Mixed er-NHC/Phosphine Pd(II) Complexes and Their Catalytic Activity in Buchwald-Hartwig Reaction under Solvent-Free Conditions

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Supporting Information

General information

All reagents were purchased from commercial sources and were used as received. NMR spectra were obtained on Bruker "Avance 600" (600 MHz ^{1}H, 151 MHz ^{13}C, 243 MHz ^{31}P). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks.[1] Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ''s", ''d", "t", "hept" or ''m" for singlet, doublet, triplet, heptet, or multiplet, respectively. The abbreviation ''br" is given for broadened signals. $^{31}P\{^{1}H\}$ NMR spectra were acquired using 15mM K_3PO_4 solution in D_2O as external reference.

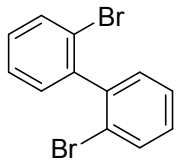
NHC complexes (6-Dipp)Pd(cinn)Cl,[2] IPrPd(cinn)Cl,[3] SIPrPd(cinn)Cl,[2] IMesPd(cinn)Cl[4] and SIMesPd(cinn)Cl[2] were synthesized according to published procedures, analytical data was in accordance with the literature.[2-4]

Crystallographic data: Crystals of **3a** ($C_{54}H_{75}Cl_2N_2O_2PPd$, M = 992.43) are triclinic, space group P-1: a = 12.8496(18), b = 19.538(3), c = 23.526(3) Å, α = 109.887(3), β = 101.799(3), γ = 91.081(3)°, V = 5411.6(13) Å^3, Z = 4, d_{calc} = 1.218 gcm^{-3}, μ(MoKα) = 0.510 cm^{-1}, F(000) = 2096. Crystals of **3f** ($C_{58}H_{83}Cl_2N_2O_2PPd$, M = 1048.53) are monoclinic, space group P2(1)/c: a =20.806(3), b = 17.258(2), c = 17.258(2) Å, β = 107.483(3)°, V = 6019.6(14) Å^3, Z = 4, d_{calc} = 1.157 gcm^{-3}, μ(MoKα) = 0.462 cm^{-1}, F(000) = 2224. Intensities of 59174 and 80271 reflections were measured at 120 K, with a Bruker APEX2 DUO CCD diffractometer [λ(MoKα) = 0.71072Å, ω-scans, $2\theta<56°$]. For further refinement, 26014 and 3482 independent reflections [R_{int} 0.0710 and 0.0581] were used for **3a** and R **3f**, respectively. The structures were solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. For **3a**, the refinement converged to wR2 = 0.1210 and GOF = 1.010 for all the independent reflections (R1 = 0.0488 was calculated against F for 18359 observed reflections with $I>2\sigma(I)$)**.** For **3f**, the refinement converged to wR2 = 0.1241 and GOF = 1.037 for all the independent reflections (R1 = 0.0572 was calculated against F for 11772 observed reflections with $I>2\sigma(I)$)**.** The unit cells of both complexes **3a** and **3f** contain disordered pentane molecules, possibly in superposition with dichloromethane, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[5] All calculations were performed using SHELXTL PLUS 5.0.[6] CCDC 1883293 and 1883294 contain the supplementary crystallographic information for **3a** and **3f**, respectively.

Synthesis of starting dibromoaryls for diarylative cyclization

3,3'-dibromo-2,2'-bithiophene[7] and 1,3,5-tribromobenzene[8] were synthesized according to published procedure, analytical data was in accordance with the literature.

2,2'-dibromobiphenyl



2,2'-dibromobiphenyl was synthesized according to published procedures.[9, 10]

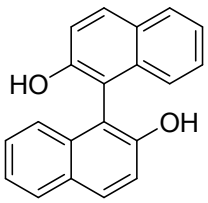
To a solution of 1,2-dibromobenzene (23.6 g, 100 mmol) in dry degassed THF (250 ml) 20 ml solution of 2.5 M *n*-BuLi (50 mmol) in hexane at was slowly added -78 °C. The reaction mixture was allowed to warm to 0 °C, hydrolyzed with aq. HCl, evaporated to dryness and extracted with dichloromethane (3x100 ml). The organic layer was filtered through a short pad of silica. Concentration of containing product fractions in vacuum and recrystallization from hexane afforded 2,2'-dibromobiphenyl as white solid (12.99 g, 83% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.24 (m, 4H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 142.2 , 132.7 , 131.1 , 129.5 , 127.2 , 123.6 .

The NMR data are in agreement with previously reported.[11]

1,1'-binaphthyl-2,2'-diol



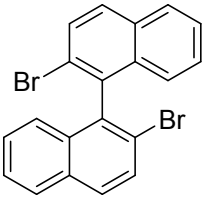
A solution of 75.8 g (276.0 mmol) $FeCl_3 \cdot 6H_2O$ and 19.9 g (138.0 mmol) 2-napthanol in water (1 L) was stirred for 1h at 50 °C. After cooling to room temperature, the precipitate was filtered, washed with H_2O and dried in vacuo. Recrystallization from ethanol afforded pure product as a light brown solid. (18.2 g, 92% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.2 (s, 2H), 7.9 (s, 4H), 7.3 (d, *J* = 8.15 Hz, 2H), 7.2 (s, 2H), 7.2 (s, 2H), 6.9 (d, *J* = 7.65 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz DMSO-d_6) δ 153.0, 134.1, 128.6, 128.1, 127.9, 125.8, 124.4, 122.3, 118.5, 115.4.

The NMR data are in agreement with previously reported.[12]

2,2'-dibromo-1,1'-binaphthyl



The title compound was synthesized according to literature procedure with minor modifications.[13]

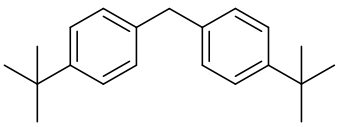
To a cooled on ice-water bath solution of triphenylphosphine (27.29 g, 0.1 mol) in dry acetonitrile (60 ml) bromine (17.6 g, 0.11 mol) was added slowly over a 1h period. To the resulting mixture 2,2'-dihydroxy-1,1'-binaphthyl (13.65 g, 0.046 mol) was added in one portion and the reaction was stirred for 0.5h at 60 °C. Then the reaction mixture was cooled to RT, the flask was equipped with a distillation head and solvent was distilled out under reduced pressure. After that the distillation head was changed to a condenser and the reaction was heated up to 260 °C and stirred at that temperature for 2h and then it was additionally stirred for 0.5h at 320 °C. The resulting melt was cooled down to 200 °C and Celite (100 ml) was added in one portion. After further cooling to ca. 70 °C the resulting mixture was extracted with a boiling 1:1 mixture of benzene and hexane (500 ml). The residual solid was filtered off and extracted again with a boiling 1:1 mixture of benzene and hexane (2x20 ml). The combined extracts were evaporated to give an orange-yellow viscous oil. Column chromatography in hexane as eluent afforded the pure product as a white solid (4.1 g, 21%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 137.2, 133.4, 132.5, 130.1, 129.9, 128.4, 127.5, 126.5, 126.0, 122.8.

The NMR data are in agreement with previously reported.[14]

bis(4-tert-butylphenyl)methane



To a mixture of diphenylmethane (30.28 g, 180 mmol) and tert-butyl chloride (38.32 g, 414 mmol) 0.12 g (0.9 mmol) of $AlCl_3$ was added at room temperature and stirred for 30 min.(*CAUTION*: vigorous evolution of HCl_g) The resulting mixture was dissolved in ethanol and

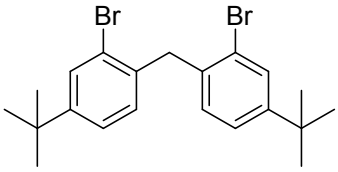
crystallized at -24 °C from ethanol. Recrystallization of resulting solid from minimal amount of ethanol at -24 °C afforded pure bis(4-tert-butylphenyl)methane as white needles (20.54 g, 41% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.3 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 4H), 3.96 (s, 2H), 1.34 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 148.9 , 138.4 , 128.7 , 125.5 , 41.1 , 34.5 , 31.6 .

The NMR data are in agreement with previously reported.[15]

bis(2-bromo-4-tert-butylphenyl)methane



Bis(2-bromo-4-tert-butylphenyl)methane was synthesized according to published procedure.[15]

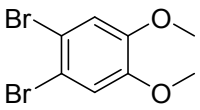
To a stirred mixture of bis(4-tert-butylphenyl)methane (15 g, 53.5 mmol) and Fe powder (0.18 g, 3.2 mmol) in 50 ml of dichloromethane (50 ml) was slowly added 5.8 ml (112.3 mmol) of Br_2 in dichloromethane (26 ml) at 10 °C for 30 min. The reaction mixture was stirred overnight at room temperature and washed with 10% aqueous HCl (2x100 ml), saturated solution of Na_2CO_3 (2x100 ml), dried over anhydrous Na_2SO_4 and evaporated to dryness. The solid was dissolved in 50 ml of hexane and filtered through short pad of silica. Concentration of containing product fractions in vacuum and crystallization at -24 °C from ethanol afforded pure bis(2-bromo-4-tert-butylphenyl)methane as white solid (10.3 g, 87% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 1.8 Hz, 2H), 7.24 (dd, *J* = 8.1, 1.8 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 4.14 (s, 2H), 1.31 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 151.6 , 136.1 , 130.4 , 129.9 , 125.0 , 124.8 , 41.2 , 34.7 , 31.4 .

The NMR data are in agreement with previously reported.[15]

1,2-dibromo-4,5-dimethoxybenzene



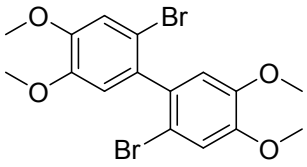
To a stirred solution of 1,2-dimethoxybenzene (2.8 g, 20.3 mmol) in 40 ml of dichloromethane was slowly added 0.1 g (0.4 mmol) of I_2 and solution of 8.2 g (51 mmol) of Br_2 in 10 ml of dichloromethane at 0 °C for 30 min. The reaction mixture was stirred overnight at room temperature and washed with H_2O, Na_2CO_3 and Na_2SO_3, dried over anhydrous Na_2SO_4, evaporated to dryness. Resulting solid was recrystallized from isopropanol at -24 °C as white solid (5.3 g, 89% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.05 (s, 2H), 3.85 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 149.0 , 116.1 , 114.9 , 56.4 .

The NMR data are in agreement with previously reported.[16]

2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl



2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl was synthesized according to published procedure.[17]

To a solution of 1,2-dibromo-4,5-dimethoxybenzene (29.6 g, 100 mmol) in dry degassed THF (250 ml) 20 ml solution of 2.5 M *n*-BuLi (50 mmol) in hexane was slowly added at -78 °C. The reaction mixture was stirred for 1 h at -78 °C and was allowed to warm to room temperature, stirred for 1 h and hydrolyzed with aq. HCl and extracted with dichloromethane (3x100 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. Purification by dry column vacuum chromatography on silica (hexane as eluent) followed by recrystallization from hexane afforded pure product as a colorless crystals (13.8 g, 64% yield).

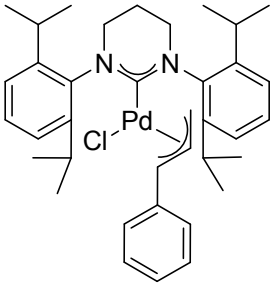
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.11 (s, 2H), 6.76 (s, 2H), 3.91 (s, 6H), 3.86 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 149.2 , 148.1 , 134.1 , 115.2 , 114.0 , 56.3 , 56.3 .

The NMR data are in agreement with previously reported.[17]

Preparation of (NHC)$PdCl_2$-PR_3

*(6-Dipp)Pd(cinn)Cl (**1a**)*



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 4H), 7.08 – 7.03 (m, 3H), 6.87 – 6.82 (m, 2H), 4.65 – 4.57 (m, 1H), 3.87 (d, *J* = 12.2 Hz, 1H), 3.67 – 3.61 (m, 4H), 3.58 – 3.51 (m, 4H), 2.38 – 2.32 (m, 2H), 1.41 (d, *J* = 6.5 Hz, 12H), 1.21 (d, *J* = 6.8 Hz, 12H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 213.5 , 146.7 , 143.6 , 139.0 , 128.6 , 128.1 , 127.4 , 126.2 , 124.3 , 108.9 , 86.6 , 49.3 , 48.2 , 28.7 , 27.1 , 23.7 , 20.8 .

HRMS (APPI) calc. for $C_{37}H_{49}N_2Pd$ $[M\text{-}Cl]^+$: 626.2945, 627.2939, 628.2965, 629.2935; found: 626.2942, 627.2939, 628.2962, 629.2932.

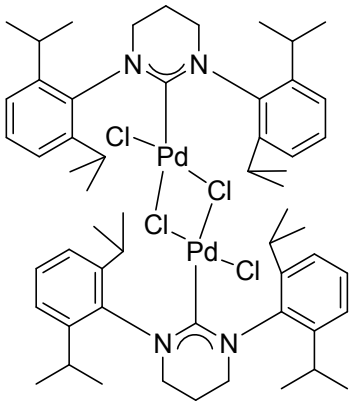
IR (KBr, υ/cm^{-1}): 2965 (s), 2928 (m), 2866 (m), 1490 (vs), 1443 (s), 1382 (m), 1320 (s), 1320 (s), 1257 (m), 1200 (s), 802 (s), 755 (s), 689 (s).

The NMR data are in agreement with previously reported.[2]

General procedure for the preparation of (NHC)$PdCl_2$-PR_3 complexes (2a, 3a-j)

A mixture of corresponding (NHC)Pd(cinn)Cl complex (0.1-0.5 mmol) in DCM (5 ml) and 1 ml of 3.8M hydrogen chloride in 1,4-dioxane was stirred until TLC showed full conversion of starting complex. The resulting orange solution was evaporated to dryness and dried in vacuum (0.5-1 torr). The solid residue was dissolved in DCM (5 ml) followed by addition of phosphine (1.05 equiv.) and stirred until TLC showed full conversion to the product. The reaction mixture was filtered through a short silica pad (elution with DCM) and filtrate was evaporated to dryness. The yellow residue was crystallized from DCM-pentane mixture (approx. 1:5) to give the pure product as light yellow microcrystalline solid.

*[(6-Dipp)PdCl$_2$]$_2$ (**2a**)*



The title compound was synthesized following General procedure for the preparation of (NHC)PdCl$_2$-PR$_3$ complexes, but without addition of phosphine ligand.

Orange solid (>99 % yield)

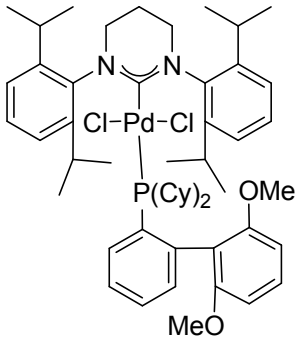
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (t, *J* = 7.58 Hz, 4H), 7.28 (d, *J* = 6.85 Hz, 4H), 7.21 (d, *J* = 6.79 Hz, 4H), 3.56 – 3.45 (m, 8H), 3.35 – 3.23 (m, 4H), 3.07 – 2.94 (m, 4H), 2.21 – 2.05 (m, 4H), 1.49 (d, *J* = 5.34 Hz, 12H), 1.19 – 1.09 (m, 24H), 1.03 (d, *J* = 5.37 Hz, 12H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 178.0 , 147.0 , 146.7 , 141.1 , 140.9 , 129.4 , 125.2 , 124.6 , 67.2 , 51.8 , 29.1 , 28.8 , 27.1 , 27.0 , 24.5 , 24.1 , 21.7 .

HRMS (APPI) calc. for $C_{28}H_{40}ClN_2Pd$ [M-Cl]$^+$: 544.1928, 545.1917, 546.1925, 547.1909; found: 544.1927, 545.1916, 546.1922, 547.1908.

IR (KBr, υ/cm^{-1}): 3067 (w), 2965 (s), 2866 (m), 1589 (w), 1503 (vs), 1452 (m), 1394 (m), 1384 (m), 1363 (w), 1321 (s), 1303 (s), 1258 (m), 1210 (m), 1175 (w), 1110 (w), 1055 (w), 994 (w), 931 (w), 799 (m), 753 (s), 644 (m), 576 (w), 551 (m).

*(6-Dipp)PdCl$_2$-SPhos (**3a**)*



Yellowish microcrystalline solid (600 mg, 98% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 2H), 7.32 – 7.22 (m, 6H), 7.19 (t, *J* = 8.3 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.79 (d, *J* = 7.3 Hz, 1H), 6.47 – 6.41 (m, 2H), 3.77 – 3.70

(m, 4H), 3.62 (p, *J* = 6.6 Hz, 4H), 3.50 (s, 6H), 2.30 – 2.23 (m, 2H), 1.64 – 1.54 (m, 2H), 1.47 (d, *J* = 6.4 Hz, 14H), 1.35 (d, *J* = 12.5 Hz, 2H), 1.30 – 1.23 (m, 4H), 1.16 (d, *J* = 6.8 Hz, 14H), 0.92 – 0.82 (m, 4H), 0.82 – 0.73 (m, 2H), 0.74 – 0.63 (m, 4H).

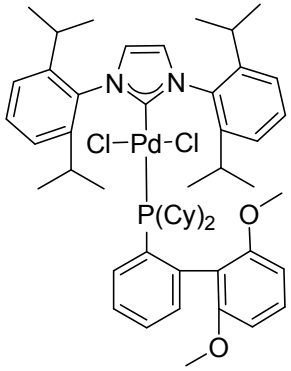
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 198.5 (d, *J* = 182.6 Hz), 157.9 , 147.9 , 142.7 , 140.2 (d, *J* = 21.3 Hz), 138.2 (d, *J* = 2.6 Hz), 131.5 (d, *J* = 5.7 Hz), 128.7 , 128.5 , 128.3 , 128.1 (d, *J* = 7.8 Hz), 124.2 (d, *J* = 13.5 Hz), 123.7 , 119.5 , 103.1 , 55.0 , 53.6 , 50.6 (d, *J* = 5.2 Hz), 31.5 (d, *J* = 20.0 Hz), 30.0 , 29.3 , 28.0 , 27.5 , 27.4 (d, *J* = 11.9 Hz), 26.9 (d, *J* = 11.5 Hz), 26.0 , 23.7 , 20.0 .

$^{31}P\{^{1}H\}$ NMR (243 MHz, Chloroform-d) δ 39.0 .

HRMS (APPI) calc. for $C_{54}H_{75}Cl_2N_2O_2PPd$ $[M]^+$: 989.3994, 990.3986, 991.3981, 992.3976, 993.3997; found: 989.3990, 990.3981, 991.3991, 992.3972, 993.3996.

IR (KBr, υ/cm^{-1}): 3061 (w), 2964 (s), 2926 (s), 2866 (m), 2851 (m), 1588 (s), 1492 (s), 1470 (s), 1443 (s), 1382 (m), 1321 (s), 1301 (s), 1248 (s), 1198 (s), 1111 (vs), 1034 (m), 998 (m), 928 (m), 895 (m), 852 (m), 800 (s), 783 (m), 757 (s), 729 (s).

*IPrPdCl_2-SPhos (**3b**)*



Yellowish microcrystalline solid (149 mg, 94% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (dt, *J* = 19.15, 7.85 Hz, 3H), 7.33 (d, *J* = 7.76 Hz, 4H), 7.22 (t, *J* = 8.36 Hz, 1H), 7.10 (d, *J* = 12.77 Hz, 3H), 6.84 (d, *J* = 8.79 Hz, 1H), 6.47 (d, *J* = 8.39 Hz, 2H), 3.52 (s, 6H), 3.22 (p, *J* = 6.71 Hz, 4H), 1.75 (q, *J* = 10.57, 9.64 Hz, 2H), 1.49 (s, 4H), 1.37 (d, *J* = 6.58 Hz, 12H), 1.07 (d, *J* = 6.91 Hz, 12H), 1.04 – 0.98 (m, 2H), 0.88 – 0.81 (m, 4H), 0.79 – 0.69 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 175.0 (d, *J* = 187.2 Hz), 158.0 , 147.4 , 140.0 (d, *J* = 20.9 Hz), 138.5 (d, *J* = 1.6 Hz), 135.8 , 131.8 (d, *J* = 5.3 Hz), 129.7 , 128.9 , 128.5 , 127.6 (d, *J* = 33.8 Hz), 124.3 (d, *J* = 14.0 Hz), 124.1 (d, *J* = 5.1 Hz), 123.4 , 119.4 , 103.2 , 55.0 , 31.9 (d, *J* = 21.4 Hz), 30.3 , 28.5 (d, *J* = 83.2 Hz), 27.3 (d, *J* = 12.2 Hz), 27.1 (d, *J* = 11.4 Hz), 26.7 , 26.1 , 22.9 .

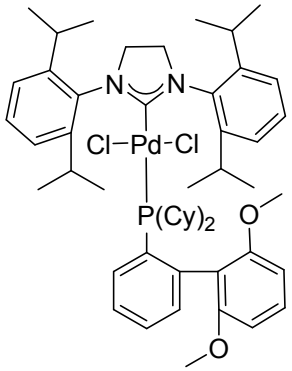
$^{31}P\{^{1}H\}$ NMR (243 MHz, Chloroform-*d*) δ 40.1 .

HRMS (APPI) calc. for $C_{53}H_{71}Cl_2N_2O_2PPd$ $[M]^+$: 974.3672, 975.3679, 976.3663, 977.3683, 978.3662; found: 974.3702, 975.3720, 976.3698, 977.3722, 978.3704.

IR (KBr, υ/cm^{-1}): 2967 (s), 2928 (s), 2866 (m), 2849 (m), 1588 (s), 1473 (s), 1453 (m), 1430 (m), 1406 (m), 1382 (m), 1362 (m), 1336 (m), 1247 (s), 1111 (vs), 1005 (m), 802 (m), 782 (m), 759 (s), 729 (s), 703 (m), 600 (m), 538 (m).

The NMR data are in agreement with previously reported.[18]

*SIPrPdCl$_2$-SPhos (**3c**)*



Yellow crystalline solid (184 mg, 91% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 3H), 7.29 (d, *J* = 7.69 Hz, 4H), 7.21 (t, *J* = 8.38 Hz, 1H), 7.07 (t, *J* = 7.58 Hz, 1H), 6.86 – 6.80 (m, 1H), 6.46 (d, *J* = 8.42 Hz, 2H), 4.10 (s, 4H), 3.67 (p, *J* = 6.67 Hz, 4H), 3.52 (s, 6H), 1.78 – 1.64 (m, 2H), 1.59 (s, 1H), 1.44 (d, *J* = 6.51 Hz, 16H), 1.38 – 1.25 (m, 7H), 1.20 (d, *J* = 6.86 Hz, 12H), 1.06 – 0.98 (m, 2H), 0.82 (t, *J* = 9.37 Hz, 4H), 0.77 – 0.66 (m, 2H).

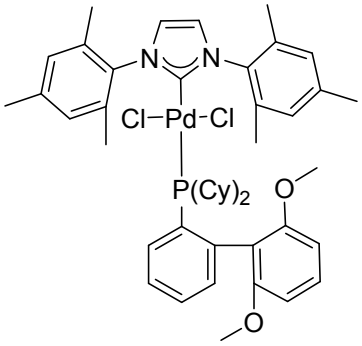
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 202.0 (d, *J* = 176.2 Hz), 157.9 , 148.6 , 140.0 (d, *J* = 21.4 Hz), 138.4 , 135.9 , 131.8 (d, *J* = 5.0 Hz), 129.0 , 128.8 , 128.5 , 127.6 (d, *J* = 32.0 Hz), 124.4 (d, *J* = 14.0 Hz), 123.8 , 119.4 , 103.1 , 53.6 (d, *J* = 6.1 Hz), 31.8 (d, *J* = 20.5 Hz), 30.3 , 28.8 , 28.1 , 27.3 , 27.3 , 27.0 (d, *J* = 11.4 Hz), 26.0 , 23.7 .

$^{31}P\{^{1}H\}$ NMR (243 MHz, Chloroform-*d*) δ 39.4 .

HRMS (APPI) calc. for $C_{53}H_{73}Cl_2N_2O_2PPd$ $[M]^+$: 976.3829, 977.3836, 978.3819, 979.3840, 980.3819; found: 976.3828, 977.3836, 978.3820, 979.3842, 980.3819.

IR (KBr, υ/cm^{-1}): 2964 (s), 2928 (s), 2866 (m), 2849 (m), 1588 (s), 1473 (vs), 1453 (s), 1430 (s), 1382 (m), 1362 (m), 1329 (m), 1287 (m), 1269 (s), 1246 (s), 1110 (vs), 999 (m), 915 (w), 850 (w), 803 (m), 782 (m), 757 (s), 727 (m), 619 (m), 600 (w), 537 (m).

*IMesPdCl$_2$-SPhos (**3d**)*



Yellowish microcrystalline solid (153 mg, 91% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 14.16, 7.81 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.06 – 6.97 (m, 7H), 6.85 (d, *J* = 7.79 Hz, 1H), 6.49 (d, *J* = 8.40 Hz, 2H), 3.55 (s, 6H), 2.40 (s, 6H), 2.35 (s, 12H), 1.75 (d, *J* = 10.51 Hz, 2H), 1.56 (s, 4H), 1.52 – 1.43 (m, 6H), 1.33 – 1.26 (m, 2H), 1.02 – 0.90 (m, 6H), 0.87 – 0.76 (m, 2H).

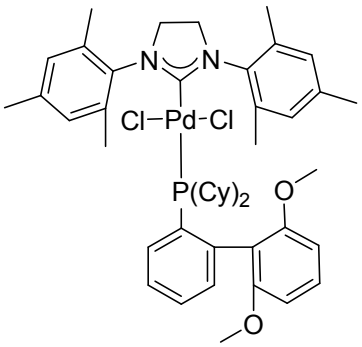
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 172.6 (d, *J* = 186.6 Hz), 158.0 , 140.1 (d, *J* = 22.5 Hz), 138.6 (d, *J* = 2.9 Hz), 138.4 , 136.6 , 135.9 , 131.8 (d, *J* = 5.6 Hz), 129.0 , 128.8 , 128.7 , 128.4 , 128.2 , 124.4 (d, *J* = 14.3 Hz), 122.8 (d, *J* = 5.5 Hz), 119.4 , 103.2 , 55.0 , 31.9 (d, *J* = 20.8 Hz), 30.2 , 28.5 , 27.4 (dd, *J* = 16.0, 11.9 Hz), 26.2 , 21.3 , 19.3 .

^{31}P{^{1}H} NMR (243 MHz, Chloroform-*d*) δ 38.9 .

HRMS (APPI) calc. for $C_{47}H_{59}ClN_2O_2PPd$ [M-Cl]$^+$: 853.3038, 854.3053, 855.3046, 856.3058, 857.3038; found: 853.3031, 854.3044, 855.3041, 856.3055, 857.3034.

IR (KBr, υ/cm^{-1}): 2925 (s), 2853 (m), 1589 (s), 1473 (s), 1443 (m), 1430 (m), 1406 (m), 1333 (w), 1248 (s), 1248 (s), 1032 (m), 1001 (m), 926 (w), 850 (m), 783 (m), 729 (m), 704 (m), 600 (w), 538 (m).

*SIMesPdCl$_2$-SPhos (**3e**)*



Yellowish microcrystalline solid (147 mg, 93% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 13.98, 7.98 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.02 – 6.95 (m, 5H), 6.84 (d, *J* = 8.50 Hz, 1H), 6.48 (d, *J* = 8.40 Hz, 2H), 3.99 (s, 4H), 3.55 (s, 6H), 2.55 (s, 12H), 2.36 (s, 6H), 1.75 – 1.64 (m, 2H), 1.57 – 1.49 (m, 4H), 1.48 – 1.39 (m, 6H), 1.19 (q, *J* = 14.93, 13.51 Hz, 2H), 0.95 – 0.88 (m, 6H), 0.79 (q, *J* = 13.35, 11.86 Hz, 2H).

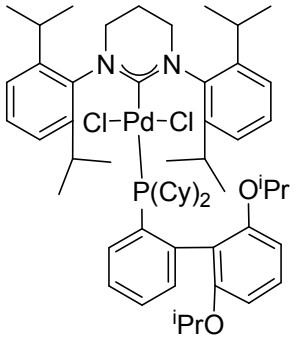
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 200.1 (d, *J* = 175.1 Hz), 158.0 , 140.1 (d, *J* = 22.1 Hz), 138.6 (d, *J* = 2.2 Hz), 137.7 , 137.6 , 131.8 (d, *J* = 5.3 Hz), 129.0 , 128.9 , 128.6 , 128.3 (d, *J* = 32.9 Hz), 124.4 (d, *J* = 14.5 Hz), 119.4 , 103.2 , 100.1 , 54.9 , 51.1 (d, *J* = 6.1 Hz), 31.8 (d, *J* = 20.5 Hz), 30.1 , 28.4 , 27.4 (dd, *J* = 16.94, 11.9 Hz), 26.2 , 21.2 , 19.5 .

^{31}P NMR{^{1}H} (243 MHz, Chloroform-*d*) δ 38.5 .

HRMS (APPI) calc. for $C_{47}H_{61}ClN_2O_2PPd$ $[M\text{-}Cl]^+$: 855.3195, 856.3209, 857.3202, 858.3214, 859.3195; found: 855.3192, 856.3206, 857.3200, 858.3212, 859.3192.

IR (KBr, υ/cm^{-1}): 2925 (m), 2851 (m), 1589 (m), 1475 (vs), 1446 (s), 1430 (s), 1300 (m), 1266 (s), 1248 (s), 1108 (vs), 1031 (m), 1001 (m), 850 (m), 783 (m), 756 (m), 727 (m), 624 (m), 538 (m).

*(6-Dipp)PdCl$_2$-RuPhos (**3f**)*



Yellowish microcrystalline solid (205 mg, 86% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 6.9 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.11 – 6.97 (m, 3H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.38 (d, *J* = 8.3 Hz, 2H), 5.30 (s, 1H), 4.27 – 4.20 (m, 2H), 3.81 – 3.69 (m, 4H), 3.67 – 3.51 (m, 4H), 2.27 (s, 2H), 1.79 – 1.57 (m, 1H), 1.47 (d, *J* = 6.3 Hz, 12H), 1.37 (d, *J* = 10.7 Hz, 4H), 1.33 – 1.20 (m, 5H), 1.15 (d, *J* = 6.8 Hz, 14H), 1.10 (d, *J* = 6.0 Hz, 6H), 0.96 (d, *J* = 5.9 Hz, 6H), 0.93 – 0.77 (m, 6H), 0.76 – 0.56 (m, 4H).

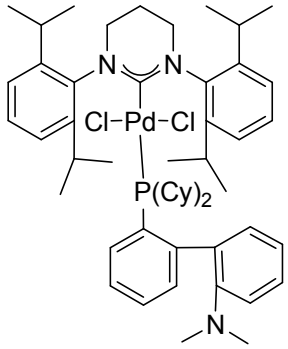
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 198.9 (d, *J* = 182.7 Hz), 157.0 , 147.8 , 142.8 , 139.9 (d, *J* = 21.1 Hz), 139.3 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 5.3 Hz), 128.9 , 128.6 , 128.4 , 128.2 , 127.2 (d, *J* = 2.1 Hz), 123.7 , 123.4 (d, *J* = 14.3 Hz), 122.6 , 105.6 , 70.4 , 53.6 , 50.6 (d, *J* = 5.3 Hz), 31.7 (d, *J* = 20.2 Hz), 29.3 , 27.6 , 27.5 (d, *J* = 12.0 Hz), 26.6 (d, *J* = 11.3 Hz), 26.1 , 23.6 , 22.0 (d, *J* = 5.9 Hz), 20.0 .

$^{31}P\{^{1}H\}$ NMR (243 MHz, Chloroform-*d*) δ 38.7 .

HRMS (APPI) calc. for $C_{58}H_{83}Cl_2N_2O_2PPd$ $[M]^+$: 1046.4613, 1047.4620, 1048.4604, 1049.4624, 1051.4626; found: 1046.4654, 1047.4665, 1048.4649, 1049.4661, 1051.4662.

IR (KBr, υ/cm^{-1}): 2966 (s), 2929 (m), 2866 (m), 2848 (m), 1590 (s), 1490 (vs), 1457 (vs), 1383 (s), 1320 (s), 1301 (s), 1247 (s), 1198 (s), 1117 (vs), 1062 (s), 800 (s), 756 (s), 732 (s).

*(6-Dipp)$PdCl_2$-DavePhos (**3g**)*



Yellowish microcrystalline solid (244 mg, 78% yield)

^{1}H NMR (600 MHz, Chloroform-d) δ 7.35 (t, J = 7.48 Hz, 2H), 7.31 (d, J = 6.99 Hz, 2H), 7.25 (s, 2H), 7.17 (s, 2H), 7.11 – 7.03 (m, 3H), 7.00 (d, J = 7.19 Hz, 1H), 6.77 (d, J = 8.16 Hz, 1H), 6.72 (t, J = 7.21 Hz, 1H), 3.74 – 3.69 (m, 4H), 3.60 (dp, *J* = 26.48, 6.61 Hz, 4H), 2.42 (s, 6H), 2.27 (s, 2H), 2.02 – 1.70 (m, 1H), 1.48 (d, *J* = 6.38 Hz, 6H), 1.40 (d, *J* = 6.45 Hz, 9H), 1.36 – 1.22 (m, 6H), 1.16 (dd, *J* = 11.22, 6.86 Hz, 14H), 1.10 – 1.02 (m, 1H), 0.88 – 0.75 (m, 4H), 0.75 – 0.55 (m, 4H), 0.48 (q, *J* = 13.05 Hz, 1H).

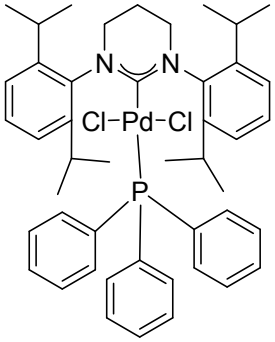
$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 198.4 (d, *J* = 182.8 Hz), 150.5 , 147.8 (d, *J* = 5.6 Hz), 145.0 , 142.6 , 139.8 (d, *J* = 20.4 Hz), 132.7 , 132.1 (d, *J* = 5.6 Hz), 128.5 , 128.3 , 128.2 , 128.0 , 127.4 , 124.3 (d, *J* = 13.72 Hz), 123.8 , 118.7 , 116.9, 50.6 (d, *J* = 5.09 Hz), 43.5 , 31.7 (d, *J* = 19.91 Hz), 30.8 , 30.2 , 29.3 , 29.2 , 28.9 , 28.1 , 27.5 (d, *J* = 7.42 Hz), 26.9 , 26.1 , 25.9 , 23.7 , 23.5 , 20.1 .

$^{31}P\{^{1}H\}$ NMR (243 MHz, Chloroform-*d*) δ 38.7 .

HRMS (APPI) calc. for $C_{54}H_{76}Cl_2N_3PPd$ $[M]^+$: 973.4196, 974.4203, 975.4187, 976.4207, 977.4186; found: 973.4197, 974.4207, 975.4188, 976.4215, 977.4191.

IR (KBr, υ/cm^{-1}): 2925 (s), 2853 (m), 1589 (s), 1473 (s), 1443 (m), 1430 (m), 1405 (m), 1248 (s), 1108 (vs), 1032 (m), 1001 (m), 850 (m), 783 (m), 756 (m), 729 (m), 704 (m), 600 (w), 538 (m).

*(6-Dipp)$PdCl_2$-PPh_3 (**3h**)*



Light yellow solid (210 mg, 98% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (t, *J* = 7.68 Hz, 2H), 7.33 (d, *J* = 7.72 Hz, 4H), 7.24 (d, *J* = 6.97 Hz, 3H), 7.17 – 7.07 (m, 12H), 3.73 (t, *J* = 5.63 Hz, 4H), 3.62 (p, *J* = 6.57 Hz, 4H), 2.34 (s, 2H), 1.32 (d, *J* = 6.50 Hz, 12H), 1.18 (d, *J* = 6.83 Hz, 12H).

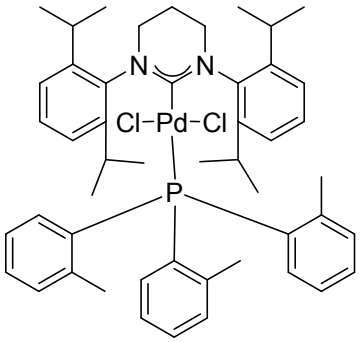
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 197.2 (d, *J* = 192.4 Hz), 147.8 , 142.1 , 135.0 (d, *J* = 10.8 Hz), 130.9 (d, *J* = 43.2 Hz), 129.5 , 128.7 , 127.4 (d, *J* = 10.3 Hz), 124.3 , 50.6 (d, *J* = 4.9 Hz), 29.2 , 27.3 , 23.8 , 20.6 .

^{31}P{^{1}H} NMR (243 MHz, Chloroform-*d*) δ 17.5 .

HRMS (APPI) calc. for $C_{46}H_{55}ClN_2PPd$ $[M\text{-}Cl]^+$: 805.2827, 806.2841, 807.2834, 808.2846, 809.2826, 810.2853; found: 805.2828 806.2844, 807.2838, 808.2850, 809.2829, 810.2853.

IR (KBr, υ/cm^{-1}): 3057 (m), 2967 (s), 2929 (m), 2866 (m), 1588 (w), 1495 (vs), 1436 (s), 1382 (m), 1362 (w), 1321 (s), 1300 (s), 1257 (m), 1200 (m), 1098 (m), 1057 (w), 1028 (w), 992 (w), 931 (w), 802 (m), 756 (m), 742 (m), 692 (s), 631 (m), 528 (s), 510 (m), 494 (m).

*(6-Dipp)$PdCl_2$-P(o-Tol)$_3$ (**3i**)*



Light yellow solid (169 mg, 94% yield)

^{1}H NMR (600 MHz, Chloroform-*d*, 323K) δ 7.40 (t, *J* = 7.57 Hz, 2H), 7.32 (s, 5H), 7.16 (s, 3H), 6.94 (s, 8H), 3.71 (s, 4H), 3.67 – 3.54 (m, 4H), 2.28 (s, 2H), 1.93 – 1.22 (m, 20H), 1.16 (d, *J* = 6.86 Hz, 13H).

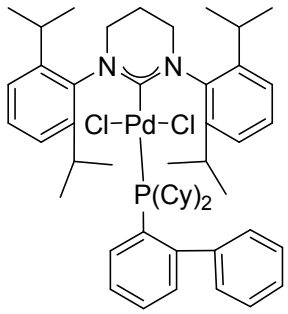
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*, 323K) δ 195.0 (d, *J* = 191.1 Hz), 147.9 , 143.5 (d, *J* = 8.3 Hz), 142.7 , 133.3 , 131.1 (d, *J* = 7.4 Hz), 129.0 , 127.2 (d, *J* = 38.8 Hz), 124.4 , 51.3 (d, *J* = 5.2 Hz), 29.3 , 27.4 , 23.8 , 20.5 .

^{31}P{^{1}H} NMR (243 MHz, Chloroform-*d*) δ 15.9 .

HRMS (APPI) calc. for $C_{49}H_{61}ClN_2PPd$ $[M\text{-}Cl]^+$: 847.3296, 848.3311, 849.3305, 850.3316, 851.3297, 852.3323; found: 847.3282, 848.3296, 849.3288, 850.3292, 851.3279, 852.3293.

IR (KBr, υ/cm^{-1}): 3052 (w), 2965 (s), 2866 (m), 1589 (w), 1565 (w), 1493 (vs), 1443 (s), 1382 (m), 1320 (s), 1299 (s), 1257 (w), 1203 (m), 1130 (w), 1102 (w), 1029 (w), 995 (w), 929 (w), 802 (m), 750 (vs), 680 (w), 664 (w), 633 (m), 558 (m), 534 (m), 462 (m).

*(6-Dipp)PdCl$_2$-CyJohnPhos (**3j**)*



Yellowish microcrystalline solid (222 mg, 98% yield)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.32 (m, 2H), 7.28 (d, *J* = 7.47 Hz, 4H), 7.24 – 7.17 (m, 3H), 7.16 – 7.12 (m, 5H), 6.93 – 6.88 (m, 1H), 3.74 – 3.69 (m, 4H), 3.61 (p, *J* = 6.54 Hz, 4H), 2.29 (p, *J* = 5.55 Hz, 2H), 1.46 – 1.34 (m, 21H), 1.33 – 1.23 (m, 5H), 1.16 (d, *J* = 6.81 Hz, 12H), 0.83 – 0.67 (m, 8H).

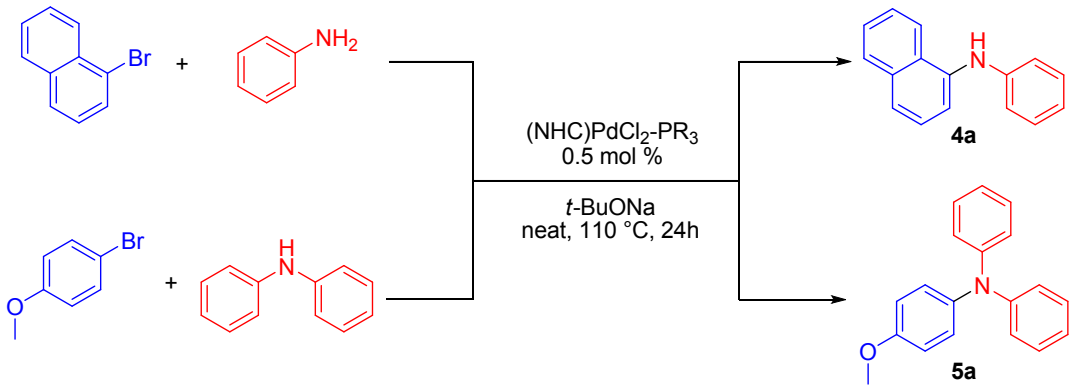
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 197.8 (d, *J* = 182.7 Hz), 147.7 , 145.9 , 142.6 , 131.1 (d, *J* = 6.2 Hz), 129.7 , 128.7 , 127.8 (d, *J* = 36.2 Hz), 126.7 , 125.0 (d, *J* = 12.4 Hz), 124.0 , 50.8 (d, *J* = 4.9 Hz), 34.3 , 30.1 , 29.2 , 28.4 , 27.4 , 27.2 (d, *J* = 10.9 Hz), 26.9 (d, *J* = 11.1 Hz), 26.1 , 23.7 , 22.5 , 20.3 , 14.2 .

^{31}P{^{1}H} NMR (243 MHz, Chloroform-*d*) δ 32.2 .

HRMS (APPI) calc. for $C_{52}H_{71}ClN_2PPd$ $[M\text{-}Cl]^+$: 893.4079, 894.4094, 895.4088, 896.4100, 897.4081; found: 893.4083, 894.4090, 895.4083, 896.4098, 897.4076.

IR (KBr, υ/cm^{-1}): 2961 (s), 2929 (s), 2852 (m), 1493 (vs), 1466 (s), 1443 (s), 1380 (m), 1320 (s), 1301 (s), 1254 (m), 1198 (s), 1111 (m), 853 (m), 800 (s), 757 (s), 700 (s), 634 (m).

Screening of catalytic systems in BHA reaction of 1-bromonaphthalene with aniline and 1-bromo-4-methoxybenzene with diphenylamine



General procedure for screening of catalytic systems in solvent free BHA reaction of 1-bromonaphthalene with aniline

A one neck round bottom 10 ml flask equipped with a reflux condenser with argon inlet and a magnetic stir bar was charged with 1 mmol of 1-bromonaphthalene, aniline (1 equiv.), (NHC)$PdCl_2$-PR_3 (0.5 mol %), and finally 1.2 equiv. of powdered *t*-BuONa. The reaction mixture was degassed with 3 Freeze-Pump-Thaw cycles. A flask was transferred to a preheated oil bath (110 °C). After 24 h reaction mixture was cooled, dissolved in EtOAc and filtered through short pad (0.5 cm) of silica gel. Purification by dry column vacuum chromatography using hexanes-EtOAc (50-10:1) as eluent gave N-phenylnaphthalen-1-amine (**4a**).

General procedure for screening of catalytic systems in solvent free BHA reaction of 1-bromo-4-methoxybenzene with diphenylamine

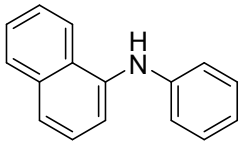
A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol of 1-bromo-4-methoxybenzene, diphenylamine (1 equiv.), (NHC)$PdCl_2$-PR_3 (0.5 mol %), and finally 1.2 equiv. of powdered *t*-BuONa. The vial was transferred to a preheated oil bath (110 °C). After 24h reaction mixture was cooled, dissolved in EtOAc and filtered through short pad (0.5 cm) of silica gel. Purification by dry-column-vacuum chromatography using hexanes-EtOAc (50-10:1) as eluent gave 4-methoxy-N,N-diphenylaniline (**5a**).

Entry	Catalyst	Isolated yield (%)	
		4a	**5a**
1	**(6-Dipp)$PdCl_2$-SPhos (3a)**	98	95
2	IPr$PdCl_2$-SPhos (**3b**)	86	84
3	SIPr$PdCl_2$-SPhos (**3c**)	90	82
4	IMes$PdCl_2$-SPhos (**3d**)	0	85
5	SIMes$PdCl_2$-SPhos (**3e**)	0	92
6	(6-Dipp)$PdCl_2$-RuPhos (**3f**)	86	93
7	(6-Dipp)$PdCl_2$-DavePhos (**3g**)	86	84
8	(6-Dipp)$PdCl_2$-PPh_3 (**3h**)	48	15
9	(6-Dipp)$PdCl_2$-P(*o*-Tol)$_3$ (**3i**)	98	14
10	(6-Dipp)$PdCl_2$-CyJohnPhos (**3j**)	98	70

General procedure for solvent free preparation of diarylamines via arylation of primary amines

A one neck round bottom 10 ml flask equipped with a reflux condenser with argon inlet and a magnetic stir bar was charged with 1 mmol of aryl or (het)arylhalide, primary amine (1 equiv.), (6-Dipp)$PdCl_2$-SPhos (0.5 or 1 mol %), and finally 1.2 equiv. of powdered *t*-BuONa. The reaction mixture was degassed with 3 Freeze-Pump-Thaw cycles. A flask was transferred to a preheated oil bath (110 °C). After 24h reaction mixture was cooled, dissolved in EtOAc and filtered through short pad (0.5 cm) of silica gel. In some cases additional purification by dry column vacuum chromatography using hexanes-EtOAc (50-10:1) as eluent was required.

*N-phenylnaphthalen-1-amine (**4a**)*



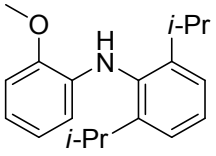
Yellow solid (215 mg, 98% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 (dq, *J* = 15.0, 6.8 Hz, 2H), 7.41 (d, *J* = 11.7 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 5.98 (br. s, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 144.9 , 138.9 , 134.8 , 129.5 , 128.7 , 127.9 , 126.3 , 126.2 , 125.8 , 123.1 , 121.9 , 120.7 , 117.5 , 116.0 .

The NMR data are in agreement with previously reported.[19]

*2,6-diisopropyl-N-(2-methoxyphenyl)aniline (**4b**)*



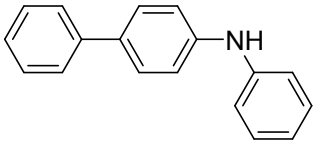
Colorless oil (282 mg, >99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.70 (dt, *J* = 22.9, 7.4 Hz, 2H), 6.13 (d, *J* = 7.6 Hz, 1H), 5.64 (s, 1H), 3.97 (s, 3H), 3.17 (p, *J* = 6.8 Hz, 2H), 1.16 (d, *J* = 6.8 Hz, 12H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 147.8 , 146.4 , 138.1 , 135.5 , 127.2 , 123.9 , 121.3 , 116.8 , 111.1 , 109.8 , 55.8 , 28.3 .

The NMR data are in agreement with previously reported.[20]

*N-phenylbiphenyl-4-amine (**4c**)*



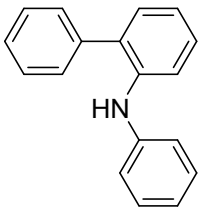
White solid (244 mg, >99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.35 Hz, 2H), 7.53 (d, *J* = 8.47 Hz, 2H), 7.44 (t, *J* = 7.65 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.15 (dd, *J* = 11.92, 8.16 Hz, 4H), 6.97 (t, *J* = 7.33 Hz, 1H), 5.79 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.9 , 142.6 , 140.9 , 133.8 , 129.5 , 128.9 , 128.1 , 126.7 , 126.7 , 121.3 , 118.2 , 117.9 .

The NMR data are in agreement with previously reported.[21]

*N-phenylbiphenyl-2-amine (**4d**)*



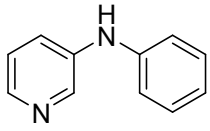
Beige oil (197 mg, 80% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 – 7.45 (m, 5H), 7.42 (t, *J* = 7.03 Hz, 1H), 7.32 (q, *J* = 7.35 Hz, 4H), 7.12 – 7.05 (m, 3H), 6.99 (t, *J* = 7.31 Hz, 1H), 5.67 (s, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 143.5 , 140.3 , 139.1 , 131.6 , 131.0 , 129.4 , 129.0 , 128.3 , 127.6 , 121.2 , 118.3 , 117.6 .

The NMR data are in agreement with previously reported.[22]

*N-phenylpyridin-3-amine (**4e**)*



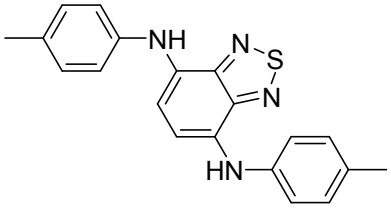
White solid (116 mg, 68% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 2.5 Hz, 1H), 8.18 – 8.14 (m, 1H), 7.41 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.16 (dd, *J* = 8.2, 4.7 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 5.94 (br. s, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 142.1 , 142.0 , 140.3 , 140.0 , 129.7 , 123.8 , 123.5 , 122.1 , 118.4 .

The NMR data are in agreement with previously reported.[19]

*N^4,N^7-di-p-tolylbenzo[c][1,2,5]thiadiazole-4,7-diamine (**4f**)*



Purple solid (309 mg, 89% yield).

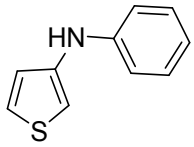
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.14 (s, 8H), 7.10 (s, 2H), 6.58 (s, 2H), 2.34 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 149.5 , 139.7 , 131.3 , 130.1 , 128.5 , 119.0 , 109.2 , 20.9 .

HRMS (ESI) calc. for $C_{20}H_{19}N_4S$ $[M+H]^+$: 347.1330; found: 347.1329.

IR (KBr, υ/cm^{-1}): 3024 (m), 2965 (m), 2909 (w), 1604 (m), 1585 (m), 1519 (vs), 1333 (m), 1313 (m), 1296 (s), 1261 (m), 1240 (m), 1111 (m), 1047 (m), 893 (m), 805 (s), 700 (w), 620 (w), 530 (w), 504 (m).

*N-phenylthiophen-3-amine (**4g**)*



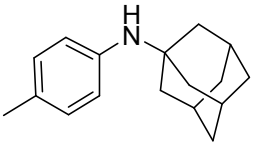
White solid (175 mg, 64% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.27 (m, 3H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.95 (dd, *J* = 5.1, 1.6 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.77 (dd, *J* = 2.9, 1.3 Hz, 1H), 5.72 (br. s, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 144.8 , 141.6 , 129.5 , 125.3 , 123.0 , 120.0 , 115.7 , 106.7 .

The NMR data are in agreement with previously reported.[19]

*N-(p-Tolyl)adamantan-1-amine (**4h**)*



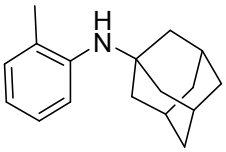
Beige solid (123 mg, 51% yield).

H NMR (600 MHz, Chloroform-*d*) δ 7.00 – 6.96 (d, *J* = 7.9 Hz, 2H), 6.77 – 6.72 (d, *J* = 7.9 Hz, 2H), 3.00 (br. s, 1H), 2.26 (s, 3H), 2.09 (s, 3H), 1.82 (s, 6H), 1.66 (q, *J* = 12.1 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 143.3 , 129.5 , 129.3 , 121.0 , 52.5 , 43.8 , 36.6 , 29.9 , 20.7 .

The NMR data are in agreement with previously reported.[23]

*N-(o-Tolyl)adamantan-1-amine (**4i**)*



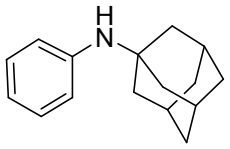
White solid (174 mg, 72% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.06 (t, *J* = 5.9 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 3.27 (br. s, 1H), 2.15 (s, 3H), 2.13 (s, 3H), 1.96 (s, 6H), 1.70 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 144.6 , 130.6 , 126.5 , 124.5 , 117.8 , 116.4 , 52.3 , 43.6 , 36.7 , 29.9 , 18.5 .

HRMS (APCI) calc. for $C_{17}H_{24}N$ $[M+H]^{+}$: 242.1909; found: 242.1909.

*N-(1-adamantyl)-N-phenylamine (**4j**)*



Beige solid (211 mg, 93% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.15 (t, *J* = 7.8 Hz, 2H), 6.79 (t, *J* = 7.9 Hz, 3H), 3.21 (s, 1H), 2.11 (s, 3H), 1.88 (s, 6H), 1.68 (q, *J* = 12.0 Hz, 6H).

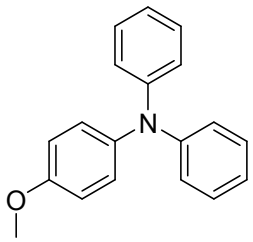
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 146.2 , 128.9 , 119.3 , 119.2 , 52.4 , 43.6 , 36.6 , 29.9 .

The NMR data are in agreement with previously reported.[24]

General procedure for solvent free preparation of triarylamines via arylation of secondary amines

A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol of aryl or (het)arylhalide, secondary amine (1 equiv.), (6-Dipp)PdCl2-SPhos (0.5 or 1 mol %), and finally 1.2 equiv. of powdered *t*-BuONa. The vial was transferred to a preheated oil bath (110 °C). After 24h reaction mixture was cooled, dissolved in EtOAc and filtered through short pad (0.5 cm) of silica gel. In some cases additional purification by dry column vacuum chromatography using hexanes-EtOAc (50:1) as eluent was required.

*4-methoxy-N,N-diphenylaniline (**5a**)*



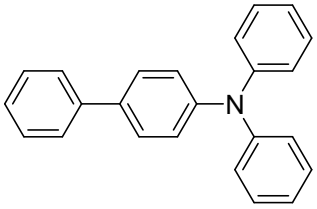
White solid (262 mg, 95% yield in case of amination with diphenylamine and 124 mg, 90% yield in case of one-pot two-step amination).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.9 Hz, 4H), 7.09 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 7.7 Hz, 4H), 6.96 (t, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 156.3 , 148.3 , 140.9 , 129.2 , 127.4 , 123.0 , 122.0 , 114.9 , 55.6 .

The NMR data are in agreement with previously reported.[19]

*N,N-diphenylbiphenyl-4-amine (**5b**)*



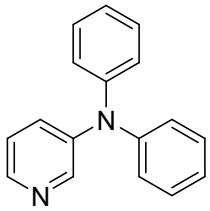
White solid (312 mg, 97% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.25 Hz, 2H), 7.49 (d, *J* = 8.57 Hz, 2H), 7.43 (t, *J* = 7.71 Hz, 2H), 7.34 – 7.27 (m, 5H), 7.15 (d, *J* = 8.49 Hz, 6H), 7.05 (t, *J* = 7.34 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 147.8 , 147.3 , 140.8 , 135.3 , 129.4 , 128.9 , 127.9 , 126.9 , 126.8 , 124.6 , 124.0 , 123.1 .

The NMR data are in agreement with previously reported.[25]

*N,N-diphenylpyridin-3-amine (**5c**)*



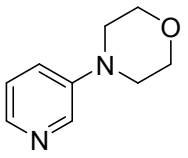
White solid (193 mg, 78% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.21 (d, *J* = 3.8 Hz, 1H), 7.36 (ddd, *J* = 8.2, 2.5, 1.3 Hz, 1H), 7.31 – 7.27 (m, 4H), 7.14 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.11 – 7.06 (m, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 147.0 , 145.2 , 144.5 , 143.0 , 129.7 , 129.4 , 124.6 , 123.8 , 123.8 .

The NMR data are in agreement with previously reported.[26]

*4-(pyridin-3-yl)morpholine (**5d**)*



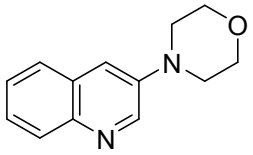
Beige oil (163 mg, >99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.13 – 8.10 (m, 1H), 7.18 (d, *J* = 2.4 Hz, 2H), 3.88 – 3.85 (m, 4H), 3.20 – 3.17 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 147.1 , 140.9 , 138.1 , 123.7 , 122.4 , 66.8 , 48.7 .

The NMR data are in agreement with previously reported.[27]

*4-(quinolin-3-yl)morpholine (**5e**)*



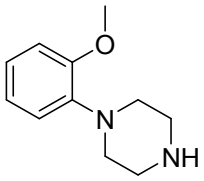
Colorless solid (212 mg, >99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 2.7 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 2.4 Hz, 1H), 3.95 – 3.91 (m, 4H), 3.30 – 3.26 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 144.9 , 144.6 , 143.2 , 129.0 , 128.8 , 127.2 , 126.7 , 116.9 , 66.8 , 49.5 .

The NMR data are in agreement with previously reported.[27]

*1-(2-methoxyphenyl)piperazine (**5f**)*



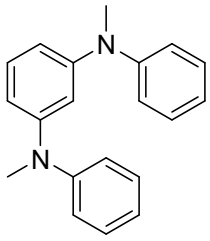
Beige oil (115 mg, 60% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.00 (t, *J* = 7.2 Hz, 1H), 6.97 – 6.89 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.12 – 3.00 (m, 8H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 152.3 , 141.6 , 123.2 , 121.1 , 118.4 , 111.2 , 55.4 , 51.7 , 46.1 .

The NMR data are in agreement with previously reported.[28]

*N^1,N^3-dimethyl-N^1,N^3-diphenylbenzene-1,3-diamine (**5g**)*



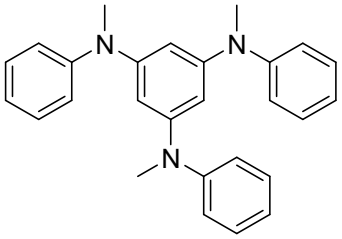
Colorless oil (286 mg, >99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.26 (m, 4H), 7.17 (t, *J* = 8.05 Hz, 1H), 7.04 (d, *J* = 7.70 Hz, 4H), 6.94 (t, *J* = 7.32 Hz, 2H), 6.71 (s, 1H), 6.63 (dd, *J* = 8.06, 2.17 Hz, 2H), 3.29 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 150.0 , 149.1 , 129.8 , 129.2 , 121.2 , 120.5 , 113.8 , 112.9 , 40.4 .

HRMS (APCI) calc. for $C_{20}H_{21}N_2$ $[M+H]^+$: 289.1705; found: 289.1712.

*N^1,N^3,N^5-trimethyl-N^1,N^3,N^5-triphenylbenzene-1,3,5-triamine (**5h**)*



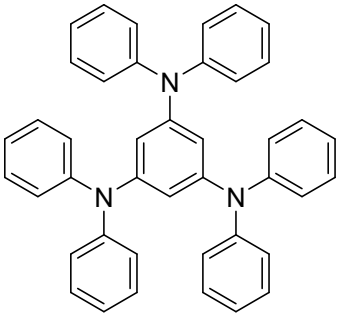
White solid (386 mg, 98% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.55 Hz, 6H), 7.03 (d, *J* = 7.80 Hz, 6H), 6.90 (t, *J* = 7.31 Hz, 3H), 6.33 (s, 3H), 3.25 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 150.5 , 148.9 , 129.2 , 121.0 , 120.2 , 106.9 , 40.4 .

