Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Facile Synthesis of 4-Substituted 3,4-Dihydrocoumarins via an Organocatalytic Double Decarboxylation Process

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Supporting Information

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1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$ δ 7.26, DMSO δ 2.50), carbon ($CDCl_3$ δ 77.0, DMSO δ 39.5) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode and API 3000™ in APCI (Heated Nebulizer) mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

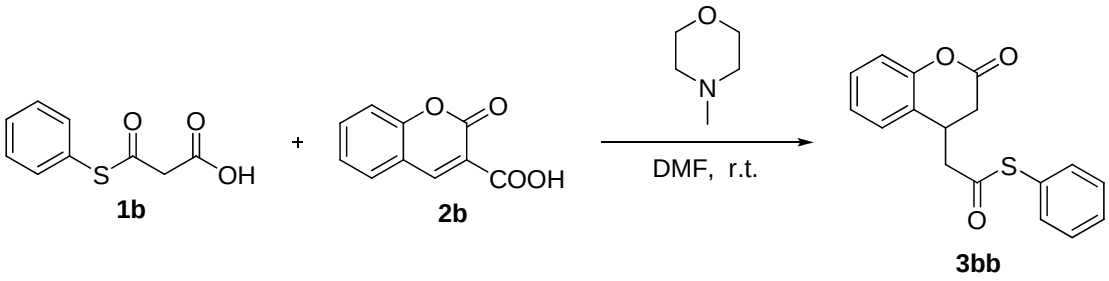
2. Starting materials

Compounds **1b-1h**[1a], **1i**[1b], **1j**[1c]and **2b-2j**[1b] were prepared according to literature, respectively.

Reference:

[1] (a) *Youji Huaxue*, **2008**, *28*, 2011-2015; (b) *Journal of Organic chemistry* , **2009**, *74*, 6190-6198; (c) *Bioorganic & Medicinal Chemistry Letters*, **2009**, *19*, 3632-3636.

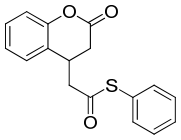
3. Representative Procedure



To a solution of **1b** (0.4 mmol) and **2b** (0.2 mmol) in 0.4 mL *N*,*N*-Dimethylformamide (DMF), *N*-Methylmorpholine (0.02 mmol) was added. The reaction mixture was stirred at r.t. for 12h. The crude product was purified by column chromatography on silica gel, eluted by hexane/ethyl acetate to afford the desired product **3a** (90% yield).

4. NMR data of compounds 3.

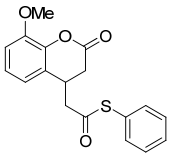
3bb



yield: 90% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.20 (m, 7H), 7.18–7.01 (m, 2H), 3.67 (ddd, *J* = 12.4, 7.2, 5.2 Hz, 1H), 3.06–2.69 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.97, 167.19, 151.30, 134.36, 129.70, 129.28, 129.02, 127.61, 126.86, 124.68, 124.45, 117.29, 77.43, 77.00, 76.58, 47.31, 34.28, 31.87. LC−MS (ESI): m/z = 321 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{14}O_3SNa$ ($M+Na^+$); 321.0556. Found: 321.0557.

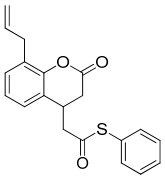
3bc



yield: 96% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.31 (m, 5H), 7.13–7.01 (m, 1H), 6.90 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.80 (dd, *J* = 7.7, 1.0 Hz, 1H), 3.90 (s, 3H), 3.66 (dq, *J* = 7.2, 5.0 Hz, 1H), 3.03–2.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.02, 166.56, 147.83, 140.61, 134.39, 129.71, 129.30, 126.94, 125.63, 124.66, 118.95, 111.65, 77.42, 77.00, 76.58, 56.05, 47.24, 34.17, 32.17. LC−MS (ESI): m/z = 351 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{18}H_{16}O_4SNa$ ($M+Na^+$); 351.0661. Found: 351.0658.

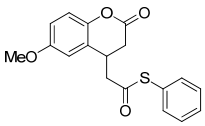
3bd



yield: 94% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.33 (m, 5H), 7.21-7.14 (m, 1H), 7.12–7.03 (m, 2H), 6.08–5.85 (m, 1H), 5.11 (tt, *J* = 3.0, 1.7 Hz, 1H), 5.07 (dq, *J* = 3.3, 1.7 Hz, 1H), 3.66 (ddd, *J* = 10.0, 7.0, 5.0 Hz, 1H), 3.47 (dd, *J* = 6.6, 1.0 Hz, 2H), 3.03–2.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.00, 167.20, 149.08, 135.70, 134.38, 129.69, 129.68, 129.28, 128.65, 126.92, 125.60, 124.52, 124.43, 116.37, 77.42, 77.00, 76.58, 47.31, 34.27, 33.57, 32.14. LC−MS (ESI): m/z = 361 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{20}H_{18}O_3SNa$ ($M+Na^+$); 361.0869. Found: 361.0862.

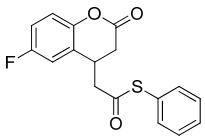
3be



yield: 91% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.31 (m, 5H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.82 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.73 (d, *J* = 2.9 Hz, 1H), 3.77 (s, 3H), 3.61 (ddd, *J* = 12.3, 7.2, 5.1 Hz, 1H), 3.03–2.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.11, 167.22, 160.14, 152.12, 134.37, 129.69, 129.29, 128.22, 126.95, 116.24, 110.74, 102.73, 77.42, 77.00, 76.58, 55.52, 47.71, 34.58, 31.35. LC−MS (ESI): m/z = 351 ($M+Na^+$). HRMS(ESI): exact mass calcd for $C_{18}H_{16}O_4SNa$ ($M+Na^+$); 351.0661. Found: 351.0663.

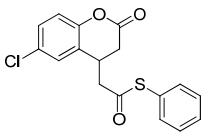
3bf



yield: 82% (24h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.31 (m, 5H), 7.12–6.87 (m, 3H), 3.64 (ddd, *J* = 12.4, 7.2, 5.2 Hz, 1H), 3.05–2.73 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.78, 166.74, 160.65, 157.41, 147.34, 134.39, 129.82, 129.35, 126.67, 126.15, 126.05, 118.70, 118.59, 115.90, 115.59, 114.49, 114.17, 77.42, 77.00, 76.58, 46.97, 33.93, 31.87. LC−MS (ESI): m/z = 339 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{13}FO_3SNa$ ($M+Na^+$); 339.0461. Found: 339.0477.

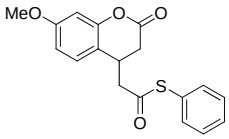
3bg



yield: 86% (24h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.26 (m, 5H), 7.23–7.12 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 3.62–3.49 (m, 1H), 2.95–2.70 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.80, 166.47, 149.85, 134.43, 129.83, 129.76, 129.36, 129.07, 127.60, 126.64, 126.06, 118.68, 77.42, 77.00, 76.58, 47.00, 33.93, 31.84. LC−MS (ESI): m/z = 355 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{13}ClO_3SNa$ ($M+Na^+$); 355.0166. Found: 355.0169.

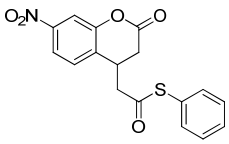
3bh



yield: 82% (24h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.30 (m, 5H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.82 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.73 (d, *J* = 2.9 Hz, 1H), 3.77 (s, 3H), 3.61 (ddd, *J* = 12.4, 7.2, 5.1 Hz, 1H), 2.96–2.79 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.02, 167.40, 156.30, 145.13, 134.37, 129.71, 129.29, 126.88, 125.35, 118.08, 114.19, 112.47, 77.42, 77.00, 76.58, 55.67, 47.24, 34.22, 32.20. LC−MS (ESI): m/z = 351 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{18}H_{16}O_4SNa$ ($M+Na^+$); 351.0661. Found: 351.0673.

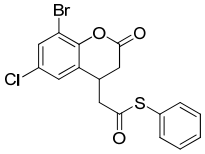
3bi



yield: 60% (24h)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25–8.16 (m, 2H), 7.49–7.31 (m, 5H), 7.21 (d, *J* = 8.6 Hz, 1H), 3.82–3.74 (m, 1H), 3.08–2.85 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.51, 165.20, 155.71, 144.25, 134.41, 129.97, 129.44, 126.35, 125.62, 124.94, 123.66, 118.31, 77.42, 77.00, 76.58, 46.72, 33.59, 31.78. LC−MS (ESI): m/z = 366 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{13}NO_5SNa$ ($M+Na^+$); 366.0406. Found: 366.0406.

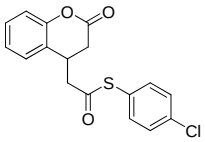
3bj



yield: 74% (24h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 2.4 Hz, 1H), 7.48–7.29 (m, 5H), 7.19 (d, *J* = 2.3 Hz, 1H), 3.73–3.55 (m, 1H), 3.01–2.73 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.66, 165.28, 147.16, 134.44, 132.44, 130.03, 129.93, 129.42, 127.37, 126.89, 126.52, 111.76, 77.42, 77.00, 76.58, 46.77, 33.84, 32.35. LC−MS (ESI): m/z = 433 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{12}BrClO_3SNa$ ($M+Na^+$); 432.9271. Found: 432.9270.

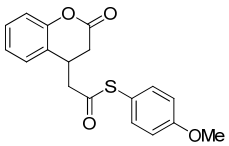
3cb



yield: 94% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.35 (m, 2H), 7.35–7.25 (m, 3H), 7.22 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.14 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.11–7.05 (m, 1H), 3.73–3.59 (m, 1H), 3.04–2.77 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.47, 167.13, 151.31, 136.18, 135.59, 129.56, 129.12, 127.62, 125.26, 124.73, 124.32, 117.37, 77.42, 77.00, 76.58, 47.42, 34.30, 31.90. LC−MS (ESI): m/z = 355 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{13}ClO_3SNa$ ($M+Na^+$); 355.0166. Found: 355.0177.

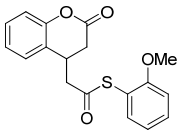
3db



yield: 97% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.23 (m, 4H), 7.21–7.08 (m, 2H), 7.02–6.93 (m, 2H), 3.86 (s, 3H), 3.70 (ddd, *J* = 12.4, 7.2, 5.2 Hz, 1H), 2.90–2.87 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.07, 167.25, 160.83, 151.29, 135.98, 128.98, 127.62, 124.66, 124.52, 117.51, 117.27, 114.94, 77.42, 77.00, 76.58, 55.31, 47.03, 34.27, 31.85. LC−MS (ESI): m/z = 351 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{18}H_{16}O_4SNa$ ($M+Na^+$); 351.0661. Found: 351.0661.

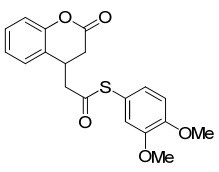
3eb



yield: 93% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 1H), 7.26-7.14 (m, 3H), 7.08–6.95 (m, 2H), 6.92-6.87 (m, 2H), 3.75 (s, 3H), 3.65–3.49 (m, 1H), 2.99–2.61 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.36, 167.29, 159.05, 151.29, 136.45, 131.98, 128.89, 127.45, 124.67, 124.60, 121.08, 117.21, 115.10, 111.55, 77.42, 77.00, 76.58, 55.88, 46.95, 34.12, 31.83. LC−MS (ESI): m/z = 351 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{18}H_{16}O_4SNa$ ($M+Na^+$); 351.0661. Found: 351.0673.

3fb

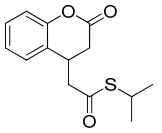


yield: 96% (12h)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.12 (m, 2H), 7.11–6.96 (m, 2H), 6.89-6.77 (m, 3H), 3.81 (d, *J* = 5.8 Hz, 6H), 3.59 (ddd, *J* = 12.2, 7.3, 5.2 Hz, 1H), 2.95–2.66 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.01, 167.22, 151.29, 150.43, 149.23, 128.98,

127.67, 127.59, 124.62, 124.49, 117.62, 117.26, 117.08, 111.54, 77.42, 77.00, 76.58, 55.93, 55.84, 47.01, 34.22, 31.81. LC−MS (ESI): m/z = 381 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{19}H_{18}O_5SNa$ ($M+Na^+$); 381.0767. Found: 381.0774.

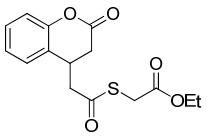
3gb



yield: 92% (12h)

^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.23 (m, 1H), 7.19 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.11 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.08–7.01 (m, 1H), 3.89–3.53 (m, 2H), 2.88–2.72 (m, 4H), 1.28 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.71, 167.29, 151.26, 128.86, 127.45, 124.65, 124.60, 117.20, 77.42, 77.00, 76.58, 47.80, 35.07, 34.20, 31.82, 22.78, 22.71. LC−MS (ESI): m/z = 287 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{14}H_{16}O_3SNa$ ($M+Na^+$); 287.0712. Found: 287.0723.

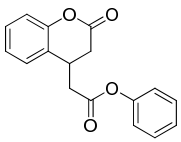
3hb



yield: 88% (12h)

^1H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.18 (m, 1H), 7.17–7.11 (m, 1H), 7.09–6.95 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.66–3.45 (m, 3H), 2.97–2.61 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.85, 168.15, 167.09, 151.25, 129.04, 127.44, 124.72, 124.37, 117.28, 77.42, 77.00, 76.58, 61.95, 47.42, 34.14, 31.86, 31.41, 14.04. LC−MS (ESI): m/z = 331 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{15}H_{16}O_5SNa$ ($M+Na^+$); 331.0610. Found: 331.0613.

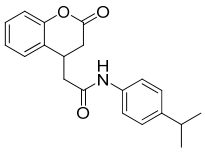
3ib



yield: 98% (24h)

^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.21 (m, 4H), 7.19–7.12 (m, 1H), 7.11–7.00 (m, 2H), 6.98–6.91 (m, 2H), 3.72–3.53 (m, 1H), 2.90–2.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.36, 167.30, 151.36, 150.22, 129.46, 129.10, 127.58, 126.08, 124.75, 124.62, 121.32, 117.37, 77.42, 77.00, 76.58, 38.99, 34.54, 31.59. LC−MS (ESI): m/z = 305 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{14}O_4Na$ ($M+Na^+$); 305.0784. Found: 305.0794.

