Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Homoleptic and heteroleptic bis-NHC Cu(I) complexes as carbene transfer reagents

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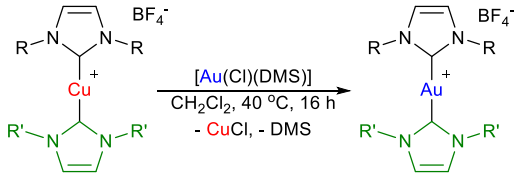
Contents

1. General Information

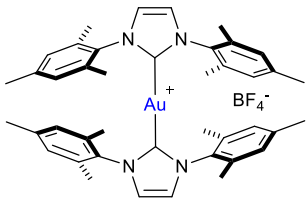
All reactions were carried out under argon atmosphere using standard Schlenk and glovebox techniques. Chemicals were used as received unless otherwise noted. Bis-NHC copper complexes were synthesised following the reported procedures.[1] Dry CH_2Cl_2 was obtained from a PureSolv SPS-400-5 solvent purification system. ^{1}H, and ^{13}C-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker-400 MHz or 300 MHz spectrometers using the residual solvent peak as reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm, CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 53.84 ppm) at 298K.
Elemental analyses were performed at London Metropolitan University 166-220, Holloway Road, London, N7 8DB.

2. General procedure for the transmetallation from Cu to Au



In a glovebox, a 3 mL vial was charged with the copper complex (250 mg, 1 equiv.), [Au(Cl)(DMS)] (1 equiv.) and CH_2Cl_2 (2 mL). The reaction mixture was stirred at 40 °C for 16 h. The reaction mixture was filtered in air through a plug of Celite and concentrated under reduced pressure. Pentane (12 mL) was then added and the precipitate was collected by filtration.

2.1 Synthesis of $[Au(IMes)_2]BF_4$ (2b)[1]



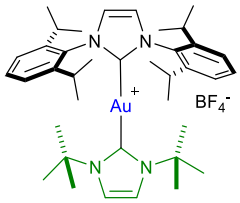
2b 88%

The reaction between $[Cu(IMes)_2]BF_4$ **2a** (250 mg, 0.33 mmol, 1 equiv.) and [Au(Cl)(DMS)] (99 mg, 0.33 mmol, 1 equiv.) afforded **2b** as a colourless solid in 88% yield (0.29 mmol, 259 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.68 (s, 24H, C*H*$_3$), 2.42 (s, 12H, C*H*$_3$), 6.87 (s, 8H, C*H* phenyl), 7.10 (s, 4H, H^4 and H^5).
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.2 (s, *C*H$_3$), 21.3 (s, *C*H$_3$), 123.2 (s, C^{IV} Ar), 129.6 (s, *C*H Ar), 134.1 (s, C^4 and C^5), 134.2 (s, C^{IV} Ar), 139.4 (s, C^{IV} Ar), 185.1 (s, C^2).
^{19}F-{^{1}H} NMR (282 Hz, $CDCl_3$, 298K): δ (ppm) = -154.3 (s, BF_4), -154.3 (s, BF_4).

Anal. Calcd for $C_{42}H_{48}BAuF_4N_4$: C, 56.51; H, 5.42; N, 6.28. Found: C, 56.39; H, 5.44; N, 6.34.

2.2 Synthesis of [Au(IPr)((I^{t}Bu)]BF$_4$ (4b)[2]

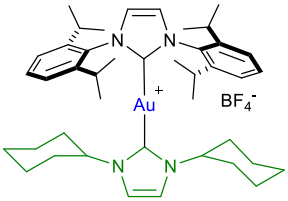


4b 83%

The reaction between [Cu(IPr)((I^{t}Bu)]BF$_4$ **4a** (250 mg, 0.35 mmol, 1 equiv.) and [Au(Cl)(DMS)] (97 mg, 0.33 mmol, 1 equiv.) afforded **4b** as a colourless solid in 83% yield (0.29 mmol, 247 mg).

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 1.24 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH-C*H*$_3$), 1.26 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH-C*H*$_3$ IPr), 1.27 (s, 18H, C(C*H*$_3$)$_3$ I^{t}Bu), 2.65 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, C*H*-CH$_3$), 7.12 (s, 2H, *H*^{4} and *H*^{5} I^{t}Bu), 7.34 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, C*H* phenyl), 7.45 (s, 2H, *H*^{4} and *H*^{5} IPr), 7.54 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, C*H* phenyl).
^{13}C-{^{1}H} NMR (75 MHz, CDCl$_3$, 298 K): δ (ppm) = 23.8 (s, CH-*C*H$_3$), 24.8 (s, CH-*C*H$_3$), 28.9 (s, *C*H-CH$_3$), 31.8 (s, C(*C*H$_3$)$_3$), 58.2 (s, *C*(CH$_3$)$_3$), 117.9 (s, *C*^{4} and *C*^{5} I^{t}Bu), 124.7 (s, *C*^{4} and *C*^{5} IPr), 124.8 (s, *C*H Ar), 131.0 (s, *C*H Ar), 134.5 (s, C^{IV}), 145.7 (s, C^{IV} Ar), 179.8 (s, *C*^{2} I^{t}Bu), 185.6(s, *C*^{2} IPr).
^{19}F-{^{1}H} NMR (282 Hz, CDCl$_3$, 298K): δ (ppm) = -154.16 (s, BF$_4$), -154.21 (s, BF$_4$).
Anal. Calcd for $C_{38}H_{56}BAuF_4N_4$: C, 53.53; H, 6.62; N, 6.57. Found: C, 53.66; H, 6.68; N, 6.39.

2.3 Synthesis of [Au(IPr)(ICy)]BF$_4$ (5b)[2]



5b 86%

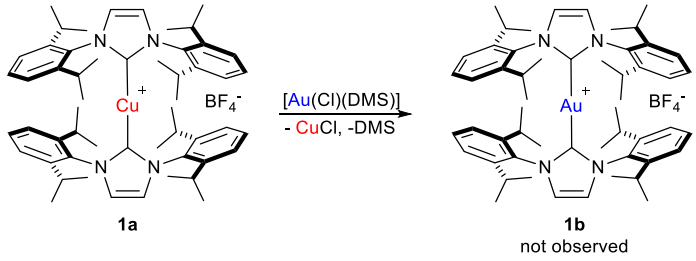
The reaction between [Cu(IPr)(ICy)]BF$_4$ **5a** (250 mg, 0.32 mmol, 1 equiv.) and [Au(Cl)(DMS)] (97 mg, 0.33 mmol, 1 equiv.) afforded **5b** as a colourless solid in 86% yield (0.28 mmol, 252 mg).

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ (ppm) = 0.89 – 1.06 (m, 4 H, C*H*$_2$ ICy), 1.09 – 1.14 (m, 2H, C*H*$_2$ ICy) 1.27 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 24H, CH-C*H*$_3$ IPr), 1.59 – 1.67 (m, 4H, C*H*$_2$ ICy 2.65) 2.57 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, C*H*-CH$_3$ IPr), 7.01 (s, 2H, *H*^{4} and *H*^{5} ICy), 7.37 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, C*H* phenyl), 7.41 (s, 2H, *H*^{4} and *H*^{5} IPr), 7.58 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, C*H* phenyl).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) = 23.9 (s, CH-*C*H$_3$), 24.6 (s, *C*H$_2$ ICy), 25.0 (s, *C*H$_2$ ICy), 25.9 (s, CH-*C*H$_3$), 28.9 (s, *C*H-CH$_3$), 33.8 (s, *C*H$_2$ ICy), 60.8 (s, *C*H ICy), 118.8 (s, *C*^{4} and *C*^{5} ICy), 124.5 (s, *C*H Ar), 124.8 (s, *C*^{4} and *C*^{5} IPr), 131.2 (s, *C*H Ar), 133.8 (s, C^{IV} Ar), 146.2 (s, C^{IV} Ar), 178.6 (s, *C*^{2} IPr), 187.3 (s, *C*^{2} ICy).
^{19}F-{^{1}H} NMR (282 Hz, $CDCl_3$, 298K): δ (ppm) = -154.0 (s, BF_4), -154.0 (s, BF_4).

