Supporting Information

for

Analysis of six “neuro-enhancing” phenidate analogs

Dr. Helge Klare[1], Dr. Simon D. Brandt[2], Dr. Jörg M. Neudörfl[3], Dr. Elisabeth Mischler[1], Sigrid Meier-Giebing[1], Dr. Kathrin Deluweit[1], Dr. Folker Westphal[4], Dr. Tim Laussmann[1]*

Table of contents

Experimental

NMR

4-Methylmethylphenidate 2 HCl

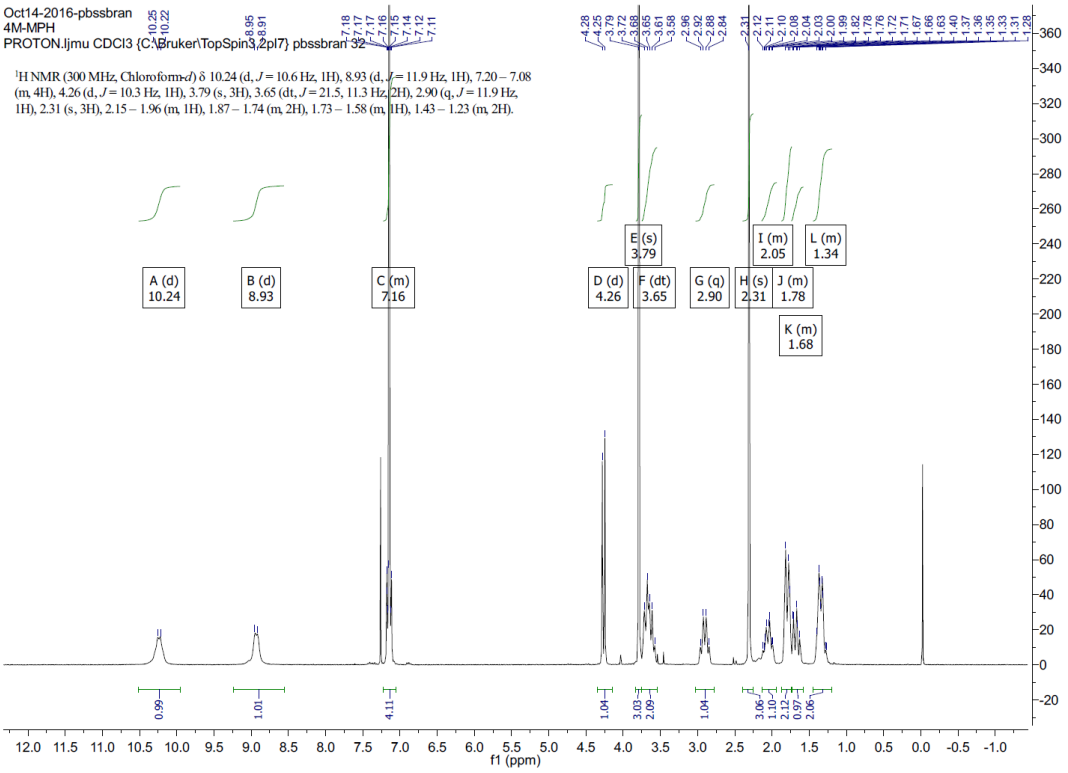


Figure S 1: ^{1}H NMR of 4-methylmethylphenidate **2** HCl (300 MHz, 298 K, $CDCl_3$).

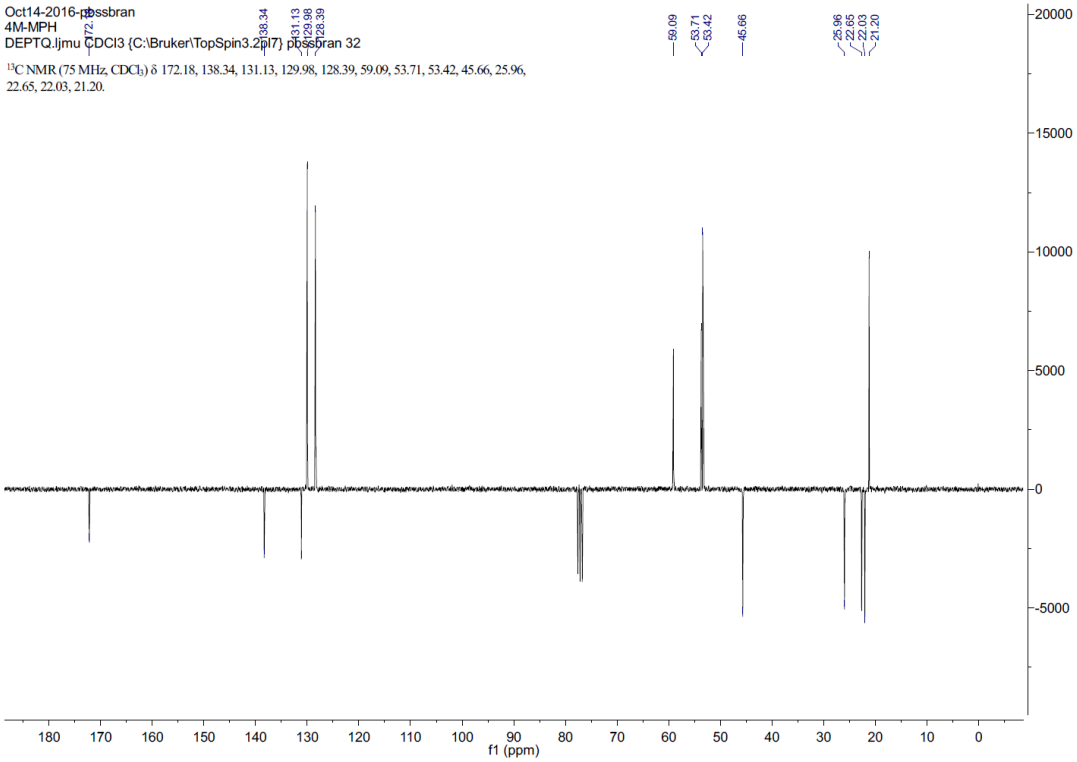


Figure S 2: ^{13}C NMR of 4-methylmethylphenidate **2** HCl (75 MHz, 298 K, $CDCl_3$).

3,4-dichloromethylphenidate 3 HCl

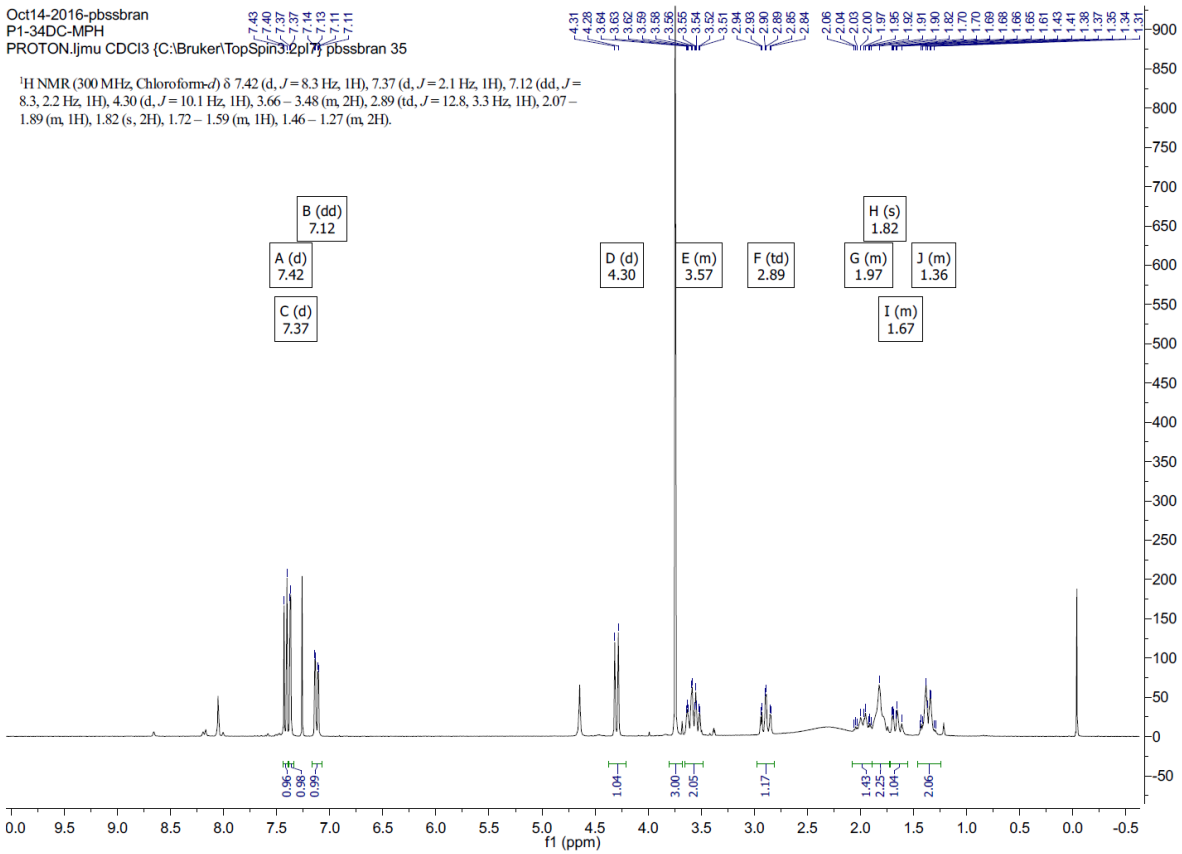


Figure S 3: ^{1}H NMR of 3,4-dichloromethylphenidate **3** HCl (300 MHz, 298 K, $CDCl_3$ + 40 µl MeOD).

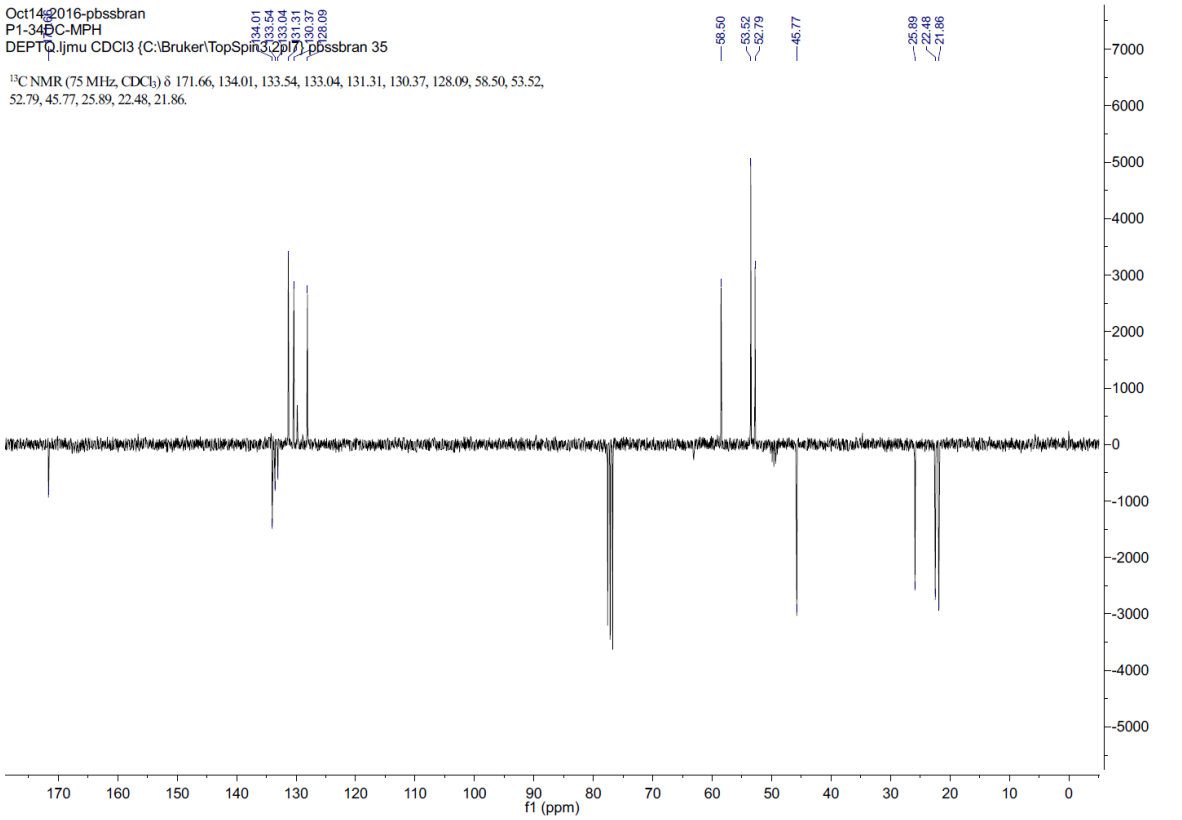
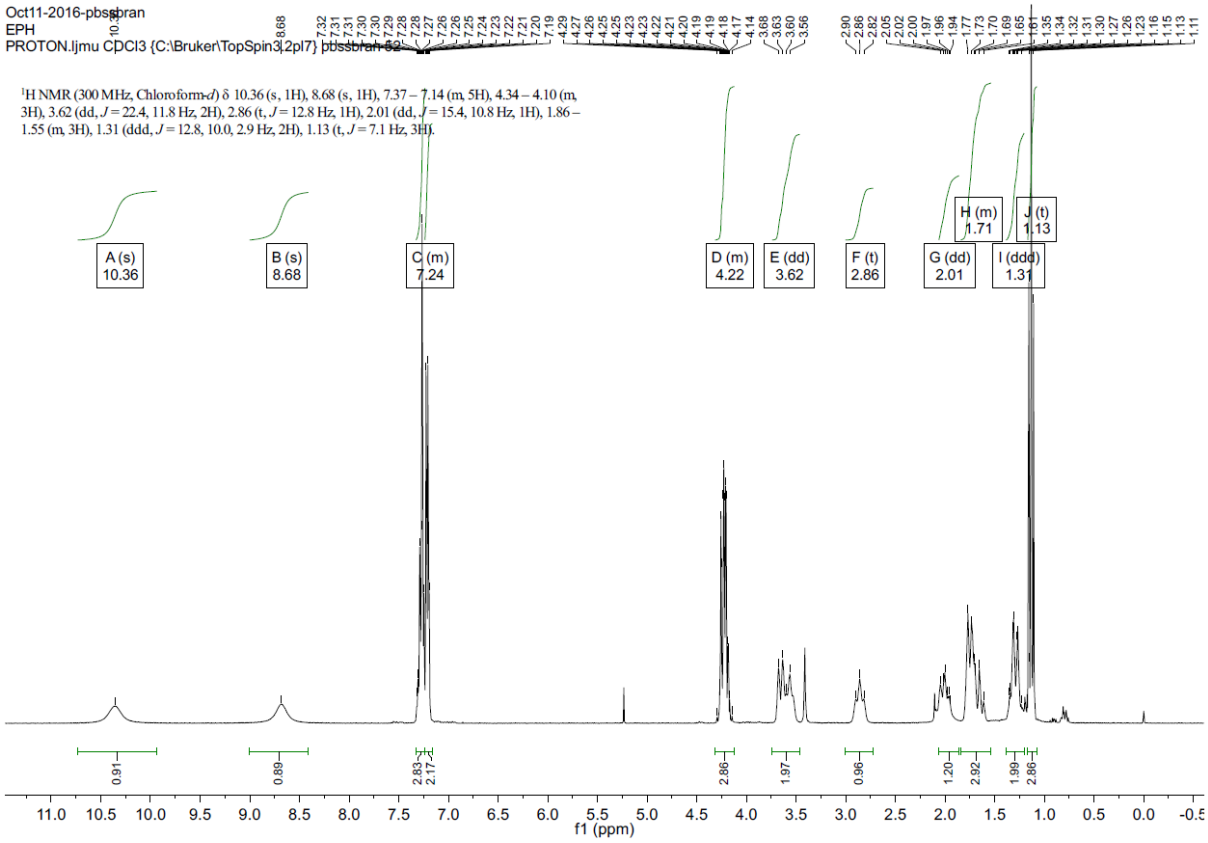


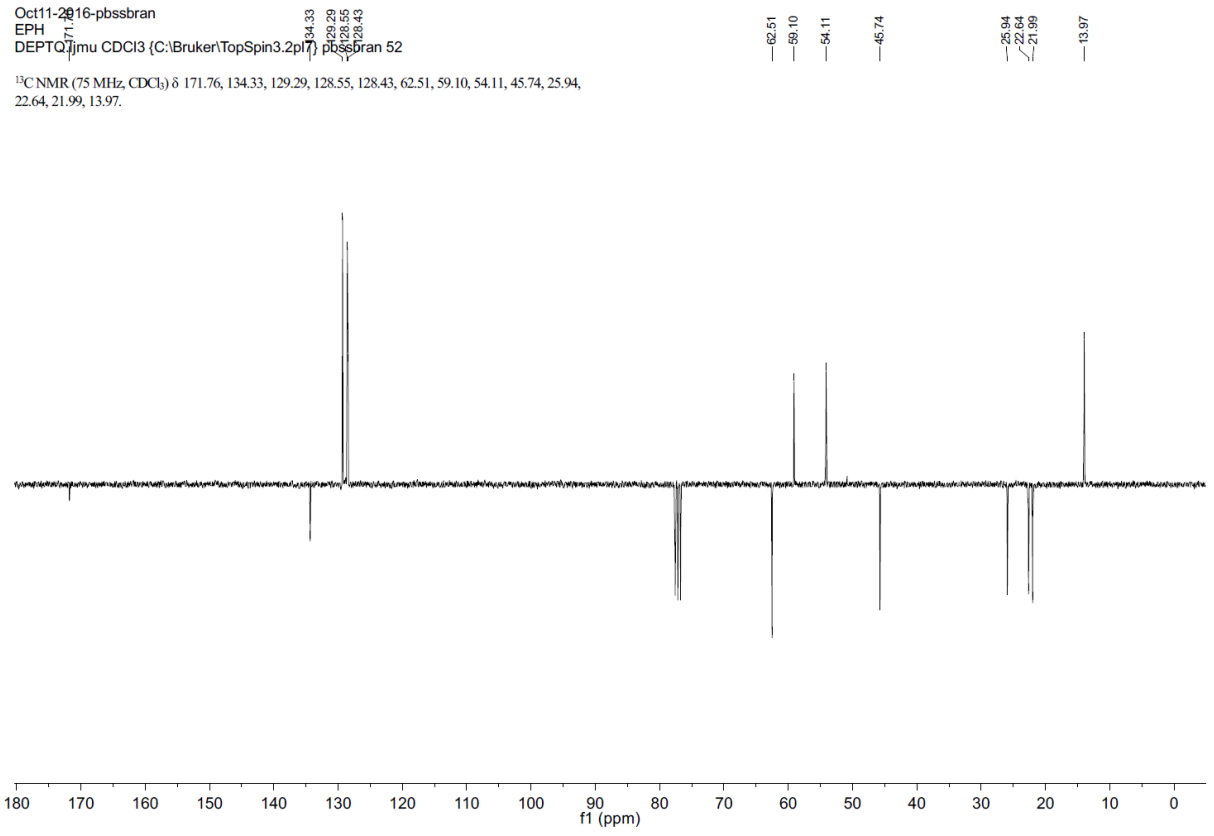
Figure S 4: ^{13}C NMR of 3,4-dichloromethylphenidate **3** HCl (75 MHz, $CDCl_3$ + 40 µl MeOD).

Ethylphenidate 4 HCl



^{1}H NMR (300 MHz, Chloroform-*d*) δ 10.36 (s, 1H), 8.68 (s, 1H), 7.37 – 7.14 (m, 5H), 4.34 – 4.10 (m, 3H), 3.62 (dd, *J* = 22.4, 11.8 Hz, 2H), 2.86 (t, *J* = 12.8 Hz, 1H), 2.01 (dd, *J* = 15.4, 10.8 Hz, 1H), 1.86 – 1.55 (m, 3H), 1.31 (ddd, *J* = 12.8, 10.0, 2.9 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H).

Figure S 5: ^{1}H NMR of ethylphenidate **4** HCl (300 MHz, 298 K, $CDCl_3$).



^{13}C NMR (75 MHz, $CDCl_3$) δ 171.76, 134.33, 129.29, 128.55, 128.43, 62.51, 59.10, 54.11, 45.74, 25.94, 22.64, 21.99, 13.97.

Figure S 6: ^{13}C NMR of ethylphenidate **4** HCl (75 MHz, 298 K, $CDCl_3$).

3,4-dichloroethylphenidate 5 HCl

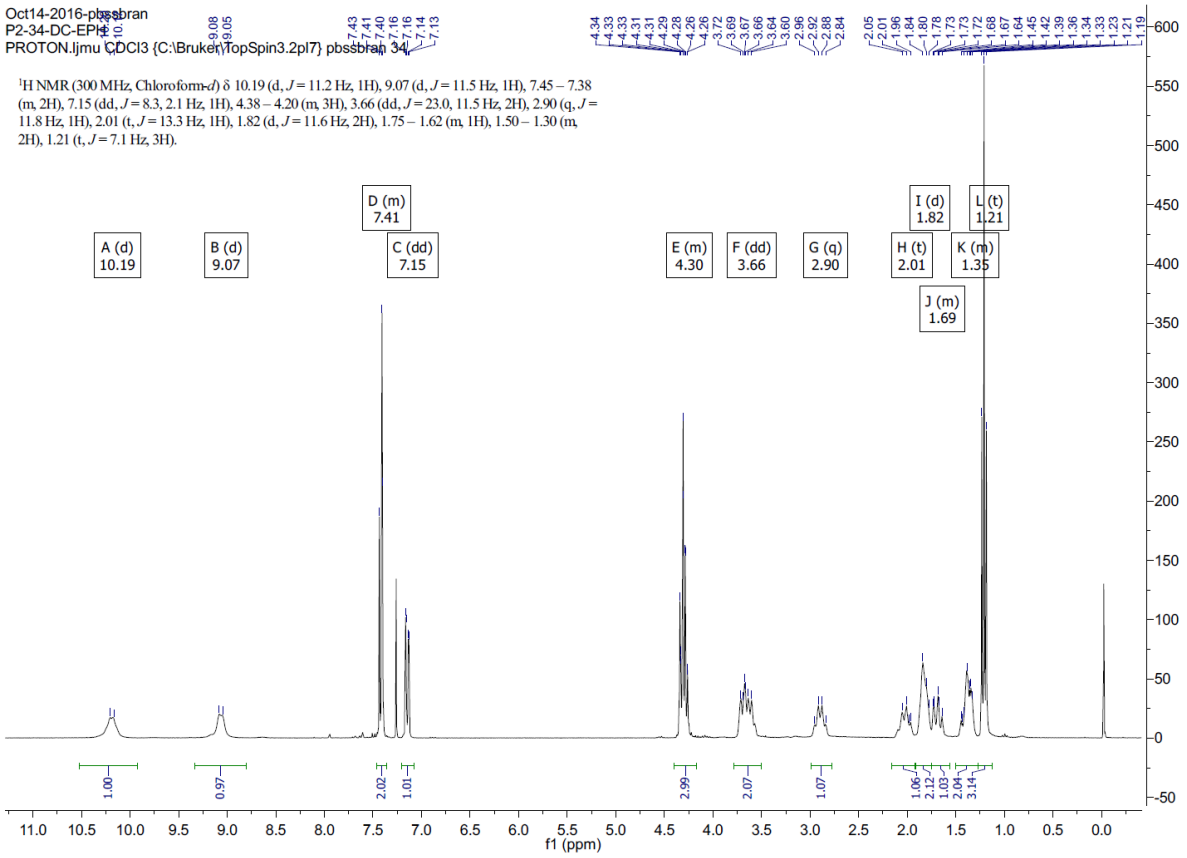


Figure S 7: ^{1}H NMR of 3,4-dichloroethylphenidate **5** HCl (300 MHz, 298 K, $CDCl_3$).

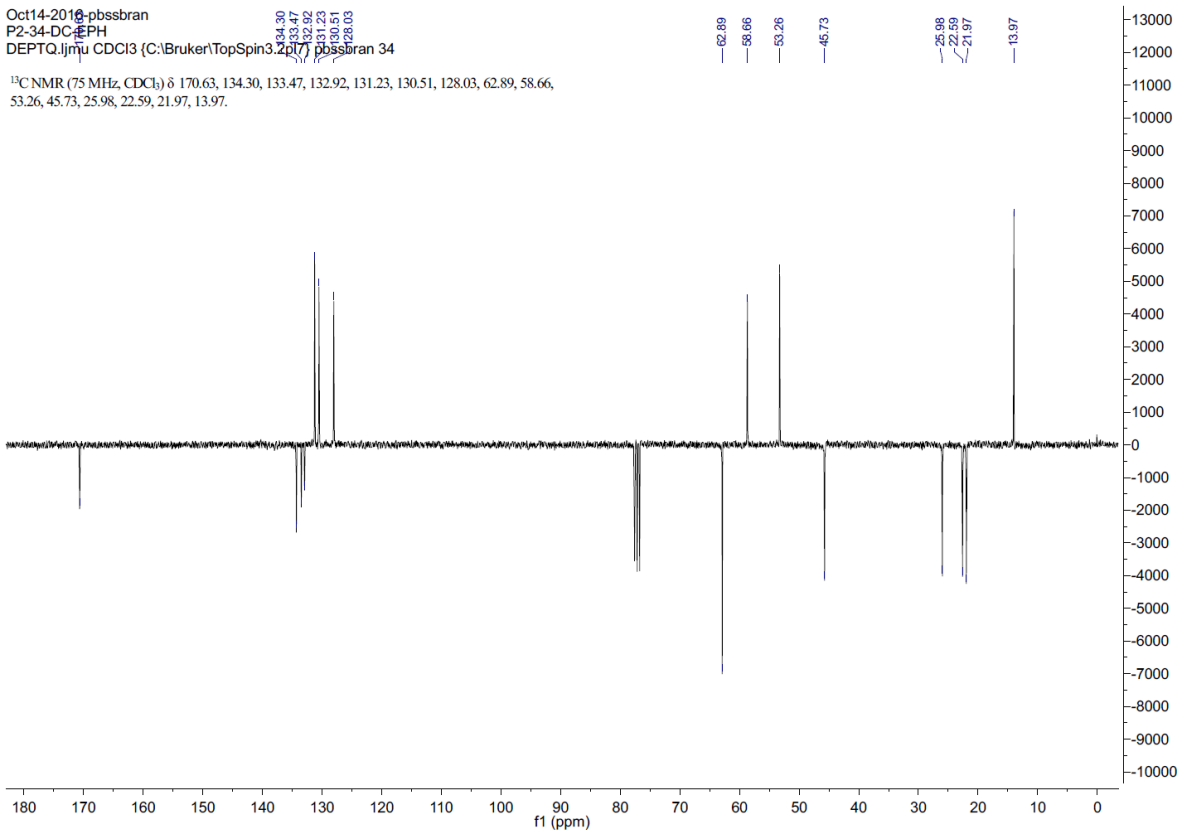


Figure S 8: ^{13}C NMR of 3,4-dichloroethylphenidate **5** HCl (75 MHz, 298 K, $CDCl_3$).

