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Diastereoselective Synthesis of Octahedral Cationic Iridium Hydride Complexes with a Stereogenic Metal Centre

by

Nicolas Humbert and Clément Mazet*

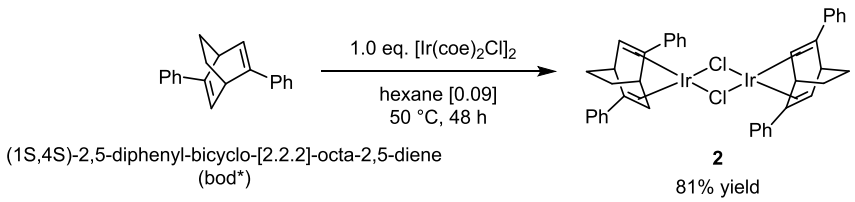
Department of Organic Chemistry, University of Geneva, 30 quai Ernest Ansermet, 1211 Geneva, Switzerland.

Email: clement.mazet@unige.ch

General information

Commercial reagents were purchased from Sigma-Aldrich, Acros Organics or Strem Chemicals and used without purification unless otherwise noted. Air sensitive compounds such as phosphines or metal complexes were stored under inert atmosphere inside a MBraun glovebox. Solvents were dried over activated alumina columns and further degassed by three successive "freeze-pump-thaw" cycles if necessary. Oxazoline ligands **2a-d**,[1] $[Ir(cod)Cl]_2$[2] and $NaBAr_F$[3] were prepared according to literature procedures. All reactions were carried out under an inert atmosphere of nitrogen using either two-manifold vacuum/inert gas lines or a MBraun glovebox unless otherwise noted. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Silicycle. ^{1}H, $^{31}P\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra were recorded on ARX-300, ARX-400 and ARX-500 Bruker Avance spectrometers. ^{1}H and ^{13}C NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. ^{31}P NMR chemical shifts are reported in ppm relative to H_3PO_4. ^{19}F NMR chemical shifts are reported in ppm relative to $CFCl_3$. Data are reported as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constant (Hz) and integration. Melting points were measured on a Büchi Melting Point M-565. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer using neat samples on a diamond ATR Golden Gate sampler. Optical rotations were measured on a Jasco P-1030 polarimeter equipped with a Na-lamp and are reported as follows: $[\alpha]^{T}_{D}$, concentration ($g.mL^{-1}$) and solvent. MALDI spectra were measured using a Brucker Daltonics Autoflex TOF spectrometer.

Synthesis of $[Ir((S,S)\text{-bod*})Cl]_2$



(1S,4S)-2,5-diphenyl-bicyclo-[2.2.2]-octa-2,5-diene (bod*)

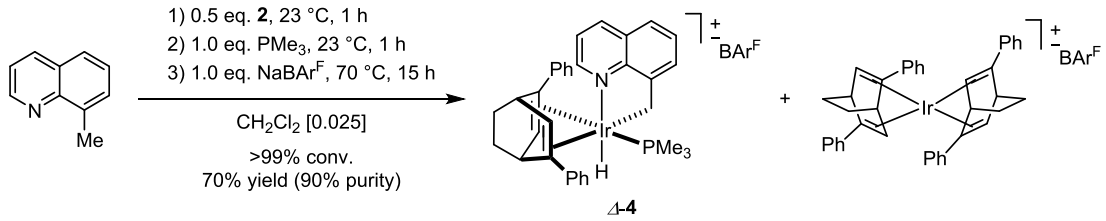
2

81% yield

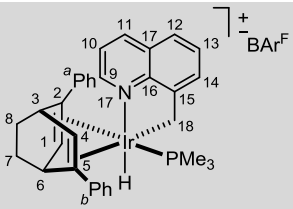
In a Schlenk equipped with a J-Young-valve, (1*S*,4*S*)-2,5-diphenyl-bicyclo-[2.2.2]-octa-2,5-diene (bod*) (1.0 eq., 0.1 mmol) was added to a solution of $[Ir(coe)_2Cl]_2$ (0.5 eq., 0.05 mmol) in degassed hexane (1.0 mL, 0.1 M) at 23 °C. The Schlenk was sealed and placed in a preheated oil bath (50 °C) and stirred for 48 hours. The reaction was cooled to room temperature. The red precipitate obtained

was isolated by filtration and washed with a small amount of hexanes to yield in analytically pure form (68% yield). All analyses were in agreement with those reported in the literature.[4]

Synthesis of *Δ*-4



In a Schlenk equipped with a J-Young-valve, 8-methylquinoline (1.0 eq., 7.0 μL, 0.051 mmol) was added to a solution of **2** (0.5 eq., 25 mg, 0.026 mmol) in degassed CH_2Cl_2 (1.0 mL, 0.025 M) at 23 °C. The reaction was stirred for one hour and then brought into a glove box. Trimethylphosphine (1.0 eq., 5.3 μL, 0.051 mmol) was then added in one portion and the resulting solution stirred for one hour under inert atmosphere. Outside of the glove box, in open-air, $NaBAr_F$ (1.0 eq., 47 mg, 0.51 mmol) was added to the mixture and the resulting suspension vigorously stirred for 15 hours at 70 °C. The reaction was cooled down to room temperature before evaporation of the solvent under reduced pressure. The crude mixture was purified by column chromatography (eluent: CH_2Cl_2; R_f = 0.9). A purple, air-stable solid was obtained (56 mg, 70% yield). The product was obtained along with ca. 10% of $[Ir(cod)_2]BAr_F$.



***Δ*-4**

Purple solid.

Yield = 70% (90% purity).

dr >30:1

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.42 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H-9), 8.13 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H-11), 7.73 (m, 9H, *o*-H_{BArF}, $H_{Ph\text{-}b}$), 7.52 (m, 4H, *p*-H_{BArF}), 7.48 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 5.0 Hz, 1H, H-10), 7.38–7.45 (m, 4H, $H_{Ph\text{-}b}$), 7.25 (m, 1H, H-12), 7.21 (m, 2H, H-13,14), 6.66 (m, 1H, $H_{Ph\text{-}a}$), 6.50 – 6.60 (m, 4H, $H_{Ph\text{-}a}$), 5.59 (ddd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, H-1), 4.65 (m, 1H, H-6), 4.59 (m, 2H, H-3,4), 3.23 (dd, $^2J_{HH}$ = 16.9 Hz, $^3J_{HP}$ = 7.5 Hz, 1H, H-18), 2.61 (d, $^3J_{HP}$ = 16.8 Hz, 1H, H-18), 1.47–1.52 (m, 1H, H-8), 1.34–1.39 (m, 1H, H-8), 1.17–1.23 (m, 2H, H-7), 0.57 (d, $^2J_{HP}$ = 10.9 Hz, 9H, H_{PMe3}) [for the other isomer: 0.98 (d, $^2J_{HP}$ = 10.6 Hz, 9H, H_{PMe3})], −15.86 (d, $^2J_{HP}$ = 15.4 Hz, 1H, Ir–H) [for the other isomer: –16.46 (d, $^2J_{HP}$ = 20.8 Hz, 1H, Ir–H).].

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ (ppm) = 161.70 (1:1:1:1 patern, $^1J_{CB}$ = 49.5 Hz, *ipso*-C-B_{BArF}), 152.37 (s, C-9), 150.03 (s, C-16), 148.68 (s, C-15), 139.04 (s, C-11), 136.66 (s, $C^{IV}_{Ph\text{-}b}$), 134.80 (bs, *o*-C_{BArF}), 132.84 (s, C-14), 129.98 (s, C-17), 129.61 (s, $C_{Ph\text{-}b}$), 129.28 (s, $2C_{Ph\text{-}b}$), 129.11 (s, $C_{Ph\text{-}a}$), 128.91 (qq, $^2J_{CF}$ = 31.4 Hz, $^5J_{CF}$ = 2.8 Hz, *m*-C_{BArF}), 128.65 (s, C-13), 128.47 (s, $C^{IV}_{Ph\text{-}a}$), 127.67 (s, $2C_{Ph\text{-}a}$), 126.26 (s, $C_{Ph\text{-}b}$), 124.91 (s, C-12), 124.54 (q, $^1J_{CF}$ = 270.9 Hz, C_{CF3}), 123.53 (bs, $2C_{Ph\text{-}a}$), 123.02 (s, C-10), 117.38–117.54 (m, *p*-C_{BArF}), 97.04 (s, C-5), 95.59 (d, $^2J_{CP}$ = 12.2 Hz, C-2), 72.49 (d, $^2J_{CP}$ = 11.3 Hz, C-1), 64.24 (s, C-4), 47.77 (d, $^3J_{CP}$ = 0.8 Hz, C-6), 36.60 (d, $^3J_{CP}$ = 2.4 Hz, C-3), 30.73 (d, $^4J_{CP}$ = 2.3 Hz, C-6), 28.86 (d, $^3J_{CP}$ = 1.5 Hz, C-7), 13.97 (d, $^1J_{CP}$ = 40.5 Hz, C_{PMe3}), 7.65 (d, $^2J_{CP}$ = 4.4 Hz, C-18).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ = −30.81 [for the minor isomer: −35.49]

$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 298 K): δ = –61.61 (s).

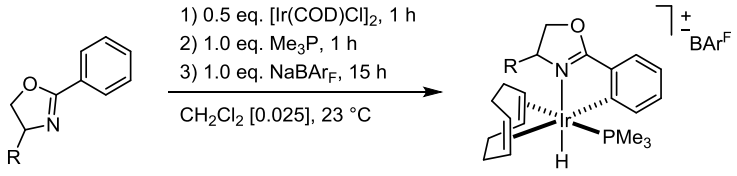
HR-MS (MALDI TOF) $C_{33}H_{36}IrNP$ $[M]^+$: 670.221, found 670.319.

IR: ν [cm^{-1}] = 1354, 1274, 1121, 952, 885, 837, 713, 676.

$[\alpha]^{20}_D$: +14.2 (c 0.1, CH_2Cl_2).

T_{decomp}: 55 °C.

General procedure for the synthesis of iridium hydride complexes with ligands 2a,c-d

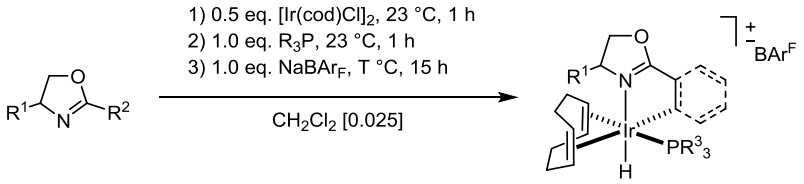


2a,c-d

6a,c-d

2a: R = Ph
2c: R = *i*-Pr
2d: R = *t*-Bu

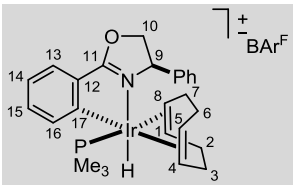
General procedure: In a Schlenk equipped with a J-Young-valve, the appropriate oxazoline precursor (1.0 eq., 0.15 mmol) was added to a solution of $[Ir(cod)Cl]_2$ (0.5 eq., 50 mg, 0.07 mmol) in degassed CH_2Cl_2 (3.0 mL, 0.025 M) at 23 °C. The reaction was stirred for one hour and then brought into a glove box. The phosphine (1.0 eq., 0.15 mmol) was then added in one portion and the resulting solution stirred for one hour under inert atmosphere. Outside of the glove box, in open-air, $NaBAr_F$ (1.0 eq., 139 mg, 0.16 mmol) was added to the mixture and the resulting suspension vigorously stirred for 15 hours at 70 °C. After evaporation of the solvent under reduced pressure, the crude mixture was purified by column chromatography (CH_2Cl_2:pentane 1:1).