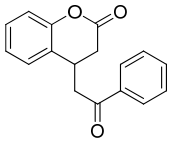
3jb



yield: 80% (24h)

^{1}H NMR (300 MHz, DMSO): δ = 9.86 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.36–7.25 (m, 2H), 7.19–7.03 (m, 4H), 3.59 (dd, *J* = 11.5, 6.6 Hz, 1H), 3.08-3.00 (m, 1H), 2.93–2.52 (m, 4H), 1.20–1.00 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, DMSO): δ = 168.28, 167.71, 151.09, 143.38, 136.62, 128.44, 127.87, 126.42, 126.01, 124.34, 119.30, 116.54, 40.96, 40.36, 40.08, 39.80, 39.52, 39.24, 38.96, 38.69, 33.89, 32.86, 31.19, 23.95. LC−MS (ESI): m/z = 346 (M+Na$^+$). HRMS (ESI): exact mass calcd for $C_{20}H_{21}NO_3$ Na (M+Na$^+$); 346.1413. Found: 346.1419.

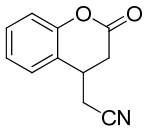
3kb



yield: 93% (12h)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93–7.91 (m, 2H), 7.60–7.57 (m, 1H), 7.48–7.45 (m, 2H), 7.38–7.21 (m, 2H), 7.19–6.95 (m, 2H), 3.98–3.78 (m, 1H), 3.35–3.24 (m, 2H), 2.98–2.88 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.78, 167.90, 151.41, 136.30, 133.54, 128.67, 127.96, 127.85, 125.80, 124.66, 117.13, 77.25, 77.00, 76.75, 42.82, 34.64, 30.39. LC−MS (ESI): m/z = 267 (M+H$^+$). HRMS (ESI): exact mass calcd for $C_{17}H_{15}O_3$ (M+H$^+$); 267.1021. Found: 267.1022.

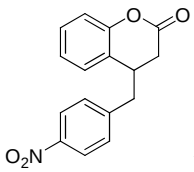
3lb



yield: 94% (12h)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.34 (m, 1H), 7.33–7.28 (m, 1H), 7.22-7.19 (m, 1H), 7.12-7.11 (m, 1H), 3.50–3.39 (m, 1H), 3.05–2.84 (m, 2H), 2.69-2.67 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.00, 151.14, 129.95, 127.31, 125.14, 122.29, 117.62, 116.65, 77.25, 77.00, 76.75, 34.11, 32.20, 22.88. LC−MS (ESI): m/z = 210 (M+Na$^+$). HRMS (ESI): exact mass calcd for $C_{11}H_9NO_2$ Na (M+Na$^+$); 210.0531. Found: 210.0528.

3mb



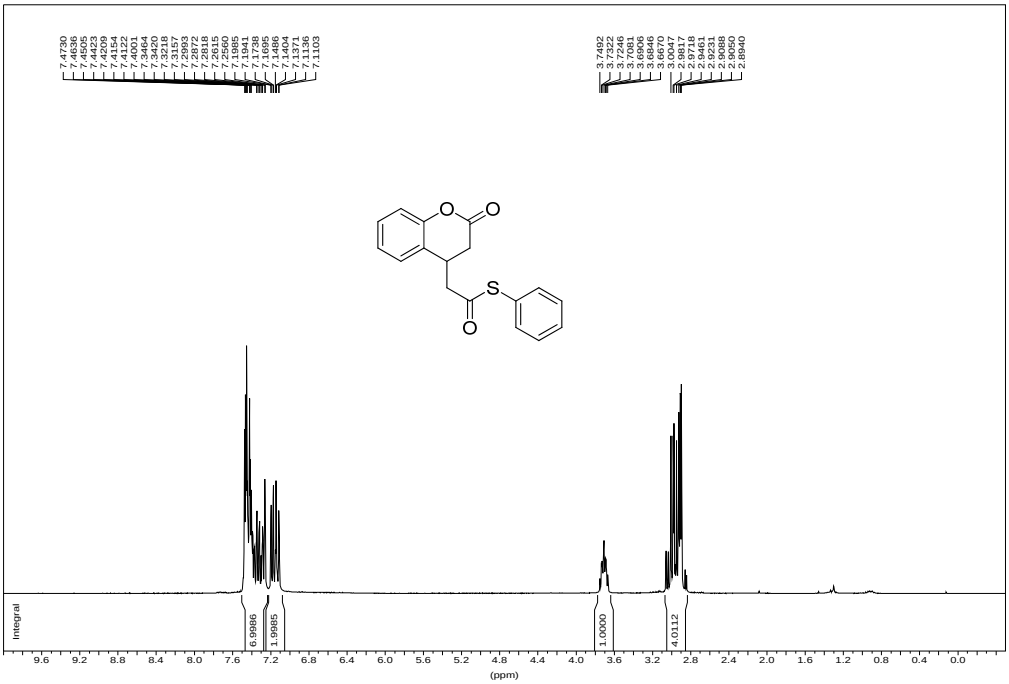
yield: 93% (12h)

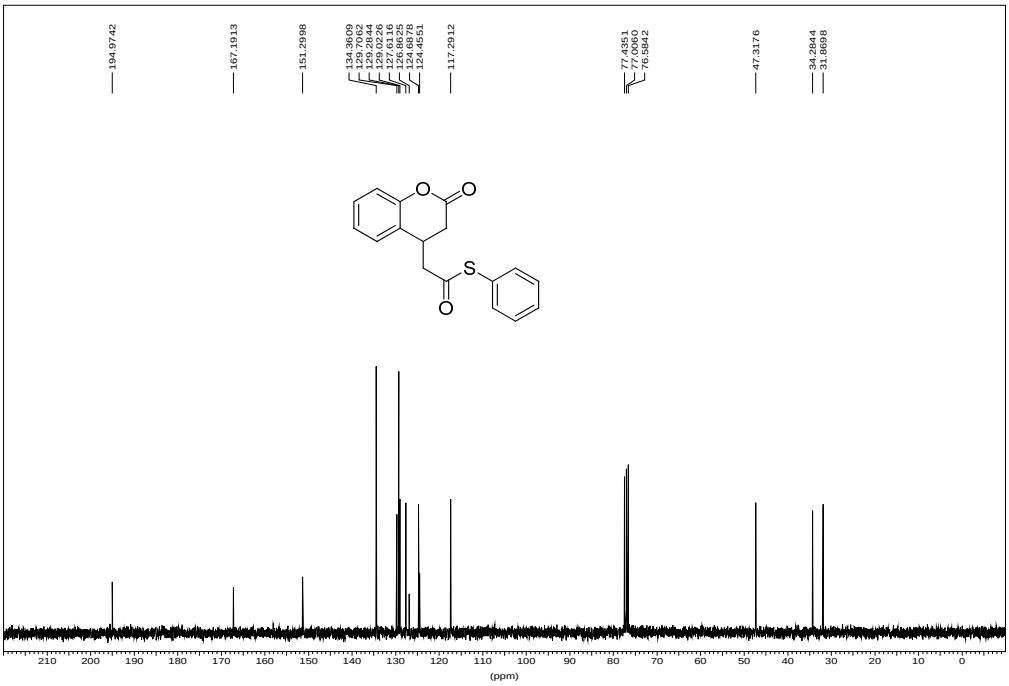
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.5 Hz, 2H), 7.33–7.23 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.13–6.98 (m, 1H), 6.91-6.89 (m, 1H), 3.29 (qd, *J* = 8.0, 3.3 Hz, 1H),

3.03-2.99 (m, 1H), 2.94-2.89 (m, 1H), 2.84-2.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.38, 151.20, 146.94, 145.42, 130.13, 128.95, 127.81, 124.70, 124.46, 123.74, 117.28, 77.25, 77.00, 76.75, 41.04, 37.04, 34.10. LC−MS (ESI): m/z = 306 ($M+Na^+$). HRMS (ESI): exact mass calcd for $C_{16}H_{13}NO_4Na$ ($M+Na^+$); 306.0742. Found: 306.0751.

5. NMR spectrun of compounds 3

3bb

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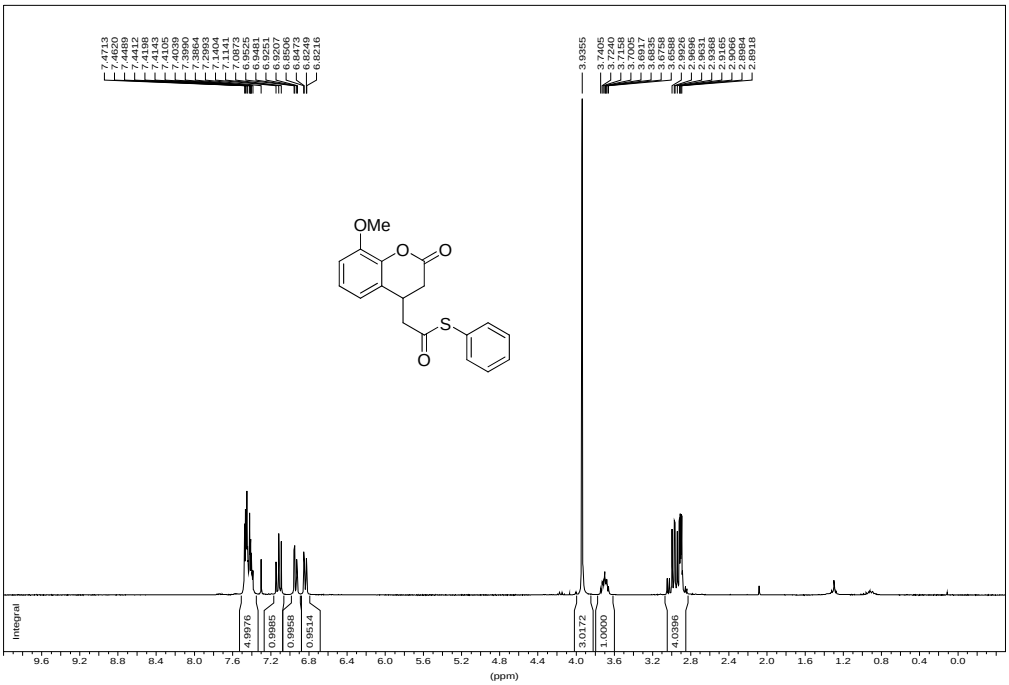
151.2998
134.3609
129.7062
129.2844
129.0226
127.6116
126.8825
124.6870
124.4551
117.2912
77.4351
77.0000
76.5842
47.3176
34.2844
31.8698
O
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3bc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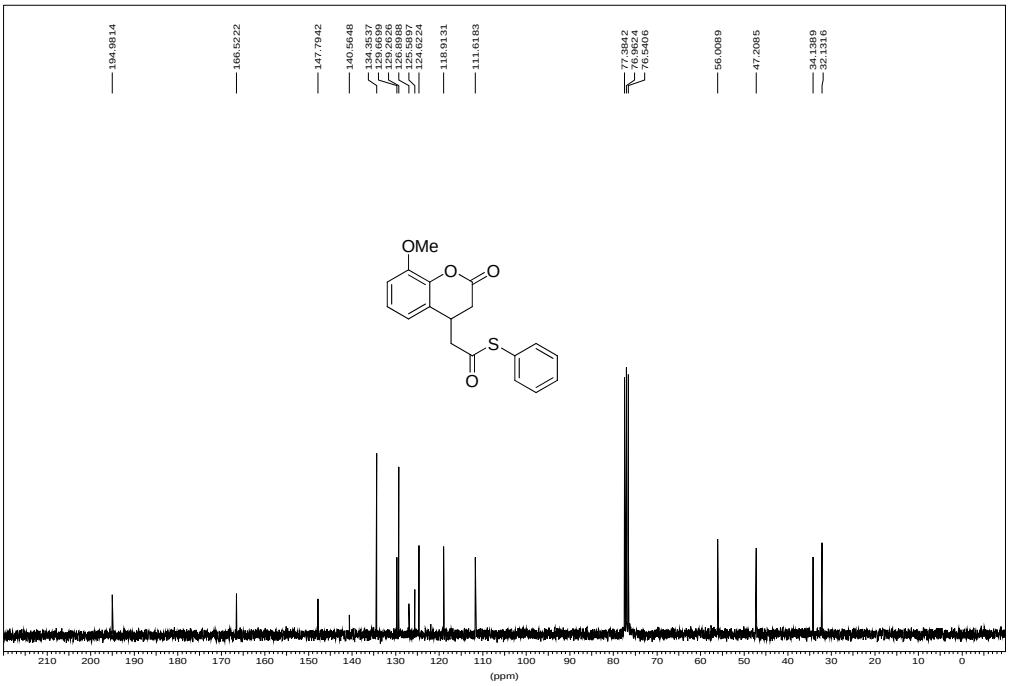
7.4489
7.4412
7.4198
7.4143
7.4105
7.4039
7.3960
7.3864
7.2993
7.1464
7.1141
7.0873
6.9525
6.9441
6.9251
6.9207
6.8956
6.8473
6.8249
6.8216
3.9355
3.7405
3.7240
3.7158
3.7005
3.6917
3.6835
3.6753
3.6588
2.9926
2.9696
2.9631
2.9368
2.9165
2.9066
2.8984
2.8918
OMe
O
O
S
O
Integral
4.9976
0.9985
0.9958
0.9514
3.0172
1.0000
4.0396
9.6 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 0.0
(ppm)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147.7942
140.5648
134.3537
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129.2626
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124.6224
118.9131
111.6183
77.3842
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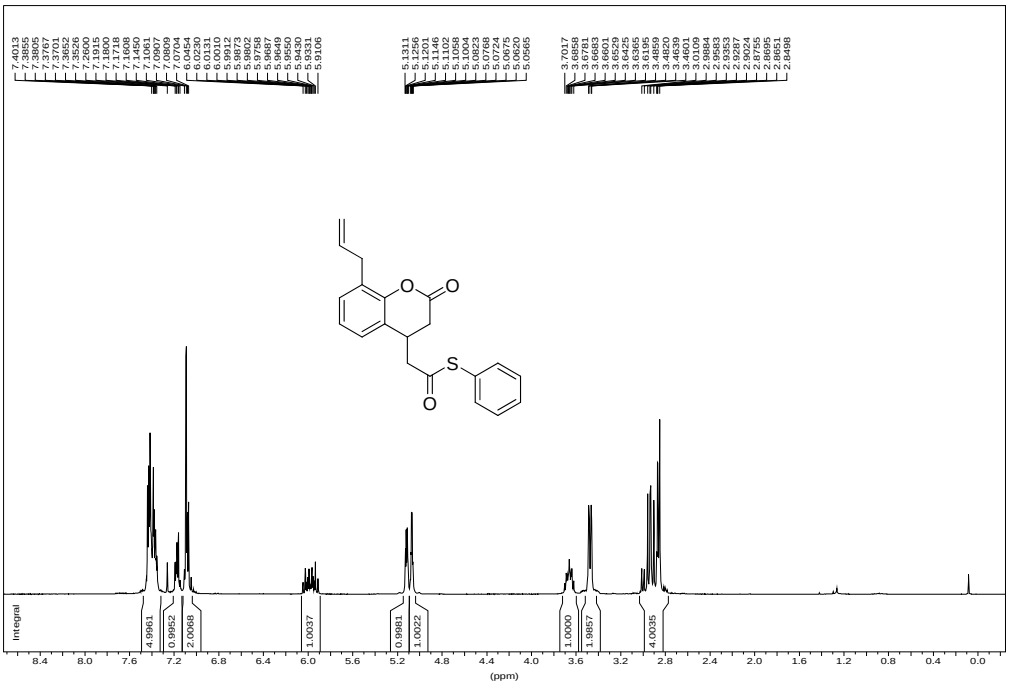
56.0089
47.2085
34.1389
32.1316
OMe
O
O
S
O
(ppm)