Ethylnaphthidate 6 CH_3SO_3H

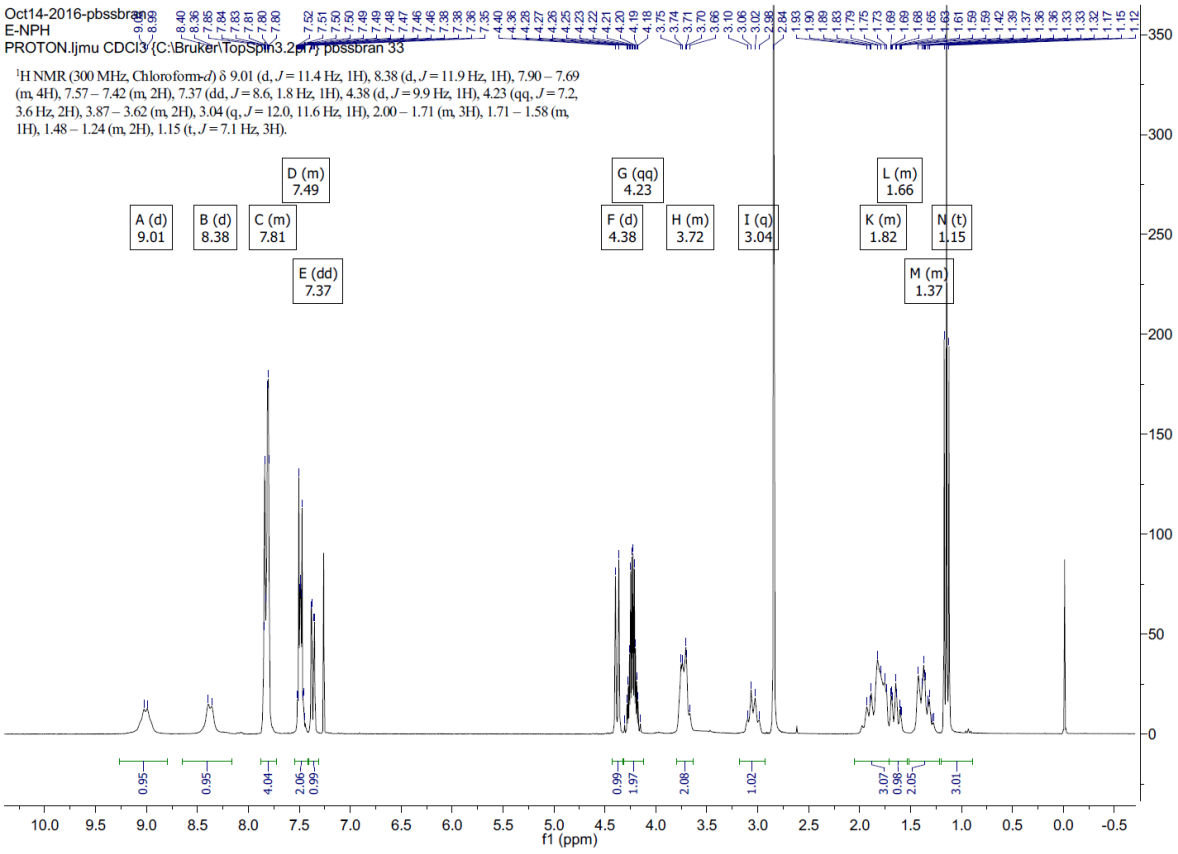


Figure S 9: ^{1}H NMR of ethylnaphthidate **6** CH_3SO_3H (300 MHz, 298 K, $CDCl_3$).

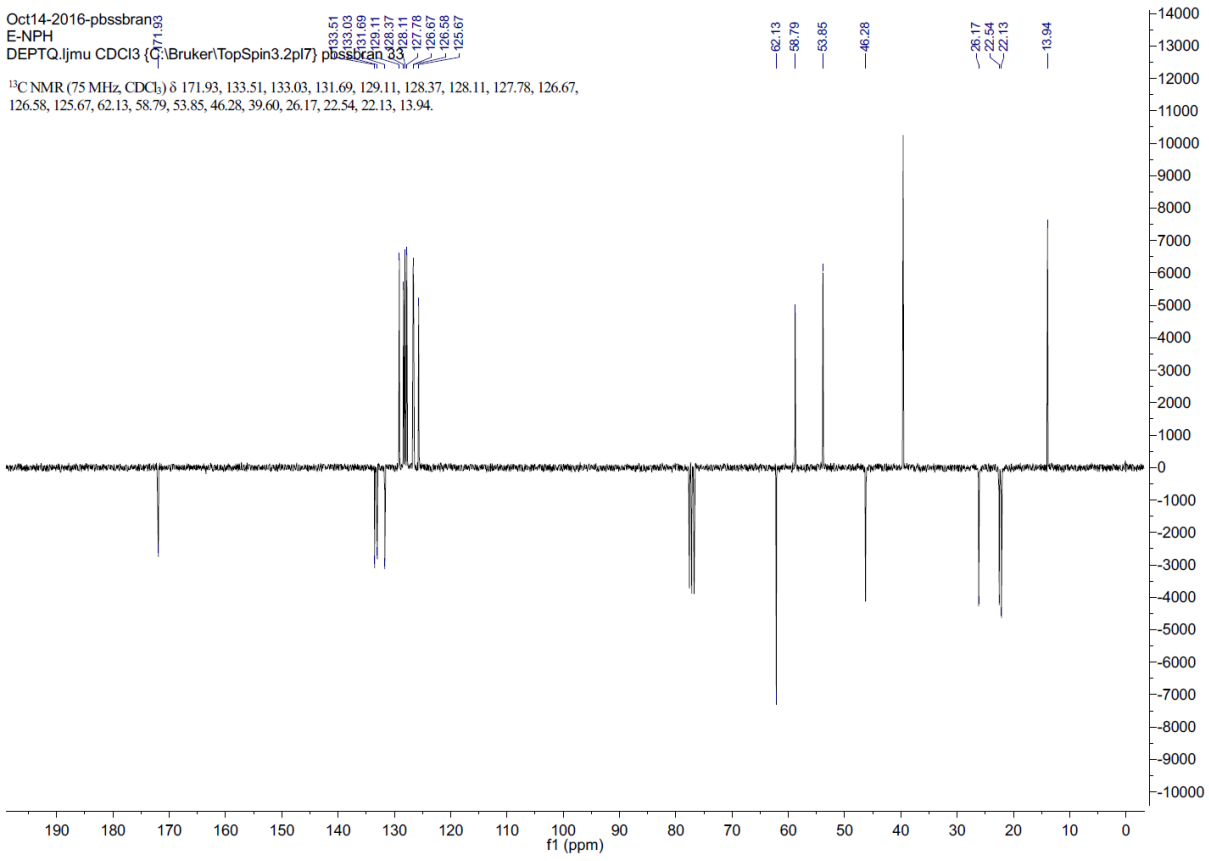


Figure S 10: ^{13}C NMR of ethylnaphthidate **6** CH_3SO_3H (75 MHz, 298 K, $CDCl_3$).

N-Benzyl-ethylphenidate 7 HCl

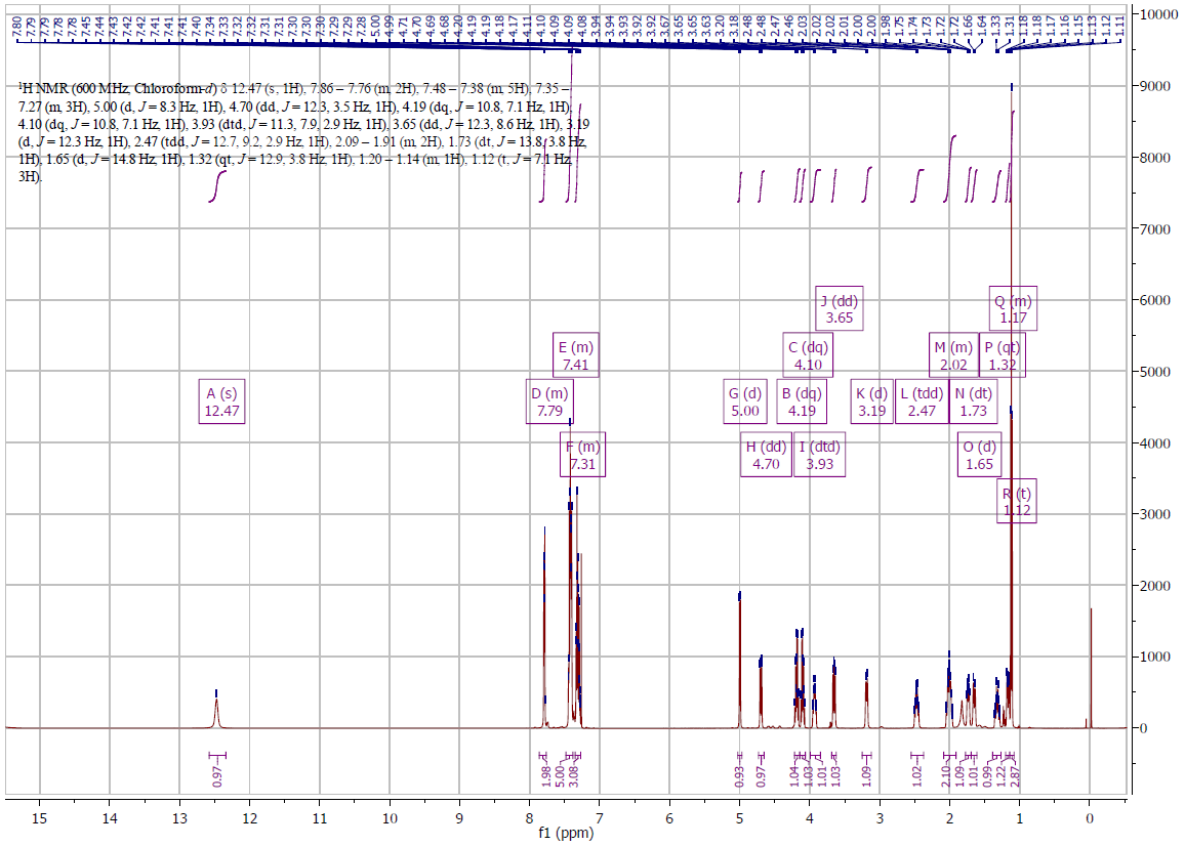


Figure S 11: ^{1}H NMR of *N*-benzyl ethylphenidate **7** HCl (600 MHz, 298 K, $CDCl_3$).

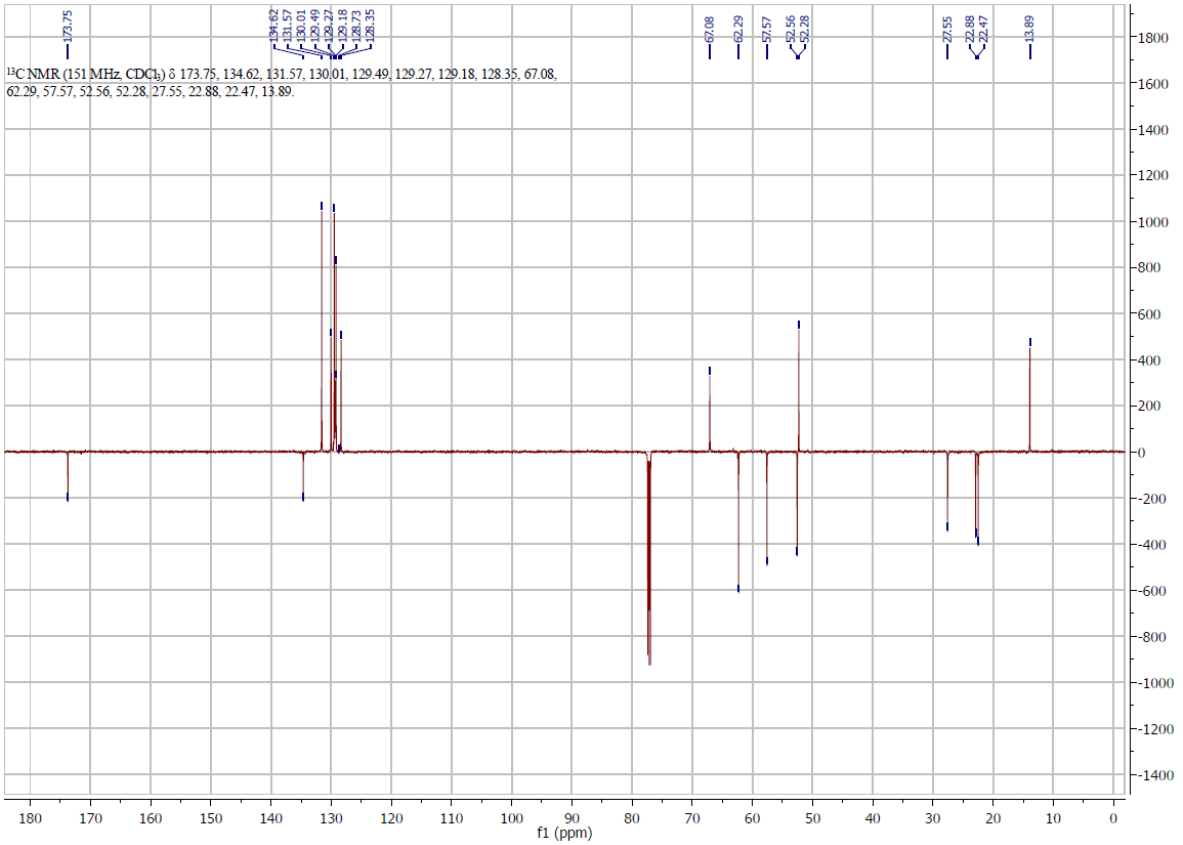


Figure S 12: ^{13}C NMR of *N*-benzyl ethylphenidate **7** HCl (600 MHz, 298 K, $CDCl_3$).

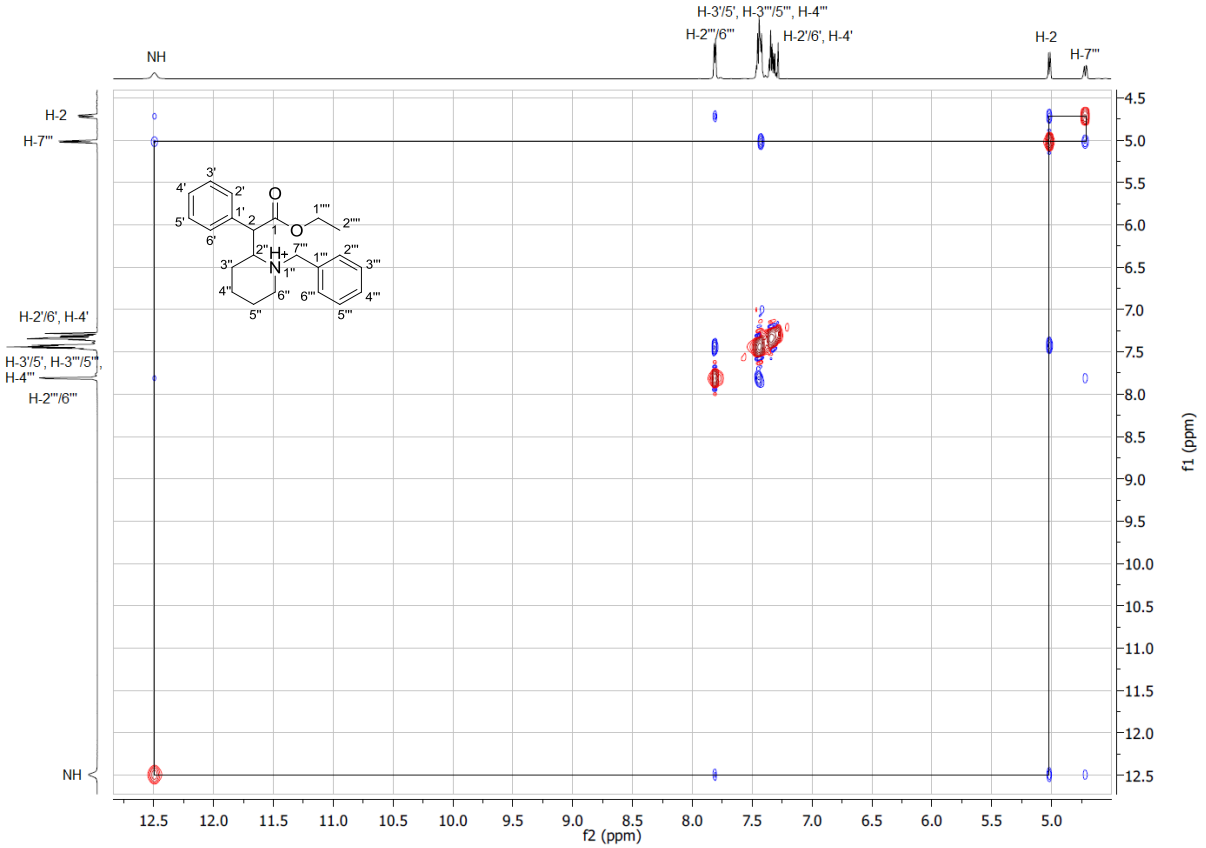


Figure S 13: $^{1}H/^{1}H$-NOESY of *N*-benzyl-ethylphenidate **7** with NOE-contacts between NH / H-2 and H-2 / H-7'''α (highlighted) showing the preferred equatorial substitution of the piperidine moiety in solution (600 MHz, 298 K, $CDCl_3$).

GC-Chromatograms with EI-spectra of the main peaks employing the standard protocol

4-Methylmethylphenidate 2 HCl

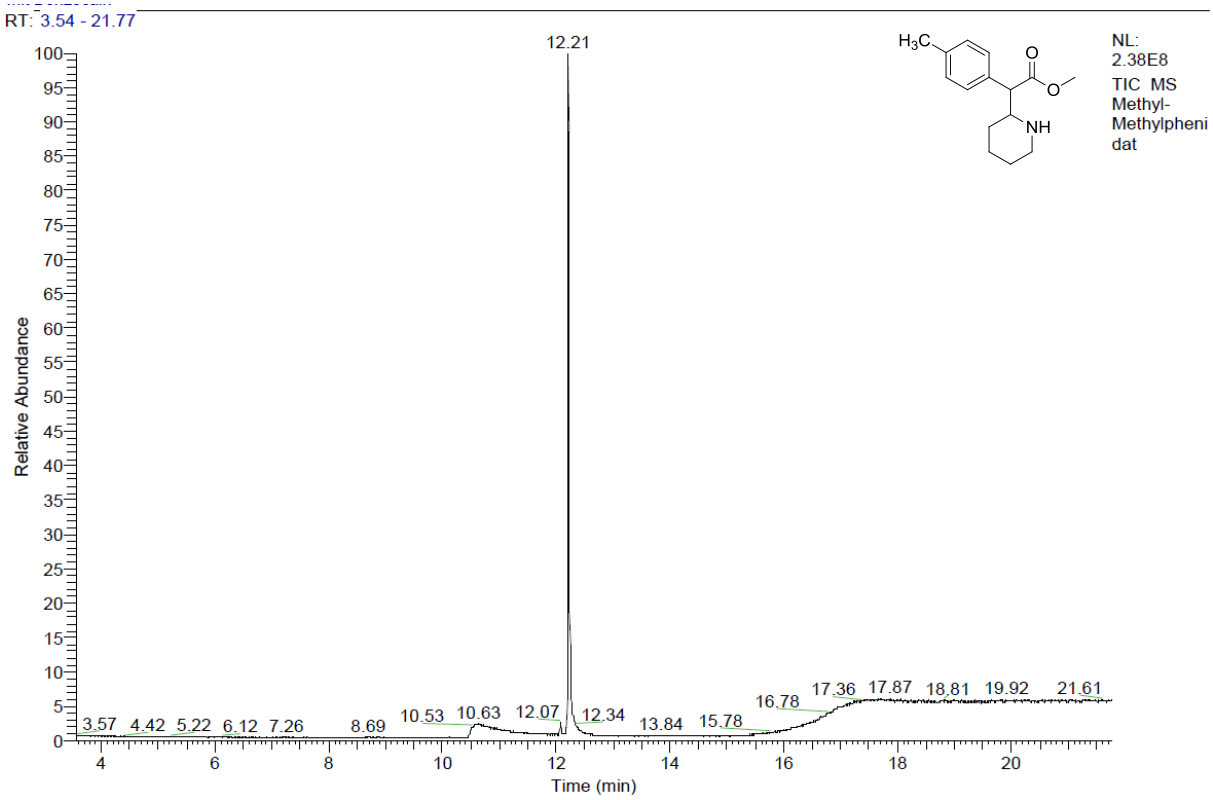


Figure S 14: Chromatogram under standard GC-conditions of 4-Methylmethylphenidate **2** HCl.

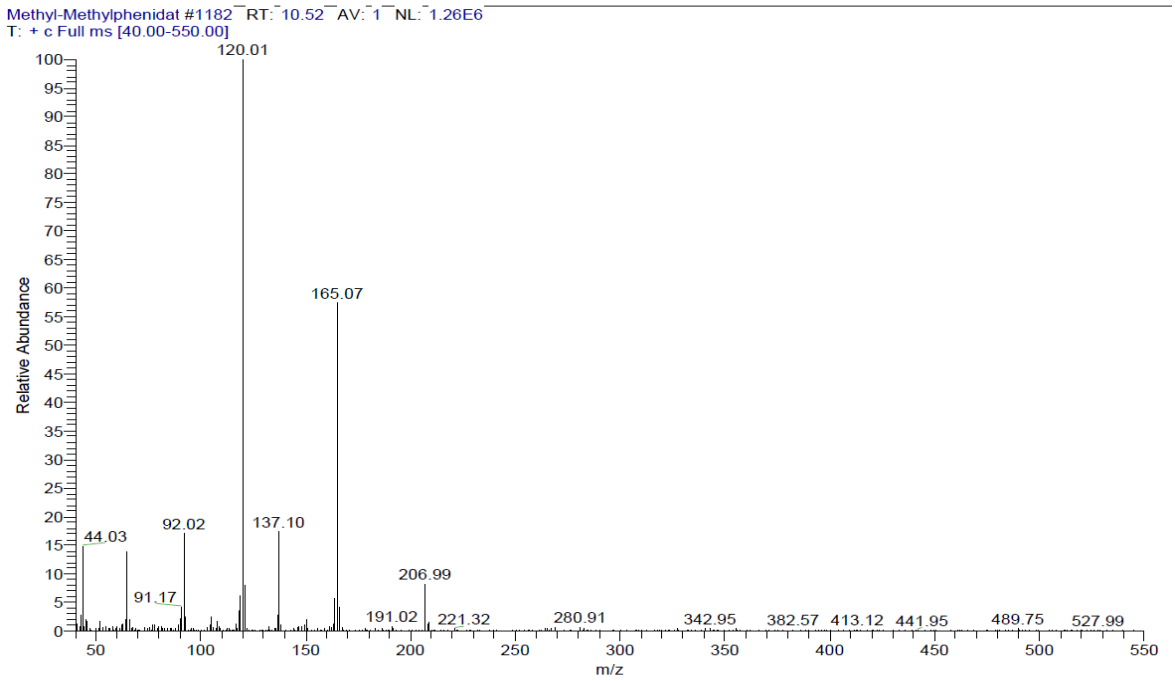


Figure S 15: EI spectrum (70 eV) of 4-Methylmethylphenidate **2** HCl at10.52 min.

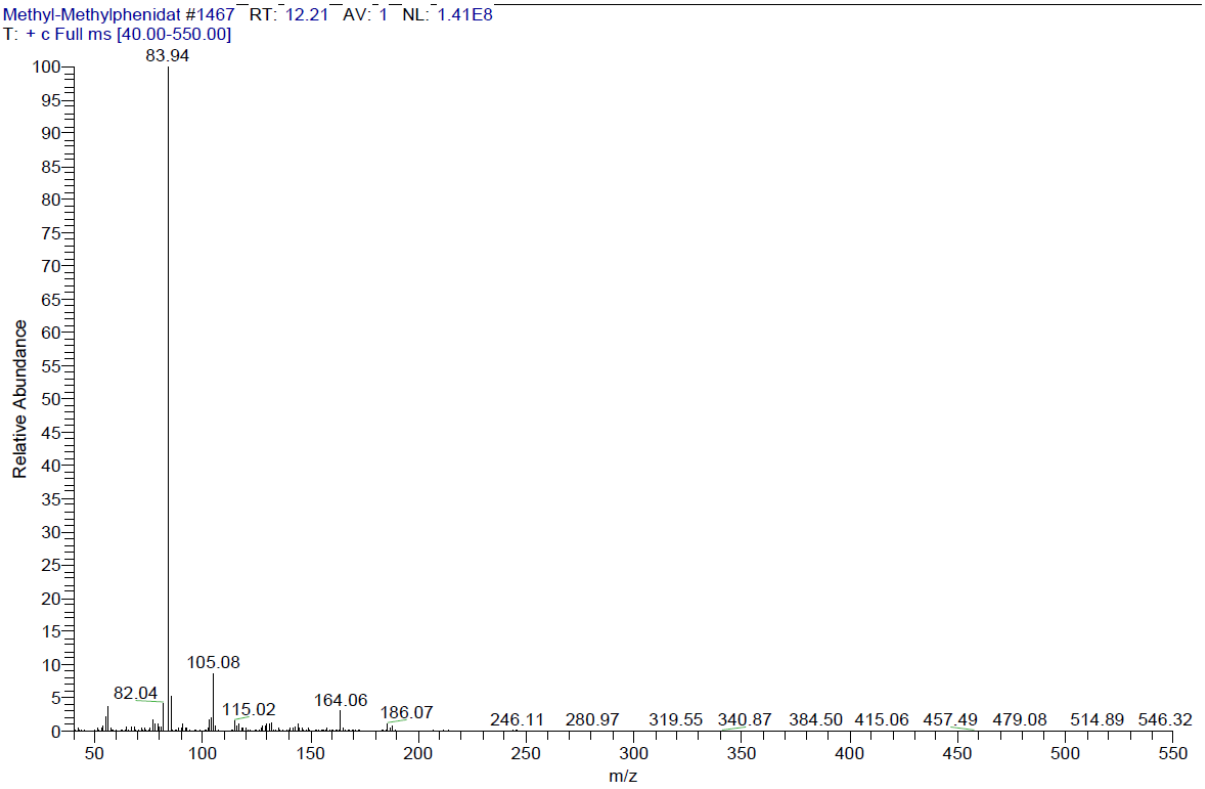


Figure S 16: EI spectrum (70 eV) of 4-Methylmethylphenidate **2** HCl at12.21 min.

3,4-dichloromethylphenidate 3 HCl

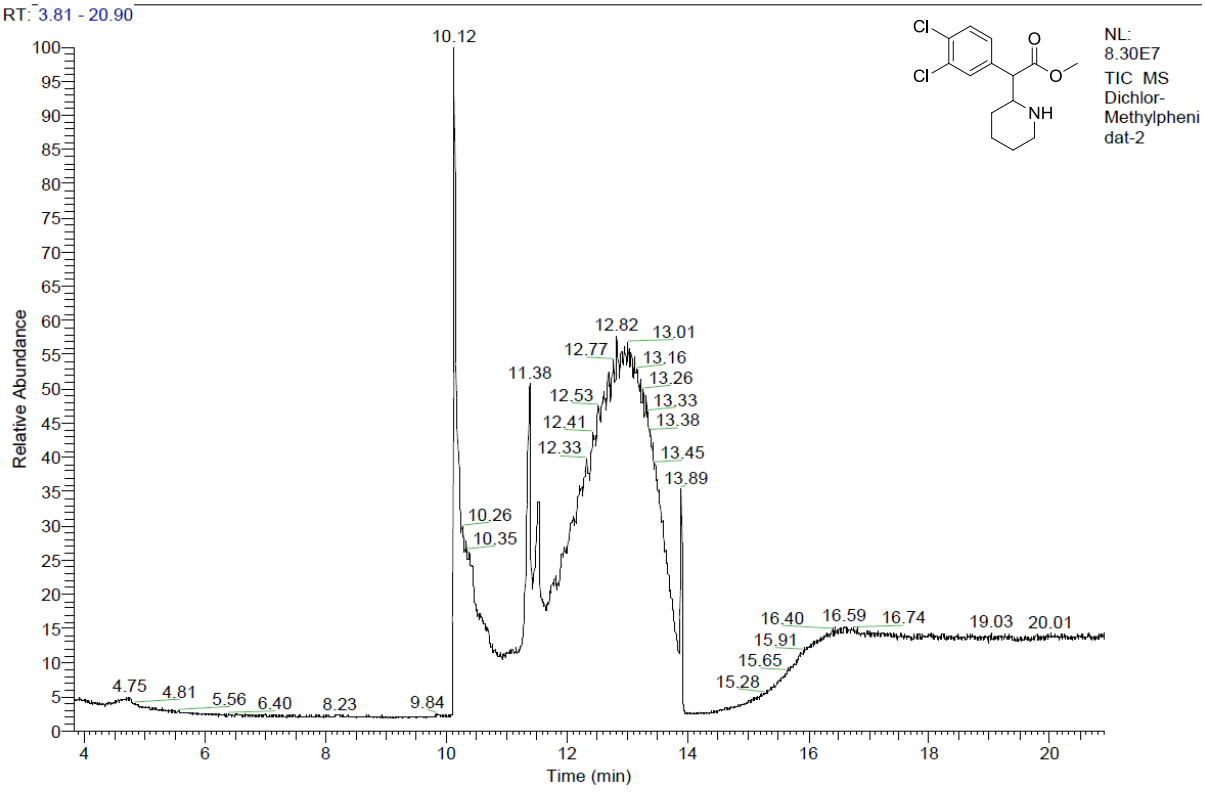


Figure S 17: Chromatogram under standard GC-conditions of 3,4-dichloromethylphenidate **3** HCl.

