Supplementary Information for

Synthesis and Full Characterization of an Iridium B–H Activation Intermediate of the Monocarba-*closo*-dodecaborate Anion

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I General Information

Chemicals

If not otherwise specified, reagents and organic solvents were commercially available and used without further purification. Acetone-d_6 and acetonitrile-d_3 were purchased from Cambridge Isotope Laboratories and filtered through Al_2O_3 prior to use. $[Me_3NH][CB_{11}H_{12}]$ (starting material) and $[IrCp^*(OAc)_2]$ (for preparation of iridium complex **2**) were prepared according to the literature [1–3]. Anhydrous solvents were prepared by passage through activated Al_2O_3 and stored over 3 Å molecular sieves.

Reaction Conditions

Glassware for air-sensitive reations was dried at 150 °C for at least 12 h and allowed to cool in a vacuum.

The iridium complex **2** was prepared in a glovebox under a nitrogen atmosphere with O_2, H_2O < 1 ppm.

Characterization

Thin-layer chromatography (TLC) was carried out using silica gel 60, F254 with a thickness of 0.25 mm. Column chromatography was performed on silica gel 60 (200-30 mesh).

NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (^{1}H NMR 500.13 MHz, ^{13}C NMR 125.77 MHz, ^{11}B NMR 160.46 MHz) or a Bruker AVANCE III 400 spectrometer (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.62 MHz, ^{11}B NMR 128.38 MHz) at 23 °C. Data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation. Signals were referenced against solvent peaks (^{1}H: residual $CHCl_3$ = 7.26 ppm, residual $CHD_2C(O)CD_3$ = 2.05 ppm, residual CHD_2CN = 1.94 ppm, $^{13}C\{^1H\}$: $CDCl_3$ = 77.00 ppm $CD_3C(O)CD_3$ = 29.84 ppm, CD_3CN = 1.32 ppm). ^{11}B and $^{11}B\{^1H\}$ NMR spectra were calibrated against external BF_3*Et_2O = 0 ppm (BF_3*Et_2O capillary in C_6D_6).

^{11}B-^{11}B COSY NMR spectra were recorded at 160 MHz (500 MHz for ^{1}H) under ^{1}H decoupling for all new compounds. For iridium complex **2**, clear $^1J_{B\text{-}B}$ correlation signals could not be found for all B–B connections. A detailed study by Grimes addressed this phenomenon,[6] and an explanatory summary is given in the following.

The detection of cross peaks requires that several criteria be fulfilled: (a) Sufficient electron density must exist directly between the respective boron atoms; (b) the relaxation times T_1 and T_2 relaxation times must be long enough and (c) the individual ^{11}B resonances in the 1D spectrum are fully or at partially resolved. All of these conditions influence scalar coupling and heavily depend on the number, nature and position of the cage substituents. They cannot be changed by the measurement parameters, except for (c) where recording data at a higher field is beneficial.

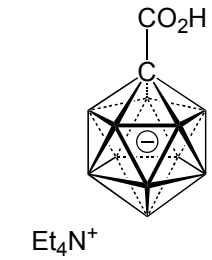
Low-resolution ESI-MS data were recorded on Advion Expression CMS instrument. High-resolution MS data were recorded using IT-TOF detection (Shimadzu, Japan) equipped with an electrospray ionization source (ESI). Accurate mass determination was corrected by calibration using sodium trifluoroacetate clusters as a reference.

IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer as KBr pellets or dry film and are reported as wavenumbers (ν, cm^{-1}).

Single-crystal X-ray diffraction studies were performed on an Oxford Diffraction Gemini A Ultra diffractometer equipped with an 135mm Atlas CCD detector and using Mo K-α radiation.

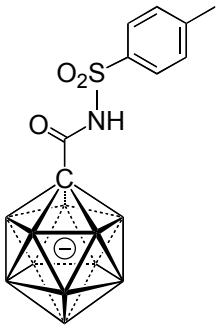
Elemental analysis: Satisfactory results were obtained for **1** and **2**. For **3**, N and H values were satisfactory, but for C the measured value was too low (52.54% *vs* calc. 55.51%). Other groups have observed discrepancies between calculated and found values for certain boron cage compounds as well, see: J. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, L. M. Rendina, P. J. Low, L. Weber, M. A. Fox, Dalton Trans. 2015, 44, 9766–9781; E. Justus, K. Rischka, J. F. Wishart, K. Werner, D. Gabel, Chem. Eur. J. 2008, 14, 1918–1923 and references cited therein. There seem to be two issues: (1) An inherent complication is the formation of boron carbide and boron nitride species during combustion, which can also depend on the presence of other elements; (2) The results depend on the laboratory/instrumentation where the analysis is performed, which again may be the result of incomplete combustion even at high temperatures.

II Experimental Section



Carborane carboxylic acid $[Et_4N][1\text{-}COOH\text{-}CB_{11}H_{11}]$ was synthesized by a modified literature procedure.[4,5] A dry 50 mL round bottom flask equipped with magnetic stir bar was charged with $[Me_3NH][CB_{11}H_{12}]$ (250 mg, 1.23 mmol) and capped with a rubber septum. Anhydrous THF (15 mL) was then added to the flask and the resulting solution cooled to 0 °C in an ice bath. A solution of 1.6 M n-BuLi in hexane (2.3 mL, 3.69 mmol) was slowly added to the reaction flask. After 1 h of stirring at 0 °C, aslightly turbid, yellowish solution was obtained. Dry CO_2 gas was then bubbled through the mixture at 0 °C (2-3 bubbles/s) for 5 h. Water (2 mL) was slowly added and the solution was concentrated on a rotary evaporator, the residue was dissolved in water, washed with diethyl ether (under these basic conditions the dianionic product was in the water layer), the aqueous phase was acidified with 1 M HCl (pH = 2) and extracted with diethyl ether (3 x 20 mL). The combined organic extracts were evaporated under reduced pressure, the crude product was dissolved in water (10 mL) and filtered through a glass frit. $[Et_4N]^+ Br^-$ (400 mg, 1.9 mmol) was added to the filtrate, and the resulting white precipitate was collected in a glass frit and dried in a vacuum to give salt $[Et_4N][1\text{-}COOH\text{-}CB_{11}H_{11}]$ (320 mg, 82%) as a colorless solid.

$^1H\{^{11}B\}$ NMR (500 MHz, acetone-d_6, 23 °C): δ 3.46 (q, J = 7.3 Hz, 8H, CH_2 of cation), 2.30-1.10 (broad m, 11H, BH), 1.38 (tt, J = 7.3Hz, 1.9 Hz, 12H, CH_3 of cation).
^{11}B NMR (160 MHz, acetone-d_6, 23 °C): δ -6.32 (d, J = 135.8 Hz, 1B), -13.09 (d, J = 135.2 Hz, 5B), -13.95 (d, J = 148.5 Hz, 5B).
$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6, 23 °C): δ -6.32 (1B), -13.09 (5B), -13.95 (5B).
$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6, 23 °C): δ 168.17 (CO), 68.52 (cage C), 52.96 (CH_2 of cation), 7.62 (CH_3 of cation).



Compound 1: To a stirred suspension of salt $[Et_4N][1\text{-}COOH\text{-}CB_{11}H_{11}]$ (300 mg, 0.95 mmol) in dry CH_2Cl_2 (7 mL) were added dimethylformamide (ca. 5 drops) and oxalyl chloride (0.084 mL, 0.98 mmol). The reaction mixture was allowed to stir for 30 min at room temperature. All volatile components were then removed in *vacuo* and the residue was dissolved in dry THF (12 mL), *p*-toluene sulfonamide (163 mg, 0.95 mmol), triethylamine (0.277 mL, 2 mmol), and DMAP (1.5 mg, 0.012 mmol) were added and the resulting mixture was stirred at room temperature for 24 h. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, eluent dichloromethane/acetonitrile 5:1 *v/v*) to afford **1** (322 mg, 72%) as a colorless solid.

$^1H\{^{11}B\}$ NMR (500 MHz, acetonitrile-d_3, 23 °C): δ 8.65 (s, 1H, NH), 7.81 (d, J = 8.3 Hz, 2H, ArH), 7.39 (d, J = 8.3 Hz, 2H, ArH), 3.16 (q, J = 7.3 Hz, 8H, CH_2 of cation), 2.43 (s, 3H, $ArCH_3$), 1.93-1.25 (overlapping m, 11H, BH), 1.21 (tt, J = 7.3 Hz, 1.8 Hz, 12H, CH_3 of cation).

$^{13}C\{^1H\}$ NMR (101 MHz, acetonitrile-d_3, 19 °C): δ 164.29 (CO), 146.40, 136.51, 130.55, 129.03, 70.03 (cage C), 53.05 (CH_2 of cation), 21.67 ($ArCH_3$), 7.66 (CH_3 of cation).

^{11}B NMR (160 MHz, acetonitrile-d_3, 23 °C): δ -6.11 (d, J = 138 Hz, 1B), -12.95 (d, J = 140 Hz, 5B), -14.59 (d, J = 155 Hz, 5B).

$^{11}B\{^1H\}$NMR (160 MHz, acetonitrile-d_3, 23 °C): δ -6.11, -12.95, -14.59.

HRMS (ESI): *m/z* Calcd. for $[C_9H_{19}B_{11}NO_3S]^-$, 340.2188; found, 340.2171.

IR (KBr): 3291, 2995, 2543, 1712, 1597, 1484, 1398, 1344, 1186, 1166, 1089, 1025, 875, 658, 552, 542.

M.p.: 146–147 °C.

Elemental analysis: Calc. for $C_{17}H_{39}B_{11}N_2O_3S$: C 43.40%, H 8.36%, N 5.95%; found: C 43.47%, H 8.35%, N 5.72%.

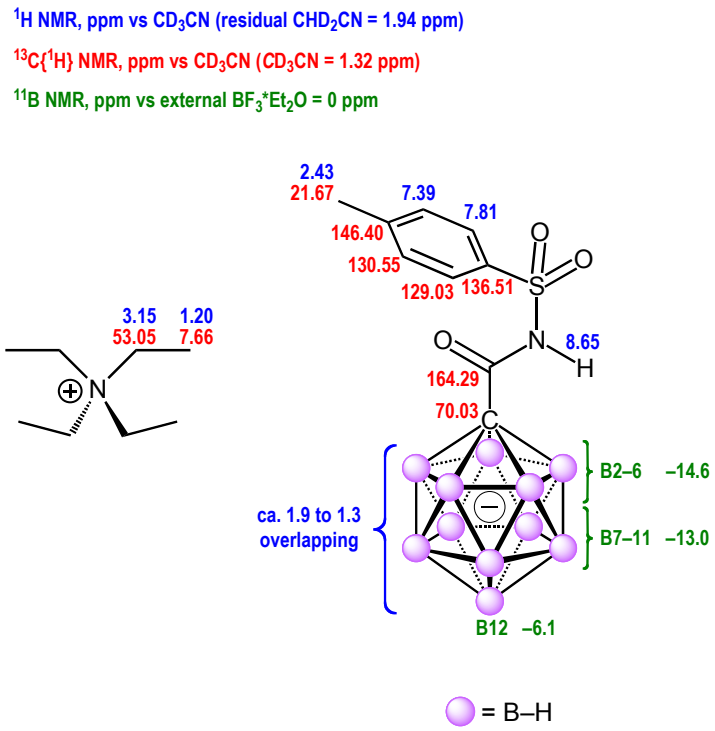
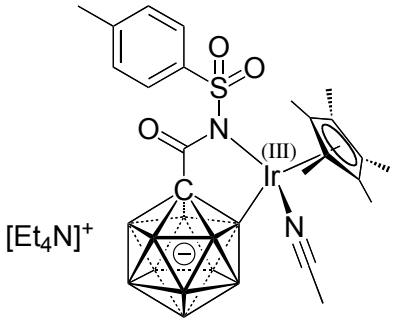


Figure S1 Summary of NMR data for **1** (^{1}H and ^{13}C assignments were made based on HSQC and HMBC spectra)



Compound 2: In a glovebox, IrCp*(OAc)2 (23 mg, 0.052 mmol) was added to a stirred solution of tosyl amide **1** (24 mg, 0.051 mmol) in acetonitrile (0.2 mL). The resulting mixture was stirred at 25 °C for 5 h. The yellow precipitate formed was filtered through a fine glass frit and washed with hexane. The filtrate was left to evaporate slowly at room temperature (evaporation of *ca.* 50% of the solvent) to yield yellow crystals, which were collected by filtration. The combined solids were dried at 25 °C in a vacuum to give iridium complex **2** (34 mg, 80%).

$^{1}H\{^{11}B\}$ NMR (500 MHz, acetonitrile-d_3, 23 °C): δ 7.58 (d, J = 8.1 Hz, 2H, ArH), 7.21 (d, J = 8.1 Hz, 2H, ArH), 3.15 (q, J = 7.3 Hz, 8H, CH_2 of cation), 2.36 (s, 3H, $ArCH_3$), *ca.* 1.9-1.2 (overlapping m, 10H, BH), 1.72 (s, 15H, CH_3 of Cp*), 1.20 (tt, J = 7.3 Hz, 1.6 Hz, 12H, CH_3 of cation).

$^{13}C\{^{1}H\}$ NMR (126 MHz, acetonitrile-d_3, 23 °C): δ 179.58 (CO), 142.03, 141.99, 129.13, 128.44, 90.85 (Cp* ring C), 76.06 (cage C), 53.05 (CH_2 of cation), 21.40 ($ArCH_3$), 9.94 (Cp* CH_3), 7.68 (CH_3 of cation).

^{11}B NMR (160 MHz, acetonitrile-d_3, 23 °C): δ -7.61 (d, J = 133 Hz, 1B), *ca.* -10.2 to -14.7 (overlapping signals, 8B), *ca.* -14.7 to -17.2 (overlapping signals, 2B).

$^{11}B\{^{1}H\}$NMR (160 MHz, acetonitrile-d_3, 23 °C): δ -7.61 (1B), *ca.* -10.8 to -14.5 (overlapping signals, 8B), *ca.* -14.9 to -17.4 (overlapping signals, 2B).

HRMS (ESI): *m/z* Calcd. for $[C_{19}H_{32}B_{11}NIrO_3S]^-$, 666.2824; found, 666.2825.

IR (KBr): 2922, 2531, 1995, 1314, 1156, 1084, 1024, 897, 669, 552.

M.p.: Decomposition at *ca.* 125 °C.

Elemental analysis: Calc. for $C_{29}H_{55}B_{11}IrN_3O_3S$: C 41.62%, H 6.62%, N 5.02%; found: C 41.89%, H 6.65%, N 5.52%.

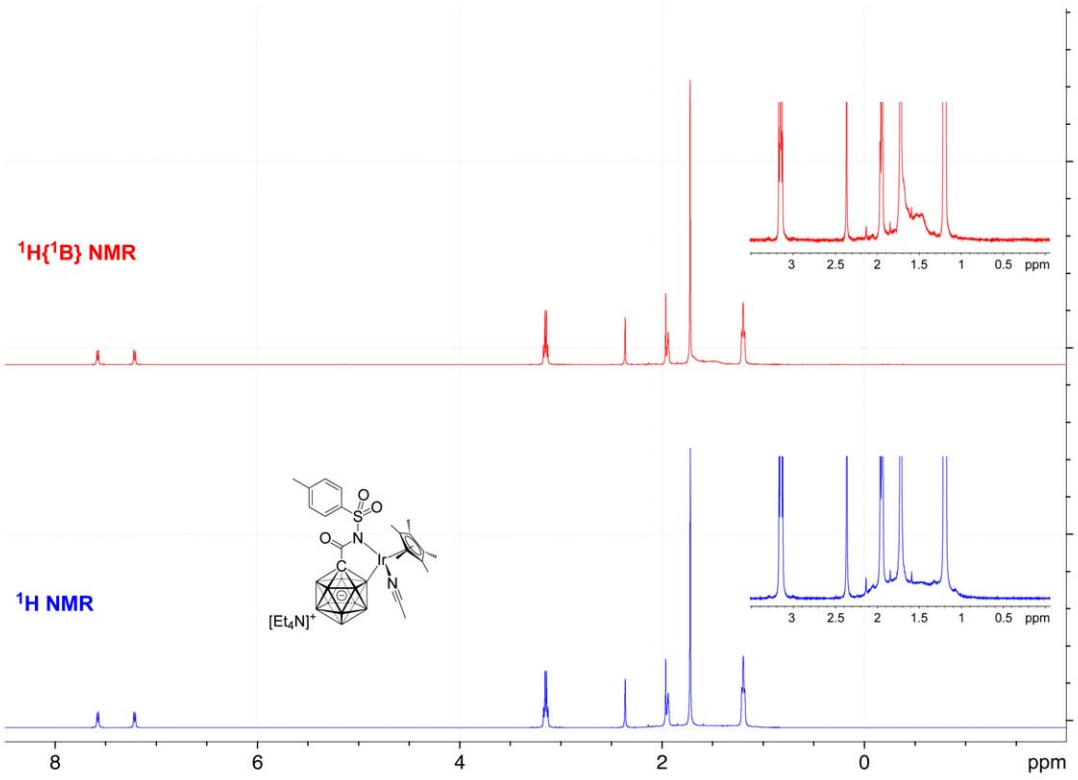


Figure S2. Comparison of ^{1}H and ^{1}H{^{11}B} NMR spectra of **2** showing only a slight increase in resolution of the B–H resonances upon decoupling from ^{11}B. Conditions: 500 MHz, 8 mg in 0.6 mL CD_3CN, 23 °C.

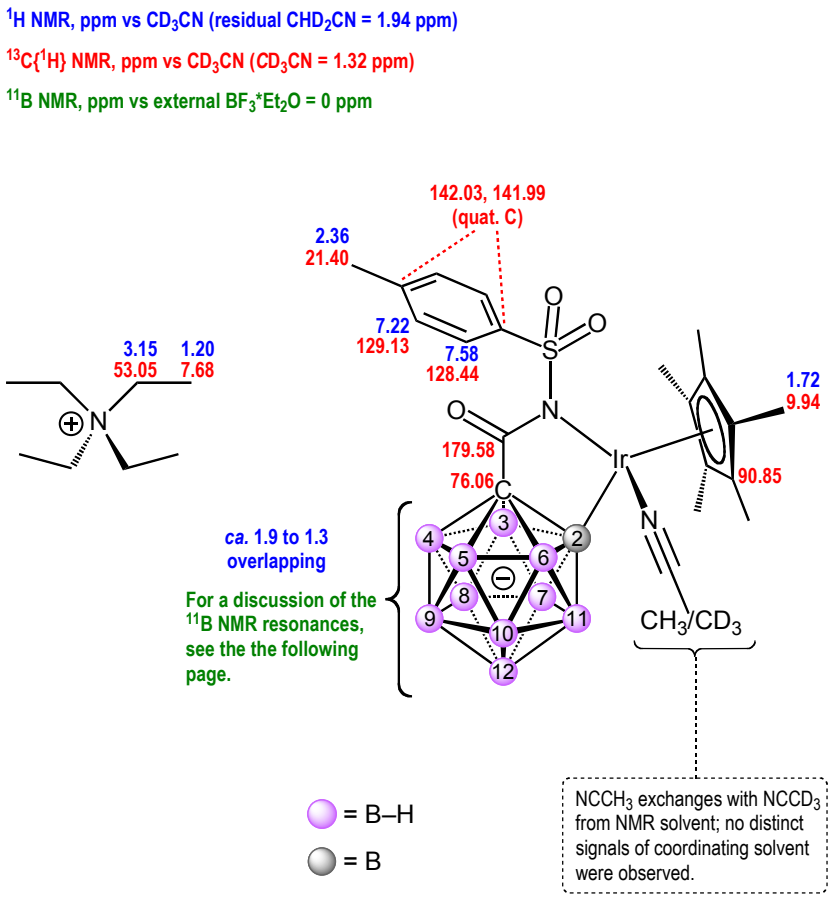


Figure S3 Summary of NMR data for **2** (^{1}H and ^{13}C assignments were made based on HSQC and HMBC spectra).

Assignment of the ^{11}B NMR signals of 2:

The ^{11}B and ^{11}B{^{1}H} NMR spectra of **2** showed signals in the region of –7.5 to –17 ppm; no other peaks were detected in the range of +180 to –80 ppm (Figure S1and pp. NMR8–NMR10). Three groups of signals with relative integration 1, 8 and 2 were consistent with 11 boron vertices, including B2–Ir, which is the only B atom not bound to H. Based on a comparison of the ^{11}B and ^{11}B{^{1}H} spectra, the most deshielded signal stems from a single B–H vertex. Assuming time-averaged C_s symmetry of **2** due to solvent exchange, B3 and B6 / B4 and B5 / B7 and B11 / B8 and B10 are related by a plane of symmetry, giving rise to a total integration of 8. Only three vertices are expected to exhibit an integration of 1, namely B2, B9 and B12. The set with integration 2 appears to be an overlap of a doublet and a singlet at –15.7 and –16.2 ppm, respectively. Thus, the most shielded signal is attributed to B2–Ir. The ^{11}B-^{11}B COSY spectrum showed weak but detectable ^{1}J correlations; see pp. S2/3 for an explanation why in certain ^{11}B-^{11}B COSY spectra the cross signals are of low intensity. Specifically, a correlation between the signals at –7.6 and –15.7 ppm is observed. Provided that for compounds **1**, **3**, the parent carborane $[CB_{11}H_{12}]^-$ and also many derivatives $[R\text{-}CB_{11}H_{11}]^-$ the B12 position is much more deshielded than B9, the following assignment is made:

–7.6 ppm B12; –10.2 to –14.7 ppm B3,4,5,6,7,8,10,11; –15.7 ppm B9; –16.2 ppm B2.

