

## Syntheses, analytical and pharmacological characterizations of the “legal high” 4-[1-(3-methoxyphenyl)cyclohexyl]morpholine (3-MeO-PCMo) and analogues

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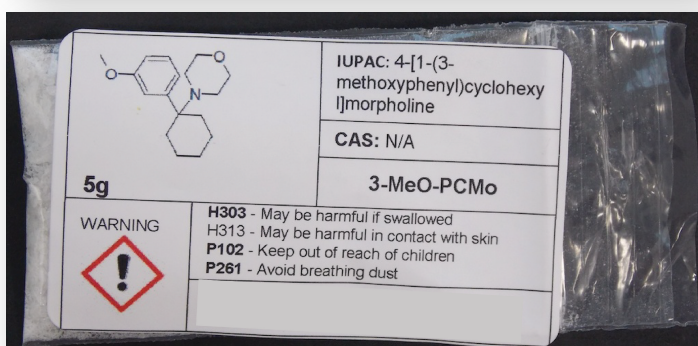
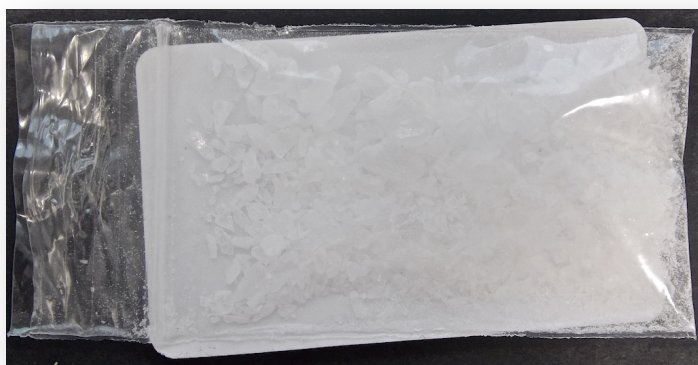
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<sup>c</sup> Alere Forensics (Forensics Ltd), Malvern Hills Science Park, Geraldine Road, WR14 3SZ, UK

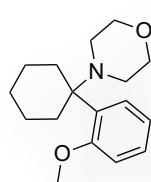
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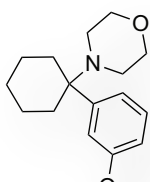
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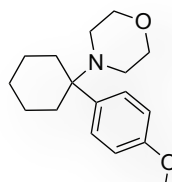
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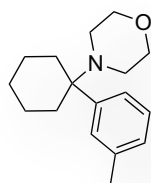
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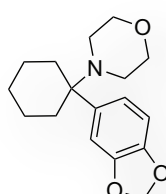
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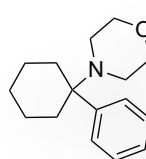
4-MeO-PCMo



3-Me-PCMo



3,4-MD-PCMo



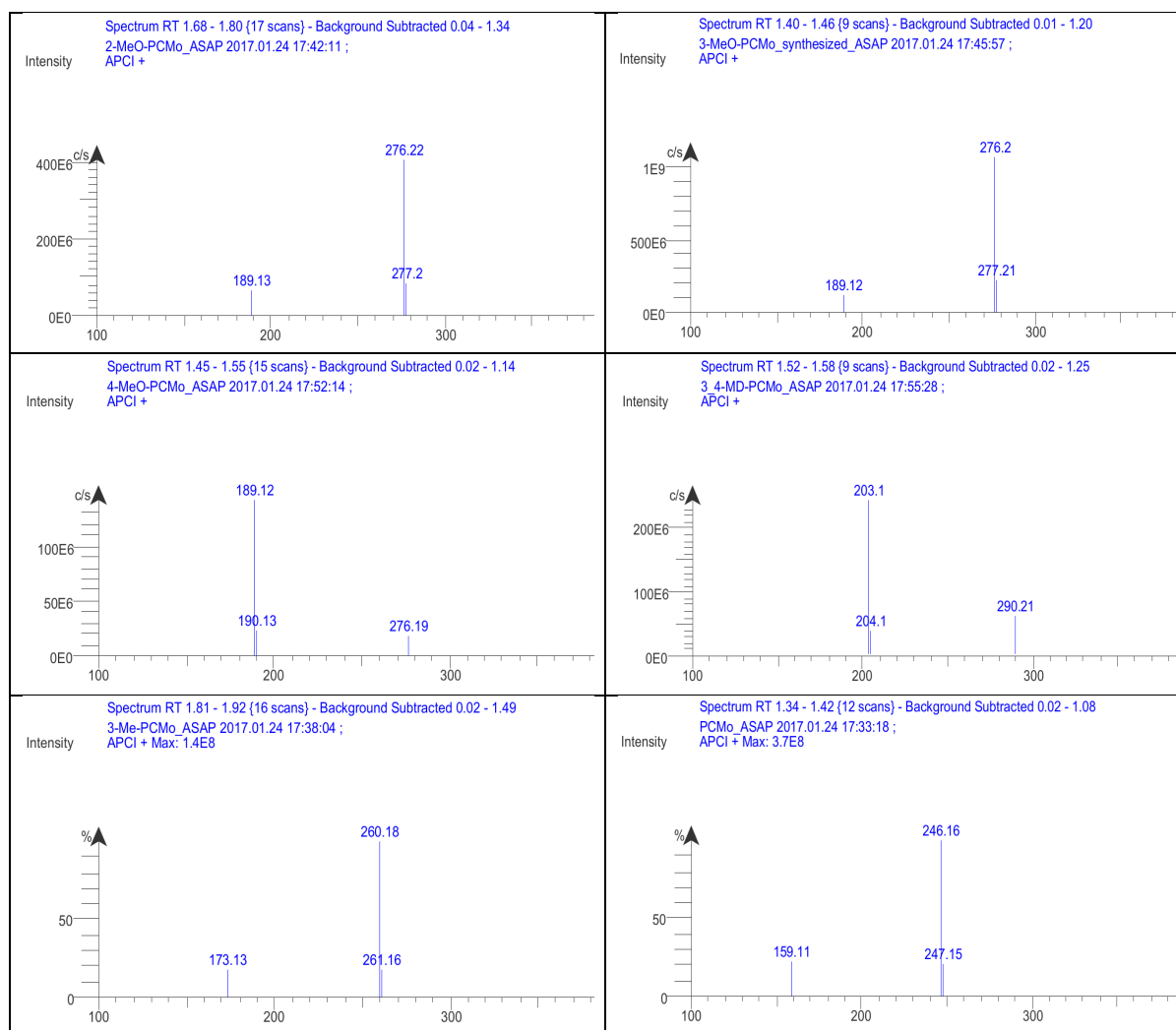
PCMo

## Alternative PCMo PCC synthesis route description

Cyclohexanone (0.0504 mol, 5.3 g) was added to a solution consisting of NaHSO<sub>3</sub> (6.3 g) in 100 mL distilled water (dH<sub>2</sub>O) resulting in an amber solution. With vigorous stirring there was simultaneously added NaCN (0.0605 mol, 2.95 g) dissolved in 20 mL dH<sub>2</sub>O and morpholine (0.0555 mol, 4.83 mL). The solution became very cloudy and was allowed to stir overnight at ambient temperature. The reaction was then removed from stir plate and allowed to sit which resulted in the formation of two separate layers. The top oil layer was obtained by extracting with ethyl acetate (2 x 60 mL). The organic extractions were pooled, washed with dH<sub>2</sub>O (100 mL), saline (2 x 10 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvents evaporated under vacuum to provide 7.0 g (71.5% yield) of 1-(morpholin-4-yl)cyclohexane-1-carbonitrile as an amber oil which solidified on storage in the freezer (but melted at ambient temperature). Bromobenzene (0.0756 mol, 7.91 mL) was added to a stirred suspension of crushed magnesium (0.227 mol, 1.8 g) in Et<sub>2</sub>O (20 mL) under argon. A small crystal of iodine was added to initiate reaction. The exothermic reaction was cooled on ice as needed and allowed to sit for approximately 20 minutes at which point the nitrile (0.036 mol, 7.0 g) dissolved in 10 mL of dry THF was slowly added with vigorous stirring under argon. This led to a violent exothermic reaction and the precipitate of white solids. The solution was allowed to sit overnight at which point the reaction appeared complete (MS and TLC). To work-up the reaction, Et<sub>2</sub>O (100 mL) was added and the suspension extracted with 0.5 N aqueous HCl solution (2 x 150 mL). The pooled aqueous phase was washed with ethyl acetate (2 x 50 mL), made basic with KOH pellets and extracted with ethyl acetate (3 x 60 mL). The organic extractions were pooled, washed with saline (10 mL) dried with Mg<sub>2</sub>SO<sub>4</sub>, filtered and solvents evaporated under vacuum to give crude PCMo as a yellow oil. The material was purified using flash column chromatography as described previously and the desired fractions (TLC and MS) pooled and evaporated to give (1.5 g) PCMo, a colorless oil in 17% yield. The true yield was higher as a large number of fractions also contained product contaminated with unreacted nitrile a common issue encountered with this route. An attempt at short-path vacuum distillation was only partially successful so the material was thus discarded. The purified freebase was converted to the HCl salt as described previously.

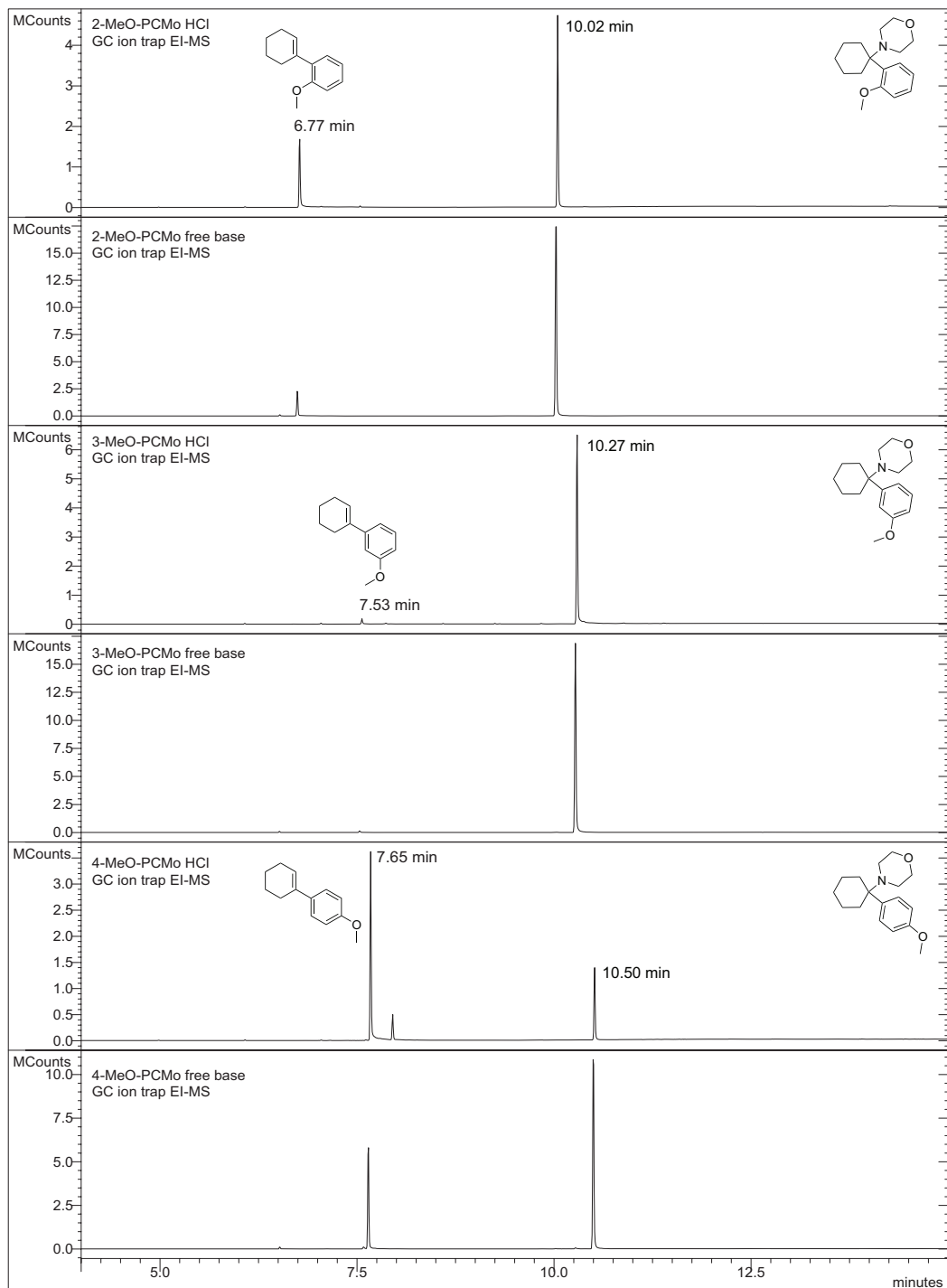
## Atmospheric solids analysis probe mass spectrometry

Flash chromatography fractions of PCMo products were recorded on an Advion expression<sup>S</sup> CMS system (New York, USA) using an atmospheric solids analysis probe (ASAP) source from Advion. Nitrogen was used as the source gas. Capillary temperature was set at 150°C, with the capillary voltage of 120 V, source voltage offset was set to 20 and source voltage span to 0. Source gas temperature was 200°C and APCI corona discharge set to 5 mA. Spectra were analyzed using Advion Data Express software, version 2.2.29.2. This method of analysis particularly helpful for the analysis of fractions obtained from flash column chromatography.

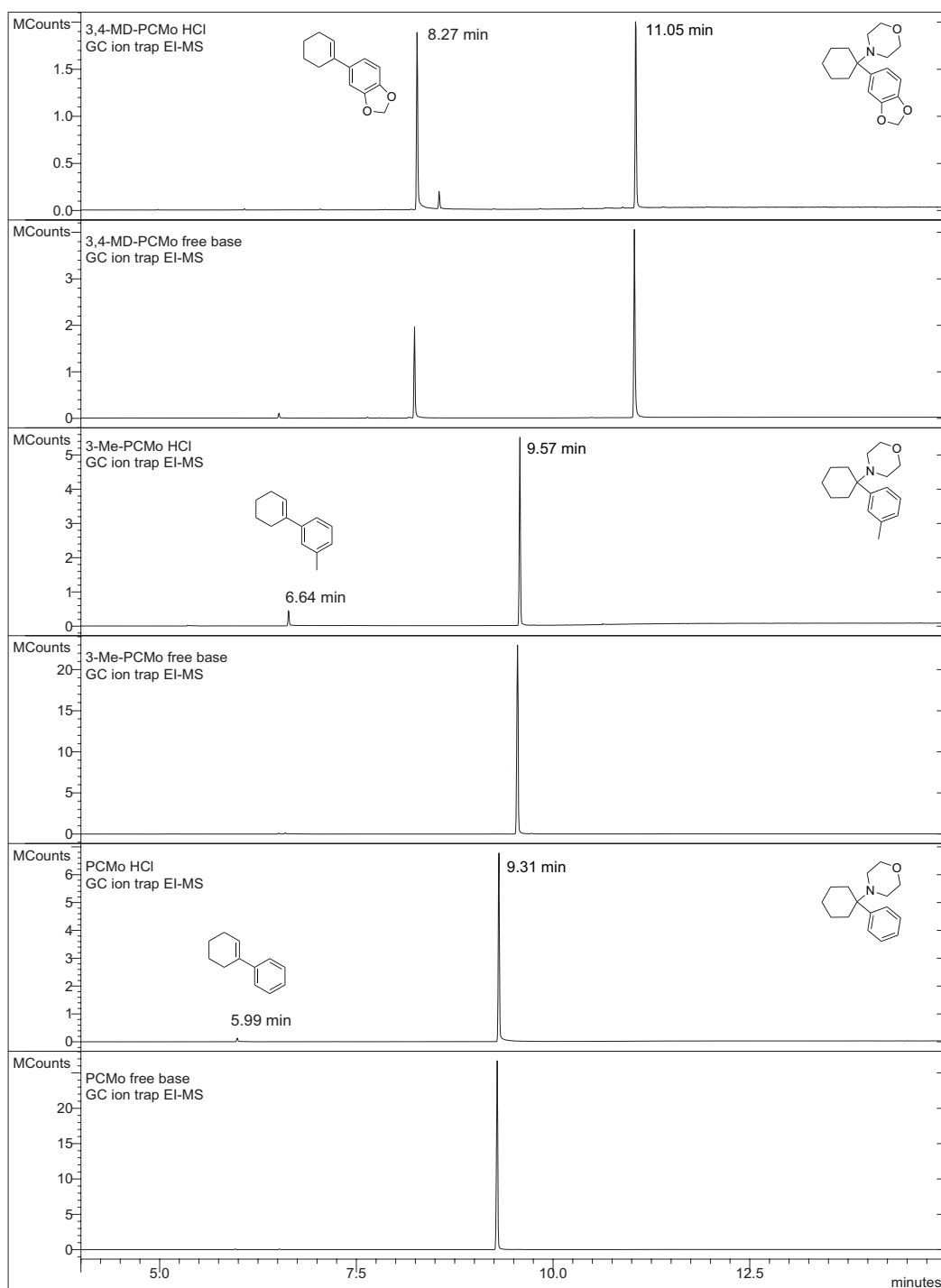




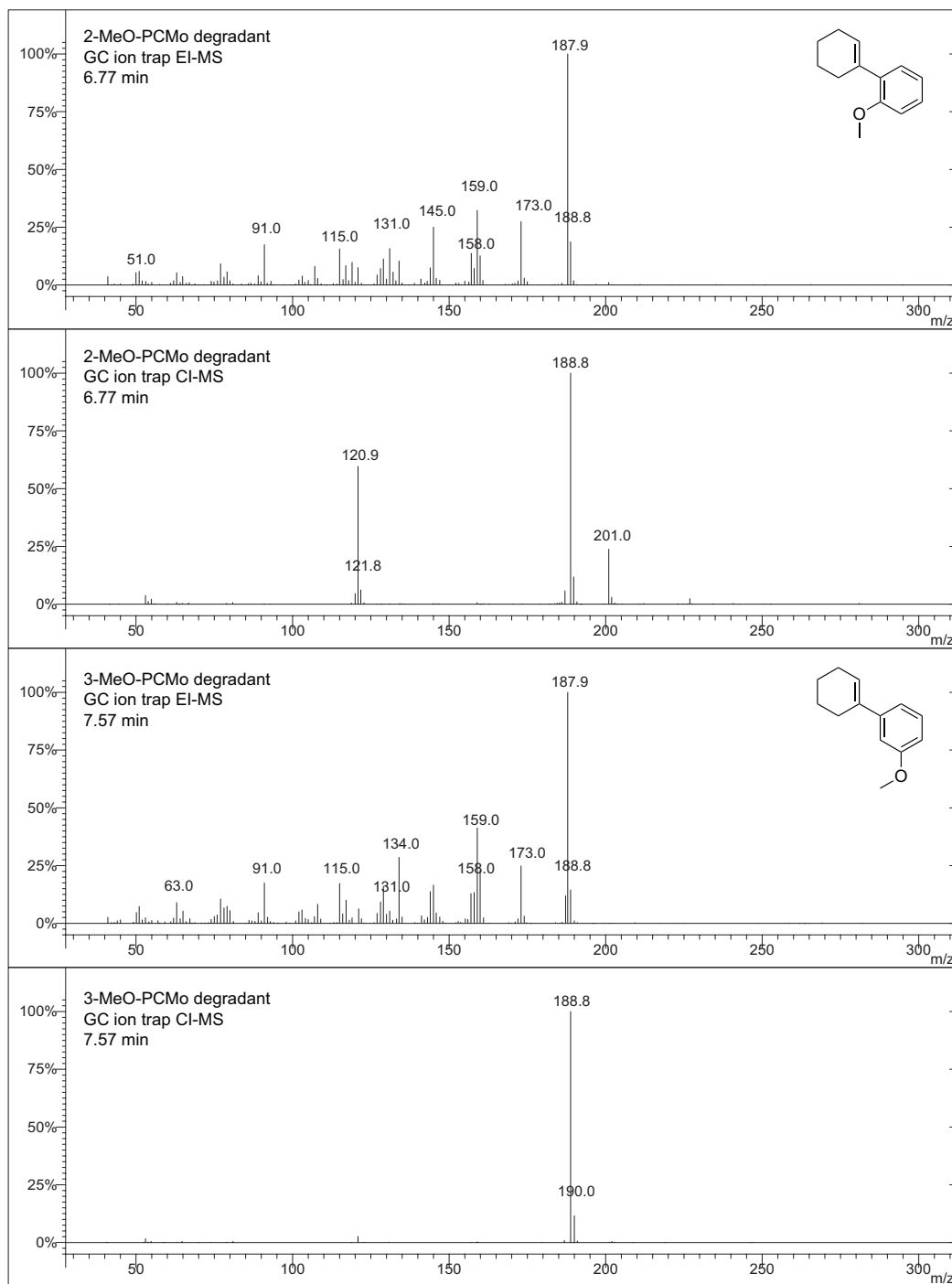
GC ion trap MS full scan traces HCl vs. freebase to compare GC-induced degradation

