Hydroxyl-functionalized triazolylidene-based PEPPSI complexes: Metallacycle formation effect toward the Suzuki coupling reaction

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Supporting information

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Experimental section

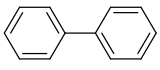
General methods

Commercially available reagents and solvents were used as received. Triazoliums **1a-c**,[1] and complexes **3-4**,[2] were synthesized as reported in the literature. IPr-Pd-PEPPSI complex 5 was purchased from Aldrich as used as received. Synthesis of all metal complexes was performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. IR spectra were recorded on a Bruker Alpha FT-IR/ATR spectrometer. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. NMR spectra were obtained with a Bruker Ascend (400 MHz) spectrometer. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin Elmer Series II CHNS/O 2400 instruments. X-Ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo Kα radiation (l = 0.71073 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELX 2014 and refined by full matrix least squares against F^2.[3] All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters. The crystallographic data and some details of the data collection and refinement are given in Table 1.

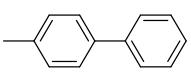
Catalytic trials

General procedure for the Suzuki-Miyarura coupling of aryl chlorides and boronic acids.

Sodium *tert*-butoxide (2 mmol) and boronic acid (1.3 mmol) were charged in a 10 mL screw capped vial equipped with a magnetic bar. The catalyst (1 mol%, based on metal) and 5 mL of anhydrous dioxane were added and the mixture was stirred for 15 minutes. The aryl chloride (1 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 2 hours and monitored by ^{1}H NMR spectroscopy. Water was added to the reaction mixture, the organic layer was extracted with ethyl acetate, dried with magnesium sulfate, and the solvent was evaporated under vacuum. When necessary the product was purified by column chromatography on silica gel using a proper mixture of ethyl acetate/hexanes as eluent.

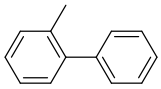


Biphenyl (Table 2, entry 1): The general procedure afforded the title compound in 99% (152 mg, off white solid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent (R_f = 0.78). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.62-7.64 (dd, *J* = 7.8 Hz, 4H, Ar*H*), 7.46-7.49 (t, *J* = 7.8 Hz, 4H, Ar*H*), 7.37-7.39 (t, *J* = 7.8 Hz, 2H, Ar*H*). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 141.4, 128.9, 127.4, 127.3. Spectroscopy data is consistent with the literature.[4]

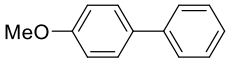


4-Methylbiphenyl (Table 2, entry 2): The general procedure afforded the title compound in 95% (160 mg, off white solid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent (R_f = 0.69). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.69-7.70 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.60-7.62 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.52-7.54 (t,

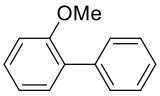
J = 7.8 Hz, 2H, Ar*H*), 7.42-7.44 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.35-7.36 (d, *J* = 7.8 Hz, 2H, Ar*H*), 2.50 (s, 3H, C*H*$_3$). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 141.3, 138.5, 137.1, 6 130.9, 129.6, 128.8, 127.2, 127.1, 21.2. Spectroscopy data is consistent with the literature.[4]



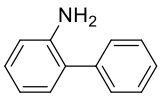
2-Methylbiphenyl (Table 2, entry 3): The general procedure afforded the title compound in 97% (163 mg, off white solid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eulent (R_f = 0.70). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.12-7.56 (m, 9H, Ar*H*), 2.38 (s, 3H, C*H*$_3$). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 21.6, 124.3, 127.2, 128.0, 128.0, 128.6, 128.7, 138.3, 141.4. Spectroscopy data is consistent with the literature.[5]



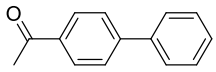
4-Methoxybiphenyl (Table 2, entry 4): The general procedure afforded the title compound in 99% (182 mg, white solid) isolated yield after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent (R_f = 0.54). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.55-7.28 (m, 7H, Ar*H*), 6.96 (d, 2H, *J* = 9.1 Hz, Ar*H*), 3.81 (s, 3H, OC*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 156.5, 138.5, 130.0, 130.8, 129.6, 128.6, 128.0, 126.9, 120.9, 111.3, 55.6. Spectroscopy data is consistent with the literature.[5]



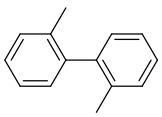
2-Methoxybiphenyl (Table 2, entry 5): The general procedure afforded the title compound in 93% (171 mg, white solid) isolated yield after column chromatography using a mixture of 85:15 ethyl acetate/hexane as eluent (R_f = 0.51). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.51 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.39 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.29 (t, *J* = 7.8 Hz, 3H, Ar*H*), 6.94-7.02 (m, 2H, ArH), 3.76 (s, 3H, OCH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 159.3, 140.9, 133.9, 128.8, 128.3, 126.8, 126.7, 114.3, 55.4. Spectroscopy data is consistent with the literature.[5]



2-Aminobiphenyl (Table 2, entry 6): The general procedure afforded the title compound in 89% (151 mg, white solid) isolated yield after column chromatography using a mixture of 30:70 ethyl acetate/hexane as eluent (R_f = 0.47). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.28-7.44 (m, 4H, Ar*H*), 6.62-7.21 (m, 5H, Ar*H*), 3.71-3.95 (m, 2H, N*H*$_2$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 115.7, 118.7, 127.2, 127.7, 128.5, 128.9, 129.1, 130.5, 139.6, 143.5. Spectroscopy data is consistent with the literature.[5]

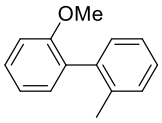


4-Acetylbiphenyl (Table 2, entry 7): The general procedure afforded the title compound in 96% (188 mg, white solid) isolated yield after column chromatography using a mixture of 25:72 ethyl acetate/hexane as eluent (R_f = 0.42). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.03 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.68-7.70 (m, 2H, Ar*H*), 7.62-7.64 (m, 2H, ArH), 7.45-7.49 (m, 2H, Ar*H*), 7.42 (t, *J* = 6.8 Hz, 1H, Ar*H*), 2.64 (s, 3H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 197.7, 145.8, 139.9, 135.9, 128.9, 128.2, 127.3, 26.6. Spectroscopy data is consistent with the literature.[6]

