Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Regioselective Zn(OAc)$_2$-catalyzed azide-alkyne cycloaddition in water: the green click-chemistry

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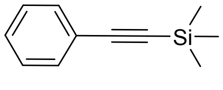
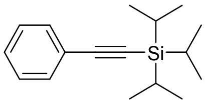
	Table of Contents	**pp**
	General experimental remarks	
	General Procedure for Preparation 1,4-disubstituted-1,2,3-triazoles from azides (**1a-l**) and terminal alkynes (**2a-d**)	
	General Procedure for Preparation 1,4-disubstituted-1,2,3-triazoles from arenediazoniumtosylates (**4a-e**) and phenylacetylene (**2a**).	
	General Procedure for Preparation 1,4,5-trisubstituted-1,2,3-triazoles from aromatic azides (**1a, 1d,1g, 1e, 1m**) and disubstituted acetylenes (**2e–j**).	
	General Procedure for Preparation Intermediate (**Iia**)	
	Spectra of products	
	References	

1. General experimental remarks

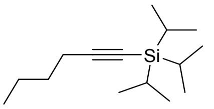
^{1}H NMR spectra were recorded on a BRUKER 300 (300 MHz) or a BRUKER AM 400 (400 MHz) spectrometer. Chemical shifts are given in parts per million (δ/ppm), referenced to dimethylsulfoxide (2.51) as internal standards. All coupling constants are absolute values and are expressed in Hertz (Hz). The description of signals include: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt doublet of triplets, m = multiplet. ^{13}C NMR spectra were recorded on Bruker 300 (75 MHz) and Bruker AM 400 (100 MHz) spectrometers. High Resolution mass-spectra were recorded on Agilent 1260 Infinity LC/6530 QTOF LC/MS with ESI ionization (column Zorbax Eclipse Plus C18 Rapid Resolution HD 2.1x50mm 1.8-Micron). GC-MS measurements were obtained with an Agilent 7890/5975C instrument. The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100 %). Routine monitoring of reactions were performed using silica gel coated aluminium plates (Merck, silica gel 60, F254) which were analyzed under UV-light at 254 nm and dipped into a solution of 2-naphthol (5 % naphthol in 10 % NaOH aqueous, dipping solution). Solvent mixtures are understood as volume/volume. Solvents, reagents and chemicals were purchased from Sigma/Aldrich. Solvents, reagents and chemicals were used as purchased unless stated otherwise. *Trimethyl(phenylethynyl)silane* **5c** was prepared according to the reported procedure [1], *hex-1-yn-1-yltriisopropylsilane* **5f**, *triisopropyl(phenylethynyl)silane* **5d** were prepared according to the reported procedure [2], *1-methyl-3-((trimethylsilyl)ethynyl)indole* **5e** was prepared according to the reported procedure [3], a*renediazonium tosylates* **4a-4e** were prepared according to the reported procedure [4], *azides* **1a-1m** were prepared according to the reported procedure [5].



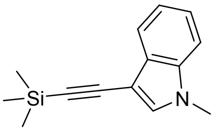
Trimethyl(phenylethynyl)silane 5c^1. Yield 87 %, yellow oil. ^{1}HNMR (300 MHz, DMSO-d$_6$): δ 7.46-7.43 (m, 2H), 7.40-7.34 (m, 3H), 0.22 (s, 9H).



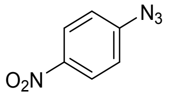
Triisopropyl(phenylethynyl)silane 5d^2. Yield 97 %, yellow oil. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.45-7.43 (m, 2H), 7.39-7.34 (m, 3H), 1.20 (m, 3H), 0.98 (m, 18H).



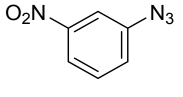
Hex-1-yn-1-yltriisopropylsilane 5f^2. Yield 97 %, yellow oil. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2.89-2.85 (m, 2H), 1.50-1.43 (m, 3H), 1.14-1.05 (m, 20H), 0.99-0.94 (m, 2H), 0.70-0.67 (m, 3H).



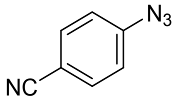
3-((trimethylsilyl)ethynyl)indole 5e^3. Yield 65 %, yellow oil. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.94 (s, 1H), 7.83-7.80 (m, 2H), 7.51-7.48 (m, 1H), 7.44-7.39 (m, 1H), 4.02 (s, 3H), 0.51 (s, 9H);



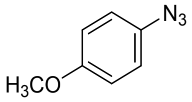
1-Azido-4-nitrobenzene 1a[5].Yield 98 %, pale yellow solid, m.p. = 72–74 °C (lit.[5], m.p. 72–73 °C).



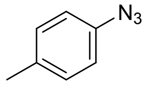
1-Azido-3-nitrobenzene 1b[5]. Yield 93 %, orange solid, m.p. = 51–52 °C (lit.[5], m.p. 52–53 °C).



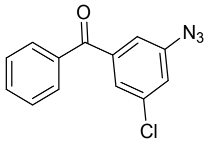
4-Azidobenzonitrile 1c[5]. Yield 97 %, white solid, m.p. = 66–67 °C (lit.[5], m.p. 66–67 °C).



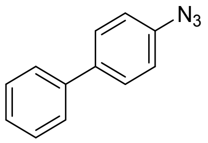
1-Azido-4-methoxybenzene 1d[5]. Yield 95 %, yellow oil. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.05 (d, J = 9.3 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 3.39 (s, 3H).



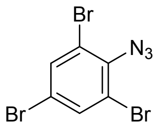
1-Azido-4-methylbenzene 1f[5]. Yield 72 %, brown oil. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.22 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 2.28 (s, 3H).



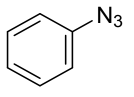
(3-Azido-5-chlorophenyl)phenylmethanone 1h[5]. Yield 98 %, beige solid, m.p. = 80–82 °C (lit.[5], m.p. 81–82 °C).



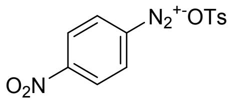
4-Azidobiphenyl 1k[5]. Yield 63 %, pale brown solid, m.p. = 72–73 °C (lit.[5], m.p. 72–73 °C).



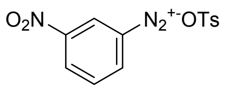
2-Azido-1,3,5-tribromobenzene 1i[5]. Yield 93 %, beige solid, m.p. = 82–84 °C (lit.[5], m.p. 83–84 °C).



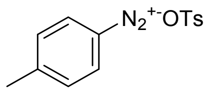
Azidobenzene 1n[5]. Yield 67 %, pale yellow oil.^{1}H NMR (300 MHz, DMSO-d_6): δ 7.39 (m, 2H), 7.17 (m, 1H), 7.07 (d, J = 7.8 Hz, 2H).



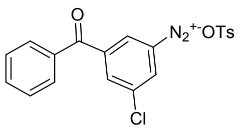
4-nitrobenzenediazoniumtosylate 4a[4]. Yield 84 %, yellow solid, m.p. = 133–134 ºC (lit.[4], m.p. 132–133 °C).



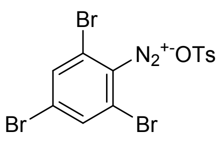
3-nitrobenzenediazonium tosylate 4b[4].Yield 85 %, yellow solid, m.p. = 133–134 ºC (lit.[4], m.p. 133–134 °C).



4-metylbenzenediazoniumtosylate 4c[4]. Yield 87 %, beige solid, m.p. = 95–97 ºC (lit.[4], m.p. 96–97 °C).



(3-diazo-5-chlorophenyl)(phenyl)methanonetosylate 4d[4]. Yield 85 %, beige solid, m.p. = 125–127 ºC (lit.[4], m.p. 126–127 °C).



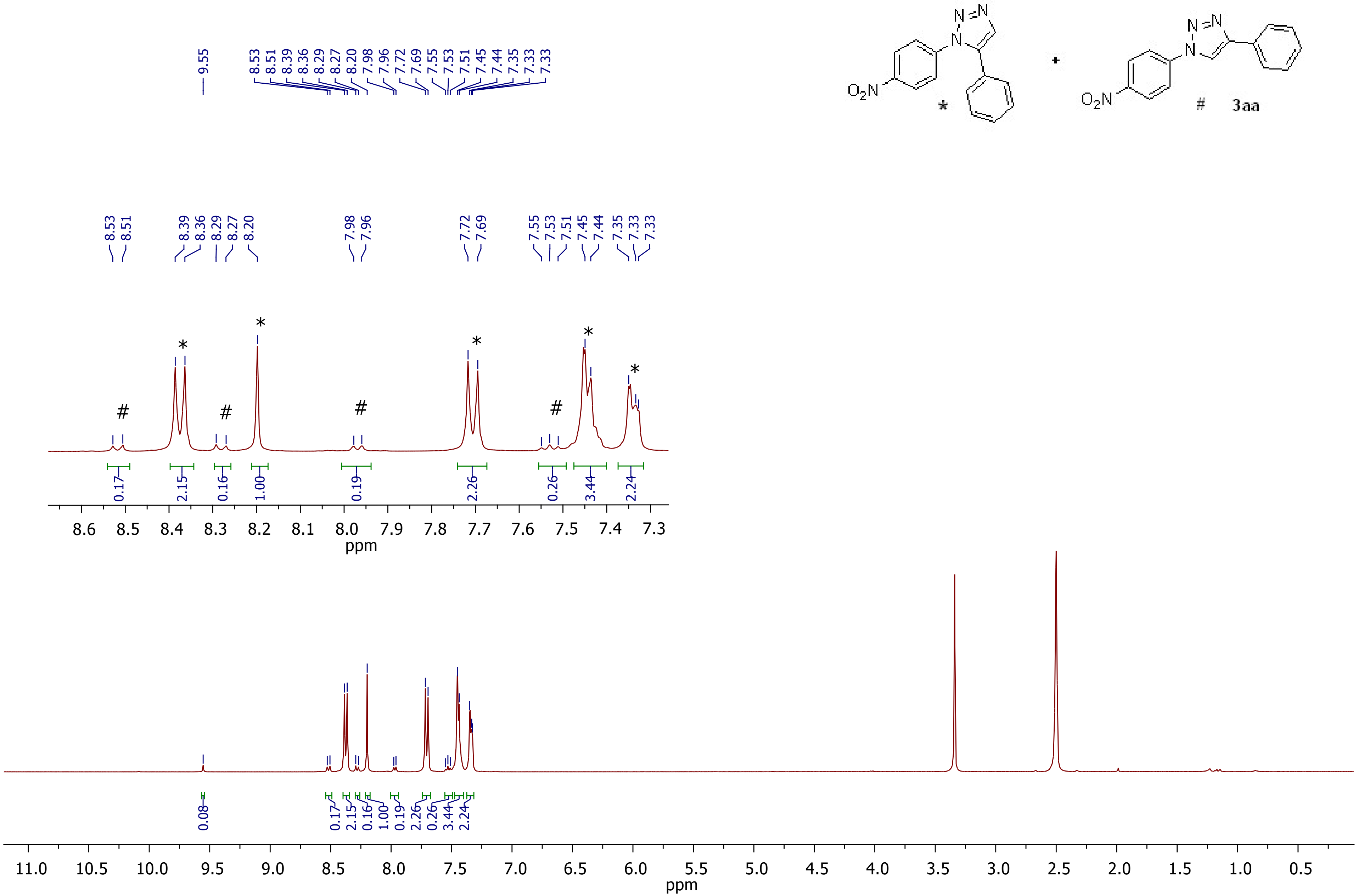
2,4,6-tribromobenzenediazonium tosylate 4e[4]. Yield 58 %, m.p. = 151–152 ºC (lit.[4], m.p. 152–153 °C).

Procedure for the AAC between 1-azido-4-nitrobenzene 1a and phenylacetylene 2a without catalyst.

The mixture of 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) in water (10 ml) was vigorously stirred during 2–3 minutes.The reaction vessel was then placed to microwave reactor (t = 75 °C and P = 80 B) and heated during 6 hours (TLC, hexane:EtOAc = 7:3). After the reaction mixture was extracted with CH_2Cl_2 (3×20 mL), washed by water, brine and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo to give the reaction mass which were purified by column chromatography (silica gel, eluent hexane:EtOAc = 9:1).

1-(4-nitrophenyl)-5-phenyl-*1H*-1,2,3-triazole. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.37 (d, *J* = 9 Hz, 2H), 8.19 (s, 1H), 7.71 (d, *J* = 9 Hz, 2H), 7.46-7.42 (m, 3H), 7.35-7.32 (m, 2H);

1-(4-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.55 (s, 1H), 8.52 (d, *J* = 8 Hz, 2H), 8.28 (d, *J* = 8 Hz, 2H), 7.97 (d, *J* = 8 Hz, 2H), 7.55-7.51 (m, 3H).


N=N
N
O2N
*
+
N=N
N
O2N
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3aa

9.55
8.53
8.51
8.39
8.36
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8.27
8.20
7.98
7.96
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7.5
7.0
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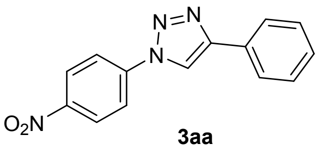
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

General Procedure for Preparation 1,4-disubstituted-1,2,3-triazoles from azides (1a-m) and terminal alkynes (2a-d).

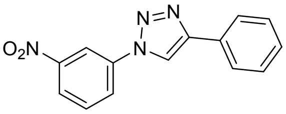
The mixture of azide (**1a-m**) (0.5 mmol) and alkyne (**2a-d**) in water (10 ml) was vigorously stirred during 2–3 minutes. After the 10 mol % Zn(OAc)$_2$ (0.05 mmol, 0.011 g) and 20 mol % ascorbic acid (0.10 mmol, 0.017 g) were added to reaction mixture. The reaction vessel was placed to microwave reactor (t = 75 °C and P = 80 B) and heated until full conversion of starting materials and intermediate (TLC, hexane:EtOAc = 7:3). After completing reaction, the reaction mixture was extracted with CH_2Cl_2 (3×20 mL), washed by water, brine and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo to give the crude 1,4-disubstitions-1,2,3-triazoles (**3aa-ma, 3ab, 3ac, 3dc, 3ad, 3fd**) which were purified by column chromatography (silica gel, eluent hexane:EtOAc = 9:1).



3aa

1-(4-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole (3aa).

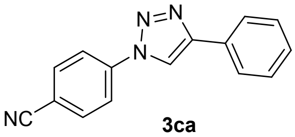
The reaction 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 6 hours afforded 1-(4-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **3aa** 0.129 g (yield 97 %) as an light yellow solid. m.p. = 151–152 °C (lit.[6], m.p. 152–154 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.55 (s, 1H), 8.52 (d, *J* = 8 Hz, 2H), 8.28 (d, *J* = 8 Hz, 2H), 7.97 (d, *J* = 8 Hz, 2H), 7.55-7.51 (m, 3H); ^{13}C NMR (100 MHz, , CDCl$_3$): δ 147.50, 140.99, 138.11, 133.91, 129.66, 129.10, 128.76, 126.47, 125.86, 125.06. HRMS (ESI-positive mode): calcd for $C_{14}H_{11}N_4O_2$ ([M]+H$^+$) = 267.0882; Found 267.0870.



3ba

1-(3-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole (3ba).

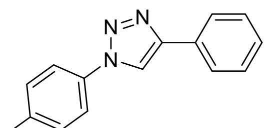
The reaction 1-azido-3-nitrobenzene **1b** (0.5 mmol, 0.082 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 7 hours afforded 1-(3-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **3ba** 0.125 g (yield 94 %) as a light yellow solid. m.p = 191–192 °C (lit.[6], m.p. 192–194 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.39 (d, *J* = 7.6 Hz, 1H), 8.32 (s, 1H), 8.19 (s, 1H), 7.85-7.79 (m, 2H), 7.44-7.42 (m, 3H), 7.36-7.34 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 148.09, 138.04, 136.91, 133.59, 131.76, 131.14, 129.59, 129.02, 128.78, 125.85, 124.27, 120.47.



3ca

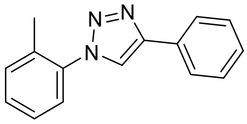
4-(4-phenyl-*1H*-1,2,3-triazol-1-yl)-benzonitrile (3ca).

The reaction 4-azidobenzonitrile **1c** (0.5 mmol, 0.072 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 7 hours afforded 4-(4-phenyl-*1H*-1,2,3-triazol-1-yl)benzonitrile **3ca** 0.113 g (yield 92 %) as a light beige solid. m.p = 220–222 °C (lit.[7], m.p. 220–221 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.17 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.44-7.43 (m, 3H), 7.32-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.64, 137.89, 133.83, 129.56, 129.02, 128.69, 126.23, 125.90, 120.36, 117.98, 112.19.


3da

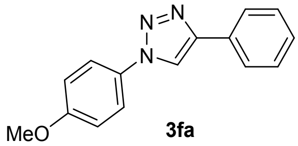
4-phenyl-1-(p-tolyl)-*1H*-1,2,3-triazole (3da).

The reaction 1-azido-4-methylbenzene **1d** (0.5 mmol, 0.067 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 9 hours afforded 4-phenyl-1-(p-tolyl)-*1H*-1,2,3-triazole **3da** 0.105 g (yield 90 %) as a light beige solid. m.p. = 163–164 °C (lit.[6], m.p. 165–167 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.26 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 8,4 Hz, 2H), 7.49 (t, *J* = 7,6 Hz 2H), 7.44-7.36 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.23, 138.36, 134.43, 130.34, 130.29, 129.01, 128.21, 125.33, 119.89, 119.52, 20.65.


3ea

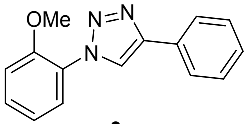
4-phenyl-1-(o-tolyl)-*1H*-1,2,3-triazole (3ea).

The reaction 1-azido-2-methylbenzene **1e** (0.5 mmol, 0.067 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 7 hours afforded 4-phenyl-1-(p-tolyl)-*1H*-1,2,3-triazole **3ea** 0.071 g (yield 61 %) as a brown solid. m.p. = 58–60 °C (lit.[8], m.p. 57–59 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.97 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.52-7.51 (m, 5H), 7.47-7.43 (m, 1H), 7.39-7.35 (m, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 146.47, 136.31, 133.07, 131.45, 130.44, 129.92, 129.00, 128.15, 127.08, 126.03, 125.33, 123.09, 17.49.


3fa

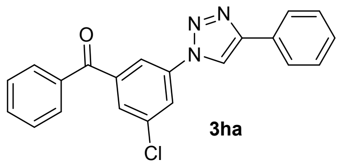
1-(4-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole (3fa).

The reaction 1-azido-4-methoxybenzene **1f** (0.5 mmol, 0.075 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 5 hours afforded 1-(4-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole **3fa** 0.116 g (yield 92 %) as a light beige solid; m.p. = 163–164 °C (lit.[6], m.p.160–162 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11 (s, 1H), 7.40-7.39 (m, 3H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.29-7.27 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.81, 137.68, 134.55, 132.93, 129.17, 128.87, 128.39, 127.17, 126.47, 114.65, 55.55.


3ga

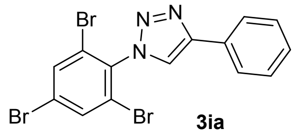
1-(2-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole (3ga).

The reaction 1-azido-2-methoxybenzene **1g** (0.5 mmol, 0.075 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 7 hours afforded 1-(2-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole **3ga** 0.116 g (yield 69 %) as an yellow oil (lit.[6]).^{1}H NMR (400 MHz, DMSO-d_6): δ 8.92 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.68-7.66 (m, 1H), 7.59-7.54 (m, 1H), 7.50-7.46 (m, 2H), 7.39-7.34 (m, 2H), 7.19-7.15 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.89, 146.23, 130.97, 130.49, 128.99, 128.09, 126.02, 125.74, 125.36, 123.47, 120.92, 113.03, 56.18.


3ha

(3-chloro-5-(4-phenyl-*1H*-1,2,3-triazol-1-yl)phenyl)(phenyl)methanone (3ha).

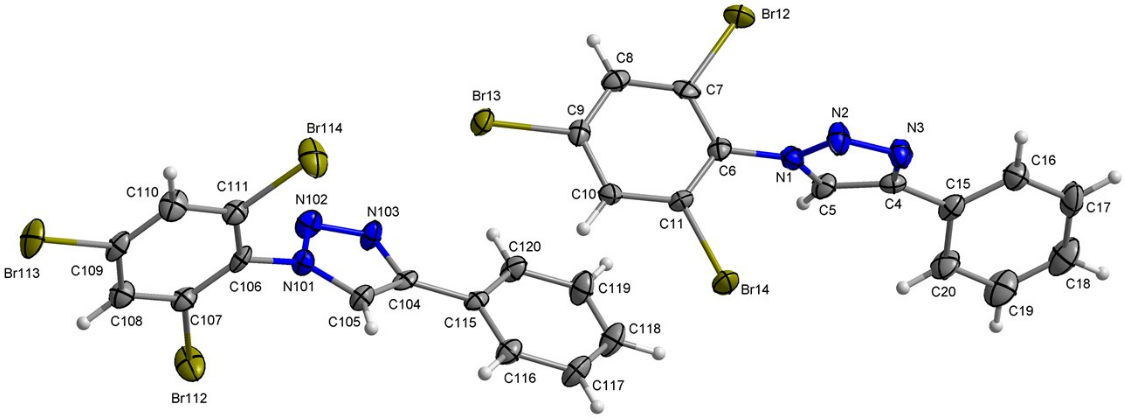
The reaction (3-azido-5-chlorophenyl)(phenyl)methanone **1h** (0.5 mmol, 0.129 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 9 hours afforded (3-chloro-5-(4-phenyl-*1H*-1,2,3-triazol-1-yl)phenyl)(phenyl)methanone **3ha** 0.126 g (yield 70 %) as an yellow solid; m.p. = 151–152 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ 9.08 (s, 1H), 7.98-7.93 (m, 2H), 7.82 (d, *J* = 2 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.64-7.62 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.39 (m, 4H), 7.36-7.32 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.43, 147.14, 135.56, 135.35, 134.11, 133.63, 133.04, 131.69, 129.81, 129.40, 129.01, 128.98, 128.63, 128.34, 125.87, 125.29, 122.05. HRMS (ESI-positive mode): calcd for $C_{21}H_{15}{}^{35}ClN_3O$ ([M]+H$^+$) 360.0904; Found: 360.0896, calcd for $C_{21}H_{15}{}^{37}ClN_3O$ ([M]+H$^+$) 362.0882; Found: 362.0913.


3ia

4-phenyl-1-(2,4,6-tribromophenyl)-*1H*-1,2,3-triazole (3ia).

The reaction 2-azido-1,3,5-tribromobenzene **1i** (0.5 mmol, 0.178 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 7 hours afforded 4-phenyl-1-(2,4,6-tribromophenyl)-*1H*-1,2,3-triazole **3ia** 0.178 g (yield 78 %) as a white solid, m.p. = 140–142 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.33 (s, 1H), 8.28 (s, 2H), 7.45-7.43 (m, 3H), 7.31-7.28 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 138.43, 135.35, 134.39, 132.53, 129.83, 129.30, 127.08, 125.65, 125.38, 124.03. HRMS (ESI-positive mode): calcd for $C_{14}H_8{}^{79}Br_3N_3$ ([M]+H$^+$) 457.8327; Found 457.8277; calcd for $C_{14}H_8{}^{81}Br_3N_3$ ([M]+H$^+$) 459.8305; Found 459.8271.

The crystal suitable for X-Ray study was obtained by slow evaporation of ether solution of **3ia.**



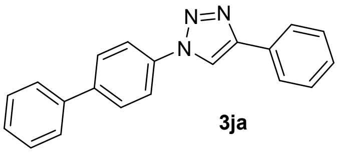
The structure **3ia** ($C_{14}H_8Br_3N_3$) was measured using D8 VENTURE with multilayer monochromator and a Mo-Kα Incoatec microfocus sealed tube ($\lambda = 0.71073$ Å) radiation at 180 K and PHOTON CMOS detector. The structure was in monoclinic system, $P2_1/n$ space group with lattice parameters $a = 16.2913$ (7) Å $b = 10.0932$ (4) Å $c = 19.7897$ (8) Å, $\beta = 112.8945$ (12) °, $Z = 8$, $V = 2997.4$ (2) Å^3, $D_c = 2.029$ g cm^{-3}, μ(Mo-Kα) = 8.07 mm^{-1}. The data reduction and absorption correction were done with Apex3 software[14]. The structure was solved by charge flipping methods[15] and refined by full matrix least squares on F squared value using Crystals software[16] to final values $R = 0.037$ an $R_w = 0.096$ using 6136 independent reflections ($\Theta_{max} = 26.4$ °), 362 parameters and 0 restrains. The MCE software[17] was used for visualization of electron density maps. According to common practice the hydrogen atoms attached to carbon atoms were place geometrically with $U_{iso}(H)$ in range 1.2-1.5 U_{eq} of parent atom (C). The structure was deposited into Cambridge Structural Database under number CCDC 1513616.

The asymmetric unit is formed by two independent molecules of **3ia**. In the absence of strong hydrogen bond donors the noncovalent intermolecular interactions are dominated by C–H···N interactions supported by Br···π and Br···Br interactions, forming a well developed 3D system. For further information on intermolecular interactions see table 1.

Table 1 The intermolecular interactions in 3ia (Å, °)

Interaction	D–H	H···A	D···A	D–H···A
C19–H191···N102^{i}	0.95	2.67	3.579 (9)	162
C105–H1051···N102^{ii}	0.95	2.37	3.250 (8)	155
C110–H1101···N2^{iii}	0.95	2.70	3.574 (8)	154
Br13···Br112^{iv}			3.6233 (9)	
Br113···Br113^{v}			3.5599 (12)	

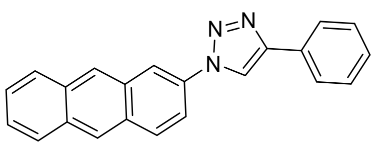
Symmetry codes: (*i*) x+1/2, -y+1/2, z-1/2 (*ii*) -x+1/2, y+1/2, -z+3/2 (*iii*) -x, -y+1, -z+1 (*iv*) x-1/2, -y+1/2, z-1/2 (*v*) -x, -y+1, -z+2



3ja

1-([1,1'-biphenyl]-4-yl)-4-phenyl-*1H*-1,2,3-triazole (3ja).

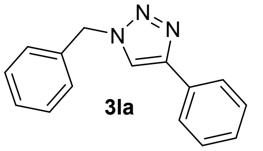
The reaction 4-azido-1,1'-biphenyl **1j** (0.5 mmol, 0.098 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 8 hours afforded 1-([1,1'-biphenyl]-4-yl)-4-phenyl-*1H*-1,2,3-triazole **3ja** 0.111 g (yield 75 %) as a light-beige solid; m.p. = 152–153 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.15 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.52-7.48 (m, 4H), 7.43-7.42 (m, 4H), 7.36-7.34 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 148.19, 147.60, 146.88, 142.26, 140.46, 136.75, 136.03, 132.00, 130.26, 129.52, 127.38, 126.72, 124.82, 124.19; HRMS (ESI-positive mode): calcd for $C_{20}H_{16}N_3$ ([M]+H$^+$) 298.1339; Found 298.1368



3ka

1-(anthracen-2-yl)-4-phenyl-*1H*-1,2,3-triazole (3ka).

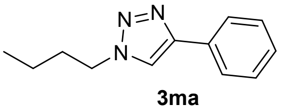
The reaction 2-azidoanthracene **1k** (0.5 mmol, 0.110 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 6 hours afforded 1-(anthracen-2-yl)-4-phenyl-*1H*-1,2,3-triazole **3ka** 0.113 g (yield 71 %) as a brown solid; m.p. = 200–202 °C (lit.[9], m.p. 200 °C). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 8.54-8.48 (m, 2H), 8.42-8.38 (m, 2H), 8.10-8.06 (m, 1H), 8.03-7.99 (m, 1H), 7.95 (s, 1H), 7.54-7.51 (m, 3H), 7.40-7.36 (m, 2H), 7.34-7.32 (m, 2H).



3la

1-benzyl-4-phenyl-*1H*-1,2,3-triazole (3la).

The reaction (azidomethyl)benzene **1l** (0.5 mmol, 0.067 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 6 hours afforded 1-benzyl-4-phenyl-*1H*-1,2,3-triazole **3la** 0.102 g (yield 87 %) as a white solid; m.p. = 125–126 °C (lit.[6], m.p.126–128 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.95 (s, 1H), 7.46-7.43 (m, 5H), 7.41-7.37 (m, 5H), 5.68 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 146.67, 136.04, 130.67, 128.92, 128.83, 128.19, 127.91, 126.84, 125.17, 121.59, 53.03.

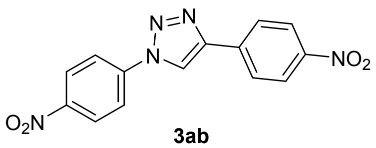


3ma

1-butyl-4-phenyl-1H-1,2,3-triazole (3ma).

The reaction 1-azidobutane **1m** (0.5 mmol, 0.0957 g) and phenylacetylene **2a** (0.5 mmol, 0.051 g, 55 µl) according to the general procedure during 6 hours afforded 1-butyl-4-phenyl-1H-1,2,3-triazole **3ma** 0.066 g (yield 66 %) as a Colorless liquid; (lit.[6]). ^{1}H NMR (400 MHz, CDCl3): δ 7.83 (t, J = 7.2 Hz, 2 H), 7.73 (s, 1 H), 7.44–7.32 (m, 3 H), 7.42 (t, J = 6.9

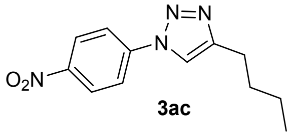
Hz, 2 H), 1.89–1.83 (m, 2 H), 1.44–1.36 (m, 2 H), 0.97 (t, J = 6.9 Hz, 3 H) ; ^{13}C NMR (100 MHz, CDCl3): δ 151.07, 130.78, 128.32, 128.09, 125.45, 119.19, 50.88, 32.63, 19.71, 13.15.



3ab

1,4-bis(4-nitrophenyl)-*1H*-1,2,3-triazole (3ab).

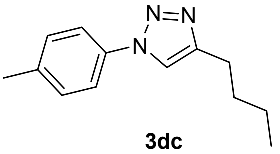
The reaction 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and 1-ethynyl-4-nitrobenzene **2b** (0.5 mmol, 0.073 g) according to the general procedure during 5 hours afforded 1,4-bis(4-nitrophenyl)-*1H*-1,2,3-triazole **3ab** 0.120 g (yield 77 %) as a white solid; m.p. = 299–300 °C (lit.[10], m.p. 305-310(dec) °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.40-8.38 (m, 3H), 8.24 (d, *J* = 9.2 Hz, 2H), 7.75 (d, *J* = 9.2 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.79, 147.72, 140.58, 136.31, 134.91, 132.32, 130.15, 126.68, 125.22, 124.13.



3ac

1-(4-nitrophenyl)-4-butyl-*1H*-1,2,3-triazole (3ac).

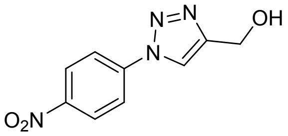
The reaction 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and hexyne-1 **2c** (0.5 mmol, 0.042 g, 30 μl) according to the general procedure during 6 hours afforded 1-(4-nitrophenyl)-4-butyl-*1H*-1,2,3-triazole **3ac** 0.113 g (yield 92 %) as a yellow solid, m.p.= 198–200 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.79 (s, 1H), 8.43 (d, *J* = 9.2 Hz, 2H), 8.19 (d, *J* = 9.2 Hz, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 1.69-1.62 (m, 2H), 1.42-1.34 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.87, 146.42, 141.04, 125.59, 120.53, 120.17, 30.73, 24.59, 21.66, 13.68.



3dc

4-butyl-1-(p-tolyl)-*1H*-1,2,3-triazole (3dc).

The reaction 1-azido-4-methylbenzene **1d** (0.5 mmol, 0.067 g) and hexyne-1 **2c** (0.5 mmol, 0.0415 g, 30 μl) according to the general procedure during 5 hours afforded 4-butyl-1-(p-tolyl)-*1H*-1,2,3-triazole **3dc** 0.086 g (yield 80 %) as a light beige solid. m.p. = 185–186 °C (lit.[12], m.p. 187-188 °C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.70 (s, 1H), 7.42 (s, 4H), 2.66-2.61 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.54-1.44 (m, 2H), 1.30-1.20 (m, 3H), 0.83-0.78 (t, *J* = 7.4 Hz, 3H).

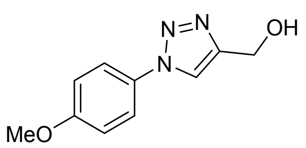


3ad

(1-(4-nitrophenyl)-*1H*-1,2,3-triazol-4-yl)methanol (3ad).

The reaction 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and propargyl alcohol **2d** (0.5 mmol, 0.028 g, 27 μl) according to the general procedure during 6 hours afforded (1-(4-nitrophenyl)-*1H*-1,2,3-triazol-4-yl)methanol **3ad** 0.102 g (yield 93 %) as an yellow solid, m.p. = 201–202 °C (lit.[11], m.p. 201–202 °C). ^{1}H NMR

(400 MHz, DMSO-d$_6$): δ 8.243 (d, *J* = 9.2 Hz, 2H), 8.05 (d, *J* = 9.2 Hz, 2H), 7.92 (s, 1H), 5.74 (t, *J* = 5.7 Hz, 1H), 5.41 (t, *J* = 5.6 Hz, 1H).



3fd

(1-(4-methoxyphenyl)-*1H*-1,2,3-triazol-4-yl)methanol (3fd).

The reaction 1-azido-4-methoxybenzene **1f** (0.5 mmol, 0.075 g) and propargyl alcohol **2d** (0.5 mmol, 0.028 g, 27 µl) according to the general procedure during 7 hours afforded (1-(4-methoxyphenyl)-*1H*-1,2,3-triazol-4-yl)methanol **3fd** 0.062 g (yield 61 %) as a light yellow solid; m.p. = 127-128 °C (lit.[11], m.p. 127-129 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.58 (s, 1H), 7.80 (d, *J* = 6.8, 2H), 7.145 (d, *J* = 4.8, 2H), 4.58 (s, 2H), 3.82 (s, 3H).

