Application of iron-based metal-organic frameworks in catalysis: Oxidant-promoted formation of coumarins using $Fe_3O(BPDC)_3$ as an efficient heterogeneous catalyst

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Supporting Information

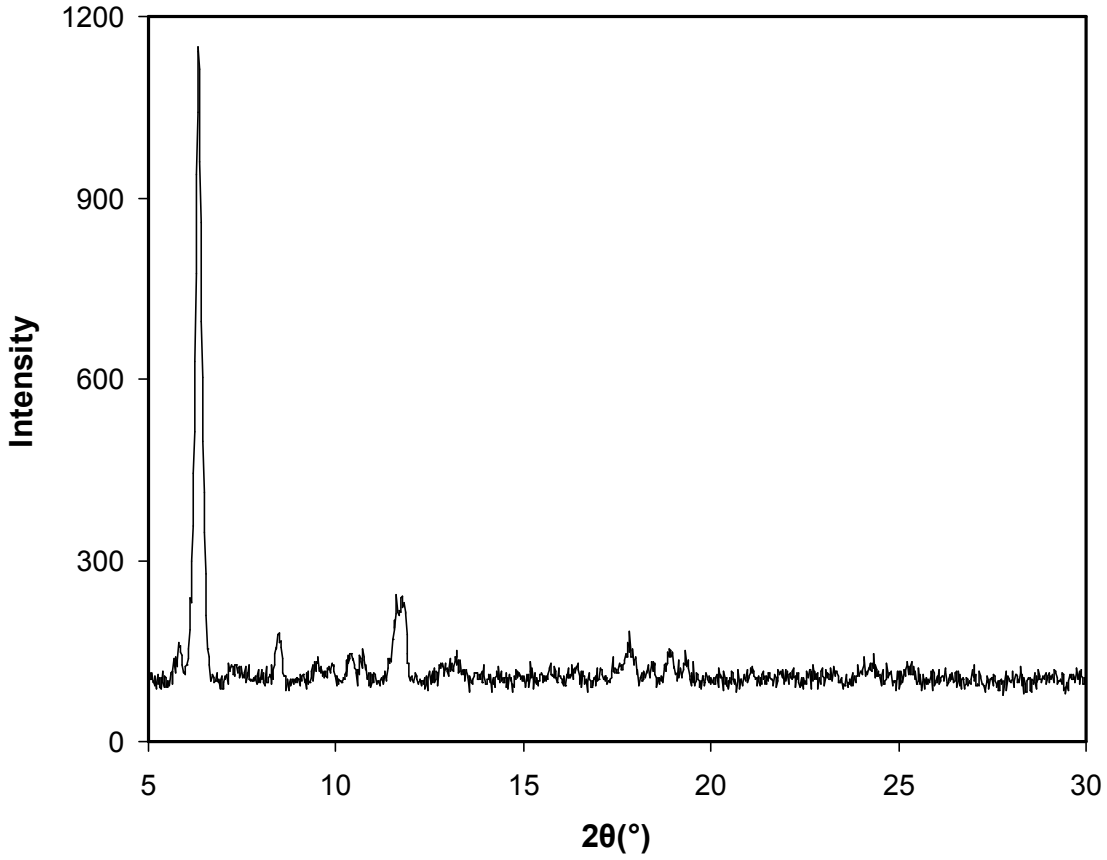


Fig. S1. X-ray powder diffractograms of the $Fe_3O(BPDC)_3$.

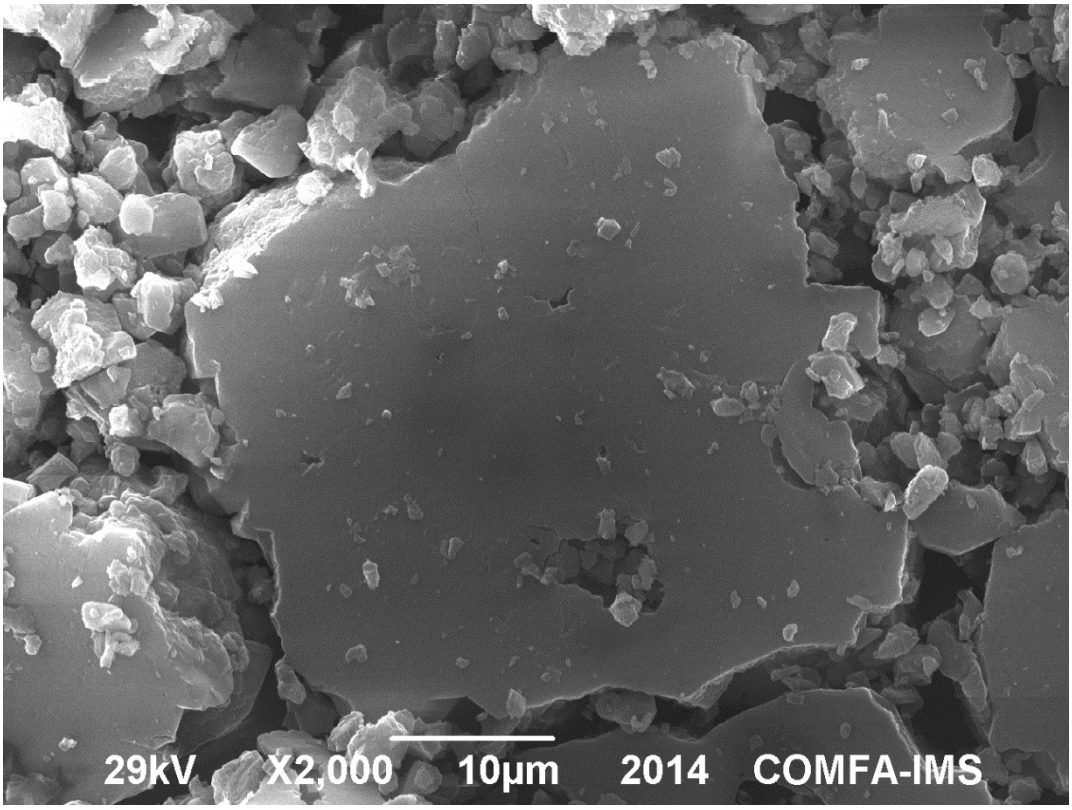


Fig. S2. SEM micrograph of the $Fe_3O(BPDC)_3$.

AAS of $Fe_3O(OH)(H_2O)_2(BPDC)_3$ provided the value of 17.32 % Fe, which is line with the theoretical value of 17.55 %

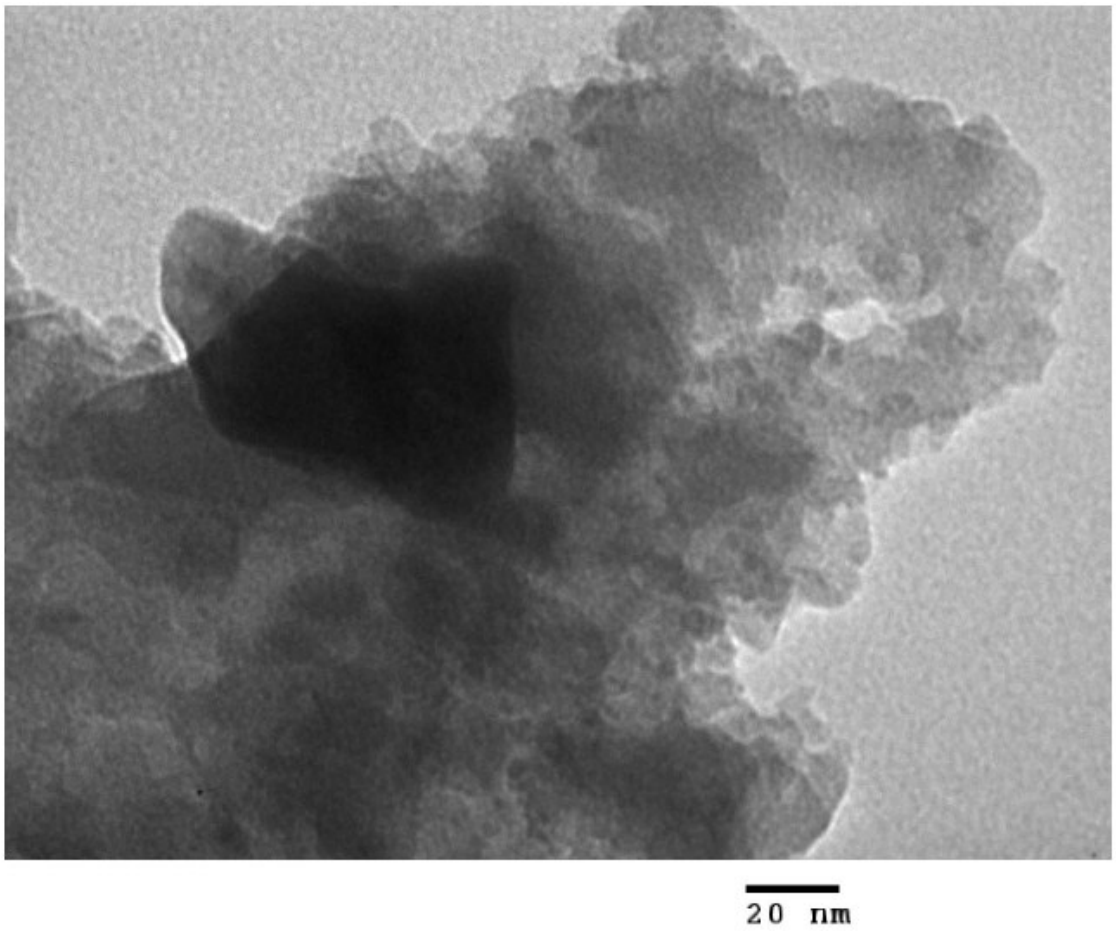


Fig. S3. TEM micrograph of the $Fe_3O(BPDC)_3$.

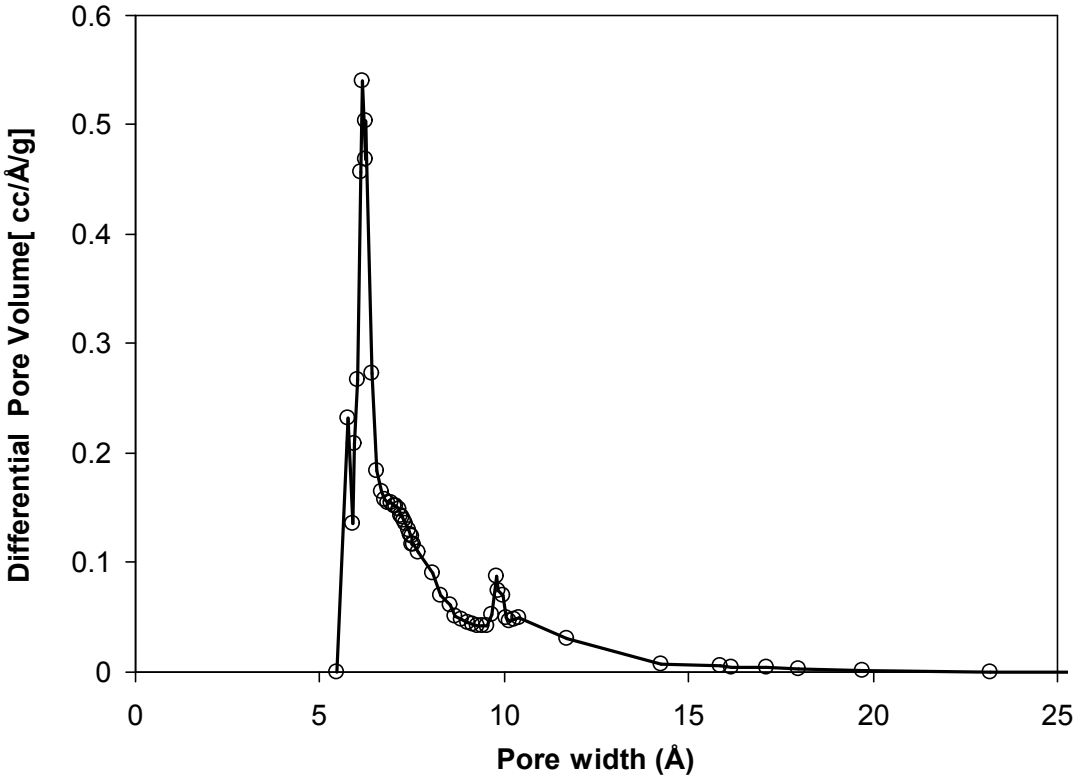


Fig. S4. Pore size distribution of the $Fe_3O(BPDC)_3$.

