

Carbazole-, Aspidofractinine-, and Aspidocarpamine-Type Alkaloids from *Pleiocarpa pycnantha*

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Table of Content

Figure S1: UV/vis spectrum of 1a in MeOH.	5
Figure S2: Stereo view of 2 in the DFT-calculated main conformation (Boltzmann factor = 0.353).	5
Figure S3: Stereo view of 2 , four DFT-calculated main conformations (Σ Boltzmann factors = 0.730).	6
Figure S4: Stereo view of 2 , two DFT-calculated minor conformations (Σ Boltzmann factors = 0.182).	6
Figure S5: ECD spectra of 2 ; green: exp. spectrum in methanol, blue = calculated spectrum of 2 , and experimental spectrum (red) of <i>N</i> ¹ -methylkopsinin in methanol for comparison.	7
Figure S6: UV/vis spectrum of 3a in Methanol.	7
Figure S7: Stereo view of 3a in the DFT-calculated main conformation (Boltzmann factor = 0.512).	8
Figure S8: ECD spectra of 3a , experimental in methanol (green) and calculated (blue), and of 3b (red) in MeOH.	8
Figure S9: UV/vis spectrum of 6 in Methanol.	9
Figure S10: Plot of $\Delta\delta$ values of experimental ¹³ C NMR shifts of 6 in CDCl ₃ minus calculated shifts for (15S,16S)- 6 [green line, $\sum abs(\delta_{exp} - \delta_{(16S)calcd}) = 19.0$] or (15S,16R)- 6 [red line, $\sum abs(\delta_{exp} - \delta_{(16R)calcd}) = 38.8$], respectively.	9
Figure S11: ECD spectra of 6 ; green = experimental spectrum in methanol, blue = calculated spectrum of (15S,16S)- 6 , orange = (15S,16R)- 6 .	10
Figure S12: Detail of the NOESY spectrum of 6 : Correlations of H-15 with H-16, in comparison with H15 / CH _{2α,β} -14.	10
Figure S13: Main conformations of (16S)- 6 (left figure, H-12/H-16 distance 2.53 Å) and of the nonnatural (16R)- 6 (right, H-12/H-16 distance 3.28 Å).	11
Figure S14: Crystal structure of 5 .	12
Figure S15: Crystal structure of 13 .	16
Figure S16: ¹ H NMR spectrum (300 MHz, Methanol- <i>d</i> ₄) of 1a .	21
Figure S17: ¹³ C NMR spectrum (125 MHz, Methanol- <i>d</i> ₄) of 1a .	22
Figure S18: ¹ H, ¹ H COSY spectrum (600 MHz, Methanol- <i>d</i> ₄) of 1a .	23
Figure S19: HSQC spectrum (600 MHz, Methanol- <i>d</i> ₄) of 1a .	24
Figure S20: HSQC spectrum (600 MHz, Methanol- <i>d</i> ₄) of 1a .	25
Figure S21: HSQC spectrum (600 MHz, Methanol- <i>d</i> ₄) of 1a .	26
Figure S22: ¹ H NMR spectrum (600 MHz, CDCl ₃) of 2 .	27
Figure S23: ¹³ C NMR spectrum (125 MHz, CDCl ₃) of 2 .	28
Figure S24: ¹ H, ¹ H COSY spectrum (600 MHz, CDCl ₃) of 2 .	29
Figure S25: HSQC spectrum (600 MHz, CDCl ₃) of 2 .	30
Figure S26: HMBC spectrum (600 MHz, CDCl ₃) of 2 .	31
Figure S27: NOESY spectrum (600 MHz, CDCl ₃) of 2 .	32

Figure S28: ^1H NMR spectrum (600 MHz, Methanol- d_4) of 3a	33
Figure S29: ^{13}C NMR spectrum (125 MHz, Methanol- d_4) of 3a	34
Figure S30: ^1H , ^1H COSY spectrum (600 MHz, Methanol- d_4) of 3a	35
Figure S31: HSQC spectrum (600 MHz, Methanol- d_4) of 3a	36
Figure S32: HMBC spectrum (600 MHz, Methanol- d_4) of 3a	37
Figure S33: NOESY spectrum (600 MHz, Methanol- d_4) of 3a	38
Figure S34: ^1H NMR spectrum (300 MHz, CDCl_3) of 6	39
Figure S35: ^{13}C NMR spectrum (125 MHz, CDCl_3) of 6	40
Figure S36: ^1H , ^1H COSY spectrum (600 MHz, CDCl_3) of 6	41
Figure S37: HSQC spectrum (600 MHz, CDCl_3) of 6	42
Figure S38: HMBC spectrum (600 MHz, CDCl_3) of 6	43
Figure S39: NOESY spectrum (600 MHz, CDCl_3) of 6	44

ABSTRACT: Three new alkaloids, janetinine (**1a**), pleiokomenine A (**2**), and huncaniterine B (**3a**), and 13 known compounds, pleiomutinin (**3b**), huncaniterine A (**3c**), 1-carbomethoxy- β -carboline (**4**), exoxanthine (**5**), deformyltalbotine acid lactone (**6**), pleiocarpamine (**7**), N^4 -methyl-10-hydroxygeissoschizol (**8**), spegatrine (**9**), neosarpagine (**10**), aspidofractinine (**11**), N^1 -methylkopsinin (**12**), pleiocarpine (**13**), and N^1 -methylkopsinin- N^4 -oxide (**14**), were isolated from the stem bark of *Pleiocarpa pycnantha*. Janetinine (**1a**) is a carbazole alkaloid; in pleiokomenine A (**2**), two aspidofractinine-type alkaloids are bridged by a methylene unit in an unprecedented way, and huncaniterine B (**3a**) is a pleiocarpamine-aspidofractinine type dimer. The structures and relative configurations of these compounds were elucidated on the basis of NMR and MS analyses. Their absolute configurations were defined by means of experimental and calculated ECD data, and additionally, the structures of **5** and **13** were determined by X-ray diffraction data analysis. Compounds **1a**, **2**, **3b**, **4**, **6**, **9**, and **12** displayed cancer chemopreventive properties through either quinone reductase induction ($C_D = 30.7, 30.2, 29.9, 43.5$, and $36.7 \mu\text{M}$ for **1a**, **4**, **6**, **9**, and **12**, respectively), and/or NF- κ B inhibition with IC_{50} values of $13.1, 8.4, 9.4$, and $8.8\mu\text{M}$ for **2**, **3b**, **6**, and **12**, respectively.

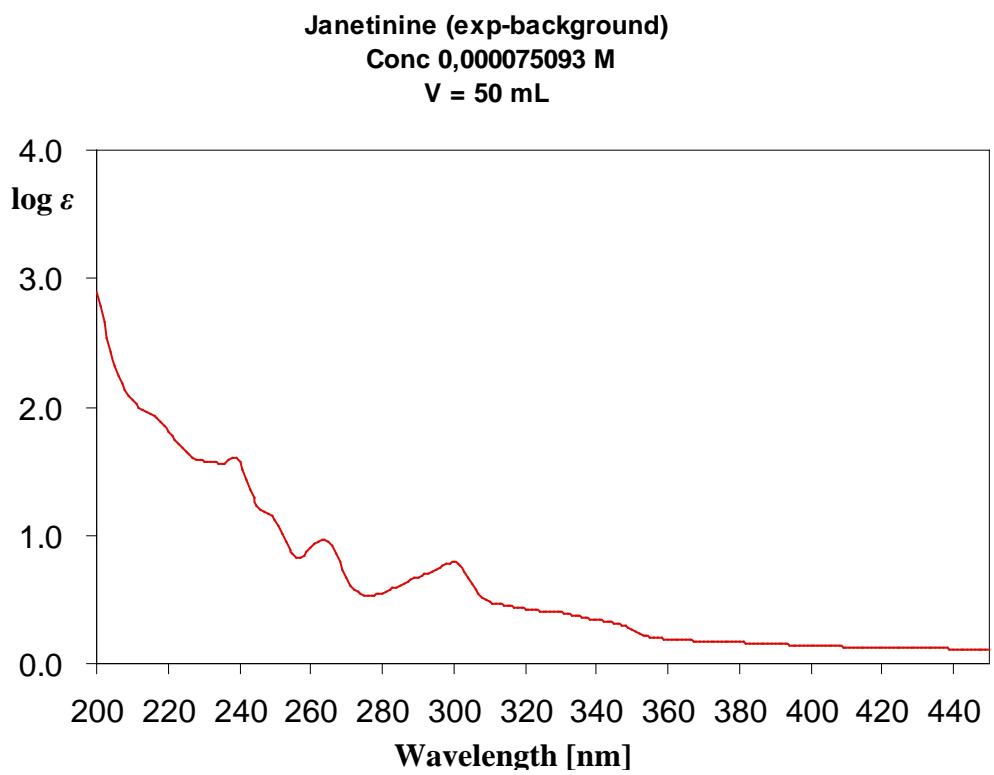


Figure S1: UV/vis spectrum of **1a** in MeOH.

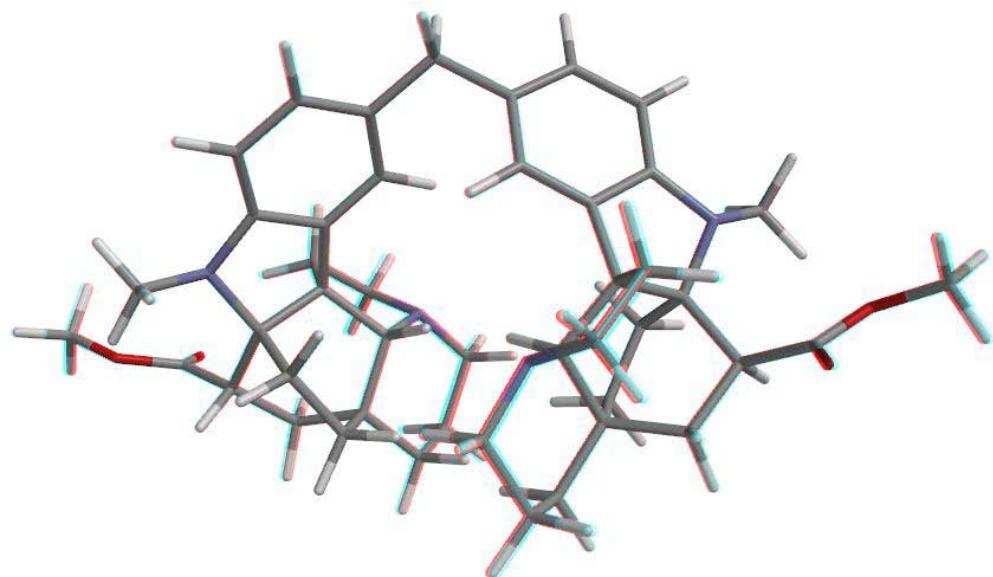


Figure S2: Stereo view of **2** in the DFT-calculated main conformation (Boltzmann factor = 0.353)

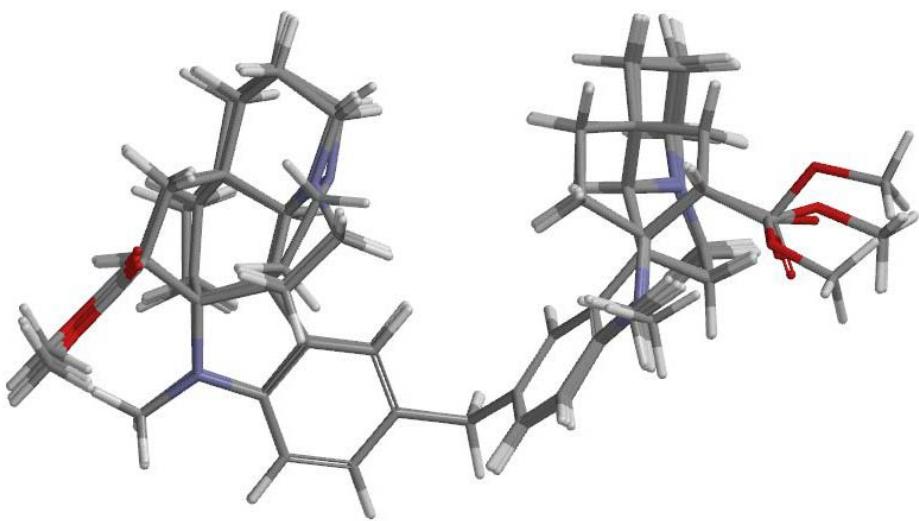


Figure S3: Stereo view of **2**, four DFT-calculated main conformations (Σ Boltzmann factors = 0.730).

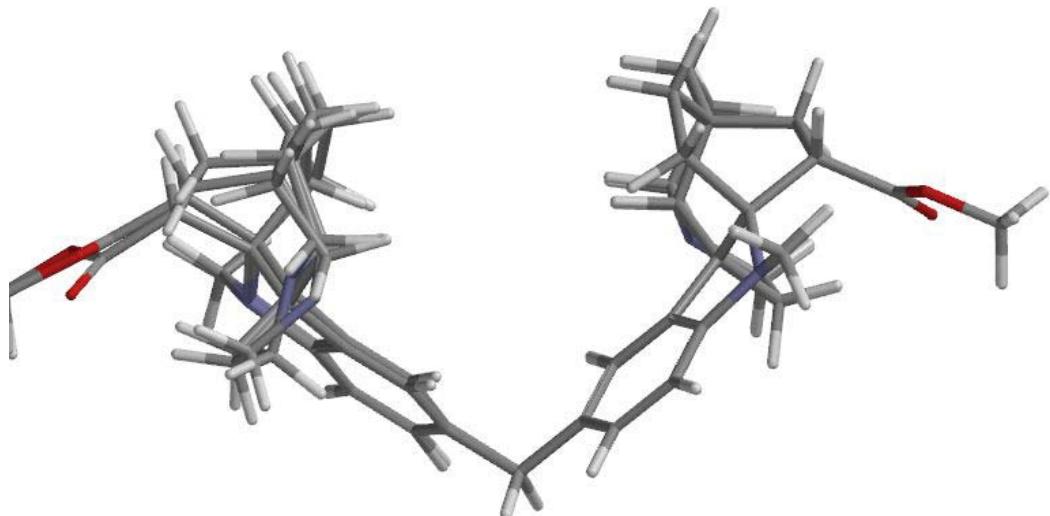


Figure S4: Stereo view of **2**, two DFT-calculated minor conformations (Σ Boltzmann factors = 0.182).

