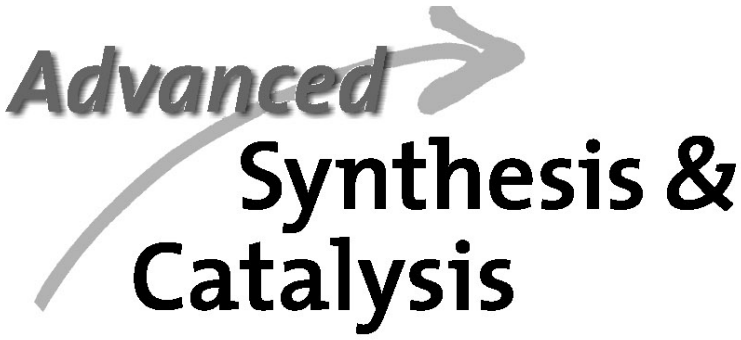

Supporting Information

An Efficient Intramolecular Stetter Reaction in Room Temperature Ionic Liquids Promoted By Microwave Irradiation

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Supporting Information

Experimental Section

Melting points were uncorrected. Mass spectroscopy was measured on a Finnigan Trace MS spectrometer. NMR were recorded in CDCl3 on a Varian Mercury 400 spectrometer and resonances are given in ppm (δ) relative to TMS. HPLC were performed on an Agilent 1100 MWD instrument. Microwave irradiation reactions were carried out on a SmithsynthesizerTM instrument (Fig.1). Crystallographic data for the structure 4 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-612700. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internal) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk

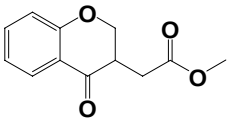
Fig.1 Microwave Reactor from Personal Chemistry

General procedures for Microwave-assisted Intramolecular Stetter reaction in RTILs (Take methyl 2-(3,4-dihydro-4-oxo-2H-chromen-3-yl) acetate as an example): In a microwave tube, Et_3N (0.20g, 2mmol) and methyl 4-(2-formylphenoxy)but-2-enoate **1a** (0.44g, 2mmol) were added into a suspension of 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide (76mg, 15mol %) in [bmim][BF_4]. Then, the sealed microwave tube was placed in a Smithsynthesizer TM and irradiated at 80°C for 20 min. After completion of the reaction, the product was extracted with Et_2O (3 x 25 mL). The organic phase was dried and the solvent was removed under reduced pressure. The residue was purified by chromatography on SiO_2 to afford **2a**.

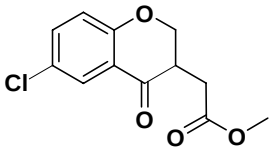
General procedures for Intramolecular Stetter reaction in RTILs under conventional heating (Take methyl 2-(3,4-dihydro-4-oxo-2H-chromen-3-yl) acetate as an example): Et_3N (0.20g, 2mmol) and methyl 4-(2-formylphenoxy)but-2-enoate **1a** (0.44g, 2mmol) were added into a suspension of 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide (76mg, 15mol %) in [bmim][BF_4]. Then, the resulted mixture was heated at 80°C for 2.5h. After completion of the reaction, the product was extracted with Et_2O (3 × 25 mL). The organic phase was dried and the solvent was removed under reduced pressure. The residue was purified by chromatography on SiO_2 to afford **2a**.

General procedures for Intramolecular Stetter reaction performed in DMF (Take methyl 2-(3, 4-dihydro-4-oxo-2H-chromen-3-yl) acetate as an example): A mixture of 1.54g (7mmol) of ester **1a,** 0.12 g (0.48mmol) of 3-ethyl-5- (2-hydroxyethyl)-4-methylthiazolium bromide **3**, 0.4ml (0.3g, 3mmol) of Et_3N, and 7ml of DMF was stirred at room temperature for 1h. After that, additional catalyst **3** (0.25g, 1mmol) and 0.8ml (0.6g, 6mmol) of Et_3N were added. The resulted mixture was stirred for further 30min. $CHCl_3$ (30ml) and 10ml of 10% aq. HCl were added, the aqueous layer was extracted with 2×30ml of $CHCl_3$. The combined extracts were washed with water, 5% aq $NaHCO_3$, and brine. The organic phase was dried and the solvent was removed under reduced pressure. The residue was purified by chromatography on SiO_2 to afford **2a**.