5a-d **6a-d**

Entry	Ligand	R^1	R^2	R_3P	T (°C)	Products	Yield (%)	*dr* (Λ:Δ) [a,b]
1	(*R*)-**5a**	Ph	Ph	Cy_3P	70	(*R*)-Λ-**6a**/(*R*)-Δ-**6a**	*nr*[c]	-
2	(*R*)-**5a**	Ph	Ph	Me_3P	23	(*R*)-Λ-**6a**/(*R*)-Δ-**6a**	43	1.4:1 (2.9:1)
3	(*R*)-**5a**	Ph	Ph	Me_3P	70	(*R*)-Λ-**6a**/(*R*)-Δ-**6a**	78	5.5:1 (12:1)
4	(*R*)-**5b**	Ph	*t*-Bu	Me_3P	70	(*R*)-Λ-**6b**/(*R*)-Δ-**6b**	*nr*	-
5	(*S*)-**5c**	*i*-Pr	Ph	Me_3P	23	(*R*)-Λ-**6c**/(*R*)-Δ-**6c**	65	2.7:1
6	(*S*)-**5c**	*i*-Pr	Ph	Me_3P	70	(*R*)-Λ-**6c**/(*R*)-Δ-**6c**	86	1:9
7	(*S*)-**5d**	*t*-Bu	Ph	Me_3P	23	(*R*)-Λ-**6d**/(*R*)-Δ-**6d**	57	1:>30
8	(*S*)-**5d**	*t*-Bu	Ph	Me_3P	70	(*R*)-Λ-**6d**/(*R*)-Δ-**6d**	96	1:>30

[a] Determined by ^{1}H NMR of the crude reaction mixture. [b] The ratio in brackets was obtained after purification by column chromatography. [c] *nr* = no reaction.



(*R*)-*Λ*-6a

Light-brown solid.

Yield = 78%.

dr 5.5:1 (crude); 12:1 (after column)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.70 (m, 8H, *o*-H_{BArF}), 7.52 (m, 6H, H-13,16, *p*-H_{BArF}), 7.40 (s, 5H, H_{Ph}), 7.24 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H-15), 7.17 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H-14), 5.37 (dd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 4.4 Hz, 1H, H-9), 5.24 (dd, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 9.6 Hz, 1H, H-10), 5.12 (dd, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 4.2 Hz, 1H, H-10), 4.99 (m, 1H, H-1), 4.53 (m, 1H, H-5), 4.46 (m, 1H, H-4), 3.46 (m, 1H, H-8), 3.16 (dd, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, H-3), 2.87 (m, 1H, H-7), 2.67 (m, 1H, H-6), 2.40–2.59 (m, 3H, H-2,3,7), 2.08 (m, 1H, H-6), 1.81 (m, 1H, H-2), 0.69 (d, $^2J_{HP}$ = 10.4 Hz, 9H, H_{PMe3}), –15.90 (d, $^2J_{HP}$ = 15.6 Hz, 1H, Ir–H). [for the minor isomer: −16.58 (d, $^2J_{HP}$ = 14.8 Hz, 1H, Ir–H).]

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ (ppm) = 178.59 (s, C-11), 161.68 (1:1:1:1 pattern, $^1J_{CB}$ = 49.6 Hz, *ipso*-C_{BArF}), 153.03 (d, $^2J_{CP}$ = 8.6 Hz, C-17), 139.78 (s, C-16), 139.45 (s, *ipso*-C_{Ph}), 135.29 (s, C-15), 134.79 (bs, *o*-C_{BArF}), 130.13 (s, *o*-C_{Ph}), 129.10 (s, C-13), 129.09 (s, C-12), 128.88 (qq, $^2J_{CF}$ = 31.3 Hz, $^5J_{CF}$ = 2.9 Hz, *m*-C_{BArF}), 127.82 (s, *m*-C_{Ph}), 127.01 (s, *p*-C_{Ph}), 124.53 (q, $^1J_{CF}$ = 270.9 Hz, C_{CF3}), 124.15 (s, C-14), 117.41–117.49 (m, *p*-C_{BArF}), 95.77 (d, $^2J_{CP}$ = 10.5 Hz, C-1), 93.55 (d, $^2J_{CP}$ = 15.1 Hz, C-8), 87.31 (s, C-4),

80.23 (s, C-5), 78.45 (s, C-10), 69.35 (s, C-9), 36.89 (d, $^4J_{CP}$ = 3.5 Hz, C-3), 31.51 (d, $^3J_{CP}$ = 1.9 Hz, C-7), 28.53 (s, C-2), 27.30 (d, $^4J_{CP}$ = 2.8 Hz, C-6), 14.54 (d, $^1J_{CP}$ = 40.1 Hz, C_{PMe3}).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ = –36.60 (bs). [for the minor isomer: −33.59 (bs).]

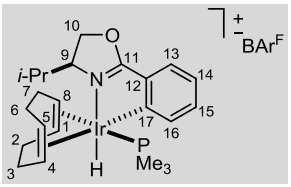
$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 298 K): δ = –61.63 (s).

HR-MS (MALDI TOF) $C_{26}H_{34}IrNOP$ $[M]^+$: 600.200, found 600.366.

IR: ν [cm^{-1}] = 3282, 2947, 2222, 1613, 1550, 1484, 1460, 1406, 1354, 1272, 1159, 1116, 1047, 946, 887, 837, 761, 740, 710, 680, 668.

$[\alpha]^{20}_D$: –51.3 (c 1.0, CH_2Cl_2).

T.dec.: 147 °C.



(*S*)-Δ-6c

Light-brown solid.

Yield = 86%.

dr = 9:1

^1H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.70 (m, 8H, *o*-H_{BArF}), 7.53 (m, 6H, H-13,16, *p*-H_{BArF}), 7.24 (ddd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H-15), 7.13 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H-14), 5.02 (m, 1H, H-1), 4.83 (dd, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H-10), 4.76 (t, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, H-10), 4.65 (m, 1H, H-4), 4.58 (m, 1H, H-5), 4.40 (ddd, $^3J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 2.4 Hz, 1H, H-9), 3.40 (m, 1H, H-8), 2.93 (m, 1H, H-3), 2.38 – 2.66 (m, 5H, H-2,3,6,7,7), 2.19 (m, 1H, H-6), 2.03 (m, 2H, H-2, C$H_{i\text{-}Pr}$), 1.21 (d, $^2J_{HP}$ = 10.4 Hz, 9H, H_{PMe3}), 1.06 (d, $^3J_{HH}$ = 7.2 Hz, 3H, $H_{i\text{-}Pr}$), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $H_{i\text{-}Pr}$), –15.85 (d, $^2J_{HP}$ = 17.2 Hz, 1H, Ir–H). [for the minor isomer: −16.34 (d, $^2J_{HP}$ = 14.4 Hz, 1H, Ir–H).]

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ (ppm) = 178.72 (s, C-11), 161.68 (1:1:1:1 pattern, $^1J_{CB}$ = 49.5 Hz, *ipso*-C_{BArF}), 151.95 (d, $^2J_{CP}$ = 8.9 Hz, C-17), 139.80 (s, C-16), 135.09 (s, C-15), 134.77 (bs, *o*-C_{BArF}), 129.41 (s, C-12), 129.26 (s, C-13), 128.88 (qq, $^2J_{CF}$ = 31.3 Hz, $^5J_{CF}$ = 2.8 Hz, *m*-C_{BArF}), 124.53 (q, $^1J_{CF}$ = 270.9 Hz, C_{CF3}), 124.17 (s, C-14), 117.38–117.54 (m, *p*-C_{BArF}), 96.37 (d, $^2J_{CP}$ = 10.1 Hz, C-1), 94.27 (d, $^2J_{CP}$ = 15.8 Hz, C-8), 87.17 (s, C-4), 81.05 (s, C-5), 70.49 (s, C-10), 70.36 (s, C-9), 35.43 (d, $^4J_{CP}$ = 3.3 Hz, C-3), 30.50 (s, *C*$H_{i\text{-}Pr}$), 30.44 (d, $^3J_{CP}$ = 2.0 Hz, C-7), 30.16 (d, $^3J_{CP}$ = 0.9 Hz, C-2), 28.16 (d, $^3J_{CP}$ = 3.3 Hz, C-6), 20.40 (s, $Me_{i\text{-}Pr}$), 15.67 (d, $^1J_{CP}$ = 39.8 Hz, C_{PMe3}), 14.86 (s, $Me_{i\text{-}Pr}$).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ = –38.02 (bs). [for the minor isomer: −33.00 (bs).]

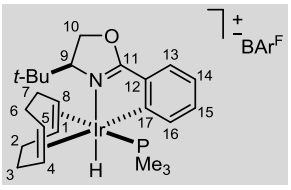
$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$, 298 K): δ = –61.62 (s).

HR-MS (MALDI TOF) $C_{23}H_{36}IrNOP$ $[M]^+$: 566.216, found 566.352.

IR: ν [cm^{-1}] = 2966, 2239, 1616, 1548, 1461, 1393, 1354, 1272, 1159, 1116, 1047, 951, 887, 838, 739, 713, 681, 668.

$[\alpha]^{20}_D$: +50.3 (c 1.0, CH_2Cl_2).

T_{decomp}: 162 °C.



(*S*)-Δ-6d

Light-brown solid.

