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New Pd-PEPPSI complexes with fluorinated tricyclic NHC ligands: synthesis and catalytic activity

Pavel S. Gribanov, Anna N. Philippova, Alexander A. Kazakov, Konstantin A. Palagin, Alexander F. Smol'yakov and Sergey N. Osipov

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General Information

All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were distilled as necessary. All reagents were used as purchased. Analytical TLC was performed with Merck silica gel 60 F 254 plates; visualization was accomplished with UV light or iodine vapors. Chromatography was carried out using Merck silica gel (Kieselgel 60, 0.063–0.200 mm) and petroleum ether/ethyl acetate as an eluent. Previously known NHC-CuCl complexes **1a** and **1b** were prepared according to the published methods, analytical data were in accordance with the literature data.[S1] NMR spectra were recorded on a Bruker Avance 400 instrument (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F ($CFCl_3$ as reference)). High-resolution mass spectra (HRMS) were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Electrospray ionization (ESI) mass spectra (MS) were obtained from acetonitrile solution.

General procedure for the synthesis of Pd-PEPPSI-NHC complexes 3a,b-5a,b.

Under argon in a Schlenk tube with a magnetic stirring bar, a mixture of NHC-CuCl complex **1a** or **1b** (70 mg, 1 equiv) and [$PdCl_2(MeCN)_2$] (1 equiv) was stirred at 40°C for 2 h in 5 mL of dry and degassed dichloromethane. The mixture was allowed to cool to room temperature, and to this solution was added the corresponding pyridine derivative (3.0 equiv) solution in dichloromethane (1 mL). The resulting mixture was stirred for 1 h at room temperature and was passed through a short layer of celite, which was additionally washed with CH_2Cl_2. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (gradient elution: petroleum ether/ethyl acetate = 8:1, petroleum ether/ethyl acetate = 4:1) to give the desired product.

[2-Mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1H-benzo[d]imidazo-[5,1-b][1,3]oxazin-1-ylidene](pyridyl)palladium(II) dichloride **3a**: following the general procedure **3a** was obtained as pale-yellow solid (69%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.56 (dd, *J* = 6.4, 1.3 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.37 (s, 1H), 7.30 (s, 1H), 7.19 – 7.14 (m, 2H), 7.04 (s, 1H), 6.97 (s, 1H), 5.67 (d, *J* = 6.6 Hz, 1H), 4.43 (dd, *J* = 13.2, 6.6 Hz, 1H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.38 (s, 3H), 2.53 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H). ^{19}F NMR (282 MHz, Chloroform-*d*) δ -71.73 (q, *J* = 9.5 Hz), -73.25 (q, *J* = 9.2 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.5, 151.4, 139.2, 137.9, 137.1, 136.6, 135.2, 134.4, 134.2, 133.8, 129.8, 129.6, 128.6 (q, *J* = 288.8 Hz), 125.2, 124.3, 121.7 (q, *J* = 287.8 Hz), 118.1, 84.1, 78.5 (hept, *J* = 31.0 Hz), 57.6, 22.3,

21.5, 21.3, 20.0, 19.0. HRMS (ESI) of $C_{28}H_{27}Cl_2F_6N_3OPd$, m/z: calcd for $[M\text{-}2Cl\text{-}H\text{-}Py+MeCN]^+$ 602.0864, found: 602.0873.

[2-Mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1H-benzo[d]imidazo-[5,1-b][1,3]oxazin-1-ylidene](4-methylpyridyl)palladium(II) dichloride **4a**: following the general procedure **4a** was obtained as pale-yellow solid (65%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 6.3 Hz, 2H), 7.36 (s, 1H), 7.29 (s, 1H), 7.03 (s, 1H), 6.99 – 6.93 (m, 3H), 5.66 (d, *J* = 6.3 Hz, 1H), 4.42 (dd, *J* = 13.3, 6.6 Hz, 1H), 3.83 (d, *J* = 13.3 Hz, 1H), 3.38 (s, 3H), 2.53 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 2.26 (s, 3H). ^{19}F NMR (282 MHz, Chloroform-*d*) δ -71.72 (q, *J* = 9.0 Hz), -73.25 (q, *J* = 8.9 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.0, 150.8, 139.2, 137.1, 136.6, 136.6, 135.2, 134.5, 134.2, 133.9, 129.8, 129.6, 125.2, 122.9 (q, *J* = 290.2 Hz), 121.7 (q, *J* = 288.2 Hz), 118.1, 84.1, 78.2 (hept, *J* = 30.0 Hz), 57.6, 22.4, 21.5, 21.3, 21.0, 20.0, 19.0. HRMS (ESI) of $C_{29}H_{29}Cl_2F_6N_3OPd$, m/z: calcd for $[M\text{-}2Cl\text{-}H]^+$ 654.1177, found: 654.1192.

[2-Mesityl-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1H-benzo[d]imidazo-[5,1-b][1,3]oxazin-1-ylidene](3-chloropyridyl)palladium(II) dichloride **5a**: following the general procedure **5a** was obtained as pale-yellow solid (61%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 2.4 Hz, 1H), 8.54 (d, *J* = 5.2 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.38 (s, 1H), 7.31 (s, 1H), 7.14 (dd, *J* = 8.1, 5.6 Hz, 1H), 7.05 (s, 1H), 6.98 (s, 1H), 5.68 (d, *J* = 6.1 Hz, 1H), 4.44 (dd, *J* = 13.3, 6.6 Hz, 1H), 3.86 (d, *J* = 13.4 Hz, 1H), 3.35 (s, 3H), 2.52 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H). ^{19}F NMR (282 MHz, Chloroform-*d*) δ -71.71 (q, *J* = 9.6 Hz), -73.25 (q, *J* = 9.2 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 150.5, 149.5, 139.4, 137.9, 137.1, 136.8, 136.6, 135.3, 134.4, 134.1, 133.8, 132.4, 129.9, 129.7, 125.3, 124.7, 122.9 (q, *J* = 290.3 Hz), 121.7 (q, *J* = 287.5 Hz), 118.1, 84.1, 57.6, 22.4, 21.5, 21.3, 20.0, 19.0. HRMS (ESI) of $C_{28}H_{26}Cl_3F_6N_3OPd$, m/z: calcd for $[M\text{-}2Cl\text{-}H\text{-}Py+MeCN]^+$ 602.0864, found: 602.0874.

[2-(2,6-Diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1H-benzo[d]imidazo[5,1-b][1,3]oxazin-1-ylidene](pyridyl)palladium(II) dichloride **3b**: following the general procedure **3b** was obtained as pale-yellow solid (67%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 5.0 Hz, 2H), 7.60 (tt, *J* = 7.7, 1.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.29 (s, 1H), 7.25 (s, 1H), 7.20 – 7.13 (m, 2H), 5.65 (d, *J* = 6.3 Hz, 1H), 4.53 (dd, *J* = 13.2, 6.5 Hz, 1H), 3.94 (d, *J* = 13.1 Hz, 1H), 3.67 (p, *J* = 6.6 Hz, 1H), 3.42 (s, 3H), 3.11 (p, *J* = 6.6 Hz, 1H), 2.39 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.46 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 3H). ^{19}F NMR (282 MHz, Chloroform-*d*) δ -71.68 (q, *J* = 8.8 Hz), -73.39 (q, *J* = 9.2 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.1, 151.4, 147.9, 147.1, 137.8, 136.6, 135.2, 134.6, 133.9, 130.3, 125.2, 124.8, 124.4, 122.9 (q, *J* = 290.2 Hz), 121.7 (q, *J* = 287.9 Hz), 118.1, 84.1, 59.8, 29.5,

28.1, 27.1, 26.3, 24.0, 23.3, 22.2, 21.5. HRMS (ESI+) of $C_{34}H_{39}Cl_2F_6N_4OPd$, m/z: calcd for $[M+H]^+$ 754.1012, found: 754.1012. $[M-Py+Na+MeCN]^+$ 738.0681, found: 738.0696.

[2-(2,6-Diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1H-benzo[d]imidazo[5,1-b][1,3]oxazin-1-ylidene](4-methylpyridyl)palladium(II) dichloride **4b**: following the general procedure **4b** was obtained as pale-yellow solid (71%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 5.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.29 (s, 1H), 7.23 (s, 1H), 6.97 (d, *J* = 5.4 Hz, 2H), 5.64 (d, *J* = 6.0 Hz, 1H), 4.52 (dd, *J* = 13.2, 6.2 Hz, 1H), 3.93 (d, *J* = 13.1 Hz, 1H), 3.70 – 3.61 (m, 1H), 3.42 (s, 3H), 3.15 – 3.05 (m, 1H), 2.39 (s, 3H), 2.26 (s, 3H), 1.49 (d, *J* = 6.4 Hz, 3H), 1.45 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.7 Hz, 3H), 1.12 (d, *J* = 6.7 Hz, 3H). ^{19}F NMR (282 MHz, Chloroform-*d*) δ -71.66 (q, *J* = 9.2 Hz), -73.39 (q, *J* = 9.3 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.2, 150.4, 149.4, 147.6, 146.7, 136.2, 134.9, 134.3, 134.3, 133.7, 129.9, 124.9, 124.5, 124.0, 117.8, 83.8, 59.5, 29.2, 27.8, 26.8, 25.9, 23.7, 23.0, 21.9, 21.2, 20.8. HRMS (ESI+) of $C_{34}H_{39}Cl_2F_6N_4OPd$ *m/z*: calcd for $[M+H+MeCN]^+$ 809.1440, found 809.1472.

[2-(2,6-Diisopropylphenyl)-7,9-dimethyl-5,5-bis(trifluoromethyl)-2,3,3a,5-tetrahydro-1H-benzo[d]imidazo[5,1-b][1,3]oxazin-1-ylidene](3-chloropyridyl)palladium(II) dichloride **5b**: following the general procedure **5b** was obtained as pale-yellow solid (64%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 8.53 (d, *J* = 5.3 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.12 (dd, *J* = 8.1, 5.6 Hz, 1H), 5.66 (d, *J* = 6.3 Hz, 1H), 4.54 (dd, *J* = 13.1, 6.5 Hz, 1H), 3.95 (d, *J* = 13.2 Hz, 1H), 3.64 (p, *J* = 6.7 Hz, 1H), 3.39 (s, 3H), 3.10 (p, *J* = 6.4 Hz, 1H), 2.39 (s, 3H), 1.49 (d, *J* = 6.4 Hz, 3H), 1.45 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H). ^{19}F NMR (282 MHz, Chloroform-*d*) δ -71.67 (q, *J* = 9.8 Hz), -73.38 (q, *J* = 9.7 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.8, 150.4, 149.4, 147.8, 147.0, 137.9, 136.8, 135.2, 134.5, 134.4, 133.9, 132.4, 130.4, 125.2, 124.8, 124.8, 124.4, 122.8 (q, *J* = 290.3 Hz), 121.7 (q, *J* = 287.7 Hz), 118.1, 84.2, 78.1 (hept, *J* = 29.0 Hz), 59.9, 29.5, 28.1, 27.1, 26.3, 24.0, 23.3, 22.2, 21.5. HRMS (ESI) of $C_{31}H_{32}Cl_3F_6N_3OPd$, m/z: calcd for $[M-2Cl-H-Py+MeCN]^+$ 644.1333, found: 644.1340.