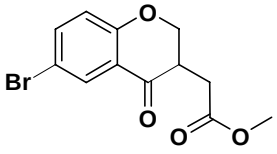
Data for Characterization for 2:



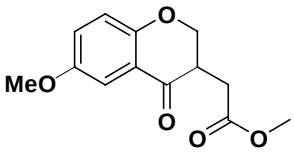
Methyl 2-(3, 4-dihydro-4-oxo-2H-chromen-3-yl) acetate 2a[1]: mp 44 – 46 ℃ (no literature data); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (dd, J = 16.8 Hz, J = 8.0 Hz, 1H), 2.93 (dd, J = 16.8 Hz, J = 5.6 Hz, 1H), 3.30 ~ 3.38 (m, 1H), 3.72 (s, 3H), 4.27 (t, J = 11.6 Hz, 1 H), 4.59 (dd, J = 11.6 Hz, J = 5.2 Hz, 1H), 6.96 ~ 7.04 (m, 2H), 7.46 ~ 7.50 (m, 1H), 7.88 (dd, J = 8 Hz, J = 1.6 Hz, 1H); EI - Ms (*m/z*): 220 (M^+)



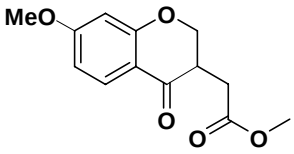
Methyl 2-(6-chloro-3, 4-dihydro-4-oxo-2H-chromen-3-yl) acetate 2b[1,2]: mp 70 - 72 ℃ (no literature data); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (dd, J = 17.0 Hz, J = 8.2 Hz, 1H), 2.93 (dd, J = 17.2 Hz, J = 5.6 Hz, 1H), 3.30 ~ 3.35 (m, 1H), 3.73 (s, 3H), 4.30 (t, J = 11.8 Hz, 1 H), 4.60 (dd, J = 11.2 Hz, J = 5.2 Hz, 1H), 6.93 (d, J = 8.8 Hz, 1H), 7.41 (dd, J = 8.6 Hz, J = 2.6 Hz, 1H), 7.88 (d, J = 2.8 Hz, 1H); EI - Ms (*m/z*): 254 (M^+), 255 ($(M+1)^+$), 255 ($(M+2)^+$)



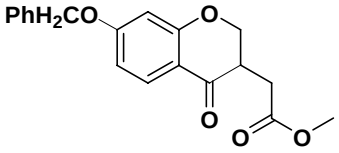
Methyl 2-(3, 4-dihydro-4-oxo-2H-chromen-3-yl) acetate 2c[2]: mp 71 - 73 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (dd, J = 17.2 Hz, J = 8.0 Hz, 1H), 2.94 (dd, J = 17.0 Hz, J = 4.6 Hz, 1H), 3.28 ~ 3.36 (m, 1H), 3.73 (s, 3H), 4.30 (t, J = 11.8 Hz, 1 H), 4.60 (dd, J = 11.4 Hz, J = 5.4 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 7.54 (dd, J = 8.6 Hz, J = 2.2 Hz, 1H), 7.88 (d, J = 2.0 Hz, 1H); EI - Ms (*m/z*): 297 ($(M-2)^+$), 299 (M^+).



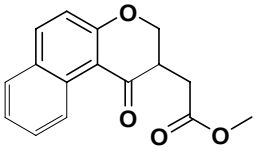
Methyl 2-(3, 4-dihydro-6-methoxy-4-oxo-2H-chromen-3-yl) acetate 2d[2]: oil (Lit.oil); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (dd, J = 16.8 Hz, J = 8.8 Hz, 1H), 2.91 (dd, J = 17.2 Hz, J = 4.8 Hz, 1H), 3.27 ~ 3.35 (m, 1H), 3.73 (s, 3H), 3.79 (s, 3H), 4.26 (t, J = 11.4 Hz, 1 H), 4.56 (dd, J = 11.4 Hz, J = 5.0 Hz, 1H), 6.90 (d, J = 9.2 Hz, 1H), 7.10 (dd, J = 9.0 Hz, J = 3.0 Hz, 1H), 7.30 (d, J = 3.2 Hz, 1H); EI - Ms (*m/z*): 250 (M^+).



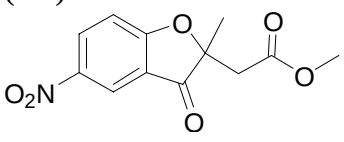
Methyl 2-(3, 4-dihydro-7-methoxy-4-oxo-2H-chromen-3-yl) acetate 2e[1]:mp: 127 ~ 128 ℃(no literature data); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (dd, J = 17.2 Hz, J = 8.8 Hz, 1H), 2.91 (dd, J = 17.0 Hz, J = 4.6 Hz, 1H), 3.25 ~ 3.30 (m, 1H), 3.73 (s, 3H), 3.85 (s, 3H), 4.27 (t, J = 11.2 Hz, 1 H), 4.56 (dd, J = 11.2 Hz, J = 5.2 Hz, 1H), 6.40 （dd, J = 2.4 Hz, 1H), 6.59 (dd, J = 8.8 J = 2.0 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H); EI - Ms (*m/z*): 250 (M^+).



