Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2017

Eight-Membered-Ring Diaminocarbenes Bearing Naphthalene Moiety in the Backbone: DFT Studies, Synthesis of Amidinium Salts, Generation of Free Carbene, Metal Complexes, and Solvent-free Copper Catalyzed Azide-Alkyne cycloaddition (CuAAC) reaction

Gleb A. Chesnokov,[a] Maxim A. Topchiy,[b,c] Pavel B. Dzhevakov,[a,b] Pavel S. Gribanov,[b] Aleksandr A. Tukov,[b] Victor N. Khrustalev,[c,d] Andrey F. Asachenko,[b] Mikhail S. Nechaev*[a,b]

[a] M. V. Lomonosov Moscow State University, Leninskie Gory 1 (3), Moscow, 119991, Russia

[b] A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prospect 29, Moscow, 119991, Russia

[c] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, Moscow, 119991, Russia

[d] Department of Inorganic Chemistry, Peoples' Friendship University of Russia, Miklukho-Maklay Street 6, Moscow, 117198, Russia

E-mail: Mikhail S. Nechaev m.nechaev@ips.ac.ru and m.s.nechaev@org.chem.msu.ru

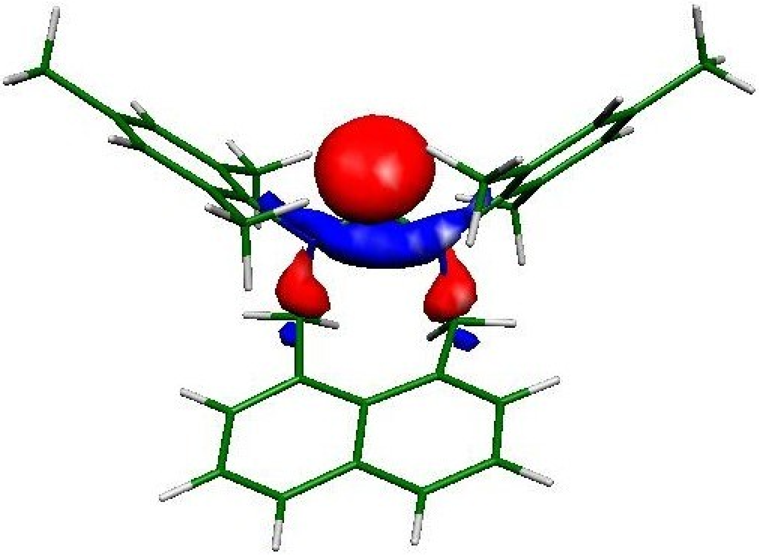
Supplementary information

Contents

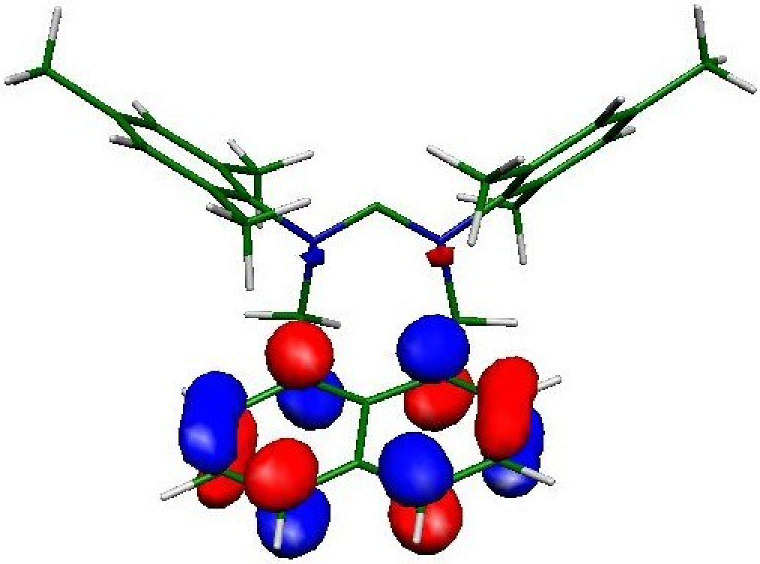
Orbital plots

Figure S0

MOLEKEL 4.3 plots of the frontier orbitals of the NaphtDHD-Mes.



HOMO, -4.21 eV



LUMO, -2.28 eV

X-ray structure determination

Data were collected using a Bruker APEX-II CCD diffractometer (λ(MoK_{α})-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the *SADABS* program.[1] For details, see Table 2. The crystal structures of [(Naph-8-Dipp)H]Br (**4b**), [(Naph-8-Dipp)AgBr] (**7b**) and [(Naph-8-Dipp)CuBr] (**8b**) were determined by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The crystal of [(Naph-8-Dipp)H]Br (**4b**) contained a solvate water molecule statistically disordered with the total positional occupancy of 0.75. The water hydrogen atoms were objectively localized in the difference-Fourier map and included into the refinement with fixed positional (the riding model) and isotropic displacement ($U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})$) parameters. The other hydrogen atoms in all compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters ($U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for the CH_3-groups and $1.2U_{\mathrm{eq}}(\mathrm{C})$ for the other groups). All calculations were carried out using the *SHELXTL* program.[2] Crystallographic data for [(Naph-8-Dipp)H]Br • ¾H_2O, [(Naph-8-Dipp)AgB] (**7b**) and [(Naph-8-Dipp)CuBr] (**8b**) have been deposited with the Cambridge Crystallographic Data Center. CCDC 1458374, CCDC 1458375 and CCDC 1458376 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Table S1

Crystallographic data for [(NaphtDHD-Dipp)H]Br • ¾H_2O, (NaphtDHD-Dipp)AgBr (**7b**) and (NaphtDHD-Dipp)CuBr (**8b**).

Compound	[(NaphtDHD-Dipp)H]Br • ¾H_2O	(NaphtDHD-Dipp)AgBr (**7b**)	(NaphtDHD-Dipp)CuBr (**8b**)
empirical formula	$C_{37}H_{46.5}N_2O_{0.75}Br$	$C_{37}H_{44}N_2AgBr$	$C_{37}H_{44}N_2CuBr$
fw	611.17	704.52	660.19
T, K	120.0(2)	120.0(2)	120.0(2)
crystal size, mm	0.15×0.20×0.20	0.15×0.15×0.20	0.20×0.20×0.25
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1$/c	$P2_1$/c	$P2_1$/c
a, Å	11.1858(4)	11.0455(5)	11.0973(11)
b, Å	19.2430(7)	19.3025(8)	19.2875(19)
c, Å	15.5488(6)	16.4884(7)	16.1494(16)
α, deg.	90	90	90
β, deg.	102.702(1)	102.290(1)	102.137(2)
γ, deg.	90	90	90
V, Å^3	3264.9(2)	3434.9(3)	3379.3(6)
Z	4	4	4
d_c, g · cm^{-3}	1.243	1.362	1.298
F(000)	1294	1448	1376
μ, mm^{-1}	1.289	1.776	1.855
$2\theta_{max}$, deg.	61.0	64.0	61.0
index range	$-15 <= h <= 15$	$-16 <= h <= 16$	$-15 <= h <= 15$
	$-27 <= k <= 26$	$-28 <= k <= 28$	$-27 <= k <= 27$
	$-22 <= l <= 22$	$-24 <= l <= 24$	$-22 <= l <= 23$
no. of rflns collected	43057	51750	43668
no. of unique rflns	9942	11938	10273
no. of rflns with $I > 2\sigma(I)$	6696	7466	5351
data/restraints/parameters	9942 / 0 / 378	11938 / 0 / 378	10273 / 0 / 378
R_1; wR_2 ($I > 2\sigma(I)$)	0.0481; 0.1070	0.0507; 0.1140	0.0564; 0.1127
R_1; wR_2 (all data)	0.0849; 0.1228	0.0971; 0.1279	0.1345; 0.1416
GOF on F^2	1.025	0.972	0.968
T_{min}; T_{max}	0.757; 0.818	0.718; 0.777	0.636; 0.696

Experimental Procedures

General Experimental Procedures

All manipulations with unstable compounds were carried out using standart Schlenk technique under argon atmosphere. Tetrahydrofuran was distilled over sodium-benzophenone. Chemicals and solvents were obtained from commercial sources and used without further purification. All acetylenes except 3-nitrophenylacetylene were purchased from Aldrich Inc, 3-nitrophenylacetylene was purchased from ABCR and used as received. Benzyl azide,[3] 4-bromobenzyl azide,[4] phenyl azide,[5] 4-azidotoluene,[6] 1-azido-3,5-bis(trifluoromethyl)benzene and 1-azido-4-fluorobenzene[7] were prepared according to published methods, all characterization data were in good agreement with previously reported. NMR spectra were obtained on a Bruker "Avance 600" (600 MHz ^{1}H, 151 MHz ^{13}C). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. 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” or ‘‘m” for singlet, doublet, triplet or multiplet, respectively. The abbreviation ‘‘br” is given for broadened signals.

Copper complexes

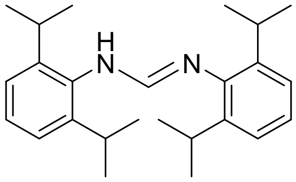
Copper complexes [(SIMes)CuBr], [(SIPr)CuBr],[8] (THP-Mes)-, (THP-Dipp)-, (THD-Mes)-, (THD-Dipp)CuBr[9] were prepared according to published methods, all characterization data were in good agreement with previously reported.

Amidines

General procedure for the preparation of formamidines

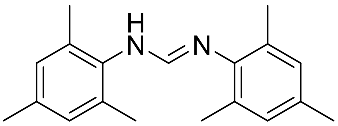
A mixture of 1 equivalent of 2,6-disubstituted aniline, 0.5 equivalent of triethyl orthoformate and catalytic amount of glacial acetic acid was heated until distillation of ethanol from reaction mixture ceased. Recrystallization of cooled reaction mixture from acetone gave pure crystalline product.

*N,N’-bis(2,6-diisopropylphenyl)formamidine (**3b**)*



According to general procedure N,N'-bis(2,6-diisopropylphenyl)formamidine was obtained from 2,6-diisopropylaniline in 85% yield as white needles. The ^{1}H and ^{13}C NMR data were in good agreement with those reported in the literature.[10]

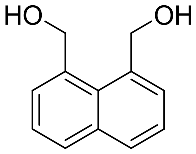
*N,N'-bis(2,4,6-trimethylphenyl)formamidine (**3a**)*



According to general procedure N,N'-bis(2,4,6-trimethylphenyl)formamidine was obtained from 2,4,6-trimethylaniline in 82% yield as white needles. The ^{1}H and ^{13}C NMR data were in good agreement with those reported in the literature.[10]

Amidinium salts

*Naphthalene-1,8-diyldimethanol[11] (**1**)*



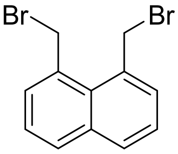
Method A. To a stirred slurry of 0.228 g (6 mmol) of $LiAlH_4$ and anhydrous 0.409 g (3 mmol) $ZnCl_2$ in 20 ml of dry THF was slowly added 0.99 g (5 mmol) of 1,8-naphthalic anhydride at room temperature. The reaction mixture was stirred for 6h, and then excess of $LiAlH_4$ was neutralized by careful addition 5 ml of water. The reaction mixture was acidified with 1M HCl to pH 5 and extracted with 3x15 ml portions of ethyl acetate. Organic phase was washed with brine, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Resulting solid was purified by recrystallization from 1:1 benzene-methanol mixture to give 0.79 g (84%) of naphthalene-1,8-diyldimethanol as white needles. Mp = 161-162°C.

Method B. The stirred slurry of 0.946 g (25 mmol) of $NaBH_4$ in 10 ml of dry 1,2-dimethoxyethane was cooled to -20°C and 0.57 ml (11 mmol) of bromine was slowly added dropwise over 30 min. The reaction mixture was stirred for additional 1h until disappearance of brown color, allowed to warm to -5°C and added 0.991 g (5 mmol) of 1,8-naphthalic anhydride. After 30 min 15 ml of 1M aqueous HCl an 15 ml of ethyl acetate was added, stirred for 5 minutes, organic phase was separated and washed twice with 15 ml of 1M K_2CO_3 followed by 15 ml of water. Organic extract was dried over anhydrous Na_2SO_4 and all volatiles were evaporated. Resulting solid was purified by recrystallization from 1:1 benzene-methanol mixture to give 0.574 g (61%) of naphthalene-1,8-diyldimethanol as white needles. Mp = 161-162°C.

^{1}H NMR (600 MHz, DMSO-d6) δ 7.86 (dd, J = 8.2, 1.5 Hz, 2H), 7.63 (dd, J = 7.0, 1.4 Hz, 2H), 7.46 (dd, J = 8.1, 7.0 Hz, 2H), 5.28 (t, J = 5.5 Hz, 2H), 5.09 (d, J = 5.5 Hz, 4H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d6) δ 138.5, 135.1, 130.0, 129.0, 128.1, 124.9, 63.7.

1,8-Bis(bromomethyl)naphthalene[11a, 12] *(**2**)*



To a stirred solution of 20.44 g (0.108 mol) naphthalene-1,8-diyldimethanol (**1**) in 100 ml of 1,4-dioxane was slowly added 30 ml (0.316 mol) of phosphorous tribromide at room temperature. Resulting reaction mixture was stirred overnight. Reaction mixture was poured in 1200 ml of ice water, stirred for 1h and filtered. Recrystallization of resulting solid from benzene gave 32.05 g (93%) of 1,8-bis(bromomethyl)naphthalene as white microcrystalline solid. Mp = 132-133°C. R_f=0.38 (hexane).

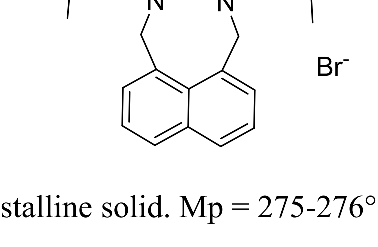
^{1}H NMR (600 MHz, Chloroform-d) δ 7.89 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 7.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 5.31 (s, 4H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 136.3, 133.6, 133.2, 132.1, 129.2, 125.9, 37.3.

General procedure for preparation of amidinium salts

N,N-Diisopropylethylamine (0.142 g, 1.1 mmol, 1.1 eq) was added to mixture of appropriate N,N'-diarylformamidine (1 mmol, 1 eq) and 0.314 g (1 mmol, 1 eq) of 1,8-bis(bromomethyl)naphthalene in 5 ml of dry DMF. Reaction mixture was heated at 125°C for 3 h. After cooling to r.t., water (50 ml) was added and resulting mixture was extracted with CH_2Cl_2 (3x25 ml), organic phase was washed with saturated solution of K_2CO_3 and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude solid was recrystallized from toluene or hexane-dichloromethane mixture, filtered and dried in vacuum.

*2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4a**)*



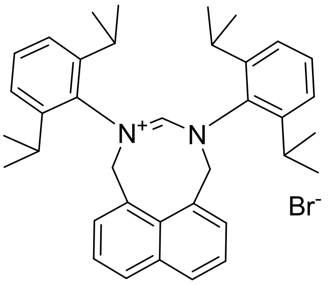
Yield 87%. White microcrystalline solid. Mp = 275-276°C

^{1}H NMR (600 MHz, Chloroform-d) δ 8.10 (d, J = 16.5 Hz, 2H), 7.94 (d, J = 7.0 Hz, 2H), 7.39 (dd, J = 8.2, 7.0 Hz, 2H), 7.33 (s, 1H), 7.19 (d, J = 7.0 Hz, 2H), 6.99 (s, 2H), 6.76 (s, 2H), 4.48 (d, J = 16.3 Hz, 2H), 2.65 (s, 6H), 2.24 (s, 6H), 1.39 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 154.9, 140.5, 140.2, 135.9, 135.7, 132.9, 132.3, 132.0, 131.5, 130.9, 130.7, 129.7, 126.0, 60.0, 21.0, 19.4, 17.8.

E.A. found (calcd.), %: C 72.60 (72.51), H 6.42 (6.48), N 5.37 (5.46).

*2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4b**)*



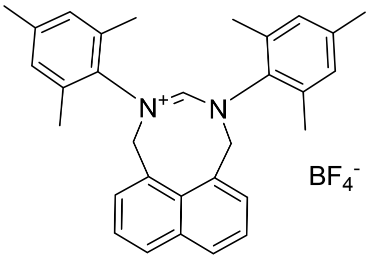
Yield 88%. White microcrystalline solid. Mp = 333-335°C

^{1}H NMR (600 MHz, DMSO-d6) δ 8.94 (s, 1H), 8.16 (dd, J = 8.1, 1.5 Hz, 2H), 7.61 (dd, J = 7.1, 1.5 Hz, 2H), 7.57 (dd, J = 8.1, 6.9 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.25 (dd, J = 7.5, 1.7 Hz, 2H), 7.20 (d, J = 16.5 Hz, 2H), 4.67 (d, J = 16.2 Hz, 2H), 2.26 – 3.30 (m, J = 6.8 Hz, 2H), 2.01 (p, J = 6.7 Hz, 2H), 1.49 (d, J = 6.7 Hz, 6H), 1.28 (d, J = 6.7 Hz, 6H), 0.83 (d, J = 6.8 Hz, 6H), 0.71 (d, J = 6.6 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d6) δ 157.1, 145.1, 144.1, 139.3, 135.2, 133.0, 131.4, 130.4, 130.2, 130.2, 125.9, 125.3, 124.8, 58.8, 28.6, 28.0, 25.2, 24.7, 24.2, 23.7.

E.A. found (calcd.), %: C 73.97 (74.35), H 7.52 (7.59), N 4.51 (4.69).

*2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (**5a**)*



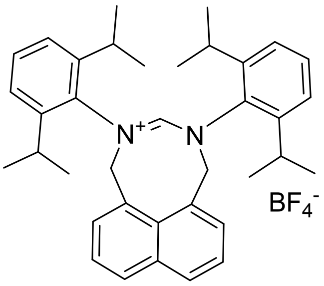
Solution of sodium tetrafluoroborate (0.367 g, 3.3 mmol) in 50 ml of water was added to solution of 1.69 g (3.3 mmol) 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4a**) in 40 ml of acetone. Acetone was slowly evaporated in vacuum from homogenous solution; precipitate was filtered and dried in vacuum over P_4O_{10}. Yield 1.67 g (97%).

^{1}H NMR (600 MHz, Chloroform-d) δ 7.99 (d, J = 7.9 Hz, 2H), 7.45 (t, J = 7.9 Hz, 2H), 7.36 (s, 1H), 7.28 – 7.21 (m, 4H), 7.05 (s, 2H), 6.81 (s, 2H), 4.55 (d, J = 16.4 Hz, 2H), 2.60 (s, 6H), 2.29 (s, 6H), 1.43 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 155.7, 140.6, 136.0, 133.0, 132.6, 131.7, 131.8, 131.1, 130.0, 126.3, 59.0, 21.0, 18.3, 17.8.

IR (υ/cm^{-1}): 2954 (w), 2919 (w), 2859 (w), 2360 (vw), 1652 (vs), 1506 (w), 1477 (m), 1452 (m), 1386 (m), 1359 (m), 1315 (w), 1189 (m), 1135 (m), 1049 (vs), 1024 (vs), 985 (m), 950 (m), 906 (m), 860 (m), 812 (m), 773 (m), 681 (m).

*2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (**5b**)*

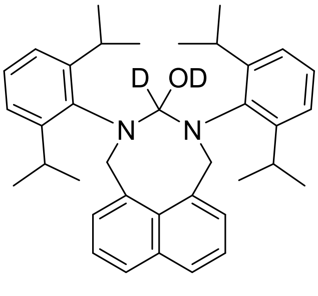


Solution of sodium tetrafluoroborate (0.367 g, 3.3 mmol) in 50 ml of water was added to solution of 2.0 g (3.3 mmol) 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4b**) in 50 ml of acetone. Acetone was slowly evaporated in vacuum from homogenous solution; precipitate was filtered and dried in vacuum over P_4O_{10}. Yield 1.98 g (98%).

^{1}H NMR (600 MHz, Chloroform-d) δ 8.00 (d, J = 7.0 Hz, 2H), 7.49 – 7.40 (m, 5H), 7.34 (dd, J = 7.8, 1.5 Hz, 2H), 7.31 (dd, J = 7.0, 1.3 Hz, 2H), 7.25 (d, J = 16.0 Hz, 2H), 7.12 (dd, J = 7.8, 1.5 Hz, 2H), 4.57 (d, J = 16.4 Hz, 2H), 3.50 (p, J = 6.6 Hz, 2H), 2.07 (p, J = 6.7 Hz, 2H), 1.52 (d, J = 6.6 Hz, 6H), 1.29 (d, J = 6.7 Hz, 6H), 0.85 (d, J = 6.9 Hz, 6H), 0.76 (d, J = 6.6 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 154.8, 146.7, 144.3, 139.3, 133.0, 132.0, 131.2, 130.3, 126.2, 126.0, 125.2, 60.3, 29.1, 28.4, 26.1, 25.2, 24.7, 24.4.

*D_2-2,4-bis(2,6-diisopropylphenyl)-2,3,4,5-tetrahydro-1H-naphtho[1,8-ef][1,3]diazocin-3-ol (**6b**)*



To the solution of 200 mg (0.3 mmol) of (E)-2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (**5b**) in 15 ml of dry, degassed THF was added solution of 55 mg (0.3 mmol) of LiHMDS in 15 ml THF at -80°C. Reaction mixture color changed to dark green. Reaction mixture was stirred for 30 min at -80°C, 2 ml of D_2O was added in one portion and reaction mixture was allowed to warm to room temperature. All volatiles were removed on rotary evaporator and residue was dissolved in 20 ml of CH_2Cl_2, dried over anhydrous Na_2SO_4 and evaporated to dryness. Drying in vacuum to constant weight gave 168 mg (95%) of white solid.

^1H NMR (600 MHz, Chloroform-d) δ 7.99 (dd, J = 8.3, 1.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.33 (dd, J = 7.8, 1.6 Hz, 2H), 7.29 (dd, J = 7.1, 1.3 Hz, 2H), 7.22 (d, J = 16.7 Hz, 2H), 7.12 (dd, J = 7.8, 1.5 Hz, 2H), 4.55 (d, J = 16.3 Hz, 2H), 3.48 (p, J = 6.7 Hz, 2H), 2.05 (p, J = 6.8 Hz, 2H), 1.50 (d, J = 6.7 Hz, 6H), 1.27 (d, J = 6.7 Hz, 6H), 0.84 (d, J = 6.9 Hz, 6H), 0.75 (d, J = 6.5 Hz, 6H).

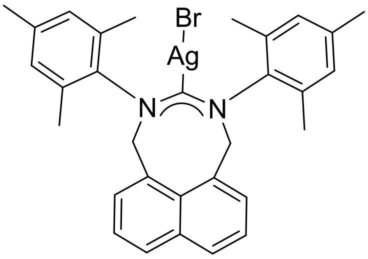
$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 154.3 (td, J = 30.0, 3.8 Hz), 146.5, 144.3, 139.2, 132.9, 132.0, 131.1, 130.5, 130.1, 126.1, 125.9, 125.2, 67.8, 67.8, 60.2, 29.0, 28.4, 26.0, 25.6, 25.1, 24.6, 24.3.

General procedure for preparation of silver complexes

A screw-cap vial equipped with a magnetic stir bar was charged with 0.232 g (1 mmol, 1 eq) of Ag_2O, 2 ml of solvent followed by 1 mmol of corresponding amidinium salt. Reaction mixture was stirred for 24 h at room temperature or at 60°C, filtered through celite and carefully diluted with equal volume of methanol. Precipitate was filtered and dried in vacuum.

Silver complexes

*(2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)silver(I) bromide (7**a**)*



Reaction of 45.1 mg (0.195 mmol) of Ag_2O and 100 mg (0.195 mmol) of 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4a**) in 2 ml of dry CH_2Cl_2 gave 53 mg (44%) of product as colorless needles.

Reaction of 45.1 mg (0.195 mmol) of Ag_2O and 100 mg (0.195 mmol) of 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4a**) in 2 ml of dry THF gave 96 mg (80 %) of product as colorless needles. Mp = 220-221°C

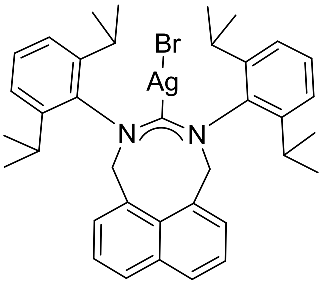
^{1}H NMR (600 MHz, Chloroform-d) δ 7.95 (d, J = 8.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.0 Hz, 2H), 6.98 (s, 2H), 6.79 (s, 2H), 6.44 (d, J = 16.0 Hz, 2H), 4.45 (d, J = 15.9 Hz, 2H), 2.42 (s, 6H), 2.26 (s, 6H), 1.44 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 210.4 (dd, J(^{109}Ag, ^{13}C) = 267.7 Hz, J(^{107}Ag, ^{13}C) = 226.7 Hz), 146.5, 137.9, 135.4, 134.1, 133.8, 133.0, 131.4, 130.7, 130.2, 130.2, 126.0, 57.2, 57.1, 21.1, 18.6, 18.3.

IR (υ/cm^{-1}): 3029 (w), 2969 (w), 2914 (w), 1740 (m), 1498 (vs), 1471 (s), 1358 (m), 1306 (m), 1284 (w), 1190 (w), 1031 (w), 993 (w), 854 (w), 820 (m), 773 (m), 678 (w).

E.A. found (calcd.), %: C 59.77 (60.02), H 5.17 (5.20), N 4.43 (4.52).

*(2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)silver(I) bromide (7**b**)*



Reaction of 38.8 mg (0.167 mmol) of Ag_2O and 100 mg (0.167 mmol) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4b**) in 2 ml of dry dichloromethane gave 47.1 mg (40%) of product as white solid.

Reaction of 38.8 mg (0.167 mmol) of Ag_2O and 100 mg (0.167 mmol) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (**4b**) in 2 ml of dry THF gave 100 mg (85%) of product as white solid. Mp = 290°C

^{1}H NMR (600 MHz, Chloroform-d) δ 7.97 (dd, J = 8.3, 1.3 Hz, 2H), 7.46 (dd, J = 8.2, 6.9 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.31 (dd, J = 7.0, 1.3 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 7.10 (dd, J = 7.7, 1.5 Hz, 2H), 6.44 (d, J = 15.9 Hz, 2H), 4.58 (d, J = 15.9 Hz, 2H), 3.30 (hept, J = 6.9 Hz, 2H), 2.30 (hept, J = 6.7 Hz, 2H), 1.47 (d, J = 6.9 Hz, 6H), 1.41 (d, J = 6.8 Hz, 6H), 1.02 (d, J = 6.8 Hz, 6H), 0.68 (d, J = 6.7 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 211.8 (dd, J(^{109}Ag, ^{13}C) = 261.3 Hz, J(^{107}Ag, ^{13}C) = 227.2 Hz), 145.3, 145.2, 145.1, 131.8, 131.0, 129.5, 125.9, 125.4, 125.3, 58.9, 58.8, 29.4, 28.1, 26.3, 25.4, 25.0, 24.1.

IR (υ/cm^{-1}): 2962 (vs), 2923 (m), 2863 (m), 1589 (w), 1496 (s), 1456 (m), 1381 (m), 1356 (m), 1300 (m), 1178 (m), 1051 (m), 812 (m), 796 (m), 765 (m).

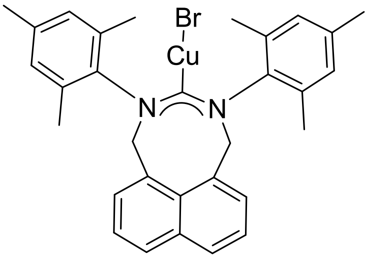
E.A. found (calcd.), %: C 63.26 (63.08), H 6.35 (6.29), N 3.70 (3.98).

Copper complexes

General procedure for preparation of copper complexes

A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol (1 eq) of corresponding silver complex, 1 mmol of copper halide and 2 ml of dichloromethane. Reaction mixture was stirred for 24 h at room temperature, filtered through celite and evaporated to dryness. Resulting solid was recrystallized from dichloromethane-diethyl ether mixture.

*(2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)copper(I) bromide (**8a**)*



Yield 84%. White microcrystalline solid. Mp = 295°C.

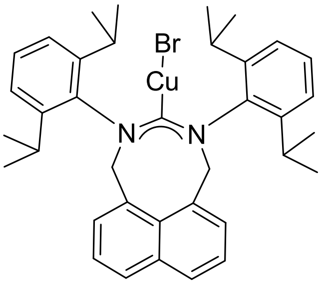
^{1}H NMR (600 MHz, Chloroform-d) δ 7.95 (dd, J = 8.3, 1.3 Hz, 2H), 7.43 (dd, J = 8.2, 7.0 Hz, 2H), 7.20 (dd, J = 7.0, 1.3 Hz, 2H), 6.98 (s, 2H), 6.80 (s, 2H), 6.43 (d, J = 15.9 Hz, 2H), 4.39 (d, J = 15.9 Hz, 2H), 2.44 (s, 6H), 2.27 (s, 6H), 1.50 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 203.6, 145.3, 137.8, 135.5, 134.3, 134.0, 133.3, 131.4, 131.3, 130.7, 130.1, 130.1, 125.9, 57.3, 21.1, 18.7, 18.5.

IR (υ/cm^{-1}): 3025 (w), 2979 (m), 2946 (w), 2913 (w), 1740 (w), 1600 (w), 1504 (vs), 1471 (s), 1432 (m), 1351 (m), 1303 (s), 1187 (m), 1031 (m), 1002 (m), 852 (m), 819 (m), 771 (s), 682 (m).

E.A. found (calcd.), %: C 62.71 (63.08), H 6.13 (6.29), N 3.71 (3.98).

*(2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)copper(I) bromide (**8b**)*



Yield 83%. White microcrystalline solid. Mp = 312°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.96 (dd, J = 8.3, 1.3 Hz, 2H), 7.45 (dd, J = 8.2, 6.9 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.31 (dd, J = 7.0, 1.3 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.10 (dd, J = 7.7, 1.5 Hz, 2H), 6.43 (d, J = 15.9 Hz, 2H), 4.52 (d, J = 15.9 Hz, 2H), 3.31 (p, J = 6.8 Hz, 2H), 2.31 (p, J = 6.8 Hz, 2H), 1.47 (d, J = 6.9 Hz, 6H), 1.43 (d, J = 6.8 Hz, 6H), 1.04 (d, J = 6.9 Hz, 6H), 0.69 (d, J = 6.7 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 204.7, 145.5, 145.3, 144.0, 135.4, 132.1, 131.7, 131.5, 130.9, 129.3, 125.9, 125.2, 125.1, 59.0, 29.4, 28.2, 26.2, 25.2, 25.0, 24.1.

IR (υ/cm^{-1}): 2958 (s), 2925 (m), 2865 (w), 1654 (vs), 1504 (w), 1462 (m), 1446 (m), 1388 (m), 1365 (m), 1321 (m), 1267 (m), 1184 (m), 1166 (m), 1056 (m), 813 (s), 790 (m), 771 (m), 727 (s).

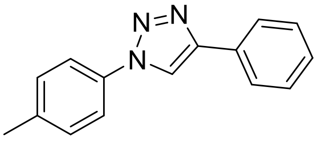
E.A. found (calcd.), %: C 62.61 (63.08), H 6.13 (6.29), N 3.71 (3.98).

General procedure for solvent free click reaction

A screw-cap vial equipped with a magnetic stir bar was charged with organic azide (1.0 mmol, 1 eq), terminal acetylene (1.03 mmol, 1.03 eq) and 1mol% (NHC)CuX. The reaction mixture was stirred at 25°C overnight (unoptimized). The reaction mixture was dissolved in 10 ml of dichloromethane and filtered through pad (4.5 cm) of silica gel. Concentration of containing product fractions in vacuum afforded 1,4-disubstitued 1,2,3-triazole.

1,2,3-triazoles

*4-phenyl-1-p-tolyl-1H-1,2,3-triazole (**9a**)*[13]

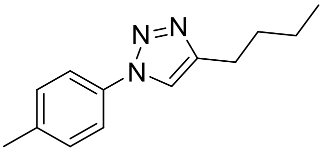


White solid. Mp = 166-167°C

^{1}H NMR (600 MHz, Chloroform-d) δ 8.16 (s, 1H), 7.91 (d, J = 7.2 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 148.3, 139.0, 134.8, 130.4, 130.4, 129.0, 128.5, 125.9, 120.5, 117.8, 21.2.

*4-Butyl-1-p-tolyl-1H-1,2,3-triazole (**9b**)*[14]

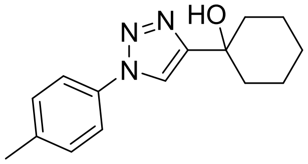


White solid. Mp = 52-54°C

^{1}H NMR (600 MHz, Chloroform-d) δ 7.85 – 7.50 (m, 3H), 7.29 (d, J = 7.9 Hz, 2H), 2.79 (s, 2H), 2.41 (s, 3H), 1.73 (s, 2H), 1.44 (d, J = 9.0 Hz, 2H), 0.96 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 149.0, 138.3, 135.0, 130.1, 120.2, 118.9, 31.5, 25.3, 22.3, 21.0, 13.8.

*1-(1-p-tolyl-1H-1,2,3-triazol-4-yl)cyclohexanol (**9c**)*[15]

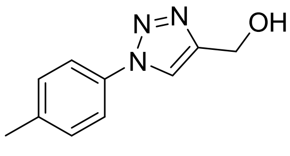


White solid. Mp = 192-195°C

^{1}H NMR (600 MHz, DMSO-d6) δ 8.45 (s, 1H), 7.76 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 4.76 (s, 1H), 2.38 (s, 3H), 2.03 – 1.92 (m, 2H), 1.84 – 1.77 (m, 2H), 1.76 – 1.70 (m, 2H), 1.57 – 1.44 (m, 3H), 1.39 – 1.29 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d6) δ 156.4, 137.6, 134.5, 129.9, 119.6, 118.8, 67.8, 37.6, 25.0, 21.5, 20.2.

*(1-p-Tolyl-1H-1,2,3-triazol-4-yl)methanol (**9d**)*[16]

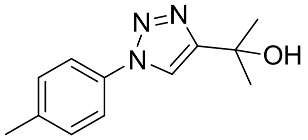


White solid. Mp = 124-125°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (s, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 4.88 (s, 2H), 3.41 (br. s, 1H), 2.40 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 148.7, 139.1, 134.9, 130.4, 120.6, 120.6, 56.4, 21.2.

*2-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)propan-2-ol (**9e**)*[17]

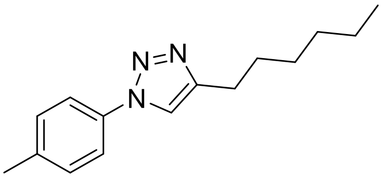


White crystals. Mp = 120–121°C

^1H NMR (600 MHz, Chloroform-d) δ 8.04 (br. s, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 2.66 (br. s, 1H), 2.40 (s, 3H), 1.73 (s, 6H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 156.3, 138.8, 134.9, 130.3, 120.5, 117.7, 68.7, 30.6, 21.2.

*4-Hexyl-1-p-tolyl-1H-1,2,3-triazole (**9f**)*[18]

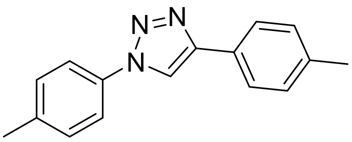


White solid. Mp = 64-66°C.

^1H NMR (600 MHz, Chloroform-d) δ 7.75 (br. s., 1H), 7.62 (d, J = 7.9 Hz, 2H), 7.30 (dd, J = 8.0, 1.0 Hz, 2H), 2.92 – 2.65 (m, 2H), 2.41 (s, 3H), 1.84 – 1.68 (m, 2H), 1.50 – 1.38 (m, 2H), 1.38 – 1.28 (m, 4H), 0.90 (t, J = 6.7 Hz, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 149.2, 138.4, 135.1, 130.2, 120.3, 119.0, 31.6, 29.4, 29.0, 25.8, 22.6, 21.1, 14.1.

*1,4-di-p-Tolyl-1H-1,2,3-triazole (**9g**)*[19]

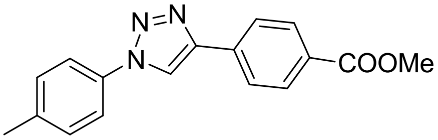


White solid. Mp = 203-205°C.

^1H NMR (600 MHz, Chloroform-d) δ 8.12 (s, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 148.4, 138.9, 138.3, 134.9, 130.3, 129.7, 127.6, 125.8, 120.5, 117.4, 21.4, 21.2.

*Methyl 4-(1-p-tolyl-1H-1,2,3-triazol-4-yl)benzoate (**9h**)*



White solid. Mp = 240-242°C.

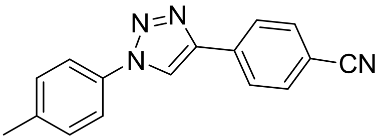
^{1}H NMR (600 MHz, DMSO-d6) δ 9.40 (s, 1H), 8.12 – 8.04 (m, 4H), 7.84 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 3.88 (s, 3H), 2.40 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d6) δ 165.9, 146.1, 138.5, 134.8, 134.3, 130.3, 129.9, 128.9, 125.4, 120.8, 119.9, 52.2, 20.6.

IR (υ/cm^{-1}): 3122 (w), 3107 (w), 2949 (w), 1709 (vs),1614 (m), 1518 (m), 1437 (m), 1408 (w), 1375 (w),1273 (s), 1230 (m), 1103 (s), 1041 (m), 815 (s), 775 (s).

E.A. found (calcd.), %: C 69.28 (69.61), H 5.16 (5.15), N 13.96 (14.33).

*4-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)benzonitrile (**9i**)*



White solid. Mp = 240-242°C.

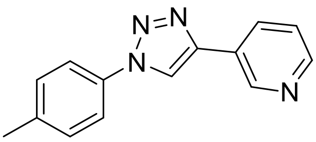
^{1}H NMR (600 MHz, DMSO-d6) δ 9.39 (s, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d6) δ 145.6, 138.6, 134.8, 134.2, 133.0, 130.3, 125.8, 121.1, 119.9, 118.7, 110.4, 20.6.

IR (υ/cm^{-1}): 3124 (w), 3103 (m), 2229 (m), 1612 (m), 1518 (m), 1487 (m), 1228 (m), 1039 (m), 816 (vs).

E.A. found (calcd.), %: C 73.50 (73.83), H 4.67 (4.65), N 21.53 (21.52).

*3-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)pyridine (**9j**)*[19]

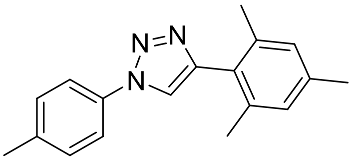


White solid. Mp = 179-181°C.

^{1}H NMR (600 MHz, DMSO-d6) δ 9.37 (s, 1H), 9.17 (s, 1H), 8.61 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.44 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d6) δ 149.1, 146.5, 144.4, 138.5, 134.3, 132.4, 130.3, 126.6, 124.2, 120.2, 119.9, 20.6.

*4-Mesityl-1-p-tolyl-1H-1,2,3-triazole (**9k**)*



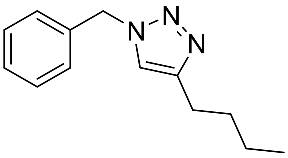
White solid. Mp = 133-135°C.

^1H NMR (600 MHz, Chloroform-d) δ 7.88 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 6.97 (s, 2H), 2.44 (s, 3H), 2.34 (s, 3H), 2.18 (s, 6H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 146.3, 138.7, 138.3, 137.9, 135.0, 130.3, 128.5, 126.9, 120.5, 120.3, 21.2, 21.1, 20.8.

E.A. found (calcd.), %: C 77.59 (77.95), H 6.93 (6.90), N 15.17 (15.15).

*1-Benzyl-4-butyl-1H-1,2,3-triazole (**10a**)*[20]

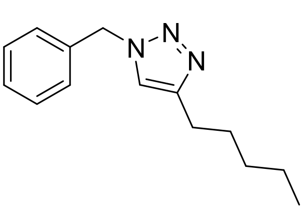


White solid. Mp = 54°C.

^1H NMR (600 MHz, Chloroform-d) δ 7.34 – 7.28 (m, 3H), 7.26 – 7.15 (m, 3H), 5.45 (s, 2H), 2.65 (t, J = 7.8 Hz, 2H), 1.60 (t, J = 7.7 Hz, 2H), 1.33 (q, J = 7.4 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 148.9, 135.0, 129.0, 128.5, 127.9, 120.6, 54.0, 31.5, 25.4, 22.3, 13.8.

*1-Benzyl-4-pentyl-1H-1,2,3-triazole (**10b**)*[20]

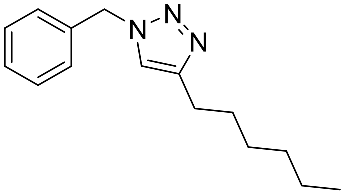


White solid. Mp = 33°C.

^1H NMR (600 MHz, Chloroform-d) δ 7.41 – 7.31 (m, 3H), 7.27 – 7.22 (m, 2H), 7.18 (s, 1H), 5.49 (s, 2H), 2.69 – 2.66 (m, 2H), 1.66 – 1.61 (m, 2H), 1.35 – 1.28 (m, 4H), 0.89 – 0.85 (m, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-d) δ 149.1, 135.1, 129.1, 128.7, 128.0, 120.6, 54.1, 31.6, 29.2, 25.8, 22.5, 14.1.

*1-Benzyl-4-hexyl-1H-1,2,3-triazole (**10c**)*[21]

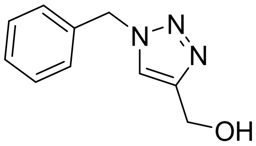


White solid. Mp = 55-56°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.37 – 7.33 (m, 2H), 7.26 – 7.22 (m, 2H), 7.18 (s, 1H), 5.48 (s, 2H), 2.69 – 2.65 (m, 2H), 1.66 – 1.60 (m, 2H), 1.34 – 1.26 (m, 6H), 0.91 – 0.74 (m, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 150.0, 134.9, 128.7, 128.2, 127.6, 121.4, 53.7, 31.3, 29.0, 28.7, 25.5, 22.3, 13.8.

*(1-Benzyl-1H-1,2,3-triazol-4-yl)methanol (**10d**)*[20b, 22]

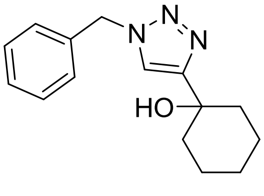


White solid. Mp = 78-79°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.52 (s, 1H), 7.26 – 7.20 (m, 3H), 7.16 – 7.11 (m, 2H), 5.34 (s, 2H), 4.87 (br. s, 1H), 4.62 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 149.2, 134.5, 128.9, 128.5, 127.9, 123.0, 55.6, 54.0.

*1-(1-Benzyl-1H-1,2,3-triazol-4-yl)cyclohexanol (**10e**)*[23]

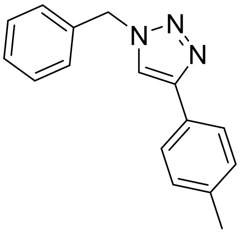


White solid. Mp = 121–122°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.44 – 7.29 (m, 4H), 7.26 – 7.21 (m, 2H), 5.47 (s, 2H), 2.64 (br. s, 1H), 1.98 – 1.87 (m, 2H), 1.87 – 1.79 (m, 2H), 1.78 – 1.66 (m, 2H), 1.63 – 1.54 (m, 1H), 1.54 – 1.46 (m, 2H), 1.37 – 1.26 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 156.3, 134.8, 129.1, 128.7, 128.2, 119.8, 69.5, 54.2, 38.2, 25.4, 22.0.

*1-Benzyl-4-p-tolyl-1H-1,2,3-triazole (**10f**)*[21]

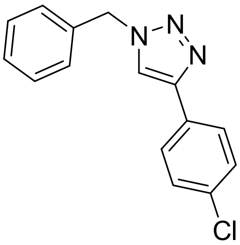


White solid. Mp = 151-153°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.69 (d, J = 8.1 Hz, 2H), 7.62 (s, 1H), 7.41 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.56 (s, 2H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 148.4, 138.1, 134.9, 129.6, 129.3, 128.9, 128.2, 127.8, 125.7, 119.3, 54.3, 21.4 .

*1-Benzyl-4-(4-chlorophenyl)-1H-1,2,3-triazole (**10g**)*[24]

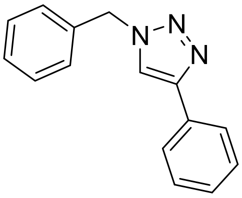


White solid. Mp = 143-145°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.72 (d, J = 8.6 Hz, 2H), 7.66 (s, 1H), 7.41 – 7.33 (m, 5H), 7.30 (dd, J = 7.6, 1.8 Hz, 2H), 5.55 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 147.2, 134.6, 133.9, 129.3, 129.2, 129.1, 128.9, 128.2, 127.0, 119.7, 54.4.

*1-Benzyl-4-phenyl-1H-1,2,3-triazole (**10h**)*[24-25]

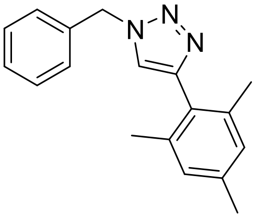


White solid. Mp = 129-130°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.83 – 7.76 (m, 2H), 7.66 (s, 1H), 7.43 – 7.35 (m, 5H), 7.34 – 7.29 (m, 3H), 5.57 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 148.4, 134.8, 130.7, 129.3, 128.9, 128.9, 128.3, 128.2, 125.8, 119.6, 54.4.

1-Benzyl-4-mesityl-1H-1,2,3-triazole ***(10i)***[26]

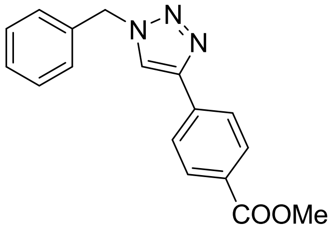


White solid. Mp = 126-128°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.41 – 7.34 (m, 4H), 7.29 – 7.26 (m, 2H), 6.91 (s, 2H), 5.62 (s, 2H), 2.30 (s, 3H), 2.08 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 146.1, 138.1, 137.8, 135.2, 129.2, 128.7, 128.4, 127.8, 127.2, 122.7, 54.1, 29.8, 21.2, 20.8.

Methyl 4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzoate ***(10j)***[25b, 27]

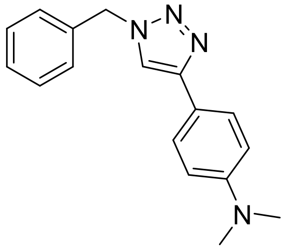


Off-white solid. Mp = 146°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.06 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.74 (s, 1H), 7.42 – 7.35 (m, 3H), 7.34 – 7.30 (m, 2H), 5.58 (s, 2H), 3.92 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 166.9, 147.3, 135.0, 134.6, 130.3, 129.7, 129.4, 129.1, 128.3, 125.6, 120.4, 54.5, 52.3.

4-(1-Benzyl-1H-1,2,3-triazol-4-yl)-N,N-dimethylaniline ***(10k)***[25b]

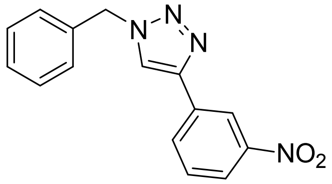


Light brown solid. Mp = 171-172°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.67 (d, J = 8.4 Hz, 2H), 7.54 (s, 1H), 7.36 (d, J = 7.4 Hz, 3H), 7.31 – 7.27 (m, 2H), 6.74 (d, J = 8.1 Hz, 2H), 5.53 (s, 2H), 2.97 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 150.5, 148.8, 135.1, 129.2, 128.7, 128.1, 126.7, 118.9, 118.2, 112.5, 54.2, 40.6

*1-Benzyl-4-(3-nitrophenyl)-1H-1,2,3-triazole (**10l**)*[25b]

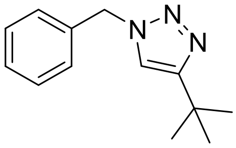


Off-white solid. Mp = 134-135°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.96 (d, J = 7.8 Hz, 1H), 7.83 – 7.73 (m, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.29 – 7.26 (m, 2H), 5.55 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 148.1, 142.6, 134.4, 132.5, 131.0, 129.1, 129.0, 128.8, 128.0, 124.7, 124.0, 123.2, 54.3.

*1-Benzyl-4-tert-butyl-1H-1,2,3-triazole (**11a**)*[28]

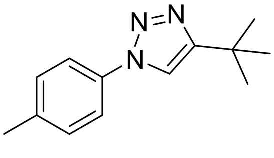


White solid. Mp = 84-86°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.34 – 7.21 (m, 3H), 7.19 – 7.14 (m, 2H), 7.08 (s, 1H), 5.39 (s, 2H), 1.23 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 158.3, 135.2, 129.1, 128.6, 128.1, 118.5, 54.0, 30.9, 30.4.

*4-tert-Butyl-1-p-tolyl-1H-1,2,3-triazole (**11b**)*



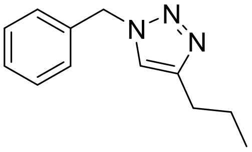
White solid. Mp = 94-95°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.63 (s, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 2.37 (s, 3H), 1.38 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 158.3, 138.4, 135.2, 130.2, 120.4, 116.9, 30.9, 30.4, 21.1.

E.A. found (calcd.), %: C 72.50 (72.52), H 7.70 (7.96), N 19.15 (19.52).

*1-Benzyl-4-propyl-1H-1,2,3-triazole (**11c**)*[28]

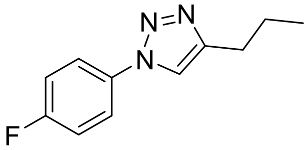


White solid. Mp = 52°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.33 – 7.28 (m, 3H), 7.26 – 7.16 (m, 3H), 5.44 (s, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.63 (q, J = 7.3 Hz, 2H), 0.90 (t, J = 7.3 Hz, 3H)

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 148.4, 135.0, 128.8, 128.3, 127.7, 120.6, 53.7, 27.5, 22.5, 13.6.

*1-(4-Fluorophenyl)-4-propyl-1H-1,2,3-triazole (**11d**)*



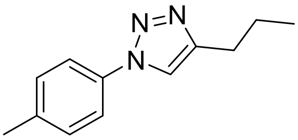
White solid. Mp = 73-74°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.71 – 7.65 (m, 3H), 7.22 – 7.16 (m, 2H), 2.76 (t, J = 7.6 Hz, 2H), 1.75 (h, J = 7.4 Hz, 2H), 1.01 (t, J = 7.4 Hz, 4H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 163.2, 161.5, 149.2, 133.7, 122.5, 122.4, 119.2, 116.8, 116.6, 27.8, 22.8, 13.9.

E.A. found (calcd.), %: C 64.60 (64.37), H 5.95 (5.89), N 20.63 (20.47).

*4-Propyl-1-p-tolyl-1H-1,2,3-triazole (**11e**)*



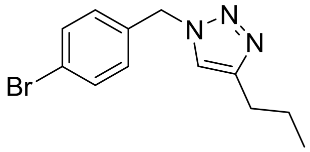
White solid. Mp = 60°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.71 (s, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H), 2.37 (s, 3H), 1.73 (q, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 148.8, 138.4, 135.1, 130.2, 120.3, 119.1, 27.7, 22.7, 21.1, 13.8.

E.A. found (calcd.), %: C 71.49 (71.61), H 7.06 (7.51), N 21.15 (20.88).

*1-(4-Bromobenzyl)-4-propyl-1H-1,2,3-triazole (**11f**)*



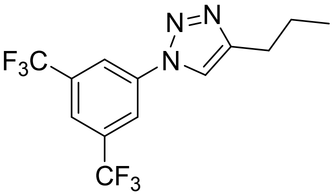
White solid. Mp = 61-62°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.47 (d, J = 8.4 Hz, 2H), 7.19 (s, 1H), 7.10 (d, J = 8.3 Hz, 2H), 5.43 (s, 2H), 2.65 (t, J = 7.6 Hz, 2H), 1.65 (h, J = 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 149.0, 134.2, 132.3, 129.6, 122.8, 120.7, 53.3, 27.8, 22.7, 13.9.

E.A. found (calcd.), %: C 51.30 (51.44), H 5.00 (5.04), N 14.75 (15.00).

