Supplementary Material

Reactivity of 2-substituted hydrazinecarbothioamides towards tetracyanoethylene and convenient synthesis of (5-amino-2-diazenylthiazolylmethylene)malononitrile derivatives

Alaa A. Hassan,[a,*] Nasr K. Mohamed,[a] Kamal M. A. El-Shaieb,[a] Hendawy N. Tawfeek,[a] Stefan Bräse,[b] and Martin Nieger [c]

[a] Chemistry Department, Faculty of Science, Minia University, 61519 El-Minia, Egypt
[b] Institute of Organic Chemistry, Karlsruhe Institute of Technology, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany
[c] Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki P.O. Box 55 (A. I. Virtasen aukio 1), 00014 Helsinki, Finland
E-mail: alaahassan2001@mu.edu.eg

Corresponding author: Prof. Dr. Alaa A. Hassan; alaahassan2001@mu.edu.eg; Chemistry Department, Faculty of Science, Minia University, 61519 El-Minia, Egypt

Received [Dates will be filled in by the Editorial office]

Single crystal X-ray structure determination of 3a

Single crystals were obtained by recrystallization from acetonitrile. The single crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123K using CuKα radiation (λ = 1.54178 Å). Direct Methods (SHELXS-97)[32] were used for structure solution and refinement was carried out using SHELXL-2014[33] (full-matrix least-squares on F2). Hydrogen atoms bound to C-atoms were refined using a riding model whilst the NH-hydrogen atoms were refined freely. A semi-empirical absorption correction was applied.

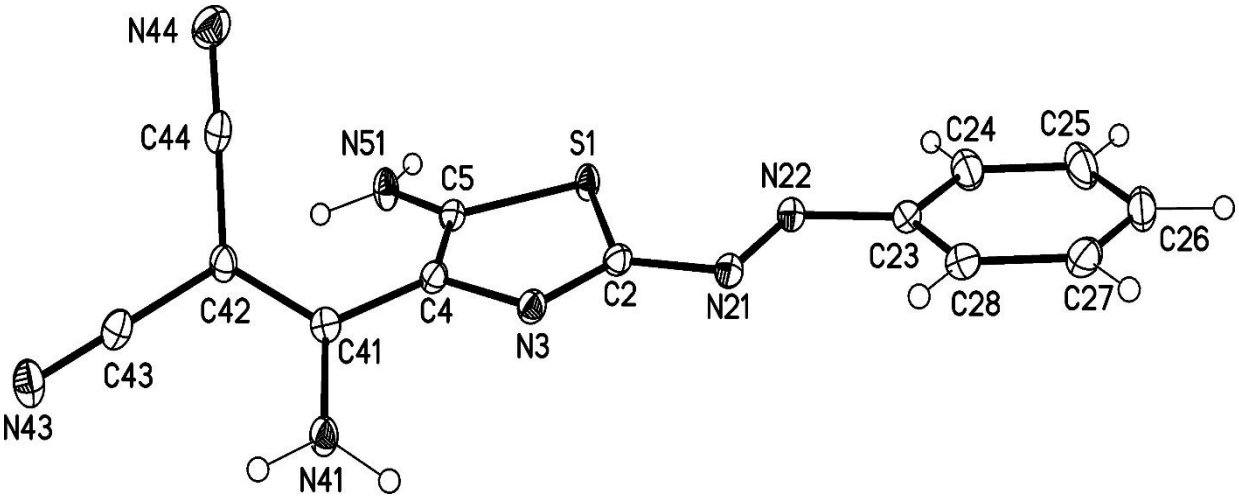


Fig. S1: Molecular Structure of **3a** in the crystal (TIF file). The crystallographic numbering does not reflect the systematic IUPAC numbering.

Table S1. Crystal data for **3a**.

$C_{13}H_9N_7S$	$Z = 2$
$M_r = 295.33$	$F(000) = 304$
Triclinic, *P*-1 (no.2)	$D_x = 1.504$ Mg m^{-3}
$a = 7.3780$ (4) Å	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$b = 7.9678$ (5) Å	Cell parameters from 8992 reflections
$c = 11.9389$ (7) Å	$\theta = 3.9$–$72.0°$
$\beta = 99.249$ (2)°	$\mu = 2.26$ mm^{-1}
$\beta = 104.589$ (2)°	$T = 123$ K
$\gamma = 100.386$ (2)°	Plates, red
$V = 652.23$ (7) Å^3	0.12 × 0.08 × 0.02 mm

Table S2.data collection for **3a**.

Bruker D8 Venture diffractometer with Photon100 detector	2405 reflections with $I > 2\sigma(I)$
Radiation source: IμS microfocus	$R_{int} = 0.030$
rotation in ϕ and ω, 1°, shutterless scans	$\theta_{max} = 72.0°$, $\theta_{min} = 3.9°$

Absorption correction: multi-scan *SADABS* (Sheldrick, 2015)	h = -9→9
T_{min} = 0.814, T_{max} = 0.929	k = -9→9
11384 measured reflections	l = -14→14
2540 independent reflections	

Table S3. Refinement data for **3a**.

Refinement on F^1	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.068$	H atoms treated by a mixture of independent and constrained refinement
S = 1.06	$W = 1/[\sigma^2(Fo^2) + (0.0215P)^2 + 0.4P]$ where $P = (Fo^2 + 2Fc^2)/3$
2540 reflections	$(\Delta/\sigma)_{max} < 0.001$
202 parameters	$\Delta\rangle_{max}$ = 0.27 e Å^{-3}
4 restraints	$\Delta\rangle_{min}$ = -0.24 e Å^{-3}

Table S4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **3a**.

