Electronic supplementary materials *Mendeleev Commun*., 2016, **26**, 72−74

Reactions of chromone-3-carboxylic acid and chromone-3-carboxamides with cyanoacetic acid hydrazide

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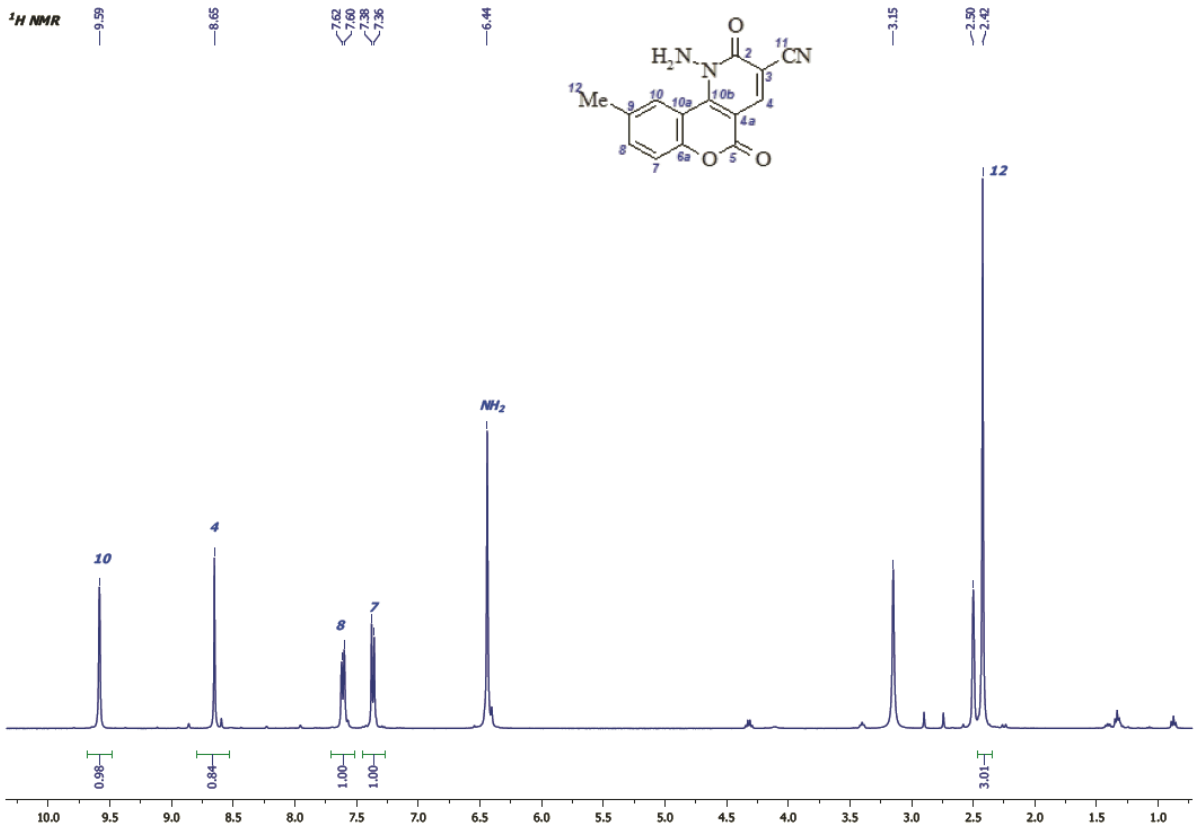
NMR spectra were recorded on Bruker DRX-400 (^{1}H – 400 MHz and ^{13}C – 100 MHz) and AVANCE-500 (^{1}H – 500 MHz and ^{13}C – 126 MHz) spectrometers in DMSO-d_6 with TMS as an internal standard. IR spectra were recorded on a Nicolet 6700 instrument (FTIR mode, ZnSe crystal). The starting chromone-3-carboxamides **8a–c** were prepared according to described procedure (A. Nohara, T. Umetani, K. Ukawa and Y. Sanno, *Chem. Pharm. Bull*., 1974, **22**, 2959; M. Yu. Kornev, V. S. Moshkin and V. Ya. Sosnovskikh, *Chem. Heterocycl. Compd*., 2015, **51**, 688).