3. Synthetic attempts towards $[Au(IPr)_2]BF_4$ (1b)

In a glovebox, a 3 mL vial was charged with $[Cu(IPr)_2]BF_4$ (**1a**) (50 mg, 0.05 mmol, 1 equiv.), [Au(Cl)(DMS)] (15 mg, 0.05 mmol, 1 equiv.) and the solvent (1 mL). The reaction mixture was stirred at the stated temperature for the time indicated. The reaction mixture was filtered in air through a plug of Celite and concentrated under reduced pressure. Pentane (5 mL) was then added and the solid obtained was collected by filtration and analysed by ^{1}H NMR and ^{13}C-{^{1}H} NMR spectroscopy.

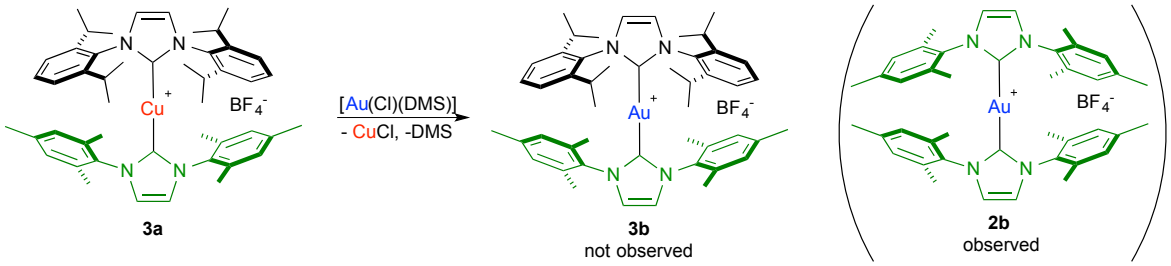


Entry	Solvent	Temperature	Time	Outcome[a]
1	CH_2Cl_2	r.t.	16 h	**1a**
2	CH_2Cl_2	40 ^{0}C	16 h	**1a** + decomposition
3	CH_2Cl_2	40 ^{0}C	24 h	**1a** + decomposition
4	CH_3CN	r.t	16 h	**1a**
5	CH_3CN	40 ^{0}C	16 h	**1a** + decomposition
6	CH_3CN	80 ^{0}C	16 h	decomposition
7	^{i}PrOH	80 ^{0}C	16 h	decomposition

Table S1 Synthetic attempts towards **1b** Reaction conditions: **1a** 50 mg (0.05 mmol, 1 equiv.), [Au(Cl)(DMS)] 16 mg (0.05 mmol, 1 equiv.), solvent (1 mL). [a] Determined by NMR spectroscopy.

4. Synthetic attempts towards [Au(IPr)(IMes)]BF_4 (3b)

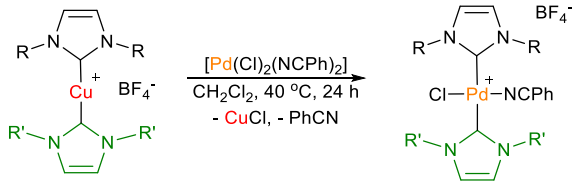
In a glovebox, a 3 mL vial was charged with the **3a** (50 mg, 0.06 mmol, 1 equiv.), [Au(Cl)(DMS)] (17 mg, 0.06 mmol, 1 equiv.) and the solvent (1 mL). The reaction mixture was stirred at the stated temperature for the time indicated. The reaction mixture was filtered through a plug of Celite and concentrated under reduced pressure. Pentane (5 mL) was then added and the solid obtained was collected by filtration and analysed by ^{1}H NMR spectroscopy.



Entry	Solvent	Temperature	Time	Outcome[a]
1	CH_2Cl_2	r.t.	16 h	**3a**
2	CH_2Cl_2	40 ^{0}C	16 h	**3a** + decomposition
3	CH_3CN	r.t	16 h	[Au(IMes)$_2$]BF_4 **2b** (46%)
4	CH_3CN	40 ^{0}C	16 h	[Au(IMes)$_2$]BF_4 **2b** (80%)
5	CH_2Cl_2	80 ^{0}C	16 h	[Au(IMes)$_2$]BF_4 **2b** (80%)

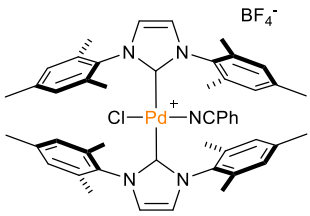
Table S2 Synthetic attempts towards **3b**. Reaction conditions: **3a** 50 mg (0.06 mmol, 1 equiv.), [Au(Cl)(DMS)] 18 mg (1 equiv.), solvent (1 mL). [a] Determined by NMR spectroscopy. Conversions in parentheses.

5. General procedure for the transmetalation from Cu to Pd



In a glovebox, a 3 mL vial was charged with the copper complex (250 mg, 1 equiv.), $[Pd(Cl)_2(NCPh)_2]$ (1 equiv.) and CH_2Cl_2 (2 mL). The reaction mixture was stirred at 40 °C for 24 h. Under argon atmosphere, the crude was filtered through a plug of Celite and concentrated under reduced pressure. Pentane (12 mL) was then added and the precipitate was collected by filtration.

5.1 Synthesis of $[Pd(Cl)(NCPh)(IMes)_2]BF_4$ (2c)

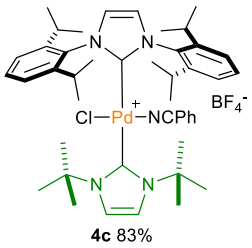


2c 77%

The reaction between **2a** (250 mg, 0.33 mmol, 1 equiv.) and $[Pd(Cl)_2(NCPh)_2]$ (127 mg, 0.33 mmol, 1 equiv.) afforded **2c** as a yellow solid in 77% yield (0.25 mmol, 235 mg). Crystals suitable for X-ray analysis were obtained from a saturated solution of **2c** in chloroform.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.63 (s, 12H, C*H*$_3$), 1.92 (s, 12H, C*H*$_3$), 2.53 (s, 12H, C*H*$_3$), 6.92 (s, 4H, C*H* phenyl), 6.97 (s, 4H, *H*^{4} and *H*^{5}), 7.02 (s, 4H, C*H* phenyl), 7.34 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, C*H* ortho PhCN), 7.74 (t, $^3J_{H\text{-}H}$ = 7.9 Hz 2H, C*H* meta PhCN), 7.89 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 1H, C*H* para PhCN).
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.9 (s, *C*H$_3$), 18.7 (s, *C*H$_3$), 21.4 (s, *C*H$_3$), 108.4 (s, C^{IV} PhCN), 121.4 (s, Ph*C*N), 124.1 (s, *C*^{4} and *C*^{5}), 129.1 (s, *C*H Ar), 130.1 (*C*H meta PhCN) 130.6 (s, *C*H Ar) 132.1 (*C*H ortho PhCN), 134.0 (s, C^{IV} Ar), 134.5 (s, C^{IV} Ar), 136.2 (*C*H para PhCN), 136.4 (s, C^{IV} Ar), 139.2 (C^{IV} Ar), 164.2 (s, *C*^{2})
^{19}F-{^{1}H} NMR (282 Hz, $CDCl_3$, 298K): δ (ppm) = -154.0 (s, BF_4), -154.0 (s, BF_4).
Anal. Calcd for $C_{49}H_{53}BClF_4N_5Pd$: C, 62.57; H, 5.68; N, 7.45. Found: C, 62.50; H, 5.56; N, 7.57.

