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Support Information

Synthesis and *in vitro* antimicrobial activity evaluation of coumarin-3-carboxylic acids obtained via cascade reaction using chitosan as a recyclable catalyst

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Estimation of the degree of deacetylation using the Sabnis and Block Method (1997)[1]

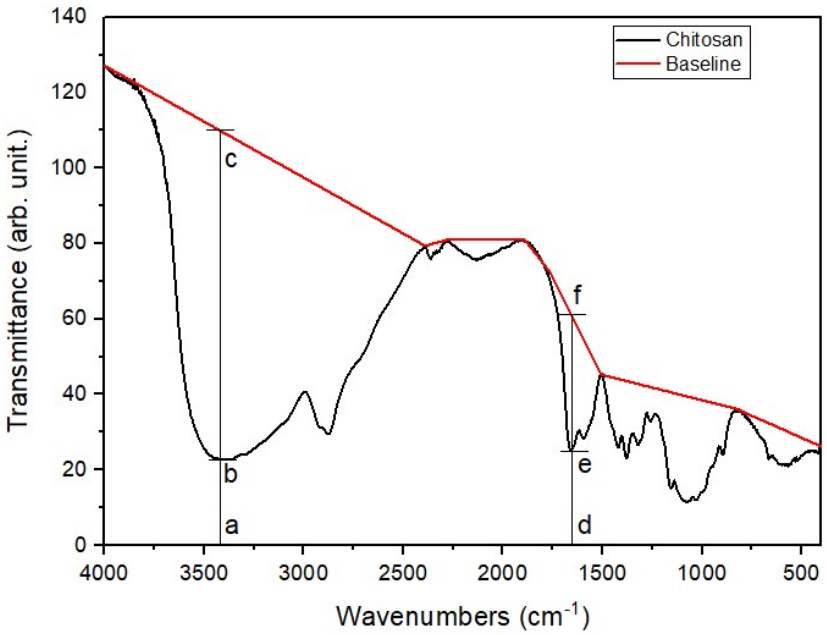


Figure S1. FT-IR spectra of commercial chitosan recorded in the range 400–4000 cm^{-1} using KBr pellets.

The hydroxyl band absorbance (3450 cm^{-1}) is given by:

$$(A)_{hydroxyl} = \log_{10} (AC/AB) \quad \text{Eq. 1}$$

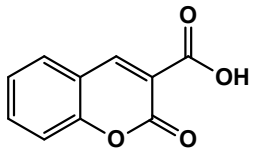
The amide band absorbance (1655 cm^{-1}) is given by:

$$(A)_{amide} = \log_{10} (DF/DE) \quad \text{Eq. 2}$$

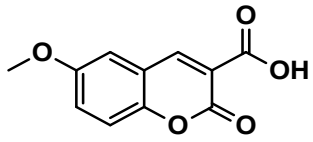
Based on the absorbances of the hydroxyl and amide I signals, the degree of deacetylation (DD) of chitosan is calculated using equation 3:

$$DD = 97.67 - [26.486 \cdot (A_{amide}/A_{hydroxyl})] \quad \text{Eq. 3}$$

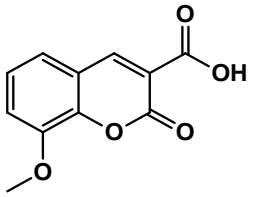
^{1}H and ^{13}C NMR shift data



2-oxo-2H-chromene-3-carboxylic acid (3a): White crystal (79 mg, 83%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 – 7.37 (m, 2H, Ar-H), 7.72 (ddd, 1H, Ar-H, J = 8.8, 7.3, 1.7 Hz), 7.90 (dd, 1H, Ar-H, J = 7.8, 1.7 Hz), 8.73 (s, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 116.16, 118.01, 118.39, 124.87, 130.22, 134.33, 148.39, 154.50, 156.76, 164.02. Displacement data consistent with Brahmachari (2015).[2]

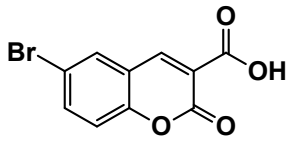


6-methoxy-2-oxo-2H-chromene-3-carboxylic acid (3b): Yellowish crystal (97 mg, 88%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.80 (s, 3H, CH_3), 7.31 (dd, 1H, Ar-H, J = 9.1, 3.0 Hz), 7.37 (d, 1H, Ar-H, J = 9.2 Hz), 7.44 (d, 1H, Ar-H, J = 2.9 Hz), 8.67 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 55.89, 111.90, 117.35, 118.46, 118.64, 122.16, 148.20, 148.99, 155.81, 157.11, 164.12. Displacement data consistent with Brahmachari (2015).[2]

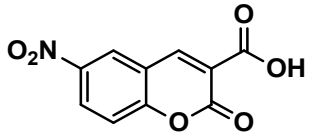


8-methoxy-2-oxo-2H-chromene-3-carboxylic acid (3c): Yellowish crystal (90 mg, 82%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.91 (s, 3H, CH_3), 7.32 (t, 1H, Ar-H, J = 7.9 Hz), 7.41 (ddd, Ar-H, 2H, J = 15.4, 7.9, 1.4 Hz), 8.69 (s, 1H, CH). ^{13}C NMR (125 MHz,

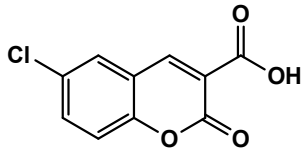
DMSO-d_6) δ 56.22, 116.28, 118.53, 121.14, 124.80, 143.85, 146.28, 148.63, 156.48, 164.02. Displacement data consistent with Chavan and Bandgar (2013).[3]



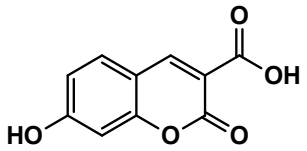
6-Bromo-2-oxo-2H-chromene-3-carboxylic acid (3d): White crystal (112 mg, 83%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.39 (d, 1H, Ar-H, J = 8.8 Hz), 7.85 (dd, 1H, Ar-H, J = 8.8, 2.4 Hz), 8.14 (d, 1H, Ar-H, J = 2.4 Hz), 8.66 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 116.31, 118.50, 119.62, 119.92, 132.04, 136.46, 146.98, 153.57, 156.19, 163.82. Displacement data consistent with Brahmachari (2015).[2]



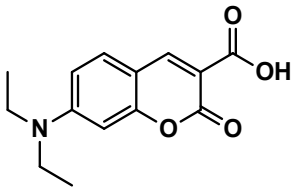
6-nitro-2-oxo-2H-chromene-3-carboxylic acid (3e): Yellowish crystal (96 mg, 82%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (d, 1H, Ar-H, J = 9.2 Hz), 8.48 (dd, 1H, Ar-H, J = 9.1, 2.8 Hz), 8.87 (s, 1H, CH), 8.88 (d, 1H, Ar-H, J = 2.7 Hz). ^{13}C NMR (125 MHz, DMSO-d_6) δ 117.76, 118.40, 120.39, 125.98, 128.38, 143.69, 147.17, 155.51, 158.09, 163.56. Displacement data consistent with Brahmachari (2015).[2]



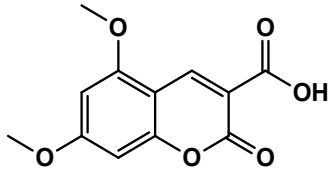
6-chloro-2-oxo-2H-chromene-3-carboxylic acid (3f): White crystal (91 mg, 81%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.47 (d, 1H, J = 8.9 Hz, Ar-H), 7.75 (ddd, 1H, J = 8.8, 2.6, 0.7 Hz, Ar-H), 8.03 (d, 1H, J = 2.6 Hz, Ar-H), 8.69 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 118.17, 119.37, 119.60, 128.42, 128.98, 133.61, 146.97, 153.11, 156.12, 163.75. Displacement data consistent with Brahmachari (2015).[2]



7-hydroxy-2-oxo-2H-chromene-3-carboxylic acid (3g): Yellowish crystal (91 mg, 88%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.73 (d, 1H, J = 2.2 Hz, Ar-H), 6.84 (dd, 1H, J = 8.6, 2.3 Hz, Ar-H), 7.74 (d, 1H, J = 8.6 Hz, Ar-H), 8.68 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 101.81, 110.64, 112.53, 114.03, 132.06, 149.42, 157.01, 157.56, 163.94, 164.24. Displacement data consistent with Brahmachari (2015).[2]



7-(diethylamino)-2-oxo-2H-chromene-3-carboxylic acid (3h): Orange crystal (104 mg, 80%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.13 (t, 6H, J = 7.0 Hz, CH_3), 3.47 (q, 4H, J = 7.1 Hz, CH_2), 6.54 (d, 1H, J = 2.4 Hz, Ar-H), 6.77 (dd, 1H, J = 9.0, 2.4 Hz, Ar-H), 7.62 (d, 1H, J = 9.0 Hz, Ar-H), 8.56 (s, 1H, CH). ^{13}C NMR (126 MHz, DMSO-d_6) δ 12.39, 44.51, 95.98, 107.16, 107.46, 110.17, 131.95, 149.54, 153.02, 157.97, 159.72, 164.62. Displacement data consistent with Bardajee and collaborators (2010).[4]



