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Divergent oriented synthesis of 2*H*-1,2,3-triazoles *via* rearrangement of furoxanylhydrazones

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Table of Contents

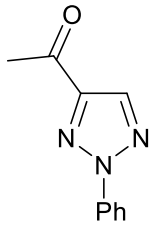
S1. Experimental Section

General remarks

All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 (300.13 and 75.47 MHz, respectively) spectrometer and referenced to residual solvent peak. The chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. High resolution mass spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization (ESI). All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range *m/z*: 50-3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for all analyzed solutions in MeCN (flow rate: 3 μL min^{-1}). Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}); interface temperature was set at 180 °C. All spectra were processed by using Bruker DataAnalysis 4.0 software package. The melting points were determined on Stuart SMP20 apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminum sheets. The visualization of the TLC plates was accomplished with a UV light. Column chromatography was performed on silica gel 60 A (0.060-0.200 mm, Acros Organics). All solvents were purified and dried using standard methods prior to use. All standard reagents were purchased from Aldrich or Acros Organics and used without further purification.

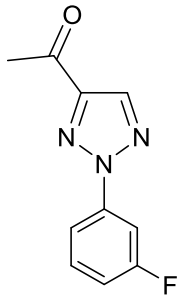
General procedure for the preparation of 2*H*-1,2,3-triazoles 2a-e.

Corresponding furoxanylhydrazone **1** (0.5 mmol) was taken in MeCN (2.5 mL) and DABCO (0.5 mmol) was added. The mixture was refluxed for 12 h, then poured into water (15 mL) and extracted with CH_2Cl_2 (3x10 mL). Organic layers were combined, washed with brine (1x10 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (PE:CH_2Cl_2 = 1:1).

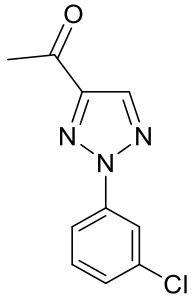


5-Acetyl-2-phenyl-2*H*-1,2,3-triazole **2a**. Yield 20 mg (21%), yellow solid, mp 102-104°C. IR (KBr), ν, cm^{-1}: 1683, 1327, 1220, 756, 672. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (s, 1H, CH), 8.15-8.09 (m, 2H, C_6H_5), 7.55-7.47 (m, 2H, C_6H_5), 7.45-7.38 (m, 1H, C_6H_5), 2.69 (s, 3H, CH_3). ^{13}C

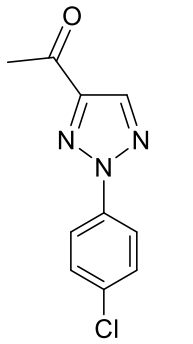
NMR (75.5 MHz, $CDCl_3$) δ: 192.3, 148.0, 139.5, 136.1, 129.6, 128.7, 119.5, 27.5. HRMS (ESI): *m/z* calcd for $C_{10}H_{10}N_3O$: 188.0818, found: 188.0817 $[M+H]^+$.



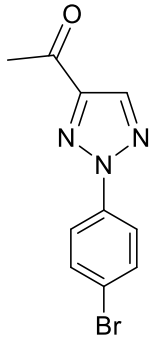
5-Acetyl-2-(3-fluorophenyl)-2*H*-1,2,3-triazole **2b**. Yield 42 mg (41%), pale yellow solid, mp 78-80°C. IR (KBr), ν, cm^{-1}: 1687, 1609, 1493, 1229, 876. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.22 (s, 1H, CH), 7.94 (dt, *J* = 8.3, 1.4 Hz, 1H, C_6H_4), 7.87 (dt, *J* = 9.6, 2.3 Hz, 1H, C_6H_4), 7.49 (td, *J* = 8.3, 5.9 Hz, 1H, C_6H_4), 7.13 (tdd, *J* = 8.3, 2.5, 1.0 Hz, 1H, C_6H_4), 2.70 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 192.1, 163.2 (d, *J* = 247.7 Hz), 148.3, 140.7, 136.3, 131.0 (d, *J* = 8.9 Hz), 115.6 (*J* = 21.3 Hz), 115.1 (d, *J* = 3.3 Hz), 107.4 (d, *J* = 27.2 Hz), 27.5. HRMS (ESI): *m/z* calcd for $C_{10}H_9FN_3O$: 206.0724, found: 206.0728 $[M+H]^+$.



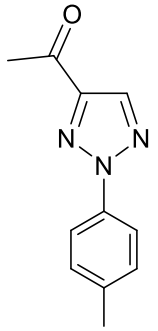
5-Acetyl-2-(3-chlorophenyl)-2*H*-1,2,3-triazole **2c**. Yield 57 mg (46%), yellow solid, mp 120-122°C. IR (KBr), ν, cm^{-1}: 1689, 1594, 1488, 1324, 782. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.22 (s, 1H, CH), 8.18-8.14 (m, 1H, C_6H_4), 8.07-8.00 (m, 1H, C_6H_4), 7.50-7.37 (m, 2H, C_6H_4), 2.70 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 192.1, 148.3, 140.3, 136.4, 135.5, 130.7, 128.7, 119.8, 117.6, 27.5. HRMS (ESI): *m/z* calcd for $C_{10}H_8{}^{35}ClN_3NaO$: 244.0248, found: 244.0253 $[M+Na]^+$; *m/z* calcd for $C_{10}H_8{}^{37}ClN_3NaO$: 246.0219, found: 246.0225 $[M+Na]^+$.



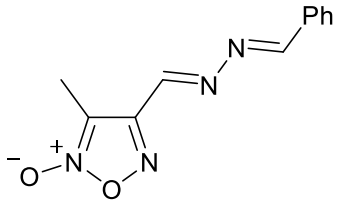
5-Acetyl-2-(4-chlorophenyl)-2*H*-1,2,3-triazole **2d**. Yield 50 mg (45%), yellow solid, mp 116-118°C. IR (KBr), ν, cm^{-1}: 1690, 1490, 1325, 967, 837. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (s, 1H, CH), 8.12-8.04 (m, 2H, C_6H_4), 7.53-7.44 (m, 2H, C_6H_4), 2.69 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 192.1, 148.2, 138.0, 136.3, 134.5, 129.8, 120.8, 27.5. HRMS (ESI): *m/z* calcd for $C_{10}H_9{}^{35}ClN_3O$: 222.0429, found: 222.0435 $[M+H]^+$; *m/z* calcd for $C_{10}H_9{}^{37}ClN_3O$: 224.0400, found: 224.0411 $[M+H]^+$.



5-Acetyl-2-(4-bromophenyl)-2*H*-1,2,3-triazole **2e**. Yield 30 mg (22%), yellow solid, mp 100-102°C. IR (KBr), ν, cm^{-1}: 1687, 1487, 1326, 966, 825. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (s, 1H, CH), 8.07-7.95 (m, 2H, C_6H_4), 7.70-7.57 (m, 2H, C_6H_4), 2.68 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 192.0, 148.3, 138.5, 136.3, 132.7, 122.5, 121.0, 27.5. HRMS (ESI): *m/z* calcd for $C_{10}H_9{}^{79}BrN_3O$: 265.9924, found: 265.9926 $[M+H]^+$; *m/z* calcd for $C_{10}H_9{}^{81}BrN_3O$: 267.9903, found 267.9908 $[M+H]^+$.



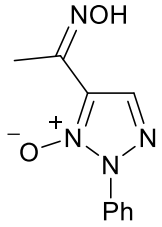
5-Acetyl-2-(*p*-tolyl)-2*H*-1,2,3-triazole **2f**. Yield 30 mg (15%), yellow solid, mp 76-78°C. IR (KBr), ν, cm^{-1}: 1686, 1493, 1328, 1218, 814. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.19 (s, 1H, CH), 8.03-7.93 (m, 2H, C_6H_4), 7.34-7.26 (m, 2H, C_6H_4), 2.68 (s, 3H, CH_3-CO), 2.41 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 192.3, 147.8, 138.8, 137.4, 135.9, 130.1, 119.4, 27.5, 21.2. HRMS (ESI): *m/z* calcd for $C_{11}H_{12}N_3O$: 202.0975, found: 202.0969 $[M+H]^+$.



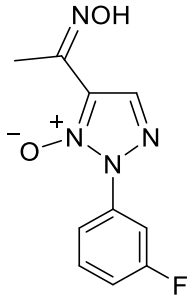
4-((*E*)-(((*E*)-Benzylidene)hydrazineylidene)methyl)-3-methylfuroxan **3** was obtained according to the same procedure as compounds **2**. Yield 37 mg (32%), yellow solid, mp 154-156°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.67 (s, 1H, CH-Ph), 8.61 (s, 1H, CH-C=N), 7.90-7.82 (m, 2H, C_6H_5), 7.54-7.43 (m, 3H, C_6H_5), 2.50 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 165.0, 153.4, 151.0, 133.2, 132.5, 129.3, 129.1, 9.8.

General procedure for preparation of 2-aryl-2*H*-1,2,3-triazoles 1-oxides 4a-d.

Corresponding furoxanylhydrazone **1** (0.5 mmol) was taken in *o*-xylene (2.5 mL) and the mixture was refluxed for 18 h. The solvent was evaporated under reduced pressure and the residue was triturated with diethyl ether. The precipitate formed was filtered off, washed with diethyl ether (2x2 mL) and dried in air.

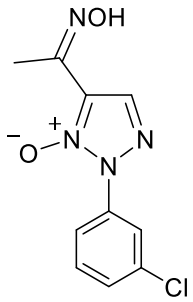


5-(1-(Hydroxyimino)ethyl)-2-phenyl-2*H*-1,2,3-triazole 1-oxide **4a**. Yield 10 mg (10%), brown solid, mp 158-205°C. IR (KBr), ν, cm^{-1}: 3207, 1498, 1295, 915, 760. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 11.85 (s, 1H, NOH), 8.22 (s, 1H, CH), 7.86-7.79 (m, 2H, C_6H_5), 7.66-7.53 (m, 3H, C_6H_5), 2.25 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 144.4, 134.4, 132.4, 129.5, 129.2, 125.2, 123.9, 10.8. HRMS (ESI): *m/z* calcd for $C_{10}H_{11}N_4O_2$: 219.0877, found: 219.0886 $[M+H]^+$.

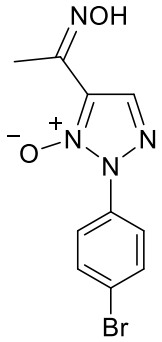


2-(3-Fluorophenyl)-5-(1-(hydroxyimino)ethyl)-2*H*-1,2,3-triazole 1-oxide **4b**. Yield 9 mg (9%), brown solid, mp 177-186°C. IR (KBr), ν, cm^{-1}: 3236, 1603, 1496, 1213, 874. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 11.88 (s, 1H, NOH), 8.26 (s, 1H, CH), 7.85-7.57 (m, 3H, C_6H_4), 7.47-7.36 (m, 1H, C_6H_4), 2.25 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 161.6 (d, J = 242.1 Hz), 144.2,

135.3 (d, J = 4.8 Hz), 132.8, 131.1 (d, J = 8.4 Hz), 125.4, 119.4, 116.3 (d, J = 20.6 Hz), 110.7 (d, J = 26.3 Hz), 10.8. HRMS (ESI): *m/z* calcd for $C_{10}H_9FN_4NaO_2$: 259.0602, found: 259.0609 $[M+Na]^+$.



2-(3-Chlorophenyl)-5-(1-(hydroxyimino)ethyl)-2H-1,2,3-triazole 1-oxide **4c**. Brown solid, yield 11 mg (9%), mp 157-163°C. IR (KBr), ν, cm^{-1}: 3220, 1585, 1489, 906, 791. ^1H NMR (300 MHz, DMSO-d_6) δ: 11.89 (s, 1H, NOH), 8.26 (s, 1H, CH), 8.02-7.98 (m, 1H, C_6H_4), 7.86-7.79 (m, 1H, C_6H_4), 7.65-7.60 (m, 2H, C_6H_4), 2.25 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 144.3, 135.4, 133.3, 132.9, 130.9, 129.3, 125.4, 123.2, 122.1, 10.8. HRMS (ESI): *m/z* calcd for $C_{10}H_{10}{}^{35}ClN_4O_2$: 253.0487, found: 253.0496 $[M+H]^+$; *m/z* calcd for $C_{10}H_{10}{}^{37}ClN_4O_2$: 255.0458, found: 255.0466 $[M+H]^+$.



2-(4-Bromophenyl)-5-(1-(hydroxyimino)ethyl)-2*H*-1,2,3-triazole 1-oxide **4d**. Brown solid, yield 26 mg (18%), mp 157-173°C. IR (KBr), ν, cm^{-1}: 3245, 1287, 1010, 909, 824. ^1H NMR (300 MHz, DMSO-d_6) δ: 11.78 (s, 1H, NOH), 8.21 (s, 1H, CH), 7.88-7.74 (m, 4H, C_6H_4), 2.25 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 144.1, 133.5, 132.6, 132.0, 129.9, 125.2, 122.1, 10.6. HRMS (ESI): *m/z* calcd for $C_{10}H_{10}{}^{79}BrN_4O_2$: 296.9982, found: 296.9980 $[M+H]^+$; *m/z* calcd for $C_{10}H_{10}{}^{81}BrN_4O_2$: 298.9962, found: 298.9963 $[M+H]^+$.

S2. Crystallographic data

Table S1. Crystal data and structure refinement for **2a**.

