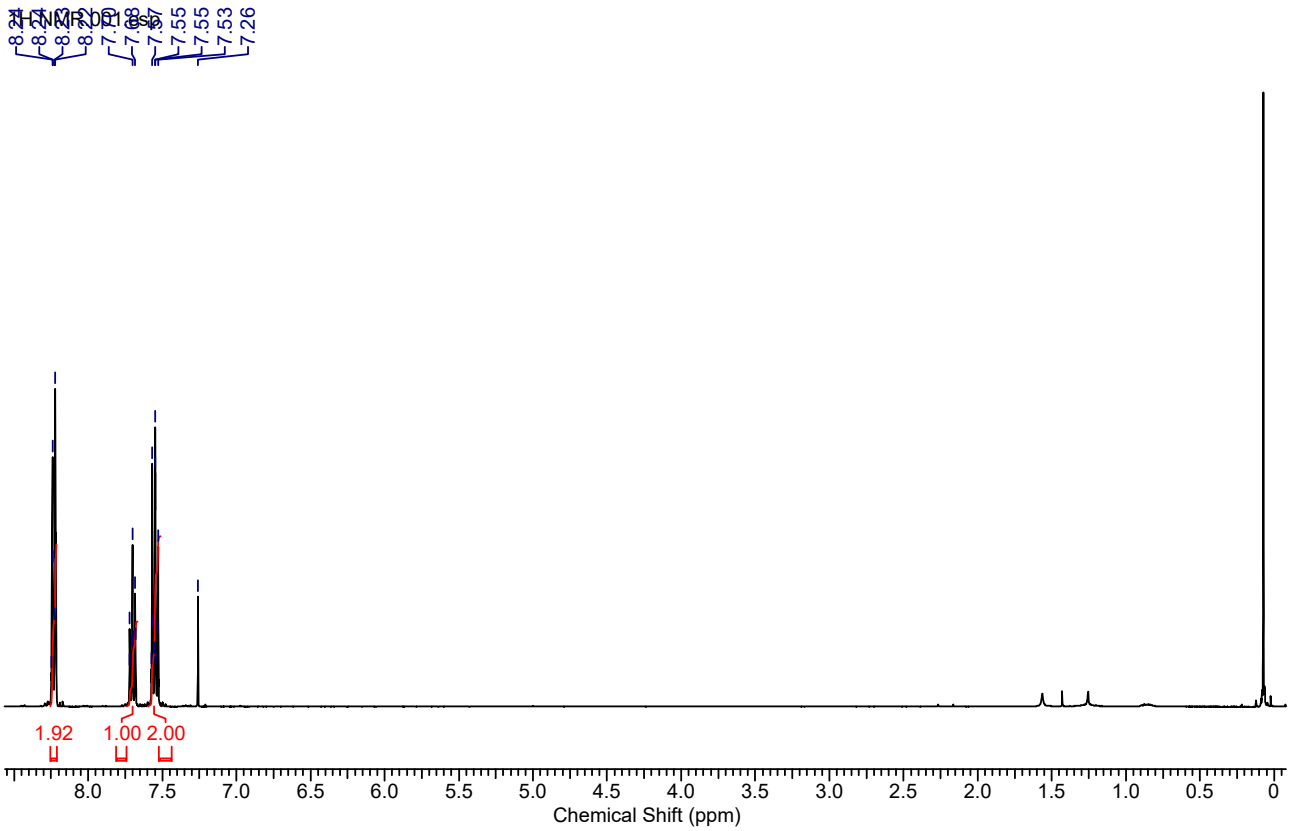


Labelling of Nitrobenzene 30

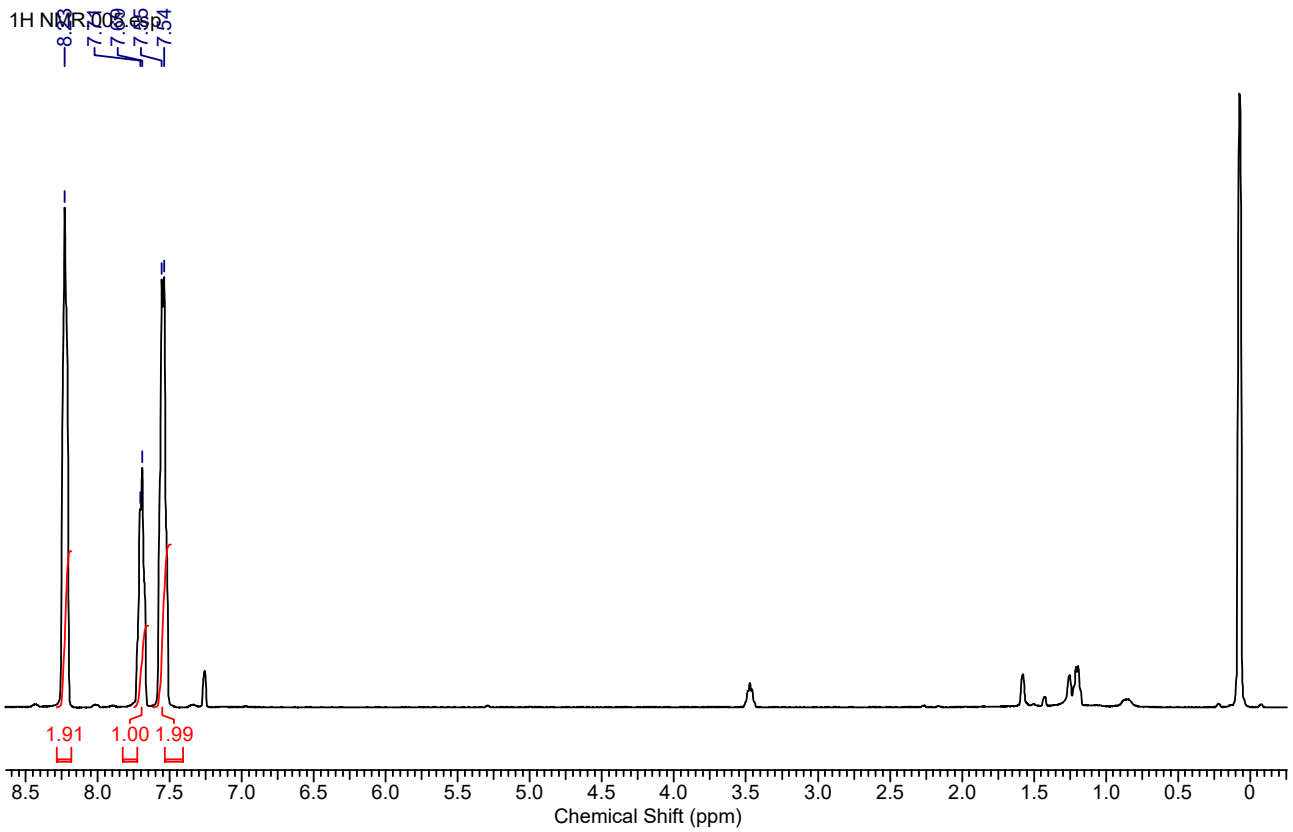
With Catalyst **6a**, 5%D



