Supporting information

A comparative study between heterogeneous stannous chloride loaded silica nanoparticles and homogeneous stannous chloride catalyst in the synthesis of 5-substituted 1H-tetrazole

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Material and methods

All chemicals were purchased from Sigma-Aldrich and Alfa aesar. Melting point of all compounds was measured using open capillary. ^{1}H NMR and ^{13}C NMR spectra's were obtained on Jeol 400 MHz spectrometer with DMSO-d_6 as a solvent and chemical shift was given in ppm in respect to tetramethylsilane. FT-IR spectra were recorded by using KBr pellets in range of 4000-400 cm^{-1} using Perkin Elmer 400 FT-IR spectrometer and some of FT-IR spectra were recorded by BRUKER Alpha instrument. Scanning electron microscopy (SEM) images were obtained on a Jeol JSM6610LV. Transmission electron microscopy (TEM) images were obtained using FEI 300 KV TechnaiG2T30. TGA data of the sample was obtained using Perkin Elmer, pyris diamond Software. X-rays analysis results were collected on Crysalis PRO (Oxford Diffraction, 2009) with graphite mono75 chromate Mo Kα radiation (λ = 0.71073 Å) and the structure was elucidated by direct method using SHELXL-86.

General procedure for the synthesis of tetrazoles using $SnCl_2$ catalyst

The representative 5-substituted 1*H*-tetrazole (1b) was synthesized by reported procedure [41]. Briefly, benzonitrile (103 mg, 1mmol) and sodium azide (97.5 mg, 1.5 mmol) were dissolved in 2 ml of anhydrous DMF in 25 ml round bottom flask and (19 mg, 10 mmol%) of $SnCl_2$ was added into it under inert atmosphere and stirred at 120 °C for 6 h. After the completion of the reaction, as monitored by TLC, the reaction mixture was diluted by 20 ml ethylacetate and 20 ml of 5M HCl solution. The aqueous layer was extracted with ethylacetate (3×20 ml). The combined organic layer was washed with 20 ml brine solution and dried over anhydrous sodium sulphate. The organic solvent was evaporated in vacuum to yield white solid compound, 5-phenyltetrazole 1b (131 mg, yield 90%). The title compound was characterized by ^{1}H, ^{13}C NMR, and IR. Melting point was recorded by open capillary method and uncorrected. The remaining tetrazoles (2b-20b) were synthesized in a similar fashion. The tetrazole 21b was synthesized by the same method by using of (128 mg, 1 mmol) of nitrile, (195 mg, 3 mmol) of sodium azide, and (38 mg, 20 mmol%) of $SnCl_2$.

General procedure for synthesis of tetrazoles using $SnCl_2$-nano-SiO_2 as catalyst

$SnCl_2$ loaded silica nanopaprticles were synthesized according to the published procedure [41]. Briefly, (77.15 mg, 5 mmol%,) of $SnCl_2$-nano-SiO_2 catalyst was added in the mixture of (103 mg, 1 mmol) of benzonitrile (1a) and (97.5 mg, 1.5 mmol) of sodium azide in 2 ml anhydrous DMF. The reaction mixture was heated to 100 ^oC for 4 hours under stirring. After the completion of reaction that shown by TLC, the reaction mixture was cooled to room temperature, and the catalyst was separated using centrifugation and washed three times with ethylacetate. The centrifugate was treated with 5 ml of ethylacetate and 8 ml of 5M HCl under vigorous stirring for 5 min. The resultant organic phase was separated. The aqueous phase was again extracted with ethylacetate. The combined organic phase was then washed with brine (2x10 ml) and water (2x10 ml). The organic phase was evaporated to give desired 5-phenyltetrazole 1b (134 mg, yield 92%). The remaining tetrazoles (2b-20b) were synthesized in a similar fashion. The tetrazole 21b was also synthesized by this method by using of (128 mg, 1 mmol) of nitrile, (195 mg, 3 mmol) of sodium azide, and (154 mg, 20 mmol%) of $SnCl_2$-nano-SiO_2.

Recyclability of catalyst:

In order to study of reusability of the $SnCl_2$-nano-SiO_2 catalyst, five batches of experiments were carried out for the preparation of 1b from 1a (Figure 7 of ms). The catalyst was separated using centrifugation of the reaction mixture and it was washed each time using EtOAc and dry at 100 °C in oven for 3 h and reused in the new reaction. Moreover, the shape and the size of $SnCl_2$-nano-SiO_2 catalyst remained same in fresh and after five time reuse as seen by TEM analysis. The recyclability experiment also confirmed that $SnCl_2$-nano-SiO_2 catalyst is very stable.

X-ray analysis data of compound 6b

Data collection: CrysAlis PRO (Oxford diffraction 2009); cell refinement: CrysAlis PRO (Oxford diffraction 2009); data reduction: CrysAlis PRO; program(s) used to solve structure. SHELXS97

(Sheldrick, 1997); program (s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Mercury (Macrae, et al. 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

Crystal data (CCDC Number 999827)

$C_7H_5BrN_4O \cdot O$	$D_x = 1.858$ Mg m^{-3}
$M_r = 257.05$	Mo Kα radiation, $\lambda = 0.71073$ Å
Orthorhombic, Pbca	Cell parameters from 2519 reflections
Hall symbol: -P 2ac 2ab	$\theta = 0.3$-$29.3°$
a = 7.169 (3) Å	$\mu = 4.45$ mm^{-1}
b = 13.975 (6) Å	T = 298 K
c = 18.344 (9) Å	Niddle, colourless
V = 1837.8 (14) Å^3	0.30 × 0.20 × 0.10 mm
Z = 8	*F*(000) = 1008.0

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer	844 reflections with I > 2σ(I)
Radiation source: fine-focus sealed tube	$R_{int} = 0.234$
Graphite monochromator	$\theta_{max} = 29.3°$, $\theta_{min} = 3.1°$
ω scan	h = -8, 9
Absorptioncorrection:multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)	k = -18, 19
$T_{min} = 0.357$, $T_{max} = 0.641$	l = -23, 25
12527 measured reflections	Standard reflection: numb; every numb reflections
2519 independent reflections	intensity decay: numb

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.119$	H-atom parameters constrained
$wR(F^2) = 0.387$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.92$	$(\Delta/\sigma)_{max} < 0.001$
2296 reflections	$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{max} = 0.70$ e Å^{-3}	$\Delta\rho_{min} = -1.53$ e Å^{-3}
0 restraints	Extinction correction: none, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	

Computational details

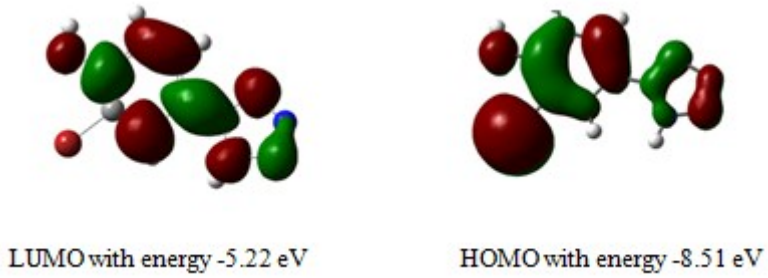


Figure S-1: HOMO and LUMO of compound **6b**

Gaussian 09 [42] program package were used to compute the optimized geometry, structural parameters, HOMO-LUMO orbitals and vibrational bands of compound 6b using Density Functional Theory with 6-311G basis sets. PED analysis along with the assignments of the vibrational levels was carried out by using VEDA program [43]. The optimized structure of the compound 6b is given in Figure 6 in ms and HOMO-LUMO orbitals are given in Figure S-1. The

calculated ^{1}H and ^{13}C NMR chemical shift without any solvent were obtained using gauge including atomic orbital (GIAO) method at the B3LYP/6-311+G(2d,p) level of theory with respect to TMS as a reference and are good agreement with the experimental data. HOMO-LUMO = -3.29 eV

Comparative study of calculated and experimental geometrical parameters of compound 6b:

The calculated geometrical parameters (bond lengths and bond angles) obtained by DFT calculations using B3LYP/6-311G basis set and experimental geometrical parameters of X-ray structure of crystal are collected in Table S-1. The calculated bond distances derived from the B3LYP/6-311G calculation also matched well with the experimental bond parameters. Calculated bond lengths of the C-C bond in aryl ring attached to tetrazole moiety is in between 1.39 and 1.46 °A, while experimentally, it ranges from 1.36 to 1.46 °A. These bond length are shorter than C-C single bond (1.54 °A) and longer than C=C double bond (1.34 °A). C-C, C-N and C-Br bond length that given in below table shown that experimental and theoretical bond length are in good agreement and very close to each other. When the X-ray structure of the title compound is compared with its optimised counterparts, minor conformational discrepancies are observed between them.

Table S-1: Calculated and experimental structural parameters (Bond lengths and bond angles) of compound 6b

Structural parameters (Bond length)	B3LYP/6-311G(d, p)	Bond lengths of X-ray structure of 6b (A°)	Structural parameters (Bond angle)	B3LYP/6-311G(d, p)	Bond angles of X-ray structure of 6b (A°)
C3-C4	1.39	1.39	C3-C4-C5	120.69	120
C4-C5	1.40	1.36	C3-C4-H4	119.91	120
C4-H4	1.08	0.93	C5-C4-H4	119.40	120
C2-C3	1.41	1.39	C2-C3-C4	120.22	119
C3-H3	1.08	0.93	C4-C3-H3	120.80	120
C2-C7	1.40	1.36	C2-C3-H3	118.98	120
C1-C2	1.46	1.46	C3-C2-C7	118.89	119
C6-C7	1.39	1.40	C1-C2-C3	119.02	119
C7-H7	1.08	0.93	C1-C2-C7	122.09	122
C5-C6	1.40	1.36	C2-C7-C6	120.68	121
C6-Br1	1.94	1.88	C2-C7-H7	121.24	120
C5-O1	1.38	1.37	C6-C7-H7	118.08	120
C1-N1	1.36	1.36	C5-C6-C7	120.31	120
C1-N4	1.34	1.33	C7-C6-Br1	119.76	119.1
O1-H1	0.97	0.82	C5-C6-Br1	119.93	121.2
N1-N2	1.39	1.36	C4-C5-C6	119.21	120
N1-H1A	1.00	0.86	C4-C5-O1	122.65	124
N2-N3	1.32	1.29	C6-C5-O1	118.14	116
N3-N4	1.39	1.36	C2-C1-N1	127.38	127
			C2-C1-N4	125.18	125
			N1-C1-N4	107.44	108
			C5-O1-H1	112.42	109
			C1-N1-N2	109.65	110
			C1-N1-H1A	131.30	125
			N2-N1-H1A	119.05	125
			N1-N2-N3	105.48	105
			N2-N3-N4	110.66	112
			C1-N4-N3	106.77	105.1

NMR and IR SPECTRA (1b - 21b)

1. **5-Phenl-1H-tetrazole** (1b): White solid, mp: 215-216 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 17.45 (1H, br), 7.99 (2H, d), 7.54 (3H, t). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.93, 131.84, 129.78, 127.33, 124.63, and 120.69. FT-IR, cm^{-1}: 2919, 1601, 1457, 1281, 722.

2. **5-(4-Chlorophenyl)-1H-tetrazole** (2b): White solid, mp: 264-266 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 16.81 (1H, br), 8.00 (2H, d), 7.61 (2H, d), ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 154.96, 135.82, 129.43, 128.61 and 123.27. FT-IR, cm^{-1}: 2696, 1650, 1349, 1083, 822.

3. **5-(4-Bromophenyl)-1H-tetrazole** (3b): Brown solid, mp: 234-235 °C. ^{1}H NMR (400MHz, DMSO-d_6) δ (ppm):16.96 (1H, br), 7.93 (2H.d), 7.77 (2H, d); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.11, 132.43, 128.83, 124.58, 123.45; FT-IR, cm^{-1}: 2919, 2849, 1721, 1595, 1046, 1010, 822, 734.

4. **5-(p-Tolyl)-1H-tetrazole** (4b): White solid, mp 246-248 °C. ^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm): 16.67 (1H, br), 7.85 (2H, d), 7.34 (2H, d), 2.32 (3H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.58, 141.75, 130.47, 127.42, 121.90 and 21.55. FT-IR cm-1: 2917, 2849, 1866, 1609, 1159, 985, 818, 736.

5. **2-Chloro-4-(1H-tetrazol-5-yl)pyridine** (5b): White solid, mp 198-200 °C. ^{1}H NMR (400MHz, DMSO-d_6) δ (ppm):15.54 (1H, br), 9.45 (1H, s), 8.76 (1H, d), 7.95 (1H, d). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 151.19, 148.23, 135.49, 129.05, 115.13 and 11316. FT-IR cm^{-1}: 3077, 2429, 1643, 1426, 1005, 752.

6. 3-**Bromo-4-(1H-tetrazole-5yl)-phenol** (6b): Brown solid, mp 175-176°C. ^{1}H NMR (400MHz, DMSO-d_6) δ (ppm): 11.09 (1H.br), 8.13 (1H.d), 7.84 (1H, dd), 7.09 (1H.d). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 157.17, 154.71, 132.00, 128.73, 117.19, 117.02 and 110.46. FT-IR cm^{-1}: 3078, 2723, 1604, 1600, 1291, 853, 740.

7. **5-(3-Bromo-4-methoxy-phenyl)-1H-tetrazole** (7b): White solid, mp 197-198 °C. ^{1}H NMR (400MHz, DMSO-d_6) δ (ppm):16.67 (1H, br), 8.19 (1H, d), 8.19 (1H, d), 8.00 (1H, d), 7.32 (1H, d), 3.70 (3H, s). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 157.47, 137.20, 128.00, 117.74, 113.31, 111.26 and 56.59; FT-IR cm^{-1}: 3065, 3011, 2976, 2906, 2839, 2314, 1604, 1489, 1012, 815.

8. **3-(1H-tetrazol-5-yl)pyridine (8b):** White solid, **mp** 238-240 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 9.21 (1H, s), 8.71-8.72 (1H, d), 8.41-8.44 (1H, t), 7.53-7.57 (1H, d). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 164.00, 155.77, 147.67, 135.99, 132.94, 124.98; FT-IR cm^{-1} 3013.16, 2313.16, 1846.22, 1642.94, 1485.37, 1005.9, 752.76.

9. **4-(1H-tetrazol-5-yl)pyridine (9b):** White solid, mp 254-256 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.71-8.72 (2H, d), 7.91-7.92 (2H, d). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 154.55, 149.45, 134.50, 121.35; FT-IR cm^{-1}: 3417, 1643, 1606, 1394, 1155, 1005, 753.

10. **4-(1H-tetrazol-5-yl) benzonitrile (10b):** White solid, mp 194-196 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.27-8.29 (2H, d), 8.06-8.08 (2H, d). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 155.77, 133.89, 128.48, 128.29, 118.89, 113.91; FT-IR cm^{-1} : 2919.35, 2899.35, 2223.82, 1721.03, 1594.76, 1423.15, 822.22.

11. **1-(4-(1H-tetrazol-5-yl)phenyl)ethanone (11b):** White solid, mp 172-175 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.04-8.06 (2H, d), 7.99-8.00 (2H, d), 2.37 (1H, s). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 197.96, 156.86, 138.24, 130.77, 129.59, 127.38, 27.38. FT-IR cm^{-1} 3324, 1668, 1572, 1423, 1362, 1267, 1153, 959, 841, 752.

12. **5-(Anthracen-9-yl)-1H-tetrazole (12b):** White solid, mp 214-216 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.05 (1H, s), 8.26-8.28 (4H, d), 7.82-7.86 (2H, t), 7.69-7.71 (2H, t). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 134.22, 133.00, 130.74, 130.43, 129.79, 127.19, 124.79, 117.41; FT-IR cm^{-1} 3363, 2916, 1701, 1520, 1443, 1363, 1227, 1162, 898, 731.

13. **N,N-Dimethyl-4-(1H-tetrazol-5-yl)aniline (13b):** Yellow solid, mp 79.0-81.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.96-7.99 (2H, d), 6.82-6.85 (2H, d), 3.05 (6H, s). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 153.90, 152.01, 128.19, 121.57, 113.25; FT-IR cm^{-1} 3473, 3354, 2211, 1621, 1600, 1512, 1315, 1173, 828.

14. **4-(1H-tetrazol-5-yl)aniline (14b):** Light orange solid, mp 266.0-269.0 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.35-7.37 (d, 2H), 6.58-6.60 (d, 2H), 6.12 (s, 2H). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm) 162.22, 153.01, 133.43, 120.69, 113.44, 95.47; FT-IR cm^{-1}: 3483.72, 3384.00, 2711.31, 1621.47, 1315.01, 1173.18, 828.59.

15. **5-Benzyl-1H-tetrazole** (15b): White solid, mp 123-124 ˚C. ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 16.15 (1H, br), 7.19-7.37 (5H, m), 4.25 (2H, s). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 155.71, 136.45, 129.46, 129.22, 129.16, 128.59, 128.11, 127.31, 29.43; FT-IR cm^{-1}: 3029, 2948, 2852, 1527, 1429, 1105, 883, 731, 691

16. **5-(3-Methylbenzyl)-1H-tetrazole** (16b): White solid, mp: 125-128 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 16.22 (1H, br), 7.15-7.19 (1H, m), 6.99-7.03 (3H, m), 4.19-4.23 (2H, s), 2.22 (3H, s). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 155.78, 138.39, 136.34, 129.75, 129.12, 128.14, 126.22, 29.35, 21.44; FT-IR cm^{-1}: 2985, 2838, 1820, 1487, 1083, 783.

17. **5-(4-Methylbenzyl)-1H-tetrazole** (17b): White solid, mp: 152-155 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.04-7.13 (4H, m), 4.16 (2H, s), 2.20 (3H, s). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 155.90, 136.63, 133.39, 129.76, 129.03, 29.02, 21.12; FT-IR cm^{-1}: 3000, 2861, 2695, 1083, 753.

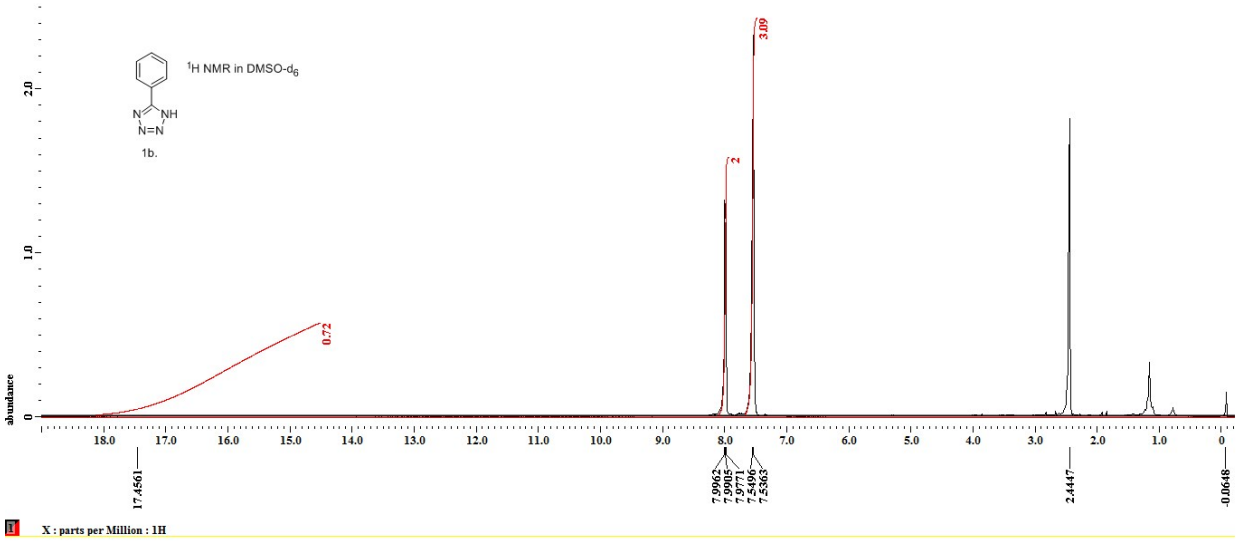
18. **5-(3-Chlorobenzyl)-1H-tetrazole** (18b): White solid, mp: 130-134˚C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 16.23 (1H, br), 7.22-7.34 (3H, m), 7.19 (1H, d), 4.27 (2H, s). ^{13}C NMR (100MHz, DMSO-d_6) δ (ppm): 155.02, 138.24, 133.15, 130.48, 128.64, 127.47, 127.00, and 29.67; FT-IR cm^{-1}: 2967, 2847, 1767, 1595, 1435, 1097, 748, 605.

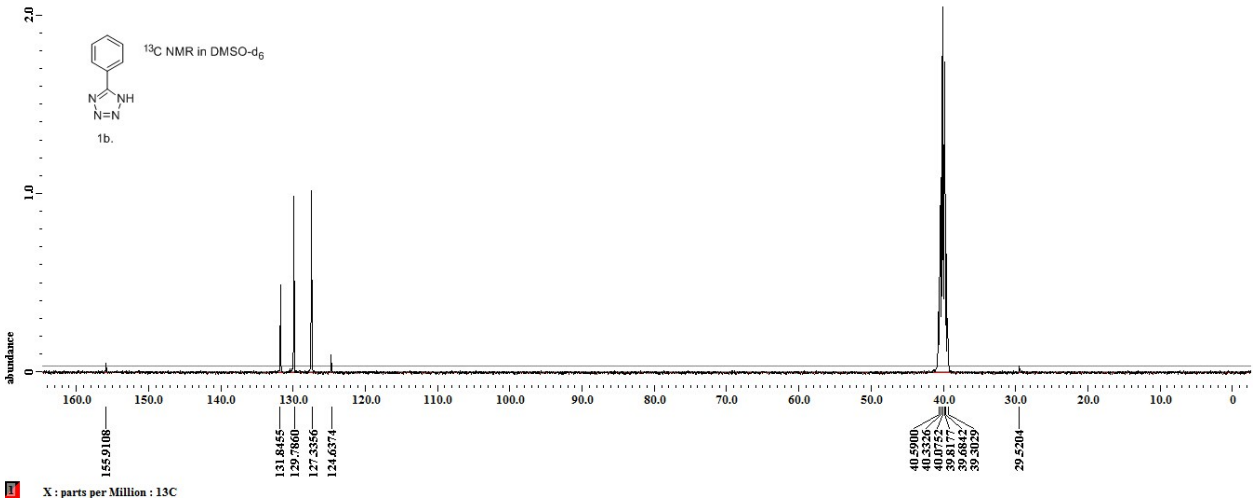
19. **5-(4-Chloro benzyl)-1H-tetrazole** (19b): White solid, mp 157-160˚C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 16.10 (1H, br), 7.36 (2H, d), 7.26 (2H, d), 4.25 (2H, s). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.80, 135.41, 132.27, 131.16, 129.16, and 28.73; FT-IR cm^{-1}: 2985, 2838, 2696, 2317, 1487, 1404, 1048, 763, 654.