3bd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7.3805
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7.3701
7.3652
7.2636
7.2600
7.1915
7.1800
7.1718
7.1608
7.1450
7.1081
7.0907
7.0809
7.0704
6.9454
6.0230
6.0131
6.0010
5.9917
5.9902
5.9769
5.9687
5.9649
5.9550
5.9430
5.9331
5.9106
5.1311
5.1256
5.1201
5.1146
5.1102
5.1058
5.1004
5.0823
5.0768
5.0714
5.0674
5.0675
5.0620
5.0565
3.7017
3.6858
3.6781
3.6693
3.6601
3.6529
3.6425
3.6365
3.6195
3.4859
3.4820
3.4658
3.4601
3.0109
2.9984
2.9583
2.9353
2.9287
2.9204
2.8755
2.8695
2.8491
2.8498
O
O
S
O
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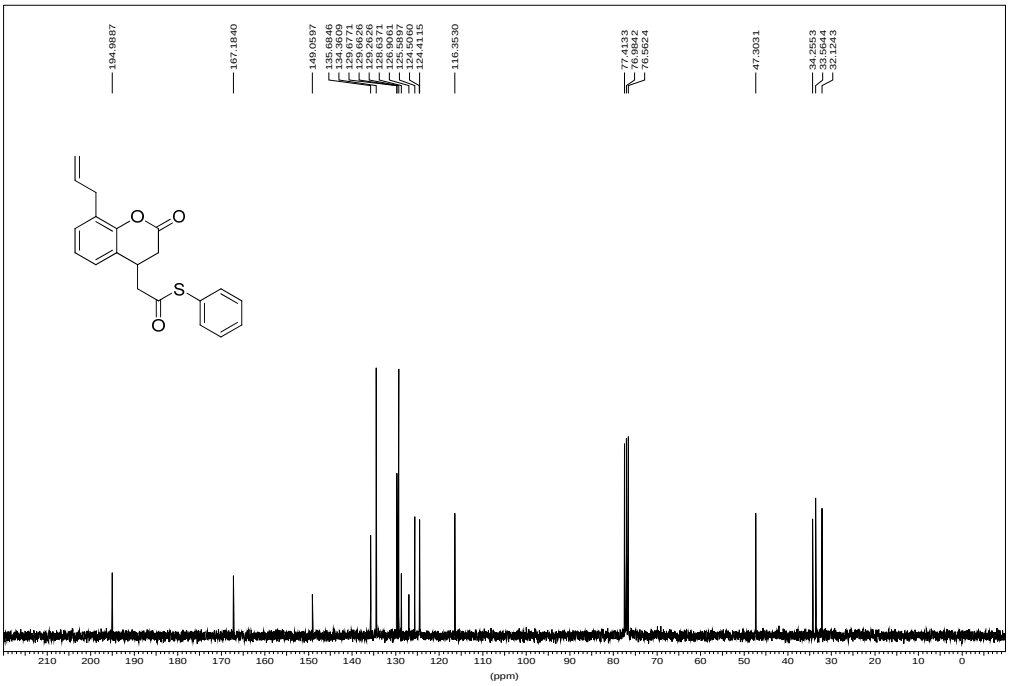
(ppm)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129.6626
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128.6371
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125.5897
124.6560
124.4115
116.3530
77.4133
76.9982
76.5824
47.3031
34.2553
33.5644
32.1243
O
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3be


7.4320
7.4222
7.4183
7.4101
7.4024
7.3970
7.3930
7.3876
7.3805
7.3750
7.3712
7.3646
7.3597
7.3553
7.3471
7.2600
7.1307
7.1222
6.6957
6.6875
6.6678
6.6598
6.6344
6.6256
3.7954
3.6513
3.6272
3.6113
3.5932
3.5691
2.9824
2.9668
2.9298
2.9210
2.9068
2.8980
2.8723
2.8673
2.8497
2.8438
2.8284
2.8202
2.7935
2.7747
MeO
O
O
S
O
Integral
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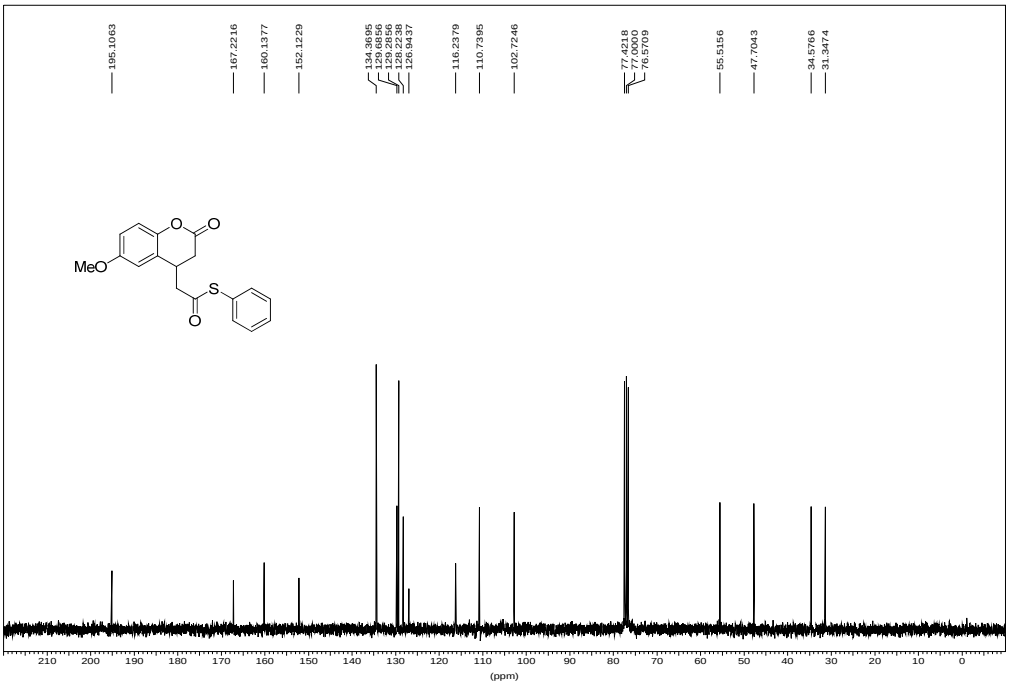
0.9986
1.9943
3.0014
1.0000
4.0023
10.4 10.0 9.6 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
(ppm)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128.6437
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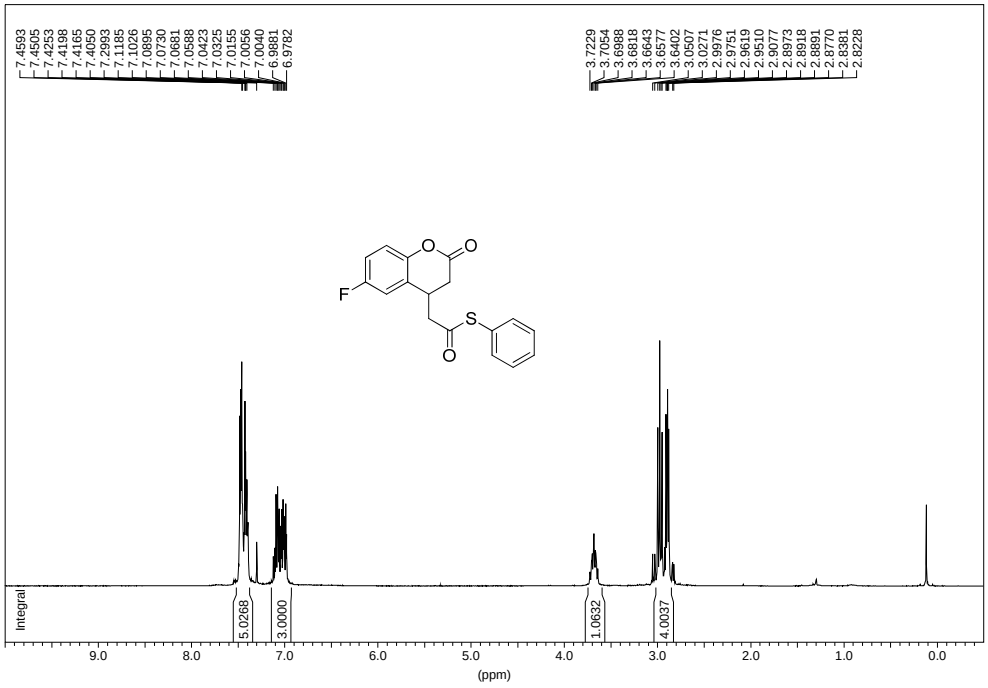
110.7395
102.7246
77.4218
77.0000
76.5709
55.5156
47.7043
34.5766
31.3474
MeO
O
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

3bf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7.4165
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7.2993
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7.1026
7.0895
7.0730
7.0681
7.0588
7.0423
7.0325
7.0155
7.0056
7.0040
6.9881
6.9782
3.7229
3.7054
3.6988
3.6818
3.6643
3.6577
3.6402
3.0507
3.0271
2.9976
2.9751
2.9619
2.9510
2.9077
2.8973
2.8918
2.8891
2.8770
2.8381
2.8228
F
O
O
S
O
Integral
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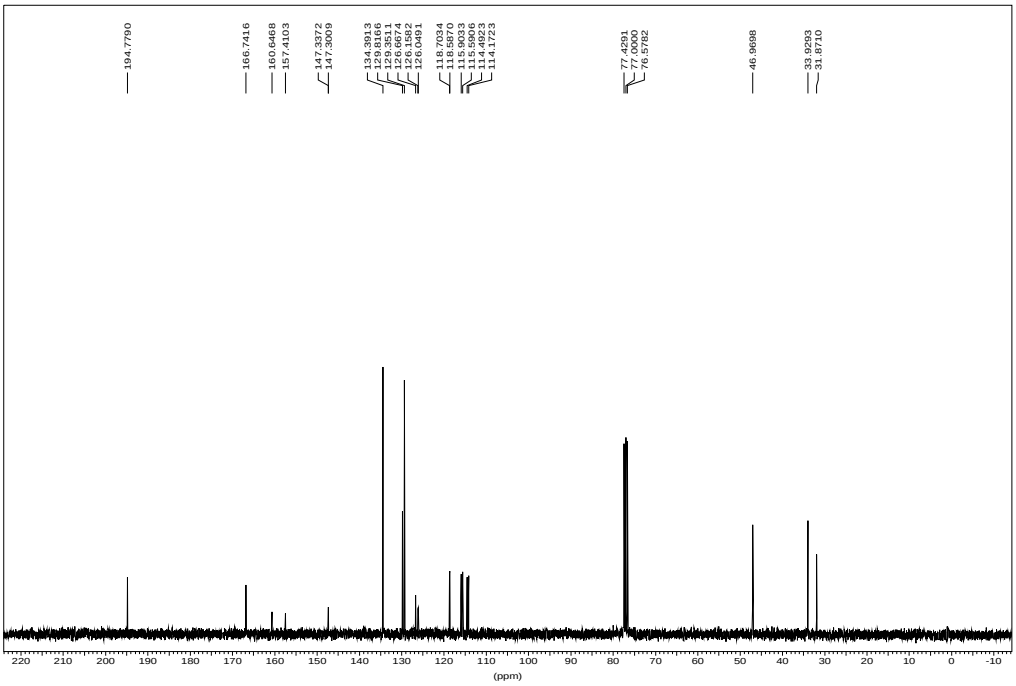
(ppm)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118.5870
115.9033
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33.9293
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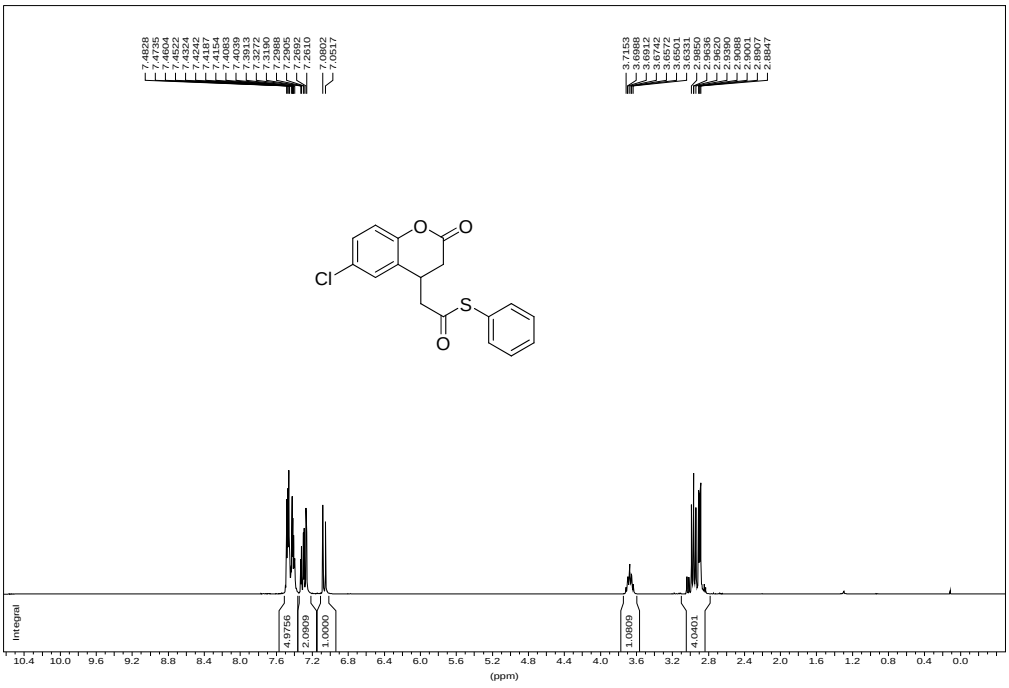
(ppm)