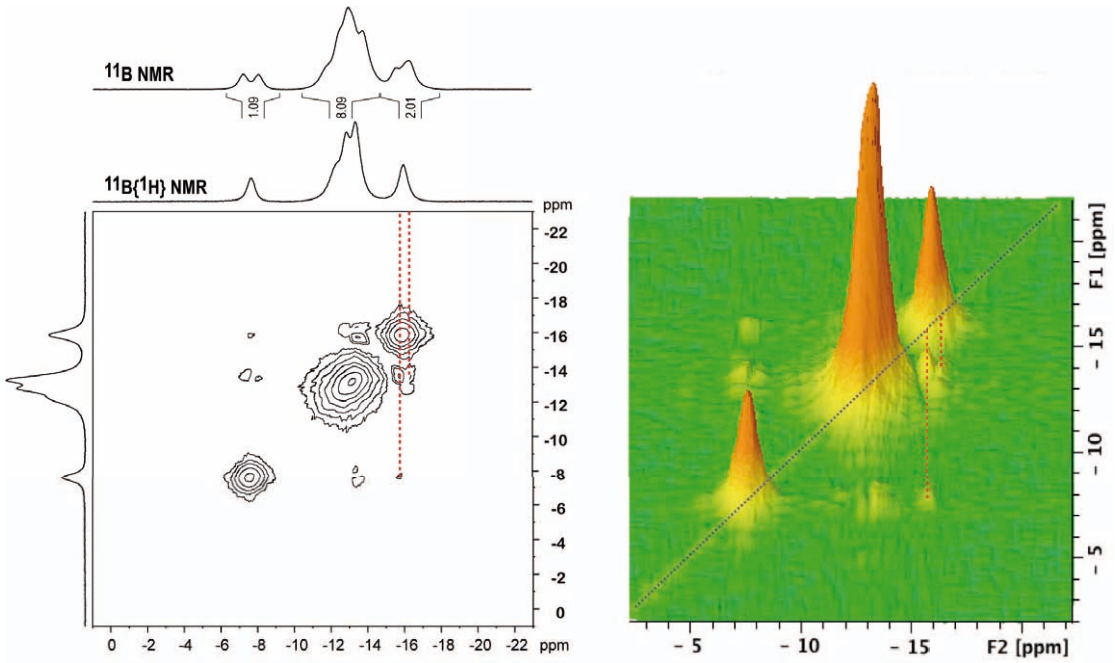
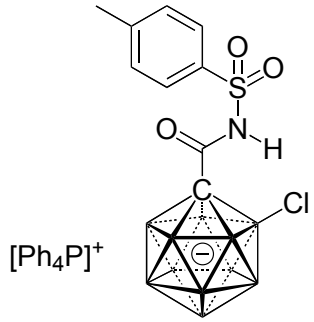


Figure S4. ^{11}B, ^{11}B{^{1}H} and ^{11}B-^{11}B COSY NMR spectra of **2** (160 MHz for ^{11}B). The colored plot is a 3D representation of the data of the black-and-white contour plot. The ^{11}B-^{11}B COSY measurement was carried out under decoupling from ^{1}H.



Compound 3: *N*-Chlorosuccinimide (3.8 mg, 0.028 mmol) was added to a stirred solution of the intermediate **2** (24 mg, 0.028 mmol) in acetonitrile (0.6 mL) at 25 °C. After stirring under N_2 for 1 h, the solvent was evaporated by rotary evaporation, and Et_2O (20 mL) and aq. HCl (2 N, 15 mL) were added. The layers were separated, and the aqueous portion was extracted with Et_2O (3 x 10 mL). The combined organic extracts were concentrated under reduced pressure, and the residue was treated with aq. Ph_4PBr solution (12 mg in 4 mL H_2O, 0.028 mmol).* The resulting precipitate was collected by filtration through a glass frit and purified by column chromatography (silica gel, eluent dichloromethane) to afford product **3** (14.0 mg, 0.020 mmol, 68%) as a colorless solid. **Note:* Without cation exchange at this point, column chromatography afforded pure monochlorinated carborane anion in comparable yield; however, NMR analysis indicated that there was a mixture of two cations, namely $[Et_4N]^+$ and $[IrCp^*(solvent)_3]^{2+}$ (solvent from aqueous workup = H_2O).

$^1H\{^{11}B\}$ NMR (500 MHz, acetonitrile-d_3, 23 °C): δ 8.76 (s, 1H, NH), 7.96-7.88 (m, 4 H, ArH of cation), 7.83 (d, J = 8.2 Hz, 2H, ArH), 7.78-7.64 (overlapping m, 16H, ArH of cation), 7.38 (d, J = 8.2 Hz, 2H, ArH), 2.42 (s, 3H, $ArCH_3$), 2.04-1.31 (overlapping m, 10H, BH).

$^{13}C\{^1H\}$ NMR (126 MHz, acetonitrile-d_3, 23 °C): δ 162.11 (CO), 146.48, 136.39 (two overlapping signals, one from tolyl ring and one from C_{para} of cation, as evident from spectrum on p. NMR13 and reference spectrum of Ph_4PBr on p. NMR15), 135.71 (d, J = 9.7 Hz, C_{meta} of cation), 131.33 (d, J = 12.6 Hz, C_{ortho} of cation), 119.29 (left half of C_{ipso} doublet of cation, as inferred from reference spectrum of Ph_4PBr on p. NMR15), 130.51, 129.25, 71.11 (cage C), 21.68 ($ArCH_3$).

δ ^{11}B NMR (160 MHz, acetonitrile-d_3, 23 °C): δ -4.45 (s, 1B), -5.90 (d, J = 137 Hz, 1B), *ca.* -10.2 to -16.0 (overlapping signals, 8 B), -17.16 (d, J = 142 Hz, 1B).

$^{11}B\{^1H\}$NMR (160 MHz, acetonitrile-d_3, 23 °C): δ -4.45 (1B), -5.90 (1B), -12.10 (2B), *ca.* -12.8 to -15.4 (overlapping signals, 6 B), -17.16 (1B).

HRMS (ESI): *m/z* Calcd. for $[C_9H_{18}B_{11}ClNO_3S]^-$, 374.1802; found, 374.1824.

M.p.: 148–150 °C.

Elemental analysis: Calc. for $C_{33}H_{38}B_{11}ClNO_3PS$: C 55.51%, H 5.36%, N 1.96%; found: C 52.54%, H 4.99%, N 1.99%.

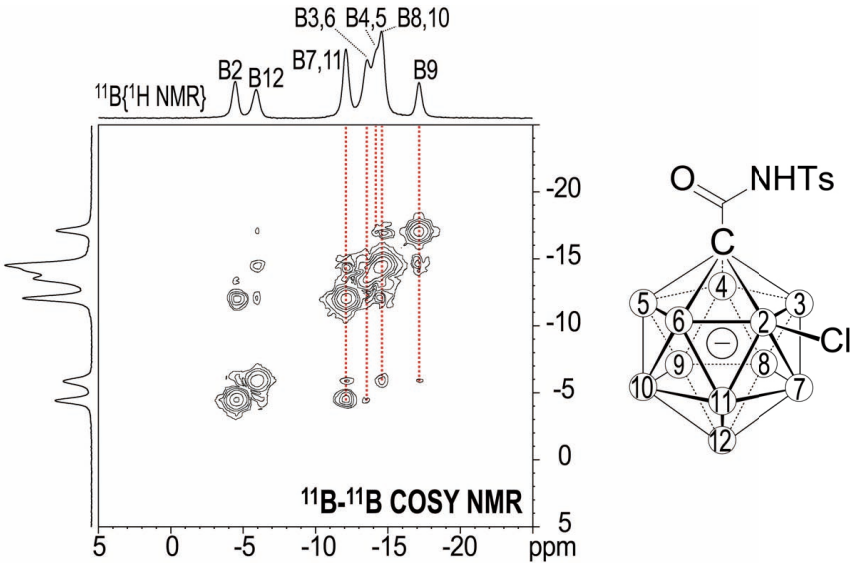


Figure S5 ^{11}B-^{11}B COSY NMR spectrum of monochloro tosyl amide **3** with key correlations indicated in red (160 MHz for ^{11}B, with decoupling from ^{1}H).

The assignments of the signals is in also in agreement with the reported ^{11}B NMR shifts of $[2\text{-Cl-}CB_{11}H_{11}]^-$, which was obtained as a by-product in a study by Michl.[7]

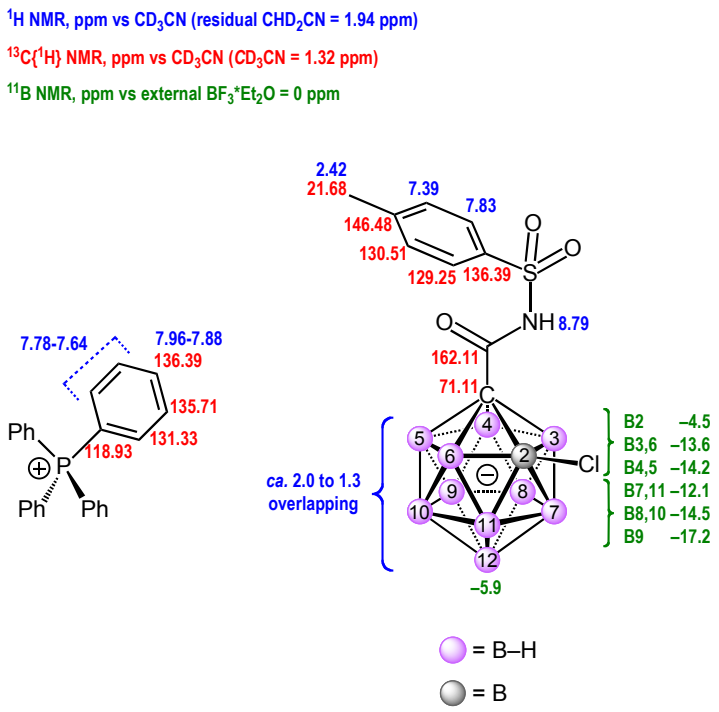
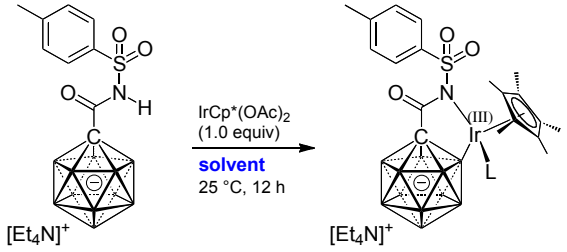


Figure S6 Summary of NMR data for **3** (^{1}H and ^{13}C assignments were made based on HSQC and HMBC spectra).

Formation of iridium complex 2 in solvents other than acetonitrile

Attempted formation of iridium complex **2** was also carried out in solvents other than acetonitrile. Specifically, DMSO-d_6, CH_2Cl_2 and 1,2-dichloroethane were tested. The reactions were carried out under conditions identical to those for the formation in acetonitrile, and the reaction mixtures were analyzed by $^1H\{^{11}B\}$ NMR spectroscopy and ESI-mass spectroscopy. Results were interpreted based on reference spectra of pure **1** and **2**. The results indicate that MeCN is not crucial for the B–H activation step and that acetate acts as the proton acceptor.

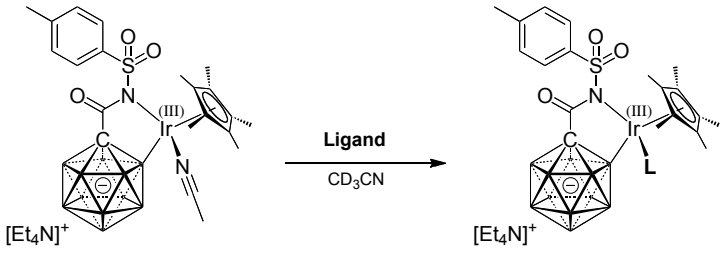


1 **2'** L = AcOH or solvent

Entry	Solvent	Result (NMR, ESI-MS)
1	DMSO-d_6	Disappearance of starting materials; formation of iridium complex. However, two sets of NMR signals observed, attributed to coordination by solvent or AcOH. In ESI-MS only detection of [Cp*Ir(carborane)]$^-$.
2	CH_2Cl_2	Disappearance of starting materials, clean formation of iridium complex. In ESI-MS only detection of [Cp*Ir(carborane)]$^-$.
3	1,2-dichloroethane	Disappearance of starting materials, clean formation of iridium complex. In ESI-MS only detection of [Cp*Ir(carborane)]$^-$.

Ligand exchange reactions of 2

Monochlorination showed substitution at the B2 vertex and formation of $[Cp^*Ir(solvent)_3]^{2+}$, *i.e.*, primarily reactivity of the cluster fragment. In order to probe the reactivity of the iridium center, ligand exchange reactions were performed. Reactions were carried out starting from isolated **2**, which was dissolved in acetonitrile-d_3 and treated with pyridine, PPh_3 or dppe (Ph_2P-$(CH_2)_2$-PPh_2), respectively. The reaction mixtures were analyzed by $^1H\{^{11}B\}$ (**4a–c)** and $^{31}P\{^1H\}$ (**4b**,**c**) NMR spectroscopy as well as ESI-mass spectroscopy. Results were interpreted based on NMR and mass reference spectra of **2** in acetonitrile-d_3. Pyridine cleanly replaced MeCN of **2**; PPh_3 lead to a partial displacement of MeCN; dppe cleanly replaced MeCN, acting as a monodentate ligand.



2 **4**

Entry	Conditions	Result (NMR, ESI-MS)	NMR spectra
1	**2** (5 mg), pyridine (1.6 equiv), 25 °C, 6 h	Replacement of MeCN ligand, clean formation of complex **4a**. In ESI-MS only detection of $[Cp^*Ir(carborane)]^-$.	NMR19
2	**2** (5 mg), PPh_3 (1.0 equiv), 25 °C/6 h, then 60 °C/12 h	Formation of **2** : **4b** in a 45 : 55 ratio; this ratio did not change upon heating to 60 °C and is interpreted as equilibrium ratio. In ESI-MS only detection of $[Cp^*Ir(carborane)]^-$.	NMR20, NMR21
3	**2** (5 mg), dppe (1.0 equiv), 25 °C/6 h, then 60 °C/12 h	Replacement of MeCN ligand, clean formation of complex **4c**. dppe is acts as a monodentate ligand, *i.e.*, one Ph_2P group is bound to Ir and the other is a free Ph2P group. In ESI-MS only detection of $[Cp^*Ir(carborane)]^-$.	NMR22, NMR23

References

[1] Plešek, J.; Jelínek, T.; Drdákova, E.; Hermánek, S.; Štibr, B.; *Collect. Czech. Chem. Commun.*, **1984**, *49*, 1559–1562.

[2] Reed, C. A. *Acc. Chem. Res*. **2010**, *43*, 121-128.

[3] Kim, H.; Shin, K.; Chang, S. *J . Am*. *Chem*. *Soc*. **2014**, *136*, 5904–5907.

[4] Valášek, M.; Štursa, J.; Pohl, R.; Michl, J. *Inorg*. *Chem*. **2010**, *49*, 10247–10254.

[5] Hailmann, M.; Konieczka, S. Z.; Himmelspach, A.; Löblein, J.; Reiss, G. J.; Finze, M. *Inorg. Chem*. **2014**, *53*, 9385–9399.

[6] Venable, T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29–37.

[7] Franken, A.; King, B. T.; Rudolph, J.; Rao, P.; Noll, B. C.; Michl, J. *Collect. Czech. Chem. Commun.* **2001**, *66*, 1238–1249.

III X-ray Crystallography

Crystal structure of 1

Compound **1** (10 mg) was dissolved in 3-butanone (1.0 mL) in a 4 mL glass vial to give a clear colorless solution. The 4 mL vial was left open and placed in a 20 mL glass vial containing hexane (4 mL). The 20 mL vial was sealed with a screw cap. Vapor diffusion afforded colorless crystals of the composition $[Et_4N][C_9H_{19}B_{11}NO_3S]$ suitable for X-ray diffraction within 2 d at 18 °C.

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=11.7040(8) b=18.1966(9) c=13.7408(7)
alpha=90 beta=105.421(7) gamma=90
Temperature: 170 K

	Calculated	Reported
Volume	2821.1(3)	2821.1(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C9 H19 B11 N O3 S, C8 H20 N	C9 H19 B11 N O3 S, C8 H20 N
Sum formula	C17 H39 B11 N2 O3 S	C17 H39 B11 N2 O3 S
Mr	470.47	470.47
Dx,g cm-3	1.108	1.108
Z	4	4
Mu (mm-1)	0.136	0.136
F000	1000.0	1000.0
F000'	1000.78	
h,k,lmax	14,21,16	14,21,16
Nref	5164	5136
Tmin,Tmax	0.941,0.968	0.976,1.000
Tmin'	0.941	

Correction method= # Reported T Limits: Tmin=0.976 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 25.350

R(reflections)= 0.0580(3565) wR2(reflections)= 0.1541(5136)

S = 1.021 Npar= 392

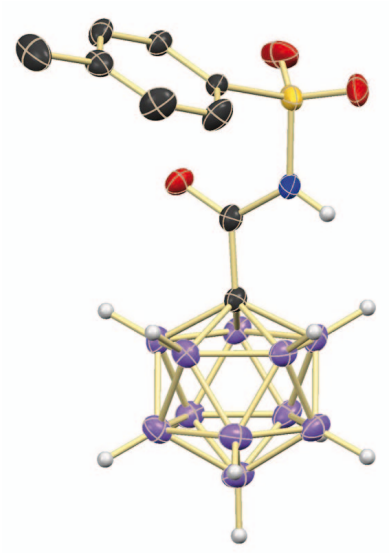


Figure S7. ORTEP representation of **1**. Cation and C-H hydrogen atoms are omitted for clarity; 25% displacement ellipsoids.

Crystal structure of 2

Compound **2** (10 mg) was dissolved in acetonitrile (0.5 mL) in a 2 mL glass vial. The resulting yellow solution was filtered into a 18 cm long NMR tube and layered with diethyl ether (1 mL). Yellow crystals of the composition $[Et_4N][C_{21}H_{35}B_{11}IrN_2O_3S]$ suitable for X-ray diffraction grew within 3 d at room temperature.

Bond precision: C-C = 0.0125 A **Wavelength=0.71073**

Cell:	a=31.5995(15)	b=11.8627(4)	c=22.3097(8)
	alpha=90	beta=107.086(5)	gamma=90
Temperature:	293 K		

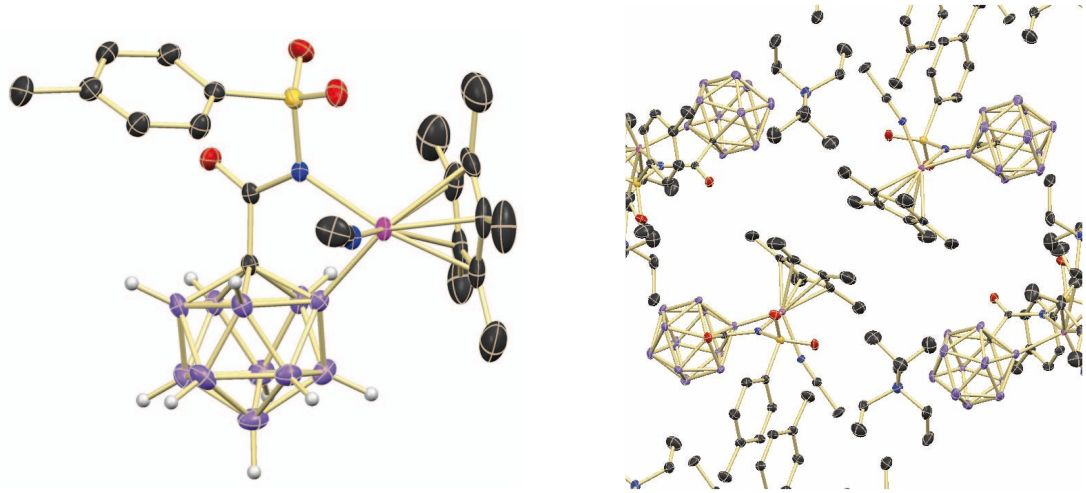
	Calculated	Reported
Volume	7993.8(6)	7993.8(6)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C21 H35 B11 Ir N2 O3 S, C8 H20 N	C21 H35 B11 Ir N2 O3 S, C8 H20 N
Sum formula	C29 H55 B11 Ir N3 O3 S	C29 H55 B11 Ir N3 O3 S
Mr	836.95	836.93
Dx,g cm-3	1.391	1.391
Z	8	8
Mu (mm-1)	3.426	3.426
F000	3376.0	3376.0
F000′	3366.50	
h,k,lmax	38,14,26	38,14,26
Nref	7328	7312
Tmin,Tmax	0.303,0.455	0.498,1.000
Tmin′	0.228	

Correction method= MULTI-SCAN

Data completeness= 0.998 **Theta(max)= 25.350**

R(reflections)= 0.0393(5890) **wR2(reflections)= 0.1095(7312)**

S = 1.050 **Npar= 444**



a) b)

Figure S8. a) ORTEP representation of **2**. Cation and C-H hydrogen atoms are omitted for clarity; 25% displacement ellipsoids. b) Packing of **2** indicating that the Cp* ligand can rotate about the Ir–centroid(Cp*) axis with a small activation energy. This leads to relatively large differences in anisotropic displacement parameters. Hydrogen atomes are omitted for clarity; 25% displacement ellipsoids.

IV Computational details

Computed structure and property results were carried out using both and GAMESS [1] and Gaussian09 [2] (for NMR) software packages. The B97-D density functional methods [3] with an army-grade grid was used in combination with the Def2-TZVPD basis set [4] in acetonitrile environment for all geometry optimizations and Hessian analyses. ^{1}H, ^{13}C, and ^{11}B chemical shielding tensor data was determined using the CSGT method [5,6] at the B97-D/Def2-QZVPPD[4]//B97-D/Def2-TZVPD level in acetonitrile environment, and data referenced using a calibration method [7] based on the following reference set that spans the respective NMR range: (^{13}C and ^{1}H): TMS, CH_4, C_2H_6, C_2H_2, C_2H_4, C_6H_6, $CH_3C(O)CH_3$, and ^{11}B: BH_3•NH_3, BH_3•$NHMe_2$, BH_3•NMe_3, BF_3•Et_2O, BH_3•Me_2O, B_2H_6, $B(OMe)_3$, BNpent, $B(CH=CH2)_3$, $BMe(CH=CH_2)_2$, $BMe_2CH=CH_2$, BMe_3. These sets were chosen as a representative set of systems with NMR signals that align with those of the experimental aggregates and complexes being studied. The resulting calibration formulas determined were: ^{13}C: -1.0609*x + 183.08 (goodness of the fit: $R^2 = 0.9983$), ^{1}H: -1.08*x + 31.35 (goodness of the fit: $R^2 = 1.00$), and ^{11}B: -0.9851*x + 102.12 (goodness of the fit: $R^2 = 0.99662$). Effects of solvent employed the COSab:*ab initio* continuum method. [5,6] Natural Bond Orbital (NBO) analysis [8] was carried out at the at the out at the B97-D/Def2-QZVPPD[4]//B97-D/Def2-TZVPD level in acetonitrile environment. Visualization and analysis of structural and property results were obtained using Avogadro, [9] WebMO [10] (NPA charges, electrophilic HOMO/LUMO maps), and Gaussview [11] (Molecular Orbitals).

References

[1] M. Schmidt, K. K. Baldridge, J. A. Boatz, S. Elbert, M. Gordon, J. H. Jenson, S. Koeski, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L.Windus, M. Dupuis, J. A. Montgomery, *J. Comp. Chem.* **1993,** *14*, 1347–1363.