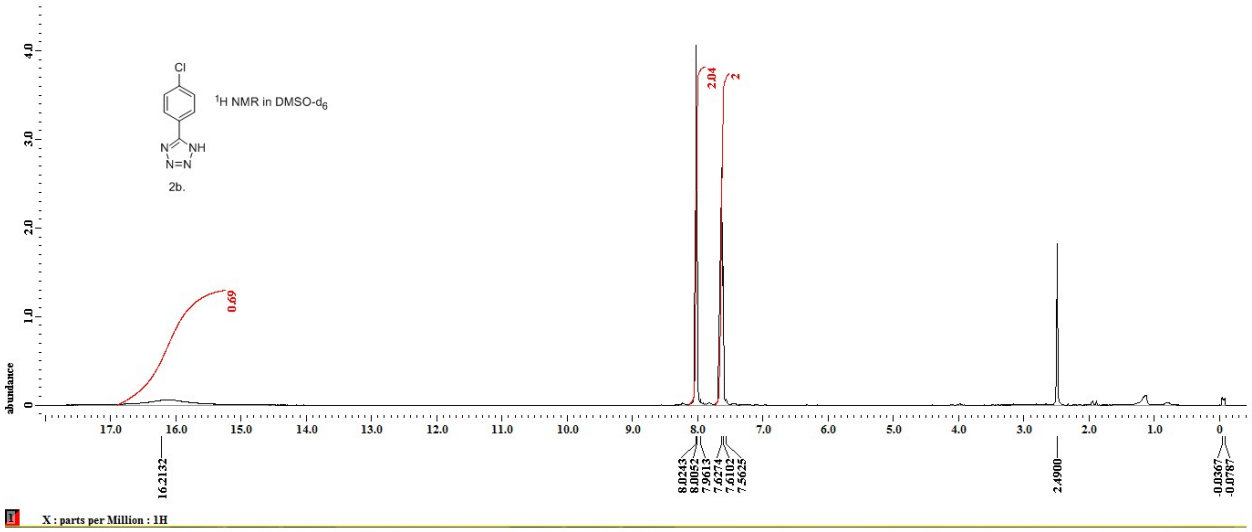
20. **5-(2,6-dichlorophenyl)-1H-tetrazole** (20b): White solid, mp 112-115˚C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.74 (2H, s), 7.53-7.47 (1H, m). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 161.81, 133.53, 131.49, 130.26, and 128.83; FT-IR cm^{-1}: 3430, 2926, 2126, 1432, 1200, 1096, 784.

21. **5,5'-(4-nitro-1,2-phenylene)bis(1H-tetrazole)** (21b): Brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.06-8.04 (1H, d), 7.73 (1H, s), 7.47-7.44 (1H, d). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.29, 145.11, 142.80, 136.70, 129.64, 125.37, and 121.61; FT-IR cm^{-1}: 3444, 3248, 2926, 2124, 1606, 1306, 1038, 834, 524.

Images of NMR Spectra's (1b-21b)



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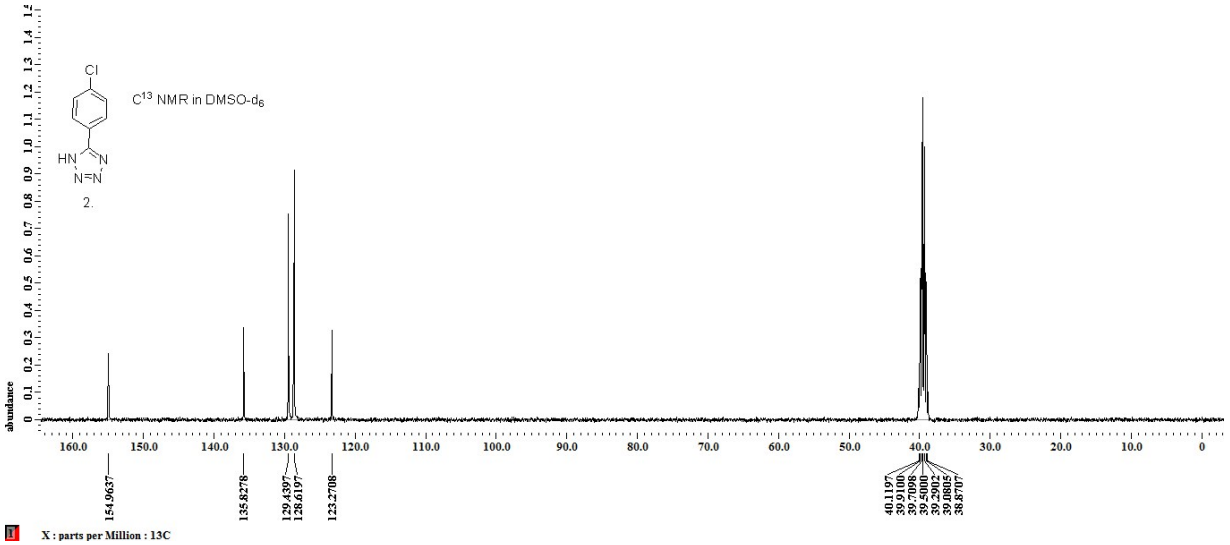
X : parts per Million : 1H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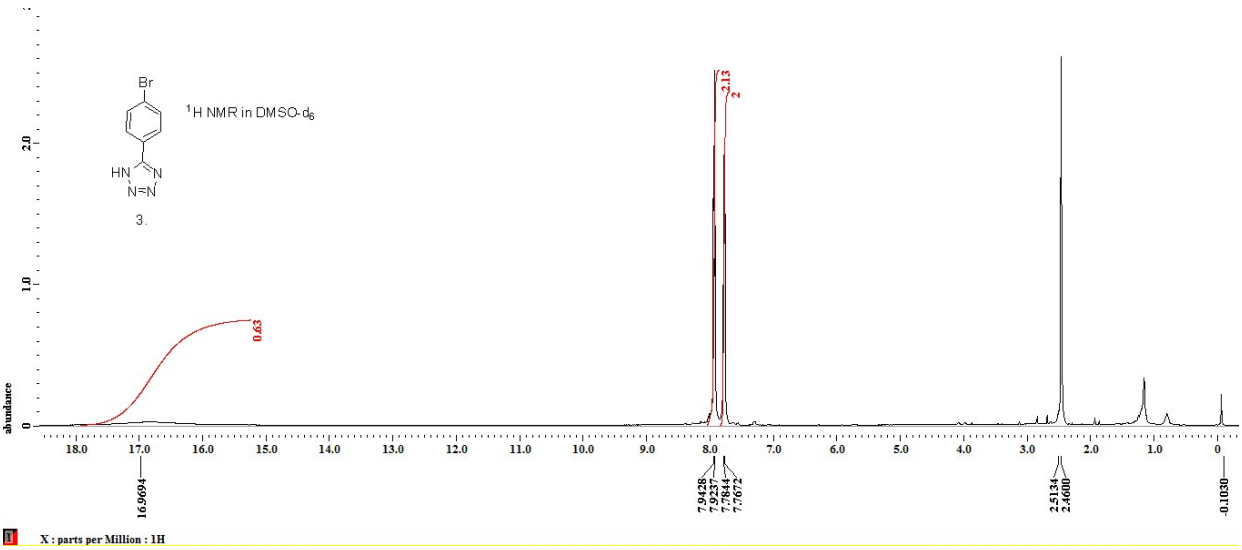
X : parts per Million : 13C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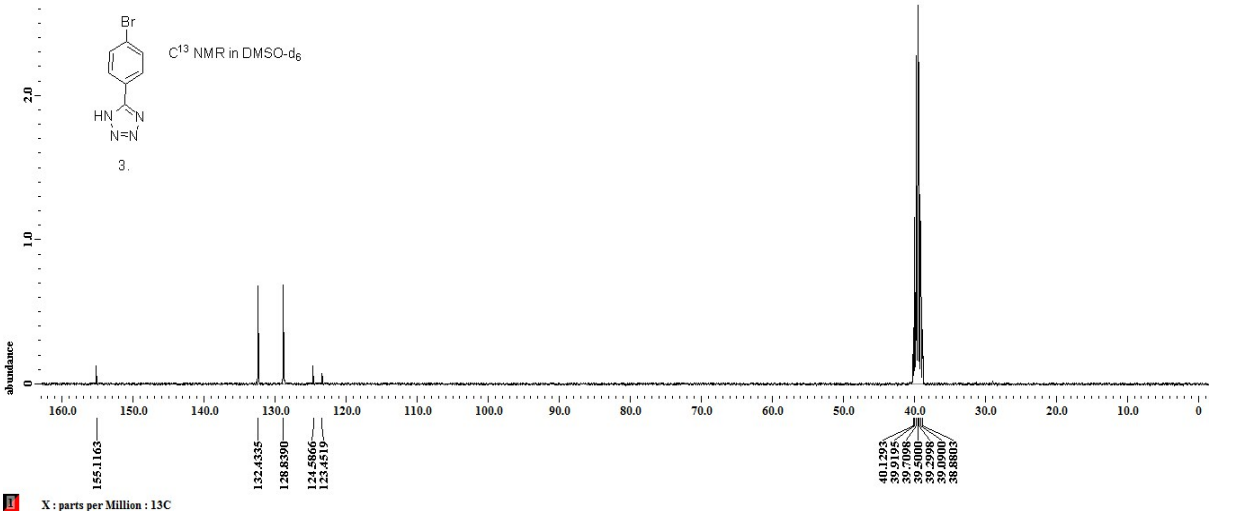
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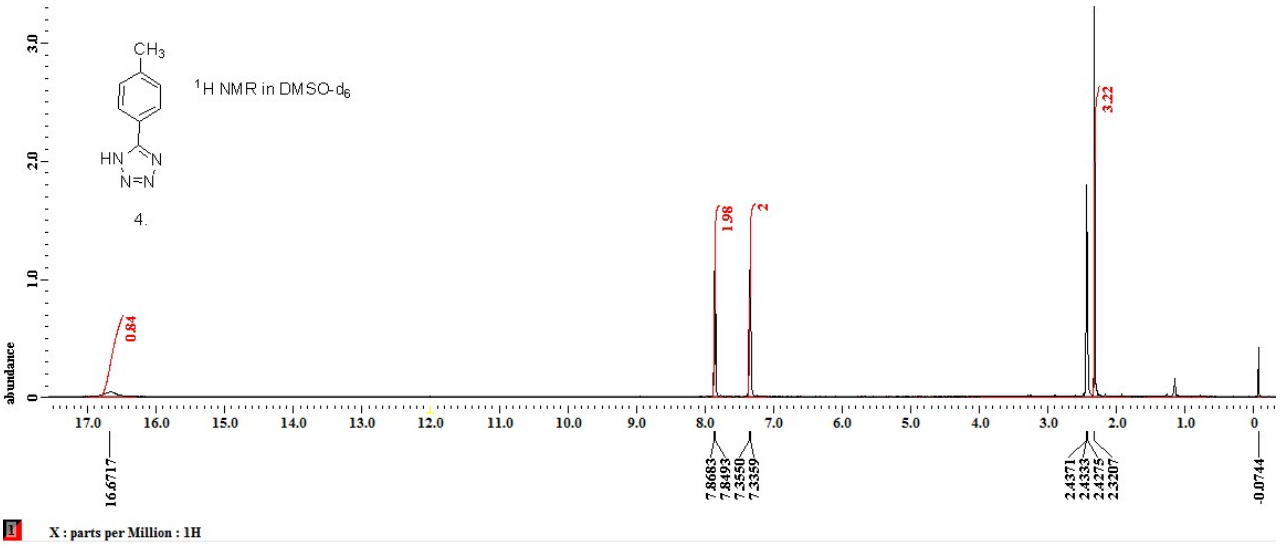
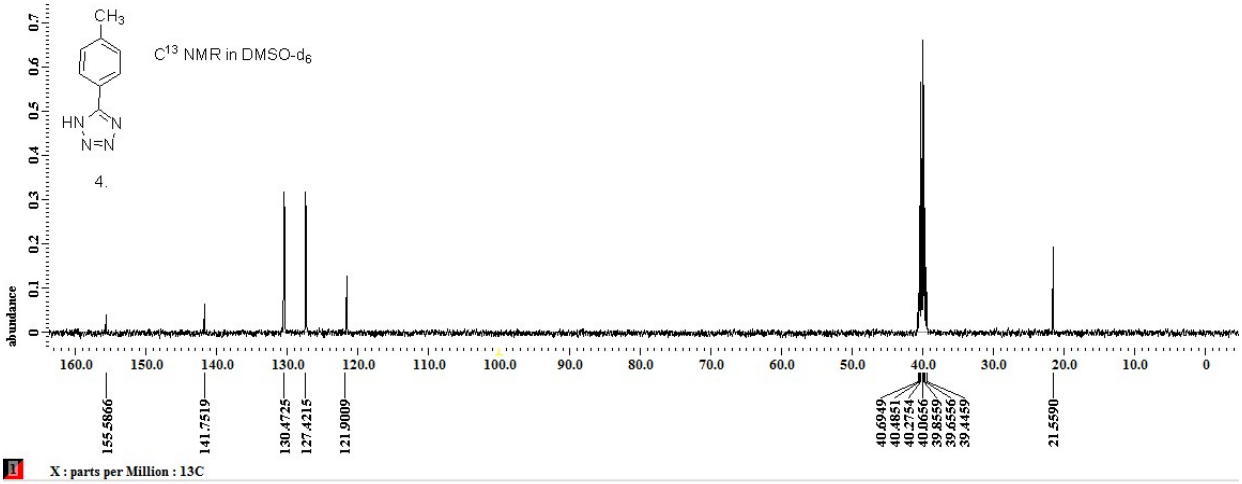
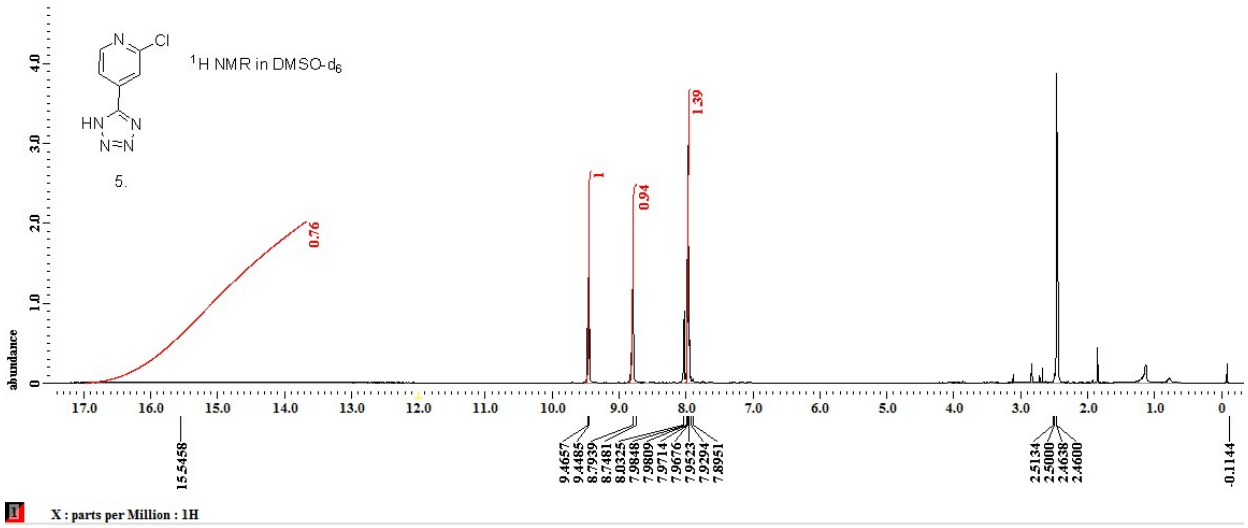
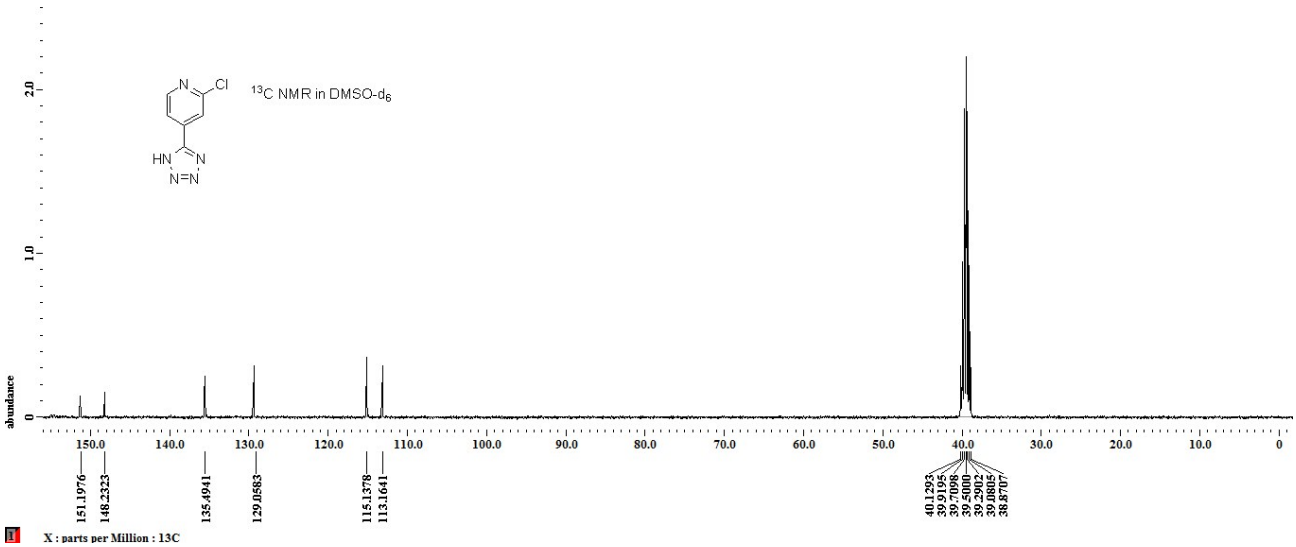
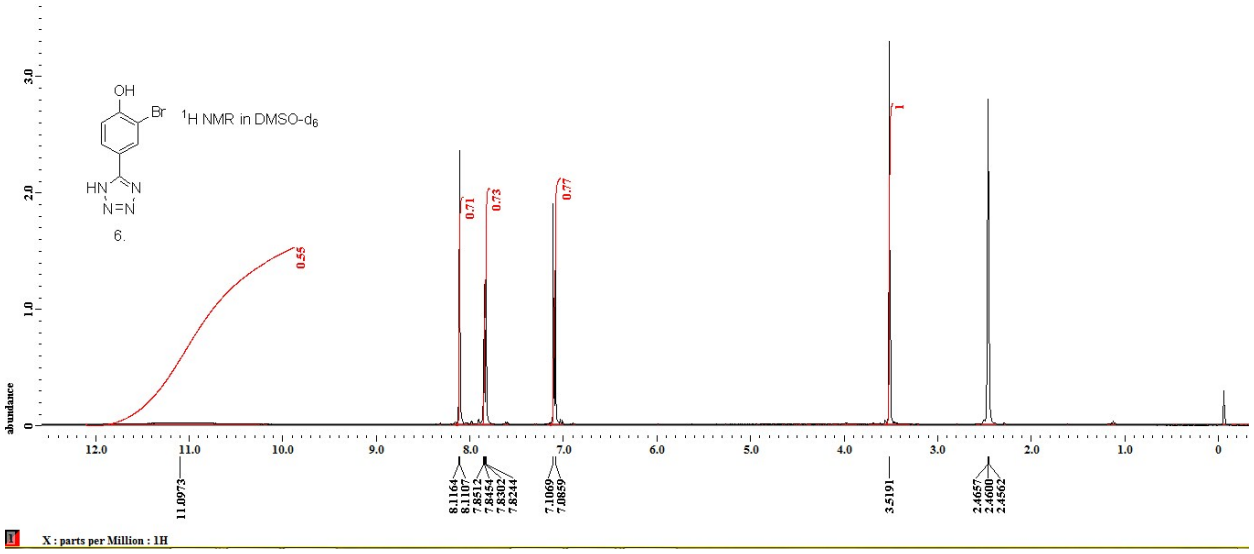
40.1293
39.9195
39.7098
39.5000
39.2903
39.0805
38.8803
X : parts per Million : 13C

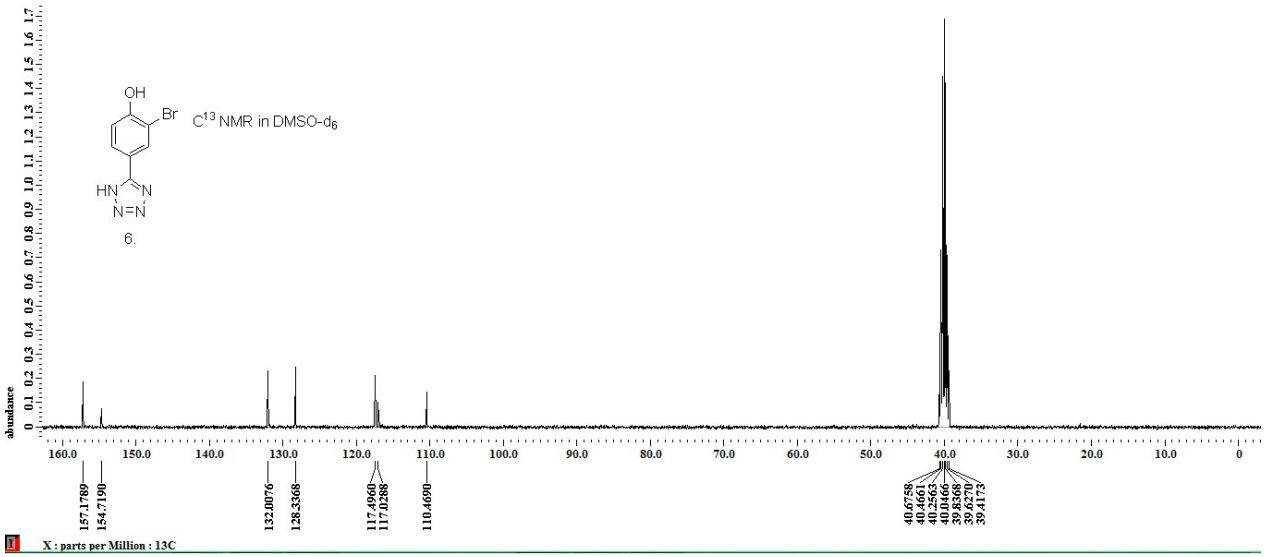

CH3
HN
N=N
N
4.
1H NMR in DMSO-d6
abundance
0.84
1.98
2
3.22
16.6717
7.8683
7.8493
7.3550
7.3359
2.4371
2.4333
2.4125
2.3207
-0.0744
X : parts per Million : 1H