Empirical formula	C10 H9 N3 O	
Formula weight	187.20	
Temperature	100.00 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 5.6693(3) Å	α= 73.036(2)°.
	b = 7.2303(3) Å	β= 89.745(2)°.
	c = 11.6096(5) Å	γ = 77.431(2)°.
Volume	443.38(4) $Å^3$	
Z	2	
Density (calculated)	1.402 g/cm^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	196	
Crystal size	0.24 x 0.18 x 0.16 mm^3	
Theta range for data collection	3.024 to 31.565°.	
Index ranges	-8<=h<=8, -10<=k<=10, -17<=l<=17	
Reflections collected	18386	
Independent reflections	2958 [R(int) = 0.0493]	
Observed reflections	2404	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.7462 and 0.6529	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2958 / 1 / 133	
Goodness-of-fit on F^2	1.102	
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1129	
R indices (all data)	R1 = 0.0702, wR2 = 0.1197	
Largest diff. peak and hole	0.463 and -0.256 e. $Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6708(2)	6754(2)	10171(1)	28(1)
N(1)	4641(2)	7552(2)	7140(1)	15(1)
N(2)	8369(2)	6124(2)	6721(1)	18(1)
C(1)	3483(2)	8177(2)	2749(1)	21(1)
C(2)	1936(2)	8724(2)	3584(1)	19(1)
C(3)	2775(2)	8337(2)	4771(1)	17(1)
C(4)	5197(2)	7427(2)	5102(1)	14(1)
N(5)	6063(2)	7034(2)	6324(1)	14(1)
C(6)	6113(2)	6943(2)	8143(1)	16(1)
C(7)	5296(2)	7303(2)	9282(1)	19(1)
C(8)	2717(9)	8387(18)	9314(13)	24(1)
C(8B)	2702(11)	8370(20)	9293(16)	24(1)
C(9)	8417(2)	6056(2)	7875(1)	19(1)
C(10)	5891(2)	7245(2)	3102(1)	21(1)
C(11)	6773(2)	6874(2)	4280(1)	18(1)

Table S3. Bond lengths [Å] and angles [°] for **2a**.

O(1)-C(7)	1.2219(15)
N(1)-N(5)	1.3256(14)
N(1)-C(6)	1.3405(15)
N(2)-N(5)	1.3446(13)
N(2)-C(9)	1.3260(17)
C(1)-H(1)	0.9500
C(1)-C(2)	1.3890(18)
C(1)-C(10)	1.3891(19)
C(2)-H(2)	0.9500
C(2)-C(3)	1.3879(17)
C(3)-H(3)	0.9500
C(3)-C(4)	1.3892(16)
C(4)-N(5)	1.4301(15)
C(4)-C(11)	1.3890(17)
C(6)-C(7)	1.4749(18)
C(6)-C(9)	1.4006(17)
C(7)-C(8)	1.507(2)
C(7)-C(8B)	1.507(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(8B)-H(8D)	0.9800
C(8B)-H(8E)	0.9800
C(8B)-H(8F)	0.9800
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(10)-C(11)	1.3865(18)
C(11)-H(11)	0.9500
N(5)-N(1)-C(6)	103.51(10)
C(9)-N(2)-N(5)	103.37(10)
C(2)-C(1)-H(1)	120.1
C(2)-C(1)-C(10)	119.82(12)
C(10)-C(1)-H(1)	120.1
C(1)-C(2)-H(2)	119.8
C(3)-C(2)-C(1)	120.48(12)
C(3)-C(2)-H(2)	119.8
C(2)-C(3)-H(3)	120.6

C(2)-C(3)-C(4)	118.80(11)
C(4)-C(3)-H(3)	120.6
C(3)-C(4)-N(5)	118.80(11)
C(11)-C(4)-C(3)	121.55(11)
C(11)-C(4)-N(5)	119.65(10)
N(1)-N(5)-N(2)	115.56(10)
N(1)-N(5)-C(4)	122.01(9)
N(2)-N(5)-C(4)	122.43(10)
N(1)-C(6)-C(7)	122.13(11)
N(1)-C(6)-C(9)	108.51(11)
C(9)-C(6)-C(7)	129.29(11)
O(1)-C(7)-C(6)	120.08(12)
O(1)-C(7)-C(8)	121.3(5)
O(1)-C(7)-C(8B)	122.3(7)
C(6)-C(7)-C(8)	118.6(5)
C(6)-C(7)-C(8B)	117.6(7)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(8B)-H(8D)	109.5
C(7)-C(8B)-H(8E)	109.5
C(7)-C(8B)-H(8F)	109.5
H(8D)-C(8B)-H(8E)	109.5
H(8D)-C(8B)-H(8F)	109.5
H(8E)-C(8B)-H(8F)	109.5
N(2)-C(9)-C(6)	109.04(11)
N(2)-C(9)-H(9)	125.5
C(6)-C(9)-H(9)	125.5
C(1)-C(10)-H(10)	119.7
C(11)-C(10)-C(1)	120.56(12)
C(11)-C(10)-H(10)	119.7
C(4)-C(11)-H(11)	120.6
C(10)-C(11)-C(4)	118.79(11)
C(10)-C(11)-H(11)	120.6

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2a**. 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)	28(1)	35(1)	19(1)	-8(1)	-8(1)	-1(1)
N(1)	14(1)	16(1)	15(1)	-5(1)	0(1)	-3(1)
N(2)	13(1)	18(1)	23(1)	-6(1)	-2(1)	0(1)
C(1)	28(1)	22(1)	14(1)	-6(1)	1(1)	-9(1)
C(2)	16(1)	24(1)	17(1)	-5(1)	-2(1)	-6(1)
C(3)	15(1)	20(1)	16(1)	-6(1)	2(1)	-4(1)
C(4)	15(1)	12(1)	15(1)	-3(1)	0(1)	-4(1)
N(5)	11(1)	14(1)	16(1)	-5(1)	0(1)	-1(1)
C(6)	17(1)	15(1)	16(1)	-4(1)	-2(1)	-3(1)
C(7)	22(1)	18(1)	17(1)	-4(1)	-3(1)	-4(1)
C(8)	24(1)	30(1)	16(1)	-8(1)	0(1)	-2(1)
C(8B)	24(1)	30(1)	16(1)	-8(1)	0(1)	-2(1)
C(9)	16(1)	18(1)	21(1)	-5(1)	-5(1)	-2(1)
C(10)	27(1)	19(1)	17(1)	-8(1)	7(1)	-5(1)
C(11)	15(1)	15(1)	21(1)	-4(1)	4(1)	-2(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2a**.

	x	y	z	U(eq)
H(1)	2896	8441	1939	25
H(2)	291	9367	3340	23
H(3)	1713	8688	5346	20
H(8A)	1807	7460	9799	35
H(8B)	1970	8948	8490	35
H(8C)	2697	9460	9673	35
H(8D)	2598	9803	9085	28
H(8E)	2120	7905	10100	28
H(8F)	1699	8102	8703	28
H(9)	9792	5495	8430	23
H(10)	6943	6859	2533	25
H(11)	8424	6252	4519	21

Table S6. Torsion angles [°] for **2a**.

N(1)-C(6)-C(7)-O(1)	-178.70(12)
N(1)-C(6)-C(7)-C(8)	0.2(6)
N(1)-C(6)-C(7)-C(8B)	0.8(8)
N(1)-C(6)-C(9)-N(2)	0.27(14)
C(1)-C(2)-C(3)-C(4)	1.14(19)
C(1)-C(10)-C(11)-C(4)	0.82(19)
C(2)-C(1)-C(10)-C(11)	-0.7(2)
C(2)-C(3)-C(4)-N(5)	179.82(11)
C(2)-C(3)-C(4)-C(11)	-1.02(18)
C(3)-C(4)-N(5)-N(1)	-1.58(16)
C(3)-C(4)-N(5)-N(2)	178.67(11)
C(3)-C(4)-C(11)-C(10)	0.05(18)
N(5)-N(1)-C(6)-C(7)	177.23(11)
N(5)-N(1)-C(6)-C(9)	-0.19(13)
N(5)-N(2)-C(9)-C(6)	-0.21(13)
N(5)-C(4)-C(11)-C(10)	179.21(11)
C(6)-N(1)-N(5)-N(2)	0.07(13)
C(6)-N(1)-N(5)-C(4)	-179.70(10)
C(7)-C(6)-C(9)-N(2)	-176.91(12)
C(9)-N(2)-N(5)-N(1)	0.09(14)
C(9)-N(2)-N(5)-C(4)	179.86(10)
C(9)-C(6)-C(7)-O(1)	-1.9(2)
C(9)-C(6)-C(7)-C(8)	177.0(6)
C(9)-C(6)-C(7)-C(8B)	177.6(8)
C(10)-C(1)-C(2)-C(3)	-0.3(2)
C(11)-C(4)-N(5)-N(1)	179.24(11)
C(11)-C(4)-N(5)-N(2)	-0.51(17)

Table S7. Hydrogen bonds for **2a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9)...O(1)#1	0.95	2.51	3.4402(16)	166.2

Symmetry transformations used to generate equivalent atoms:

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

Table S8. Crystal data and structure refinement for **3**.

Empirical formula	C11 H10 N4 O2	
Formula weight	230.23	
Temperature	99.9(3) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 6.9334(2) Å	α= 90°.
	b = 12.2596(4) Å	β= 102.724(3)°.
	c = 12.9102(4) Å	γ = 90°.
Volume	1070.43(6) $Å^3$	
Z	4	
Density (calculated)	1.429 g/cm^3	
Absorption coefficient	0.858 mm^{-1}	
F(000)	480	
Crystal size	0.166 x 0.057 x 0.052 mm^3	
Theta range for data collection	5.035 to 76.893°.	
Index ranges	-7<=h<=8, -15<=k<=15, -16<=l<=16	
Reflections collected	4147	
Independent reflections	4147 [R(int) = ?]	
Observed reflections	3875	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.89652	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4147 / 0 / 169	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0982	
R indices (all data)	R1 = 0.0365, wR2 = 0.1001	
Largest diff. peak and hole	0.233 and -0.184 e. $Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6876(2)	1749(1)	5151(1)	25(1)
C(2)	6477(2)	1940(1)	3988(1)	21(1)
N(3)	6028(1)	1131(1)	3303(1)	24(1)
O(4)	5851(1)	130(1)	3375(1)	32(1)
O(5)	5712(1)	1582(1)	2241(1)	27(1)
N(6)	6014(2)	2682(1)	2343(1)	26(1)
C(7)	6469(2)	2896(1)	3366(1)	21(1)
C(8)	6874(2)	4024(1)	3696(1)	23(1)
N(9)	7171(1)	4290(1)	4677(1)	22(1)
N(10)	7455(2)	5423(1)	4795(1)	24(1)
C(11)	7993(2)	5711(1)	5770(1)	22(1)
C(12)	8320(2)	6864(1)	6049(1)	21(1)
C(13)	8125(2)	7669(1)	5261(1)	23(1)
C(14)	8395(2)	8756(1)	5538(1)	26(1)
C(15)	8880(2)	9058(1)	6603(1)	26(1)
C(16)	9104(2)	8269(1)	7393(1)	27(1)
C(17)	8825(2)	7176(1)	7116(1)	24(1)

Table S10. Bond lengths [Å] and angles [°] for **3**.

C(1)-C(2)	1.4846(15)
C(1)-H(1A)	0.957(19)
C(1)-H(1B)	0.950(19)
C(1)-H(1C)	0.965(16)
C(2)-N(3)	1.3201(14)
C(2)-C(7)	1.4193(16)
N(3)-O(4)	1.2382(13)
N(3)-O(5)	1.4490(12)
O(5)-N(6)	1.3661(13)
N(6)-C(7)	1.3153(14)
C(7)-C(8)	1.4557(16)
C(8)-H(8)	0.9500
C(8)-N(9)	1.2800(15)
N(9)-N(10)	1.4065(13)
N(10)-C(11)	1.2810(15)
C(11)-H(11)	0.9500
C(11)-C(12)	1.4643(15)
C(12)-C(13)	1.4014(16)
C(12)-C(17)	1.3987(15)
C(13)-H(13)	0.9500
C(13)-C(14)	1.3816(17)
C(14)-H(14)	0.9500
C(14)-C(15)	1.3923(16)
C(15)-H(15)	0.9500
C(15)-C(16)	1.3894(17)
C(16)-H(16)	0.9500
C(16)-C(17)	1.3890(16)
C(17)-H(17)	0.9500
C(2)-C(1)-H(1A)	110.8(11)
C(2)-C(1)-H(1B)	107.6(11)
C(2)-C(1)-H(1C)	108.8(10)
H(1A)-C(1)-H(1B)	108.9(15)
H(1A)-C(1)-H(1C)	110.5(14)
H(1B)-C(1)-H(1C)	110.2(14)
N(3)-C(2)-C(1)	121.54(11)
N(3)-C(2)-C(7)	105.73(10)
C(7)-C(2)-C(1)	132.73(10)

C(2)-N(3)-O(5)	108.07(9)
O(4)-N(3)-C(2)	135.00(10)
O(4)-N(3)-O(5)	116.92(9)
N(6)-O(5)-N(3)	107.36(7)
C(7)-N(6)-O(5)	106.91(9)
C(2)-C(7)-C(8)	129.94(10)
N(6)-C(7)-C(2)	111.92(10)
N(6)-C(7)-C(8)	118.13(10)
C(7)-C(8)-H(8)	119.6
N(9)-C(8)-C(7)	120.71(10)
N(9)-C(8)-H(8)	119.6
C(8)-N(9)-N(10)	110.30(10)
C(11)-N(10)-N(9)	112.45(10)
N(10)-C(11)-H(11)	119.9
N(10)-C(11)-C(12)	120.26(10)
C(12)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	121.05(10)
C(17)-C(12)-C(11)	119.89(10)
C(17)-C(12)-C(13)	119.07(11)
C(12)-C(13)-H(13)	119.8
C(14)-C(13)-C(12)	120.34(11)
C(14)-C(13)-H(13)	119.8
C(13)-C(14)-H(14)	119.9
C(13)-C(14)-C(15)	120.12(11)
C(15)-C(14)-H(14)	119.9
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-C(14)	120.22(11)
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-C(15)	119.73(11)
C(17)-C(16)-H(16)	120.1
C(12)-C(17)-H(17)	119.7
C(16)-C(17)-C(12)	120.51(11)
C(16)-C(17)-H(17)	119.7

