19th International Electronic Conference on Synthetic Organic Chemistry
1–30 November 2015
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Substituted Quinolinones. Part 27. Synthesis of Some New [1,2]Diazolo and or [1,2,4]triazepino[*b*]or [*c*]quinoline Derivatives

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Presented by

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Quinolines and especially 2-Quinolinones represent one of the most active classes of heterocyclic compounds possising a wide spectrum of valuable biological activity.

The great importance of this category of heterocycles oriented our attention to the synthesis of a series of new heterocyclic derivatives combining both known biologically active heterocycles and quinoline in one molecular-frame

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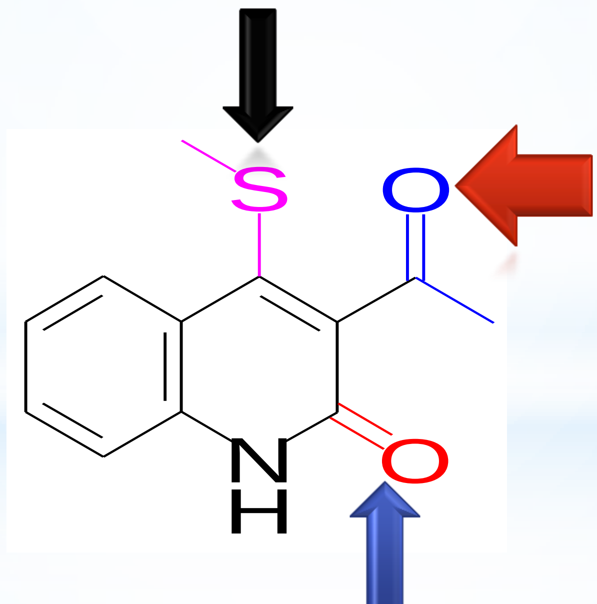
The starting material, used in this study, 3-acetyl-4-methylthioquinolin-2(1*H*)-one (1) which possesses three active centers susceptible for nucleophilic attack, *viz*.; replacement of SCH_3 group at position-4, acetyl group at position-3, and C═O at position-2.



Hassan, M. M.; Othman, E. S.; Abass, M., *Res. Chem. Intermed.* **2013**, *39*, 1209–1225