Yield = 96%.

dr >30:1

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.70 (m, 8H, *o*-H_{BArF}), 7.52 (m, 6H, H-13,16, *p*-H_{BArF}), 7.27 (ddd, $^{3}J_{HH}$ = 7.2 Hz, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 0.8 Hz, 1H, H-15), 7.14 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-14), 5.01 (m, 1H, H-1), 4.95 (dd, $^{2}J_{HH}$ = 9.6 Hz, $^{3}J_{HH}$ = 2.8 Hz, 1H, H-10), 4.88 (m, 1H, H-4), 4.70 (m, 1H, H-5), 4.67 (dd, $^{2}J_{HH}$ = 9.2 Hz, $^{3}J_{HH}$ = 9.2 Hz, 1H, H-10), 4.05 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{3}J_{HH}$ = 2.6 Hz, 1H, H-9), 3.32 (m, 1H, H-8), 2.83 (m, 1H, H-3), 2.34–2.66 (m, 5H, H-2,3,6,7,7), 2.24 (m, 1H, H-6), 2.08 (m, 1H, H-2), 1.33 (d, $^{2}J_{HP}$ = 10.4 Hz, 9H, H_{PMe3}), 1.04 (s, 9H, $H_{t\text{-}Bu}$), –17.55 (d, $^{2}J_{HP}$ = 18.8 Hz, 1H, Ir–H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ (ppm) = 180.39 (s, C-11), 161.69 (1:1:1:1 pattern, $^{1}J_{CB}$ = 49.2 Hz, *ipso*-C_{BArF}), 150.15 (d, $^{2}J_{CP}$ = 9.5 Hz, C-17), 140.15 (s, C-16), 134.98 (s, C-15), 134.77 (bs, *o*-C_{BArF}), 130.10 (s, C-12), 129.50 (s, C-13), 128.89 (qq, $^{2}J_{CF}$ = 31.3 Hz, $^{5}J_{CF}$ = 2.8 Hz, *m*-C_{BArF}), 124.53 (q, $^{1}J_{CF}$ = 270.9 Hz, C_{CF3}), 124.19 (s, C-14), 117.38–117.53 (m, *p*-C_{BArF}), 98.38 (d, $^{2}J_{CP}$ = 10.0 Hz, C-1), 96.77 (d, $^{2}J_{CP}$ = 15.9 Hz, C-8), 89.92 (s, C-4), 84.21 (s, C-5), 74.07 (s, C-9), 73.26 (s, C-10), 35.20 (s, $C^{IV}_{t\text{-}Bu}$), 35.03 (d, $^{4}J_{CP}$ = 3.1 Hz, C-3), 30.38 (d, $^{3}J_{CP}$ = 1.1 Hz, C-2), 30.10 (d, $^{3}J_{CP}$ = 2.0 Hz, C-7), 28.02 (d, $^{4}J_{CP}$ = 3.3 Hz, C-6), 26.19 (s, $Me_{t\text{-}Bu}$), 15.65 (d, $^{1}J_{CP}$ = 40.1 Hz, C_{PMe3}).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ = –38.69 (bs)

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 298 K): δ = –61.61 (s).

HR-MS (MALDI TOF) $C_{24}H_{38}IrNOP$ $[M–COD]^+$: 472.138, found 471.981.

IR: ν [cm^{-1}] = 2969, 2260, 1610, 1547, 1486, 1395, 1354, 1272, 1159, 1117, 1047, 949, 887, 838, 740, 713, 681, 668.

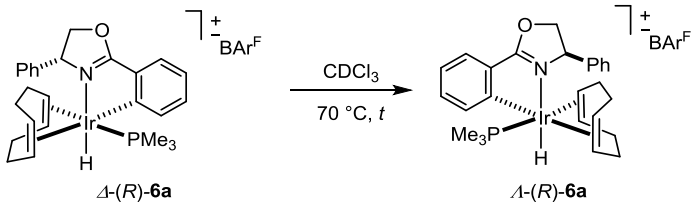
$[\alpha]^{20}_{D}$: +57.7 (c 1.0, CH_2Cl_2).

T_{decomp}: 163 °C.

Inversion of configuration at the metal-centre

A J-Young-valve NMR tube was charged with the appropriate iridium complex (20 mg). Next, 1.0 mL of $CDCl_3$ was added at room temperature. The tube was then placed into a pre-heated oil bath (70 °C). The mixture was cooled to room temperature before recording ^1H NMR experiments periodically to quantify the ratio between the two diastereoisomers.

A

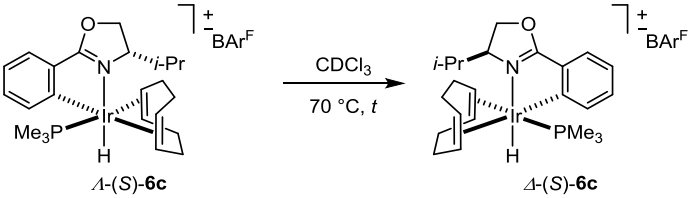


Δ-(*R*)-**6a** → Λ-(*R*)-**6a**

Entry	*t* *(h)*	dr[a] *(Λ:Δ)*
1	0	2.9:1
2	15	7.8:1
3	35	16.4:1
4	55	19.5:1
5	123	24.3:1
6	143	25:1

[a] Determined by ^1H NMR.

B

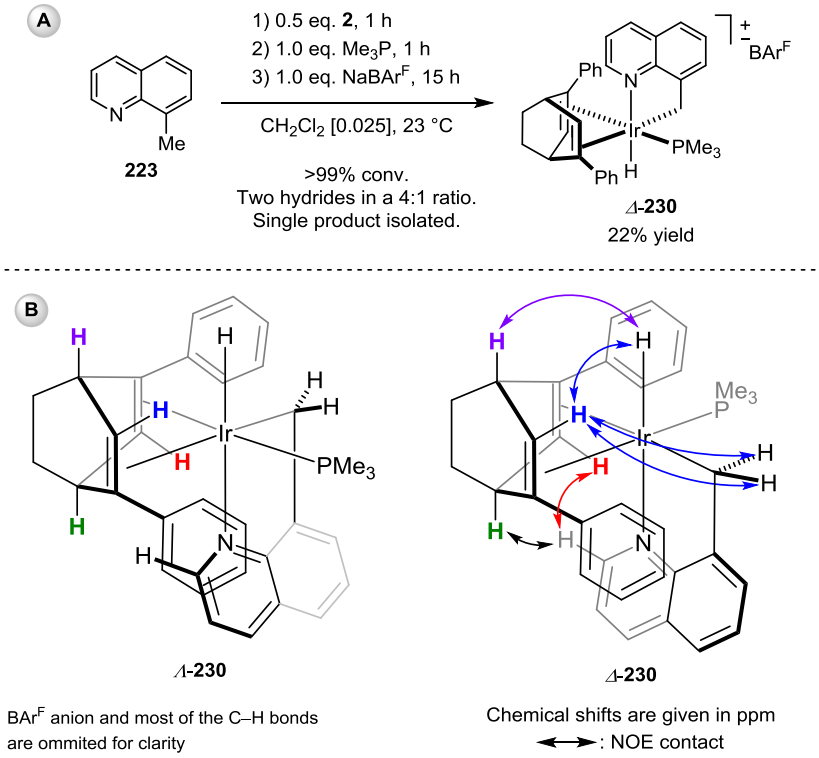


Λ-(*S*)-**6c** → Δ-(*S*)-**6c**

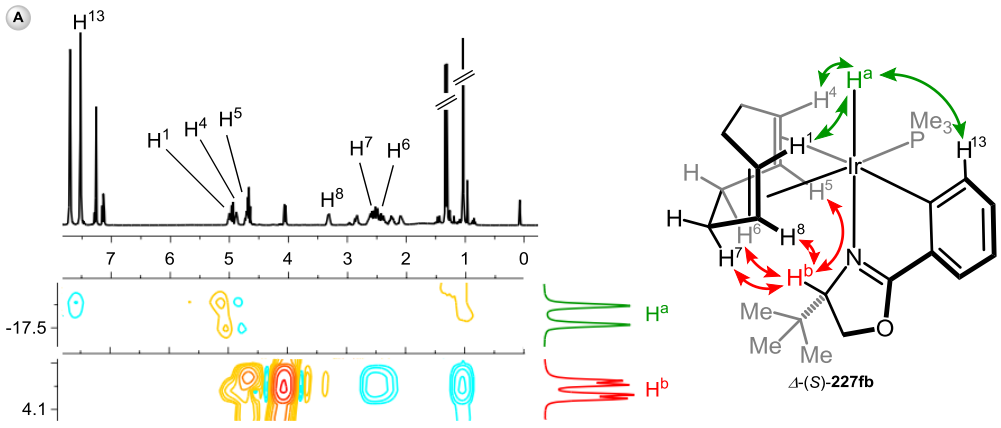
Entry	*t* *(h)*	dr[a] *(Λ:Δ)*
1	0	2.7:1
2	15	1:7.2
3	35	1:10.7
4	55	1:11.3
5	123	1:11.3

[a] Determined by ^1H NMR.

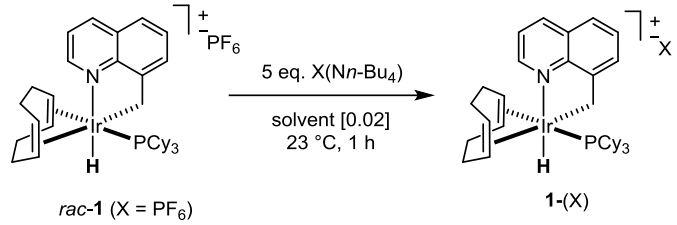
Key nOe contacts in (*S*)-Δ-4



Sections of the NOESY spectrum for (*S*)-Δ-6d



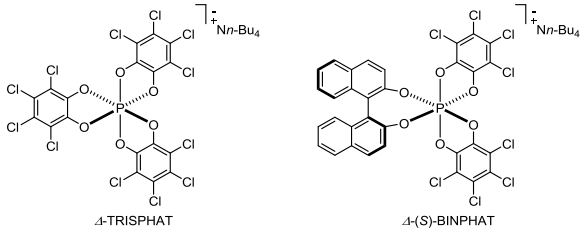
Reaction of *rac*-1 (PF_6) with chiral anions analysed by ^{1}H NMR



rac-**1** (X = PF_6) **1**-(X)

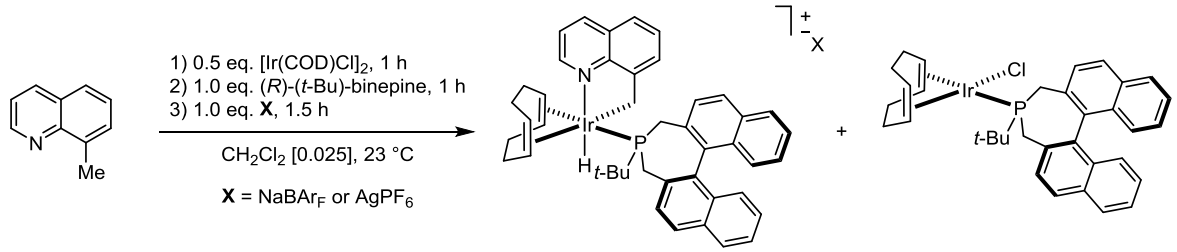
^{1}H NMR: δ($CDCl_3$) = –15.97 ppm (d, *J* = 16.2 Hz)