[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomergy, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishido, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R.

Gomperts, R. E. Stratmann, O. Yazyev, J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Doannernberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. KFarkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. G. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challocombe, P. M. W. Gill., B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, in 'Gaussian03', Wallingford, 2009.

[3] S. Grimme, *J. Comput. Chem.* **2006,** *27*, 1787–1799.

[4] D. Rappoport, F. Furche, *J. Chem. Phys.* **2010**, *133*, 134105.

[5] A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* **1993**, *5*, 799–805.

[6] K. K. Baldridge, A. Klamt, *J. Chem. Phys.* **1997**, *106*, 6622–6633.

[7] K. K. Baldridge, J. S. Siegel, *J. Phys. Chem. A.* **1999**, *103*, 4038–4042.

[8] J. P. Foster, F. J. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.

[9] M. Hanwell, D. Curtis, D. Lonie, T. Vandermeersch, E. Zurek, G. Hutchison, *J. Cheminform*. **2012**, *4*, 17.

[10] J. R. Schmidt, W. F. Polik, WebMO Enterprise, version 13.0; WebMO LLC: Holland, MI, USA, 2013; http://www.webmo.net (accessed March, 2013).

[11] GaussView, **Version 5**, R. Dennington, T. Keith, J. Millam, *Semichem Inc.*, Shawnee Mission, KS, **2009**.

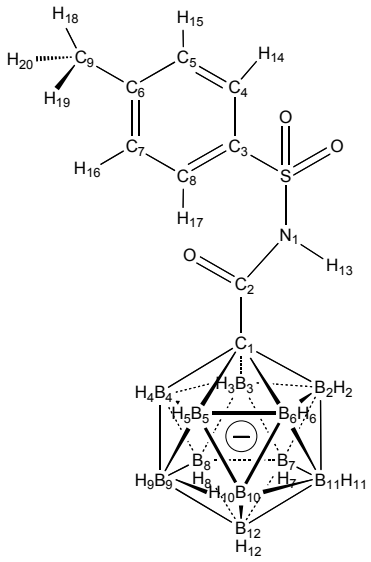


Figure S9 Numbering system for calculated *vs* experimental NMR shifts of compound **1**.

Table S1 Calculated B97-D/Def2-QZVPPD//B97-D/Def2-TZVPD *vs* experimental NMR shifts in acetonitrile of compound **1**.

Atom	**Calculated Signal (ppm)**	**Experimental Signal (ppm)**
C1	74.01	70.03
C2	168.35	164.29
C3	139.46	136.51
C4	130.46	129.03
C5	130.27	130.55
C6	152.36	146.40
C7	132.49	130.55
C8	128.13	129.03
C9	16.65	21.67
H2	-0.2912	1.3-1.9
H3	-0.4828	1.3-1.9
H4	-0.4822	1.3-1.9
H5	-1.0502	1.3-1.9
H6	-0.1695	1.3-1.9
H7	-0.7018	1.3-1.9
H8	-0.8030	1.3-1.9
H9	-0.8570	1.3-1.9
H10	-0.7664	1.3-1.9

H11	-0.7473	1.3-1.9
H12	-0.6047	1.3-1.9
H13	7.1189	8.65
H14	6.0597	7.81
H15	5.6258	7.39
H16	5.7687	7.39
H17	6.0393	7.81
H18	-0.0764	2.43
H19	0.3602	2.43
H20	0.3732	2.43
B2	-14.53	-14.59
B3	-12.30	-14.59
B4	-14.98	-14.59
B5	-12.66	-14.59
B6	-13.20	-14.59
	av. of calc. B2-B6: -13.53	
B7	-11.83	-12.95
B8	-12.64	-12.95
B9	-12.55	-12.95
B10	-11.97	-12.95
B11	-13.51	-12.95
	av. of calc. B2-B6: -12.50	
B12	-5.67	-6.11

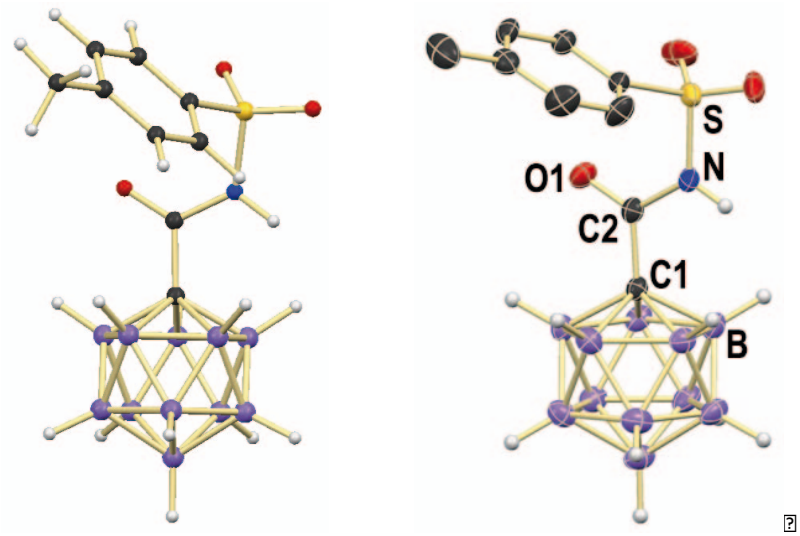


Figure S10 Calculated B97-D/Def2-TZVPD (left) and experimental X-ray crystal structure (right) of compound **1**.

Table S2 Calculated B97-D/Def2-TZVPD *vs* experimental X-ray structural parameters of compound **1**.

Parameter	**Calculated value**	**Experimental value**
C1-C2 (Å)	1.525	1.505
C2-O1 (Å)	1.220	1.206
C2-N (Å)	1.383	1.378
N-S (Å)	1.702	1.657
average of C1-B2 to C1-B6	1.733	1.714
sum of angles around C2 (°)	360.0	360.0
C1-C2-N-S torsion angle (°)	-164.74	-176.59

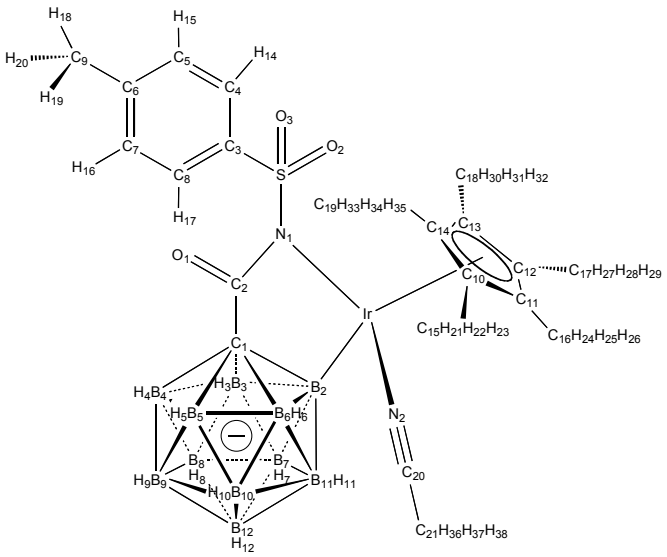


Figure S11 Numbering system for calculated *vs* experimental NMR shifts of compound **2**.

Table S3 Calculated B97-D/Def2-QZVPPD//B97-D/Def2-TZVPD *vs* experimental NMR shifts in acetonitrile of compound **2**.

Atom	**Calculated Signal (ppm)**	**Experimental Signal (ppm)**
C1	80.05	76.06
C2	179.06	179.58
C3	145.28	ca. 142
C4	128.55	128.44
C5	128.92	129.13
C6	147.85	ca. 142
C7	130.87	129.13
C8	127.97	128.44
C9	16.21	21.40
C10	103.28	90.85
C11	78.09	90.85
C12	114.09	90.85
C13	114.49	90.85
C14	86.32	90.85
	avg. of calc. C10-C14: 99.25	
C15	4.92	9.94
C16	3.08	9.94

C17	2.67	9.94
C18	5.56	9.94
C19	2.62	9.94
	avg. of calc. C15-C19: 3.77	
C20	116.57	*
C21	-4.94	*
H3	-0.40794	1.3-1.9
H4	-0.728808	1.3-1.9
H5	-1.15422	1.3-1.9
H6	-0.2248	1.3-1.9
H7	-0.3067	1.3-1.9
H8	-0.9507	1.3-1.9
H9	-1.2169	1.3-1.9
H10	-0.9580	1.3-1.9
H11	-0.7798	1.3-1.9
H12	-0.7589	1.3-1.9
H14	5.91	7.58
H15	5.48	7.22
H16	5.60	7.22
H17	5.84	7.58
H18	0.2522	2.36
H19	-0.1391	2.36
H20	0.3168	2.36
H21	-0.1172	1.72
H22	-0.6827	1.72
H23	0.1531	1.72
H24	-0.5905	1.72
H25	-0.6859	1.72
H26	-0.6993	1.72
H27	-0.2125	1.72
H28	-0.6587	1.72
H29	-0.3620	1.72
H30	0.0175	1.72
H31	-0.7116	1.72
H32	-0.2123	1.72
H33	-0.7663	1.72
H34	-0.8371	1.72
H35	-0.8139	1.72
H36	0.2066	*
H37	0.1760	*

H38	0.2857	*
B2	7.259	-16.2
B3	-10.52	-10.2 to -14.7
B4	-14.41	-10.2 to -14.7
B5	-13.08	-10.2 to -14.7
B6	-11.33	-10.2 to -14.7
B7	-12.23	-10.2 to -14.7
B8	-13.39	-10.2 to -14.7
B9	-16.99	-15.7
B10	-12.32	-10.2 to -14.7
B11	-11.58	-10.2 to -14.7
B12	-6.849	-7.6

* acetonitrile ligand exchanges with solvent molecules in CD_3CN solution; no distinct ^{1}H or ^{13}C signals detectable.

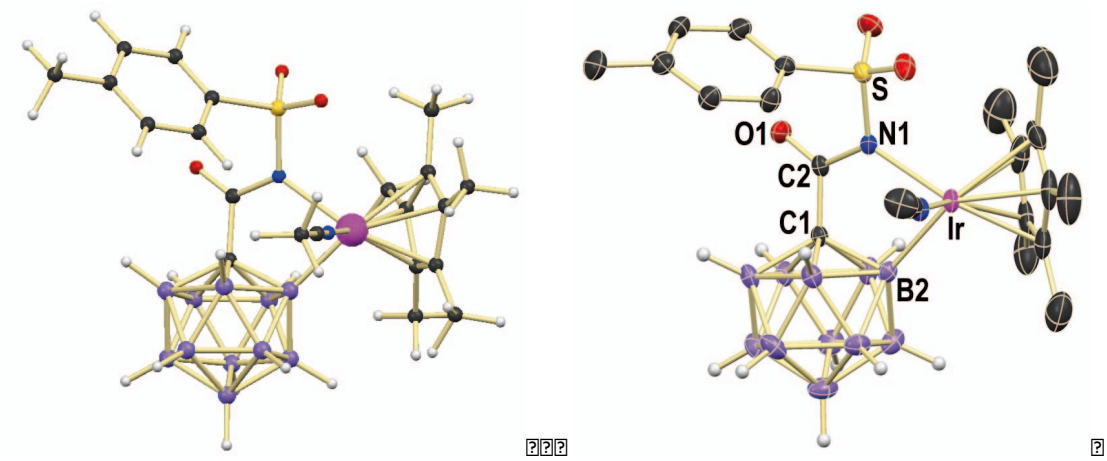


Figure S12 Calculated B97-D/Def2-TZVPD (left) and experimental X-ray crystal structure (right) of compound **2**.

Table S4 Calculated B97-D/Def2-TZVPD *vs* experimental X-ray structural parameters of compound **2**.

Parameter	**Calculated value**	**Experimental value**
B2-Ir (Å)	2.118	2.123(7)
N1-Ir (Å)	2.208	2.147(4)
C1-B2 (Å)	1.748	1.746(8)
C1-C2 (Å)	1.521	1.487(8)
C2-N1 (Å)	1.380	1.378(7)
B2-Ir-N1 (°)	78.49	79.5
B2-C1-N1 (°)	112.77	113.3
C1-C2-N1 (°)	111.62	112.0
B2-C1-C2-N1 (°)	–10.24	–12.4

HOMO and LUMO plots for the B97-D/Def2-TZVPD optimized compound **2** in acetonitrile are shown in Figure S12. The HOMO is rather localized around the Ir/ligand moities, while the LUMO is more localized on ligands with π systems.

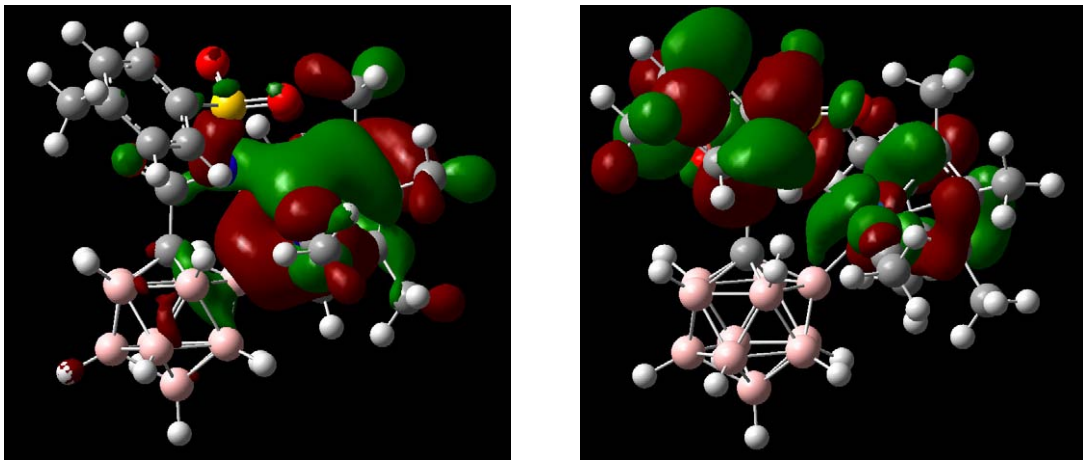


Figure S13 HOMO (left) and LUMO (right) plots for the B97-D/Def2-TZVPD optimized **2** in acetonitrile.

Electrophilic (HOMO) and nucleophilic (LUMO) frontier density plots for the B97-D/Def2-TZVPD optimized compound **2** are shown in Figure S13. The blue color indicates the highest probability of attack by a nucleophile or electrophile, respectively, i.e., the most reactive areas of the molecule. Therefore, Figure S13 (left) indicates the most probable attack by an electrophile at the site of the B2 and Ir, and Figure S13 (right) indicates the most probable attack by a nucleophile at the C3 position.

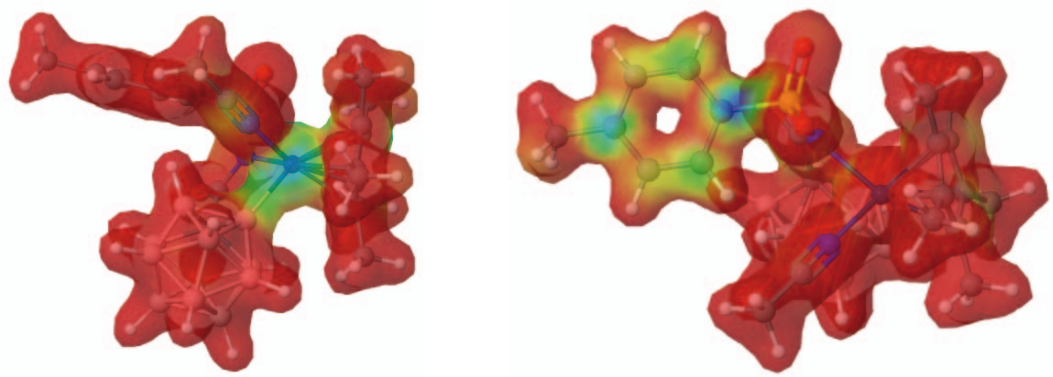


Figure S14 Electrophilic HOMO (left) and nucleophilic LUMO (right) frontier density plots for the B97-D/Def2-TZVPD optimized compound **2** in acetonitrile.

Table S5 Natural electronic configuration for Ir and B atoms of compound **2** as calculated from B97-D/Def2-QZVPPD//B97-D/Def2-TZVPD NBO analysis.

Atom	Natural Electron Configuration
Ir1	[core]$5d^{8.01}6p^{0.49}5f^{0.02}6d^{0.02}8S^{0.33}$
B2	[core]$2S^{0.65}2p^{2.03}3p^{0.03}3d^{0.01}4d^{0.01}5p^{0.01}4f^{0.01}5d^{0.01}6d^{0.01}$
B3	[core]$2S^{0.65}2p^{2.36}3p^{0.02}4p^{0.01}4d^{0.01}5d^{0.02}$
B4	[core]$2S^{0.68}2p^{2.17}3p^{0.01}4S^{0.01}4d^{0.06}$
B5	[core]$2S^{0.67}2p^{2.30}3p^{0.03}4d^{0.02}$
B6	[core]$2S^{0.65}2p^{2.34}3p^{0.02}4p^{0.01}4d^{0.01}5d^{0.02}$
B7	[core]$2S^{0.66}2p^{2.54}3p^{0.03}4d^{0.02}4f^{0.01}$
B8	[core]$2S^{0.68}2p^{2.35}3S^{0.01}3p^{0.01}4d^{0.07}$
B9	[core]$2S^{0.68}2p^{2.36}3S^{0.02}3p^{0.01}3d^{0.02}4f^{0.01}$
B10	[core]$2S^{0.68}2p^{2.35}3S^{0.01}3p^{0.01}4d^{0.06}$
B11	[core]$2S^{0.67}2p^{2.41}3p^{0.01}3d^{0.05}5S^{0.01}4d^{0.01}$
B12	[core]$2S^{0.68}2p^{2.32}3S^{0.01}3p^{0.01}3d^{0.02}4d^{0.05}$

Table S6 B97-D/Def2-QZVPPD//B97-D/Def2-TZVPD Natural population analysis (NPA) charges for Ir atom, carborane B and H atoms, and select ligand atoms, with Ir-B bond atoms highlighted.

Atom	Charge		Atom	Charge		Atom	Charge
Ir	0.1493		B2	0.2262		H3	0.0367
			B3	-0.0773		H4	0.0379
C1	-0.6856		B4	0.0719		H5	0.0548
C2	0.6822		B5	-0.0329		H6	0.0304
C10	-0.0306		B6	-0.0616		H7	0.0431
C11	-0.0726		B7	-0.2681		H8	0.0299
C12	0.0168		B8	-0.1241		H9	0.0327
C13	-0.0596		B9	-0.0922		H10	0.0278
C14	-0.0270		B10	-0.1226		H11	0.0272
			B11	-0.1688		H12	0.0243
N2	-0.2111		B12	-0.0982			
N1	-0.7998						

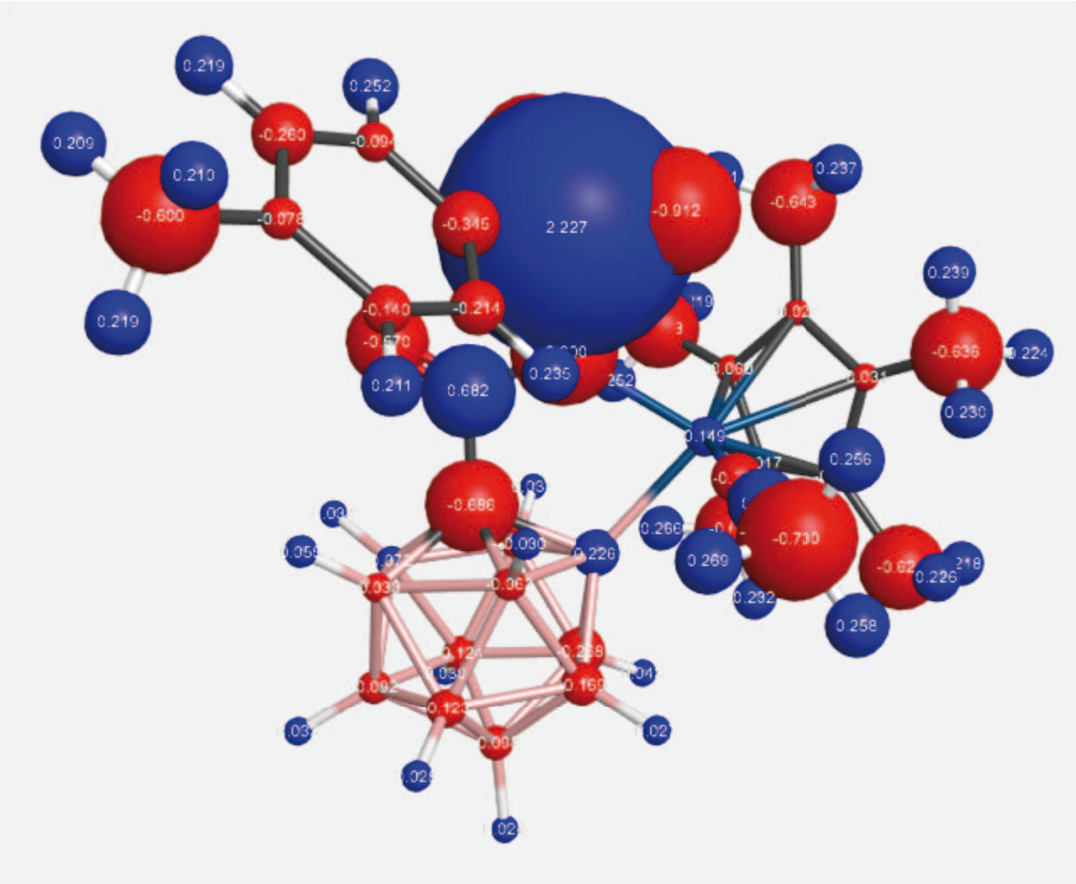


Figure S15 B97-D/Def2-QZVPPD//B97-D/Def2-TZVPD depiction of Natural Population Analysis charges. Blue = positive partial charge, red = negative partial charge.

Table S7 B97-D/Def2-QZVPPD//B97-D/Def2-TZVPD NBO analysis of compound **2** highlighting Donor/Acceptor interactions involving Ir and B2 of carborane.