General procedure for the Suzuki–Miyaura coupling

The Suzuki–Miyaura coupling of 1-bromo-4-methylbenzene and 4-methoxyphenylboronic acid was performed according to literature procedures[S2,S3] with minor modifications. A screw-cap vial equipped with a magnetic stir bar was charged with corresponding Pd-PEPPSI-NHC complex **3-5** (2 mol%) in ethanol (1 mL), 0.3 mmol (1.0 equiv) of 1-bromo-4-methylbenzene or bromobenzene,

0.45 mmol (1.5 equiv) of 4-methoxyphenylboronic acid, and K_2CO_3 (3.0 equiv.). The vial was transferred to a preaheated oil bath (70°C). After 24 h reaction mixture was cooled, concentrated in vacuo, and the corresponding products isolated by chromatography with hexane-ethyl acetate mixture.

Coupling product 6a: 4-methoxy-4'-methyl-1,1'-biphenyl

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 4H), 2.39 (s, 3H).

Analytical data was in accordance with the literature.[S4]

Coupling product 6b: 4-methoxy-1,1'-biphenyl

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 4H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H).

Analytical data was in accordance with the literature.[S5]

NMR spectra

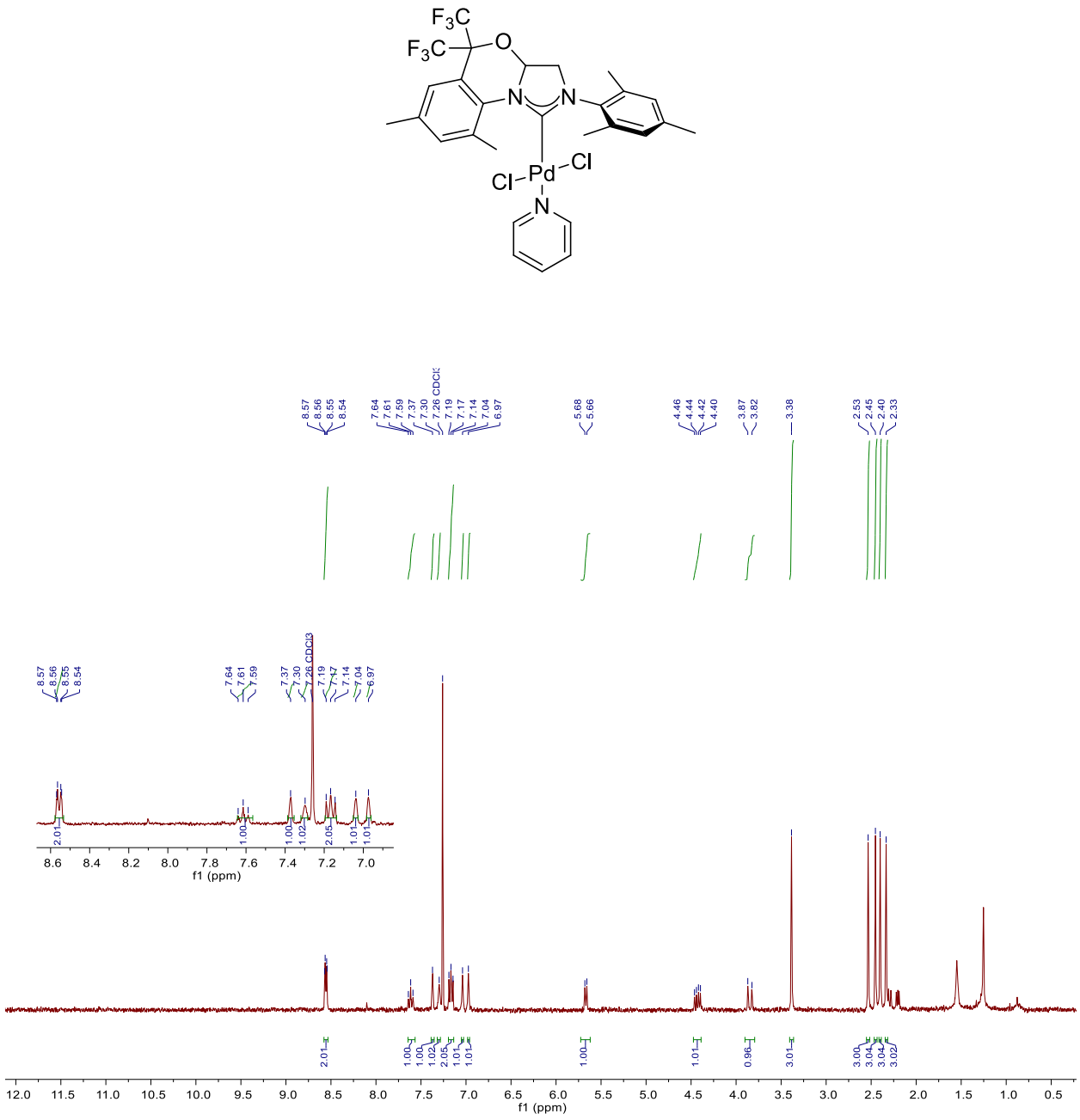


Figure S1. ^{1}H NMR (400 MHz) of **3a** in $CDCl_3$.

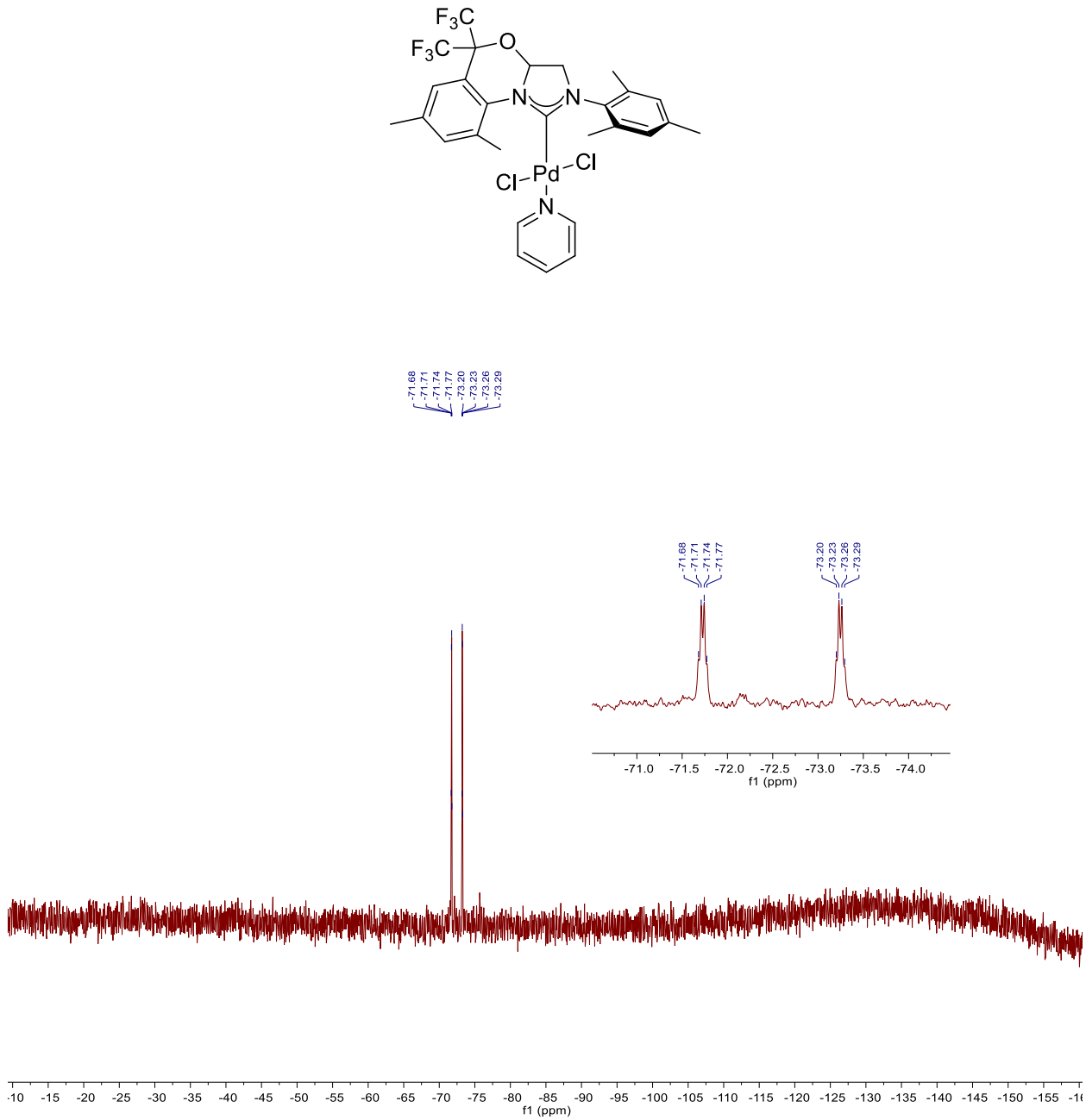


Figure S2. ^{19}F NMR (282 MHz) of **3a** in $CDCl_3$.

