Supporting Information

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Synthesis, characterization and theoretical studies of novel sulfonamide-aldehydes derivatives having tautomeric forms

Mehmet Gümüş[1,*], Yusuf Sert[2] and İrfan Koca[3]

[1]Akdagmadeni Health College, Yozgat Bozok University, Yozgat, Türkiye
[2]Sorgun Vocational School, Yozgat Bozok University, Yozgat, Türkiye
[3]Department of Chemistry, Faculty of Art & Sciences, Yozgat Bozok University, Yozgat, Türkiye

Table of content **Page**

*General Procedure for the Synthesis of Compound **M:***

The aromatic sulfonamide derivatives (1 mmol) were converted to the amine salt in an acidic medium (HCl) and then converted to the diazonium salt by reaction with an aqueous solution of the equivalent amount of sodium nitrite at 0 ° C. This diazonium salt solution was added dropwise to a mixture of enaminone (**L**, 1 mmol) and sodium acetate (1 mmol) in the reaction flask fixed at 0 ° C. This reaction was carried out in ethanol solvent. After five minutes, the yellow diazo compound (**M**) which precipitated in the reaction medium was filtered off under vacuum with the aid of water trump. The crude product was purified by recrystallization from n-butanol to get compounds **M**.

*4-(2-(1,3-dioxo-1-(p-tolyl)propan-2-ylidene)hydrazinyl)benzenesulfonamide **(M1)***

Color: Yellow, Yield 0.304 g, 88%, mp 188-190 ºC, FT-IR (ATR, cm^{-1}): υ_{max} 3367, 3255 (NH_2), 3104-2920 (CH, aromatic and aliphatic), 2891 (C-H, aldehyde), 1646 (C=O, aldehyde), 1623 (C=O, ketone), 1603-1503 (C=N and C=C), SO_2 (1313, 1148). ^{1}H-NMR (400 MHz; DMSO-d_6, ppm): δ 14.03 (s, NH, keto-hydrazo form); 11.92 (s, OH, enol-azo form); 9.97 and 9.57 (s, 2H, 2 x CHO); 7.85-7.37 (m, 16H, Ar-H); 7.35 and 7.29 (s, 4H, SO_2NH_2); 2.41 and 2.40 (s, 6H, 2 x CH_3). ^{13}C-NMR (100 MHz; DMSO-d_6, ppm): δ 192.6 (C=O, ketone, keto-hydrazo form); 190.7 (C-OH, enol-azo form); 189.6 and 189.2 (2 x CHO); 146.0, 145.7, 144.8, 143.3, 141.4, 140.8, 139.0, 134.3, 133.5, 133.4, 130.9, 130.1, 129.8, 129.2, 127.8, 117.0, 117.0, 115.4 (C=C and C=N) ; 21.8, 21.7 (2 x CH_3). Calcd. for $C_{16}H_{15}N_3O_4S$ (345.08): C, 55.64; H, 4.38; N, 12.17; S, 9.28. Found: C, 55.78; H, 4.50; N, 12.29; S, 9.37 %.