HRMS (APCI) calc. for $C_{27}H_{28}N_3$ $[M+H]^+$: 394.2283; found: 394.2286.

*N^1,N^1,N^3,N^3,N^5,N^5-hexaphenylbenzene-1,3,5-triamine (**5i**)*



White solid (476 mg, 82% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.16 (t, *J* = 7.9 Hz, 12H), 7.02 (d, *J* = 8.3 Hz, 12H), 6.91 (t, *J* = 7.3 Hz, 6H), 6.42 (s, 3H).

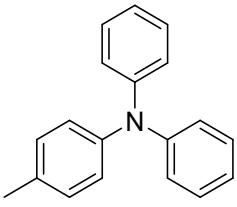
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 149.1 , 147.4 , 129.1 , 124.0 , 122.7 , 114.7 .

The NMR data are in agreement with previously reported.[25]

General procedure for solvent free one-pot two-step preparation of triarylamines via arylation of primary amines

A one neck round bottom 10 ml flask equipped with a reflux condenser with argon inlet and a magnetic stir bar was charged with 2 mmol of aryl or (het)arylhalide, primary amine (1 equiv.), (6-Dipp)$PdCl_2$-SPhos (2 mol %), and finally 2.4 equiv. of powdered *t*-BuONa. The reaction mixture was degassed with 3 Freeze-Pump-Thaw cycles. A flask was transferred to a preheated oil bath (110, 150 or 170 °C). After 24h reaction mixture was cooled, dissolved in EtOAc and filtered through short pad (0.5 cm) of silica gel. In some cases additional purification by dry column vacuum chromatography using hexanes-EtOAc (50:1) as eluent was required.

*4-methyl-N,N-diphenylaniline (**6a**)*



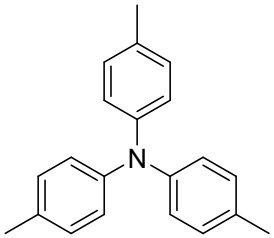
White solid (122 mg, 94% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.93 Hz, 4H), 7.07 (t, *J* = 7.06 Hz, 6H), 7.01 (d, *J* = 8.35 Hz, 2H), 6.97 (t, *J* = 7.34 Hz, 2H), 2.32 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 148.2 , 145.4 , 132.9 , 130.1 , 129.2 , 125.1 , 123.7 , 122.4 , 21.0 .

The NMR data are in agreement with previously reported.[27]

*Tri-p-tolylamine (**6b**)*



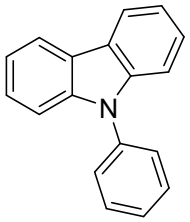
White solid (128 mg, 89% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.04 (d, *J* = 8.14 Hz, 6H), 6.97 (d, *J* = 8.26 Hz, 6H), 2.31 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 145.8 , 131.9 , 129.9 , 124.0 , 20.9 .

The NMR data are in agreement with previously reported.[29]

*9-phenyl-9H-carbazole (**6c**)*



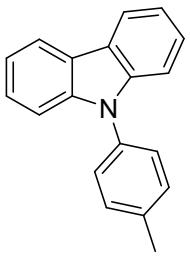
White solid (121 mg, >99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.77 Hz, 2H), 7.63 (dt, *J* = 14.18, 7.48 Hz, 4H), 7.52 – 7.43 (m, 5H), 7.37 – 7.32 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.0 , 137.8 , 130.0 , 127.6 , 127.3 , 126.0 , 123.5 , 120.4 , 120.0 , 109.9 .

The NMR data are in agreement with previously reported.[30]

*9-p-tolyl-9H-carbazole (**6d**)*



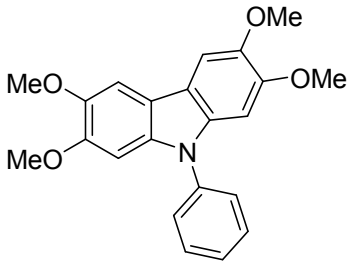
Colorless needles (128 mg, >99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.73 Hz, 2H), 7.46 – 7.38 (m, 8H), 7.30 – 7.27 (m, 2H), 2.50 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.2 , 137.5 , 135.1 , 130.6 , 127.1 , 126.0 , 123.4 , 120.4 , 119.8 , 109.9 , 21.4 .

The NMR data are in agreement with previously reported.[30]

*2,3,6,7-tetramethoxy-9-phenyl-9H-carbazole (**6e**)*



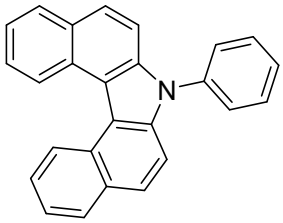
White solid (111 mg, 61% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (t, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.47 (s, 3H), 6.88 (s, 2H), 4.03 (s, 6H), 3.88 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 148.4 , 144.8 , 138.2 , 135.3 , 130.1 , 127.3 , 126.9 , 115.7 , 101.8 , 93.7 , 56.7 , 56.3 .

The NMR data are in agreement with previously reported.[31]

*7-phenyl-7H-dibenzo[c,g]carbazole (**6f**)*



White solid (76 mg, 44% yield).

^{1}H NMR (600 MHz, Chloroform-d) δ 9.31 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.75 (t, J = 7.2 Hz, 2H), 7.67 (t, J = 7.6 Hz, 2H), 7.62 – 7.54 (m, 7H).

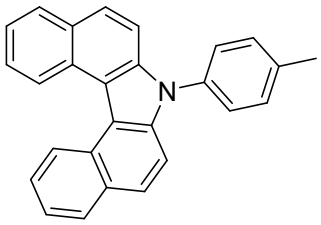
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 138.1 , 137.1 , 130.3 , 130.1 , 129.3 , 129.2 , 128.5 , 128.4 , 126.9 , 125.6 , 125.4 , 123.6 , 117.7 , 111.9 .

IR (KBr, υ/cm^{-1}): 3048 (s), 1589 (s), 1520 (s), 1502 (vs), 1452 (s), 1437 (m), 1397 (s), 1383 (s), 1354 (s), 1320 (s), 1300 (s), 1248 (m), 1206 (m), 1174 (m), 1154 (m), 1143 (m), 1124

(m), 1080 (m), 1041 (m), 1027 (m), 1012 (s), 951 (m), 922 (m), 856 (m), 800 (vs), 767 (s), 747 (vs), 702 (s), 686 (m), 666 (m), 614 (m), 556 (w), 521 (m), 504 (m), 460 (m), 421 (m).

HRMS (APCI) calc. for $C_{26}H_{18}N$ $[M+H]^+$: 344.1439; found: 344.1436.

*7-p-tolyl-7H-dibenzo[c,g]carbazole (**6g**)*



White solid (93 mg, 52% yield).

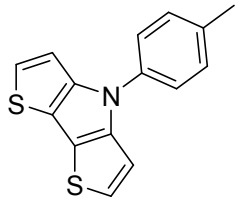
^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.29 (d, *J* = 8.39 Hz, 2H), 8.05 (d, *J* = 7.90 Hz, 2H), 7.84 (d, *J* = 8.75 Hz, 2H), 7.72 (t, *J* = 7.55 Hz, 2H), 7.59 – 7.53 (m, 4H), 7.46 (s, 4H), 2.55 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 138.5 , 138.3 , 134.4 , 130.7 , 130.3 , 129.3 , 128.2 , 126.8 , 125.6 , 125.4 , 123.5 , 117.6 , 112.0 , 21.4 .

IR (KBr, υ/cm^{-1}): 3047 (m), 1616 (m), 1594 (m), 1579 (m), 1518 (s), 1457 (m), 1439 (m), 1400 (m), 1380 (m), 1310 (m), 1297 (m), 1251 (m), 1207 (m), 1110 (m), 1044 (m), 1015 (m), 942 (w), 840 (m), 796 (vs), 766 (m), 733 (s), 670 (w), 633 (w), 613 (w), 556 (w), 514 (m), 505 (m), 460 (w), 425 (w).

HRMS (APCI) calc. for $C_{27}H_{20}N$ $[M+H]^+$: 358.1596; found: 358.1592.

*4-p-tolyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (**6h**)*



Yellow needles (95 mg, 70% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.21 Hz, 2H), 7.33 (d, *J* = 7.97 Hz, 2H), 7.20 – 7.12 (m, 4H), 2.44 (s, 3H).

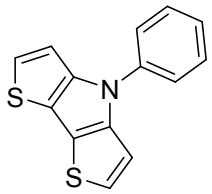
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 144.3 , 137.5 , 136.0 , 130.4 , 123.5 , 122.8 , 116.7 , 112.4 , 21.2 .

IR (KBr, υ/cm^{-1}): 3107 (m), 3080 (m), 3032 (m), 1898 (m), 1712 (w), 1608 (m), 1516 (vs), 1407 (s), 1382 (s), 1304 (m), 1117 (m), 1107 (s), 1085 (s), 1054 (m), 1014 (m), 856 (m), 836 (m), 805 (s), 744 (m), 702 (vs), 656 (s), 558 (m), 508 (m), 484 (m).

HRMS (APCI) calc. for $C_{15}H_{12}NS_2$ $[M+H]^+$: 270.0411; found: 270.0411.

The NMR data are in agreement with previously reported.[32]

*4-phenyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (**6i**)*



Yellow needles (101 mg, 70% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 9.24 Hz, 2H), 7.54 (t, *J* = 7.90 Hz, 2H), 7.34 (t, *J* = 7.39 Hz, 1H), 7.18 (s, 4H).

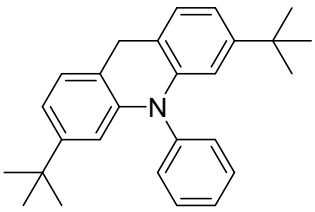
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 144.1 , 140.0 , 129.9 , 126.1 , 123.6 , 122.8 , 117.1 , 112.4 .

IR (KBr, υ/cm^{-1}): 3098 (s), 3084 (s), 3047 (s), 1596 (s), 1508 (vs), 1402 (vs), 1303 (s), 1104 (s), 1084 (s), 859 (m), 765 (s), 727 (s), 690 (vs), 649 (s), 478 (s).

HRMS (APCI) calc. for $C_{14}H_{10}NS_2$ $[M+H]^+$: 256.0255; found: 256.0251.

The NMR data are in agreement with previously reported.[32]

*3,6-di-tert-butyl-10-phenyl-9,10-dihydroacridine (**6j**)*



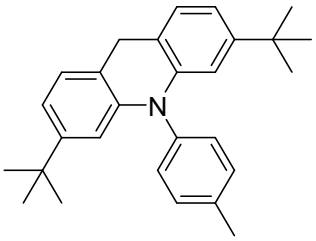
Beige oil (115 mg, 62% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (t, *J* = 7.03 Hz, 2H), 7.51 (t, *J* = 7.43 Hz, 1H), 7.36 (d, *J* = 8.03 Hz, 2H), 7.08 (d, *J* = 7.66 Hz, 2H), 6.89 (d, *J* = 7.81 Hz, 2H), 6.26 (s, 2H), 4.19 (s, 2H), 1.13 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 149.8 , 142.7 , 131.5 , 130.7 , 128.1 , 118.3 , 117.5 , 111.6 , 34.6 , 31.4 , 31.2 .

HRMS (APCI) calc. for $C_{27}H_{30}N$ $[M-H]^+$: 368.2378; found: 368.2381.

*3,6-di-tert-butyl-10-p-tolyl-9,10-dihydroacridine (**6k**)*



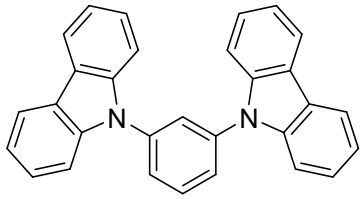
Yellow solid (104 mg, 54% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.93 Hz, 2H), 7.21 (d, *J* = 8.11 Hz, 2H), 7.06 (d, *J* = 7.82 Hz, 2H), 6.87 (dd, *J* = 7.82, 1.79 Hz, 2H), 6.28 (d, *J* = 1.70 Hz, 2H), 4.16 (s, 2H), 2.50 (s, 3H), 1.13 (s, 18H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 149.7 , 142.8 , 138.5 , 137.8 , 131.3 , 131.0 , 128.0 , 118.3 , 117.3 , 111.5 , 34.6 , 31.4 , 31.2 , 21.5 .

HRMS (APCI) calc. for $C_{28}H_{32}N$ $[M-H]^{+}$: 382.2535; found: 382.2535.

*1,3-di(9H-carbazol-9-yl)benzene (**6l**)*



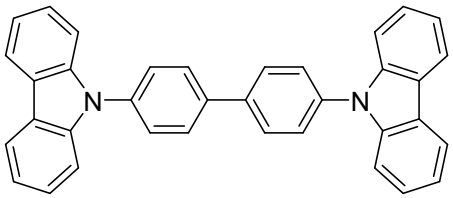
White solid (141 mg, 69% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 7.7 Hz, 4H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.73 (dd, *J* = 7.9, 1.9 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 4H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 140.7 , 139.5 , 131.3 , 126.3 , 126.0 , 125.5 , 123.7 , 120.6 , 120.5 , 109.8 .

The NMR data are in agreement with previously reported.[33]

*4,4'-di(9H-carbazol-9-yl)biphenyl (**6m**)*



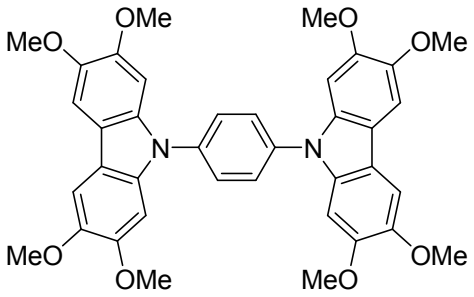
White solid (185 mg, 76% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.8 Hz, 4H), 7.92 (d, *J* = 8.3 Hz, 4H), 7.73 (d, *J* = 8.3 Hz, 4H), 7.55 (d, *J* = 8.2 Hz, 4H), 7.48 (t, *J* = 8.1 Hz, 4H), 7.35 (t, *J* = 7.8 Hz, 4H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.0 , 139.4 , 137.4 , 128.6 , 127.6 , 126.2 , 123.6 , 120.5 , 120.2 , 110.0 .

The NMR data are in agreement with previously reported.[34]

*1,4-bis(2,3,6,7-tetramethoxy-9H-carbazol-9-yl)benzene (**6n**)*



White solid (82 mg, 25% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 (s, 4H), 7.50 (s, 4H), 7.06 (s, 4H), 4.06 (s, 12H), 3.93 (s, 12H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 148.6 , 145.2 , 137.0 , 135.0 , 128.0 , 116.2 , 102.1 , 94.1 , 56.8 , 56.6 .

The NMR data are in agreement with previously reported.[35]

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NMR spectra

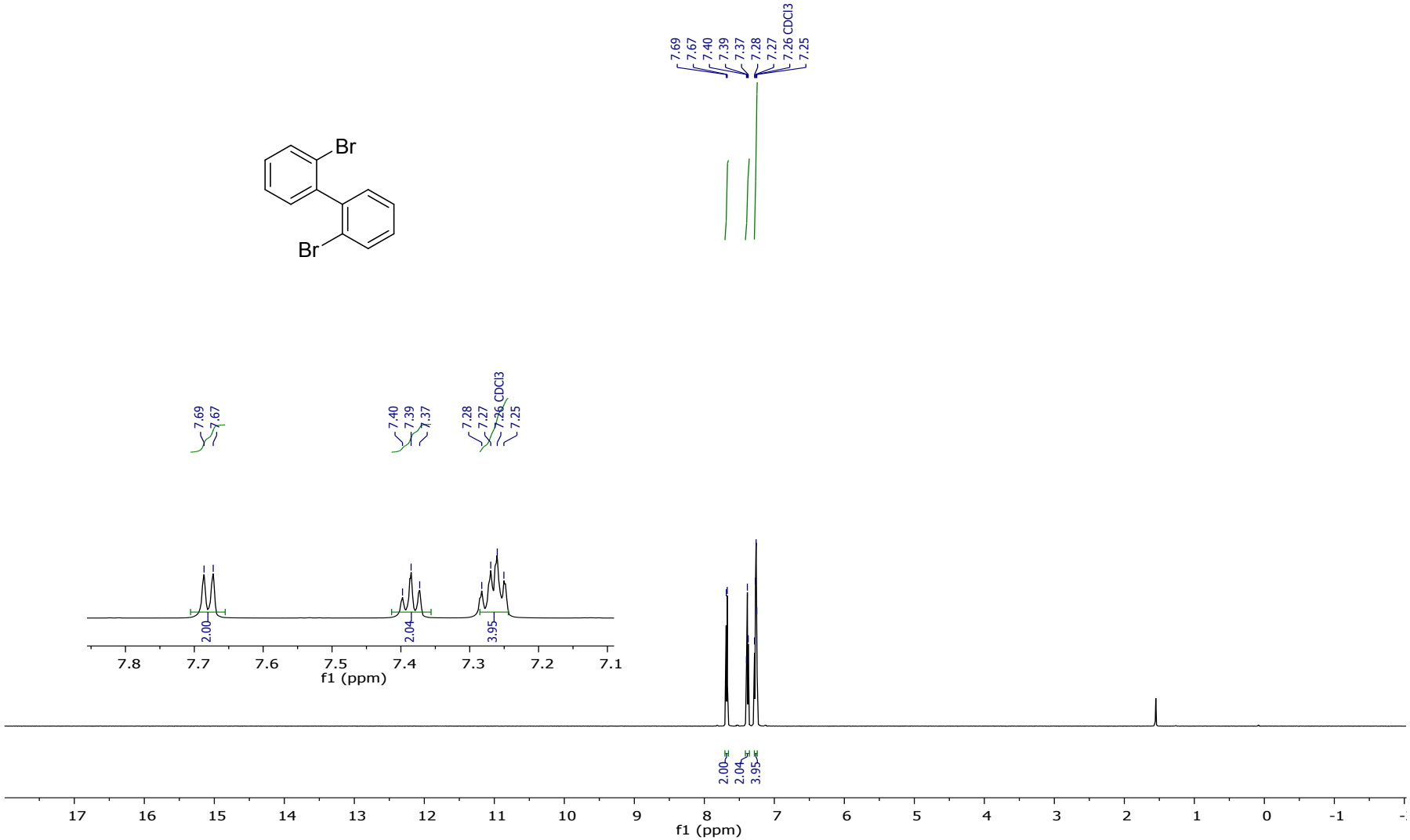

Figure S1. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,2'-dibromobiphenyl

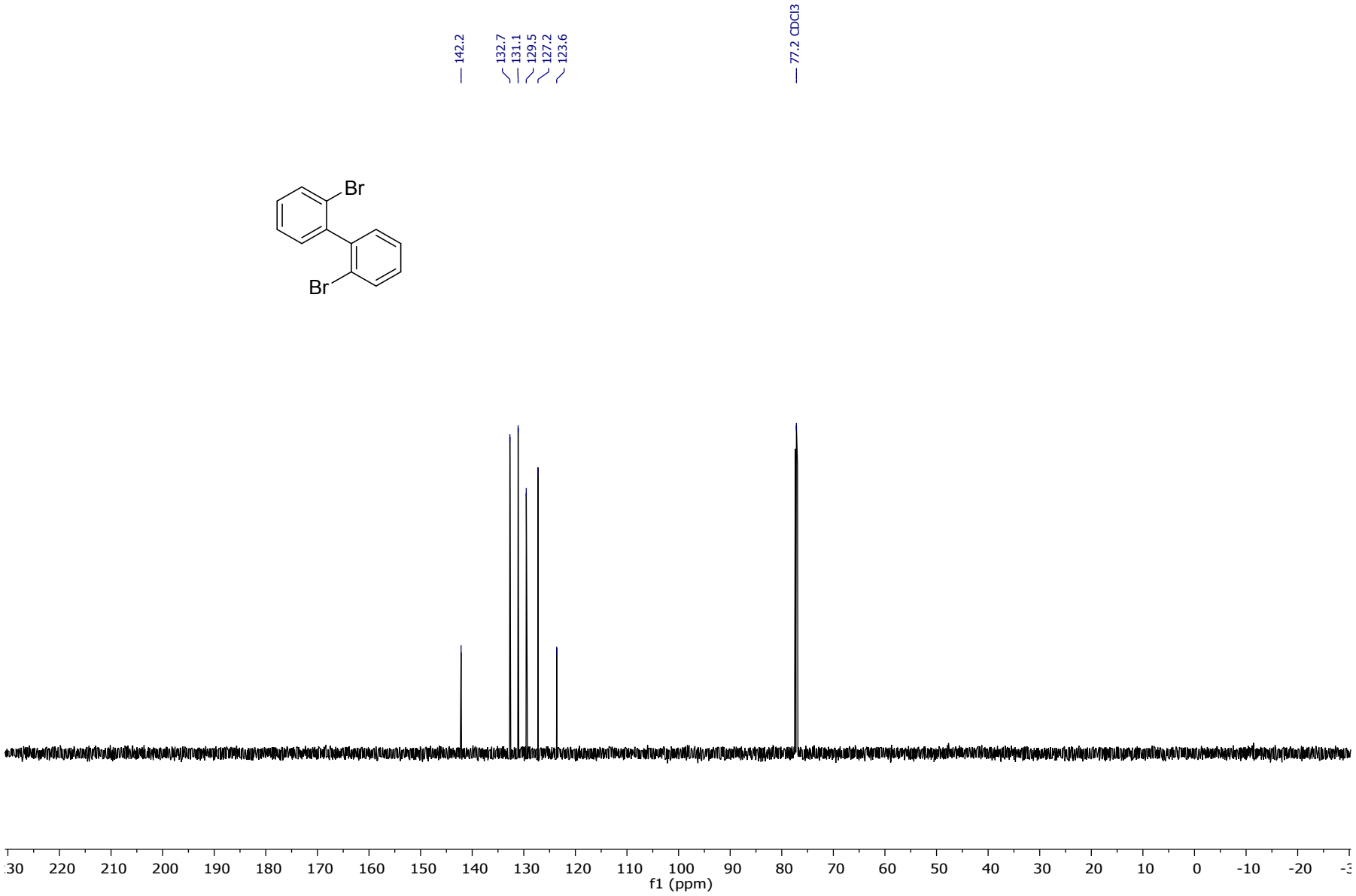

Figure S2. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,2'-dibromobiphenyl

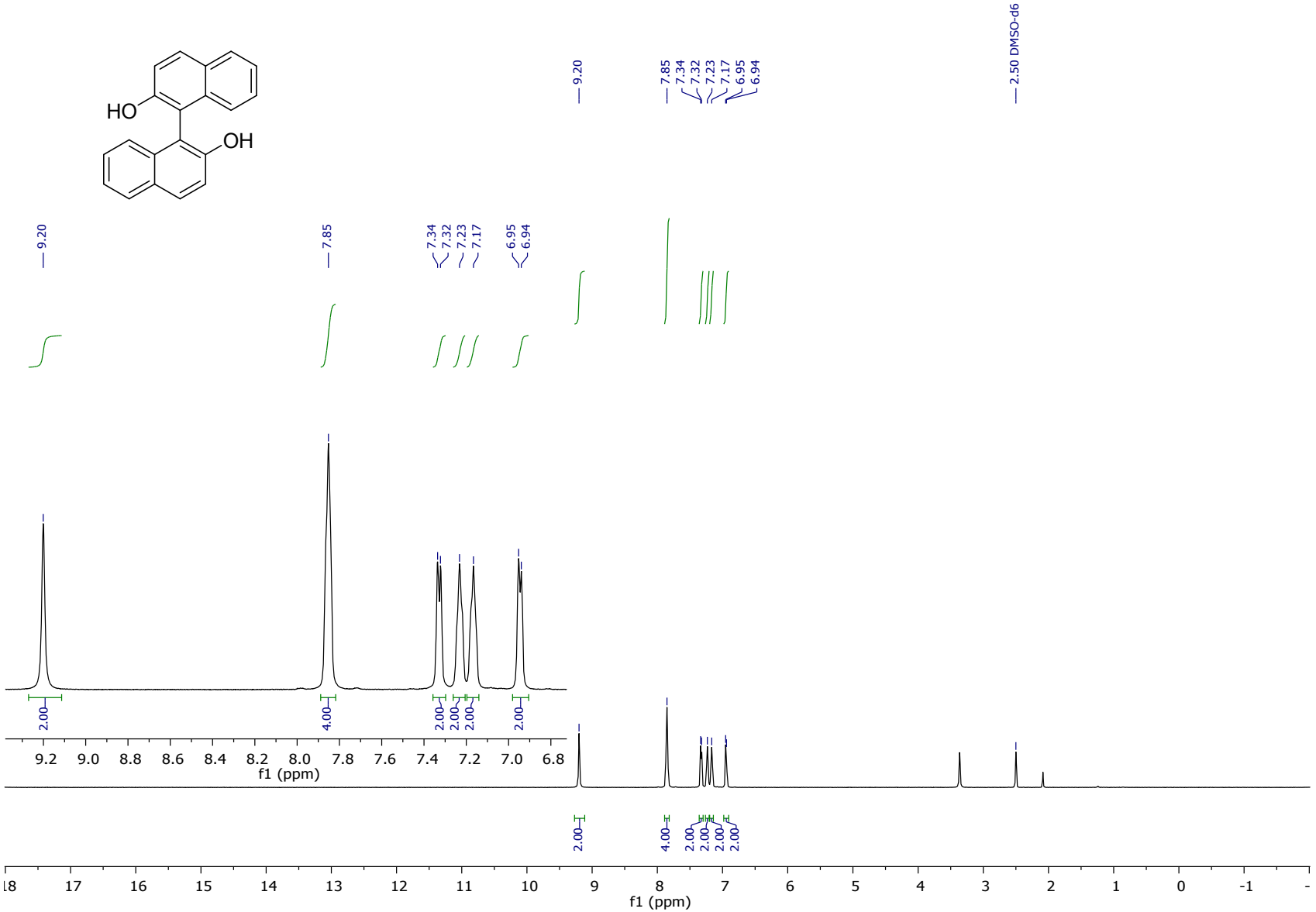

Figure S3. ^{1}H NMR (600 MHz, DMSO-*d6*) of 1,1'-binaphthyl-2,2'-diol.

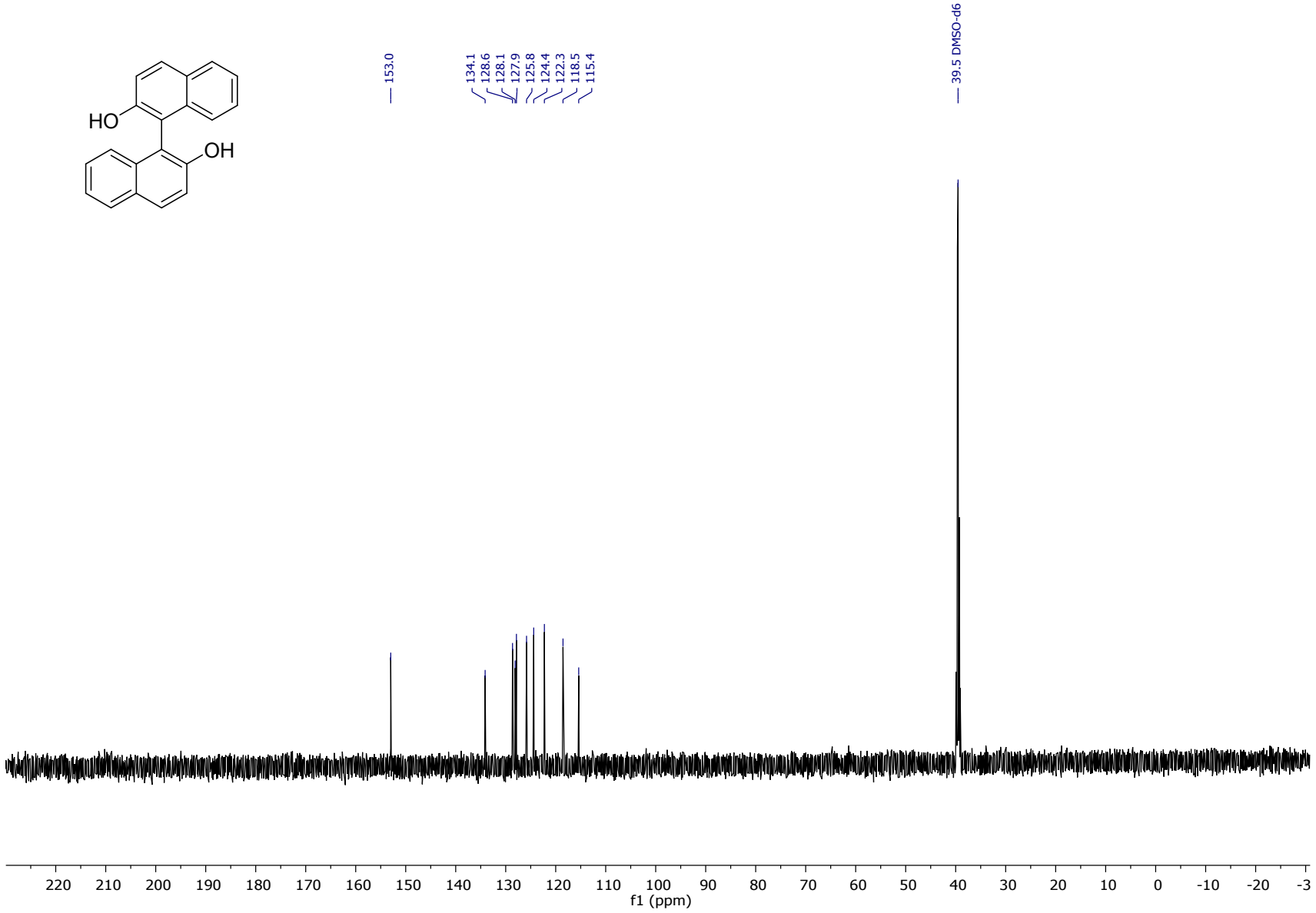

Figure S4. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-*d6*) of 1,1'-binaphthyl-2,2'-diol.

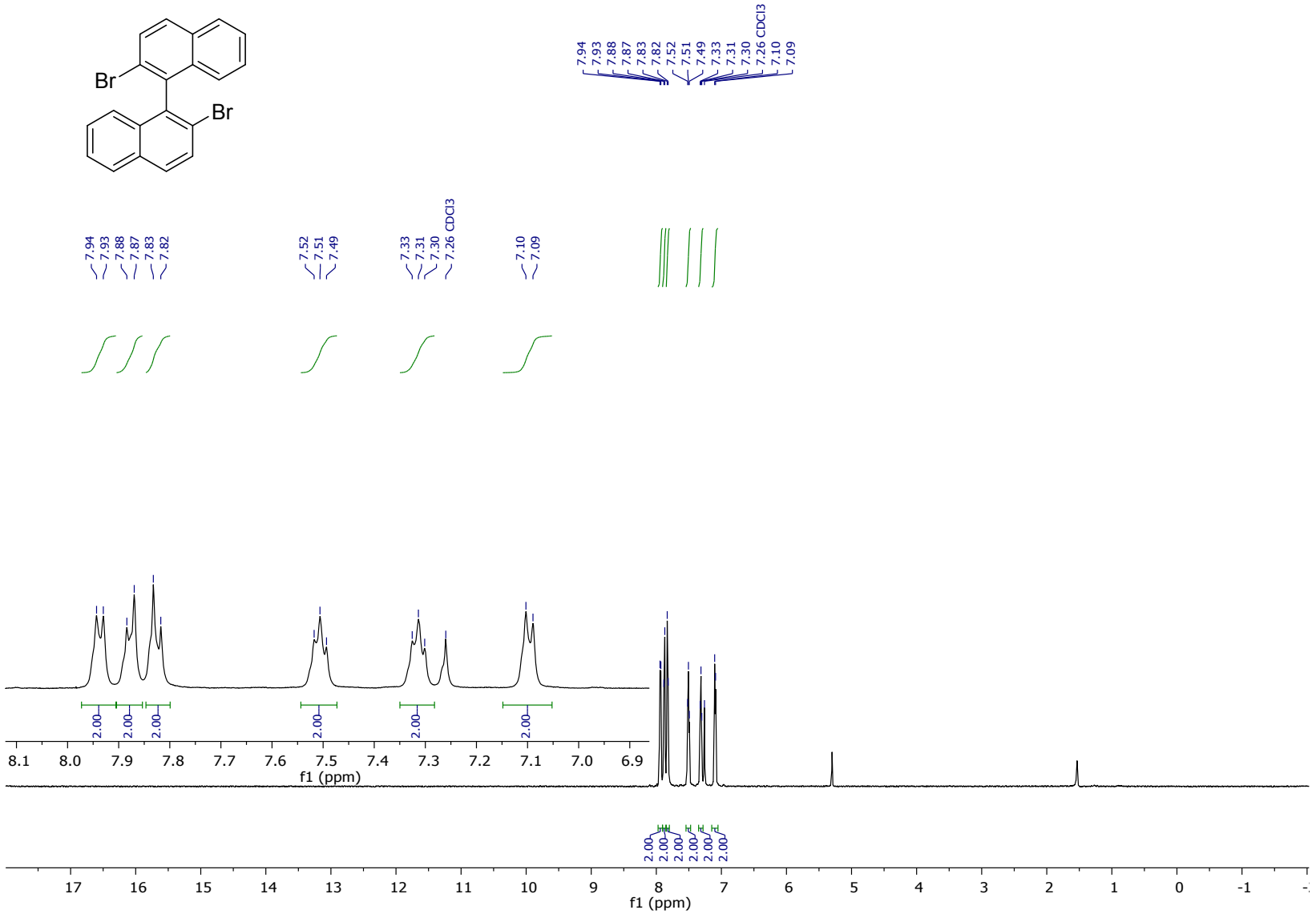

Figure S5. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,2'-dibromo-1,1'-binaphthyl.

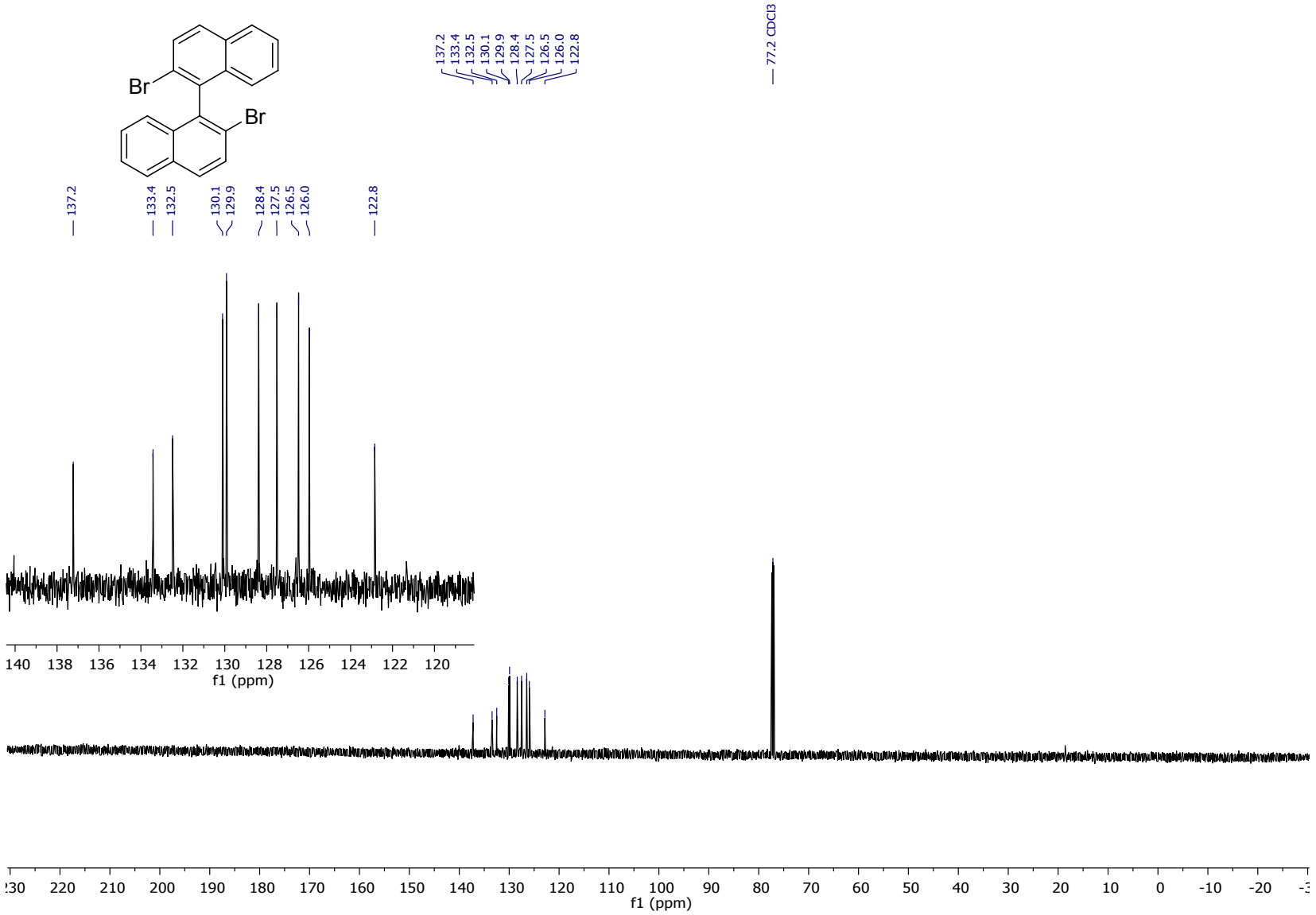

Figure S6. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,2'-dibromo-1,1'-binaphthyl.

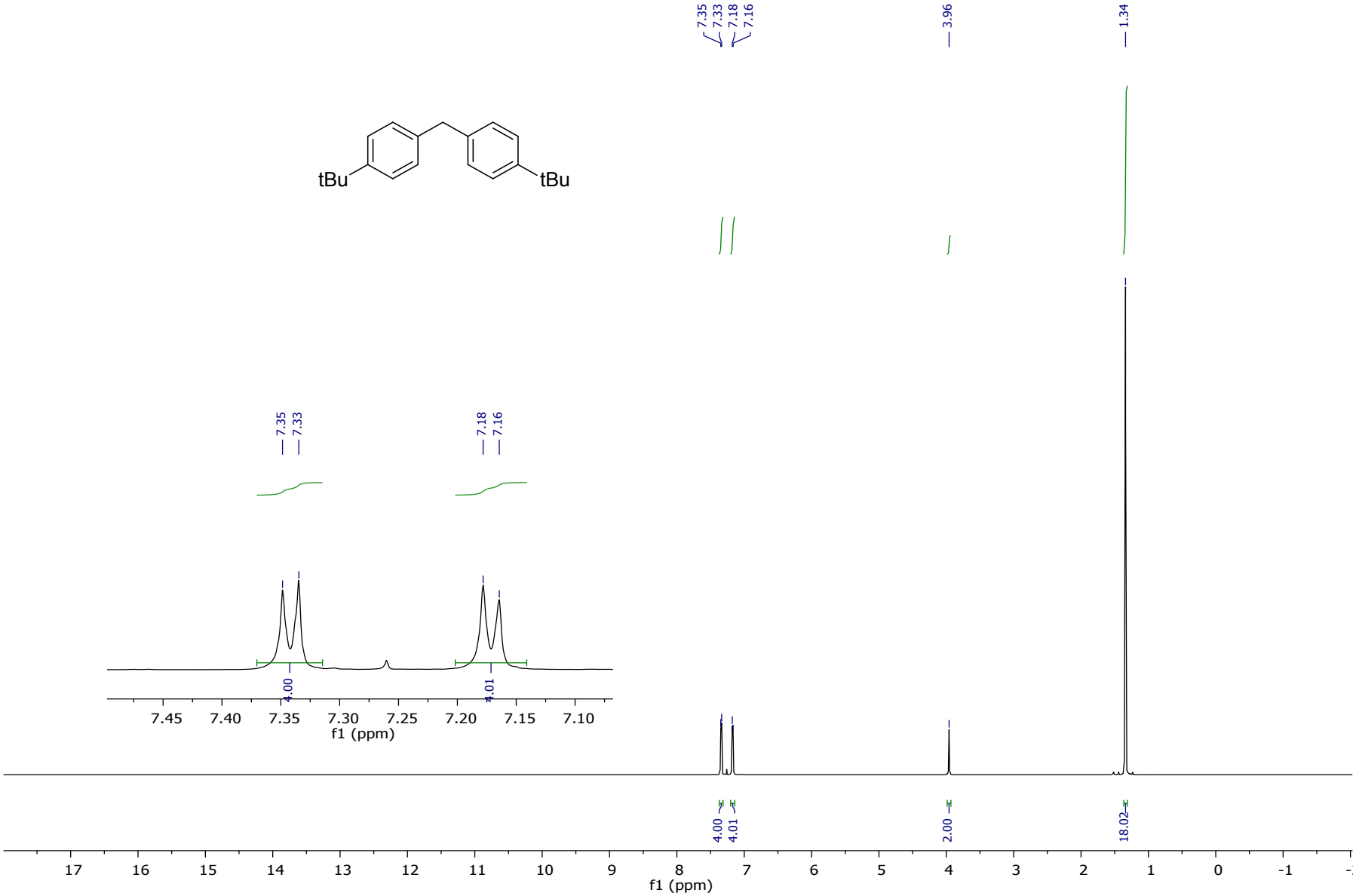

Figure S7. ^{1}H NMR (600 MHz, Chloroform-*d*) of bis(4-tert-butylphenyl)methane

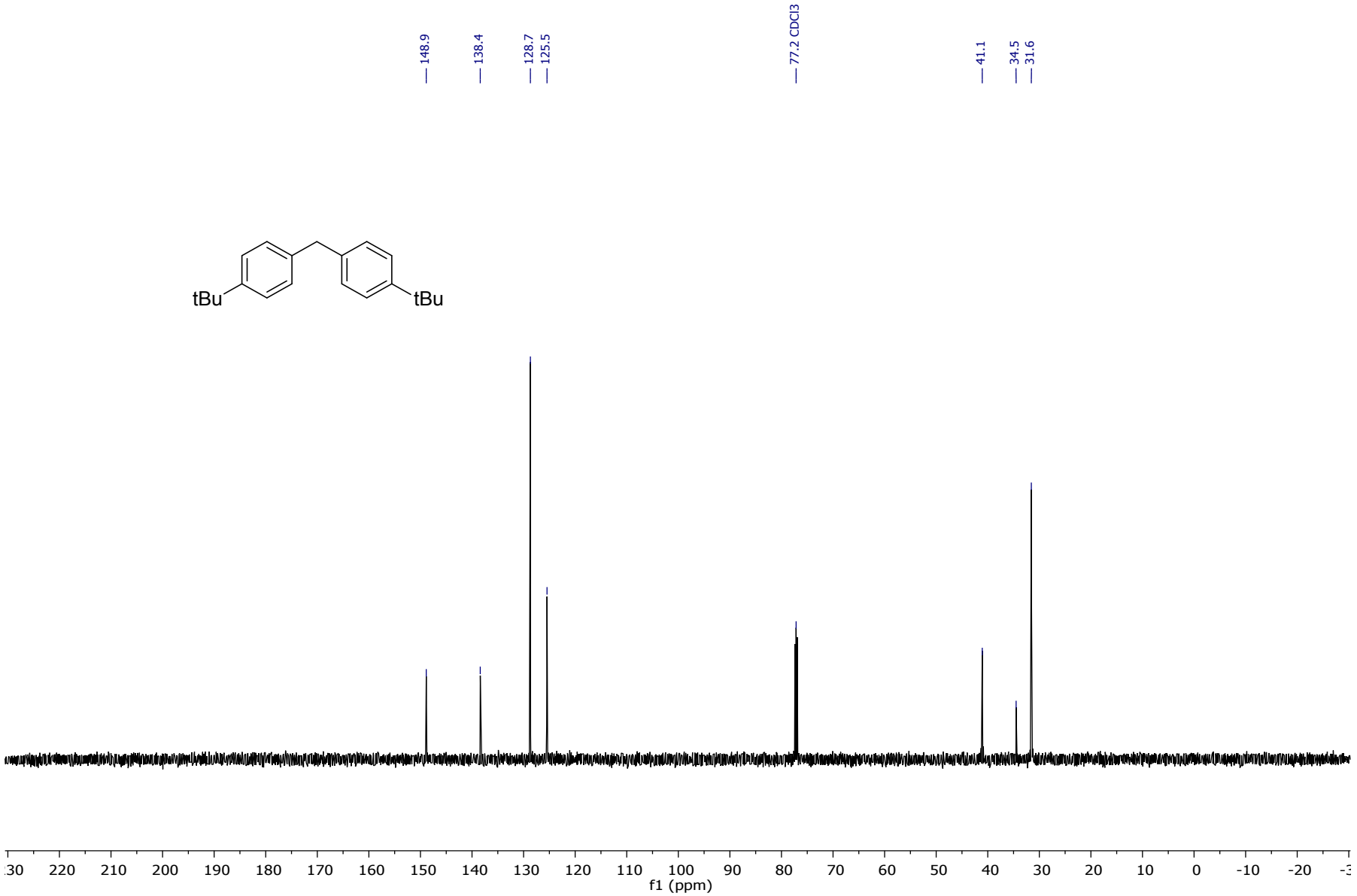

Figure S8. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of bis(4-tert-butylphenyl)methane

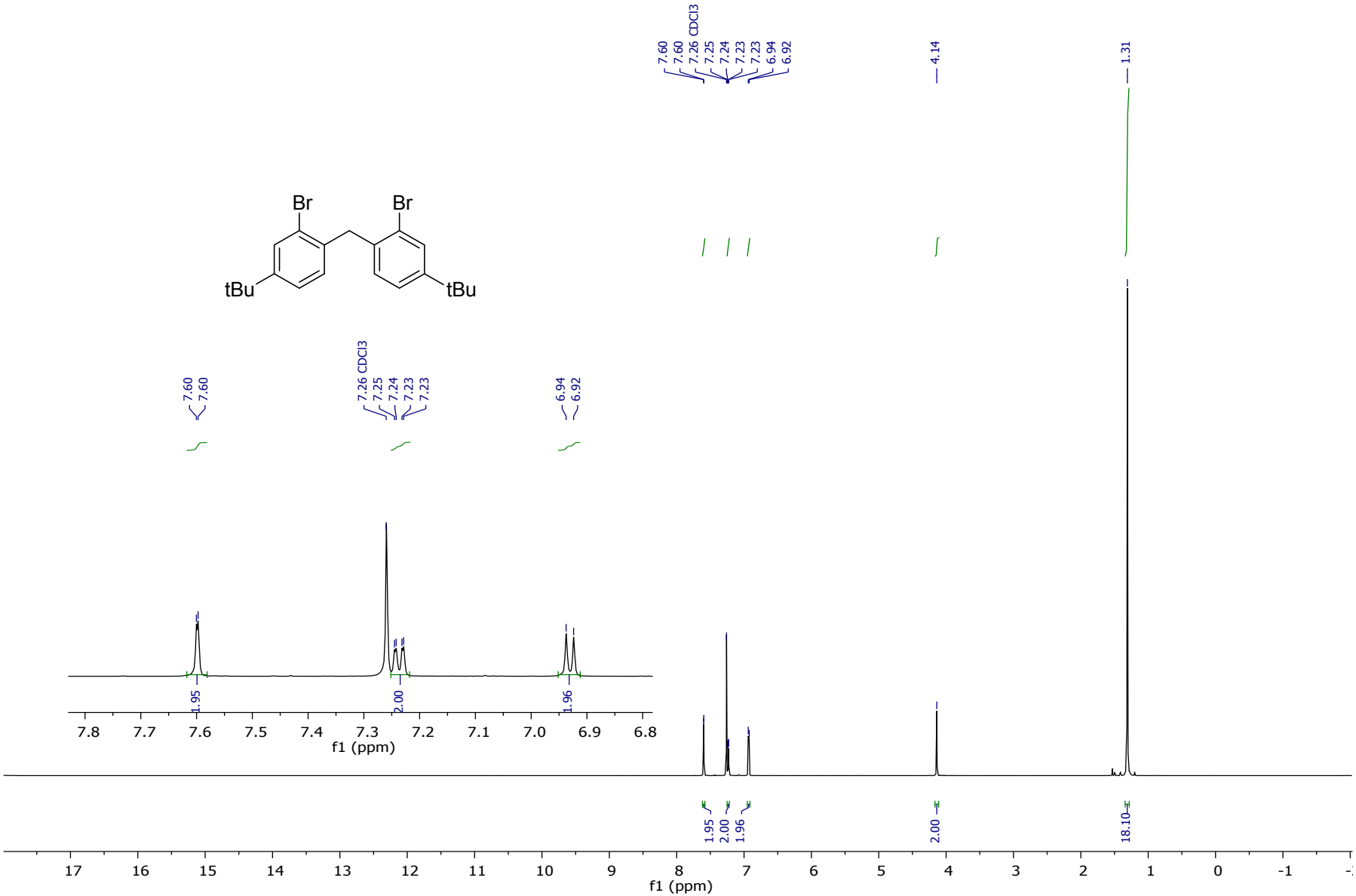

Figure S9. ^{1}H NMR (600 MHz, Chloroform-*d*) of bis(2-bromo-4-tert-butylphenyl)methane

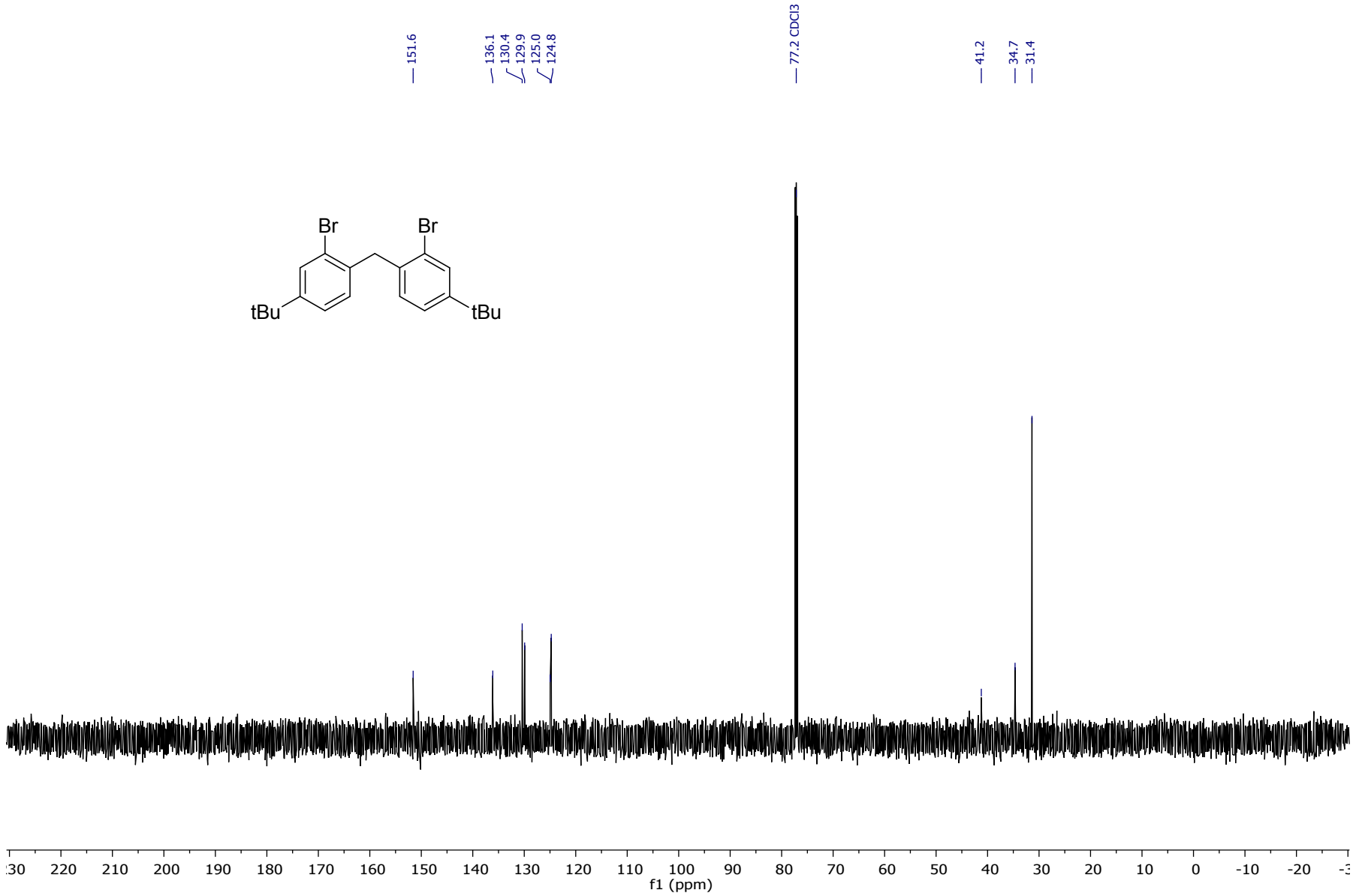

Figure S10. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of bis(2-bromo-4-tert-butylphenyl)methane

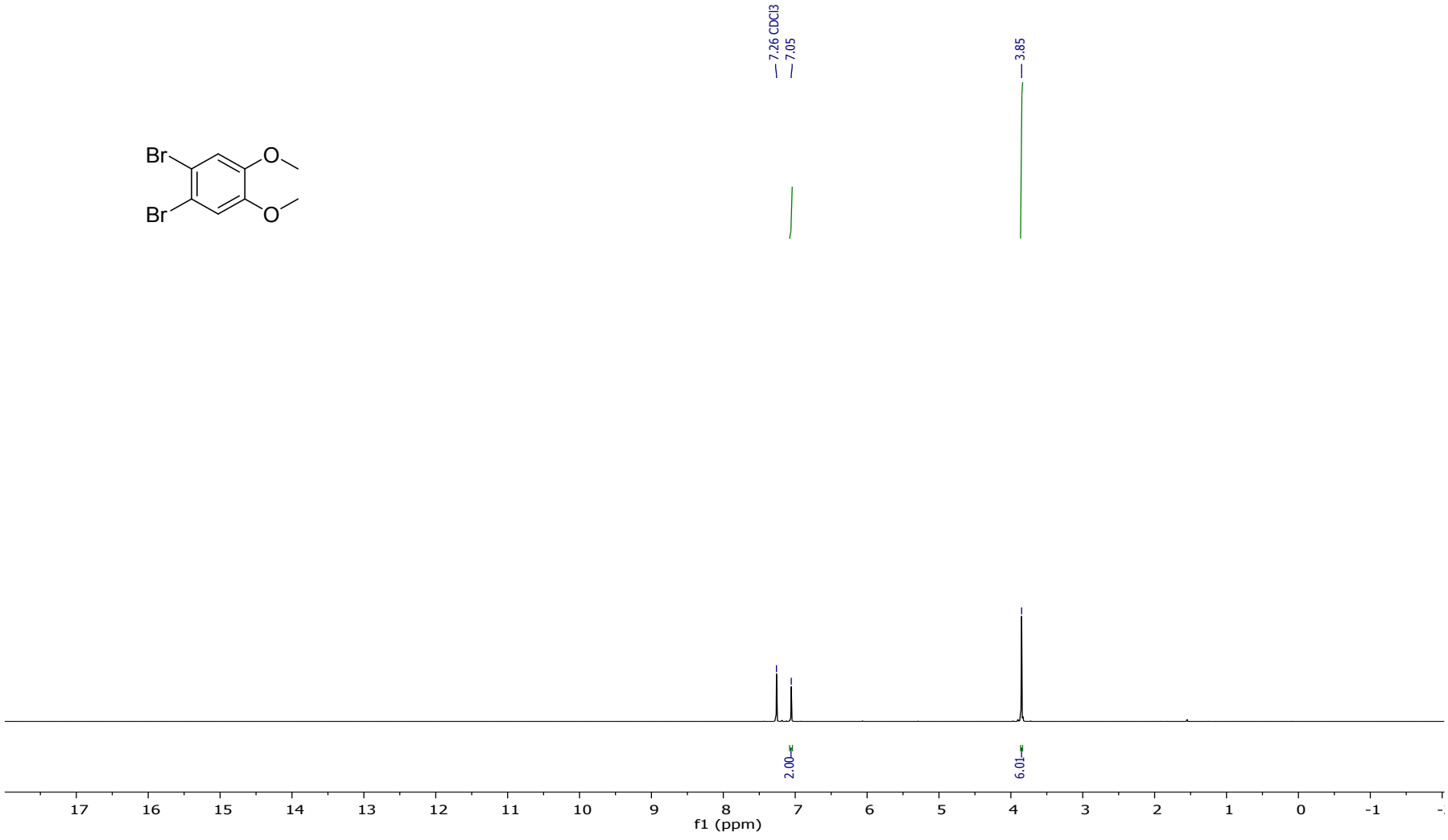

Figure S11. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1,2-dibromo-4,5-dimethoxybenzene

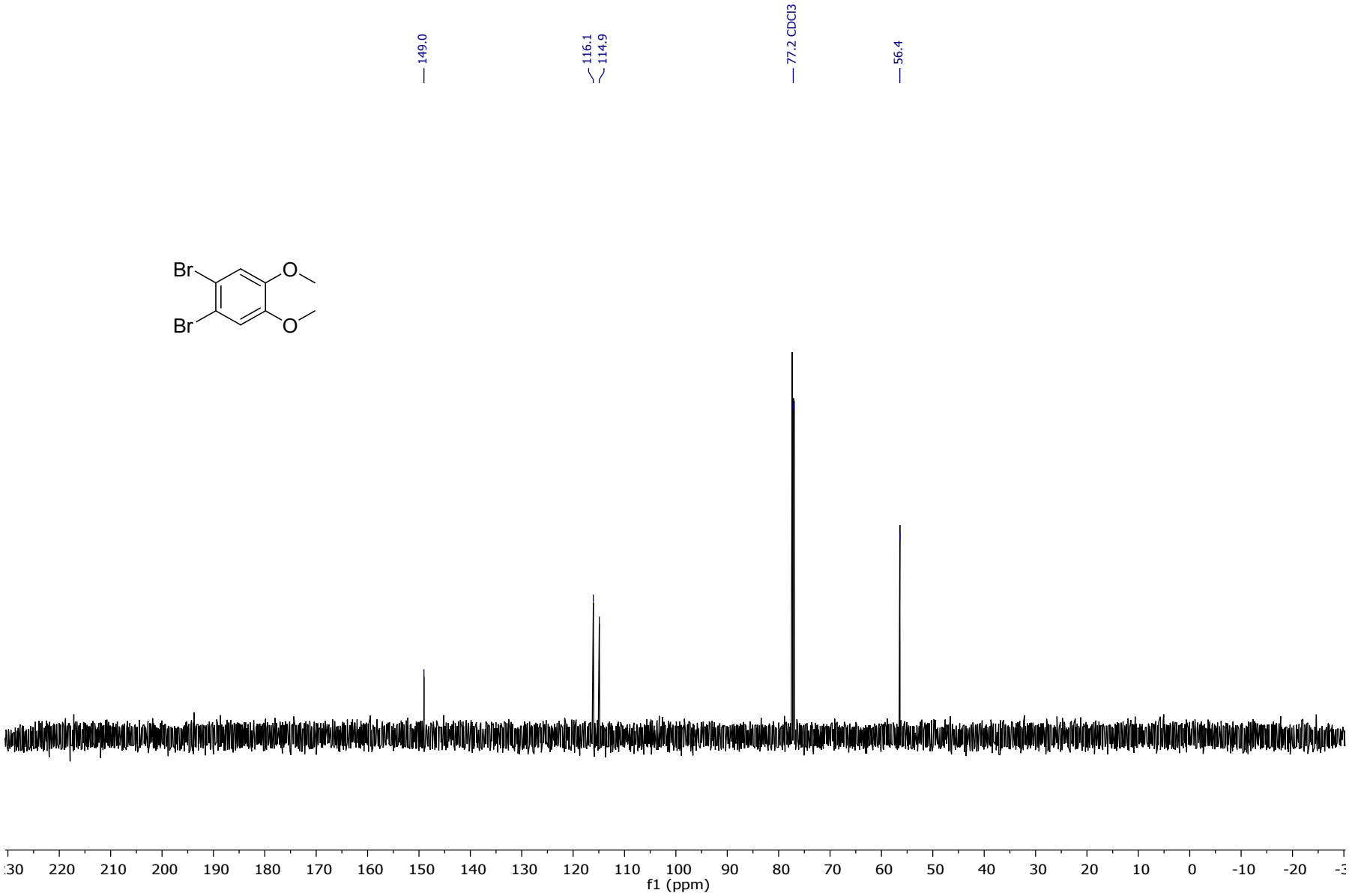

Figure S12. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1,2-dibromo-4,5-dimethoxybenzene