5,7-dimethoxy-2-oxo-2H-chromene-3-carboxylic acid (3i): Yellowish crystal (96 mg, 77%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.89 (s, 3H, CH_3), 3.94 (s, 3H, CH_3), 6.54 (s, 1H, Ar-H), 6.63 (s, 1H, Ar-H), 8.63 (s, 1H, CH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 56.40, 56.63, 93.05, 95.29, 102.75, 111.35, 143.51, 157.14, 157.65, 158.12, 164.06, 166.28. Displacement data consistent with Chavan and Bandgar (2013).[3]

References

1 S. Sabnis and L. H. Block, *Polym. Bull.,* 1997, **39**, 67-71.

2 G. Brahmachari, *ACS Sustain. Chem. Eng.***,** 2015, **3**, 2350-2358.

3 H. V. Chavan and B. P. Bandgar, *ACS Sustain. Chem. Eng.,* 2013, **1**, 929-936.

4 G. Bardajee, F. Jafarpour and H. Afsari, *Open Chem.,* 2010, **8**, 370-374.

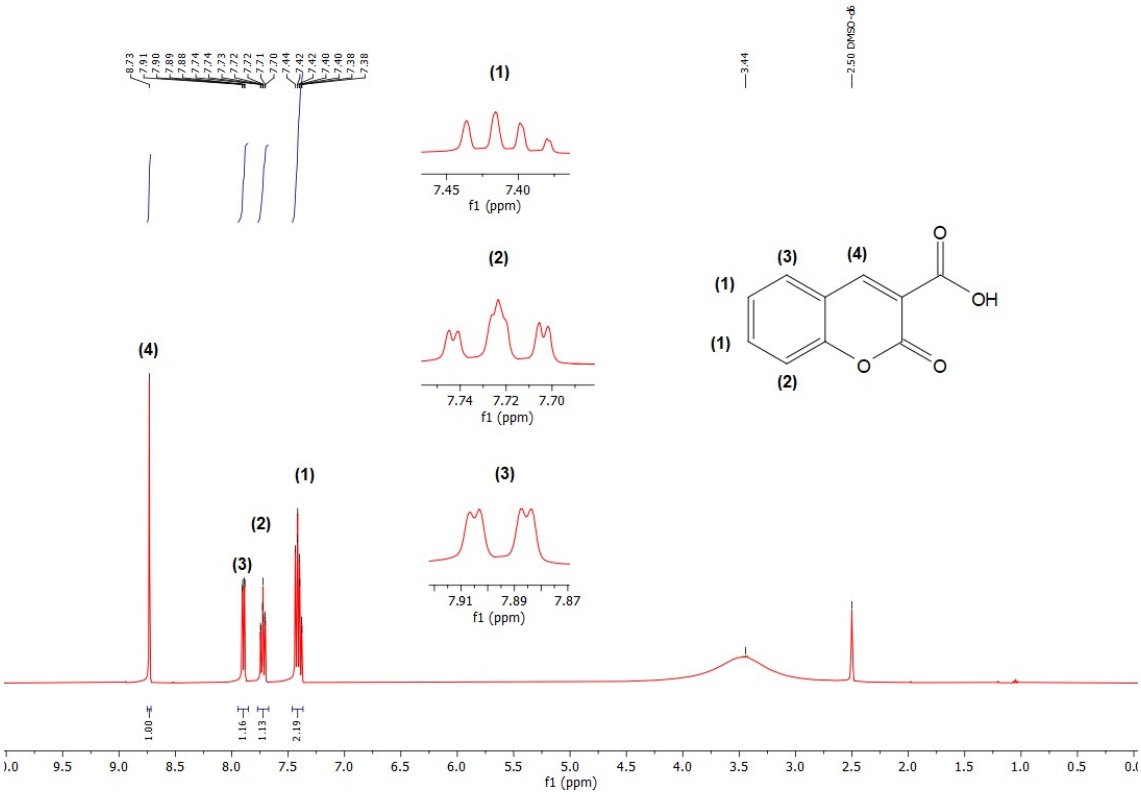


Figure S2. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of Compound (3a).

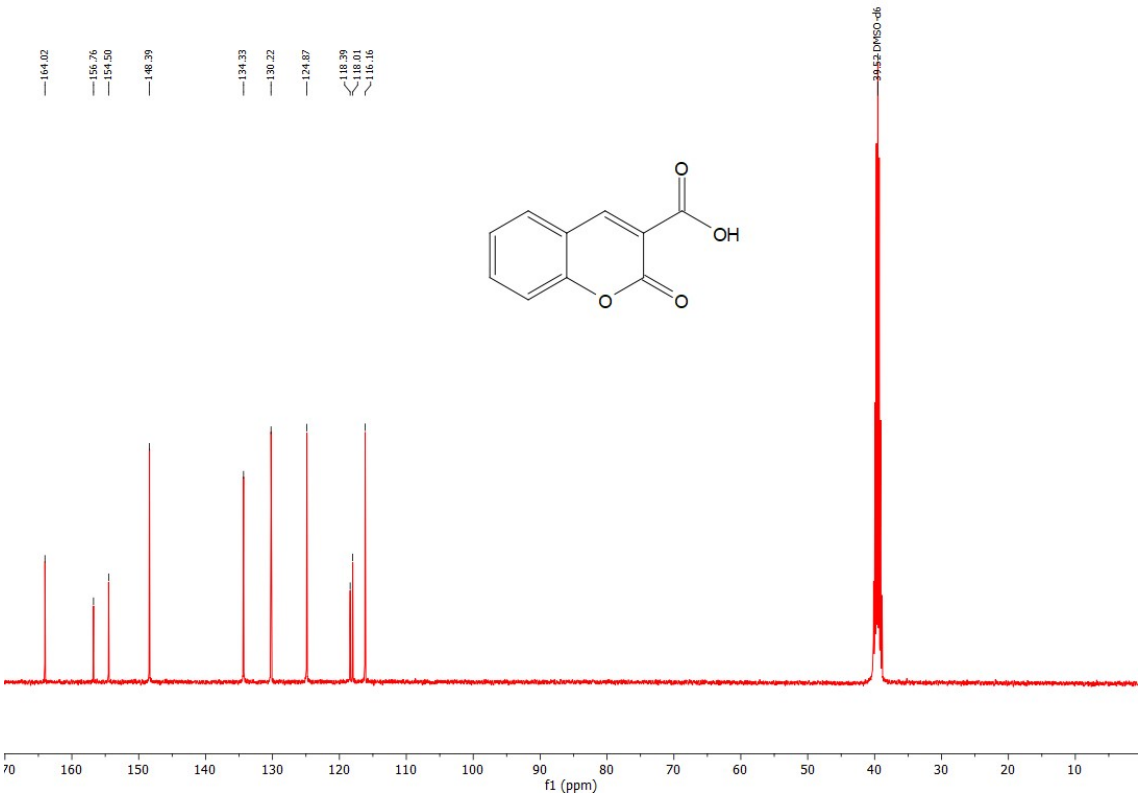


Figure S3. ^{13}C NMR spectrum (DMSO-d_6, 100 MHz) do Compound (3a).

