Supplementary Material

"Efficient, mild synthesis of *N*- unsubstituted 1,2,3-triazoles from methanolysis of 1-sulfonyl-1,2,3-triazoles"

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CONTENTS:

1. - General Considerations

The starting materials were purchased from Aldrich Chemical Co. and were used without further purification. 1-(*p*-Toluenesulfonyl)-1,2,3-triazoles were prepared according to the literature.[1,2] Solvents were distilled before use. Silica gel (230–400 mesh) was purchased from Merck. Silica plates of 0.20 mm thickness were used for thin layer chromatography. Melting points were determined with a Krüss Optronic melting point apparatus and they are uncorrected.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 300 MHz, and a Varian 500 MHz, The chemical shifts (δ) are given in ppm relative to TMS as internal standard (0.00). For analytical purposes the mass spectra were recorded on a Shimadzu GCMS-QP2010 Plus in the EI mode, 70 eV, 200 °C via direct inlet probe. Only the molecular and parent ions (m/z) are reported. IR spectra were recorded on a Bruker TENSOR 27 FT instrument.

For the X-ray diffraction studies, crystals of compounds **5** and **8** were obtained by slow evaporation of a dilute MeOH solution, and the reflections were acquired with a Bruker APEX DUO diffractometer equipped with an Apex II CCD detector using CuKa (k = 1.54178 Å) for Incoatec IlS microsource and Helios optic monochromator. Frames were integrated with SAINT. Multi-scan absorption correction (SADABS) was applied. The structures were solved by using direct methods (SHELXT) and refined using fullmatrix least-squares on F2 with SHELXL using the ShelXle GUI. Weighted R factors, Rw and all goodness-of-fit indicators are based on F2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the CAH bonds were placed in idealized positions, whereas the hydrogen atoms from the NH, NH_2 and OH moieties were localized from the difference electron density map; their position was refined with Uiso tied to the parent atom with distance restraints (DFIX or SADI). Three standard reflections every 97 reflections were used to monitor the crystal stability. The structure was solved by direct methods; missing atoms were found by difference-Fourier synthesis, and refined on F2 by a full-matrix least-squares procedure using anisotropic displacement parameters using SHELX-97. Crystallographic data for the structures reported herein have been deposited with the

Cambridge Crystallographic Data Centre (CCDC). Copies of available materials can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (facsimile: (44) 01223 336033); e-mail: deposit@ccdc.ac.uk.

2. - General procedure for the synthesis of *N*- unsubstituted 1,2,3-triazoles from methanolysis of 1-sulfonyl-1,2,3-triazoles

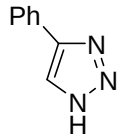
Typical procedure. A solution of the appropriate 1-(*p*-toluenesulfonyl)-1,2,3-triazole (1 mmol) in MeOH (10 mL) was heated at reflux temperature for 8 h. The mixture was cooled to room temperature and the solvent was removed under reduced pressure, the final product was purified by column chromatography (SiO_2, hexane/AcOEt 7:3).

3. - References.

1.- Raushel, J.; Fokin, V. V. *Org. Lett*. **2010**, *12*, 4952-4955.

2.- Valencia, R. A.; Corona, D.; Cuevas-Yañez, E. *J. Mex. Chem. Soc*. **2012**, *56*, 152-155.

4. Spectroscopic data of compounds

4-Phenyl-1,2,3-triazole (2): 

4-Phenyl-1-(toluene-4-sulfonyl)-1,2,3-triazole afforded 4-Phenyl-1,2,3-triazole as a white solid m.p. 119 ºC. Yield: 119 mg (82%).

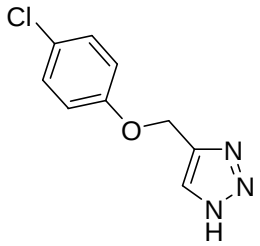
IR (ATR, cm^{-1}): 3154, 3116, 1607, 1465, 915, 692.

HRMS (EI): for $C_8H_7N_3$ calcd. 145.0640, found 145.0643.

MS [EI+] m/z (%): 145$[M]^+$ (39), 118 $[M - HCN]^+$ (83), 89 $[M - CH_2N_3]^+$ (100), 77 $[C_6H_5]^+$ (51)

^{1}H NMR: (300 MHz, $CDCl_3$) δ =14.33 (s, 1H), 7.92 (s, 1H), 7.82 (d, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 1H)

^{13}C NMR: (75 MHz, $CDCl_3$) δ =131.82 (C), 130.29 (C), 128.25 (2xCH), 128.18 (CH), 127.72 (CH), 125.41 (2xCH).

4-(4-chlorophenoxymethyl)-1,2,3-triazole (3): 

4-(4-Chlorophenoxymethyl)-1-(toluene-4-sulfonyl)-1,2,3-triazole afforded 4-(4-chlorophenoxymethyl)-1,2,3-triazole as a white solid m.p. 95 ºC. Yield: 134 mg (67%).

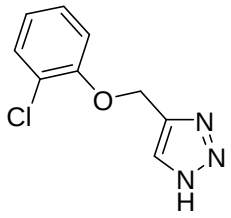
IR (ATR, cm^{-1}): 3175, 3092, 1487, 1288, 1116, 825, 640.

HRMS (EI): for $C_9H_8ClN_3O$ calcd. 209.6323, found 205.6929.

MS [EI+] m/z (%): 209$[M]^+$ (53), 128 $[M - C_3H_3N_3]^+$ (96), 82 $[C_3H_4N_3]^+$ (100).

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 12.63 (s, 1H), 7.80 (s, 1H), 7.24 (d, *J* = 6.9 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.21 (s, 2H).

^{13}C NMR: (75 MHz, $CDCl_3$) δ =156.67 (C), 143.25 (C), 130.84 (C), 129.47 (2xCH), 126.15 (CH), 116.15 (2xCH), 61.77 (CH_2).



4-(2-Chlorophenoxymethyl)-1,2,3-triazole (4) :

4-(2-Chlorophenoxymethyl)-1-(toluene-4-sulfonyl)-1,2,3-triazole afforded 4-(2-chlorophenoxymethyl)-1,2,3-triazole as a white solid m.p. 78 ºC. Yield: 122.5 mg (61%).

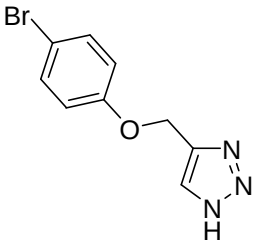
IR (ATR, cm^{-1}): 3139, 3074, 1483, 1276, 1059, 747, 682.

HRMS (EI): for $C_9H_8ClN_3O$ calcd. 209.6323, found 205.6926.

MS [EI+] m/z (%): 209$[M]^+$ (23), 174 $[M - Cl]^+$ (25), 82 $[C_3H_4N_3]^+$ (100).

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 14.54 (s, 1H), 7.77 (s, 1H), 7.35 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 5.29 (s, 2H).

^{13}C NMR: (75 MHz, $CDCl_3$) δ = 148.95 (C), 138.00 (C), 128.11 (CH), 125.46 (CH), 122.95 (CH), 118.22 (C), 117.19 (CH), 109.50 (CH), 58.08 (CH_2).



4-(4-Bromophenoxymethyl)-1,2,3-triazole (5) :

4-(4-Bromophenoxymethyl)-1-(toluene-4-sulfonyl)-1,2,3-triazole afforded 4-(4-nromophenoxymethyl)-1,2,3-triazole as a white solid m.p. 157 ºC. Yield: 152.9 mg (63%).

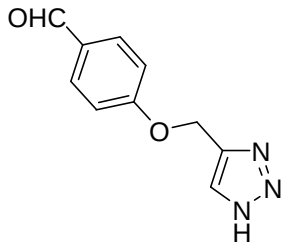
IR (ATR, cm^{-1}): 3133, 3076, 1485, 1283, 1033, 823.

HRMS (EI): for $C_9H_8BrN_3O$ calcd. 252.9851, found 252.9856.

MS [EI+] m/z (%): 253$[M]^+$ (31), 171 $[M - HBr]^+$ (78), 82 $[C_3H_4N_3]^+$ (100).

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 12.61 (s, 1H), 7.80 (s, 1H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.21 (s, 2H).

^{13}C NMR:(125 MHz, $CDCl_3$) δ =157.19 (C), 143.45 (C), 132.48 (2xCH), 131.33 (CH), 116.65 (2xCH), 113.75 (C), 61.74 (CH_2).

4-(1,2,3-Triazol-4-ylmethoxy)benzaldehyde (6) : 

4-[1-(Toluene-4-sulfonyl)-1,2,3-triazol-4-ylmethoxy]-benzaldehyde afforded 4-(1,2,3-triazol-4-ylmethoxy)benzaldehyde as a white solid m.p. 152 ºC. Yield: 122 mg (58%).

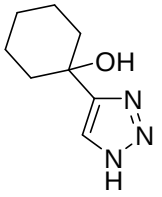
IR (ATR, cm^{-1}): 2959, 2918, 2851, 1726, 1599, 1257, 1038, 853, 614.

HRMS (EI): for $C_{10}H_9N_3O$ calcd. 203.0695, found 203.0697.

MS [EI+] m/z (%): 203$[M]^+$ (11), 149 $[M - CN_3]^+$ (100).

^{1}H NMR: (300 MHz, $CDCl_3$+DMSO-d_6) δ = 14.83 (s, 1H), 9.87 (s, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.78 (s, 1H), 7.14 (d, *J* = 8.7 Hz, 2H), 5.30 (s, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$+DMSO-d_6) δ = 190.73 (C), 163.28 (C), 131.91 (2xCH), 131.18 (C), 130.18 (CH), 128.80 (C), 115.22 (2xCH), 61.84 (CH_2).

1-(1,2,3-Triazol-4-yl)cyclohexanol (7): 

1-[1-(Toluene-4-sulfonyl)-1,2,3-triazol-4-yl]-cyclohexanol afforded 1-(1,2,3-triazol-4-yl)cyclohexanol as a white solid m.p. 75 ºC. Yield: 167.2 mg (63%).

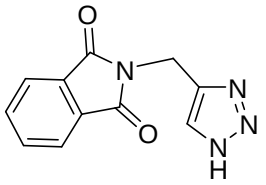
IR (ATR, cm^{-1}): 3140, 3117, 2932, 2917, 1450, 1223, 918.

HRMS (EI): for $C_8H_{13}N_3O$ calcd. 167.1059, found 167.1057.

MS [EI+] m/z (%): 167 $[M]^+$ (1), 149 $[M - H_2O]^+$ (70), 134 $[M - H_3NO]^+$ (100).

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 12.97 (s, 1H), 7.69 (s, 1H), 3.07 (s, 1H), 2.08 (m, 2H), 1.99 – 1.85 (m, 2H), 1.82 – 1.33 (m, 6H).

