Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Classifying donor strengths of dipyrrinato/aza-dipyrrinato ligands

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Experimental Procedures

General Remarks

All NMR spectra were recorded using a 500 MHz spectrometer unless otherwise noted. ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane using the $CDCl_3$ residual solvent signal at δ = 7.26 as an internal standard. ^{13}C NMR spectra were recorded using the proton-decoupled UDEFT pulse sequence,[1] and chemical shifts are reported in ppm referenced to the $CDCl_3$ signal at δ = 77.2. The chemical shifts of the carbene carbon, from which HEP2 values originate, are highlighted in bold. HEP2 values are calculated by adding 0.5 ppm to the carbene ^{13}C chemical shift to enable comparison to other values referenced to 77.7 ppm.[2,3] Analysis of HMBC correlations enabled assignment of the carbene ^{13}C resonances. Mass spectrometry was performed using a TOF spectrometer operating in ESI$^+$ or APCI mode. UV-Visible spectrophotometry was performed using a Varian Cary 100 Bio spectrophotometer and a 10mm screw-top quartz cuvette. X-ray crystallography was performed using a Bruker APEX II CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K. Specific experimental details about each structure reported herein are included below.

All chemicals were used as received. 1,3-Diisopropylbenzimidazolium bromide (**1**), di-μ-bromobis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromopalladium (II) (**2**),[4,5] tetraphenyl aza-dipyrrin **3a**,[6] benzannulated aza-dipyrrin **3c**,[7] benzannulated *meso*-methine dipyrrin **3d**,[8] and *meso*-mesityl core-unsubstituted dipyrrin **3m**[9,10] were synthesized according to literature methods. Thin-layer chromatography was performed on silica. No precautions were taken to exclude air or moisture during any synthetic step.

(*Z*)-2-((3,5-Diphenyl-1*H*-pyrrol-2-yl)methylene)-3,5-diphenyl-2*H*-pyrrolium bromide (3b·HBr)

2,4-Diphenyl-1*H*-pyrrole[11] (100 mg, 0.46 mmol) was dissolved in 98% formic acid (1 mL) and aqueous HBr (11.5 M, 0.5 mL). The solution was stirred at 110°C for 4 hr, during which a large amount of lustrous golden solid precipitated. The precipitate was collected via suction filtration, then washed with water and pentane to yield the title compound as a shiny golden powder (112 mg, 94% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 13.88 (br s, 2H), 8.41 (d, 4H, *J* = 7.4 Hz), 7.60 – 7.48 (m, 6H), 7.44 – 7.30 (m, 11H), 7.03 (s, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 162.5, 154.7, 151.5, 133.0, 131.8, 129.7, 129.32, 129.28 (two overlapping signals), 129.0, 128.6, 128.3, 115.2. HRMS-ESI$^+$-TOF (m/z): [m-Br]$^+$ calc'd. for $C_{33}H_{25}N_2$: 449.2012; found 449.2017.

(*Z*)-2-((3,5-Diphenyl-2*H*-pyrrol-2-ylidene)methyl)-3,5-diphenyl-1*H*-pyrrole (3b)

A solution of **3b·Hbr**[12] in dichloromethane was treated with excess base (e.g. DIPEA or sodium hydroxide) and stirred for 5 min at room temperature. The organic phase was washed with water and volatiles then removed in vacuo to yield the title compound in quantitative yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.97 (d, 4H, *J* = 7.4 Hz), 7.55 – 7.49 (m, 8H), 7.47 – 7.39 (m, 6H), 7.38 – 7.33 (m, 2H), 7.24 (s, 1H), 6.97 (s, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 153.4, 144.9, 139.7, 135.1, 133.1, 129.2, 128.9 (two overlapping signals), 127.8, 126.4, 123.7, 114.7 (one signal not observed).

General procedure 1 (GP1) for the synthesis of Series 1 sensor complexes a-d

To a solution of **2** (0.032 mmol) and (aza) dipyrrin (0.064 mmol) in dichloromethane (6 mL) was added DIPEA (0.064 mmol). The resulting solution was stirred overnight at room temperature. Silica gel was added to adsorb the crude mixture and volatiles were removed in vacuo; the resulting solid was dry-loaded directly onto a silica chromatography column and purified using a gradient of dichloromethane/hexanes (0 to 60% dichloromethane) as an eluent.

General procedure 2 (GP2) for the synthesis of Series 2 sensor complexes e-m

To a solution of **2** (0.032 mmol) and dipyrrin or dipyrrin·HX (0.064 mmol) in dichloromethane (6 mL) was added DIPEA (0.064 mmol for dipyrrin, 0.128 mmol for dipyrrin·HX). The resulting solution was stirred overnight at room temperature. Celite was added to adsorb the crude mixture and volatiles were removed in vacuo; the resulting solid was dry-loaded directly onto a silica chromatography column and purified using a gradient of ethyl acetate/hexanes (0 to 40% ethyl acetate) or methanol/dichloromethane (0 to 4% methanol) as an eluent.

PdBr(iPr$_2$-bimy)(3a)] (4a)

Following GP1, **3a** was reacted with **2** to give a red-blue crystalline solid, 56% yield. R_f = 0.12 (40% dichloromethane/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.48 (d, 2H, *J* = 7.1 Hz), 8.06 (d, 2H, *J* = 7.1 Hz), 7.99 (d, 2H, *J* = 7.3 Hz), 7.58 – 7.49 (m, 3H), 7.46 – 7.34 (m, 9H), 7.26 (s, 1H, obscured by chloroform residual), 7.22 (d, 1H, *J* = 7.8 Hz), 7.19 – 7.15 (m, 3H), 7.13 – 7.04 (m, 2H), 6.72 (s, 1H), 5.72 (septet, 1H, *J* = 7 Hz), 5.59 (7et, 1H, *J* = 7 Hz), 1.73 (d, 3H, *J* = 7 Hz), 1.53 (d, 3H, obscured by water resonance), 1.45 (d, 3H, *J* = 7 Hz), 1.24 (d, 3H, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **167.2**, 166.9, 161.8, 148.2, 146.2, 145.9, 142.7, 136.4, 135.5, 134.9, 134.2, 133.7, 133.1, 130.3, 129.8, 129.6, 128.9, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 122.2, 120.0, 118.5, 112.7, 55.1, 54.0, 31.8, 22.8, 22.11, 22.06, 21.5, 21.2. Carbene resonance assignment confirmed by 2D HMBC; no correlations were observed for this resonance, while the correlations for the adjacent ^{13}C resonance suggest it originates from an internal pyrrolic α-carbon. HRMS-ESI$^+$-TOF (m/z): [m+H]$^+$ calc'd. for $C_{45}H_{41}BrN_5Pd$: 836.1575; found 836.1536.

PdBr(iPr$_2$-bimy)(3b)] (4b)

Following GP1, **3b** was reacted with **2** to give a bright red solid, 15% yield. R_f = 0.11 (40% dichloromethane/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.53 (d, 2H, *J* = 7.3 Hz), 7.59 – 7.49 (m, 7H), 7.48 – 7.38 (m, 8H), 7.37 – 7.30 (m, 2H), 7.25 (app s, 1H, obscured by chloroform residual), 7.22 – 7.18 (m, 3H), 7.13 – 7.04 (app qu, 2H), 6.98 (s, 1H), 6.49 (s, 1H), 5.71 (7et, 2H, *J* = 7 Hz), 1.64 (d, 3H, *J* = 7 Hz), 1.49 (d, 3H, *J* = 7 Hz), 1.44 (d, 3H, *J* = 7 Hz), 1.14 (d, 3H, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **168.1**, 163.7, 161.1, 147.9, 145.3, 138.8, 137.8, 136.8, 136.3, 135.7, 135.4, 133.6, 133.2, 132.0, 129.3, 129.2, 129.1, 129.0, 128.9, 128.7, 127.97, 127.94, 127.69, 127.64, 122.1, 118.4, 117.8, 112.8, 112.7, 54.8, 54.2, 21.94, 21.89, 21.5, 21.1. HRMS-ESI$^+$-TOF (m/z): [m+H]$^+$ calc'd. for $C_{46}H_{41}BrN_4Pd$: 834.1544; found 834.1561.

PdBr(iPr$_2$-bimy)(3c)] (4c)

Following GP1, **3c** was reacted with **2** to give a green crystalline solid, 62% yield. R_f = 0.12 (40% dichloromethane/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.39 (d, 2H, *J* = 7.2 Hz), 8.25 – 8.19 (app t, 2H), 7.89 (d, 1H, *J* = 7.8 Hz), 7.61 (t, 2H, *J* = 7.7 Hz), 7.56 – 7.52 (app t, 1H), 7.46 (t, 1H, *J* = 7.4 Hz), 7.41 – 7.28 (m, 3H), 7.24 – 7.06 (m, 10H), 5.54 (app br s, 1H), 5.38 (app br s, 1H), 1.73 (app br s, 3H), 1.35 (app br s, 3H), 1.17 (app br s, 3H), 1.03 (app br s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **166.3**, 160.4, 154.6, 140.8, 139.0, 137.2, 136.0, 135.2, 134.8, 133.1, 132.0, 130.8, 129.7, 128.8, 128.5, 128.3, 128.22, 128.17, 127.0, 125.7, 124.6, 122.3, 120.8, 120.6, 120.4, 112.6, 54.9, 53.7, 22.2, 21.8, 21.4, 20.0. HRMS-ESI$^+$-TOF (m/z): $[m+H]^+$ calc'd. for $C_{41}H_{36}BrN_5Pd$: 783.1183; found 783.1213.

PdBr(iPr$_2$-bimy)(3d)] (4d)

Following GP1, **3d** was reacted with **2** to give a blue crystalline solid, 42% yield. R_f = 0.23 (40% dichloromethane/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.46 (d, 2H, *J* = 7.6 Hz), 8.03 – 7.93 (m, 4H), 7.62 (t, 2H, *J* = 7.6 Hz), 7.51 (t, 1H, *J* = 7.3 Hz), 7.41 – 7.34 (m, 2H), 7.32 – 7.25 (m, 3H), 7.25 – 7.16 (m, 6H), 7.13 – 7.06 (m, 2H), 7.06 – 7.01 (t, 1H, *J* = 7.3 Hz), 5.56 (septet, 1H, *J* = 7 Hz), 5.39 (7et, 1H, *J* = 7 Hz), 1.57 (d, 3H, *J* = 7 Hz), 1.11 (d, 3H, *J* = 7 Hz), 0.90 (d, 3H, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **167.1**, 157.7, 153.9, 138.2, 136.8, 136.0, 135.9, 133.7, 133.1, 131.8, 131.2, 131.1, 130.5, 130.4, 128.9, 128.72, 128.66, 128.1, 128.0, 126.6, 125.7, 123.9, 123.0, 122.2, 121.8, 120.5, 118.9, 118.6, 118.0, 112.71, 112.65, 54.4, 54.0, 22.0, 21.6, 21.4, 20.1. HRMS-ESI$^+$-TOF (m/z): $[m+H]^+$ calc'd. for $C_{42}H_{37}BrN_4Pd$: 782.1231; found 782.1256.

PdBr(iPr$_2$-bimy)(3e)] (4e)

Following GP2, **3e** was reacted with **2** to give an orange solid, 58% yield. R_f = 0.62 (20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.60 – 7.52 (m, 2H), 7.23 – 7.17 (m, 2H), 6.91 (s, 1H), 6.09 (app br s, 2H), 2.64 (s, 3H), 2.34 (q, 2H, *J* = 7.5 Hz), 2.21 – 2.14 (m, 8H, two overlapping signals), 1.71 (app br s, 6H, two overlapping signals), 1.62 – 1.44 (m, 8H, two overlapping signals), 1.01 (t, 3H, *J* = 7.5 Hz), 0.85 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **171.1**, 164.0, 153.3, 137.6, 135.2, 134.7, 133.4, 132.9, 132.8, 128.7, 122.4, 122.2, 113.0, 54.4, 21.4, 20.4, 19.5, 18.4, 18.3, 16.7, 15.0, 14.7, 10.2, 10.0. HRMS-ESI$^+$-TOF (m/z): $[m+Na]^+$ calc'd. for $C_{30}H_{41}BrN_4Pd$: 665.1442; found 665.1452.

PdBr(iPr$_2$-bimy)(3f)] (4f)

Following GP2, **3f·HBr** was reacted with **2** to give an orange-yellow solid, 58% yield. R_f = 0.79 (75% dichloromethane/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.63 – 7.58 (m, 2H), 7.29 – 7.23 (m, 2H, overlaps chloroform residual), 6.92 (s, 1H), 6.67 (app d, 1H), 6.31 (7et, 2H, *J* = 7.0 Hz), 6.01 – 5.98 (m, 1H), 5.97 (s, 1H), 2.72 (s, 3H), 2.36 (q, 2H, *J* = 7.5 Hz), 2.16 (s, 3H), 1.77 (d, 6H, *J* = 7.0 Hz), 1.54 (d, 6H, *J* = 7.0 Hz), 1.04 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **170.3**, 143.0, 140.2, 139.0, 135.7, 133.5, 133.4, 125.2, 122.8, 122.7, 113.2, 112.9, 54.6, 34.9, 31.7, 22.8, 21.0, 20.7, 20.3, 18.4, 14.4, 14.3. HRMS-ESI$^+$-TOF (m/z): $[m+Na]^+$ calc'd. for $C_{26}H_{33}BrN_4Pd$: 609.0816; found 609.0813.