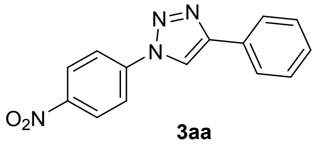
Table 2 Preparation of 1,4-disubstituted-1,2,3-triazoles from ADTs

Entry	ADT, R=	Triazole, Yield [%]^b	*t* [h]
1	4a, 4-O$_2$N	**3aa**, 95	6
2	4b, 3-O$_2$N	**3ba**, 89	7
3	4c, 4-Me	**3da**, 86	9
4	4d, 2-(PhCO)-5-Cl	**3ha**, 67	9
5	4e, 2,4,6-Br$_3$	**3ia**, 81	7

[a] reactions conditions: ADT (1 equiv), NaN$_3$ (1.3 equiv), acetylene (1 equiv), water (10 ml), microwave irradiation (75 °C, constant power 80 W); [b] isolated yield

General Procedure for Preparation 1,4-disubstituted-1,2,3-triazoles from arenediazonium tosylates (4a-e) and phenylacetylene (2a).

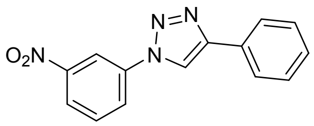
The mixture of arenediazonium tosylates (**4a-e**) (0.5 mmol) and NaN$_3$ (0.65 mmol, 0.042 g) in water (10 ml) was vigorously stirred during 2–3 minutes. After the phenylacetylene **2a** (0.55 mmol, 0.051 g, 55 µl), 10 mol % Zn(OAc)$_2$ (0.05 mmol, 0.011 g) and 20 mol % ascorbic acid (0.10 mmol, 0.017 g) were added to reaction mixture. The reaction vessel was placed to microwave reactor (t = 75 °C and P = 80 B) and heated until full conversion of starting materials and intermediate (TLC, hexane:EtOAc = 7:3). After completing reaction, the reaction mixture was extracted with CH$_2$Cl$_2$ (3×20 mL), washed by (water, brine) and dried with anhydrous Na$_2$SO$_4$. The solvent was removed in vacuo to give the crude 1,4-disubstitions-1,2,3-triazoles (**3aa, 3ba, 3da, 3ha, 3ia**) which were purified by column chromatography(silica gel, eluent hexane:EtOAc=9:1).



3aa

1-(4-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole (3aa).

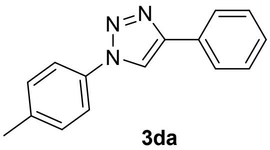
The reaction 4-nitroarenediazonium tosylate **4a** (0.5 mmol, 0.16 g) according to the general procedureduring 6 hours afforded 1-(4-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **3aa** 0.126 g (yield 95 %) as a light yellow solid. m.p = 151-152 °C (lit.[6], m.p. 152–154 °C).



3ba

1-(3-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole (3ba).

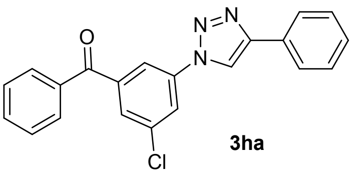
The reaction 3-nitroarenediazonium tosylate **4b** (0.5 mmol, 0.16 g) according to the general procedure during 7 hours afforded 1-(3-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **3ba** 0.118 g (yield 89 %) as a light yellow solid. m.p = 191–192°C (lit.[6], m.p. 192–194 °C).



3da

4-phenyl-1-(p-tolyl)-*1H*-1,2,3-triazole (3da).

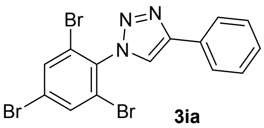
The reaction 4-nitroarenediazonium tosylate **4d** (0.5 mmol, 0.145 g) and according to the general procedure during 9 hours afforded 4-phenyl-1-(p-tolyl)-*1H*-1,2,3-triazole **3da** 0.101 mg (yield 86 %) as a light beige solid. m.p = 163–164 °C(lit.[6], m.p. 165–167 °C).



3ha

3-chloro-5-(4-phenyl-*1H*-1,2,3-triazol-1-yl)phenyl)(phenyl) methanone (3ha).

The reaction 3-diazo-5-chlorophenyl)(phenyl)methanone tosylate **4h** (0.5 mmol, 0.207 g) according to the general procedure during 9 hours afforded (3-chloro-5-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)(phenyl)methanone **3ha** 0.120 mg (yield 67 %) as an yellow solid; m.p. = 151–152°C.



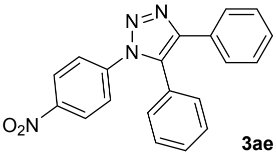
3ia

4-phenyl-1-(2,4,6-tribromophenyl)-*1H*-1,2,3-triazole (3ia).

The reaction 2,4,6-tribromoarendiazonium tosylate **4i** (0.5 mmol, 0.224 g) according to the general procedure during 7 hours afforded 4-phenyl-1-(2,4,6-tribromophenyl)-*1H*-1,2,3-triazole **3ia** 0.185 g (yield 81 %) as a white solid; m.p. = 140–142 °C.

General Procedure for Preparation 1,4,5-trisubstituted-1,2,3-triazoles from aromatic azides (1a, 1d, 1g, 1e, 1n) and disubstituted acetylenes (2e-j).

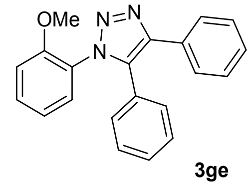
The mixture of azide (**1a, 1d, 1g, 1e, 1o**) (0.5 mmol) and disubstituted acetylenes (**2e-j**) in water (10 ml) was vigorously stirred during 2–3 minutes. After the 10 mol % $Zn(OAc)_2$ (0.05 mmol, 0.011 g) and 20 mol % ascorbic acid (0.10 mmol, 0.017 g) were added to reaction mixture. The reaction vessel was placed to microwave reactor (t = 130 °C and P = 150 B) and heated until full conversion of starting materials and intermediate (TLC, hexane:EtOAc = 7:3). After completing reaction, the reaction mixture was extracted with CH_2Cl_2 (3×20 mL), washed by water, brine and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo to give the crude 1,4,5-trisubstitued-1,2,3-triazoles (**3ae, 3ee, 3ge, 3af, 3ng, 3ah, 3dh, 3nh, 3ai, 3aj**) which were purified by column chromatography (silica gel, eluent hexane:EtOAc = 9:1).



3ae

1-(4-nitrophenyl)-4,5-diphenyl-*1H*-1,2,3-triazole (3ae).

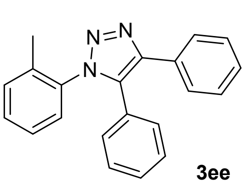
The reaction 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and tolane **2e** (0.5 mmol, 0.089 g) according to the general procedure during 7 hours afforded 1-(4-nitrophenyl)-4,5-diphenyl-*1H*-1,2,3-triazole **3ae** 0.164 g (yield 96 %) as a light yellow solid, m.p. = 239-240 °C (lit.[6], m.p. 238–240 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.32 (d, *J*= 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.53-7.45 (m, 5H), 7.41-7.33 (m, 5H).



3ge

1-(2-methoxyphenyl)-4,5-diphenyl-*1H*-1,2,3-triazole (3ge).

The reaction 1-azido-2-methoxybenzene **1g** (1 mmol, 0.149 g) and tolane **2e** (0.5 mmol, 0.089 g) according to the general procedure during 8 hours afforded 1-(2-methoxyphenyl)-4,5-diphenyl-*1H*-1,2,3-triazole **3ge** 0.083 g (yield 51 %) as a brown solid, m.p. = 223–224°C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.55-7.52 (m, 3 H), 7.49-7.45 (m, 1H), 7.37-7.31 (m, 6H), 7.24-7.22 (m, 2H), 7.11-7.04 (m, 2H), 3.55 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 153.77, 142.66, 131.89, 130.75, 129.49, 129.39, 128.96, 128.68, 127.90, 127.40, 126.50, 124.65, 120.59, 112.56, 55.58; HRMS (ESI-positive mode): calcd for $C_{21}H_{18}N_3O$ ([M] +H$^+$) 328.1450; Found 328.1426.

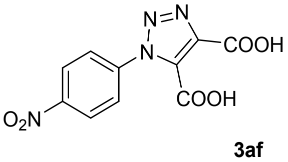


3ee

4,5-diphenyl-1-(o-tolyl)-*1H*-1,2,3-triazole (3ee).

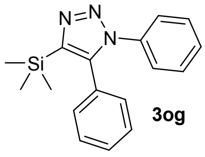
The reaction 1-azido-2-methylbenzene **1e** (1 mmol, 0.130 g) and tolane **2e** (0.5 mmol, 0.089 g) according to the general procedure during 8 hours afforded 4,5-diphenyl-1-(o-tolyl)-*1H*-1,2,3-triazole **3ee** 0.073 g (yield 47 %) as an yellow solid, m.p. = 215–216 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.57-7.55 (m, 2H), 7.48-7.46 (m, 4H), 7.43-7.42 (m, 4H), 7.11 (d, *J* = 7.6 Hz, 4H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 153.13, 142.03, 131.26, 130.12, 128.87, 128.77, 128.33, 128.09, 128.06, 127.27, 126.77, 125.88, 119.97, 111.93, 20.85; HRMS (ESI-positive mode): calcd for $C_{21}H_{18}N_3$ ([M]+H$^+$) 312.1574; Found 312.1565.

1-(4-nitrophenyl)-*1H*-1,2,3-triazole-4,5-dicarboxylic acid (3af).



3af

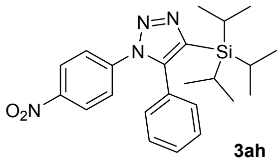
The reaction 1-azido-4-nitrobenzene **1a** (0.5mmol, 0.082 g) and but-2-ynedioic acid **2f** (0.5 mmol, 0.057 g) according to the general procedure during 3 hours afforded 1-(4-nitrophenyl)-*1H*-1,2,3-triazole-4,5-dicarboxylic acid **3af** 0.083 g (yield 60 %) as an yellow solid, m.p. = 200–202°C (lit.[13], m.p. 200-202 °C). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.93 (d, *J* = 9.2 Hz, 2H), 6.68 (broad s, 2H), 6.59 (d, *J*= 9.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 155.73, 135.61, 126.42, 125.61, 120.70, 112.38; HRMS (ESI-positive mode): calcd for $C_{10}H_7N_4O_6$ ([M]+H$^+$) 279.0366; Found 279.0332.



3og

1,5-diphenyl-4-(trimethylsilyl)-*1H*-1,2,3-triazole (3ng).

The reaction azidobenzene **1o** (0.5 mmol, 0.060 g) and trimethyl(phenylethynyl)silane **2g** (0.5 mmol, 0.087 g) according to the general procedure during 6 hours afforded 1,4-diphenyl-5-(trimethylsilyl)-*1H*-1,2,3-triazole **3og** 0.095 g (yield 65 %) as a light beige solid, m.p. = 94–95 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.44-7.38 (m, 6H), 7.35-7.31 (m, 2H), 7.29-7.26 (m, 2H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 143.74, 143.64, 136.03, 130.05, 129.31, 129.22, 129.07, 128.41, 128.08, 125.38, -0.81. HRMS (ESI-positive mode): calcd for $C_{17}H_{20}N_3Si$ ([M]+H$^+$) 294.1421; Found 294.1411.

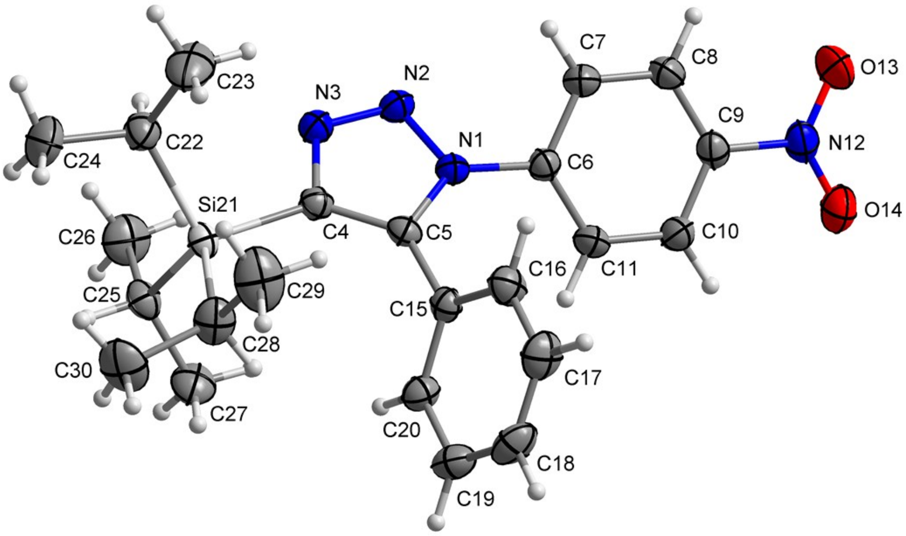


3ah

1-(4-nitrophenyl)-5-phenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole (3ah).

The reaction 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and triisopropyl(phenylethynyl)silane **2h** (0.5 mmol, 0.142 g) according to the general procedure during 5.5 hours afforded 1-(4-nitrophenyl)-5-phenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **3ah** 0.169 g (yield 80 %) as a slight yellow solid, m.p. = 84–85 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.46-7.39 (m, 3H), 7.36-7.34 (m, 2H), 1.23-1.14 (m, 3H), 0.98-0.96 (m, 18H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 147.08, 144.47, 140.99, 140.77, 130.35, 129.90, 128.55, 127.90, 126.29, 124.65, 18.54, 11.11; HRMS (ESI-positive mode): calcd for $C_{23}H_{31}N_4O_2Si$ ([M]+H$^+$) 423.2216, Found 423.2214.

The crystal suitable for X-Ray study was obtained by slow evaporation of ether solution of **3ah.**



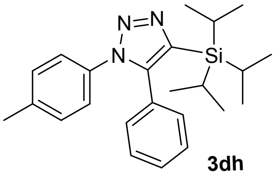
The structure **3ha** ($C_{14}H_8Br_3N_3$) was measured using D8 VENTURE with multilayer monochromator and a Mo-Kα Incoatec microfocus sealed tube ($\lambda = 0.71073$ Å) radiation at 180 K and PHOTON CMOS detector. The structure was in orthorhombic system, *Pbca* space group with lattice parameters $a = 15.6516\ (5)$ Å $b = 14.7041\ (4)$ Å $c = 20.8303\ (6)$ Å, $Z = 8$, $V = 4793.9\ (2)$ Å^3, $D_c = 1.171$ g cm^{-3}, μ(Mo-Kα) = 0.12 mm^{-1}. The data reduction and absorption correction were done with Apex3 software[14]. The structure was solved by charge flipping methods[15] and refined by full matrix least squares on F squared value using Crystals software[16] to final values $R = 0.039$ an $R_w = 0.101$ using 4899 independent reflections ($\Theta_{max} = 26.4$ °), 271 parameters and 0 restrains. The MCE software[17] was used for visualization of electron density maps. According to common practice the hydrogen atoms attached to carbon atoms were place geometrically with U_{iso}(H) in range 1.2-1.5 U_{eq} of parent atom (C). The structure was deposited into Cambridge Structural Database under number CCDC 1513617.

The asymmetric unit is formed by a single molecule of **3ha**. In the absence of strong hydrogen bond donors the noncovalent intermolecular interactions are dominated by C–H···N and C–H···O interactions, with C–H···N interaction forming a supramolecular dimer and the remaining interactions connecting the dimmers throughout the structure. For further information on intermolecular interactions see table 3.

Table 3 The intermolecular interactions in 3ha (Å, °)

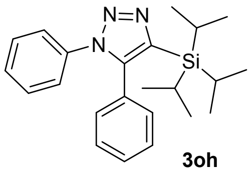
Interaction	D–H	H···A	D···A	D–H···A
C7–H71···N2^{i}	0.95	2.47	3.261 (2)	140
C17–H171···O14^{ii}	0.95	2.65	3.284 (2)	125
C20–H201···O14^{iii}	0.95	2.72	3.434 (2)	130

Symmetry codes: (*i*) -x+1, -y+2, -z+1 (*ii*) x-1/2, y, -z+3/2 (*iii*) -x+3/2, y-1/2, z


3dh

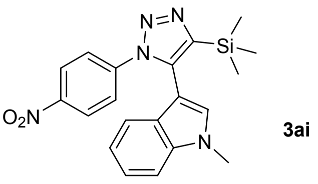
5-phenyl-1-(p-tolyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole (3dh).

The reaction 1-azido-4-methylbenzene **1d** (0.5 mmol, 0.0665 g) and triisopropyl(phenylethynyl)silane **2h** (0.5 mmol, 0.142 g) according to the general procedure during 6.5 hours afforded 5-phenyl-1-(p-tolyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **3dh** 0.154 g (yield 79 %) as a light yellow solid, m.p. = 62-63 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.40-7.35 (m, 3H), 7.28-7.26 (m, 2H), 7.22-7.17 (m, 4H), 2.28 (s, 3H), 1.23-1.15 (m, 3H), 0.98-0.97 (m, 18H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.21, 139.66, 138.53, 133.69, 130.22, 129.45, 129.28, 128.56, 128.11, 125.23, 20.48, 18.47, 11.03. HRMS (ESI-positive mode): calcd for $C_{24}H_{34}N_3Si$ ([M]+H$^+$) 392.2522, Found: 392.2509.


3oh

1,5-diphenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole (3nh).

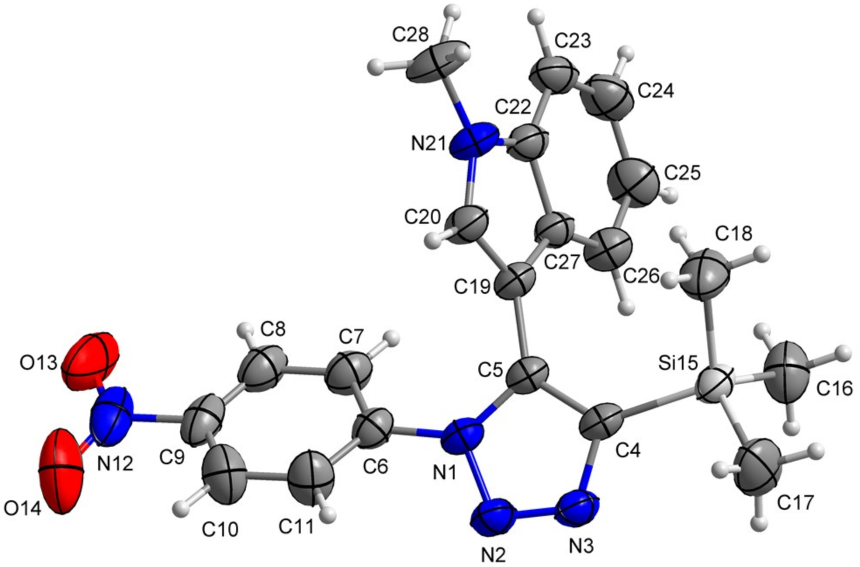
The reaction azidobenzene **1o** (0.5 mmol, 0.060 g) and triisopropyl(phenylethynyl)silane **2h** (0.5 mmol, 0.142 g) according to the general procedure during 7 hours afforded 1,5-diphenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **3oh** 0.131 g (yield 70 %) as a light yellow solid, m.p. = 68–70 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.42-7.37 (m, 6H), 7.34-7.30 (m, 2H), 7.28-7.25 (m, 2H), 1.23 (m, 3H), 0.98-0.96 (m, 18H);^{13}C NMR (100 MHz, DMSO-d_6): δ 143.18, 143.08, 135.47, 129.50, 128.75, 128.66, 128.52, 127.85, 127.52, 124.83, 18.549, 11.11. HRMS (ESI-positive mode): calcd for $C_{25}H_{32}N_3Si$ ([M]+H$^+$) 378.2365; Found: 378.2361.


3ai

1-methyl-3-(1-(4-nitrophenyl)-4-(trimethylsilyl)-*1H*-1,2,3-triazol-5-yl)-indole (3ai).

The reaction 1-azido-4-nitrobenzene **1a** (1 mmol, 0.164 g) and 1-methyl-3-((trimethylsilyl)ethynyl)-indole **2i** (0.5 mmol, 0.114 g) according to the general procedure during 8 hours afforded 1-methyl-3-(1-(4-nitrophenyl)-5-(trimethylsilyl)-*1H*-1,2,3-triazol-4-yl)-indole **3ai** 0.139 g (yield 69 %) as an orange solid, m.p. = 130–131 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20 (d, *J* = 9.2 Hz, 2H), 7.68 (d, *J* = 9.2 Hz, 2H), 7.62 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 6.8, 9.6 Hz, 1H), 7.00-6.92 (m, 2H), 3.86 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 146.84, 145.87, 141.44, 137.78, 136.45, 131.09, 126.79, 125.14, 124.70, 122.02, 120.18, 118.48, 110.47, 99.58, 32.81, -0.90. HRMS (ESI-positive mode): calcd for $C_{20}H_{22}N_5O_2Si$ ([M]+H$^+$) 392.2522; Found: 392.2509.

The crystal suitable for X-Ray study was obtained by slow evaporation of ether solution of **3ai.**



The structure **3ai** ($C_{20}H_{21}N_5O_2Si$) was measured using D8 VENTURE with multilayer monochromator and a Cu-Kα Incoatec microfocus sealed tube (λ = 1.54178 Å) radiation at 180 K and PHOTON CMOS detector. The structure was in triclinic system, *P*-1 space group with lattice parameters $a = 9.4684$ (3) Å, $b = 10.4692$ (4) Å, $c = 12.7710$ (4) Å, $\alpha = 96.2634$ (12) °, $\beta = 95.7478$ (12) °, $\gamma = 113.6438$ (11) °, $Z = 2$, $V = 1138.27$ (7) Å^3, $D_c = 1.142$ g cm^{-3}, μ(Cu-Kα) = 1.10 mm^{-1}. The data reduction and absorption correction were done with Apex3 software[14]. The structure was solved by charge flipping methods[15] and refined by full matrix least squares on F squared value using Crystals software[16] to final values $R = 0.047$ an $R_w = 0.132$ using 4161 independent reflections ($\Theta_{max} = 68.4$ °), 253 parameters and 0 restrains. The MCE software[17] was used for visualization of electron density maps. According to common practice the hydrogen atoms attached to carbon atoms were place geometrically with U_{iso}(H) in range 1.2-1.5 U_{eq} of parent atom (C). The loosely bound disordered hexene was located in vicinity of inversion center, resulting in unclear atomic positions and significant refinement instability; therefore it was removed from the structure using PLATON squeeze utility, resulting in void channels in the structure of 142 Å^3 for unit cell. The structure was deposited into Cambridge Structural Database under number CCDC 1513614.

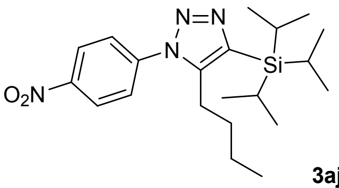
The asymmetric unit is formed by one independent molecule of **3ai**. Full analysis of non-covalent interactions cannot be done, since the disordered solvent was excluded from the structure, but the interactions of **3ai** itself can still provide some information about the structure packing. The C–H···O and C–H···π interactions connect **3ai** molecules into strips, which are further connected by π···π interactions into a well developed framework. For further information on intermolecular interactions see table 4.

Table 4 The intermolecular interactions in 3ia (Å, °)

Interaction	D–H	H···A	D···A	D–H···A

C24–H241···O13^{i}	0.95	2.51	3.303 (3)	141
C18–H181···C25^{ii}	0.95	2.886	3.823 (3)	169

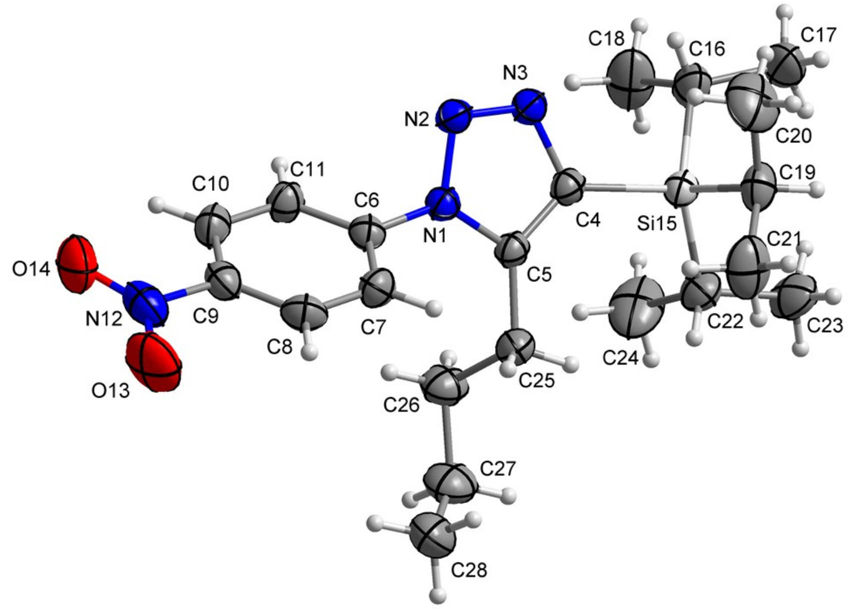
Symmetry codes: (*i*) -x+1, -y+1, -z (*ii*) -x+2, -y+1, -z+1



3aj

5-butyl-1-(4-nitrophenyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole (3aj). The reaction 1-azido-4-nitrobenzene **1a** (0.5 mmol, 0.082 g) and hex-1-yn-1-yltriisopropylsilane **2j** (0.5 mmol, 0.119 g) according to the general procedure during 7 hours afforded 5-butyl-1-(4-nitrophenyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **3aj** 0.138 g (yield 69 %) as a light yellow solid, m.p. = 59–60 °C.^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.44 (d, *J* = 9.2 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 2.89-2.85 (m, 2H), 1.50-1.43 (m, 3H), 1.14-1.09 (m, 22H), 0.71-0.67 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 147.58, 144.68, 138.88, 126.36, 125.15, 23.14, 21.96, 18.62, 13.28, 11.12; HRMS (ESI-positive mode): calcd for $C_{21}H_{35}N_4O_2Si$ ([M]+H$^+$) 403.2529; Found: 403.2517.

The crystal suitable for X-Ray study was obtained by slow evaporation of hexane solution of **3aj.**



The structure **3aj** ($C_{21}H_{34}N_4O_2Si$) was measured using D8 VENTURE with multilayer monochromator and a Cu-Kα Incoatec microfocus sealed tube (λ = 1.54178 Å) radiation at 180 K and PHOTON CMOS detector. The structure was in orthorhombic system, *Pbca* space group with lattice parameters $a = 8.9462$ (5) Å, $b = 11.9145$ (6) Å, $c = 43.549$ (2) Å, $Z = 8$, $V = 4641.8$ (4) Å^3, $D_c = 1.152$ g cm^{-3}, μ(Cu-Kα) = 1.07 mm^{-1}. The data reduction and absorption correction were done with Apex3 software[14]. The structure was solved by charge flipping methods[15] and refined by full matrix least squares on F squared value using Crystals software[16] to final values $R = 0.058$ an $R_w = 0.116$ using 4237 independent reflections ($\Theta_{max} = 68.3$ °), 253 parameters and 0 restrains. The MCE software[17] was used for visualization of electron density maps. According to common practice the hydrogen atoms attached to carbon atoms were place geometrically with $U_{iso}(H)$ in range 1.2-1.5 U_{eq} of parent atom (C). The structure was deposited into Cambridge Structural Database under number CCDC 1513615.

The asymmetric unit is formed by one independent molecule of **3aj**. The C–H···O and C–H···N interactions are the driving force of layer formation in the structure, the layers stack in direction of c axis and are held together by London forces. For further information on intermolecular interactions see table 5.

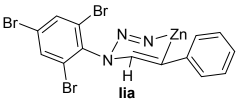
Table 5 The intermolecular interactions in 3ia (Å, °)

Interaction	D–H	H···A	D···A	D–H···A
C7–H71···N2^{i}	0.95	2.68	3.462 (3)	140
C7–H71···N3^{i}	0.95	2.57	3.470 (4)	158
C10–H101···O13^{ii}	0.95	2.49	3.278 (4)	141
C28–H282···O14^{iii}	0.95	2.60	3.499 (4)	159

Symmetry codes: (*i*) -x+1/2, y-1/2, z (*ii*) -x+1, y+1/2, -z+3/2 (*iii*) x-1/2, y, -z+3/2

Isolation and characterization of Zn-containing six-membered metallacycle (Iia).

The mixture of 2-azido-1,3,5-tribromobenzene **1i** (0.5 mmol, 0.177 g) and phenylacetylene **2a** (2 mmol, 0.204 g, 220 µl) in water (10 ml) was vigorously stirred during 2-3 minutes. After the $Zn(OAc)_2$ (2 mmol, 0.438 g) were added to reaction mixture. The reaction mixture was stirred until full conversion of 2-azido-1,3,5-tribromobenzene **1i** (TLC, hexane:EtOAc = 7:3). After, the reaction mixture was extracted with CH_2Cl_2 (3×20 mL), washed by water, brine and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo to give the crude mixture of **3ia** and **Iia** which was purified by column chromatography (silica gel, eluent hexane:EtOAc = 9:1): 0.114 g of **3ia** (yield 50 %) and 0.134 g of **Iia** (yield 48 %) as a white solid; m.p. = 128–130 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00 (s, 1H), 8.31 (s, 2H), 7.94 (d, *J* = 7.2 Hz, 2H), 7.52-7.48 (m, 2H), 7.41-7.37 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.25, 135.50, 130.33, 129.57, 128.90, 125.87, 125.76, 123.94, 123.82. HRMS (ESI-positive mode): calcd for $C_{16}H_{11}{}^{79}Br_3N_4Zn$ (M+MeCN) 562.7702, Found 562.7745; calcd for $C_{16}H_{11}{}^{81}Br_3N_4Zn$ ([M]+MeCN) 564.7665, Found 564.7729. $C_{16}H_{11}{}^{79}Br_3N_4Zn$ ([M]+MeCN).



Iia

The decomposition of intermediate Iia in acetone solution.

The solution of intermediate **Iia** (0.25 mmol, 0.134 g) in acetone was refluxed during 12 h until full conversion of intermediate **Iia**. After that, the cloudy solution was filtered through the silica pad and solvent was removed in vacuo to give the 0.115 g (100% yield) of **3ia** as a white solid; m.p. = 140–142 °C.

Fig. S1– GC-MS analysis Zn-containing six-membered metallacycle **Iia**

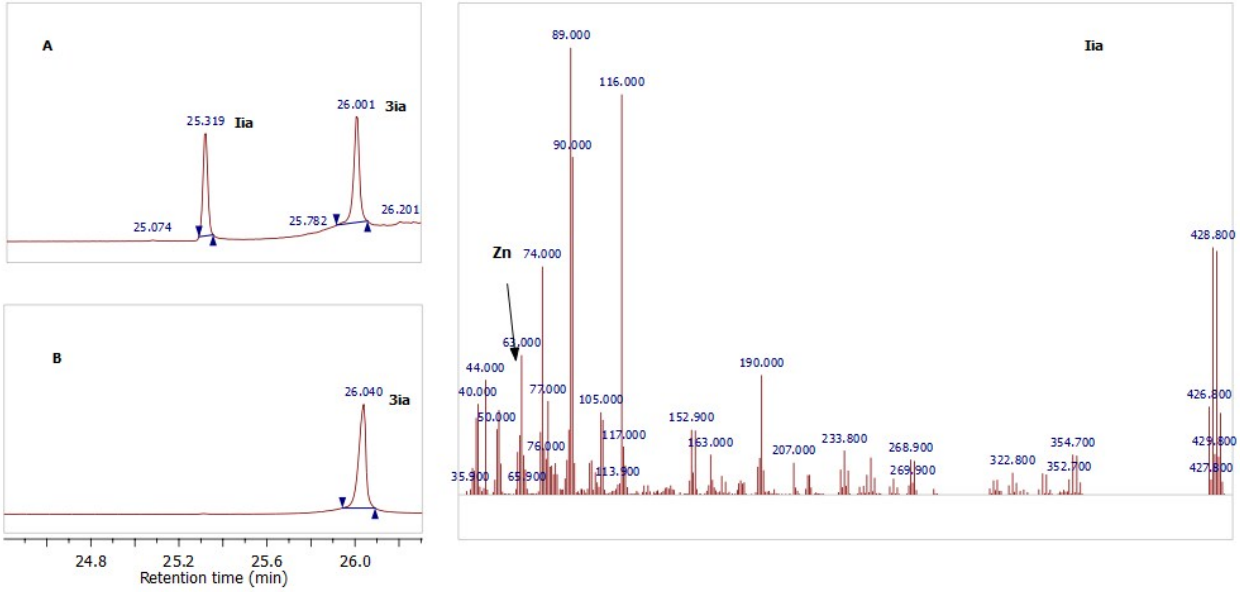


Fig. S2. The high resolution mass-spectrum of intermediate **Iia**.

