Versatile halogenation via a C_{NHC}^C_{sp3} palladacycle intermediate

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Electron donating abilities of the monodentate and C_{NHC}^C_{sp3} bidentate ligands. The $^{i}Pr_2$-bimy $^{13}C_{carbene}$ resonances of complexes **3a-d** and **6** (HEP values) are in the range of 178.1−179.2 ppm (Table S1), which are at lower field compared to those of IMes (177.2 ppm) and IPr (177.5 ppm) suggesting stronger donating powers of the dialkyl substituted imidazolin-2-ylidenes.[1] A closer look at the HEP values shows that they increase in the order of **3a** < **6** < **3d** < **3b** < **3c** in line with an increasing electron donating power of the respective ligands. This difference clearly originates from the increasing positive inductive effects (+*I*) of the N_3 substituents in these ligands, which is -$(CH_2)_2$CN (**3a**) < -$(CH_2)_2CH_2$BrCN (**6**) < -$(CH_2)_3$CN (**3d**) < -$(CH_2)_2$COOMe (**3b**) < -$(CH_2)_2$COPh (**3c**). The additional methylene group in **3d** makes the N_3 substituent and thus the whole carbene ligand more electron donating. The Br substitution, on the other hand, weakens the +*I* of the whole substituent in **6**.

Table S1 Summary of the $^{i}Pr_2$-bimy ^{13}Ccarbene signals (HEP& HEP2) in complexes **3-10**.

Ligand	Complex	n	R	HEP/HEP2[a]
C_{NHC}	**3a**	1	CN	178.1
	3b	1	COOMe	179.1_8[b]
	3c	1	COPh	179.2_4[b]
	3d	2	CN	178.5
	6	2	CN	178.2
$N_{imidazole}$	**5**	-	-	161.8
	10	-	-	161.5
C_{NHC}^C_{sp3}	**4a**	1	CN	185.8
	4b	1	COOMe	189.4
	4c	1	COPh	187.8
	4d	2	CN	188.4

[a]Measured in $CDCl_3$ and internally referenced to the solvent signal at 77.7 ppm. [b]The second decimal was kept for comparison of closer values. Detailed discussion on the standard deviations of HEP can be found in references 1.

The order of the -$(CH_2)_2$R groups in the monodentate NHC ligands is not easy to rationalize at first sight but is undoubtedly determined by the inductive effects of the R groups. By using substituted bicyclooctane carboxylic acids instead of substituted benzoic acids, Hansch and Leo could successfully deconvolute the σ Hammett values into their inductive components.[2] Both the σ_m and σ_p values of the present R groups rank in the order -CN (0.56, 0.66) > -CO_2Me (0.37, 0.45) > -COPh (0.34, 0.43), suggesting greater -*I* effects of the -CN followed by the -CO_2Me and the -COPh substituents. This order is reflected in the HEP values of the monodentate NHC ligands, which only differ in these remote substituents six bonds away from the reporter atom.

The HEP value for **5** was found at a much higher field at 161.8 ppm due to the significantly weaker electron donating ability of N donors in general. For comparison, we have also prepared the non-brominated analogue [$PdBr_2$(^{i}Pr_2-bimy)(Bn-Imi)] (**10**) bearing a simple *N*-benzylimidazole. The HEP of the latter is at higher field of 161.5 ppm, suggesting a net electron donating nature of the Br substituent on the imidazole ring due to the dominance of the +*M* effect.

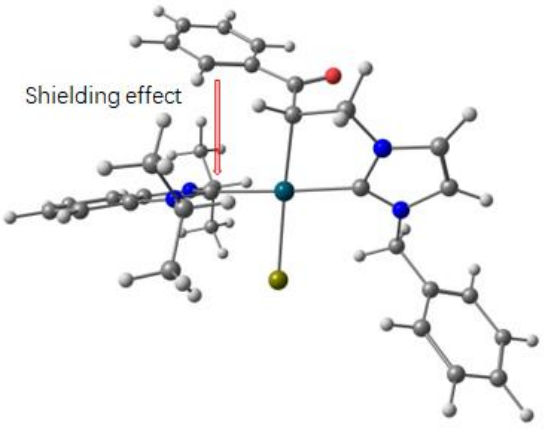


Figure S1. Optimized structure of **4c** at the B3LYP/def2-TZVP level.

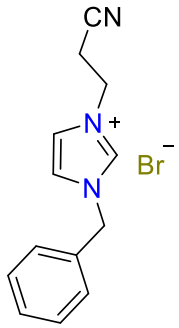
The HEP2 order within the chelate complexes **4a**-**b** shows a slightly different trend with -$(CH_2)_2$CN (**4a**, L1) < -$(CH_2)_2$COPh (**4c**, L3) < -$(CH_2)_3$CN (**4d**, L4) < -$(CH_2)_2$COOMe (**4b**, L2) (Figure 2 and Table S1). Surprisingly, the least inductively withdrawing -COPh group leads to a somewhat smaller HEP2 value. This is probably

due to the shielding effect exerted by the phenyl group near the reporter carbon atom, which induces a shift to the higher field. Regrettably, single crystals of **4c** were not obtained but geometry optimization using DFT calculation confirmed the spatial arrangement (Figure S1).[3] Such an anisotropy effect has been observed for arylated expanded-ring NHCs and represents a limitation of the HEP method.[4]

Experimental Section.

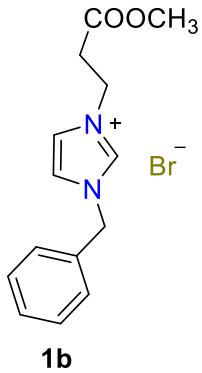
General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 298 K on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane. ESI mass spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on an ElementarVario Micro Cube elemental analyzer. 3-(1*H*-imidazol-1-yl) propanentrile [5], methyl 3-(1*H*-imidazol-1-yl) propanoate, 3-(1*H*-imidazol-1-yl)-1-phenylpropan-1-one were prepared following literature procedures. [6] DFT calculation was performed using Gaussian 09 [7] with B3LYP/def2-TZVP. The ground state was validated by the absence of imaginary frequencies.

General procedure for the preparation of salt precursors. For **1a**–**1c**, mono-substituted imidazole (1.00 mmol) and benzyl bromide (5.00 mmol) were dissolved in toluene (5 mL) in a sealed tube and stirred at 90 ºC overnight. The resulting suspension was separated and the residue washed with toluene, diethyl ether or DCM before drying under vacuum to afford the products. Salt **1d** was prepared in analogous way from 1-benzylimidazole (475 mg, 3.00 mmol) and 4-bromobutyronitrile (327 μL, 3.30 mmol).



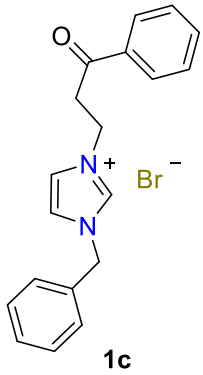
1a

1a, white sticky solid (232 mg, 0.85 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$ + CD_3OD): δ 9.83 (s, ^{1}H, NCHN), 7.83 (d, 1H, ^{3}J = 2 Hz, Imi-H), 7.30–7.34 (m, 6H, Ar-H & Imi-H), 5.40 (s, 2H, NCH_2Ph), 4.66–4.71 (m, 2H, NCH_2), 3.17–3.22 (m, 2H, $NCCH_2$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$ + CD_3OD): δ 137.3 (NCHN), 133.0, 130.2, 130.0, 129.3, 123.8, 122.8 (Ar-C), 117.3 (CN), 54.1, 45.9 (CH_2), 20.4 (CCN). Anal. Calcd. for $C_{13}H_{14}BrN_3$: C 53.44, H 4.83, N 14.38; found: C 53.67, H 4.82, N 14.02. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{13}H_{14}N_3$ 212, found 212.



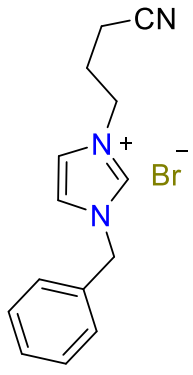
1b

1b, white solid (318 mg, 0.98 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.14 (s, 1H, NCHN), 7.63 (t, ^{3}J = 2 Hz, 1H, Imi-H), 7.42–7.45 (m, 2H, Ar-H), 7.30-7.33 (m, 4H, Ar-H & Imi-H), 5.52 (s, 2H, NCH_2), 4.61 (t, ^{3}J = 6 Hz, 2H, NCH_2), 3.58 (s, 3H, CH_3), 3.03 (t, ^{3}J = 6 Hz, 2H, CH_2CO); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 171.4 (CO), 137.4 (NCHN), 133.6, 129.9 129.8, 129.5, 123.8, 122.4 (Ar-C), 53.7, 52.8, 45.9, 35.0 (CH_2 & CH_3). Anal. Calcd. for $C_{14}H_{17}BrN_2O_2$: C 51.71, H 5.27, N 8.61; found: C 51.88, H 5.87, N 8.98 (the best result after multiple tests). MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{14}H_{17}BrN_2O_2$ 245, found 245.



1c

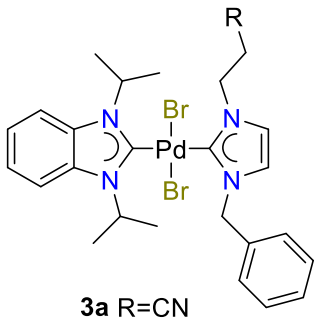
1c, white solid (286 mg, 0.77 mmol, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.42 (s, 1H, NCHN), 7.94 (d, ^{3}J = 3 Hz, 2H, Ar-H), 7.68 (s, 1H, Imi-H), 7.51–7.55 (m, 1H, Ar-H), 7.33–7.49 (m, 7H, Ar-H), 7.19 (s, 1H, Imi-H), 5.46 (s, 2H, NCH_2), 4.76 (d, ^{3}J = 6 Hz, 2H, NCH_2), 3.84 (d, ^{3}J = 6 Hz, 2H, CH_2); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 197.6 (CO), 137.9 (NCHN), 136.1, 134.6, 133.4, 130.1, 130.1, 129.4, 129.4, 128.9, 124.5, 121.8 (Ar-C), 54.1, 45.4, 39.9 (CH_2). Anal. Calcd. for $C_{19}H_{19}BrN_2O$: C 61.47, H 5.16, N 7.55; found: C 61.58, H 5.43, N 7.76. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{19}H_{19}N_2O$ 291, found 291.



1d

1d, white sticky solid (254 mg, 0.83 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.44 (s, 1H, NCHN), 7.65 (d, ^{3}J = 3 Hz, 1H, Imi-H), 7.37–7.45 (m, 5H, Ar-H), 7.23 (d, ^{3}J = 3 Hz, 1H, Imi-H), 5.50 (s, 2H, NCH_2Ph), 4.62 (t, ^{3}J = 6 Hz, 2H, NCH_2), 2.69 (t, ^{3}J = 6 Hz, 2H, $NCCH_2$), 2.33–2.42 (m, 2H, CH_2); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 137.9 (NCHN), 133.1, 130.4, 130.2, 129.7, 123.4, 122.4 (Ar-C), 119.3 (CN), 54.4, 49.2, 26.8, 15.3 (CH_2). Anal. Calcd. for $C_{14}H_{16}BrN_3$:C 54.92, H 5.27, N 13.72; found: C 55.02, H 5.39, N 13.48. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{14}H_{16}N_3$ 226, found 226.

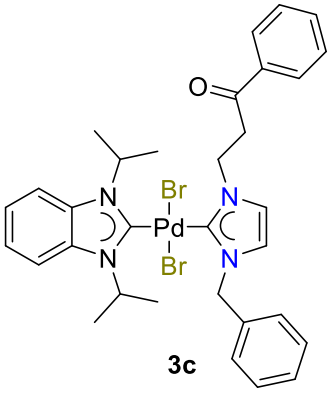
General procedure for the preparation of hetero-bis(carbene) complexes. Salt precursor **1** (294 mg, 1.00 mmol), dimeric complex **2** (470 mg, 0.50 mmol) and Ag_2O (139 mg, 0.59 mmol) were suspended in CH_2Cl_2 (20 mL) and stirred overnight. The resulting suspension for **1a** and **1d** were directly filtered and dried to give **3a** and **3d**, respectively, while those for **3b** and **3c** need further purification by column chromatography. SiO_2: PE/EA/DCM V/V/V 2/1/1 (**3b**), 8/1/1 (**3c**). All are yellow solids.



3a R=CN
3b R=$COOCH_3$

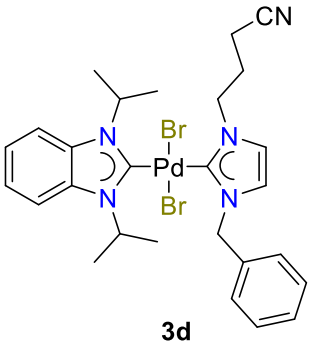
3a, 616 mg, 0.93 mmol, 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.59 (m, 4H, Ar-H), 7.33–7.45 (m, 3H, Ar-H), 7.19–7.22 (m, 2H, Ar-H), 7.02 (d, ^3J = 2 Hz, 1H, Imi-H), 6.77 (d, ^3J = 2 Hz, 1H, Imi-H), 6.13 (m, ^3J = 7 Hz, 1H, NCH), 5.99 (m, ^3J = 7 Hz, 1H, NCH), 5.76 (s, 2H, NCH_2), 4.88 (t, ^3J = 7 Hz, 2H, NCH_2), 3.40 (t, ^3J = 7 Hz, 2H, $NCCH_2$), 1.84 (d, ^3J = 7 Hz, 6H, CH_3), 1.68 (d, ^3J = 7 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 178.1 ($C_{carbene\text{-}benz}$), 172.9 ($C_{carbene\text{-}imi}$), 136.2, 134.21, 134.17, 129.6, 129.3, 129.1, 122.8, 122.2, 121.1 (Ar-C, two are coincident), 117.9 (CN), 113.32, 113.27 (Ar-C), 55.4, 54.8, 54.5, 47.4, 21.7, 21.6, 20.4 (CH, CH_2 and CH_3). Anal. Calcd. for $C_{26}H_{31}Br_2N_5Pd$: C 45.94, H 4.60, N 10.30; found: C 45.78, H 4.83, N 10.06. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{26}H_{31}BrN_5Pd$ 598, found 598.

3b, 519 mg, 0.73 mmol, 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51–7.57 (m, 4H, Ar-H), 7.33–7.42 (m, 3H, Ar-H), 7.16–7.21 (m, 2H, Ar-H), 7.00 (d, ^3J = 2 Hz, 1H, Imi-H), 6.70 (d, ^3J = 2 Hz, 1H, Imi-H), 6.22 (m, ^3J = 7 Hz, 1H, NCH), 5.99 (m, ^3J = 7 Hz, 1H, NCH), 5.75 (s, 2H, NCH_2), 4.86 (t, ^3J = 7 Hz, 1H, NCH_2), 3.75 (s, 3H, OCH_3), 3.31 (t, ^3J = 7 Hz, 2H, $COCH_2$), 1.81 (d, ^3J = 7 Hz, 6H, CH_3), 1.68 (d, ^3J = 7 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 179.2 ($C_{carbene\text{-}benz}$), 172.4 (CO), 171.6 ($C_{carbene\text{-}imi}$), 136.7, 134.3, 134.2, 129.5, 129.3, 128.9, 122.9, 122.6, 121.3, 113.2 (Ar-C, three are coincident), 55.3, 54.6, 54.4, 52.7, 47.1, 36.2, 21.7, 21.6 (CH, CH_2 and CH_3). Anal. Calcd. for $C_{27}H_{34}Br_2N_4O_2Pd$: C 45.49, H 4.81, N 7.86; found: C 45.78, H 4.83, N 7.75. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{27}H_{34}BrN_4O_2Pd$ 631, found 631.