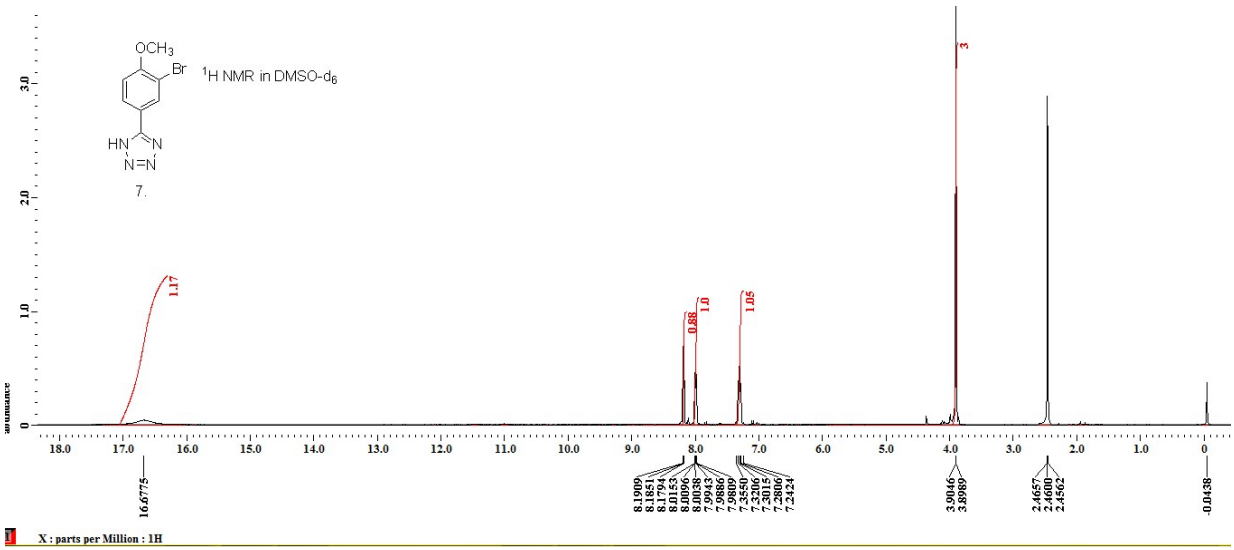

CH3
HN
N=N
N
4.
C13 NMR in DMSO-d6
abundance
155.5866
141.7519
130.4725
127.4215
121.9009
40.6949
40.4851
40.2754
40.0656
39.8559
39.6556
39.4459
21.5590
X : parts per Million : 13C

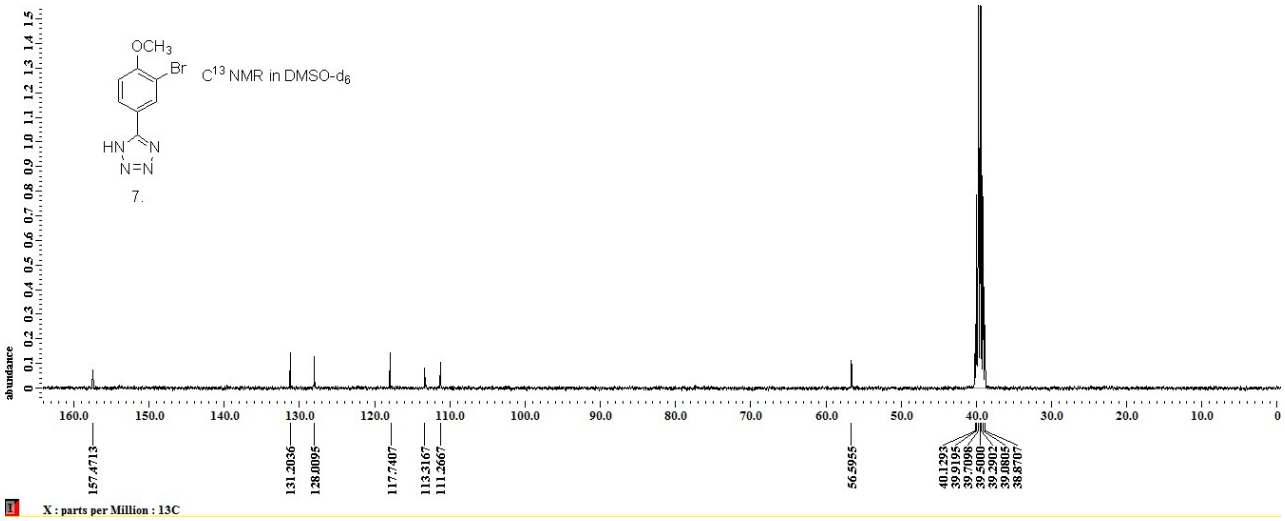

^{1}H NMR in DMSO-d$_6$
5.
abundance
0.76
1
0.94
1.39
15.5458
9.4657
9.4485
8.7939
8.7481
8.0325
7.9848
7.9809
7.9714
7.9676
7.9523
7.9294
7.8951
2.5134
2.5000
2.4638
2.4600
-0.1144
X : parts per Million : 1H

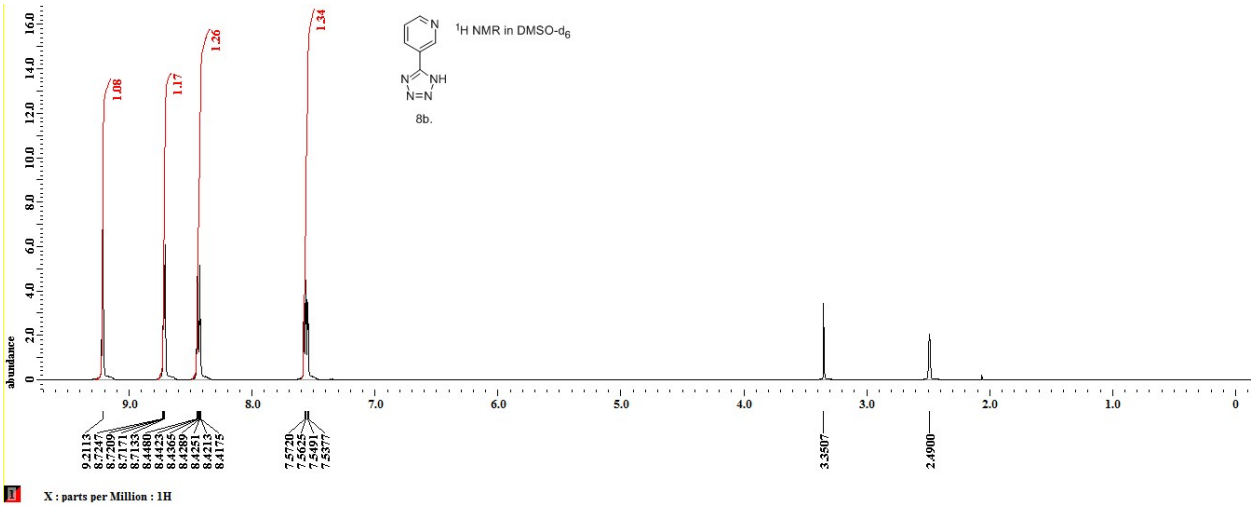

^{13}C NMR in DMSO-d$_6$
abundance
151.1976
148.2323
135.4941
129.0583
115.1378
113.1641
40.1293
39.9195
39.7098
39.5000
39.2902
39.0805
38.8707
X : parts per Million : 13C

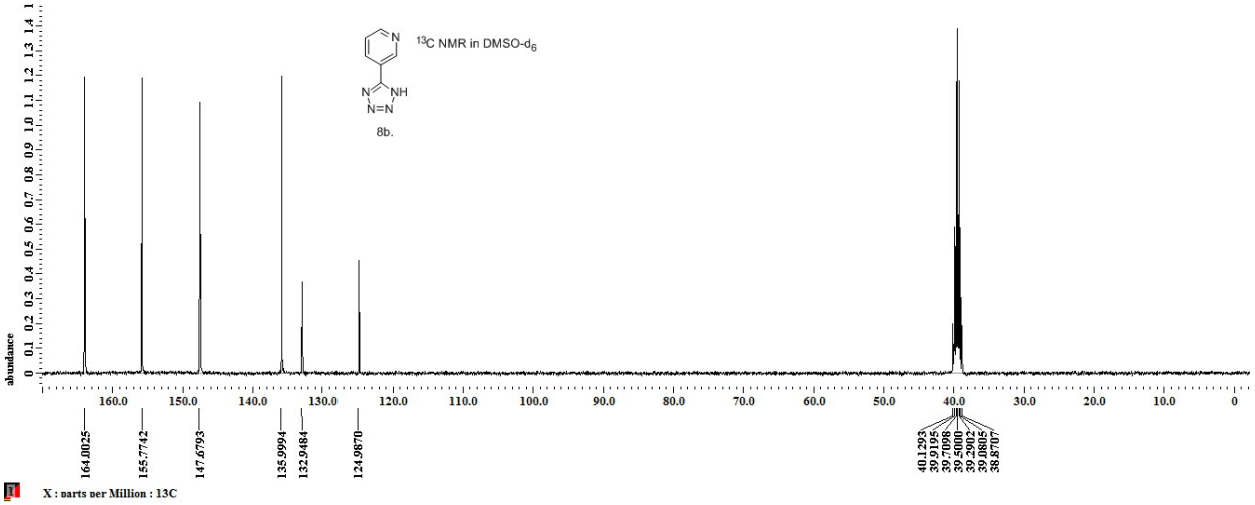

OH
Br
HN
N
N=N
6.
^{1}H NMR in DMSO-d$_6$
0.55
0.71
0.73
0.77
1
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
11.0973
8.1164
8.1107
7.8512
7.8454
7.8302
7.8244
7.1069
7.0859
3.5191
2.4657
2.4600
2.4502
X : parts per Million : 1H

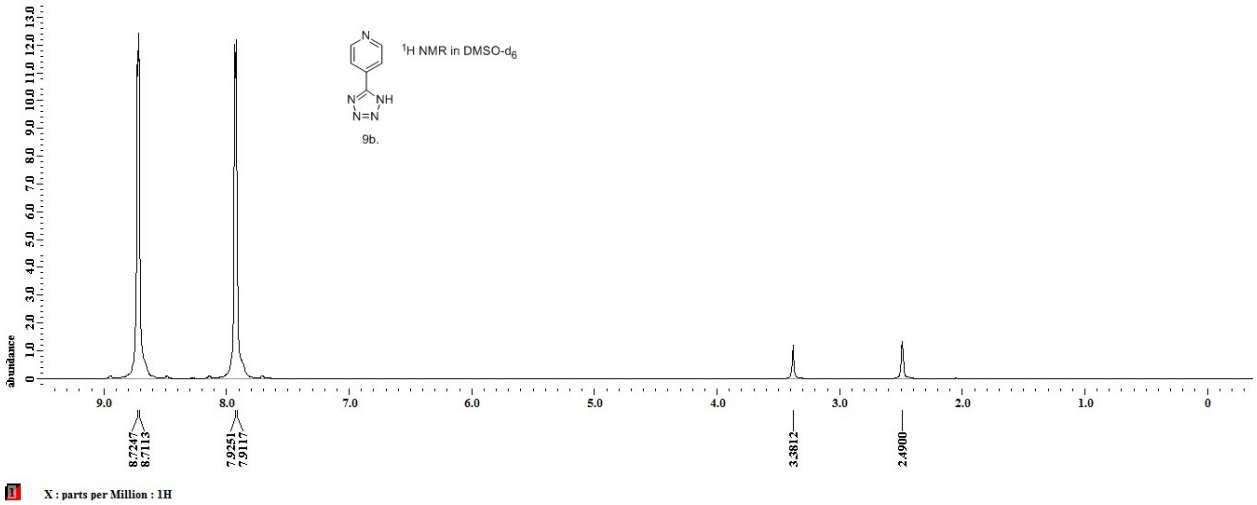

OH
Br
HN
N
N=N
6.
C^{13} NMR in DMSO-d$_6$
abundance
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.1789
154.7190
132.0076
128.3368
117.4960
117.0288
110.4690
40.6758
40.4661
40.2563
40.0466
39.8368
39.6270
39.4173
X : parts per Million : 13C

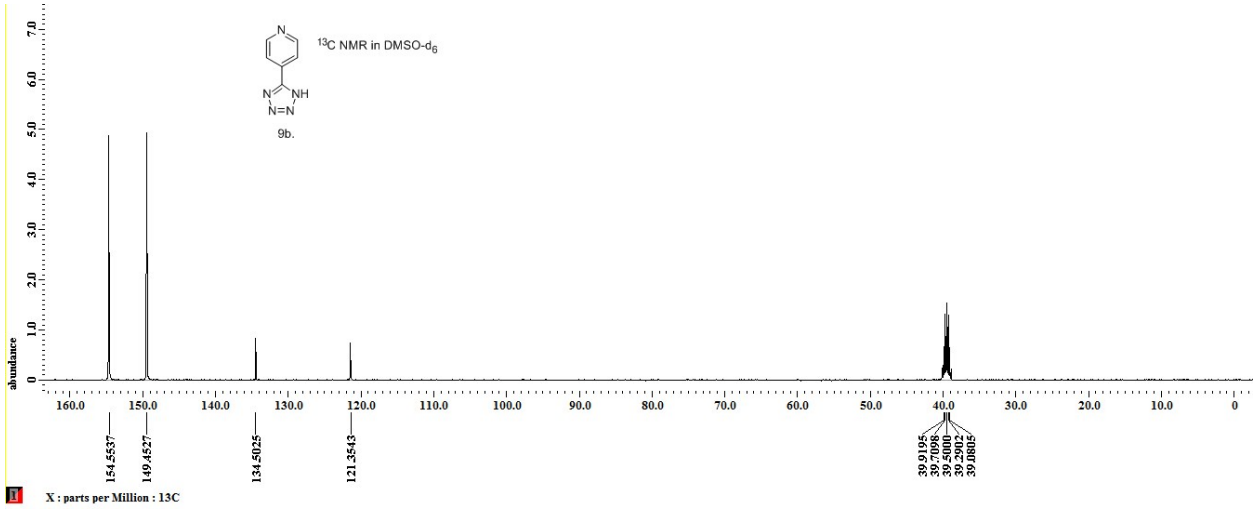

OCH3
Br
HN
N
N=N
7.
1H NMR in DMSO-d6
abundance
X : parts per Million : 1H

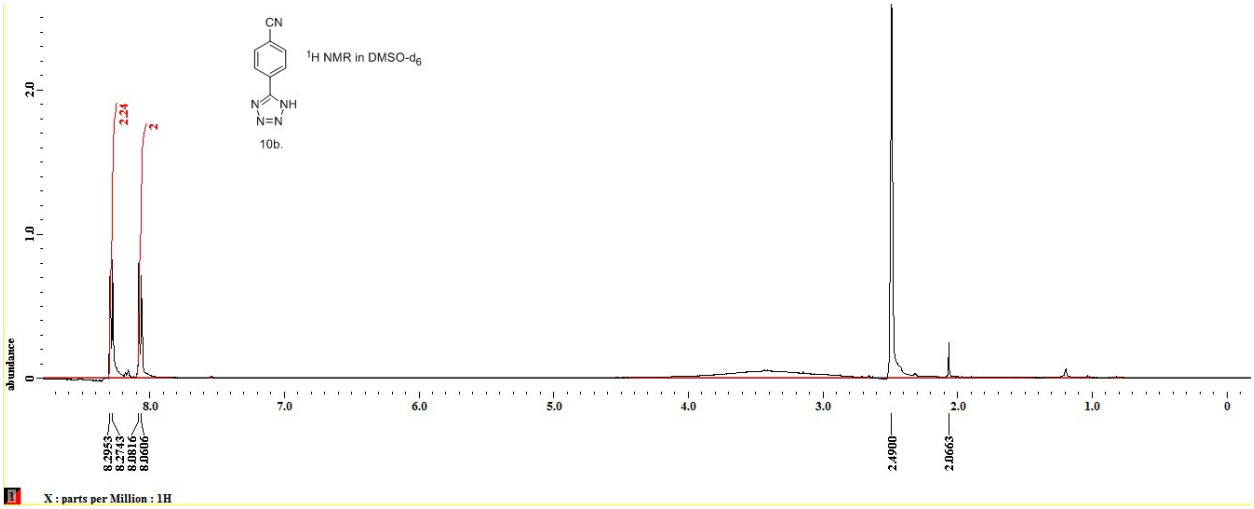

OCH3
Br
HN
N
N=N
7.
C13 NMR in DMSO-d6
abundance
X : parts per Million : 13C

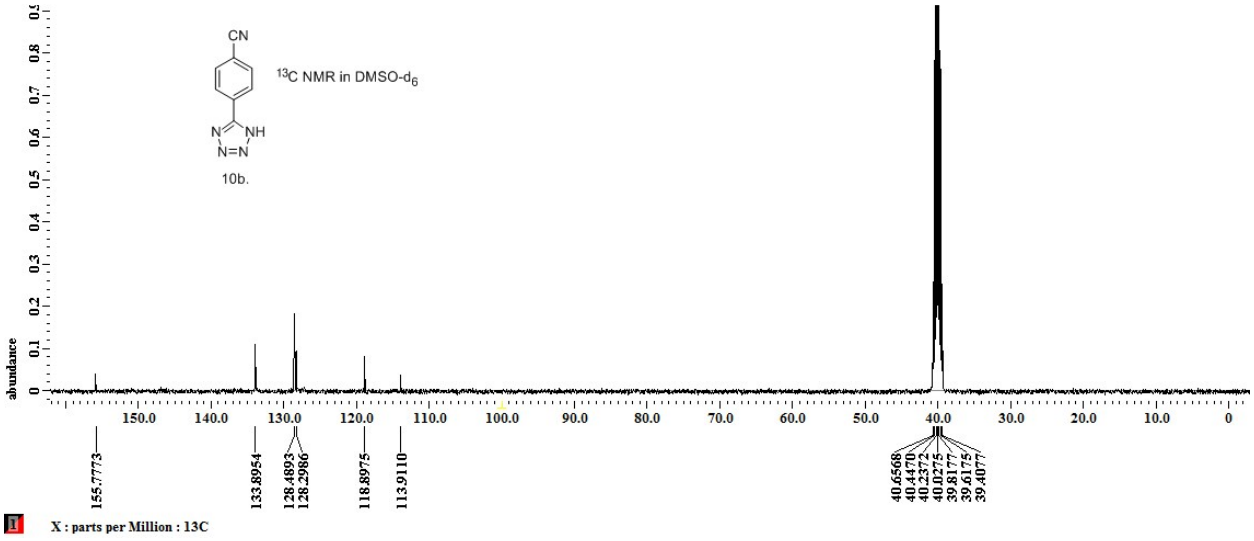

^{1}H NMR in DMSO-d$_6$
8b.
1.08
1.17
1.26
1.34
abundance
9.2113
8.7247
8.7209
8.7171
8.7133
8.4460
8.4423
8.4365
8.4289
8.4251
8.4213
8.4175
7.5720
7.5681
7.5491
7.5377
3.3507
2.4900
X : parts per Million : 1H

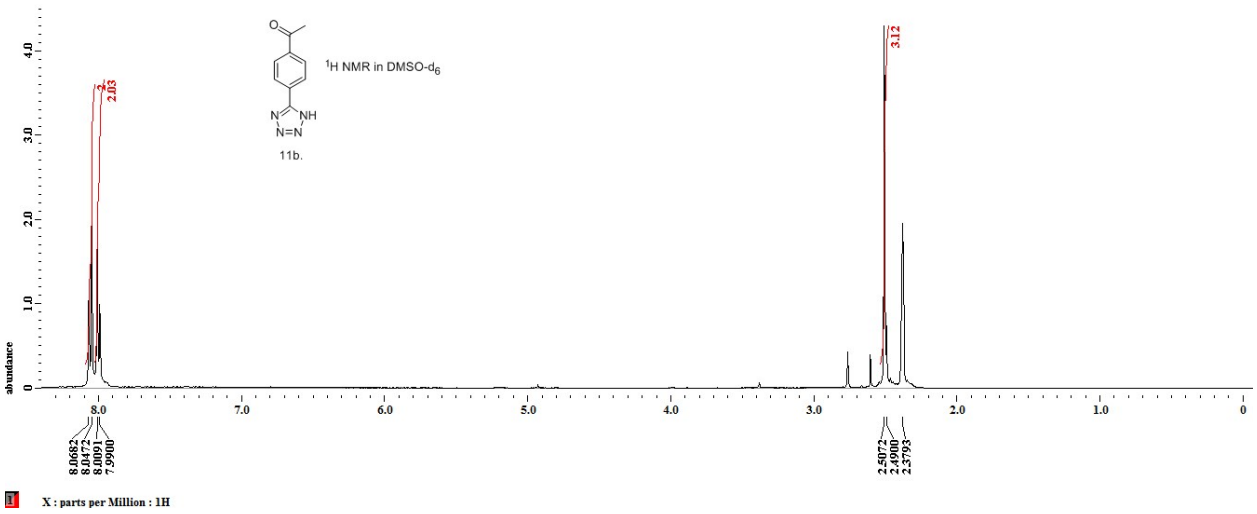

^{13}C NMR in DMSO-d$_6$
8b.
abundance
164.0025
155.7742
147.6793
135.9994
132.9484
124.9870
40.1293
39.9196
39.7098
39.5000
39.2902
39.0805
38.8707
X : parts per Million : 13C