*1-(3,5-Bis(trifluoromethyl)phenyl)-4-propyl-1H-1,2,3-triazole (**11g**)*



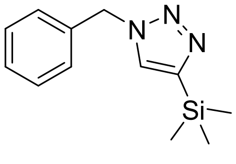
White solid. Mp = 47-48°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.23 (s, 2H), 7.91 (s, 1H), 7.88 (s, 1H), 2.79 (t, J = 7.6 Hz, 2H), 1.78 (h, J = 7.4 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 150.2, 138.4, 134.0, 133.7, 133.5, 133.3, 125.5, 123.7, 121.9, 121.8, 121.8, 120.3, 120.2, 118.8, 27.7, 22.6, 13.8.

E.A. found (calcd.), %: C 48.42 (48.30), H 3.27 (3.43), N 13.04 (13.00).

*1-Benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole (**11h**)*[29]

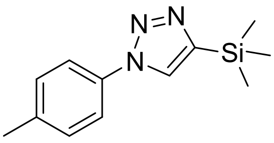


White solid. Mp = 75°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.61 – 7.29 (m, 4H), 7.27 – 7.23 (m, 2H), 5.54 (s, 2H), 0.30 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 147.1, 135.0, 129.0, 128.6, 128.1, 53.6, -1.1.

*1-p-Tolyl-4-(trimethylsilyl)-1H-1,2,3-triazole (**11i**)*[30]

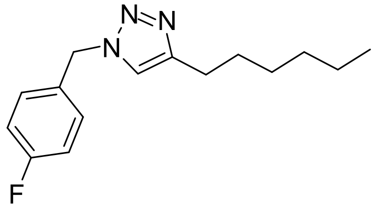


White solid. Mp = 105°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.91 (s, 1H), 7.62 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 2.41 (s, 3H), 0.40 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 147.0, 138.3, 134.7, 130.0, 127.1, 120.5, 20.9, -1.2.

*1-(4-Fluorobenzyl)-4-hexyl-1H-1,2,3-triazole (**11j**)*



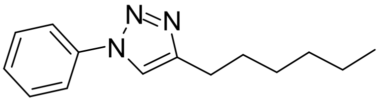
White solid. Mp = 46°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.23 (m, 2H), 7.17 (s, 1H), 7.08 – 6.98 (m, 2H), 5.44 (s, 2H), 2.70 – 2.64 (m, 2H), 1.62 (p, J = 7.6 Hz, 2H), 1.34 – 1.24 (m, 6H), 0.85 (t, J = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 163.7, 162.0, 149.1, 131.0, 129.9, 129.8, 120.5, 116.2, 116.0, 53.3, 31.6, 29.4, 29.0, 25.8, 22.6, 14.1.

E.A. found (calcd.), %: C 68.63 (68.94), H 7.68 (7.71), N 15.94 (16.08).

*4-Hexyl-1-phenyl-1H-1,2,3-triazole (**11k**)*[31]

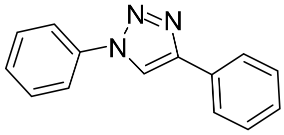


White solid. Mp = 41°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.74 – 7.69 (m, 3H), 7.51 – 7.47 (m, 2H), 7.43 – 7.35 (m, 1H), 2.80 – 2.77 (m, 2H), 1.72 (p, J = 7.6 Hz, 2H), 1.42 – 1.37 (m, 2H), 1.33 – 1.30 (m, 4H), 0.90 – 0.87 (m, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 149.3, 137.4, 129.8, 128.5, 120.5, 118.9, 31.7, 29.5, 29.0, 25.8, 22.7, 14.2.

*1,4-Diphenyl-1H-1,2,3-triazole (**11l**)*[31b]



White solid. Mp = 171°C.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.19 (s, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.54 (t, J = 7.9 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.37 (t, J = 7.4 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 148.6, 137.3, 130.5, 129.9, 129.1, 128.9, 128.6, 126.1, 120.7, 117.7.

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

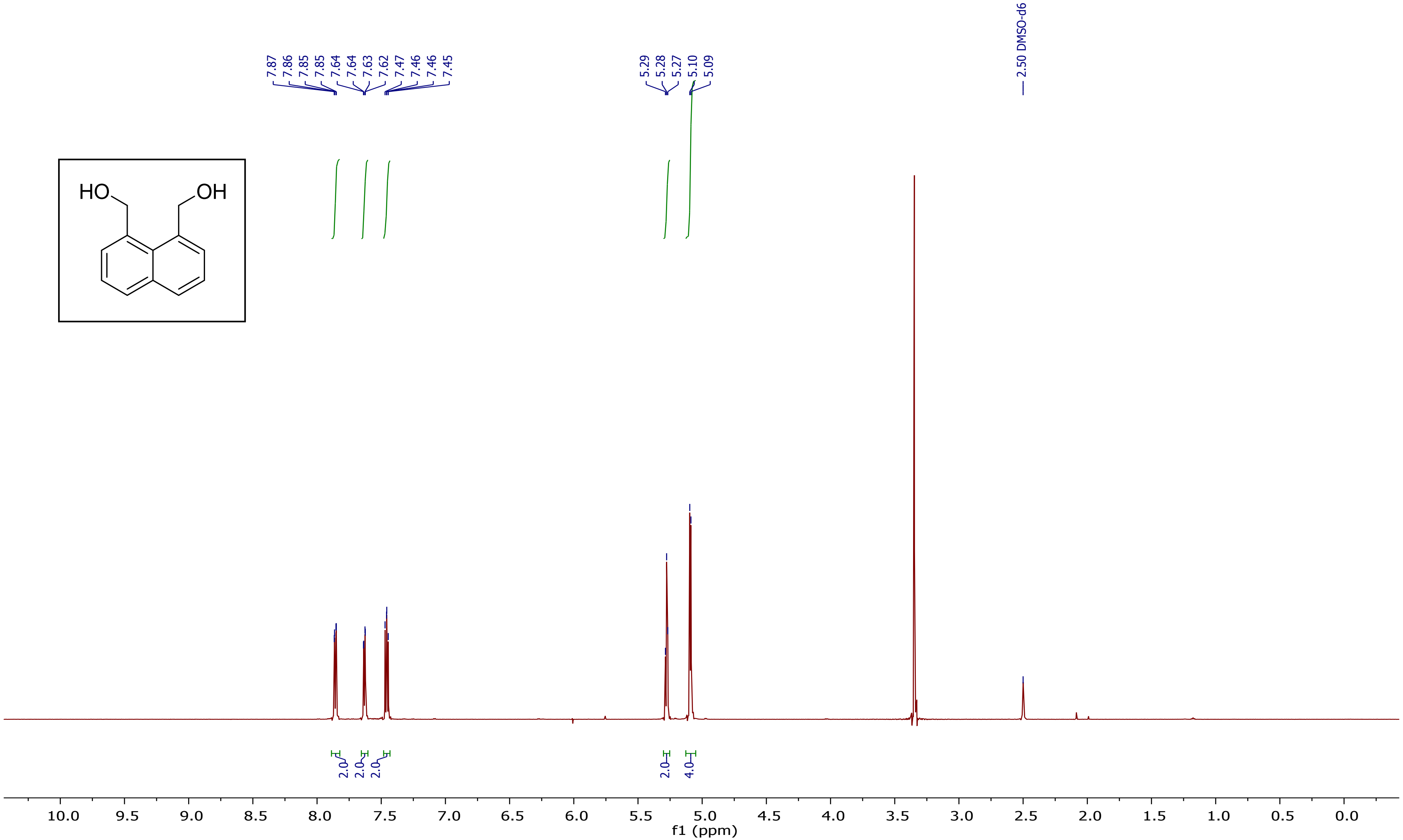


Figure S1. ^{1}H NMR (600 MHz, Chloroform-*d*) of Naphthalene-1,8-diyldimethanol (1).

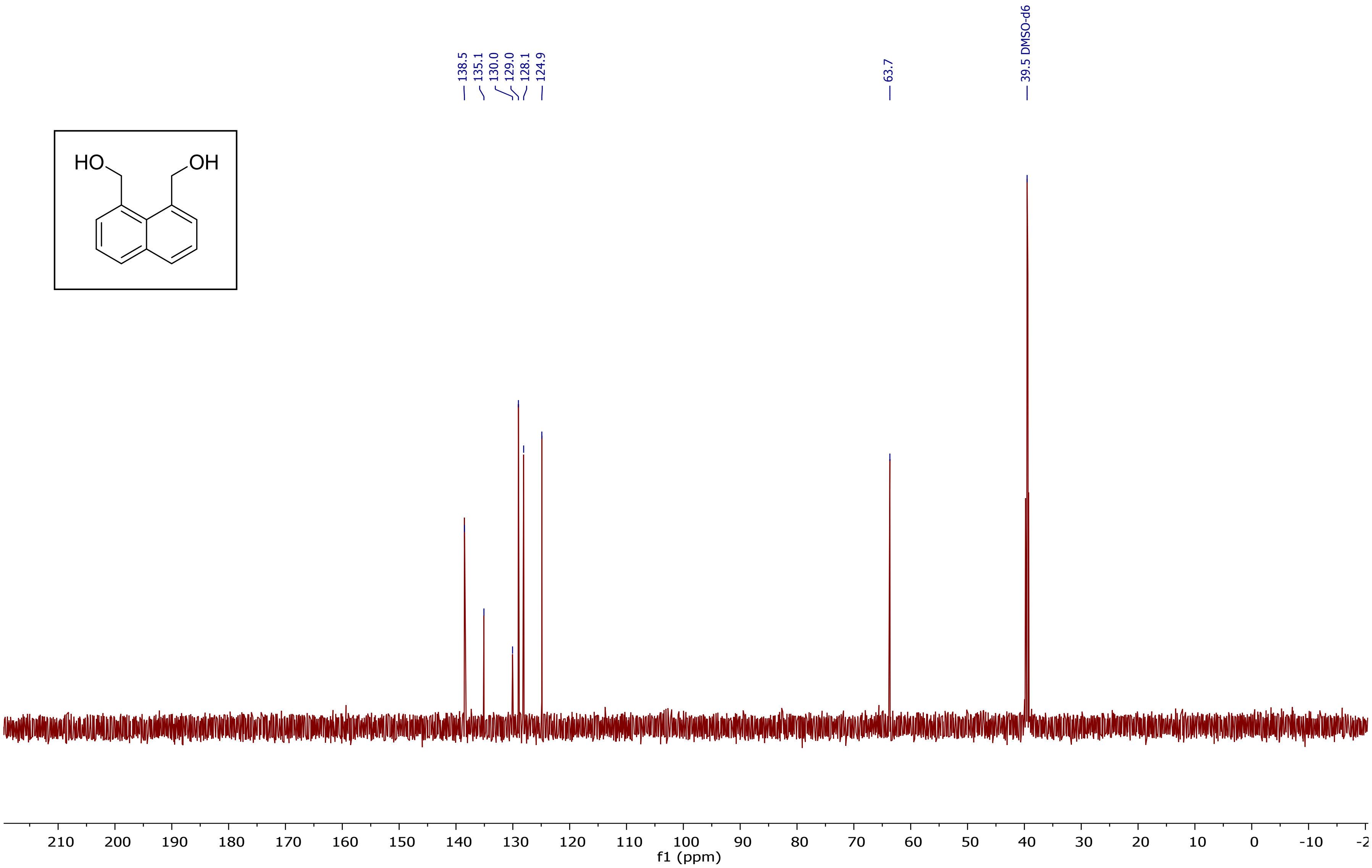


Figure S2. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) of Naphthalene-1,8-diyldimethanol (1).

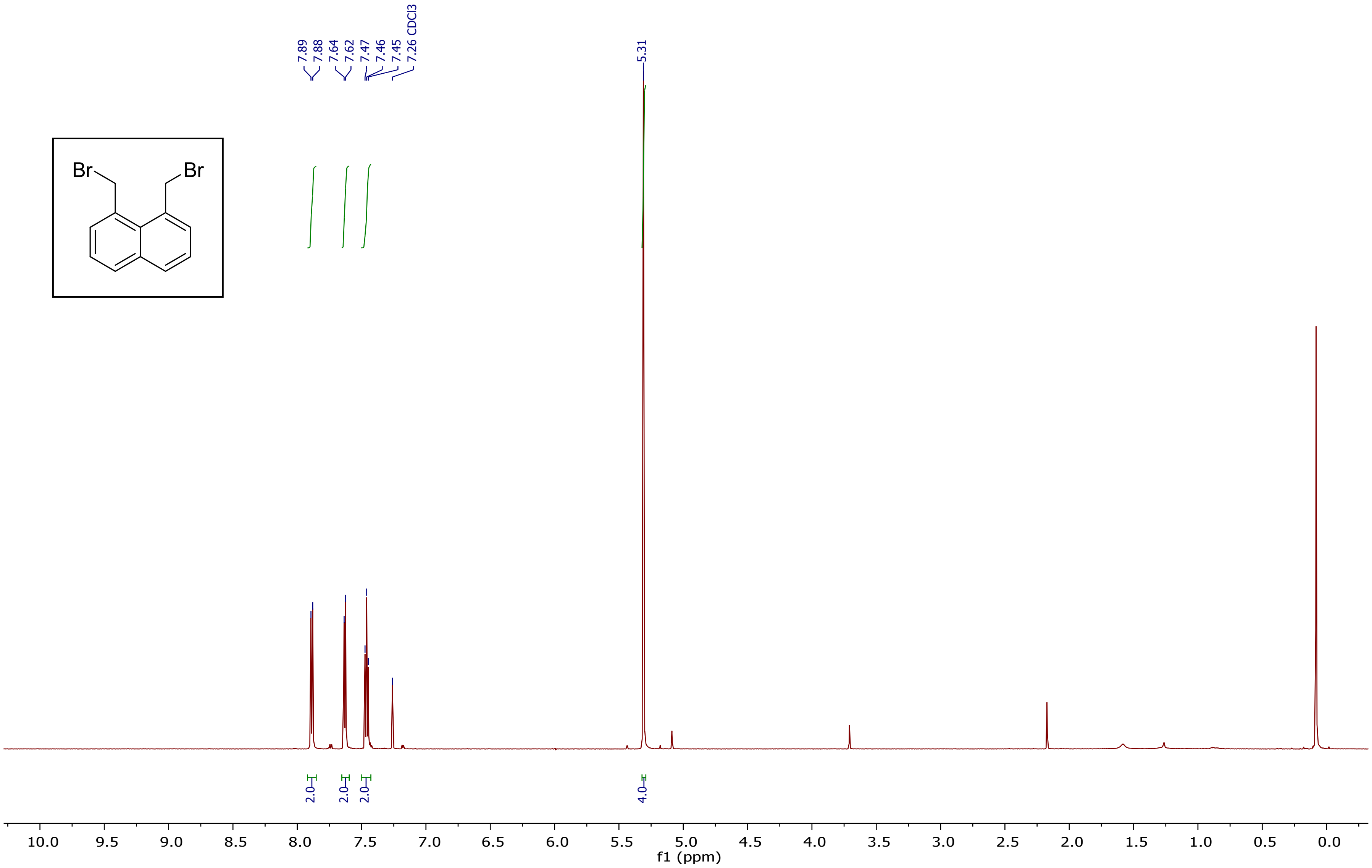


Figure S3. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1,8-Bis(bromomethyl)naphthalene (2).

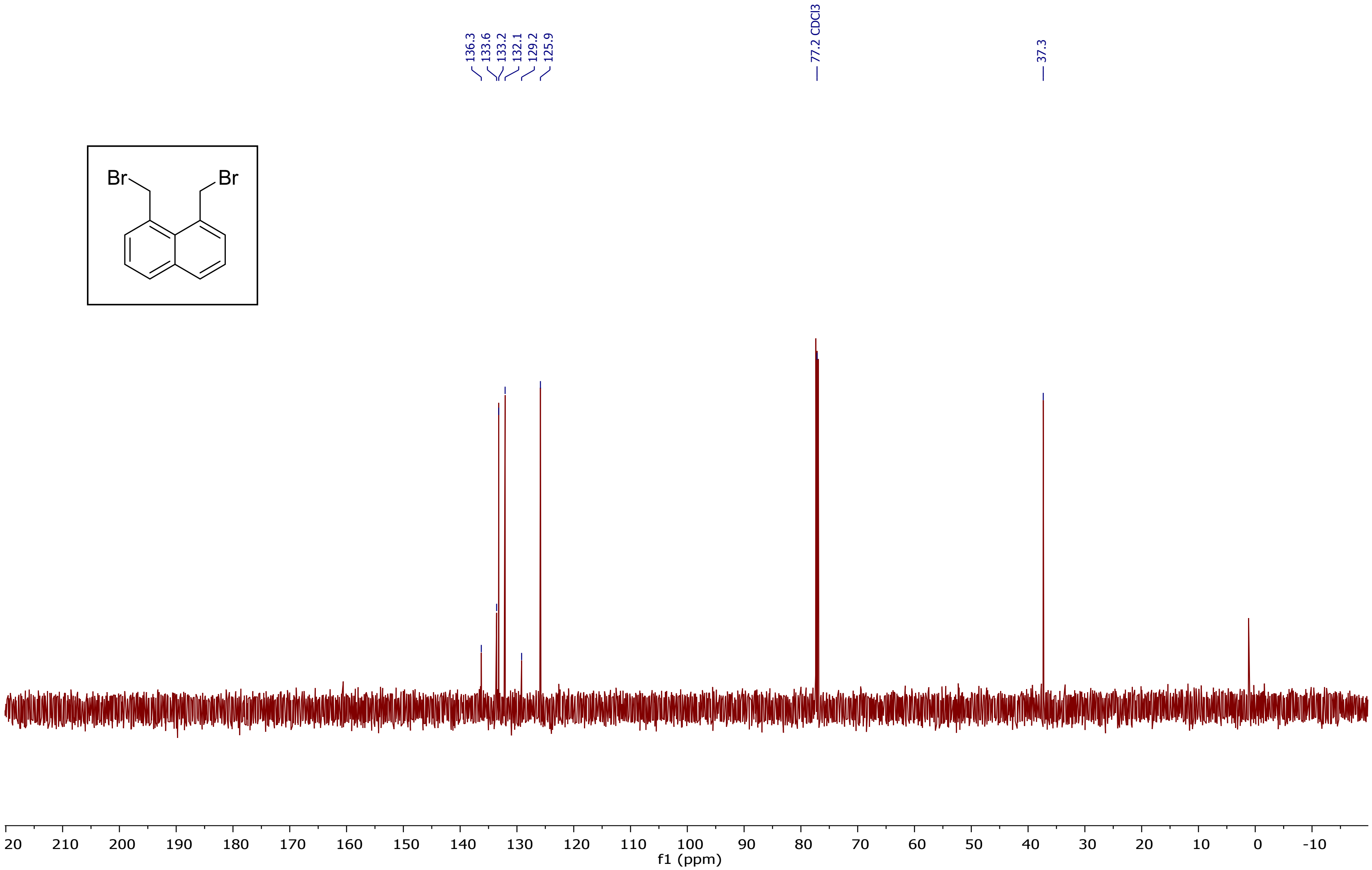


Figure S4. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1,8-Bis(bromomethyl)naphthalene (2).**

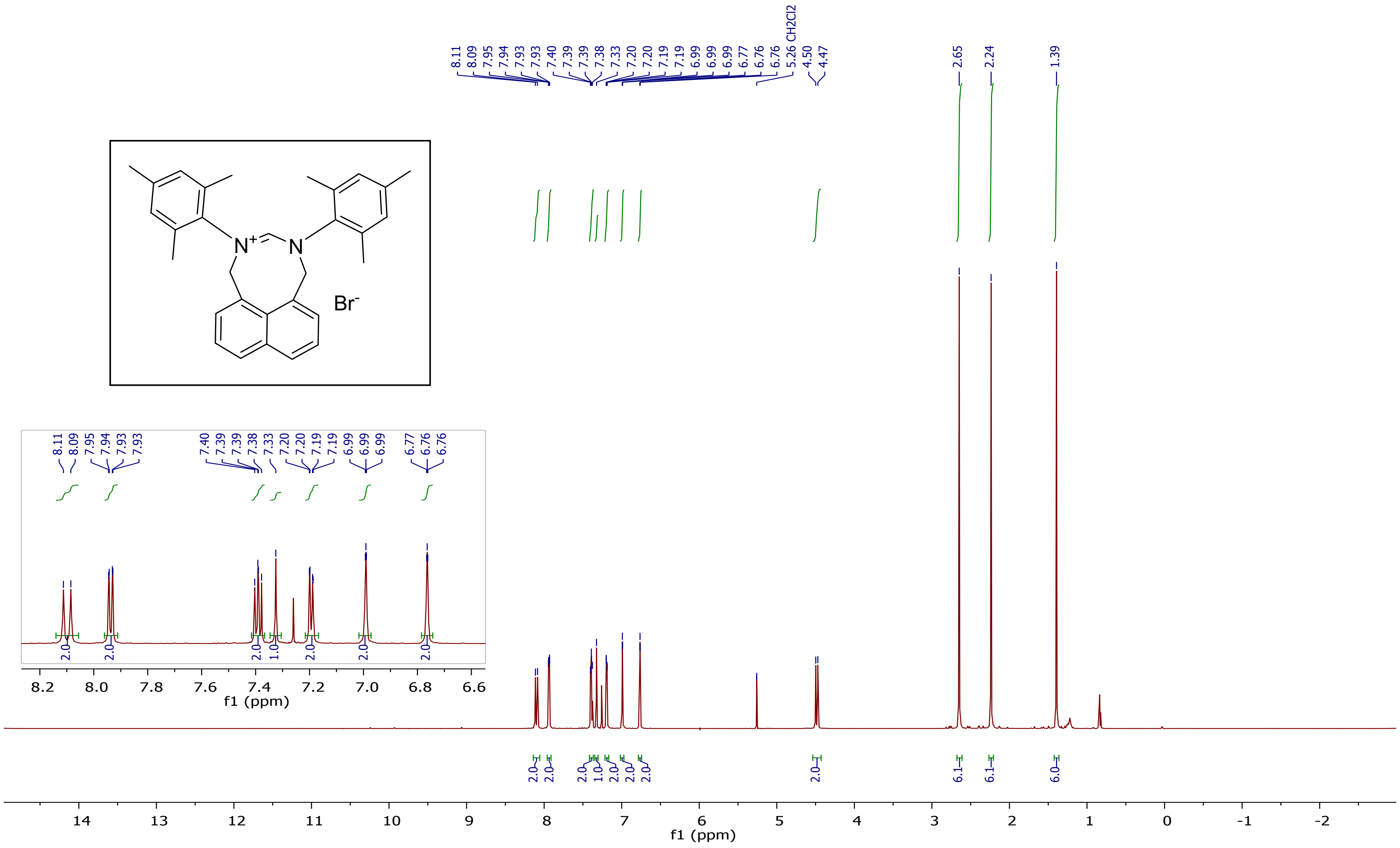


Figure S5. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (4a).

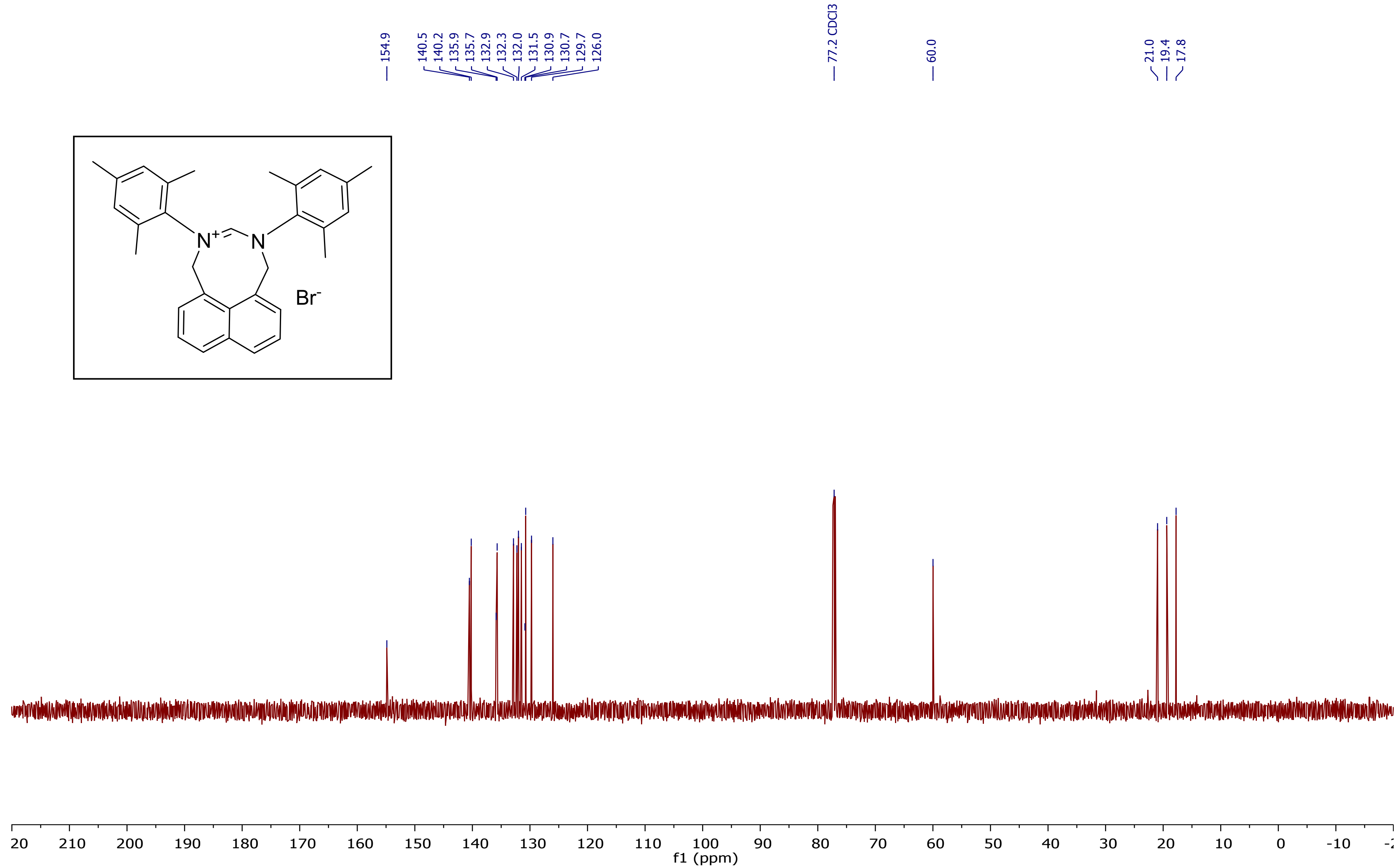


Figure S6. ^{13}C{^{1}H} **NMR (151 MHz, Chloroform-*d*) of 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (4a).**

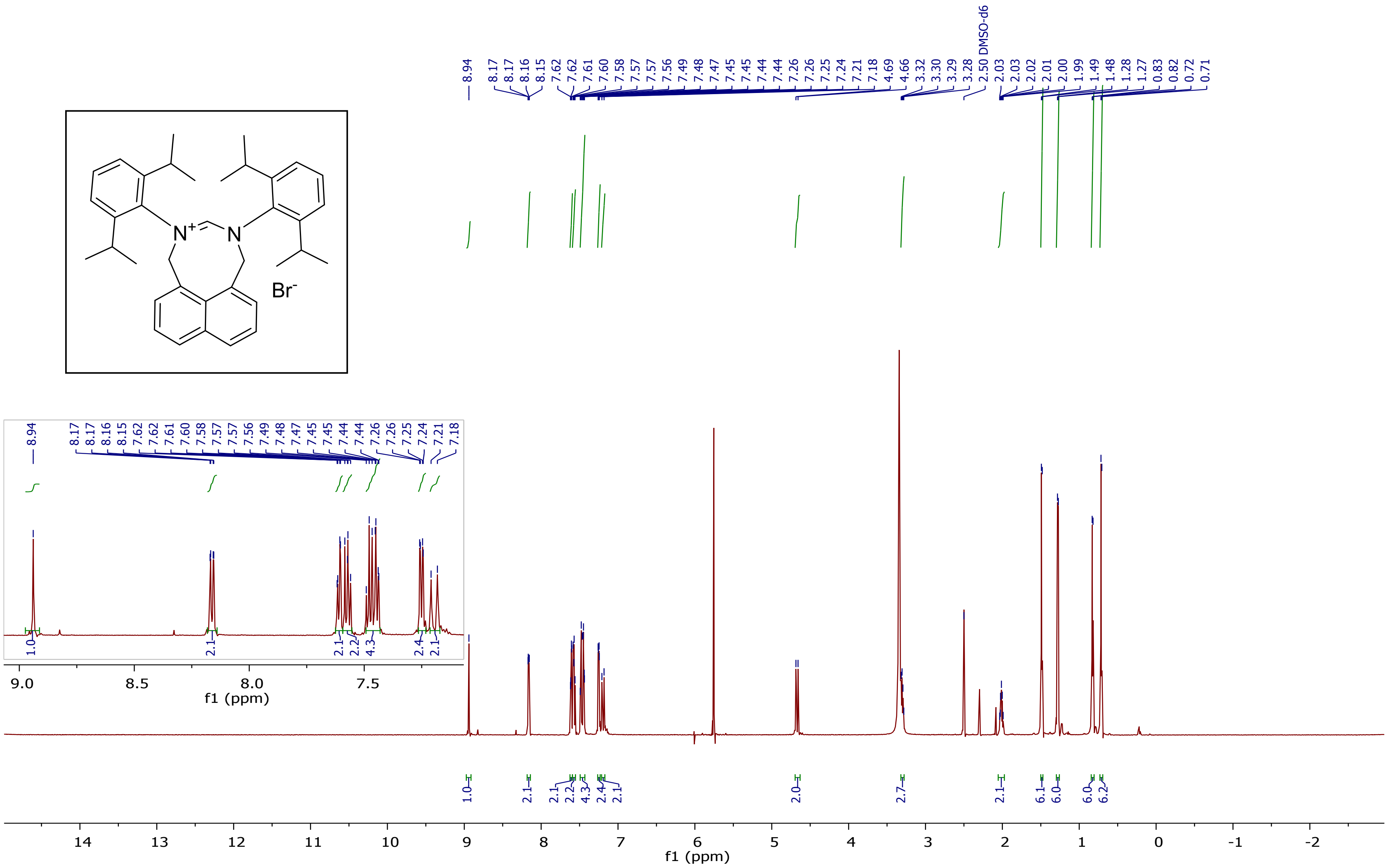


Figure S7. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (4b).

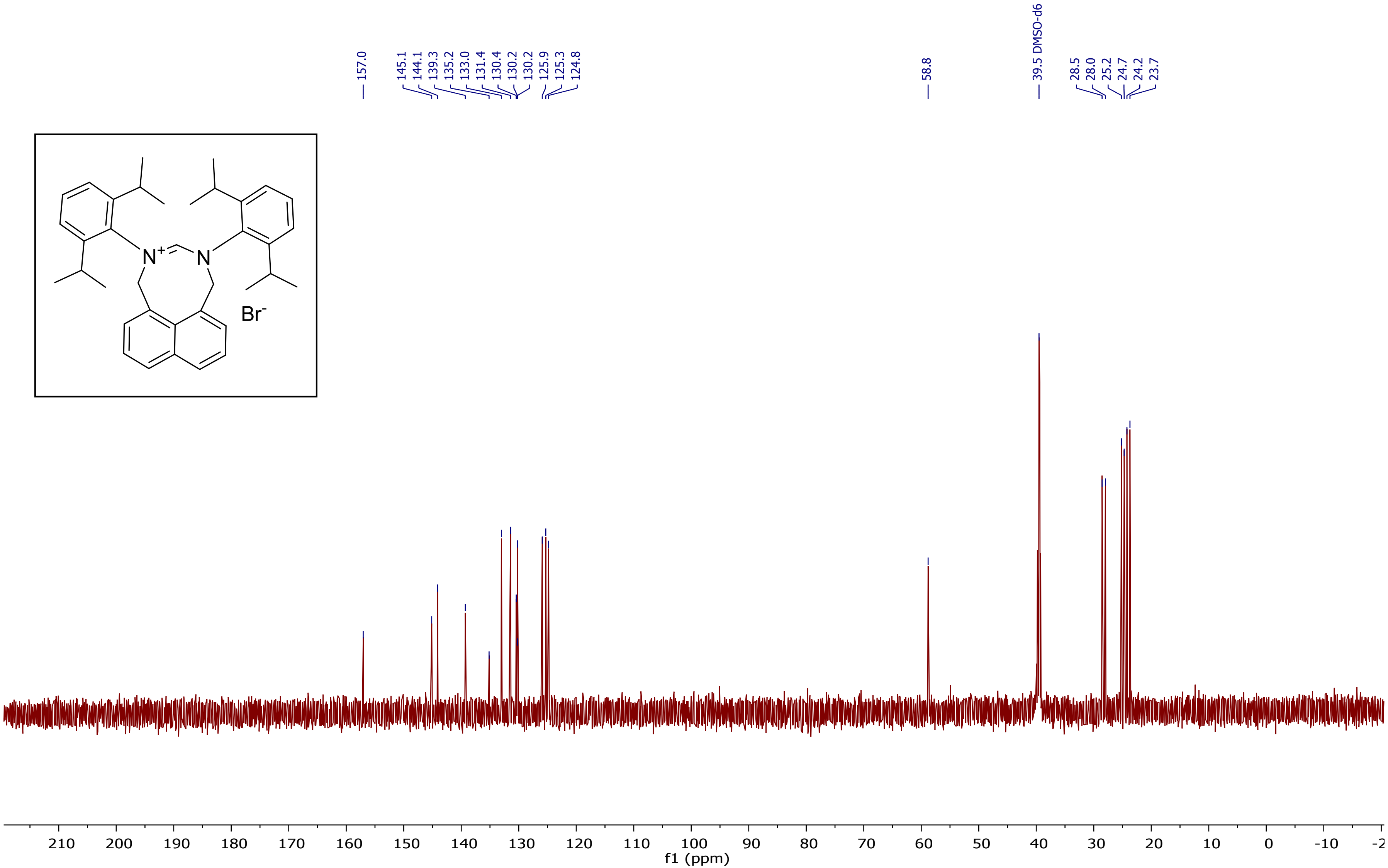


Figure S8. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium bromide (4b).**

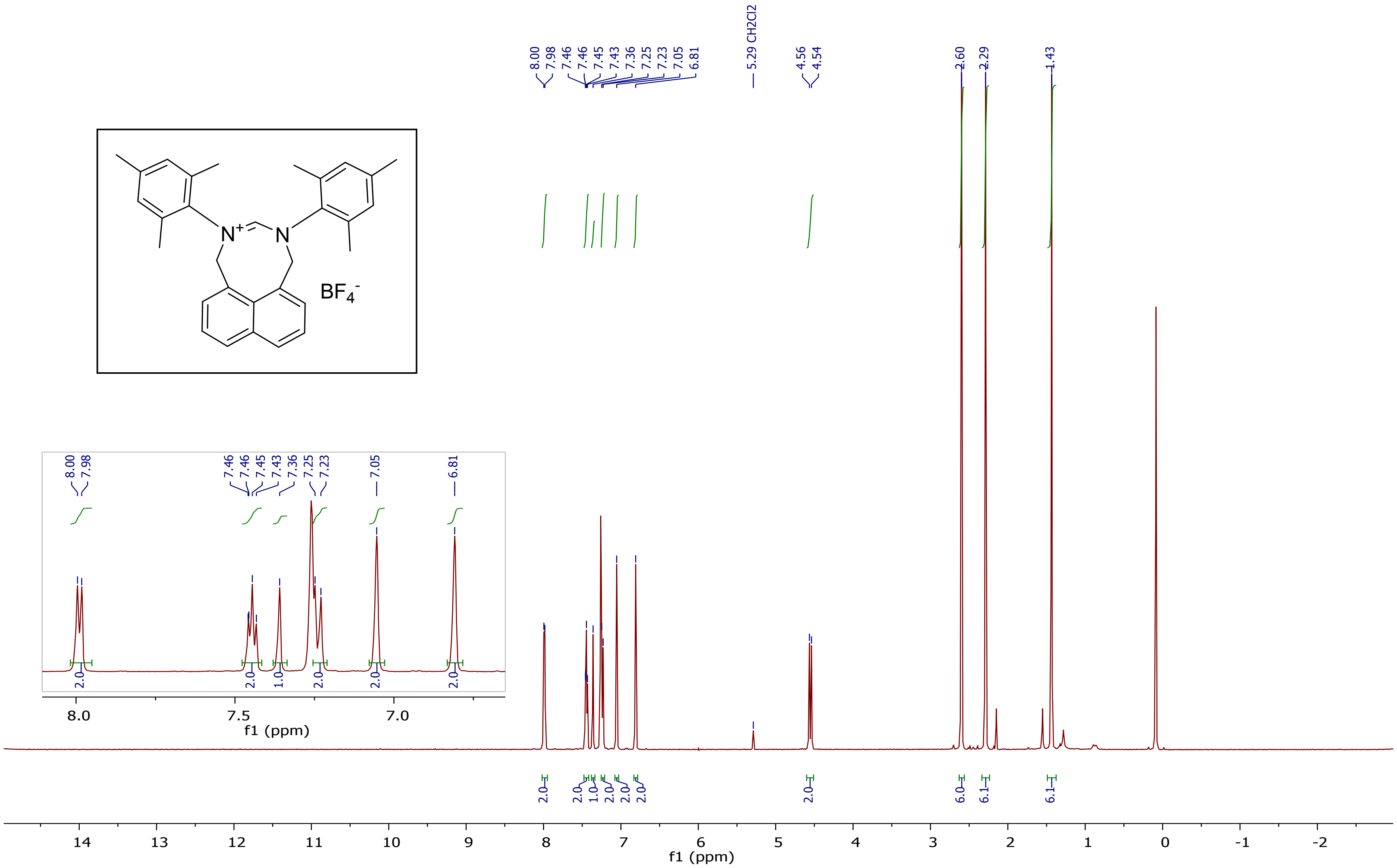


Figure S9. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (5a).

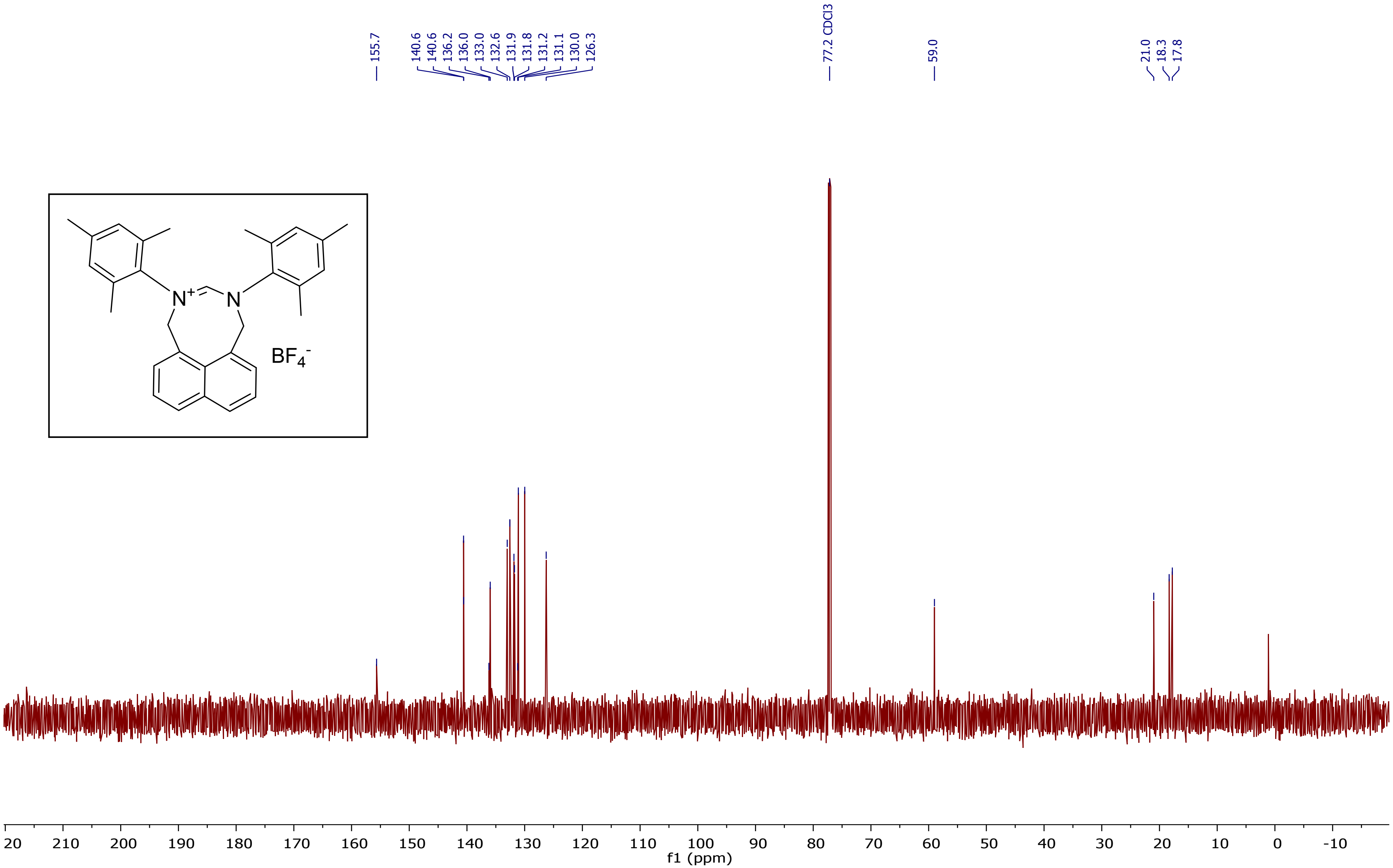


Figure S10. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (5a).**

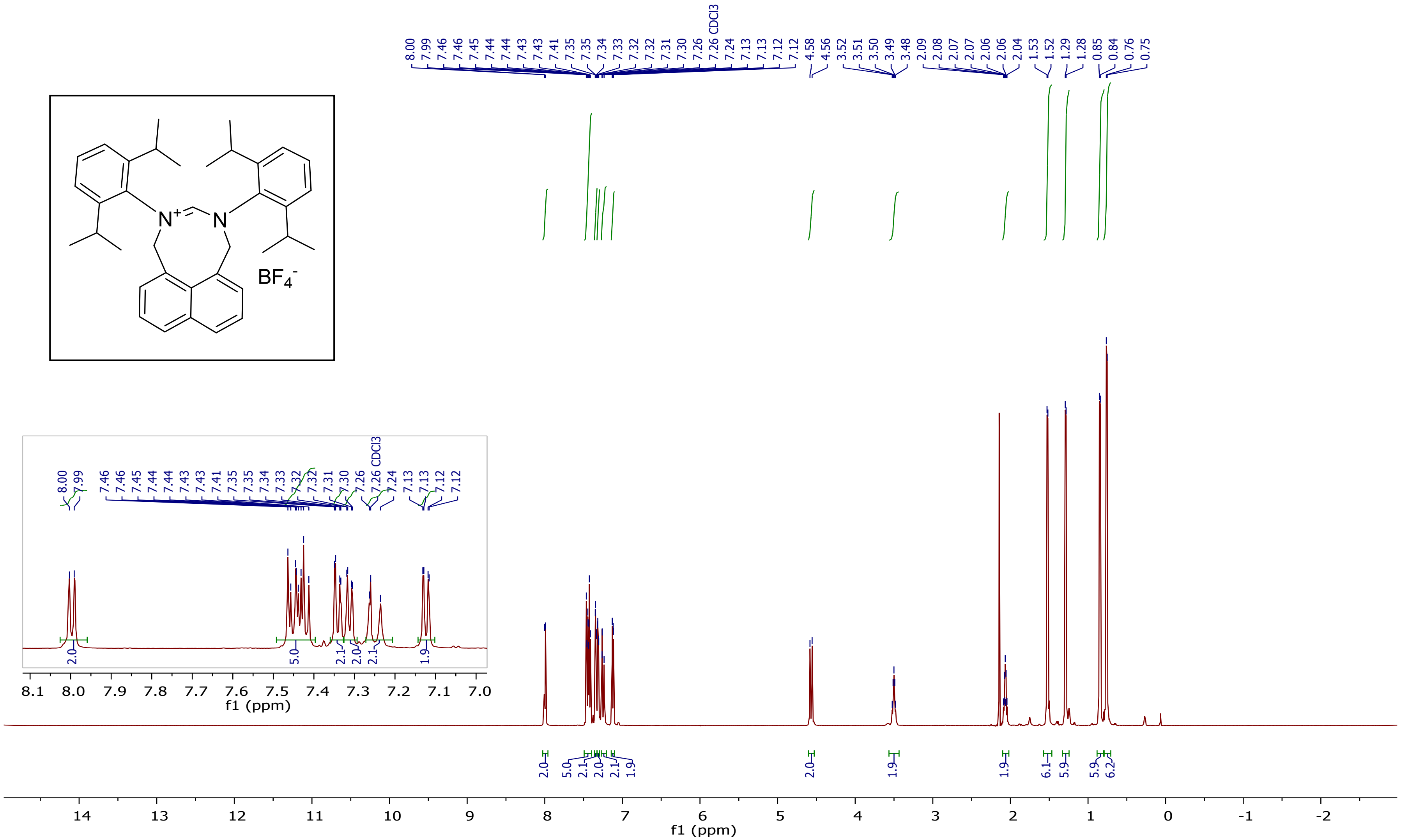


Figure S11. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (5b).

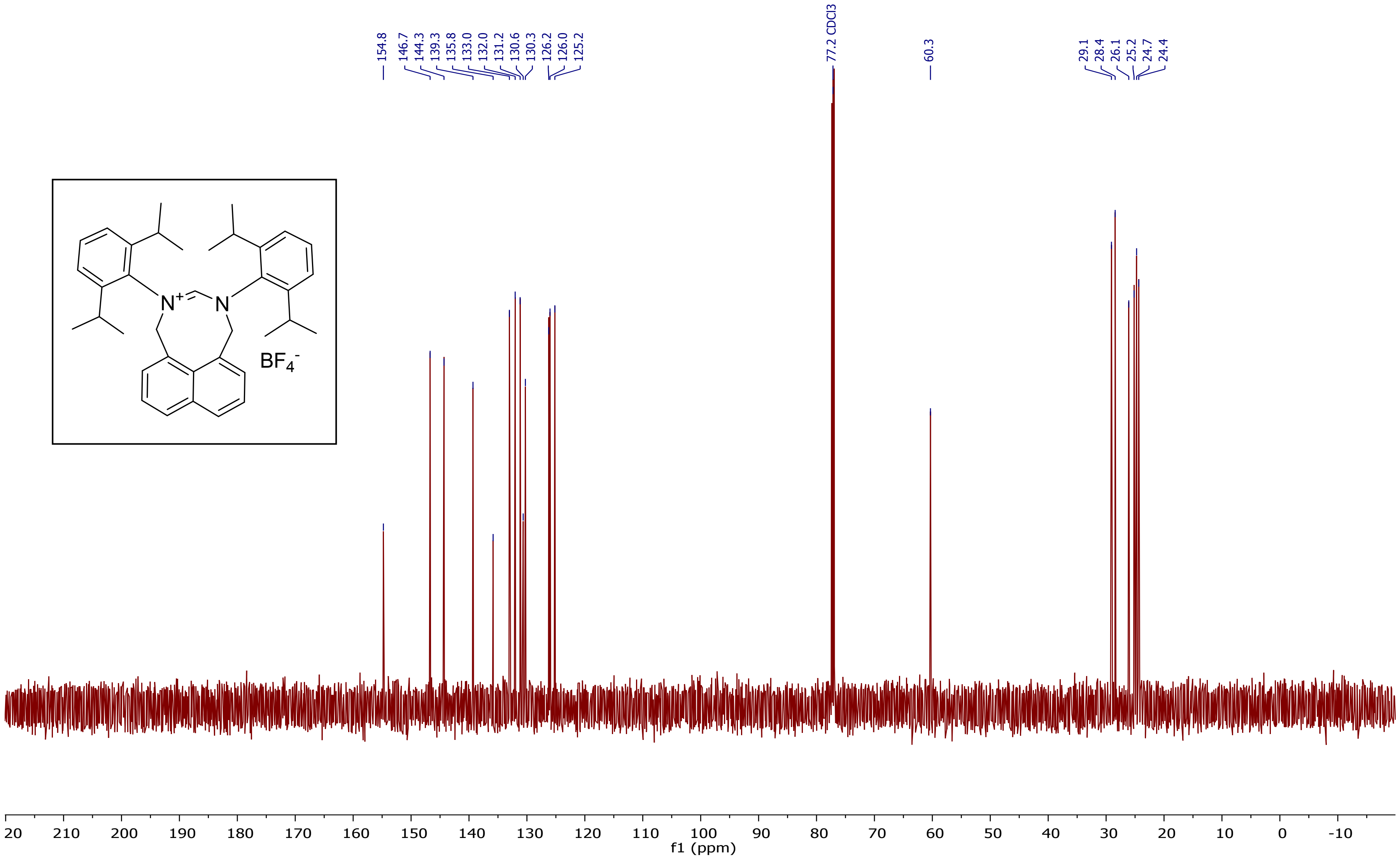


Figure S12. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocinium tetrafluroborate (5b).**

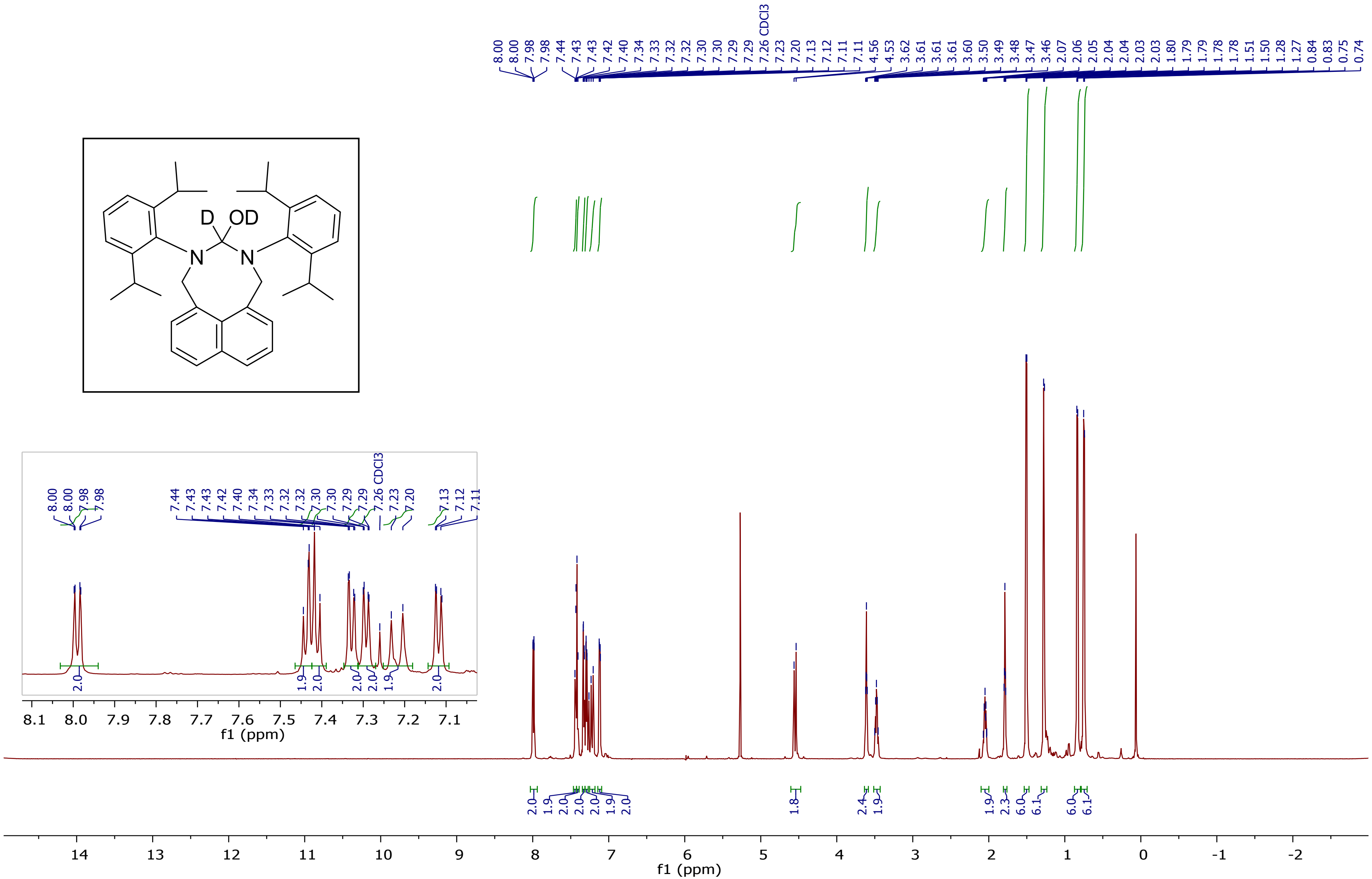


Figure S13. ^{1}H NMR (600 MHz, Chloroform-*d*) of *D2*-2,4-bis(2,6-diisopropylphenyl)-2,3,4,5-tetrahydro-1H-naphtho[1,8-ef][1,3]diazocin-3-ol (6b).