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. 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}
C(1)	31(1)	25(1)	19(1)	0(1)	4(1)	-1(1)
C(2)	19(1)	23(1)	20(1)	-4(1)	4(1)	0(1)
N(3)	25(1)	26(1)	20(1)	-3(1)	3(1)	0(1)
O(4)	42(1)	22(1)	32(1)	-5(1)	3(1)	-2(1)
O(5)	32(1)	31(1)	18(1)	-4(1)	4(1)	-3(1)
N(6)	27(1)	29(1)	22(1)	-2(1)	4(1)	-4(1)
C(7)	18(1)	28(1)	19(1)	-1(1)	4(1)	0(1)
C(8)	21(1)	24(1)	22(1)	2(1)	4(1)	0(1)
N(9)	22(1)	21(1)	23(1)	-1(1)	5(1)	0(1)
N(10)	26(1)	21(1)	24(1)	0(1)	6(1)	-1(1)
C(11)	20(1)	23(1)	22(1)	2(1)	6(1)	2(1)
C(12)	18(1)	23(1)	22(1)	0(1)	5(1)	2(1)
C(13)	24(1)	26(1)	20(1)	1(1)	5(1)	0(1)
C(14)	28(1)	25(1)	26(1)	4(1)	4(1)	1(1)
C(15)	27(1)	22(1)	30(1)	-2(1)	4(1)	1(1)
C(16)	28(1)	29(1)	22(1)	-4(1)	3(1)	2(1)
C(17)	26(1)	25(1)	21(1)	2(1)	5(1)	3(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3**.

	x	y	z	U(eq)
H(8)	6920	4567	3178	27
H(11)	8180	5175	6313	26
H(13)	7806	7465	4533	28
H(14)	8249	9298	5000	32
H(15)	9059	9807	6790	32
H(16)	9446	8476	8120	32
H(17)	8979	6637	7657	29
H(1A)	8260(30)	1669(15)	5437(15)	53(5)
H(1B)	6410(30)	2368(15)	5466(15)	48(5)
H(1C)	6170(20)	1104(13)	5286(13)	35(4)

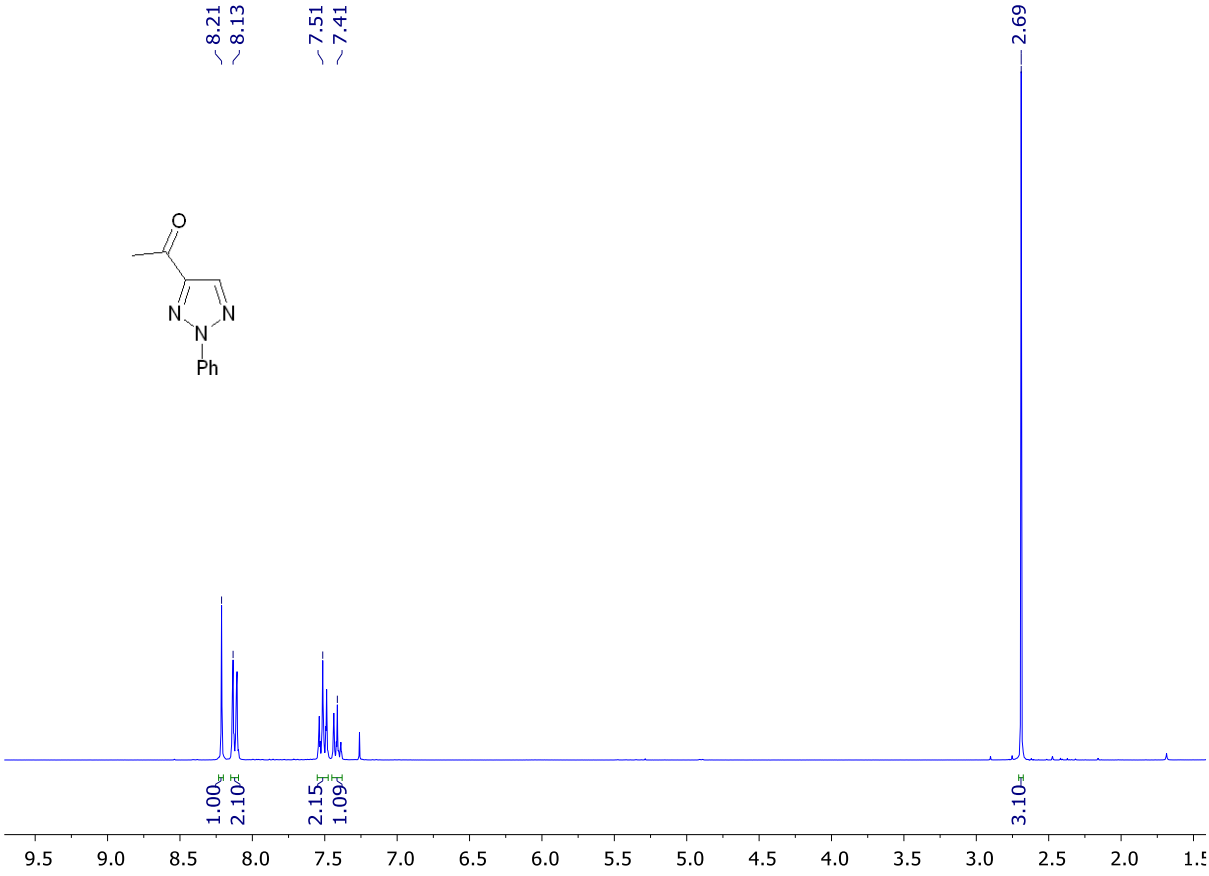
Table S13. Torsion angles [°] for **3**.

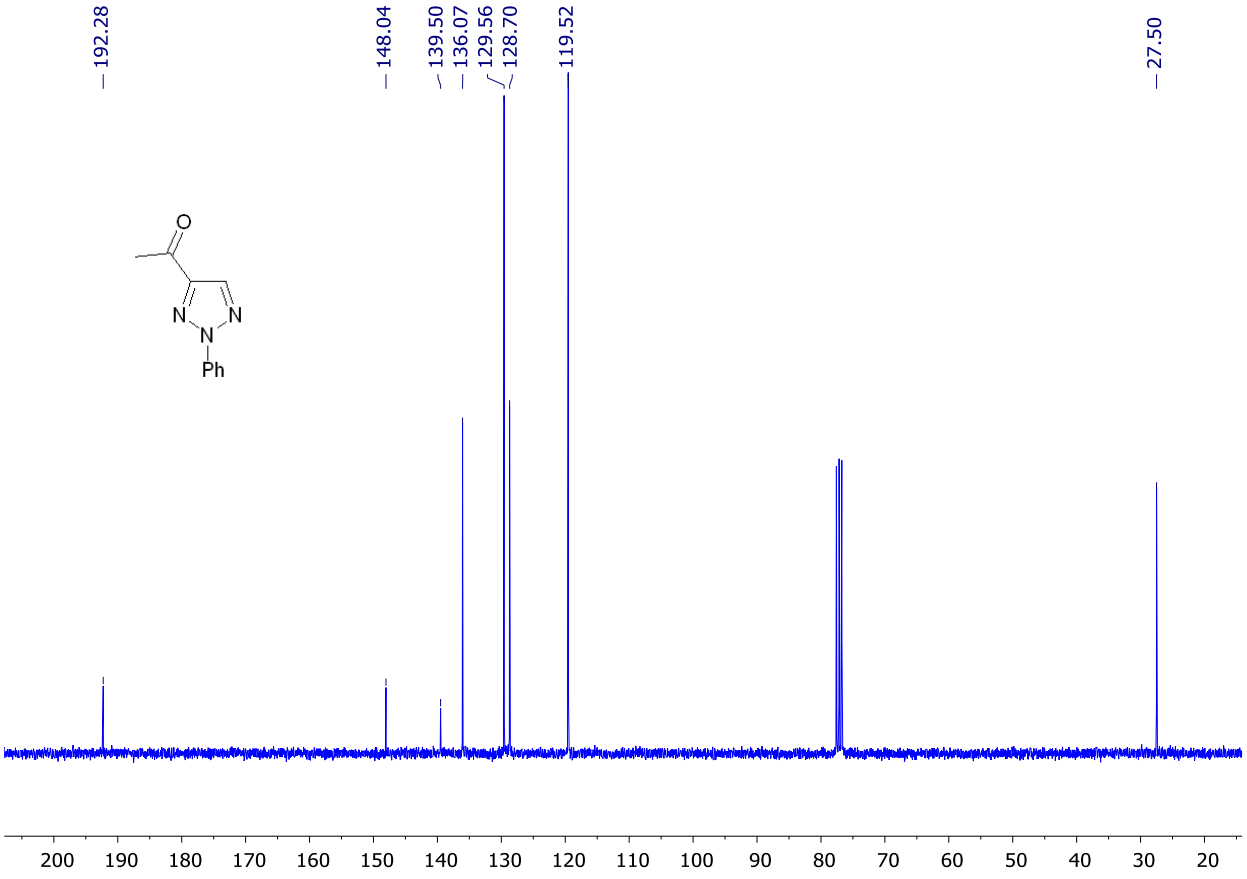
C(1)-C(2)-N(3)-O(4)	-1.3(2)
C(1)-C(2)-N(3)-O(5)	179.54(10)
C(1)-C(2)-C(7)-N(6)	-179.61(12)
C(1)-C(2)-C(7)-C(8)	0.3(2)
C(2)-N(3)-O(5)-N(6)	0.51(12)
C(2)-C(7)-C(8)-N(9)	-5.44(19)
N(3)-C(2)-C(7)-N(6)	0.62(14)
N(3)-C(2)-C(7)-C(8)	-179.50(11)
N(3)-O(5)-N(6)-C(7)	-0.12(12)
O(4)-N(3)-O(5)-N(6)	-178.85(9)
O(5)-N(6)-C(7)-C(2)	-0.29(13)
O(5)-N(6)-C(7)-C(8)	179.81(9)
N(6)-C(7)-C(8)-N(9)	174.44(10)
C(7)-C(2)-N(3)-O(4)	178.55(12)
C(7)-C(2)-N(3)-O(5)	-0.65(12)
C(7)-C(8)-N(9)-N(10)	-177.78(9)
C(8)-N(9)-N(10)-C(11)	-172.08(10)
N(9)-N(10)-C(11)-C(12)	-178.73(9)
N(10)-C(11)-C(12)-C(13)	-2.35(17)
N(10)-C(11)-C(12)-C(17)	177.28(10)
C(11)-C(12)-C(13)-C(14)	178.51(10)
C(11)-C(12)-C(17)-C(16)	-178.78(10)
C(12)-C(13)-C(14)-C(15)	0.57(18)
C(13)-C(12)-C(17)-C(16)	0.85(17)
C(13)-C(14)-C(15)-C(16)	0.27(19)
C(14)-C(15)-C(16)-C(17)	-0.53(19)
C(15)-C(16)-C(17)-C(12)	-0.04(18)
C(17)-C(12)-C(13)-C(14)	-1.12(17)

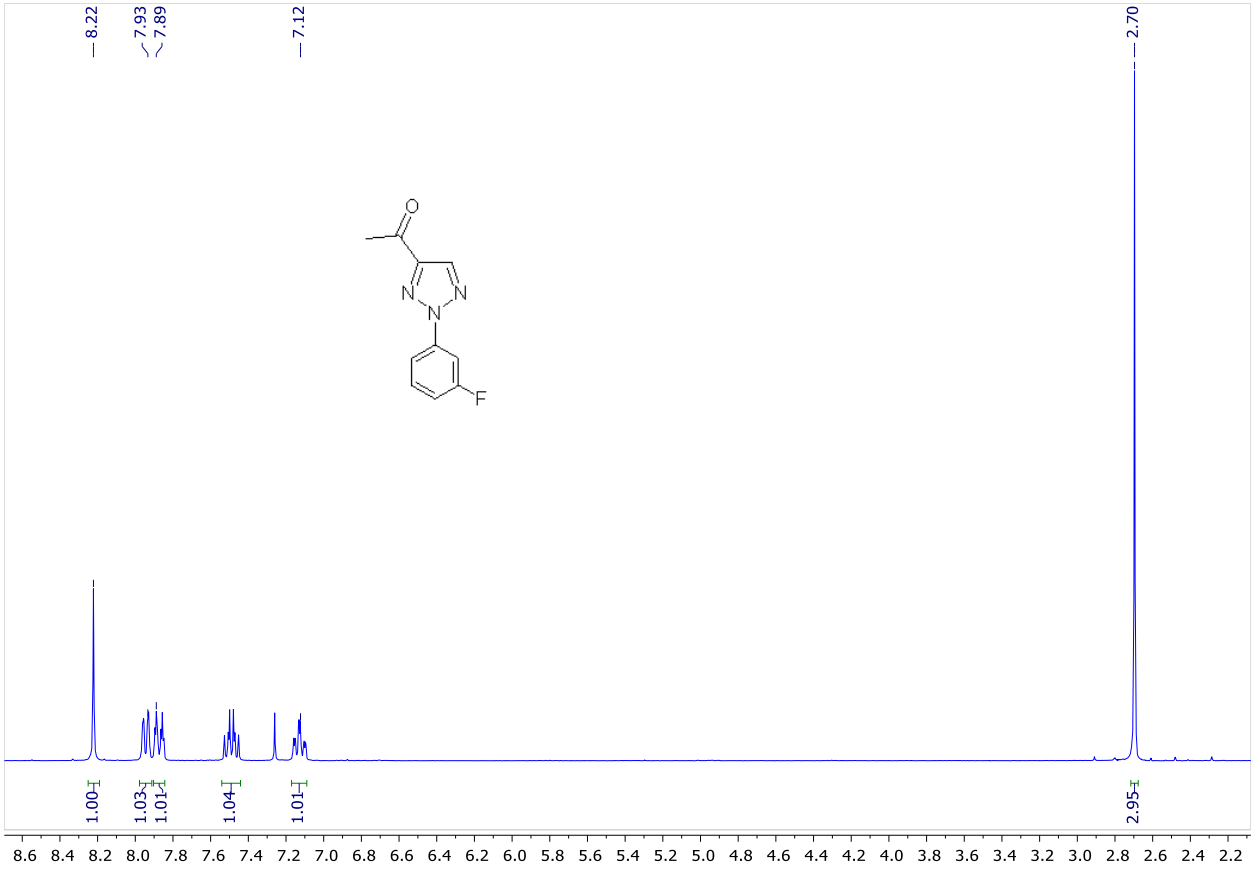
Table S14. Hydrogen bonds for **3** [E and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