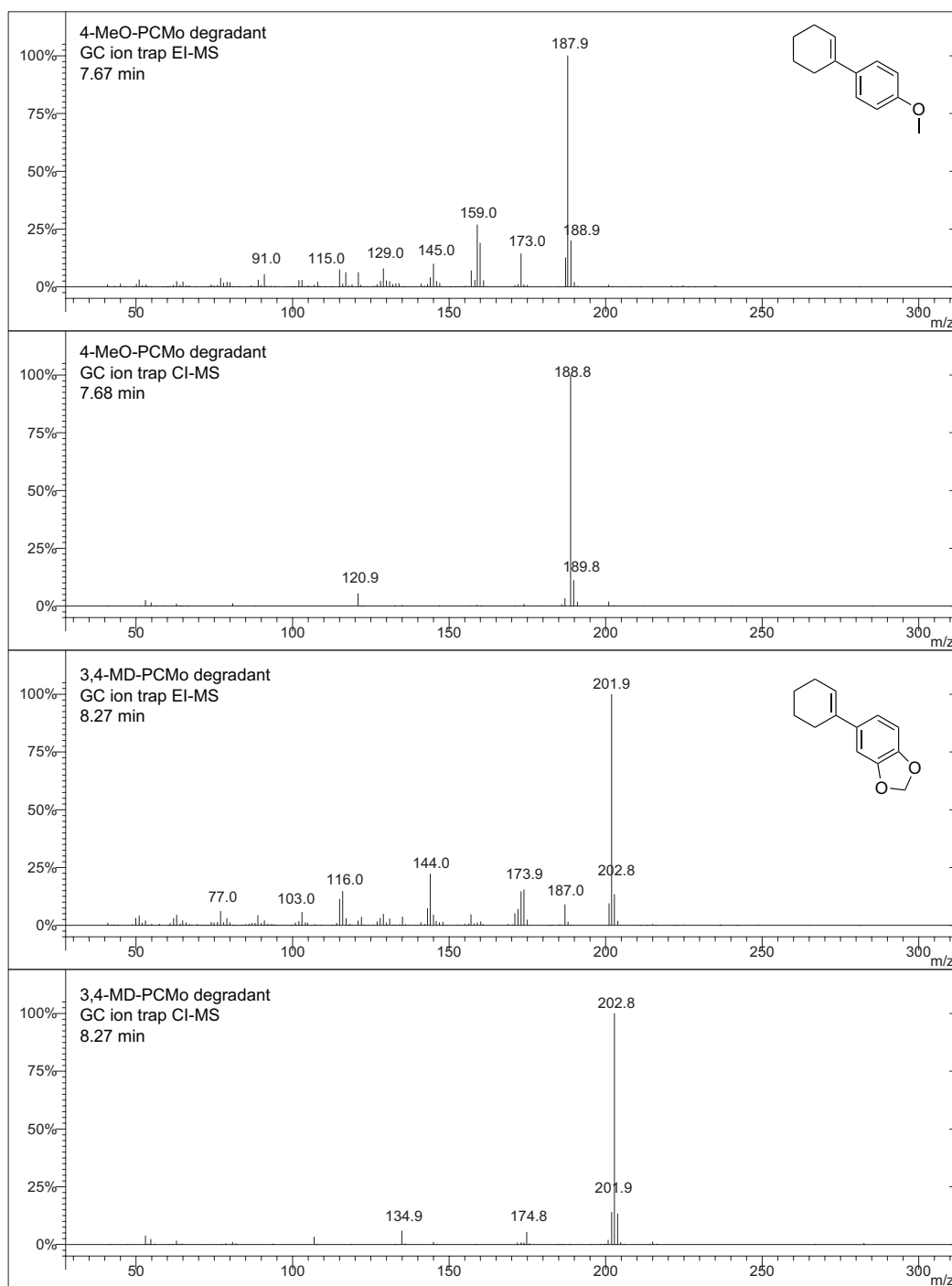


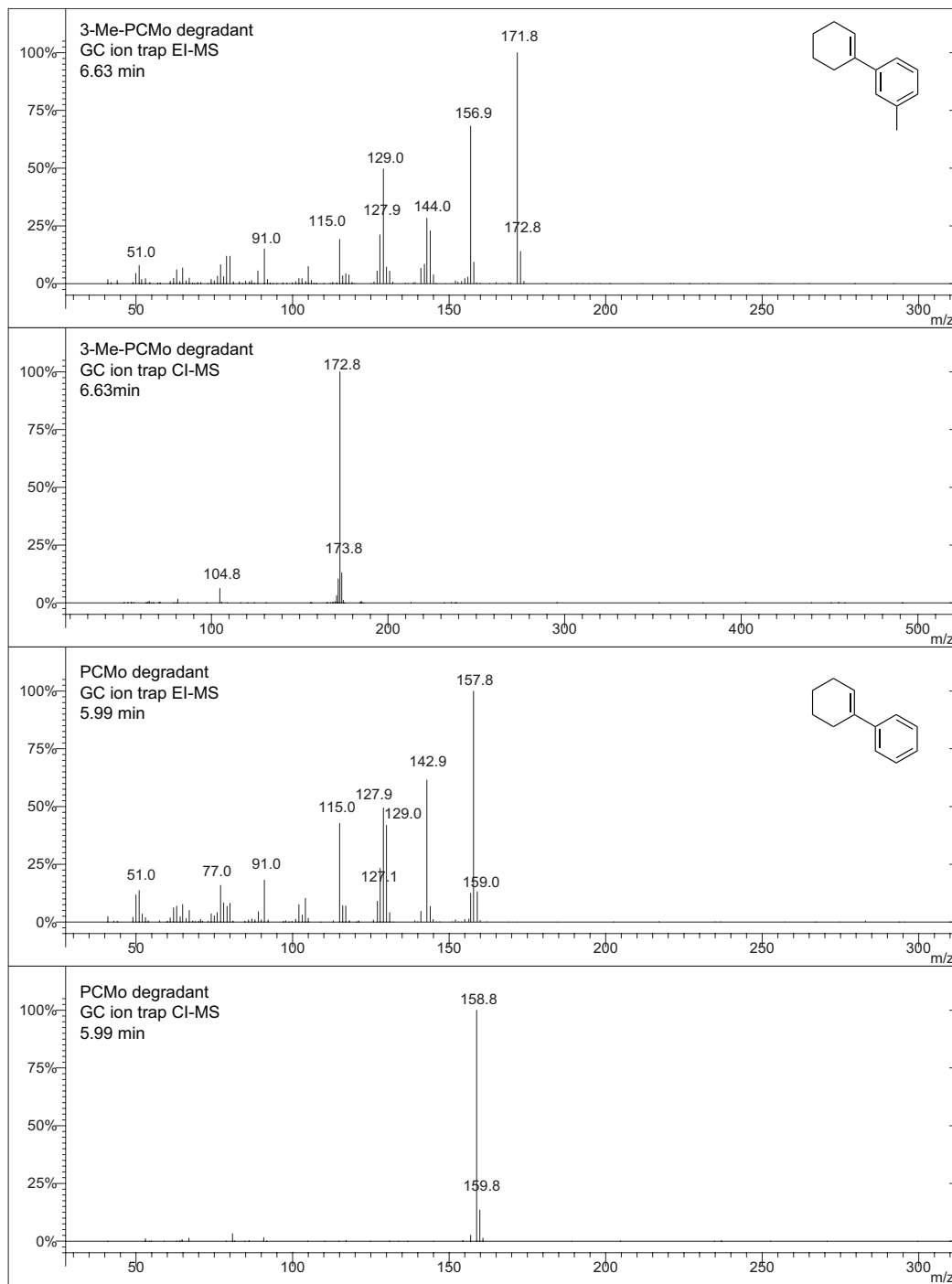
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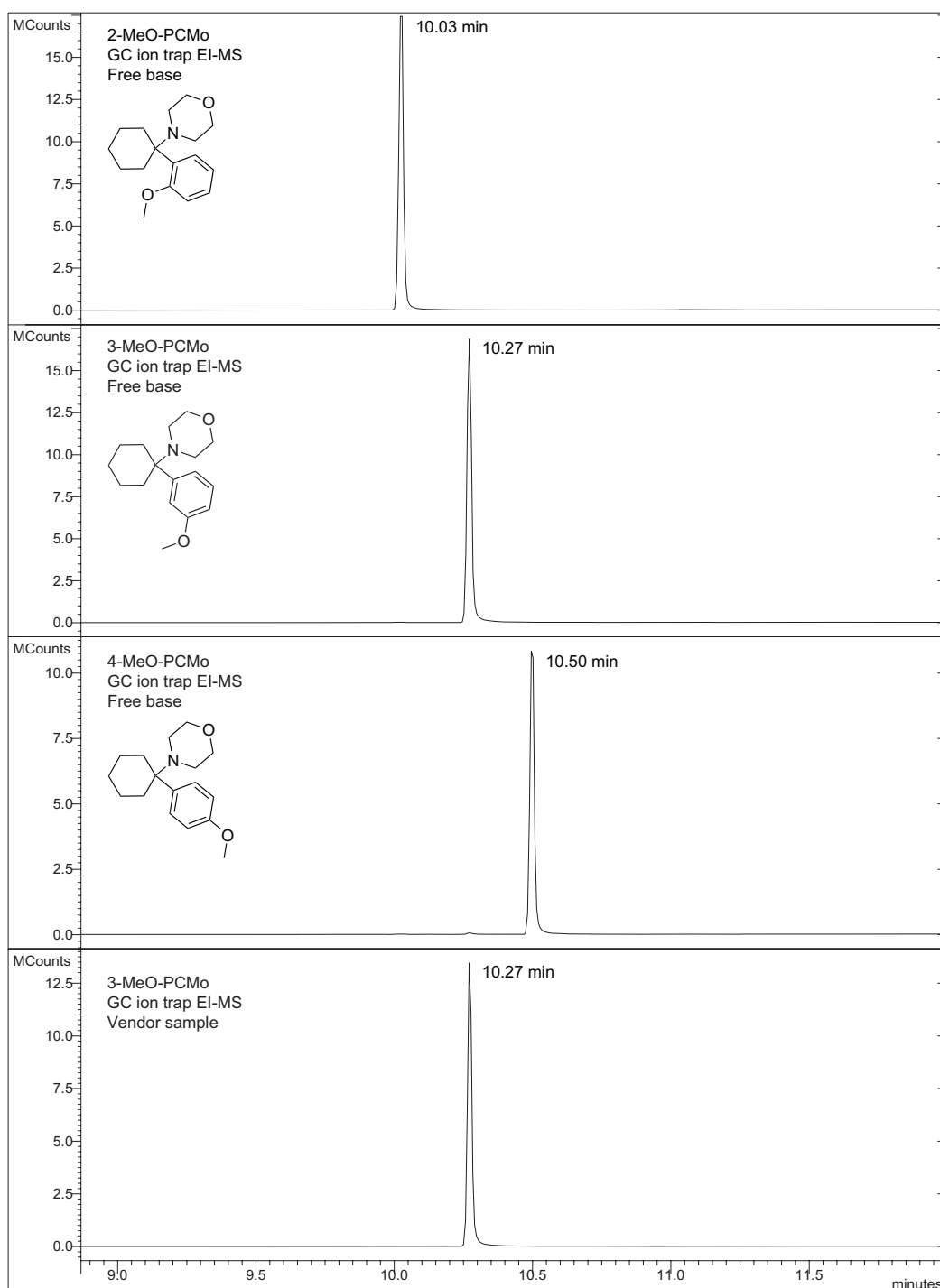
Ion trap EI/CI mass spectra of GC-induced PCMo degradation products



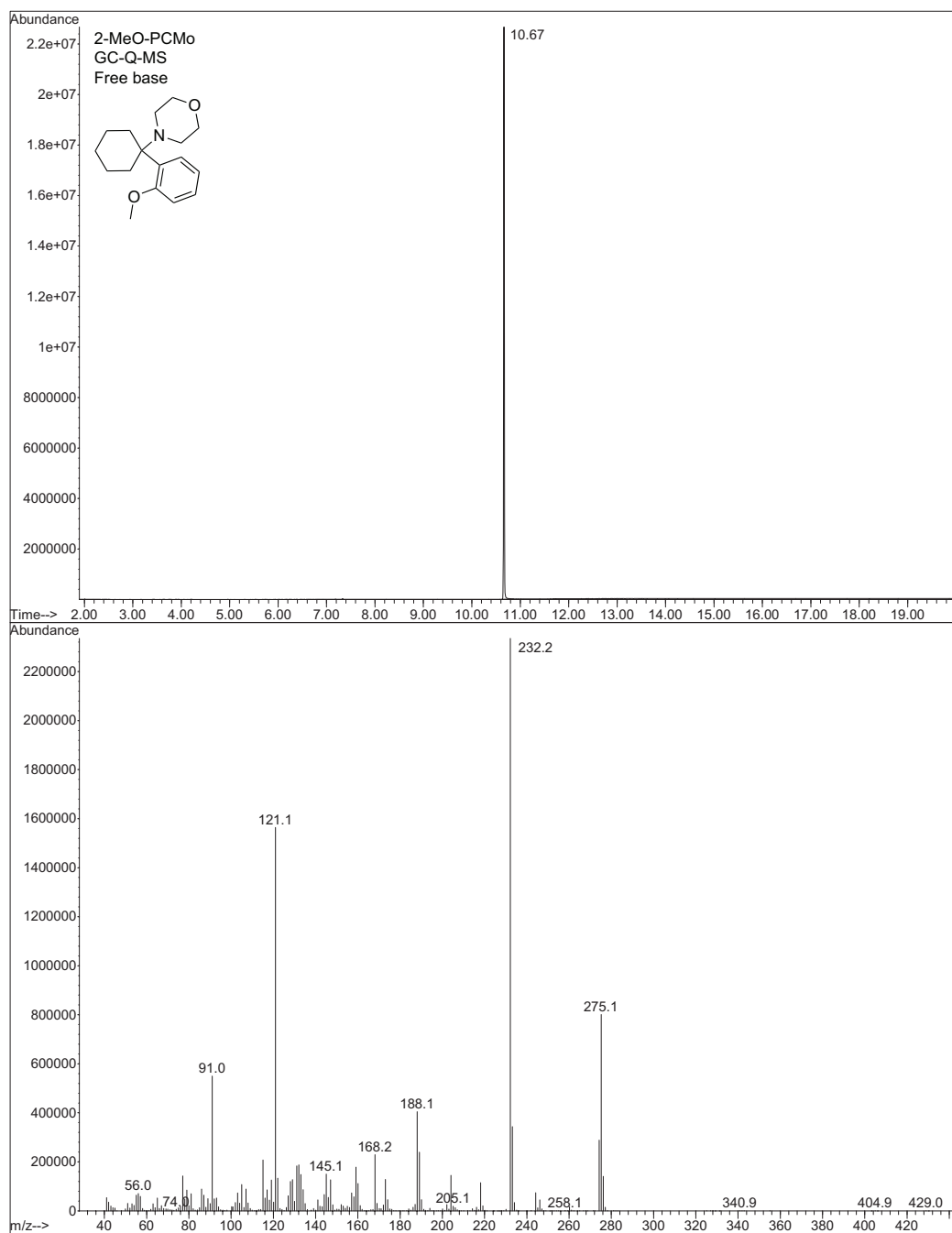




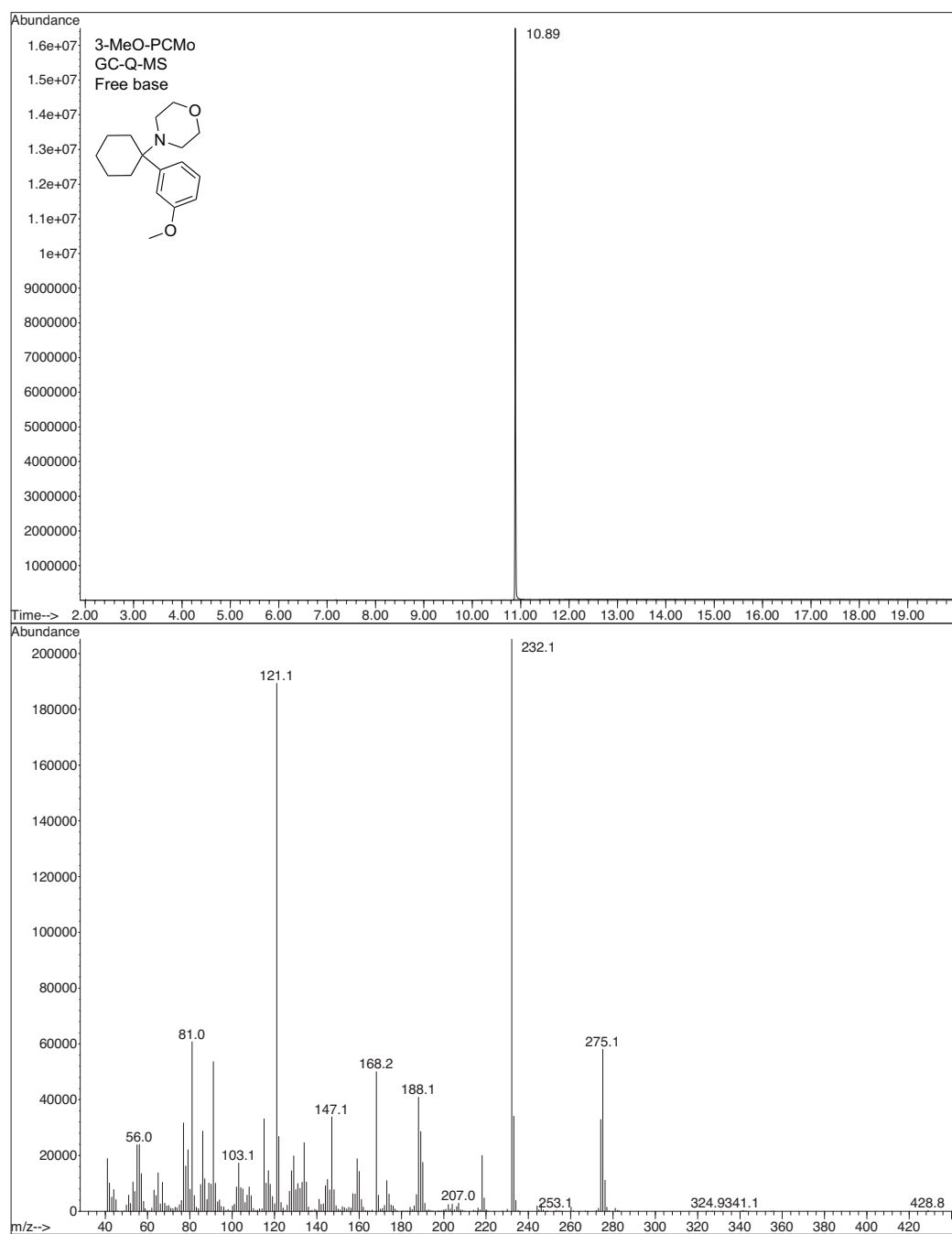
Partial GC ion trap MS full scan traces of MeO isomers vs. 3-MeO-PCMo vendor sample



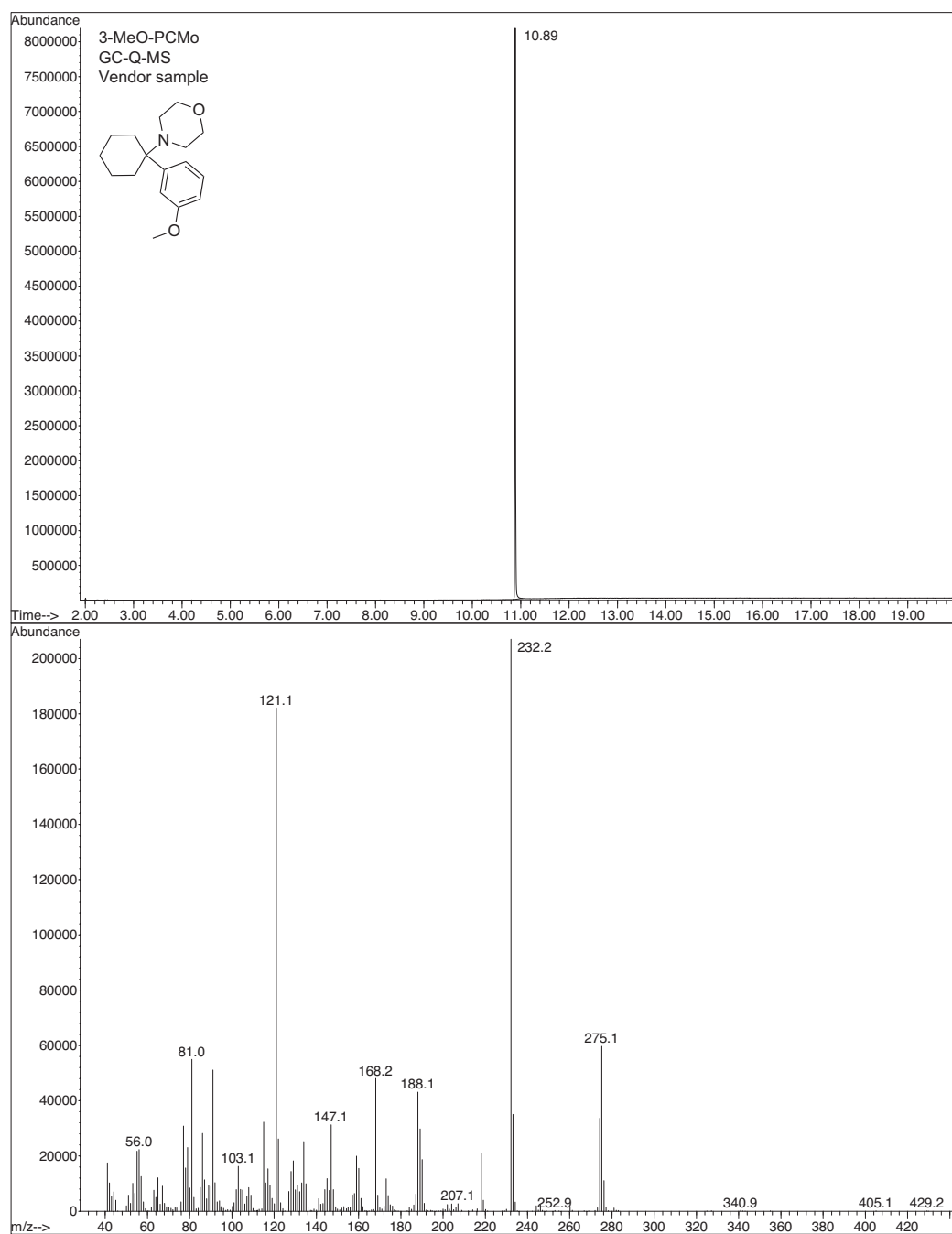
GC quadrupole EI-MS (GC-Q-MS) full scan traces of PCMo analogues



