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3-Amino-1,2,4-triazolium salts as NHC-proligands: synthesis and postmodification of a new type of amino-functionalized Pd/NHC complexes

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Table of contents

S1. Synthetic procedures and characterization of isolated compounds

General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 (500 and 125 MHz, respectively) and Bruker Avance Neo 300 (300 and 75 MHz, respectively) spectrometers. Chemical shifts are given relative to the residual signals of protons of chloroform-*d*, methylene chloride-d_2, or DMSO-d_6 (7.26, 5.32, and 2.50 ppm for ^{1}H NMR, respectively) or carbon signals in chloroform-*d*, methylene chloride-d_2, or DMSO-d_6 (77.16, 53.00, and 39.52 ppm for ^{13}C NMR, respectively).

Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer.

High-resolution mass spectra (HRMS) were recorded on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The measurements were performed in a positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: –500 V) with a scan range of *m/z* 50 – 1500. External calibration of the mass spectrometer was achieved using a low-concentration tuning mix solution (Agilent Technologies). Direct syringe injection was applied for the analysed solutions at a flow rate 3 μL min^{-1}. Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}). The dry temperature was established at 250 °C. All the spectra were recorded with 1 Hz frequency and processed using the Bruker Data Analysis 4.0 software package.

Melting points were determined in open capillary tubes using a Thiele apparatus and are uncorrected.

Materials.

3-Acetamido-1-(*tert*-butyl)-1*H*-1,2,4-triazole (1) was obtained as described [V. M. Chernyshev, A. G. Vlasova, A. V. Astakhov, S. V. Shishkina, O. V. Shishkin, *J. Org. Chem*., 2015,

80, 375].

General procedure for the synthesis of compounds 2a-e. Compound **1** (1 mmol), corresponding alkyl halide (1.2 mmol) and acetonitrile (5 mL) were heated at 80 °C and stirring within 24 h. Then volatiles were removed in vacuo and the residue obtained was recrystallized from a MeCN-EtOAc (1:2) mixture and dried in vacuo.

3-Acetamido-1-(*tert*-butyl)-4-methyl-1*H*-1,2,4-triazol-4-ium iodide (2a). Yield 0.298 g (92%), white crystals, mp 211-214 ºC. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.73 (s, 9H, $3CH_3$). 2.41 (s, 3H, CH_3), 4.01 (s, 3H, CH_3), 10.12 (s, 1H, NH), 11.00 (s, 1H, CH).^{13}C NMR ($CDCl_3$, 75 MHz): 23.7, 28.7, 34.7, 64.5, 139.7, 148.4, 170.6. ESI-MS(TOF) calcd. for $C_9H_{17}N_4O^+$ $[M - I]^+$ *m/z* 197.1397, found *m/z* 197.1397. Anal. calcd. for $C_9H_{17}N_4OI$ (%): C, 33.35; H, 5.29; N, 17.28. Found (%):C, 33.30; H, 5.22; N, 17.19.

3-Acetamido-1-(*tert*-butyl)-4-ethyl-1*H*-1,2,4-triazol-4-ium iodide (2b). Yield 0.290 g (86%), white crystals, mp 191−194 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (t, *J* = 7.3 Hz, 3H, CH_3). 1.73 (s, 9H, $3CH_3$), 2.41 (s, 3H, CH_3), 4.47 (q, *J* = 7.3 Hz, 2H, CH_2), 10.14 (s, 1H, CH), 10.39 (s, 1H, CH).^{13}C NMR (75 MHz, $CDCl_3$) δ. 15.2, 24.1, 28.9, 43.8, 64.8, 139.3, 147.1, 170.6. ESI-MS(TOF) calcd. for $C_{10}H_{19}N_4O^+$ $[M - I]^+$ *m/z* 211.1553, found *m/z* 211.1556. Anal. calcd. for $C_{10}H_{19}N_4OI$ (%): C, 35.52; H, 5.66; N, 16.57. Found (%):C, 35.39; H, 5.73; N, 16.48.

3-Acetamido-1-(*tert*-butyl)-4-butyl-1*H*-1,2,4-triazol-4-ium bromide (2c). Yield 0.267 g (84%), white crystals, mp 144−147 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): 0.91 (t, *J* = 7.4 Hz, 3H, CH_3), 1.36-1.28 (m, 2H, CH_2), 1.60 (s, 9H, $3CH_3$), 1.85-1.79 (m, 2H, CH_2), 2.18 (s, 3H, CH_3); 4.04-4.01 (m, 2H, CH_2), 10.16 (s, 1H, NH), 11.23 (s, 1H, CH). ^{13}C NMR (DMSO-d_6, 125 MHz): 13.4. 19.0, 22.8, 27.7 30.1, 46.3, 63.1, 141.0,146.7,170.3. ESI-MS(TOF) calcd. for $C_{12}H_{23}N_4O^+$ $[M - Br]^+$ *m/z* 239.1866, found *m/z* 239.1871. Anal. calcd. for $C_{12}H_{23}N_4OBr$ (%): C, 45.15; H, 7.26; N, 17.55. Found (%):C, 45.08; H, 7.33; N, 17.42.

3-Acetamido-4-benzyl-1-(*tert*-butyl)-1*H*-1,2,4-triazol-4-ium bromide (2d). Yield 0.254 g (72%), white crystals, mp 211-214 ºC. The spectral characteristics of the product obtained are identical to the ones described in the literature.[1]

3-Acetamido-1-(*tert*-butyl)-4-benzyl-1*H*-1,2,4-triazol-4-ium chloride (2e). Yield 0.267 g (84%), white crystals, mp 144−147 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.63 (s, 9H, $3CH_3$), 2.33 (s, 3H, CH_3), 5.83 (s, 2H, NH_2), 7.26 – 7.54 (m, 5H, Ph), 10.70 (s, 1H, CH), 11.98 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 23.6, 28.7, 50.3, 64.2, 129.3, 129.5, 129.6, 132.4, 139.3, 147.6, 170.1. Anal. calcd. for $C_{12}H_{23}N_4OCl$ (%): C, 58.34; H, 6.85; N, 18.14. Found (%):C, 58.29; H, 6.87; N, 17.96.

General procedure for the synthesis of compounds 3a-e. A mixture of the corresponding **2** from the previous step (1 mmol), ethanol (7 ml) and concentrated HCl (in the synthesis of compounds **3a,b,e**) or 48% aq. HBr (in the synthesis of compounds **2c,d**) (0.2 ml) was refluxed for 2 h, then evaporated to dryness in vacuo. The residue obtained was dissolved in water (5 mL) and the solution was evaporated to dryness at reduced pressure to remove excess of HCl or HBr. The residue obtained was recrystallized from MeCN to give desired product.

Despite that HCl was used for the hydrolysis of iodides acetamides, compounds **3a,b** were obtained in the form of iodides, only iodide anions were detected in the mass-spectra of **3a,b** recorded in negative ion mode.

3-Amino-1-(*tert*-butyl)-4-methyl-1*H*-1,2,4-triazol-4-ium iodide (3a). Yield 0.322 g (90%), white crystals, mp 166-167 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.51 (s, 9H, $3CH_3$), 3.56 (s, 3H, CH_3), 7.19 (s, 2H, NH_2), 9.59 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 27.7, 31.4, 60.9, 137.4, 154.5. Anal. calcd. for $C_7H_{15}N_4I$ (%): C, 29.80; H, 5.36; N, 19.86. Found (%):C, 29.83; H, 5.37; N, 19.88

3-Amino-1-(*tert*-butyl)-4-ethyl-1*H*-1,2,4-triazol-4-ium iodide (3b). Yield 0.204 g (69%), white crystals, mp 153-157 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (t, *J* = 6.9 Hz, 3H, CH_3), 1.65 (s, 9H, $3CH_3$), 4.57 (q, *J* = 7.0 Hz, 2H, CH_2), 6.00 (s, 2H, NH_2), 9.99 (s, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8. 28.7, 42.3, 62.9, 136.5, 154.1. Anal. calcd. for $C_8H_{17}N_4I$ (%): C, 32.45; H, 5.79; N, 18.92. Found (%):C, 32.47; H, 5.81; N, 18.95.

3-Amino-1-(*tert*-butyl)-4-butyl-1*H*-1,2,4-triazol-4-ium bromide (3c). Yield 0.216 g (78%), white crystals, mp 136-138 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3H), 1.35 – 1.45 (m, 2H), 1.59 (s, 9H), 1.83 – 1.93 (m, 2H), 4.40 (t, *J* = 7.4 Hz, 2H), 6.22 (c, 2H),δ 10.03 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 19.6, 28.6, 30.8, 46.4, 62.1, 134.7, 154.2. ESI-MS(TOF) calcd. for $C_{10}H_{21}N_4^+$ $[M - Br]^+$ *m/z* 197.1761, found *m/z* 197.1761. Anal. calcd. for $C_{10}H_{21}N_4Br$ (%): C, 43.33; H, 7.64; N, 20.21. Found (%):C, 43.27; H, 7.75; N, 20.15**.**

3-Amino-4-benzyl-1-(tert-butyl)-1*H*-1,2,4-triazol-4-ium bromide (3d). Yield 0.273 g (88%), white crystals, mp 194-196 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.54 (s, 9H, $3CH_3$), 5.33 (s, 2H, NH_2), 7.35 – 7.46 (m, 5H, Ar), 9.94 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 27.7, 47.2, 61.5, 128.0, 128.4, 128.8, 133.8, 137.2, 154.0. Anal. calcd. for $C_{13}H_{19}N_4Br$ (%): C, 50.17; H, 6.15; N, 18.00. Found (%):C, 50.10; H, 6.13; N, 18.06.

3-Amino-4-benzyl-1-(tert-butyl)-1*H*-1,2,4-triazol-4-ium chloride (3e). Yield 0.273 g (88%), white crystals, mp 194-196 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.54 (s, 9H, $3CH_3$), 5.35 (s, 2H, CH_2), 7.30 – 7.52 (m, 7H, Ph + NH_2), 9.98 (s, 1H, CH). ^{13}C NMR (75 MHz, DMSO-d_6) δ 27.7, 47.2, 61.4, 128.1, 128.8, 128.5, 133.9, 137.3, 154.1. Anal. calcd. for $C_{13}H_{19}N_4Cl$ (%): C, 58.53; H, 7.18; N, 21.00. Found (%):C, 58.42; H, 7.21; N, 21.10.

General procedure for the synthesis of compounds 4a-g. A mixture of azolium salt **3** (0.55 mmol), KBr (357 mg, 3.0 mmol) in the synthesis of **4c,d** or KI (498 mg, 3.0 mmol) in the synthesis of **4a,b,e,f**, anhydrous K_2CO_3 (345 mg, 2.5 mmol), $PdCl_2$ (89 mg, 0.5 mmol), and 4 mL of dry pyridine (in the synthesis of **4a-d,g**) or lutidine (in the synthesis of **4e,f**) was heated at vigorous stirring for 12 h at 80 °C. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and passed through a short pad of silica gel eluting with CH_2Cl_2. The solvent was removed on a rotary evaporator under vacuum. The residue obtained was chromatographed on silica gel (CH_2Cl_2 as an eluent). The pure product was obtained after recrystallization from CH_2Cl_2-hexane (1:5) and dried under vacuum at 40 °C.

(5-Amino-2-*tert*-butyl-4-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(diiodo)(pyridine)palladium (4a). Yield 0.134 g (78%) Light-orange crystals. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.86 (s, 9H, $3CH_3$), 3.79 (s, 3H, CH_3), 6.43 (s, 2H, NH_2),7.52 (t, *J* = 6.7 Hz, 2H, Ar), 7.92 – 7.96 (m, 1H, Ar), δ 8.84 – 8.85 (m, 2H, Ar). ^{13}C NMR (125 MHz, DMSO-d_6) δ 30.2, 34.6, 59.5, 125.0, 138.5, 143.3, 153.3, 153.8. Anal. calcd. for $C_{12}H_{19}I_2N_5Pd$ (%): C, 24.28; H, 3.23; N, 11.80. Found (%): C, 24.19; H, 3.16; N, 11.82.

(5-Amino-2-*tert*-butyl-4-ethyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(diiodo)(pyridine)palladium (4b). Yield 0.266 g (88 %). Light-orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (t, *J* = 7.4 Hz, 3H, CH_3), 1.96 (s, 9H, $3CH_3$), 4.10 (s, 2H, NH_2), 4.55 (q, *J* = 7.4 Hz, 2H, Ar), 7.30 – 7.35 (m, 2H, Ar), 7.70 – 7.77 (m, 1H, Ar), 8.98 – 9.00 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3, 31.0, 43.8, 61.3, 124.7, 137.8, 145.3, 151.9, 154.2. Anal. calcd. for $C_{13}H_{21}I_2N_5Pd$ (%): C, 25.70; H, 3.48; N, 11.53. Found (%): C, 25.74; H, 3.32; N, 11.55.

(5-Amino-4-butyl-2-*tert*-butyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(di bromo)(pyridine)palladium (4c). Yield 0.167 g (62 %) light-yellow crystals. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.01 (t, *J* = 7.4 Hz, 3H, CH_3), 1.46 (h, *J* = 7.4 Hz, 2H, CH_2), 1.90 (s, 9H, $3CH_3$), 2.02-2.10 (m, 2H, CH_2), 4.42 (t, *J* = 8.3 Hz, 2H, CH_2), 6.45 (s, 2H, NH_2), 7.42 – 7.57 (m, 2H, Ar), 7.94 – 8.00 (m, 1H, Ar), δ 8.78 – 8.81 (m, 2H, Ar).^{13}C NMR (75 MHz, DMSO-d_6) δ 13.6. 19.3, 29.5, 30.4, 46.3, 59.8, 125.1, 138.7, 145.4, 152.1, 153.4. Anal. calcd. for $C_{15}H_{25}Br_2N_5Pd$ (%): C, 33.26; H, 4.65; N, 12.93. Found (%):C, 33.23; H, 4.62; N, 12.90.

(5-Amino-4-benzyl-2-*tert*-butyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(dibromo)(pyridine)palladium (4d). Yield 0.147 g (83%) light-yellow crystals. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.95 (s, 9H, $3CH_3$), 5.81 (s, 2H, CH_2), 6.26 (s, 2H, NH_2), 7.30 (d, *J* = 7.3 Hz, 1H, Ar), 7.35 (t, *J* = 7.4 Hz, 2H, Ar), 7.50-7.53 (m, 4H, Ar), 7.95 (t, *J* = 7.6 Hz, 1H, Ar), 8.76 (d, *J* = 5.0 Hz, 2H, Ar). ^{13}C NMR (125 MHz, DMSO-d_6) δ 30.5, 50.1, 60.1, 125.0, 127.5, 128.08, 128.11, 134.8, 138.7, 147.0, 152.2, 153.6. Anal. calcd. for $C_{18}H_{23}Br_2N_5Pd$ (%): C, 37.56; H, 4.03; N, 12.17. Found (%):C, 37.60; H, 3.88; N, 12.18.

(5-Amino-2-*tert*-butyl-4-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(2,6-dimethylpyridine)diiodopalladium (4e). Yield 0.228 g (74%) Light-orange crystals. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.84 (s, 9H, 3CH_3), 2.99 (s, 3H, CH_3), 3.17 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 6.46 (s, 2H, NH_2),7.29 (d, *J* = 7.7 Hz, 2H, Ar), 7.70 (t, *J* = 7.7 Hz, 1H, Ar). ^{13}C NMR (75 MHz, DMSO-d_6) δ 27.0, 27.3, 30.3, 34.0, 60.0, 122.7, 123.0, 138.8, 144.1, 154.1, 158.4, 159.3. Anal. calcd. for $C_{14}H_{23}I_2N_5Pd$ (%): C, 27.05; H, 3.73; N, 11.27. Found (%): C, 26.94; H, 3.70; N, 11.24.

(5-Amino-2-*tert*-butyl-4-ethyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(2,6-dimethylpyridine)diiodopalladium (4f). 2,6-dimethylpyridine was used instead of pyridine. Yield 0.228 g (72%) Light-orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (t, *J* = 7.4 Hz, 3H, CH_3), 1.94 (s, 9H, 3CH_3), 3.09 (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 4.12 (s, 2H, NH_2), 4.64 (q, *J* = 7.4 Hz, MeC$\underline{H}_2$, Ar), 7.04 – 7.11 (m, 2H, Ar), 7.49 (t, *J* = 7.7 Hz, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 27.9, 28.1, 31.0, 43.0, 61.7, 122.9, 123.1, 138.2, 147.6, 152.1, 159.5, 159.7. Anal. calcd. for $C_{15}H_{25}I_2N_5Pd$ (%): C, 28.34; H, 3.96; N, 11.02. Found (%): C, 28.19; H, 3.97; N, 10.97.

(5-amino-4-benzyl-2-*tert*-butyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(dichloro)(pyridine)palladium (4g). Yield 0.147 g (78%), light-yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05 (s, 9H), 3.80 (s, 2H, CH_2), 6.06 (s, 2H, NH_2), 7.33 – 7.42 (m, 5H), 7.61-7.64 (m, 2H), 7.72-7.78 – 7.80 (m, 1H), 8.95–8.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.0, 52.3, 61.7, 124.7, 128.3, 129.1, 129.6, 133.8, 138.2, 150.5, 151.6, 152.2. Anal. calcd. for $C_{18}H_{23}Cl_2N_5Pd$ (%): C, 44.42; H, 4.76; N, 14.39. Found (%):C, 44.37; H, 4.73; N, 14.28.

General procedure for the synthesis of compounds 5a-e. A solution of corresponding acid chloride (0.17 mmol) in anhydrous acetonitrile (1 mL) was added drop by drop to a vigorously stirred mixture of compound **4a** (89 mg, 0.15 mmol), anhydrous pyridine (0.5 mL) and anhydrous acetonitrile (1 mL) at 0-5 °C within 2-3 min. The reaction mixture was then stirred within 6 h at 20 °C. The progress of the reaction was monitored by TLC until the disappearance of the starting compound **4a**. The resulting mixture was diluted with 5 mL of water, and the product was extracted with chloroform (2 × 25 mL). The chloroform extract was dried with anhydrous magnesium sulfate and evaporated in vacuo. The residue obtained was chromatographed on silica gel (CH_2Cl_2 as an eluent). The pure product was obtained after recrystallization from a mixture CH_2Cl_2 - hexane (1:5).

{2-*tert*-Butyl-4-methyl-5-[(2-methylpropanoyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}(diiodo)(pyridine)palladium (5a) Yield 0.077 g (78%), pale-yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$) 1.28 (d, *J* = 6.9 Hz, 6H, 2CH_3), 2.00 (s, 9H, 3CH_3), 2.61-2.70 (m, 1H, CH), 3.97 (s, 3H, CH_3), 7.30 – 7.35 (m, 2H, Ar), 7.53 (s, 1H, NH), 7.72 – 7.77 (m, 1H, Ar), δ 8.98 – 9.01 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 31.0, 35.7, 37.1, 62.5, 124.8, 137.9, 146.1, 151.9, 154.3, 176.4. Anal. calcd. for $C_{16}H_{25}I_2N_5OPd$ (%): C, 28.96; H, 3.80; N, 10.55. Found (%): C, 28.93; H, 3.81; N, 10.50.

[5-(Benzoylamino)-2-*tert*-butyl-4-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene](diiodo)(pyridine)palladium (5b) Yield 0.083 g (74%), pale-orange crystals.^{1}H NMR (300 MHz, $CDCl_3$) 2.03 (s, 9H, 3CH_3). 4.07 (s, 3H, CH_3), 7.31 – 7.37 (m, 2H, Ar), 7.51 – 7.56 (m, 2H, Ar), 7.61 – 7.67 (m, 1H, Ar), 7.72 – 7.79 (m, 1H, Ar), 7.86 (d, *J* = 7.6 Hz, 2H, Ar), 8.14 (s, 1H, NH), δ 9.03 – 9.00 (m, 2H, Ar).^{13}C NMR (75 MHz, $CDCl_3$) δ 31.0. 37.5, 62.6, 124.8, 128.0, 129.2, 131.6, 133.5, 137.9, 146.5, 152.2, 154.3, 166.2. Anal. calcd. for $C_{19}H_{23}I_2N_5OPd$ (%): C, 32.71; H, 3.32; N, 10.04. Found (%): C, 32.58; H, 3.34; N, 10.11.

{2-*tert*-butyl-4-methyl-5-[(4-methylbenzoyl)amino]-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}(diiodo)(pyridine)palladium (5c) Yield 0.077 g (73%), pale-orange crystals.^{1}H NMR (500 MHz, CD_2Cl_2) δ 2.04 (s, 9H, 3CH_3). 2.48 (s, 3H, CH_3), 4.04 (s, 3H, CH_3), 7.38 – 7.42 (m, 4H, Ar), 7.82-7.85 (m, 3H, Ar), 8.05 (s, 1H, NH), 9.01 – 9.02 (m, 2H, Ar).^{13}C NMR (125 MHz, CD_2Cl_2) δ 22.0, 31.2, 37.8, 62.8, 125.2, 128.3, 129.2, 129.7, 130.3, 138.5, 145.1, 147.0, 154.5, 166.6. Anal. calcd. for $C_{20}H_{25}I_2N_5OPd$ (%): C, 33.75; H, 3.54; N, 9.84. Found (%): C, 33.48; H, 3.29; N, 9.67.

{2-*tert*-butyl-5-[(4-chlorobenzoyl)amino]-4-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}(diiodo)(pyridine)palladium (5d) Yield 0.077 g (73 %), pale-orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (s, 9H, $3CH_3$). 4.05 (s, 3H, CH_3), 7.31 – 7.36 (m, 2H, Ar), 7.51 (d, *J* = 8.6 Hz, 2H, Ar), 7.73 – 7.78 (m, 1H, Ar), 7.89 (d, *J* = 8.3 Hz, 2H, Ar), 8.49 (s, 1H, NH), 9.00 – 9.03 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.0, 37.4, 62.6, 124.8, 129.4, 129.5, 130.0, 137.9, 140.0, 146.3, 152.4, 154.3, 165.3. Anal. calcd. for $C_{19}H_{22}ClI_2N_5OPd$ (%): C, 31.17; H, 3.03; N, 9.57. Found (%): C, 31.24; H, 2.92; N, 9.57.

{2-*tert*-butyl-5-[(2-ethylhexanoyl)amino]-4-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene}(diiodo)(pyridine)palladium (5e) Yield 0.106 g (84 %), pale-orange crystals.^{1}H NMR (300 MHz, $CDCl_3$) 0.86 – 0.94 (m, 3H, CH_3). 0.99 (t, *J* = 7.4 Hz, 3H, CH_3), 1.26 – 1.39 (m, 4H, $2CH_2$), 1.46 – 1.63 (m, 2H, CH_2), 1.65 – 1.80 (m, 2H), 2.00 (s, 9H, $3CH_3$), 2.21 – 2.33 (m, 1H, CH), 3.99 (s, 3H , CH_3), 7.30 – 7.35 (m, 2H, Ar), 7.44 (s, 1H, NH),7.72 – 7.77 (m, 1H, Ar),δ 8.98 – 9.01 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.2, 14.1, 22.9, 25.8, 29.9, 31.0, 32.1, 62.5, 124.8, 137.9, 146.1, 152.0, 154.2, 158.7 (some signals of aliphatic carbons are overlapped). Anal. calcd. for $C_{20}H_{33}I_2N_5OPd$ (%): C, 33.38; H, 4.62; N, 9.73. Found (%): C, 33.51; H, 4.60; N, 9.50.

[2-*tert*-Butyl-5-(dibenzoylamino)-4-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene](diiodo)(pyridine)palladium (6). A mixture of compound **4a** (89 mg, 0.15 mmol), anhydrous pyridine (0.5 mL), anhydrous acetonitrile (1 mL) and benzoyl chloride (46 mg, 0.33 mmol) was stirred within 6 h at 20 °C, then was diluted with water (5 mL) and extracted with chloroform (2 × 25 ml). The chloroform extract was dried with anhydrous magnesium sulfate and evaporated to dryness in vacuo. The residue obtained was chromatographed on silica gel (CH_2Cl_2 as an eluent). The pure product was obtained after recrystallization with hexane. Yield 0.087 g (73%), pale-orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$) 1.74 (s, 9H, $3CH_3$). δ 4.05 (s, 3H, CH_3), 7.30 – 7.35 (m, 2H, Ar), 7.46 – 7.51 (m, 4H, Ar), 7.56 – 7.61 (m, 2H, Ar), 7.69 – 7.77 (m, 5H, Ar), 9.00 (d, *J* = 5.3 Hz, 2H, Ar).^{13}C NMR (75 MHz, $CDCl_3$) δ 30.5. 36.6, 62.8, 124.7, 129.0, 129.2, 132.0, 133.6, 137.8, 147.9, 154.0, 154.17, 170.03. Anal. calcd. for $C_{26}H_{27}I_2N_5O_2Pd$ (%): C, 38.95; H, 3.39; N, 8.74. Found (%): C, 38.94; H, 3.53; N, 8.70.

(2-*tert*-Butyl-4-methyl-5-{[(4-methylphenyl)sulfonyl]amino}-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(diiodo)(pyridine)palladium (7). A mixture of compound **4a** (89 mg, 0.15 mmol), 4-methylbenzenesulfonyl chloride (38 mg, 0.2 mmol) and dry pyridine (1 mL) was heated at 110 °C and vigorous stirring overnight. The resulted mixture was diluted with water (5 mL) and extracted with chloroform (2 × 25 ml), the organic solution was dried with anhydrous magnesium sulfate, and evaporated in vacuo. The residue obtained was chromatographed on silica gel (CH_2Cl_2 as an eluent). The pure product was obtained after recrystallization from hexane. Yield 0.108 g (77 %), dark-orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89 (s, 9H, $3CH_3$). 2.42 (s, 3H, CH_3), 4.24 (s, 3H, CH_3), 7.30 (d, *J* = 8.2 Hz, 2H, Ar), 7.34 – 7.39 (m, 2H, Ar), 7.68 (d, *J* = 8.4 Hz, 2H, Ar), 7.76 – 7.81 (m, 1H, Ar), 8.94 – 8.96 (m, 2H, Ar) (signal of NH is broadened and merged into background). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8. 30.8, 35.5, 62.8, 124.8, 128.2, 129.9, 134.7, 138.4, 145.0, 145.2, 151.5, 155.6. Anal. calcd. for $C_{19}H_{25}I_2N_5O_2PdS$ (%): C, 30.52; H, 3.37; N, 9.37. Found (%): C, 30.50; H, 3.24; N, 9.19.

2-*tert*-Butyl-4-methyl-5-{[(*E*)-(4-nitrophenyl)methylidene]amino}-2,4-dihydro-3*H*-1,2,4-triazol-3-ylidene)(diiodo)(pyridine)palladium (**8**). A mixture of complex **4a** (178 mg, 0.3 mmol), 4-nitrobenzaldehyde (60 mg, 0.4 mmol) and ethanol (5 mL) was heated under reflux within 5 h. Then ethanol was removed on a rotary evaporator and methylene chloride (5 mL) was added. Resulting mixture was washed several times with water (4 x 10 mL), the organic phase was dried with anhydrous sodium sulfate and evaporated in vacuo. The residue obtained was chromatographed on silica gel (CH_2Cl_2 as an eluent). The pure product was obtained by recrystallization from hexane. Yield 0.112 g (69%), dark-orange crystals. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.93 (s, 9H, CH_3), 3.90 (s, 3H, CH_3), 7.34 – 7.36 (m, 2H, Ar), 7.78 – 7.80 (m, 1H, Ar),

8.07 (d, *J* = 8.8 Hz, 2H, Ar), 8.38 (d, *J* = 8.6 Hz, 2H, Ar), 8.96 (d, *J* = 4.9 Hz, 2H, Ar), 10.15 (s, 1H, CH).^{13}C NMR (125 MHz, CD_2Cl_2) δ 31.1. 35.6, 61.3, 100.6, 124.8, 125.1, 130.2, 131.0, 138.4, 140.7, 152.9, 154.4, 191.0. Anal. calcd. for $C_{19}H_{22}I_2N_6O_2Pd$ (%): C, 31.41; H, 3.05; N, 11.57. Found (%): C, 31.22; H, 3.12; N, 11.63.