Donor (i)	Type	ED[1]/ e	Acceptor (j)	Type	ED/ e	E(2) (kcal/mol)
Ir-N1	σ	1.9335	Ir	LP*(4)	0.6479	21.86
Ir-N1	σ	1.9335	Ir	LP*(7)	0.1372	20.83
Ir-N1	σ	1.9335	Ir-N1	σ*	0.6938	20.82
Ir-N1	σ	1.9335	B2	LP	0.9381	30.54
Ir-N2	σ	1.9753	B2	LP	0.9381	22.87
N2-C20	σ	1.9845	C14-C13	σ*	0.0342	21.54
N2-C20	π	1.9769	C14-C13	σ*	0.0342	31.14
N2-C20	π	1.9769	B2	LP*(3)	0.6391	25.67

Ir	LP[2](1)	1.9116	Ir	LP*(4)	0.6479	47.32
Ir	LP(1)	1.9116	Ir	LP*(6)	0.1901	64.82
Ir	LP(1)	1.9116	Ir	LP*(7)	0.1372	36.50
Ir	LP(1)	1.9116	Ir-N1	σ*	0.6938	46.72
Ir	LP(1)	1.9116	Ir-N2	σ*	0.6181	40.23
Ir	LP(1)	1.9116	C12	LP	0.9278	26.48
Ir	LP(1)	1.9116	B2	LP(1)	0.9381	48.33
Ir	LP(2)	1.8543	Ir	LP*(4)	0.6479	21.44
Ir	LP(2)	1.8543	Ir	LP*(6)	0.1901	36.22
Ir	LP(2)	1.8543	B3	LP*(2)	0.1372	31.00
Ir	LP(3)	1.7823	C12	LP	0.9278	34.15
Ir	LP(3)	1.7823	C11	LP	1.0116	70.94
Ir	LP(3)	1.7823	C13	LP	0.9871	48.25
Ir	LP(3)	1.7823	C11-C10	σ*	0.0357	43.76
Ir	LP(3)	1.7823	C14-C13	σ*	0.0342	88.66
C12-C11	σ	1.9503	C14-C13	σ*	0.0342	22.42
C10-C14	π	1.6672	C13	LP	1.0116	137.00
C14-C13	σ	1.9419	Ir	LP*(7)	0.1372	24.82
C12	LP	0.9278	Ir	LP*(6)	0.1901	20.93
C12	LP	0.9278	Ir-N1	σ*	0.6938	29.50
C12	LP	0.9278	B2	LP*(3)	0.6391	70.46
C11	LP	1.0116	Ir	LP*(6)	0.1901	22.68
C11	LP	1.0116	Ir-N2	σ*	0.6181	20.73
C11	LP	1.0116	C12	LP	0.9278	136.40
C11	LP	1.0116	C13	LP	0.9871	225.90
C13	LP	0.9871	Ir-N2	σ*	0.6181	34.59
C13	LP	0.9871	C12	LP	0.9278	267.20

[1]ED: electron density

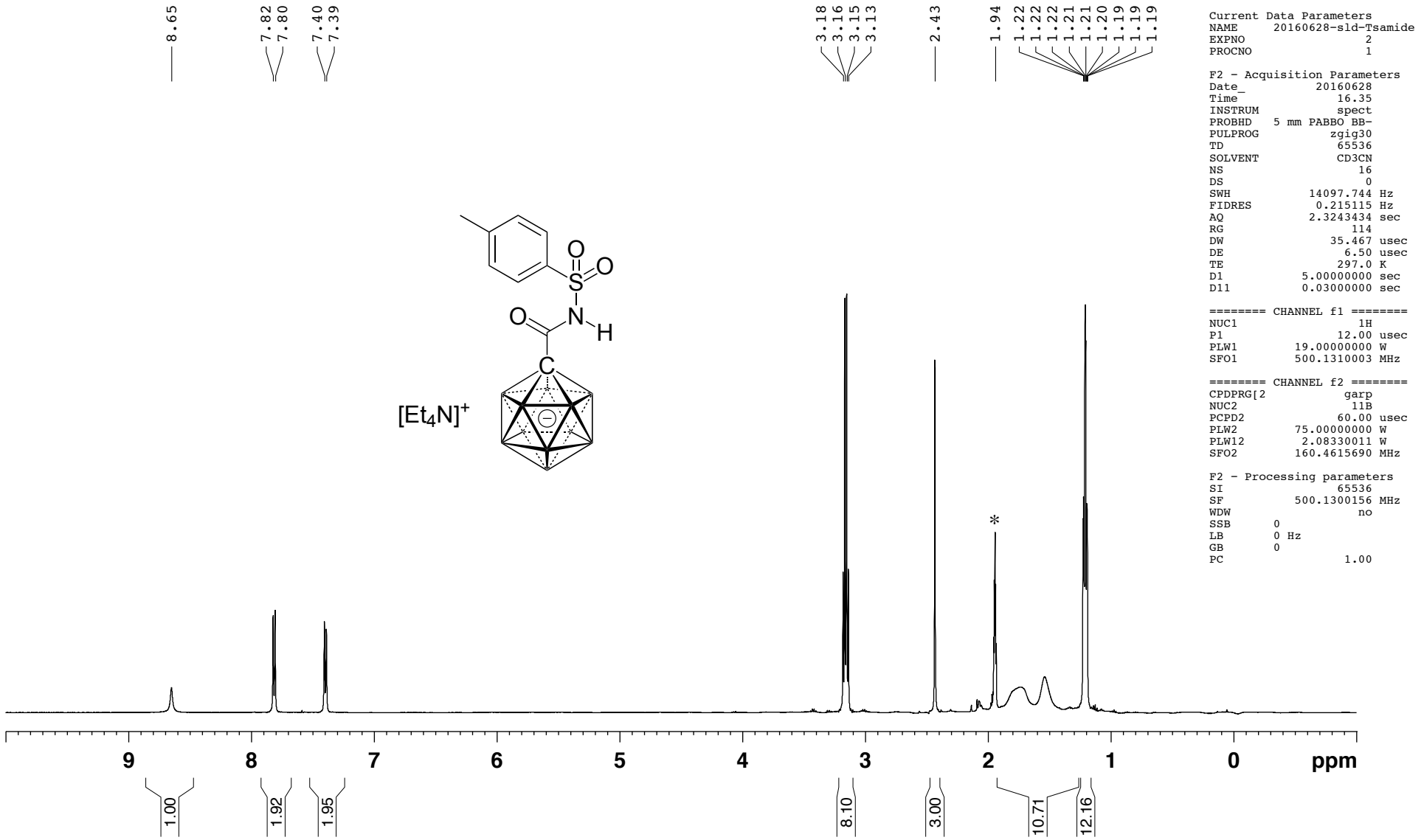
[2]LP: lone paired

V NMR Spectra

VI Mass Spectra

VII IR Spectra

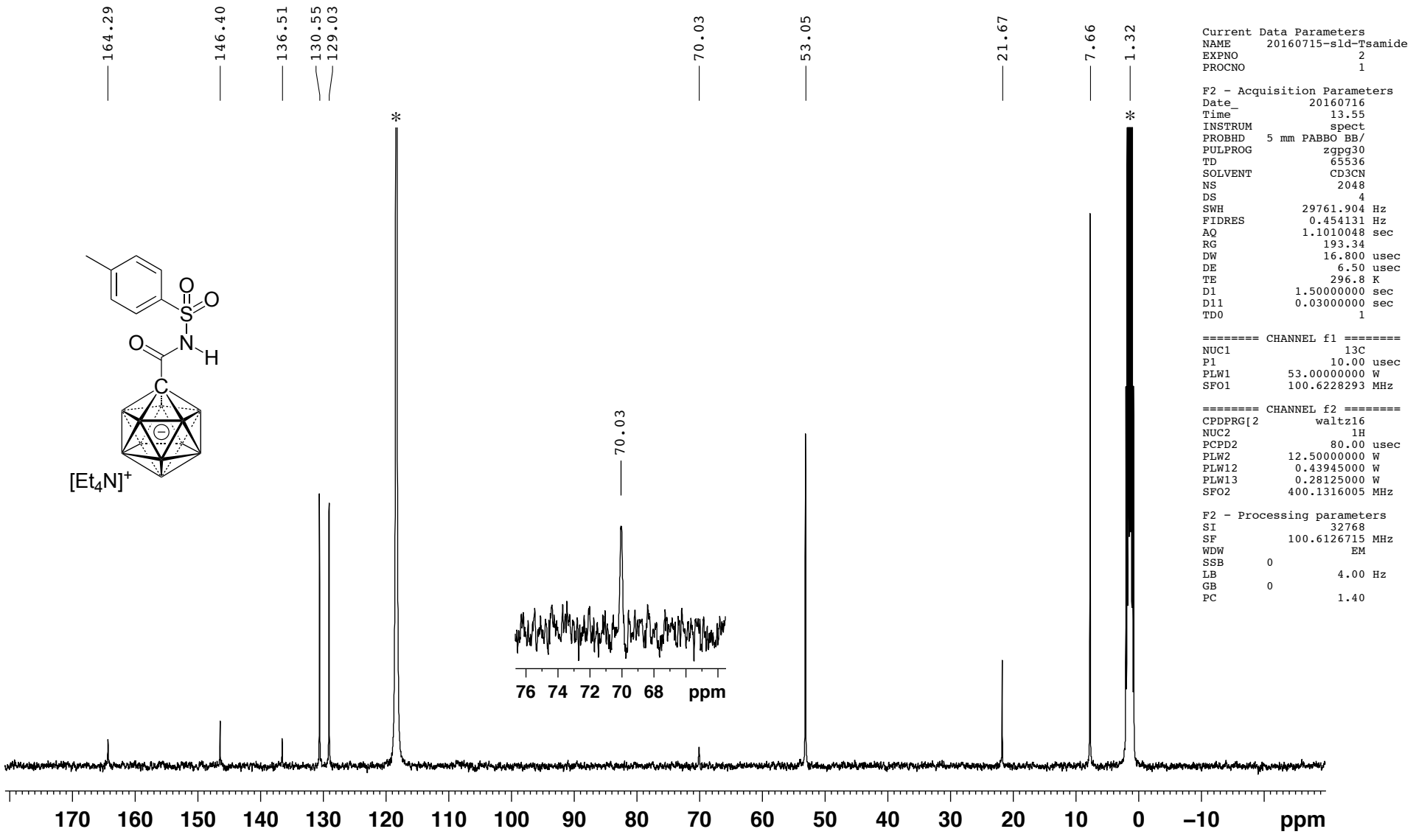
NHTs amide 12 mg in CD3CN*
1H{11B} NMR, Bruker 500 MHz, T = 23 C




```
Current Data Parameters
NAME      20160628-sld-Tsamide
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160628
Time                 16.35
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgig30
TD                   65536
SOLVENT              CD3CN
NS                      16
DS                       0
SWH              14097.744 Hz
FIDRES            0.215115 Hz
AQ                2.3243434 sec
RG                     114
DW                  35.467 usec
DE                   6.50 usec
TE                  297.0 K
D1               5.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.00 usec
PLW1           19.00000000 W
SFO1           500.1310003 MHz

======== CHANNEL f2 ========
CPDPRG[2                garp
NUC2                     11B
PCPD2                 60.00 usec
PLW2           75.00000000 W
PLW12           2.08330011 W
SFO2           160.4615690 MHz

F2 - Processing parameters
SI                    65536
SF             500.1300156 MHz
WDW                      no
SSB       0
LB        0 Hz
GB        0
PC                     1.00
```

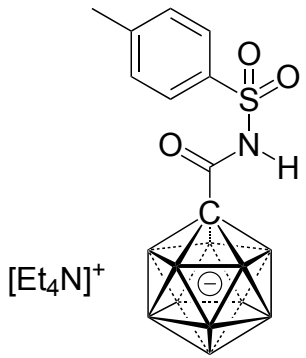
NMR1

NHTs amide 12 mg in CD3CN *
13C{1H} NMR, Bruker 400 MHz, T = 23 C



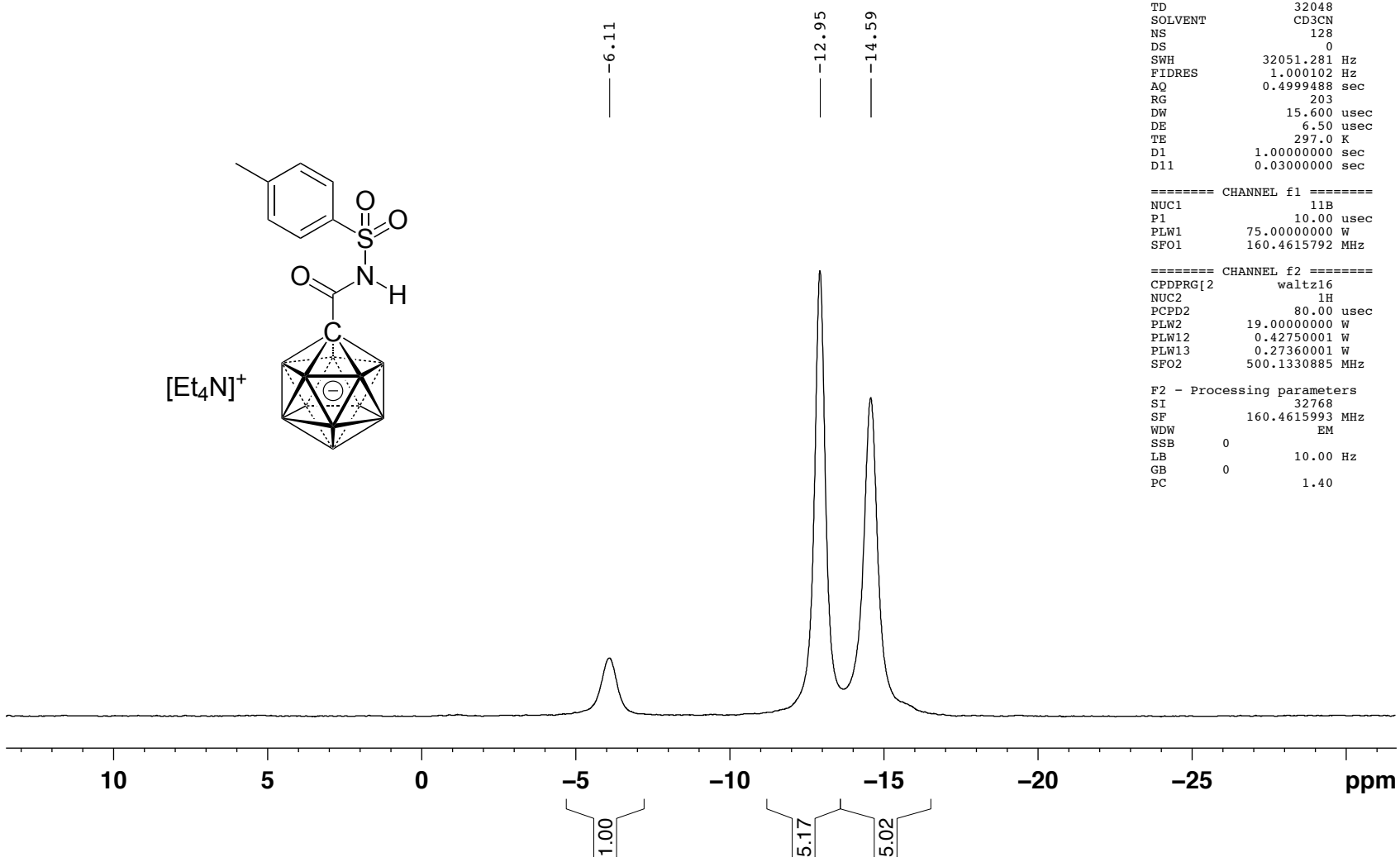

```
Current Data Parameters
NAME      20160715-sld-Tsamide
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160716
Time                   13.55
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CD3CN
NS                     2048
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                   193.34
DW                   16.800 usec
DE                    6.50 usec
TE                   296.8 K
D1             1.50000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.00 usec
PLW1          53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PLW2          12.50000000 W
PLW12          0.43945000 W
PLW13          0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF           100.6126715 MHz
WDW                      EM
SSB       0
LB                    4.00 Hz
GB        0
PC                    1.40
```

NHTs amide 12 mg in CD3CN
11B NMR, Bruker 500 MHz, T = 23 C



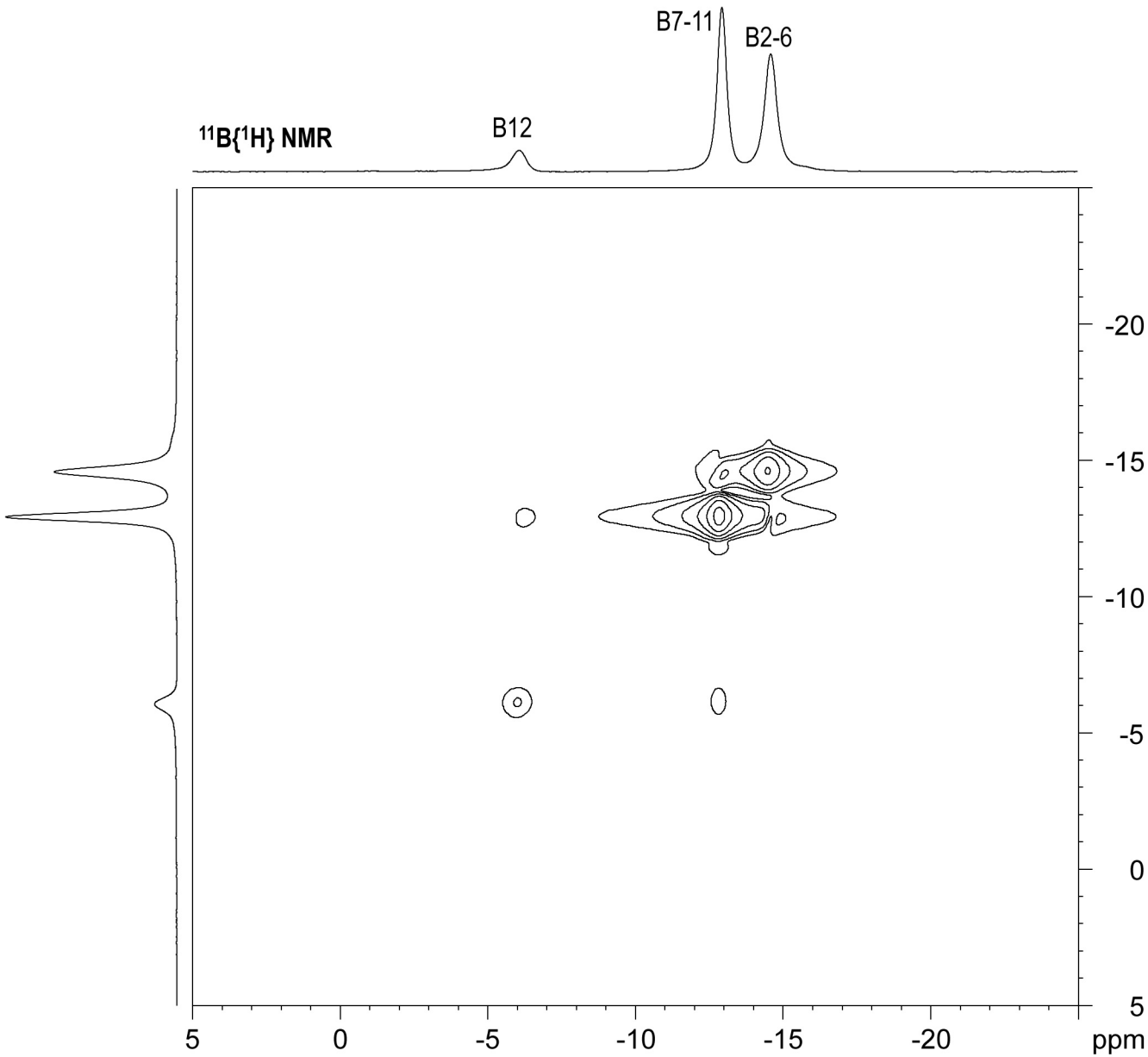

```
Current Data Parameters
NAME      20160628-sld-Tsamide
EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160628
Time                  16.38
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                   zg
TD                     32048
SOLVENT               CD3CN
NS                       128
DS                         0
SWH               32051.281 Hz
FIDRES             1.000102 Hz
AQ                0.4999488 sec
RG                       203
DW                    15.600 usec
DE                    16.00 usec
TE                    296.5 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                     11B
P1                    10.00 usec
PLW1           75.00000000 W
SFO1           160.4615792 MHz

F2 - Processing parameters
SI                     32768
SF             160.4615993 MHz
WDW                       EM
SSB          0
LB                    10.00 Hz
GB           0
PC                     1.40
```

NHTs amide 12 mg in CD3CN
11B{11H} NMR, Bruker 500 MHz, T = 23 C

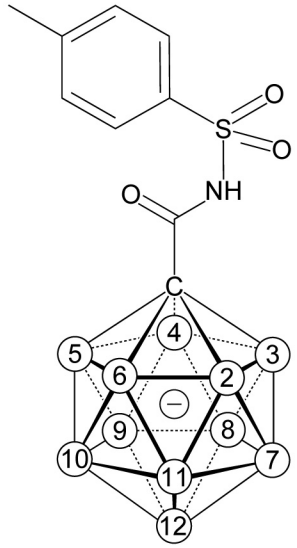



```
Current Data Parameters
NAME      20160628-sld-Tsamide
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160628
Time                 16.43
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                   32048
SOLVENT              CD3CN
NS                     128
DS                       0
SWH              32051.281 Hz
FIDRES            1.000102 Hz
AQ               0.4999488 sec
RG                     203
DW                  15.600 usec
DE                   6.50 usec
TE                  297.0 K
D1              1.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   11B
P1                   10.00 usec
PLW1          75.00000000 W
SFO1         160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W
PLW13          0.27360001 W
SFO2         500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF           160.4615993 MHz
WDW                    EM
SSB       0
LB                   10.00 Hz
GB        0
PC                    1.40
```