Entry	X(N*n*-Bu_4)	Solvent	Observation in ^{1}H NMR
1	*Δ*-**TRISPHAT**	$CDCl_3$	No change
2	*Δ*-(*S*)-**BINPHAT**	$CDCl_3$	δ = –16.01 ppm (d, *J* = 16.4 Hz); –16.02 ppm (d, *J* = 15.6 Hz)
3	*Δ*-**TRISPHAT**	toluene-d_8	No change
4	*Δ*-(*S*)-**BINPHAT**	toluene-d_8	δ = –16.30 ppm (m)



Δ-TRISPHAT *Δ*-(*S*)-BINPHAT

Attempt to synthesise an analogue of complex 1 using a chiral monodentate *binepine* ligand



not observed 51% yield

References

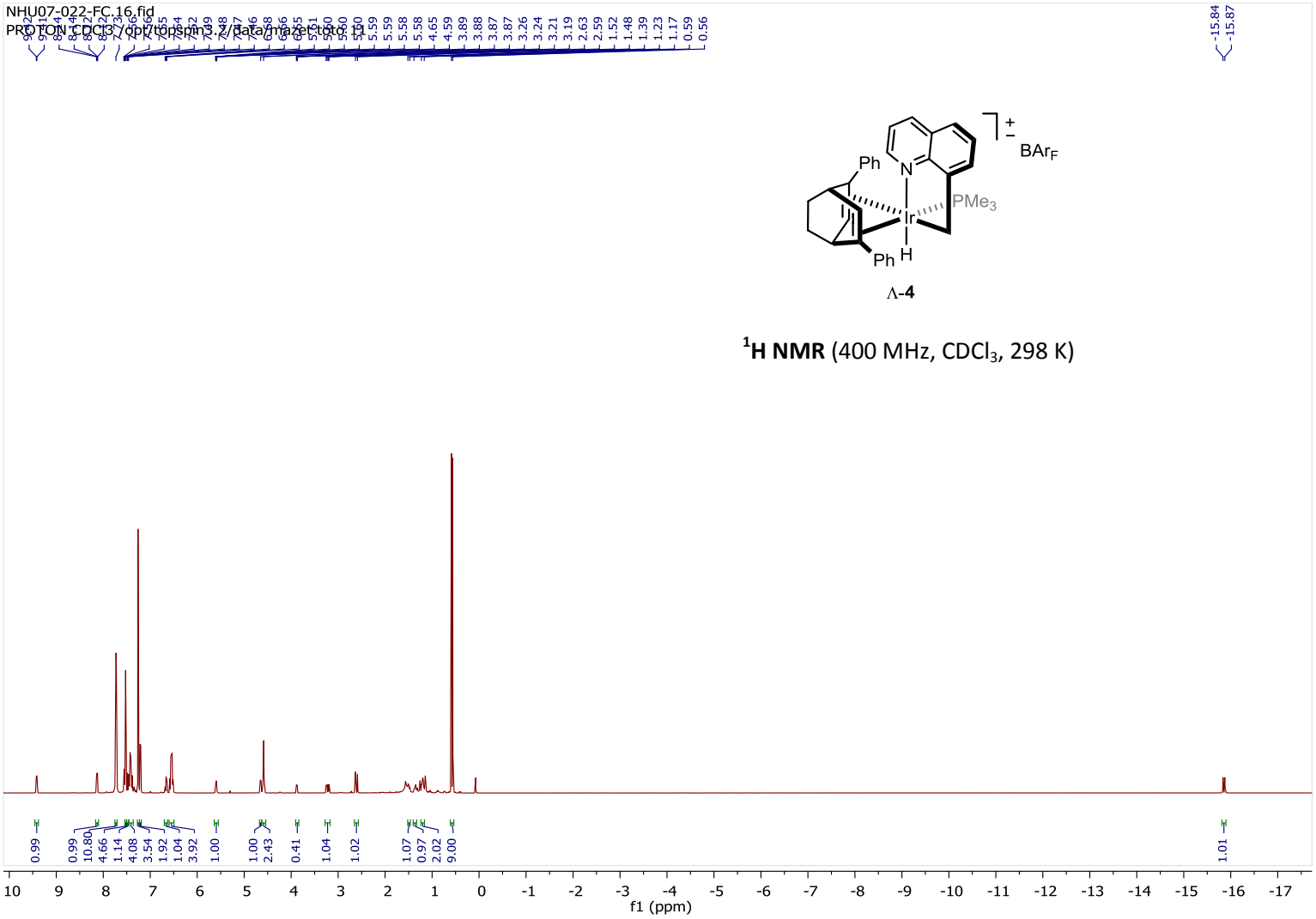
1) S. Nanchen and A. Pfaltz, *Chem. Eur. J.,* 2006, **12**, 4550.

2) J. Choudhury, S. Podder and S. Roy, *J. Am. Chem. Soc.,* 2005, **127**, 6162.

3) D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba and M. D. Smith, *Inorg. Chem.,* 2001, **40**, 3810.

4) T. Nishimura, Y. Yasuhara, T. Sawano and T. Hayashi, *J. Am. Chem. Soc.*, 2010, **132**, 7872.

NMR data for all new compounds



Λ-**4**

^{1}**H NMR** (400 MHz, $CDCl_3$, 298 K)

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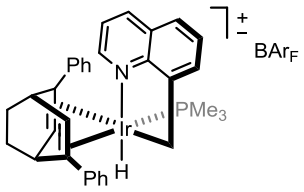
C13CPD CDCl3 /opt/topspin3.2/data/mazet.cdc11

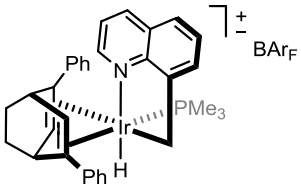


Λ-**4**

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K)

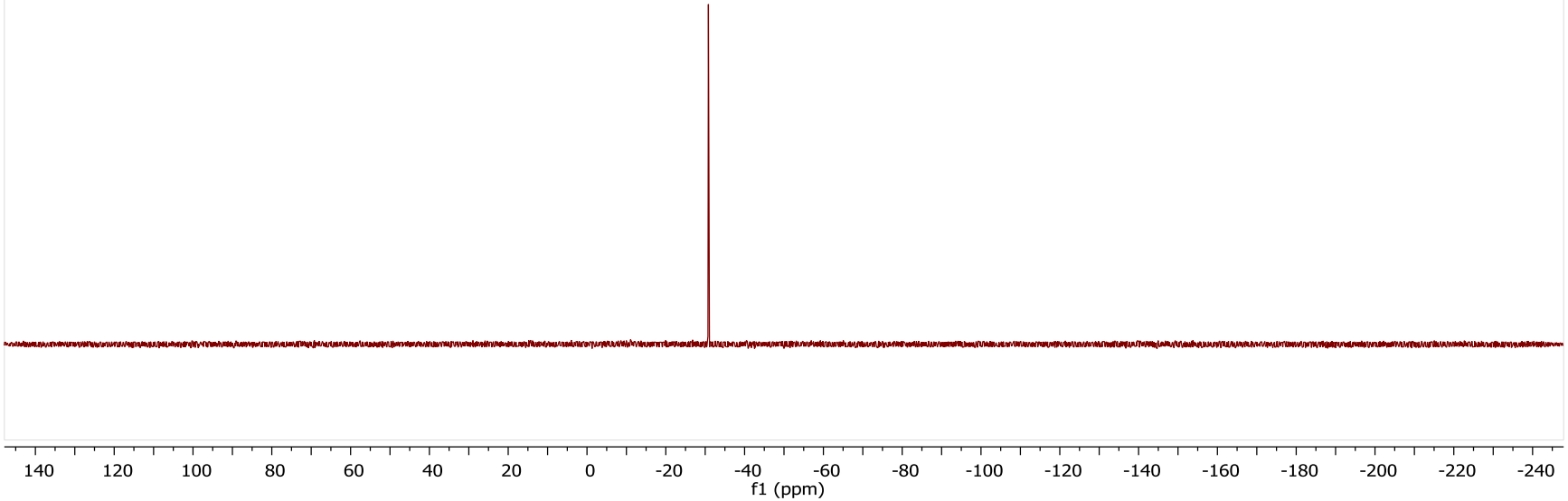
NHU07-022-FC.17.fid
P31CPD CDCl3 /opt/topspin3.2/data/mazet toto 11

-30.81

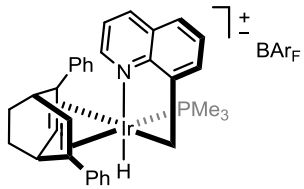


Λ-**4**

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K)