1 V. M. Chernyshev, A. G. Vlasova, A. V. Astakhov, S. V. Shishkina and O. V. Shishkin, *J. Org. Chem.*, 2015, **80**, 375.

S2. X-Ray investigation of compound 4a

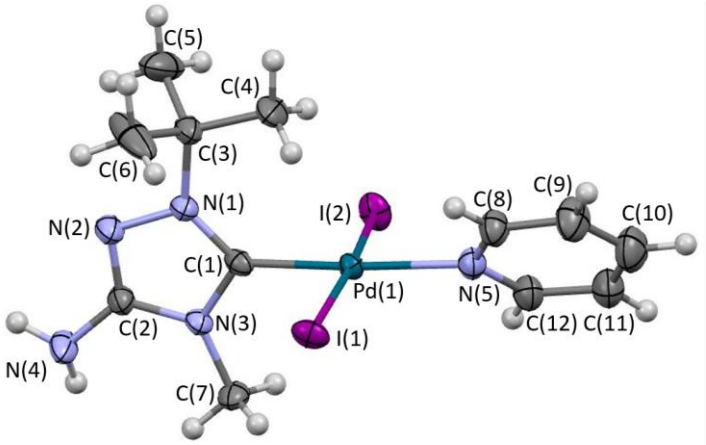

Figure S1 General view of complex **4a** in the representation of atoms via thermal ellipsoids at the 50% probability level. Selected bond lengths (Å): Pd(1)—C(1) 1.950(5), Pd(1)—N(5) 2.104(4), Pd(1)—I(2) 2.6039(8), Pd(1)—I(1) 2.6116(9), N(1)—C(1) 1.324(6), N(1)—N(2) 1.396(5), N(2)—C(2) 1.315(6), N(3)—C(1) 1.375(6), N(3)—C(2) 1.374(6), N(4)—C(2) 1.356(6), N(5)—C(8) 1.330(7), N(5)—C(12) 1.348(6); selected bond angles (°): C(1)—Pd(1)—N(5) 176.65(17), C(1)—Pd(1)—I(1) 86.97(13), C(1)—Pd(1)—I(2) 86.32(13), N(5)—Pd(1)—I(1) 93.58(11), N(5)—Pd(1)—I(2) 93.44(11), I(2)—Pd(1)—I(1) 171.356(19).

In the crystal, molecules of **4a** form centrosymmetric H-bonded dimers by the strong N─H···N hydrogen bonds (Figure 2, Table 1). Further, the dimers are bound into three-dimensional framework by the weak N─H···I hydrogen bonds (Table 1) and non-valent I···I interactions of 3.7645(12) Å (Figure 3).

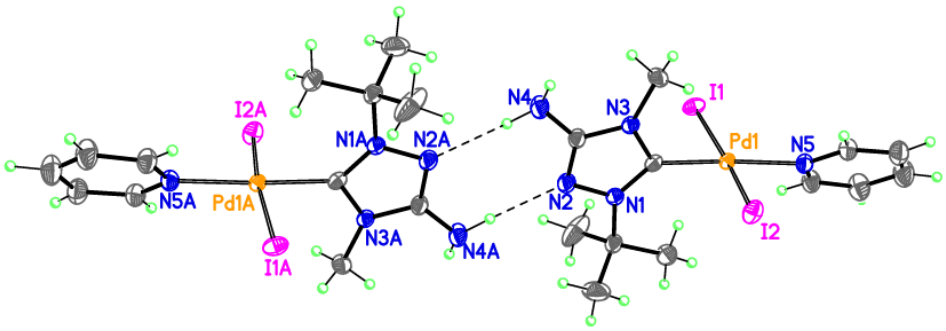

Figure S2. The centrosymmetric H-bonded dimers of **4a**. The strong N─H···N hydrogen bonds are depicted by dashed lines.

Table S1. Hydrogen bonds in **4a** (Å and °).

D─H···A	d(D─H)	d(H···A)	d(D···A)	∠(DHA)
N4─H4D···I1[a]	0.92	3.09	3.763(4)	132
N4─H4D···I2[b]	0.92	3.06	3.891(5)	152
N4─H4E···N2[c]	0.91	2.12	3.022(6)	171

Symmetry transformations used to generate equivalent atoms:
[a] -*x*+1, -*y*, -*z*+1; [b] -*x*+3/2, *y*-1/2, -*z*+3/2; [c] -*x*+2, -*y*, -*z*+1

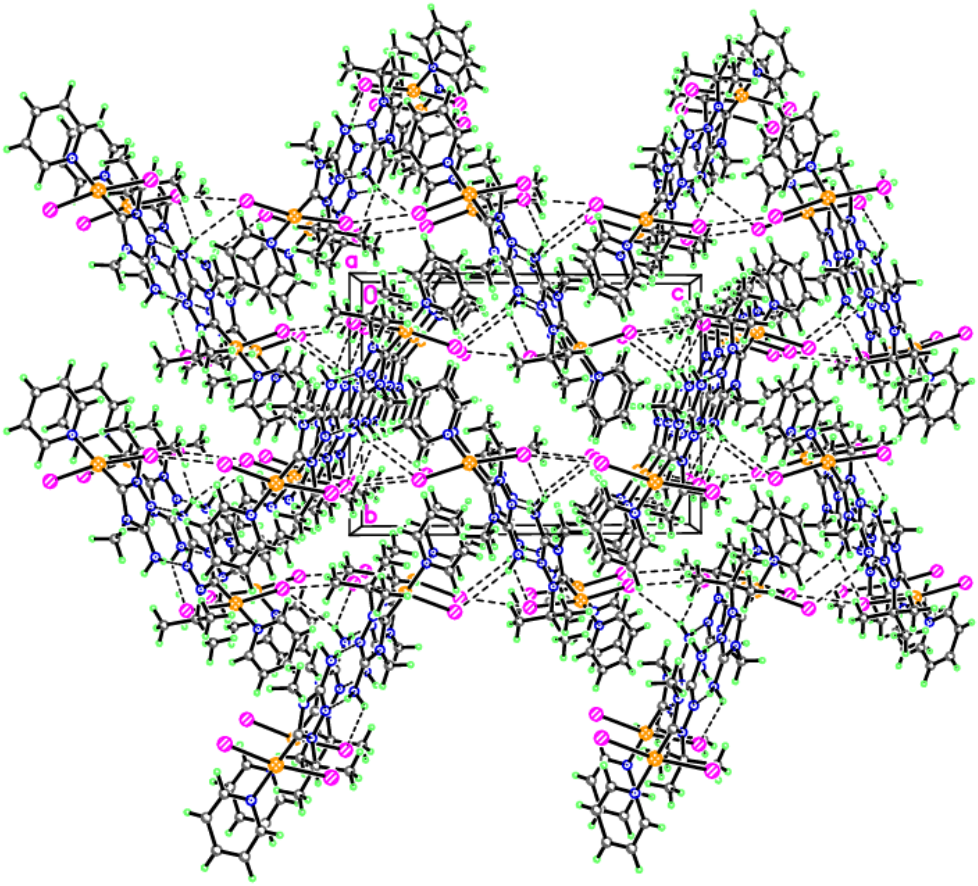

Figure S3. Crystal structure of **4a**. The N─H···N and N─H···I hydrogen bonds as well as the non-valent I···I interactions are depicted by dashed lines.

Table S2. Crystal data for compound **4a**.

$C_{12}H_{19}I_2N_5Pd$	$F(000)$ = 1112
M_r = 593.52	D_x = 2.210 Mg m^{-3}
Monoclinic, $P2_1/n$	Synchrotron radiation, λ = 0.80246 Å
a = 9.2838 (19) Å	Cell parameters from 600 reflections
b = 11.924 (2) Å	θ = 2.4–30.0°
c = 16.256 (3) Å	μ = 6.16 mm^{-1}
β = 97.55 (3)°	T = 100 K
V = 1783.9 (6) Å^3	Prism, orange
Z = 4	0.32 × 0.28 × 0.20 mm

Table S3. Data collection for compound **4a**.

Rayonix SX165 CCD diffractometer	3775 reflections with $I > 2\sigma(I)$
φ scan	$R_{int} = 0.112$
Absorption correction: semi-empirical, Scala (Evans, 2006)	$\theta_{max} = 30.8°$, $\theta_{min} = 2.4°$
$T_{min} = 0.130$, $T_{max} = 0.260$	$h = -11 \rightarrow 11$
30410 measured reflections	$k = -15 \rightarrow 15$
3835 independent reflections	$l = -20 \rightarrow 20$

Table S4. Refinement for compound **4a**.

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.112$	$w=1/[\sigma^2(F_o^2)+6P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3835 reflections	$\Delta \rho_{max} = 1.51$ e Å^{-3}
186 parameters	$\Delta \rho_{min} = -1.47$ e Å^{-3}
0 restraints	Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: difference Fourier map	Extinction coefficient: 0.0077 (6)

Special details (Geometry):

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

1. P. Evans, *Acta Crystallogr.*, 2006, **62**, 72.

2. T. G. G. Battye, L. Kontogiannis, O. Johnson, H. R. Powell and A. G. W. Leslie, *Acta Crystallogr.*, 2011, **67**, 271.

3. G. Sheldrick, *Acta Crystallogr.*, 2015, **71**, 3.

S3. ^{1}H and ^{13}C NMR spectra

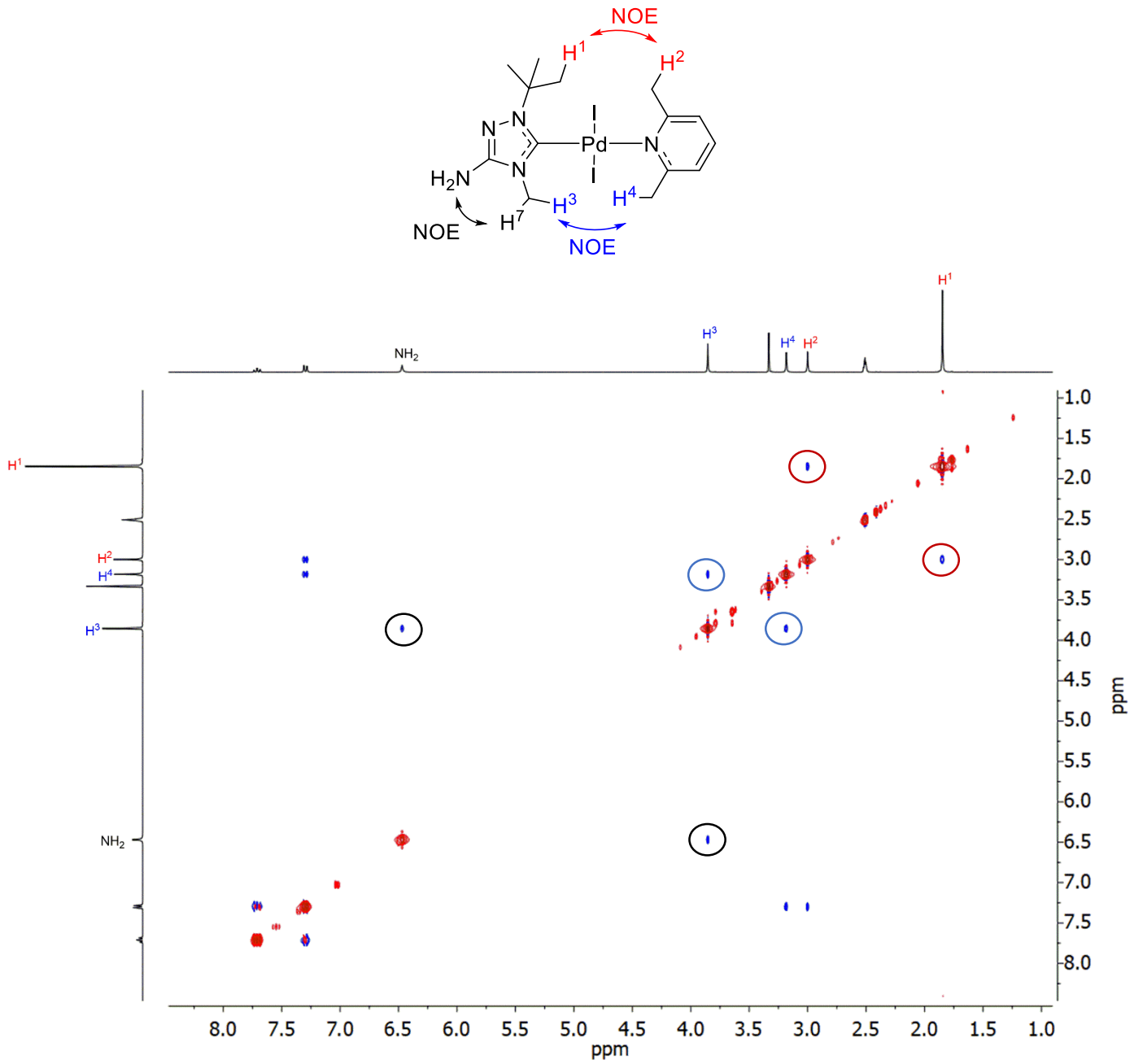

Figure S4. ^{1}H-^{1}H NOESY spectrum of compound **4e** (DMSO-d_6)

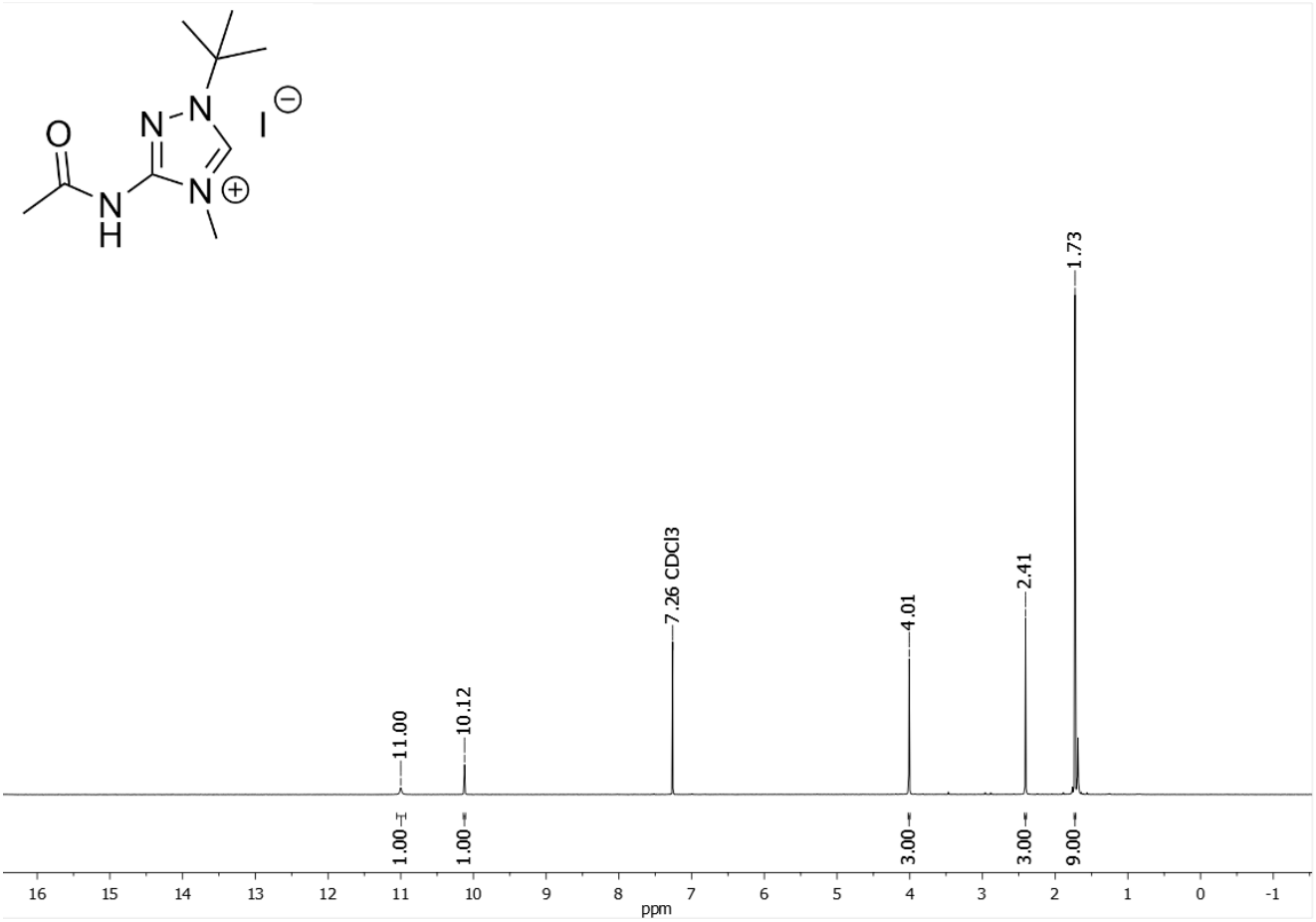

Figure S5 ^{1}H NMR spectrum of **2a** ($CDCl_3$), 300 MHz

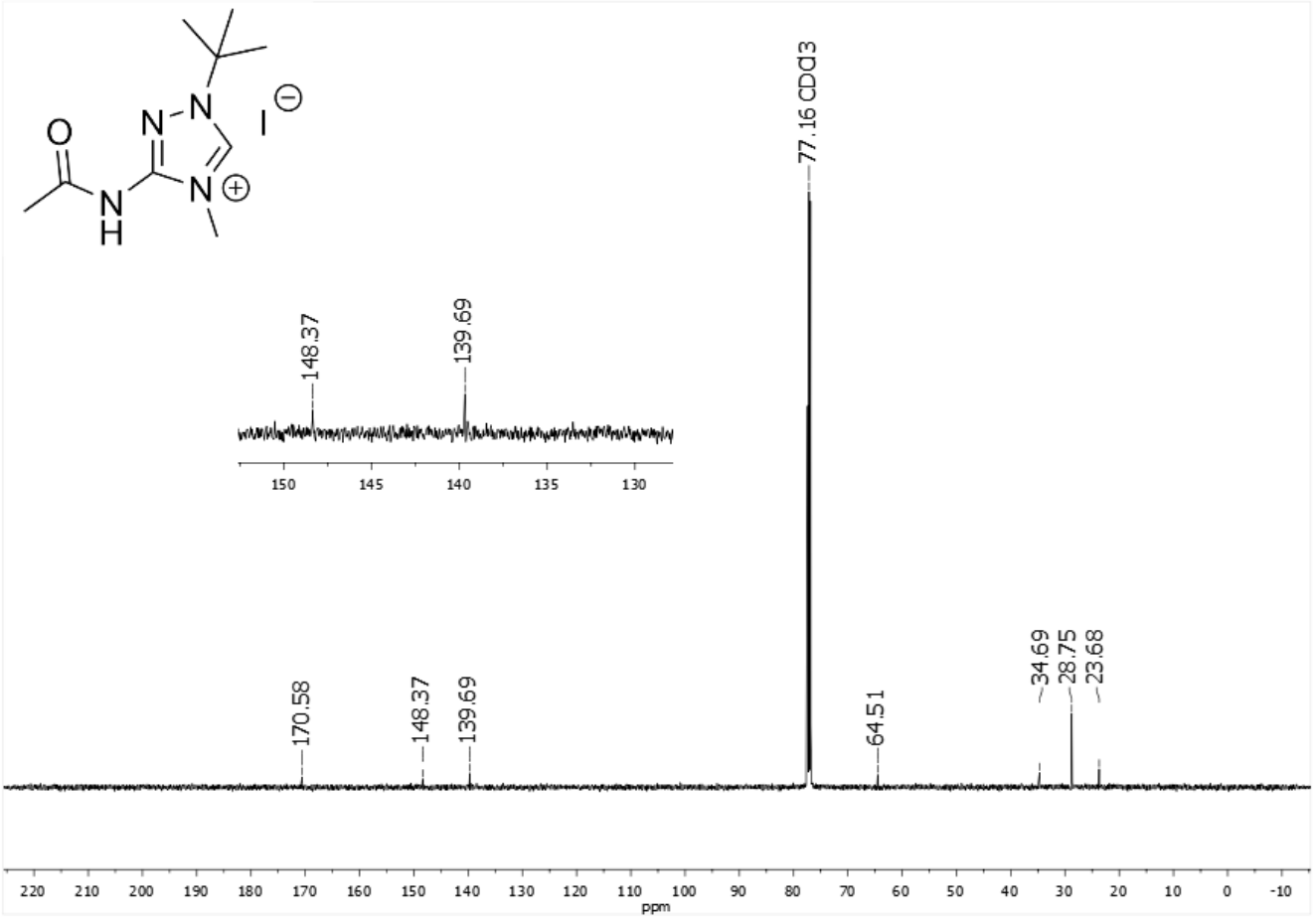

Figure S6 ^{13}C NMR spectrum of **2a** ($CDCl_3$, 75 MHz)

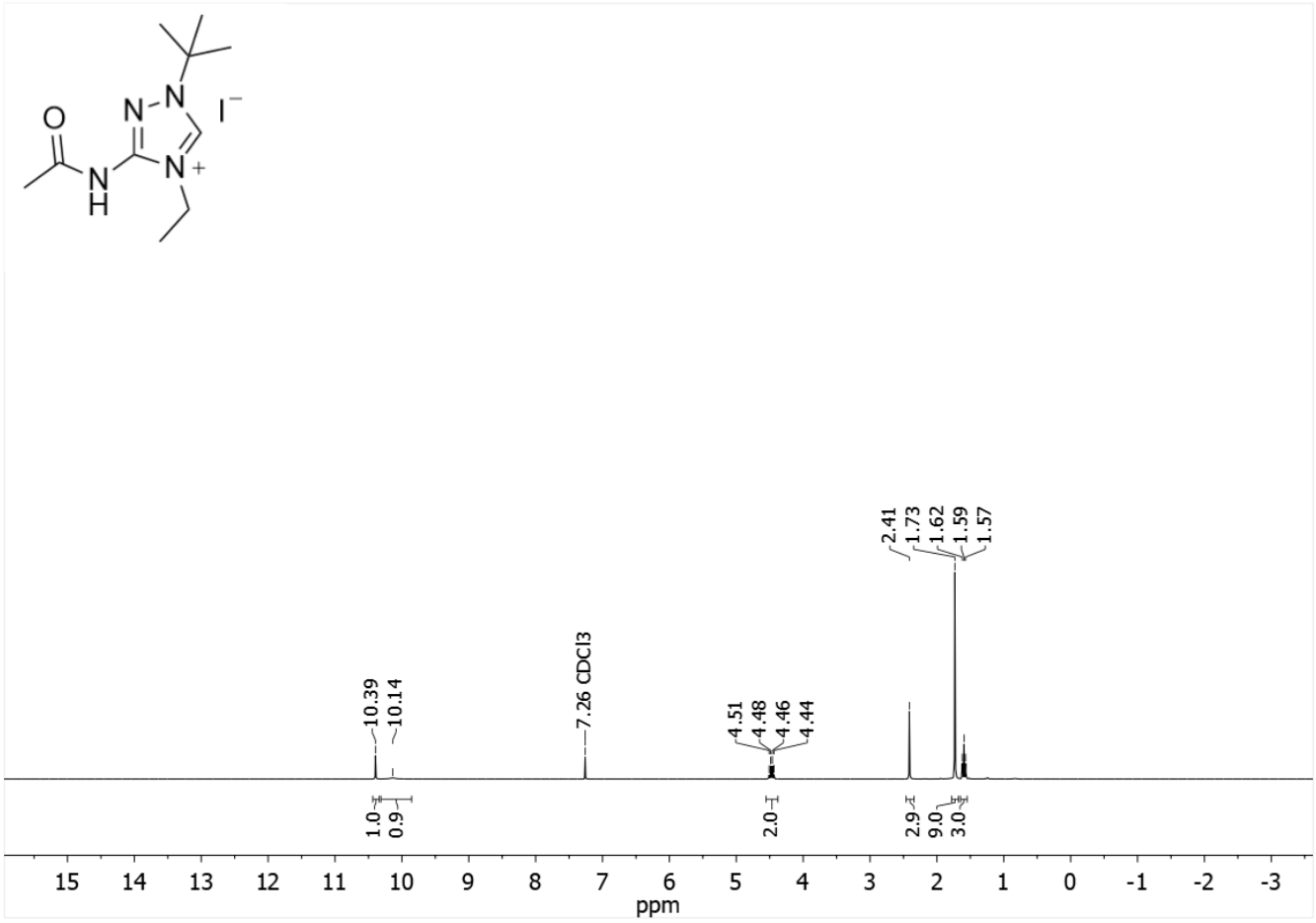

Figure S7 ^{1}H NMR spectrum of **2b** ($CDCl_3$, 300 MHz)

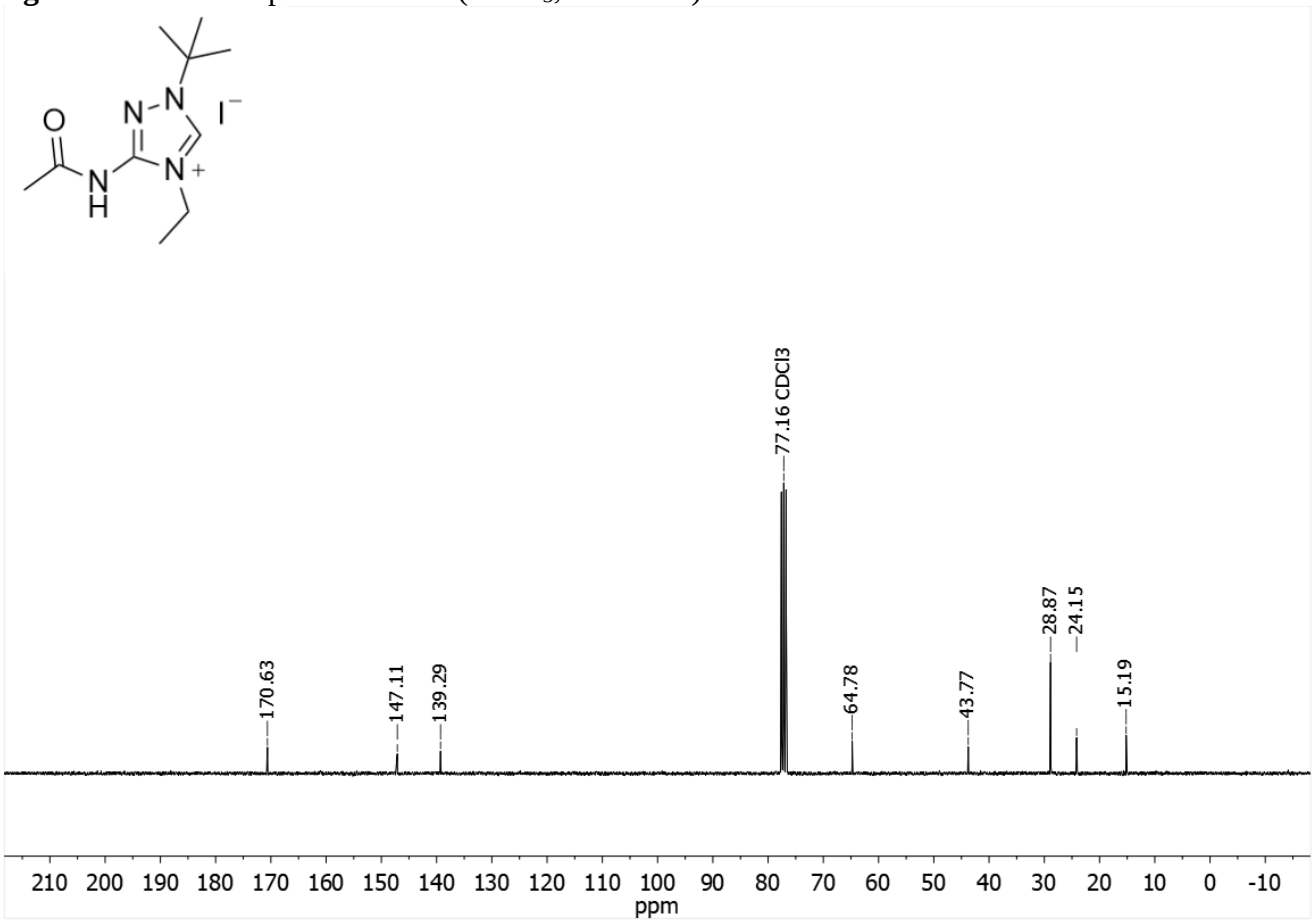

Figure S8 ^{13}C NMR spectrum of **2b** ($CDCl_3$, 75 MHz)

