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# Electronic supplementary information

## Amine functionalized MCM-41: an efficient heterogeneous recyclable catalyst for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones from carbon dioxide and 2-aminobenzonitriles in water

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# 1. Experimental section

## 1.1 *Materials*

All chemicals were procured from firms of repute. Cetyltrimethyl ammonium bromide (CTAB), tetraethyl *ortho*-silicate (TEOS), sodium hydroxide (NaOH), 3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane (AEPTMS), methanol, and absolute ethanol were all purchased from Sigma-Aldrich Ltd., India. $CO_2$ was acquired from Rakhangi Gases Ltd., Mumbai, India with a purity of 99.99 %. Various substrates of 2-aminobenzonitrile were procured from Sigma-Aldrich (purity >99%). All other chemicals or solvents were purchased from S. D. Fine Chem. Ltd. India and used without any further purification/pre-treatment. IR spectra were recorded on FT-IR Perkin Elmer using KBr. Products were isolated and identified by comparison of their $^{1}$H NMR and $^{13}$C NMR signals with literature data recorded on Varian-400 and 100 MHz NMR spectrometer using TMS as an internal standard. All chemicals were procured from firms of repute. The various amine functionalized MCM-41 catalysts were prepared according to the procedure reported in previous literature with some modification.[1]

## 1.2 *General procedure for preparation of amine functionalized MCM-41 catalysts*

The mixture of CTAB (0.5 g, 5.49 mmol), $H_2O$ (480 g, 26.67 mmol), and 2 M of NaOH (aqueous) (7 mL, 14 mmol) were heated at 80 °C for 30 min. at 12.4 pH. In this clear solution, TEOS (9.34 g, 44.8 mmol) and AEPTMS (1.5 mL) were added sequentially and promptly. After the addition, a white precipitation was observed after 3 minute of stirring. The reaction temperature was sustained at 80 °C for 2 hours. The products were isolated by a hot filtration, washed with sufficient amount of water followed by methanol and dried under reduced pressure. For acid extraction, obtained materials were treated with a mixture of ethanol (100 mL) and concentrated HCl (1 mL) at 80 °C for 6 hours with vigorous stirring. The resulting (surfactant removed) solid products were filtered and washed with ethanol, and then dried under vacuum at 60 °C. We have prepared the various modified MCM-41 catalysts by varying the loading of

amine from 2.8 wt % to 14.6 wt % on MCM-41. The modified samples were designated as 2.8 wt %, 4.2 wt %, 10.2 wt %, 12.8 wt % and 14.6 wt %, respectively.

### 1.3 *Characterization of amine functionalized MCM-41 catalysts*

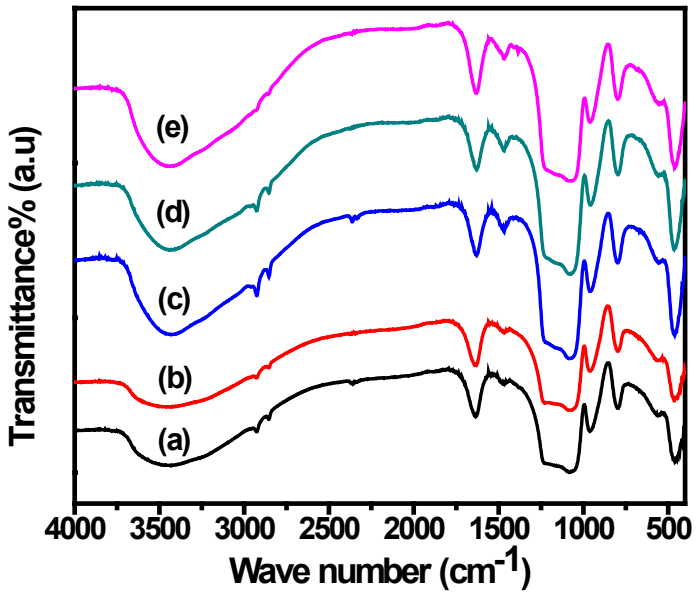
The powder X-ray patterns of the dried amine functionalized MCM-41 samples were signified that the mesoporous structure with stronger intensity band recorded on a Rigaku D/Max III VC diffractometer with Cu Kα radiation at 40 kV and 40 mA in the range of 2θ = 5–80°. The Fourier Transfer Infra red spectroscopy (FT-IR) analysis of amine functionalized MCM-41 were recorded on Varian FT-IR 800 (with anhydrous KBr as standard in the range of 1700–1000 $cm^{-1}$) to the study of successful embedded of organic amines onto the surface of catalysts. Thermal gravimetric analysis (TG/DTA) was carried out in nitrogen atmosphere using a NETZSCH thermal analyser in the temperature range 30–1000 °C at heating rate of 10 °C $min^{-1}$. The TEM analysis of MCM-41 demonstrated the mesoporosity of the catalyst. The SEM measurements were carried out using a JEOL JSM-6100 microscope. The images were taken with an emission current = 100 μA by a Tungsten (W) filament and an accelerator voltage = 12 kV. The catalysts were secured onto brass stubs with carbon conductive tape, sputter coated with gold and viewed in JEOL JSM-6100 microscope. TEM study exhibits that the mesoporosity of particles for amine modified MCM-41 are well porous and spherical in nature. The transmission electron micrograph of AEPTMS@MCM-41 sample was recorded using a TECNAI-G2 microscope with a CCD camera. The solid state $^{29}$Si CP MAS (Cross polarization and magic-angle spinning) NMR spectra were recorded at 79.49 MHz applying 90° pulses, 300 s pulse delays and 5.0 ms contact time and the NMR spectra were obtained by using a Bruker Avance spectrometer.

### 1.4 *Typical procedure for the synthesis of quinazoline-2,4(1H,3H)-diones from $CO_2$ and 2-aminobenzonitriles*

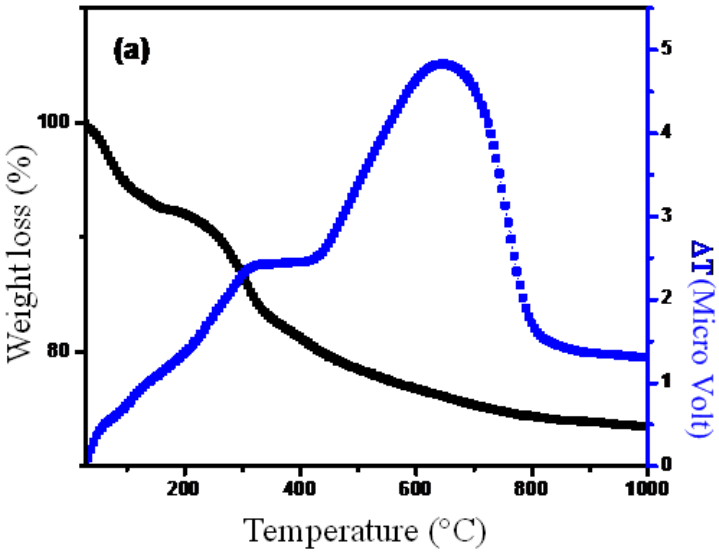
The quinazoline-2,4(1H,3H)-dione was synthesized by coupling reaction of $CO_2$ with 2-aminobenzonitrile in water using amine functionalized MCM-41 as catalyst. The experiments were carried out in a 100 mL stainless steel autoclave, which was similar to that used

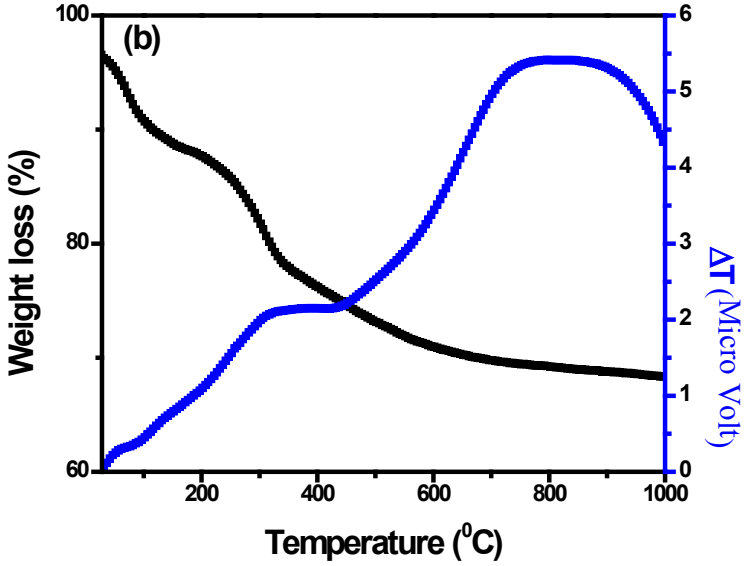
previously.[2] In a typical reaction procedure, the catalyst was introduced into a reactor containing 2-aminobenzonitrile (2 mmol) and 5 mL water at room temperature and then pressurized to 3.5 MPa of $CO_2$ pressure and heated to a specified temperature. Once the reaction was completed, the autoclave was cooled to room temperature and then the excess $CO_2$ was released slowly. The reaction mixture was poured in to the 20 mL water. After centrifugation to remove aqueous layer, the mixture of catalyst and products washed out with absolute ethanol followed by t-BuOMe (10 × 2 mL). Then above mixture was taken in 10 mL dimethylformamide for separation of product and catalyst by simple filtration through Buckner funnel. The dimethylformamide was evolved through distillation and the solid residue obtained as pure product. The isolated products (**2a**–**l**) were confirmed by IR, $^{1}$H NMR, and $^{13}$C NMR (Varian 400 MHz, 100 MHz) spectra recorded on NMR spectrometer using TMS as internal standard. Chemical shifts ($\delta$) were reported in parts per million (ppm) and referenced to the residual solvent peaks.