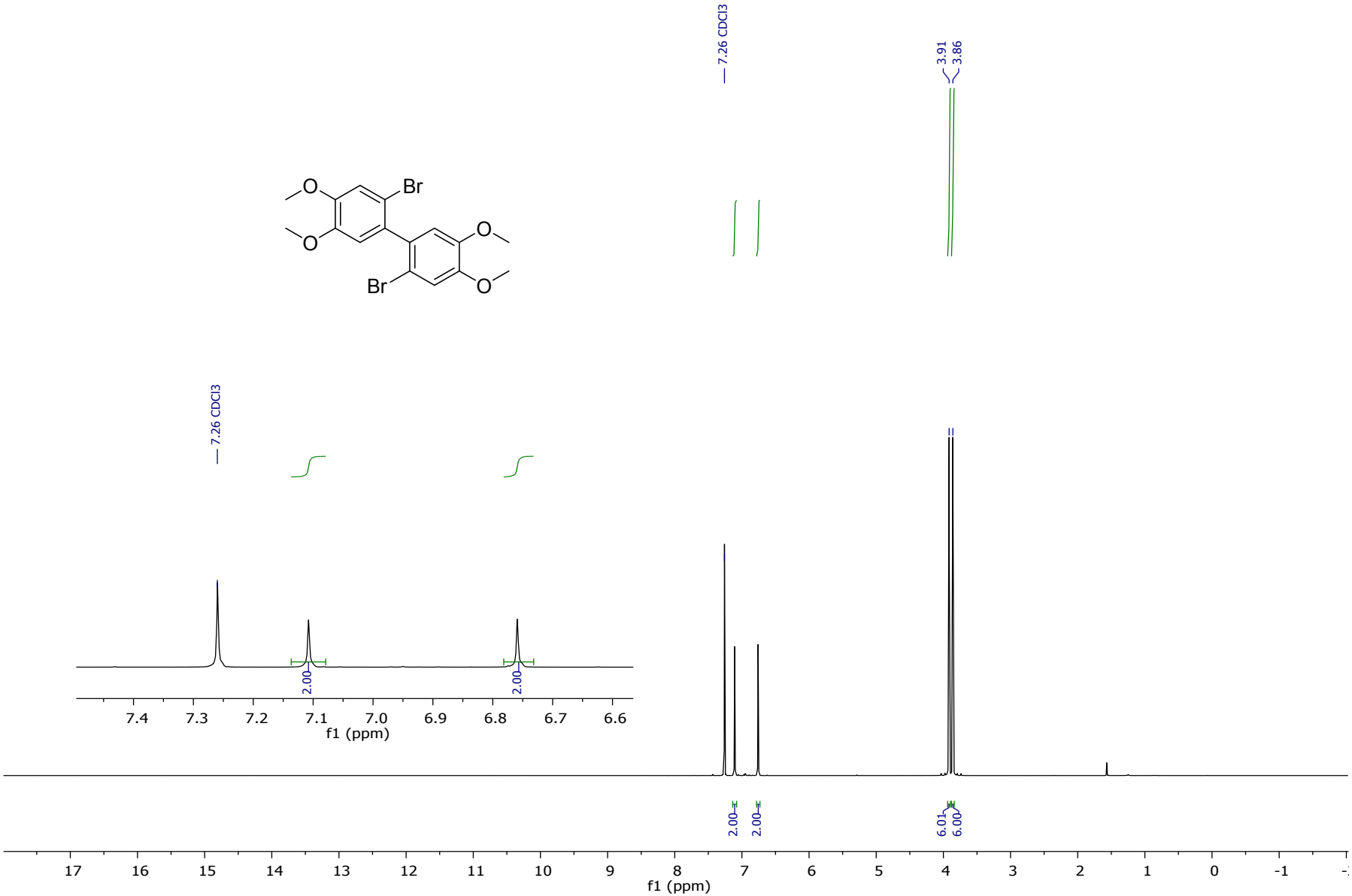

Figure S13. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl

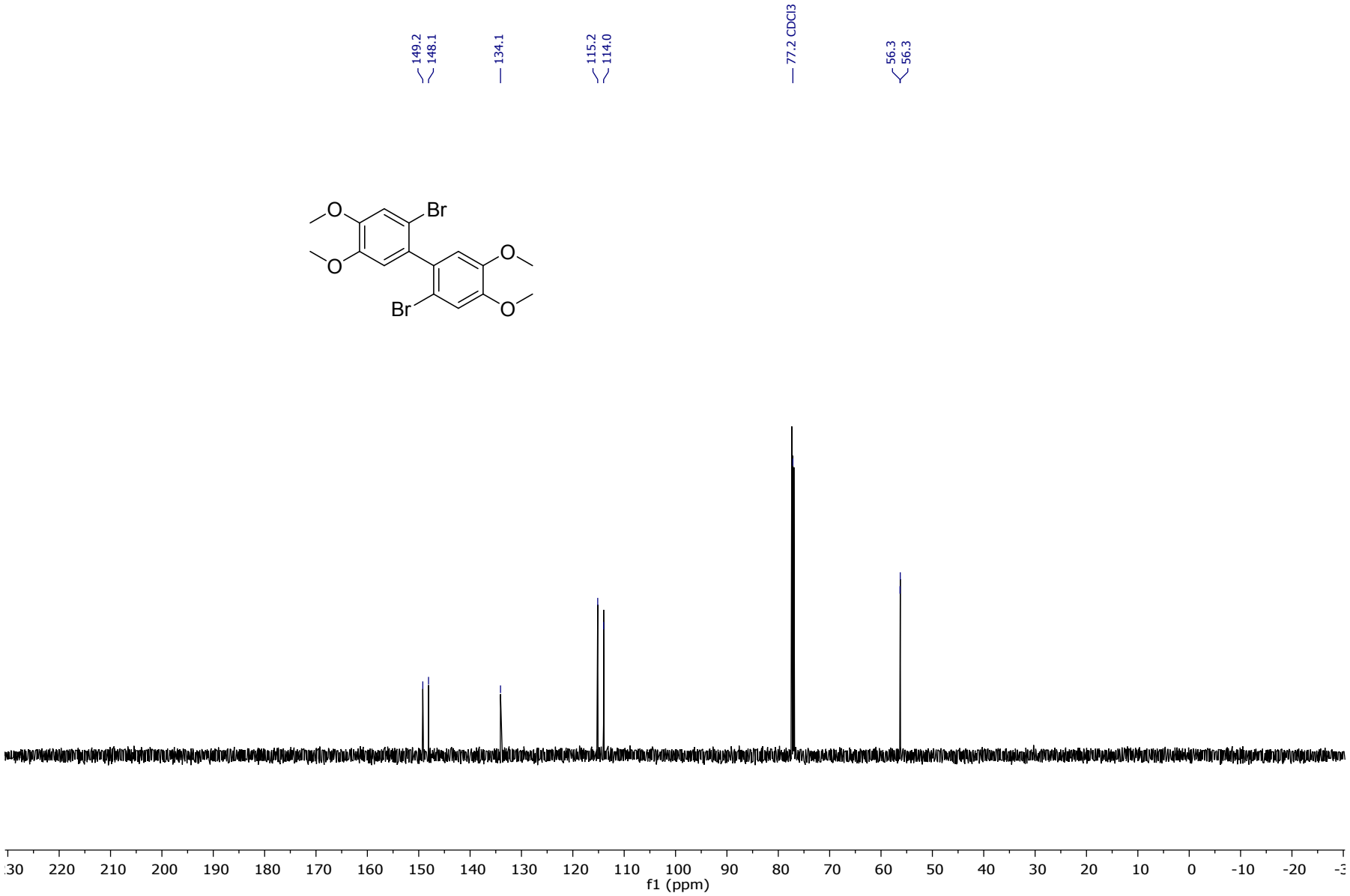

Figure S14. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl

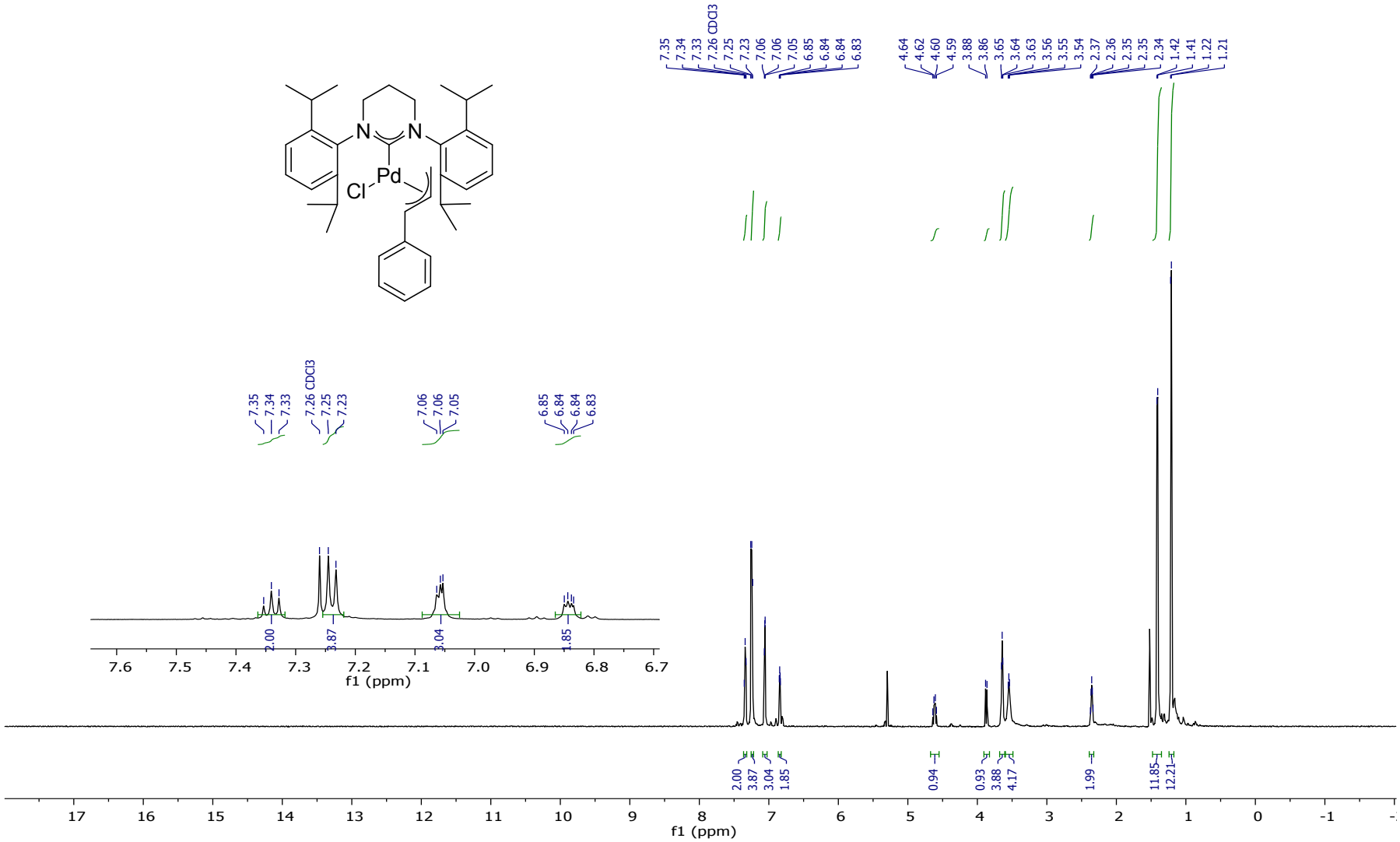

Figure S15. ^{1}H NMR (600 MHz, Chloroform-*d*) of 6-DippPd(cinn)Cl (1a)

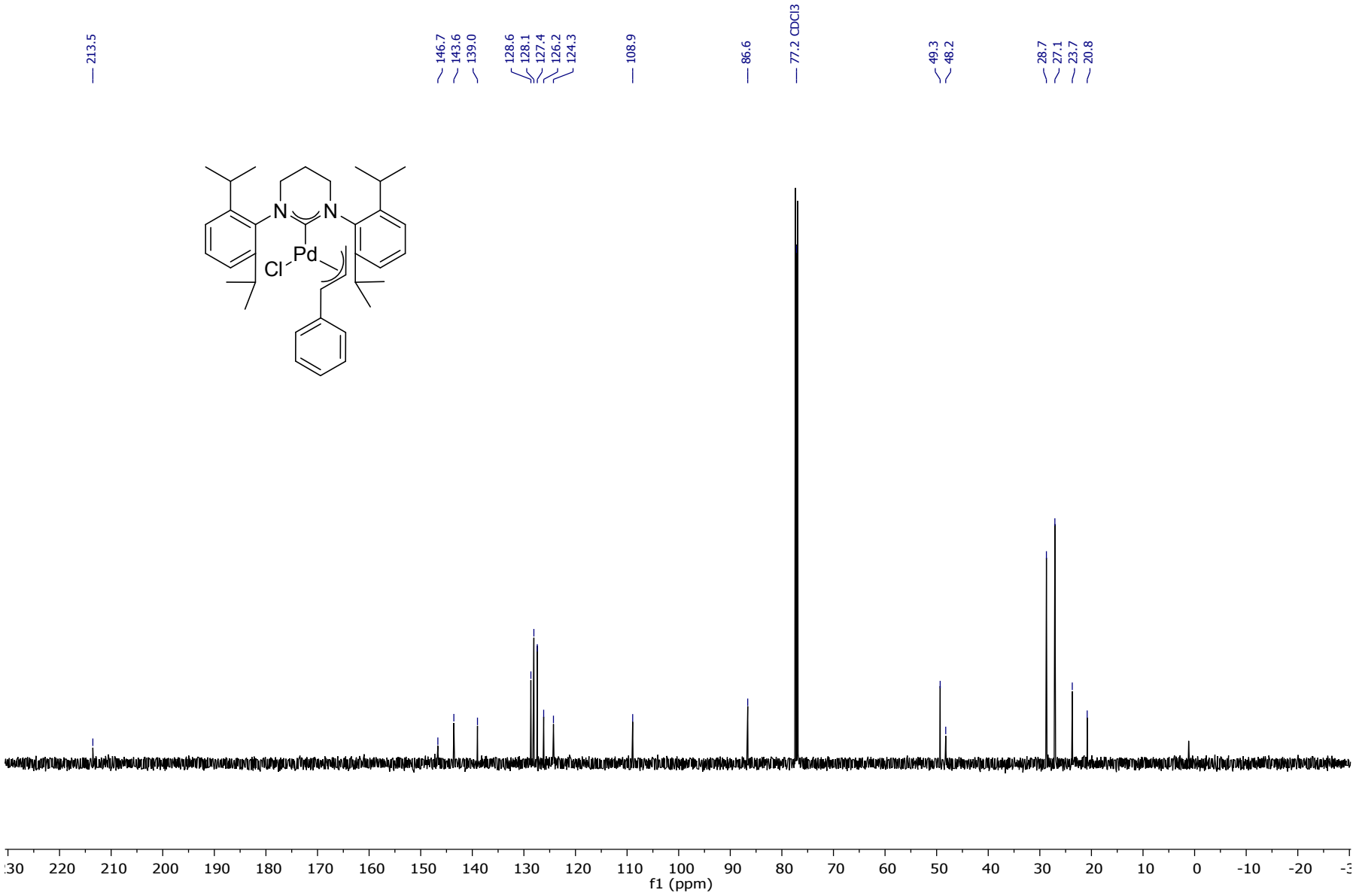

Figure S16. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 6-DippPd(cinn)Cl (1a)

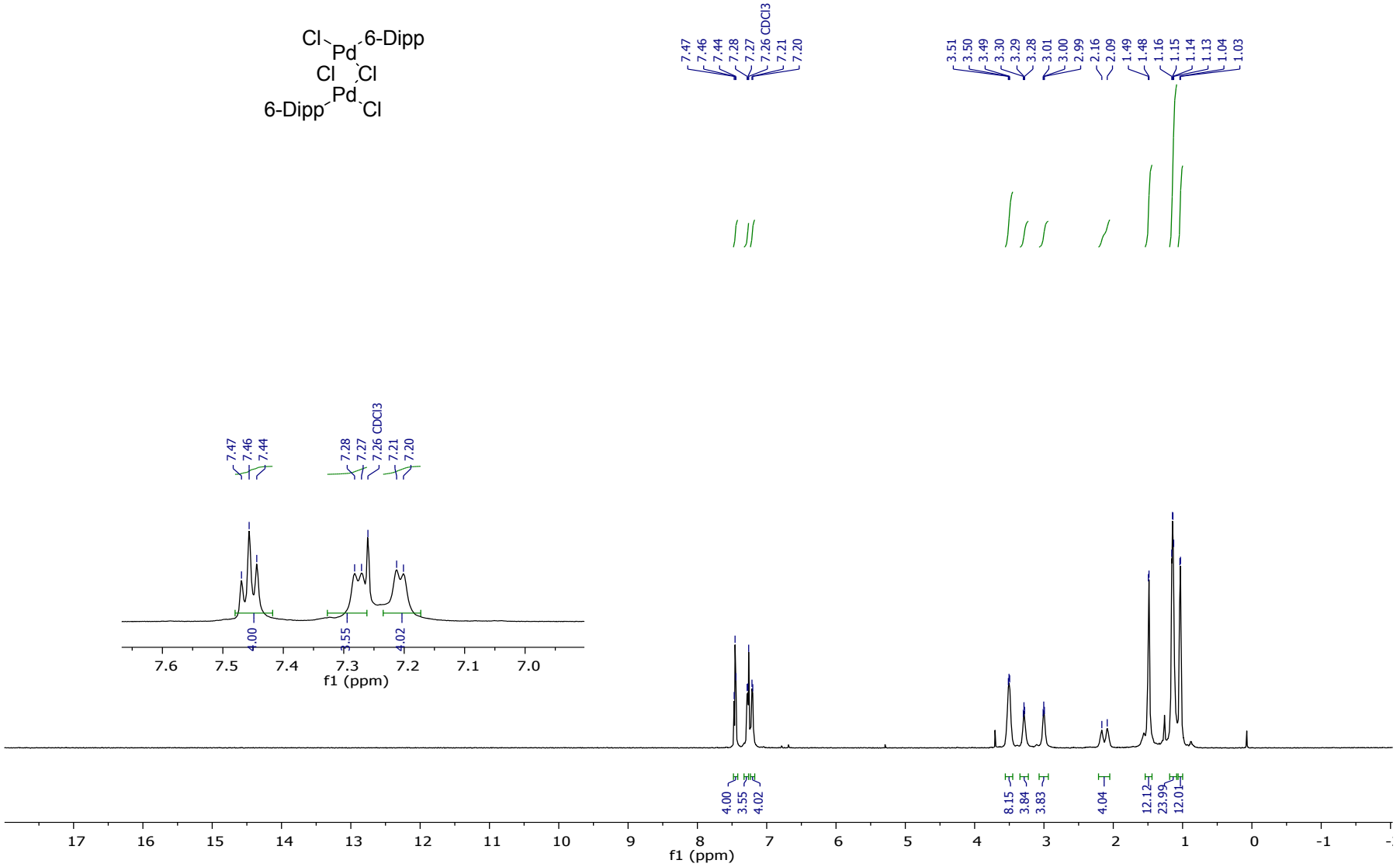

Figure S17. ^{1}H NMR (600 MHz, Chloroform-*d*) of [(6-Dipp)PdCl$_2$]$_2$ (2a)

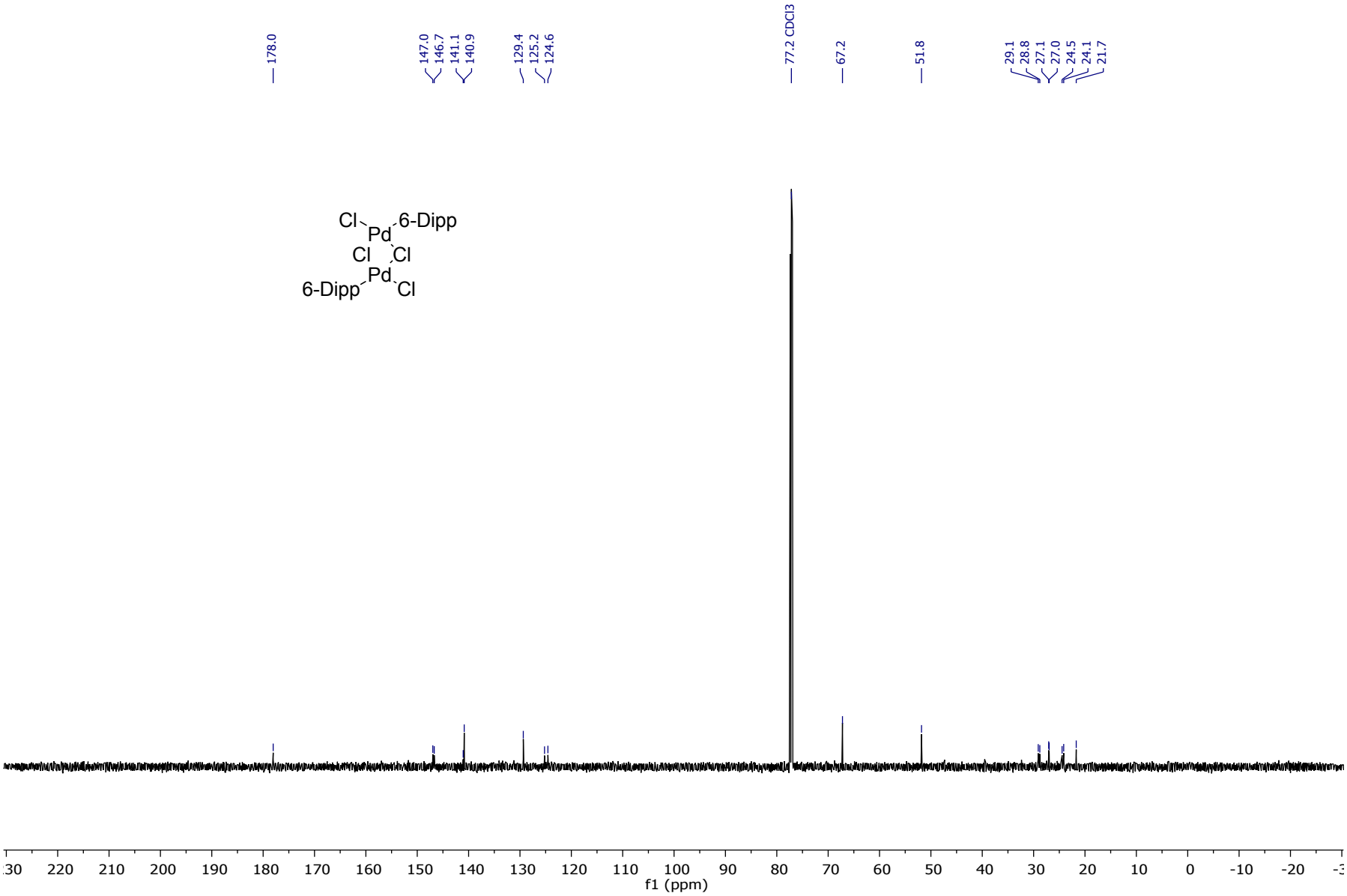

Figure S18. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of $[(6\text{-Dipp})PdCl_2]_2$ (2a)

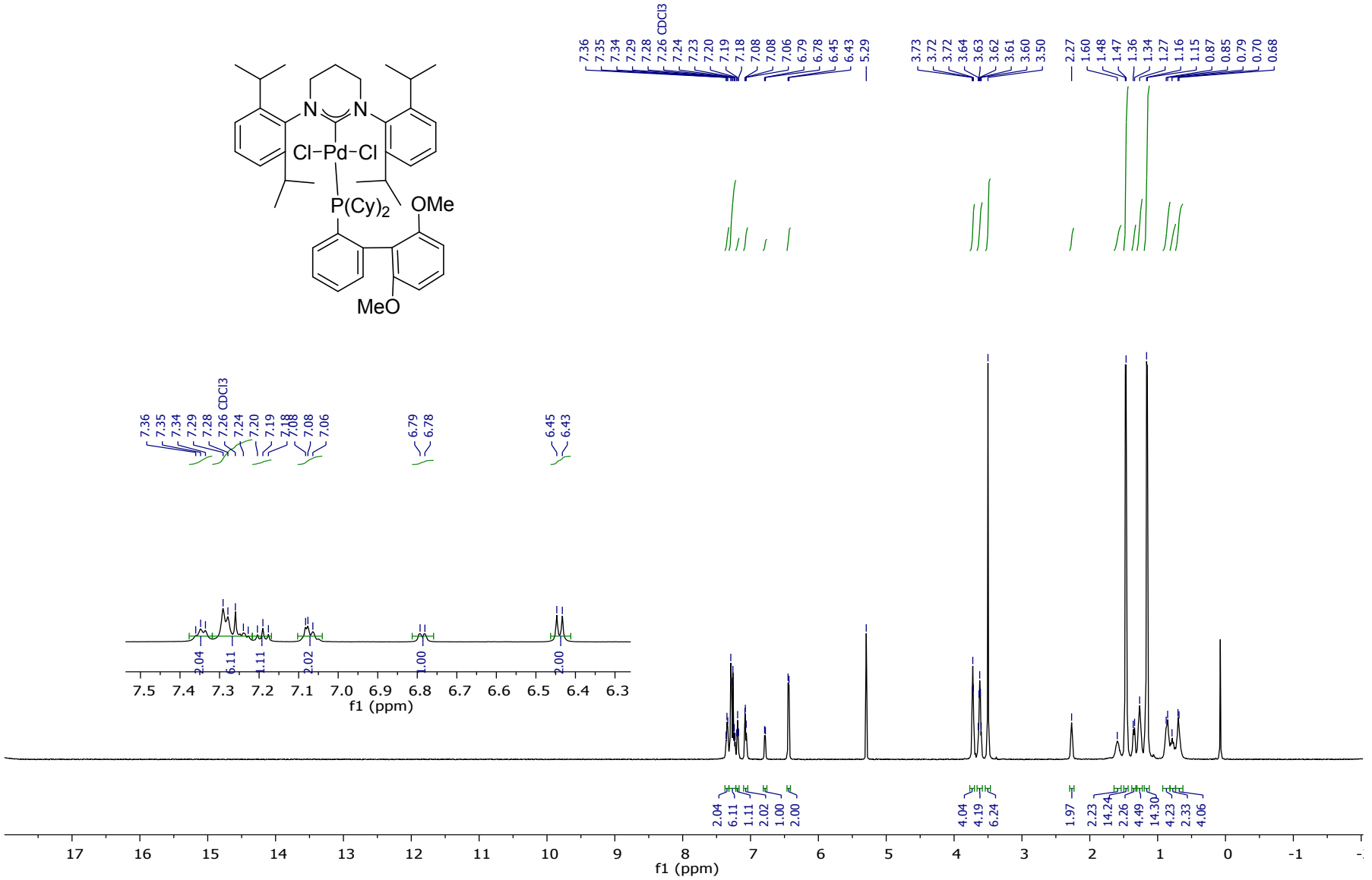

Figure S19. ^{1}H NMR (600 MHz, Chloroform-*d*) of (6-Dipp)PdCl$_2$-SPhos (3a)

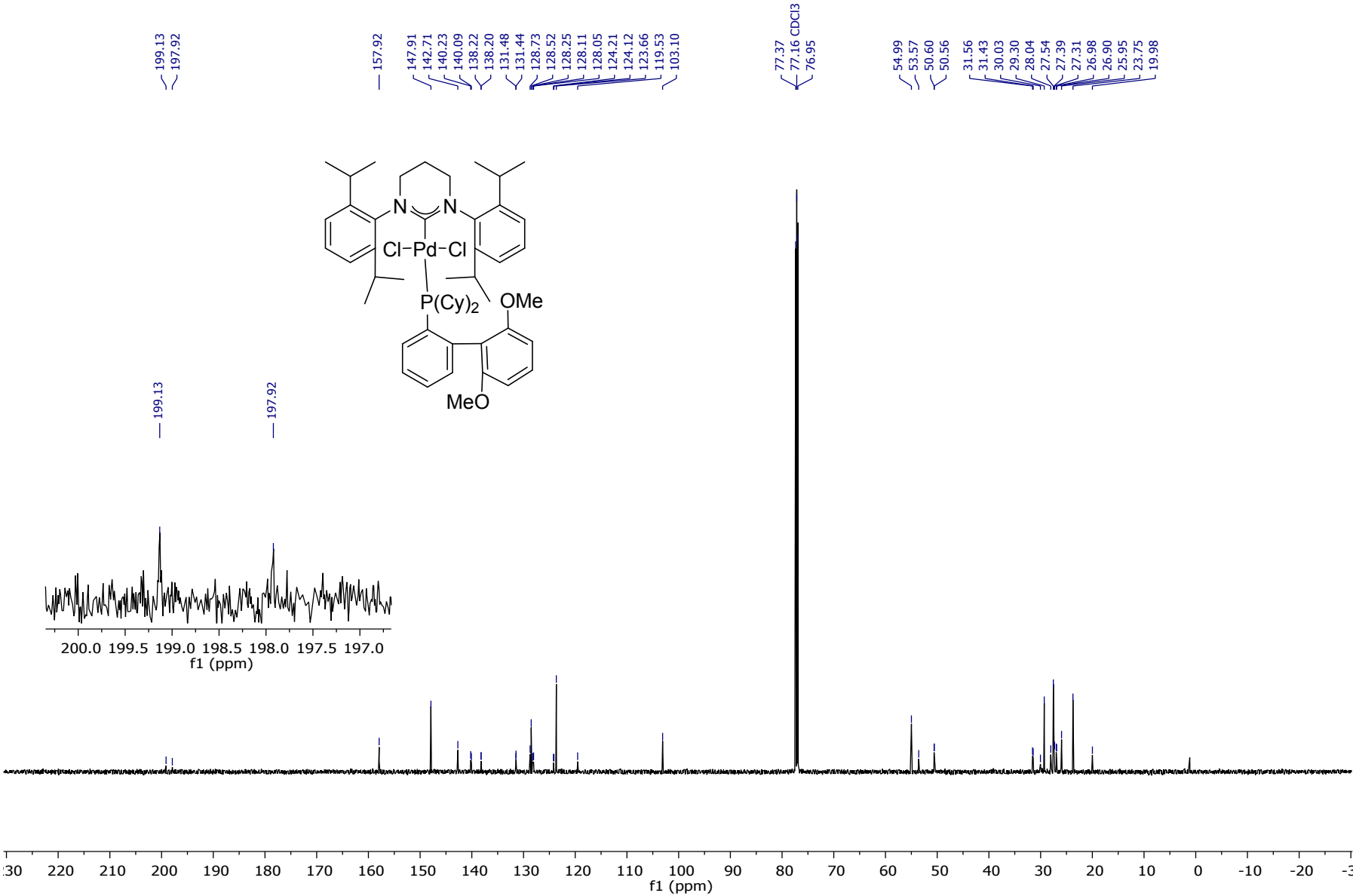

Figure S20. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of (6-Dipp)$PdCl_2$-SPhos (3a)

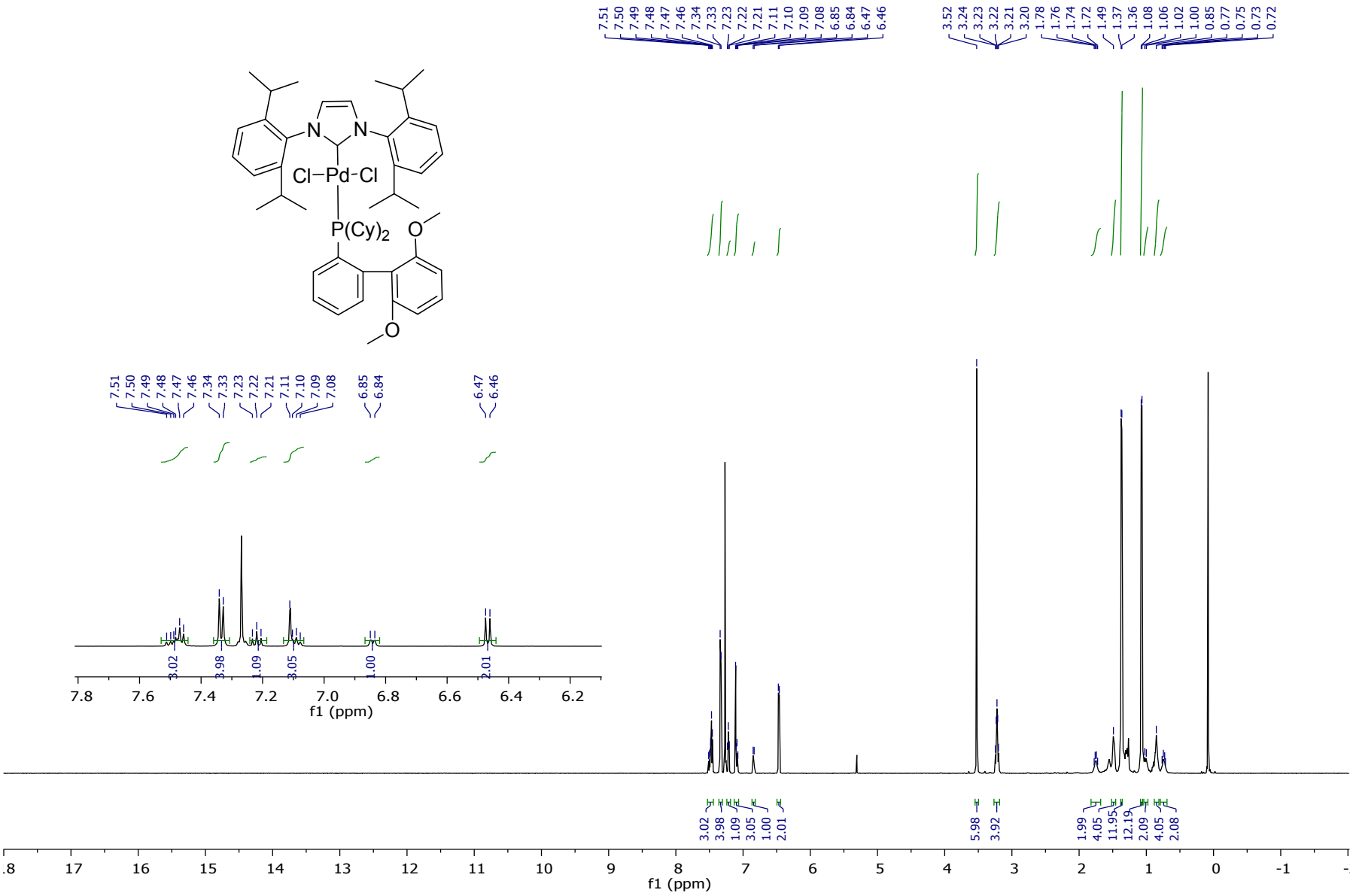

Figure S21. ^{1}H NMR (600 MHz, Chloroform-*d*) of IPrPdCl$_2$-SPhos (3b)

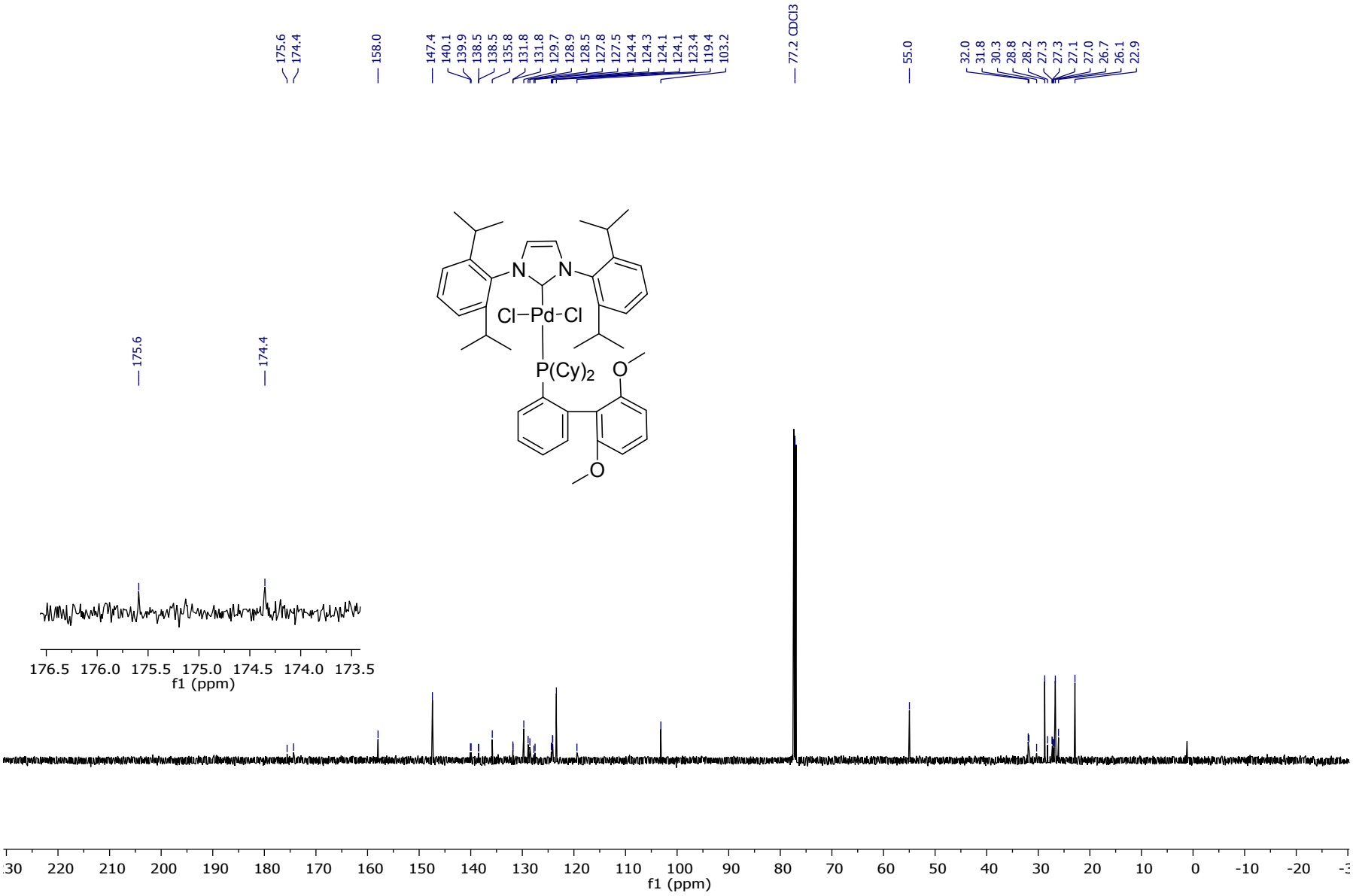

Figure S22. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of of $IPrPdCl_2$-SPhos (3b)

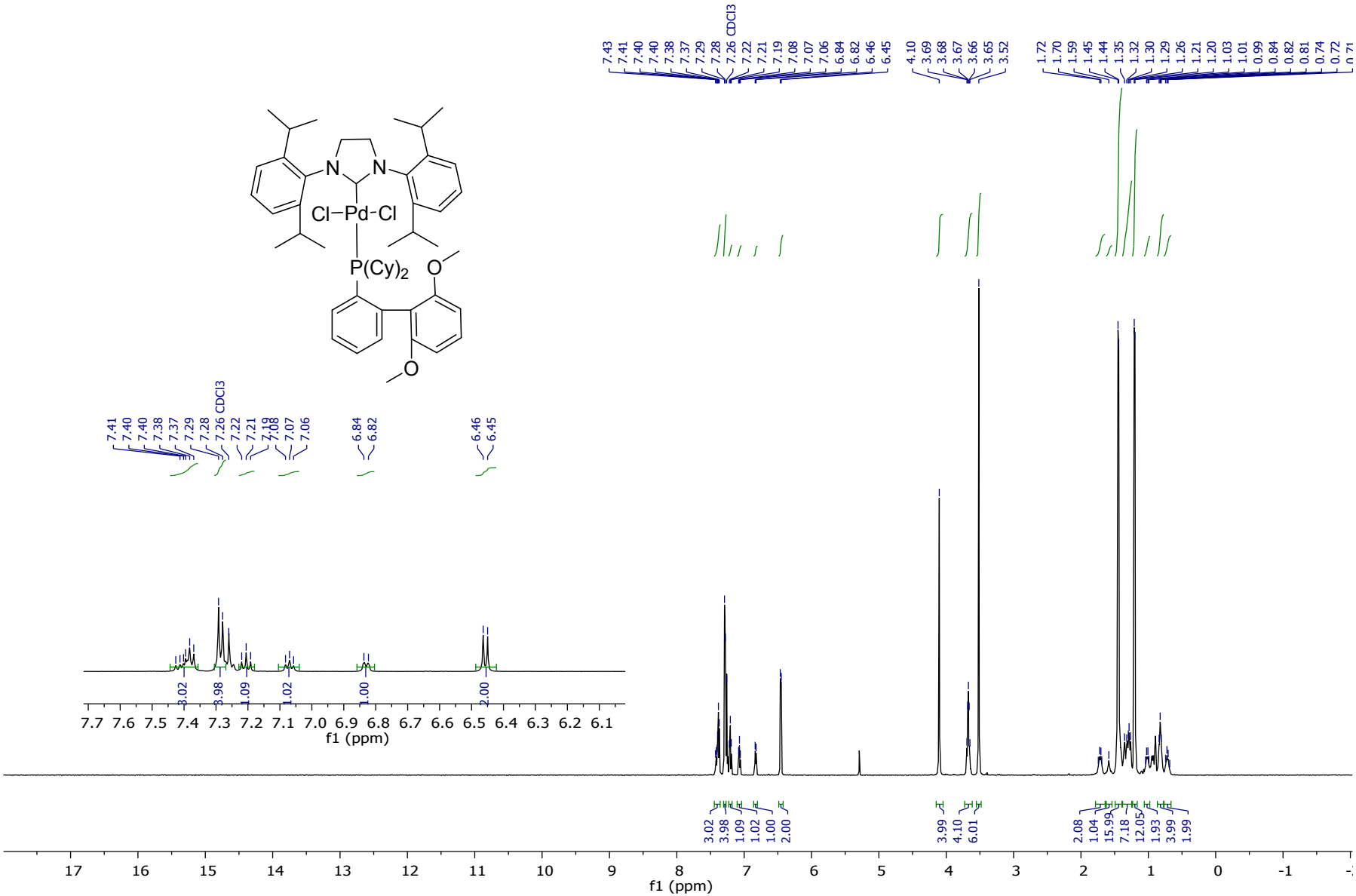

Figure S23. ^{1}H NMR (600 MHz, Chloroform-*d*) of SIPrPdCl$_2$-SPhos (3c)

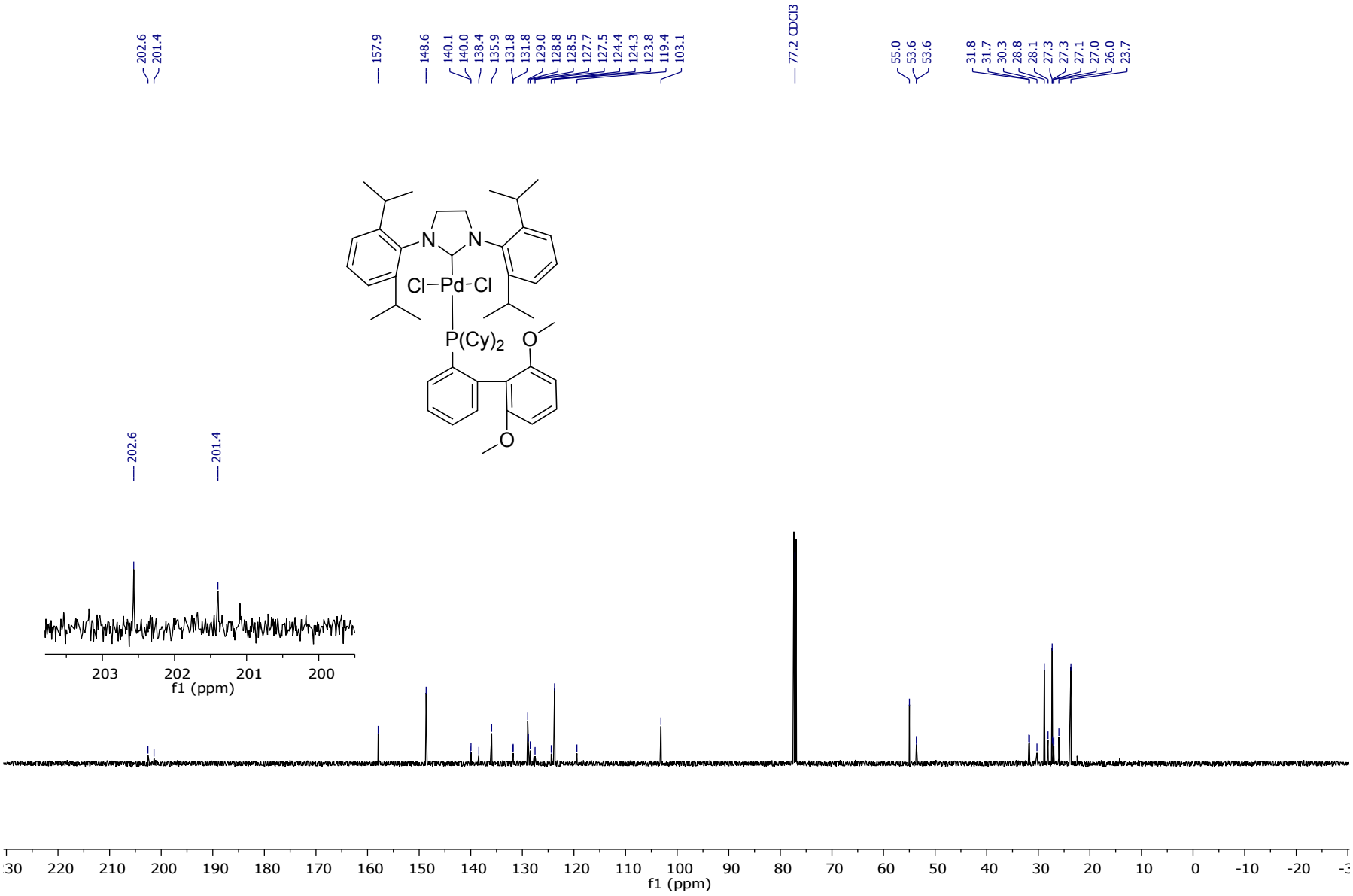

Figure S24. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of $SIPrPdCl_2$-SPhos (3c)

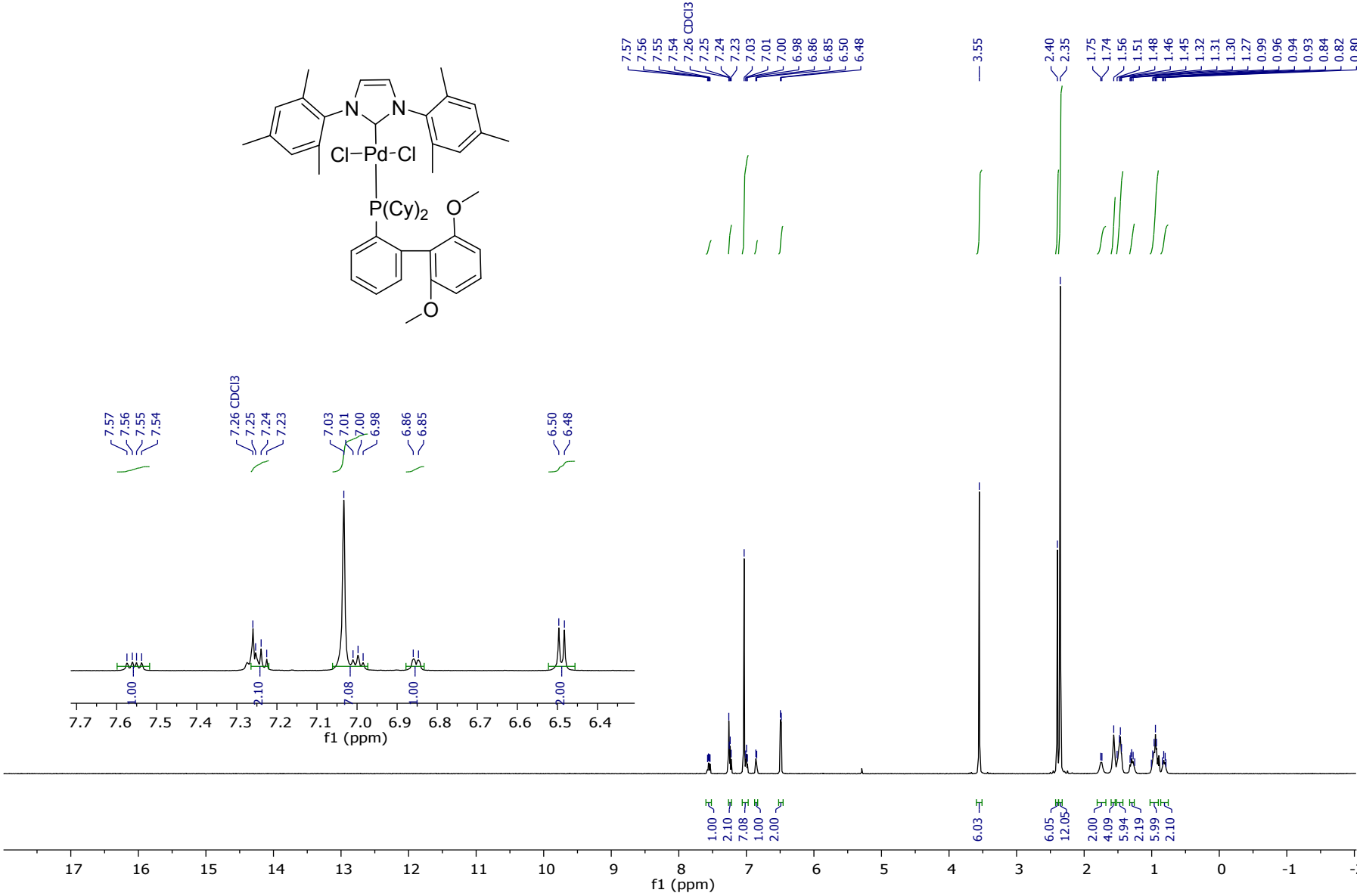

Figure S25. ^{1}H NMR (600 MHz, Chloroform-*d*) of IMesPdCl$_2$-SPhos (3d)

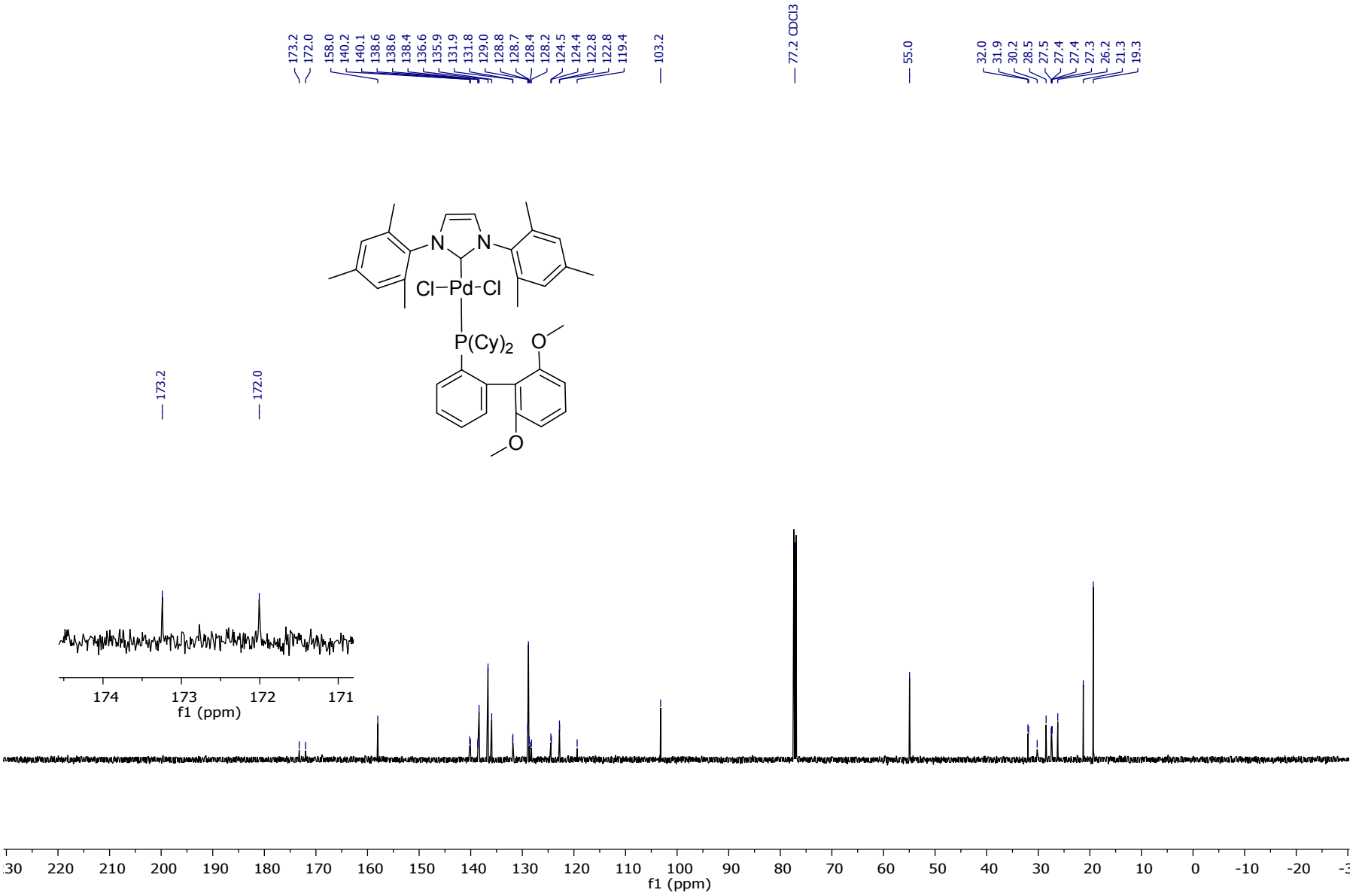

Figure S26. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of $IMesPdCl_2$-SPhos (3d)

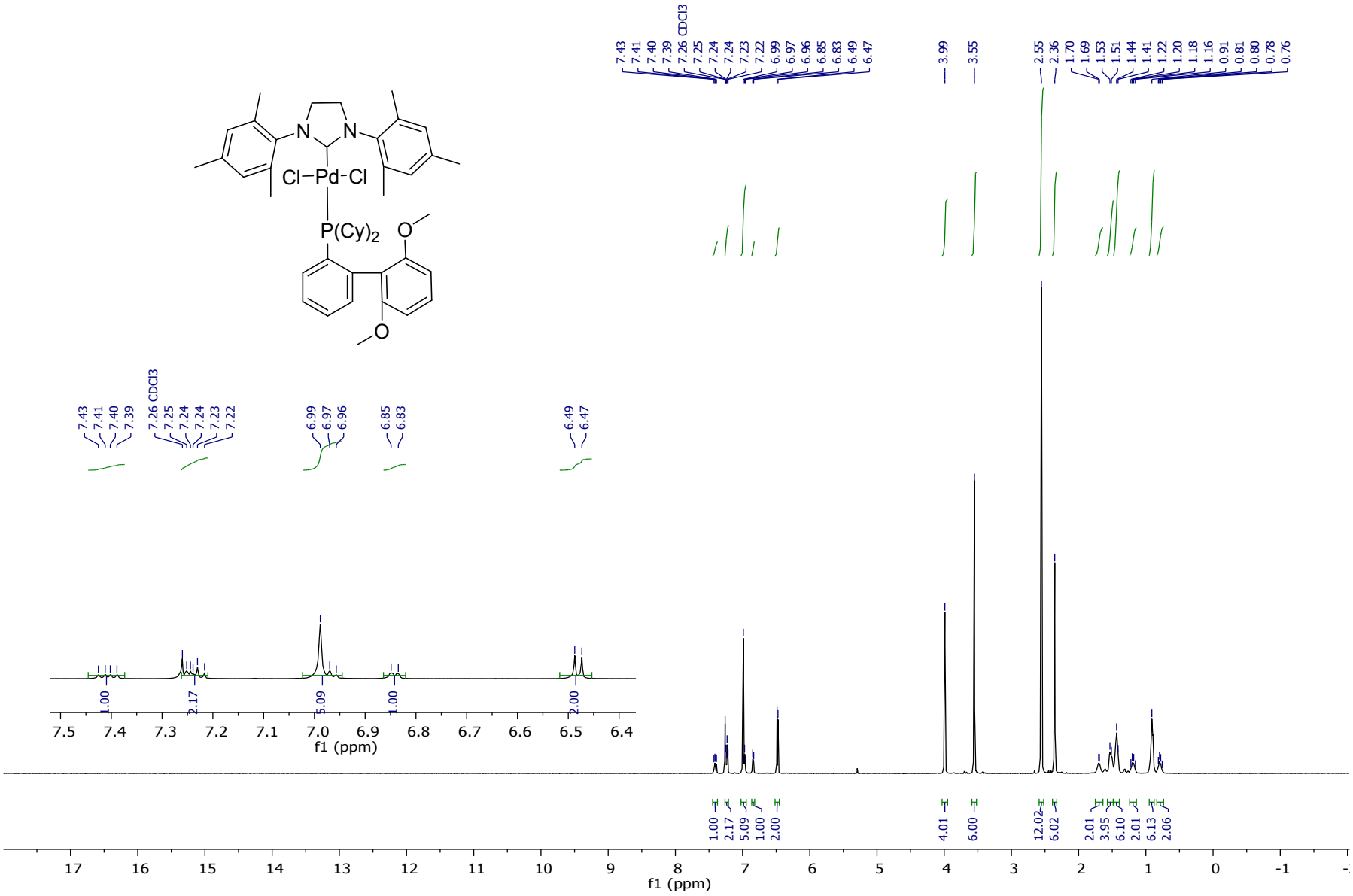

Figure S27. ^{1}H NMR (600 MHz, Chloroform-*d*) of SIMesPdCl$_2$-SPhos (3e)