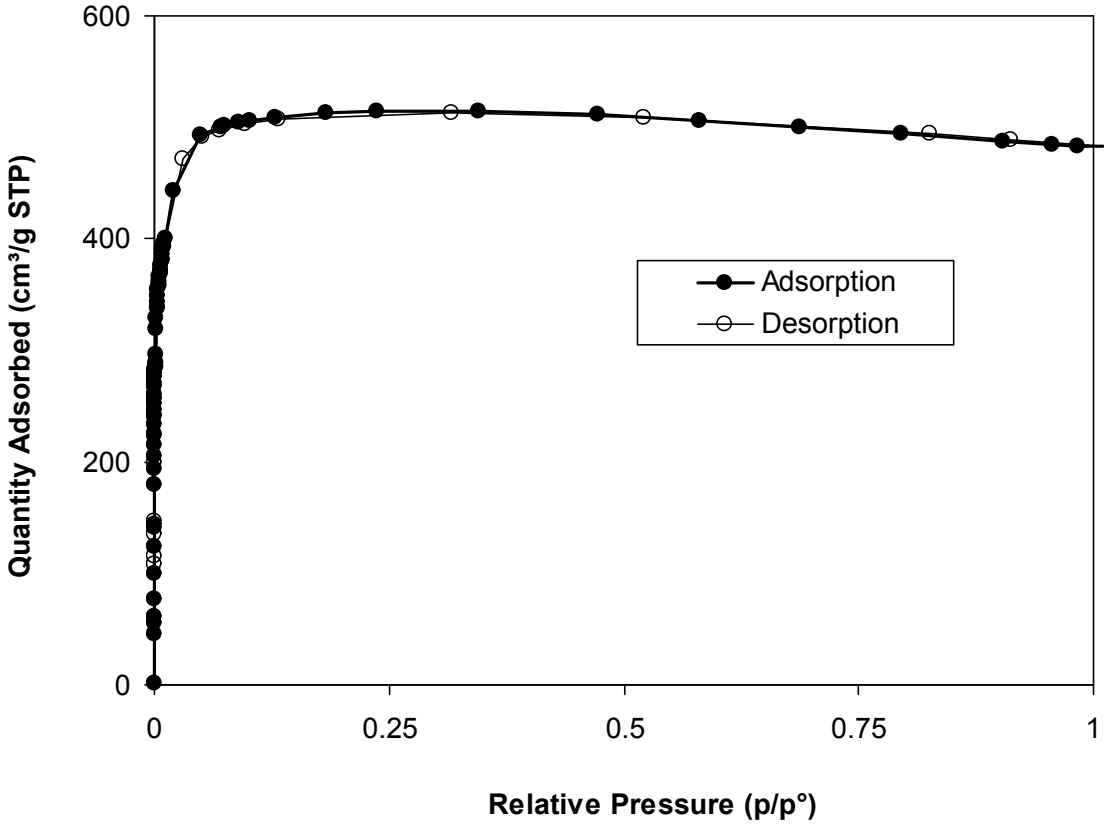


Fig. S5. Nitrogen adsorption/desorption isotherm of the $Fe_3O(BPDC)_3$. Adsorption data are shown as closed circles and desorption data as open circles.

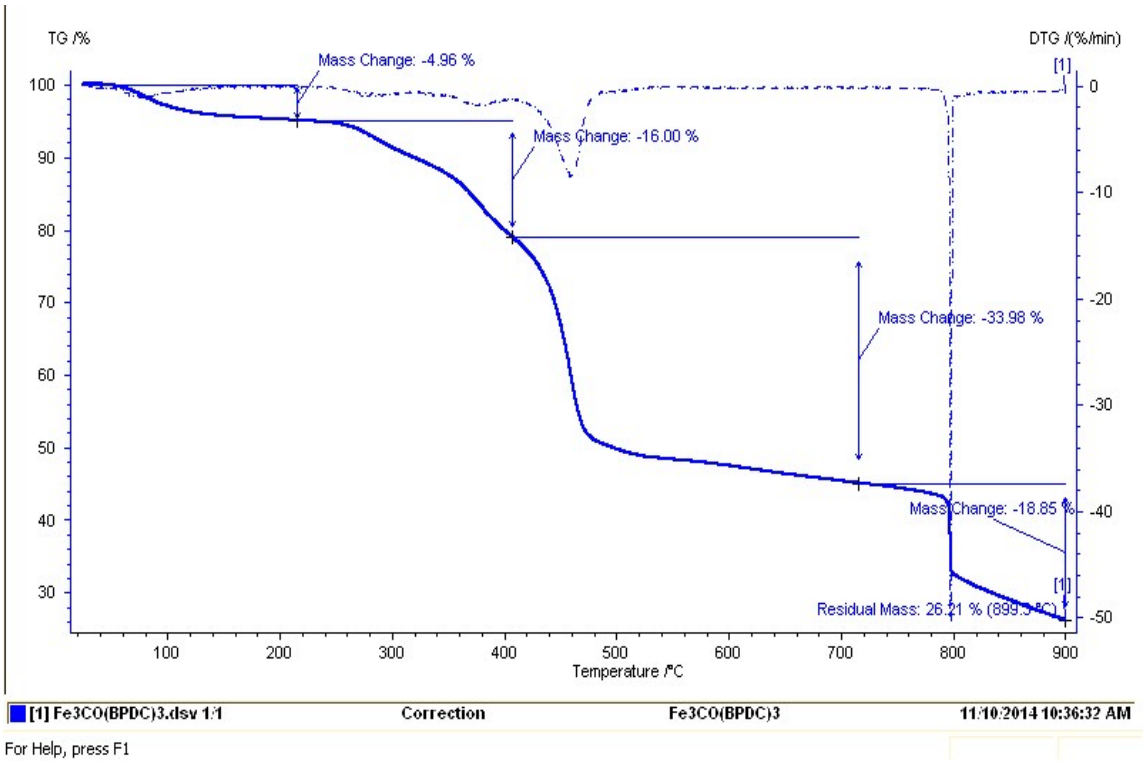


Fig. S6. TGA analysis of the $Fe_3O(BPDC)_3$.

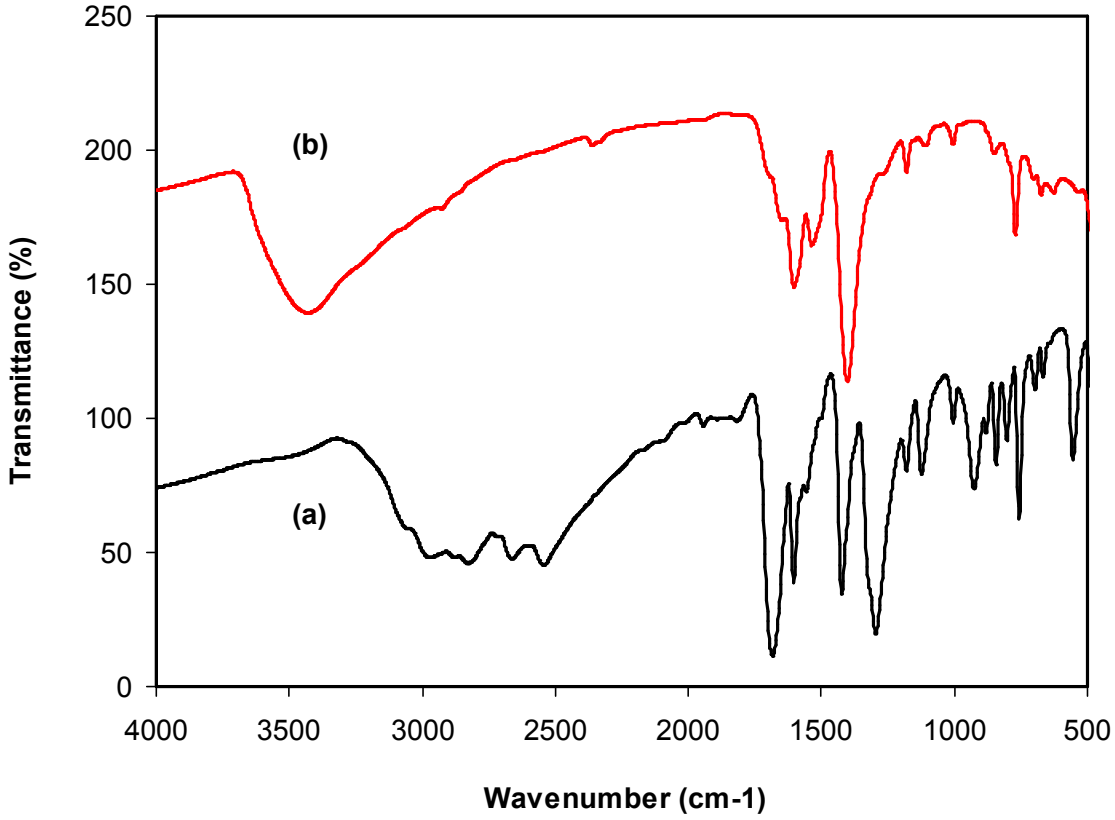


Fig. S7. FT-IR spectra of biphenyl-4,4'-dicarboxylic acid (a), and the $Fe_3O(BPDC)_3$ (b).

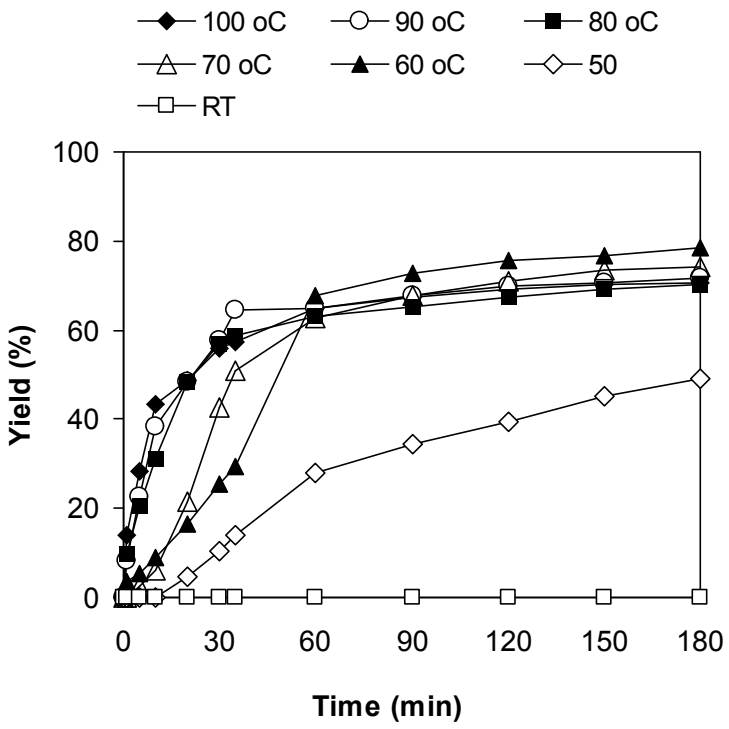


Fig. S8. Effect of temperature on the reaction yield with aliquots taken at 5 min intervals at early reaction time.

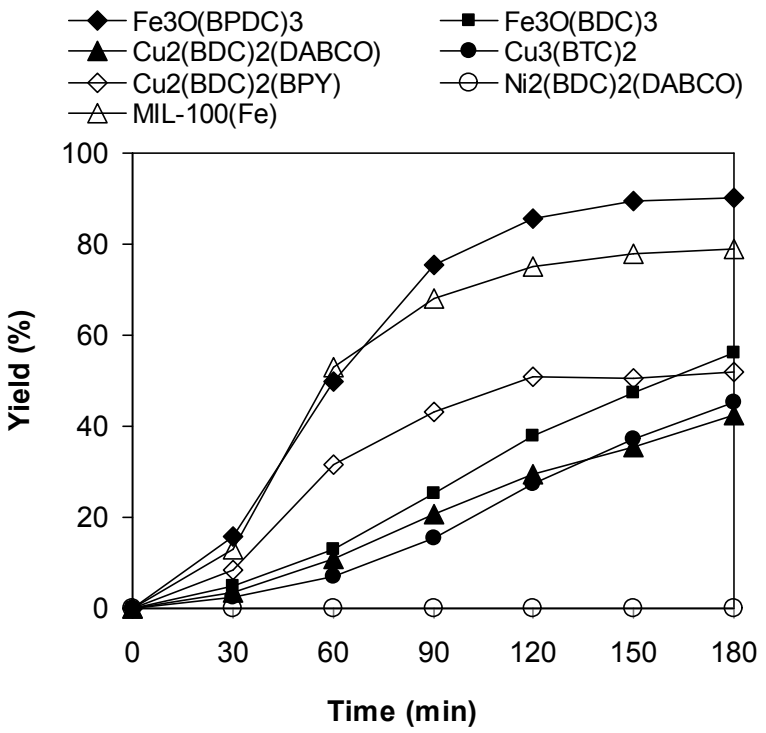
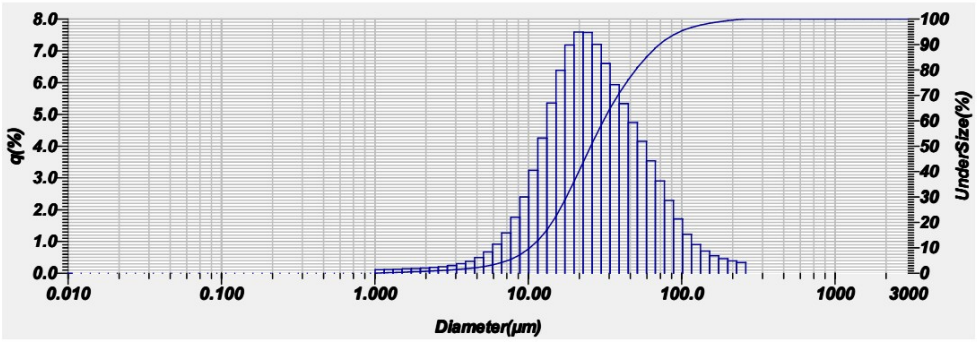
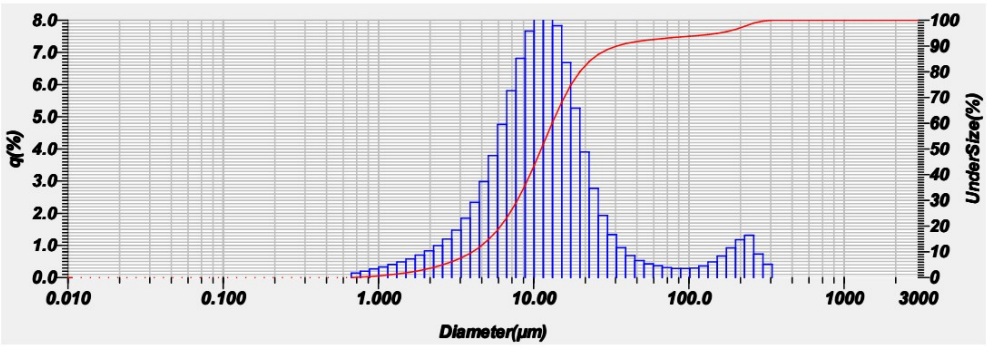


Fig. S9. Different MOFs as catalyst for the synthesis of 3-acetylcoumarin.