S3. Copies of NMR spectra



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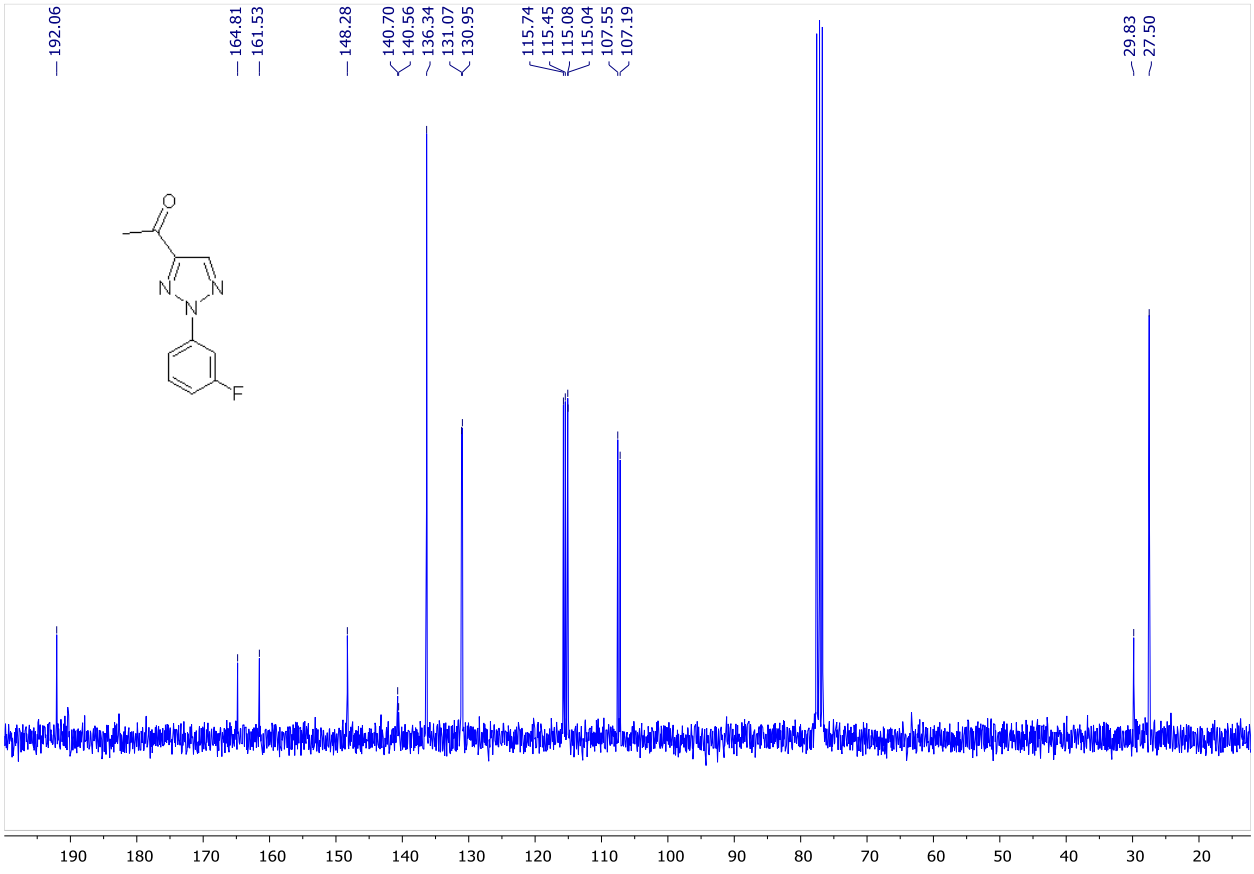
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29.83
27.50
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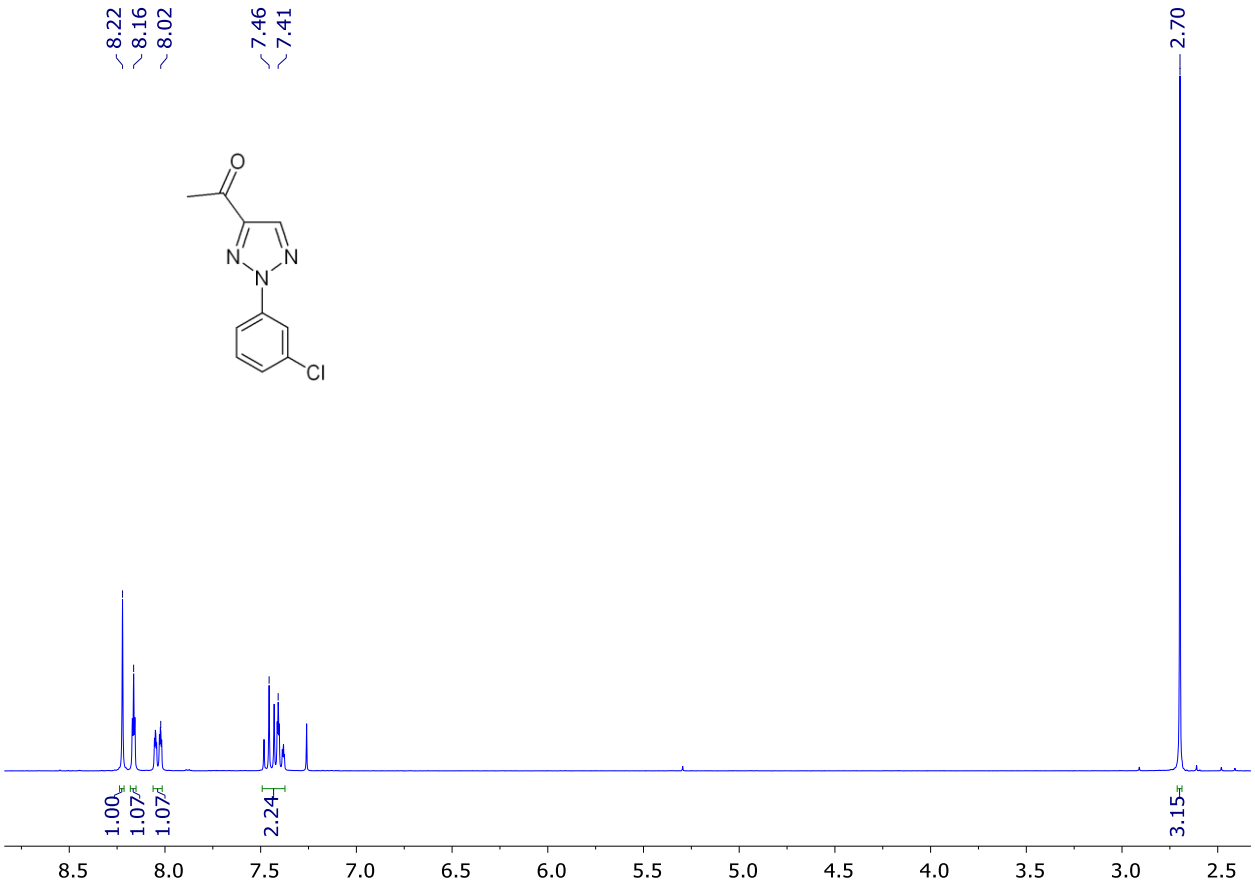
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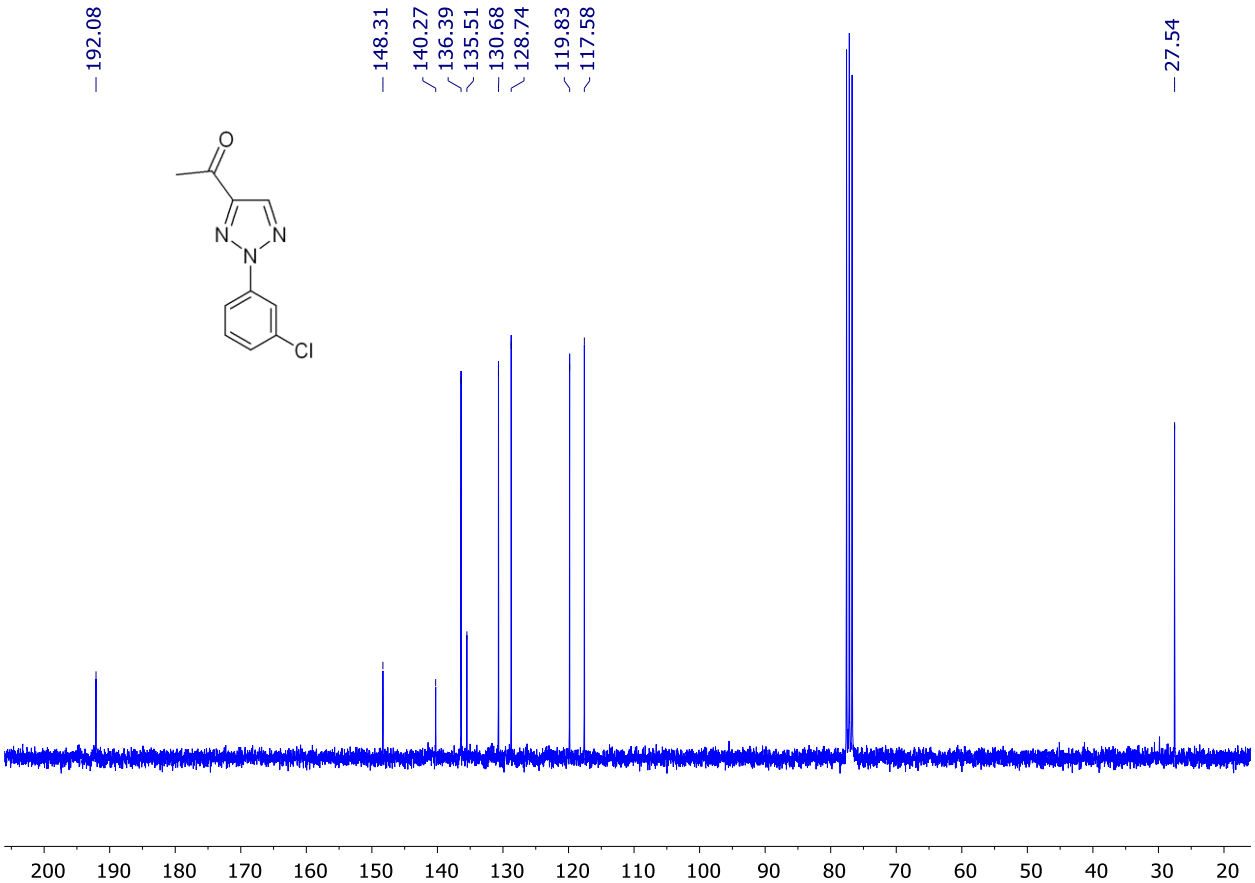
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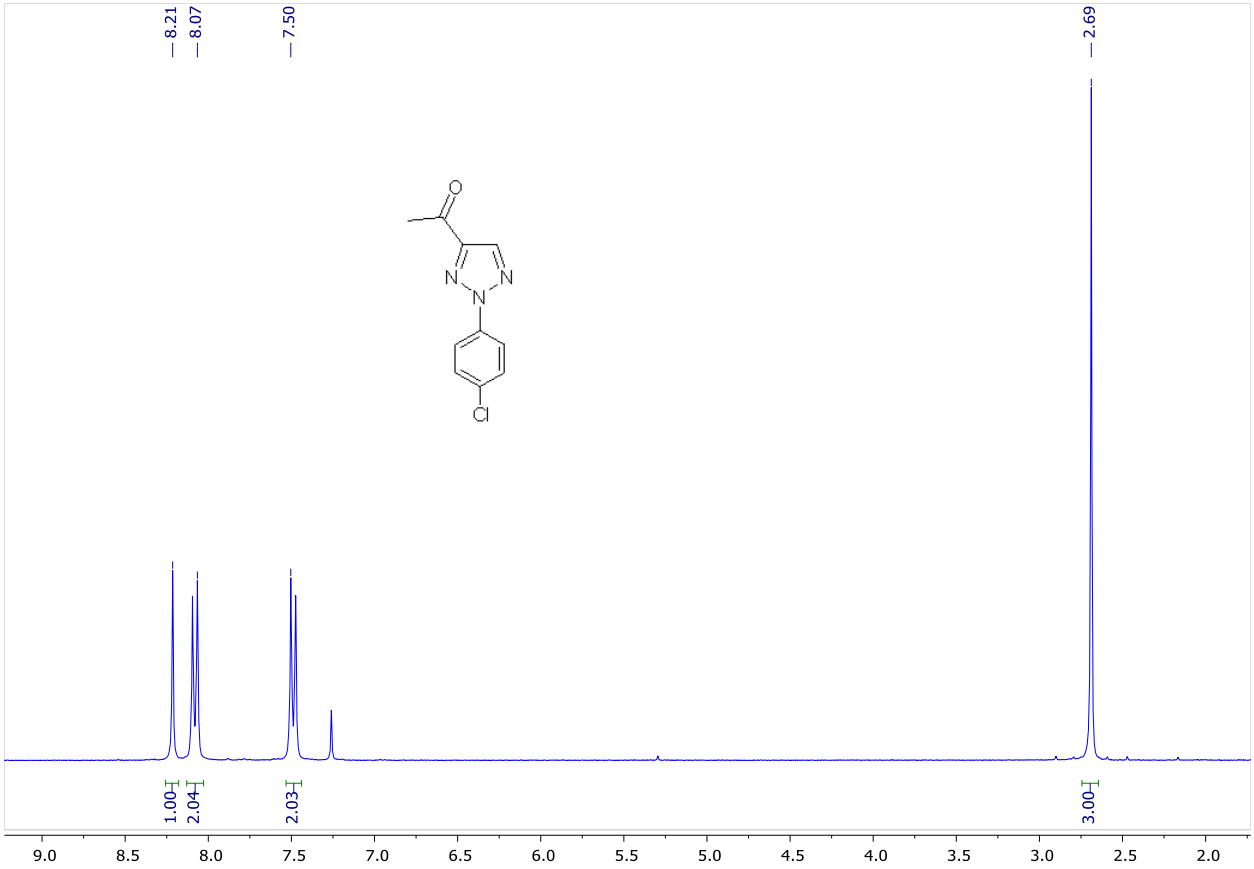
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N
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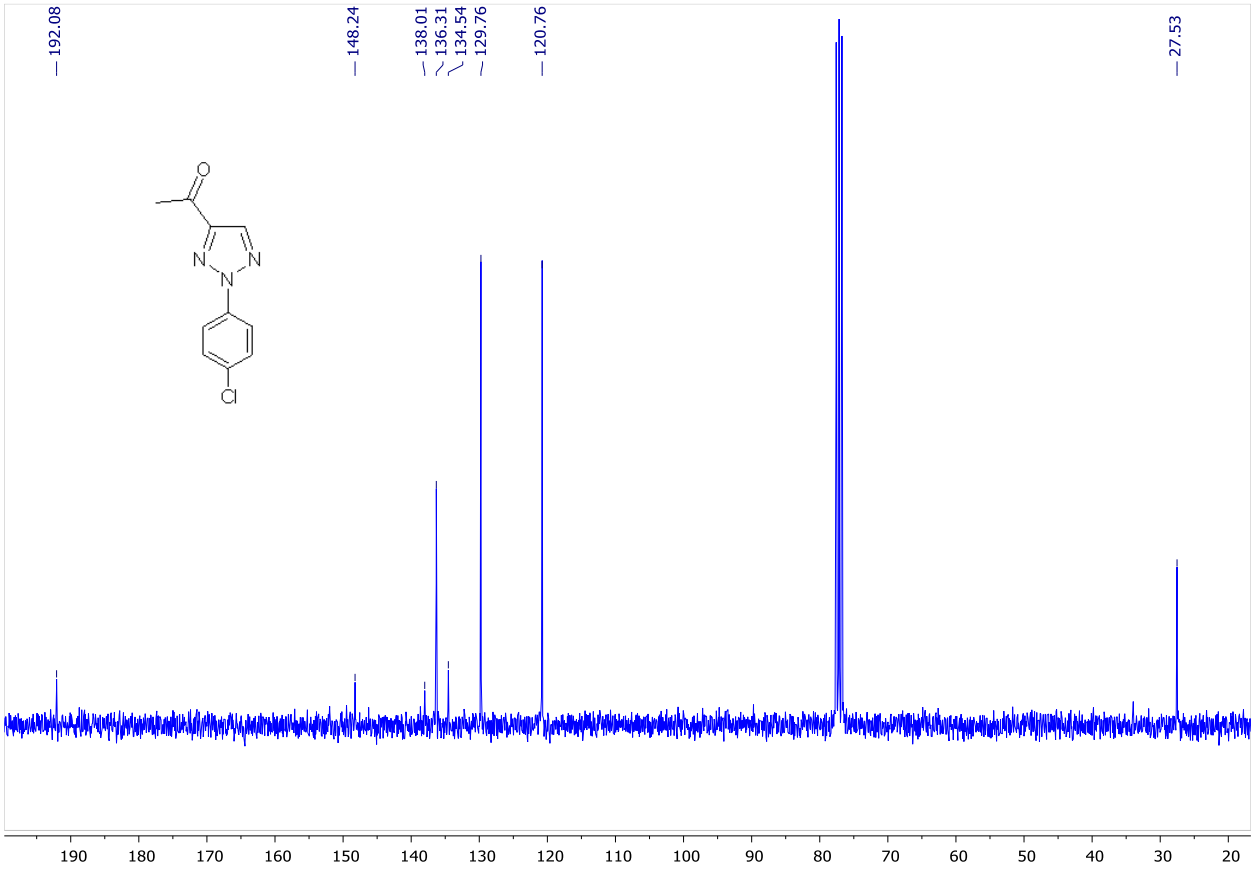