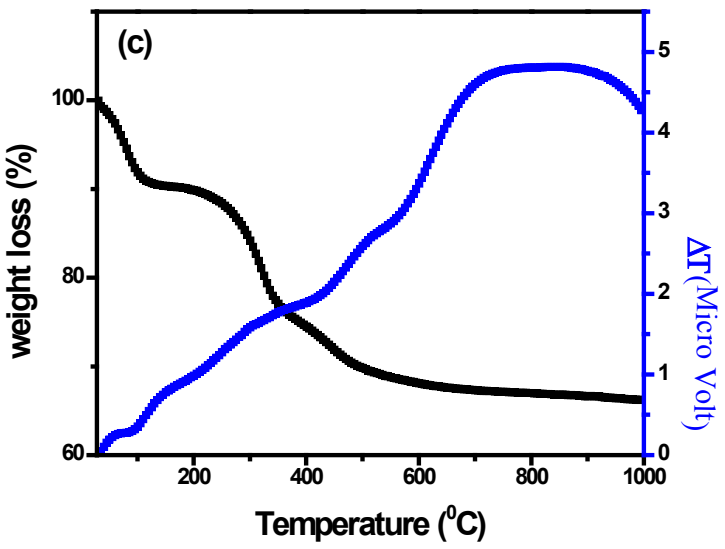
**2. FT-IR analysis of (a) 2.8 wt% AEPTMS@MCM-41, (b) 4.2 wt% AEPTMS@MCM-41, (c) 10.2 wt% AEPTMS@MCM-41, (d) 12.8 wt% AEPTMS@MCM-41, (e) 14.6 wt% AEPTMS@MCM-41 catalysts** *(Fig. S1)*



3. **TG/DTA analysis of (a) 2.8 wt% AEPTMS@MCM-41, (b) 4.2 wt% AEPTMS@MCM-41, (c) 10.2 wt% AEPTMS@MCM-41, (d) 12.8 wt% AEPTMS@MCM-41, (e) 14.6 wt% AEPTMS@MCM-41 catalysts** *(Fig. S2)*

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200
400
600
800
1000
Temperature ($^0$C)
ΔT(Micro Volt)
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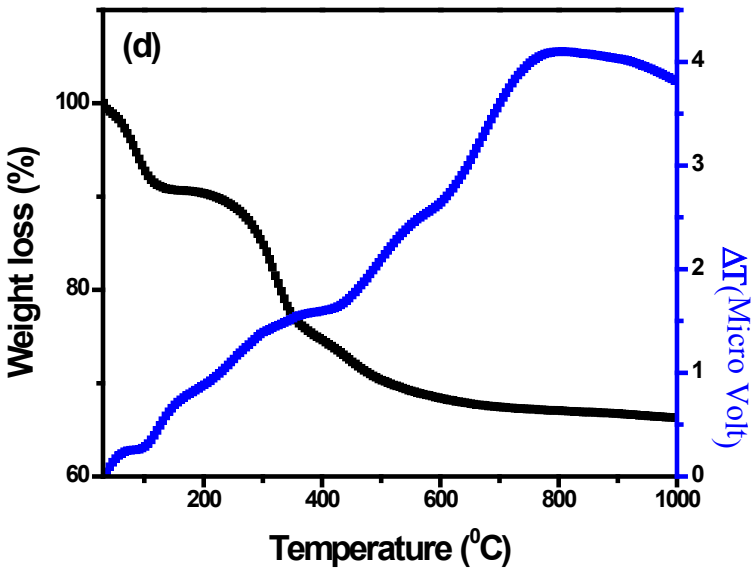
2
3
4
5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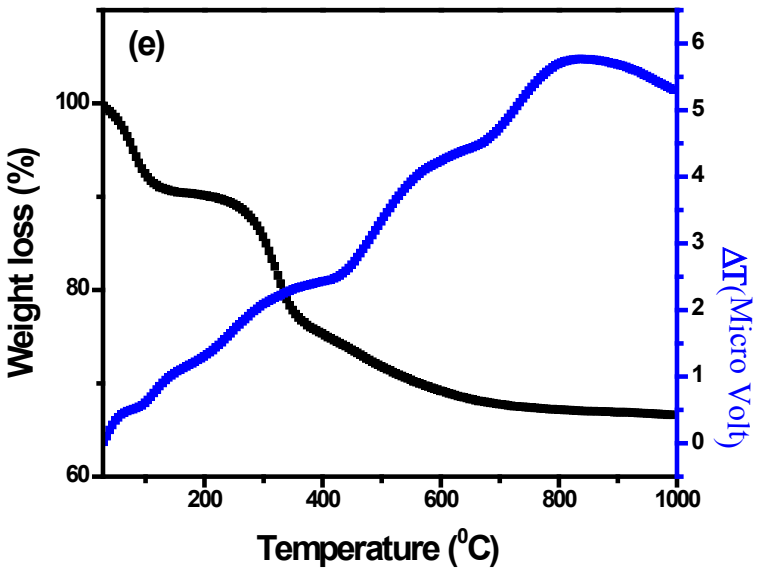
(e)
Weight loss (%)
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200
400
600
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1000
Temperature ($^0$C)
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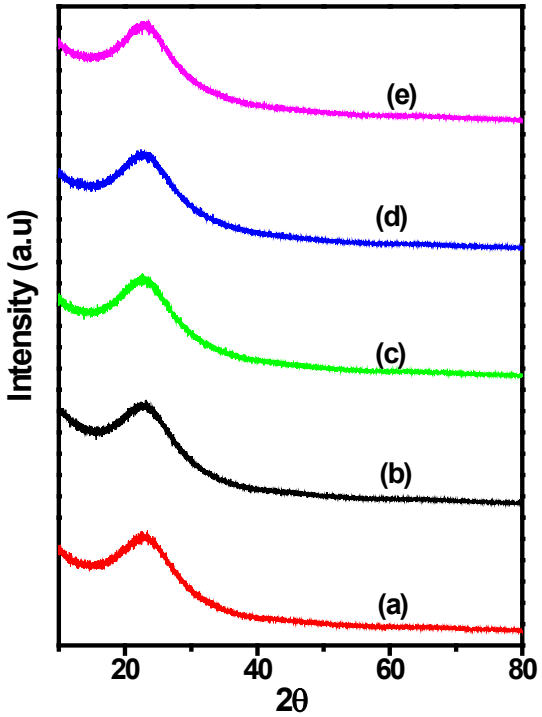
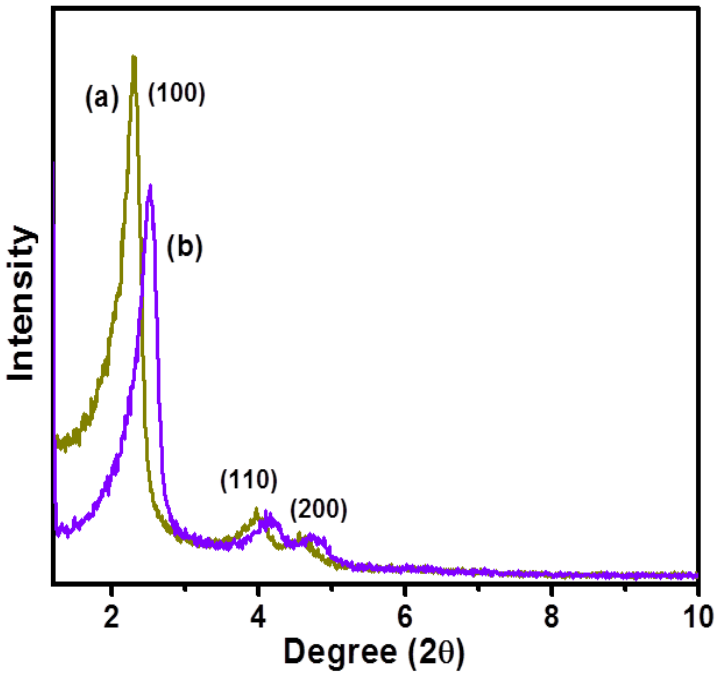
5
4
3
2
1
0
ΔT(Micro Volt)

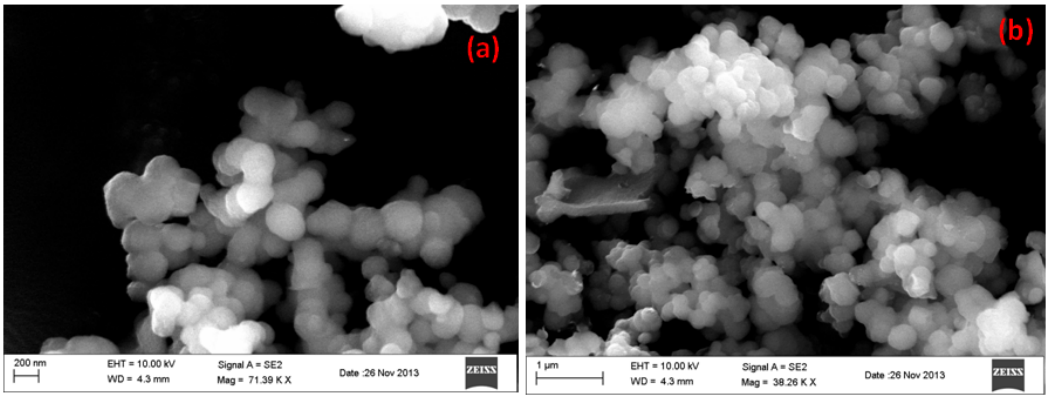
4. **High angle X-Ray diffraction analysis of (a) 2.8 wt% AEPTMS@MCM-41, (b) 4.2 wt% AEPTMS@MCM-41, (c) 10.2 wt% AEPTMS@MCM-41, (d) 12.8 wt% AEPTMS@MCM-41, (e) 14.6 wt% AEPTMS@MCM-41 catalysts** *(Fig. S3A)*



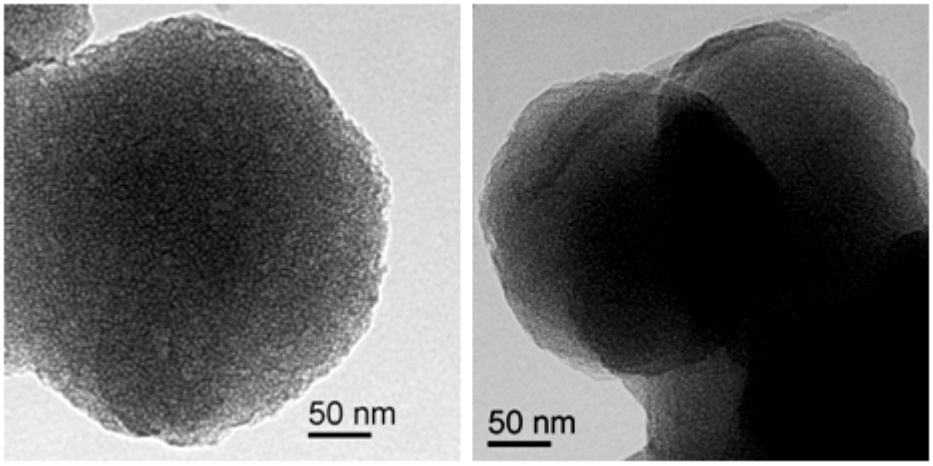

**Small angle X-Ray diffraction analysis of MCM-41 (a) and 14.6 wt% AEPTMS@MCM-41 (b) catalysts** *(Fig. S3B)*



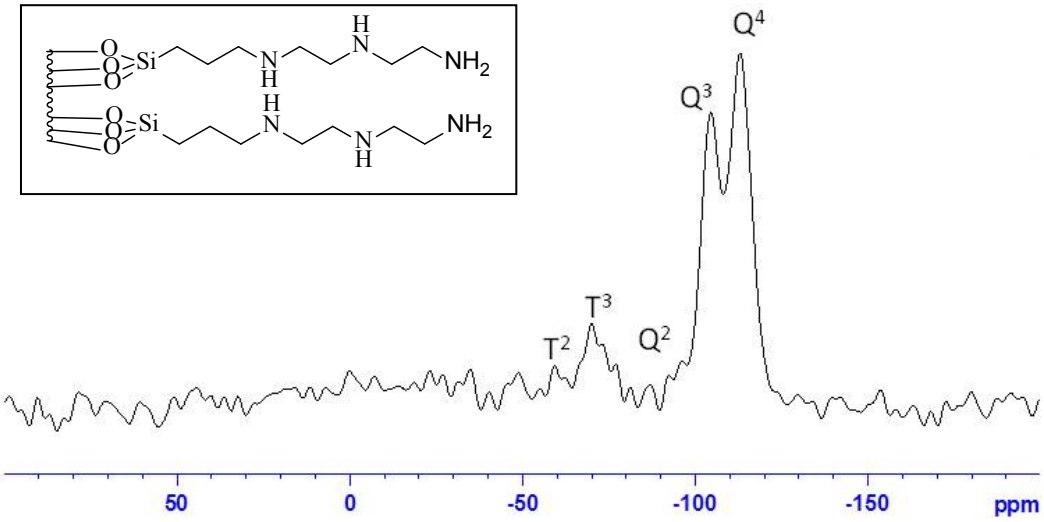
**5. SEM image of different magnification of 14.6 wt% AEPTMS@MCM-41 catalyst** *(Fig. S4)*