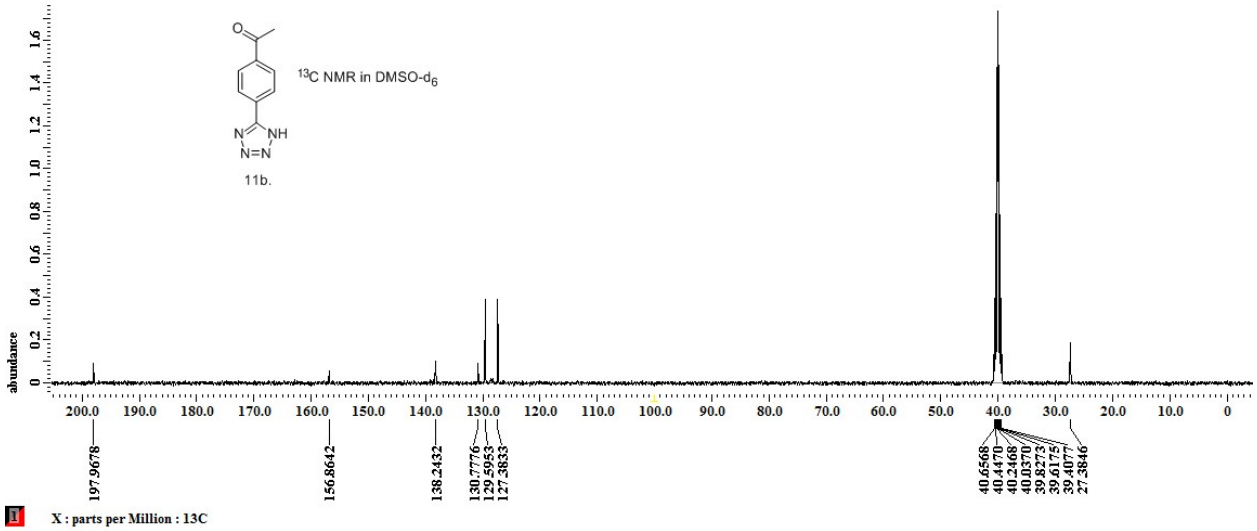

^{1}H NMR in DMSO-d$_6$
9b.
abundance
8.7247
8.7113
7.9251
7.9117
3.3812
2.4900
X : parts per Million : 1H

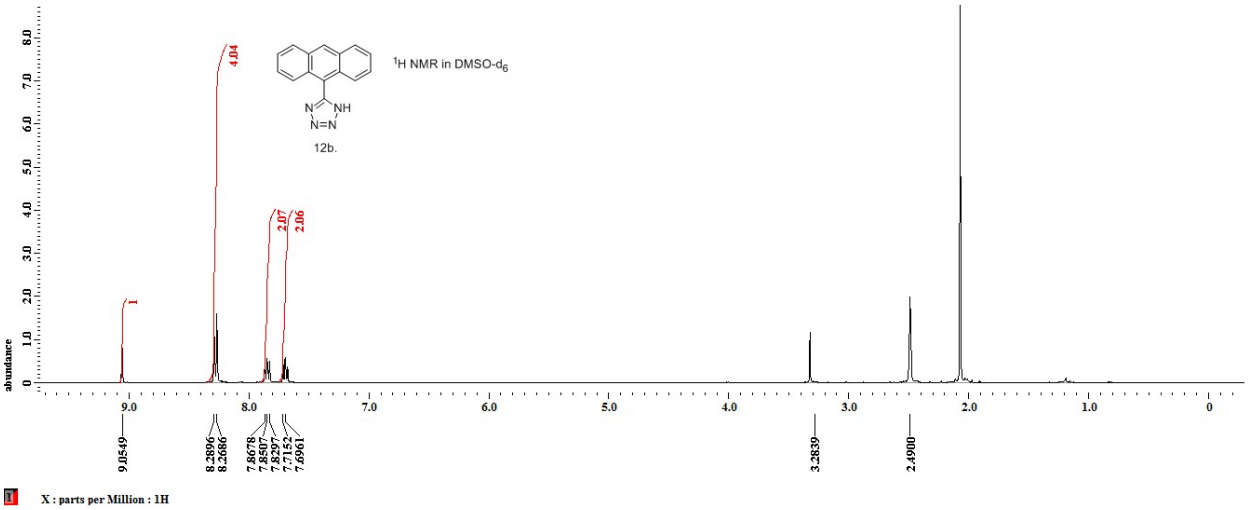

^{13}C NMR in DMSO-d$_6$
9b.
abundance
154.5537
149.4527
134.5025
121.3543
39.9195
39.7098
39.5001
39.2903
39.0805
X : parts per Million : 13C

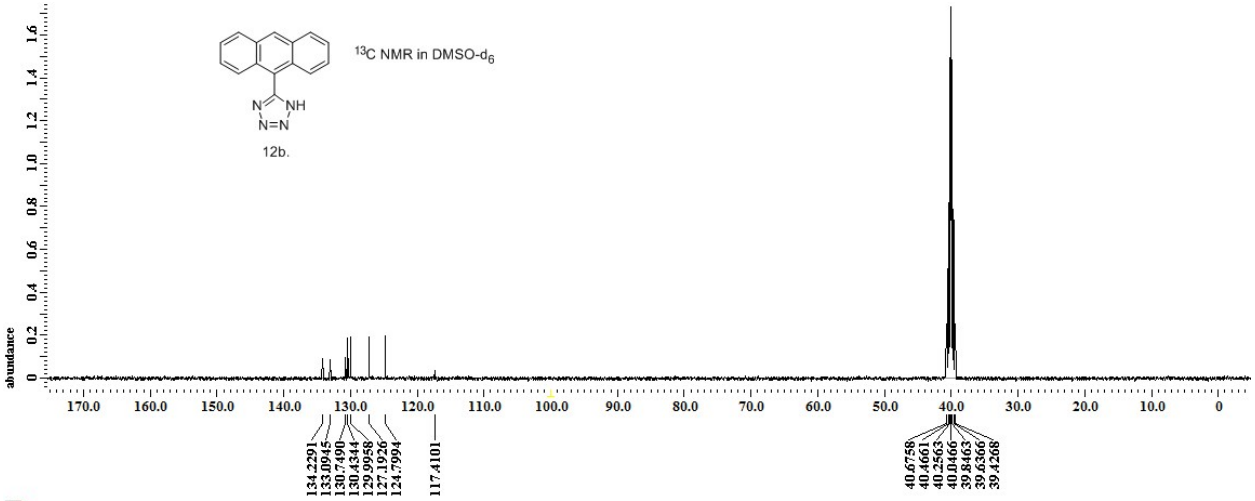

CN
NH
N=N
10b.
^{1}H NMR in DMSO-d$_6$
2.24
2
abundance
8.2953
8.2743
8.0816
8.0606
2.4900
2.0663
X : parts per Million : 1H

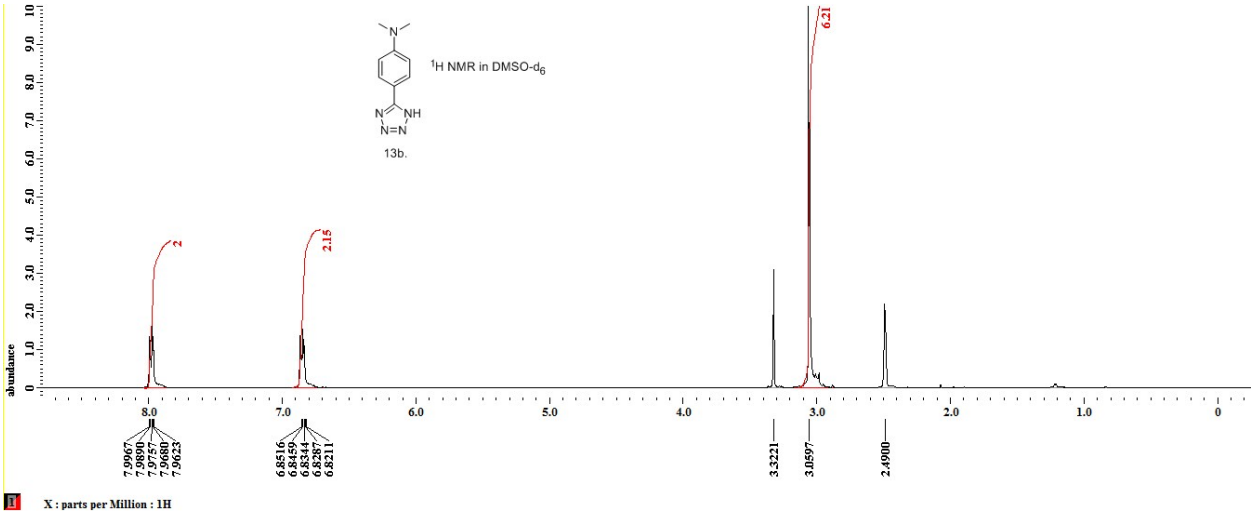

CN
NH
N=N
10b.
^{13}C NMR in DMSO-d$_6$
abundance
155.7773
133.8954
128.4893
128.2986
118.8975
113.9110
40.6568
40.4470
40.2372
40.0275
39.8177
39.6175
39.4077
X : parts per Million : 13C

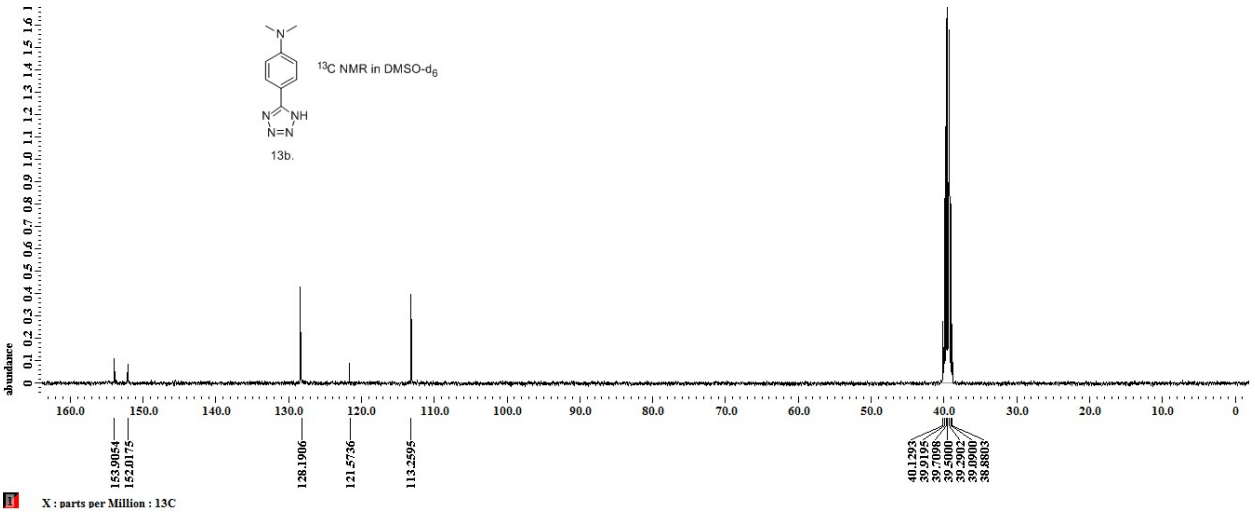

^{1}H NMR in DMSO-d_6
11b.
abundance
8.0682
8.0472
8.0091
7.9900
2.5072
2.4900
2.3793
X : parts per Million : 1H

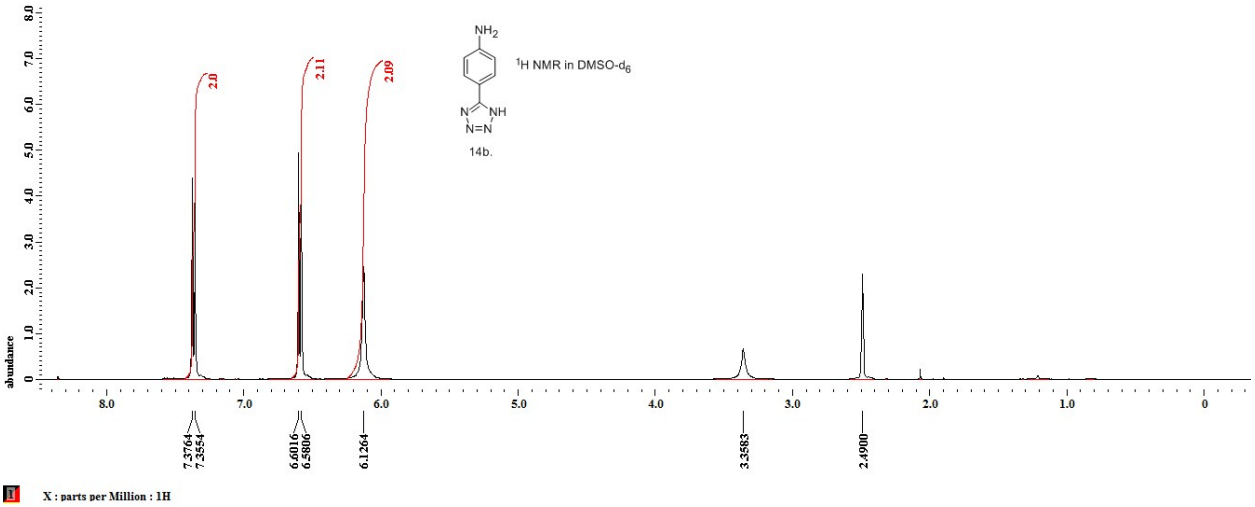

^{13}C NMR in DMSO-d_6
11b.
abundance
197.9678
156.8642
138.2432
130.7776
129.5953
127.3833
40.6568
40.4470
40.2468
40.0370
39.8273
39.6175
39.4077
27.3846
X : parts per Million : 13C

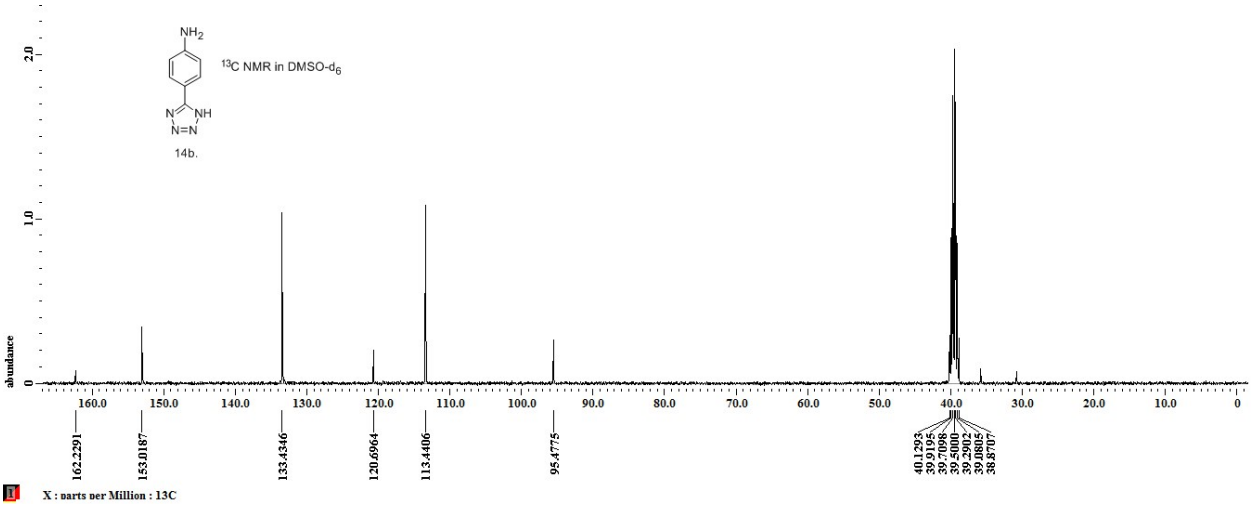

^{1}H NMR in DMSO-d$_6$
12b.
4.04
2.07
2.06
1
9.0549
8.2896
8.2686
7.8678
7.8507
7.8297
7.7153
7.6961
3.2839
2.4900
abundance
X : parts per Million : 1H

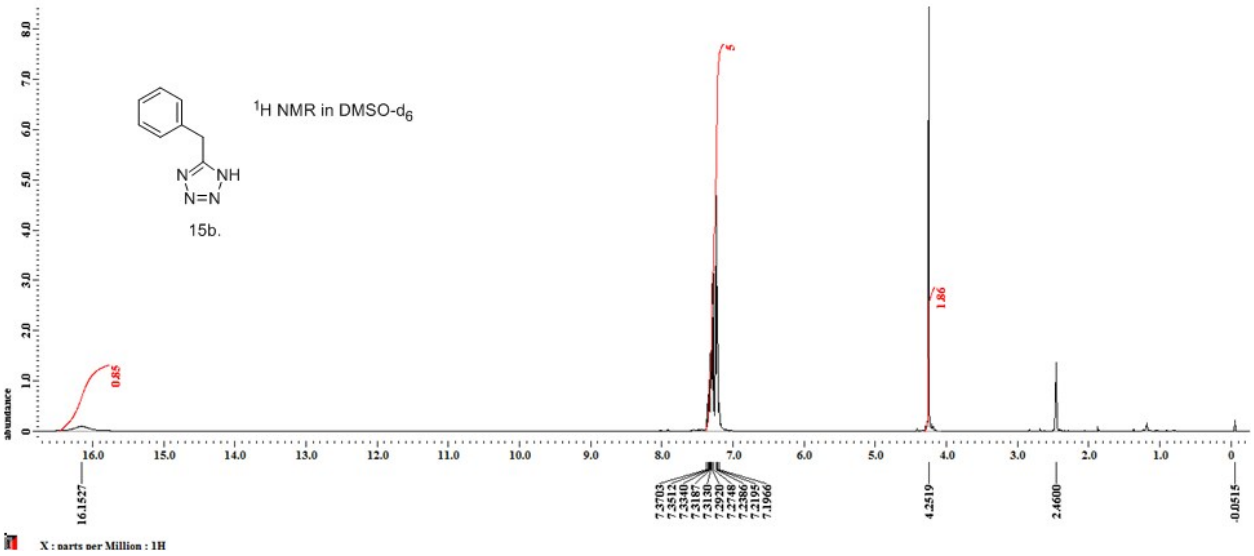

^{13}C NMR in DMSO-d$_6$
12b.
134.2291
133.0945
130.7490
130.4344
129.9958
127.1926
124.7994
117.4101
40.6758
40.4661
40.2563
40.0466
39.8463
39.6366
39.4268
abundance
X : parts per Million : 13C

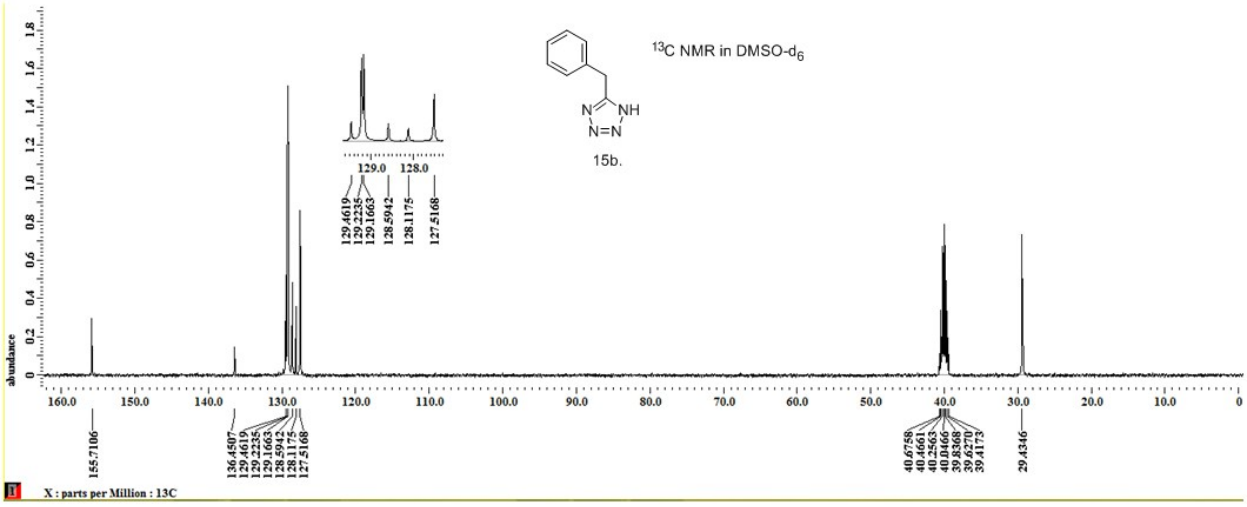

^{1}H NMR in DMSO-d_6
13b.
abundance
2
2.15
6.21
7.9967
7.9890
7.9757
7.9680
7.9623
6.8516
6.8459
6.8344
6.8287
6.8211
3.3221
3.0597
2.4900
X : parts per Million : 1H

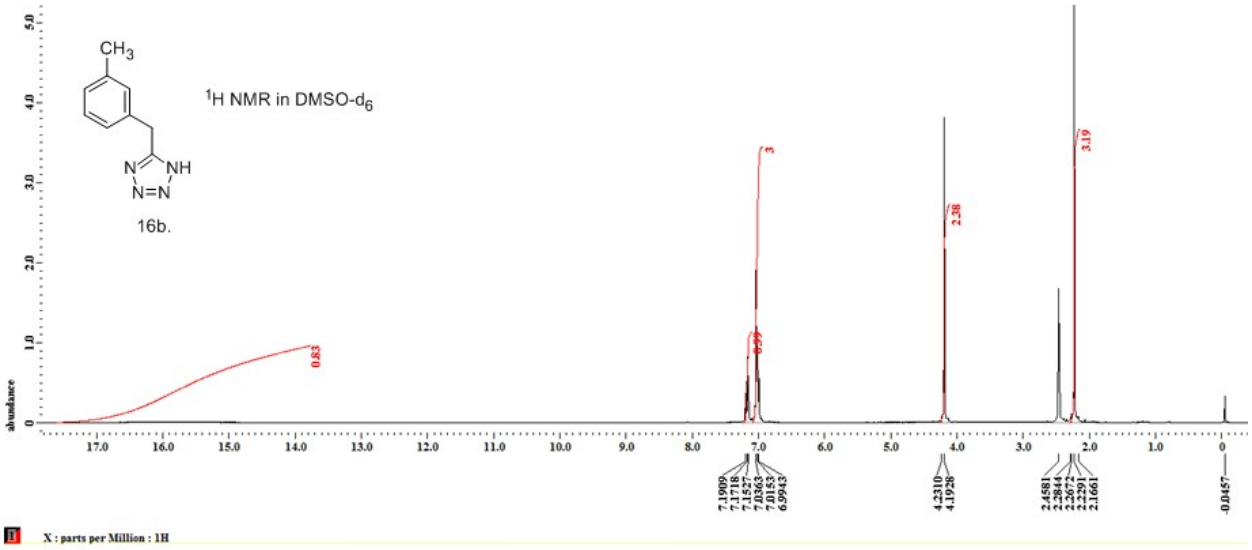

^{13}C NMR in DMSO-d_6
13b.
abundance
153.9054
152.0175
128.1906
121.5736
113.2595
40.1293
39.9195
39.7098
39.5000
39.2902
39.0805
38.8803
X : parts per Million : 13C