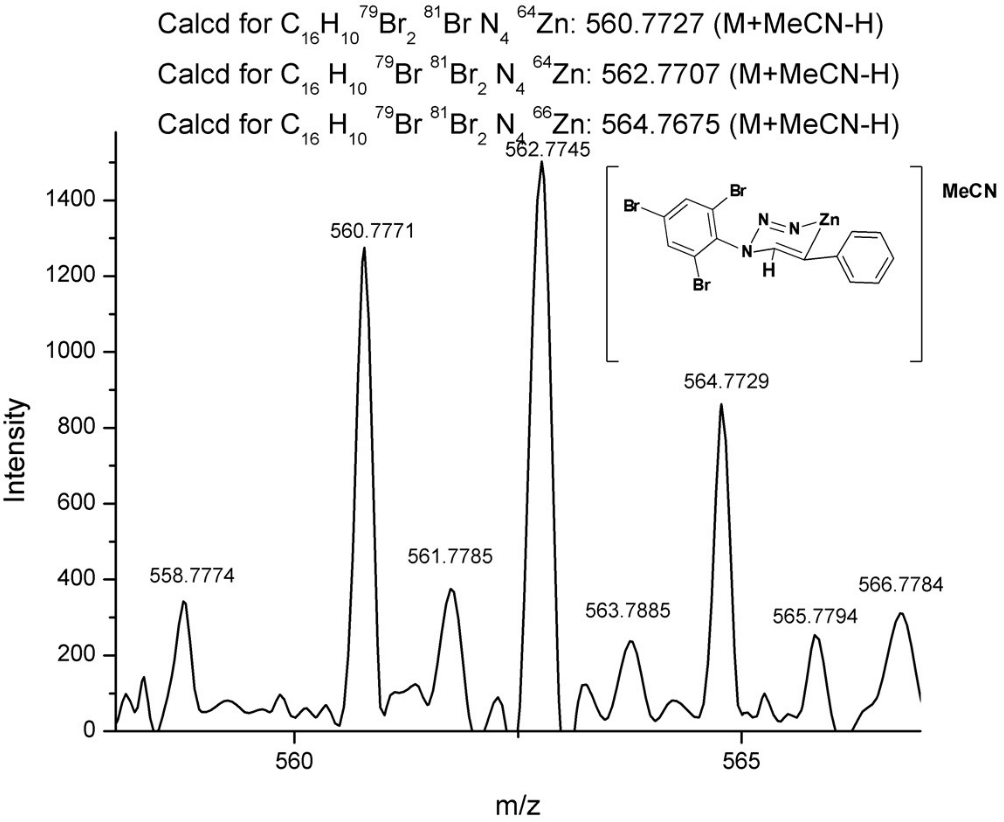


Fig. S3 – ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of Zn-containing six-membered metallacycle **Iia.**

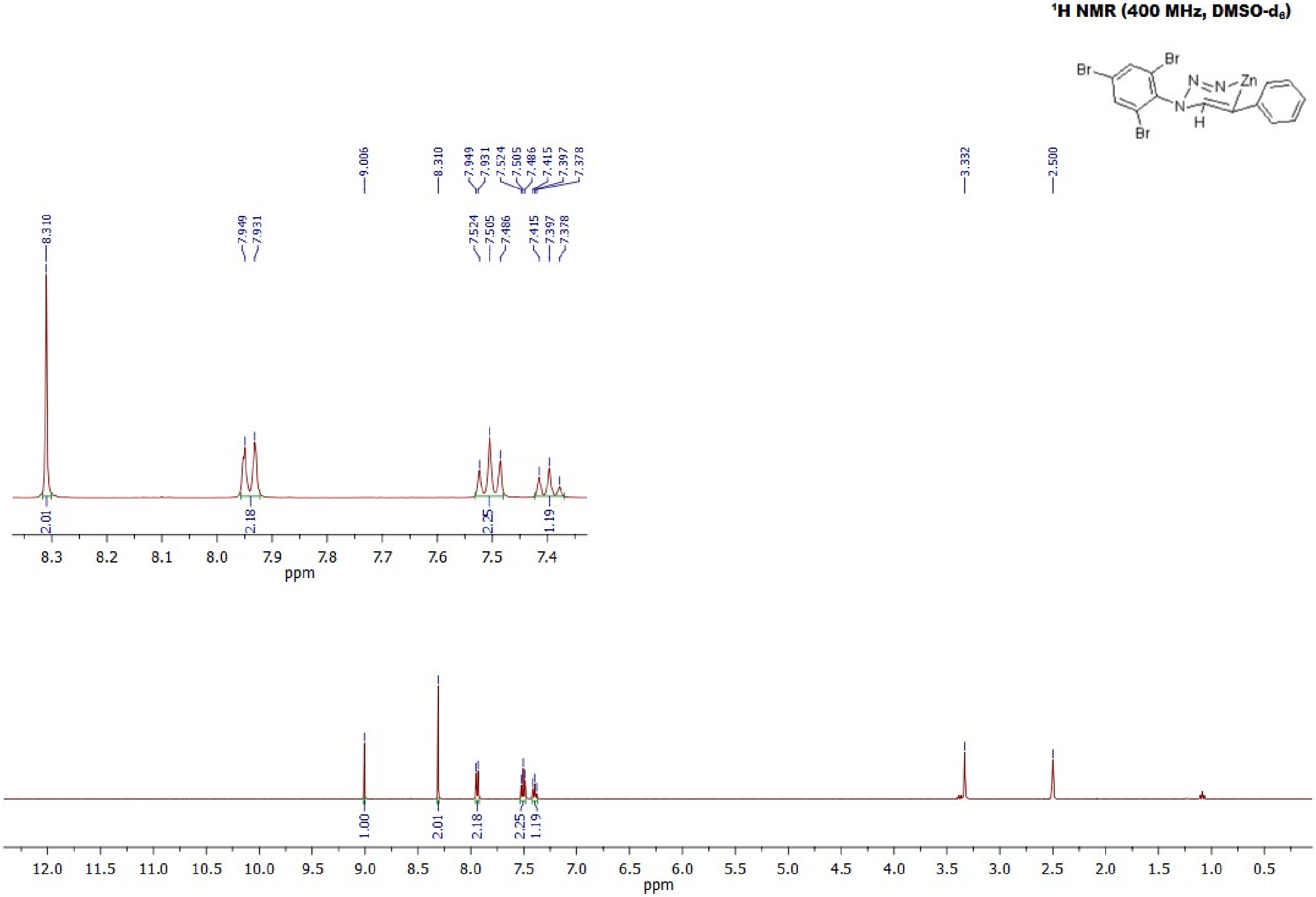


Fig. S4 – ^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of Zn-containing six-membered metallacycle **Iia.**

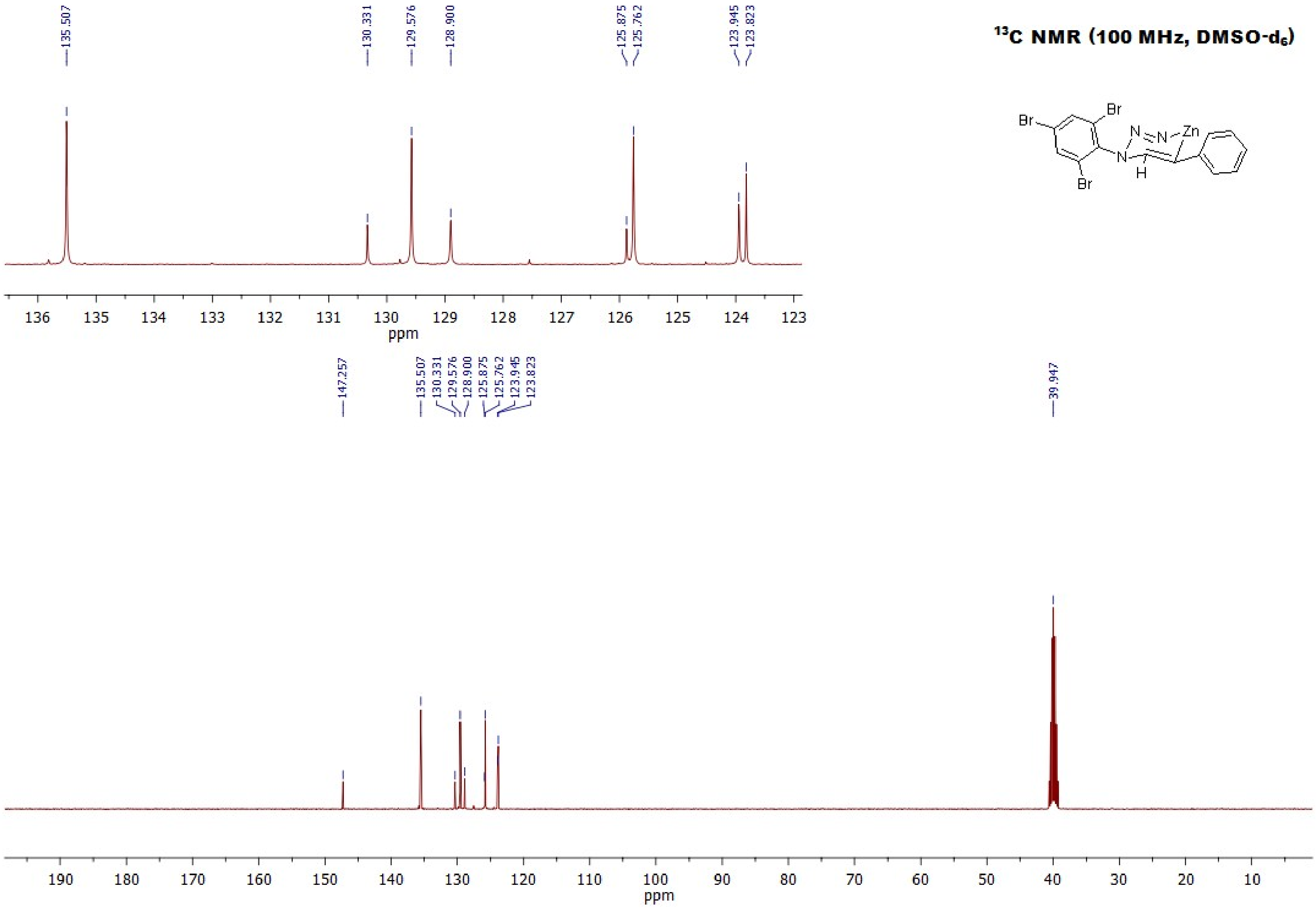


Fig. S5 – HMBC NMR (400 MHz, DMSO-d_6) spectrum of Zn-containing six-membered metallacycle **Iia.**

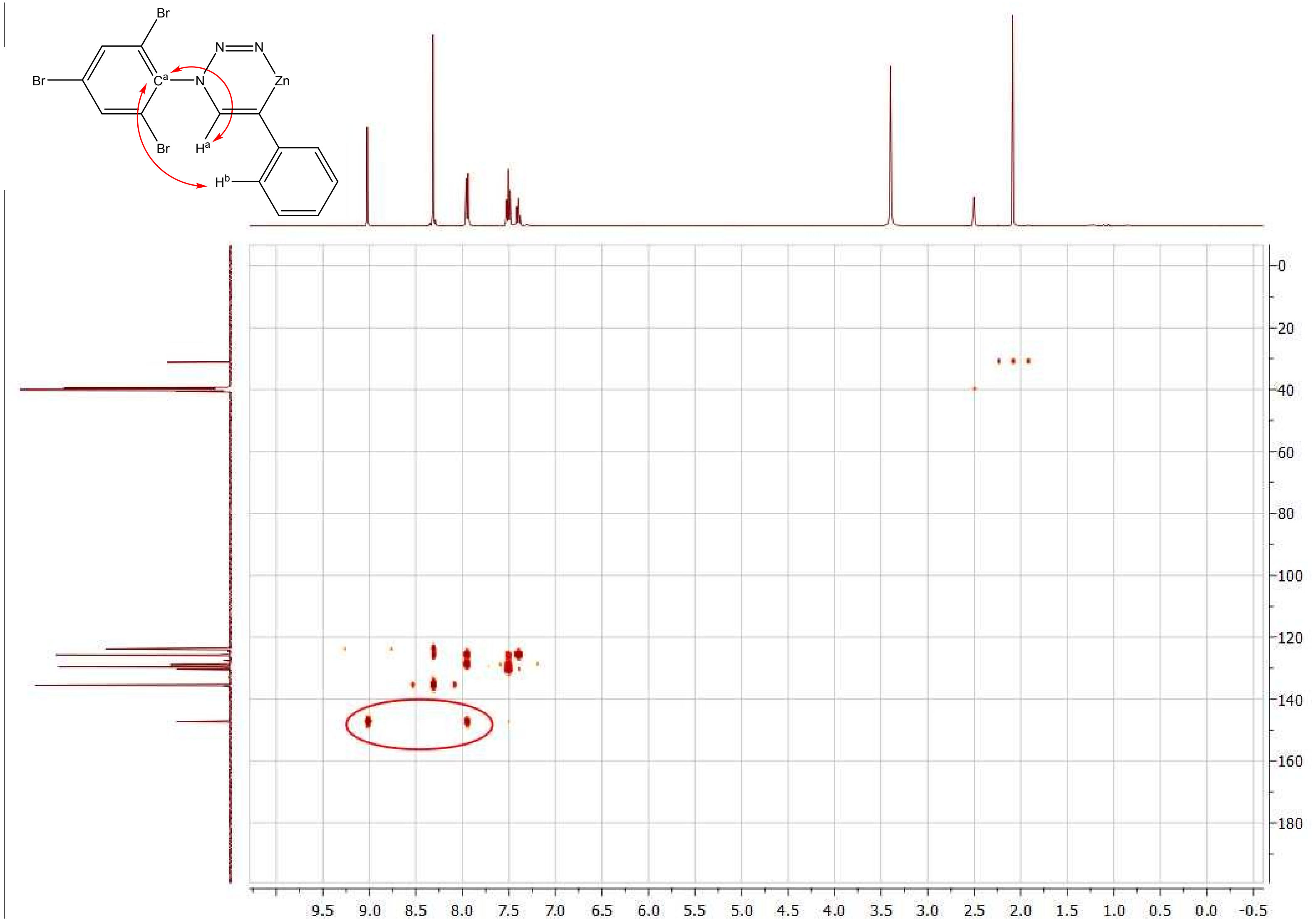


Fig. S6. The comparison of 1H NMR spectra intermediate **Iia**, 1,2,3-triazole **3ia** and mixture azide **1i** with alkyne **2a**

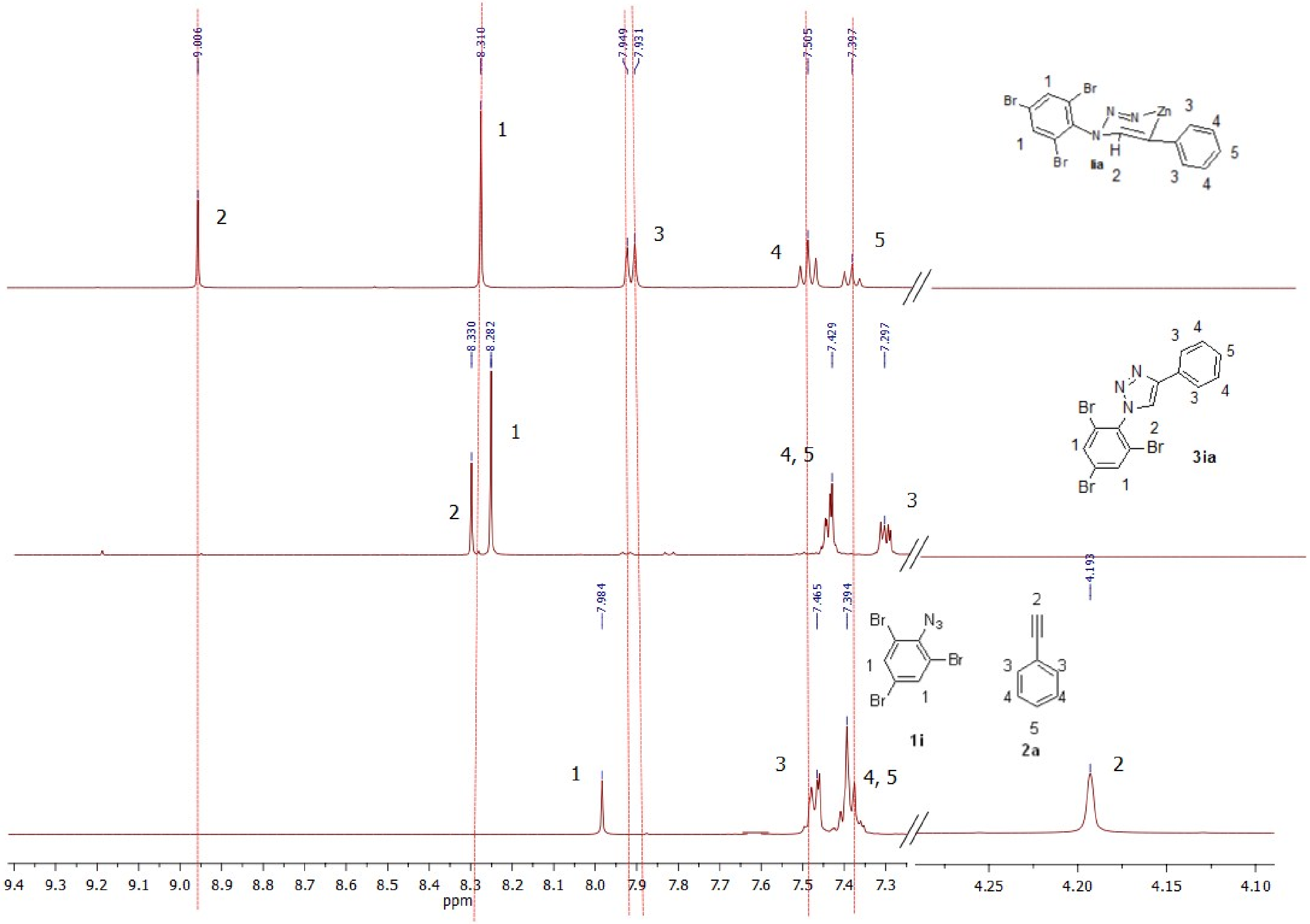
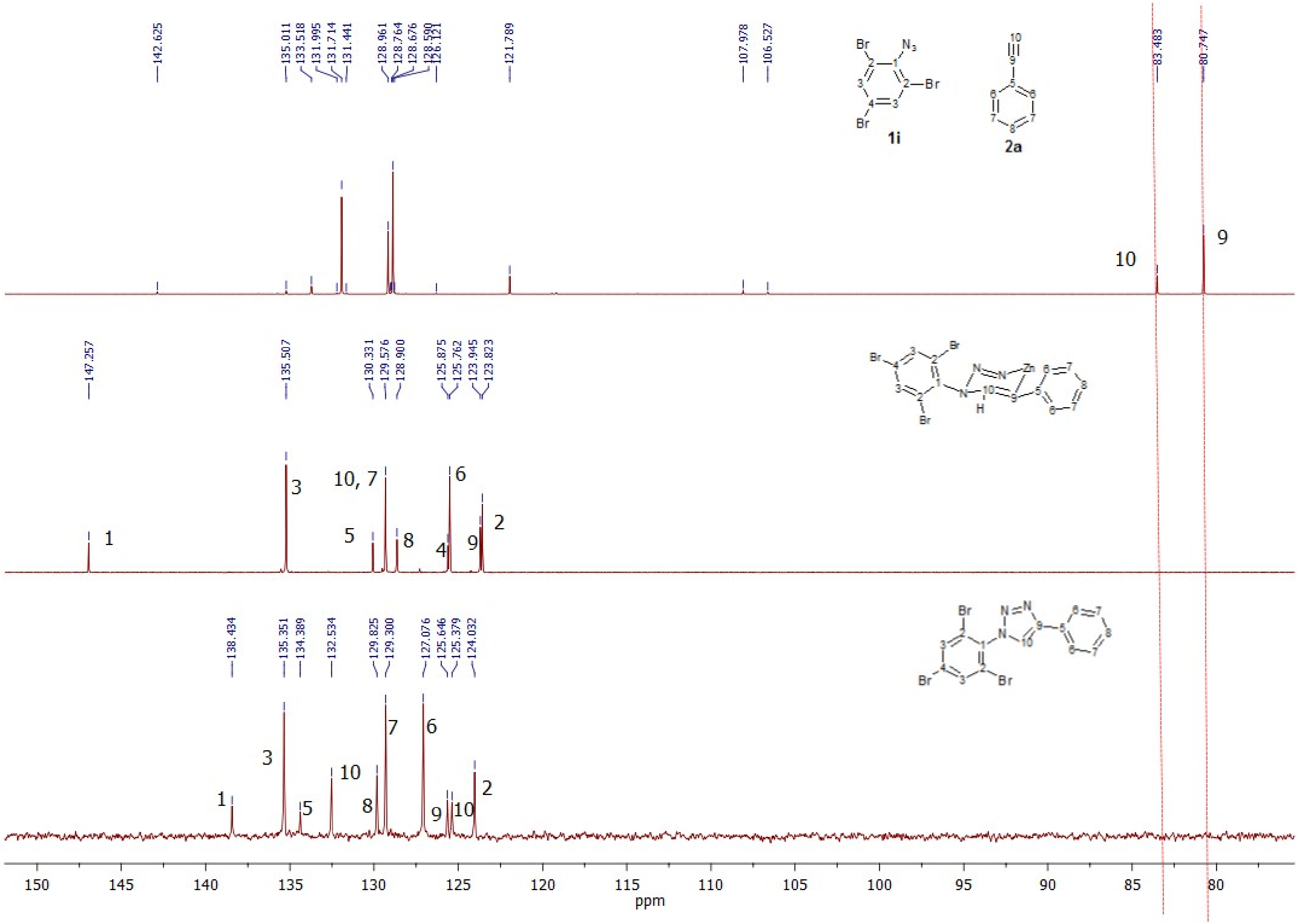
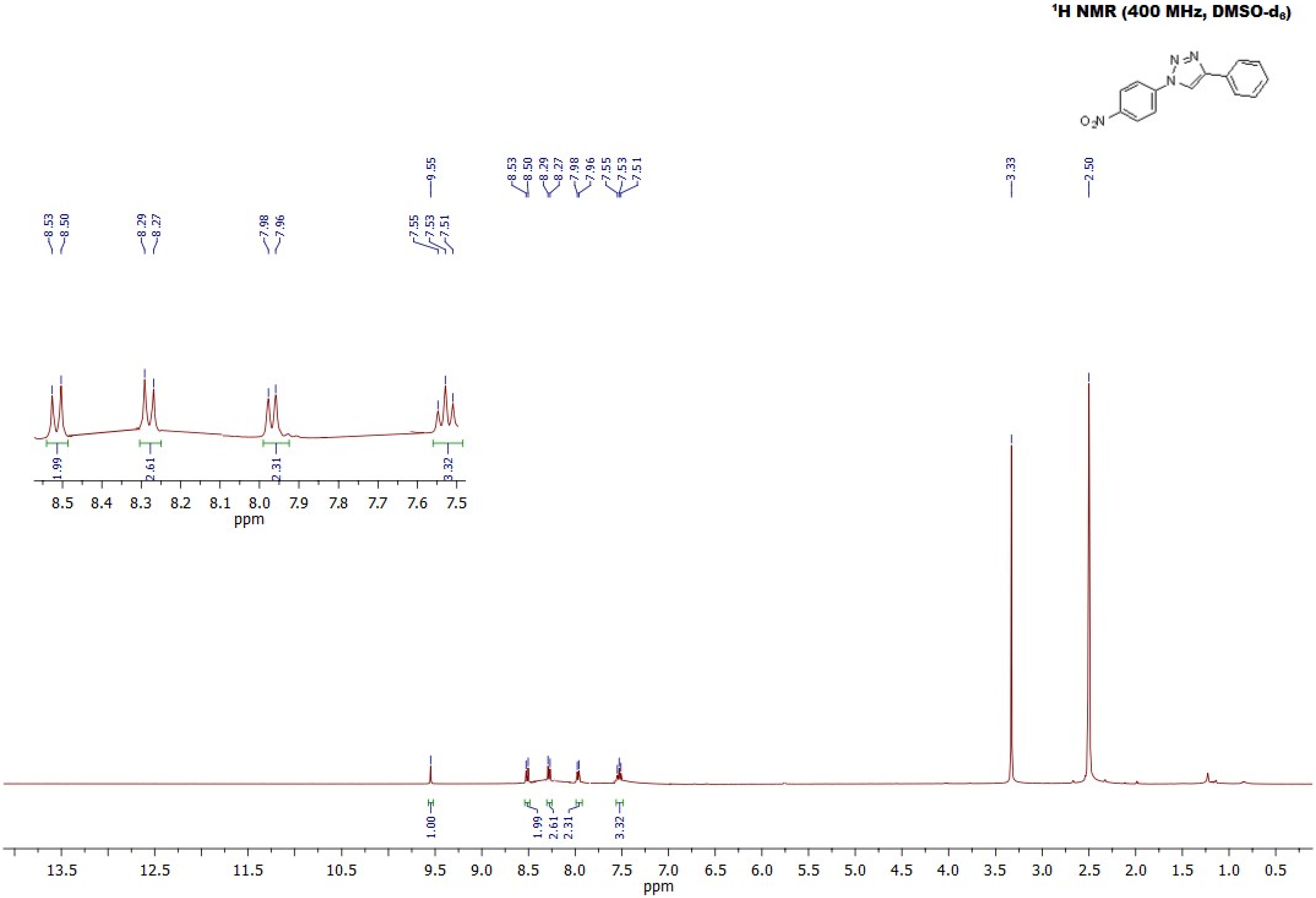


Fig. S7 – The comparison of^{13}C NMR spectraZn-containing six-membered metallacycle **Iia,** 1,2,3-triazole **3ia** and mixture azide **1i** with alkyne **2a**

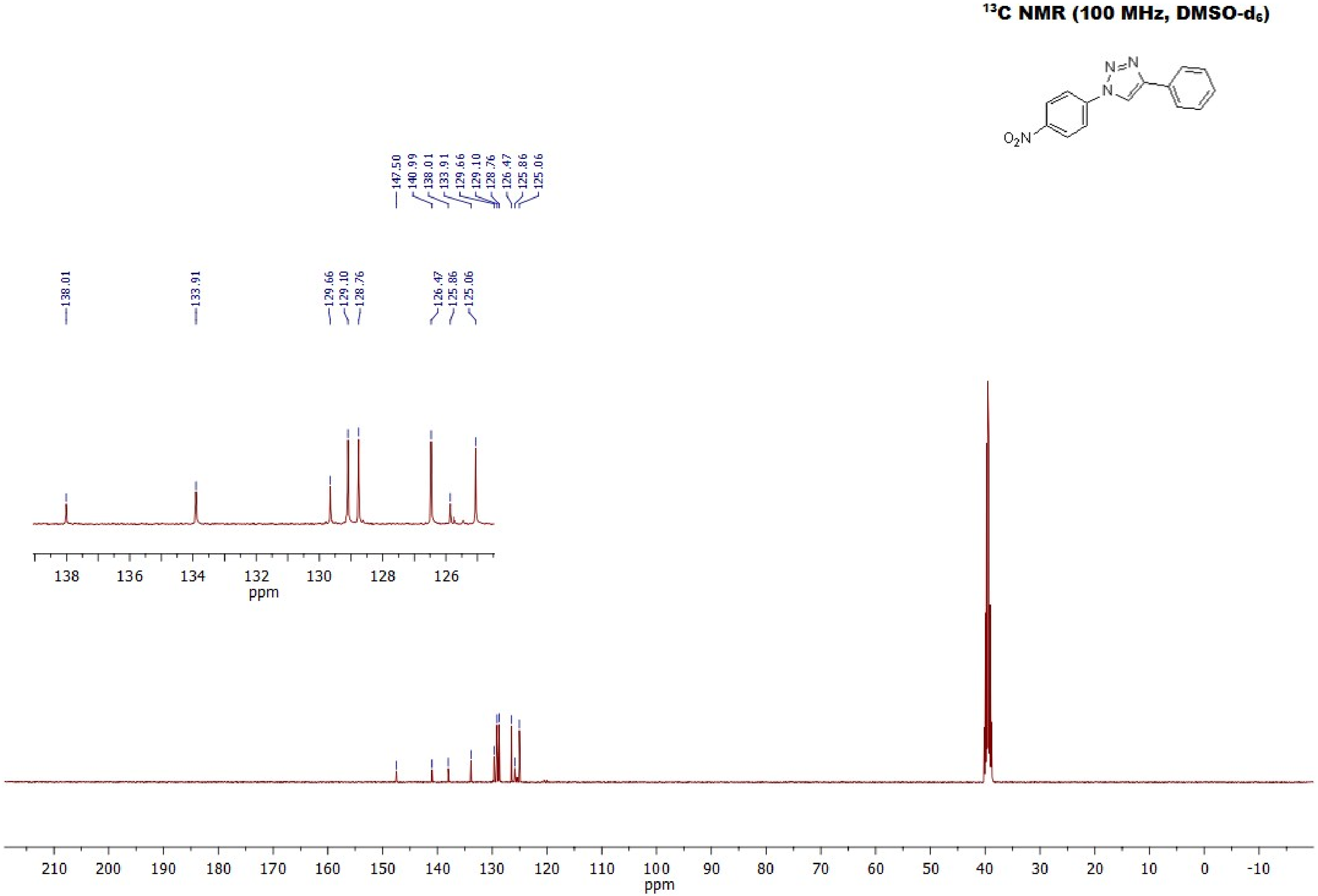


Spectra ^{1}H, ^{13}C NMR of products

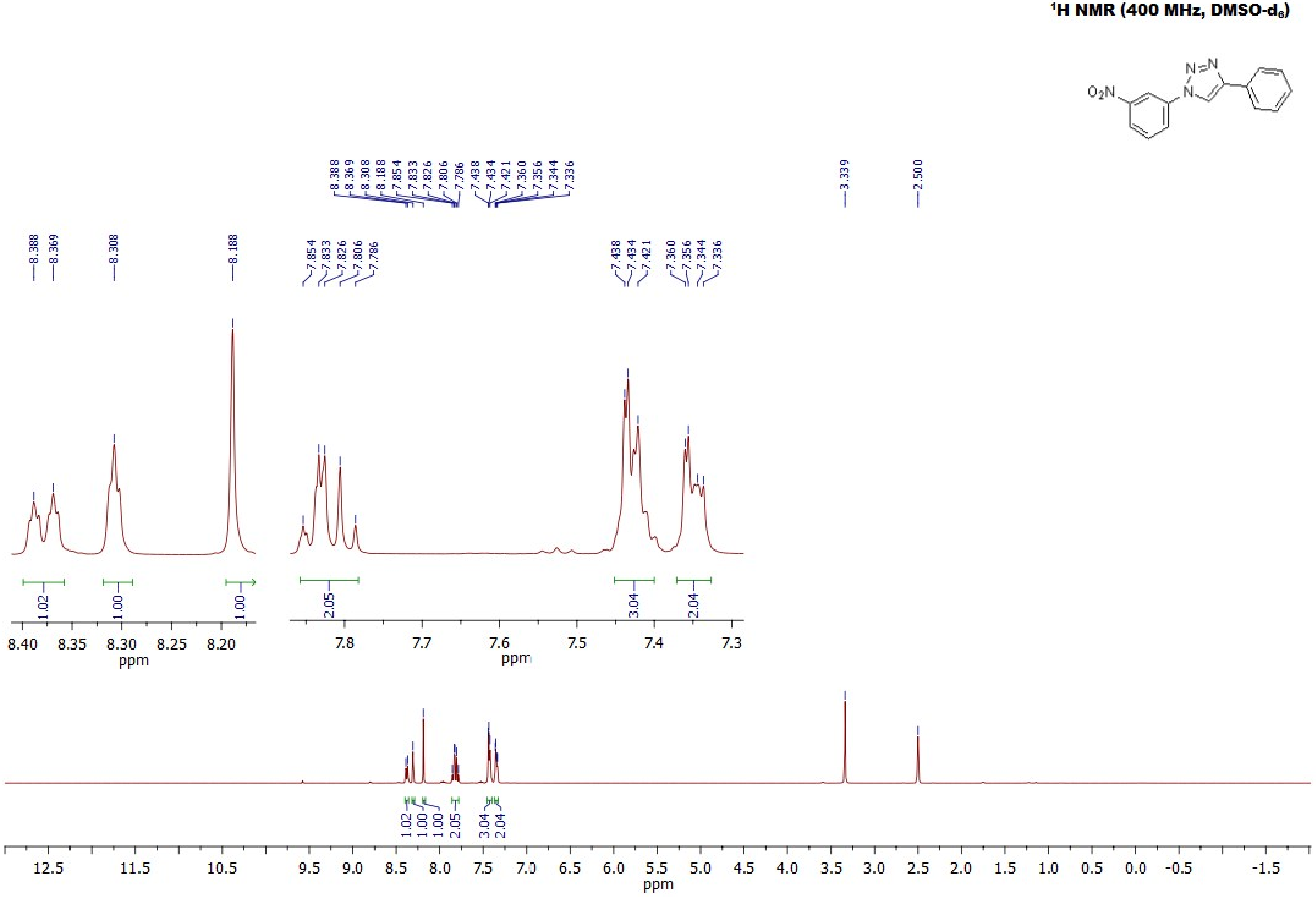
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-(4-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **(3aa).**



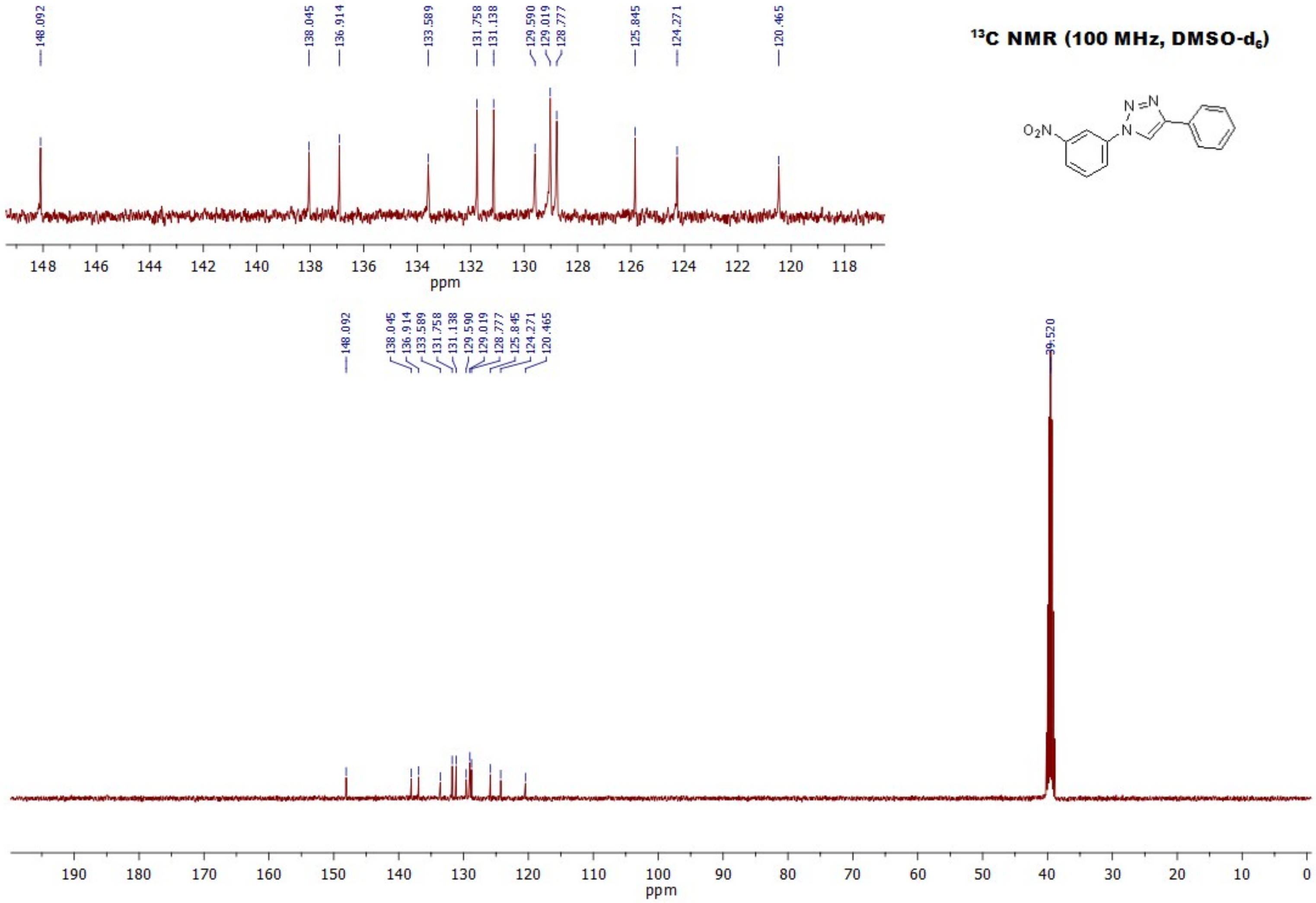
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-(4-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **(3aa)**