5.2 Synthesis of [Pd(Cl)(NCPh)(IPr)(I^{t}Bu)]BF_4 (4c)



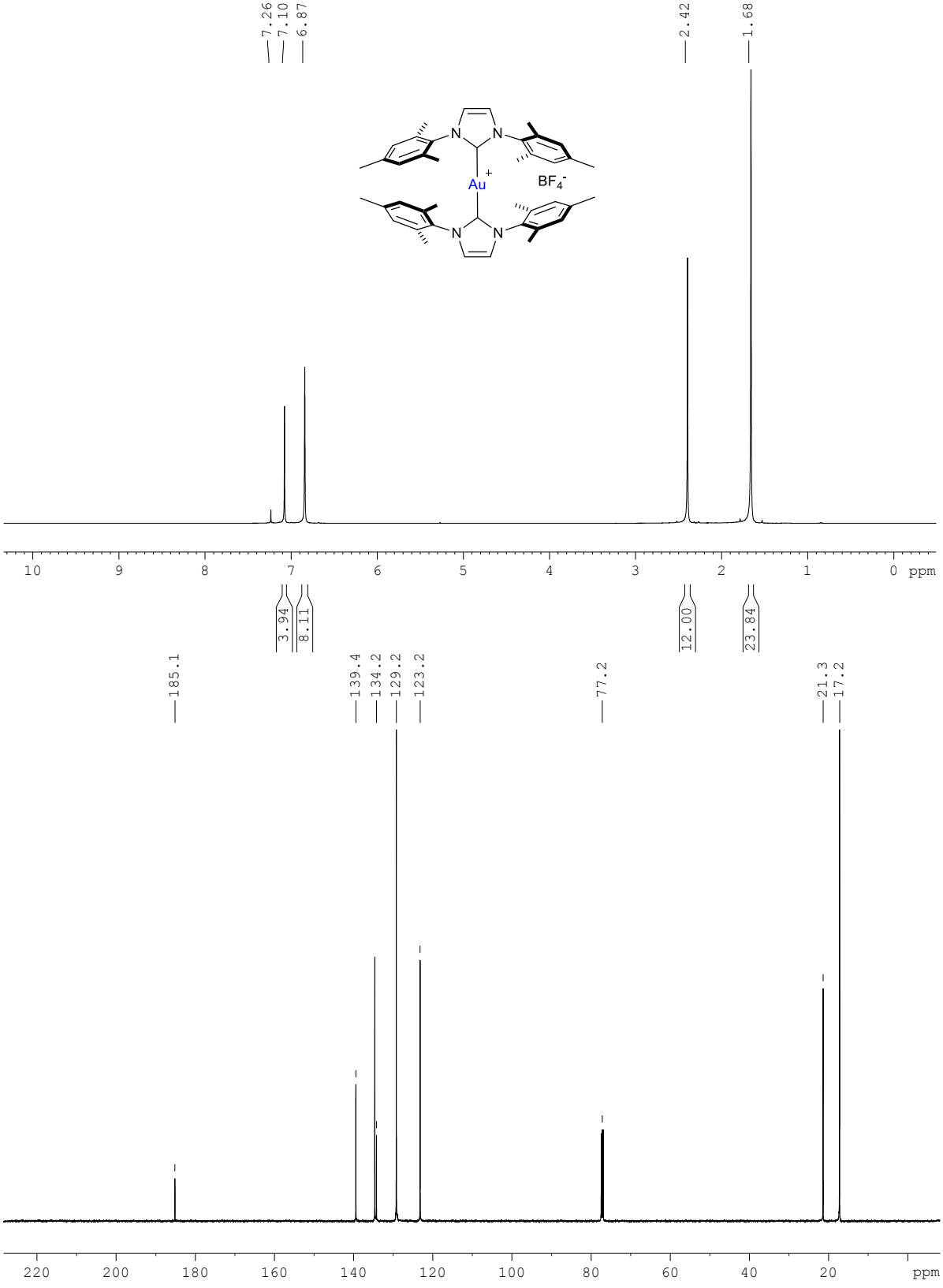
4c 83%

The reaction between **4a** (250 mg, 0.35 mmol, 1 equiv.) and $[Pd(Cl)_2(NCPh)_2]$ (134 mg, 0.35 mmol, 1 equiv.) afforded **4c** as a yellow solid in 83% yield (0.29 mmol, 249 mg). Crystals suitable for X-ray analysis were obtained from a saturated solution of **4c** in chloroform.

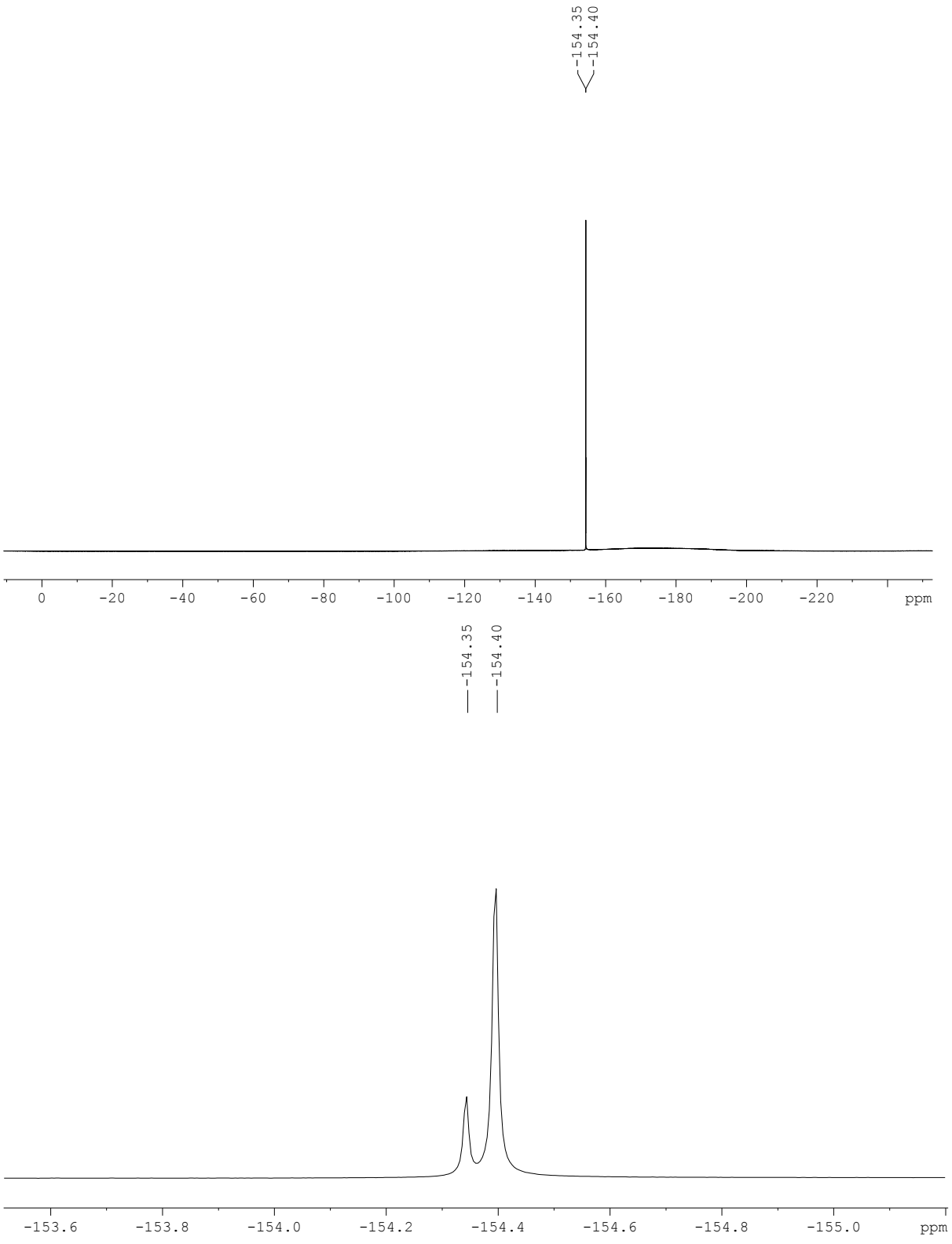
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.13 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH-C*H*$_3$), 1.26 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH-C*H*$_3$ IPr), 1.49 (s, 18H, C(C*H*$_3$)$_3$ I^{t}Bu), 2.88 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, C*H*-CH$_3$), 7.17 (s, 2H, *H*^{4} and *H*^{5} I^{t}Bu), 7.29 (s, 2H, *H*^{4} and *H*^{5} IPr), 7.41 (m, 6H, C*H* phenyl overlapped with C*H* ortho PhCN), 7.63 (m, 4H, C*H* phenyl overlapped with C*H* meta PhCN), 7.78 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 1H, C*H* para PhCN).
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) = 22.6 (s, CH-*C*H$_3$), 26.6 (s, CH-*C*H$_3$), 28.9 (s, *C*H-CH$_3$), 31.8 (s, C(*C*H$_3$)$_3$), 59.3 (s, *C*(CH$_3$)$_3$), 108.1 (s, C^{IV} PhCN) 120.3 (s, *C*^{4} and *C*^{5} I^{t}Bu), 123.1 (s, Ph*C*N), 124.5 (s, *C*^{4} and *C*^{5} IPr), 125.9 (s, *C*H Ar), 130.8 (s, *C*H Ar), 131.2 (*C*H meta PhCN), 132.8 (s, *C*H ortho PhCN), 135.2 (s, C^{IV}), 136.2 (s, *C*H para PhCN), 146.6 (bs, C^{IV} Ar), 156.7 (s, *C*^{2} I^{t}Bu), 168.1 (s, *C*^{2} IPr).
^{19}F-{^{1}H} NMR (282 Hz, $CDCl_3$, 298K): δ (ppm) = -153.3 (s, BF_4), -153.6 (s, BF_4).
Anal. Calcd for $C_{45}H_{61}BClF_4N_5Pd$: C, 60.01; H, 6.83; N, 7.78. Found: C, 60.18; H, 6.94; N, 7.65.