^{13}C NMR: (75 MHz, $CDCl_3$) δ = 147.93 (C), 128.56 (CH), 71.46 (C), 32.43 (2xCH_2), 23.08 (CH_2), 19.40 (2xCH_2).

2-(1,2,3-Triazol-4-ylmethyl)isoindole-1,3-dione (8) : 

2-[1-(Toluene-4-sulfonyl)-1,2,3-triazol-4-ylmethyl]-isoindole-1,3-dione afforded 2-(1,2,3-triazol-4-ylmethyl)isoindole-1,3-dione as a white solid m.p. 125 ºC. Yield: 129.9 mg (57%).

IR (ATR, cm^{-1}): 3116, 3095, 2923, 2853, 1707, 1583, 1465, 709.

HRMS (EI): for $C_{11}H_8N_4O_2$ calcd. 228.0647, found 228.0650.

MS [EI+] m/z (%): 228 $[M]^+$ (100), 104 $[C_7H_4O]^+$ (97), 76 $[C_6H_4]^+$ (69).

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 14.44 (s, 1H), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.64 (s, 1H), 4.98 (s, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ = 166.96 (2xC), 142.04 (C), 133.79 (2xCH), 131.45 (2xC), 128.24 (CH), 122.83 (2xCH), 36.18 (CH_2).

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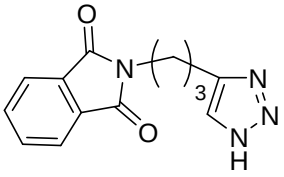
2-[3-(1,2,3-Triazol-4-yl)propyl]isoindole-1,3-dione (9): 

2-{3-[1-(Toluene-4-sulfonyl)-1,2,3-triazol-4-yl]-propyl}-isoindole-1,3-dione afforded 2-[3-(1,2,3-Triazol-4-yl)propyl]isoindole-1,3-dione as white solid m.p. 116 ºC. Yield: 133.1 mg (52%).

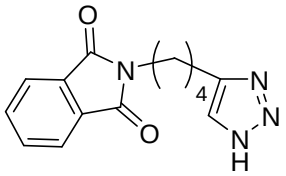
IR (ATR, cm^{-1}): 3284, 3134, 2955, 2941, 1704, 1131, 1118, 717.

HRMS (EI): for $C_{13}H_{12}N_4O_2$ calcd. 256.0960, found 256.0965.

MS [EI+] m/z (%): 256 $[M]^+$ (32), 104 $[C_7H_4O]^+$ (88), 76 $[C_6H_4]^+$ (100).

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 12.76 (s, 1H), 7.86 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 7.56 (s, 1H), 3.77 (m, 2H), 2.81 (m, 2H), 2.10 (m, 2H).

^{13}C NMR: (75 MHz, $CDCl_3$) δ = 168.58 (2xC), 144.69 (C), 134.05 (2xCH), 131.98 (2xC), 130.89 (CH), 123.30 (2xCH), 37.29 (CH_2), 27.98 (CH_2), 22.27 (CH_2).

2-[4-(1,2,3-Triazol-4-yl)butyl]isoindole-1,3-dione (10): 

2-{4-[1-(Toluene-4-sulfonyl)-1,2,3-triazol-4-yl]butyl}isoindole-1,3-dione afforded 2-[4-(1,2,3-triazol-4-yl)butyl]isoindole-1,3-dione as white solid m.p. 106 ºC. Yield: 145.8 mg (54%).

IR (ATR, cm^{-1}): 3126, 3067, 2940, 2871, 1702, 718, 710.

HRMS (EI): for $C_{14}H_{14}N_4O_2$ calcd. 270.1117, found 270.1119.

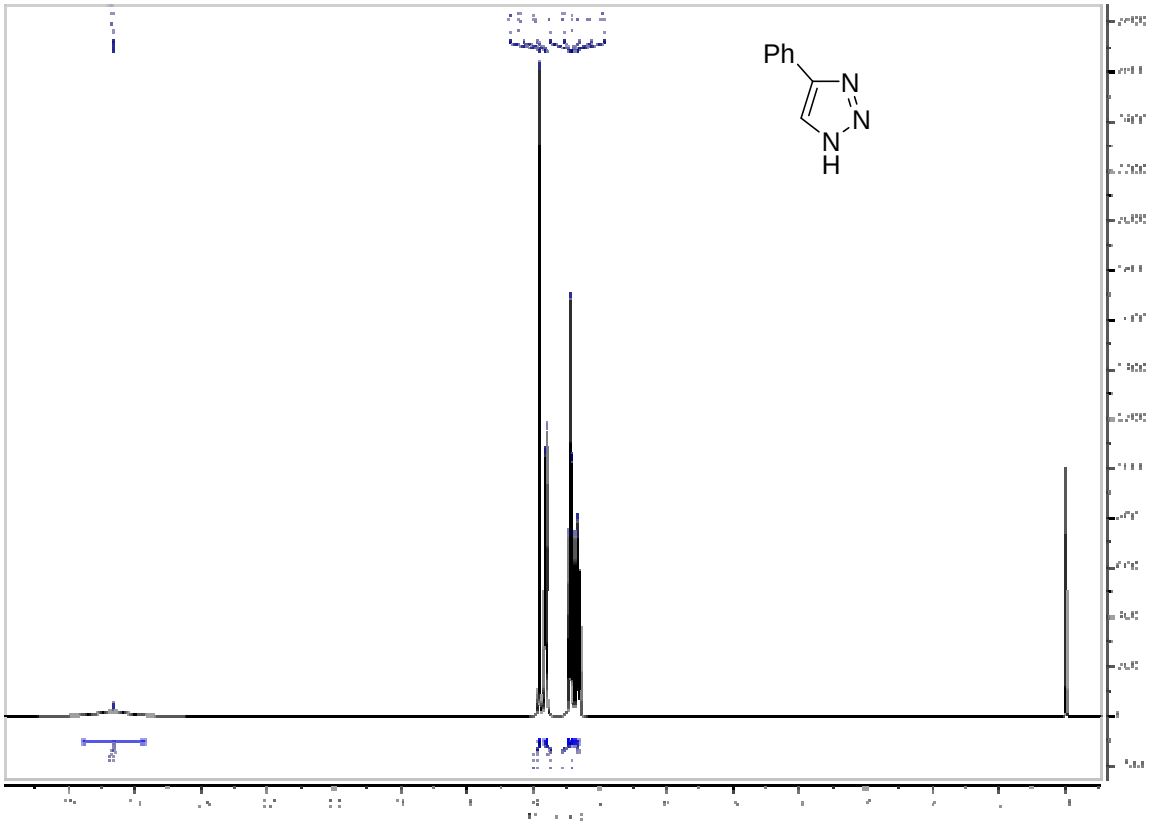
MS [EI+] m/z (%): 270 $[M]^+$ (40), 104 $[C_7H_4O]^+$ (100), 76 $[C_6H_4]^+$ (80)

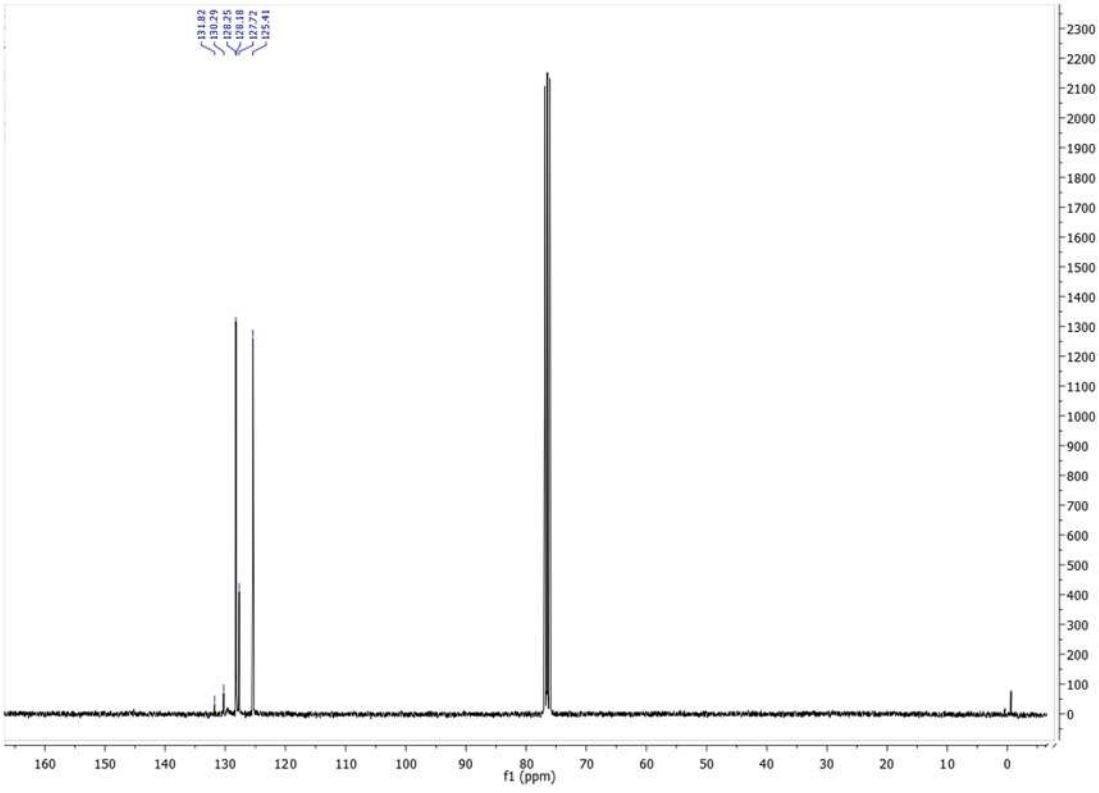
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 13.14 (s, 1H), 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.52 (s, 1H), 3.73 (s, 2H), 2.81 (s, 2H), 1.82 – 1.70 (m, 4H).

^{13}C NMR: (75 MHz, $CDCl_3$) δ = 167.35(2xC), 144.58 (C), 132.78 (2xCH), 130.84 (2xC), 129.70 (CH), 122.06 (2xCH), 36.32 (CH_2), 26.82 (CH_2), 25.20 (CH_2), 23.15 (CH_2).