PdBr(iPr$_2$-bimy)(3g)] (4g)

Following GP2, **3g** was reacted with **2** to give an orange solid, 54% yield. R_f = 0.51 (20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.37 (s, 1H), 7.8 – 7.76 (m, 1H), 7.53 – 7.44 (m, 2H), 7.44 – 7.39 (m, 3H), 7.30 – 7.26 (m, 1H), 7.17 – 7.07 (m, 2H), 6.56 (7et, 1H, *J* = 7.1 Hz), 5.06 (7et, 1H, *J* = 7.0 Hz), 3.07 (s, 3H), 2.57 – 2.50 (m, 2H), 2.49 (s, 3H), 2.35 (q, 2H, *J* = 7.6 Hz), 1.81 (d, 3H, *J* = 7.1 Hz), 1.73 (d, 3H, *J* = 7.1 Hz), 1.52 (s, 3H), 1.48 (d, 3H, *J* = 7.0 Hz), 1.36 (d, 3H, *J* = 7.0 Hz), 1.19 (s, 3H), 1.14 (t, 3H, *J* = 7.5 Hz), 1.02 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 167.8, **164.0**, 146.1, 144.3, 142.7, 140.0, 139.3, 138.1, 134.5, 133.7, 133.5, 131.9, 131.5, 129.9, 128.8, 128.2, 128.0, 127.2, 122.0, 121.9, 112.6, 54.3, 54.0, 20.80, 20.76, 20.6, 20.3, 18.53. 18.47, 18.3, 15.6, 14.6, 13.0, 12.5, 12.1. Carbene resonance assignment confirmed by 2D HMBC; correlations only to the isopropylic C-H were observed. HRMS-ESI$^+$-TOF (m/z): $[m+H]^+$ calc'd. for $C_{36}H_{45}BrN_4Pd$: 719.1935; found 719.1946.

PdBr(iPr$_2$-bimy)(3h)] (4h)

Following GP2, **3h·HBr** was reacted with **2** to give a brown-orange solid, 77% yield. R_f = 0.63 (2% methanol/dichloromethane). ^{1}H NMR ($CDCl_3$, 300 MHz @ 324K) δ: 7.61 – 7.49 (m, 2H), 7.37 (s, 1H), 7.26 – 7.19 (m, 2H, overlaps chloroform residual), 6.00 (br s, 2H), 2.92 (s, 3H), 2.59 – 2.52 (two overlapping s, 6H), 2.45 (s, 3H), 2.33 (s, 3H), 1.91 (s, 3H), 1.88 – 1.18 (br m, 12H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 194.9, 194.4, 167.7, **166.9**, 160.8, 147.2, 141.9, 137.3, 135.0, 133.3, 131.3, 128.4, 127.1, 122.9, 113.2, 54.6, 31.7, 31.5, 23.8, 21.4, 21.0, 20.5, 13.5, 13.3. Carbene resonance assignment confirmed by 2D HMBC; no correlations were observed for this resonance where the surrounding carbonyl and pyrrolic carbon resonances gave distinct correlations. HRMS-ESI$^+$-TOF (m/z): $[m+Na]^+$ calc'd. for $C_{30}H_{37}BrN_4O_2Pd$: 693.1027; found 693.1017.

PdBr(iPr$_2$-bimy)(3i)] (4i)

Following GP2, **3i·HBr** was reacted with **2** to give an orange solid, 70% yield. R_f = 0.28 (20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz @ 324 K) δ: 7.61 – 7.50 (m, 2H), 7.34 (s, 1H), 7.26 – 7.17 (m, 2H), 6.01 (br s, 2H), 4.29 (q, 2H, *J* = 7.1 Hz), 4.18 (q, 2H, *J* = 7.1 Hz), 2.91 (s, 3H), 2.6 – 2.49 (two overlapping s, 6H), 1.89 (s, 3H), 1.85 – 1.39 (br m, 12H), 1.35 (t, 3H, *J* = 7.1 Hz), 1.26 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 168.0, **167.4**, 165.0, 164.9, 160.6, 149.5, 144.4, 136.9, 134.6, 133.3, 126.9, 122.8, 121.9, 118.4, 113.2, 59.7, 59.6, 54.6, 23.0, 21.2, 20.4, 20.1, 14.6, 14.5, 12.7, 12.5. Carbene resonance assignment confirmed by 2D HMBC; no correlations observed for this resonance where the surrounding carbonyl, ester and pyrrolic carbon resonances gave distinct correlations. HRMS-ESI$^+$-TOF (m/z): $[m+H]^+$ calc'd. for $C_{32}H_{41}BrN_4O_4Pd$: 753.1238; found 753.1265.

PdBr(iPr$_2$-bimy)(3j)] (4j)

Following GP2, **3j** was reacted with **2** to give a yellow solid, 28% yield. R_f = 0.44 (20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.72 (s, 1H), 7.72 – 7.65 (m, 2H), 7.50 – 7.37 (m, 5H), 7.34 – 7.28 (m, 2H), 6.62 (dd, 1H, *J* = 4.5 and 1.0 Hz), 6.47 – 6.34 (m, 4H, two overlapping signals), 6.12 (s, 1H), 6.06 (dd, 1H, *J* = 4.4 and 1.6 Hz), 1.81 (d, 6H, *J* = 7 Hz), 1.65 (d, 6H, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **171.9**, 155.1, 148.9, 147.7, 138.7, 136.2, 134.8, 133.6, 133.2, 130.6, 129.3, 128.5, 127.3, 122.9, 119.2, 115.3, 113.2, 54.7, 20.9, 20.8. HRMS-APCI-TOF (m/z): $[m+H]^+$ calc'd. for $C_{28}H_{29}BrN_4Pd$: 607.0683; found 607.0674.

PdBr(iPr$_2$-bimy)(3k**)] (4k)**

Following GP2, **3k** was reacted with **2** to give a yellow-orange solid, 28% yield. R_f = 0.63 (2% methanol/dichloromethane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.71 (s, 1H), 7.71 – 7.65 (m, 2H), 7.37 – 7.28 (m, 4H, two overlapping signals), 6.90 – 6.84 (m, 2H), 6.67 (d, 1H, *J* = 4.25 Hz), 6.50 (d, 1H, *J* = 4.1 Hz), 6.44 (d, 1H, *J* = 4.25 Hz), 6.39 (7et, 2H, *J* = 7 Hz), 6.11 (s, 1H), 6.08 – 6.04 (m, 1H), 1.80 (d, 6H, *J* = 7 Hz), 1.64 (d, 6H, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **172.0**, 156.1, 154.9, 148.8, 147.6, 136.4, 135.1, 133.6, 133.1, 132.3, 131.4, 129.2, 122.9, 119.1, 115.2, 114.3, 113.2, 54.6, 20.9, 20.8. HRMS-ESI$^+$-TOF (m/z): $[m+Na]^+$ calc'd. for $C_{28}H_{29}BrN_4OPd$: 645.0452; found 645.0438.

PdBr(iPr$_2$-bimy)(3l**)] (4l)**

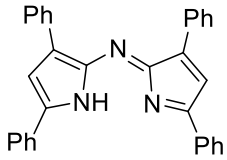
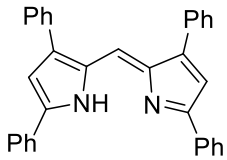
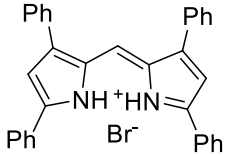
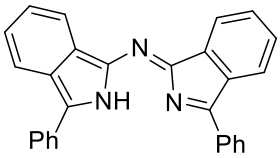
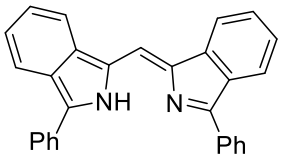
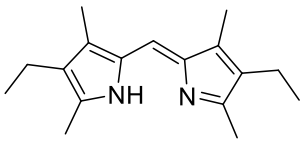
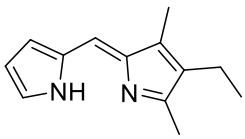
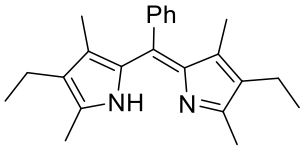
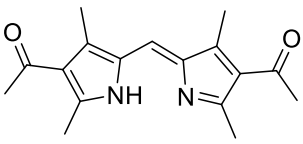
Aza-dipyrrin **3l** (23 mg) was combined with **2** (20 mg) in dichloromethane (3 mL), and DIPEA (8 uL) was added. The reaction mixture was stirred overnight at room temperature. Celite was added to adsorb the crude mixture and volatiles were removed in vacuo; the dry Celite was loaded directly onto a silica chromatography column and purified using a gradient of ethyl acetate/hexanes (0 to 25% ethyl acetate) to give a red-blue solid, 43% yield. R_f = 0.43 (20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.47 (d, 2H, *J* = 7.2 Hz), 7.58 – 7.36 (m, 7H), 7.13 – 7.01 (m, 5H), 6.86 (s, 1H), 6.84 – 6.64 (m, 4H), 6.40 (s, 1H), 5.95 (app br s, 1H), 5.48 (app br s, 1H), 2.40 – 2.20 (m, 12H), 1.99 – 1.80 (m, 6H), 1.79 – 1.43 (m, 12H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **167.8**, 167.1, 160.9, 147.8, 147.5, 145.7, 143.5, 137.2, 136.9, 136.4, 136.3, 135.9, 132.1, 131.2, 129.9, 129.7, 128.6, 128.0, 127.7, 127.63, 127.61, 123.4, 122.1, 121.6, 112.6, 54.7, 54.2, 22.4 – 21.3 (several overlapping signals), 21.18, 21.15. Carbene resonance assignment confirmed by 2D HMBC; no correlations were observed for this resonance, while the correlations for the adjacent resonance suggest it originates from an internal pyrrolic α-carbon. HRMS-ESI$^+$-TOF (m/z): $[m+H]^+$ calc'd. for $C_{51}H_{52}BrN_5Pd$: 920.2514; found 920.2508.

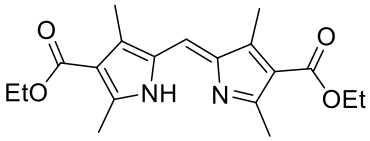
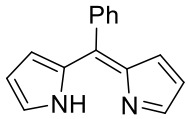
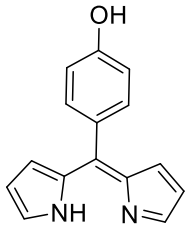
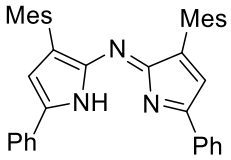
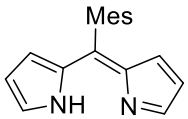
PdBr(iPr$_2$-bimy)(3m**)] (4m)**

Following GP2, **3m** was reacted with **2** to give a yellow-orange solid, 33% yield. R_f = 0.73 (20% EtOAc/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.64 (s, 1H), 7.75 – 7.63 (m, 2H), 7.35 – 7.28 (m, 2H), 6.90 (s, 2H), 6.51 (app d, 1H), 6.46 – 6.35 (m, 3H, two overlapping signals), 6.31 (app d, 1H), 6.06 (app s, 1H), 5.99 (app d, 1H), 2.35 (s, 3H), 2.10 (s, 6H), 1.80 (d, 6H, *J* = 7.0 Hz), 1.64 (d, 6H, *J* = 7.0 Hz).). ^{13}C NMR ($CDCl_3$, 126 MHz) δ: **172.1**, 154.6, 148.2, 147.2, 137.3, 136.7, 135.9, 135.2, 134.2, 133.6, 131.6, 127.7, 127.3, 122.9, 119.4, 115.2, 113.1, 54.6, 21.3, 20.92, 20.89, 20.1. HRMS-APCI (m/z): $[M+H]^+$ calc'd for $C_{31}H_{36}BrN_4Pd$: 649.1153; found 649.1173.

Photophysical Data

Table S1. Photophysical properties of free ligands **3a-m** in chloroform.

Compound		λ_{abs} (nm)	ε (logE)
	**3a**	597	4.21
	**3b**	531	4.61
	**3b·HBr**	563	5.02
	**3c**	653	4.28
	**3d**	592	4.50
	**3e**	449 481 (sh)	4.49 -
	**3f**	396	4.36
	**3g**	462	4.39
	**3h**	460	4.71

	**3i**	455	4.63
	**3j**	435 312	3.93 3.45
	**3k**[a]	432 370 (sh)	4.07 -
	**3l**	575 550 (sh)	4.53 -
	**3m**	432[b] 465 (sh) 484 (sh)	4.32 - -

[a] Data collected in DMSO, as this dipyrrin is insoluble in chloroform.

[b] This dipyrrin was observed to fluoresce at 494 nm.

Crystallographic Information

[PdBr(iPr$_2$-bimy)(3a)] (4a)

The crystal chosen was attached to the tip of a 300 µm MicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K.[11] The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 10 second frames and 366 frames per series at varying ϕ angles (ϕ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT[12] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS[13]). The structure was solved using SHELXT-2014[14] and was refined using a full-matrix least-squares method on F^2 with SHELXL-2018.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2U_{eq} of the parent carbon atom or 1.5U_{eq} for methyl hydrogens.