6. ^{1}H-, ^{13}C-{^{1}H} and ^{19}F-{1H} NMR spectra

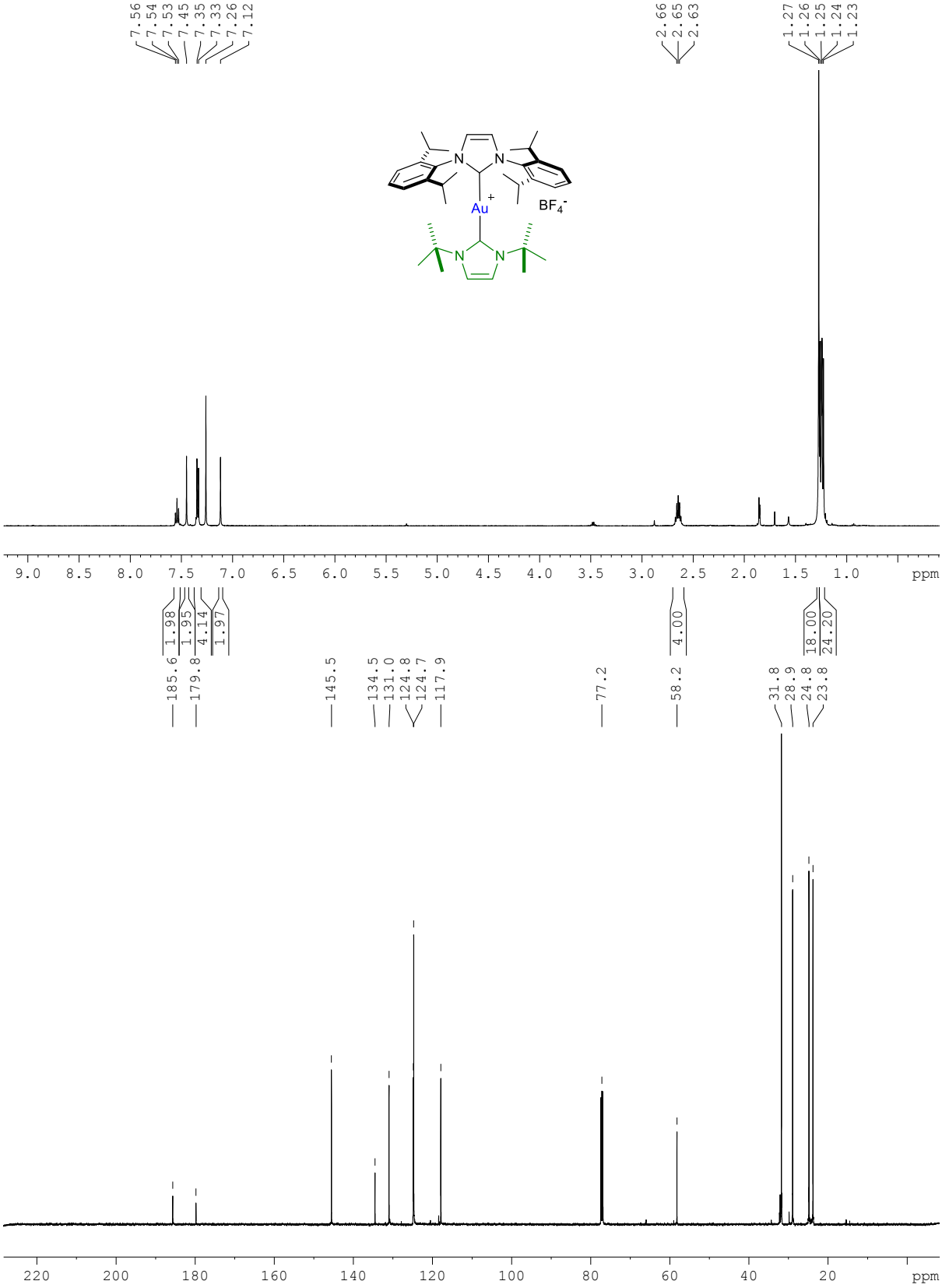
[Au(IMes)$_2$]BF$_4$ (**2b**), ^{1}H NMR, $CDCl_3$, 298K and ^{13}C-{^{1}H} NMR, $CDCl_3$, 298 K



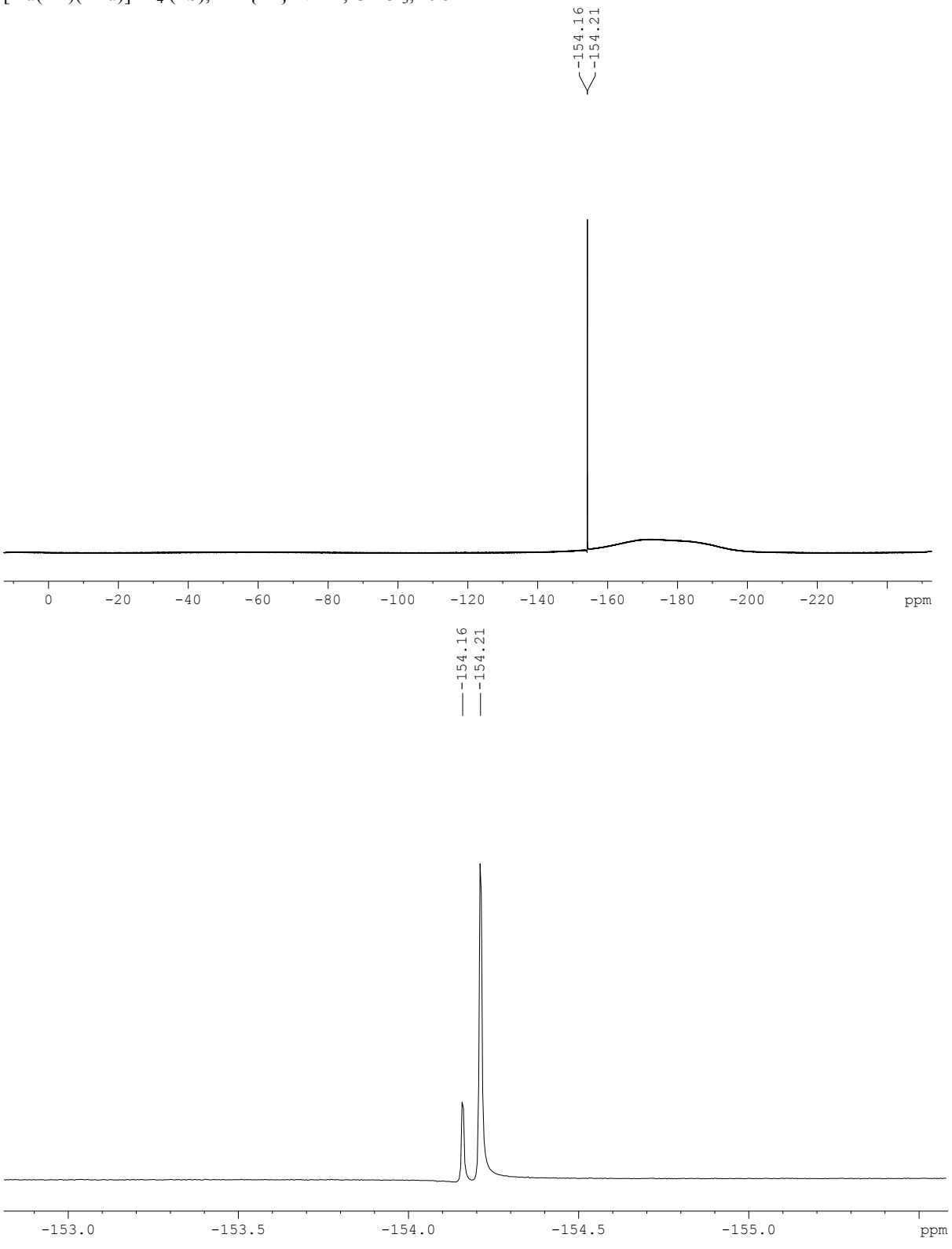
$[Au(IMes)_2]BF_4$ (**2b**), ^{19}F-{^1H} NMR, $CDCl_3$, 298 K