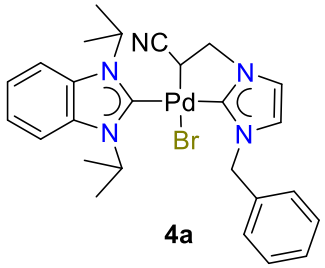
3c

3c, 577 mg, 0.76 mmol, 76%. Single crystals were obtained by slow evaporation of a concentrated solution in THF and hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, ^{3}J = 7 Hz 2H, Ar-H), 7.35–7.53 (m, 10H, Ar-H), 7.16–7.19 (m, 2H, Ar-H), 7.04 (br-s, 1H, Imi-H), 6.68 (br-s, 1H, Imi-H), 6.17 (m, ^{3}J = 7 Hz, 1H, NCH), 6.01 (m, ^{3}J = 7 Hz, 1H, NCH), 5.75 (s, 2H, NCH_2), 5.01 (t, ^{3}J = 7 Hz, 2H, NCH_2), 4.01 (t, ^{3}J = 7 Hz, 2H, CH_2CO), 1.70 (d, ^{3}J = 7 Hz, 12H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 198.6 (C=O), 179.2 ($C_{carbene\text{-}benz}$), 171.2 ($C_{carbene\text{-}imi}$), 137.1, 136.6, 134.2, 129.5, 129.4, 129.3, 128.9, 128.8, 123.3, 122.6, 121.0, 113.2 (Ar-C, two are coincident), 55.2, 54.5, 54.4, 46.5, 40.9, 21.6, 21.5 (CH, CH_2 and CH_3). Anal. Calcd. for : $C_{32}H_{36}Br_2N_4OPd$: C 50.65, H 4.78, N 7.38; found: C 50.78, H 4.99, N 7.36. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{32}H_{36}Br_2N_4OPd$ 677, found 677.



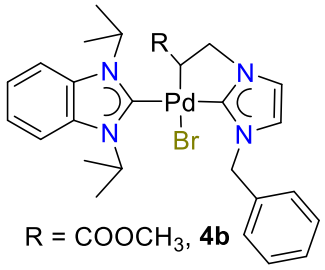
3d

3d, 652 mg, 0.94 mmol, 94%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.58 (m, 4H, Ar-H), 7.35–7.43 (m, 3H, Ar-H), 7.17–7.20 (m, 2H, Ar-H), 6.94 (d, ^{3}J = 2 Hz, 1H, Imi-H), 6.78 (d, ^{3}J = 2 Hz, 1H, Imi-H), 6.11 (m, ^{3}J = 7 Hz, 1H, NCH), 6.03 (m, ^{3}J = 7 Hz, 1H, NCH), 5.81 (s, 2H, NCH_2), 4.67 (t, ^{3}J = 7 Hz, 1H, NCH_2), 2.52–2.65 (m, 4H, $NCCH_2$ & CH_2), 1.81 (d, ^{3}J = 7 Hz, 6H, CH_3), 1.63 (d, ^{3}J = 7 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 178.5 ($C_{carbene\text{-}benz}$), 171.8 ($C_{carbene\text{-}imi}$), 136.5, 134.1, 134.2, 129.6, 129.0, 128.9, 122.7, 122.5, 122.0 (Ar-C, two are coincident), 119.5 (CN), 113.3, 113.2 (Ar-C), 55.3, 54.6, 54.4, 49.8, 27.1, 21.66, 21.45, 15.3 (CH, CH_2 and CH_3). Anal. Calcd. for $C_{27}H_{33}Br_2N_5Pd$: C 46.74, H 4.79, N 10.09; found: C 46.87, H 4.98, N 10.45. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{27}H_{33}BrN_5Pd$ 612, found 612.



4a

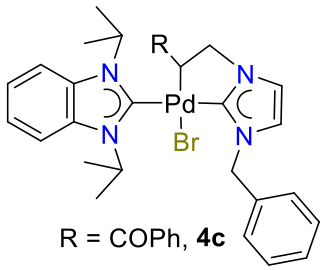
Complex **3a** (85 mg, 0.12 mmol) was dissolved in CH_3CN (5 mL) and THF (5 mL) before NaOH (8 mg, 0.20 mmol) was added. The suspension was stirred overnight, and the solvent was removed by vacuum distillation before DCM (10 mL) was added, which was filtered, dried and washed with Et_2O (3 × 5 mL) to afford **4a** as an off-white solid (65 mg, 0.11 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61–7.64 (m, 1H, Ar-H), 7.56–7.58 (m, 1H, Ar-H), 7.45–7.47 (m, 2H, Ar-H), 7.30–7.40 (m, 3H, Ar-H), 7.20–7.23 (m, 2H, Ar-H), 6.99 (d, ^3J = 2 Hz, 1H, Imi-H), 6.72 (d, ^3J =2 Hz, 1H, Imi-H), 5.85–6.08 (m, 4H, NCH & NCH_2), 4.08–4.20 (m, 2H, NCH_2), 2.95–2.99 (m, 1H, CH), 1.87 (d, ^3J = 7 Hz, 3H, CH_3), 1.74–1.79 (m, 9H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ185.8 ($C_{carbene\text{-}benz}$), 175.9 ($C_{carbene\text{-}imi}$), 137.6, 134.7, 134.1, 129.4, 129.3, 128.6, 127.2, 122.7, 122.6, 121.9 (Ar-C), 118.4 (CN), 113.7, 113.2 (Ar-C), 54.9, 54.8, 54.6, 54.5, 22.4, 22.1, 21.8, 21.6 (CH, CH_2 and CH_3), 8.0 (Pd-C). Anal. Calcd. for $C_{26}H_{30}BrN_5Pd$: C 52.14, H 5.05, N 11.69; found: C 52.46, H 4.97, N 11.58. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{26}H_{30}BrN_5Pd$ 518, found 518.



R = $COOCH_3$, **4b**

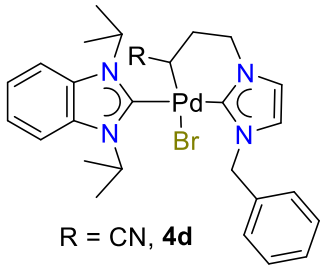
Complex **3b** (42 mg, 0.06 mmol) and NaOH (8 mg, 0.20 mmol) were suspended in CH_3CN (5 mL) and stirred for 4 h. The resulting suspension was filtered, concentrated and subjected to flash chromatography (SiO_2: PE/EA/DCM V/V/V 8/1/1 to MeOH/DCM V/V 1/30) to give complex **4b** as an off-white solid (13 mg, 0.02 mmol, 34%). Single crystals were obtained by slow evaporation of a concentrated solution in THF and hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57–7.60 (m, 2H, Ar-H), 7.43–7.46 (m, 2H, Ar-H), 7.29–7.37 (m, 3H, Ar-H), 7.16–7.21 (m, 2H, Ar-H), 6.99 (d, ^3J = 2 Hz, 1H, Imi-H), 6.69 (d, ^3J = 2 Hz, 1H, Imi-H), 6.12 (m, ^3J = 7 Hz, 1H, NCH), 5.93 (br-s, 2H, NCH_2), 5.80 (m, ^3J = 7 Hz, 1H, NCH), 4.41 (dd, ^3J = 7 Hz, ^2J = 12 Hz, 1H, NC*H*H), 4.00 (dd, ^3J = 7 Hz, ^2J = 12 Hz, 1H, NCH*H*), 3.53 (t, ^3J = 7 Hz, 1H, COCH), 2.96 (s, 3H, OCH_3), 1.75–1.82 (m, 9H, CH_3),

1.71 (d, ^3J = 7 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 189.4 ($C_{carbene\text{-}benz}$), 180.3 (C=O), 175.7 ($C_{carbene\text{-}imi}$), 138.2, 134.3, 134.0, 129.2, 128.4, 122.4, 122.3, 121.4, 118.3, 113.4, 113.1 (Ar-C, two are coincident), 54.8, 54.6, 54.3, 54.2, 50.7 (CH and CH_2), 31.9 (Pd-C), 22.0, 21.7, 21.3, 21.1 (CH_2 and CH_3). Anal. Calcd. for $C_{27}H_{33}BrN_4O_2Pd$: C 51.32; H 5.26; N 8.87; found: C 51.48, H 5.62, N 8.53. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{27}H_{334}O_2Pd$ 551, found 551.



R = COPh, **4c**

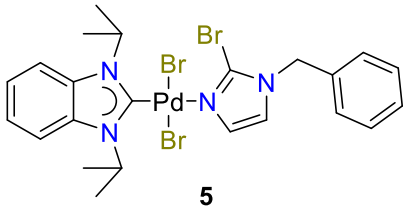
4c was prepared in analogy to **4a** from **3c** (60 mg, 0.08 mmol), NaOH (6 mg, 0.14 mmol) as a yellow solid (53 mg, 0.08 mmol, 98%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, ^3J = 8 Hz, 1H, Ar-H), 7.41–7.45 (m, 4H, Ar-H), 7.30–7.37 (m, 4H, Ar-H), 7.14–7.19 (m, 3H, Ar-H), 7.06 (d, ^3J = 2 Hz, 1H, Imi-H), 6.87 (t, ^3J = 8 Hz, 2H, Ar-H), 6.71 (d, ^3J = 2 Hz, 1H, Imi-H), 6.19 (m, ^3J = 7 Hz, 1H, NCH), 5.93 (d, ^3J = 15 Hz, 1H, NC*H*H), 5.86 (d, ^3J = 15 Hz, 1H, NCH*H*), 5.35 (m, ^3J = 7 Hz, 1H, NCH), 4.70–4.73 (m, 1H, CHCO), 4.30–4.35 (m, 2H, NCH_2), 1.82 (d, ^3J = 7 Hz, 3H, CH_3), 1.75 (d, ^3J = 7 Hz, 3H, CH_3), 1.53 (d, ^3J = 7 Hz, 3H, CH_3), 0.78 (d, ^3J = 7 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 201.9 (C=O), 187.8 ($C_{carbene\text{-}benz}$), 175.2 ($C_{carbene\text{-}imi}$), 138.8, 138.1, 134.8, 134.0, 131.7, 129.2, 129.1, 128.5, 128.2, 128.0, 122.4, 122.3, 121.3, 118.3, 113.3, 113.0 (Ar-C), 54.5, 54.4, 54.3, 54.2, 22.1, 21.9, 21.7 (CH, CH_2 and CH_3), 21.2 (Pd-C), 20.4 (CH_3). Anal. Calcd. for : $C_{32}H_{35}BrN_4OPd$: C 56.69, H 5.20, N 8.26; found: C 56.89, H 5.48, N 8.46. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{32}H_{35}N_4OPd$ 597, found 597.



R = CN, **4d**

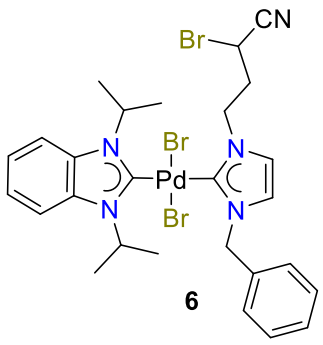
Under nitrogen atmosphere, complex **3d** (310 mg, 0.45 mmol) was dissolved in THF (15 mL) before t-BuOK (76 mg, 0.67 mmol) was added and reacted at 60°C for 12 h. The solvent was removed by vacuum distillation to give a crude product before DCM (10 mL) was added. The suspension was filtered, and the filtrate was dried and washed with Et_2O (10 mL × 3)

to afford **4d** as a yellow solid (261mg, 0.43 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54–7.60 (m, 2H, Ar-H), 7.47–7.49 (m, 2H, Ar-H), 7.32–7.42 (m, 3H, Ar-H), 7.18–7.22 (m, 2H, Ar-H), 6.88 (d, ^{3}J = 2 Hz, 1H, Imi-H), 6.74 (d, ^{3}J = 2 Hz, 1H, Imi-H), 6.17 (d, ^{2}J = 15 Hz, 1H, C*H*H), 5.85–5.96 (m, ^{3}J = 7 Hz, 2H, NCH), 5.59 (d, ^{2}J = 15 Hz, 1H, CH*H*), 4.08–4.15 (m, 2H, NCH_2), 2.66 (t, ^{3}J = 7 Hz 1H, CH), 2.09–2.20 (m, 1H, CH_2), 1.66–1.79 (m, 13H, CH_2 & CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 188.4 ($C_{carbene\text{-}benz}$), 175.9 ($C_{carbene\text{-}imi}$), 137.8, 134.4, 134.0, 129.4, 129.1, 128.8, 128.4, 122.7, 122.6, 121.5 (Ar-C), 120.9 (CN), 113.5, 113.2 (Ar-C), 55.2, 54.6, 54.5, 52.5, 30.6, 22.3, 22.0, 21.7, 21.5 (CH, CH_2 and CH_3), -2.3 (Pd-C). Anal. Calcd. for $C_{27}H_{32}BrN_5Pd$: C 52.91, H 5.26, N 11.43, found: C 52.79, H 5.60, N 11.67. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{27}H_{32}BrN_5Pd$ 532, found 532.



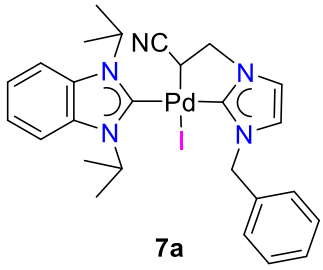
5

Complex **4a** (60 mg, 0.10 mmol) was dissolved in DCM (5 mL) before bromine (6 µL, 0.12 mmol) in $CHCl_3$ (5 mL) were added dropwise. The mixture was stirred for 2 h, concentrated and subjected to column chromatography (SiO_2: PE/EA/DCM V/V/V 8/1/1 to 4/1/1) to give complex **5** as a yellow solid (54 mg, 0.08 mmol, 76%). Single crystals were obtained by slow evaporation of a concentrated solution in $CHCl_3$ and hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56–7.79 (m, 2H, Ar-H), 7.36–7.38 (m, 3H, Ar-H), 7.30 (d, ^{3}J = 2 Hz, 1H, Imi-H), 7.17–7.22 (m, 4H, Ar-H), 6.90 (d, ^{3}J = 2 Hz, 1H, Imi-H), 6.45 (m, ^{3}J = 7 Hz, 2H, NCH), 5.13 (s, 2 H, NCH_2), 1.81 (d, ^{3}J = 7 Hz, 12H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.8 ($C_{carbene}$), 134.5, 134.2, 131.7, 129.9, 129.5, 128.4, 122.9, 122.8, 113.3 (Ar-C), 55.1, 53.0, 21.4 (CH, CH_2 and CH_3). Anal. Calcd. for $C_{23}H_{27}Br_3N_4Pd$: C 39.15, H 3.86, N 7.94; found: C 39.53, H 3.98, N 7.87. MS-EI (*m/z*): $[M - L - Br]^+$ calcd for $C_{13}H_{18}BrN_2Pd$ 387, found 387.