N
Cl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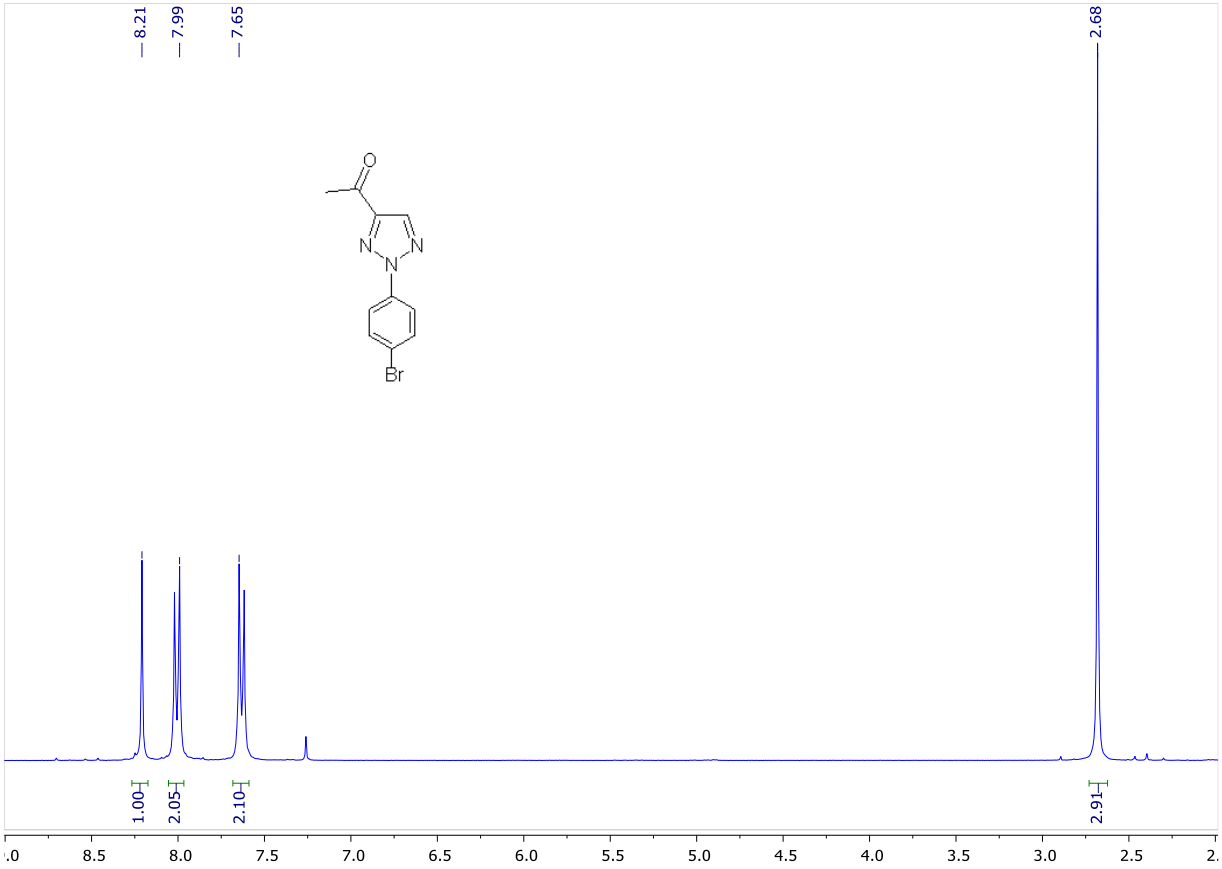
N
N
Cl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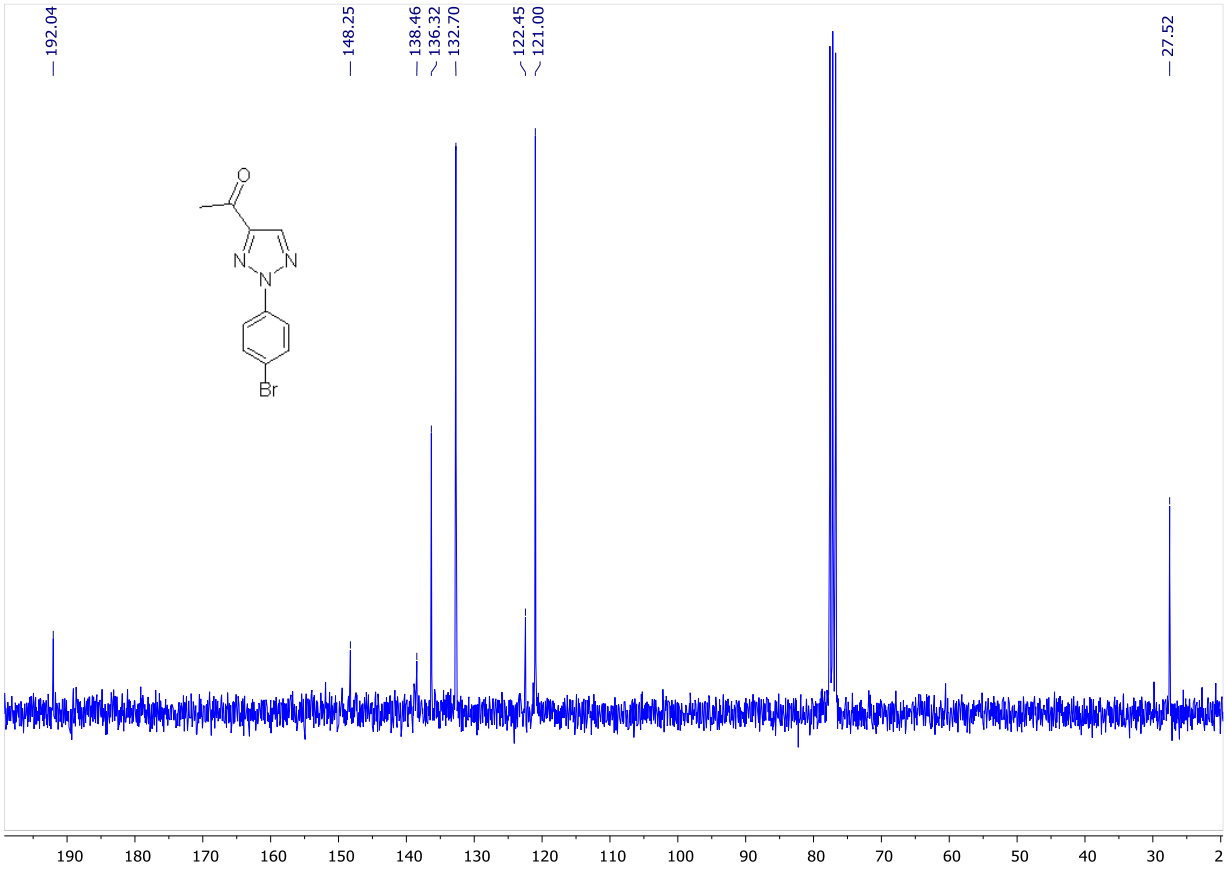
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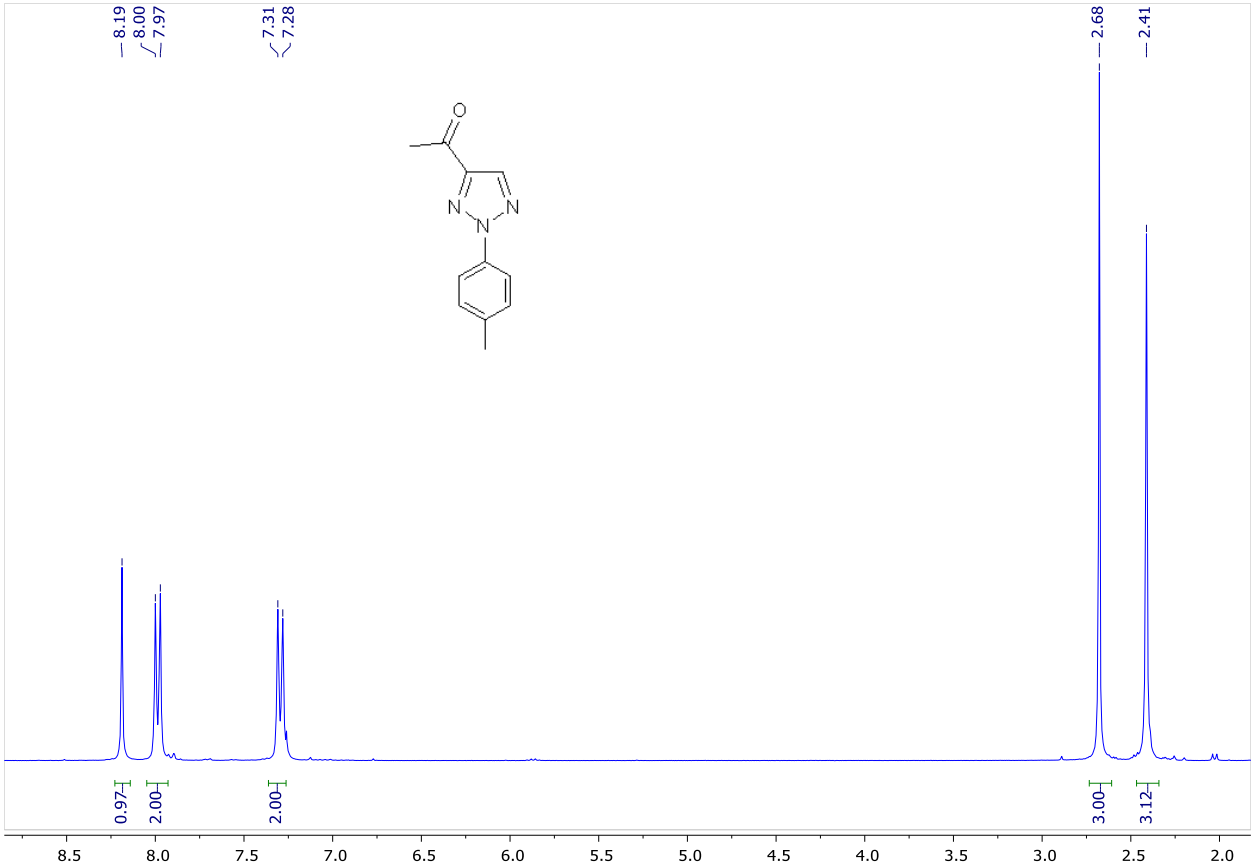
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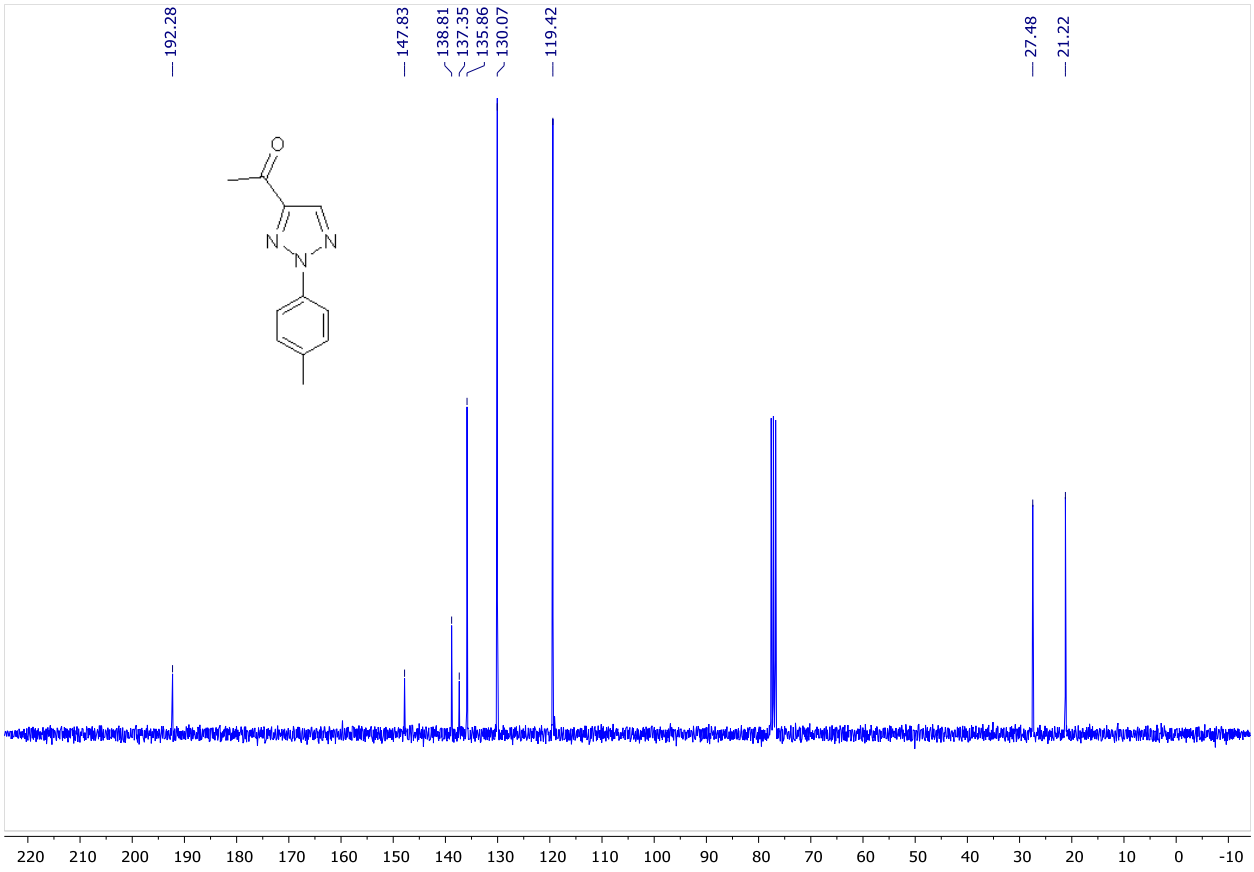
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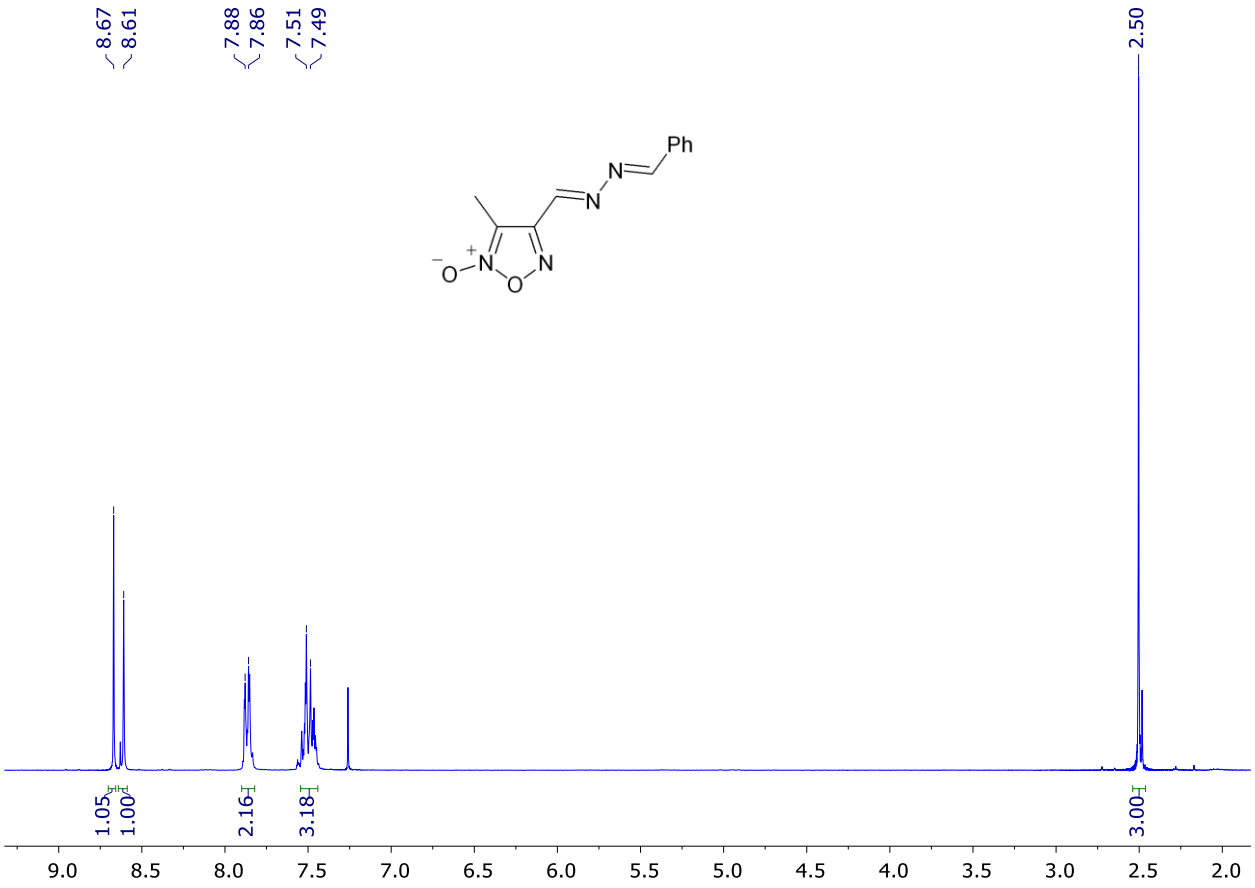
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2.16