The chemical reactivity of Acetylquinolinone studied was towards

- 1,2-Dinucleophiles
- 1,4-Dinucleophiles

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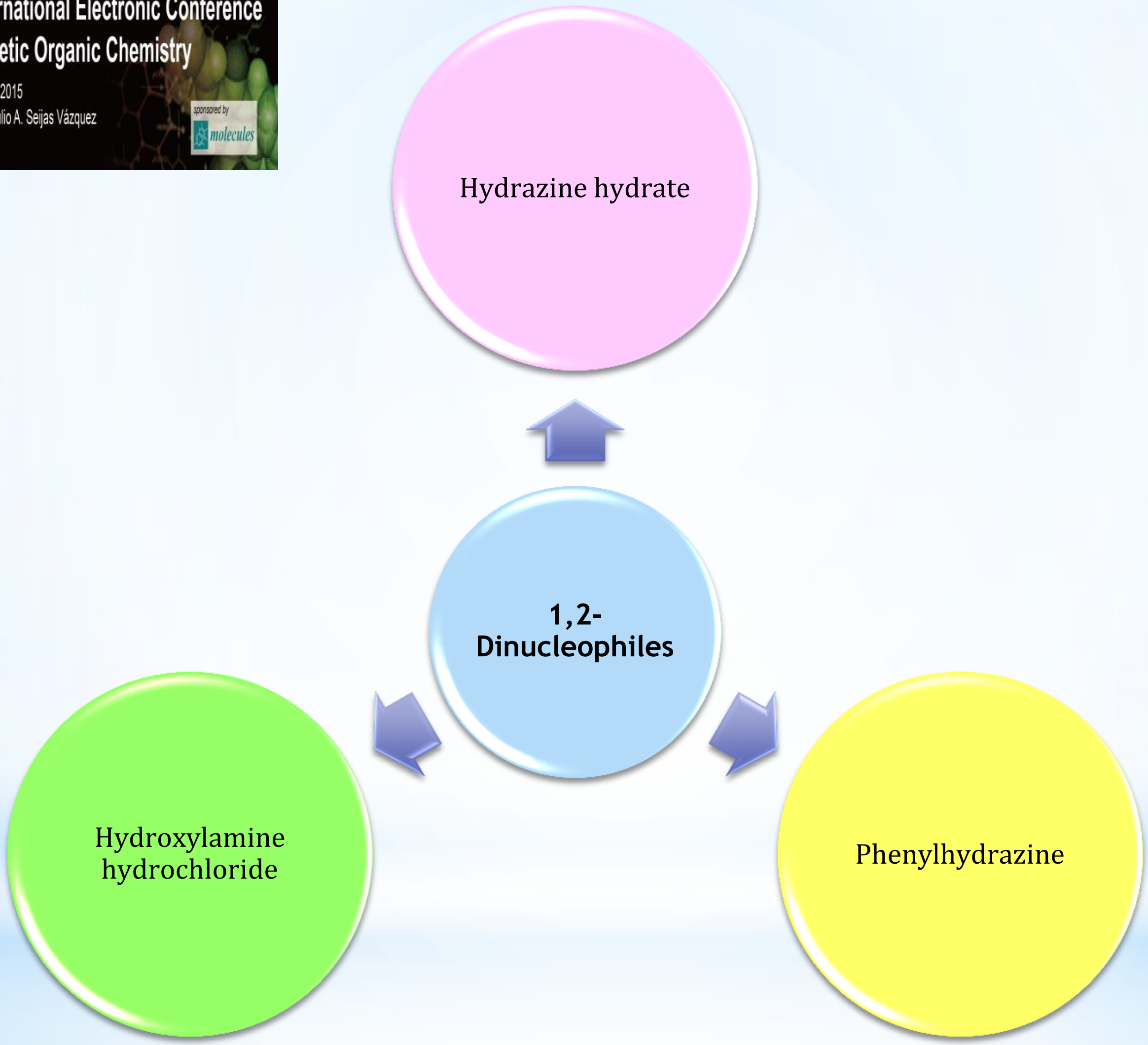
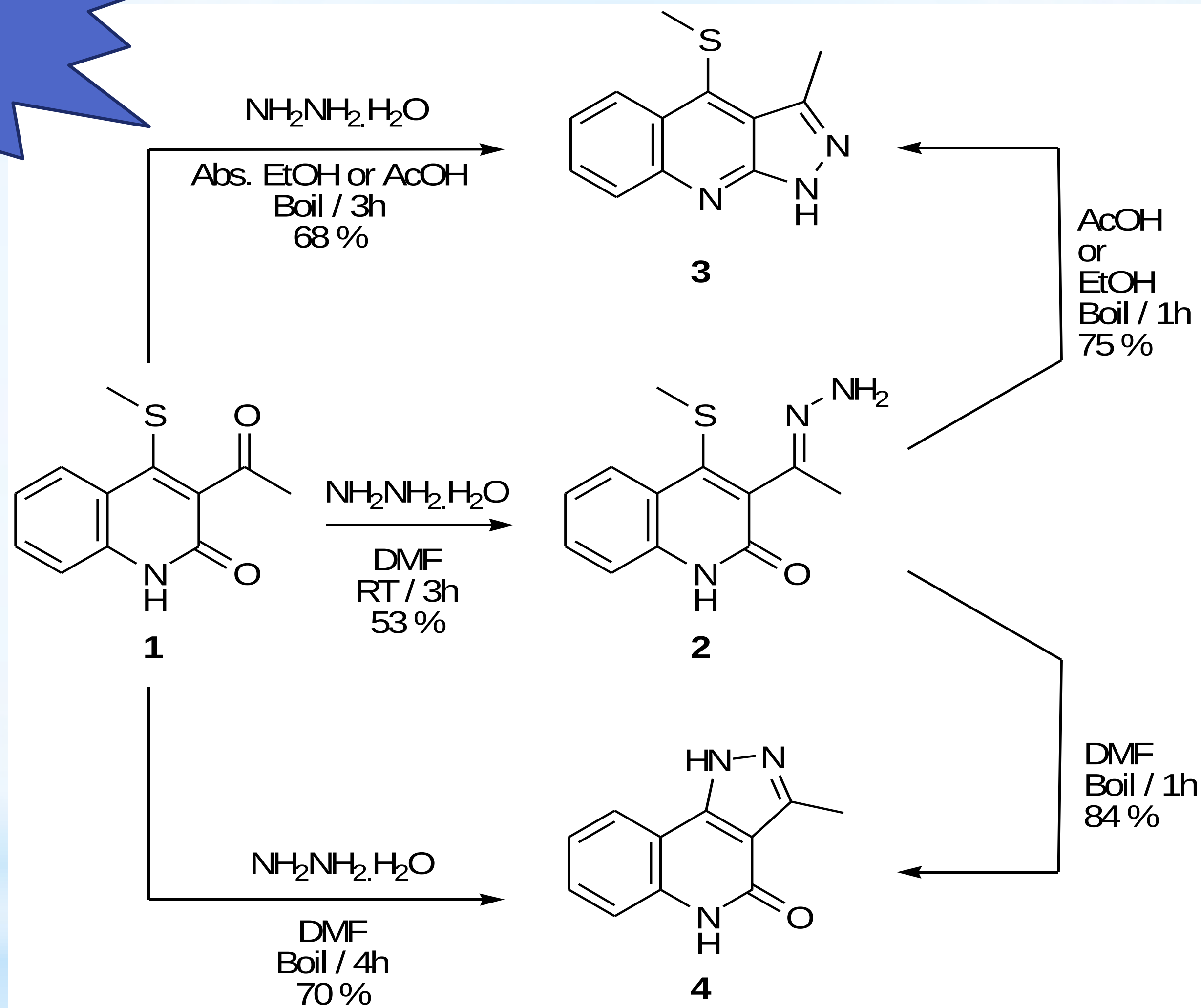
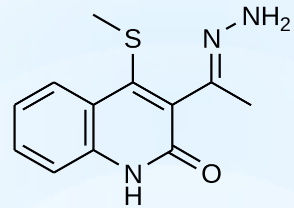
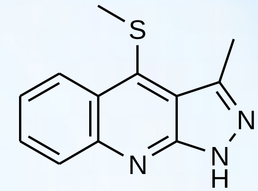