	X	*Y*	*Z*	U_{iso}*/U_{eq}
S1	0.22630 (4)	0.54720 (4)	0.71753 (3)	0.01311 (10)
C2	0.20729 (18)	0.38502 (16)	0.59433 (11)	0.0125 (3)
N3	0.17526 (15)	0.22467 (14)	0.60771 (9)	0.0128 (2)
C4	0.16602 (17)	0.21888 (16)	0.72124 (11)	0.0119 (2)
C5	0.17979 (18)	0.38281 (16)	0.79265 (11)	0.0127 (3)
N21	0.22992 (15)	0.43001 (14)	0.49025 (9)	0.0138 (2)
N22	0.26642 (15)	0.59539 (14)	0.50166 (9)	0.0140 (2)
C23	0.29595 (18)	0.65728 (17)	0.40190 (11)	0.0150 (3)
C24	0.31345 (19)	0.83666 (18)	0.41213 (13)	0.0192 (3)

H24	0.3044	0.9064	0.4820	0.023*
C25	0.3442 (2)	0.9131 (2)	0.31970 (14)	0.0242 (3)
H25	0.3564	1.0353	0.3263	0.029*
C26	0.3571 (2)	0.8106 (2)	0.21805 (13)	0.0251 (3)
H26	0.3760	0.8624	0.1543	0.030*
C27	0.3427 (2)	0.6320 (2)	0.20868 (12)	0.0233 (3)
H27	0.3540	0.5631	0.1391	0.028*
C28	0.31200 (19)	0.55379 (19)	0.29974 (12)	0.0183 (3)
H28	0.3019	0.4318	0.2932	0.022*
N41	0.02420 (17)	-0.08515 (15)	0.66484 (10)	0.0157 (2)
H41A	0.005 (2)	-0.1922 (19)	0.6764 (15)	0.024*
H41B	-0.023 (2)	-0.070 (2)	0.5926 (13)	0.024*
C41	0.12421 (18)	0.05130 (16)	0.75214 (11)	0.0121 (3)
C42	0.18269 (18)	0.03057 (16)	0.86981 (11)	0.0130 (3)
C43	0.09506 (19)	-0.11891 (17)	0.90360 (11)	0.0141 (3)
N43	0.02161 (17)	-0.23716 (15)	0.93361 (10)	0.0194 (3)
C44	0.34342 (19)	0.14578 (17)	0.95815 (11)	0.0152 (3)
N44	0.47467 (18)	0.23502 (16)	1.03036 (11)	0.0235 (3)
N51	0.15596 (17)	0.42280 (15)	0.89979 (10)	0.0153 (2)
H51A	0.153 (2)	0.5297 (19)	0.9267 (15)	0.023*
H51B	0.116 (2)	0.340 (2)	0.9346 (14)	0.023*

Table S5. Atomic displacement parameters (Å2) for **3a**.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01995 (17)	0.00882 (16)	0.01054 (16)	0.00298 (12)	0.00424 (12)	0.00271 (11)
C2	0.0138 (6)	0.0112 (6)	0.0106 (6)	0.0020 (5)	0.0016 (5)	0.0016 (5)
N3	0.0150 (5)	0.0121 (5)	0.0104 (5)	0.0026 (4)	0.0025 (4)	0.0023 (4)
C4	0.0132 (6)	0.0121 (6)	0.0099 (6)	0.0032 (5)	0.0024 (5)	0.0026 (5)
C5	0.0134 (6)	0.0116 (6)	0.0122 (6)	0.0025 (5)	0.0016 (5)	0.0042 (5)

N21	0.0151 (5)	0.0134 (5)	0.0121 (5)	0.0020 (4)	0.0027 (4)	0.0038 (4)
N22	0.0146 (5)	0.0137 (5)	0.0132 (5)	0.0021 (4)	0.0028 (4)	0.0048 (4)
C23	0.0120 (6)	0.0184 (7)	0.0137 (6)	0.0013 (5)	0.0019 (5)	0.0065 (5)
C24	0.0184 (7)	0.0196 (7)	0.0221 (7)	0.0048 (5)	0.0076 (5)	0.0083 (6)
C25	0.0202 (7)	0.0257 (8)	0.0334 (8)	0.0070 (6)	0.0104 (6)	0.0191 (7)
C26	0.0157 (7)	0.0415 (9)	0.0233 (7)	0.0054 (6)	0.0067 (6)	0.0211 (7)
C27	0.0168 (7)	0.0367 (9)	0.0141 (6)	0.0014 (6)	0.0035 (5)	0.0061 (6)
C28	0.0158 (6)	0.0216 (7)	0.0147 (6)	0.0003 (5)	0.0025 (5)	0.0035 (5)
N41	0.0243 (6)	0.0089 (5)	0.0118 (5)	0.0020 (4)	0.0026 (5)	0.0023 (4)
C41	0.0132 (6)	0.0111 (6)	0.0131 (6)	0.0044 (5)	0.0047 (5)	0.0021 (5)
C42	0.0178 (6)	0.0094 (6)	0.0121 (6)	0.0037 (5)	0.0041 (5)	0.0026 (5)
C43	0.0196 (6)	0.0137 (6)	0.0099 (6)	0.0071 (5)	0.0041 (5)	0.0013 (5)
N43	0.0285 (6)	0.0144 (6)	0.0173 (6)	0.0055 (5)	0.0088 (5)	0.0052 (5)
C44	0.0209 (7)	0.0138 (6)	0.0134 (6)	0.0071 (5)	0.0054 (5)	0.0059 (5)
N44	0.0264 (7)	0.0218 (6)	0.0176 (6)	0.0036 (5)	-0.0001 (5)	0.0031 (5)
N51	0.0260 (6)	0.0093 (5)	0.0128 (5)	0.0057 (4)	0.0083 (5)	0.0032 (4)

