Electronic Supplementary Material (ESI) for RSC Advances.

Cholinium ionic liquids as cheap and reusable catalysts for the synthesis of coumarins via Pechmann reaction under solvent-free condition

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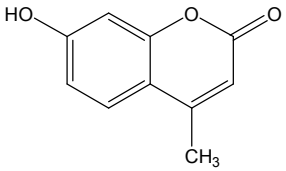
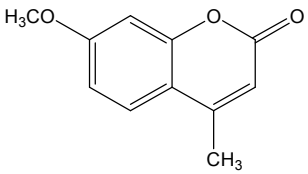
Selected spectra data for the target compound:



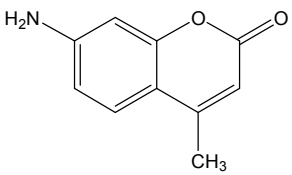
1. 7-Hydroxy-4-methyl-chromen-2-one[1]

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.36 (s, 3H,-CH_3), 6.12(s, 1H), 6.70(d, 1H, Ar-H), 6.78-6.81 (m, 1H, Ar-H), 7.57-7.59(d, 1H, Ar-H), 10.52(s, 1H, -OH).



2. 7-Methoxy-4-methyl-chromen-2-one[1]

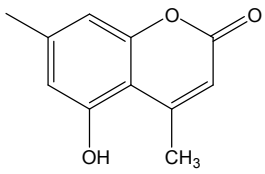
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.39 (s, 3H,-CH_3), 3.86(s, 3H,-OCH_3), 6.21(s, 1H), 6.97 (d, 2H, Ar-H), 7.67-7.69 (d, 1H, Ar-H). [1]



3. 7-Amino-4-methyl-chromen-2-one[1]

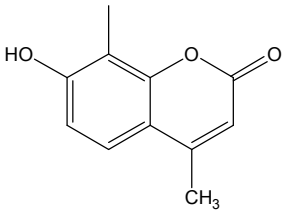
^{1}HNMR (400 MHz, DMSO-d_6): δ 7.4 (d,1H, J=8.8 Hz), 6.56 (d, 1H,

J=7.2 Hz), 6.39 (s, 1H), 6.09 (s,2H), 5.89 (s, 1H), 2.39 (s, 3H). [1]

4. 

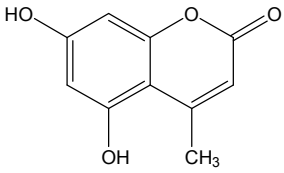
5-Hydroxy-4,7-dimethyl-chromen-2-one[1]

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.27(s, 3H,-CH_3), 2.54(s, 3H,-CH_3), 6.03(s, 1H), 6.57(s, 1H, Ar-H), 6.61(s, 1H, Ar-H), 10.48(s, 1H, -OH).

5. 

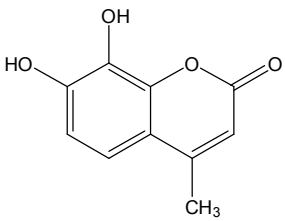
7-Hydroxy-4,8-dimethyl-chromen-2-one[2]

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.15(s, 3H,-CH_3), 2.35(s, 3H,-CH_3), 6.11(s, 1H), 6.84-6.87(d, 1H, Ar-H), 7.42-7.45(d, 1H, Ar-H), 10.37(s, 1H, -OH).

6. 

5,7-Dihydroxy-4-methyl-chromen-2-one[1]

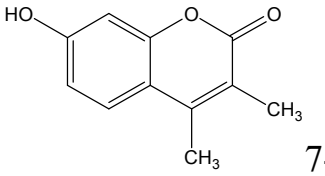
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.41(s, 3H,-CH_3), 5.76(s, 1H), 6.09(s, 1H, Ar-H), 6.18(s, 1H, Ar-H), 10.19(s, 1H, -OH), 10.42(s, 1H, -OH).

7. 