(a)



(b)

Fig. S10. The particle size analysis (DLS) of non-grinded $Fe_3O(BPDC)_3$(a) and grinded $Fe_3O(BPDC)_3$(b)

Table S1. Particle size of grinded and non-grinded $Fe_3O(BPDC)_3$

MOFs	Median size (μm)	Mean size (μm)
non-grinded $Fe_3O(BPDC)_3$	25.60	35.85
grinded $Fe_3O(BPDC)_3$	11.22	25.61

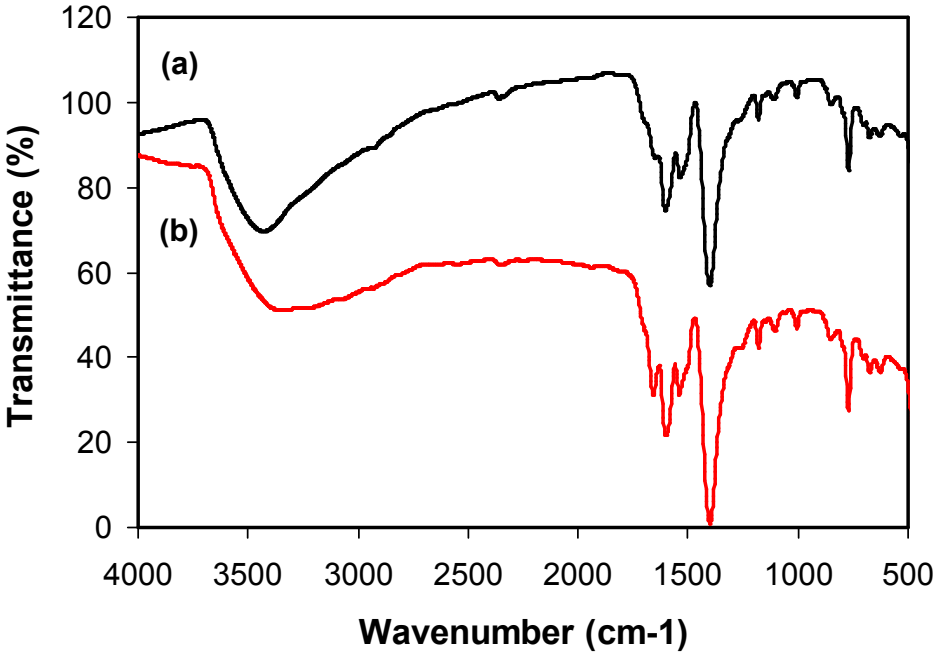


Fig. S11. FT-IR spectra of the fresh (a) and 4th used (b) $Fe_3O(BPDC)_3$ catalyst.

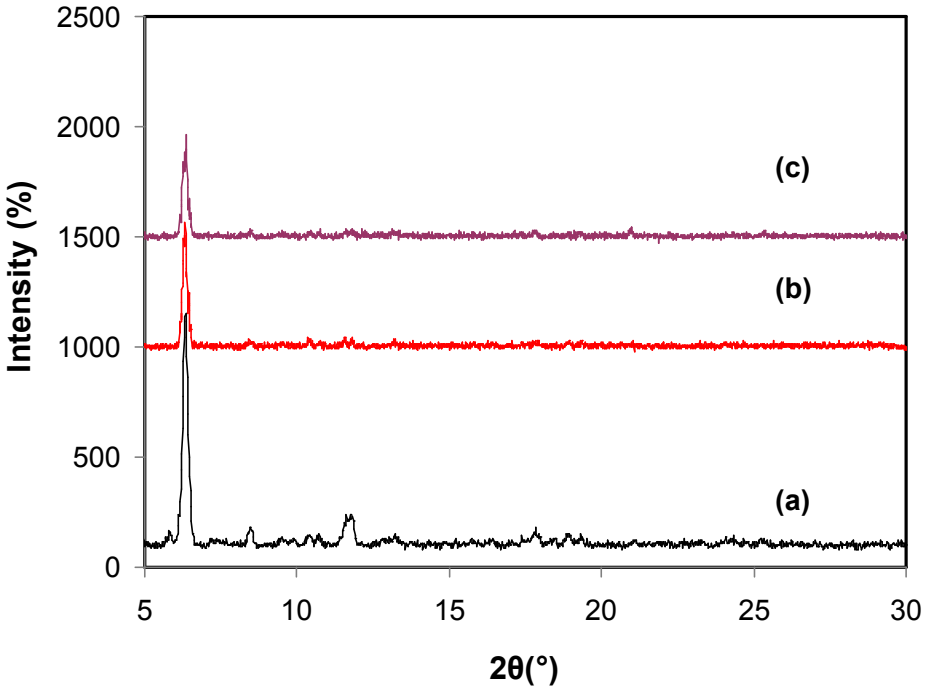


Fig. S12. X-ray powder diffractograms of the fresh (a), 2nd (b), and 4th (c) used $Fe_3O(BPDC)_3$ catalyst.

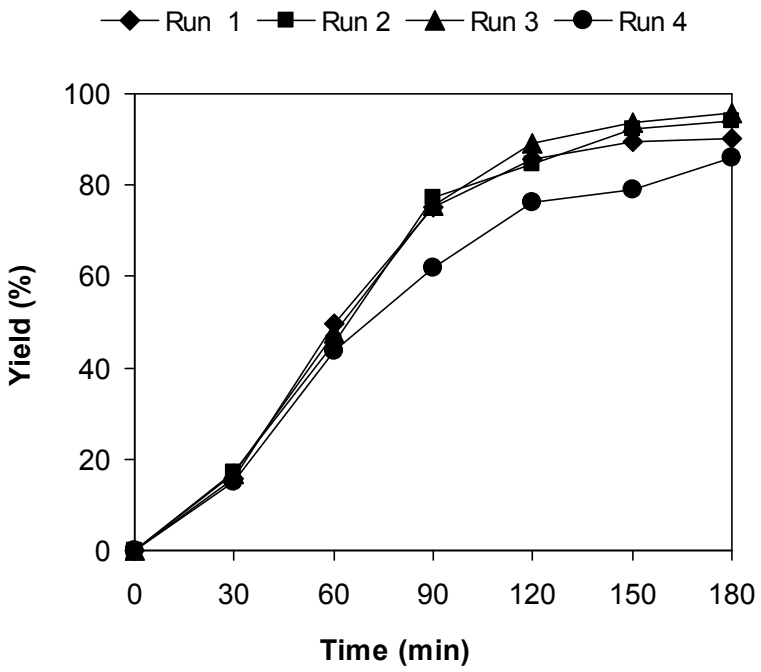
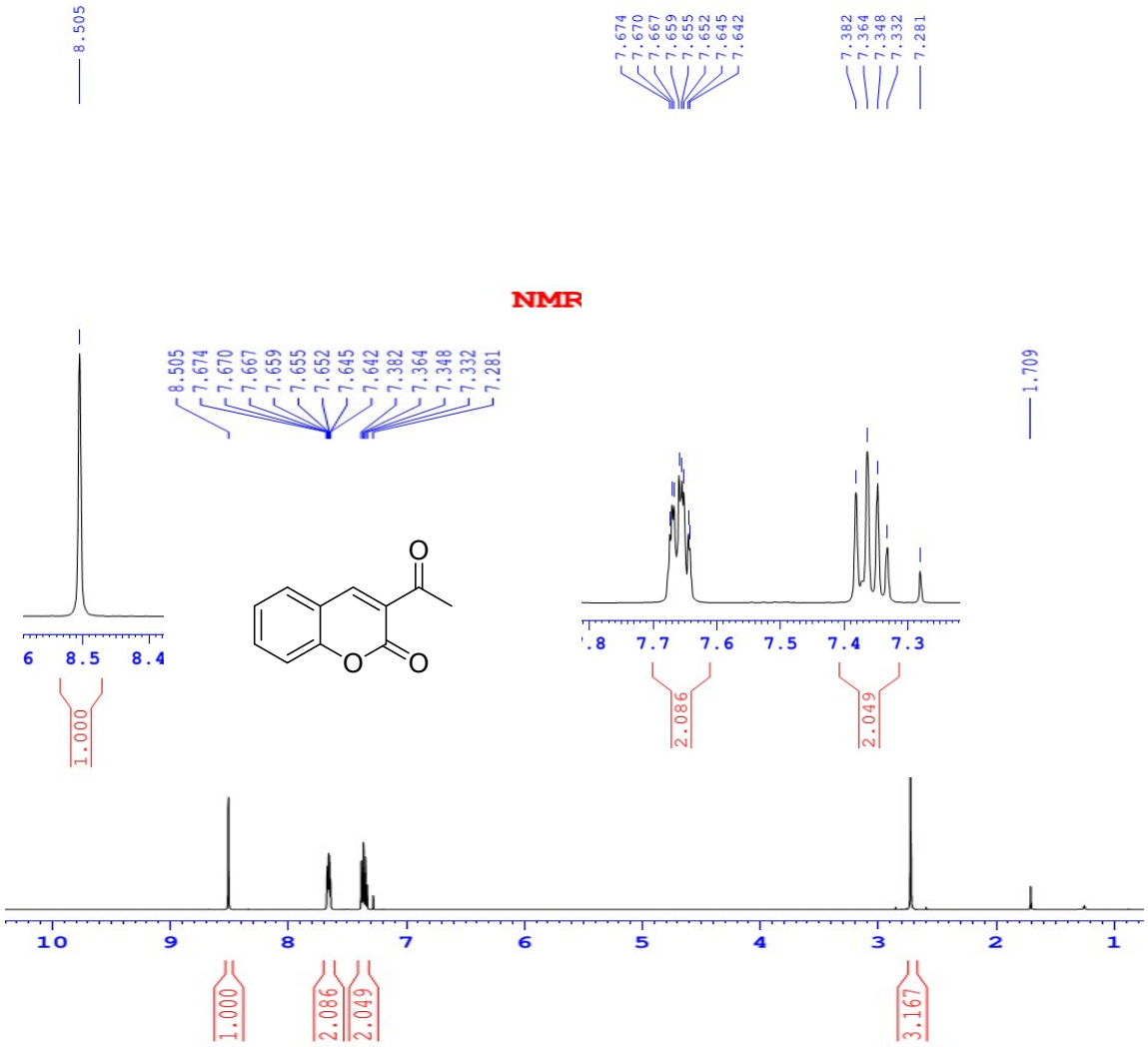
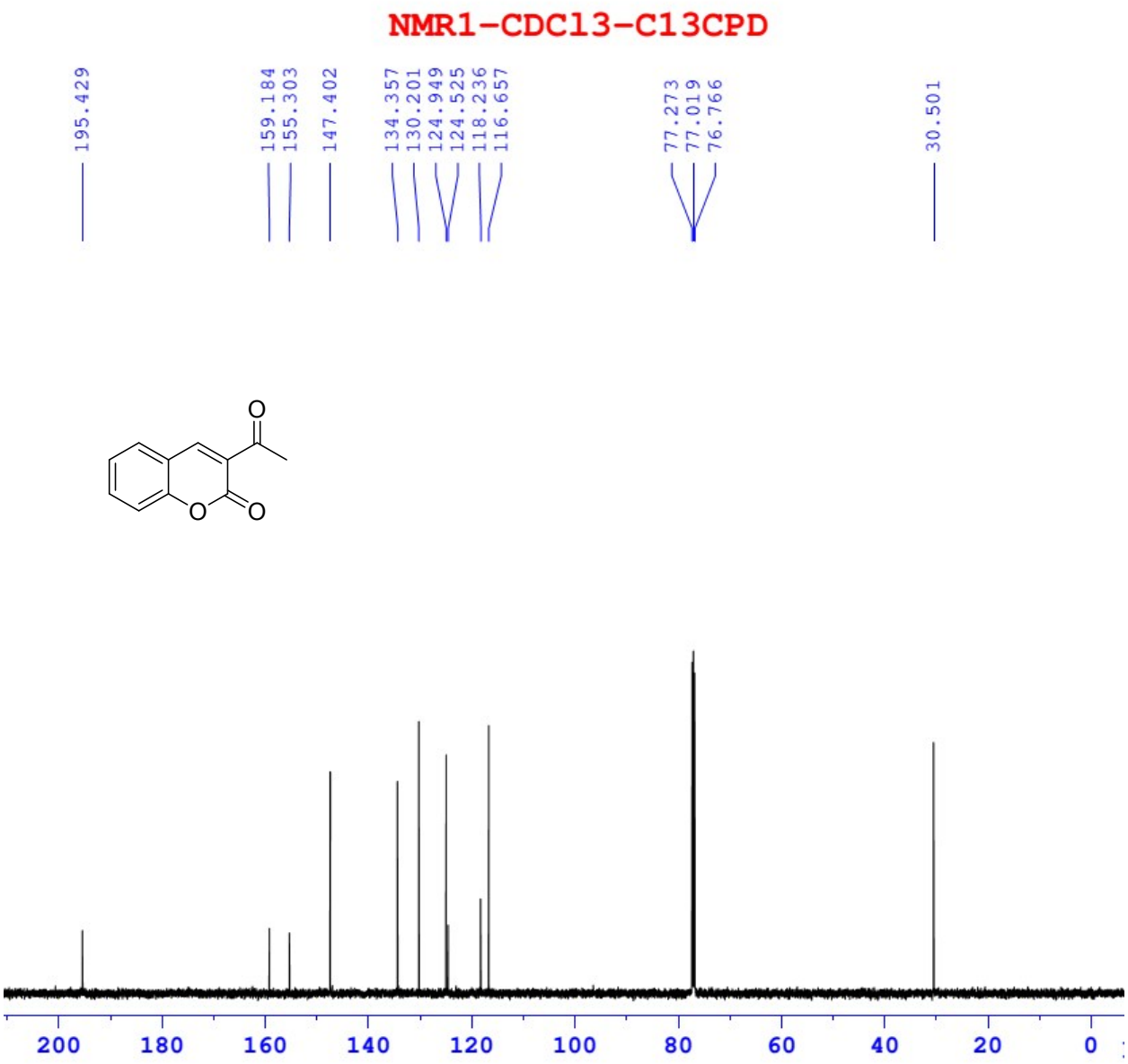