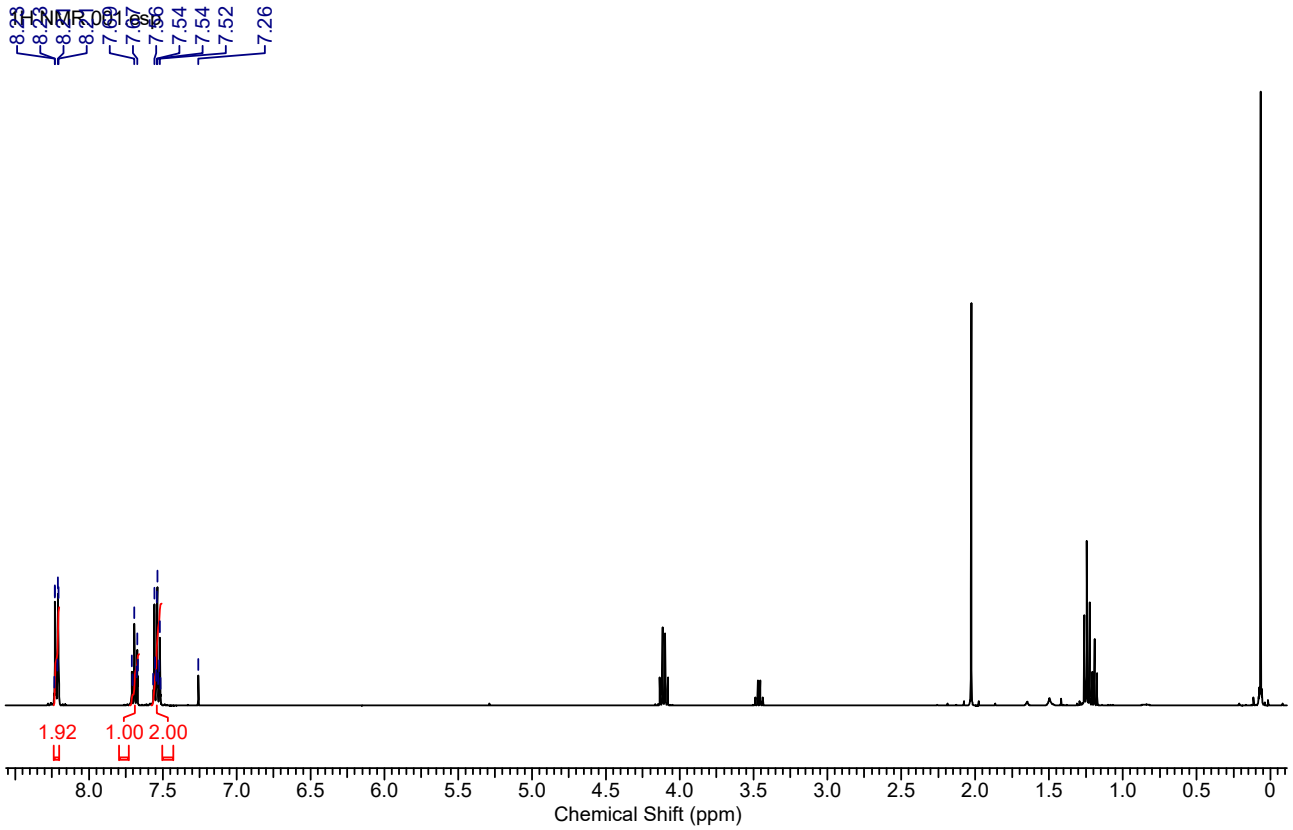
With Catalyst **6b**, 4%D



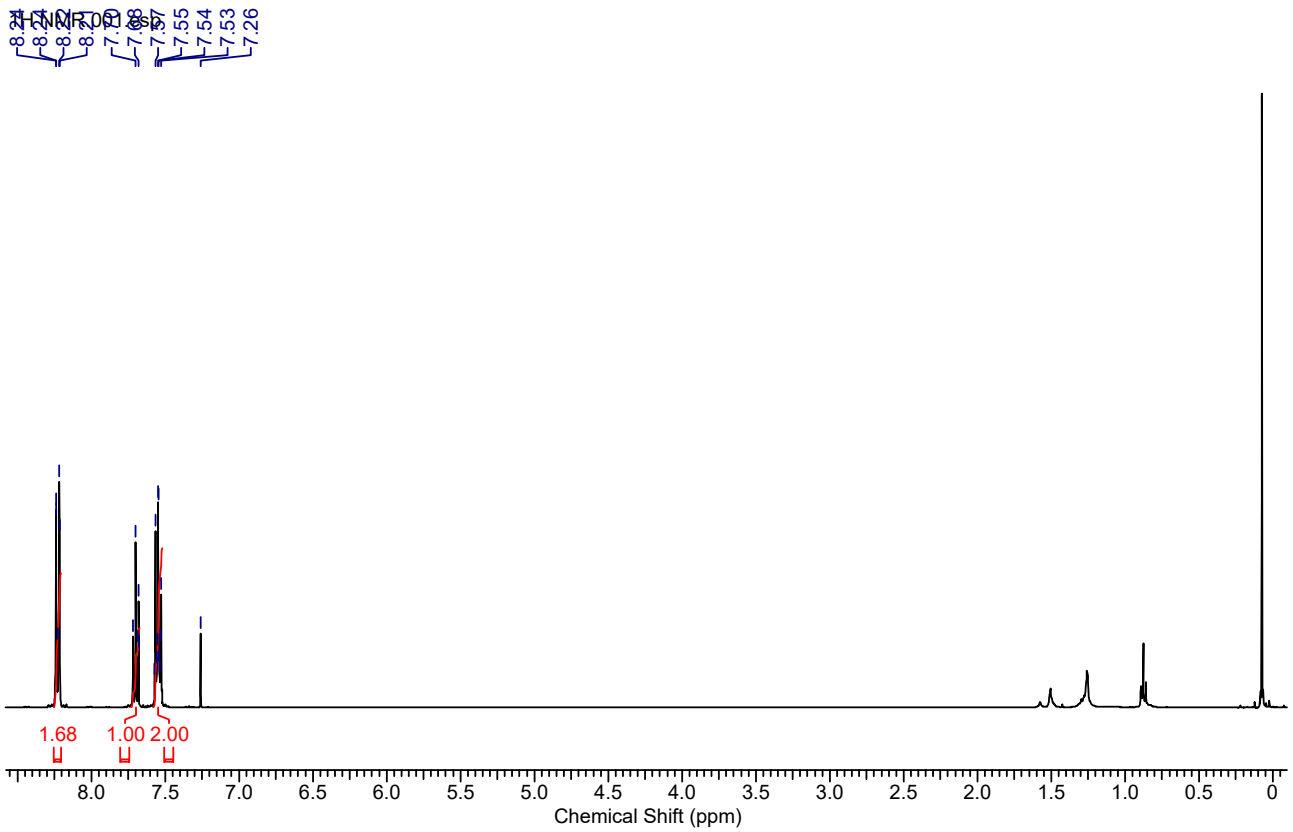
With Catalyst **6c**, 5%D



With Catalyst **6d**, 4%D



With Catalyst **6e**, 16%D



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