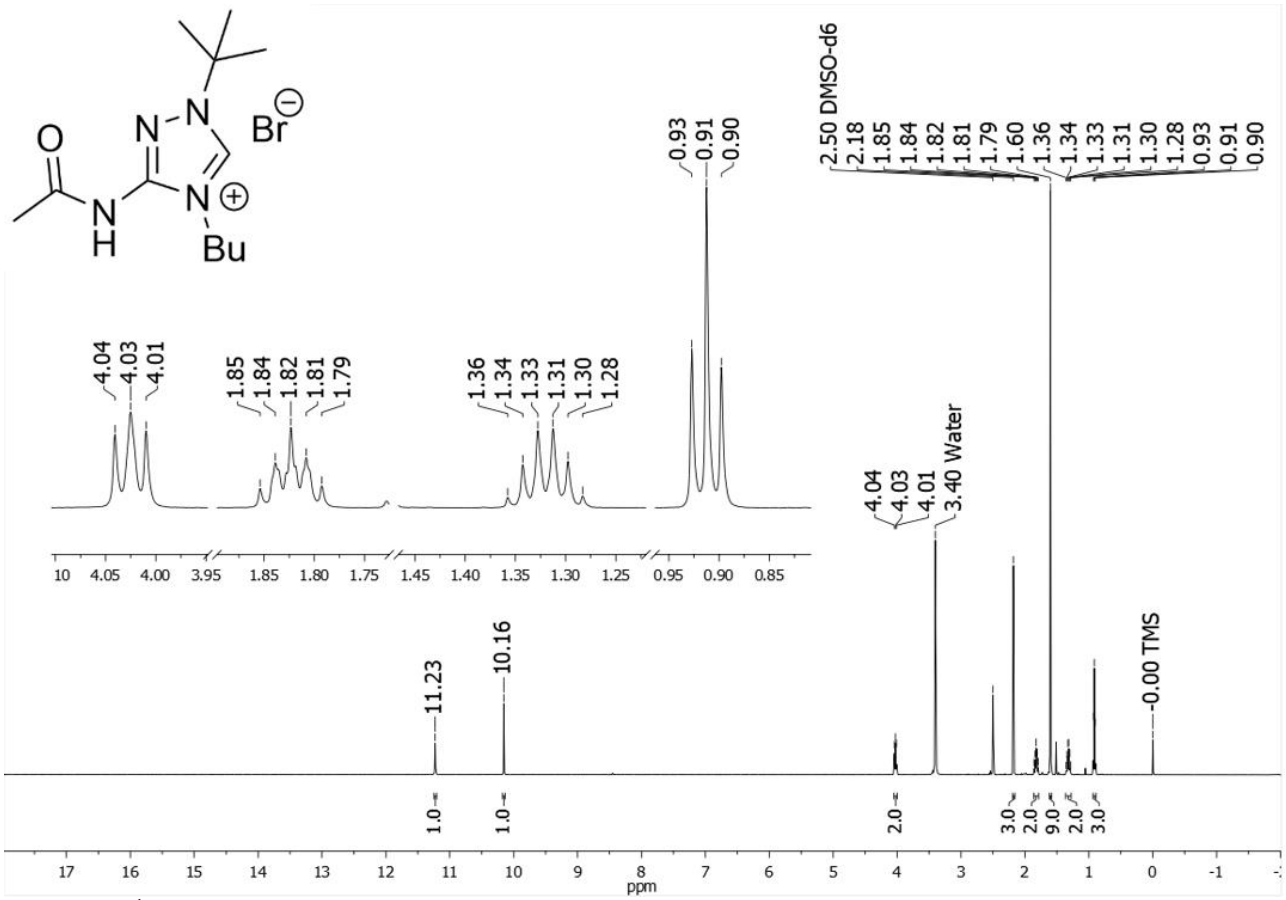

Figure S9 ^{1}H NMR spectrum of **2c** (DMSO-d_6, 500 MHz)

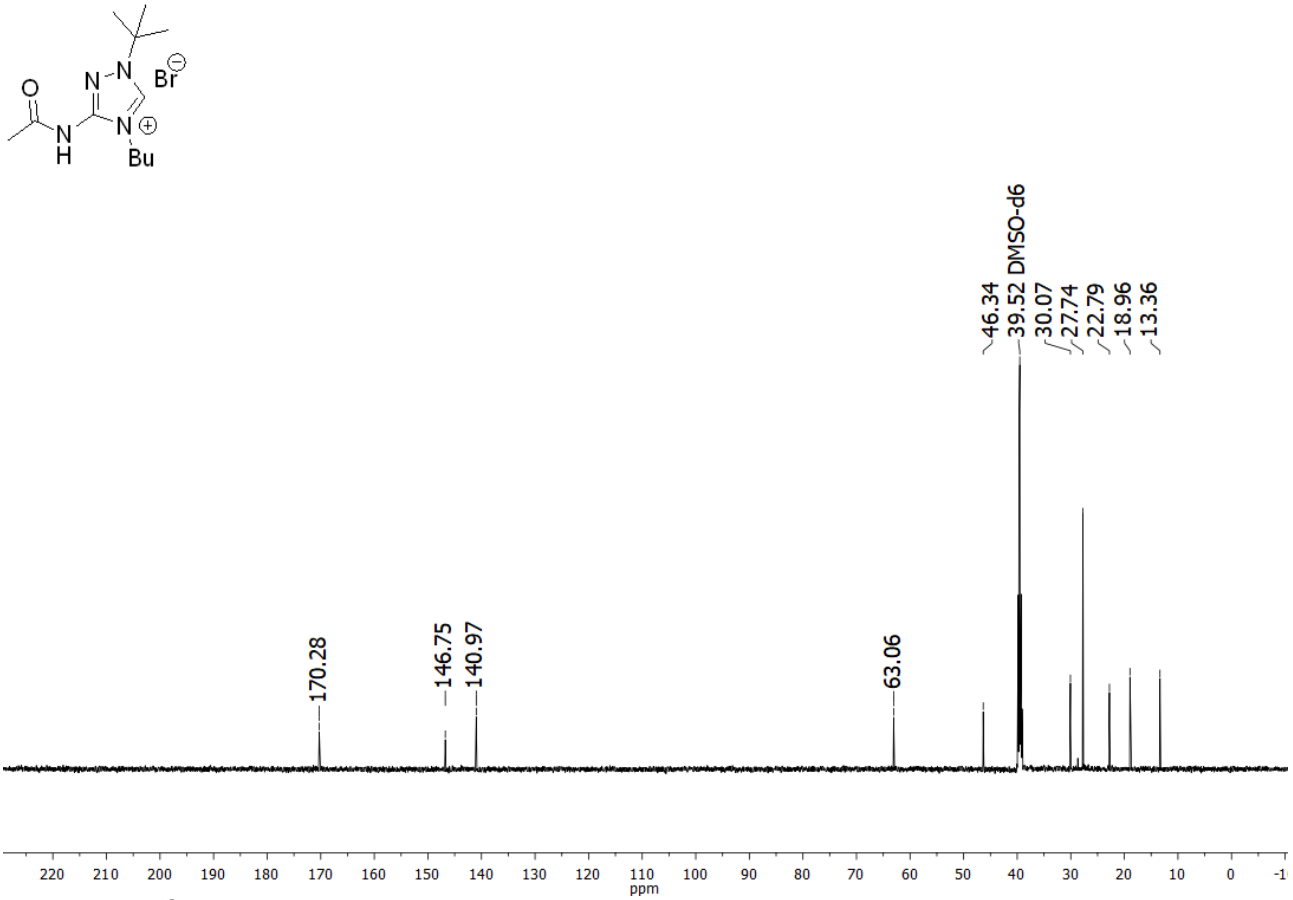

Figure S10 ^{13}C NMR spectrum of **2c** (DMSO-d_6, 125 MHz)

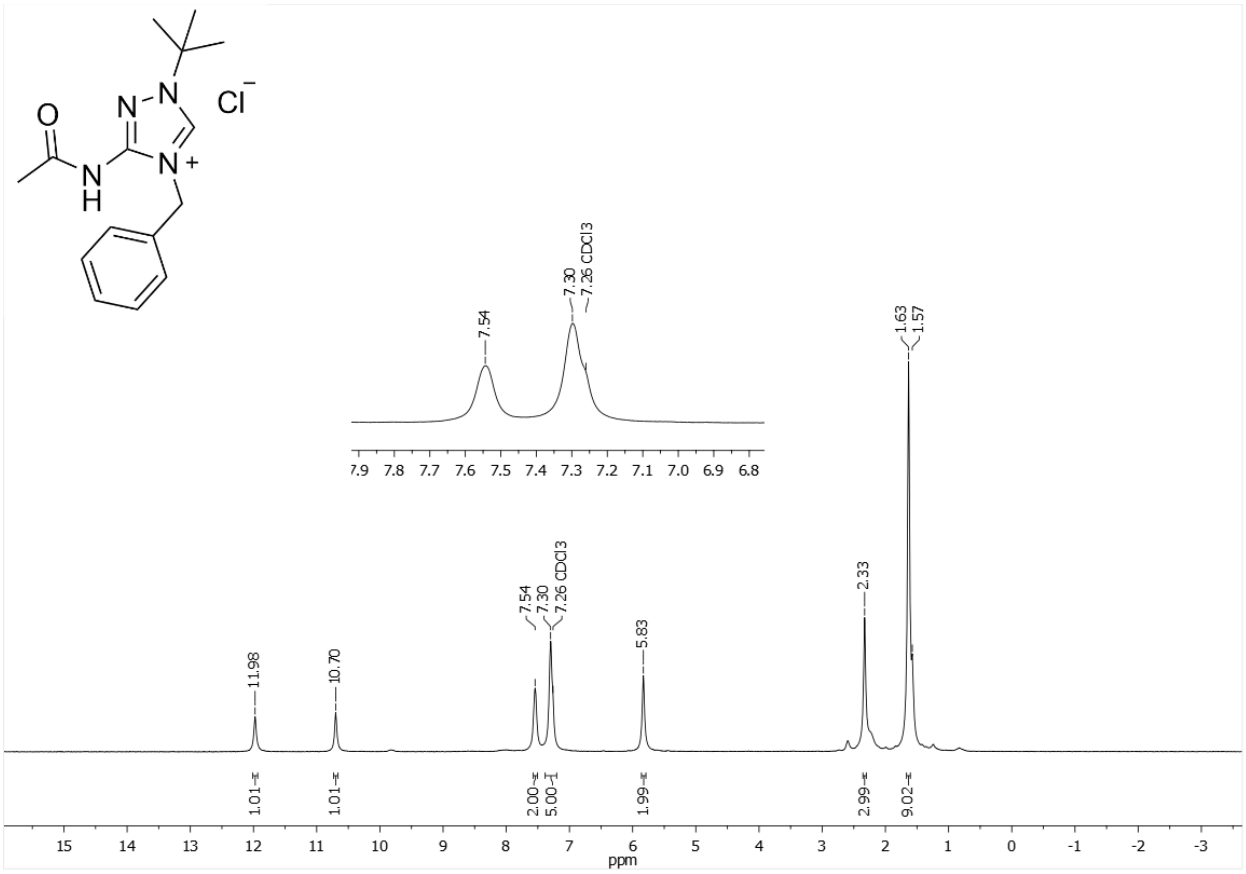

Figure S11 ^{1}H NMR spectrum of **2e** ($CDCl_3$, 300 MHz)

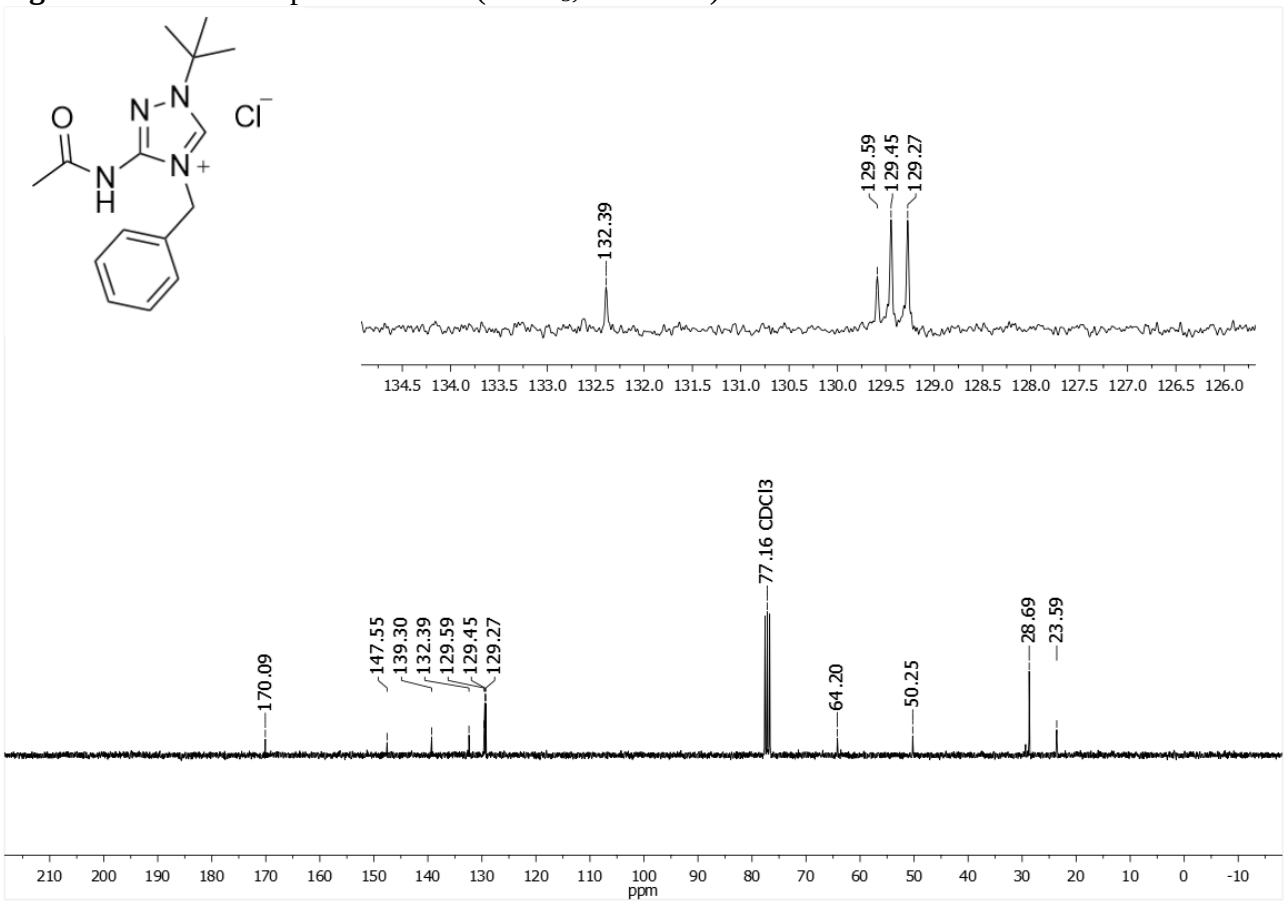

Figure S12 ^{13}C NMR spectrum of **2e** ($CDCl_3$, 75 MHz)

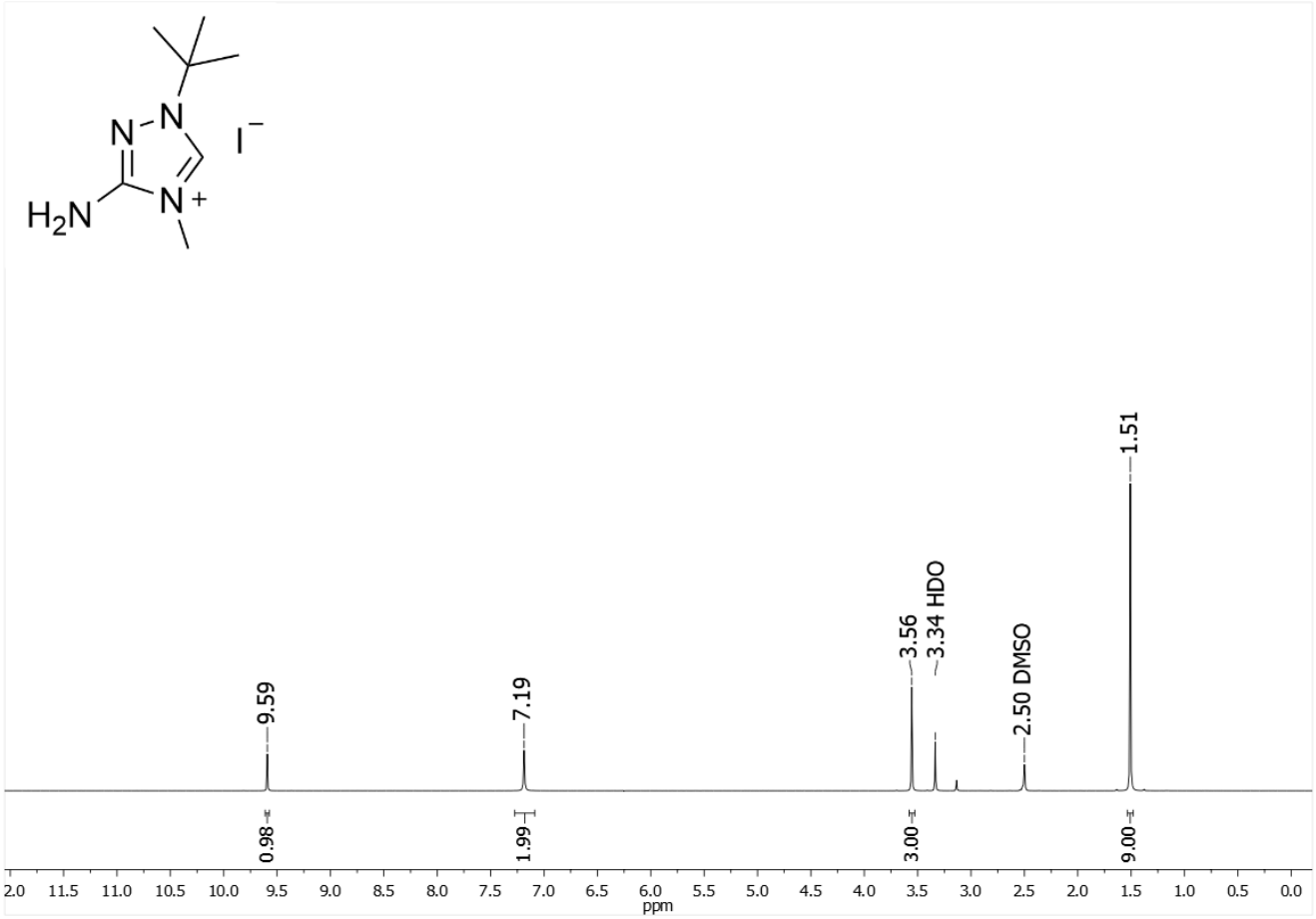

Figure S13 ^{1}H NMR spectrum of **3a** (DMSO-d_6, 500 MHz)

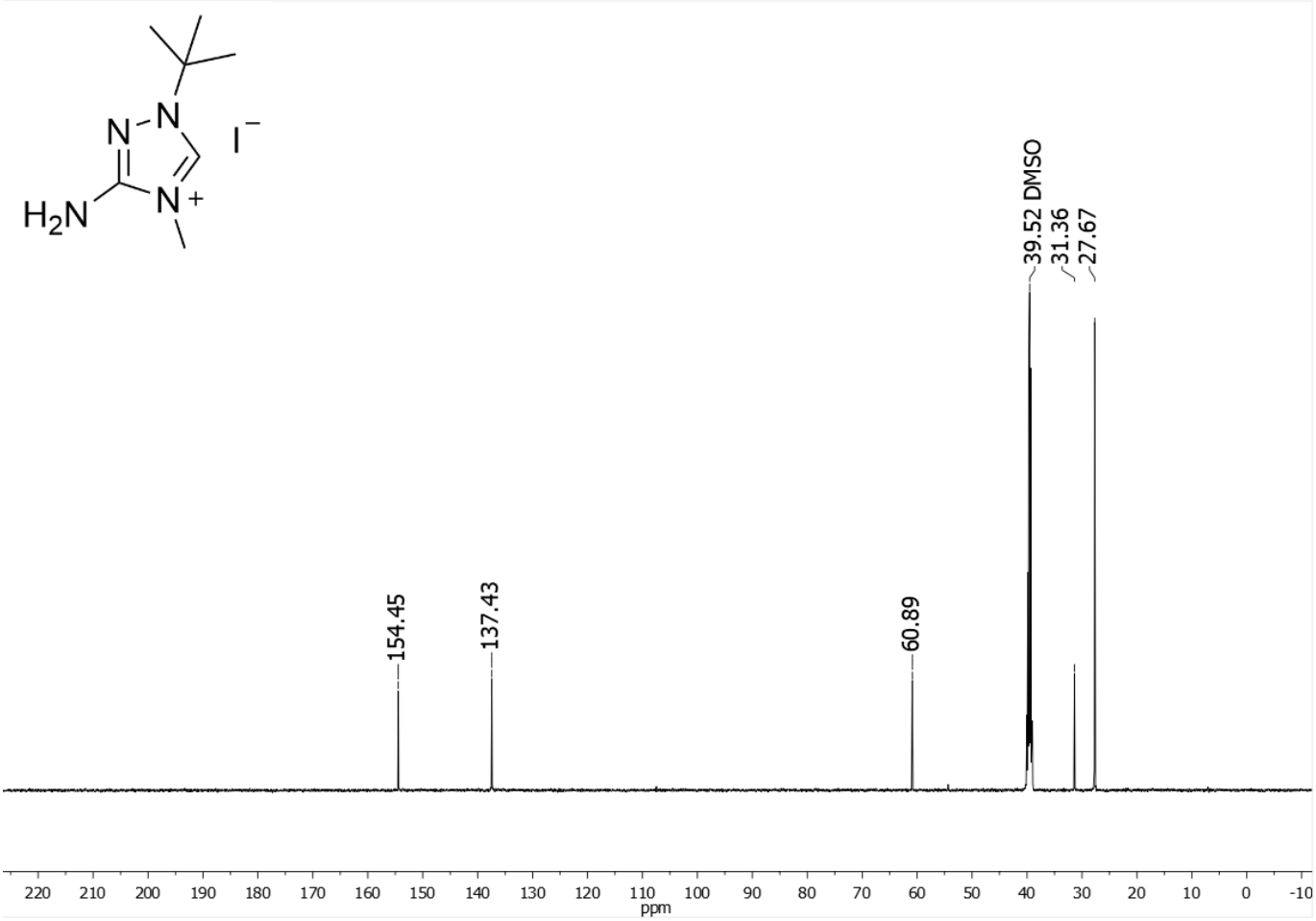

Figure S14 ^{13}C NMR spectrum of **3a** (DMSO-d_6, 125 MHz)

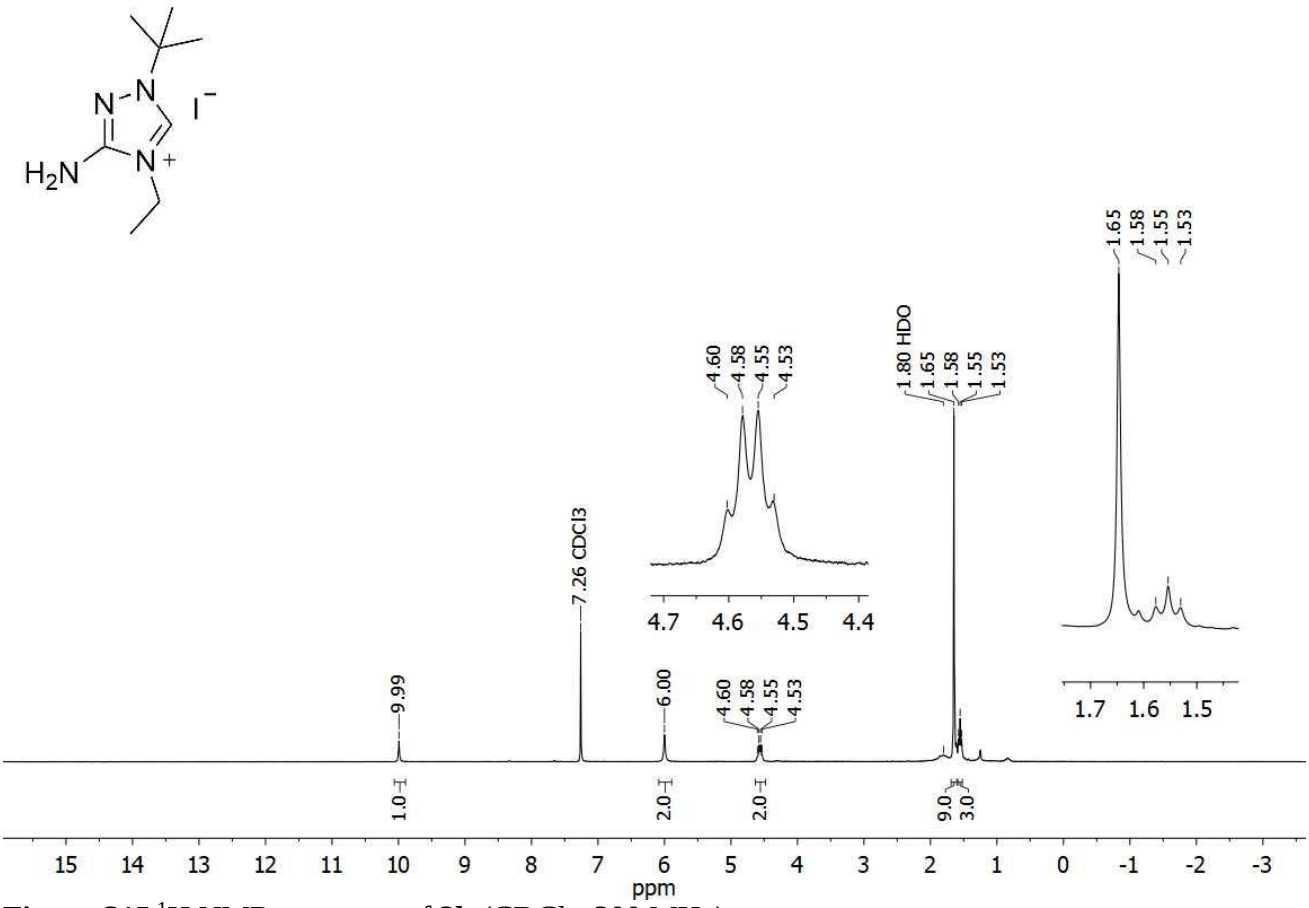

Figure S15 ^{1}H NMR spectrum of **3b** ($CDCl_3$, 300 MHz)