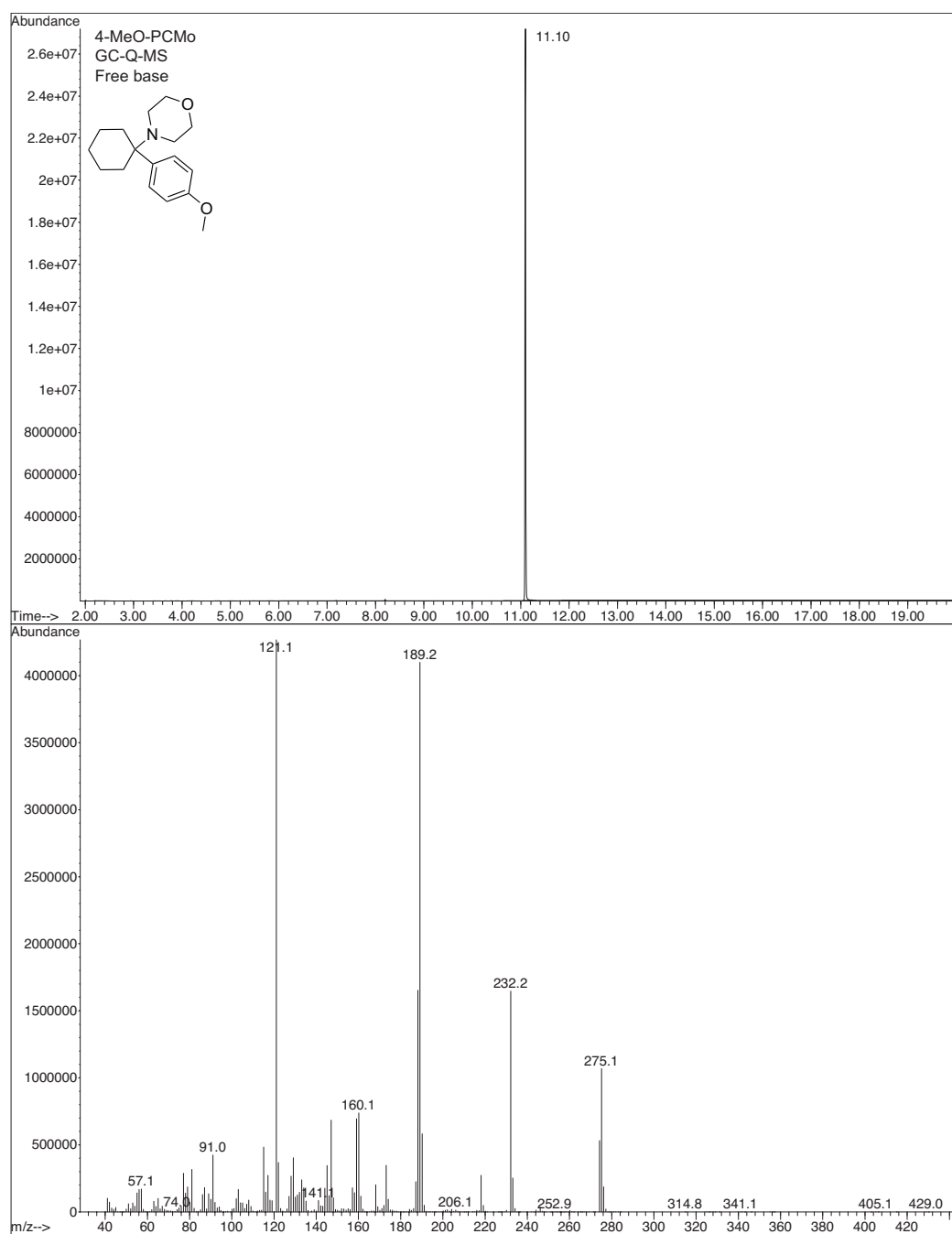




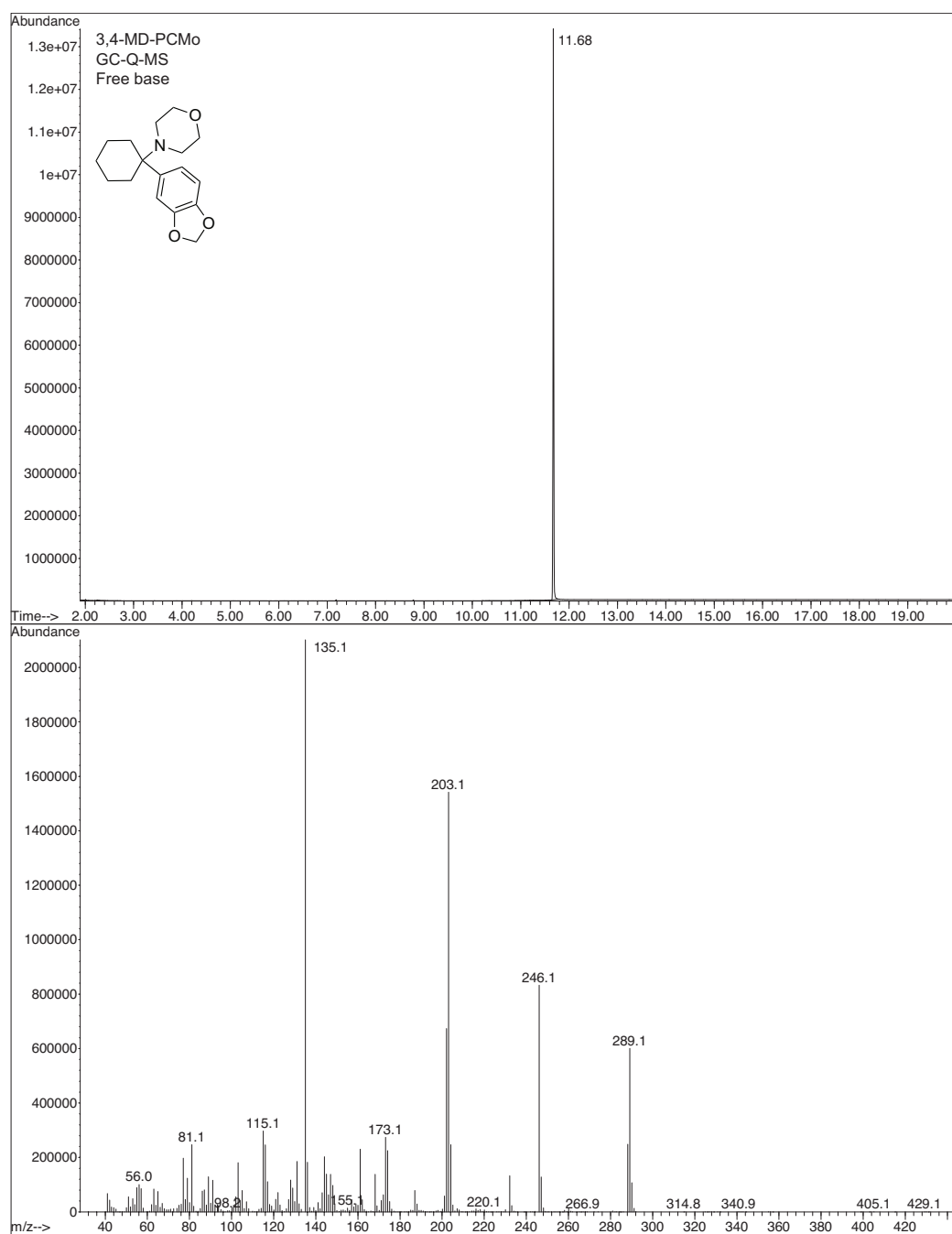
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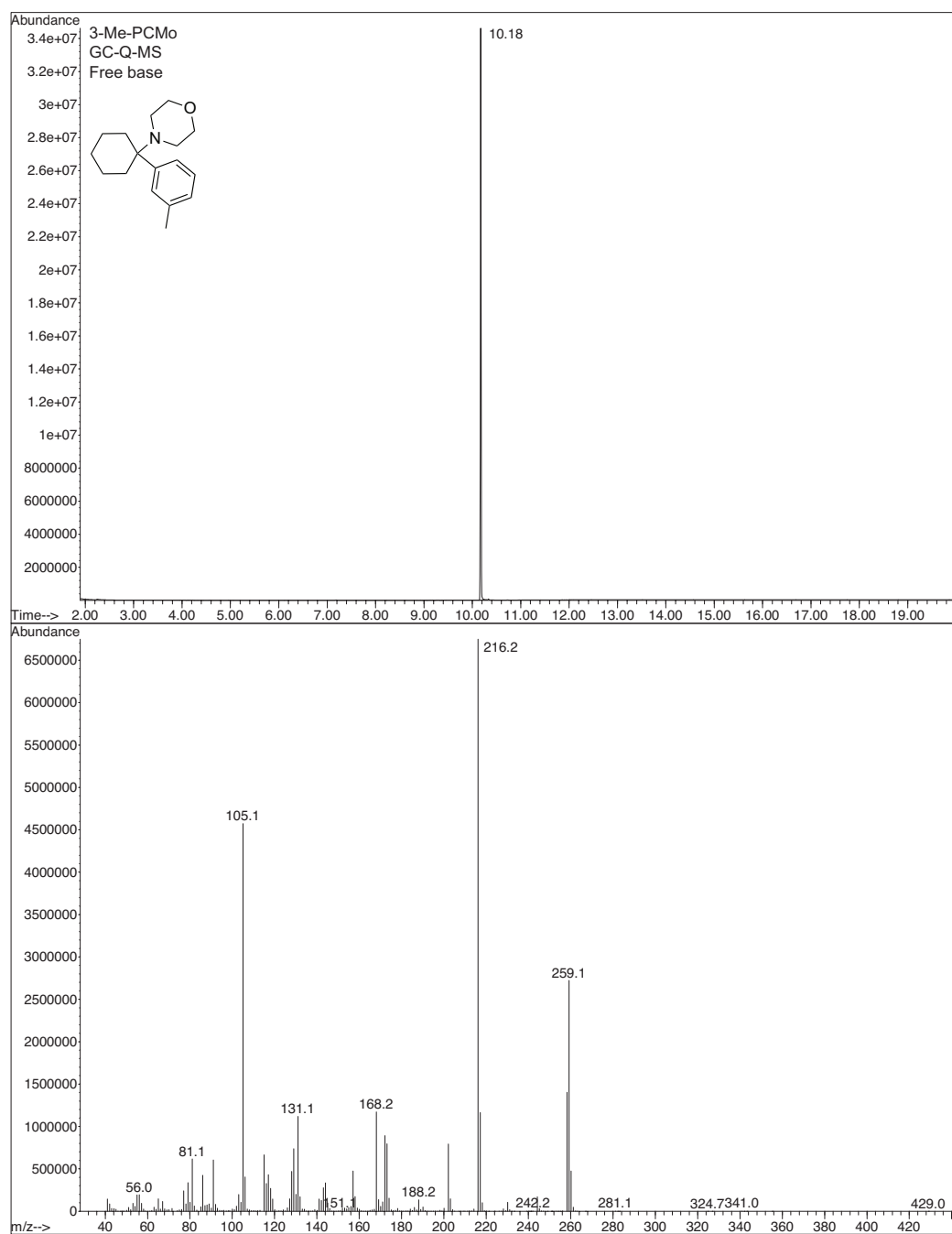
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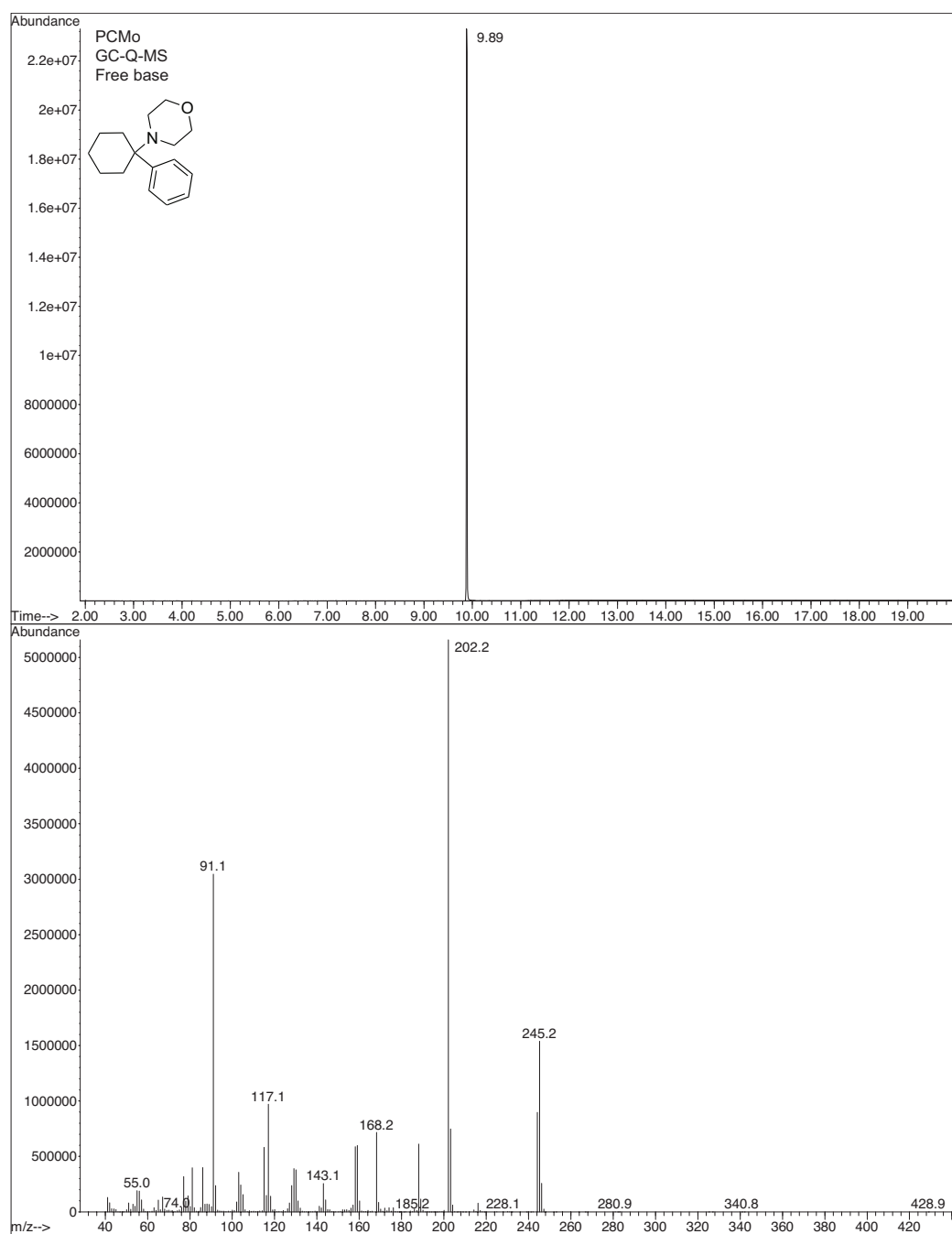
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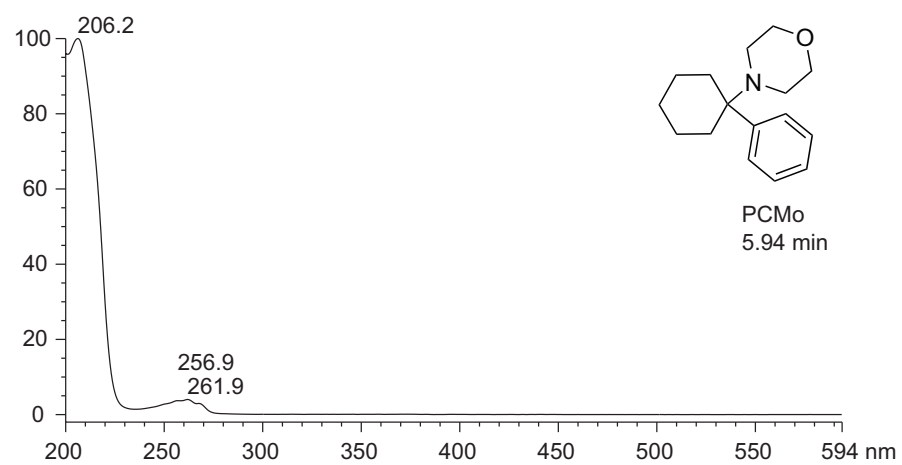
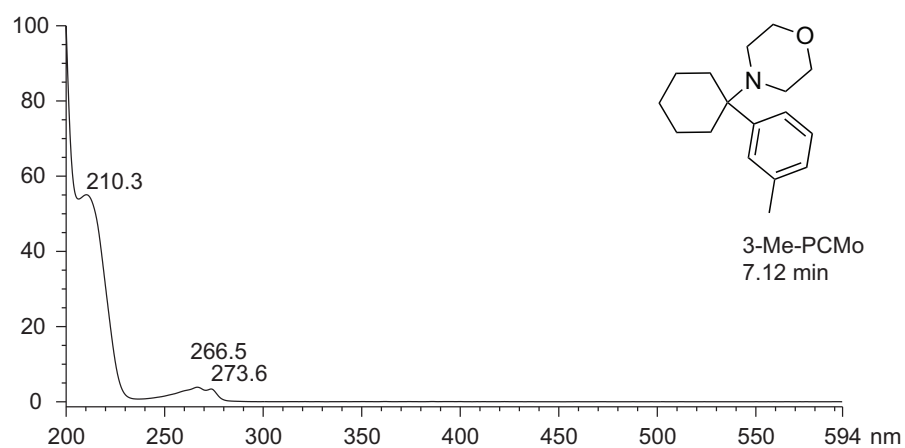
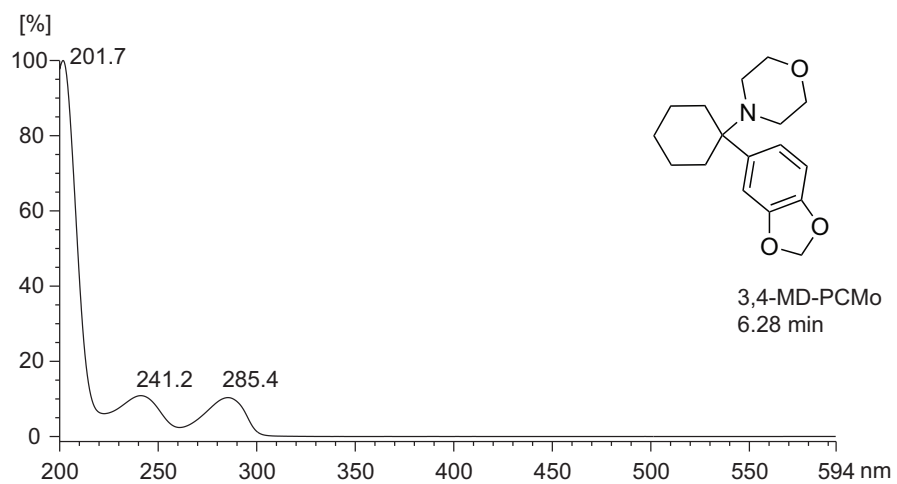
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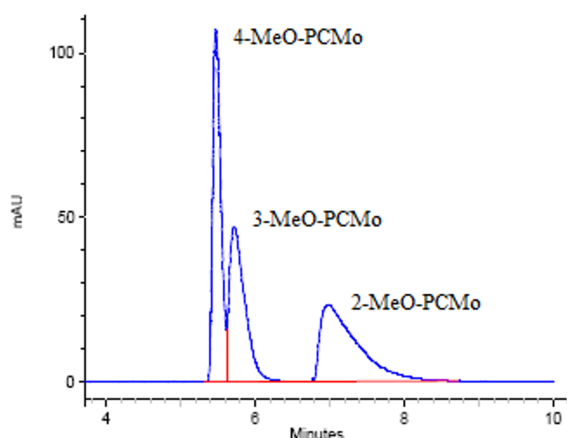
UV full scan spectra via HPLC-DAD of 3,4-MD-PCMo, 3-Me-PCMo and PCMo





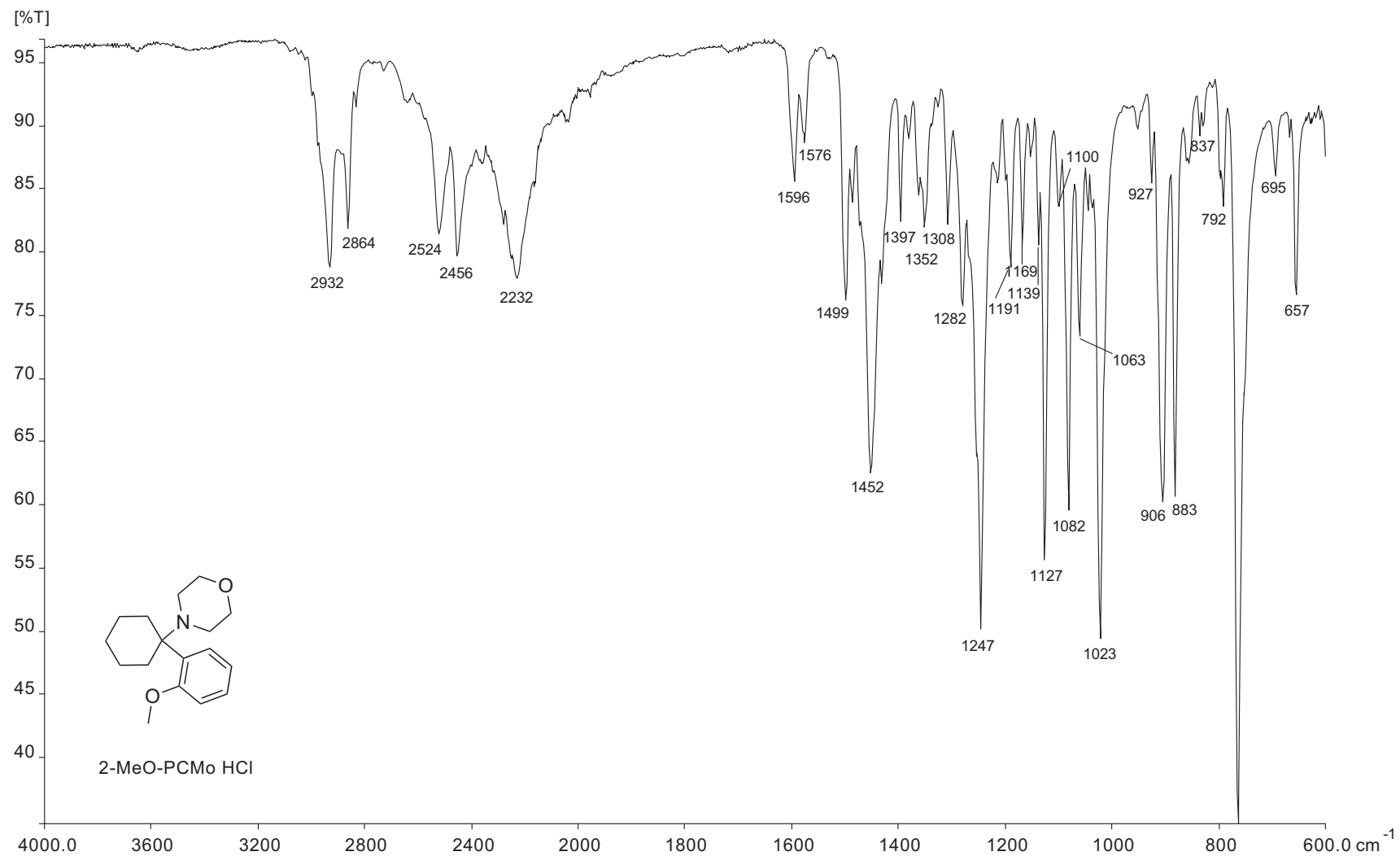
## Alternative HPLC method to attempt separation between 2-, 3-, and 4-MeO-PCMo

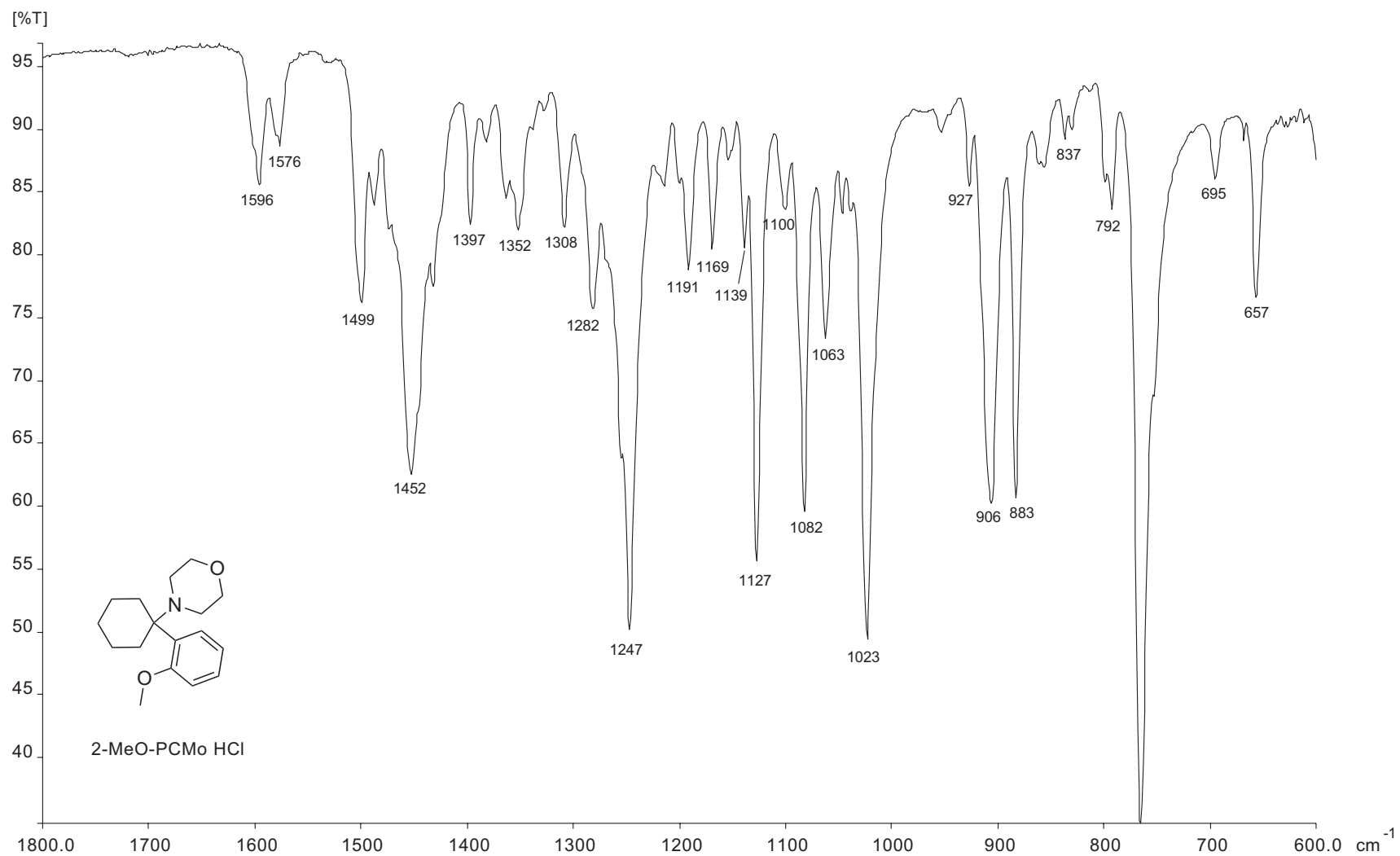
RP-HPLC analyses were performed on a Hitachi LaChrom Elite system with L-2130 pump, L-2200 autosampler, L-2300 column oven, and L-2400 UV detector, respectively (Hitachi High Technologies America, Inc., San José, CA, USA). The detection wavelength was set at 250 nm. Individual samples were prepared in acetonitrile at a concentration of 1 mg/mL, and then combined into a mixture of three equal parts with 1% 2-propanol (v/v). Separation was obtained using a Zorbax Eclipse Plus C18 column (5  $\mu$ m, 250 mm  $\times$  4.6mm) from Agilent Technologies (Santa Clara, CA, USA). Mobile phase A consisted of water with 10 mM formate; mobile phase B was acetonitrile with 1% 2-propanol (v/v). The following gradient was used for elution: 0–4.5 min 93% B, followed by an increase to 100% within 0.5 min and held for 2min. This was followed by a decrease to 93% B within 1 min and held for 2 min to give a total run time of 10 min. Injection volume was 10  $\mu$ L, flow rate was 1 mL/min, and column temperature was maintained at 35°C using an external column oven from Cole-Palmer (Cole-Palmer, Indiana, USA) due to the long column length. Chromatograms were analyzed using Agilent OpenLAB CDS EZChrom Edition (Agilent Technologies, Santa Clara, CA, USA).



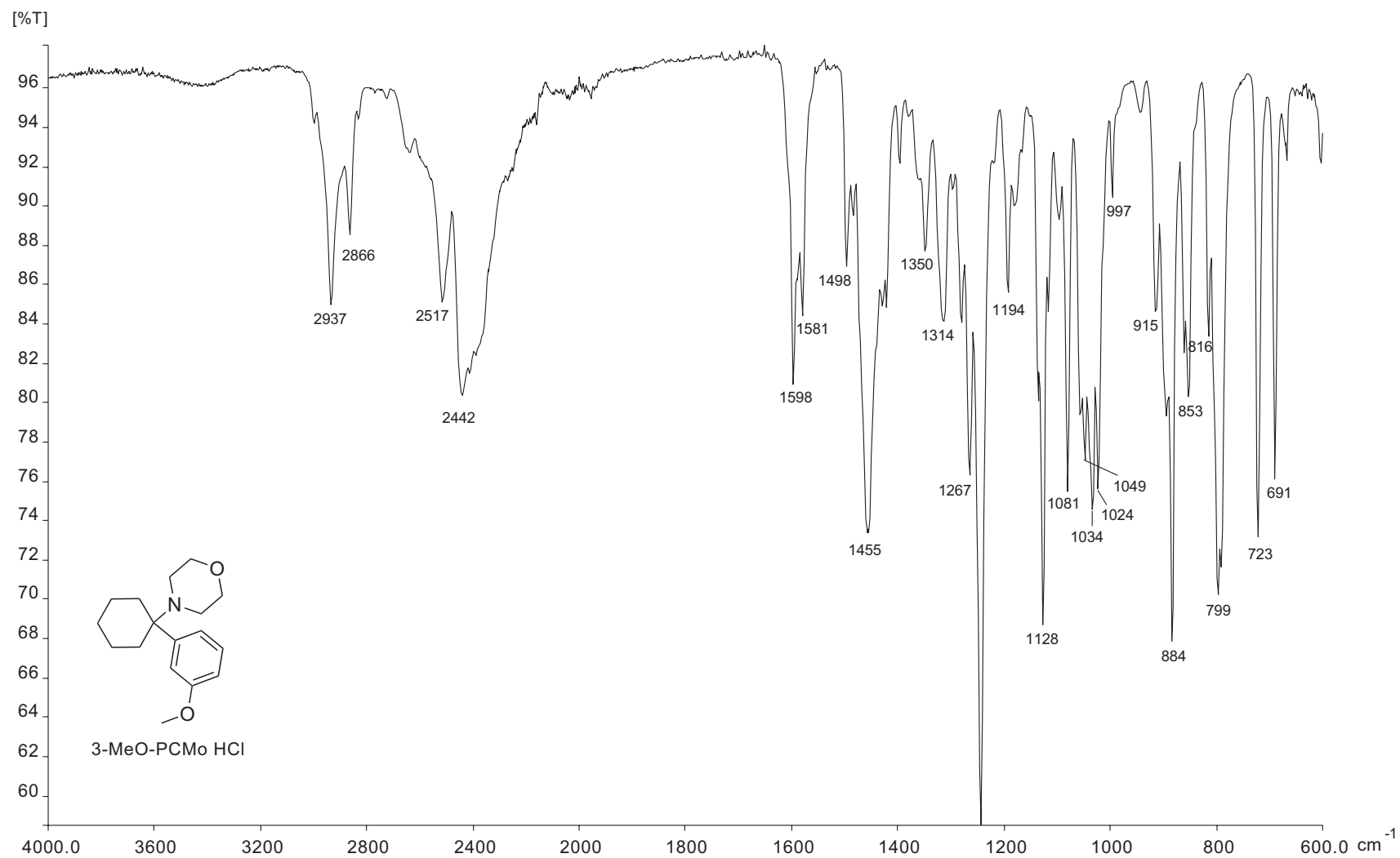
Using the method described, and despite various modifications of the mobile phase compositions, complete separation between the 3- and 4-MeO isomers were not achieved. 4-MeO-PCMo eluted at 5.473 minutes, 3-MeO-PCMo at 5.717 minutes, and 2-MeO-PCMo at 6.980 minutes, respectively. An improvement of tailing observed with 2-MeO-PCMo was not achieved under the conditions used without compromising separation.

ATR-IR spectra of PCMo analogues (HCl salts)