Methyl 2-(7-(benzyloxy)-3, 4-dihydro-4-oxo-2H-chromen-3-yl) acetate 2f: mp 96 ~ 97℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (dd, J = 16.8 Hz, J = 8.4 Hz, 1H), 2.91 (dd, J = 16.8 Hz, J = 4.8 Hz, 1H), 3.23 ~ 3.31 (m, 1H), 3.72 (s, 3H), 4.26 (t, J = 11.4 Hz, 1 H), 4.57 (dd, J = 11.2 Hz, J = 5.2 Hz, 1H), 5.11 (s, 2H), 6.47 (d, J = 2.4 Hz, 1H), 6.64 (dd, J = 8.2 J = 2.2 Hz, 1H), 7.32 ~ 7.41 (m, 5H), 7.83 (d, J = 8.8 Hz, 1H); EI - Ms (*m/z*): 326 (M^+).



Methyl 2-(2, 3-dihydro-1-oxo-1H-benzo[f]chromen-2-yl) acetate 2g[1]: oil (Lit. oil); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (dd, J = 17.0 Hz, J = 8.2 Hz, 1H), 2.97 (dd, J = 17.0 Hz, J = 5.4 Hz, 1H), 3.41 ~ 3.46 (m, 1H), 3.75 (s, 3H), 4.41 (t, J = 11.4 Hz, 1 H), 4.68 (dd, J = 11.2 Hz, J = 5.2 Hz, 1H), 7.08 (d, J = 9.2 Hz, 1H), 7.26 ~ 7.44 (m, 1H), 7.60 ~ 7.64 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 9.40 (d, J = 9.2 Hz, 1H); EI - Ms (*m/z*): 270 (M^+).

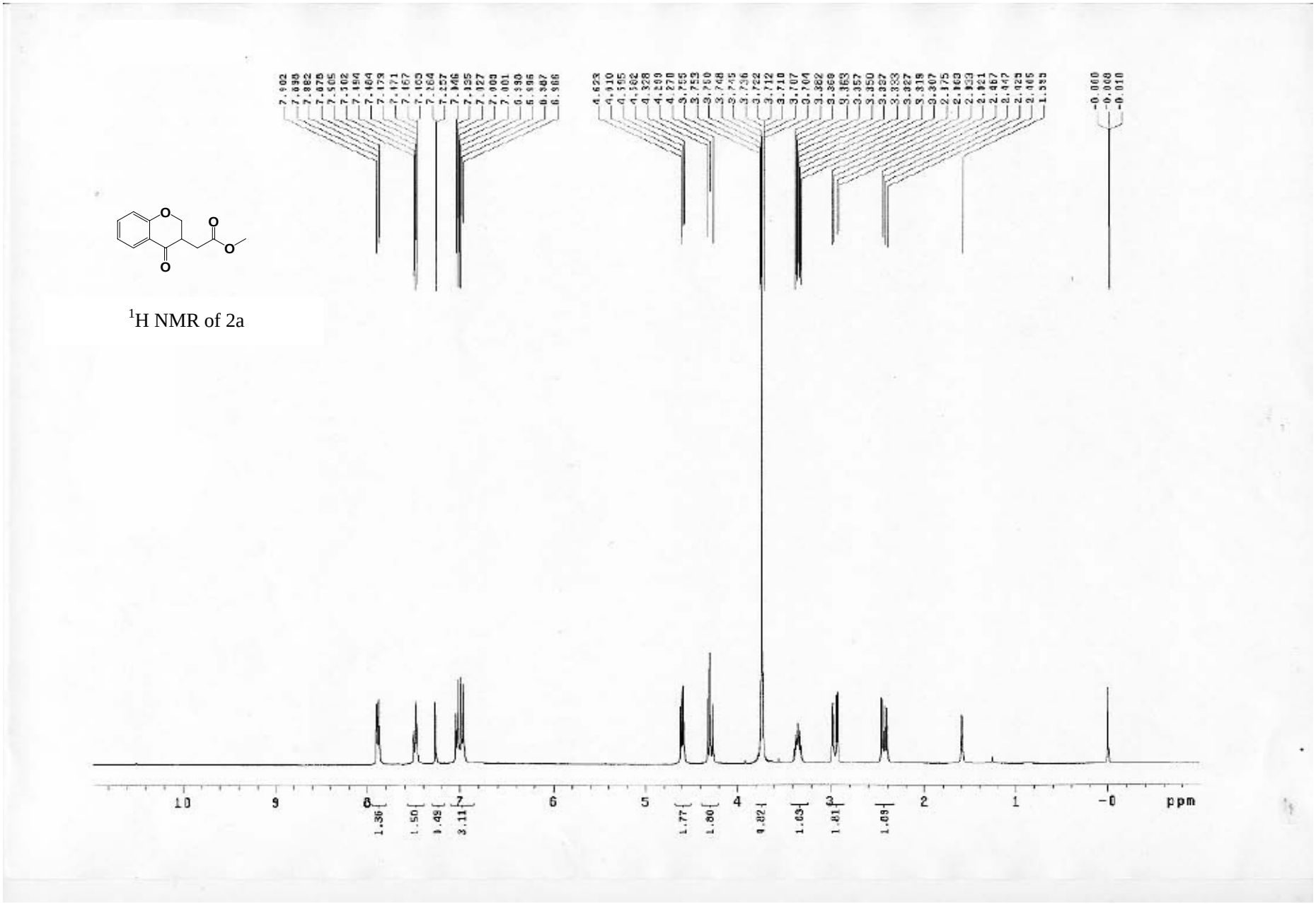


Methyl 2-(2-methyl-5- nitro-3-oxo-2,3-dihydrobenzofuran-2-yl)acetate 4: mp 125~126℃;