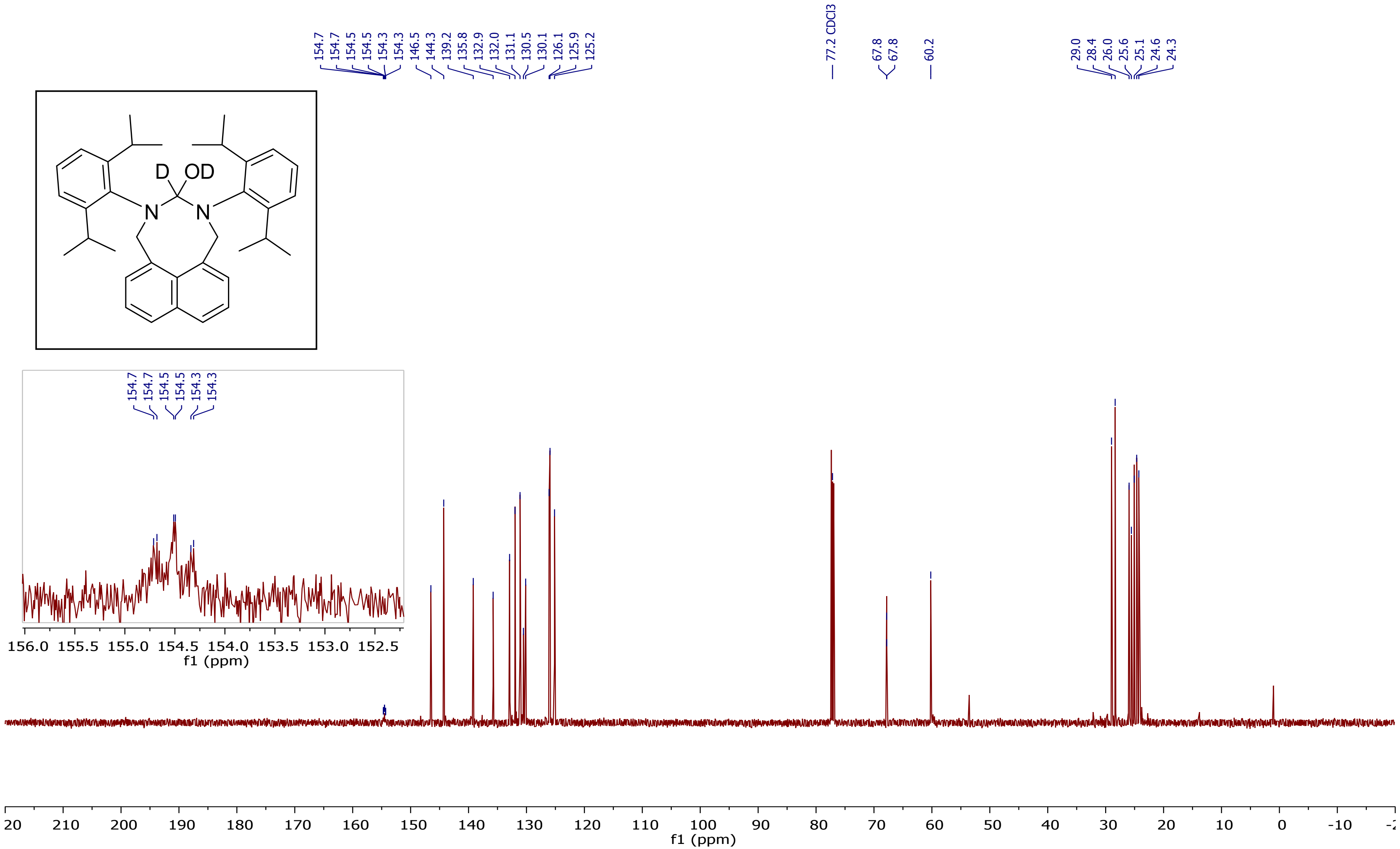


Figure S14. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of *D2*-2,4-bis(2,6-diisopropylphenyl)-2,3,4,5-tetrahydro-1H-naphtho[1,8-ef][1,3]diazocin-3-ol (6b).

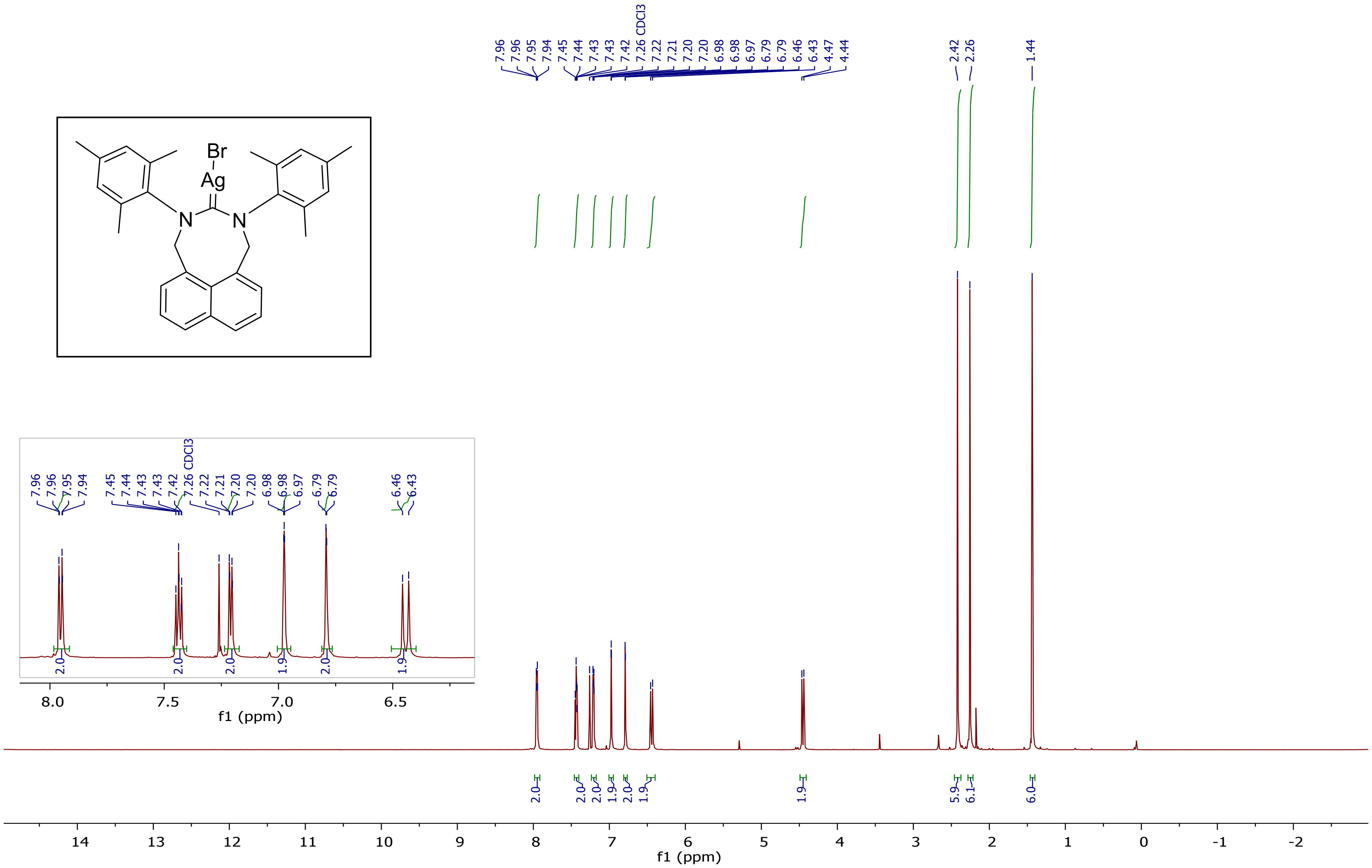


Figure S15. ^1H NMR (600 MHz, Chloroform-*d*) of (2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)silver(I) bromide (7a).

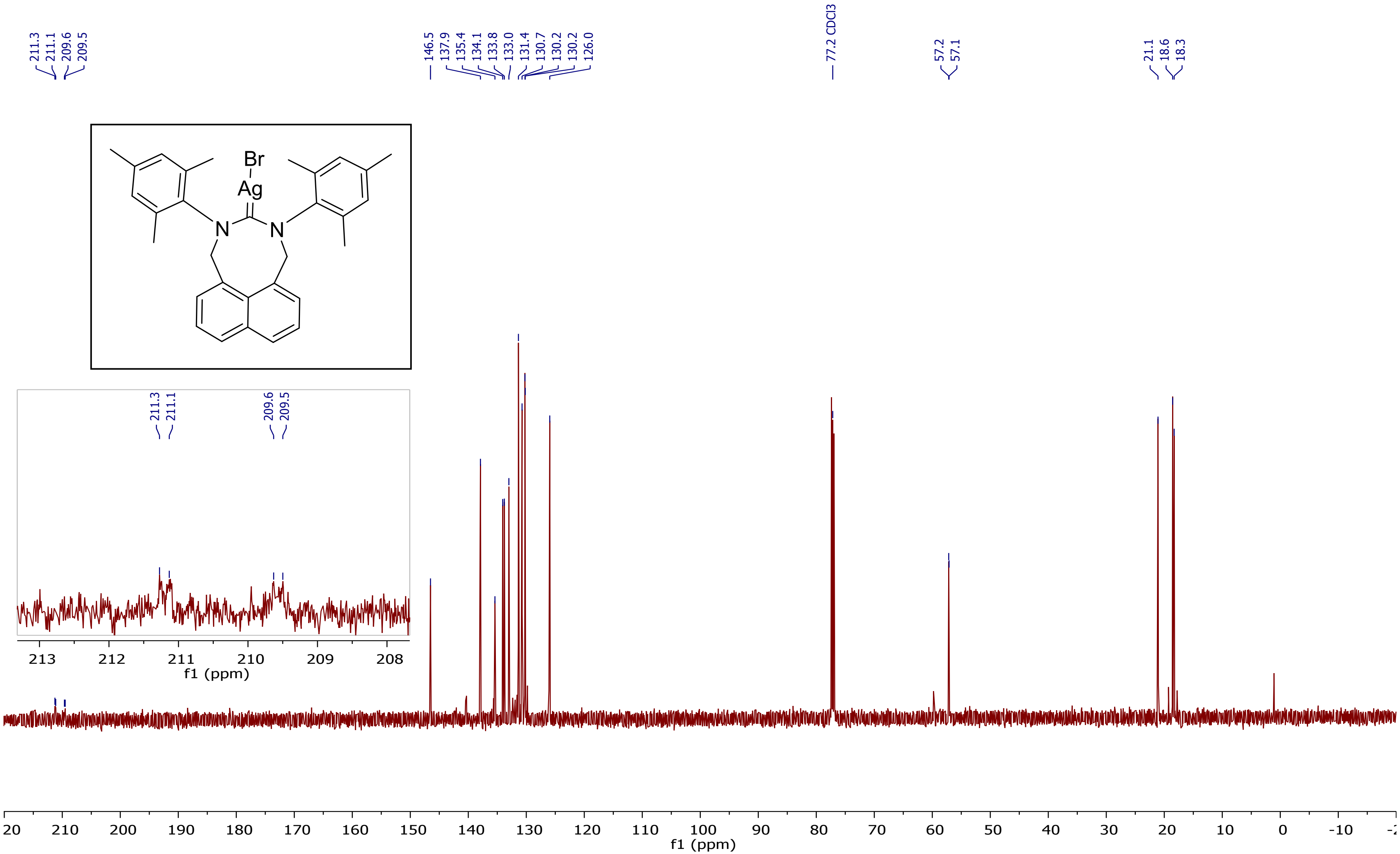


Figure S16. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of (2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)silver(I) bromide (7a).**

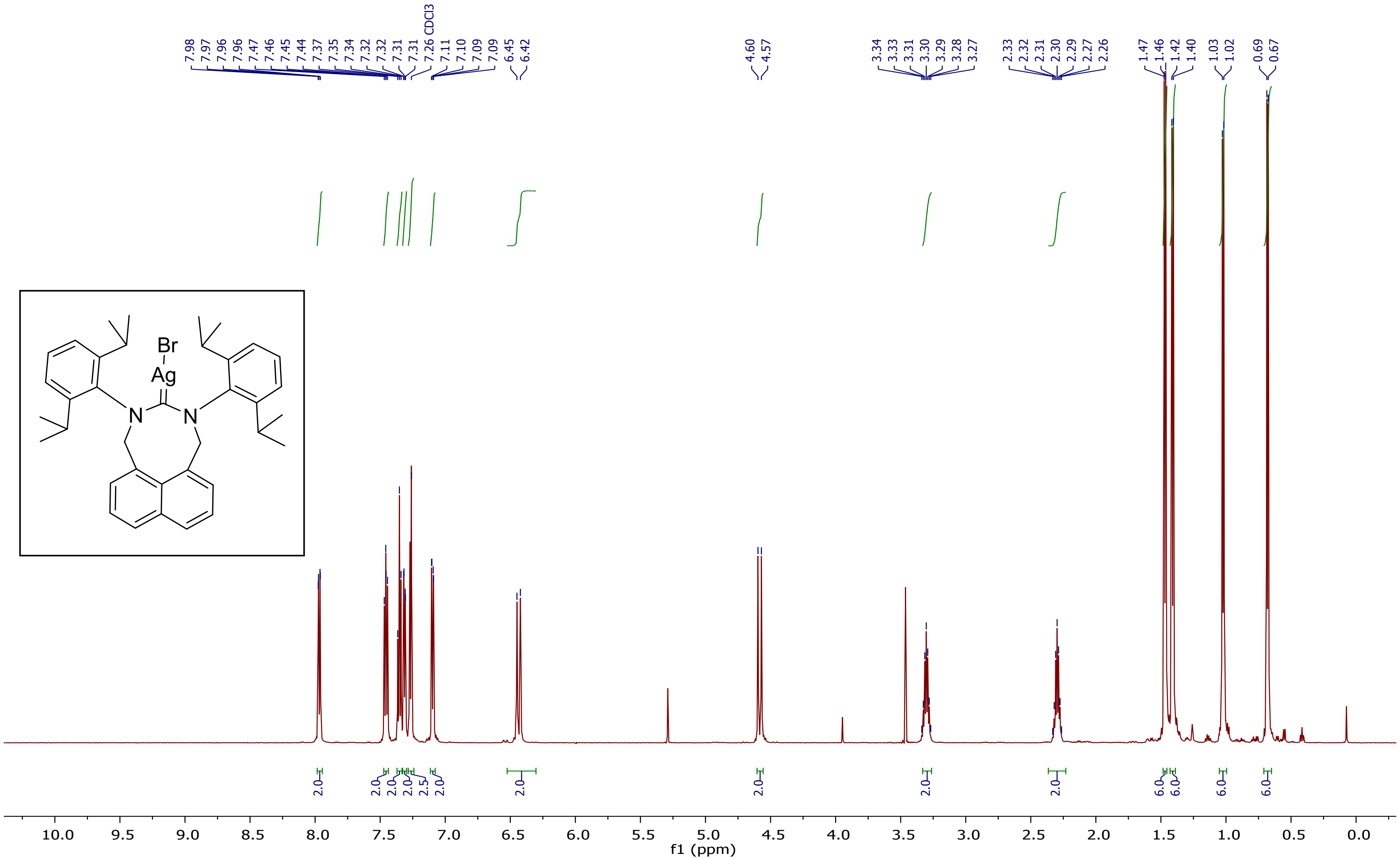


Figure S17. ^{1}H NMR (600 MHz, Chloroform-*d*) of (2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)silver(I) bromide (7b).

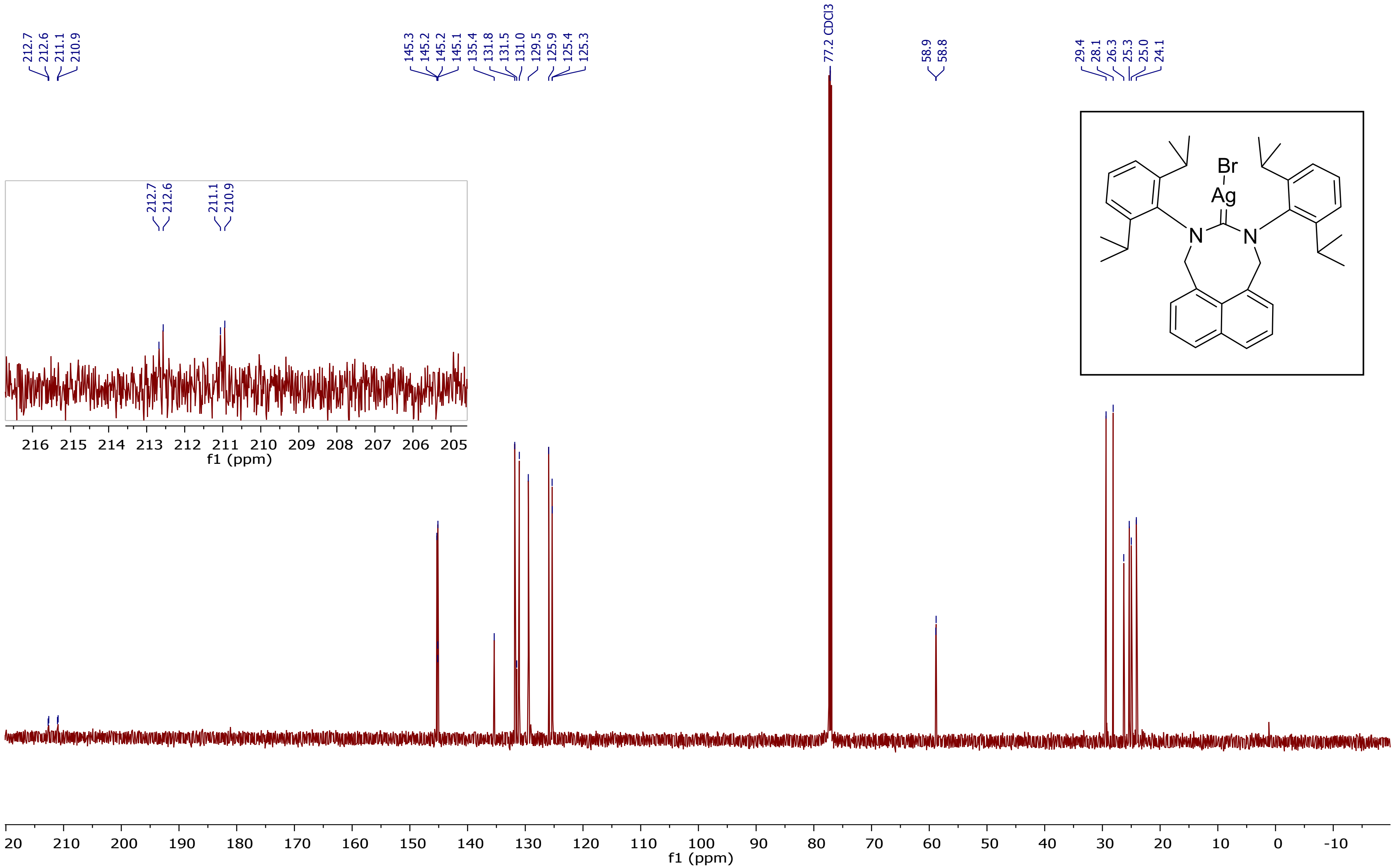


Figure S18. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) of (2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)silver(I) bromide (7b).

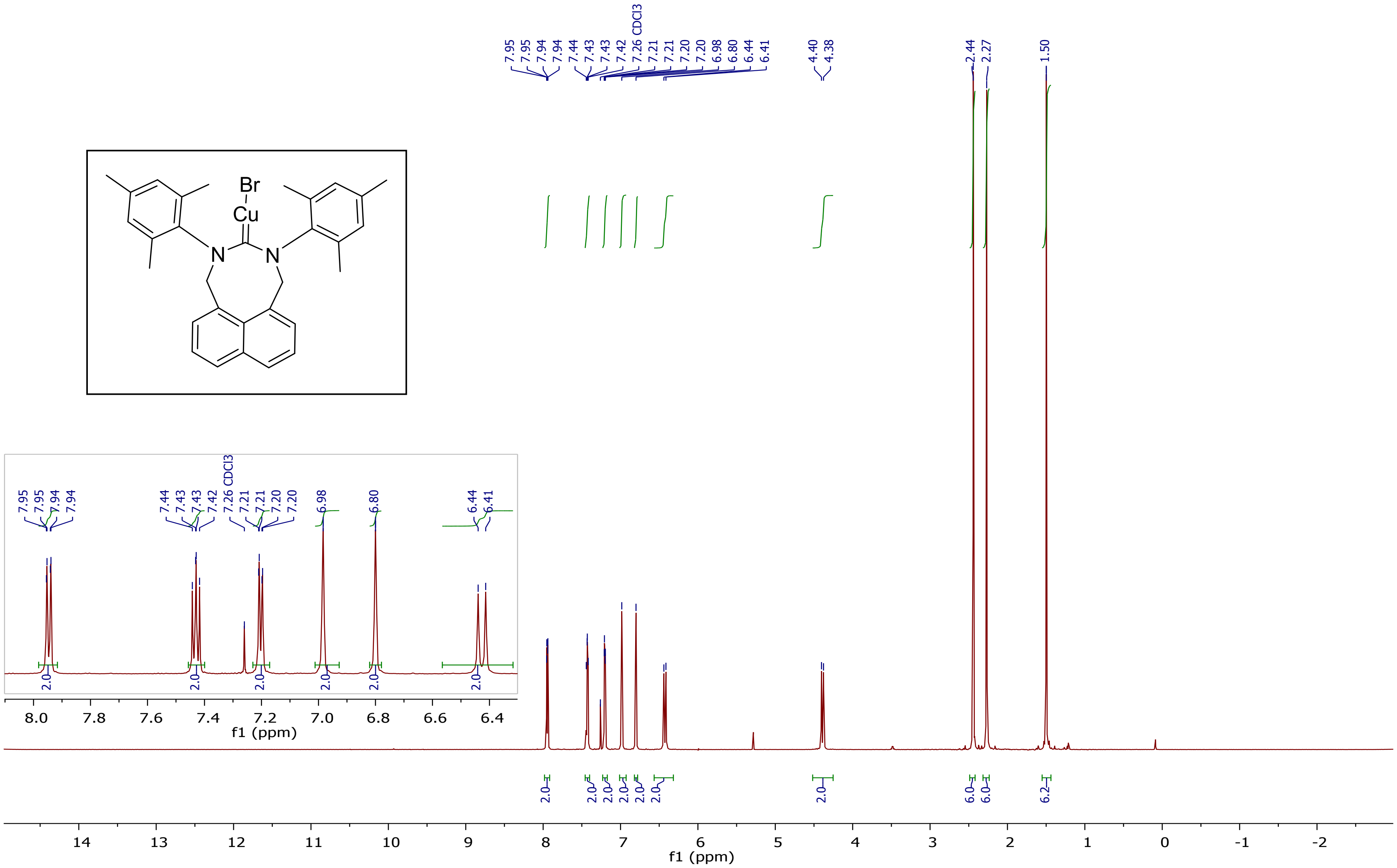


Figure S19. ^{1}H NMR (600 MHz, Chloroform-*d*) of (2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)copper(I) bromide (8a).

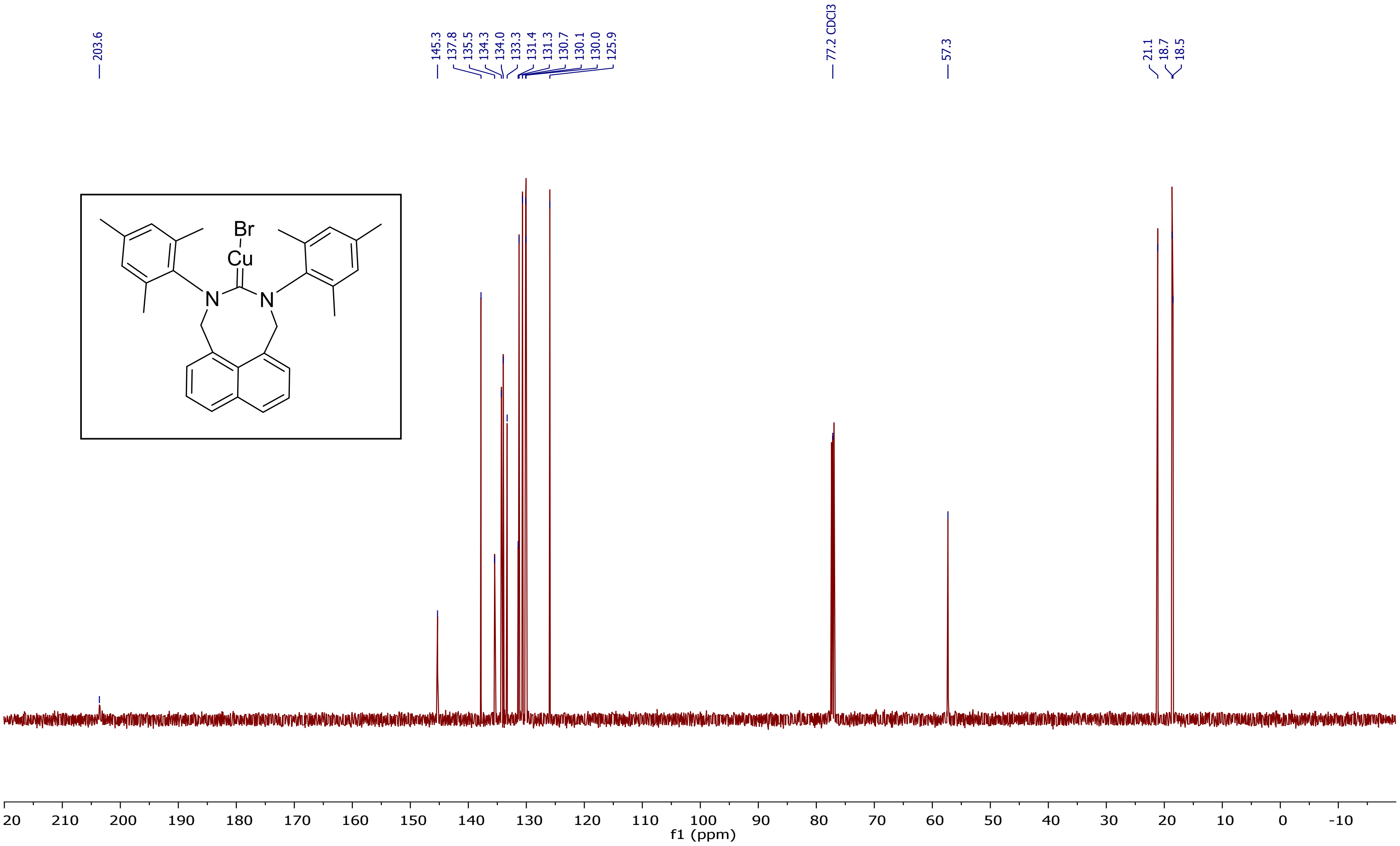


Figure S20. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of (2,4-dimesityl-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)copper(I) bromide (8a).**

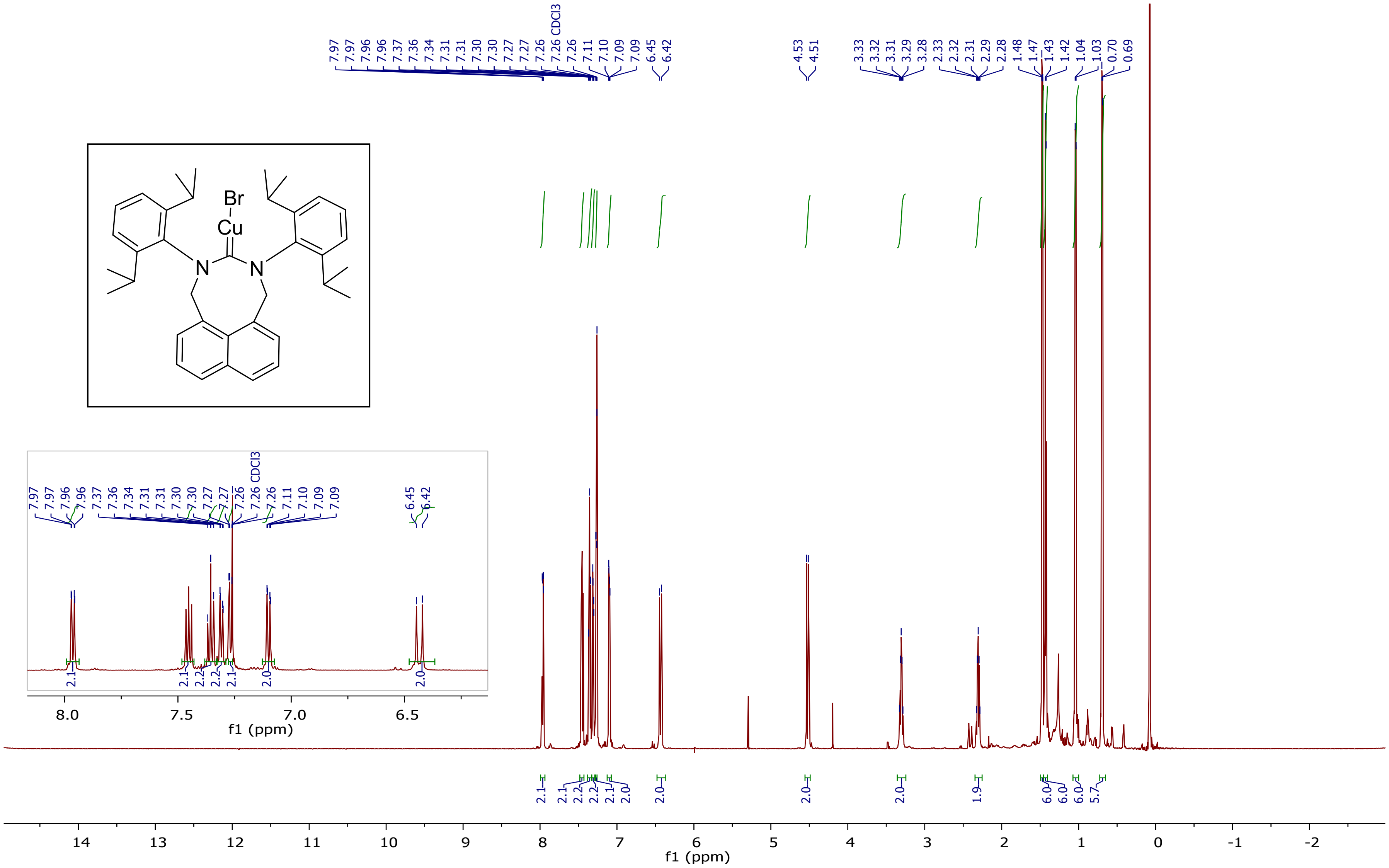


Figure S21. ^{1}H NMR (600 MHz, Chloroform-*d*) of (2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)copper(I) bromide (8b).

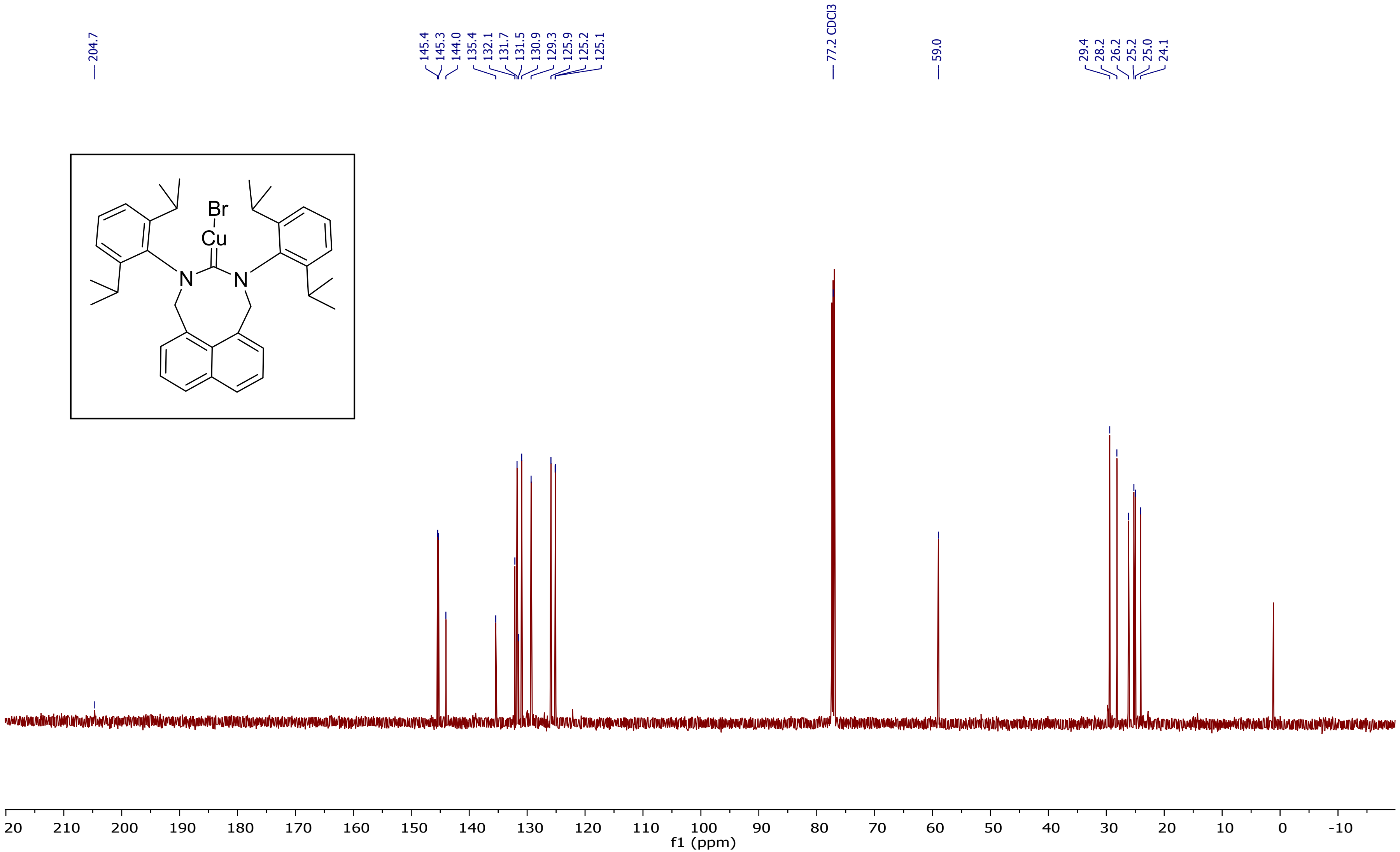


Figure S22. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of (2,4-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-naphtho[1,8-ef][1,3]diazocin-3(2H)-ylidene)copper(I) bromide (8b).

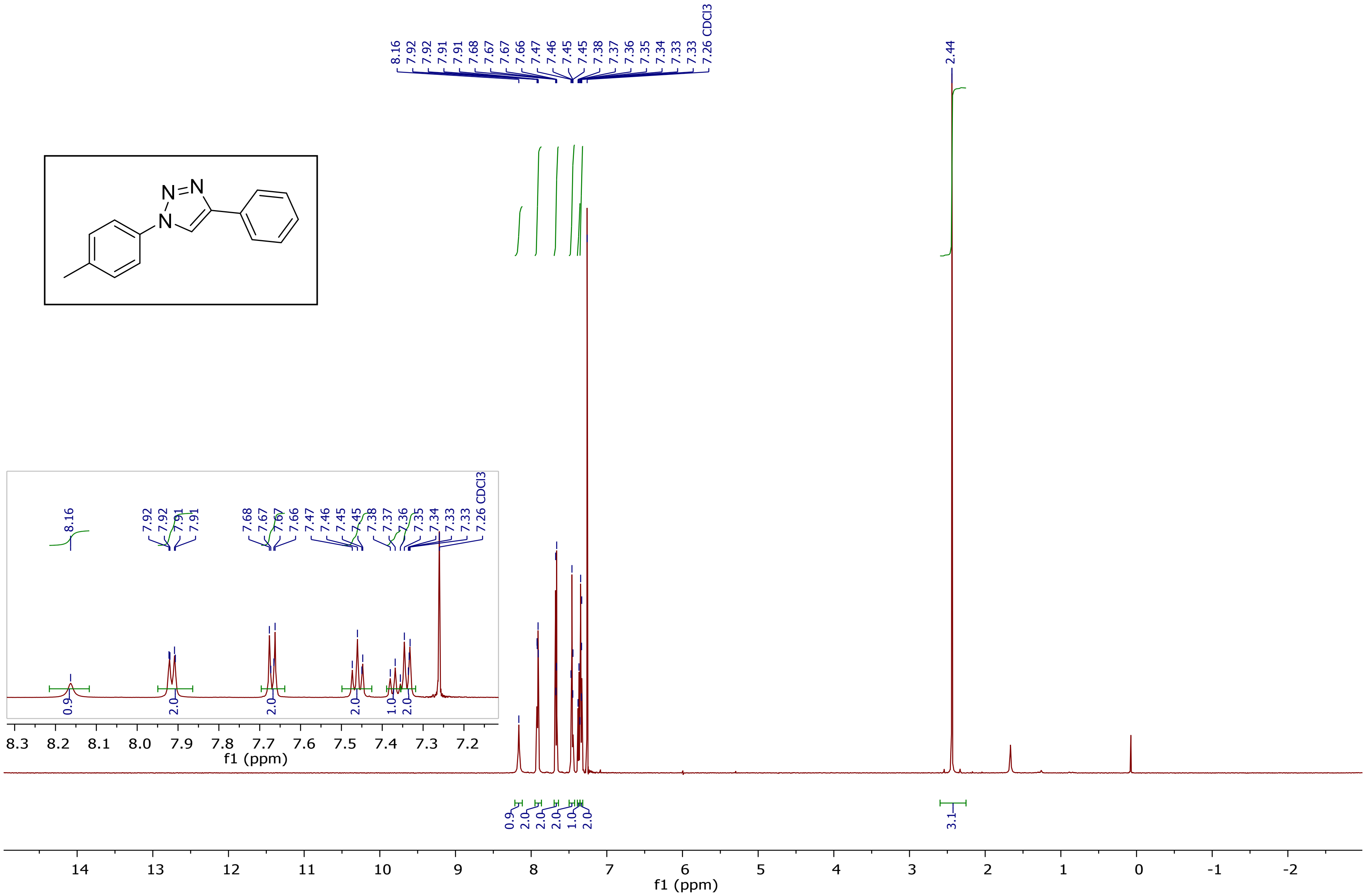


Figure S23. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-phenyl-1-p-tolyl-1H-1,2,3-triazole (9a).

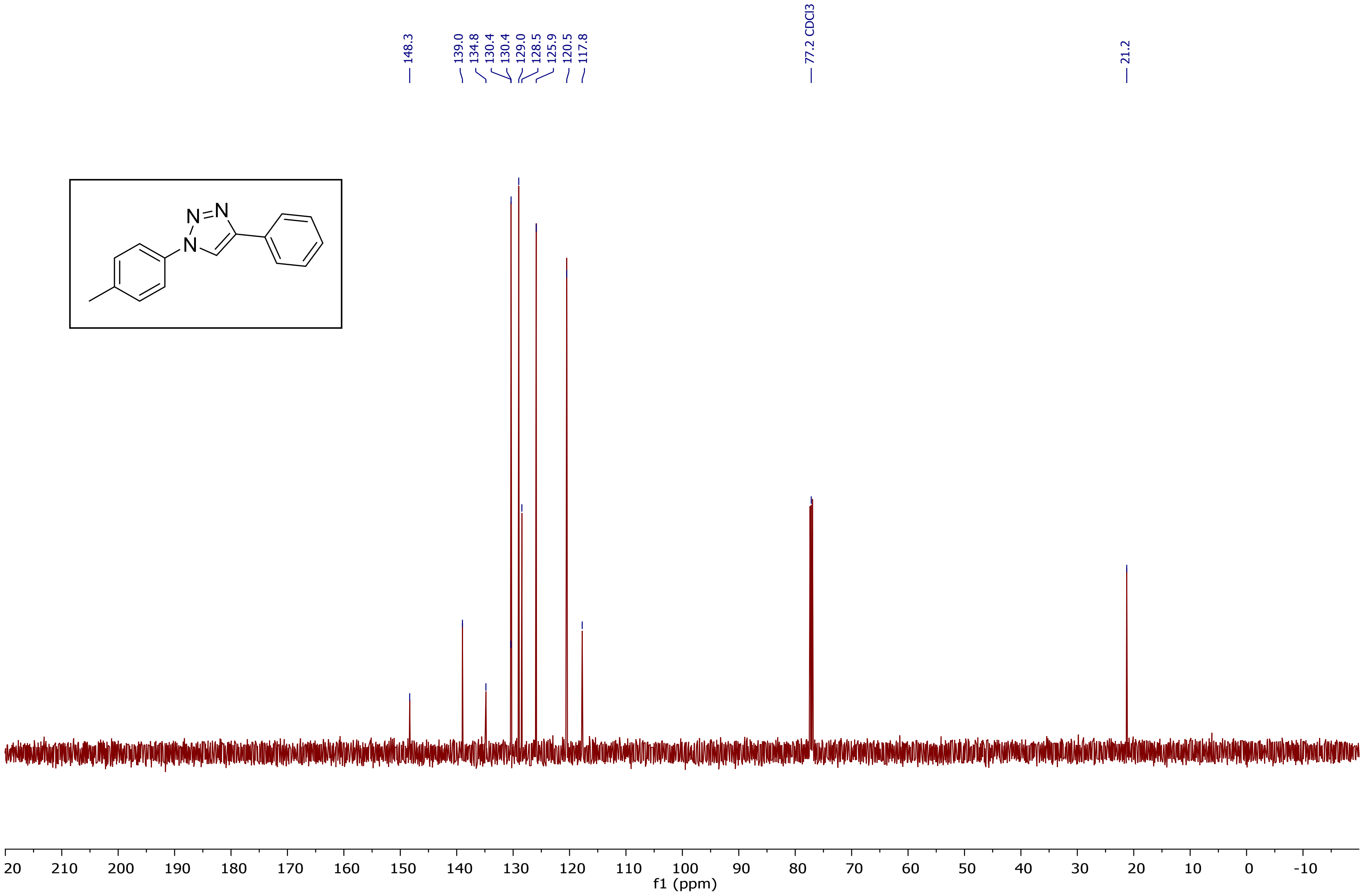


Figure S24. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 4-phenyl-1-p-tolyl-1H-1,2,3-triazole (9a).**

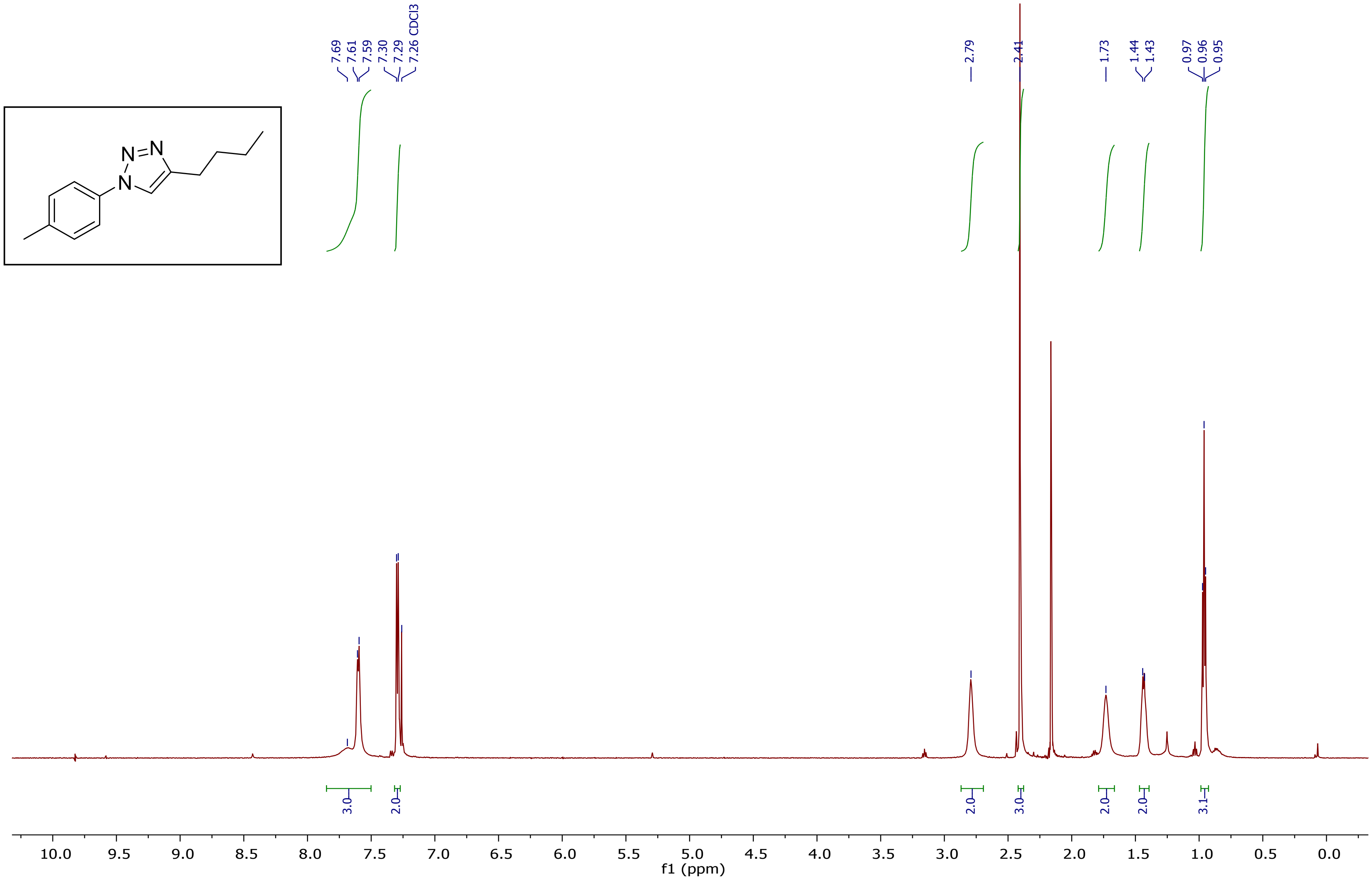


Figure S25. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-Butyl-1-p-tolyl-1H-1,2,3-triazole (9b).

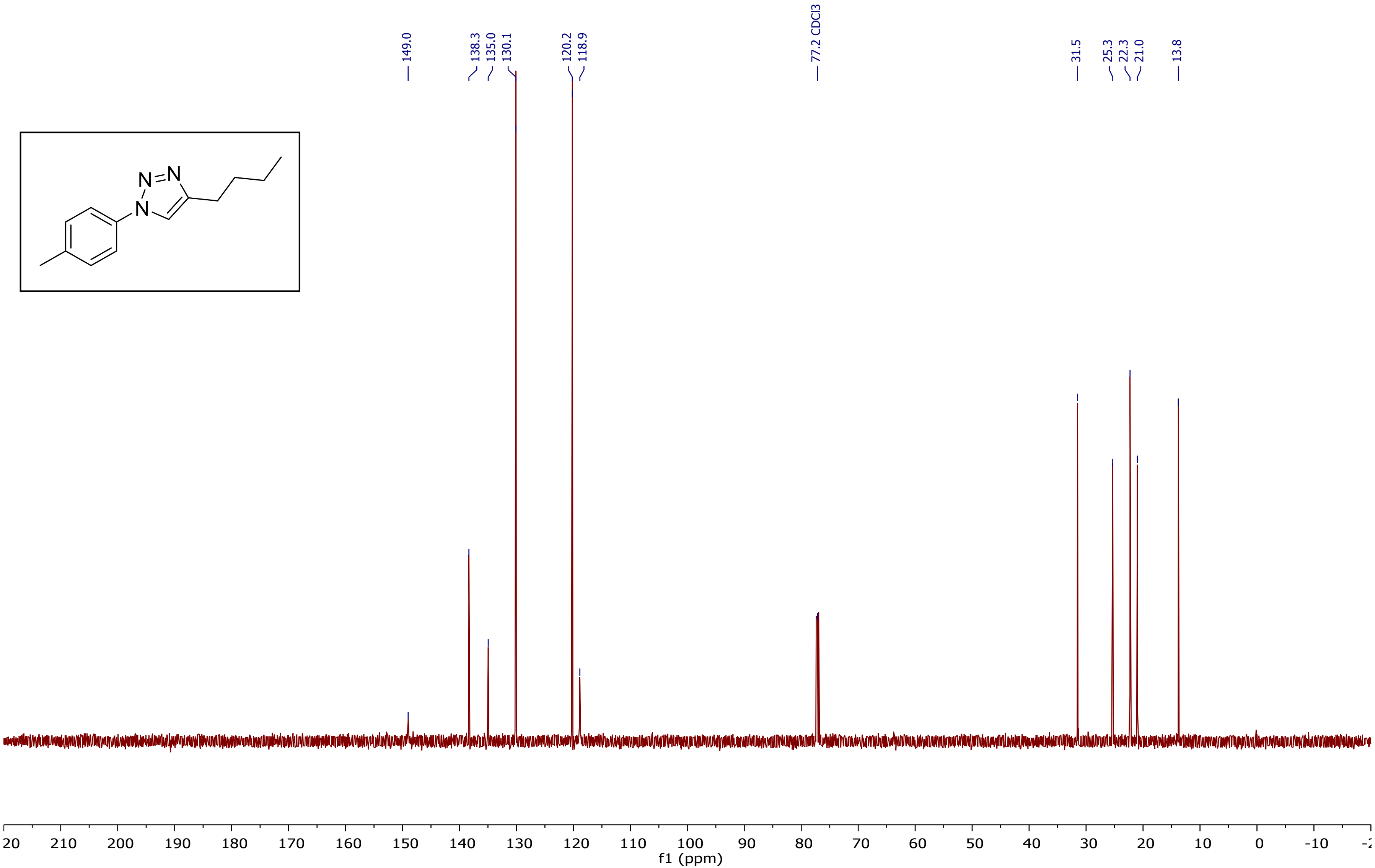


Figure S26. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of 4-Butyl-1-p-tolyl-1H-1,2,3-triazole (9b).