Fig. S13. Reaction yields along the time for the different reuses in catalyst recycling study.


8.505
7.674
7.670
7.667
7.659
7.655
7.652
7.645
7.642
7.382
7.364
7.348
7.332
7.281
NMR
1.709
O
O
O
6
8.5
8.4
.8
7.7
7.6
7.5
7.4
7.3
1.000
2.086
2.049
10
9
8
7
6
5
4
3
2
1
1.000
2.086
2.049
3.167

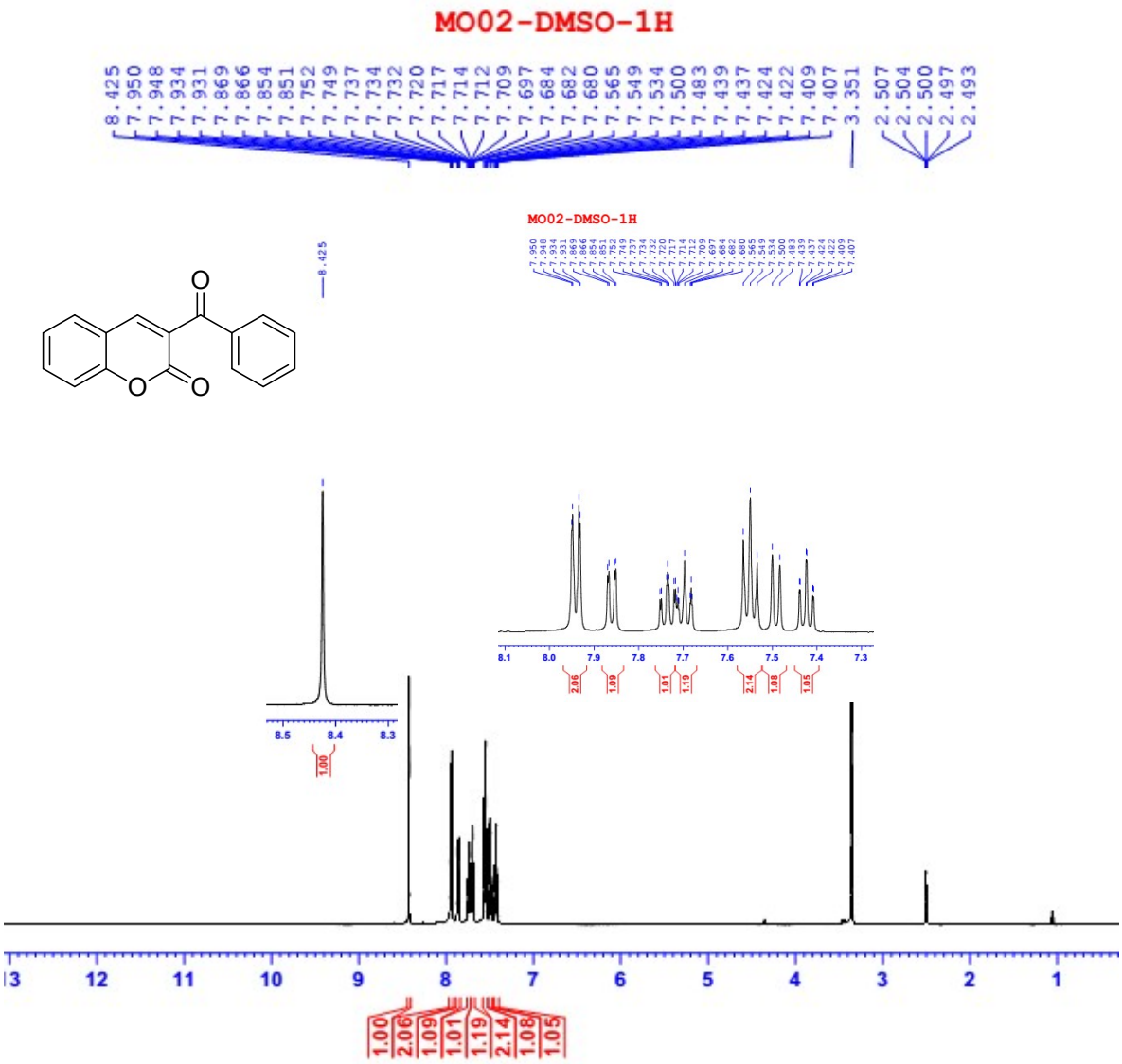
(a)



(b)

Figure S14. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of 3-acetyl-2H-chromen-2-one in $CDCl_3$.

3-acetyl-2H-chromen-2-one. Salicylaldehyde (0.122 g, 1.0 mmol), methyl acetoacetate (0.348 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 60 ^{o}C, 3 h. After recrystallization (ethanol/water = 1:1), 167 mg yellow solid was obtained (89%). This compound is known. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 8.51 (s, 1H), 7.66 (m, 2H), 7.37 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 195.4, 159.2, 155.3, 147.4, 134.4, 130.2, 125.0, 124.5, 118.2, 116.7, 30.5.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7.950
7.948
7.934
7.931
7.869
7.866
7.854
7.851
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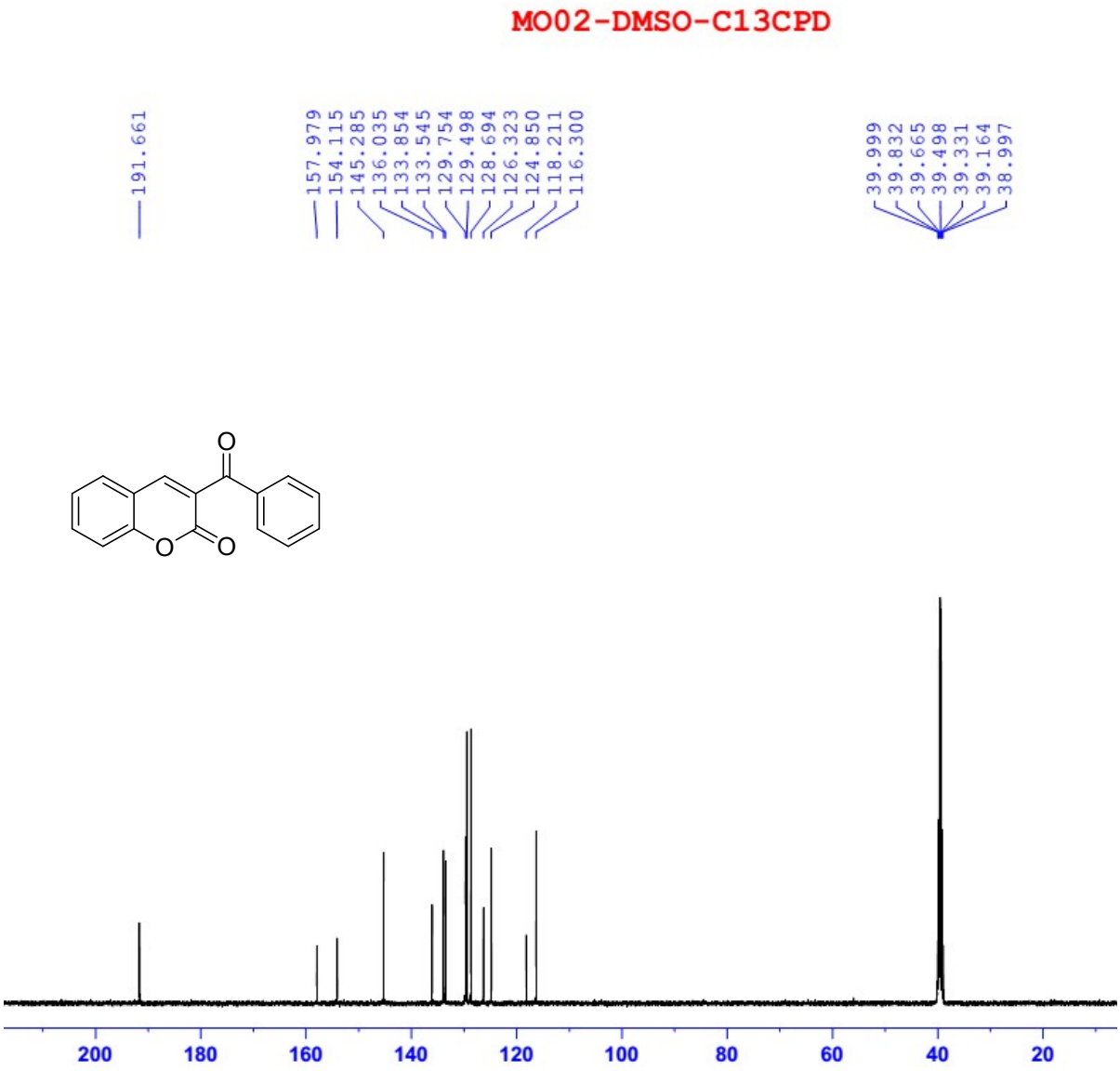
7.749
7.737
7.734
7.732
7.720
7.717
7.714
7.712
7.709
7.697
7.684
7.682
7.680
7.565
7.549
7.534
7.500
7.483
7.439
7.437
7.424
7.422
7.409
7.407
3.351
2.507
2.504
2.500
2.497
2.493
O
O
O
1.00
2.06
1.09
1.01
1.19
2.14
1.08
1.05