**6. TEM of 14.6% wt AEPTMS@MCM-41 catalyst** *(Fig. S5)*



## 7. Solid state $^{29}$Si NMR of 14.6 wt % AEPTMS@MCM-41 (*Fig. S6*)



## 8. Spectroscopic data of some selected compounds

*i. Quinazoline-2,4(1H,3H)-dione (**2a**)(Table 3, entry 1):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.15 (s, 1H), 11.29 (s, 1H), 7.89 (d, J= 7.6 Hz, 1H), 7.66–7.62 (m, 1H), 7.20–7.16 (m, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 162.79, 150.25, 140.82, 134.92, 126.91, 122.28, 115.27, 114.29 ppm. MS: *m/z* = 162 ($M^+$), 119, 92, 64, 44. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3167, 3055, 2848, 1702, 1672, 1617, 1444, 1300, 1142, 1039, 859, 756, 684, 491.

*ii. 6,7-Dimethoxyquinazoline-2,4(1H,3H)-dione (**2b**)(Table 3, entry 2):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS); $\delta$ = 11.09 (s, 2H), 7.26 (s, 1H), 6.68 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 162.39, 154.86, 150.37, 144.98, 136.51, 107.10, 106.14, 97.73, 55.77, 55.66 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3467, 3168, 3026, 2832, 1707, 1657, 1626, 1511, 1426, 1265, 1100.

*iii. 6-Chloroquinazoline-2,4(1H,3H)-dione (**2c**)(Table 3, entry 3):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.41–11.38 (s, 1H), 11.48 (s, 1H), 7.81 (d, $J$ = 2.4 Hz, 1H), 7.68 (dd, $J$ = 8.8, 2.4 Hz, 1H), 7.19 (d, $J$ = 8.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 162.78, 150.22, 138.66, 135.90, 131.48, 126.42, 115.23, 114.11 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3200, 3060, 2845, 1728, 1700, 1446, 1294, 832, 752, 502.

*iv. 6-Fluoroquinazoline-2,4(1H,3H)-dione (**2d**)(Table 3, entry 4):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.20 (s, 1H), 11.08 (s, 1H), 7.77 (d, $J$ = 8 Hz, 1H), 7.00 (d, $J$ = 8 Hz, 1H), 6.95 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 162.66, 150.41, 145.55, 140.89, 126.86, 123.61, 115.01, 112.00 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3218, 3062, 2800, 1709, 1674, 1629, 1425, 1288, 1033, 818, 561.

v. *6-Bromoquinazoline-2,4(1H,3H)-dione (**2e**)(Table 3, entry 5):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.46 (s, 1H), 11.29 (s, 1H), 7.94 (d, $J$ = 2 Hz, 1H), 7.80 (dd, $J$ = 8.4, 2 Hz, 1H), 7.12 (d, $J$ = 8.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 161.69, 150.00, 140.04, 137.48, 128.88, 117.74, 116.17, 113.79 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3198, 3067, 2828, 1701, 1615, 1483, 1435, 1288, 1144, 838, 751, 511.

vi. *7-Chloroquinazoline-2,4(1H,3H)-dione (**2f**)(Table 3, entry 6):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.40–11.31 (s, 2H), 7.88 (d, $J$ = 8.4 Hz, 1H), 7.22–7.17 (m, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 162.09, 150.23, 142.10, 139.21, 128.98, 122.36, 114.72, 113.30 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3306, 3052, 2840, 1741, 1684, 1618, 1430, 1286, 1082, 864, 793.

vii. *7-Methylquinazoline-2,4(1H,3H)-dione (**2g**)(Table 3, entry 7):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.17–11.03 (s, 2H), 7.77 (s, 1H), 7.41–7.23 (m, 2H), 2.30 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 169.06, 151.22, 134.56, 128.16, 127.02, 124.67, 118.39, 113.33, 25.09 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3429, 3351, 1647, 1601, 1550, 1502, 1438, 1323, 1308, 1157, 1043, 607, 523.

viii. *6-Methylquinazoline-2,4(1H,3H)-dione (**2h**)(Table 3, entry 8):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.20 (s, 1H), 11.04 (s, 1H), 7.69 (s, 1H), 7.46 (d, $J$ = 8.4 Hz, 1H), 7.07 (d, $J$ = 8.4 Hz, 1H), 2.32 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 161.81, 150.07, 139.81, 134.72, 126.18, 125.86, 117.54, 115.75, 20.09 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3199, 3059, 2825, 1741, 1712, 1668, 1483, 1428, 1330, 1285, 1145, 1025, 829, 532.

ix. *5-Methylquinazoline-2,4(1H,3H)-dione (**2i**)(Table 3, entry 9):* $^{1}$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): $\delta$ = 11.07–11.02 (s, 2H), 7.45 (t, $J$ = 8, 7.6 Hz, 1H), 7.01 (d, $J$ = 8 Hz, 1H), 6.94 (d, $J$ = 7.2 Hz, 1H), 2.65 (s, 3H) ppm. $^{13}$C NMR (100 MHz,

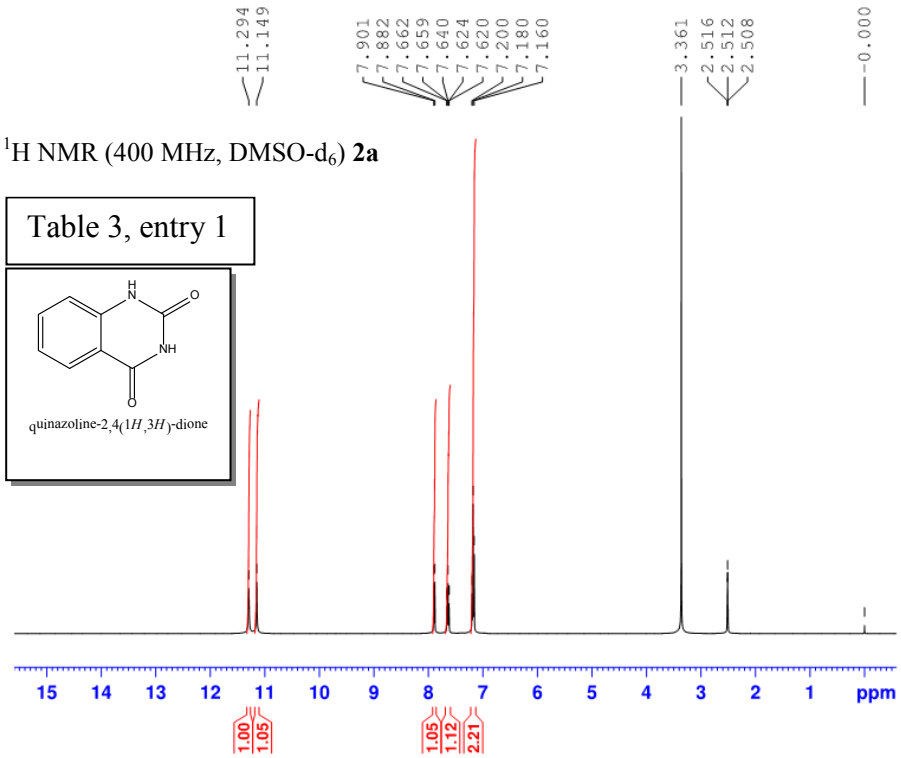
DMSO-$d_6$, 25 °C, TMS): $\delta$ = 163.60, 150.01, 142.13, 140.93, 133.74, 125.13, 113.42, 112.44, 22.04 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3190, 3063, 2835, 1731, 1703, 1673, 1614, 1515, 1444, 1288, 1090, 798, 470.

x. *6-Nitroquinazoline-2,4(1H,3H)-dione (**2j**)(Table 3, entry 10):* $^1$H NMR (400 MHz, DMSO-$d_6$, 25 °C, TMS): $\delta$ = 11.39–11.21 (s, br, 2H), 7.61–7.53 (m, 2H), 7.21 (dd, *J* = 8.8, 4.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$, 25 °C, TMS): $\delta$ = 162.07, 158.41, 156.03, 150.04, 137.56, 122.72, 117.51, 115.38 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3199, 3061, 2840, 1715, 1677, 1499, 1438, 1343, 1288, 1133, 828, 507.