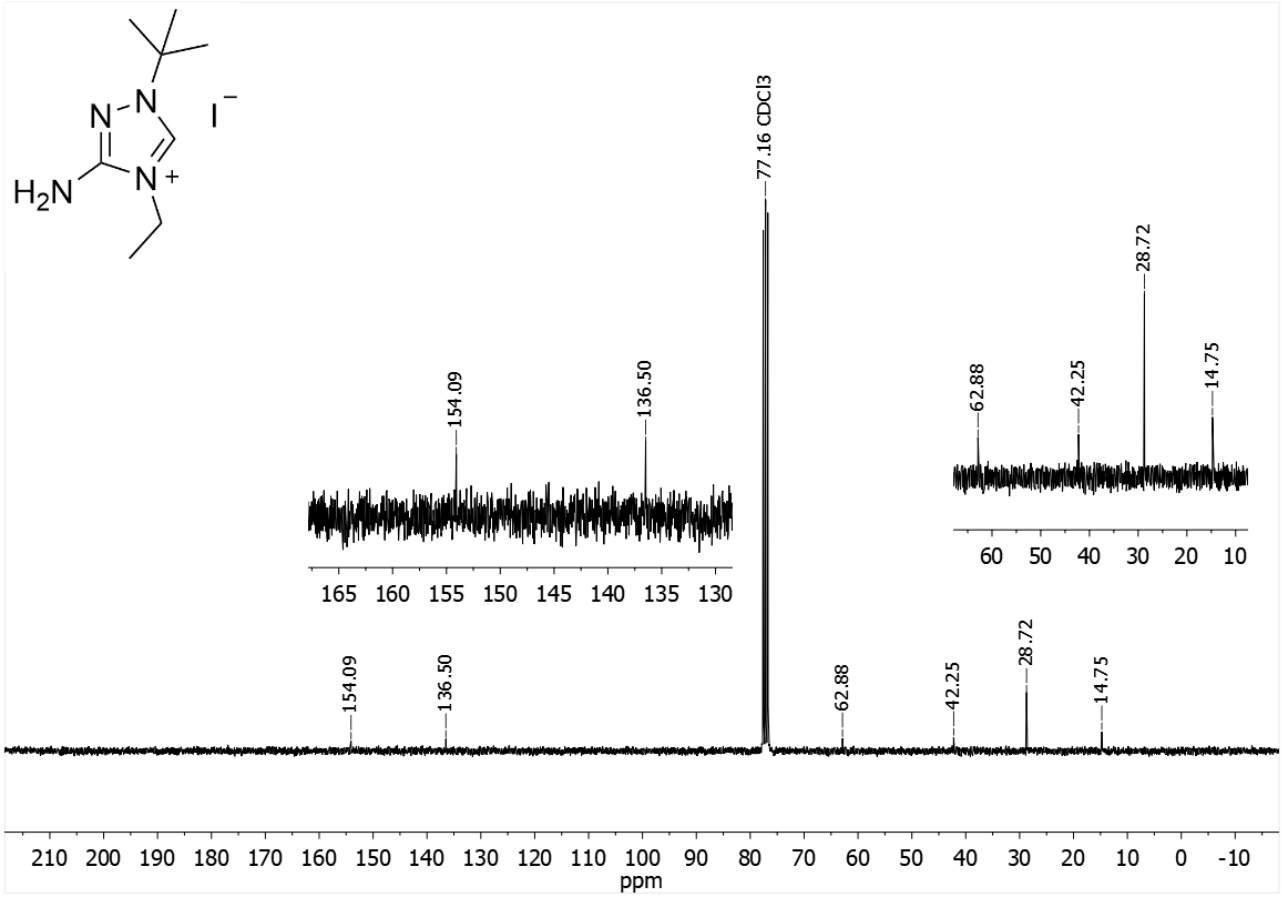

Figure S16 ^{13}C NMR spectrum of **3b** ($CDCl_3$, 75 MHz)

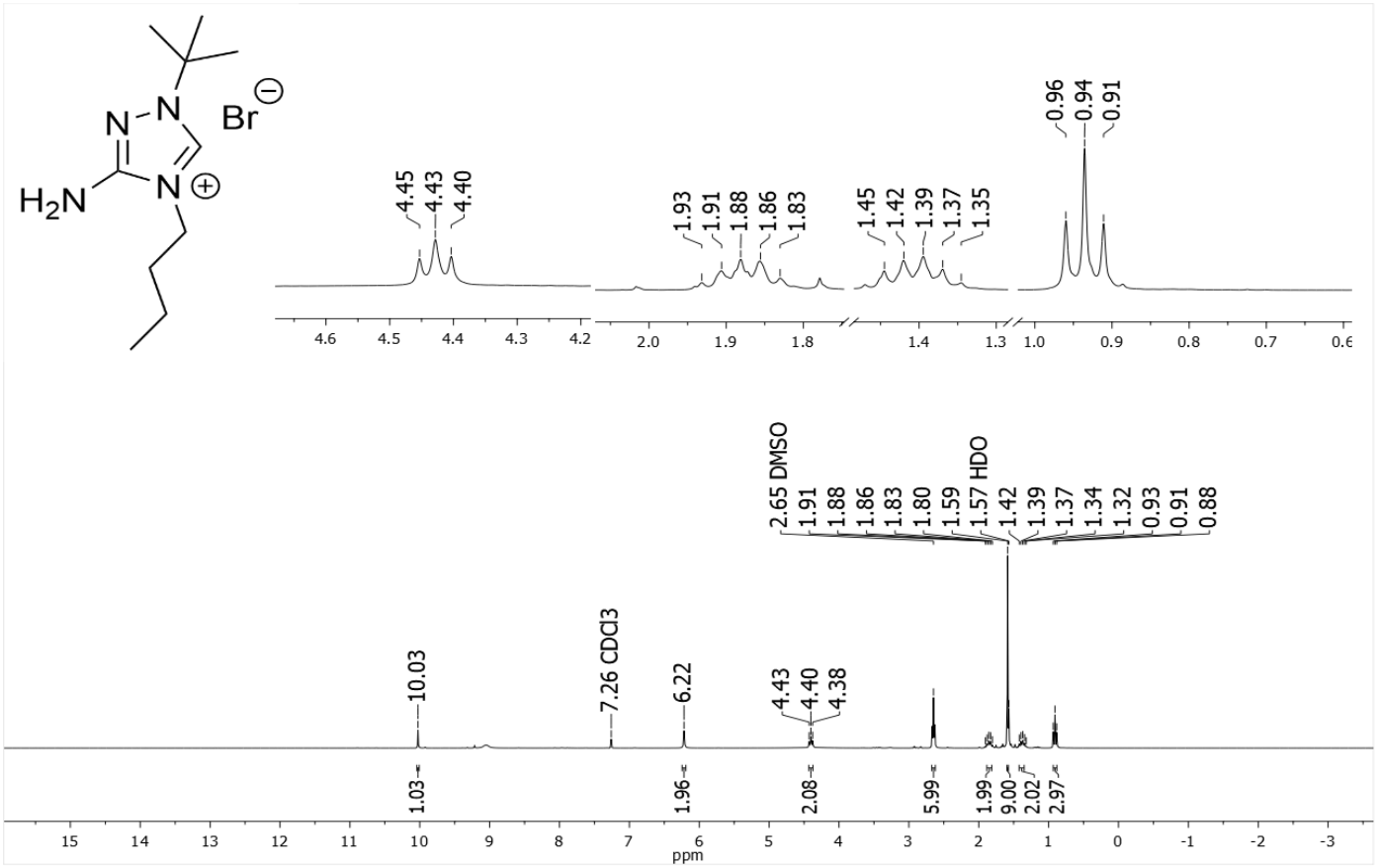

Figure S17 ^{1}H NMR spectrum of **3c** ($CDCl_3$, 300 MHz)

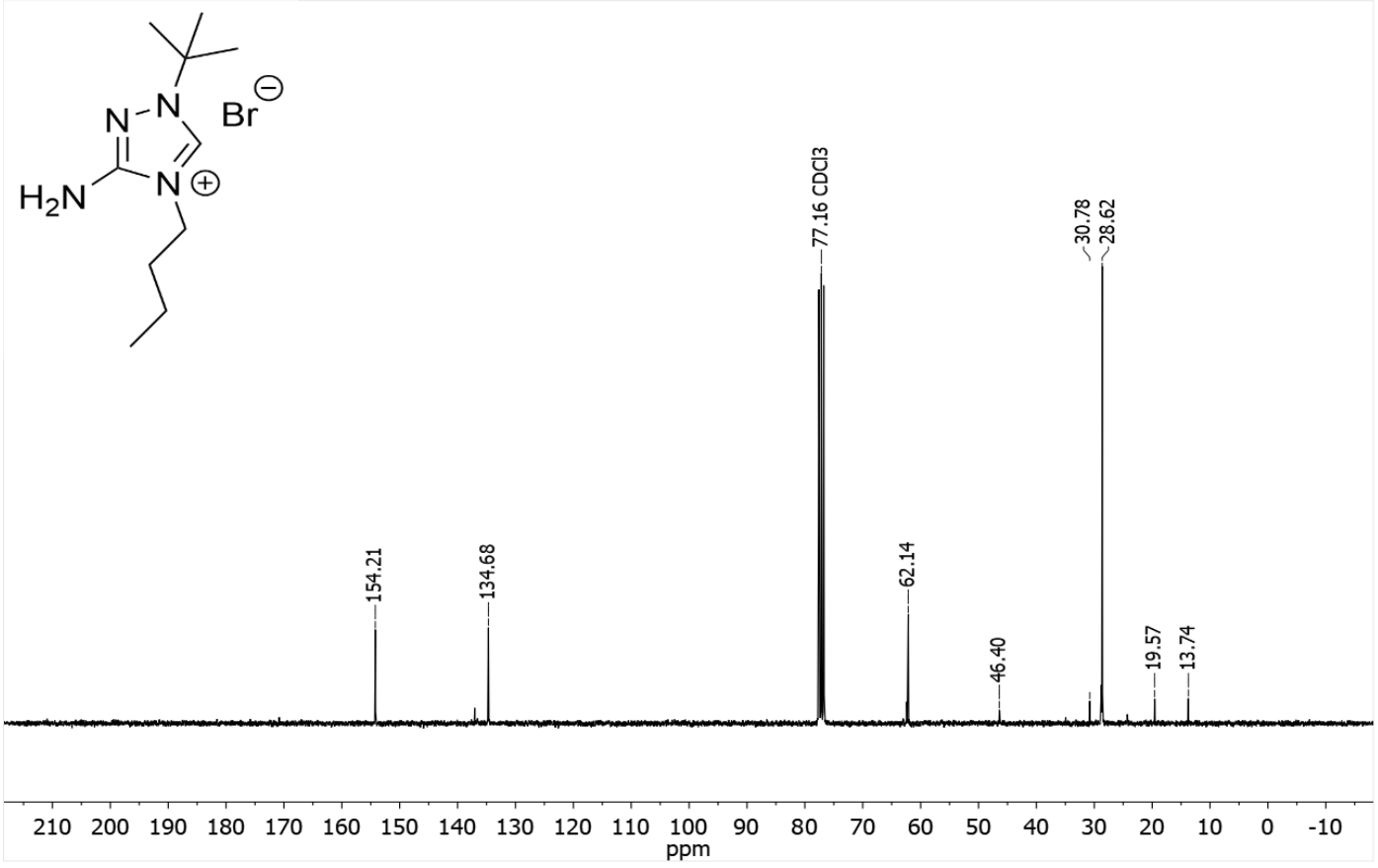

Figure S18 ^{13}C NMR spectrum of **3c** ($CDCl_3$, 75 MHz)

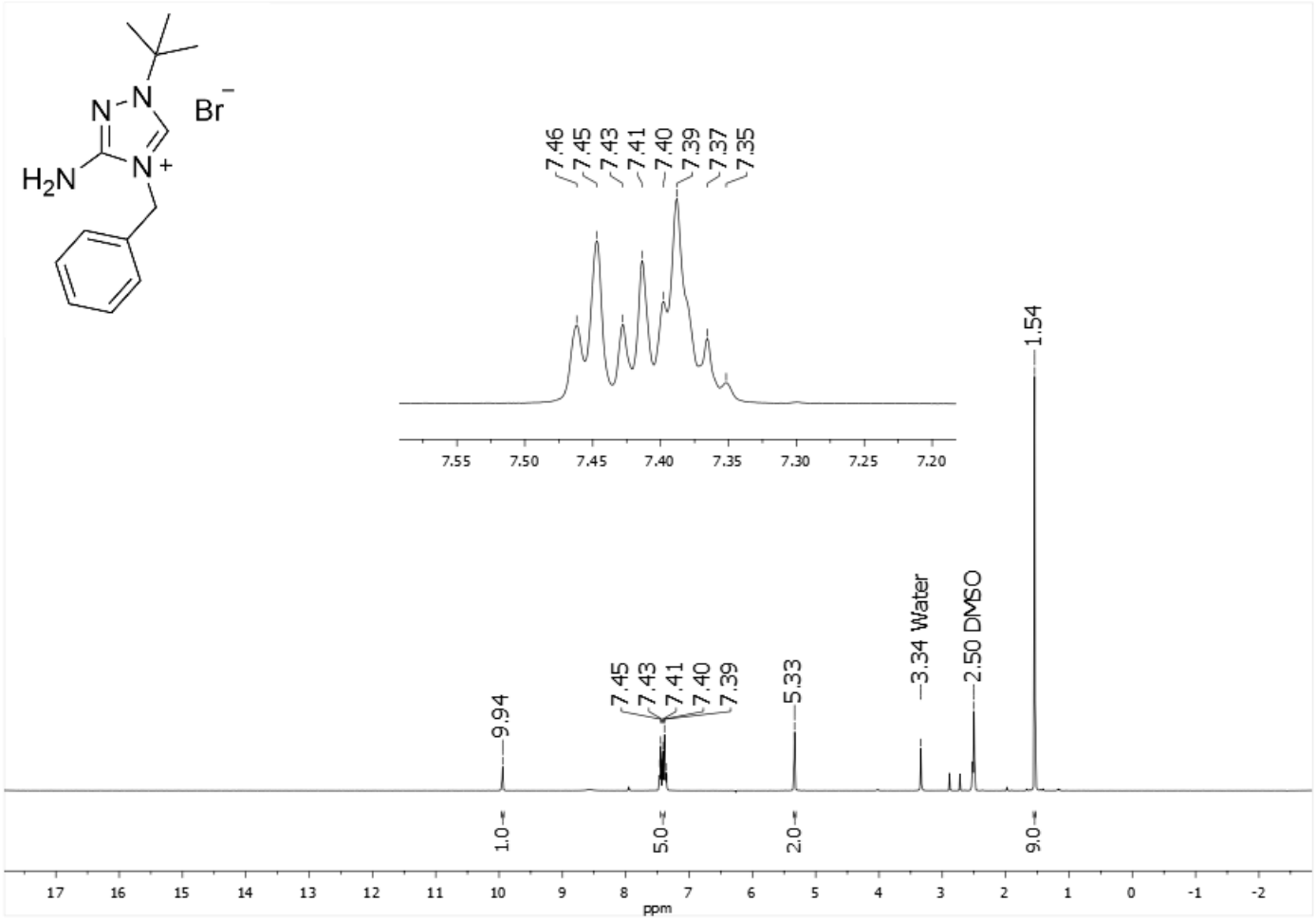

Figure S19 ^{1}H NMR spectrum of **3d** (DMSO-d_6, 500 MHz)

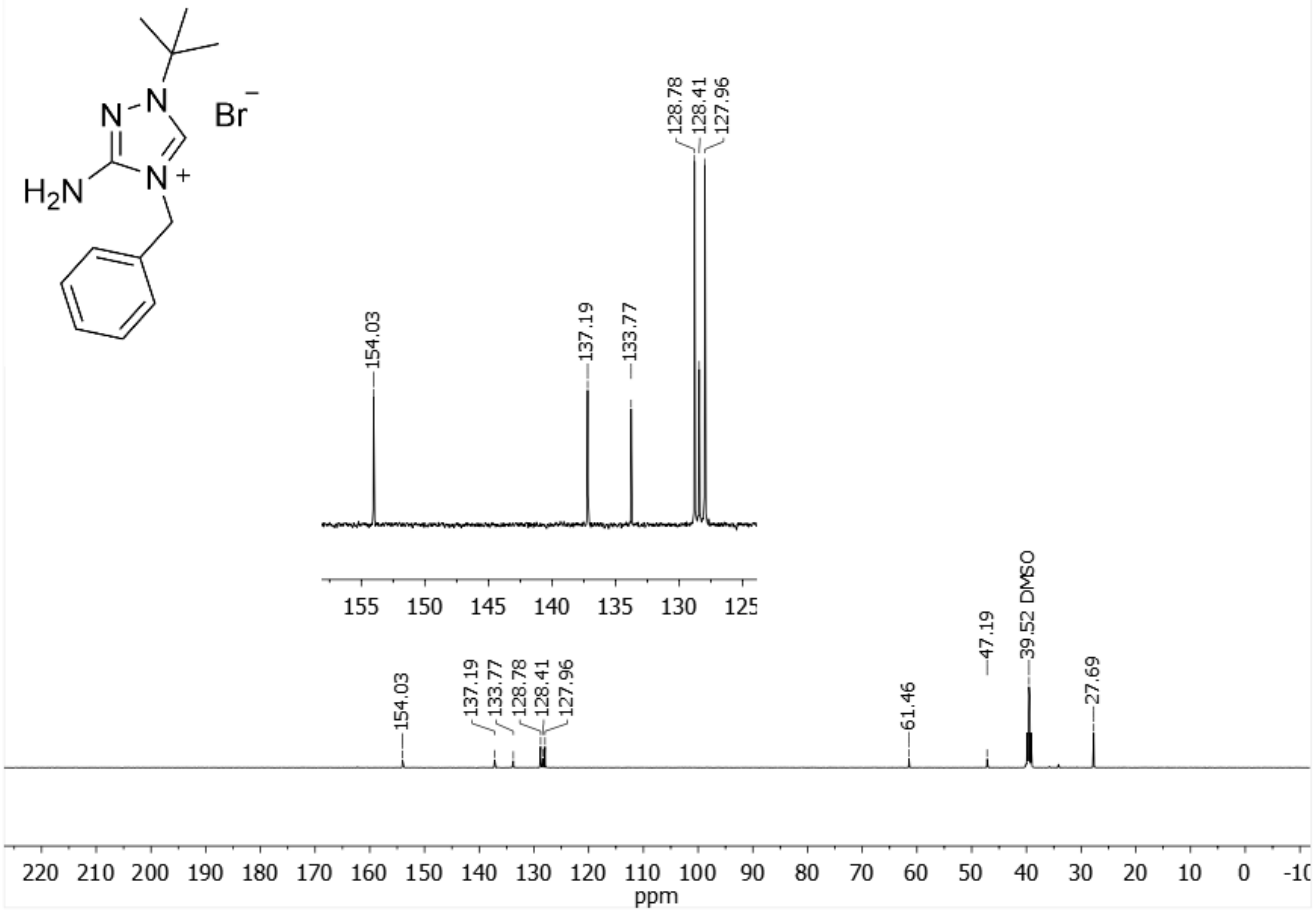

Figure S20 ^{13}C NMR spectrum of **3d** (DMSO-d_6, 125 MHz)

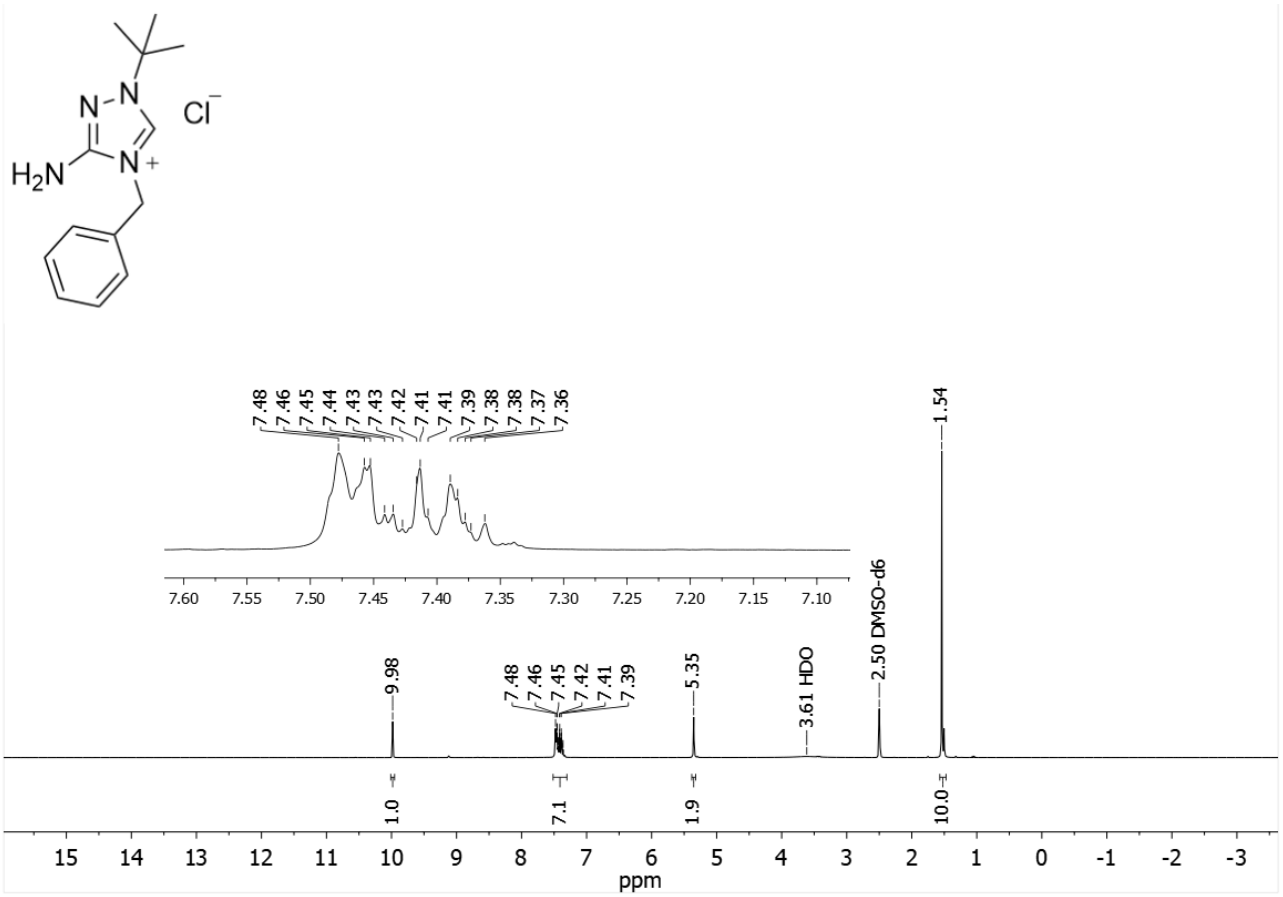

Figure S21 ^{1}H NMR spectrum of **3e** (DMSO-d_6, 300 MHz)

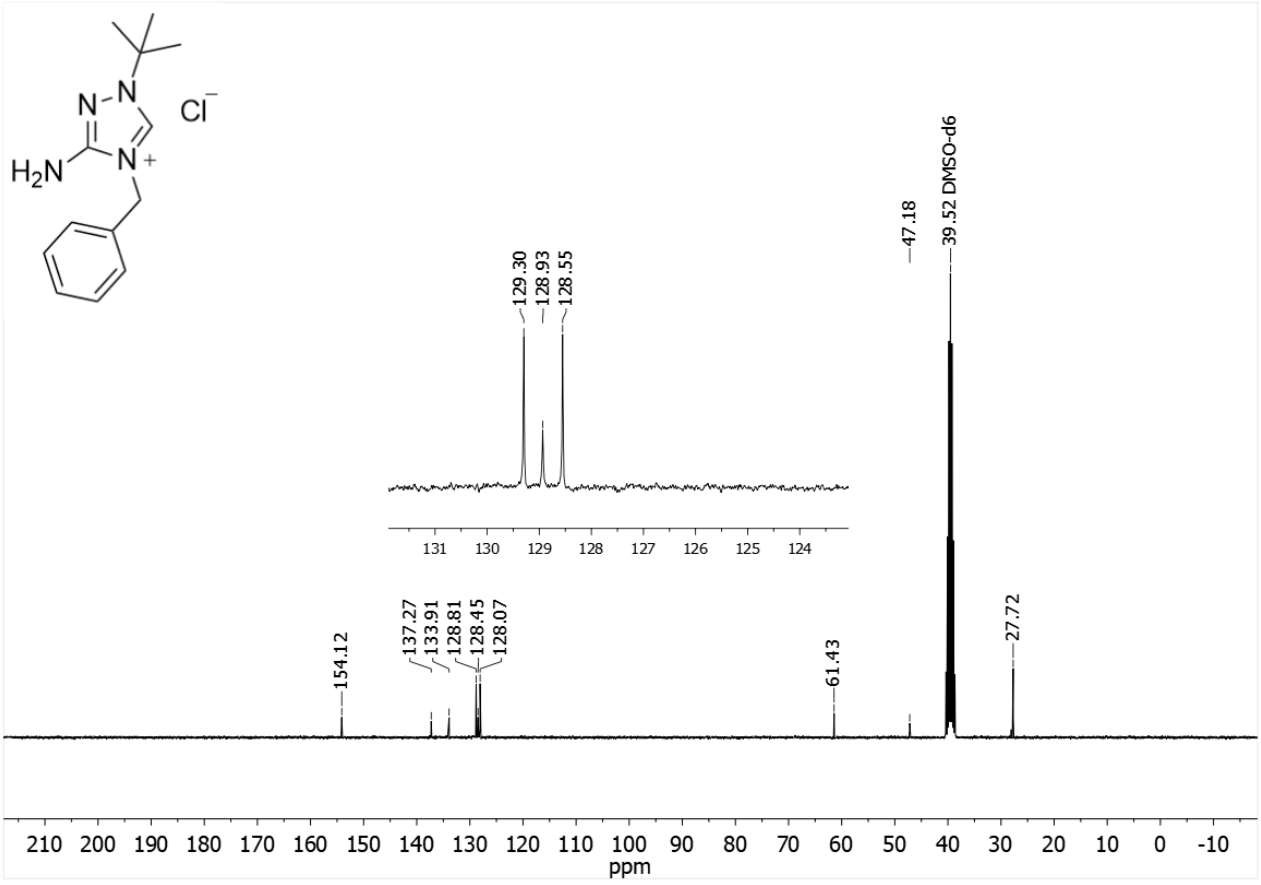

Figure S22 ^{13}C NMR spectrum of **3e** (DMSO-d_6, 75 MHz)

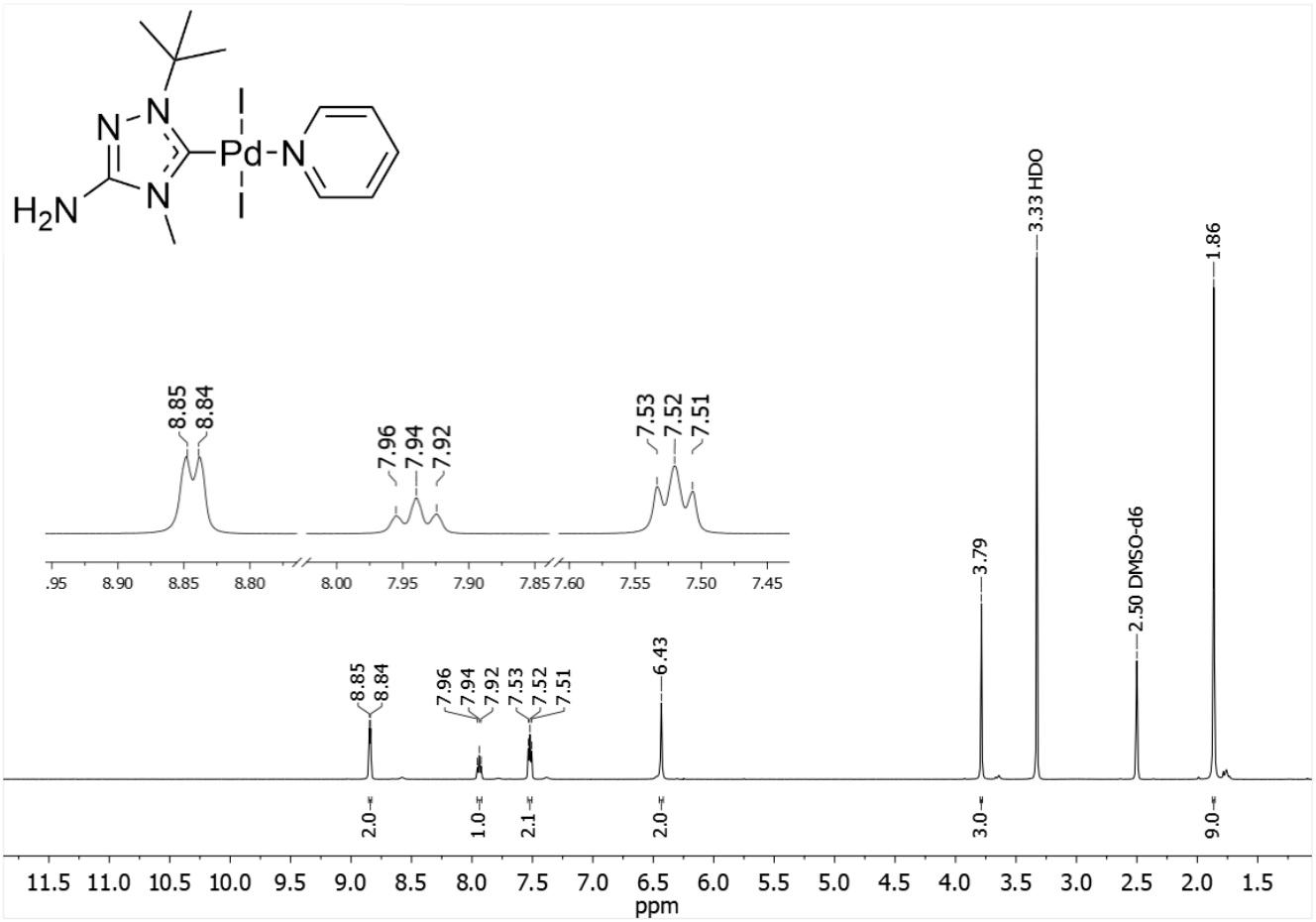

Figure S23 ^{1}H NMR spectrum of **4a** (DMSO-d_6, 500 MHz)