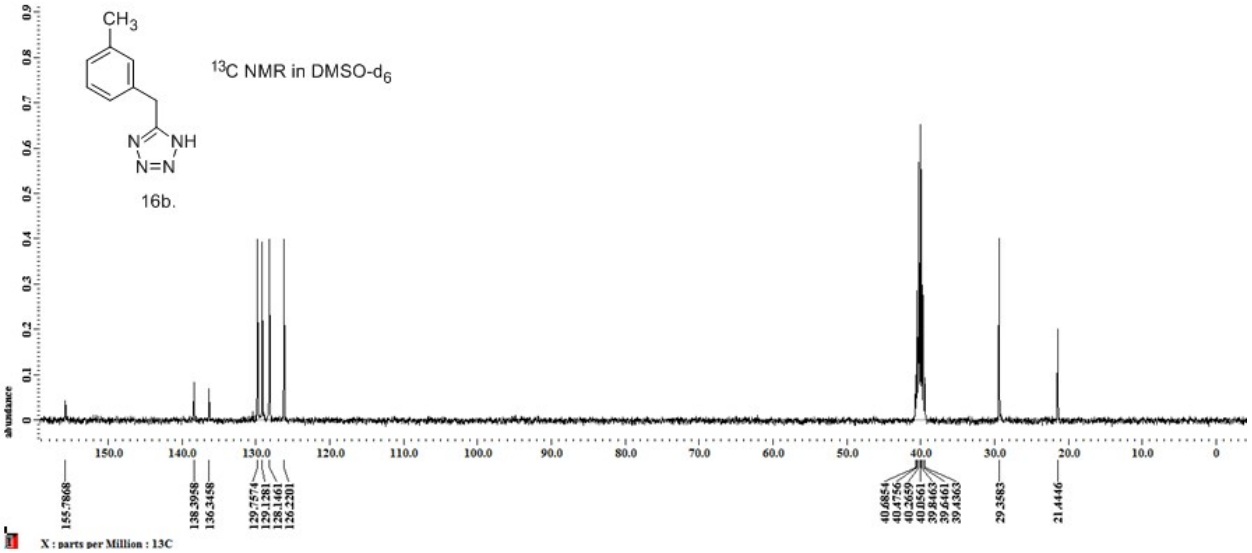

NH2
1H NMR in DMSO-d6
N
NH
N=N
14b.
2.0
2.11
2.09
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3764
7.3554
6.6016
6.5806
6.1264
3.3583
2.4900
X : parts per Million : 1H

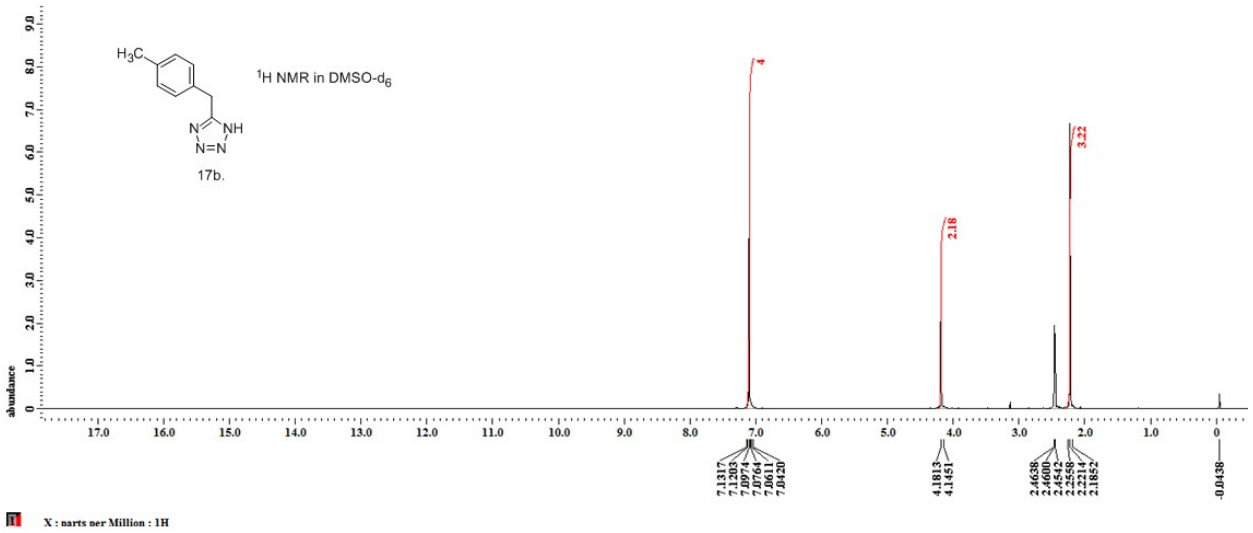

NH2
13C NMR in DMSO-d6
N
NH
N=N
14b.
abundance
2.0
1.0
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.2291
153.0187
133.4346
120.6964
113.4406
95.4775
40.1293
40.0195
39.7098
39.5000
39.2902
39.0805
38.8707
X : parts per Million : 13C

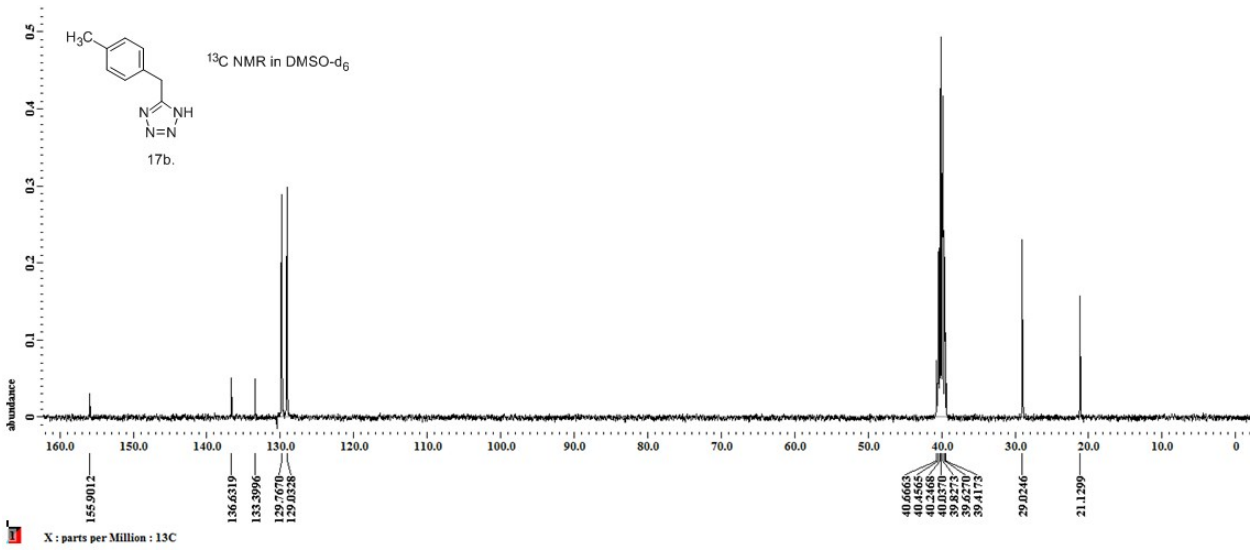

^{1}H NMR in DMSO-d$_6$
15b.
abundance
0.85
1.86
16.1527
7.3703
7.3512
7.3340
7.3187
7.3130
7.2930
7.2748
7.2386
7.2195
7.1966
4.2519
2.4600
-0.0515
X : parts per Million : 1H

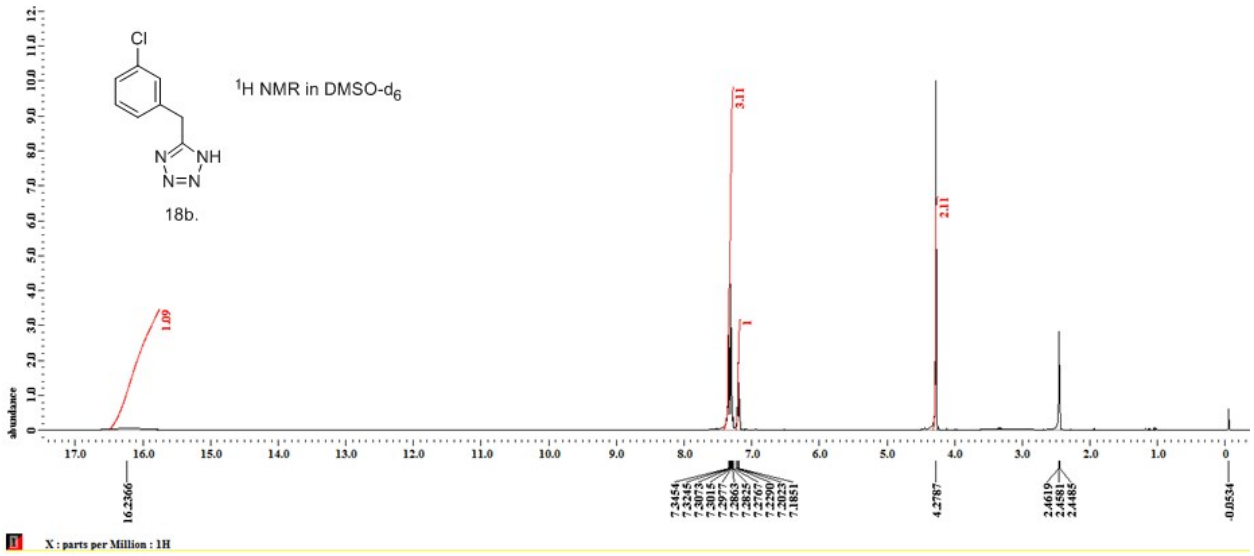

^{13}C NMR in DMSO-d$_6$
15b.
abundance
129.4619
129.2238
129.1663
128.5942
128.1175
127.5168
155.7106
136.4507
40.6758
40.4661
40.2563
40.0466
39.8368
39.6270
39.4173
29.4346
X : parts per Million : 13C

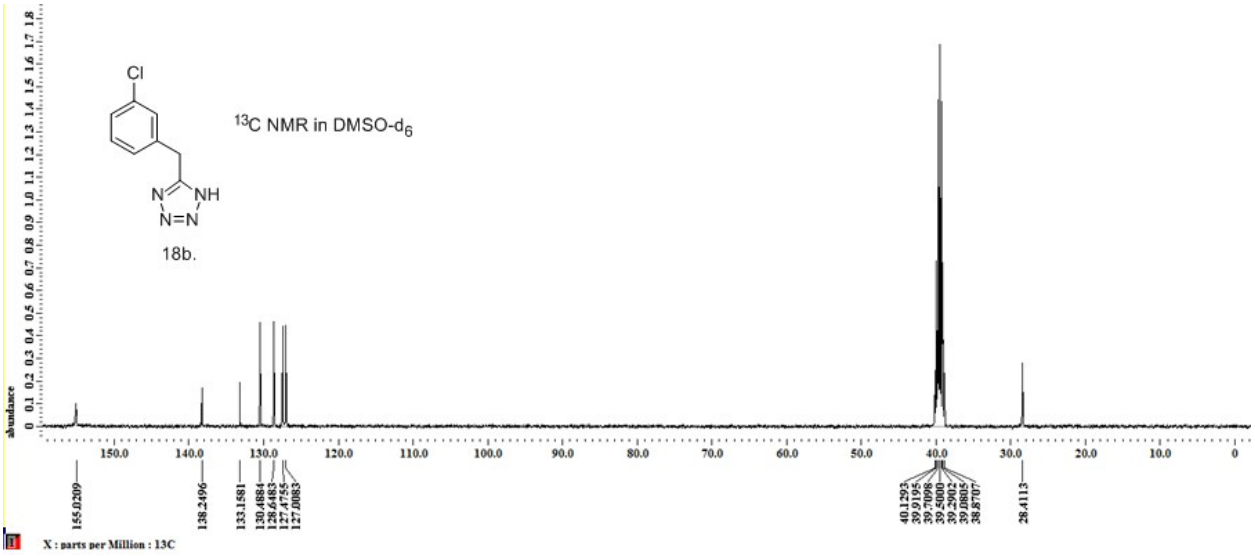

CH3
NH
N=N
16b.
1H NMR in DMSO-d6
abundance
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.1909
7.1718
7.1526
7.0358
7.0153
6.9943
4.2310
4.1928
2.4581
2.2844
2.2672
2.2500
2.1661
-0.0457
X : parts per Million : 1H

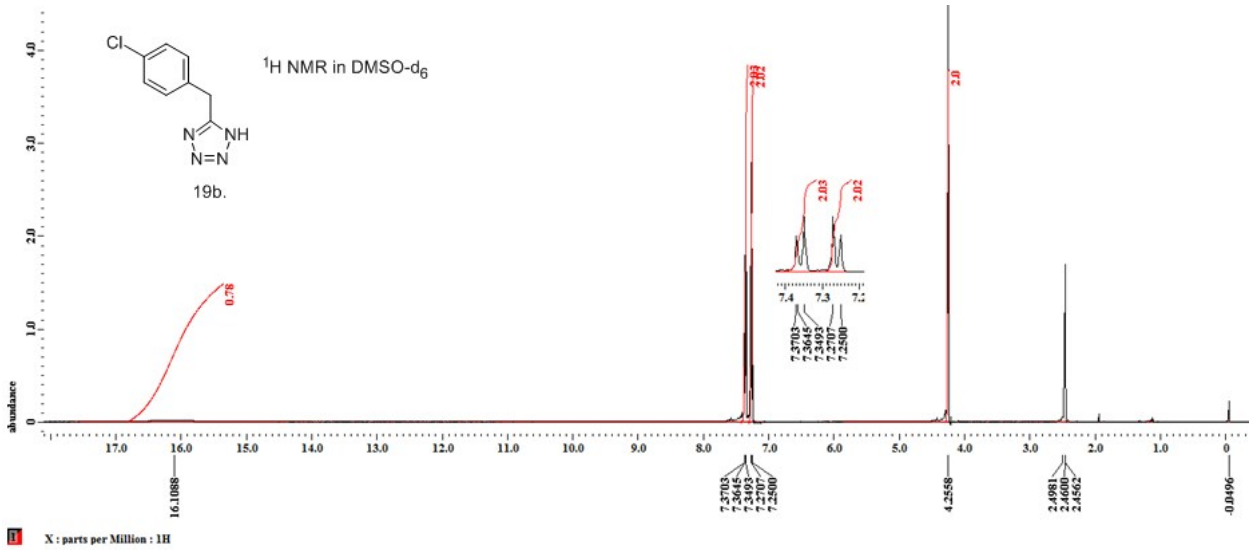

CH3
NH
N=N
16b.
13C NMR in DMSO-d6
abundance
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
155.7868
138.3958
136.3458
129.7574
129.1281
128.1461
126.2301
40.6854
40.4756
40.2659
40.0561
39.8463
39.6461
39.4363
29.3583
21.4446
X : parts per Million : 13C

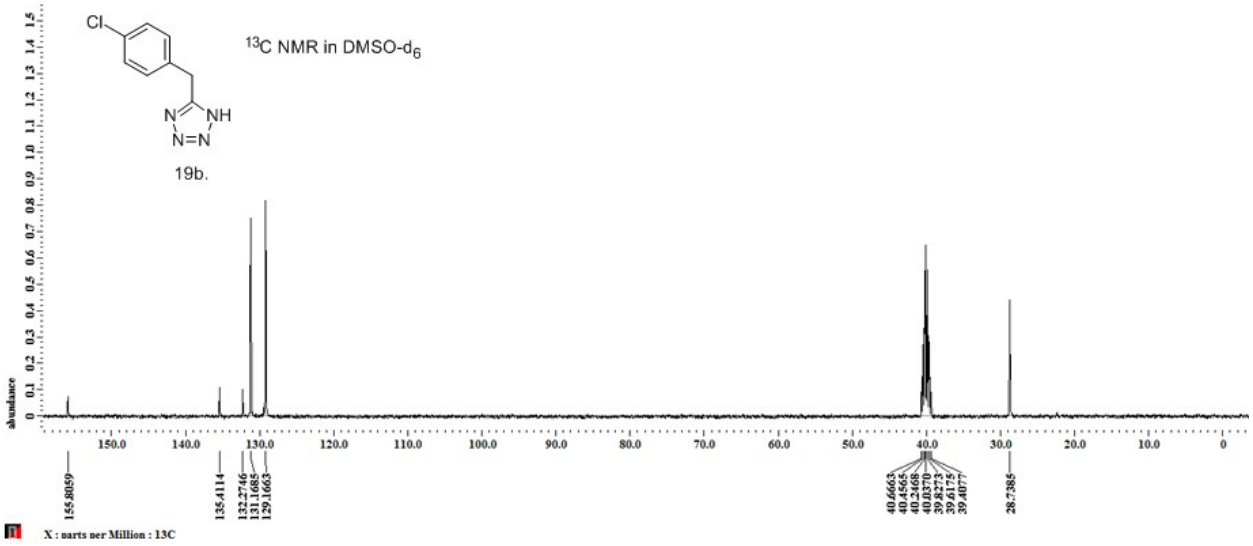

^{1}H NMR in DMSO-d$_6$
17b.
abundance
4
2.18
3.22
7.1317
7.1203
7.0974
7.0764
7.0611
7.0420
4.1813
4.1451
2.4638
2.4600
2.4542
2.4506
2.2214
2.1852
-0.0438
X : parts per Million : 1H

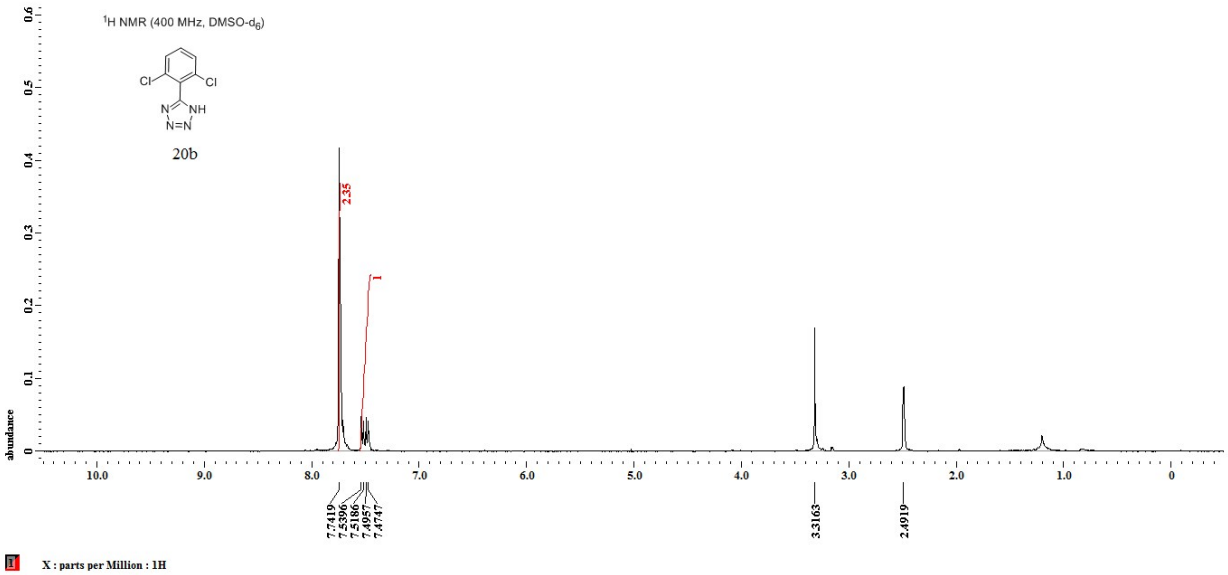

^{13}C NMR in DMSO-d$_6$
17b.
abundance
155.9012
136.6319
133.3996
129.7670
129.0328
40.6663
40.4565
40.4468
40.0370
39.8273
39.6270
39.4173
29.0246
21.1299
X : parts per Million : 13C

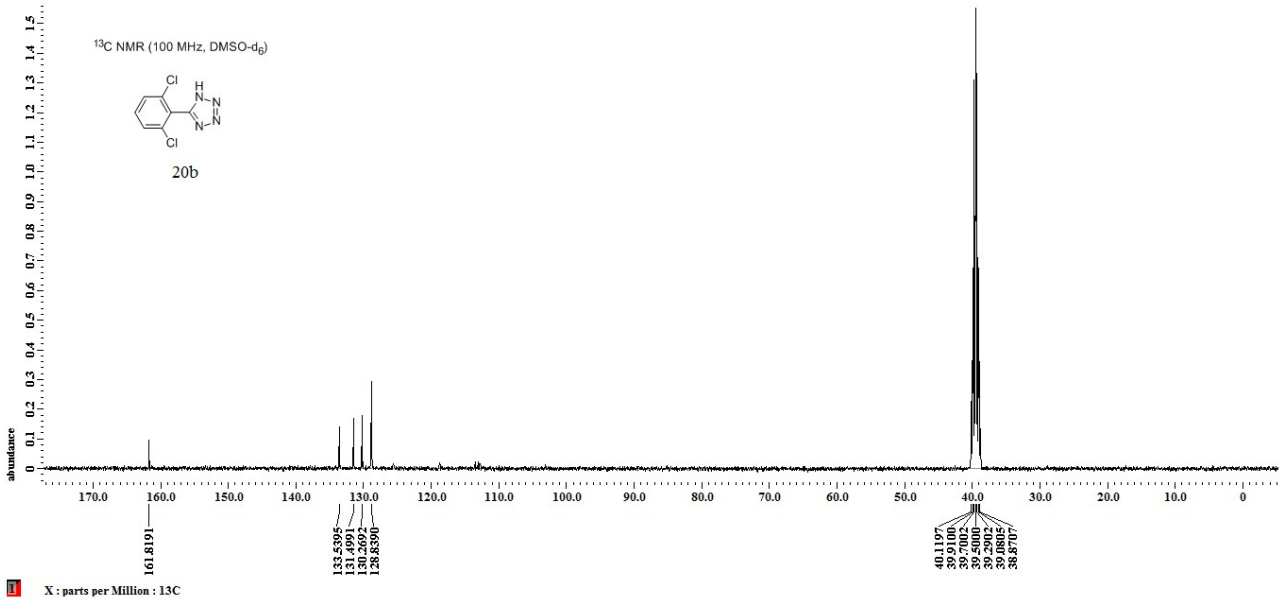

Cl
NH
N=N
18b.
^{1}H NMR in DMSO-d$_6$
3.11
2.11
1
1.09
abundance
16.2566
7.3454
7.3245
7.3073
7.3015
7.2973
7.2853
7.2767
7.2290
7.2023
7.1851
4.2787
2.4619
2.4581
2.4485
-0.0534
X : parts per Million : 1H