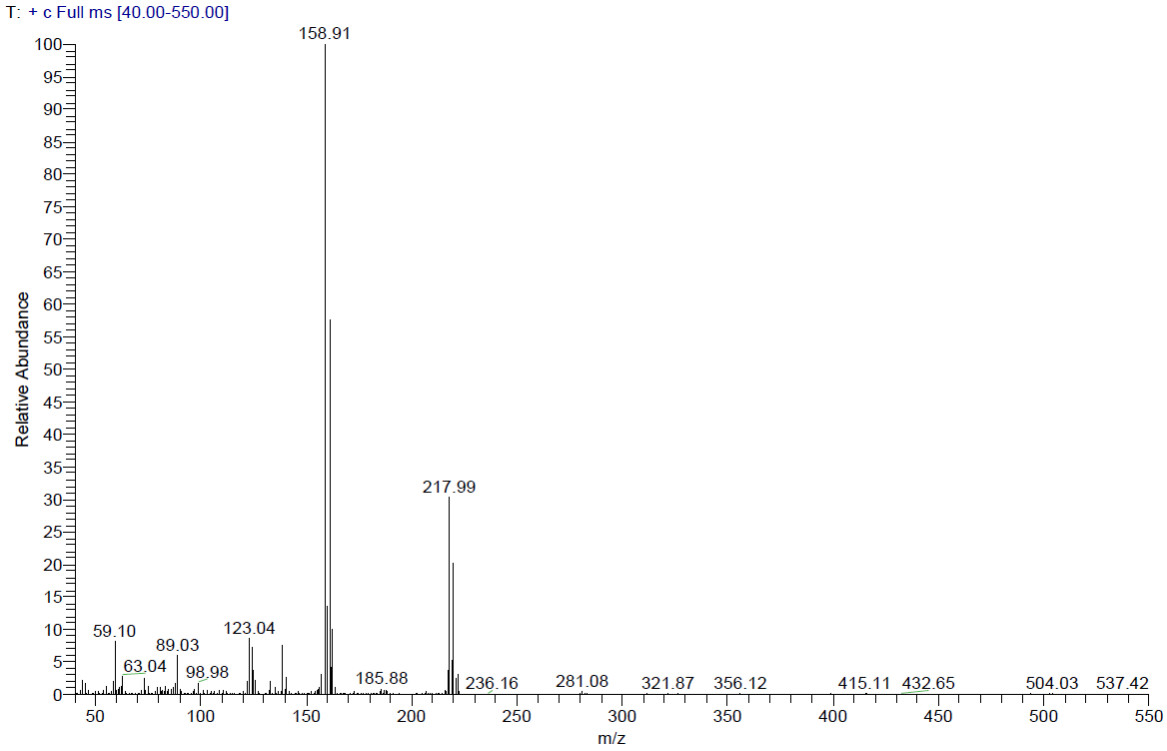


Figure S 18: EI spectrum (70 eV) of 3,4-Dichloromethylphenidate **3** HCl at12.93 min.

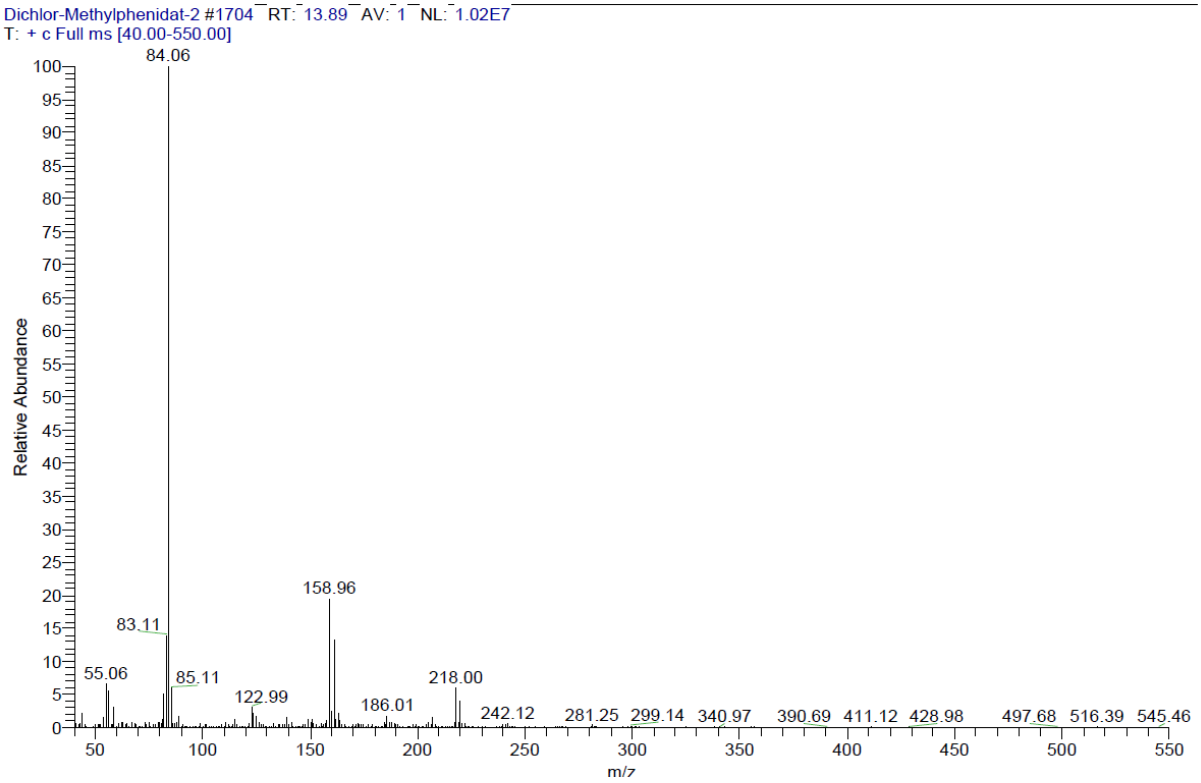


Figure S 19: EI spectrum (70 eV) of 3,4-Dichloromethylphenidate **3** HCl at13.89 min.

Ethylphenidate 4 HCl

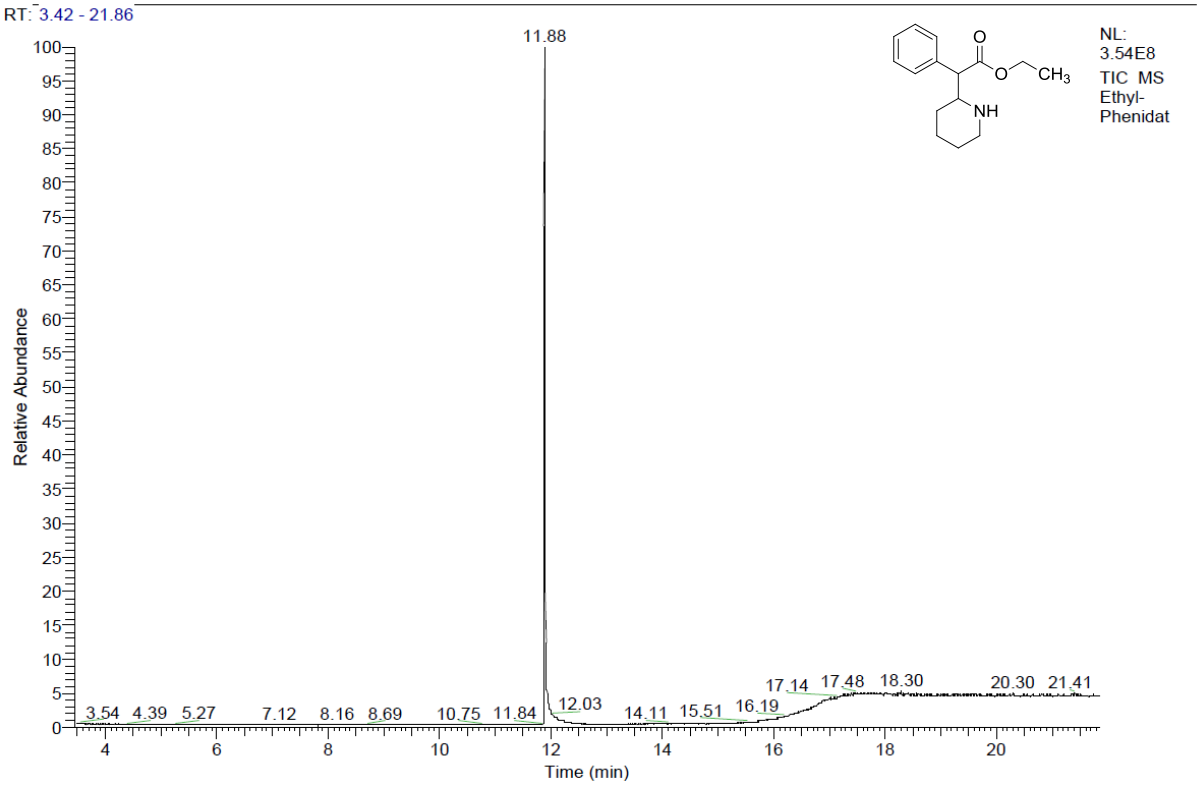


Figure S 20: Chromatogram under standard GC-conditions of ethylphenidate **4** HCl.

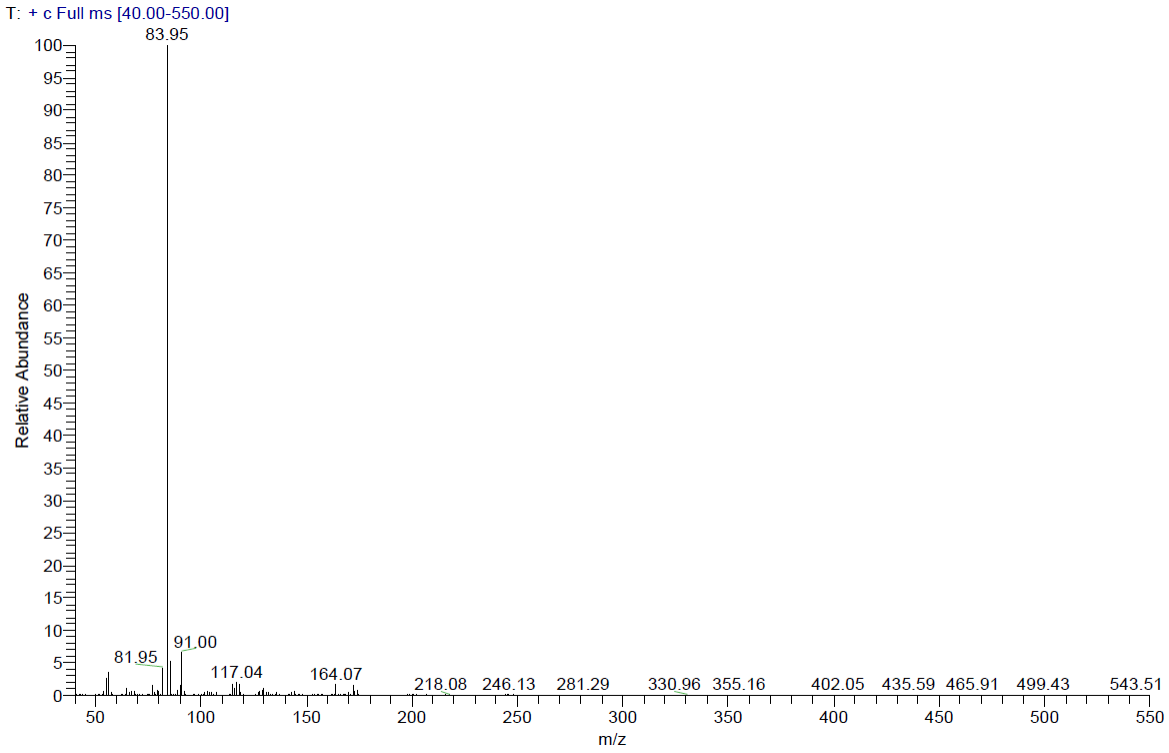


Figure S 21: EI spectrum (70 eV) of ethylphenidate **4** HCl at 11.88min.

3,4-dichloroethylphenidate 5 HCl

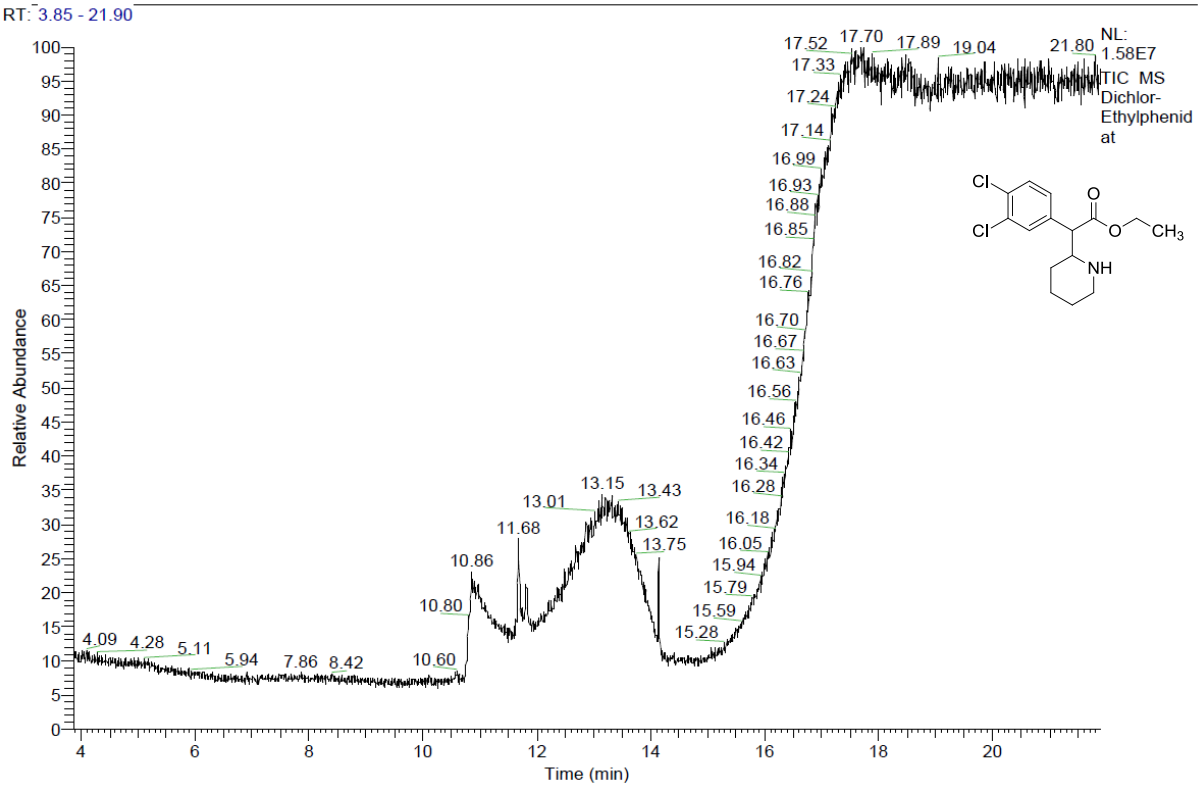


Figure S 22: Chromatogram under standard GC-conditions of 3,4-dichloroethylphenidate **5** HCl.

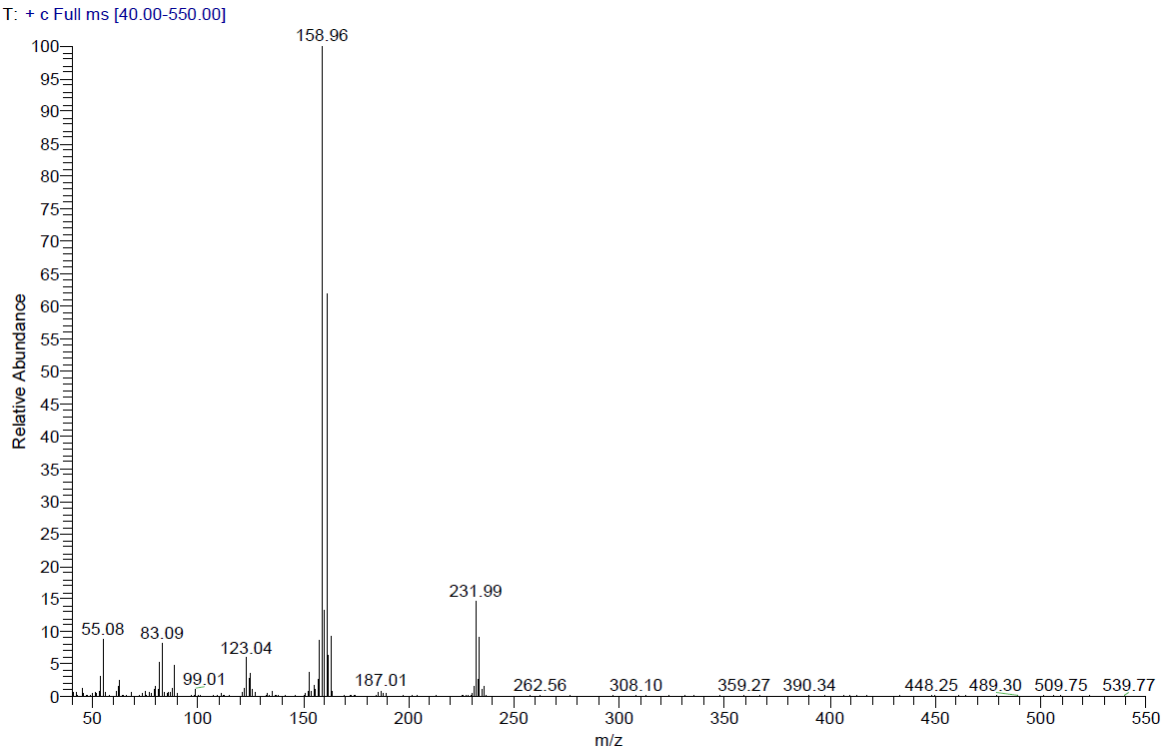


Figure S 23: EI spectrum (70 eV) of 3,4-dichloroethylphenidate **5** HCl at13.15 min.

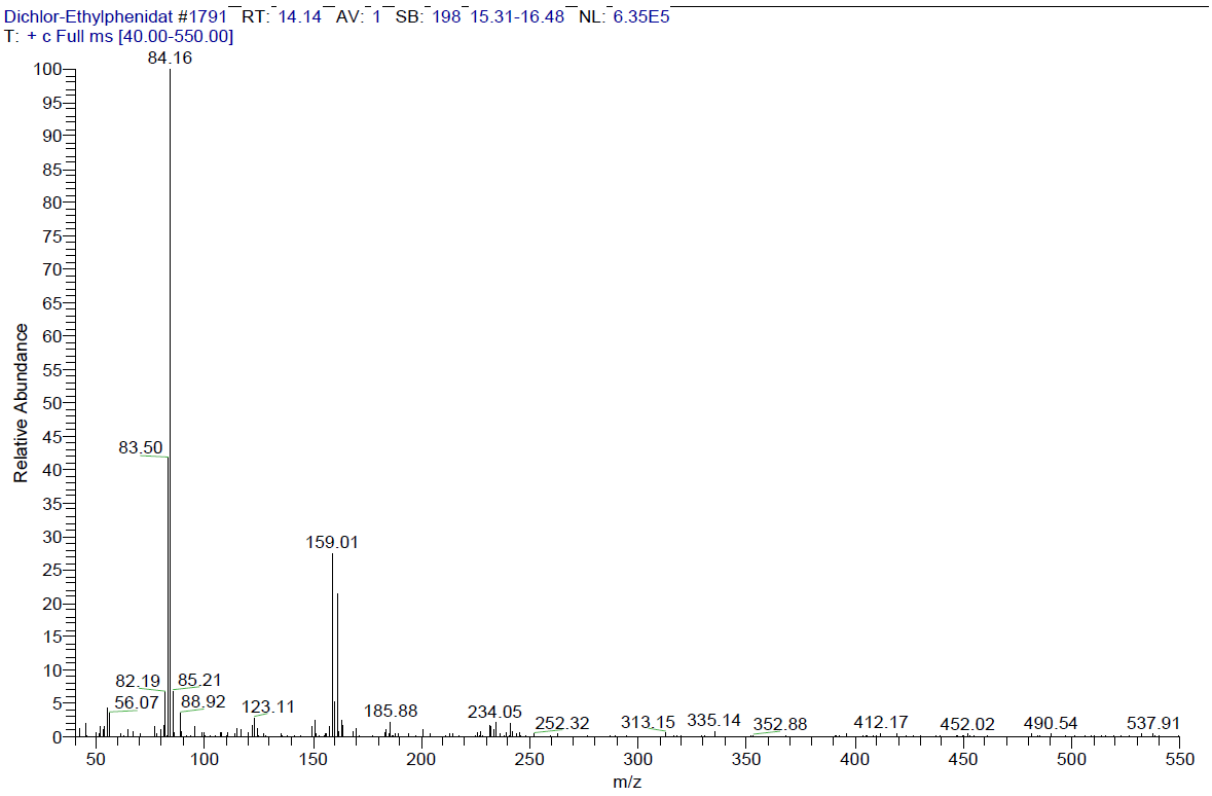


Figure S 24: EI spectrum (70 eV) of 3,4-dichloroethylphenidate **5** HCl at14.14 min.

3,4-dichloroethylphenidate 5 HCl and free base with modified GC-method

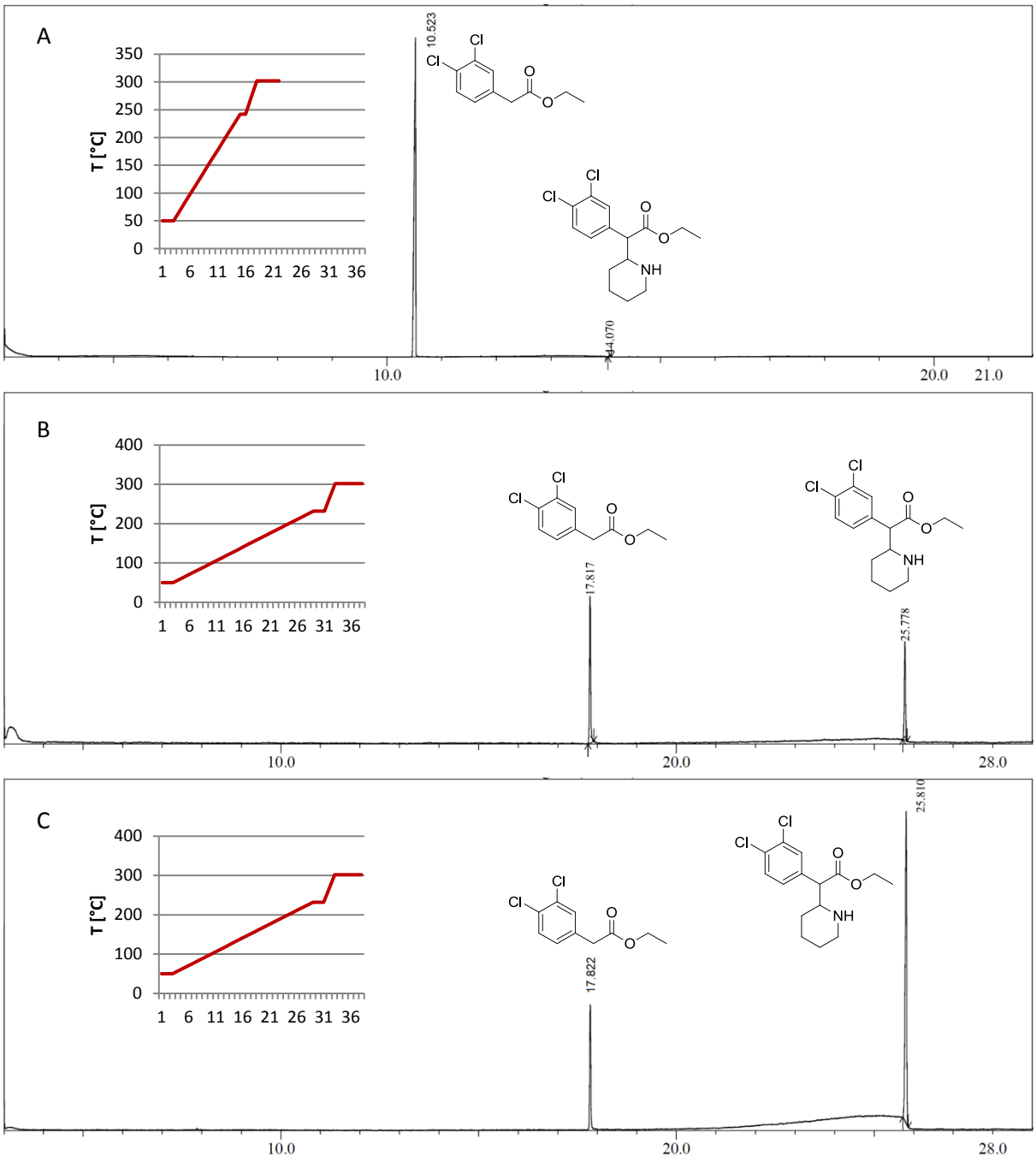


Figure S 25: GC traces of 3,4-dichloroethylphenidate **5** with different temperature programs: a) standard-method with injection of the HCl-salt; b) ramp to 230 °C with injection of the HCl-salt; c) ramp to 230 °C with injection of the free base.

Ethylnaphthidate 6 HCl

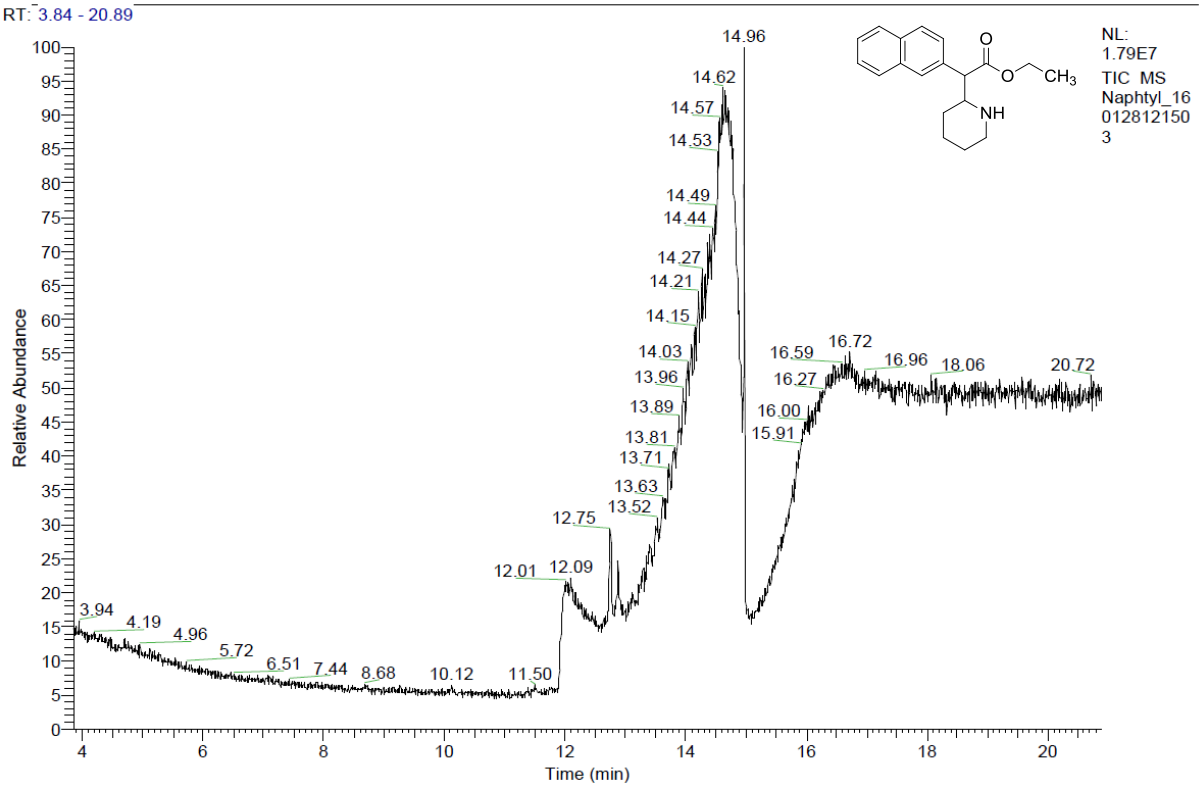


Figure S 26: Chromatogram under standard GC-conditions of ethylnaphtidate **6** HCl.