3bg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7.4039
7.3913
7.3272
7.3190
7.2988
7.2935
7.2892
7.2610
7.0802
7.0517
3.7153
3.6998
3.6912
3.6742
3.6572
3.6501
3.6331
2.9850
2.9658
2.9530
2.9390
2.9088
2.9001
2.8907
2.8847
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O
Cl
S
O
Integral
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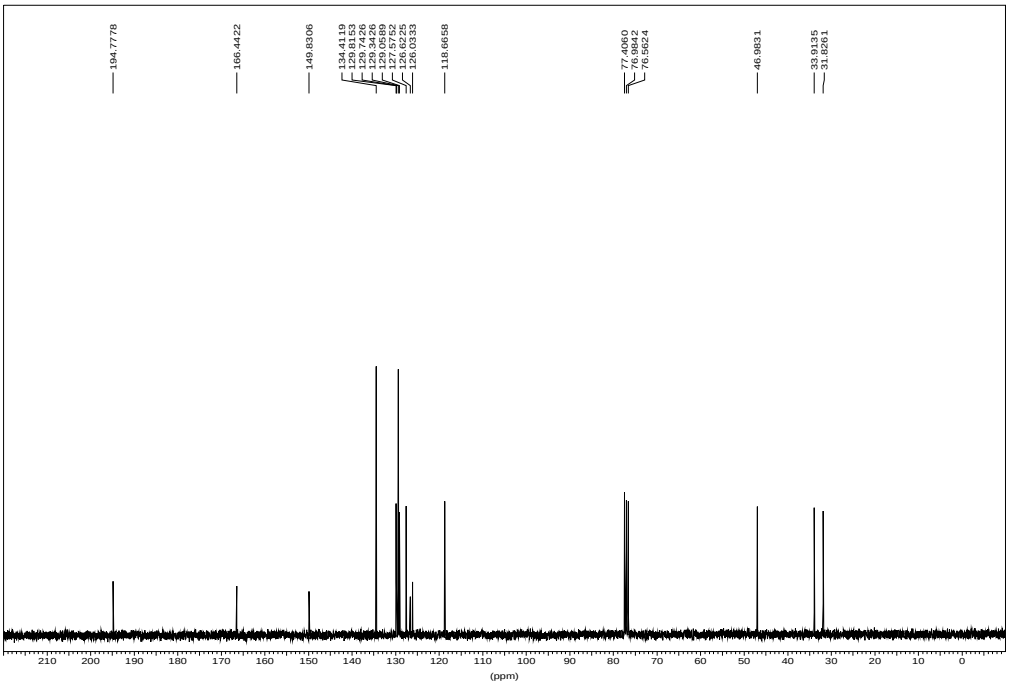
(ppm)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77.4060
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76.5624
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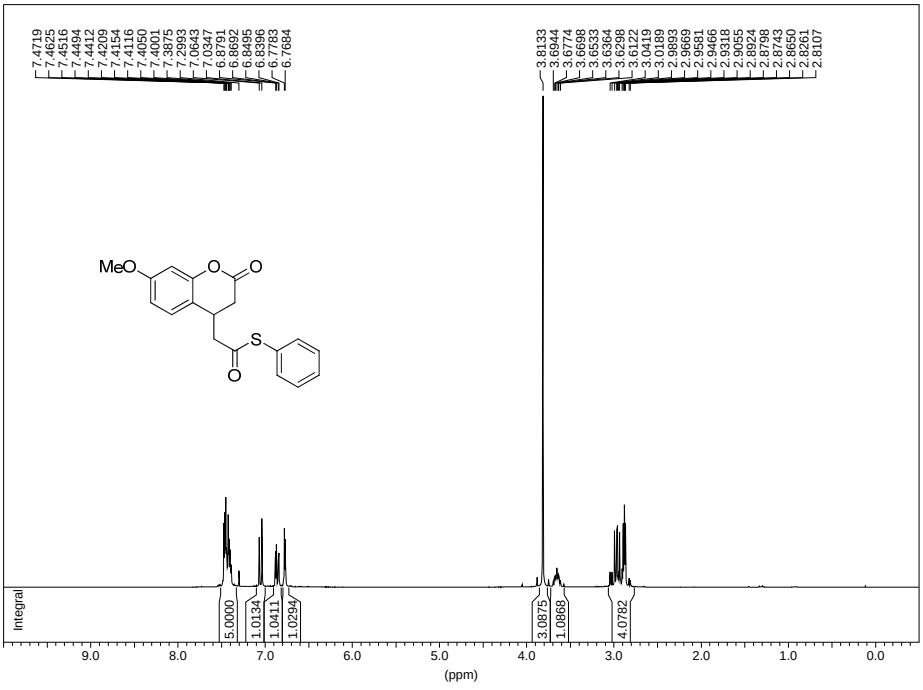
31.8261
(ppm)

3bh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7.4154
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7.4001
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7.0643
7.0347
6.8791
6.8692
6.8495
6.8396
6.7783
6.7684
3.8133
3.6944
3.6774
3.6698
3.6533
3.6364
3.6298
3.6122
3.0419
3.0189
2.9893
2.9669
2.9581
2.9466
2.9318
2.9055
2.8924
2.8798
2.8743
2.8550
2.8261
2.8107
MeO
O
O
S
O
Integral
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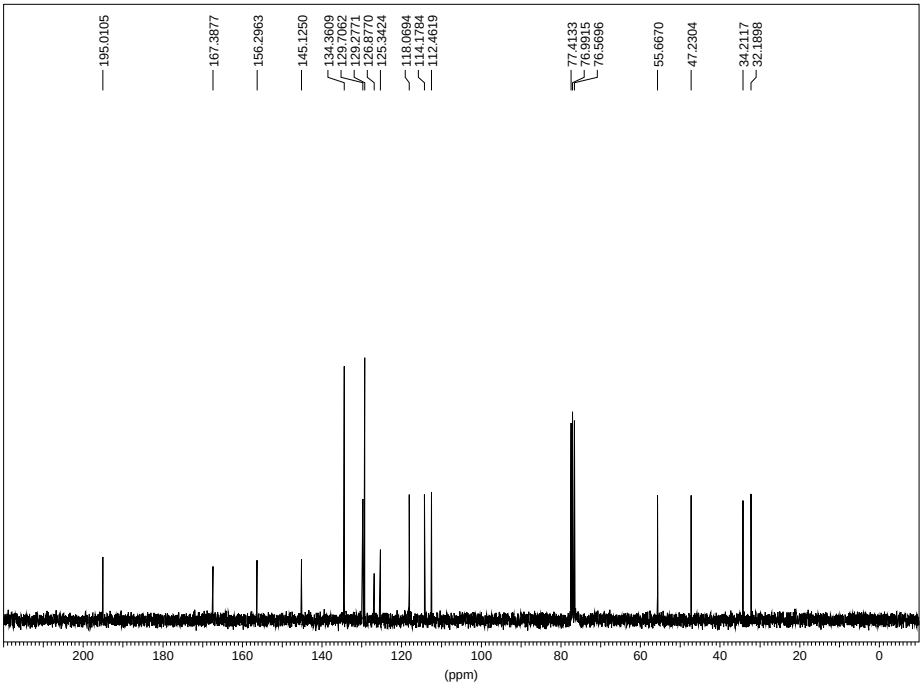
(ppm)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112.4619
77.4133
76.9915
76.5696
55.6670
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120
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80
60
40
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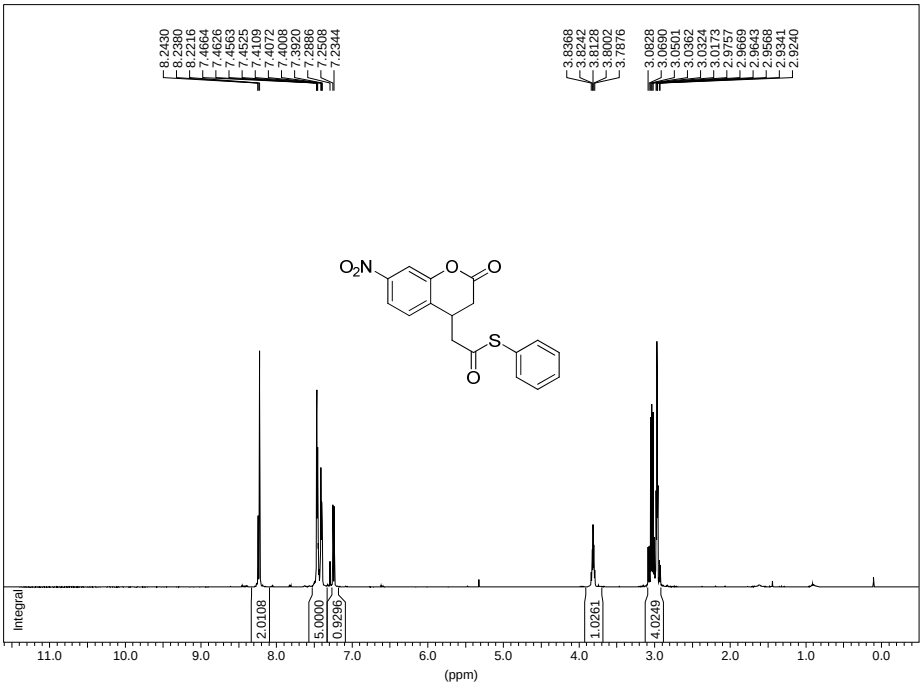
(ppm)

3bi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7.2508
7.2344
3.8368
3.8242
3.8128
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3.7876
3.0828
3.0690
3.0501
3.0362
3.0324
3.0173
2.9757
2.9669
2.9643
2.9568
2.9341
2.9240
O2N
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O
S
O
Integral
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7.0
6.0
5.0
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3.0
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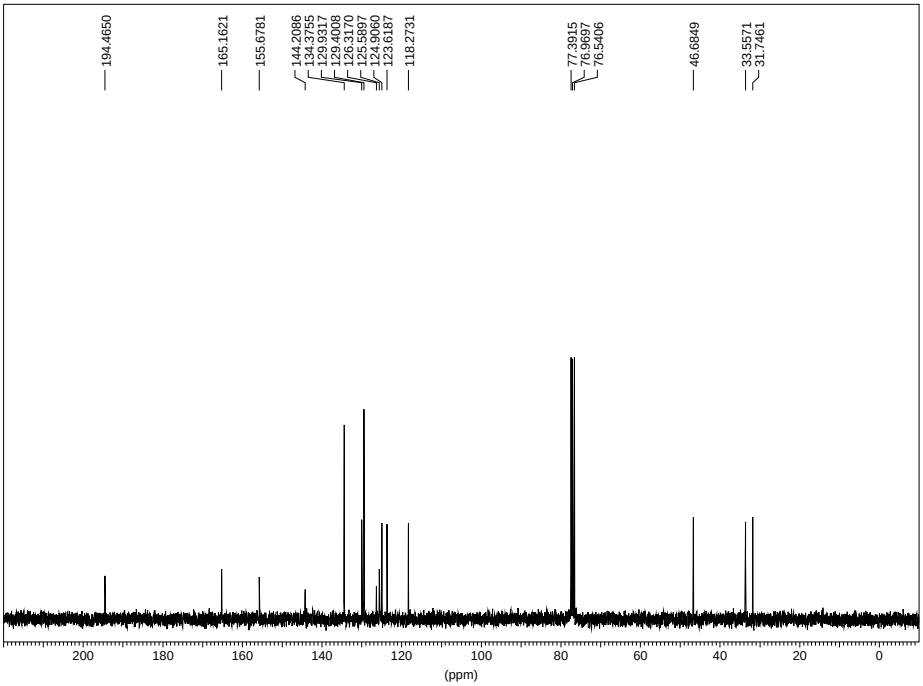
(ppm)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124.9060
123.6187
118.2731
77.3915
76.9697
76.5406
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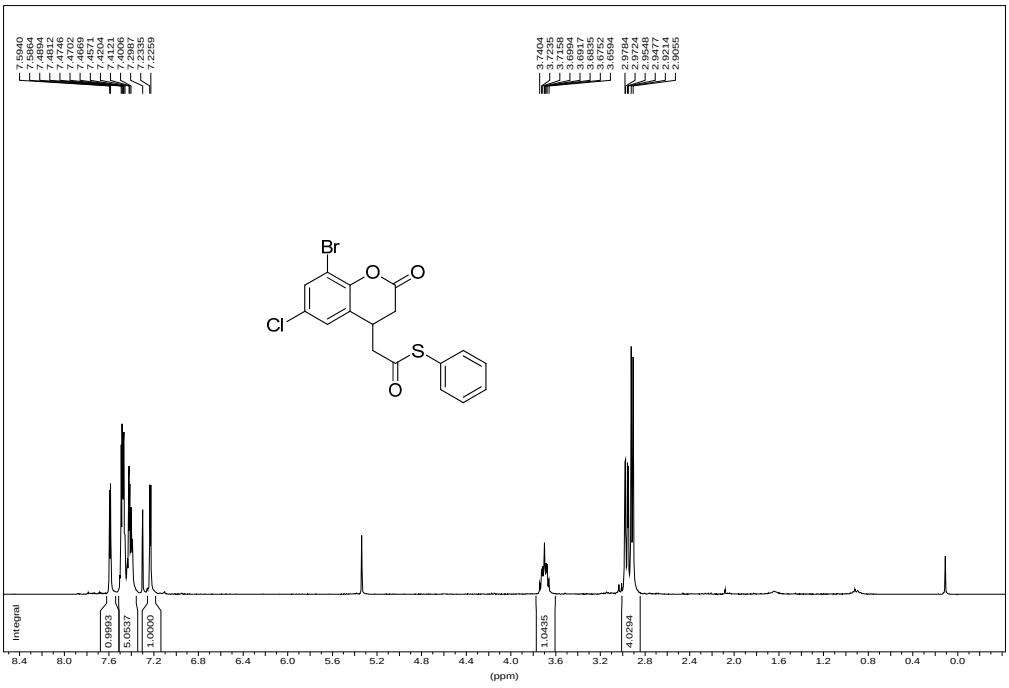
31.7461
200
180
160
140
120
100
80
60
40
20
0
(ppm)