With Hydrazine hydrate

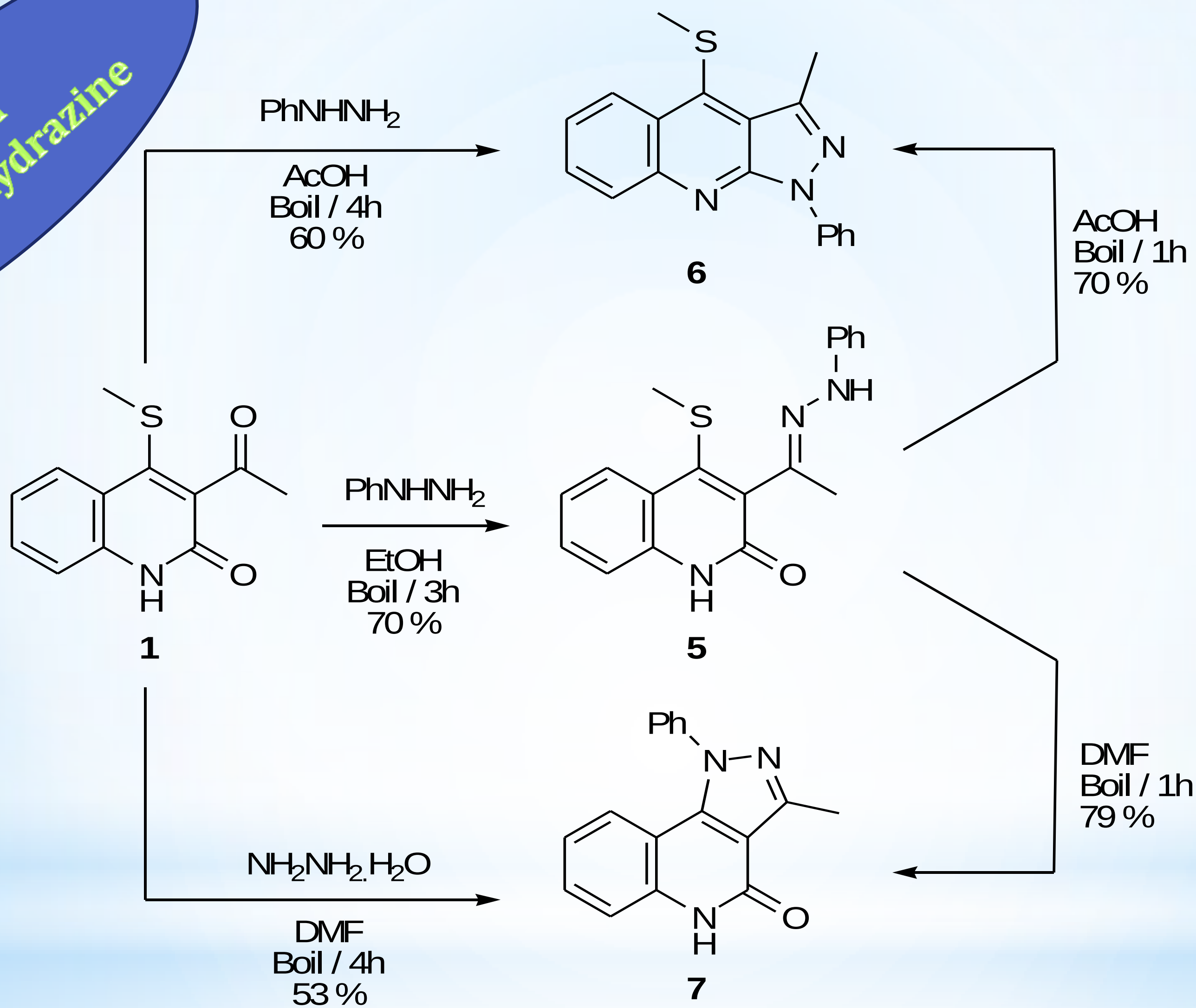


Scheme1. Reaction of acetylquinolinone **1** with hydrazine hydrate at different conditions.

Hassan, M. M.; Othman, E. S.; Abass, M., *Res. Chem. Intermed.* 2013, *39*, 1209–1225

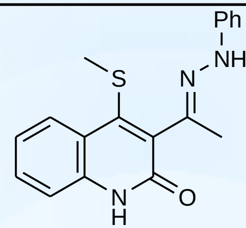
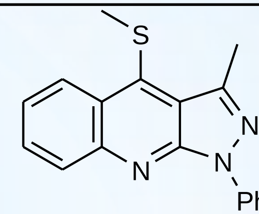
		
IR (KBr, cm^{-1}), ν_{max}	**3355 (NH_2), 3243, 3198, 3129 (N–H), 3064, 2963, 1620, 1603, 1555, 1513, 1480, 1362, 1349, 759.**	**3213, 3132 (N–H), 3027, 2919, 1629 (C=N), 1586, 1567, 1518, 1376, 1349, 1294, 763, 756**
^{1}H NMR (300 MHz, DMSO-d_6)	**2.49 (3H, s, N=C–CH_3), 2.63 (3H, s, S–CH_3), 4.50 (2H, s, NH_2 disappeared on addition of D_2O), 7.32 (1H, t, J = 6.6, 6-CH), 7.67 (2H, m, 7,8-CH), 8.07 (1H, d, J = 8.1, 5-CH), 10.80 (1H, s, N–H disappeared on addition of D_2O).**	**2.43 (s, 3H, (N=C–CH_3), 2.70 (s, 3H, S–CH_3), 7.55 (t, J = 6.6 Hz, 1H, 6-CH), 7.67 (d, J = 8.4 Hz, 1H, 8-CH), 7.94 (t, J = 8.1 Hz, 1H, 7-CH), 8.28 (d, J = 7.8 Hz, 1H, 5-CH), 13.93 (s, 1H, N–H disappeared on addition of D_2O)**
^{13}C NMR (75 MHz, DMSO-d_6), δ	V	**155.06, 144.94, 143.16, 141.17, 129.44, 128.27, 125.72, 122.35, 114.92, 114.26, 15.09, 11.90**