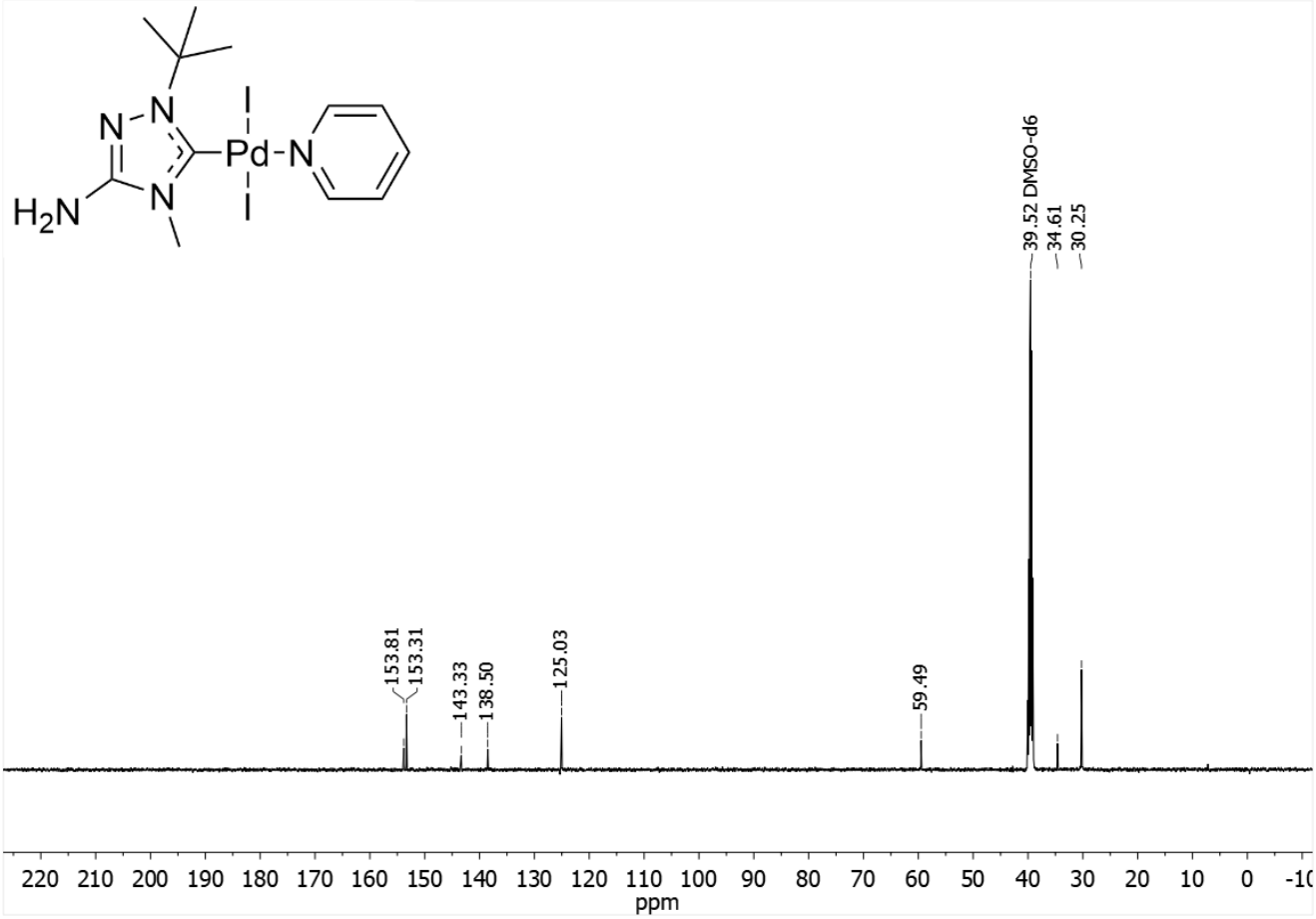

Figure S24 ^{13}C NMR spectrum of **4a** (DMSO-d_6, 125 MHz)

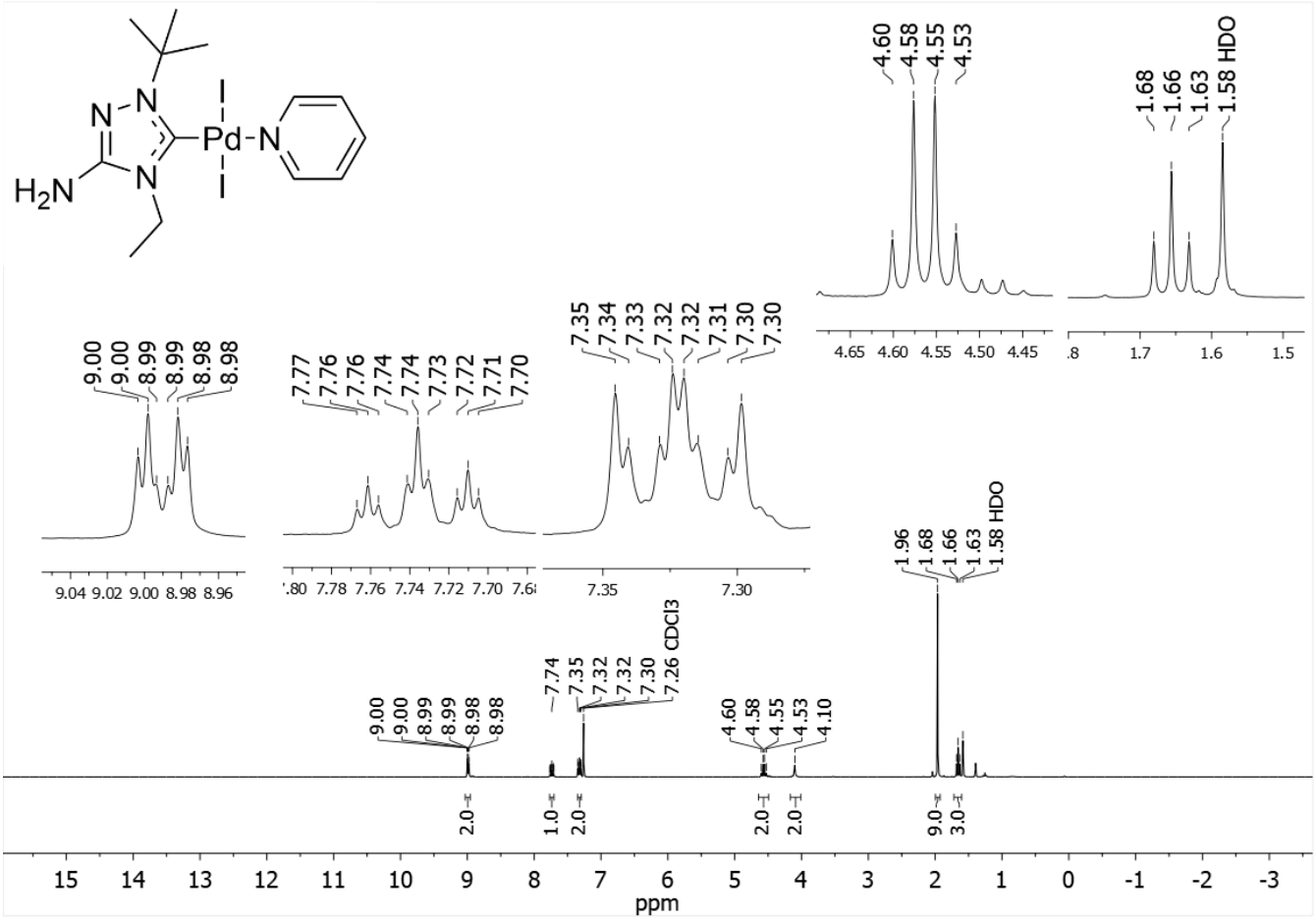

Figure S25 ^{1}H NMR spectrum of **4b** ($CDCl_3$, 300 MHz)

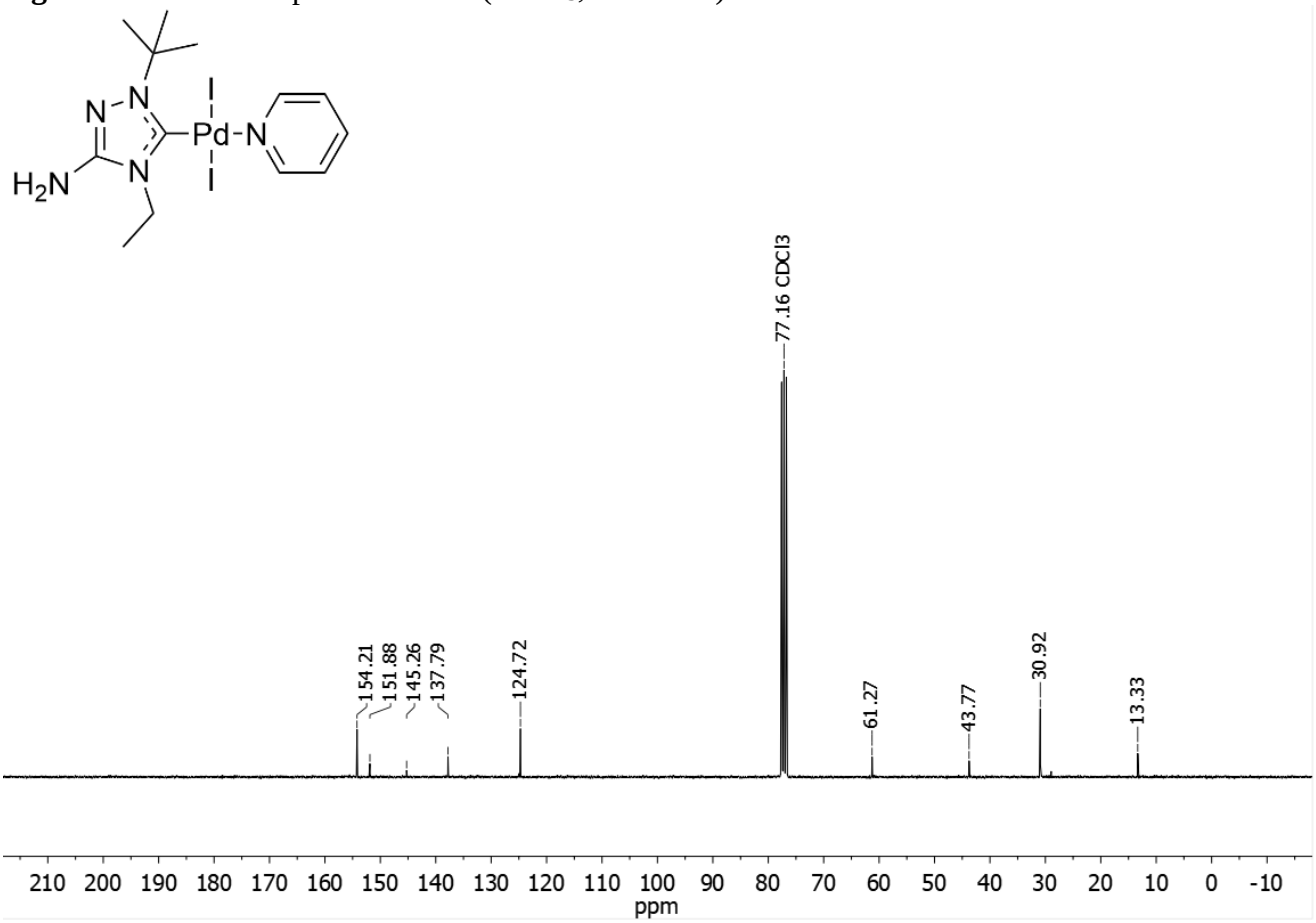

Figure S26 ^{13}C NMR spectrum of **4b** ($CDCl_3$, 75 MHz)

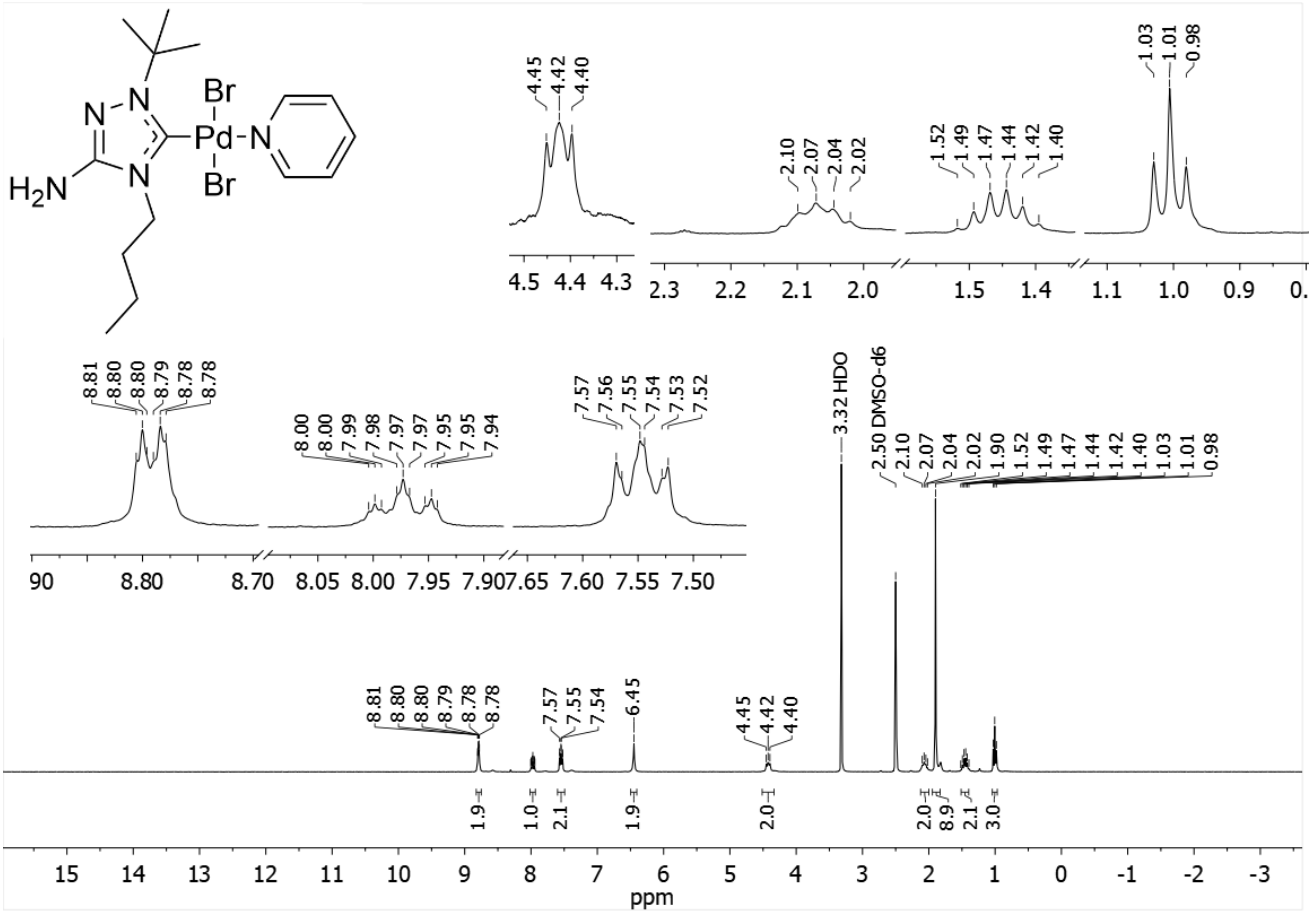

Figure S27 ^{1}H NMR spectrum of **4c** (DMSO-d_6, 300 MHz)

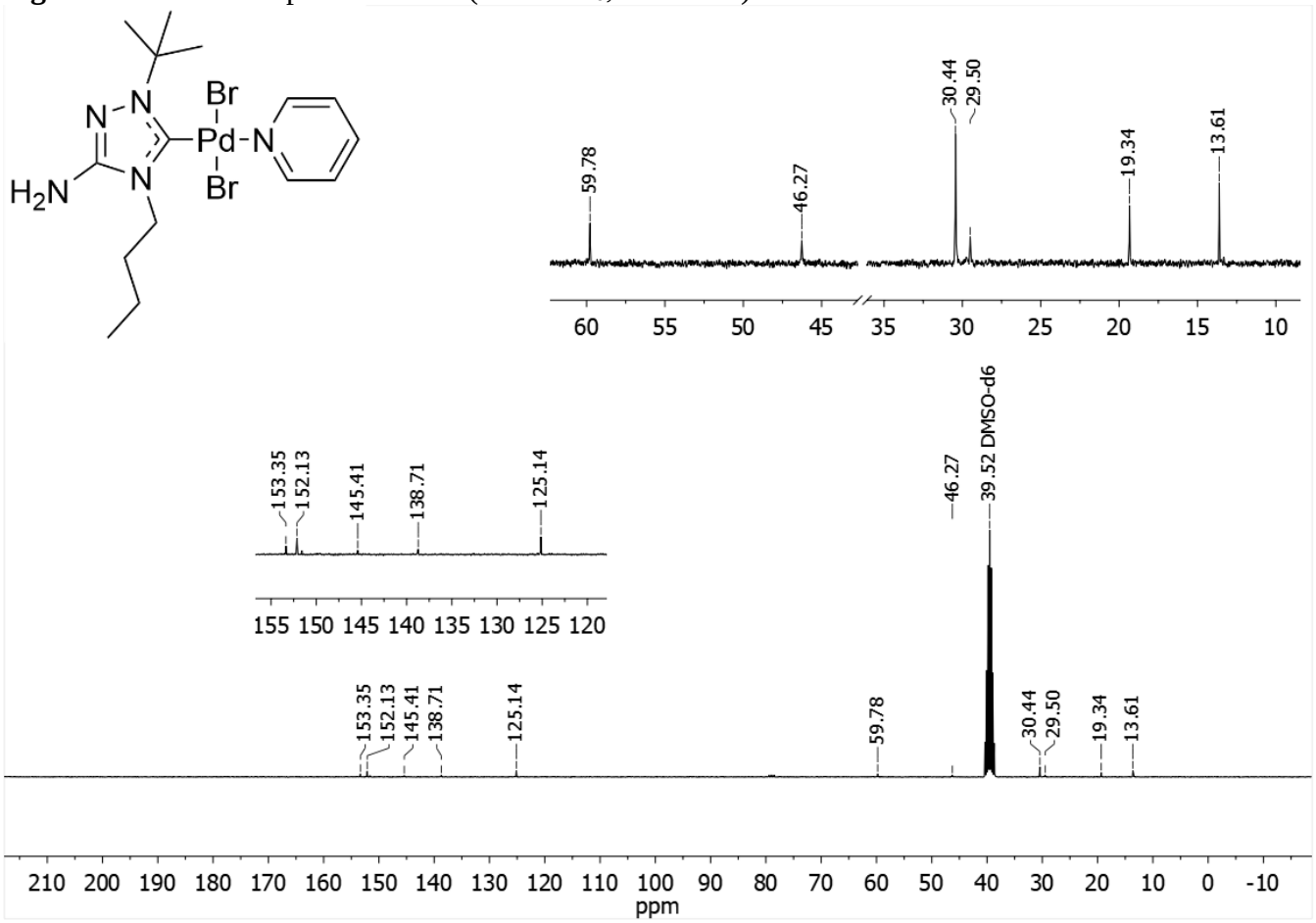

Figure S28 ^{13}C NMR spectrum of **4c** (DMSO-d_6, 75 MHz)

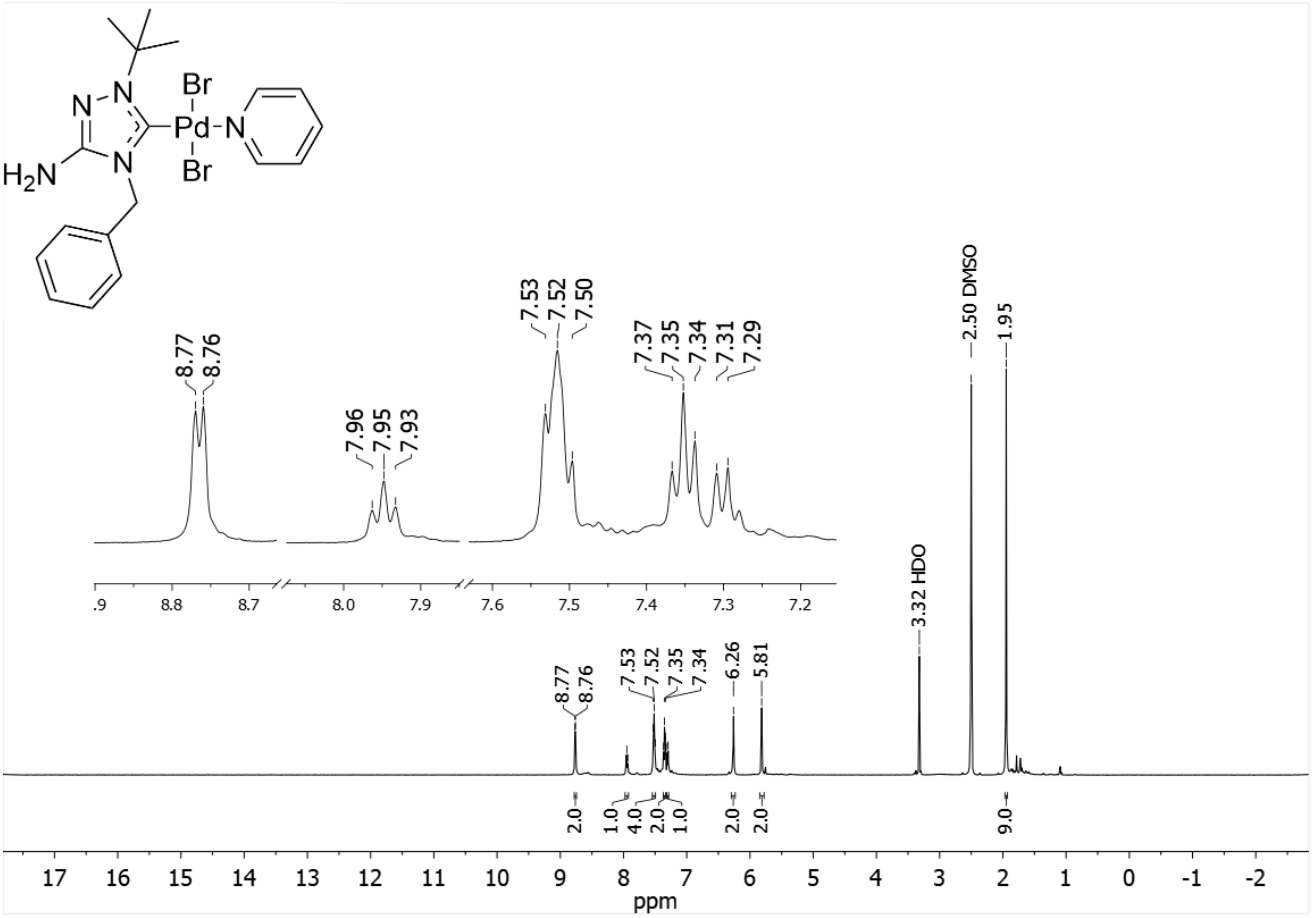

Figure S29 ^{1}H NMR spectrum of **4d** (DMSO-d_6, 500 MHz)

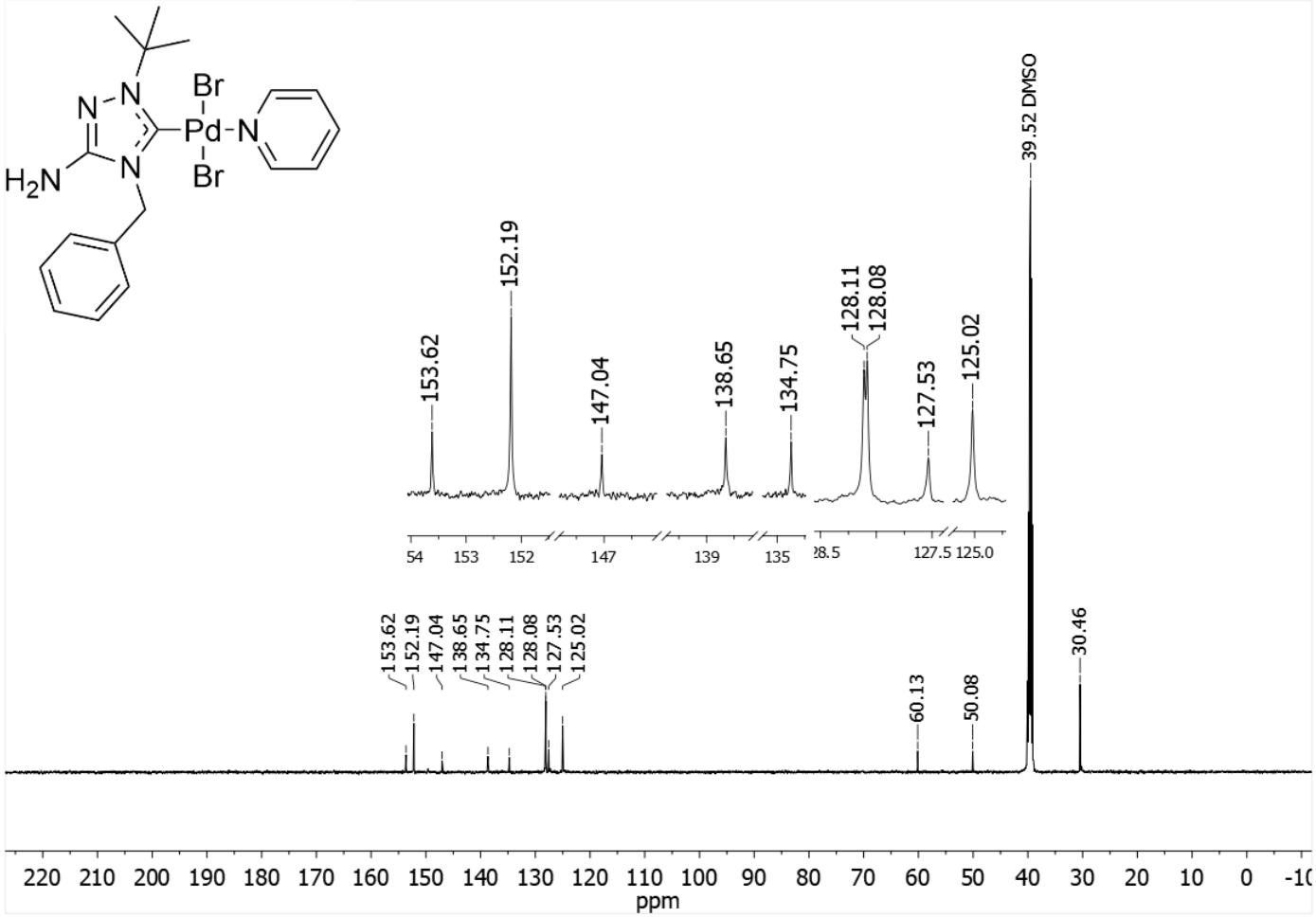

Figure S30 ^{13}C NMR spectrum of **4d** (DMSO-d_6, 125 MHz)