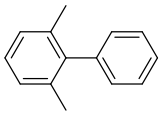


2,2-dimethyl-1,1´-biphenyl (Table 3, entry 1): The general procedure afforded the title compound in 96% (175 mg, colorless liquid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent (R_f = 0.74). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.19-7.26 (m, 6H, Ar*H*), 7.09 (d, *J* = 6.8 Hz, 2H,

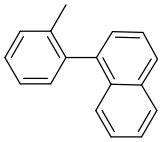
Ar*H*), 2.05 (s, 6H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 19.8, 125.5, 127.1, 129.3, 129.8, 135.8, 141.6. Spectroscopy data is consistent with the literature.[5]



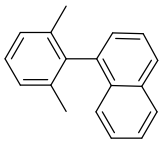
2-methoxy-2´-methyl-1,1´-biphenyl (Table 3, entry 2): The general procedure afforded the title compound in 93% (184 mg, colorless liquid) isolated yield after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent (R_f = 0.55). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.30-7.32 (m, 1H, Ar*H*), 7.14-7.23 (m, 5H, ArH), 6.94-7.02 (m, 2H, ArH), 3.73 (s, 3H, OC*H*$_3$), 2.13 (s, 3H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 19.9, 55.4, 110.7, 120.5, 125.5, 127.3, 128.6, 129.6, 130.0, 130.9 131.0, 136.8, 138.7, 156.5. Spectroscopy data is consistent with the literature.[5]



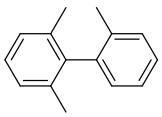
2,6-dimethyl-biphenyl (Table 3, entry 3): The general procedure afforded the title compound in 96% (175 mg, colorless liquid) isolated yield after column chromatography using a mixture of 10:90 ethyl acetate/hexane as eluent (R_f = 0.68). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.39 (t, *J* = 7.4 Hz, 2H, ArH), 7.31 (d, *J* = 6.8 Hz, 1H, ArH), 7.07-7.13 (m, 5H, ArH), 2.01 (s, 6H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 20.9, 126.5, 127.1, 127.3, 128.5, 129.1, 136.1, 141.1, 141.9. Spectroscopy data is consistent with the literature.[5]



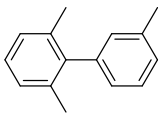
1-(o-tolyl)naphthalene (Table 3, entry 4): The general procedure afforded the title compound in 90% (196 mg, while solid) isolated yield after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent (R_f = 0.38). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.89 (d, *J* = 8.0 Hz, 1H, Ar*H*) ,7.85 (d, *J* = 8.4 Hz, 1H, ArH),7.51 (dt, *J* = 1.5, 7.7 Hz, 1H, Ar*H*) ,7.44-7.48 (m, 2H, ArH), 7.23-7.39 (m, 6H, ArH), 2.02 (s, 3H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 20.0, 125.4, 125.6, 125.7, 125.9, 126.1, 126.6, 127.4, 127.5, 128.2, 129.8, 130.4, 132.0, 133.5, 136.8, 139.8, 140.2. Spectroscopy data is consistent with the literature.[7]



1-(2,6-dimtehylphenyl)naphthalene (Table 3, entry 5): The general procedure afforded the title compound in 88% (204 mg, while solid) isolated yield after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent (R_f = 0.44). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.91 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.87 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.55 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.47 (t, *J* = 6.9 Hz, 1H, Ar*H*), 7.38–7.32 (m, 2H, Ar*H*), 7.30–7.22 (m, 2H, Ar*H*), 7.20–7.15 (m, 2H, Ar*H*), 1.92 (s, 6H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 20.4, 125.4, 125.6, 125.7, 126.0, 126.4, 127.1, 127.2, 127.3, 128.3, 131.7, 133.7, 137.0, 138.7, 139.6. Spectroscopy data is consistent with the literature.[8]



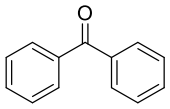
2,2´,6-trimethyl-biphenyl (Table 3, entry 6): The general procedure afforded the title compound in 89% (174 mg, colorless liquid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent (R_f = 0.62). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.09-7.29 (m, 6H, Ar*H*), 6.99-7.02 (m, 1H, ArH), 1.96 (s, 3H, C*H*$_3$), 1.92 (s, 6H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 19.4 20.3, 126.0, 126.9, 127.0, 127.2, 128.8, 130.0, 135.6, 135.8 140.5, 141.1. Spectroscopy data is consistent with the literature.[5]



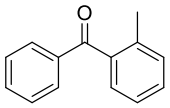
2,3´,6-trimethyl-biphenyl (Table 3, entry 7): The general procedure afforded the title compound in 90% (177 mg, colorless liquid) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent (R_f = 0.64). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.13-7.17 (m, 1H, Ar*H*), 6.96-7.01 (m, 4H, ArH), 6.78-6.83 (m, 2H, Ar*H*), 2.22 (s, 3H, C*H*$_3$), 1.90 (s, 6H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 20.9, 21.6, 126.1, 127.0, 127.3, 127.4, 128.4, 129.8, 136.1, 138.0, 141.1, 142.1. Spectroscopy data is consistent with the literature.[5]

General procedure for the Suzuki-Miyarura coupling of amides and boronic acids.

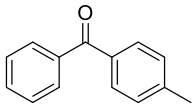
In a Schlenk flask were charged sequentially the amide substrate (1.0 mmol), potassium carbonate (3.0 mmol), boronic acid (2.0 mmol) and the catalyst (3 mol %). Under nitrogen, dry THF (5 mL) was added with vigorous stirring at room temperature and then heated at 60 ^{o}C for 15 h. The reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product.