6

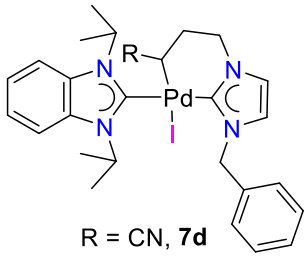
Complex **4d** (91 mg, 0.15 mmol) was dissolved in DCM (5 mL) before bromine (6 μL, 0.12 mmol) in $CHCl_3$ (5 mL) were added dropwise. The mixture was stirred for 2 h, concentrated and subjected to column chromatography (SiO_2: PE/EA/DCM V/V/V 8/1/1) to give complex **6** as a yellow solid (58 mg, 0.08 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.60 (m, 4H, Ar-H), 7.36–7.45 (m, 3H, Ar-H), 7.18–7.20 (m, 2H, Ar-H), 6.93 (d, ^3J = 2 Hz, 1H, Imi-H), 6.78 (d, ^3J = 2 Hz, 1H, Imi-H), 5.99–6.16 (m, ^3J = 7 Hz 2H, NCH), 5.87 (d, ^2J = 15 Hz, 1H, NC*H*H), 5.79 (d, ^2J = 15 Hz, 1H, NCH*H*), 4.69–4.76 (m, 2H, NCH_2), 3.27–3.38 (m, 1H, C*H*H), 3.06–3.18 (m, 1H, CH*H*), 1.78–1.81 (m, 6H, CH_3), 1.79 (d, ^3J = 7 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 178.2 ($C_{carbene\text{-}benz}$), 172.0 ($C_{carbene\text{-}imi}$), 136.4, 134.2, 134.0, 129.6, 129.0, 128.9, 122.8, 122.7, 122.1 (Ar-C, two are coincident), 117.5 (CN), 113.4, 113.3 (Ar-C), 55.4, 54.7, 54.5, 48.5, 37.7, 25.1, 21.6, 21.5, 21.4 (CH, CH_2 and CH_3, two are coincident). Anal. Calcd. for $C_{27}H_{32}Br_3N_5Pd$: C 41.97, H 4.17, N 9.06; found: C 41.87, H 4.52, N 8.98. MS-EI (*m/z*): $[M - Br]^+$ calcd for $C_{27}H_{32}Br_3N_5Pd$ 692, found 692.



7a

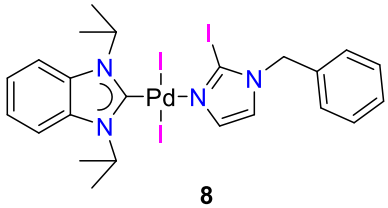
Complex **4a** (120 mg, 0.20 mmol) and KI (100 mg, 0.20 mmol) were suspended in CH_3CN (10 mL). The suspension was stirred overnight, and the solvent was removed by vacuum evaporation before DCM (10 mL) was added, which was filtered afford **7a** as a yellow solid (127 mg, 0.20 mmol 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–7.63 (m, 3H, Ar-H), 7.42–7.45 (m, 2H, Ar-H), 7.37–7.39 (m, 2H, Ar-H), 7.31–7.34 (m, 2H, Ar-H), 7.19–7.23 (m, 2H, Ar-H), 7.02 (d, ^3J = 2 Hz, 1H, Imi-H), 6.73 (d, ^3J =2 Hz, 1H, Imi-H), 5.89–5.97 (m, 4H, NCH & NCH_2), 4.18–4.21 (m, 2H, NCH_2), 2.98–3.02 (m, 1H, CH), 1.84 (d, ^3J = 7 Hz, 3H, CH_3), 1.71–1.76 (m, ^3J = 7 Hz, 9H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 184.5 ($C_{carbene\text{-}benz}$), 176.4 ($C_{carbene\text{-}imi}$), 137.4, 134.8, 134.2, 129.2, 129.1, 128.6, 127.1, 122.6, 122.6, 121.8 (Ar-C), 118.5 (CN), 113.6, 113.1 (Ar-C), 56.5, 54.8, 54.7, 54.3,

22.5, 22.0, 21.3, 21.04 (CH, CH_2 and CH_3), 11.8 (Pd-C). Anal. Calcd. for $C_{26}H_{30}IN_5Pd$: C 48.35, H 4.68, N 10.84; found: C 48.13, H 4.92, N 10.98. MS-EI (*m/z*): $[M - I]^+$ calcd for $C_{26}H_{30}N_5Pd$ 518, found 518.



R = CN, **7d**

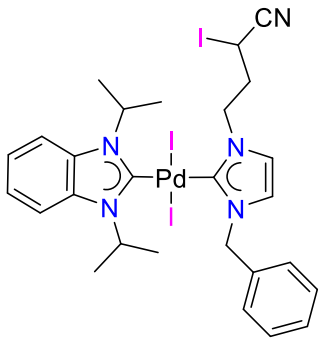
Complex **7d** was prepared in analogy to **7a** from **4d** (61 mg, 0.10 mmol) and KI (83 mg, 0.50 mmol). Yield: 63 mg, 0.10 mmol, 95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.58 (m, 2H, Ar-H), 7.45–7.47 (m, 2H, Ar-H), 7.38–7.42 (m, 3H, Ar-H), 7.18–7.22 (m, 2H, Ar-H), 6.90 (d, ^3J = 2 Hz, 1H, Imi-H), 6.76 (d, ^3J = 2 Hz, 1H, Imi-H), 6.07 (d, ^3J = 15 Hz, 1H, NCH*H*), 5.75–5.81 (m, ^3J = 7 Hz, 2H, NCH), 5.61 (d, ^3J = 15 Hz, 1H, NC*H*H) , 4.13–4.14 (m, 2H, NCH_2), 2.63 (t, ^3J = 7 Hz, 1H, CH), 2.12–2.13 (m, 1H, CH_2), 1.67–1.76 (m, 13H, CH_2 & CH_3); $^{13}C\{^1H\}$ NMR (75 MHz,$CDCl_3$): δ 187.9 ($C_{carbene\text{-}benz}$), 177.1 ($C_{carbene\text{-}imi}$), 137.5, 134.6, 134.2, 129.4, 129.3, 128.9, 128.5, 122.6, 122.5, 121.6 (Ar-C), 120.8 (CN), 113.5, 113.2 (Ar-C), 56.4, 54.5, 54.4, 52.9, 30.6, 22.3, 22.0, 21.7, 21.5 (CH, CH_2 and CH_3), 0.56 (Pd-C). Anal. Calcd. for $C_{27}H_{32}IN_5Pd$: C 49.14, H 4.89, 10.61, found: C 49.49, H 5.04, N 10.38. MS-EI (*m/z*): $[M - I]^+$ calcd for $C_{27}H_{32}N_5Pd$ 532, found 532.



8

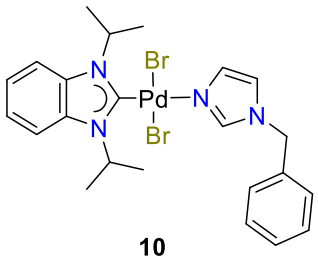
Complex **7a** (128 mg, 0.20 mmol) was dissolved in DCM (15 mL) before iodine (60 mg, 0.24 mmol) in $CHCl_3$ (10 mL) were added dropwise. The mixture was stirred for 2 h, concentrated and subjected to column chromatography (SiO_2: PE/EA V/V 10/1) to give complex **8** as a yellow solid (52 mg, 0.06 mmol, 31%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (br-s, 2H, Ar-H), 7.31–7.37 (m, 4H, Ar-H), 7.17 (br-s, 4H, Ar-H & Imi-H), 6.98 (br-s, 1H, Imi-H), 6.26 (br-s, 2H, NCH), 5.14 (s, 2 H, NCH_2), 1.78 (d, ^3J = 5 Hz, 12H, CH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 159.4 ($C_{carbene}$), 134.8, 134.7, 134.3, 129.9, 129.4, 128.2, 124.2, 122.6, 113.2 (Ar-C), 55.0, 21.4 (CH, CH_2 and CH_3, two are coincident). Anal. Calcd. for $C_{23}H_{27}I_3N_4Pd$: C 32.63, H 3.21, N 6.62; found: C 32.53, H 3.08, N 6.44. MS-EI (*m/z*): $[M - L + I]^-$ calcd

for $C_{13}H_{28}I_3N_2Pd$ 689, found 689.



9

Complex **7d** (198 mg, 0.30 mmol) was dissolved in DCM (15 mL) before iodine (91 mg, 0.36 mmol) in $CHCl_3$ (5 mL) were added dropwise. The mixture was stirred for 2 h, concentrated and subjected to column chromatography (SiO_2: PE/EA V/V 10/1) to give complex **9** as a yellow solid (88 mg, 0.10 mmol, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.58 (m, 4H, Ar-H), 7.39–7.42 (m, 3H, Ar-H), 7.18–7.20 (m, 2H, Ar-H), 6.99 (d, ^3J = 2 Hz, 1H, Imi-H), 6.78 (d, ^3J = 2 Hz, 1H, Imi-H), 5.77–5.90 (m, ^3J = 7 Hz, 2H, NCH), 5.73 (d, ^2J = 15 Hz, 1H, NC*H*H), 5.66 (d, ^2J = 15 Hz, 2H, NCH*H*), 4.58 (t, ^2J = 6 Hz, 2H, CH_2), 4.37 (t, ^2J = 7 Hz, 1H, NCCH), 3.12–3.20 (m, 1H, C*H*H), 2.95–3.02 (m, 1H, CH*H*), 1.77 (d, ^3J = 7 Hz, 6H, CH_3), 1.63–1.66 (m, 6H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 175.9 ($C_{carbene\text{-}benz}$), 170.0 ($C_{carbene\text{-}imi}$), 135.8, 134.4, 134.3, 129.6, 129.5, 129.1, 123.5, 122.6, 122.4 (Ar-C, two are coincident), 119.2 (CN) 113.4, 113.3 (Ar-C), 56.1, 54.7, 54.4, 51.0, 37.9, 30.3, 21.1, 21.04, 21.01, 20.8 (CH, CH_2 and CH_3). Anal. Calcd. for $C_{27}H_{32}I_3N_5Pd$: C 35.49, H 3.53, N 7.66; found: C 35.88, H 3.68, N 7.92. MS-EI (*m/z*): $[M - I]^+$ calcd for $C_{27}H_{32}I_2N_5Pd$ 786, found 786.



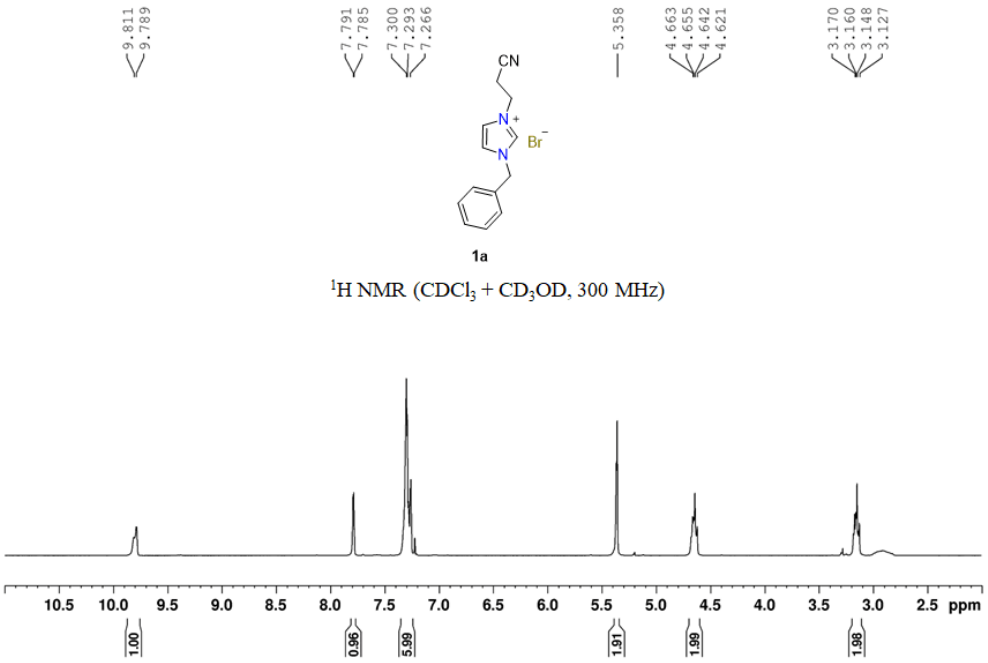
10

The dimeric complex **2** (94 mg, 0.10 mmol) and benzylimidazole (32 mg, 0.20 mmol) were mixed in DCM (10 mL) and stirred for 2 h before the solvent was evaporated off to afford the product as a yellow solid (123 mg, 0.20 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (s, 1H, NCHN), 7.71 (s, 1H, Imi-H), 7.56–7.59 (m, 2H, Ar-H), 7.35–7.38 (m, 3H, Ar-H), 7.18–7.21 (m, 4H, Ar-H), 6.80 (s, 1H, Imi-H), 6.34 (m, ^3J = 7 Hz, 2H, NCH), 5.07 (s, 2 H, NCH_2), 1.75 (d, ^3J = 7 Hz, 12H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.5 ($C_{carbene}$), 140.6, 135.4, 134.2, 131.1, 129.8, 129.4, 128.4, 122.8, 119.6, 113.2

(Ar-C), 55.0, 52.4, 21.2 (CH, CH_2 and CH_3). Anal. Calcd. for $C_{23}H_{28}Br_2N_4Pd$: C 44.08, H 4.50, N 8.94; found: C 44.35, H 4.67, N 8.63. MS-EI (*m/z*): $[M - L - Br]^+$ calcd for $C_{13}H_{18}BrN_2Pd$ 387, found 387.

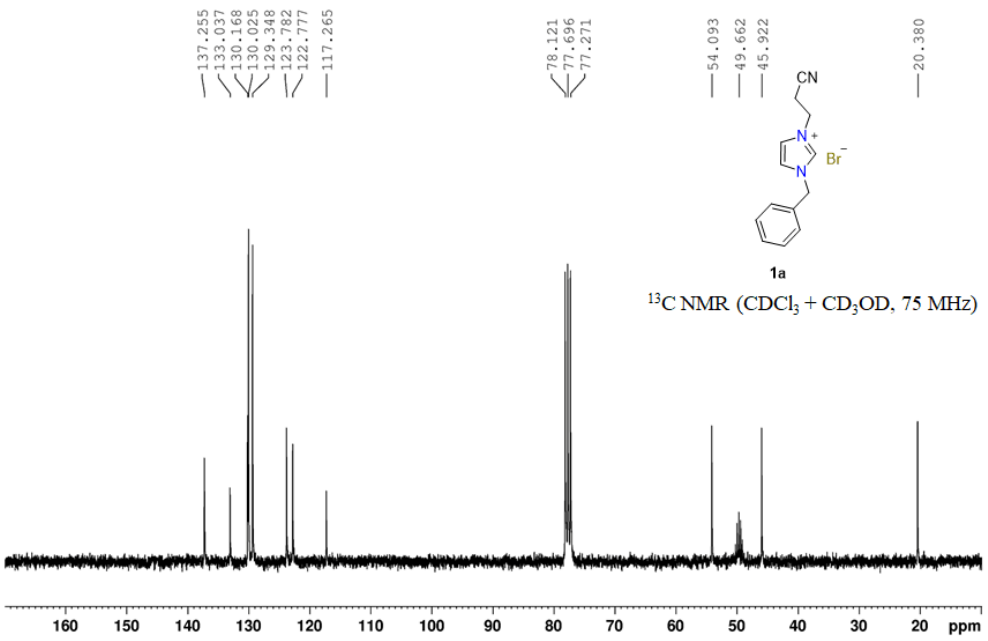
NMR Spectra

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1a**.