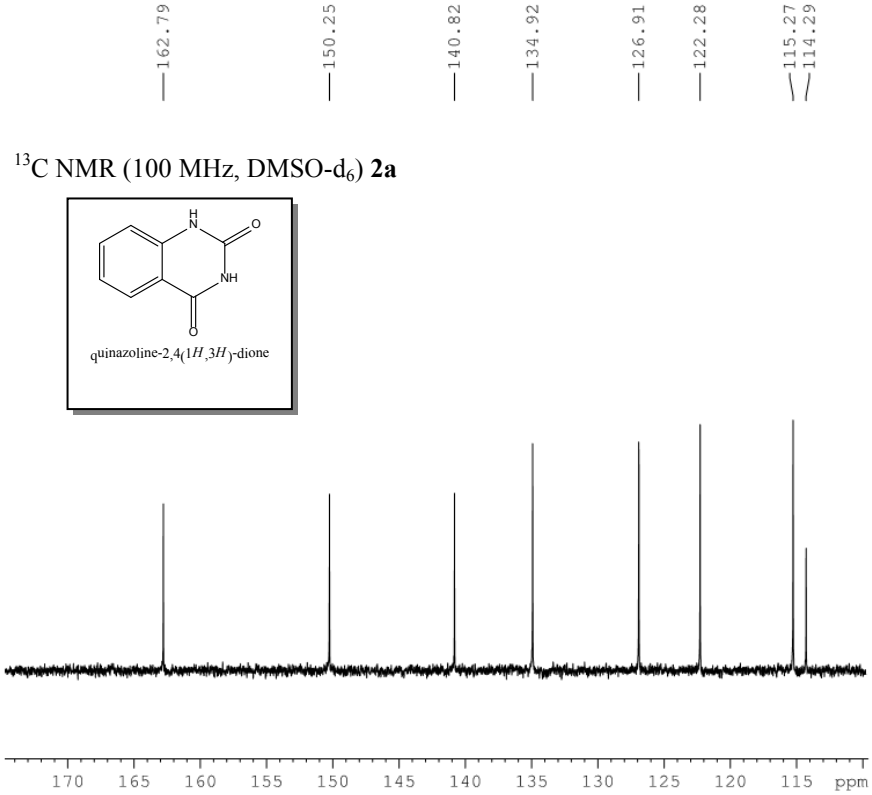
xi. *8-Chloro-6-nitroquinazoline-2,4(1H,3H)-dione (**2k**)(Table 3, entry 11):* $^1$H NMR (400 MHz, DMSO-$d_6$, 25 °C, TMS): $\delta$ = 11.07–11.01 (s, 2H), 8.58 (s, 1H), 8.42 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$, 25 °C, TMS): $\delta$ = 169.61, 150.80, 147.25, 141.22, 129.38, 123.12, 114.47, 111.99 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3068, 2830, 1708, 1626, 1485, 1338, 1153, 836, 748, 496.

xii. *2H-pyrazolo[3,4-d]pyrimidine-4,6(5H,7H)-dione (**2l**)(Table 3, entry 12):* $^1$H NMR (400 MHz, DMSO-$d_6$, 25 °C, TMS): $\delta$ = 13.31 (s, 1H), 11.37 (s, 1H), 10.69 (s, 1H), 8.34 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$, 25 °C, TMS): $\delta$ = 162.29, 159.67, 151.70, 129.08, 100.22 ppm. IR (KBr) $\nu_{max}$/cm$^{-1}$: 3187, 2828, 1693, 1617, 1476, 1330, 1249, 1184, 944, 768, 524, 488.