Table S6. Geometric parameters (Å, º) for **3a.**

S1—C5	1.7345 (13)	C26—C27	1.392 (2)
S1—C2	1.7529 (13)	C26—H26	0.9500
C2—N3	1.2998 (17)	C27—C28	1.383 (2)
C2—N21	1.3881 (16)	C27—H27	0.9500
N3—C4	1.3819 (16)	C28—H28	0.9500
C4—C5	1.4120 (18)	N41—C41	1.3311 (17)
C4—C41	1.4426 (18)	N41—H41A	0.879 (14)
C5—N51	1.3308 (17)	N41—H41B	0.882 (14)
N21—N22	1.2741 (15)	C41—C42	1.4079 (17)
N22—C23	1.4106 (16)	C42—C43	1.4169 (18)

C23—C24	1.3943 (19)	C42—C44	1.4239 (18)
C23—C28	1.4023 (19)	C43—N43	1.1540 (18)
C24—C25	1.390 (2)	C44—N44	1.1492 (18)
C24—H24	0.9500	N51—H51A	0.868 (14)
C25—C26	1.385 (2)	N51—H51B	0.879 (14)
C25—H25	0.9500		
C5—S1—C2	88.31 (6)	C25—C26—H26	119.8
N3—C2—N21	123.17 (11)	C27—C26—H26	119.8
N3—C2—S1	116.35 (9)	C28—C27—C26	120.58 (14)
N21—C2—S1	120.47 (9)	C28—C27—H27	119.7
C2—N3—C4	110.77 (10)	C26—C27—H27	119.7
N3—C4—C5	114.43 (11)	C27—C28—C23	118.99 (14)
N3—C4—C41	119.08 (11)	C27—C28—H28	120.5
C5—C4—C41	126.15 (11)	C23—C28—H28	120.5
N51—C5—C4	130.37 (12)	C41—N41—H41A	121.9 (11)
N51—C5—S1	119.65 (10)	C41—N41—H41B	120.2 (11)
C4—C5—S1	109.92 (9)	H41A—N41—H41B	117.9 (16)
N22—N21—C2	110.69 (10)	N41—C41—C42	120.40 (12)
N21—N22—C23	115.91 (11)	N41—C41—C4	117.45 (11)
C24—C23—C28	120.46 (12)	C42—C41—C4	122.15 (11)
C24—C23—N22	114.51 (12)	C41—C42—C43	120.84 (11)
C28—C23—N22	125.02 (12)	C41—C42—C44	123.01 (12)
C25—C24—C23	119.80 (13)	C43—C42—C44	115.83 (11)
C25—C24—H24	120.1	N43—C43—C42	177.77 (13)
C23—C24—H24	120.1	N44—C44—C42	178.21 (14)
C26—C25—C24	119.76 (14)	C5—N51—H51A	118.2 (12)
C26—C25—H25	120.1	C5—N51—H51B	120.6 (11)
C24—C25—H25	120.1	H51A—N51—H51B	119.5 (16)

C25—C26—C27	120.40 (13)		
C5—S1—C2—N3	-1.77 (10)	C28—C23—C24—C25	0.9 (2)
C5—S1—C2—N21	179.51 (11)	N22—C23—C24—C25	179.58 (12)
N21—C2—N3—C4	177.75 (11)	C23—C24—C25—C26	0.1 (2)
S1—C2—N3—C4	-0.93 (14)	C24—C25—C26—C27	-1.1 (2)
C2—N3—C4—C5	4.05 (15)	C25—C26—C27—C28	1.1 (2)
C2—N3—C4—C41	177.72 (11)	C26—C27—C28—C23	-0.1 (2)
N3—C4—C5—N51	171.91 (12)	C24—C23—C28—C27	-0.91 (19)
C41—C4—C5—N51	-1.2 (2)	N22—C23—C28—C27	-179.41 (12)
N3—C4—C5—S1	-5.31 (14)	N3—C4—C41—N41	-26.14 (17)
C41—C4—C5—S1	-178.47 (10)	C5—C4—C41—N41	146.72 (13)
C2—S1—C5—N51	-173.76 (11)	N3—C4—C41—C42	154.95 (12)
C2—S1—C5—C4	3.81 (9)	C5—C4—C41—C42	-32.19 (19)
N3—C2—N21—N22	-177.70 (11)	N41—C41—C42—C43	-17.55 (19)
S1—C2—N21—N22	0.93 (14)	C4—C41—C42—C43	161.33 (12)
C2—N21—N22—C23	178.88 (10)	N41—C41—C42—C44	155.74 (12)
N21—N22—C23—C24	172.96 (11)	C4—C41—C42—C44	-25.38 (19)
N21—N22—C23—C28	-8.47 (18)		