3.18
3.00
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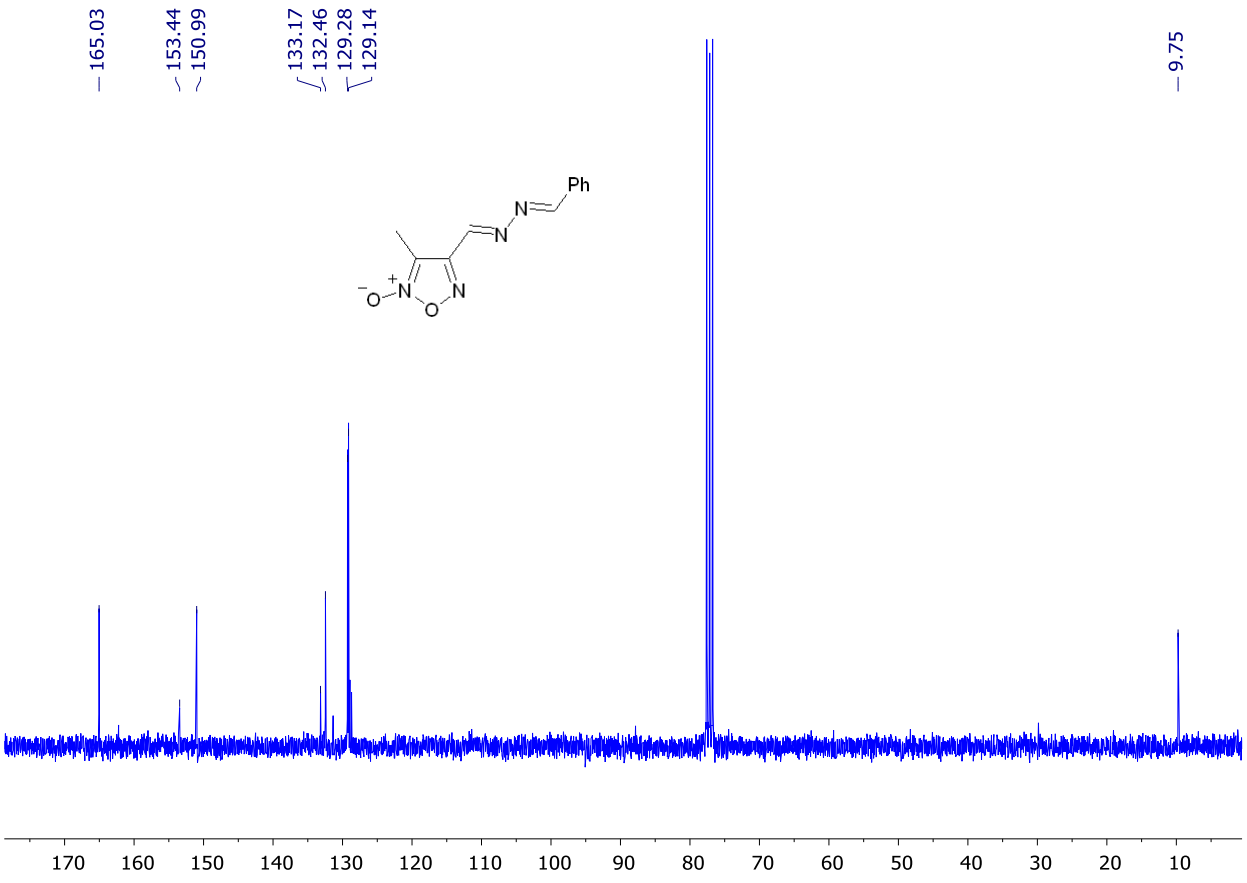
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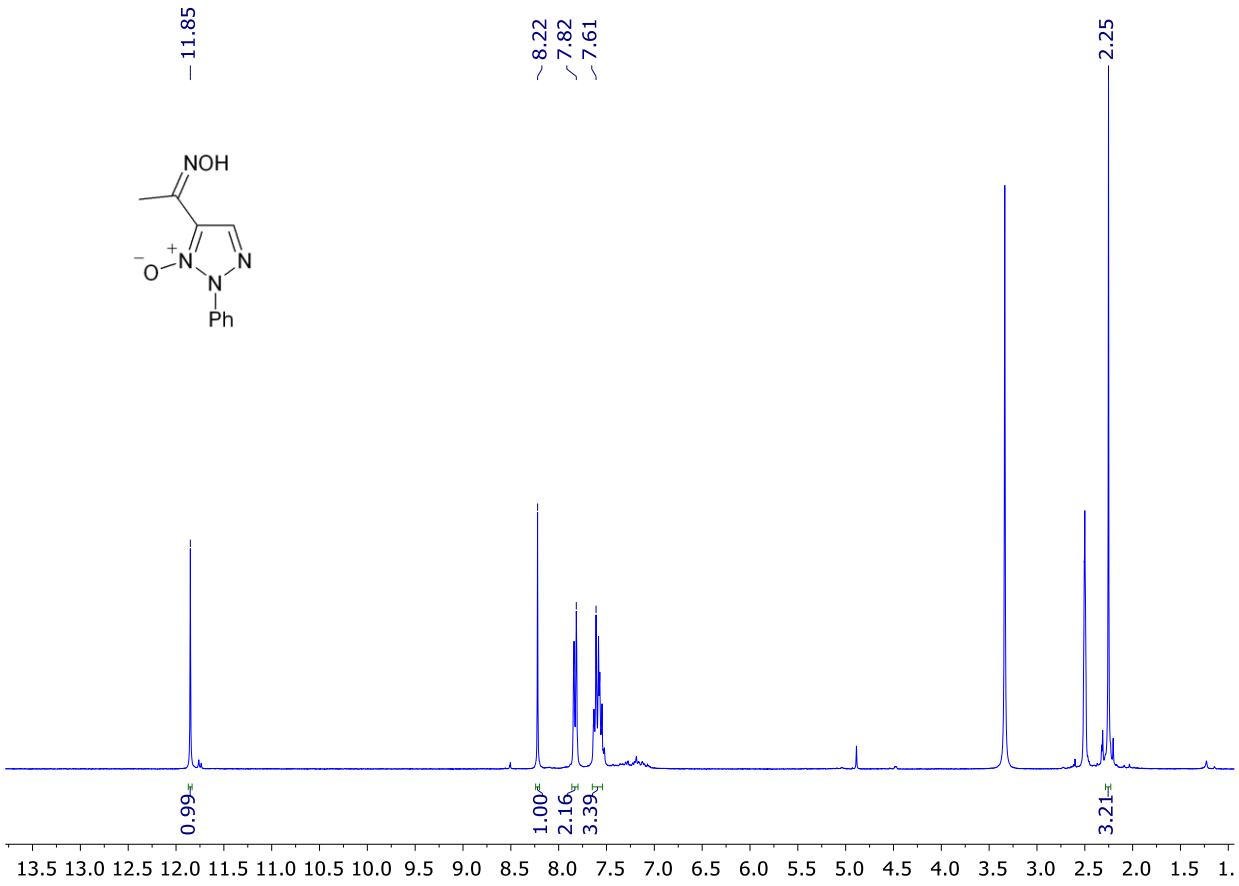
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7.61
2.25
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N
N
Ph
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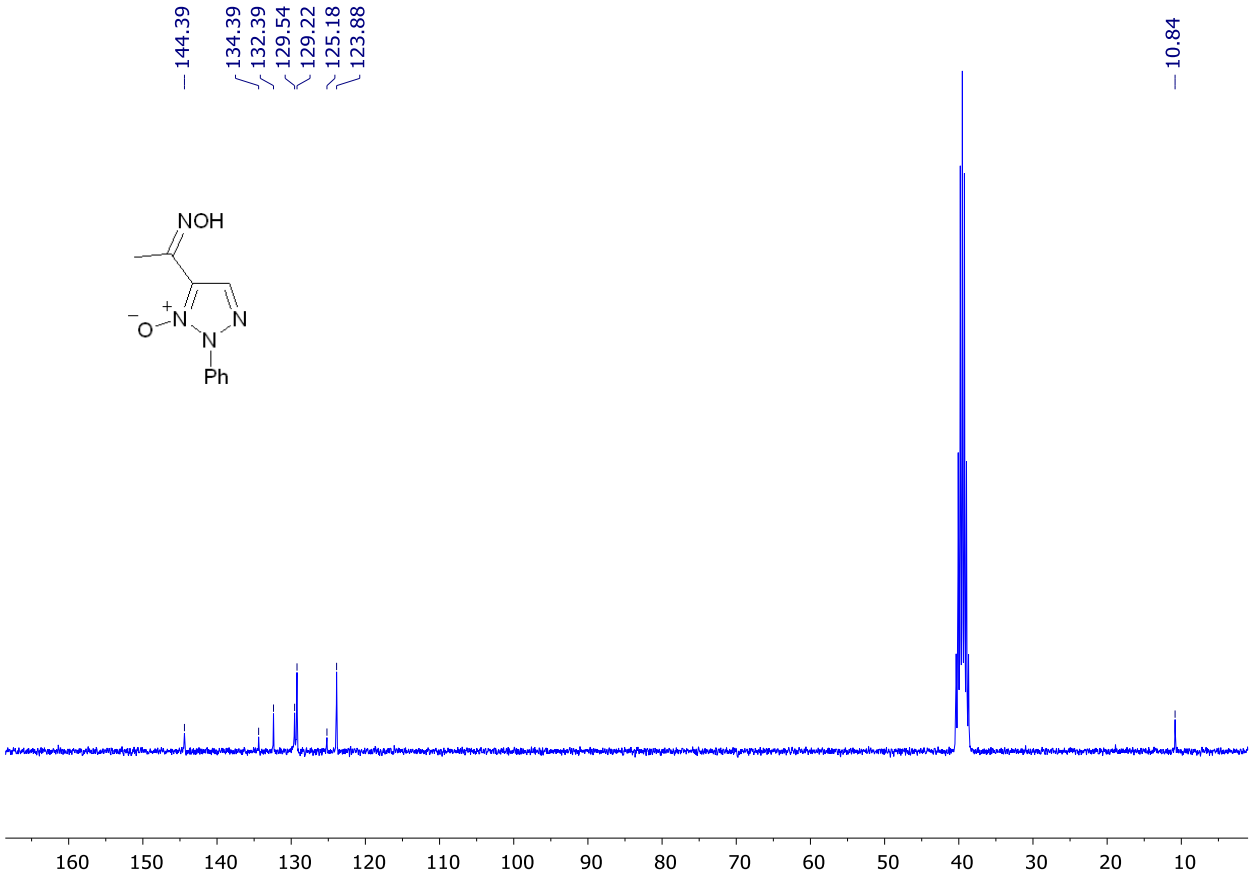
1.00
2.16
3.39
3.21
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.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Ph