## 9. $^{1}$H and $^{13}$C NMR spectra of some selected products

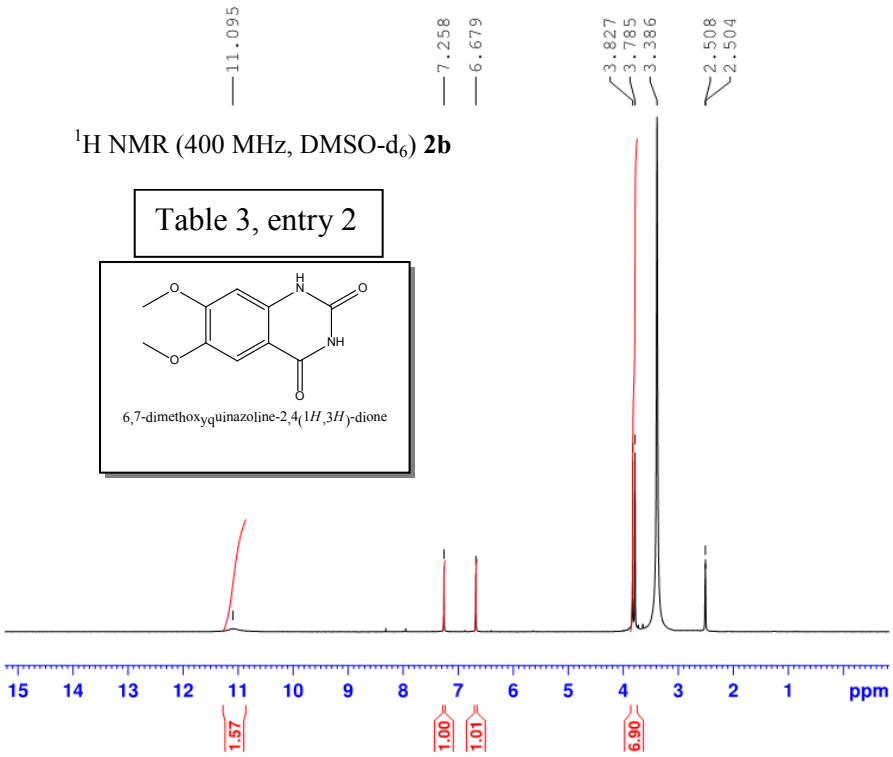


$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2a**

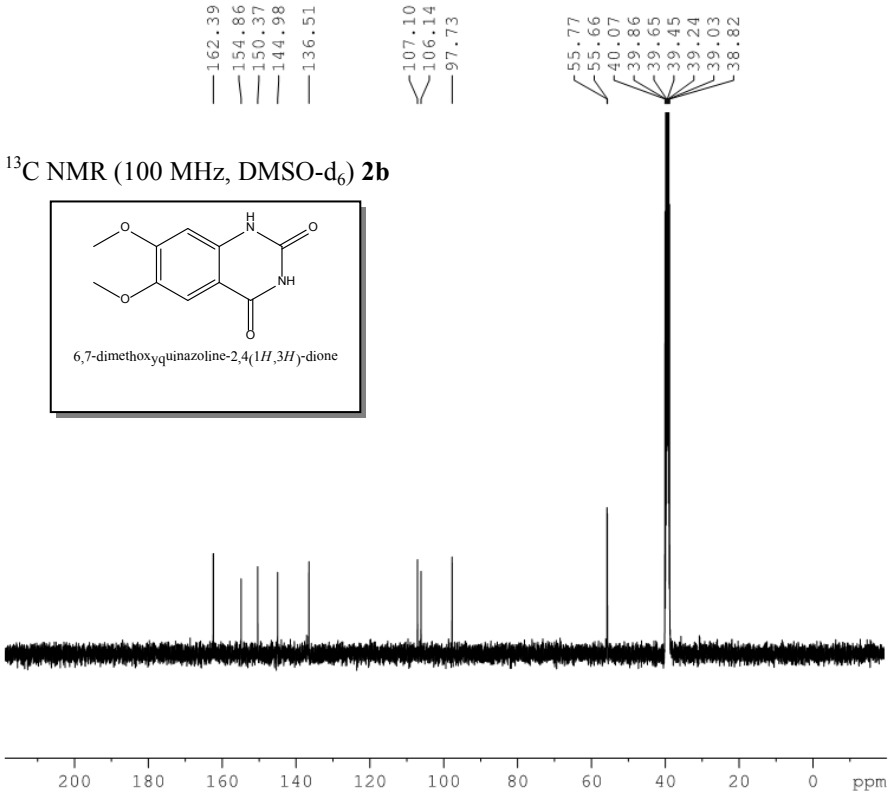



$^{1}$H NMR (400 MHz, DMSO-d$_6$) **2b**

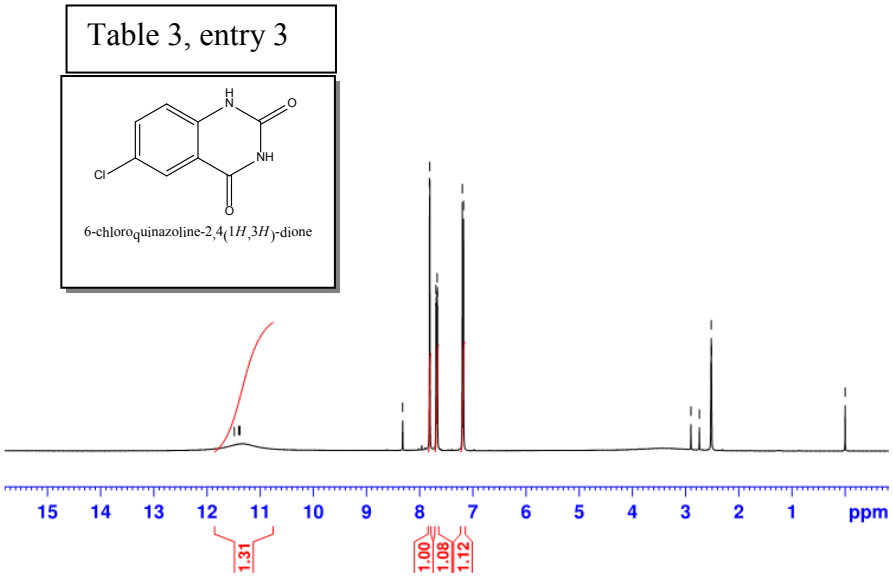
Table 3, entry 2



$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2b**

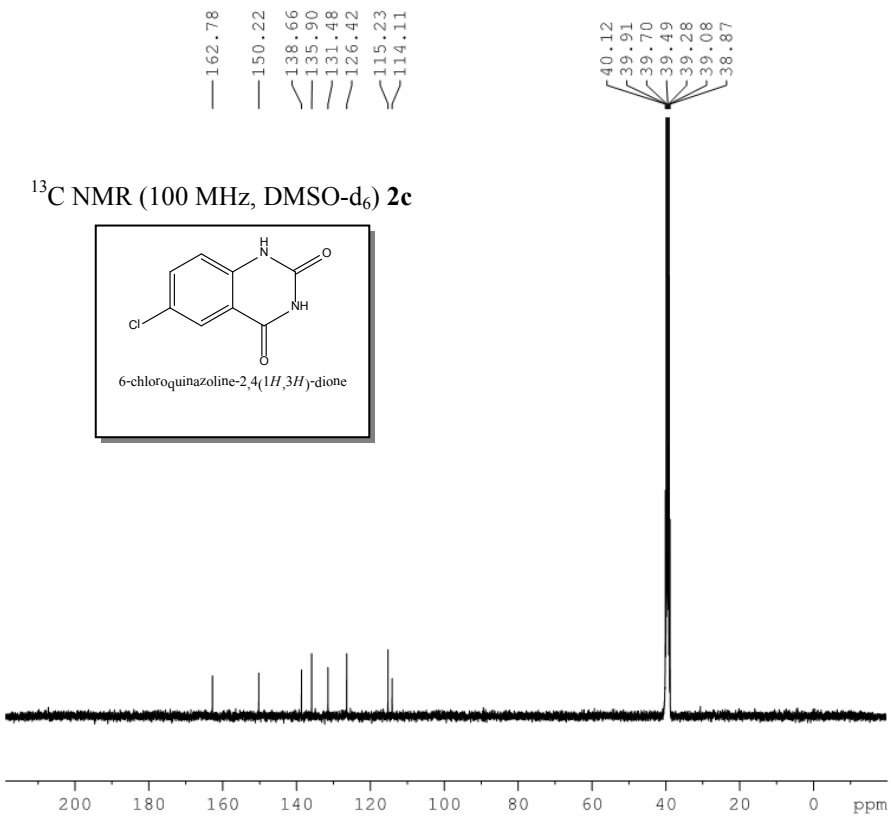



$^{1}$H NMR ( 400 MHz, DMSO-d$_6$) **2c**



$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2c**

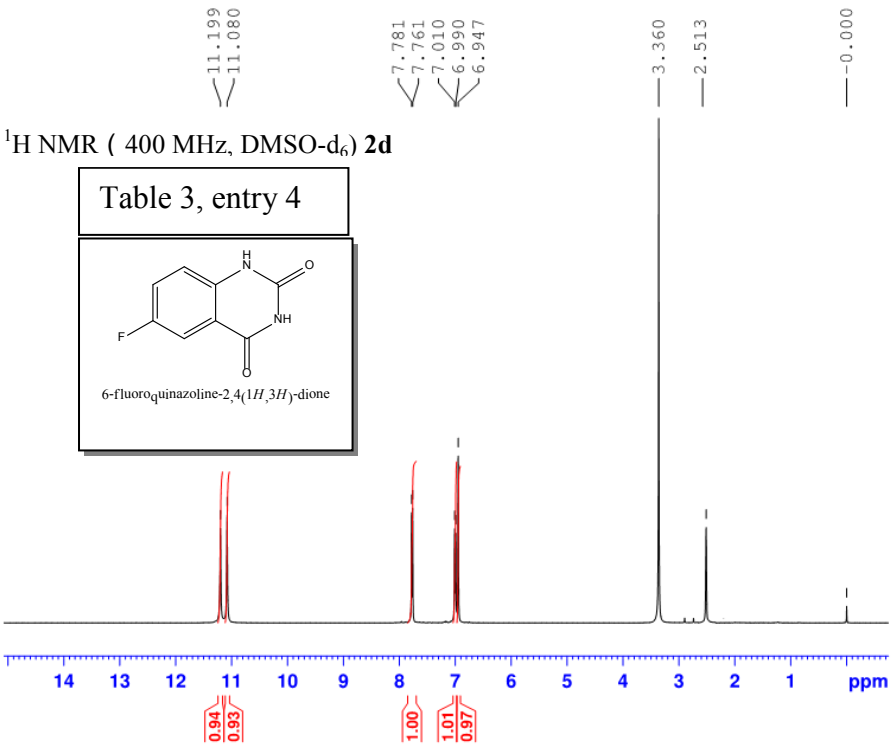


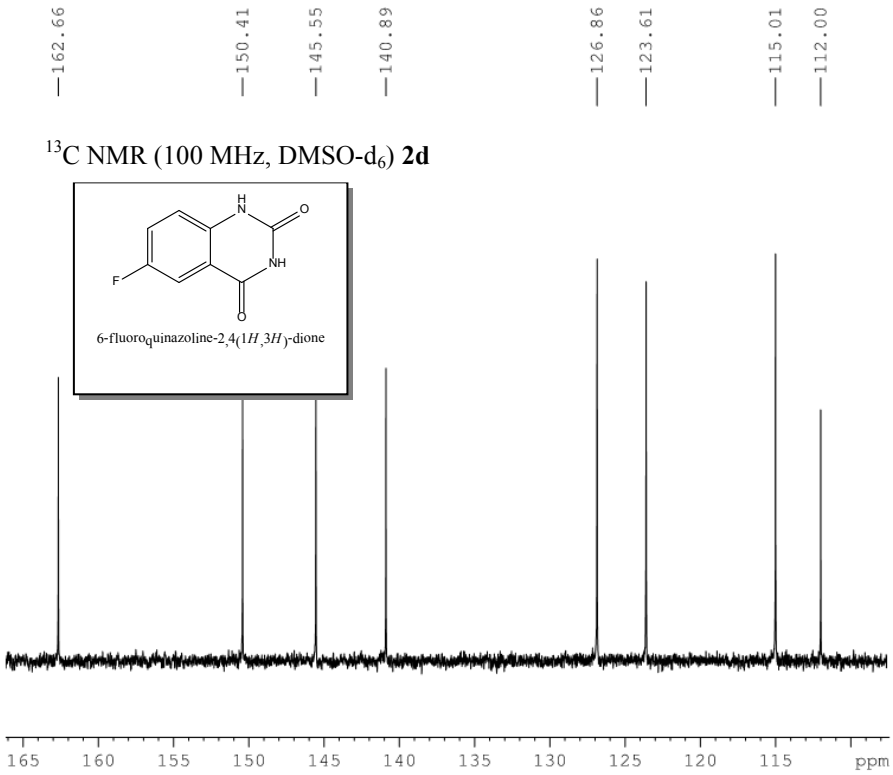



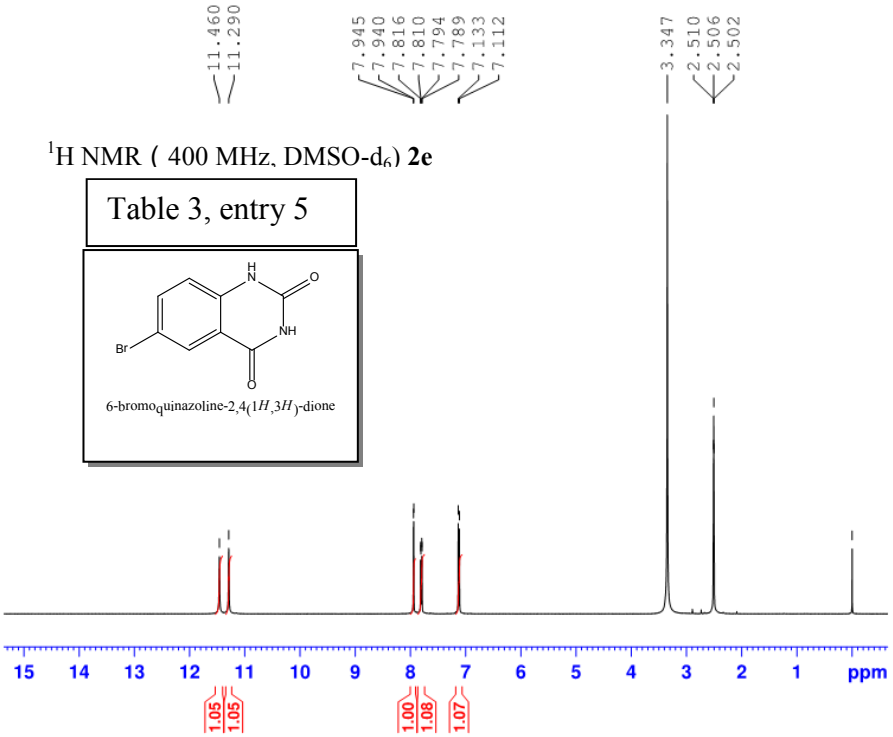

$^{1}$H NMR ( 400 MHz, DMSO-d$_6$) **2d**

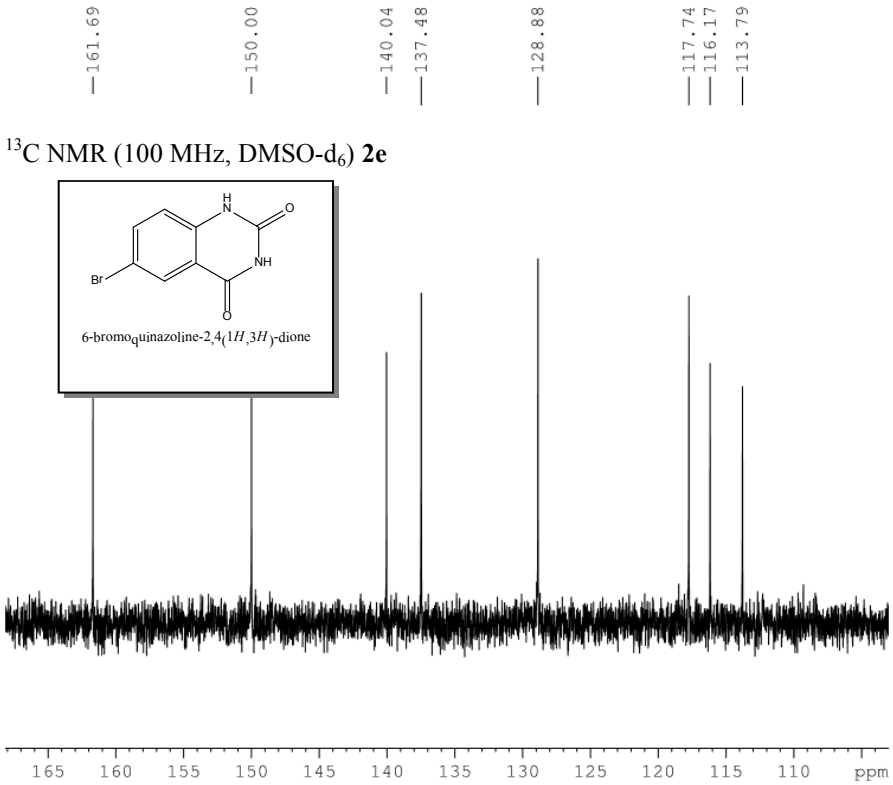
Table 3, entry 4



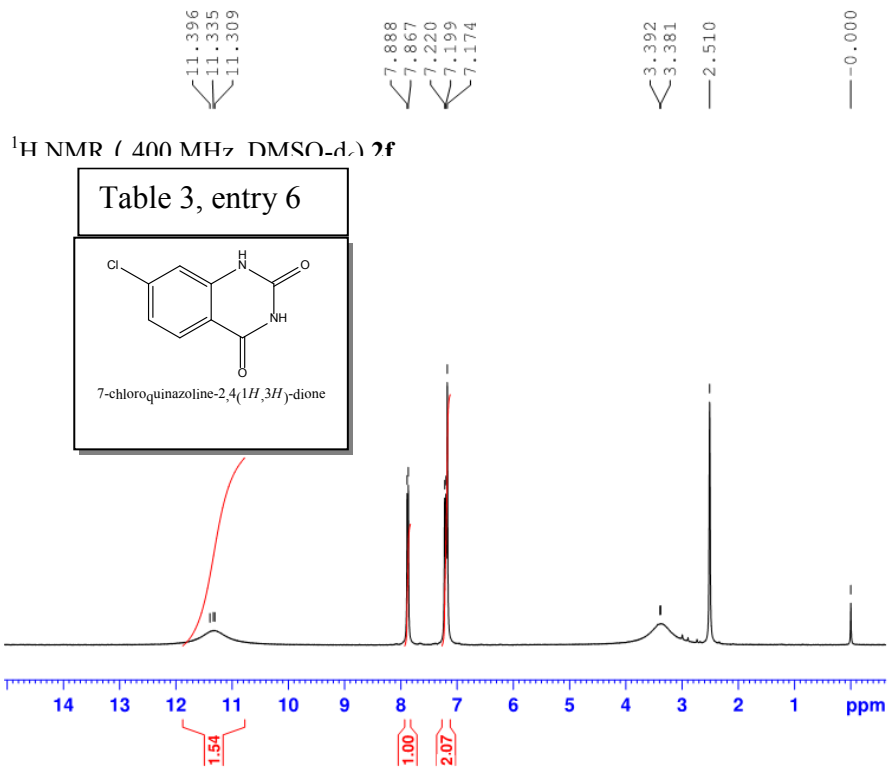




162.66
150.41
145.55
140.89
126.86
123.61
115.01
112.00
13C NMR (100 MHz, DMSO-d6) 2d
6-fluoroquinazoline-2,4(1H,3H)-dione
165 160 155 150 145 140 135 130 125 120 115 ppm