With phenylhydrazine

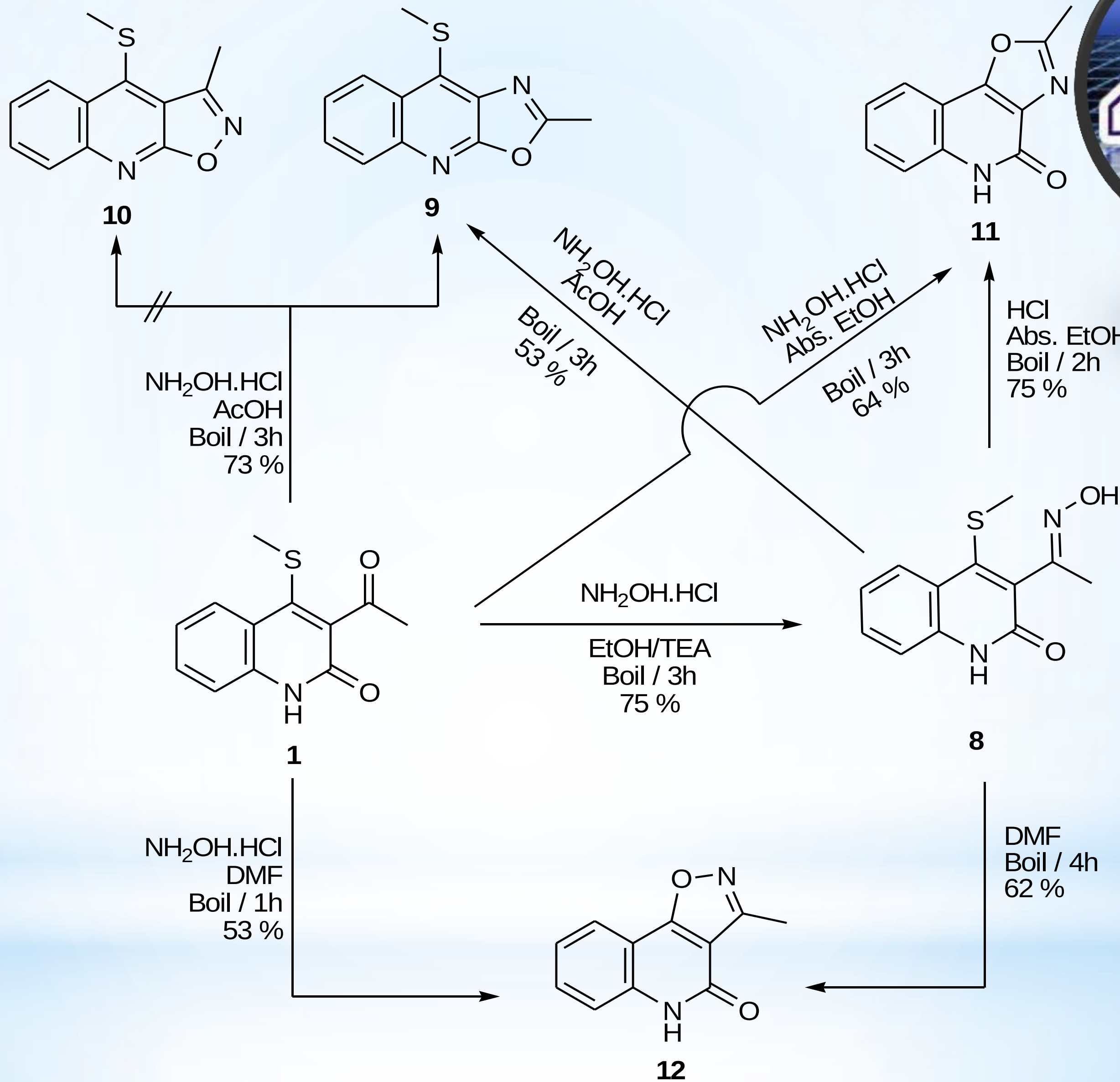


Scheme2. Reaction of acetylquinolinone **1** with phenylhydrazine at different conditions.

Stadlbauer, W.; Hojas, G. *J. Heterocycl. Chem.* **2004**, *41*, 681–690.

		
IR (KBr, cm^{-1}), ν_{max}	3620 (O–H), 3188 (N–H), 3069, 2965, 1620 (C=N), 1559, 1528, 756, 752.	3069, 2974, 1617 (C=N), 1597, 1562, 776, 749.
^{1}H NMR (300 MHz, DMSO-d_6)	2.13 (3H, s, (N=C–CH_3), 2.60 (3H, s, S–CH_3), 6.63–8.08 (9H, m, H_{arom}), 8.50 (1H, s, hydrazone N–$H_{E\text{-}form}$), 9.00 (1H, s, hydrazone N–$H_{Z\text{-}form}$), 11.04 (1H, s, quinolinone N–$H_{Z\text{-}form}$), 11.20 (1H, s, quinolinol O–$H_{E\text{-}form}$)	2.84 (3H, s, N=C–CH_3), 2.88 (3H, s, S–CH_3), 7.18 (1H, t, J = 8, 6-CH), 7.43 (1H, d, J = 8, 8-CH), 7.45–7.61 (6H, m, H_{arom} + 7-CH), 8.04 (1H, d, J = 8, 5-CH).
^{13}C NMR (75 MHz, DMSO-d_6), δ	174.49, 149.49, 146.74, 140.00, 132.09, 129.09, 128.80, 125.42, 124.00, 123.75, 122.62, 118.99, 118.28, 113.05,112.80, 112.43, 23.65, 17.23	155.20, 145.86, 143.85, 140.61, 139.75, 130.27, 129.60, 128.84, 127.65, 125.36, 121.67, 115.65, 114.84, 15.02, 12.07.