Table S7. Hydrogen-bond geometry (Å, º)For **3a.**

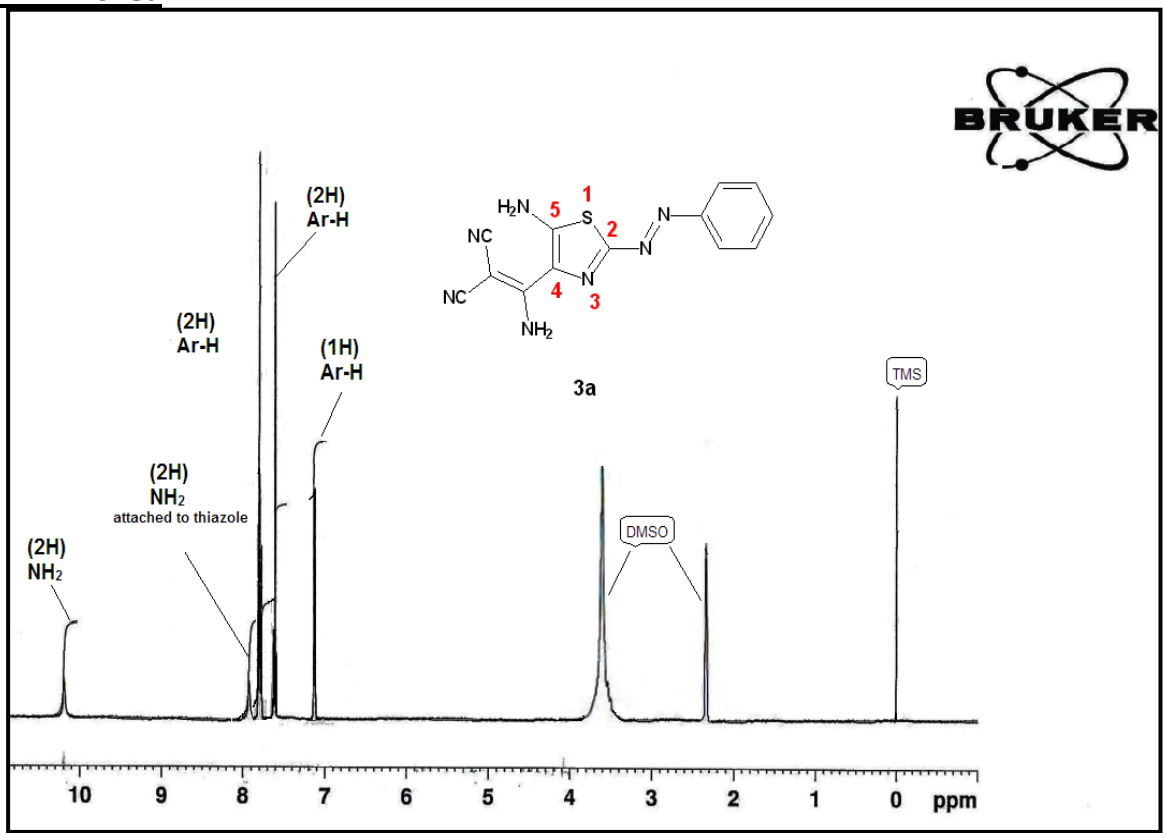
D—H···A	D—H	H···A	D···A	D—H···A
N41—H41A···S1i	0.88 (1)	2.89 (2)	3.5910 (12)	138 (1)
N41—H41B···N3ii	0.88 (1)	2.39 (2)	3.1344 (15)	143 (2)
N51—H51A···N43iii	0.87 (1)	2.24 (2)	3.0504 (16)	155 (2)
N51—H51B···N43iv	0.88 (1)	2.26 (2)	3.0693 (16)	153 (2)

Symmetry codes: (i) x, y-1, z; (ii) -x, -y, -z+1; (iii) x, y+1, z; (iv) -x, -y, -z+2.

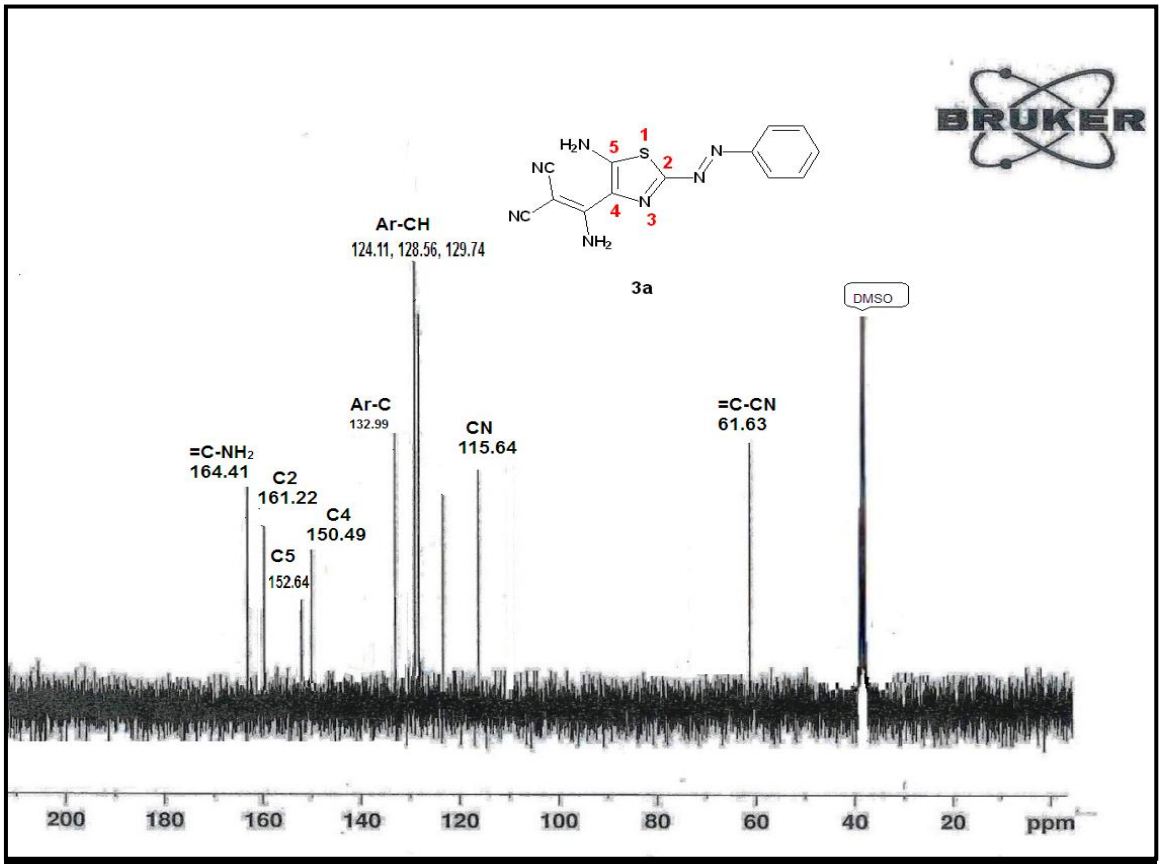
Document origin: publCIF [Westrip, S. P. (2010). J. Apply. Cryst., 43, 920-925].