NHTs amide 12 mg in CD3CN
11B-11B-COSY NMR, Bruker 500 MHz, T = 23 C



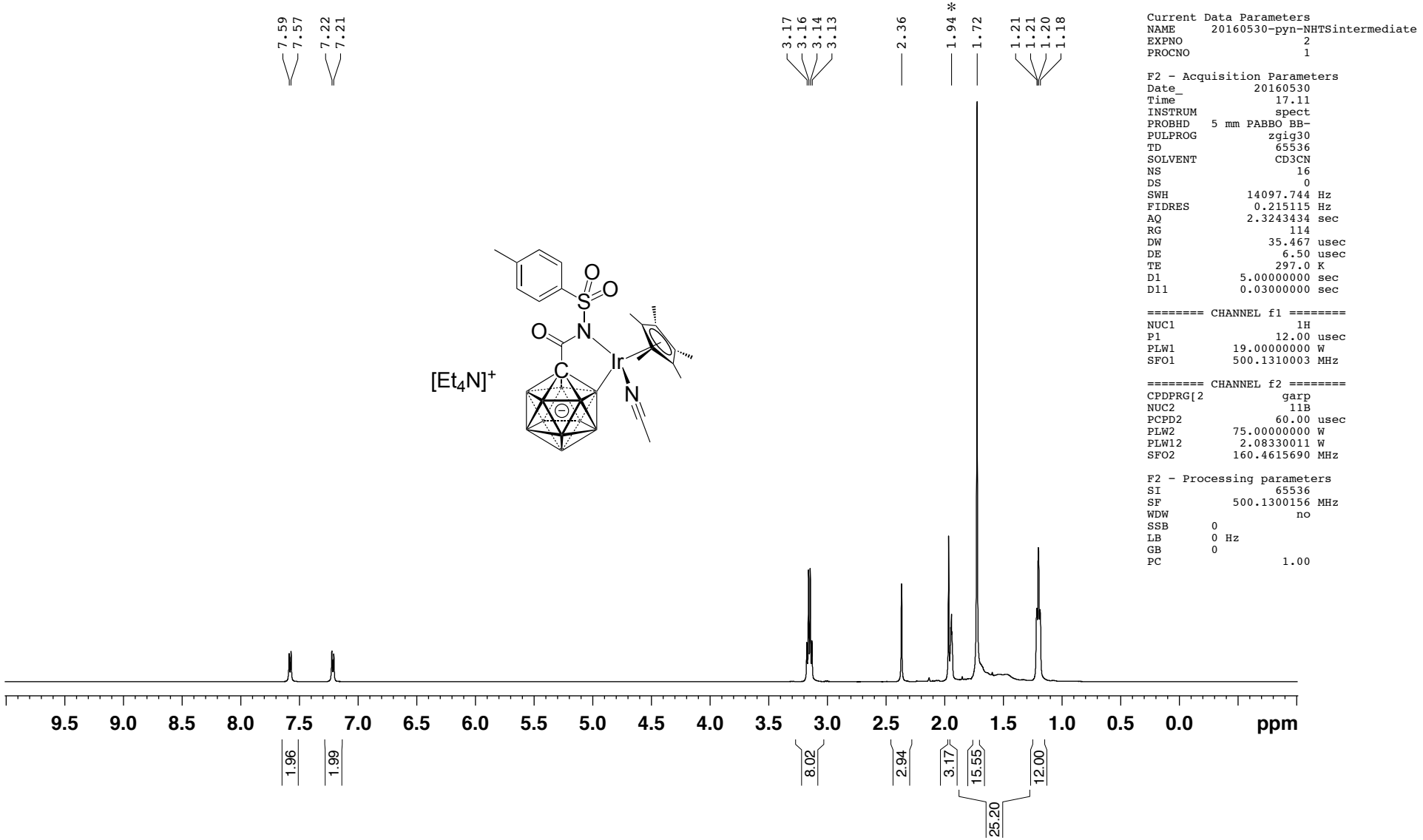
NMR5



$[Et_4N]^+$

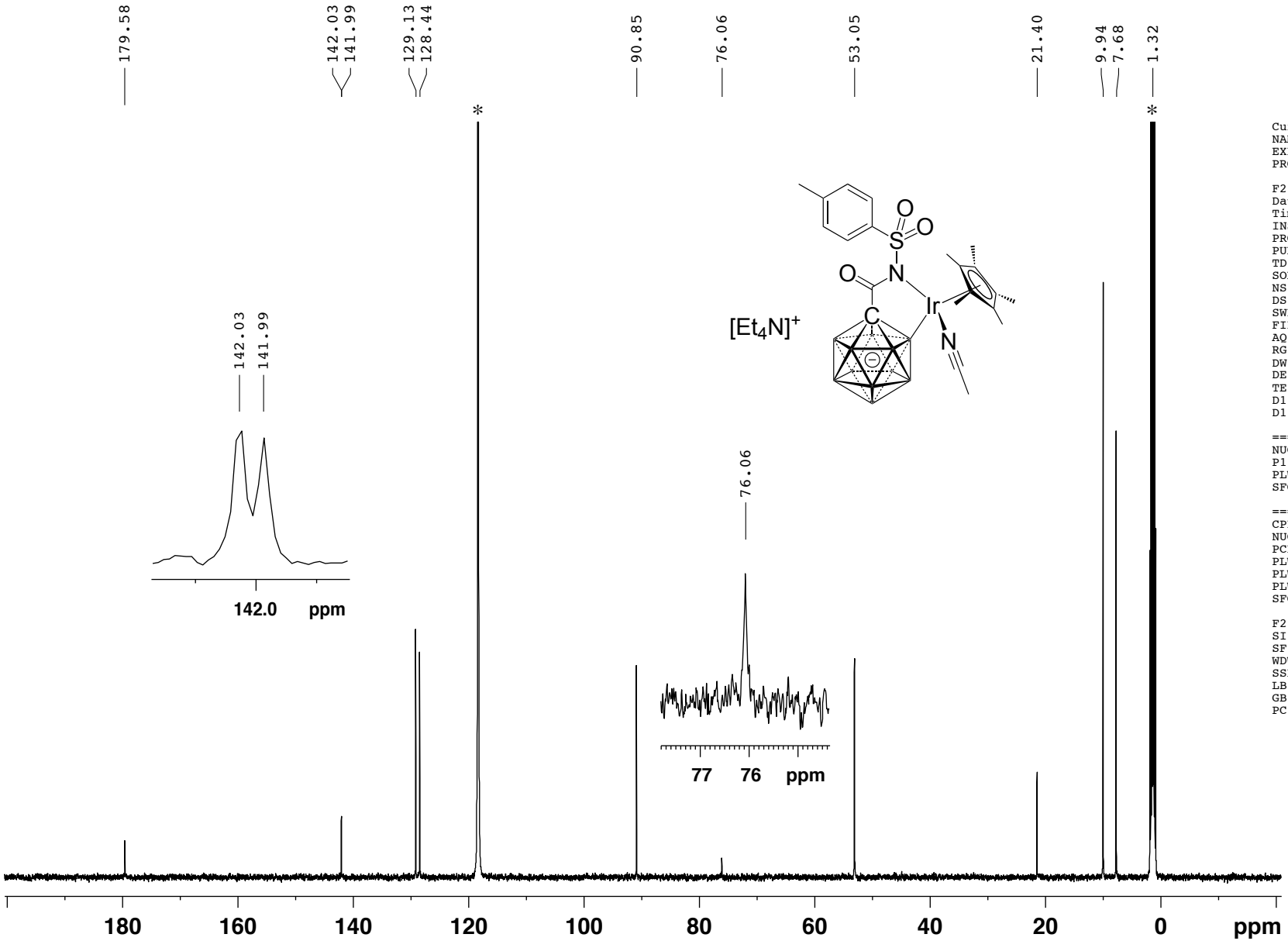
```
Current Data Parameters
NAME      20160628-sld-Tsamide
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160628
Time                   16.47
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpqfdec
TD                     2566
SOLVENT              CD3CN
NS                        8
DS                       16
SWH                6421.233 Hz
FIDRES             2.502429 Hz
AQ                 0.1998059 sec
RG                       203
DW                    77.867 usec
DE                     6.50 usec
TE                    296.7 K
D0                 0.00000300 sec
D1                 0.30000001 sec
D11                0.03000000 sec
D13                0.00000400 sec
D16                0.00020000 sec
IN0                0.00015580 sec

======== CHANNEL f1 ========
NUC1                      11B
P0                      13.10 usec
P1                      13.10 usec
PLW1               95.00000000 W
SFO1              160.4604558 MHz

======== CHANNEL f2 ========
CPDPRG[2               waltz16
NUC2                       1H
PCPD2                   80.00 usec
PLW2               19.00000000 W
PLW12               0.42750001 W
SFO2              500.1312000 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1                    10.00 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         64
SFO1                160.4605 MHz
FIDRES             100.287483 Hz
SW                     40.000 ppm
FnMODE                     QF

F2 - Processing parameters
SI                       4096
SF                160.4615850 MHz
WDW                        EM
SSB       0
LB                     20.00 Hz
GB        0
PC                      1.40

F1 - Processing parameters
SI                       1024
MC2                        QF
SF                160.4615986 MHz
WDW                      SINE
SSB       0
LB        0 Hz
GB        0
```

NHTS Ir intermediate 8 mg in CD3CN*
1H{11B} NMR, Bruker 500 MHz, T = 23 C




```
Current Data Parameters
NAME      20160530-pyn-NHTSintermediate
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20160530
Time              17.11
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgig30
TD                65536
SOLVENT           CD3CN
NS                   16
DS                    0
SWH           14097.744 Hz
FIDRES         0.215115 Hz
AQ            2.3243434 sec
RG                  114
DW               35.467 usec
DE                6.50 usec
TE               297.0 K
D1           5.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PLW1        19.00000000 W
SFO1        500.1310003 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp
NUC2                 11B
PCPD2             60.00 usec
PLW2        75.00000000 W
PLW12        2.08330011 W
SFO2        160.4615690 MHz

F2 - Processing parameters
SI                65536
SF           500.1300156 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

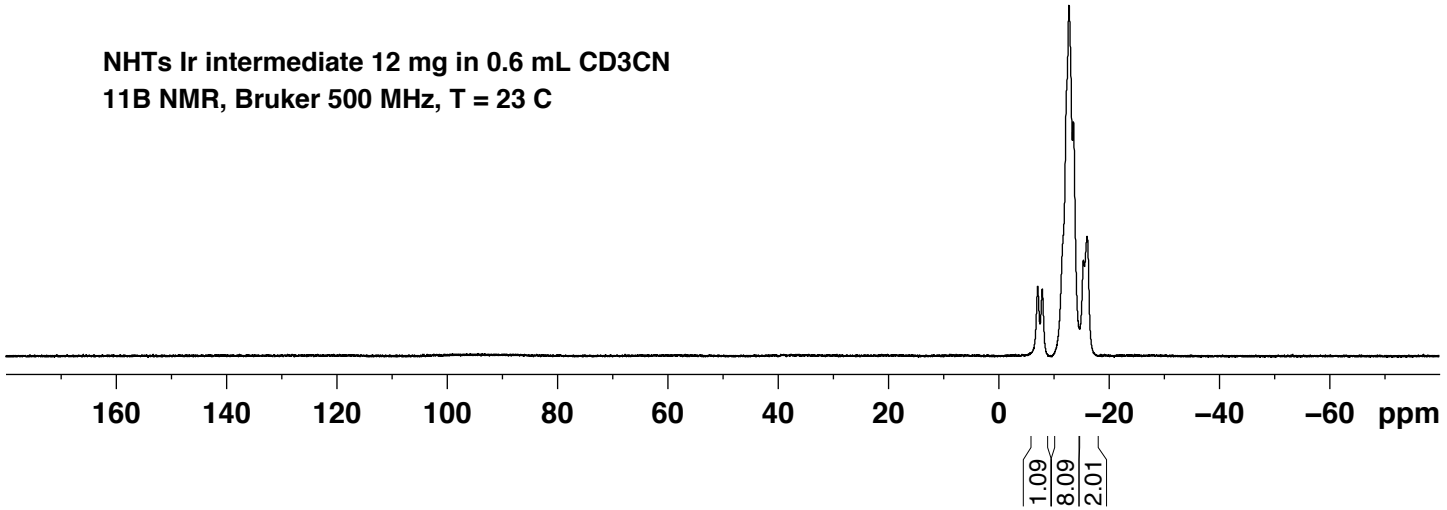
NHTS Ir intermediate 12 mg in 0.6 mL CD3CN*
13C{1H} NMR, Bruker 500 MHz, T = 23 C

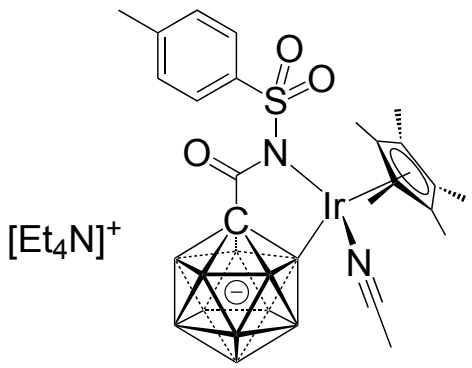


NMR7

```
Current Data Parameters
NAME      20160520-pyn-intermediate
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20160521
Time               0.15
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
NS                2048
DS                   4
SWH          37878.789 Hz
FIDRES        0.577984 Hz
AQ            0.8650752 sec
RG                 203
DW              13.200 usec
DE               6.50 usec
TE              297.0 K
D1           1.50000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1               13C
P1               10.50 usec
PLW1        95.00000000 W
SFO1       125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2               1H
PCPD2            80.00 usec
PLW2        19.00000000 W
PLW12        0.39947000 W
PLW13        0.25566000 W
SFO2       500.1320005 MHz

F2 - Processing parameters
SI               32768
SF         125.7576661 MHz
WDW                EM
SSB       0
LB               2.00 Hz
GB        0
PC               1.40
```

NHTs Ir intermediate 12 mg in 0.6 mL CD3CN
11B NMR, Bruker 500 MHz, T = 23 C

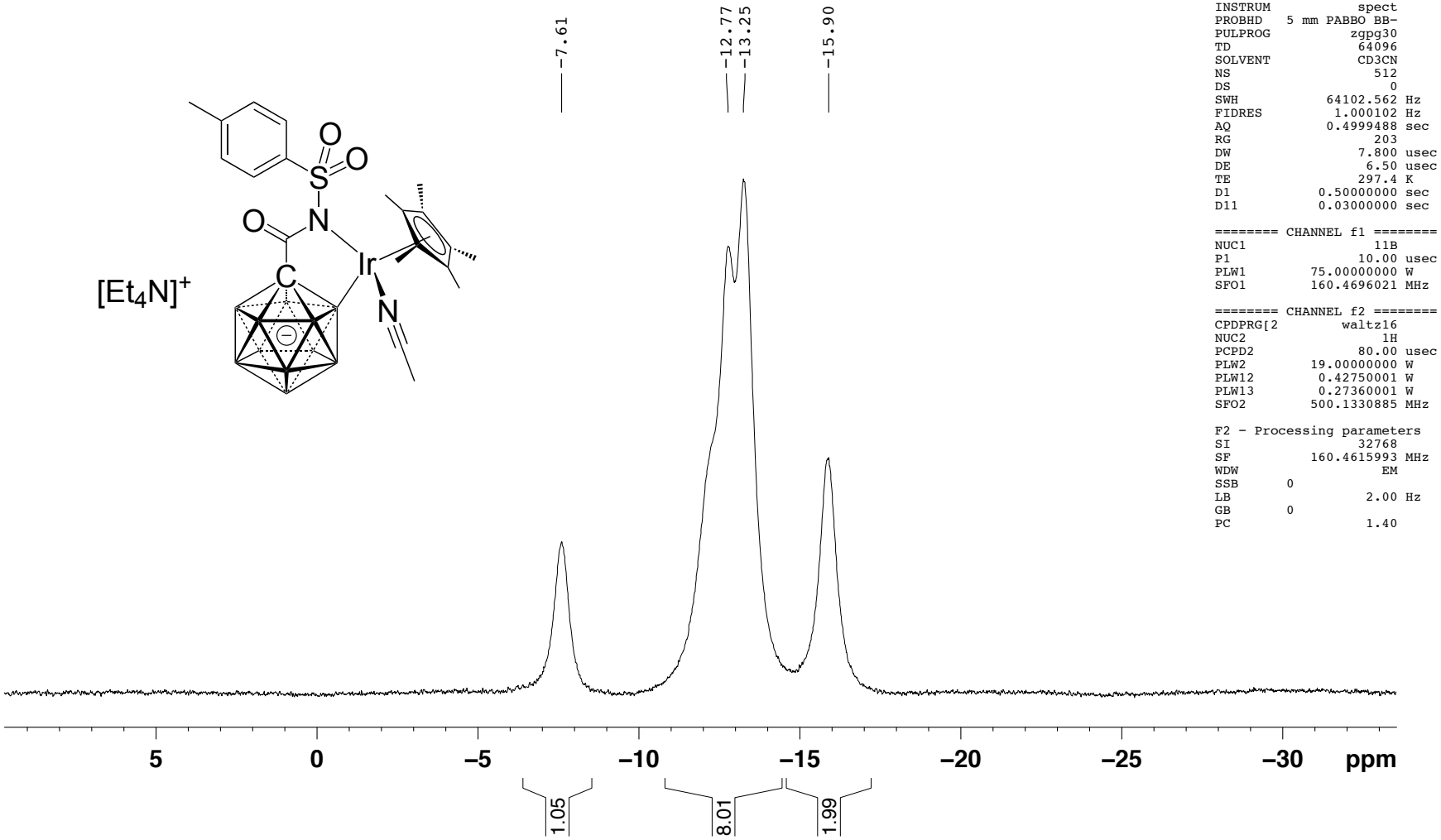




$[Et_4N]^+$

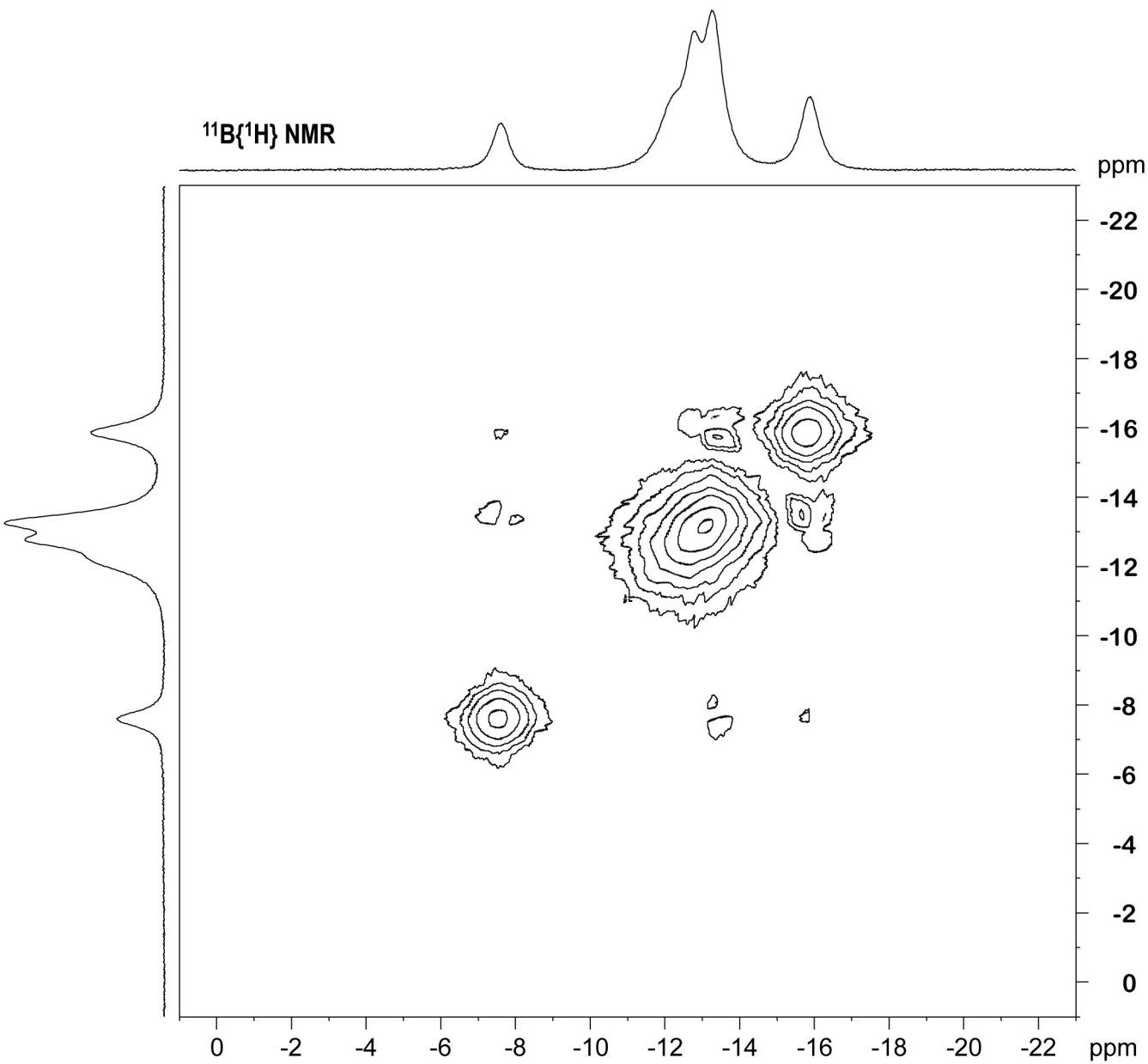

```
Current Data Parameters
NAME      20160718-yjs-Ts-Ir
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_            20160718
Time                16.36
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG                zg
TD                  32048
SOLVENT             CD3CN
NS                    512
DS                      0
SWH             48076.922 Hz
FIDRES           1.500154 Hz
AQ              0.3332992 sec
RG                    203
DW                10.400 usec
DE                16.00 usec
TE                297.0 K
D1             0.50000000 sec

======== CHANNEL f1 ========
NUC1                  11B
P1                  10.00 usec
PLW1          75.00000000 W
SFO1          160.4696021 MHz

F2 - Processing parameters
SI                    32768
SF            160.4615993 MHz
WDW                     EM
SSB       0
LB                   2.00 Hz
GB        0
PC                   1.40
```

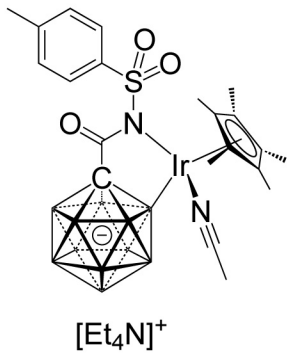
NHTs Ir intermediate 12 mg in 0.6 mL CD3CN
11B{1H} NMR, Bruker 500 MHz, T = 23 C




```
Current Data Parameters
NAME      20160718-yjs-Ts-Ir
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_           20160718
Time              16.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                64096
SOLVENT           CD3CN
NS                  512
DS                    0
SWH           64102.562 Hz
FIDRES         1.000102 Hz
AQ            0.4999488 sec
RG                  203
DW                7.800 usec
DE                6.50 usec
TE                297.4 K
D1           0.50000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                11B
P1                10.00 usec
PLW1         75.00000000 W
SFO1         160.4696021 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2             80.00 usec
PLW2         19.00000000 W
PLW12         0.42750001 W
PLW13         0.27360001 W
SFO2         500.1330885 MHz