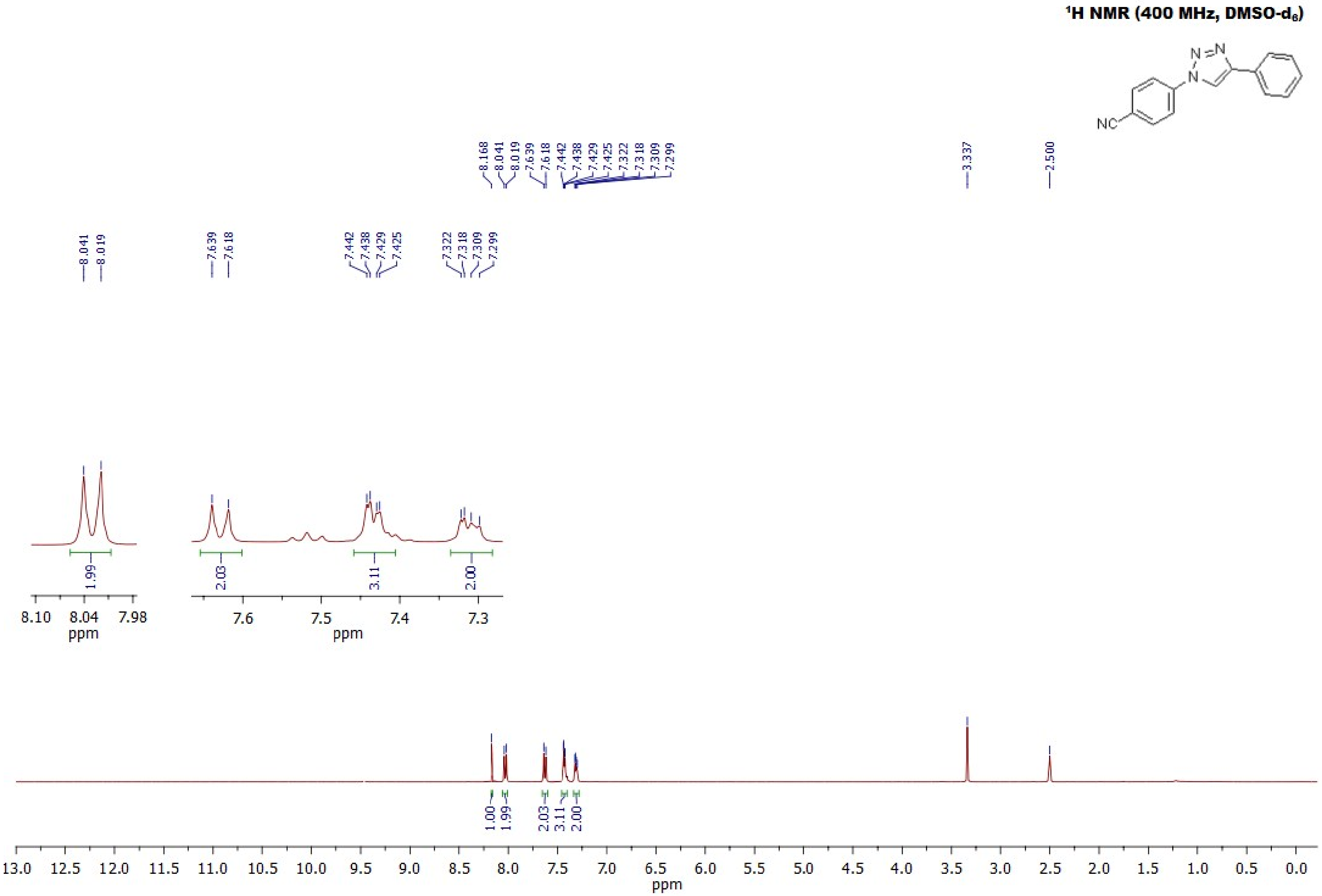
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1-(3-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **(3ba).**



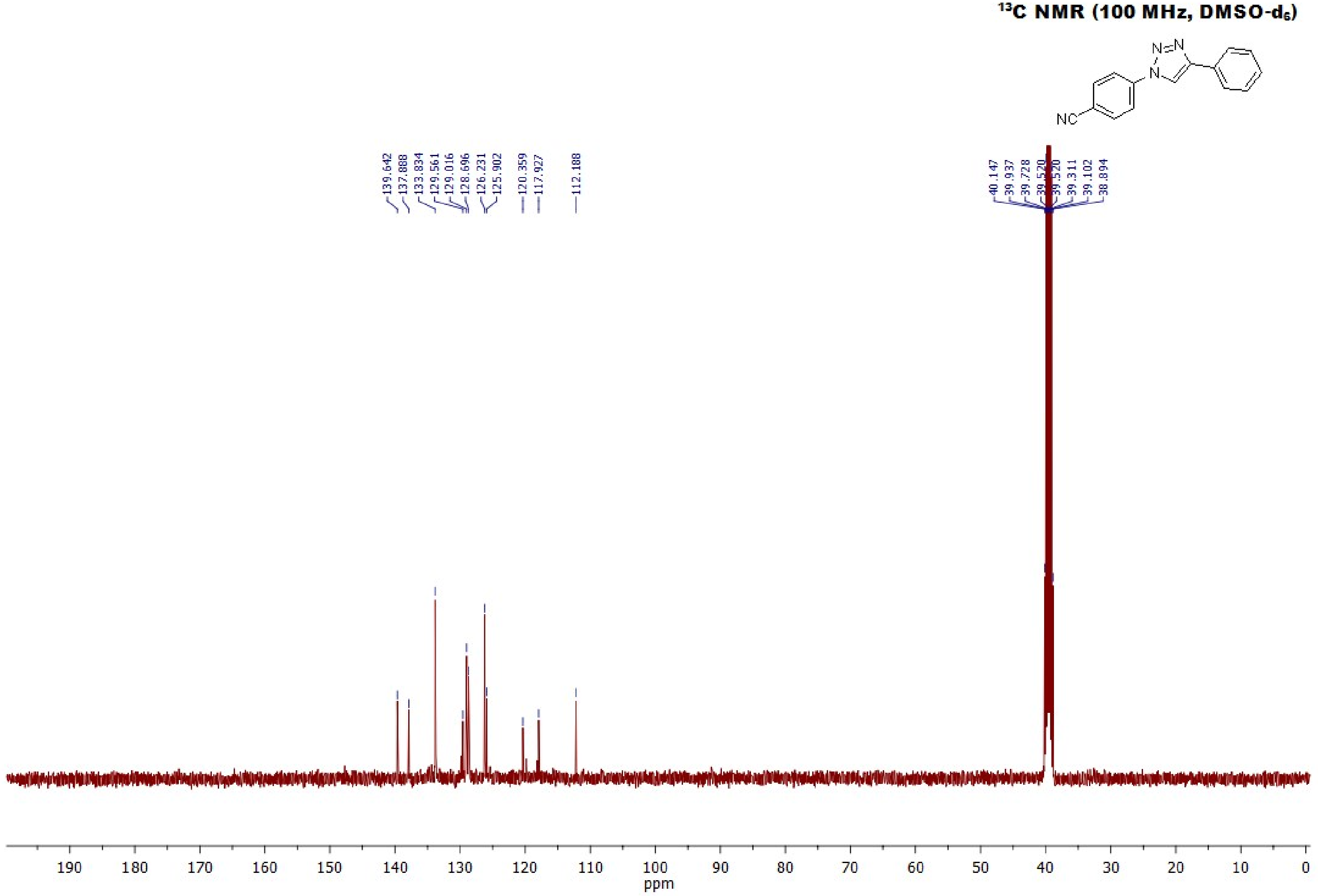
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-(3-nitrophenyl)-4-phenyl-*1H*-1,2,3-triazole **(3ba).**



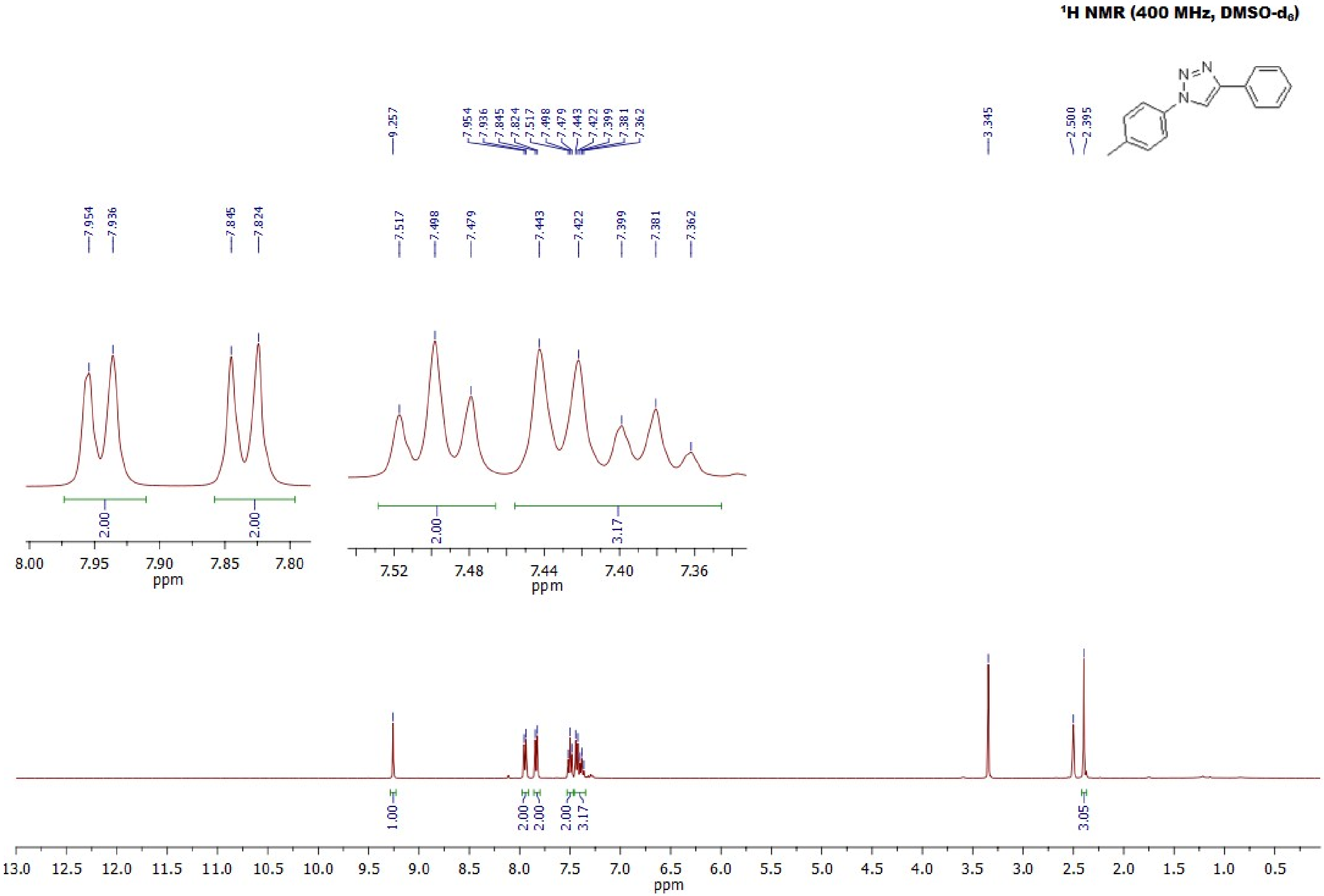
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 4-(4-phenyl-*1H*-1,2,3-triazol-1-yl)benzonitrile **(3ca).**



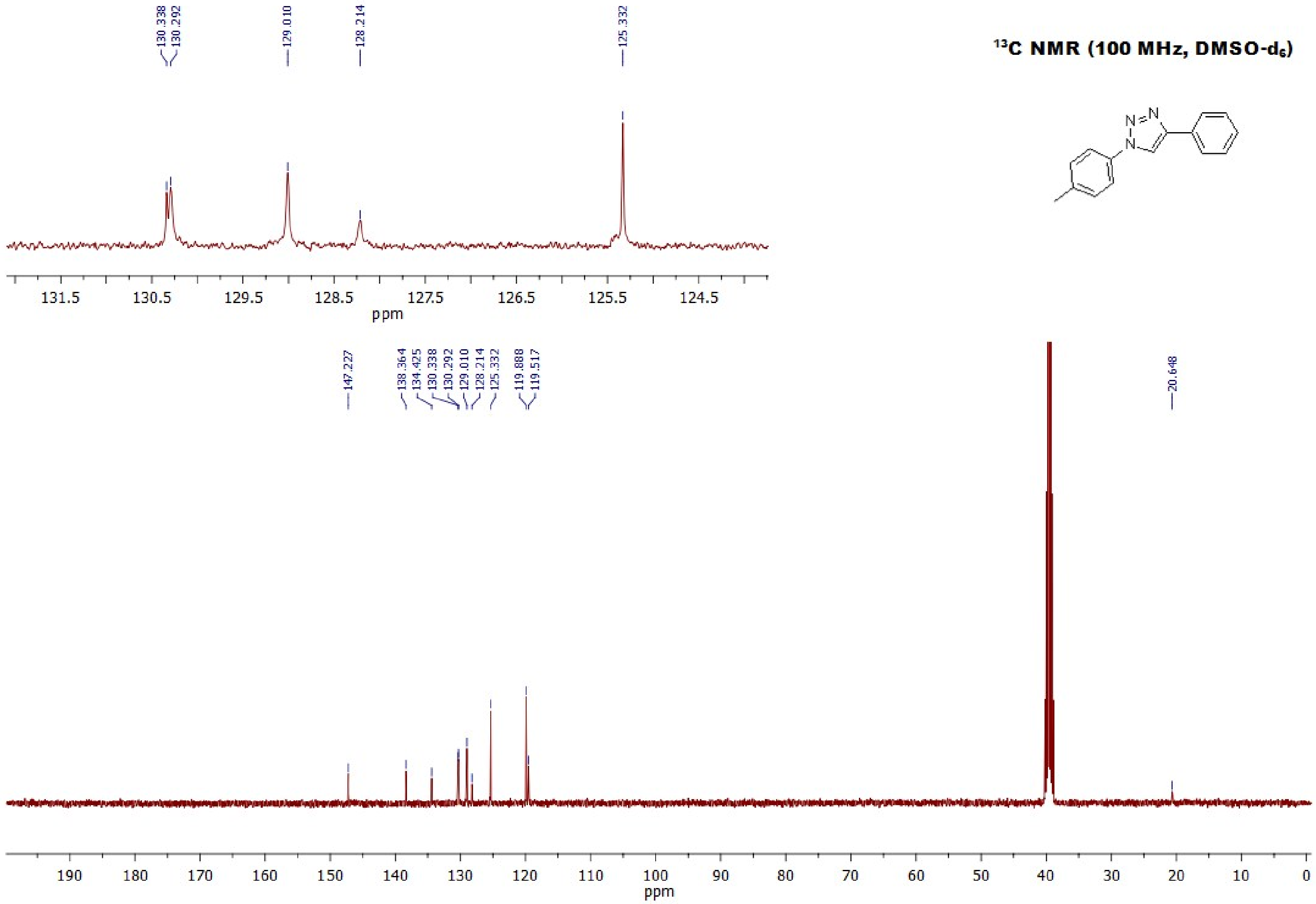
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 4-(4-phenyl-*1H*-1,2,3-triazol-1-yl)benzonitrile **(3ca).**



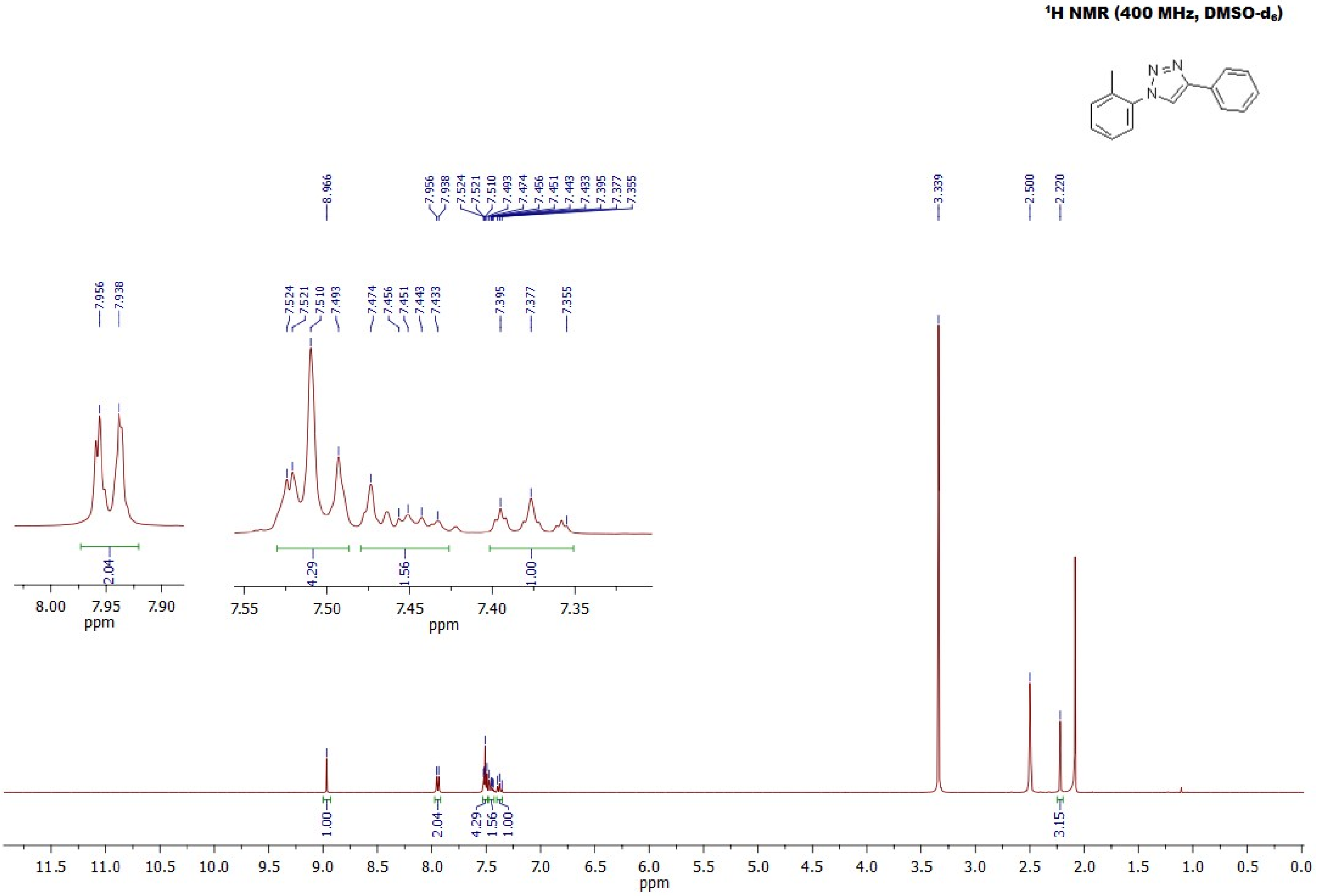
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of (4-phenyl-1-(p-tolyl)-*1H*-1,2,3-triazole) **(3da).**



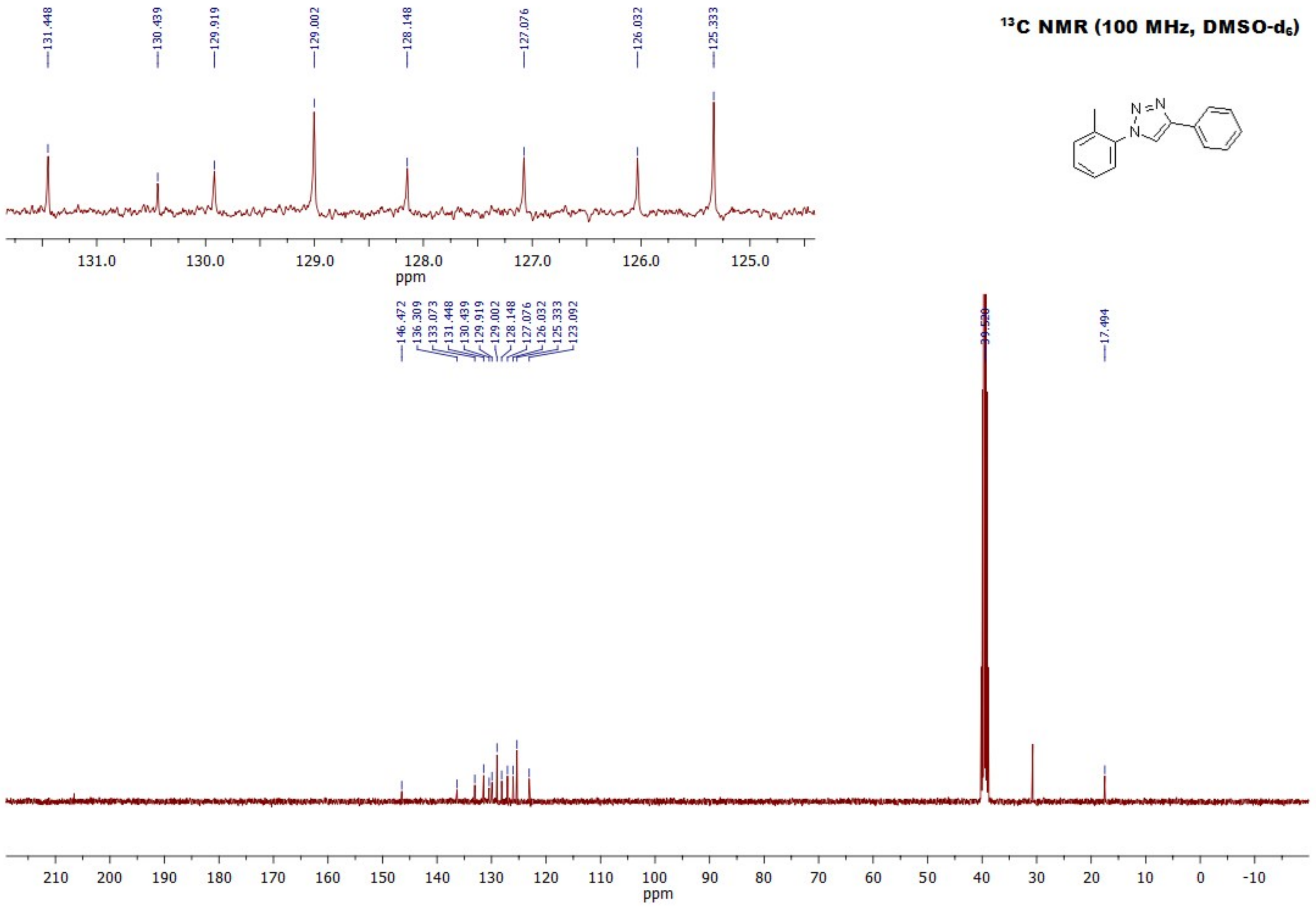
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of (4-phenyl-1-(p-tolyl)-*1H*-1,2,3-triazole) **(3da).**



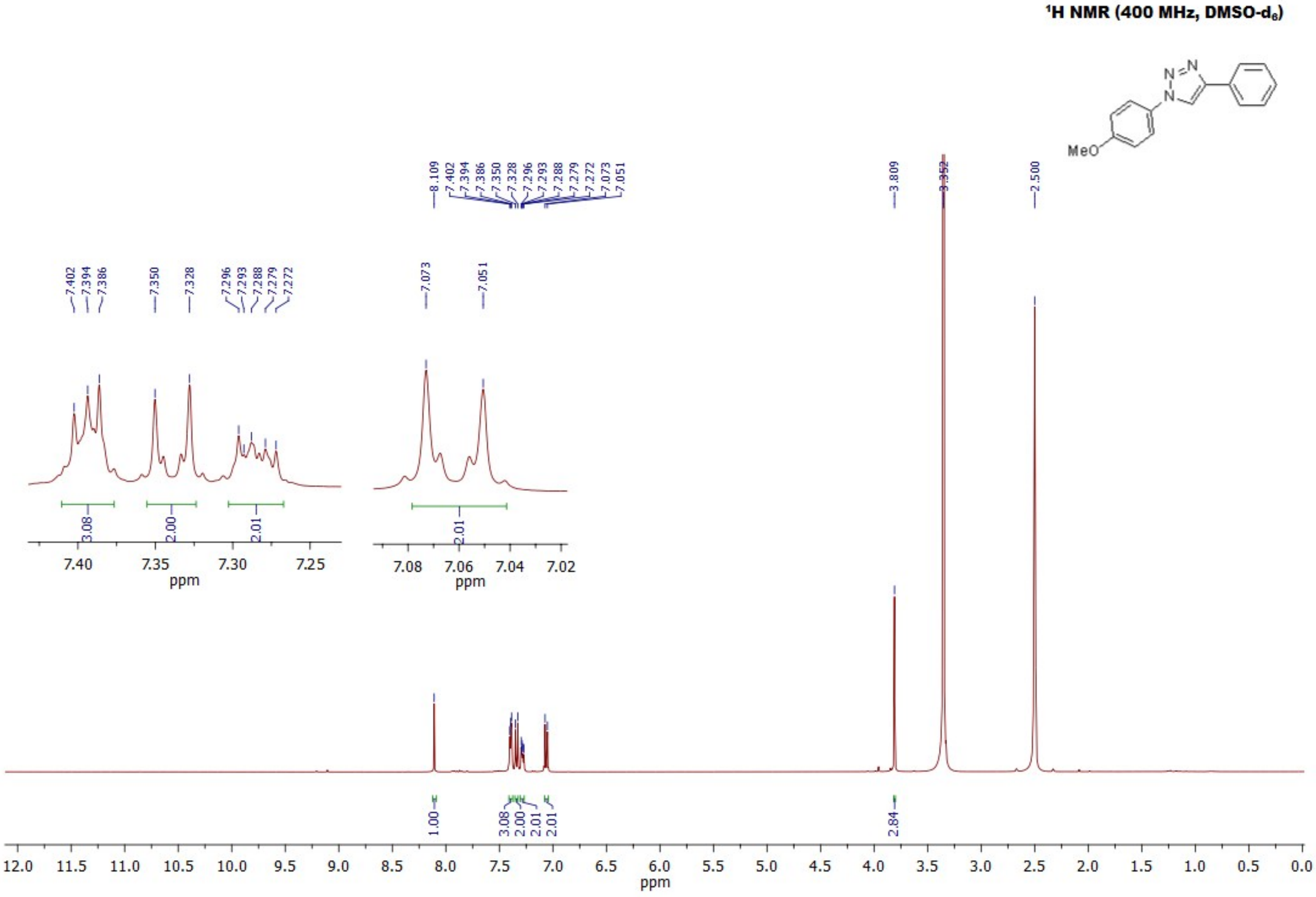
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 4-phenyl-1-(o-tolyl)-*1H*-1,2,3-triazole **(3ea).**



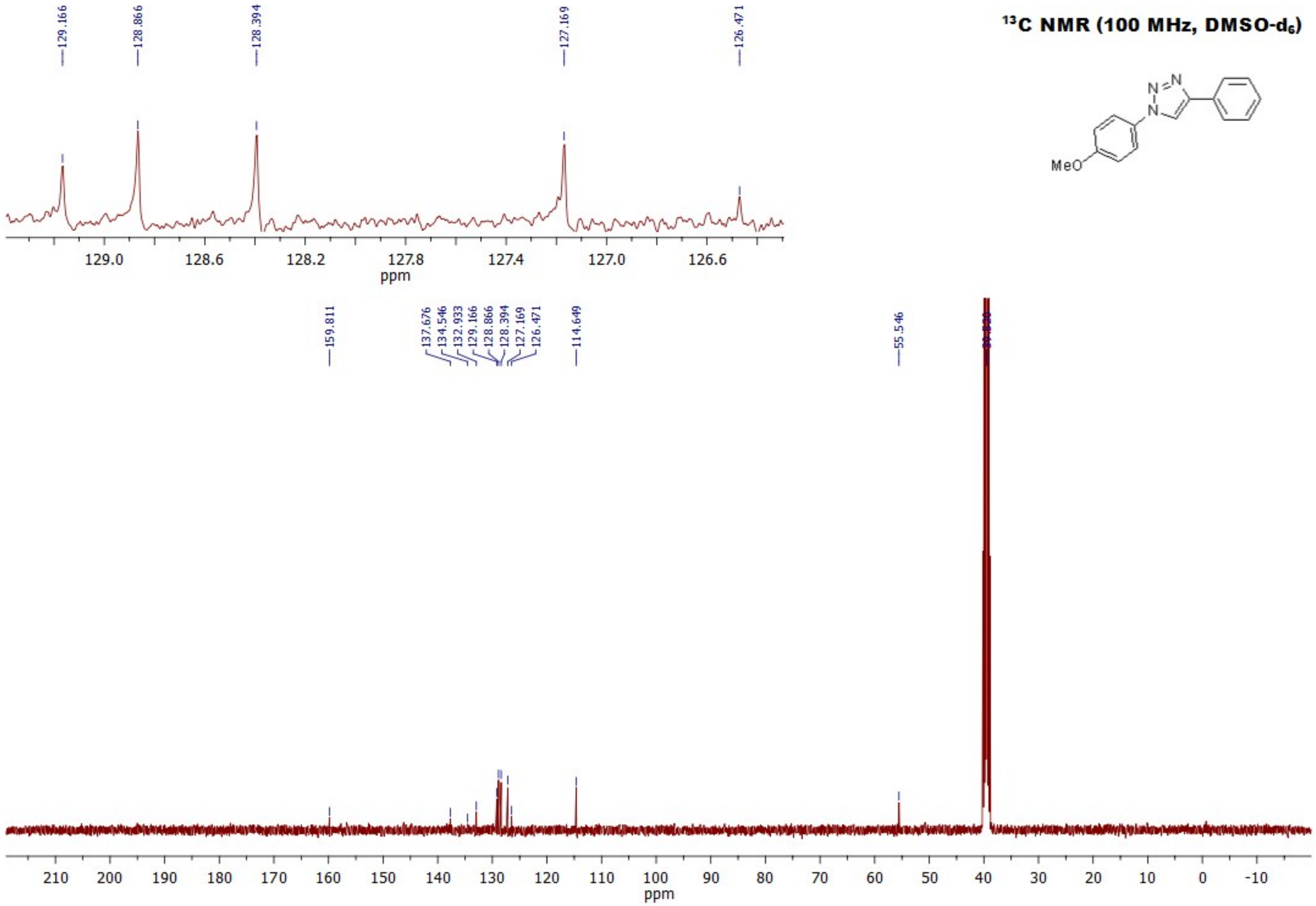
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 4-phenyl-1-(o-tolyl)-*1H*-1,2,3-triazole **(3ea).**



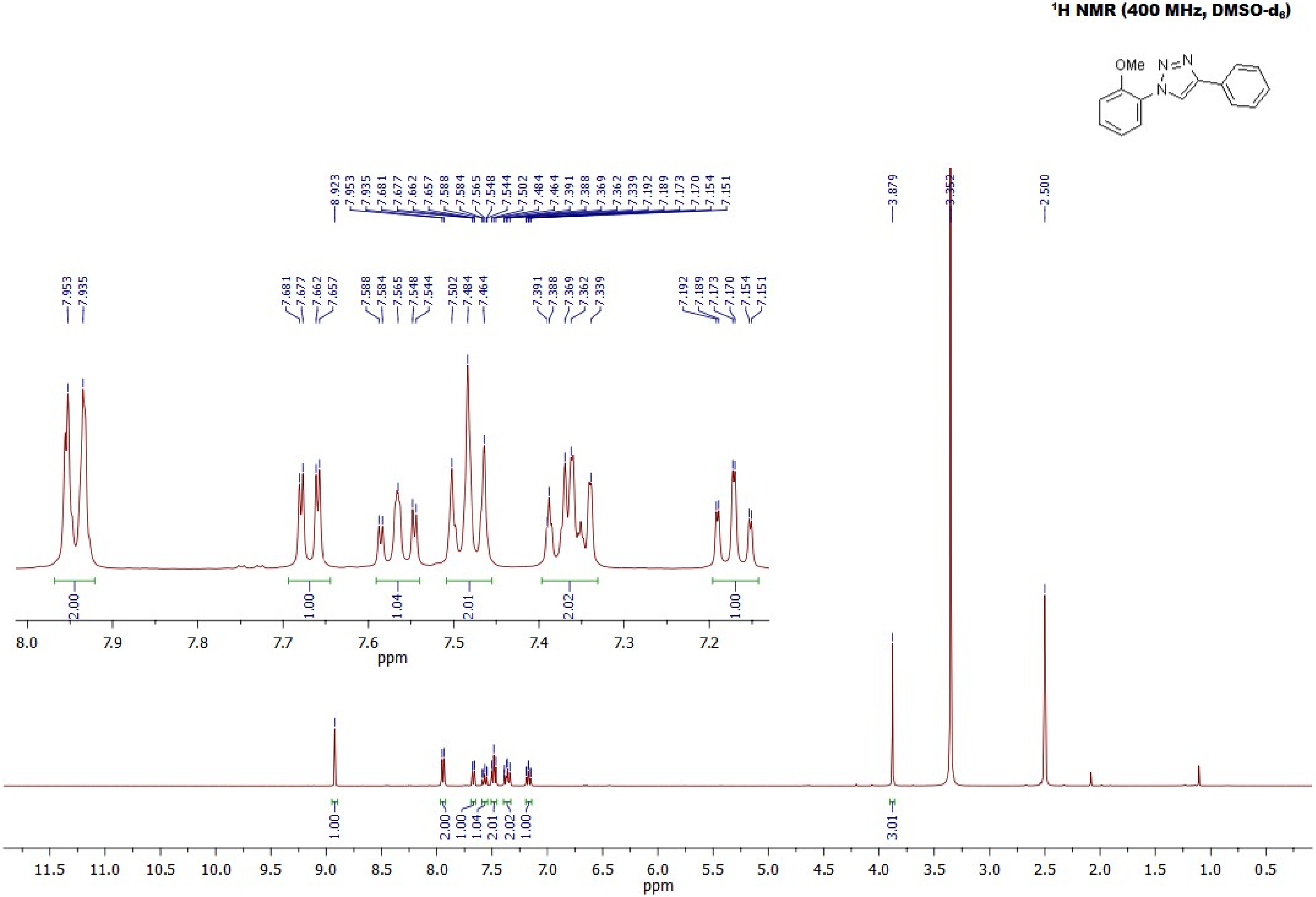
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1-(4-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole **(3fa).**