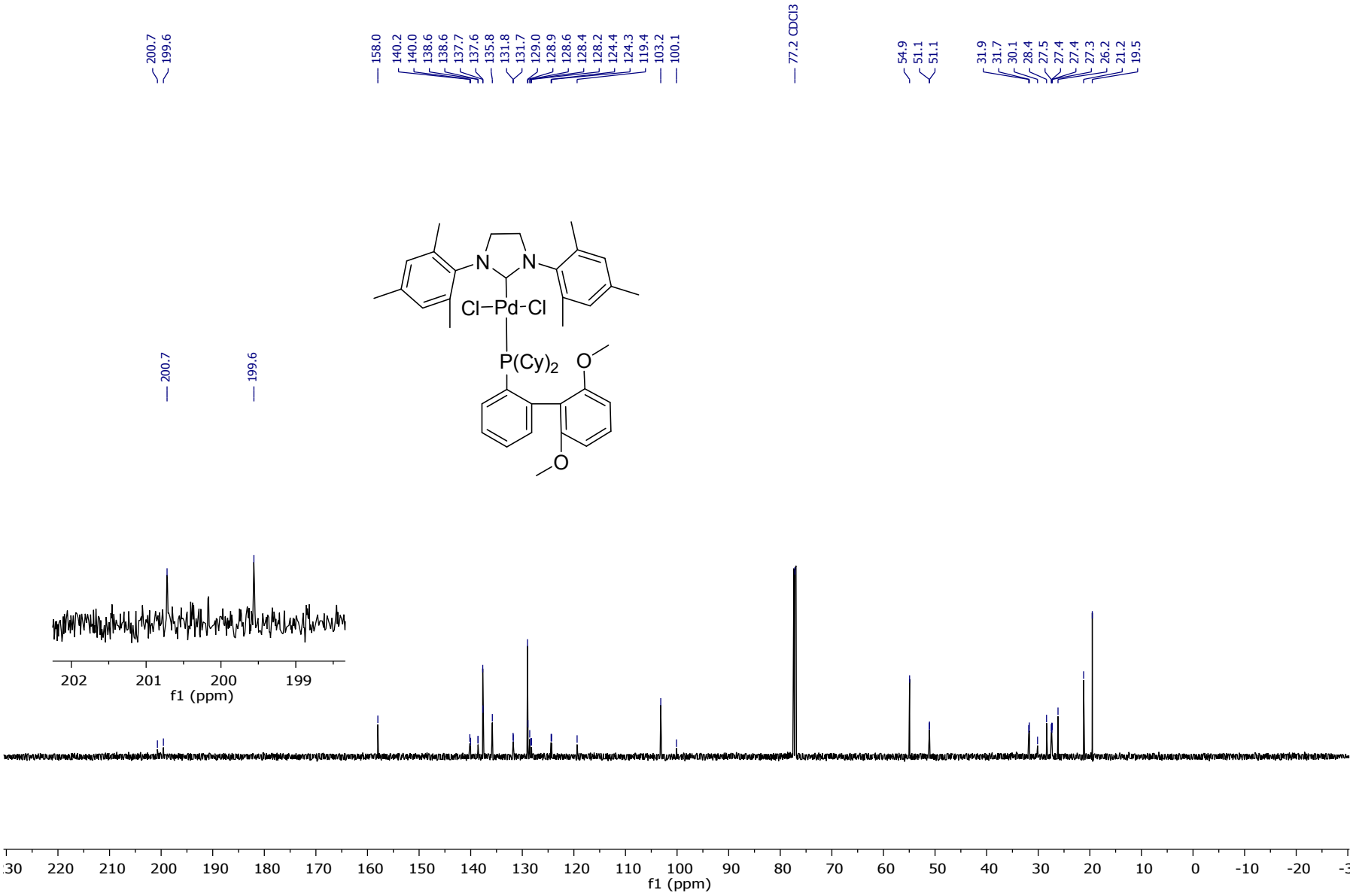

Figure S28. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of $SIMesPdCl_2$-SPhos (3e)

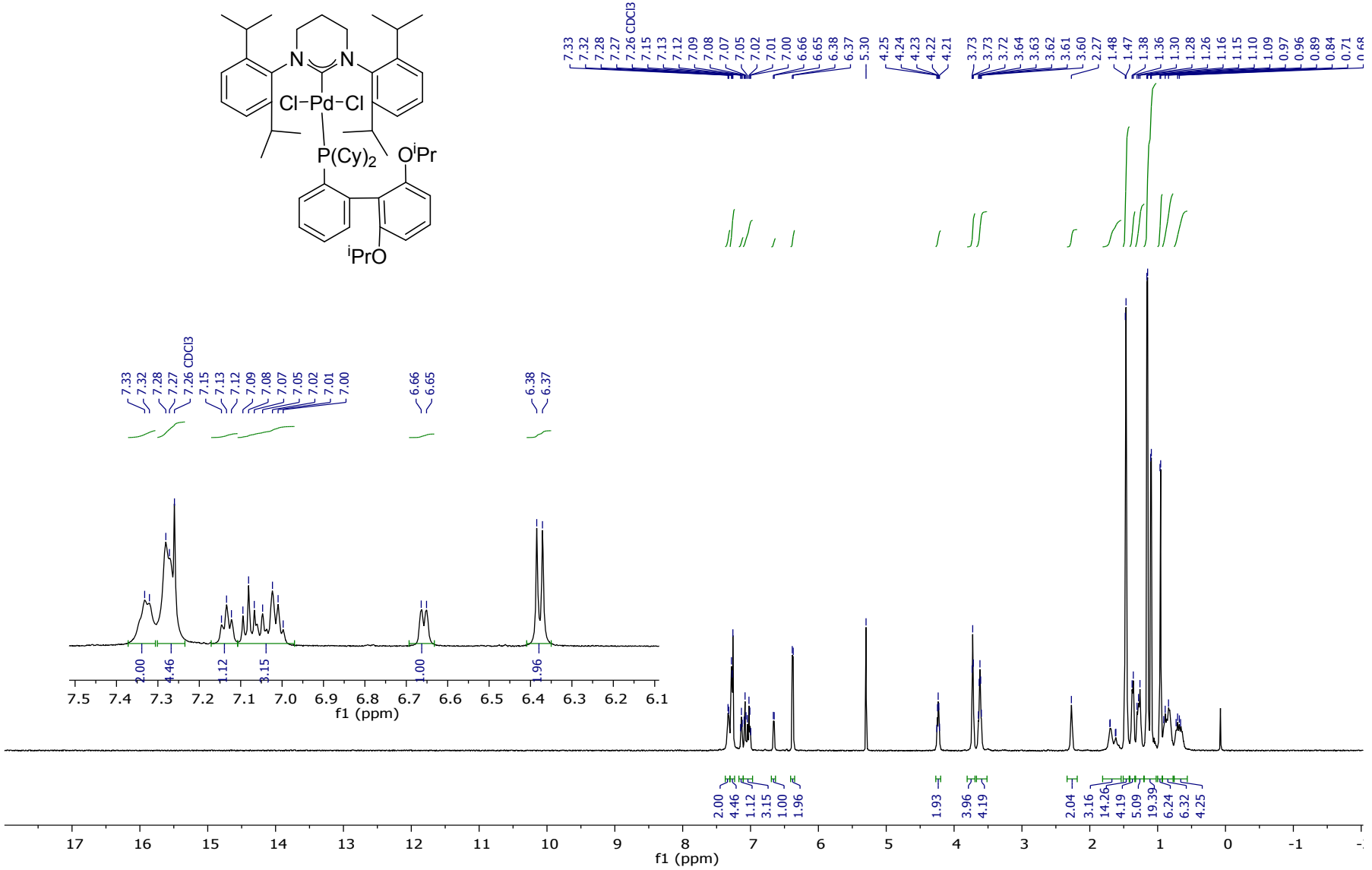

Figure S29. ^{1}H NMR (600 MHz, Chloroform-*d*) of (6-Dipp)PdCl$_2$-RuPhos (3f)

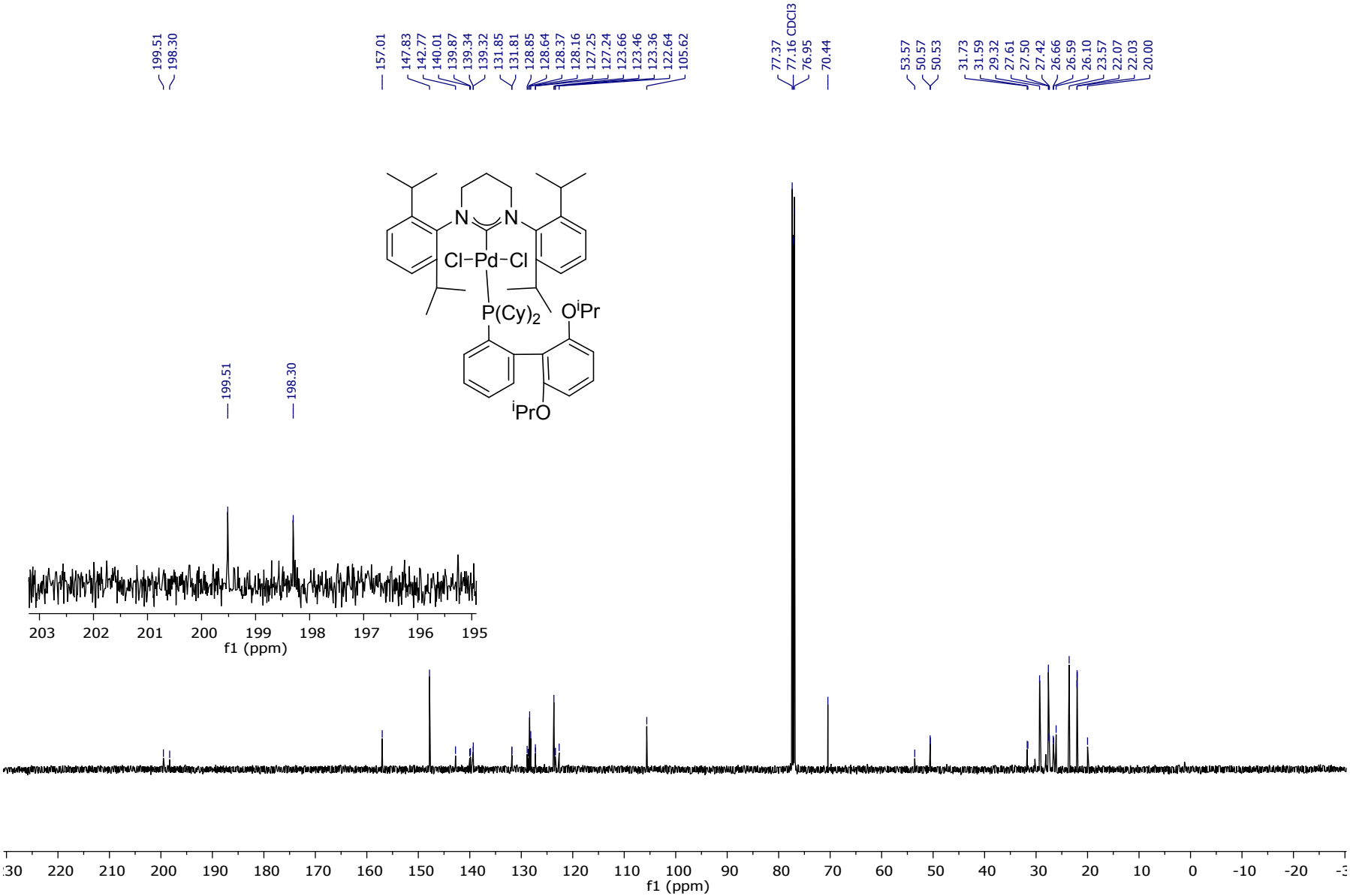

Figure S30. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of (6-Dipp)$PdCl_2$-RuPhos (3f)

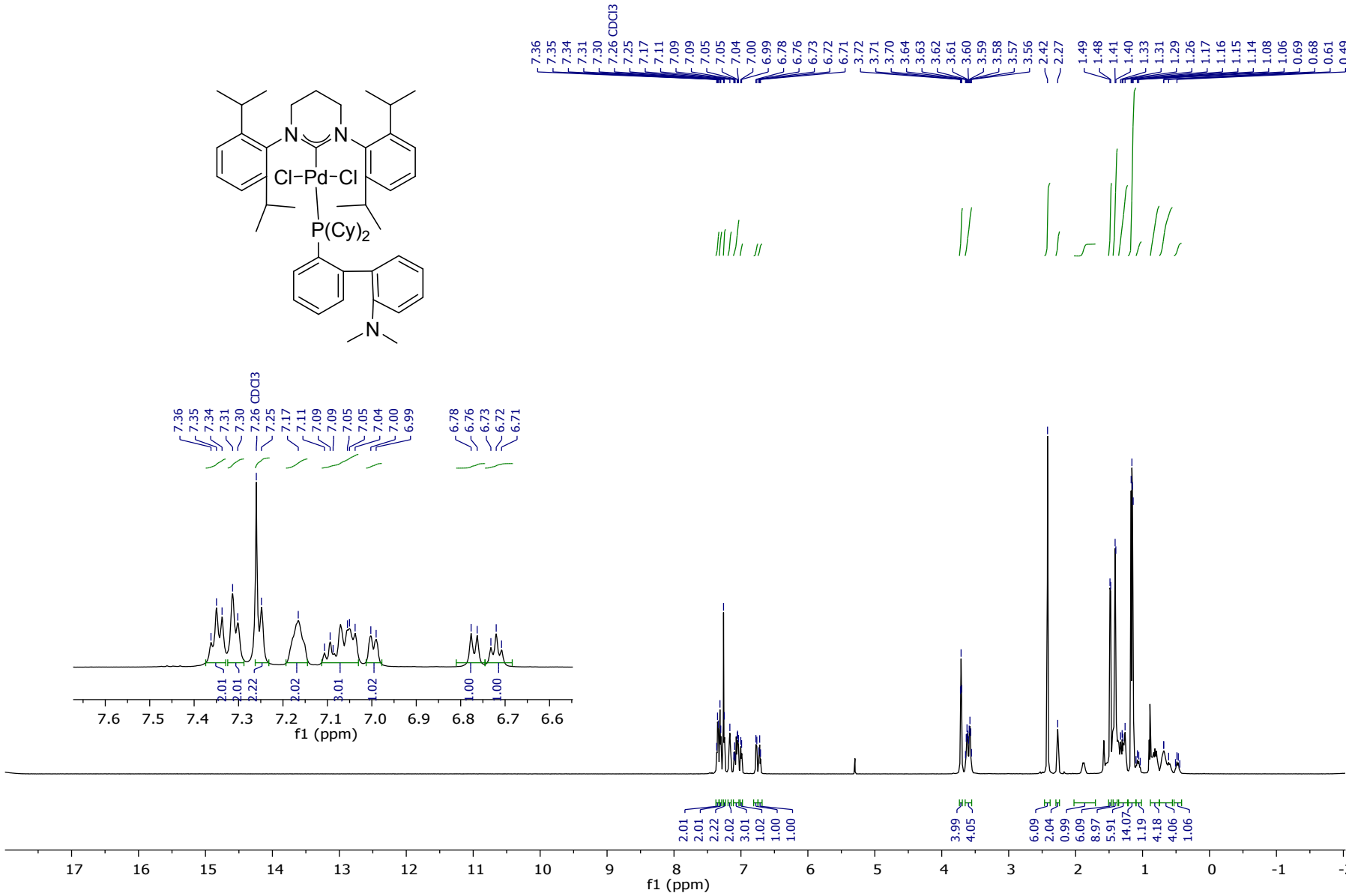

Figure S31. ^{1}H NMR (600 MHz, Chloroform-*d*) of (6-Dipp)PdCl$_2$-DavePhos (3g)

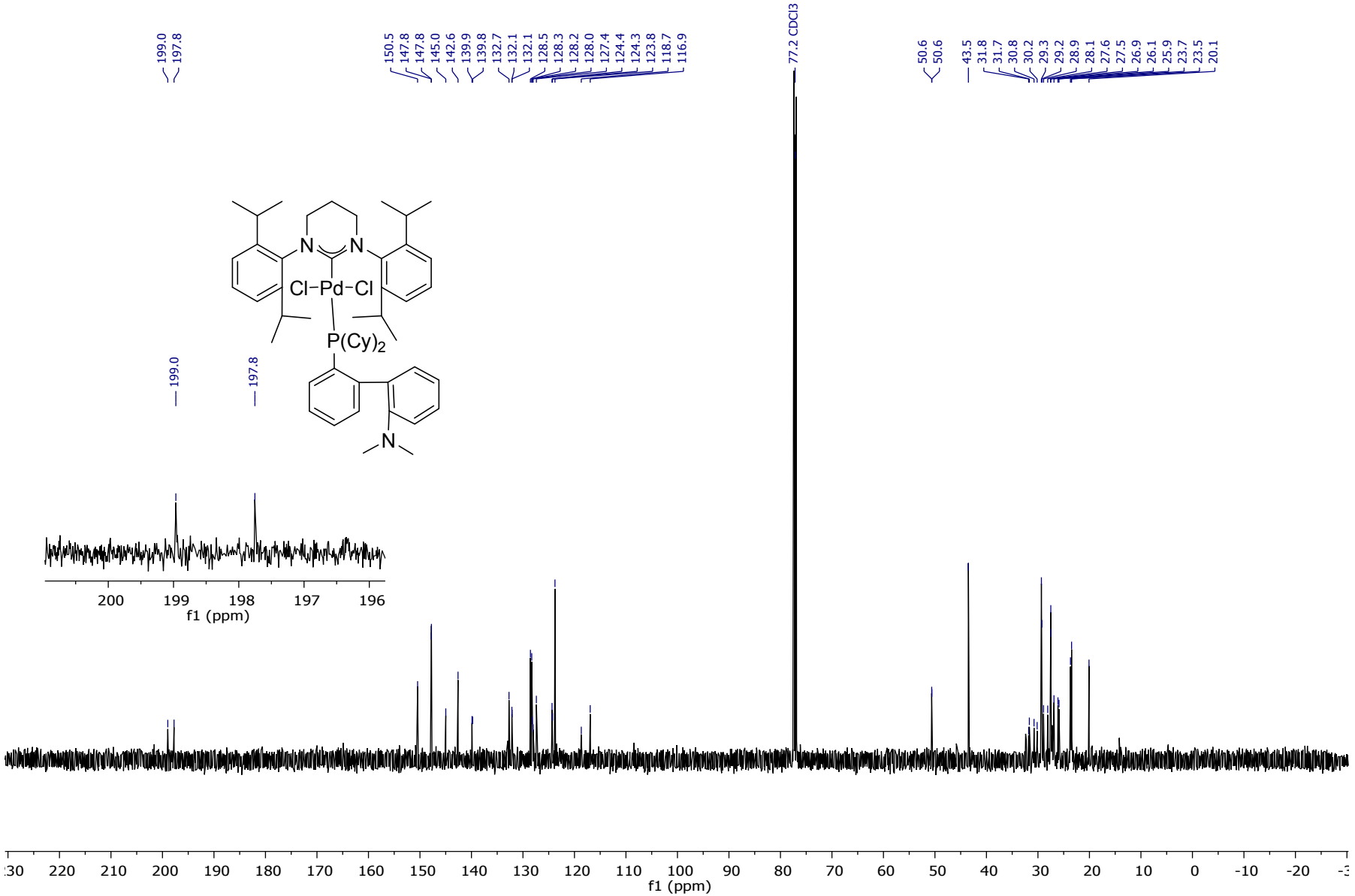

Figure S32. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of (6-Dipp)$PdCl_2$-DavePhos (3g)

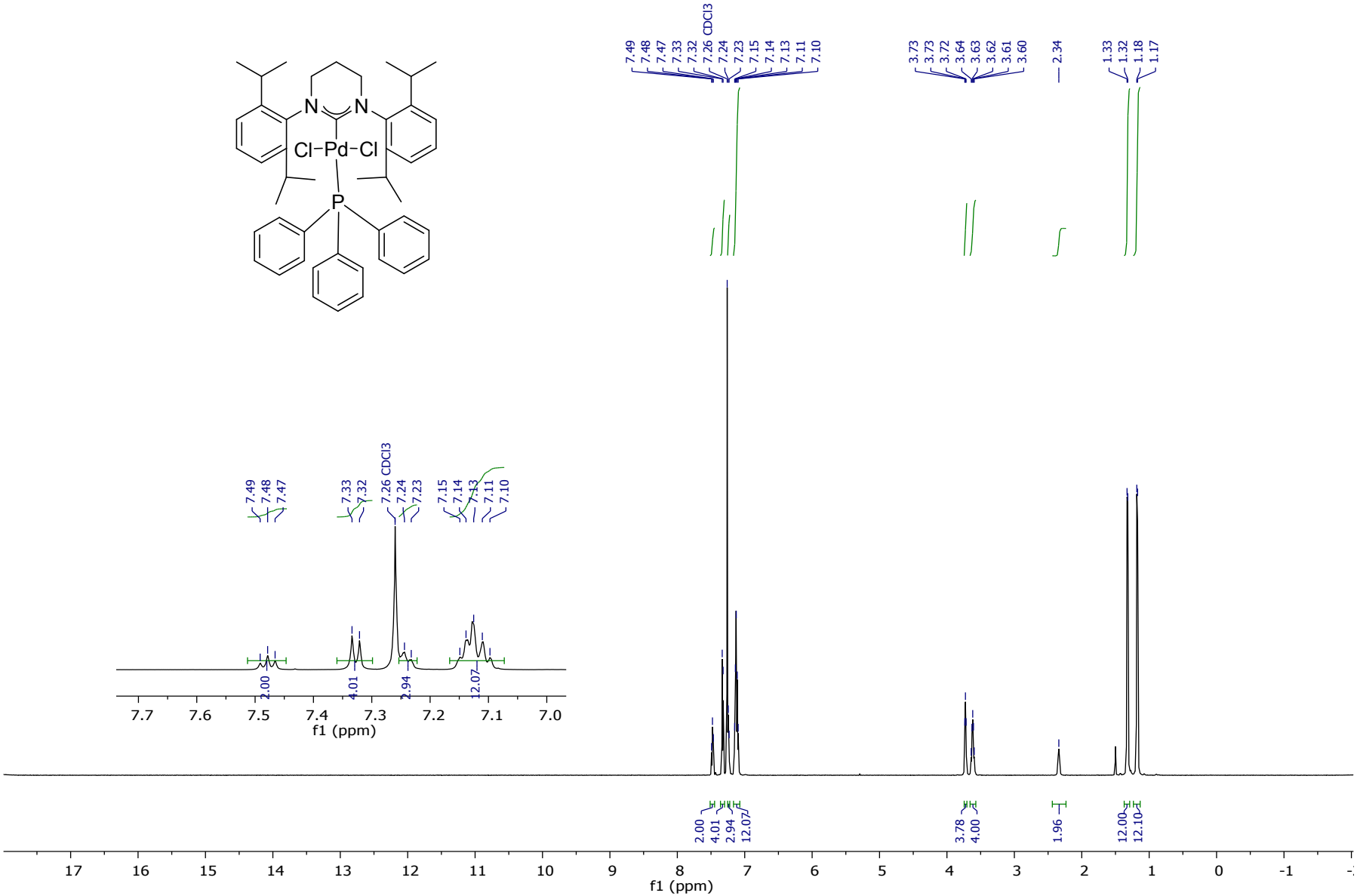

Figure S33. ^{1}H NMR (600 MHz, Chloroform-*d*) of (6-Dipp)PdCl$_2$-PPh$_3$ (3h)

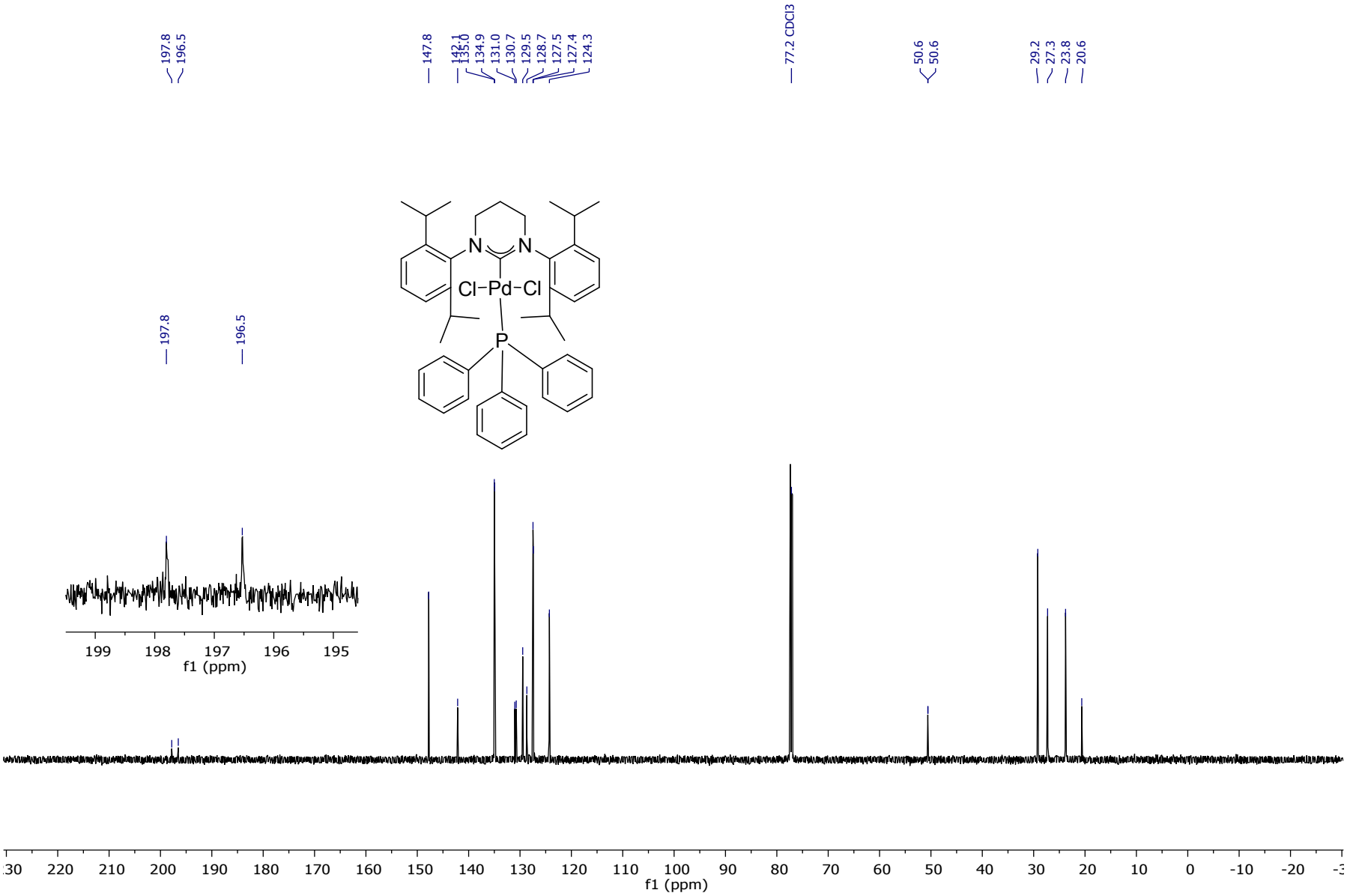

Figure S34. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of (6-Dipp)$PdCl_2$-PPh_3 (3h)

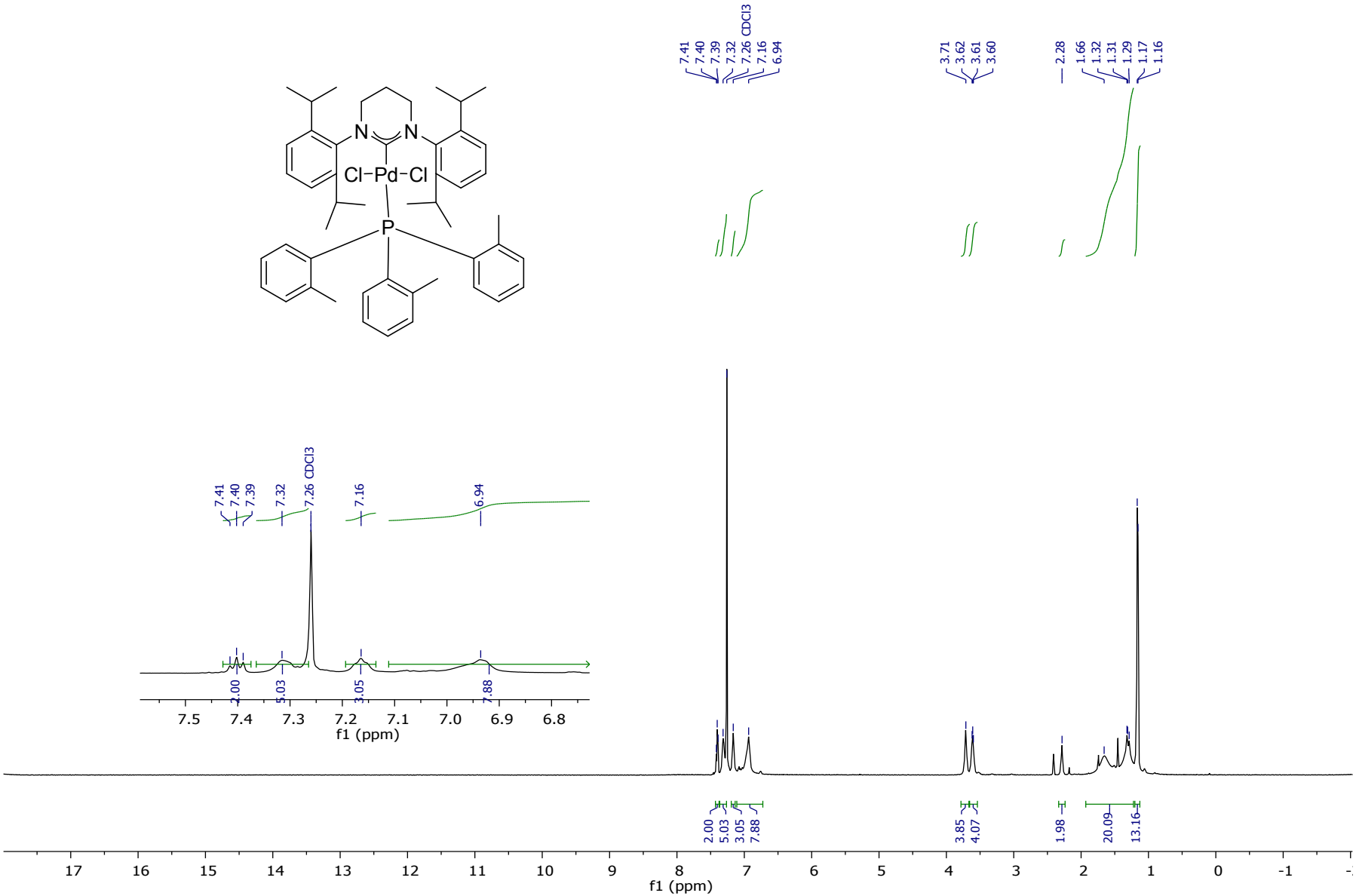

Figure S35. ^{1}H NMR (600 MHz, Chloroform-*d*) of (6-Dipp)PdCl$_2$-P(*o*-Tol)$_3$ (3i)

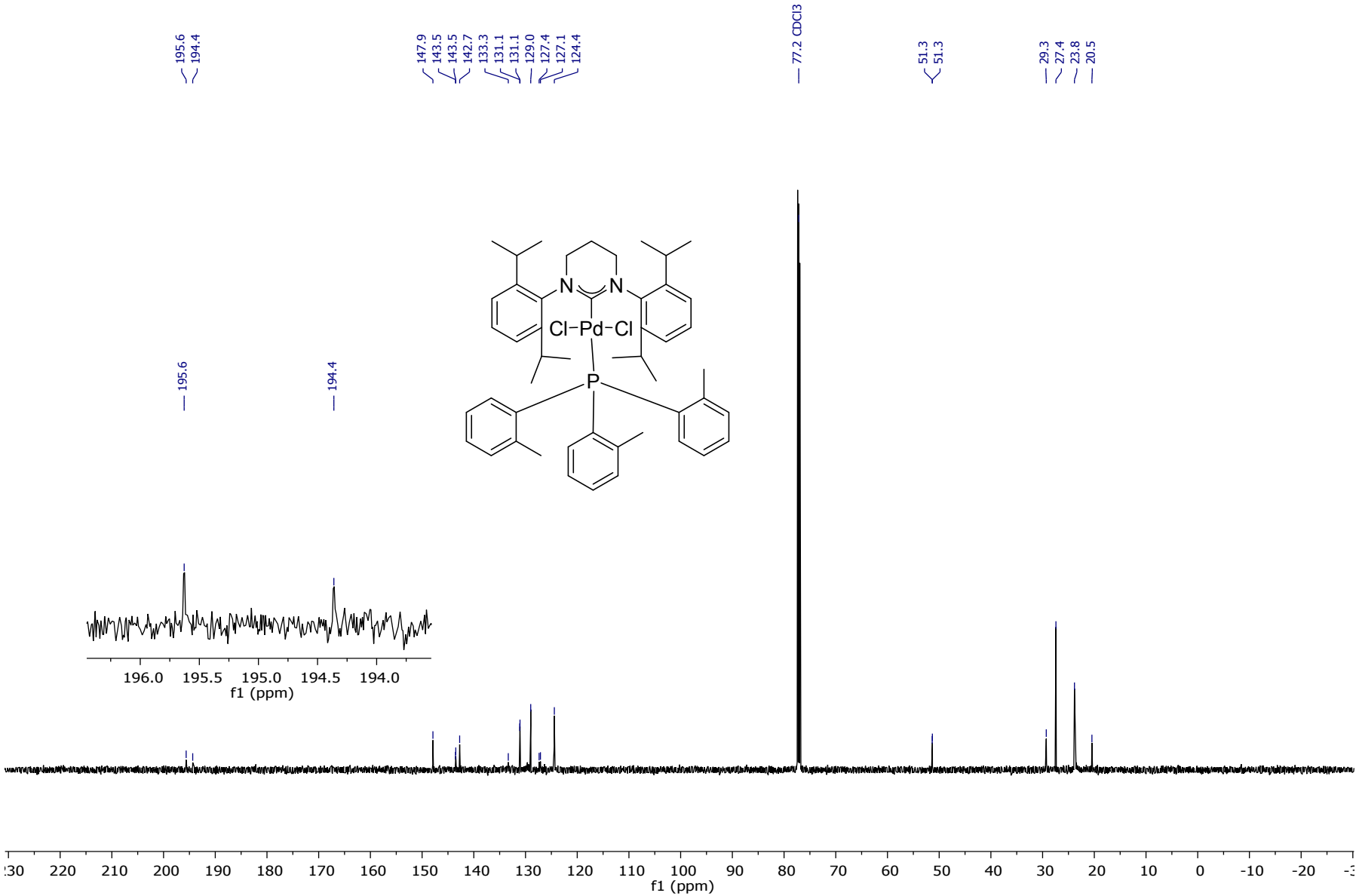

Figure S36. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of (6-Dipp)$PdCl_2$-P(*o*-Tol)$_3$ (3i)

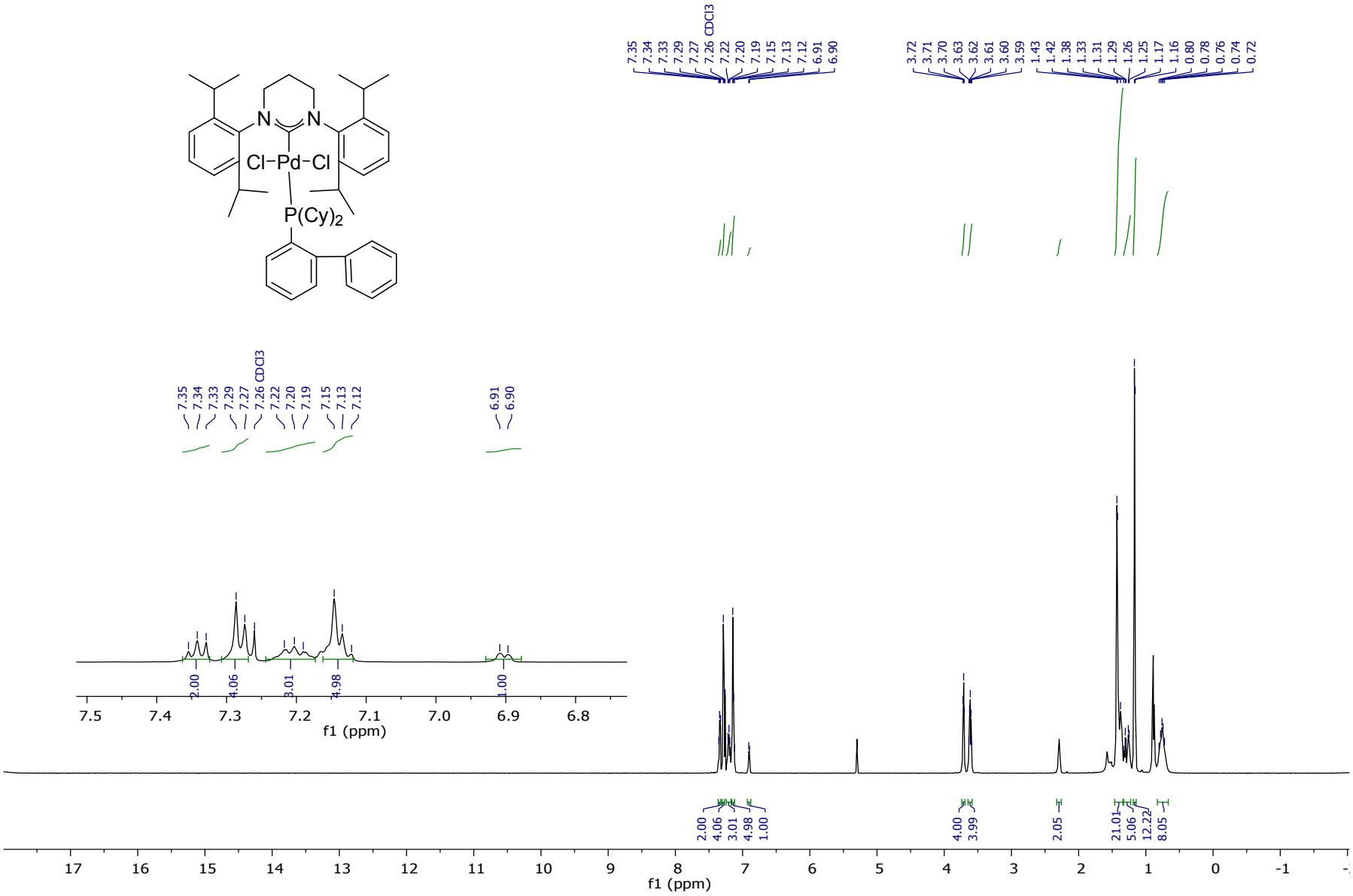

Figure S37. ^{1}H NMR (600 MHz, Chloroform-*d*) of (6-Dipp)PdCl$_2$-CyJohnPhos (3j)

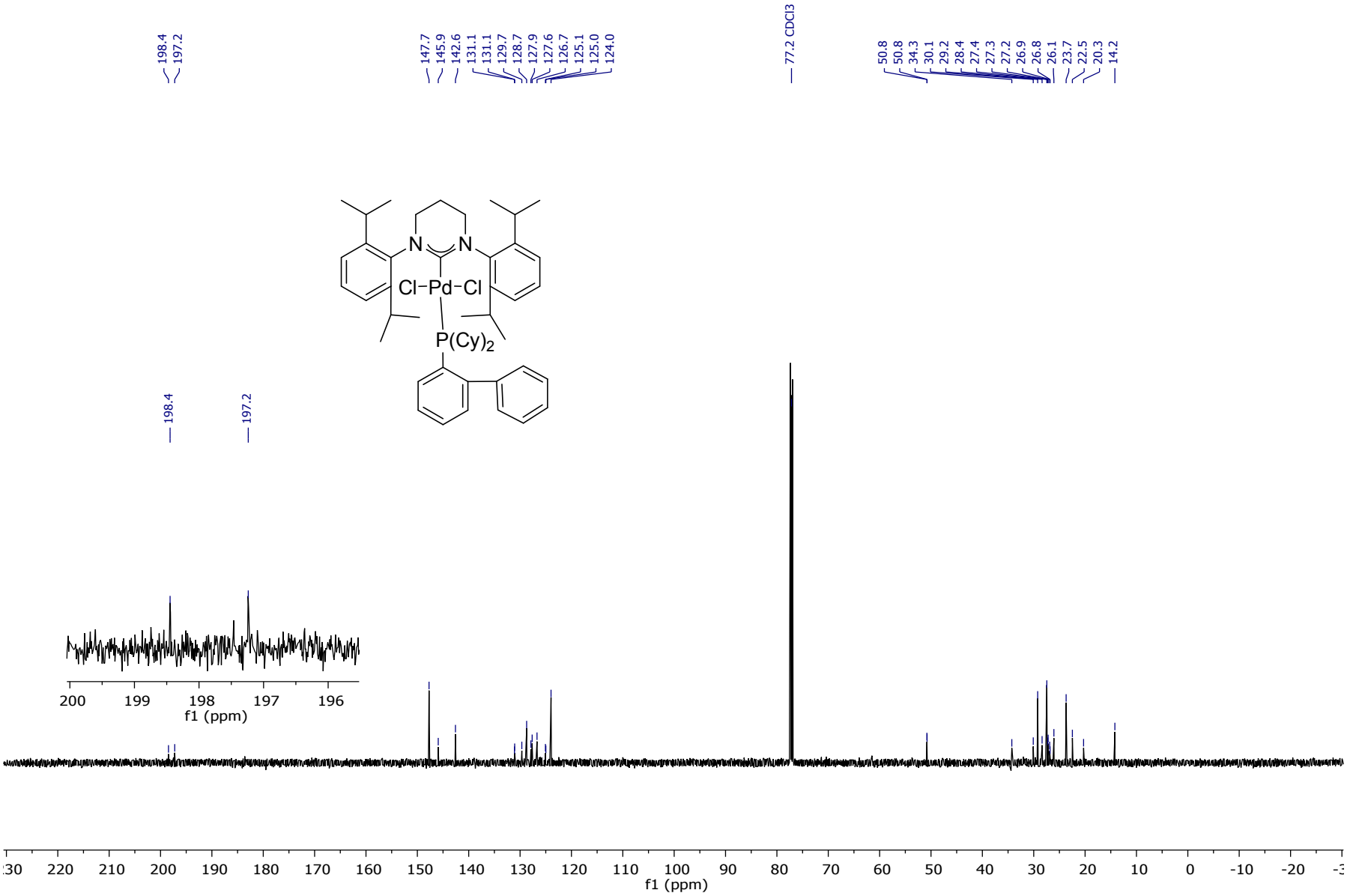

Figure S38. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of (6-Dipp)$PdCl_2$-(Cy)JohnPhos (3j)

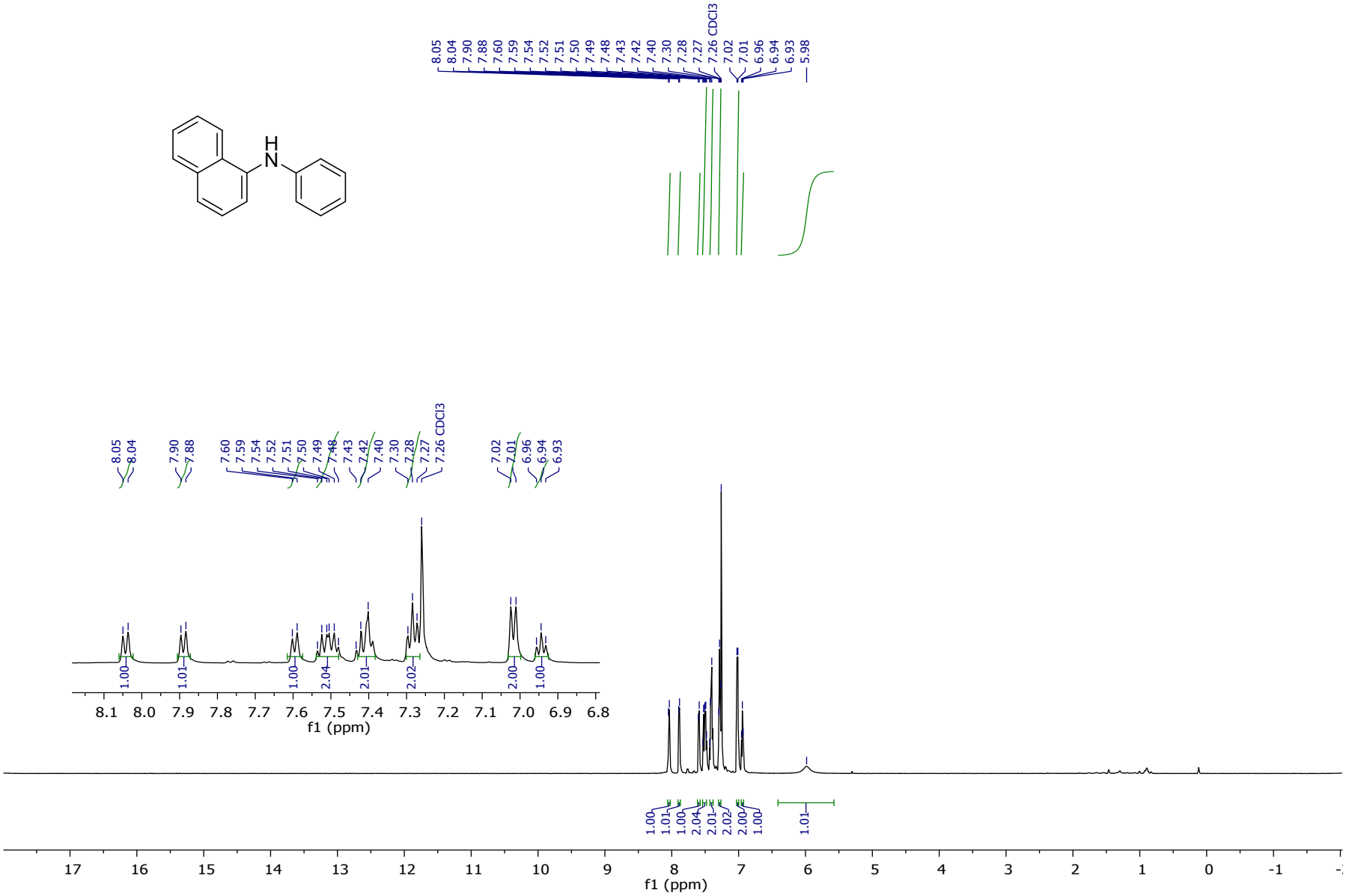

Figure S39. ^{1}H NMR (600 MHz, Chloroform-*d*) of *N*-phenylnaphthalen-1-amine (4a)

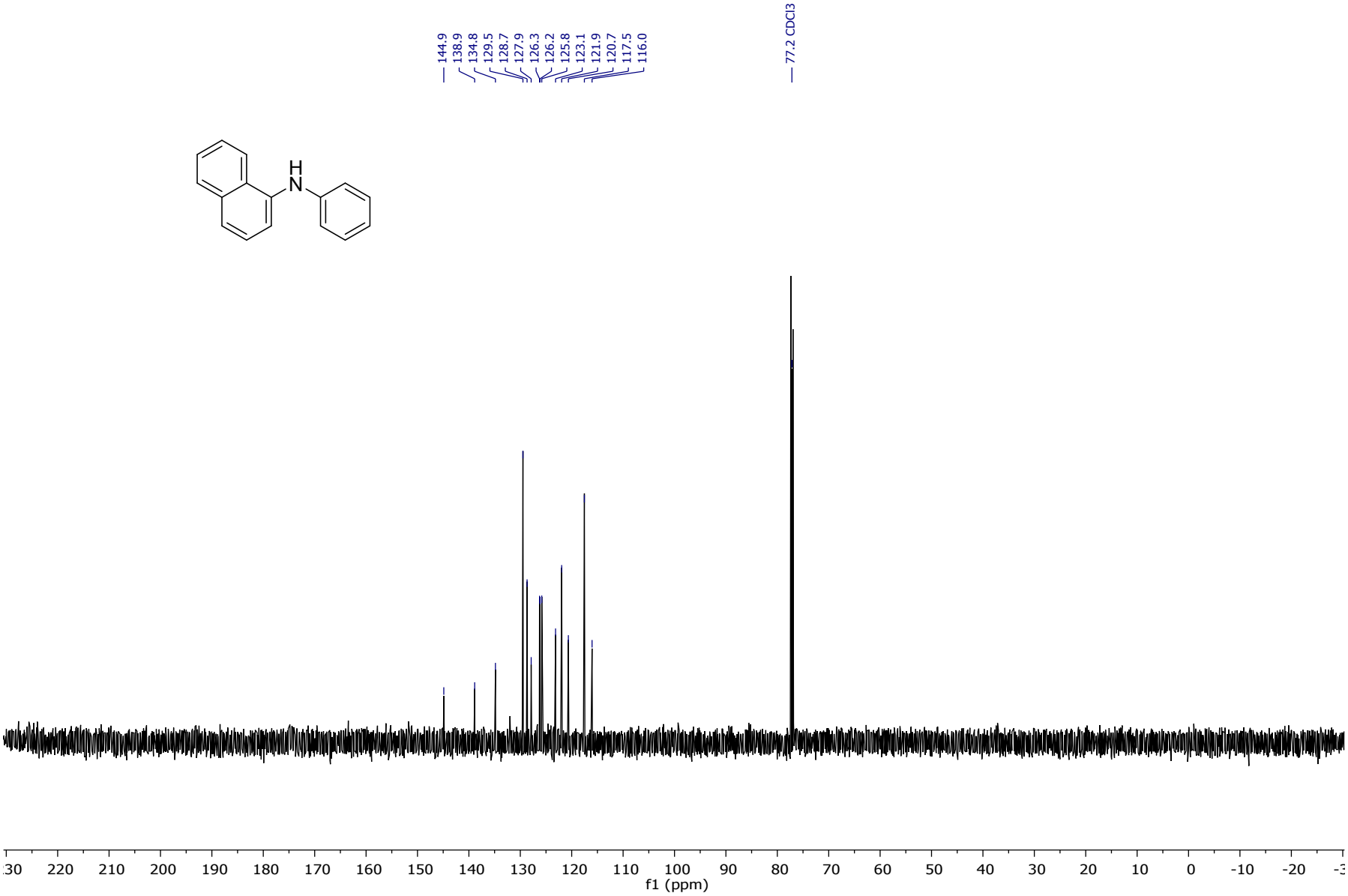

Figure S40. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of *N*-phenylnaphthalen-1-amine (4a)

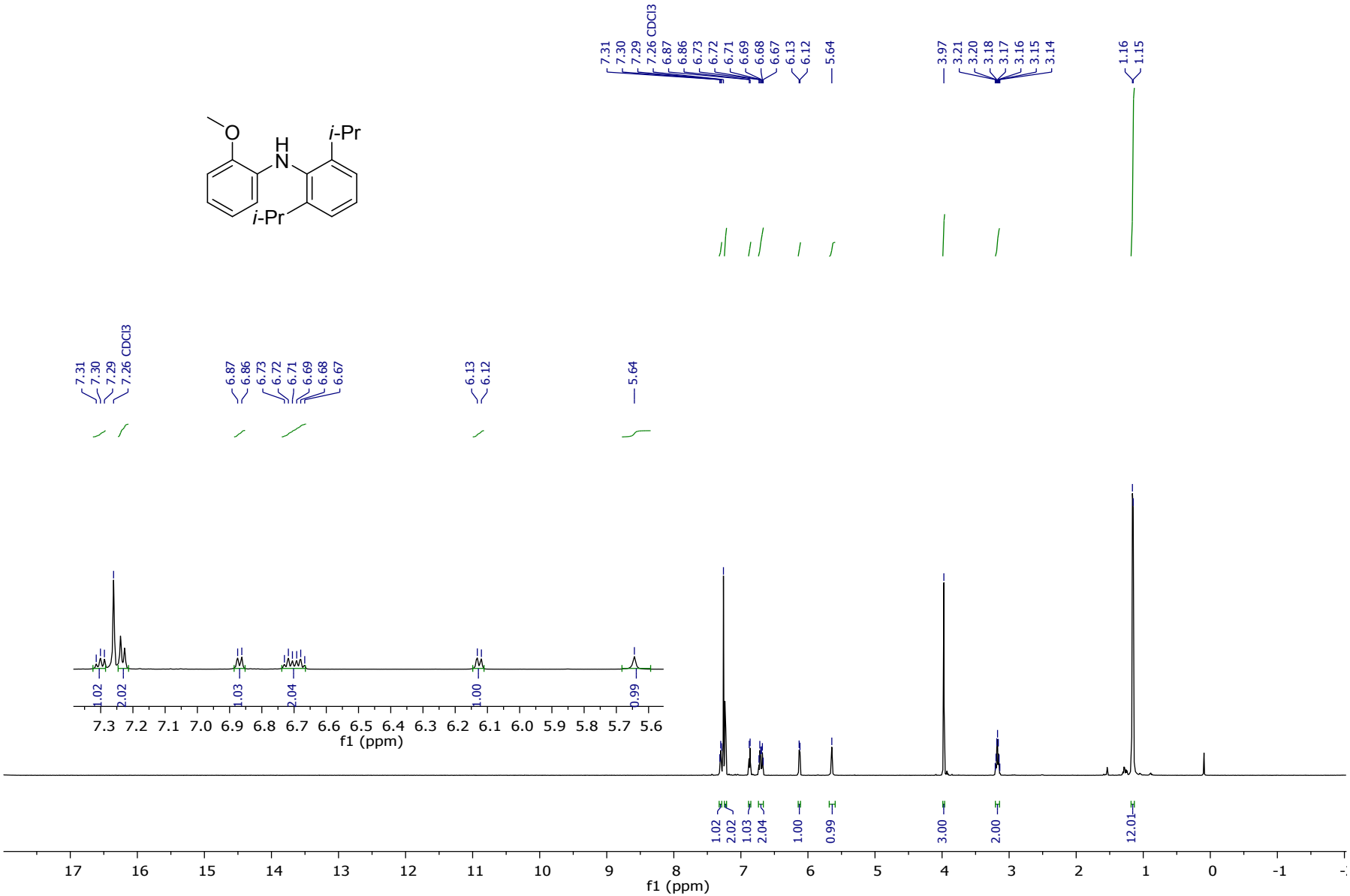

Figure S41. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,6-diisopropyl-*N*-(2-methoxyphenyl)aniline (4b)

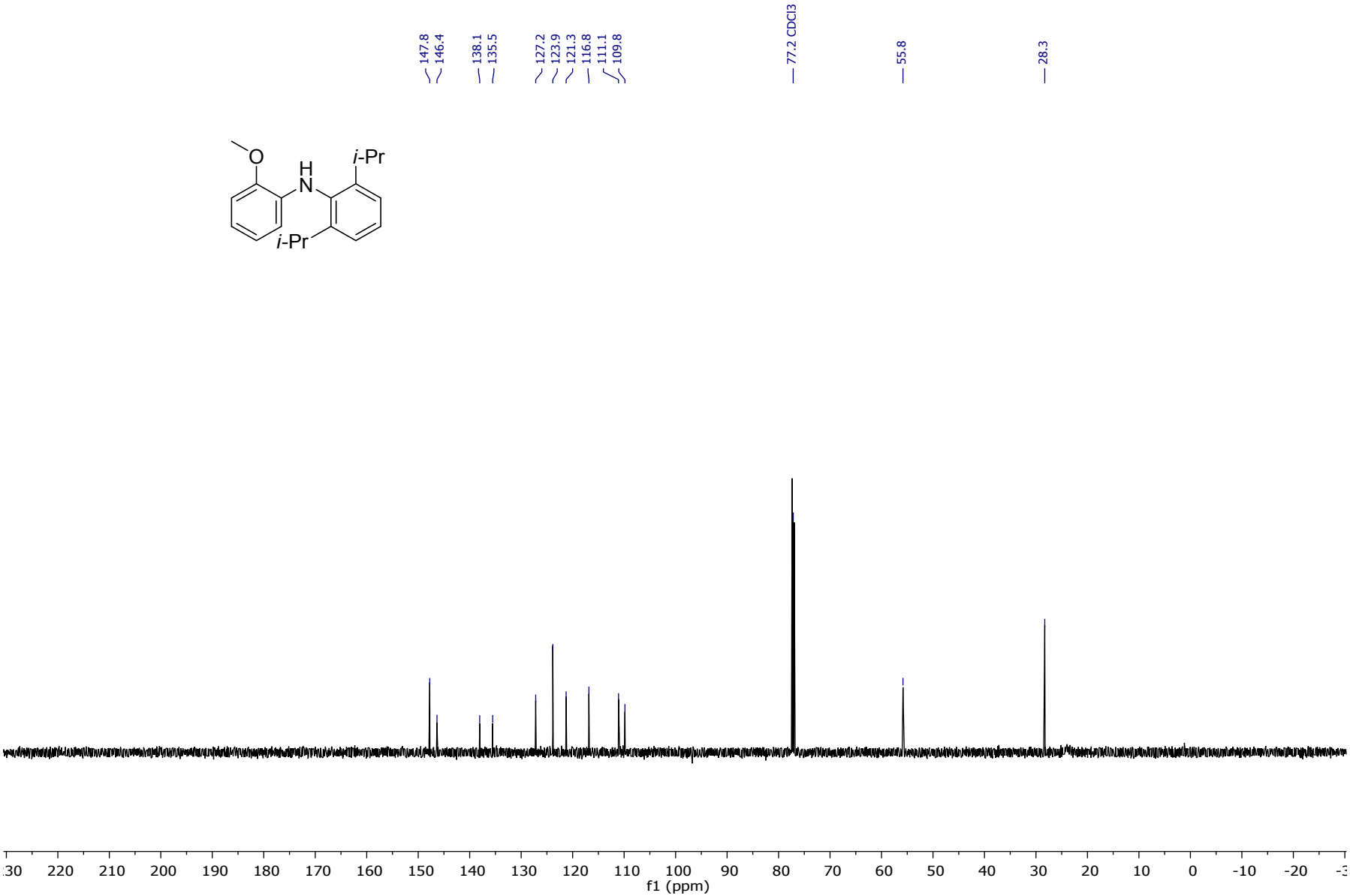

Figure S42. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,6-diisopropyl-*N*-(2-methoxyphenyl)aniline (4b)

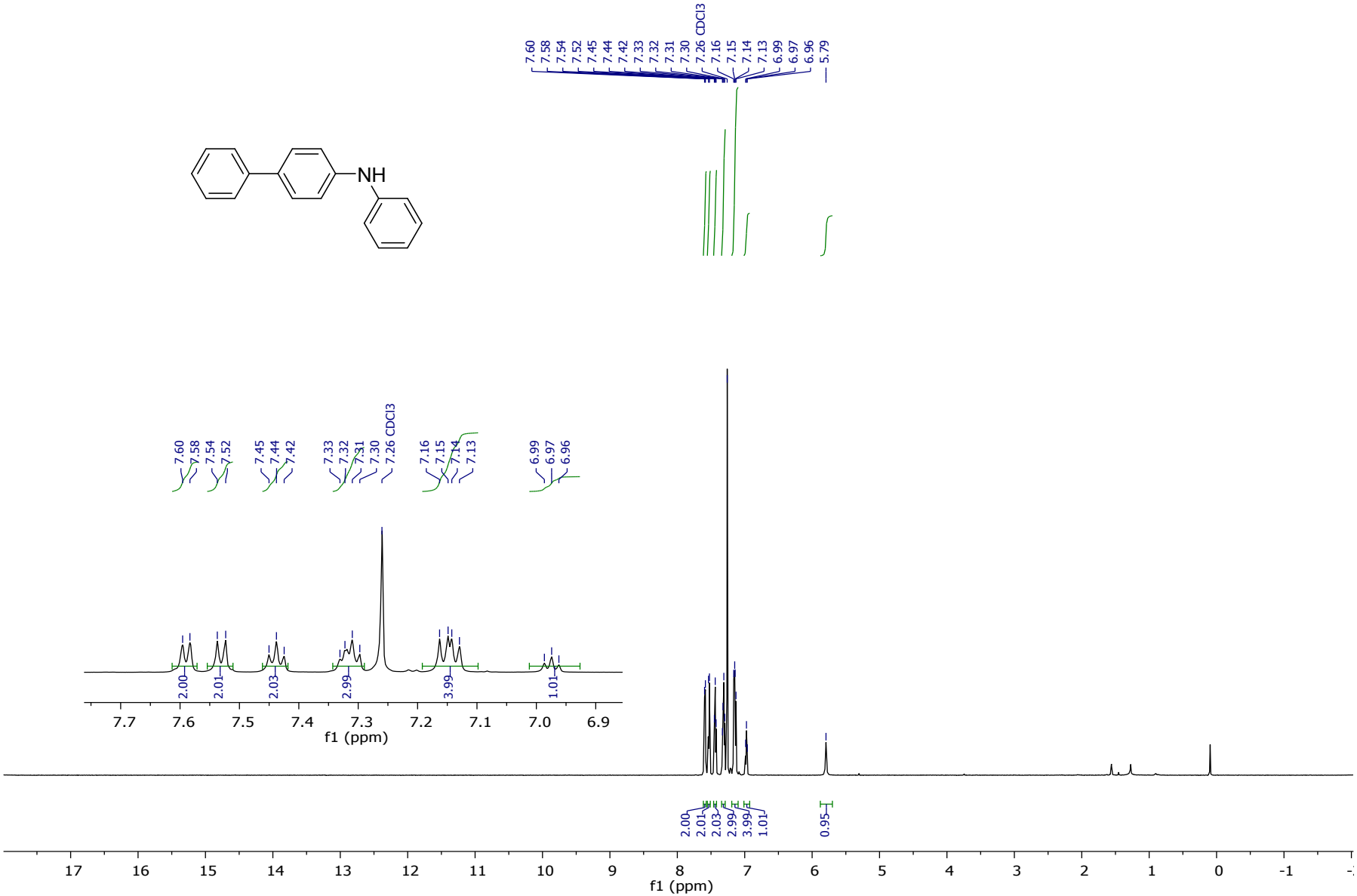

Figure S43. ^{1}H NMR (600 MHz, Chloroform-*d*) of N-phenylbiphenyl-4-amine (4c)