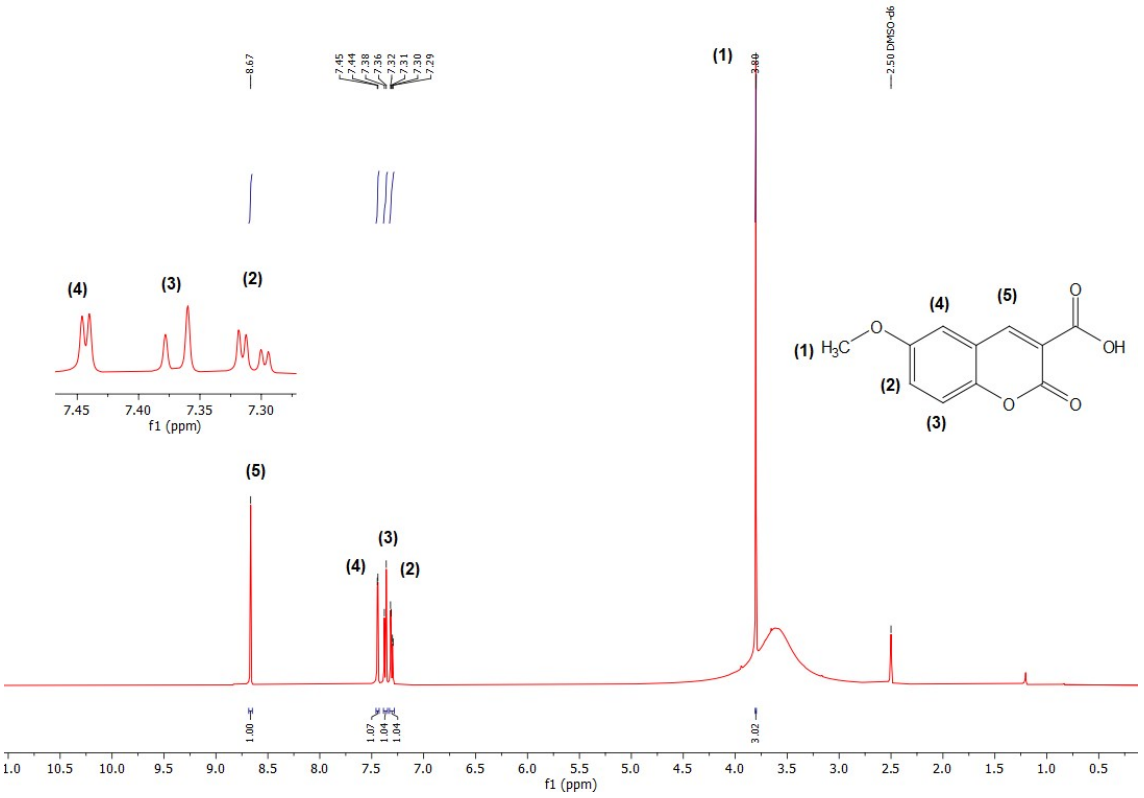


Figure S4. [1]H NMR spectrum (DMSO-d_6, 500 MHz) of Compound (3b).

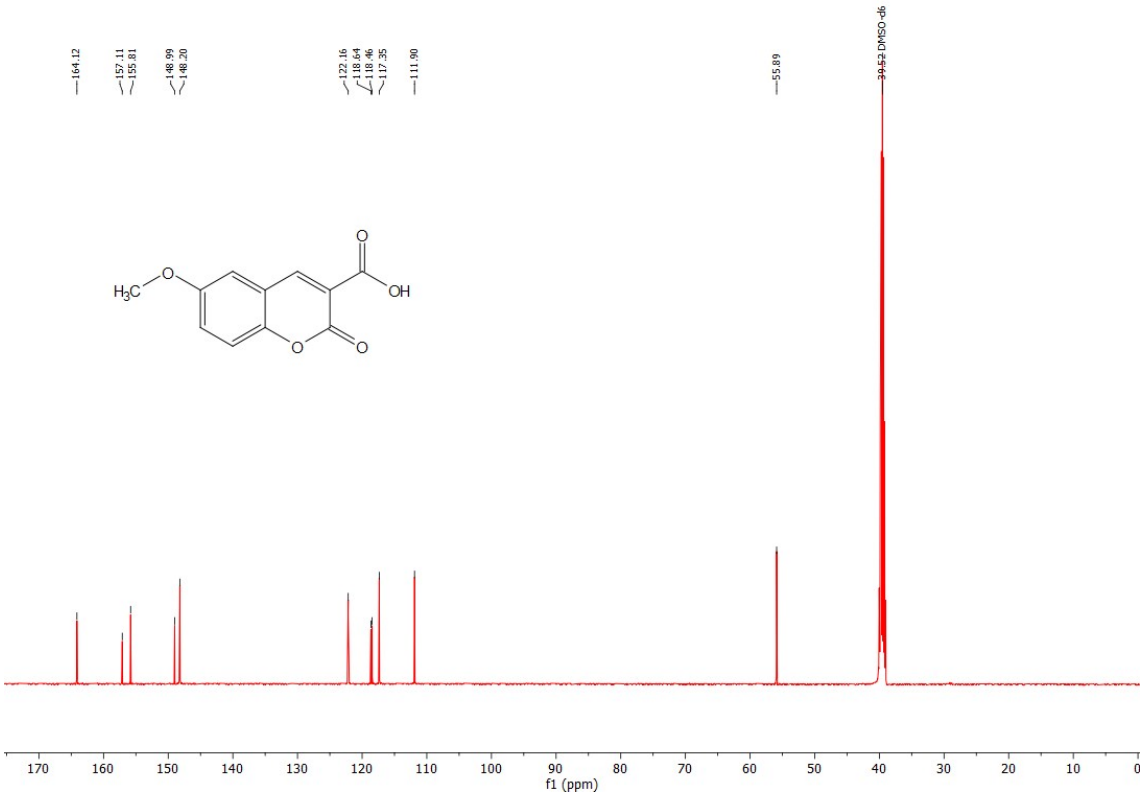


Figure S5. [13]C NMR spectrum (DMSO-d_6, 125 MHz) do Compound (3b).

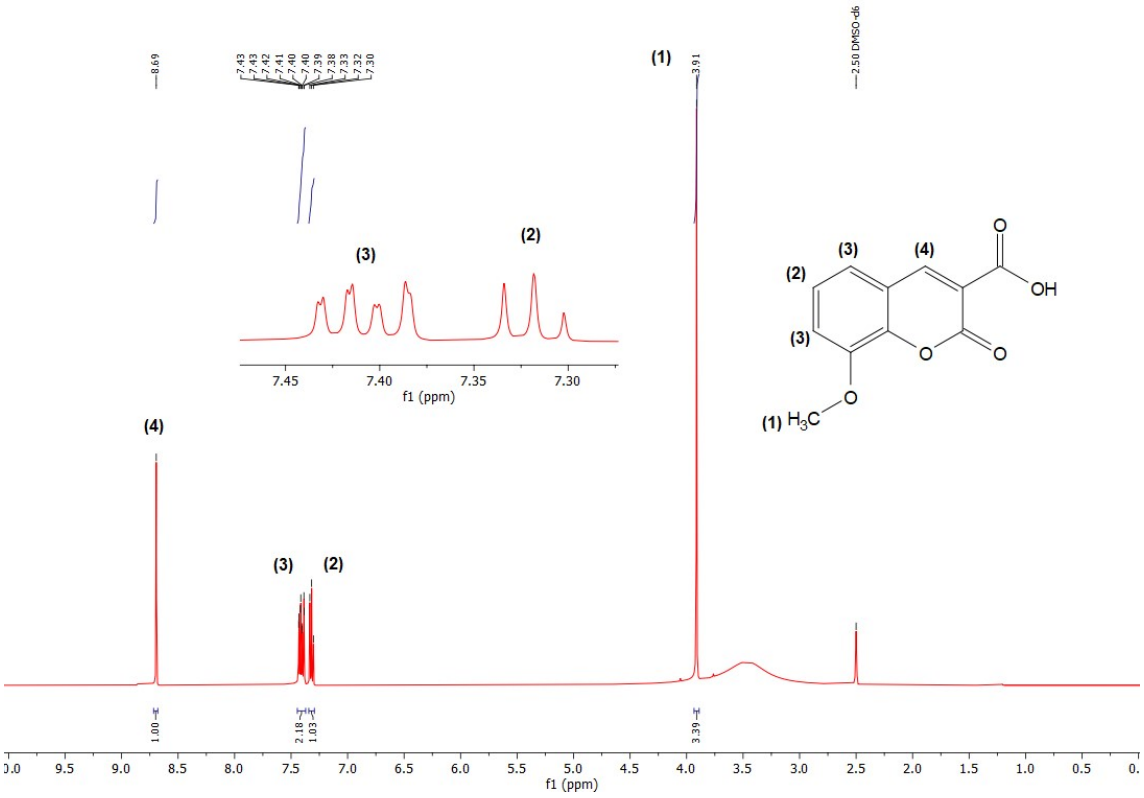


Figure S6. [1]H NMR spectrum (DMSO-d_6, 500 MHz) of Compound (3c).