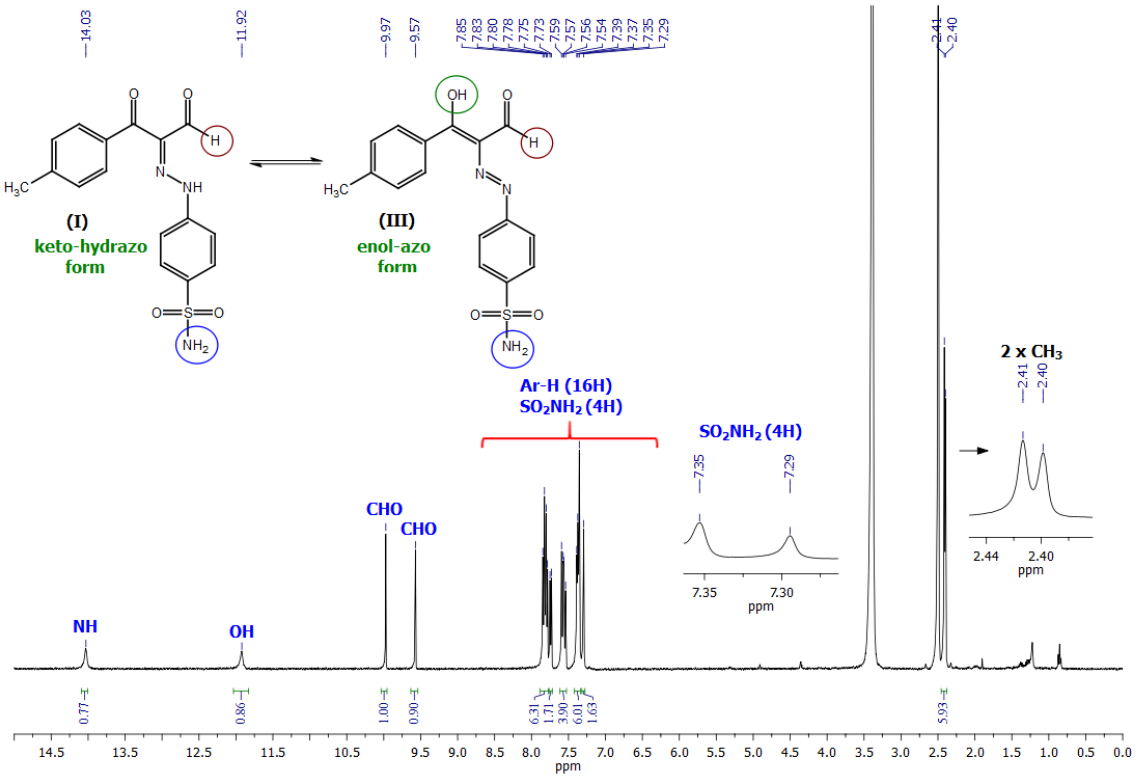

Figure S1: ^{1}H NMR spectrum of **M1**

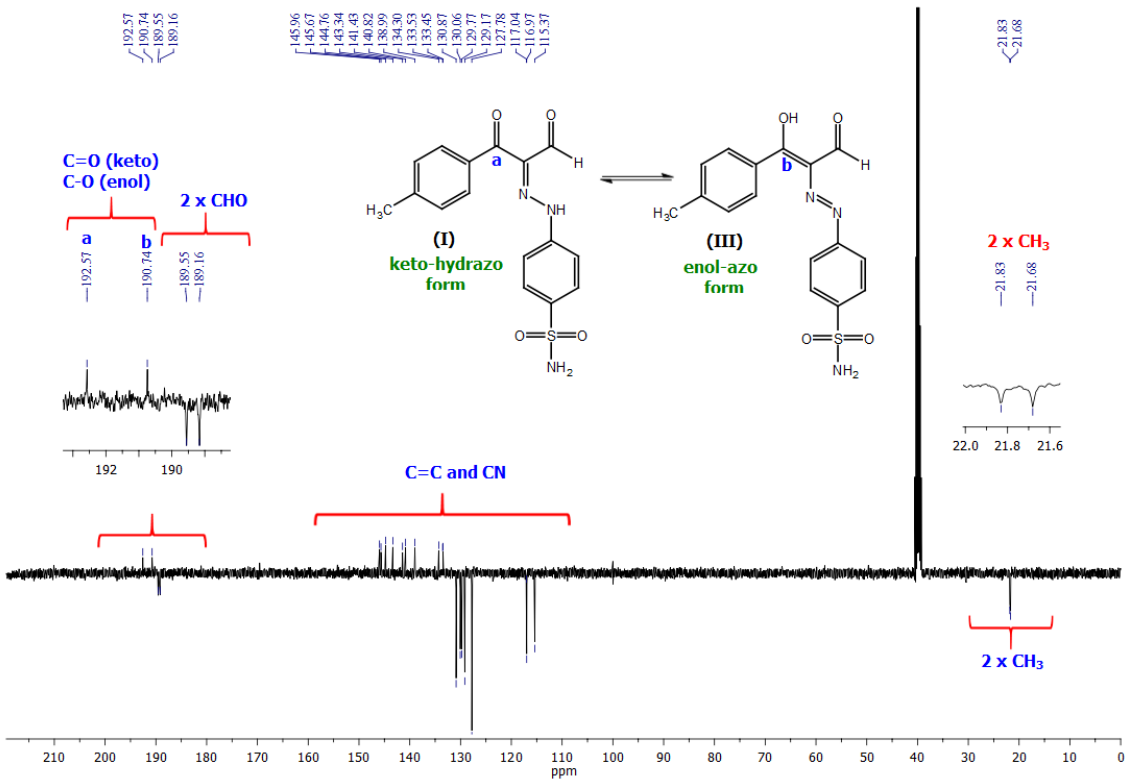

Figure S2: ^{13}C NMR spectrum of **M1**

4-(2-(1,3-dioxo-1-(p-tolyl)propan-2-ylidene)hydrazinyl)-N-(pyrimidin-2-yl)benzenesulfonamide ***(M2)***

Color: Yellow, Yield 0.381 g, 90%, mp 258-260 ^{o}C, FT-IR (ATR, cm^{-1}): υ_{max} 3222 (NH), 3112-2937 (CH, aromatic and aliphatic), 2868 (C-H, aldehyde), 1647 (C=O, aldehyde), 1631 (C=O, ketone), 1604-1445 (C=N and C=C), SO_2 (1316, 1160). ^{1}H-NMR (400 MHz; DMSO-d_6, ppm): δ 13.98 (s, NH, keto-hydrazo form); 11.89 (s, OH, enol-azo form); 11.74 (s, NH, 2H, enol and keto forms); 9.97 and 9.57 (s, 2H, 2 x CHO); 8.50-7.05 (m, 22H, Ar-H); 2.42 and 2.00 (s, 6H, 2 x CH_3). ^{13}C-NMR (100 MHz; DMSO-d_6, ppm): δ 192.6 (C=O, ketone, keto-hydrazo form); 190.9 (C-OH, enol-azo form); 189.8, 189.2, 158.8, 157.2, 157.1, 146.6, 146.2, 146.2, 145.5, 143.6, 141.9, 140.0, 139.2, 138.2, 136.6, 134.5, 134.0, 133.7, 133.2, 130.8, 130.1, 129.9, 129.9, 129.7, 129.6, 129.2, 116.7, 115.2 (C=C and C=N); 21.8 and 21.6 (2 x CH_3). Calcd. for $C_{20}H_{17}N_5O_4S$ (423.10): C, 56.73; H, 4.05; N, 16.54; S, 7.57. Found: C, 56.84; H, 4.33; N, 16.37; S, 7.73 %.