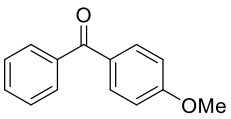
Benzophenone (Table 5, entry 1): The general procedure afforded the title compound in 94% (171 mg, white solid) isolated yield after column chromatography using a mixture of 25:75 ethyl acetate/hexane as eluent (R_f = 0.61). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.47-7.50 (m, 4H, Ar*H*), 7.57-7.61 (m, 2H, Ar*H*), 7.81 (d, *J* = 7.8 Hz, 4H, Ar*H*). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 196.8, 137.6, 132.4, 130.1, 128.3. Spectroscopy data is consistent with the literature.[9]



2-Methylbenzophenone (Table 5, entry 2): The general procedure afforded the title compound in 98% (192 mg, clear oil) isolated yield after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent (R_f = 0.57). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.61 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.48 (t, *J* = 7.4 Hz, 2H, Ar*H*), 7.42 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.33 (t, *J* = 9.4 Hz, 2H, Ar*H*), 7.28 (d, *J* = 5.9 Hz, 1H, Ar*H*), 2.36 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 138.6, 137.8, 136.8, 133.2, 131.0, 130.3, 130.2, 128.5, 128.5, 125.2, 20.0. Spectroscopy data is consistent with the literature.[9]

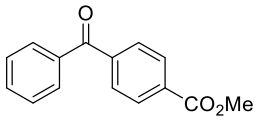


4-Methylbenzophenone (Table 5, entry 3): The general procedure afforded the title compound in 97% (190 mg, off white solid) isolated yield after column chromatography using a mixture of 10:90 ethyl acetate/hexane as eluent (R_f = 0.55). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.72 (d, *J* = 7.4 Hz, 2H, Ar*H*), 7.58 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.47 (t, *J* = 7.4 Hz, 2H, Ar*H*), 7.28 (d, *J* = 7.6 Hz, 2H, Ar*H*), 2.44 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.5, 143.3, 138.0, 134.9, 132.2, 130.3, 130.0, 129.0, 128.2, 21.7. Spectroscopy data is consistent with the literature.[9]

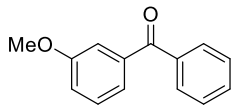


4-Methoxybenzophenone (Table 5, entry 4): The general procedure afforded the title compound in 96% (204 mg, off white solid) isolated yield after column chromatography using a mixture of 10:80 ethyl acetate/hexane as eluent (R_f = 0.37). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.76 (d,

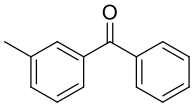
J = 7.5 Hz, 2H, Ar*H*), 7.56 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.47 (t, *J* = 7.3 Hz, 2H, Ar*H*), 6.97 (d, *J* = 8.4 Hz, 2H, Ar*H*), 3.89 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 163.2, 138.3, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5. Spectroscopy data is consistent with the literature.[9]



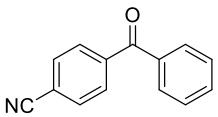
4-Acetatebenzophenone (Table 5, entry 5): The general procedure afforded the title compound in 90% (216 mg, white solid) isolated yield after column chromatography using a mixture of 10:90 ethyl acetate/hexane as eluent (R_f = 0.41). ^1H-NMR ($CDCl_3$, 400 MHz): δ = 8.15 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.83 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.81 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.62 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.51 (t, *J* = 7.5 Hz, 2H, Ar*H*), 3.97 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 166.3, 141.3, 137.0, 133.2, 133.1, 130.0, 129.8, 129.5, 128.5, 52.6. Spectroscopy data is consistent with the literature.[9]



3-Methoxybenzophenone (Table 5, entry 6): The general procedure afforded the title compound in 93% (197 mg, white solid) isolated yield after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent (R_f = 0.39). ^1H-NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.59 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.49 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.40−7.33 (m, 3H, Ar*H*), 7.15 (d, *J* = 7.2 Hz, 1H, Ar*H*), 3.86 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.6, 159.5, 139.0, 137.7, 132.3, 130.1, 129.2, 128.3, 122.9, 118.9, 114.2, 55.6. Spectroscopy data is consistent with the literature.[9]



3-Methylbenzophenone (Table 5, entry 7): The general procedure afforded the title compound in 96% (188 mg, colorless oil) isolated yield after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^1H-NMR ($CDCl_3$, 400 MHz): δ = 7.81−7.79 (m, 2H, Ar*H*), 7.63 (s, 1H, Ar*H*), 7.62− 7.59 (m, 2H, Ar*H*), 7.48 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.42−7.37 (m, 2H, Ar*H*), 2.43 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.1, 138.2, 137.8, 137.8, 133.2, 132.3, 130.5, 130.1, 128.3, 128.1, 127.4, 21.3. Spectroscopy data is consistent with the literature.[10]



4-Cyanobenzophenone (Table 5, entry 8): The general procedure afforded the title compound in 90% (187 mg, off white oil) isolated yield after column chromatography using a mixture of 10:90 ethyl acetate/hexane as eluent (R_f = 0.63). ^1H-NMR ($CDCl_3$, 400 MHz): δ = 7.88 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.82−7.74 (m, 4H, Ar*H*), 7.64 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.52 (t, *J* = 7.3 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.1, 141.3, 136.4, 133.4, 132.2, 130.3, 130.1, 128.7, 118.0, 115.5. Spectroscopy data is consistent with the literature.[9]

Catalytic poisoning tests in the formation of benzophenone using catalyst 6a-b

To the reaction mixture of the appropriate catalyst (3 mol%), phenyl *N*-glutaramide (1.0 mmol), potassium carbonate (3.0 mmol), and phenylboronic acid (2.0 mmol) in 5 mL of dry THF, an excess amount of Hg (5 mmol) was added at different reaction times (t = 0, 2, 4 and 6 h). Every reaction mixture was stirred at 60°C for a period of 16 h. Aliquots of ~ 10 μL were removed every 2 hours via a micropipette and the contents were analyzed by means of gas chromatography. The results depicted in Figures 5 and 6 are the average of two independent runs.

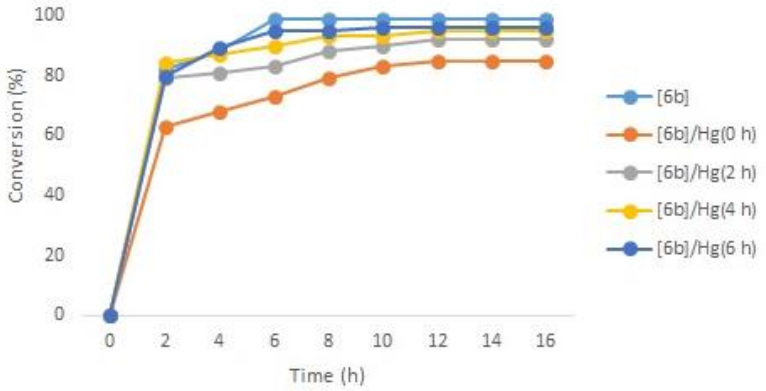


Figure S1. Mercury poisoning tests at different reaction times for the formation of benzophenone catalyzed for complex **6b**.