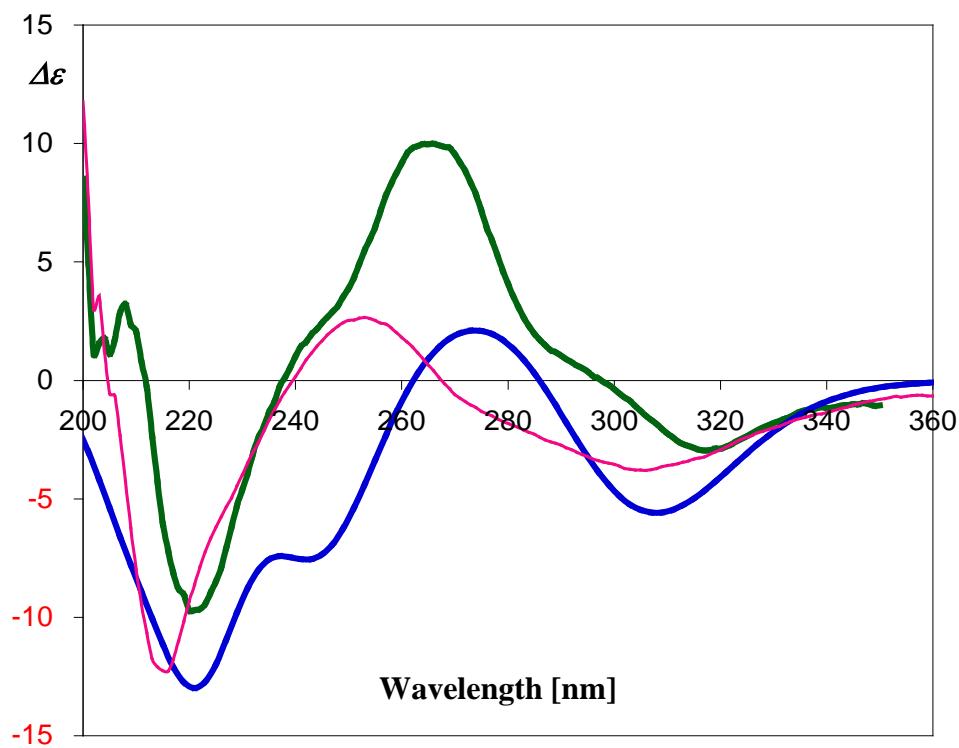


Figure S5: ECD spectra of **2**; green: exp. spectrum in methanol, blue = calculated spectrum of **2**, and experimental spectrum (red) of *N*¹-methylkopsinin in methanol for comparison.

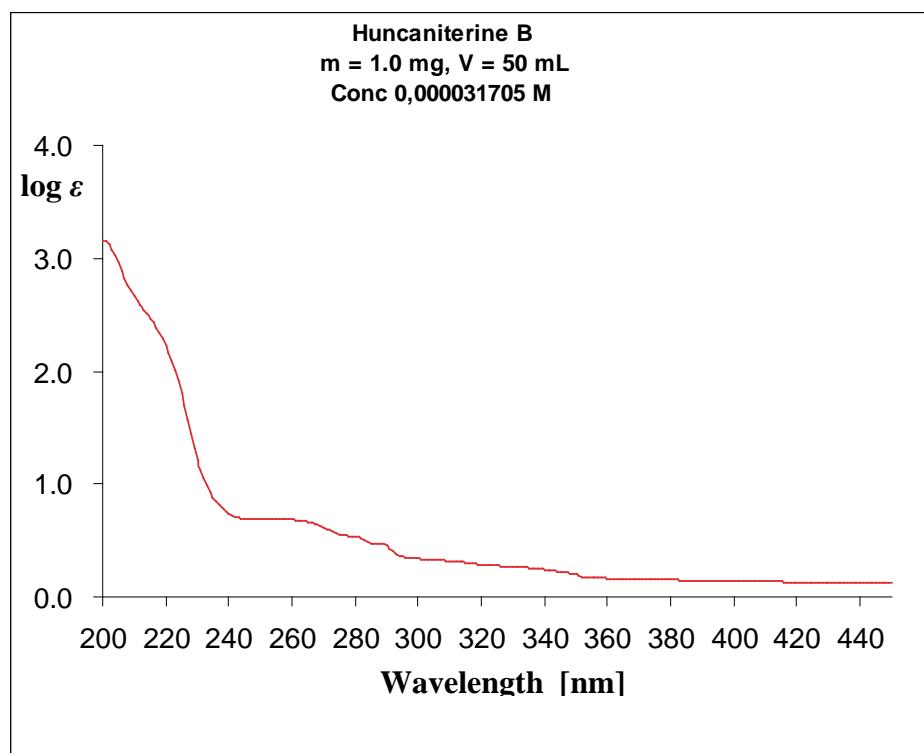


Figure S6: UV/vis spectrum of **3a** in Methanol

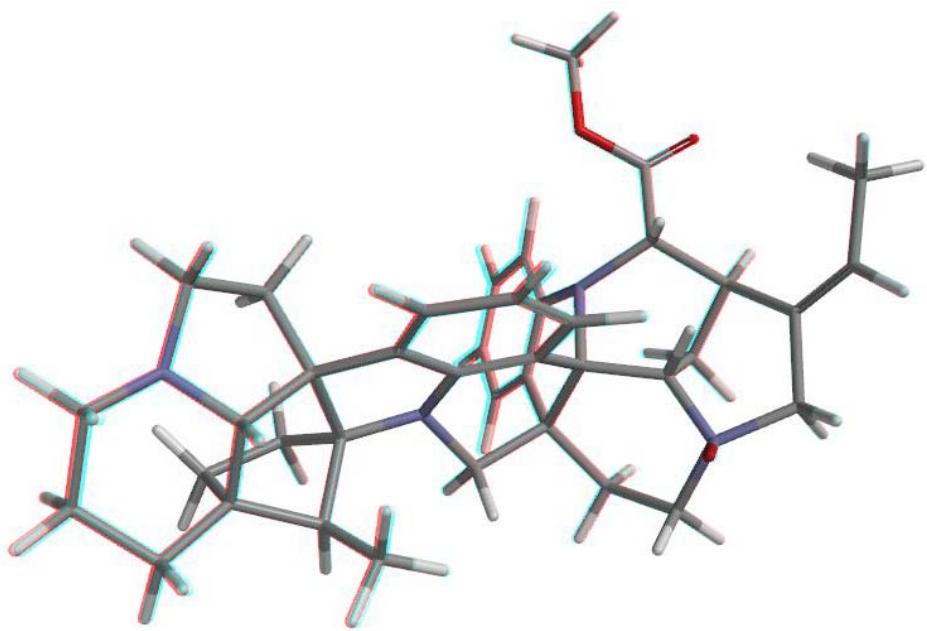


Figure S7: Stereo view of **3a** in the DFT-calculated main conformation (Boltzmann factor = 0.512).

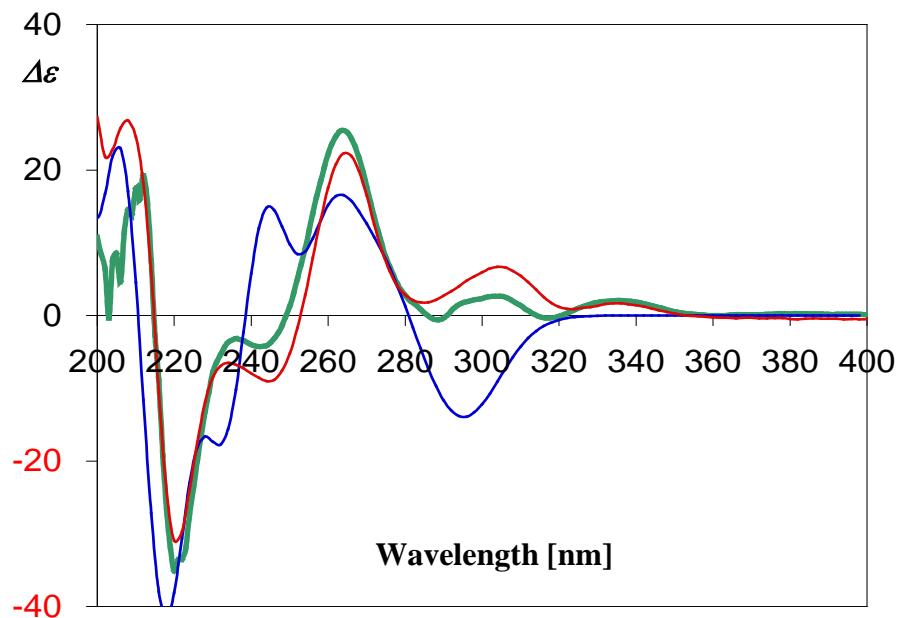


Figure S8: ECD spectra of **3a**, experimental in methanol (green) and calculated (blue), and of **3b** (red) in methanol

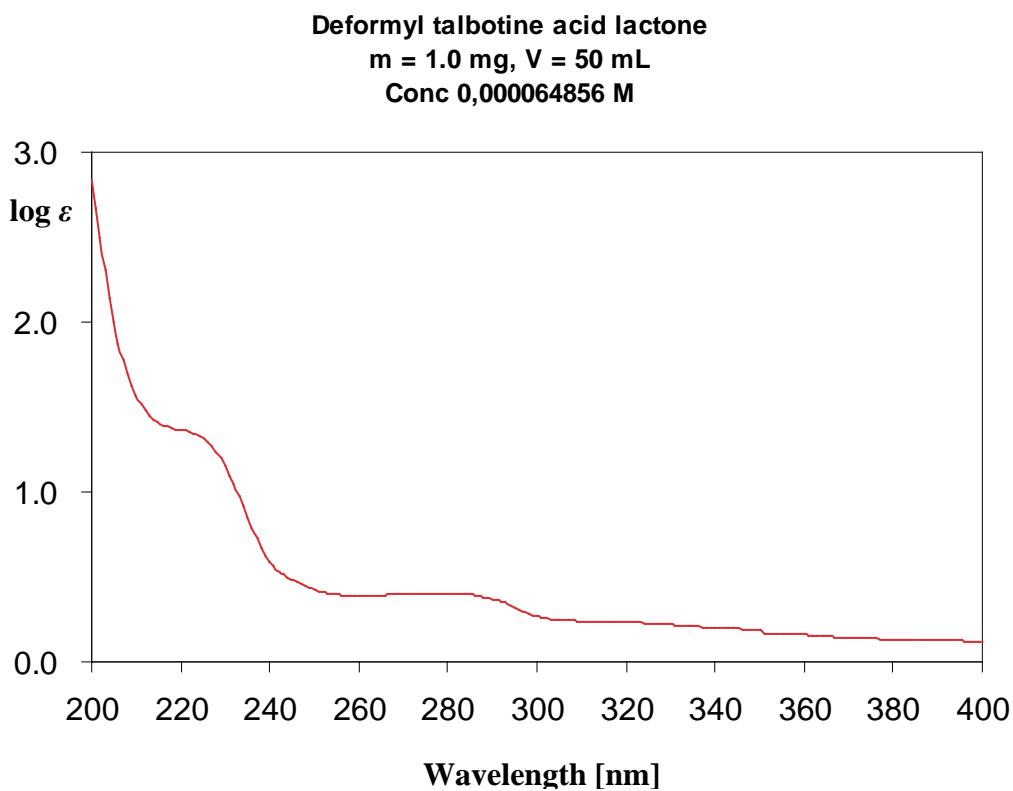


Figure S9: UV/vis spectrum of **6** in methanol.

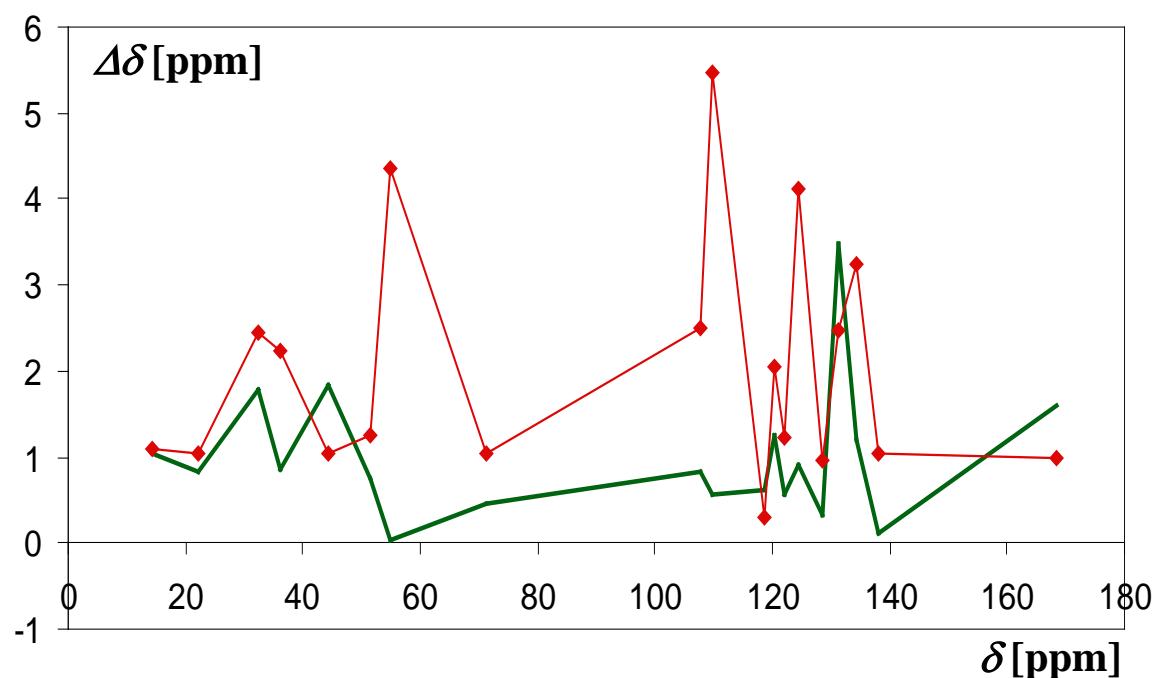


Figure S10: Plot of $\Delta\delta$ values of experimental ^{13}C NMR shifts of **6** in CDCl_3 minus calculated shifts for (15S,16S)-**6** [green line, $\sum \text{abs}(\delta_{\text{exp}} - \delta_{(16S)\text{calcd}}) = 19.0$] or (15S,16R)-**6** [red line, $\sum \text{abs}(\delta_{\text{exp}} - \delta_{(16R)\text{calcd}}) = 38.8$], respectively.