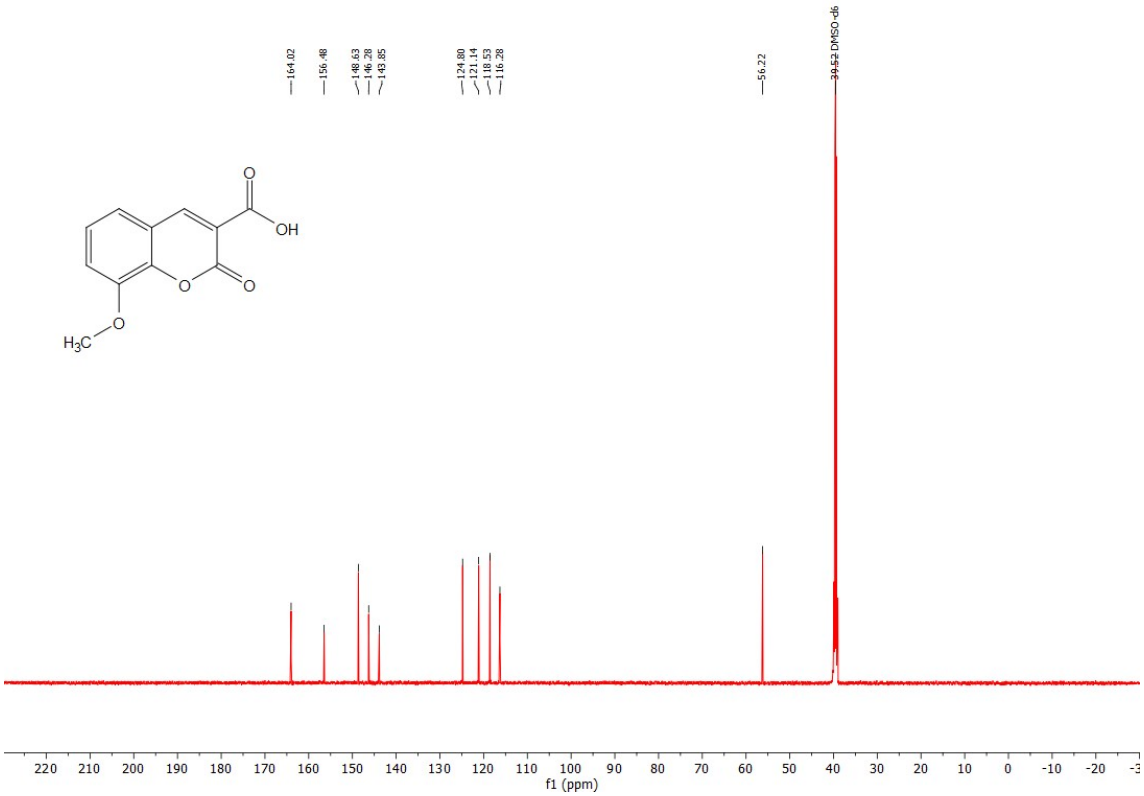


Figure S7. [13]C NMR spectrum (DMSO-d_6, 125 MHz) do Compound (3c).

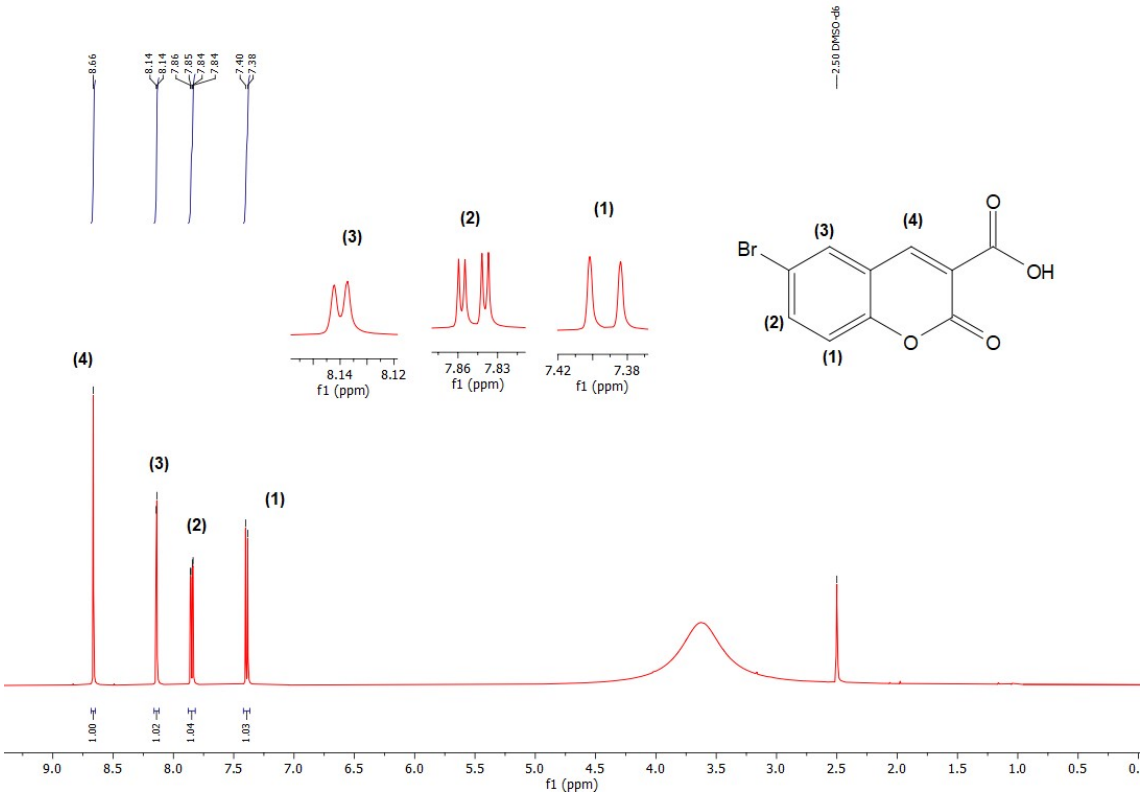


Figure S8. [1]H NMR spectrum (DMSO-d_6, 500 MHz) of Compound (3d).

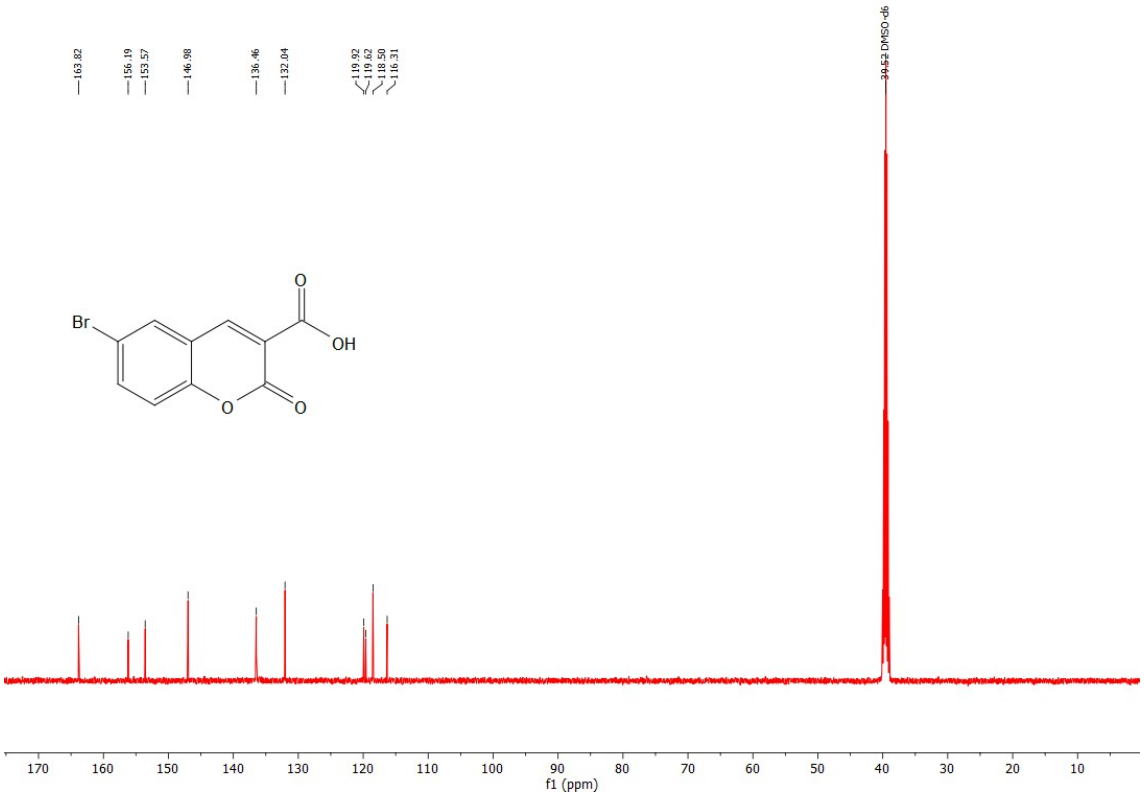


Figure S9. [13]C NMR spectrum (DMSO-d_6, 125 MHz) do Compound (3d)