The structure was found to be solvated, with one molecule of dichloromethane (CH_2Cl_2) in the asymmetric unit. The solvent was not disordered and refined nicely.

All diagrams were prepared using the program Mercury CSD 3.10.[15] The data has been deposited with the Cambridge Crystallographic Data Centre under deposition number 1898705.

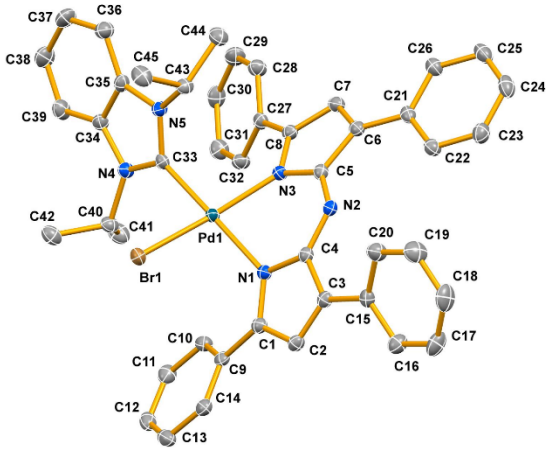


Figure S1. ORTEP Diagram of **4a.** Thermal ellipsoids are shown at 50% probability, and hydrogen atoms are omitted for clarity.

Table S2. Selected bond lengths and angles around palladium of **4a**.

Bond	Length (Å)	Entry	Angle (°)
N1 – Pd1	2.0517(16)	N1 – Pd1 – N3	85.41(6)
N3 – Pd1	2.0494(17)	N1 – Pd1 – Br1	91.39(5)
Br1 – Pd1	2.4366(3)	Br1 – Pd1 – C33	88.72(6)
C33 – Pd1	1.979(2)	C33 – Pd1 – N3	94.86(7)
		Br1 – Pd1 – N3	164.35(5)
		C33 – Pd1 – N1	178.56(7)

[PdBr(iPr$_2$-bimy)(3k)] (4k)

The crystal chosen was attached to the tip of a 300 µm MicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K.[11] The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 30 second frames and 366 frames per series at varying ϕ angles (ϕ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT[12] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS[13]). The structure was solved using SHELXT-2014[14] and was refined using a full-matrix least-squares method on F^2 with SHELXL-2018.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2U_{eq} of the parent carbon atom or 1.5U_{eq} for methyl hydrogens. The hydrogen bonded to oxygen was located in the Fourier difference map. It was allowed to refine with the bond length restrained to 0.85 (0.02) Å and with U_{iso} = 1.5 U_{eq} of oxygen.

The structure was found to be solvated, with 1.5 molecules of chloroform ($CHCl_3$) and one molecule of $C_{28}H_{29}BrN_4OPd$ in the asymmetric unit. The solvent molecules were disordered and had to be restrained during refinement. The C-Cl bond lengths were restrained to a reasonable distance and the thermal parameters of the chlorine atoms were restrained to be similar to the others in each molecule. The second (half) solvate molecule was found to be disordered across a center of symmetry and had to be restrained a bit more rigorously than the first molecule.

All diagrams were prepared using the program Mercury CSD 3.10.[15] The data has been deposited with the Cambridge Crystallographic Data Centre under deposition number 1898706.

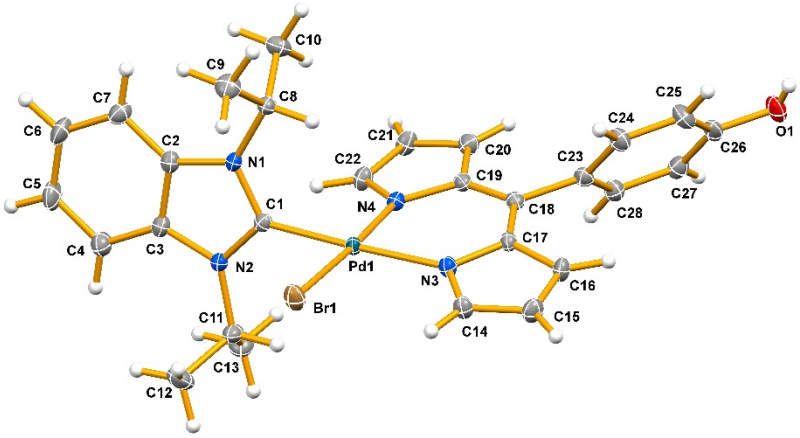


Figure S2. ORTEP Diagram of **4k.** Thermal ellipsoids are shown at 50% probability.

Table S3. Selected bond lengths and angles around palladium of **4k**.

Bond	Length (Å)	Entry	Angle (°)
N3 – Pd1	2.064(2)	N3 – Pd1 – N4	89.34(8)
N4 – Pd1	2.023(2)	N3 – Pd1 – Br1	94.60(6)
Br1 – Pd1	2.4332(5)	Br1 – Pd1 – C1	85.12(7)
C1 – Pd1	1.976(2)	C1 – Pd1 – N4	90.94(9)
		Br1 – Pd1 – N4	176.05(6)
		C1 – Pd1 – N3	177.36(9)

[PdBr(iPr$_2$-bimy)(3h)] (4h)

The crystal chosen was attached to the tip of a 300 µm MicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K.[11] The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 30 second frames and 366 frames per series at varying ϕ angles (ϕ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT[12] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS[13]). The structure was solved using SHELXT-2014[14] and was refined using a full-matrix least-squares method on F^2 with SHELXL-2018[14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2U_{eq} of the parent carbon atom or 1.5U_{eq} for methyl hydrogens. The refinement was uneventful and there was one complete molecule (with no solvent) in the asymmetric unit.

There were two distinctly different looking types of crystals present in this sample after recrystallization. The majority of the crystals were large, dark red-orange, plates that were roughly square in shape. A crystal of this type was used in this data collection.

All diagrams were prepared using the program Mercury CSD 3.10.[15] The data has been deposited with the Cambridge Crystallographic Data Centre under deposition number 1898708.

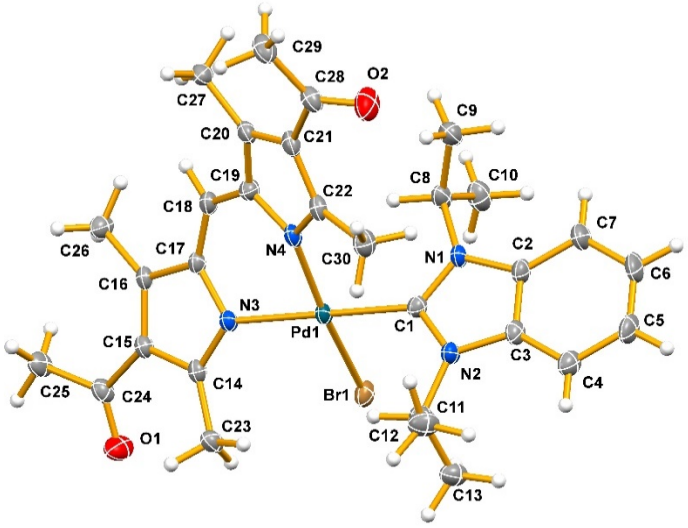
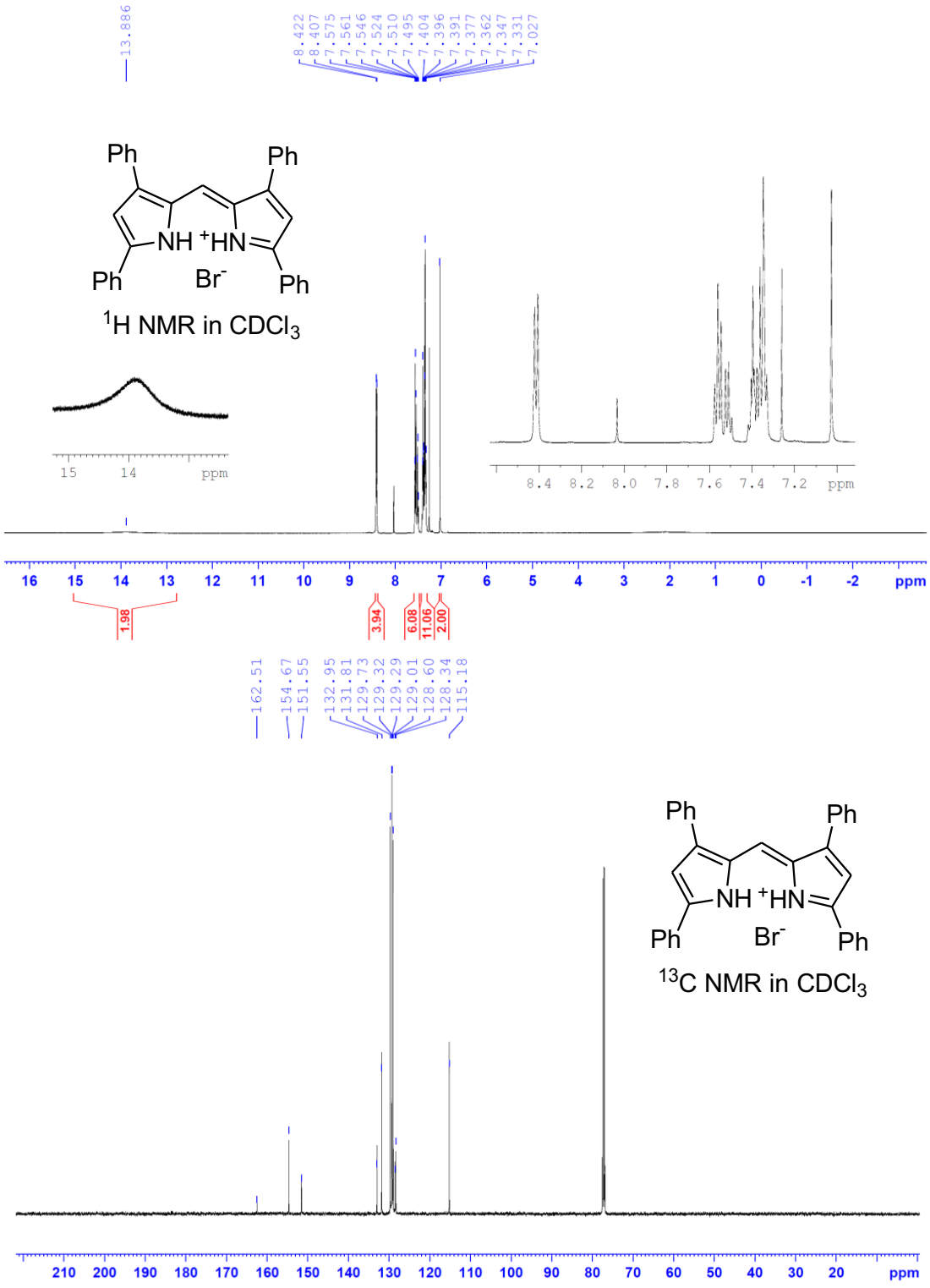


Figure S3. ORTEP Diagram of **4h.** Thermal ellipsoids are shown at 50% probability.

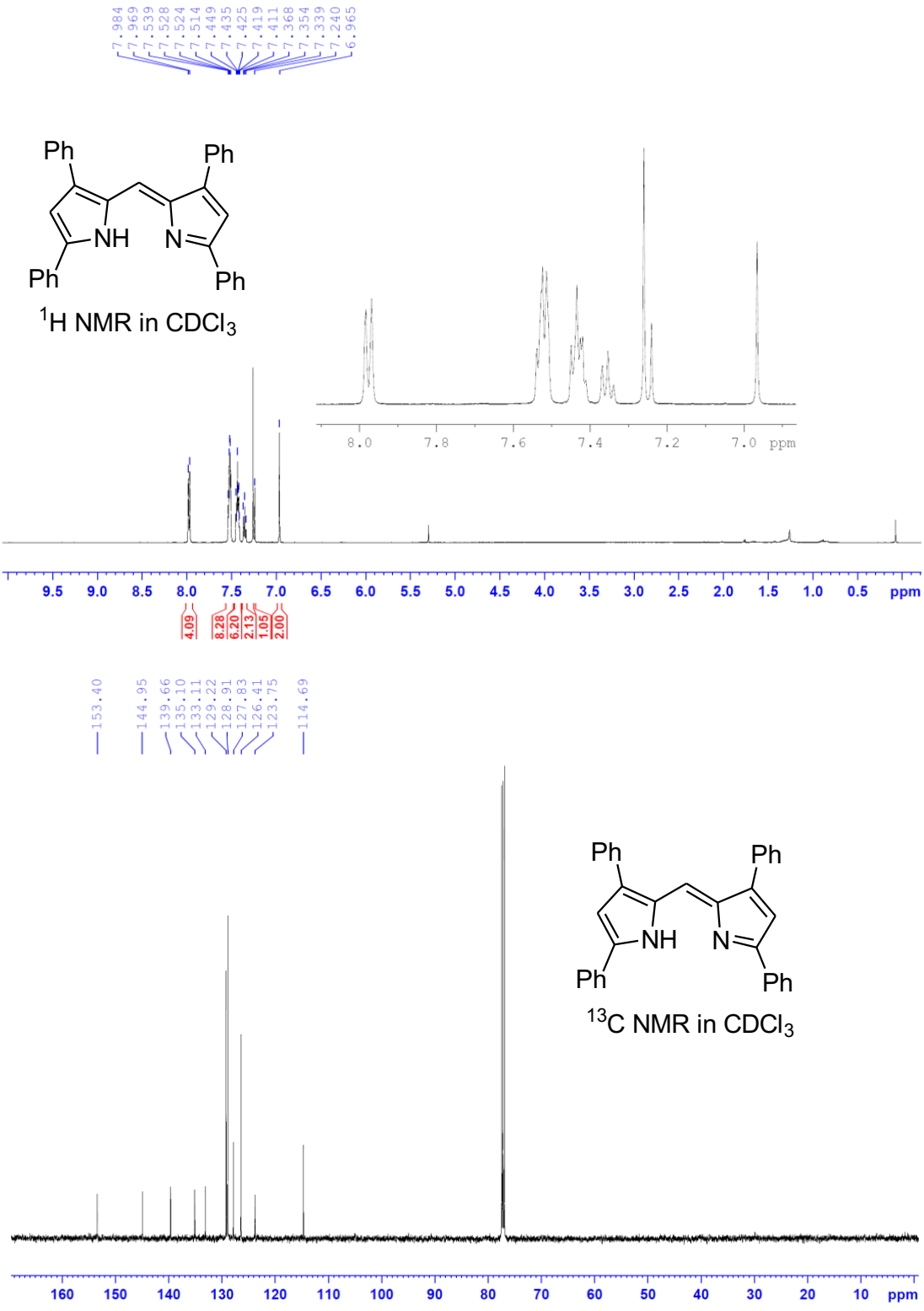
Table S4. Selected bond lengths and angles around palladium of **4h**.