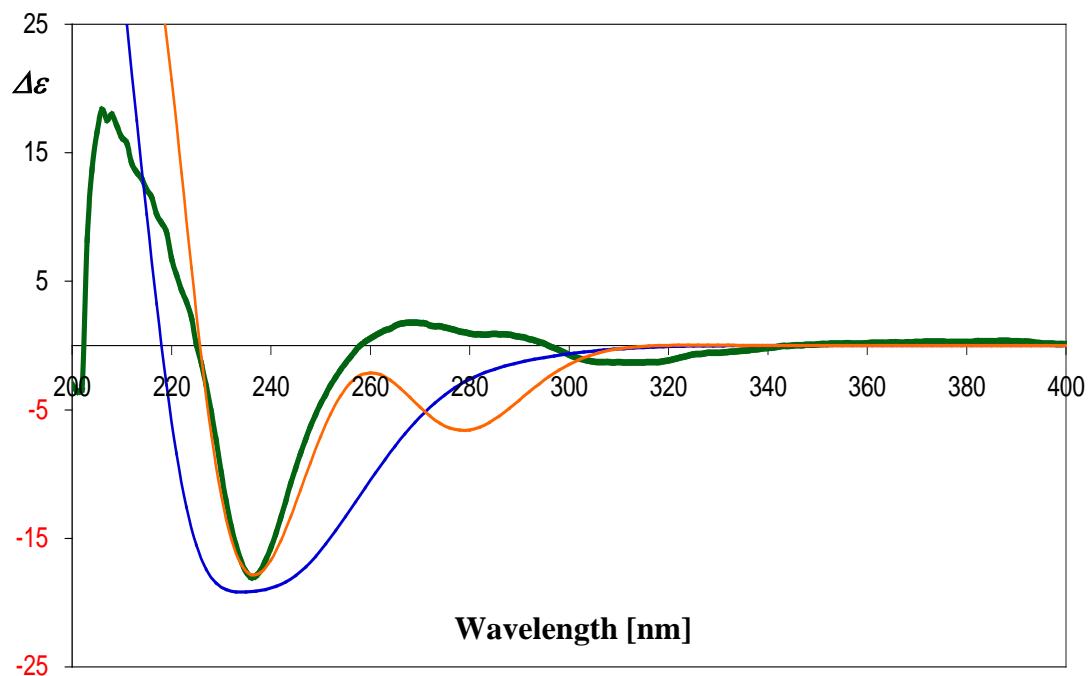


Figure S11: ECD spectra of **6**; green = experimental spectrum in methanol, blue = calculated spectrum of (15*S*,16*S*)-**6**, orange = (15*S*,16*R*)-**6**.

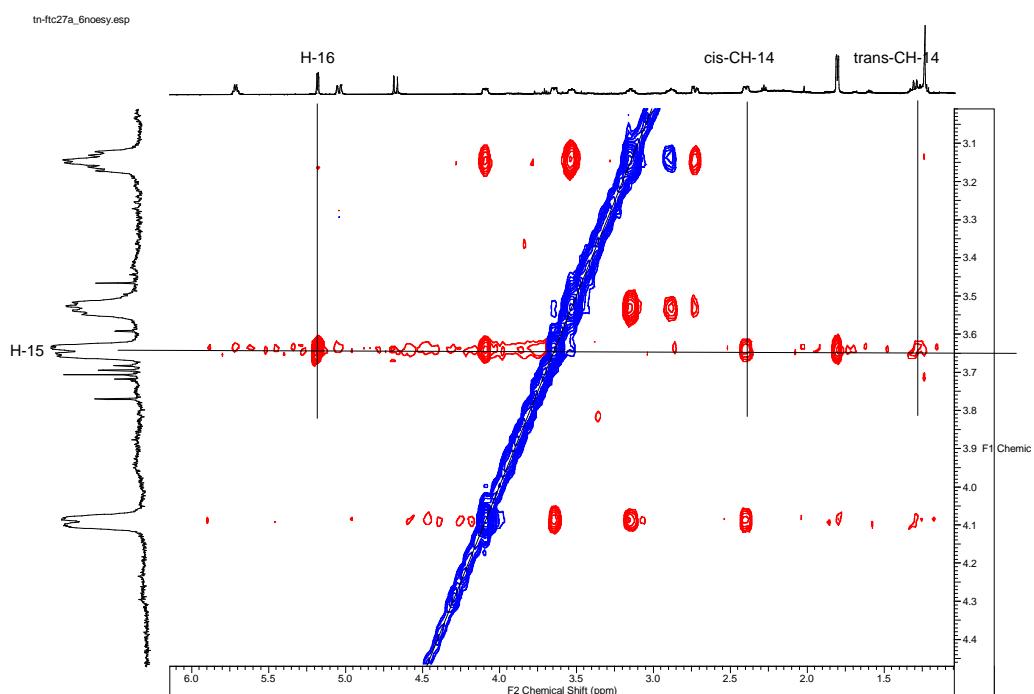


Figure S12: Detail of the NOESY spectrum of **6**: Correlations of H-15 with H-16, in comparison with H-15 / CH_{2α,β}-14

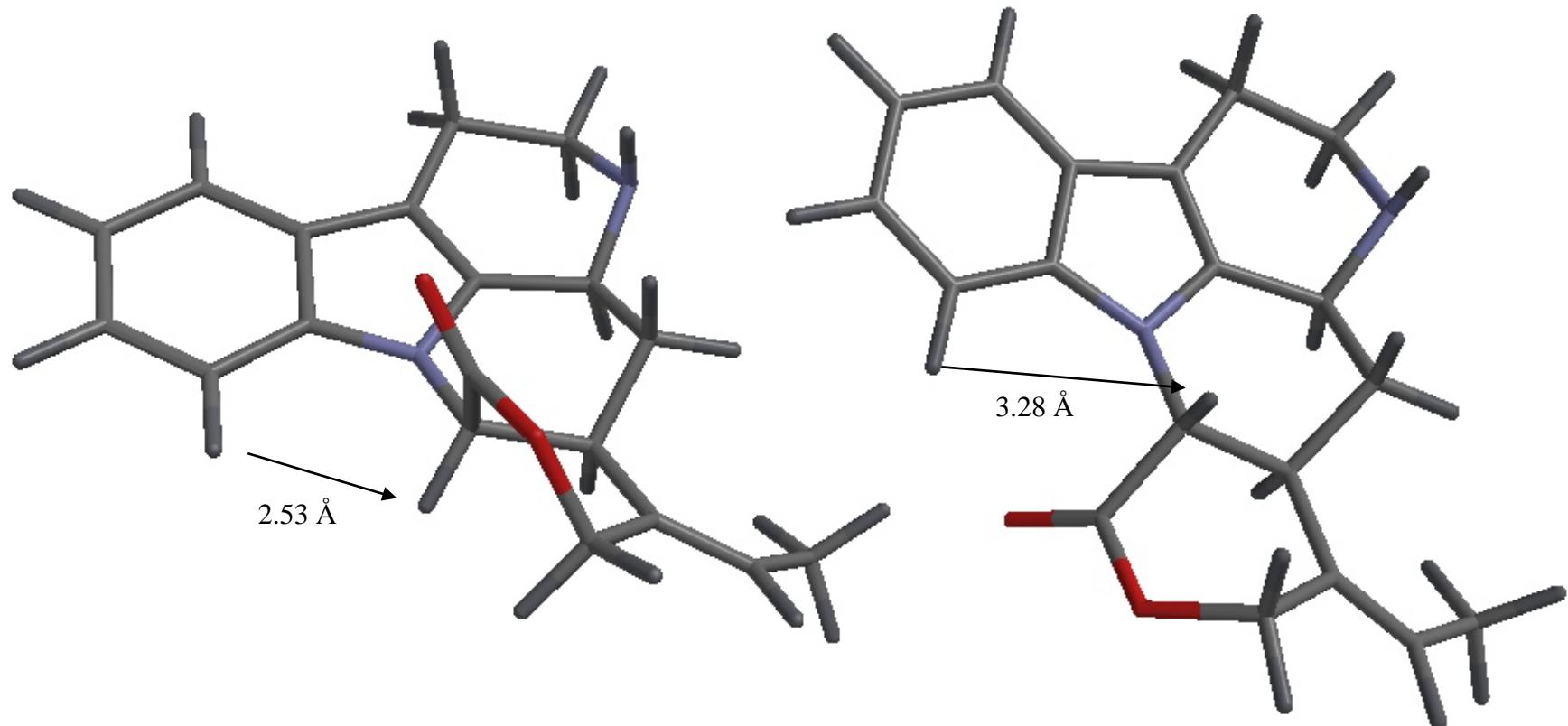


Figure S13: Main conformations of (16*S*)-6 (left figure, H-12/H-16 distance 2.53 Å) and of the nonnatural (16*R*)-6 (right, H-12/H-16 distance 3.28 Å)

Evoxanthine (5)

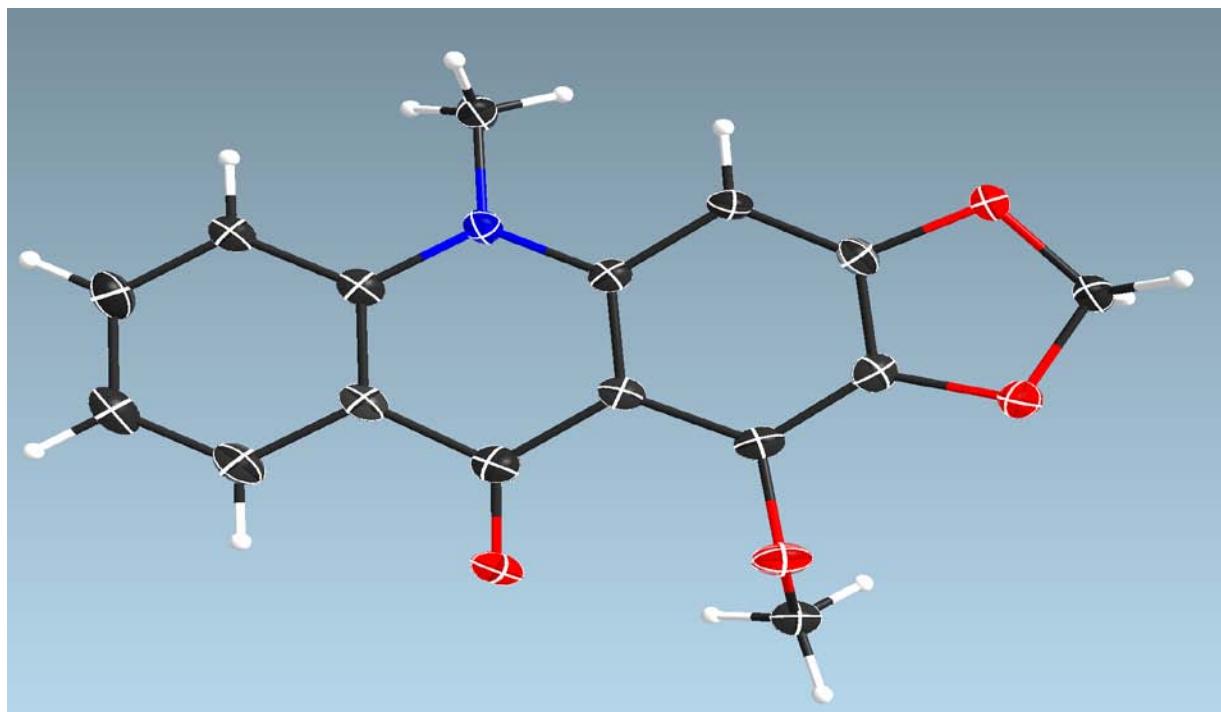


Figure S14: Crystal structure of **5**

Computing details for the crystal structure of 5

Data collection: *APEX2* v2014.11-0; cell refinement: *SAINT* V8.37A (Bruker AXS, 2013); data reduction: *SAINT* V8.37A (Bruker AXS, 2013); program(s) used to solve structure: The structure was known; program(s) used to refine structure: Volkov, A.; Macchi, P.; Farrugia, L. J.; Gatti, C.; Mallinson, P. R.; Richter, T. and Koritsanszky, T. (2006) XD2006 - a computer program for multipole refinement, topological analysis and evaluation of intermolecular energies from experimental and theoretical structure factors; molecular graphics: *ShelXle*, Hübschle, (2011); software used to prepare material for publication: *enCIFer* 1.5.1, CCDC, 2014.

References

NOT FOUND

Evoxanthine (5)

Crystal data

$C_{16}H_{13}NO_4$
 $M_r = 283.27$
Monoclinic, $P2_1/c$
 $a = 7.4572 (8) \text{ \AA}$
 $b = 8.9283 (10) \text{ \AA}$
 $c = 18.5642 (19) \text{ \AA}$
 $\beta = 92.91 (3)^\circ$
 $V = 1234.4 (2) \text{ \AA}^3$
 $Z = 4$

$F(000) = 592$
 $D_x = 1.524 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$
Cell parameters from 9258 reflections
 $\theta = 2.2\text{--}33.2^\circ$
 $\mu = 0.11 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
Plate
 $0.22 \times 0.09 \times 0.08 \text{ mm}$

Data collection

Huber Type 512 with Bruker APEX I diffractometer
Radiation source: INCOATEC Mo Microsource
 ϕ scans
Absorption correction: empirical (using intensity measurements)
SADABS 2015/1
 $T_{\min} = 0.516$, $T_{\max} = 0.747$

74625 measured reflections
4724 independent reflections
3677 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.099$
 $\theta_{\max} = 33.2^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -11 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
Least-squares matrix: full $R[F^2] > 2\sigma(F^2)] = 0.042$ $wR(F^2) = 0.08$
 $S = 1.87$
3677 reflections
203 parameters
0 restraints
0 constraints

Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from eighboring sites
 $w2 = /[\bar{s}^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for evoxanthine (5)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O(1)	0.93583 (11)	1.01502 (8)	0.38734 (3)	0.022
O(2)	0.85181 (11)	0.89529 (8)	0.28063 (3)	0.024
O(3)	0.74081 (10)	0.58727 (9)	0.27241 (3)	0.022
O(4)	0.63978 (13)	0.35347 (9)	0.35593 (4)	0.032
N(1)	0.78606 (11)	0.59506 (9)	0.53763 (4)	0.016
C(1)	0.89488 (15)	1.03880 (12)	0.31169 (5)	0.022
C(2)	0.87066 (13)	0.87690 (11)	0.40223 (5)	0.017
C(3)	0.82001 (13)	0.80410 (12)	0.33813 (4)	0.017
C(4)	0.76643 (13)	0.65778 (11)	0.33761 (4)	0.016
C(5)	0.75162 (13)	0.58314 (11)	0.40577 (5)	0.016
C(6)	0.69138 (14)	0.42803 (11)	0.40934 (5)	0.019
C(7)	0.69568 (13)	0.36109 (11)	0.48159 (5)	0.018
C(9)	0.65314 (16)	0.14117 (12)	0.55558 (6)	0.025
C(8)	0.64907 (15)	0.20957 (12)	0.48892 (6)	0.023
C(10)	0.70857 (16)	0.22397 (12)	0.61719 (6)	0.025
C(11)	0.75434 (14)	0.37299 (11)	0.61179 (5)	0.02
C(12)	0.74543 (13)	0.44526 (11)	0.54360 (5)	0.016
C(13)	0.79942 (13)	0.66210 (11)	0.47063 (4)	0.014
C(14)	0.86450 (13)	0.81146 (11)	0.46865 (4)	0.017
C(15)	0.81166 (16)	0.68371 (12)	0.60391 (5)	0.021
C(16)	0.56022 (14)	0.59093 (13)	0.24281 (5)	0.021
H(1A)	0.7814	1.1146	0.3040	0.028 (4)*
H(1B)	1.0095	1.0876	0.2863	0.026 (4)*
H(9)	0.6145	0.0249	0.5604	0.029 (4)*
H(8)	0.6091	0.1452	0.4414	0.023 (4)*
H(10)	0.7147	0.1702	0.6695	0.022 (4)*
H(11)	0.7976	0.4351	0.6596	0.017 (3)*
H(14)	0.9071	0.8708	0.5174	0.017 (3)*
H(15A)	0.9495	0.6730	0.6249	0.035 (4)*
H(15B)	0.7218	0.6432	0.6437	0.023 (4)*
H(15C)	0.7826	0.8005	0.5922	0.036 (4)*
H(16A)	0.5111	0.7065	0.2427	0.030 (4)*
H(16B)	0.4755	0.5213	0.2757	0.032 (4)*
H(16C)	0.5556	0.5481	0.1875	0.036 (4)*