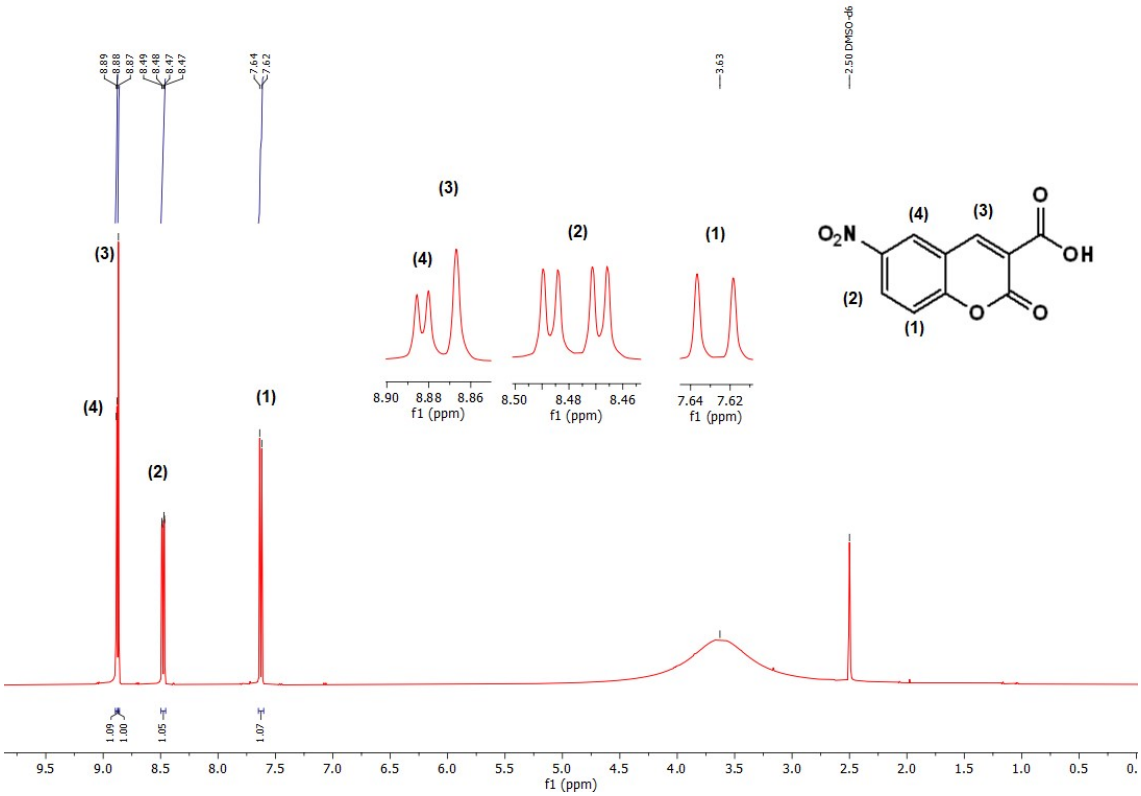


Figure S10. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of Compound (3e).

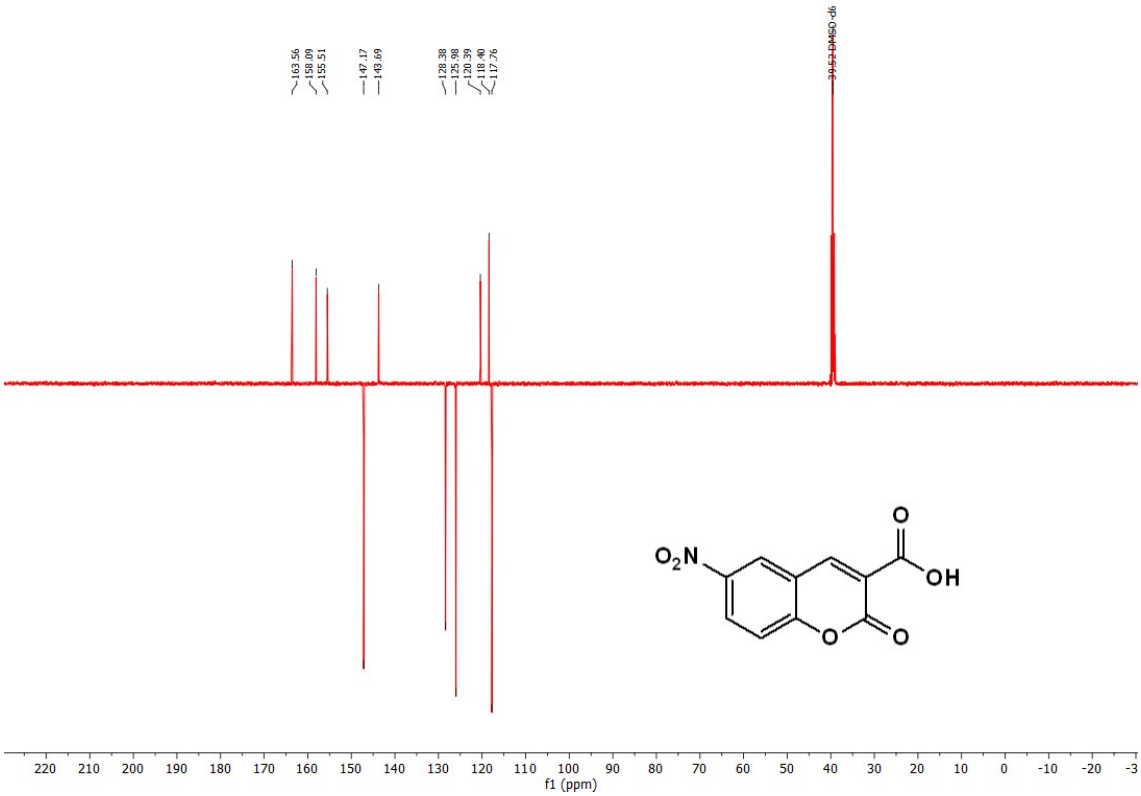


Figure S11. ^{13}C NMR spectrum (DMSO-d_6, 125 MHz) do Compound (3e).

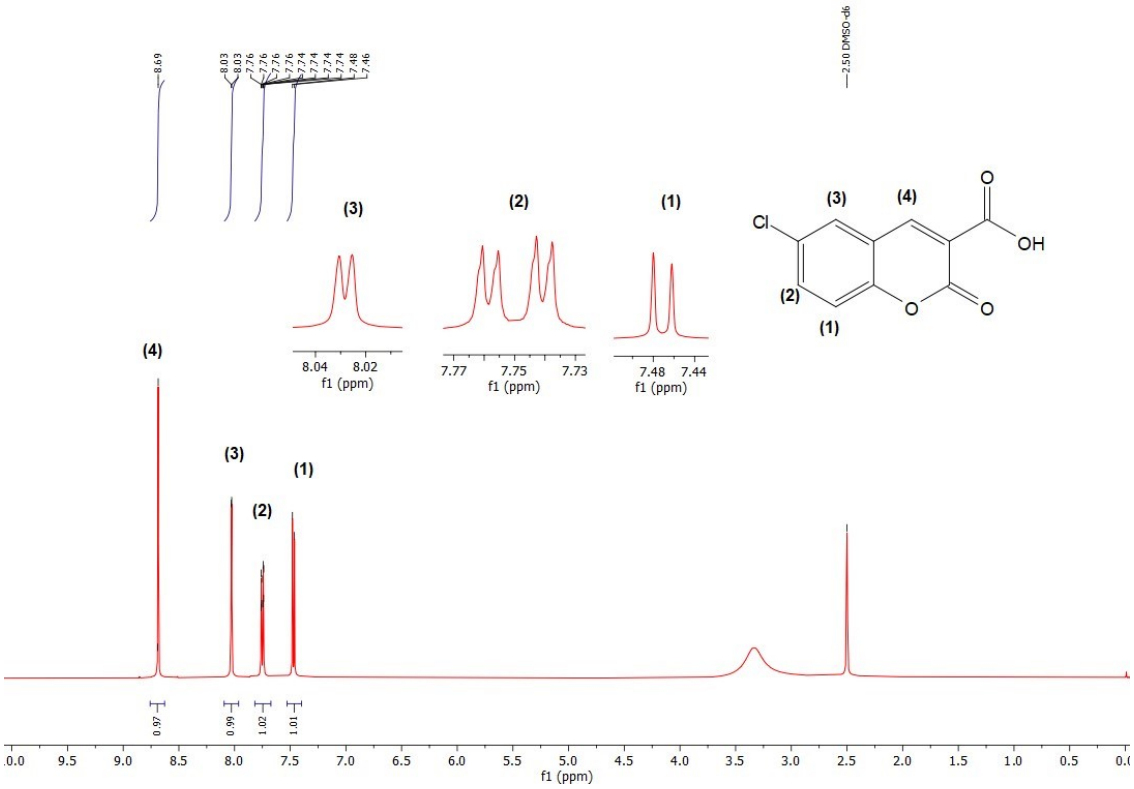


Figure S12. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of Compound (3f).