^{1}H and ^{13}C-NMR spectrums of 3a-d

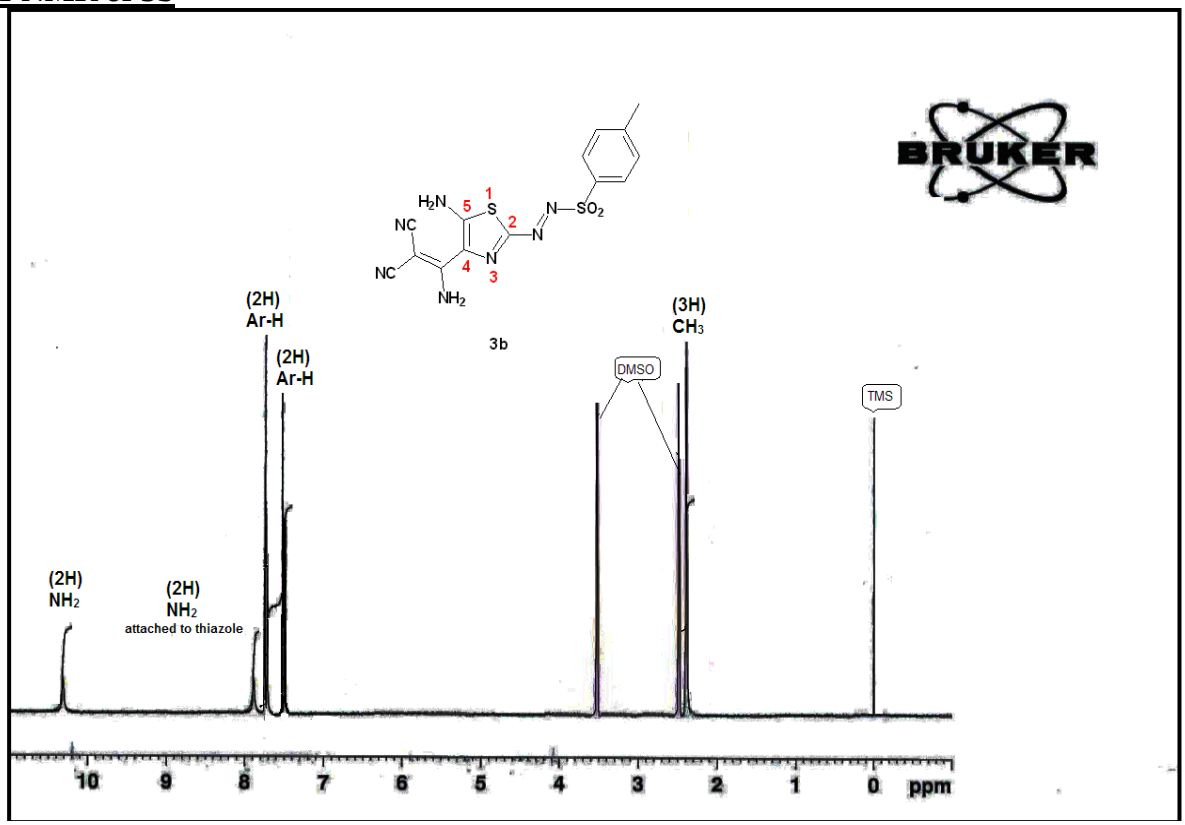
^{1}H-NMR of 3a



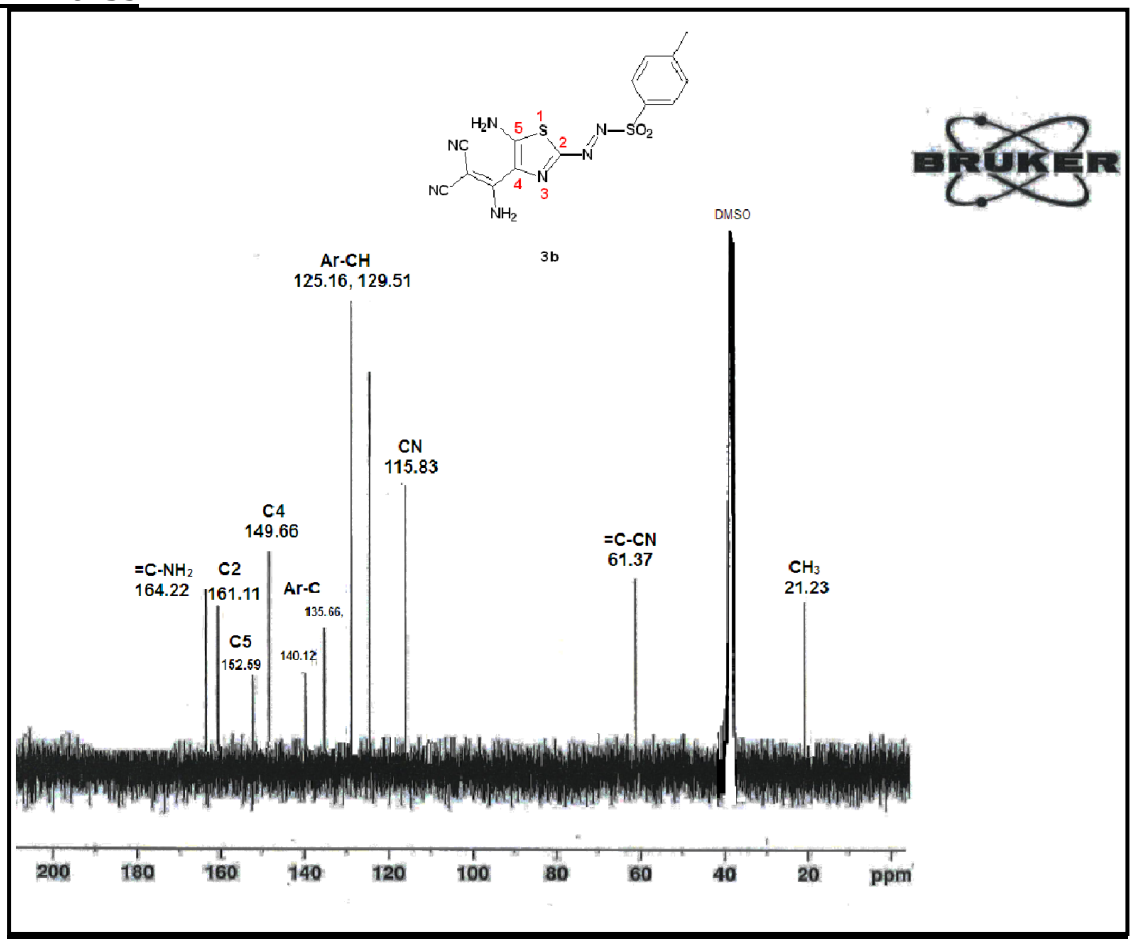