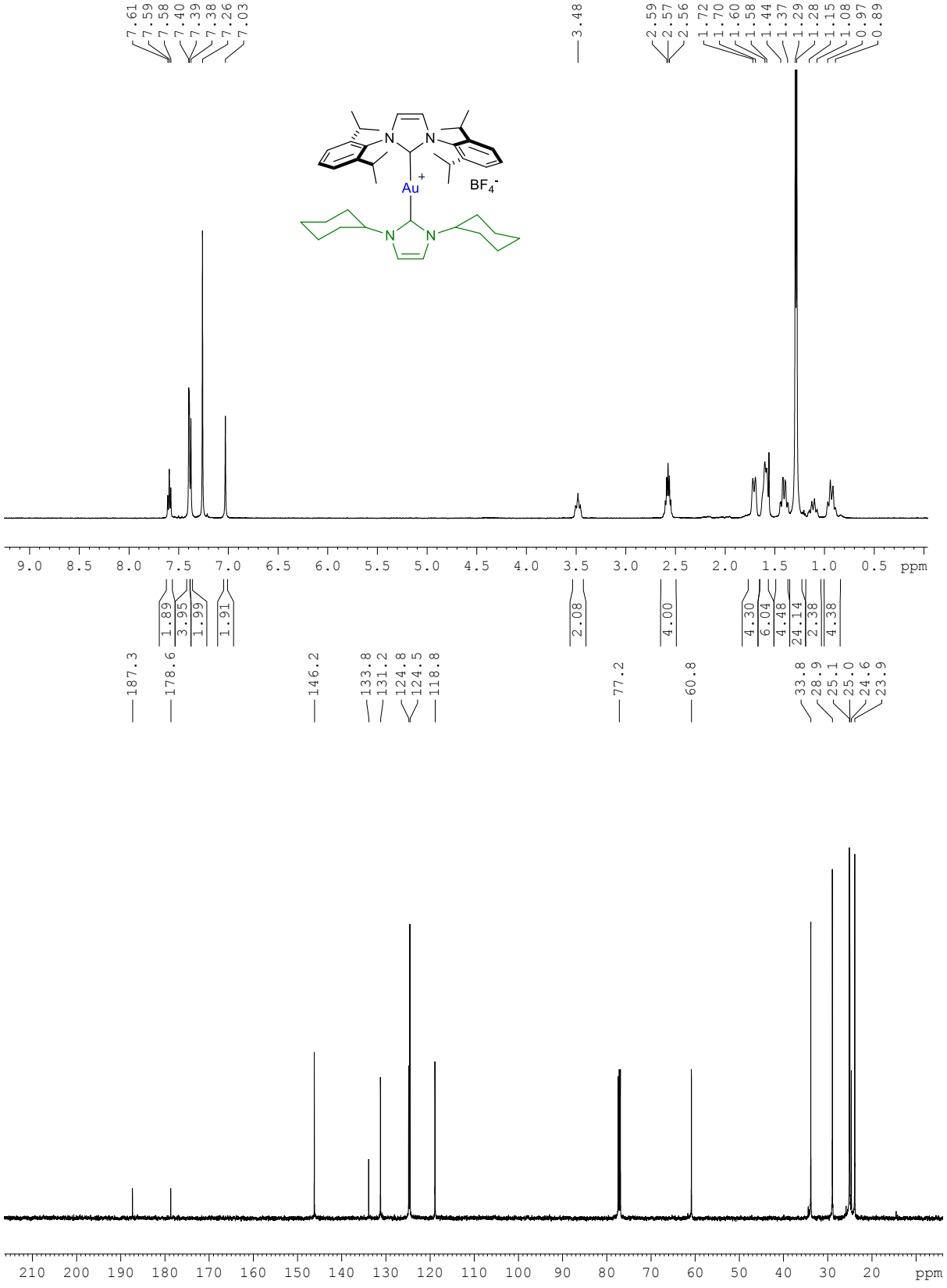
[Au(IPr)(I^{t}Bu)]BF_4 (**4b**), ^{1}H NMR, $CDCl_3$, 298K and ^{13}C-{^{1}H} NMR, $CDCl_3$, 298 K



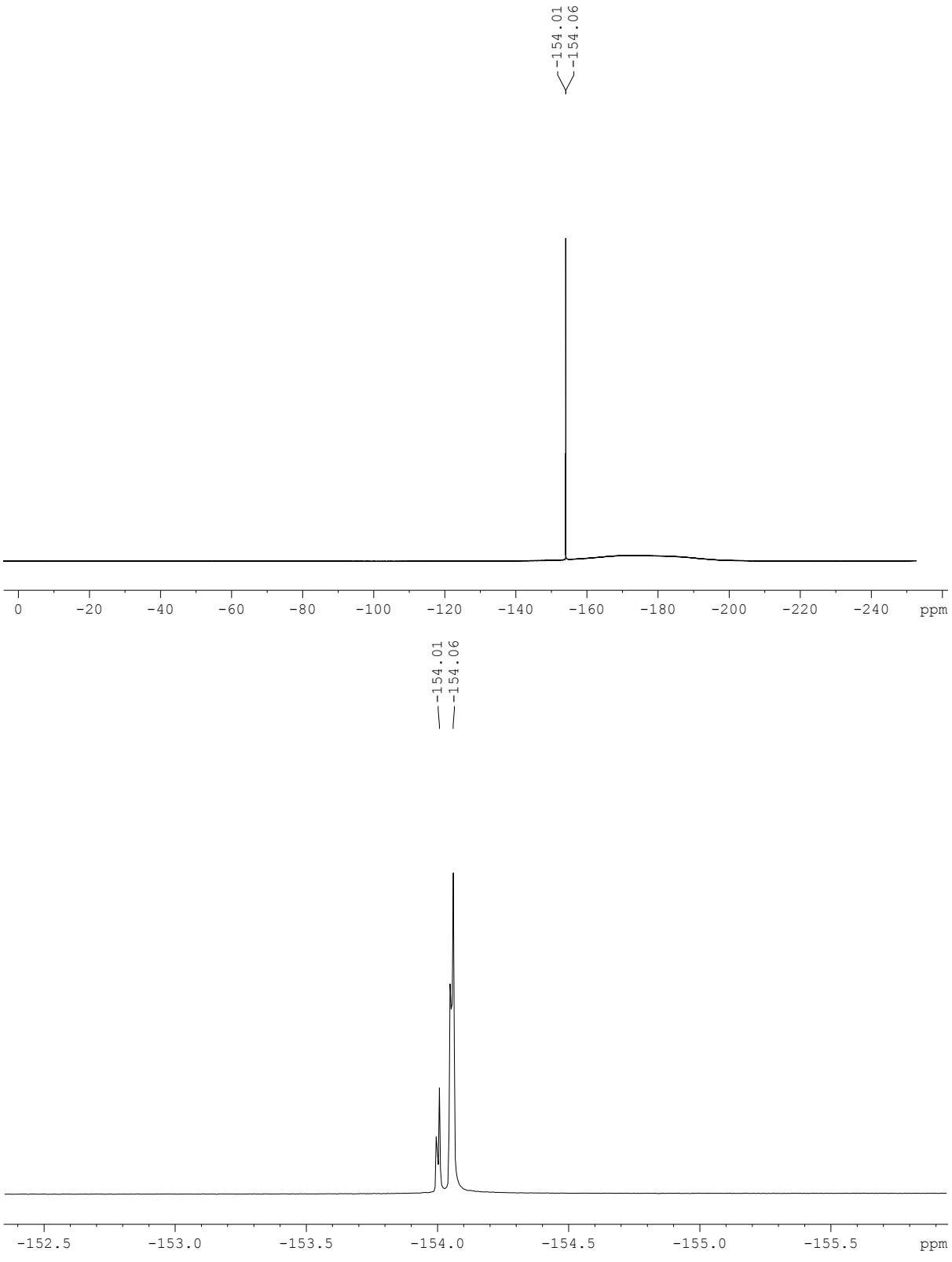
[Au(IPr)(I^{t}Bu)]BF_4 (**4b**), ^{19}F-{^1H} NMR, $CDCl_3$, 298 K