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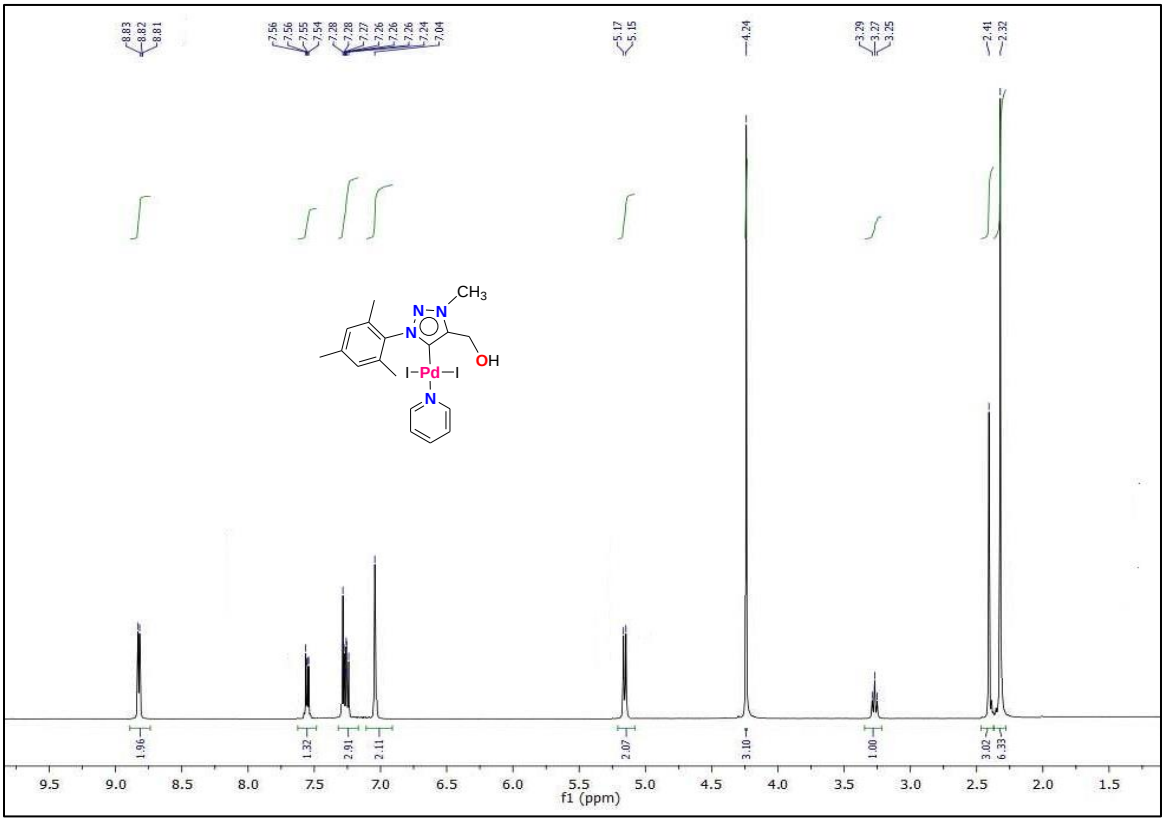

Figure S2. ^{1}H NMR (400 MHz) spectrum for **2a** in $CDCl_3$.