Hydroxylamine Hydrochloride

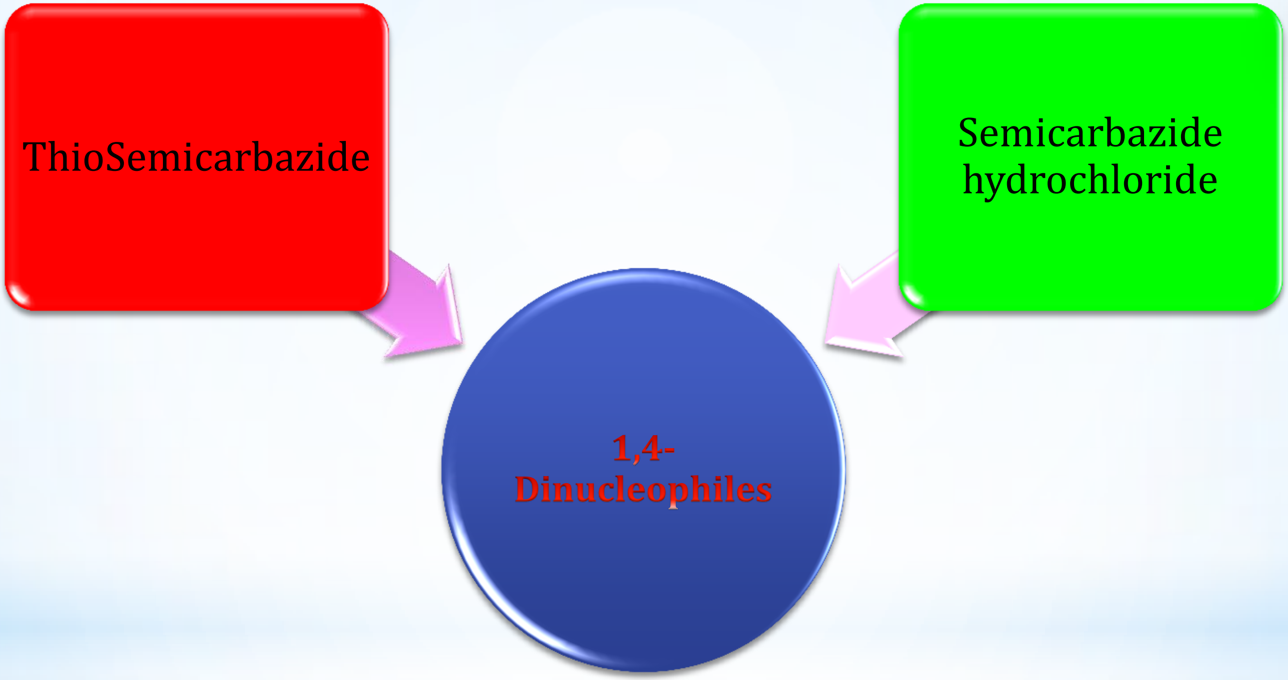


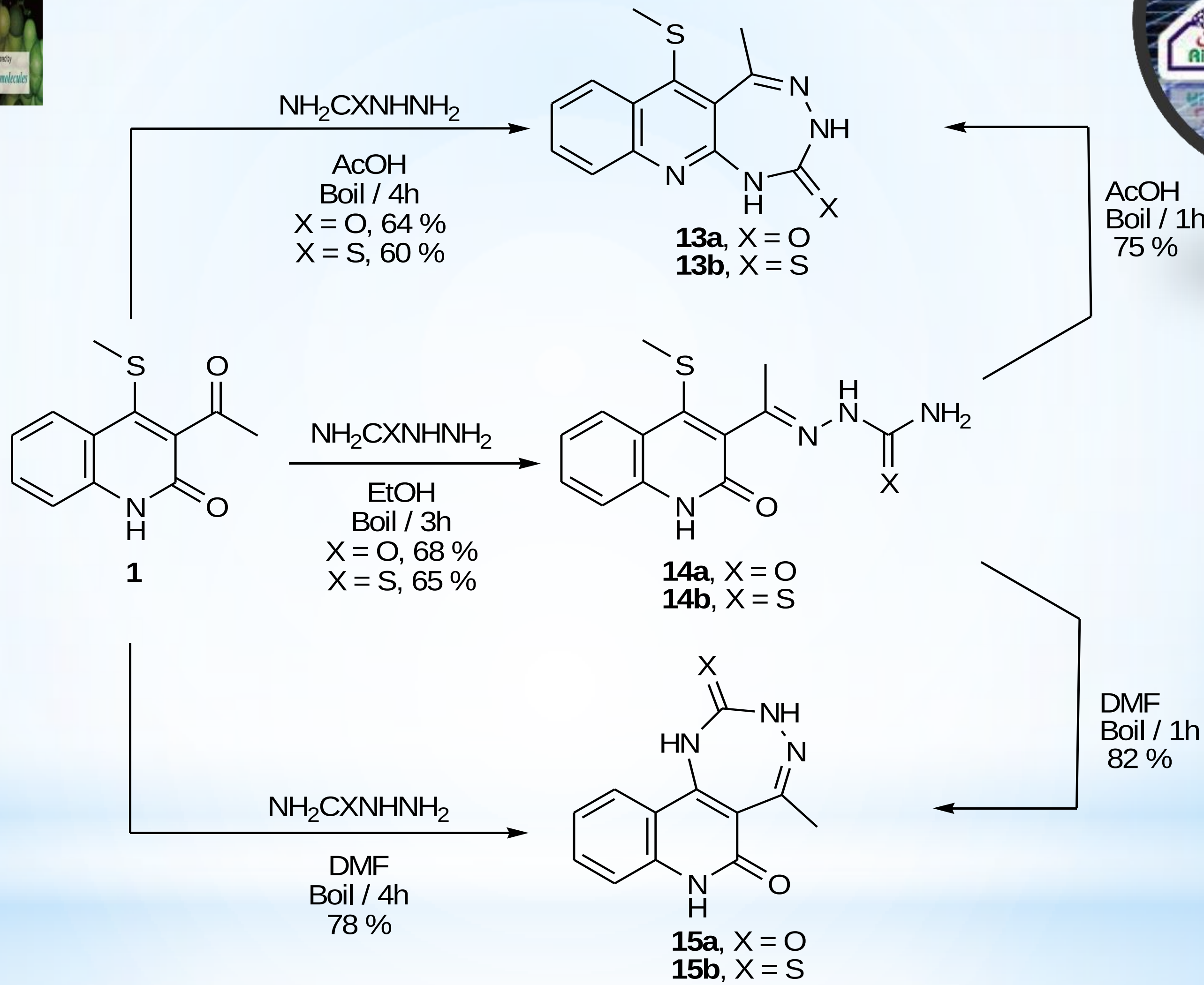
Scheme3. Reaction of acetylquinolinone **1** with hydroxylamine hydrochloride.

Hassan, M. M.; Othman, E. S.; Abass, M., *Res. Chem. Intermed.* 2013, *39*, 1209–1225

Kappe, T.; Algner, R.; Jobstl, M.; Hohengassner, P.; Stadlbauer, W. *Heterocyclic Communications* **1995**, *3*, 341–352

	 	
IR (KBr, cm^{-1}), ν_{max}	3446 (O–H), 3243 (N–H), 3061, 2957, 1625 (C=O, C=N), 1606, 1560, 1496, 1473, 758.	**3069, 2927, 1632 (C=N), 1590, 1557, 1525, 1297, 761.**
^{1}H NMR (300 MHz, DMSO-d_6)	2.08 (3H, s, N=C–CH_3), 2.50 (3H, s, S–CH_3), 7.32 (1H, t, J = 7.2, 6-CH), 7.65 (2H, m, 7,8-CH), 8.03(1H, d, J = 7.8 Hz, 5-CH), 10.87 (1H, s, N–H disappeared on addition of D_2O), 11.20 (1H, s, O–H disappeared on addition of D_2O).	**2.48 (3H, s, N=C–CH_3), 2.50 (3H, s, S–CH_3), 7.61 (1H, t, J = 6.9, 6-CH), 7.83 (1H, t, J = 7.2, 7-CH), 7.97 (1H, d, J = 6 Hz, 8-CH), 8.21 (1H, d, J = 8.4, 5-CH).**
^{13}C NMR (75 MHz, DMSO-d_6), δ	174.00, 152.77, 149.32, 140.74, 132.27, 125.53, 124.57, 123.90, 120.03, 118.31, 16.12, 15.20.	**174.00, 153.00, 149.00, 141.00, 132.00, 125.00, 124.00, 123.00, 120.00, 118.00, 16.00, 15.00.**