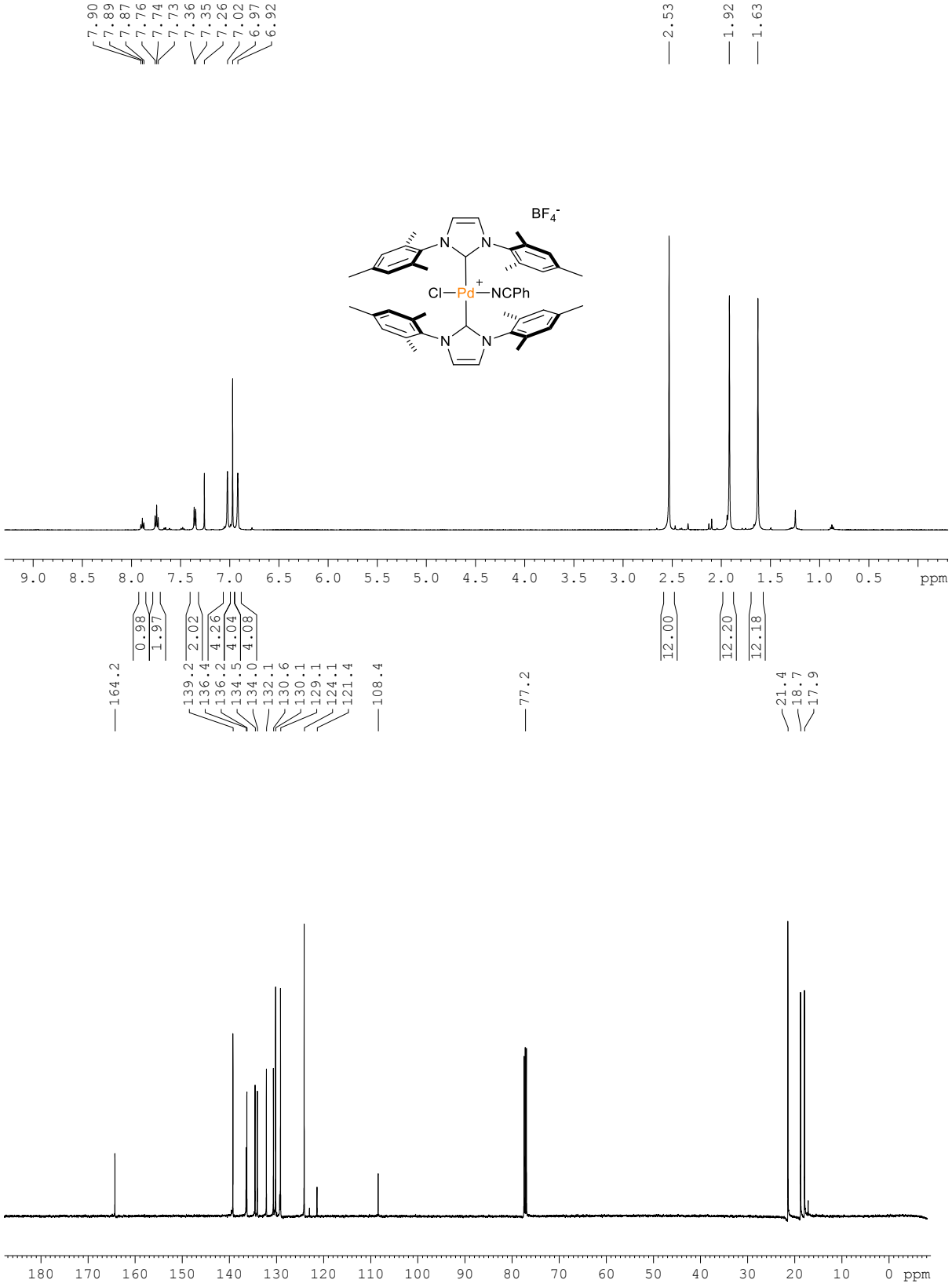
[Au(IPr)(ICy)]BF_4 (**5b**), ^{1}H NMR, $CDCl_3$, 298K and ^{13}C-{^{1}H} NMR, $CDCl_3$, 298 K



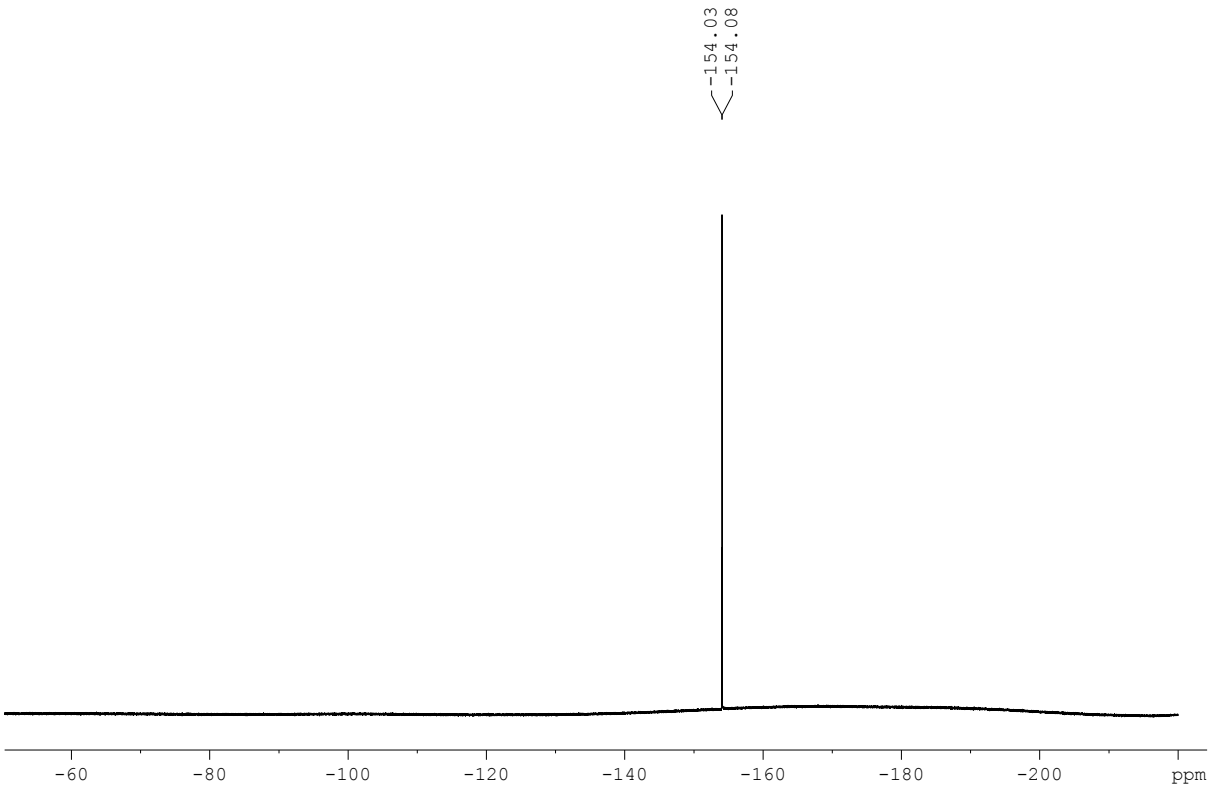
[Au(IPr)(ICy)]BF_4 (**5b**), ^{19}F-{^1H} NMR, $CDCl_3$, 298 K