3bj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7.3987
7.2335
7.2259
3.7404
3.7235
3.7158
3.6994
3.6937
3.6835
3.6752
3.6594
2.9784
2.9734
2.9548
2.9477
2.9214
2.9055
Br
O
O
Cl
S
O
Integral
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1.0000
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8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
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3.2
2.8
2.4
2.0
1.6
1.2
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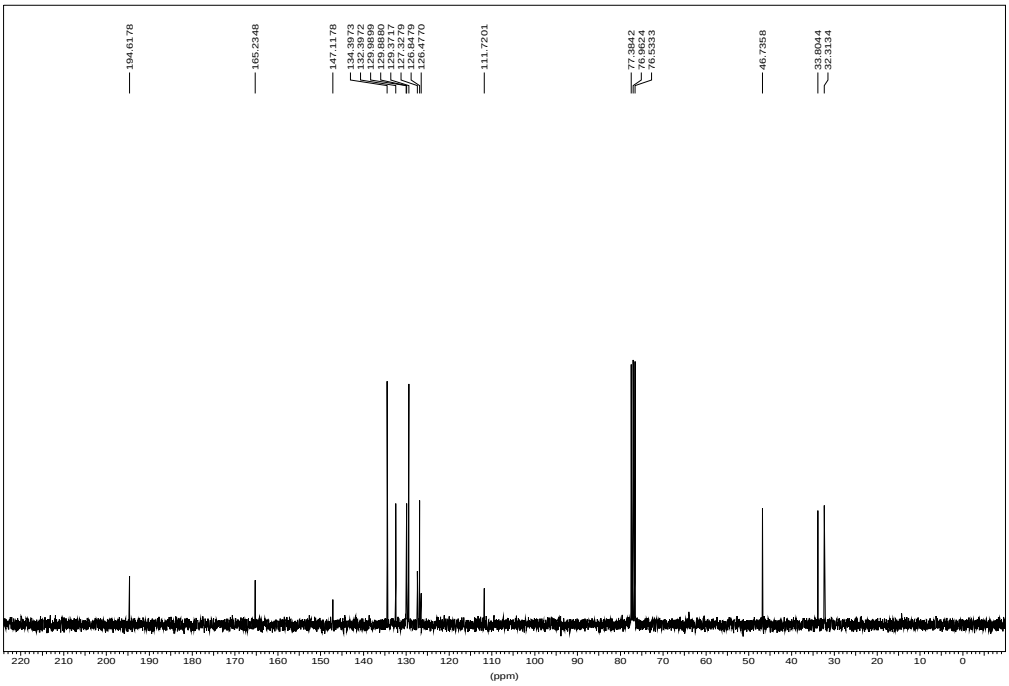
0.0
(ppm)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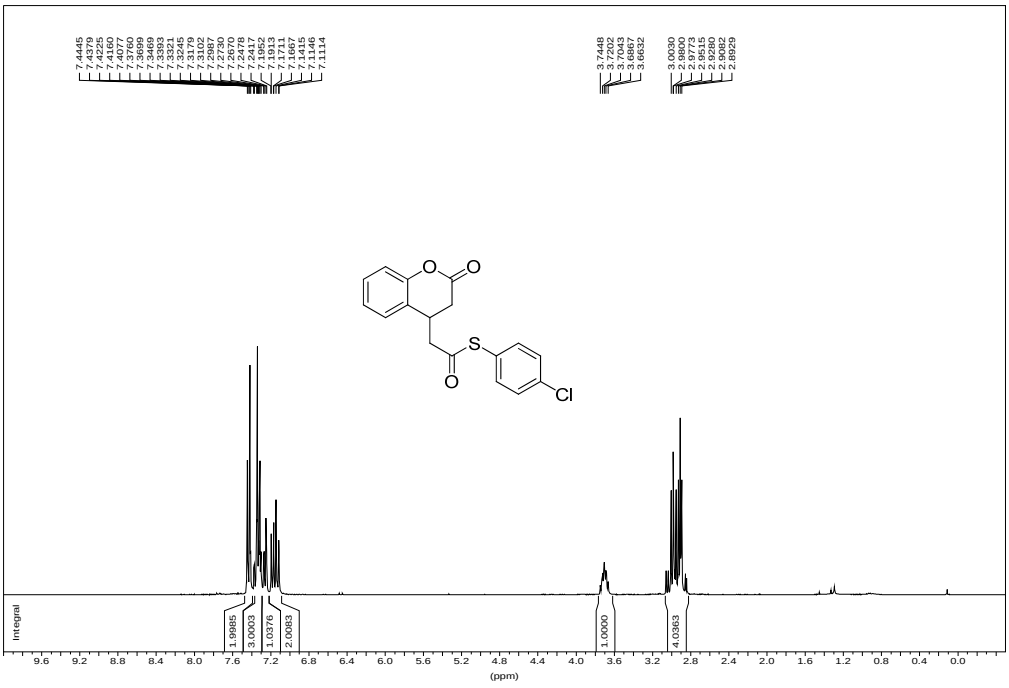
(ppm)

3cb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7.3245
7.3179
7.3102
7.2987
7.2730
7.2679
7.2578
7.2417
7.1952
7.1913
7.1711
7.1667
7.1445
7.1146
7.1114
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3.7202
3.7043
3.6867
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3.0030
2.9800
2.9573
2.9515
2.9280
2.9062
2.8829
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Cl
Integral
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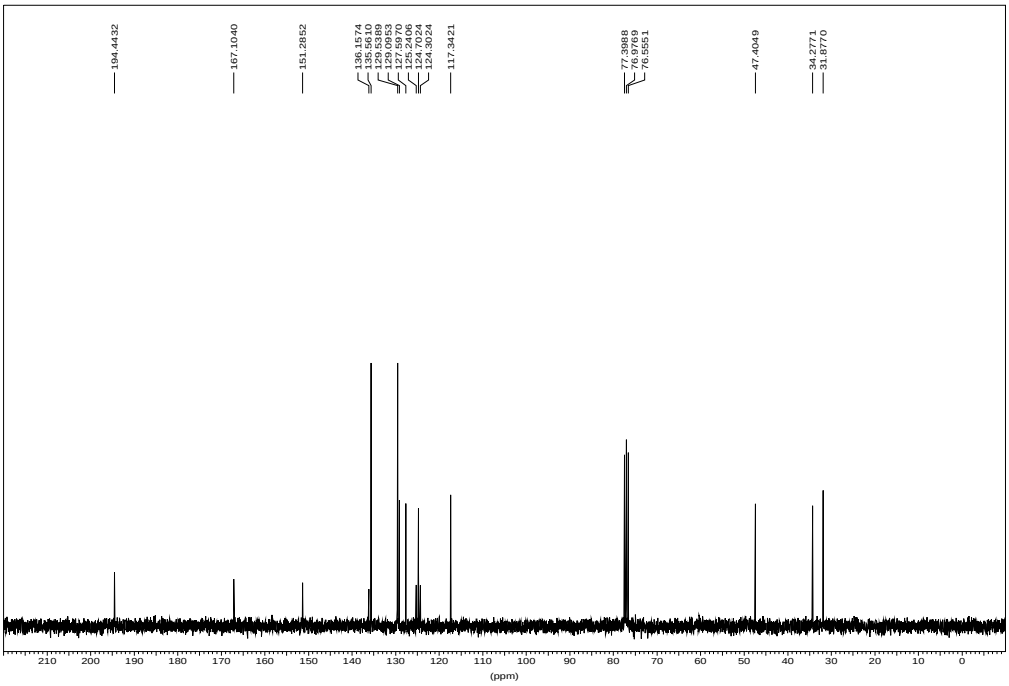
(ppm)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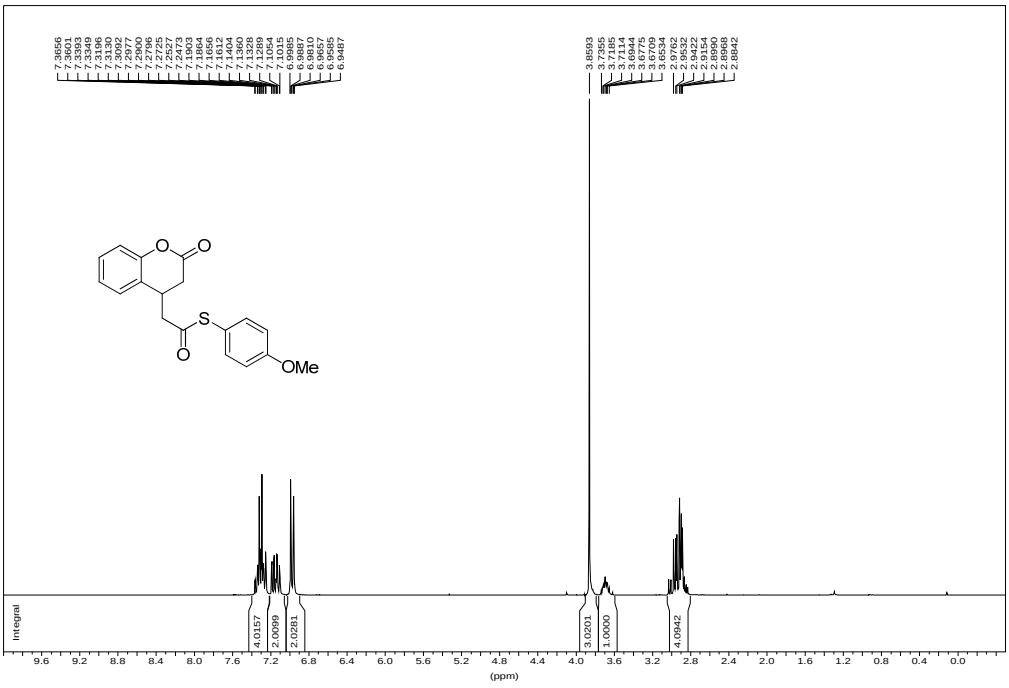
(ppm)

3db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7.2527
7.2473
7.1983
7.1884
7.1656
7.1612
7.1464
7.1360
7.1328
7.1289
7.1054
7.1015
6.9985
6.9937
6.9810
6.9667
6.9585
6.9467
3.8593
3.7355
3.7185
3.7114
3.6944
3.6775
3.6709
3.6634
2.9762
2.9532
2.9422
2.9154
2.8990
2.8968
2.8842
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O
S
O
OMe
Integral
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3.0201
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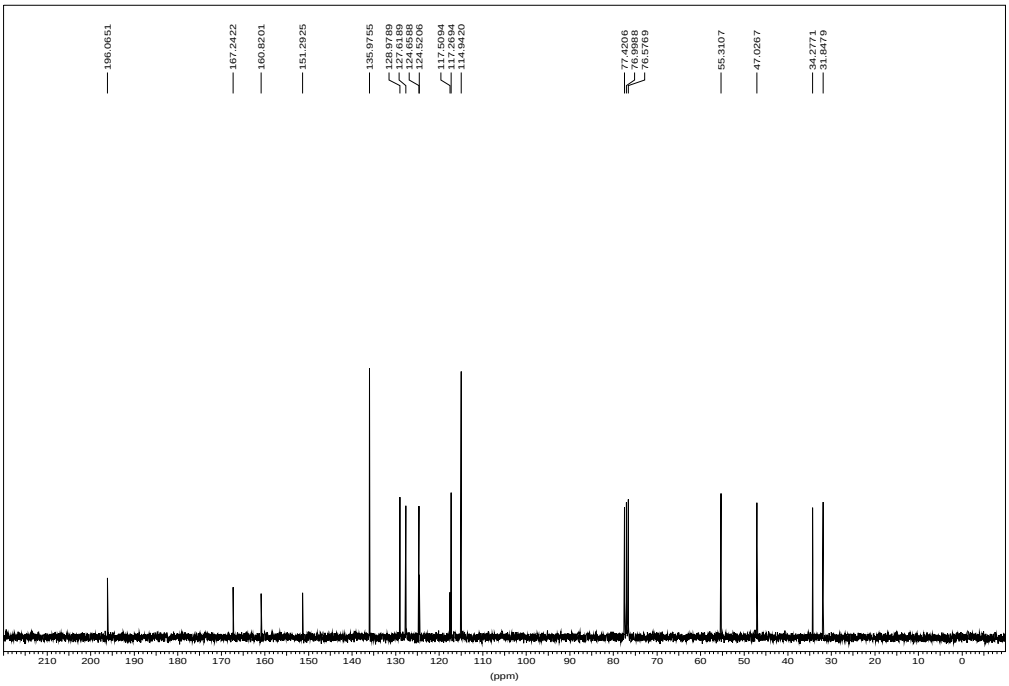
(ppm)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76.9968
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55.3107
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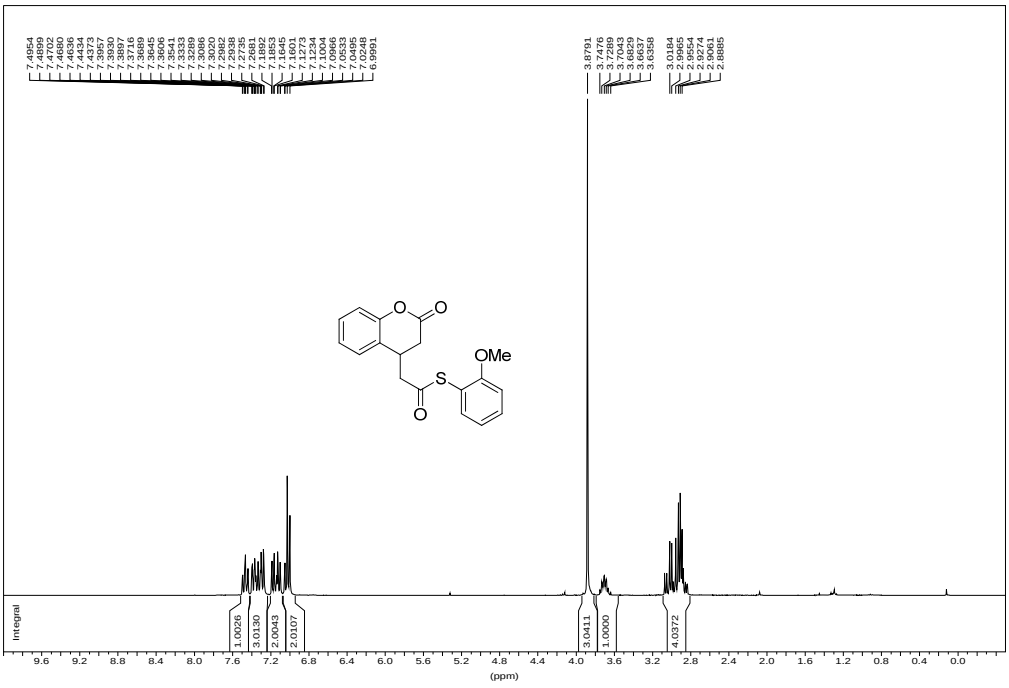
34.2771
31.8479
(ppm)