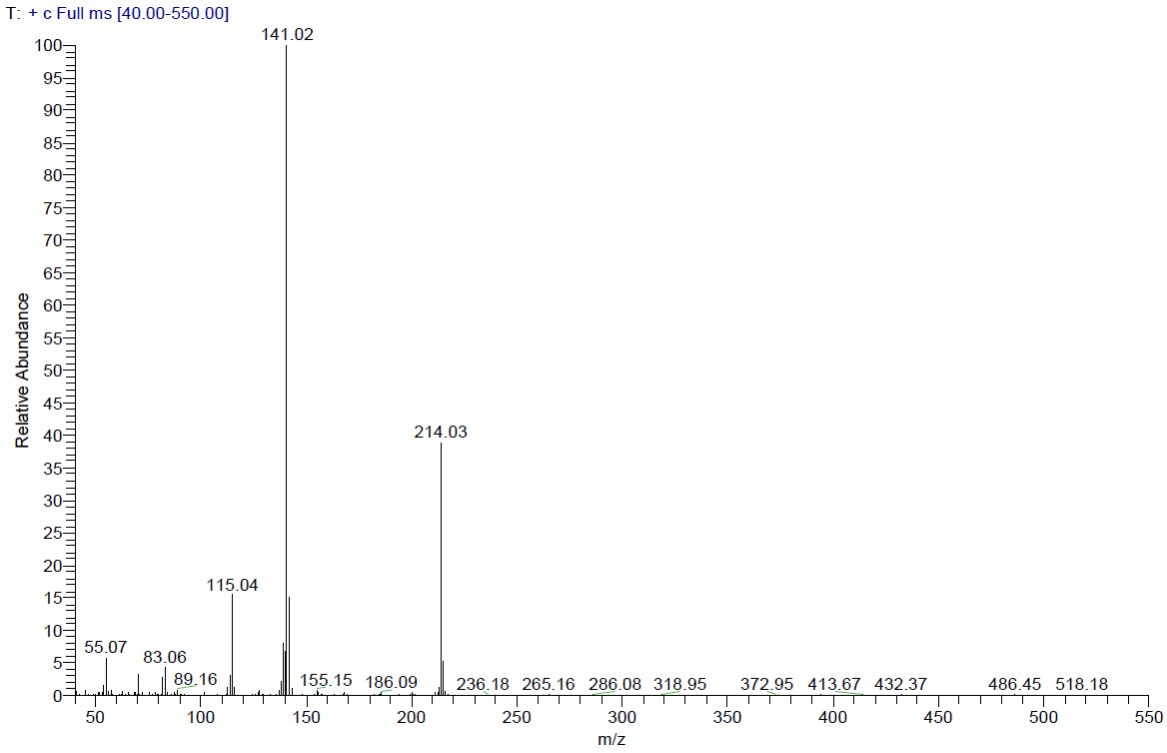


Figure S 27: EI spectrum (70 eV) of ethylnaphthidate **6** HCl at14.63 min.

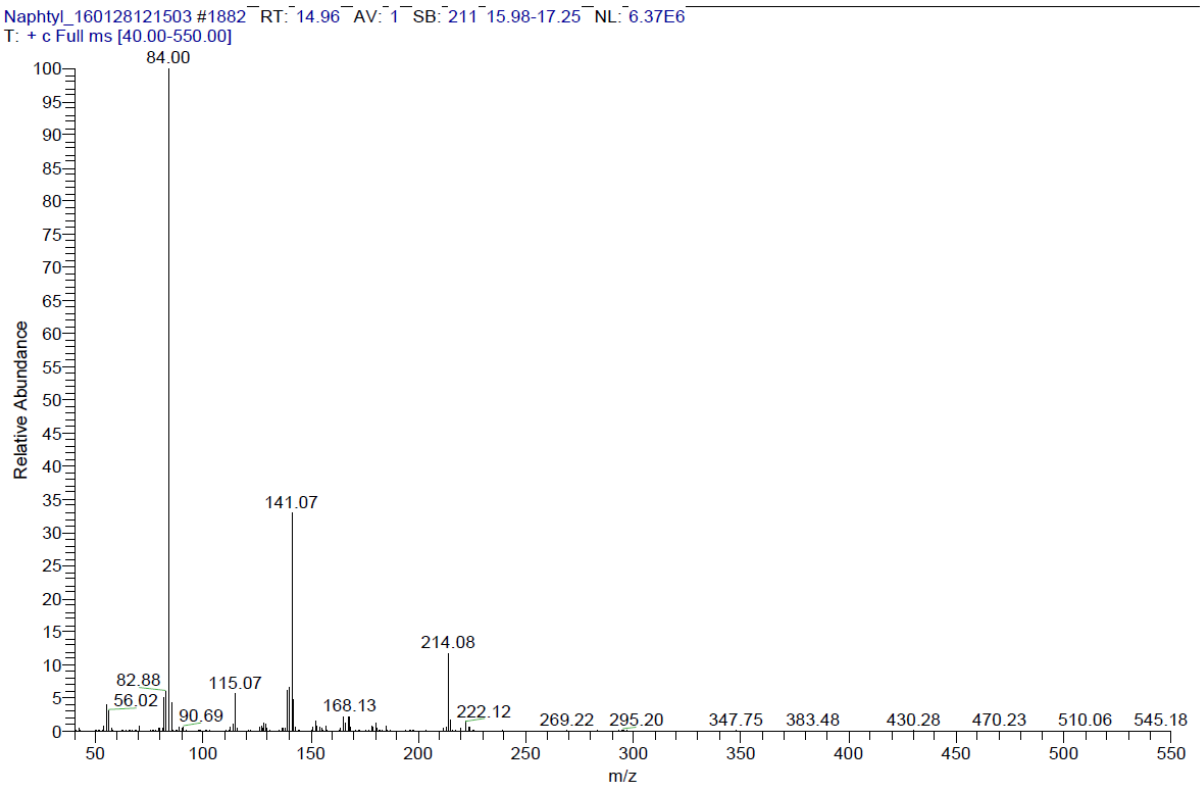


Figure S 28: EI spectrum (70 eV) of ethylnaphthidate **6** HCl at14.96 min.

N-benzyl-ethylphenidate 7 HCl

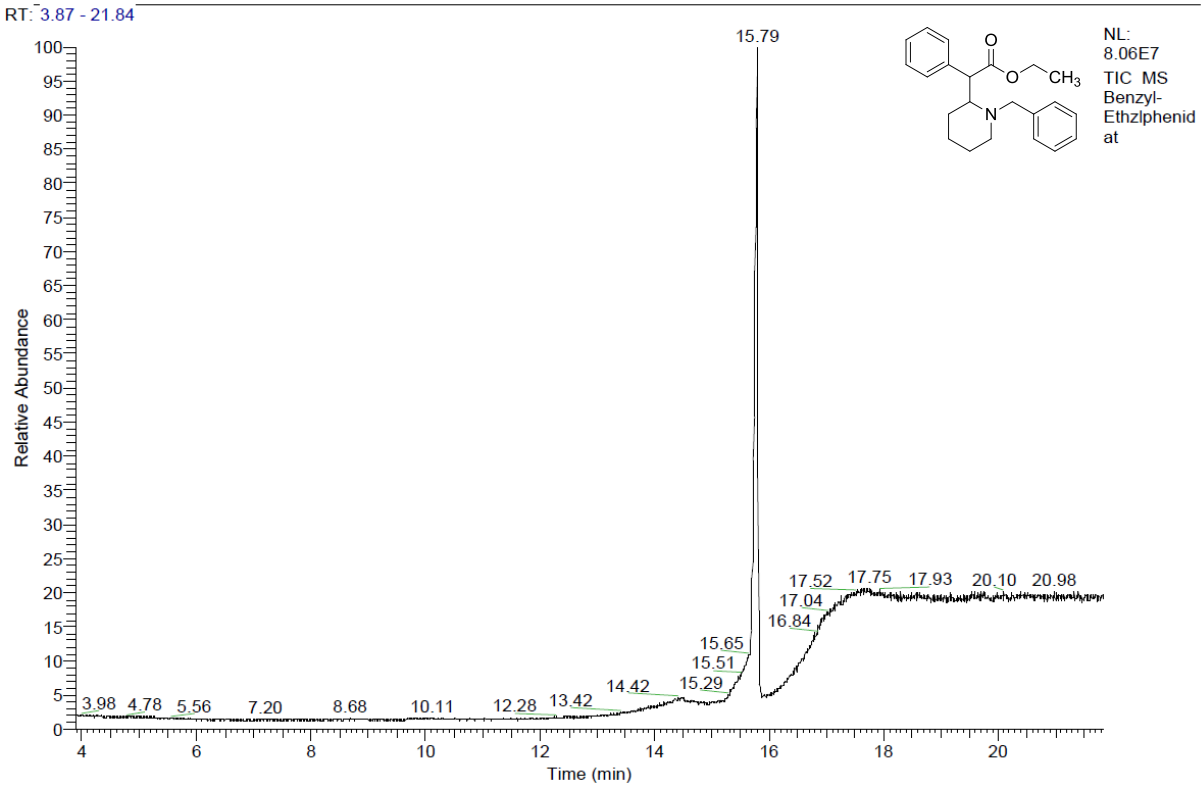


Figure S 29: Chromatogram under standard GC-conditions of *N*-benzyl-ethylphenidate **7** HCl.

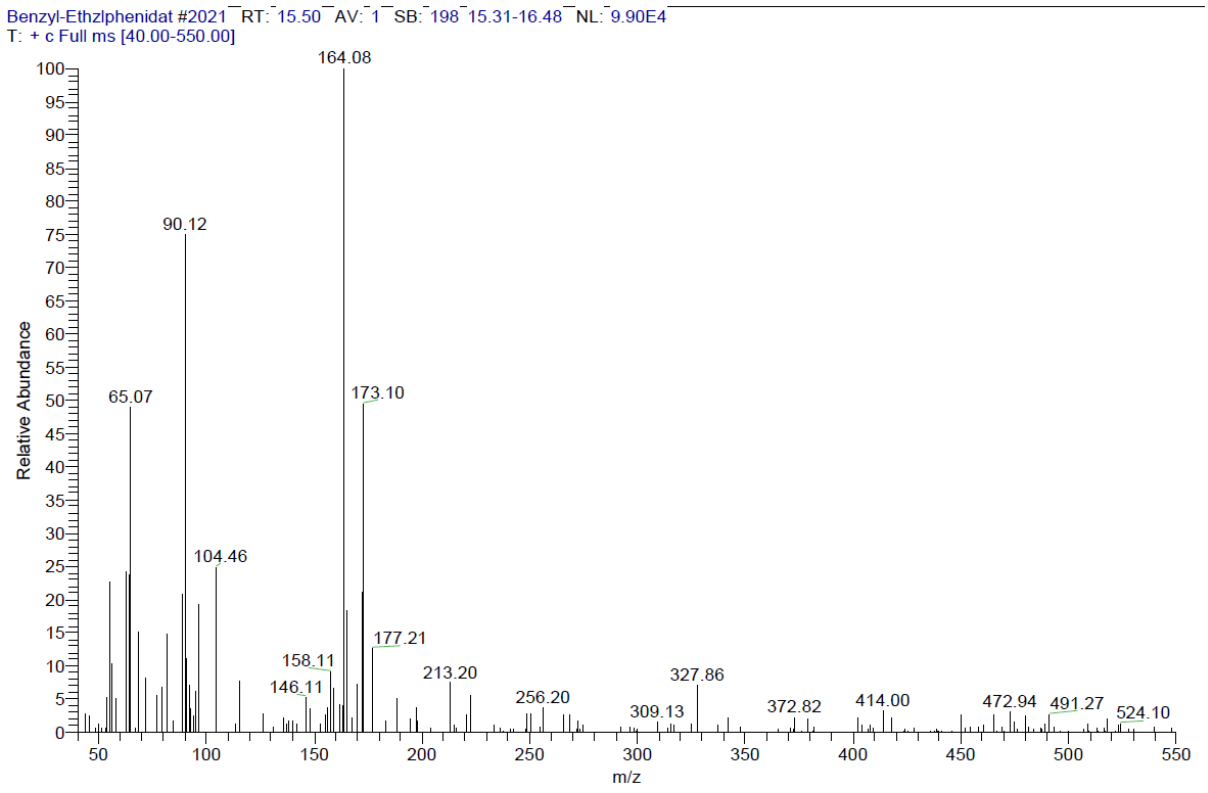


Figure S 30: EI spectrum (70 eV) of *N*-benzyl-ethylphenidate **7** HCl at15.50 min.

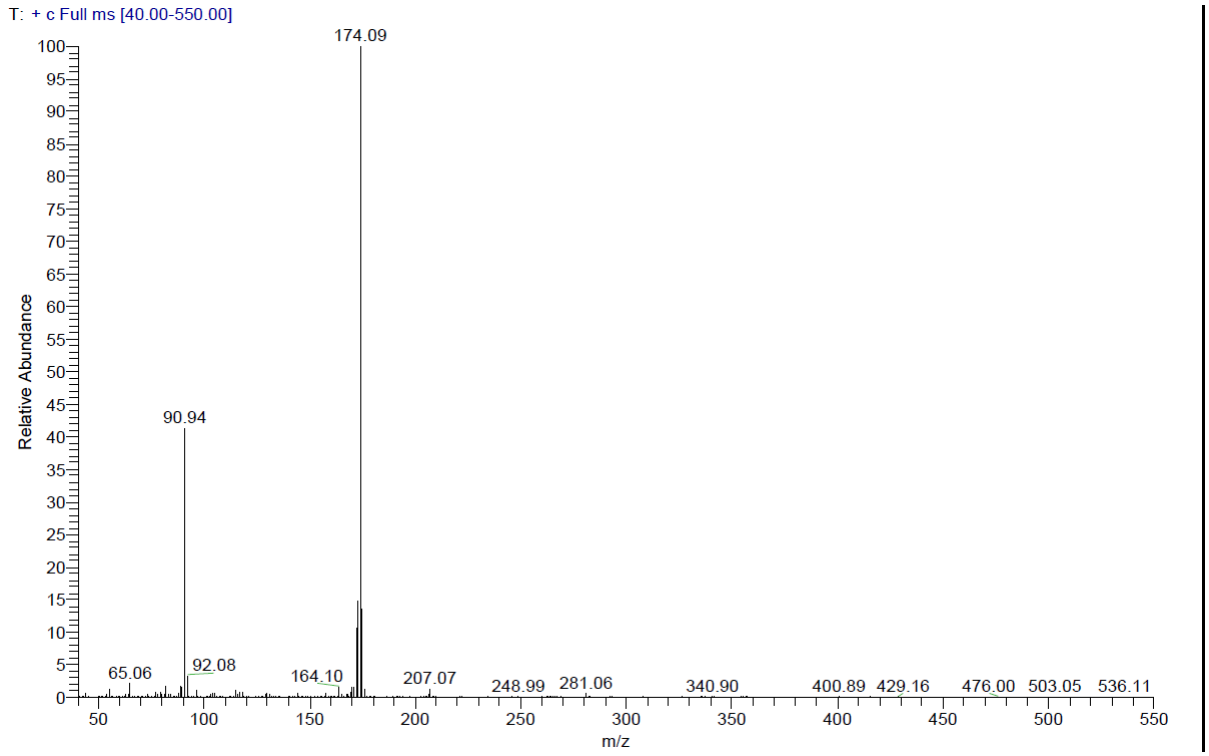


Figure S 31: EI spectrum (70 eV) of *N*-benzyl-ethylphenidate **7** HCl at15.78 min.

CI-MS and DIP-MS

Method (State Bureau of Criminal Investigation Schleswig-Holstein, Section Narcotics/Toxicology, Kiel, Germany)

Electron ionization (EI) mass spectra (70 eV) were recorded using a Finnigan TSQ 7000 triple stage quadrupole mass spectrometer coupled to a gas chromatograph (Trace GC Ultra, Thermo Electron) using a CTC CombiPAL (CTC Analytics, Switzerland) autosampler. The emission current was 200 µA and the scan time was 1 s spanning a scan range between *m/z* 29 – *m/z* 600. The ion source temperature was maintained at 175 °C. Samples were introduced via GC with splitless injection using a fused silica capillary DB-1 column (30 m x 0.25 mm, film thickness 0.25 µm). The temperature program consisted of an initial temperature of 80 °C, held for 1 min, followed by a ramp to 280 °C at 15 °C/min. The final temperature was held for 21 min. The injector temperature was 220 °C. The transfer line temperature was maintained at 280 C and the carrier gas was helium in constant flow mode at a flow rate of 1.0 mL/min. Approximately 2 mg of the appropriate phenidate was alcalized with 1 mL 5 % NaOH and extracted in 1.5 mL diethyl ether. For analysis, 1 µL sample solutions were injected into the GC-MS system. For the direct insertion probe (DIP) spectra 1 µL of the sample solution were evaporated in the direct insertion cup and were afterwards introduced directly in the ionization chamber of the mass spectrometer. The cup was heated starting with 50 °C held for 1 min, followed by a ramp to 300 °C at 200 °C/min held for 2 min.

3,4-dichloromethylphenidate 3 free base

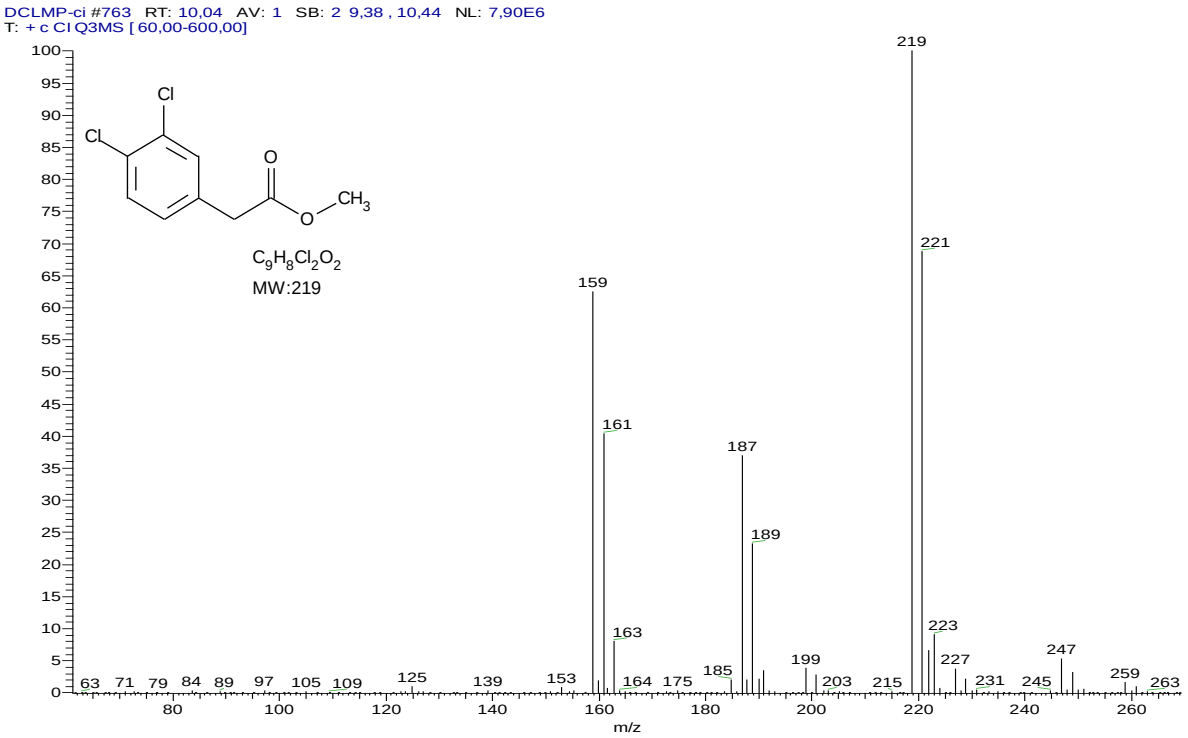


Figure S 32: CI-MS of thermal decomposition product 2-(3,4-dichloro-phenyl)-methylacetate from **3 free base**.

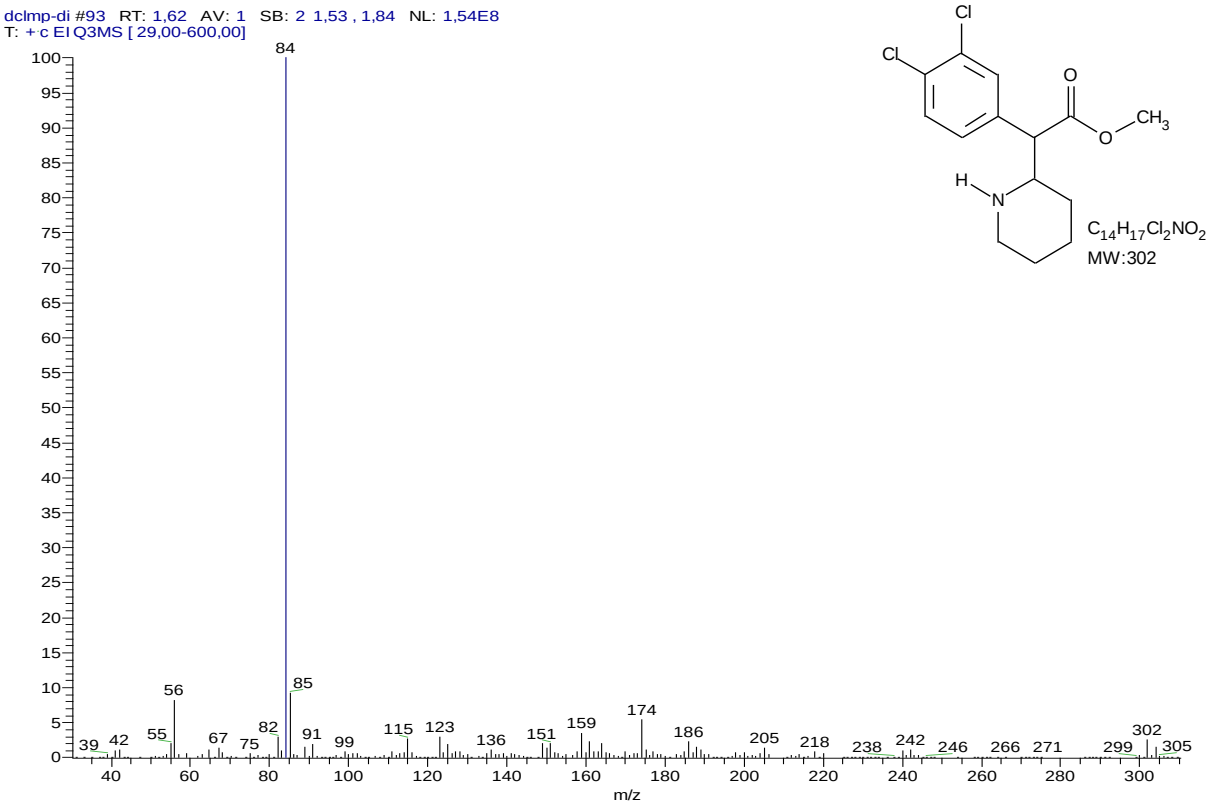


Figure S 33: DIP-EI-MS of 3,4-dichloromethylphenidate **3 free base**.

3,4-dichloroethylphenidate 5 free base

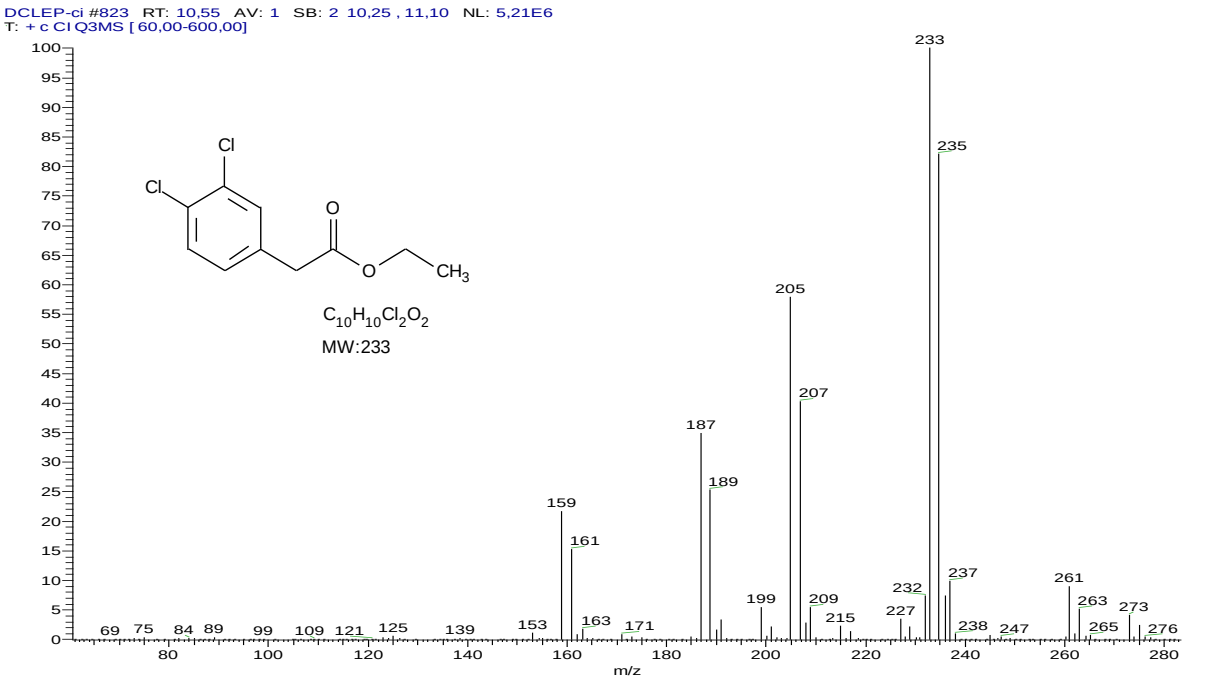


Figure S 34: CI-MS of thermal decomposition product 2-(3,4-dichloro-phenyl)-ethylacetate from **5 free base**.

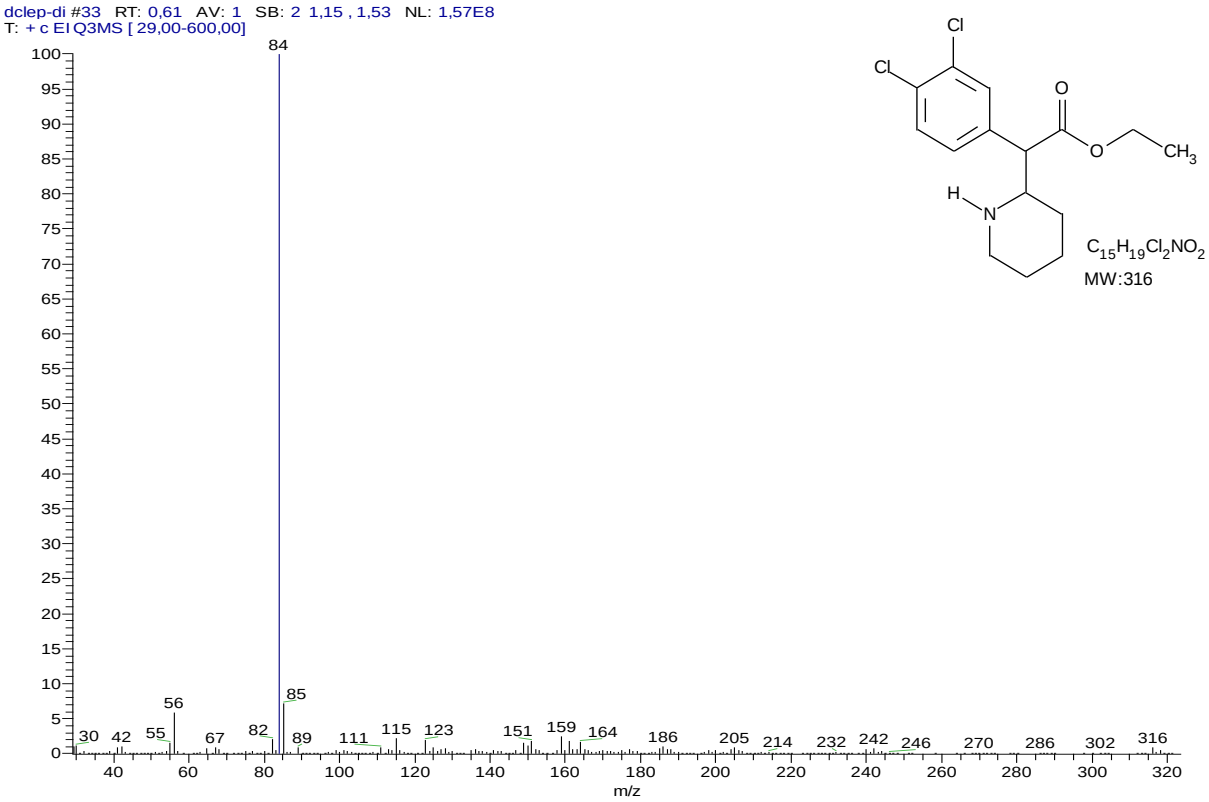


Figure S 35: DIP-EI-MS of 3,4-dichloroethylphenidate **5 free base**.