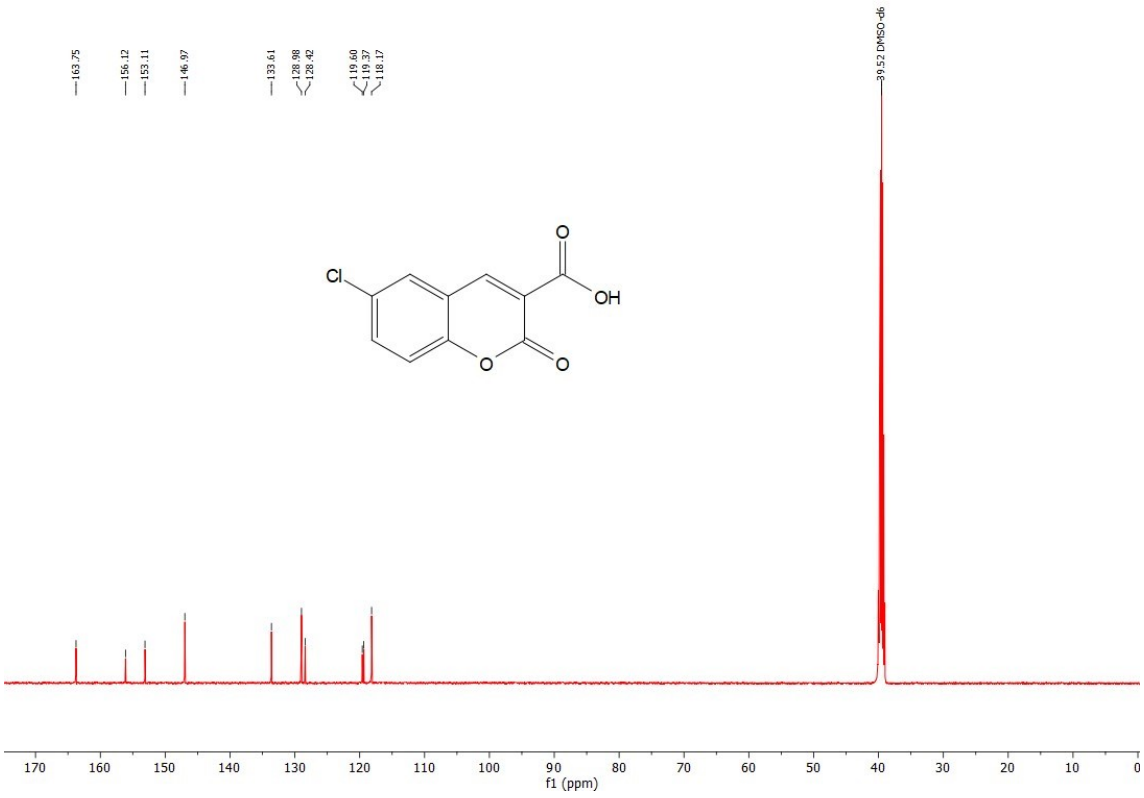


Figure S13. ^{13}C NMR spectrum (DMSO-d_6, 125 MHz) do Compound (3f).

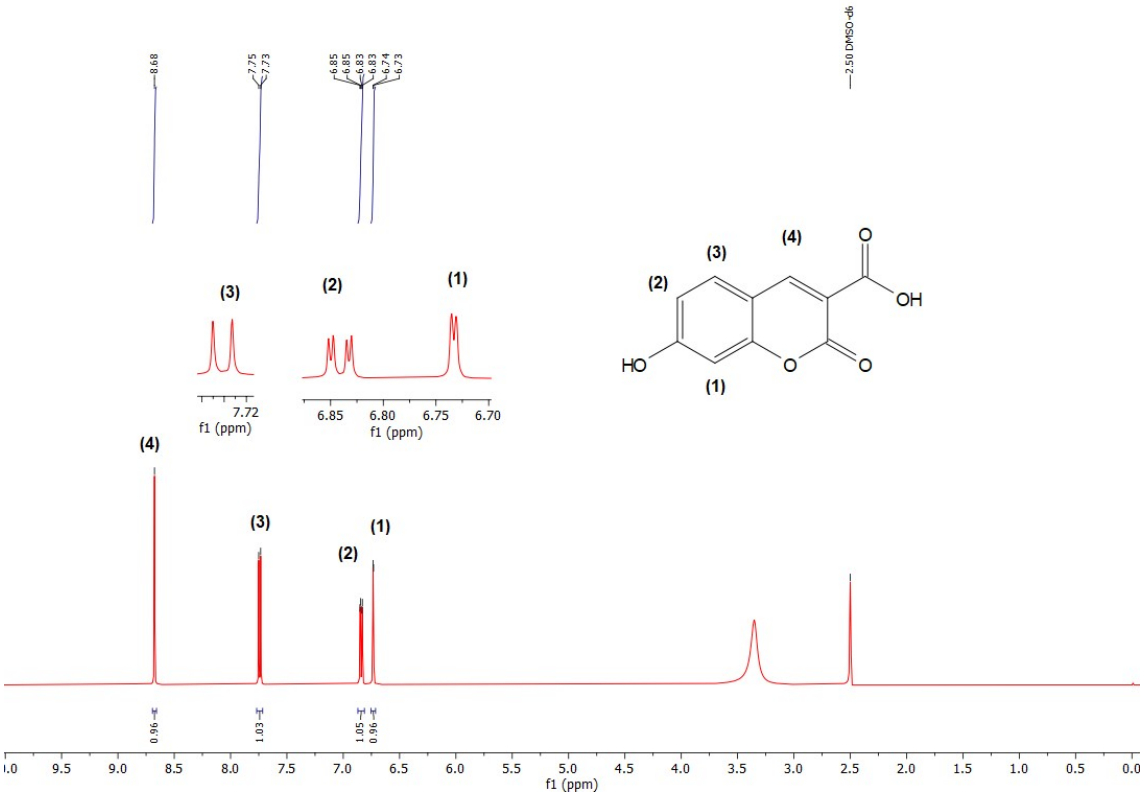


Figure S14. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of Compound (3g).

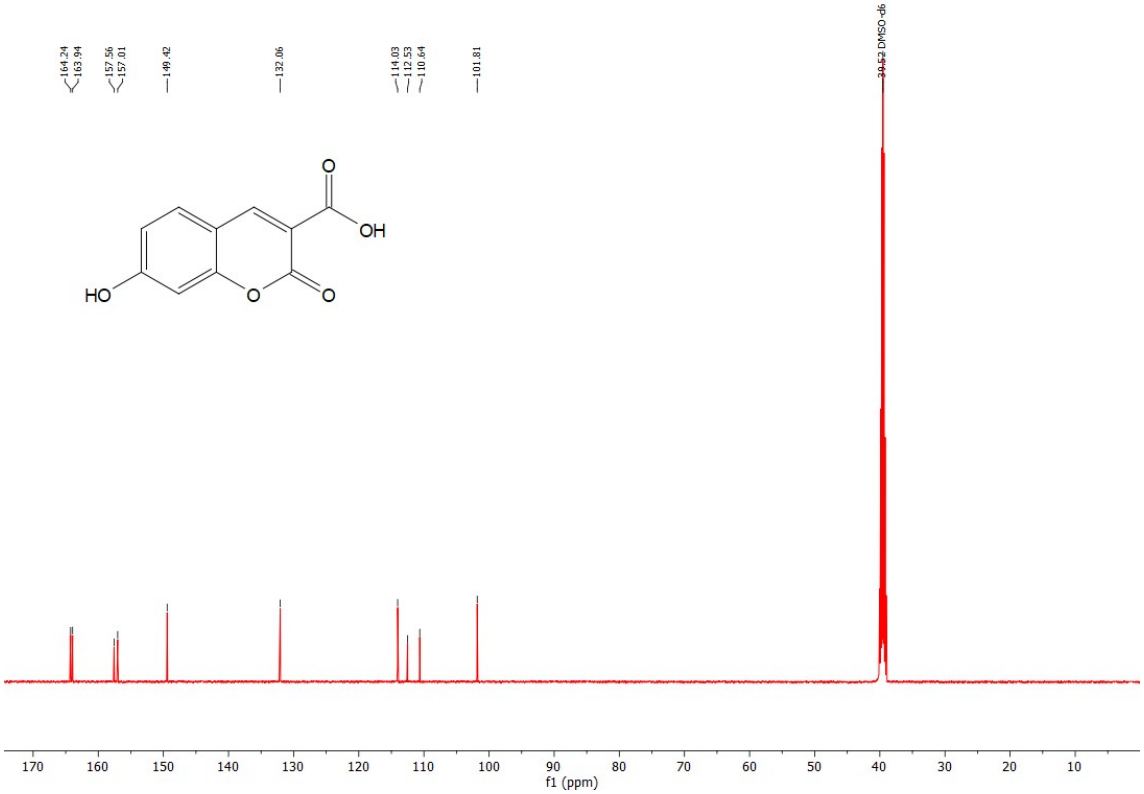


Figure S15. ^{13}C NMR spectrum (DMSO-d_6, 125 MHz) do Compound (3g).