*Atomic displacement parameters (\AA^2) for evoxanthine (**5**)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O(1)	0.0295 (4)	0.0243 (4)	0.0131 (3)	-0.0099 (3)	-0.0020 (3)	0.0030 (3)
O(2)	0.0294 (4)	0.0307 (4)	0.0106 (3)	-0.0076 (3)	0.0005 (3)	0.0002 (3)
O(3)	0.0183 (4)	0.0324 (4)	0.0143 (3)	0.0005 (3)	0.0013 (2)	-0.0099 (3)
O(4)	0.0518 (6)	0.0203 (4)	0.0232 (3)	-0.0054 (4)	-0.0141 (3)	-0.0056 (3)
N(1)	0.0201 (4)	0.0155 (4)	0.0121 (3)	-0.0030 (3)	0.0010 (3)	-0.0007 (3)
C(1)	0.0232 (6)	0.0277 (6)	0.0136 (4)	-0.0073 (4)	-0.0008 (3)	0.0040 (4)
C(2)	0.0188 (5)	0.0191 (5)	0.0116 (3)	-0.0050 (4)	0.0001 (3)	-0.0008 (3)
C(3)	0.0174 (5)	0.0244 (5)	0.0101 (3)	-0.0032 (4)	0.0009 (3)	-0.0016 (3)
C(4)	0.0156 (5)	0.0224 (5)	0.0114 (3)	-0.0007 (4)	0.0004 (3)	-0.0040 (3)
C(5)	0.0148 (5)	0.0188 (5)	0.0135 (3)	-0.0010 (4)	-0.0003 (3)	-0.0034 (3)
C(6)	0.0221 (5)	0.0168 (5)	0.0180 (4)	-0.0006 (4)	-0.0047 (3)	-0.0047 (3)
C(7)	0.0170 (5)	0.0149 (5)	0.0210 (4)	-0.0007 (4)	-0.0007 (3)	-0.0021 (3)
C(9)	0.0270 (6)	0.0157 (5)	0.0328 (5)	-0.0027 (4)	0.0042 (4)	0.0021 (4)
C(8)	0.0216 (5)	0.0165 (5)	0.0298 (5)	-0.0020 (4)	-0.0003 (4)	-0.0026 (4)
C(10)	0.0291 (6)	0.0190 (5)	0.0261 (5)	-0.0018 (4)	0.0057 (4)	0.0035 (4)
C(11)	0.0248 (6)	0.0179 (5)	0.0187 (4)	-0.0013 (4)	0.0045 (4)	0.0022 (4)
C(12)	0.0158 (5)	0.0161 (5)	0.0159 (4)	-0.0011 (4)	0.0017 (3)	-0.0005 (3)
C(13)	0.0151 (5)	0.0163 (5)	0.0115 (3)	-0.0022 (4)	0.0004 (3)	-0.0016 (3)
C(14)	0.0210 (5)	0.0176 (5)	0.0112 (3)	-0.0046 (4)	-0.0001 (3)	-0.0013 (3)
C(15)	0.0307 (6)	0.0199 (5)	0.0121 (3)	-0.0041 (4)	0.0007 (4)	-0.0004 (3)
C(16)	0.0224 (5)	0.0274 (6)	0.0141 (4)	0.0016 (4)	-0.0040 (3)	-0.0049 (4)

*Geometric parameters (\AA , $^\circ$) for evoxanthine (**5**)*

O(1)—C(2)	1.3591 (11)	C(7)—C(8)	1.4050 (14)
O(2)—C(3)	1.3727 (11)	C(7)—C(12)	1.4087 (12)
O(3)—C(4)	1.3691 (10)	C(9)—C(8)	1.3791 (15)
O(3)—C(16)	1.4289 (12)	C(9)—C(10)	1.4062 (15)
O(4)—C(6)	1.2393 (11)	C(9)—H(9)	1.0822
N(1)—C(12)	1.3770 (12)	C(8)—H(8)	1.0822
N(1)—C(13)	1.3884 (11)	C(10)—C(11)	1.3785 (14)
C(1)—H(1A)	1.0873	C(10)—H(10)	1.0823
C(1)—H(1B)	1.0873	C(11)—C(12)	1.4193 (13)
C(2)—C(3)	1.3913 (12)	C(11)—H(11)	1.0823
C(2)—C(14)	1.3672 (12)	C(13)—C(14)	1.4202 (13)
C(3)—C(4)	1.3660 (14)	C(14)—H(14)	1.0822
C(4)—C(5)	1.4393 (12)	C(15)—H(15A)	1.0848
C(5)—C(6)	1.4584 (14)	C(15)—H(15B)	1.0848
C(5)—C(13)	1.4249 (11)	C(15)—H(15C)	1.0848
C(6)—C(7)	1.4672 (13)		
C(4)—O(3)—C(16)	114.59 (7)	C(5)—C(6)—C(7)	115.84 (8)
C(12)—N(1)—C(13)	121.13 (7)	C(6)—C(7)—C(8)	119.12 (9)
O(1)—C(2)—C(3)	109.53 (8)	C(6)—C(7)—C(12)	121.49 (9)
O(1)—C(2)—C(14)	126.87 (8)	C(8)—C(7)—C(12)	119.39 (9)
C(3)—C(2)—C(14)	123.48 (9)	C(8)—C(9)—C(10)	119.29 (10)
O(2)—C(3)—C(2)	109.75 (9)	C(7)—C(8)—C(9)	121.26 (10)
O(2)—C(3)—C(4)	128.59 (8)	C(9)—C(10)—C(11)	120.79 (10)
C(2)—C(3)—C(4)	121.30 (8)	C(10)—C(11)—C(12)	120.21 (9)
O(3)—C(4)—C(3)	118.28 (8)	N(1)—C(12)—C(7)	120.14 (8)
O(3)—C(4)—C(5)	123.42 (9)	N(1)—C(12)—C(11)	120.86 (8)
C(3)—C(4)—C(5)	118.17 (8)	C(7)—C(12)—C(11)	119.00 (9)
C(4)—C(5)—C(6)	121.15 (8)	N(1)—C(13)—C(5)	121.16 (9)
C(4)—C(5)—C(13)	119.12 (9)	N(1)—C(13)—C(14)	117.91 (7)
C(6)—C(5)—C(13)	119.72 (8)	C(5)—C(13)—C(14)	120.93 (8)
O(4)—C(6)—C(5)	123.88 (9)	C(2)—C(14)—C(13)	116.85 (8)
O(4)—C(6)—C(7)	120.27 (10)		

Pleiocarpine (13)

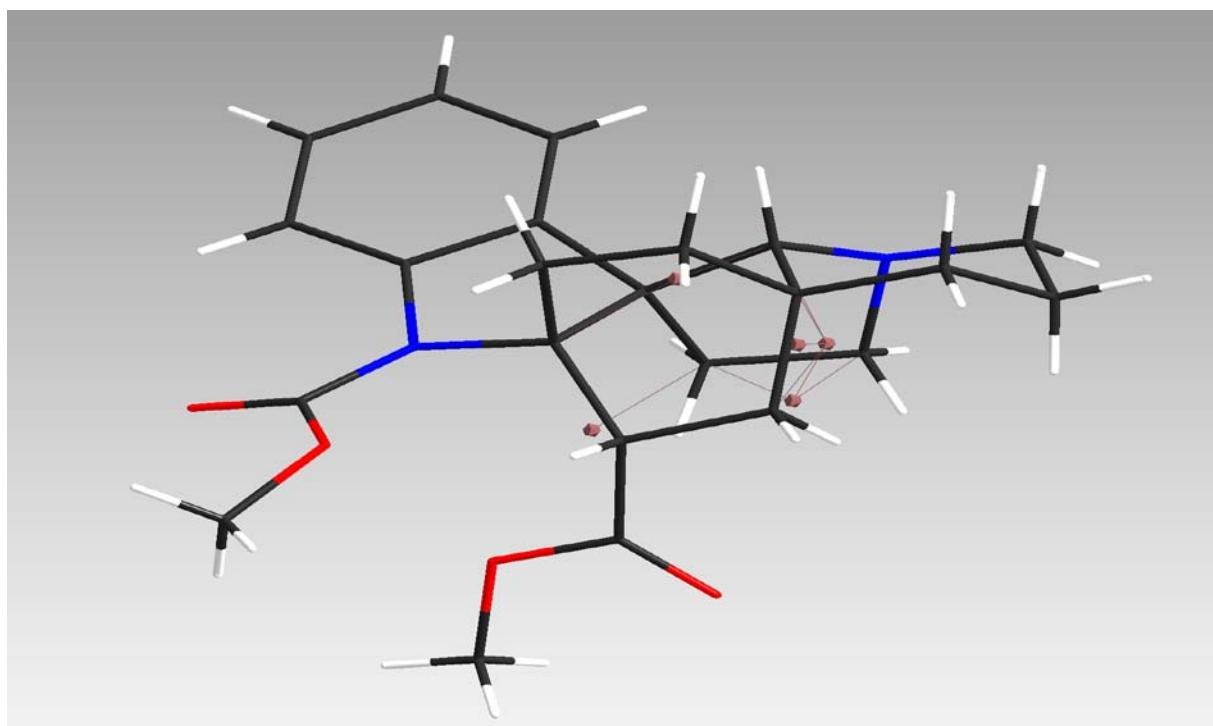


Figure S15: Crystal structure of **13**

Computing details for **13**

Data collection: *APEX2* v2014.11-0; cell refinement: *SAINT* V8.37A (Bruker AXS, 2013); data reduction: *SAINT* V8.37A (Bruker AXS, 2013); program(s) used to solve structure: The structure was known; program(s) used to refine structure: Volkov, A.; Macchi, P.; Farrugia, L. J.; Gatti, C.; Mallinson, P. R.; Richter, T. and Koritsanszky, T. (2006) XD2006 - a computer program for multipole refinement, topological analysis and evaluation of intermolecular energies from experimental and theoretical structure factors.; molecular graphics: Shelxle, Hübschle, (2011); software used to prepare material for publication: *encIFer* 1.5.1, CCDC, 2014.

Pleiocarpine (13)

Crystal data

$C_{23}H_{28}N_2O_4$
 $M_r = 396.47$
Monoclinic, $P2_1$
 $a = 7.4061 (3) \text{ \AA}$
 $b = 9.1421 (4) \text{ \AA}$
 $c = 14.8478 (6) \text{ \AA}$
 $\beta = 95.826 (2)^\circ$
 $V = 1000.11 (7) \text{ \AA}^3$
 $Z = 2$

$F(000) = 424$
 $D_x = 1.317 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Cell parameters from 9801 reflections
 $\theta = 2.8\text{--}23.2^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
Cube
 $0.31 \times 0.24 \times 0.21 \text{ mm}$

Data collection

Huber Type 512 with Bruker APEX I diffractometer
Radiation source: INCOATEC Mo Microsource
 φ scans
Absorption correction: empirical (using intensity measurements)
SADABS 2015/1
 $T_{\min} = 0.750$, $T_{\max} = 0.875$

37617 measured reflections
3491 independent reflections
2580 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.074$
 $\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 1.4^\circ$
 $h = -8 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.036$
 $S = 2.22$
1482 reflections
289 parameters
0 restraints
0 constraints
Primary atom site location: dual

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighboring sites
H-atom parameters constrained
 $w2 = 1/[s^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.14 \text{ e \AA}^{-3}$
Absolute structure: Flack x parameter could not be determined reliably

Special details

Refinement. An invariom refinement (with aspherical scattering factors predicted by DFT computations) was carried out. (Dittrich *et al.*, Acta Cryst. B69, 91-104.) Hydrogen atom positions were calculated with shelxl and their bond distances elongated to idealized values from geometry optimizations of suitable model compounds from the invariom database. The program XDLSM was used with Friedel pairs merged.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for pleiocarpine (13)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O(1)	0.6885 (2)	0.338977	0.46554 (12)	0.047
O(2)	0.6016 (2)	0.5751 (3)	0.46623 (11)	0.037
O(3)	0.0010 (2)	0.5966 (3)	0.41026 (13)	0.059
O(4)	0.2456 (2)	0.4731 (3)	0.46442 (12)	0.046
N(1)	0.5230 (2)	0.4391 (3)	0.34300 (14)	0.032
N(2)	0.0817 (3)	0.5428 (3)	0.09829 (15)	0.048
C(1)	0.3160 (3)	0.4794 (4)	0.21359 (16)	0.03
C(2)	0.4154 (3)	0.5598 (3)	0.29730 (15)	0.027
C(3)	0.2547 (3)	0.5961 (4)	0.14140 (16)	0.035
C(5)	0.4570 (3)	0.3676 (4)	0.19502 (18)	0.036
C(6)	0.4761 (4)	0.2847 (4)	0.1185 (2)	0.048
C(7)	0.6039 (4)	0.1718 (4)	0.1232 (2)	0.056
C(8)	0.7095 (4)	0.1437 (4)	0.2047 (2)	0.053
C(9)	0.6913 (3)	0.2253 (4)	0.2826 (2)	0.046
C(10)	0.5646 (3)	0.3377 (4)	0.27649 (18)	0.034
C(11)	0.6125 (3)	0.4439 (4)	0.42911 (18)	0.035
C(12)	0.6578 (4)	0.5828 (5)	0.56144 (17)	0.053
C(13)	0.2824 (3)	0.6486 (3)	0.34917 (17)	0.032
C(14)	0.1589 (3)	0.5703 (4)	0.40930 (17)	0.037
C(15)	0.1419 (4)	0.4043 (4)	0.5297 (2)	0.057
C(16)	0.1688 (3)	0.7432 (4)	0.27729 (17)	0.037
C(17)	0.5503 (3)	0.6698 (3)	0.26240 (19)	0.04
C(18)	0.4495 (3)	0.7954 (4)	0.2084 (2)	0.046
C(19)	0.2510 (3)	0.7483 (4)	0.18633 (18)	0.036
C(20)	0.1476 (3)	0.8561 (4)	0.12075 (19)	0.05
C(21)	-0.0421 (4)	0.7985 (4)	0.0875 (2)	0.052
C(22)	-0.0235 (5)	0.6501 (4)	0.0414 (2)	0.061
C(23)	-0.0128 (4)	0.4656 (4)	0.1641 (2)	0.058
C(24)	0.1363 (3)	0.3936 (4)	0.22784 (19)	0.04
H(3)	0.3536	0.5986	0.0908	0.063 (10)*
H(6)	0.3931	0.3062	0.0557	0.053 (10)*
H(7)	0.6218	0.1071	0.0637	0.077 (12)*
H(8)	0.8075	0.0555	0.2075	0.065 (11)*
H(9)	0.7741	0.2029	0.3454	0.057 (10)*
H(12A)	0.8006	0.5508	0.5738	0.103 (14)*
H(12B)	0.5748	0.5090	0.5981	0.082 (14)*
H(12C)	0.6415	0.6951	0.5849	0.068 (12)*
H(13)	0.3649	0.7249	0.3930	0.067 (11)*
H(15A)	0.0229	0.3508	0.4943	0.089 (13)*
H(15B)	0.0978	0.4873	0.5758	0.117 (17)*
H(15C)	0.2256	0.3227	0.5684	0.094 (13)*
H(16A)	0.0310	0.6992	0.2664	0.053 (10)*
H(16B)	0.1598	0.8545	0.3034	0.033 (8)*
H(17A)	0.6350	0.7163	0.3200	0.060 (10)*
H(17B)	0.6393	0.6129	0.2195	0.042 (9)*
H(18A)	0.5120	0.8150	0.1459	0.064 (11)*
H(18B)	0.4572	0.8964	0.2481	0.064 (11)*