1a

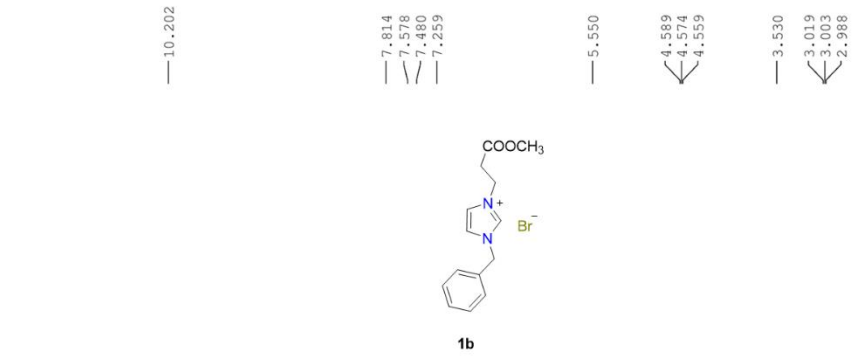
^{1}H NMR ($CDCl_3$ + CD_3OD, 300 MHz)



1a

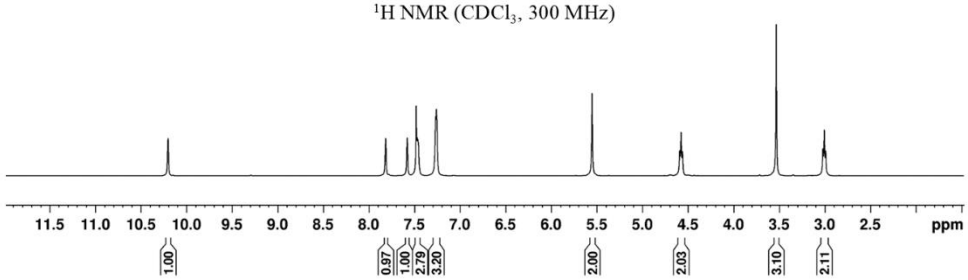
^{13}C NMR ($CDCl_3$ + CD_3OD, 75 MHz)

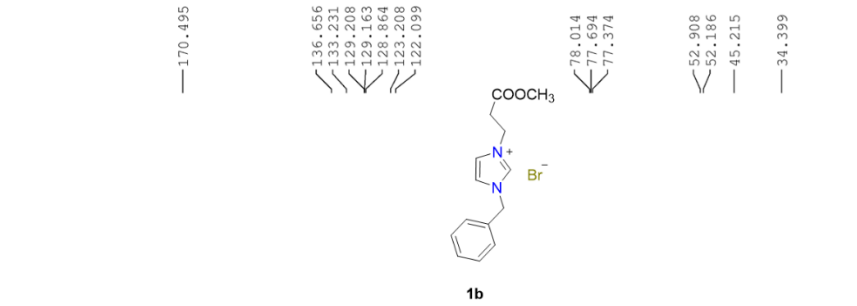
^{1}H and ^{13}C{^{1}H} NMR spectra of **1b**.



1b

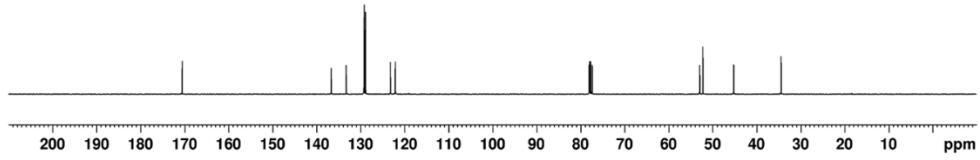
^{1}H NMR ($CDCl_3$, 300 MHz)



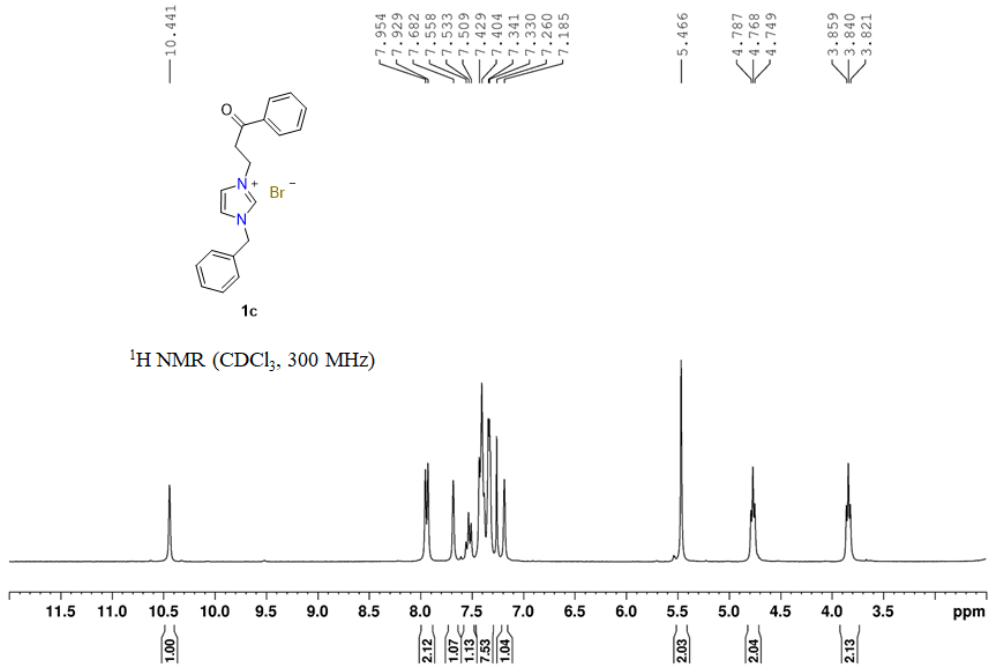


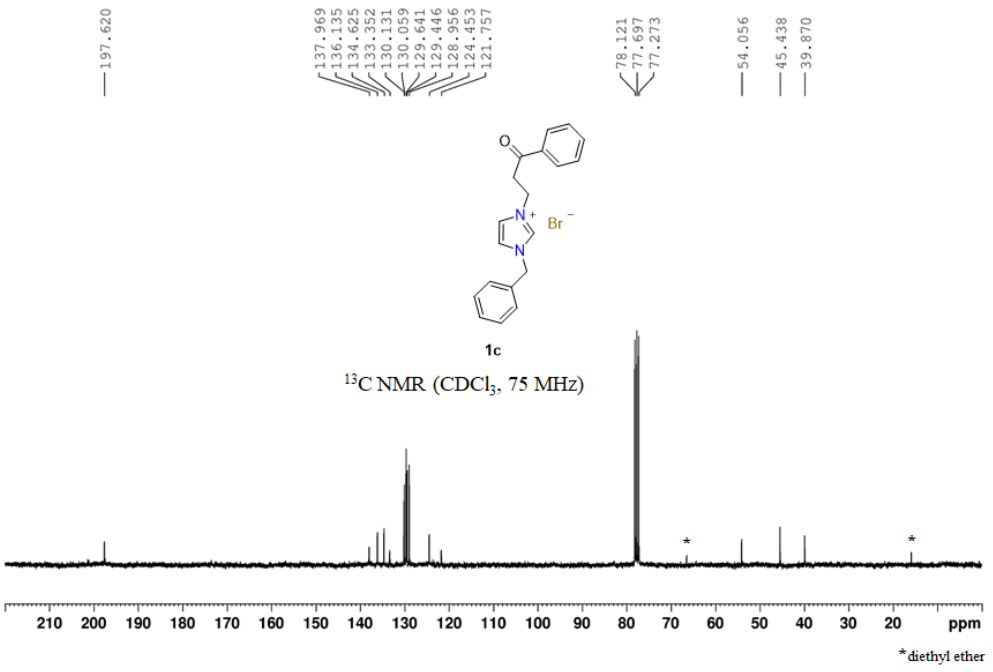
1b

^{13}C NMR ($CDCl_3$, 75 MHz)

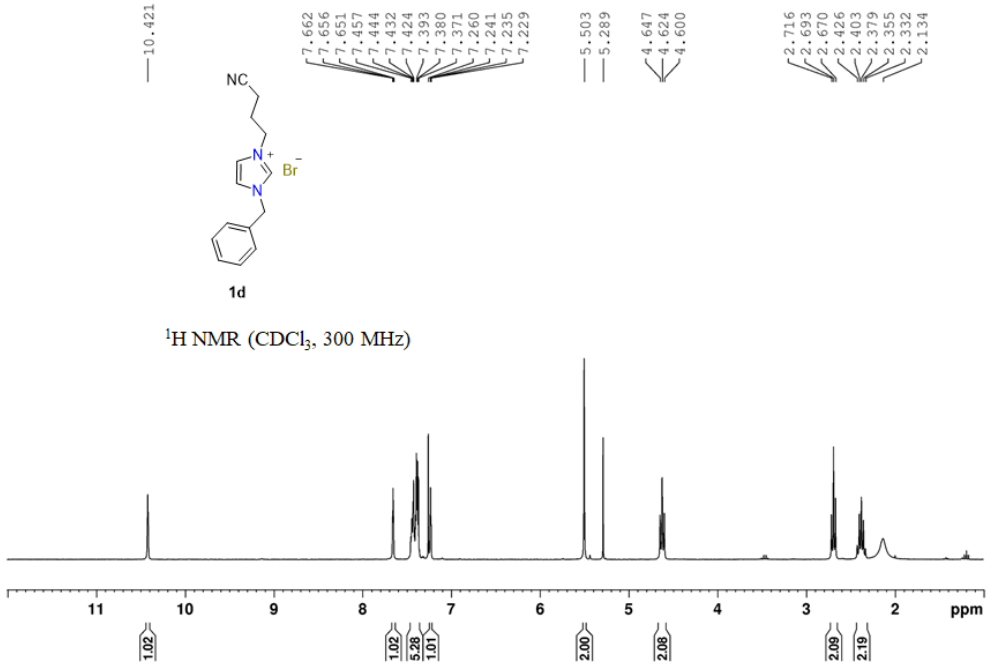


^{1}H and ^{13}C{^{1}H} NMR spectra of **1c**.

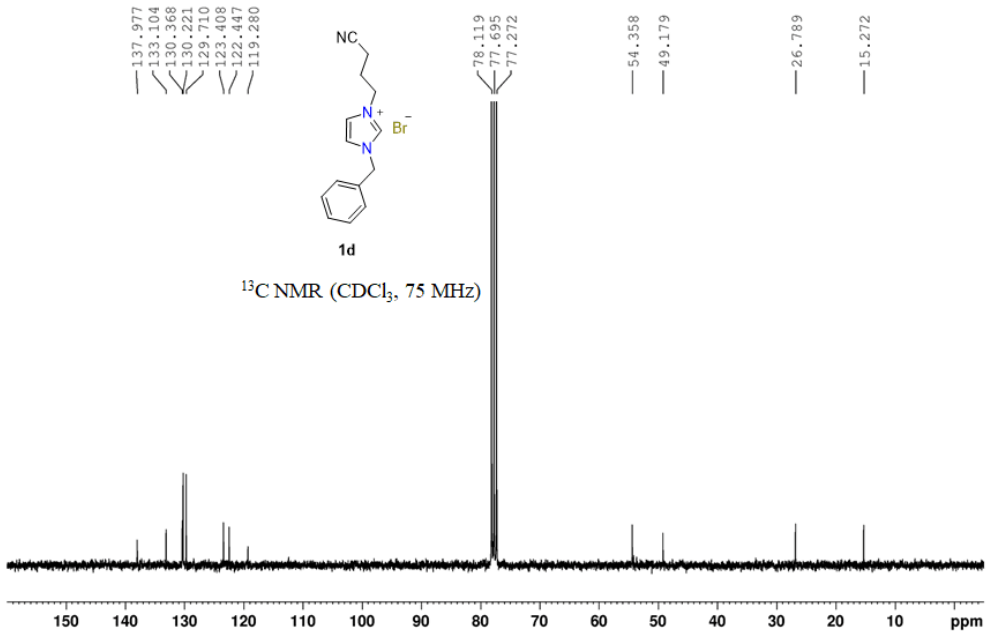




^{1}H and ^{13}C{^{1}H} NMR spectra of **1d**.

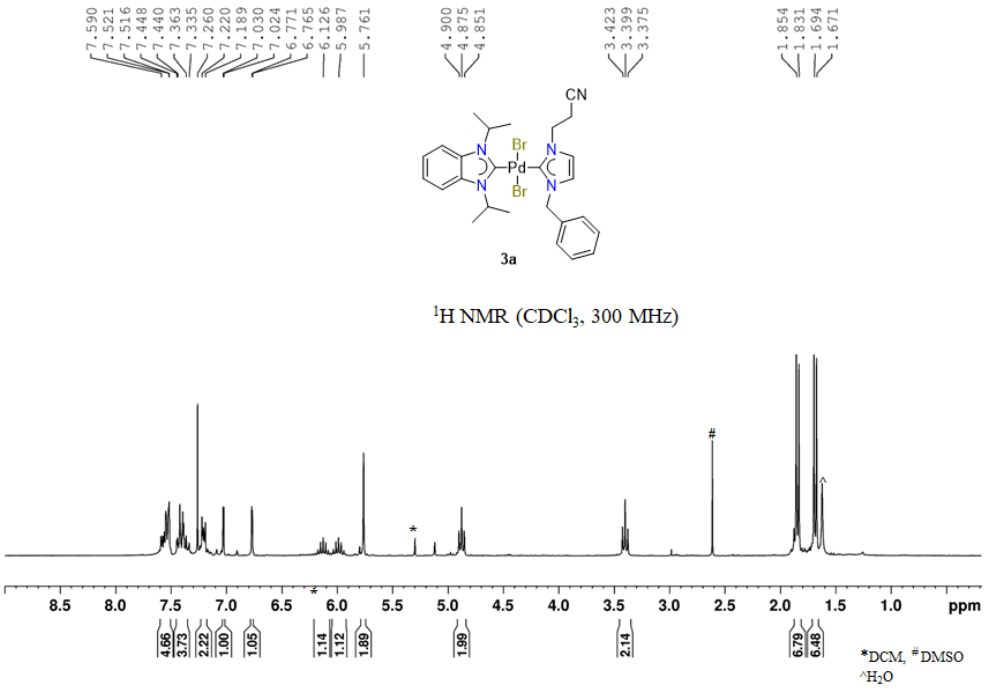


^{1}H NMR ($CDCl_3$, 300 MHz)

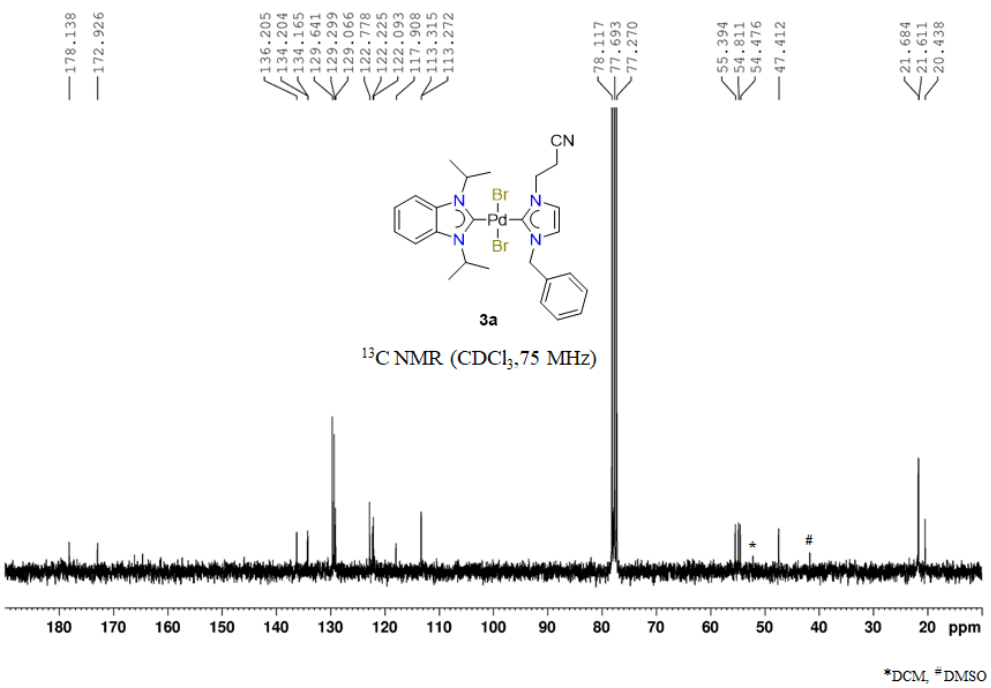


^{13}C NMR ($CDCl_3$, 75 MHz)

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3a**.