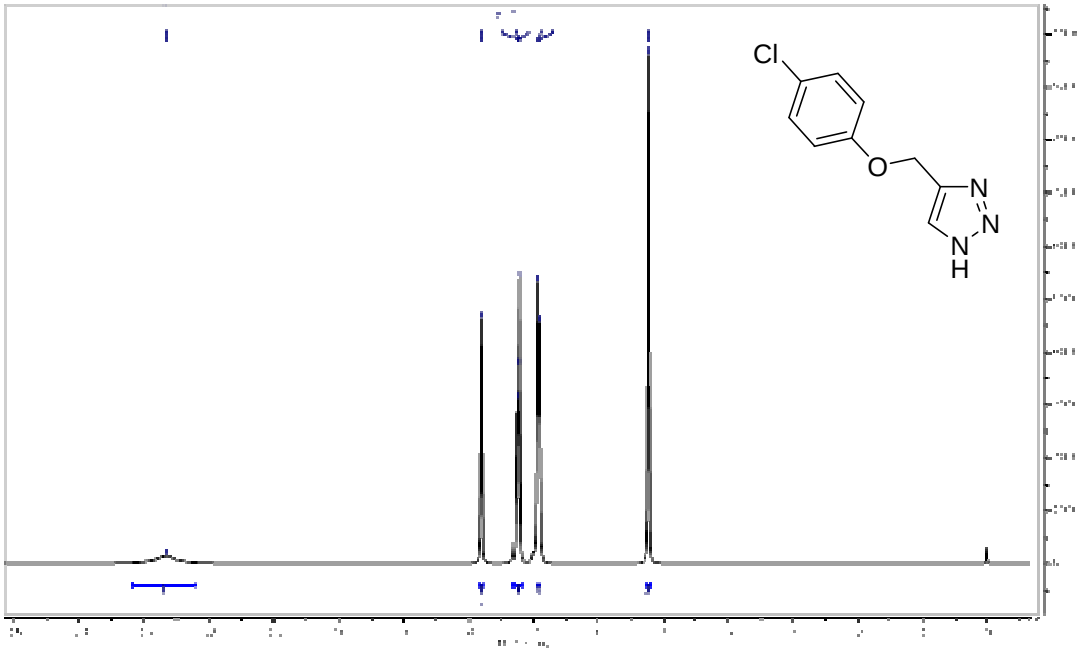
5. - ^{1}H NMR and ^{13}C NMR spectra for compounds

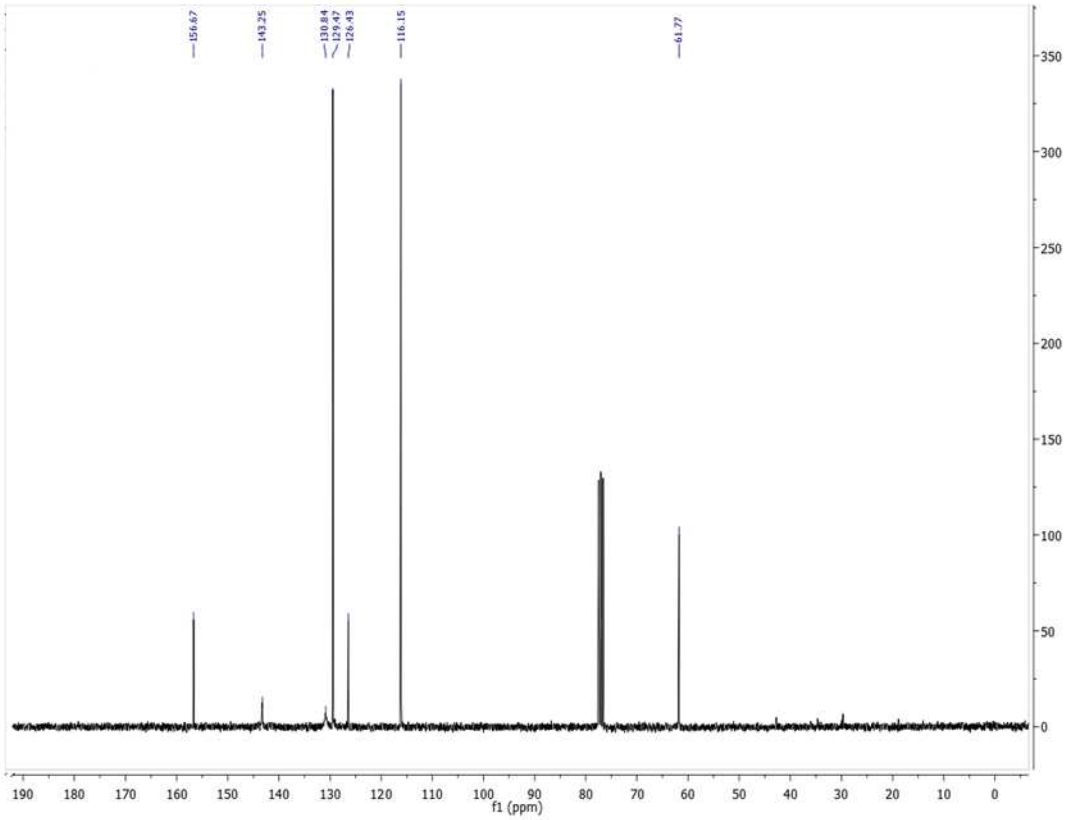
4-Phenyl-1,2,3-triazole (2)



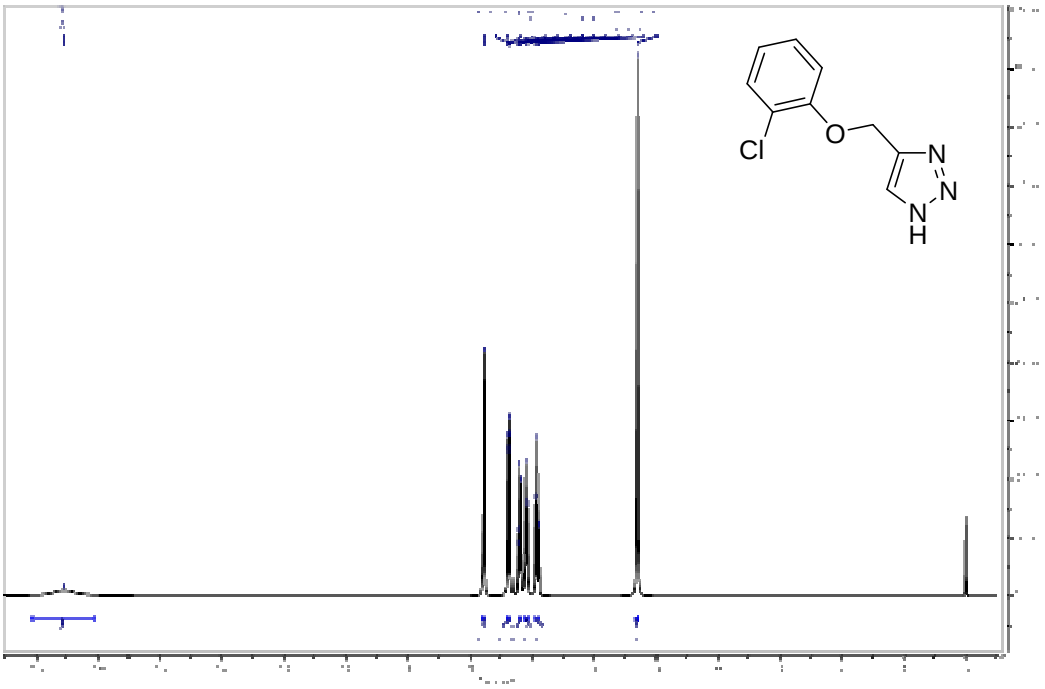


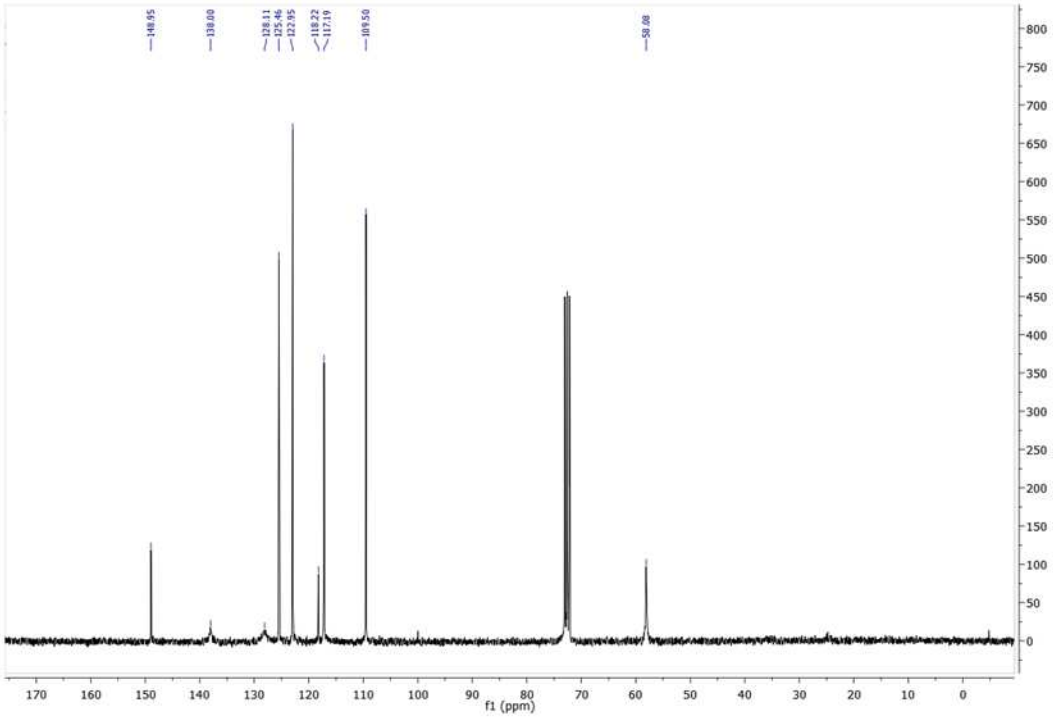
4-(4-chlorophenoxymethyl)-1,2,3-triazole (3)