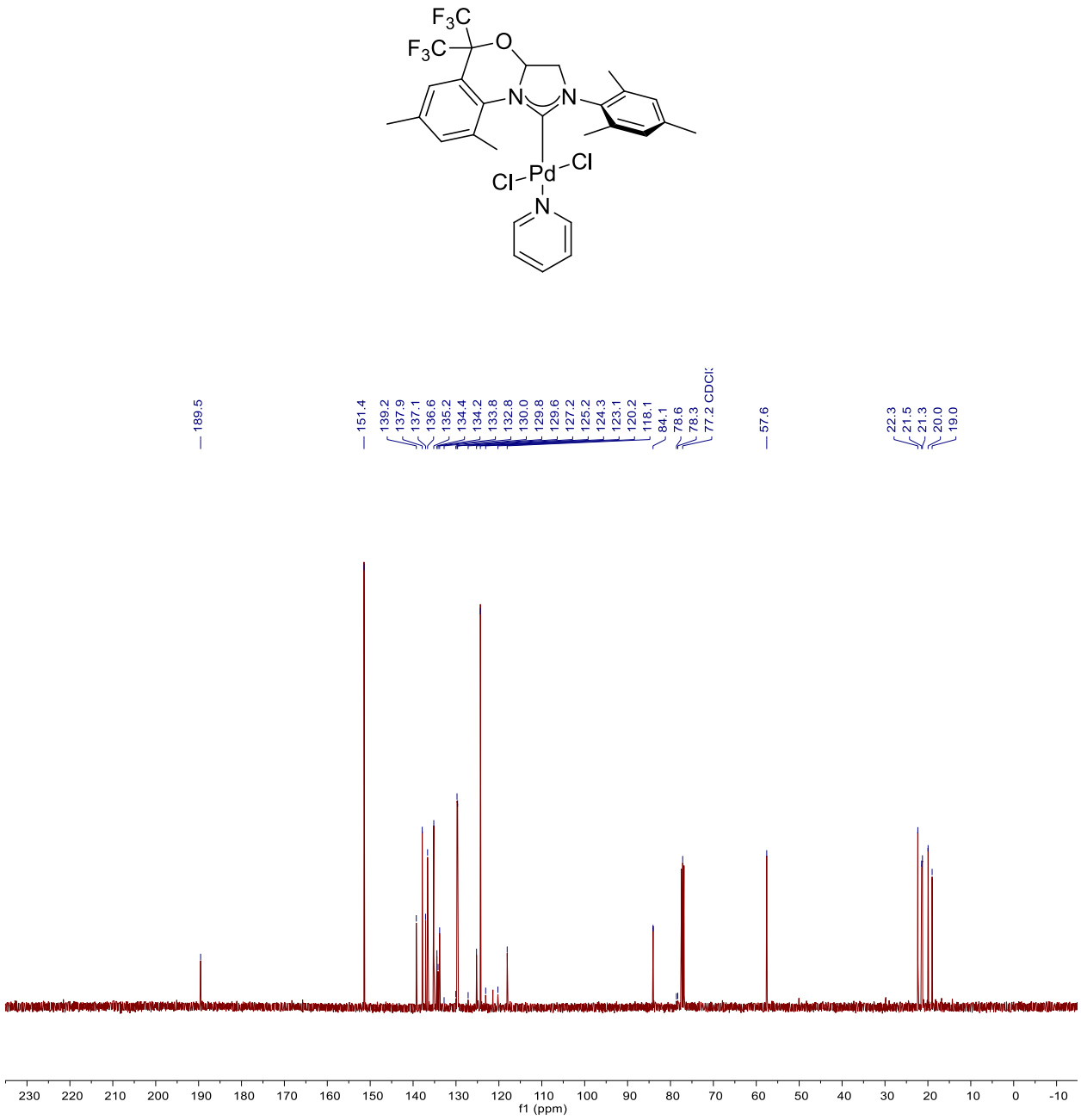


Figure S3. ^{13}C NMR (101 MHz) of **3a** in $CDCl_3$.

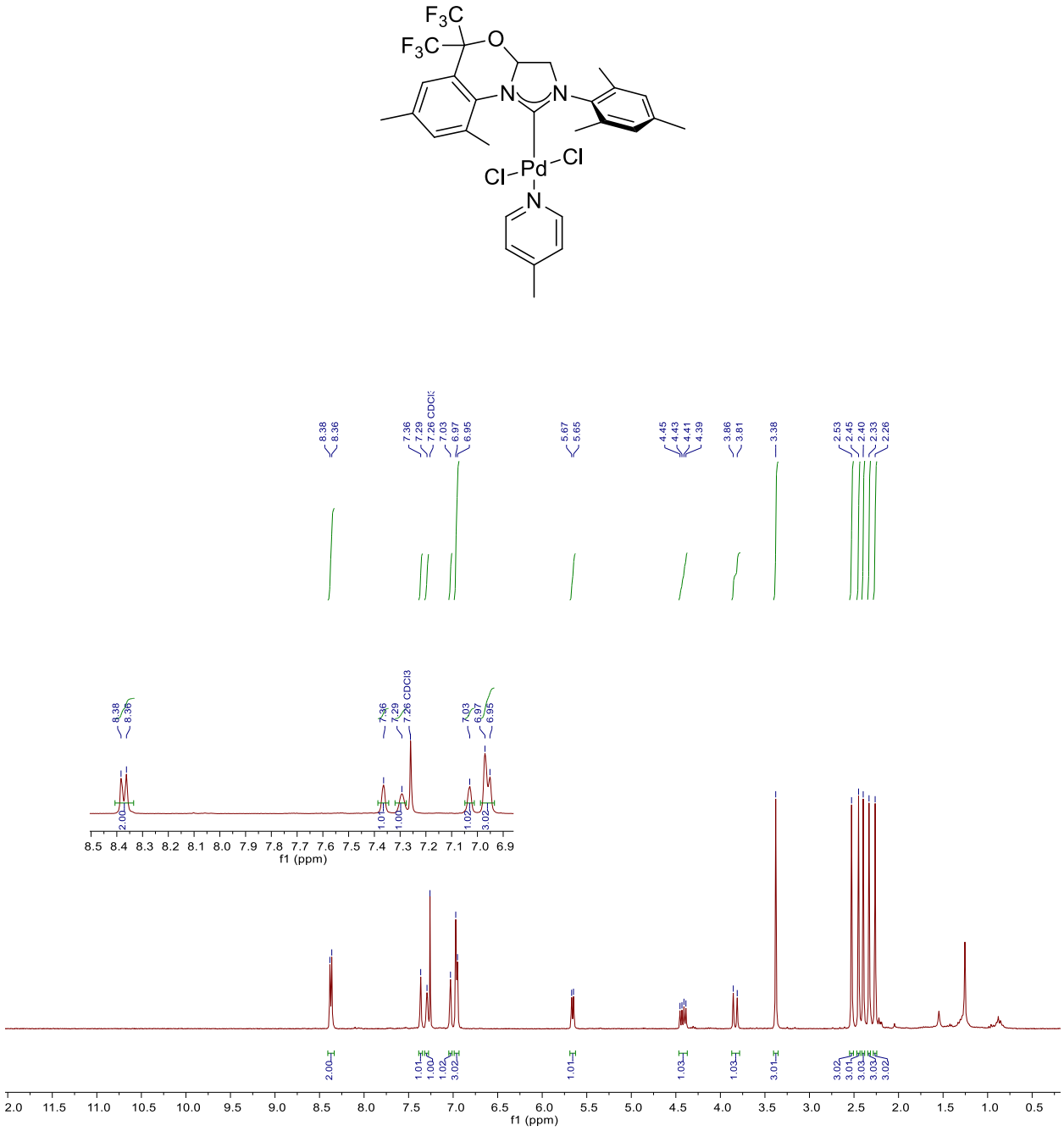


Figure S4. ^{1}H NMR (400 MHz) of **4a** in $CDCl_3$.

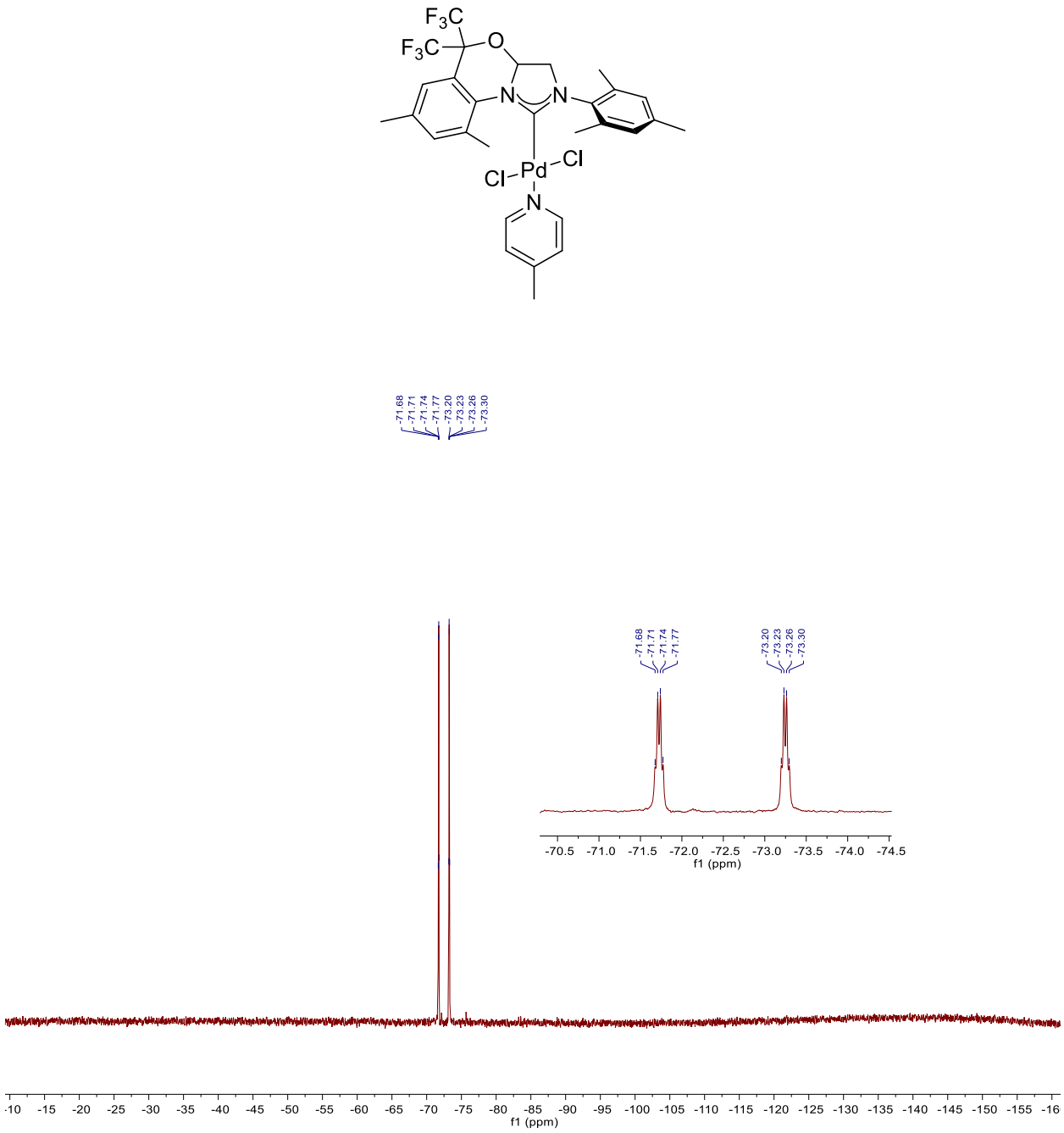


Figure S5. ^{19}F NMR (282 MHz) of **4a** in $CDCl_3$.