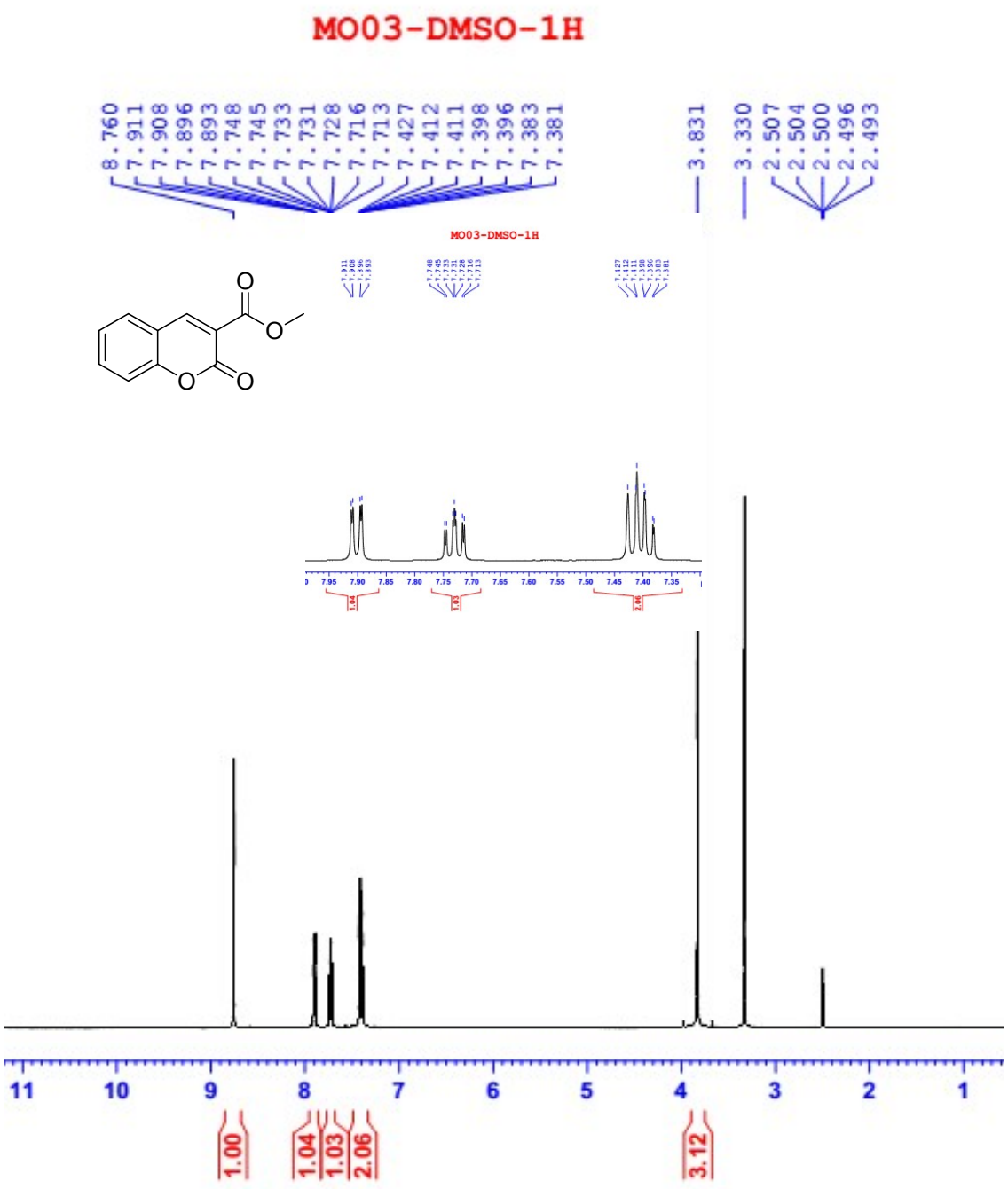
(a)



(b)

Figure S15. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of 3-benzoyl-2H-chromen-2-one in DMSO.

3-benzoyl-2H-chromen-2-one. Salicylaldehyde (0.122 g, 1.0 mmol), ethyl benzoylacetate (0.576 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 60 ^{o}C, 3 h. After chromatography (Hex/EtOAc = 3:1), 110 mg white solid was obtained (44%). This compound is known. ^{1}H NMR (500 MHz, DMSO, ppm): δ = 8.42 (s, 1H), 7.94 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 7.5 Hz, 1H), 7.73 (m, 1H), 7.71 (m, 1H). ^{13}C NMR (125 MHz, DMSO, ppm): δ = 191.6, 157.9, 154.1, 145.3, 136, 133.8, 133.5, 129.7, 129.5, 128.7, 126.3, 124.8, 118.2, 116.3, 39.5


MO03-DMSO-1H
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7.911
7.908
7.896
7.893
7.748
7.745
7.733
7.731
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7.716
7.713
7.427
7.412
7.411
7.398
7.396
7.383
7.381
3.831
3.330
2.507
2.504
2.500
2.496
2.493
O
O
O
O
11
10
9
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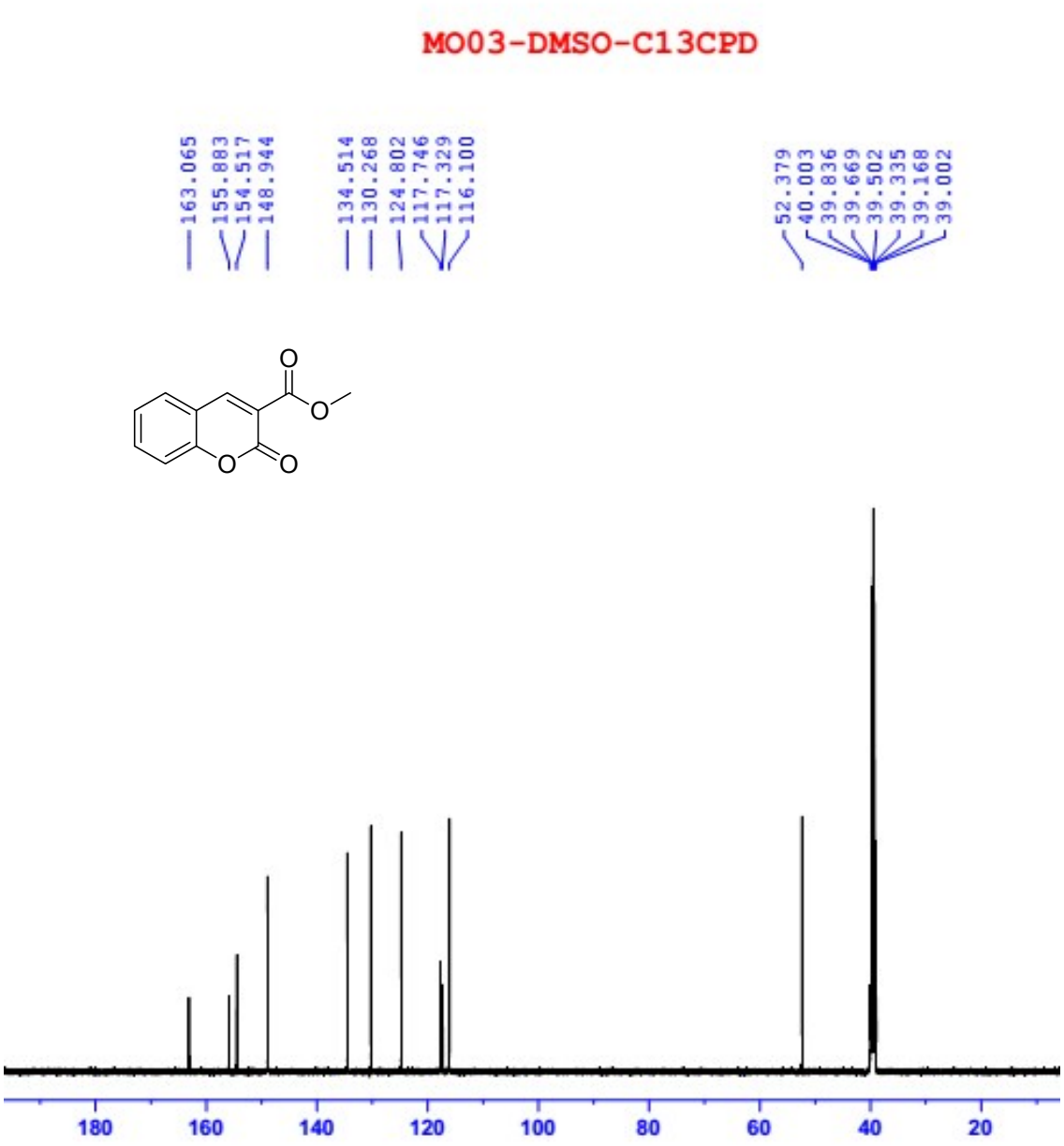
4
3
2
1
1.00
1.04
1.03
2.06
3.12

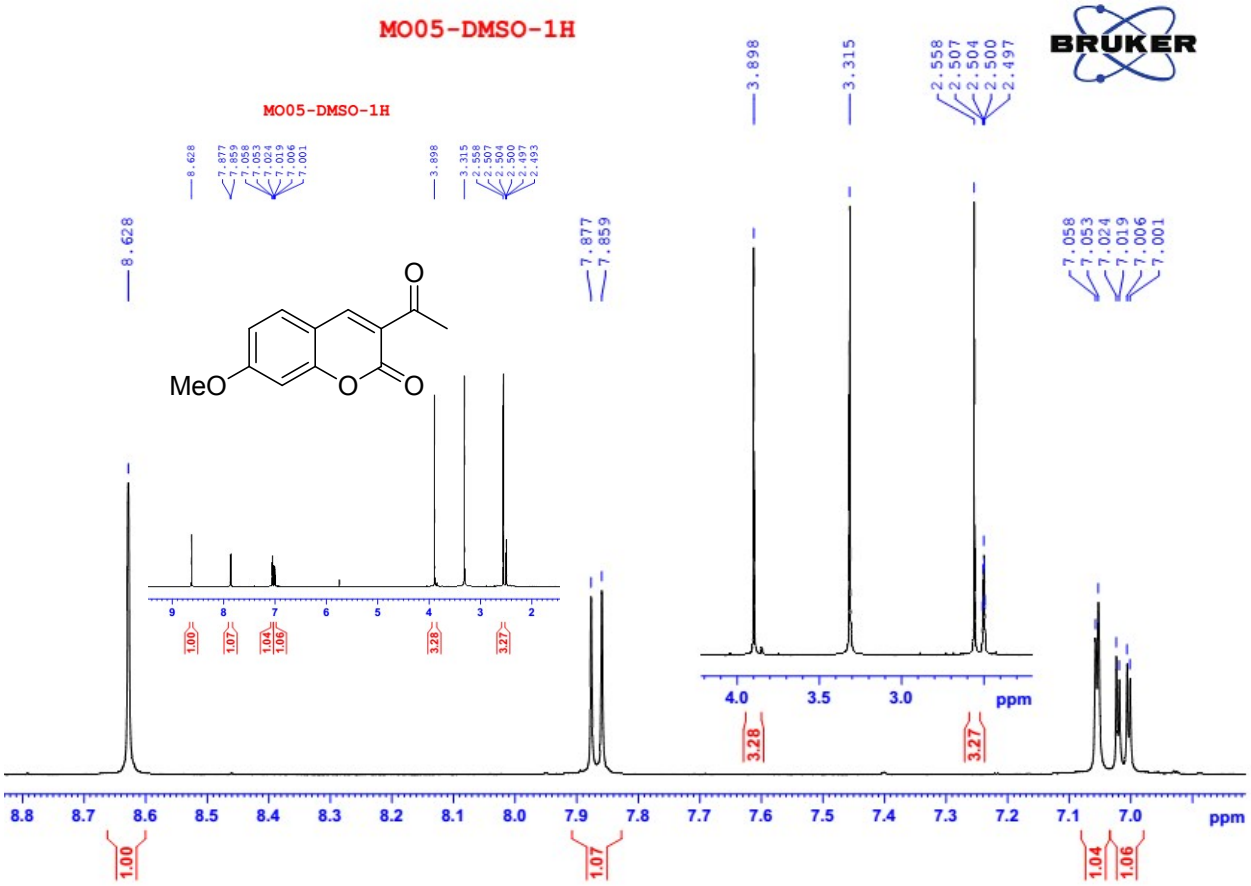
(a)