F2 - Processing parameters
SI                32768
SF           160.4615993 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.40
```

NHTs Ir intermediate 12 mg in CD3CN
11B-11B-COSY NMR, Bruker 500 MHz, T = 23 C



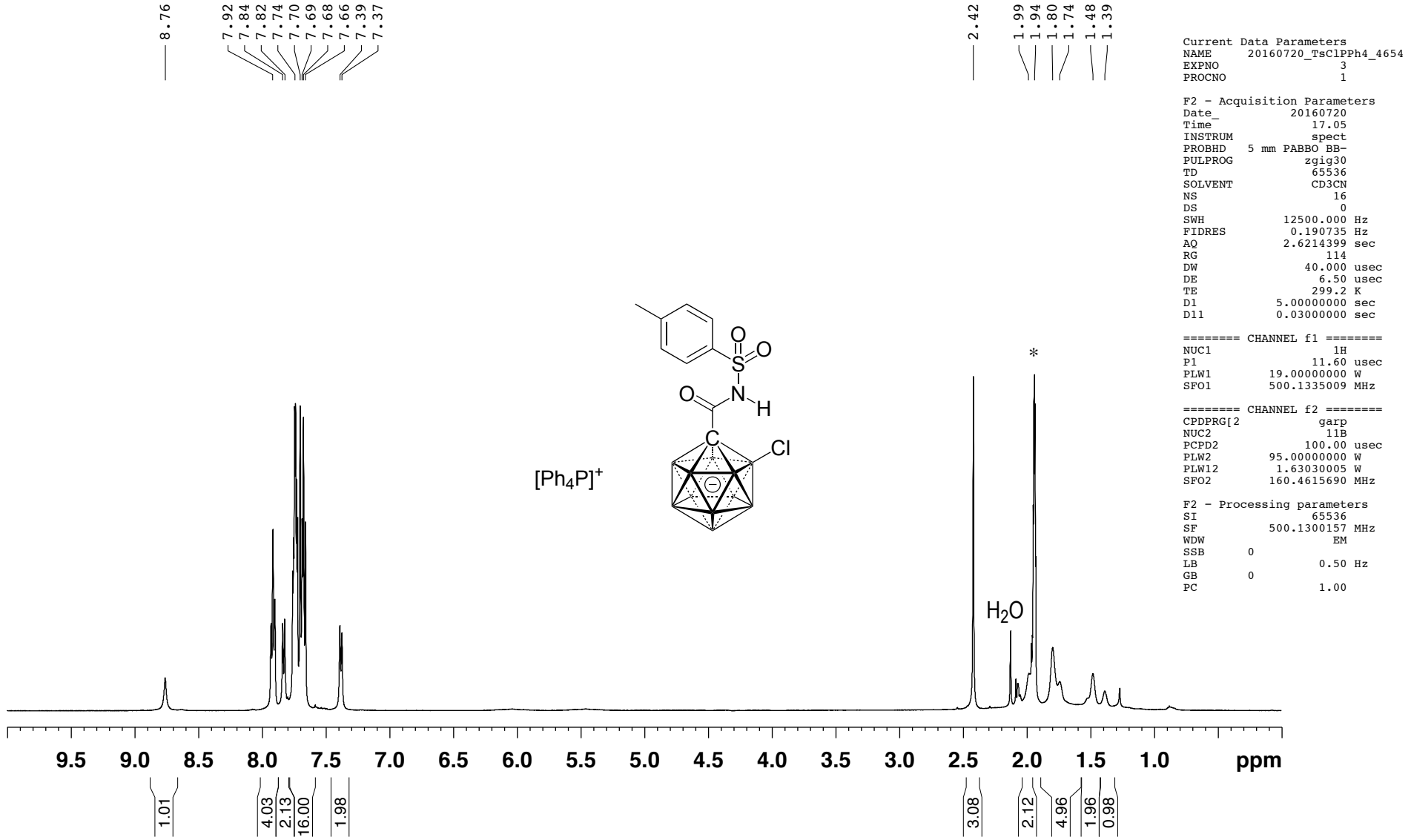


$[Et_4N]^+$

```
Current Data Parameters
NAME      20160718-yjs-Ts-Ir-intermediate
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160718
Time_              16.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG     cosygpqfdec
TD                 2566
SOLVENT            CD3CN
NS                   32
DS                   16
SWH           6421.233 Hz
FIDRES        2.502429 Hz
AQ            0.1998059 sec
RG                 203
DW               77.867 usec
DE                6.50 usec
TE                297.5 K
D0           0.00000300 sec
D1           0.30000001 sec
D11          0.03000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00015580 sec

======== CHANNEL f1 ========
NUC1                11B
P0                13.10 usec
P1                13.10 usec
PLW1        95.00000000 W
SFO1       160.4604558 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                1H
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.42750001 W
SFO2       500.1312000 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   64
SFO1          160.4605 MHz
FIDRES        100.287483 Hz
SW                40.000 ppm
FnMODE               QF

F2 - Processing parameters
SI                 4096
SF            160.4616085 MHz
WDW                  EM
SSB       0
LB                20.00 Hz
GB        0
PC                 1.40

F1 - Processing parameters
SI                 1024
MC2                  QF
SF            160.4615986 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
```

NMR10

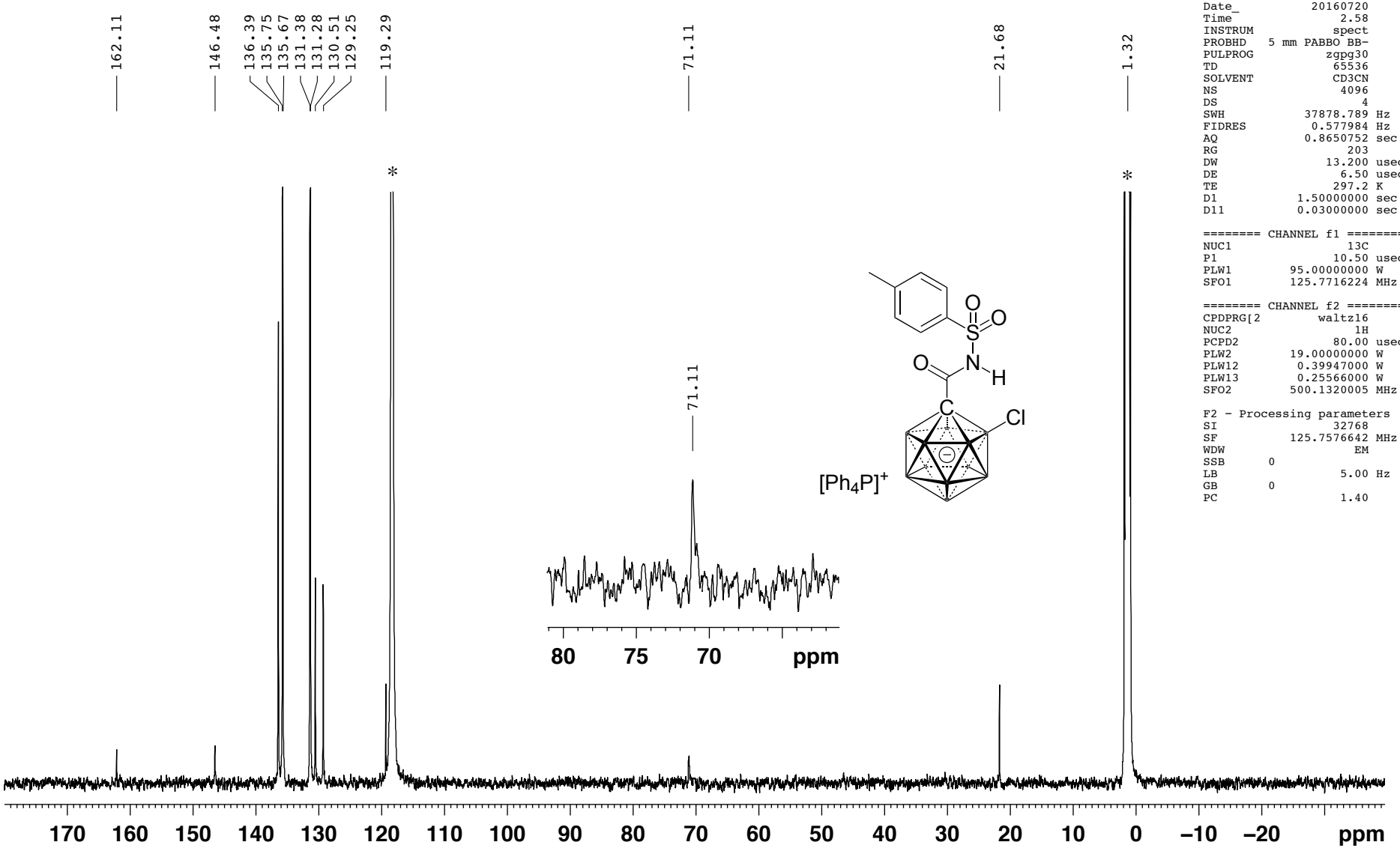
NHTs amide monochlorination product 6 mg in CD3CN *
1H{11B} NMR, Bruker 500 MHz, T = 23 C




```
Current Data Parameters
NAME      20160720_TsClPPh4_4654
EXPNO                          3
PROCNO                         1

F2 - Acquisition Parameters
Date_               20160720
Time                   17.05
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zgig30
TD                     65536
SOLVENT                CD3CN
NS                        16
DS                         0
SWH                12500.000 Hz
FIDRES                 0.190735 Hz
AQ                 2.6214399 sec
RG                       114
DW                    40.000 usec
DE                     6.50 usec
TE                     299.2 K
D1                 5.00000000 sec
D11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      11.60 usec
PLW1              19.00000000 W
SFO1              500.1335009 MHz

======== CHANNEL f2 ========
CPDPRG[2                 garp
NUC2                      11B
PCPD2                  100.00 usec
PLW2              95.00000000 W
PLW12              1.63030005 W
SFO2              160.4615690 MHz

F2 - Processing parameters
SI                     65536
SF                500.1300157 MHz
WDW                       EM
SSB       0
LB                      0.50 Hz
GB        0
PC                      1.00
```

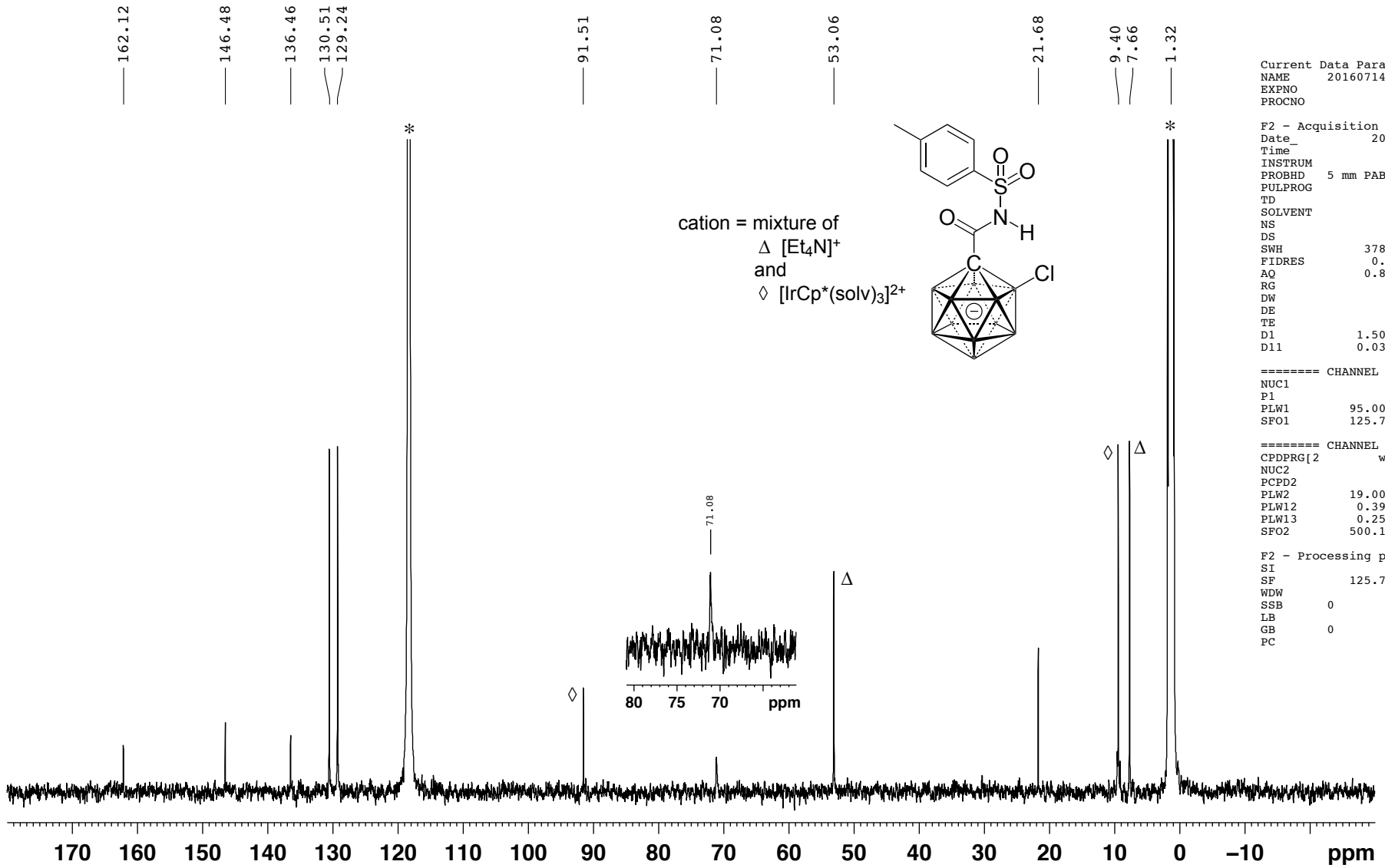
NHTs amide monochlorination product 6 mg in CD3CN*

13C{1H} NMR, Bruker 500 MHz, T = 23 C




```
Current Data Parameters
NAME     20160720_TsClPPh4_4654
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20160720
Time              2.58
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                 4096
DS                    4
SWH           37878.789 Hz
FIDRES         0.577984 Hz
AQ            0.8650752 sec
RG                  203
DW               13.200 usec
DE                6.50 usec
TE                297.2 K
D1           1.50000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1               10.50 usec
PLW1        95.00000000 W
SFO1       125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2            80.00 usec
PLW2        19.00000000 W
PLW12        0.39947000 W
PLW13        0.25566000 W
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF           125.7576642 MHz
WDW                EM
SSB       0
LB                5.00 Hz
GB        0
PC                1.40
```

NHTS amide monochlorination product 9 mg in CD3CN*
13C{1H} NMR, Bruker 500 MHz, T = 23 C




```
Current Data Parameters
NAME      20160714_yjs-tscl_02
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20160715
Time                   0.20
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CD3CN
NS                    2048
DS                       4
SWH              37878.789 Hz
FIDRES            0.577984 Hz
AQ                0.8650752 sec
RG                     203
DW                  13.200 usec
DE                   6.50 usec
TE                  297.9 K
D1             1.50000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.50 usec
PLW1          95.00000000 W
SFO1         125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PLW2          19.00000000 W
PLW12          0.39947000 W
PLW13          0.25566000 W
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                   32768
SF           125.7576652 MHz
WDW                     EM
SSB       0
LB                    5.00 Hz
GB        0
PC                    1.40
```

commercial Ph4PBr 20 mg in CDCl3 *
1H NMR, Bruker 400 MHz, T = 23 C

```
Current Data Parameters
NAME      20160728-yjs-ph4pbr
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_            20160730
Time                4.48
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                 78.69
DW               50.000 usec
DE                6.50 usec
TE                295.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                15.00 usec
PLW1        12.50000000 W
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF          400.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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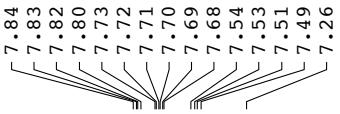
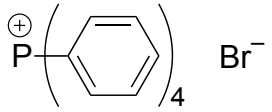
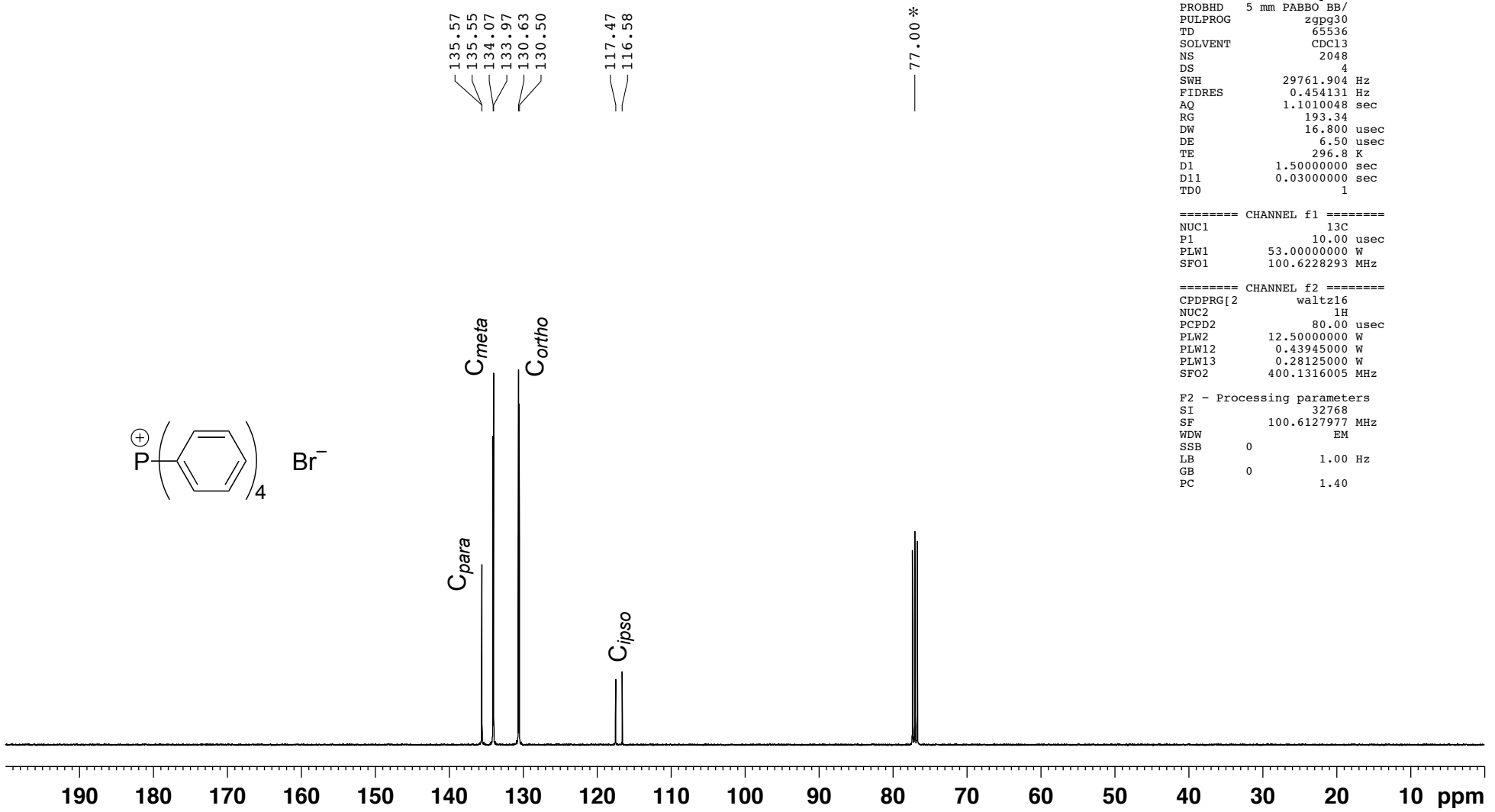