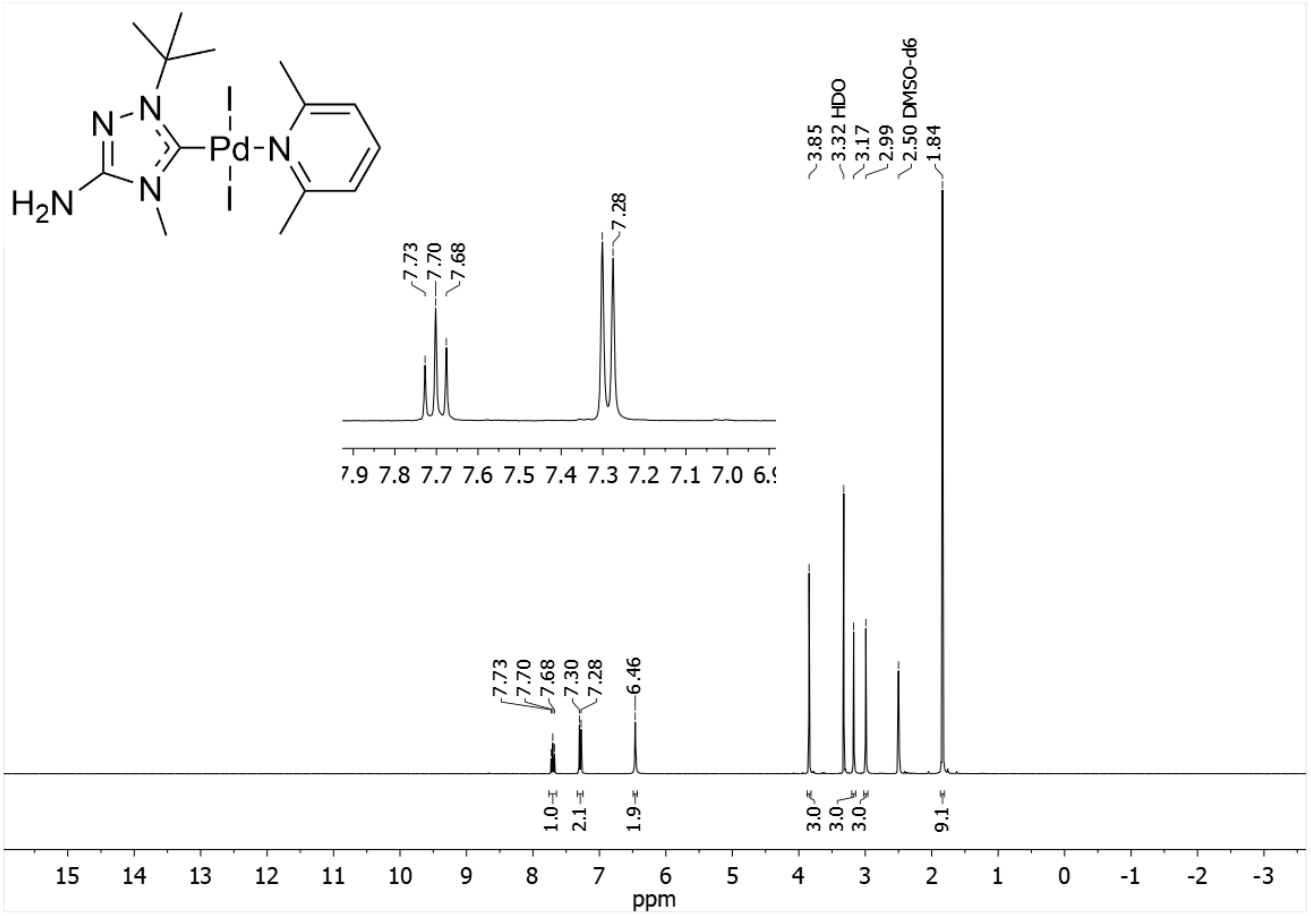

Figure S31 ^{1}H NMR spectrum of **4e** (DMSO-d_6, 300 MHz)

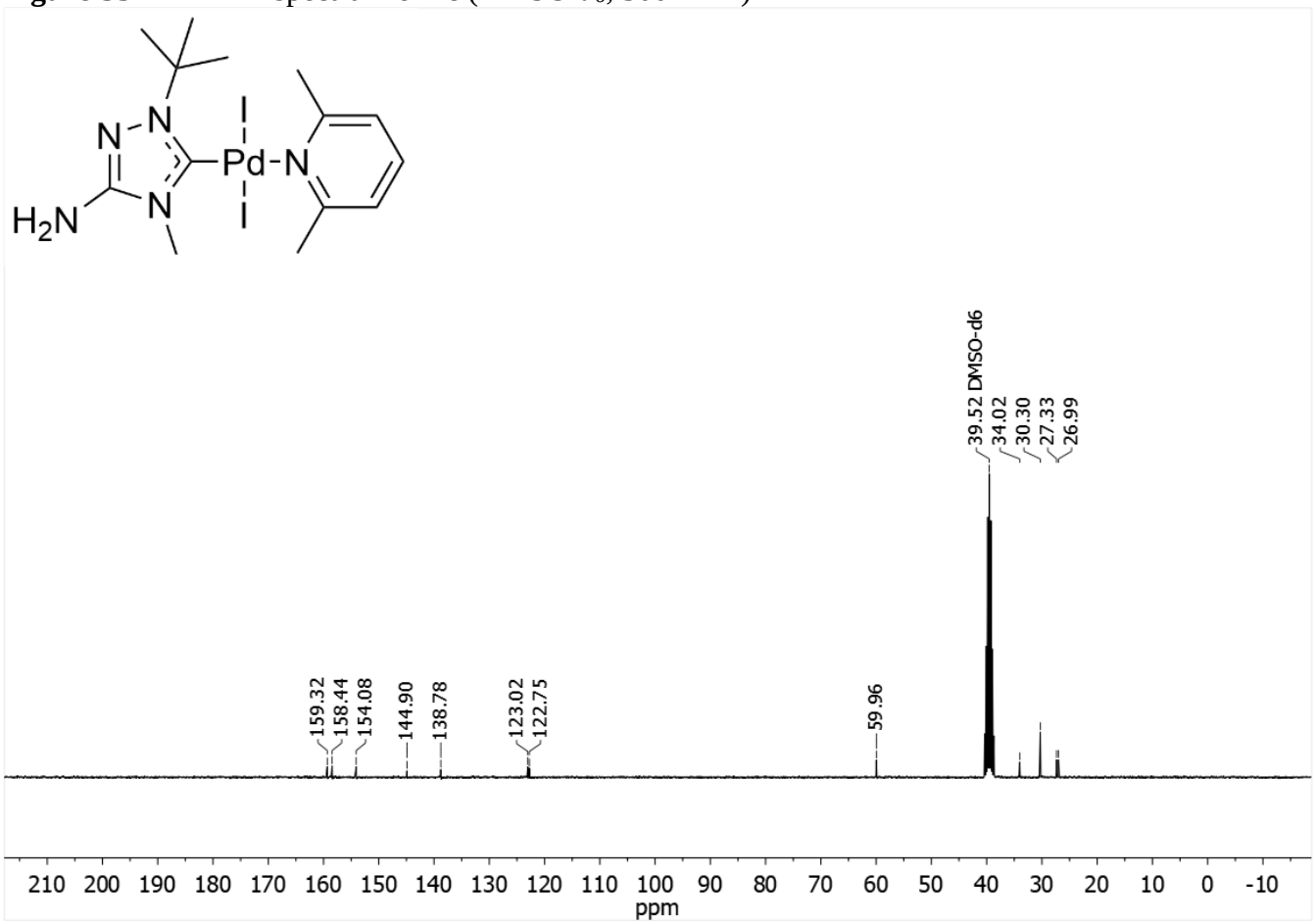

Figure S32 ^{13}C NMR spectrum of **4e** (DMSO-d_6, 75 MHz)

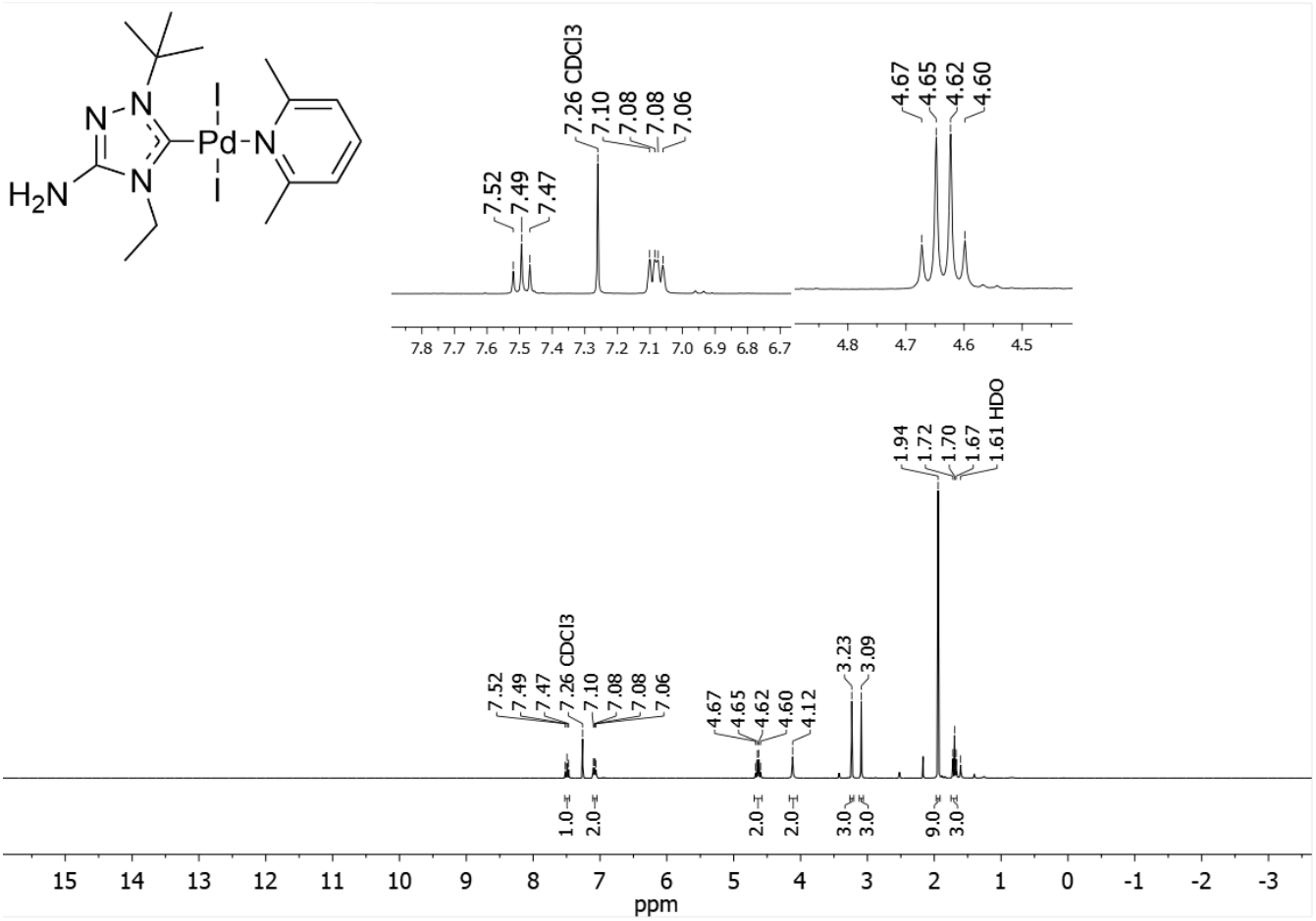

Figure S33 ^{1}H NMR spectrum of **4f** ($CDCl_3$, 300 MHz)

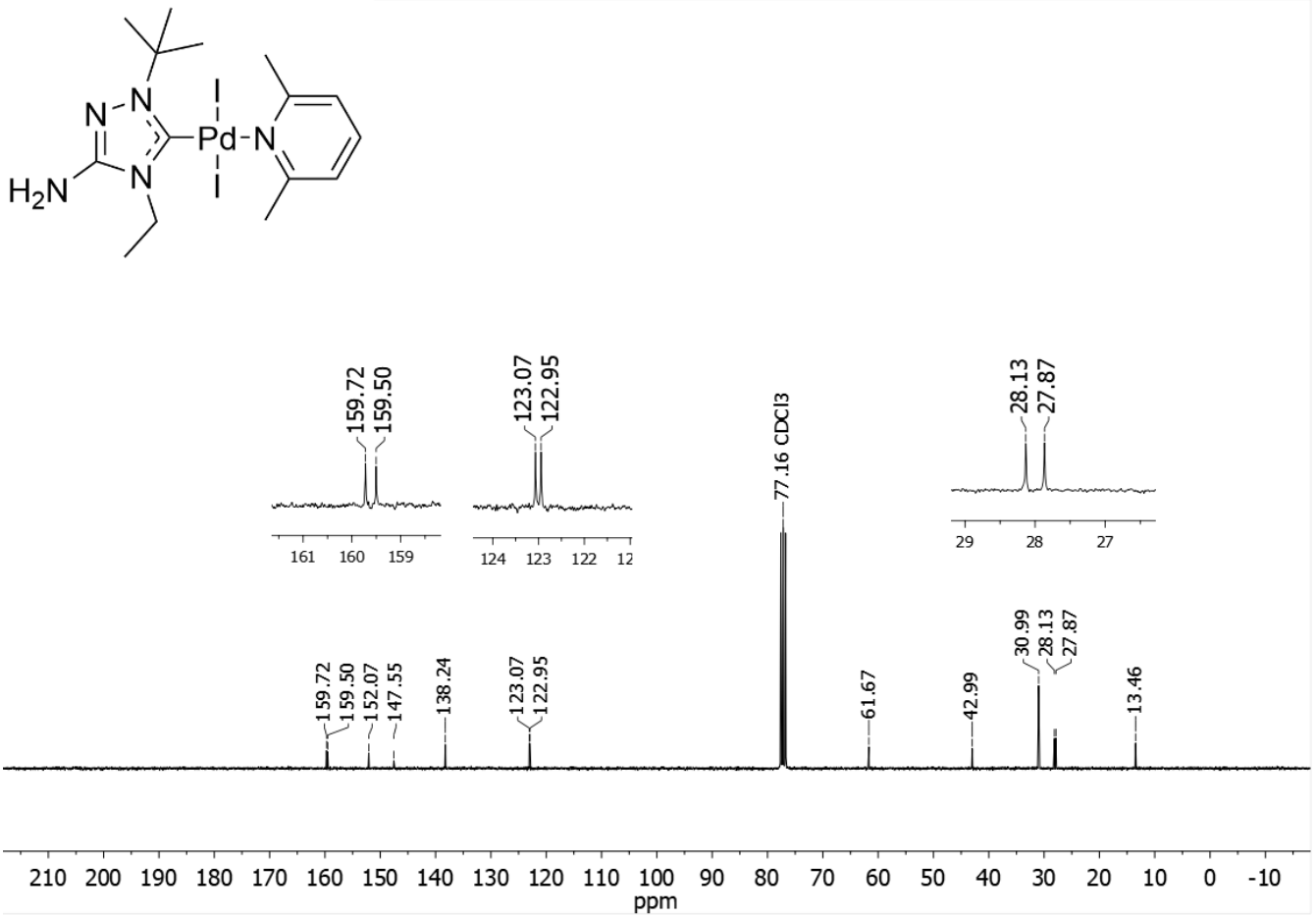

Figure S34 ^{13}C NMR spectrum of **4f** ($CDCl_3$, 75 MHz)

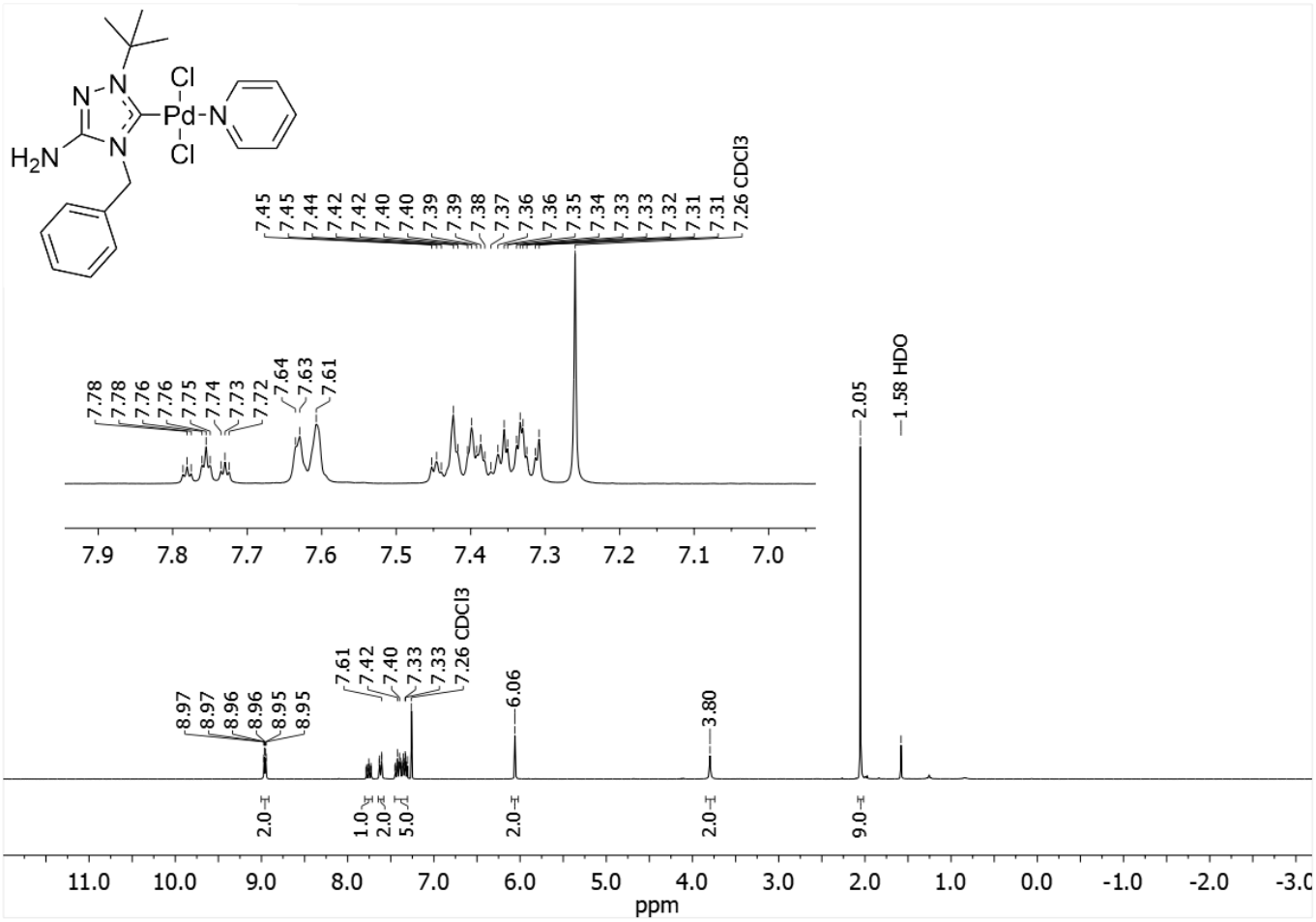

Figure S35 ^{1}H NMR spectrum of **4g** ($CDCl_3$, 300 MHz)

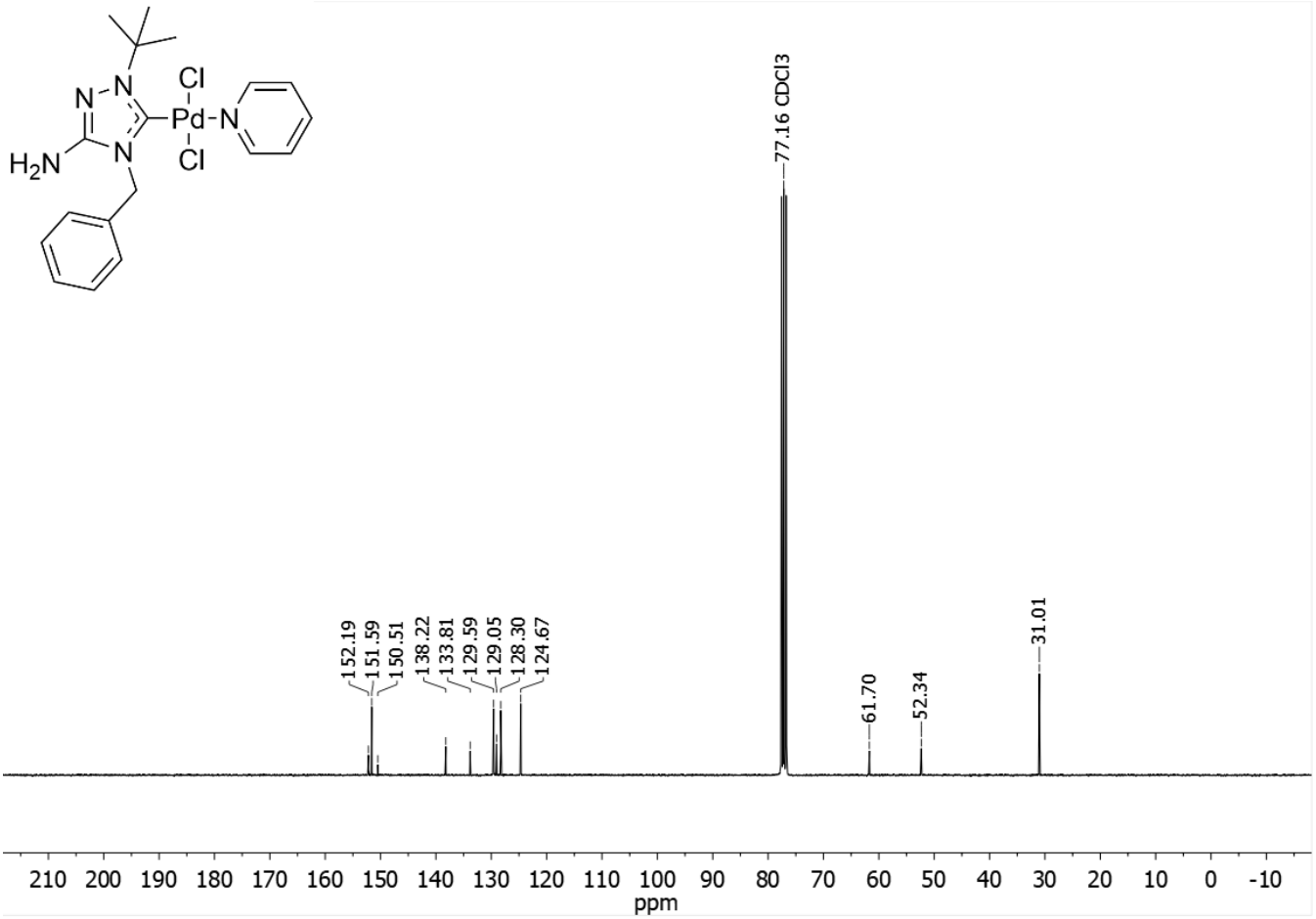

Figure S36 ^{13}C NMR spectrum of **4g** ($CDCl_3$, 75 MHz)

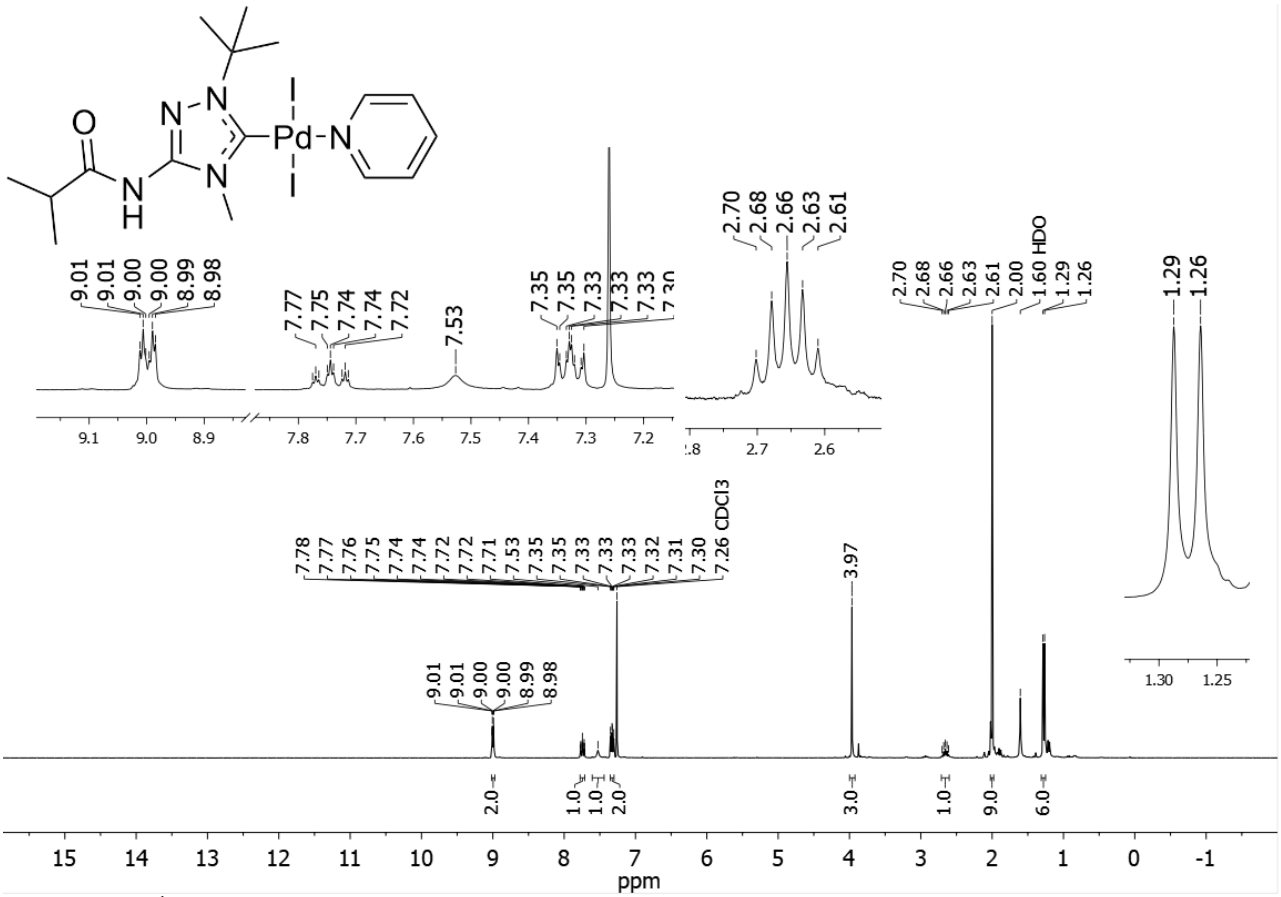

Figure S37 ^{1}H NMR spectrum of **5a** ($CDCl_3$, 300 MHz)