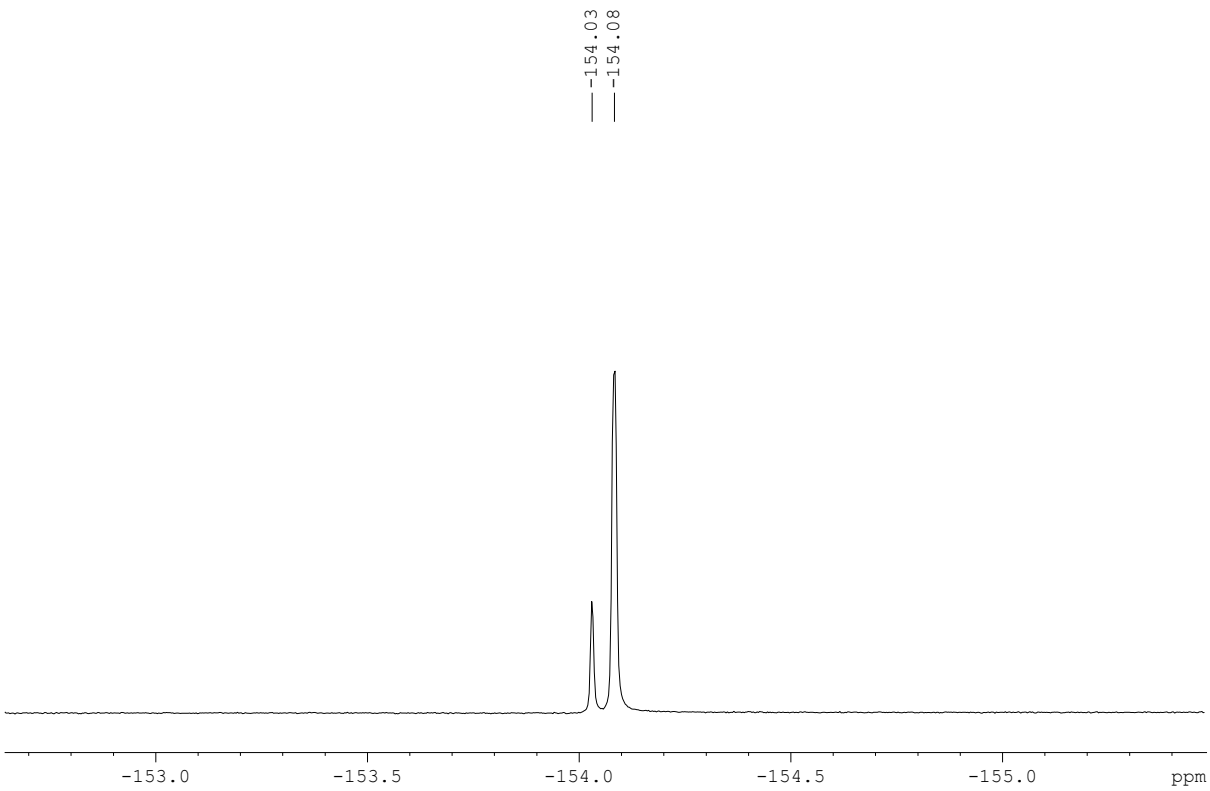


[Pd(Cl)(NCPh)(IMes)$_2$]BF$_4$ (**2c**), ^{1}H NMR, CDCl$_3$, 298K and ^{13}C-{^{1}H} NMR, CDCl$_3$, 298 K