commercial Ph4PBr 20 mg in CDCl3*

13C{1H} NMR, Bruker 400 MHz, T = 23 C




```
Current Data Parameters
NAME      20160728-yjs-ph4pbr
EXPNO                       2
PROCNO                      1

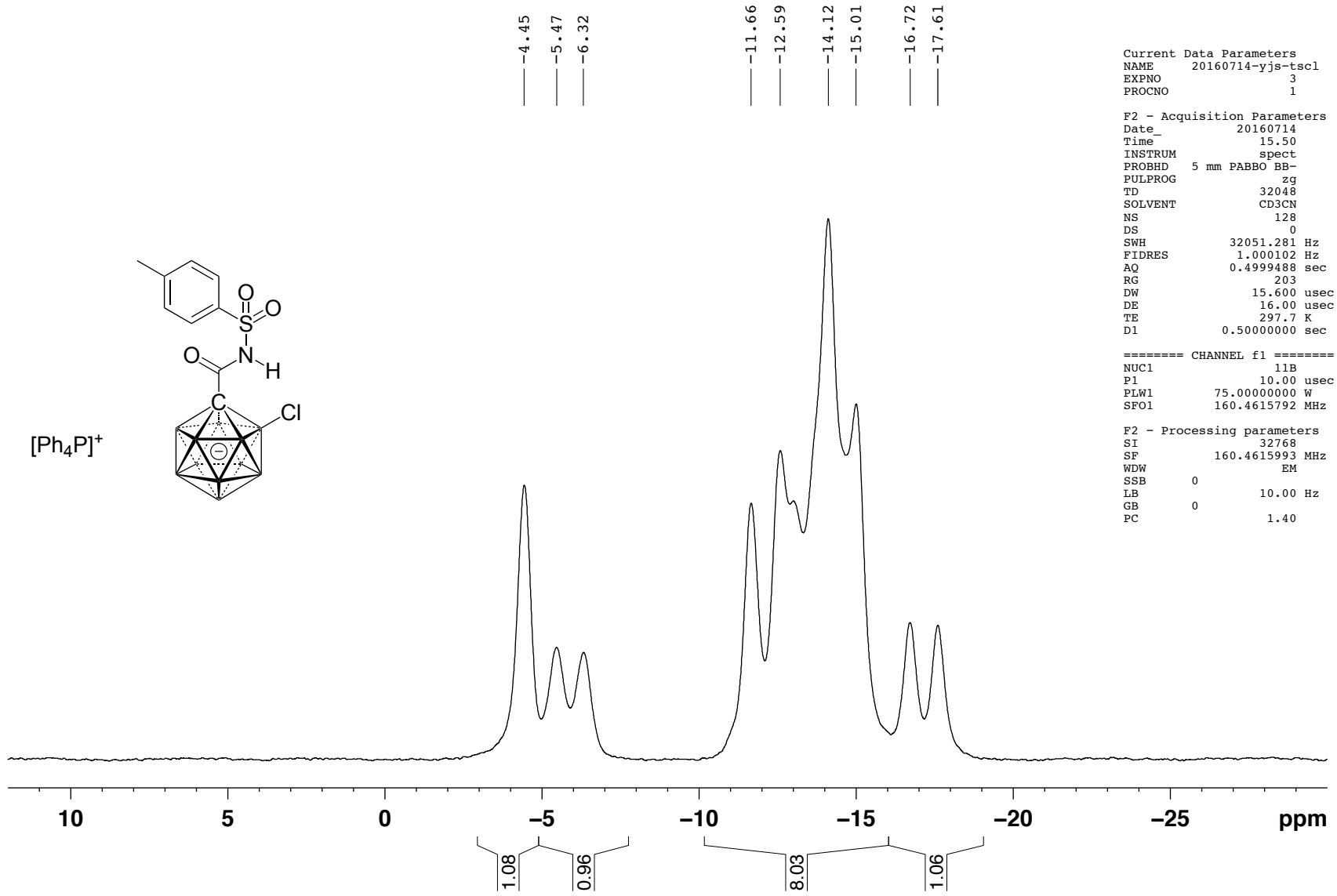
F2 - Acquisition Parameters
Date_            20160730
Time                 6.20
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2048
DS                       4
SWH             29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010048 sec
RG                  193.34
DW                16.800 usec
DE                 6.50 usec
TE                 296.8 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                 10.00 usec
PLW1          53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PLW2          12.50000000 W
PLW12          0.43945000 W
PLW13          0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6127977 MHz
WDW                     EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

NHTs amide monochlorination product 10 mg in CD3CN
11B NMR, Bruker 500 MHz, T = 23 C

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Current Data Parameters
NAME      20160714-yjs-tscl
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160714
Time              15.50
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg
TD                32048
SOLVENT           CD3CN
NS                  128
DS                    0
SWH           32051.281 Hz
FIDRES         1.000102 Hz
AQ            0.4999488 sec
RG                  203
DW               15.600 usec
DE                16.00 usec
TE                297.7 K
D1           0.50000000 sec

======== CHANNEL f1 ========
NUC1                11B
P1                10.00 usec
PLW1        75.00000000 W
SFO1        160.4615792 MHz

F2 - Processing parameters
SI                32768
SF          160.4615993 MHz
WDW                 EM
SSB       0
LB                10.00 Hz
GB        0
PC                 1.40
```
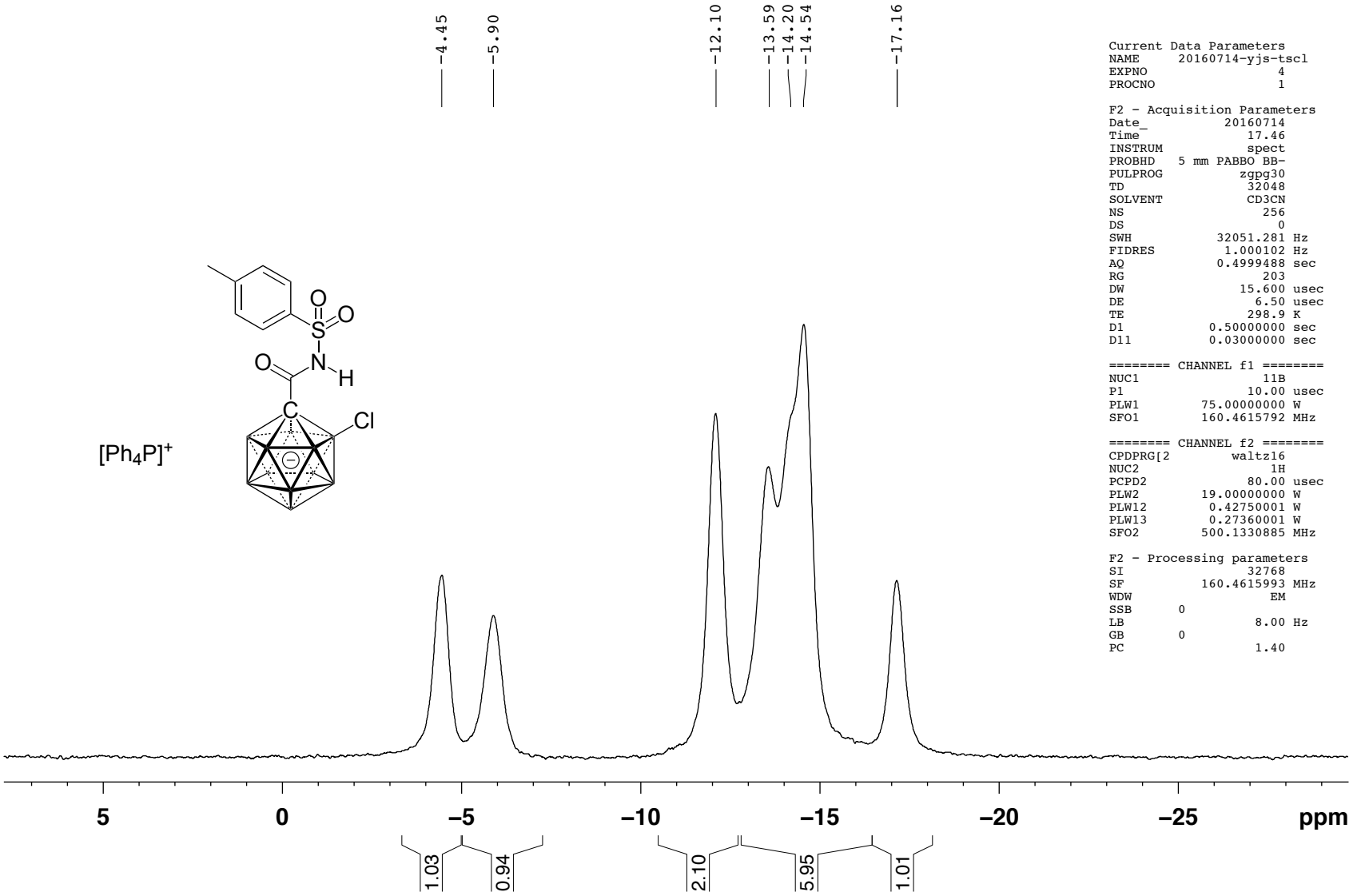

NMR16

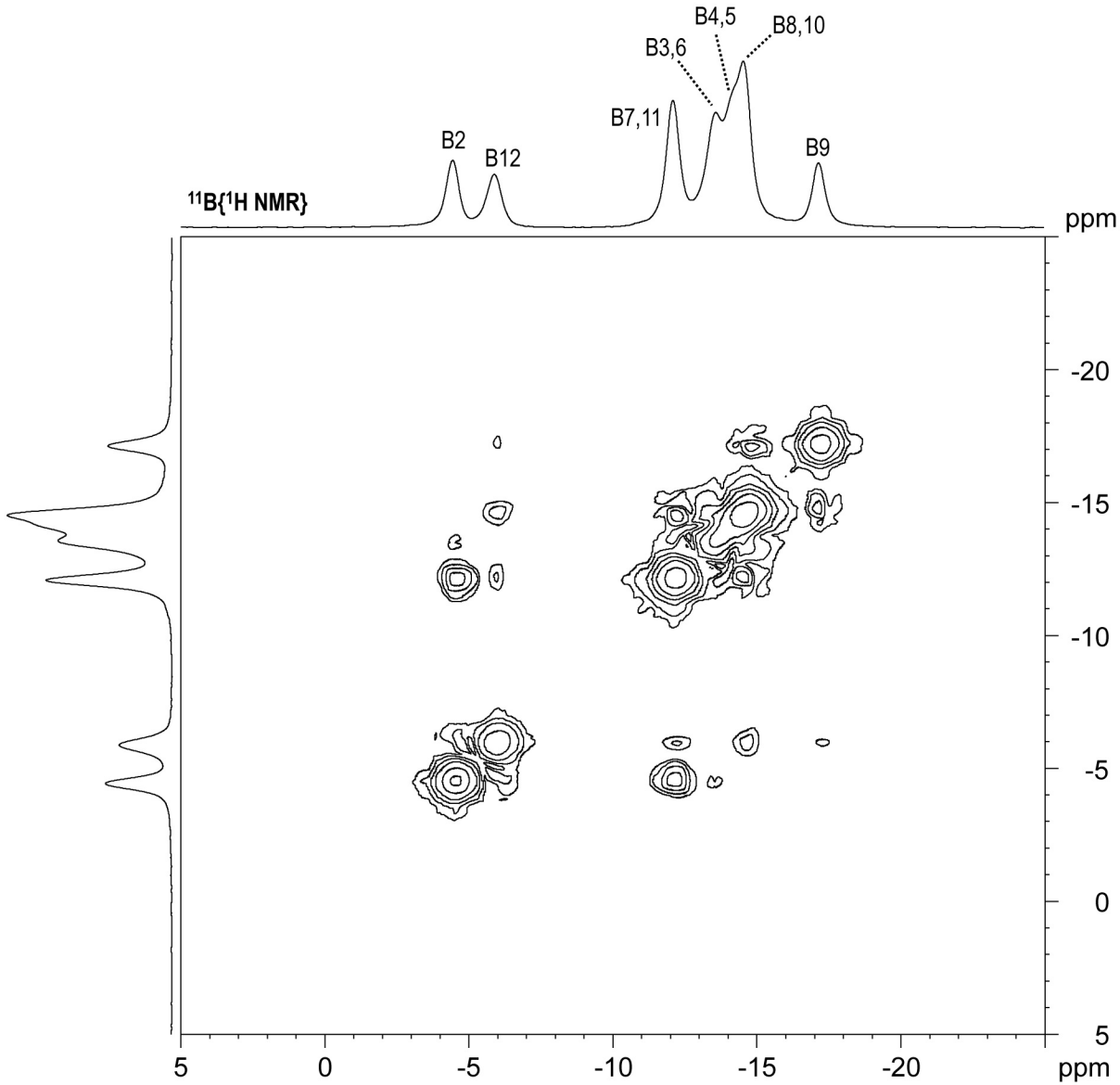
NHTs amide monochlorination product 10 mg in CD3CN
11B{1H} NMR, Bruker 500 MHz, T = 23 C

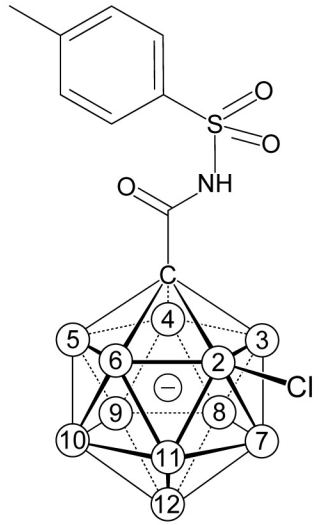



```
Current Data Parameters
NAME      20160714-yjs-tscl
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160714
Time              17.46
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                32048
SOLVENT           CD3CN
NS                  256
DS                    0
SWH           32051.281 Hz
FIDRES         1.000102 Hz
AQ            0.4999488 sec
RG                  203
DW               15.600 usec
DE                6.50 usec
TE                298.9 K
D1           0.50000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                11B
P1                10.00 usec
PLW1        75.00000000 W
SFO1       160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.42750001 W
PLW13        0.27360001 W
SFO2       500.1330885 MHz

F2 - Processing parameters
SI                32768
SF           160.4615993 MHz
WDW                  EM
SSB      0
LB                8.00 Hz
GB       0
PC                1.40
```

NMR17

NHTs amide monochlorination product 10 mg in CD3CN
11B-11B-COSY NMR, Bruker 500 MHz, T = 23 C



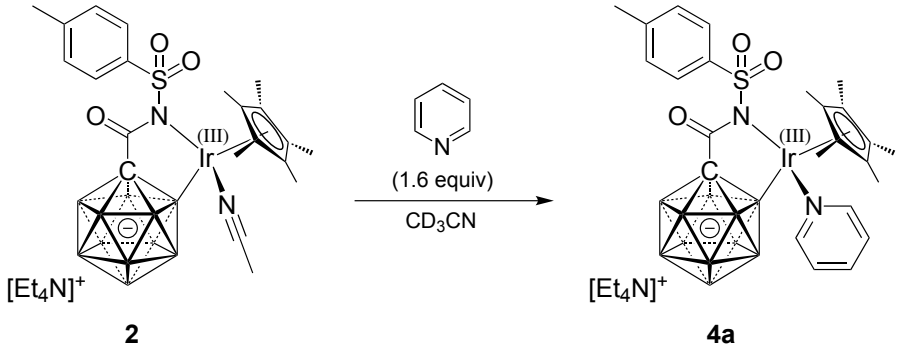


$[Ph_4N]^+$

```
Current Data Parameters
NAME      20160714-yjs-tscl
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160714
Time              17.51
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG     cosygpqfdec
TD                 2566
SOLVENT            CD3CN
NS                    8
DS                   16
SWH            6421.233 Hz
FIDRES         2.502429 Hz
AQ             0.1998059 sec
RG                   203
DW               77.867 usec
DE                6.50 usec
TE                299.1 K
D0             0.00000300 sec
D1             0.30000001 sec
D11            0.03000000 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00015580 sec

======== CHANNEL f1 ========
NUC1                 11B
P0                 13.10 usec
P1                 13.10 usec
PLW1          95.00000000 W
SFO1         160.4604558 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W
SFO2         500.1312000 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1                10.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    64
SFO1            160.4605 MHz
FIDRES        100.287483 Hz
SW                40.000 ppm
FnMODE                QF

F2 - Processing parameters
SI                  4096
SF            160.4616085 MHz
WDW                   EM
SSB       0
LB                20.00 Hz
GB        0
PC                 1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF            160.4615986 MHz
WDW                 SINE
SSB       0
LB        0 Hz
GB        0
```

NMR18

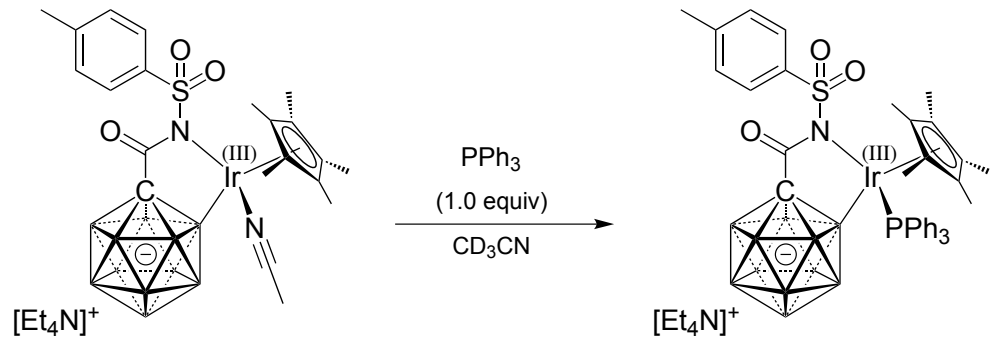
YJS_pub02_20161108_5975, Iridium intermediate + pyridine, ligand exchange
1H{11B} NMR, 500 MHz, CD3CN*



2

4a

YJS_pub02_20161108_5977, Iridium intermediate + PPh3, ligand exchange
1H{11B} NMR, 500 MHz, CD3CN

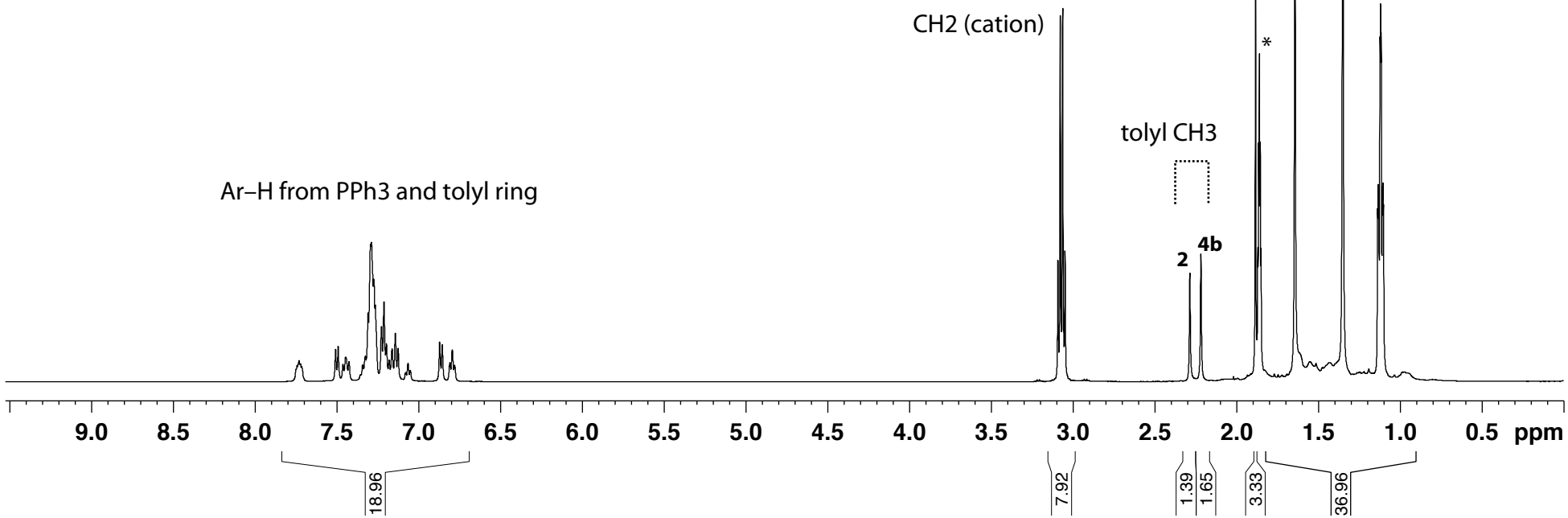


2

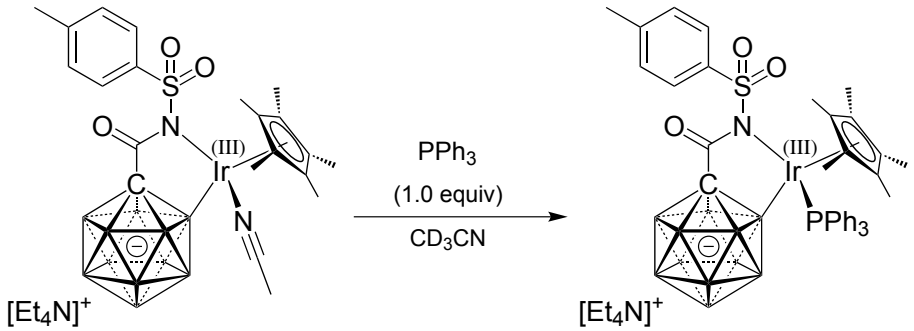
PPh_3
(1.0 equiv)
CD_3CN

ca. 45 : 55
based on integrals
of 1H and 31 P spectra

4b

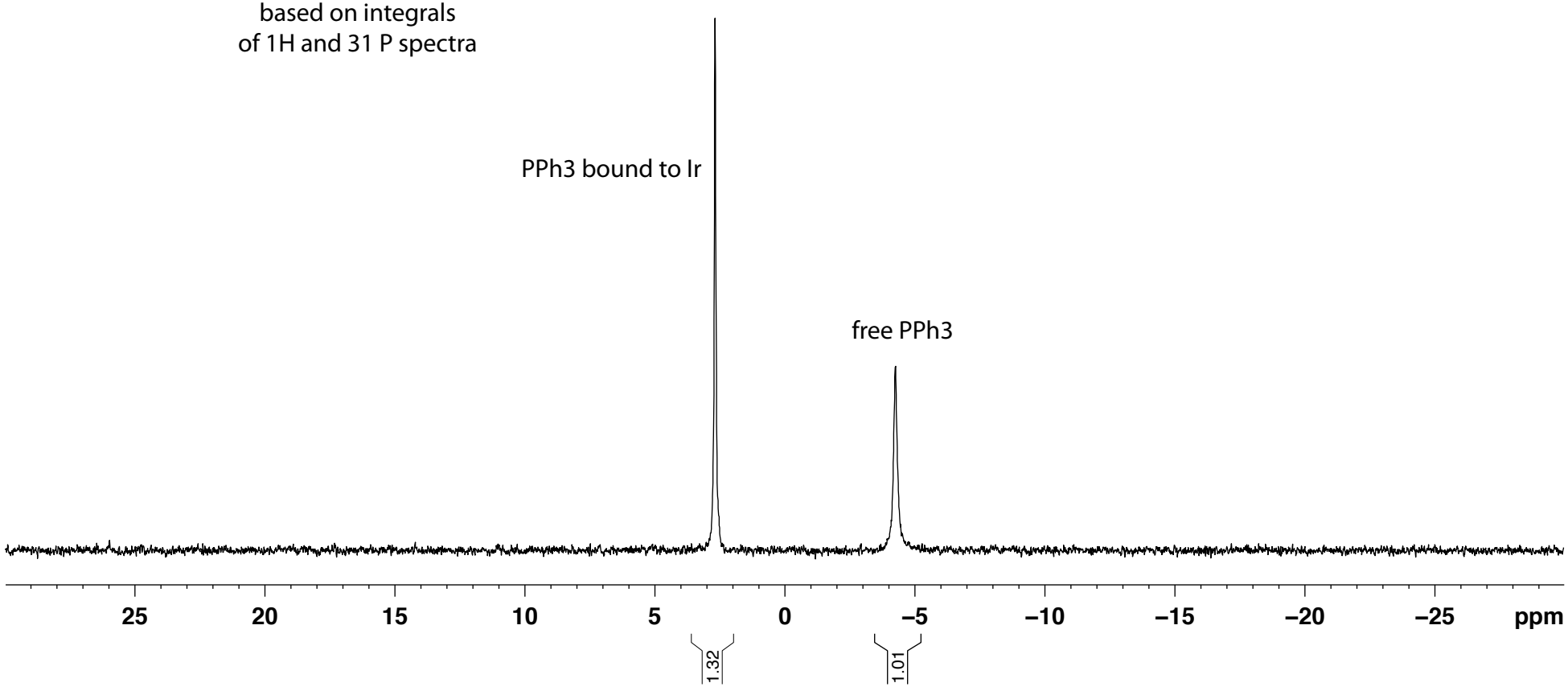


YJS_pub02_20161108_5977, Iridium intermediate + PPh3, ligand exchange
31P{1H} NMR, 202 MHz, CD3CN