7,8-Dihydroxy-4-methyl-chromen-2-one[1]

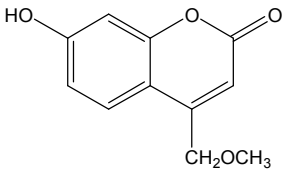
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.41(s, 3H,-CH_3), 5.76(s, 1H), 6.09(s,

1H, Ar-H), 6.18(s, 1H, Ar-H), 10.18(s, 1H, -OH), 10.41(s, 1H, -OH).

8. 

7-Hydroxy-3,4-dimethyl-chromen-2-one[1]

[1]HNMR(400MHz，DMSO-d_6)：δ=2.04 (s, 3H), 2.32 (s, 3H), 6.67 (d, 1H, *J* = 2.3 Hz), 6.77 (dd, 1H, *J* = 8.7, 2.4 Hz), 7.59 (d,1H, *J* = 8.8 Hz), 10.35 (s,1H).

9. 

7-Hydroxy-4-methoxymethyl-chromen-2-one

[1]HNMR(400MHz，DMSO-d_6)：δ= 3.38 (s, 3H), 4.62 (d, 2H, *J* = 1.3 Hz),

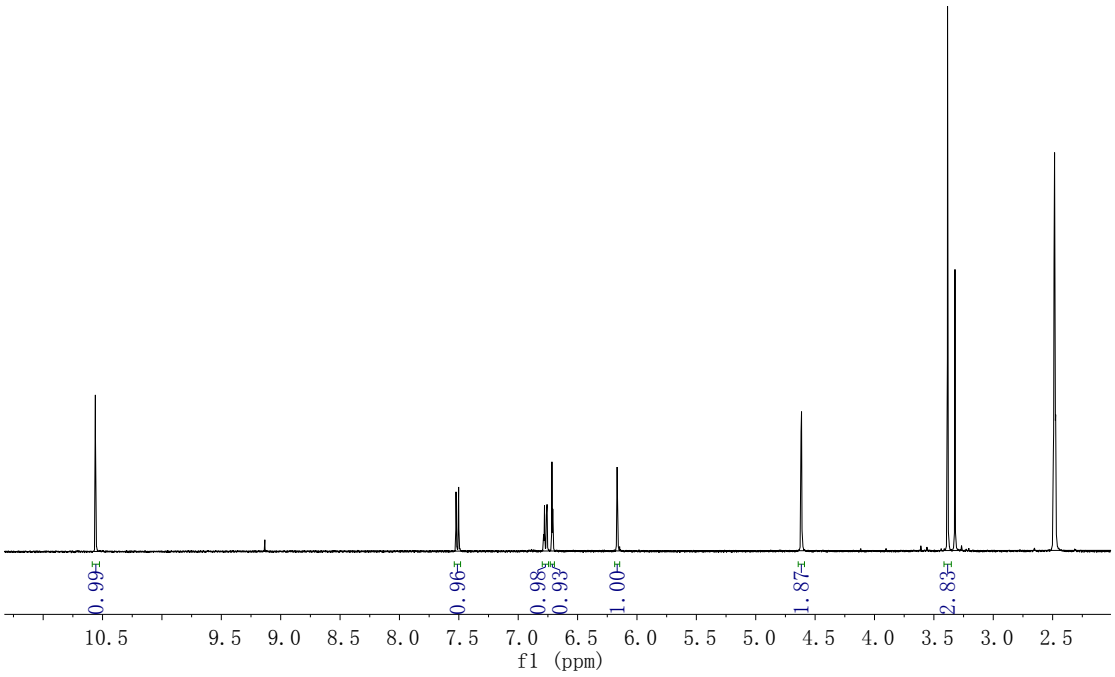
6.17 (d, 1H, *J* = 1.3 Hz), 6.71 (d,1H, *J* = 2.3 Hz), 6.77 (dd, 1H, *J* = 8.7, 2.4 Hz), 7.51 (d, 1H, *J* = 8.7 Hz), 10.56 (s,1H);