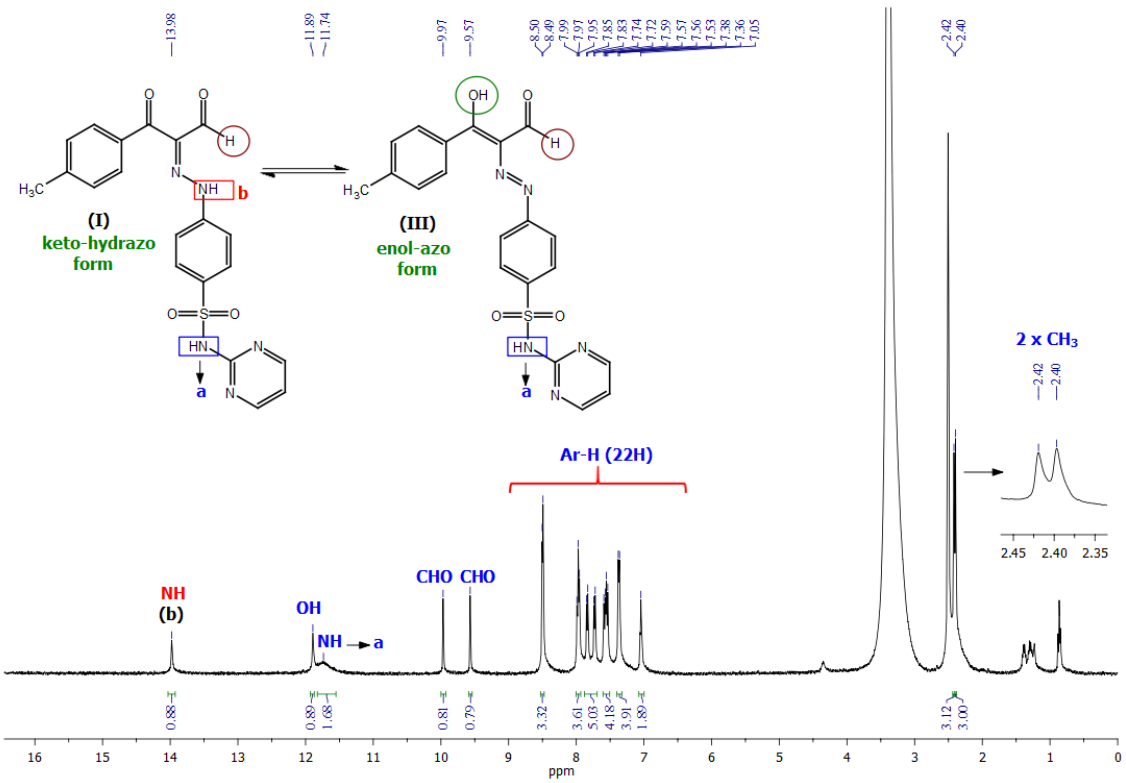

Figure S3: ^{1}H NMR spectrum of **M2**

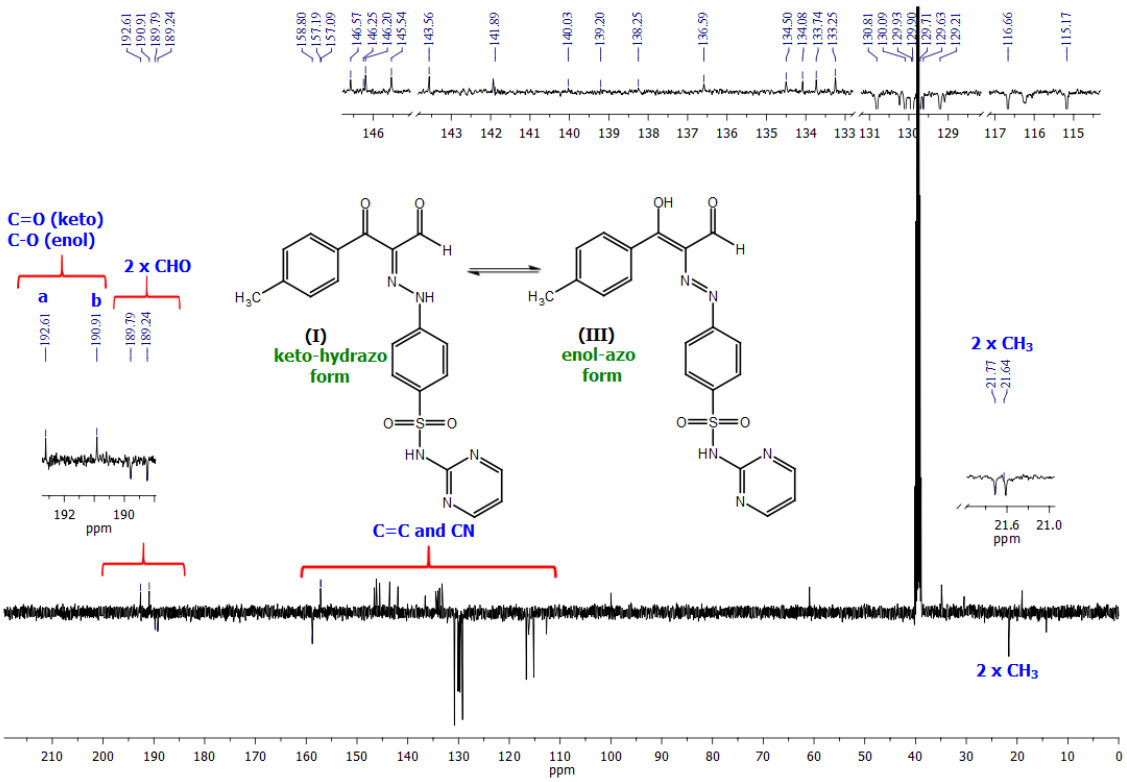

Figure S4: ^{13}C NMR spectrum of **M2**

4-(2-(1,3-dioxo-1-(p-tolyl)propan-2-ylidene)hydrazinyl)-N-(4-methylpyrimidin-2-yl)benzenesulfonamide ***(M3)***

Color: Yellow, Yield 0.367 g, 84%, mp 189-190 °C, FT-IR (ATR, cm^{-1}): υ_{max} 3085-2932 (CH, aromatic and aliphatic), 2865 (C-H, aldehyde), 1646 (C=O, aldehyde), 1633 (C=O, ketone), 1598-1448 (C=N and C=C), SO_2 (1319, 1149). ^{1}H-NMR (400 MHz; DMSO-d_6, ppm): δ 14.01 (s, NH, keto-hydrazo form); 11.90 (s, NH, 2H, enol-azo form); 9.96 and 9.56 (s, 2H, 2 x CHO); 8.30-6.90 (m, 20H, Ar-H); 2.40 and 2.30 (s, 12H, 4 x CH_3). ^{13}C-NMR (100 MHz; DMSO-d_6, ppm): δ 190.7 (C=O, ketone, keto- hydrazo form); 188.63 (C-OH, enol- azo form); 188.4 and 188.1 (2 x CHO); 169.2, 168.6, 152.6, 152.6, 144.9, 144.6, 143.8, 143.6, 143.1, 143.0, 142.9, 136.5, 136.4, 136.3, 136.0, 135.3, 129.8, 129.6, 128.3, 128.2, 128.0, 127.8, 124.8, 116.3, 115.4, 113.1, 113.0, 108.1 (C=C and C=N); in DMSO-d_6; (2 x CH_3, pyrimidine); 21.4 and 21.4 (2 x CH_3). Calcd. for $C_{21}H_{19}N_5O_4S$ (437.12): C, 57.66; H, 4.38; N, 16.01; S, 7.33. Found: C, 57.52; H, 4.49; N, 16.18; S, 7.56 %.