3eb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7.3930
7.3897
7.3716
7.3689
7.3645
7.3606
7.3541
7.3333
7.3289
7.3086
7.3020
7.2982
7.2938
7.2735
7.2681
7.1882
7.1853
7.1645
7.1601
7.1273
7.1234
7.1004
7.0966
7.0763
7.0495
7.0248
6.9991
3.8791
3.7476
3.7249
3.7043
3.6829
3.6637
3.6338
3.0184
2.9965
2.9764
2.9274
2.9061
2.8885
O
O
O
S
OMe
Integral
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2.0043
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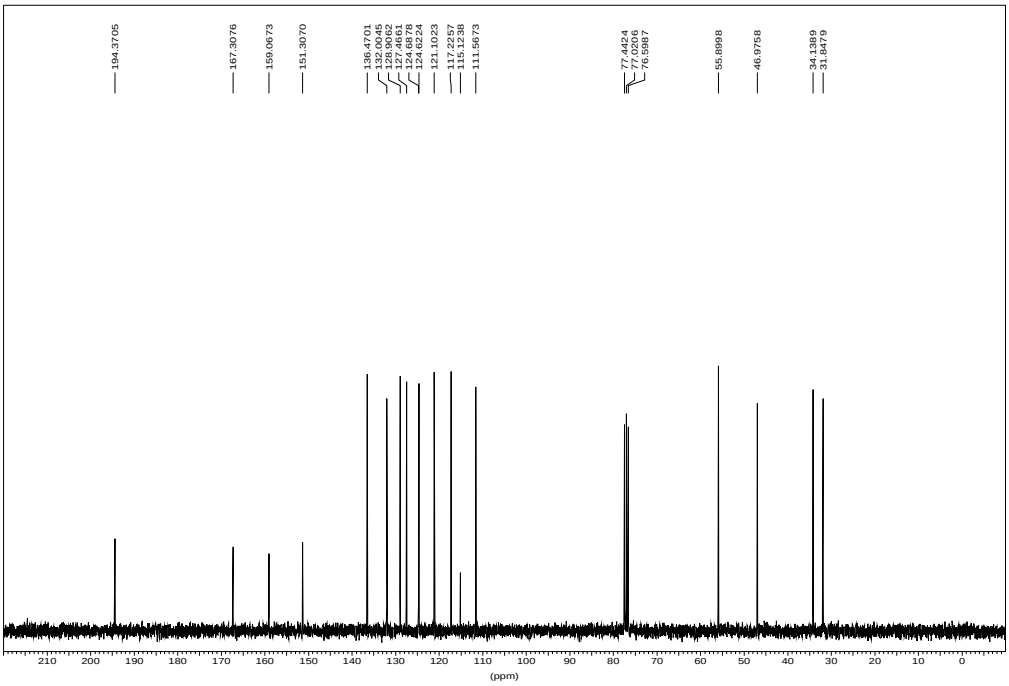
4.0372
(ppm)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159.0673
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136.4701
132.0045
128.9062
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121.1023
117.2257
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77.4424
77.0006
76.5987
55.8998
46.9758
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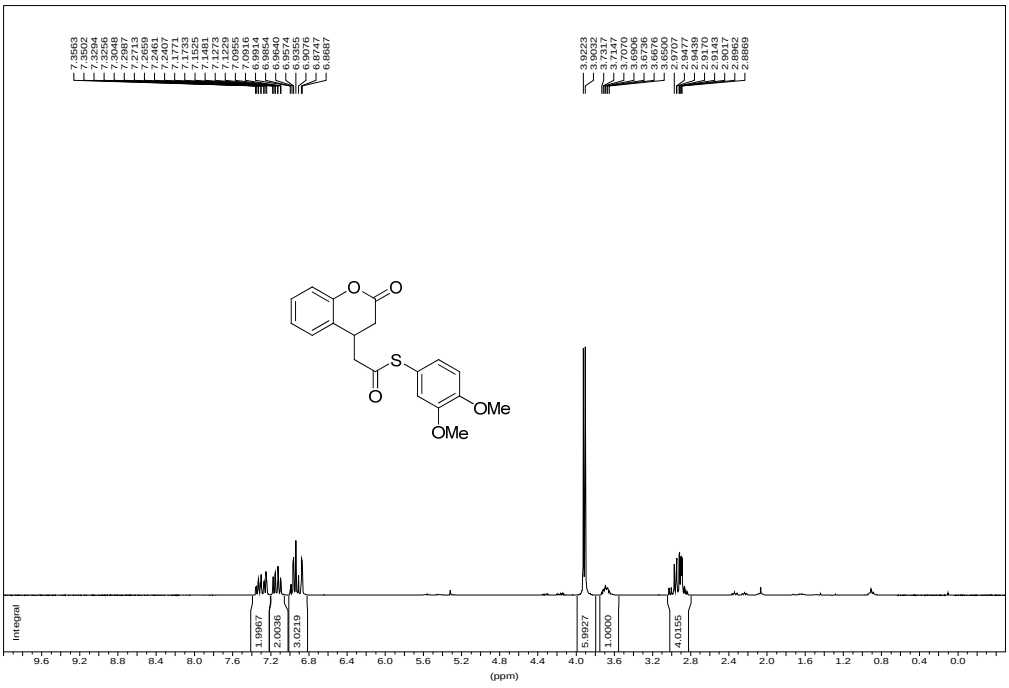
(ppm)

3fb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7.3048
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7.2713
7.2659
7.2461
7.2407
7.1771
7.1733
7.1525
7.1481
7.1273
7.1229
7.0955
7.0916
6.9914
6.9854
6.9640
6.9574
6.9355
6.9076
6.8747
6.8687
3.9223
3.9122
3.7317
3.7147
3.7070
3.6986
3.6736
3.6676
3.6569
2.9707
2.9477
2.9439
2.9170
2.9143
2.9017
2.8993
2.8883
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S
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OMe
OMe
Integral
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2.0036
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5.9927
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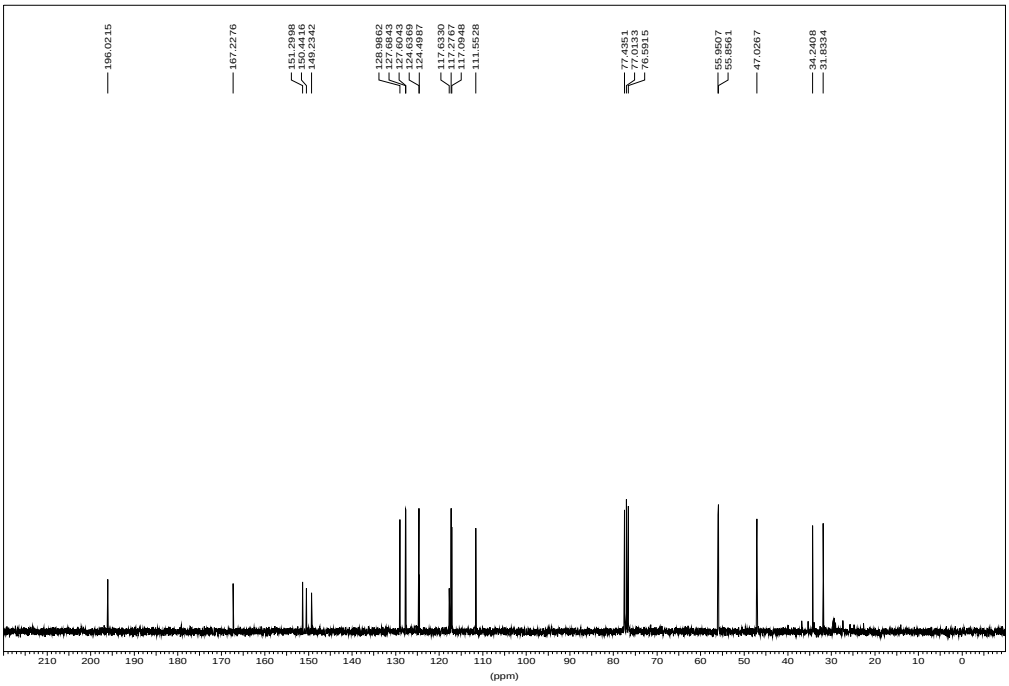
4.0155
(ppm)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151.2998
150.4416
149.2242
128.9862
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125.6589
124.4987
117.6330
117.2767
117.0948
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76.5915
55.9507
55.8561
47.0267
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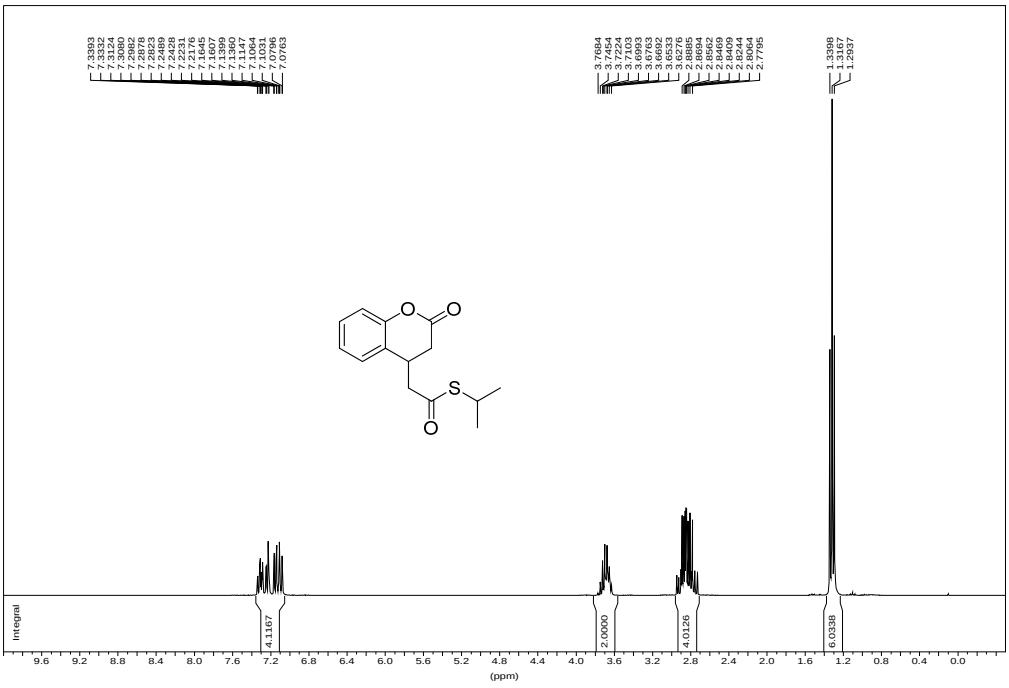
(ppm)