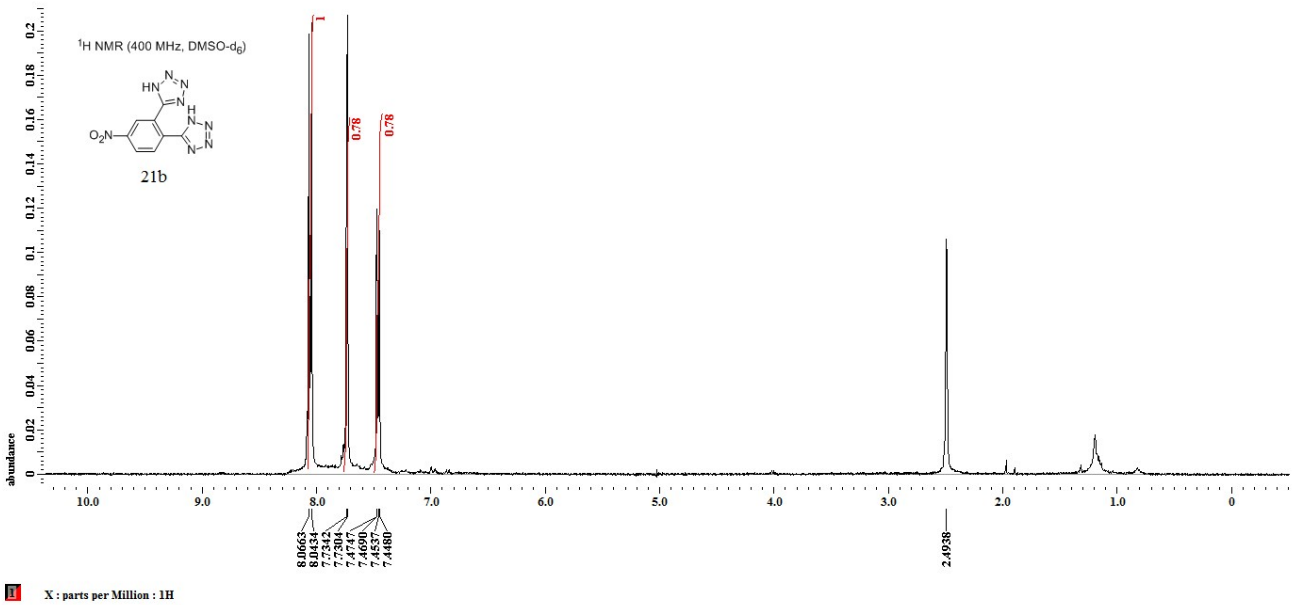

Cl
NH
N=N
18b.
^{13}C NMR in DMSO-d$_6$
abundance
155.0209
138.2496
133.1581
130.4684
130.4483
127.4755
127.0083
40.1293
40.0179
39.7098
39.5000
39.2902
39.0805
38.8707
28.4113
X : parts per Million : 13C

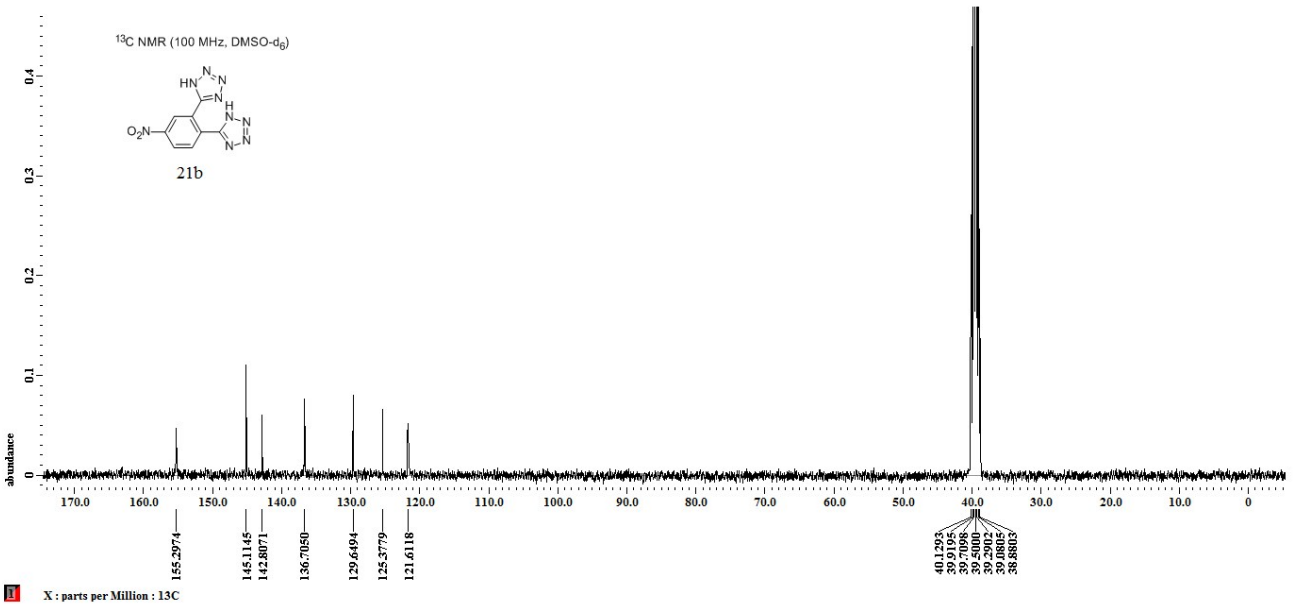

Cl
N
NH
N=N
19b.
^{1}H NMR in DMSO-d$_6$
abundance
X : parts per Million : 1H


Cl
N
NH
N=N
19b.
^{13}C NMR in DMSO-d$_6$
abundance
X : parts per Million : 13C

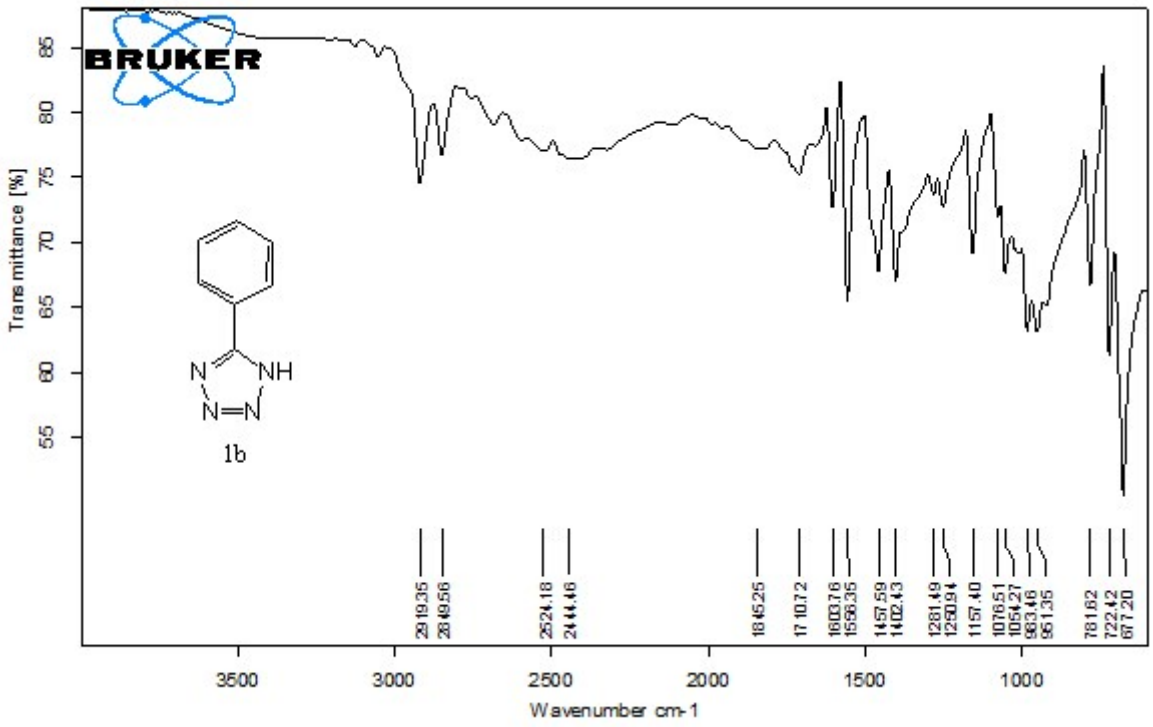

1H NMR (400 MHz, DMSO-d6)
20b
2.35
1
abundance
7.7419
7.5396
7.5186
7.4957
7.4747
3.3163
2.4919
X : parts per Million : 1H

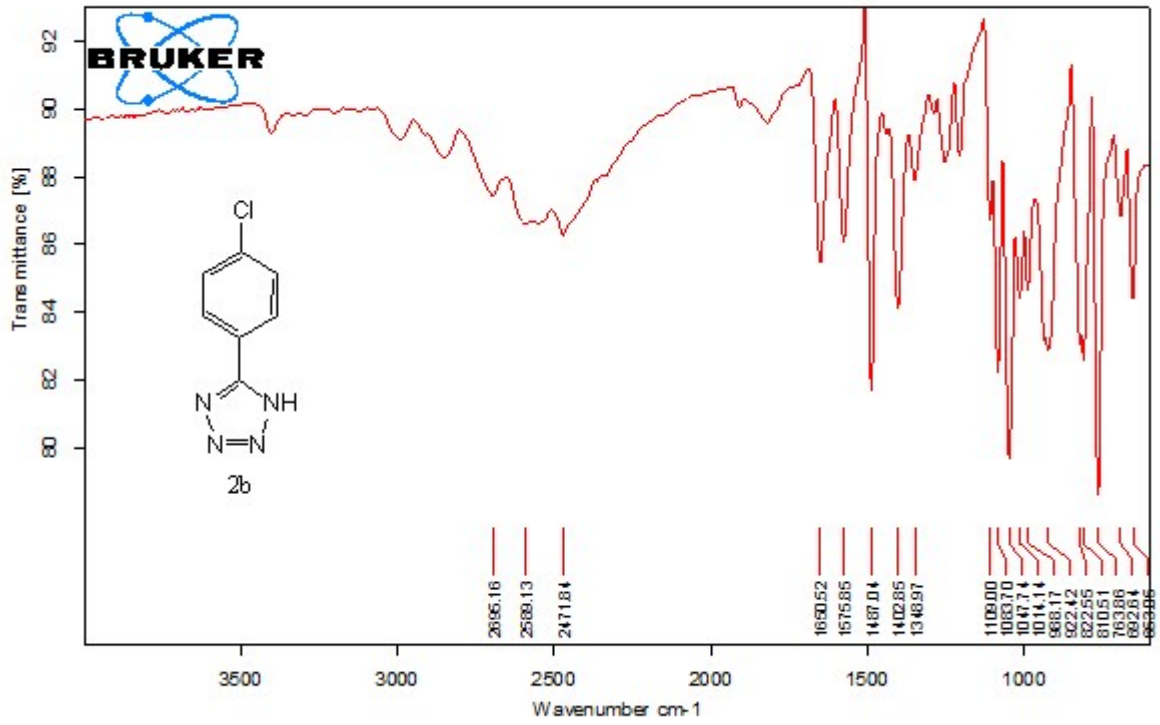

13C NMR (100 MHz, DMSO-d6)
20b
abundance
161.8191
133.5395
131.4991
130.2692
128.8390
40.1197
39.9100
39.7002
39.4900
39.2802
39.0705
38.8707
X : parts per Million : 13C

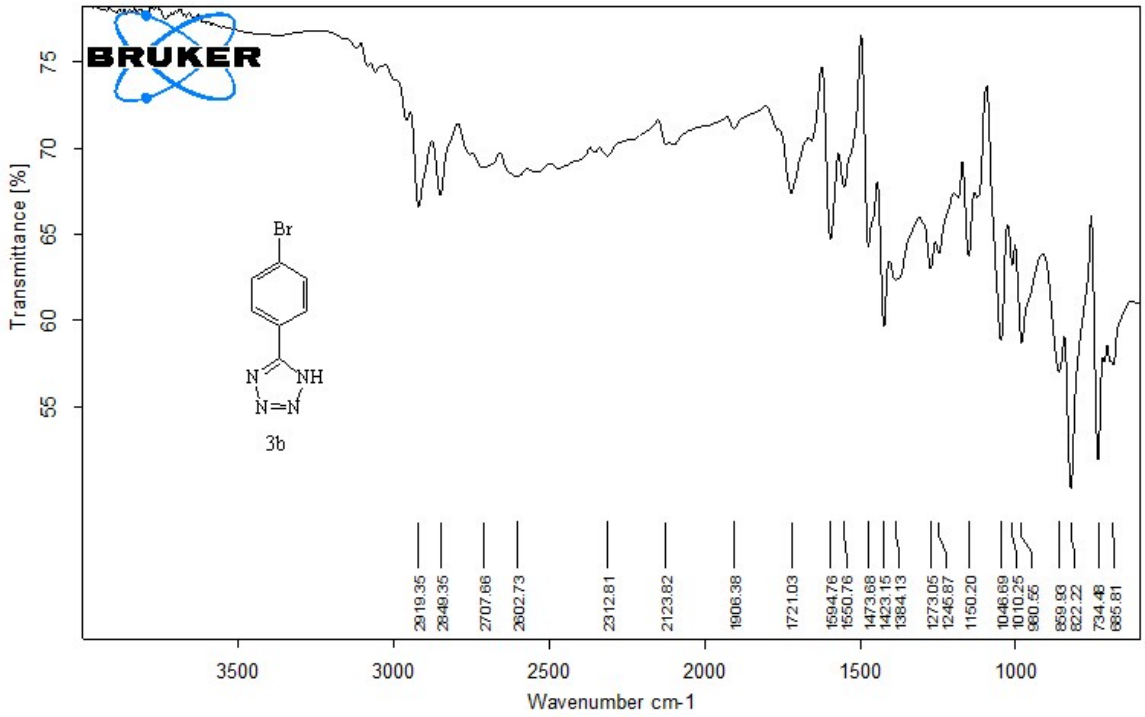

^{1}H NMR (400 MHz, DMSO-d_6)
21b
1
0.78
0.78
abundance
8.0663
8.0434
7.7384
7.7304
7.4747
7.4690
7.4537
7.4480
2.4938
X : parts per Million : 1H

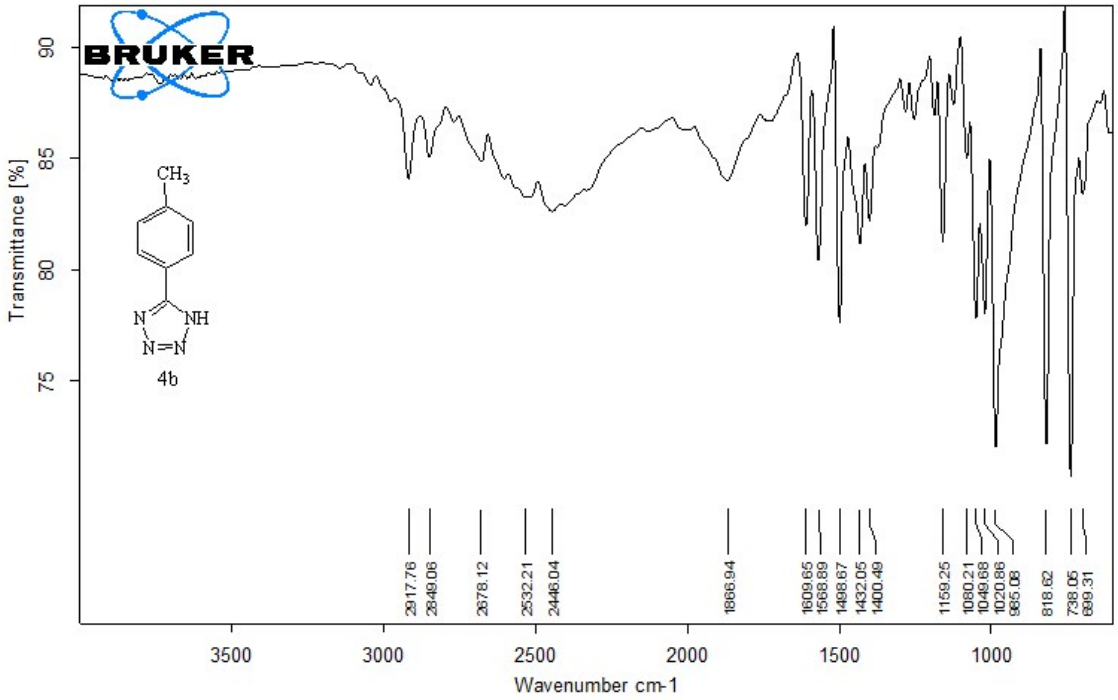

^{13}C NMR (100 MHz, DMSO-d_6)
21b
abundance
155.2974
145.1145
142.8071
136.7050
129.6494
125.3779
121.6118
40.1293
39.9195
39.7098
39.5000
39.2902
39.0805
38.8803
X : parts per Million : 13C

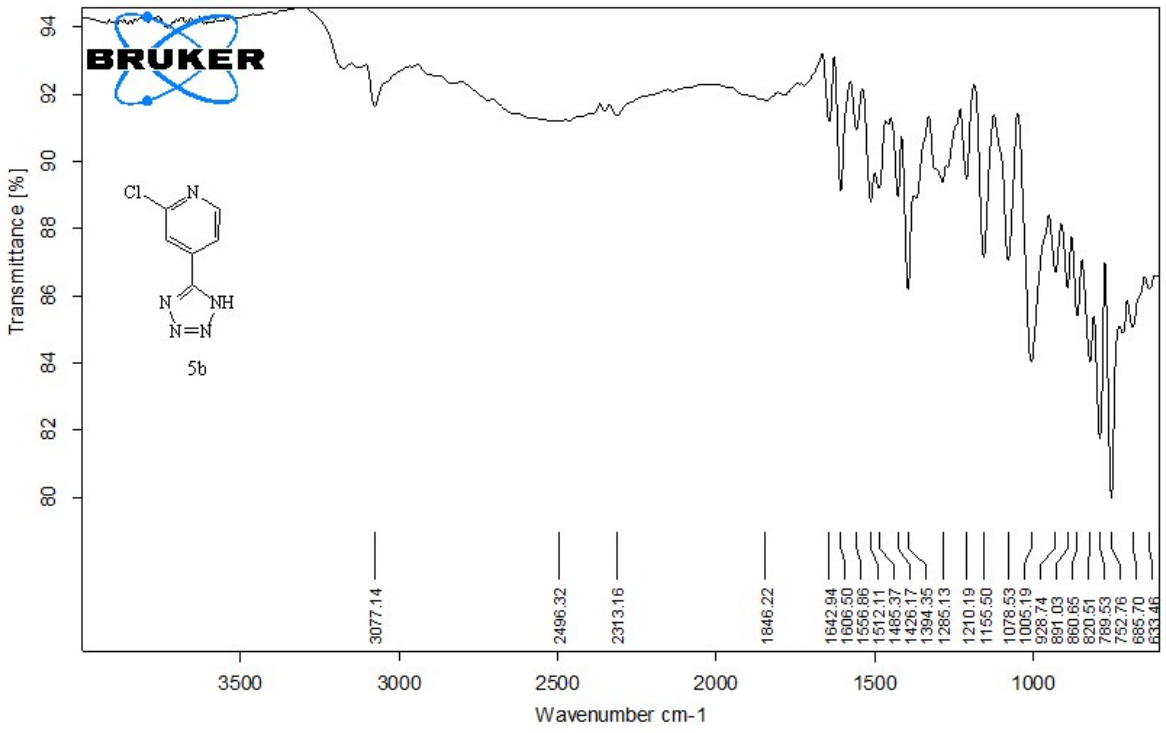
IR data (1b - 21b)