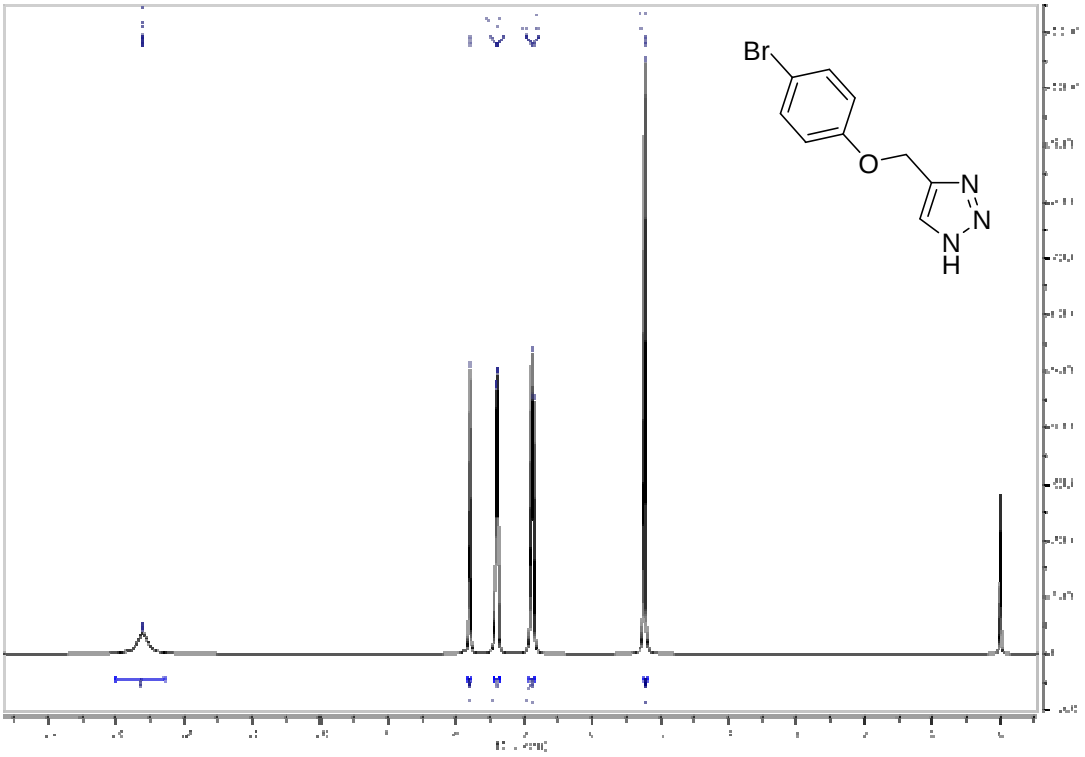


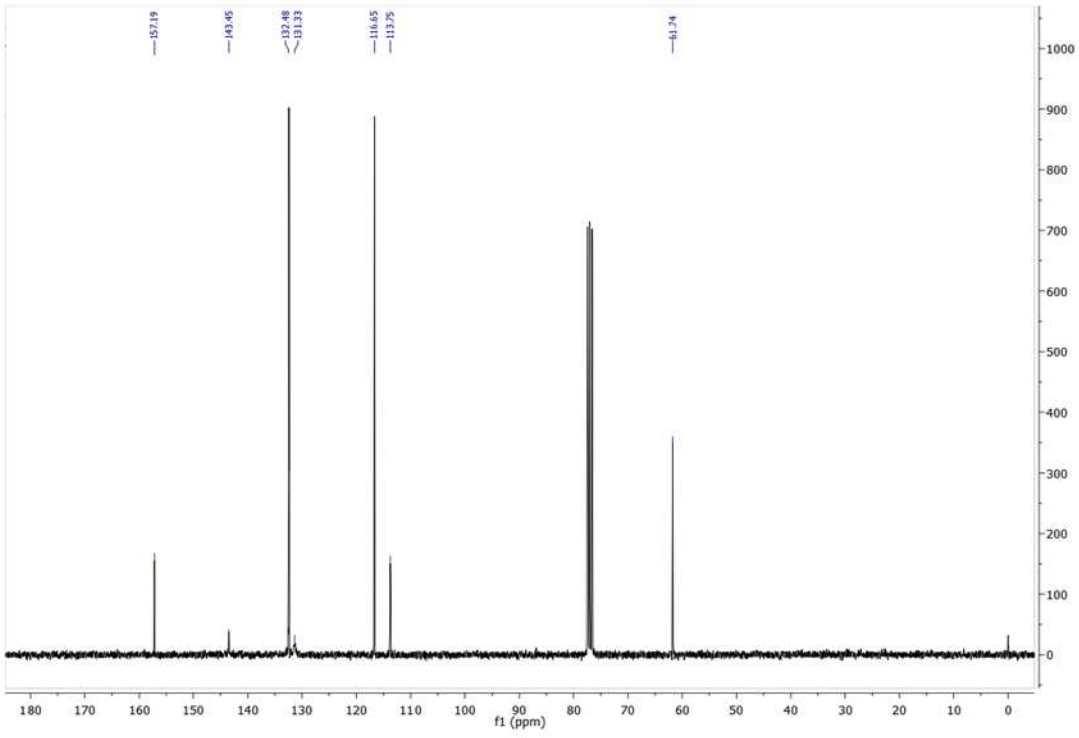
4-(2-Chlorophenoxymethyl)-1,2,3-triazole (4)



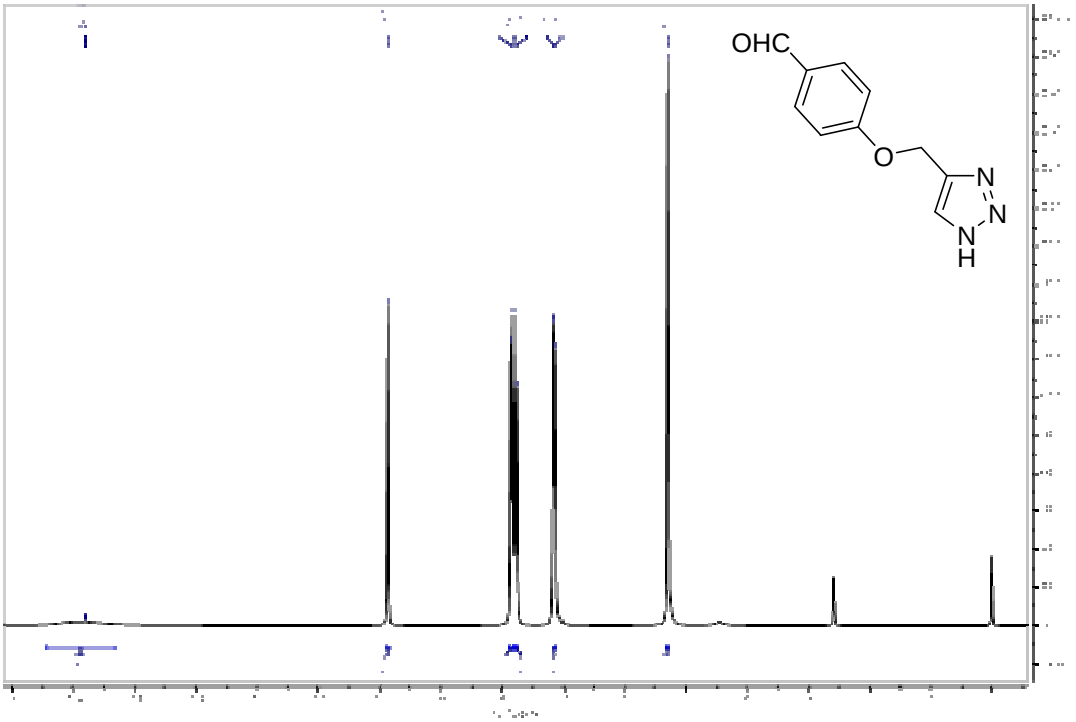


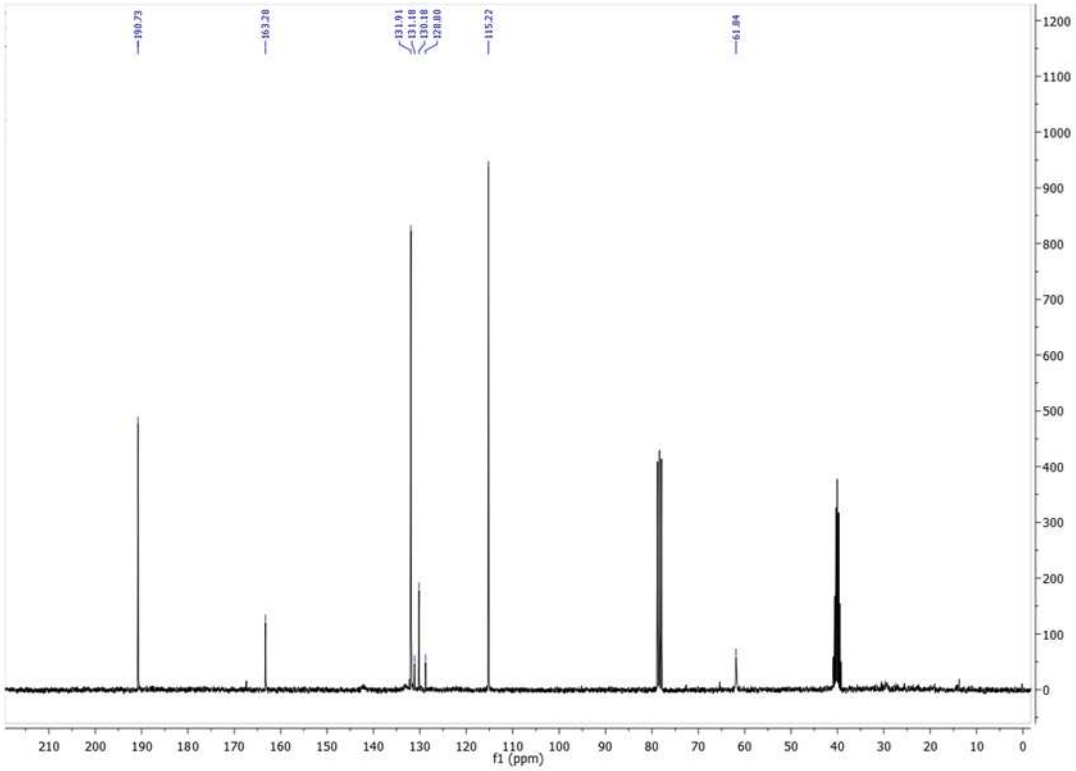
4-(4-Bromophenoxymethyl)-1,2,3-triazole (5)