H(20A)	0.1338	0.9607	0.1552	0.065 (11)*
H(20B)	0.2244	0.8753	0.0627	0.070 (11)*
H(21A)	-0.1228	0.7859	0.1447	0.071 (12)*
H(21B)	-0.1118	0.8759	0.0397	0.101 (13)*
H(22A)	-0.1599	0.6060	0.0217	0.099 (14)*
H(22B)	0.0422	0.6673	-0.0209	0.094 (14)*
H(23A)	-0.1050	0.3826	0.1316	0.085 (12)*
H(23B)	-0.0921	0.5425	0.2013	0.096 (14)*
H(24A)	0.1494	0.2778	0.2112	0.060 (11)*
H(24B)	0.1056	0.4025	0.2982	0.072 (11)*

Atomic displacement parameters (\AA^2) for (pleio)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O(1)	0.0458 (12)	0.0410 (15)	0.0522 (13)	0.0087 (10)	-0.0029 (10)	0.0122 (11)
O(2)	0.0295 (10)	0.0415 (13)	0.0399 (12)	0.0022 (10)	0.0040 (8)	-0.0013 (11)
O(3)	0.0318 (11)	0.0715 (17)	0.0786 (15)	0.0180 (11)	0.0248 (10)	0.0200 (12)
O(4)	0.0309 (11)	0.0542 (15)	0.0550 (12)	0.0057 (10)	0.0120 (9)	0.0178 (11)
N(1)	0.0262 (12)	0.0302 (16)	0.0419 (14)	0.0063 (10)	0.0072 (11)	0.0029 (13)
N(2)	0.0479 (15)	0.0428 (18)	0.0509 (16)	-0.0009 (13)	-0.0119 (13)	-0.0079 (13)
C(1)	0.0269 (15)	0.031 (2)	0.0342 (16)	-0.0005 (13)	0.0067 (12)	-0.0031 (13)
C(2)	0.0218 (13)	0.0273 (17)	0.0335 (16)	0.0008 (13)	0.0055 (11)	0.0004 (14)
C(3)	0.0327 (15)	0.037 (2)	0.0370 (17)	0.0033 (14)	0.0035 (13)	0.0026 (15)
C(5)	0.0354 (17)	0.034 (2)	0.0408 (19)	-0.0002 (14)	0.0112 (14)	-0.0055 (15)
C(6)	0.0455 (19)	0.044 (2)	0.056 (2)	0.0048 (16)	0.0170 (16)	-0.0126 (18)
C(7)	0.055 (2)	0.051 (2)	0.066 (2)	-0.0009 (18)	0.0231 (19)	-0.016 (2)
C(8)	0.0513 (19)	0.039 (2)	0.073 (3)	0.0084 (17)	0.0274 (19)	-0.0043 (19)
C(9)	0.0368 (19)	0.041 (2)	0.064 (2)	0.0094 (15)	0.0190 (17)	0.0015 (18)
C(10)	0.0252 (15)	0.032 (2)	0.0480 (19)	0.0043 (14)	0.0130 (14)	-0.0018 (16)
C(11)	0.0233 (15)	0.039 (2)	0.0431 (19)	0.0016 (14)	0.0041 (14)	0.0078 (18)
C(12)	0.056 (2)	0.069 (3)	0.0335 (18)	0.009 (2)	-0.0046 (15)	-0.0068 (19)
C(13)	0.0259 (14)	0.0280 (18)	0.0417 (17)	0.0054 (13)	0.0063 (13)	0.0026 (14)
C(14)	0.0302 (16)	0.0356 (18)	0.0454 (17)	0.0055 (15)	0.0119 (14)	0.0005 (15)
C(15)	0.045 (2)	0.070 (3)	0.059 (2)	0.002 (2)	0.0220 (18)	0.029 (2)
C(16)	0.0385 (19)	0.038 (2)	0.0357 (18)	0.0070 (14)	0.0019 (14)	0.0001 (15)
C(17)	0.0318 (16)	0.041 (2)	0.0469 (19)	-0.0077 (15)	0.0047 (15)	0.0041 (16)
C(18)	0.0374 (18)	0.043 (2)	0.058 (2)	-0.0099 (15)	0.0018 (15)	0.0114 (18)
C(19)	0.0365 (17)	0.031 (2)	0.0404 (18)	-0.0009 (14)	0.0004 (14)	0.0060 (15)
C(20)	0.051 (2)	0.047 (2)	0.049 (2)	0.0013 (16)	-0.0025 (17)	0.0120 (18)
C(21)	0.050 (2)	0.051 (3)	0.052 (2)	0.0059 (17)	-0.0085 (18)	0.0046 (18)
C(22)	0.064 (2)	0.060 (3)	0.054 (2)	0.0135 (19)	-0.019 (2)	-0.0017 (19)
C(23)	0.0308 (18)	0.056 (2)	0.084 (2)	-0.0066 (18)	-0.0071 (17)	0.003 (2)
C(24)	0.0284 (16)	0.040 (2)	0.053 (2)	-0.0098 (14)	0.0075 (14)	-0.0038 (15)

*Geometric parameters (\AA , $^{\circ}$) for pleiocarpine (**13**)*

O(1)—C(11)	1.211 (3)	C(7)—C(8)	1.396 (4)
O(2)—C(11)	1.326 (3)	C(7)—H(7)	1.0822
O(3)—C(14)	1.195 (3)	C(8)—C(9)	1.394 (3)
O(4)—C(14)	1.328 (3)	C(8)—H(8)	1.0822
N(1)—C(10)	1.411 (3)	C(9)—C(10)	1.389 (3)
N(1)—C(11)	1.380 (3)	C(9)—H(9)	1.0822
N(2)—C(3)	1.457 (3)	C(13)—C(14)	1.521 (3)
N(2)—C(23)	1.443 (3)	C(16)—C(19)	1.537 (3)
C(1)—C(5)	1.506 (3)	C(18)—C(19)	1.535 (3)
C(5)—C(6)	1.385 (3)	C(19)—C(20)	1.534 (3)
C(5)—C(10)	1.406 (3)	C(20)—C(21)	1.535 (3)
C(6)—C(7)	1.398 (4)	C(21)—C(22)	1.532 (4)
C(6)—H(6)	1.0822	C(23)—C(24)	1.528 (3)
C(10)—N(1)—C(11)	123.4 (2)	O(1)—C(11)—O(2)	125.2 (3)
C(3)—N(2)—C(23)	109.4 (2)	O(1)—C(11)—N(1)	123.1 (3)
C(1)—C(5)—C(6)	130.7 (3)	O(2)—C(11)—N(1)	111.7 (2)
C(1)—C(5)—C(10)	108.5 (2)	O(3)—C(14)—O(4)	122.6 (3)
C(6)—C(5)—C(10)	120.2 (3)	O(3)—C(14)—C(13)	124.1 (3)
C(5)—C(6)—C(7)	119.2 (3)	O(4)—C(14)—C(13)	113.2 (2)
C(6)—C(7)—C(8)	119.8 (3)	C(16)—C(19)—C(18)	106.1 (2)
C(7)—C(8)—C(9)	121.8 (3)	C(16)—C(19)—C(20)	111.1 (2)
C(8)—C(9)—C(10)	117.6 (3)	C(18)—C(19)—C(20)	111.2 (2)
N(1)—C(10)—C(5)	109.2 (2)	C(19)—C(20)—C(21)	111.4 (2)
N(1)—C(10)—C(9)	129.4 (3)	C(20)—C(21)—C(22)	109.1 (3)
C(5)—C(10)—C(9)	121.4 (3)	N(2)—C(23)—C(24)	105.1 (2)

Nov 27 2015

INSTRUMENT: MERCURY-300
PROBE atb
OBSERVE H1
Frequency 300.141 MHz
Spectral width 5109.9 Hz
Acquisition time 3.128 sec
Relaxation delay 0.000 sec
Pulse 45.0 degrees
Ambient temperature
128 repetitions
Gated decoupling
Double precision acquisition
DATA PROCESSING
FT Size 65536
Total acquisition time 6 minutes

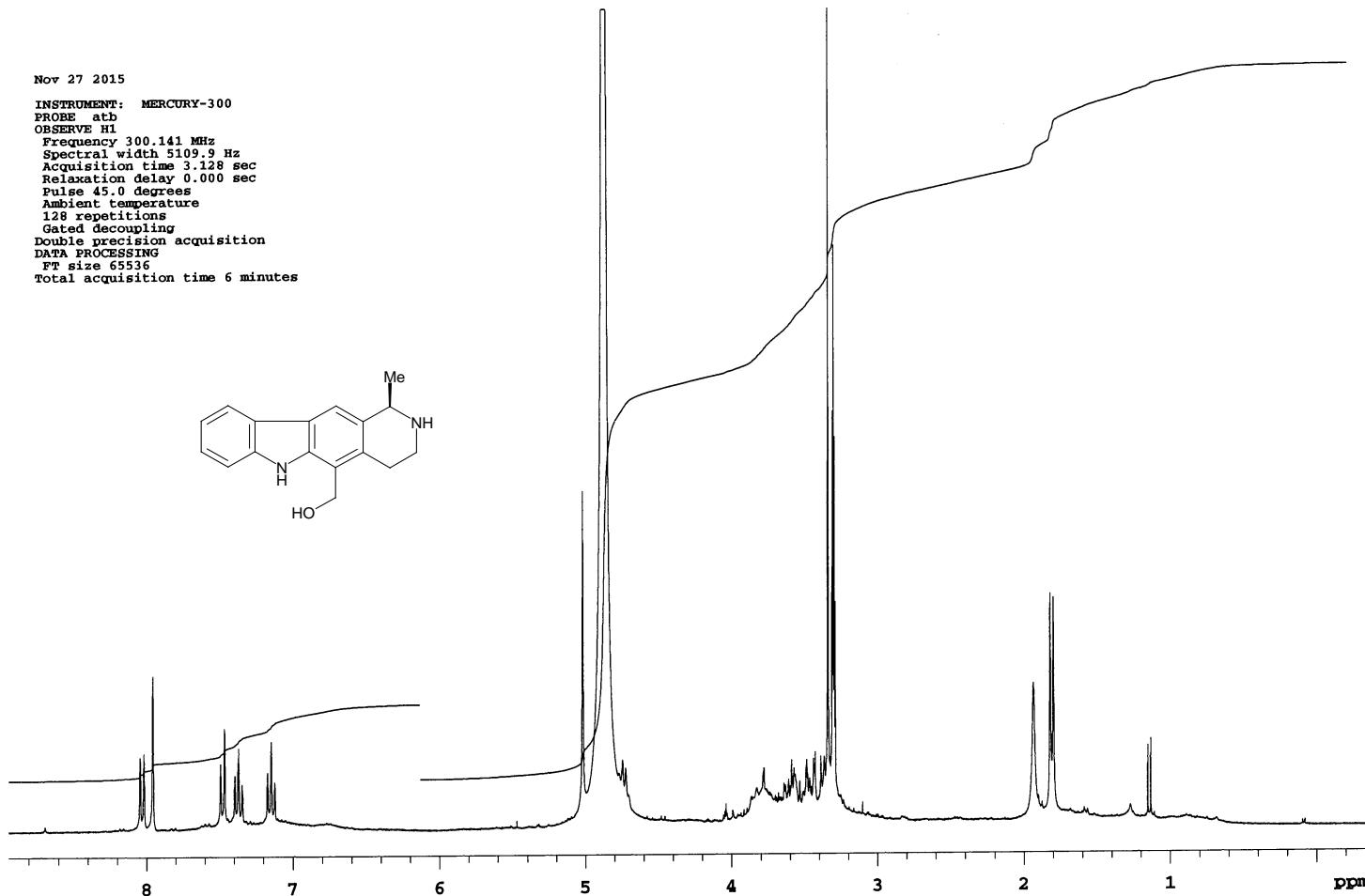
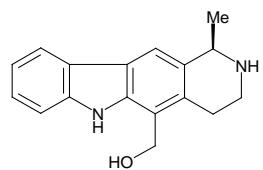
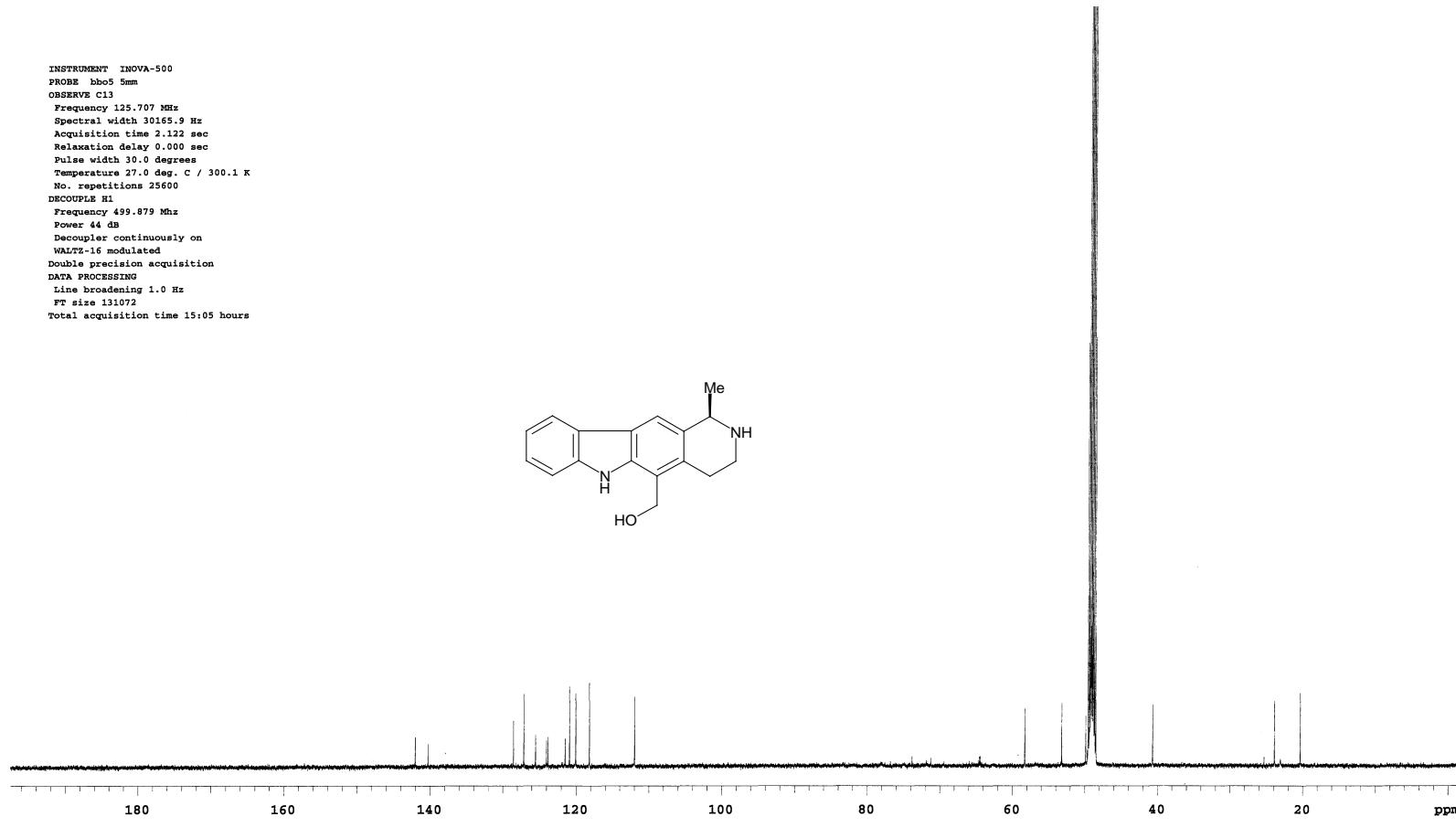
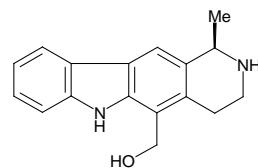