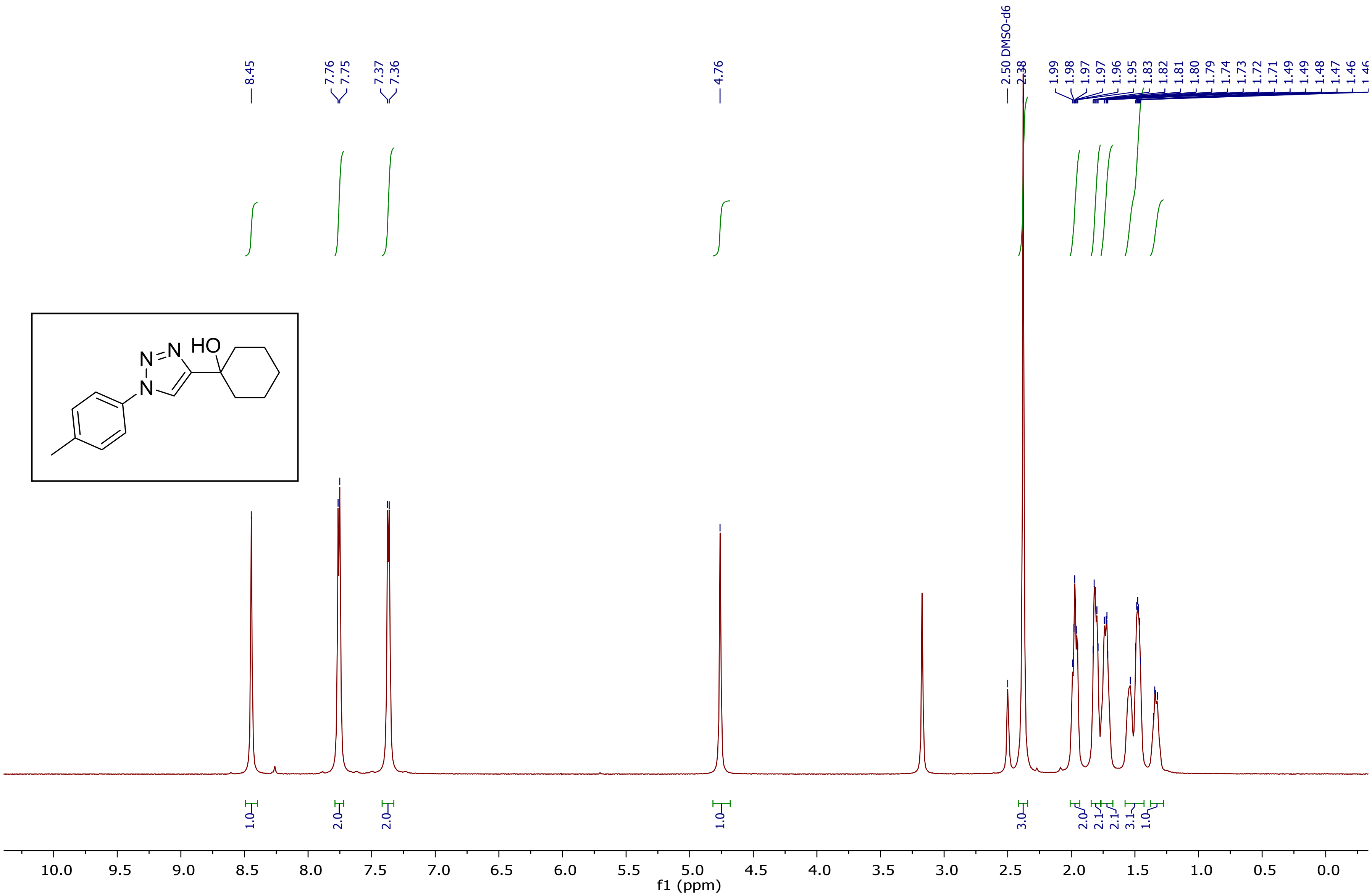


Figure S27. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(1-p-tolyl-1H-1,2,3-triazol-4-yl)cyclohexanol (9c).

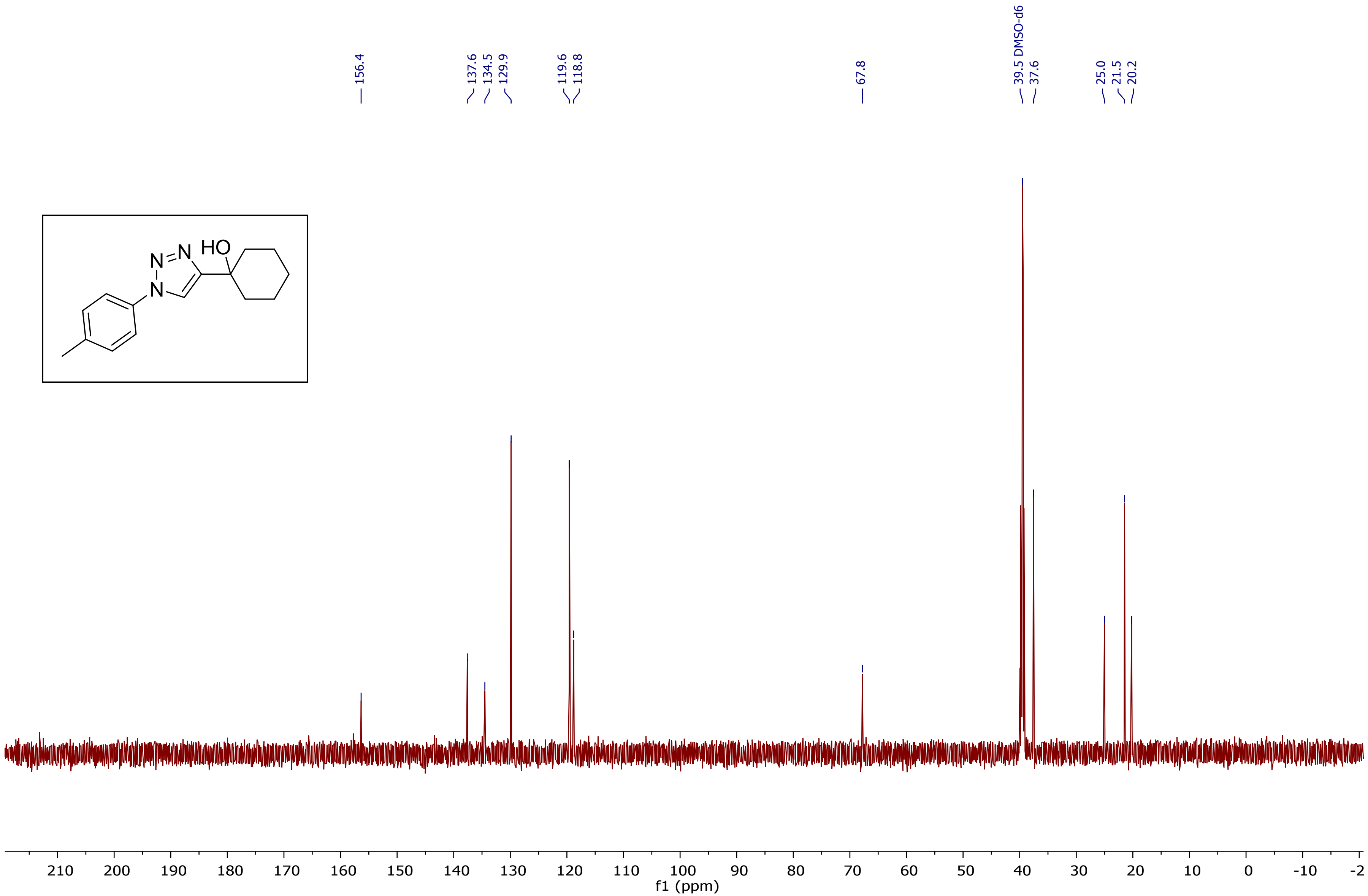


Figure S28. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) of 1-(1-p-tolyl-1H-1,2,3-triazol-4-yl)cyclohexanol (9c).

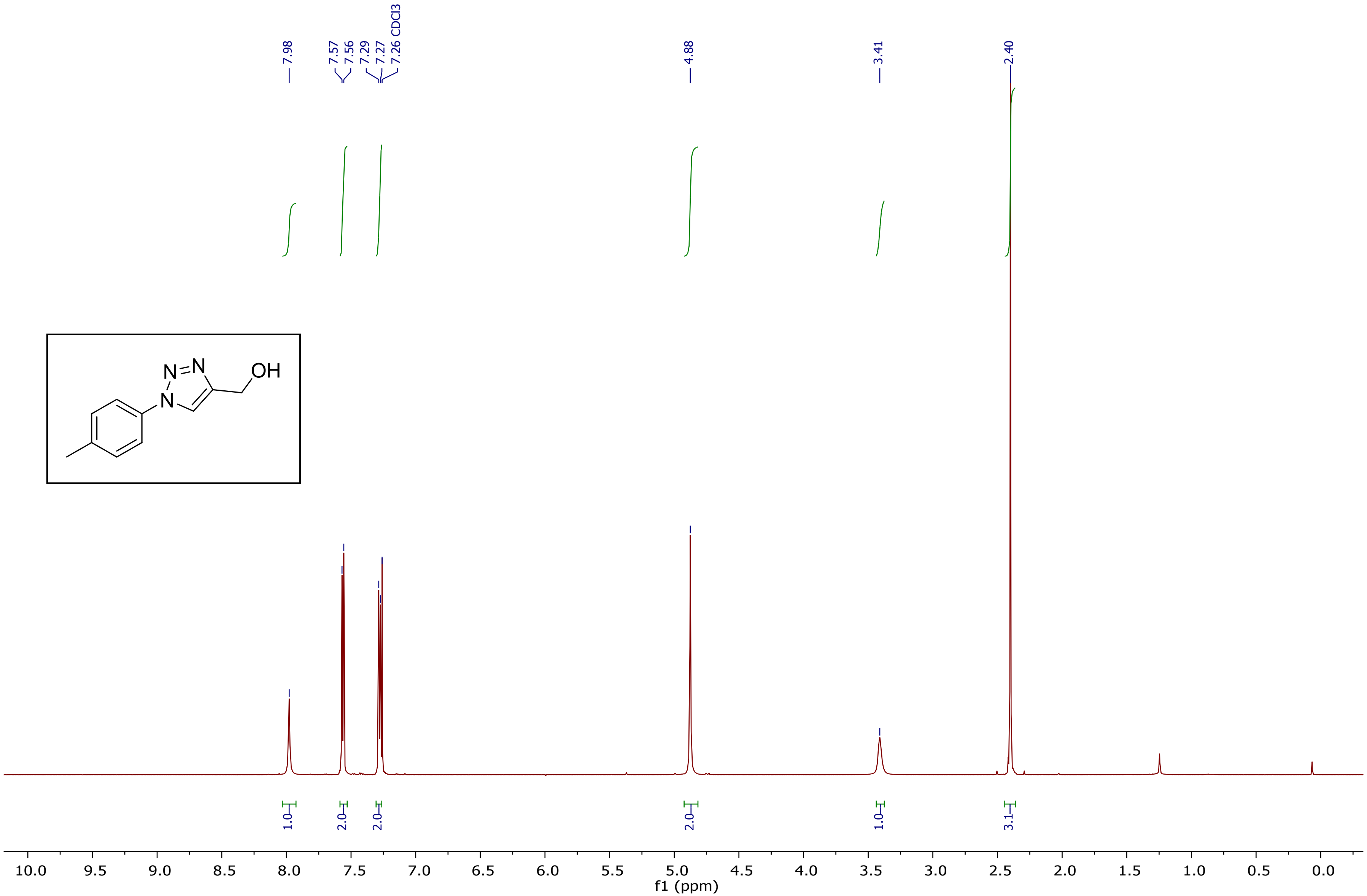


Figure S29. ^{1}H NMR (600 MHz, Chloroform-*d*) of (1-p-Tolyl-1H-1,2,3-triazol-4-yl)methanol (9d).

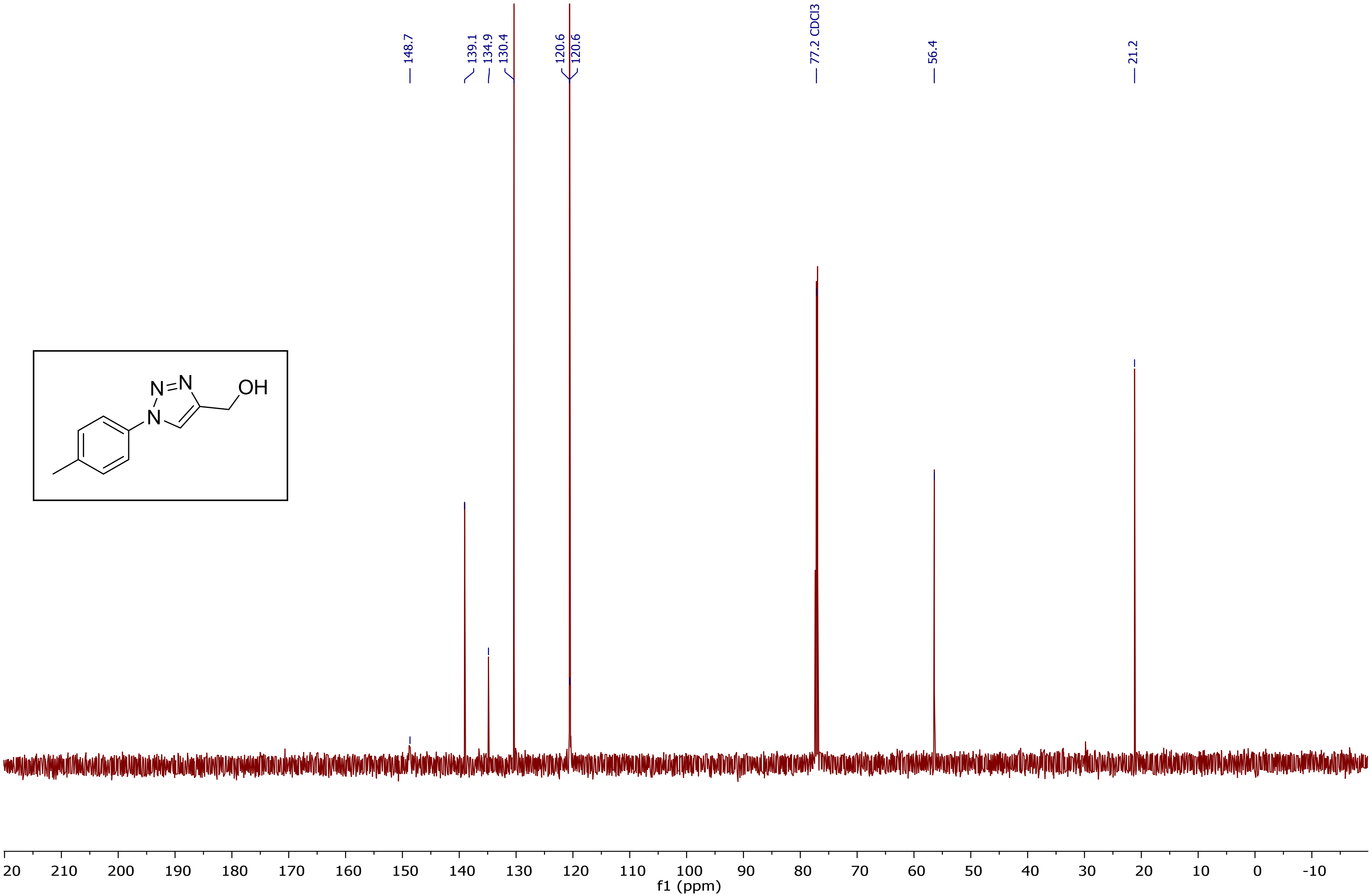


Figure S30. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) of (1-p-Tolyl-1H-1,2,3-triazol-4-yl)methanol (9d).

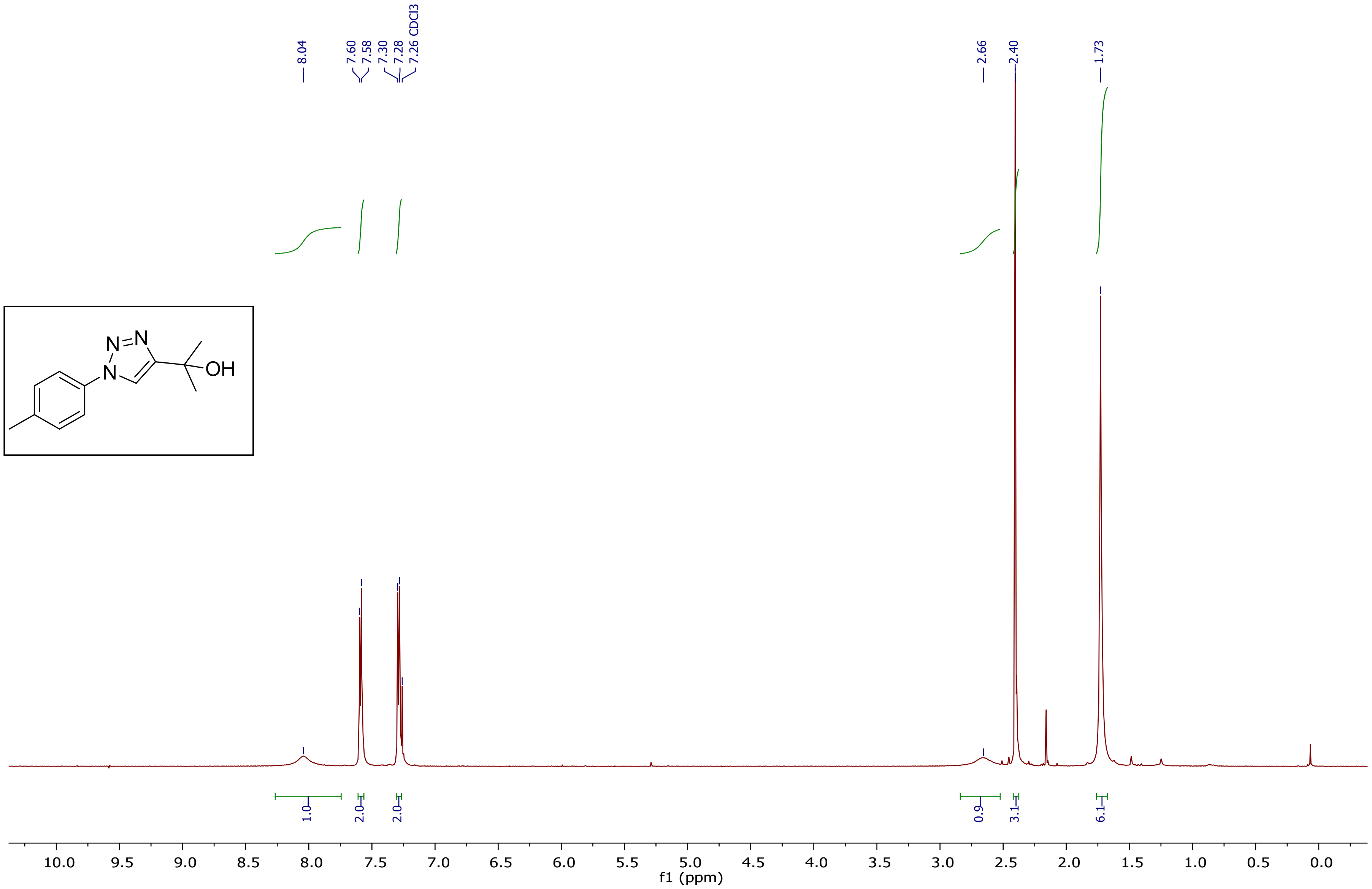


Figure S31. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)propan-2-ol (9e).

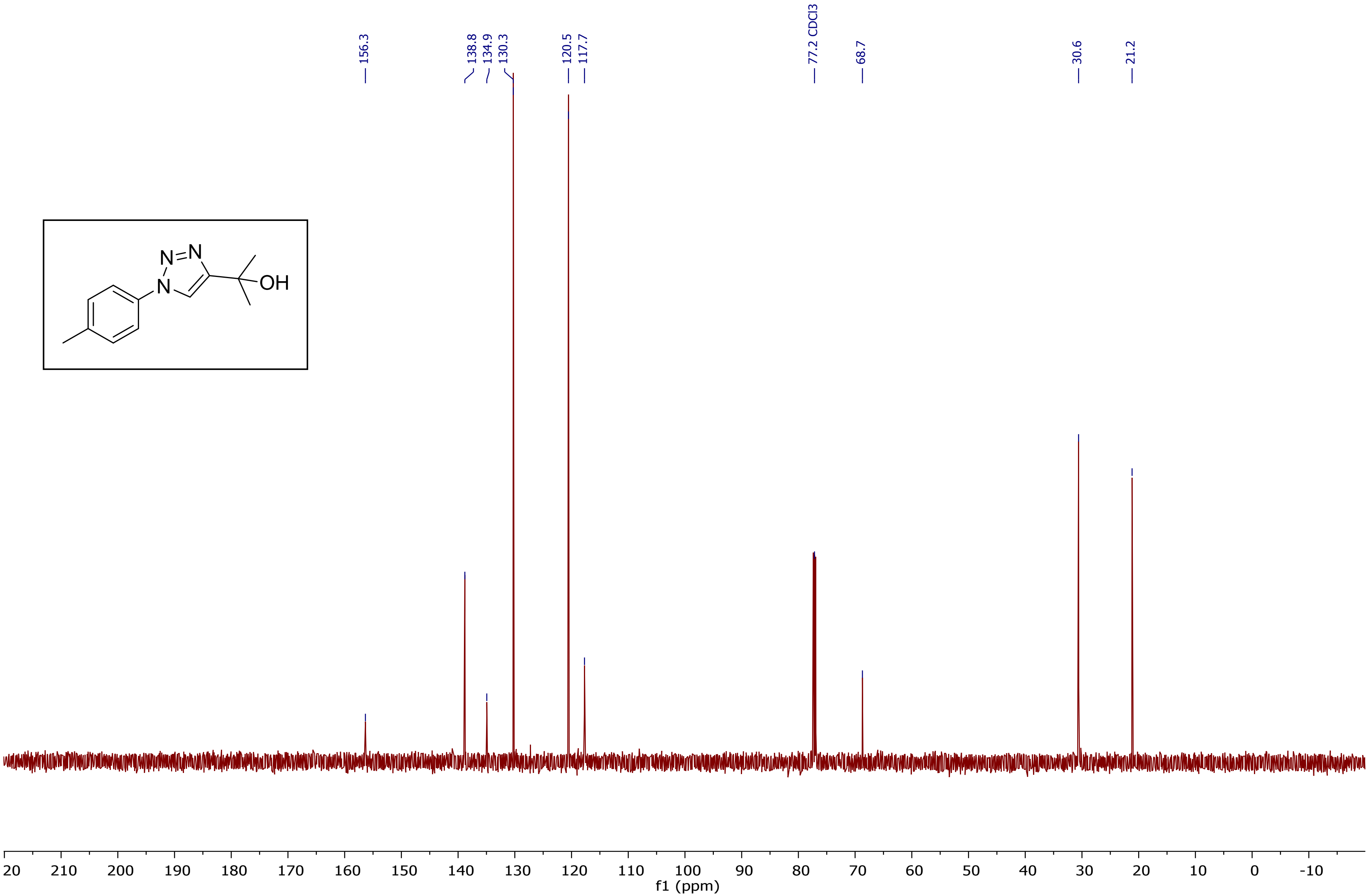


Figure S32. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 2-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)propan-2-ol (9e).**

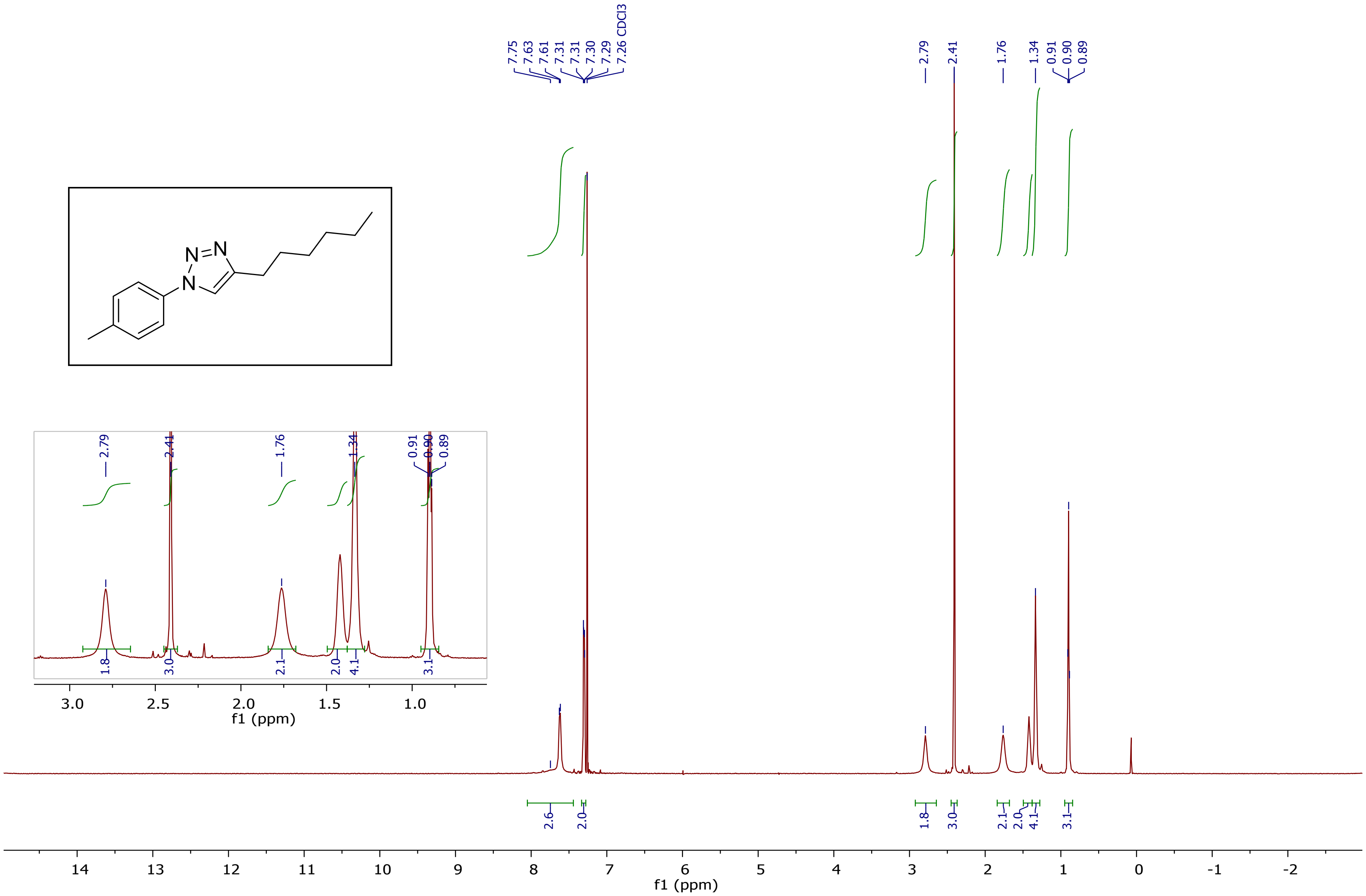


Figure S33. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-Hexyl-1-p-tolyl-1H-1,2,3-triazole (9f).

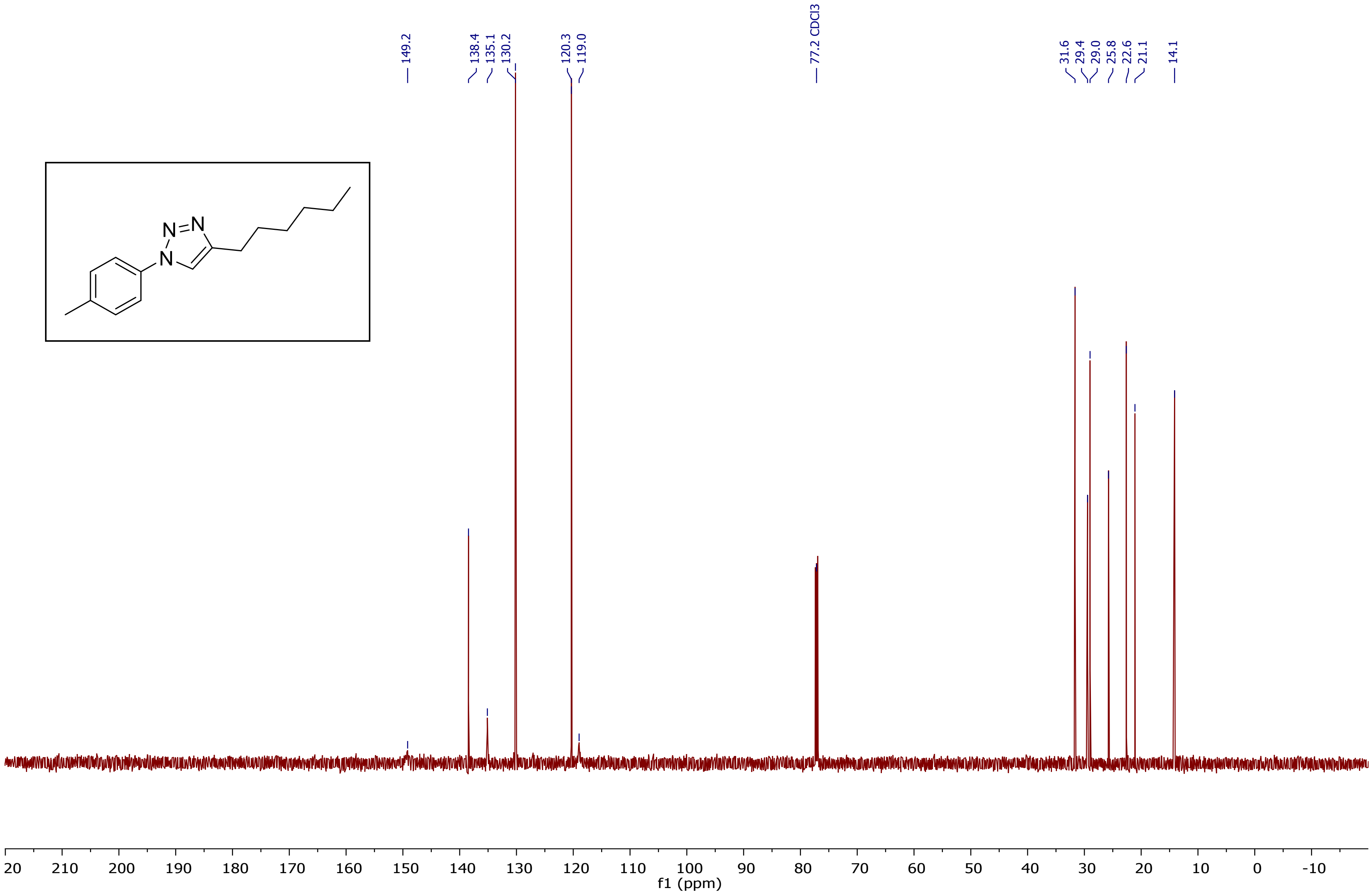


Figure S34. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of 4-Hexyl-1-p-tolyl-1H-1,2,3-triazole (9f).

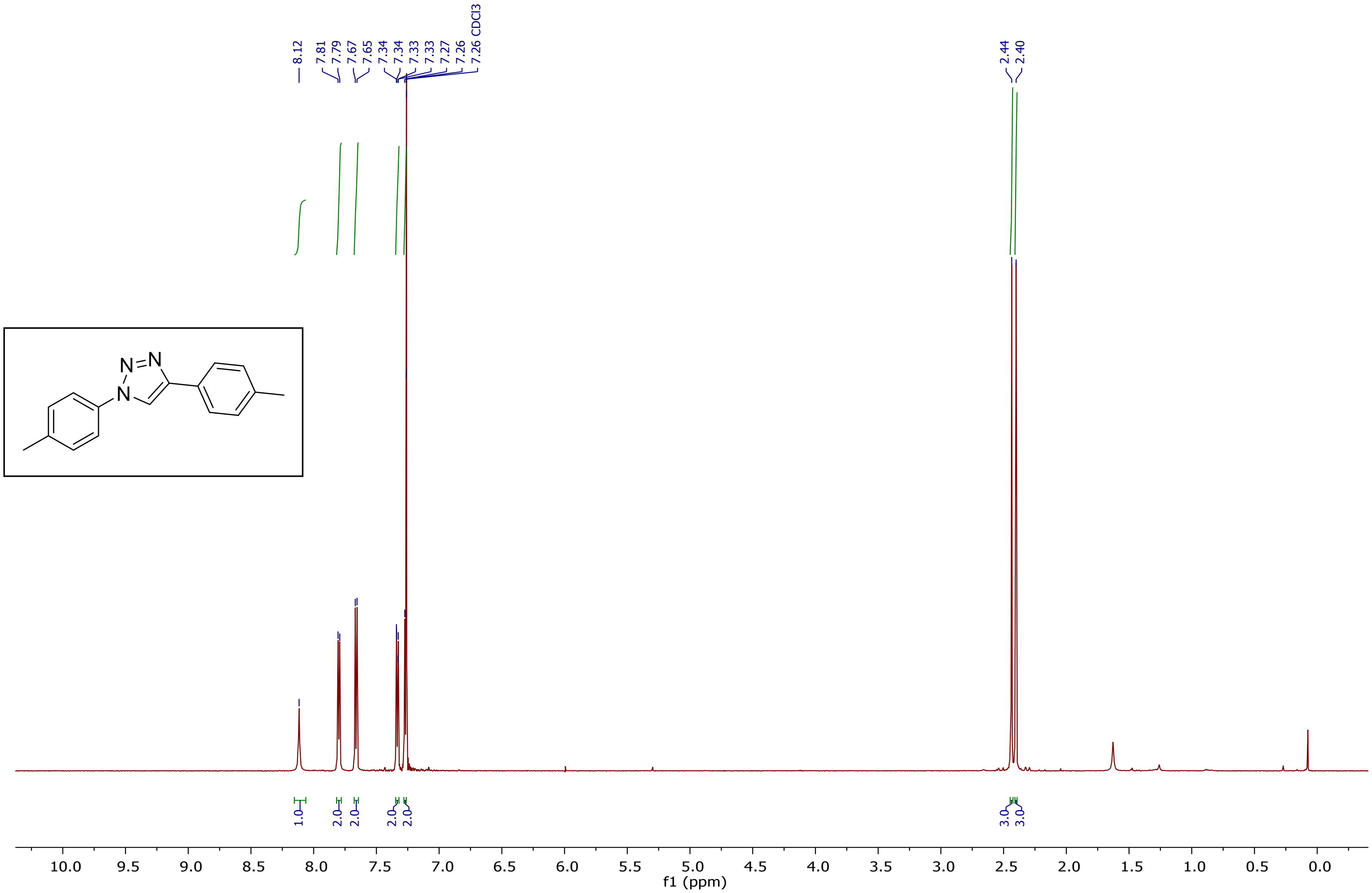


Figure S35. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1,4-di-p-Tolyl-1H-1,2,3-triazole (9g).

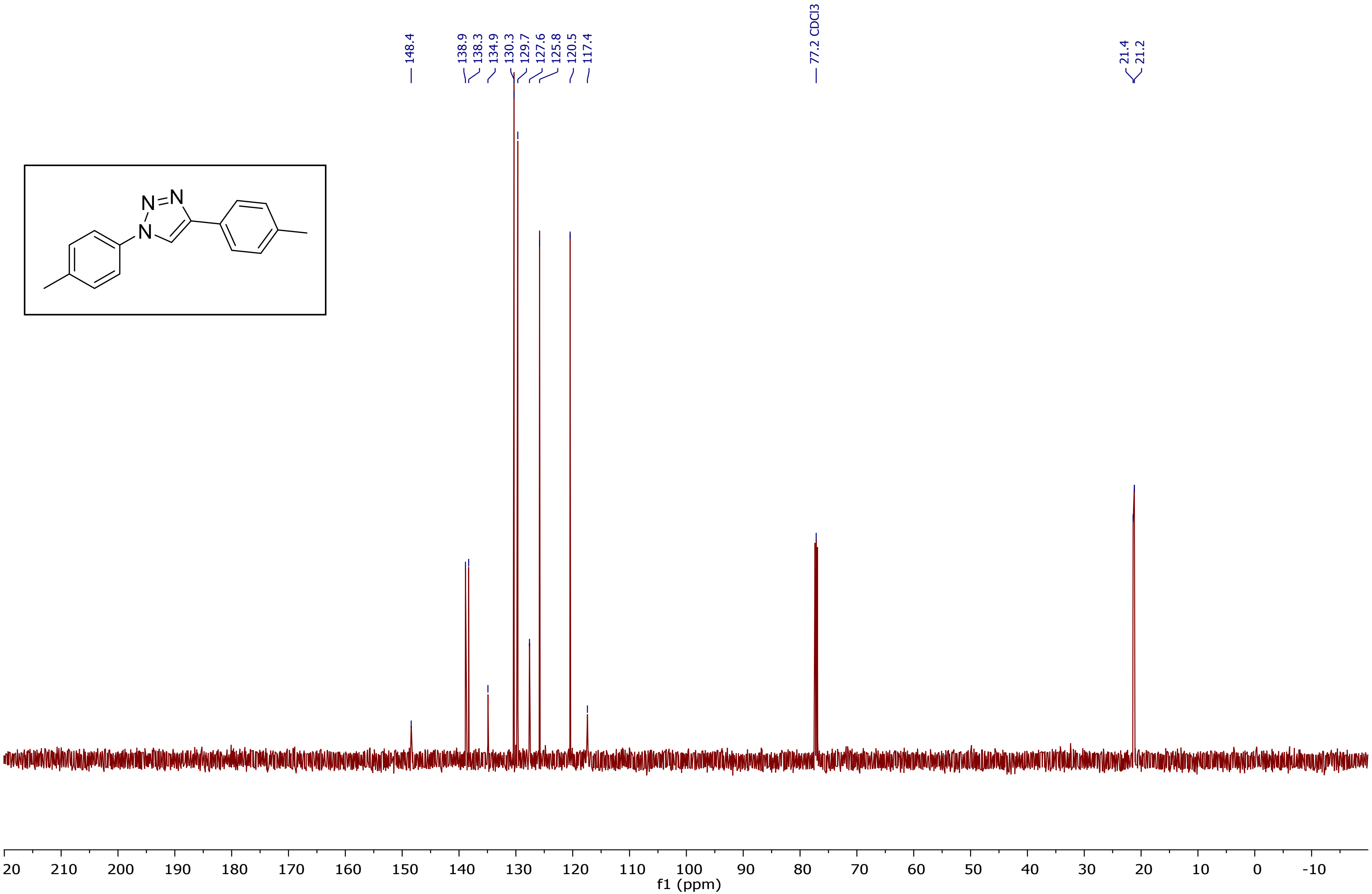


Figure S36. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 1,4-di-p-Tolyl-1H-1,2,3-triazole (9g).**

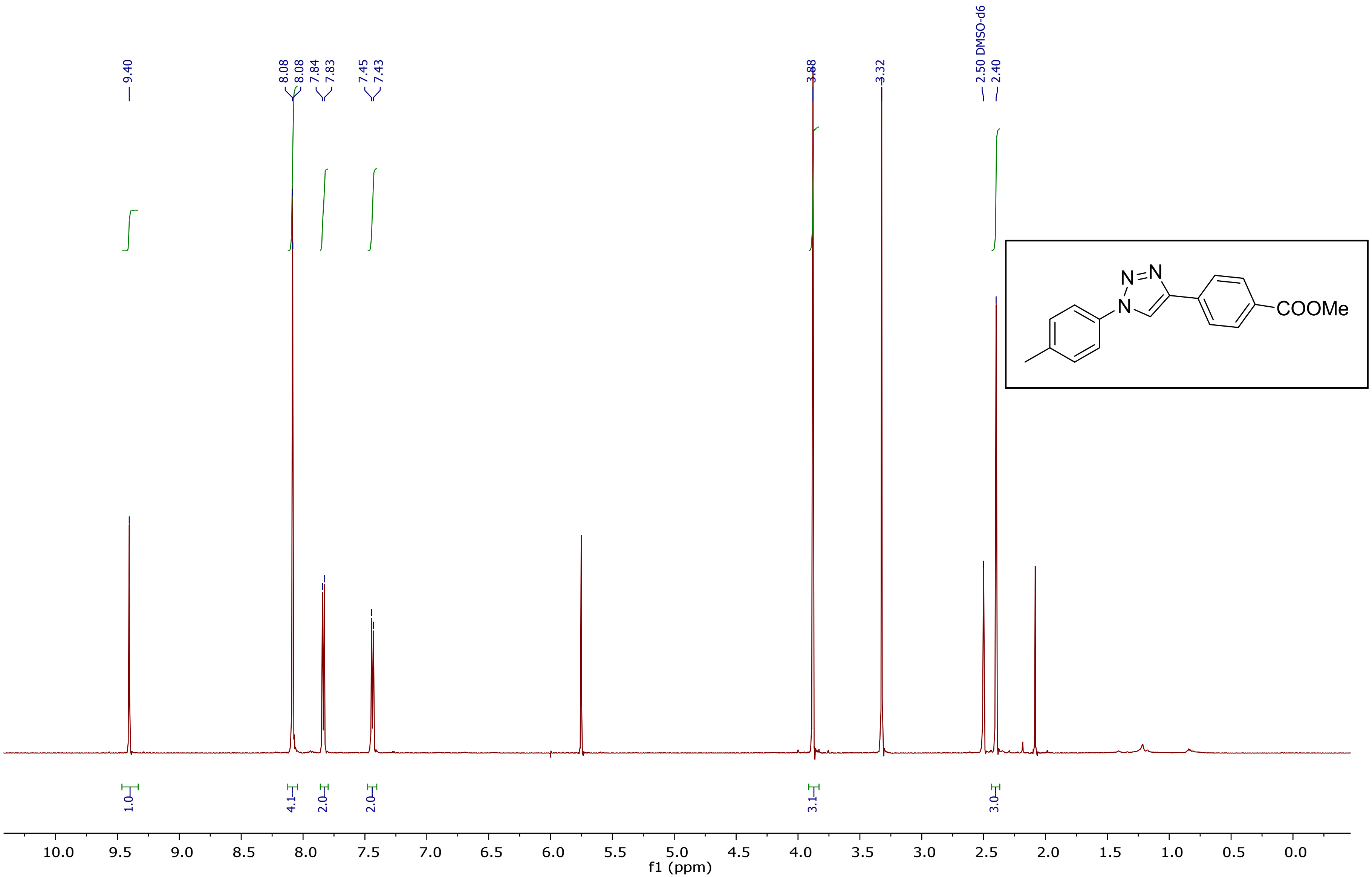


Figure S37. ^{1}H NMR (600 MHz, DMSO-d_6) of methyl 4-(1-p-tolyl-1H-1,2,3-triazol-4-yl)benzoate (9h).

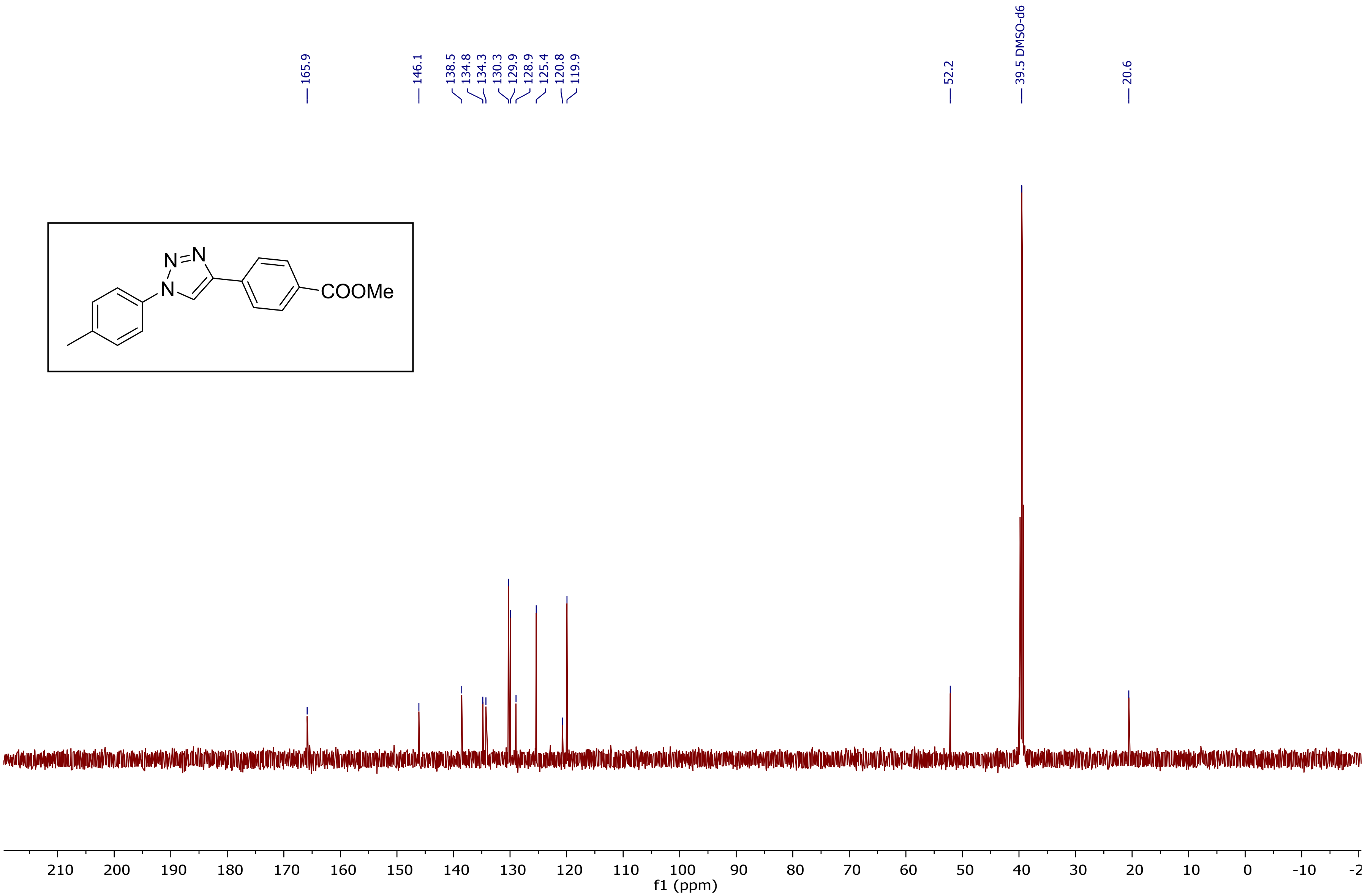


Figure S38. $^{13}C\{^{1}H\}$ **NMR (151 MHz, DMSO-d_6) of methyl 4-(1-p-tolyl-1H-1,2,3-triazol-4-yl)benzoate (9h).**

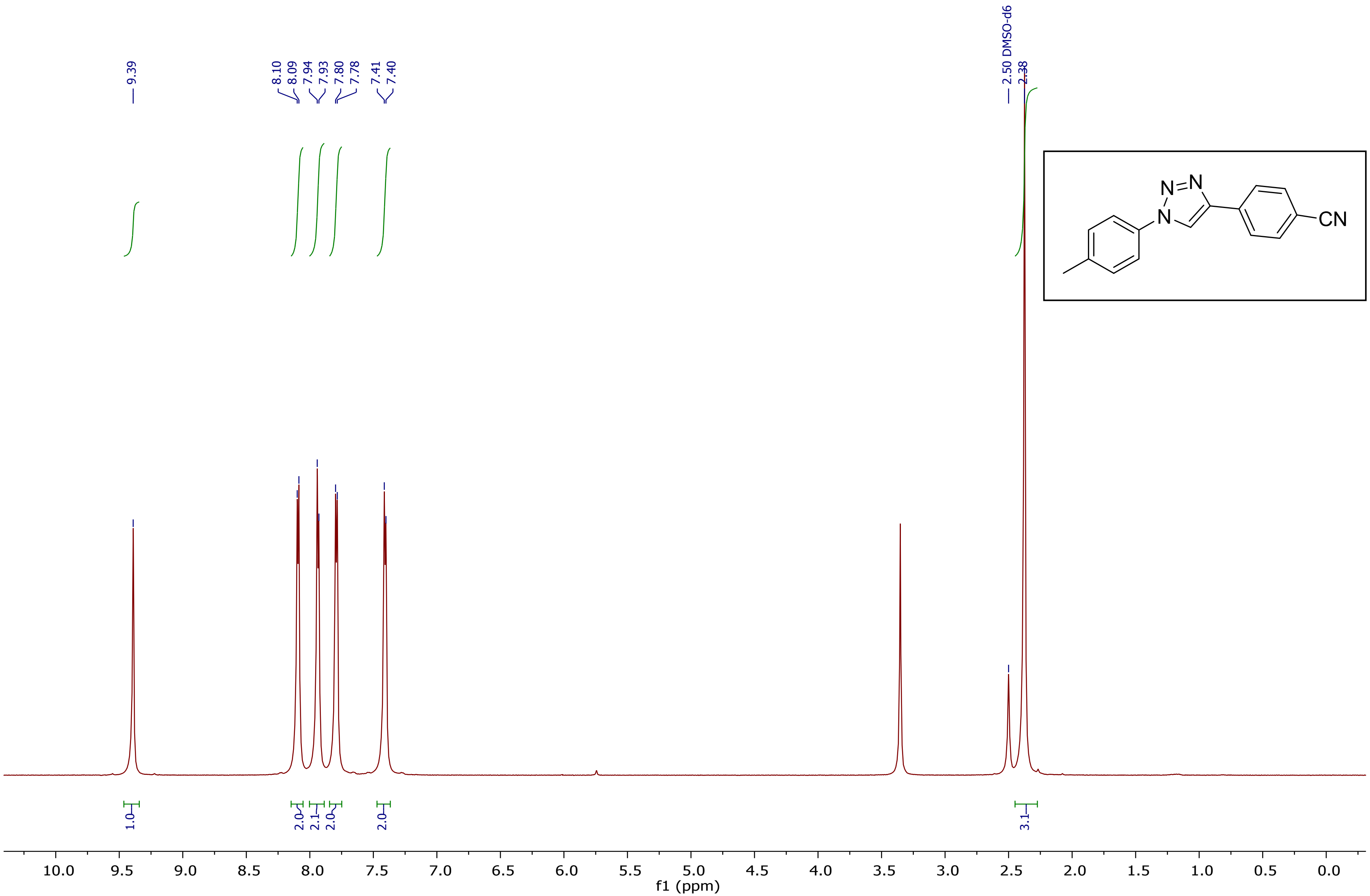


Figure S39. ^{1}H NMR (600 MHz, DMSO-d_6) of 4-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)benzonitrile (9i).