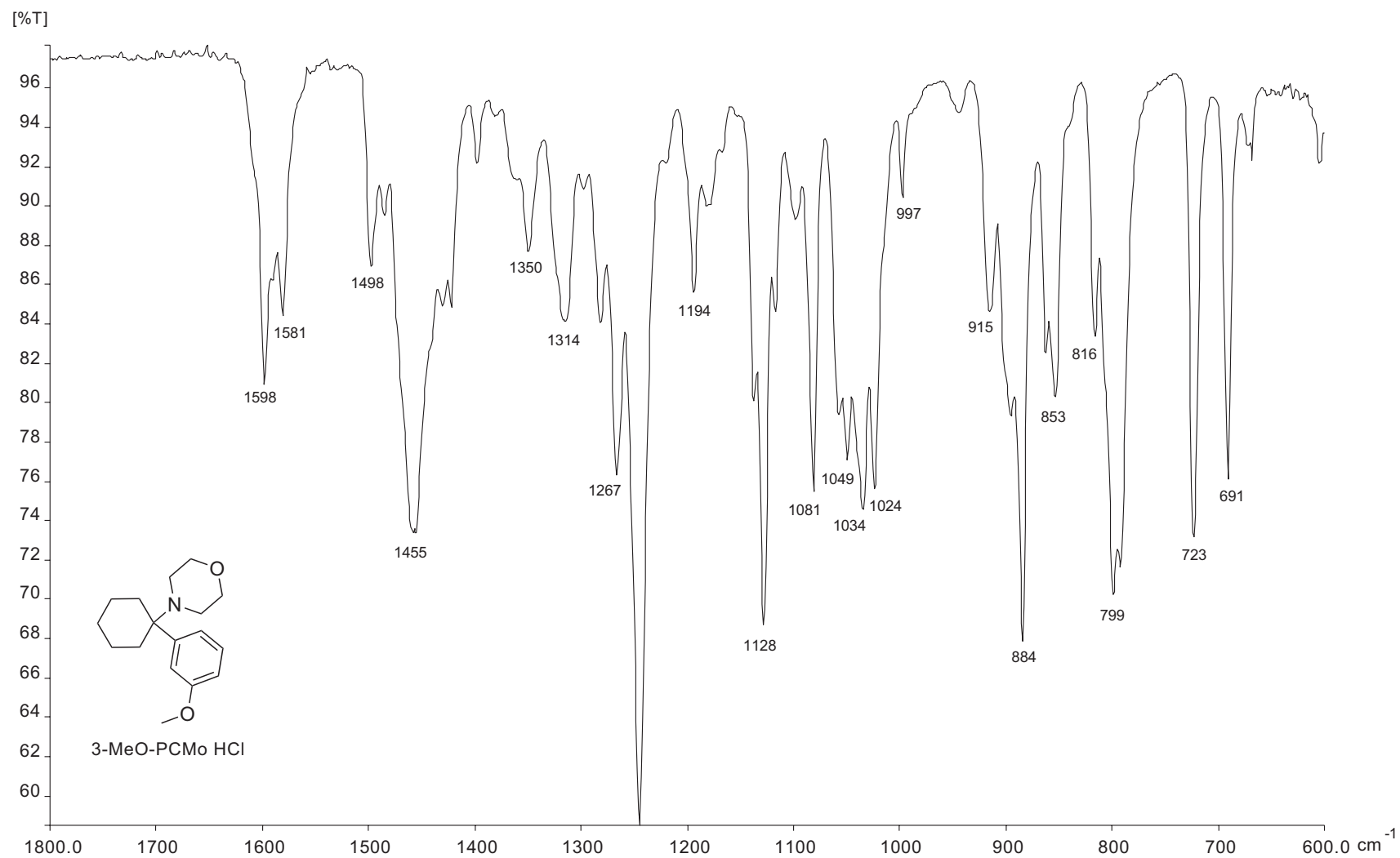


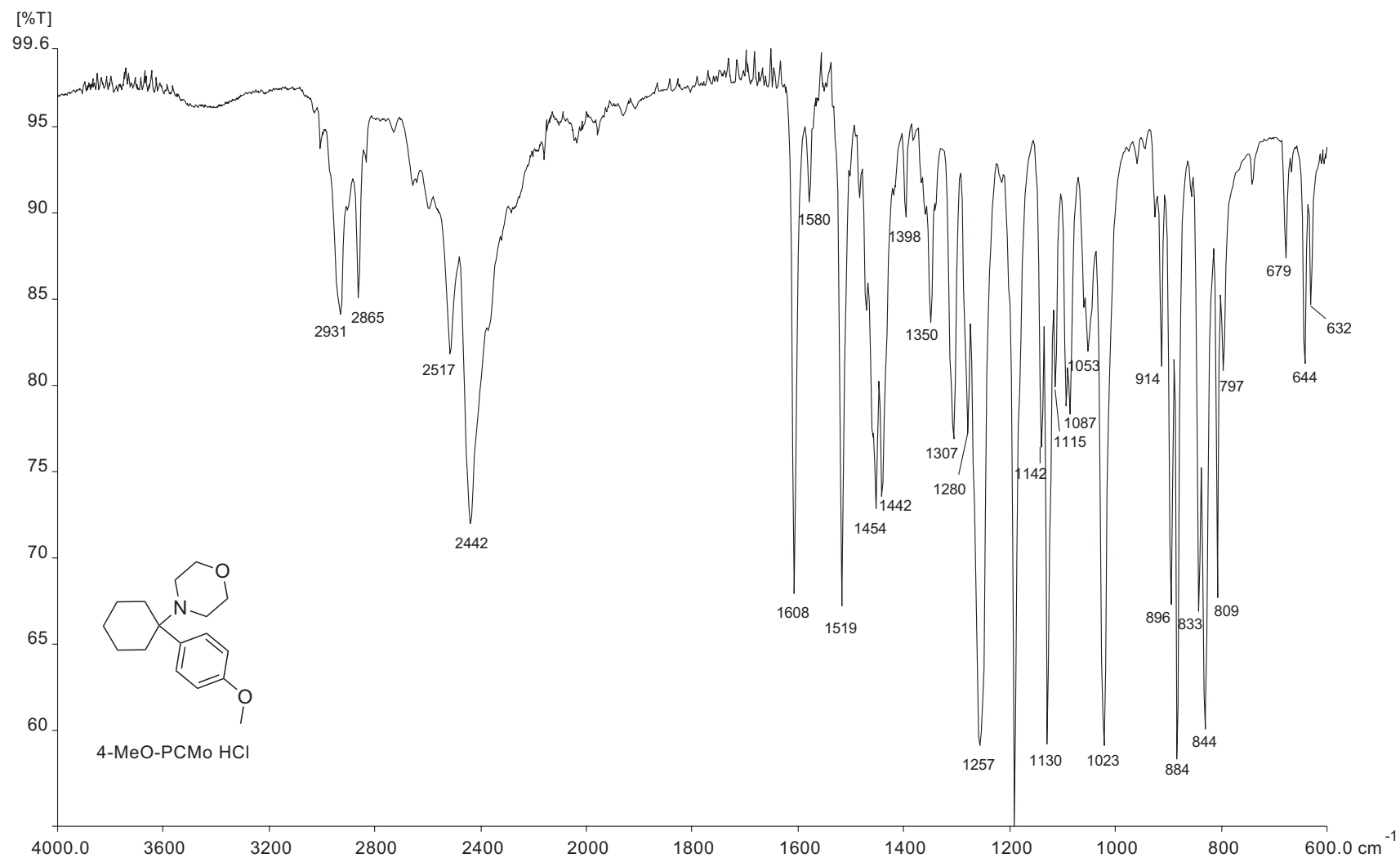


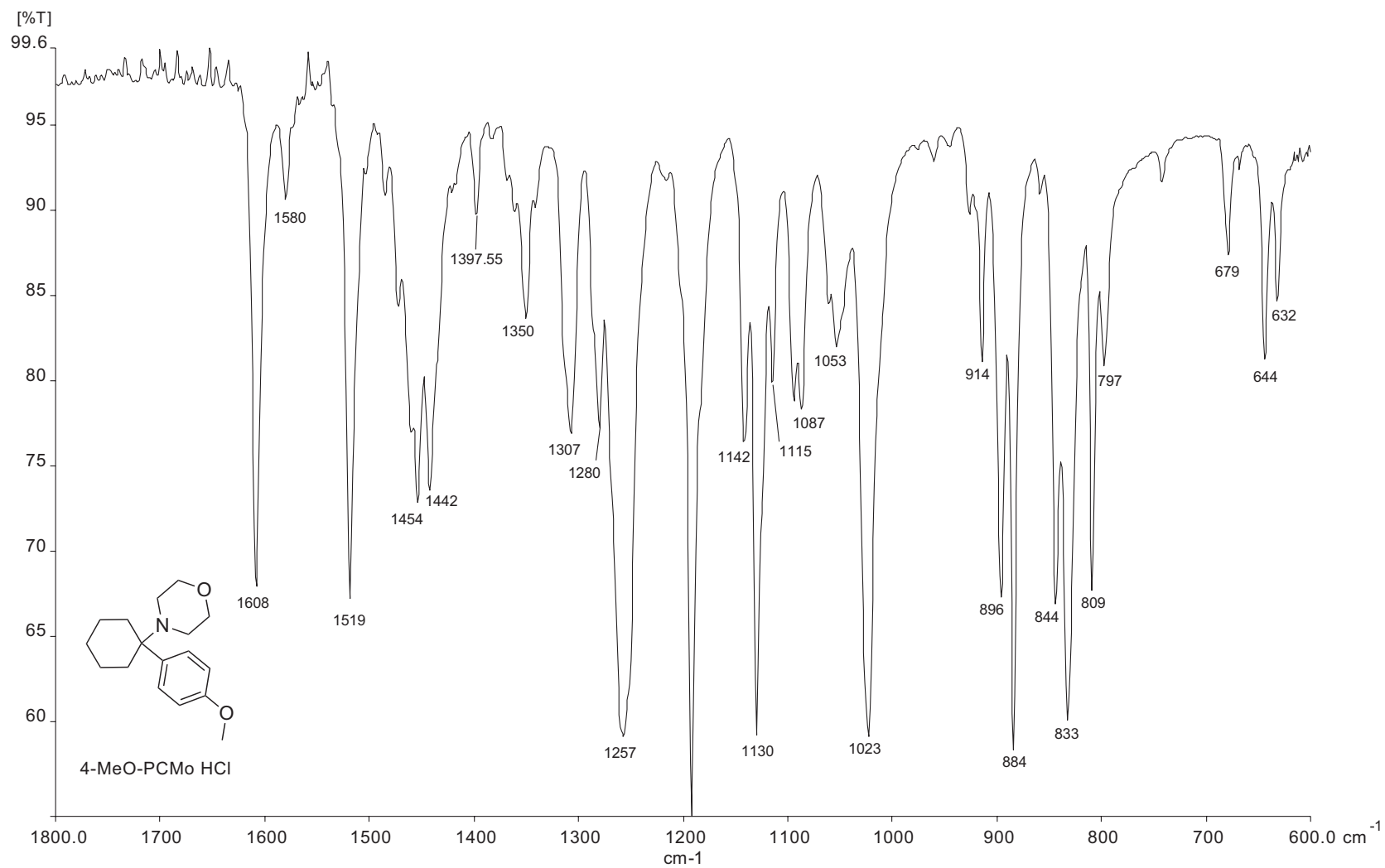
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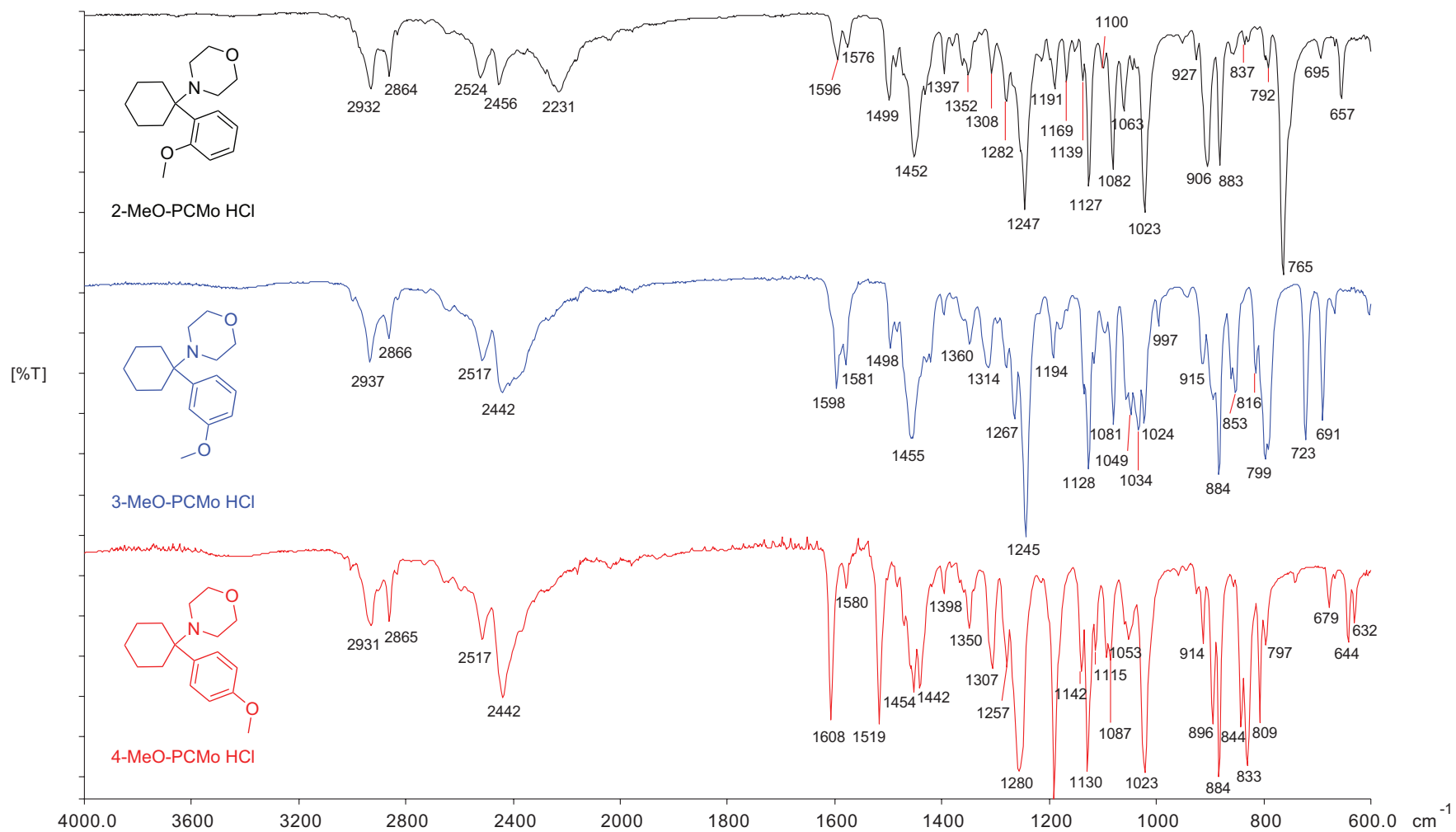




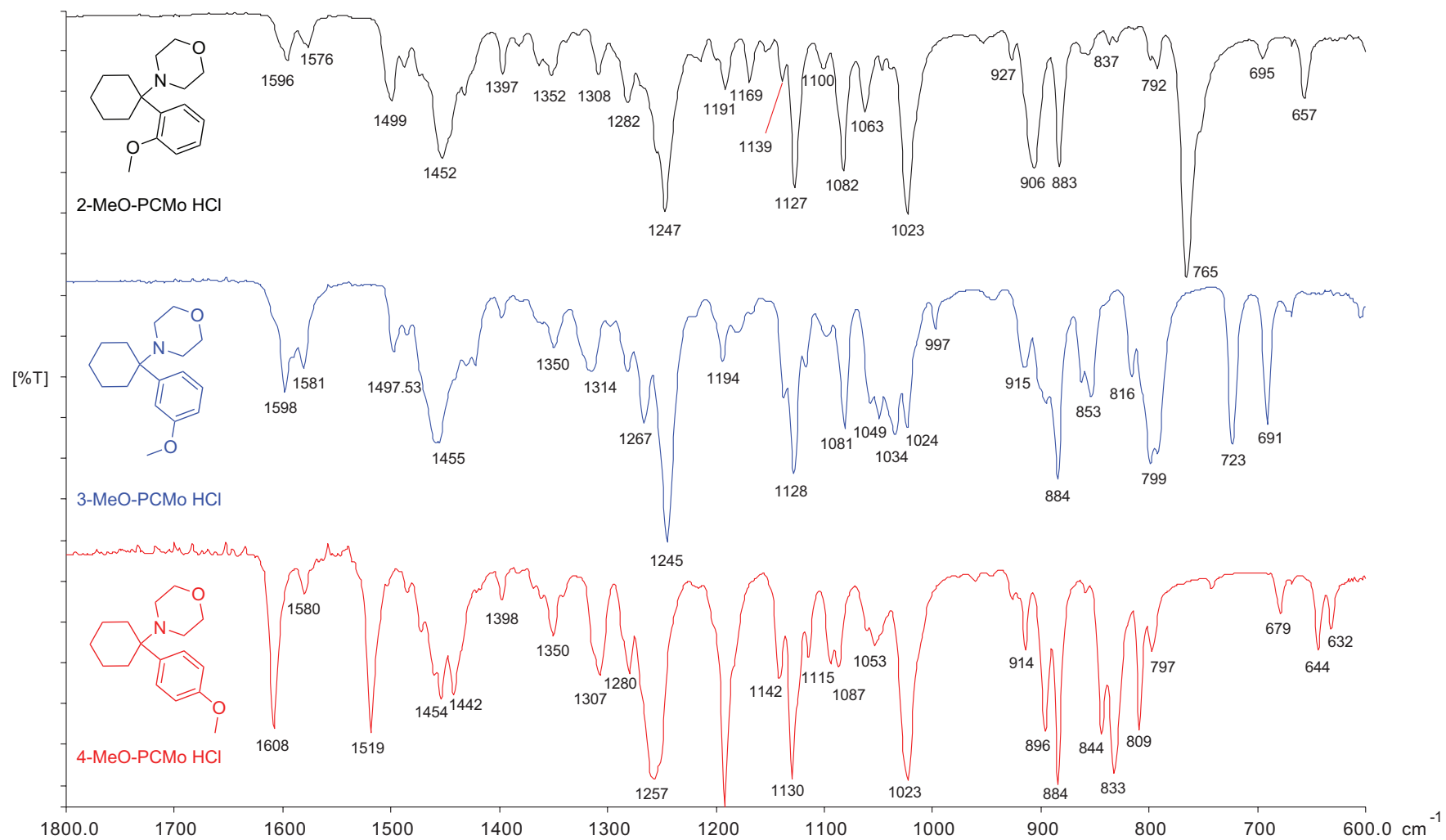




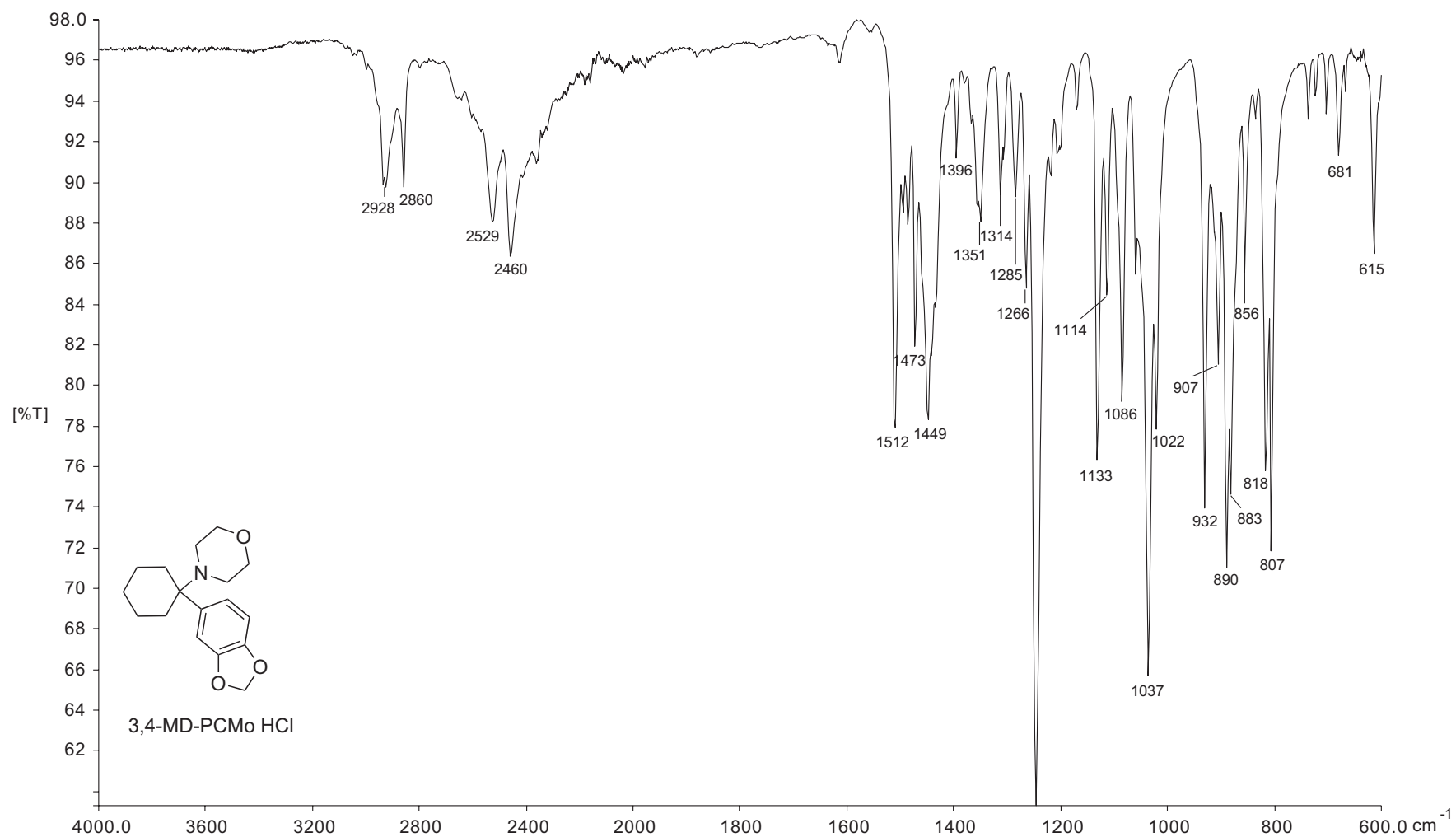
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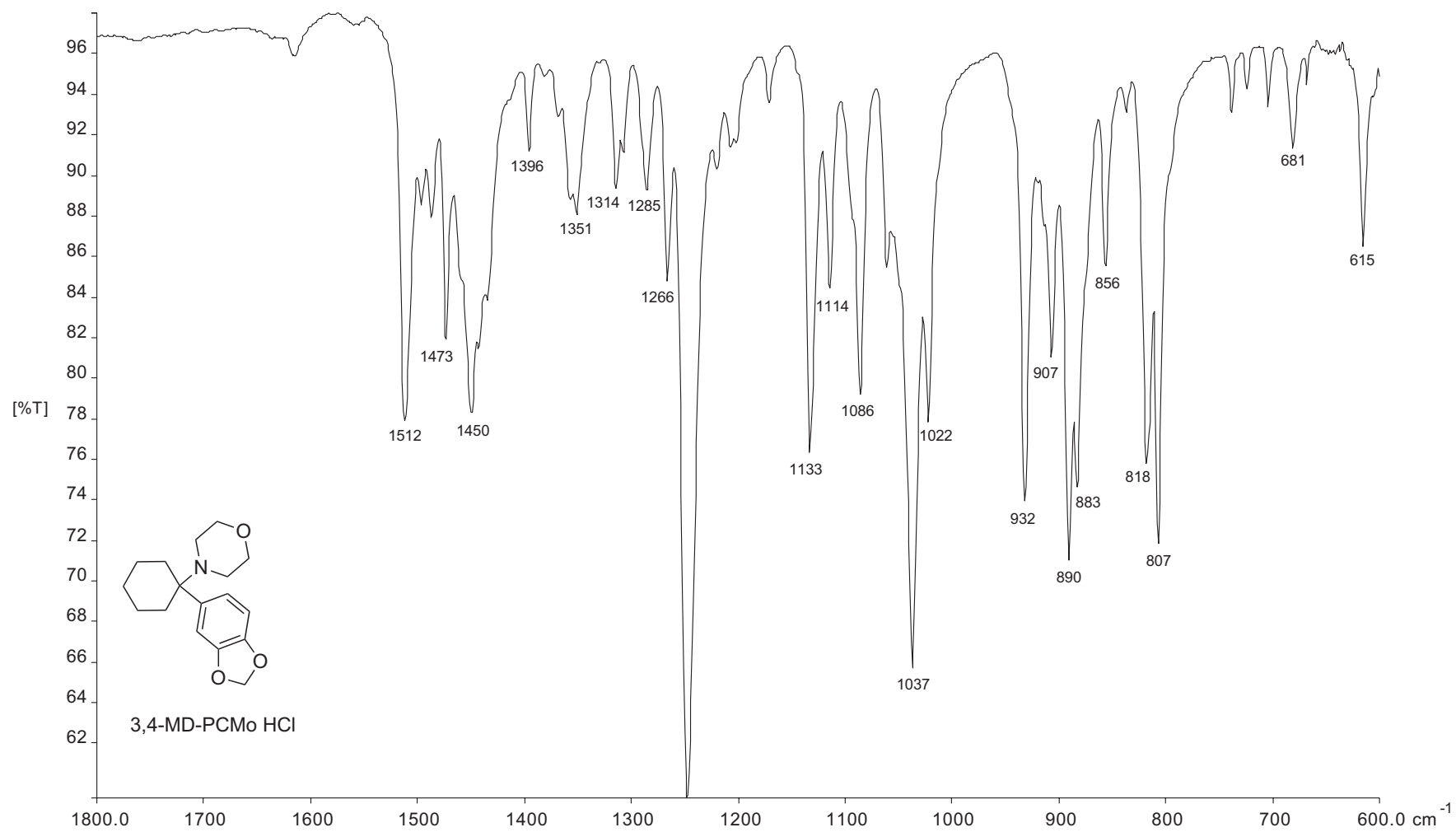


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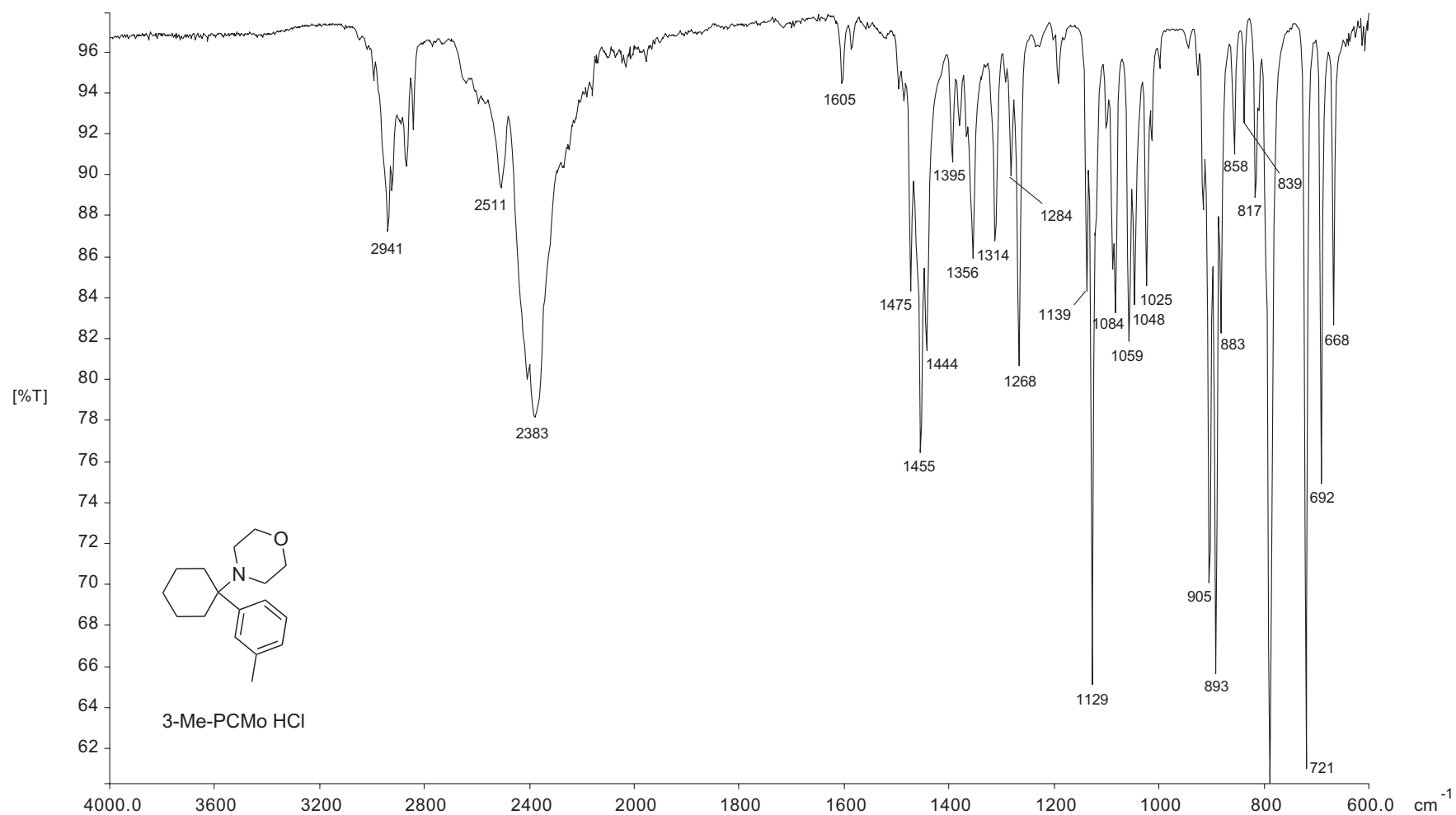


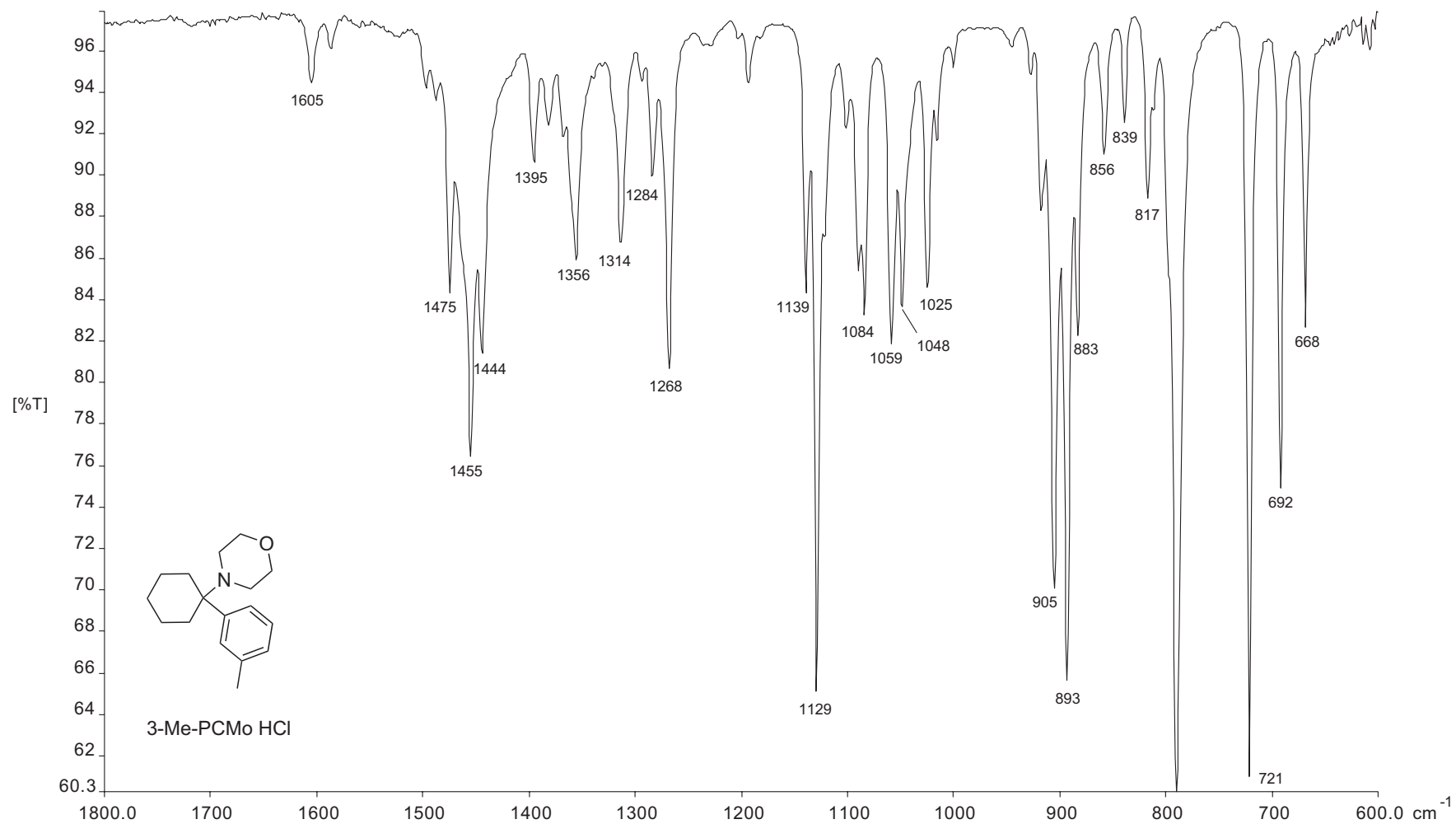
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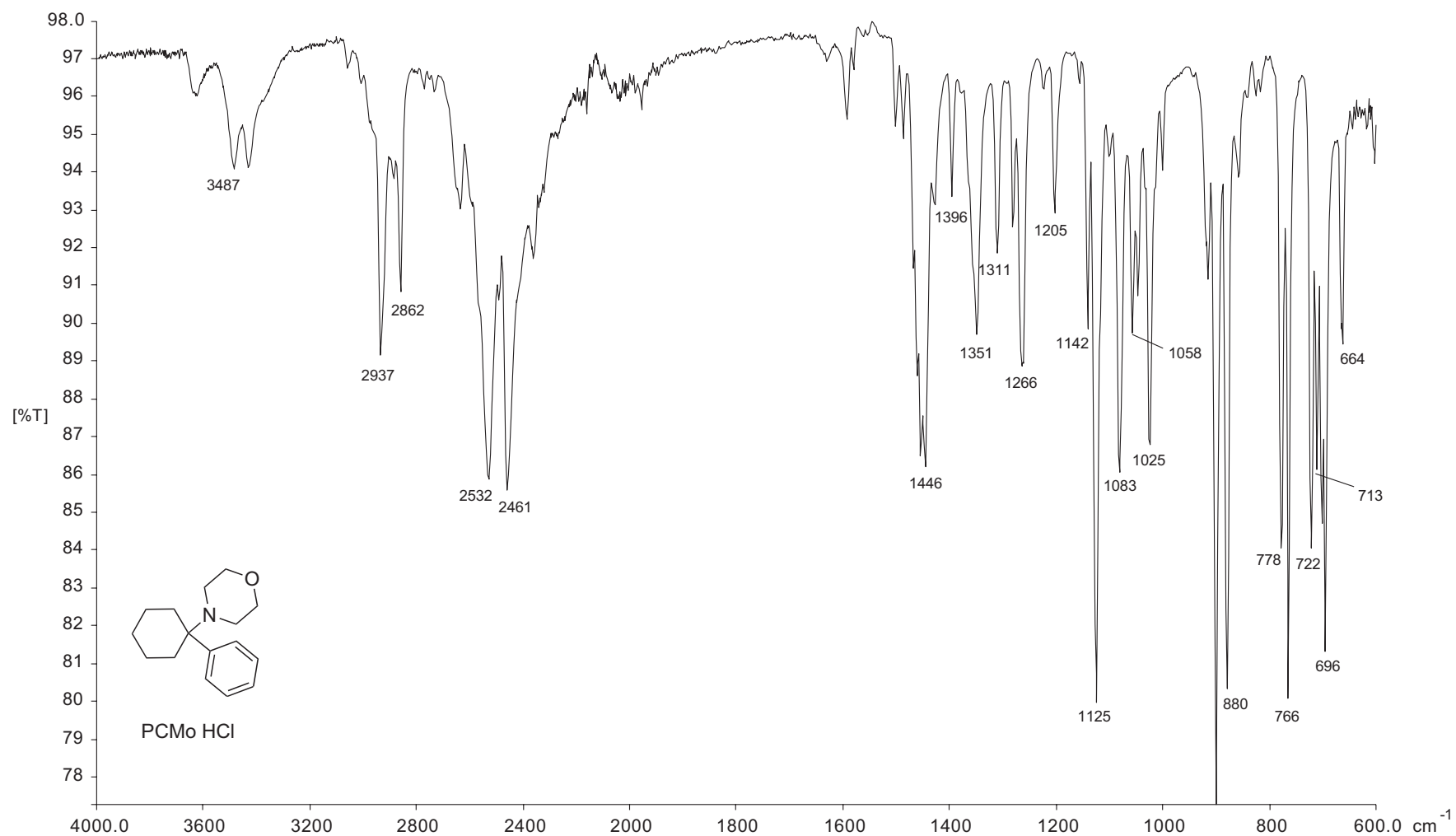