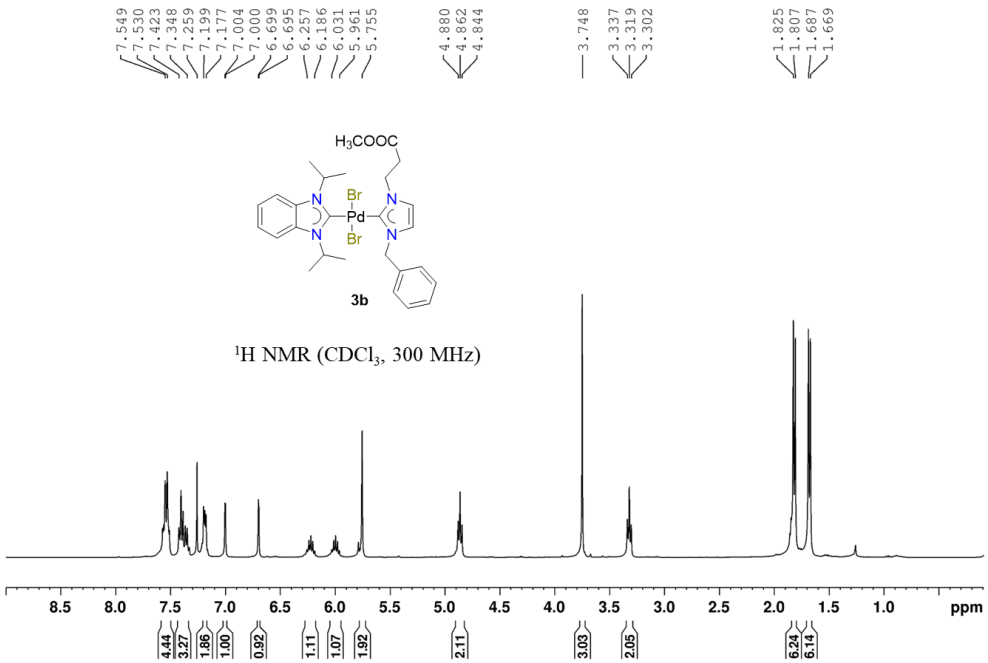


^{1}H NMR ($CDCl_3$, 300 MHz)

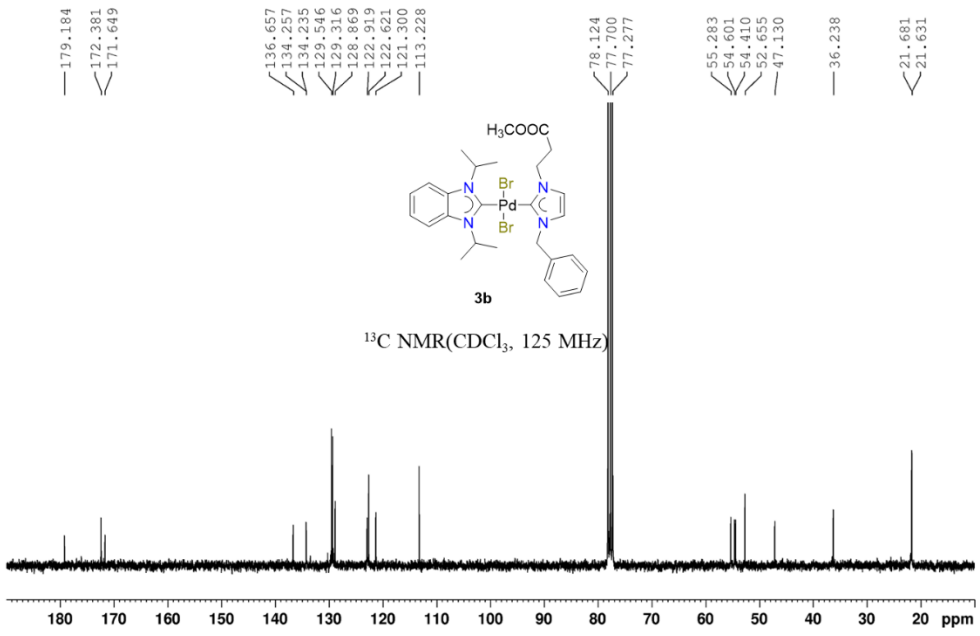


^{13}C NMR ($CDCl_3$,75 MHz)

^{1}H and ^{13}C{^{1}H} NMR spectra of **3b**.

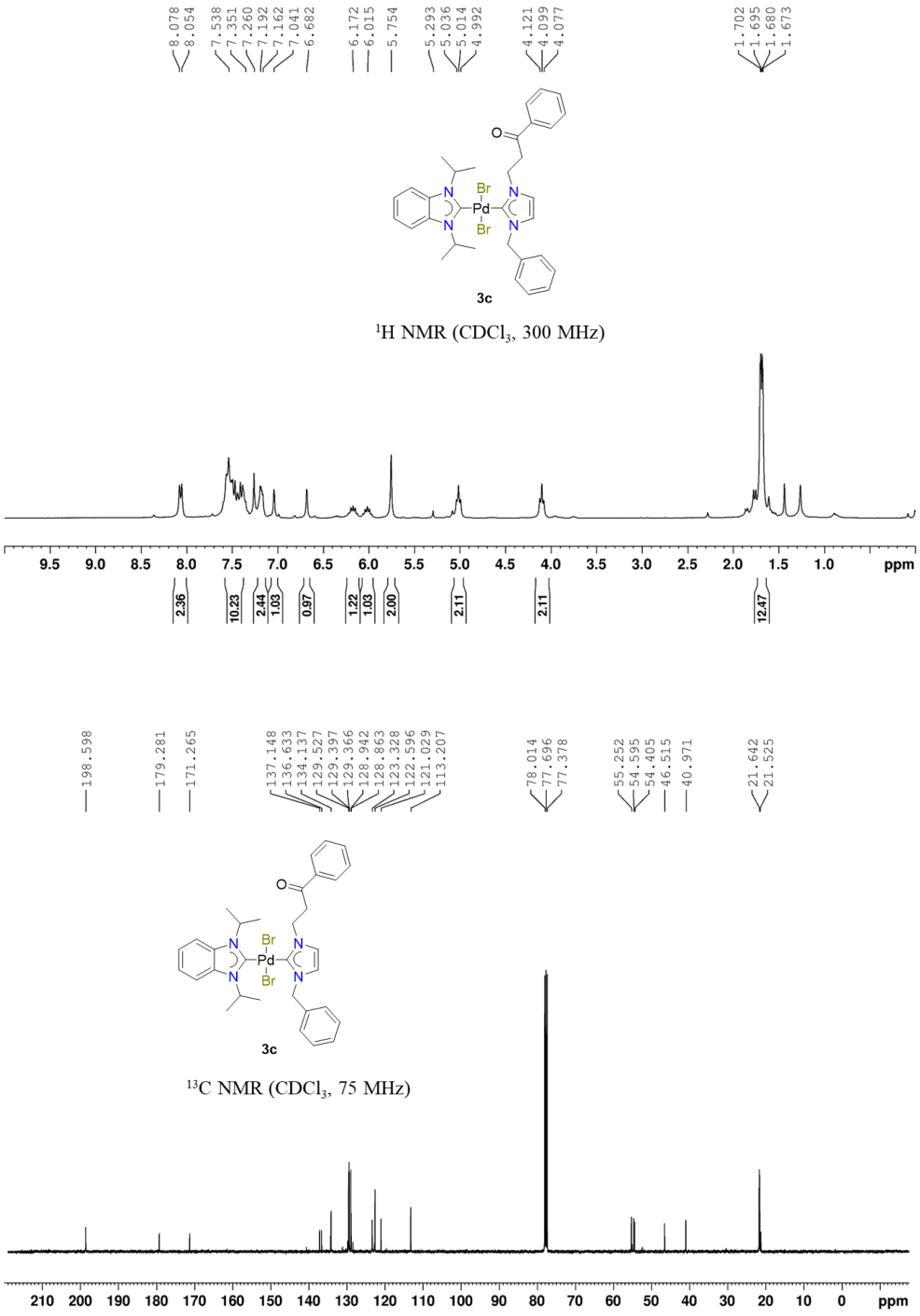


^{1}H NMR ($CDCl_3$, 300 MHz)



^{13}C NMR($CDCl_3$, 125 MHz)

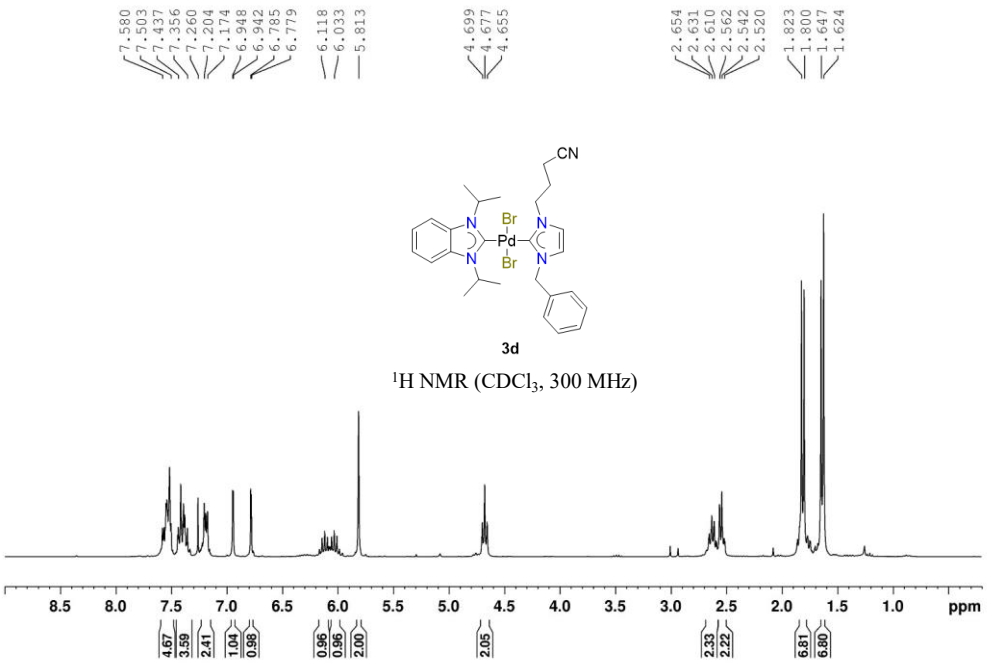
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3c**.



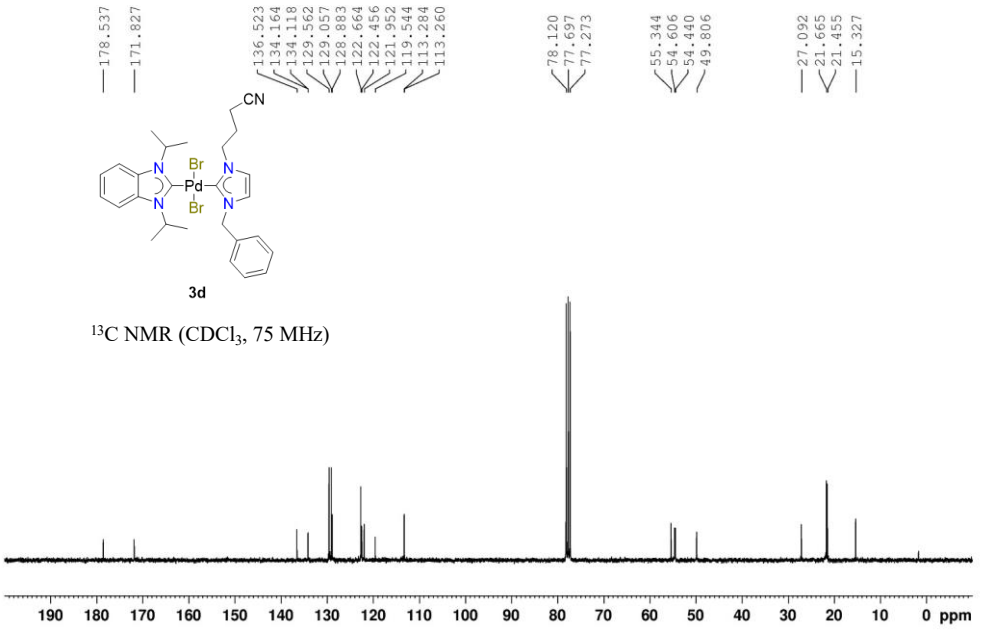
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR ($CDCl_3$, 75 MHz)

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3d**.

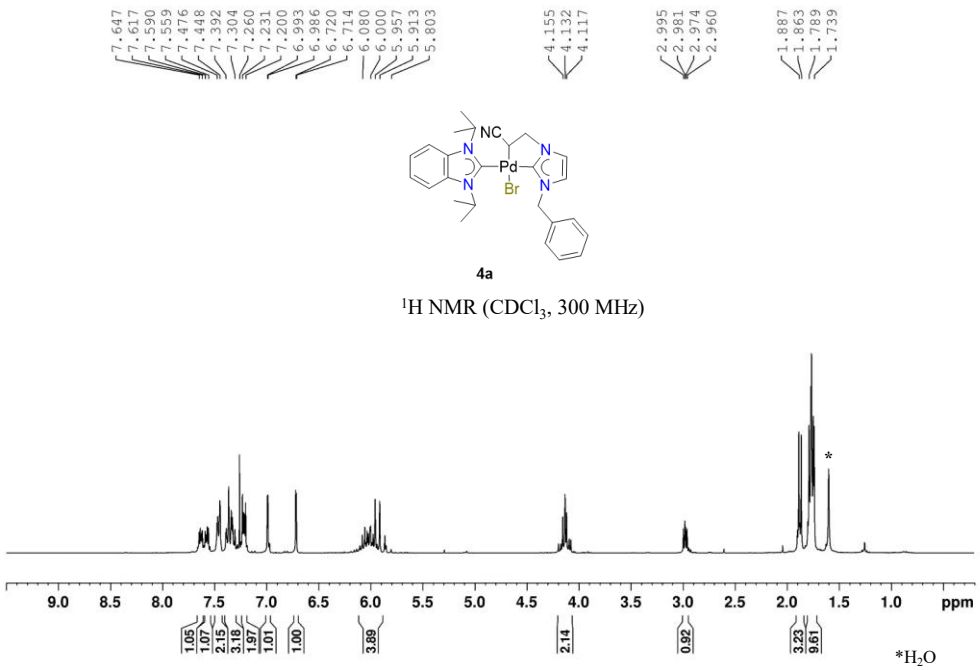


^{1}H NMR ($CDCl_3$, 300 MHz)

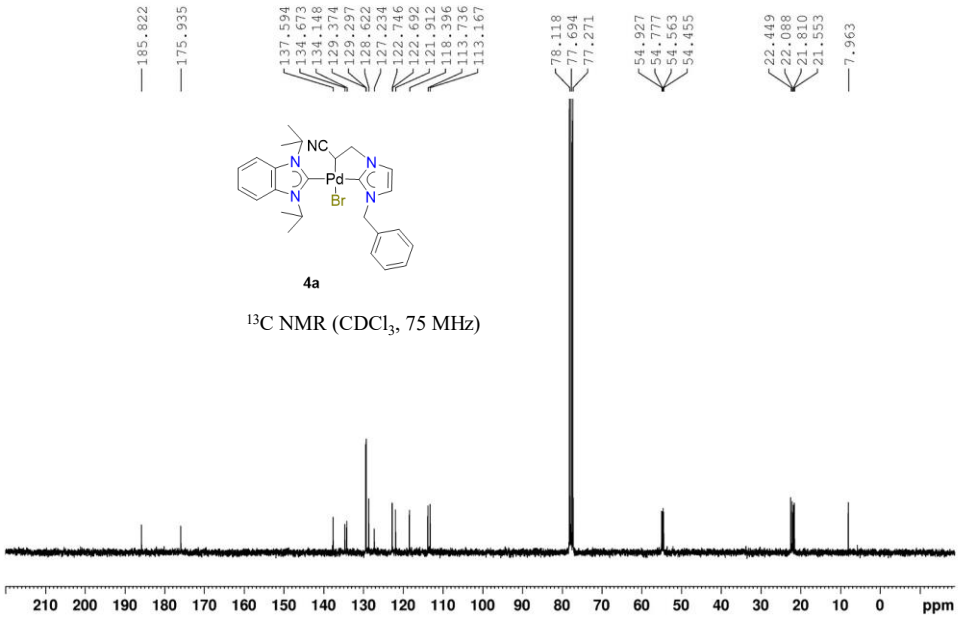


^{13}C NMR ($CDCl_3$, 75 MHz)

^{1}H and ^{13}C{^{1}H} NMR spectra of **4a**.