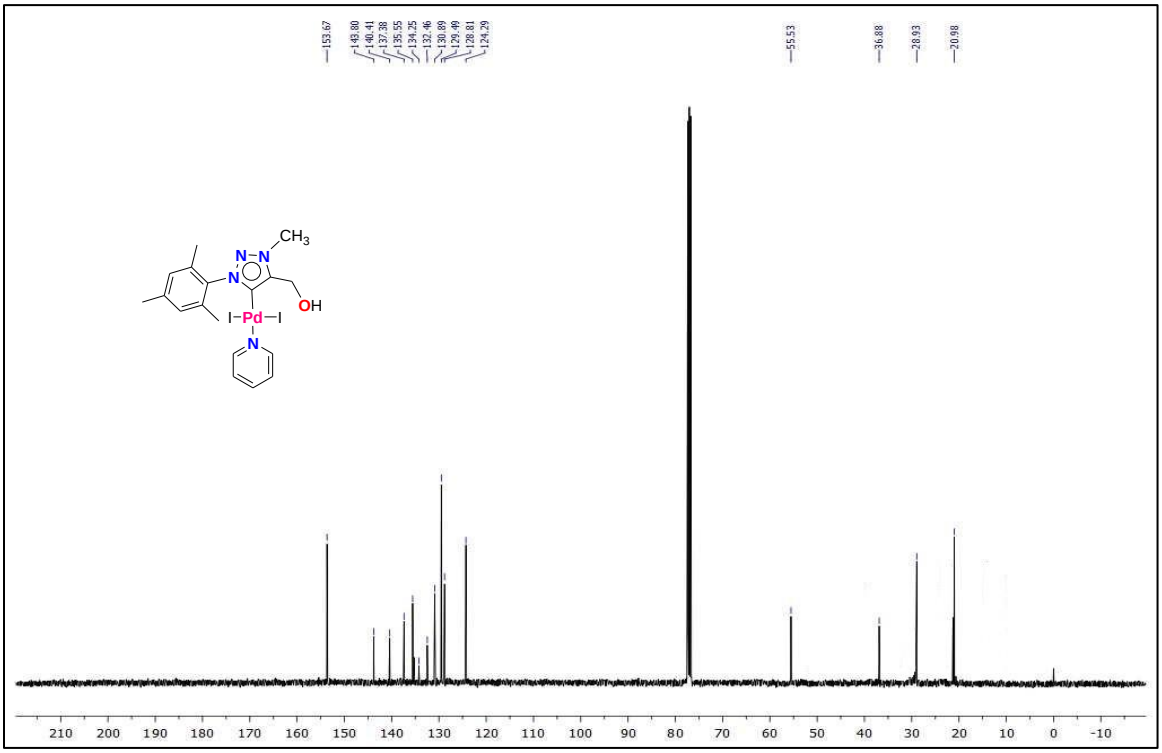

Figure S3. ^{13}C NMR (100 MHz) spectrum for **2a** in $CDCl_3$

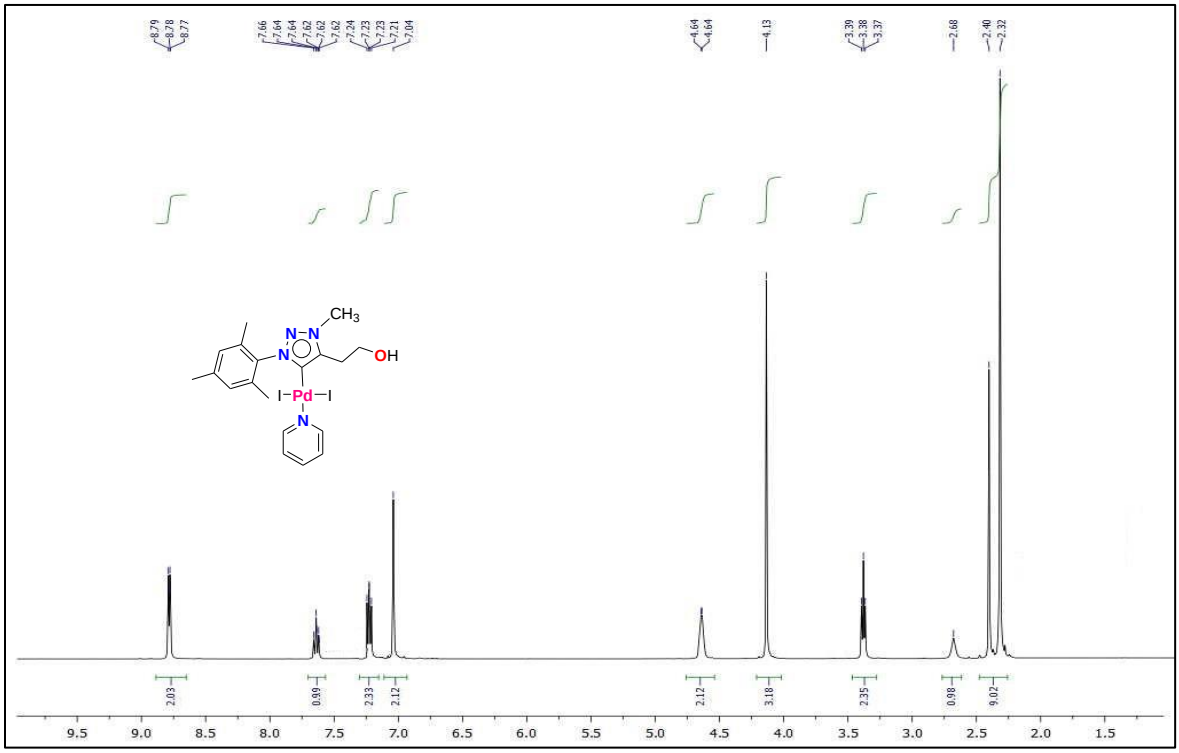

Figure S4. ^{1}H NMR (400 MHz) spectrum for **2b** in $CDCl_3$.