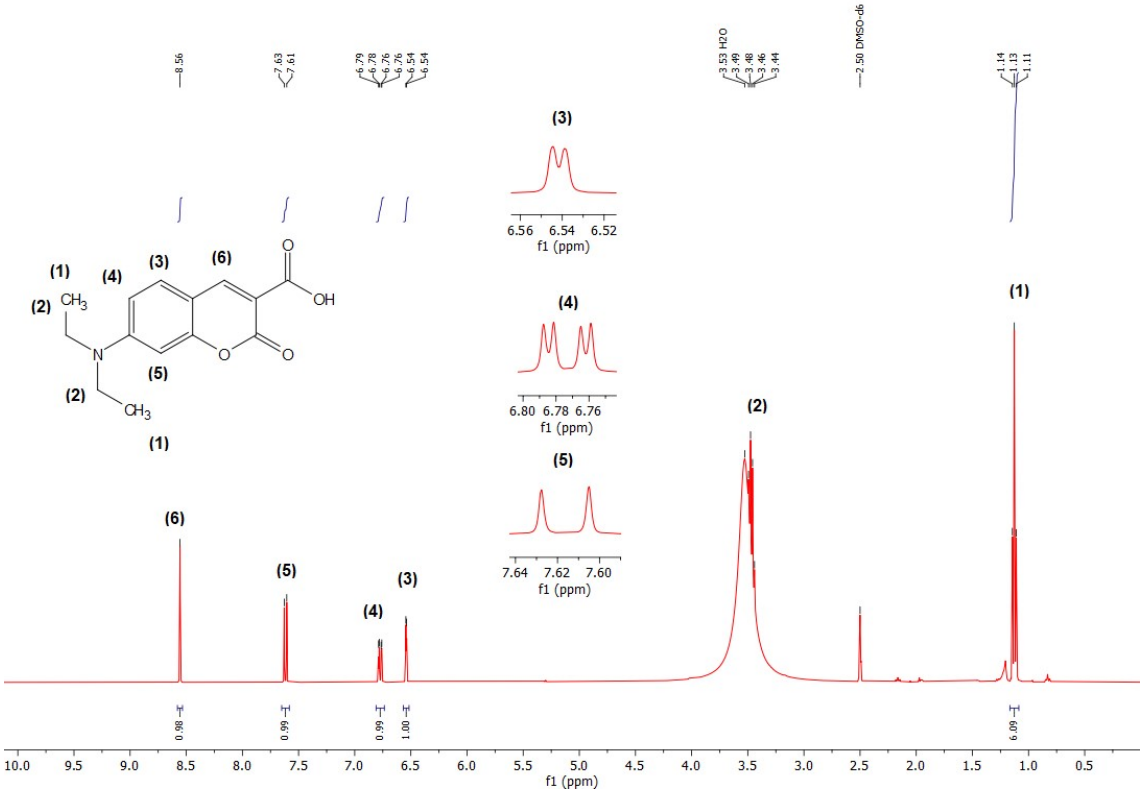


Figure S16. [1]H NMR spectrum (DMSO-d_6, 400 MHz) of Compound (3h).

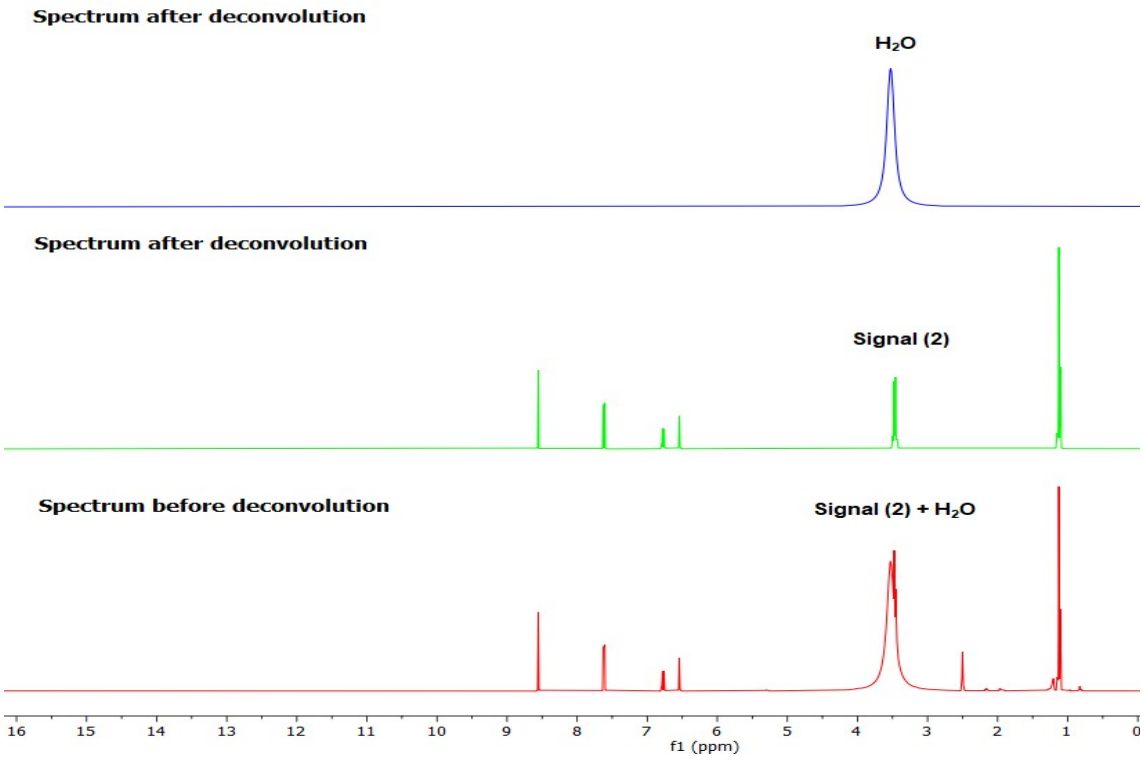


Figure S17. [1]H NMR spectrum before (red) and after (green) deconvolution (DMSO-d_6, 400 MHz) of Compound (3h).

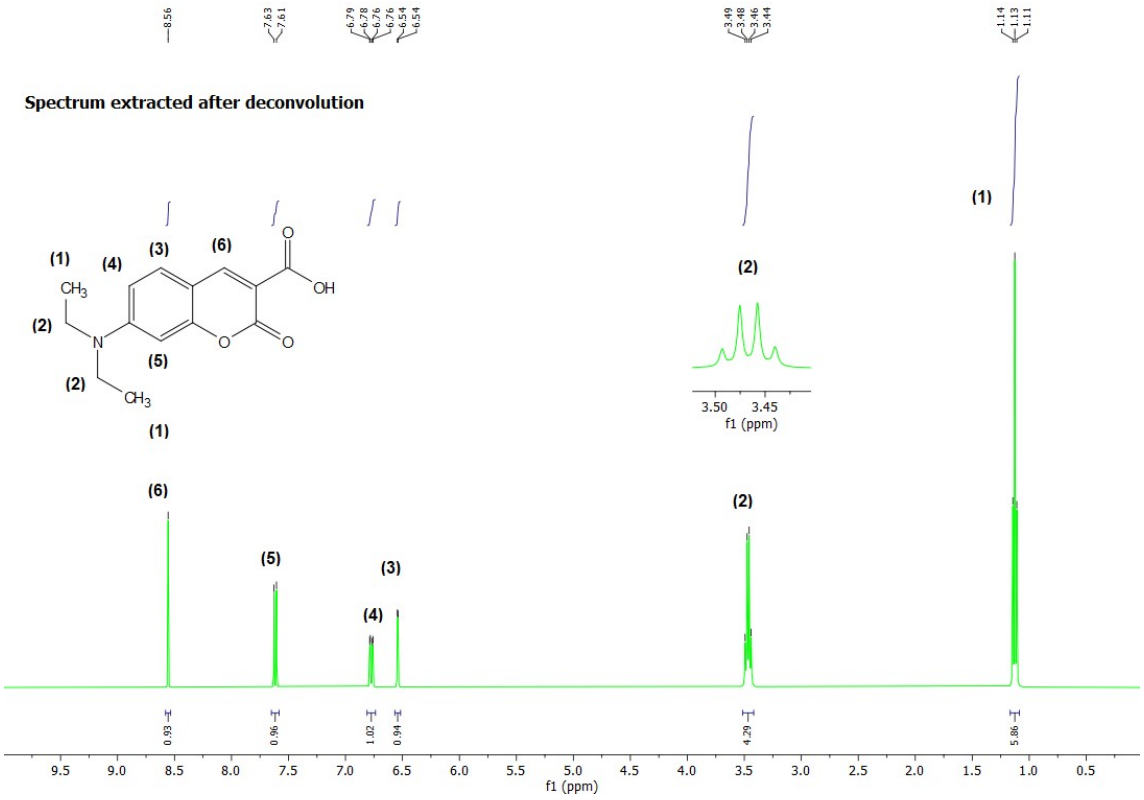


Figure S18. [1]H NMR spectrum extrated after decovolution (DMSO-d_6, 400 MHz) of Compound (3h).