Bond	Length (Å)	Entry	Angle (°)
N3 – Pd1	2.078(2)	N3 – Pd1 – N4	88.29(10)
N4 – Pd1	2.046(3)	N3 – Pd1 – Br1	91.60(7)
Br1 – Pd1	2.4306(5)	Br1 – Pd1 – C1	85.92(9)
C1 – Pd1	1.989(3)	C1 – Pd1 – N4	93.76(11)
		Br1 – Pd1 – N4	170.68(8)
		C1 – Pd1 – N3	176.47(12)

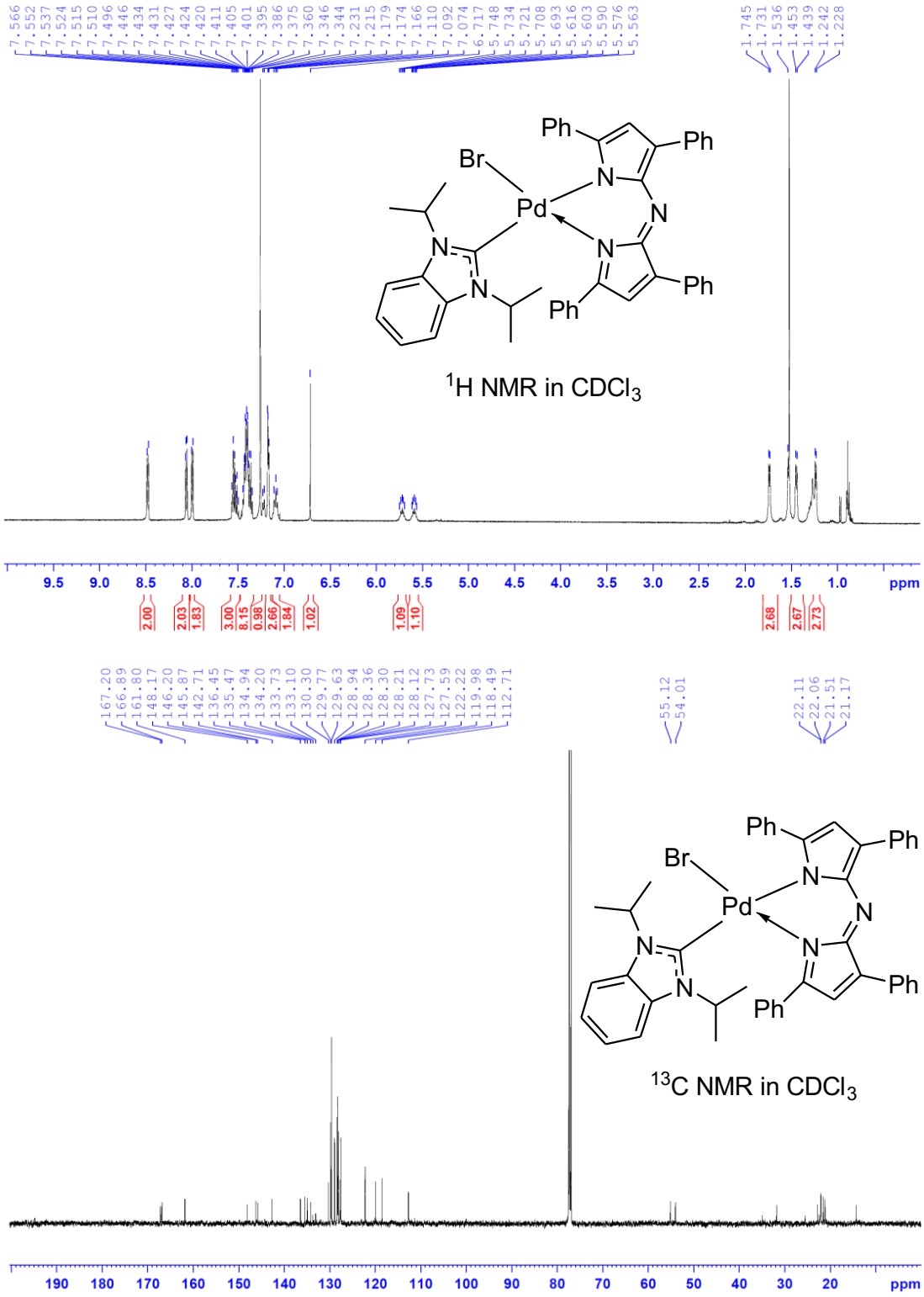
(*Z*)-2-((3,5-Diphenyl-1*H*-pyrrol-2-yl)methylene)-3,5-diphenyl-2*H*-pyrrolium bromide (3b·HBr)



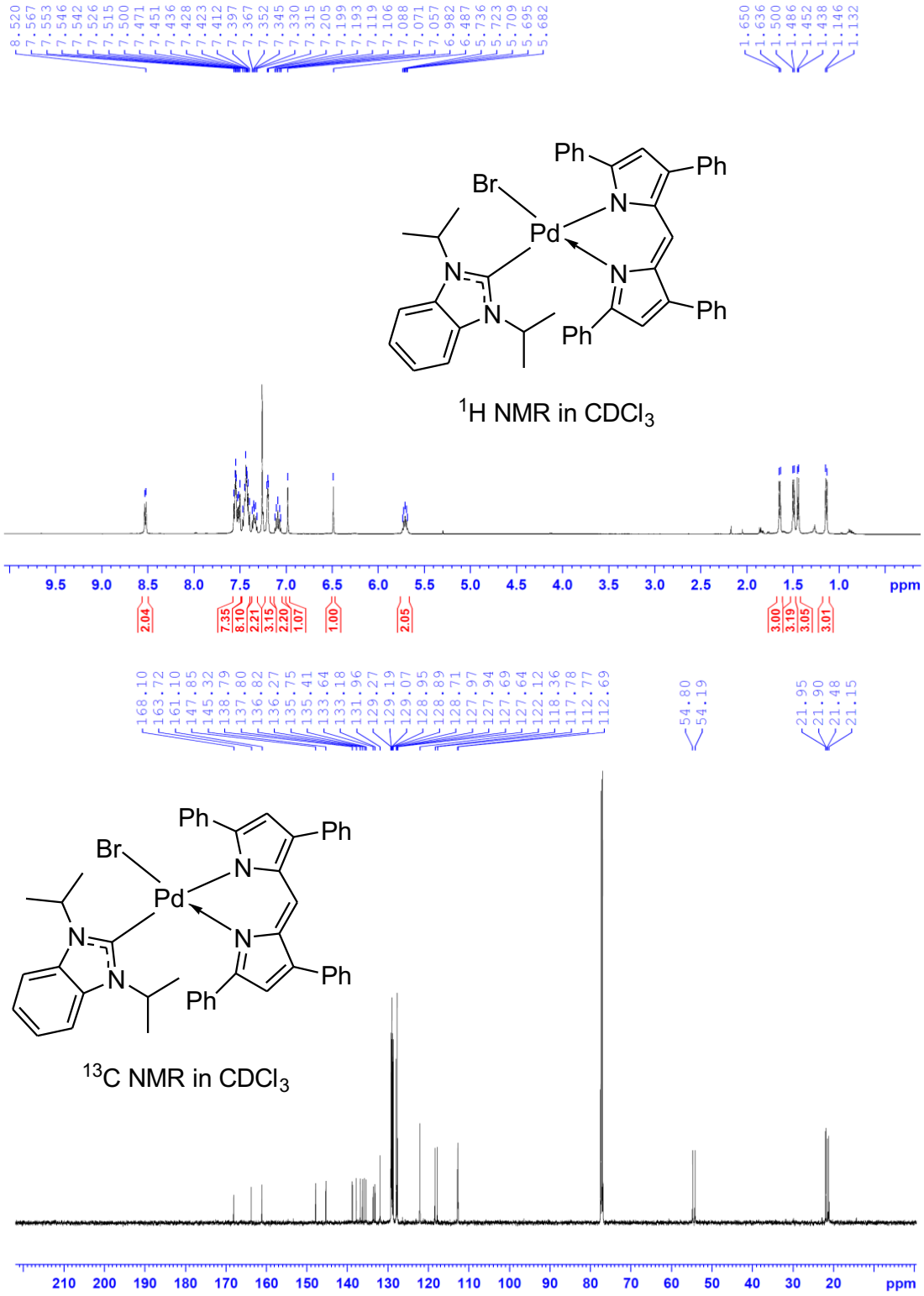
(*Z*)-2-((3,5-Diphenyl-2*H*-pyrrol-2-ylidene)methyl)-3,5-diphenyl-1*H*-pyrrole (3b)



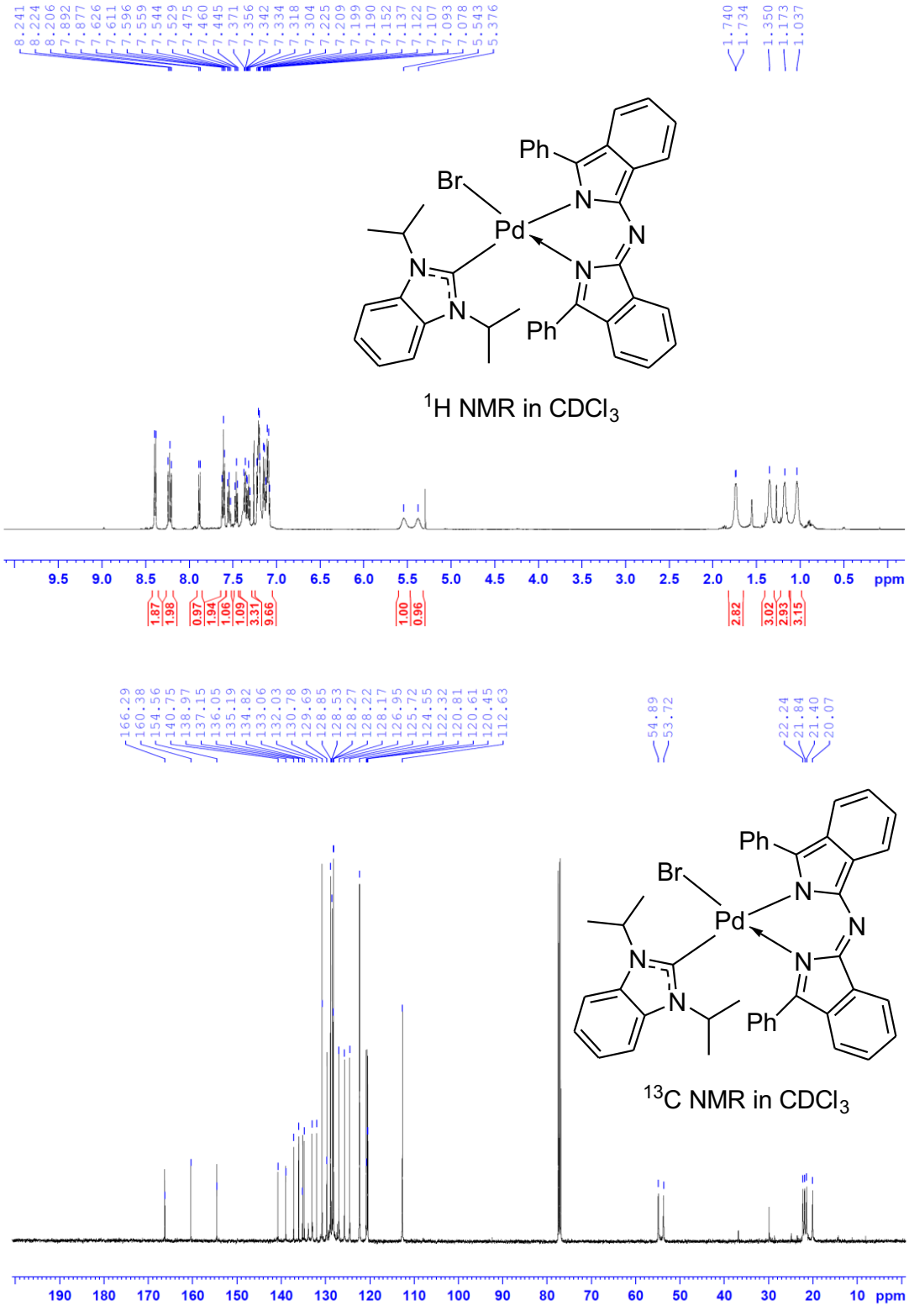
[PdBr(iPr$_2$-bimy)(3a)] (4a)