ThioSemicarbazide
Semicarbazide hydrochloride
1,4-Dinucleophiles



Scheme4. Reaction of acetylquinolinone **1** with semicarbazide derivatives at different conditions.

	 **13a**, X = O **13b**, X = S	 **14a**, X = O **14b**, X = S
IR (KBr, cm^{-1}), ν_{max}	X=O 3277 (NH_2), 3217, 3143 (N–H), 3058, 2927, 1650 (C=O), 1620 (C=N), 1609, 1567, 1532, 1489, 1380, 1297, 758. X=S 3277 (NH_2), 3217, 3143 (N–H), 3070, 2930, 1654 (C=O), 1619 (C=N), 1566, 1540, 1489, 1340, 758.	**X=O** **3248, 3135 (N–H), 3061, 2985, 1647 (C=O), 1620 ($C=N_{triazepine}$), 1603, 1560, 1510, 1474, 1344, 758.** **X=S** **3316, 3200 (N–H), 3026, 2961, 1622 ($C=N_{triazepine}$), 1592, 1498, 1472, 723.**
^1H NMR (300 MHz, DMSO-d_6)	X=O 2.50 (3H, s, N=C–CH_3), 2.70 (3H, s, S–CH_3), 4.48 (2H, s, NH_2 disappeared on addition of D_2O), 7.39 (1H, t, J = 8.1, 6-CH), 7.70 (1H, t, J = 7.2, 7-CH), 7.78 (1H, d, J = 8.4, 8-CH), 8.13 (1H, d, J = 7.8, 5-CH), 8.62 (1H, s, N–H disappeared on addition of D_2O), 10.86 (s, 1H, N–$H_{quinolinone}$ disappeared on addition of D_2O). X=S 2.20 (3H, s, N=C–CH_3), 2.67 (3H, s, S–CH_3), 4.50 (2H, s, NH_2 disappeared on addition of D_2O), 7.40 (1H, t, J = 8.1, 6-CH), 7.71 (1H, t, J = 7.2, 7-CH), 7.80 (1H, d, J = 8.4, 8-CH), 8.13 (1H, d, J = 7.8, 5-CH), 10.30 (1H, s, N–H disappeared on addition of D_2O), 10.86 (1H, s, N–$H_{quinolinone}$ disappeared on addition of D_2O)	**X=O** **2.48 (3H, s, N=C–CH_3), 2.67 (3H, s, S–CH_3), 7.37 (1H, t, J = 7.8, 9-CH), 7.65 (1H, t, J = 8.1, 8-CH), 7.79 (1H, d, J = 8.4, 7-CH), 8.11 (1H, d, J = 8.1, 10-CH), 9.79 (1H, s, N–H disappeared on addition of D_2O), 13.00 (1H, s, N–$H_{quinolinone}$ disappeared on addition of D_2O).** **X=S** **2.14 (3H, s, N=C–CH_3), 2.69 (3H, s, S–CH_3), 7.63 (1H, t, J = 8.1, 9-CH), 7.70 (2H, m, 7,8-CH), 8.07 (1H, d, J = 7.8, 10-CH), 9.66 (1H, s, N–H disappeared on addition of D_2O), 11.97 (1H, s, N–$H_{quinolinone}$ disappeared on addition of D_2O)**
^{13}C NMR (75 MHz, DMSO-d_6), δ	X=O 198.00, 178.00, 156.00, 139.00, 132.00, 131.00, 125.00, 124.00, 123.00, 119.00, 118.00, 31.00, 14.00. X=S 199.17, 179.00, 175.00, 156.70, 150.00, 139.97, 132.86, 125.62, 124.88, 120.08, 118.76, 32.04, 16.23.	**X=S** **178.55, 172.48, 149.53, 147.85, 146.58, 141.26, 132.35, 125.39, 124.87, 118.39, 116.82, 21.51, 16.16.**


Thank You