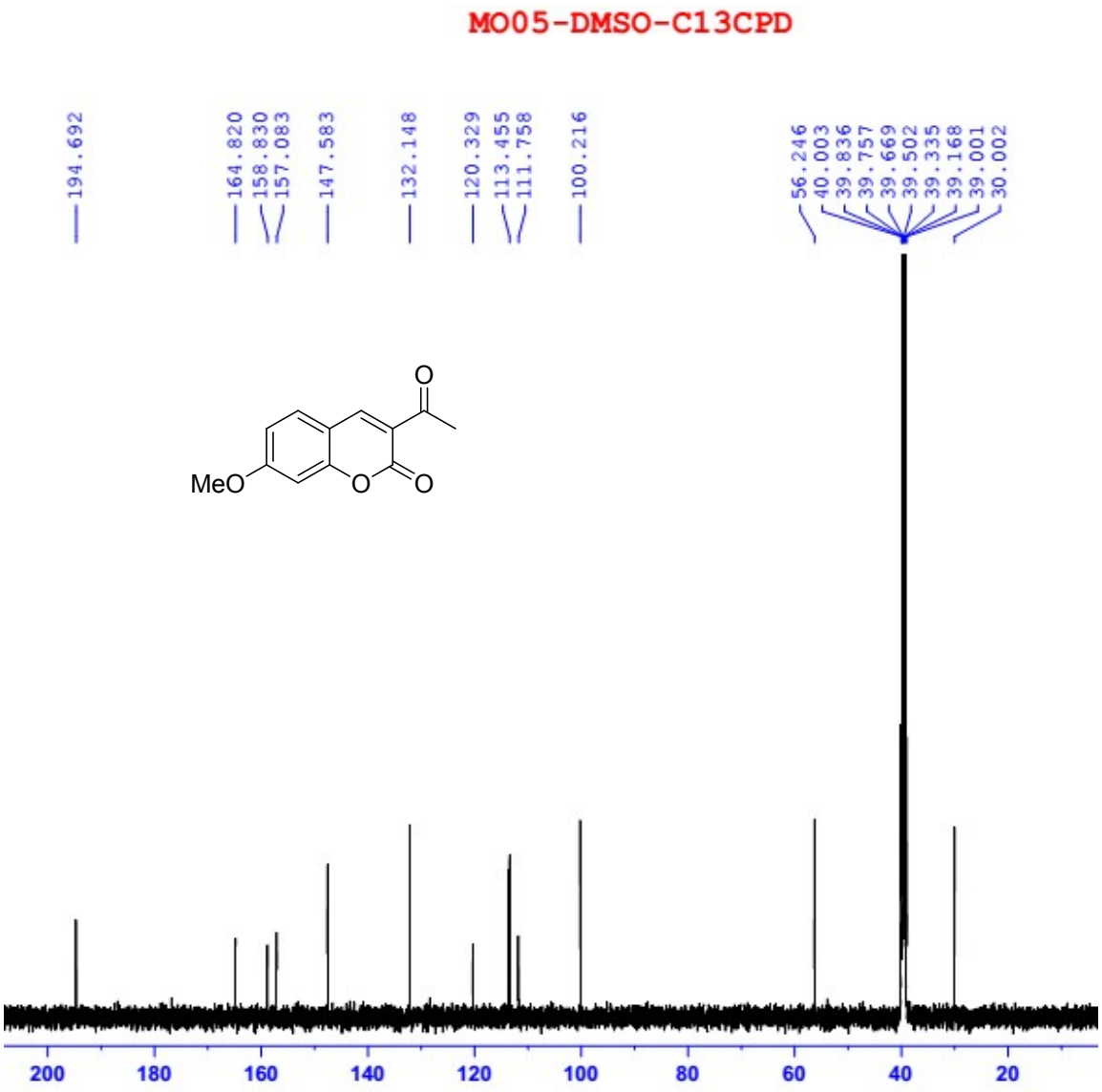
(b)

Figure S16. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of methyl 2-oxo-2H-chromene-3-carboxylate in DMSO.

methyl 2-oxo-2H-chromene-3-carboxylate. Salicylaldehyde (0.122 g, 1.0 mmol), dimethyl malonate (0.396 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 60 ^{o}C, 3 h. After recrystallization (ethanol/water = 1:1), 57.2 mg white solid was obtained (28%). This compound is known. ^{1}H NMR (500 MHz, DMSO, ppm): δ = 8.76 (s, 1H), 7.9 (dd, J = 7.5, J = 1.5, 1H), 7.731 (dt, J = 7 Hz, J = 1.5, 1H), 7.4 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, DMSO, ppm): δ = 163.1, 155.9, 154.5, 148.9, 134.5, 130.3, 124.8, 117.7, 117.3, 1161, 52.4.


MO05-DMSO-1H
BRUKER
MO05-DMSO-1H
8.628
7.877
7.859
7.058
7.053
7.024
7.019
7.006
7.001
3.898
3.315
2.558
2.507
2.504
2.500
2.497
MeO
O
O
O
ppm
1.00
1.07
1.04
1.06
3.28
3.27

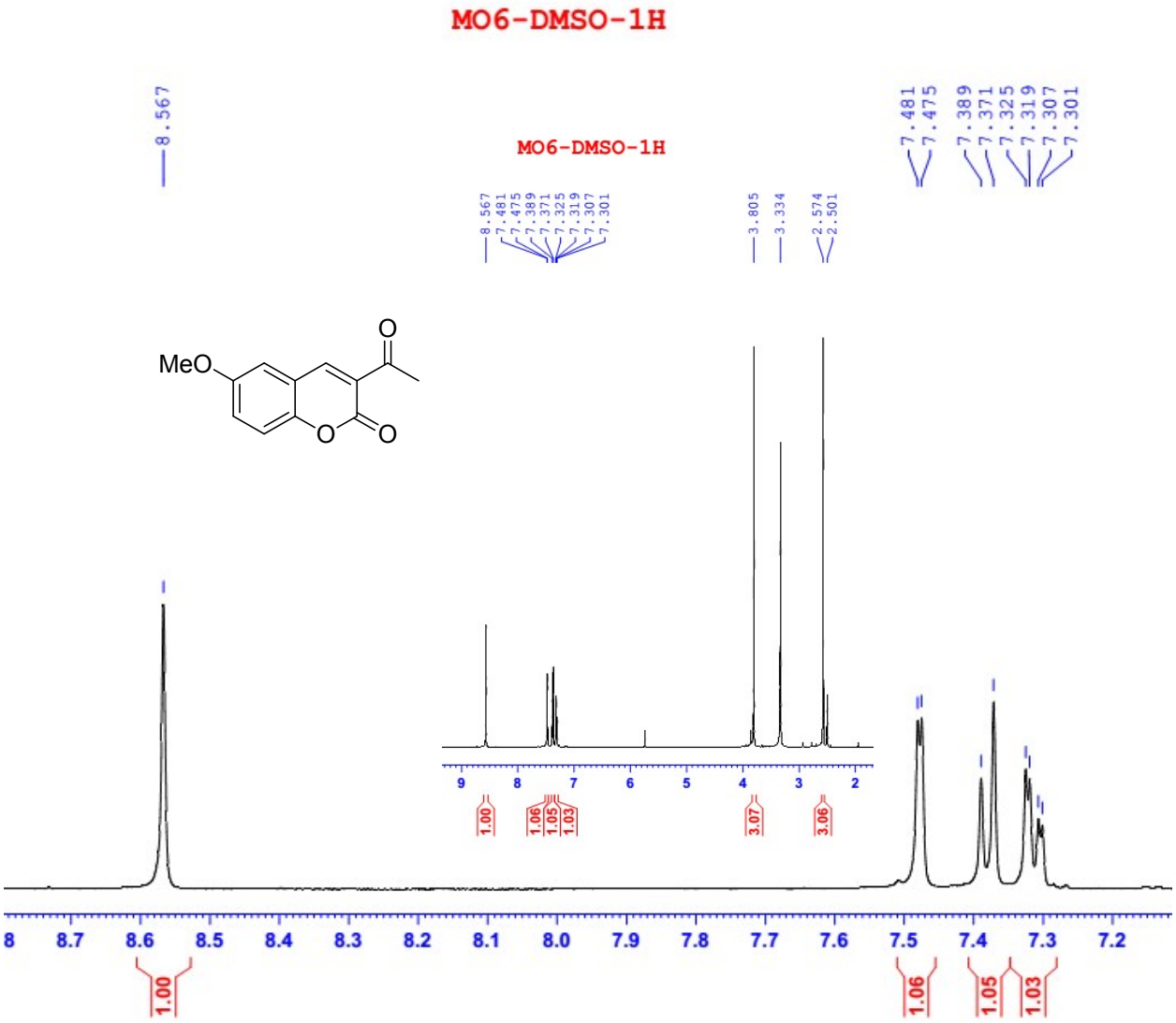
(a)



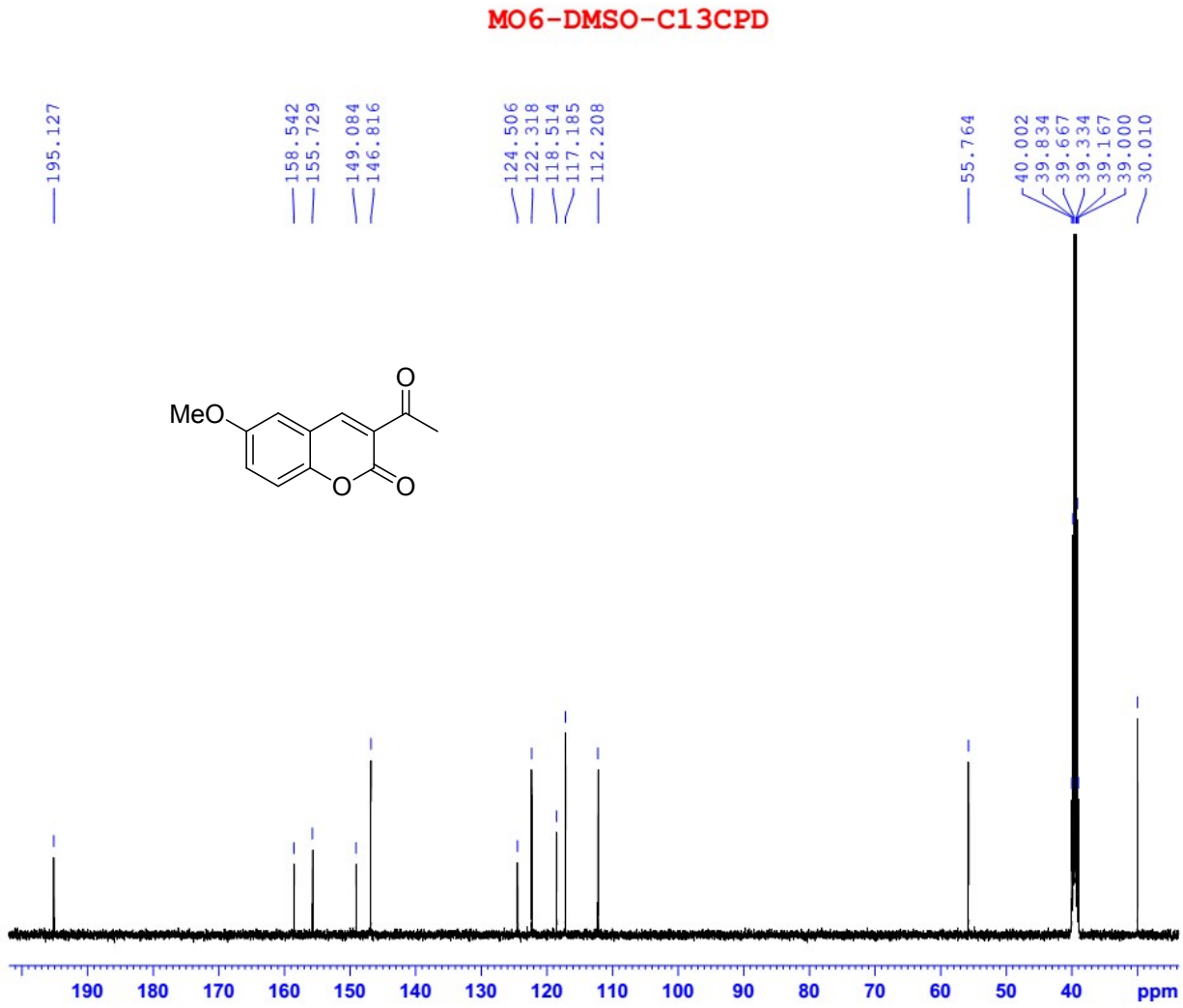
(b)

Figure S17. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of 3-acetyl-8-methoxy-2H-chromen-2-one in DMSO.

3-acetyl-8-methoxy-2H-chromen-2-one. 2-hydroxy-4-methoxy benzaldehyde (0.152 g, 1.0 mmol), methyl acetoacetate (0.348 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 80 °C, 9 h. After chromatography (Hex/EtOAc = 2:1), 141.7 mg yellow solid was obtained (65%). This compound is known. ^{1}H NMR (500 MHz, DMSO, ppm): δ = 8.63 (s, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.05 (d, J = 2.5 Hz, 1H), 7.01 (dd, J = 9 Hz, J = 2.5 Hz, 1H) 3.9 (s, 3H), 2.5 (s, 3H). ^{13}C NMR (125 MHz, DMSO, ppm): δ = 194.7, 164.8, 158.8, 157.7, 147.6, 132.1, 120.3, 113.5, 111.6, 100.2, 56.2, 30.0.