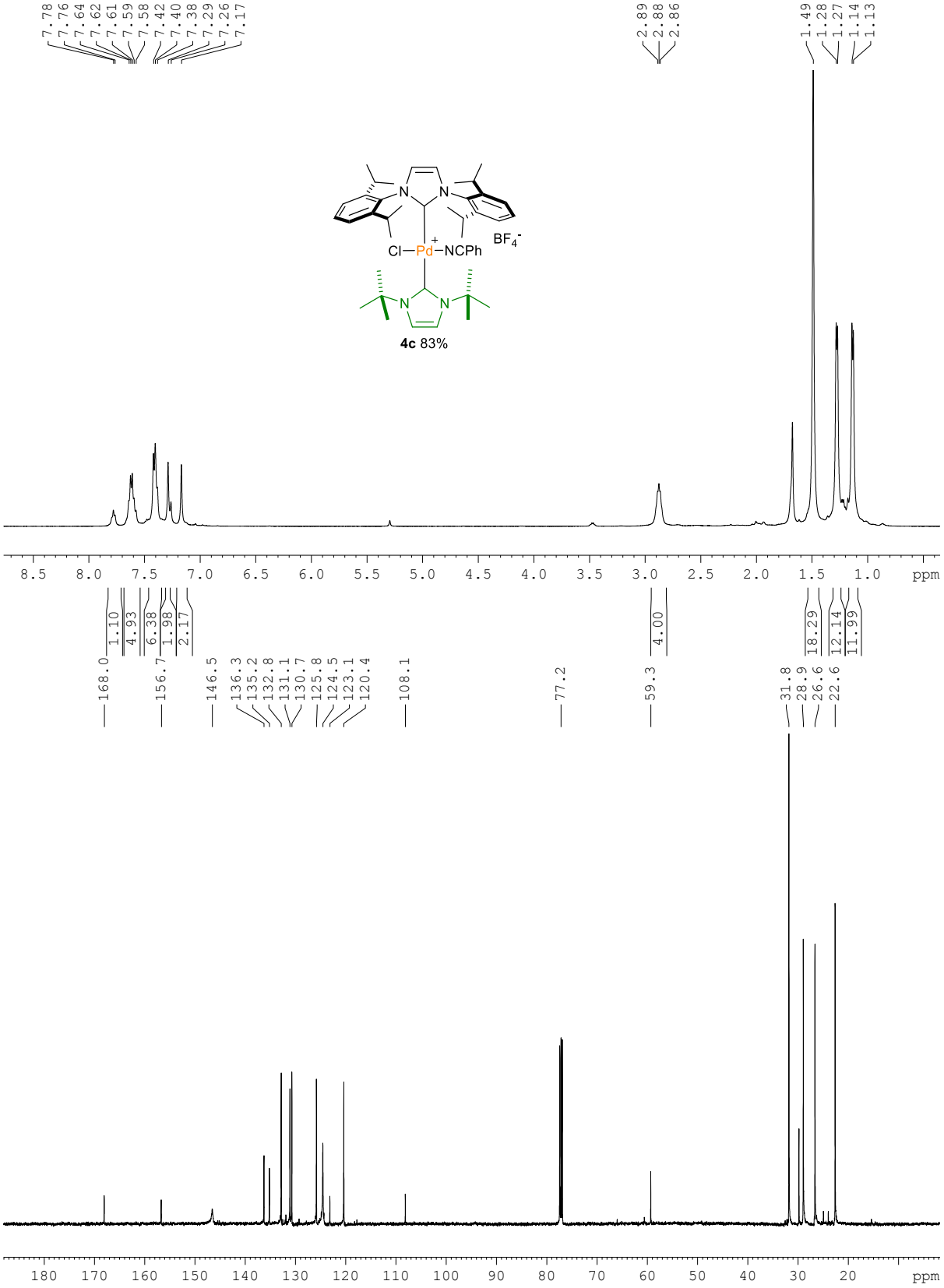


[Pd(Cl)(NCPh)(IMes)$_2$]BF$_4$ (**2c**), ^{19}F-{^{1}H} NMR, CDCl$_3$, 298 K

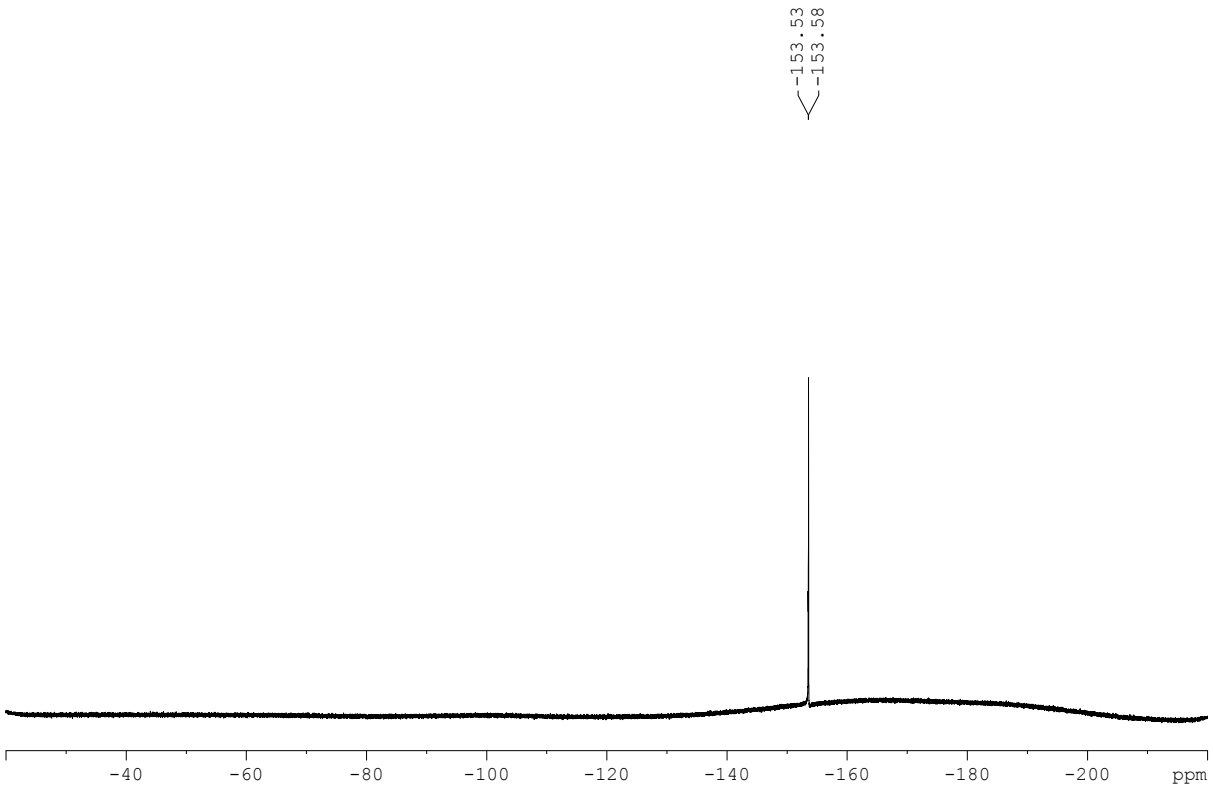


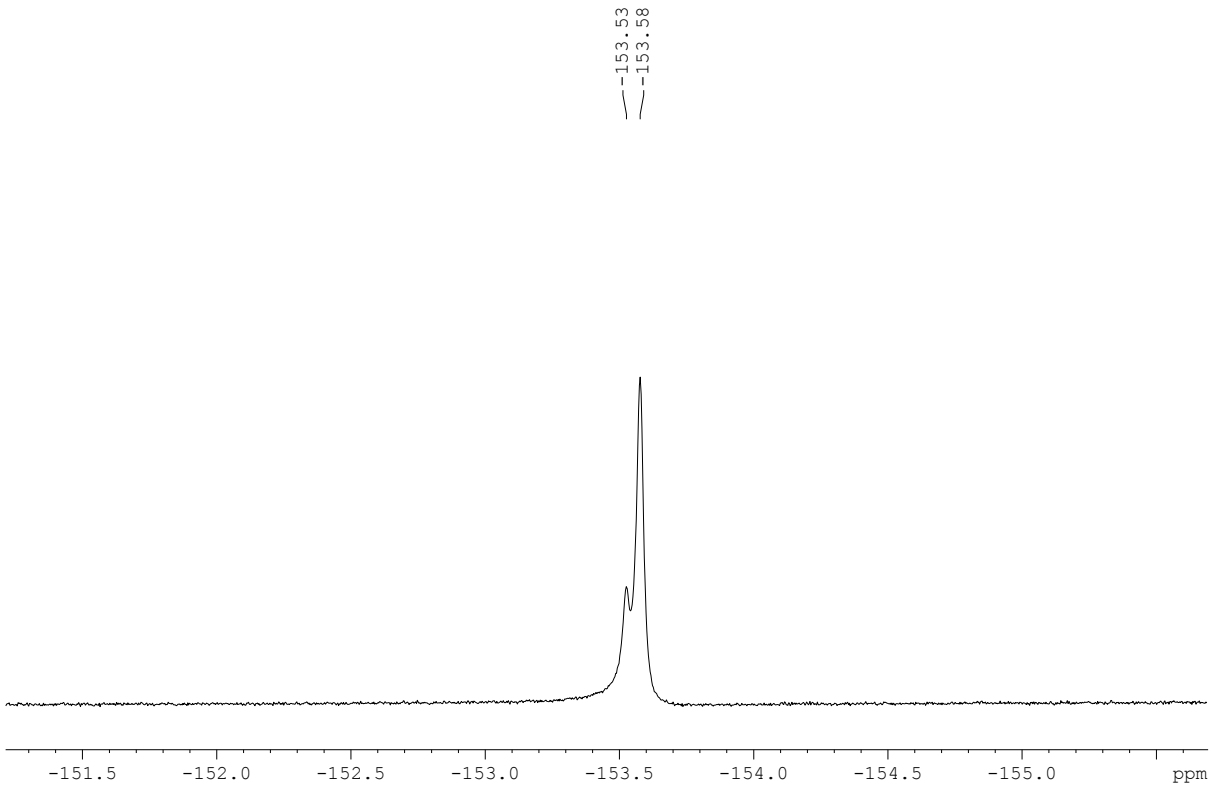


[Pd(Cl)(NCPh)(IPr)(I^{t}Bu)]BF_4 (**4c**), ^{1}H NMR, $CDCl_3$, 298K and ^{13}C-{^{1}H} NMR, $CDCl_3$, 298 K



[Pd(Cl)(NCPh)(IPr)(I^{t}Bu)]BF_4 (**4c**), ^{19}F-{^1H} NMR, $CDCl_3$, 298 K





7. Crystallographic data for complexes 2c and 4c

	2c	**4c**
CCDC number	CCDC 1435102	CCDC 1435103
Emperical formula	$C_{50}H_{54}BCl_4F_4N_5Pd$	$C_{46}H_{62}BCl_4F_4N_5Pd$
Formula Weight	1060.03	1020.04
Crystal color, Habit	colourless, prism	colorless, prism
Temperature (K)	173.15	173.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1$ (#4)	Cc (#9)
Unit cell dim.	0.300 X 0.030 X 0.030 mm	0.300 X 0.060 X 0.060 mm
Lattice type	Primitive	C-centered
Lattice parameter a,b,c (Å)	a = 11.609(4) Å b = 10.843(3) Å c = 20.674(7) Å	a = 18.242(3) Å b = 16.276(2) Å c = 18.471(3) Å
α,β,γ (°)	β = 91.013(8) ^{o}	β = 115.779(4) ^{o}
Volume (Å)^3	V = 2602.0(14) Å^3	V = 4938.4(13) Å^3
Z	2	4
Density calculated	1.353 g/cm^3	1.372 g/cm^3
Absorption coefficient (cm^{-1})	6.142 cm^{-1}	6.439 cm^{-1}
F(000)	1088.00	2112.00
Diffractometer	XtaLAB P200	XtaLAB P200
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA	45kV, 66mA
Theta range for data collection (°)	$2\Theta_{max}$ = 50.8^o	$2\Theta_{max}$ = 50.8^o
Reflexions collected	Total: 30536 Unique: 9371 (R_{int} = 0.0000)	Total: 29539 Unique: 8800 (R_{int} = 0.0631)
Correction	Lorentz-polarization Absorption (trans. factors: 0.544 - 0.982)	Lorentz-polarization Absorption (trans. factors: 0.622 - 0.962)
Structure solution	Direct Methods (SIR2004)	Direct Methods (SIR2004))
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Anomalous dispersion	All non-hydrogen atoms	All non-hydrogen atoms

No. Observations (all reflections)	9371	8800
No. variables	599	564
Reflection/parameter ratio	15.64	15.60
Goodness-of-fit on F^2	1.086	1.022
R1 (I>2.00σ(I))	0.1213	0.0532
R (All reflections)	0.1598	0.0756
Maximum peak in Final Diff Map ($e.Å^{-3}$)	3.29 $e^-/Å^3$	1.34 $e^-/Å^3$
Minimum peak in Final Diff Map ($e.Å^{-3}$)	-2.01 $e^-/Å^3$	--0.55 $e^-/Å^3$
Max shift/error in final cycle	0.000	0.000

8. References

1. F. Lazreg, D. B. Cordes, A. M. Z. Slawin and C. S. J. Cazin, *Organometallics*, 2015, **34**, 419.
2. S. Gaillard, P. Nun, A. M. Z. Slawin and S. P. Nolan, *Organometallics,* 2010, **29**, 5402.