Ethylnaphthidate 6 free base

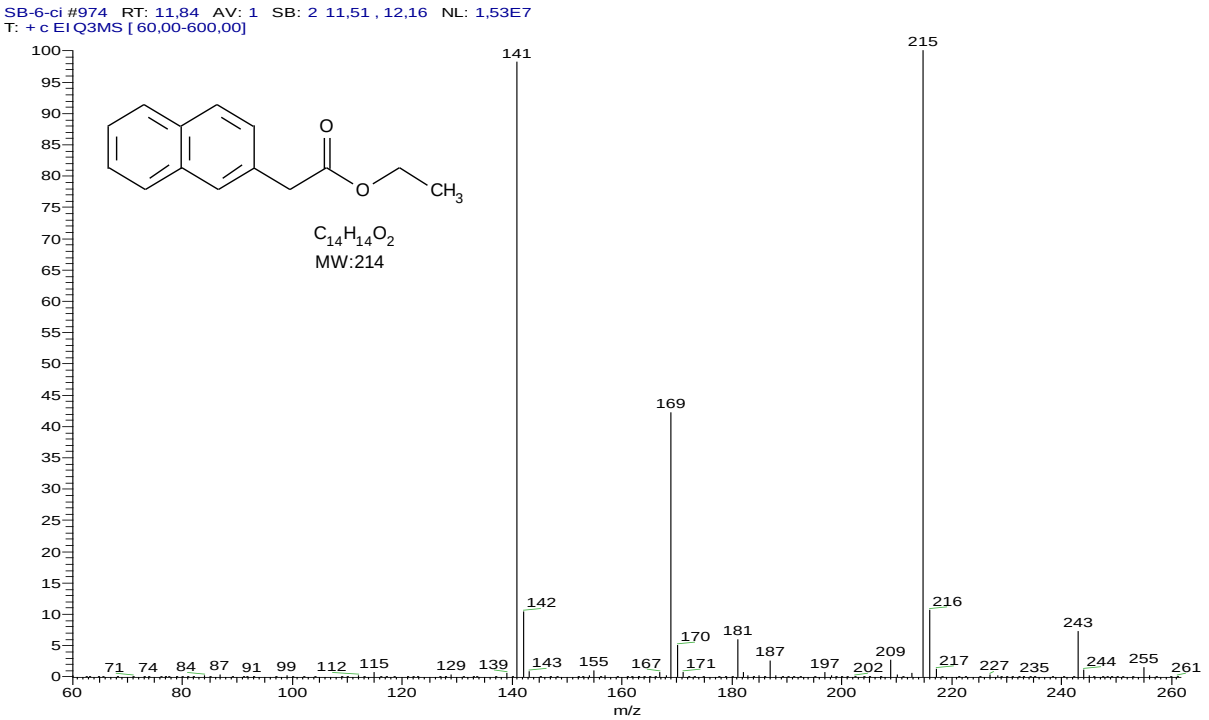


Figure S 36: CI-MS of thermal decomposition product 2-naphthyl-ethylacetate from **6 free base**.

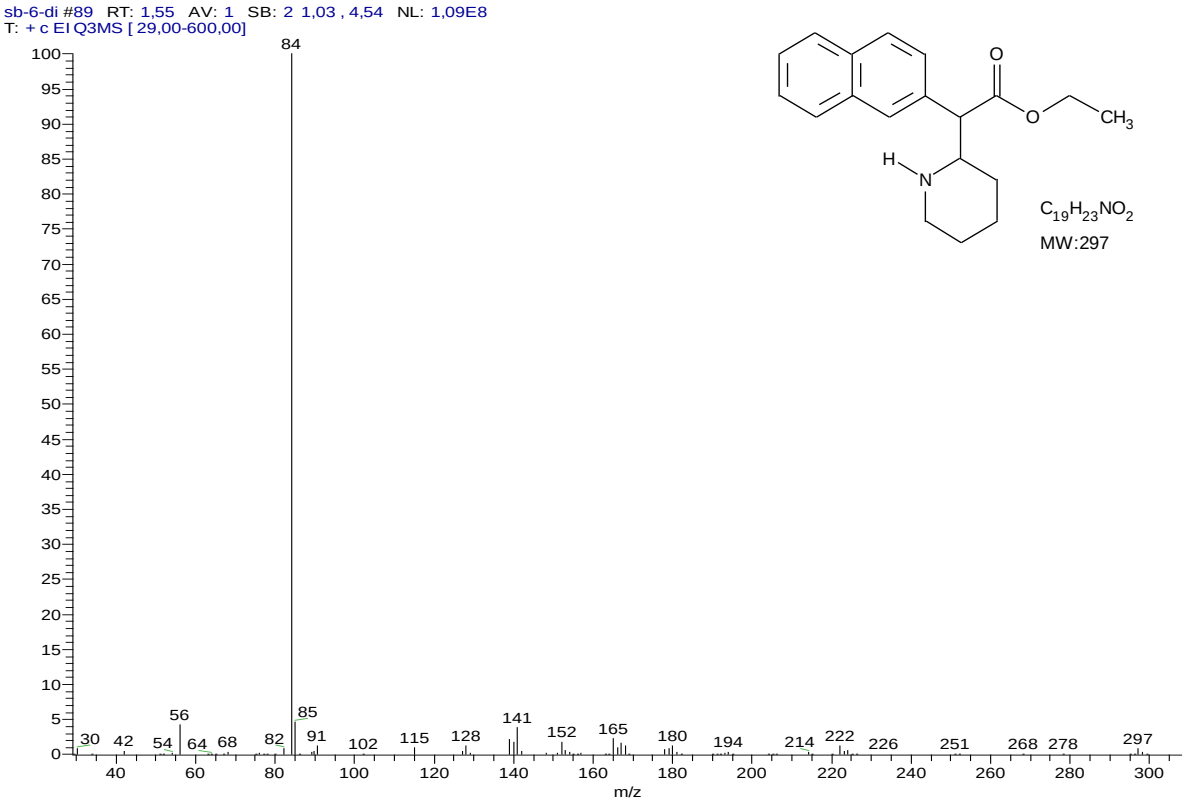


Figure S 37: DIP-EI-MS of naphthyl-ethylphenidate **6 free base**.

N-benzyl-ethylphenidate 7 free base

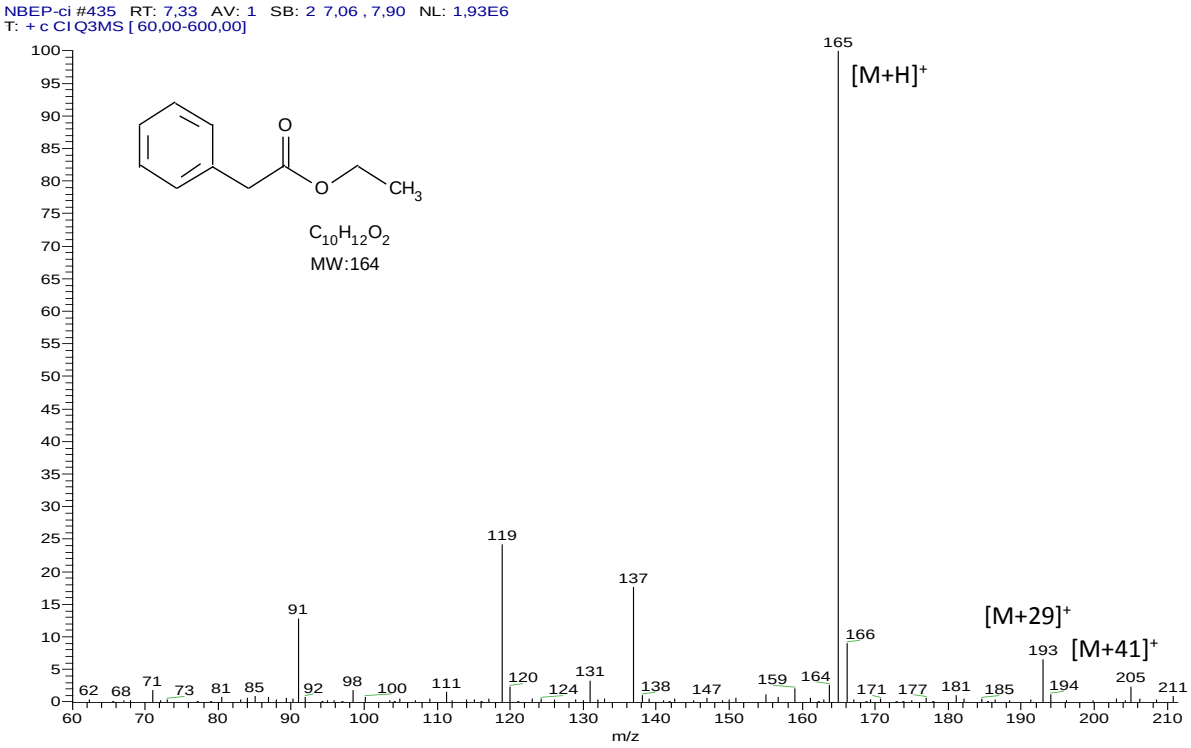


Figure S 38: CI-MS of thermal decomposition product 2-phenyl-ethylacetate from **7**.

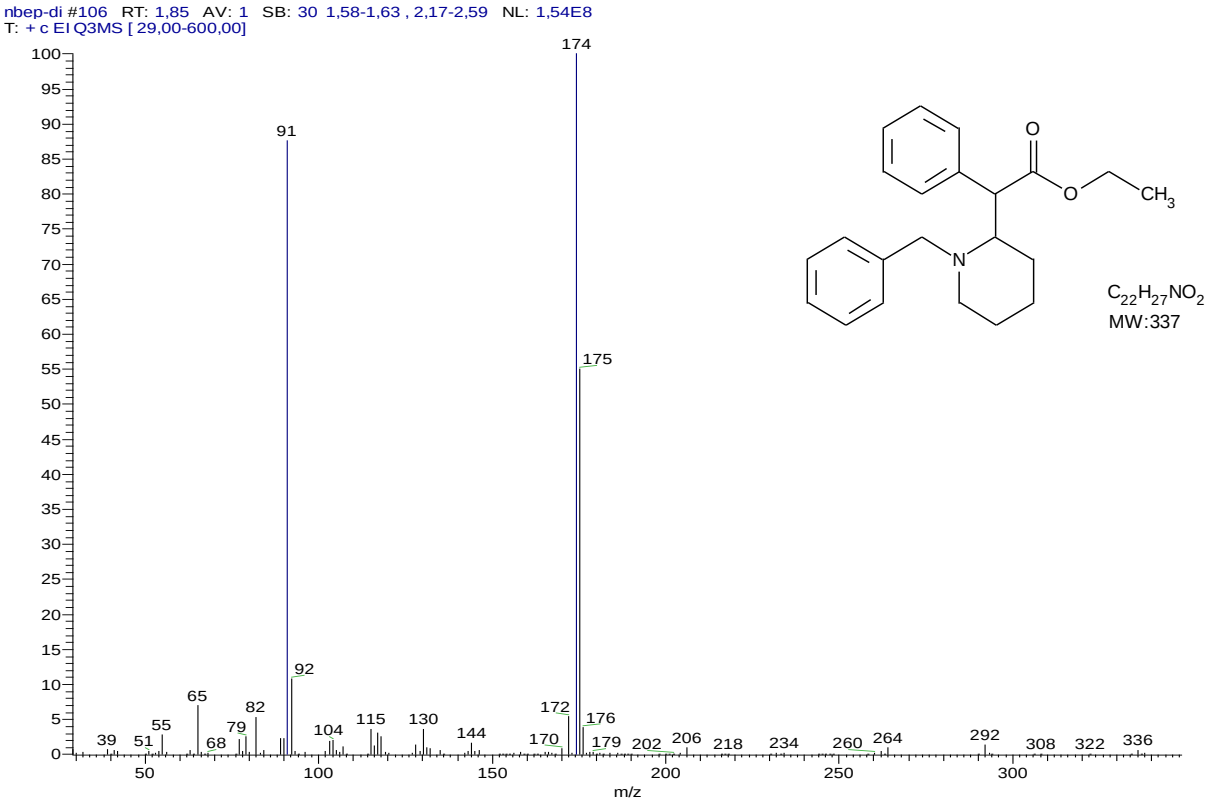


Figure S 39: DIP-EI-MS of *N*-benzyl-ethylphenidate **7**.

ESI-MS/MS

4-Methylmethylphenidate 2 HCl

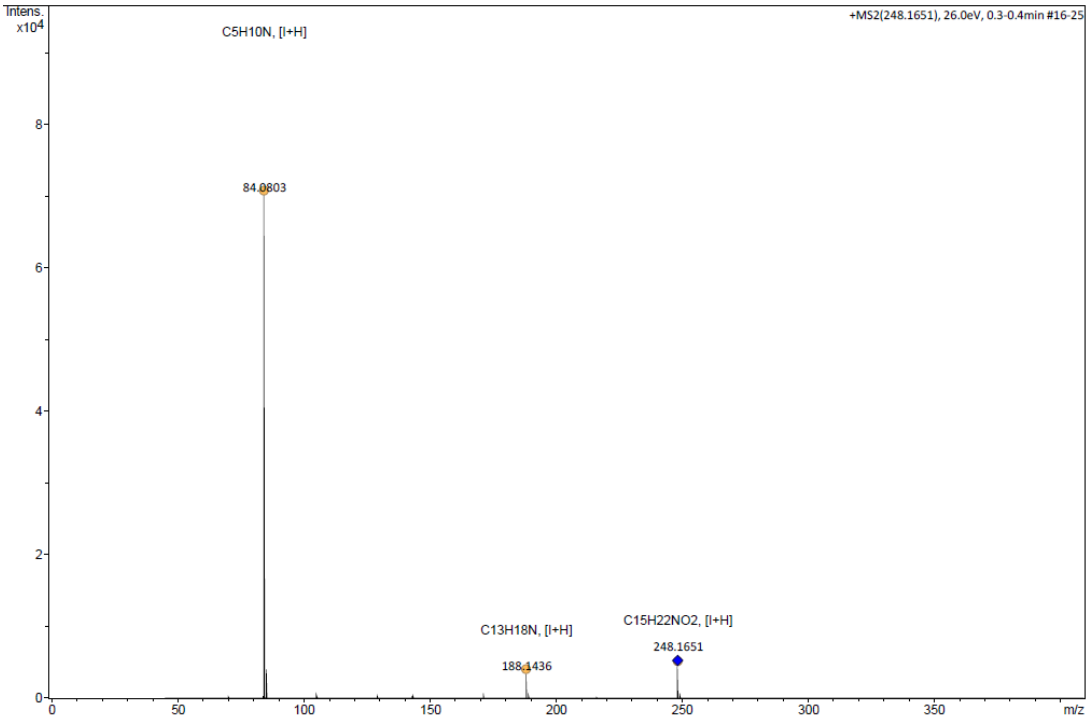


Figure S 40: MS2 of 4-methylmethylphenidate **2** (CE: 26.0 eV).

3,4-dichloromethylphenidate 3 HCl

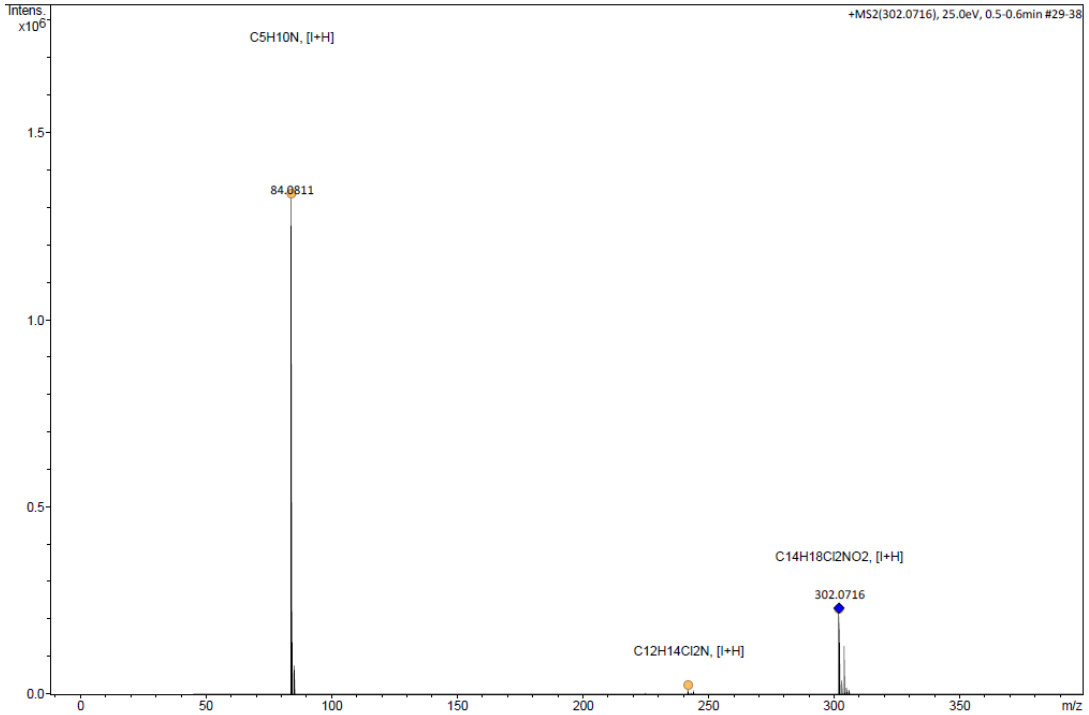


Figure S 41: MS2 of 3,4-dichloromethylphenidate **3** (CE: 25.0 eV).

Ethylphenidate 4 HCl

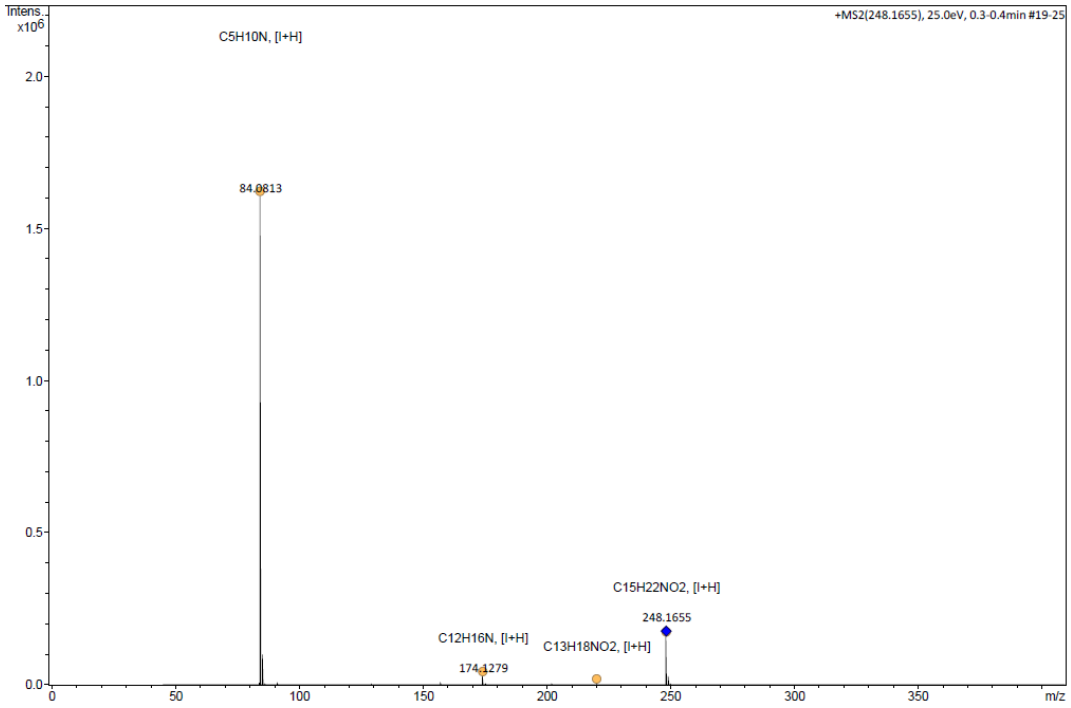


Figure S 42: MS2 of Ethylphenidate **4** (CE: 26.0 eV).

3,4-dichloroethylphenidate 5 HCl

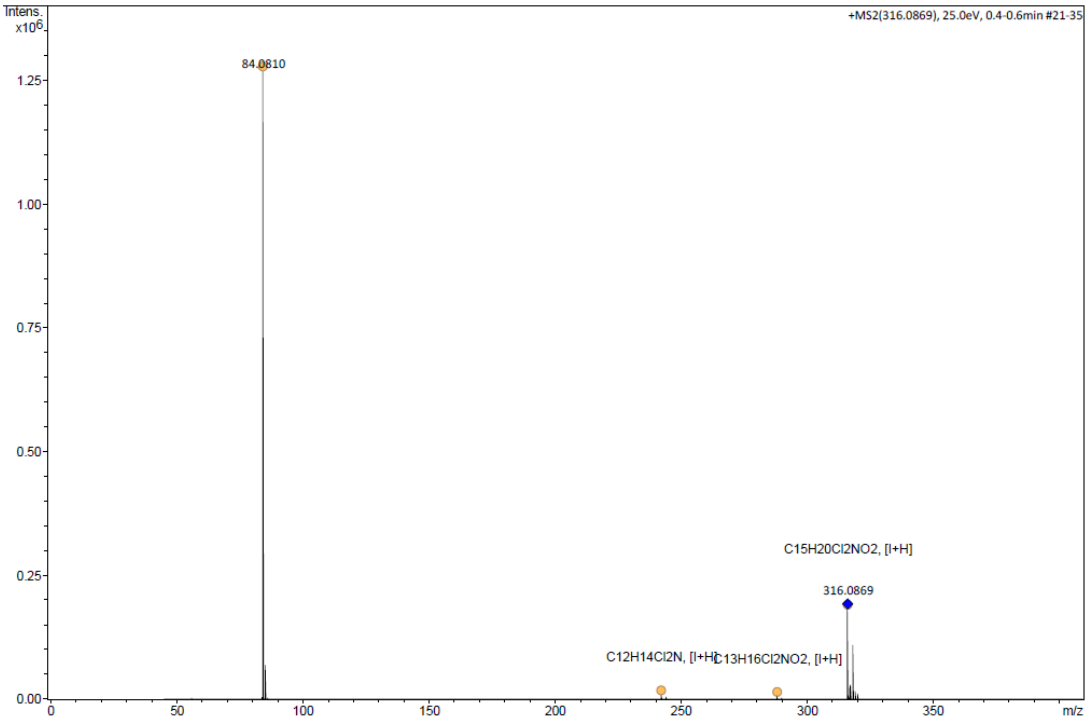


Figure S 43: MS2 of 3,4-dichloroethylphenidate **5** (CE: 25.0 eV).

Ethylnaphthidate 6 HCl

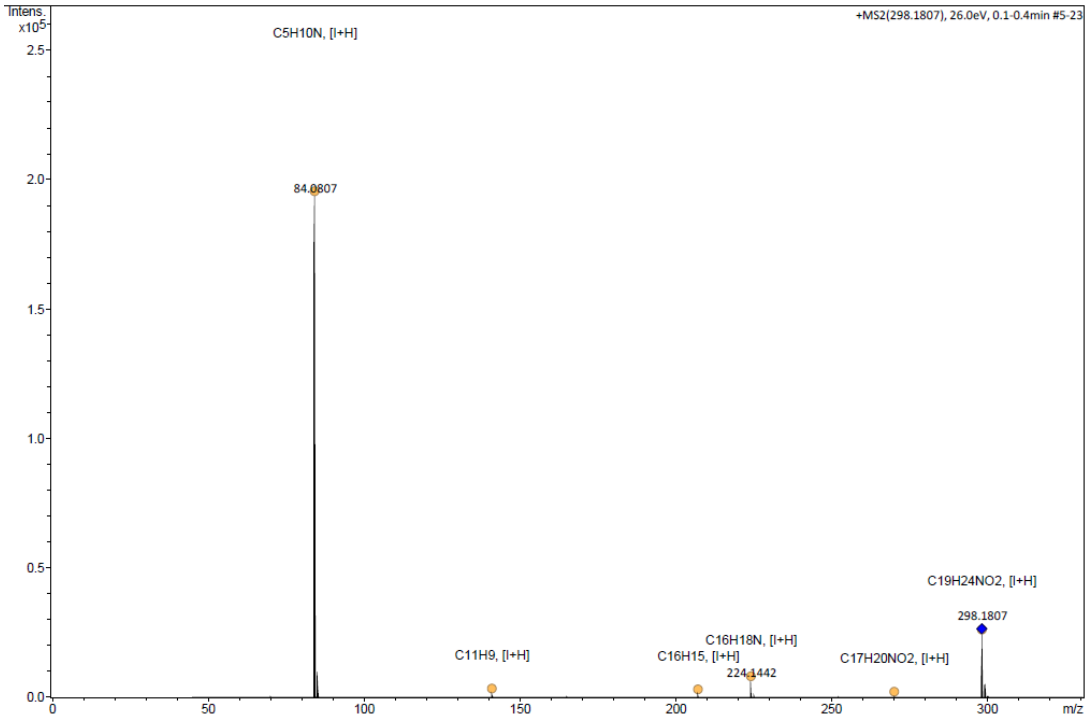


Figure S 44: MS2 of ethylnaphthidate **6** (CE: 26.0 eV).

N-benzyl-ethylphenidate 7 HCl

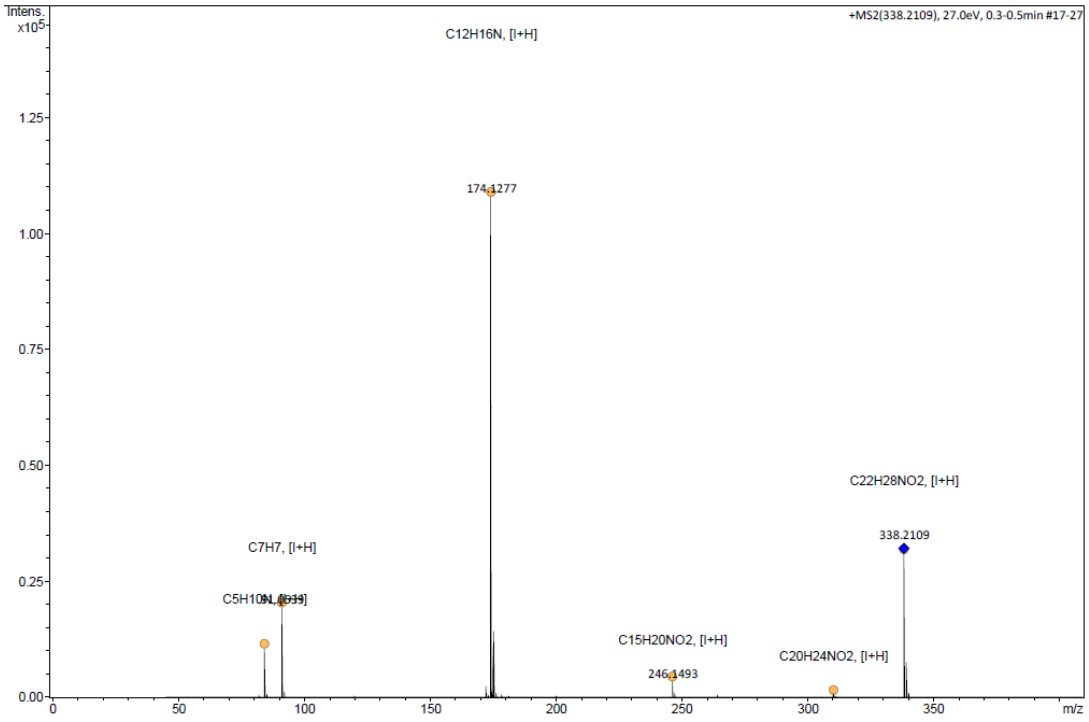


Figure S 45: MS2 of *N*-benzyl-ethylphenidate **7** (CE: 27.0 eV).