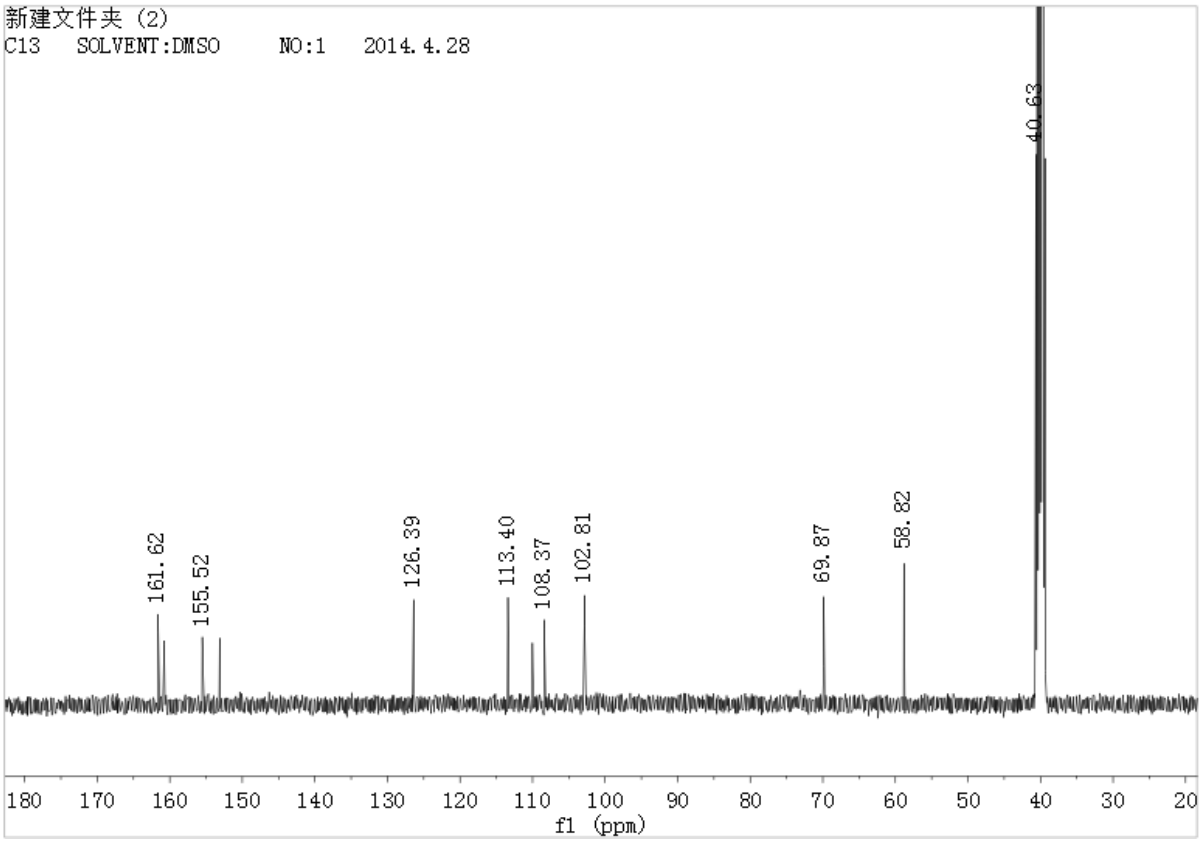
[13]CNMR: 161.62, 160.77, 155.52, 153.12, 126.39, 113.40, 110.02, 108.37, 102.81, 69.87, 58.82, 40.63, 40.42, 40.21, 40.00, 39.79, 39.58, 39.38;

HRMS: m/z calculate for ($M+H^+$) $C_{11}H_{11}O_4$: 207.0652; found: 207.0660.

1H and 13C NMR for compound **9**

1H SOLVENT:DMSO NO:2 2014-04-28





References:

1. N.G. Khaligh, *Catal. Sci. Technol*., 2012, **2**, 1633.
2. R.S. Keri, K.M. Hosamani, H.R.S. Reddy, *Catal. Lett.*, 2009, **131**, 321.