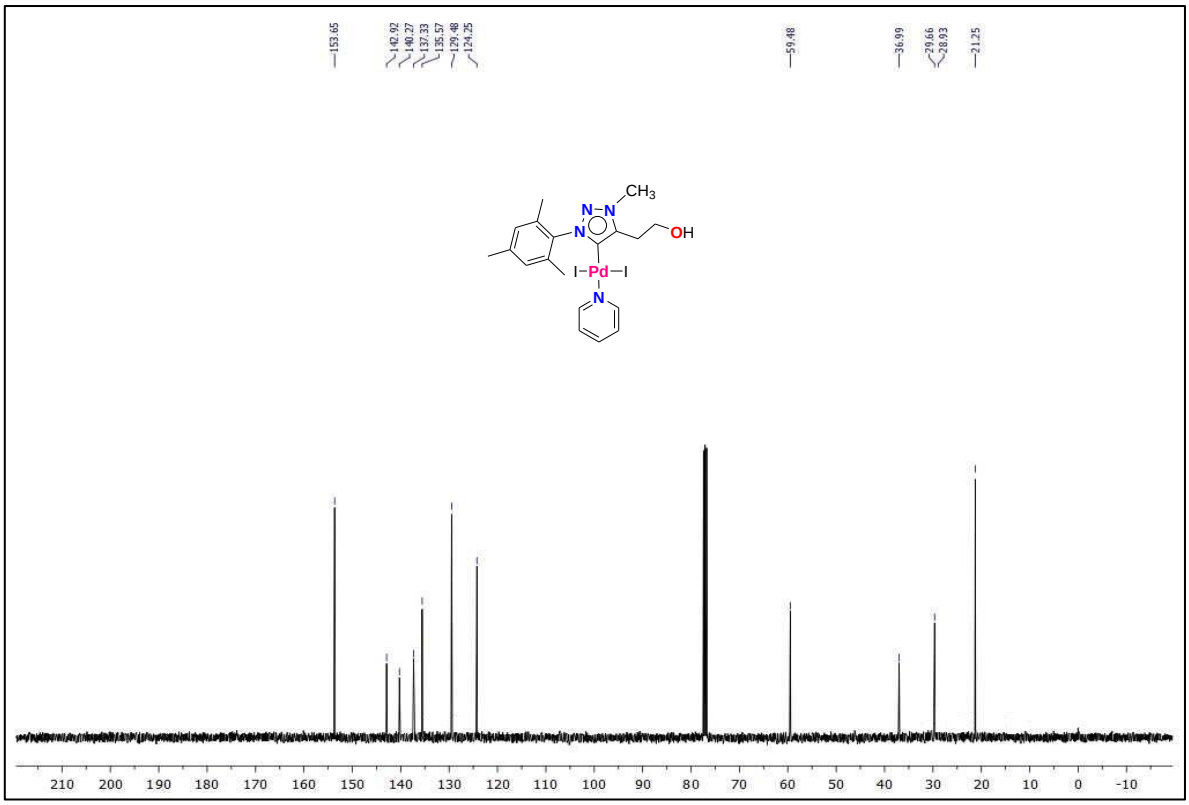

Figure S5. ^{13}C NMR (100 MHz) spectrum for **2b** in $CDCl_3$

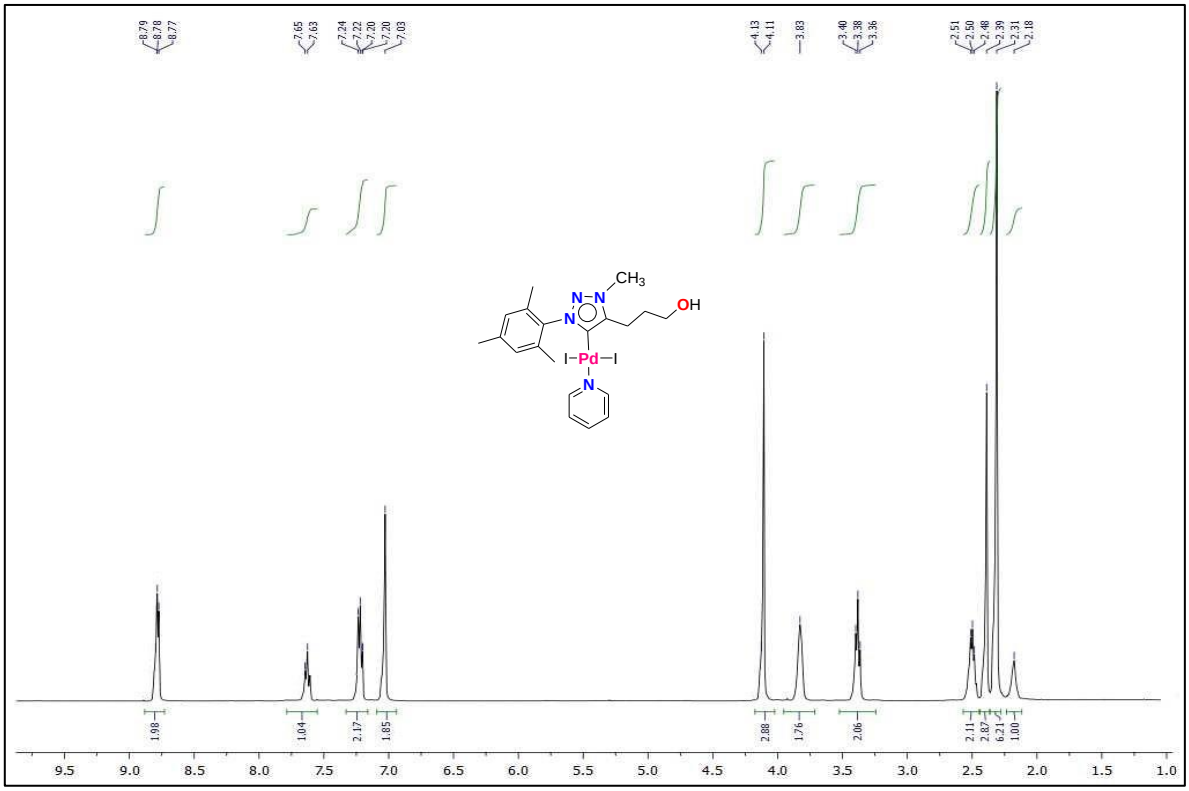

Figure S6. ^{1}H NMR (400 MHz) spectrum for **2c** in $CDCl_3$.