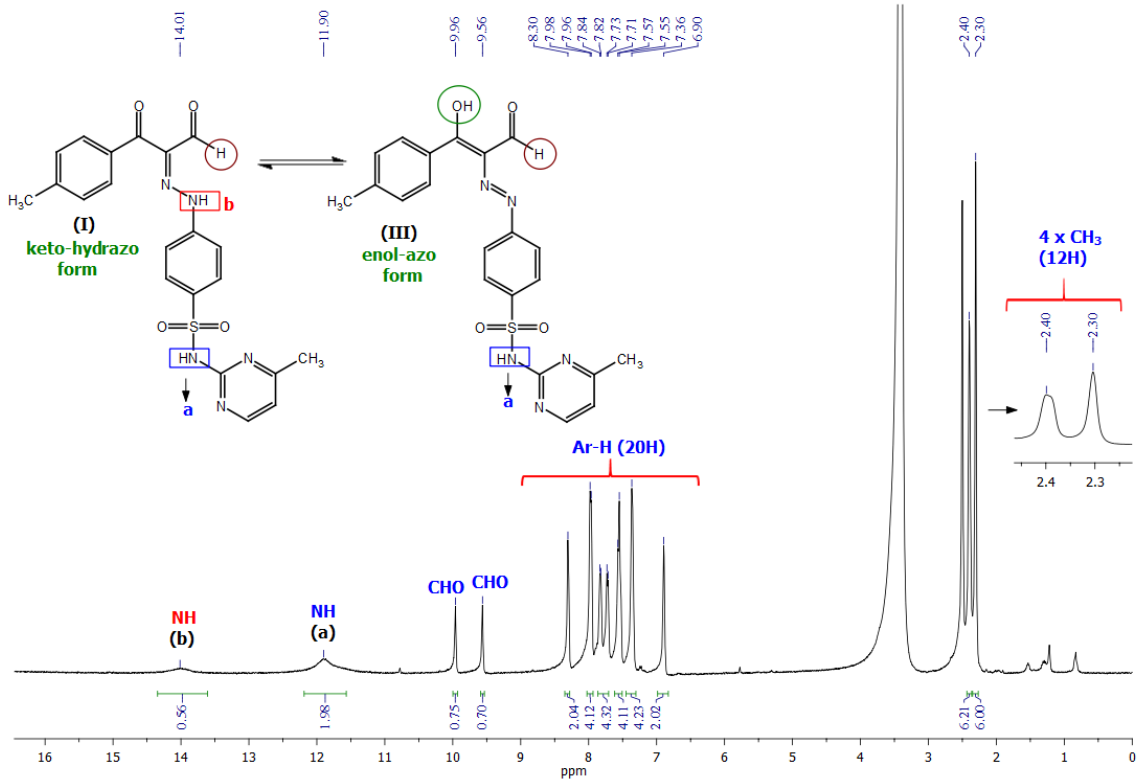

Figure S5: ^{1}H NMR spectrum of **M3**

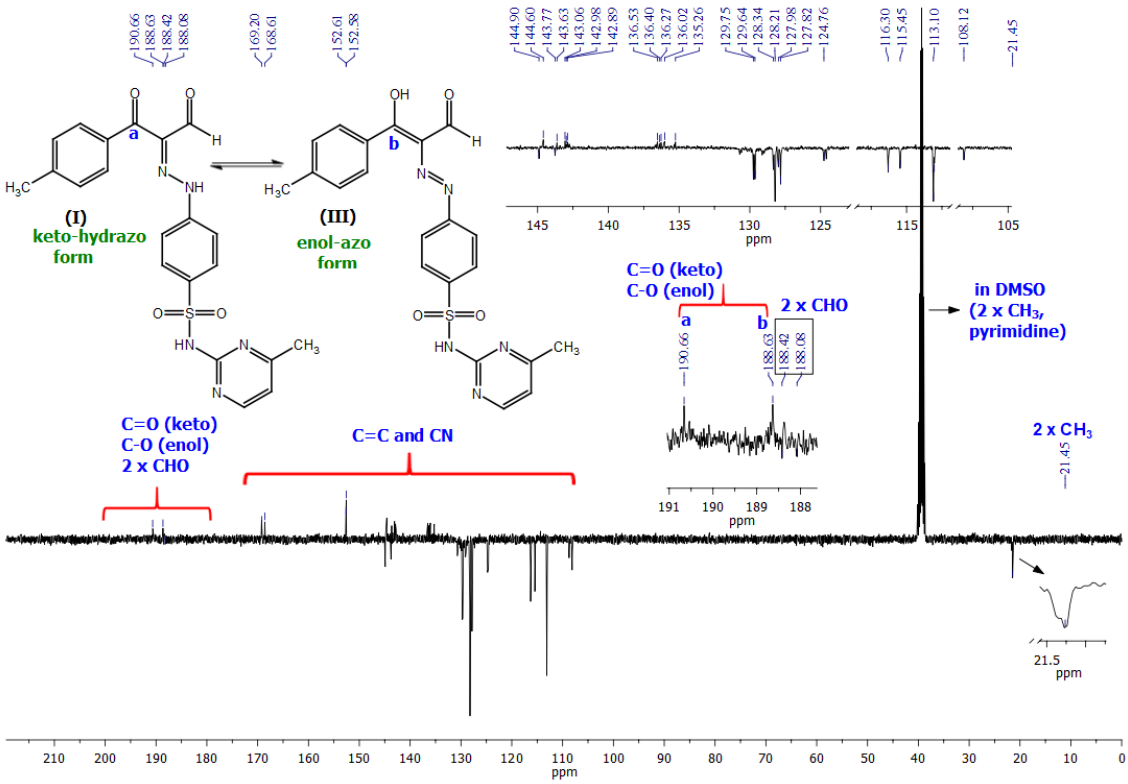

Figure S6: ^{13}C NMR spectrum of **M3**

*4-(2-(1-(4-chlorophenyl)-1,3-dioxopropan-2-ylidene) hydrazinyl) benzenesulfonamide **(M4)***

Color: Yellow, Yield 0.311 g, 85%, mp 186-188 °C, FT-IR (ATR, cm^{-1}): υ_{max} NH_2 (3366, 3255), 3101-3022 (Ar-H), 2887 (C-H, aldehyde), 1647 (C=O, aldehyde), 1630 (C=O, ketone), 1596-1486 (C=N and C=C), SO_2 (1312, 1149). ^{1}H-NMR (400 MHz; DMSO-d_6, ppm): δ 14.06 (s, NH, keto-hydrazo form); 12.13 (s, OH, enol-azo form); 9.99 and 9.57 (s, 2H, 2 x CHO); 7.94-7.58 (m, 16H, Ar-H); 7.37 and 7.32 (s, 4H, SO_2NH_2). ^{13}C-NMR (100 MHz; DMSO-d_6, ppm): δ 192.9 (C=O, ketone, keto-hydrazo form); 190.2 (C-OH, enol-azo form); 189.5 and 188.9 (2 x CHO); 145.4, 144.6, 141.0, 139.4, 138.2, 137.7, 135.8, 134.8, 133.2, 132.5, 132.5, 131.4, 131.4, 129.6, 128.7, 127.8, 117.2, 115.7 (C=C and C=N). Calcd. for $C_{15}H_{12}ClN_3O_4S$ (365.02): C, 49.25; H, 3.31; N, 11.49; S, 8.76. Found: C, 49.04; H, 3.29; N, 11.69; S, 8.61 %.