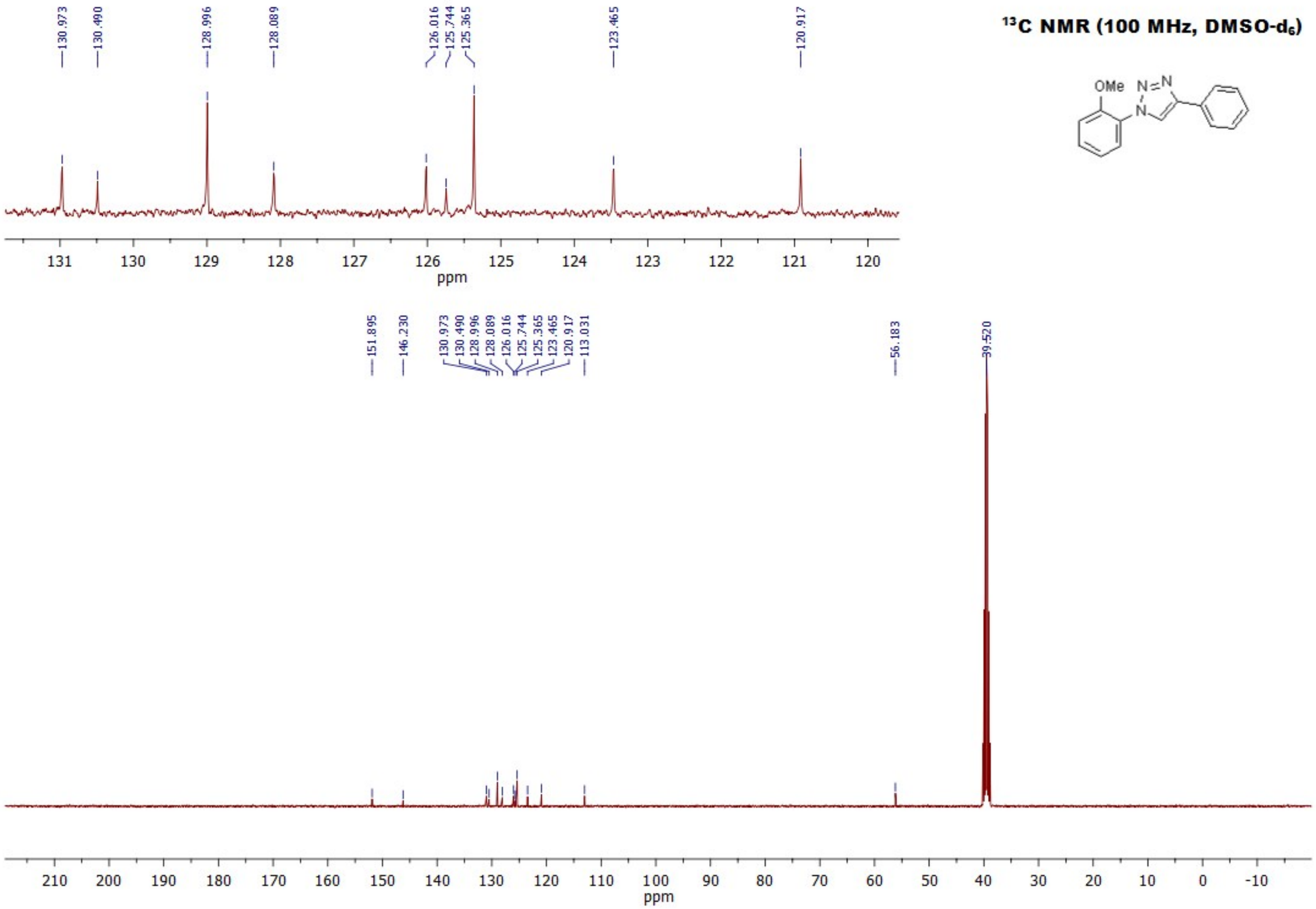
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-(4-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole **(3fa).**



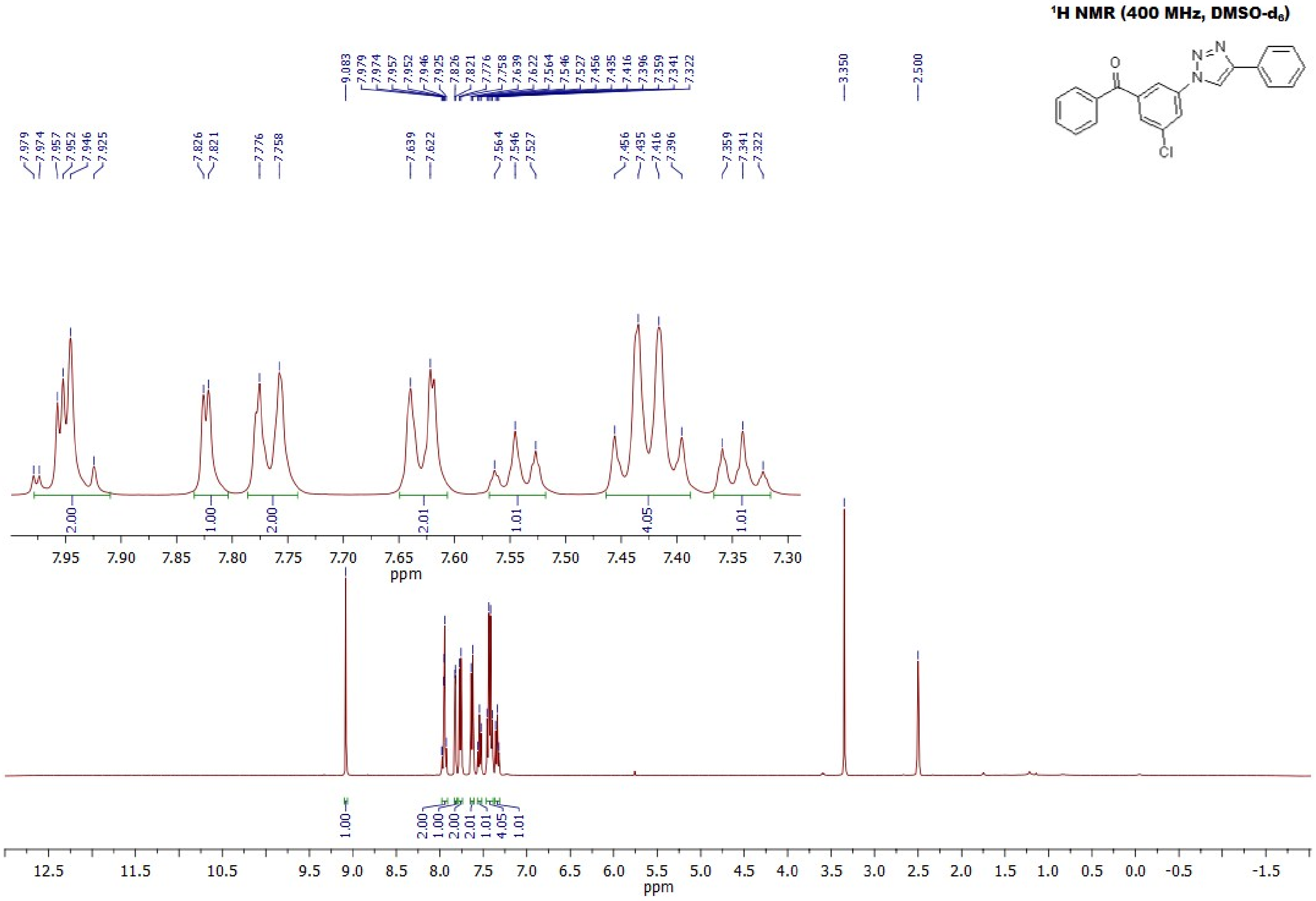
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1-(2-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole **(3ga).**



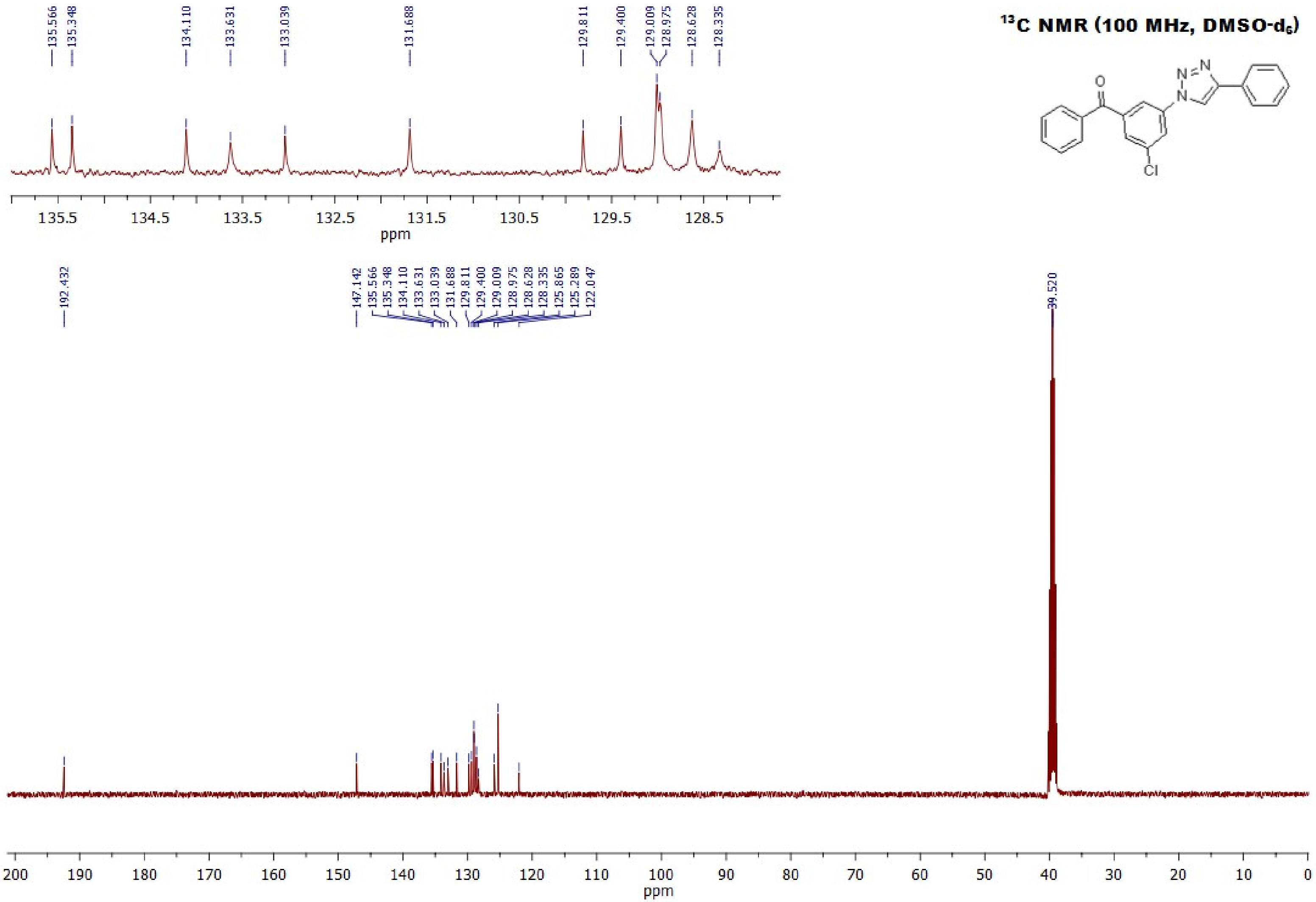
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-(2-methoxyphenyl)-4-phenyl-*1H*-1,2,3-triazole **(3ga).**



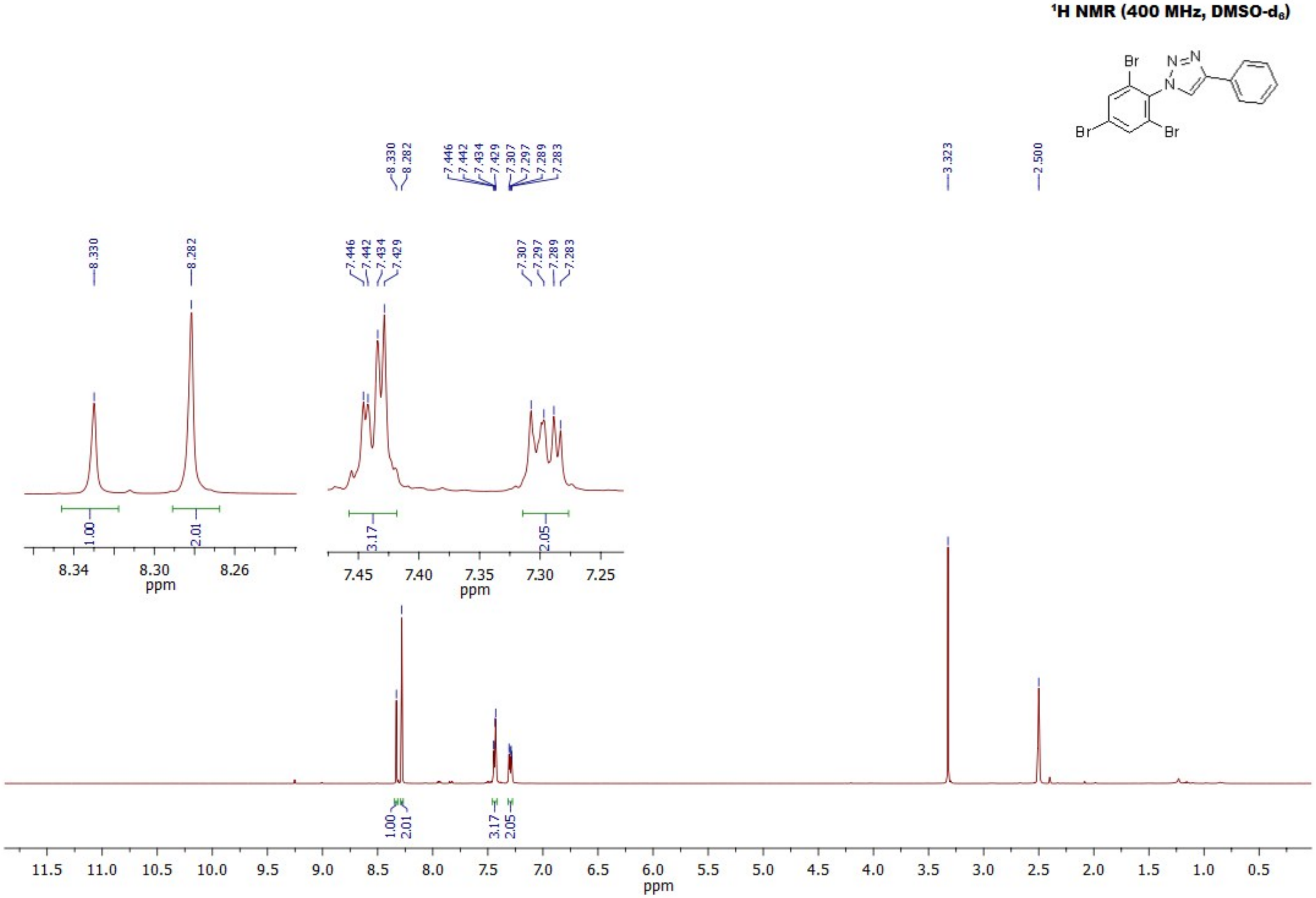
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of (3-chloro-5-(4-phenyl-*1H*-1,2,3-triazol-1-yl)phenyl)(phenyl)methanone **(3ha).**



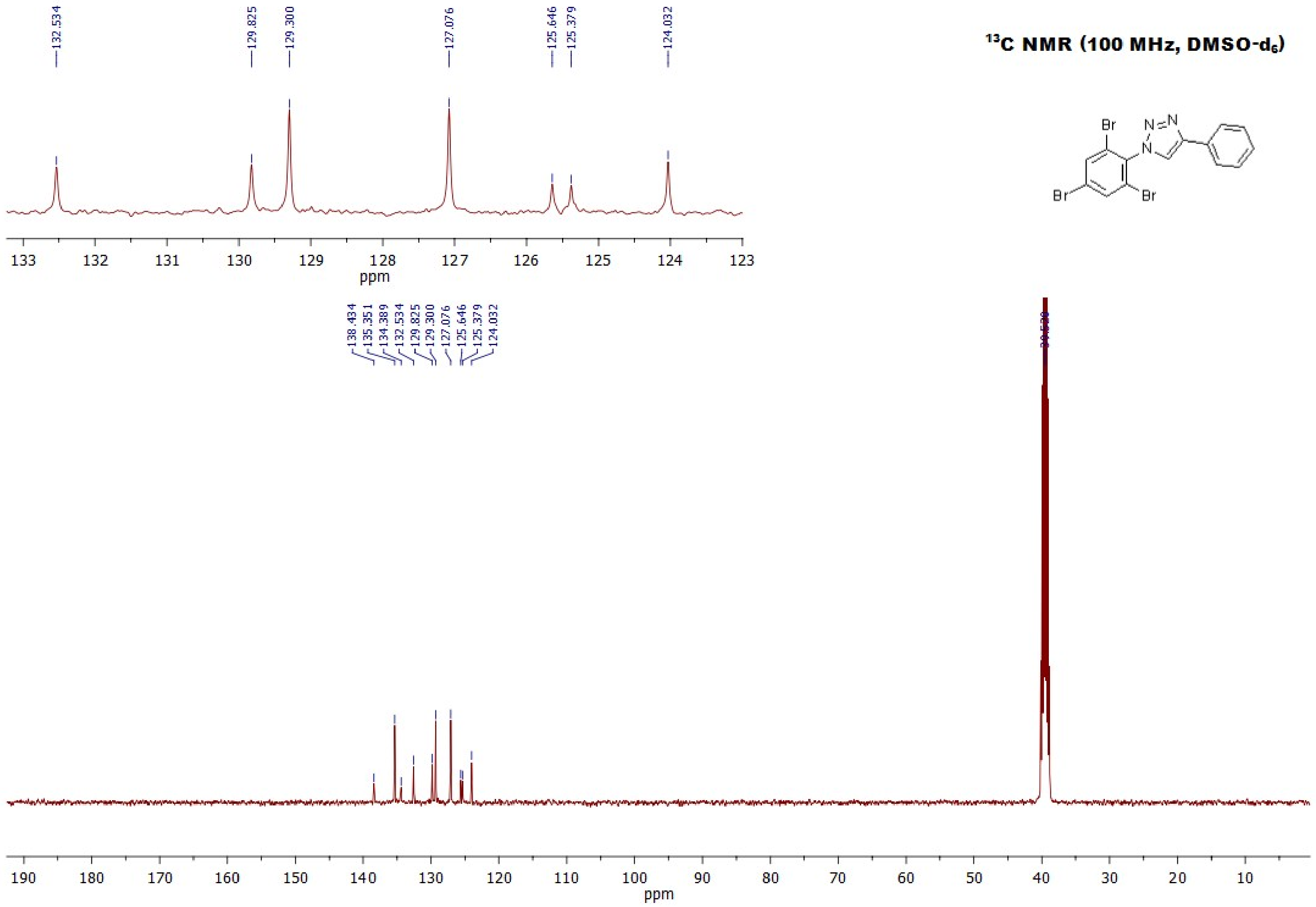
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (3-chloro-5-(4-phenyl-*1H*-1,2,3-triazol-1-yl)phenyl)(phenyl)methanone **(3ha).**



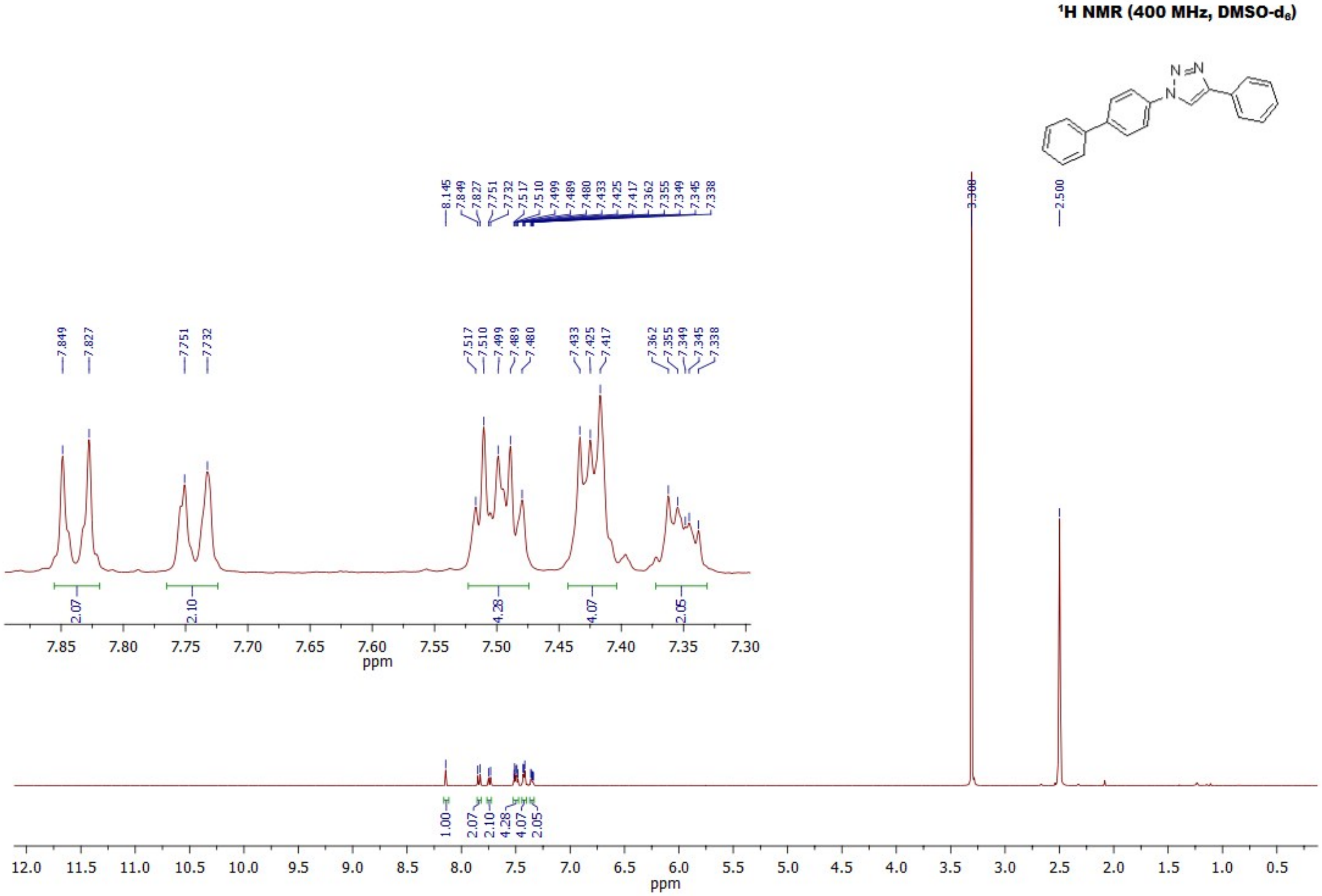
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of4-phenyl-1-(2,4,6-tribromophenyl)-*1H*-1,2,3-triazole **(3ia).**



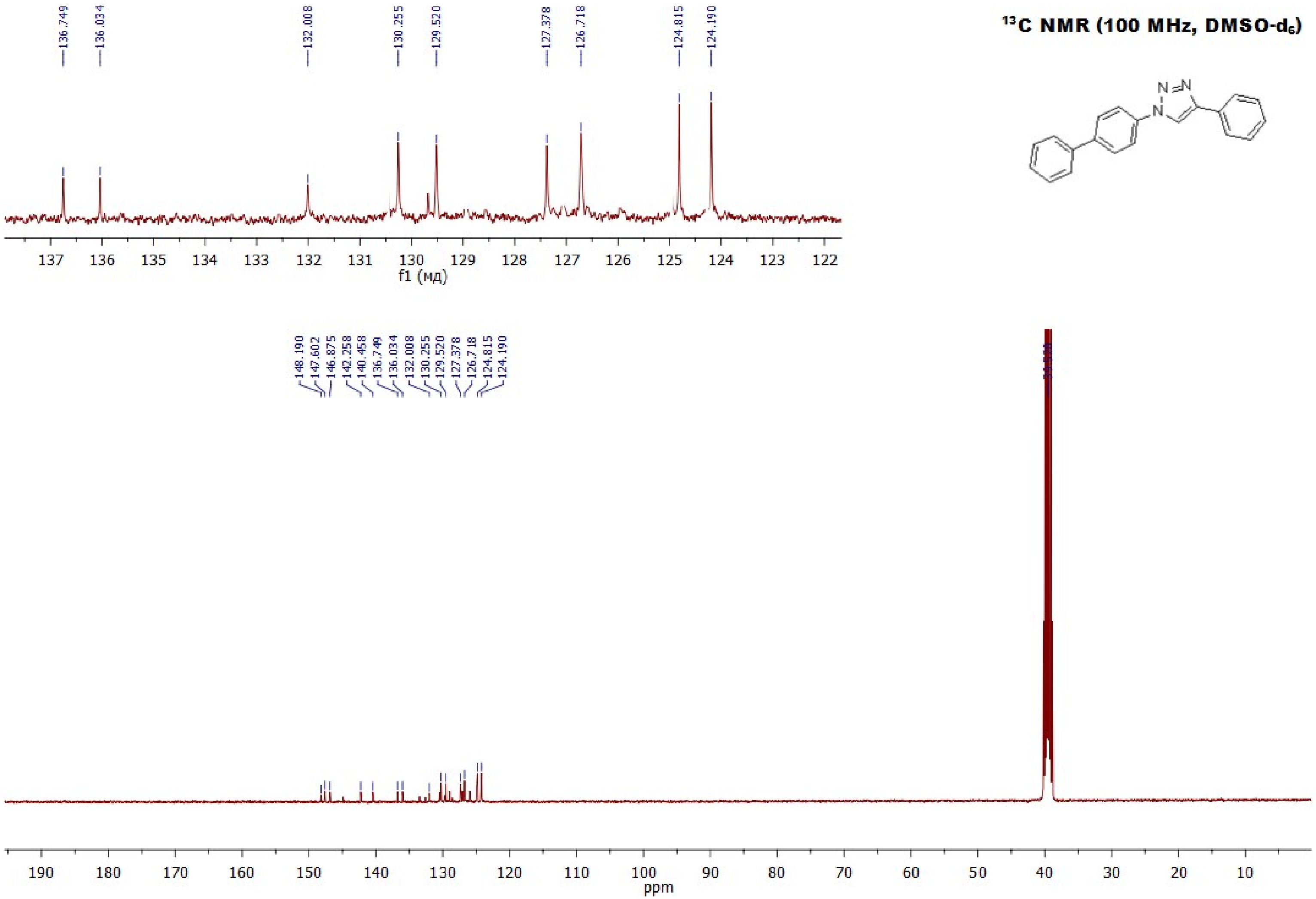
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 4-phenyl-1-(2,4,6-tribromophenyl)-*1H*-1,2,3-triazole **(3ia).**



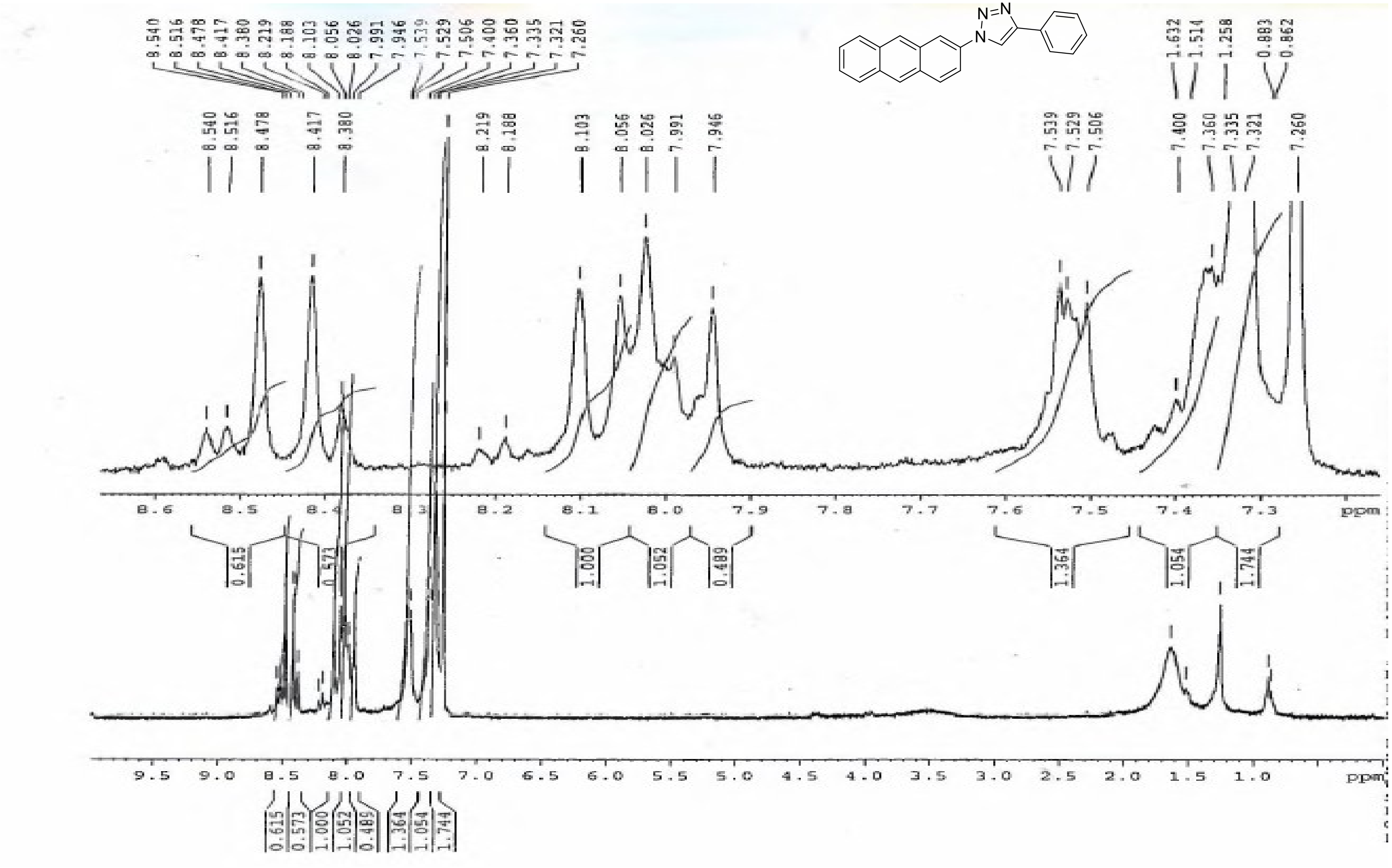
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1-([1,1'-biphenyl]-4-yl)-4-phenyl-*1H*-1,2,3-triazole **(3ja).**



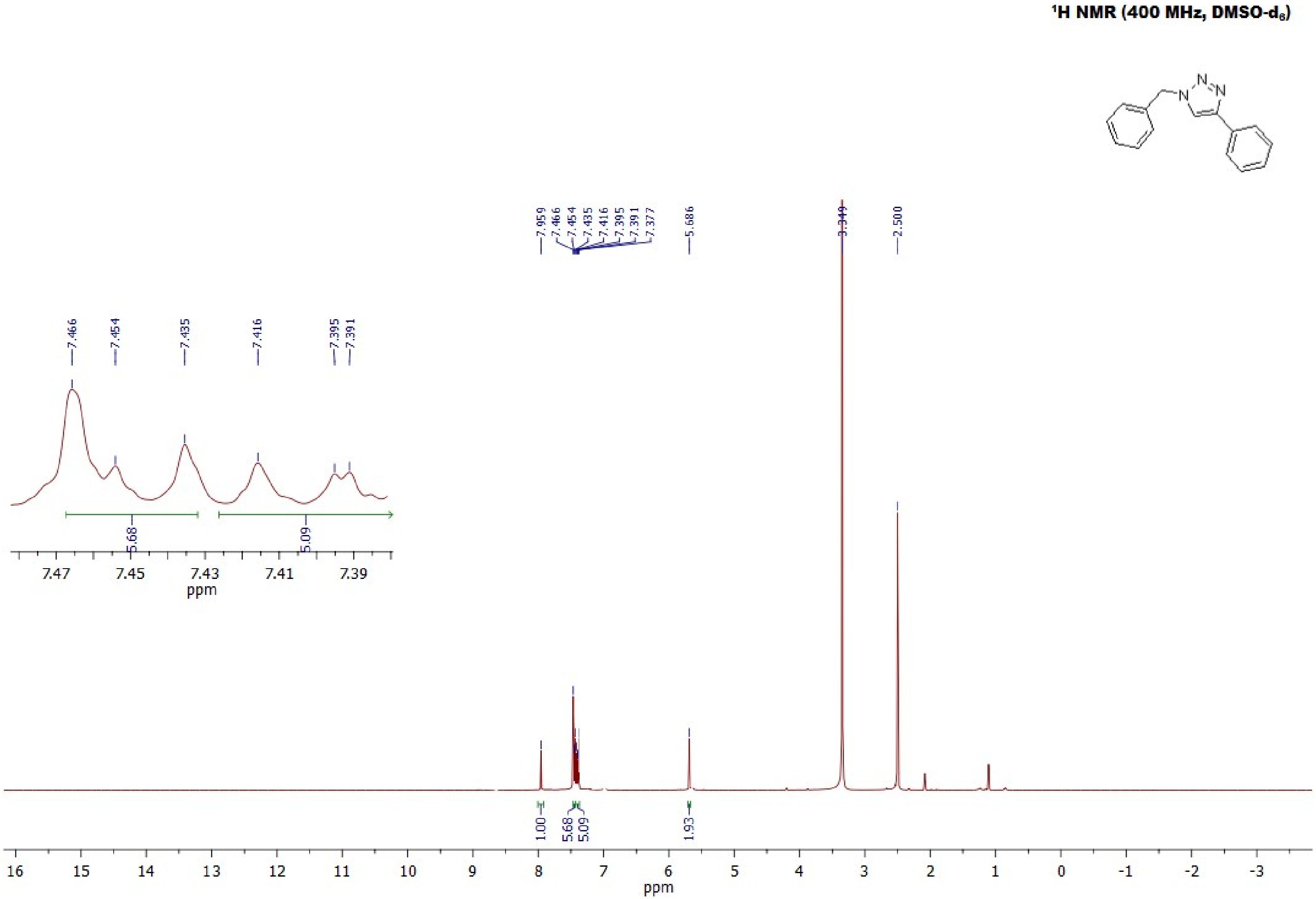
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 1-([1,1'-biphenyl]-4-yl)-4-phenyl-*1H*-1,2,3-triazole **(3ja).**