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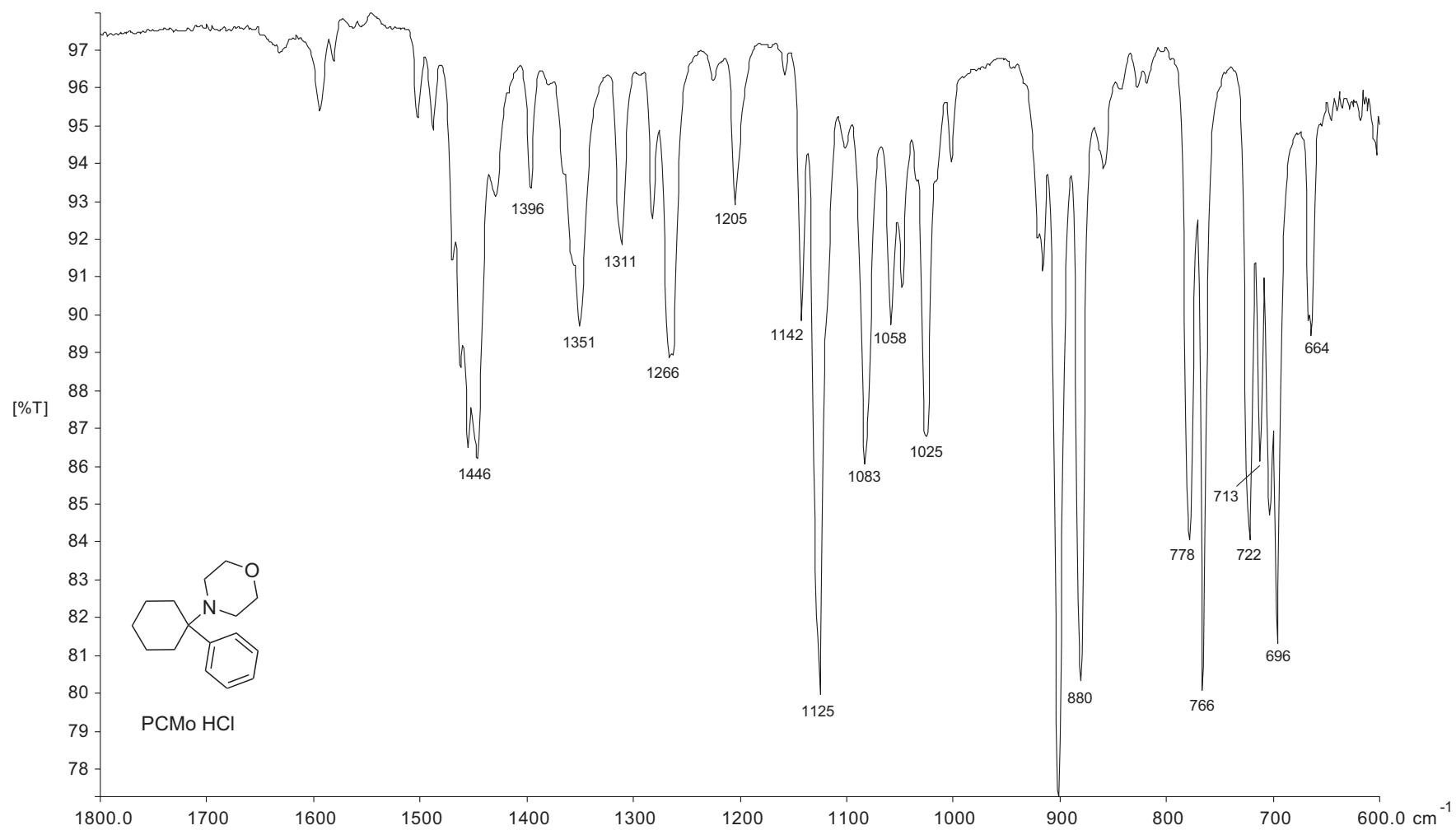






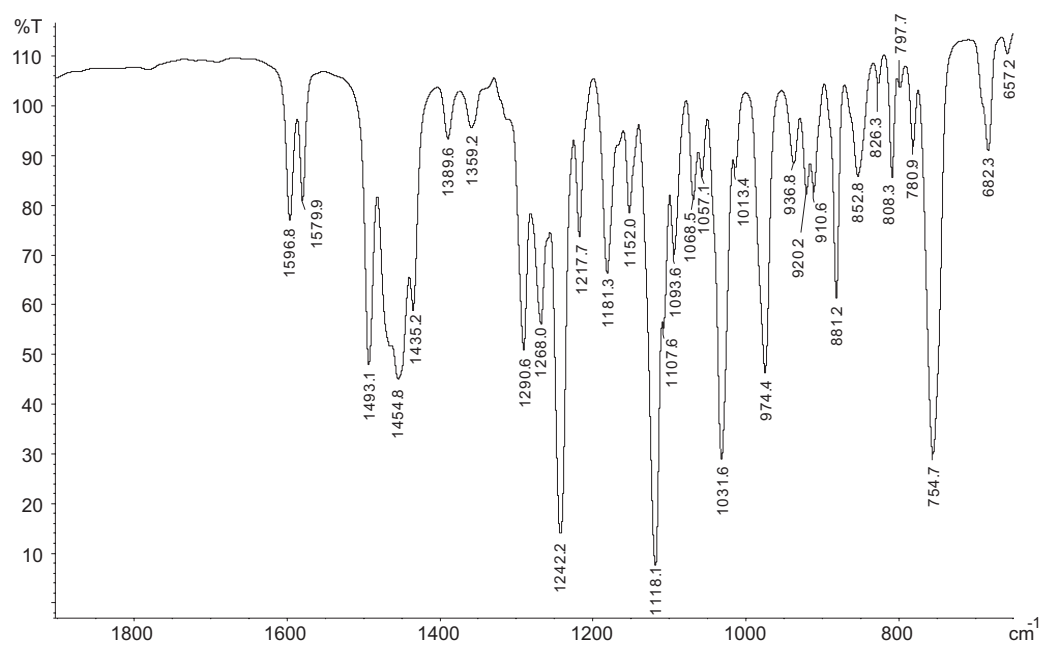
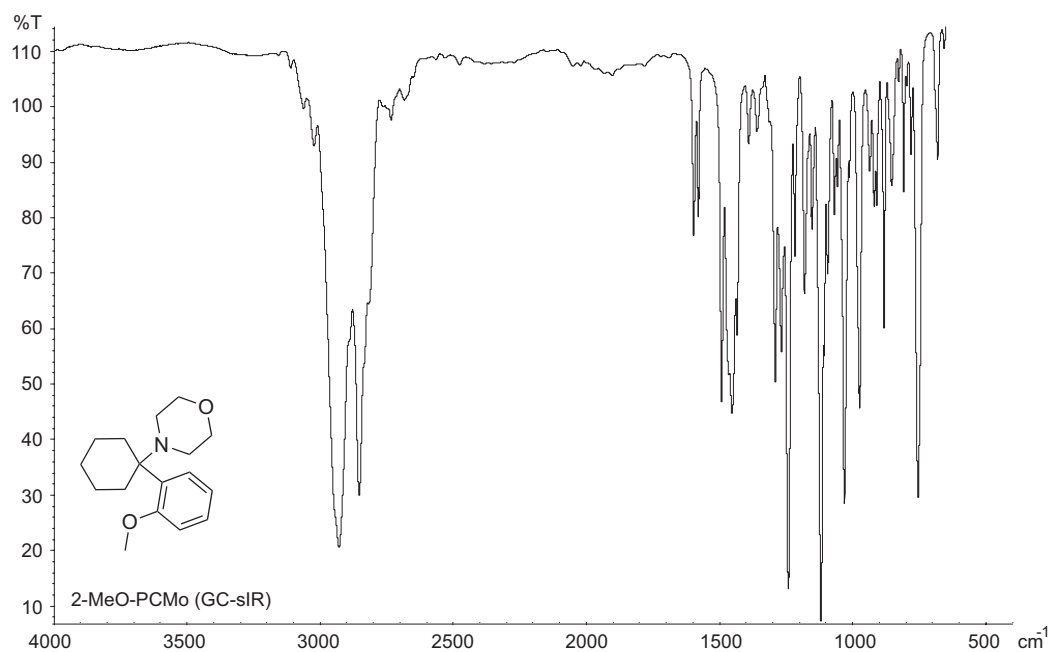


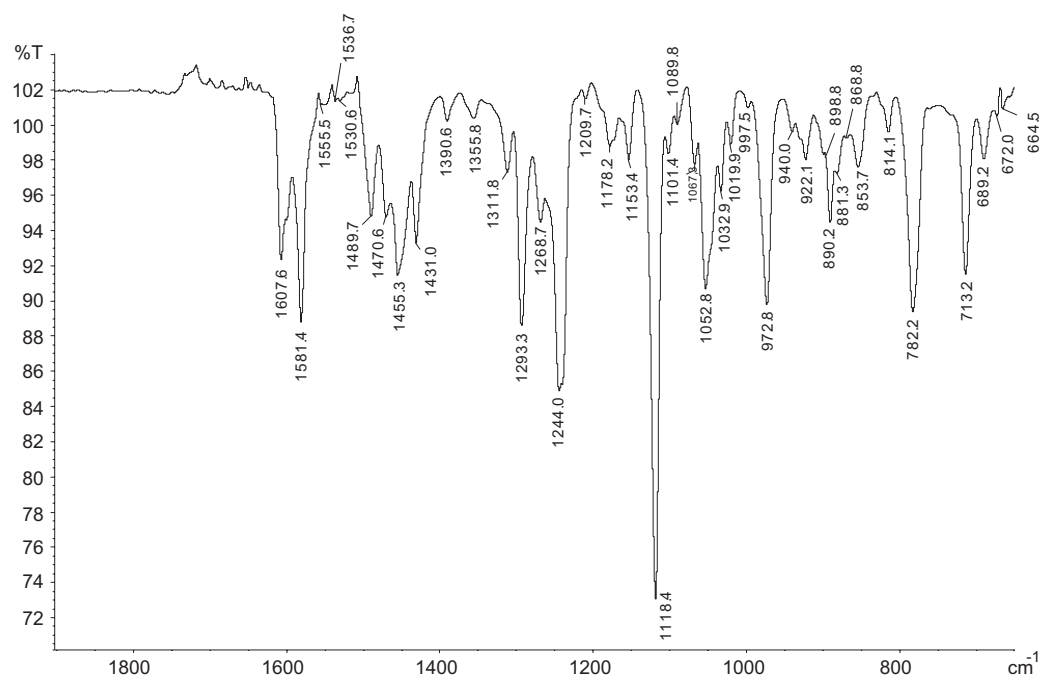
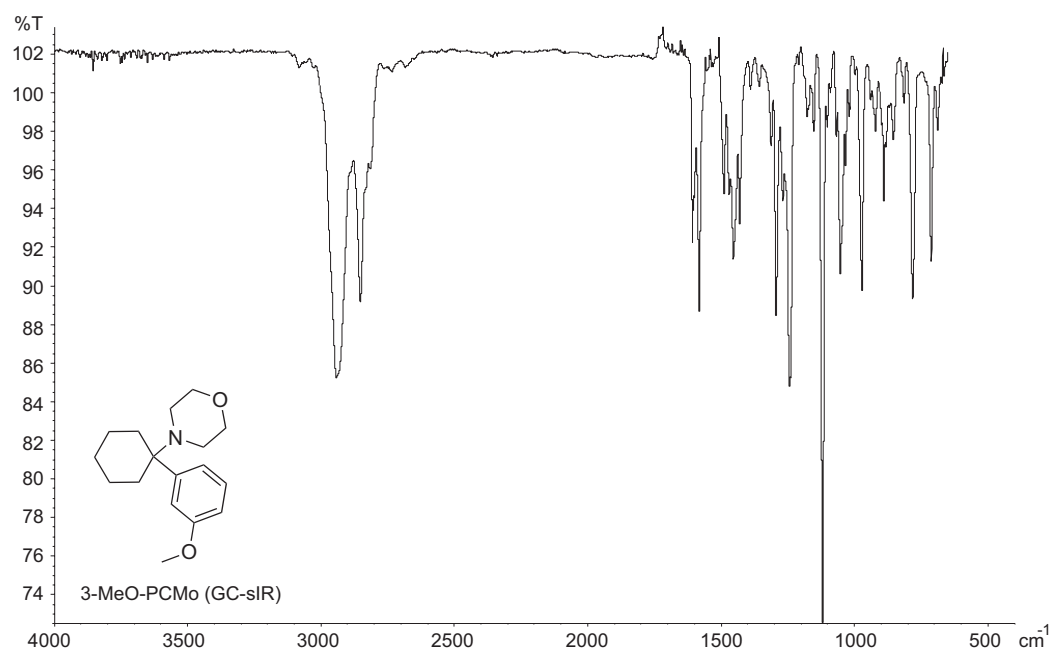
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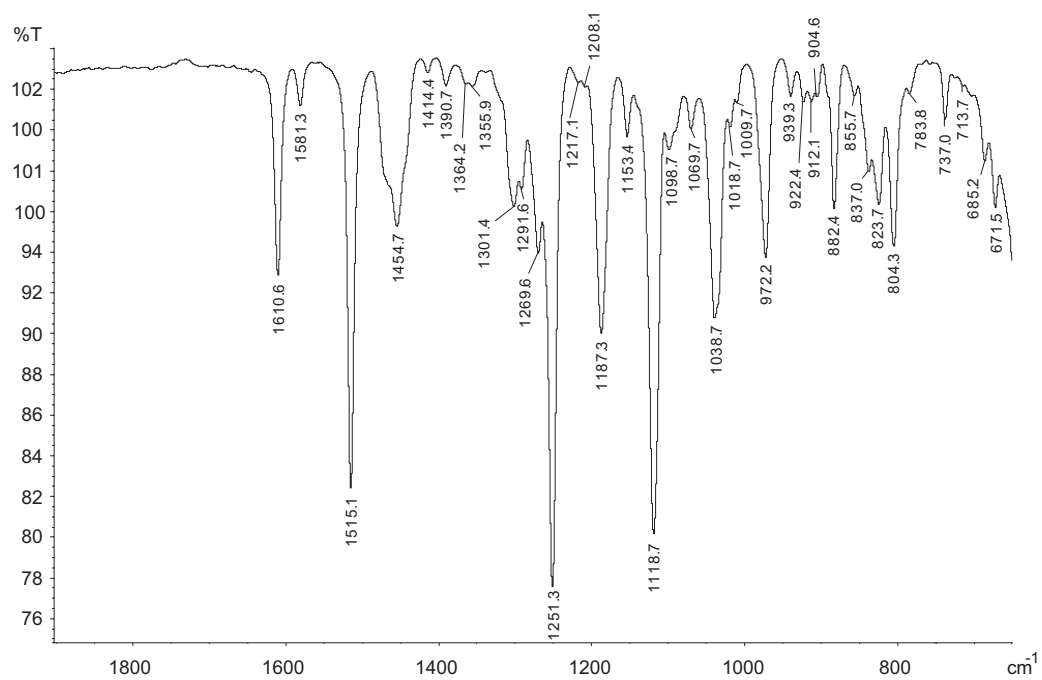
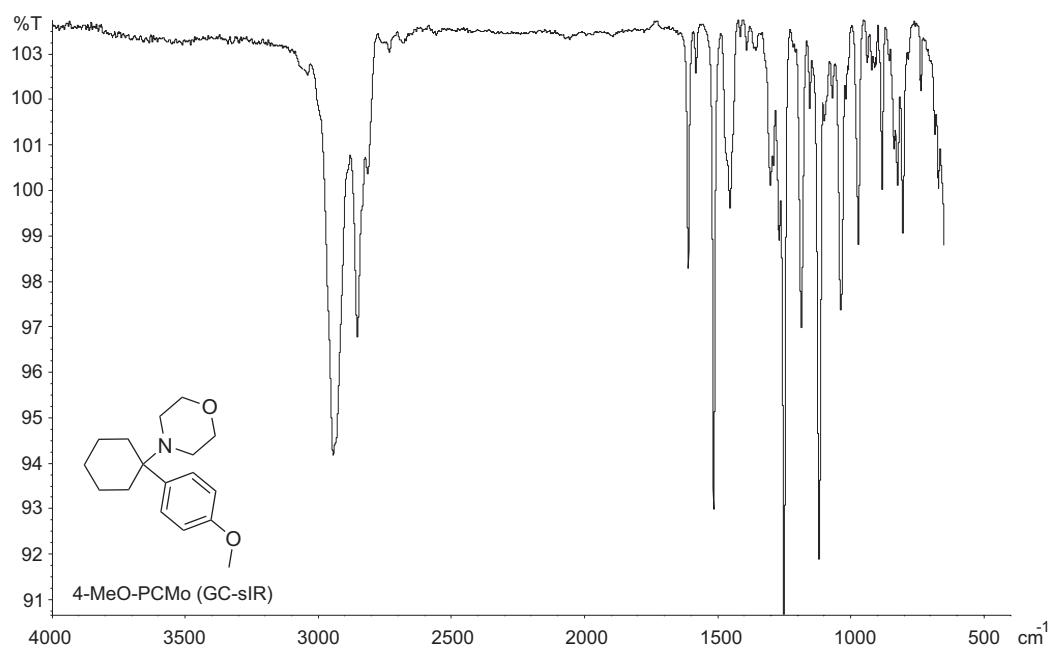


#### Gas chromatography solid-state infrared analysis (GC-sIR)

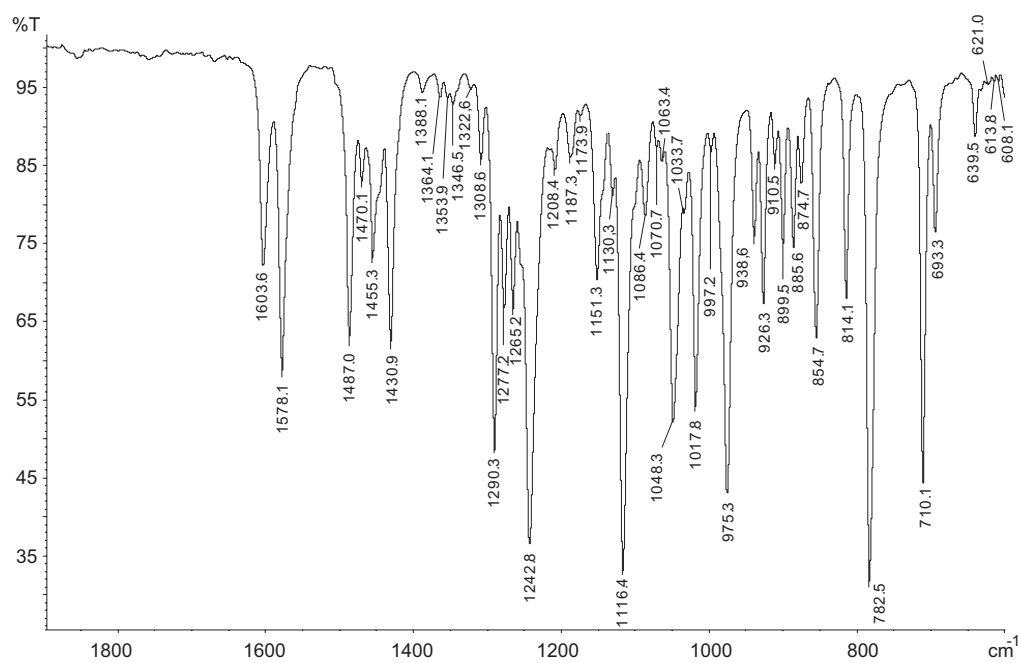
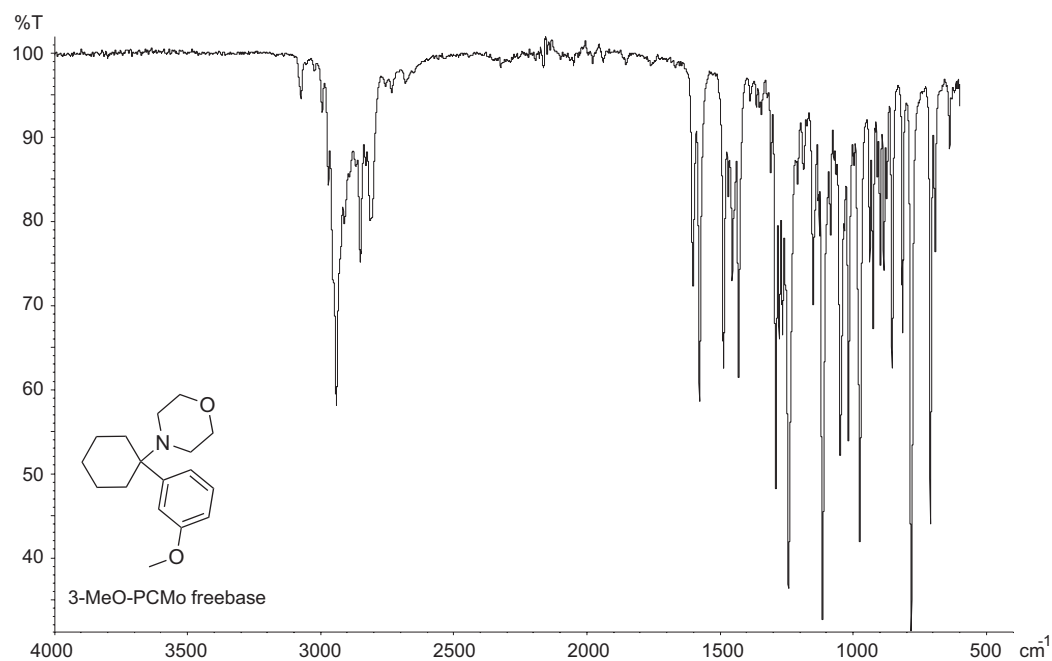
Samples were analyzed using a GC-solid phase-IR-system that consisted of an Agilent GC 7890B (Waldbronn, Germany) with probe sampler Agilent G4567A and a DiscovIR-GC™ (Spectra Analysis, Marlborough, MA, USA). The column eluent was cryogenically accumulated on a spirally rotating ZnSe disk cooled by liquid nitrogen. IR spectra were recorded through the IR-transparent ZnSe disk using a nitrogen-cooled MCT detector. GC parameters: injection in splitless mode with an injection port temperature set at 240°C and a DB-1 fused silica capillary column (30 m × 0.32 mm i.d., 0.25 µm film thickness). The carrier gas was helium with a flow rate of 2.5 mL/min and the oven temperature program was as follows: 80°C for 2 min, ramped to 290°C at 20°C/min, and held at for 20 min. The transfer line was heated at 280°C. Infrared conditions: oven temperature, restrictor temperature, disc temperature, and Dewar cap temperatures were 280°C, 280°C, -40°C, and 35°C, respectively. The vacuum was 0.2 mTorr, disc speed 3 mm/s, spiral separation was 1 mm, wavelength resolution 4 cm<sup>-1</sup> and IR range 650–4000 cm<sup>-1</sup>. Acquisition time was 0.6 s/file with 64 scans/spectrum. Data were processed using GRAMS/AI Ver. 9.1 (Grams Spectroscopy Software Suite, Thermo Fischer Scientific, Dreieich, Germany) followed by implementation of the OMNIC Software, Ver. 7.4.127 (Thermo Electron Corporation, Dreieich, Germany).