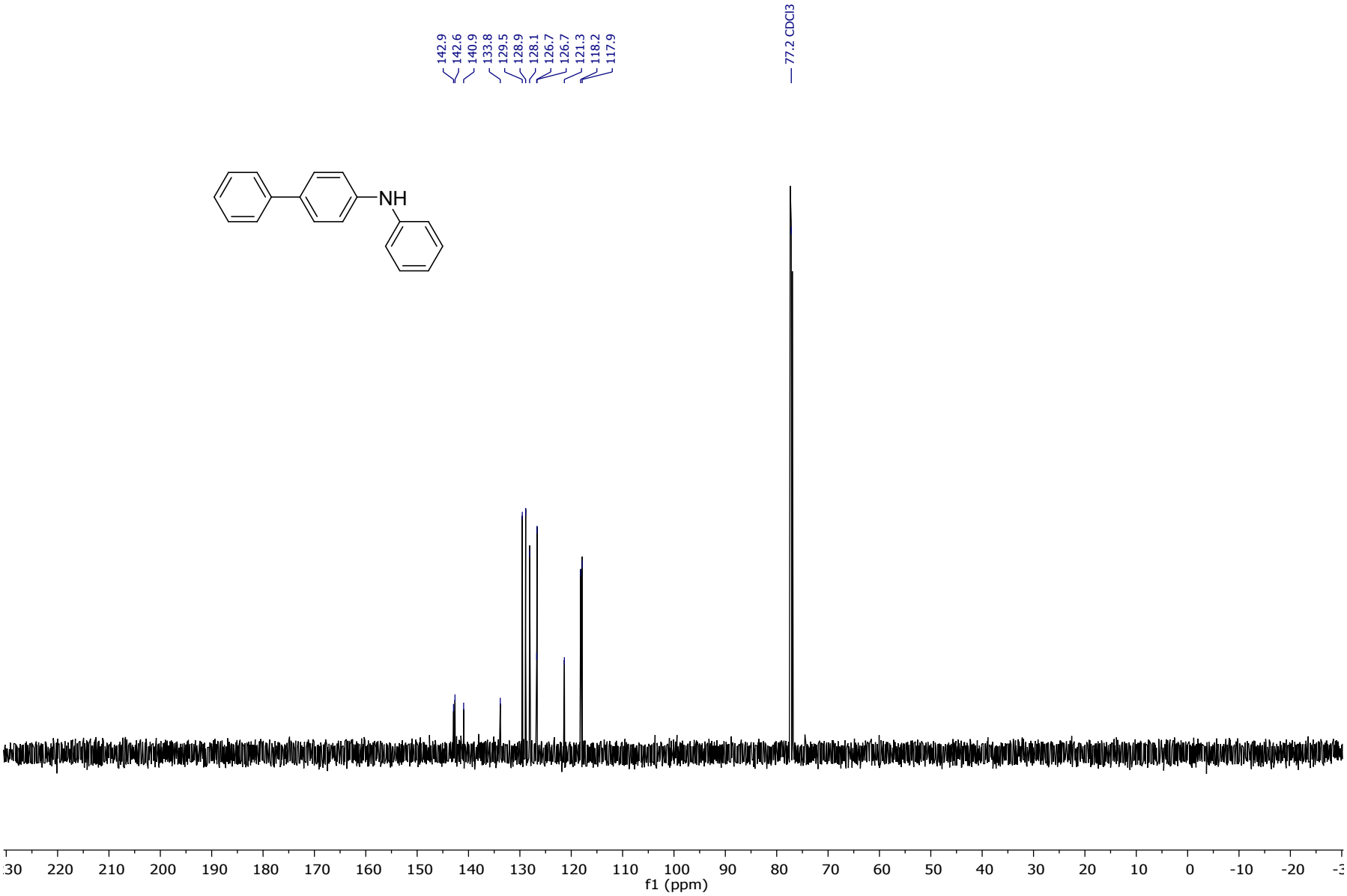

Figure S44. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N-phenylbiphenyl-4-amine (4c)

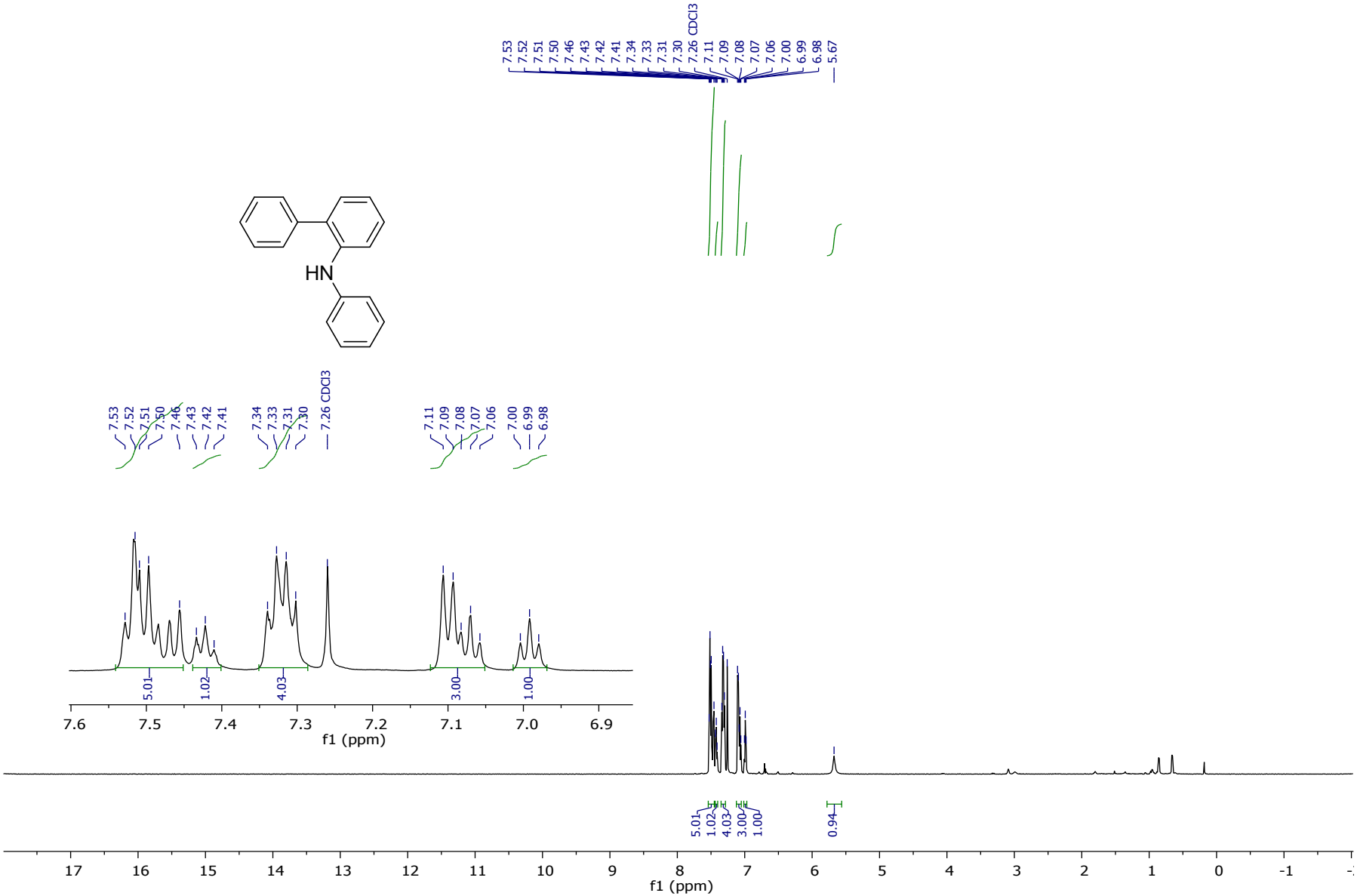

Figure S45. ^{1}H NMR (600 MHz, Chloroform-*d*) of N-phenylbiphenyl-2-amine (4d)

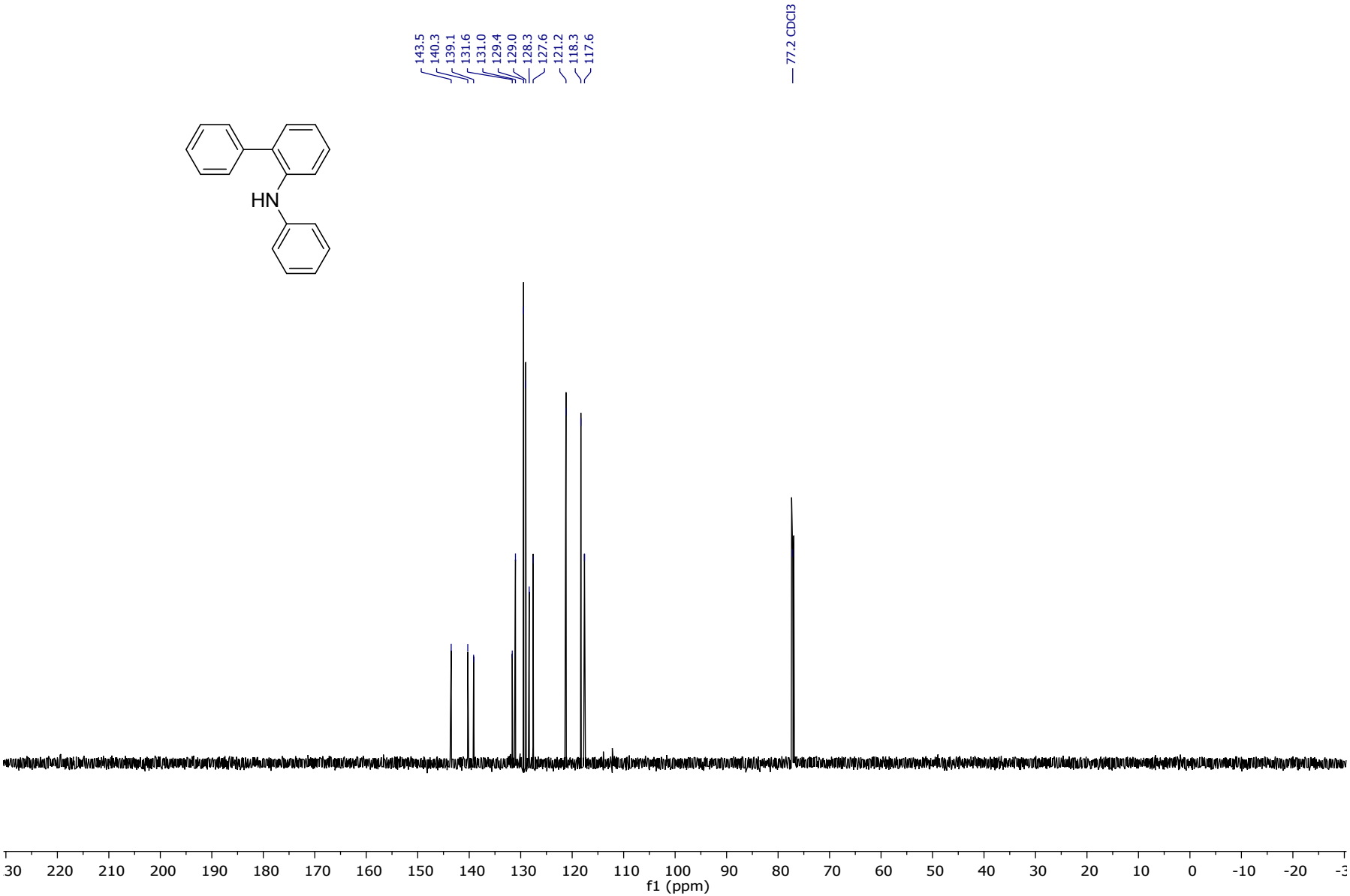

Figure S46. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N-phenylbiphenyl-2-amine (4d)

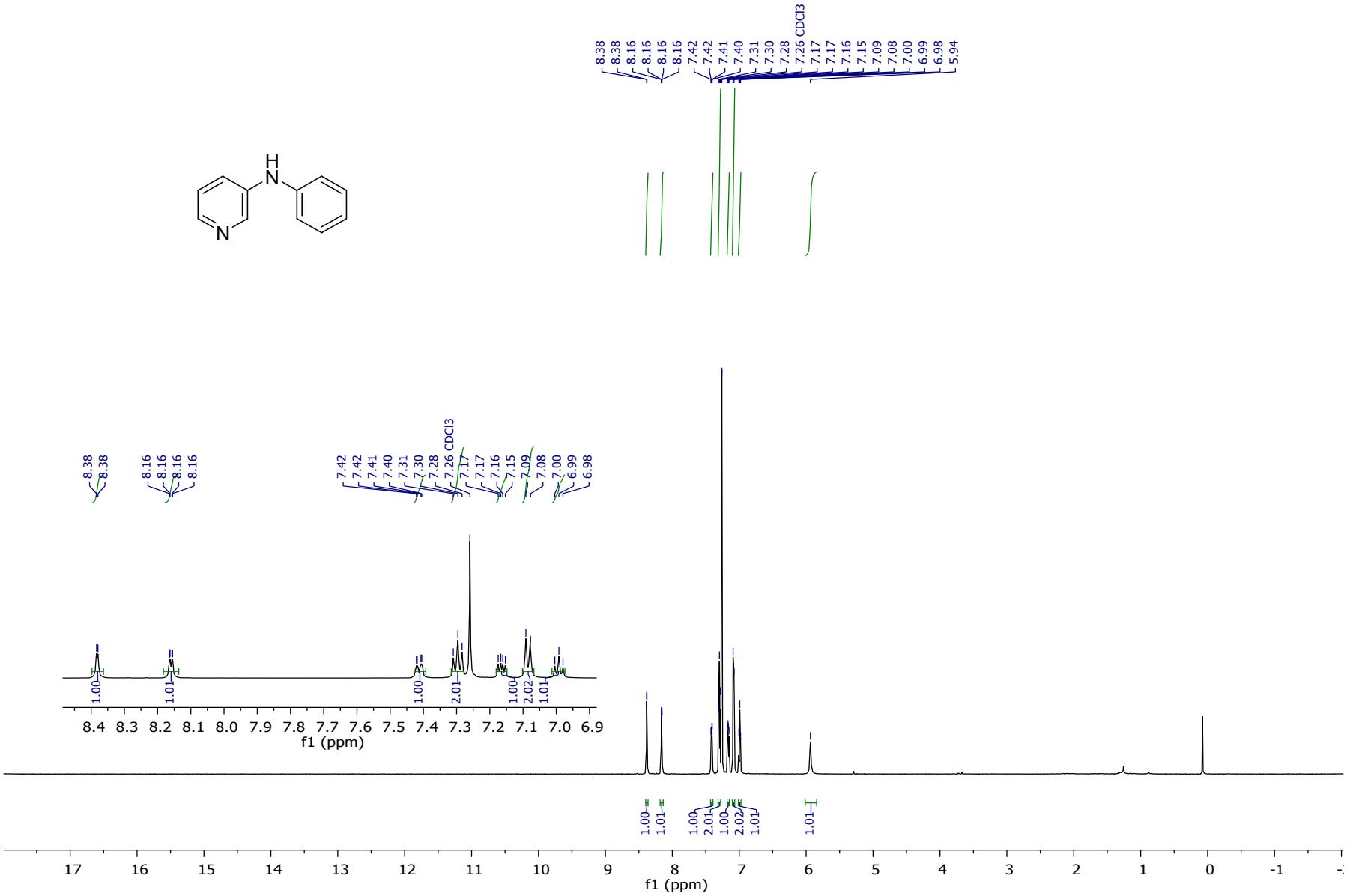

Figure S47. ^{1}H NMR (600 MHz, Chloroform-*d*) of *N*-phenylpyridin-3-amine (4e)

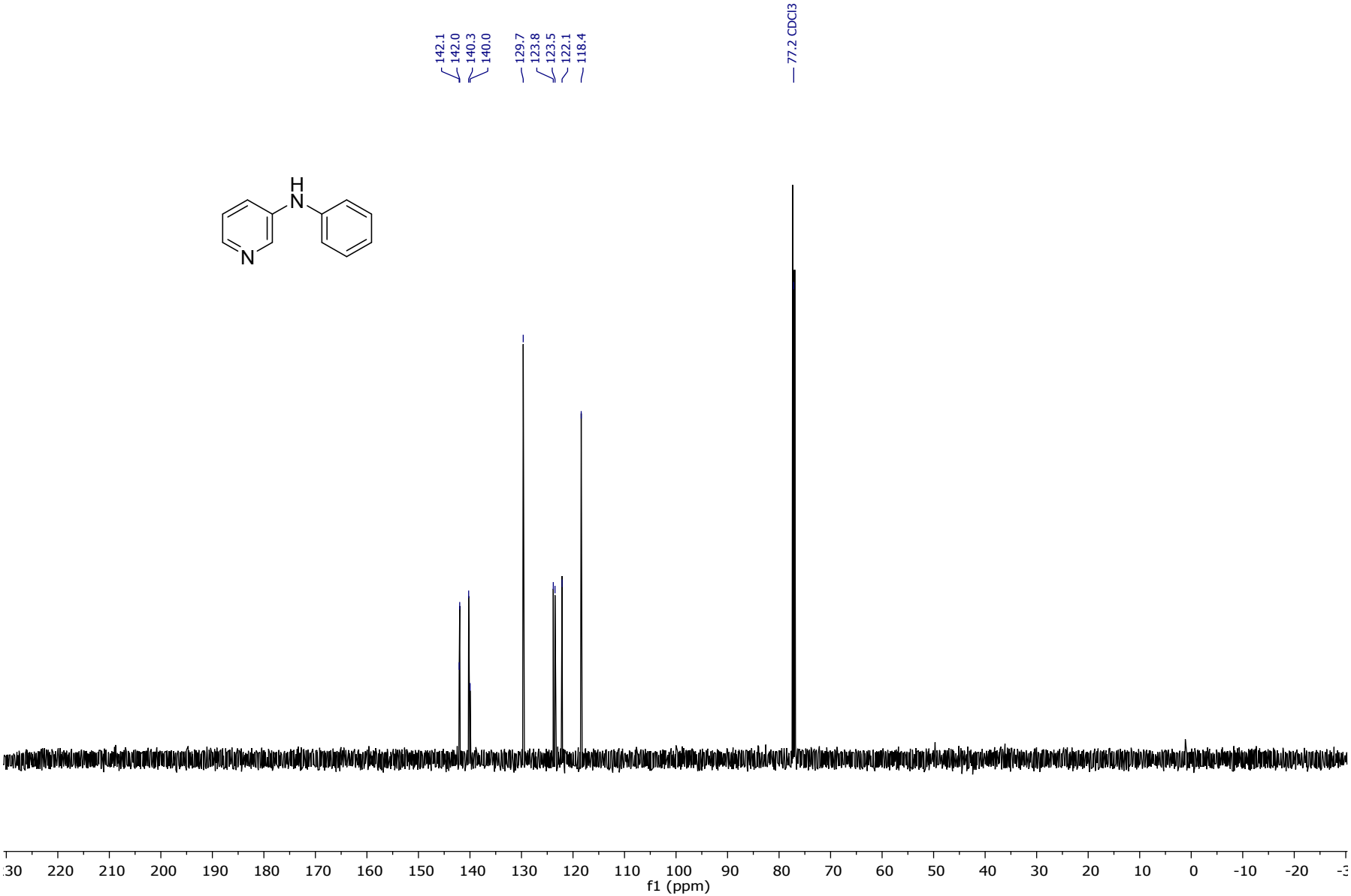

Figure S48. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of *N*-phenylpyridin-3-amine (4e)

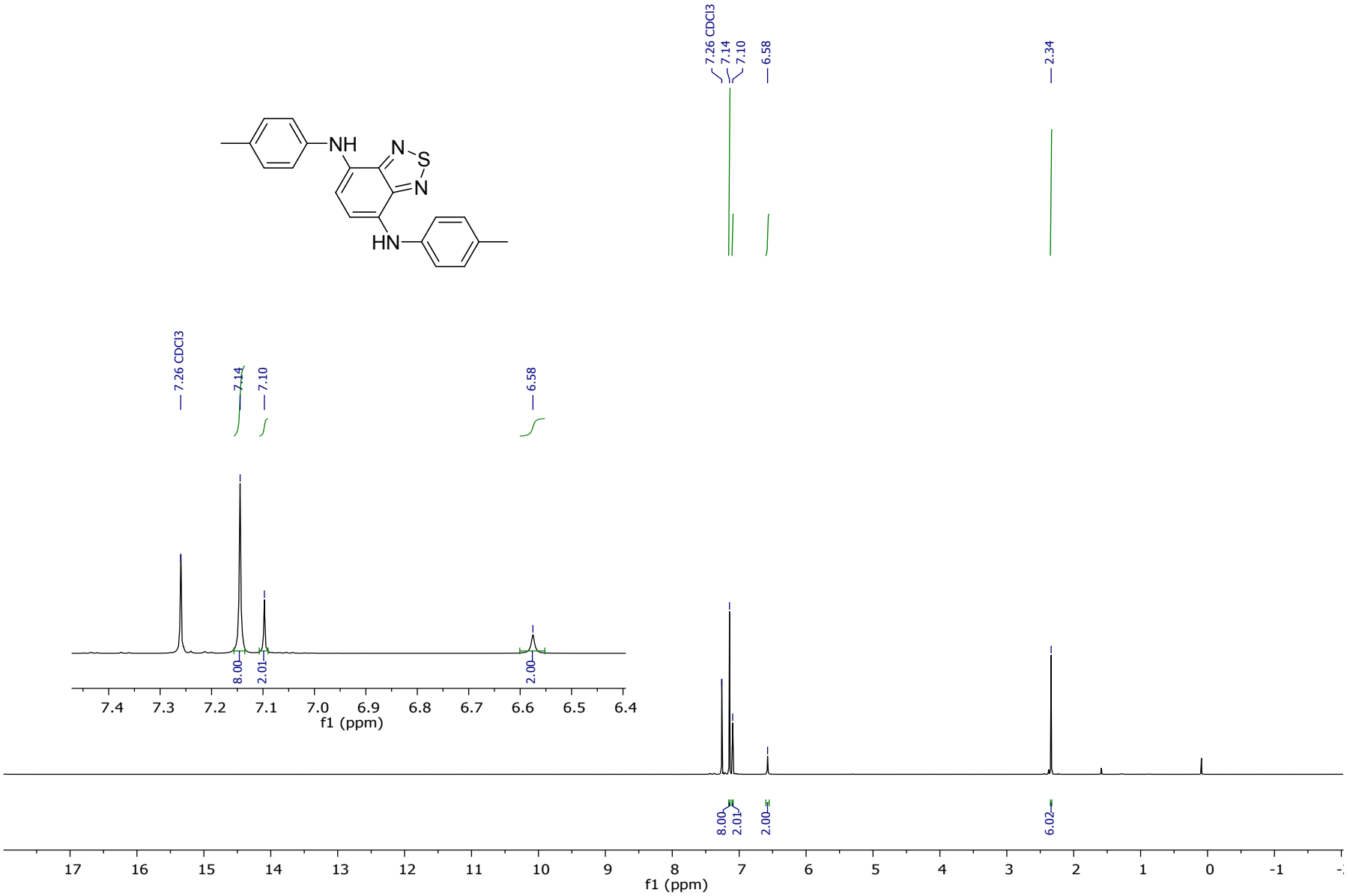

Figure S49. ^{1}H NMR (600 MHz, Chloroform-*d*) of N4,N7-di*p*-tolylbenzo[c][1,2,5]thiadiazole-4,7-diamine (4f)

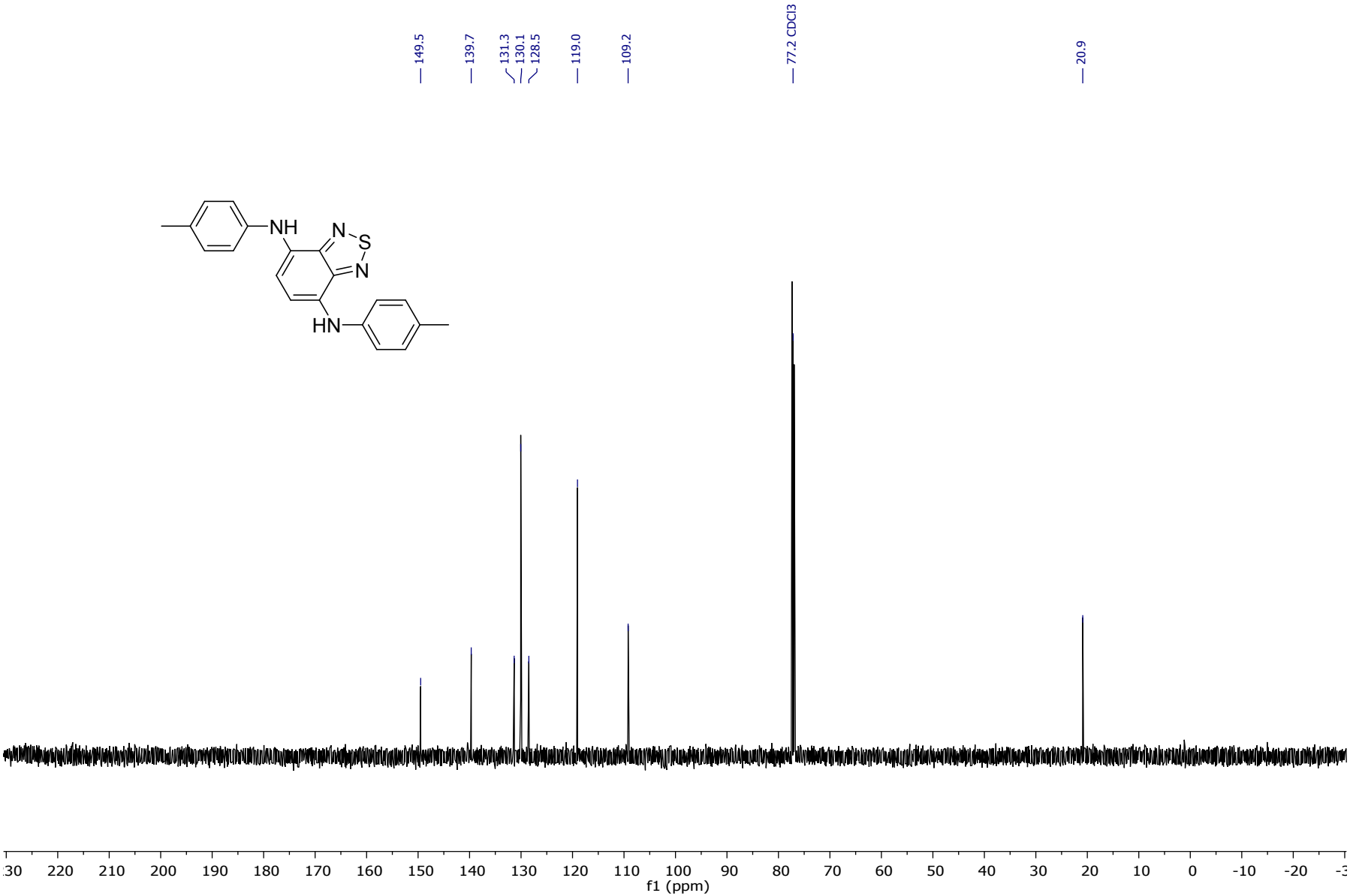

Figure S50. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N4,N7-di*p*-tolylbenzo[c][1,2,5]thiadiazole-4,7-diamine (4f)

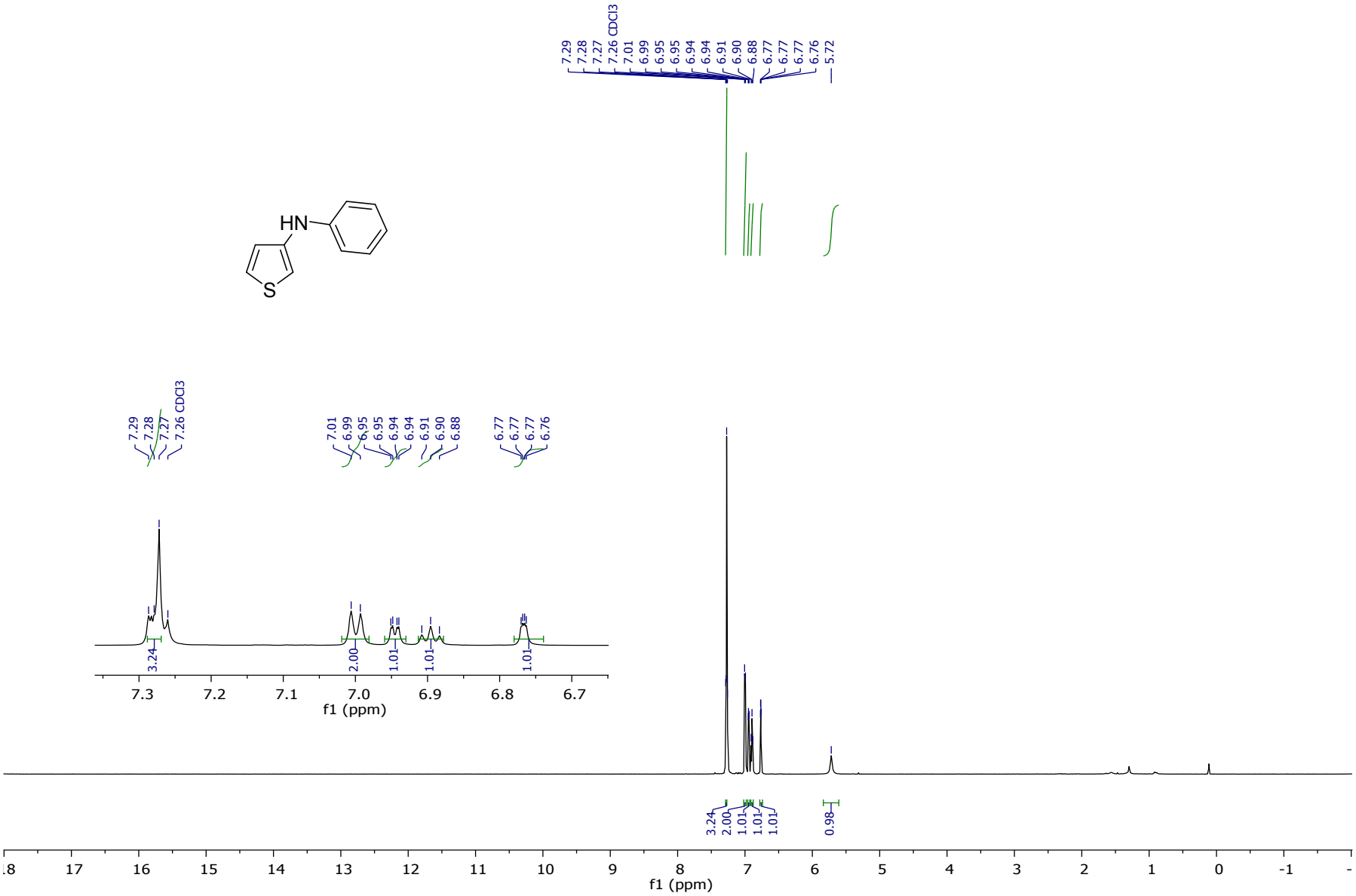

Figure S51. ^{1}H NMR (600 MHz, Chloroform-*d*) of *N*-phenylthiophen-3-amine (4g)

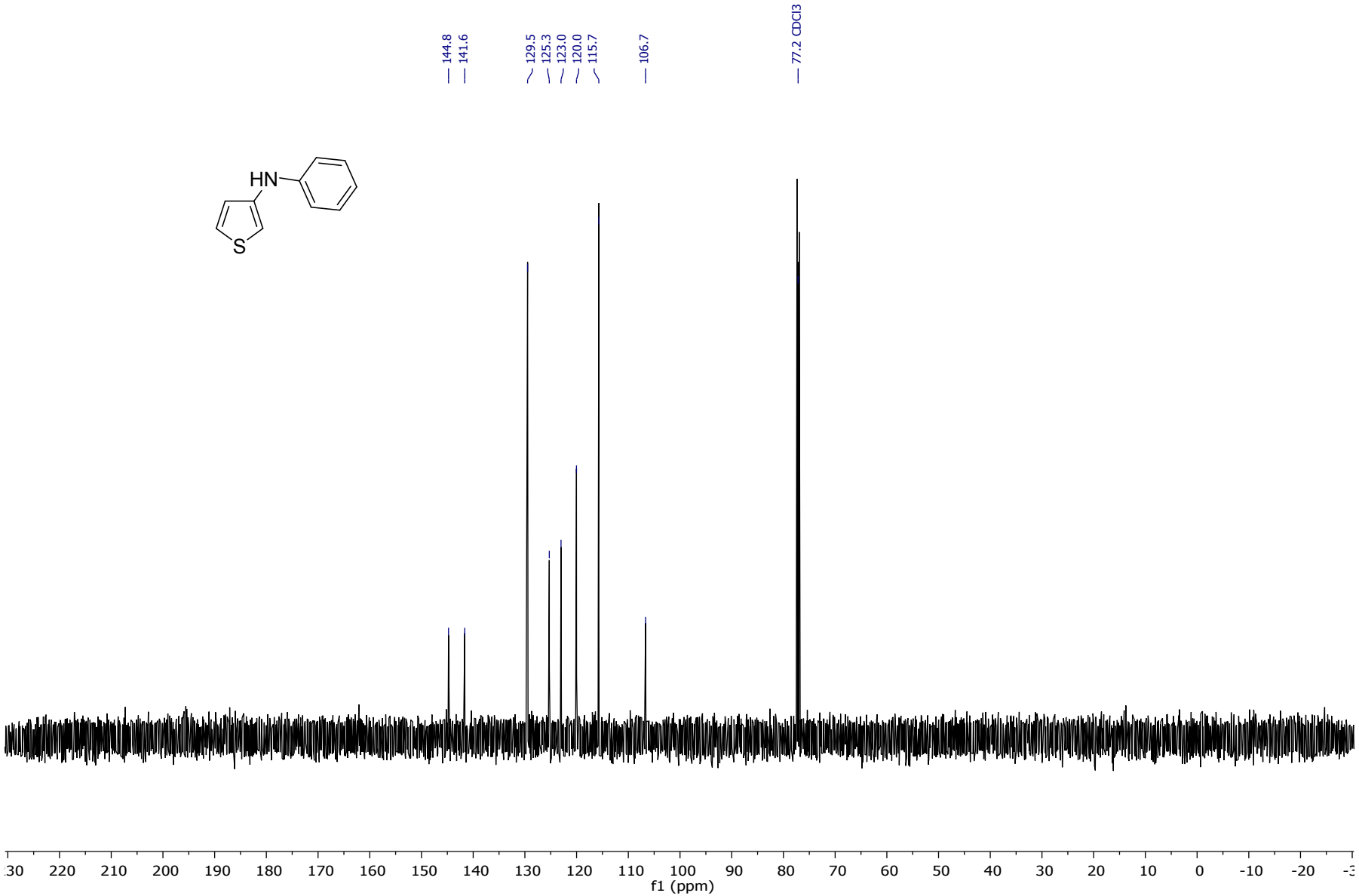

Figure S52. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of *N*-phenylthiophen-3-amine (4g)

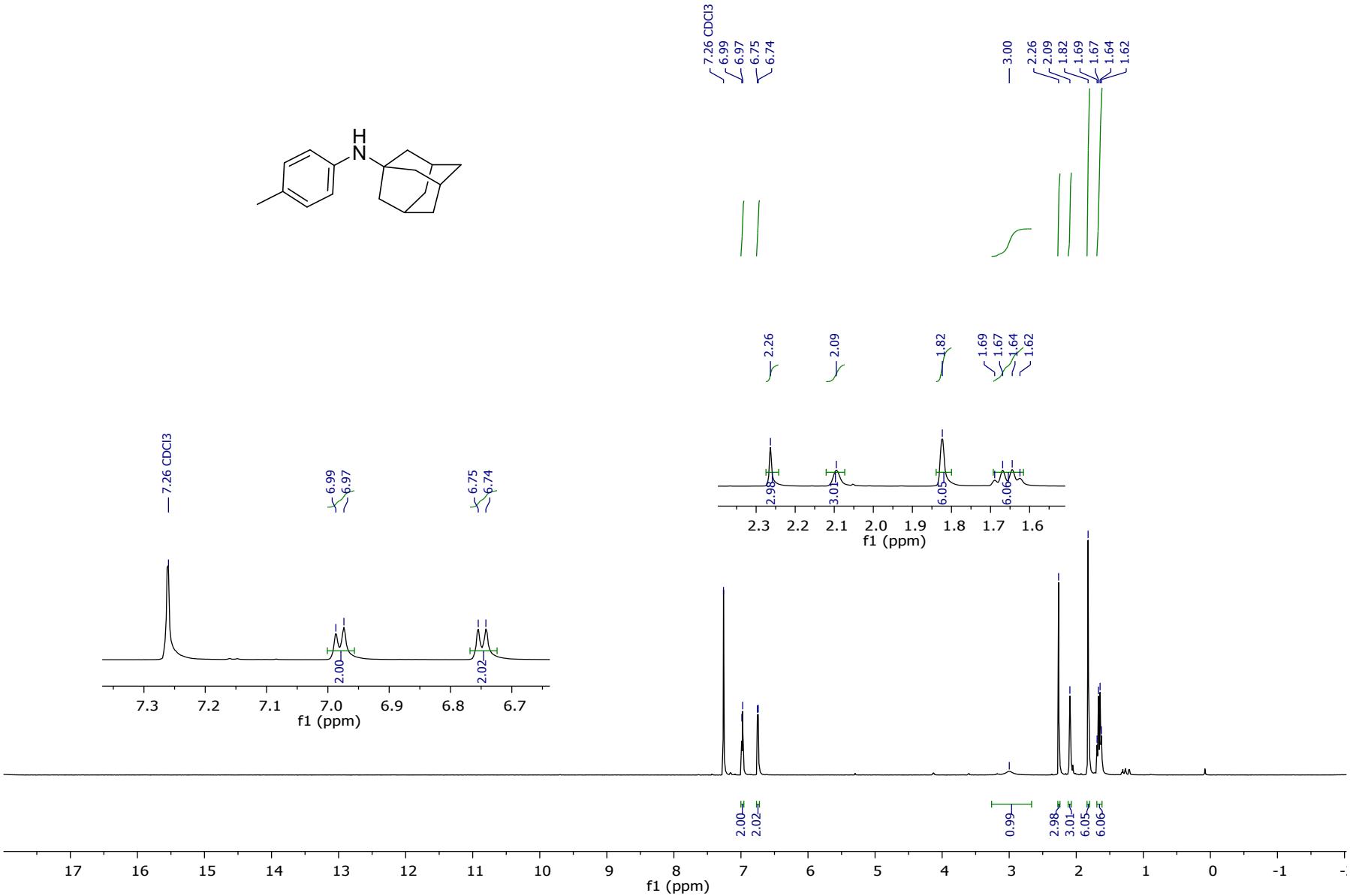

Figure S53. ^{1}H NMR (600 MHz, Chloroform-*d*) of *N*-(*p*-Tolyl)adamantan-1-amine -1-amine (4h)

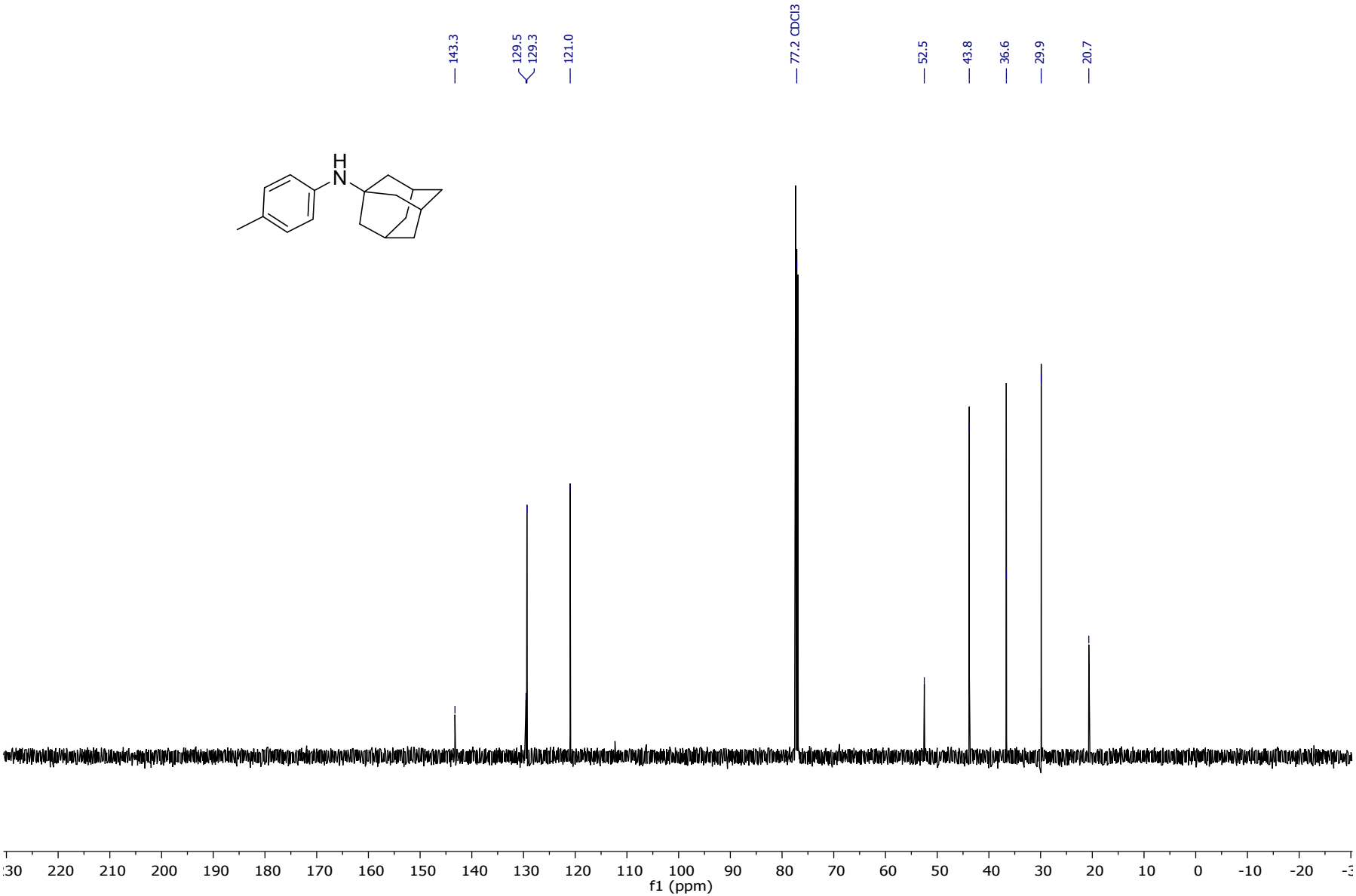

Figure S54. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of *N*-(*p*-Tolyl)adamantan-1-amine (4h)

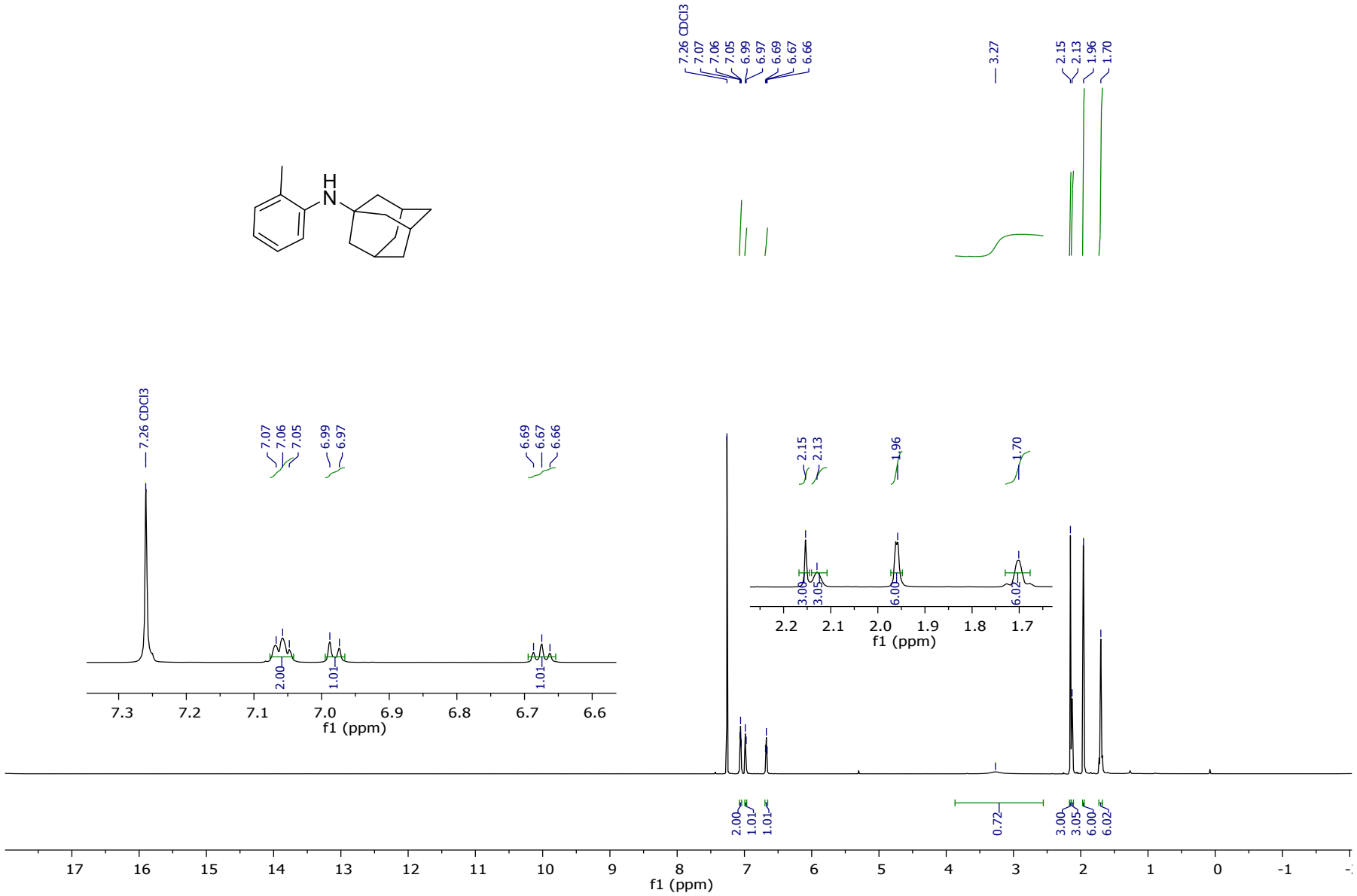

Figure S55. ^{1}H NMR (600 MHz, Chloroform-*d*) of *N*-(*o*-Tolyl)adamantan-1-amine (4i)

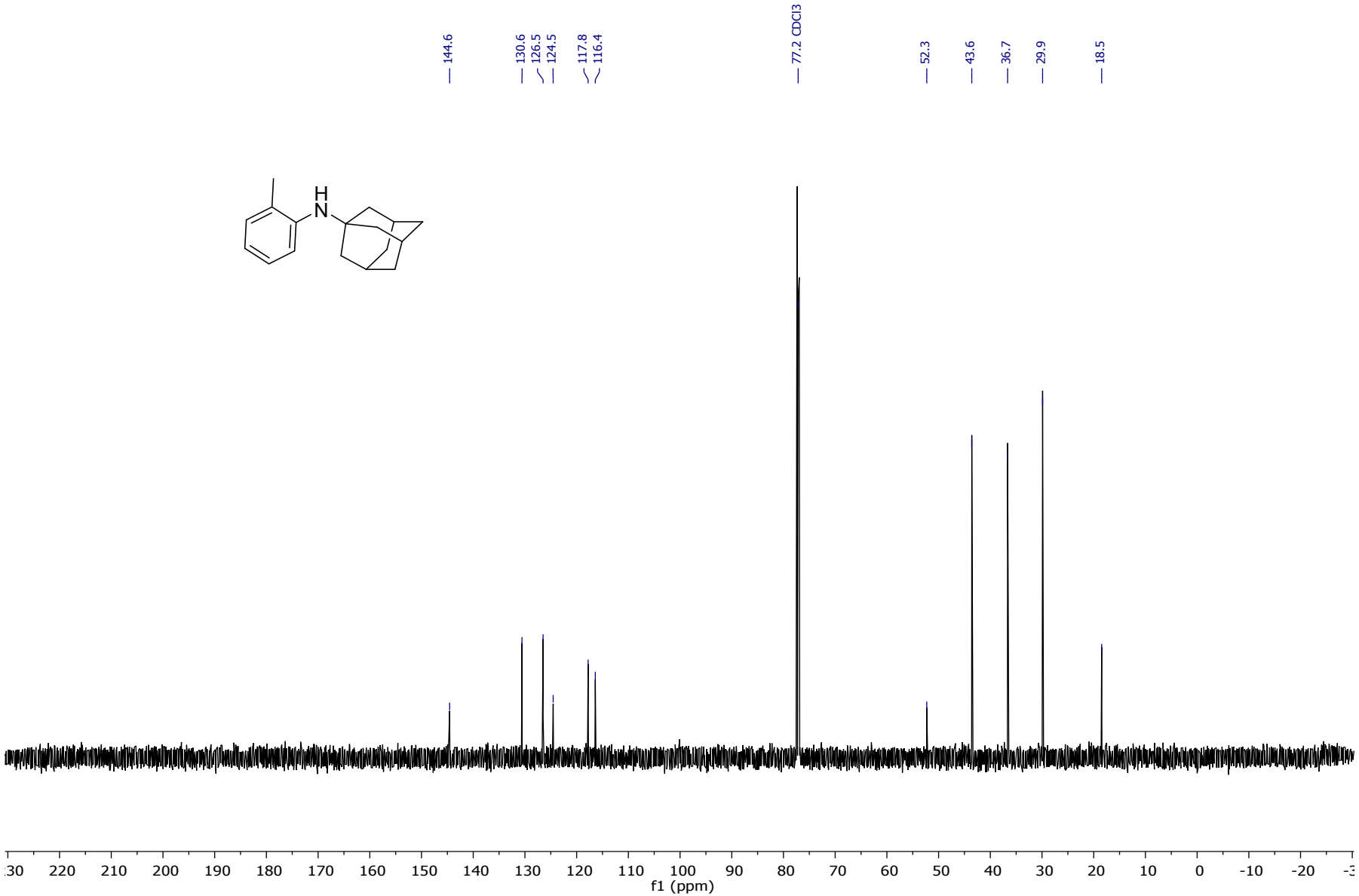

Figure S56. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of *N*-(*o*-Tolyl)adamantan-1-amine (4i)

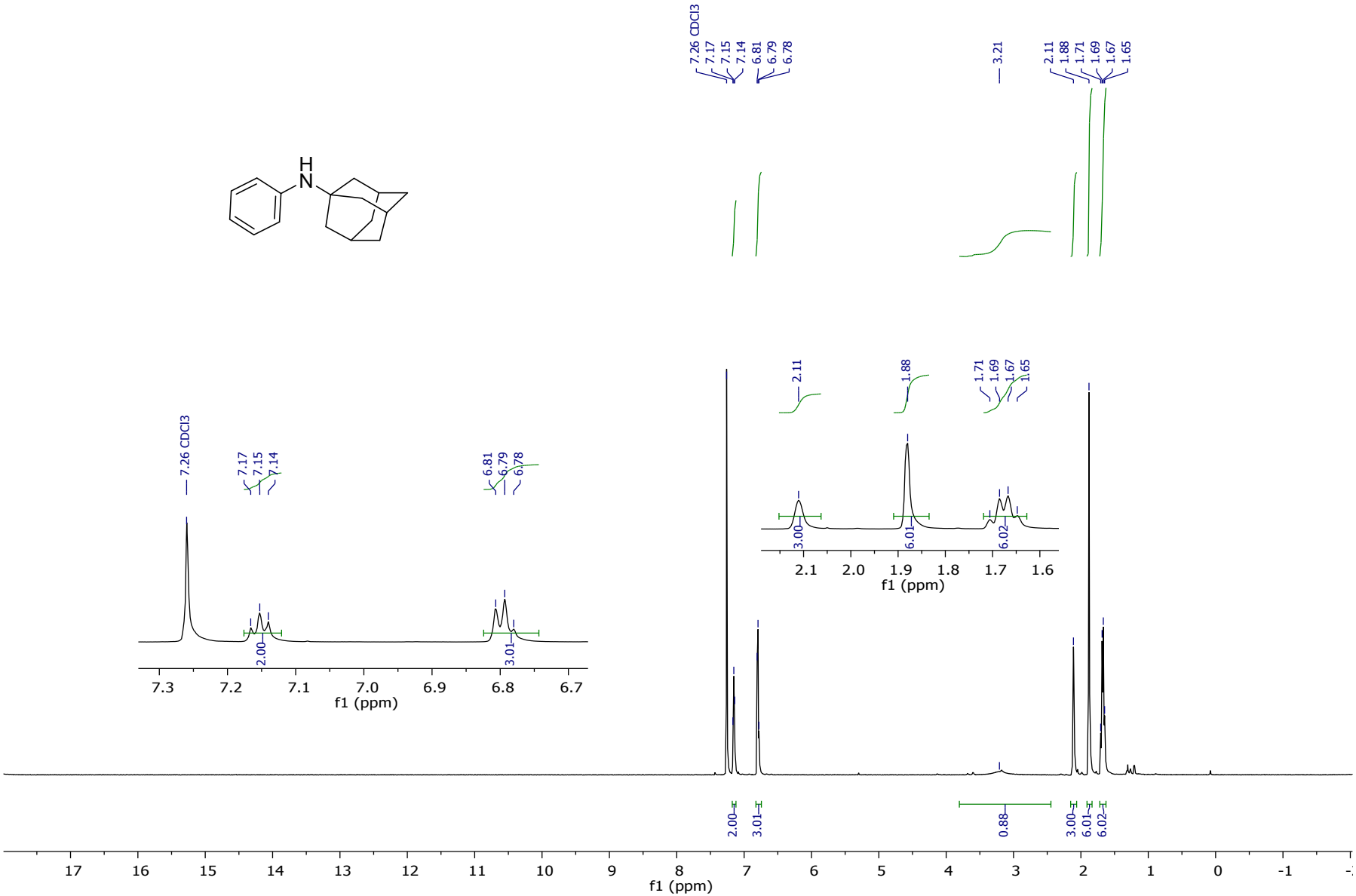

Figure S57. ^{1}H NMR (600 MHz, Chloroform-*d*) of *N*-(1-adamantyl)-*N*-phenylamine (4j)

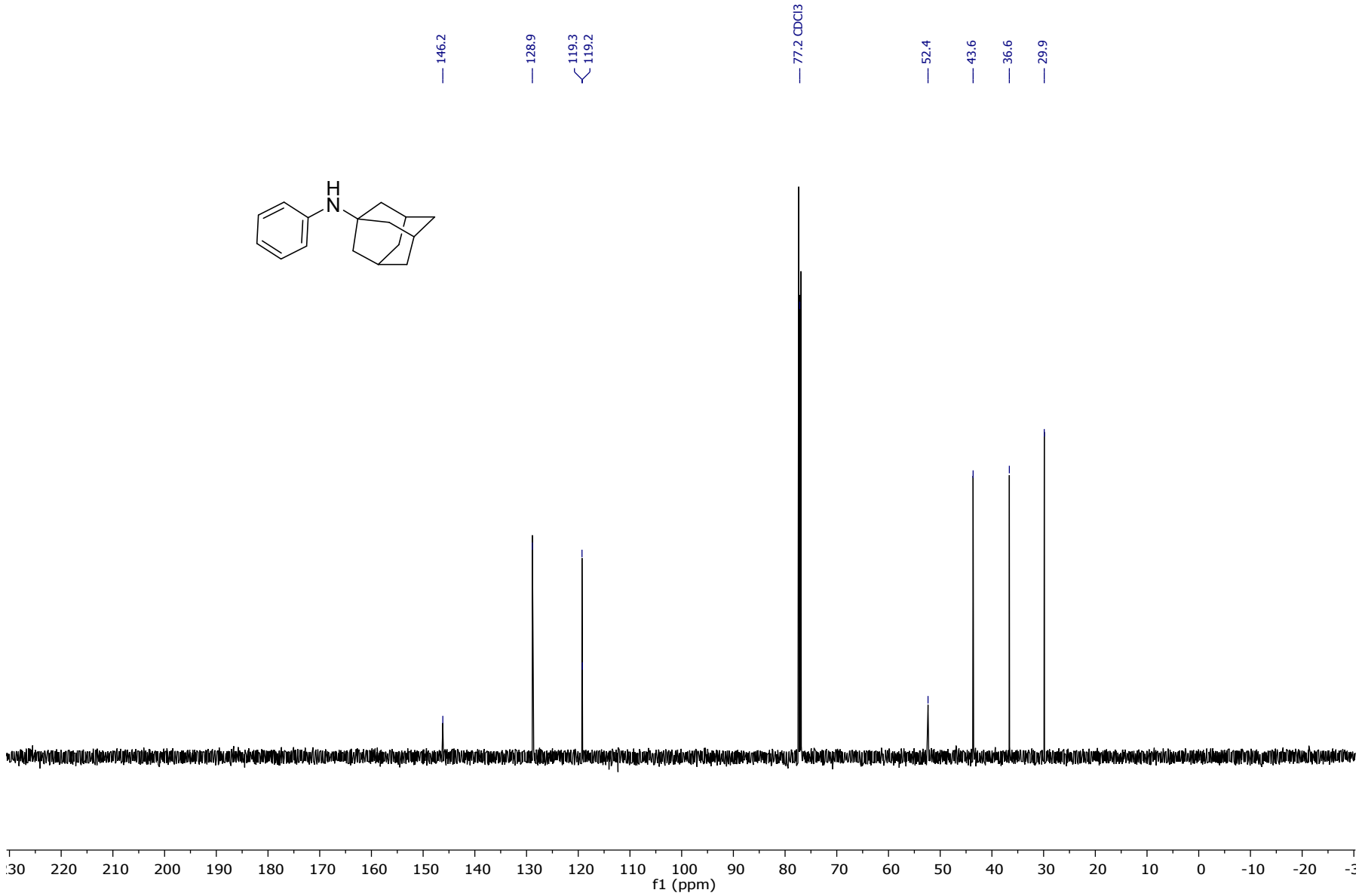

Figure S58. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of *N*-(1-adamantyl)-*N*-phenylamine (4j)