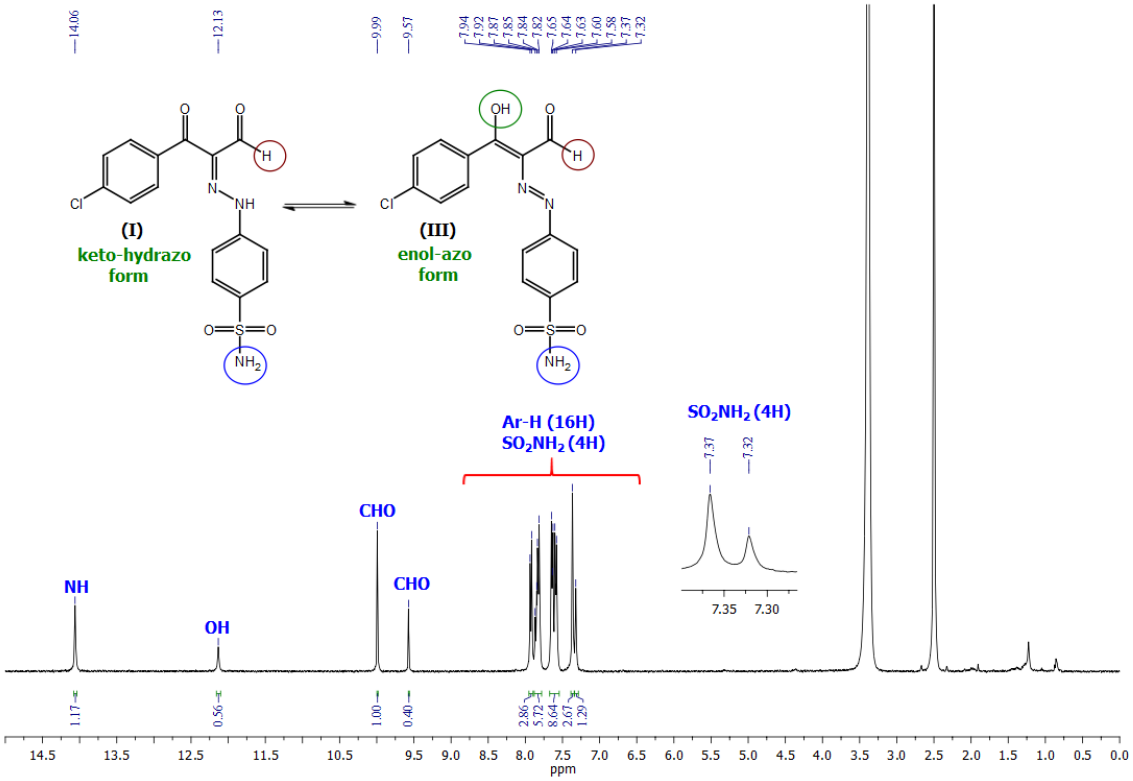

Figure S7: ^{1}H NMR spectrum of **M4**

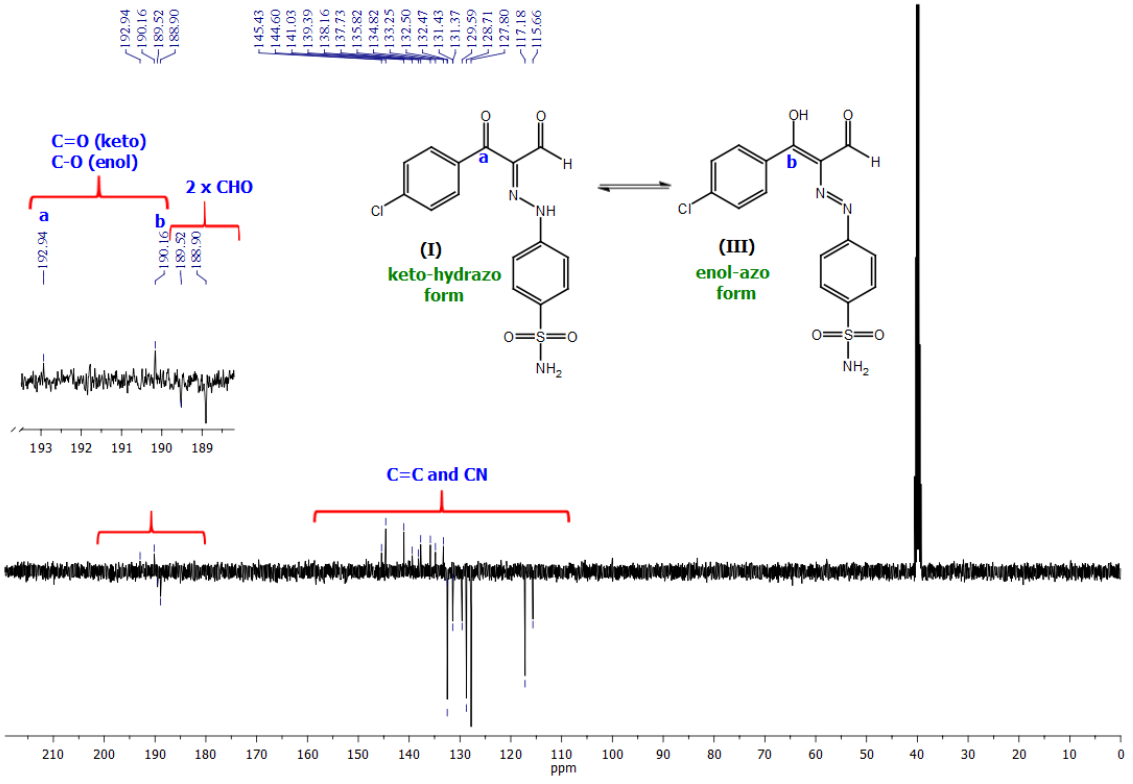

Figure S8: ^{13}C NMR spectrum of **M4**

4-(2-(1-(4-chlorophenyl)-1,3-dioxopropan-2-ylidene)hydrazinyl)-N-(pyrimidin-2-yl)benzenesulfonamide ***(M5)***