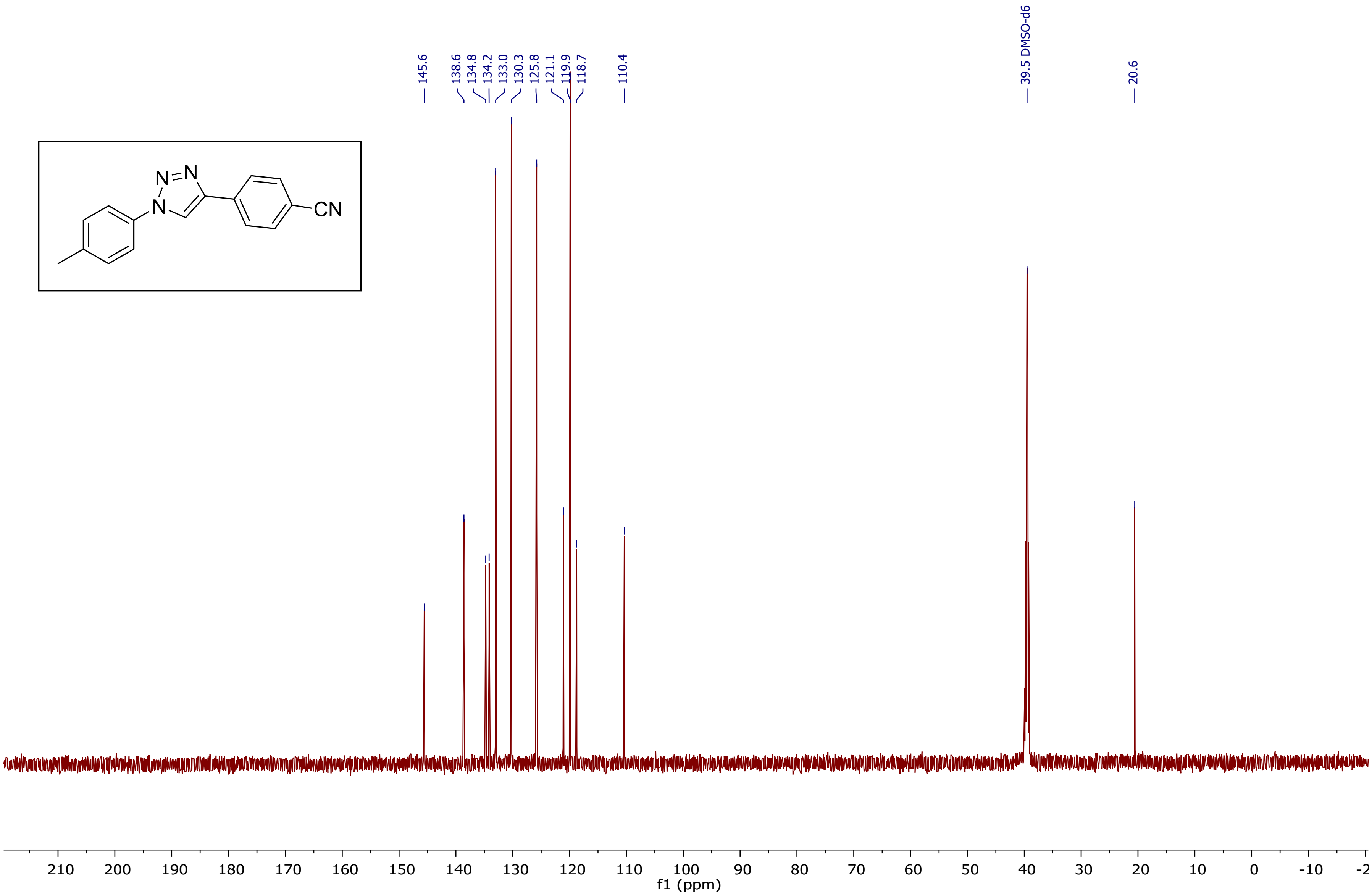


Figure S40. $^{13}C\{^1H\}$ **NMR (151 MHz, DMSO-d_6) of 4-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)benzonitrile (9i).**

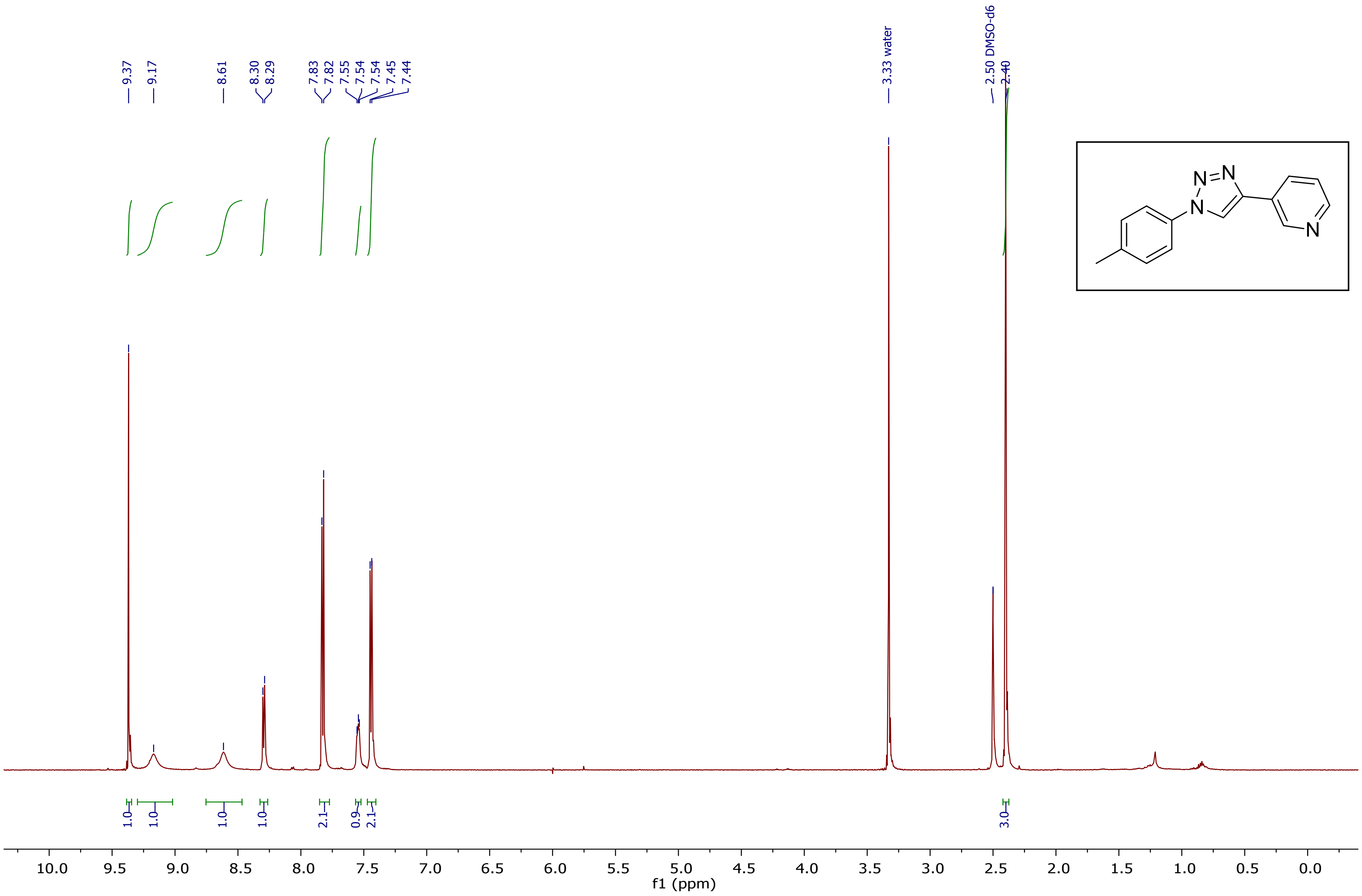


Figure S41. ^{1}H NMR (600 MHz, DMSO-d_6) of 3-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)pyridine (9j).

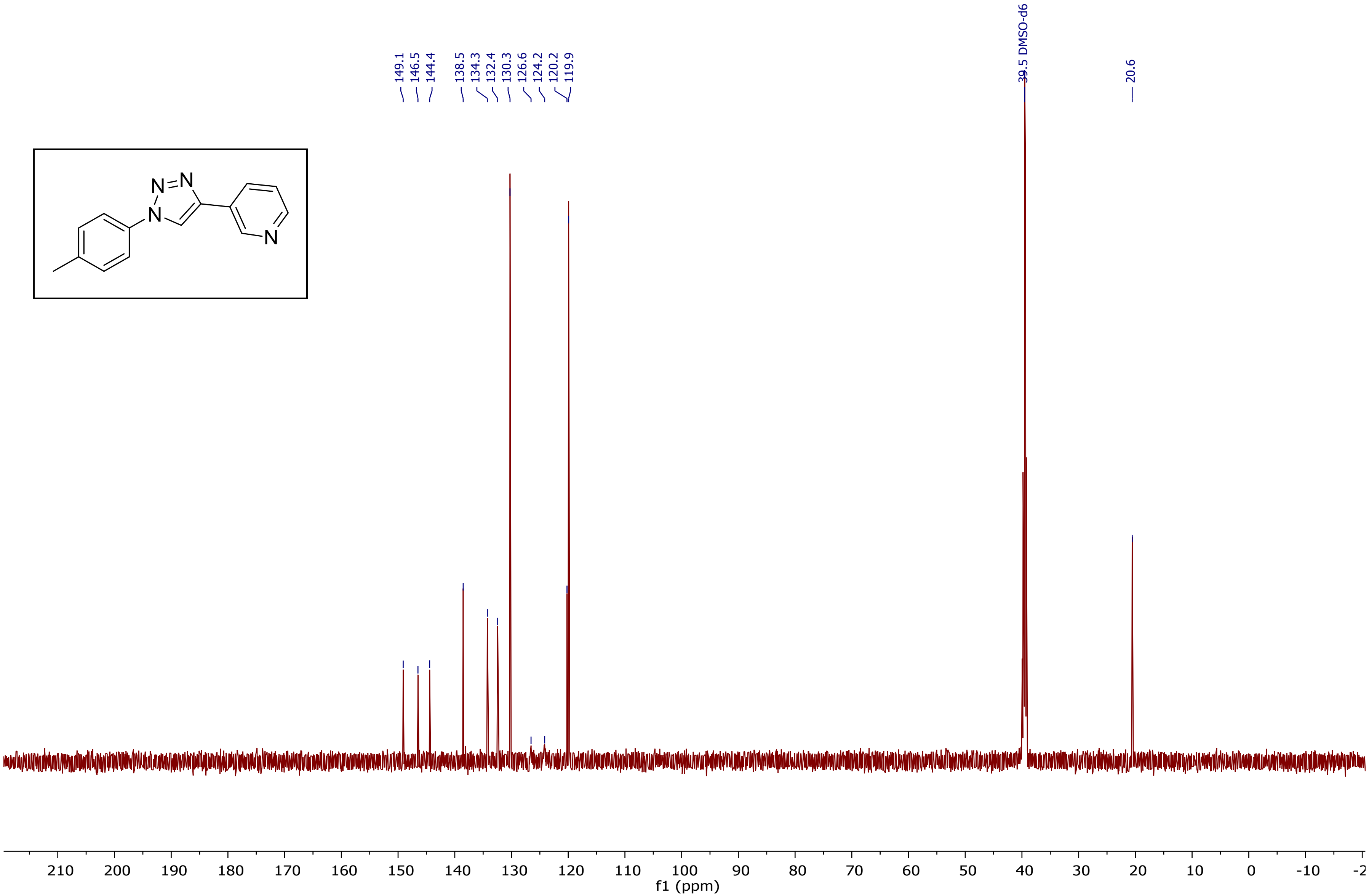


Figure S42. $^{13}C\{^1H\}$ **NMR (151 MHz, DMSO-d_6) of 3-(1-p-Tolyl-1H-1,2,3-triazol-4-yl)pyridine (9j).**

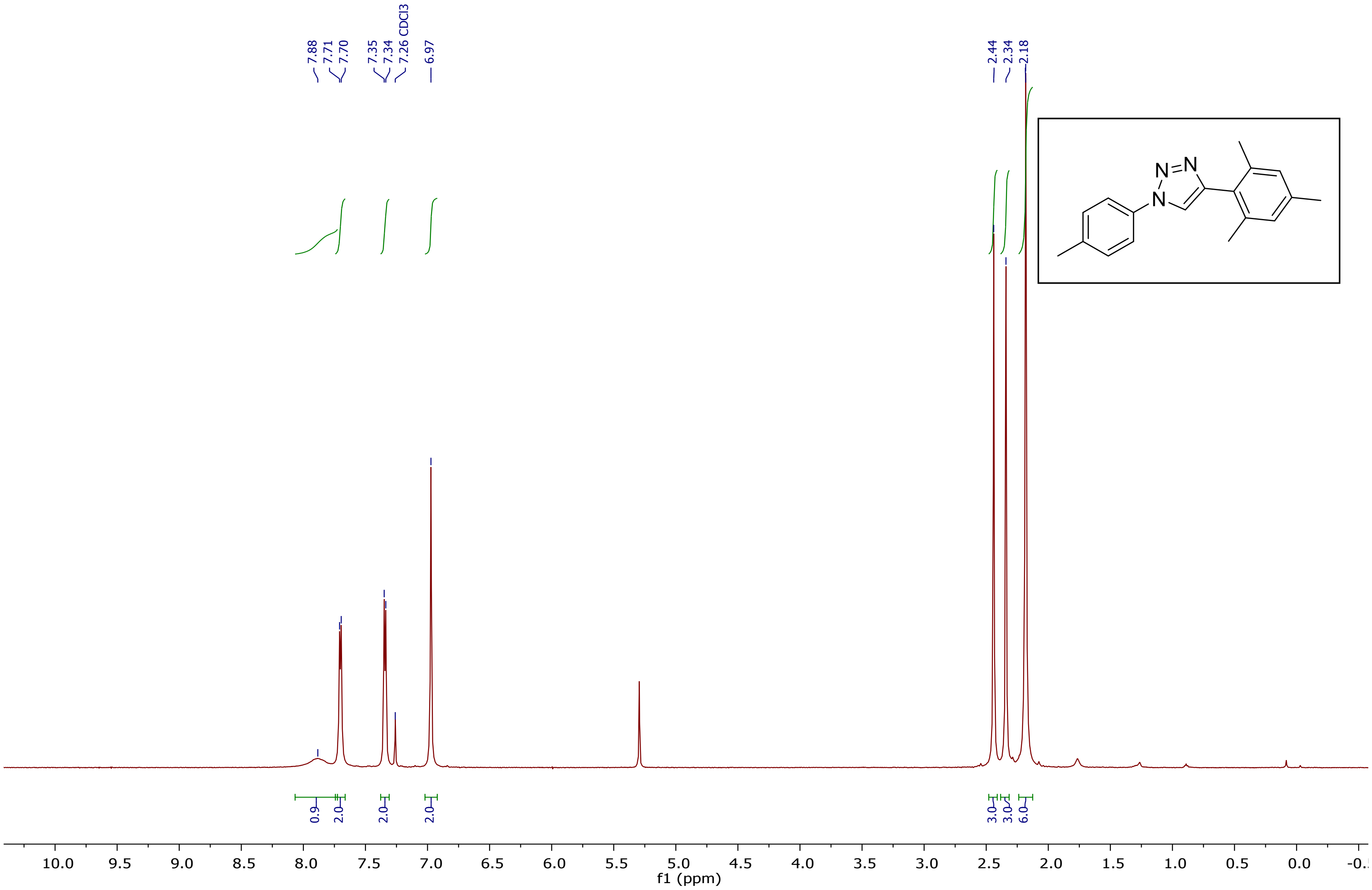


Figure S43. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-Mesityl-1-p-tolyl-1H-1,2,3-triazole (9k).

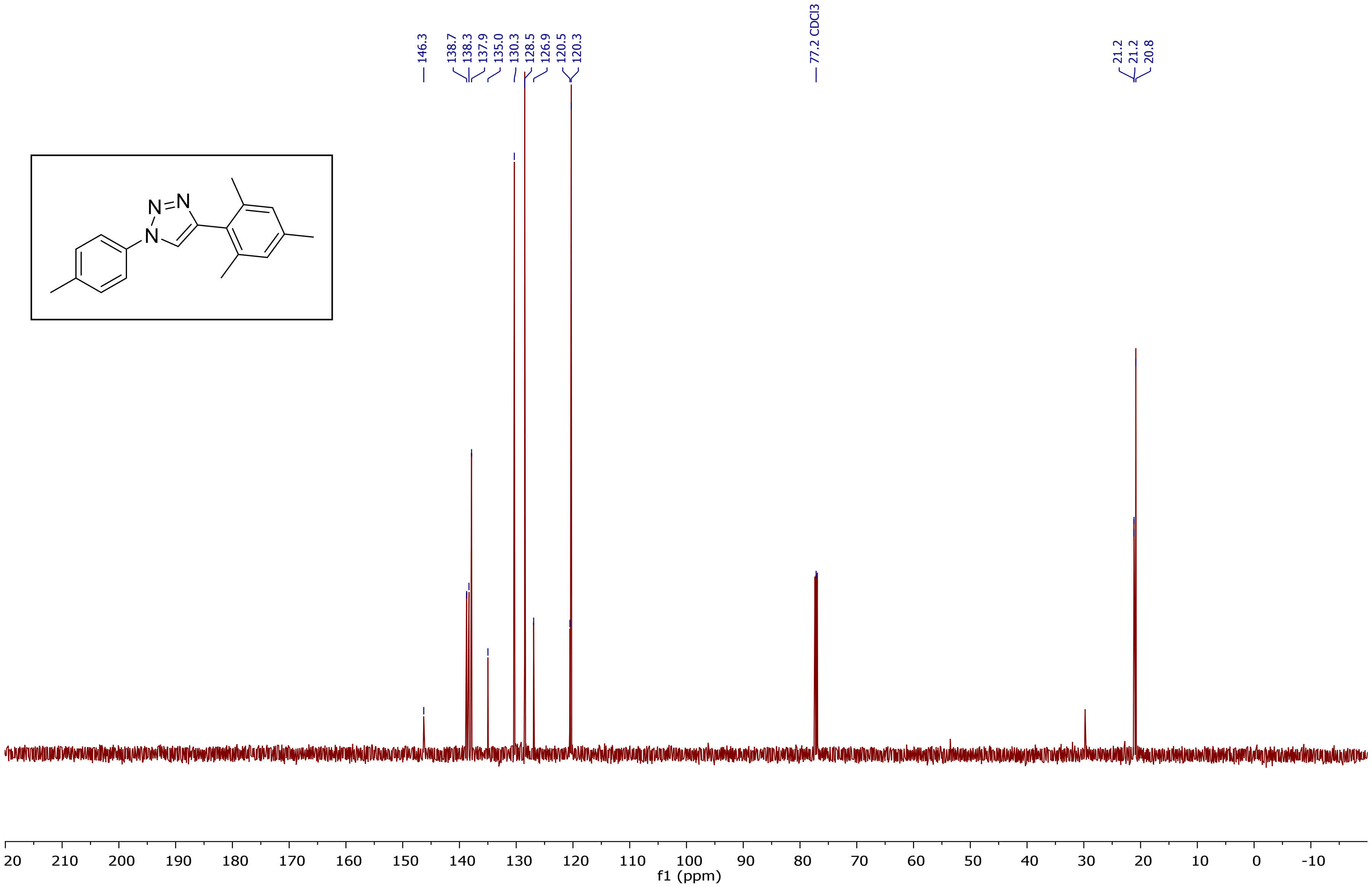


Figure S44. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 4-Mesityl-1-p-tolyl-1H-1,2,3-triazole (9k).**

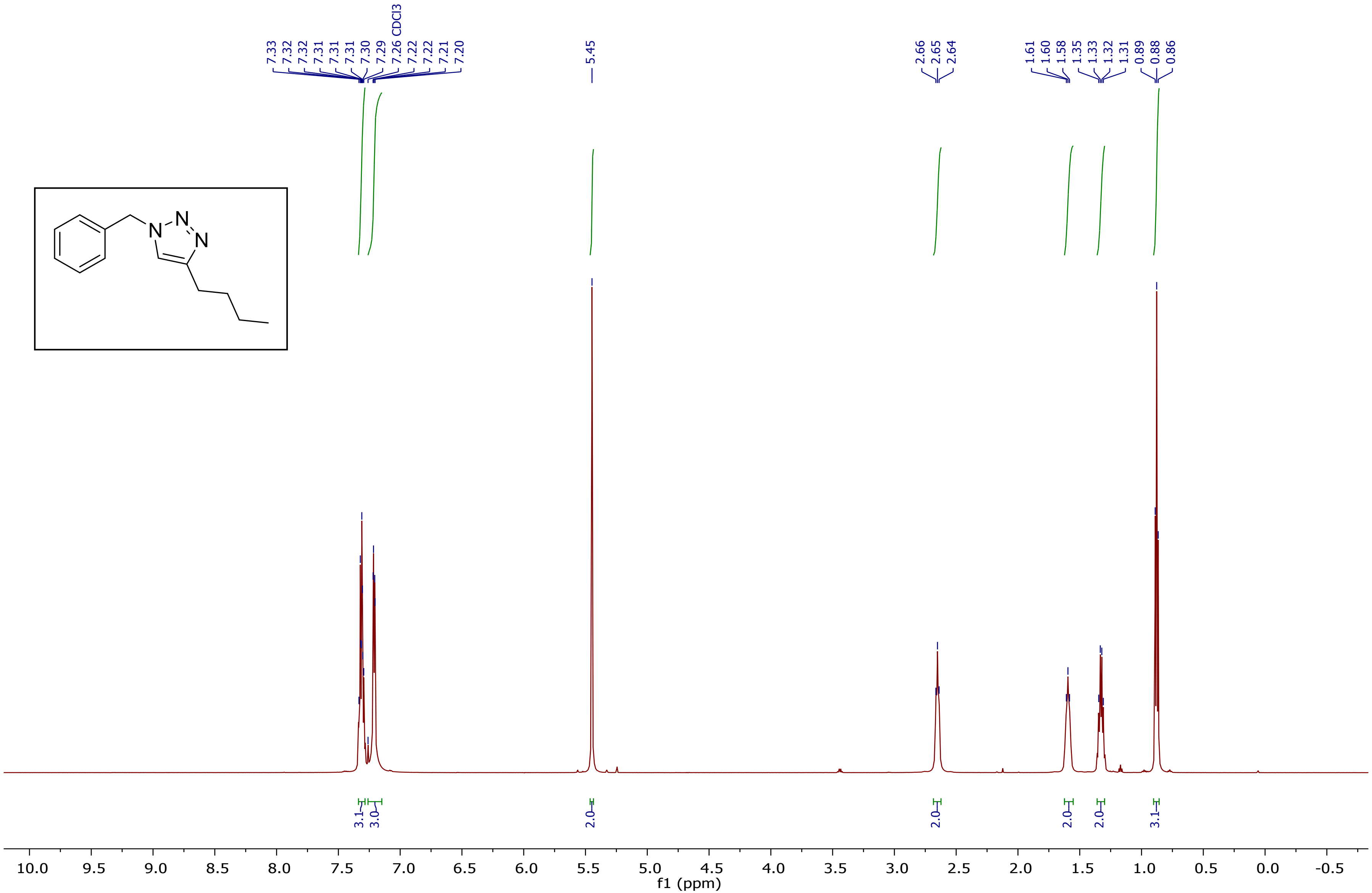


Figure S45. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-butyl-1H-1,2,3-triazole (10a).

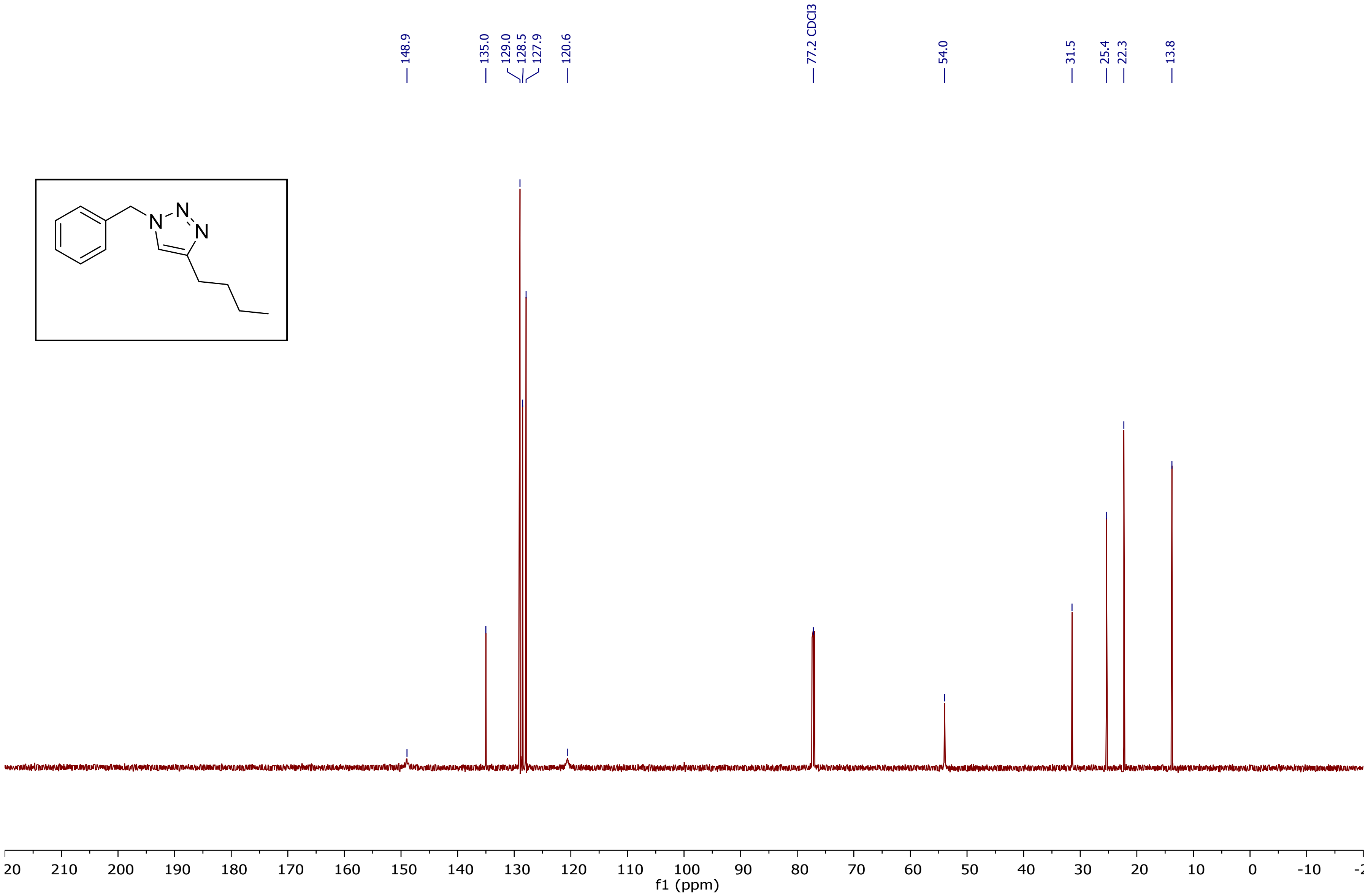


Figure S46. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-butyl-1H-1,2,3-triazole (10a).**

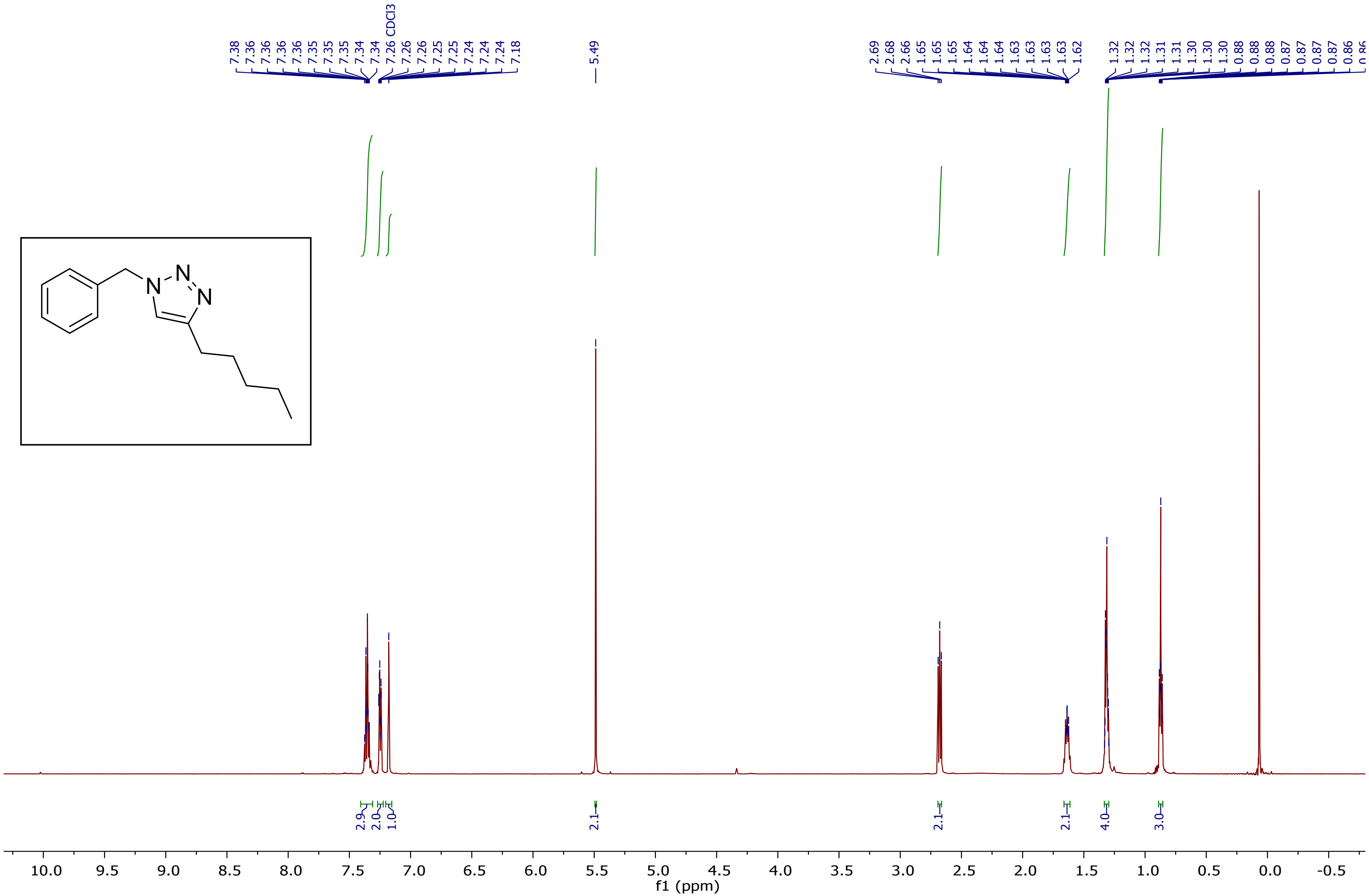


Figure S47. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-pentyl-1H-1,2,3-triazole (10b).

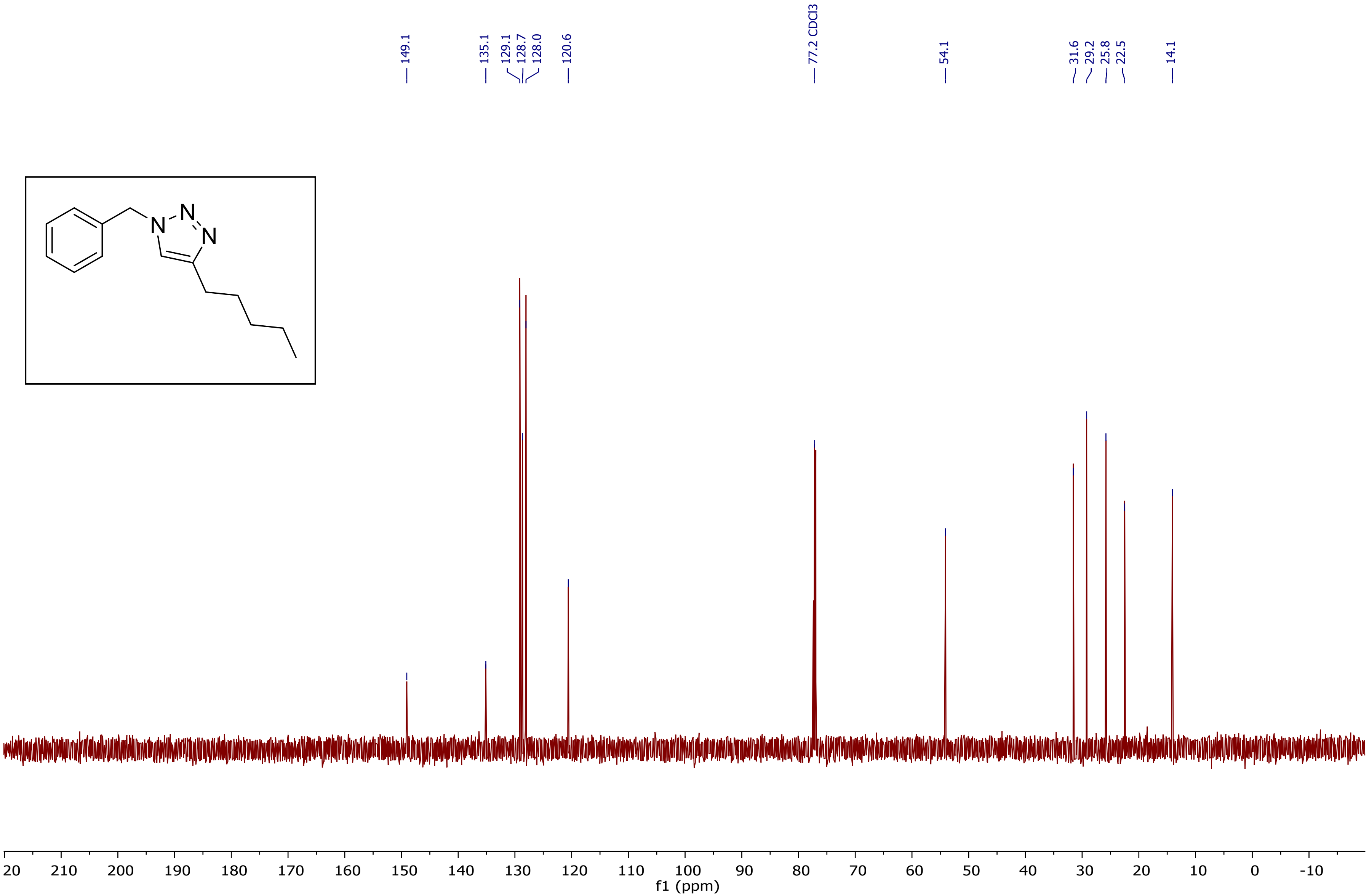


Figure S48. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-pentyl-1H-1,2,3-triazole (10b).**

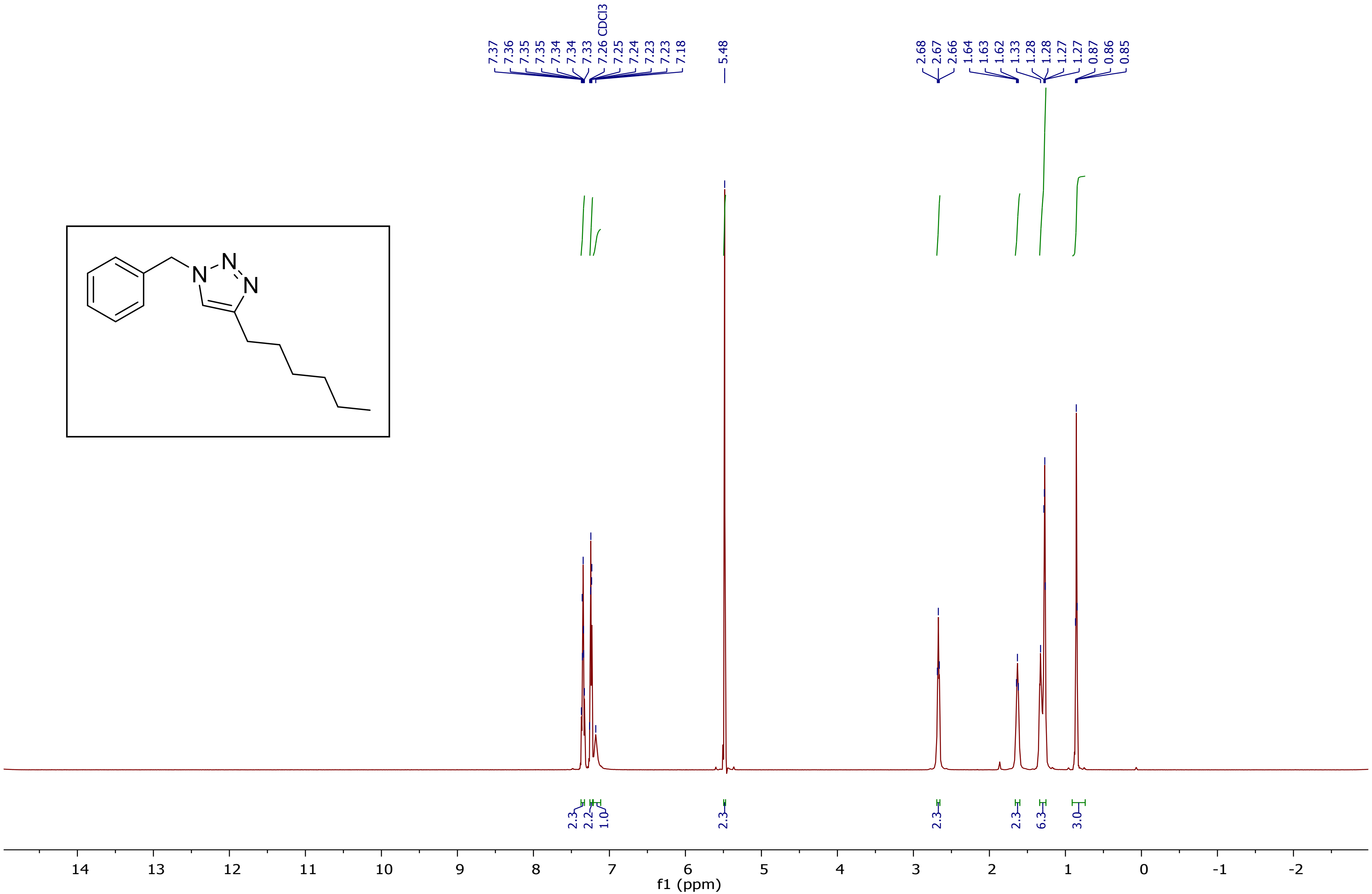


Figure S49. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-hexyl-1H-1,2,3-triazole (10c).

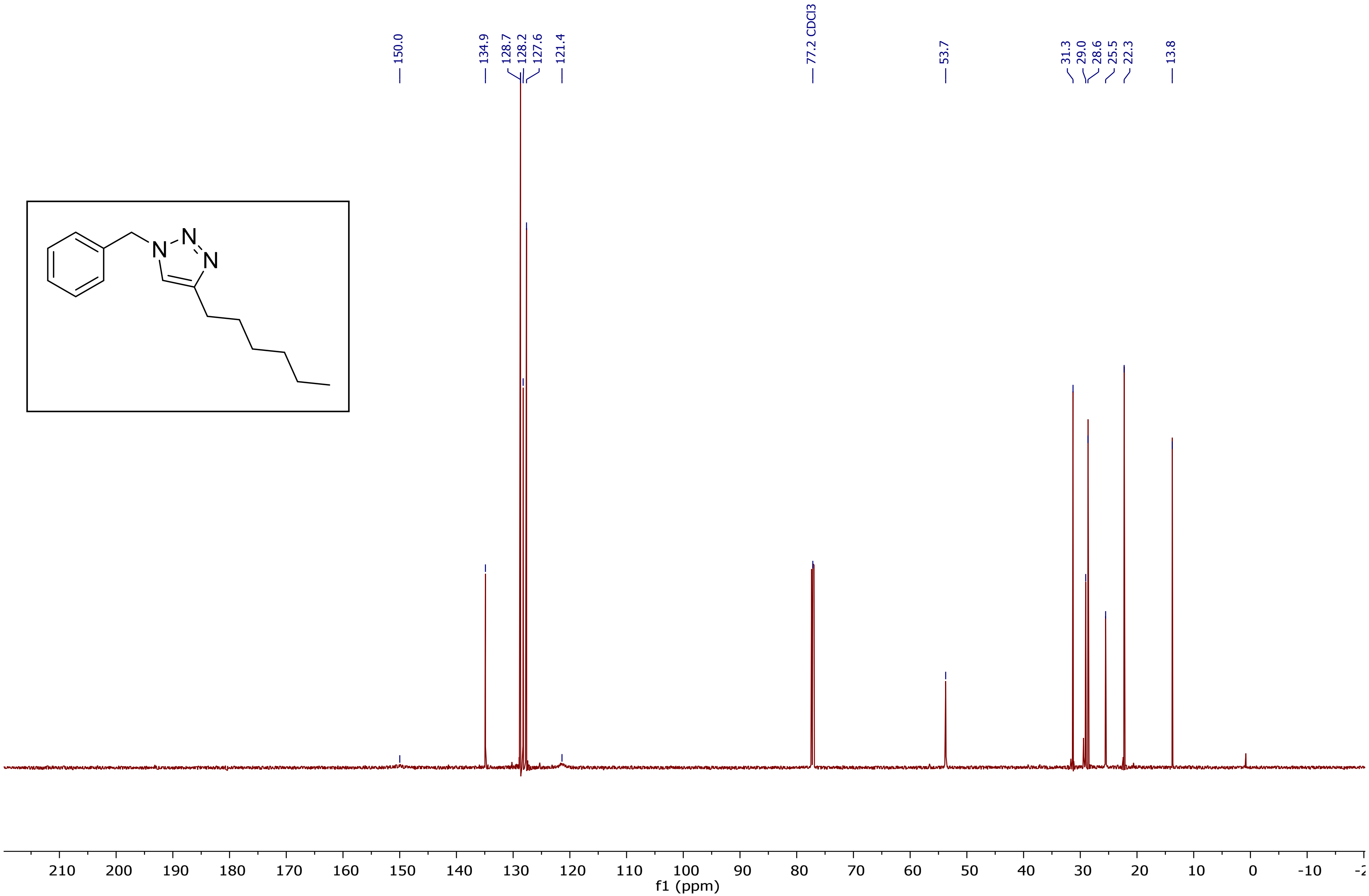


Figure S50. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-hexyl-1H-1,2,3-triazole (10c).**

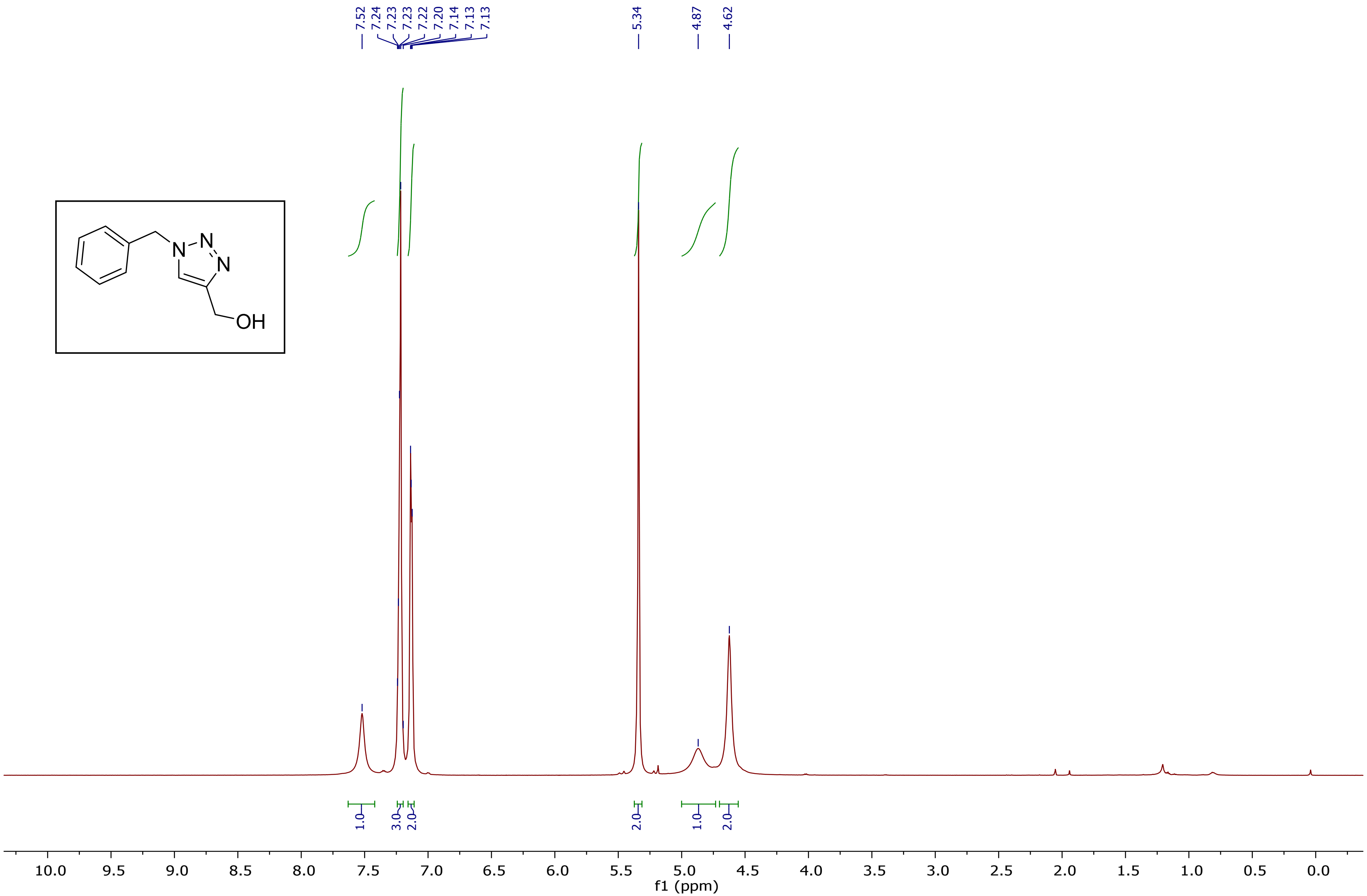


Figure S51. ^{1}H NMR (600 MHz, Chloroform-*d*) of (1-Benzyl-1H-1,2,3-triazol-4-yl)methanol (10d).

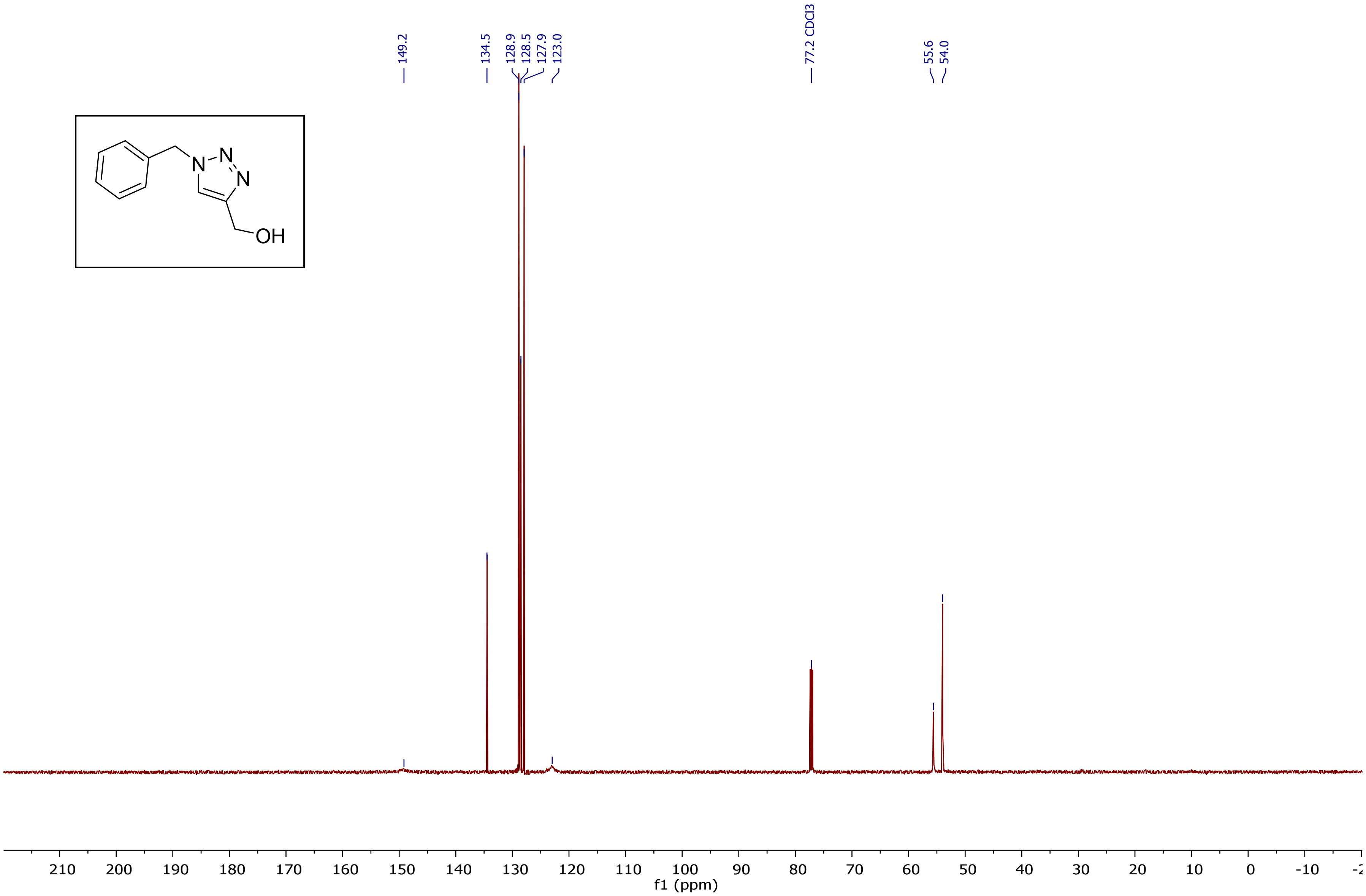


Figure S52. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of (1-Benzyl-1H-1,2,3-triazol-4-yl)methanol (10d).**

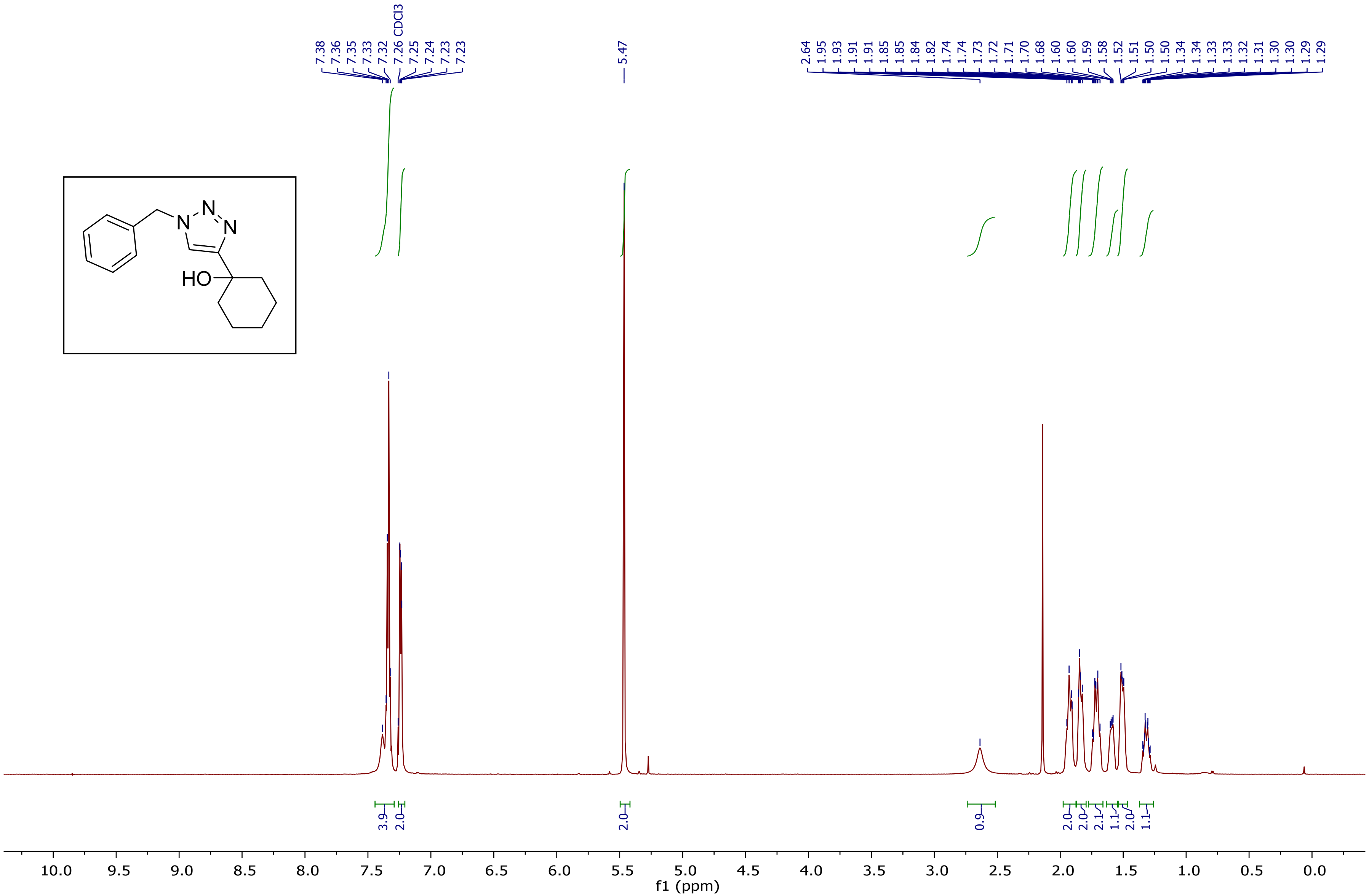


Figure S53. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(1-Benzyl-1H-1,2,3-triazol-4-yl)cyclohexanol (10e).