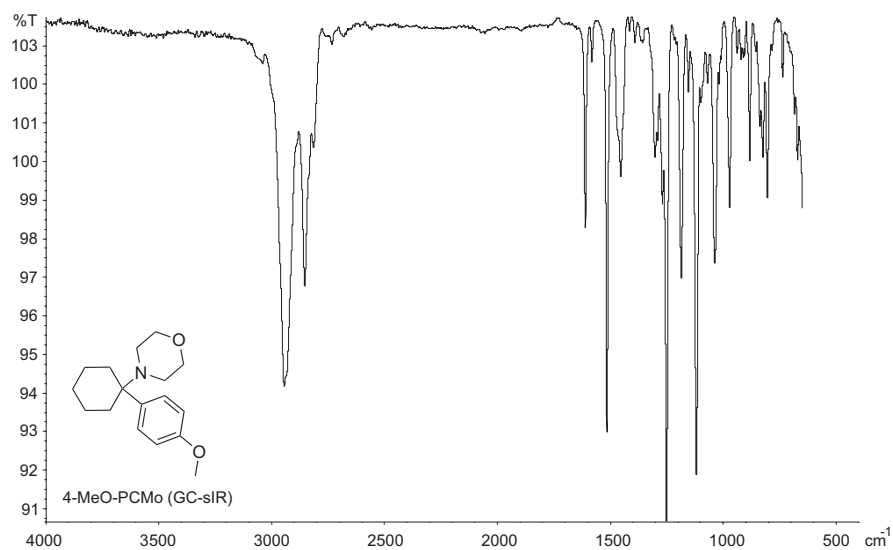
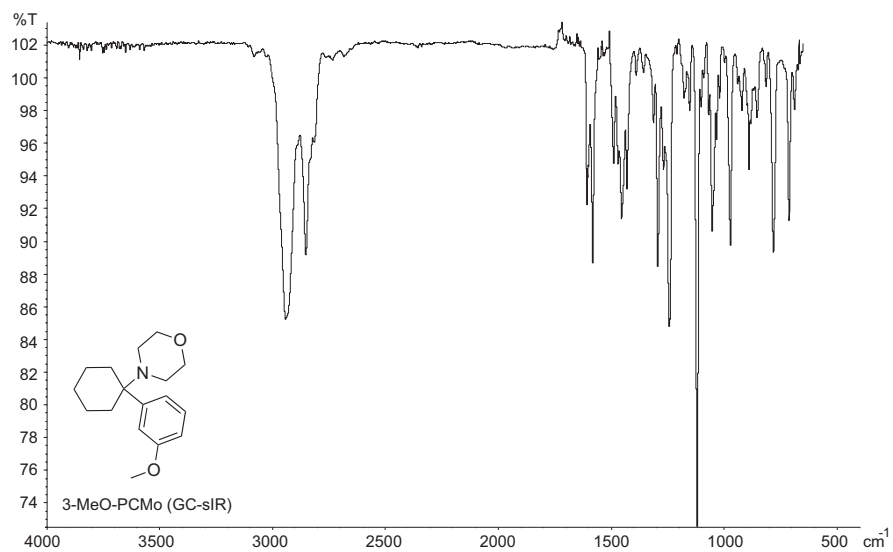
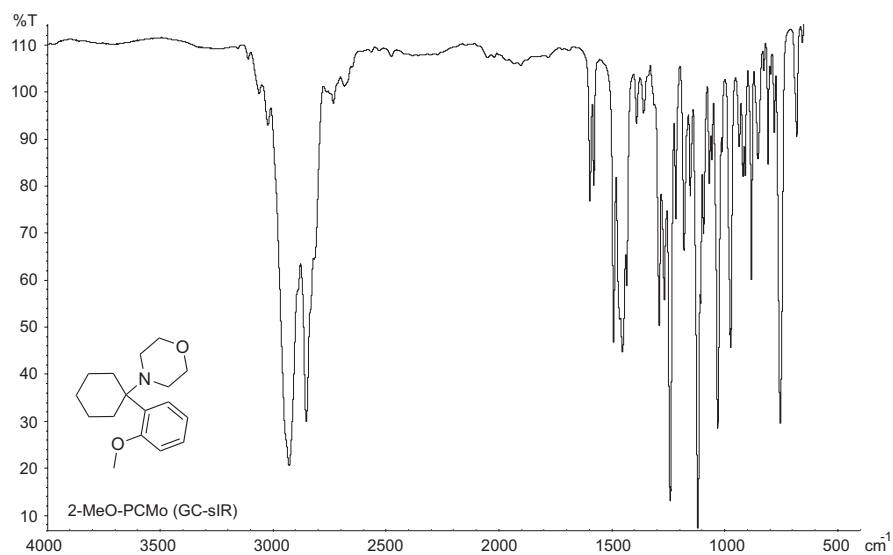




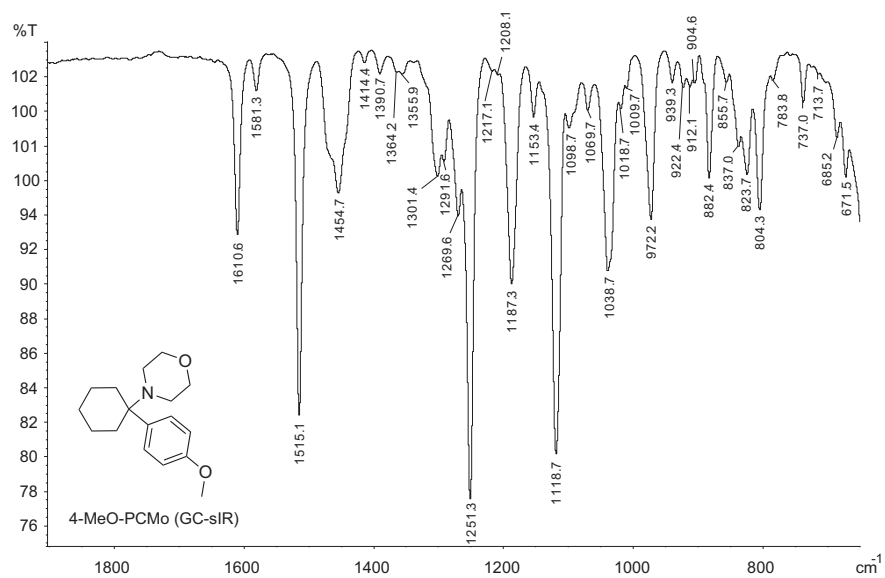
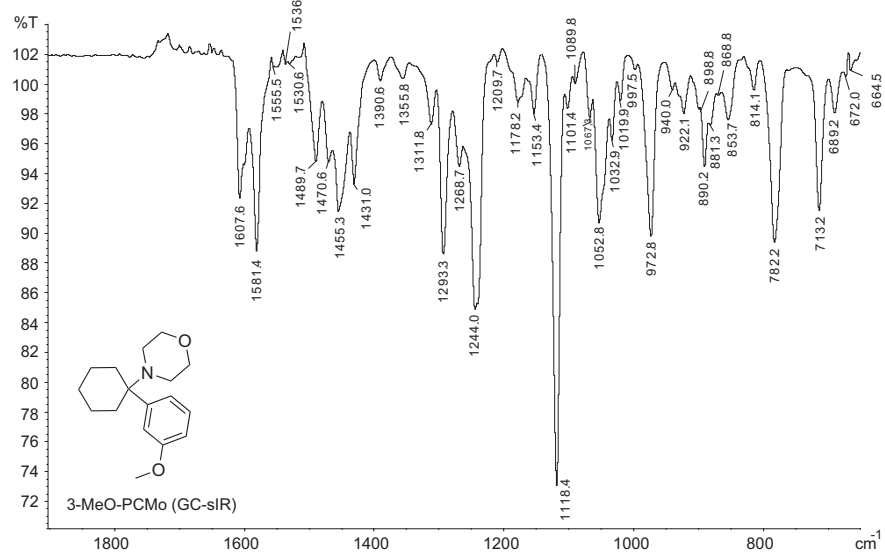
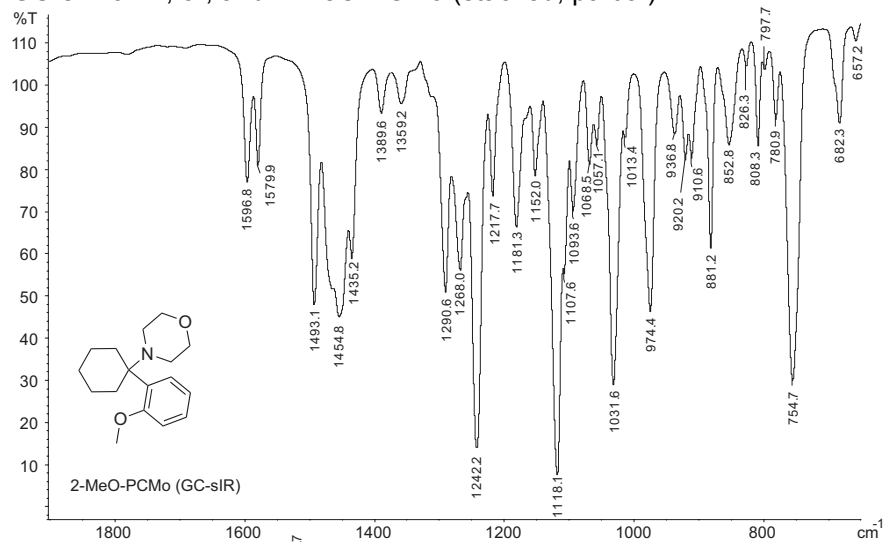
ATR-IR spectrum of 3-MeO-PCMo freebase



GC-sIR of 2-, 3-, and 4-MeO-PCMo (stacked)

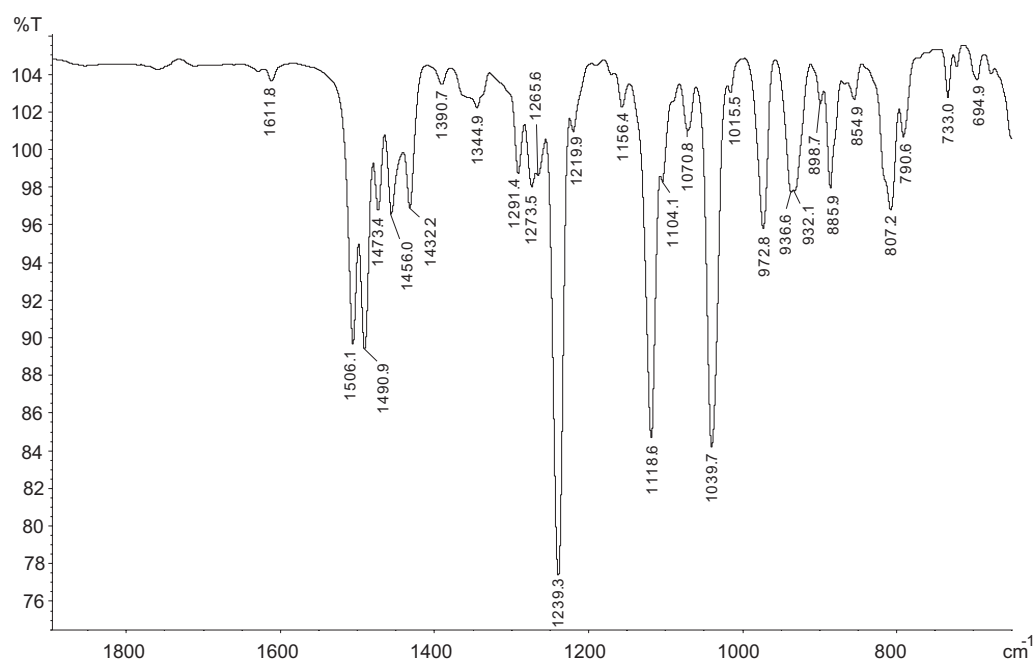
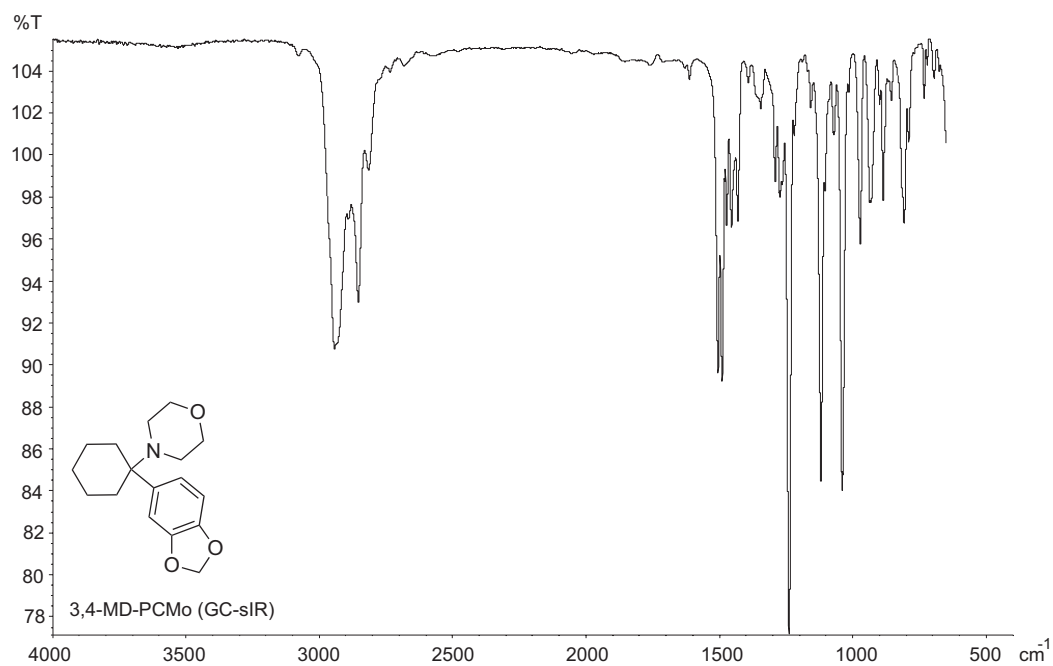


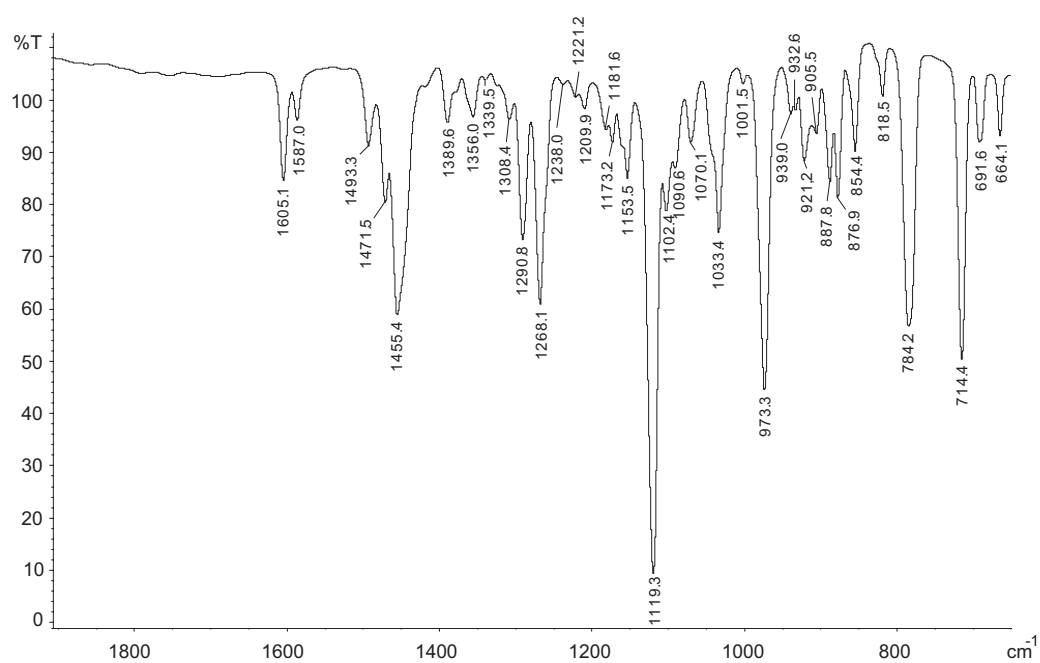
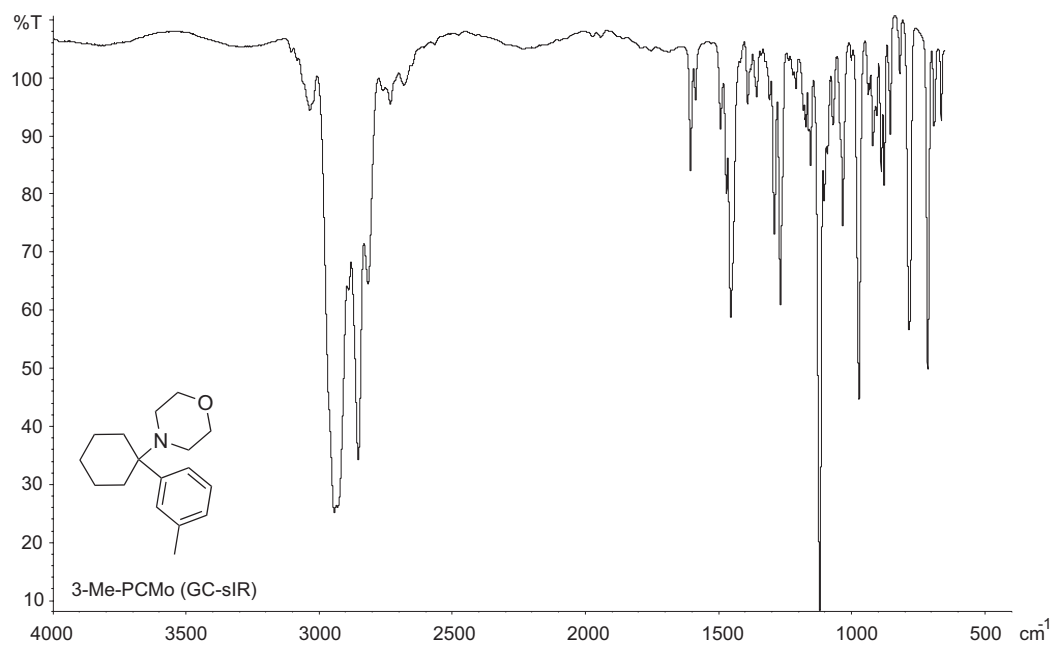
## GC-sIR of 2-, 3-, and 4-MeO-PCMo (stacked, partial)

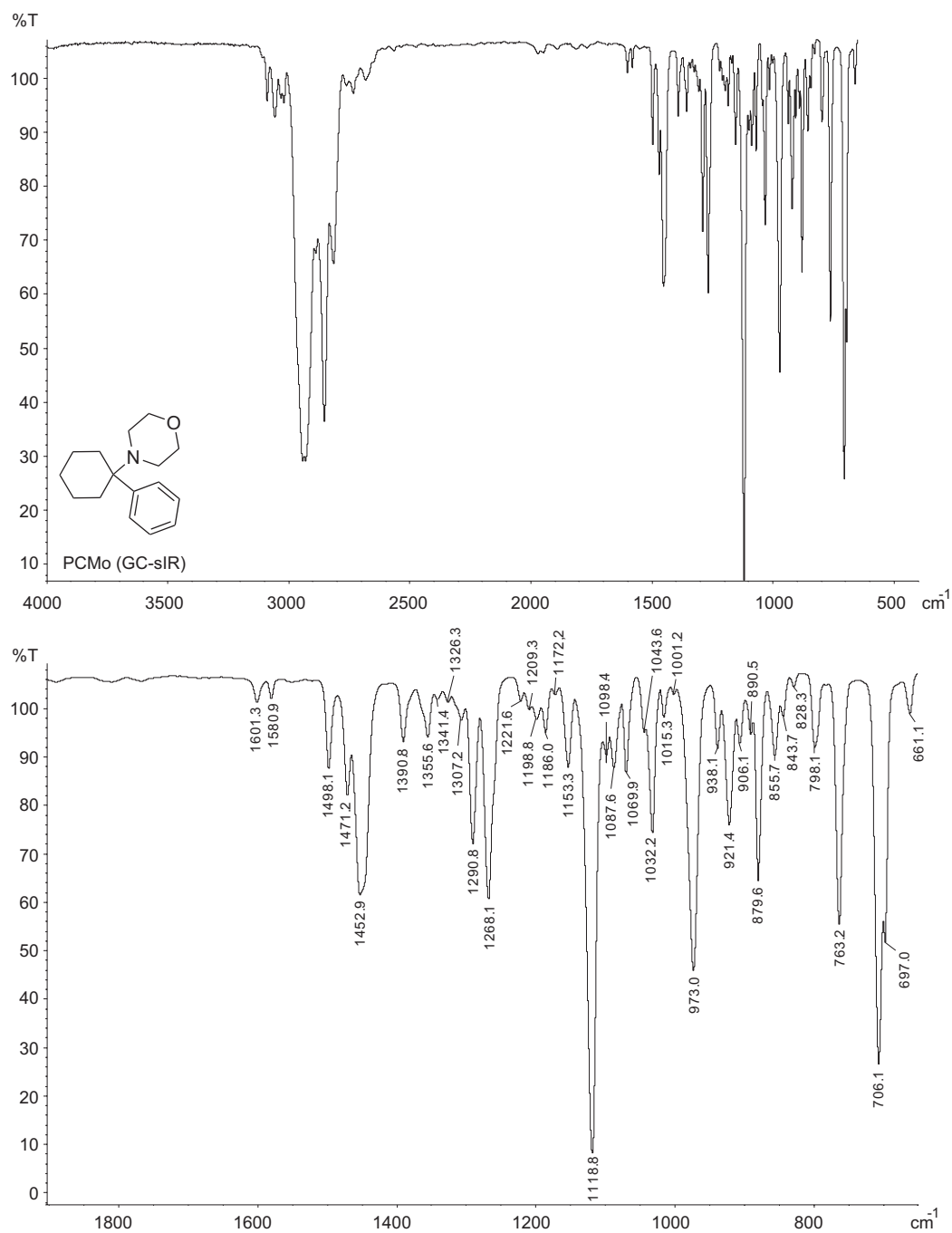




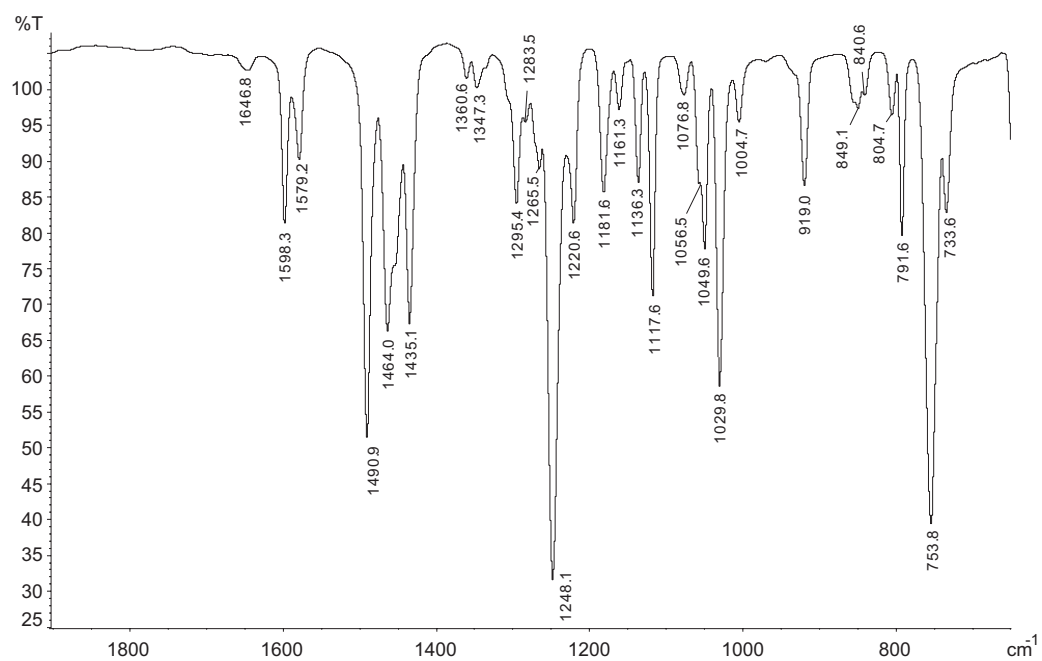
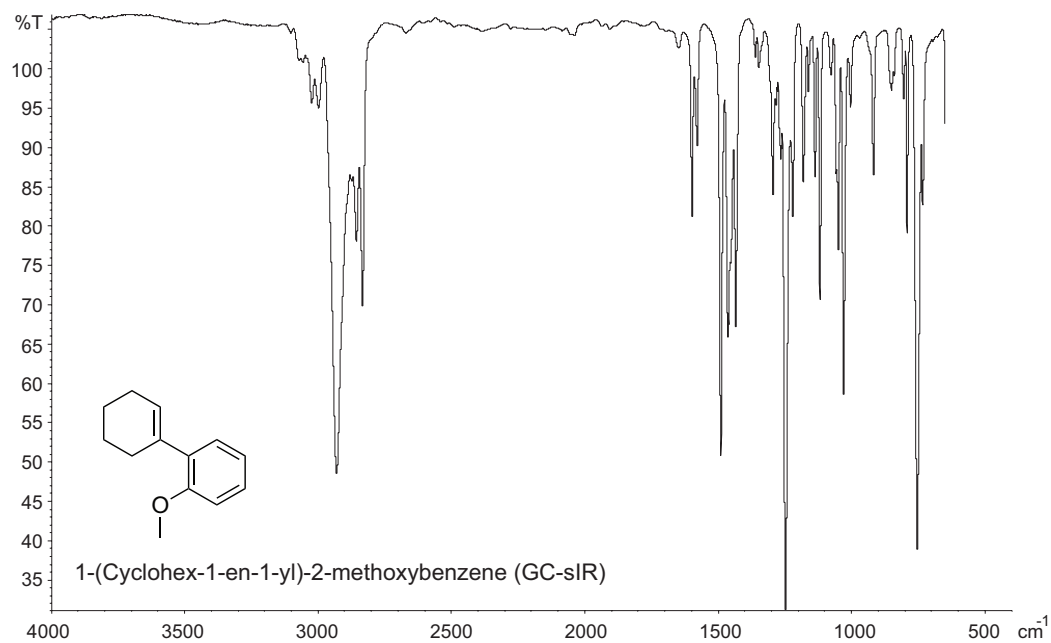
GC-sIR of 3,4-MD-PCMo, 3-Me-PCMo and PCMo

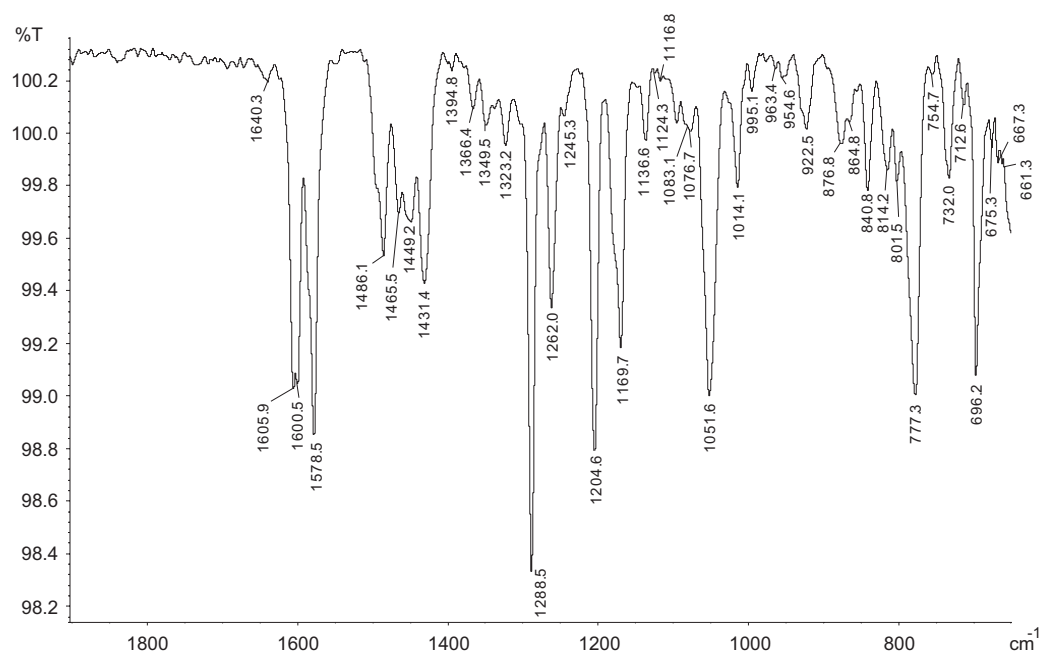
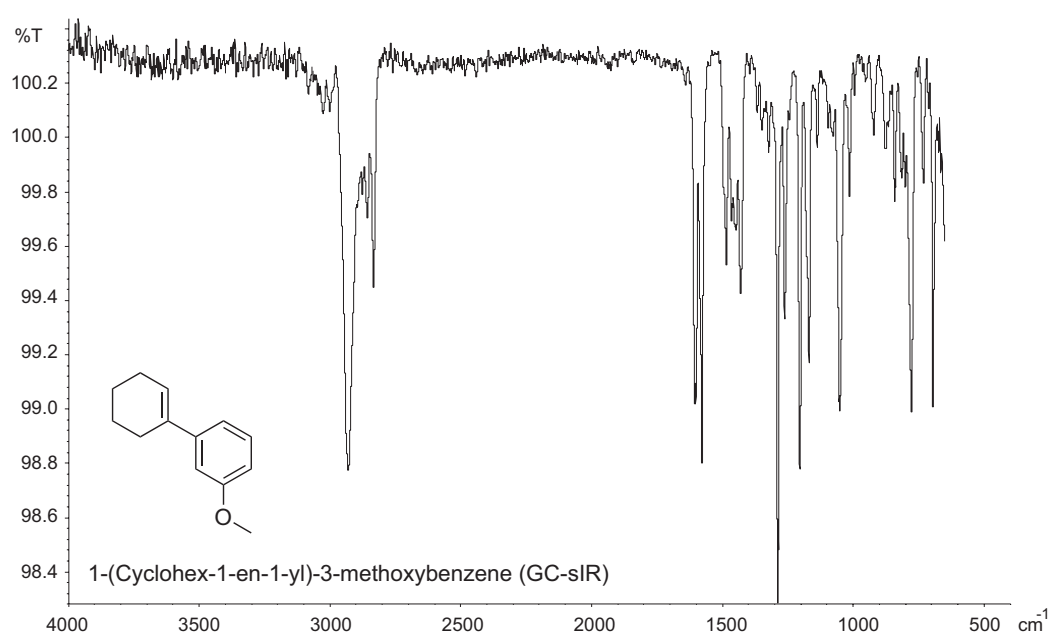