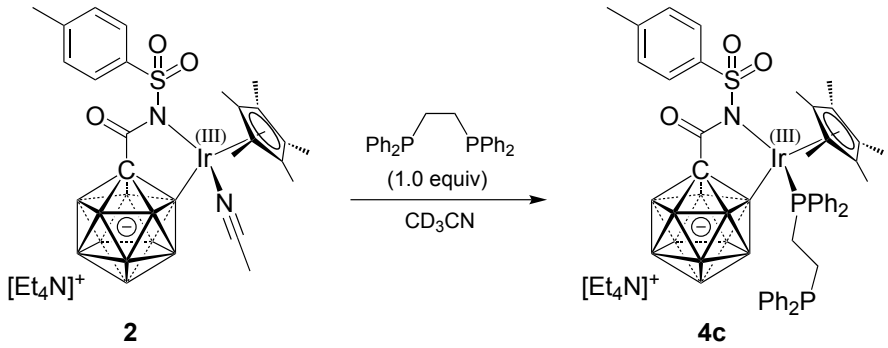
2 **4b**

ca. 45 : 55
based on integrals
of 1H and 31 P spectra



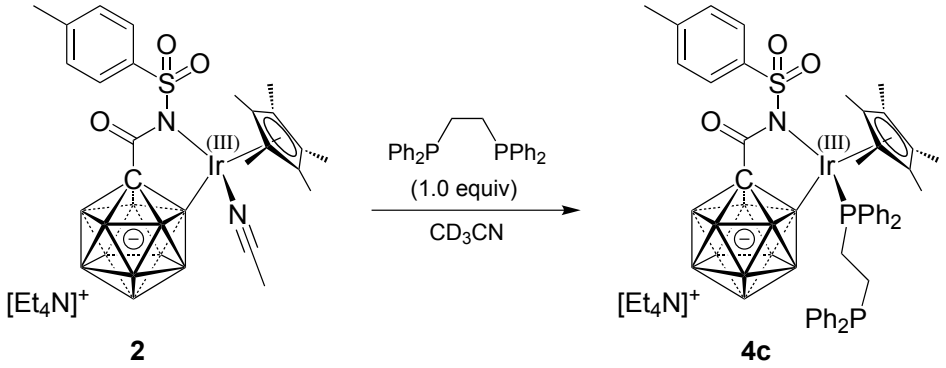
NMR21

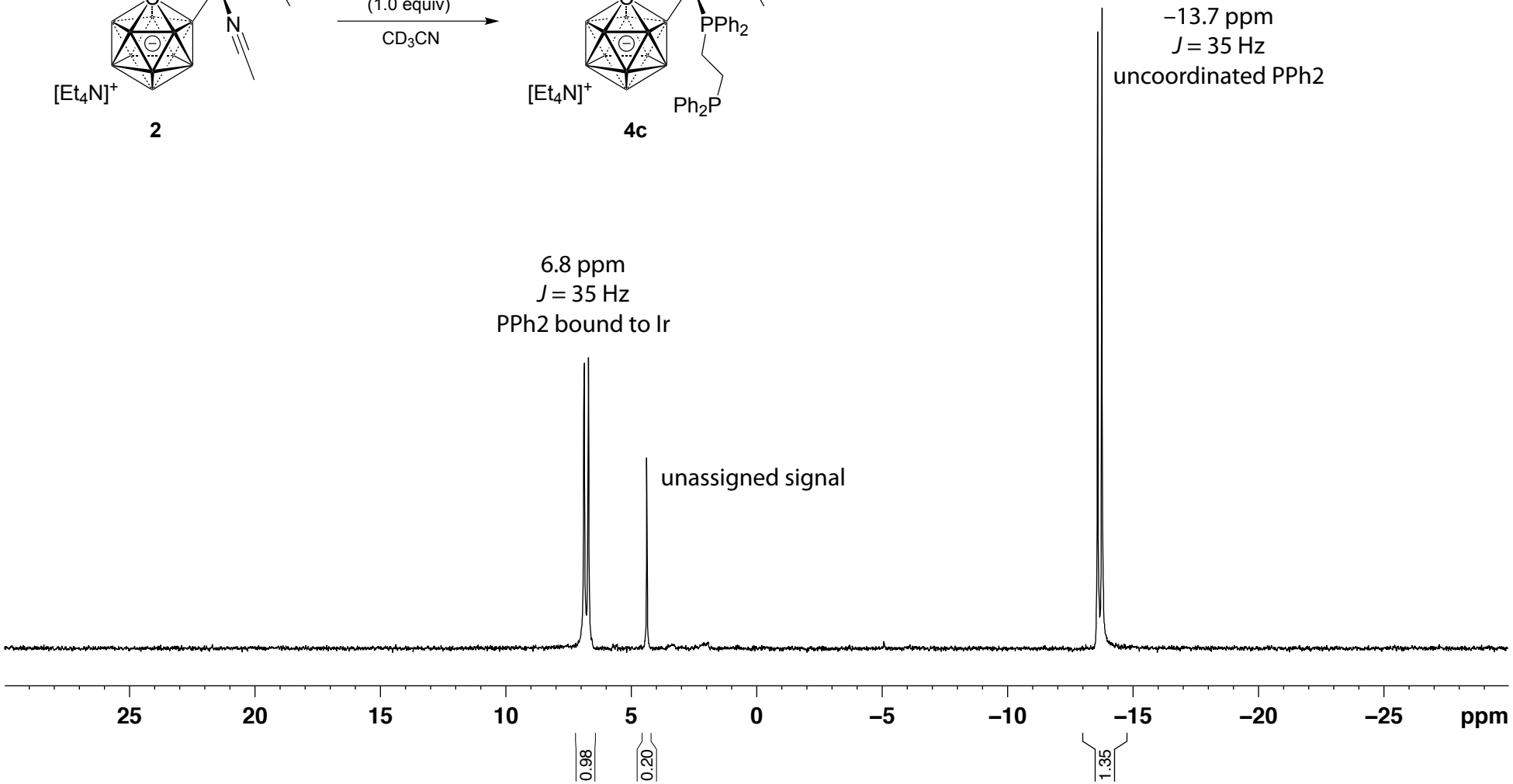
YJS_pub02_20161108_5976, Iridium intermediate + dppe, ligand exchange
1H{11B} NMR, 500 MHz, CD3CN *



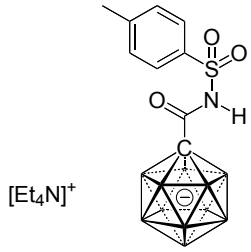
2 **4c**

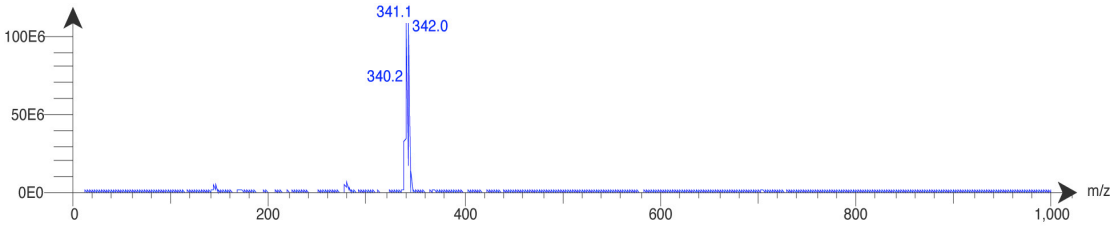
YJS_pub02_20161108_5976, Iridium intermediate + dppe, ligand exchange
31P{1H} NMR, 202 MHz, CD3CN



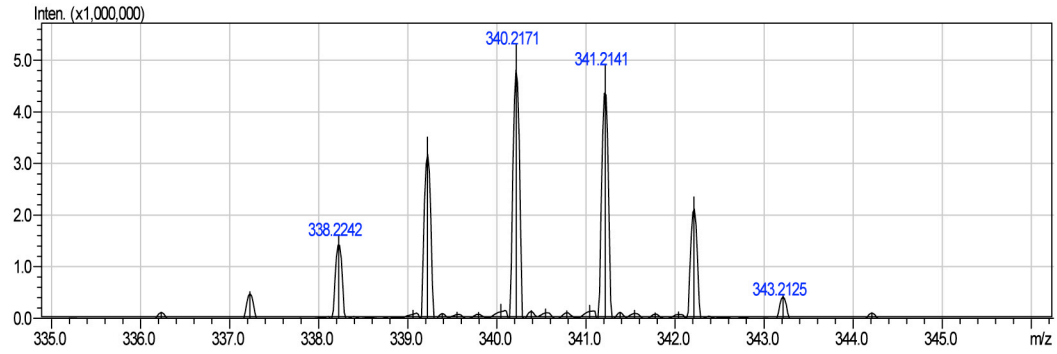


NMR23

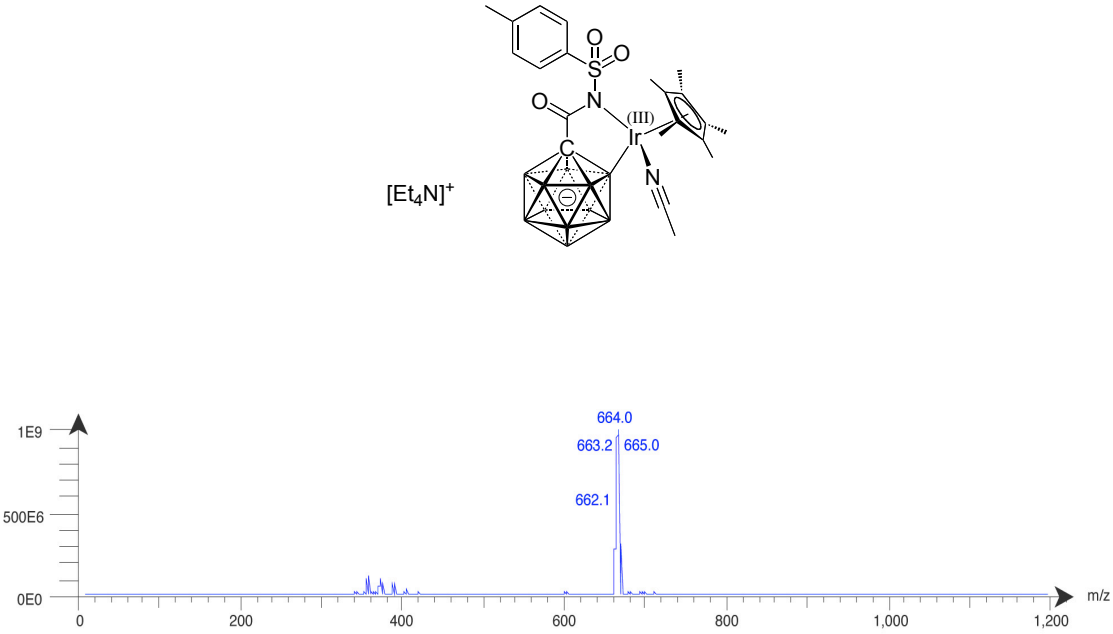




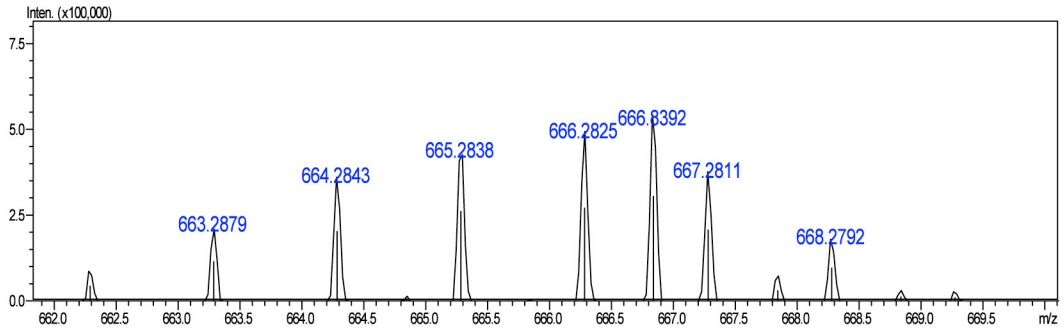
Low-resolution full-range ESI-MS negative mode



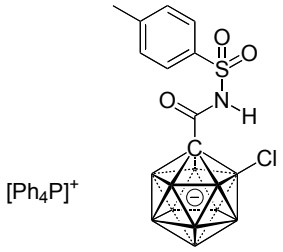
High-resolution ESI-MS negative mode



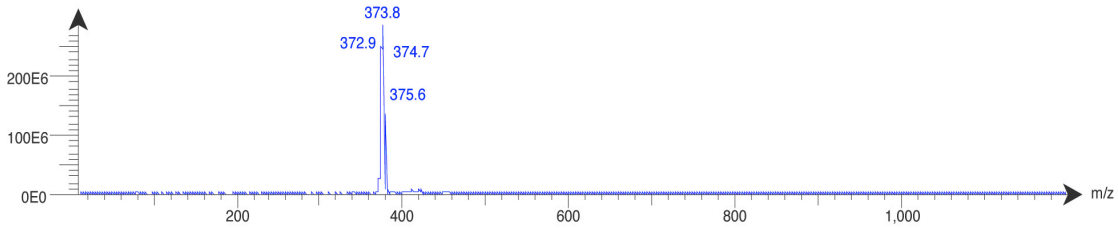
Low-resolution full-range ESI-MS negative mode



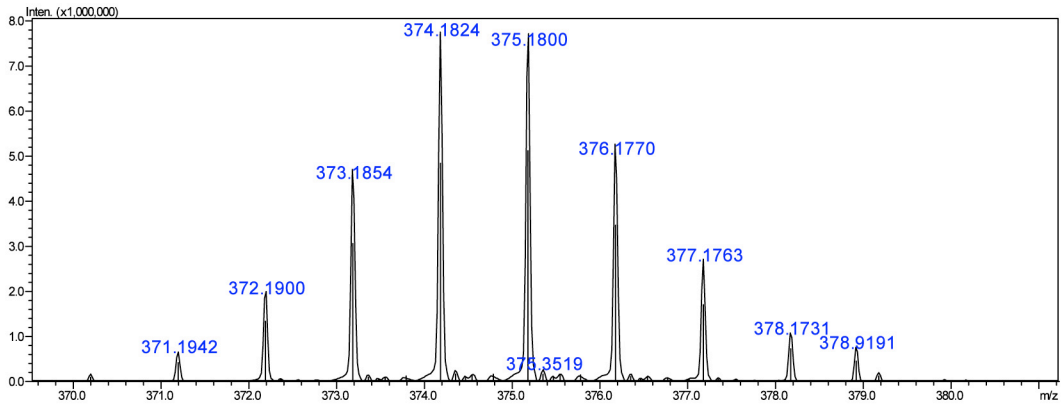
High-resolution ESI-MS negative mode



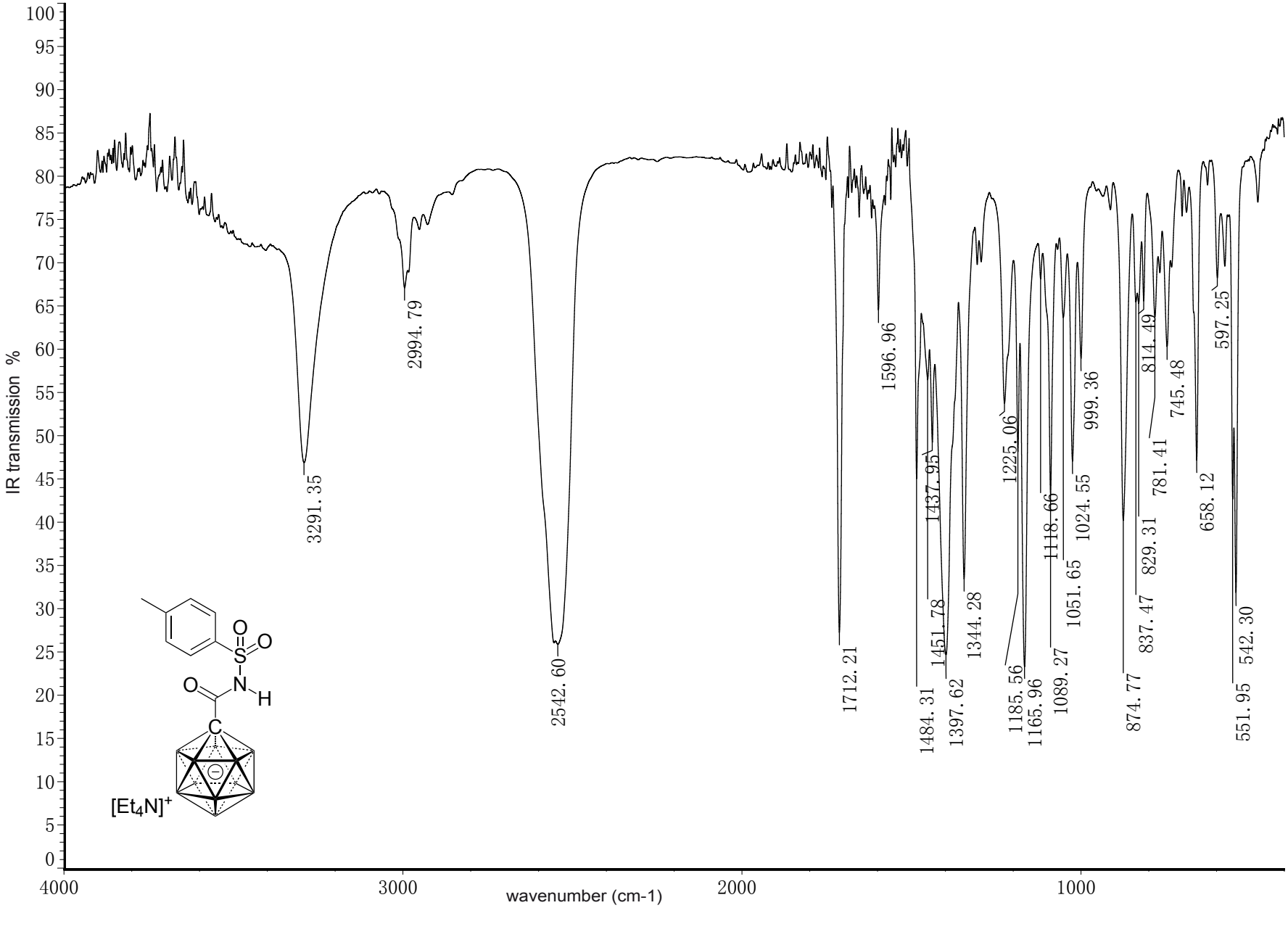
$[Ph_4P]^+$



Low-resolution full-range ESI-MS negative mode



High-resolution ESI-MS negative mode


IR transmission %
wavenumber (cm-1)
4000
3000
2000
1000
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
3291.35
2994.79
2542.60
1712.21
1596.96
1484.31
1451.78
1437.95
1397.62
1344.28
1225.06
1185.56
1165.96
1118.66
1089.27
1051.65
1024.55
999.36
874.77
837.47
829.31
814.49
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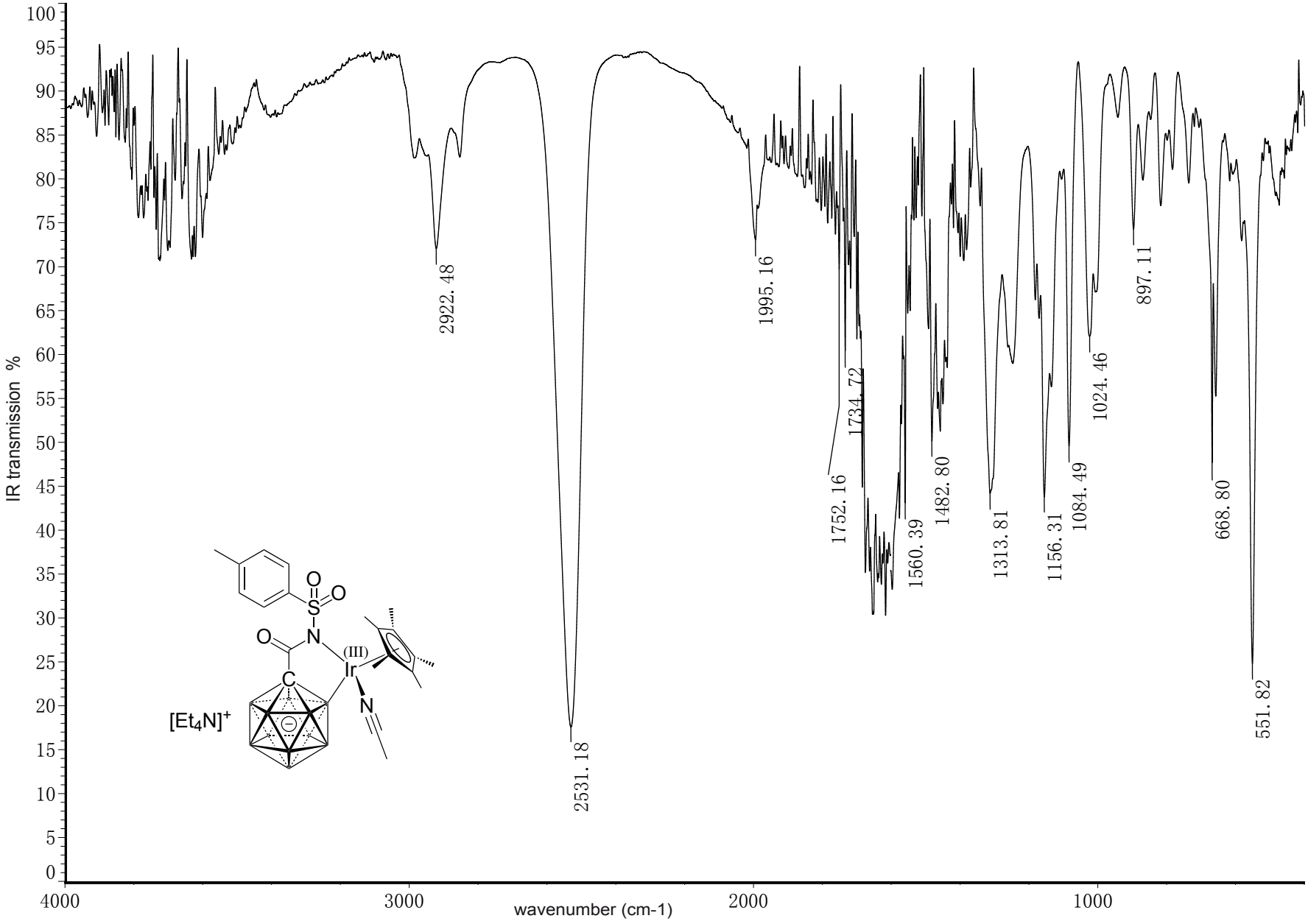
597.25
551.95
542.30
O
O
S
O
N
H
C
[Et4N]+

IR1


IR transmission %
wavenumber (cm-1)
4000
3000
2000
1000
100
95
90
85
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75
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1995. 16
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1734. 72
1560. 39
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1313. 81
1156. 31
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1024. 46
897. 11
668. 80
551. 82
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O
S
O
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(III)
Ir
C
N

IR2