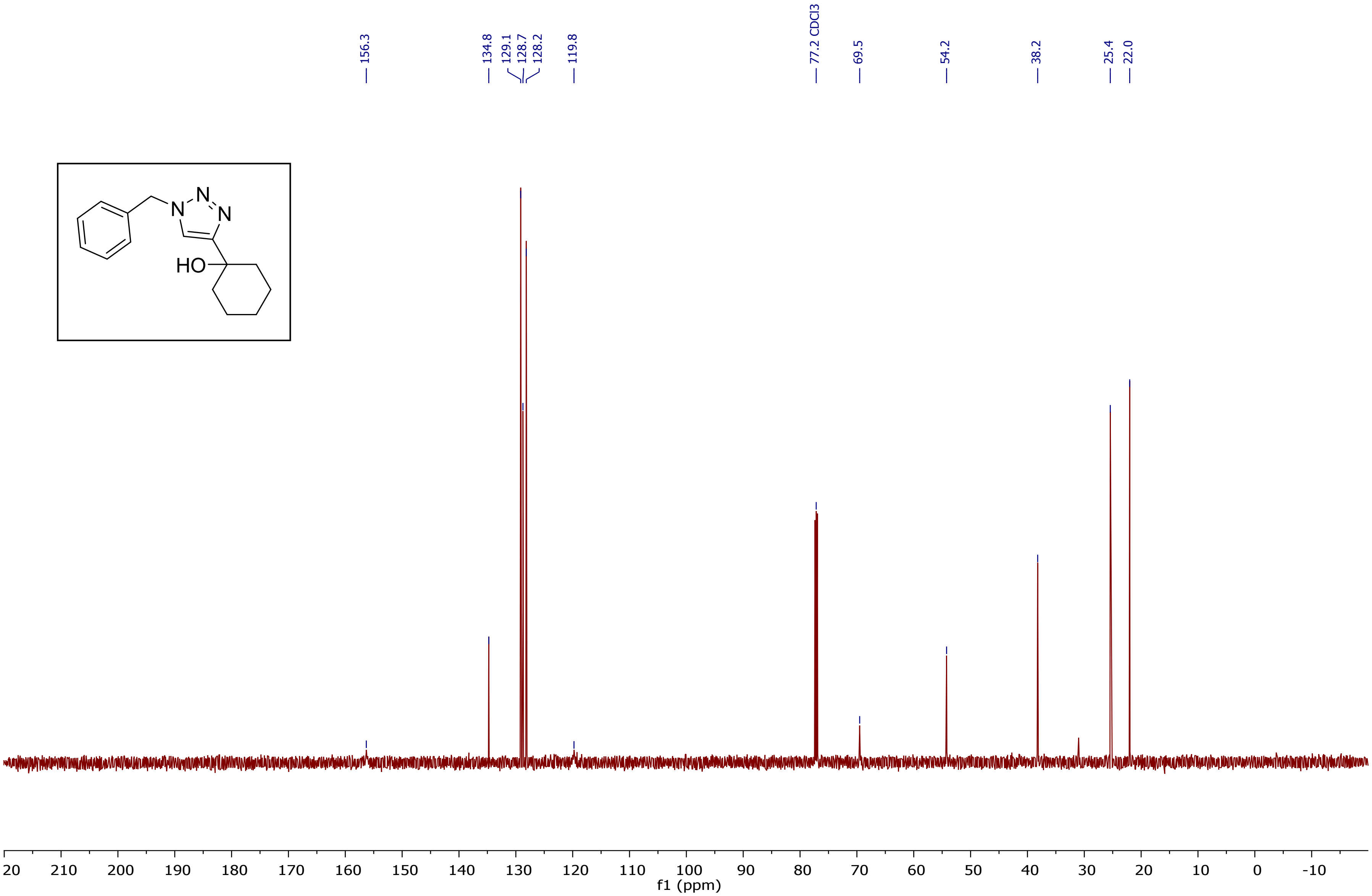


Figure S54. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-(1-Benzyl-1H-1,2,3-triazol-4-yl)cyclohexanol (10e).**

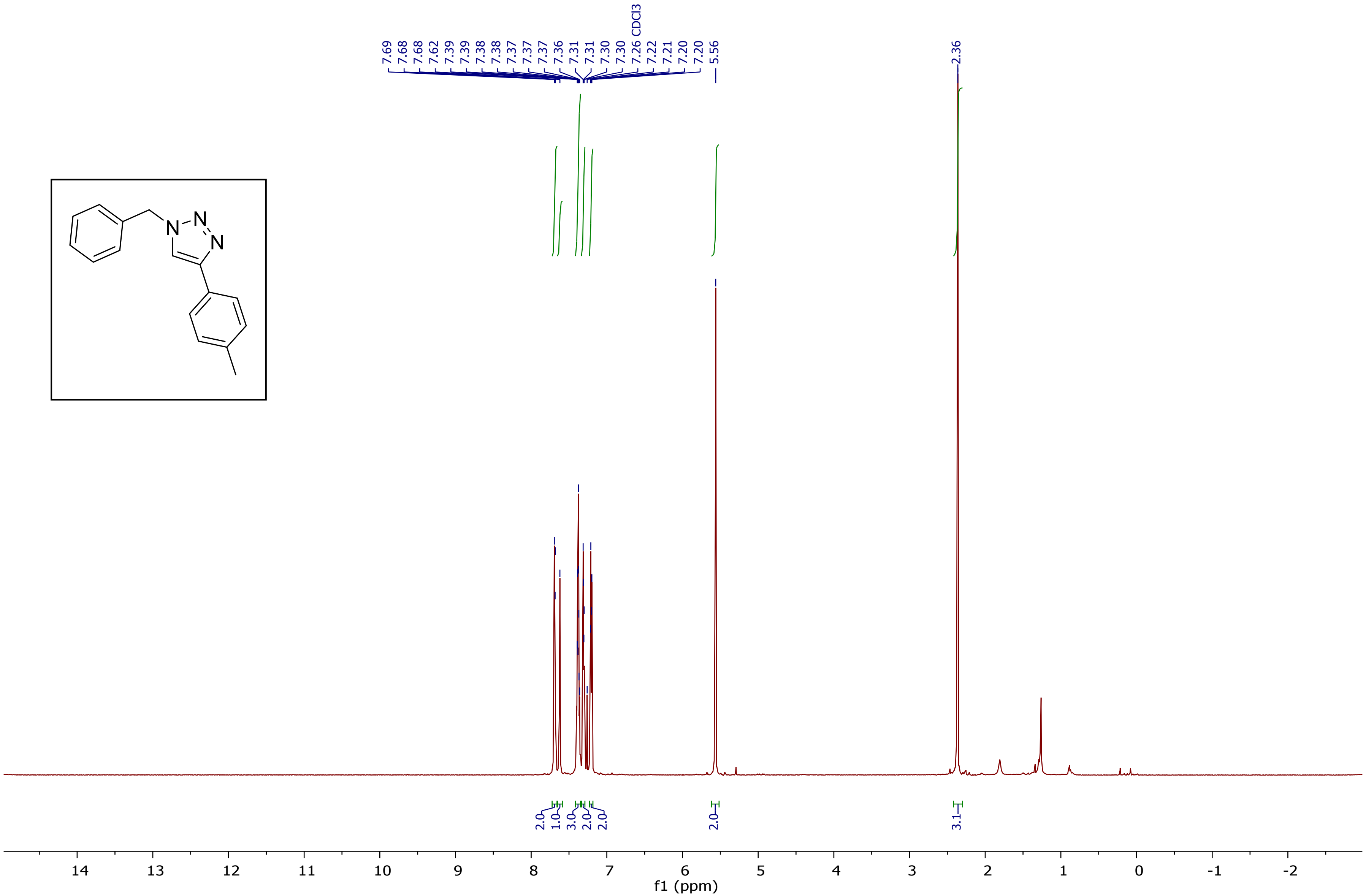


Figure S55. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-p-tolyl-1H-1,2,3-triazole (10f).

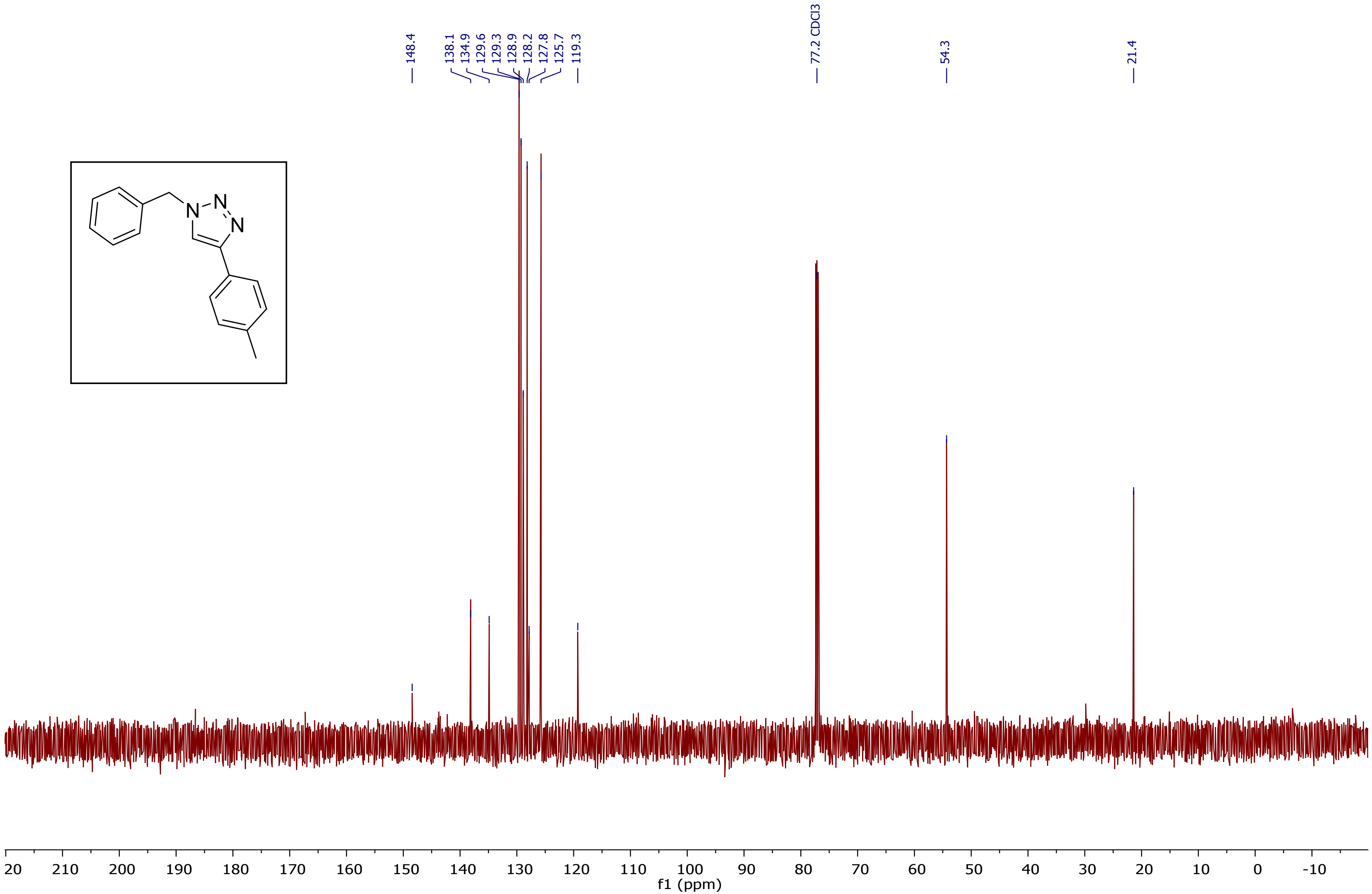


Figure S56. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-p-tolyl-1H-1,2,3-triazole (10f).**

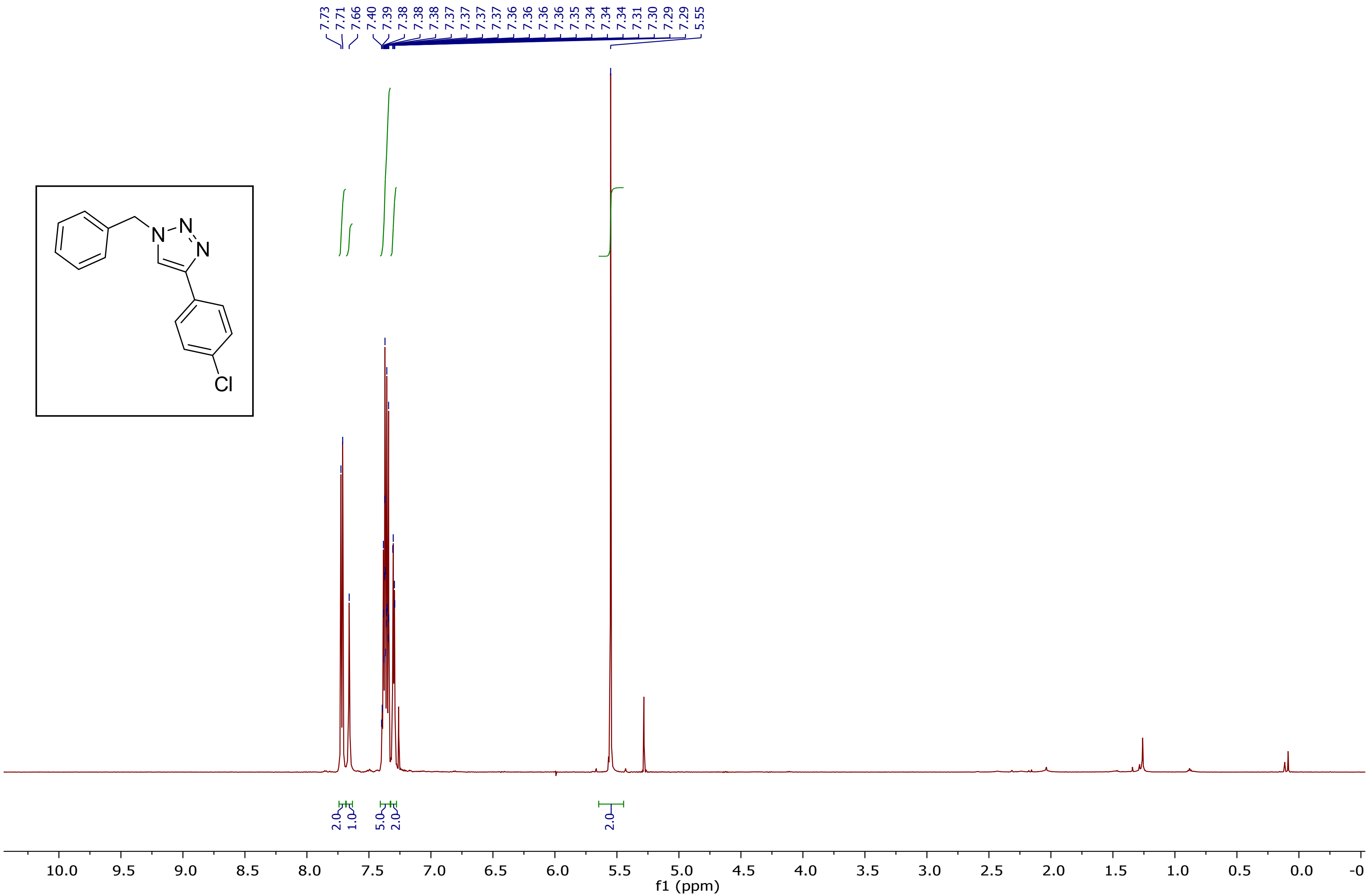


Figure S57. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-(4-chlorophenyl)-1H-1,2,3-triazole (10g).

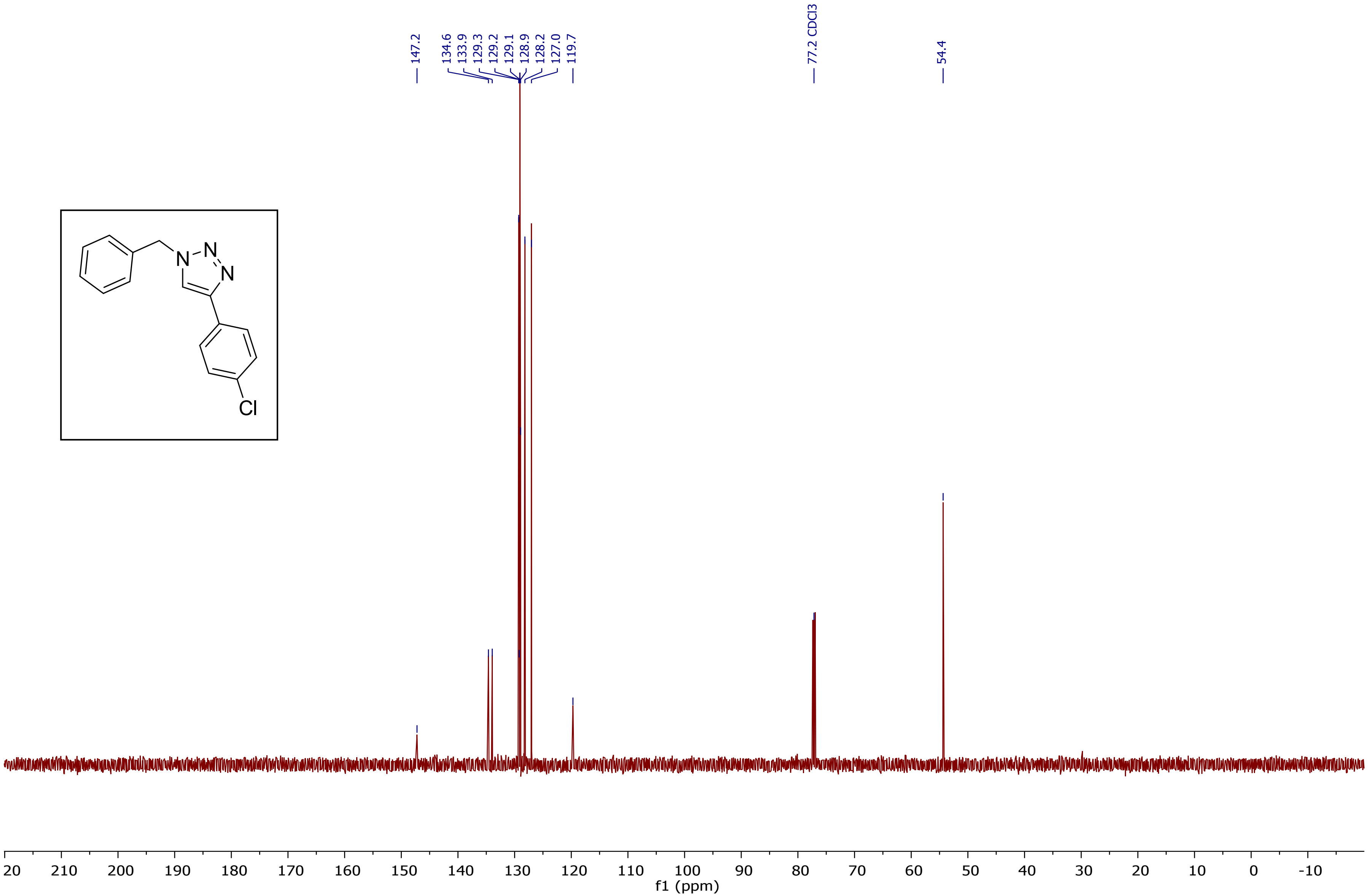


Figure S58. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-(4-chlorophenyl)-1H-1,2,3-triazole (10g).**

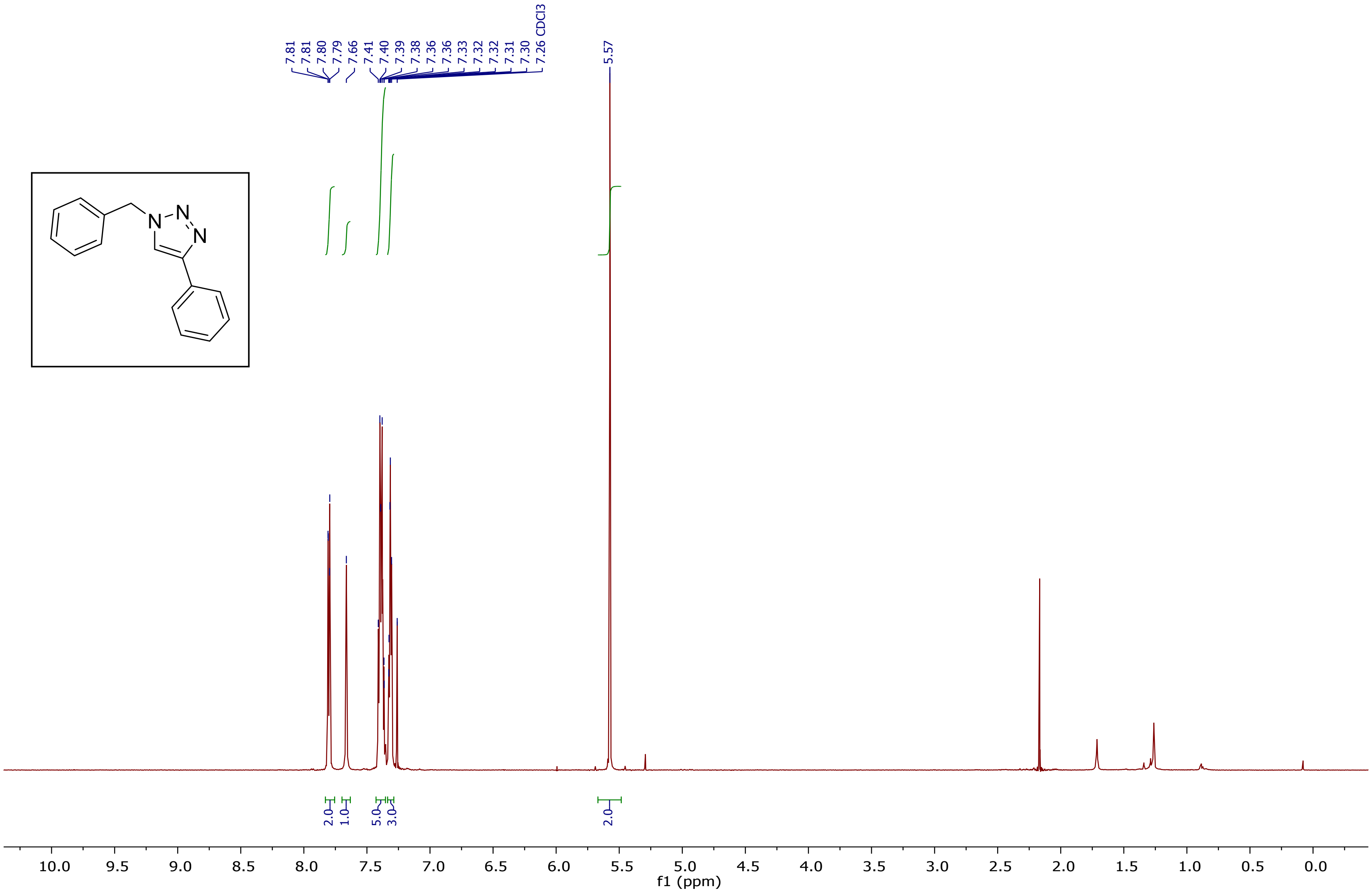


Figure S59. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-phenyl-1H-1,2,3-triazole (10h).

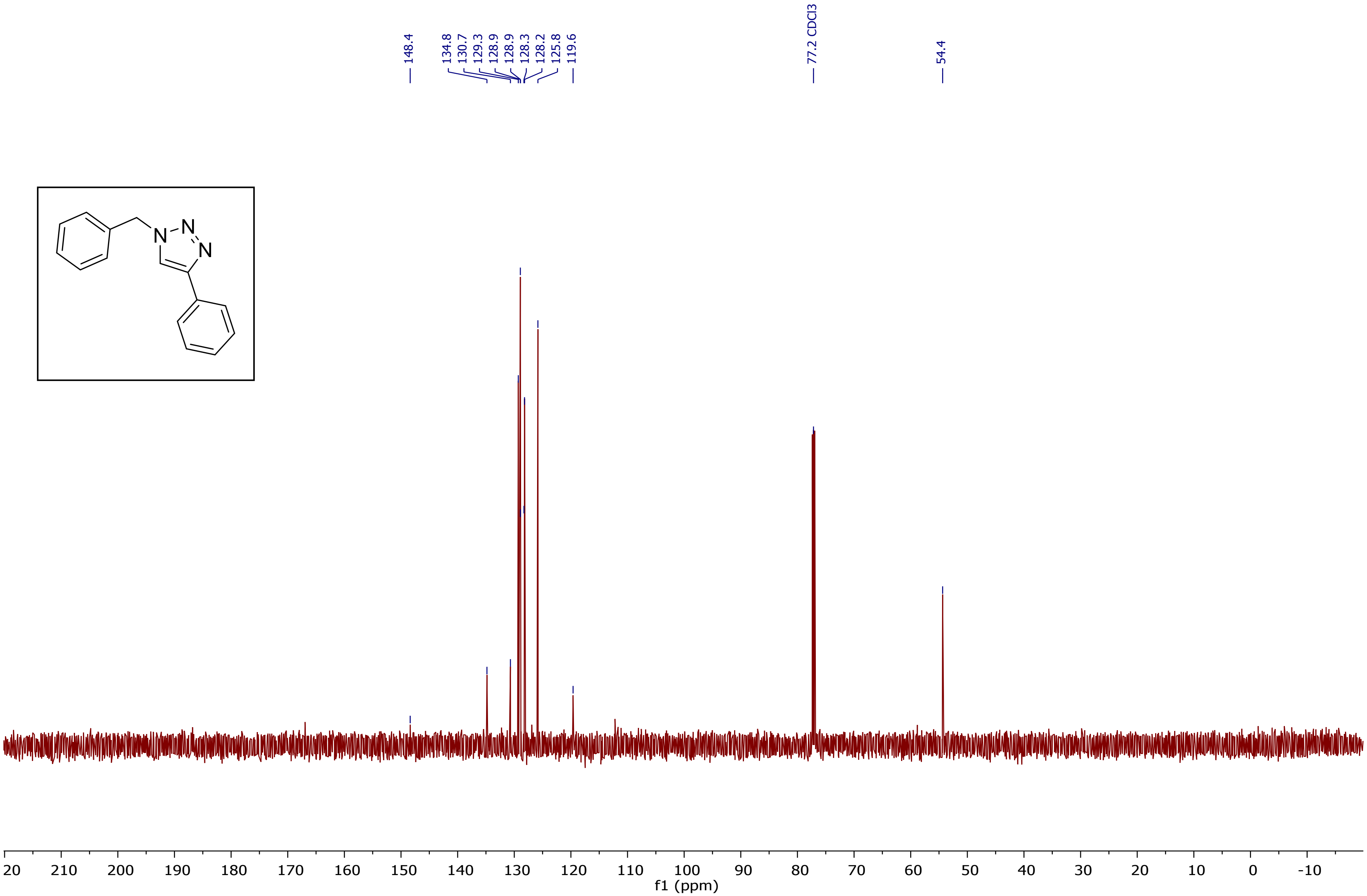


Figure S60. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-phenyl-1H-1,2,3-triazole (10h).**

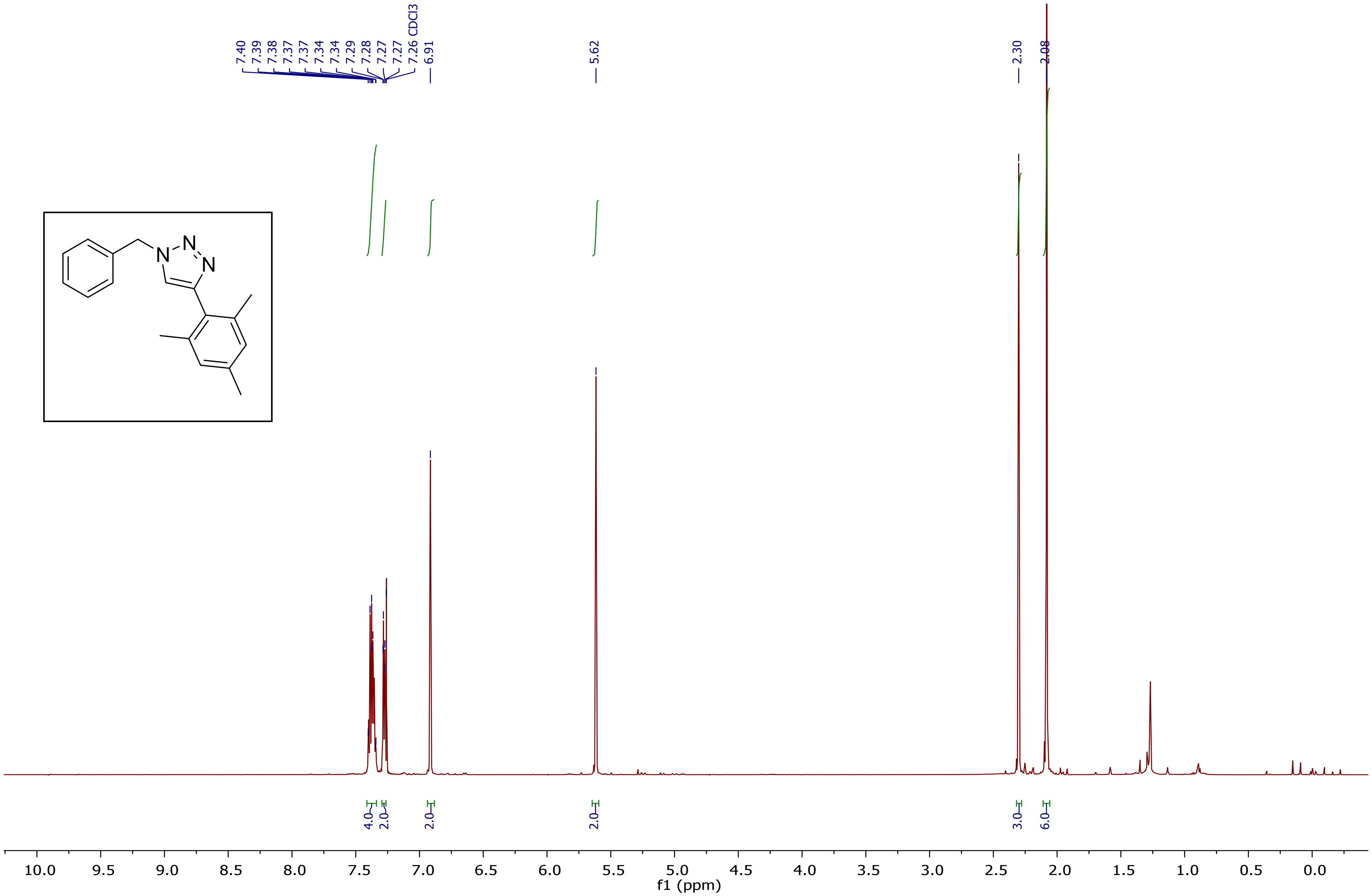


Figure S61. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-mesityl-1H-1,2,3-triazole (10i).

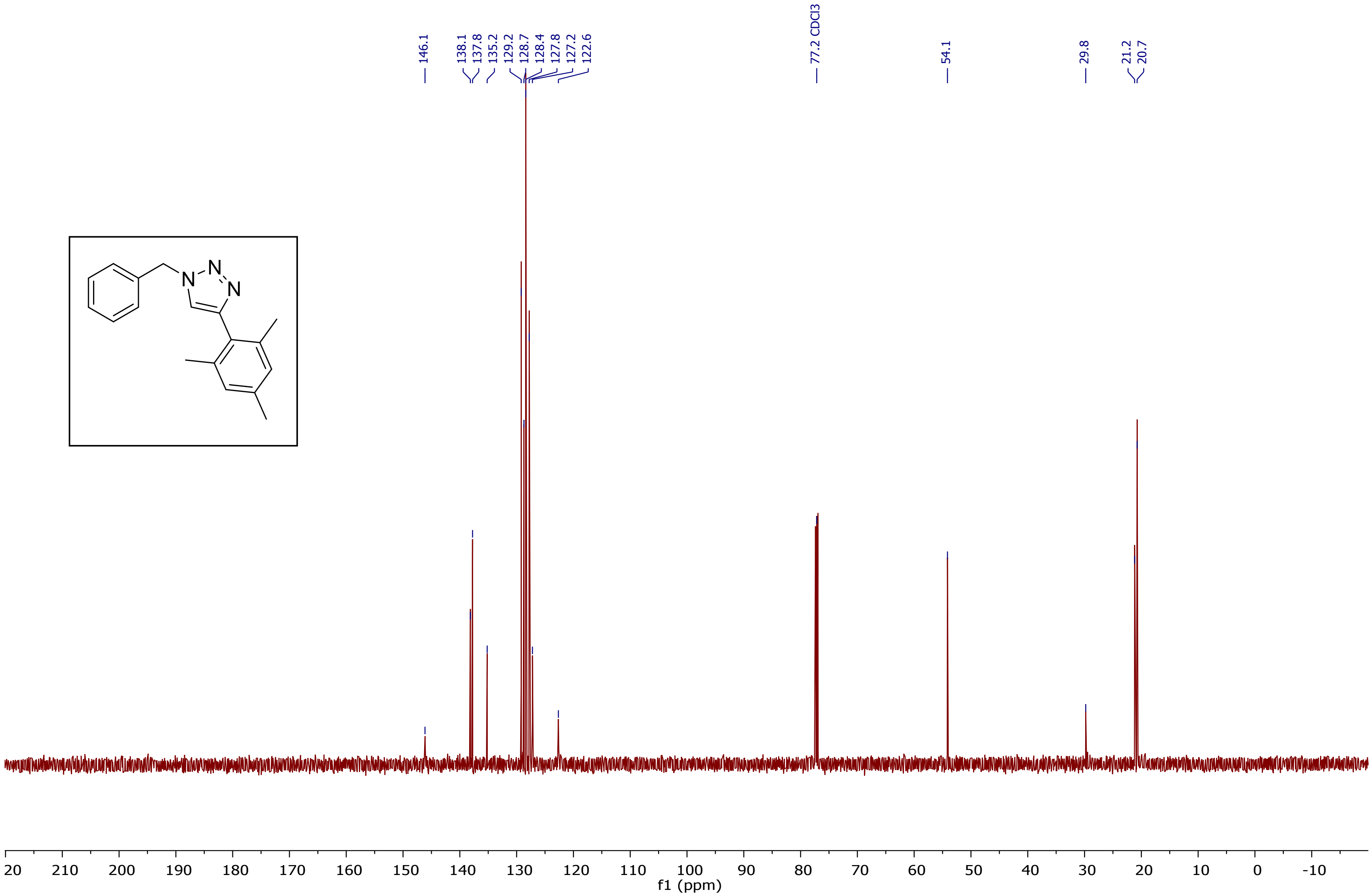


Figure S62. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-mesityl-1H-1,2,3-triazole (10i).**

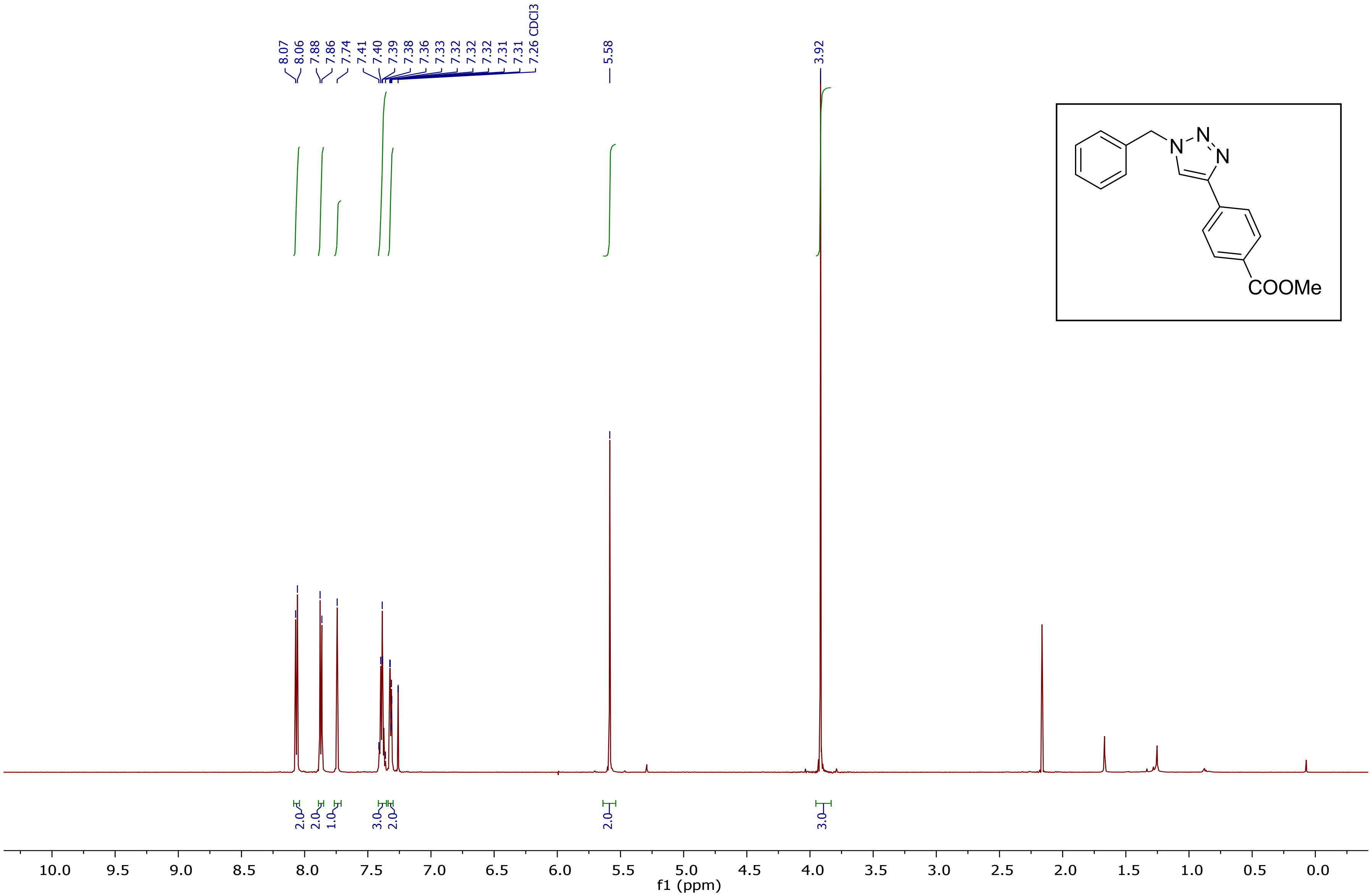


Figure S63. ^{1}H NMR (600 MHz, Chloroform-*d*) of methyl 4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzoate (10j).

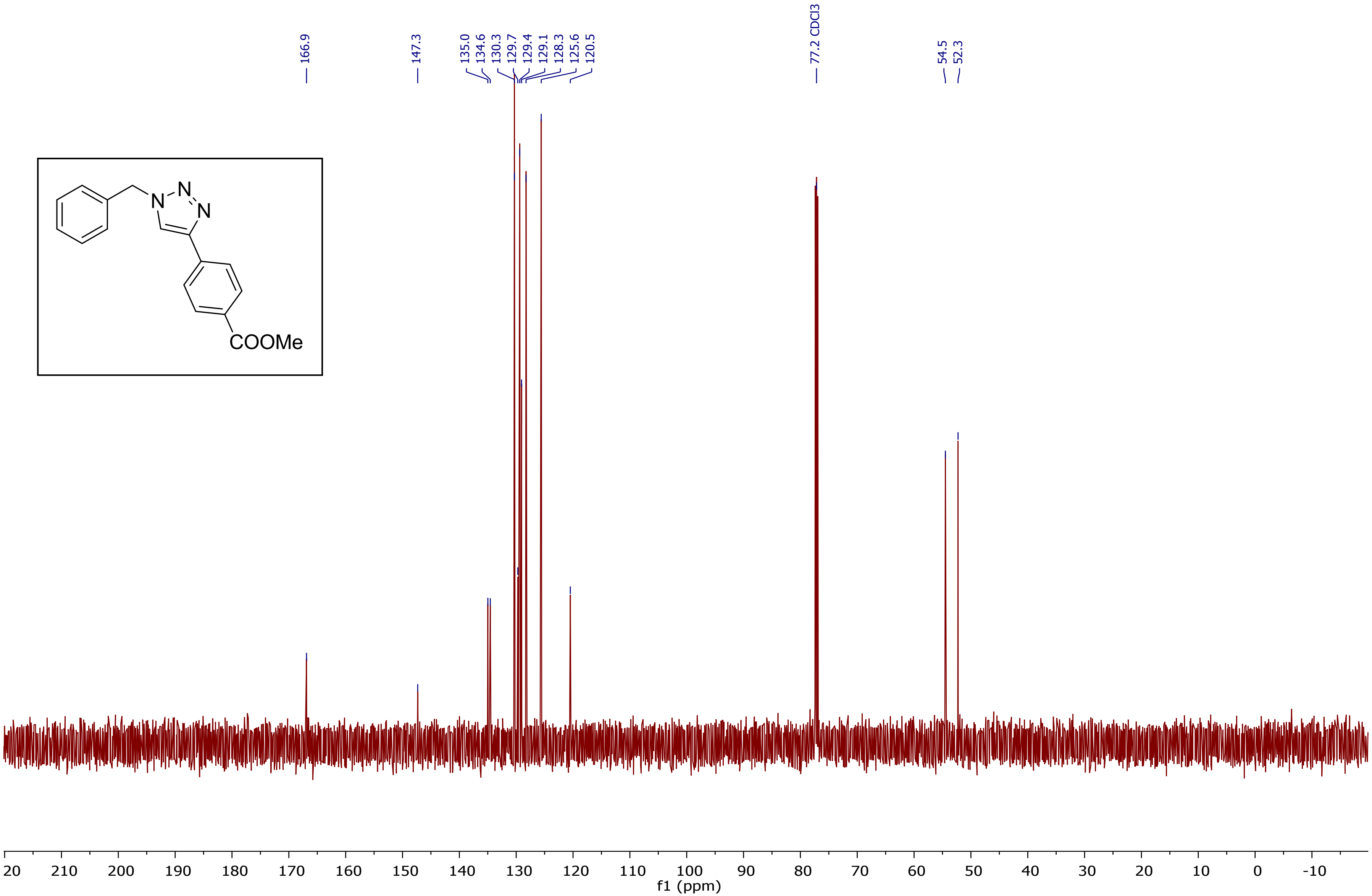


Figure S64. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of methyl 4-(1-benzyl-1H-1,2,3-triazol-4-yl)benzoate (10j).**

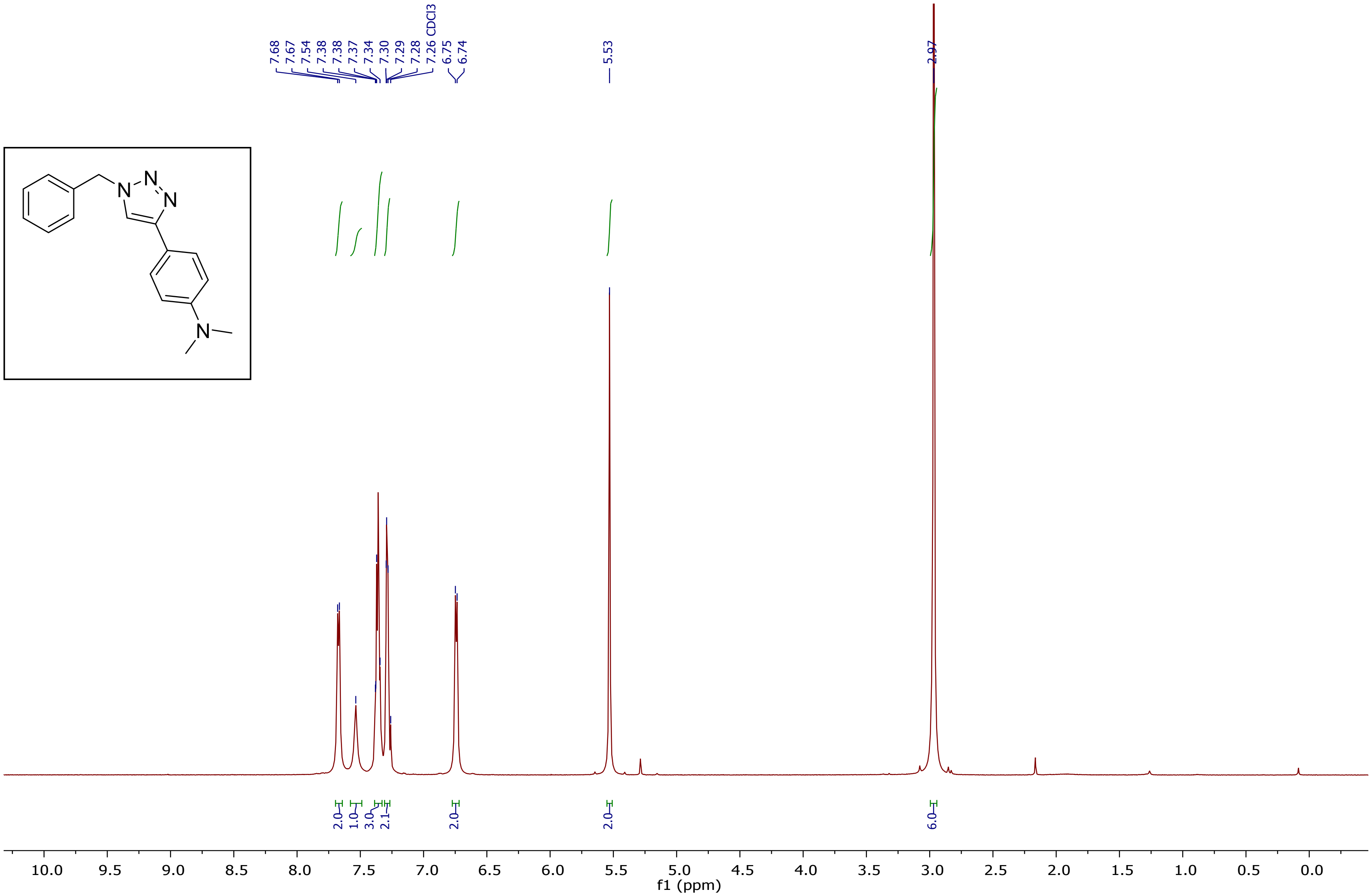


Figure S65. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-(1-Benzyl-1H-1,2,3-triazol-4-yl)-N,N-dimethylaniline (10k).

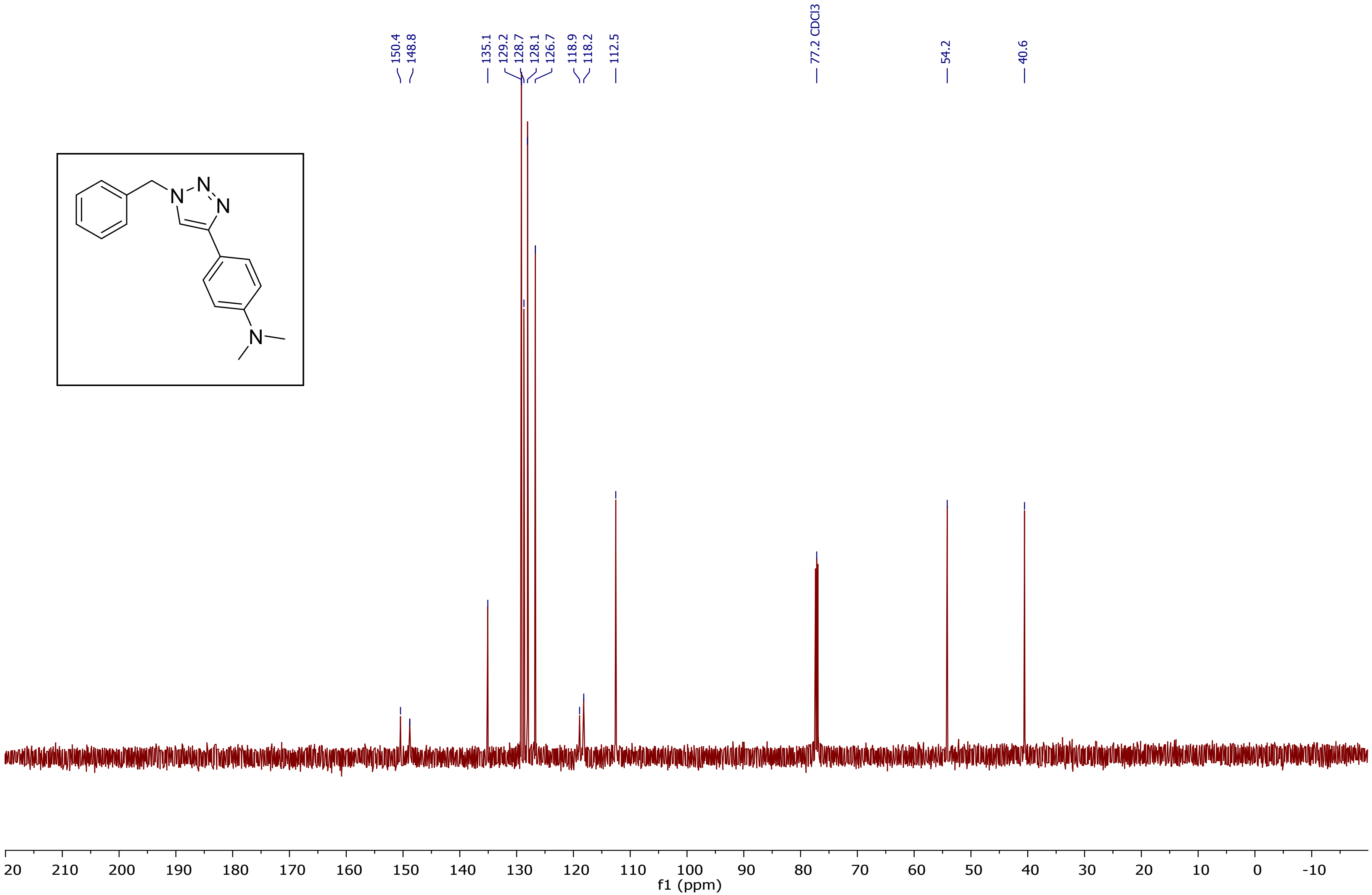


Figure S66. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 4-(1-Benzyl-1H-1,2,3-triazol-4-yl)-N,N-dimethylaniline (10k).**

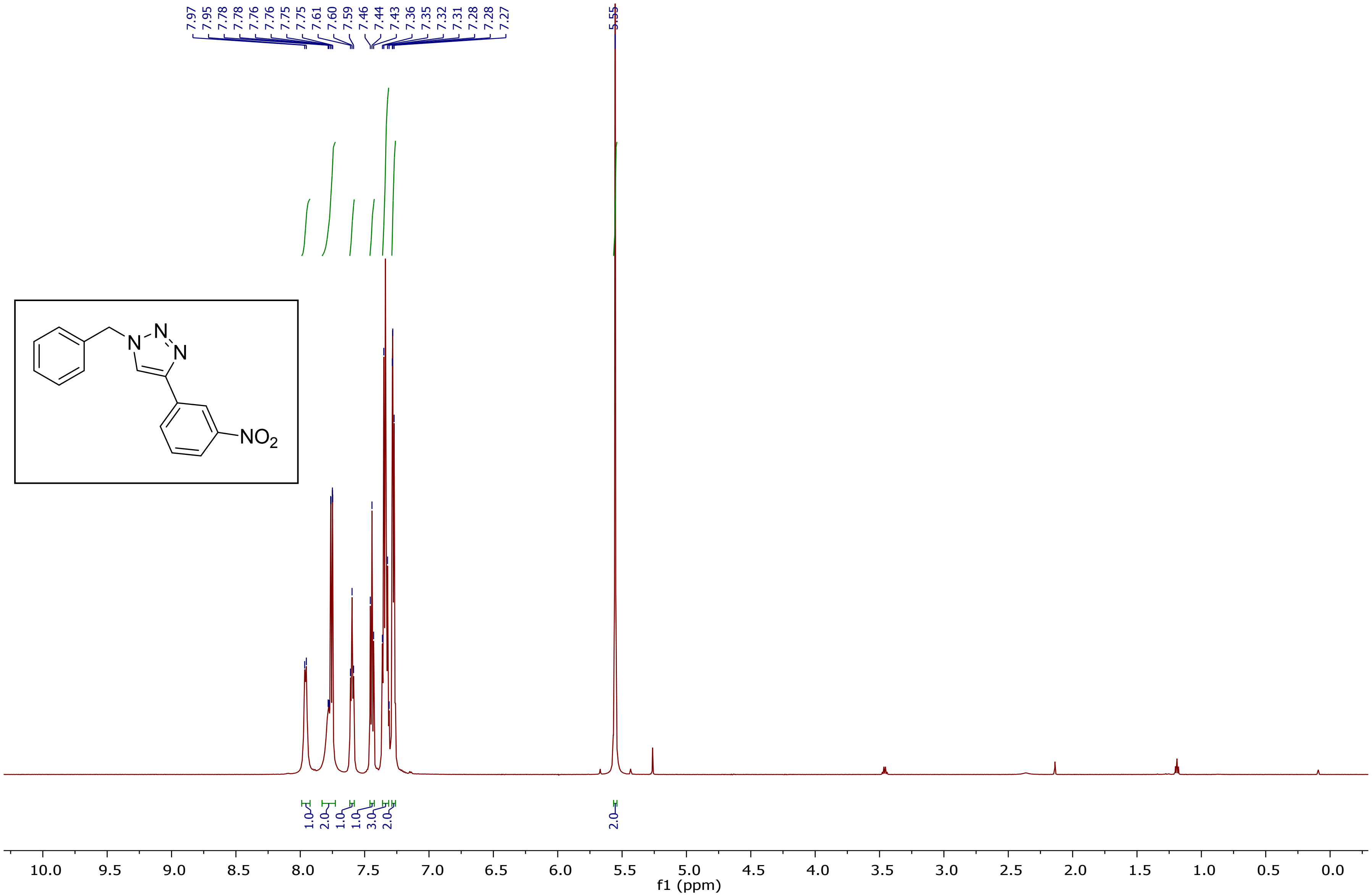


Figure S67. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-(3-nitrophenyl)-1H-1,2,3-triazole (10l).