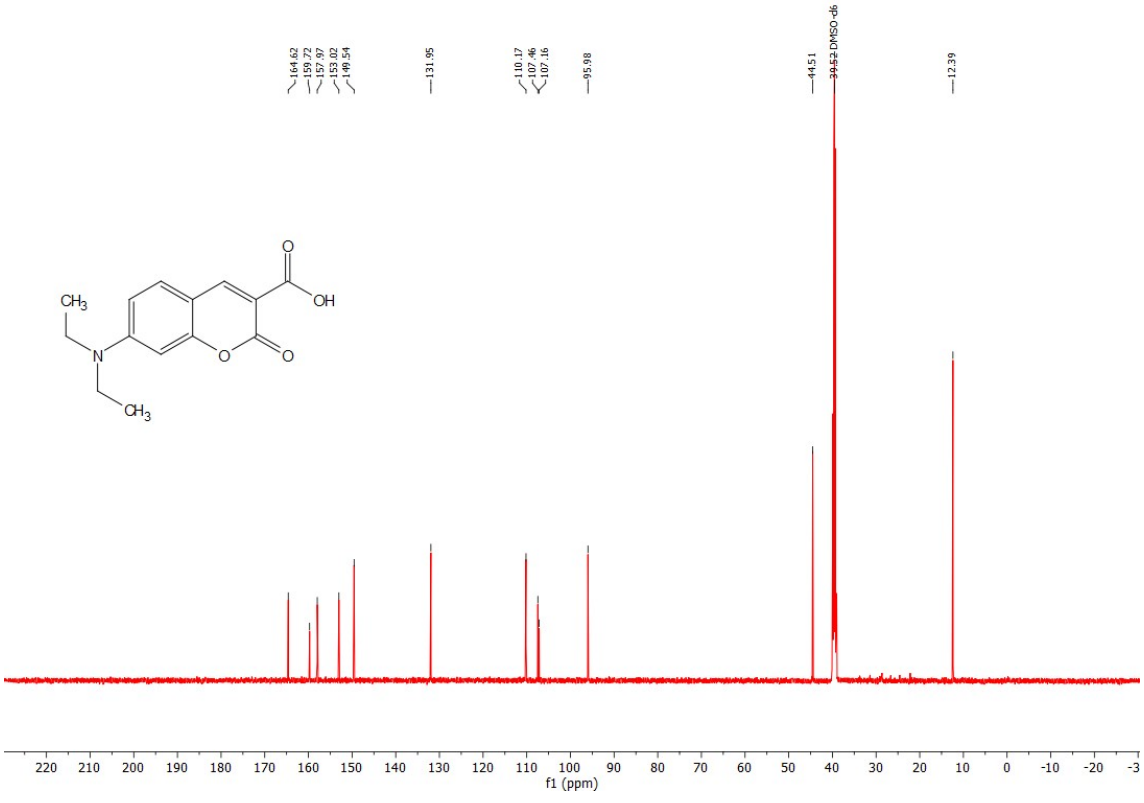


Figure S19. [13]C NMR spectrum (DMSO-d_6, 100 MHz) do Compound (3h).

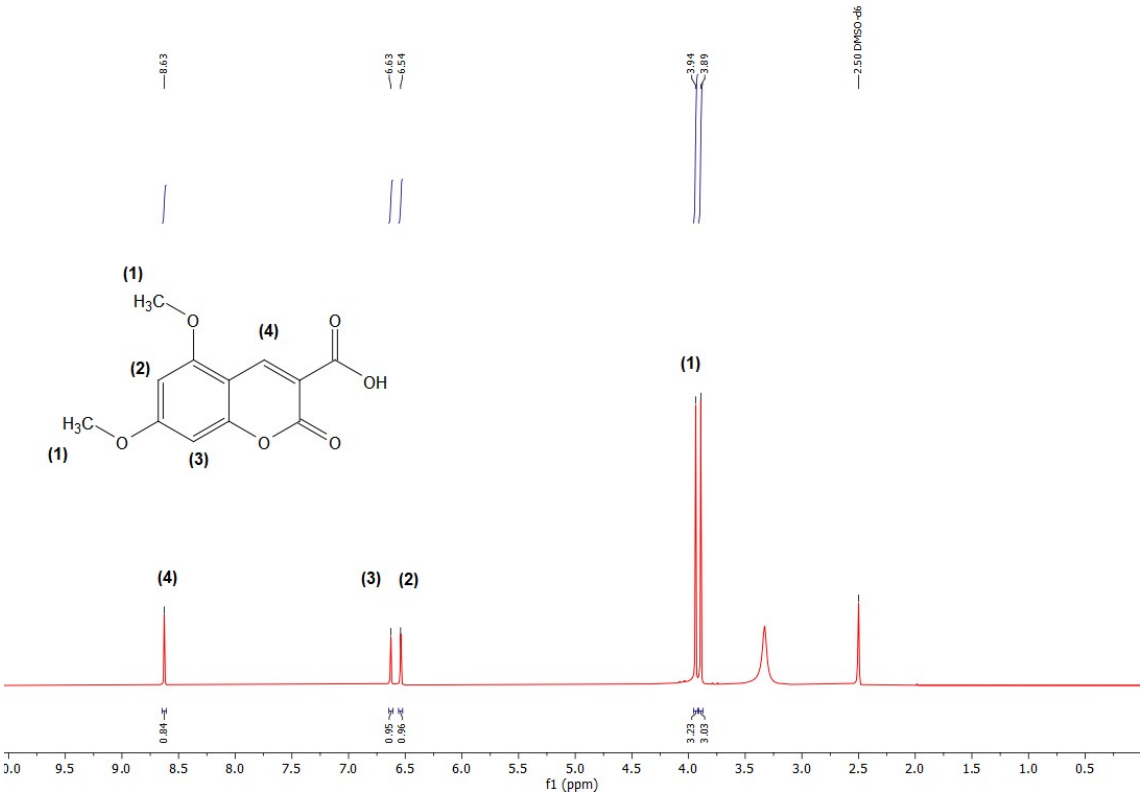


Figure S20. ^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of Compound (3i).

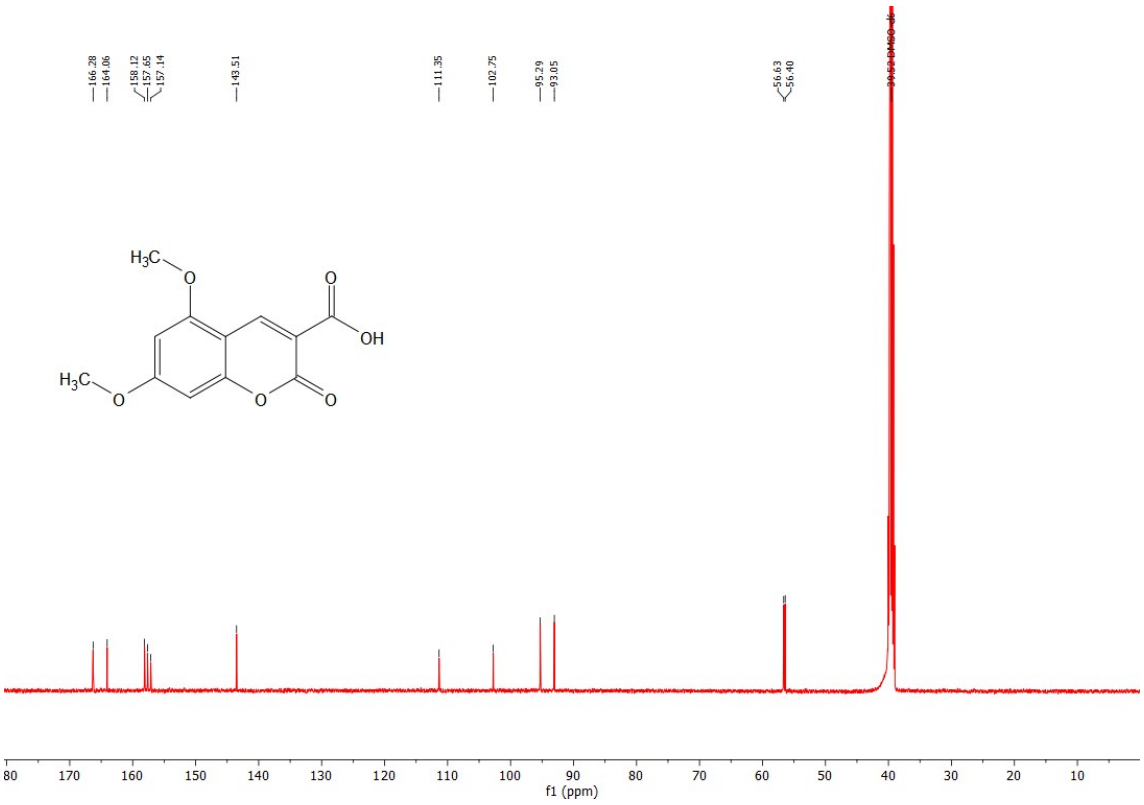


Figure S21. ^{13}C NMR spectrum (DMSO-d_6, 125 MHz) do Compound (3i).