FT-IR

4-Methylmethylphenidate 2 HCl and free base

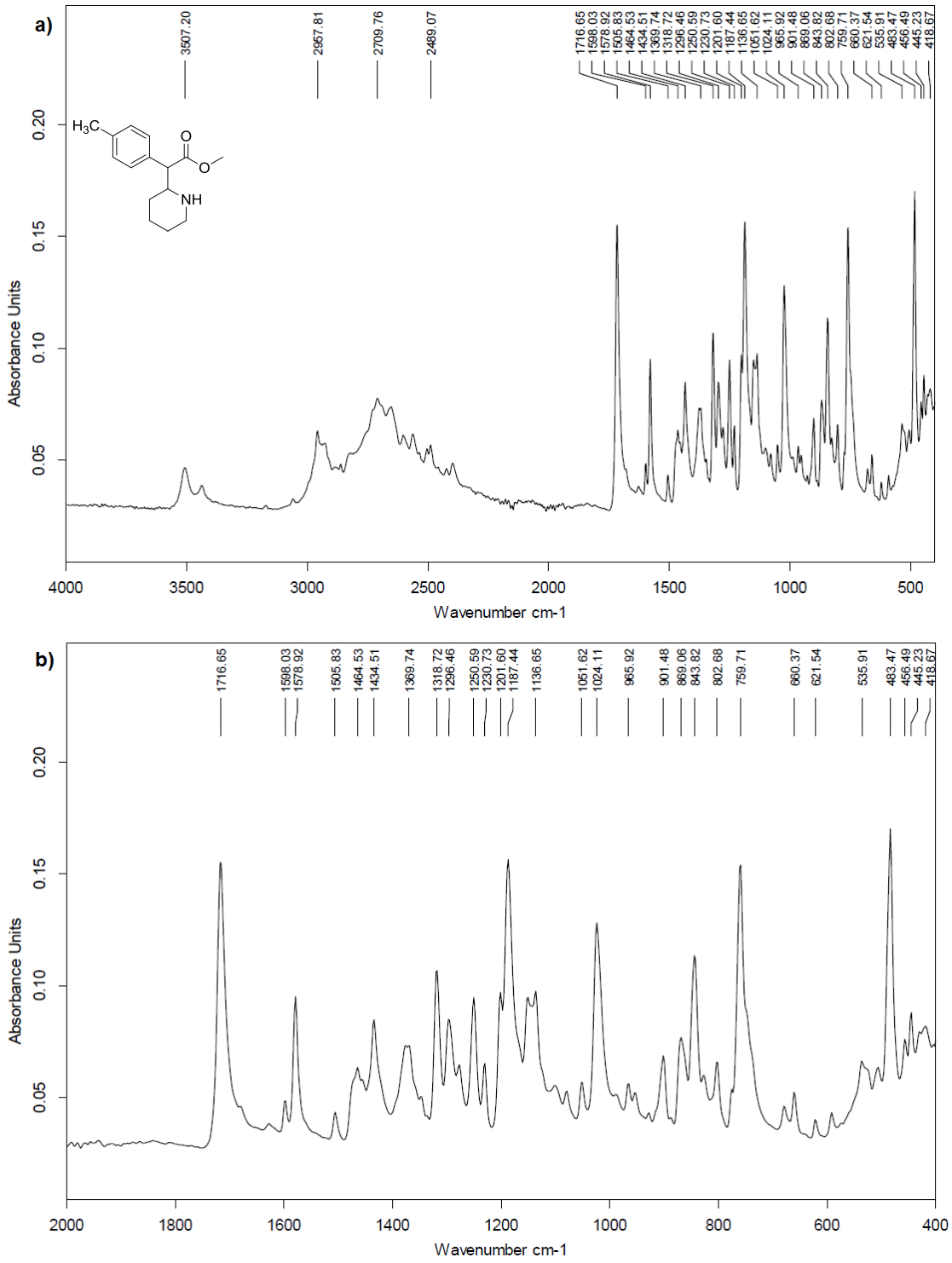


Figure S 46: IR spectrum of **2 HCl** (a) and enlarged fingerprint region (b) for identification.

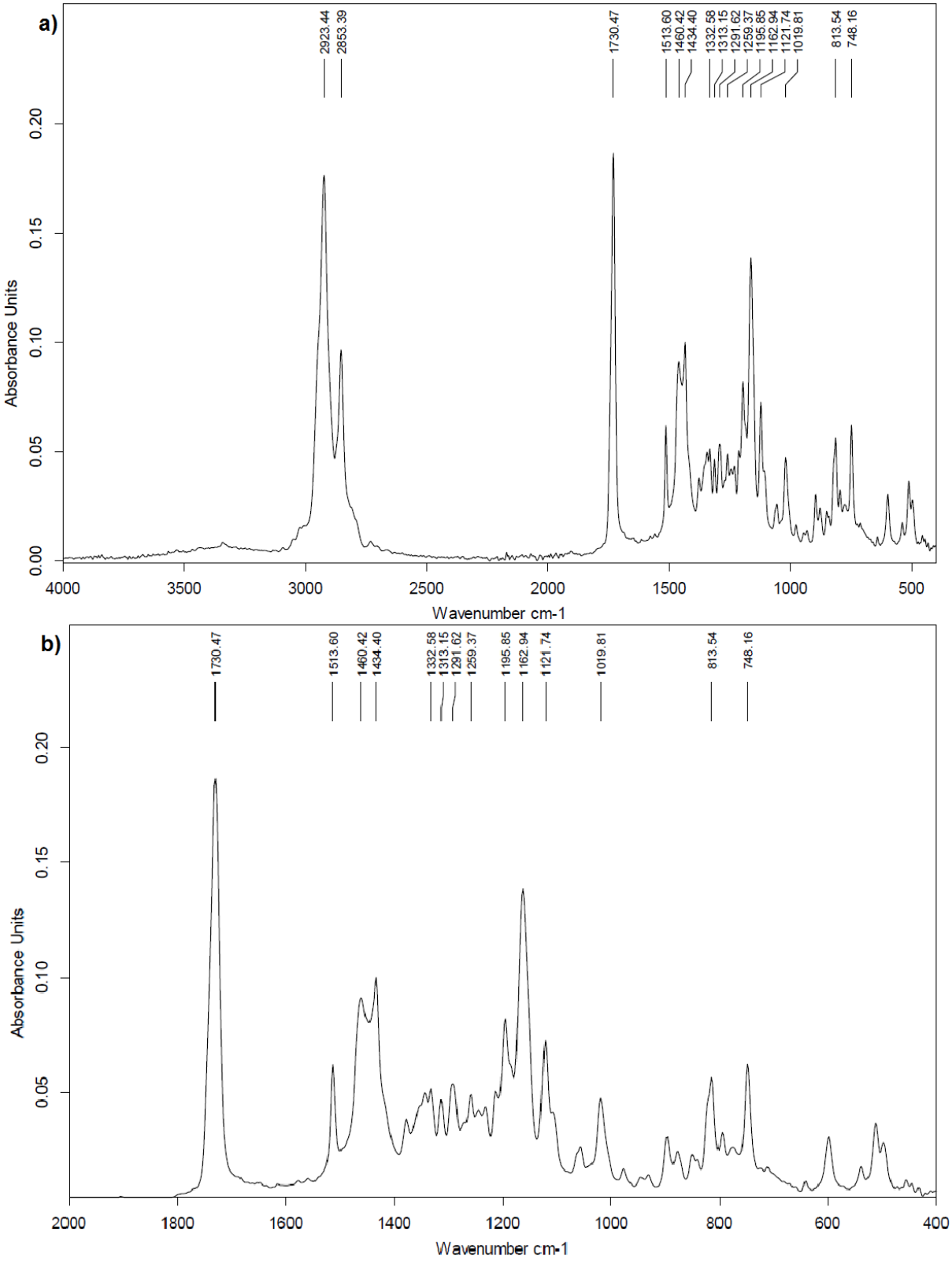


Figure S 47: IR spectrum of **2 free base**(a) and enlarged fingerprint region (b) for identification.

3,4-dichloromethylphenidate 3 HCl and free base

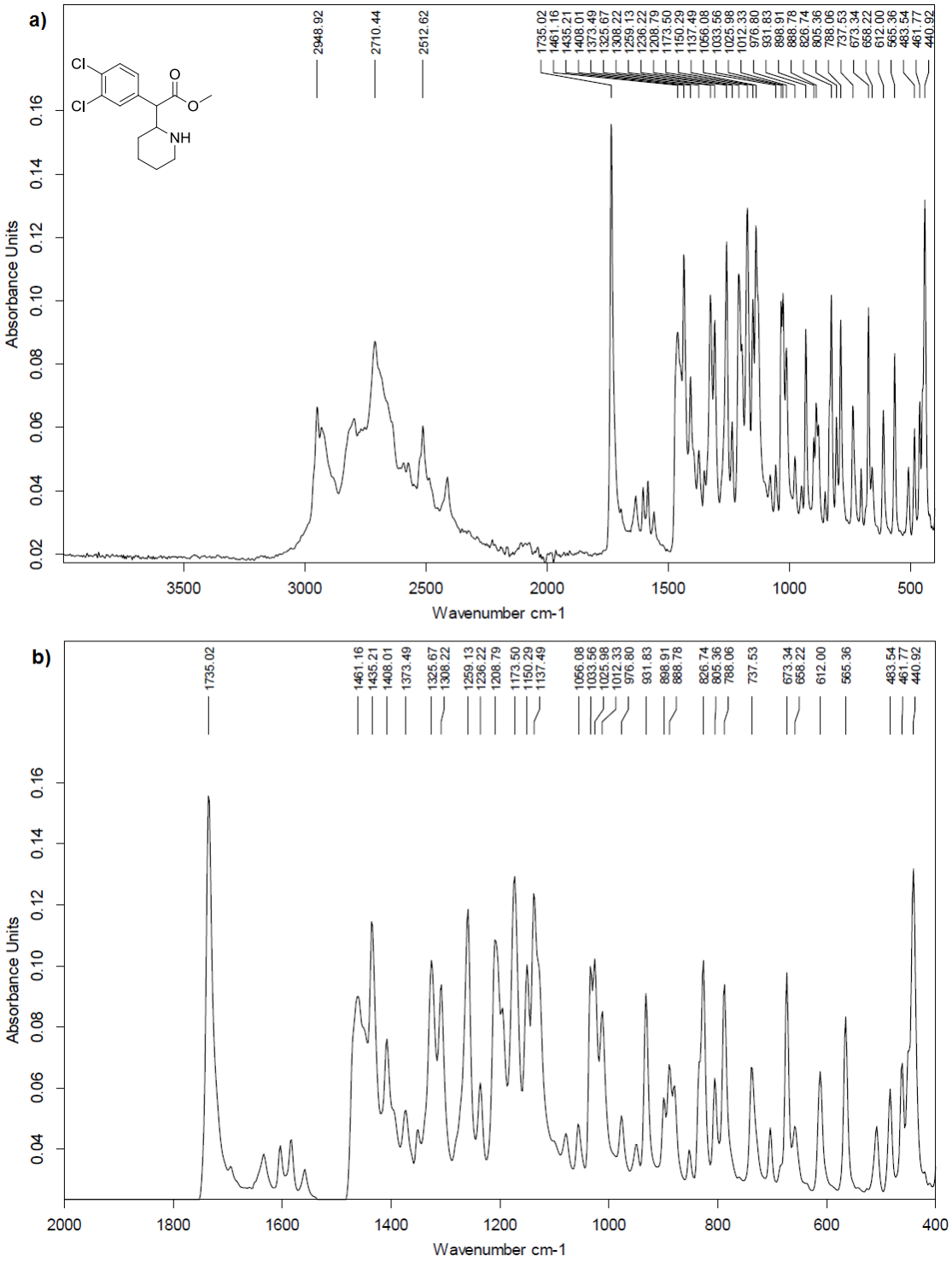


Figure S 48: IR spectrum of **3 HCl** (a) and enlarged fingerprint region (b) for identification.

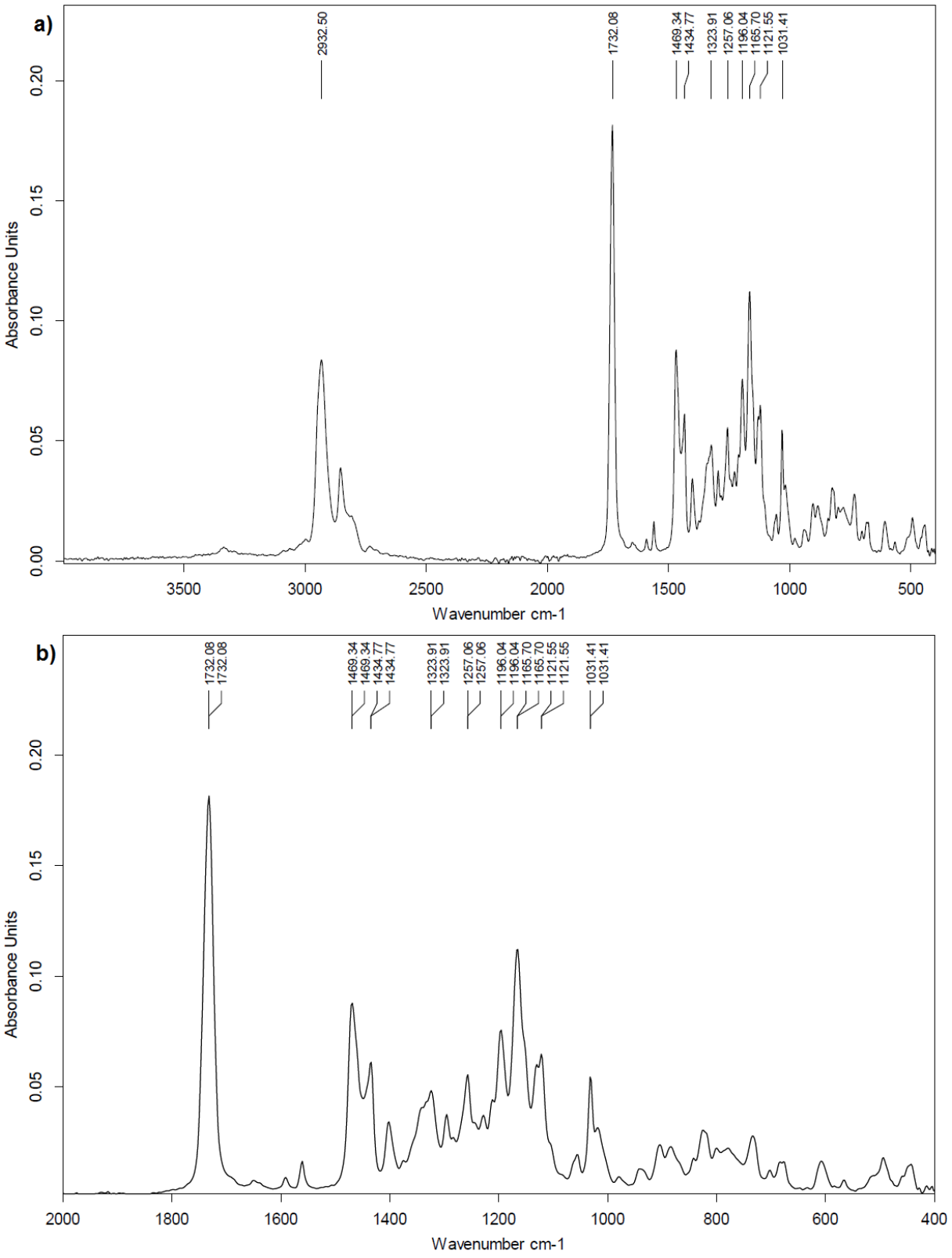


Figure S 49: IR spectrum of **3 free base** (a) and enlarged fingerprint region (b) for identification.

Ethylphenidate 4 HCl and free base

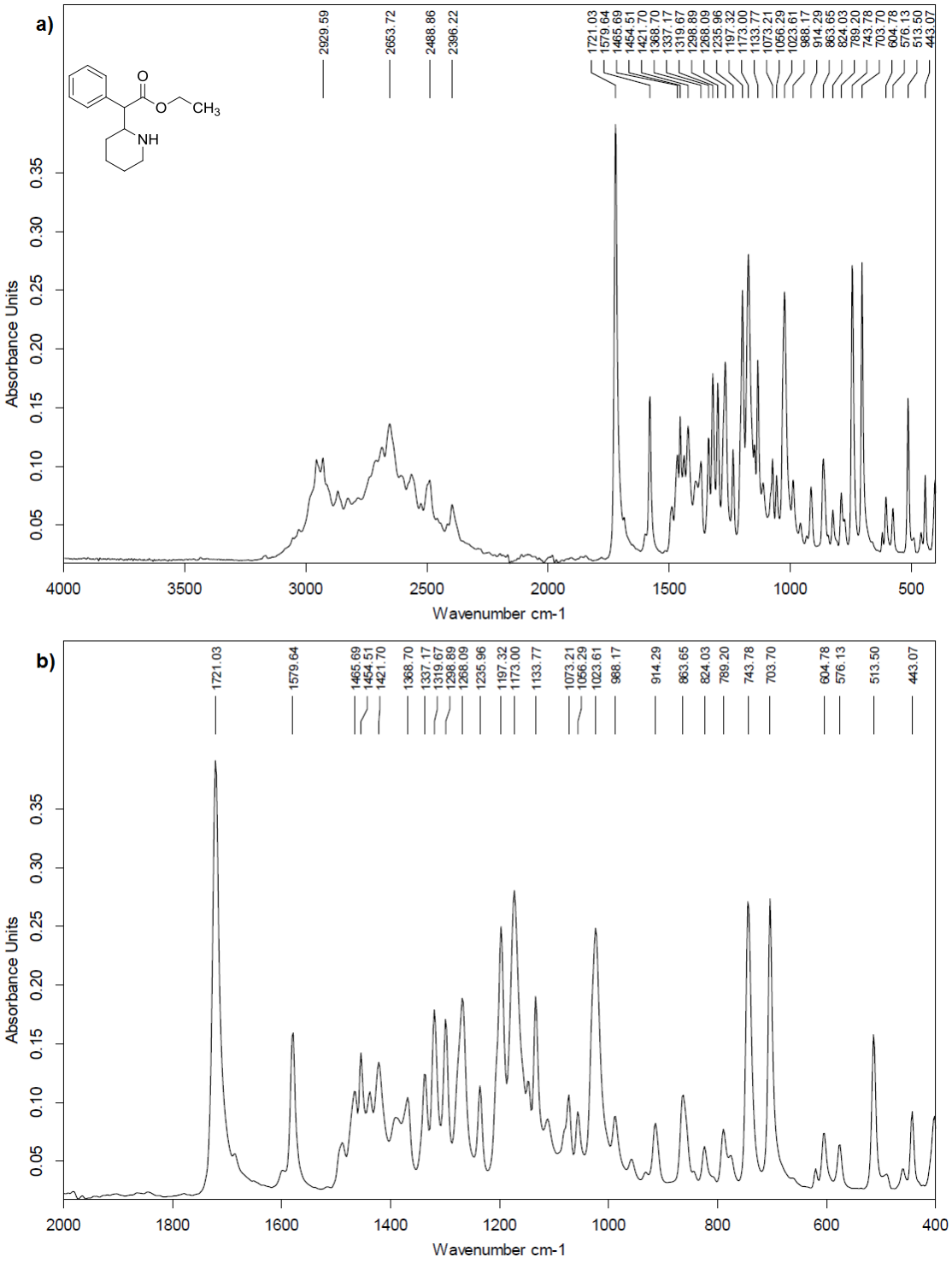


Figure S 50: IR spectrum of **4 HCl** (a) and enlarged fingerprint region (b) for identification.

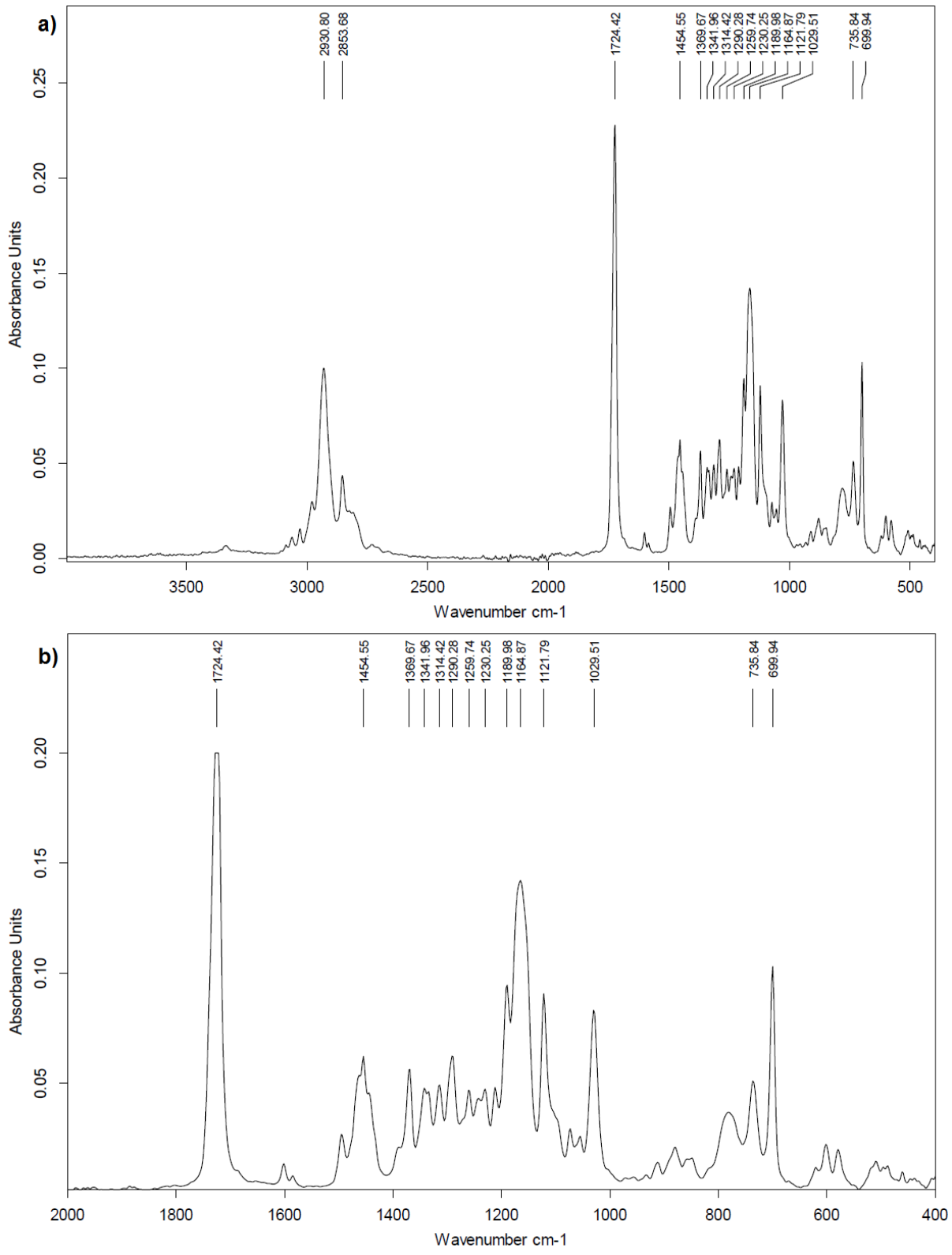


Figure S 51: IR spectrum of **4 free base** (a) and enlarged fingerprint region (b) for identification.

3,4-dichloroethylphenidate 5 HCl and free base

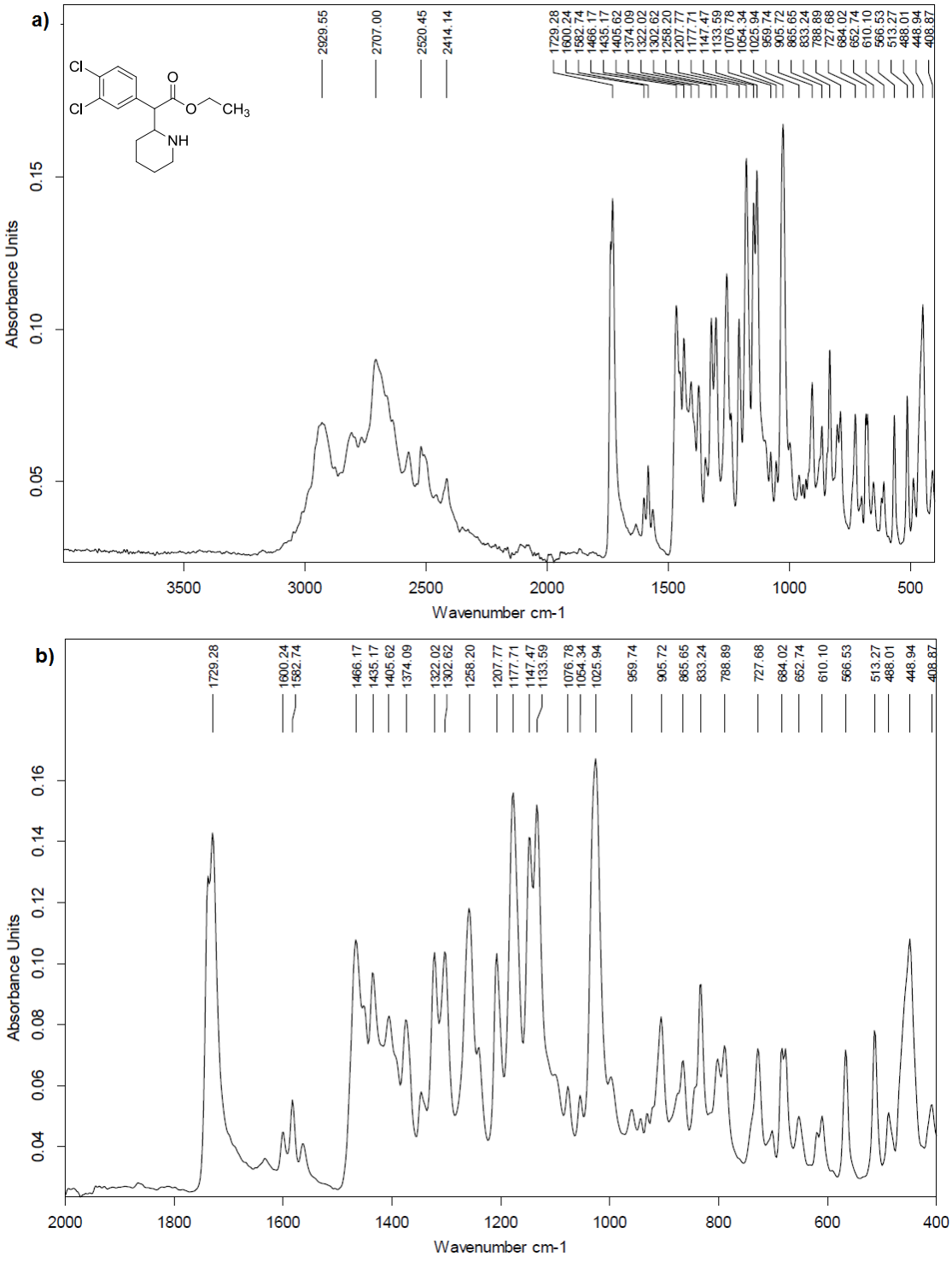


Figure S 52: IR spectrum of **5 HCl** (a) and enlarged fingerprint region (b) for identification.