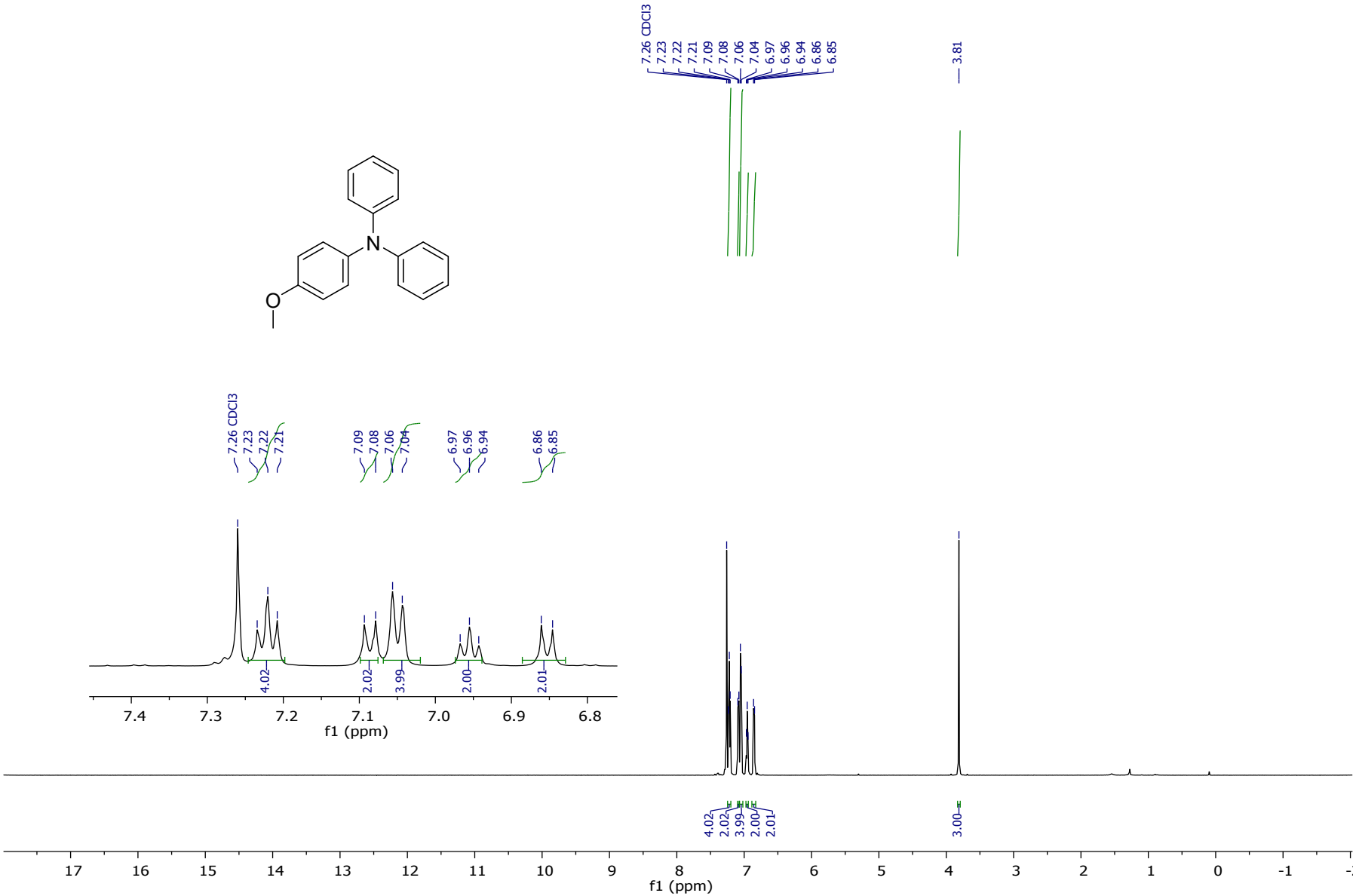

Figure S59. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-methoxy-*N*,*N*-diphenylaniline (5a)

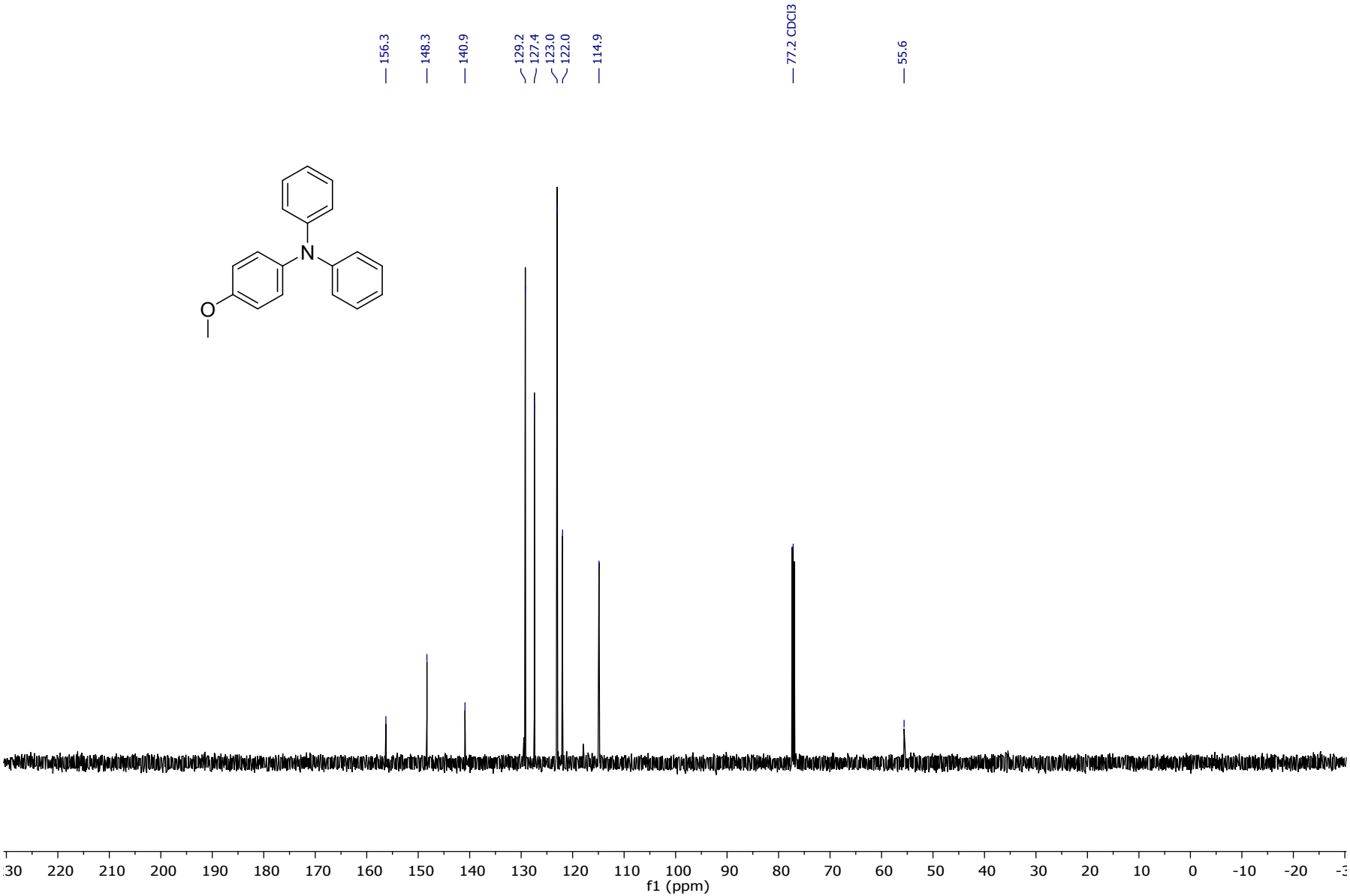

Figure S60. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4-methoxy-*N*,*N*-diphenylaniline (5a)

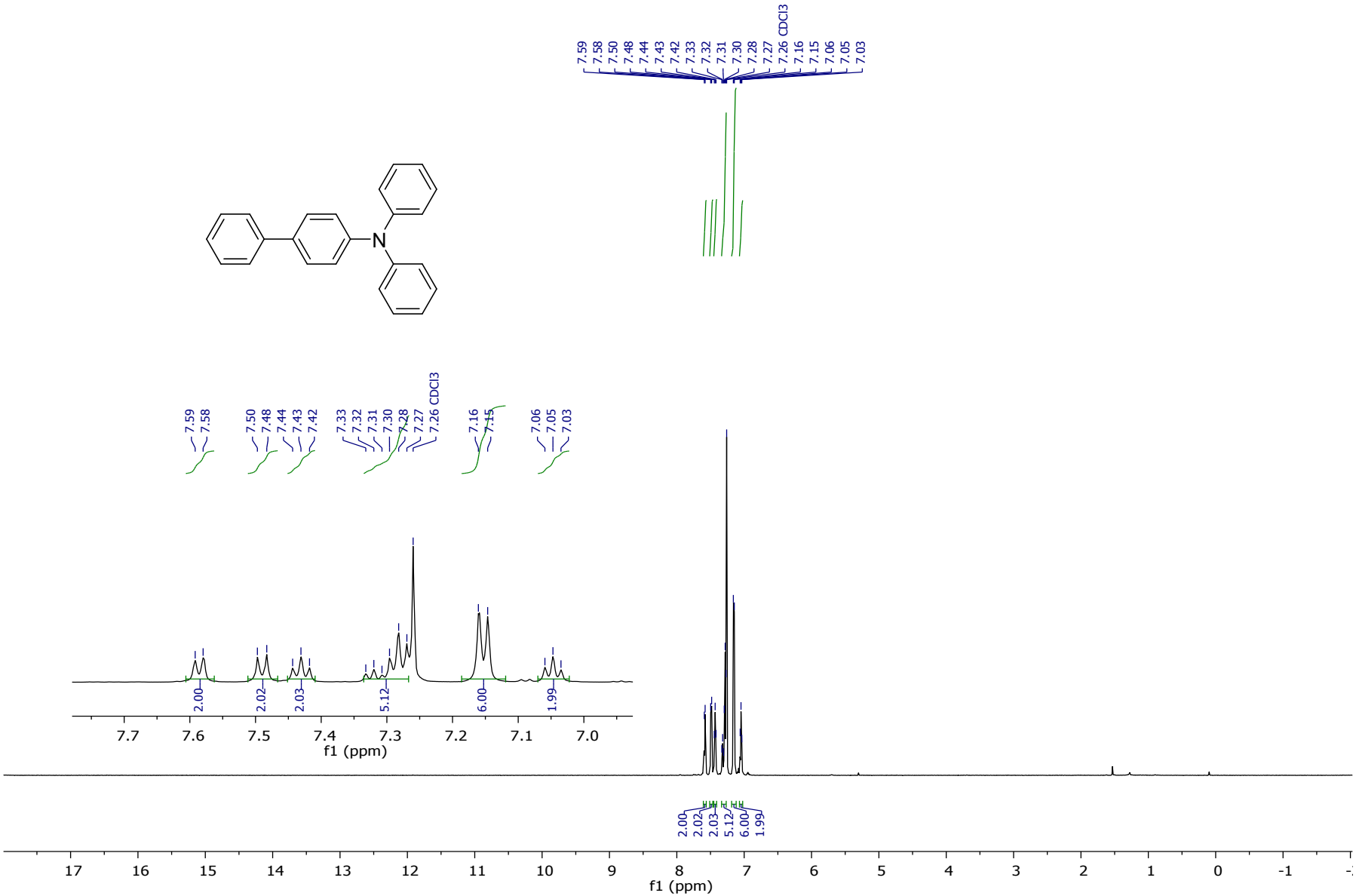

Figure S61. ^{1}H NMR (600 MHz, Chloroform-*d*) of N,N-diphenylbiphenyl-4-amine (5b)

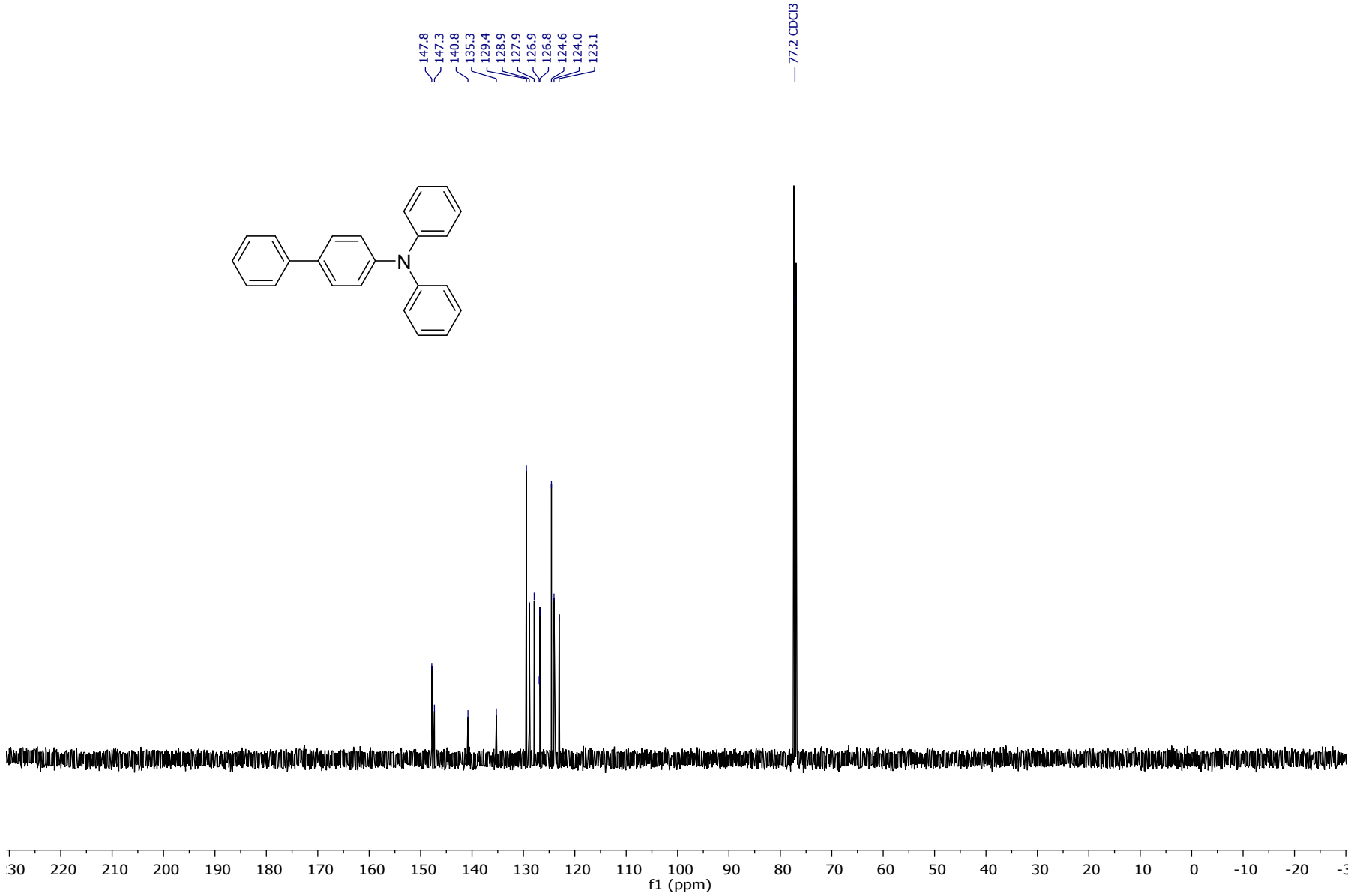

Figure S62. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N,N-diphenylbiphenyl-4-amine (5b)

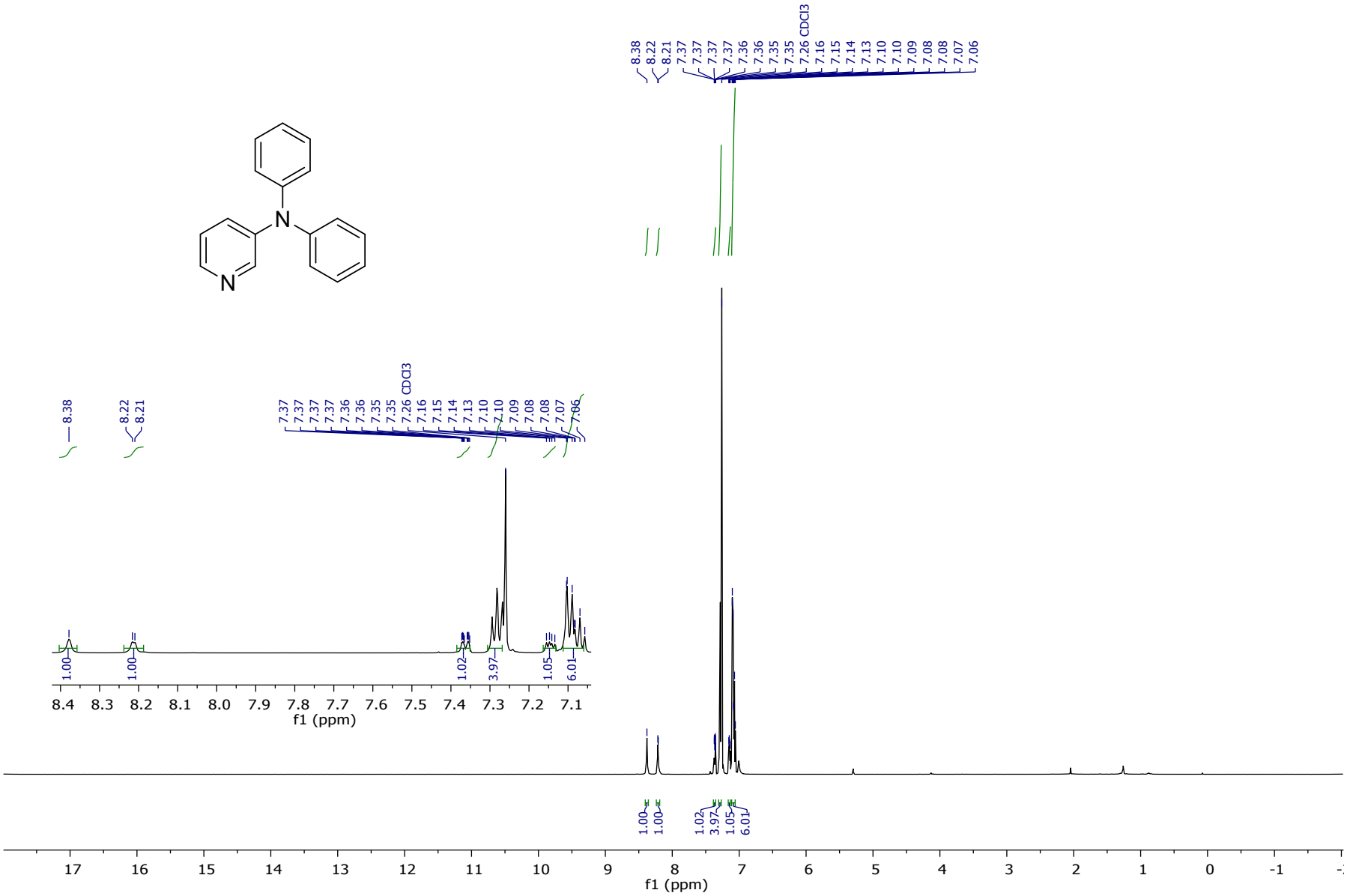

Figure S63. ^{1}H NMR (600 MHz, Chloroform-*d*) of N,N-diphenylpyridin-3-amine (5c)

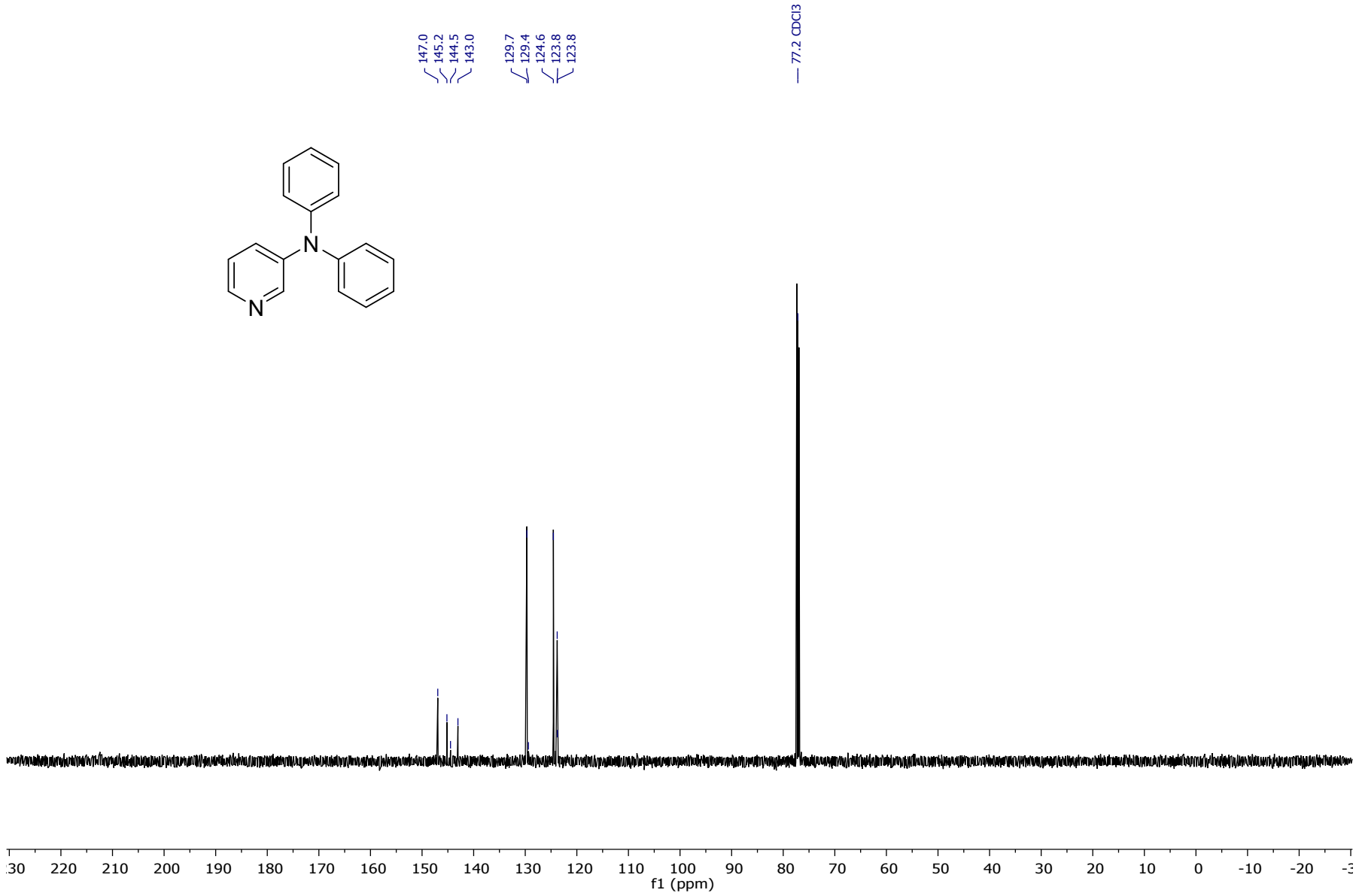

Figure S64. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N,N-diphenylpyridin-3-amine (5c)

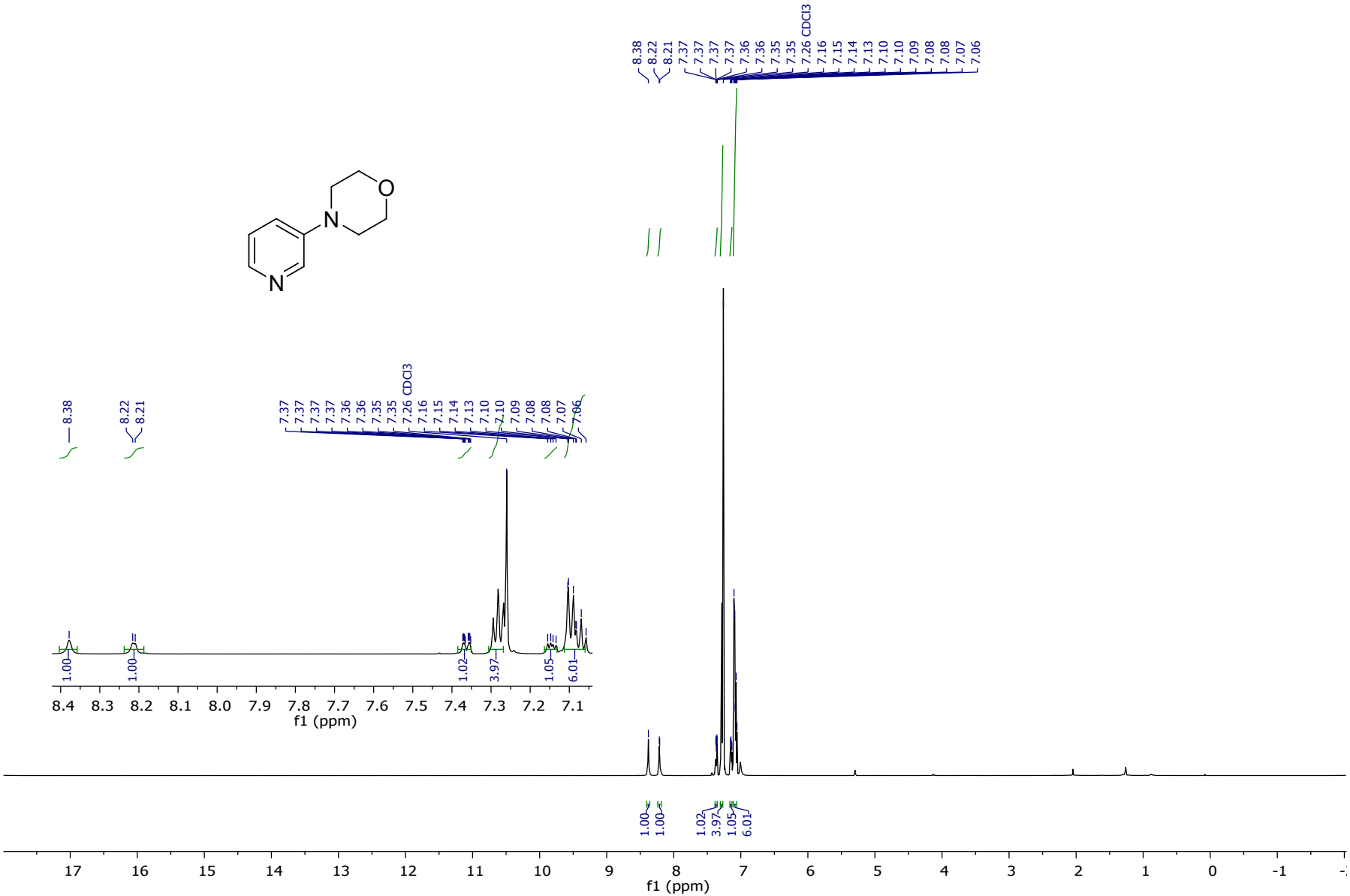

Figure S65. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-(pyridin-3-yl)morpholine (5d)

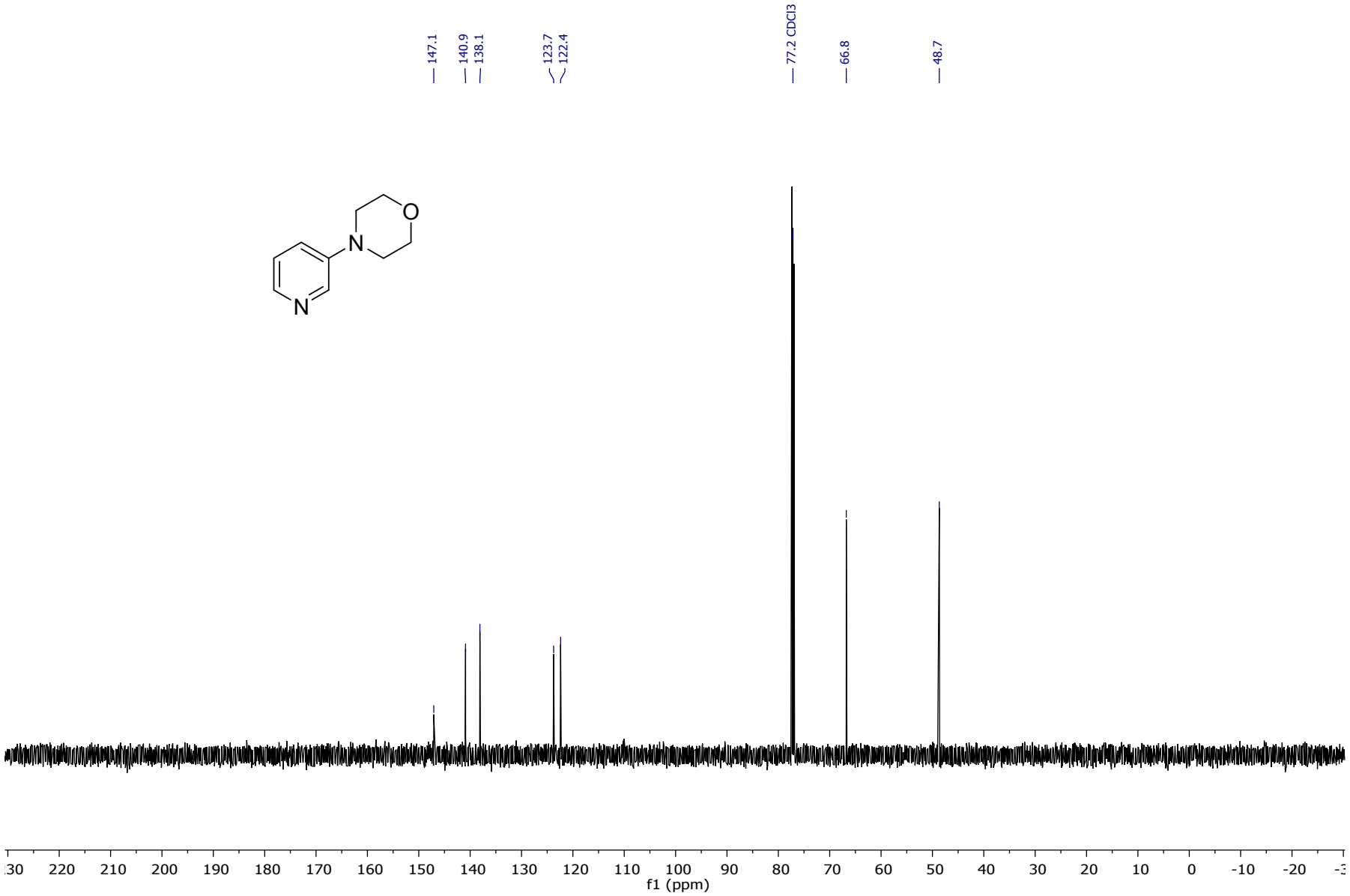

Figure S66. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4-(pyridin-3-yl)morpholine (5d)

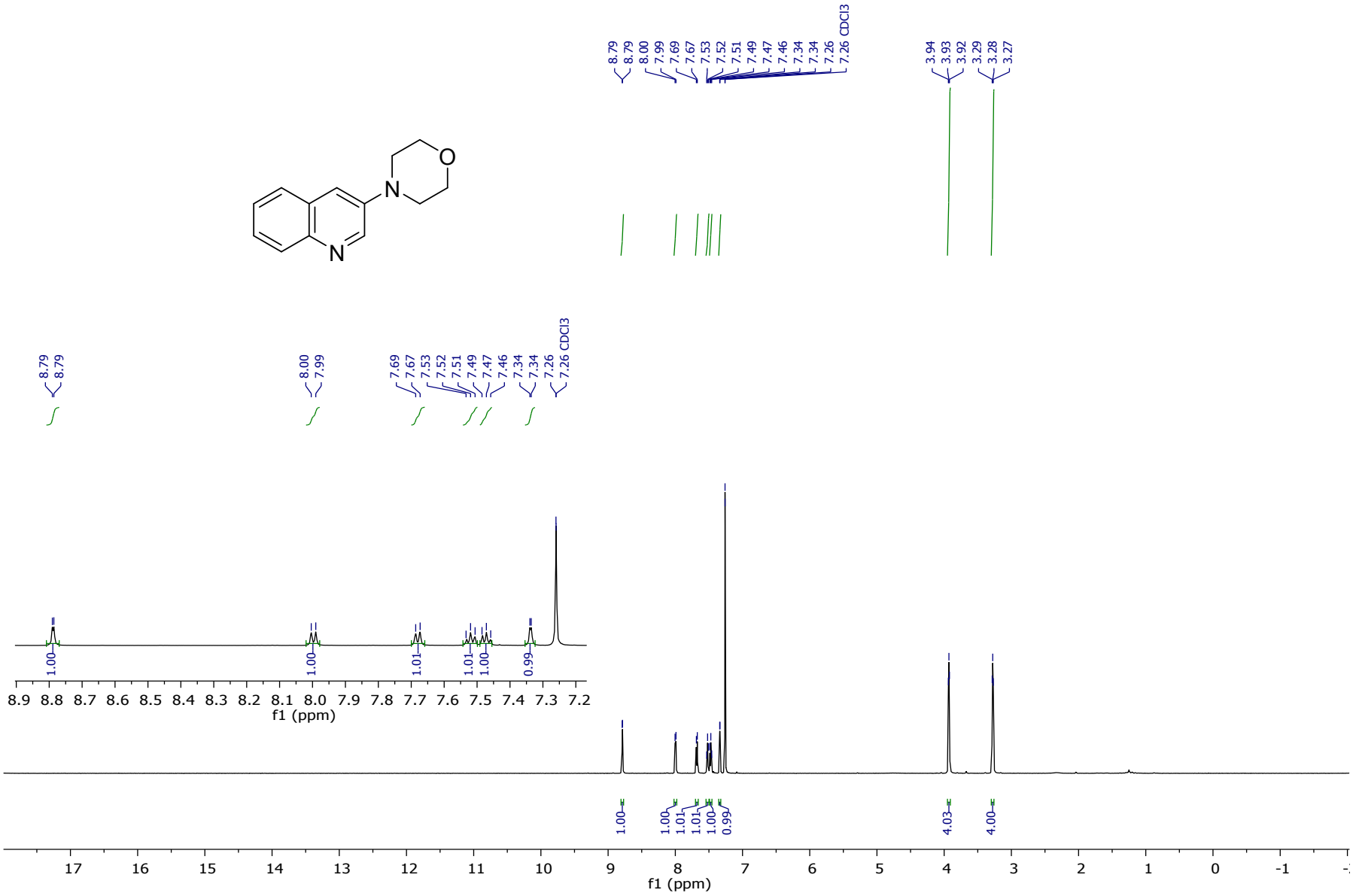

Figure S67. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-(quinolin-3-yl)morpholine (5e)

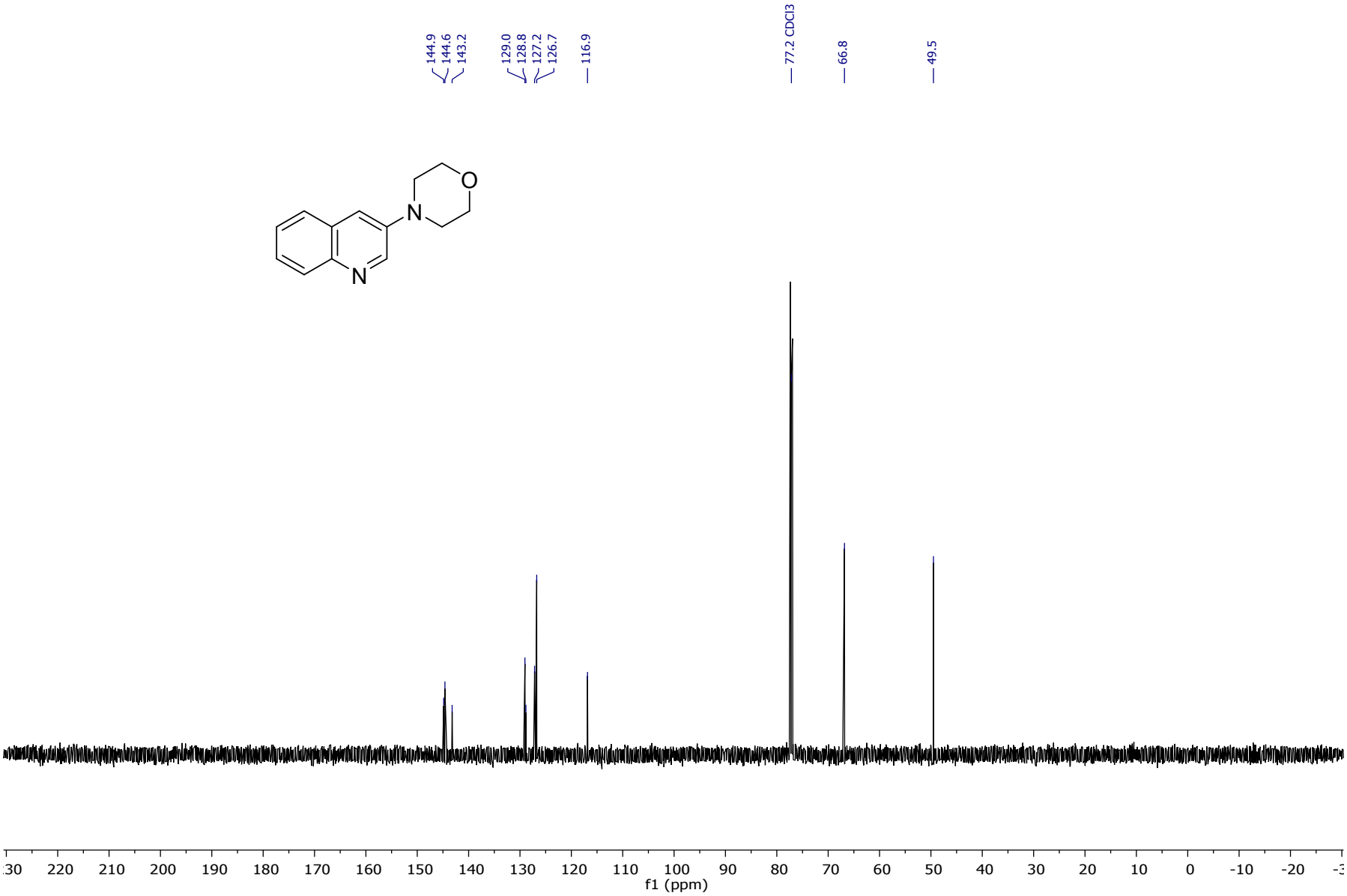

Figure S68. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4-(quinolin-3-yl)morpholine (5e)

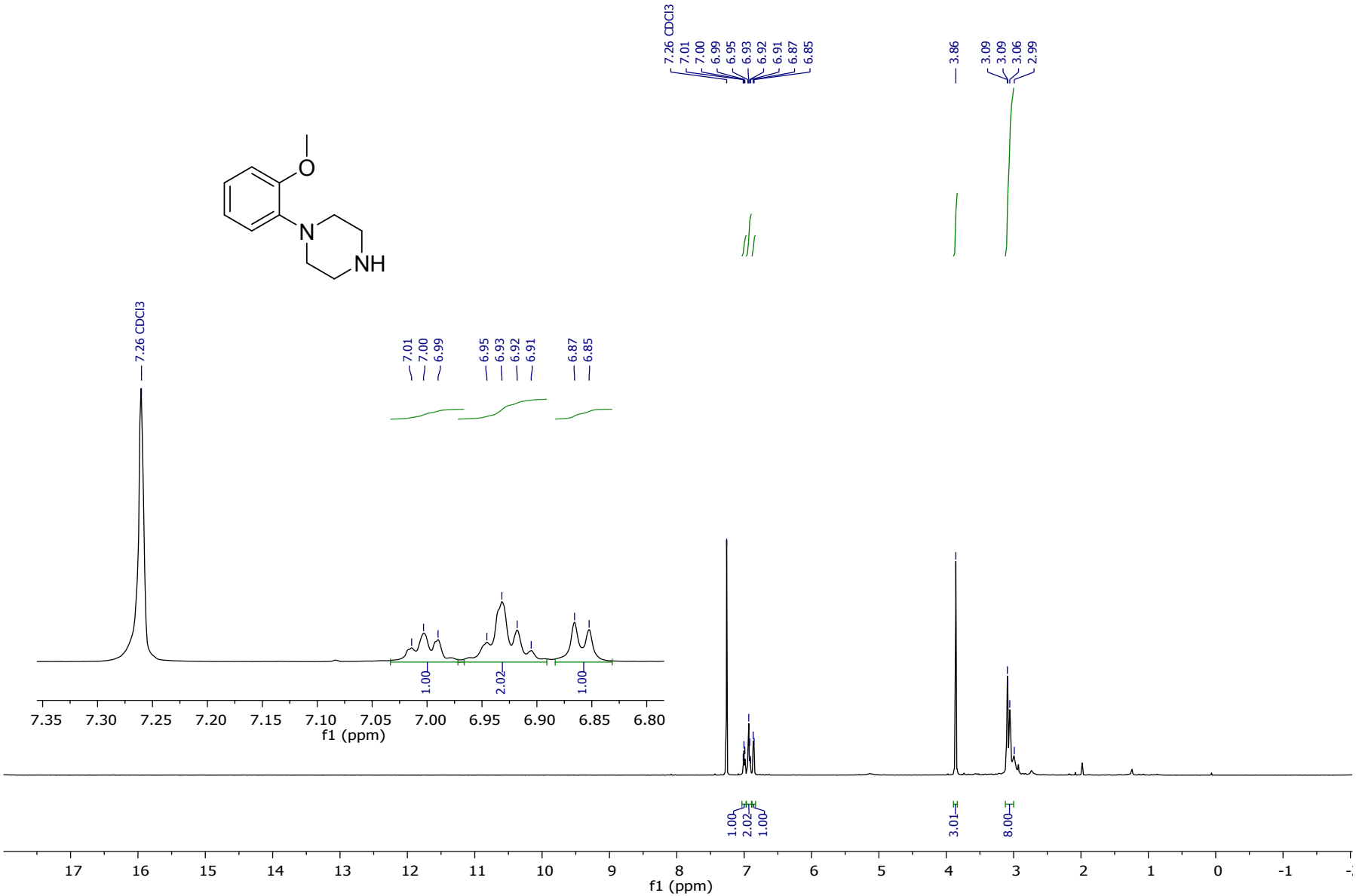

Figure S69. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(2-methoxyphenyl)piperazine (5f)

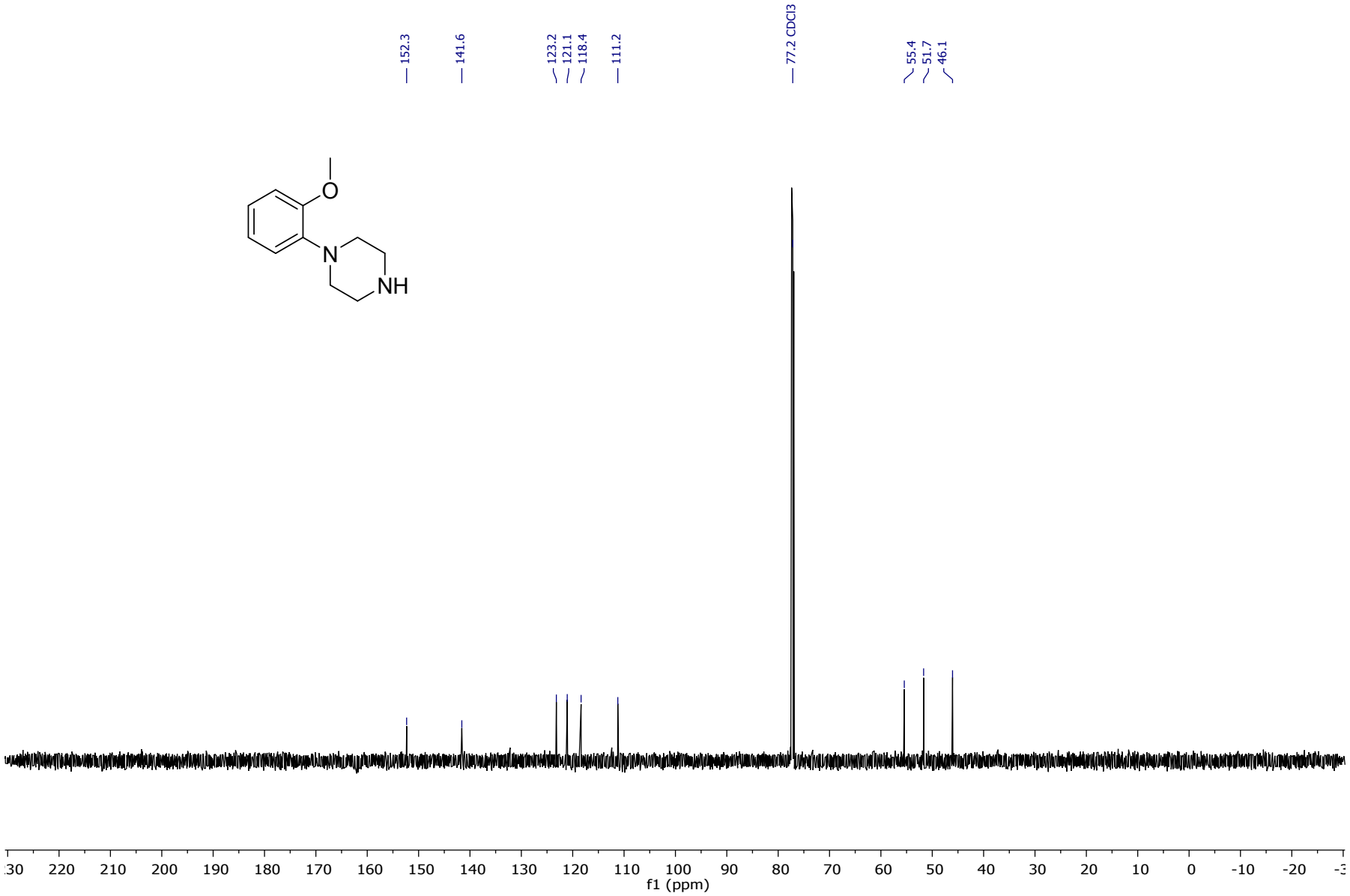

Figure S70. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(2-methoxyphenyl)piperazine (5f)

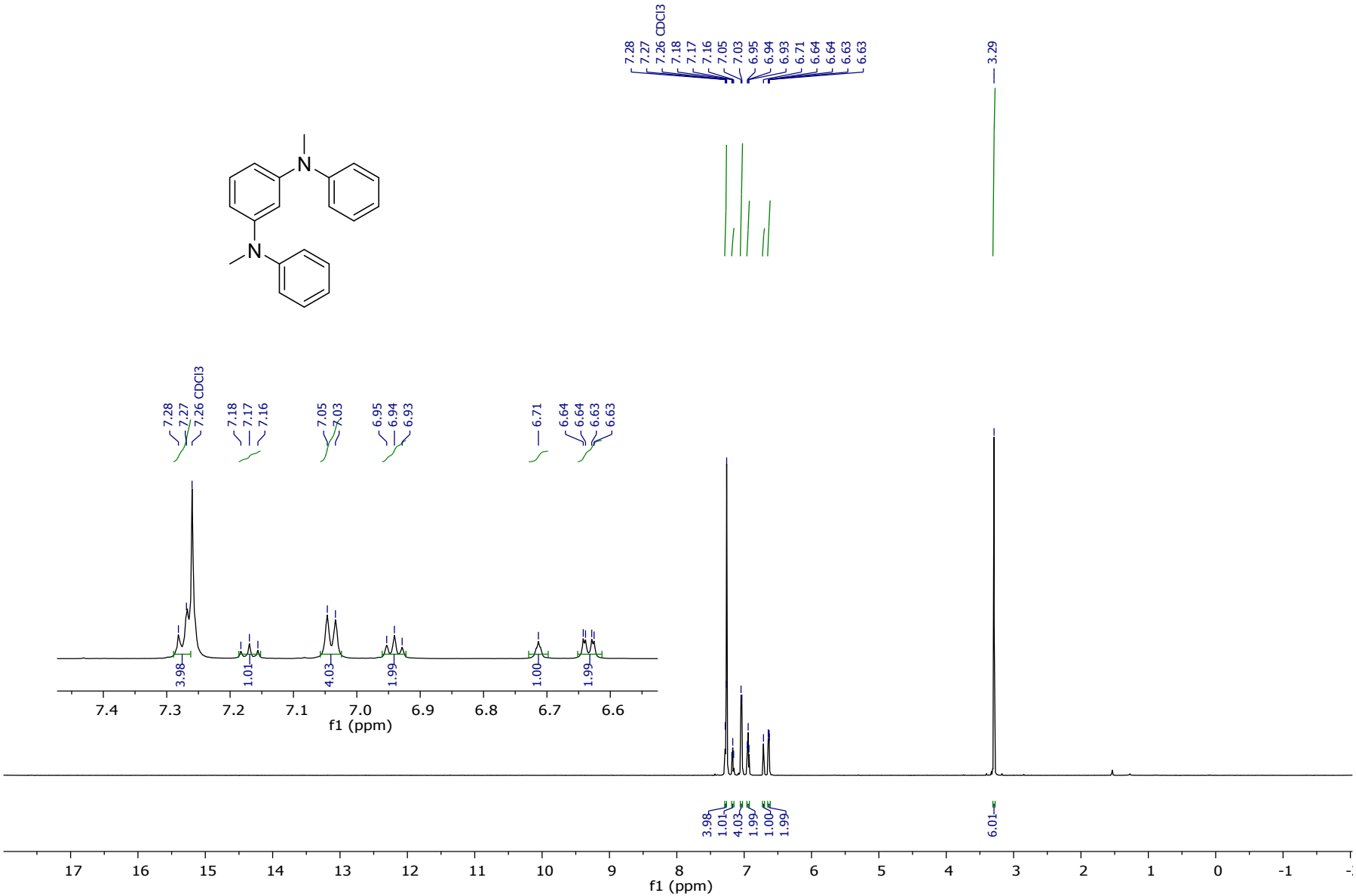

Figure S71. ^{1}H NMR (600 MHz, Chloroform-*d*) of N^{1},N^{3}-dimethyl-N^{1},N^{3}-diphenylbenzene-1,3-diamine (5g)

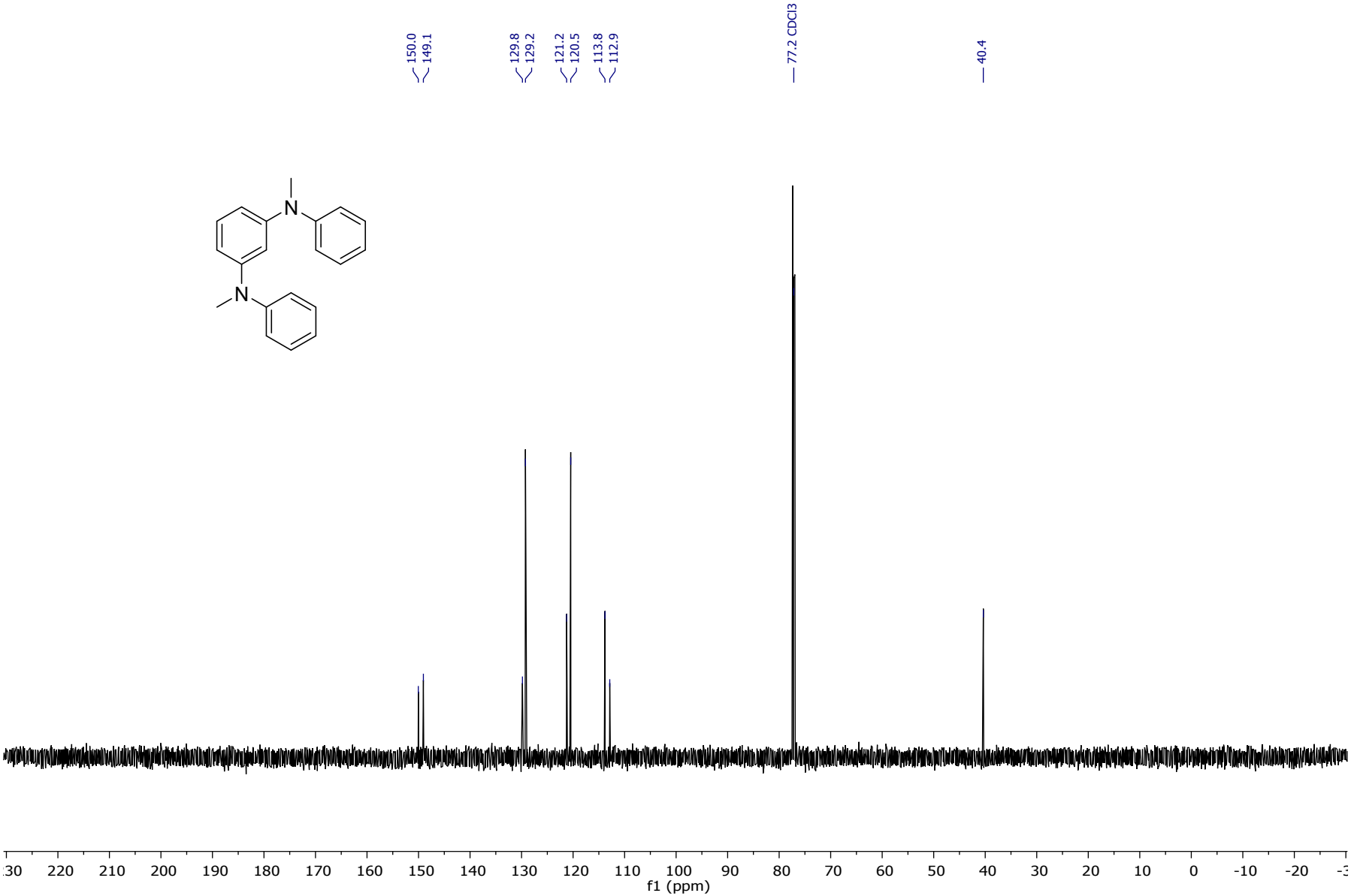

Figure S72. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N^1,N^3-dimethyl-N^1,N^3-diphenylbenzene-1,3-diamine (5g)

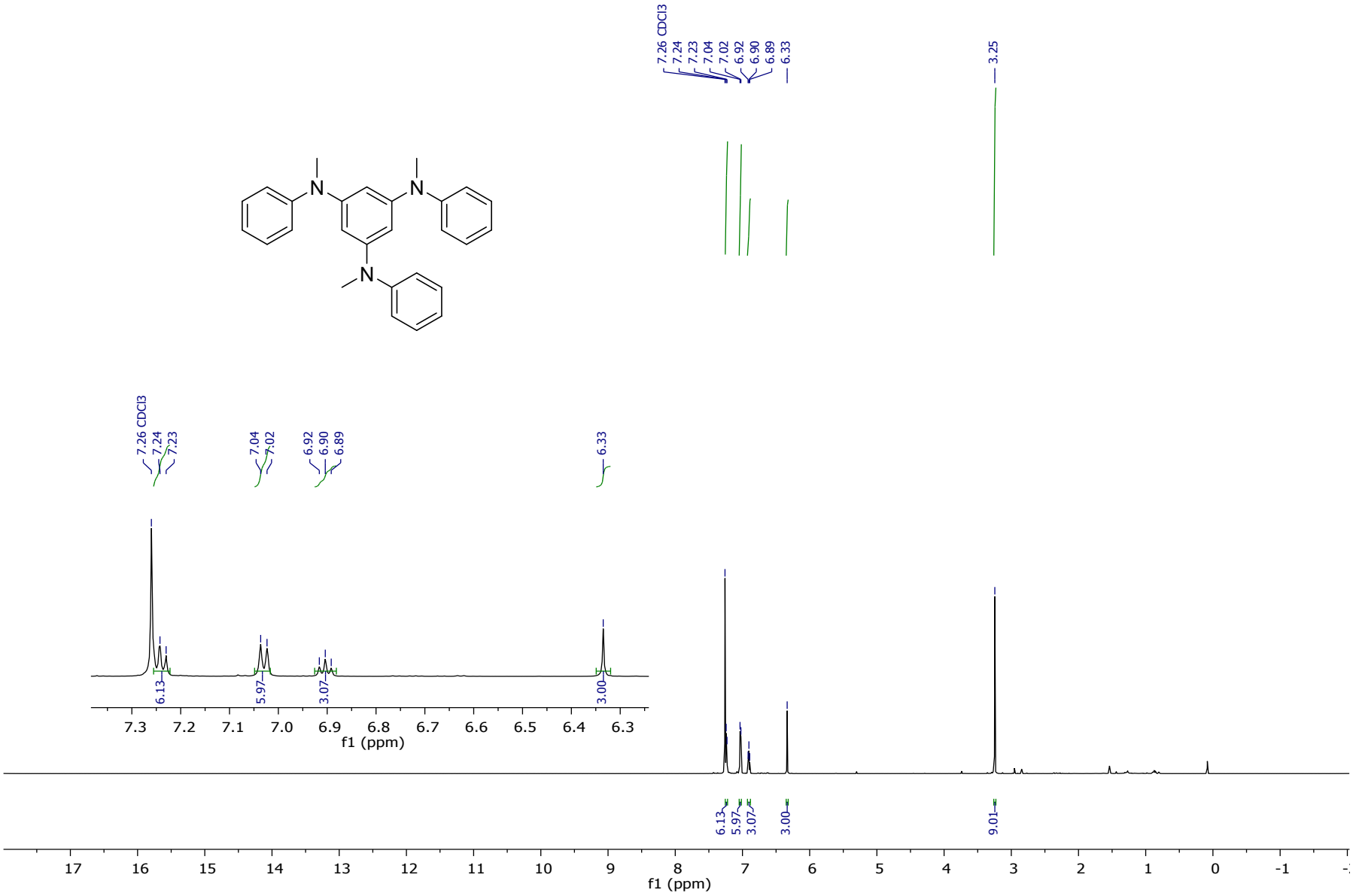

Figure S73. ^{1}H NMR (600 MHz, Chloroform-*d*) of N^{1},N^{3},N^{5}-trimethyl-N^{1},N^{3},N^{5}-triphenylbenzene-1,3,5-triamine (5h)