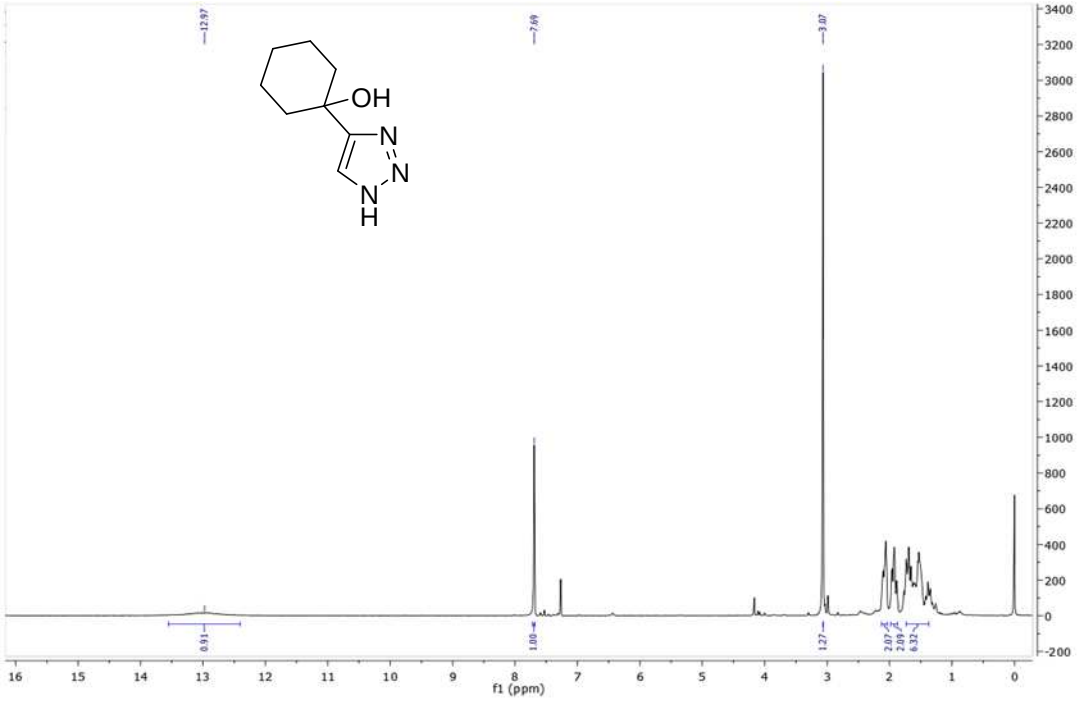


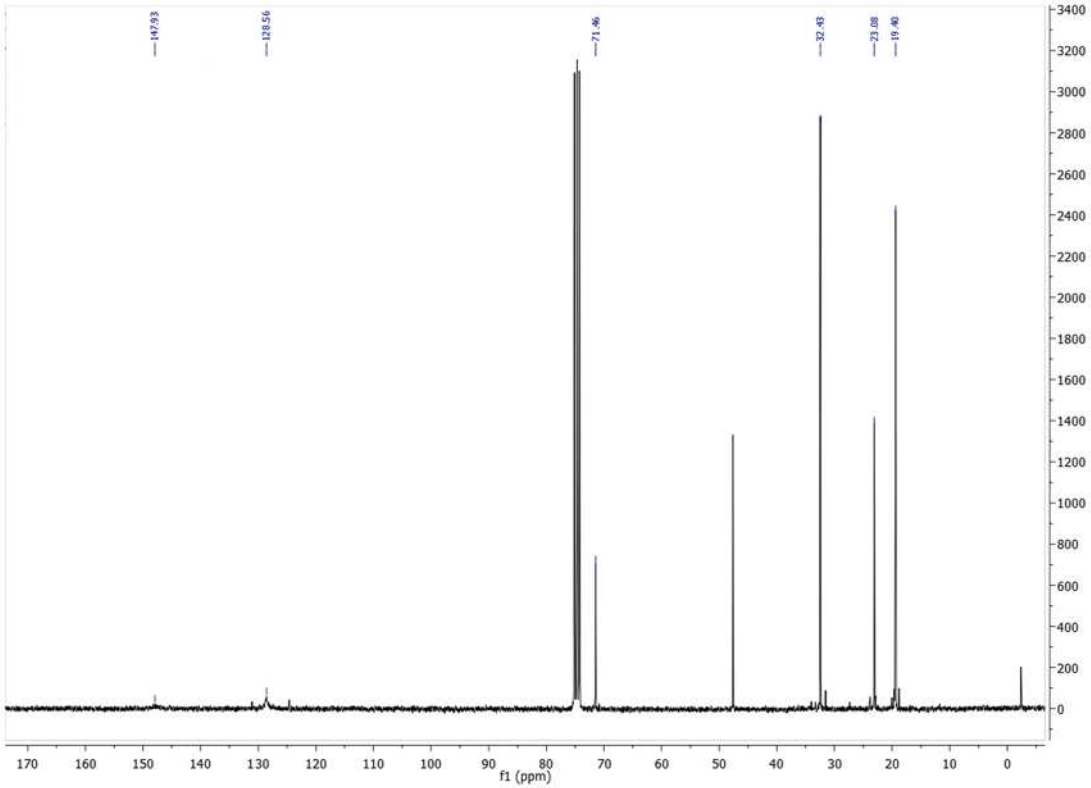
4-(1,2,3-Triazol-4-ylmethoxy)benzaldehyde (6)



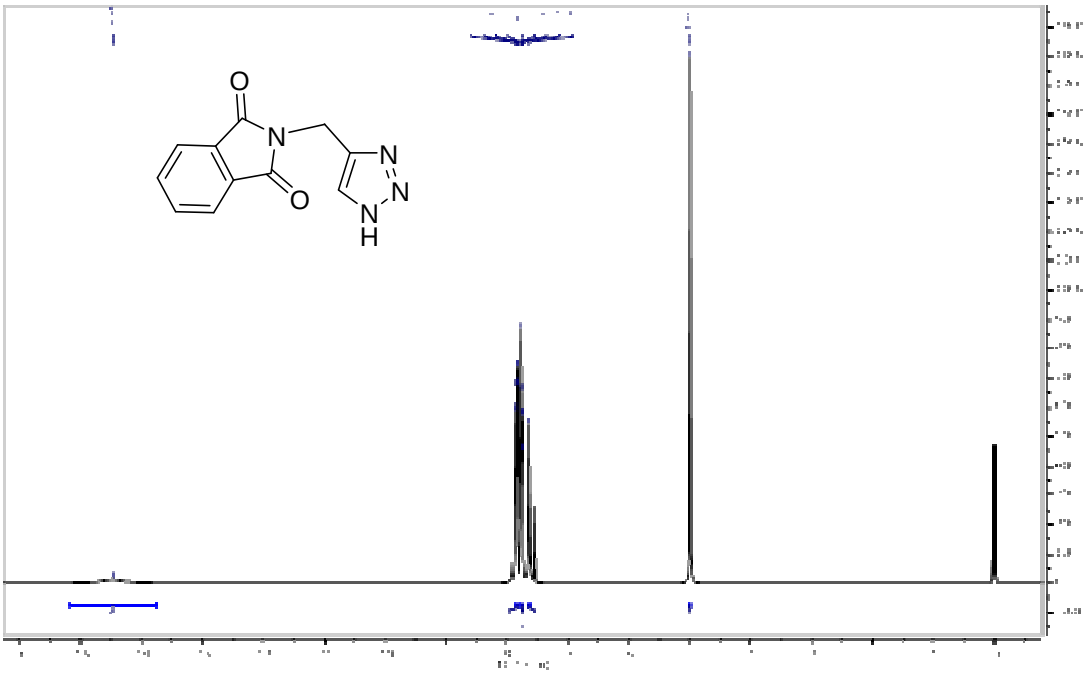


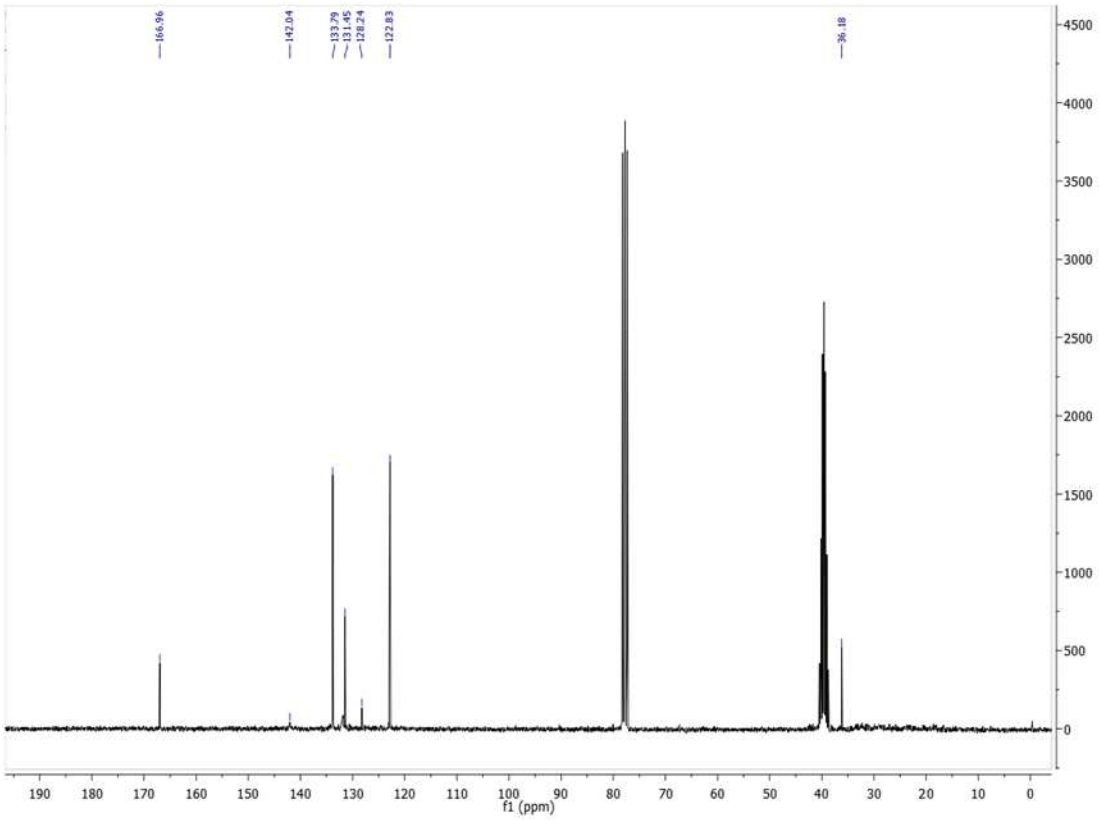
1-(1,2,3-Triazol-4-yl)cyclohexanol (7)