^{13}C-NMR of 3a



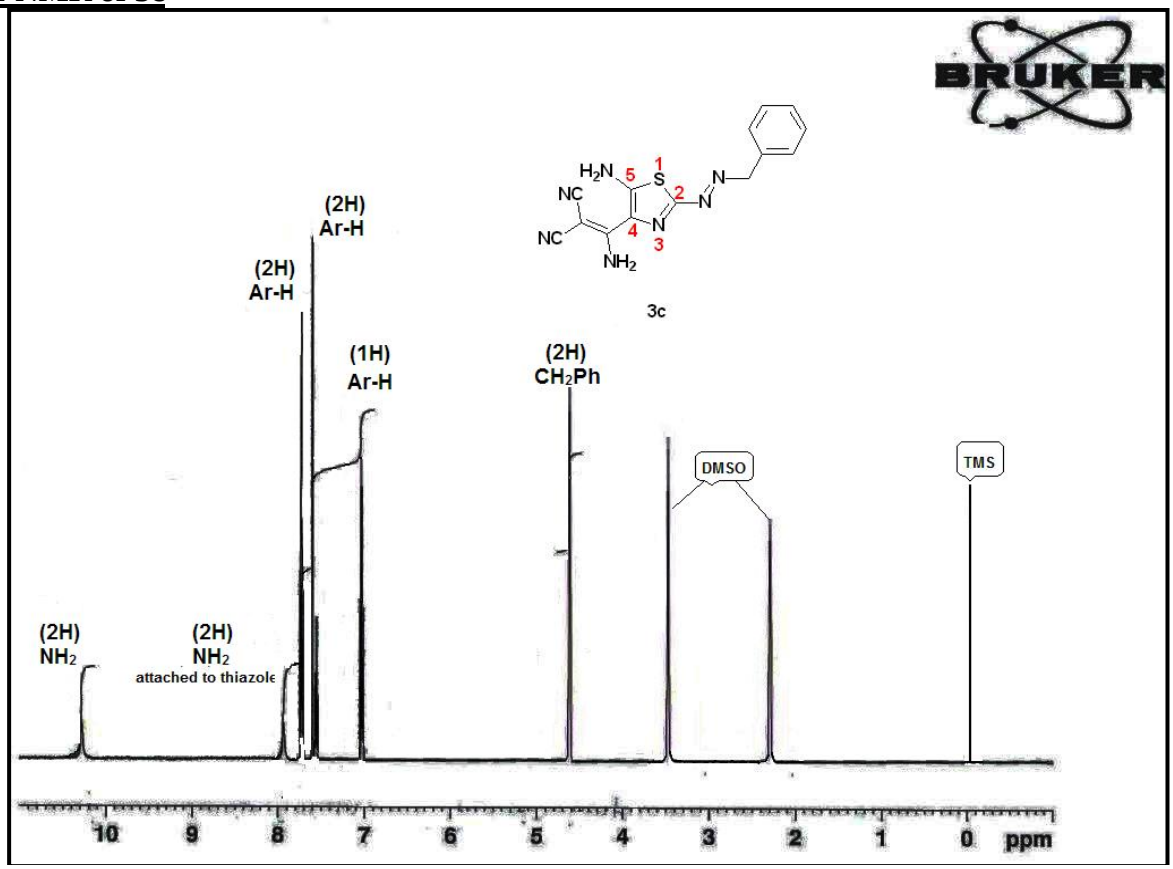
^{1}H-NMR of 3b



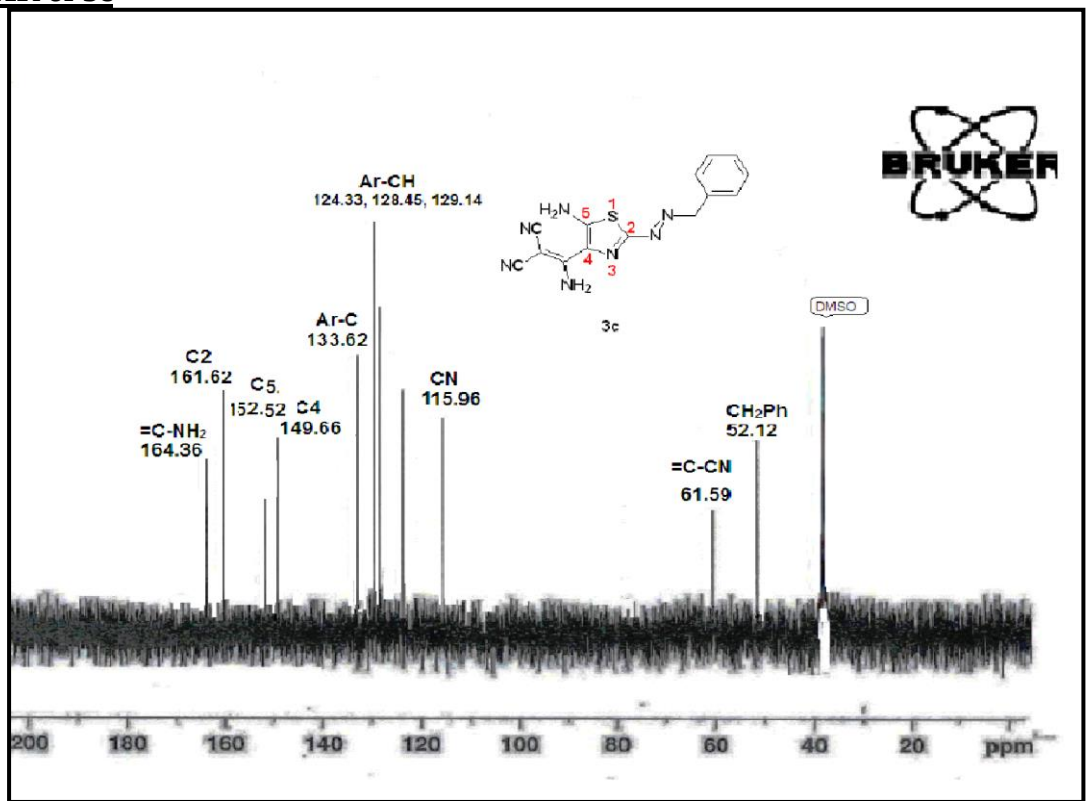