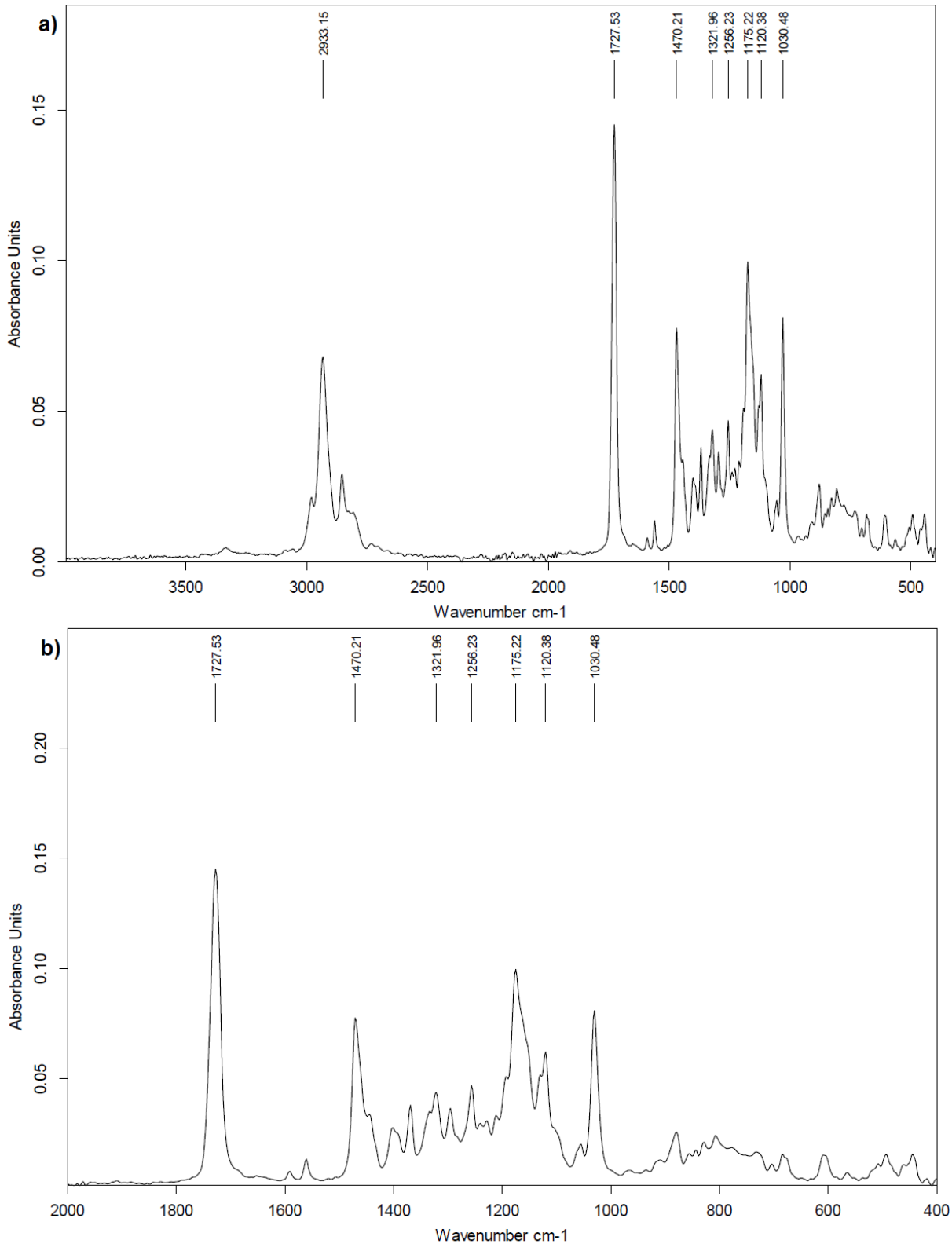


Figure S 53: IR spectrum of **5 free base** (a) and enlarged fingerprint region (b) for identification.

Ethylnaphthidate 6 HCl and free base

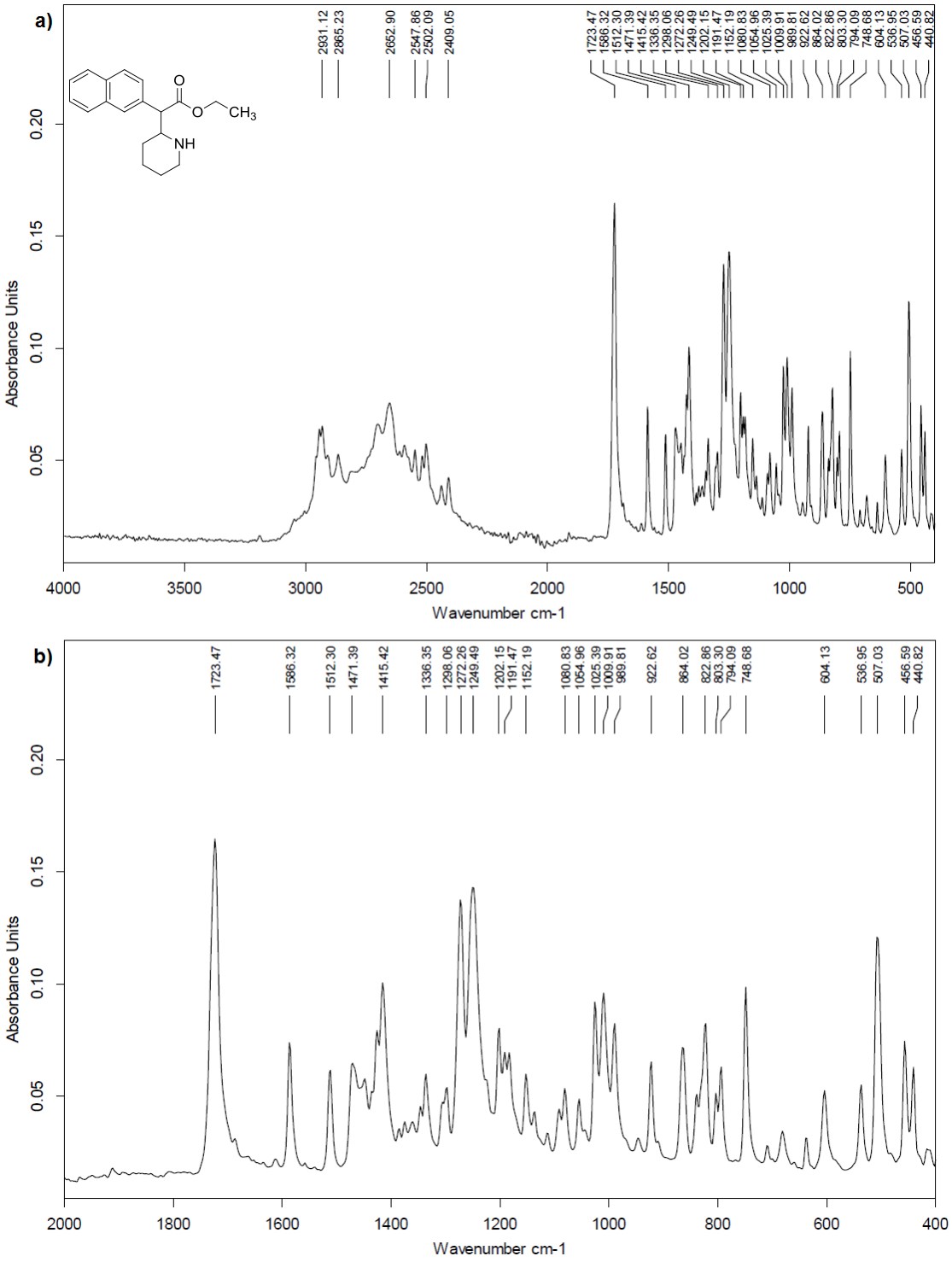


Figure S 54: IR spectrum of **6 HCl** (a) and enlarged fingerprint region (b) for identification.

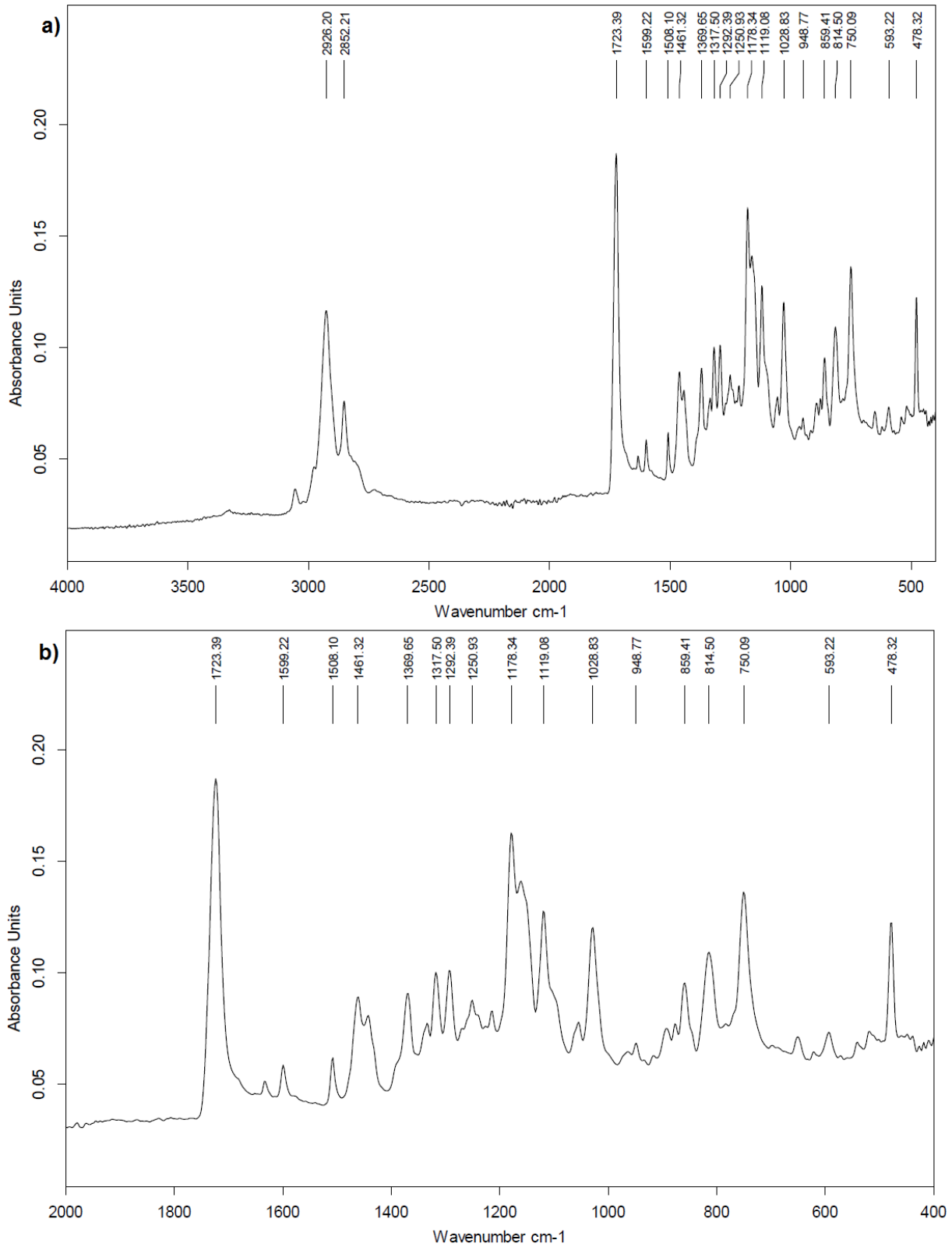


Figure S 55: IR spectrum of **6 free base**(a) and enlarged fingerprint region (b) for identification.

N-benzyl-Ethylphenidate 7 HCl and free base

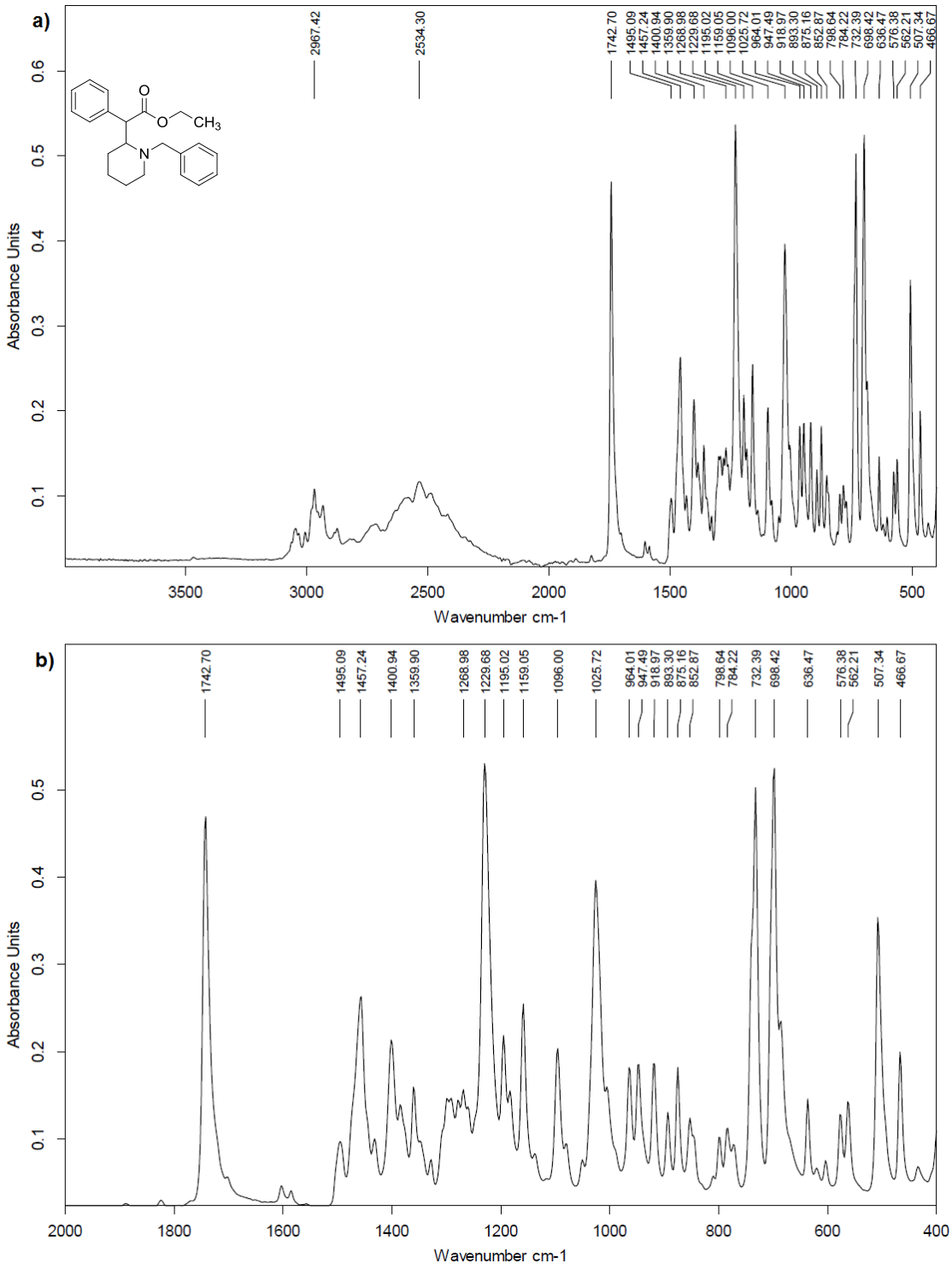


Figure S 56: IR spectrum of **7 HCl** (a) and enlarged fingerprint region (b) for identification.

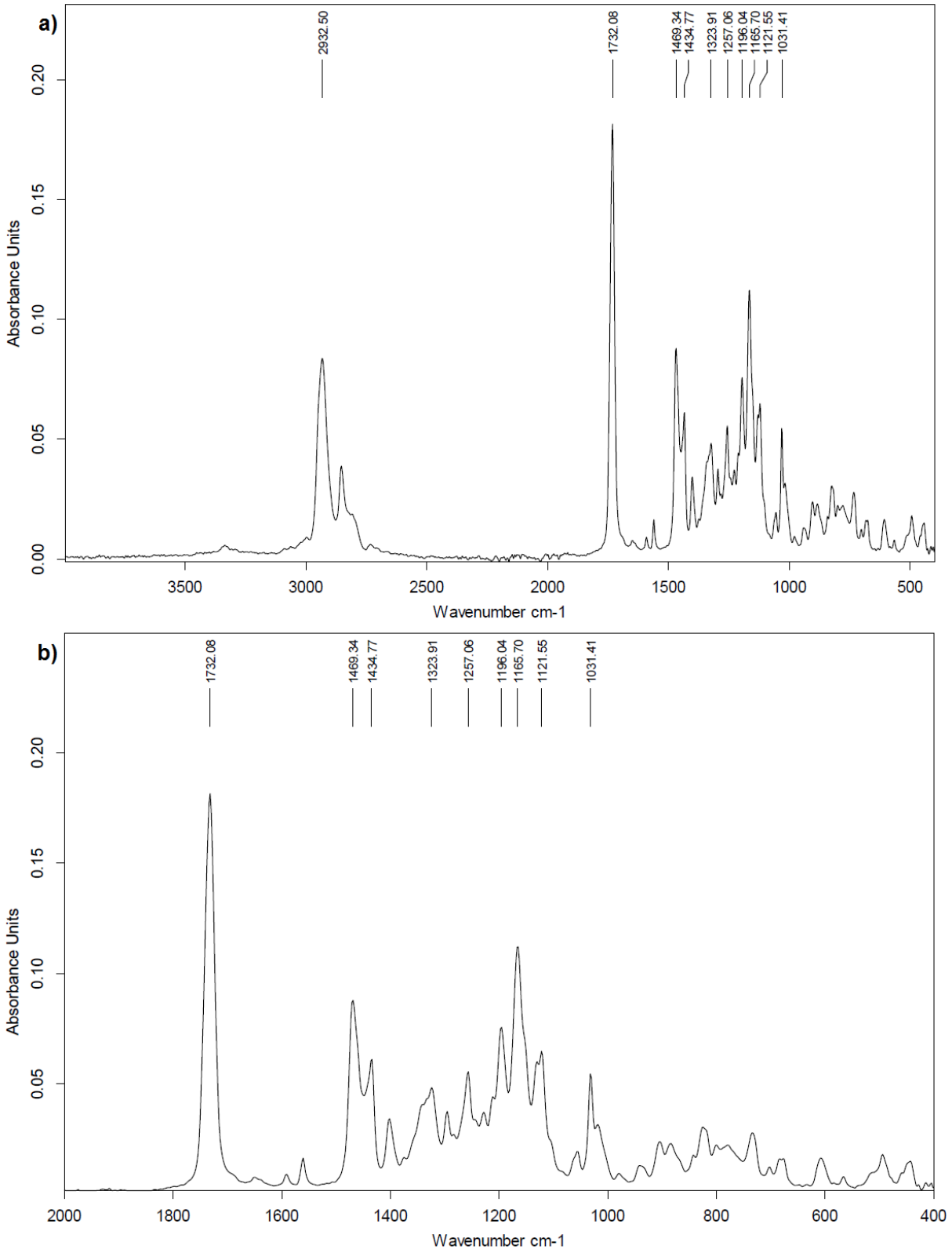


Figure S 57: IR spectrum of **7 free base** (a) and enlarged fingerprint region (b) for identification.

GC-sIR

Method (State Bureau of Criminal Investigation Schleswig-Holstein, Section Narcotics/Toxicology, Kiel, Germany)

The etheral extract of the alkalized watery solution of the phenidates was measured on a GC-solid phase-IR-system consisting of an Agilent GC 7890B (Waldbronn, Germany) with probe sampler Agilent G4567A and a DiscovIR-GC™ (Spectra Analysis, Marlborough, Massachusetts, USA). The column eluent was cryogenically accumulated on a spirally rotating ZnSe disk that was cooled by liquid nitrogen. The IR spectra were directly recorded through the IR-transparent ZnSe disk using a nitrogen cooled MCT detector. GC parameters: the injection was carried out in splitless mode with an injection port temperature of 200 °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; oven temperature program: 60 °C for 1 min, ramped to 220 °C at 5 °C/min, and held at the final temperature for 10 min. The transfer line heater was set at 240 °C. Infrared conditions: oven temperature, restrictor temperature, disc temperature, and dewar cap temperatures were 240 °C, 240 °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^{-1} and IR range 650–4000 cm^{-1}. Acquisition time was 6s/file with 64 scans/spectrum. Data were processed using GRAMS/AI Ver. 9.1 (Grams Spectroscopy Software Suite, Thermo Fischer Scientific) followed by implementation of the OMNIC Software, Ver. 7.4.127 (Thermo Electron Corporation).

3,4-dichloromethylphenidate 3 free base

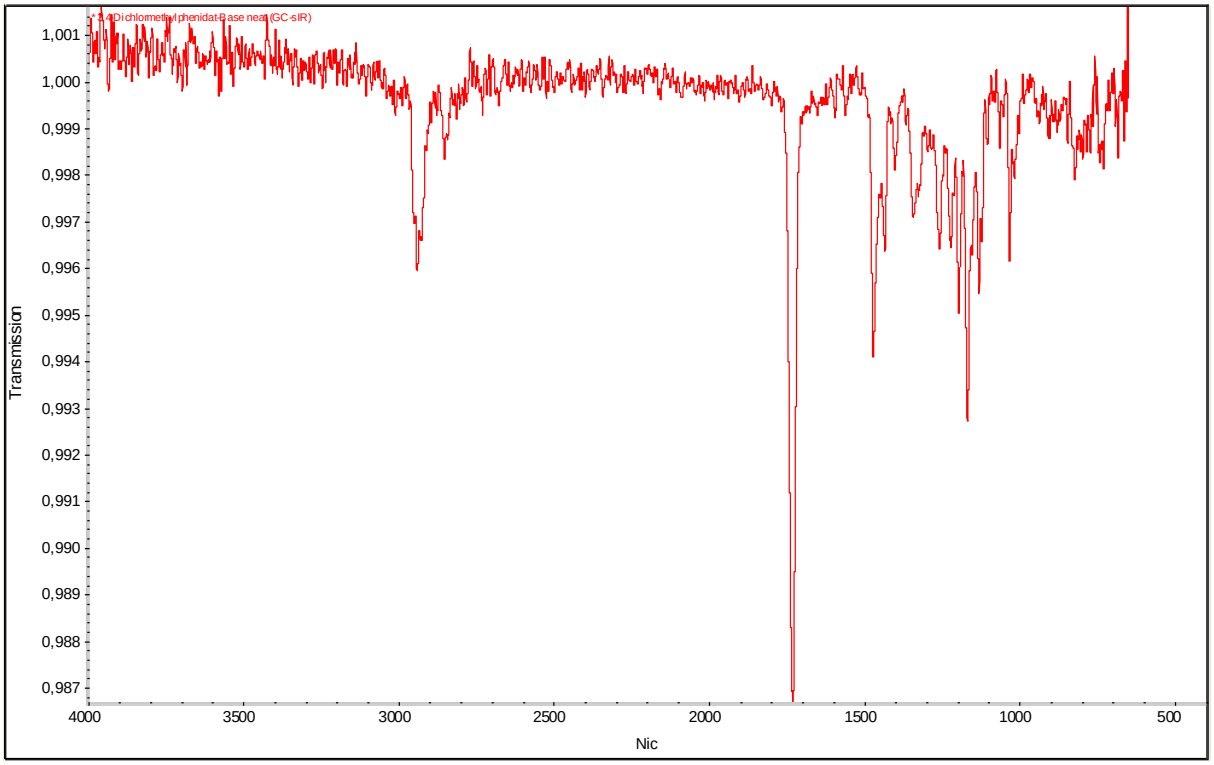


Figure S 58: 3,4-dichloromethylphenidate-base **3** neat (GC-sIR)

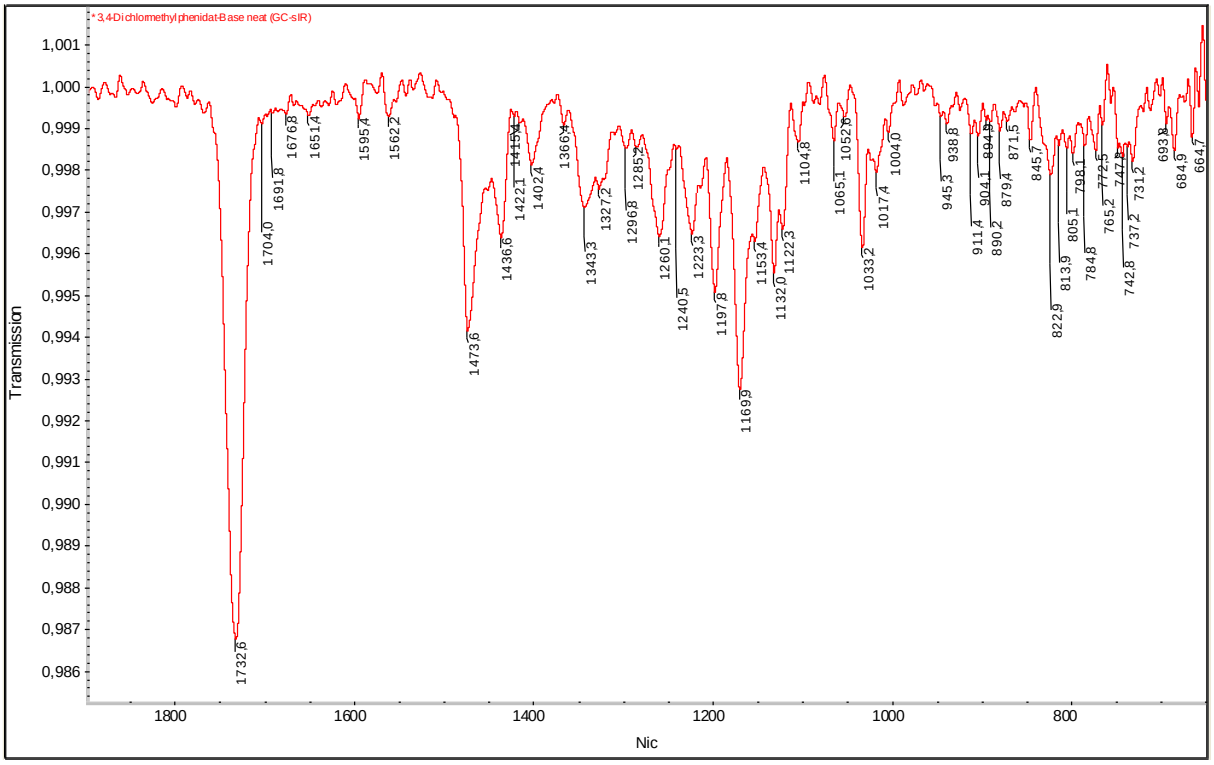


Figure S 59: 3,4-dichloromethylphenidate-base **3** neat (GC-sIR, cutout)

Ethylphenidate 4 free base

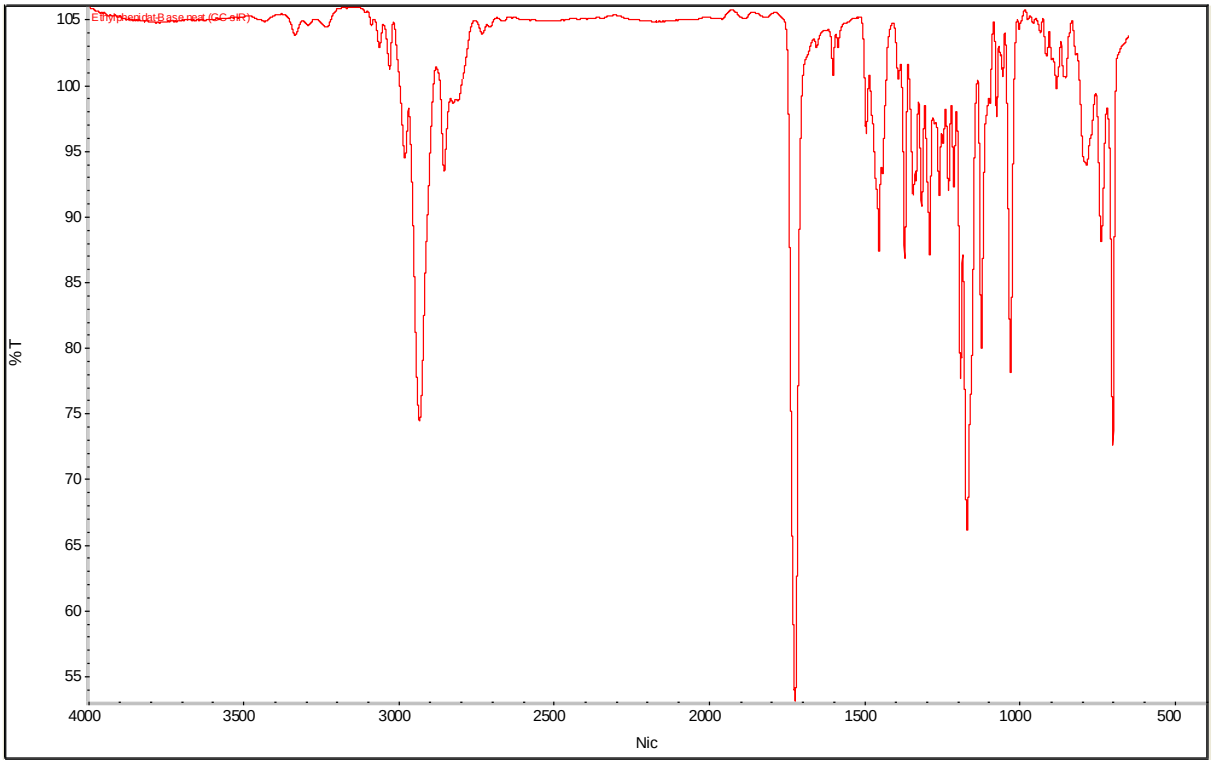


Figure S 60: Ethylphenidate-base **4** neat (GC-sIR)