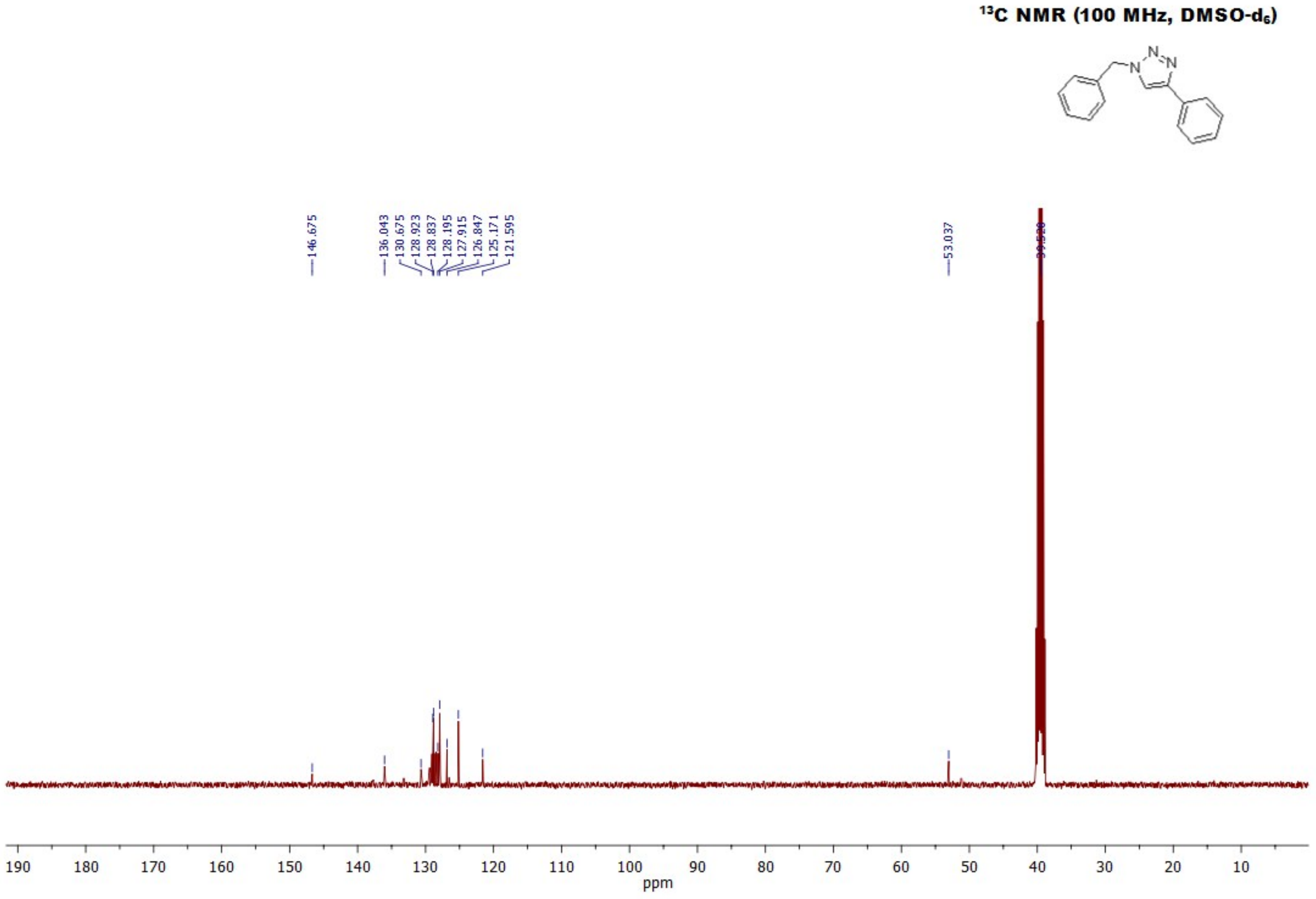
^{1}H NMR (300 MHz, DMSO-d$_6$) spectrum of 1-(anthracen-2-yl)-4-phenyl-*1H*-1,2,3-triazole **(3ka).**



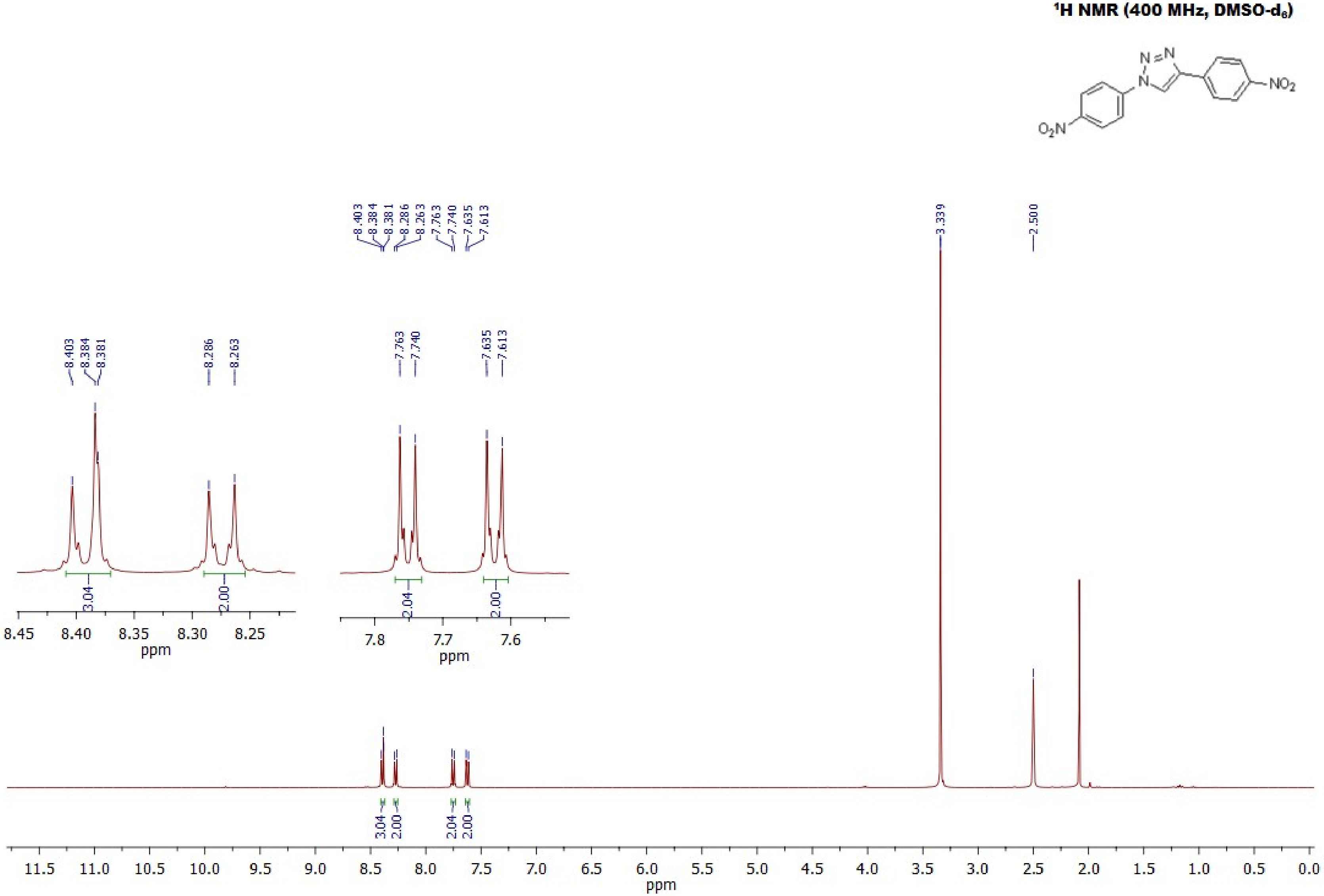
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of1-benzyl-4-phenyl-*1H*-1,2,3-triazole **(3la).**



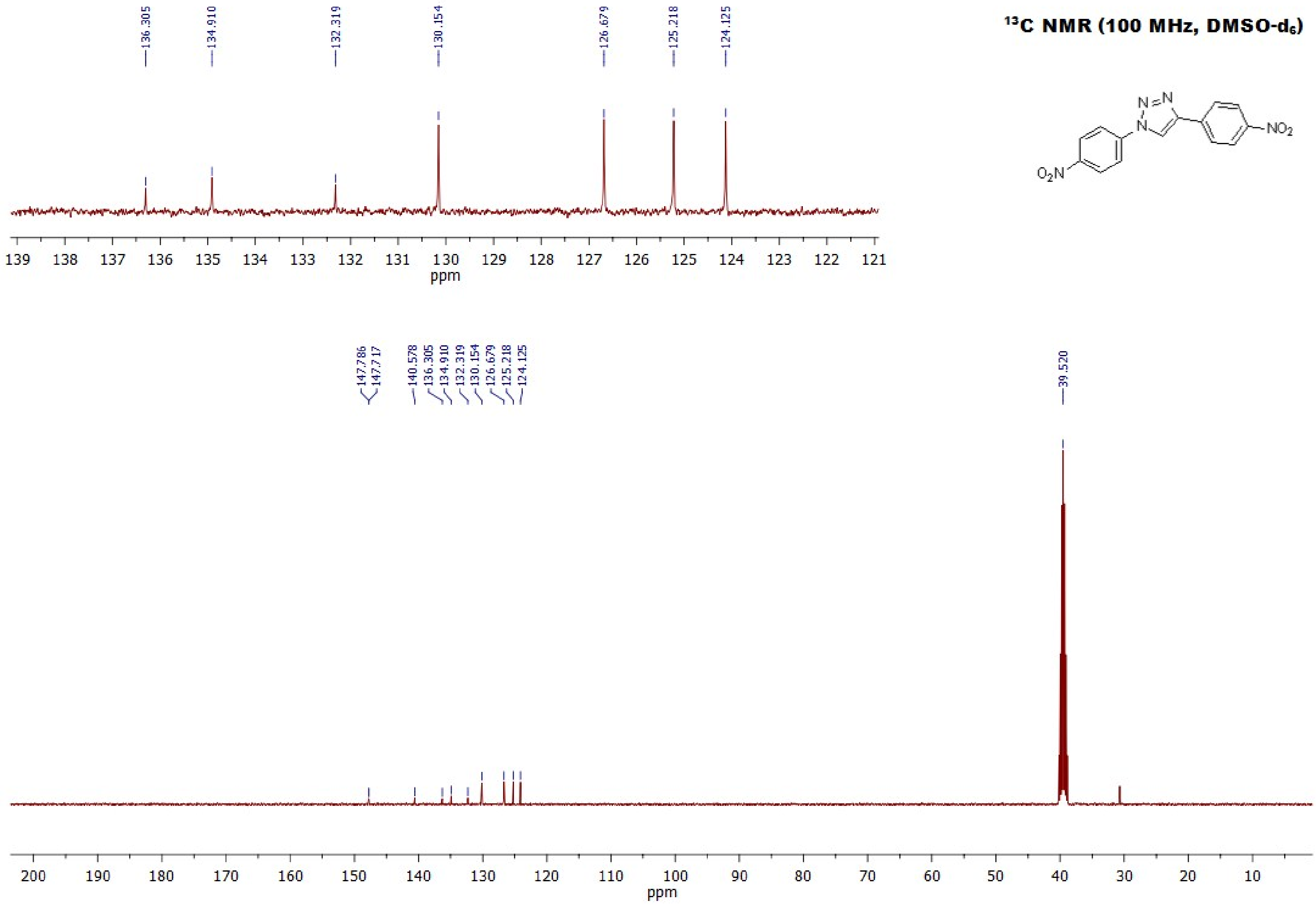
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-benzyl-4-phenyl-*1H*-1,2,3-triazole **(3la).**



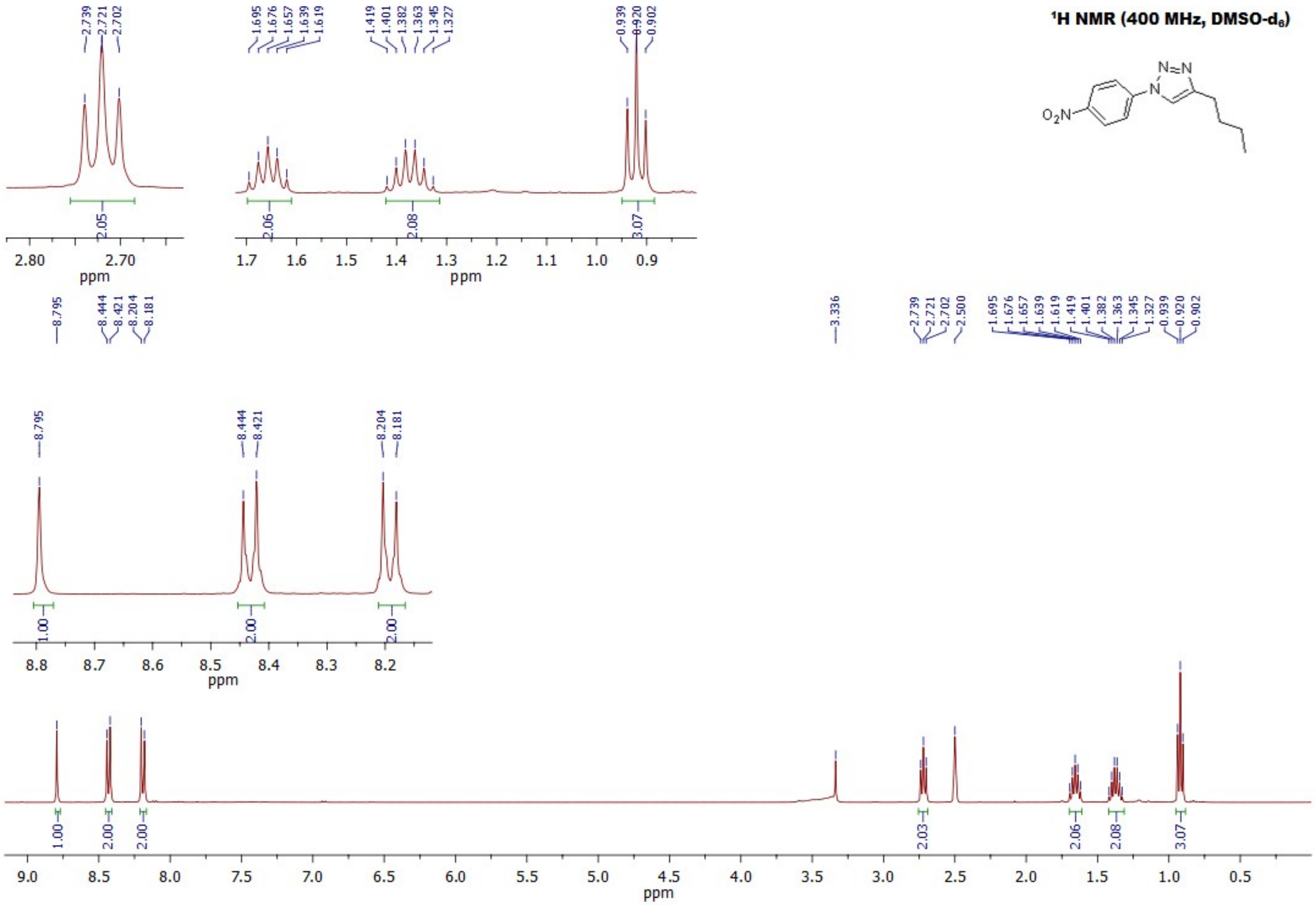
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1,4-bis(4-nitrophenyl)-*1H*-1,2,3-triazole **(3ab).**



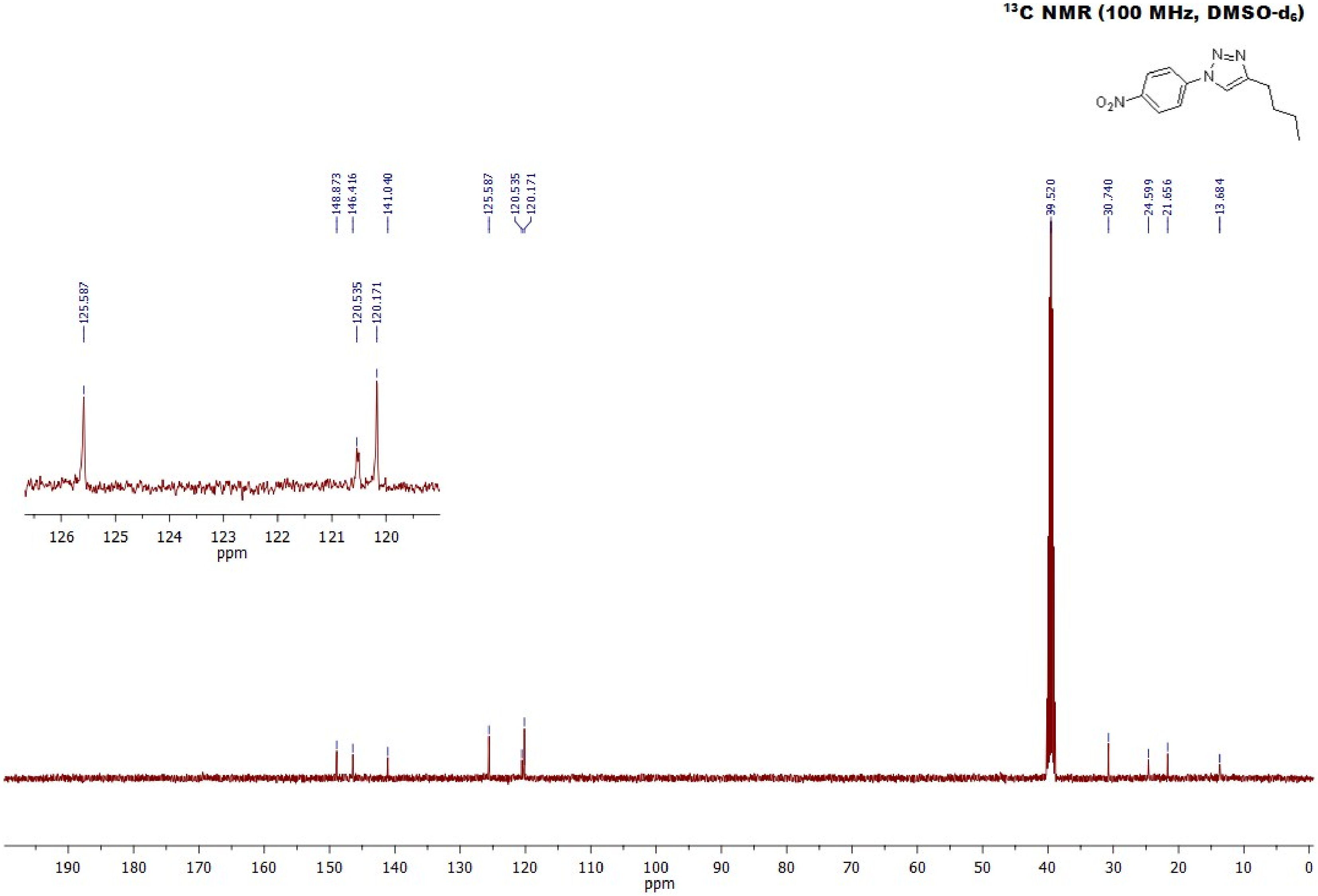
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1,4-bis(4-nitrophenyl)-*1H*-1,2,3-triazole **(3ab).**



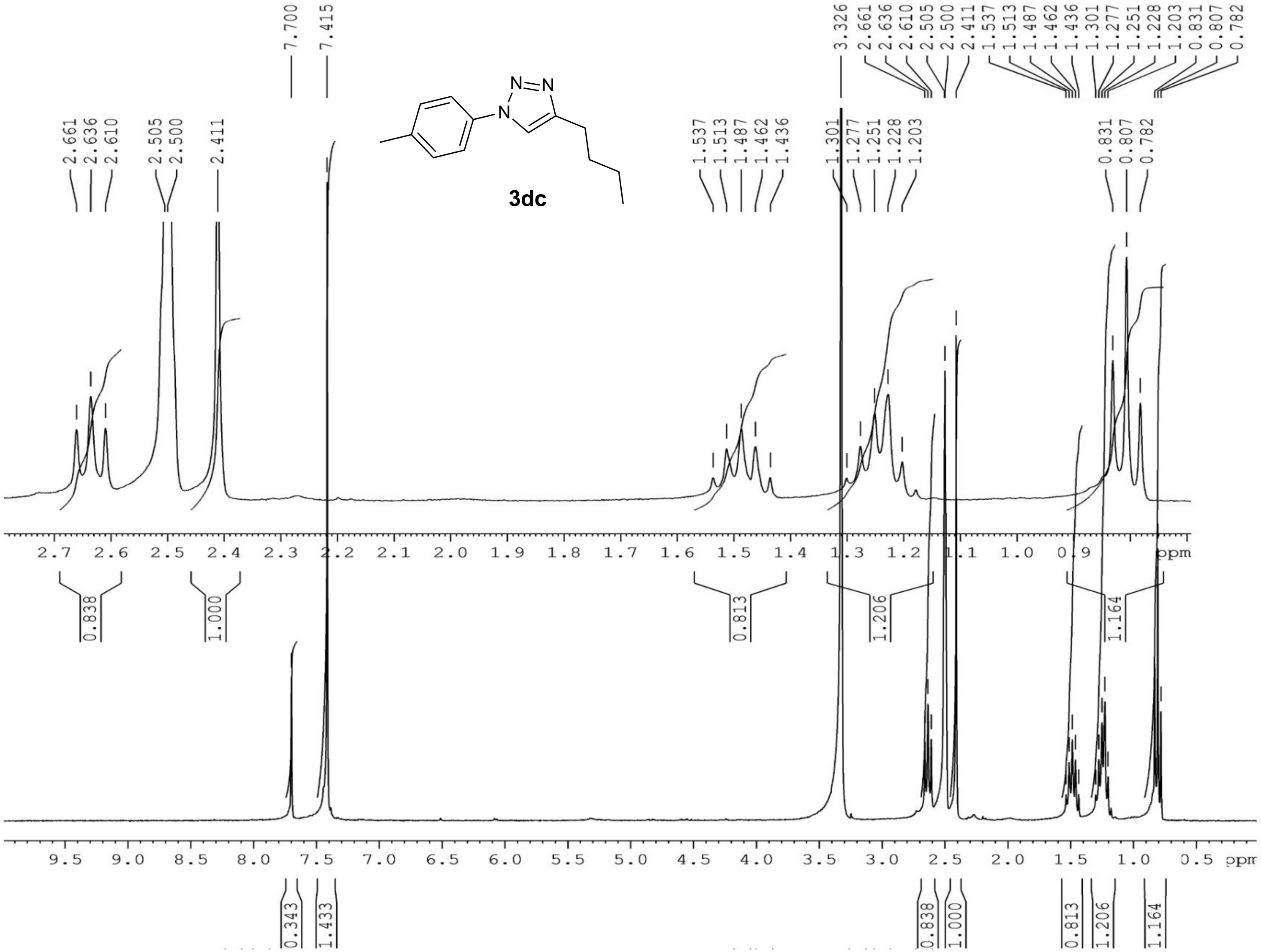
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1-(4-nitrophenyl)-4-butyl-*1H*-1,2,3-triazole **(3ac).**



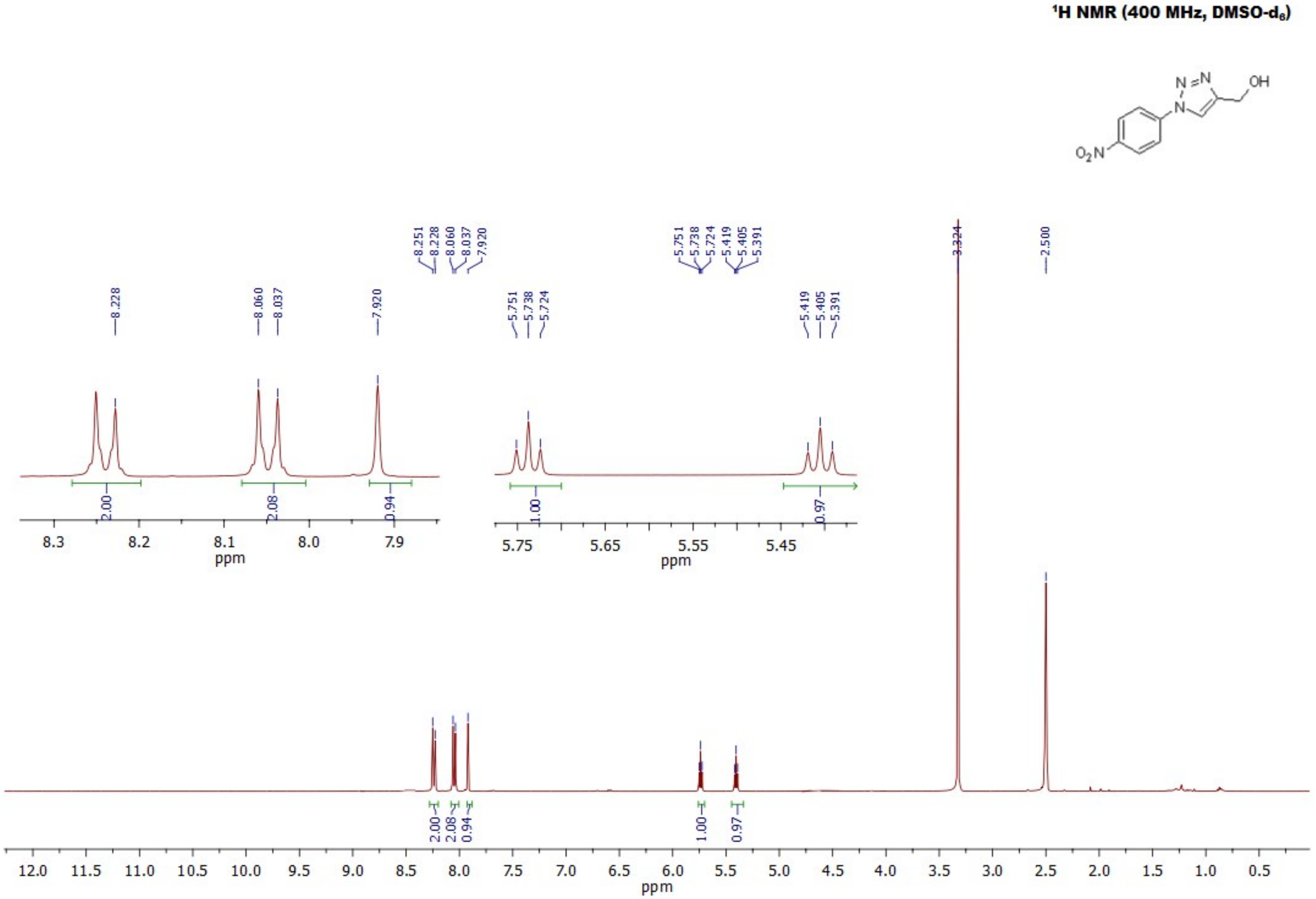
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-(4-nitrophenyl)-4-butyl-*1H*-1,2,3-triazole **(3ac).**



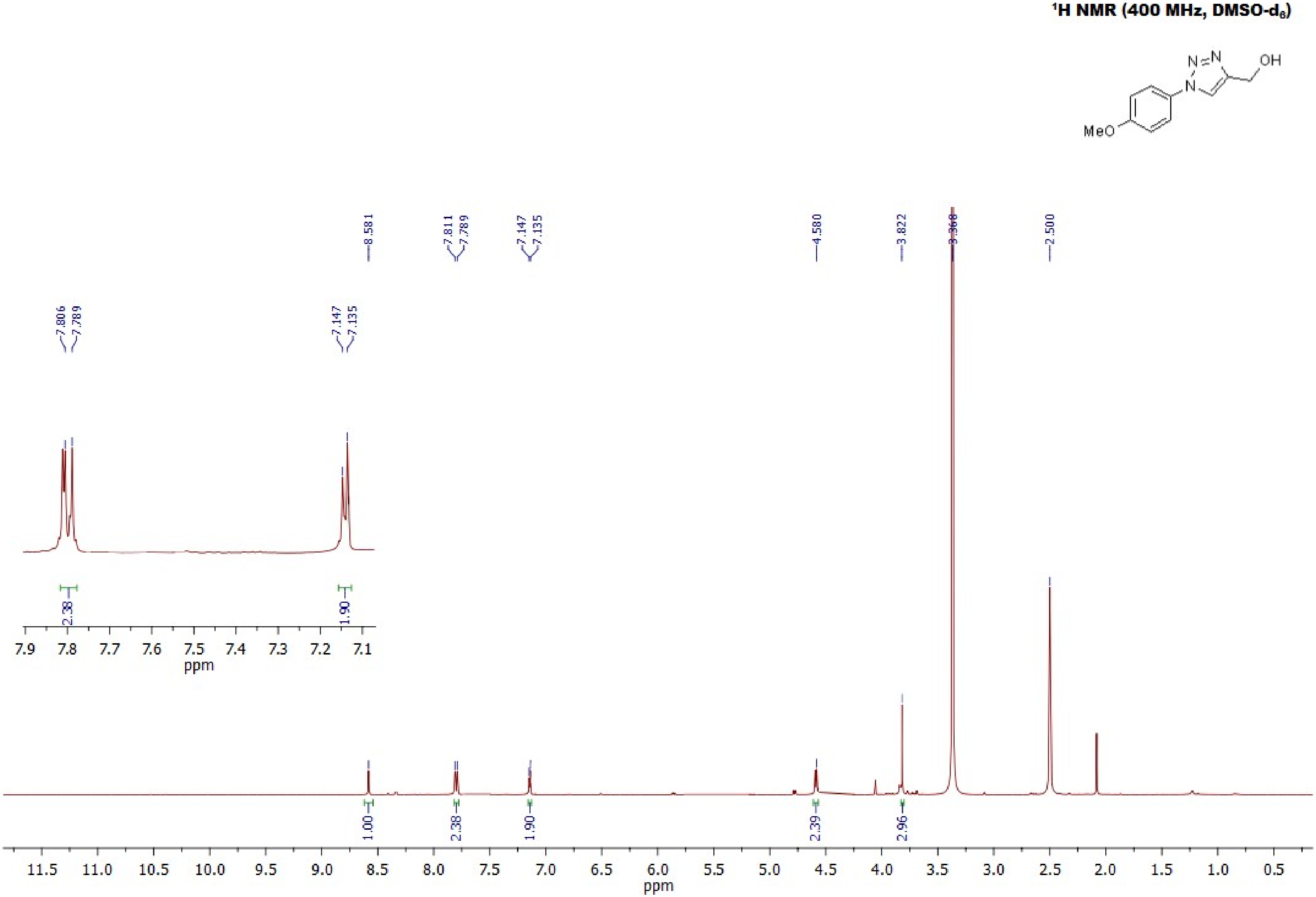
^{1}H NMR (300 MHz, DMSO-d$_6$) spectrum of 4-butyl-1-(p-tolyl)-*1H*-1,2,3-triazole **(3dc).**



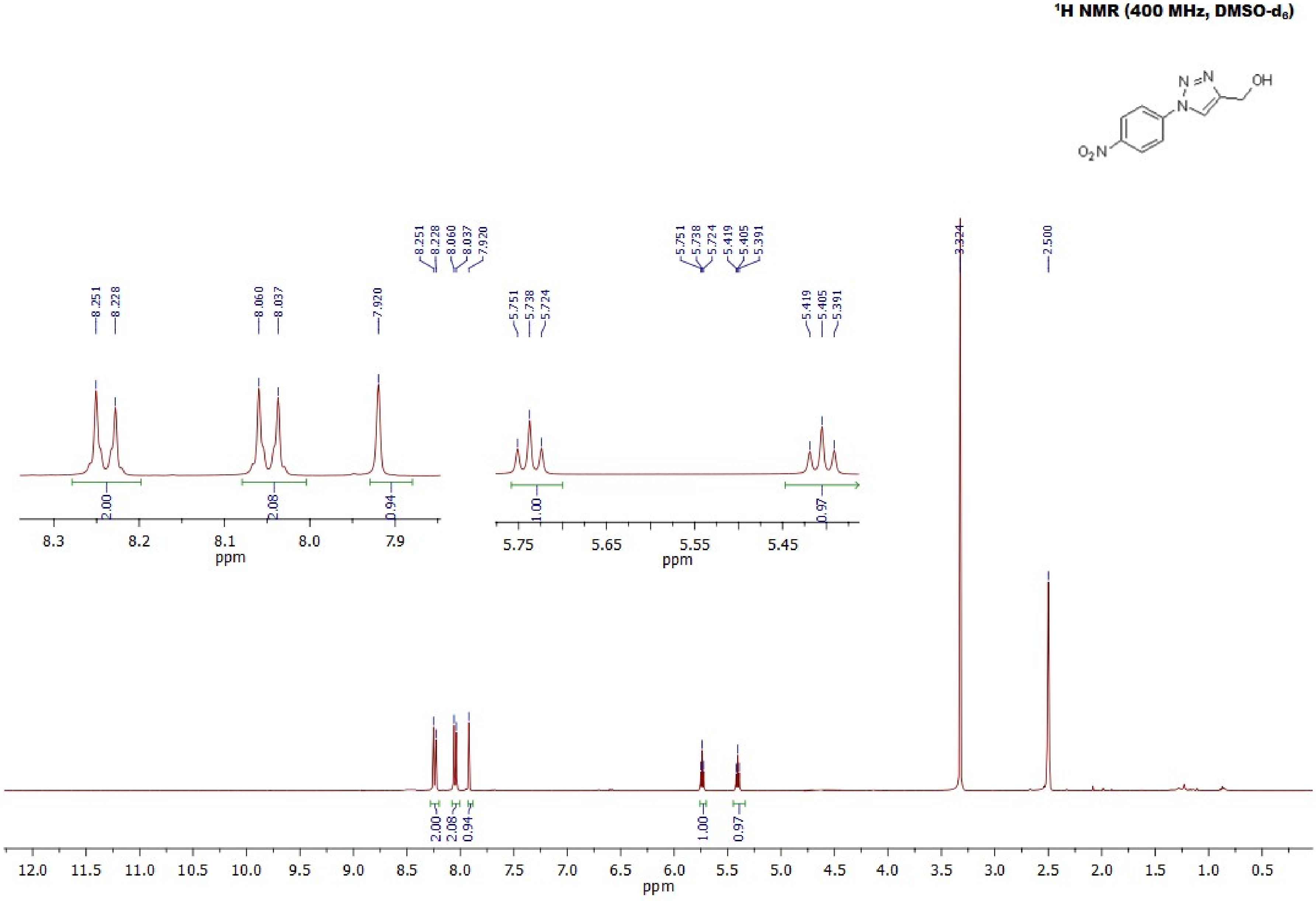
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of(1-(4-nitrophenyl)-*1H*-1,2,3-triazol-4-yl)methanol **(3ad).**