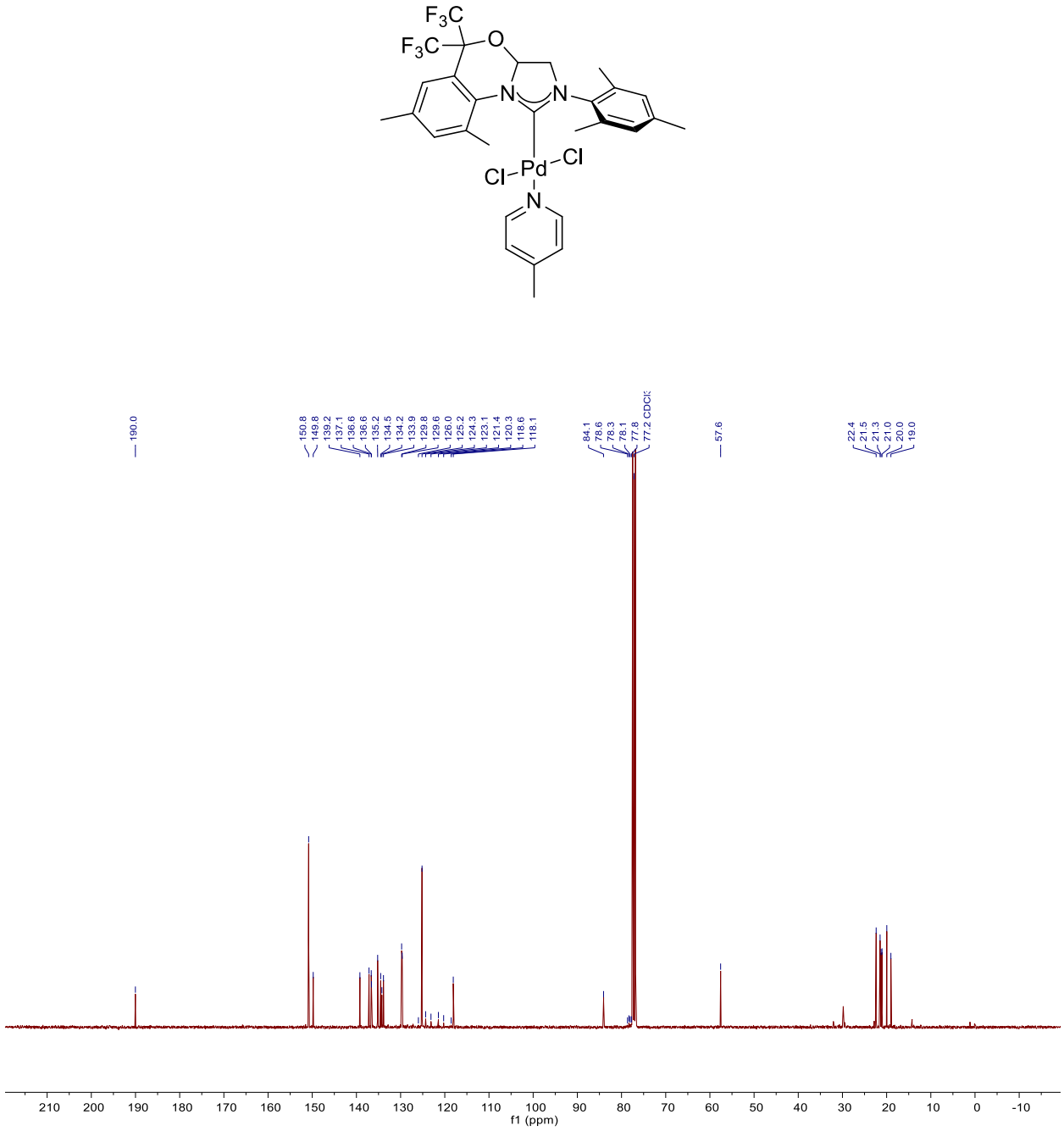


Figure S6. ^{13}C NMR (101 MHz) of **4a** in $CDCl_3$.

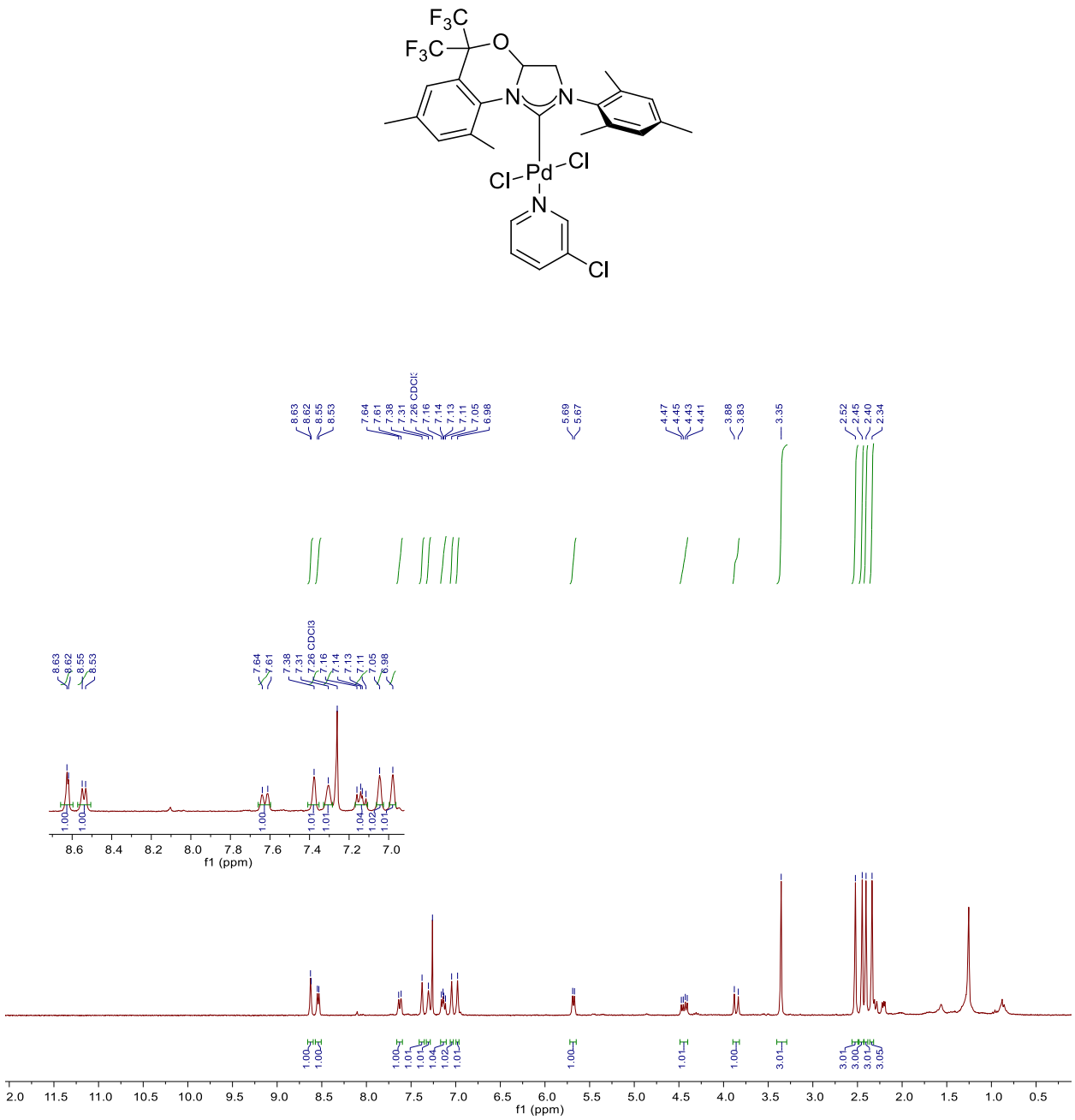


Figure S7. ^{1}H NMR (400 MHz) of **5a** in $CDCl_3$.

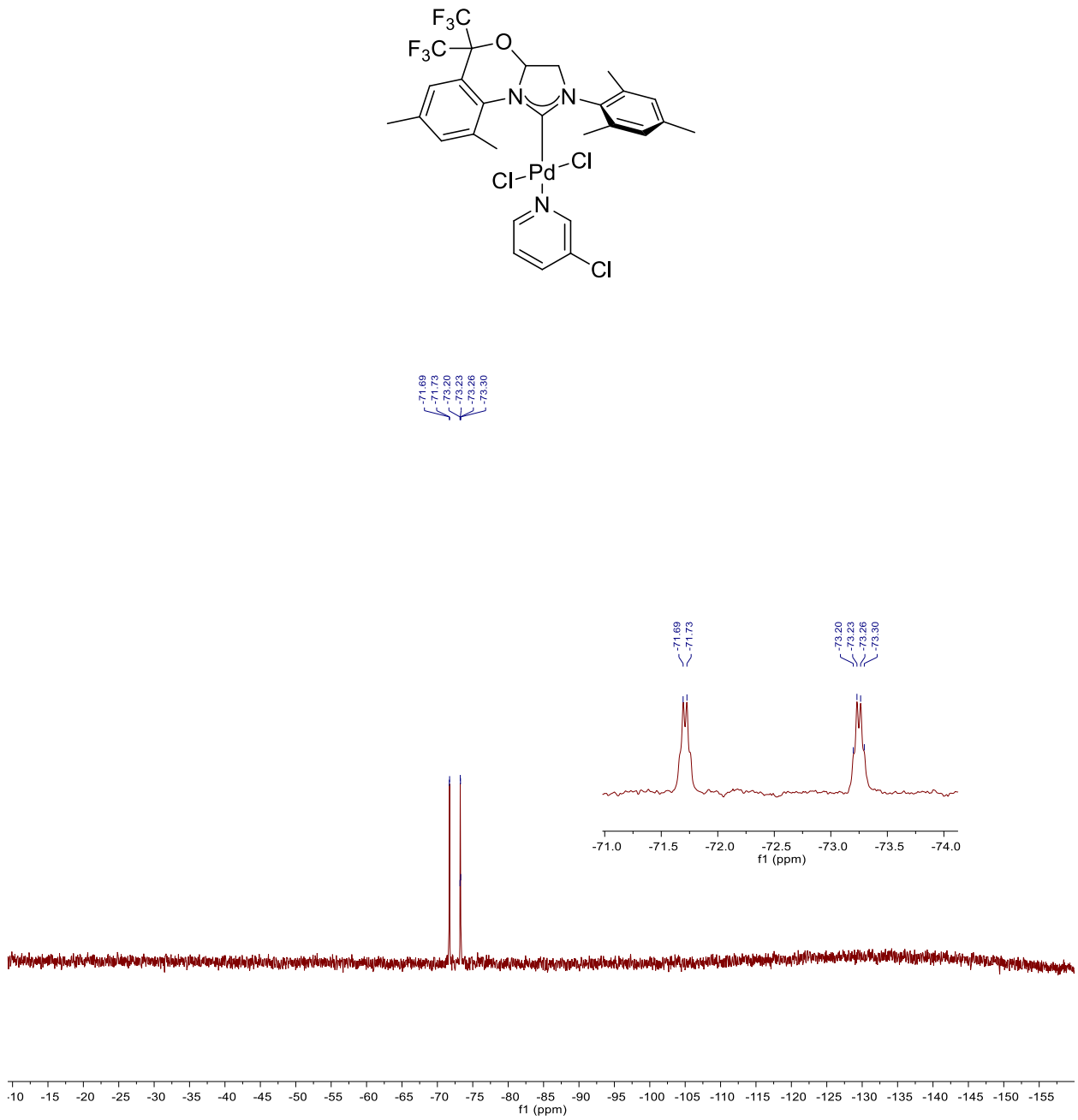


Figure S8. ^{19}F NMR (282 MHz) of **5a** in $CDCl_3$.