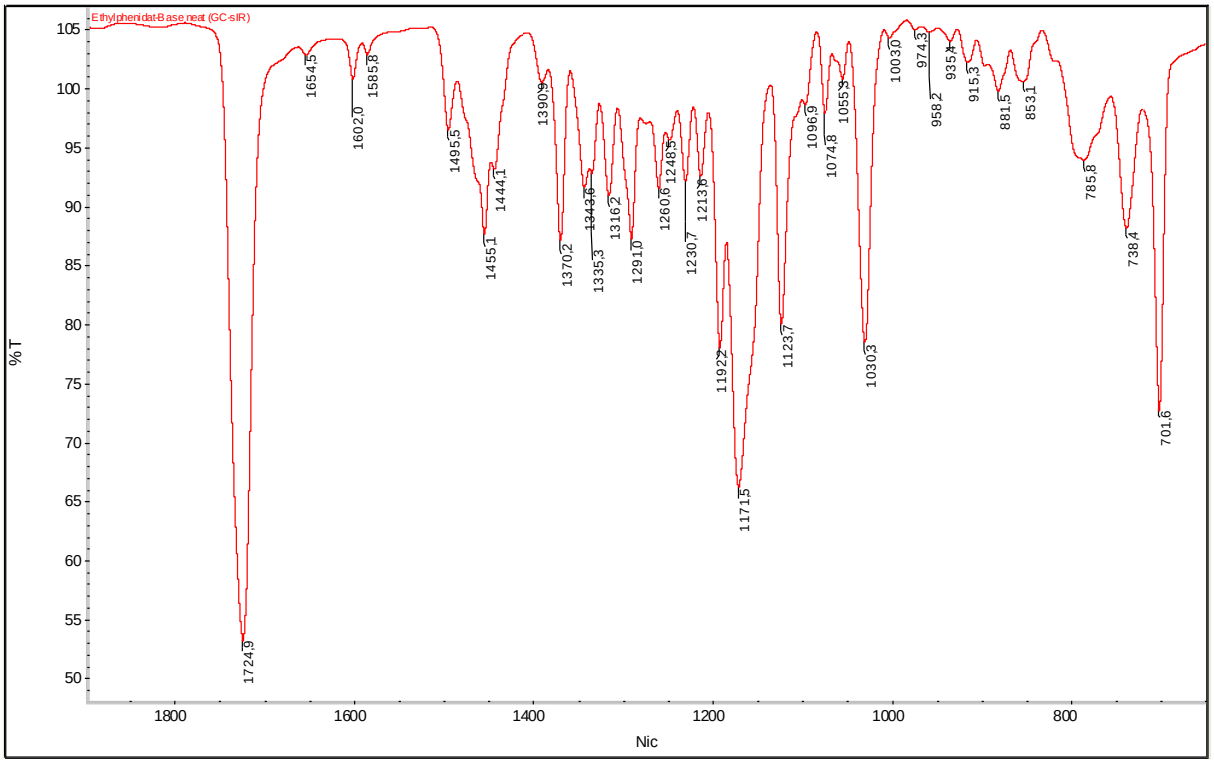


Figure S 61: Ethylphenidate-base **4** neat (GC-sIR, cutout)

3,4-dichloroethylphenidate 5 free base

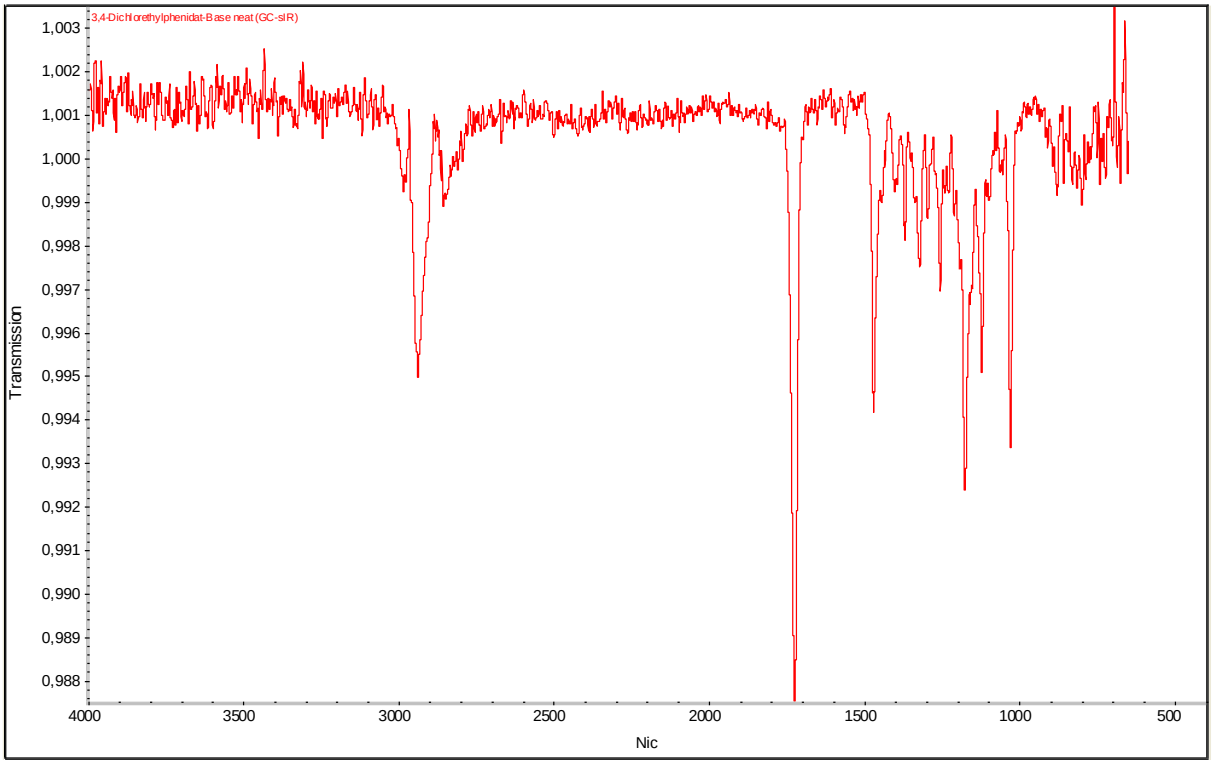


Figure S 62: 3,4-Dichloroethylphenidate-base **5** neat (GC-sIR)

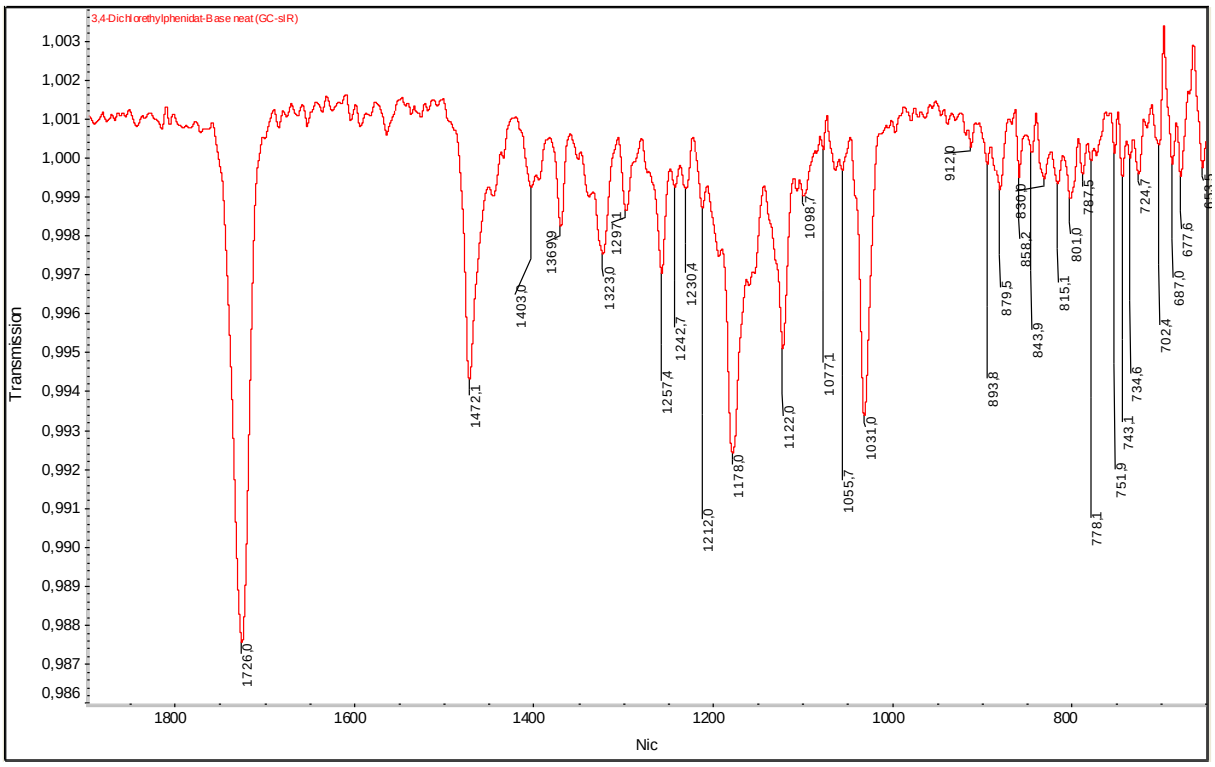


Figure S 63: 3,4-Dichloroethylphenidate-base **5** neat (GC-sIR, cutout)

N-benzyl-ethylphenidate 7 free base

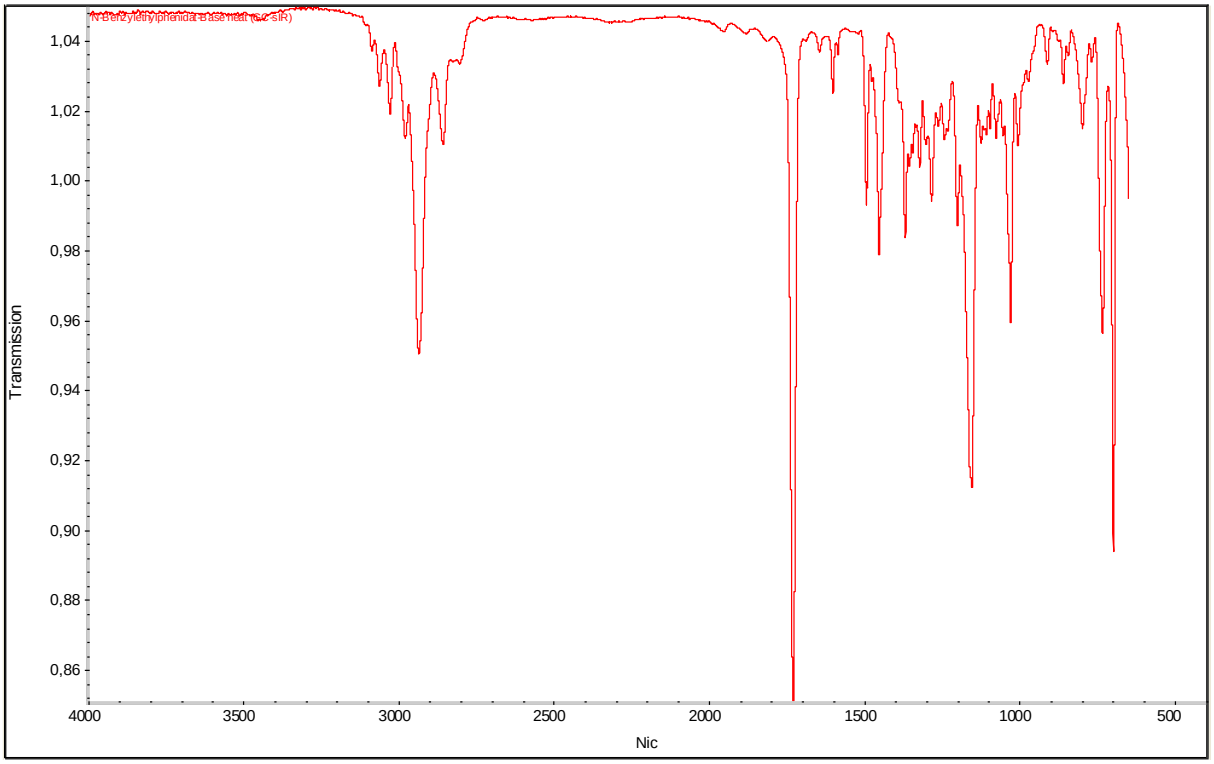


Figure S 64: *N*-benzyl-ethylphenidate **7** neat (GC-sIR)

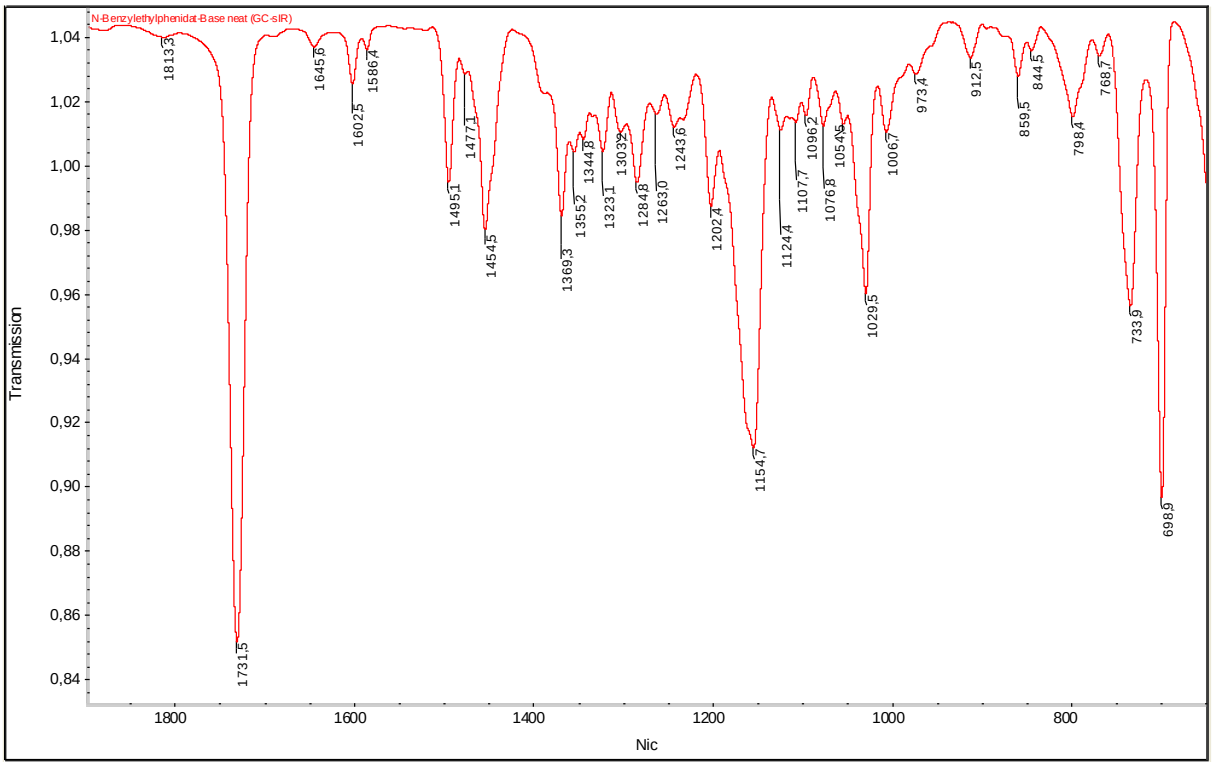


Figure S 65: *N*-benzyl-ethylphenidate-base **5** neat (GC-sIR)

Theoretical

Graphical illustration of computed *N*-benzyl-ethylphenidate conformers

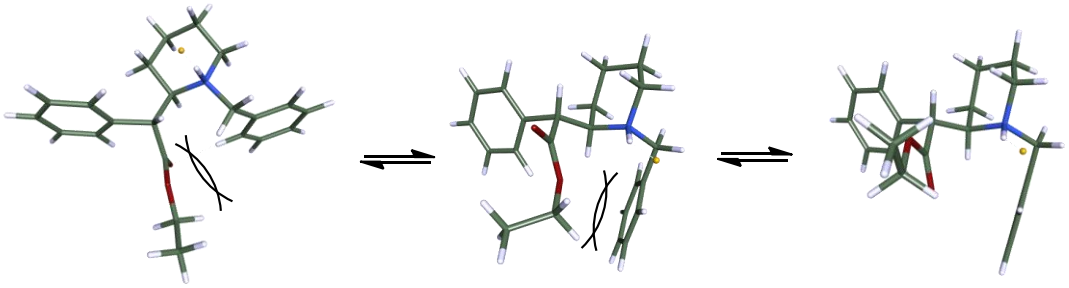


Figure S 66: Computed relative lowest energy conformers of *N*-benzyl-ethylphenidate **7** HCl in gas phase, steric strain between the ester- and *N*-benzyl moieties make *eq*-**7**-1 and *ax*-**7**-1 thermodynamically less favorable (BP86-D3(BJ)/def2-TZVP+ZPE).

Coordinates for stationary points

Eq-7-1

```
N 1.108253 -1.417747 0.402398
C 1.628488 -0.016684 0.451349
C 0.905638 0.816697 1.495505
C -0.592683 0.814812 1.207105
C -1.101218 -0.623888 1.198566
C -0.385962 -1.509978 0.173106
H 1.270284 -1.871617 1.455735
H 1.522733 0.423754 -0.551614
H 1.099190 0.394684 2.493873
H -0.788492 1.296156 0.232624
H -0.962643 -1.067042 2.197014
H -0.596842 -1.150891 -0.846540
C 1.980391 -2.269373 -0.487484
H 2.700780 -0.097737 0.674333
H 1.323036 1.833985 1.475001
H -1.136846 1.394833 1.965750
H -2.175410 -0.660714 0.978079
C -0.806835 -3.005759 0.297017
H -0.072005 -3.507179 0.944187
C -2.162095 -3.219914 0.962762
C -2.192067 -3.576976 2.317013
```

```
C -3.414128 -3.750098 2.968953
C -4.613874 -3.574515 2.274523
C -4.586649 -3.225368 0.921900
C -3.366127 -3.048789 0.267070
H -1.248507 -3.692849 2.855434
H -3.426976 -4.023022 4.024806
H -5.567931 -3.711758 2.785015
H -5.519328 -3.090335 0.372576
H -3.346843 -2.776212 -0.789076
O -0.435558 -4.983892 -0.945936
C -0.839731 -3.701619 -1.051979
O -1.215765 -3.192787 -2.096198
C -0.512101 -5.776496 -2.167704
C -0.002327 -7.162102 -1.838403
H -1.557453 -5.782634 -2.507529
H 0.089879 -5.279069 -2.941402
H 1.039263 -7.127558 -1.492503
H -0.613091 -7.630366 -1.055403
H -0.046986 -7.793713 -2.736355
H 1.473775 -3.229189 -0.631114
H 2.872643 -2.477662 0.119850
C 2.370979 -1.637092 -1.798205
C 3.674544 -1.147207 -1.960880
C 4.067491 -0.537094 -3.152903
C 3.154498 -0.405826 -4.201502
C 1.855418 -0.897846 -4.052952
C 1.464910 -1.514600 -2.862841
H 4.389295 -1.249650 -1.141623
H 5.086830 -0.165251 -3.262521
H 3.456820 0.071489 -5.134264
H 1.140633 -0.809338 -4.871922
H 0.453558 -1.911172 -2.768814
Cl 1.498325 -2.650173 2.967496
```

Ax-7-1

```
N 0.459313 -1.202493 0.173679
C 1.434891 -0.166702 -0.320824
C 1.150788 1.181826 0.353365
C -0.293235 1.646063 0.145924
C -1.274601 0.572436 0.628231
C -0.969843 -0.780626 -0.002481
C 1.427128 -0.077750 -1.860831
H 1.360500 1.091487 1.430425
H -0.468285 1.858674 -0.920865
H -1.234269 0.498544 1.726686
H -1.154673 -0.770826 -1.084829
H 0.481665 -2.198810 -0.404123
H 2.421586 -0.530425 -0.014060
H 1.861719 1.920772 -0.038264
H -0.465191 2.590512 0.681538
H -2.310389 0.842468 0.377047
H -1.579943 -1.595486 0.406301
C 0.723231 -1.651111 1.592645
```

```
H 0.391013 -0.868679 2.285583
H 0.083624 -2.536770 1.712746
C 2.166696 -1.996484 1.835239
C 2.727376 -3.142804 1.251957
C 4.073935 -3.440800 1.458898
C 4.871337 -2.606757 2.248292
C 4.314715 -1.471855 2.842051
C 2.967033 -1.170788 2.635239
H 2.094811 -3.778875 0.625932
H 4.503568 -4.334978 1.005345
H 5.923946 -2.844691 2.406716
H 4.928161 -0.821978 3.467100
H 2.530716 -0.284800 3.101609
H 0.431119 0.192774 -2.232284
C 2.400863 0.990590 -2.333525
C 1.944259 2.060914 -3.110952
C 2.825809 3.053191 -3.545170
C 4.178133 2.983893 -3.205768
C 4.643733 1.913581 -2.436698
C 3.763130 0.921372 -2.005879
H 0.888703 2.111568 -3.384166
H 2.454691 3.879511 -4.152495
H 4.868789 3.757040 -3.543824
H 5.700706 1.847531 -2.175732
H 4.135870 0.078962 -1.422569
O 2.732155 -2.064126 -1.912541
C 1.777256 -1.384334 -2.581644
O 1.296166 -1.699944 -3.647989
C 3.139504 -3.335686 -2.503368
C 4.187988 -3.123826 -3.578532
H 3.530631 -3.902844 -1.650916
H 2.236612 -3.832952 -2.877140
H 4.523718 -4.099041 -3.960024
H 3.775032 -2.551191 -4.418121
H 5.063346 -2.592658 -3.179391
Cl 0.044498 -3.812762 -0.920528
```

Ax-7-2

```
N 0.361147 -1.078846 0.198401
C 1.433497 -0.144084 -0.303797
C 1.322448 1.211303 0.399050
C -0.066970 1.836212 0.254746
C -1.137891 0.870240 0.770669
C -1.017697 -0.491918 0.100456
C 1.388096 -0.076900 -1.847027
H 1.559687 1.072195 1.465815
H -0.258651 2.076174 -0.803822
H -1.049635 0.767198 1.863969
H -1.251286 -0.432720 -0.970551
H 0.253388 -2.022299 -0.440583
H 2.385222 -0.623979 -0.039909
H 2.096638 1.875777 -0.005233
H -0.111760 2.787684 0.802873
```

```
H -2.148807 1.258744 0.579011
H -1.698306 -1.241929 0.521969
C 0.616386 -1.626807 1.582456
H 0.374924 -0.854861 2.323189
H -0.104736 -2.451691 1.676814
C 2.023889 -2.118148 1.770015
C 2.502000 -3.206039 1.024980
C 3.817120 -3.637053 1.191732
C 4.660949 -2.999290 2.105288
C 4.186769 -1.921816 2.856683
C 2.873016 -1.482020 2.684522
H 1.842047 -3.692913 0.302171
H 4.185886 -4.474115 0.598537
H 5.688904 -3.341461 2.231464
H 4.838751 -1.422043 3.574033
H 2.500406 -0.637396 3.268886
H 0.366928 0.101178 -2.205748
C 2.272096 1.034752 -2.383936
C 1.707417 2.100129 -3.094261
C 2.506778 3.141680 -3.570383
C 3.883896 3.125625 -3.341621
C 4.456790 2.058667 -2.643446
C 3.658206 1.018085 -2.169067
H 0.631938 2.108869 -3.281857
H 2.052440 3.964331 -4.123922
H 4.510367 3.937622 -3.712253
H 5.533531 2.033887 -2.471598
H 4.108134 0.175480 -1.642490
O 1.158036 -1.726606 -3.524219
C 1.868691 -1.409456 -2.435163
O 2.805201 -2.044303 -1.986444
C 1.434689 -3.040976 -4.100275
C 0.267790 -3.388006 -4.996284
H 2.389925 -2.979891 -4.642610
H 1.533259 -3.748100 -3.267056
H 0.442533 -4.367828 -5.462839
H -0.652500 -3.447099 -4.400886
H 0.136828 -2.644135 -5.794268
Cl -0.370869 -3.514390 -1.132145
```

Coordinates for transition states

TS1

```
N -0.812421 -0.786549 -0.801861
C -0.686787 0.555290 -0.810576
C -1.891065 1.467433 -0.676211
C -3.187644 0.706810 -0.340156
C -2.882184 -0.466171 0.599025
C -1.915727 -1.442991 -0.081518
H 0.150392 0.933238 -1.418813
H -1.673819 2.236224 0.092591
H -3.647388 0.313139 -1.273296
H -2.436082 -0.080493 1.540688
H -2.472658 -2.078908 -0.806744
H 0.163084 -1.221944 -0.539426
```

C 0.669777 0.867178 1.101741
H -2.004888 2.029068 -1.629778
H -3.930937 1.397822 0.107129
H -3.808491 -1.005581 0.885799
H -1.465669 -2.136873 0.660921
H 0.966400 1.916098 1.248111
C 1.617560 -0.042100 0.563567
H -0.096151 0.455838 1.772039
O 1.383573 -1.255245 0.286385
O 2.807826 0.524840 0.176060
C 3.715446 -0.335679 -0.513025
H 3.975777 -1.225021 0.097296
H 4.621423 0.268414 -0.706063
H 3.293683 -0.696510 -1.474821

TS2

C -0.685085 -0.794068 -0.880122
C -0.901781 0.662681 -0.951220
N -2.081997 1.207818 -0.552676
C -3.025091 0.566567 0.368065
C -2.560099 -0.840372 0.767296
C -1.932816 -1.566994 -0.431406
H -0.342656 1.266895 -1.677915
H -4.022187 0.516830 -0.126738
H -1.798073 -0.770071 1.571984
H -2.679115 -1.647994 -1.255152
H -0.260046 -1.164664 -1.836393
C 0.774127 1.470709 0.709722
H -2.184911 2.217615 -0.666220
H -3.153092 1.203486 1.272490
H -3.423544 -1.396544 1.185817
H -1.656262 -2.603298 -0.150253
H 1.112821 2.477698 0.424361
C 1.647556 0.371806 0.567860
H -0.009997 1.386556 1.472161
O 1.331303 -0.825976 0.819188
O 2.853724 0.654168 -0.042638
C 3.680450 -0.470129 -0.326955
H 3.893272 -1.065875 0.585497
H 4.623030 -0.062797 -0.739067
H 3.215170 -1.152455 -1.071269
H 0.185496 -0.973615 -0.089786

TS3

N -0.803293 -0.752612 -1.036308
C -0.904729 0.711057 -1.042533
C -2.230554 1.276962 -0.643006
C -2.828322 0.661359 0.642086
C -2.457884 -0.836337 0.813581
C -2.015820 -1.480090 -0.498961
H -0.379590 1.166827 -1.896541
H -2.152326 2.379678 -0.575274
H -3.927749 0.792674 0.616223
H -1.641493 -0.962039 1.555600

H -2.810125 -1.436845 -1.271357
H 0.108929 -0.998761 -0.375285
C 0.648890 1.300493 0.632544
H -2.920104 1.094279 -1.504728
H -2.478403 1.233380 1.524697
H -3.313395 -1.416331 1.211778
H -1.721256 -2.538797 -0.367352
H 0.937417 2.342499 0.431569
C 1.640226 0.251509 0.405913
H -0.036542 1.128615 1.475067
O 1.321100 -0.965827 0.336223
O 2.884340 0.667894 0.235082
C 3.911501 -0.329772 -0.005918
H 3.959697 -1.038765 0.842293
H 4.852844 0.236627 -0.096723
H 3.695635 -0.884886 -0.938827
H -0.551708 -1.109595 -1.973963