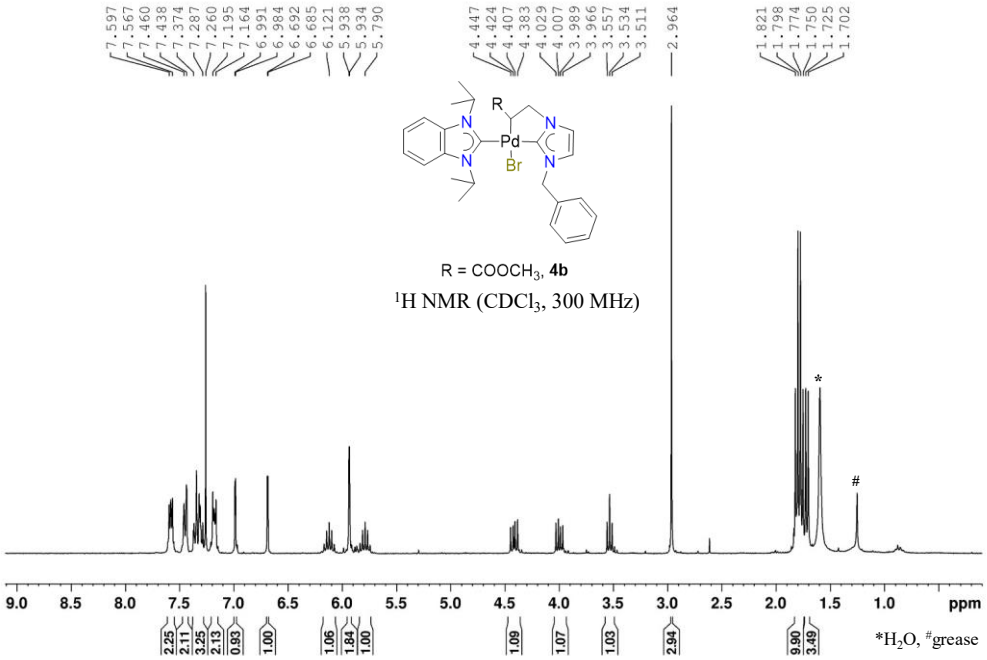


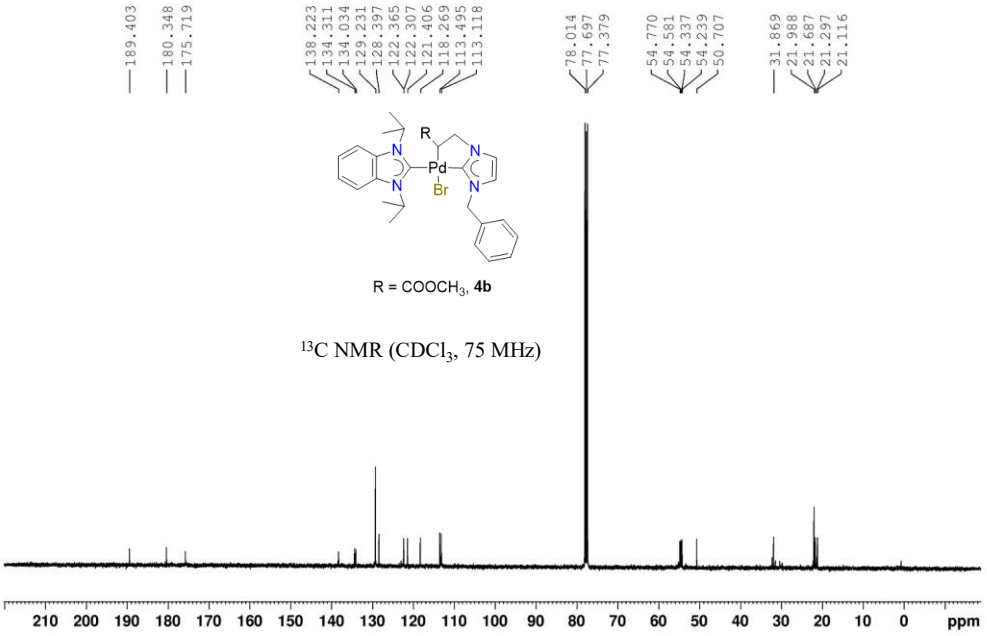
^{1}H NMR ($CDCl_3$, 300 MHz)



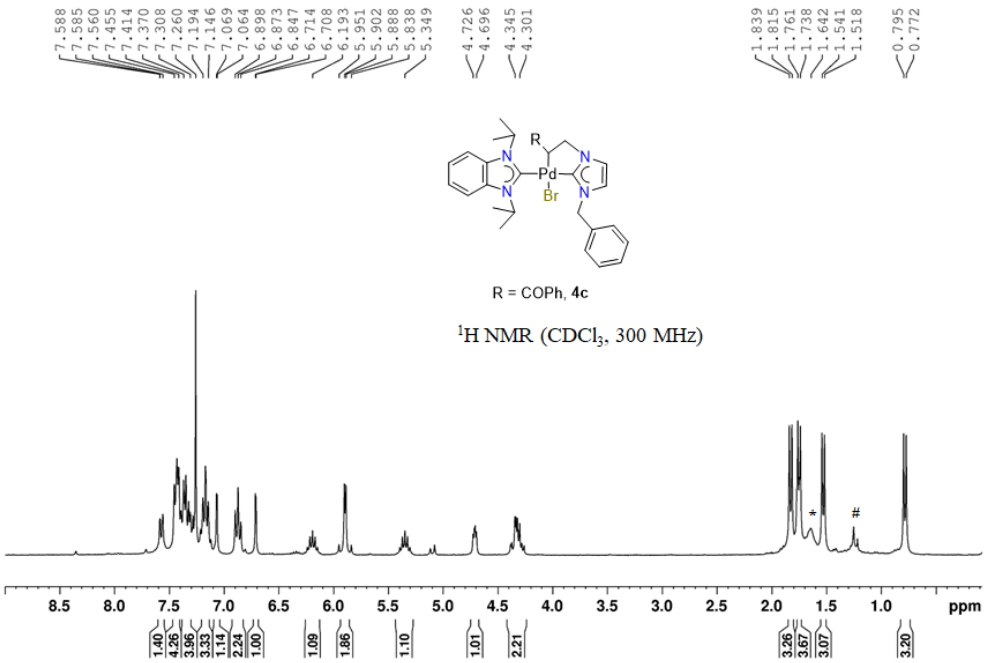
^{13}C NMR ($CDCl_3$, 75 MHz)

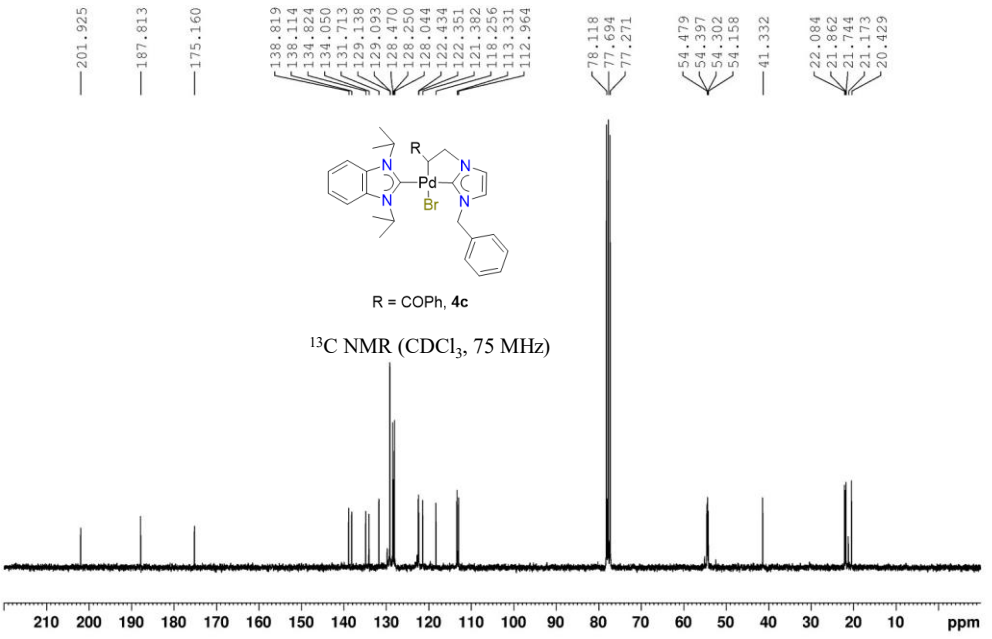
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4b**.



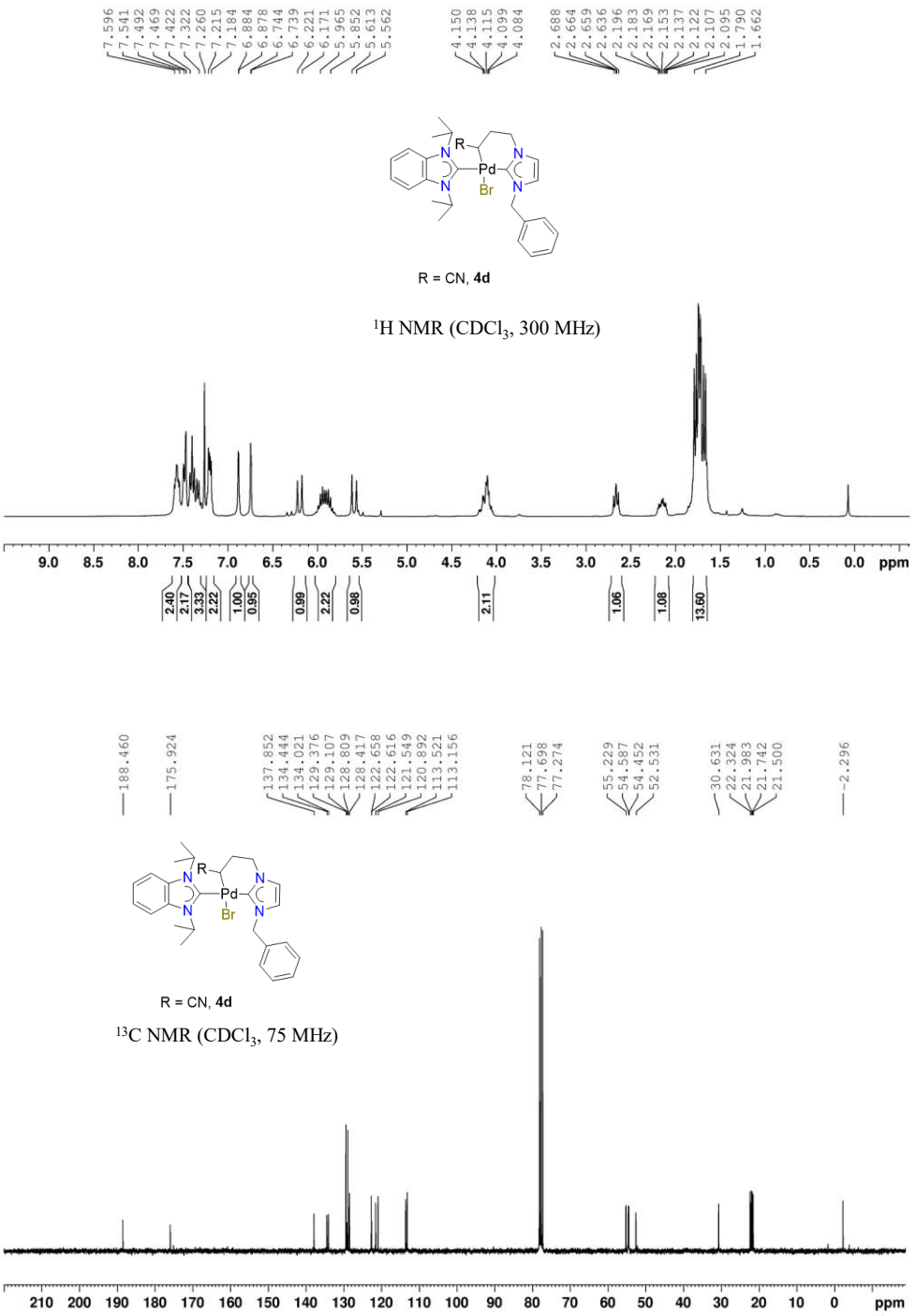


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4c**.

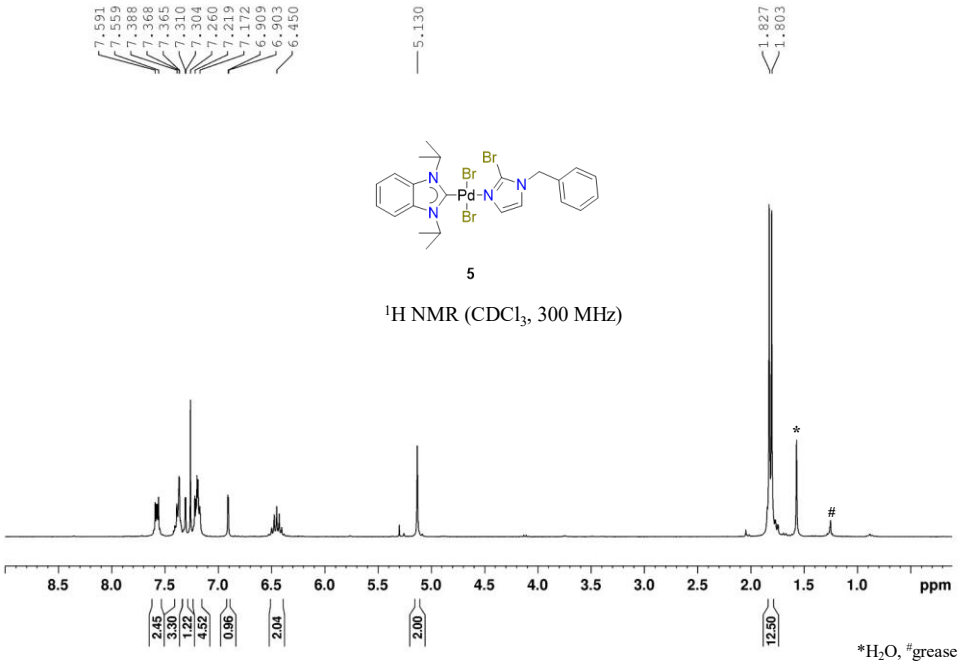




^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4d**.