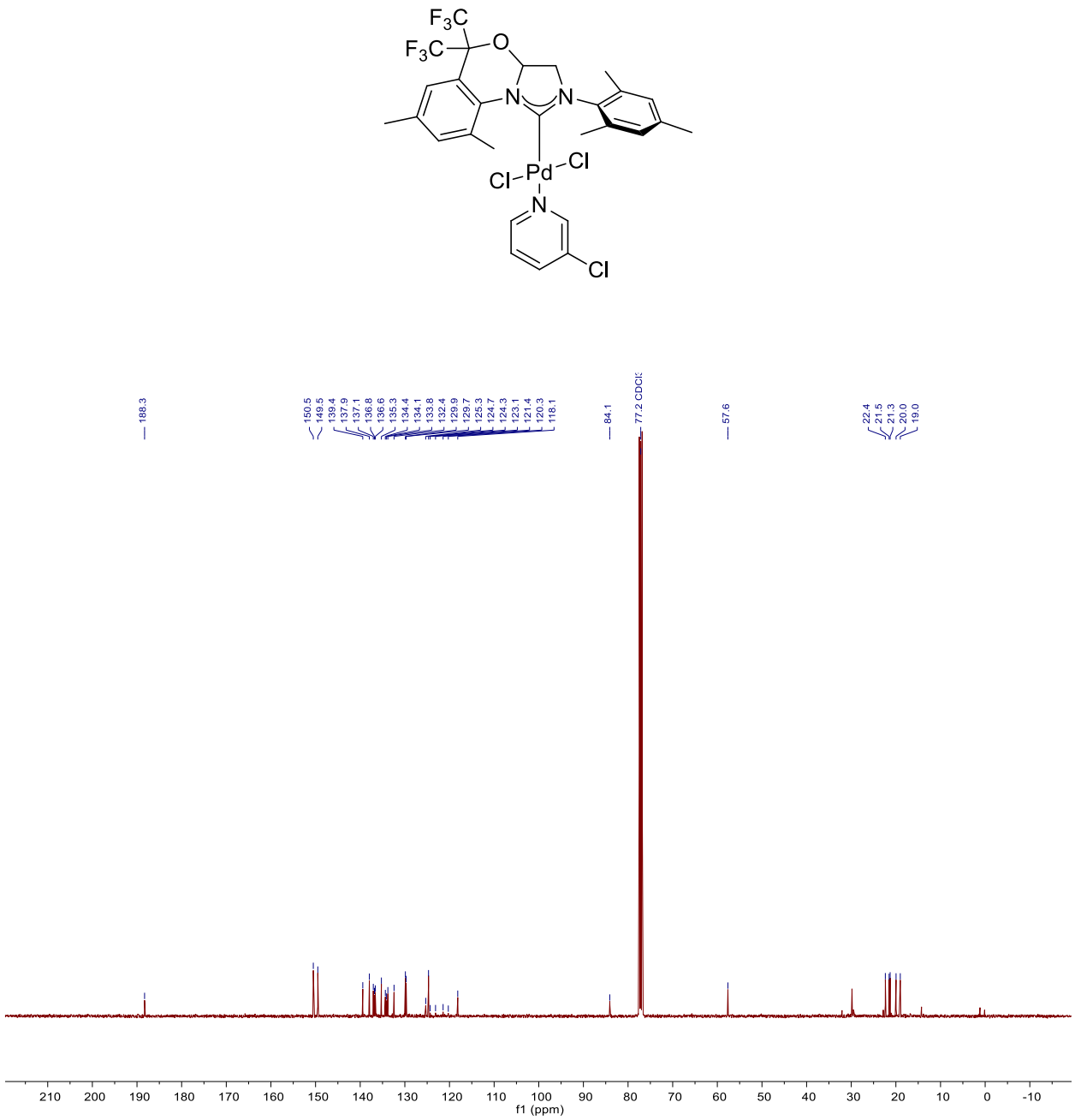


Figure S9. ^{13}C NMR (101 MHz) of **5a** in $CDCl_3$.

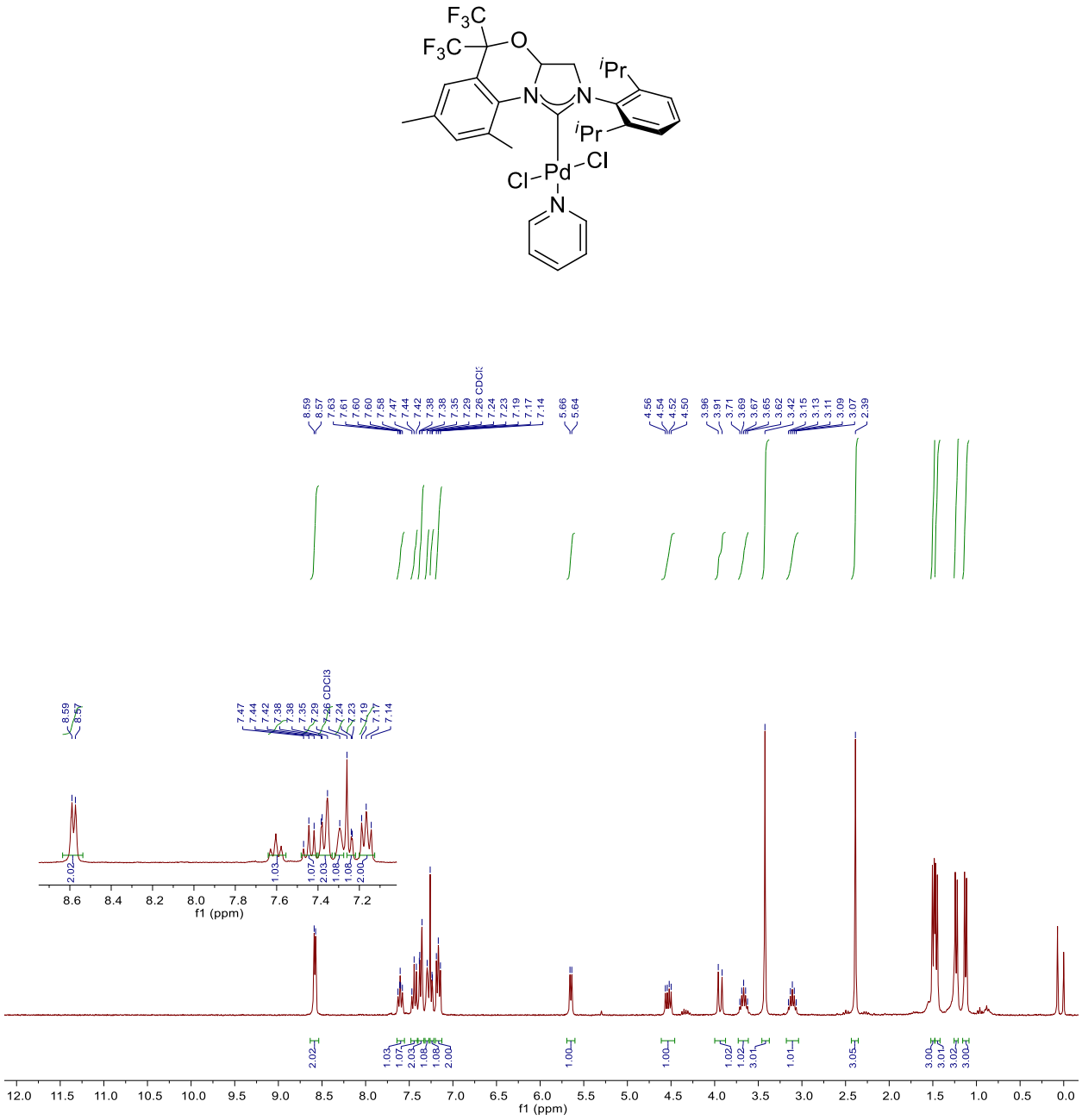


Figure S10. ^{1}H NMR (400 MHz) of **3b** in $CDCl_3$.