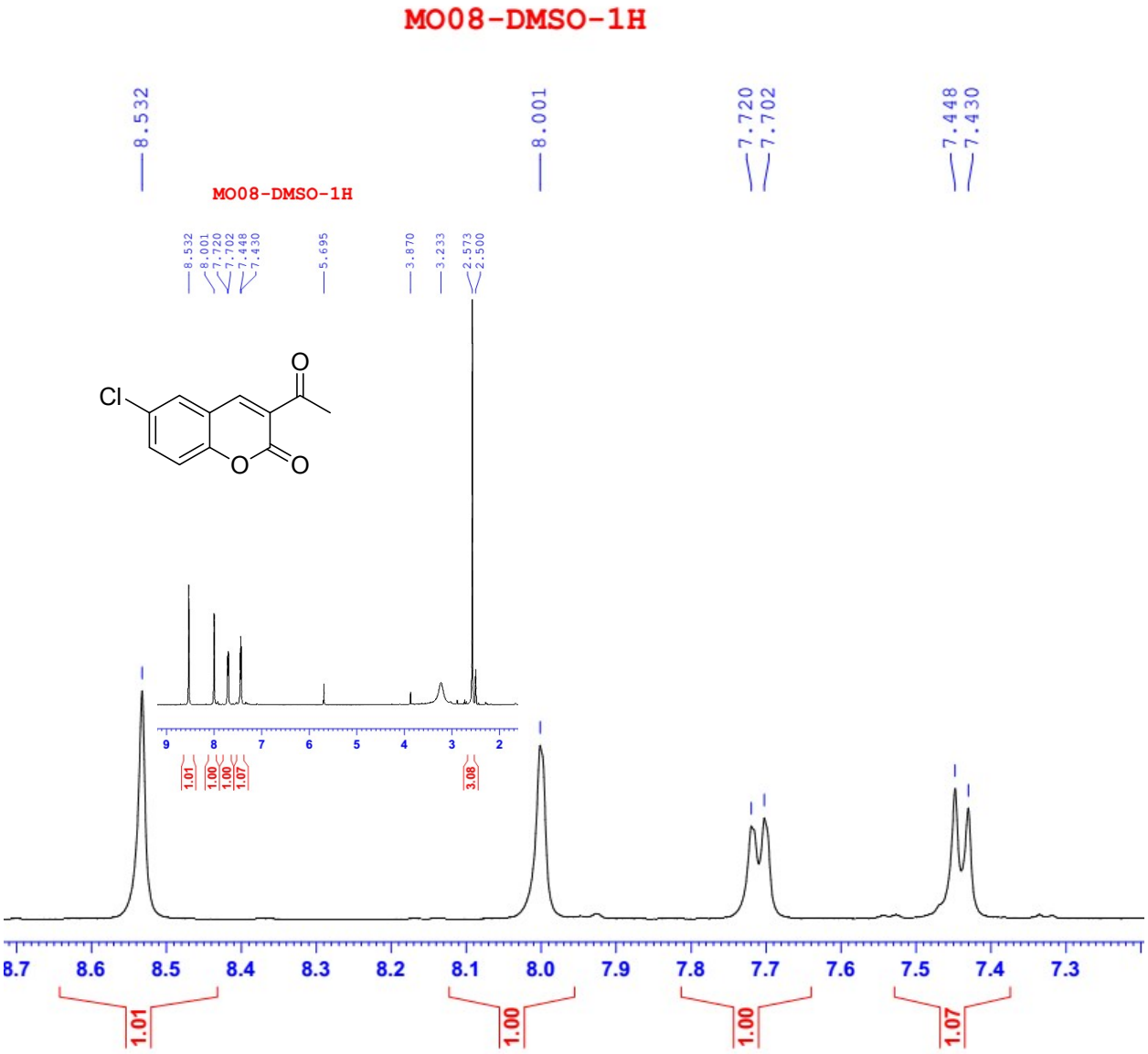
(a)



(b)

Figure S18. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of 3-acetyl-7-methoxy-2H-chromen-2-one in DMSO.

3-acetyl-7-methoxy-2H-chromen-2-one. 2-hydroxy-5-methoxy benzaldehyde (0.152 g, 1.0 mmol), methyl acetoacetate (0.348 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 80 °C, 9 h. After chromatography (Hex/EtOAc = 2:1), 207 mg yellow solid was obtained (95%). Reaction at 60 °C, 3 h afforded 42 % yield. This compound is known. ^{1}H NMR (500 MHz, DMSO, ppm): δ = 8.57 (s, 1H), 7.48 (d, J = 3.0 Hz, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.31 (dd, J = 9 Hz, J = 3 Hz, 1H), 3.81 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, DMSO, ppm): δ = 195.1, 158.5, 155.7, 149.1, 146.8, 124.5, 122.3, 118.3, 117.2, 112.2, 55.8, 30.0.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7.720
7.702
7.448
7.430
MO08-DMSO-1H
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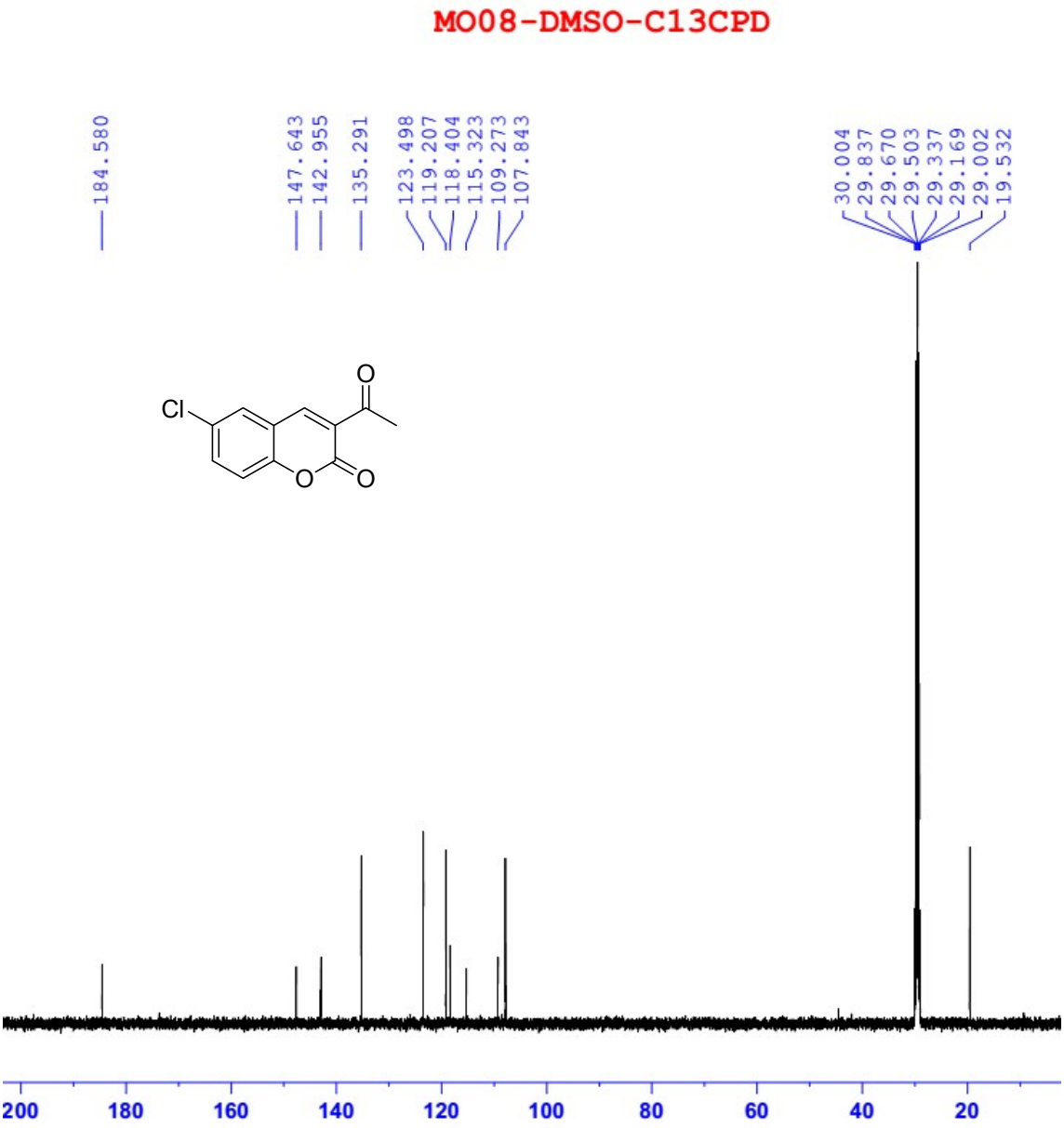
3.870
3.233
2.573
2.500
Cl
O
O
O
1.01
1.00
1.00
1.07
3.08
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
1.01
1.00
1.00
1.07

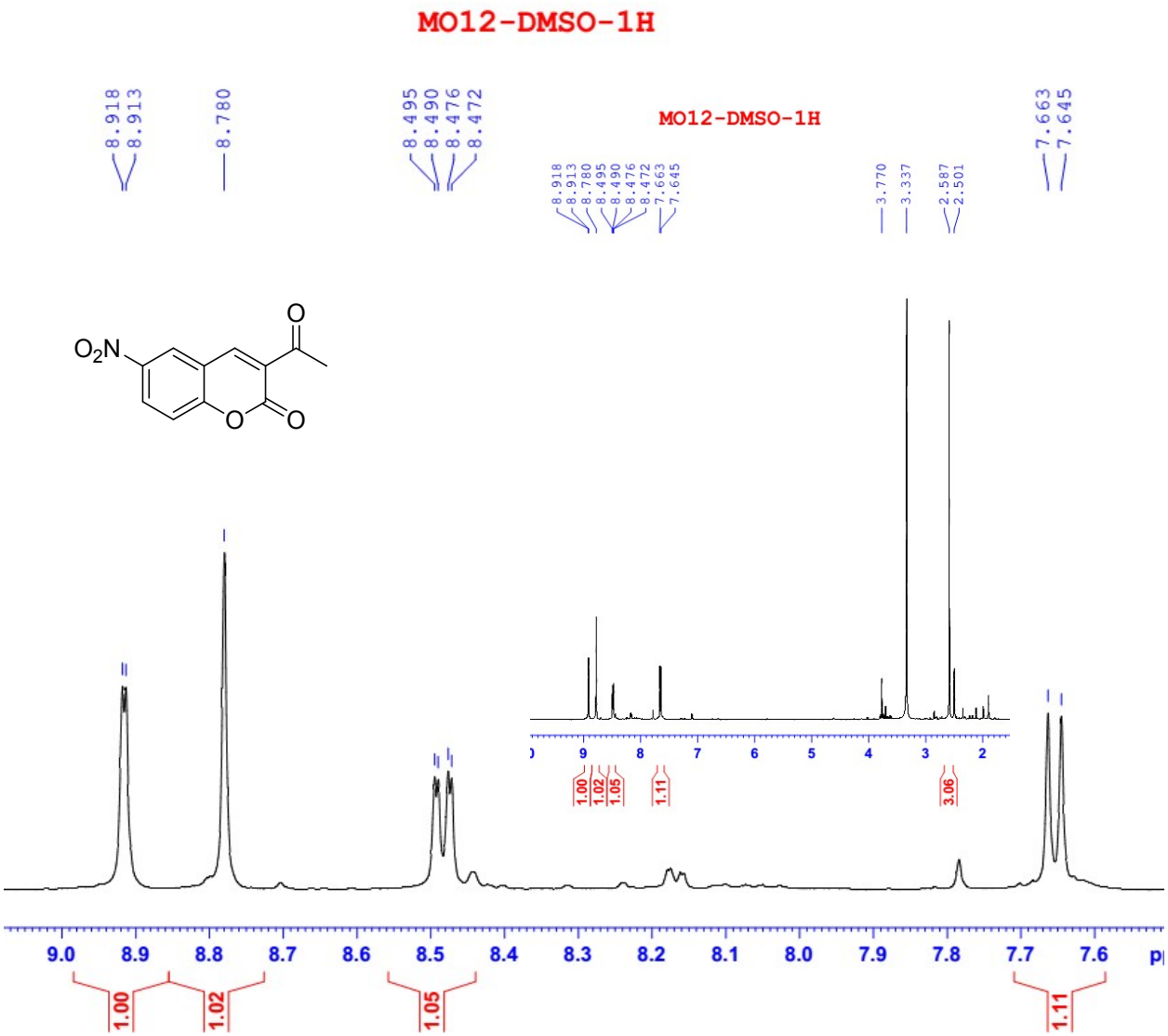
(a)



(b)

Figure S19. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of 3-acetyl-7-chloro-2H-chromen-2-one in DMSO.