6-Nitro-4-oxochromene-3-carboxamide **8d**. Yield 216 mg (89%), white powder, mp 256–258 ºC. ^{1}H NNMR (500 MHz, DMSO-d_6) δ: 7.95 (br s, 1H, NHH), 8.04 (d, 1H, *J* 9.2 Hz, H-8), 8.36 (br s, 1H, NHH), 8.64 (dd, 1H, *J* 9.2, 2.8 Hz, H-7), 8.83 (d, 1H, *J* 2.8 Hz, H-5), 9.10 (s, 1H, H-2). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 116.5, 121.0, 121.4, 124.0, 129.1, 145.0, 158.6, 162.7, 163.7, 175.4 (C=O). IR (ν/cm^{-1}): 3366, 3153, 3112, 3090, 3073, 1684, 1644, 1626, 1594, 1563, 1545, 1530, 1471, 1451. Found (%): C, 49.58; H, 2.90; N, 11.40. Calc. for $C_{10}H_6N_2O_5 \cdot 0.5H_2O$ (%): C, 49.39; H, 2.90; N, 11.52.

1-(2-Hydroxyphenyl)-1-(pyrazol-4-yl)methanone **13**. Yield 70 mg (37%), white powder, mp 121–123 ºC (lit. mp 123–125 ºC; K. Ito and J. Maruyama, *J. Heterocycl. Chem*., 1988, **25**, 1681). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.90–6.97 (m, 2H, H-3′, H-5′), 7.46 (ddd, *J* 8.6, 7.0, 1.6 Hz, 1H, H-4′), 7.94 (br s, 1H, H-3/5), 7.82 (dd, *J* 7.8, 1.2 Hz, 1H, H-6′), 8.30 (br s, 1H, H-5/3), 11.67 (s, 1H, OH), 13.47 (br s, 1H, NH).


¹H NMR
9.59
8.65
7.62
7.60
7.38
7.36
6.44
3.15
2.50
2.42
10
4
8
7
NH₂
12
0.98
0.84
1.00
1.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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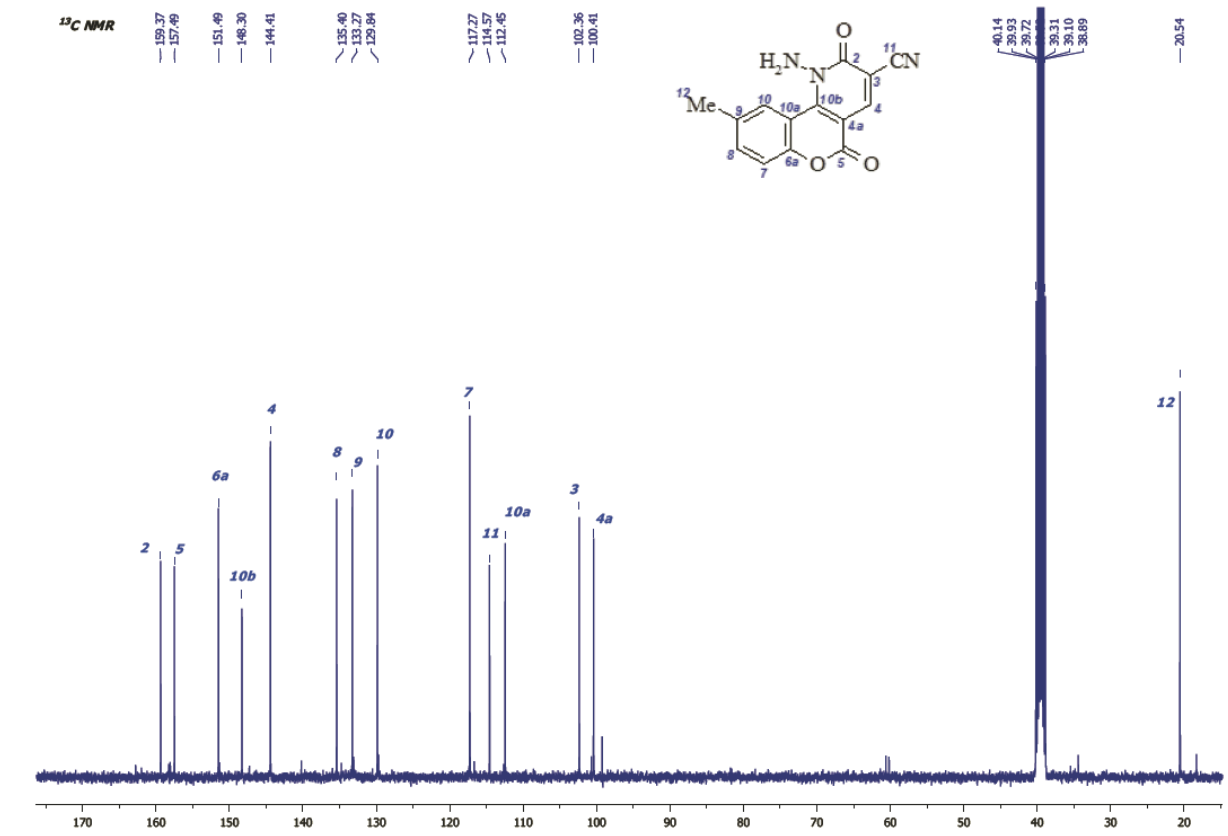