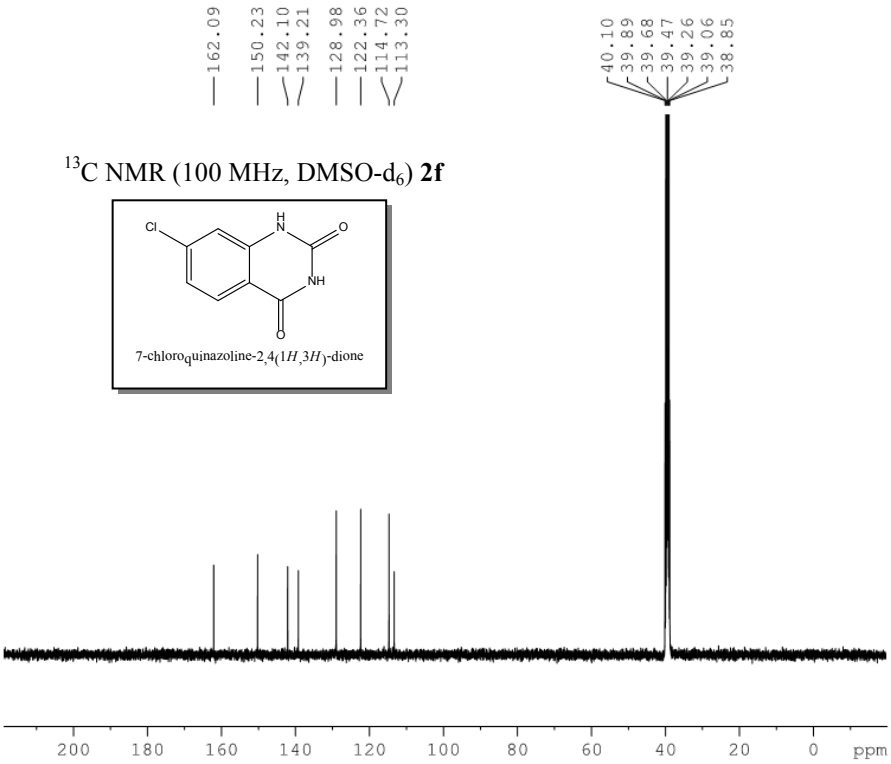

11.460
11.290
7.945
7.940
7.816
7.810
7.794
7.789
7.133
7.112
3.347
2.510
2.506
2.502
1H NMR ( 400 MHz, DMSO-d6) 2e
Table 3, entry 5
6-bromoquinazoline-2,4(1H,3H)-dione
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.05
1.05
1.00
1.08
1.07