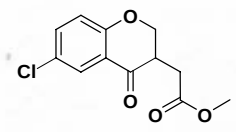
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 (s, 3H), 3.04 (d, *J* = 17.2 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 3.56 (s, 3H), 7.17 (d, *J* = 9.2Hz, 1H), 8.51 (dd, *J* = 9Hz, *J* = 2.6Hz, 1H), 8.62 (d, *J* = 2.4Hz, 1H).

References and notes

1. Engelbert Ciganek, synthesis, **1995**, 1311-1314
2. Enders, D.; Breuer, K.; Runsink, J.; Teles, J. H. *Helv. Chim. Acta.* **1996**, 79, 1899 - 1902.



^{1}H NMR of 2a



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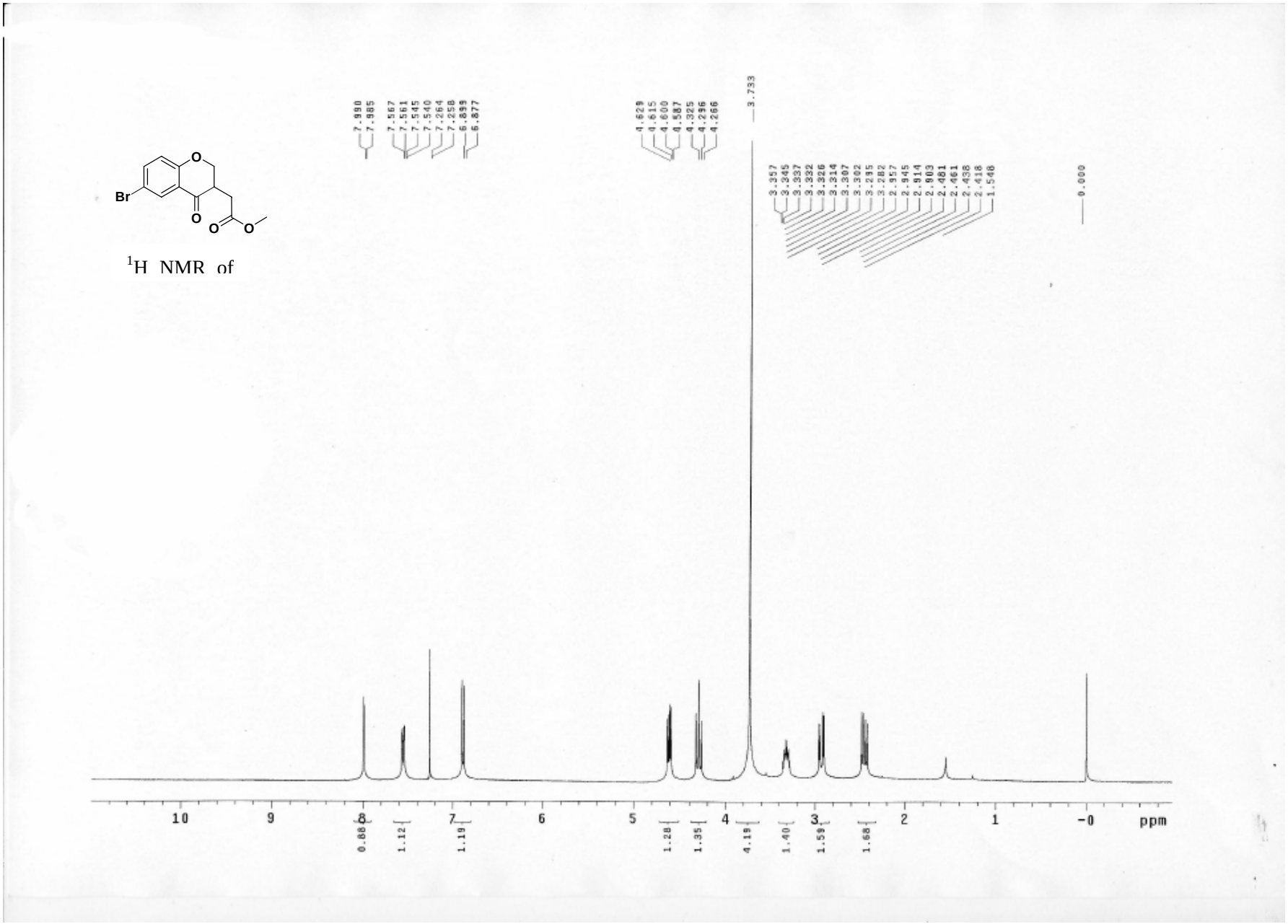
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3.733