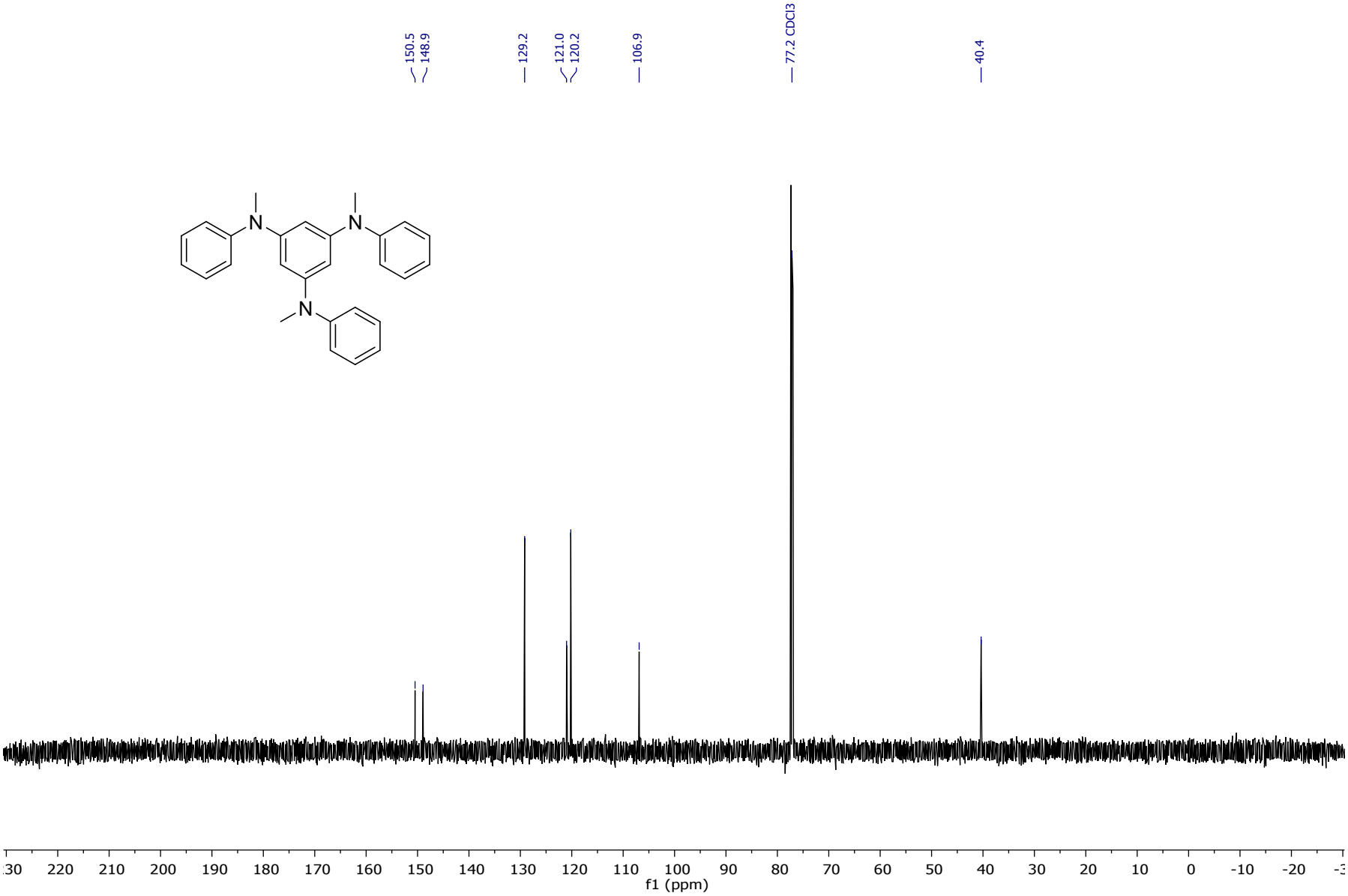

Figure S74. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N^1,N^3,N^5-trimethyl-N^1,N^3,N^5-triphenylbenzene-1,3,5-triamine (5h)

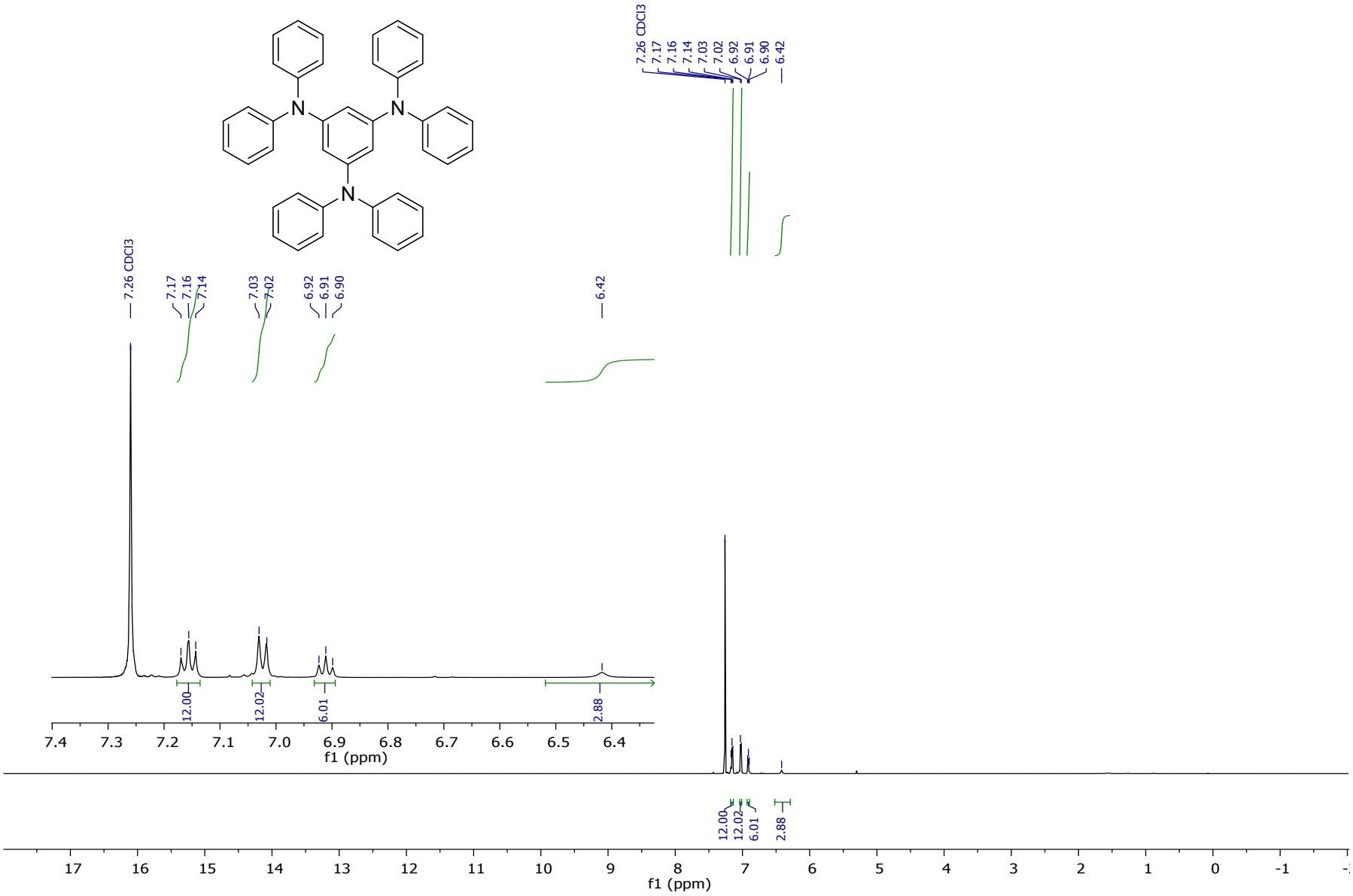

Figure S75. ^{1}H NMR (600 MHz, Chloroform-*d*) of N^{1},N^{1},N^{3},N^{3},N^{5},N^{5}-hexaphenylbenzene-1,3,5-triamine (5i)

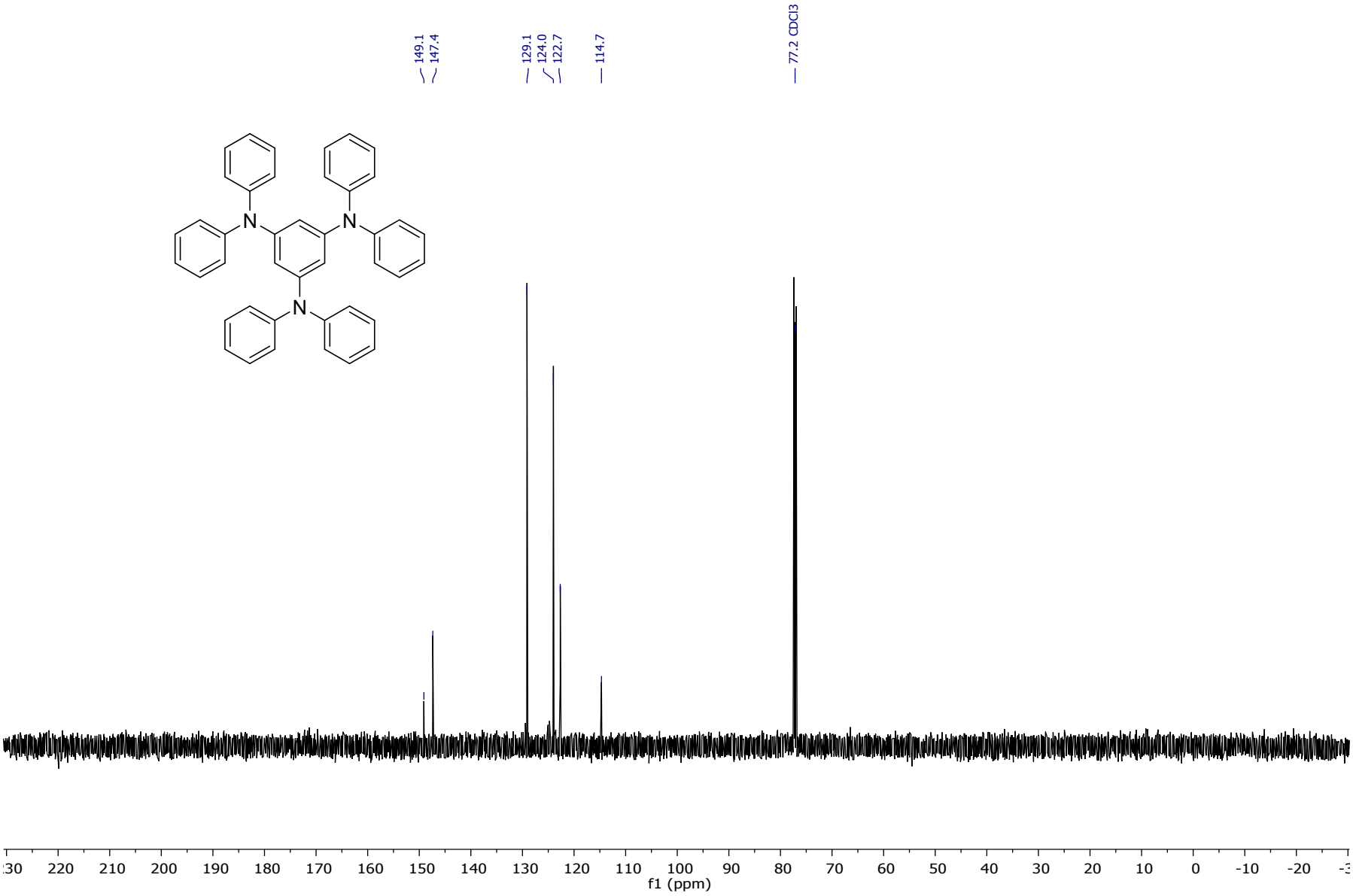

Figure S76. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of N^1,N^1,N^3,N^3,N^5,N^5-hexaphenylbenzene-1,3,5-triamine (5i)

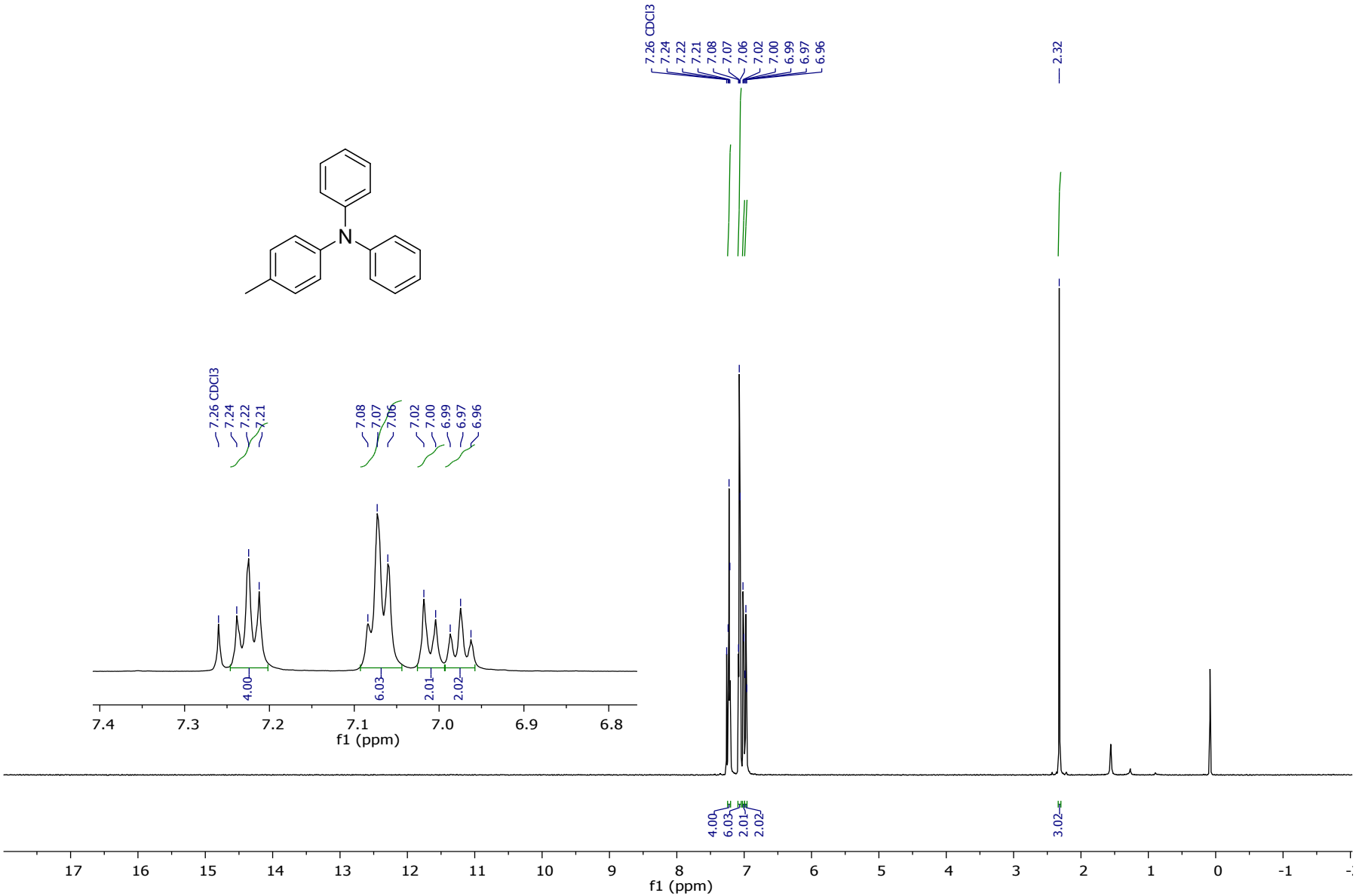

Figure S77. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-methyl-N,N-diphenylaniline (6a)

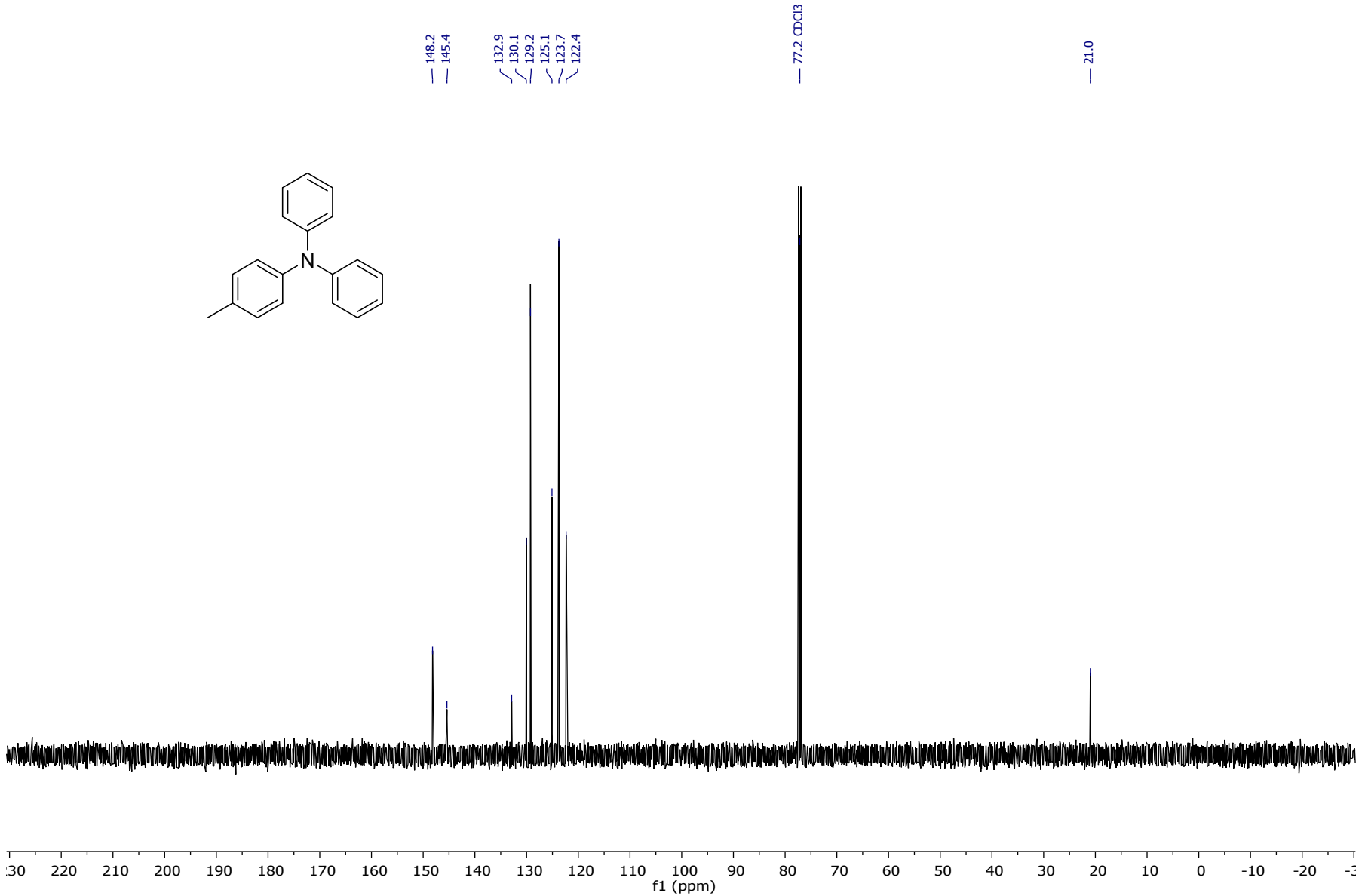

Figure S78. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4-methyl-N,N-diphenylaniline (6a)

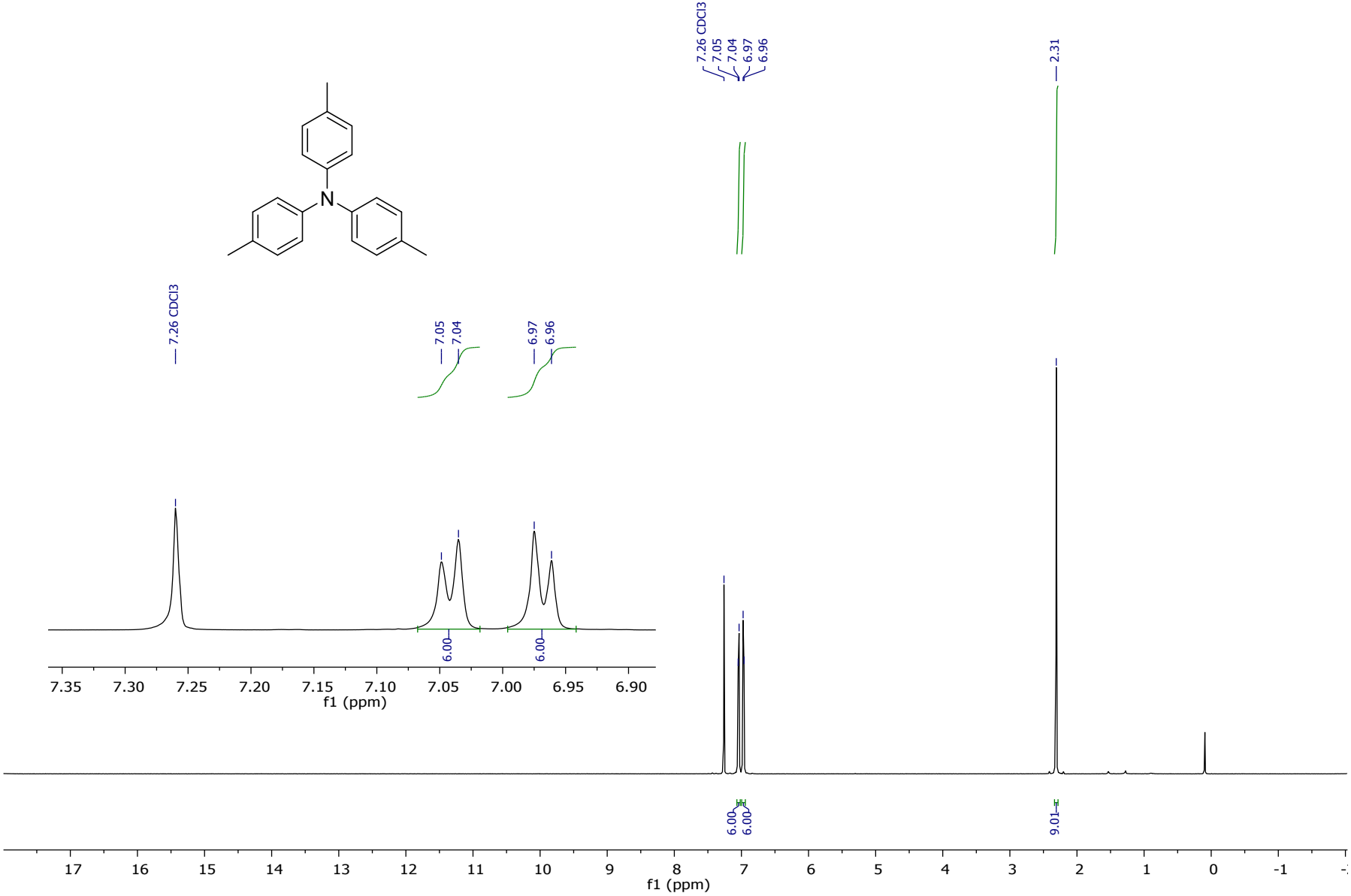

Figure S79. ^{1}H NMR (600 MHz, Chloroform-*d*) of tri*p*-tolylamine (6b)

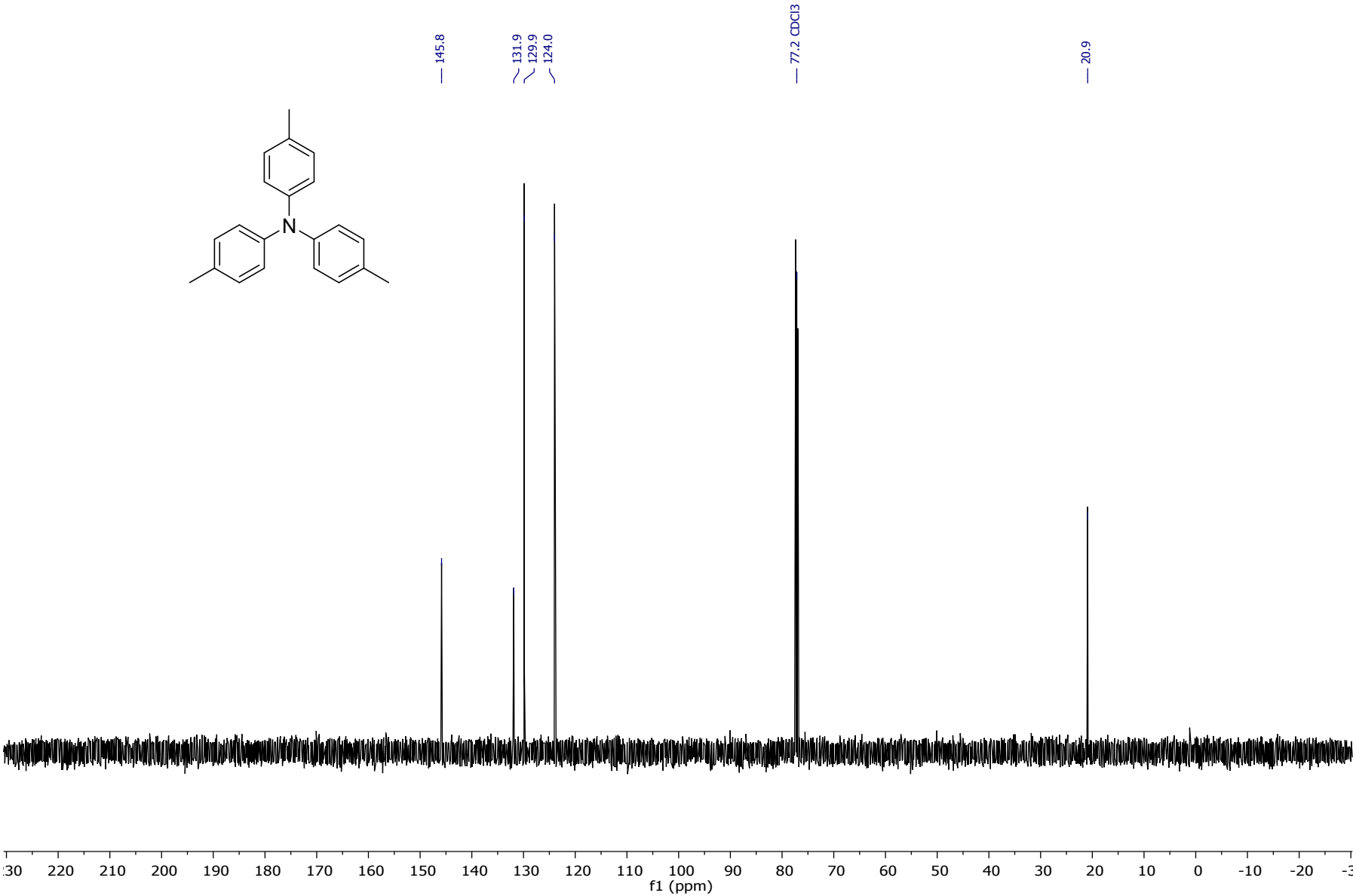

Figure S80. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of tri*p*-tolylamine (6b)

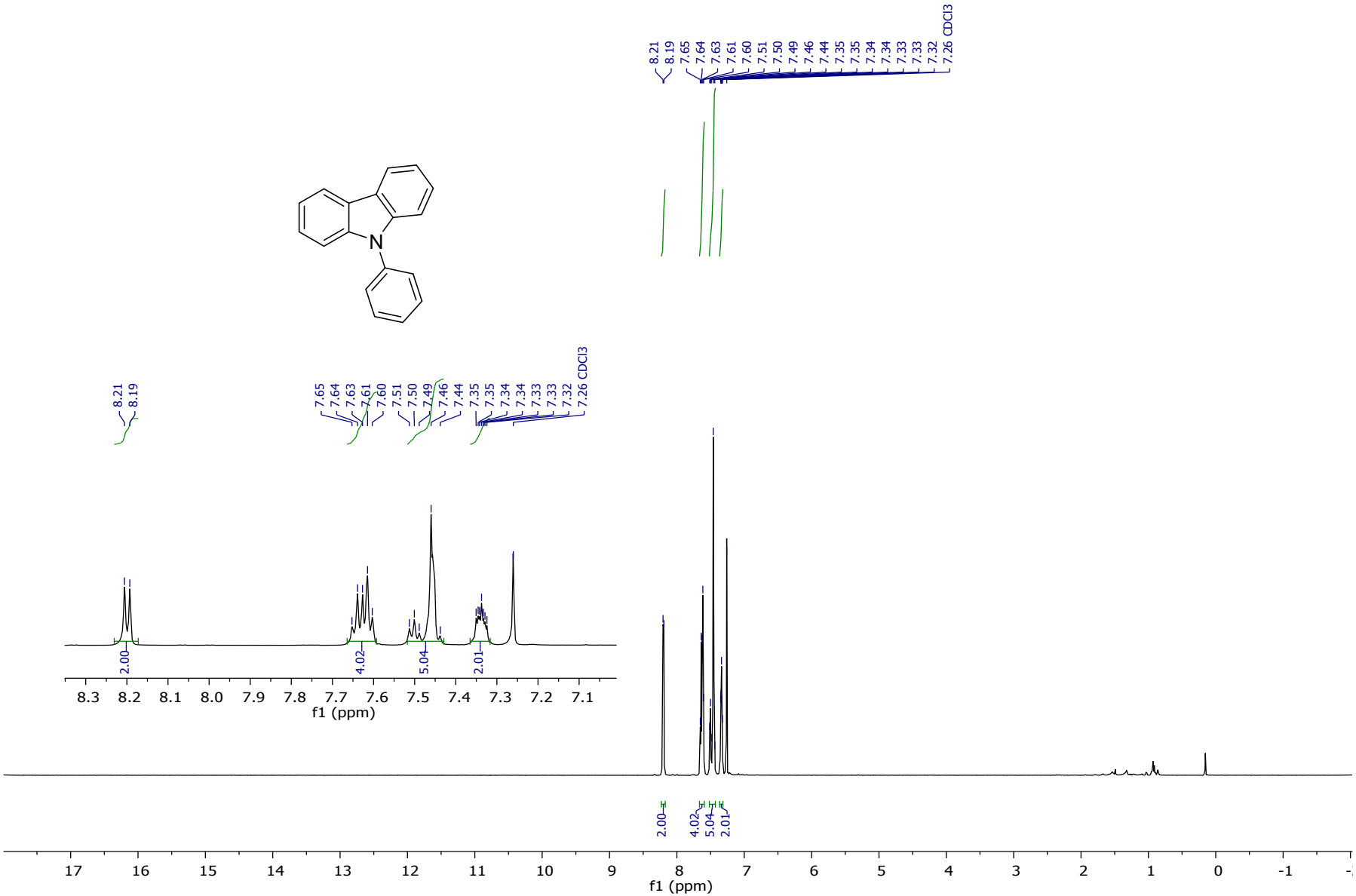

Figure S81. ^{1}H NMR (600 MHz, Chloroform-*d*) of 9-phenyl-9*H*-carbazole (6c)

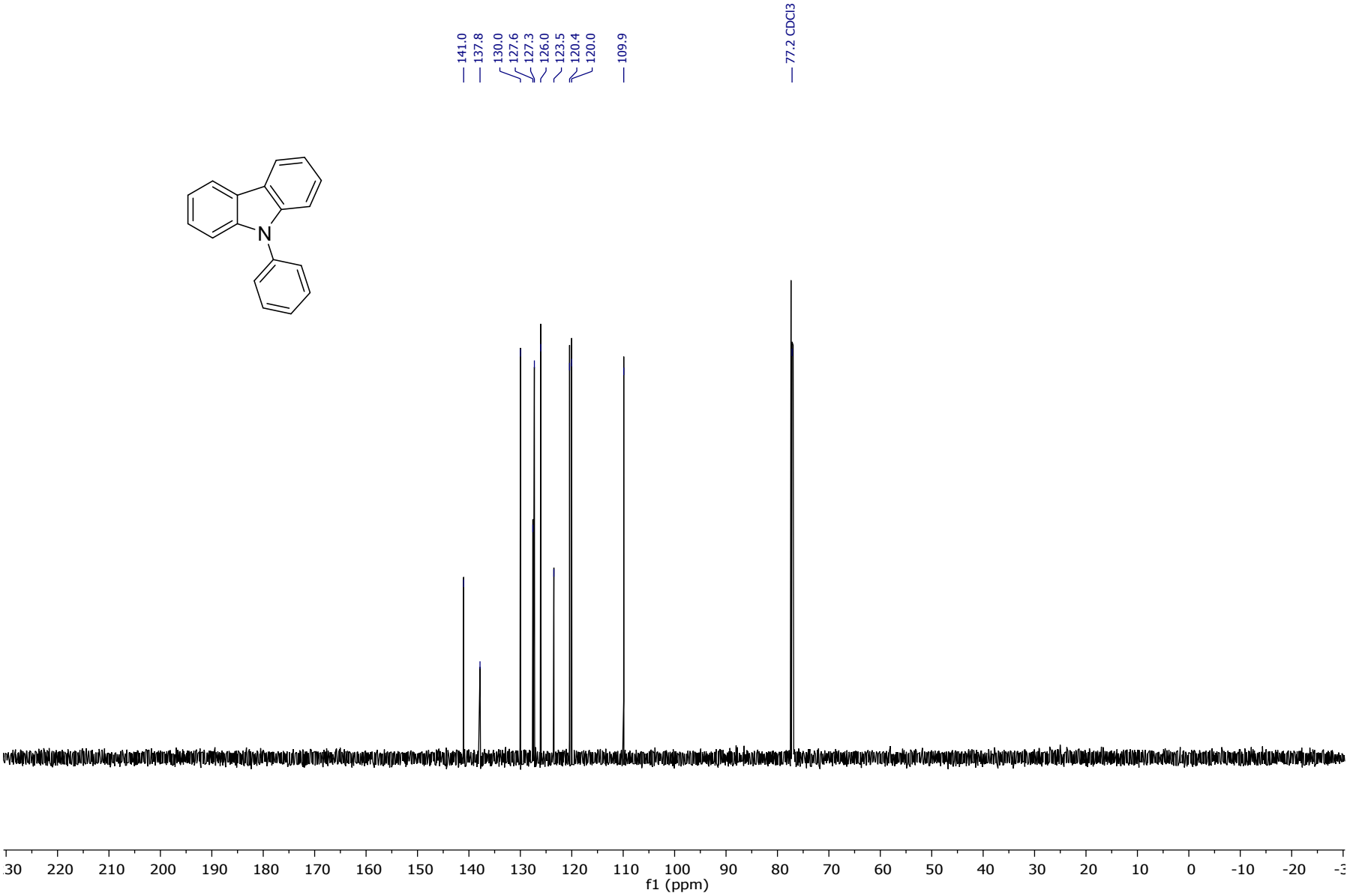

Figure S82. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 9-phenyl-9*H*-carbazole (6c)

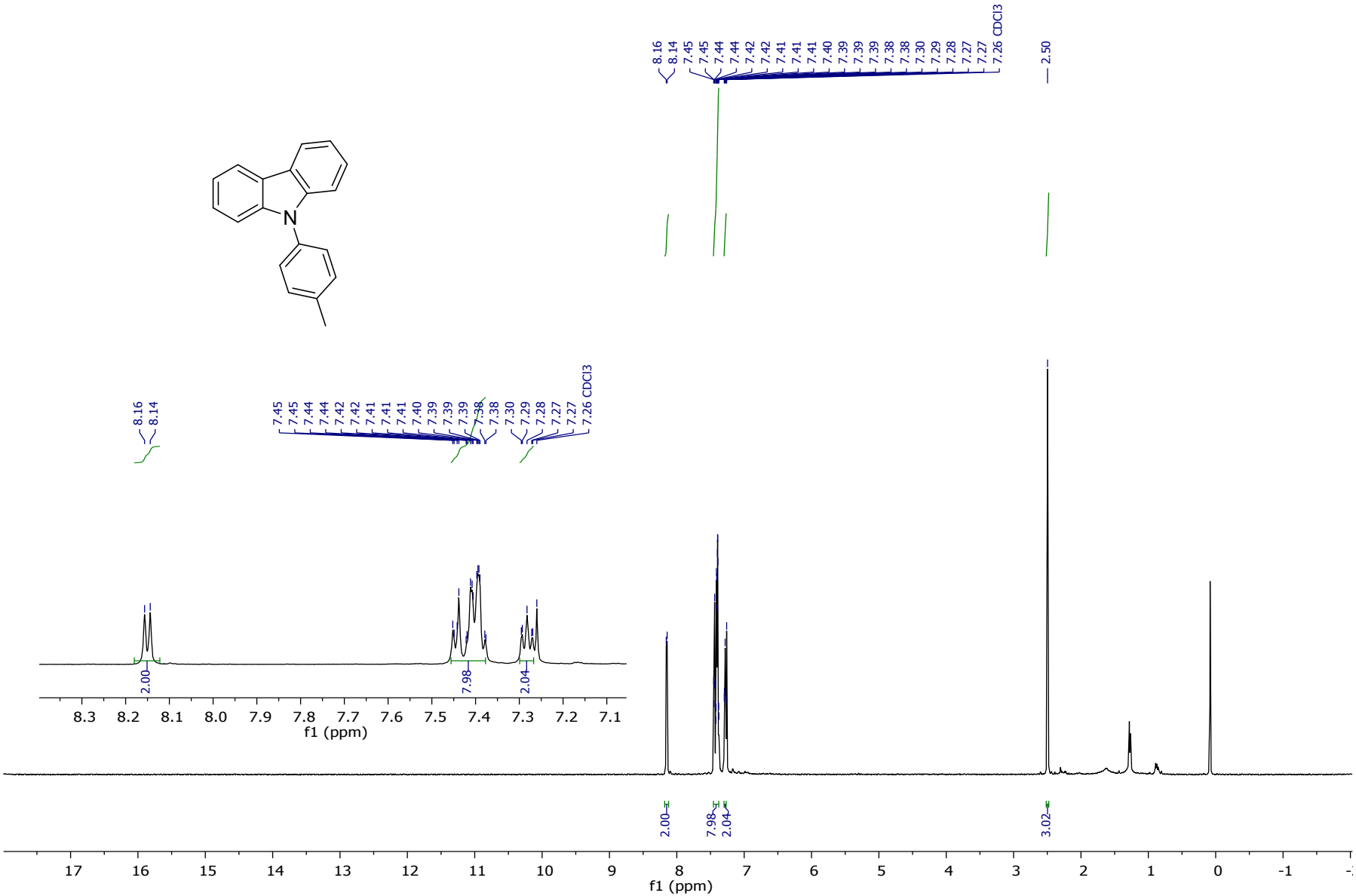

Figure S83. ^{1}H NMR (600 MHz, Chloroform-*d*) of 9-*p*-tolyl-9*H*-carbazole (6d)

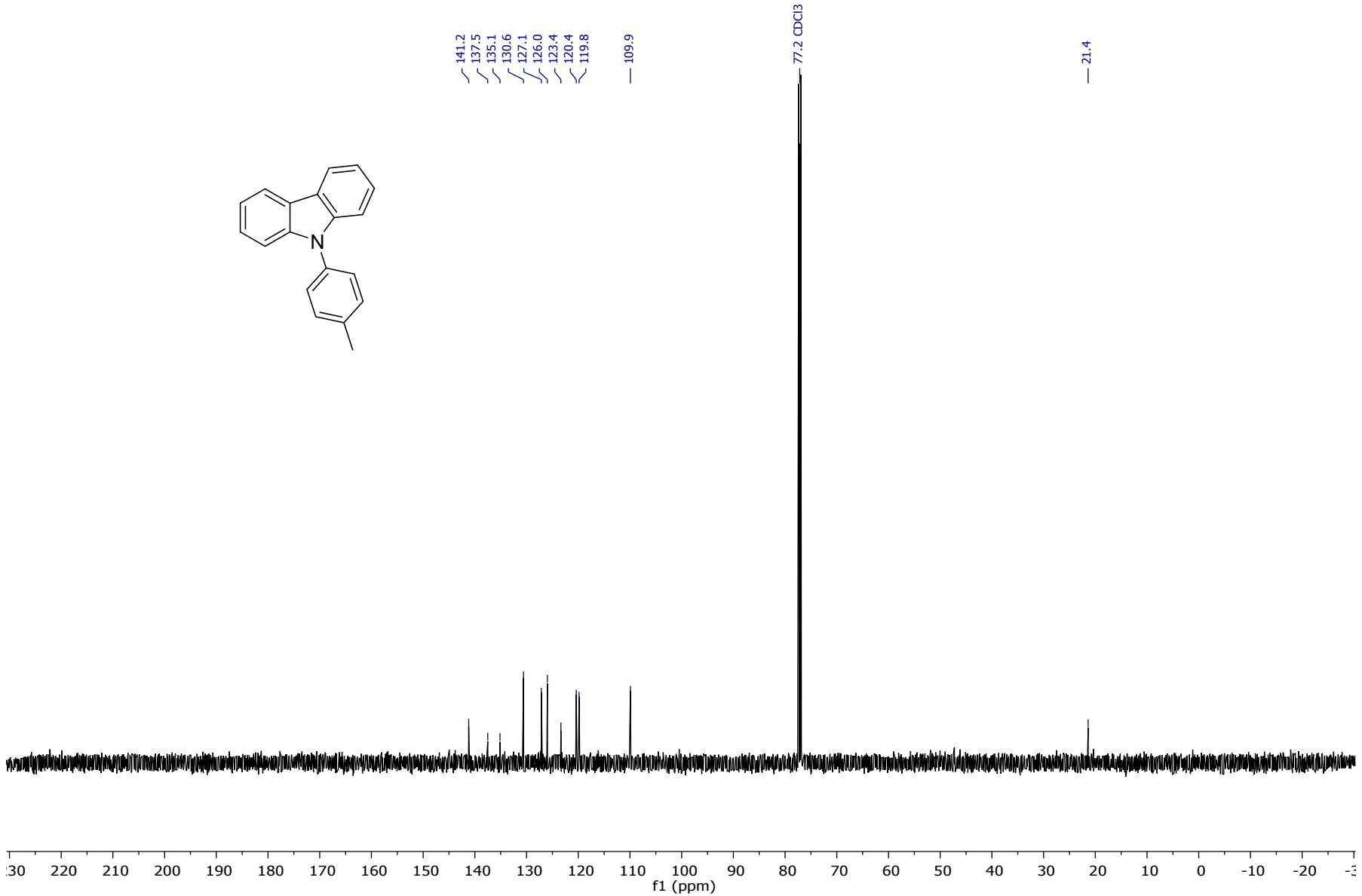

Figure S84. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 9-*p*-tolyl-9*H*-carbazole (6d)

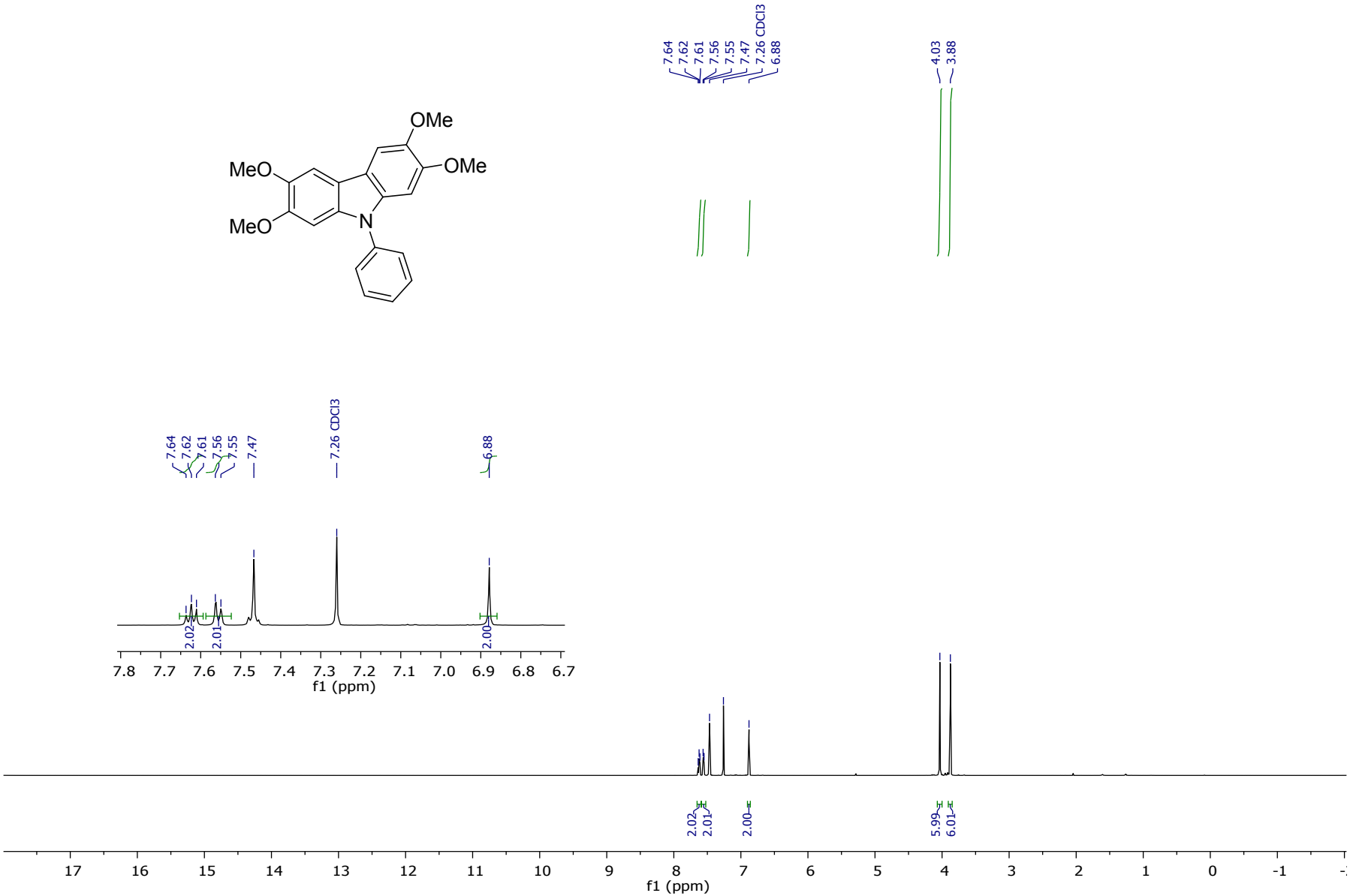

Figure S85. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,3,6,7-tetramethoxy-9-phenyl-9H-carbazole (6e)

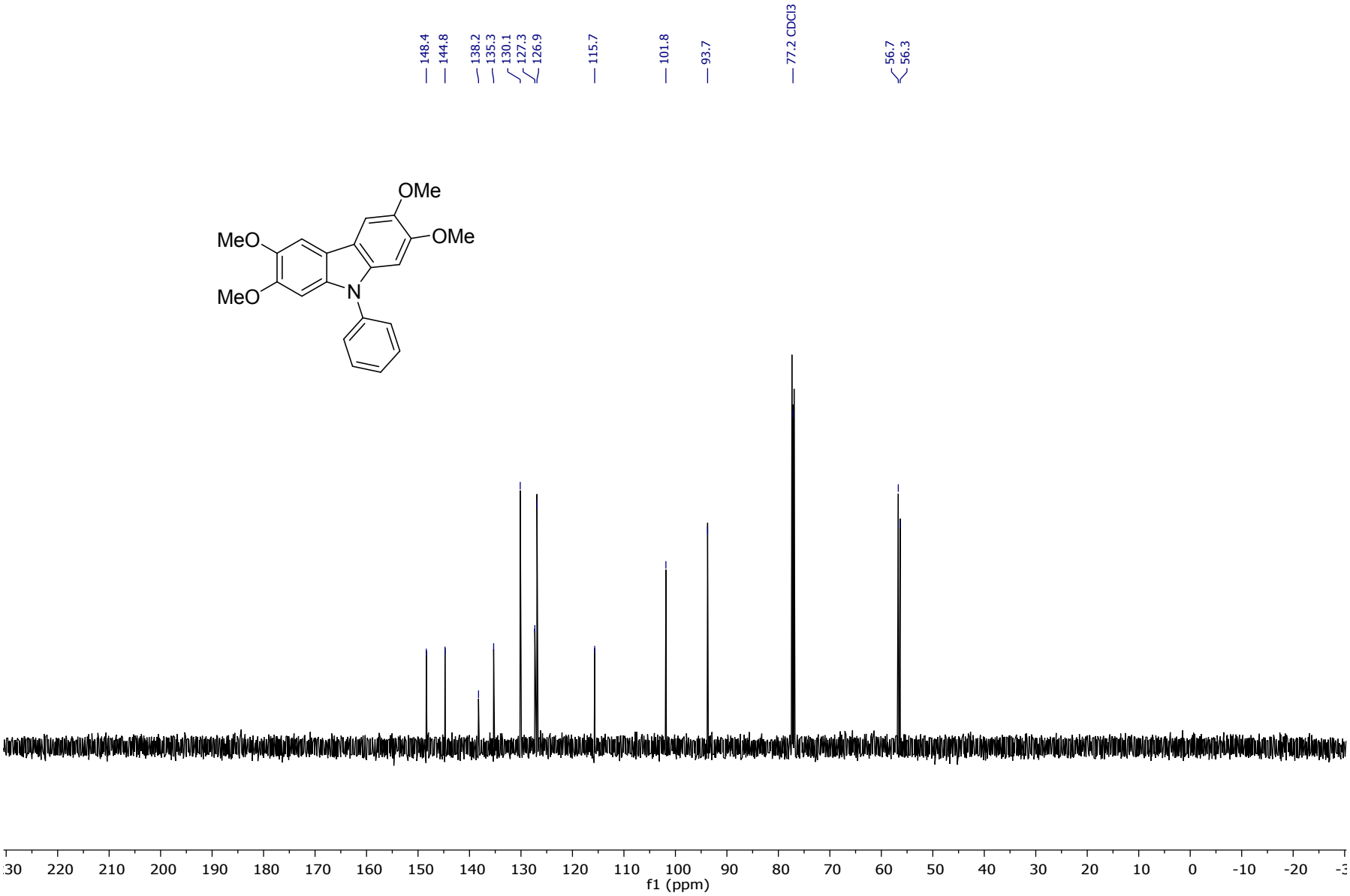

Figure S86. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,3,6,7-tetramethoxy-9-phenyl-9H-carbazole (6e)

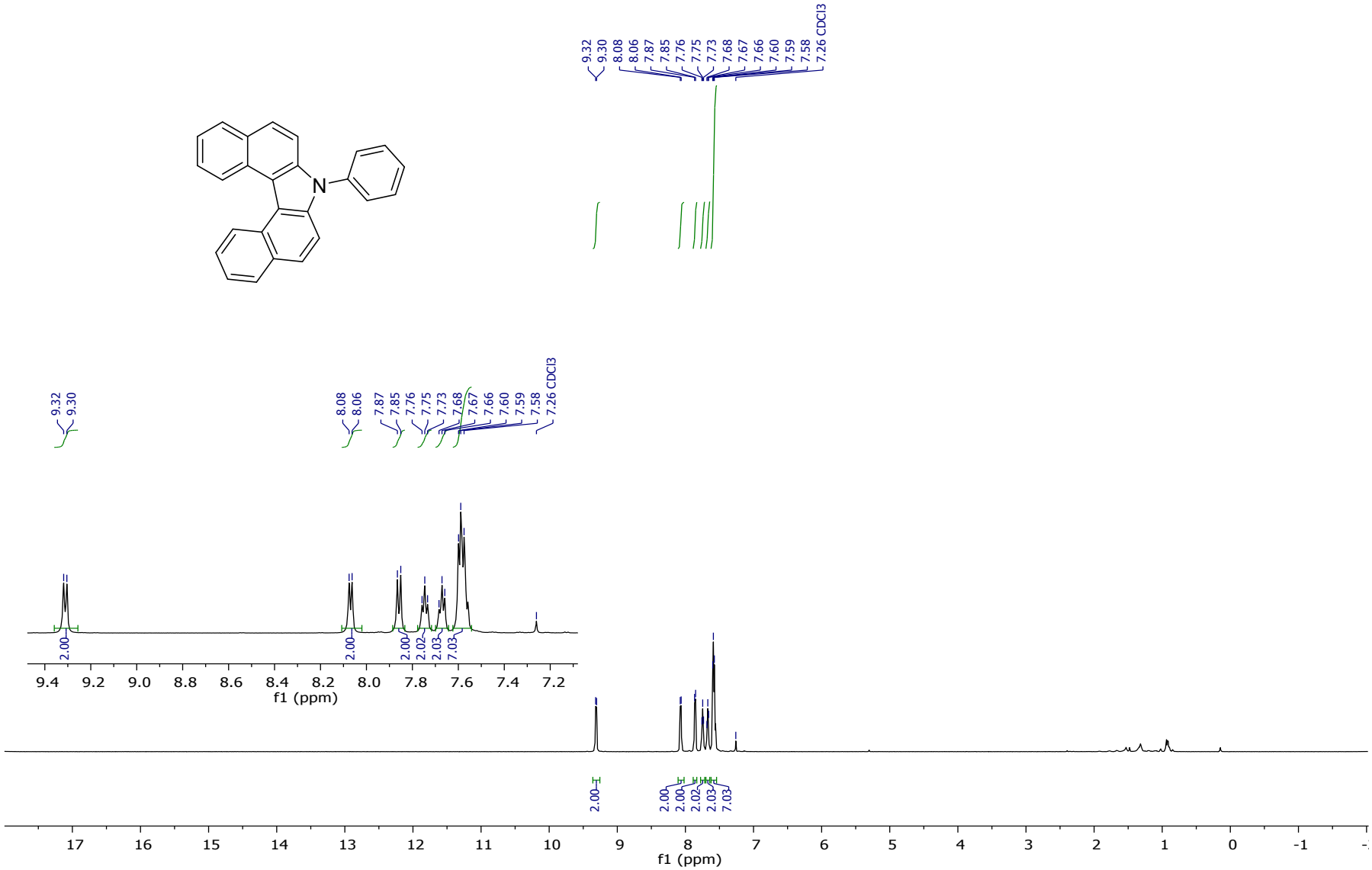

Figure S87. ^{1}H NMR (600 MHz, Chloroform-*d*) of 7-phenyl-7*H*-dibenzo[c,g]carbazole (6f)

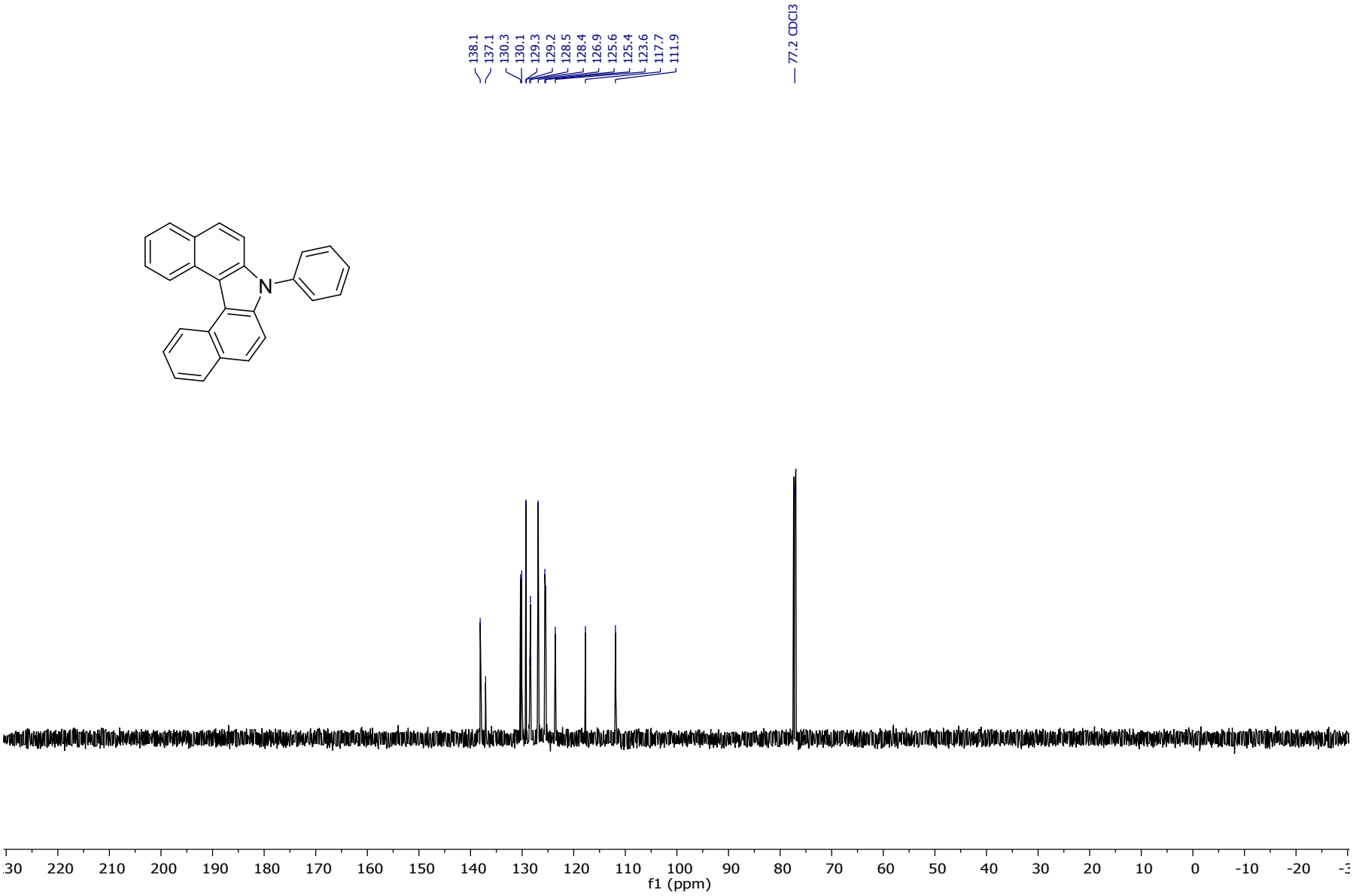

Figure S88. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 7-phenyl-7*H*-dibenzo[c,g]carbazole (6f)

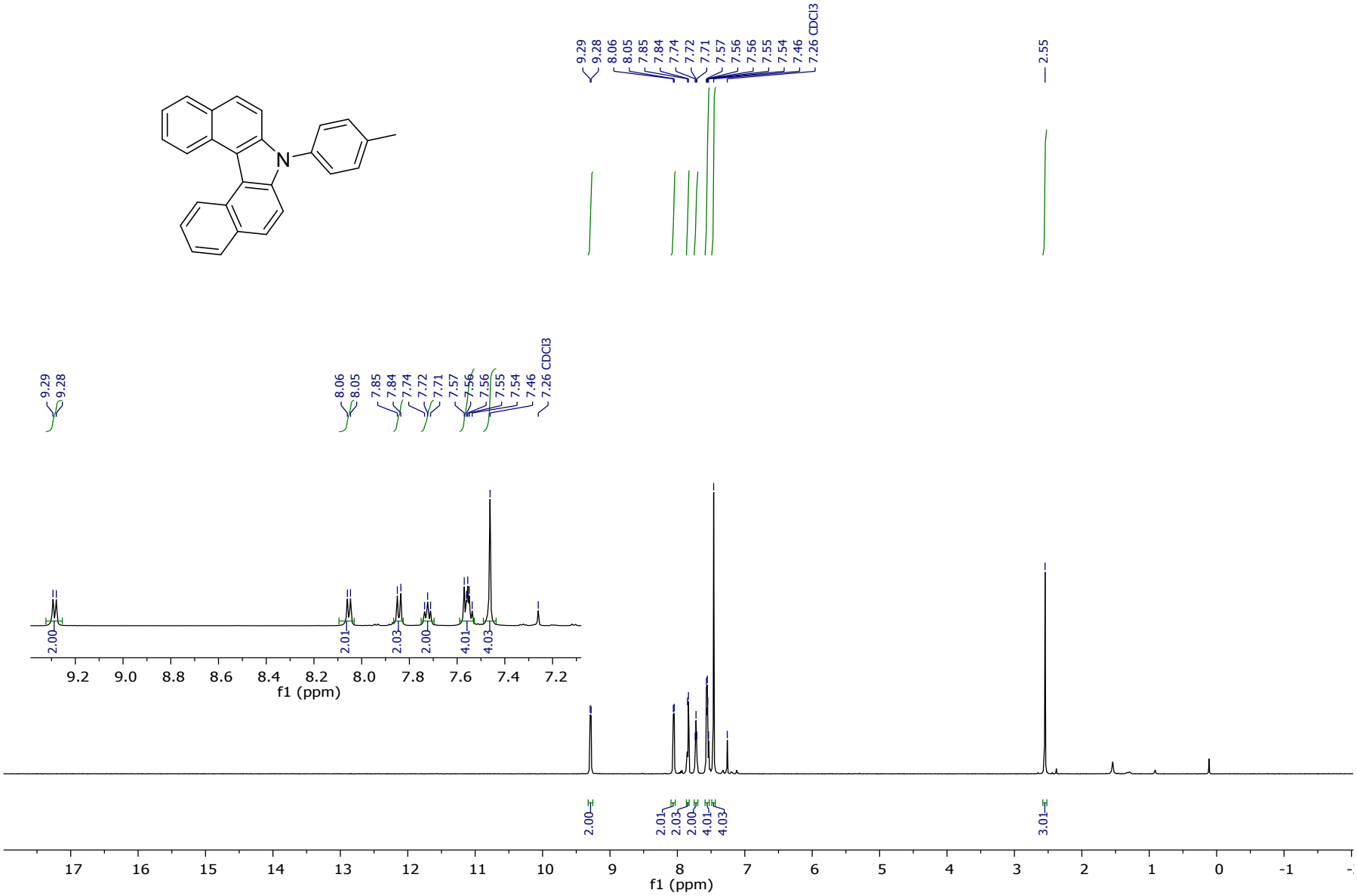

Figure S89. ^{1}H NMR (600 MHz, Chloroform-*d*) of 7-*p*-tolyl-7*H*-dibenzo[c,g]carbazole (6g)