1.5
1.0


13C NMR
159.37
157.49
151.49
148.30
144.41
135.40
133.27
129.84
117.27
114.57
112.45
102.36
100.41
40.14
39.93
39.72
39.31
39.10
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10b
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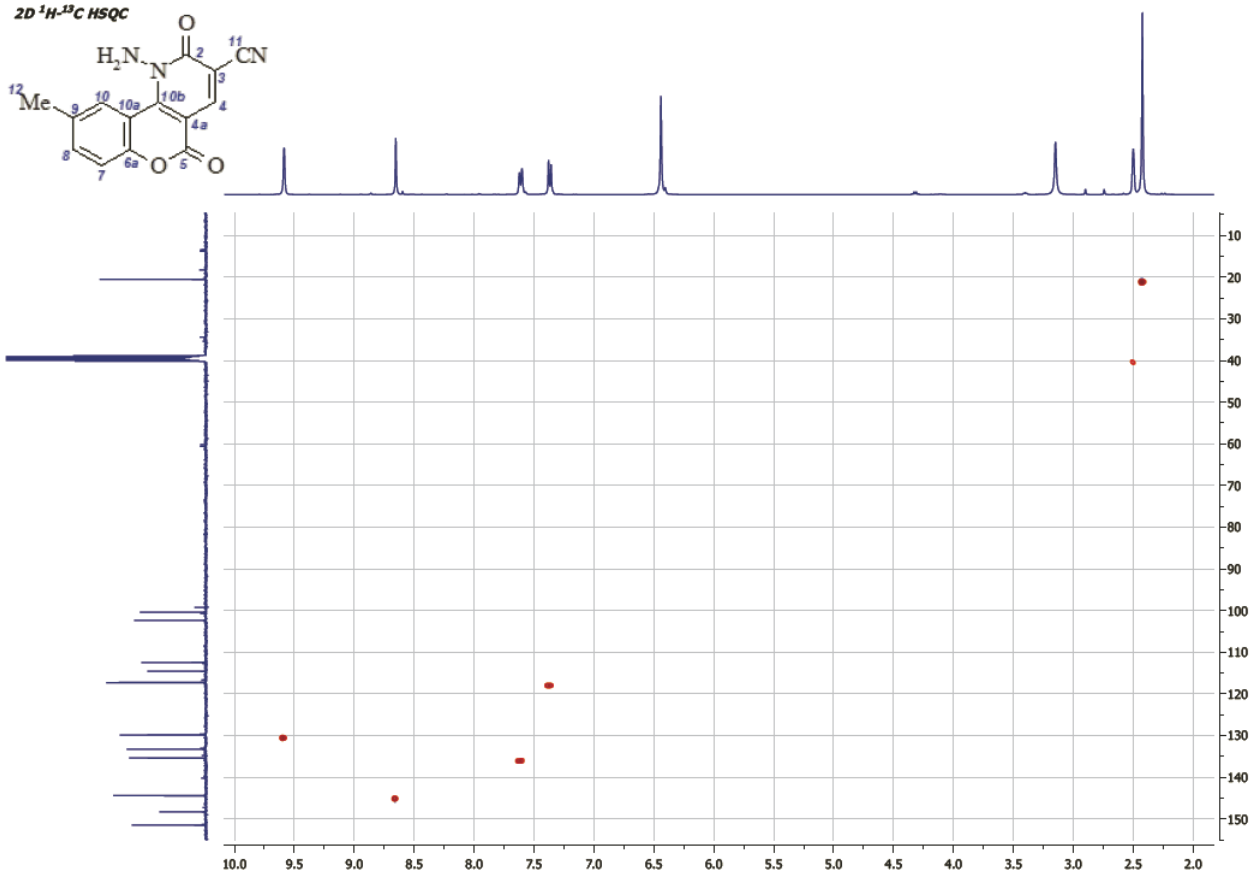
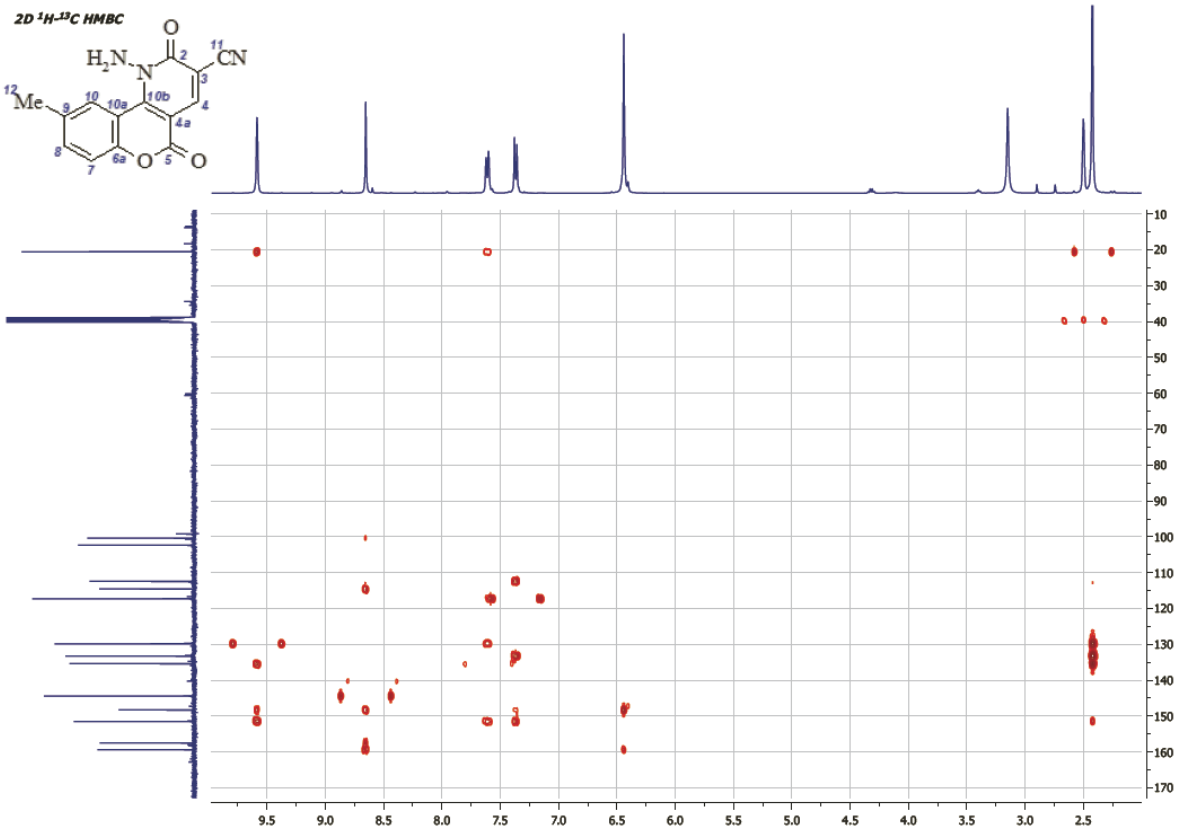
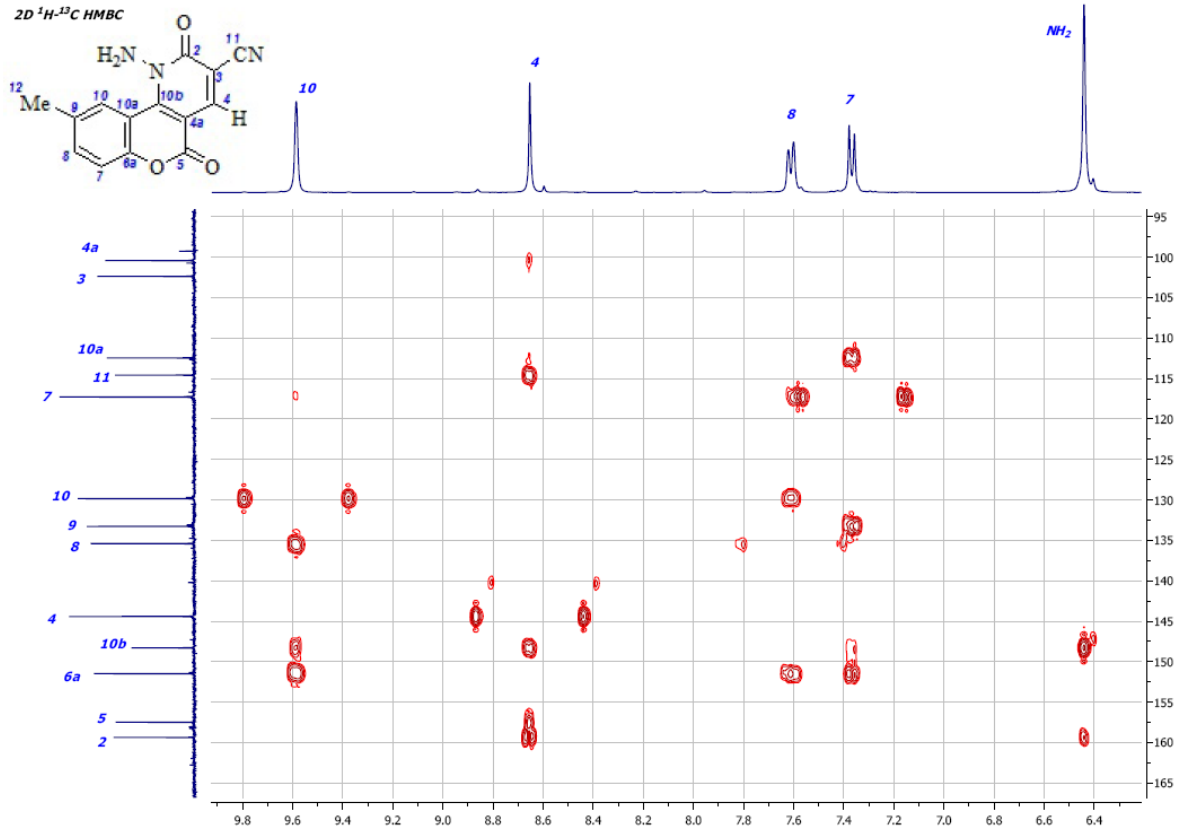
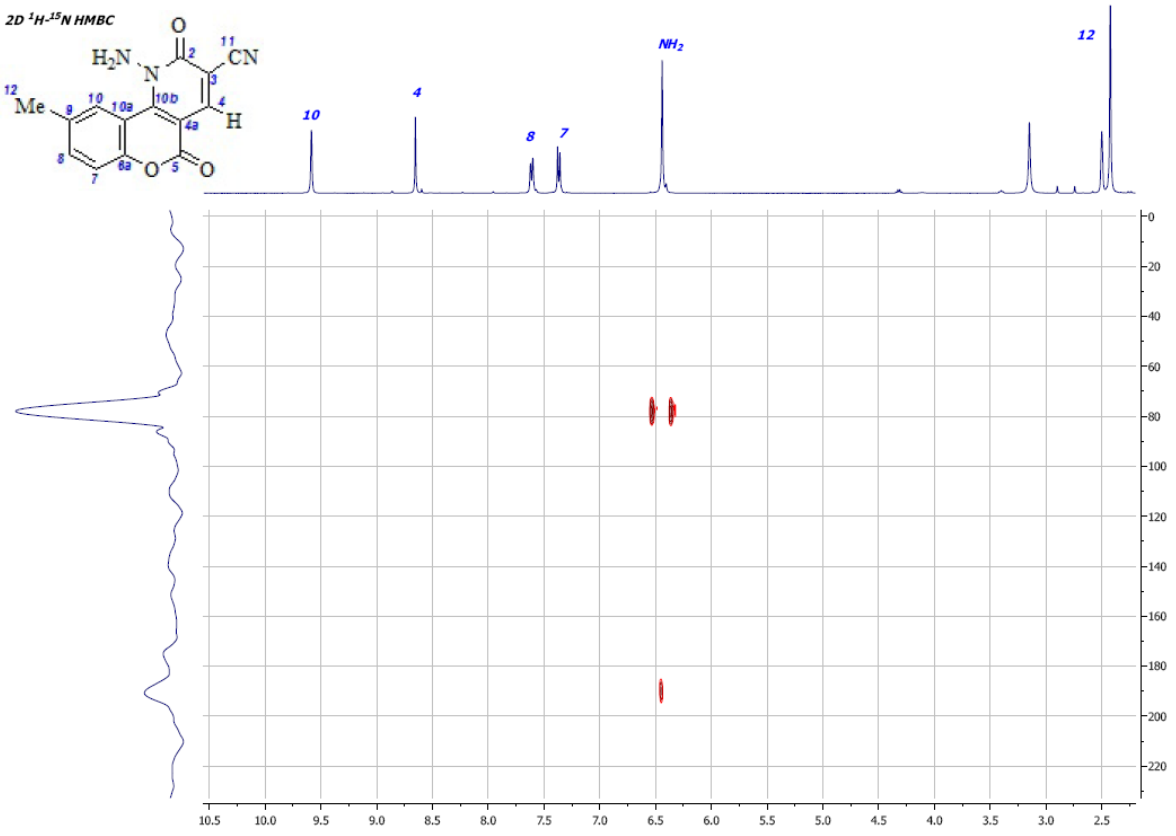
8
9
10
7
11
10a
3
4a
12


2D 1H-13C HSQC


2D ¹H-¹³C HMBC
H2N
N
O
2
11
CN
3
4
12
Me
9
10
10a
10b
4a
8
6a
7
O
5
O


2D ¹H-¹³C HMBC
H2N
N
O
2
11
CN
3
4
H
12
Me
9
10
10a
10b
4a
8
6a
7
O
5
O
10
4
8
7
NH2
4a
3
10a
11
7
10
9
8
4
10b
6a
5
2


2D ^{1}H-^{15}N HMBC
O
H_2N
N
2
11
CN
3
4
H
12
Me
9
10
10a
10b
4a
8
7
6a
O
5
O
10
4
8
7
NH_2
12
0
20
40
60
80
100
120
140
160
180
200
220
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