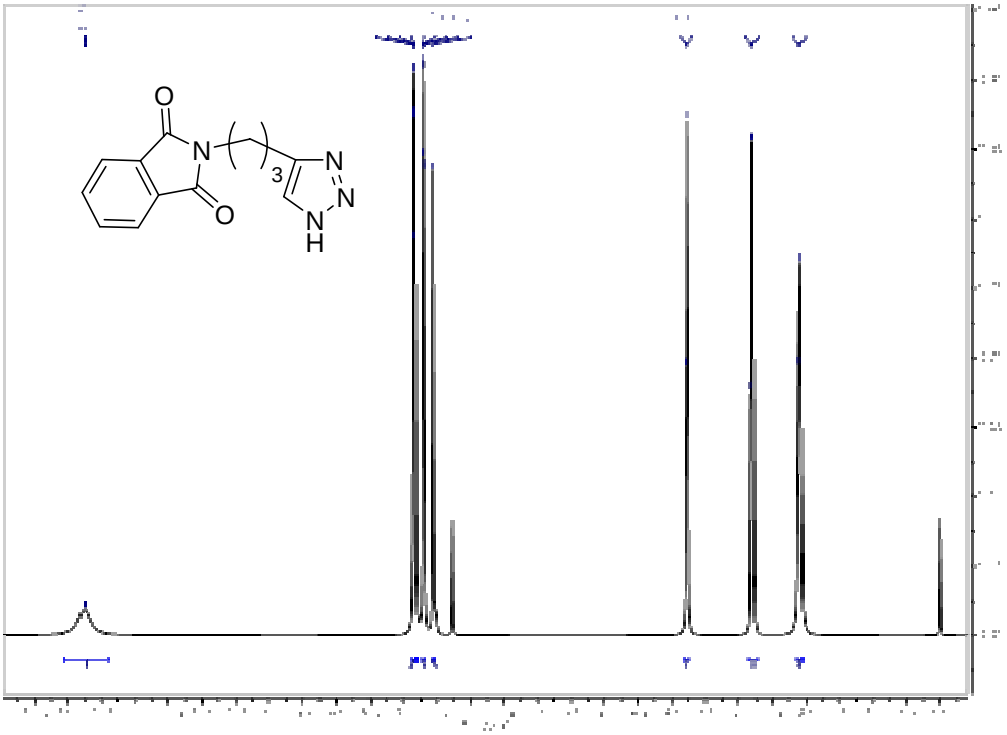


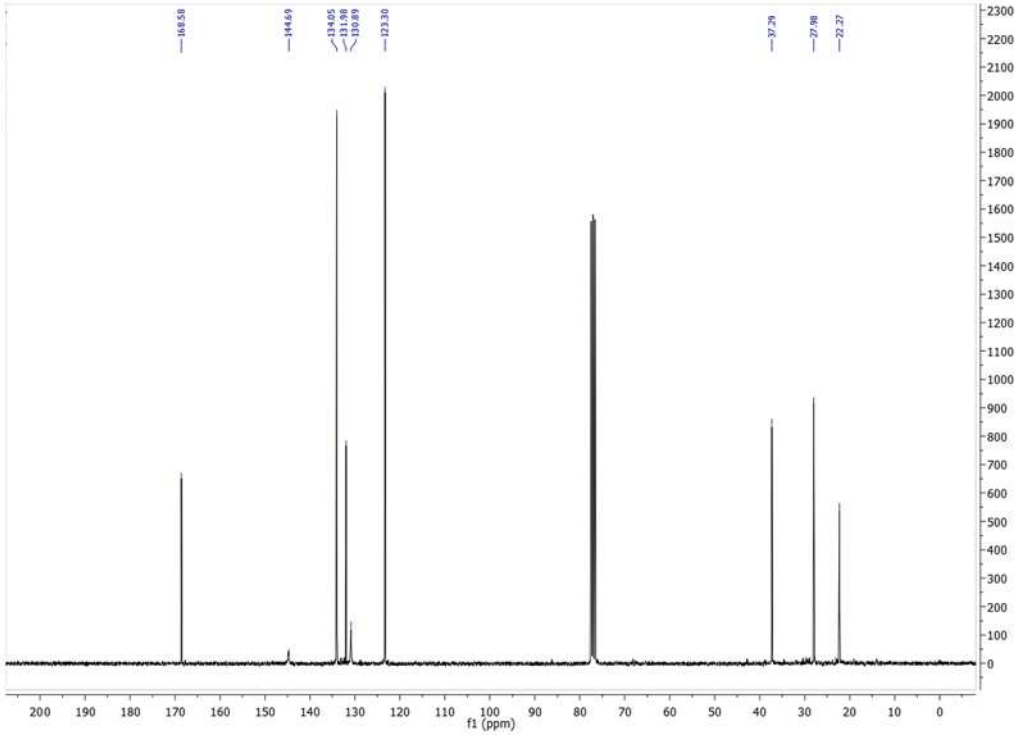
2-(1,2,3-Triazol-4-ylmethyl)isoindole-1,3-dione (8)



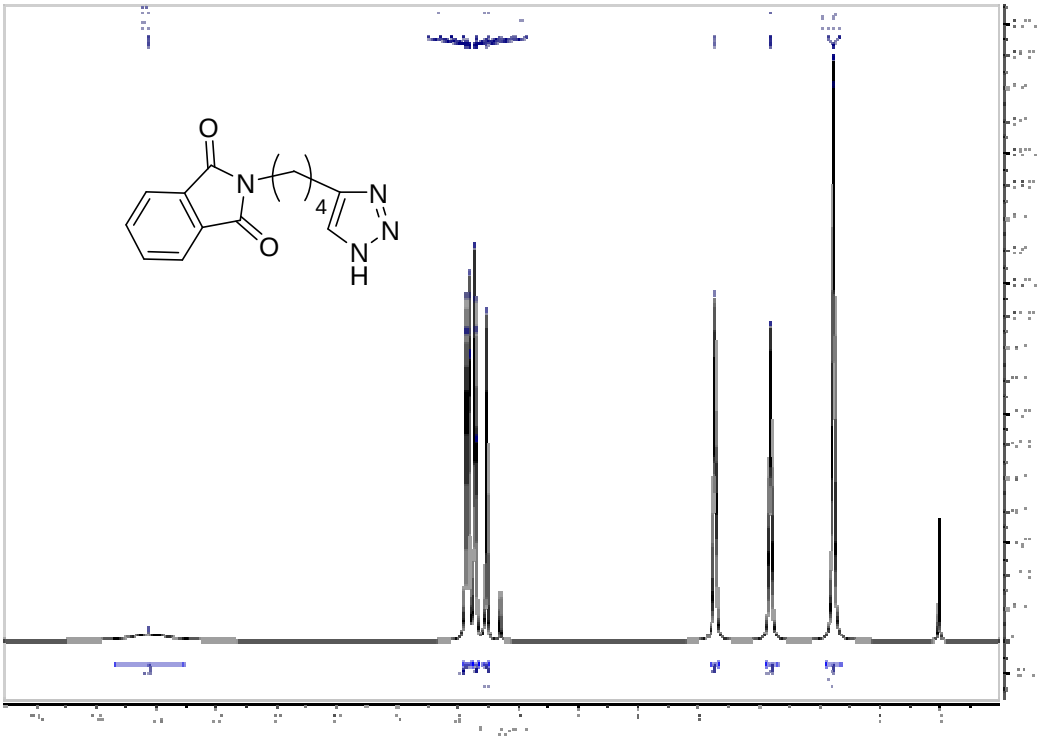


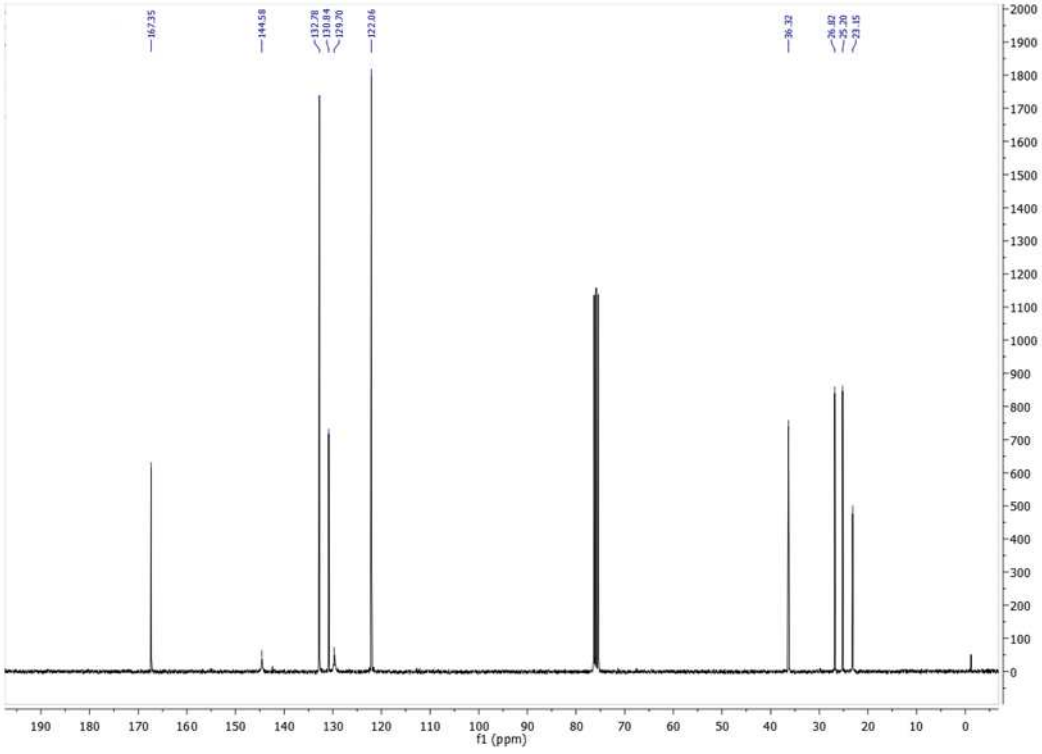
2-[3-(1,2,3-Triazol-4-yl)propyl]isoindole-1,3-dione (9)





2-[4-(1,2,3-Triazol-4-yl)butyl]isoindole-1,3-dione (10)





6.- Crystallographic data of compounds 8 and 5

6.1. Crystallographic data of compound 8

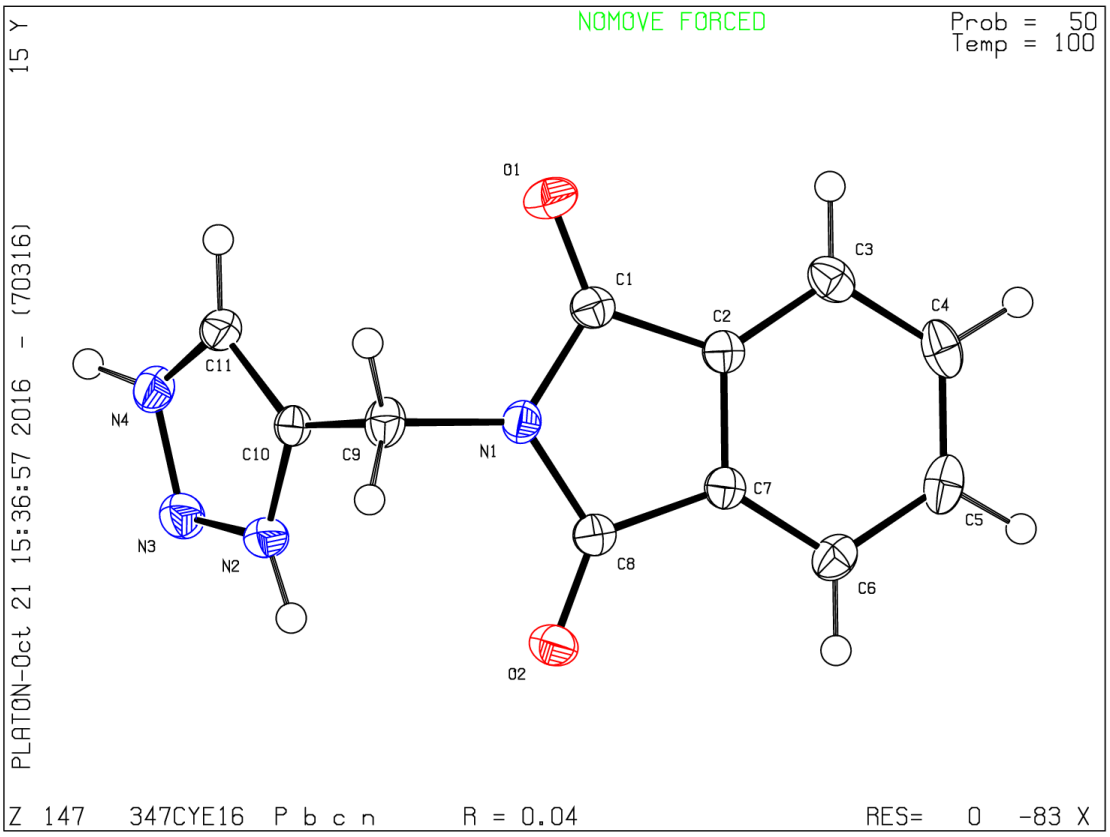


Figure 1. ORTEP diagram and atom labelling system for compound **8**

Table 1. Crystal data and structure refinement for compound 8.