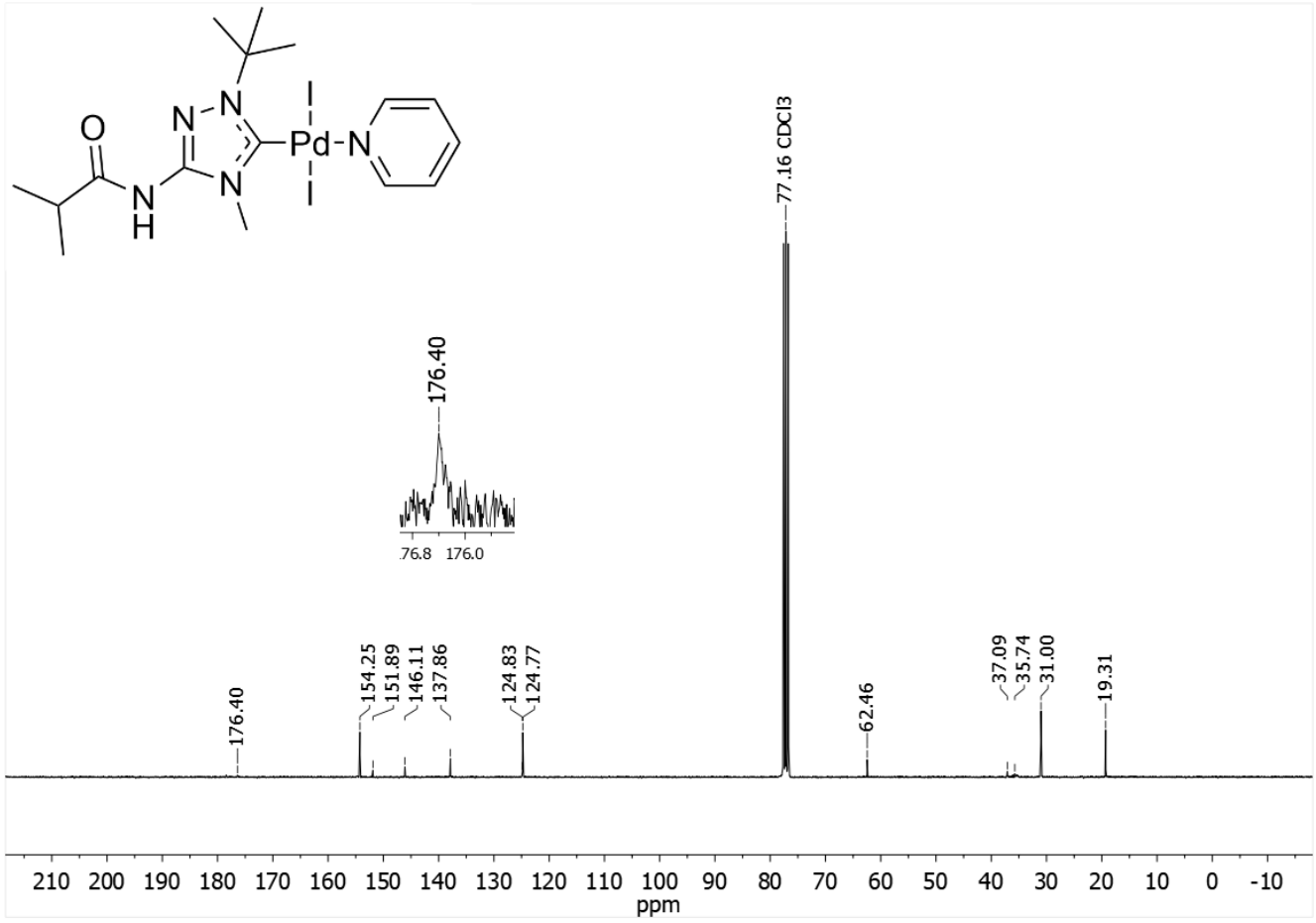

Figure S38 ^{13}C NMR spectrum of **5a** ($CDCl_3$, 75 MHz)

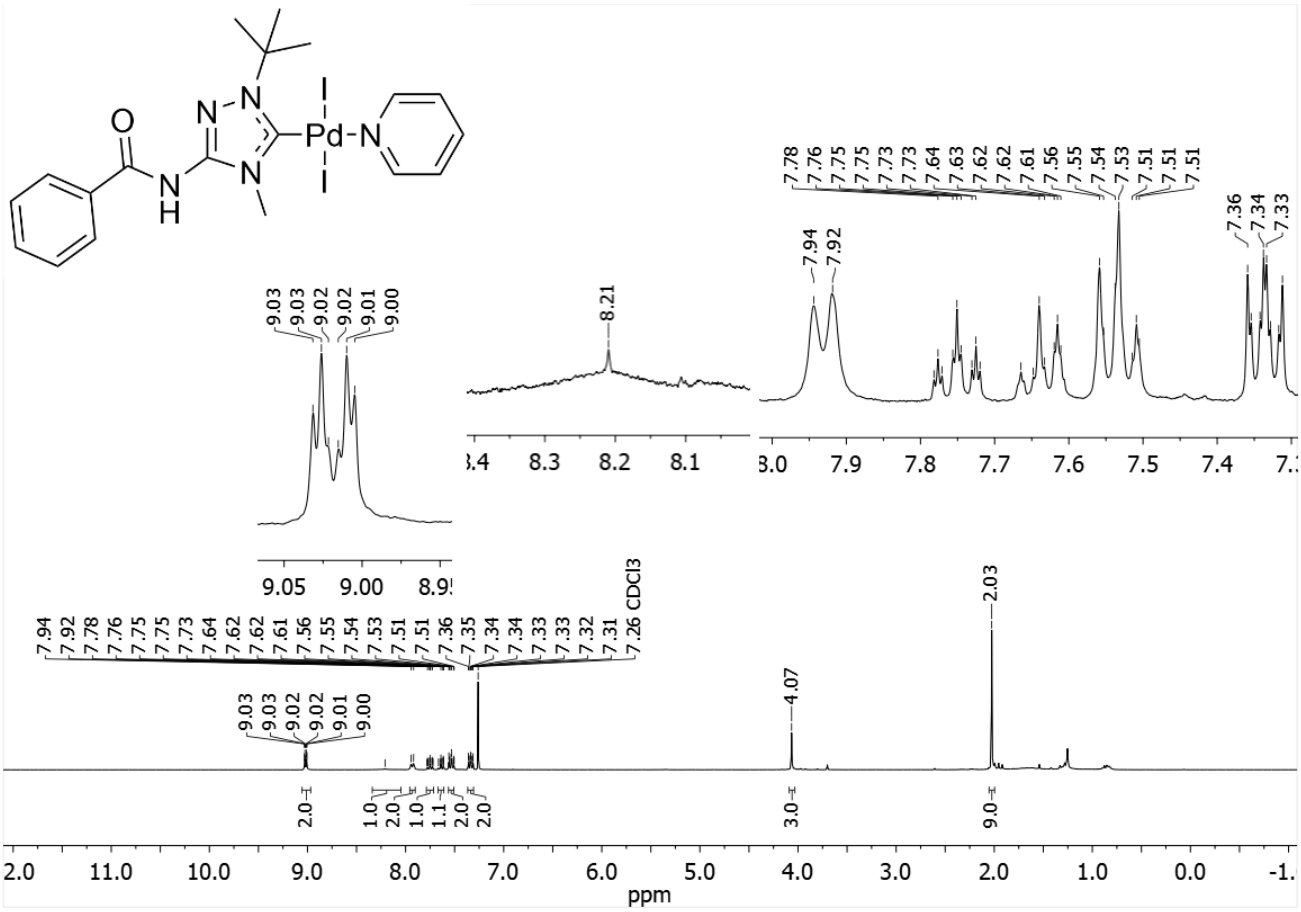

Figure S39 ^{1}H NMR spectrum of **5b** ($CDCl_3$, 300 MHz)

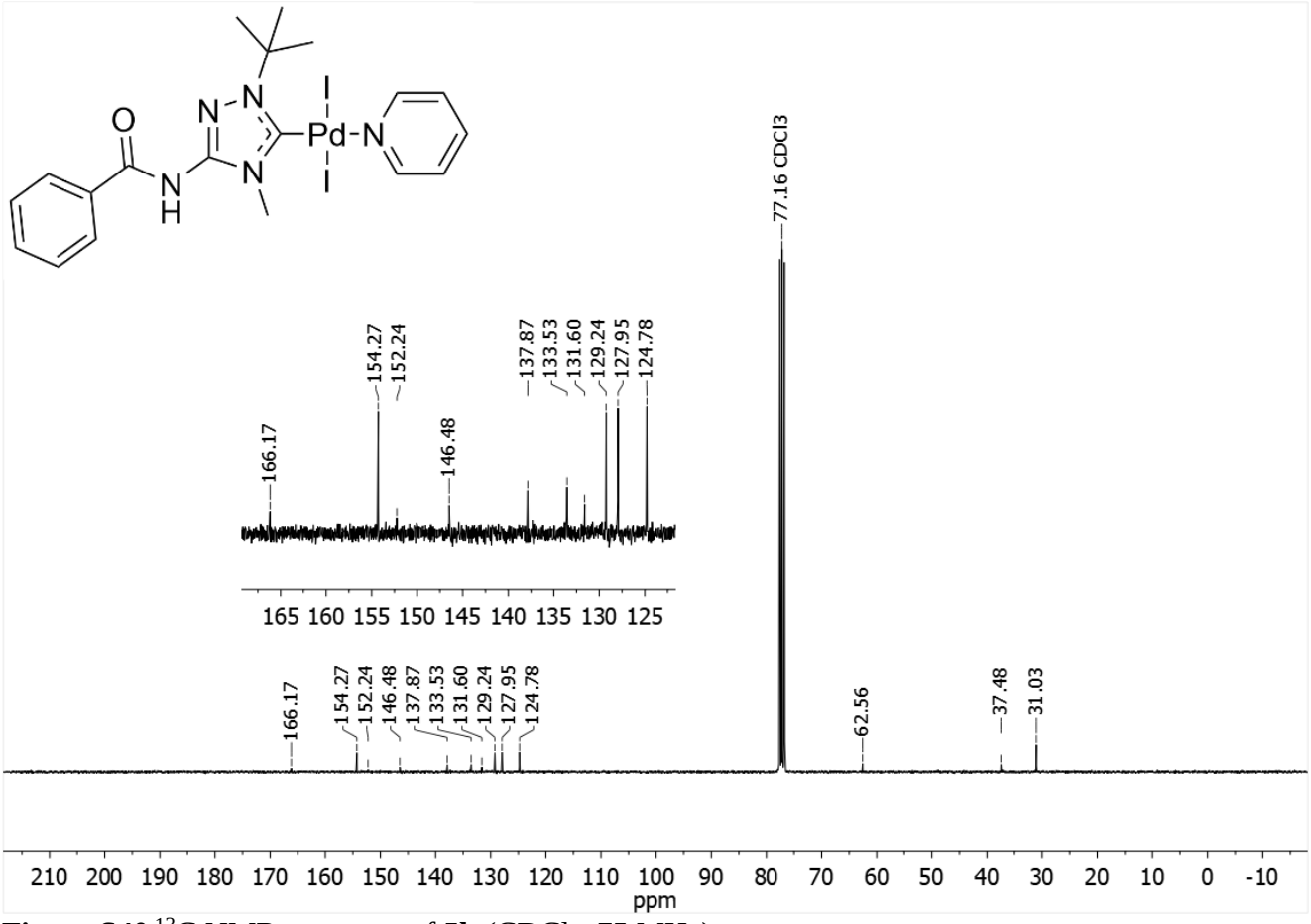

Figure S40 ^{13}C NMR spectrum of **5b** ($CDCl_3$, 75 MHz)

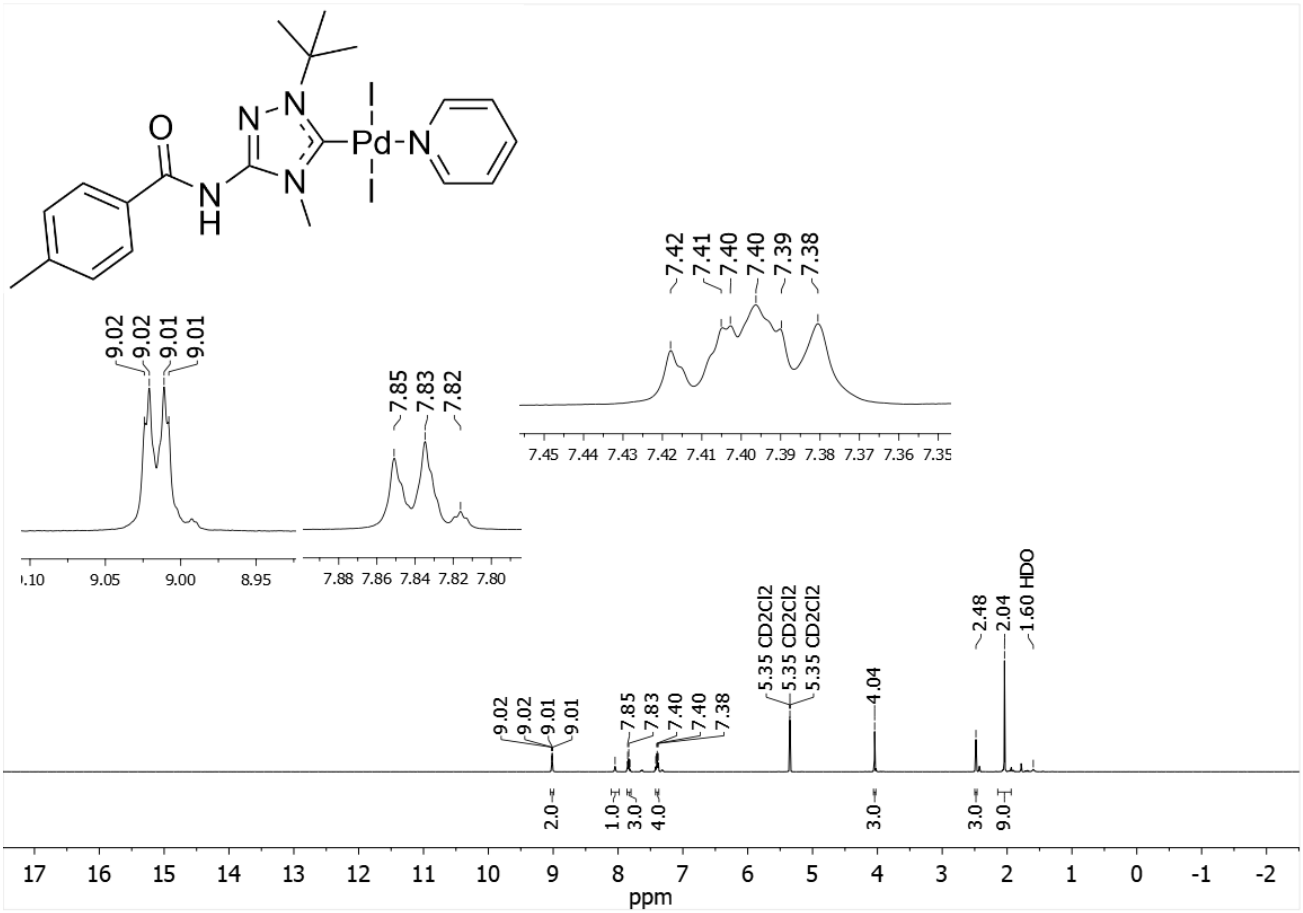

Figure S41 ^{1}H NMR spectrum of **5c** (CD_2Cl_2, 500 MHz)

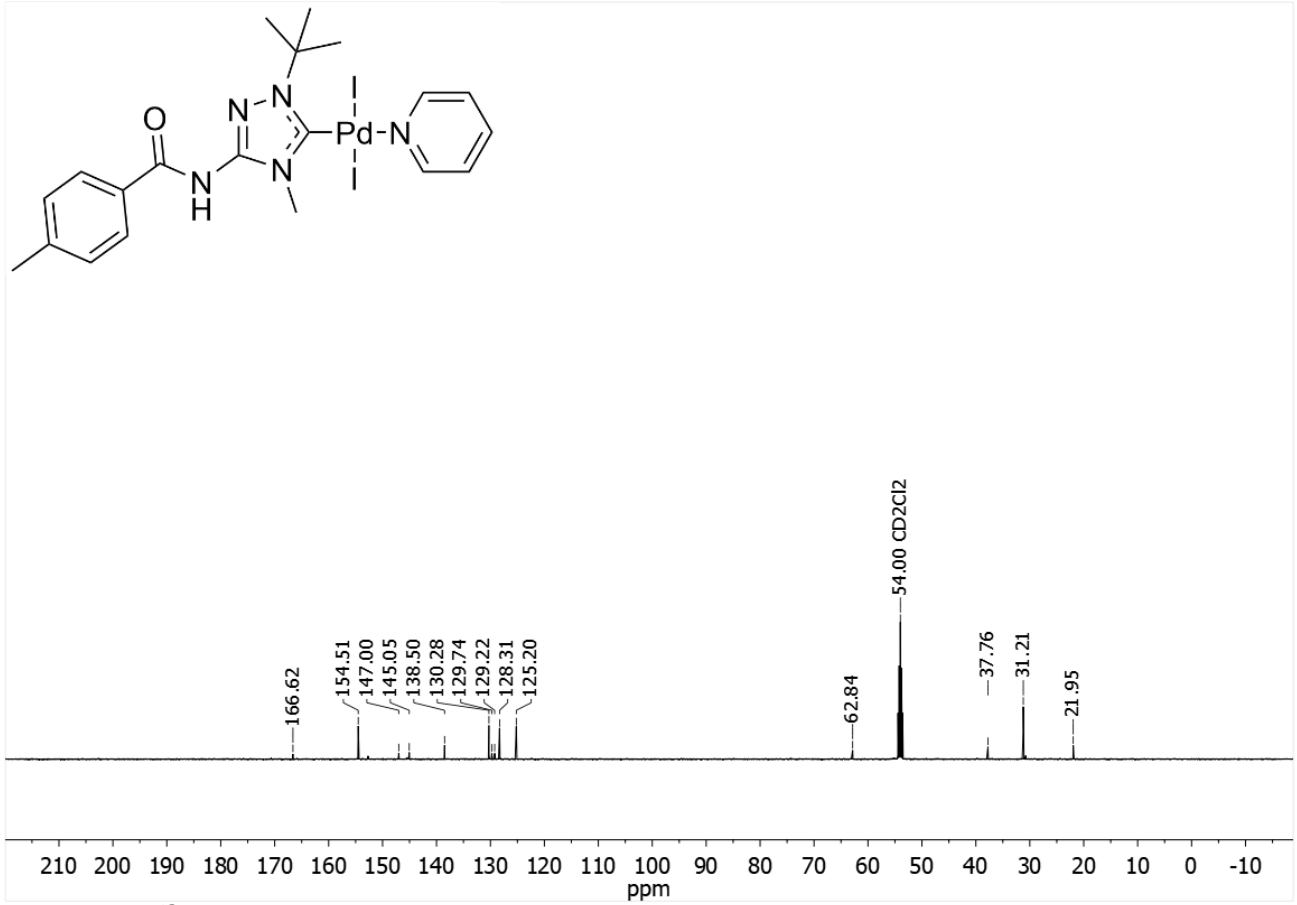

Figure S42 ^{13}C NMR spectrum of **5c** (CD_2Cl_2, 125 MHz)

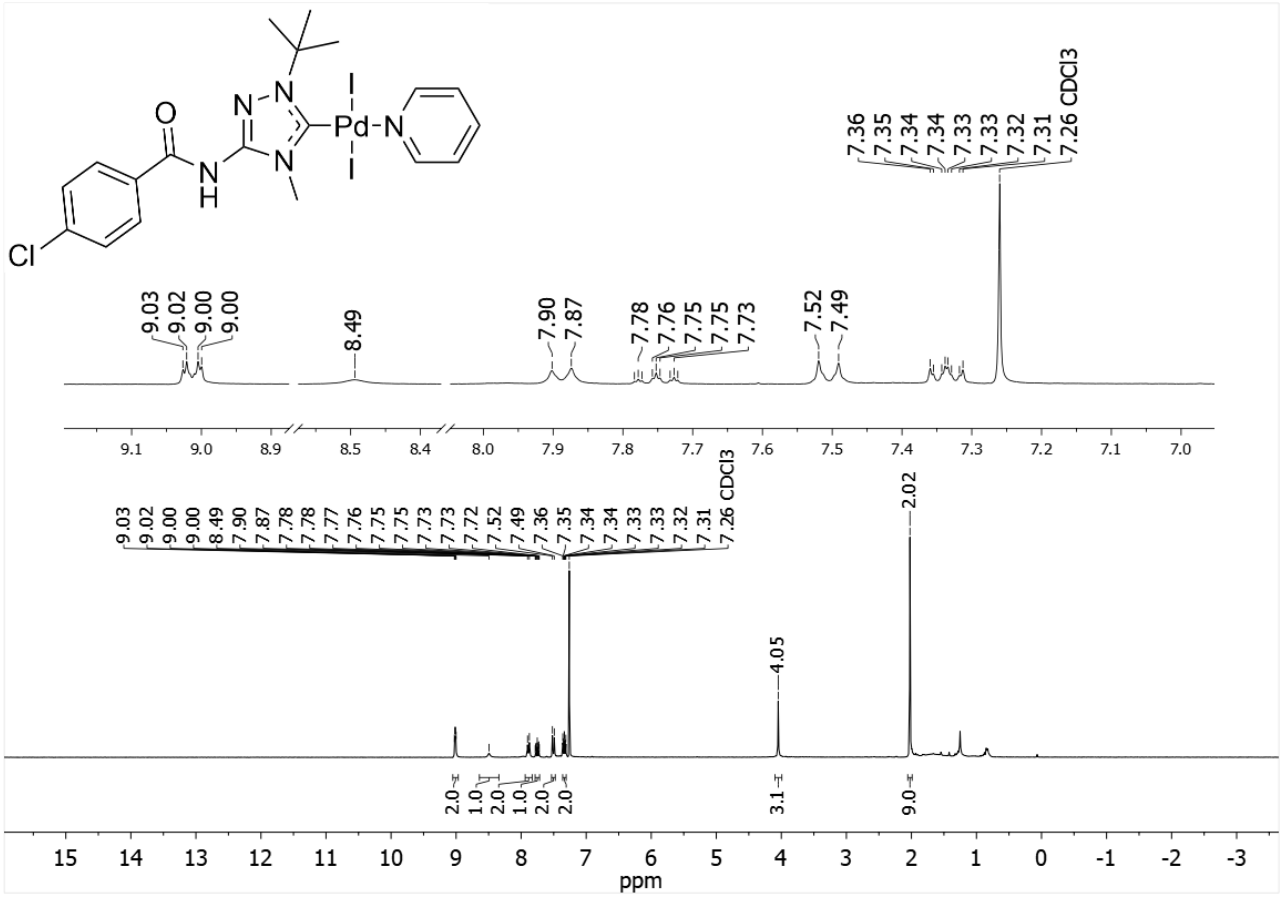

Figure S43 ^{1}H NMR spectrum of **5d** ($CDCl_3$, 300 MHz)

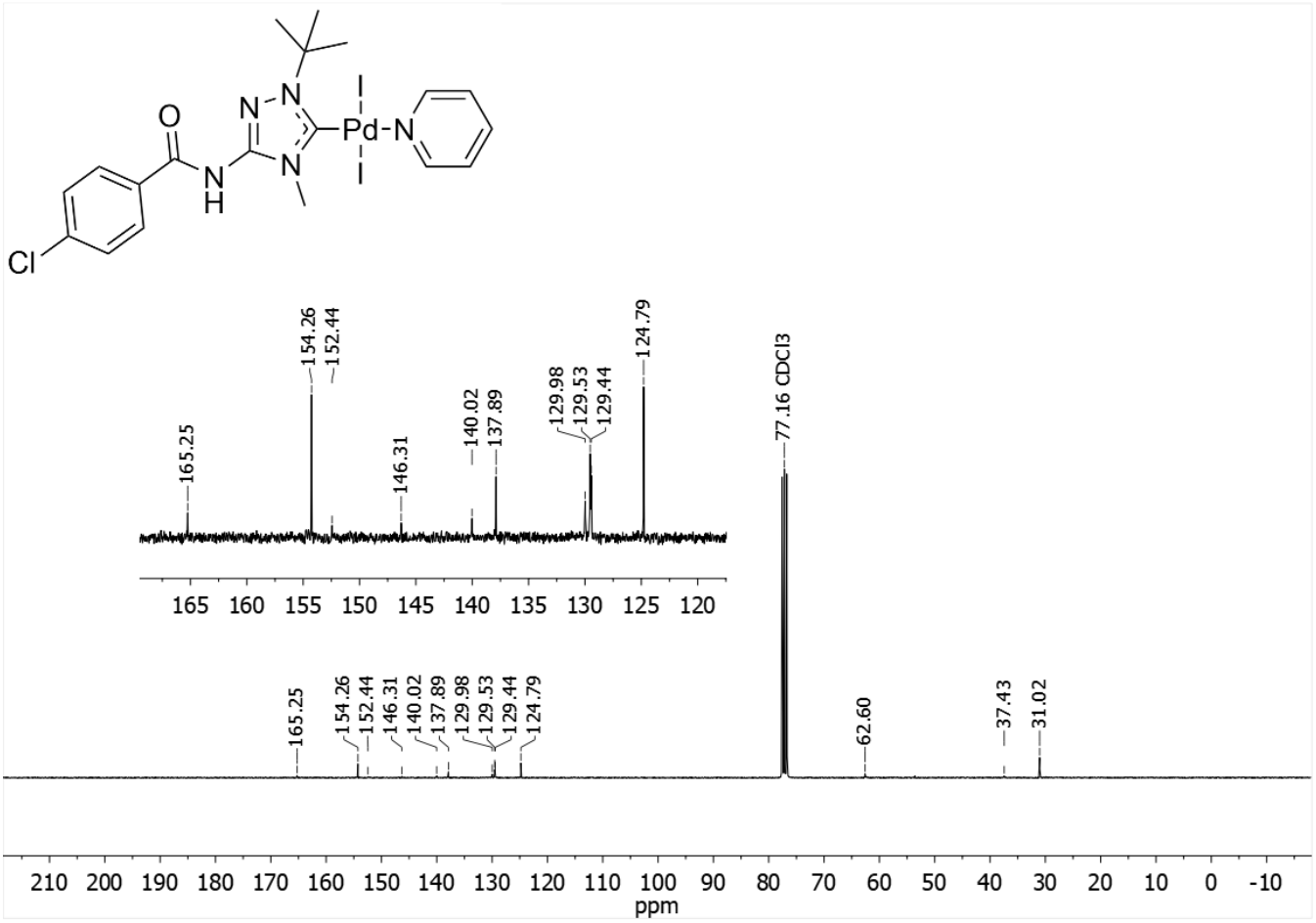

Figure S44 ^{13}C NMR spectrum of **5d** ($CDCl_3$, 75 MHz)

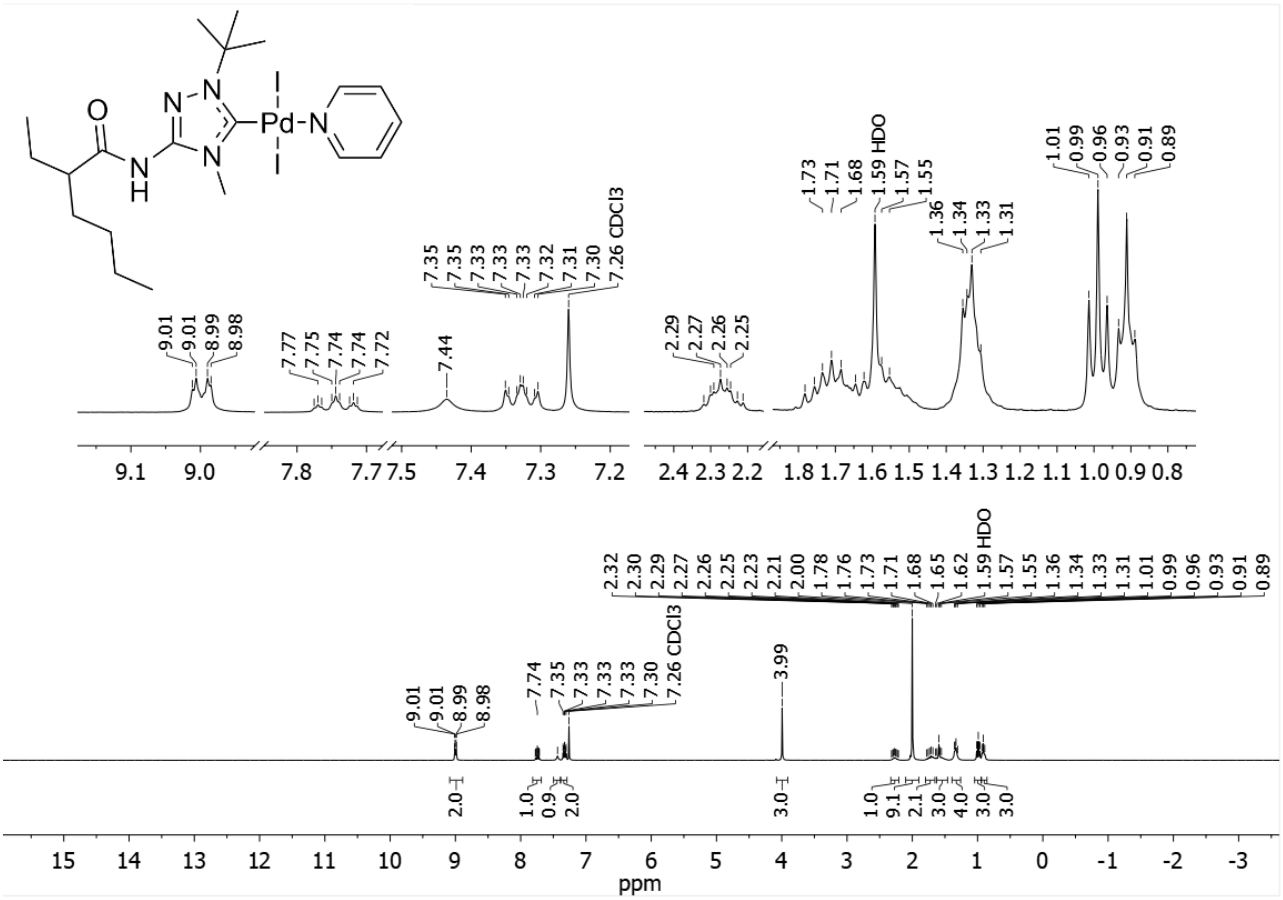

Figure S45 ^{1}H NMR spectrum of **5e** ($CDCl_3$, 300 MHz)