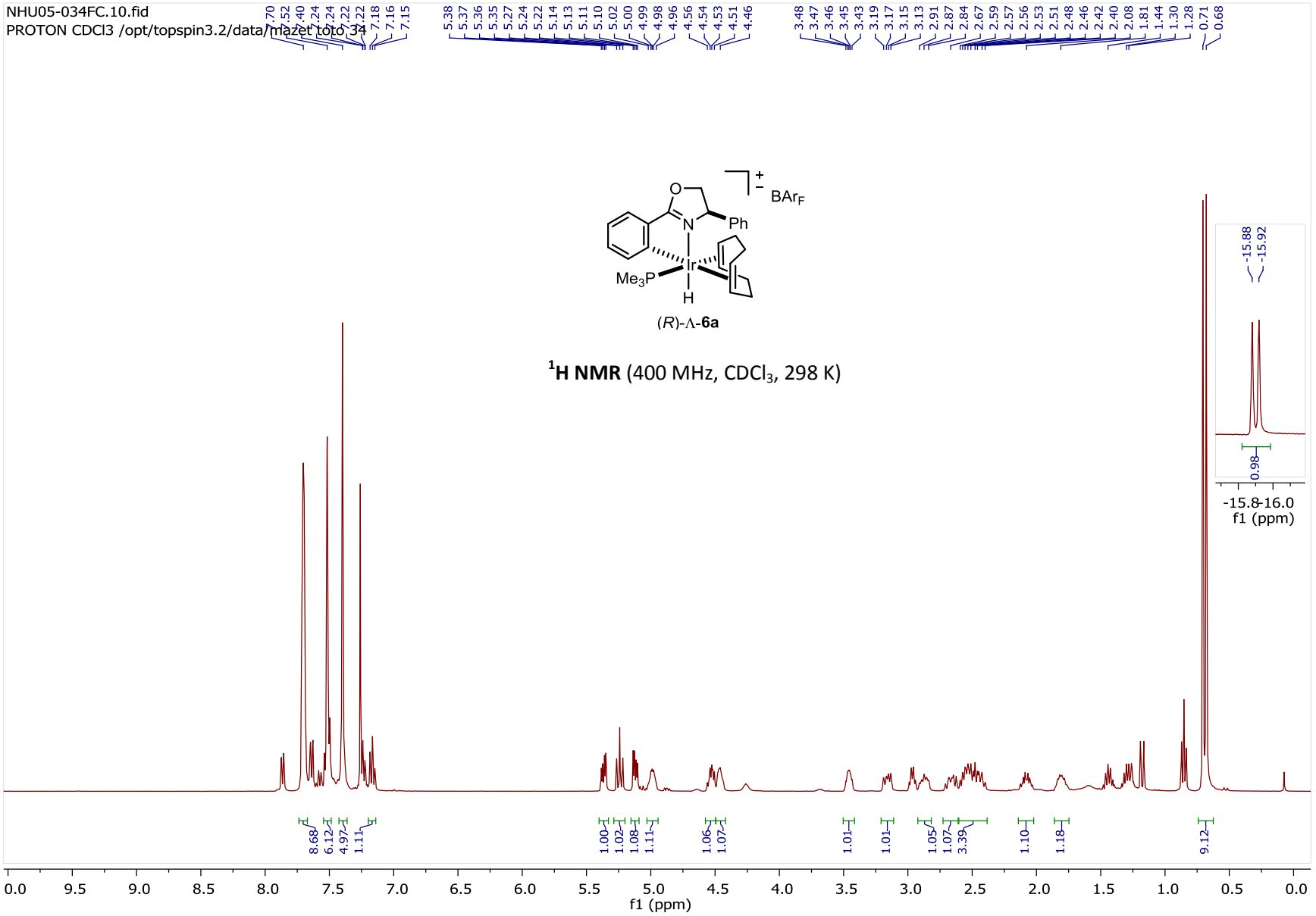


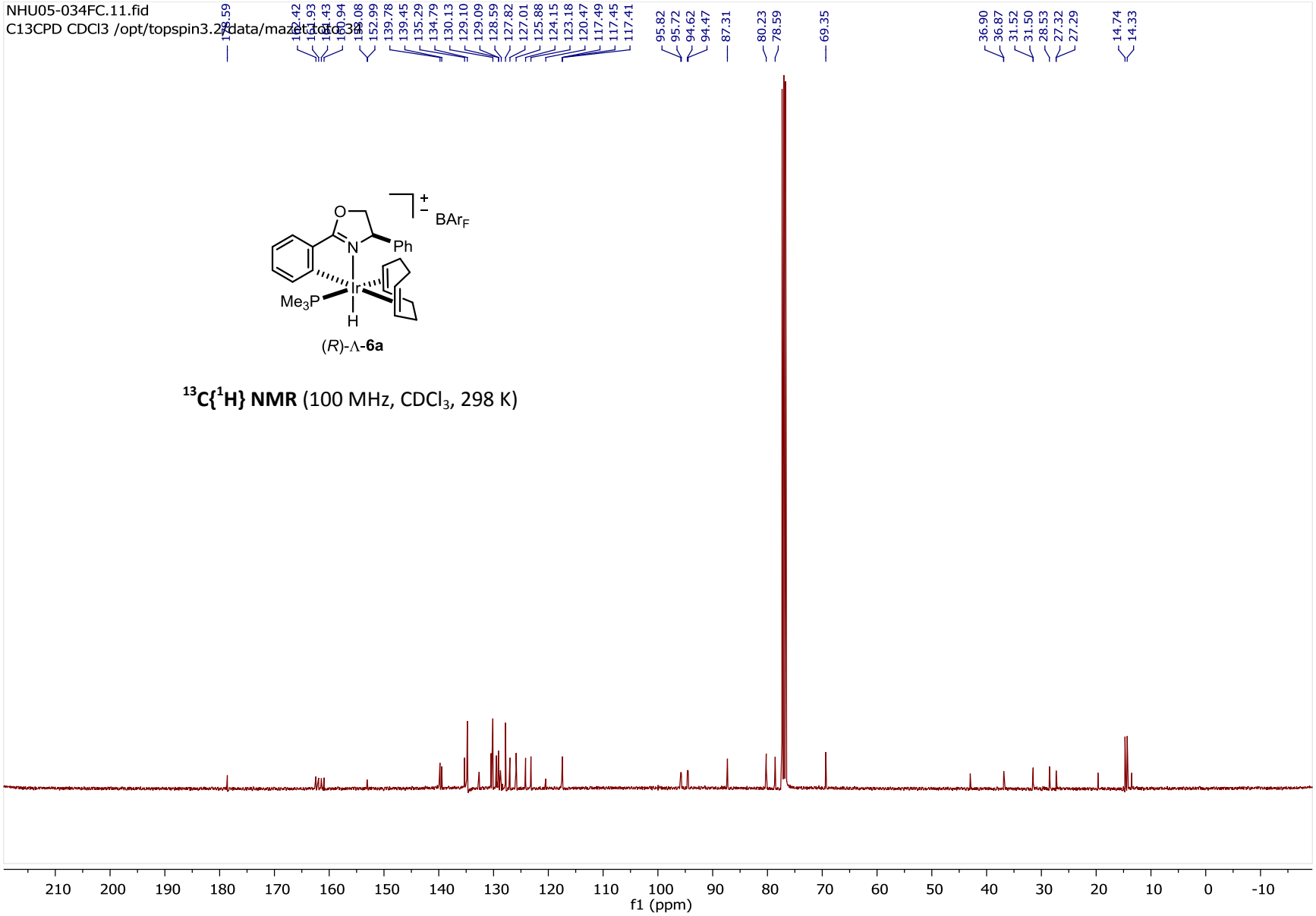
NHU07-022-F/1
F19CPD

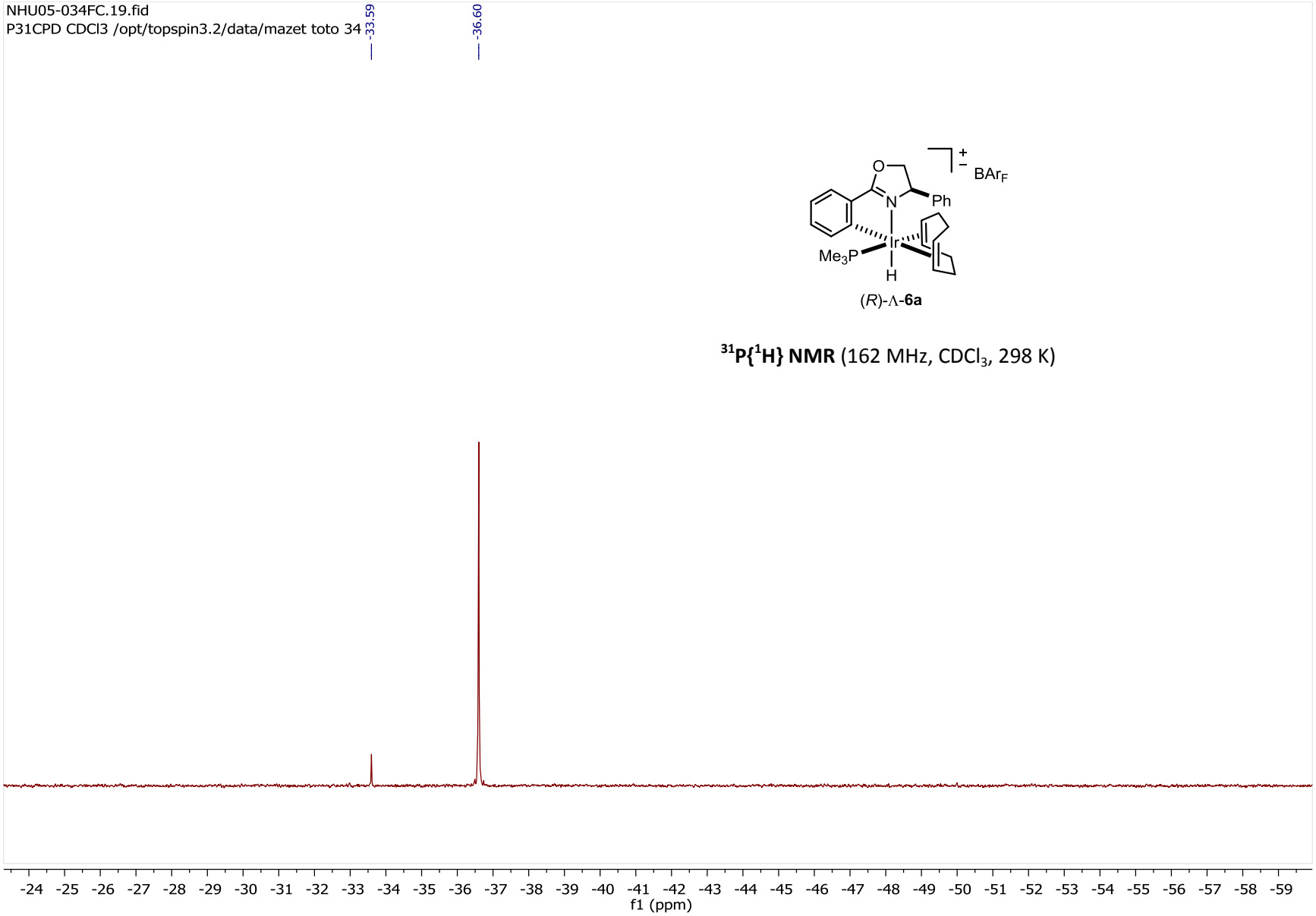


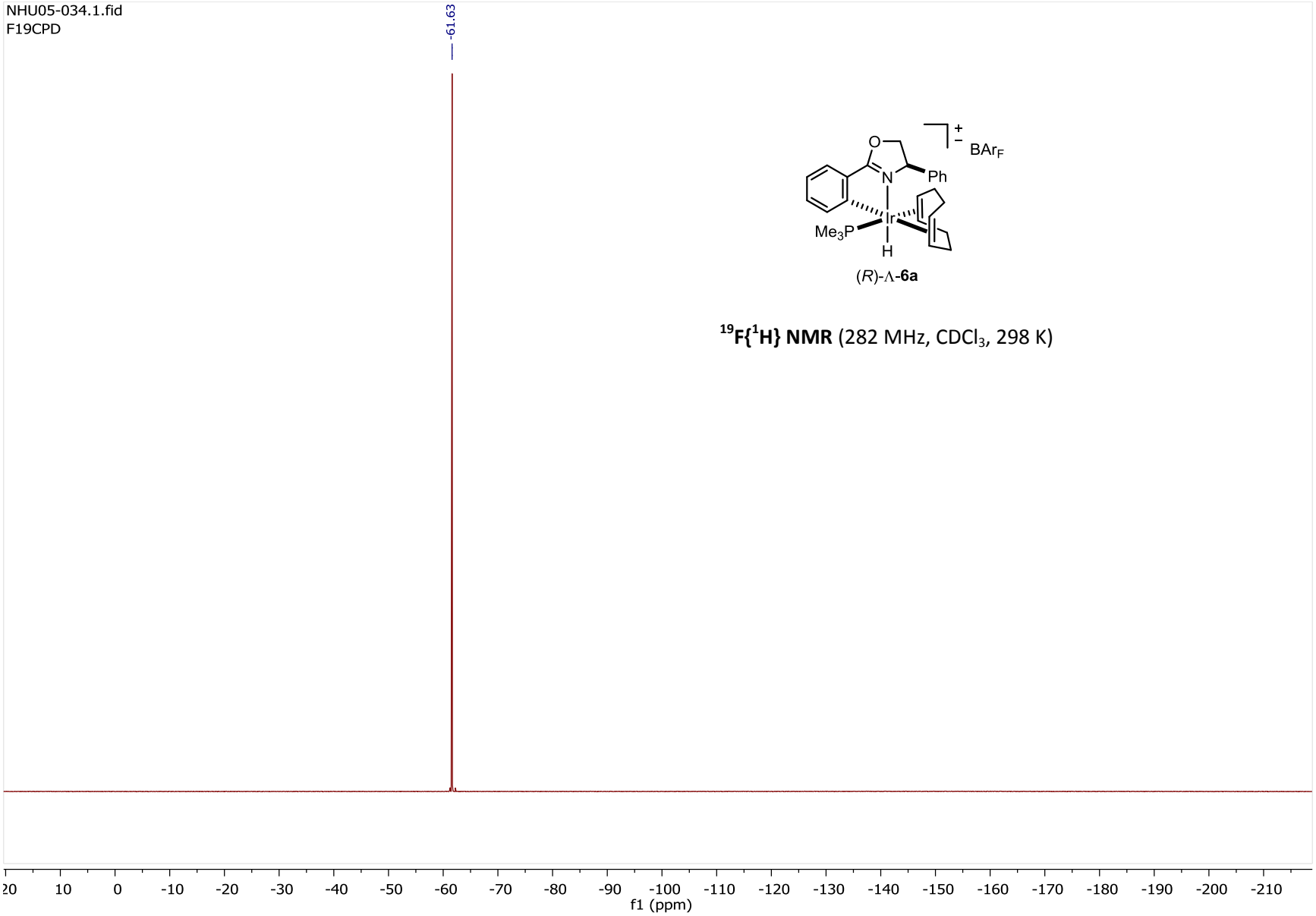
Λ-**4**

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 298 K)


NHU05-034FC.10.fid
PROTON CDCl3 /opt/topspin3.2/data/mazet toto 34
BAr$_F$
Ph
Me$_3$P
Ir
H
(*R*)-Λ-**6a**
^{1}**H NMR** (400 MHz, $CDCl_3$, 298 K)
-15.88
-15.92
0.98
-15.8-16.0
f1 (ppm)
f1 (ppm)


NHU05-034FC.11.fid
C13CPD CDCl3 /opt/topspin3.2/data/mazet/std/C13
179.59
162.42
161.93
161.43
160.94
159.08
152.99
139.78
139.45
135.29
134.79
130.13
129.10
129.09
128.59
127.82
127.01
125.88
124.15
123.18
120.47
117.49
117.45
117.41
95.82
95.72
94.62
94.47
87.31
80.23
78.59
69.35
36.90
36.87
31.52