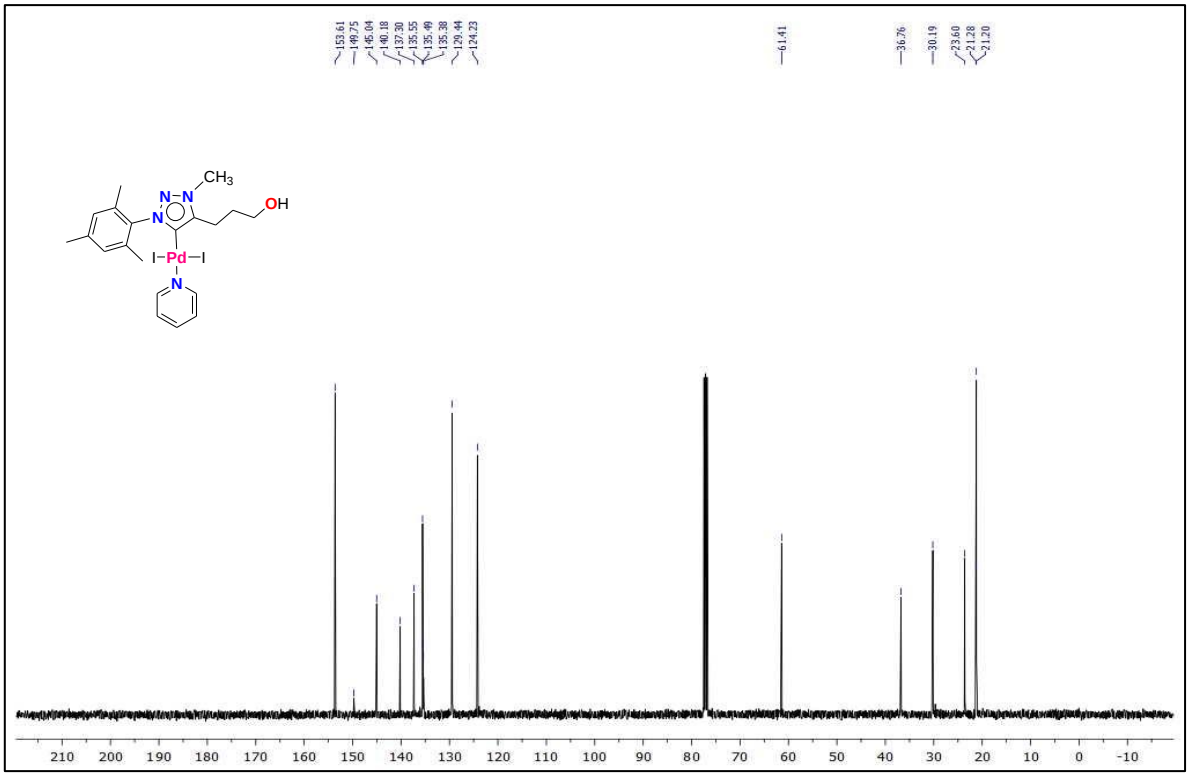

Figure S7. ^{13}C NMR (100 MHz) spectrum for **2c** in $CDCl_3$

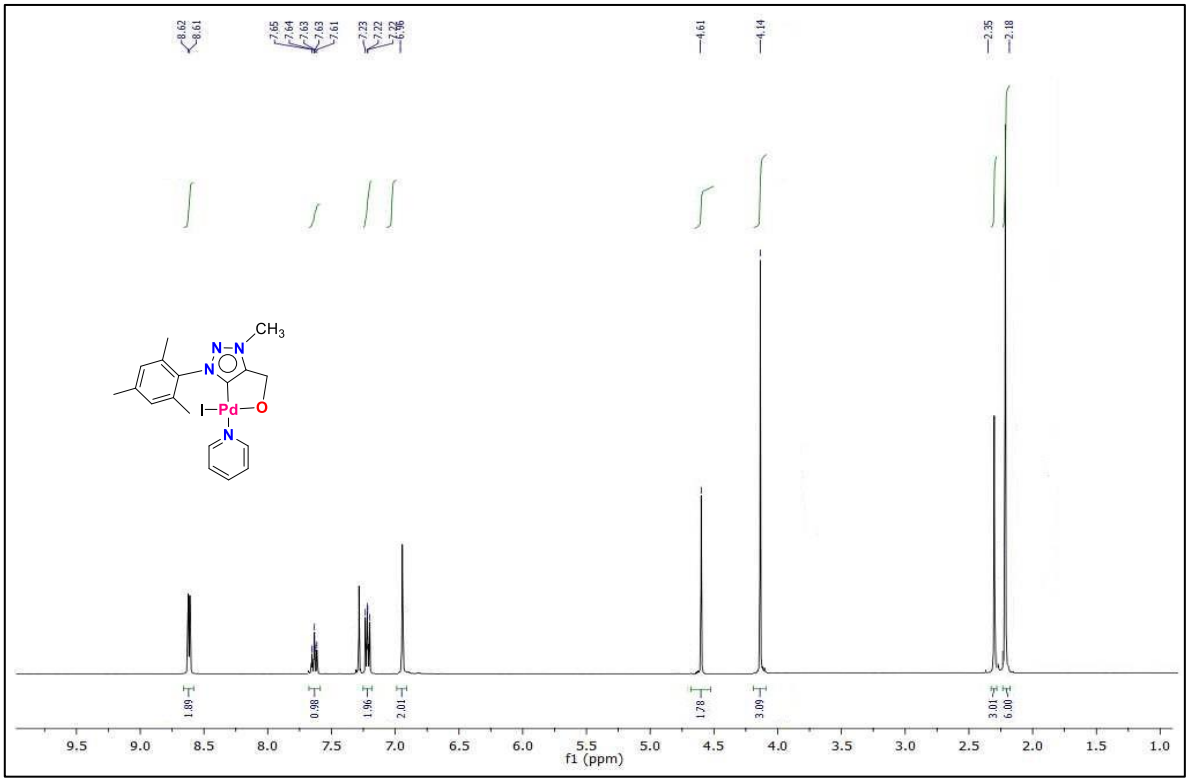

Figure S8. ^{1}H NMR (400 MHz) spectrum for **6a** in $CDCl_3$.