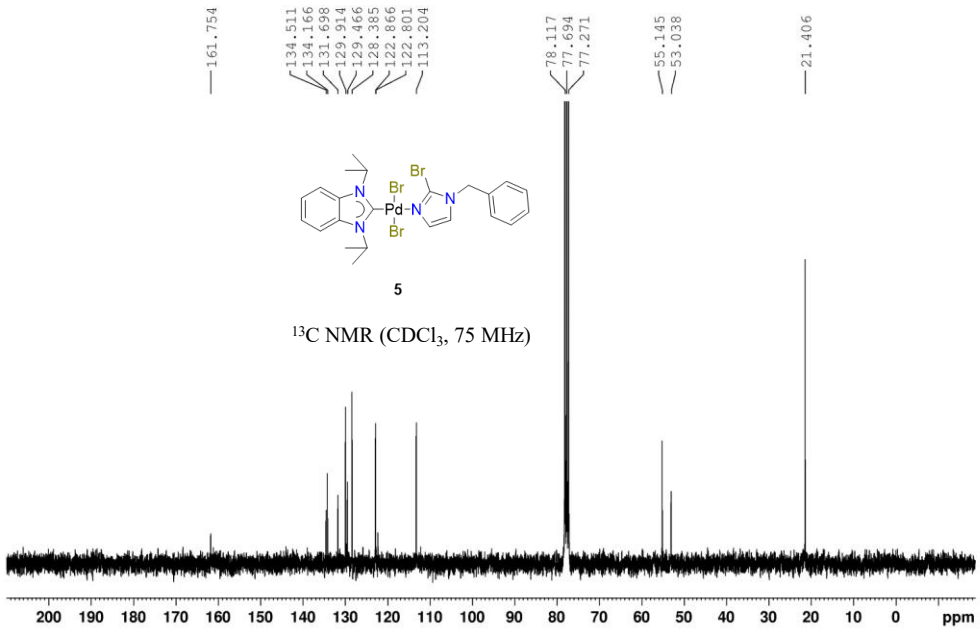


^{1}H and ^{13}C{^{1}H} NMR spectra of **5**.



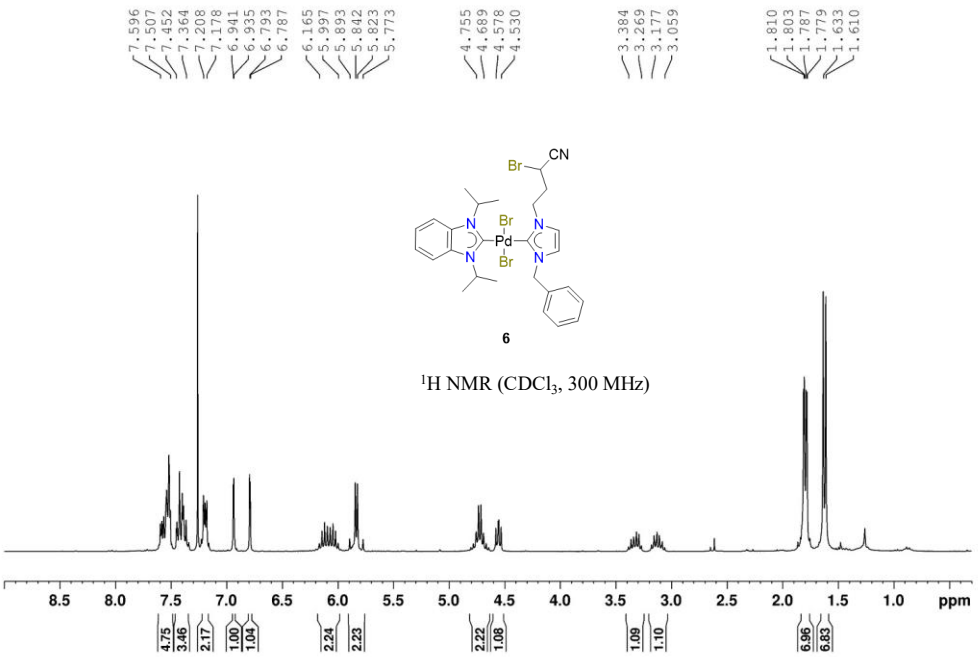
^{1}H NMR ($CDCl_3$, 300 MHz)

*H_2O, #grease

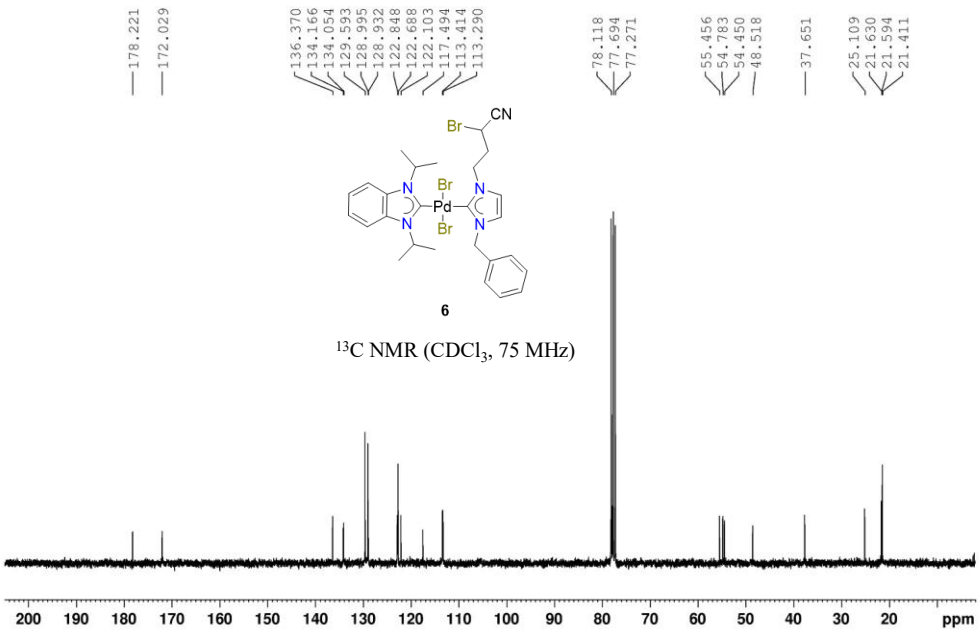


^{13}C NMR ($CDCl_3$, 75 MHz)

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **6**.

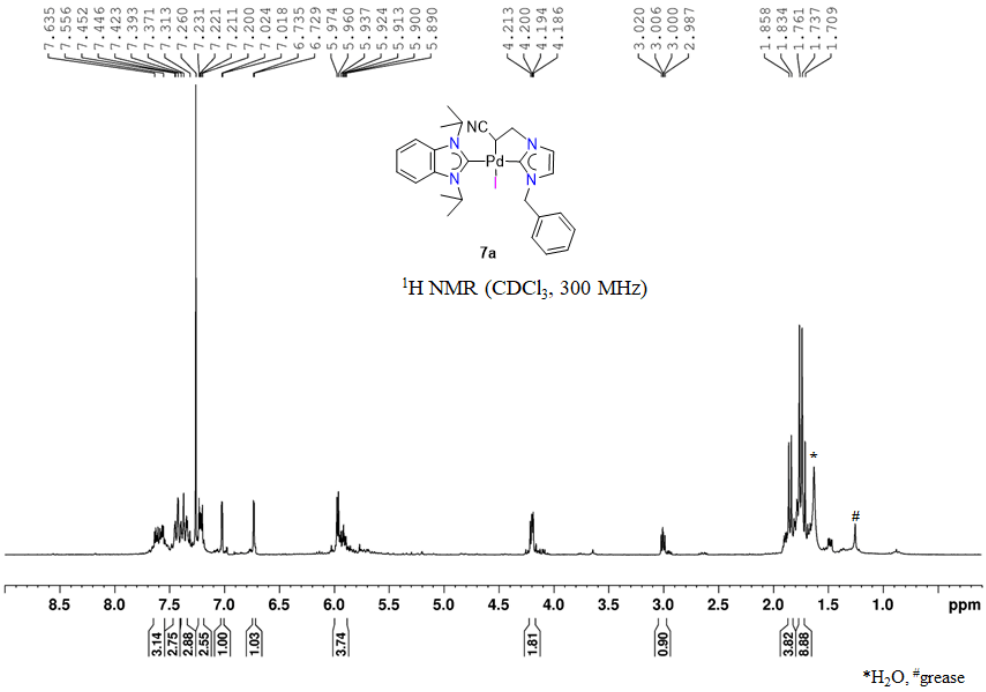


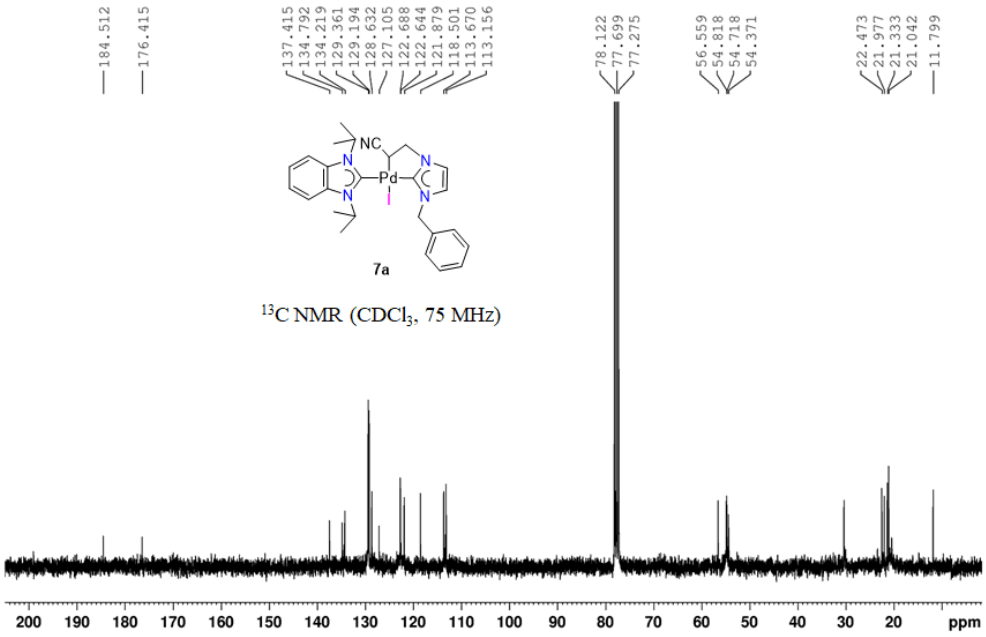
^{1}H NMR ($CDCl_3$, 300 MHz)



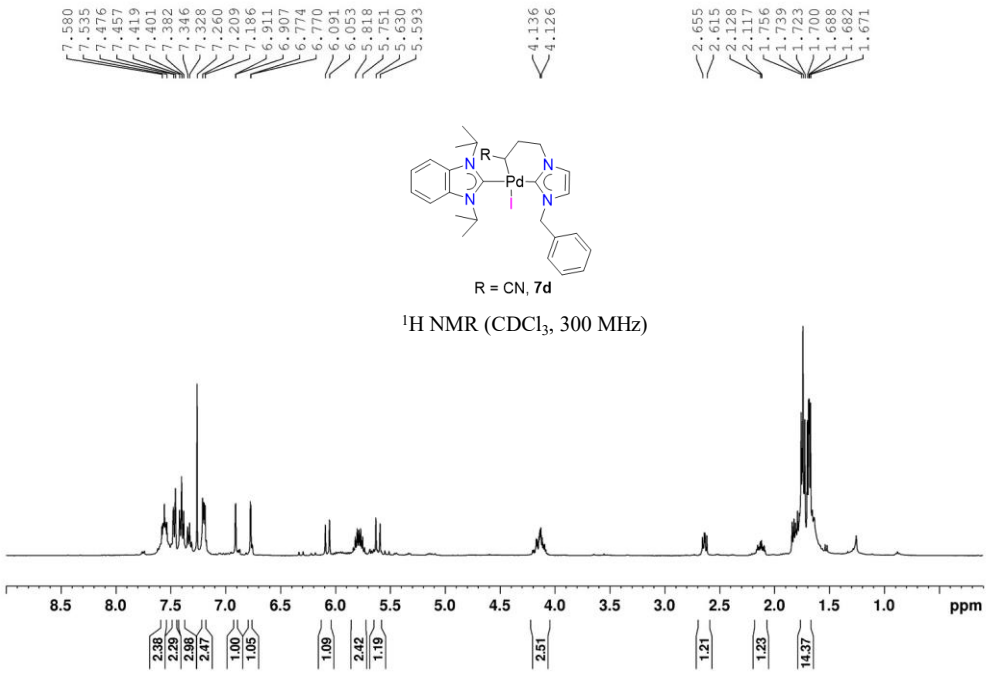
^{13}C NMR ($CDCl_3$, 75 MHz)

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **7a**.

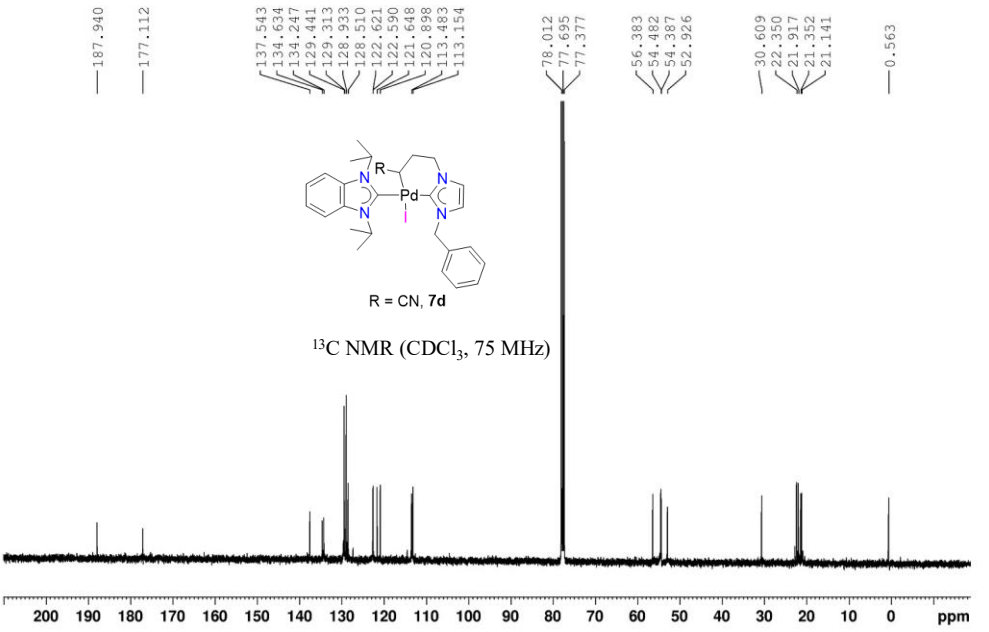




^{1}H and ^{13}C{^{1}H} NMR spectra of **7d**.