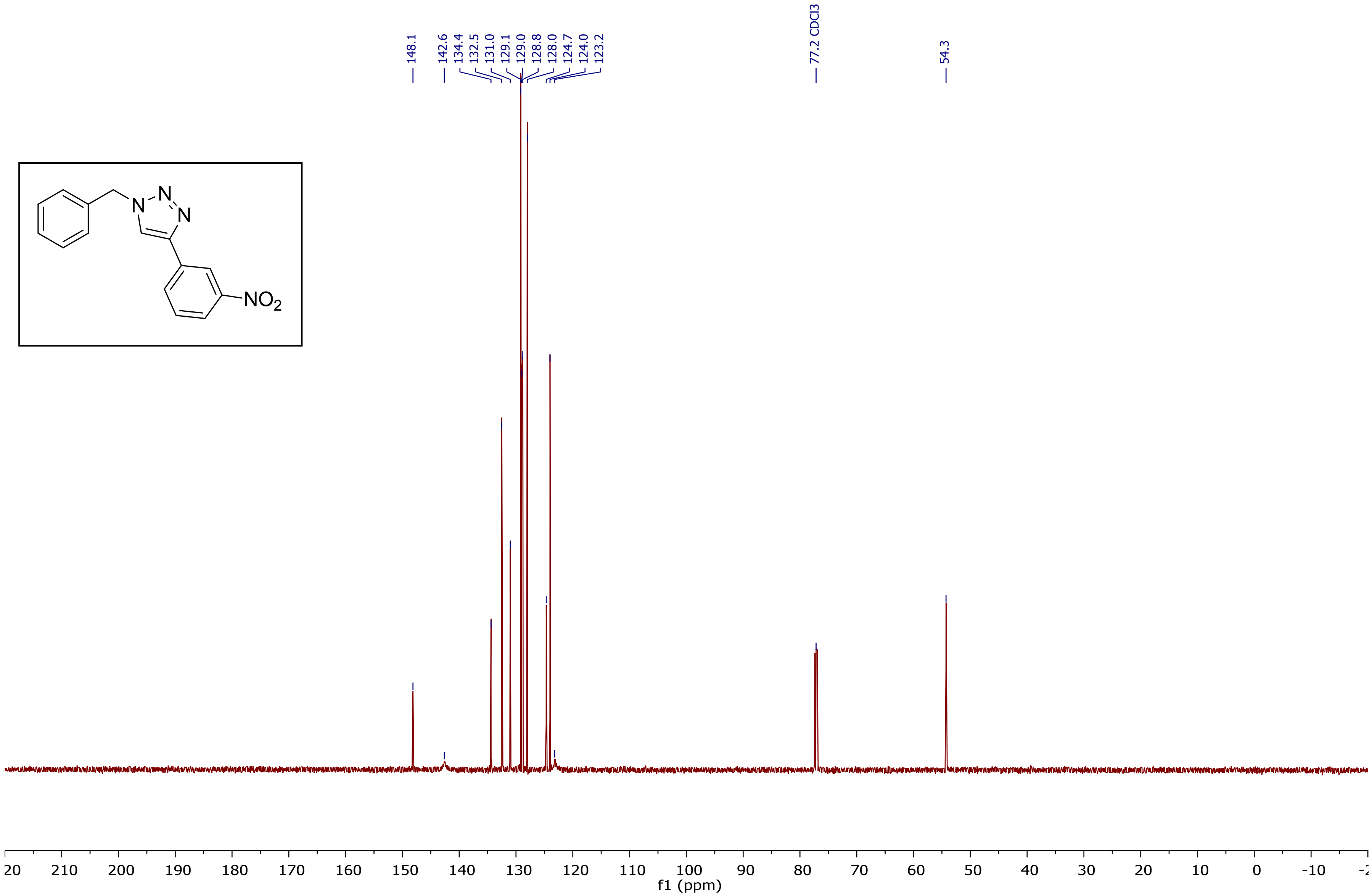


Figure S68. ^{13}C{^{1}H} **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-(3-nitrophenyl)-1H-1,2,3-triazole (10l).**

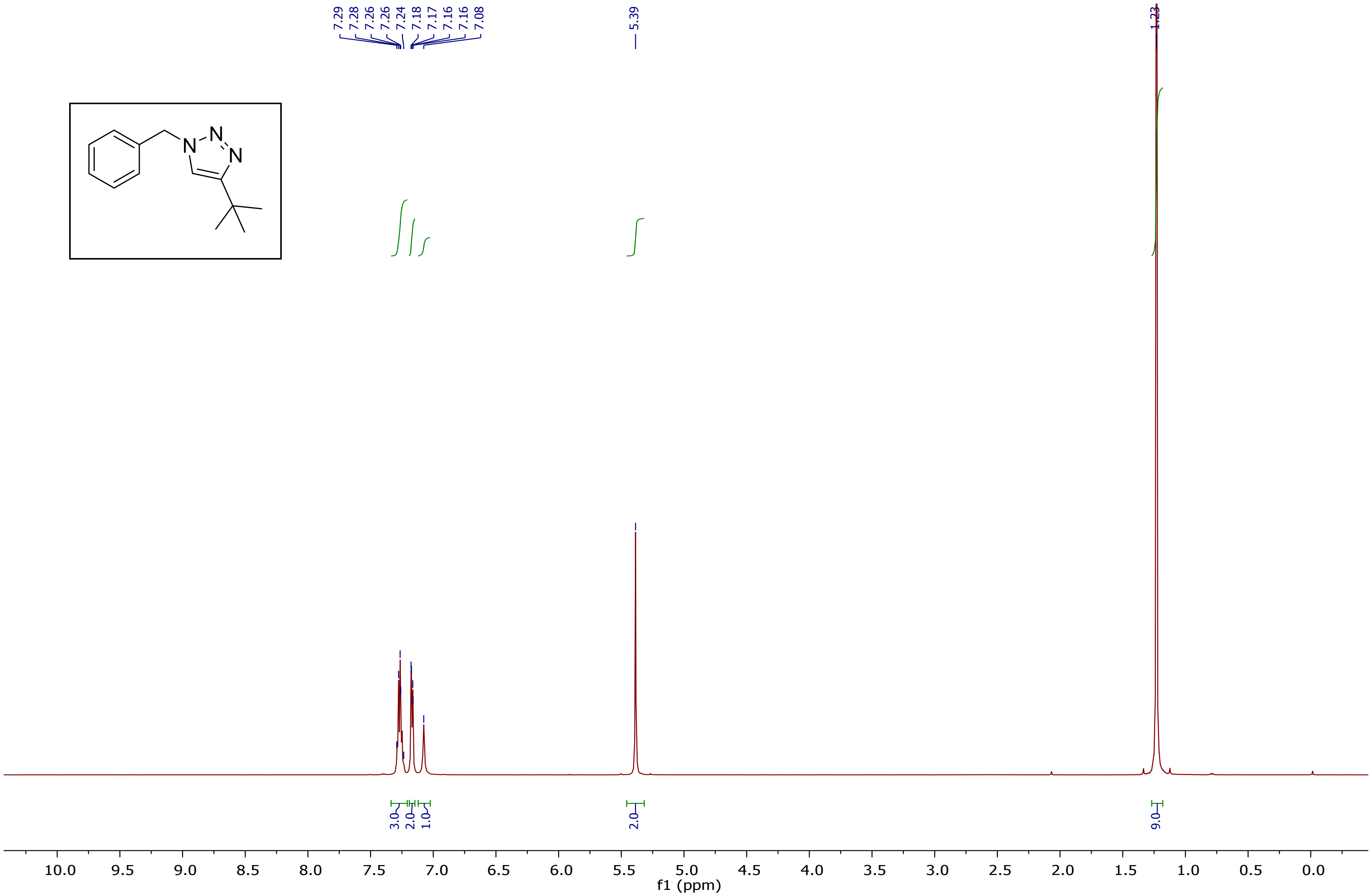


Figure S69. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-tert-butyl-1H-1,2,3-triazole (11a).

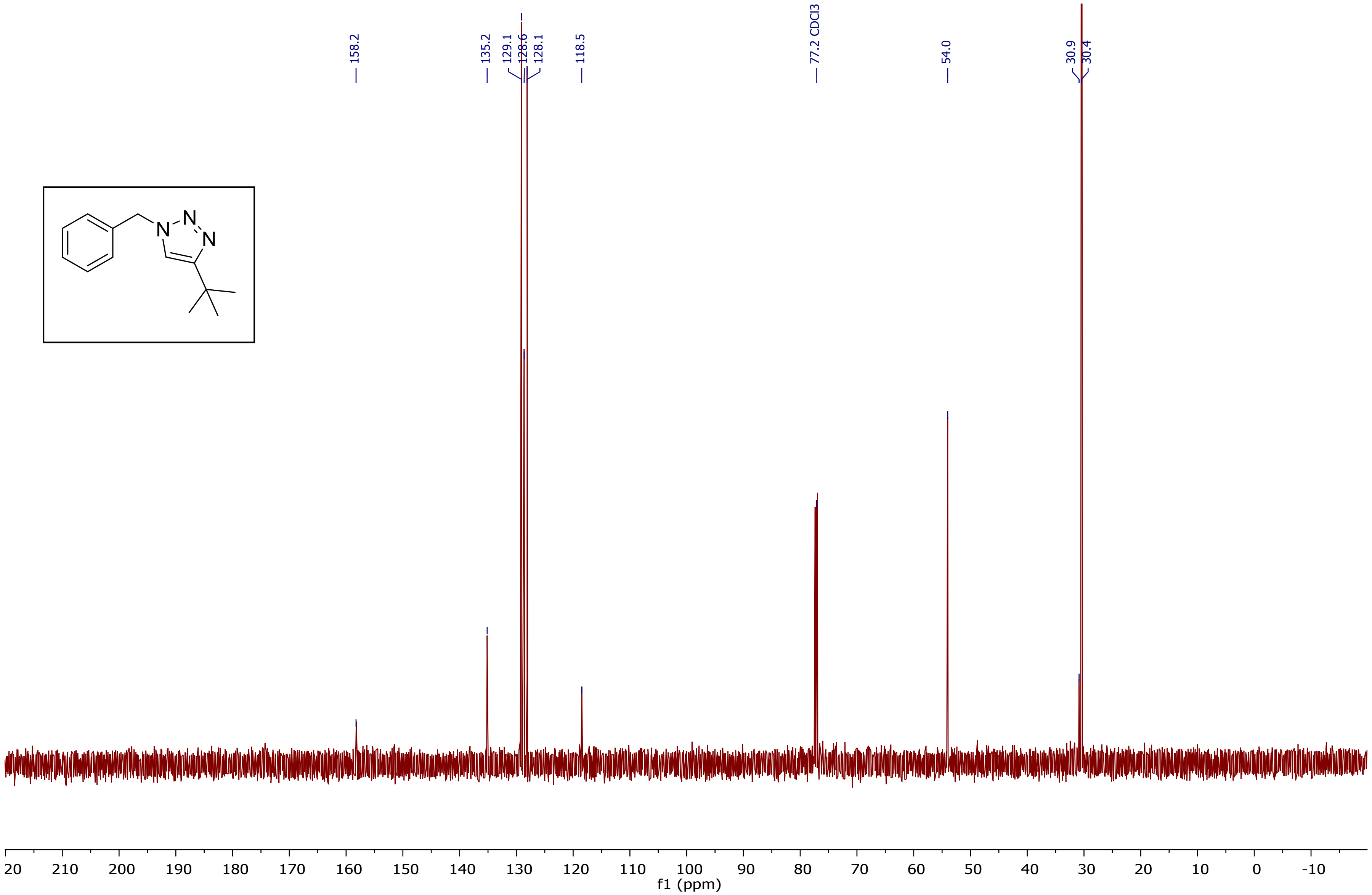


Figure S70. ^{13}C{^{1}H} **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-tert-butyl-1H-1,2,3-triazole (11a).**

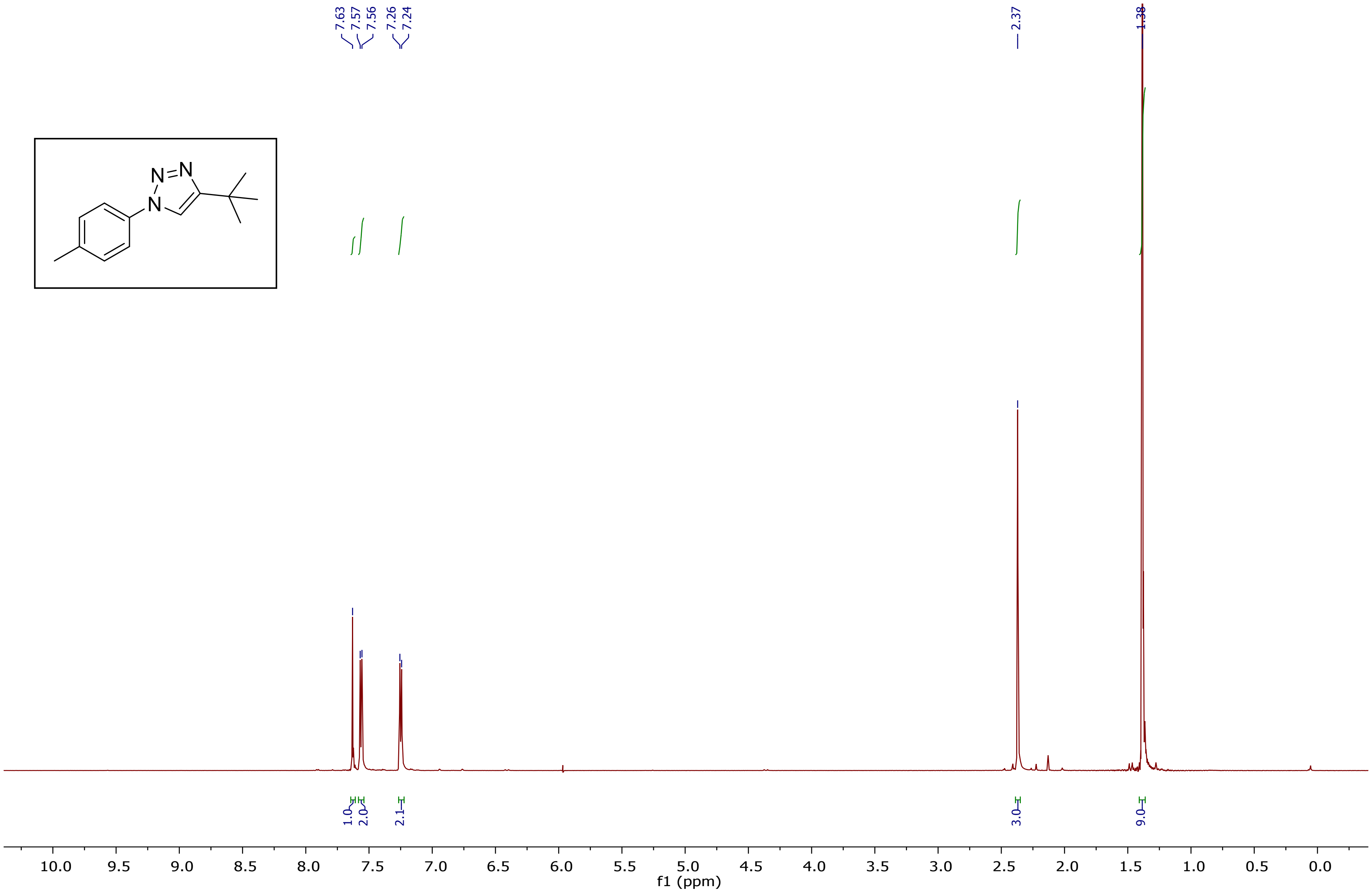


Figure S71. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-tert-Butyl-1-p-tolyl-1H-1,2,3-triazole (11b).

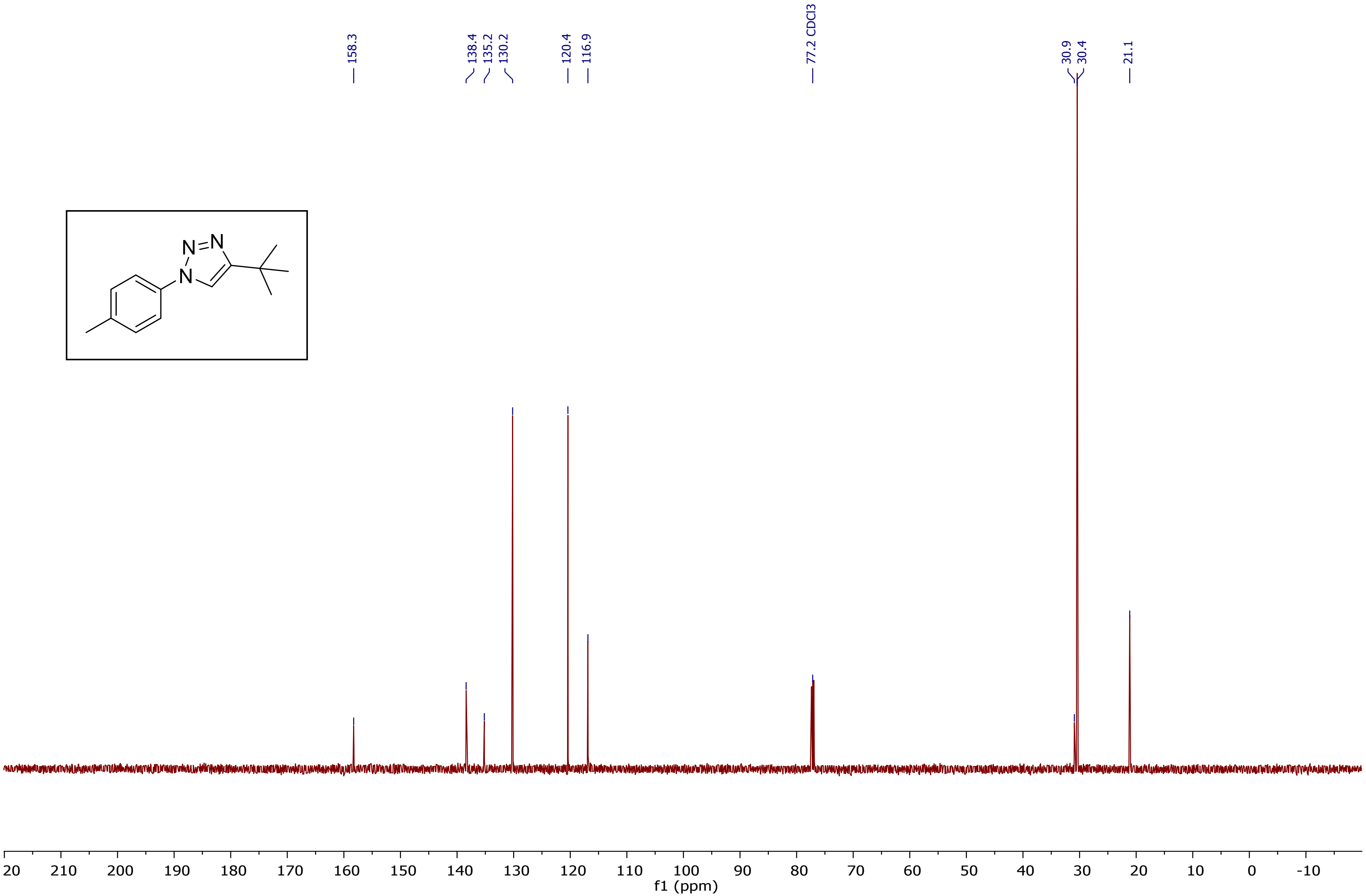


Figure S72. ^{13}C{^{1}H} **NMR (151 MHz, Chloroform-*d*) of 4-tert-Butyl-1-p-tolyl-1H-1,2,3-triazole (11b).**

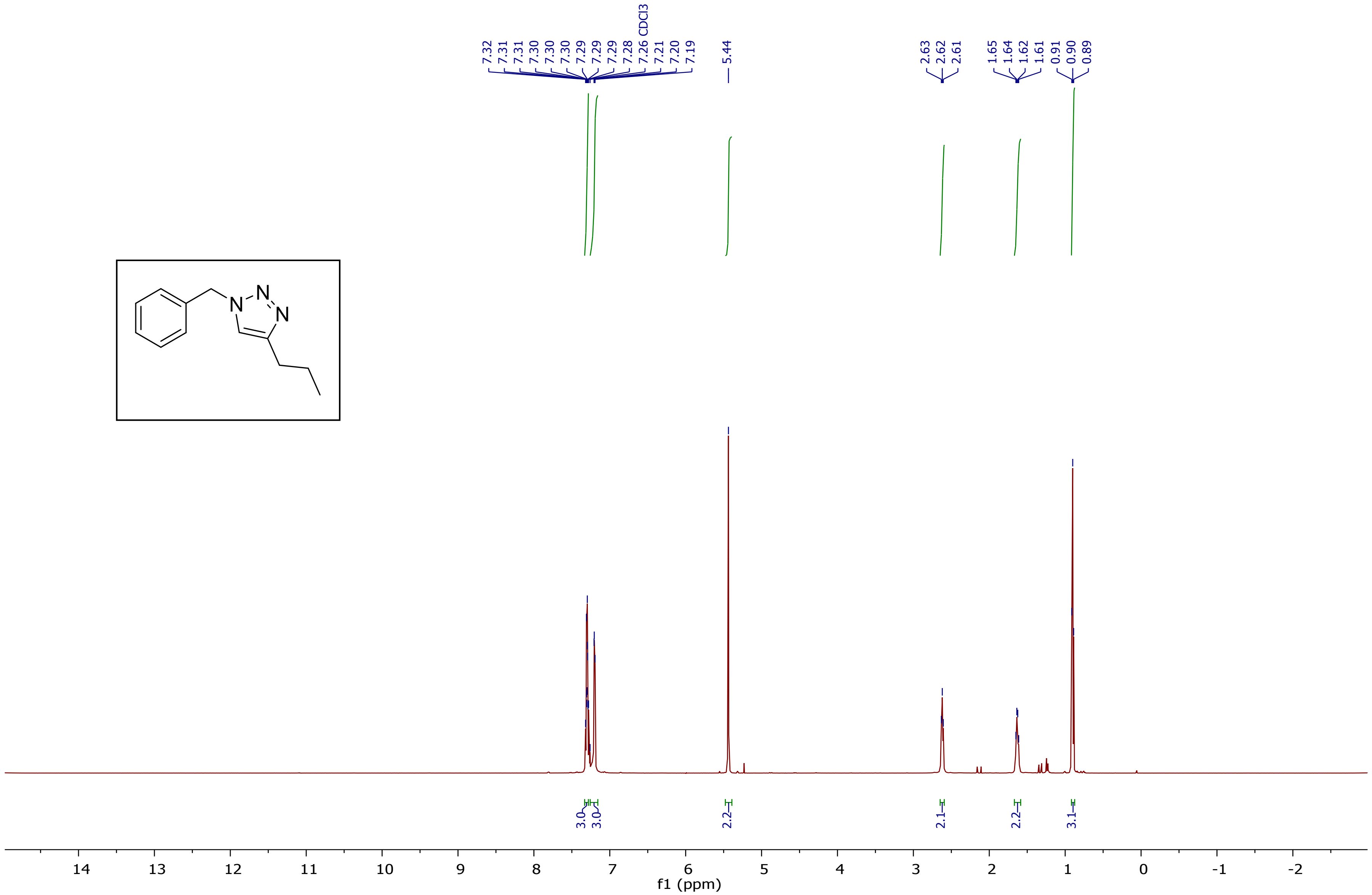


Figure S73. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-propyl-1H-1,2,3-triazole (11c).

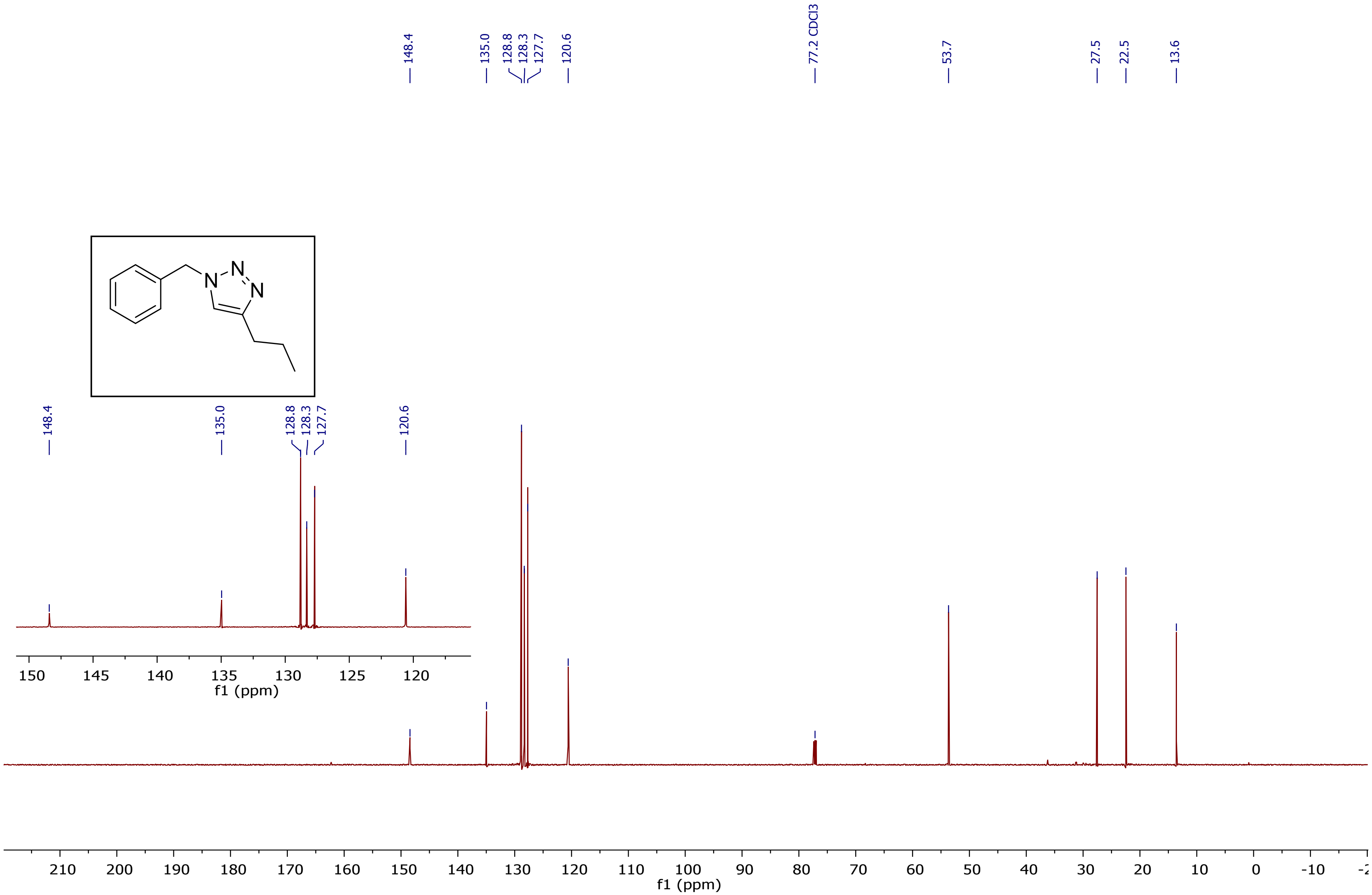


Figure S74. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-propyl-1H-1,2,3-triazole (11c).**

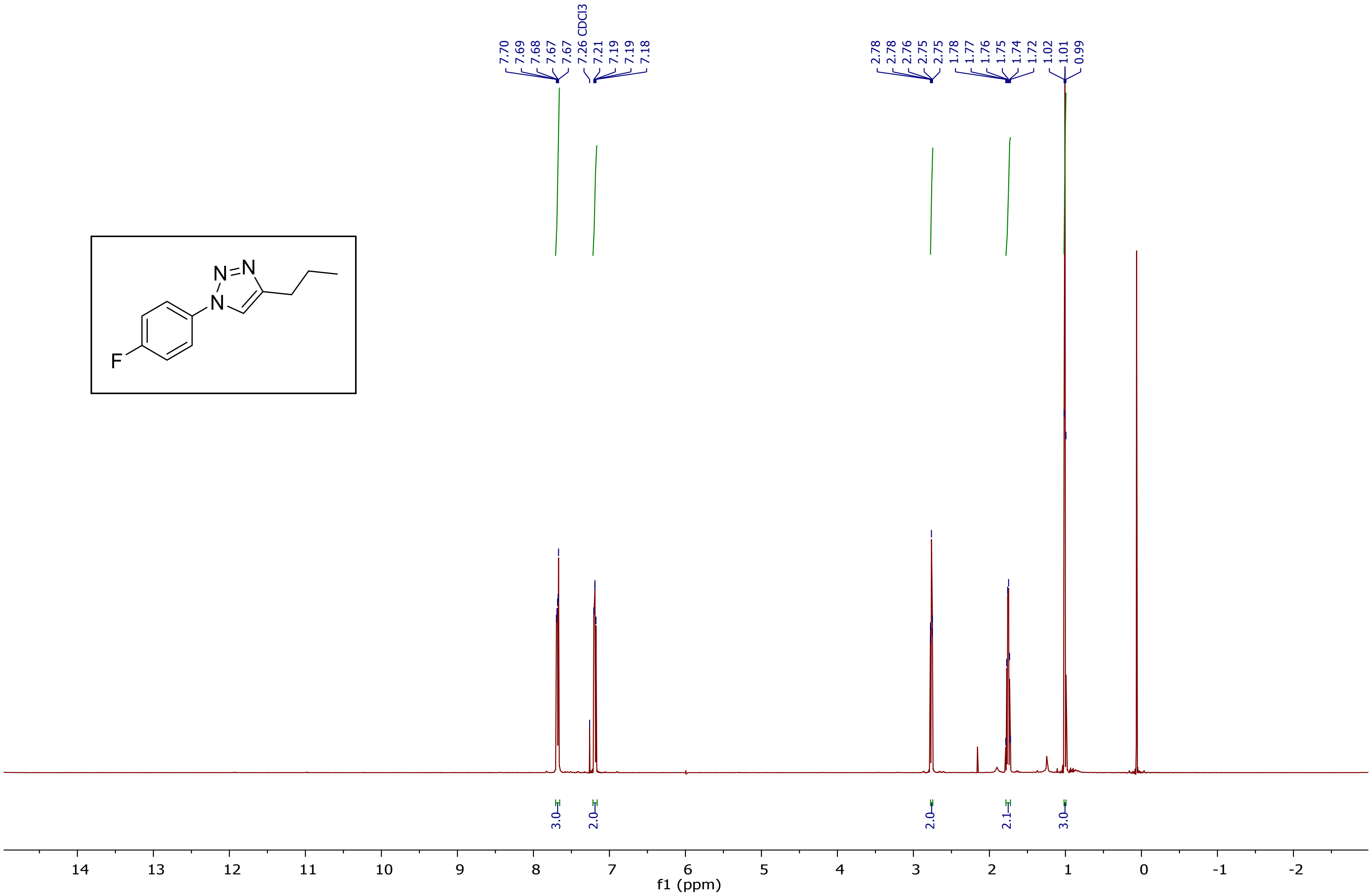


Figure S75. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(4-Fluorophenyl)-4-propyl-1H-1,2,3-triazole (11d).

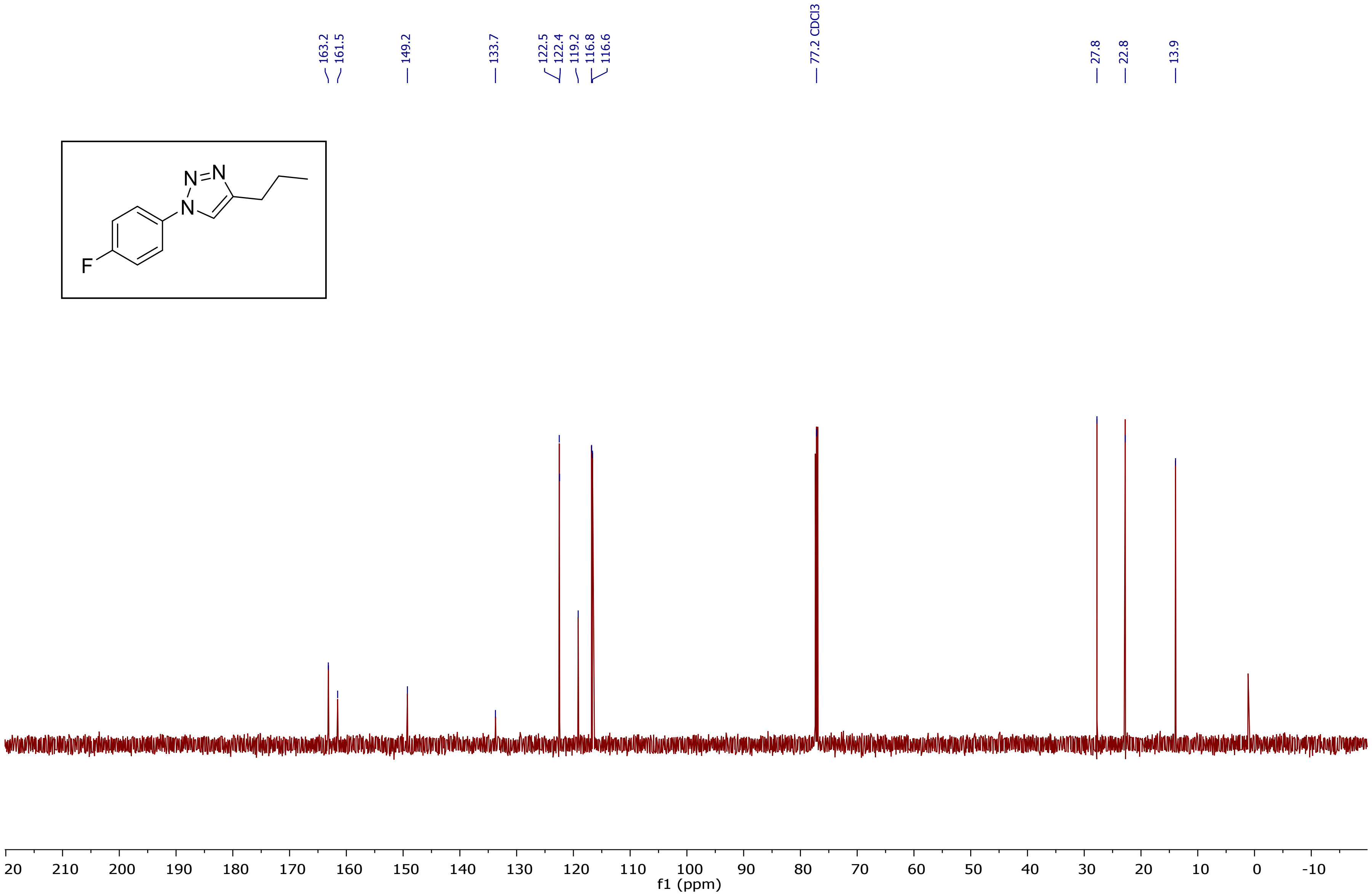


Figure S76. ^{13}C{^{1}H} **NMR (151 MHz, Chloroform-*d*) of 1-(4-Fluorophenyl)-4-propyl-1H-1,2,3-triazole (11d).**

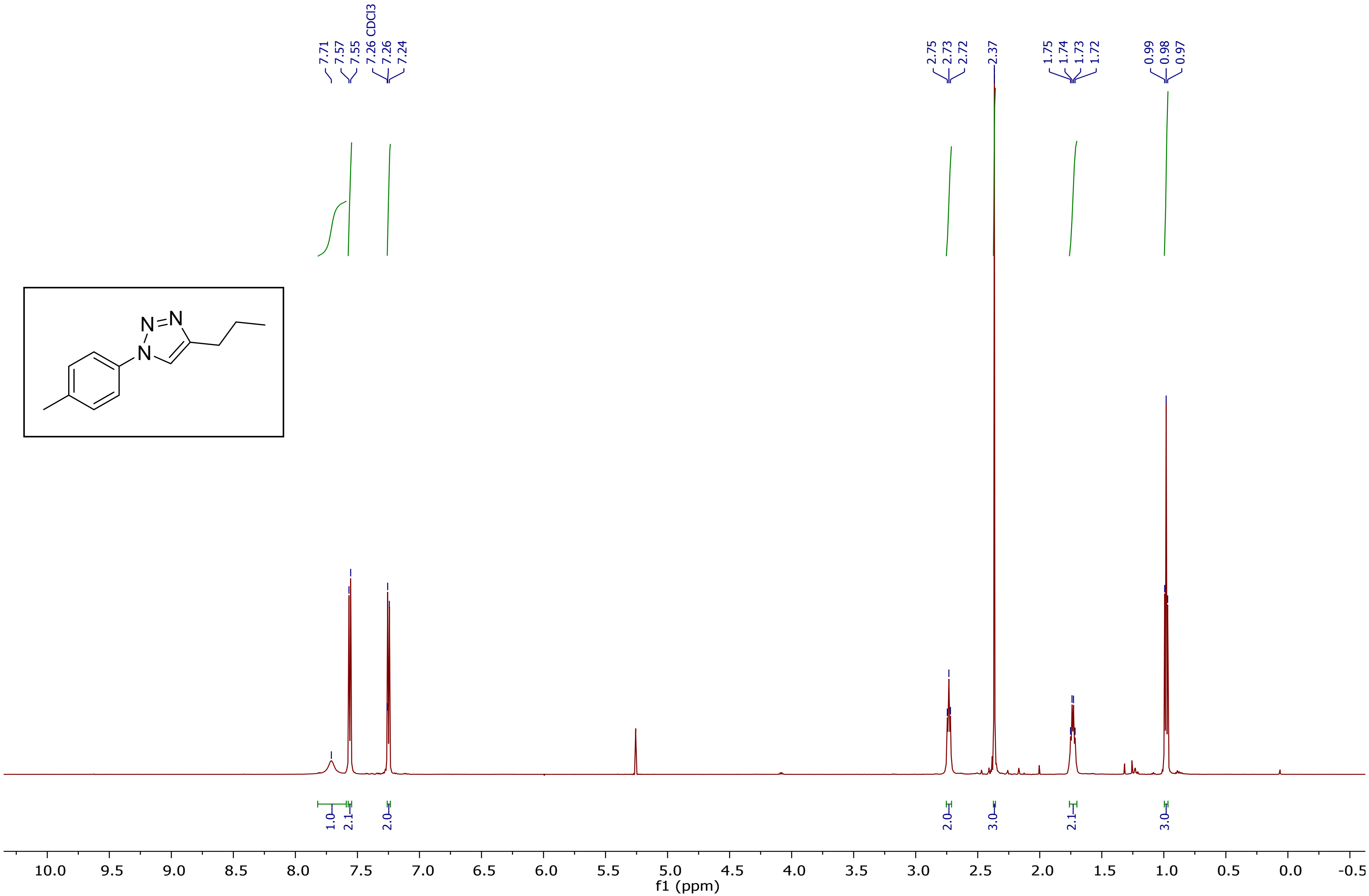


Figure S77. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-Propyl-1-p-tolyl-1H-1,2,3-triazole (11e).

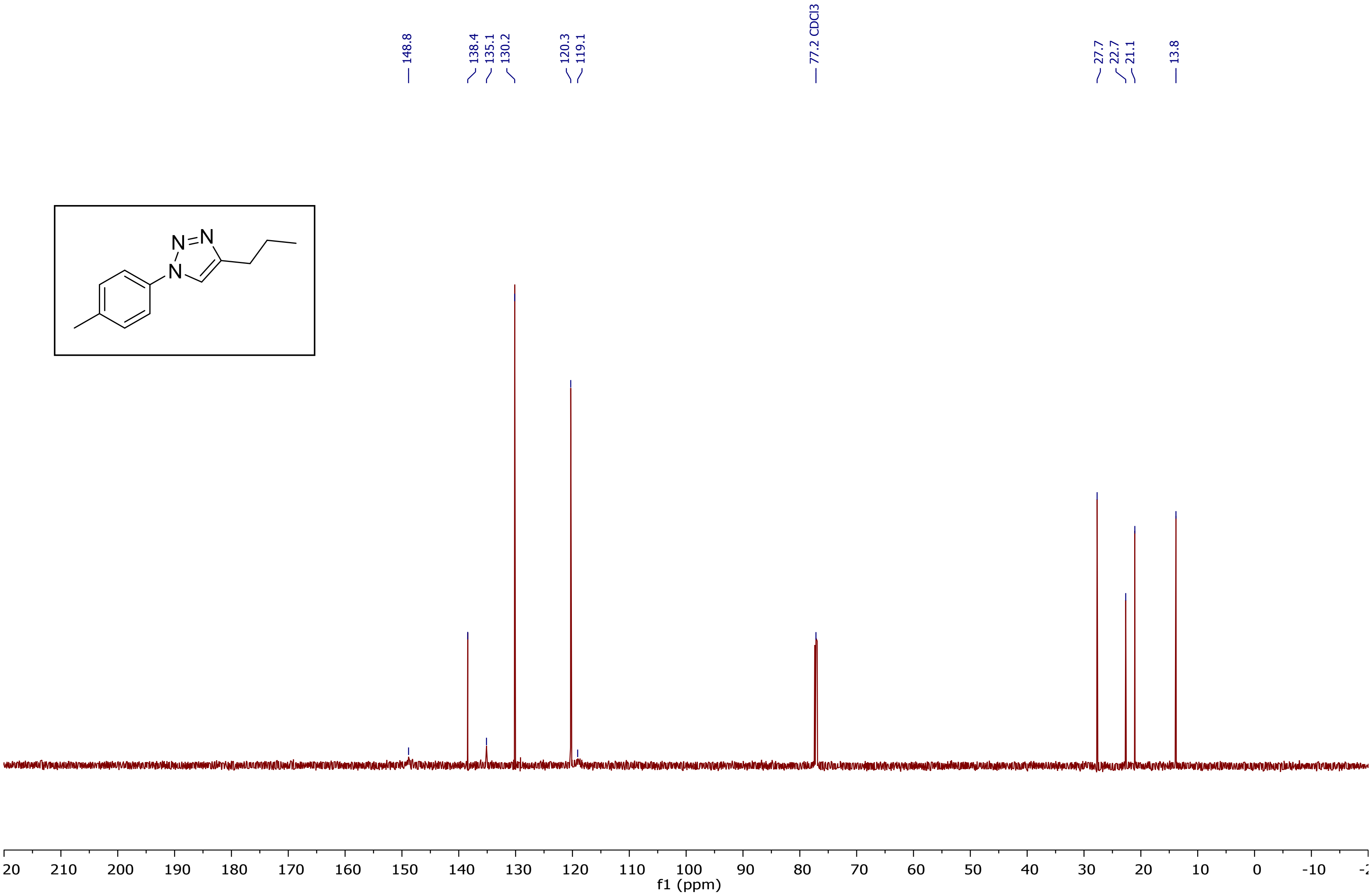


Figure S78. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) of 4-Propyl-1-p-tolyl-1H-1,2,3-triazole (11e).

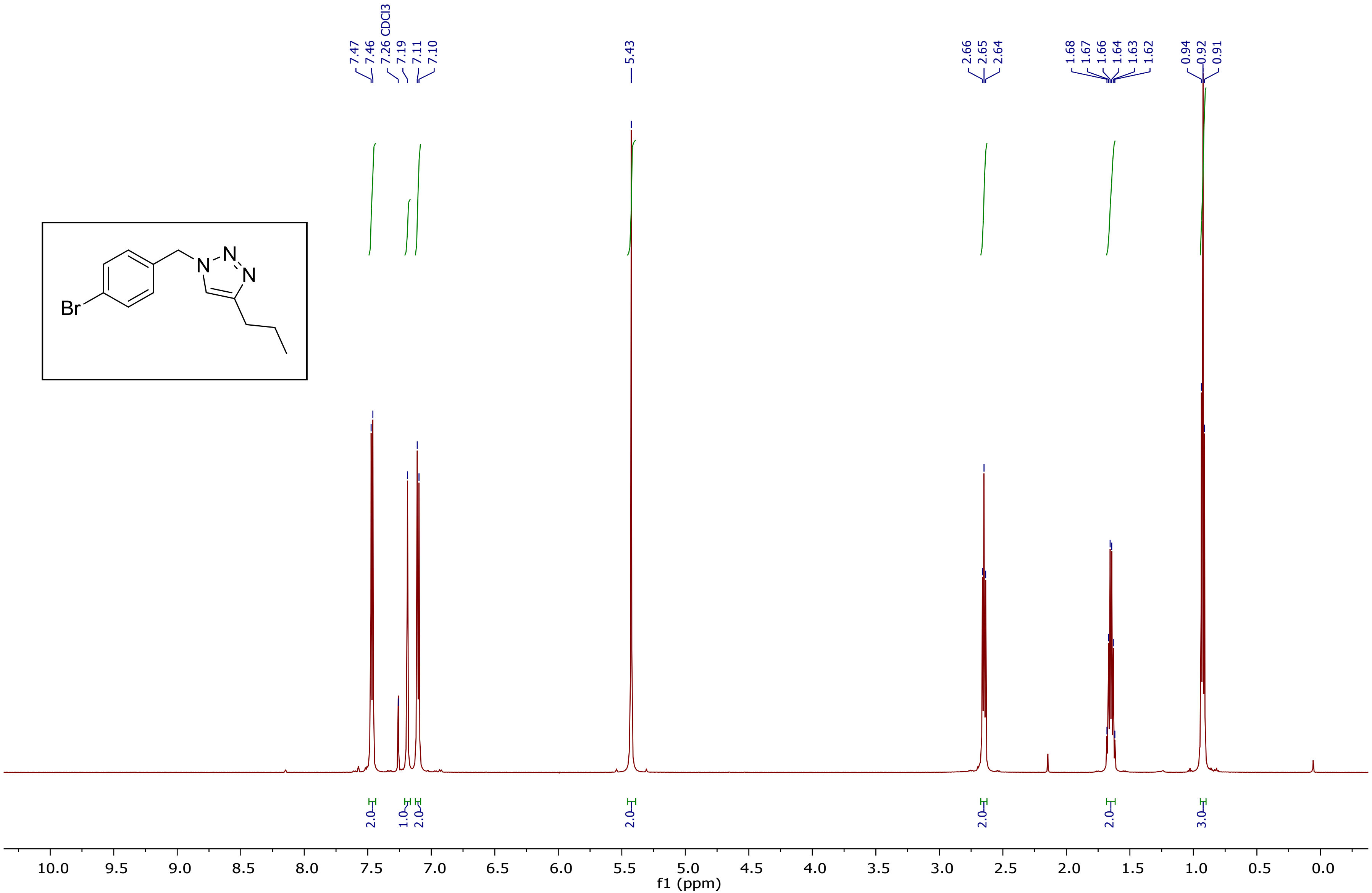


Figure S79. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(4-Bromobenzyl)-4-propyl-1H-1,2,3-triazole (11f).

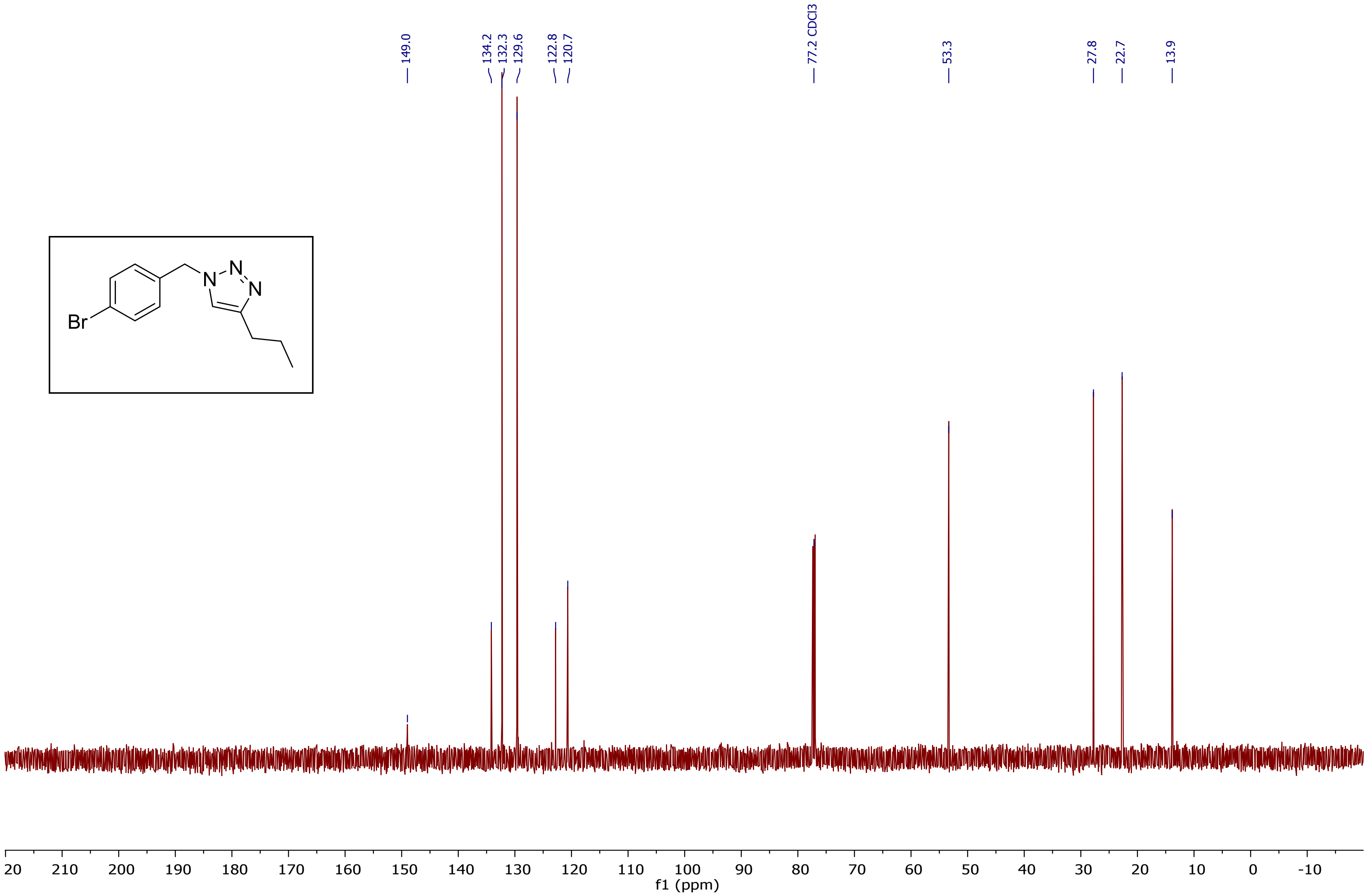


Figure S80. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-(4-Bromobenzyl)-4-propyl-1H-1,2,3-triazole (11f).**

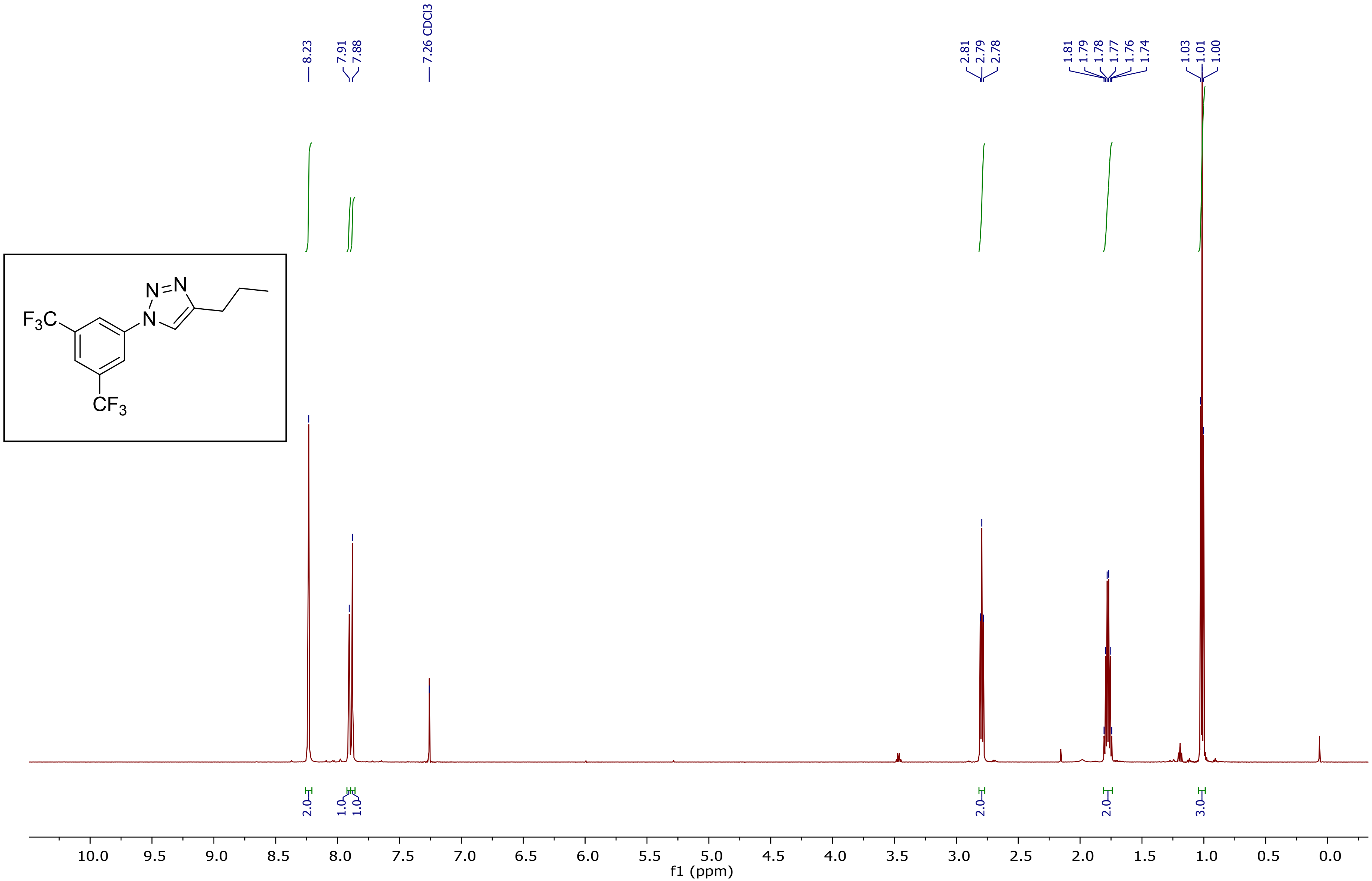


Figure S81. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(3,5-Bis(trifluoromethyl)phenyl)-4-propyl-1H-1,2,3-triazole (11g).