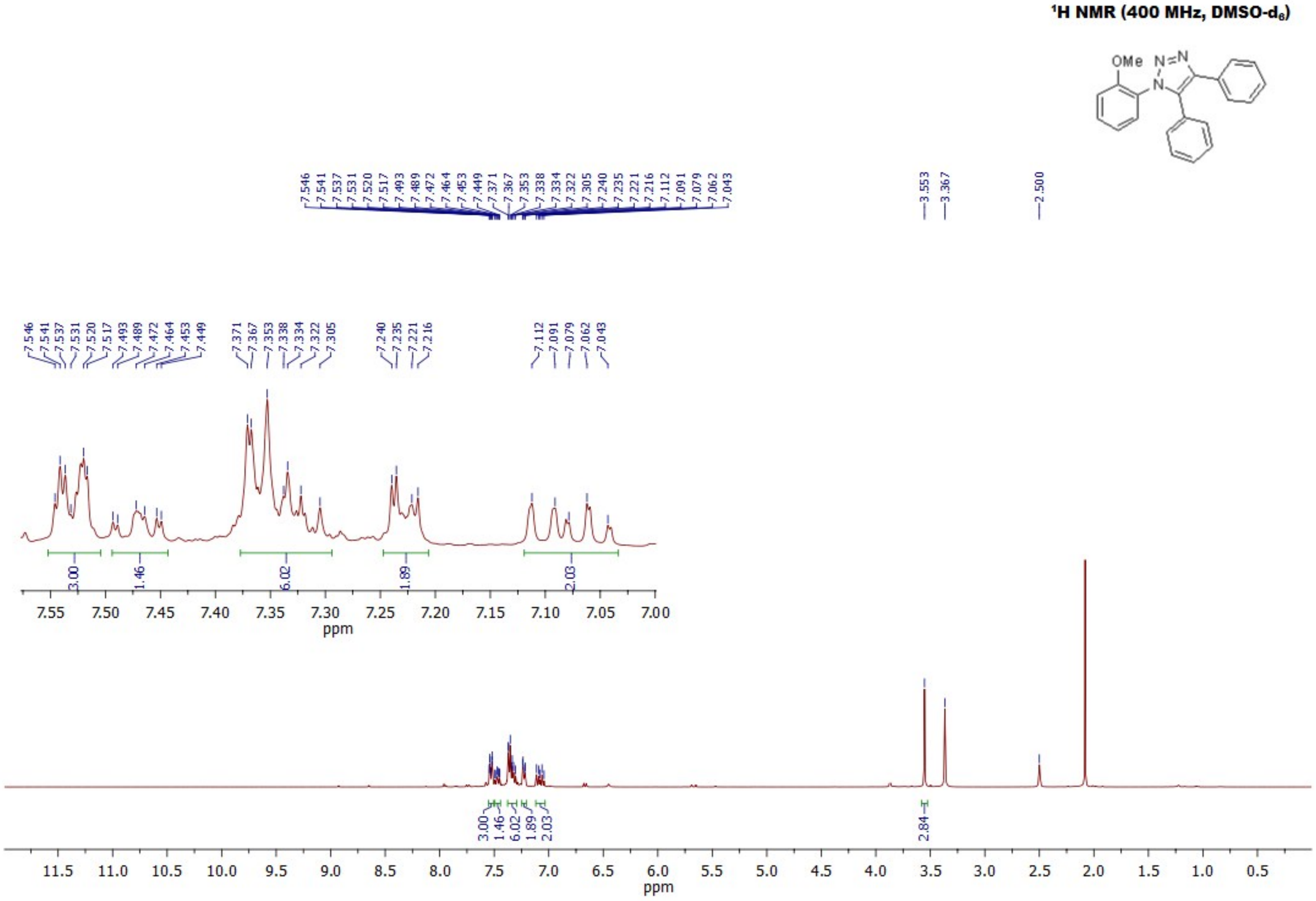
^1H NMR (400 MHz, DMSO-d$_6$) spectrum of (1-(4-methoxyphenyl)-*1H*-1,2,3-triazol-4-yl)methanol **(3fd).**



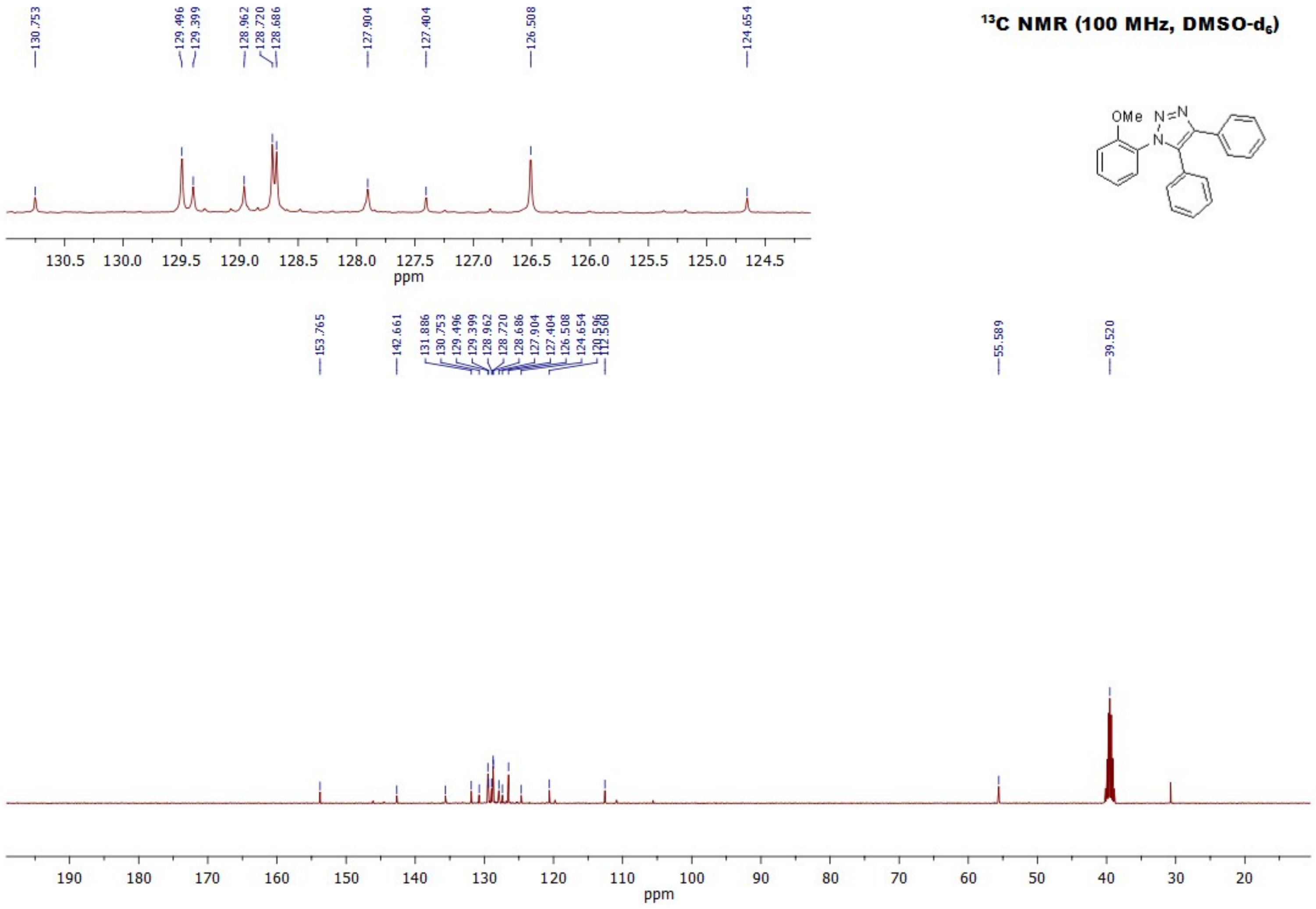
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1-(4-nitrophenyl)-4,5-diphenyl-*1H*-1,2,3-triazole **(3ae).**



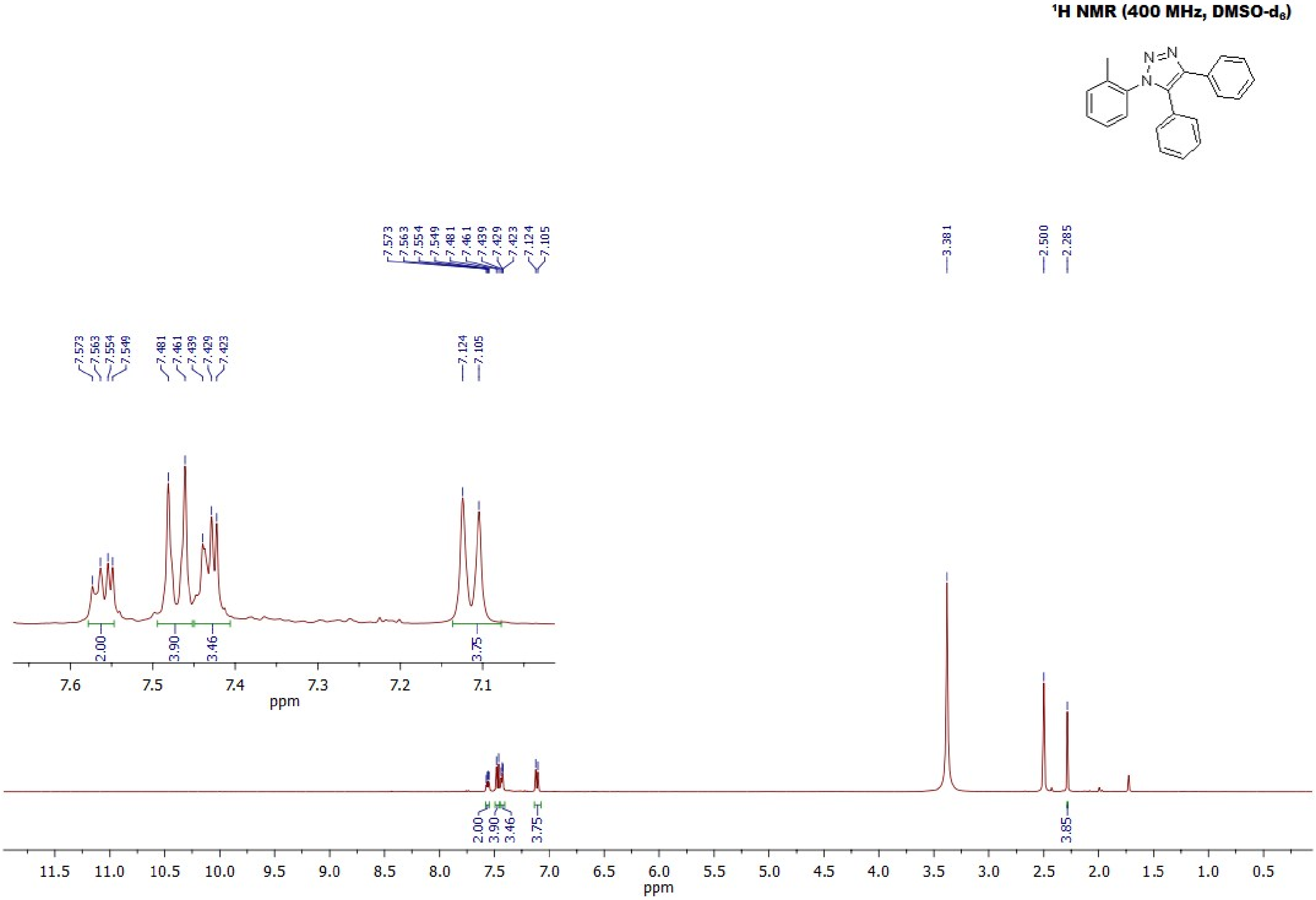
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-(2-methoxyphenyl)-4,5-diphenyl-*1H*-1,2,3-triazole **(3ge).**



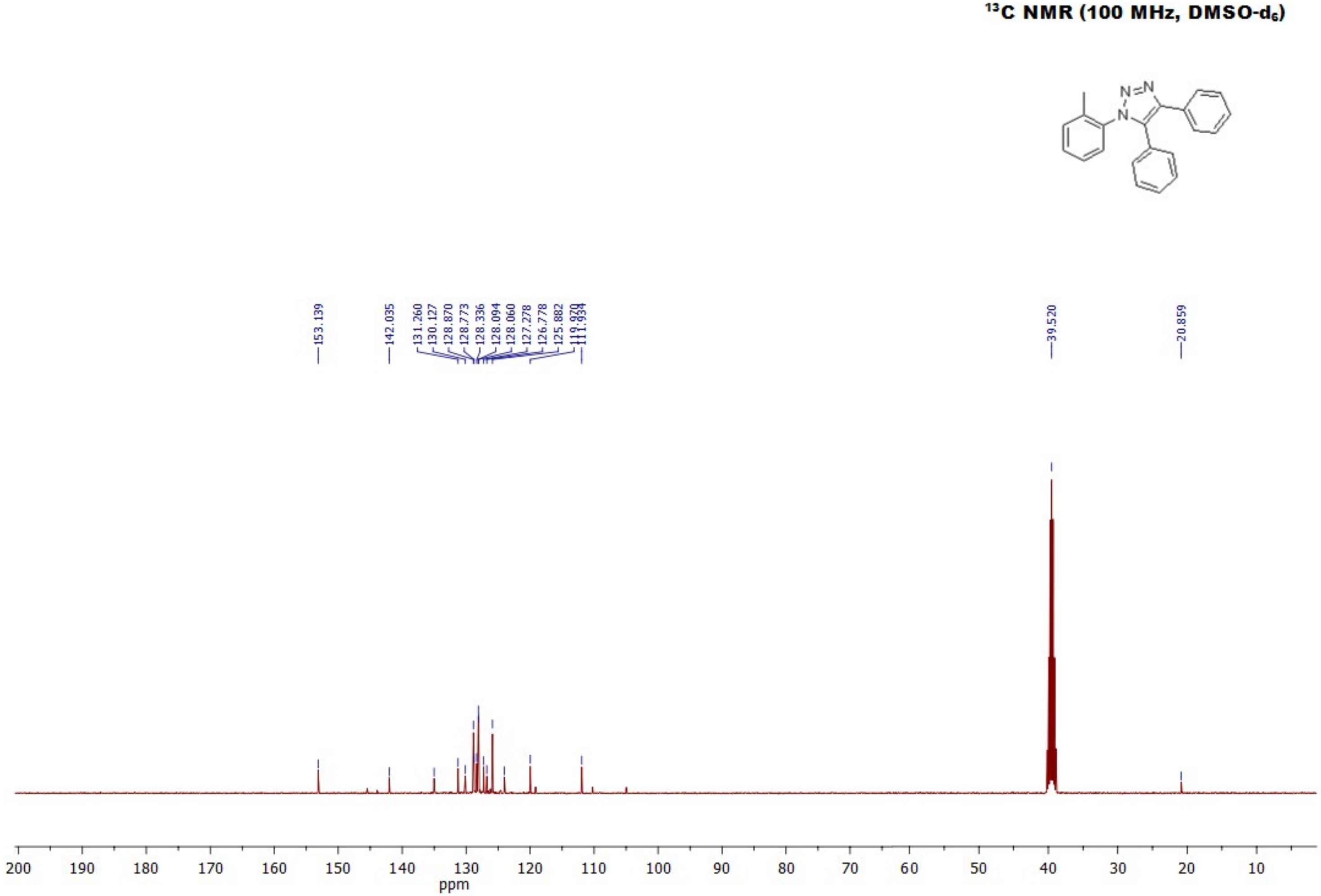
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-(2-methoxyphenyl)-4,5-diphenyl-*1H*-1,2,3-triazole **(3ge).**



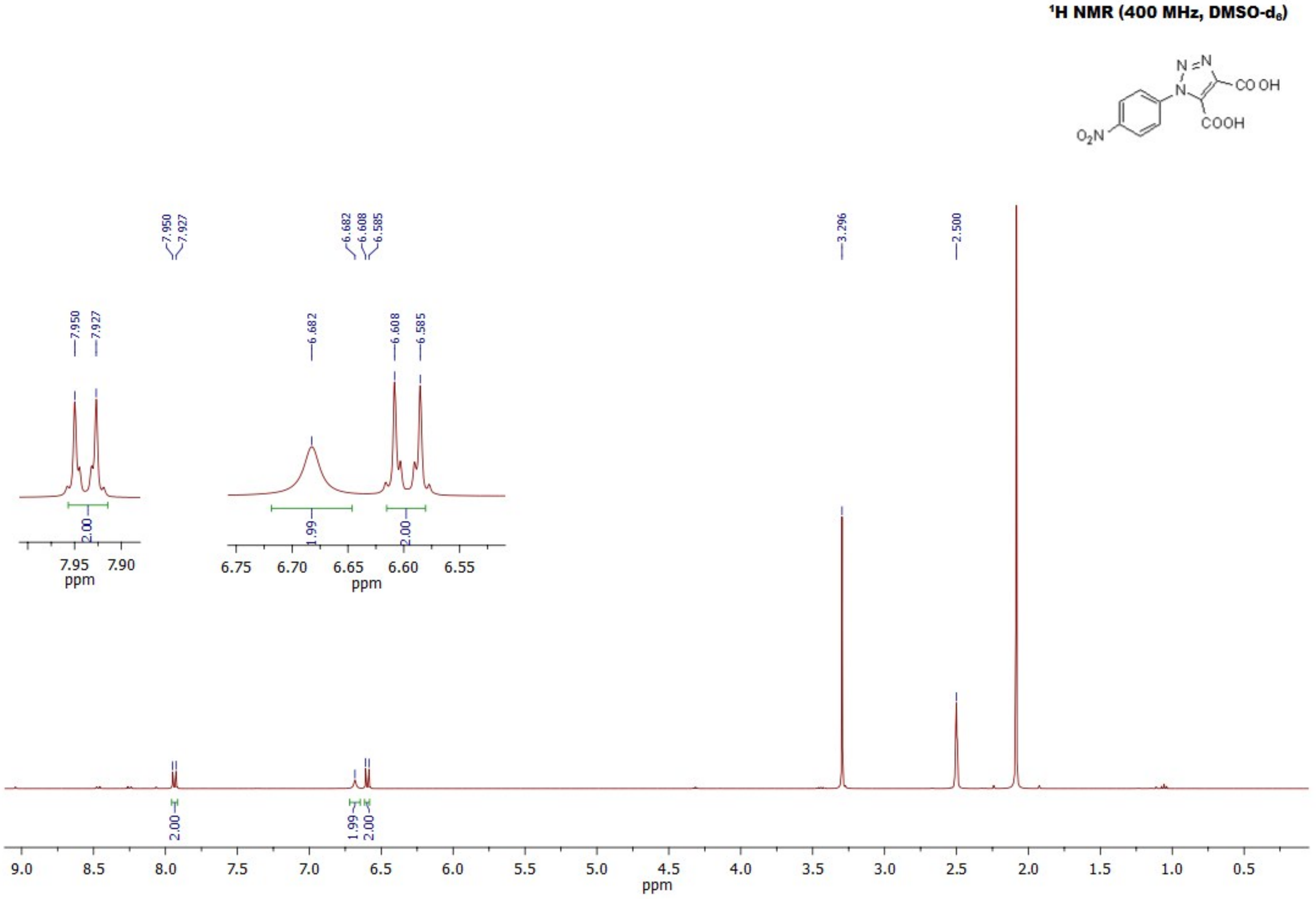
^1H NMR (400 MHz, DMSO-d_6) spectrum of 4,5-diphenyl-1-(o-tolyl)-*1H*-1,2,3-triazole**(3ee).**



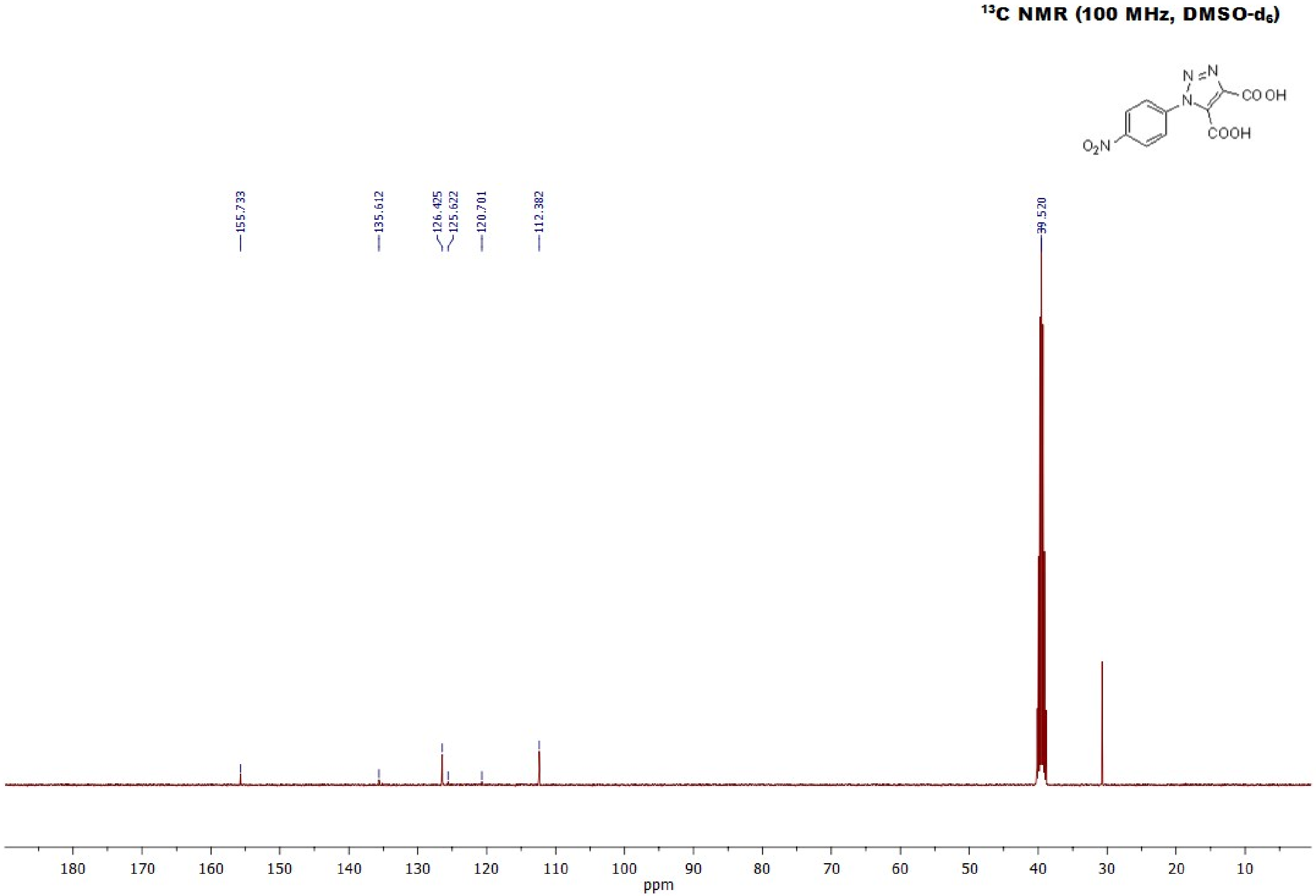
^{13}CNMR (100 MHz, DMSO-d$_6$) spectrumof4,5-diphenyl-1-(o-tolyl)-*1H*-1,2,3-triazole**(3ee).**



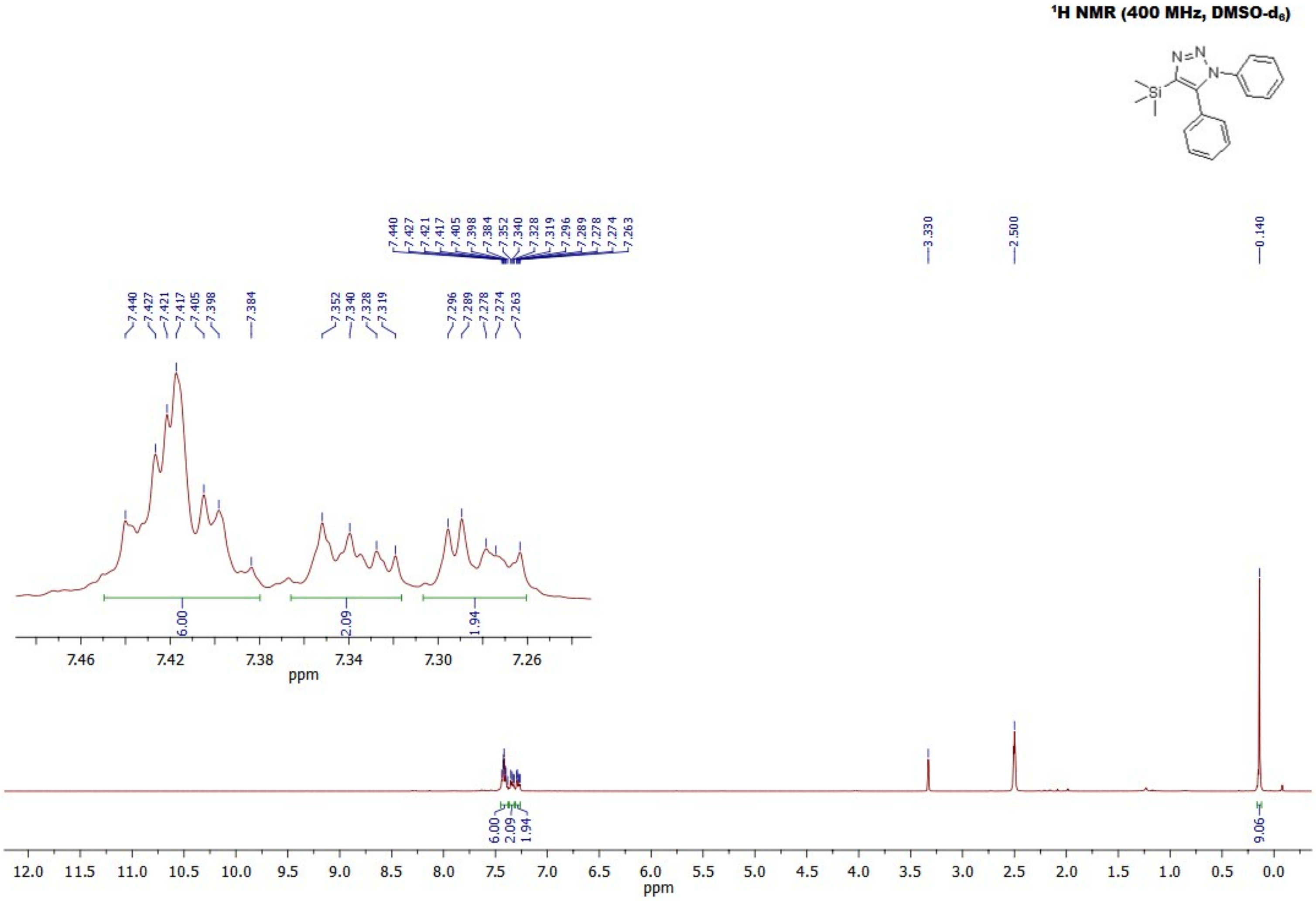
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of1-(4-nitrophenyl)-*1H*-1,2,3-triazole-4,5-dicarboxylic acid **(3af).**



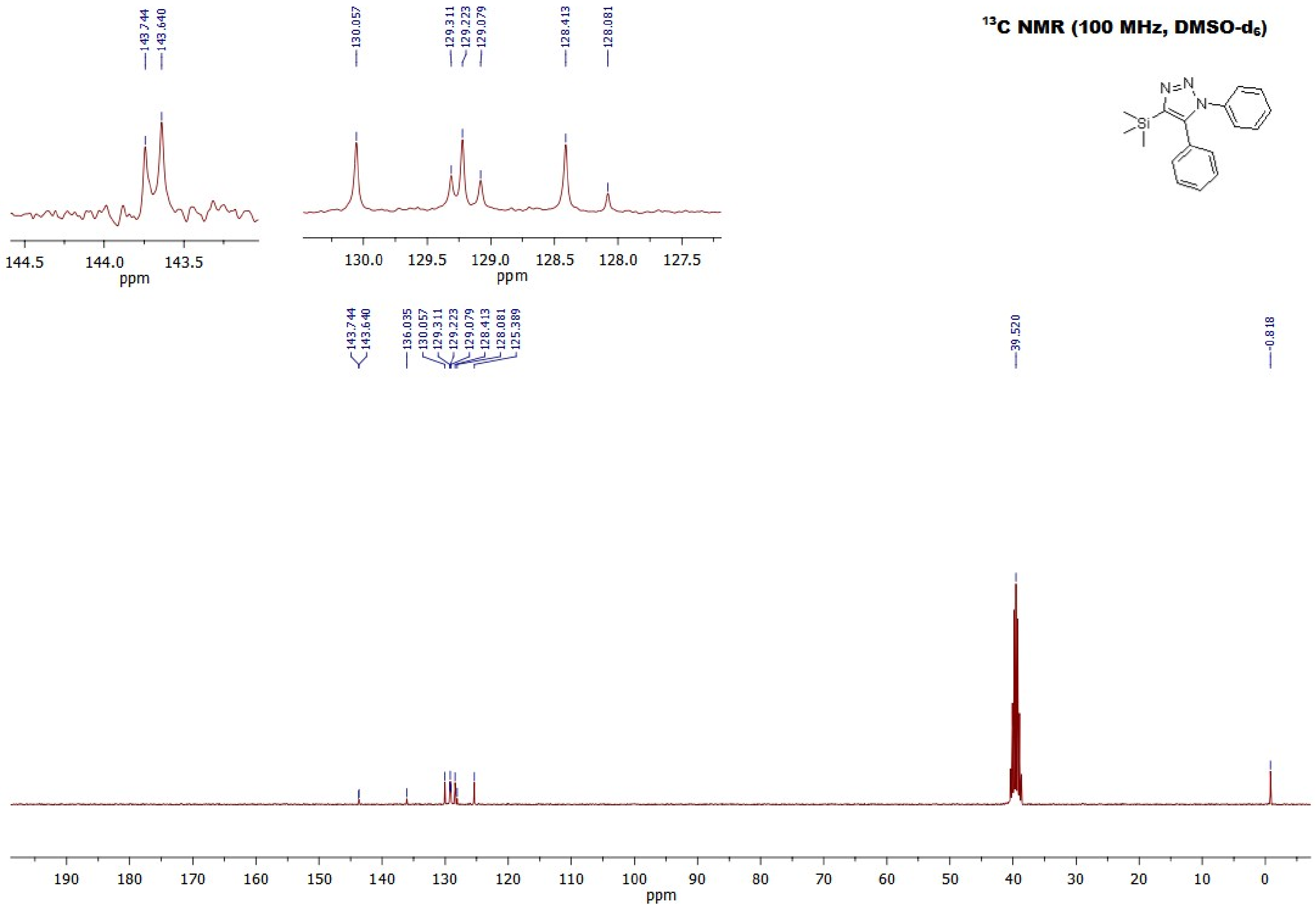
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 1-(4-nitrophenyl)-*1H*-1,2,3-triazole-4,5-dicarboxylic acid **(3af).**



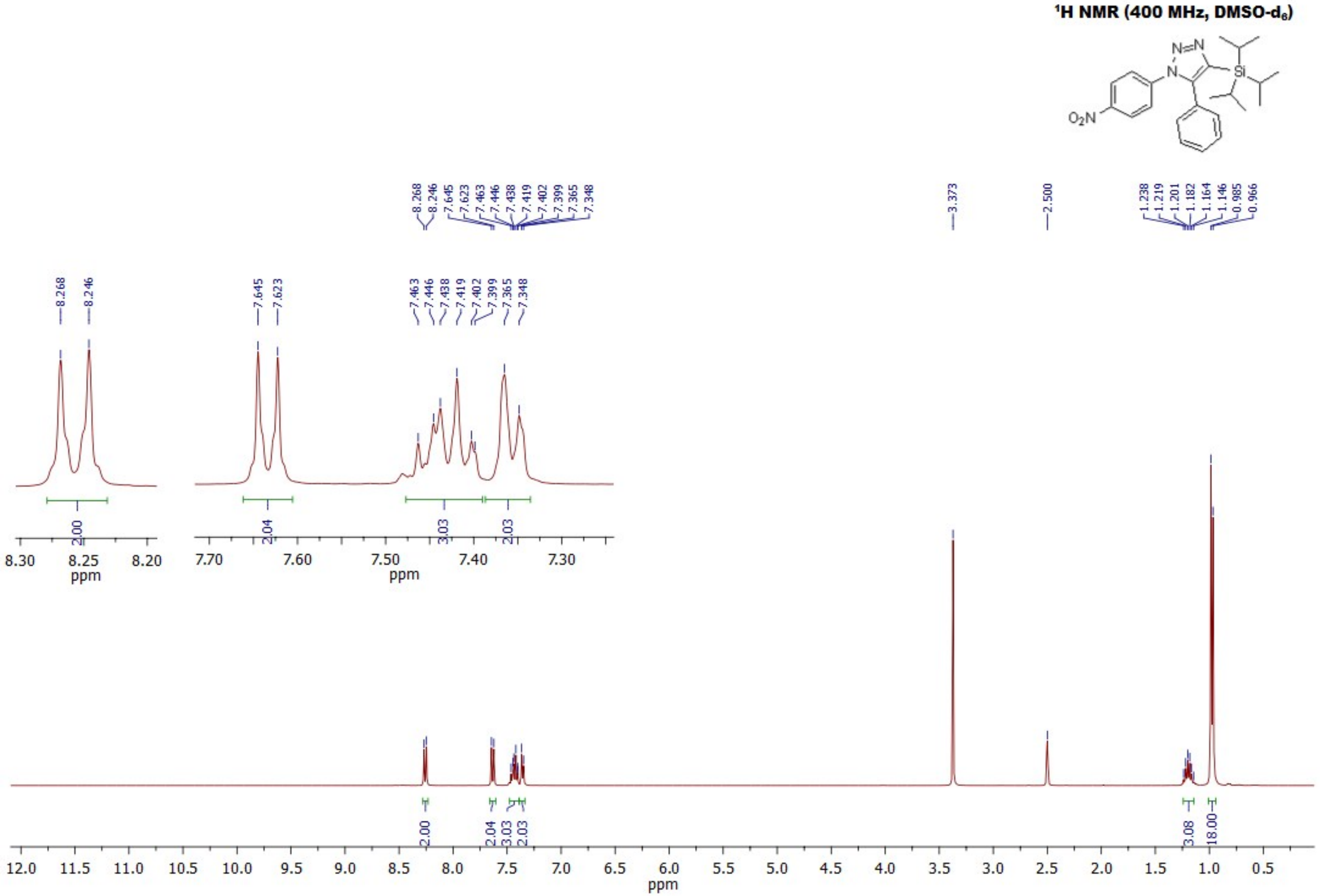
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1,5-diphenyl-4-(trimethylsilyl)-*1H*-1,2,3-triazole **(3ng).**