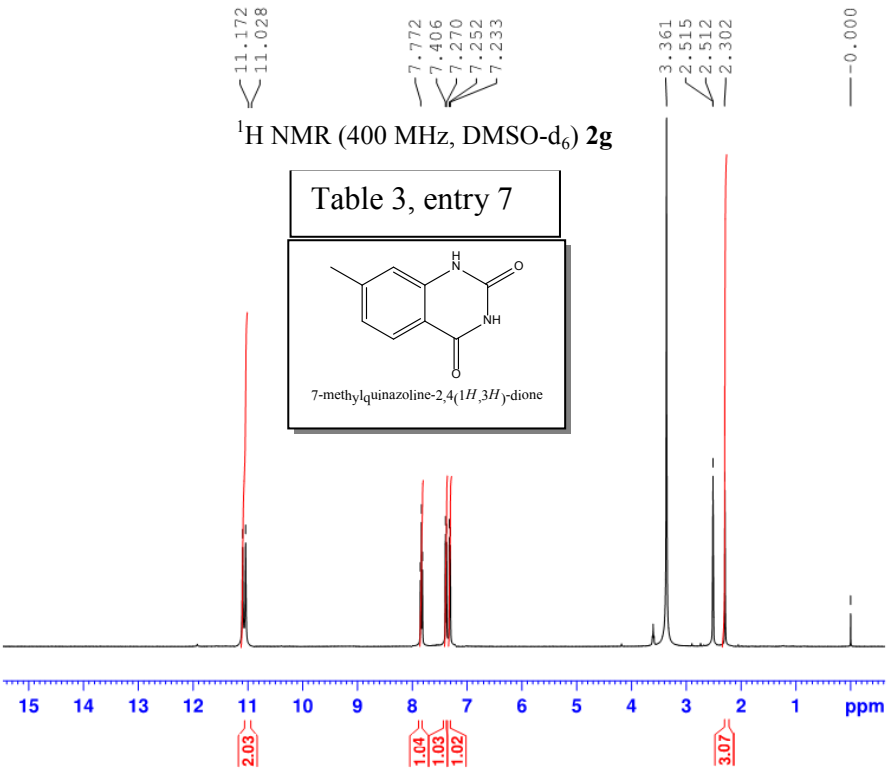


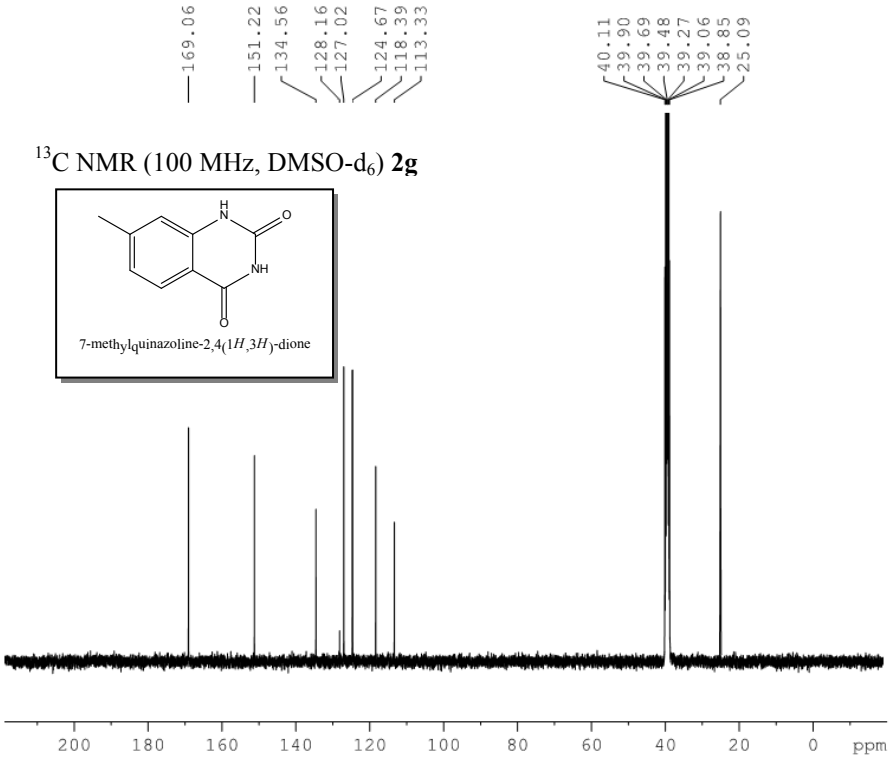

$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2e**

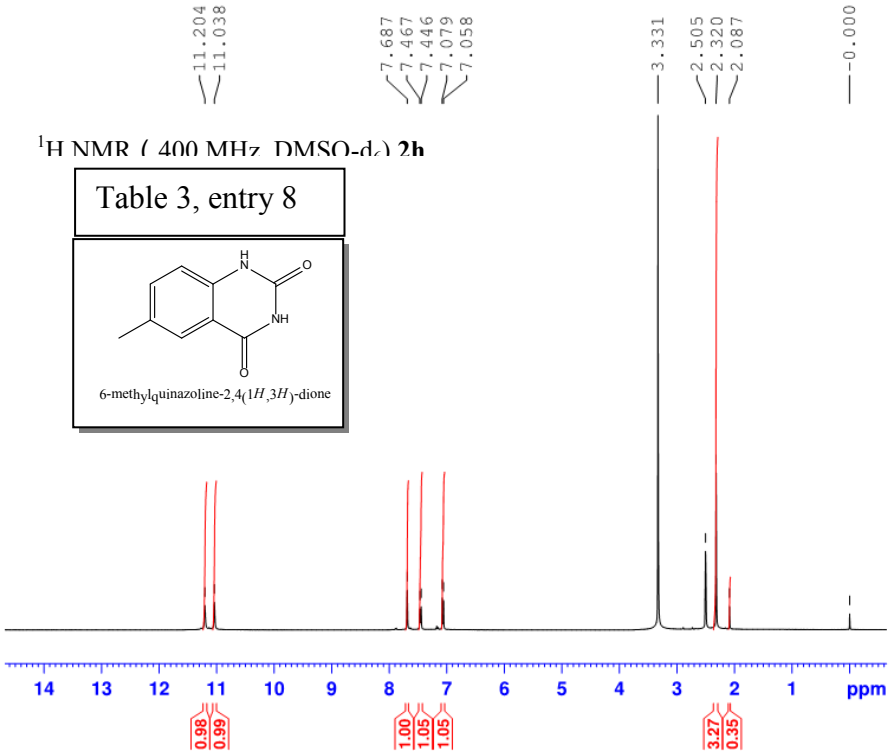


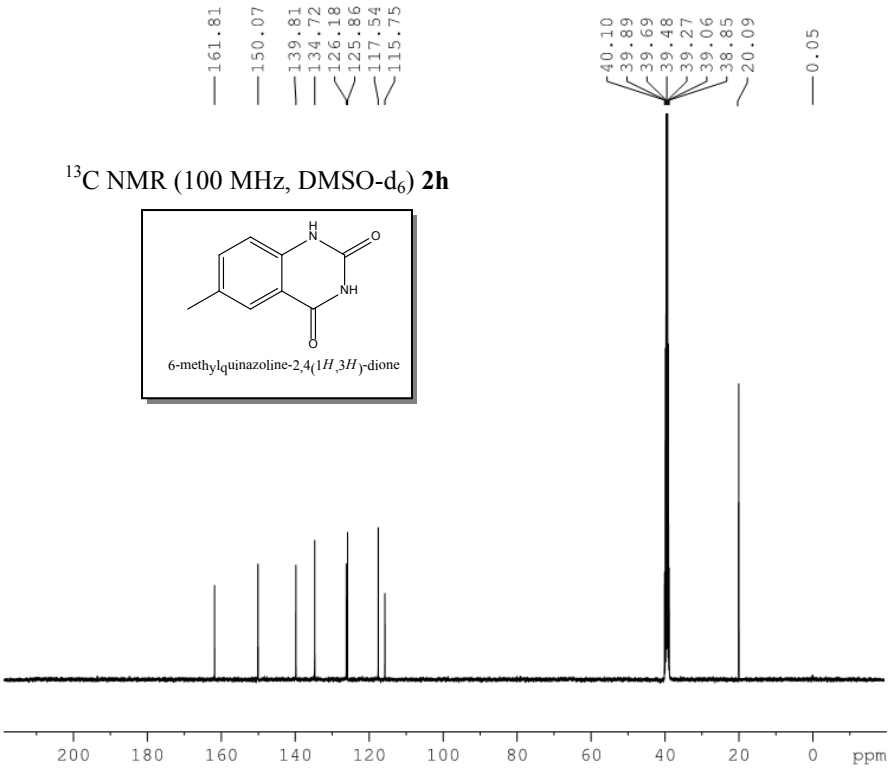

$^{1}$H NMR (400 MHz, DMSO-d$_6$) **2f**


162.09
150.23
142.10
139.21
128.98
122.36
114.72
113.30
40.10
39.89
39.68
39.47
39.26
39.06
38.85
$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2f**
Cl
H
N
O
NH
O
7-chloroquinazoline-2,4(1*H*,3*H*)-dione
200
180
160
140
120
100
80
60
40
20
0
ppm


11.172
11.028
7.772
7.406
7.270
7.252
7.233
3.361
2.515
2.512
2.302
-0.000
$^{1}$H NMR (400 MHz, DMSO-d$_6$) **2g**
Table 3, entry 7
H
N
O
NH
O
7-methylquinazoline-2,4(1*H*,3*H*)-dione
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.03
1.04
1.03
1.02
3.07


169.06
151.22
134.56
128.16
127.02
124.67
118.39
113.33
40.11
39.90
39.69
39.48
39.27
39.06
38.85
25.09
13C NMR (100 MHz, DMSO-d6) 2g
7-methylquinazoline-2,4(1H,3H)-dione
200
180
160
140
120
100
80
60
40
20
0
ppm

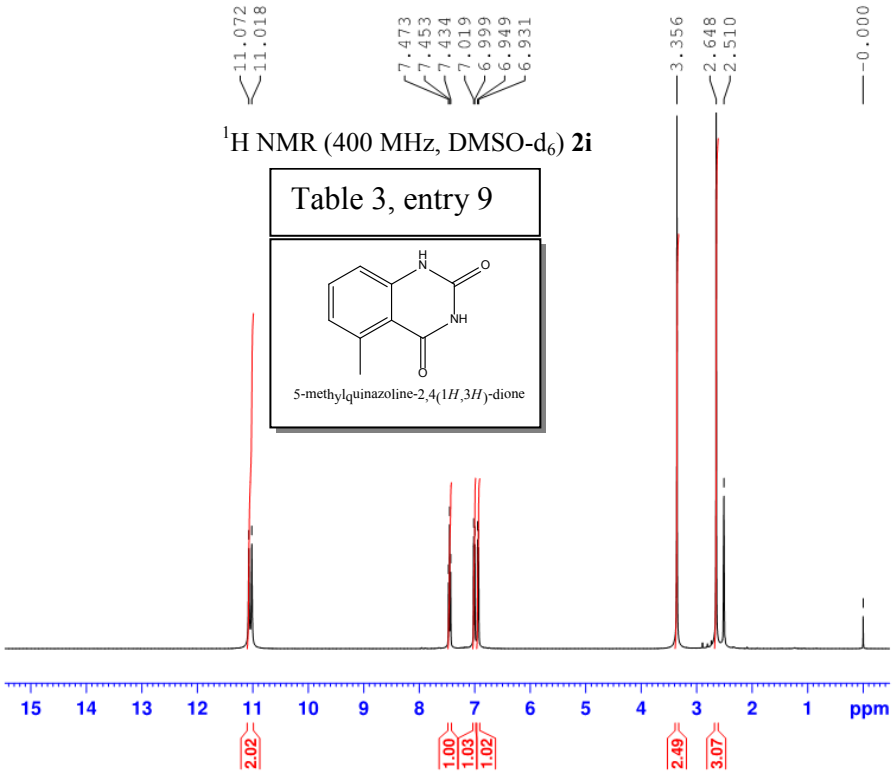

11.204
11.038
7.687
7.467
7.446
7.079
7.058
3.331
2.505
2.320
2.087
-0.000
1H NMR (400 MHz, DMSO-d6) 2h
Table 3, entry 8
6-methylquinazoline-2,4(1H,3H)-dione
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.98
0.99
1.00
1.05
1.05
3.27
0.35