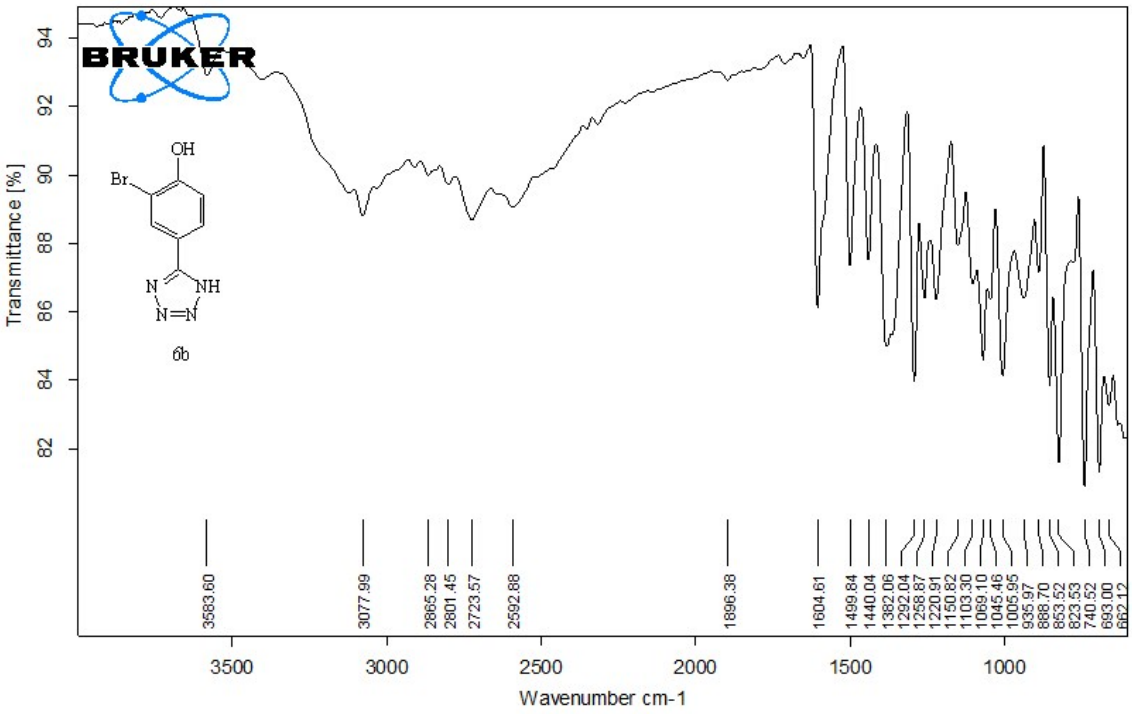


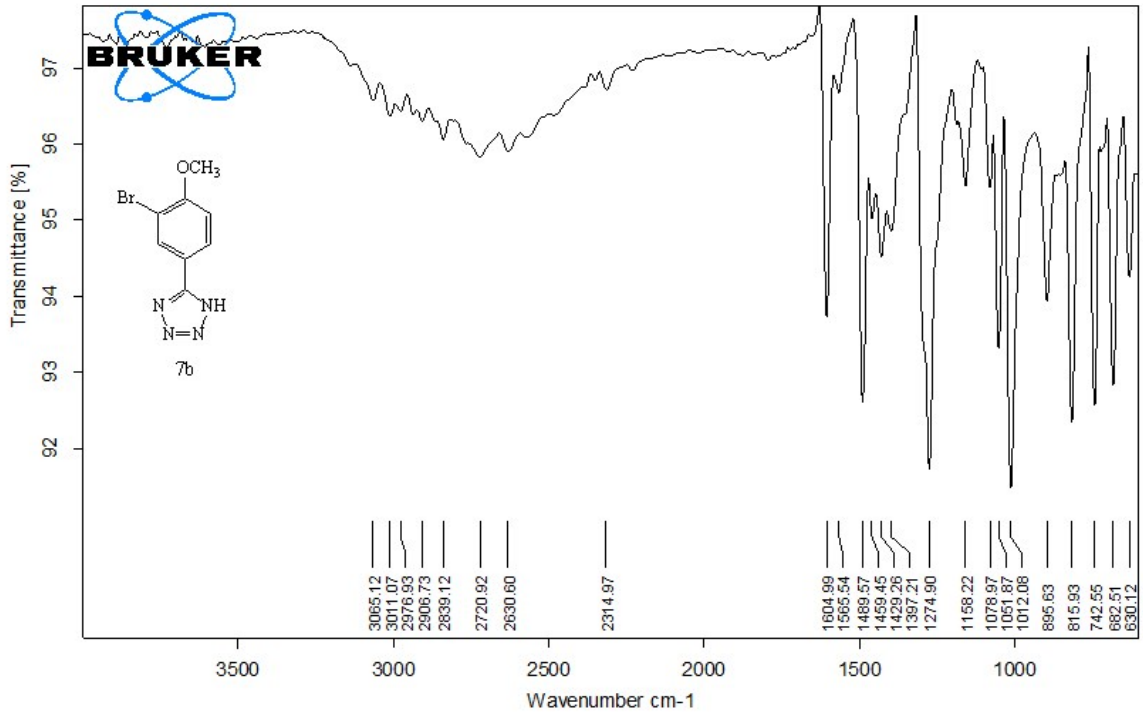


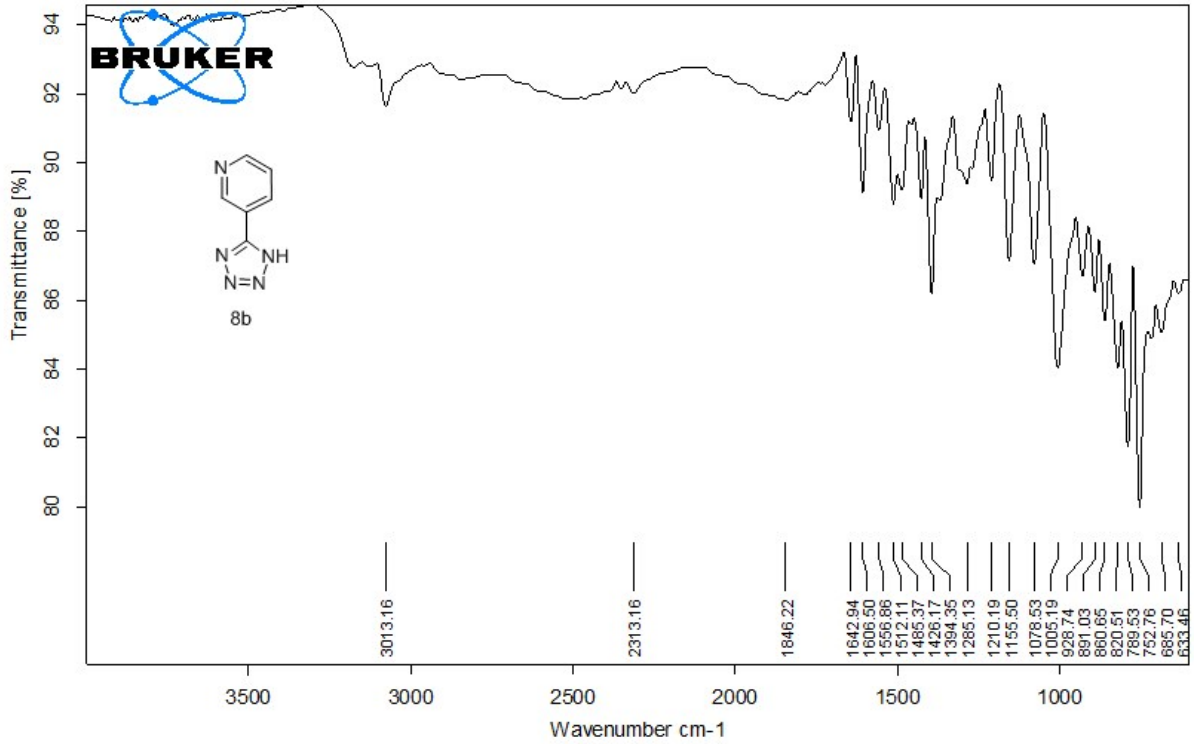

BRUKER
Transmittance [%]
75
70
65
60
55
Br
N
NH
N=N
3b
2919.35
2849.35
2707.66
2602.73
2312.81
2123.82
1906.38
1721.03
1594.76
1550.76
1473.68
1423.15
1364.13
1273.05
1245.87
1150.20
1046.69
1010.25
960.55
859.99
822.22
734.48
685.81
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

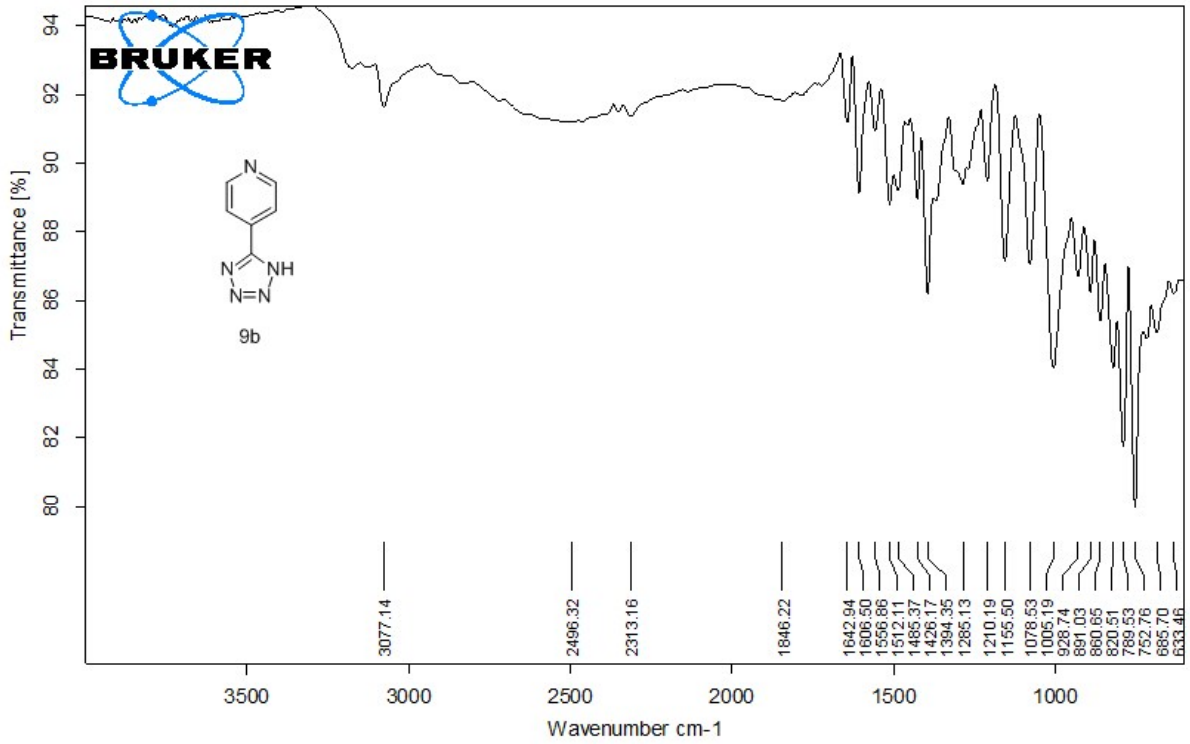

BRUKER
Transmittance [%]
90
85
80
75
CH3
N
NH
N=N
4b
2917.76
2849.06
2678.12
2532.21
2446.04
1886.94
1609.65
1568.89
1498.67
1432.05
1400.49
1159.25
1080.21
1049.68
1020.86
985.08
818.62
738.05
699.31
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

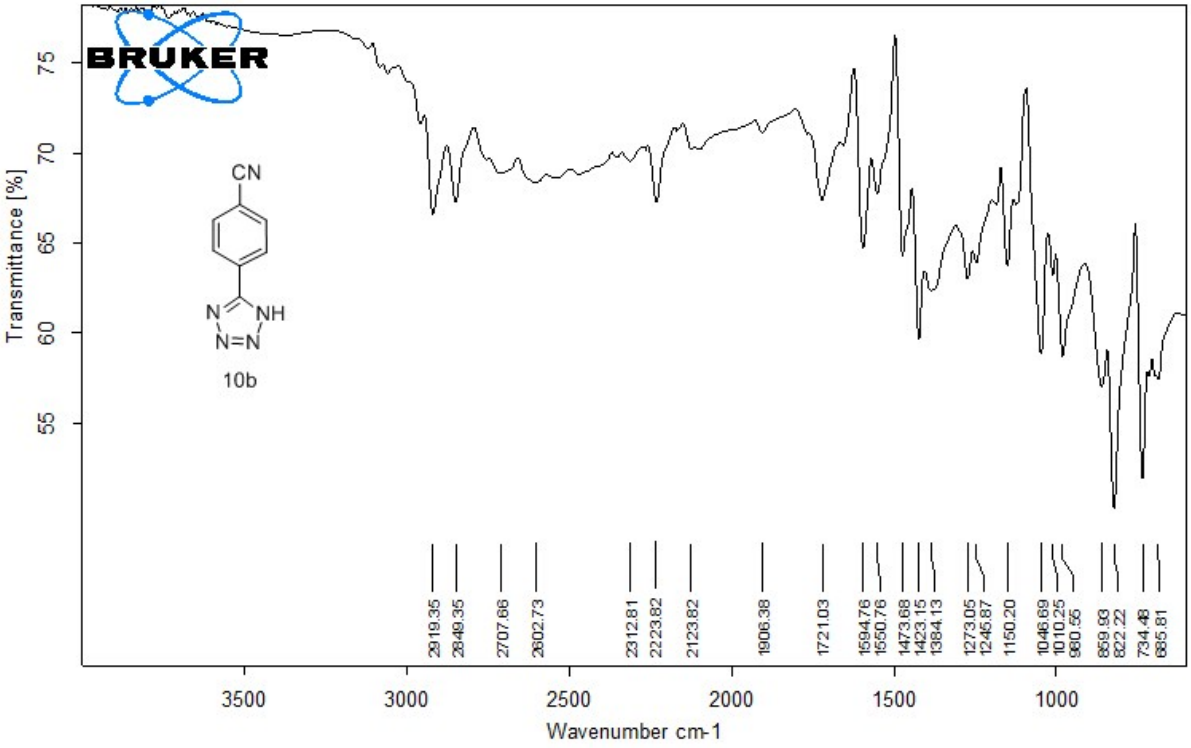

BRUKER
Cl
N
N
NH
N=N
5b
Transmittance [%]
94
92
90
88
86
84
82
80
3077.14
2496.32
2313.16
1846.22
1642.94
1606.50
1556.86
1512.11
1485.37
1426.17
1394.35
1285.13
1210.19
1155.50
1078.53
1005.19
928.74
891.03
860.65
820.51
789.53
752.76
685.70
633.46
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

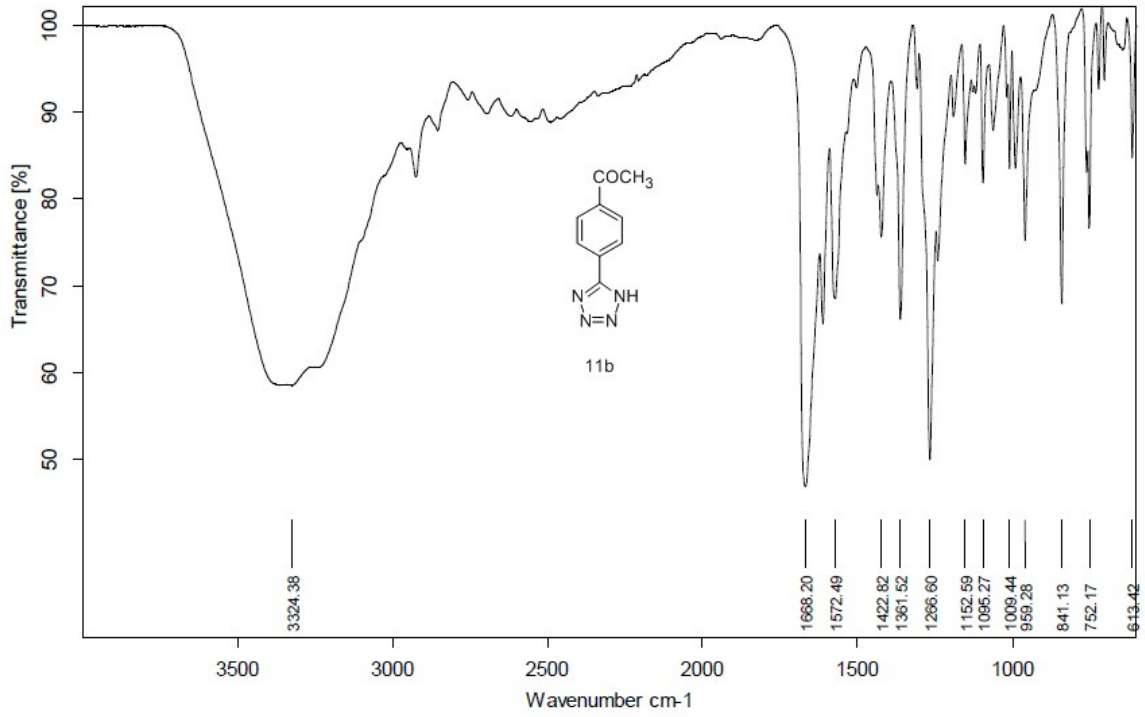

BRUKER
OH
Br
N
NH
N=N
6b
Transmittance [%]
94
92
90
88
86
84
82
3583.60
3077.99
2865.28
2801.45
2723.57
2592.88
1896.38
1604.61
1499.84
1440.04
1382.06
1292.04
1258.87
1220.91
1150.82
1103.30
1069.10
1045.46
1005.95
935.97
888.70
853.52
823.53
740.52
693.00
662.12
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

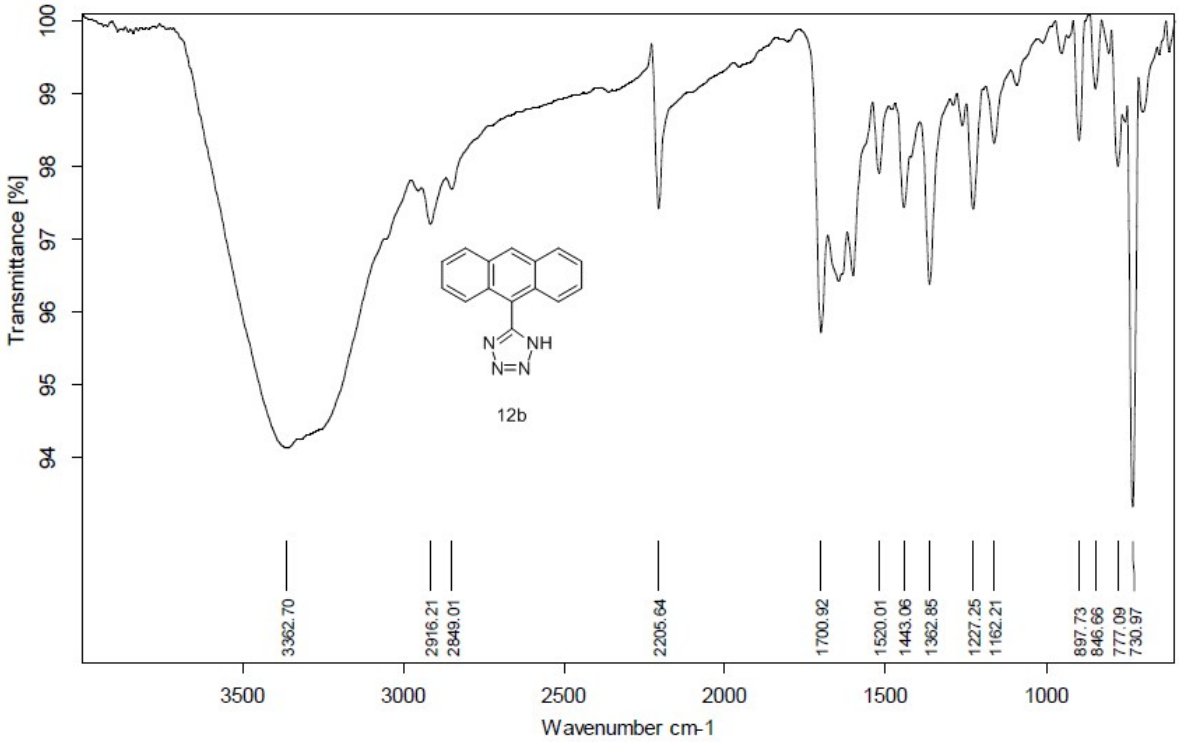

BRUKER
OCH3
Br
N
NH
N=N
7b
Transmittance [%]
97
96
95
94
93
92
3065.12
3011.07
2976.93
2906.73
2839.12
2720.92
2630.60
2314.97
1604.99
1565.54
1489.57
1459.45
1429.26
1397.21
1274.90
1158.22
1078.97
1051.87
1012.08
895.63
815.93
742.55
682.51
630.12
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

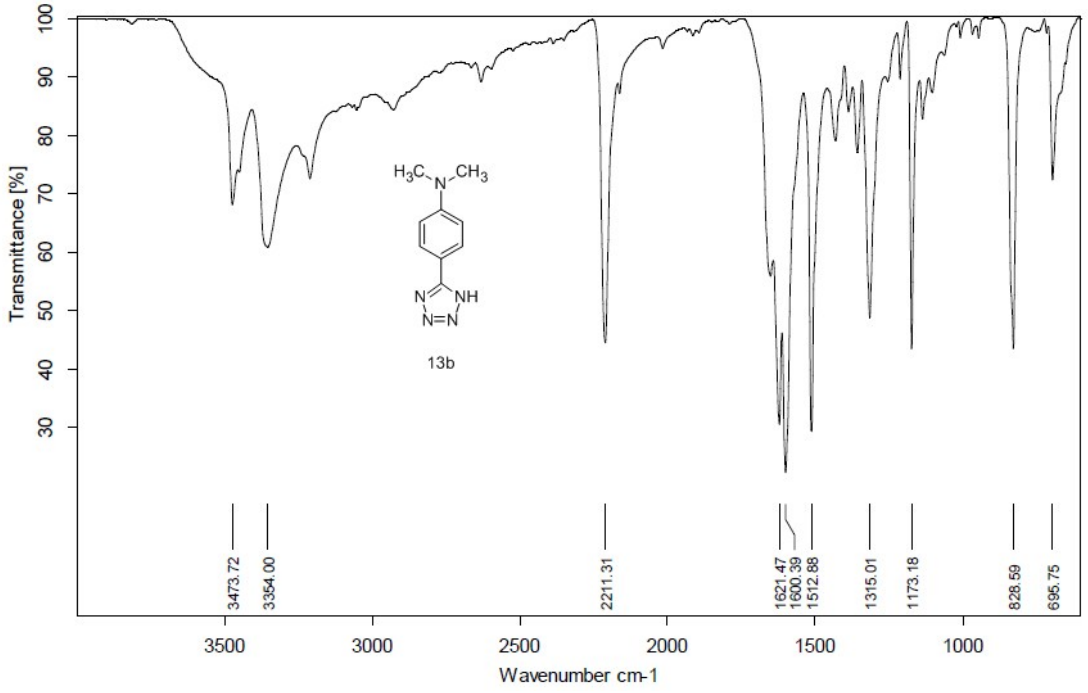

BRUKER
N
N
NH
N=N
8b
Transmittance [%]
94
92
90
88
86
84
82
80
3013.16
2313.16
1846.22
1642.94
1606.50
1556.86
1512.11
1485.37
1426.17
1394.35
1285.13
1210.19
1155.50
1078.53
1005.19
928.74
891.03
860.65
820.51
789.53
752.76
685.70
633.46
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

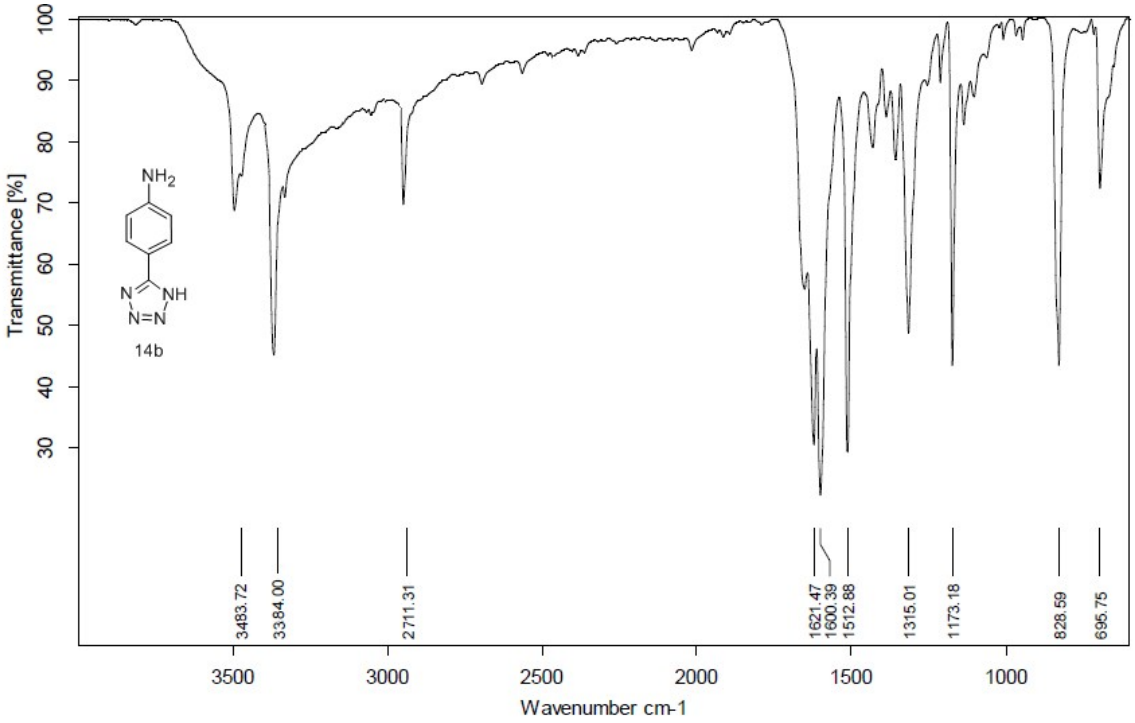

BRUKER
9b
Transmittance [%]
Wavenumber cm-1
3077.14
2496.32
2313.16
1846.22
1642.94
1606.50
1556.86
1512.11
1485.37
1426.17
1394.35
1285.13
1210.19
1155.50
1078.53
1005.19
928.74
891.03
860.65
820.51
789.53
752.76
685.70
633.46