Figure S16: ¹H NMR spectrum (300 MHz, Methanol-*d*₄) of **1a**.

INSTRUMENT INOVA-500
 PROBE bb05 5mm
 OBSERVE C13
 Frequency 125.707 MHz
 Spectral width 30165.9 Hz
 Acquisition time 2.122 sec
 Relaxation delay 0.000 sec
 Pulse width 30.0 degrees
 Temperature 27.0 deg. C / 300.1 K
 No. repetitions 25600
 DECOUPLE H1
 Frequency 499.879 Mhz
 Power 44 dB
 Decoupler continuously on
 WALTZ-16 modulated
 Double precision acquisition
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total acquisition time 15:05 hours



DATE: Dec 7 2015 FILE:nmrdata: laatsch/tn-ftc011_5c

Figure S17: ^{13}C NMR spectrum (125 MHz, Methanol- d_4) of **1a**.

Sample Name:
 Data Collected on:
 1600.nmr-inova600
 Archive directory:
 Sample directory:
 FidFile: gCOSY
 Pulse Sequence: gCOSY
 Solvent: cd3od
 Data collected on: Dec 9 2015
 Temp: 25.0 C / 298.1 K
 Operator: vmarl
 Relax. delay 1.000 sec
 Acc. time 0.150 sec
 Width 5529.4 Hz
 2D Width 5529.4 Hz
 4 repetitions
 128 increments
 OBSERVE H1, 599.7397189 MHz
 DATA PROCESSING
 Sq. sine bell 0.075 sec
 F1 DATA PROCESSING
 Sq. sine bell 0.023 sec
 FT size 2048 x 2048
 Total time 10 min

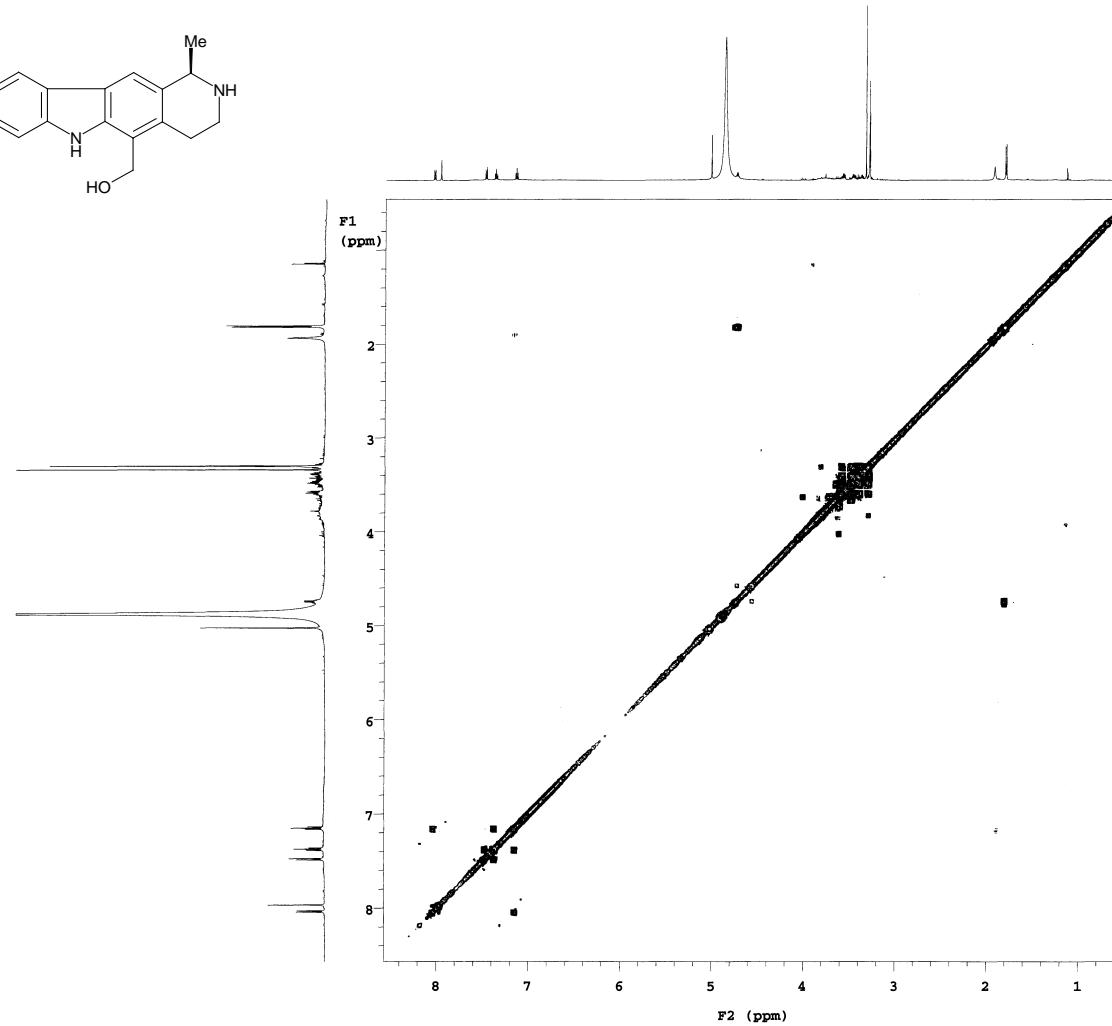
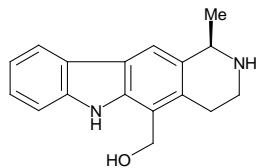


Figure S18: ¹H, ¹H COSY spectrum (600 MHz, Methanol-*d*₄) of **1a**.

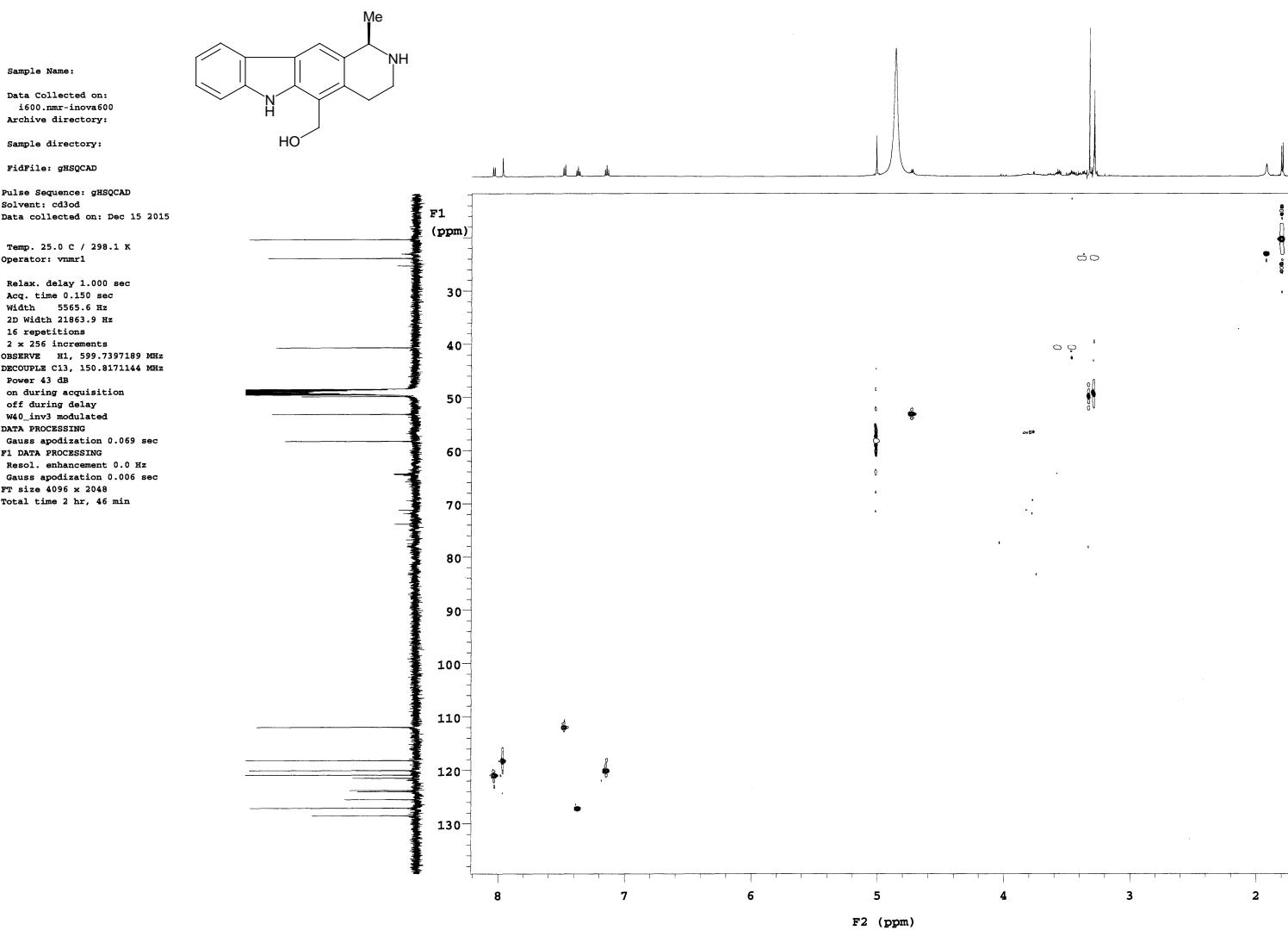


Figure S19: HSQC spectrum (600 MHz, Methanol-*d*₄) of **1a**.

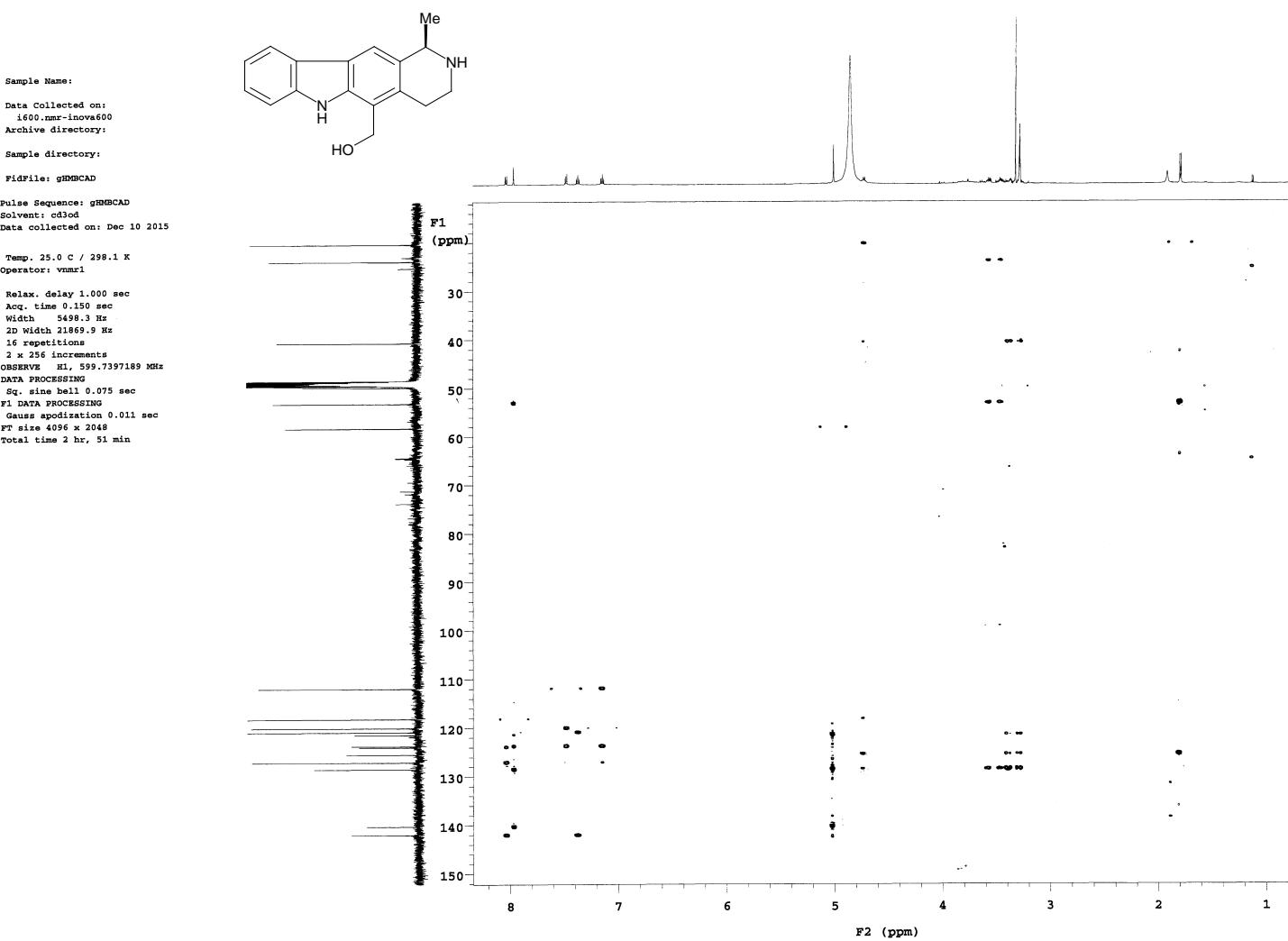


Figure S20: HSQC spectrum (600 MHz, Methanol-*d*₄) of **1a**.