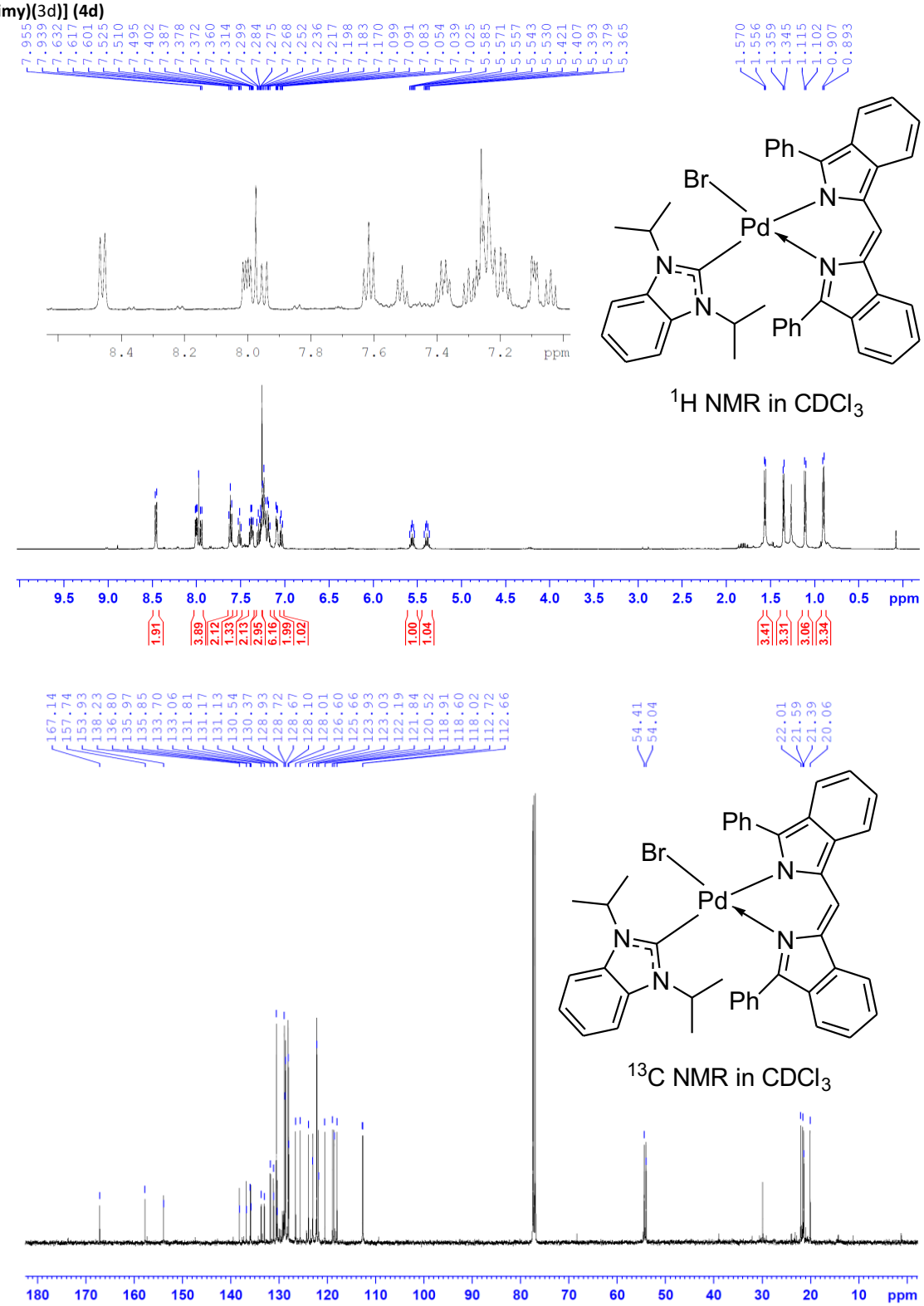
PdBr(iPr$_2$-bimy)(3b)] (4b)



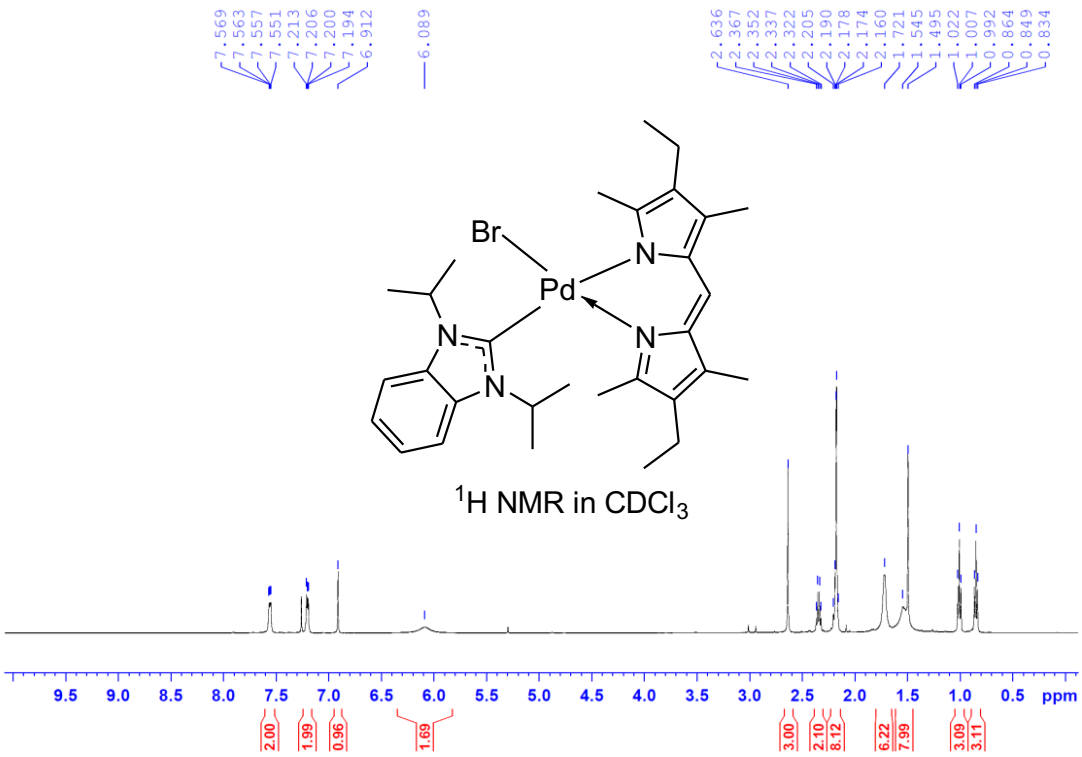
PdBr(iPr$_2$-bimy)(3c)] (4c)

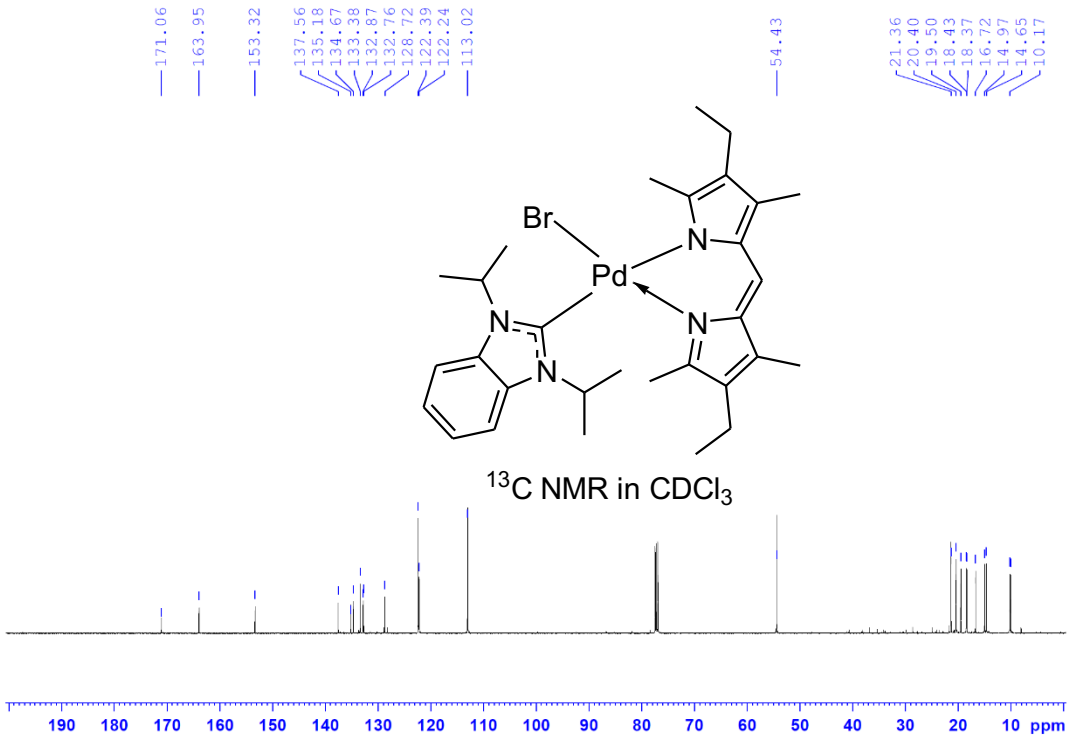


PdBr(iPr$_2$-bimy)(3d)] (4d)

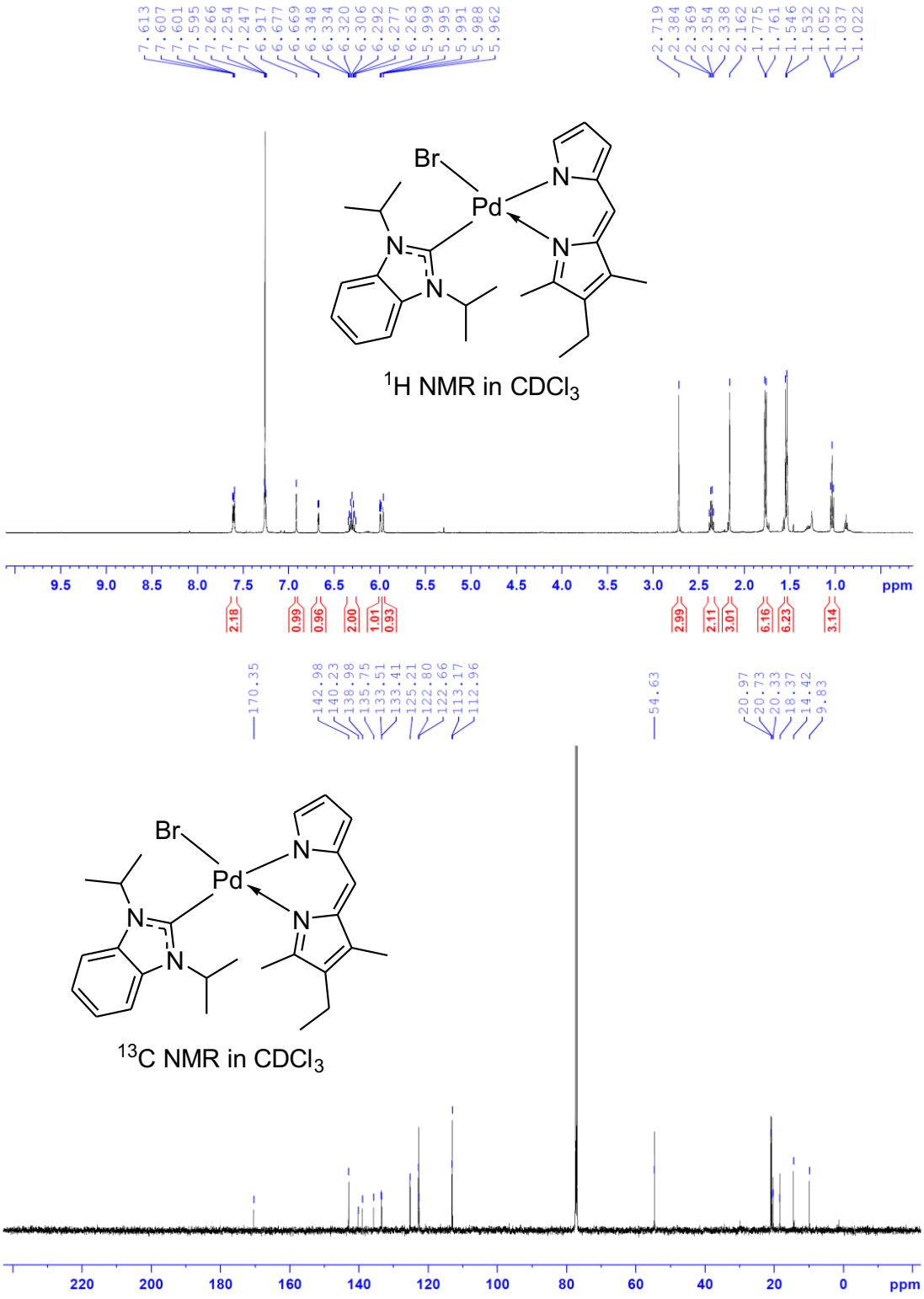


PdBr(iPr$_2$-bimy)(3e)] (4e)