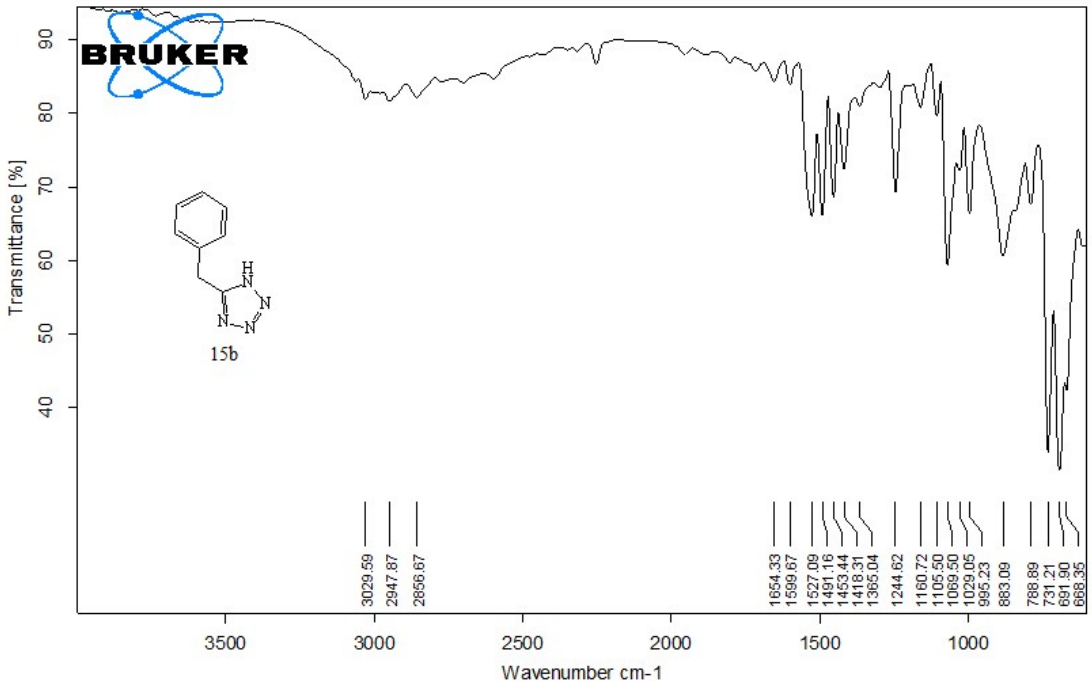

BRUKER
10b
Transmittance [%]
Wavenumber cm-1
2919.35
2849.35
2707.66
2602.73
2312.81
2223.82
2123.82
1906.38
1721.03
1594.76
1550.76
1473.68
1423.15
1384.13
1273.05
1245.87
1150.20
1046.69
1010.25
980.55
859.93
822.22
734.48
685.81

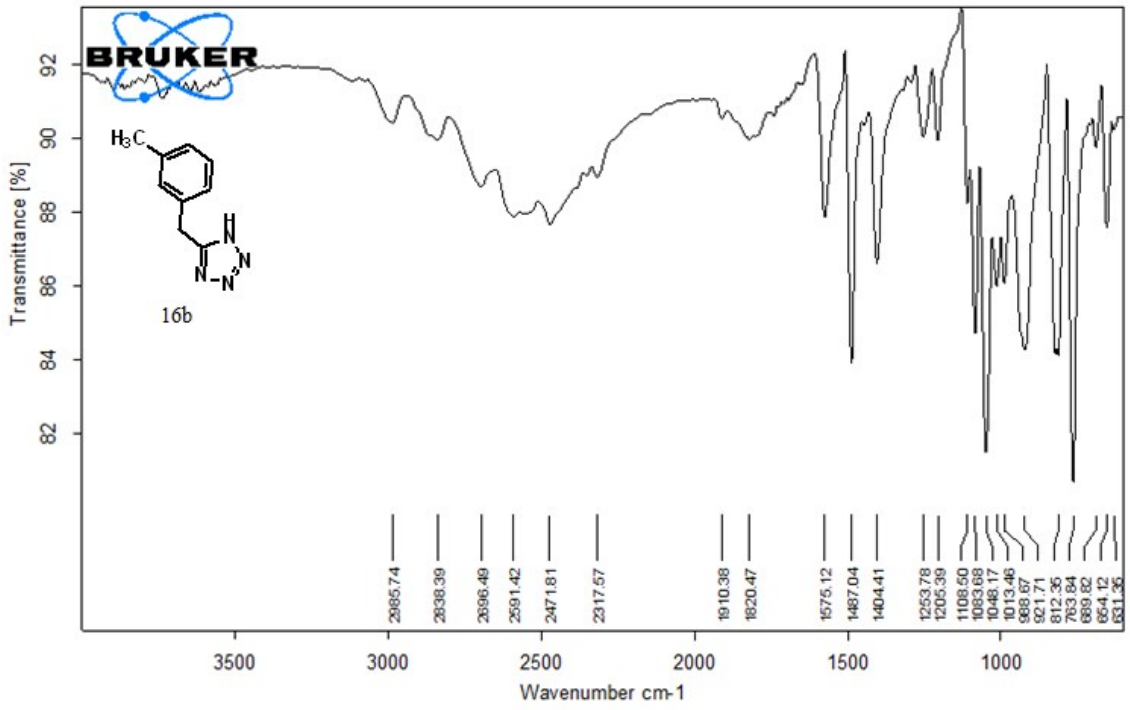

Transmittance [%]
100
90
80
70
60
50
COCH3
N
NH
N=N
11b
3324.38
1668.20
1572.49
1422.82
1361.52
1266.60
1152.59
1095.27
1009.44
959.28
841.13
752.17
613.42
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

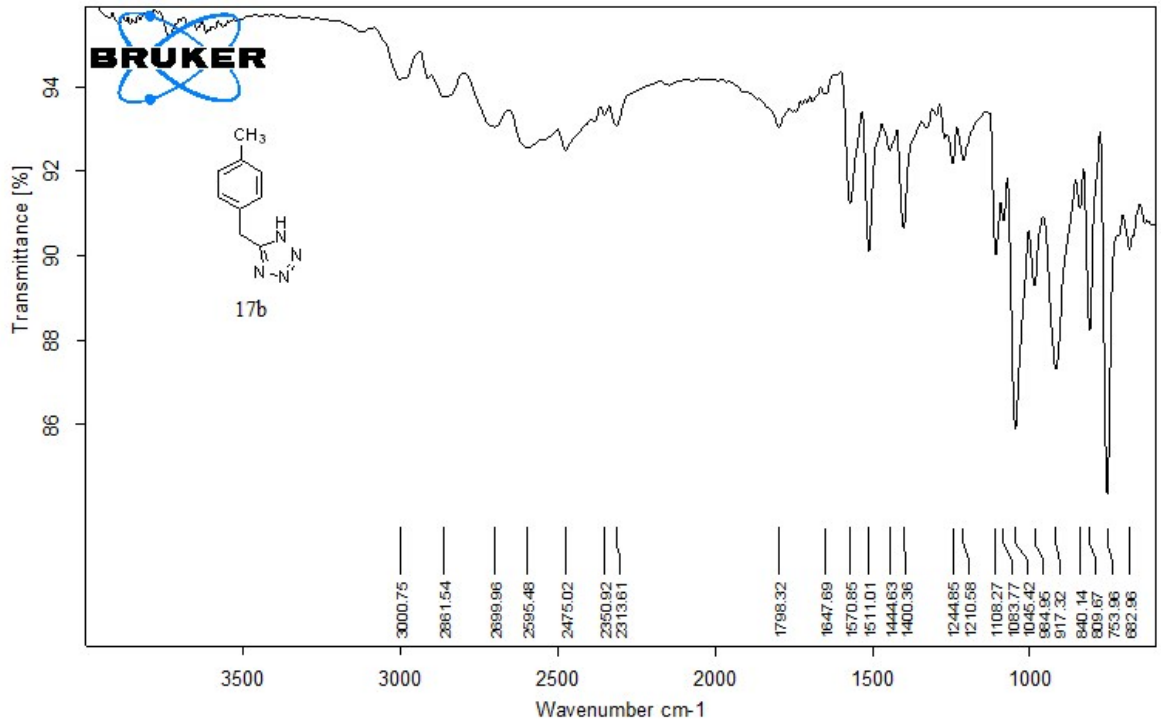

Transmittance [%]
100
99
98
97
96
95
94
N
NH
N=N
12b
3362.70
2916.21
2849.01
2205.64
1700.92
1520.01
1443.06
1362.85
1227.25
1162.21
897.73
846.66
777.09
730.97
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

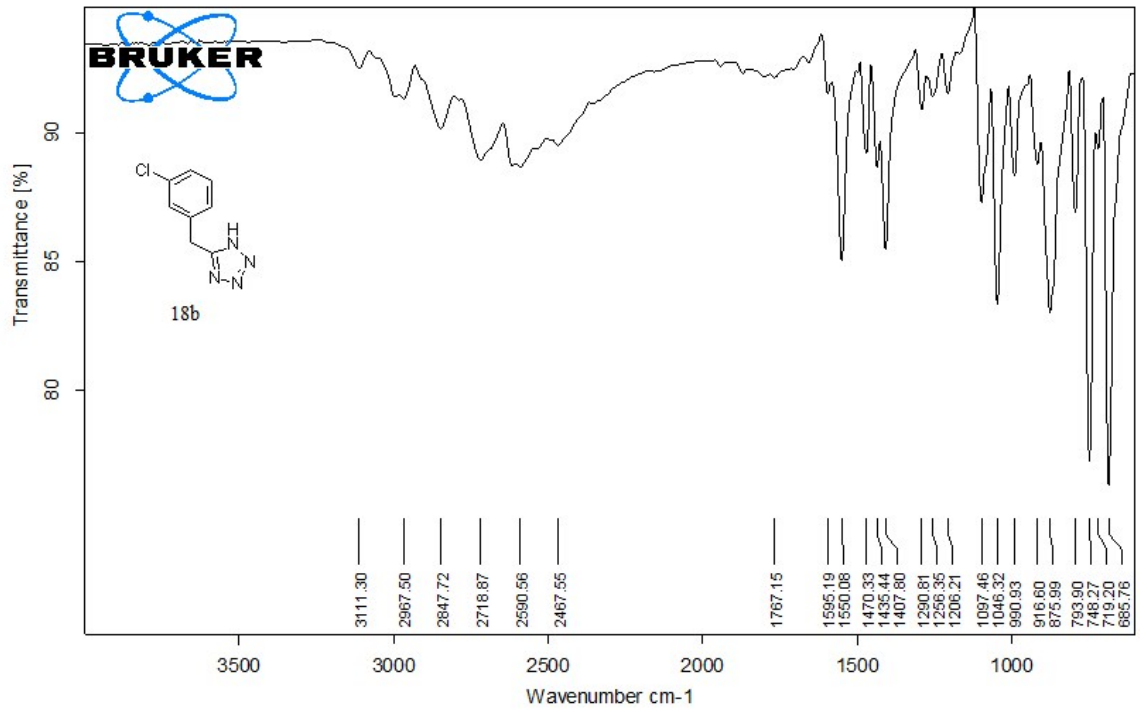

Transmittance [%]
100
90
80
70
60
50
40
30
3473.72
3364.00
2211.31
1621.47
1600.39
1512.88
1315.01
1173.18
828.59
695.75
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
13b

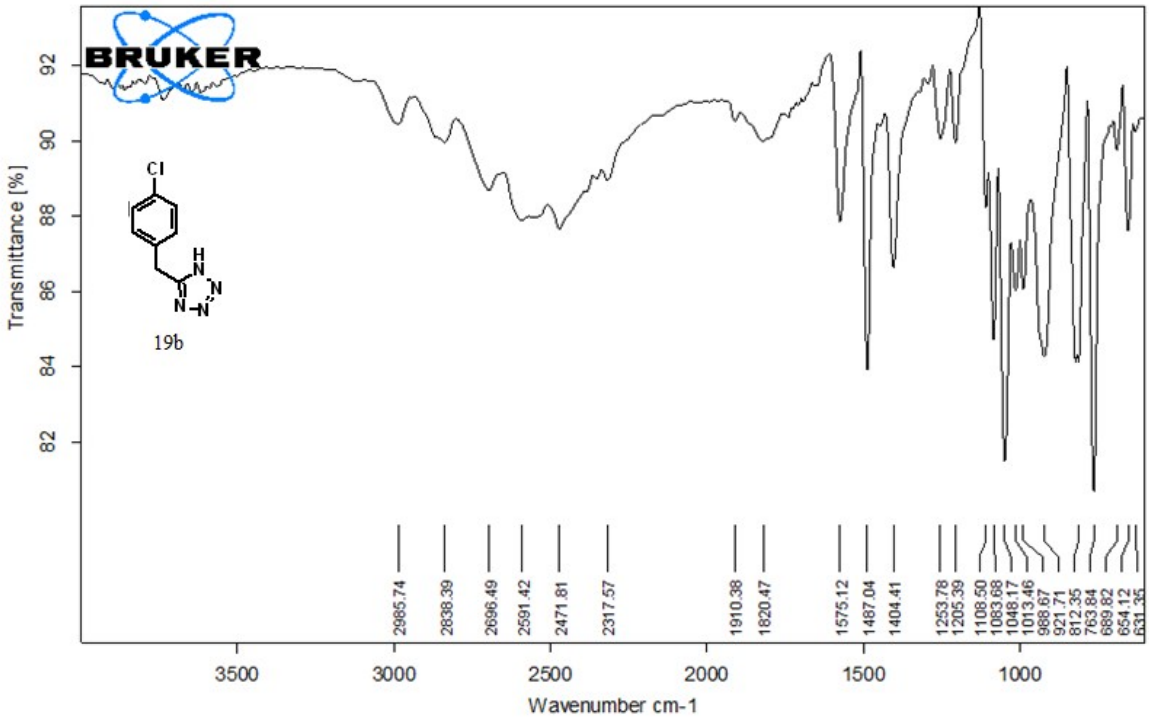

Transmittance [%]
100
90
80
70
60
50
40
30
3483.72
3384.00
2711.31
1621.47
1600.39
1512.88
1315.01
1173.18
828.59
695.75
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
14b

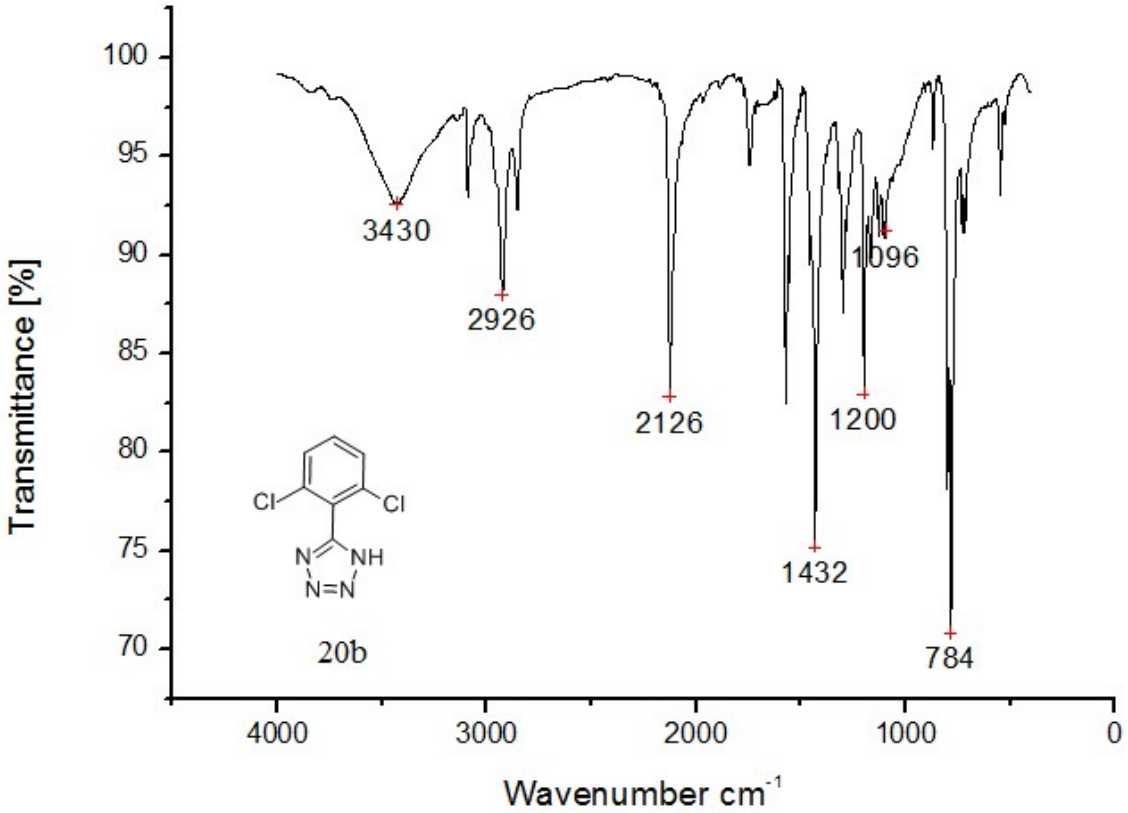

BRUKER
Transmittance [%]
Wavenumber cm-1
15b
3029.59
2947.87
2856.67
1654.33
1599.67
1527.09
1491.16
1453.44
1418.31
1365.04
1244.62
1160.72
1105.50
1069.50
1029.05
995.23
883.09
788.89
731.21
691.90
668.35

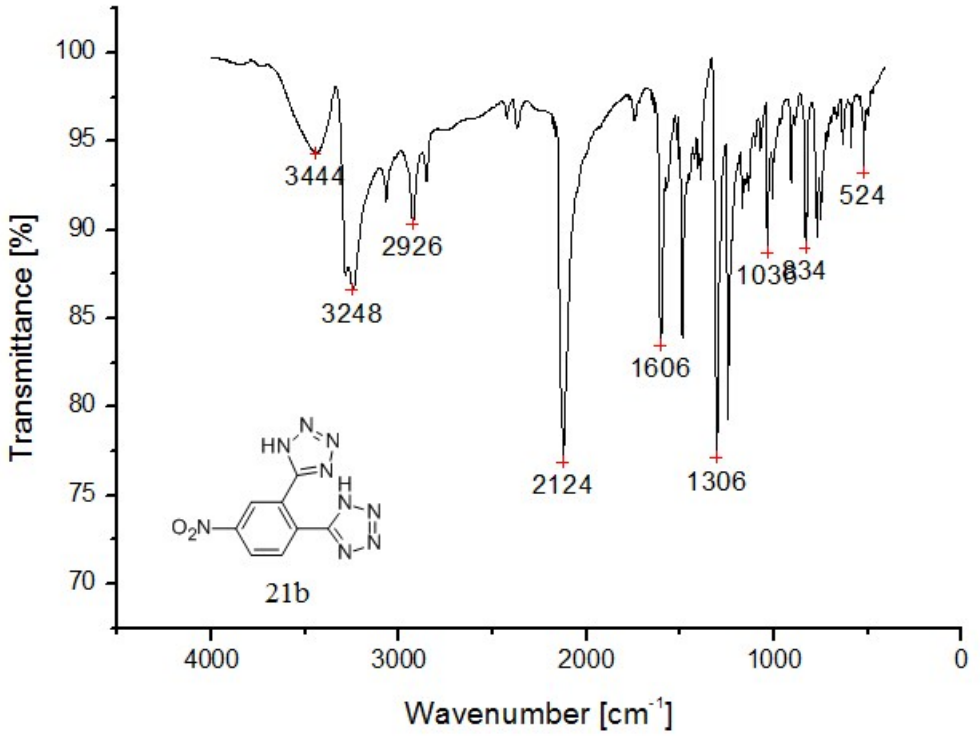

BRUKER
Transmittance [%]
Wavenumber cm-1
16b
2985.74
2838.39
2696.49
2591.42
2471.81
2317.57
1910.38
1820.47
1575.12
1487.04
1404.41
1253.78
1205.39
1108.50
1083.68
1048.17
1013.46
968.67
921.71
812.36
763.84
689.82
654.12
631.36


BRUKER
CH3
17b
Transmittance [%]
94
92
90
88
86
3000.75
2861.54
2699.96
2595.48
2475.02
2350.92
2313.61
1798.32
1647.69
1570.85
1511.01
1444.63
1400.36
1244.85
1210.58
1108.27
1083.77
1045.42
984.95
917.32
840.14
809.67
753.96
682.96
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


BRUKER
Cl
18b
Transmittance [%]
90
85
80
3111.30
2967.50
2847.72
2718.87
2590.56
2467.55
1767.15
1595.19
1550.08
1470.33
1435.44
1407.80
1290.81
1256.35
1206.21
1097.46
1046.32
990.93
916.60
875.99
793.90
748.27
719.20
685.76
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


BRUKER
Cl
H
N
N
N
19b
Transmittance [%]
92
90
88
86
84
82
2985.74
2838.39
2696.49
2591.42
2471.81
2317.57
1910.38
1820.47
1575.12
1487.04
1404.41
1253.78
1205.39
1108.50
1083.68
1048.17
1013.46
988.67
921.71
812.35
763.84
689.82
654.12
631.35
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


Transmittance [%]
100
95
90
85
80
75
70
3430
2926
2126
1432
1200
1096
784
Cl
Cl
N
NH
N=N
20b
4000
3000
2000
1000
0
Wavenumber cm-1



Reference:

[41] S. Kumar, A. Kumar, A. Agarwal and S.K. Awasthi, RSC Adv. 5 (2015) 21651-21658.

[42] Gaussian 09, Revision A.1, Frisch M. J. et al 2009 Gaussian, Inc.,Wallingford, CT, 2013.

[43] H. M. Jamroz, Spectrochim. Acta, Part A, 114 (2013) 220.