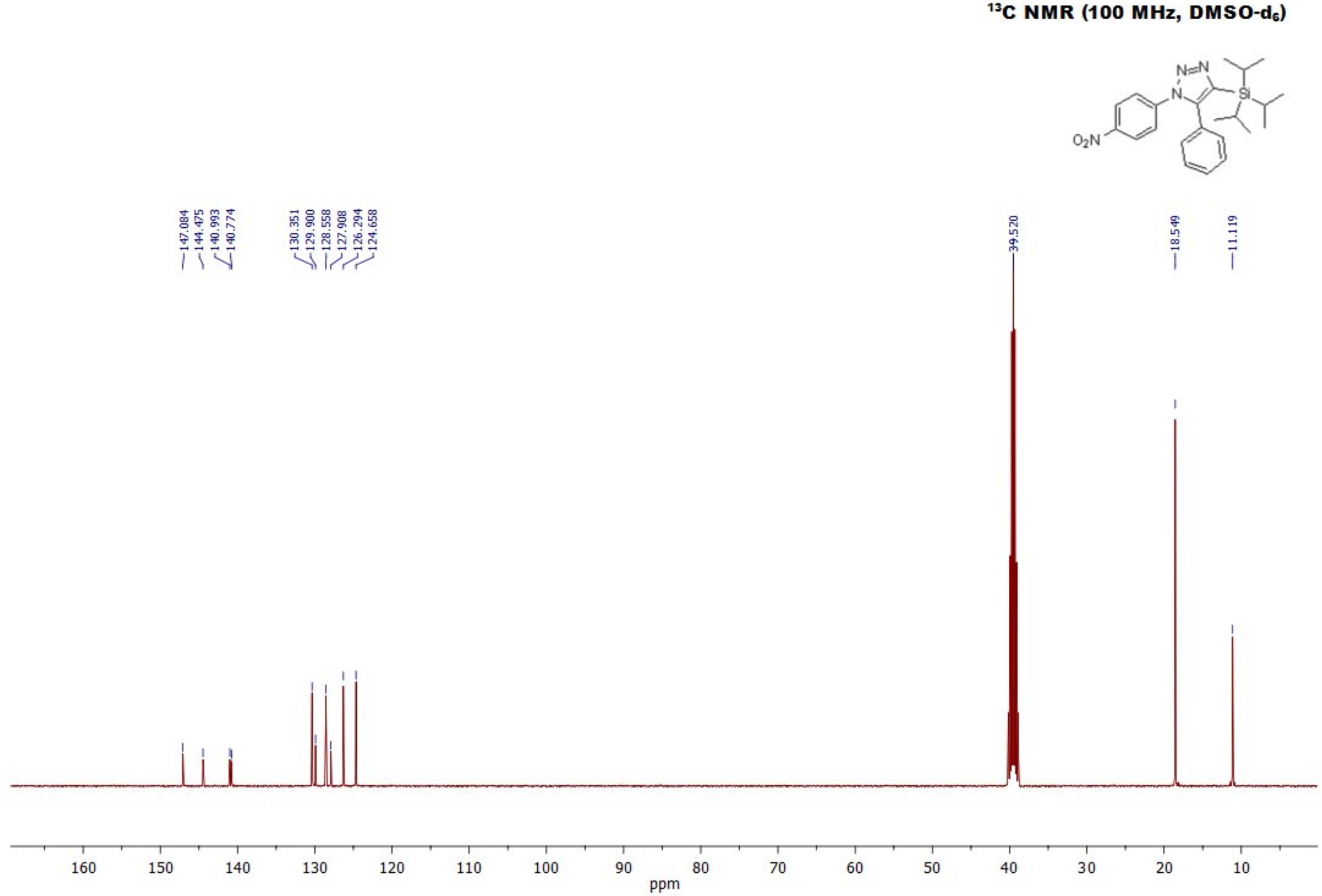
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1,5-diphenyl-4-(trimethylsilyl)-*1H*-1,2,3-triazole **(3ng).**



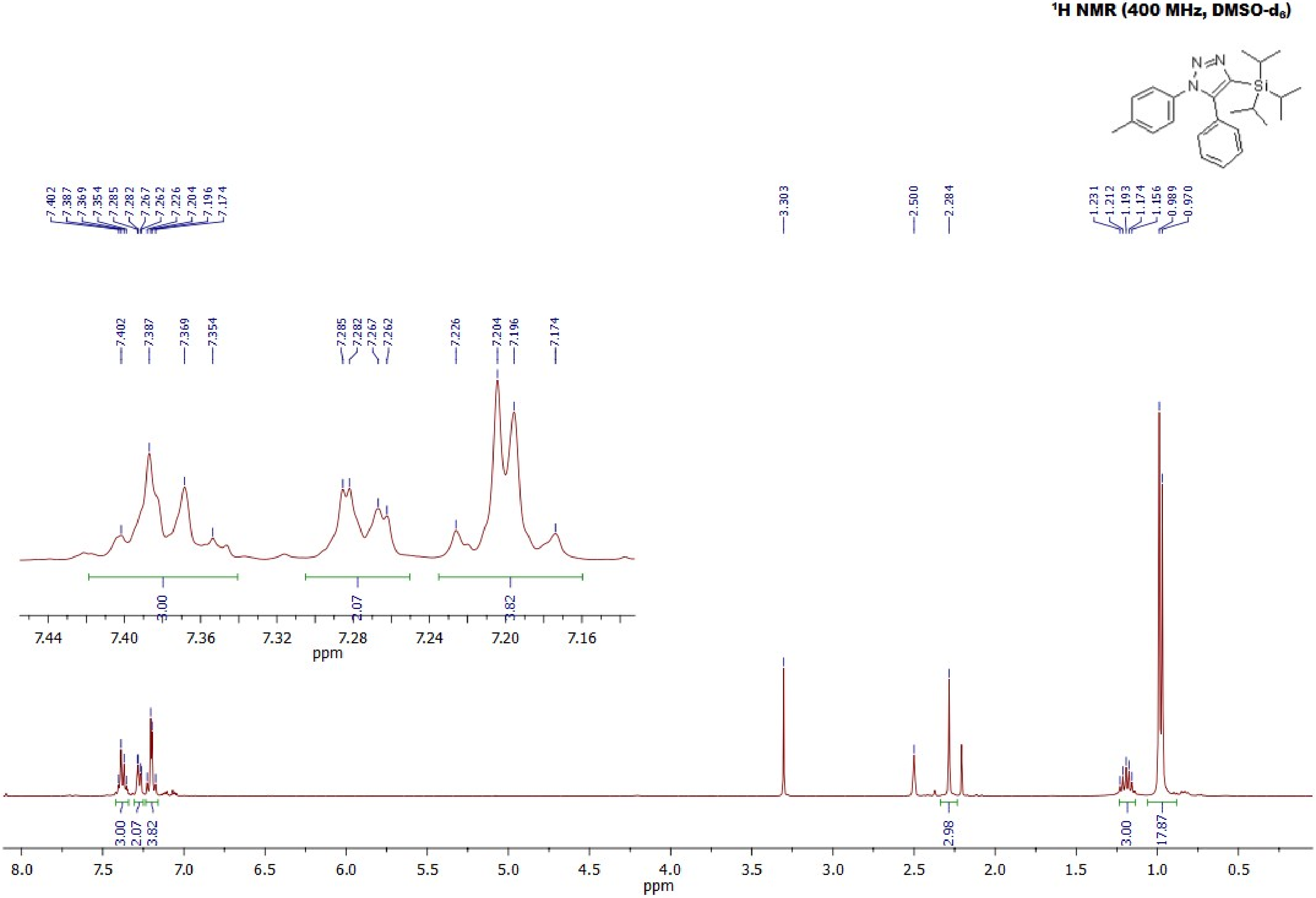
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(4-nitrophenyl)-5-phenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **(3ah).**



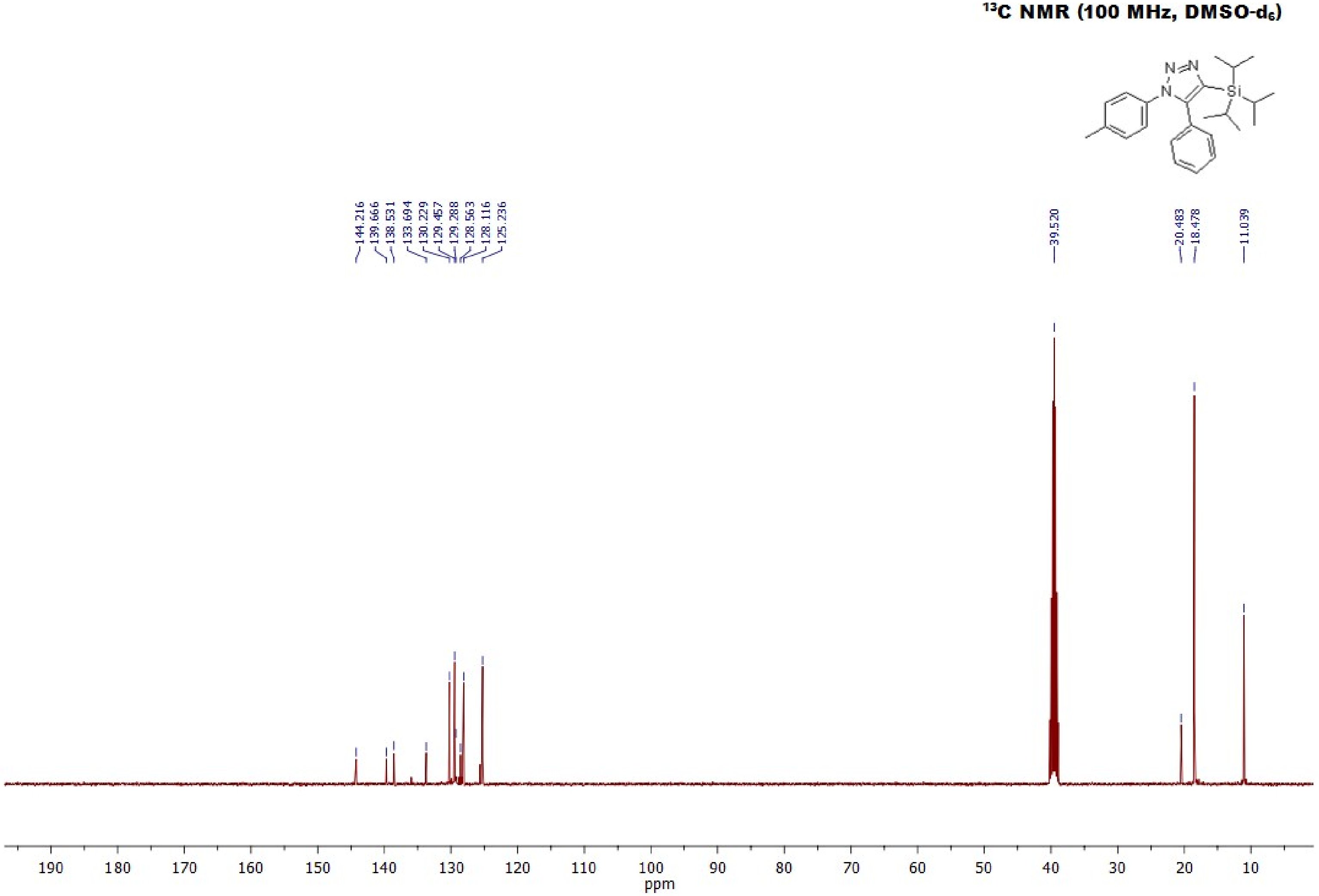
^{13}C NMR (100 MHz, CDCl$_3$) spectrum of 1-(4-nitrophenyl)-5-phenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **(3ah).**



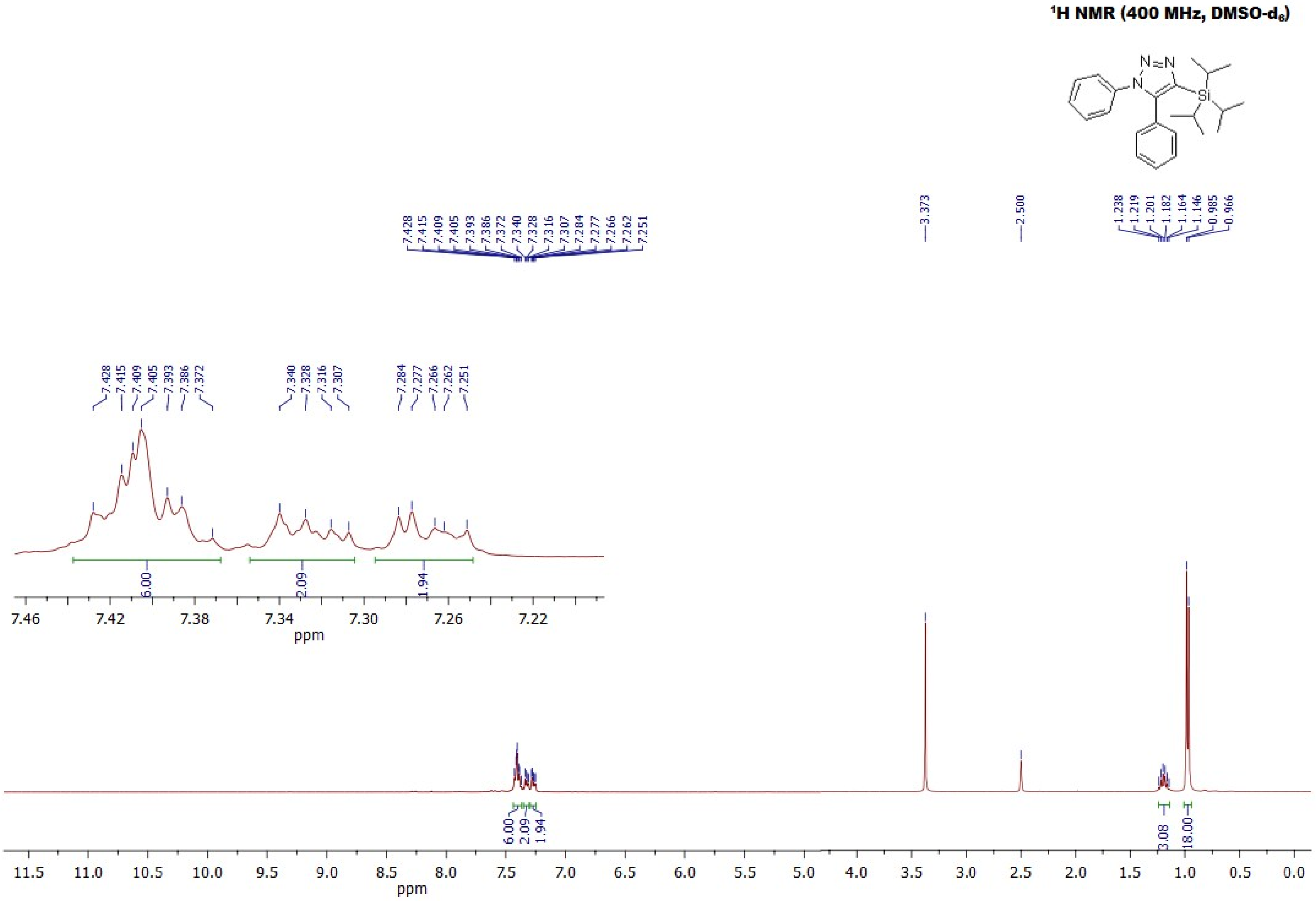
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 5-phenyl-1-(p-tolyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **(3dh).**



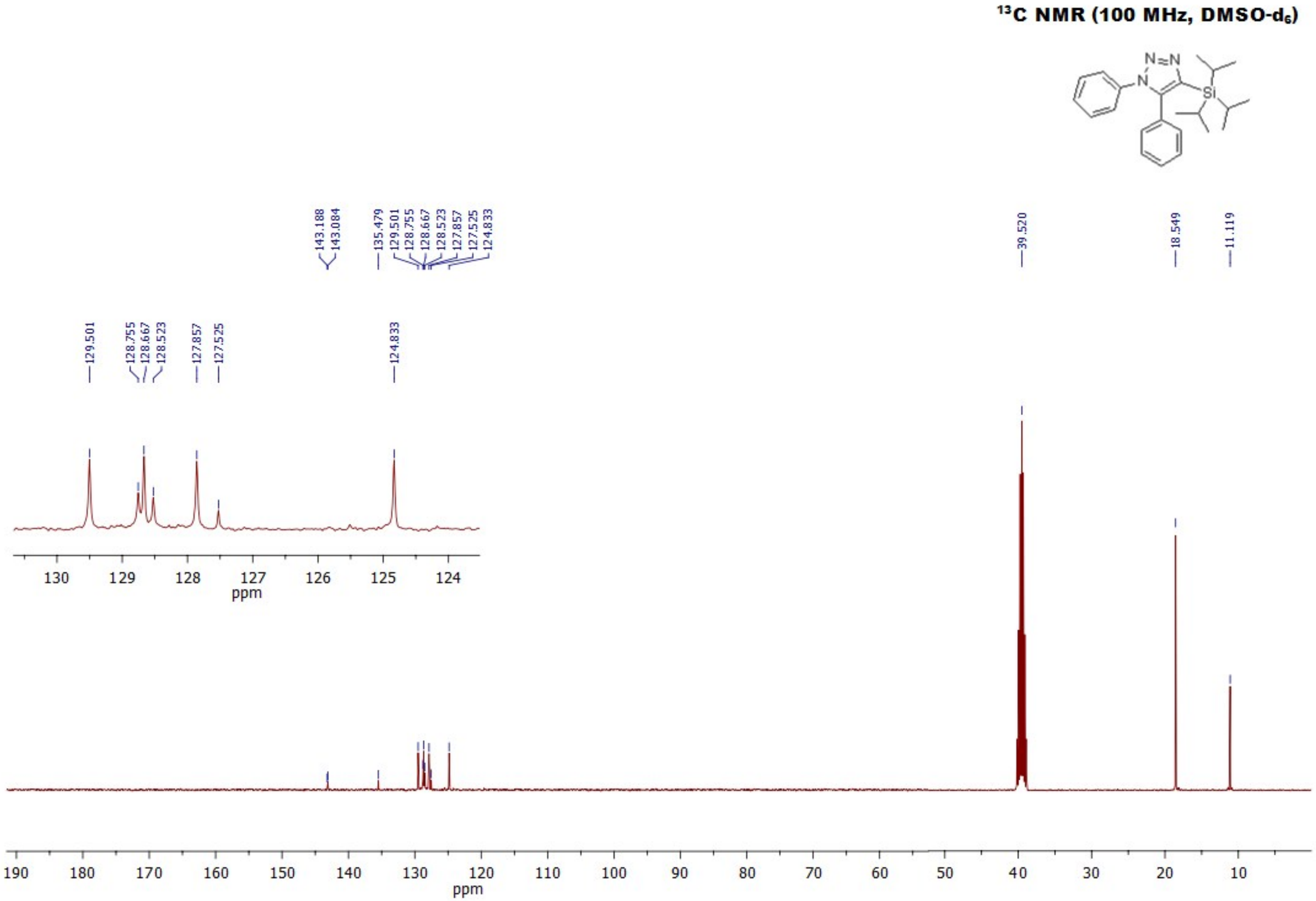
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 5-phenyl-1-(p-tolyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **(3dh).**



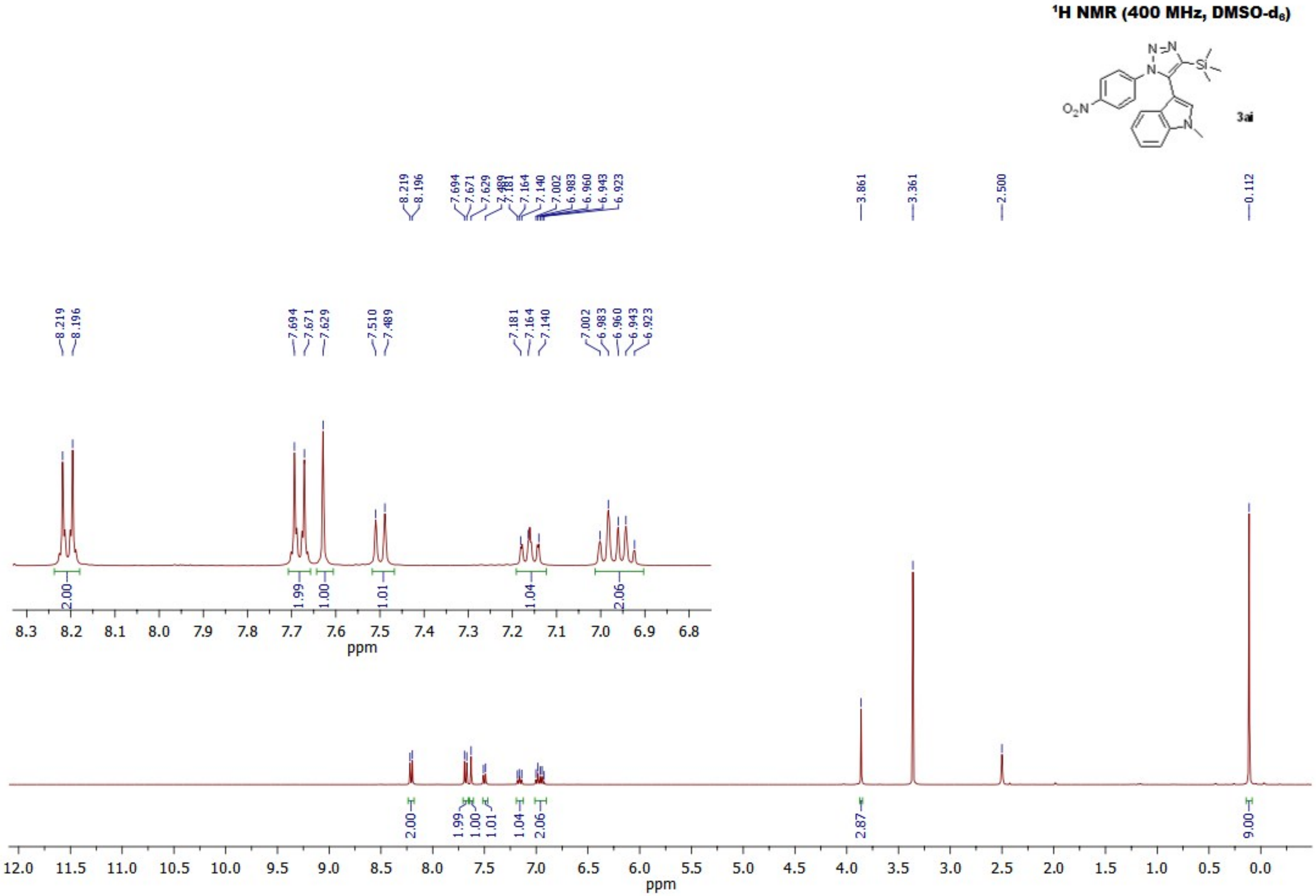
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1,5-diphenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **(3nh)**.



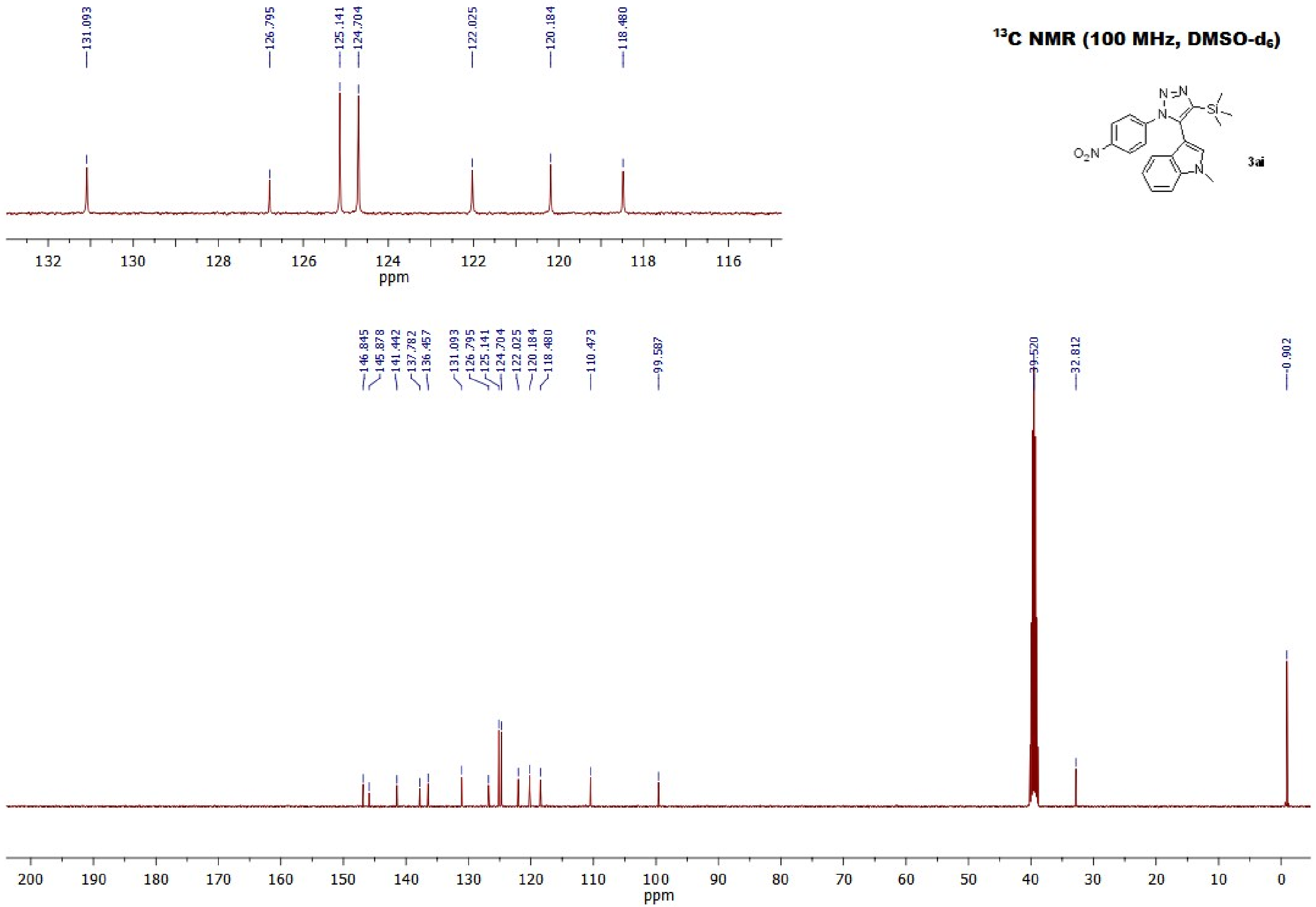
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1,5-diphenyl-4-(triisopropylsilyl)-*1H*-1,2,3-triazole **(3nh)**.



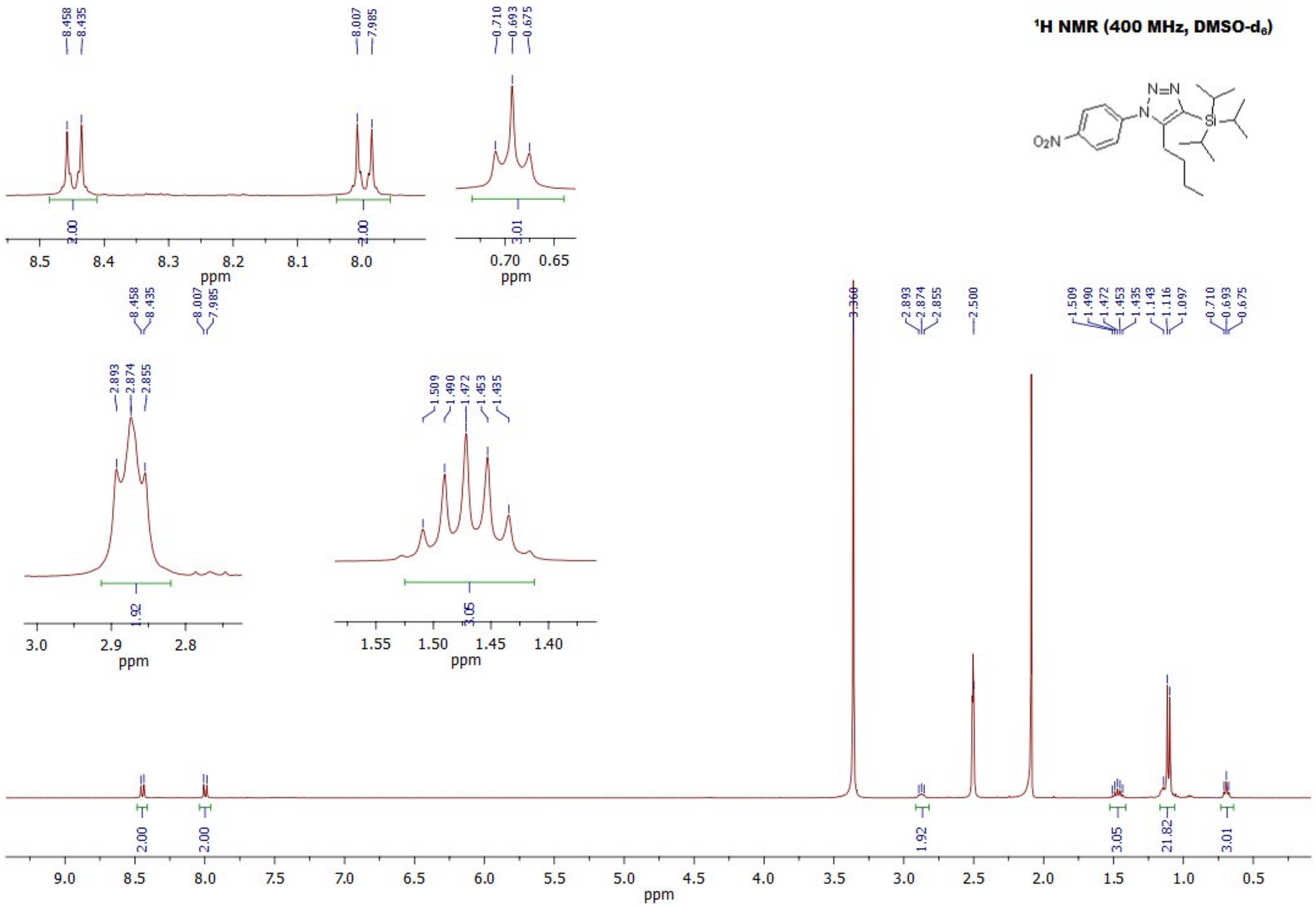
^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 1-methyl-3-(1-(4-nitrophenyl)-4-(trimethylsilyl)-*1H*-1,2,3-triazol-5-yl)-1H-indole **(3ai).**



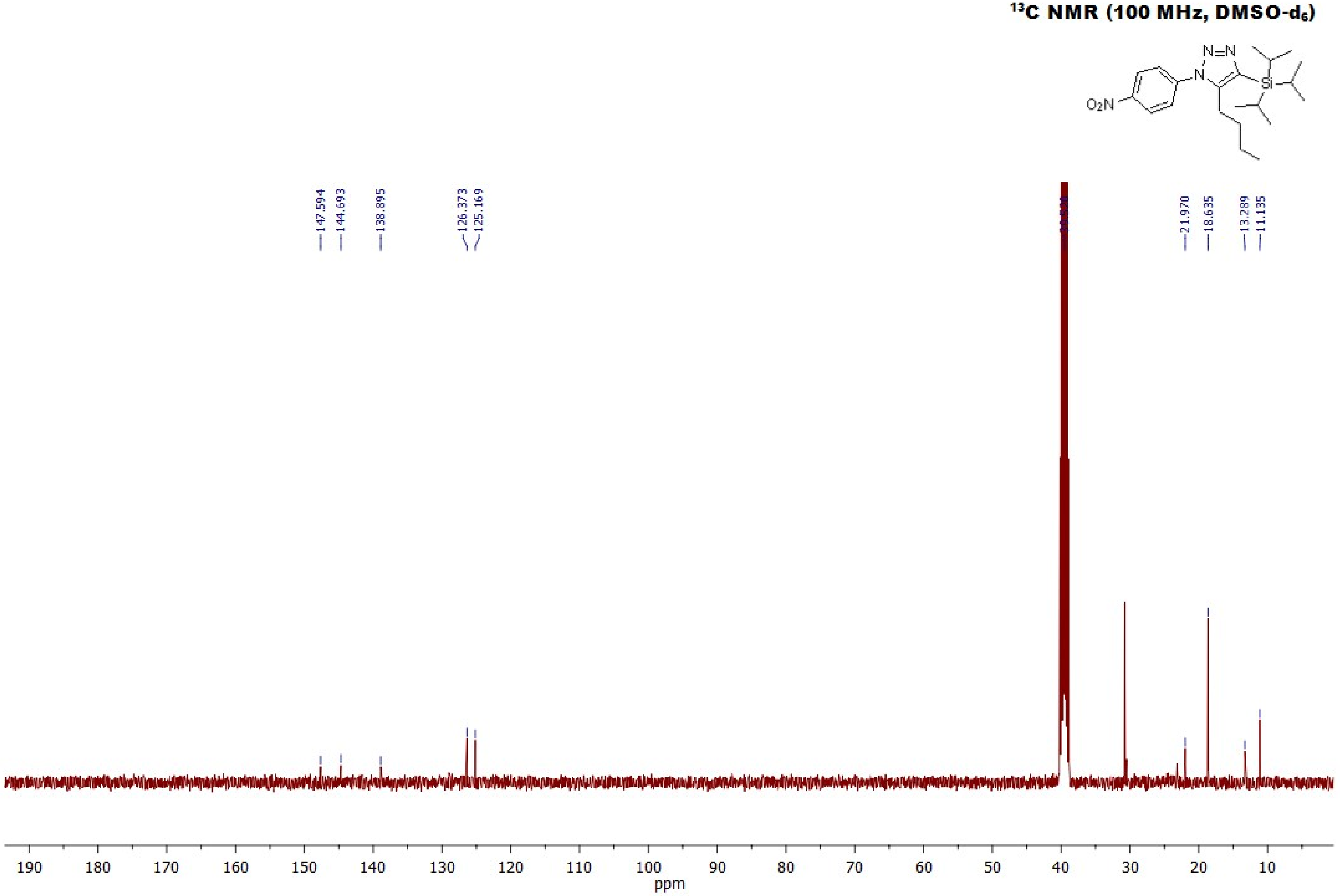
^{13}C NMR (100 MHz, DMSO-d$_6$) spectrum of 1-methyl-3-(1-(4-nitrophenyl)-4-(trimethylsilyl)-*1H*-1,2,3-triazol-5-yl)-indole **(3ai).**



^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of 5-butyl-1-(4-nitrophenyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole**(3aj).**



^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 5-butyl-1-(4-nitrophenyl)-4-(triisopropylsilyl)-*1H*-1,2,3-triazole**(3aj).**



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