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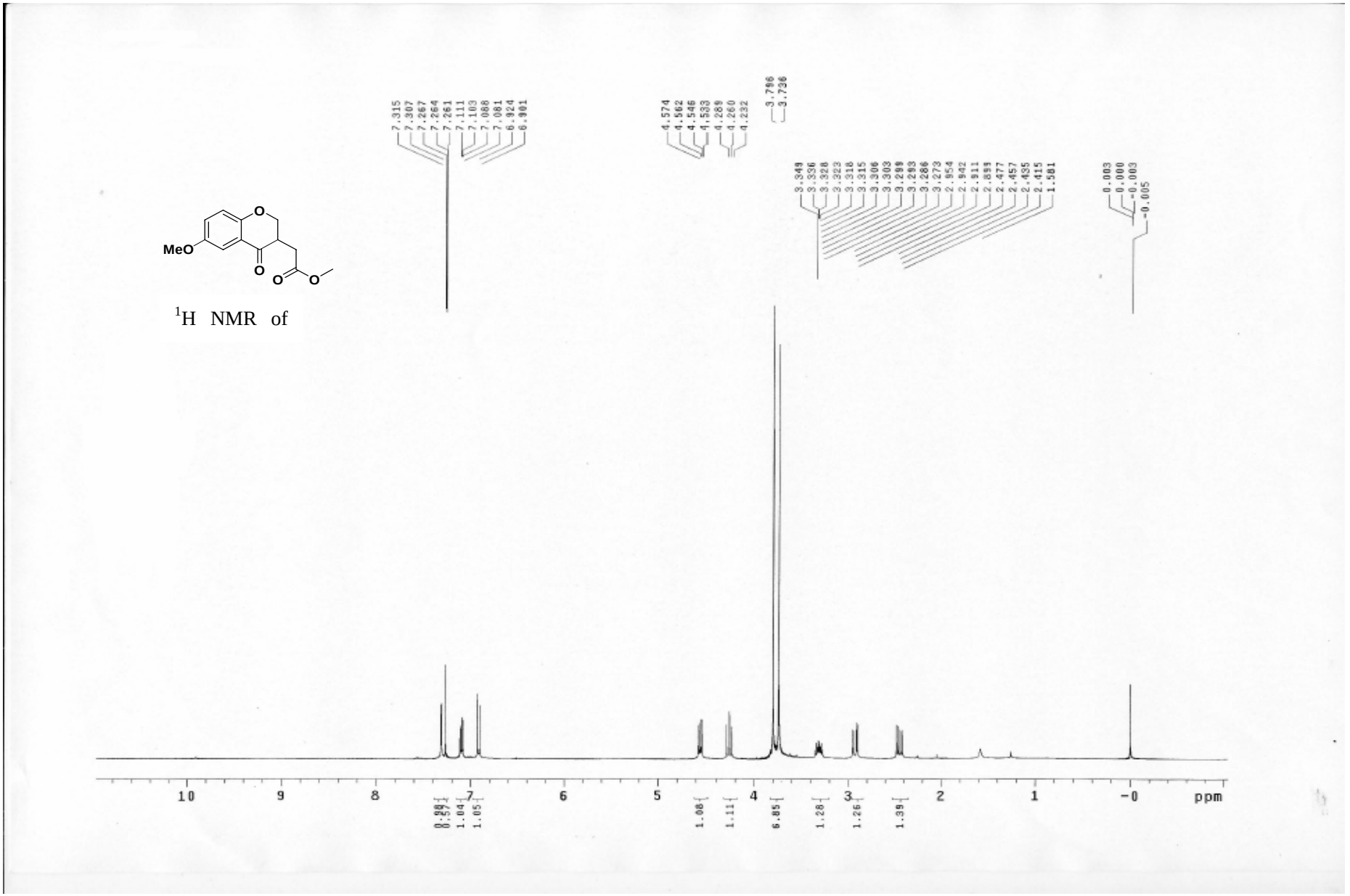
^{1}H NMR of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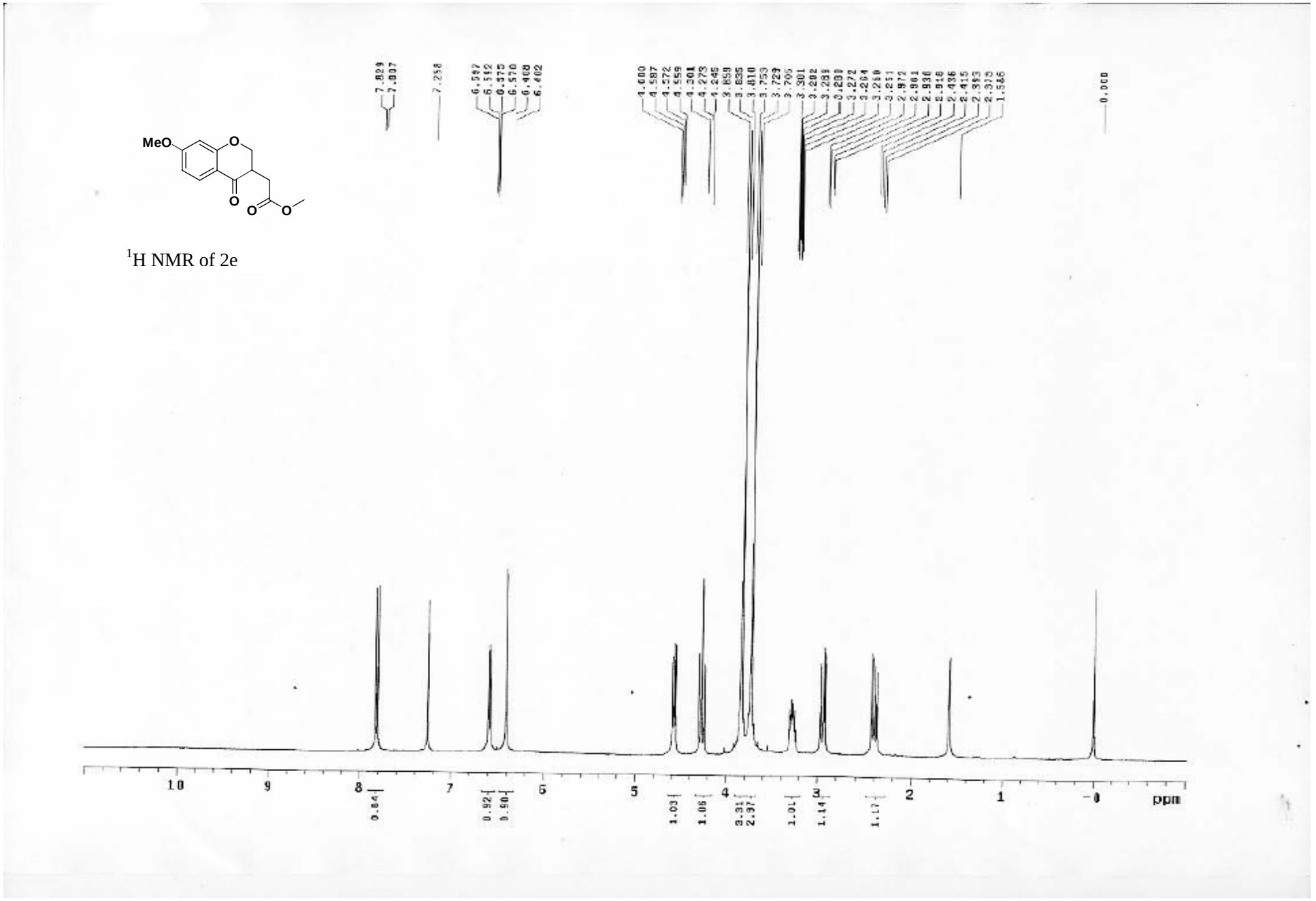
^{1}H NMR of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4.572
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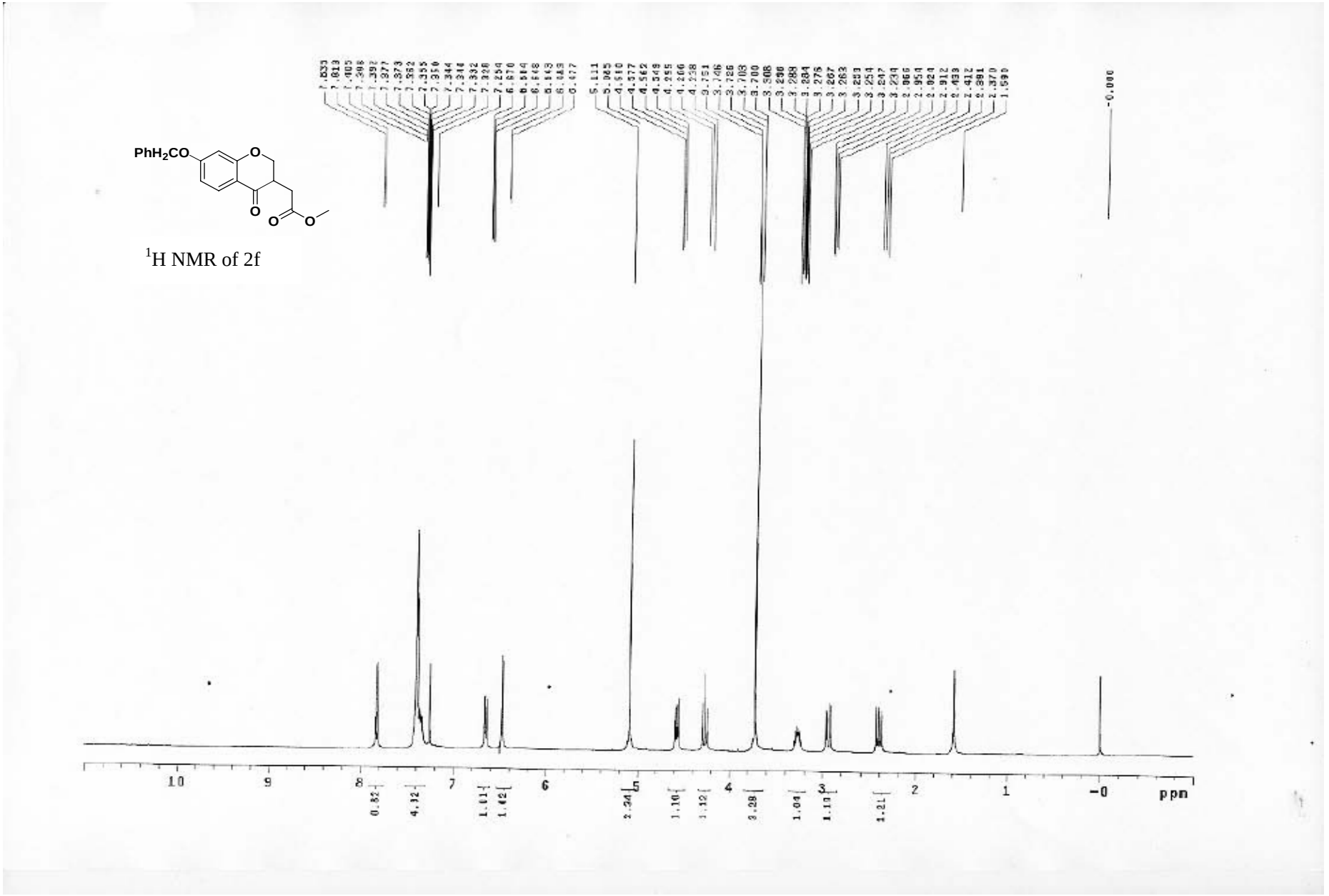
^{1}H NMR of 2e