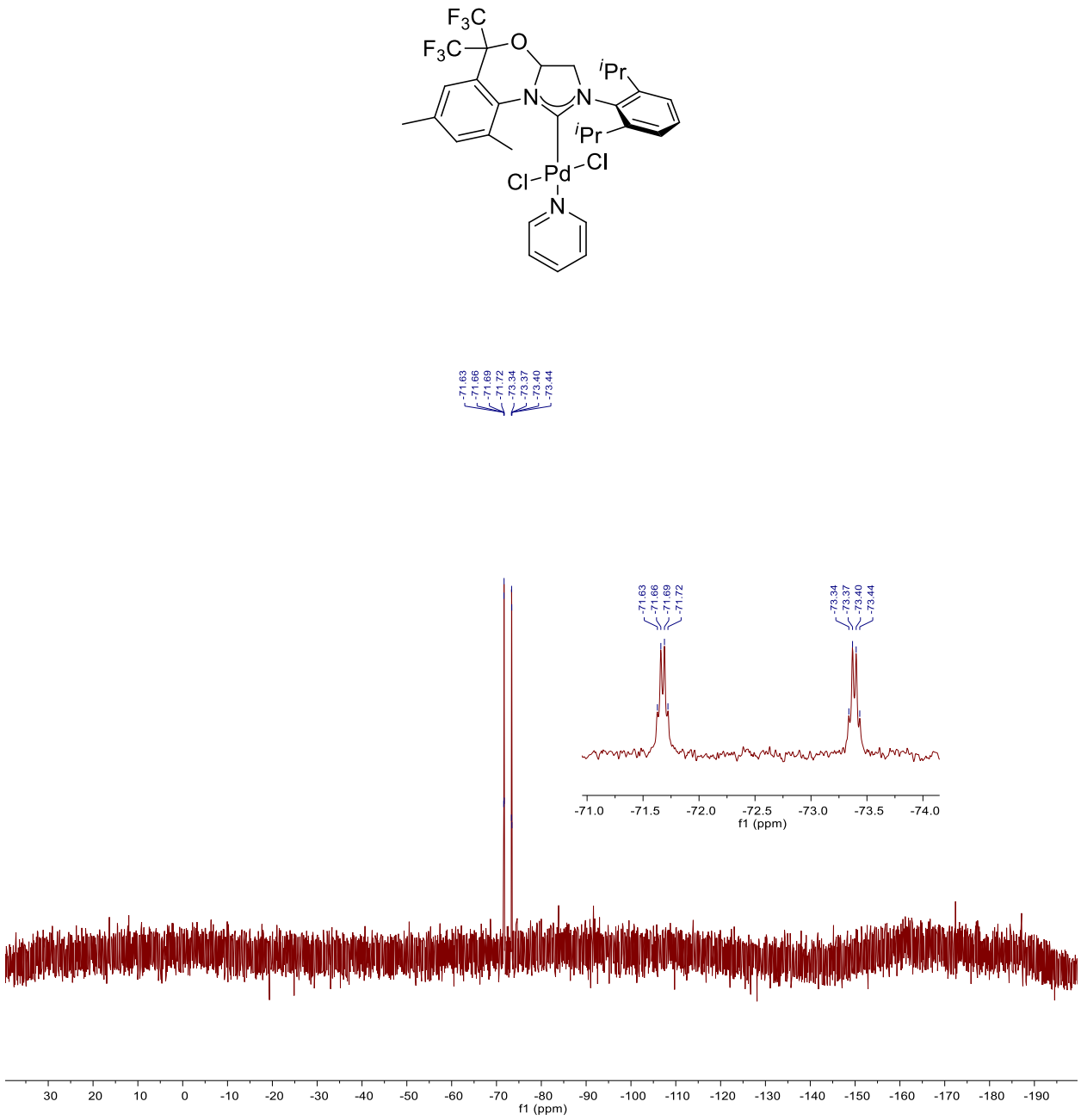


Figure S11. ^{19}F NMR (282 MHz) of **3b** in $CDCl_3$.

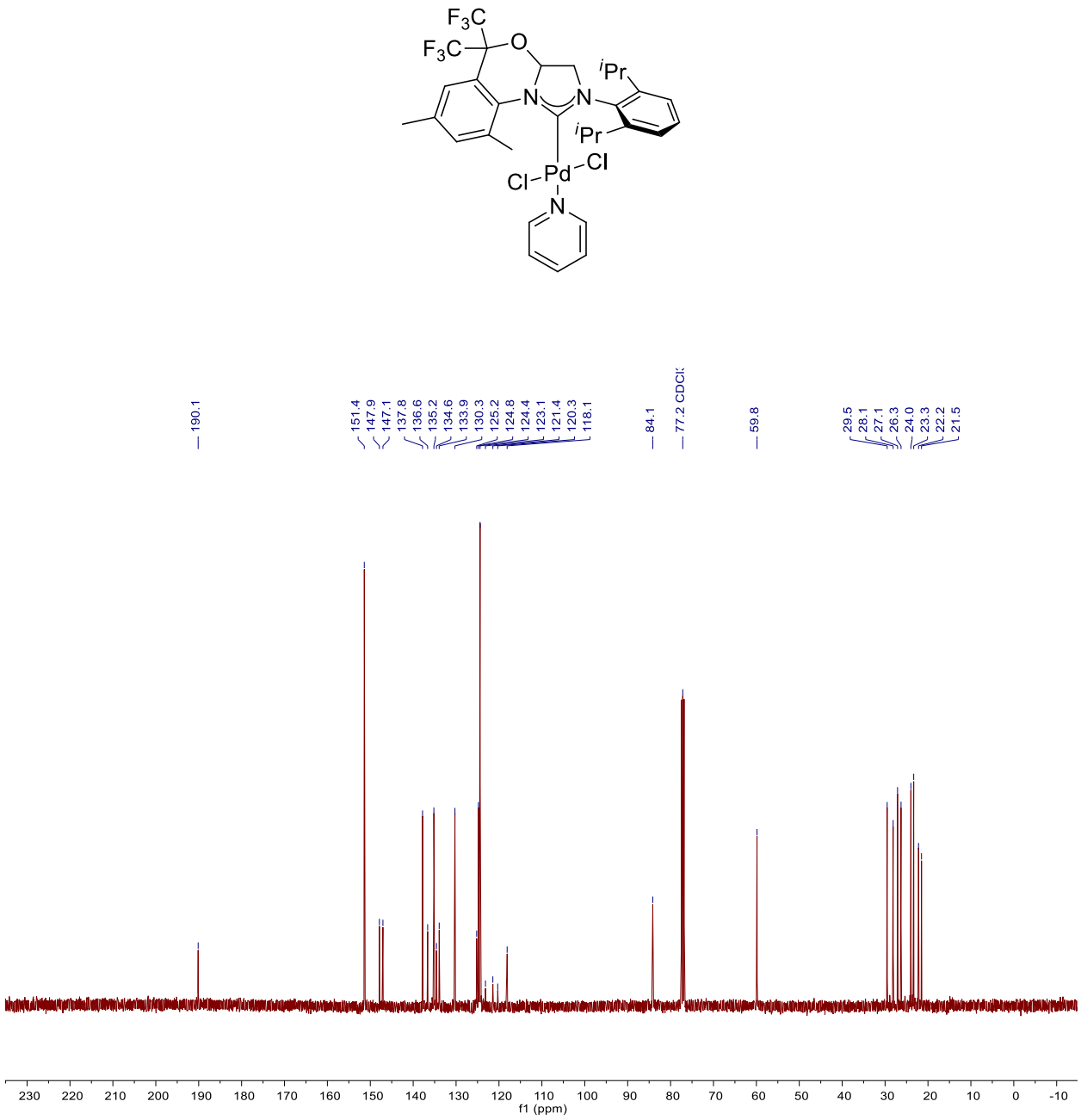


Figure S12. ^{13}C NMR (101 MHz) of **3b** in $CDCl_3$.

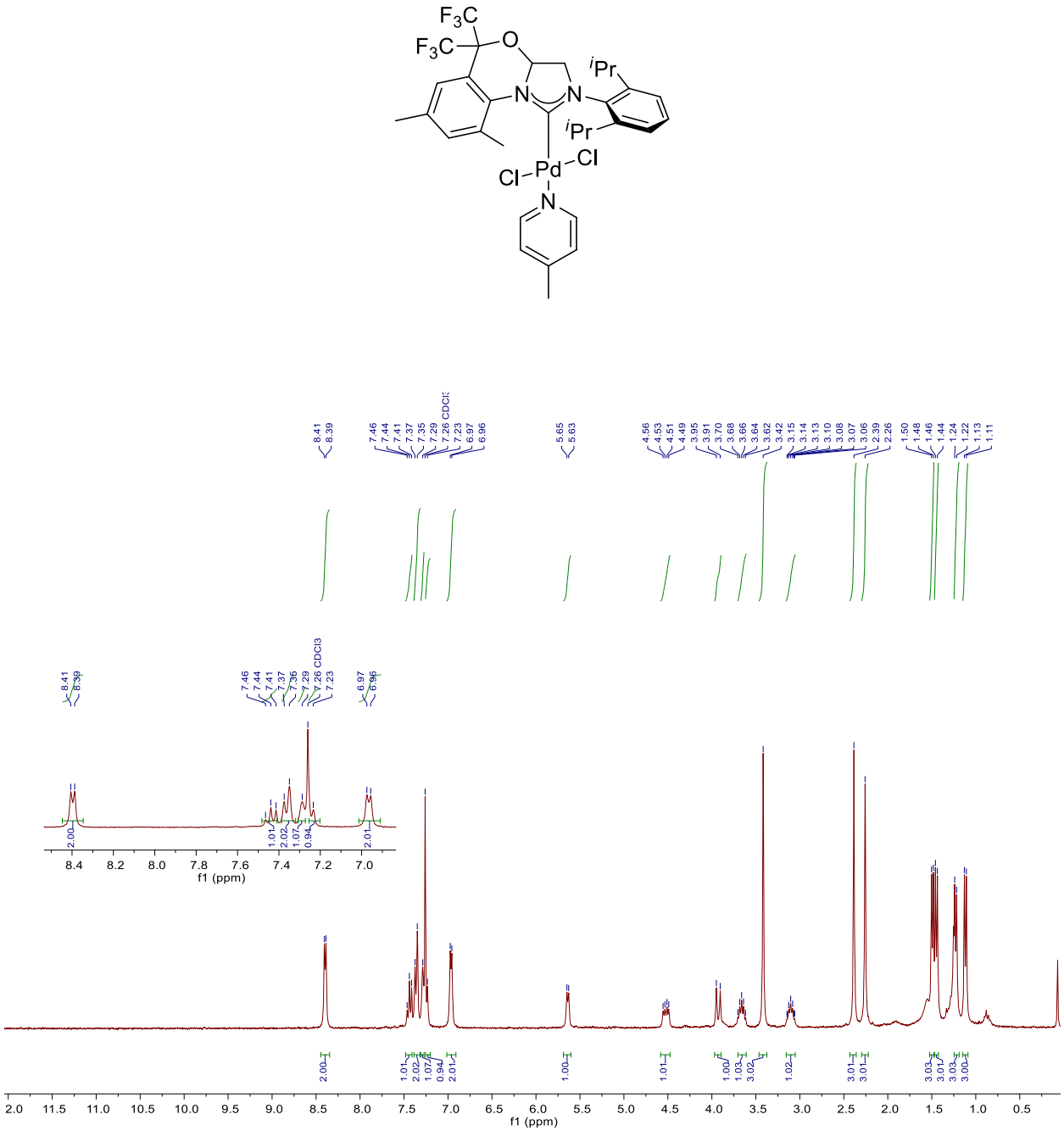


Figure S13. ^{1}H NMR (400 MHz) of **4b** in $CDCl_3$.