3-acetyl-7-chloro-2H-chromen-2-one. 2-hydroxy-5-chloro benzaldehyde (0.156 g, 1.0 mmol), methyl acetoacetate (0.348 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 80 °C, 6 h, 94% yield. Reaction at 60 °C in 3 h afforded 43 % yield. This compound is known. ^{1}H NMR (500 MHz, DMSO, ppm): δ = 8.53 (s, 1H), 8.01 (s, 1H), 7.71 (d, J = 9 Hz, 1H), 7.44 (d, J = 9 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, DMSO, ppm): δ = 184.6, 147.6, 142.9, 135.3, 123.5, 119.2, 118.4, 115.3, 109.3, 107.8, 19.5.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8.490
8.476
8.472
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7.645
3.770
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2.501
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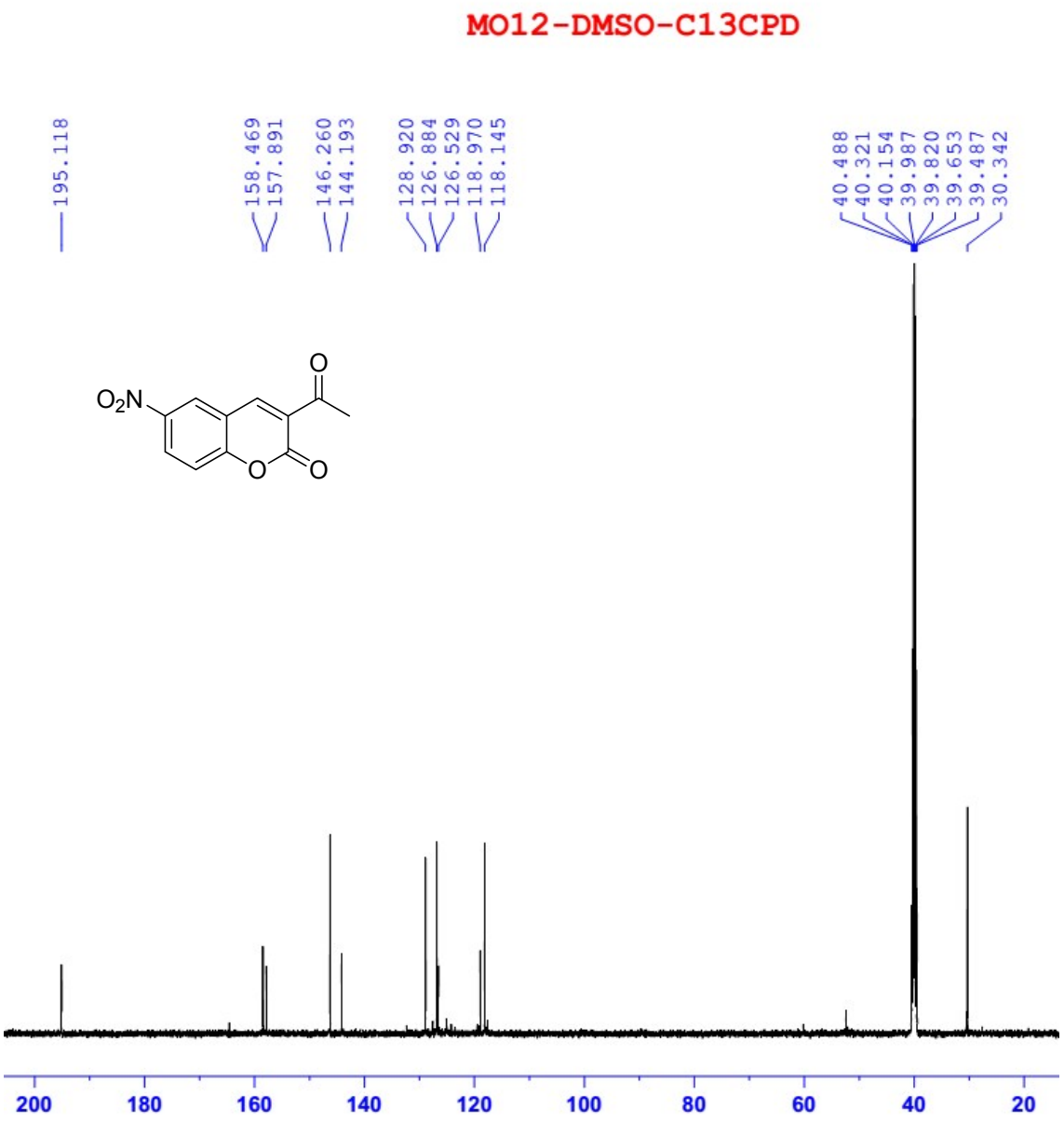
O
O
O
1.00
1.02
1.05
1.11
3.06

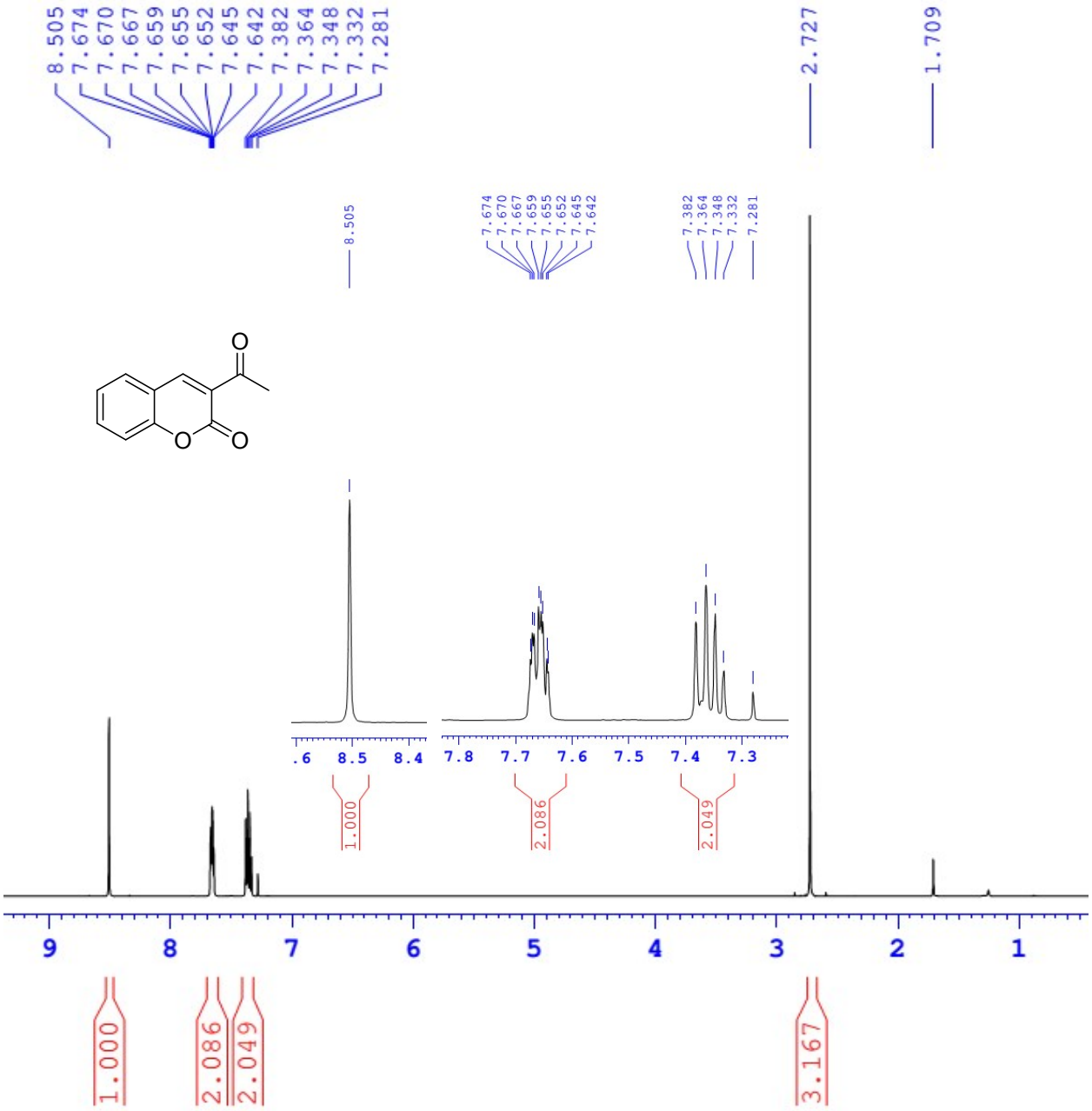
(a)



(b)

Figure S20. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of 3-acetyl-7-nitro-2H-chromen-2-one in DMSO.

3-acetyl-7-nitro-2H-chromen-2-one. 2-hydroxy-5-nitro benzaldehyde (0.167 g, 1.0 mmol), methyl acetoacetate (0.348 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 80 °C, 9 h. After chromatography (Hex/EtOAc = 4:3), 224 mg yellow solid was obtained (96%), reaction at 60 ^{o}C afforded 59 % yield. This compound is known. ^{1}H NMR (500 MHz, DMSO, ppm): δ = 8.91 (d, J = 2.5 Hz, 1H), 8.78 (s, 1H), 8.48 (dd, J = 9 Hz, J = 2.5 Hz, 1H), 7.65 (d, J = 9Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, DMSO, ppm): δ = 195.1, 158.5, 157.9, 146.3, 144.2, 128.9, 126.9, 126.5, 119, 118.1, 30.4.


8.505
7.674
7.670
7.667
7.659
7.655
7.652
7.645
7.642
7.382
7.364
7.348
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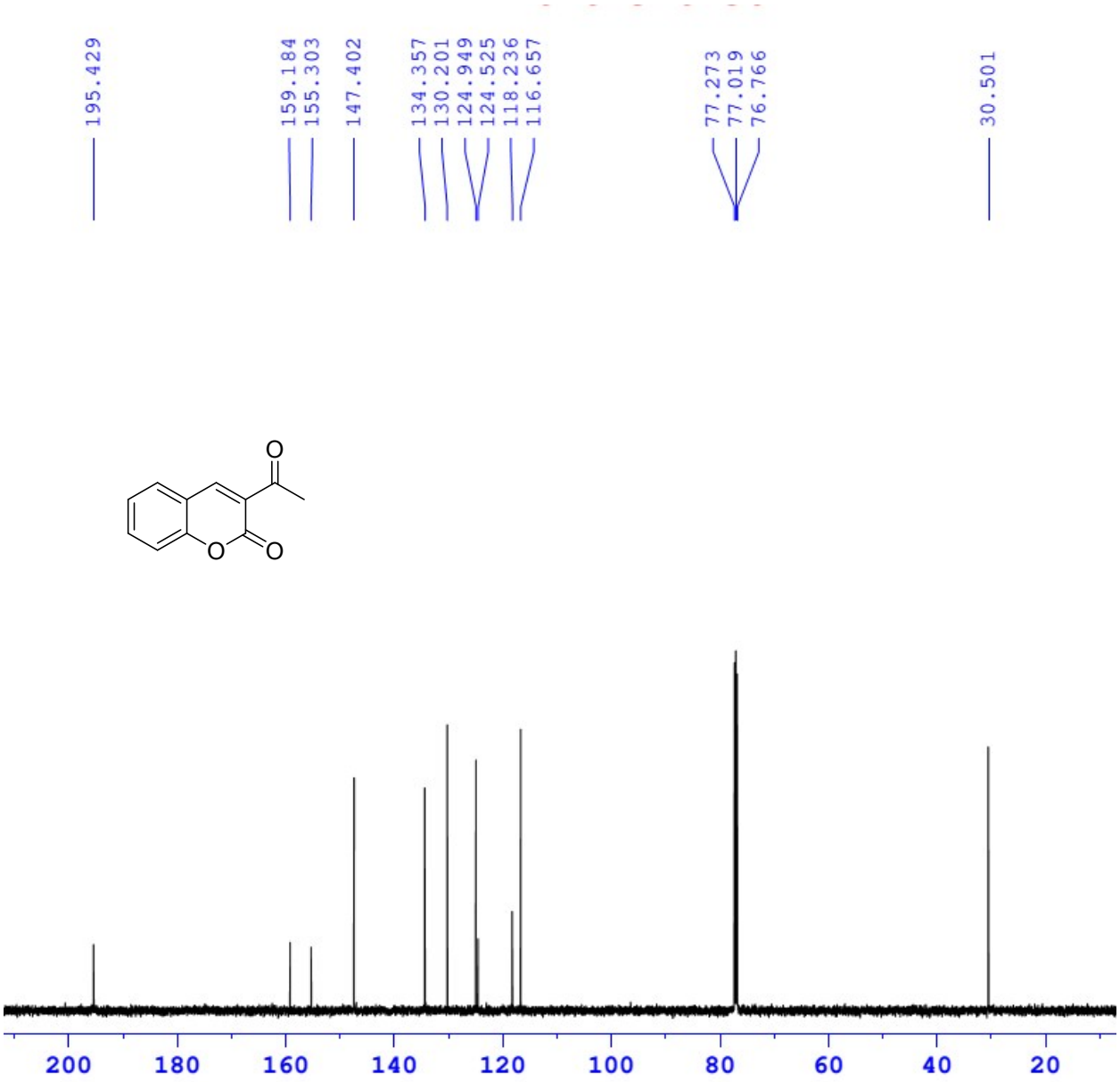
O
O
1.000
2.086
2.049
3.167

(a)



(b)

Figure S21. ^{1}H NMR spectra a) and ^{13}C NMR spectra b) of 3-acetyl-2H-chromen-2-one in $CDCl_3$.

3-acetyl-2H-chromen-2-one. Salicylaldehyde (0.122 g, 1.0 mmol), ethyl acetoacetate (0.390 g, 3.0 mmol), $Fe_3O(BPDC)_3$ (0.015g, 5 mol%), 60 °C, 3h. After recrystallization (ethanol/water = 1:1), 150 mg yellow solid was obtained (80%). This compound is known. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 8.51 (s, 1H), 7.66 (m, 2H), 7.37 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 195.4, 159.2, 155.3, 147.4, 134.4, 130.2, 125.0, 124.5, 118.2, 116.7, 30.5.