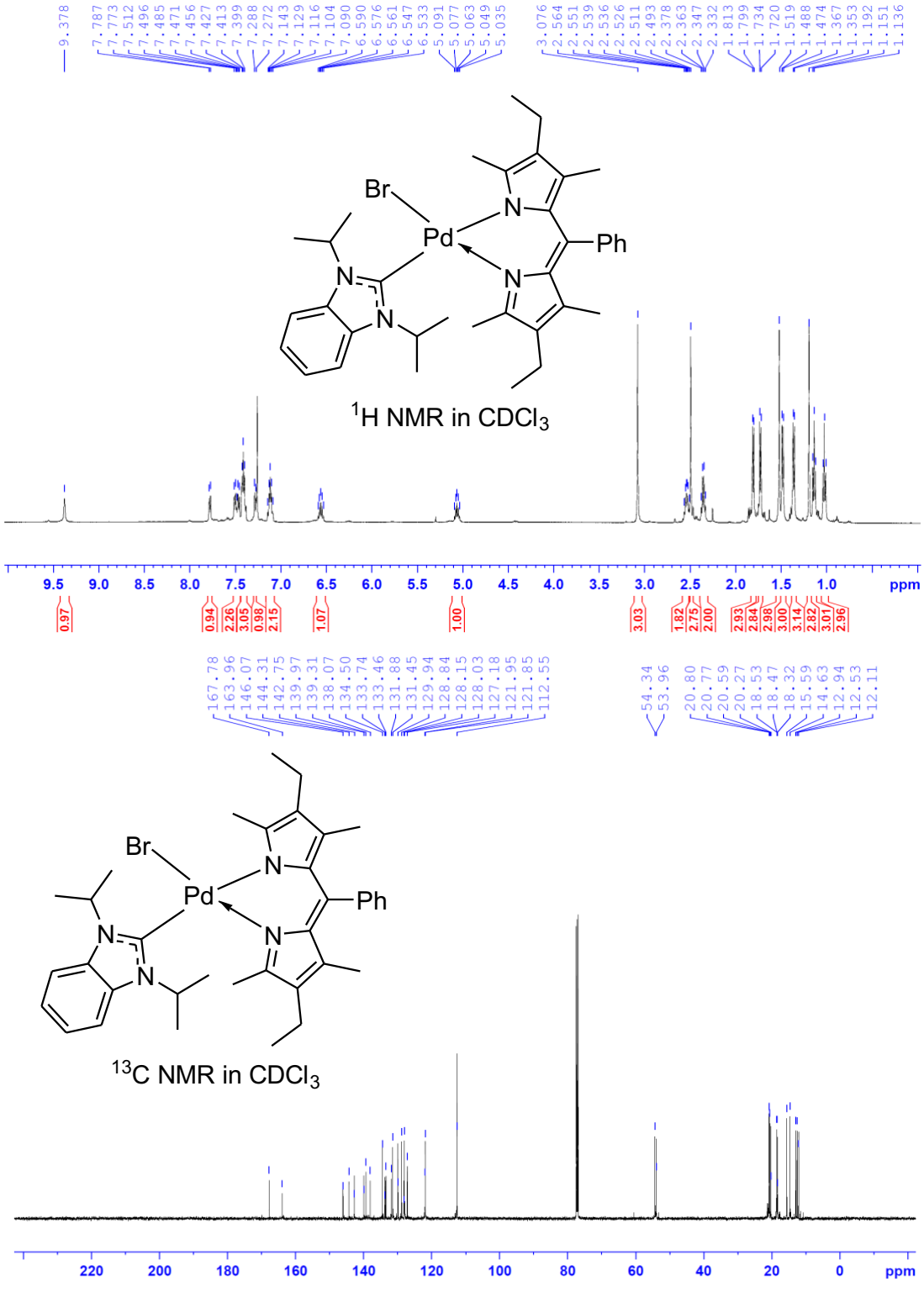




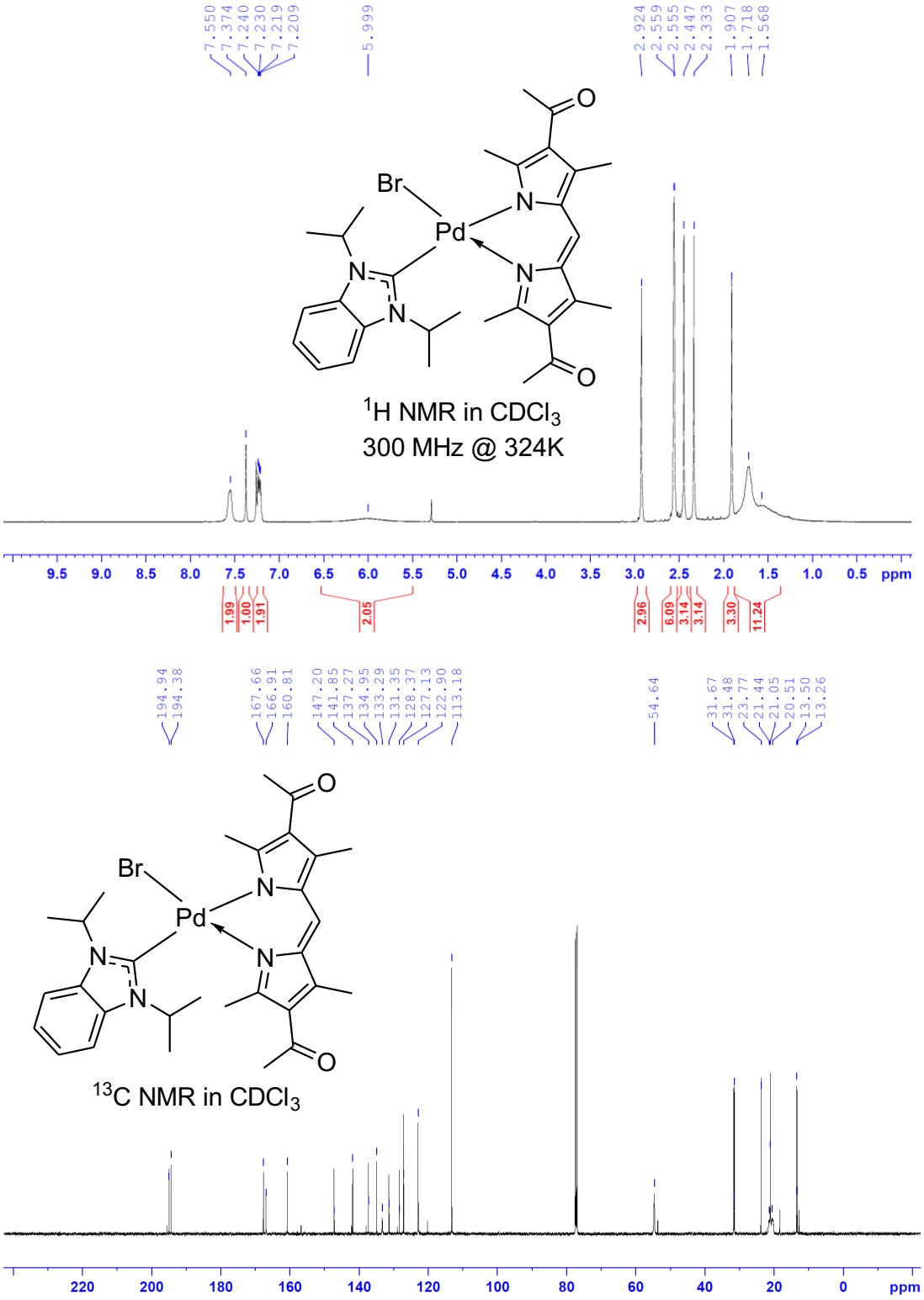
PdBr(iPr$_2$-bimy)(3f)] (4f)



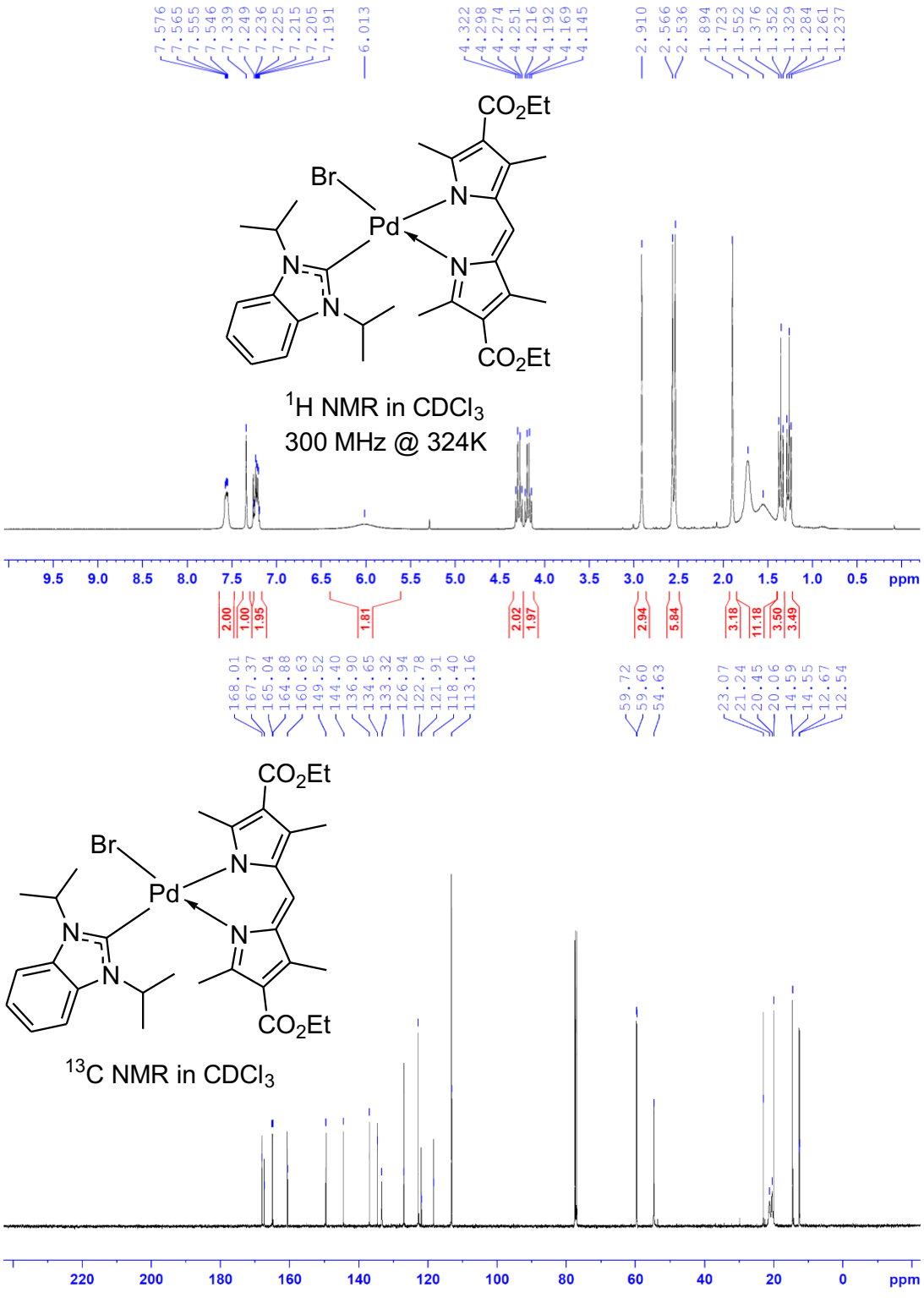
PdBr(iPr$_2$-bimy)(3g)] (4g)