$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2h**




6-methylquinazoline-2,4(1*H*,3*H*)-dione



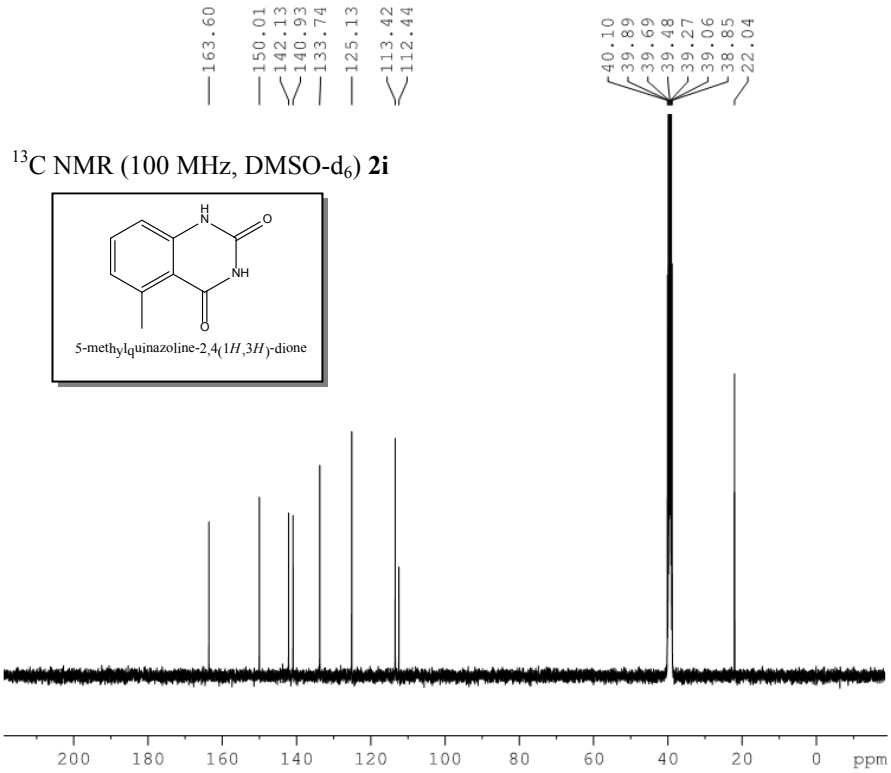

$^{1}$H NMR (400 MHz, DMSO-d$_6$) **2i**

Table 3, entry 9

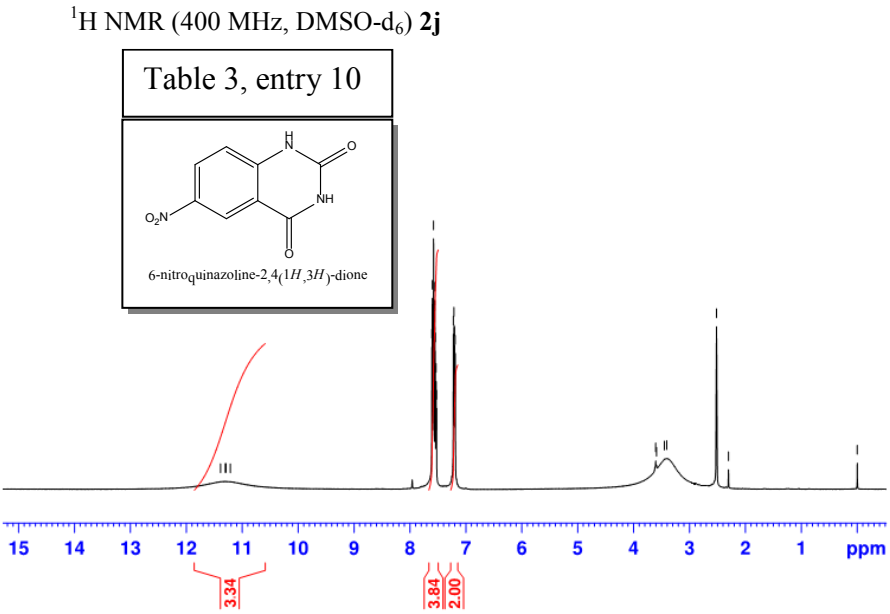


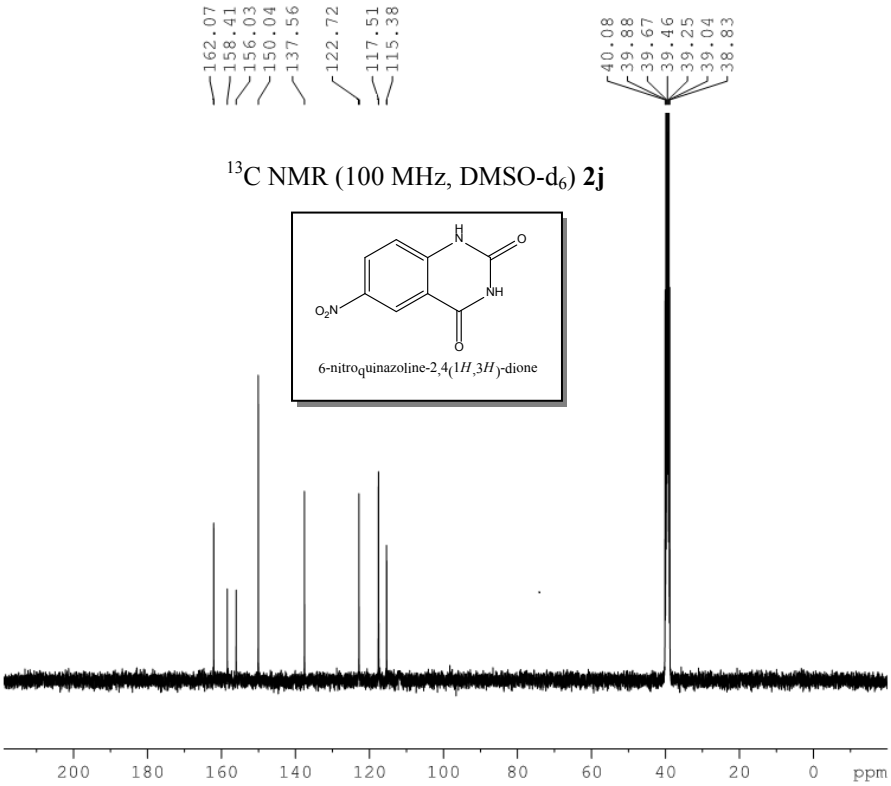

5-methylquinazoline-2,4(1*H*,3*H*)-dione

$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2i**




$^{1}$H NMR (400 MHz, DMSO-d$_6$) **2j**

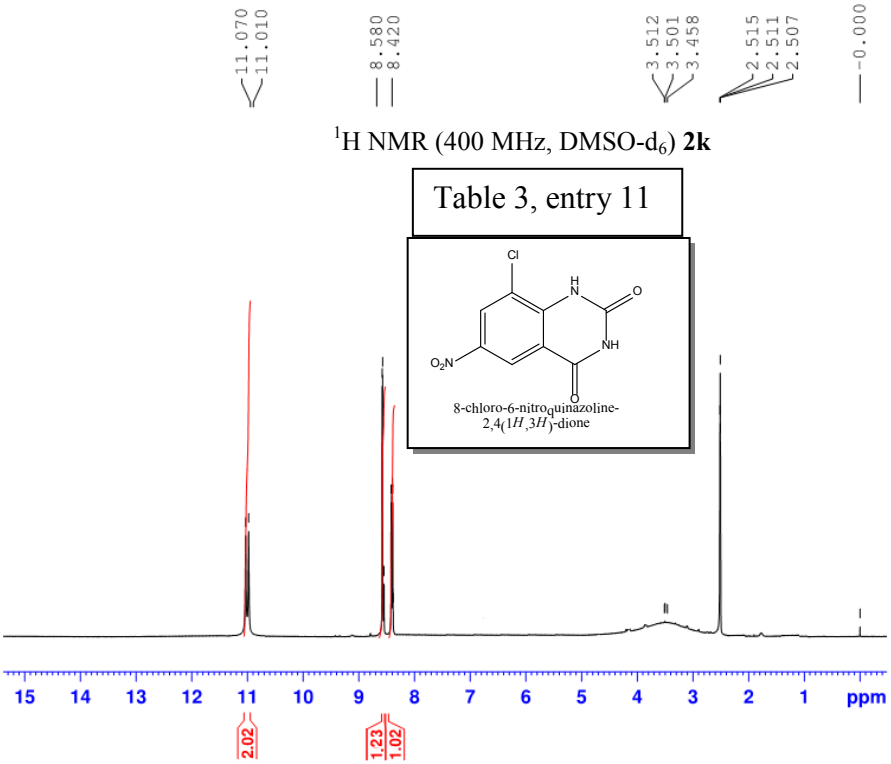





$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2j**




6-nitroquinazoline-2,4(1*H*,3*H*)-dione



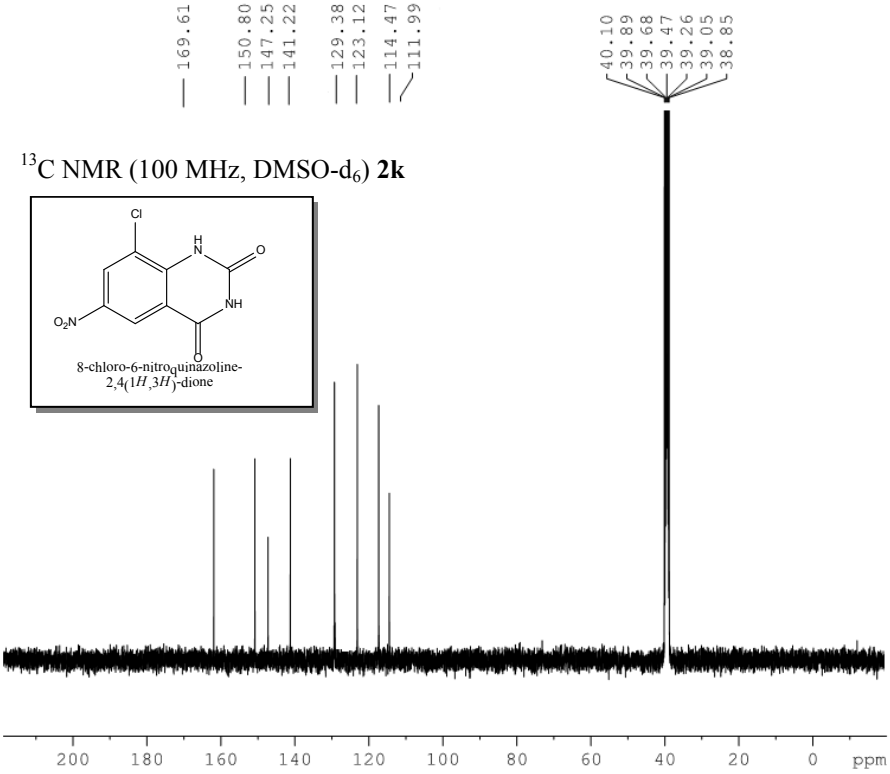

$^{1}$H NMR (400 MHz, DMSO-d$_6$) **2k**

Table 3, entry 11



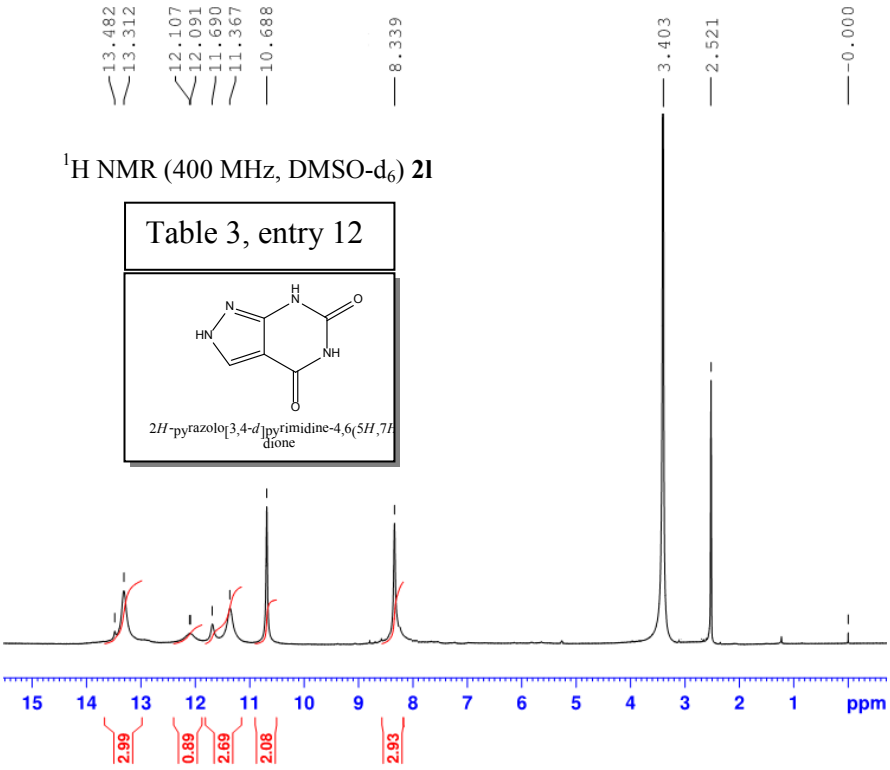

8-chloro-6-nitroquinazoline-2,4(1*H*,3*H*)-dione

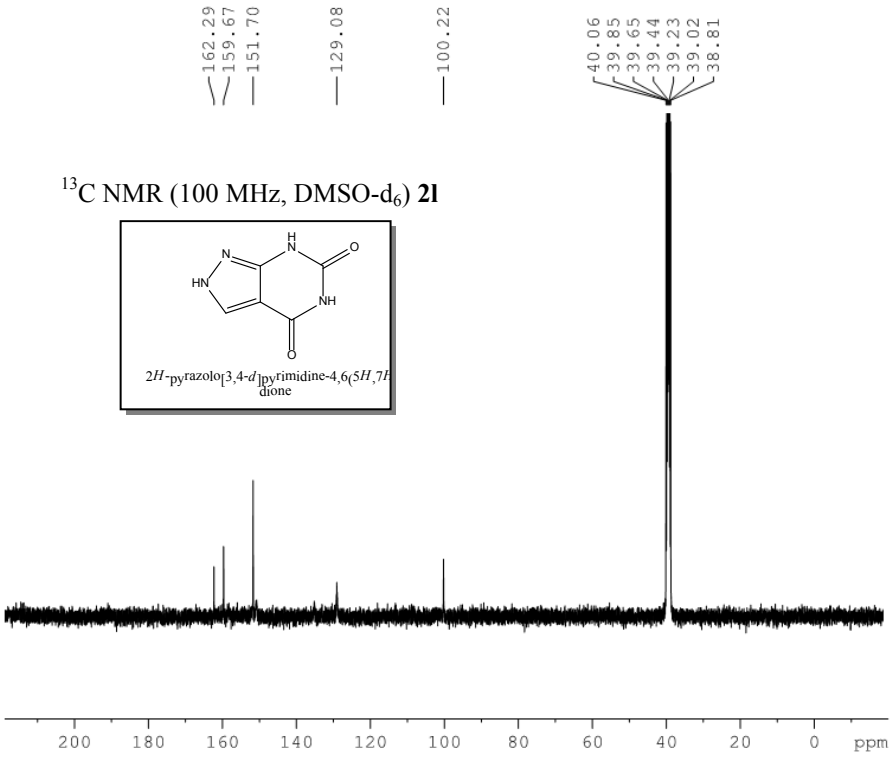
$^{13}$C NMR (100 MHz, DMSO-d$_6$) **2k**




$^{1}$H NMR (400 MHz, DMSO-d$_6$) **2l**

Table 3, entry 12






## 10. References

1. K. M. Parida, D. Rath, *J. Mol. Catal. A: Chem*. 2009, **310**, 93–100.

2. Y. P. Patil, P. J. Tambade, S. R. Jagtap, B. M. Bhanage, *J. Mol. Cat. A: Chem*., 2008, **289**, 14.