3gb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7.2992
7.2876
7.2823
7.2489
7.2436
7.2231
7.2176
7.2145
7.1607
7.1399
7.1360
7.1147
7.1064
7.1031
7.0796
7.0763
3.7684
3.7654
3.7224
3.7103
3.6993
3.6963
3.6692
3.6533
3.6376
3.8865
2.8694
2.8562
2.8469
2.8409
2.8244
2.8064
2.7795
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1.3167
1.2937
O
O
S
O
Integral
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2.0000
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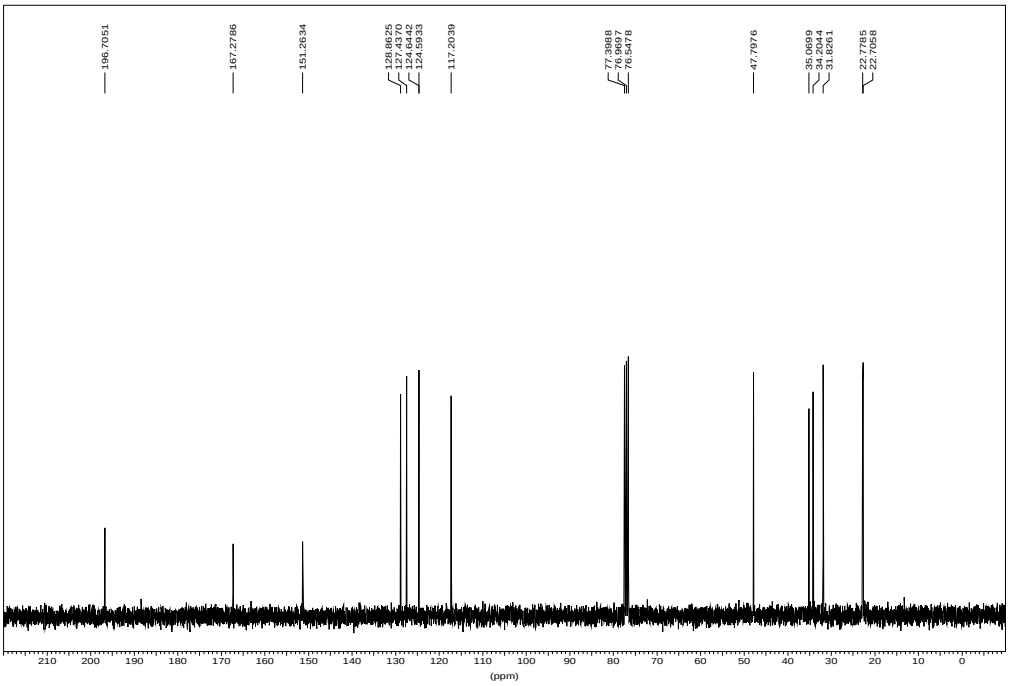
6.0338
(ppm)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151.2634
128.8625
127.4970
124.4442
124.5933
117.2039
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76.9897
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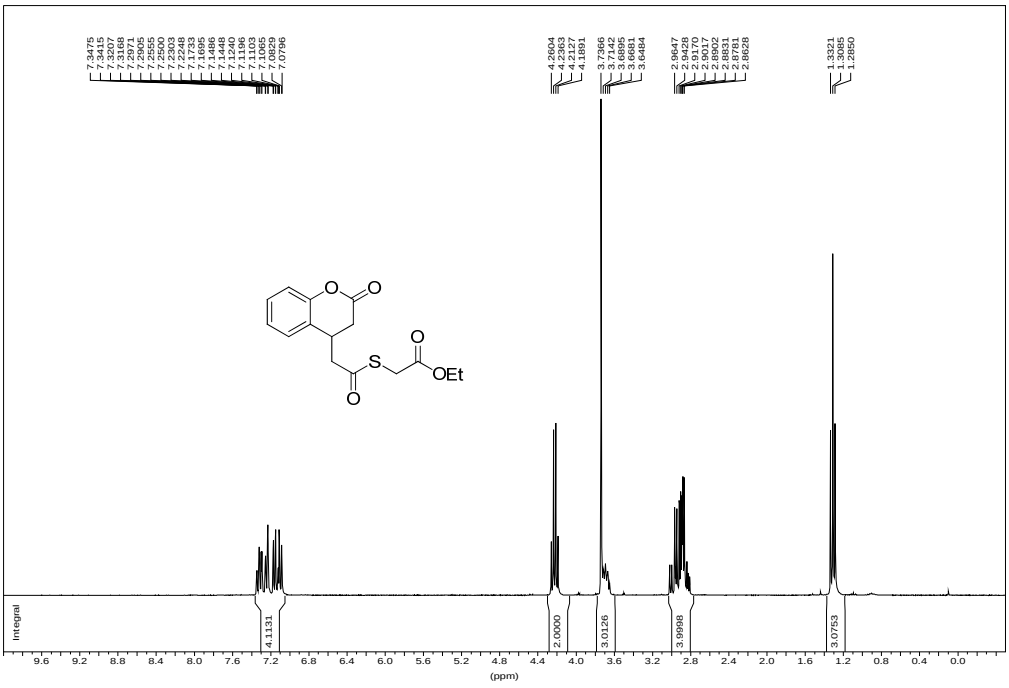
47.7976
35.0699
34.2044
31.8051
22.7785
22.7058
(ppm)

3hb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7.2905
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7.2500
7.2303
7.2248
7.1733
7.1695
7.1486
7.1448
7.1240
7.1196
7.1103
7.1065
7.0859
7.0796
4.2604
4.2363
4.2127
4.1891
3.7366
3.7142
3.6895
3.6681
3.6484
2.9647
2.9428
2.9170
2.9017
2.8902
2.8831
2.8791
2.8658
1.3321
1.3085
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O
S
OEt
O
Integral
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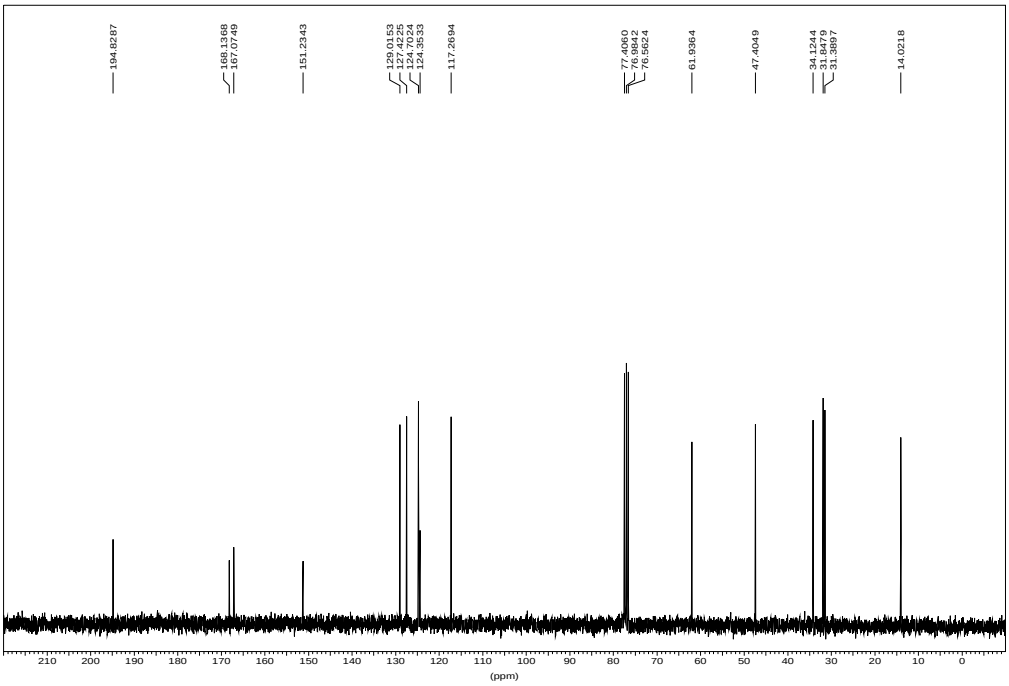
3.0126
3.9998
3.0753
(ppm)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129.0153
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117.2694
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76.5624
61.9364
47.4049
34.1244
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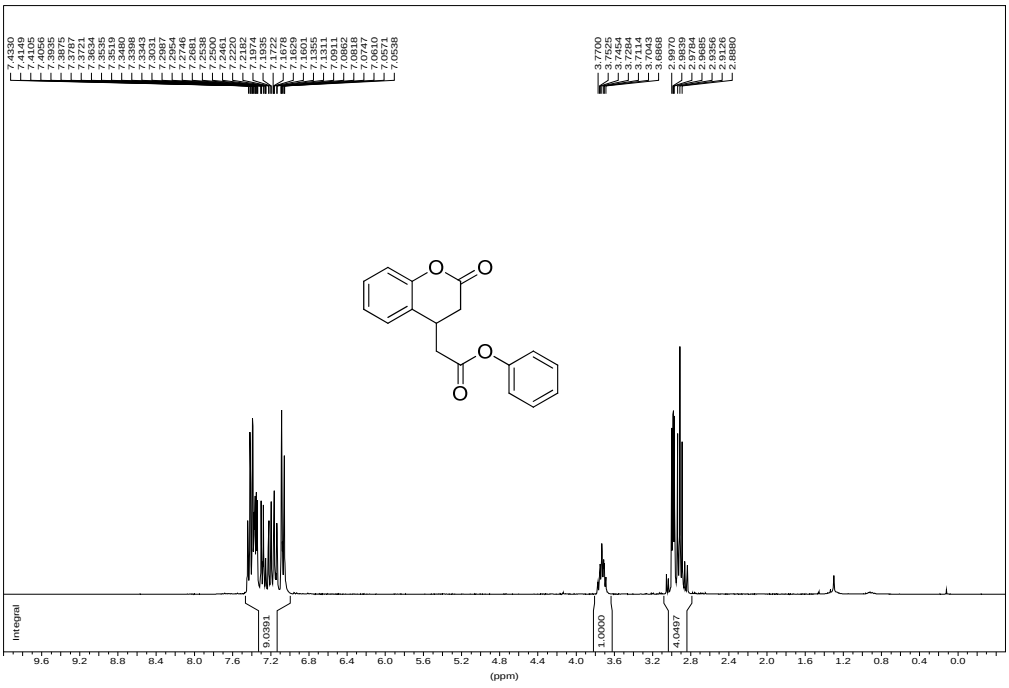
31.3897
14.0218
(ppm)

3ib


Integral
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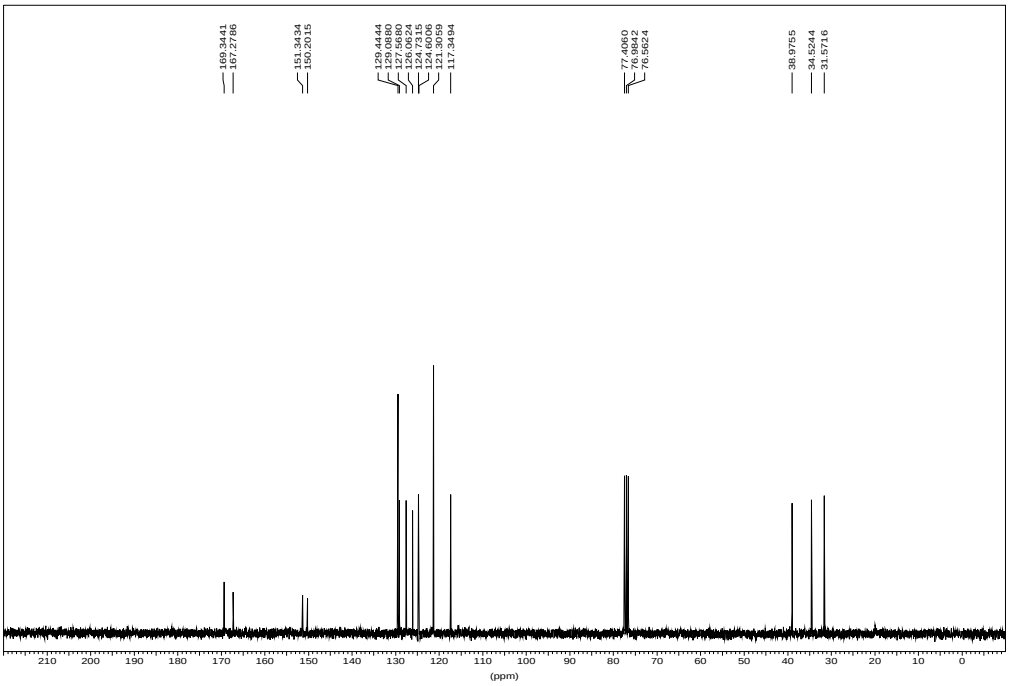
(ppm)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38.9755
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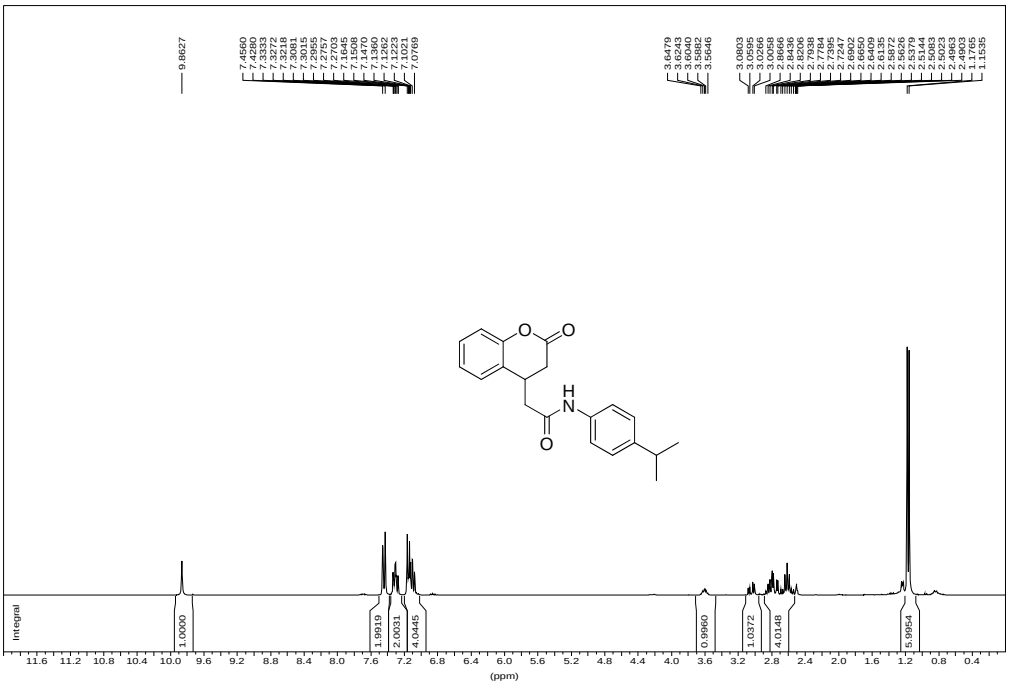
3jb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7.3333
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7.3081
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7.2955
7.2757
7.2703
7.1645
7.1496
7.1470
7.1360
7.1223
7.1021
7.0769
3.6479
3.6243
3.6040
3.5882
3.5646
3.0803
3.0595
3.0066
3.0058
2.8666
2.8498
2.8206
2.7938
2.7784
2.7596
2.7247
2.6902
2.6459
2.6249
2.6135
2.5872
2.5676
2.5379
2.5144
2.5083
2.5023
2.4963
2.4903
1.1755
1.1535
O
O
H
N
O
Integral
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1.0372
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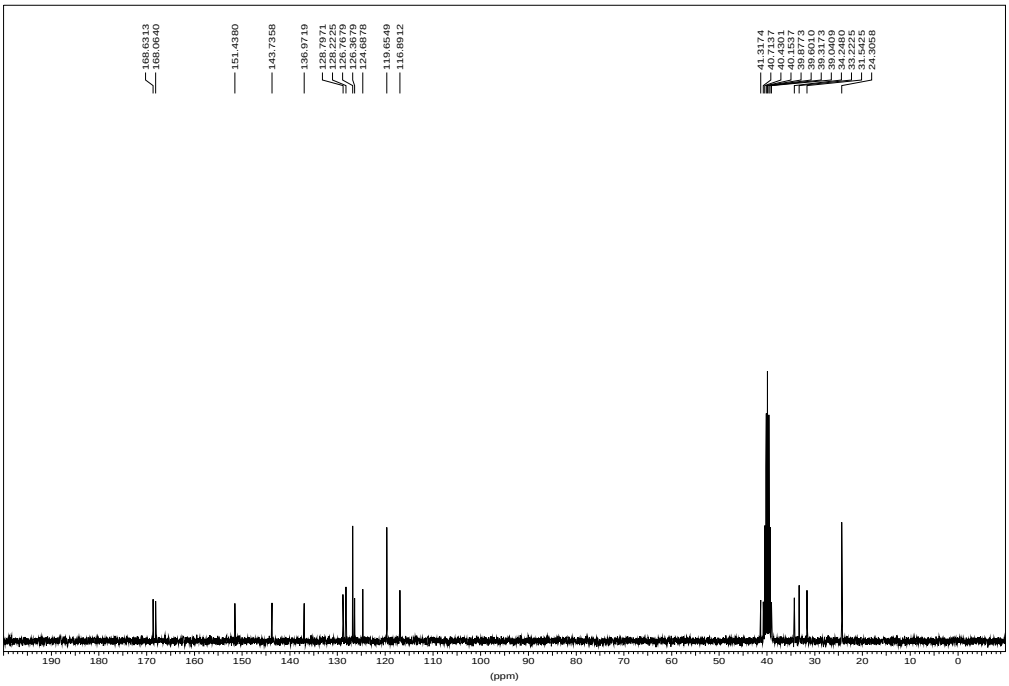
5.9954
(ppm)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116.8912
41.3174
40.7137
40.4301
40.1457
39.8773
39.6010
39.3173
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33.2225
31.5425
24.4058
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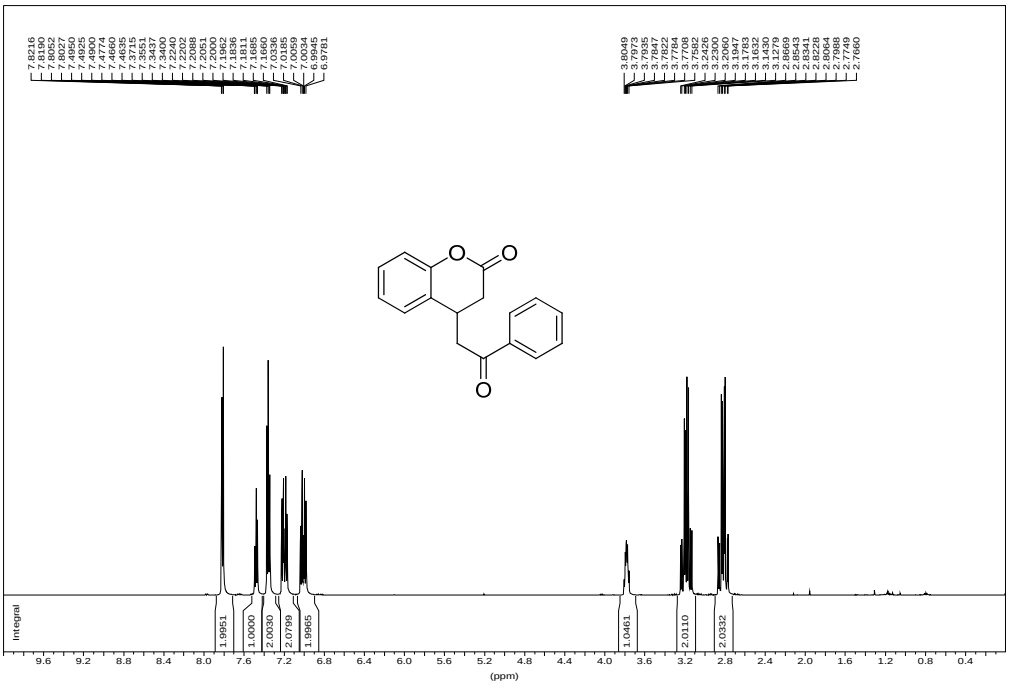
(ppm)