^{13}C-NMR of 3b



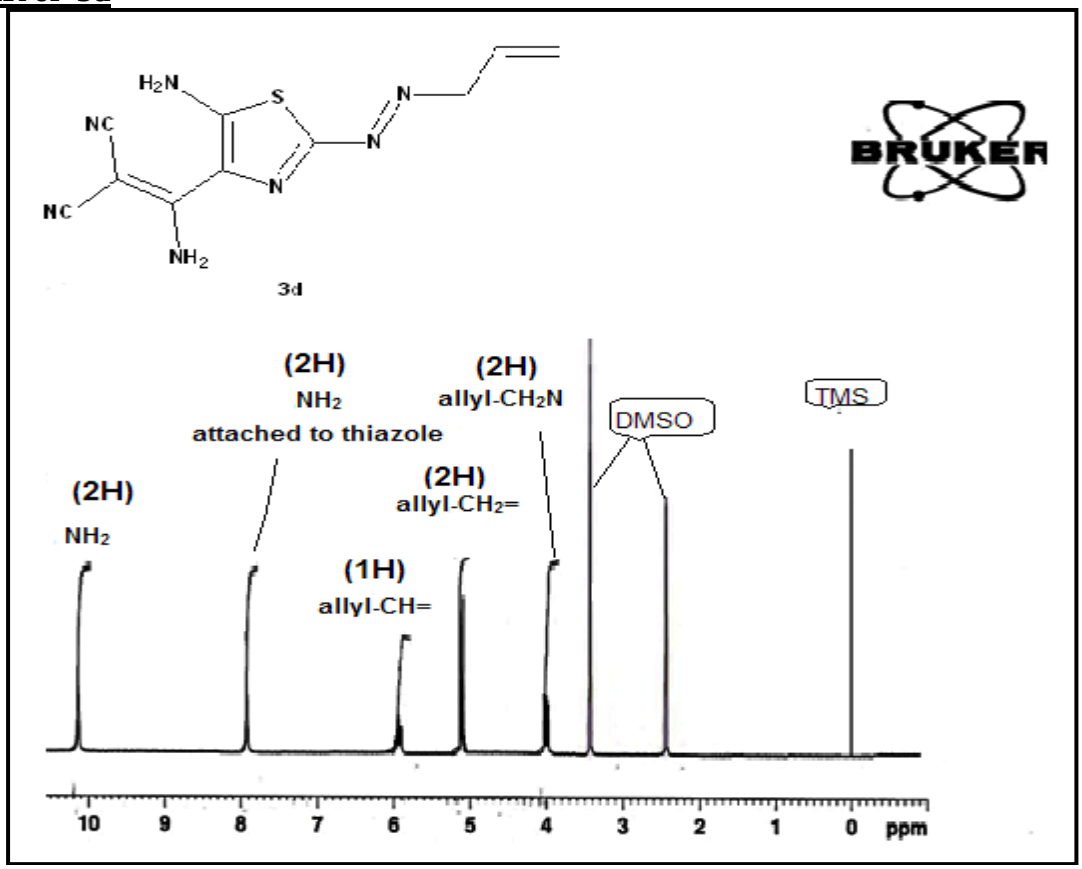
^{1}H-NMR of 3c



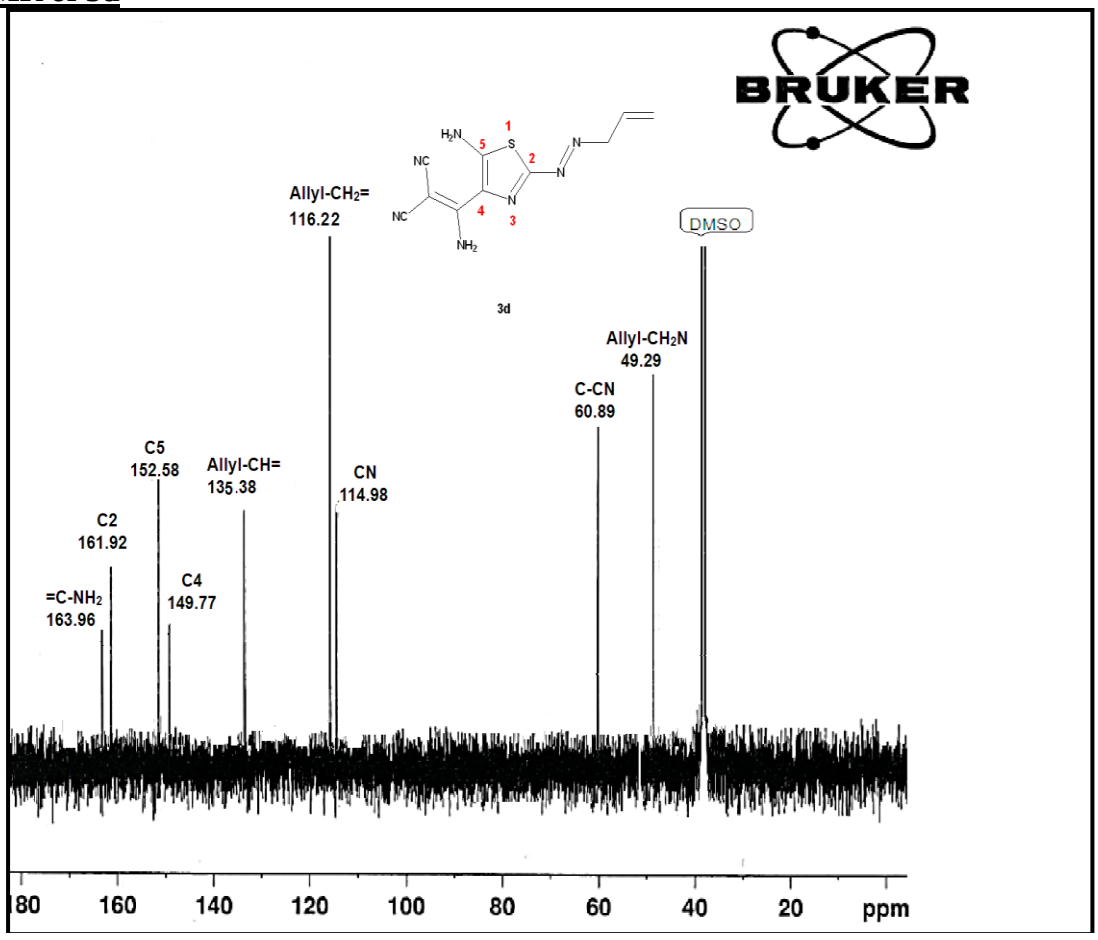