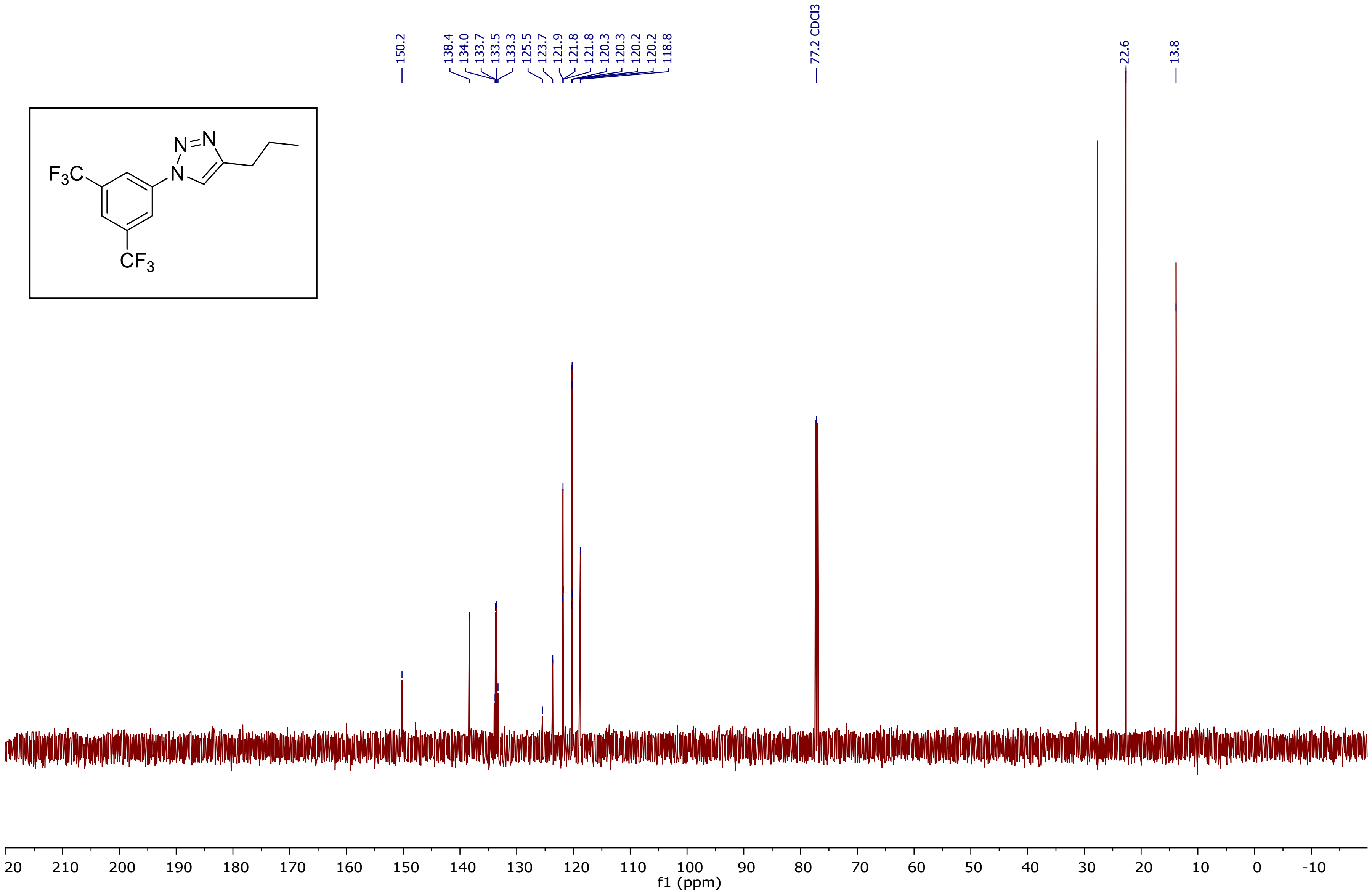


Figure S82. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 1-(3,5-Bis(trifluoromethyl)phenyl)-4-propyl-1H-1,2,3-triazole (11g).**

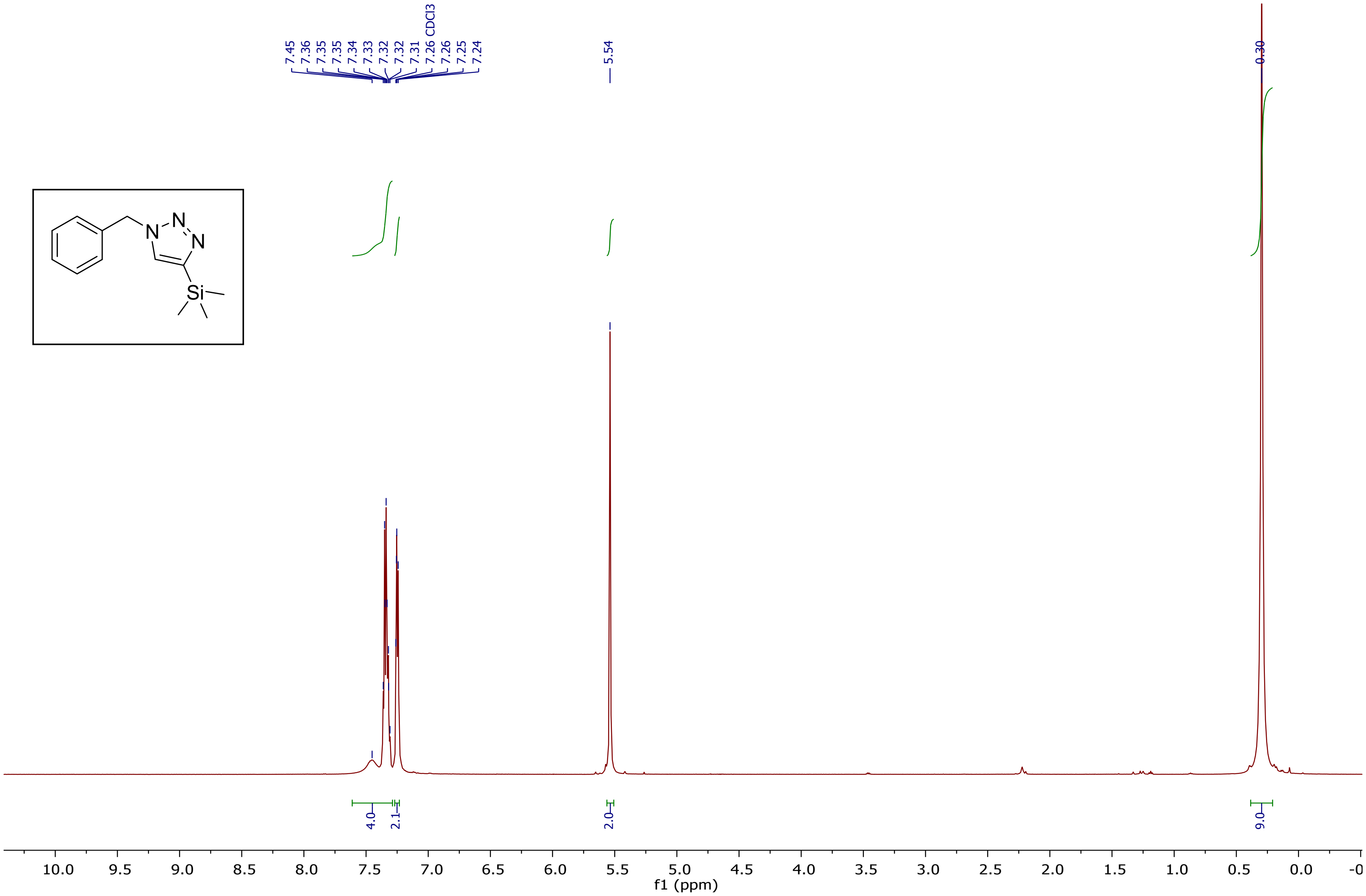


Figure S83. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-Benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole (11h).

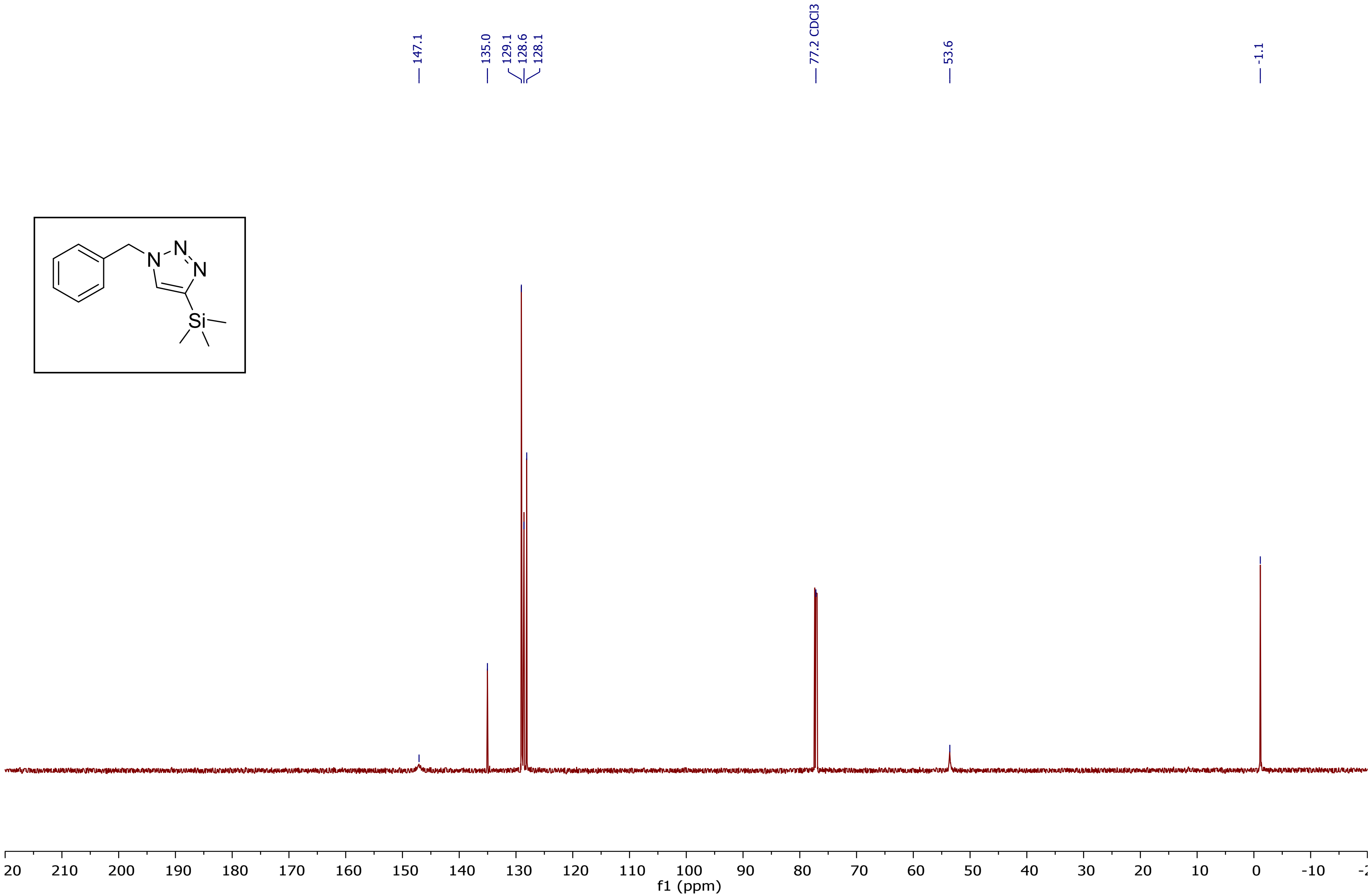


Figure S84. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) of 1-Benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole (11h).

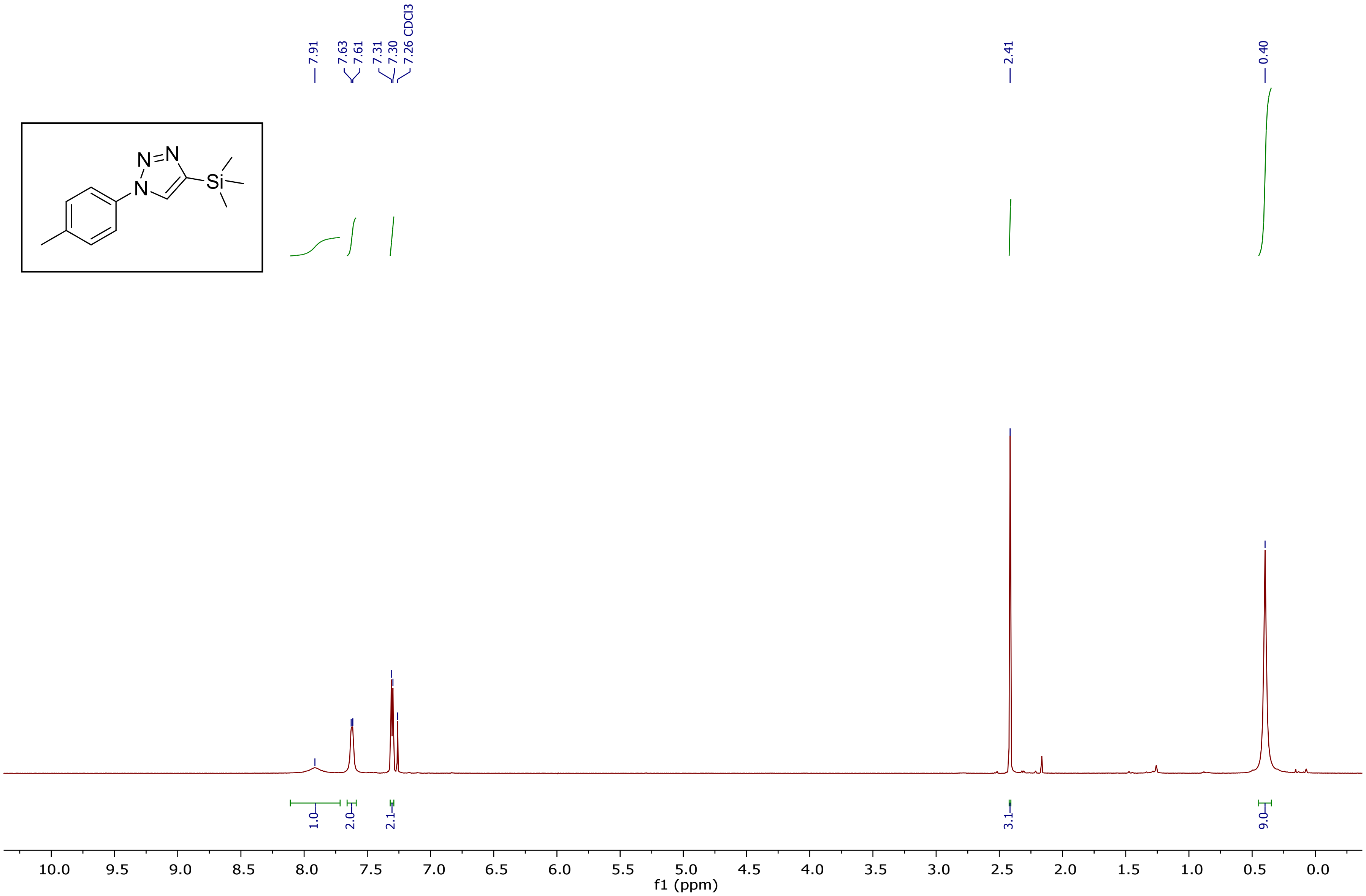


Figure S85. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-p-Tolyl-4-(trimethylsilyl)-1H-1,2,3-triazole (11i).

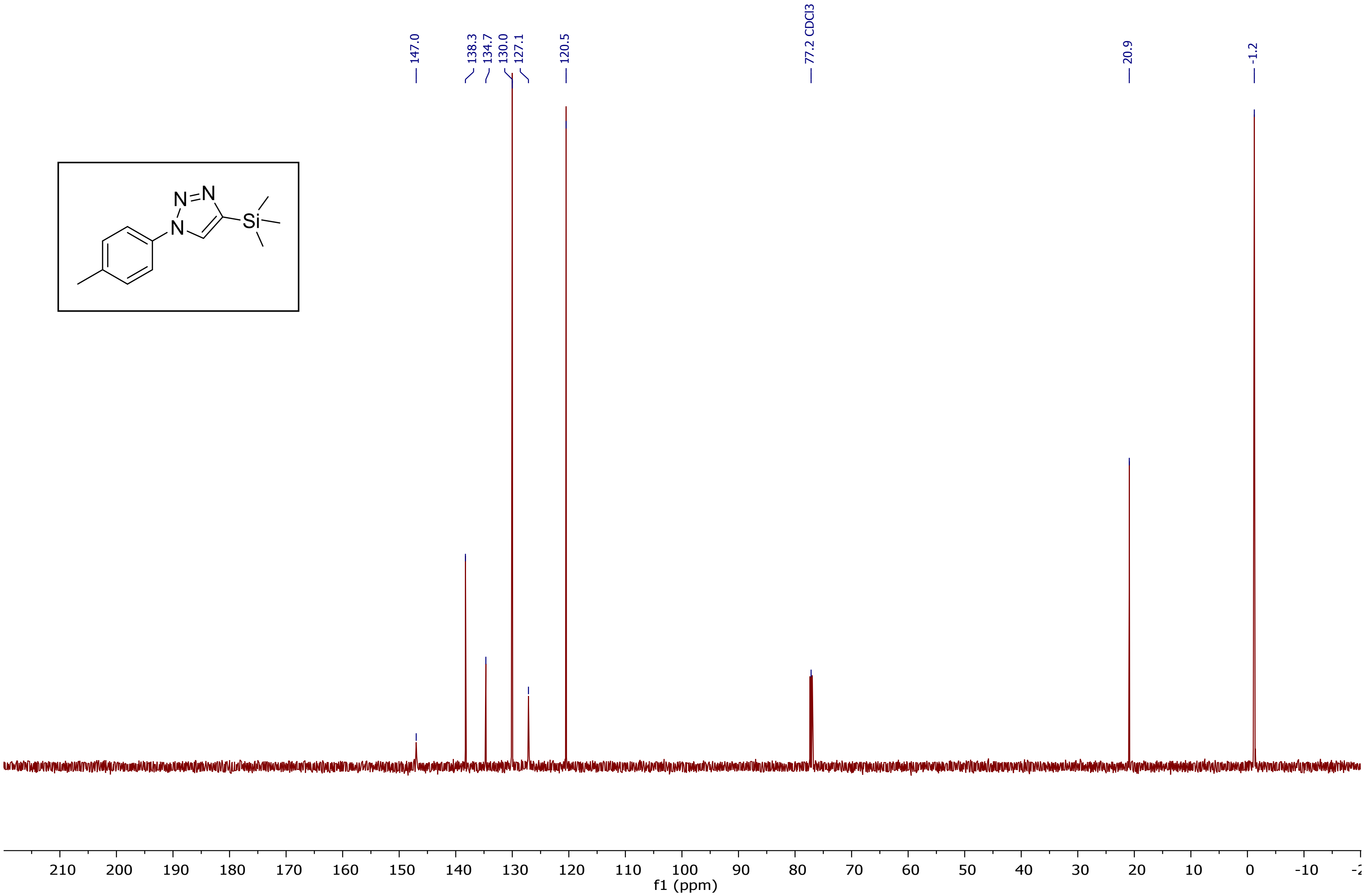


Figure S86. ^{13}C{^{1}H} **NMR (151 MHz, Chloroform-*d*) of 1-p-Tolyl-4-(trimethylsilyl)-1H-1,2,3-triazole (11i).**

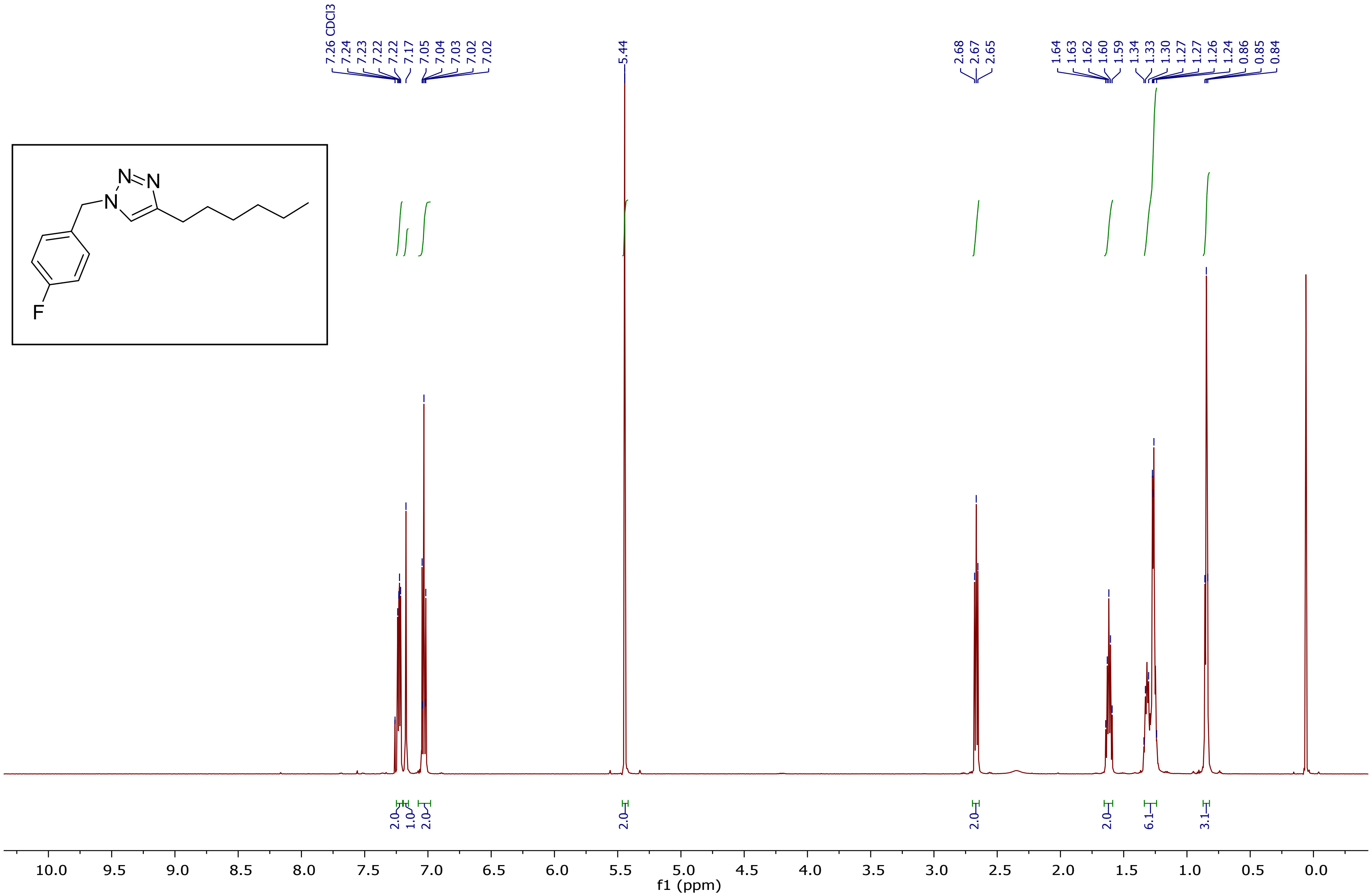


Figure S87. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(4-Fluorobenzyl)-4-hexyl-1H-1,2,3-triazole (11j).

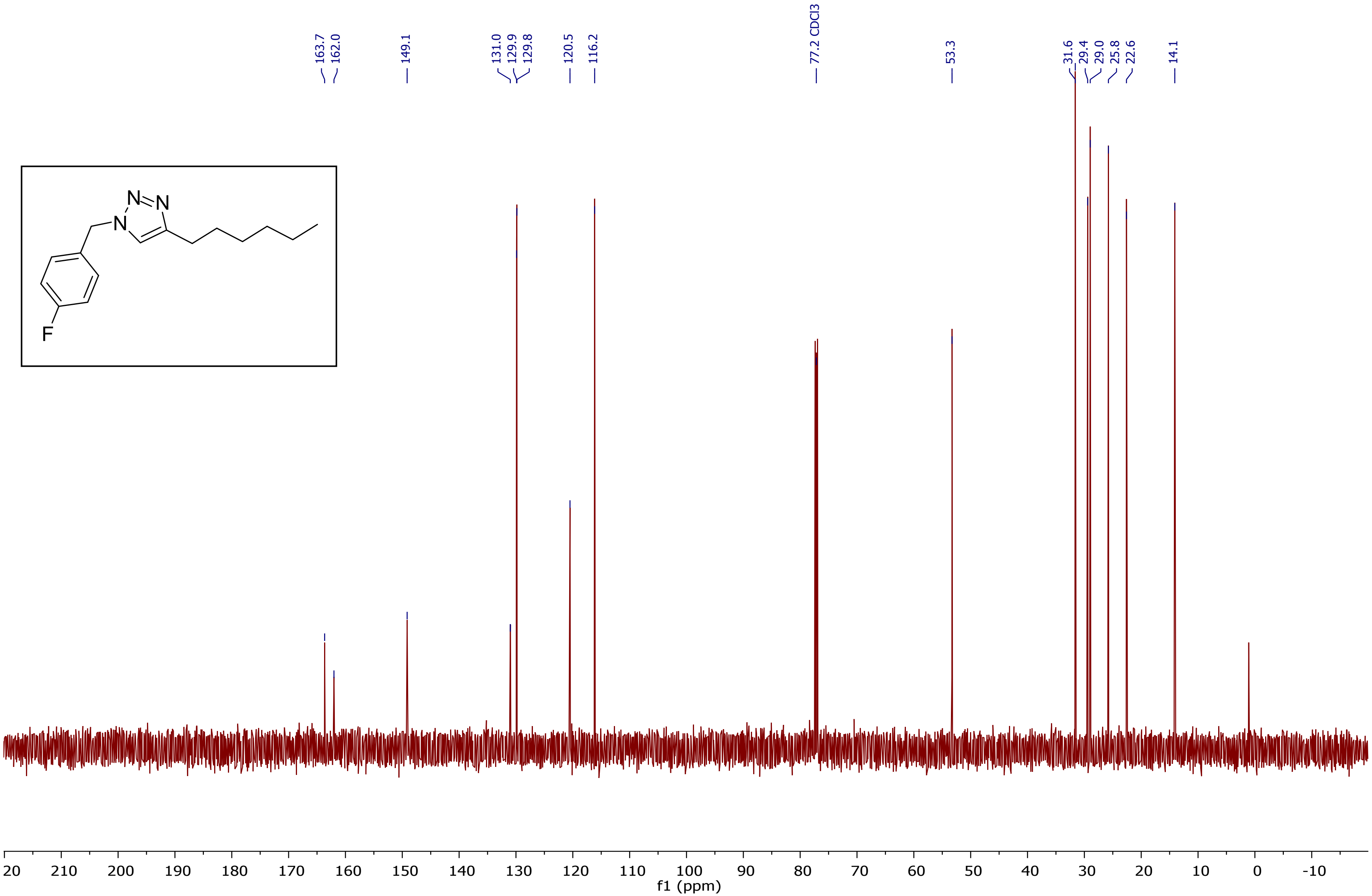


Figure S88. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) of 1-(4-Fluorobenzyl)-4-hexyl-1H-1,2,3-triazole (11j).

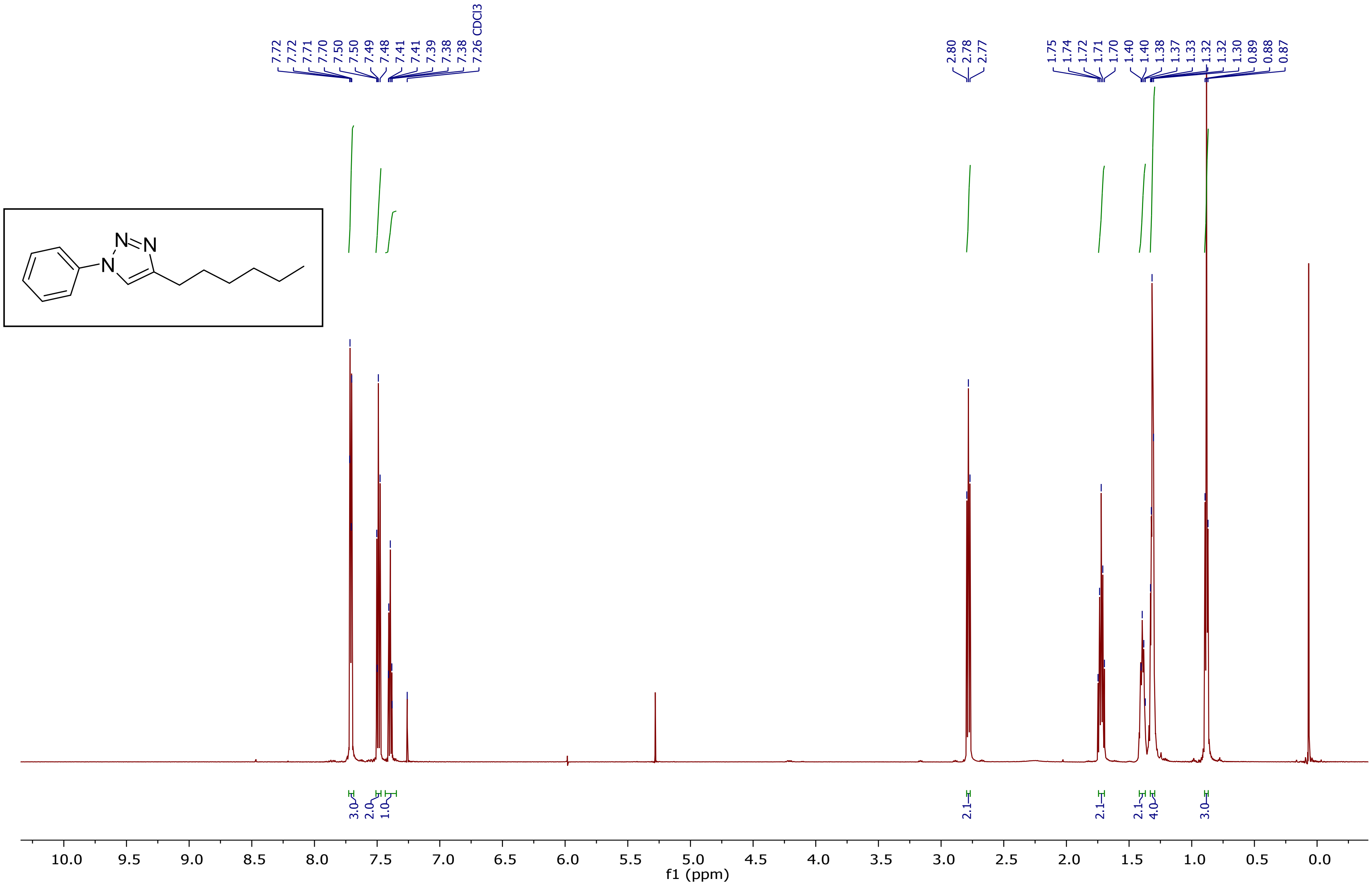


Figure S89. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-Hexyl-1-phenyl-1H-1,2,3-triazole (11k).

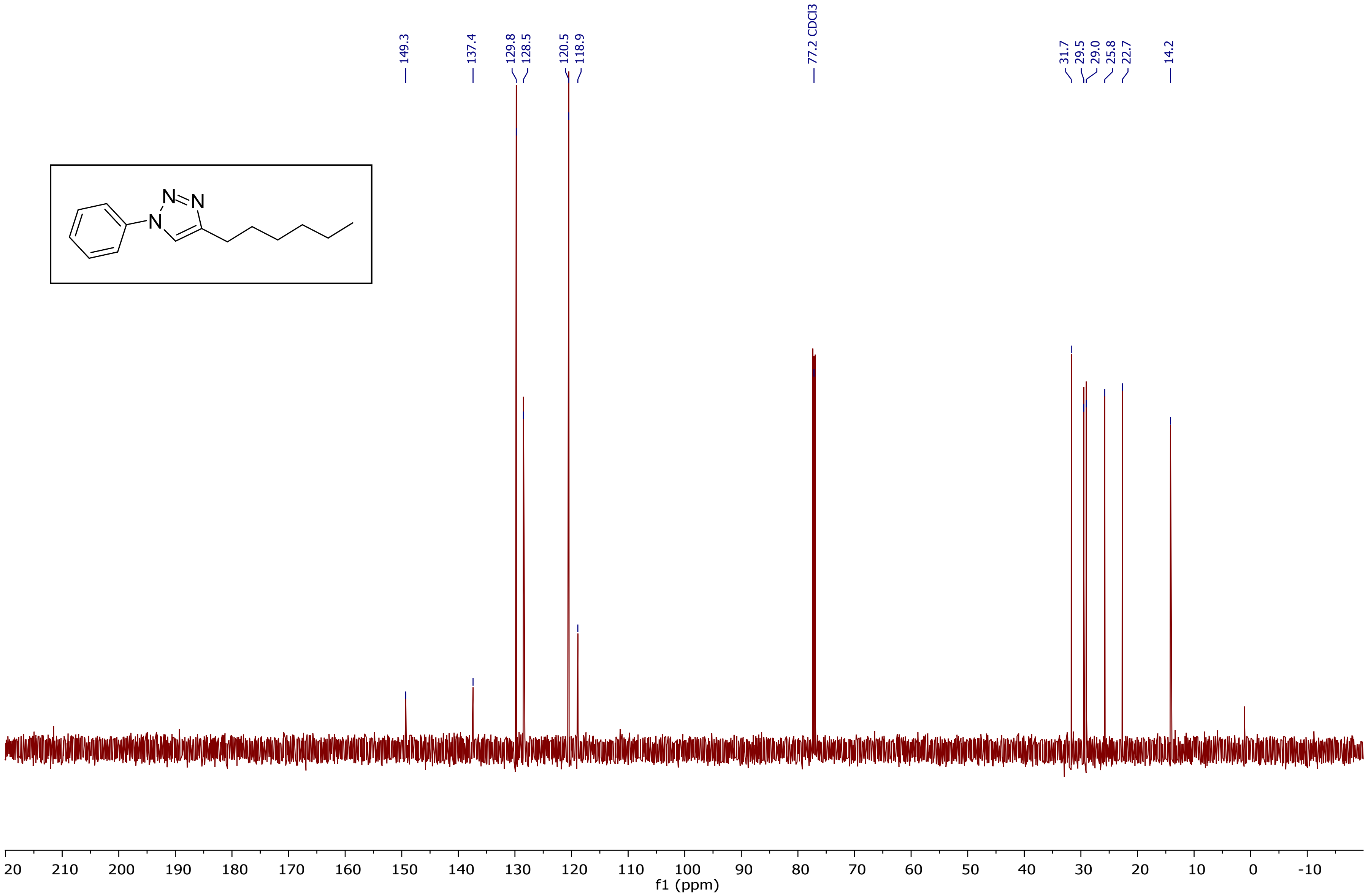


Figure S90. $^{13}C\{^{1}H\}$ **NMR (151 MHz, Chloroform-*d*) of 4-Hexyl-1-phenyl-1H-1,2,3-triazole (11k).**

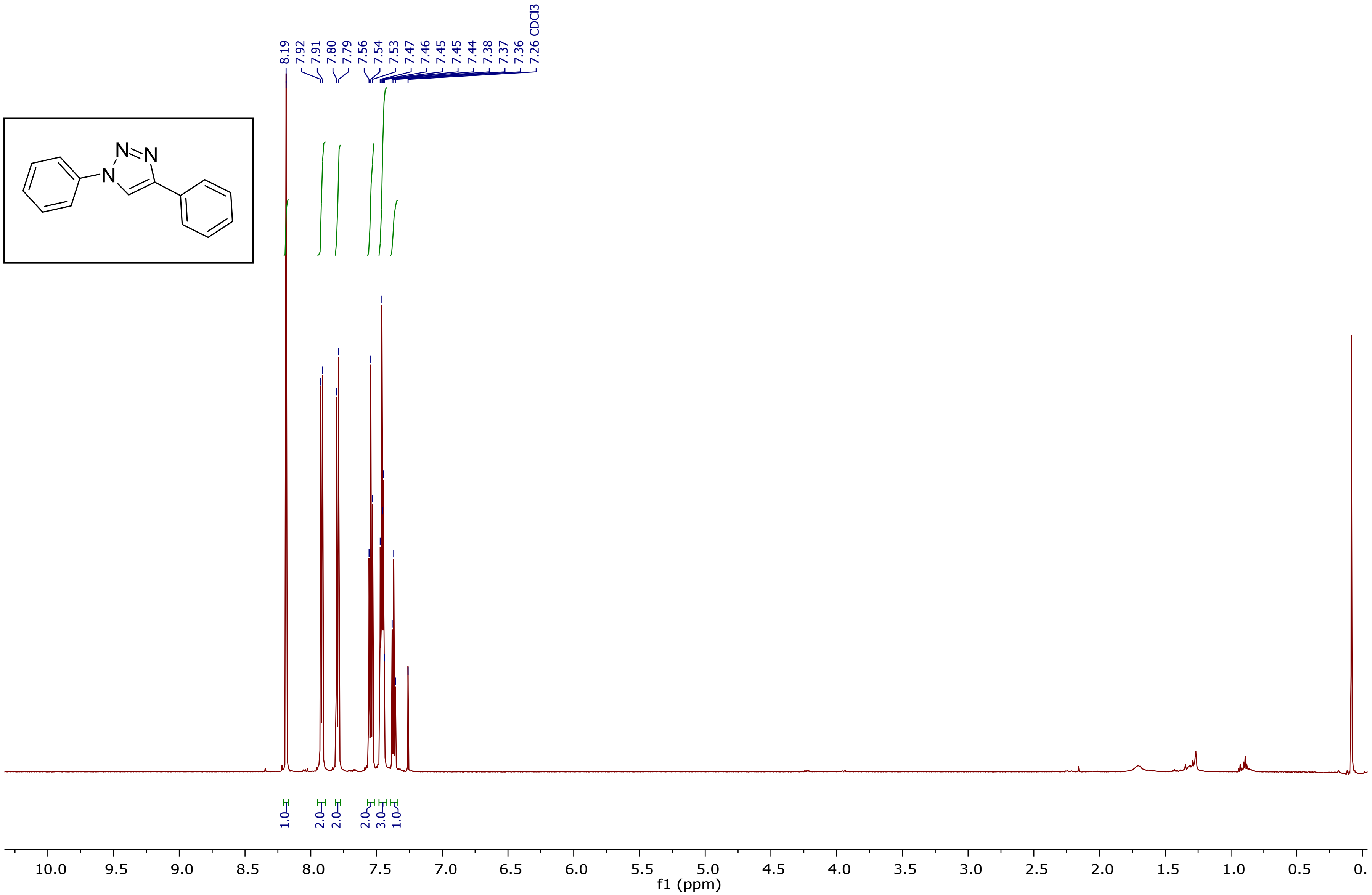


Figure S91. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1,4-Diphenyl-1H-1,2,3-triazole (11l).

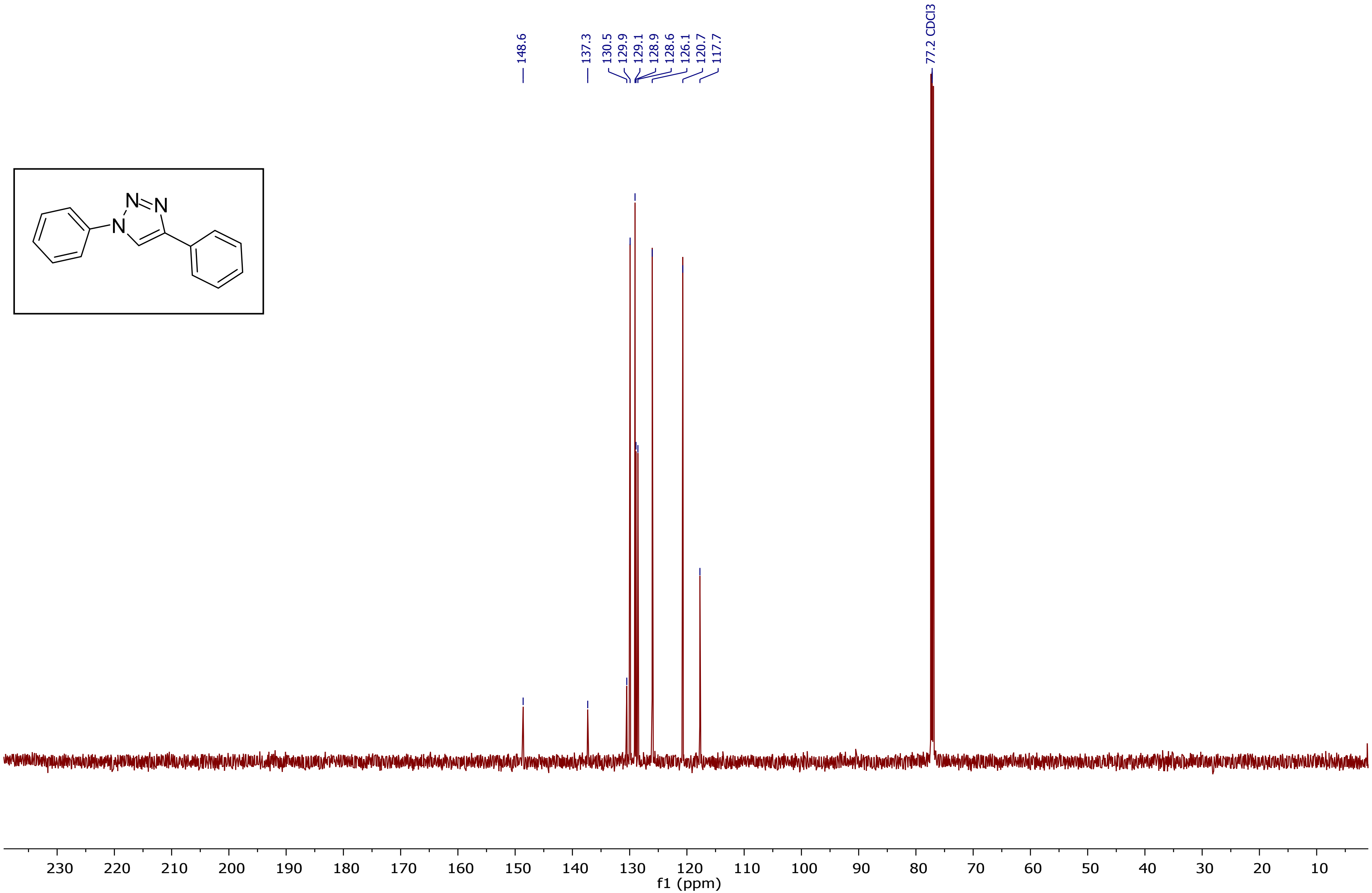


Figure S92. $^{13}C\{^1H\}$ **NMR (151 MHz, Chloroform-*d*) of 1,4-Diphenyl-1H-1,2,3-triazole (11l).**

References

1. G. M. Sheldrick, *SADABS*, *v.* 2.03, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, 2003.
2. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
3. S. G. Alvarez and M. T. Alvarez, *Synthesis*, 1997, 413-414.
4. J. C. Y. Ng, J. Z. Liu, H. M. Su, Y. N. Hong, H. K. Li, J. W. Y. Lam, K. S. Wong and B. Z. Tang, *J. Mater. Chem. C*, 2014, **2**, 78-83.
5. M. R. J. Vallee, L. M. Artner, J. Dernedde and C. P. R. Hackenberger, *Angew. Chem.-Int. Edit.*, 2013, **52**, 9504-9508.
6. S. G. Zhou, H. M. Liao, M. M. Liu, G. B. Feng, B. L. Fu, R. J. Li, M. S. Cheng, Y. F. Zhao and P. Gong, *Bioorg. Med. Chem.*, 2014, **22**, 6438-6452.
7. K. Kanakarajan, K. Haider and A. W. Czarnik, *Synthesis*, 1988, 566-568.
8. S. Diez-Gonzalez, A. Correa, L. Cavallo and S. P. Nolan, *Chem.-Eur. J.*, 2006, **12**, 7558-7564.
9. E. L. Kolychev, V. V. Shuntikov, V. N. Khrustalev, A. A. Bush and M. S. Nechaev, *Dalton Trans.*, 2011, **40**, 3074-3076.
10. E. L. Kolychev, I. A. Portnyagin, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *J. Organomet. Chem.*, 2009, **694**, 2454-2462.
11. (a) W. D. Rohrbach, F. Gerson, R. Mockel and V. Boekelheide, *J. Org. Chem.*, 1984, **49**, 4128-4132; (b) H. Luo, Q. Zeng, Z. R. Liu, Y. Z. Wei, B. G. Li and F. P. Wang, *Synth. Commun.*, 2004, **34**, 2269-2275.
12. P. G. Jones and P. Kus, *Z.Naturforsch.(B)*, 2010, **65**, 433-444.
13. X. Meng, X. Y. Xu, T. T. Gao and B. H. Chen, *Eur. J. Org. Chem.*, 2010, 5409-5414.
14. (a) S. I. Fukuzawa, E. Shimizu and K. Ogata, *Heterocycles*, 2009, **78**, 645-655; (b) C. Tirler and L. Ackermann, *Tetrahedron*, 2015, **71**, 4543-4551.
15. F. Jabeen, S. A. Shehzadi, M. Q. Fatmi, S. Shaheen, L. Iqbal, N. Afza, S. S. Panda and F. L. Ansari, *Bioorg. Med. Chem. Lett.*, 2016, **26**, 1029-1038.
16. N. Boechat, V. F. Ferreira, S. B. Ferreira, M. D. G. Ferreira, F. D. da Silva, M. M. Bastos, M. D. Costa, M. C. S. Lourenco, A. C. Pinto, A. U. Krettli, A. C. Aguiar, B. M. Teixeira, N. V. da Silva, P. R. C. Martins, F. Bezerra, A. L. S. Camilo, G. P. da Silva and C. C. P. Costa, *J. Med. Chem.*, 2011, **54**, 5988-5999.
17. R. G. Lima-Neto, N. N. M. Cavalcante, R. M. Srivastava, F. J. B. Mendonca, A. G. Wanderley, R. P. Neves and J. V. dos Anjos, *Molecules*, 2012, **17**, 5882-5892.
18. C. Z. Tao, X. Cui, J. Li, A. X. Liu, L. Liu and Q. X. Guo, *Tetrahedron Lett.*, 2007, **48**, 3525-3529.
19. X. Z. Cheng, Y. W. Yang, C. X. Kuang and Q. Yang, *Synthesis*, 2011, 2907-2912.
20. (a) S. Hanelt and J. Liebscher, *Synlett*, 2008, 1058-1060; (b) S. S. Khan, S. Hanelt and J. Liebscher, *Arkivoc*, 2009, 193-208.
21. M. Iwasaki, H. Yorimitsu and K. Oshima, *Chem.-Asian J.*, 2007, **2**, 1430-1435.
22. J. M. Aizpurua, I. Azcune, R. M. Fratila, E. Balentova, M. Sagartzazu-Aizpurua and J. I. Miranda, *Org. Lett.*, 2010, **12**, 1584-1587.
23. F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *Eur. J. Org. Chem.*, 2010, 1875-1884.
24. F. Friscourt and G. J. Boons, *Org. Lett.*, 2010, **12**, 4936-4939.
25. (a) H. Sharghi, R. Khalifeh and M. M. Doroodmand, *Adv. Synth. Catal.*, 2009, **351**, 207-218; (b) S. Ladouceur, A. M. Soliman and E. Zysman-Colman, *Synthesis*, 2011, 3604-3611.
26. (a) H. Ibrahim, R. Guillot, F. Cisnetti and A. Gautier, *Chem. Commun.*, 2014, **50**, 7154-7156; (b) S. Hohloch, D. Scheiffele and B. Sarkar, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3956-3965.
27. R. A. Kramer, M. C. Brohmer, N. V. Forkel and W. Bannwarth, *Eur. J. Org. Chem.*, 2009, 4273-4283.
28. Y. H. Zhou, T. Lecourt and L. Micouin, *Angew. Chem.-Int. Edit.*, 2010, **49**, 2607-2610.

29. I. Jlalia, F. Meganem, J. Herscovici and C. Girard, *Molecules*, 2009, **14**, 528-539.
30. F. Kloss, U. Kohn, B. O. Jahn, M. D. Hager, H. Gorls and U. S. Schubert, *Chem.-Asian J.*, 2011, **6**, 2816-2824.
31. (a) A. Ali, A. G. Correa, D. Alves, J. Zukerman-Schpector, B. Westermann, M. A. B. Ferreira and M. W. Paixao, *Chem. Commun.*, 2014, **50**, 11926-11929; (b) B. Kaboudin, R. Mostafalu and T. Yokomatsu, *Green Chem.*, 2013, **15**, 2266-2274.