3kb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7.3437
7.3400
7.2240
7.2202
7.2088
7.2051
7.2000
7.1962
7.1836
7.1811
7.1685
7.1660
7.0336
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7.0059
7.0034
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3.7784
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3.7426
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3.1632
3.1430
3.1279
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2.7749
2.7660
Integral
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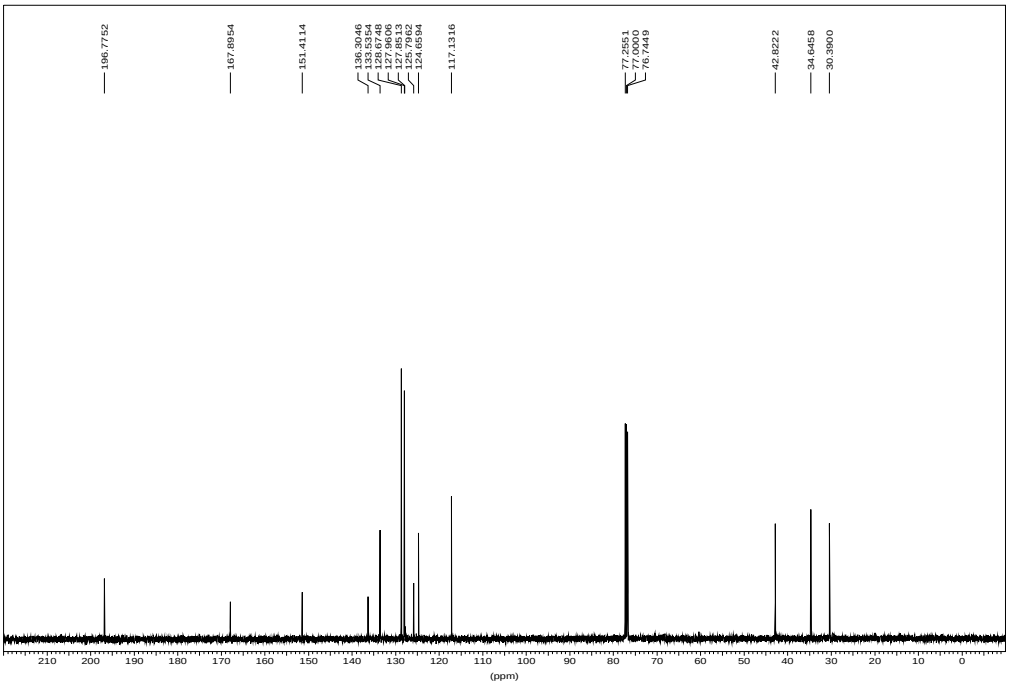
2.0799
1.9965
1.0461
2.0110
2.0332
9.6 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
(ppm)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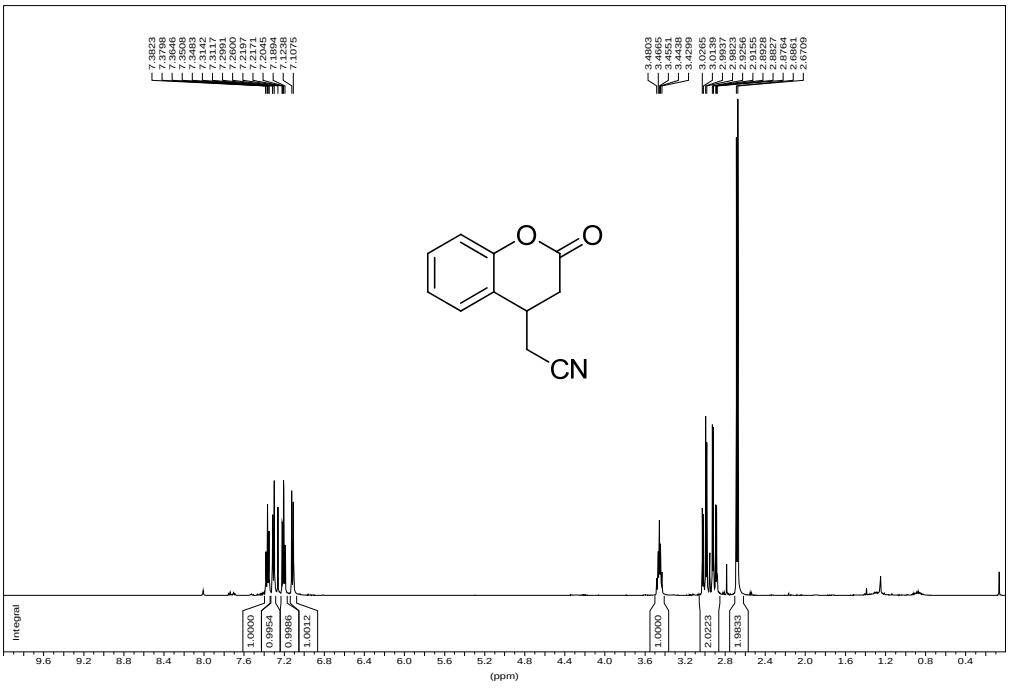
3lb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7.2600
7.2377
7.2171
7.2045
7.1894
7.1238
7.1075
3.4803
3.4665
3.4551
3.4438
3.4299
3.0265
3.0139
2.9937
2.9833
2.9256
2.9155
2.8939
2.8827
2.8764
2.6861
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CN
Integral
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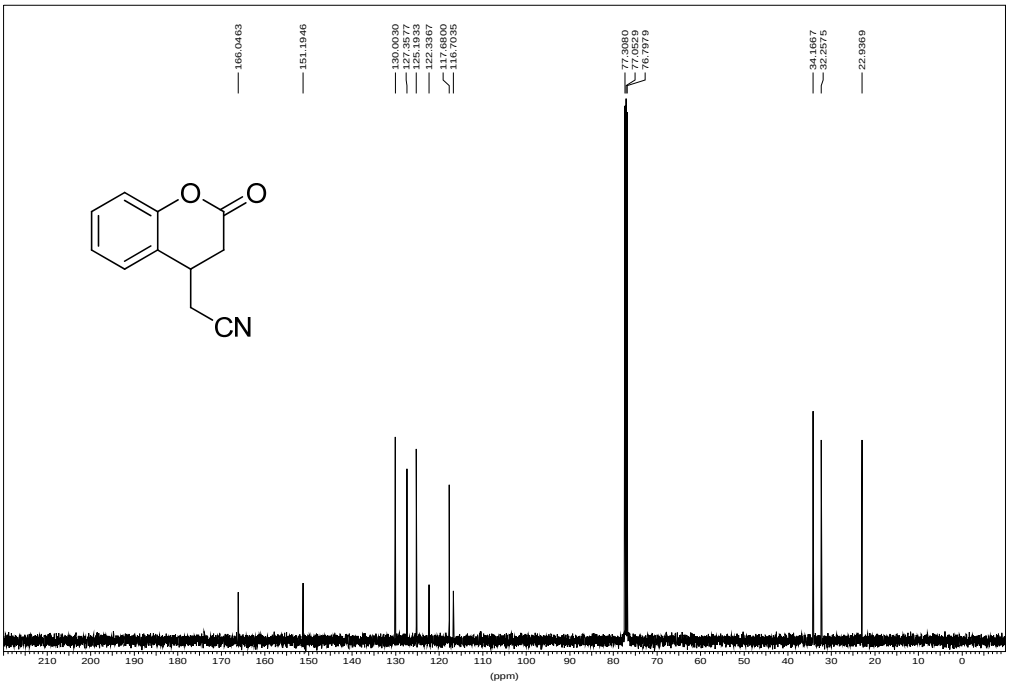
(ppm)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22.9369
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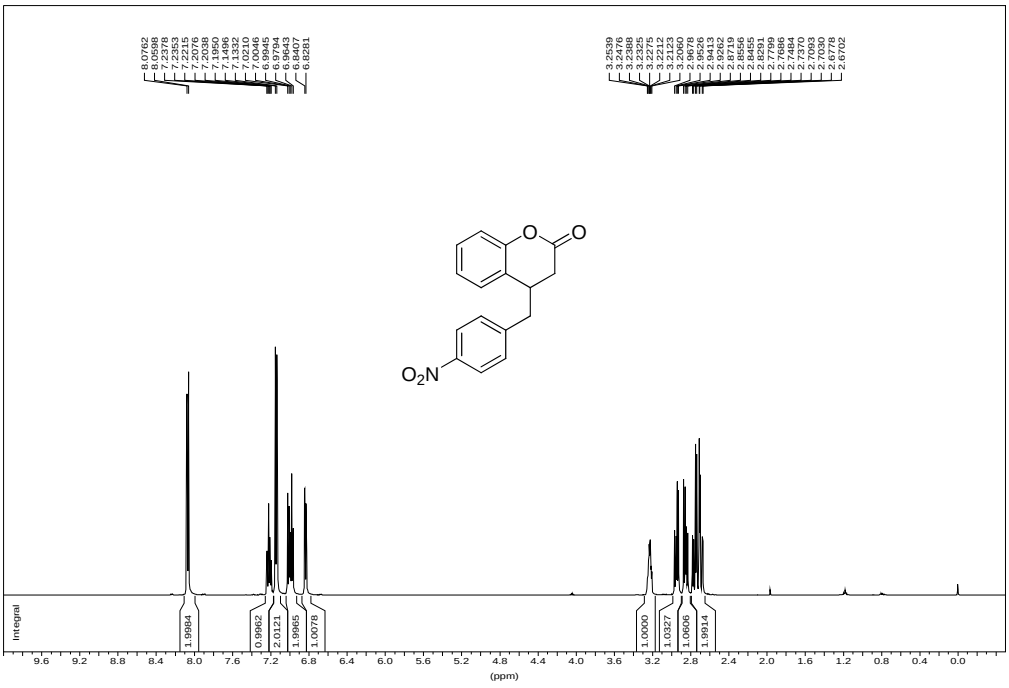
O
CN
(ppm)

3mb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7.1332
7.0210
7.0046
6.9945
6.9794
6.8643
6.8407
6.8281
3.2539
3.2478
3.2388
3.2325
3.2275
3.2212
3.2123
3.2060
3.1979
2.9526
2.9413
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2.8719
2.8556
2.8455
2.8291
2.7799
2.7686
2.7494
2.7370
2.7093
2.7030
2.6778
2.6702
O
O
O2N
Integral
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1.9965
1.0078
1.0000
1.0327
1.0606
1.9914
(ppm)