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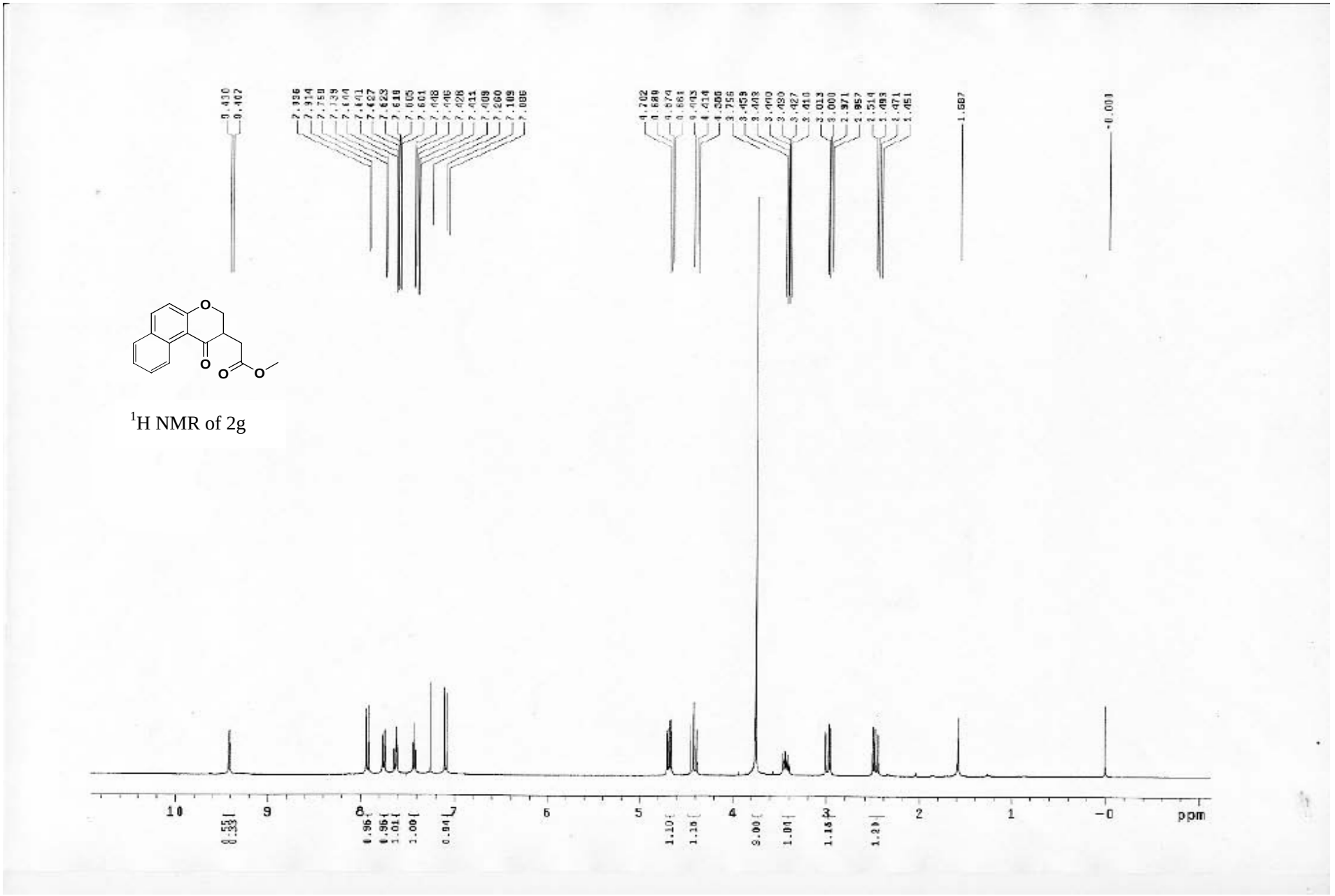