31.50
28.53
27.32
27.29
14.74
14.33
O
N
Ph
Ir
Me3P
H
BArF
(R)-Λ-6a
13C{1H} NMR (100 MHz, CDCl3, 298 K)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

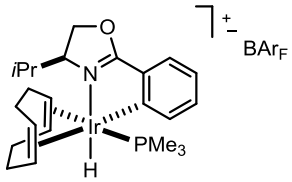

NHU05-034FC.19.fid
P31CPD CDCl3 /opt/topspin3.2/data/mazet toto 34
-33.59
-36.60
O
N
Ph
Ir
Me3P
H
BArF
+
−
(R)-Λ-6a
31P{1H} NMR (162 MHz, CDCl3, 298 K)
-24 -25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35 -36 -37 -38 -39 -40 -41 -42 -43 -44 -45 -46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59
f1 (ppm)



(*R*)-Λ-**6a**

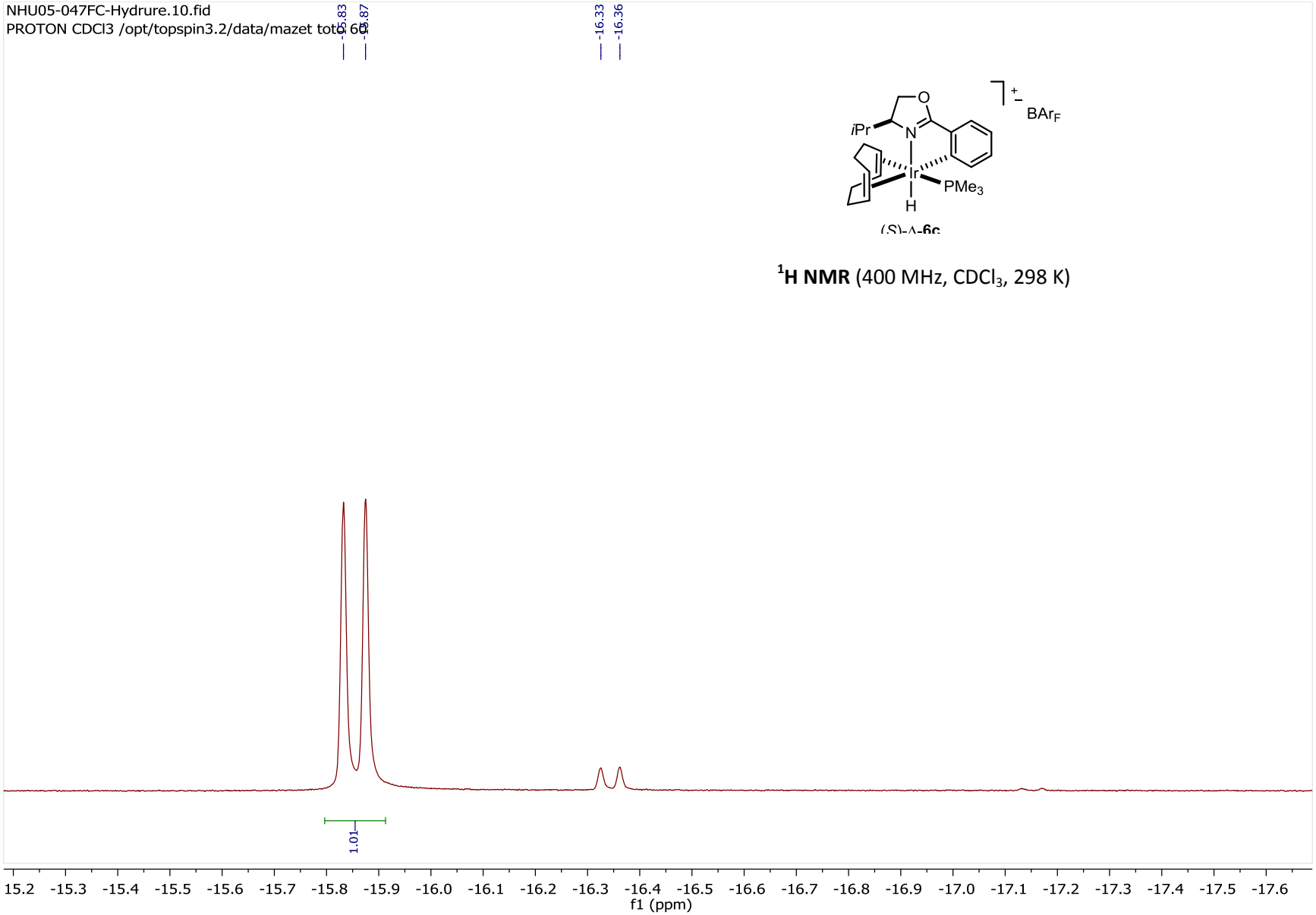
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 298 K)

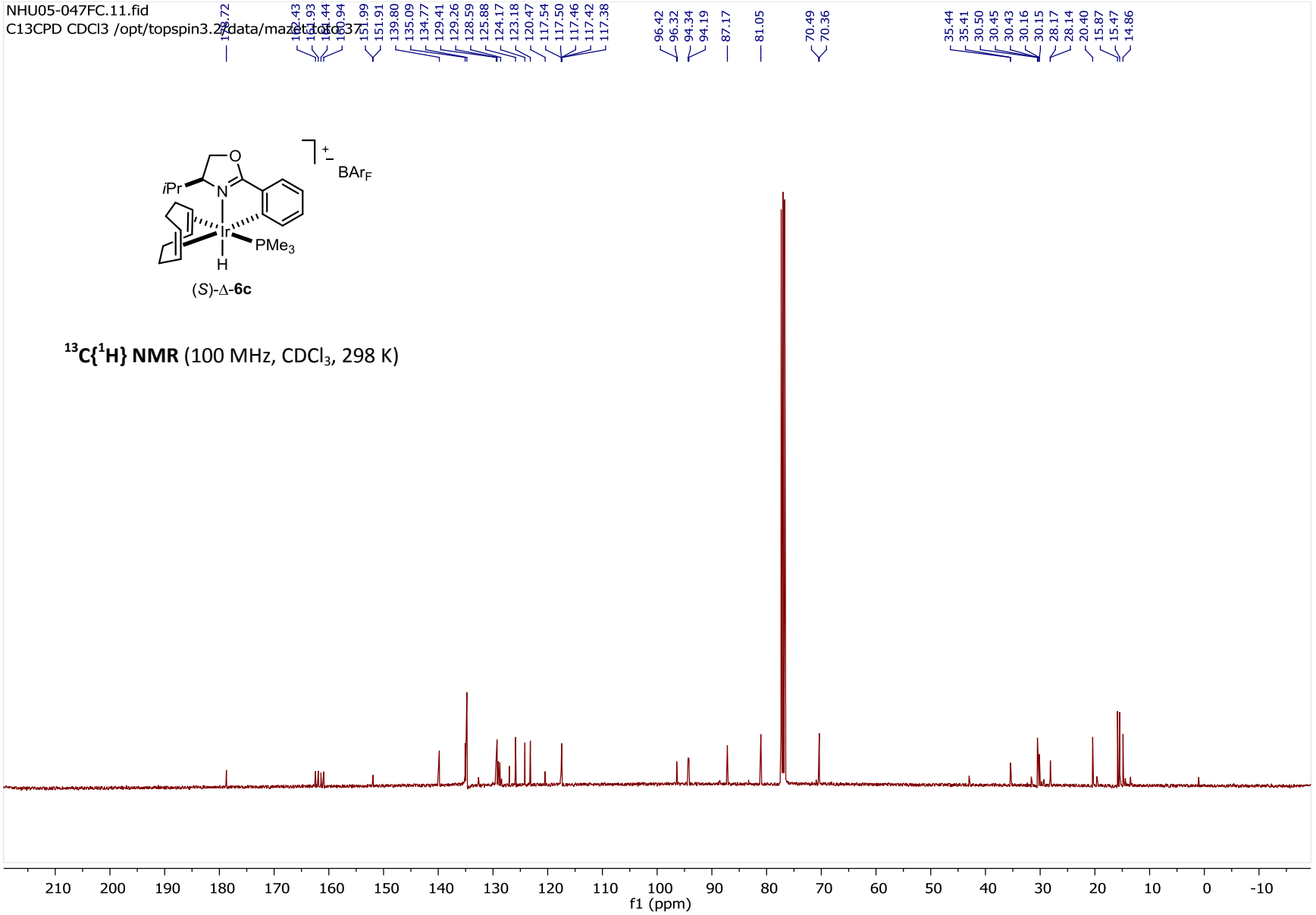
NHU05-047FC.10.fid
PROTON CDCl3 /opt/topspin3.2/data/mazet toto 37