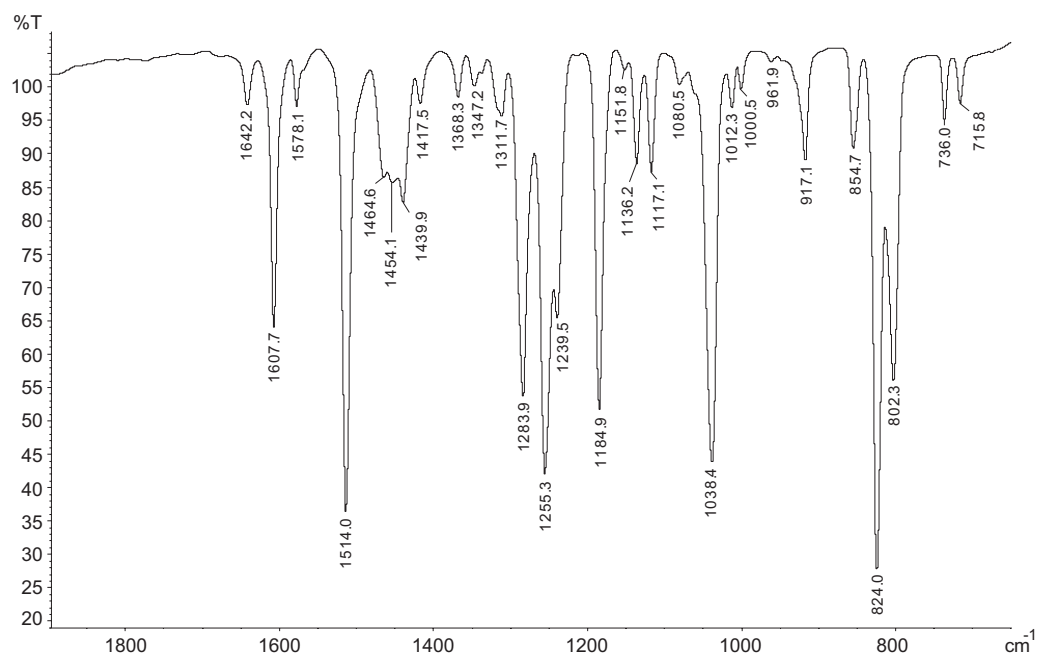
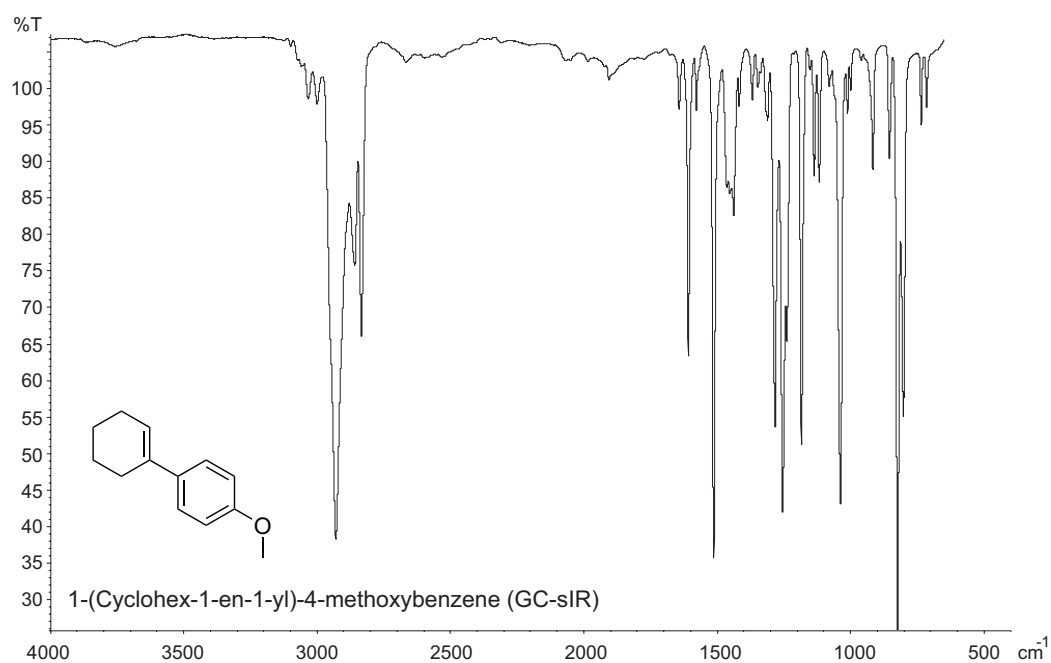


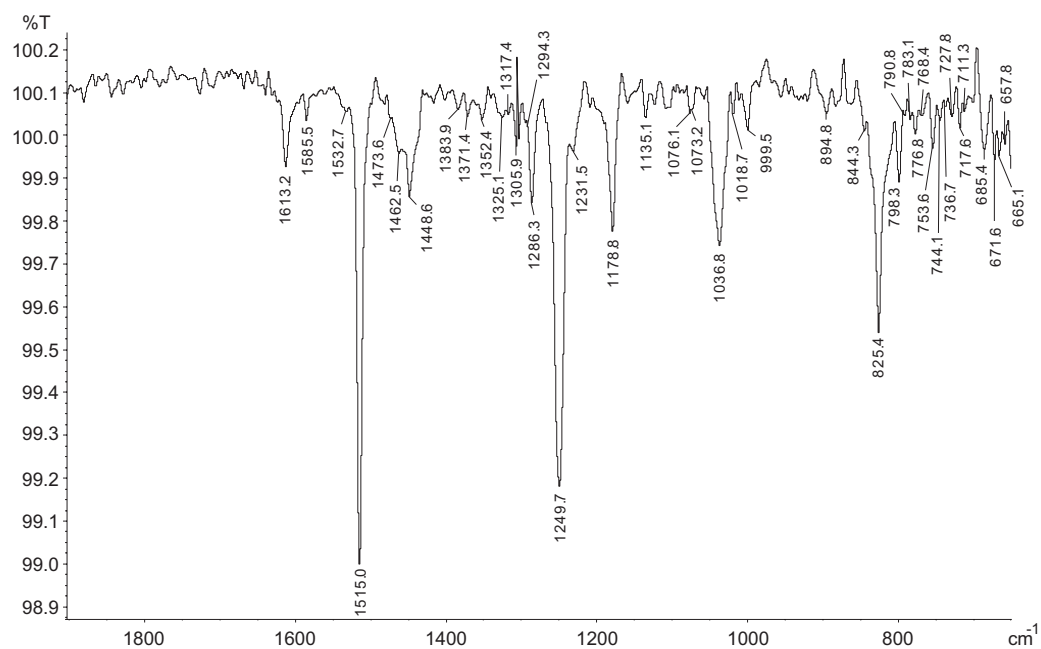
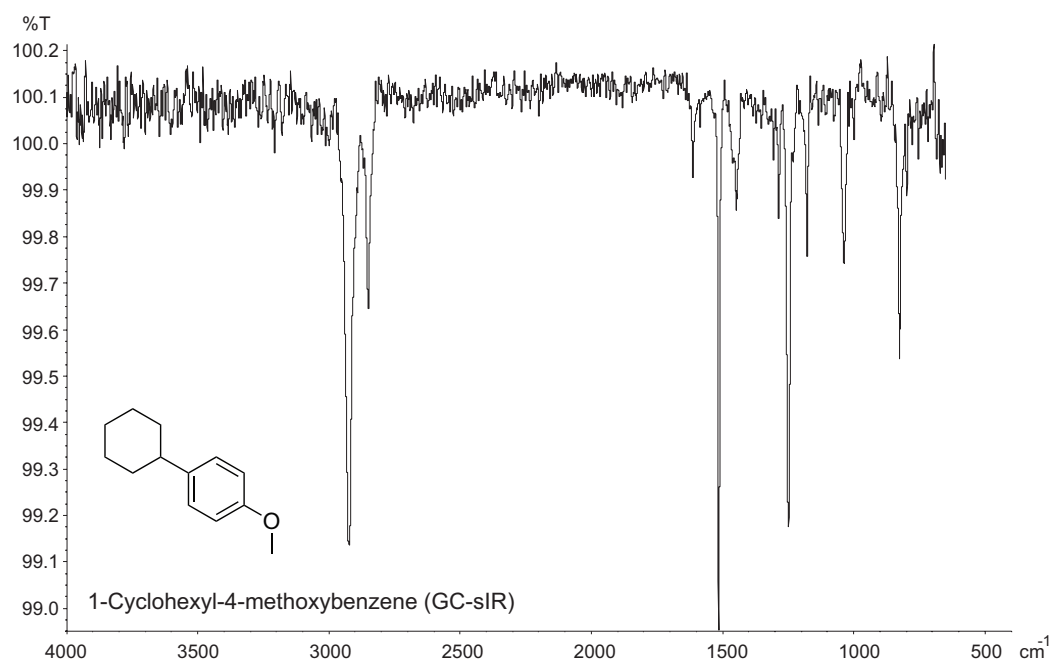


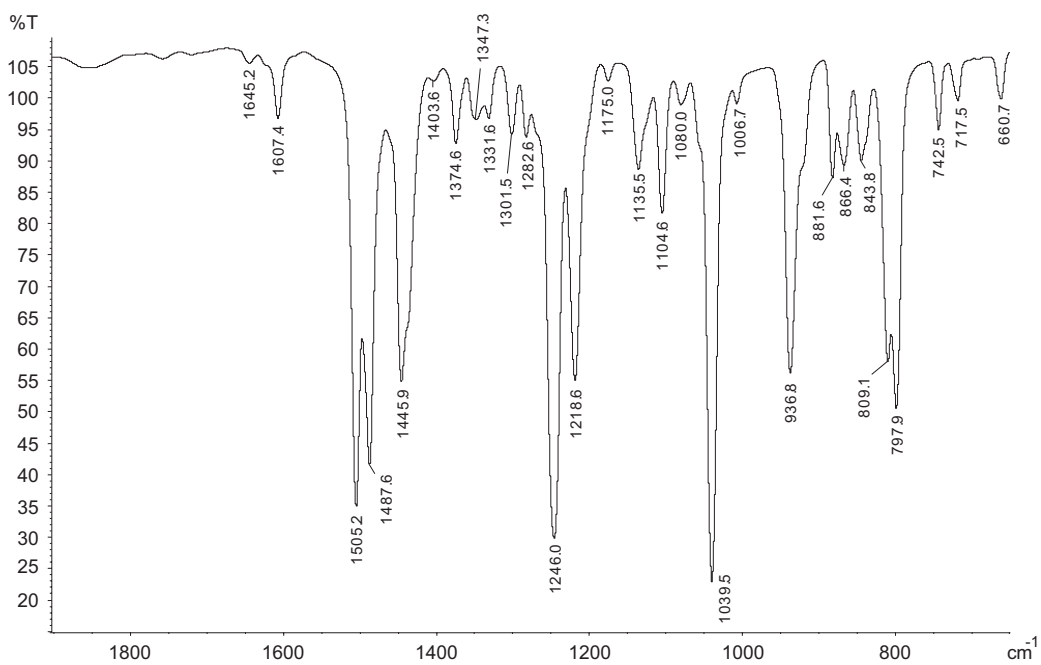
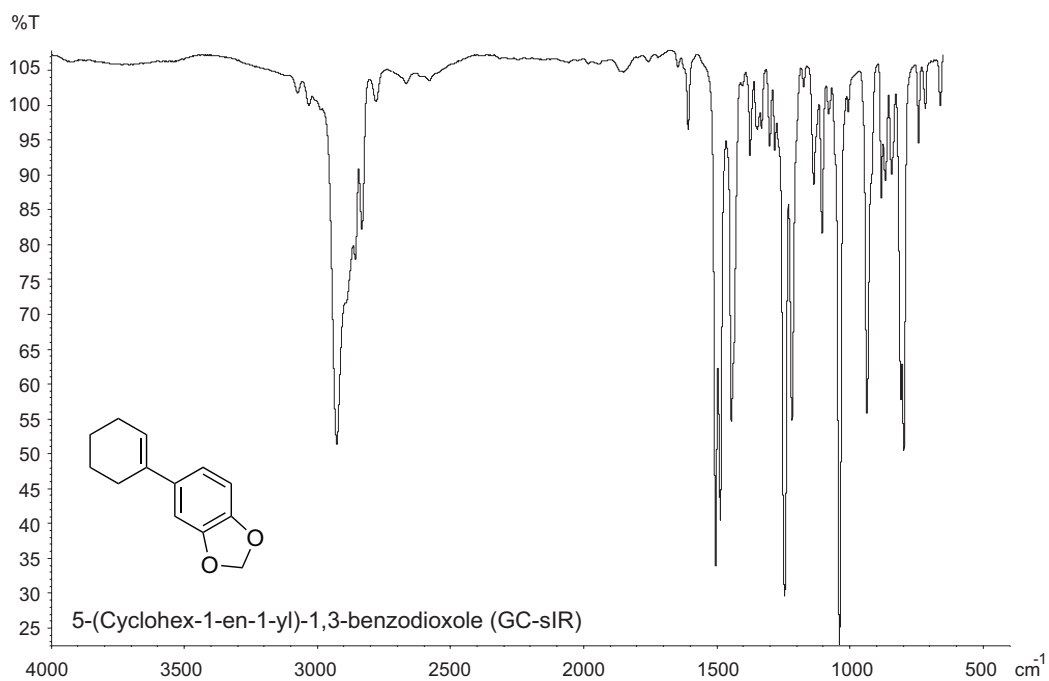
GC-sIR data of GC-induced degradation products



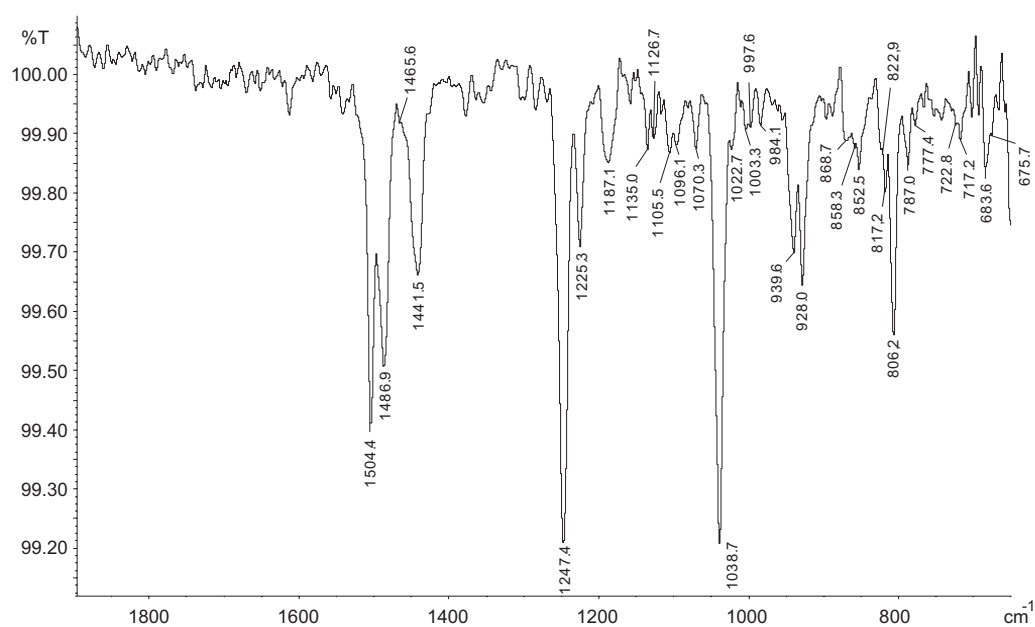
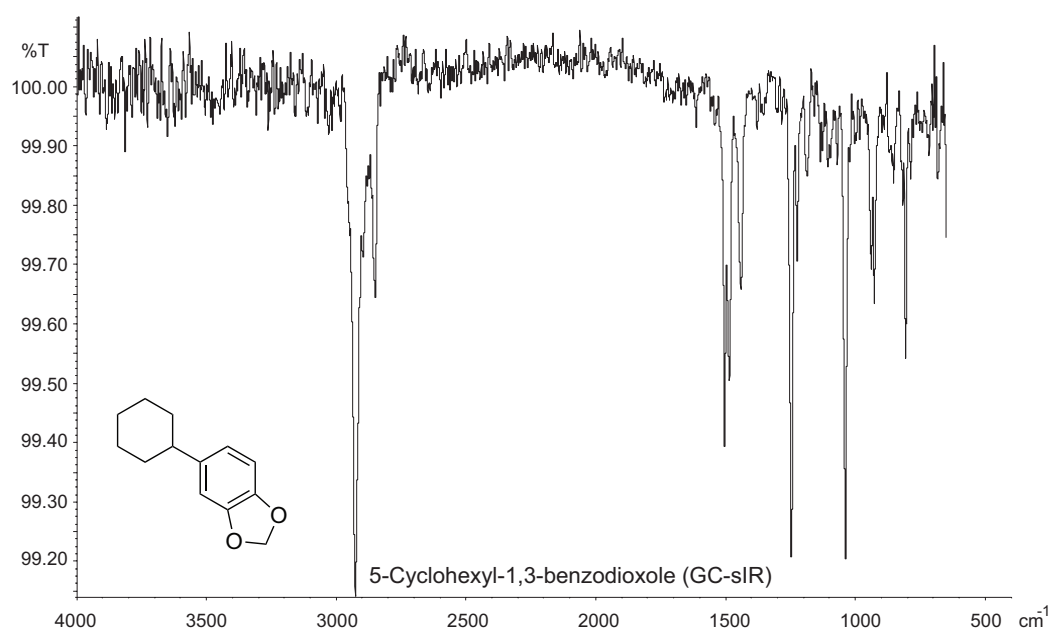


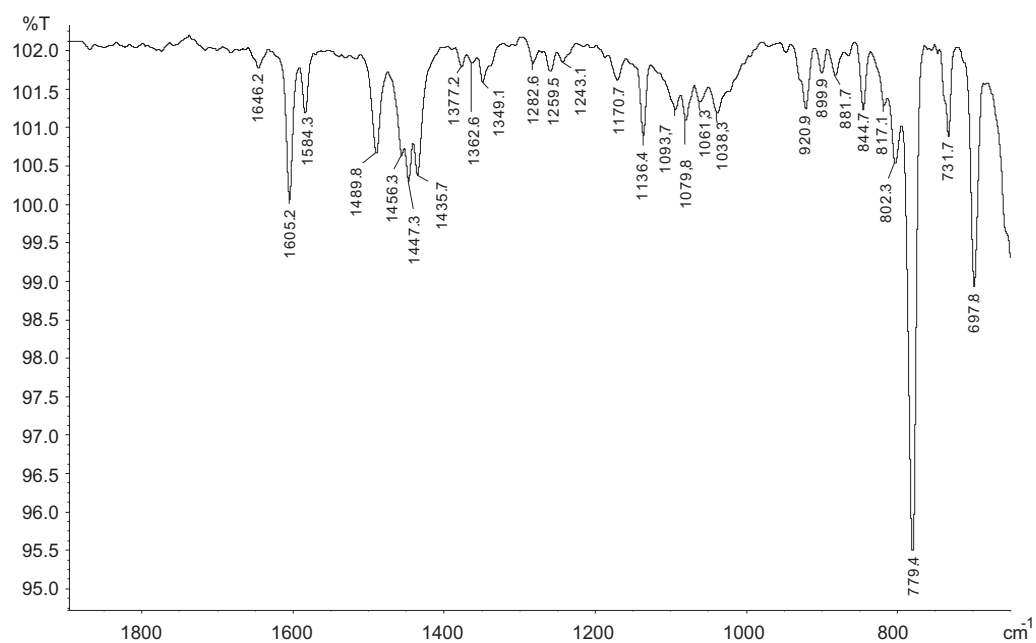
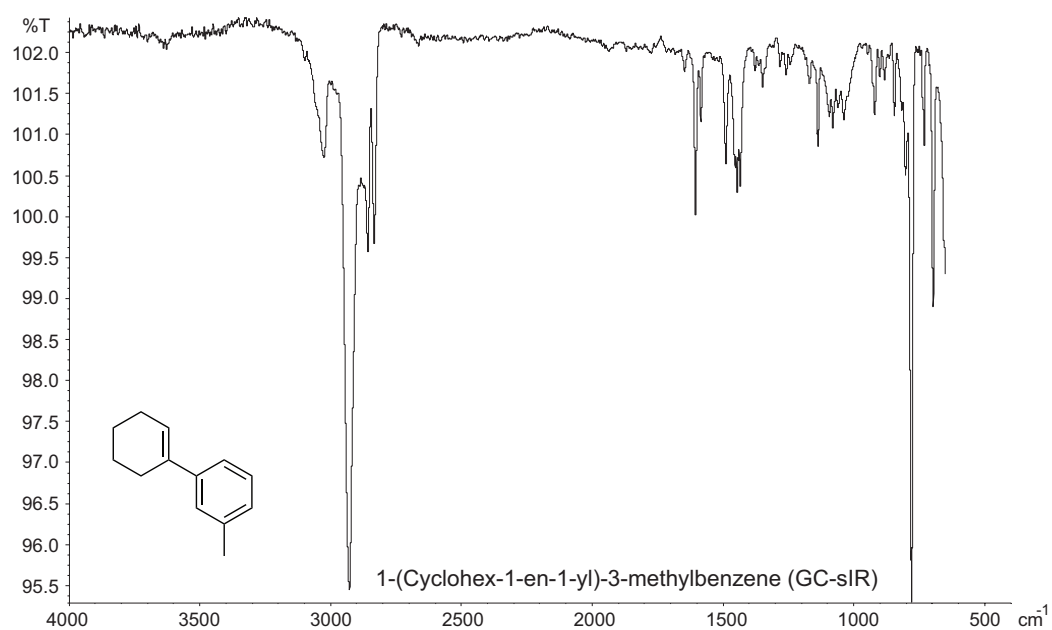


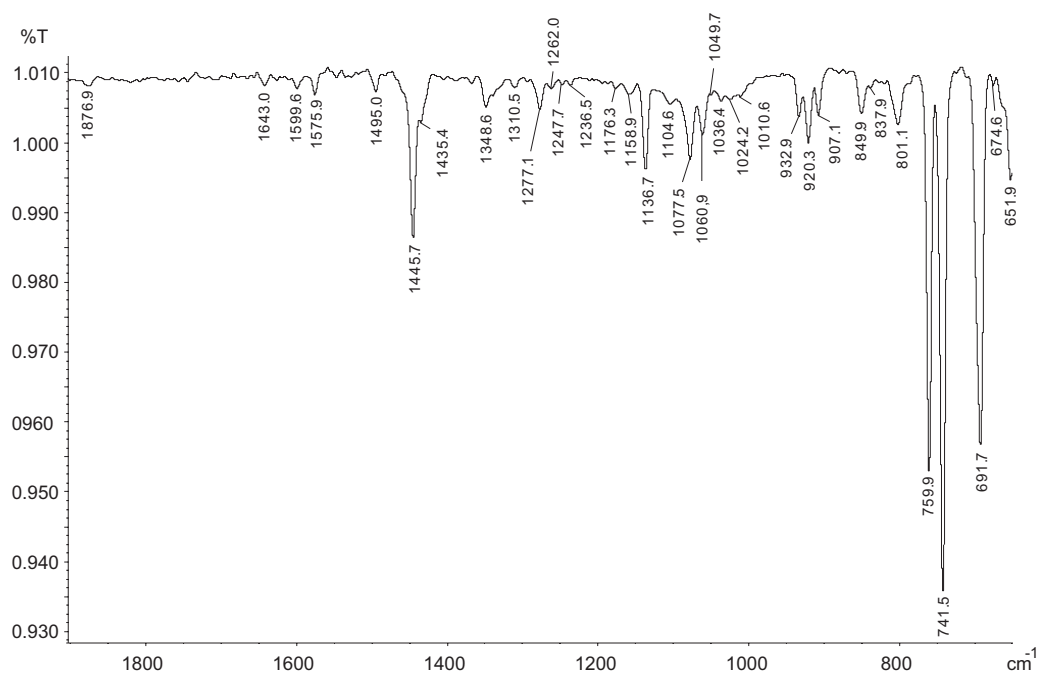
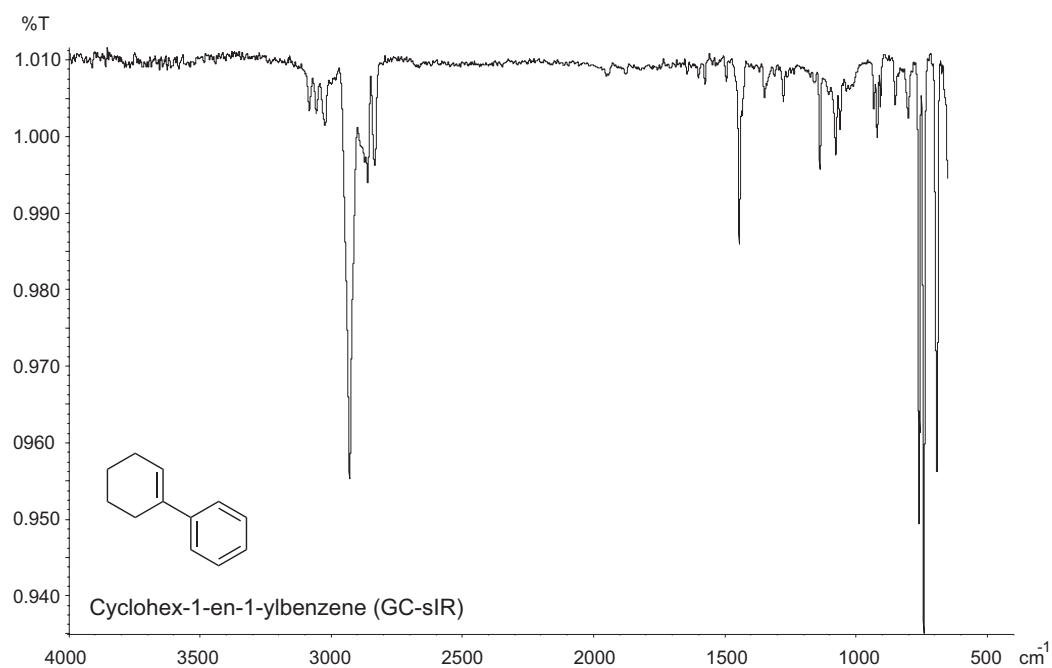