Sample Name:
 Data Collected on:
 i600.nmr-inova600
 Archive directory:
 Sample directory:
 FidFile: NOESY
 Pulse Sequence: NOESY
 Solvent: cd3od
 Data collected on: Dec 10 2015
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width 5498.3 Hz
 2D Width 5498.3 Hz
 16 Repeition
 2 x 16 scans
 OBSERVE H1, 599.7397189 MHz
 DATA PROCESSING
 Gauss apodization 0.069 sec
 F1 DATA PROCESSING
 Gauss apodization 0.043 sec
 FT size 2048 x 2048
 Total time 4 hr, 59 min

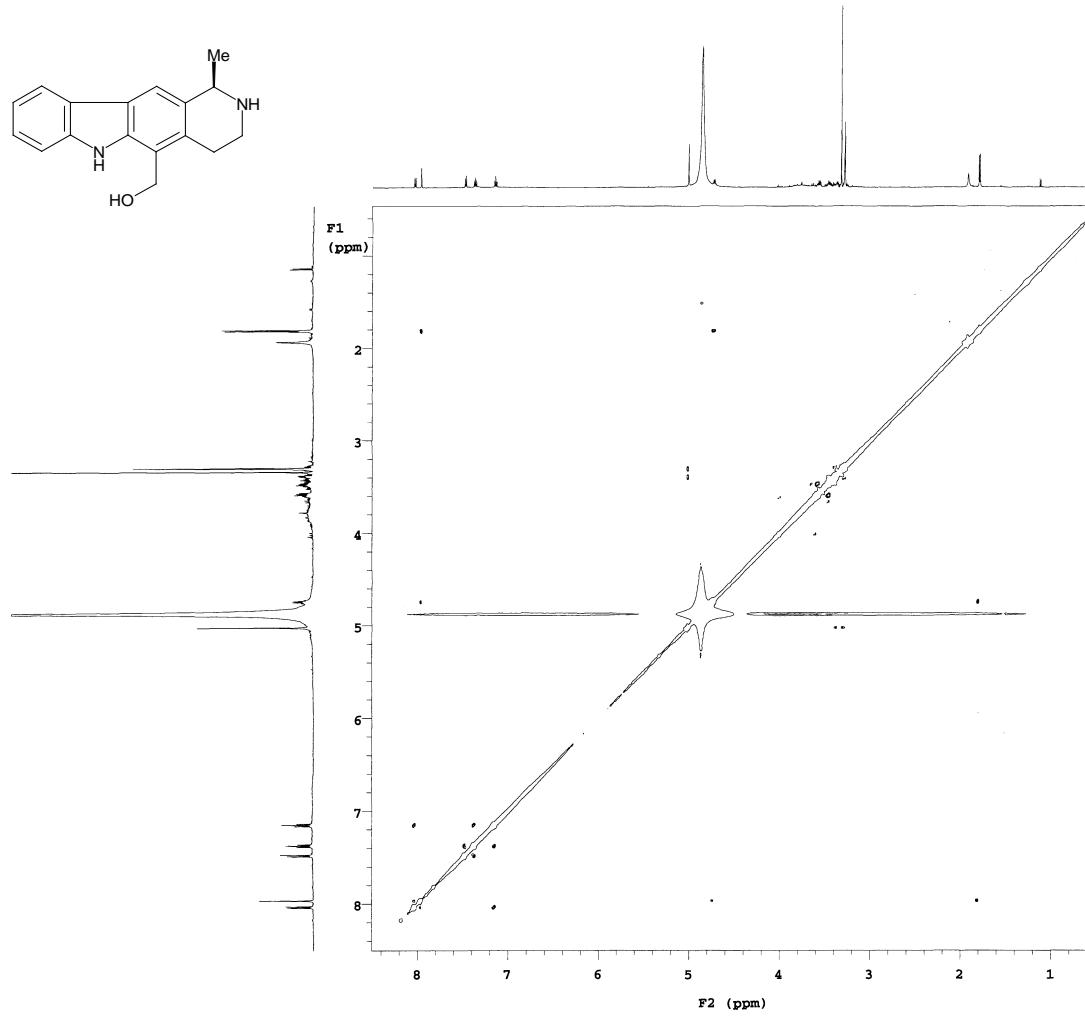
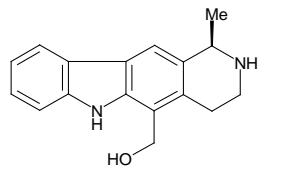


Figure S21: HSQC spectrum (600 MHz, Methanol-*d*₄) of **1a**.

Sample Name:
 Data Collected on:
 i600.nmr-inova600
 Archive directory:
 Sample directory:
 FidFile: PROTON
 Pulse Sequence: PROTON (s2pul)
 Solvent: cdcl3
 Data collected on: Feb 15 2016
 Temp. 25.0 C / 298.1 K
 Operator: vnmri
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.707 sec
 Width 9595.8 Hz
 32 repetitions
 OBSERVE: H1, 599.7373650 MHz
 DATA PROCESSING
 FT size 32768
 Total time 1 min 27 sec

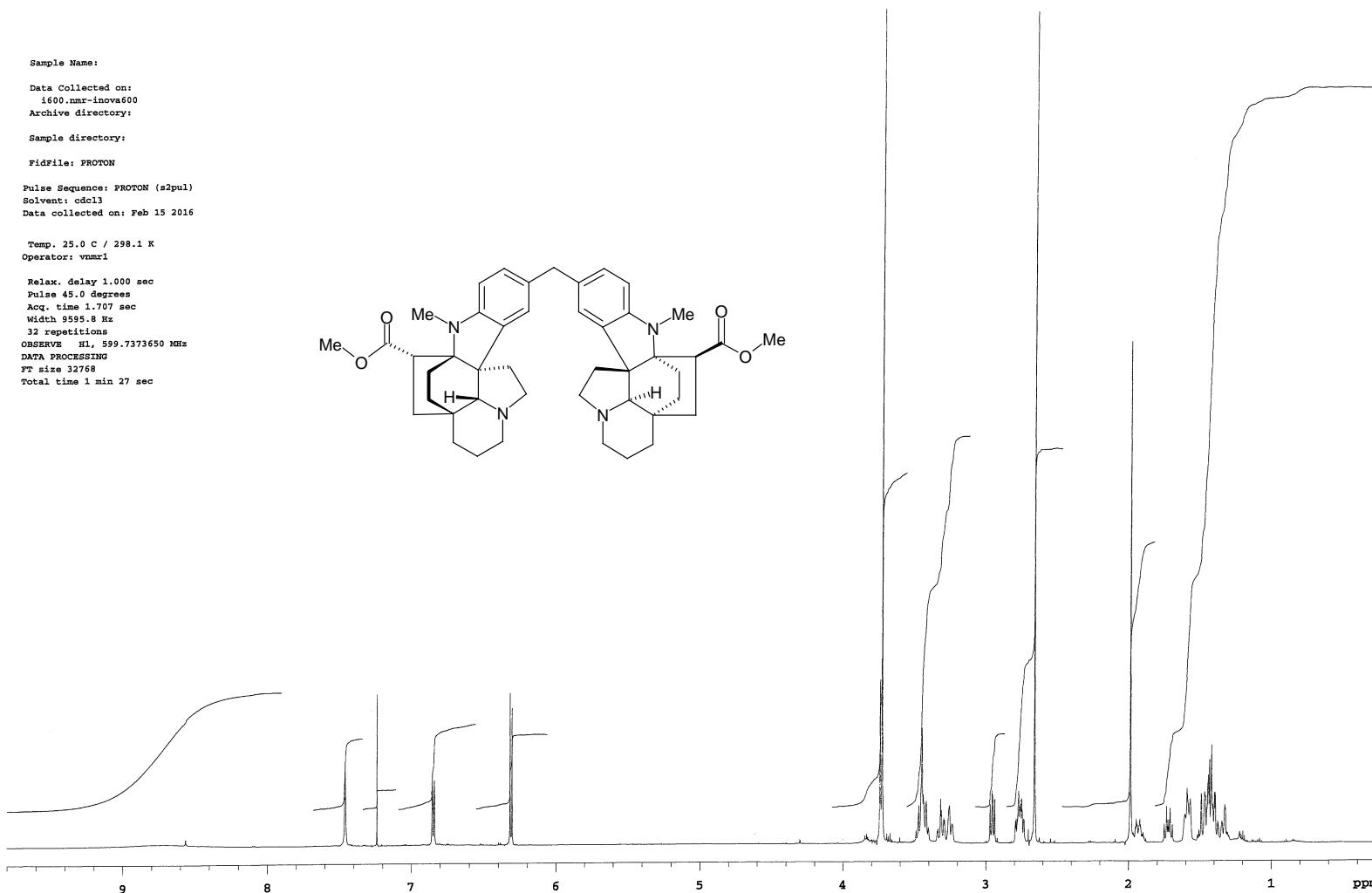
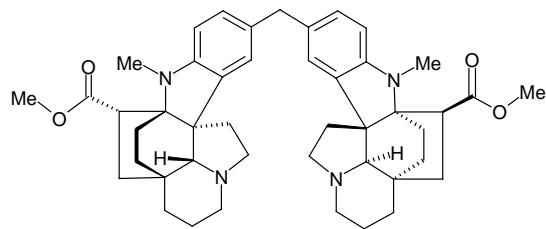


Figure S22: ¹H NMR spectrum (600 MHz, CDCl₃) of **2**.

INSTRUMENT INNOVA-500
 PROBE bbo5 3mm
 OBSERVE C13
 Frequency 125.707 MHz
 Spectral width 30165.9 Hz
 Acquisition time 2.122 sec
 Relaxation delay 0.000 sec
 Pulse width 30.0 degrees
 Temperature 27.0 deg. C / 300.1 K
 No. repetitions 1664
 DECOUPLE H1
 Frequency 499.877 MHz
 Power 44 dB
 Decoupler continuously on
 WALTZ-16 modulated
 Double precision acquisition
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total acquisition time 58 minutes

INDEX	FREQ	PPM	HEIGHT
1	21931.5	174.48	40.1
2	18714.9	148.89	32.7
3	17268.2	137.38	14.6
4	16777.5	133.48	27.0
5	16048.9	127.68	39.4
6	15370.4	122.28	42.4
7	13596.0	108.17	48.0
8	9710.6	77.26	197.8
9	9678.9	77.00	200.0
10	9646.6	76.75	196.9
11	8884.4	70.68	44.7
12	8403.4	66.86	50.2
13	7205.2	57.32	47.9
14	6588.0	52.41	59.8
15	6342.6	50.46	37.0
16	5889.7	46.86	37.5
17	5233.8	41.64	53.1
18	5203.9	41.40	19.9
19	4315.5	34.33	30.9
20	4251.5	33.82	35.8
21	4234.0	33.69	40.3
22	4068.3	32.37	39.7
23	3917.8	31.17	67.0
24	3786.2	30.12	57.6
25	3001.8	23.88	38.7
26	2835.2	22.56	35.6
27	2002.5	15.93	36.0

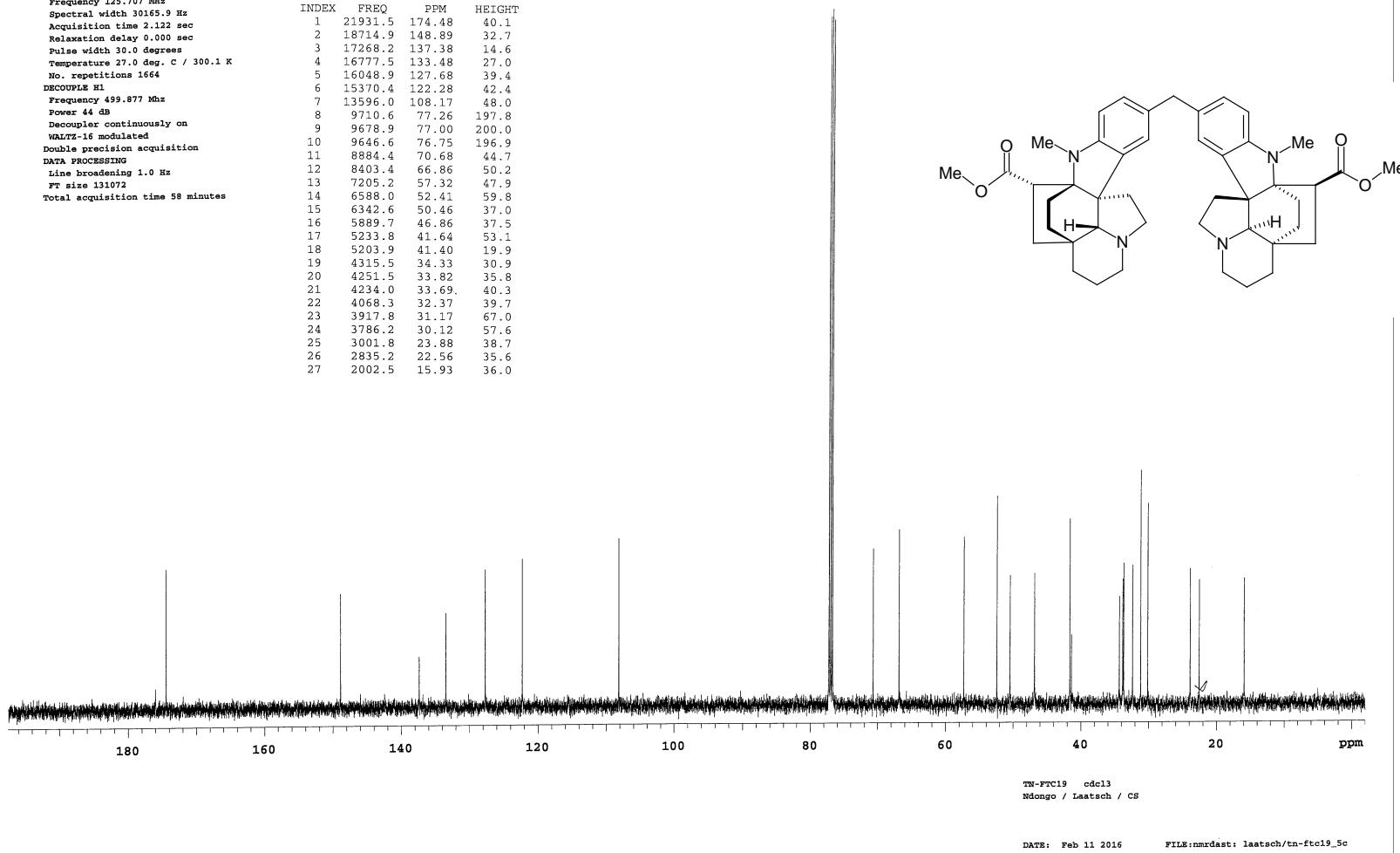


Figure S23: ^{13}C NMR spectrum (125 MHz, CDCl_3) of **2**.