(*S*)-Δ-**6c**

^{1}H NMR (400 MHz, $CDCl_3$, 298 K)


NHU05-047FC-Hydrure.10.fid
PROTON CDCl3 /opt/topspin3.2/data/mazet tot
-15.83
-15.87
-16.33
-16.36
iPr
O
N
Ir
H
PMe3
BArF
(S)-Λ-6c
1H NMR (400 MHz, CDCl3, 298 K)
1.01
15.2 -15.3 -15.4 -15.5 -15.6 -15.7 -15.8 -15.9 -16.0 -16.1 -16.2 -16.3 -16.4 -16.5 -16.6 -16.7 -16.8 -16.9 -17.0 -17.1 -17.2 -17.3 -17.4 -17.5 -17.6
f1 (ppm)

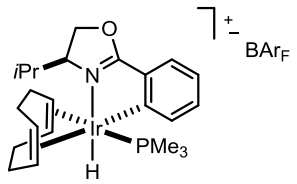


(*S*)-Δ-**6c**

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K)

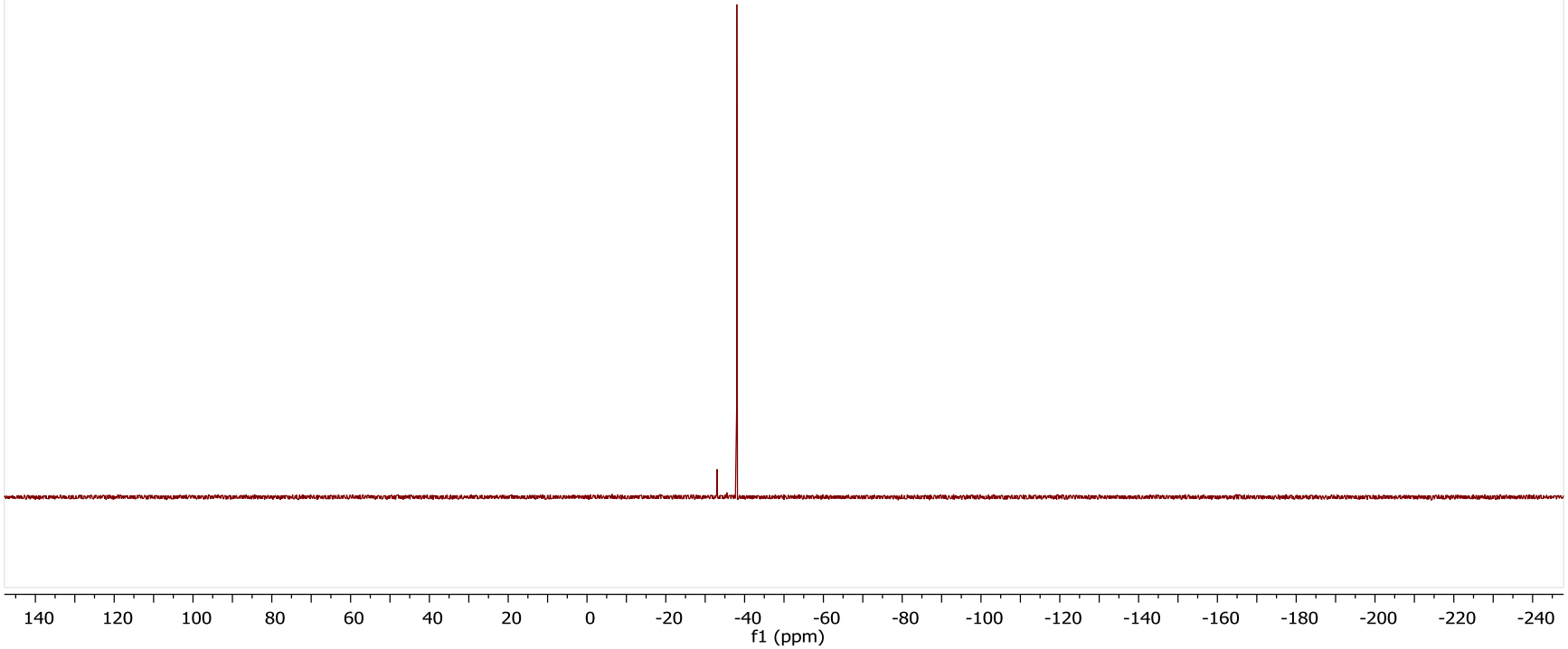
NHU05-047FC.19.fid
P31CPD CDCl3 /opt/topspin3.2/data/mazet toto 37

-32.99
-33.01
-38.02



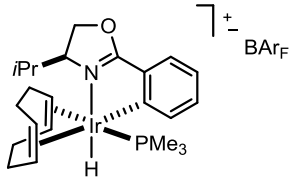
(*S*)-Δ-**6c**

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K)