Color: Yellow, Yield 0.390 g, 88%, mp 237-239 °C, FT-IR (ATR, cm^{-1}): υ_{max} 3115 (NH), 3085-2991 (Ar-H), 2874 (C-H, aldehyde), 1659 (C=O, aldehyde), 1626 (C=O, ketone), 1579-1440 (C=N and C=C), SO_2 (1316, 1164). ^{1}H-NMR (400 MHz; DMSO-d_6, ppm): δ 14.01 (s, NH, keto-hydrazo form); 12.15 (s, OH, enol-azo form); 11.81 (s, 2 x NH, enol and keto forms); 9.99 and 9.57 (s, 2H, 2 x CHO); 8.49-7.05 (m, 22H, Ar-H). ^{13}C-NMR (100 MHz; DMSO-d_6, ppm): δ 190.4 (C=O, ketone, keto-hydrazo form); 190.3 (C-OH, enol-azo form); 189.8 and 189.0 (2 x CHO); 158.8, 157.1, 157.0, 146.3, 145.3, 140.0, 137.9, 137.9, 136.8, 135.6, 134.9, 134.6, 133.4, 132.4, 132.4, 131.6, 131.3, 130.2, 129.9, 129.6, 129.2, 128.7, 116.8, 116.2, 115.5, 112.8 (C=C and C=N). Calcd. for $C_{19}H_{14}ClN_5O_4S$ (443.04): C, 51.41; H, 3.18; N, 15.78; S, 7.22. Found: C, 51.53; H, 3.30; N, 15.54; S, 7.37 %.