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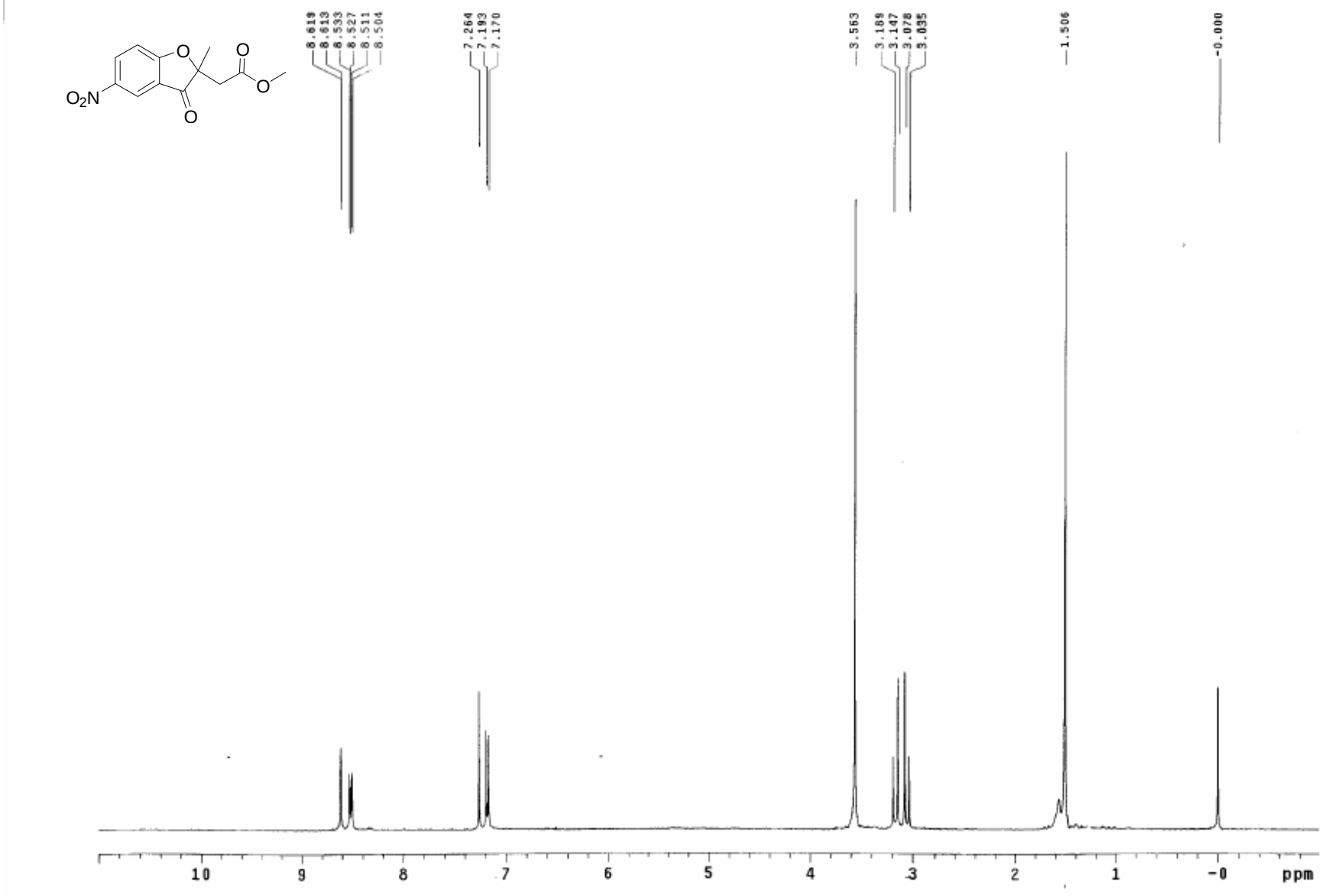
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7
6
5
4
3
2
1
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ppm