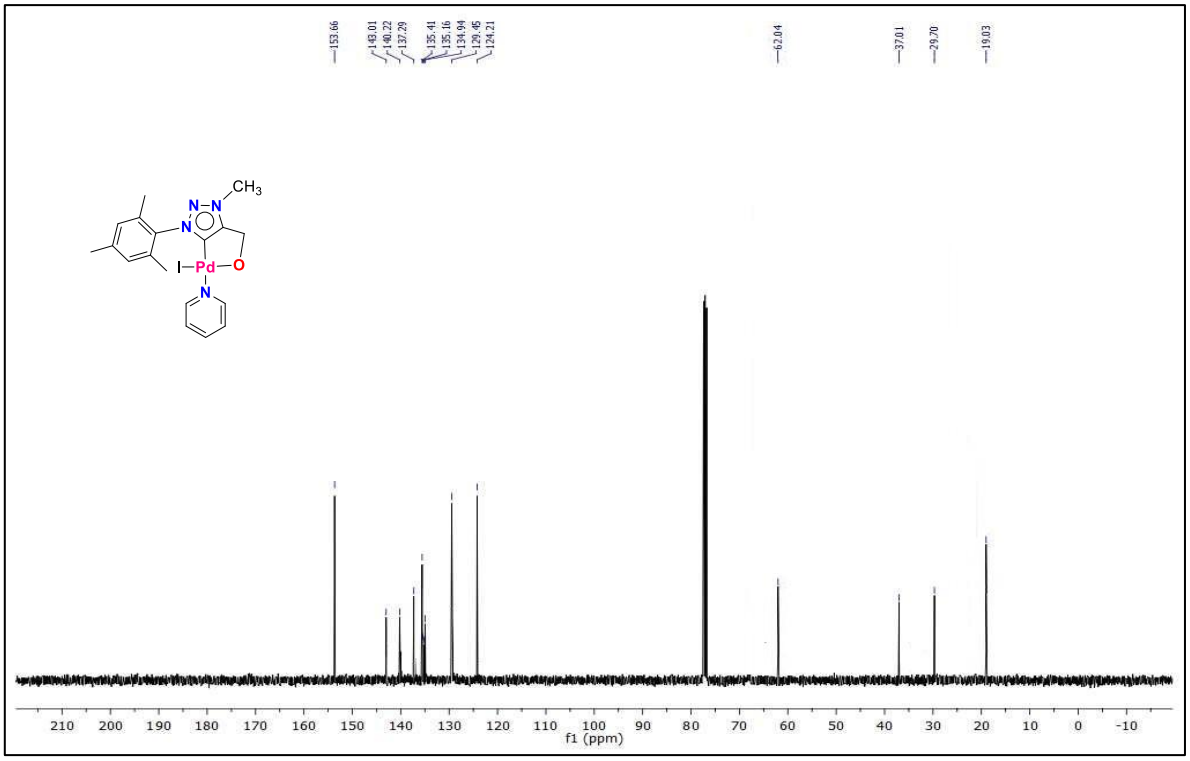

Figure S9. ^{13}C NMR (100 MHz) spectrum for **6a** in $CDCl_3$

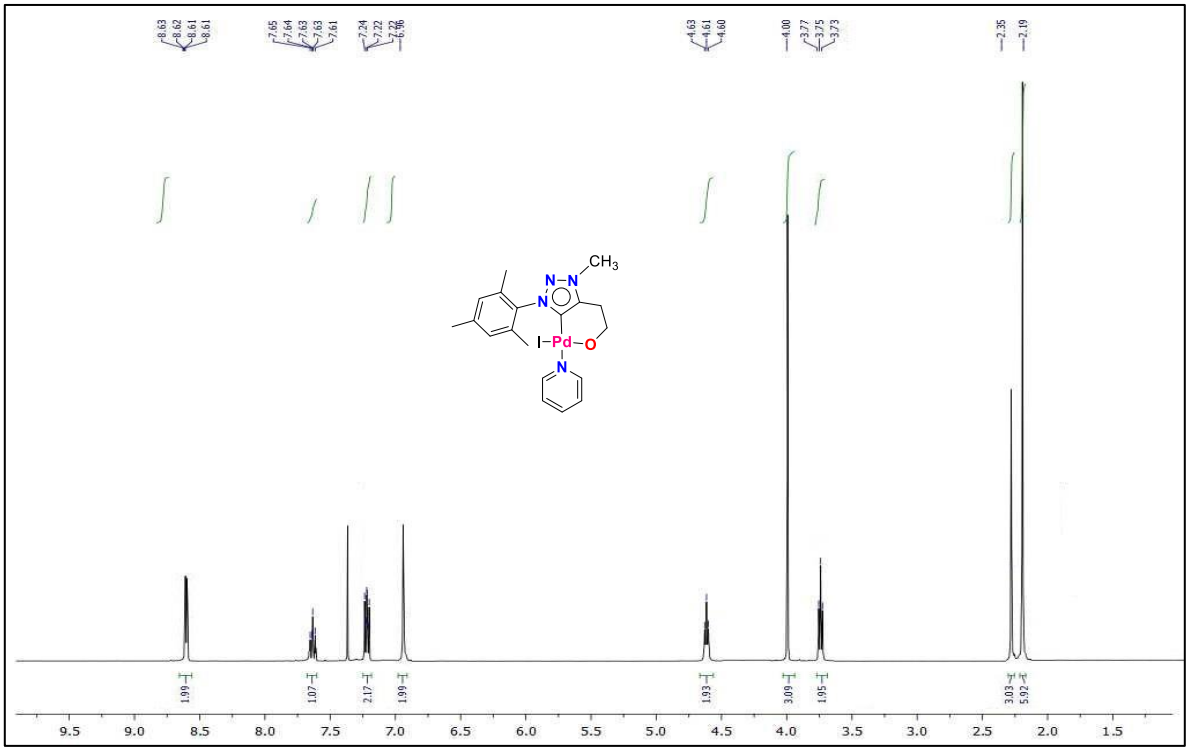

Figure S10. ^{1}H NMR (400 MHz) spectrum for **6b** in $CDCl_3$.

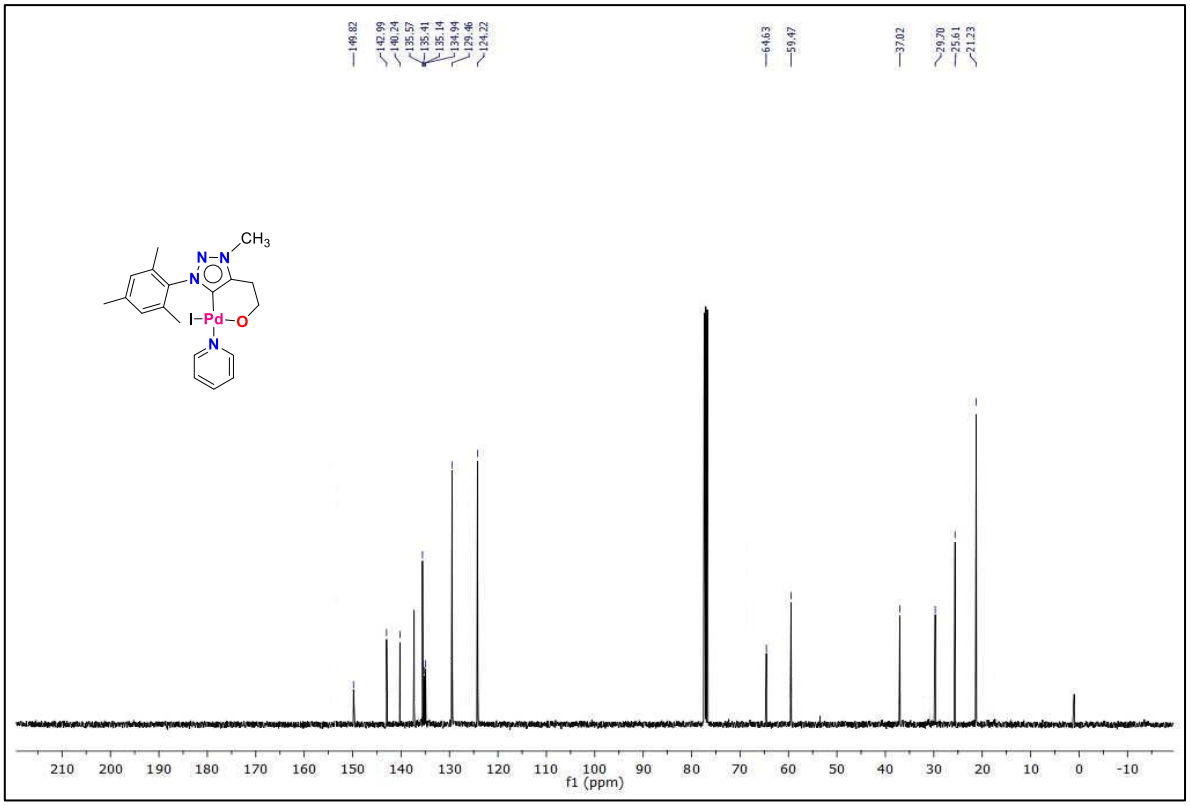

Figure S11. ^{13}C NMR (100 MHz) spectrum for **6b**