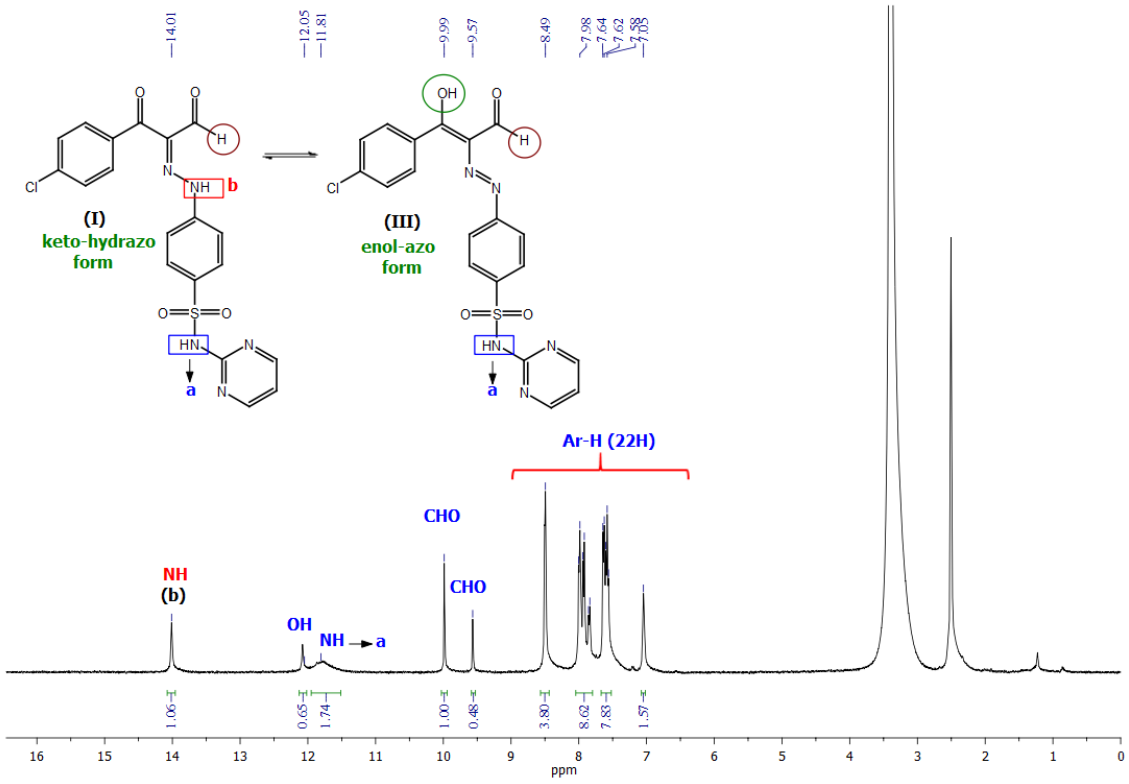

Figure S9: ^{1}H NMR spectrum of **M5**

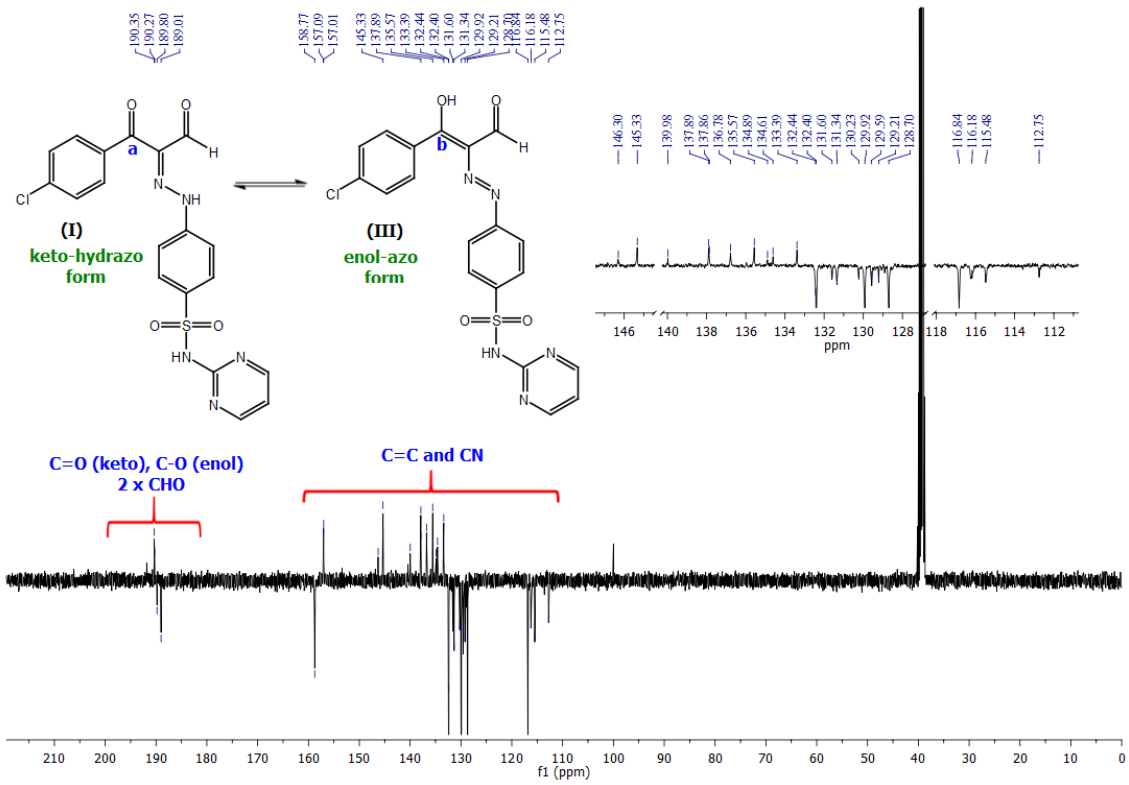

Figure S10: ^{13}C NMR spectrum of **M5**

*4-(2-(1-(4-chlorophenyl)-1,3-dioxopropan-2-ylidene)hydrazinyl)-N-(4-methylpyrimidin-2-yl)benzenesulfonamide **(M6)***

Color: Yellow, Yield 0.398 g, 87%, mp 198-200 °C, FT-IR (ATR, cm^{-1}): υ_{max} 3138 (NH), 3099-3032 (Ar-H), 2971-2947 (aliphatic CH), 2860 (C-H, aldehyde), 1651 (C=O, aldehyde), 1633 (C=O, ketone), 1588-1447 (C=N and C=C), SO_2 (1316, 1149). ^{1}H-NMR (400 MHz; DMSO-d_6, ppm): δ 14.02 (s, NH, keto-hydrazo form); 12.07 (s, OH, enol-azo form); 11.72 (s, 2 x NH, enol and keto forms); 9.98 and 9.56 (s, 2H, 2 x CHO); 8.30-7.57 (m, 20H, Ar-H); 2.31 (s, 6H, 2 x CH_3). ^{13}C-NMR (100 MHz; DMSO-d_6, ppm): δ 191.8 (C=O, ketone, keto-imine form); 190.3 (C-OH, enol-imine form); 189.7 and 189.9 (2 x CHO); 169.3, 168.6, 152.6, 145.6, 144.7, 140.0, 139.9, 138.9, 137.8, 135.7, 134.7, 133.2, 132.4, 131.4, 129.6, 129.2, 128.7, 128.2, 128.1, 127.8, 124.8, 124.6, 117.2, 115.8, 113.0, 108.1 (C=C and C=N); in DMSO-d_6 (2 x CH_3). Calcd. for $C_{20}H_{16}ClN_5O_4S$ (457.06): C, 52.46; H, 3.52; N, 15.30; S, 7.00. Found: C, 52.65; H, 3.29; N, 15.57; S, 6.84 %.