Empirical formula	C16 H16 Br N3 O4 S	
Formula weight	426.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 40.1663(19) Å	α= 90°.
	b = 5.4766(3) Å	β= 107.9868(17)°.
	c = 16.3526(8) Å	γ = 90°.
Volume	3421.4(3) $Å^3$	
Z	4	
Density (calculated)	1.655 Mg/m^3	
Absorption coefficient	2.552 mm^{-1}	
F(000)	1728	
Crystal size	0.373 x 0.177 x 0.097 mm^3	
Theta range for data collection	2.132 to 27.441°.	
Index ranges	-52<=h<=52, -7<=k<=7, -21<=l<=21	
Reflections collected	35244	
Independent reflections	3893 [R(int) = 0.0527]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3893 / 3 / 233	
Goodness-of-fit on F^2	1.129	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1272	
R indices (all data)	R1 = 0.0488, wR2 = 0.1295	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.024 and -0.803 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_021CYE17_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	5200(1)	8202(1)	4042(1)	28(1)
S(1)	6919(1)	1987(1)	5131(1)	13(1)
O(1)	6875(1)	556(4)	5858(1)	17(1)
O(2)	6991(1)	4546(4)	5362(1)	20(1)
O(3)	7166(1)	842(4)	4766(1)	20(1)
O(4)	6423(1)	4646(4)	6984(1)	17(1)
N(1)	7441(1)	2296(5)	8664(1)	15(1)
N(2)	7353(1)	970(4)	7961(1)	16(1)
N(3)	7096(1)	2194(4)	7424(1)	14(1)
C(1)	7246(1)	4339(5)	8594(2)	15(1)
C(2)	7018(1)	4273(5)	7770(2)	13(1)
C(3)	6743(1)	5987(5)	7257(2)	16(1)
C(4)	6152(1)	5620(5)	6328(2)	14(1)
C(5)	6168(1)	7852(5)	5932(2)	16(1)
C(6)	5881(1)	8592(5)	5242(2)	17(1)
C(7)	5587(1)	7142(5)	4976(2)	18(1)
C(8)	5567(1)	4932(5)	5377(2)	19(1)
C(9)	5852(1)	4187(5)	6054(2)	17(1)
C(10)	6508(1)	1885(5)	4322(2)	13(1)
C(11)	6429(1)	-136(5)	3779(2)	18(1)
C(12)	6107(1)	-247(6)	3146(2)	20(1)
C(13)	5861(1)	1620(6)	3042(2)	19(1)
C(14)	5945(1)	3617(6)	3596(2)	20(1)
C(15)	6268(1)	3755(5)	4235(2)	18(1)
C(16)	5513(1)	1461(7)	2342(2)	28(1)

Table 3. Bond lengths [Å] and angles [°] for mo_021CYE17_0m.

Br(1)-C(7)	1.903(3)
S(1)-O(3)	1.448(2)
S(1)-O(2)	1.457(2)
S(1)-O(1)	1.4794(19)
S(1)-C(10)	1.769(3)
O(4)-C(4)	1.378(3)
O(4)-C(3)	1.427(3)
N(1)-N(2)	1.313(3)
N(1)-C(1)	1.351(4)
N(1)-H(1)	0.848(14)
N(2)-N(3)	1.314(3)
N(3)-C(2)	1.351(3)
N(3)-H(3)	0.851(14)
C(1)-C(2)	1.376(3)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.495(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(9)	1.391(4)
C(4)-C(5)	1.394(4)
C(5)-C(6)	1.400(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.379(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.390(4)
C(8)-C(9)	1.386(4)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-C(15)	1.384(4)
C(10)-C(11)	1.393(4)
C(11)-C(12)	1.387(4)
C(11)-H(11)	0.9500
C(12)-C(13)	1.394(4)
C(12)-H(12)	0.9500

C(13)-C(14)	1.394(4)
C(13)-C(16)	1.512(4)
C(14)-C(15)	1.393(4)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

O(3)-S(1)-O(2)	114.73(12)
O(3)-S(1)-O(1)	111.60(12)
O(2)-S(1)-O(1)	111.35(11)
O(3)-S(1)-C(10)	106.11(12)
O(2)-S(1)-C(10)	106.77(12)
O(1)-S(1)-C(10)	105.60(12)
C(4)-O(4)-C(3)	117.5(2)
N(2)-N(1)-C(1)	113.1(2)
N(2)-N(1)-H(1)	114(2)
C(1)-N(1)-H(1)	133(2)
N(1)-N(2)-N(3)	104.2(2)
N(2)-N(3)-C(2)	112.8(2)
N(2)-N(3)-H(3)	118(2)
C(2)-N(3)-H(3)	129(2)
N(1)-C(1)-C(2)	104.7(2)
N(1)-C(1)-H(1A)	127.7
C(2)-C(1)-H(1A)	127.7
N(3)-C(2)-C(1)	105.2(2)
N(3)-C(2)-C(3)	121.4(2)
C(1)-C(2)-C(3)	133.3(3)
O(4)-C(3)-C(2)	106.9(2)
O(4)-C(3)-H(3A)	110.3
C(2)-C(3)-H(3A)	110.3
O(4)-C(3)-H(3B)	110.3
C(2)-C(3)-H(3B)	110.3
H(3A)-C(3)-H(3B)	108.6
O(4)-C(4)-C(9)	115.4(2)

O(4)-C(4)-C(5)	124.2(2)
C(9)-C(4)-C(5)	120.4(2)
C(4)-C(5)-C(6)	118.9(3)
C(4)-C(5)-H(5)	120.6
C(6)-C(5)-H(5)	120.6
C(7)-C(6)-C(5)	119.9(3)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
C(6)-C(7)-C(8)	121.5(3)
C(6)-C(7)-Br(1)	119.1(2)
C(8)-C(7)-Br(1)	119.5(2)
C(9)-C(8)-C(7)	118.6(3)
C(9)-C(8)-H(8)	120.7
C(7)-C(8)-H(8)	120.7
C(8)-C(9)-C(4)	120.7(3)
C(8)-C(9)-H(9)	119.7
C(4)-C(9)-H(9)	119.7
C(15)-C(10)-C(11)	120.5(3)
C(15)-C(10)-S(1)	120.9(2)
C(11)-C(10)-S(1)	118.6(2)
C(12)-C(11)-C(10)	119.1(3)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	121.4(3)
C(11)-C(12)-H(12)	119.3
C(13)-C(12)-H(12)	119.3
C(12)-C(13)-C(14)	118.4(3)
C(12)-C(13)-C(16)	120.3(3)
C(14)-C(13)-C(16)	121.2(3)
C(15)-C(14)-C(13)	120.8(3)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(10)-C(15)-C(14)	119.7(3)
C(10)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2
C(13)-C(16)-H(16A)	109.5

C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

6.2. Crystallographic data of compound 5

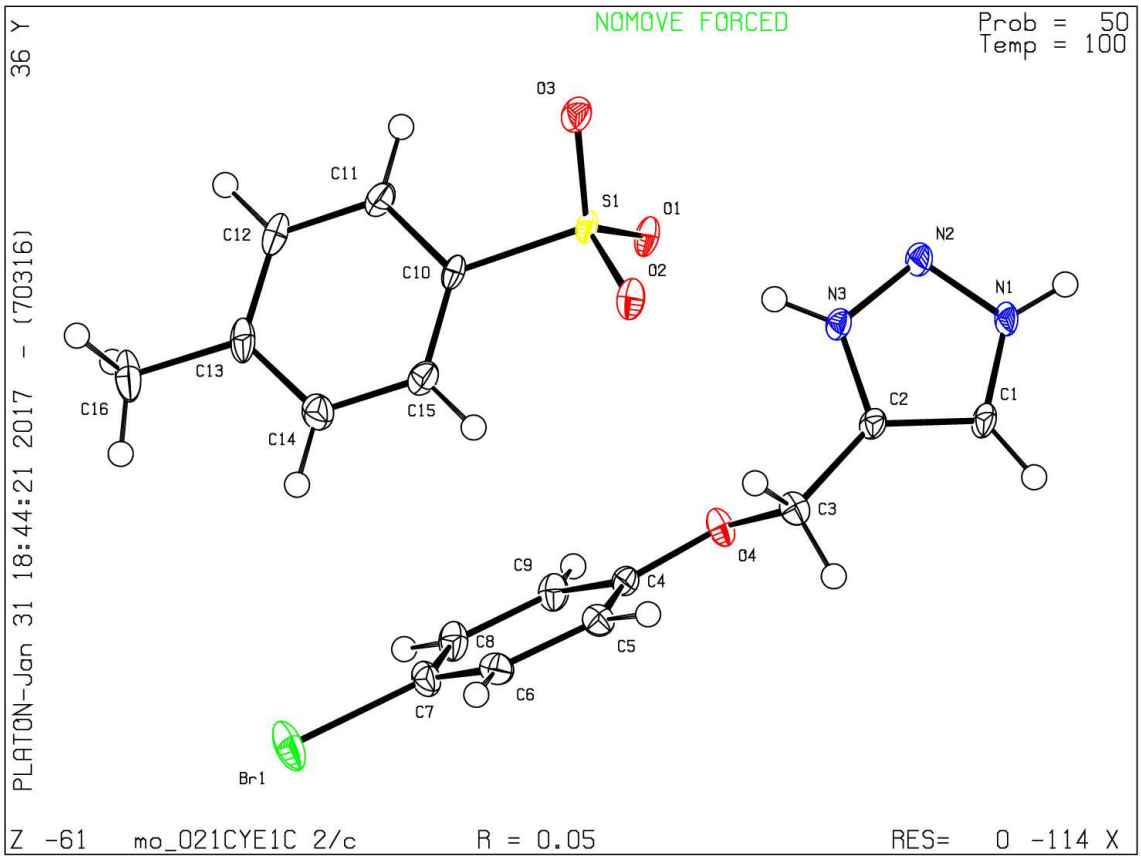


Figure 2. ORTEP diagram and atom labelling system for *p*-toluenesulfonic salt of compound **5**.