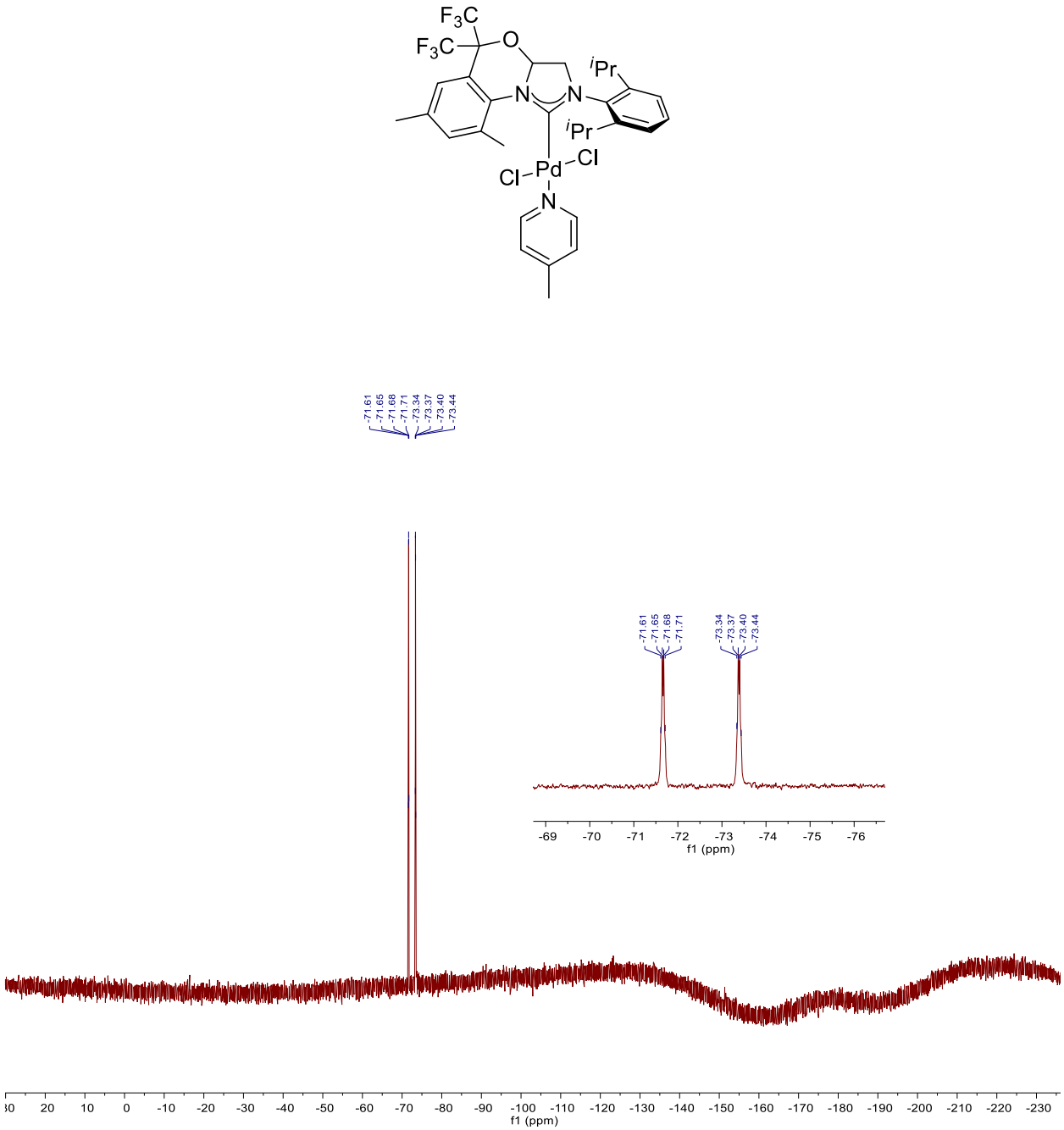


Figure S14. ^{19}F NMR (282 MHz) of **4b** in $CDCl_3$.

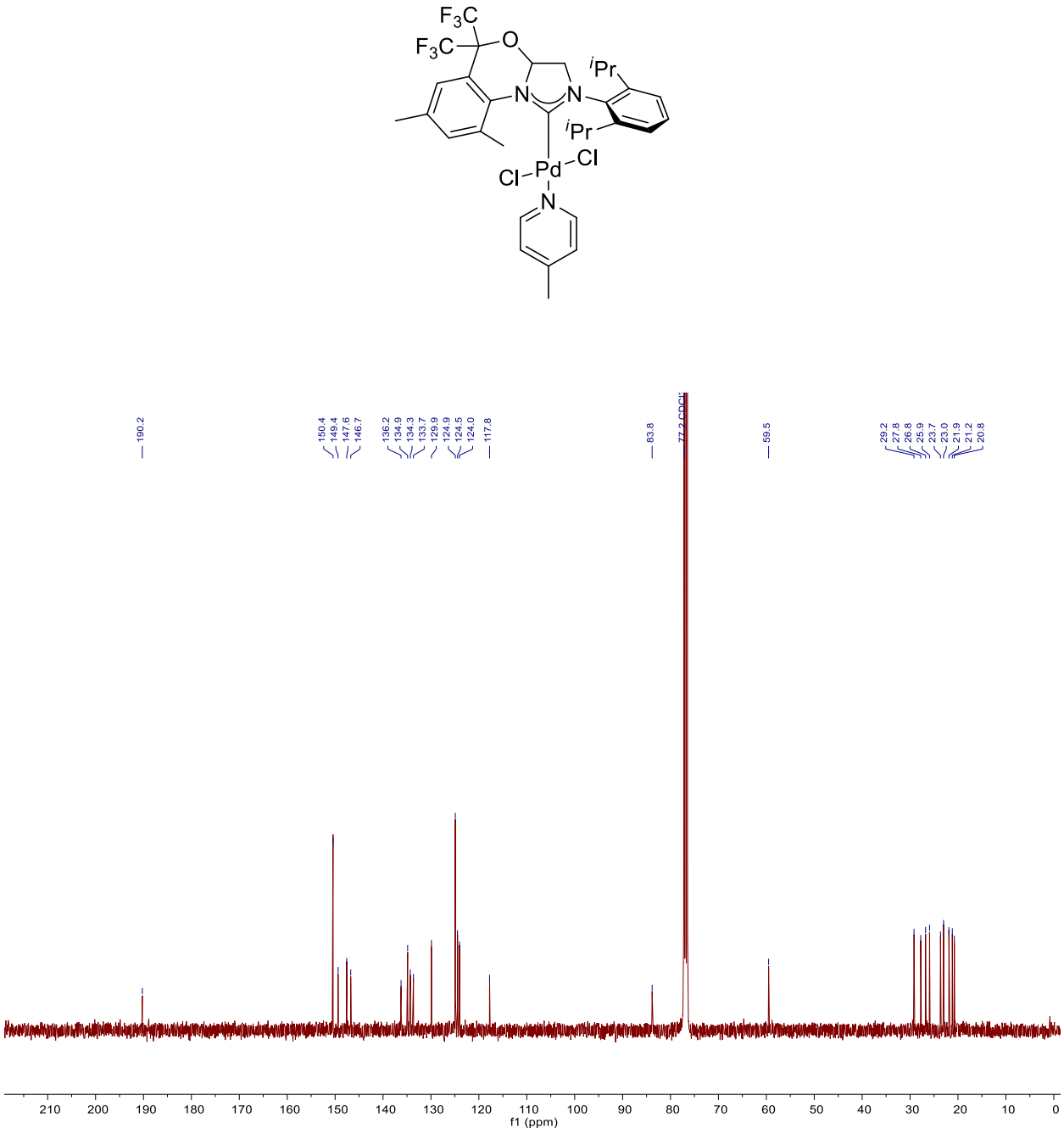


Figure S15. ^{13}C NMR (101 MHz) of **4b** in $CDCl_3$.

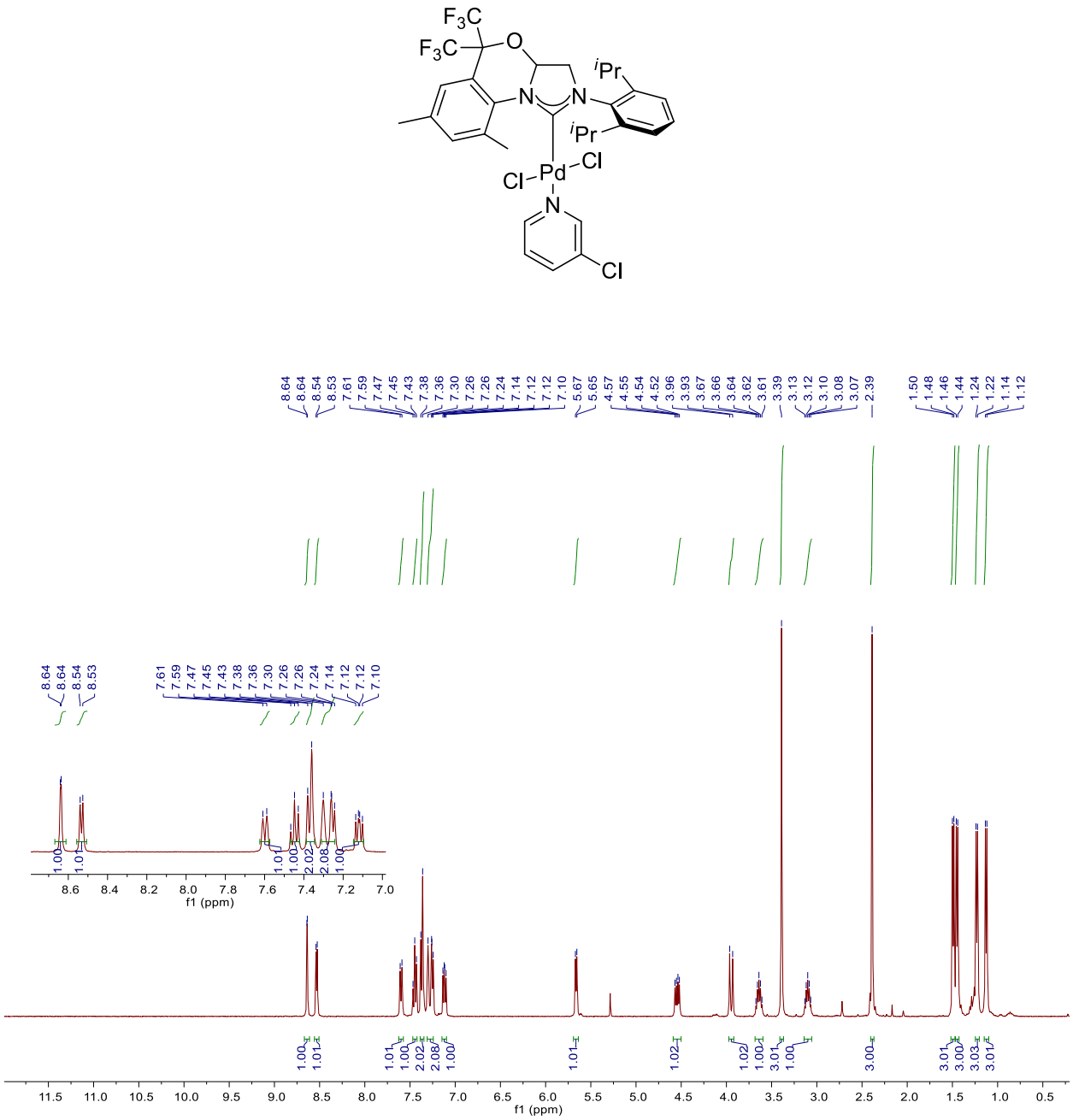


Figure S16. ^{1}H NMR (400 MHz) of **5b** in $CDCl_3$.