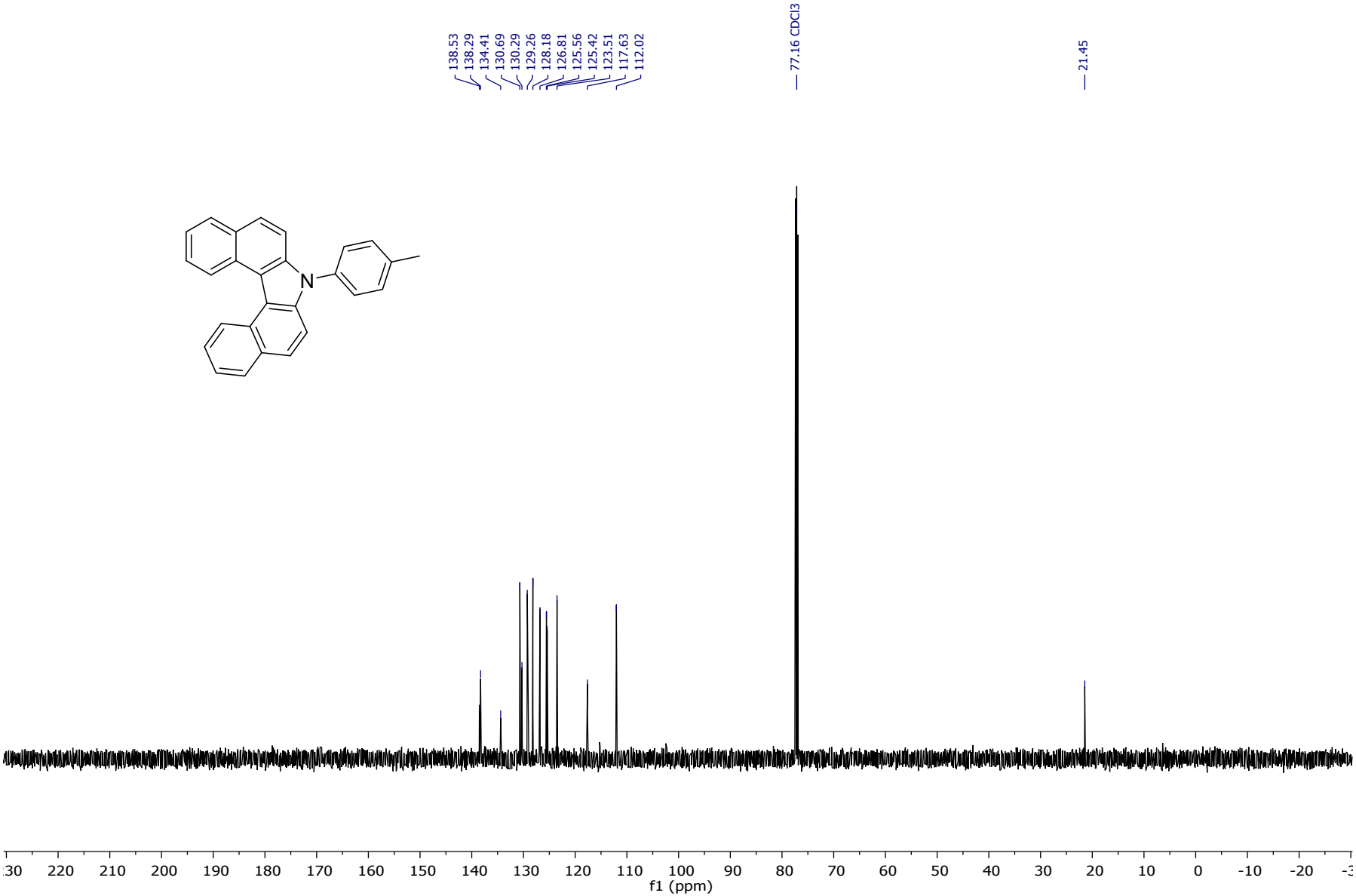

Figure S90. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 7-*p*-tolyl-7*H*-dibenzo[c,g]carbazole (6g)

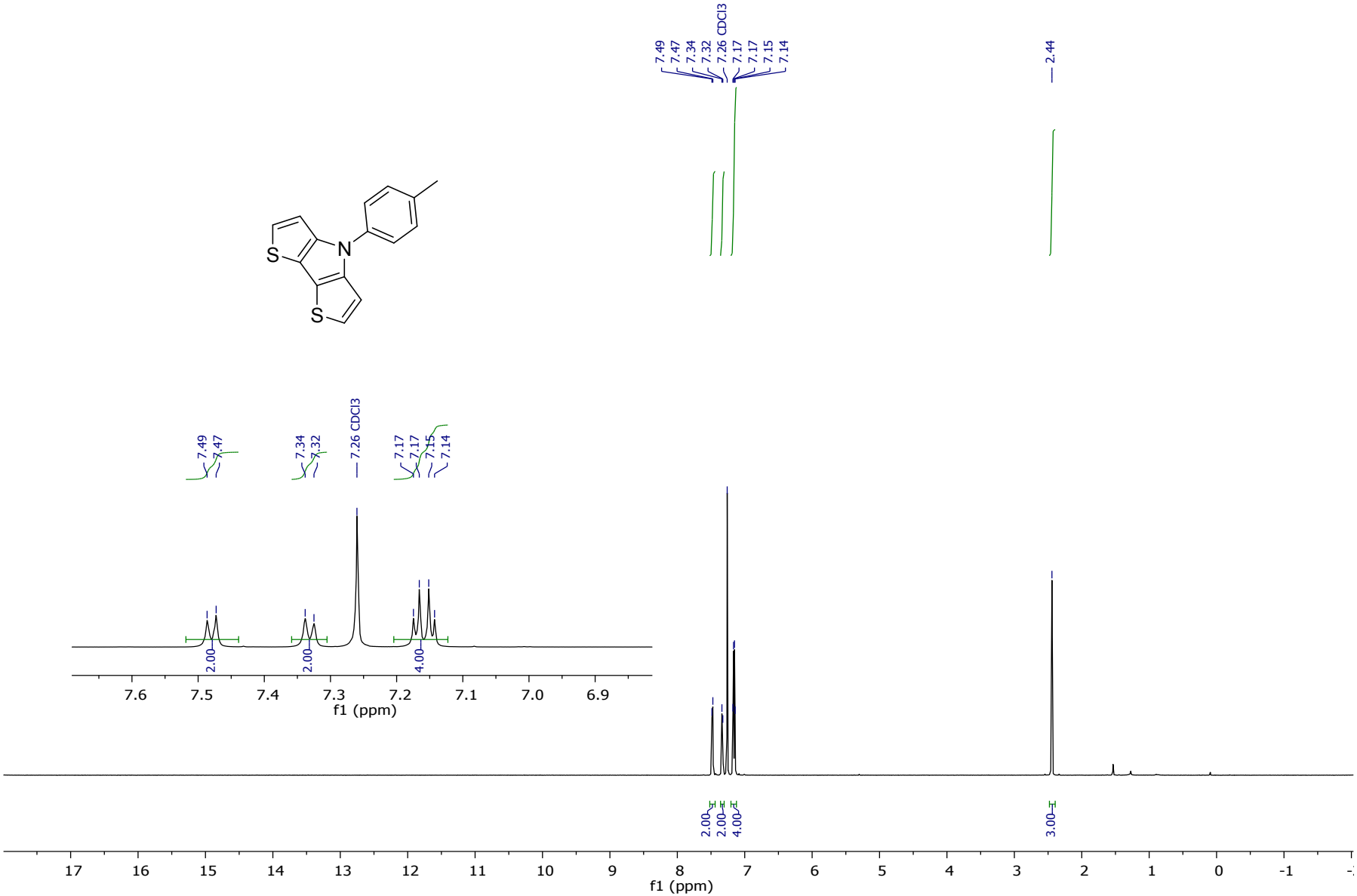

Figure S91. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-*p*-tolyl-4*H*-dithieno[3,2-b:2',3'-d]pyrrole (6h)

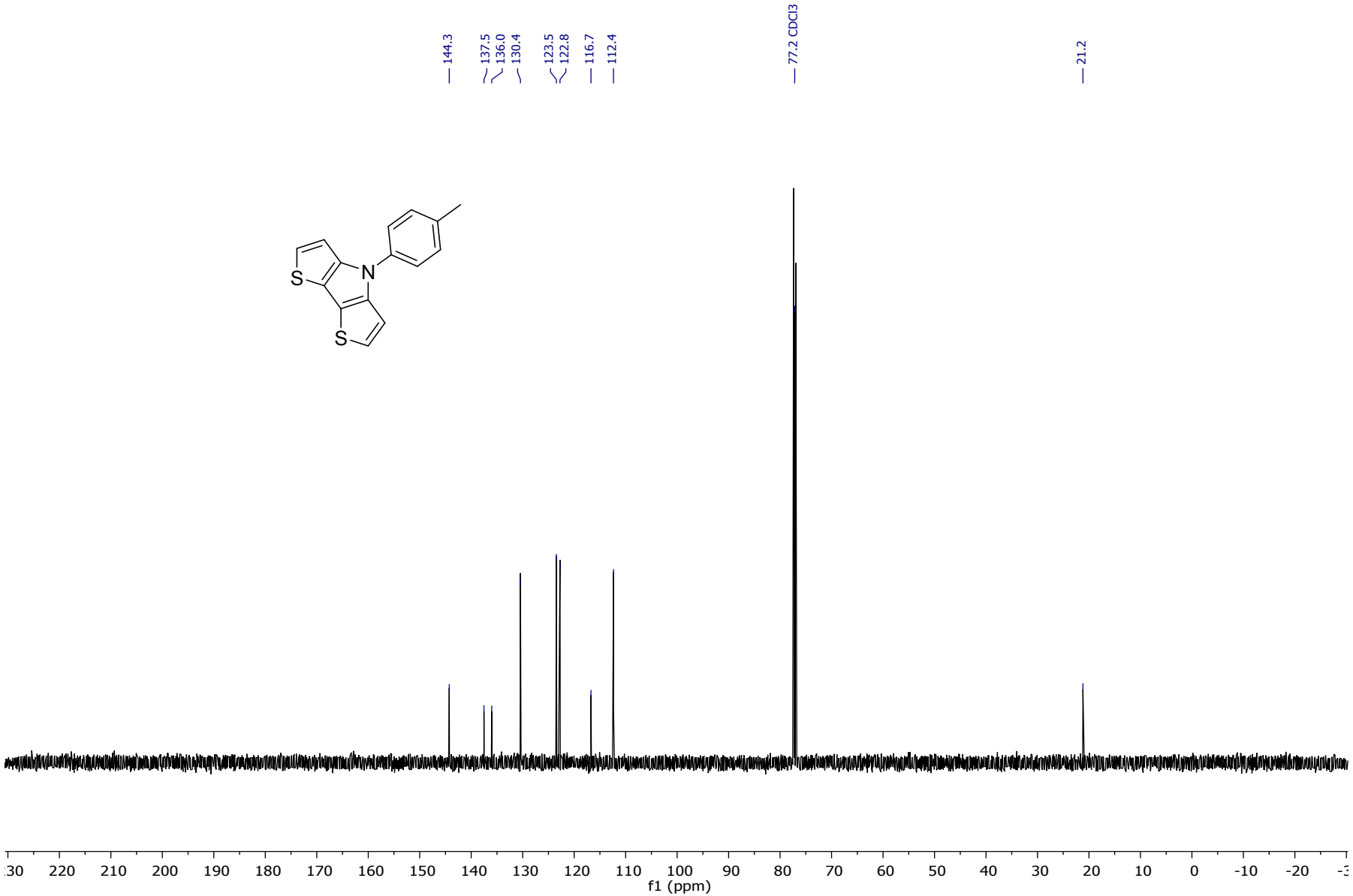

Figure S92. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4-*p*-tolyl-4*H*-dithieno[3,2-b:2',3'-d]pyrrole (6h)

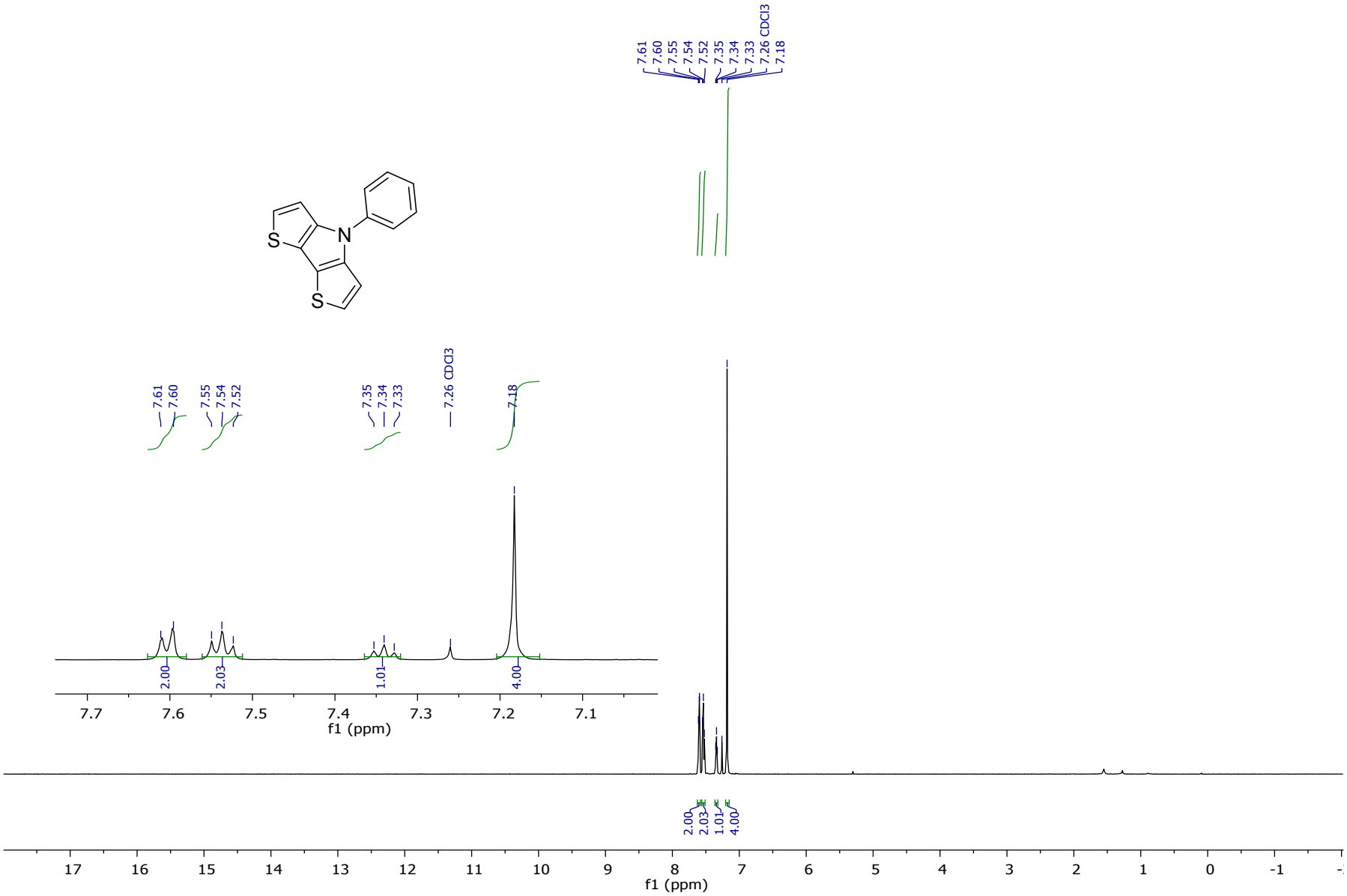

Figure S93. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-phenyl-4*H*-dithieno[3,2-b:2',3'-d]pyrrole (6i)

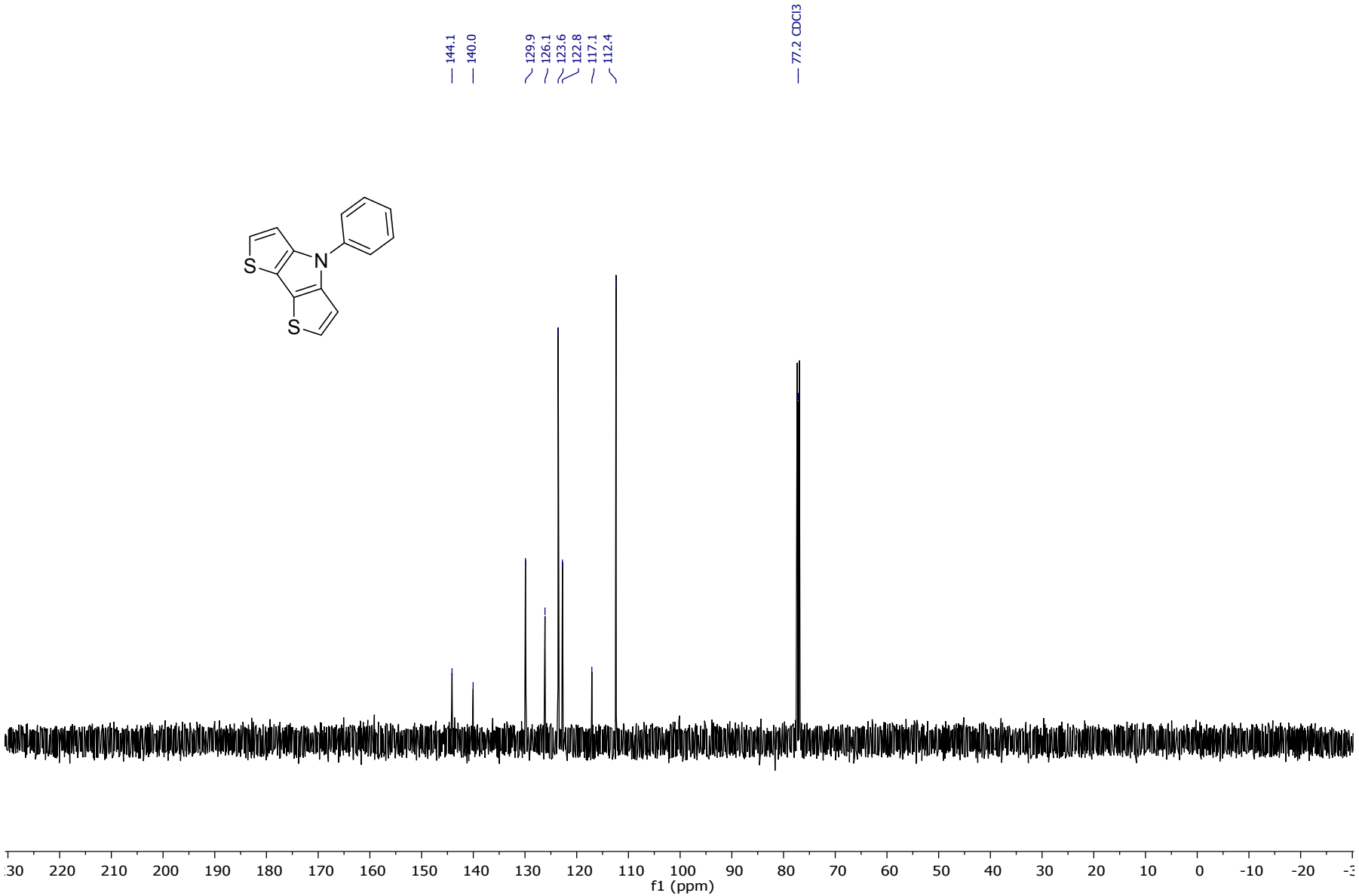

Figure S94. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4-phenyl-4*H*-dithieno[3,2-b:2',3'-d]pyrrole (6i)

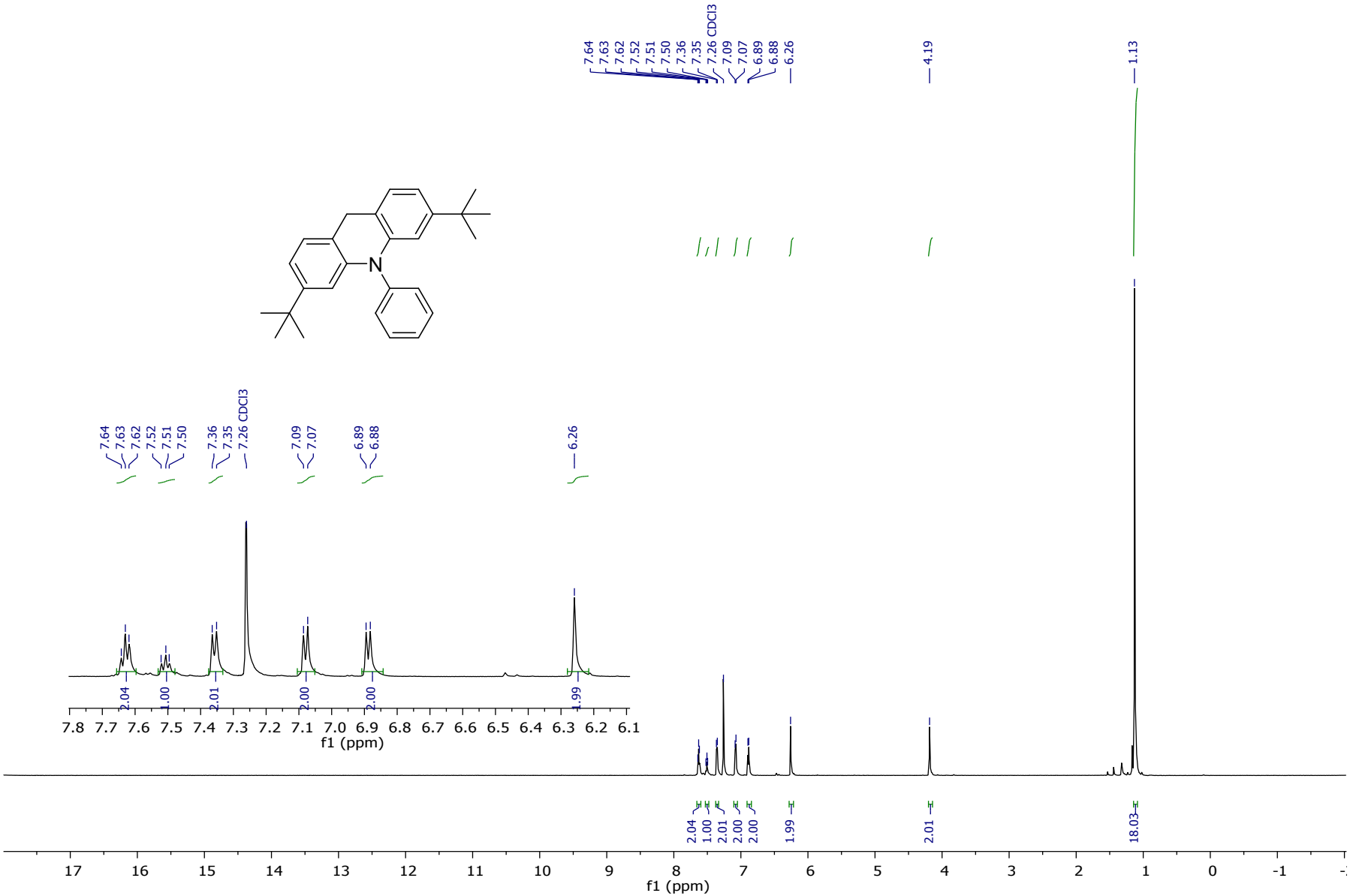

Figure S95. ^{1}H NMR (600 MHz, Chloroform-*d*) of 3,6-di-tert-butyl-10-phenyl-9,10-dihydroacridine (6j)

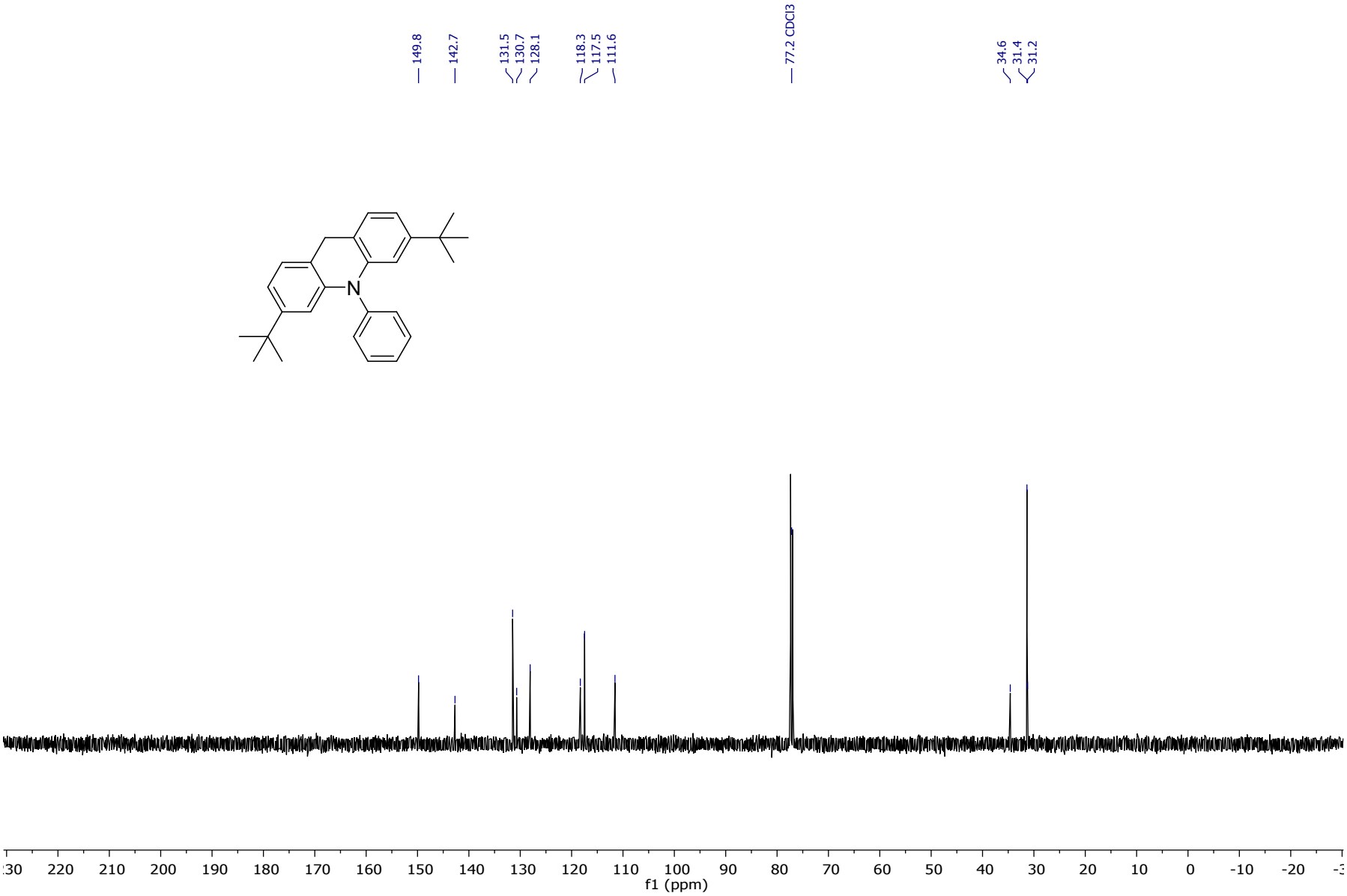

Figure S96. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 3,6-di-tert-butyl-10-phenyl-9,10-dihydroacridine (6j)

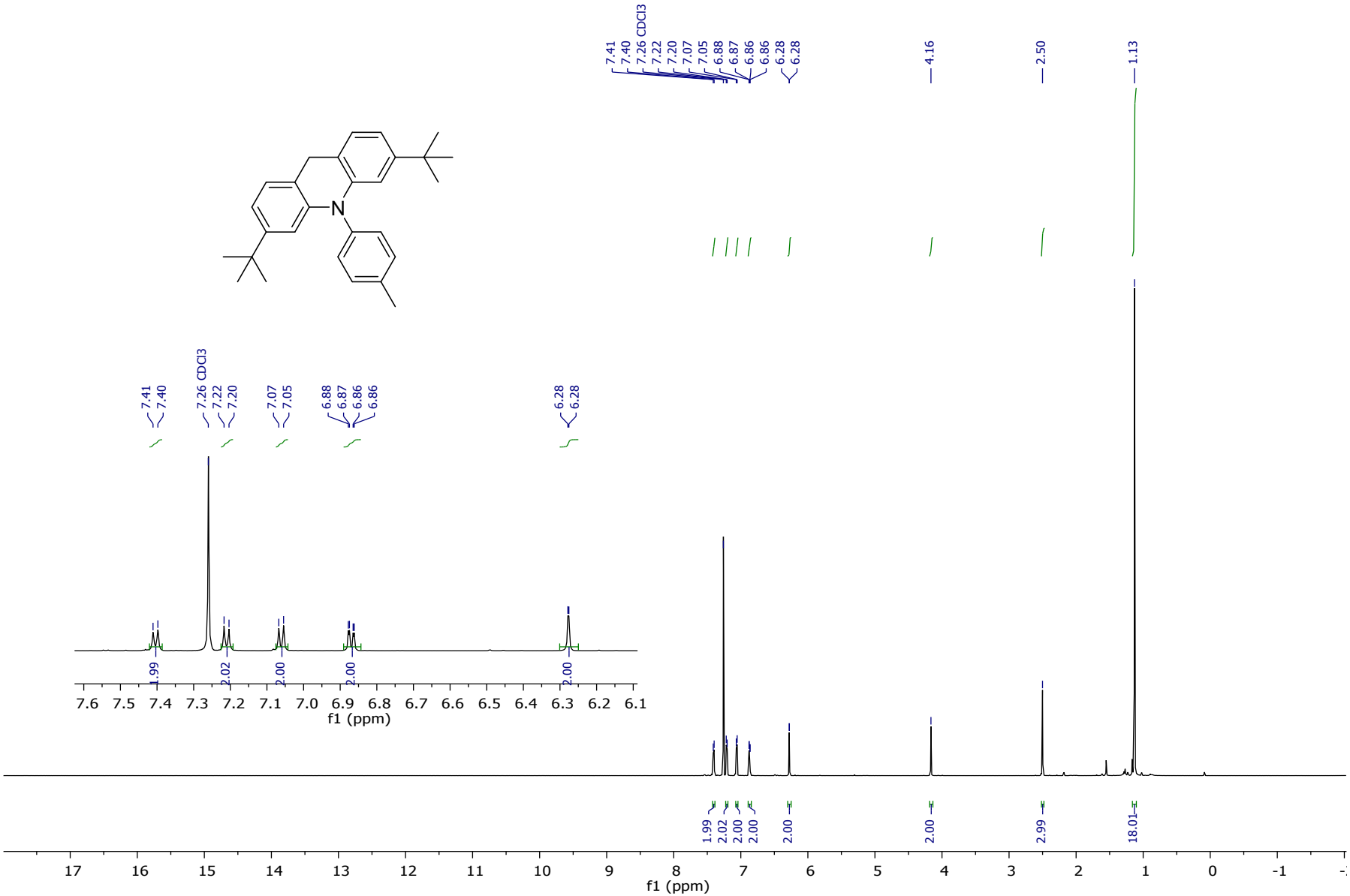

Figure S97. ^{1}H NMR (600 MHz, Chloroform-*d*) of 3,6-di-tert-butyl-10-*p*-tolyl-9,10-dihydroacridine (6k)

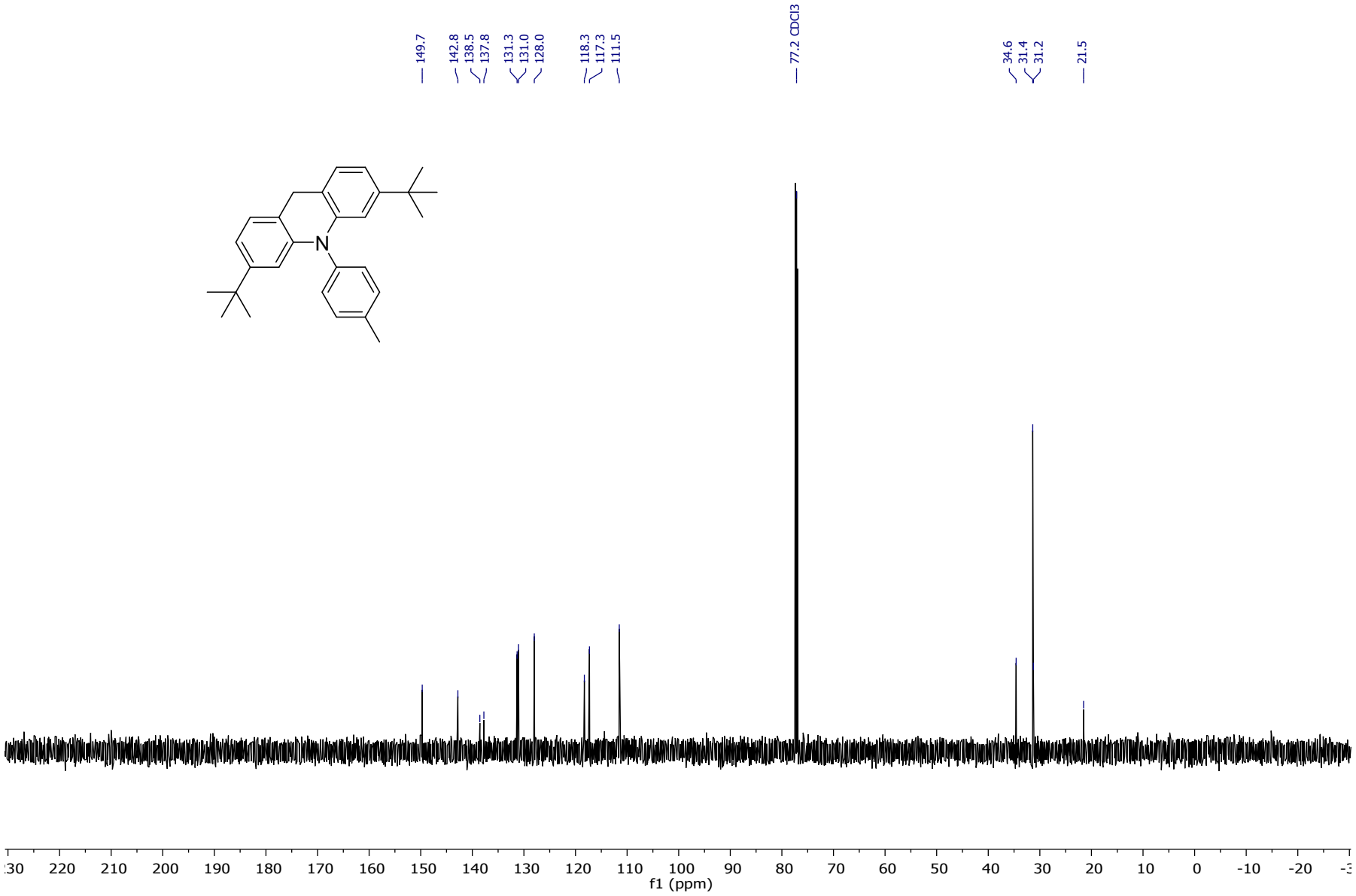

Figure S98. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 3,6-di-tert-butyl-10-*p*-tolyl-9,10-dihydroacridine (6k)

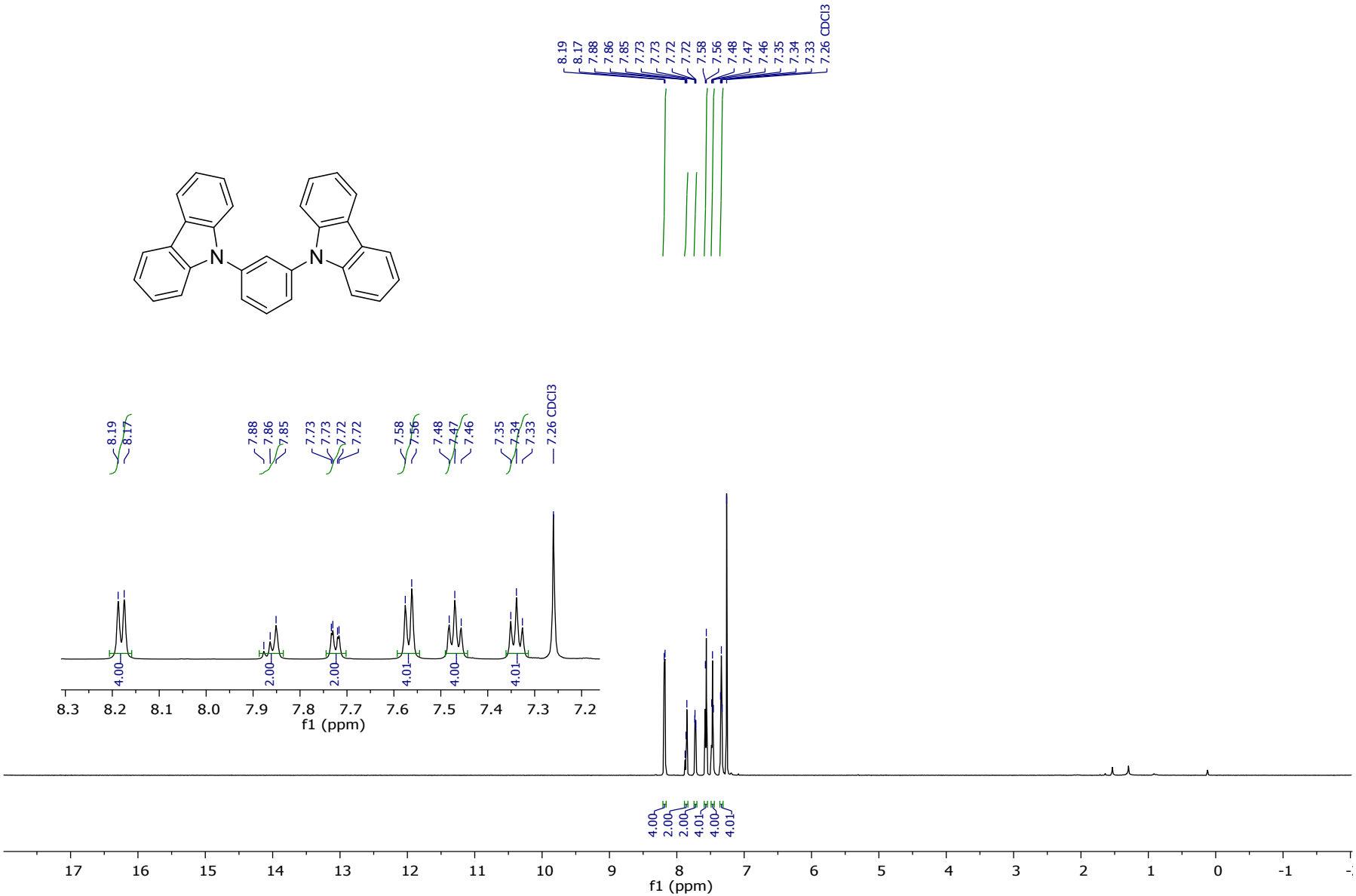

Figure S99. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1,3-di(9H-carbazol-9-yl)benzene (6l)

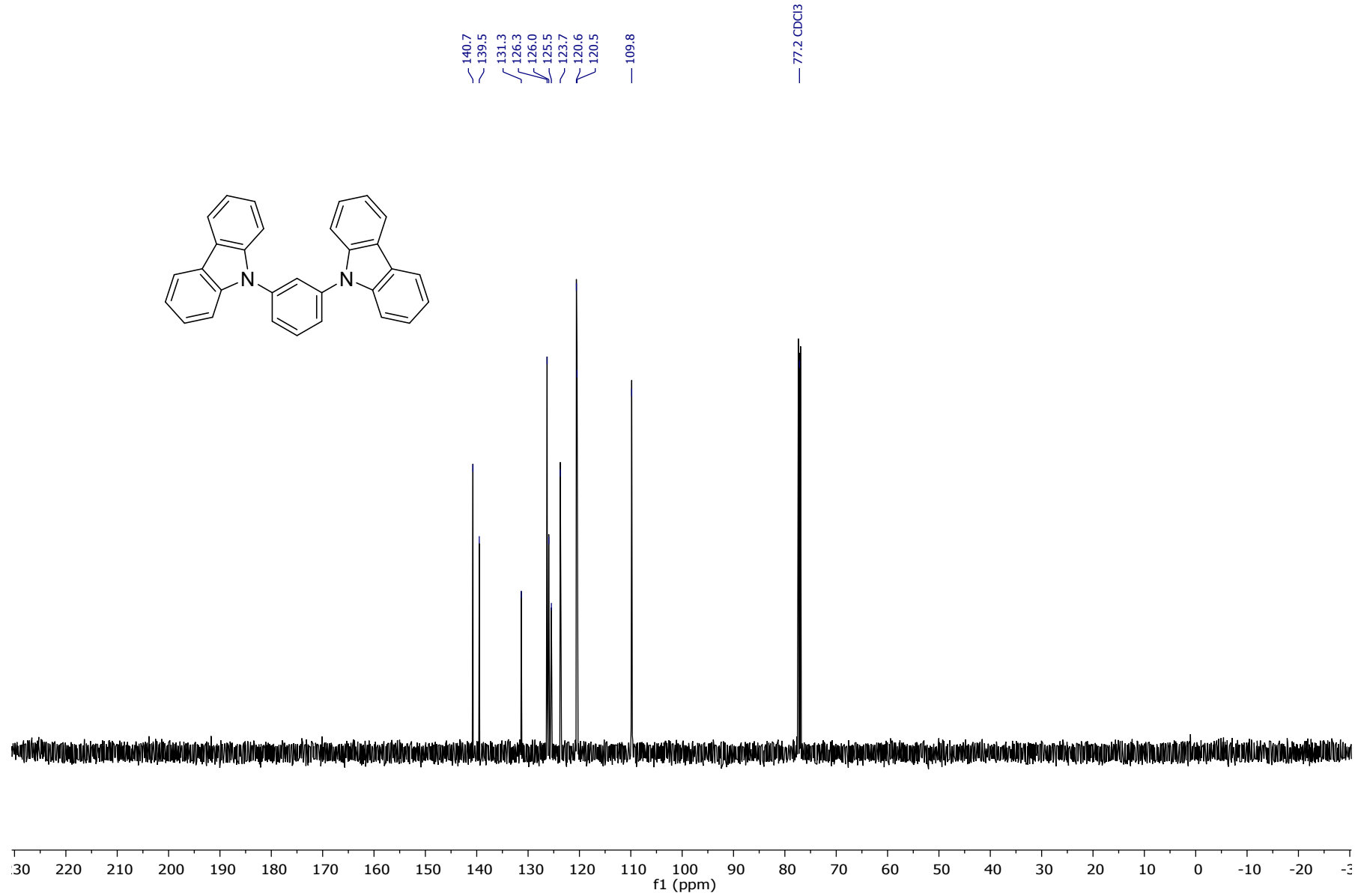

Figure S100. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1,3-di(9H-carbazol-9-yl)benzene (6l)

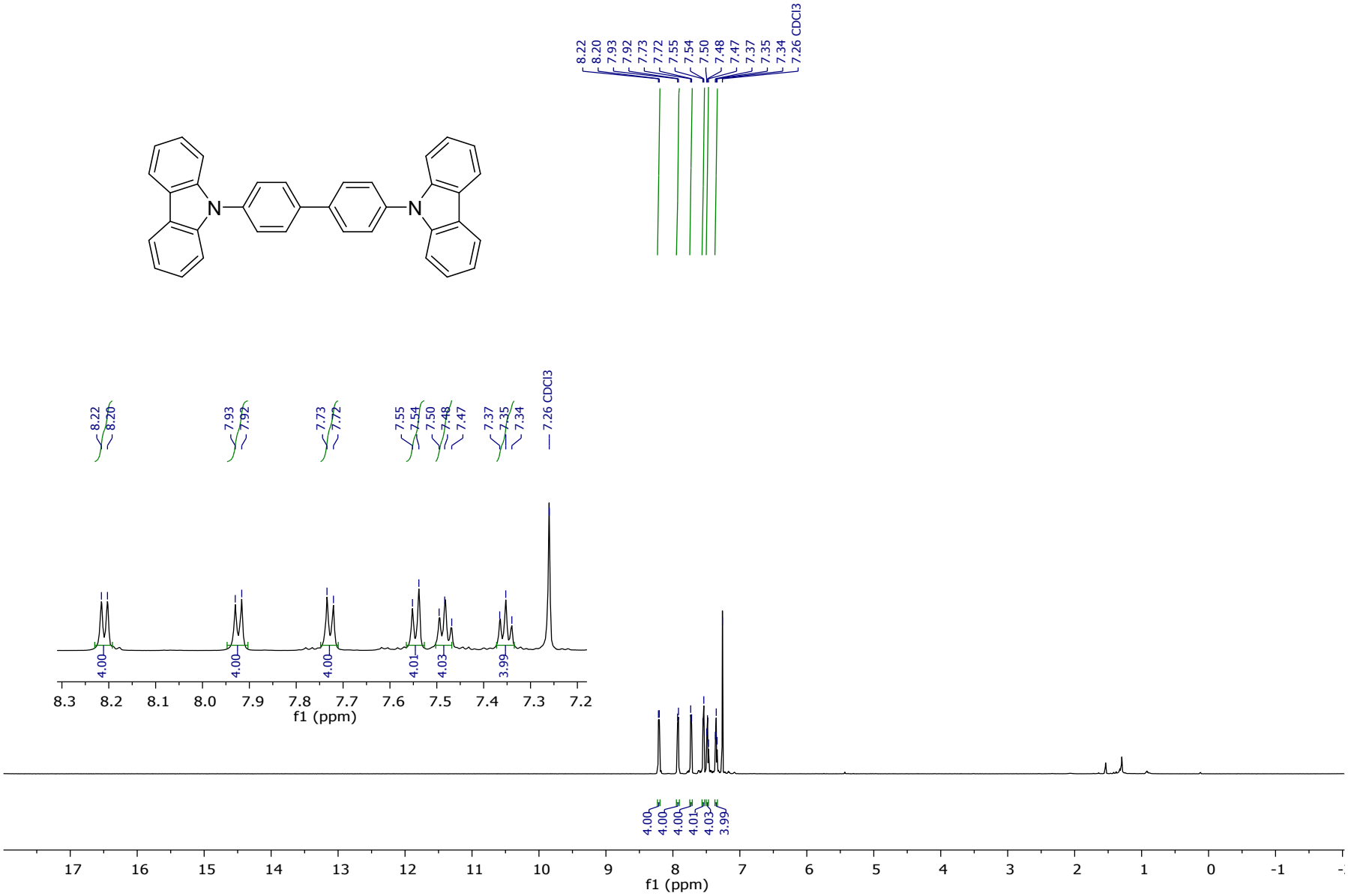

Figure S101. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4,4'-di(9H-carbazol-9-yl)biphenyl (6m)

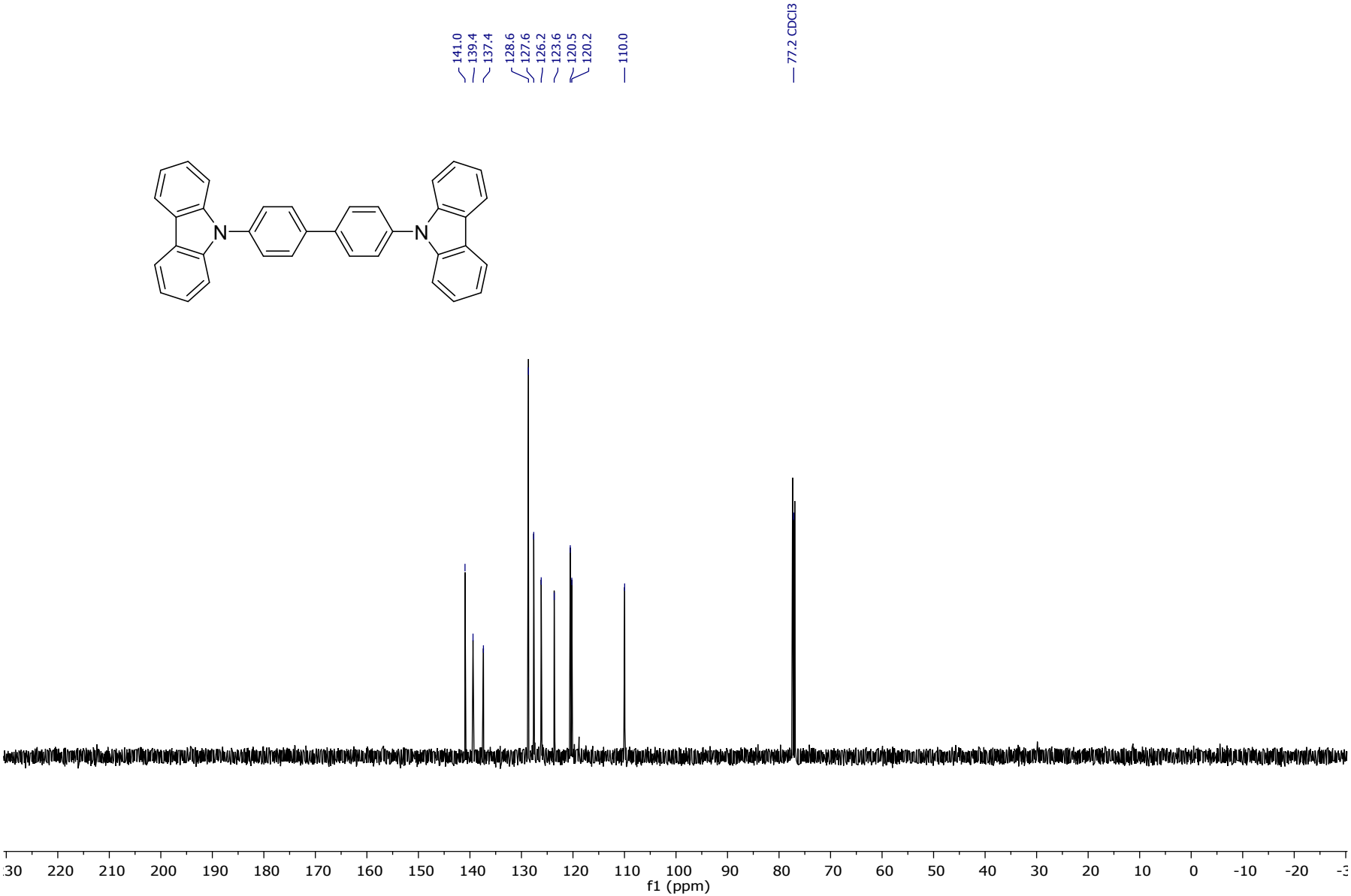

Figure S102. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4,4'-di(9H-carbazol-9-yl)biphenyl (6m)

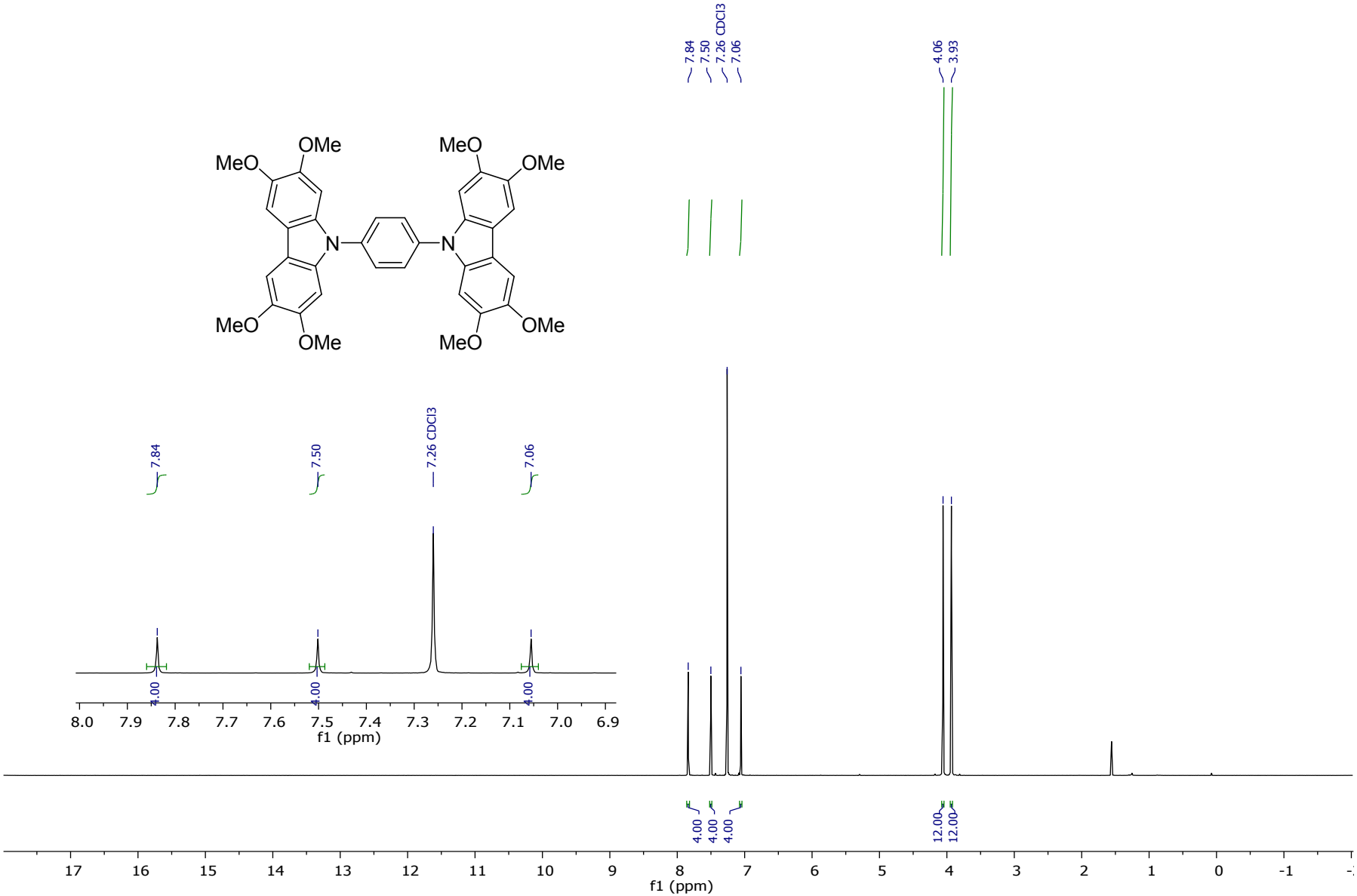

Figure S103. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1,4-bis(2,3,6,7-tetramethoxy-9*H*-carbazol-9-yl)benzene (6n)

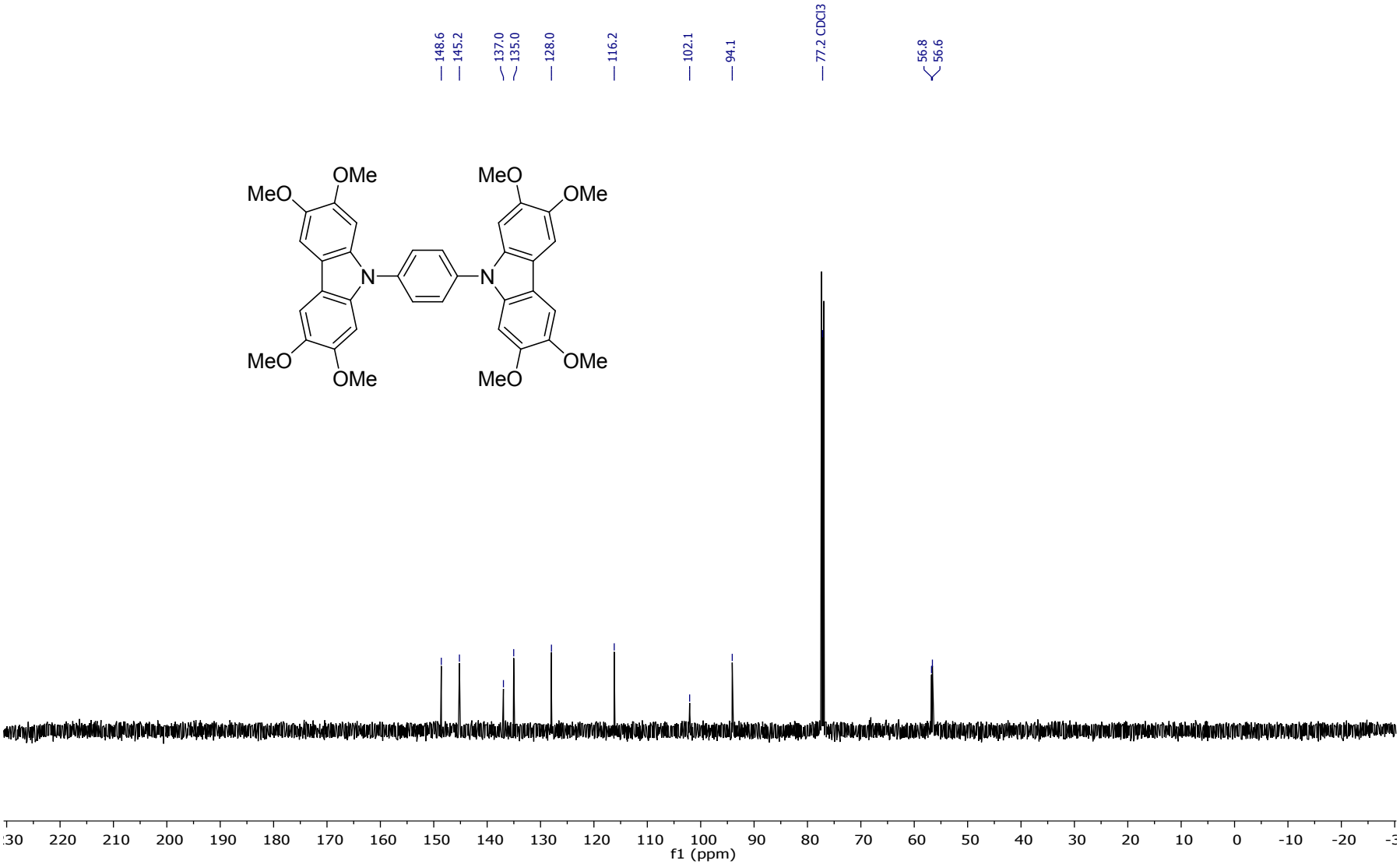

Figure S104. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1,4-bis(2,3,6,7-tetramethoxy-9*H*-carbazol-9-yl)benzene (6n)