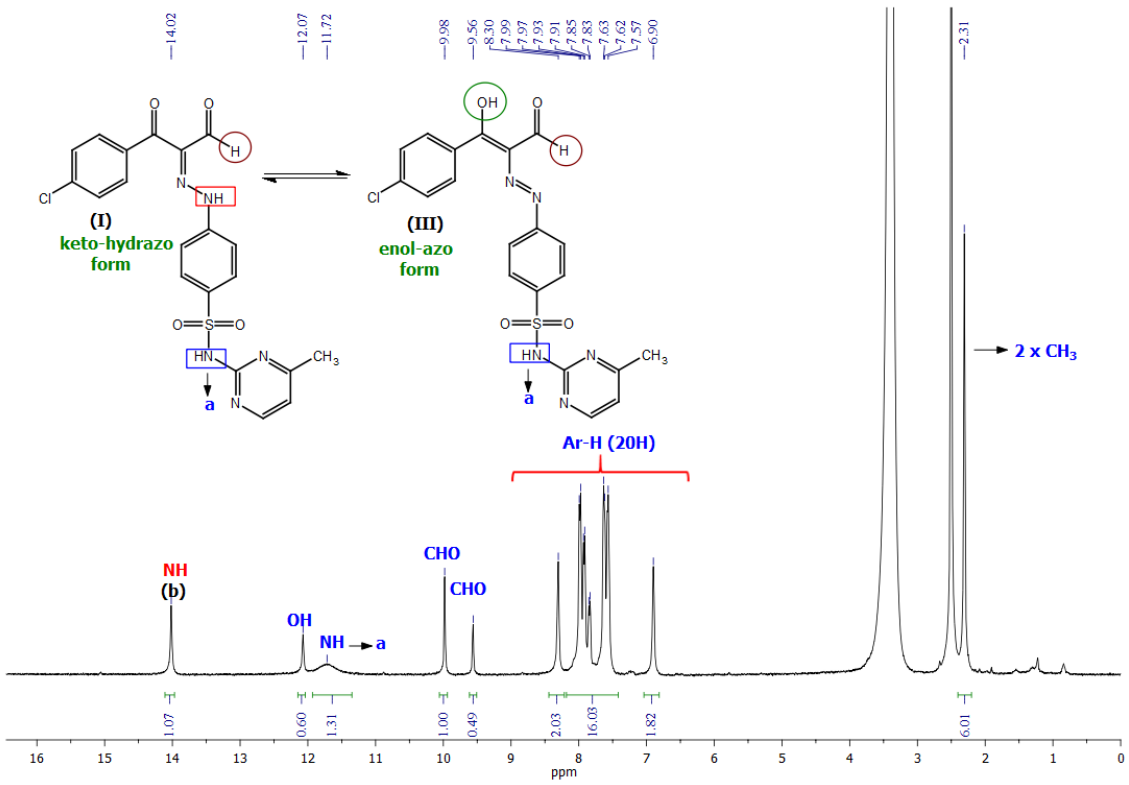

Figure S11: ^{1}H NMR spectrum of **M6**

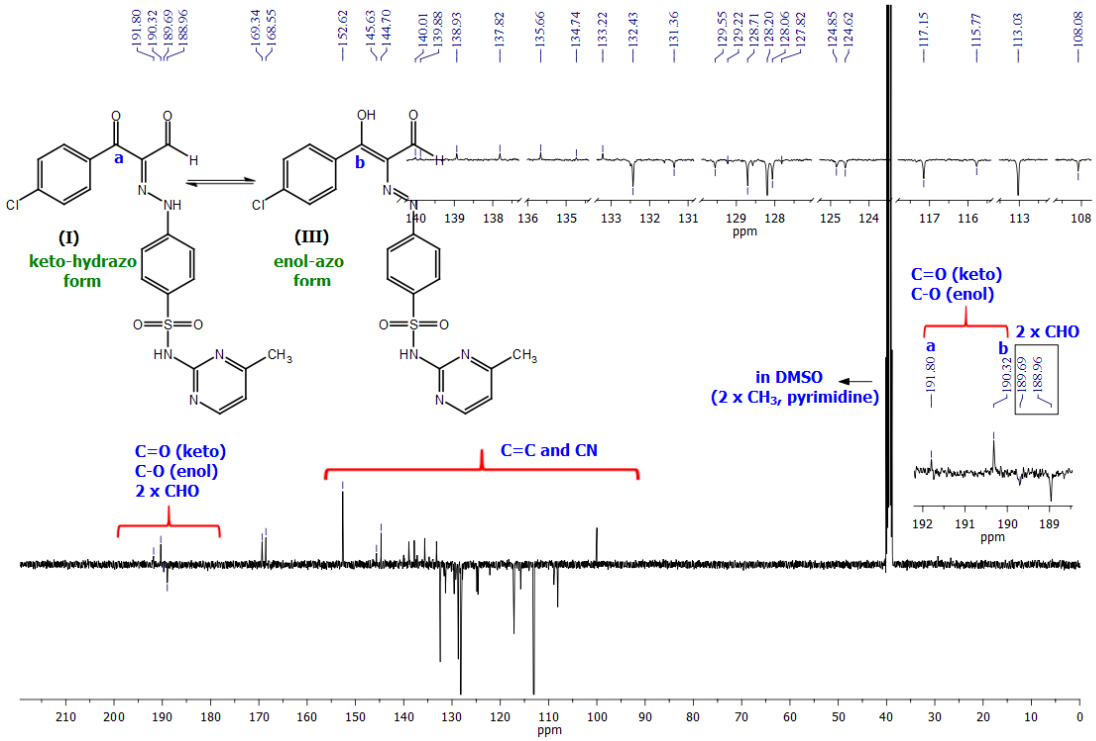

Figure S12: ^{13}C NMR spectrum of **M6**

Table S1. The experimental and computed ^{1}H and ^{13}C-NMR isotropic chemical shifts (with respect to TMS, all values are in ppm) of **M1** and **M4** compounds (forms **I** and **III**).

M1/^{13}C-form I			**M1**/^{13}C-form III			**M4**/^{13}C-form I			**M4**/^{13}C-form III		
Atoms	$\delta_{exp.}$	$\delta_{cal.}$	Atoms	$\delta_{exp.}$	$\delta_{cal.}$	Atoms	$\delta_{exp.}$	$\delta_{cal.}$	Atoms	$\delta_{exp.}$	$\delta_{cal.}$
C1		137.09	C1		136.69	C1		136.98	C1		136.43
C2		137.40	C2		137.87	C2		139.30	C2		139.42
C3		142.79	C3		135.89	C3		144.58	C3		137.60
C4		140.94	C4		144.16	C4		141.47	C4		145.06
C5		135.59	C5		135.36	C5		135.09	C5		134.93
C6		156.88	C6		157.48	C6	**141.0**	157.39	C6		158.21
C11	**145.7**	143.77	C11	**117.0**	140.46	C12		142.40	C12	**115.7**	140.66
C15	**144.8**	154.54	C14	**146.0**	163.93	C16	**144.6**	153.61	C15	**145.4**	163.85
C16	**115.4**	121.79	C15		138.58	C17	**115.7**	122.01	C16		138.62
C17	**115.4**	122.11	C16		122.14	C18	**117.2**	122.73	C17		122.11
C18		137.05	C17		135.87	C19		137.03	C18		135.69
C20		136.31	C19		135.46	C21		136.36	C20		135.50
C22		146.43	C21		151.74	C23		147.28	C22	**139.4**	152.32
C25	**189.6**	186.94	C24	**189.2**	197.08	C26	**189.5**	187.20	C25	**188.9**	198.06
C34	**192.6**	200.64	C33	**190.7**	192.24	C35	**192.9**	199.95	C34	**190.2**	190.61

M1/^{1}H- form I			**M1**/^{1}H- form III			**M4**/^{1}H- form I			**M4**/^{1}H- form III		
Atoms	$\delta_{exp.}$	$\delta_{cal.}$	Atoms	$\delta_{exp.}$	$\delta_{cal.}$	Atoms	$\delta_{exp.}$	$\delta_{cal.}$	Atoms	$\delta_{exp.}$	$\delta_{cal.}$
H7		7.86	H7		7.87	H7		7.84	H7		7.90
H8		8.45	H8		8.43	H8		8.32	H8		8.46
H9		7.93	H9		8.15	H9		7.91	H9		8.07
H10		7.65	H10		7.69	H10		7.75	H10		7.72
H14	**14.03**	10.39	H18		8.29	H15	**14.06**	10.32	H19		8.32
H19		7.71	H20		7.96	H20		7.64	H21		7.79
H21		7.29	H22		8.36	H22		7.37	H23		8.34
H23		7.96	H23		8.11	H24		7.96	H24		8.07
H24		8.14	H25	**9.97**	10.64	H25		8.12	H26	**9.99**	10.64
H26	**9.57**	10.92	H31	**7.35**	4.62	H27	**9.57**	10.90	H32	**7.37**	4.59
H32	**7.29**	3.93	H32	**7.35**	4.01	H33	**7.32**	3.92	H33	**7.37**	4.02
H33	**7.29**	4.58	H35	**11.92**	16.16	H34	**7.32**	4.55	H36	**12.13**	16.01
H37	**2.41**	2.42	H37	**2.40**	2.54						
H38	**2.41**	2.54	H38	**2.40**	2.86						
H39	**2.41**	2.86	H39	**2.40**	2.50						