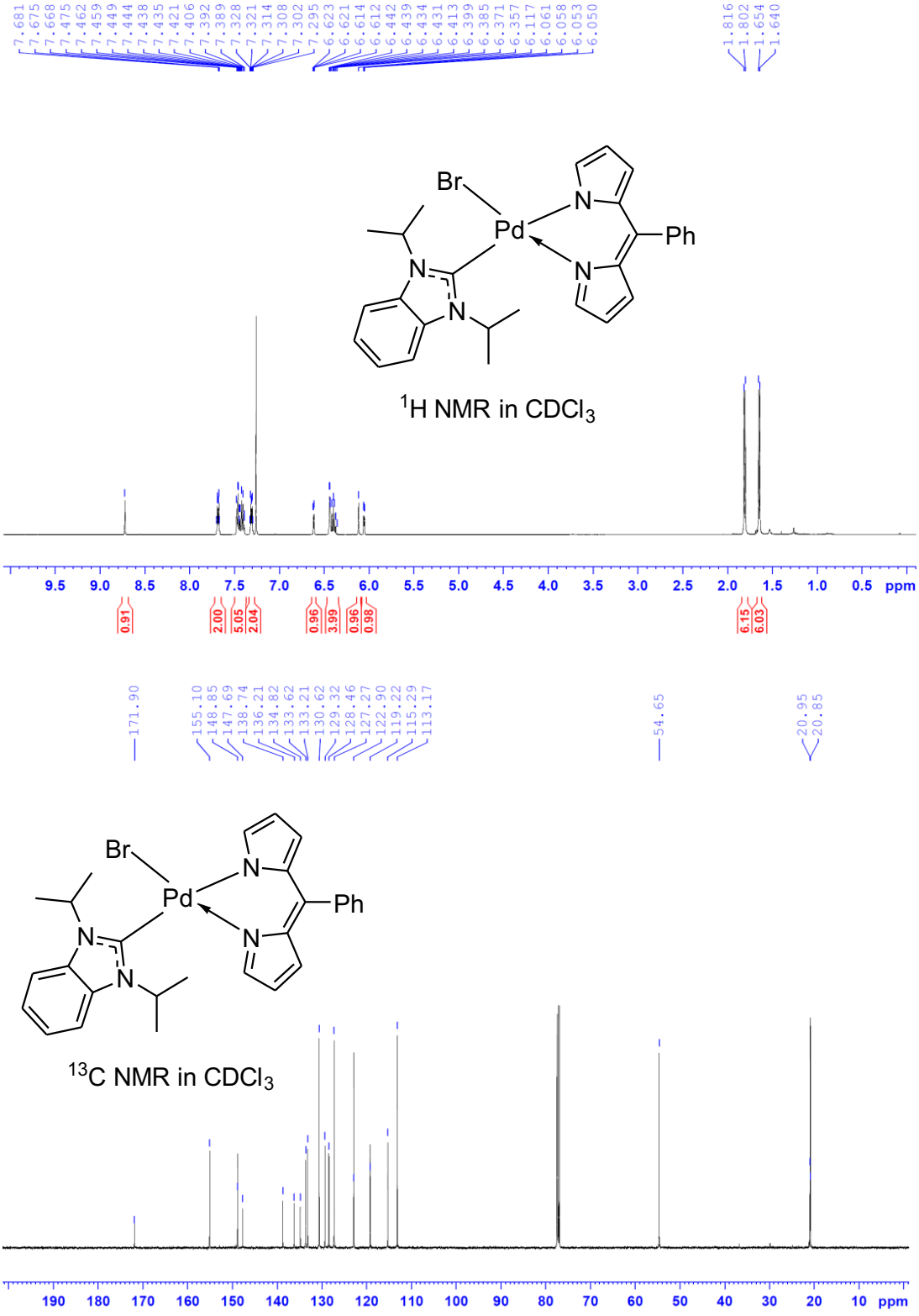
PdBr(iPr$_2$-bimy)(3h)] (4h)



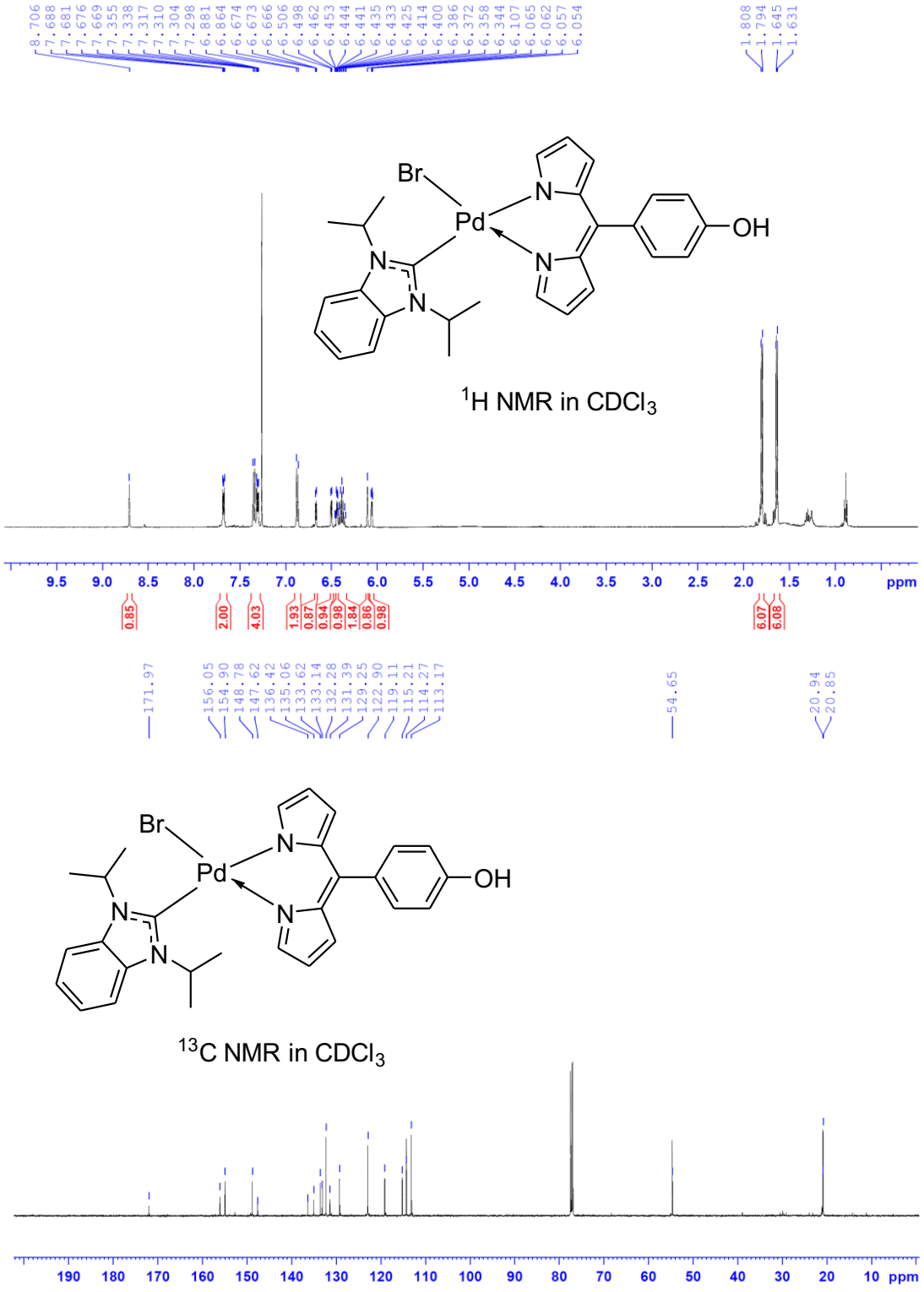
PdBr(iPr$_2$-bimy)(3i)] (4i)



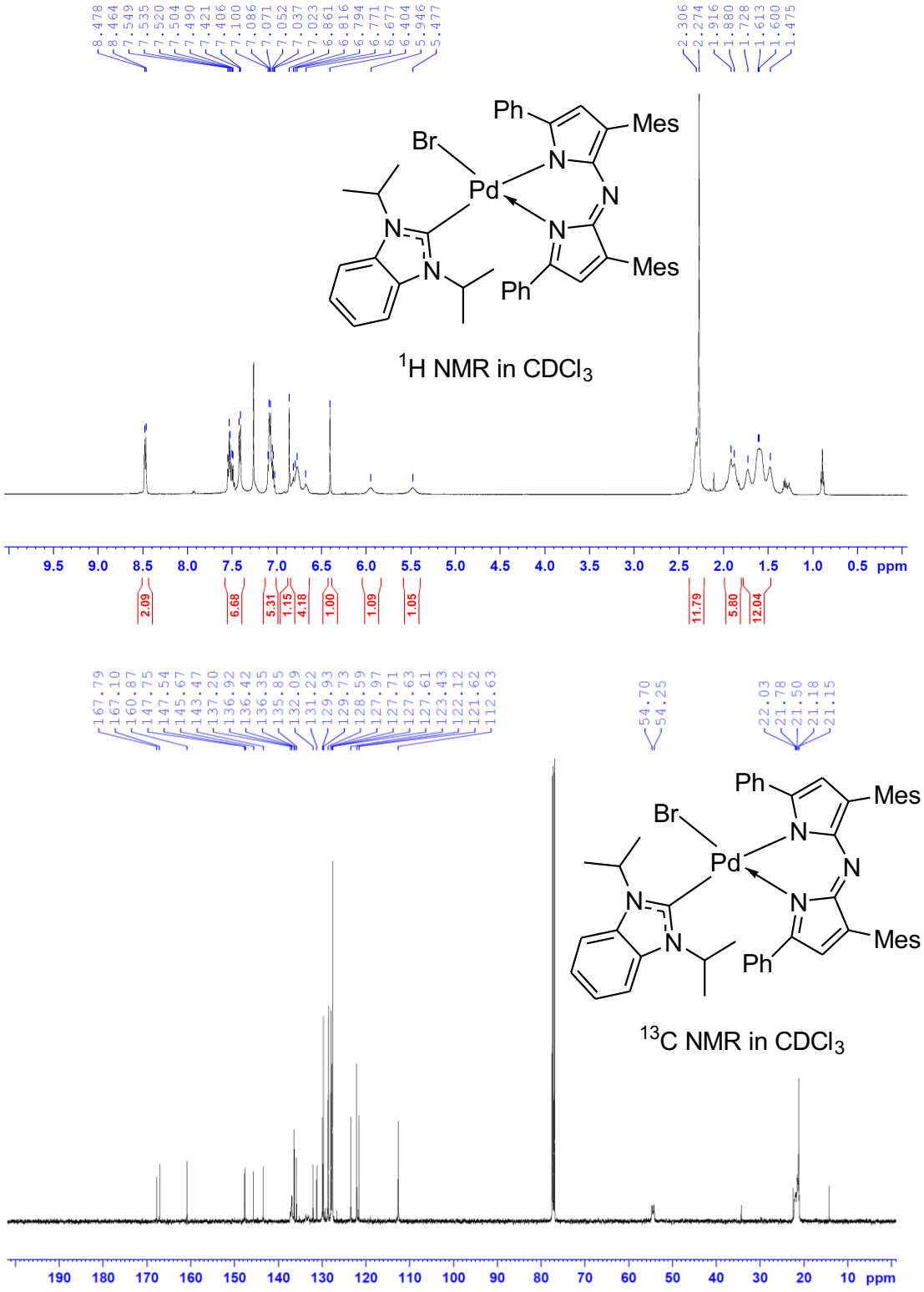
PdBr(iPr$_2$-bimy)(3j)] (4j)



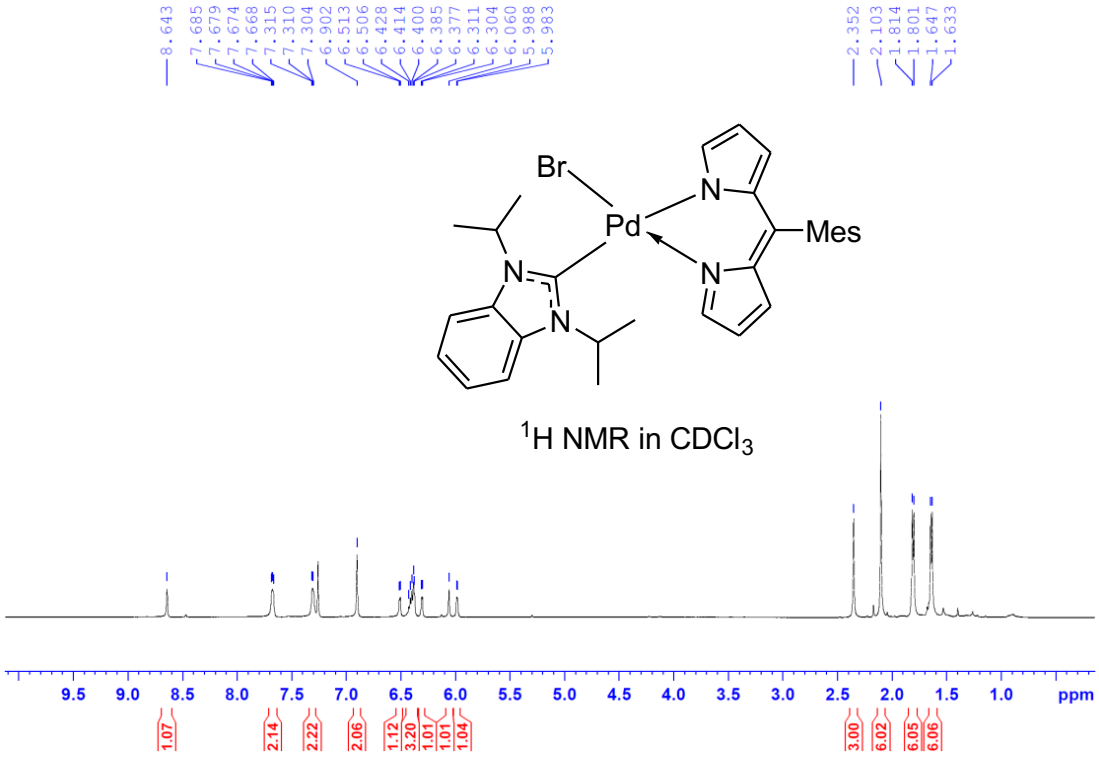
PdBr(iPr$_2$-bimy)(3k)] (4k)