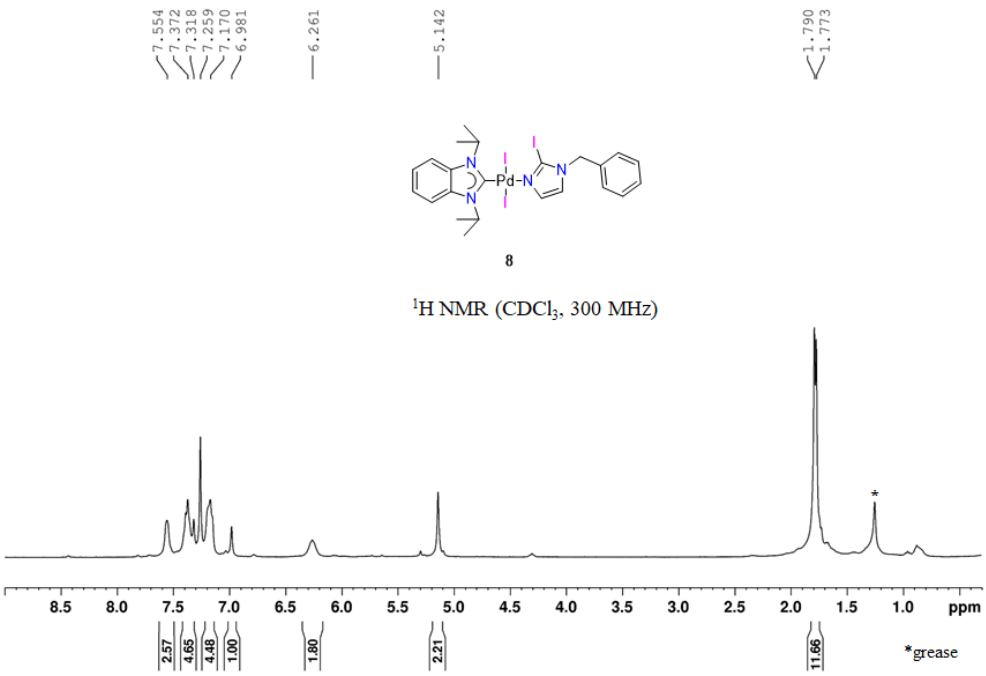


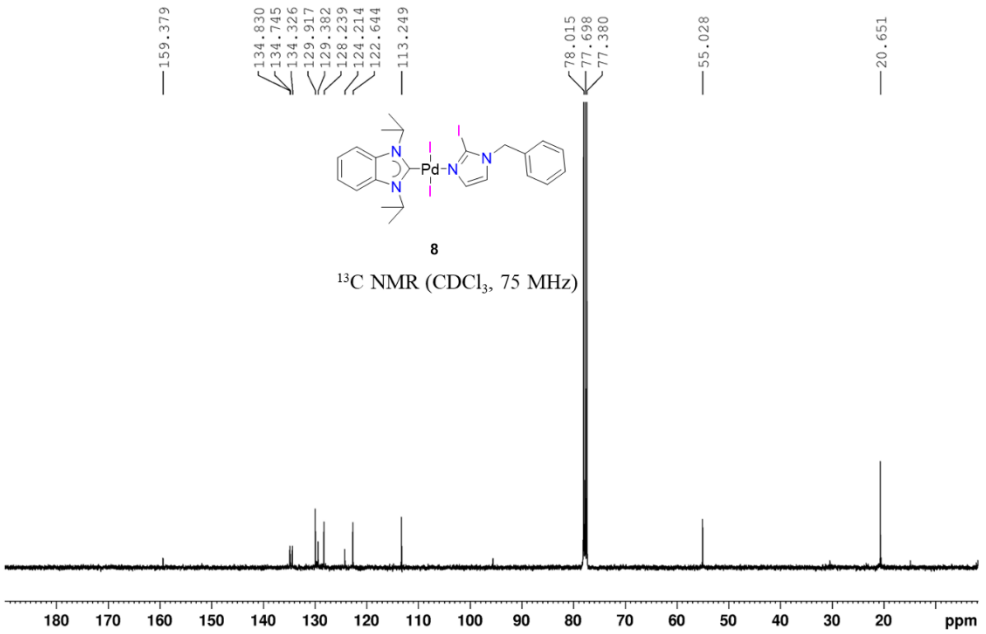
^{1}H NMR ($CDCl_3$, 300 MHz)



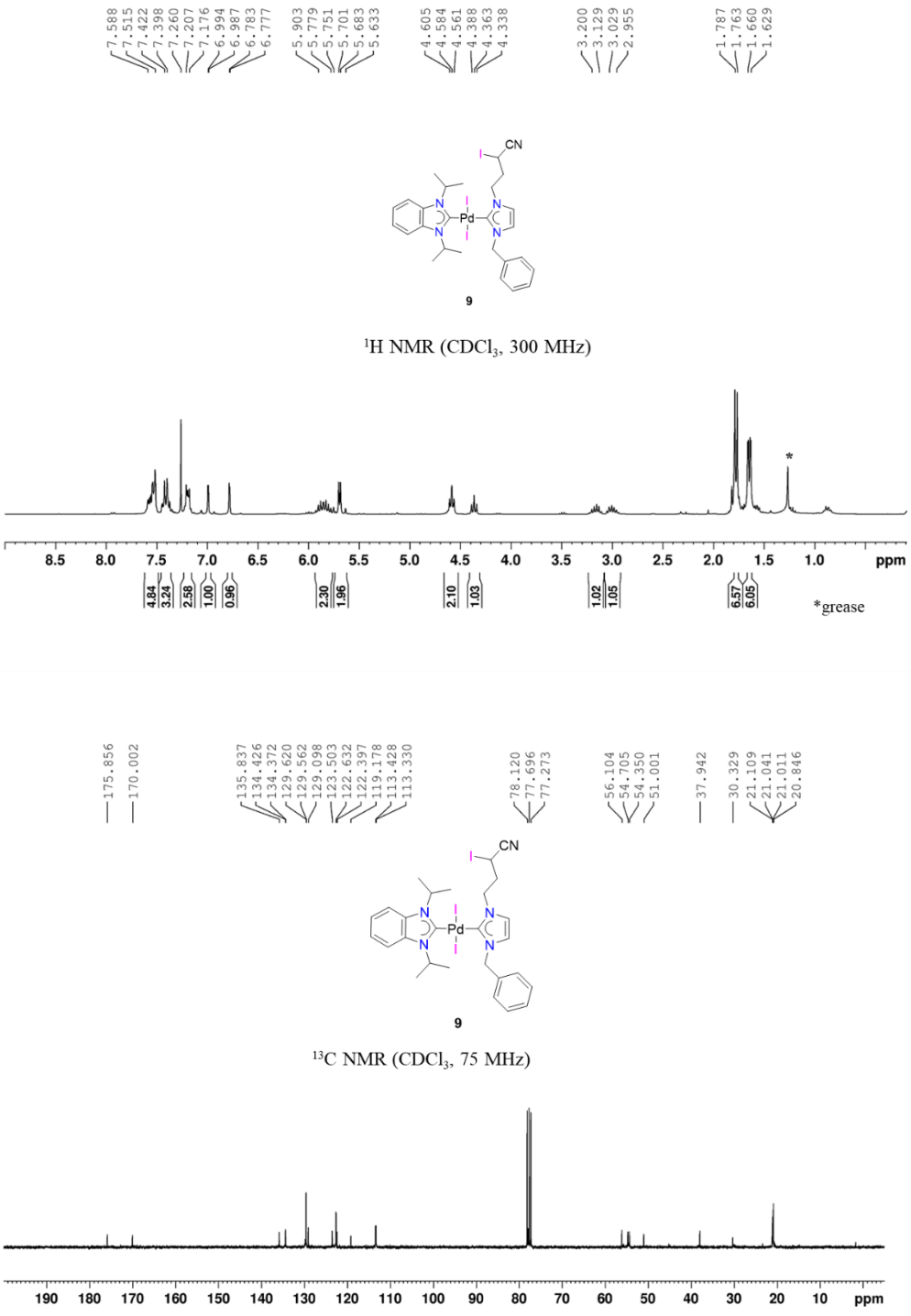
^{13}C NMR ($CDCl_3$, 75 MHz)

^{1}H and ^{13}C{^{1}H} NMR spectra of **8**.





^{1}H and ^{13}C{^{1}H} NMR spectra of **9**.

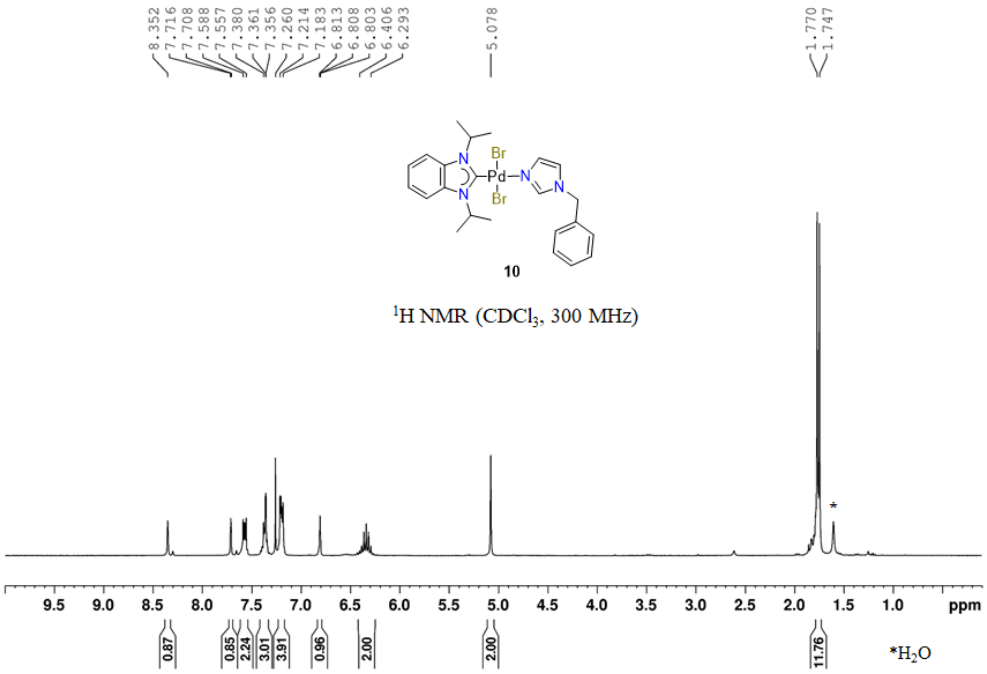


^{1}H NMR ($CDCl_3$, 300 MHz)

*grease

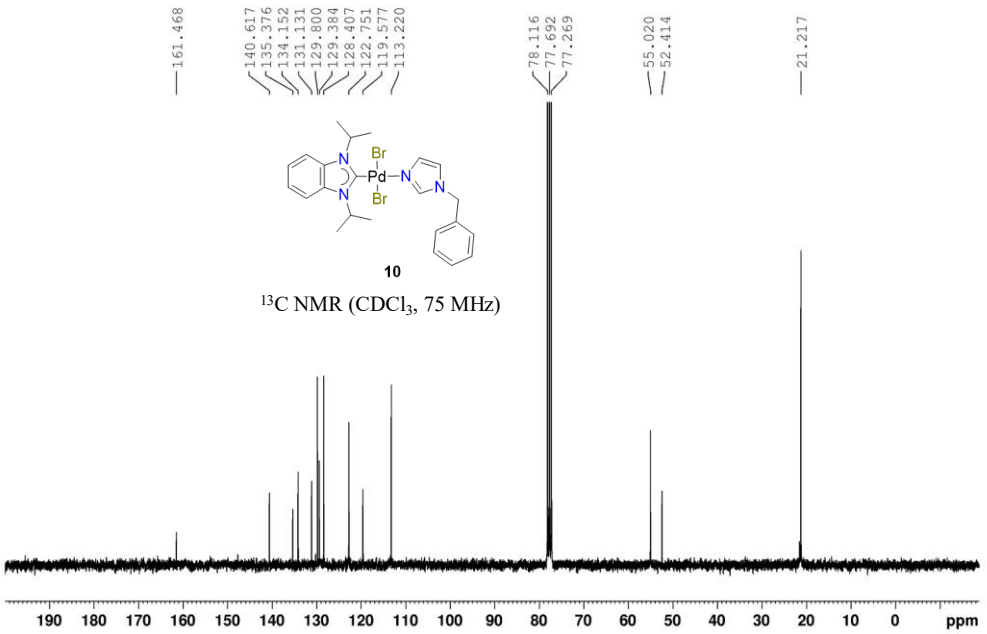
^{13}C NMR ($CDCl_3$, 75 MHz)

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **10**.



^{1}H NMR ($CDCl_3$, 300 MHz)

*H_2O



^{13}C NMR ($CDCl_3$, 75 MHz)

X-ray Diffraction Studies. X-ray data were collected with a Bruker D8 VENTURE diffractometer, using Mo-Kα radiation with the SMART suite of Programs.1 The structures were deposited to CCDC database and assigned with numbers of 2226577−2226579. Data were processed and corrected for Lorentz and polarization effects with SAINT, 2 and for absorption effect with SADABS.3 Structural solution and S23 refinement were carried out with the SHELXTL suite of programs.4 The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table S2.

Table S2. Selected X-ray crystallographic data for complexes **3c**, **4b** and **5**

	3c·THF	**4b**	**5**
formula	$C_{32}H_{36}Br_2N_4OPd·C_4H_8O$	$C_{27}H_{33}BrN_4O_2Pd$	$C_{23}H_{27}Br_3N_4Pd$
formula weight	830.97	631.885	705.61
color, habit	colorless	colorless	colorless
temperature [K]	150.0	160.0	170.0
crystal size [mm]	0.12 × 0.08 × 0.05	0.15 × 0.08 × 0.06	0.12 × 0.08 × 0.05
crystal system	triclinic	monoclinic	monoclinic
space group	P-1	$P2_1/c$	$P2_1/c$
a [Å]	9.5373(5)	16.1679(6)	10.6138(6)
b [Å]	12.3311(7)	9.3786(3)	13.7132(9)
c [Å]	16.2241(9)	35.7626(15)	17.3306(11)
α [°]	93.233(2)	90	90
β [°]	92.079(2)	96.1070(10)	97.572(2)
γ [°]	110.721(2)	90	90
V [$Å^3$]	1778.54(17)	5392.0(3)	2500.5(3)
Z	2	8	4
Dc (g cm^{-3})	1.552	1.557	1.874
radiation used	Mo Kα	Mo Kα	Mo Kα

μ [mm^{-1}]	2.805	2.201	5.554
θ range (°)	4.192–50.736	4.492–52.804	3.872–52.786
no. of unique data	6404	47847	5091
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0414 wR_2 = 0.0855	R_1 = 0.0489 wR_2 = 0.0978	R_1 = 0.0821 wR_2=0.1548
R indices (all data)	R_1 = 0.0614 wR_2 = 0.0958	R_1 = 0.0886 wR_2 = 0.1157	R_1 = 0.1408 wR_2 = 0.1747
goodness-of-fit on F^2	0.990	1.028	1.066
peak/hole [e Å^{-3}]	0.88/-0.56	1.29/-1.02	1.90/-1.35

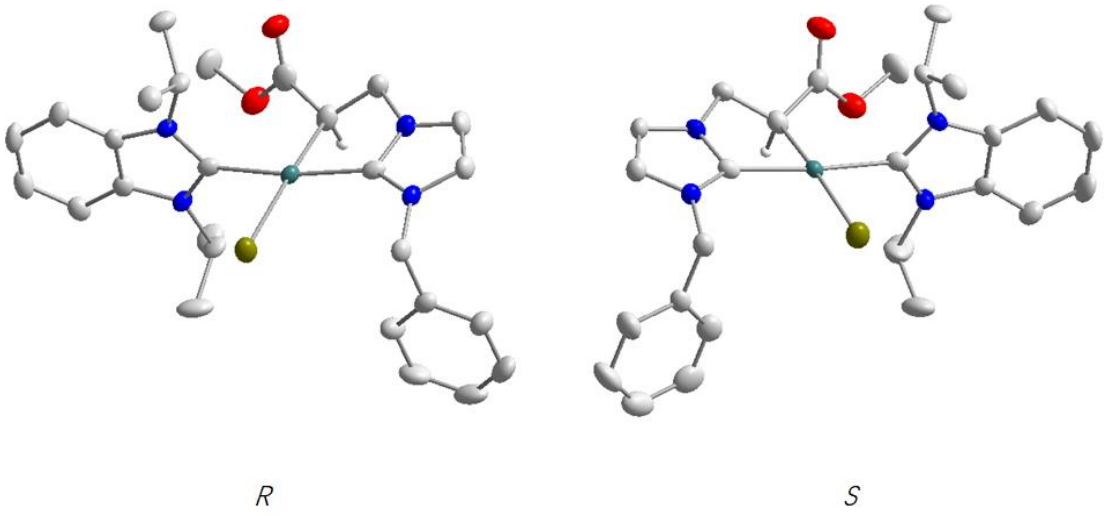


Figure S2 Molecular structure of racemic **4b** showing 50% probability ellipsoids; most hydrogen atoms are omitted for clarity.

Reference

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