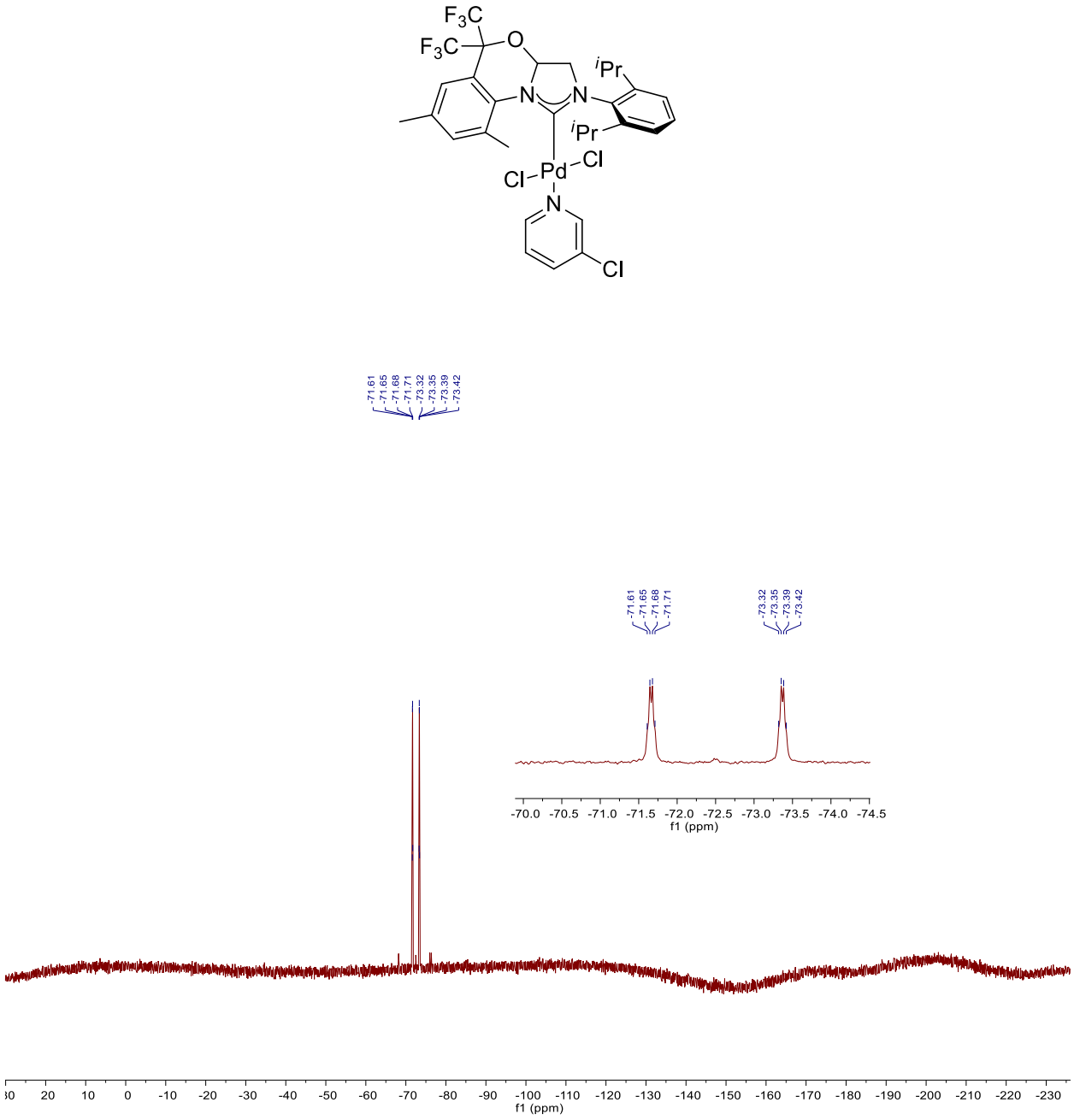


Figure S17. ^{19}F NMR (282 MHz) of **5b** in $CDCl_3$.

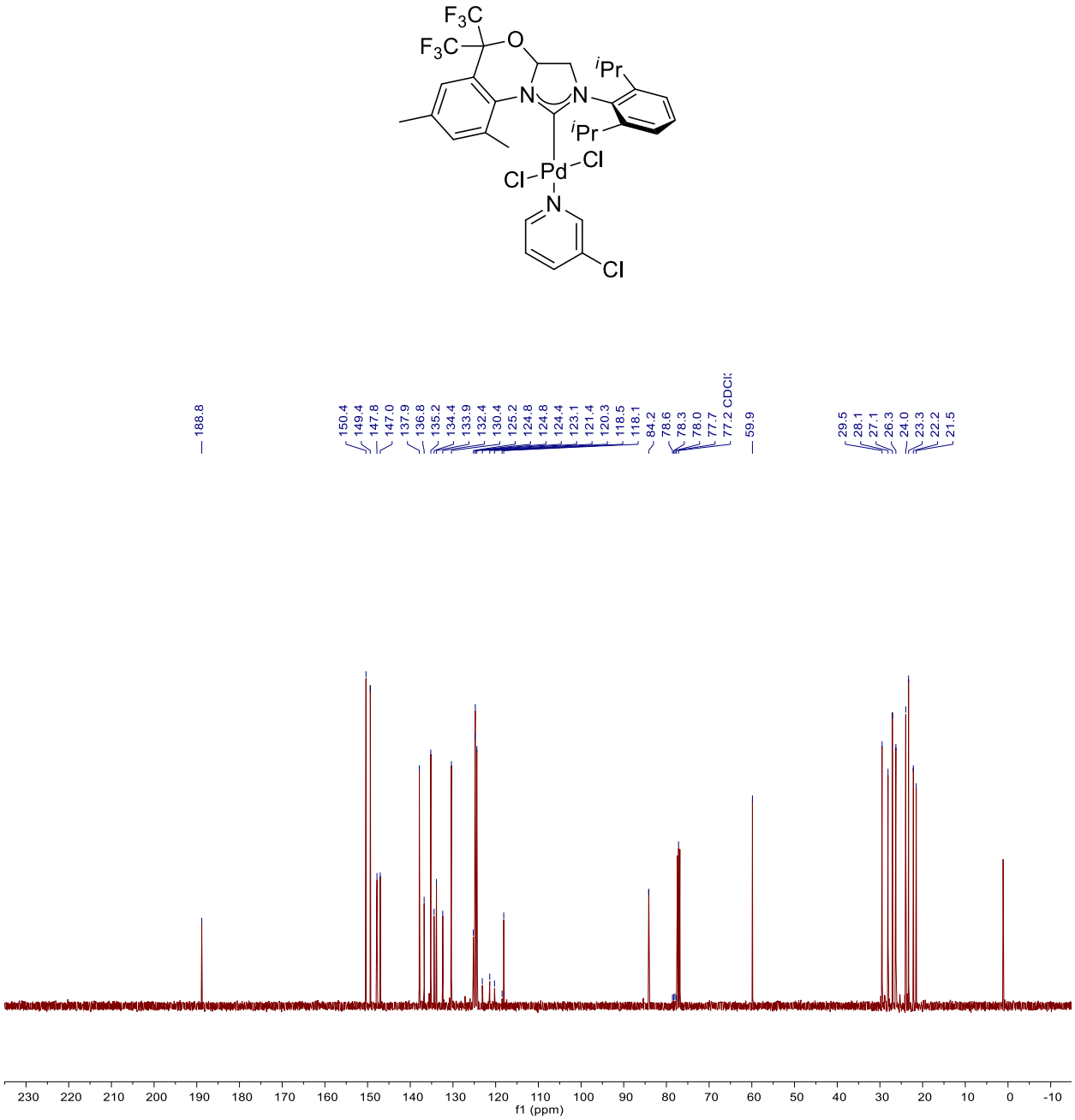


Figure S18. ^{13}C NMR (101 MHz) of **5b** in $CDCl_3$.

X-ray crystallography of 3a and 4b

Crystals of **3a** and **4b** were obtained by slow interdiffusion of a two-phase system containing petroleum ether and a solution of the compound in dichloromethane. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX CCD area detector diffractometer. The crystal was kept at 120 K during data collection. Using Olex2,[S6] the structures were solved with the SHELXT[S7] structure solution program using Intrinsic Phasing and refined with the XL[S8] refinement package using Least Squares minimisation.

Table S1. Crystal data and structure refinement parameters for **3a** (CCDC 2582199) and **4b** (CCDC 2582198).

Identification code	**3a**	**4b**
Empirical formula	$C_{28}H_{27}N_3F_6Cl_2PdO$	$C_{33}H_{36}Cl_5F_6N_3OPd$
Formula weight	712.82	888.30
Temperature/K	150.15	120
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.1545(4)	9.9446(3)
b/Å	16.6054(4)	23.6774(7)
c/Å	14.1819(3)	16.0893(5)
α/°	90	90
β/°	111.3381(9)	98.5300(10)
γ/°	90	90
Volume/Å^3	2885.47(13)	3746.5(2)
Z	4	4
ρ_{calc}g/cm^3	1.641	1.575
μ/mm^{-1}	0.895	0.913
F(000)	1432.0	1792.0
Crystal size/mm^3	0.28 × 0.26 × 0.08	0.37 × 0.24 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.372 to 59.996	3.44 to 51.996
Index ranges	$-18 \le h \le 18$, $-23 \le k \le 23$, $-17 \le l \le 19$	$-12 \le h \le 12$, $-28 \le k \le 29$, $-19 \le l \le 19$
Reflections collected	35530	40693
Independent reflections	8413 [R_{int} = 0.0596, R_{sigma} = 0.0610]	7353 [R_{int} = 0.0445, R_{sigma} = 0.0404]
Data/restraints/parameters	8413/0/375	7353/0/449
Goodness-of-fit on F^2	1.055	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.0938	R_1 = 0.0306, wR_2 = 0.0739
Final R indexes [all data]	R_1 = 0.0786, wR_2 = 0.1029	R_1 = 0.0450, wR_2 = 0.0774
Largest diff. peak/hole / e Å^{-3}	0.74/-1.11	1.05/-0.45

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