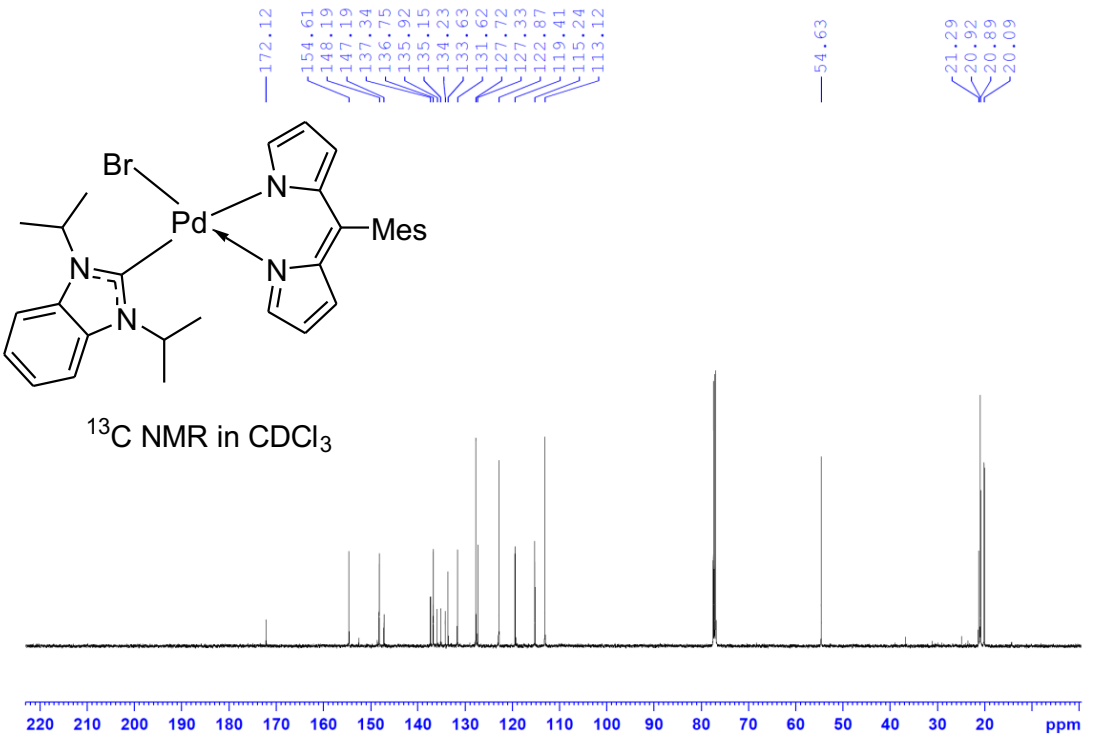


PdBr(iPr$_2$-bimy)(3I)] (4I)

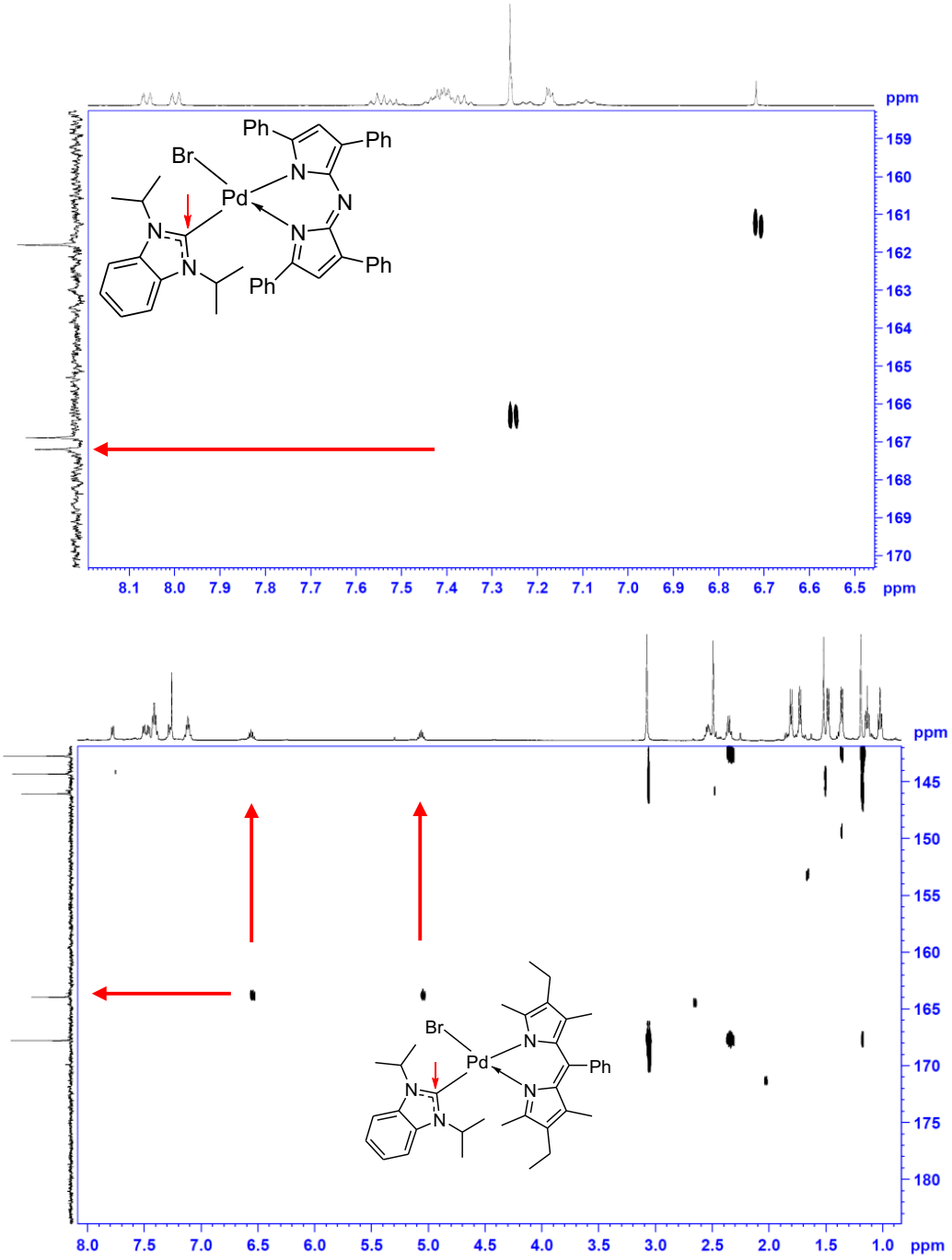


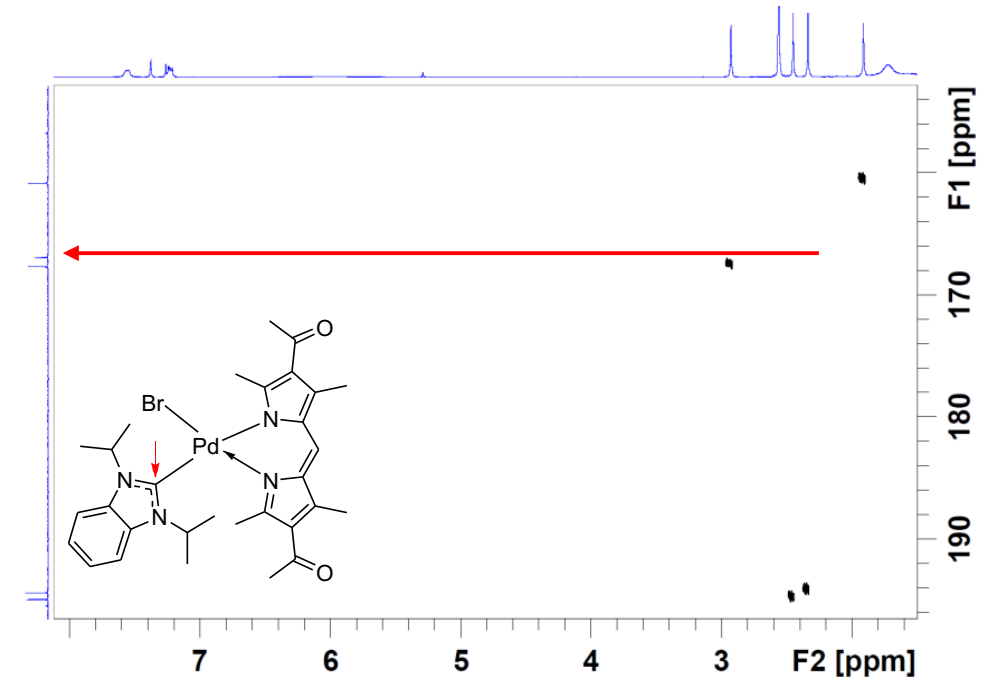
PdBr(iPr$_2$-bimy)(3m)] (4m)





HMBC spectra enabling characterization of complexes 4a,g,h,i,l

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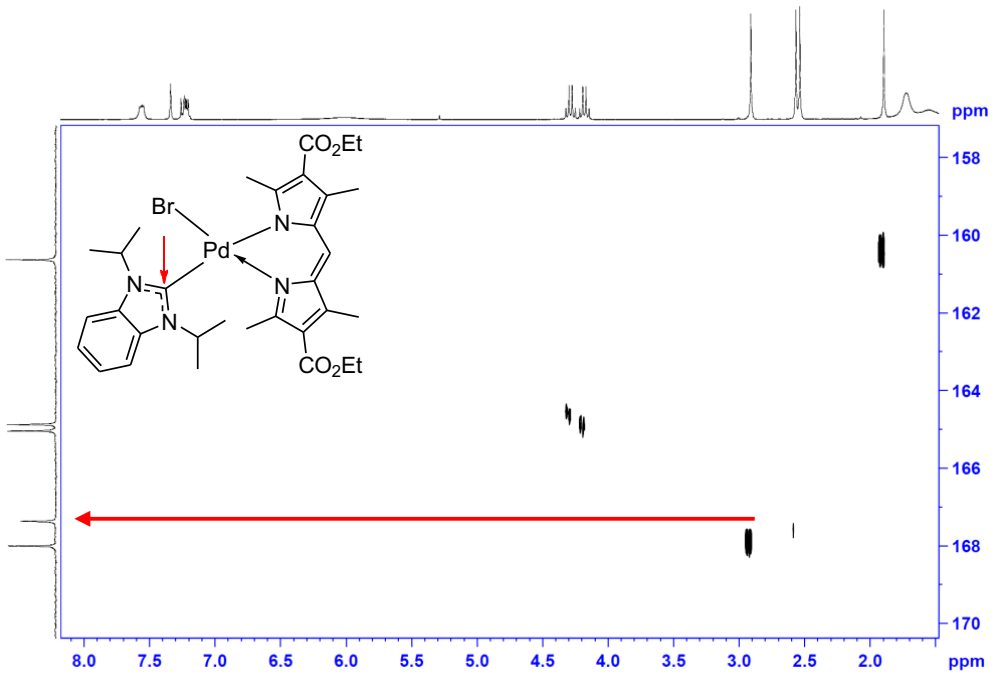
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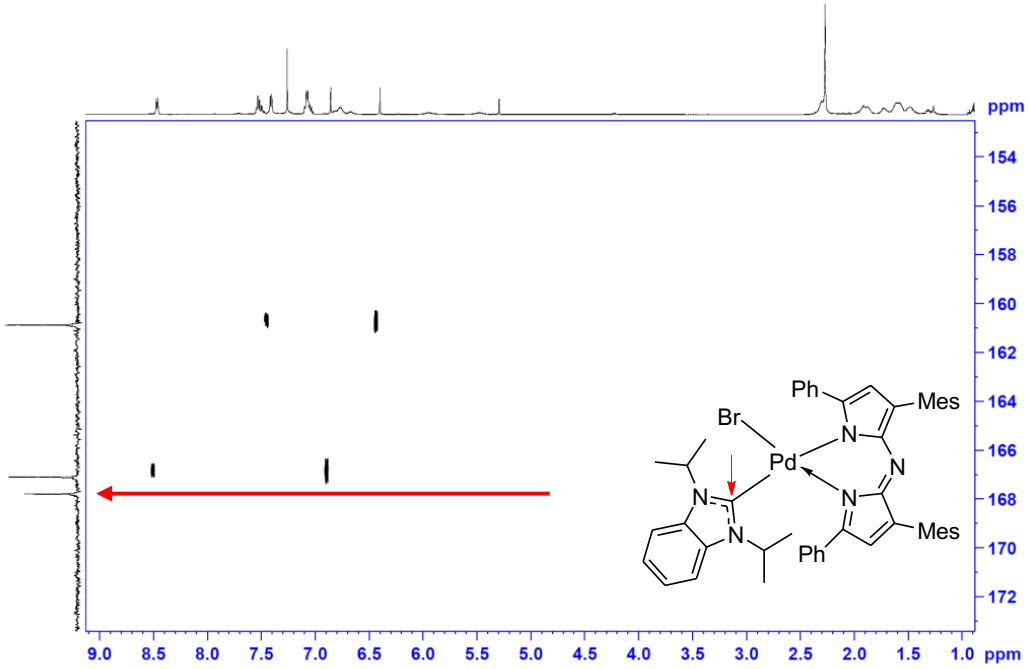

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[1] M. Piotto, M. Bourdonneau, K. Elbayed, J. M. Wieruszeski, G. Lippens, *Magn. Reson. Chem.* **2006**, *44*, 943–947.

[2] Q. Teng, H. V. Huynh, *Dalt. Trans.* **2017**, *46*, 614–627.

[3] X. Yan, R. Feng, C. Yan, P. Lei, S. Guo, H. V. Huynh, *Dalt. Trans.* **2018**, *47*, 7830–7838.

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