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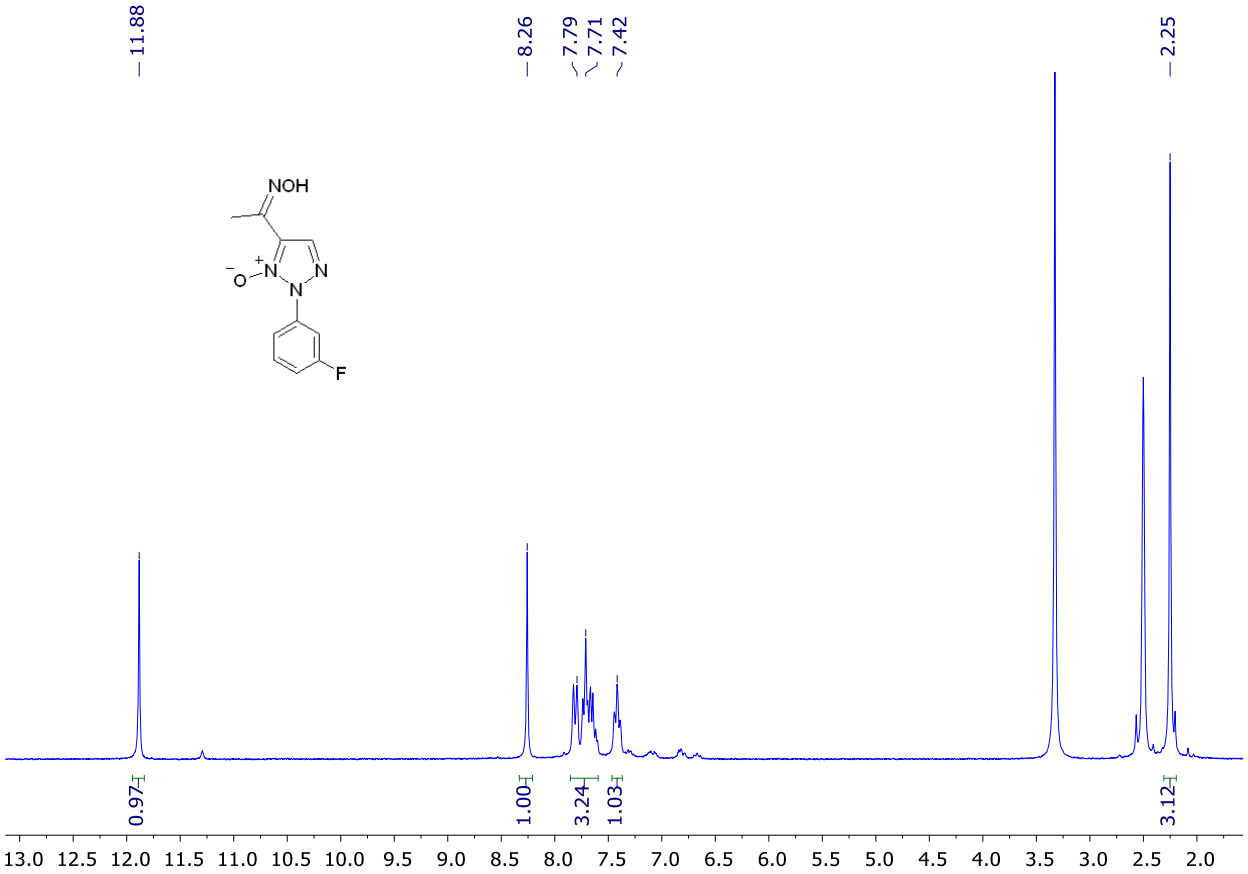
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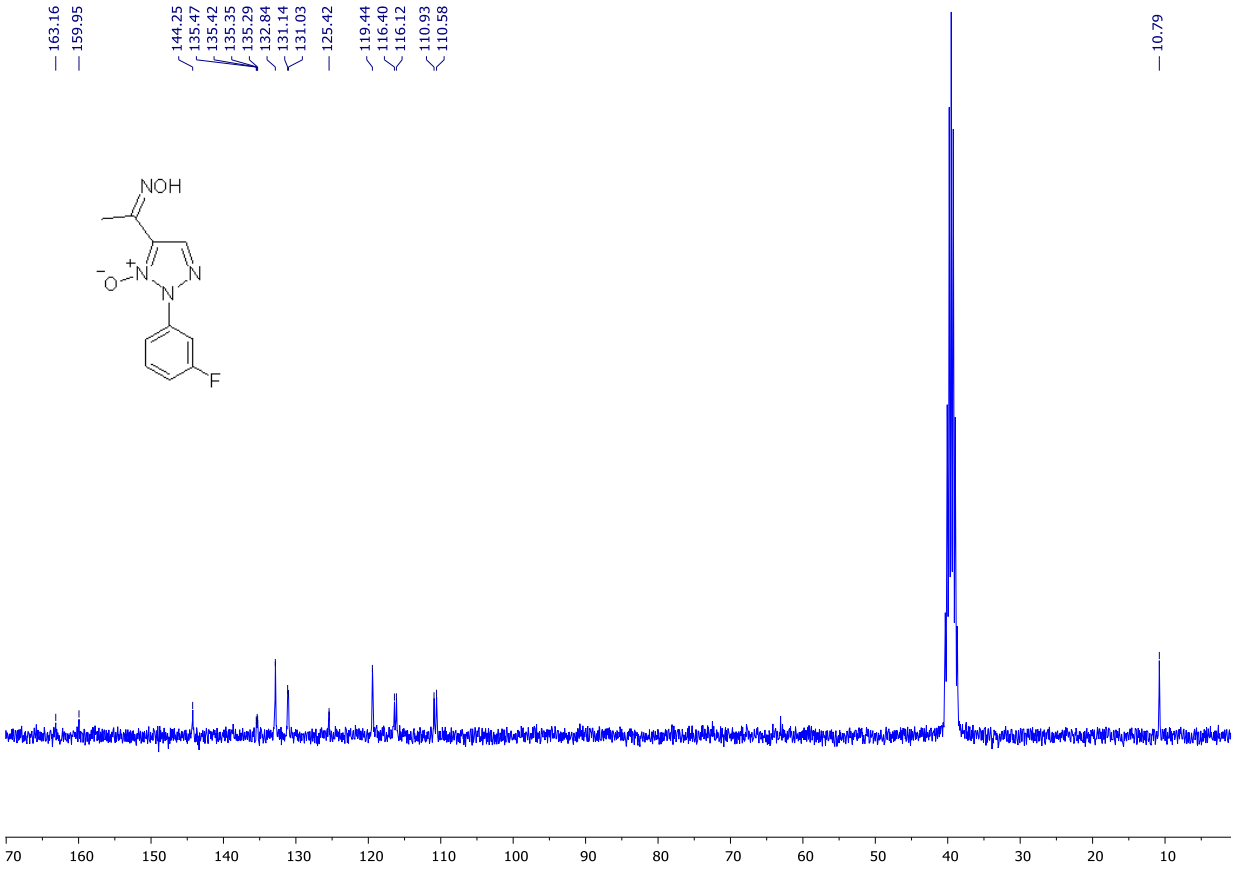
3.24
1.03
3.12
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0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125.42
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N
F
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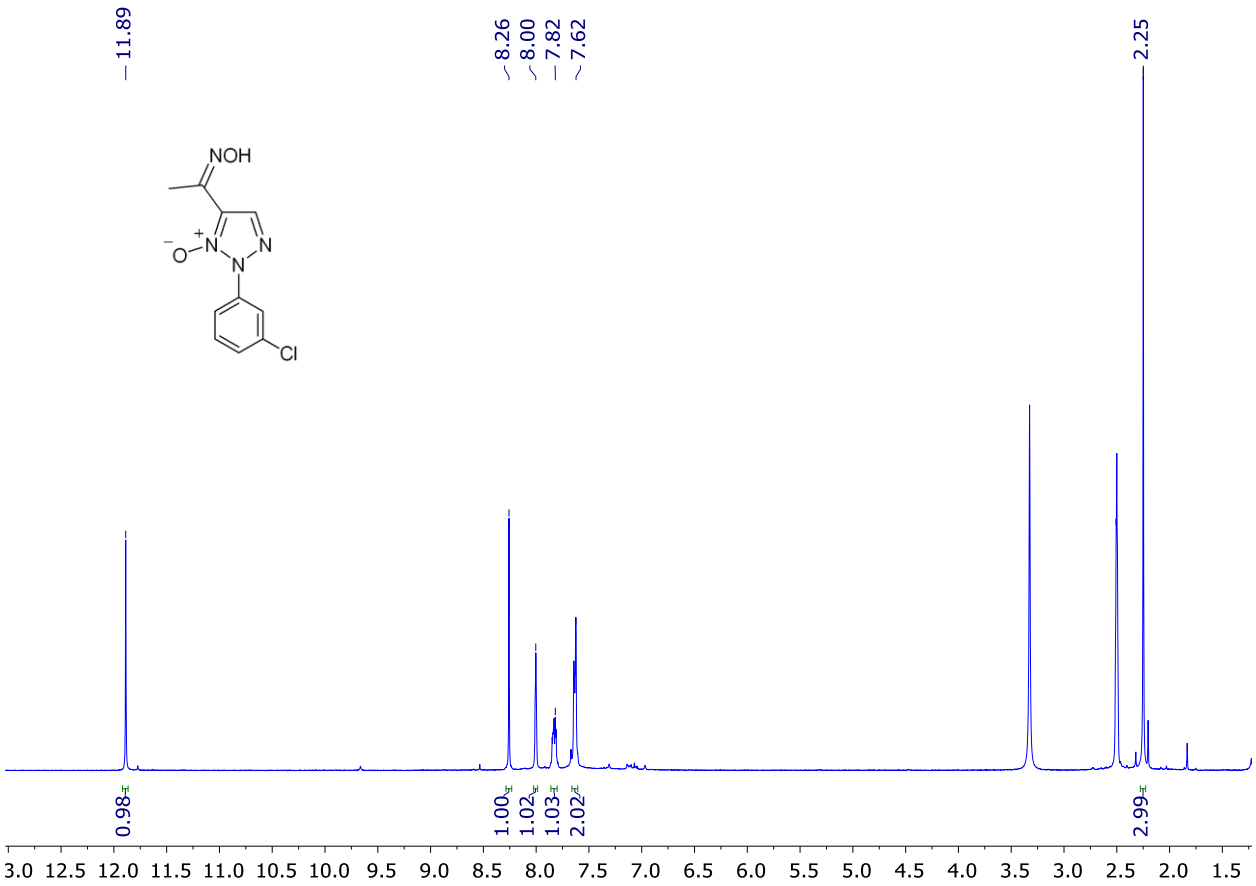
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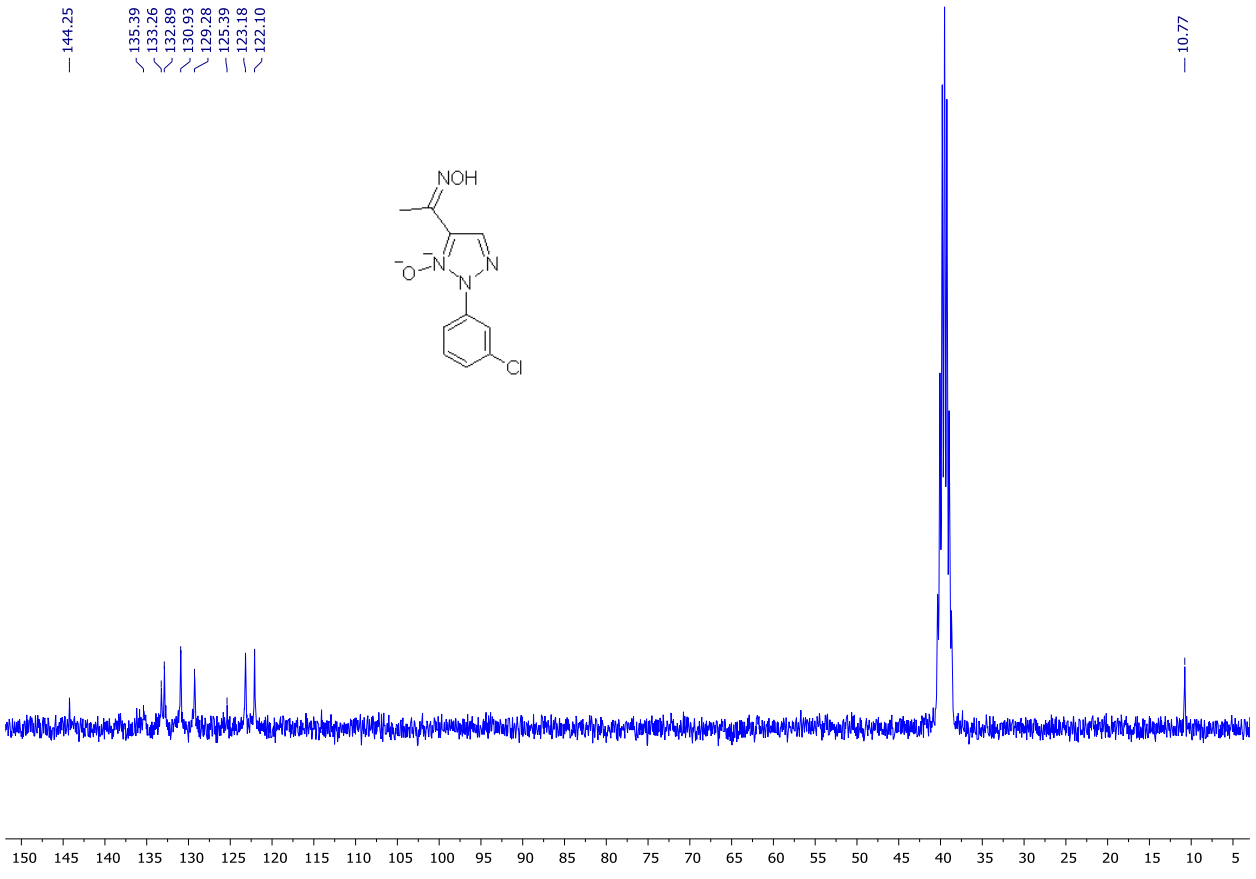
1.03
2.02
2.99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123.18