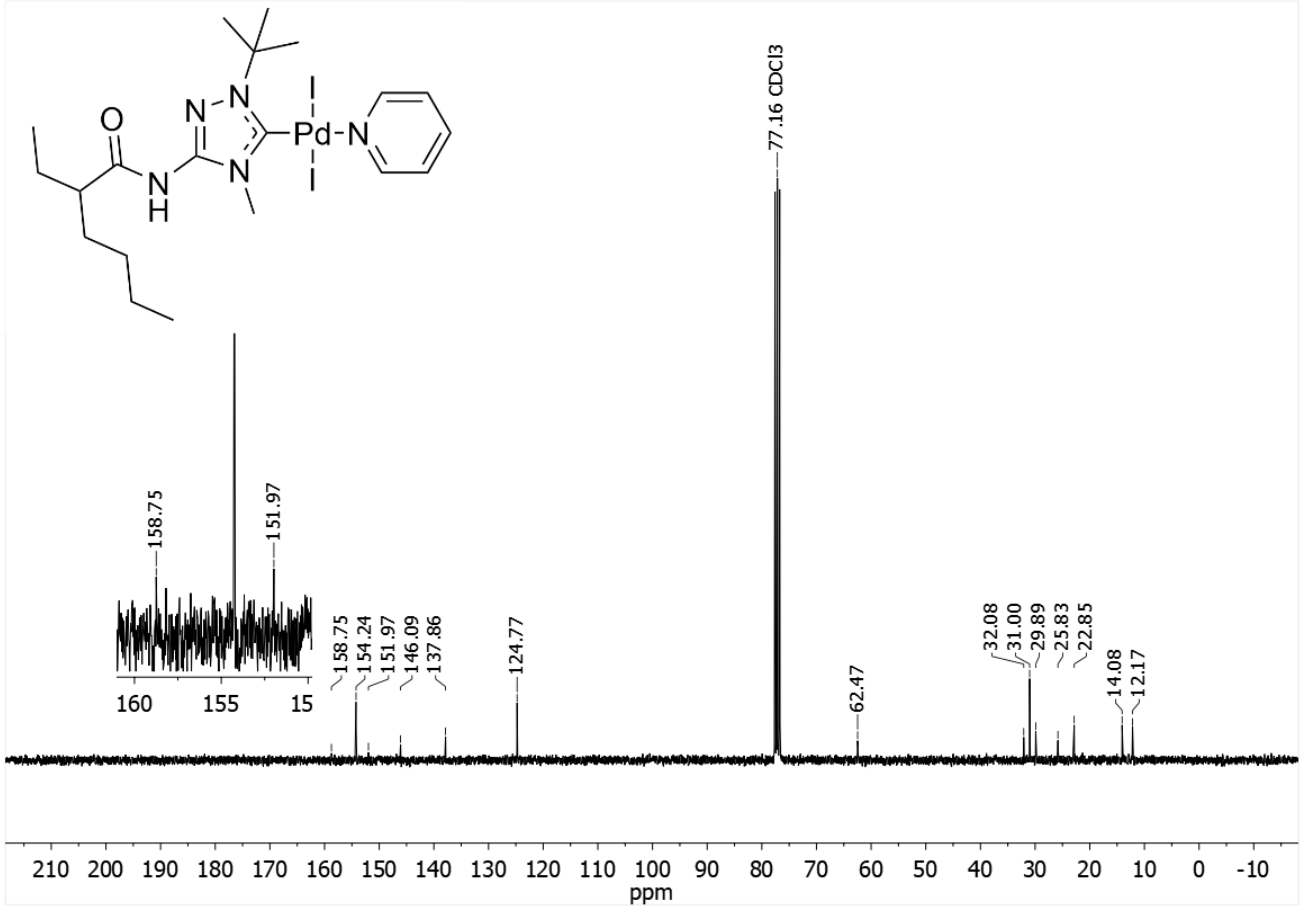

Figure S46 ^{13}C NMR spectrum of **5e** ($CDCl_3$, 75 MHz)

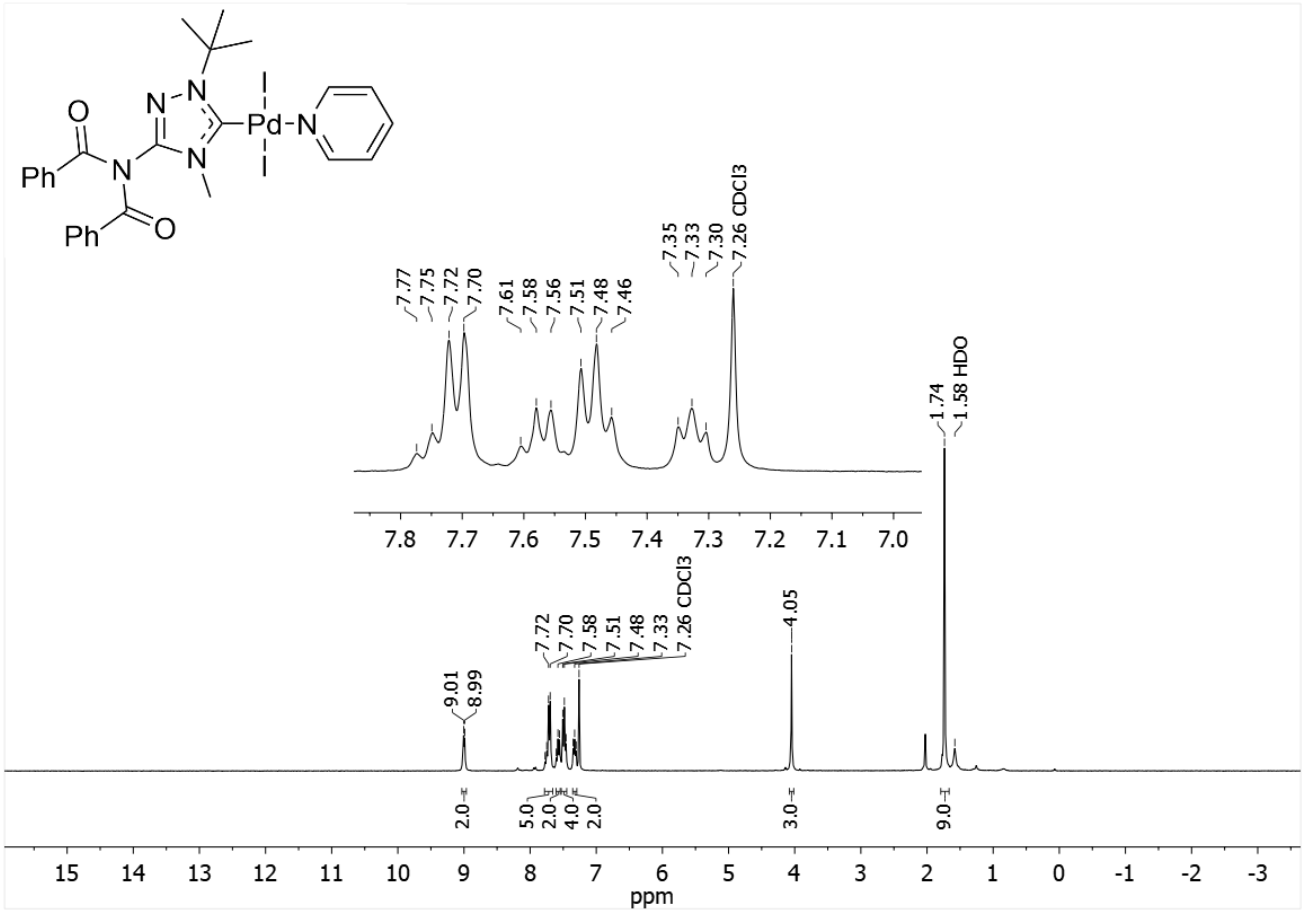

Figure S47 ^{1}H NMR spectrum of **6** ($CDCl_3$, 300 MHz)

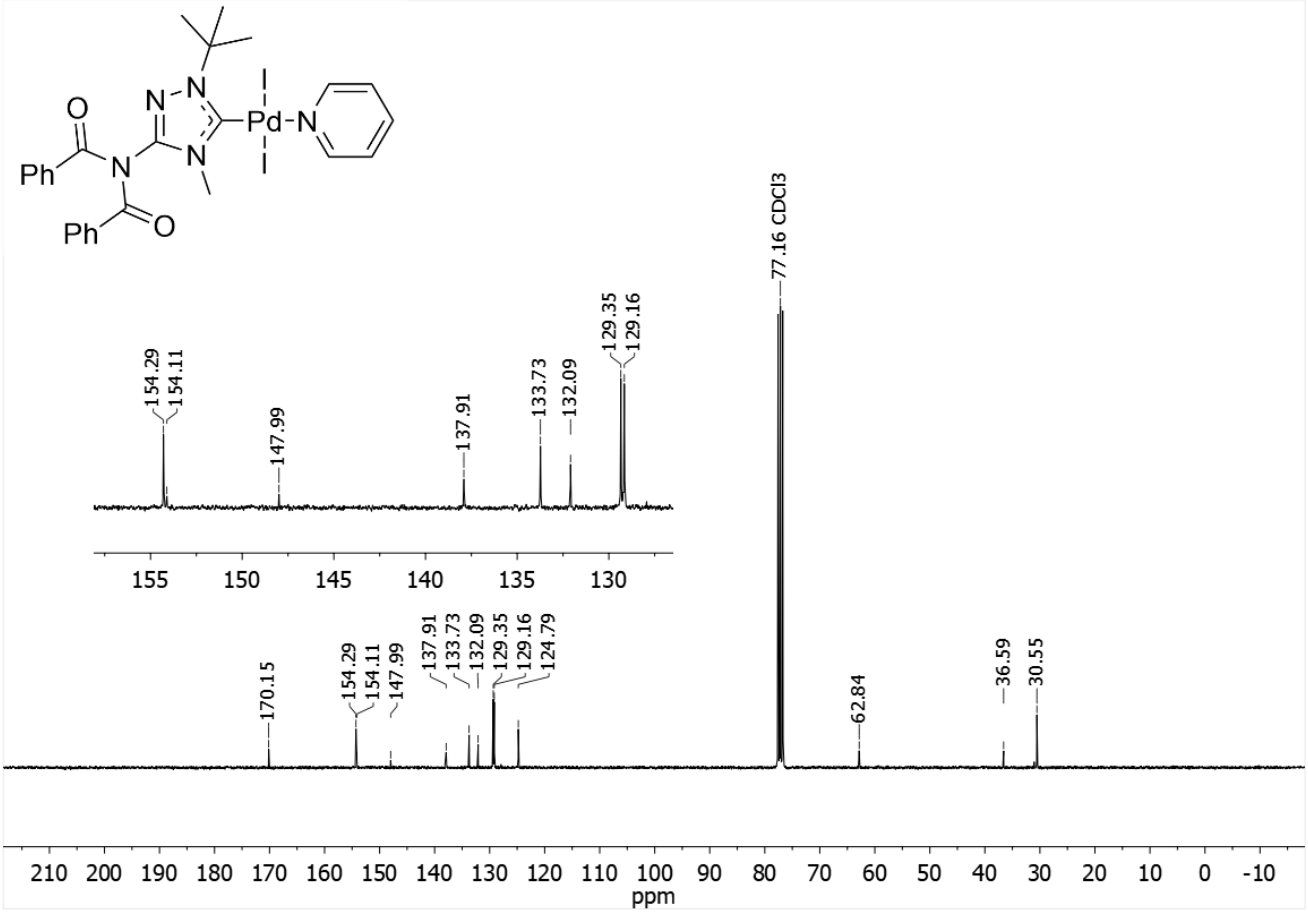

Figure S48 ^{13}C NMR spectrum of **6** ($CDCl_3$, 75 MHz)

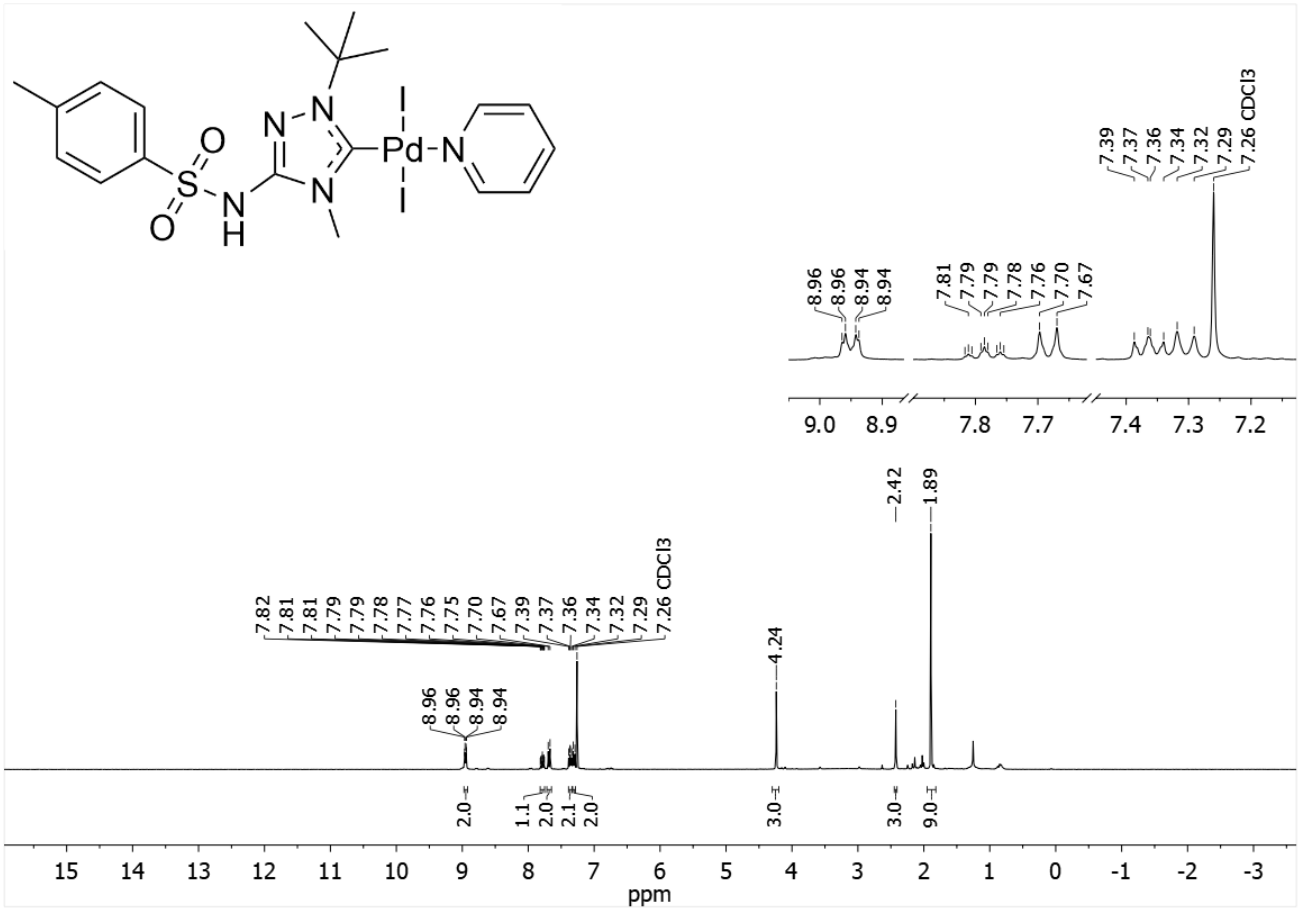

Figure S49 ^{1}H NMR spectrum of **7** ($CDCl_3$, 300 MHz)

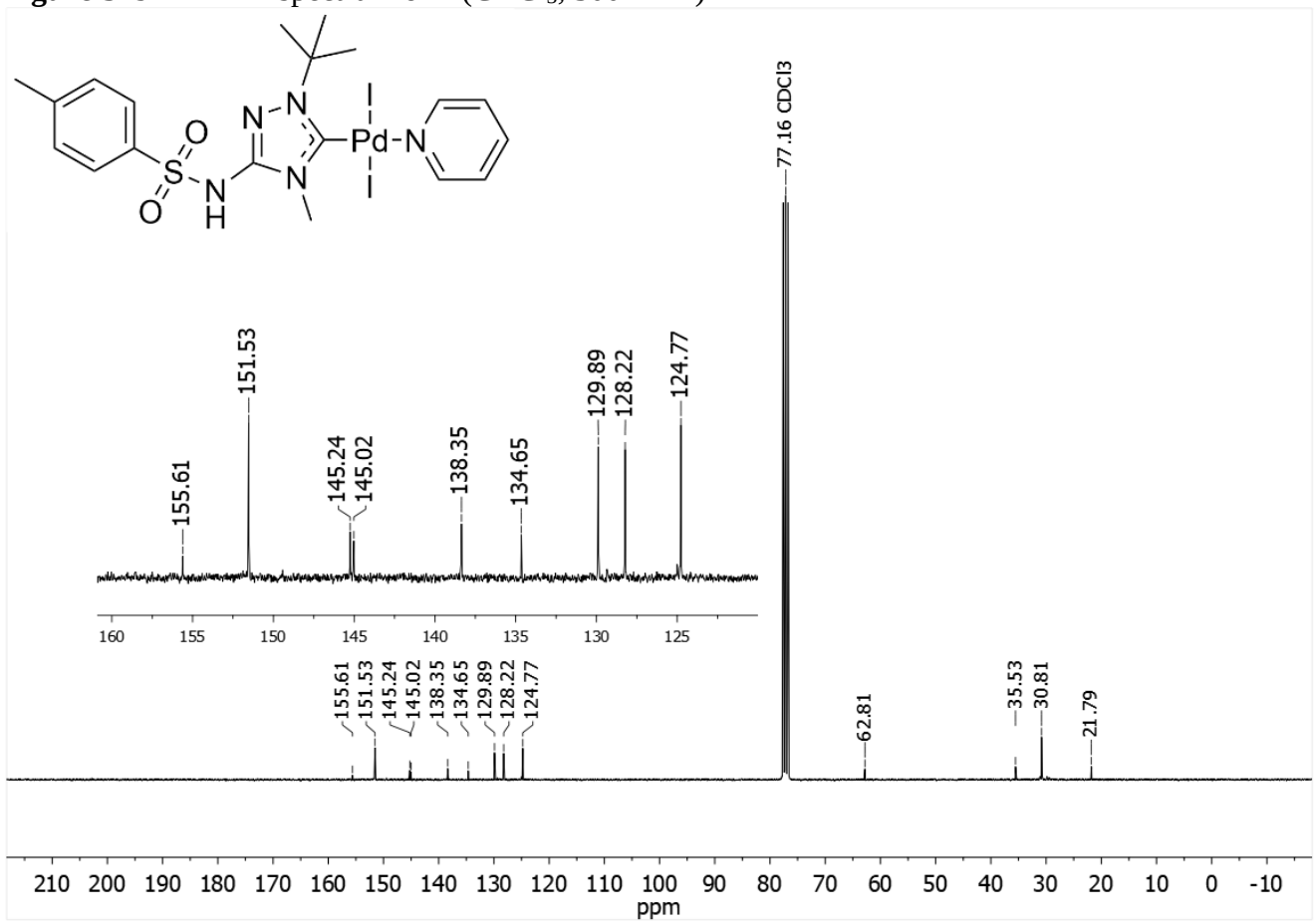

Figure S50 ^{13}C NMR spectrum of **7** ($CDCl_3$, 75 MHz)

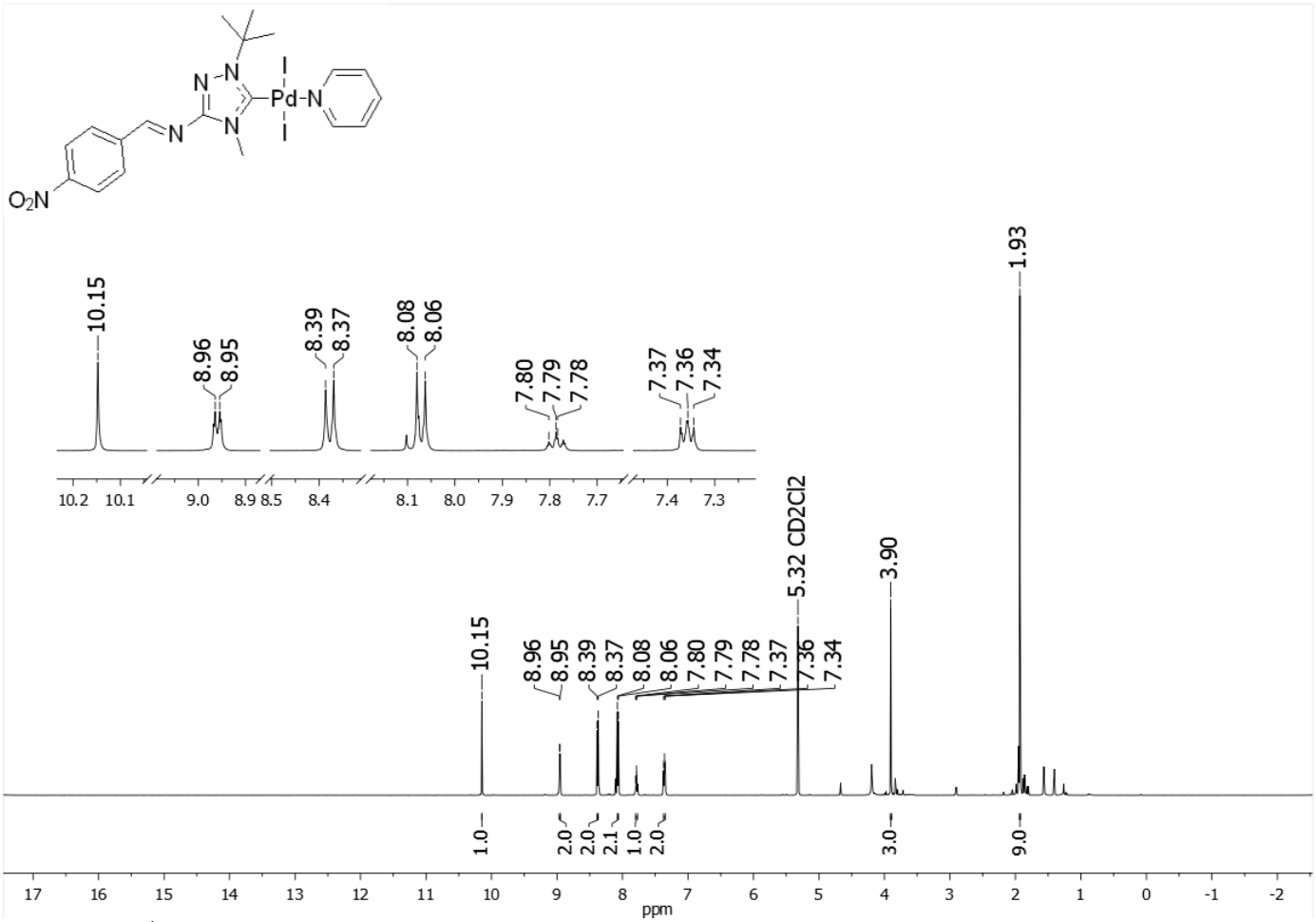

Figure S51 ^{1}H NMR spectrum of **8** (CD_2Cl_2, 500 MHz)

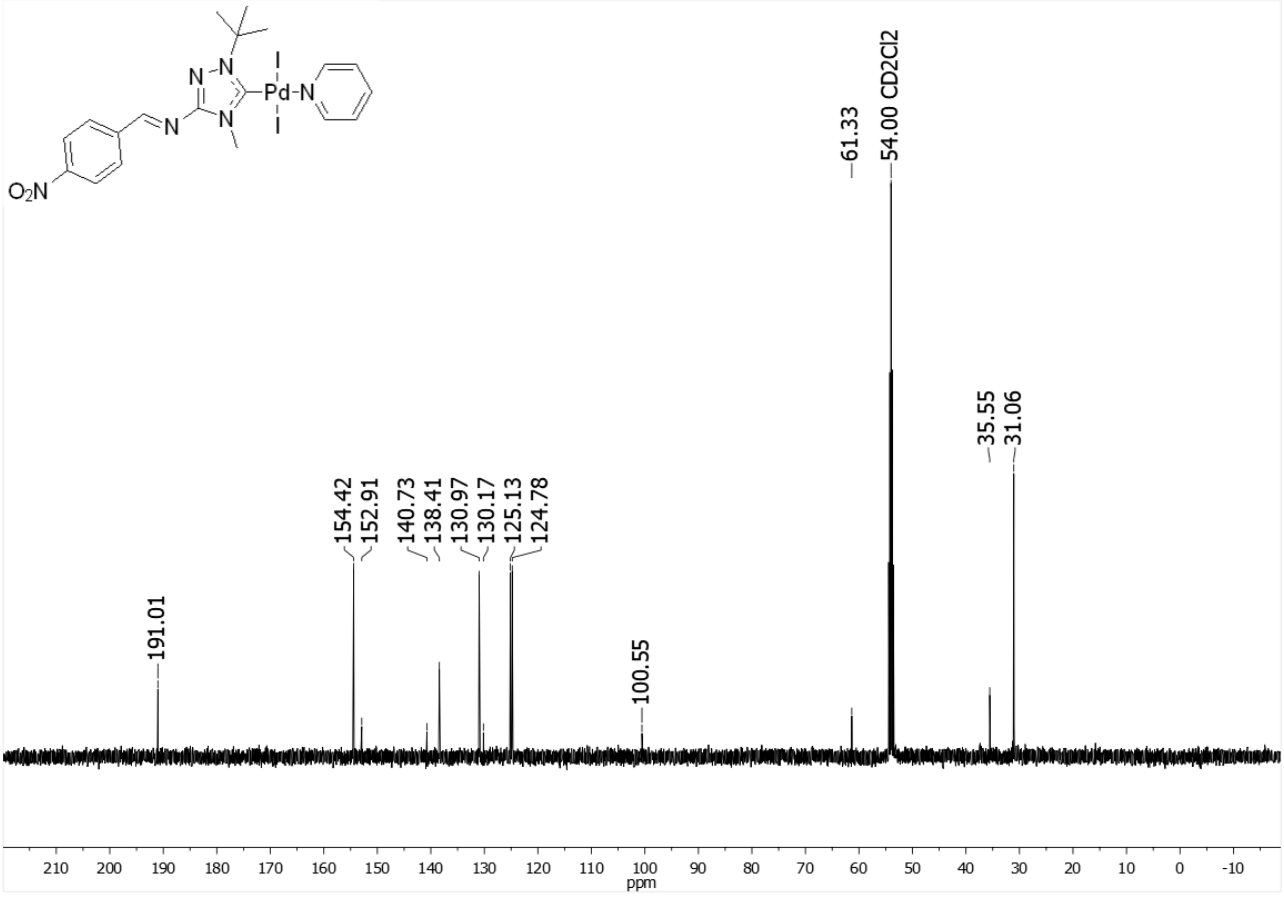

Figure S52^{13}C NMR spectrum of **8** (CD_2Cl2, 125 MHz)