^{13}C-NMR of 3c



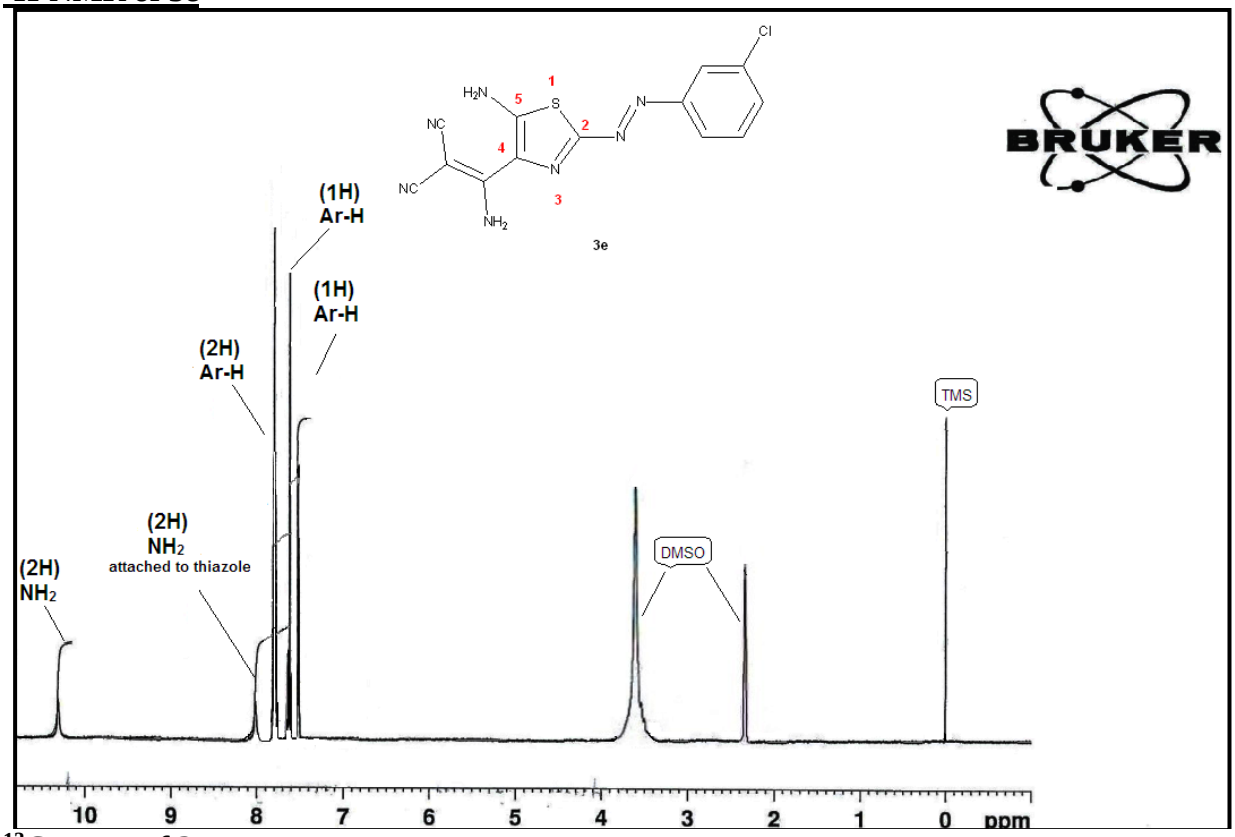
^{1}H-NMR of 3d



^{13}C-NMR of 3d



^{1}H-NMR of 3e



^{13}C-NMR of 3e