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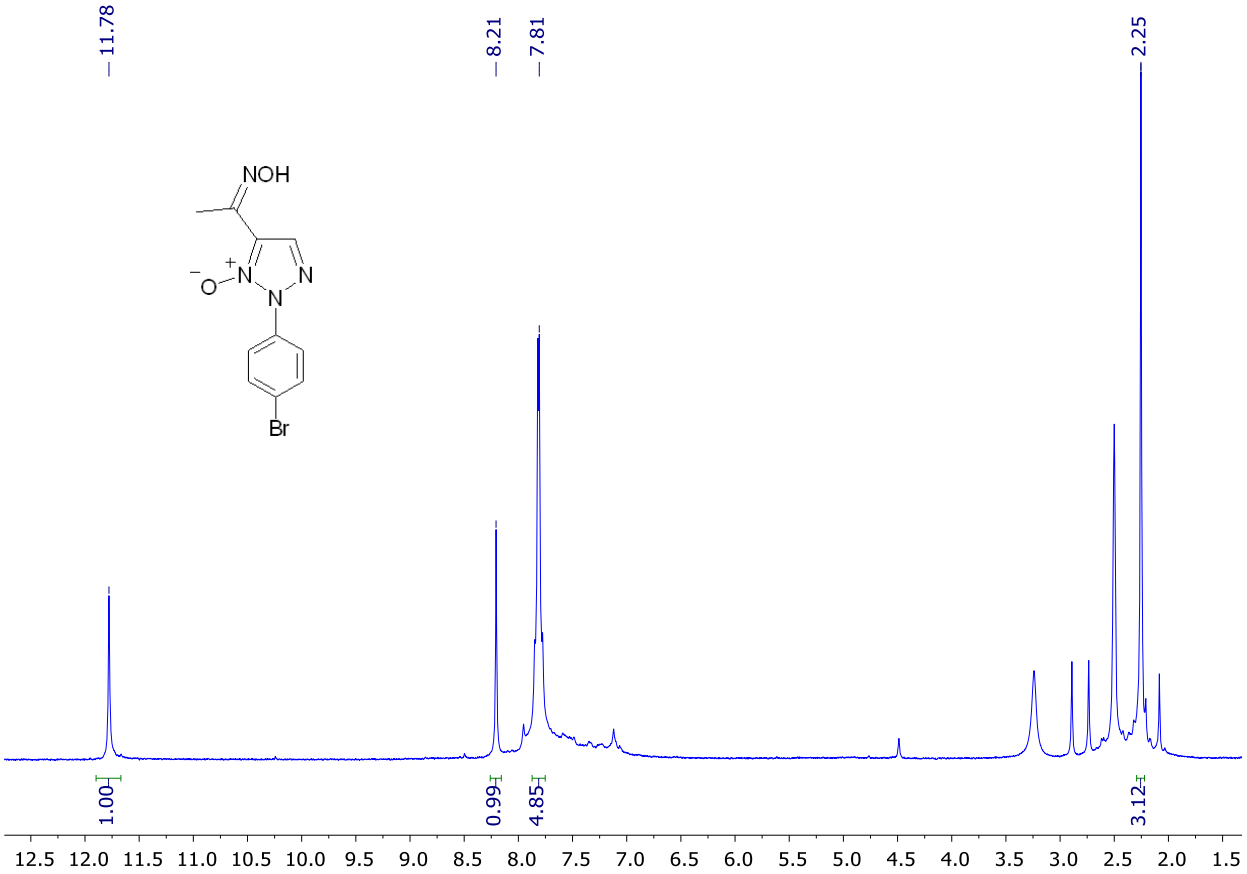
NOH
Cl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8.21
7.81
2.25
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O
Br
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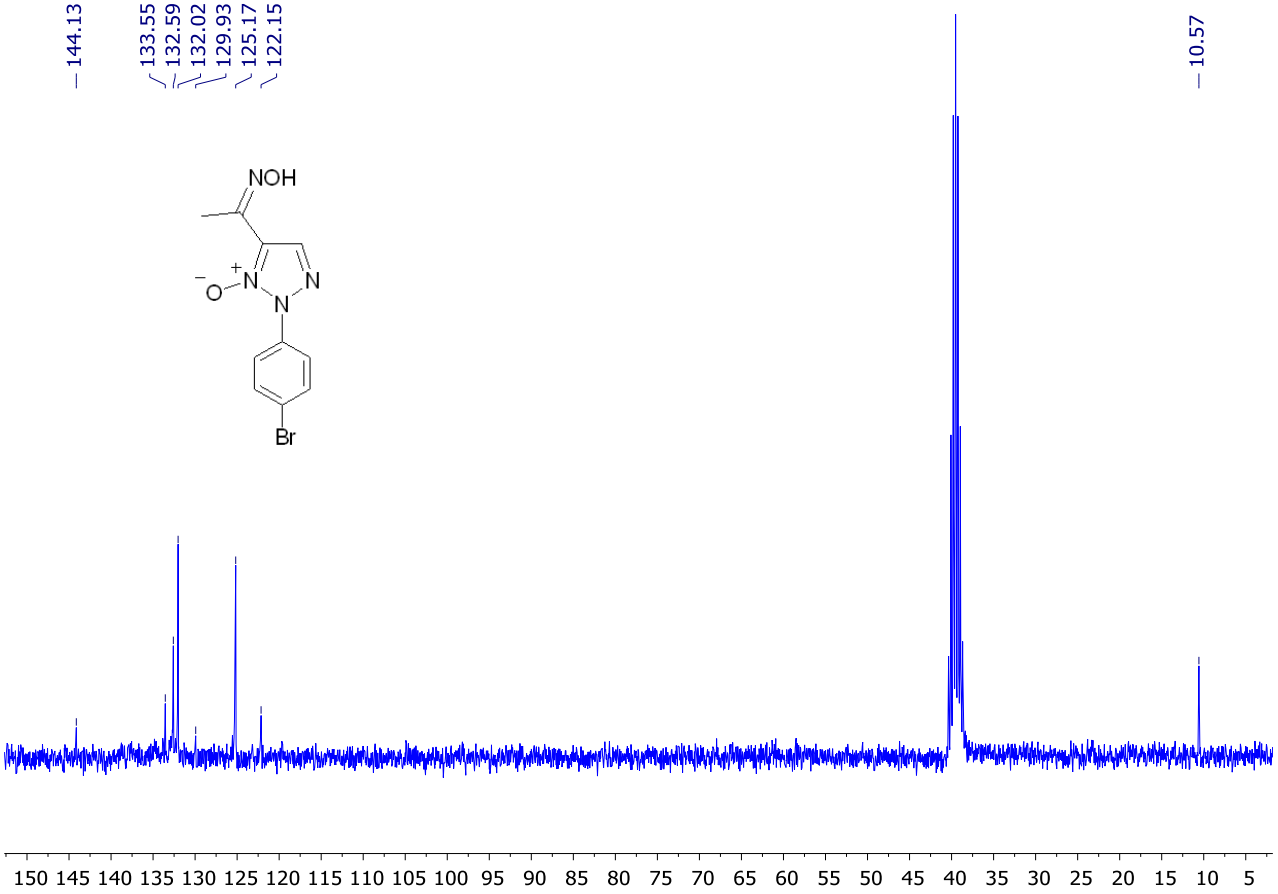
0.99
4.85
3.12
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5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N
N
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Br
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