Table 1. Crystal data and structure refinement for compound 5.

Empirical formula	C11 H8 N4 O2	
Formula weight	228.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 20.1462(6) Å	α= 90°.
	b = 6.8229(2) Å	β= 90°.
	c = 15.1018(4) Å	γ = 90°.
Volume	2075.83(10) $Å^3$	
Z	8	
Density (calculated)	1.460 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	944	
Crystal size	0.300 x 0.243 x 0.210 mm^3	
Theta range for data collection	2.022 to 27.405°.	
Index ranges	-26<=h<=25, -8<=k<=8, -19<=l<=17	
Reflections collected	18333	
Independent reflections	2357 [R(int) = 0.0379]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2357 / 3 / 160	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.1002	
R indices (all data)	R1 = 0.0439, wR2 = 0.1038	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.326 and -0.204 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 347CYE16. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2863(1)	6482(2)	4443(1)	30(1)
O(2)	4032(1)	6209(2)	1852(1)	24(1)
N(1)	3589(1)	6384(2)	3259(1)	19(1)
N(2)	4770(1)	3304(2)	3371(1)	21(1)
N(3)	4933(1)	1582(2)	3712(1)	24(1)
N(4)	4717(1)	1587(2)	4543(1)	23(1)
C(1)	2961(1)	6382(2)	3655(1)	20(1)
C(2)	2479(1)	6247(2)	2913(1)	18(1)
C(3)	1793(1)	6187(2)	2930(1)	22(1)
C(4)	1469(1)	6043(2)	2118(1)	26(1)
C(5)	1821(1)	5975(2)	1329(1)	27(1)
C(6)	2515(1)	6038(2)	1314(1)	23(1)
C(7)	2833(1)	6171(2)	2122(1)	18(1)
C(8)	3554(1)	6246(2)	2337(1)	18(1)
C(9)	4209(1)	6426(2)	3760(1)	22(1)
C(10)	4450(1)	4411(2)	3974(1)	18(1)
C(11)	4413(1)	3297(2)	4729(1)	22(1)

Table 3. Bond lengths [Å] and angles [°] for 347CYE16.

O(1)-C(1)	1.2077(17)
O(2)-C(8)	1.2114(17)
N(1)-C(8)	1.3981(18)
N(1)-C(1)	1.3993(17)
N(1)-C(9)	1.4610(17)
N(2)-N(3)	1.3240(16)
N(2)-C(10)	1.3481(18)
N(2)-H(2)	0.872(13)
N(3)-N(4)	1.3273(17)
N(4)-C(11)	1.3477(19)
N(4)-H(4A)	0.872(13)
C(1)-C(2)	1.4854(19)
C(2)-C(3)	1.383(2)
C(2)-C(7)	1.3920(18)
C(3)-C(4)	1.392(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.387(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.399(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.3813(19)
C(6)-H(6)	0.9500
C(7)-C(8)	1.4885(18)
C(9)-C(10)	1.4928(19)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.3730(19)
C(11)-H(11)	0.9500

C(8)-N(1)-C(1)	112.33(11)
C(8)-N(1)-C(9)	124.10(12)
C(1)-N(1)-C(9)	123.51(11)
N(3)-N(2)-C(10)	110.65(12)
N(3)-N(2)-H(2)	118(2)

C(10)-N(2)-H(2)	131(2)
N(2)-N(3)-N(4)	106.58(11)
N(3)-N(4)-C(11)	110.36(12)
N(3)-N(4)-H(4A)	117(2)
C(11)-N(4)-H(4A)	132(2)
O(1)-C(1)-N(1)	124.58(13)
O(1)-C(1)-C(2)	129.84(13)
N(1)-C(1)-C(2)	105.59(11)
C(3)-C(2)-C(7)	121.76(13)
C(3)-C(2)-C(1)	129.90(13)
C(7)-C(2)-C(1)	108.33(12)
C(2)-C(3)-C(4)	117.04(13)
C(2)-C(3)-H(3)	121.5
C(4)-C(3)-H(3)	121.5
C(5)-C(4)-C(3)	121.26(13)
C(5)-C(4)-H(4)	119.4
C(3)-C(4)-H(4)	119.4
C(4)-C(5)-C(6)	121.60(14)
C(4)-C(5)-H(5)	119.2
C(6)-C(5)-H(5)	119.2
C(7)-C(6)-C(5)	116.82(13)
C(7)-C(6)-H(6)	121.6
C(5)-C(6)-H(6)	121.6
C(6)-C(7)-C(2)	121.51(13)
C(6)-C(7)-C(8)	130.31(13)
C(2)-C(7)-C(8)	108.18(11)
O(2)-C(8)-N(1)	124.31(13)
O(2)-C(8)-C(7)	130.12(13)
N(1)-C(8)-C(7)	105.57(11)
N(1)-C(9)-C(10)	111.81(11)
N(1)-C(9)-H(9A)	109.3
C(10)-C(9)-H(9A)	109.3
N(1)-C(9)-H(9B)	109.3
C(10)-C(9)-H(9B)	109.3
H(9A)-C(9)-H(9B)	107.9
N(2)-C(10)-C(11)	106.05(12)

N(2)-C(10)-C(9)	121.76(12)
C(11)-C(10)-C(9)	132.19(13)
N(4)-C(11)-C(10)	106.36(12)
N(4)-C(11)-H(11)	126.8
C(10)-C(11)-H(11)	126.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 347CYE16. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	34(1)	38(1)	17(1)	-2(1)	3(1)	4(1)
O(2)	22(1)	28(1)	24(1)	1(1)	5(1)	2(1)
N(1)	20(1)	20(1)	18(1)	-1(1)	-2(1)	3(1)
N(2)	21(1)	23(1)	19(1)	2(1)	3(1)	1(1)
N(3)	22(1)	25(1)	25(1)	4(1)	2(1)	3(1)
N(4)	22(1)	28(1)	21(1)	6(1)	-2(1)	1(1)
C(1)	23(1)	16(1)	20(1)	0(1)	2(1)	3(1)
C(2)	21(1)	13(1)	20(1)	1(1)	1(1)	2(1)
C(3)	21(1)	17(1)	29(1)	2(1)	4(1)	3(1)
C(4)	19(1)	19(1)	40(1)	2(1)	-4(1)	3(1)
C(5)	29(1)	23(1)	29(1)	2(1)	-11(1)	3(1)
C(6)	28(1)	20(1)	20(1)	1(1)	-2(1)	1(1)
C(7)	20(1)	14(1)	20(1)	2(1)	1(1)	2(1)
C(8)	22(1)	14(1)	19(1)	1(1)	1(1)	2(1)
C(9)	22(1)	22(1)	23(1)	-3(1)	-6(1)	-1(1)
C(10)	14(1)	24(1)	16(1)	-2(1)	-2(1)	-1(1)
C(11)	19(1)	30(1)	17(1)	1(1)	-1(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 347CYE16.

	x	y	z	U(eq)
H(2)	4898(17)	3560(40)	2831(12)	26
H(4A)	4859(16)	640(40)	4880(20)	28
H(3)	1553	6241	3471	27
H(4)	998	5990	2104	31
H(5)	1585	5884	786	32
H(6)	2756	5992	774	27
H(9A)	4140	7162	4318	27
H(9B)	4551	7122	3411	27
H(11)	4214	3661	5275	26

Table 6. Torsion angles [°] for 347CYE16.

C(10)-N(2)-N(3)-N(4)	-0.31(15)
N(2)-N(3)-N(4)-C(11)	0.56(15)
C(8)-N(1)-C(1)-O(1)	179.75(13)
C(9)-N(1)-C(1)-O(1)	2.6(2)
C(8)-N(1)-C(1)-C(2)	-0.48(14)
C(9)-N(1)-C(1)-C(2)	-177.63(11)
O(1)-C(1)-C(2)-C(3)	-0.4(2)
N(1)-C(1)-C(2)-C(3)	179.82(13)
O(1)-C(1)-C(2)-C(7)	179.84(14)
N(1)-C(1)-C(2)-C(7)	0.10(14)
C(7)-C(2)-C(3)-C(4)	0.11(19)
C(1)-C(2)-C(3)-C(4)	-179.57(13)
C(2)-C(3)-C(4)-C(5)	-0.4(2)
C(3)-C(4)-C(5)-C(6)	0.3(2)
C(4)-C(5)-C(6)-C(7)	0.0(2)
C(5)-C(6)-C(7)-C(2)	-0.26(19)
C(5)-C(6)-C(7)-C(8)	179.32(13)
C(3)-C(2)-C(7)-C(6)	0.21(19)
C(1)-C(2)-C(7)-C(6)	179.95(12)
C(3)-C(2)-C(7)-C(8)	-179.46(12)
C(1)-C(2)-C(7)-C(8)	0.29(14)
C(1)-N(1)-C(8)-O(2)	-179.54(12)
C(9)-N(1)-C(8)-O(2)	-2.4(2)
C(1)-N(1)-C(8)-C(7)	0.66(14)
C(9)-N(1)-C(8)-C(7)	177.78(11)
C(6)-C(7)-C(8)-O(2)	0.0(2)
C(2)-C(7)-C(8)-O(2)	179.64(13)
C(6)-C(7)-C(8)-N(1)	179.81(13)
C(2)-C(7)-C(8)-N(1)	-0.57(14)
C(8)-N(1)-C(9)-C(10)	-87.10(15)
C(1)-N(1)-C(9)-C(10)	89.71(15)
N(3)-N(2)-C(10)-C(11)	-0.05(15)
N(3)-N(2)-C(10)-C(9)	-179.83(12)
N(1)-C(9)-C(10)-N(2)	79.30(16)

N(1)-C(9)-C(10)-C(11)	-100.41(17)
N(3)-N(4)-C(11)-C(10)	-0.59(15)
N(2)-C(10)-C(11)-N(4)	0.38(15)
C(9)-C(10)-C(11)-N(4)	-179.87(13)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 347CYE16 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...N(2)#1	0.872(13)	1.942(16)	2.788(2)	163(3)
N(4)-H(4A)...N(3)#2	0.872(13)	2.642(18)	3.4807(17)	162(3)
N(4)-H(4A)...N(4)#2	0.872(13)	1.947(14)	2.809(2)	169(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 -x+1,-y,-z+1