NMR data for PCMo analogues (HCl salts, CDCl<sub>3</sub>, 400/100 MHz)

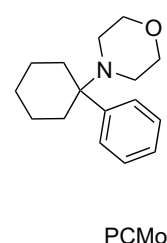
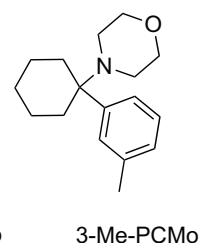
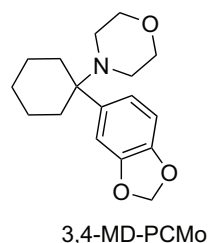
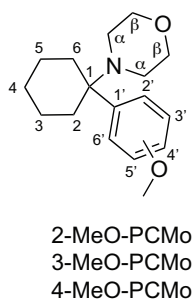
Carbon	2-MeO- PCMo	3-MeO- PCMo	4-MeO- PCMo	3,4-MD-PCMo	3-Me-PCMo	PCMo
C <sub>1</sub>	73.01	71.33	71.42	71.54	71.42	71.42
C <sub>2,6</sub>	31.74 32.59	30.29	30.34	30.61	30.26	30.19
C <sub>3,5</sub>	22.82	22.60	22.54	22.56	22.59	22.53
C <sub>4</sub>	24.70	24.51	24.63	24.52	24.57	24.58
C <sub>1'</sub>	117.38	131.48	121.39	123.30	129.62	129.74
C <sub>2'</sub>	160.28	116.83	130.86	109.37	129.82	129.46
C <sub>3'</sub>	113.47	160.29	114.60	148.72	139.18	129.37
C <sub>4'</sub>	131.81	113.68	160.44	148.89	126.57	129.91
C <sub>5'</sub>	121.37	130.33	114.60	108.70	129.18	129.37
C <sub>6'</sub>	132.76	121.46	130.86	123.73	130.62	129.46
C <sub>α</sub>	45.39 46.99	45.63	45.35	45.46	45.49	45.53
C <sub>β</sub>	63.89	63.61	65.59	63.60	63.32	63.59
C <sub>c</sub>	55.54 (OCH <sub>3</sub> )	55.51 (OCH <sub>3</sub> )	55.38 (OCH <sub>3</sub> )	101.88 (OCH <sub>2</sub> O)	21.67 (CH <sub>3</sub> )	-

Proton	2-MeO- PCMo	3-MeO- PCMo	4-MeO- PCMo	3,4-MD-PCMo	3-Me-PCMo	PCMo
H <sub>1</sub>	-	-	-	-	-	-
H <sub>2,6</sub>	2.35 t ( <i>J</i> = 12.3 Hz, 1H)  2.73–2.50 (1H) <sup>a</sup>  2.84 d ( <i>J</i> = 12.1 Hz)  3.62 s (1H)	2.59 td ( <i>J</i> = 13.0, 3.3 Hz, 2H <sub>ax</sub> ) <sup>c</sup>  2.77 d ( <i>J</i> = 12.4 Hz, 2H <sub>eq</sub> )	2.58–2.47 m (2H <sub>ax</sub> ) <sup>e</sup>  2.82–2.73 m (2H <sub>eq</sub> )	2.65–2.49 m (2H <sub>ax</sub> ) <sup>i</sup>  2.70 d ( <i>J</i> = 12.2 Hz, 2H <sub>eq</sub> )	2.56–2.41 m (2H <sub>ax</sub> ) <sup>k</sup>  2.73 d ( <i>J</i> = 12.5 Hz, 2H <sub>eq</sub> )	2.59 td ( <i>J</i> = 12.9, 3.3 Hz, 2H <sub>ax</sub> ) <sup>m</sup>  2.88–2.78 m (2H <sub>eq</sub> )
H <sub>3,5</sub>	1.12–0.96 m (1H)  1.31–1.12 m (1H)  1.81 d ( <i>J</i> = 13.1 Hz, 2H)	1.18 qt ( <i>J</i> = 13.4, 3.6 Hz, 2H <sub>ax</sub> )  1.82 dm ( <i>J</i> = 13.3 Hz, 2H <sub>eq</sub> )	1.17 qt ( <i>J</i> = 13.4, 3.4 Hz, 2H <sub>ax</sub> )  1.83–1.76 m (2H <sub>eq</sub> )	1.18 qt ( <i>J</i> = 13.4, 3.4 Hz, 2H <sub>ax</sub> )  1.82 d ( <i>J</i> = 13.1 Hz, 2H <sub>eq</sub> )	1.11 qt (13.4, 3.4 Hz, 2H <sub>ax</sub> )  1.75 d ( <i>J</i> = 13.4 Hz, 2H <sub>eq</sub> )	1.16 qt ( <i>J</i> = 13.5, 3.6 Hz, 2H <sub>ax</sub> )  1.84 dm ( <i>J</i> = 13.1 Hz, 2H <sub>eq</sub> )
H <sub>4</sub>	1.43 qt ( <i>J</i> = 13.1, 4.2 Hz, 1H <sub>ax</sub> )  1.59–1.49 m (1H <sub>eq</sub> )	1.43 qt ( <i>J</i> = 13.1, 3.9 Hz, 1H <sub>ax</sub> )  1.48 dm ( <i>J</i> = 13.1 Hz, H <sub>eq</sub> )	1.43 qt ( <i>J</i> = 13.1, 4.1 Hz, 1H <sub>ax</sub> )  1.57 d ( <i>J</i> = 13.2 Hz, 1H <sub>eq</sub> )	1.38 qt ( <i>J</i> = 13.1, 4.0 Hz, 1H <sub>ax</sub> )  1.58 d ( <i>J</i> = 13.1 Hz, 1H <sub>eq</sub> )	1.37 qt ( <i>J</i> = 13.1, 4.2 Hz, 1H <sub>ax</sub> )  1.49 d ( <i>J</i> = 13.0 Hz, 1H <sub>eq</sub> )	1.45 qt ( <i>J</i> = 13.1, 4.1 Hz, 1H <sub>ax</sub> )  1.65–1.53 m (1H <sub>eq</sub> )

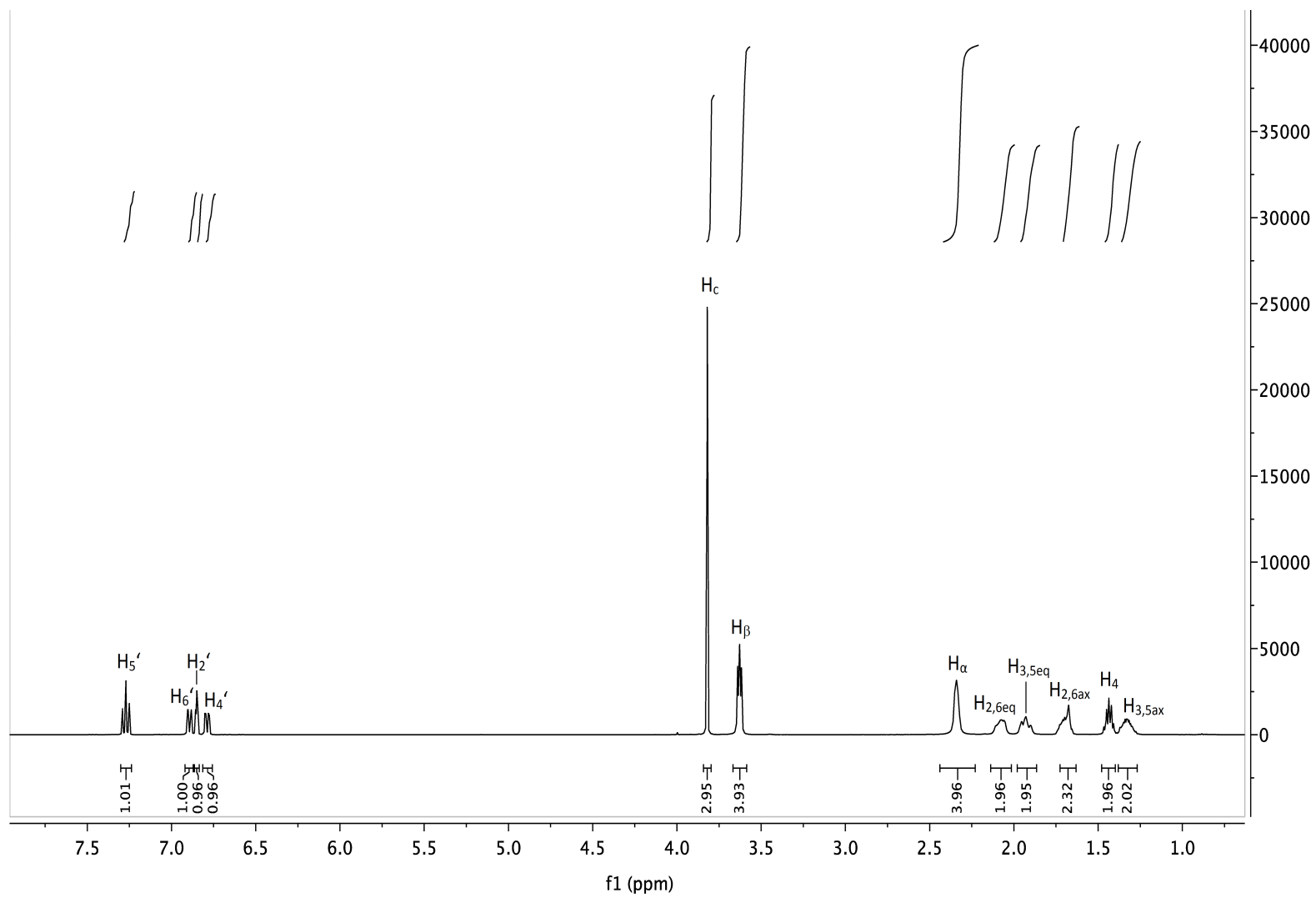
Supporting Information - Colestock *et al.* - Drug Testing and Analysis

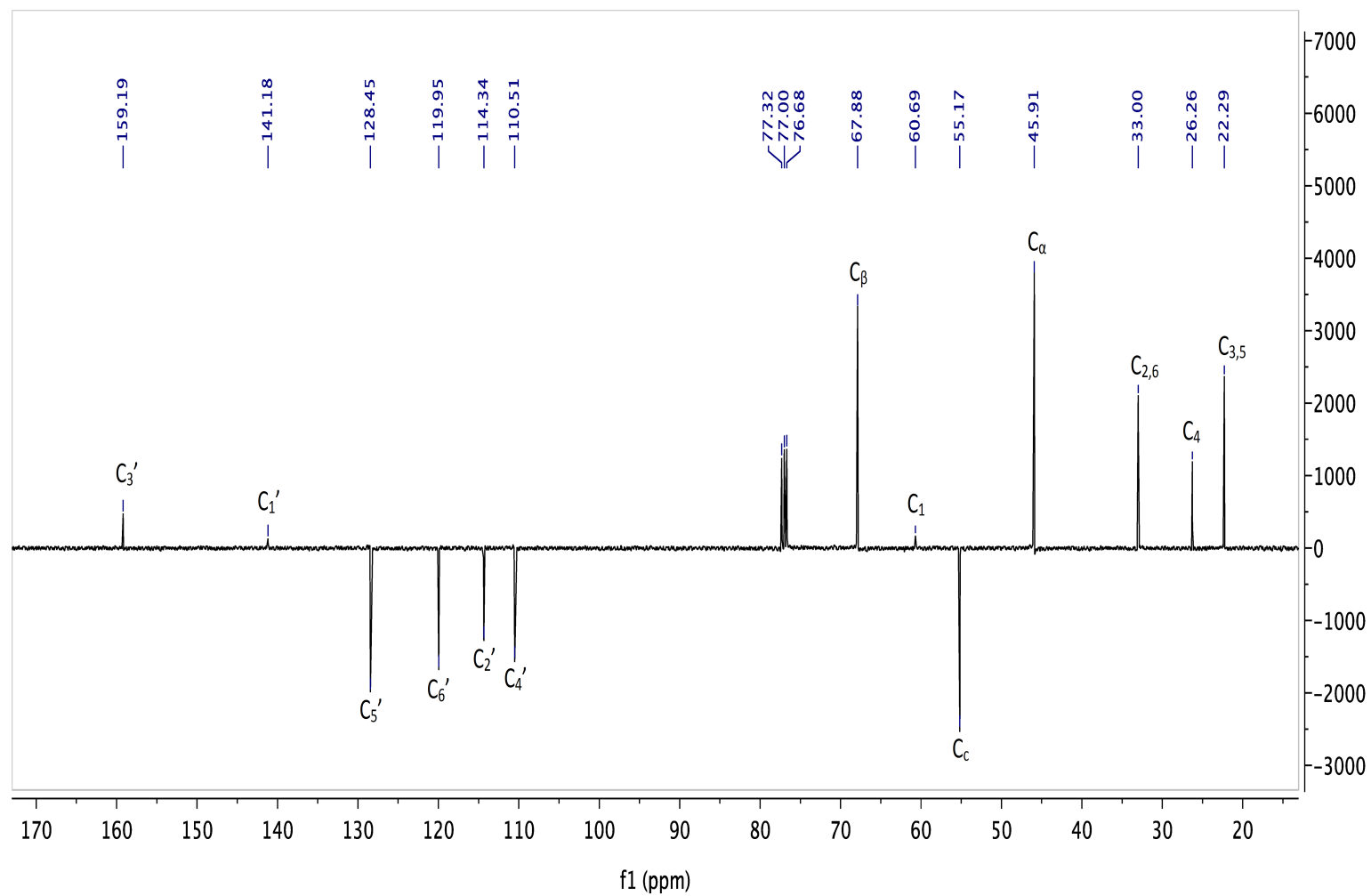
H <sub>1'</sub>	-	-	-	-	-	-
H <sub>2'</sub>	-	7.01 dd ( <i>J</i> = 8.1, 2.3 Hz, 1H)	7.42 dm ( <i>J</i> = 8.94 Hz, 1H)	6.95 d ( <i>J</i> = 1.9 Hz, 1H)	7.20 s (1H)	7.61–7.45 m (1H)
H <sub>3'</sub>	7.06 dd ( <i>J</i> = 8.4, 1.1 Hz, 1H)	-	7.02 dm ( <i>J</i> = 8.95 Hz, 1H)	-	-	7.61–7.45 m (1H)
H <sub>4'</sub>	7.47 ddd ( <i>J</i> = 8.5, 7.2, 1.6 Hz, 1H)	7.01 dd ( <i>J</i> = 8.1, 2.3 Hz, 1H)	-	-	7.34–7.19 m (1H)	7.61–7.45 m (1H)
H <sub>5'</sub>	7.10 ddd ( <i>J</i> = 8.1, 7.2, 1.2 Hz, 1H)	7.45 t ( <i>J</i> = 8.0 Hz, 1H)	7.02 dm ( <i>J</i> = 8.95 Hz, 1H)	6.93 d ( <i>J</i> = 8.2 Hz, 1H)	7.34 t ( <i>J</i> = 7.6 Hz, 1H)	7.61–7.45 m (1H)
H <sub>6'</sub>	7.40 dd ( <i>J</i> = 8.1, 1.7 Hz, 1H)	7.06 dd ( <i>J</i> = 8.1, 1.7 Hz, 1H)	7.42 dm ( <i>J</i> = 8.94 Hz, 1H)	6.98 dd ( <i>J</i> = 8.2, 2.0 Hz, 1H)	7.34–7.19 m (1H)	7.61–7.45 m (1H)
H <sub>α</sub>	2.73–2.45 m (2H) <sup>b</sup>  3.45 d ( <i>J</i> = 12.1 Hz, 1H)  3.76 d ( <i>J</i> = 12.2 Hz, 1H)	2.65–2.53 m (2H <sub>ax</sub> ) <sup>d</sup>  3.46 d ( <i>J</i> = 12.1 Hz, 2H <sub>eq</sub> )	2.58–2.47 m (2H <sub>ax</sub> ) <sup>f</sup>  3.46 dm ( <i>J</i> = 11.8 Hz, 2H <sub>eq</sub> )	2.65–2.49 m (2H <sub>ax</sub> ) <sup>j</sup>  3.45 d ( <i>J</i> = 11.7 Hz, 2H <sub>eq</sub> )	2.56–2.41 m (2H <sub>ax</sub> ) <sup>l</sup>  3.41 d ( <i>J</i> = 11.8 Hz, 2H <sub>eq</sub> )	2.88–2.78 m (2H <sub>ax</sub> ) <sup>n</sup>  3.50 d ( <i>J</i> = 12.0 Hz, 2H <sub>eq</sub> )
H <sub>β</sub>	3.82 dd ( <i>J</i> = 13.2, 3.3 Hz, 2H <sub>eq</sub> )  4.53 td ( <i>J</i> = 12.5, 2.1 Hz, 2H <sub>ax</sub> )	3.87 dd ( <i>J</i> = 13.1, 3.4 Hz, 2H <sub>eq</sub> )  4.50 t ( <i>J</i> = 12.5 Hz, 2H <sub>ax</sub> )	3.83 dd ( <i>J</i> = 13.1, 3.4 Hz, 2H <sub>eq</sub> ) <sup>g</sup>  4.49 td ( <i>J</i> = 12.5, 2.1 Hz, 2H <sub>ax</sub> )	3.86 dd ( <i>J</i> = 12.6, 3.5 Hz, 2H <sub>eq</sub> )  4.50 t ( <i>J</i> = 12.4 Hz, 2H <sub>ax</sub> )	3.77 dd ( <i>J</i> = 12.8, 3.6 Hz, 2H <sub>eq</sub> )  4.43 t ( <i>J</i> = 12.0 Hz, 2H <sub>ax</sub> )	3.84 dd ( <i>J</i> = 13.0, 3.6 Hz, 2H <sub>eq</sub> )  4.50 td ( <i>J</i> = 12.5, 2.0 Hz, 2H <sub>ax</sub> )
Cc	3.87 s (OCH <sub>3</sub> )	3.88 s (OCH <sub>3</sub> )	3.87 s (OCH <sub>3</sub> ) <sup>h</sup>	6.07 s (OCH <sub>2</sub> O)	2.37 s (CH <sub>3</sub> )	-
NH <sup>+</sup>	12.11 s (1H)	12.32 s (1H)	12.21 s (1H)	12.29 s (1H)	12.22 s (1H)	12.37 s (1H)

- a. Overlap with H<sub>α</sub>  
b. Overlap with H<sub>2,6</sub>  
c. Overlap with H<sub>α<sub>ax</sub></sub>  
d. Overlap with H<sub>2,6ax</sub>  
e. Overlap with H<sub>α<sub>ax</sub></sub>  
f. Overlap with H<sub>2,6ax</sub>  
g. Overlap with Cc  
h. Overlap with H<sub>β<sub>eq</sub></sub>  
i. Overlap with H<sub>α<sub>ax</sub></sub>  
j. Overlap with H<sub>2,6ax</sub>  
k. Overlap with H<sub>α<sub>ax</sub></sub>  
l. Overlap with H<sub>2,6ax</sub>  
m. Overlap with H<sub>α<sub>ax</sub></sub>  
n. Overlap with H<sub>2,6ax</sub>

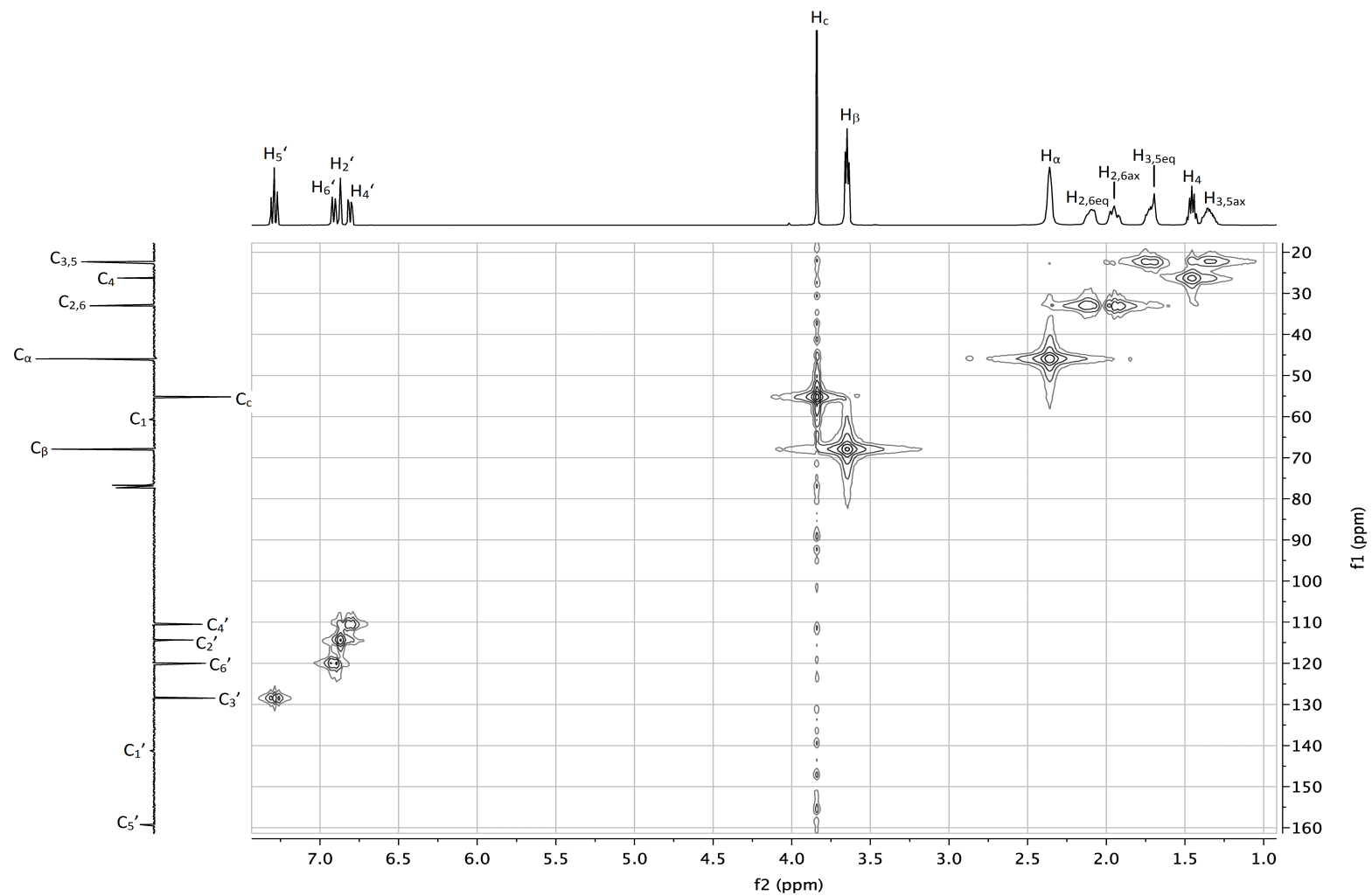


$^1\text{H}$  NMR of 3-MeO-PCMo freebase (400 MHz,  $\text{CDCl}_3$ )



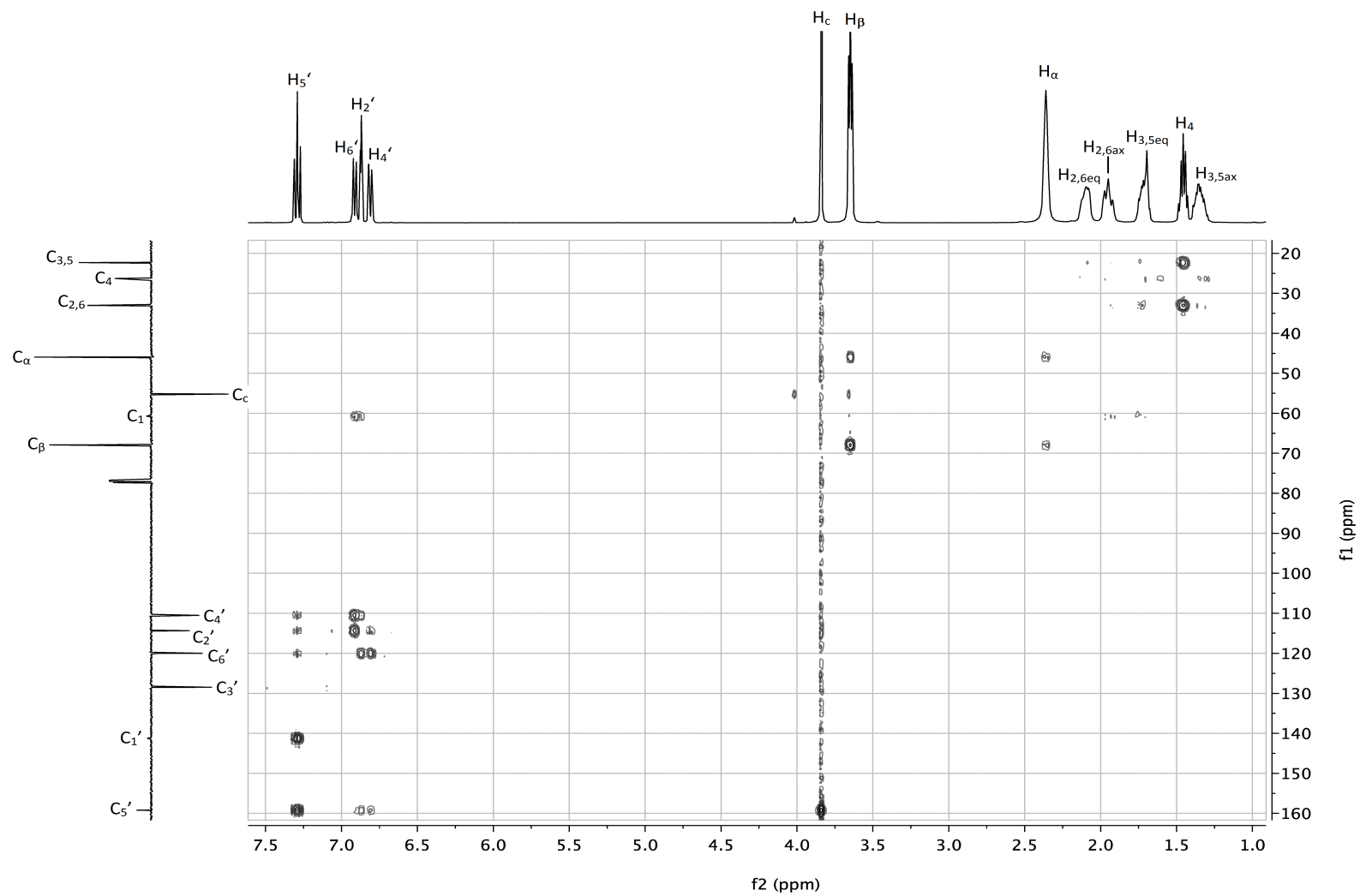
<sup>13</sup>C PENDANT NMR of 3-MeO-PCMo freebase (100 MHz, CDCl<sub>3</sub>)

HMQC 2-D NMR of 3-MeO-PCMo freebase ( $\text{CDCl}_3$ )





HMBC 2-D NMR of 3-MeO-PCMo freebase (CDCl<sub>3</sub>)



COSY-45 2-D NMR of 3-MeO-PCMo freebase (CDCl<sub>3</sub>)