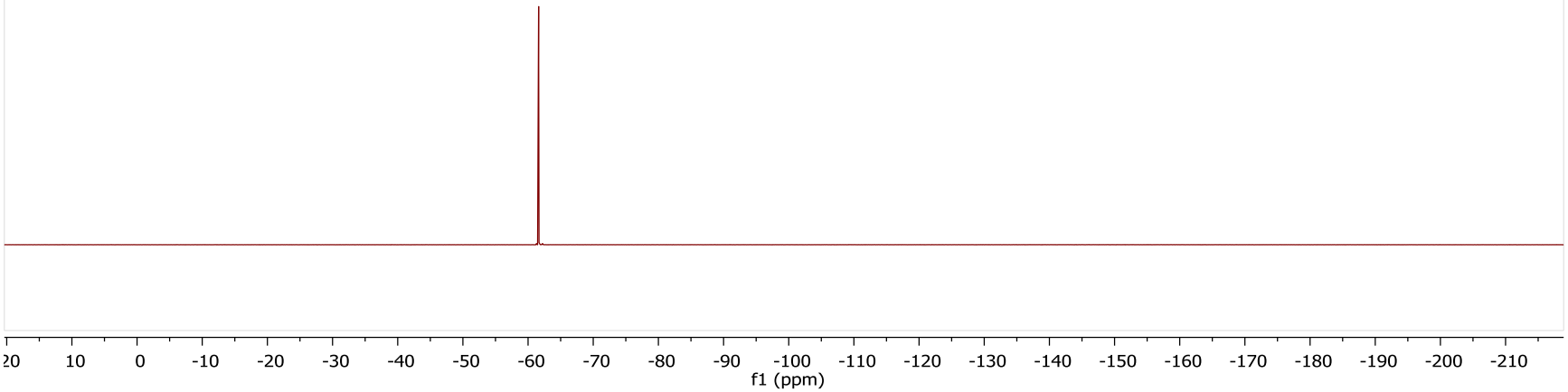
NHU05-047.1.fid
F19CPD

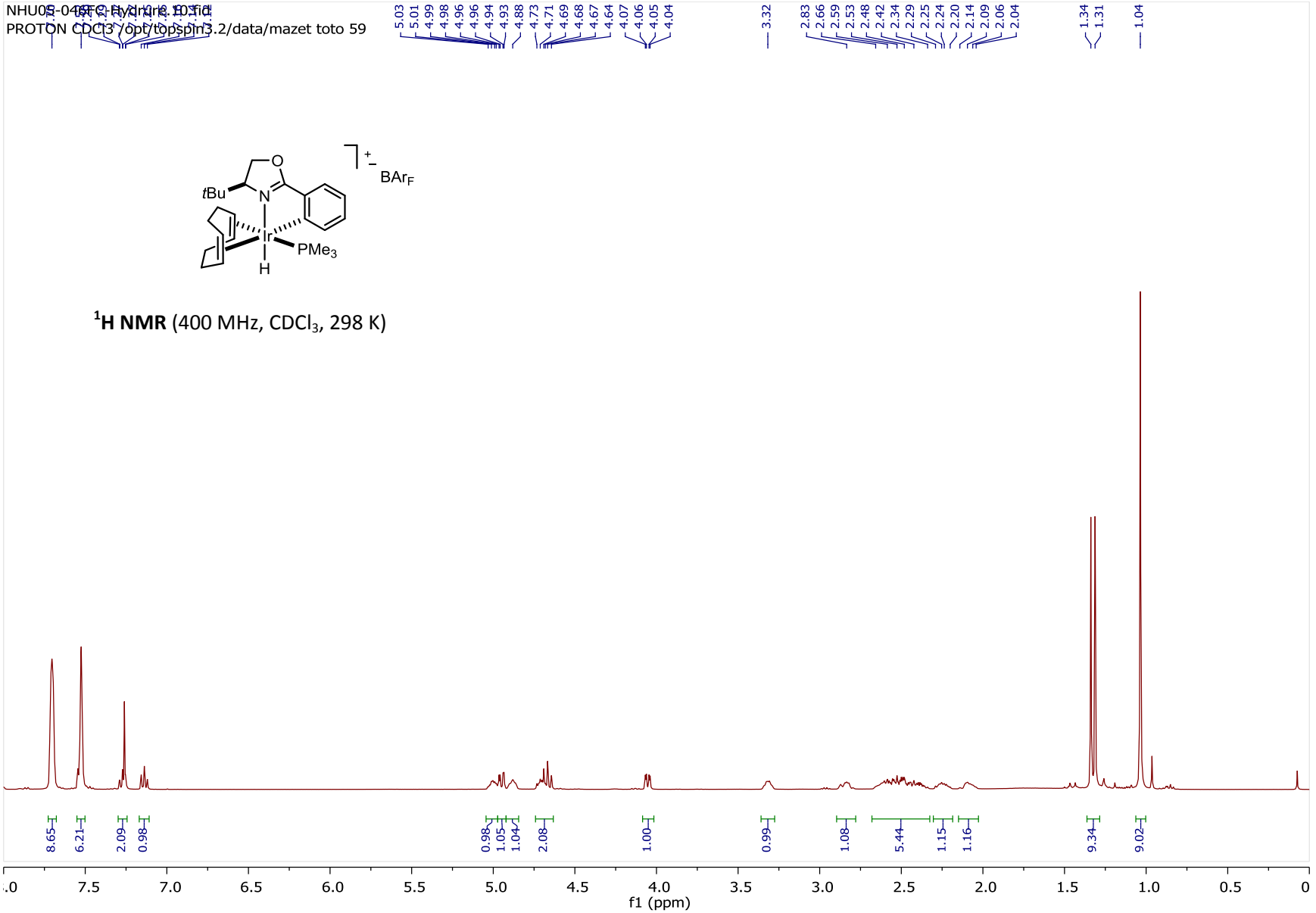
-61.62



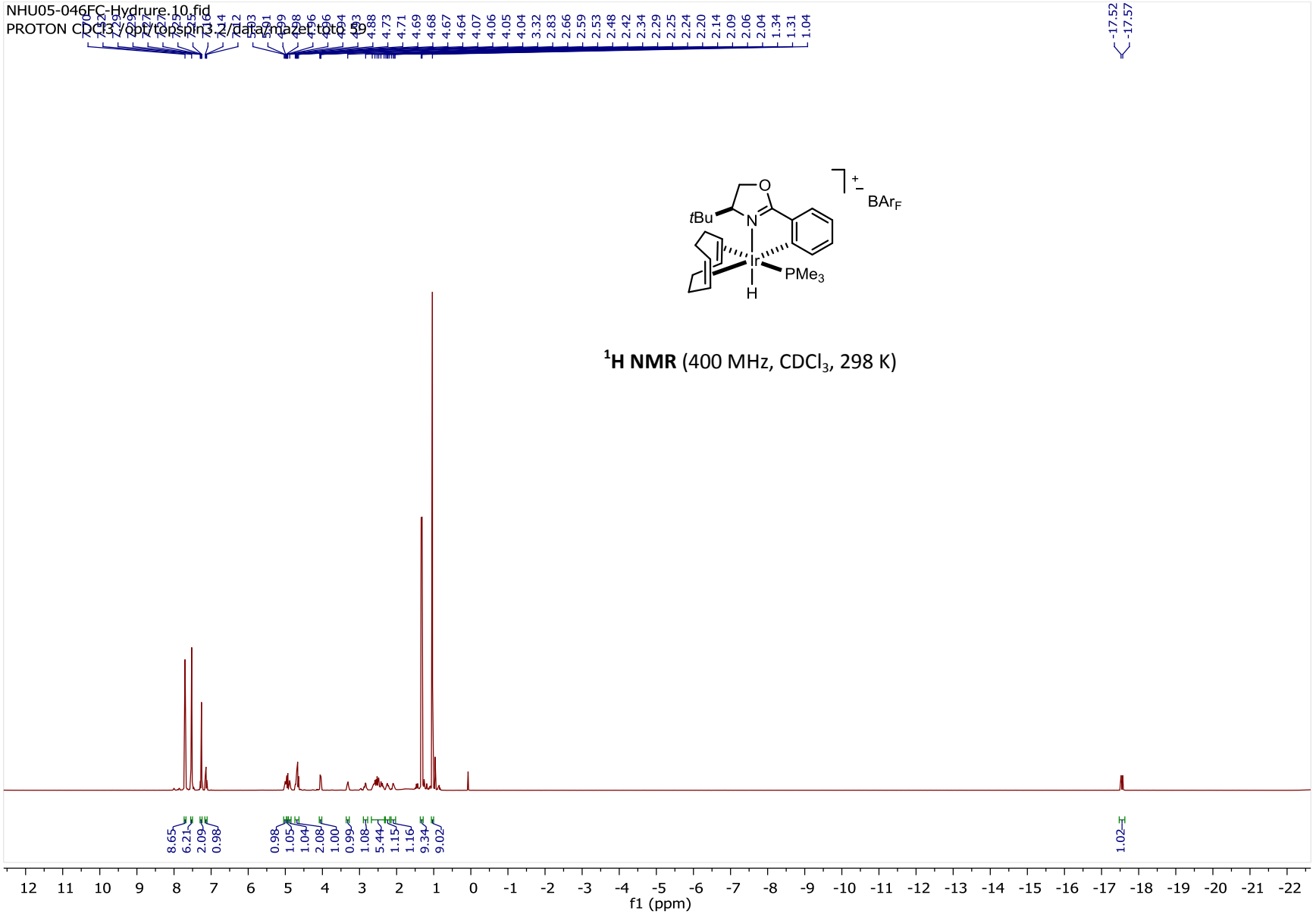
(*S*)-Δ-**6c**

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 298 K)





^{1}H NMR (400 MHz, $CDCl_3$, 298 K)


NHU05-046FC-Hydrure.10.fid
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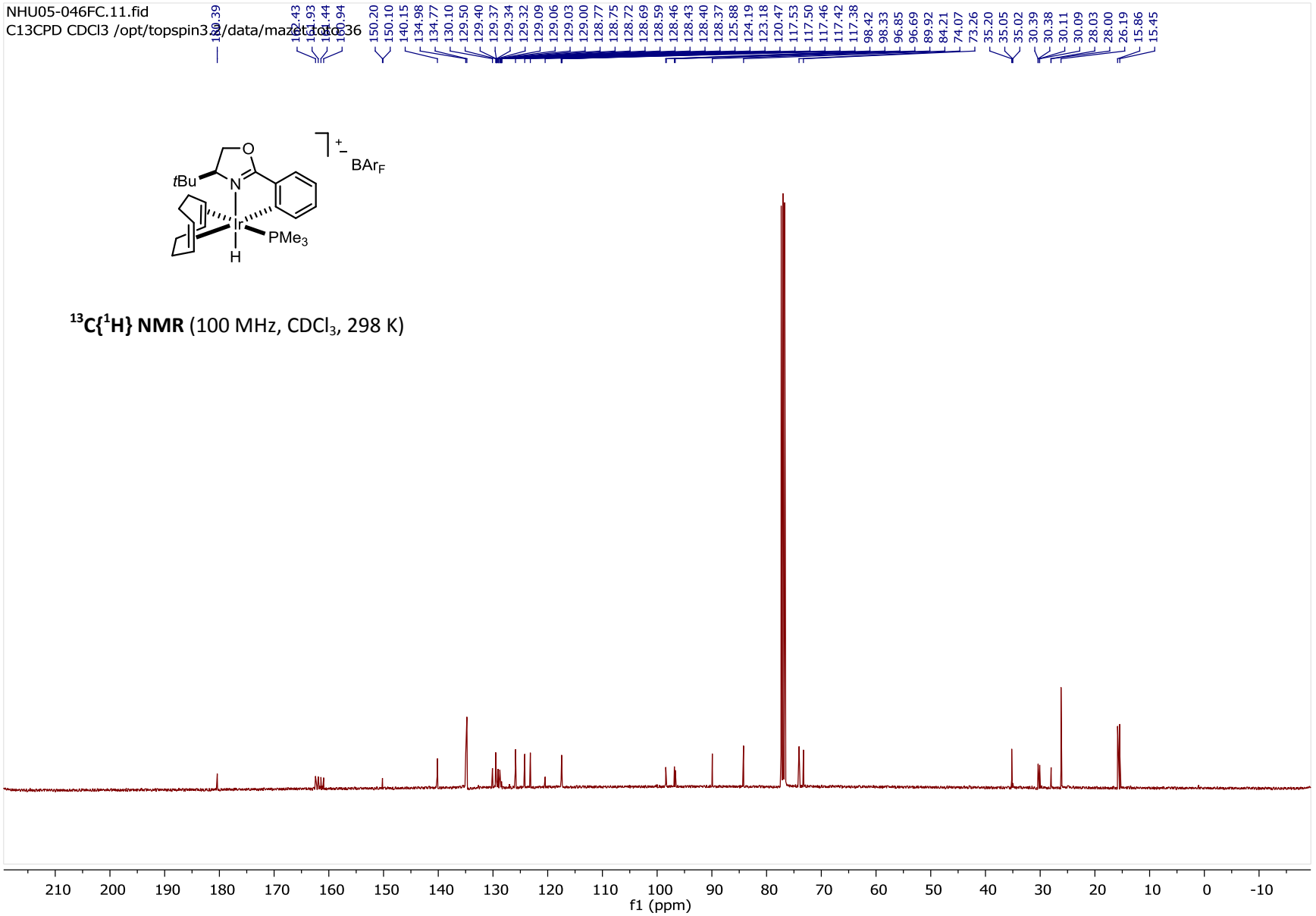
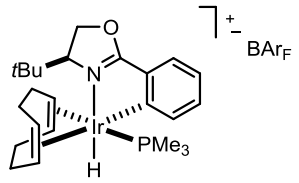
-17.52
-17.57
tBu
O
N
Ir
H
PMe3
BArF
+
−
1H NMR (400 MHz, CDCl3, 298 K)
8.65
6.21
2.09
0.98
0.98
1.05
1.04
2.08
1.00
0.99
1.08
5.44
1.15
1.16
9.34
9.02
1.02
f1 (ppm)



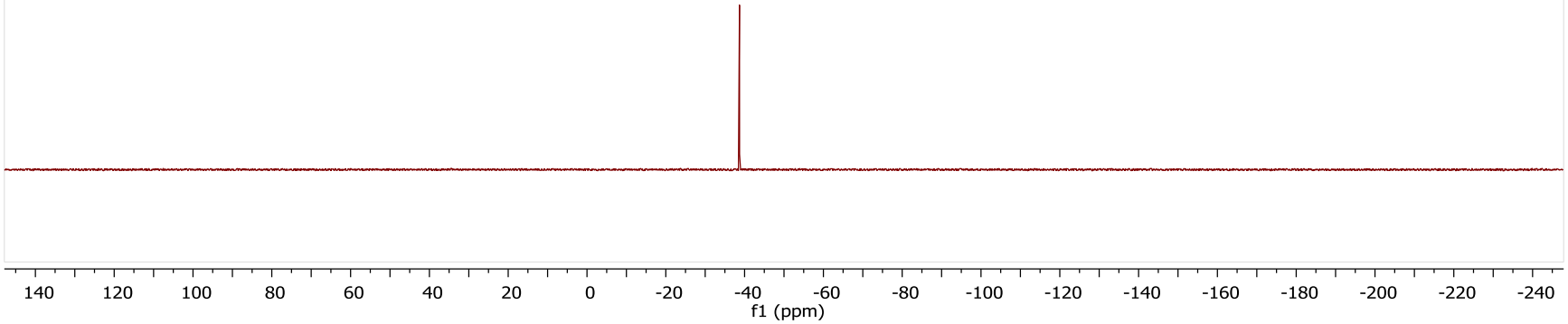
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K)

NHU05-046FC.19.fid
P31CPD CDCl3 /opt/topspin3.2/data/mazet toto 36

-38.68
-38.70



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K)



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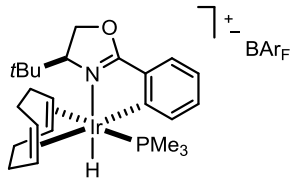
F19CPD

-61.61



$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$, 298 K)