Sample Name:
 Data Collected on:
 i600.nmr-inova600
 Archive directory:
 Sample directory:
 Fidfile: gCOSY
 Pulse Sequence: gCOSY
 Solvent: cdcl₃
 Data collected on: Feb 15 2016
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width 6027.7 Hz
 2D Width 6027.7 Hz
 4 repetitions
 128 increments
 OBSERVE H1, 599.7373650 MHz
 DATA PROCESSING
 Sq. sine bell 0.075 sec
 F1 DATA PROCESSING
 Sq. sine bell 0.021 sec
 FT size 2048 x 2048
 Total time 10 min

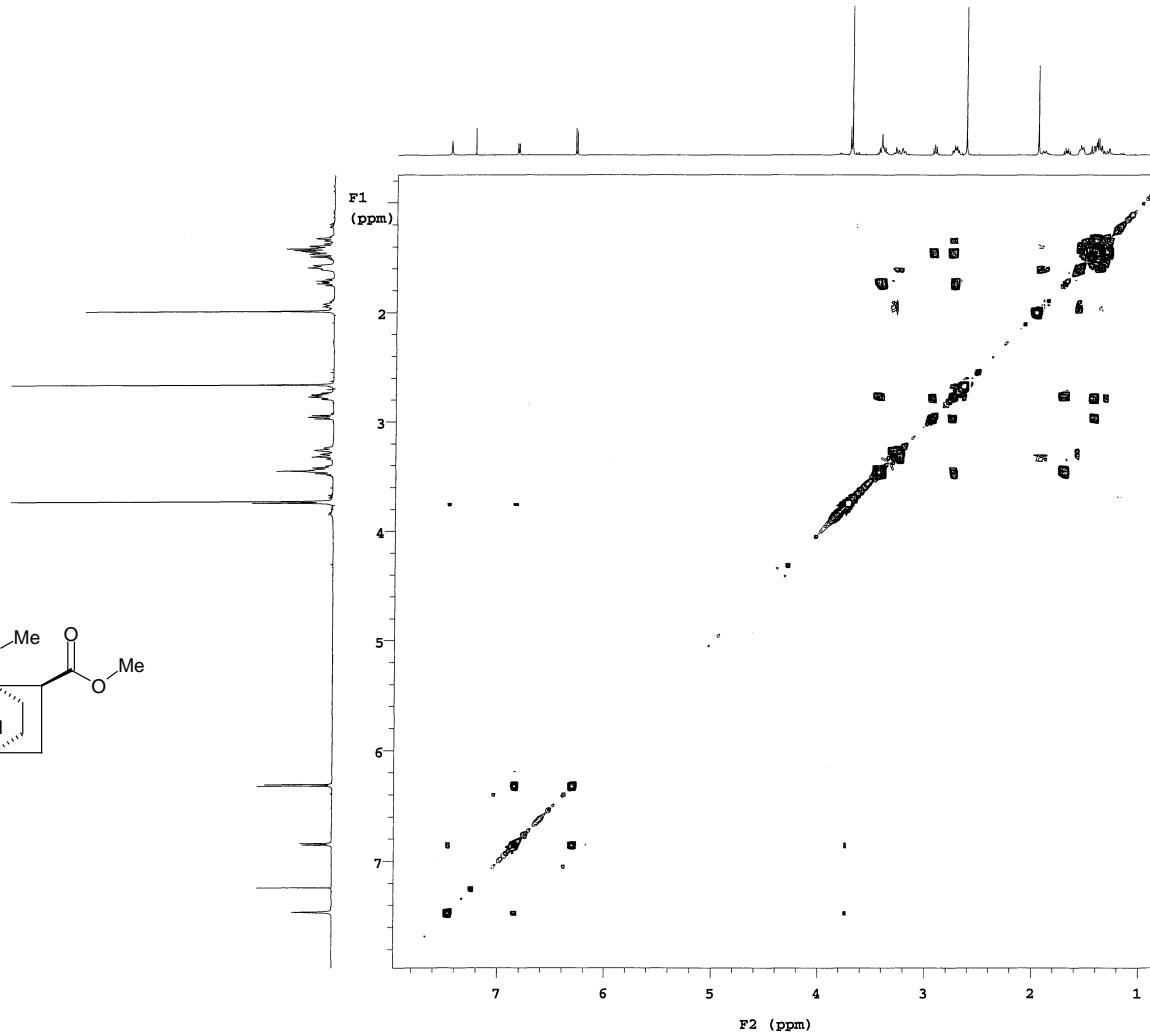
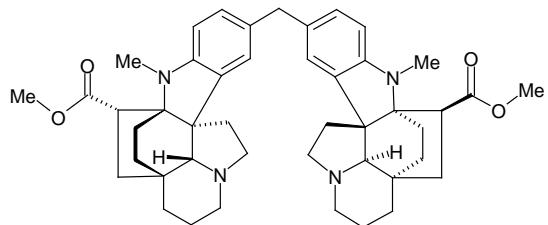


Figure S24: ¹H, ¹H COSY spectrum (600 MHz, CDCl₃) of **2**.

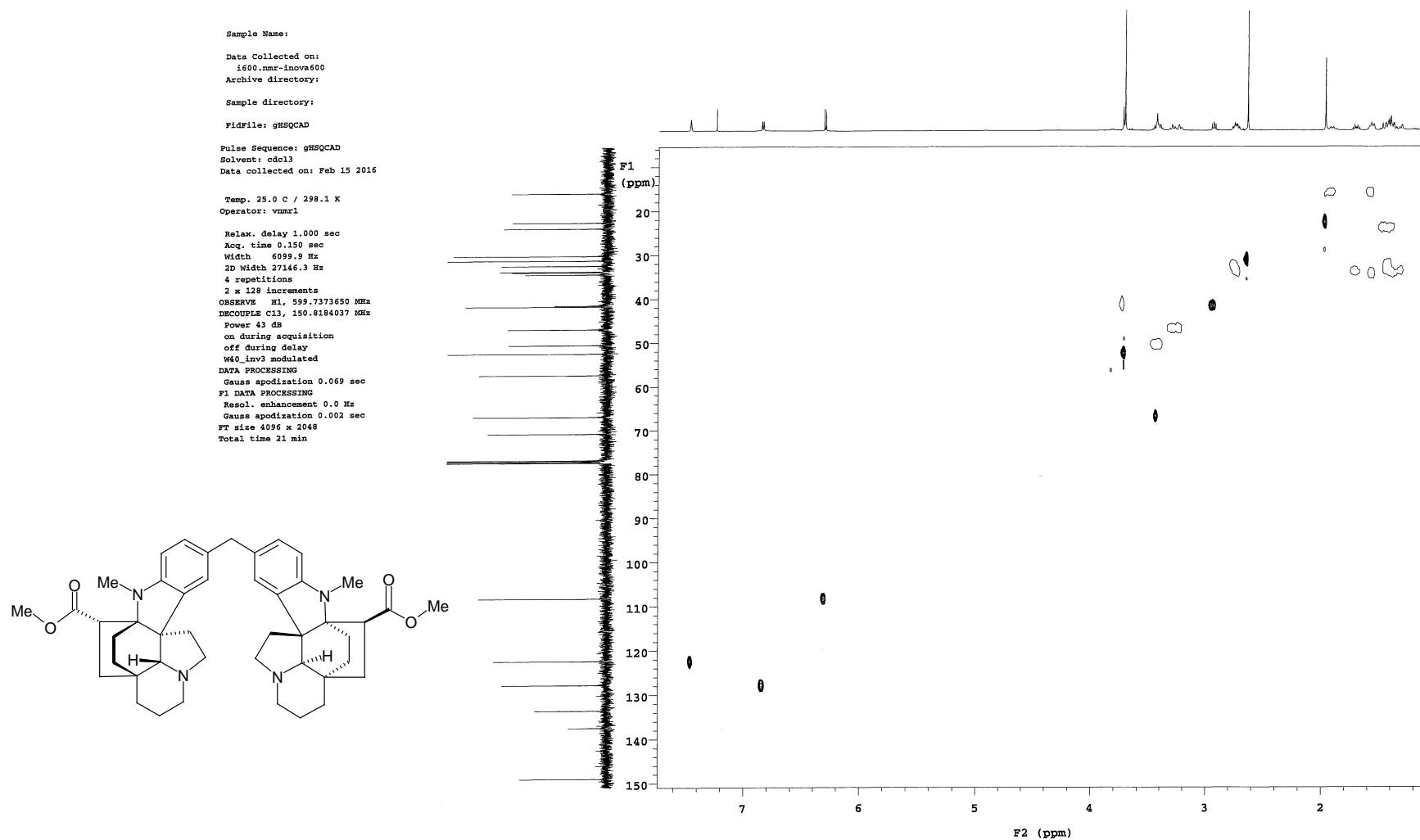


Figure S25: HSQC spectrum (600 MHz, CDCl₃) of **2**.

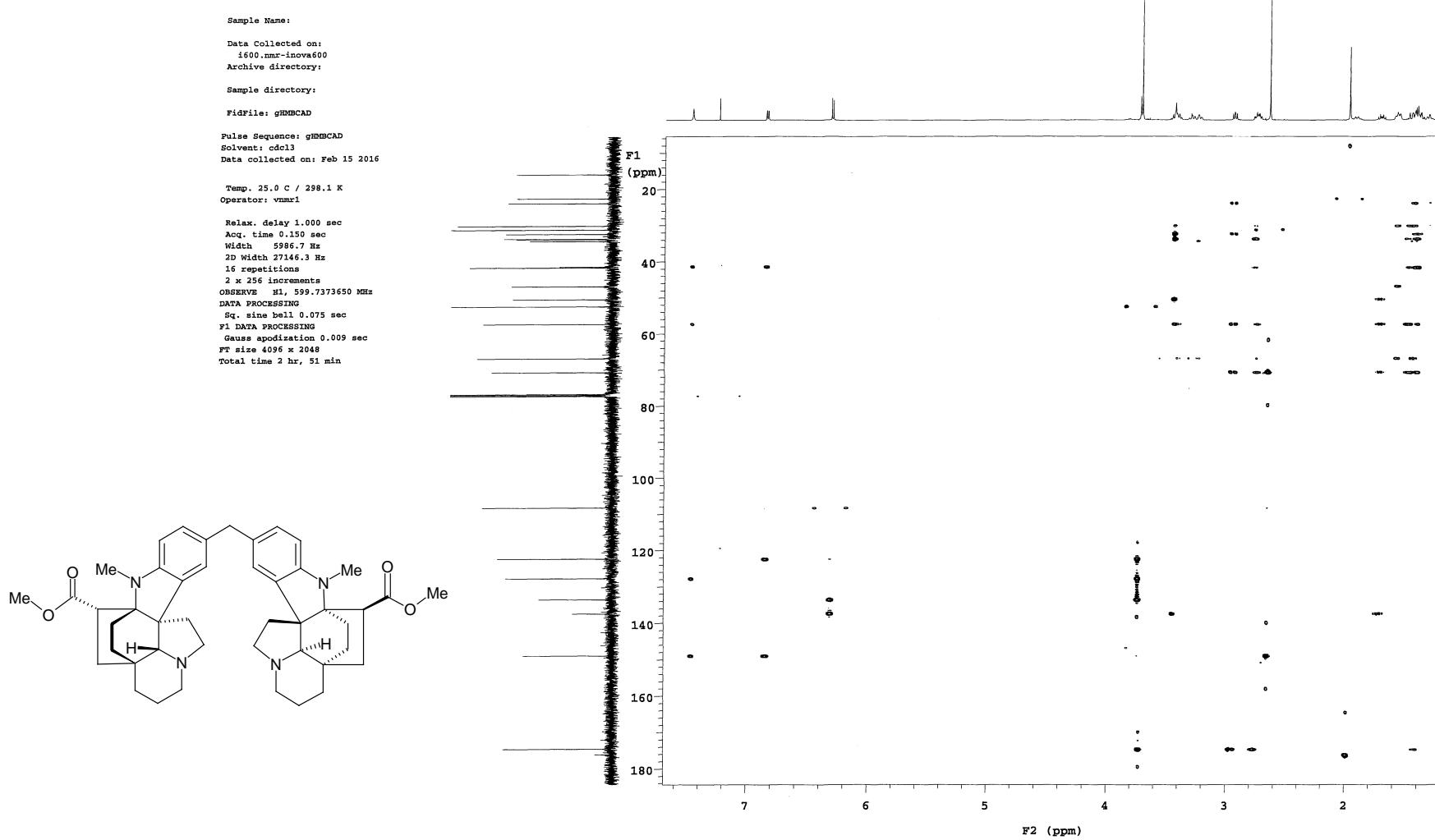


Figure S26: HMBC spectrum (600 MHz, CDCl₃) of **2**.

Sample Name:
 Data Collected on:
 i600.mmr-inova600
 Archive directory:
 Sample directory:
 FidFile: NOESY
 Pulse Sequence: NOESY
 Solvent: cdcl₃
 Data collected on: Feb 15 2016
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width 5960.8 Hz
 2D Width 5960.8 Hz
 4 repetitions
 2 x 256 increments
 OBSERVE H1, 599.7373650 MHz
 DATA PROCESSING
 Gauss apodization 0.069 sec
 F1 DATA PROCESSING
 Gauss apodization 0.040 sec
 FT size 2048 x 2048
 Total time 1 hr, 15 min

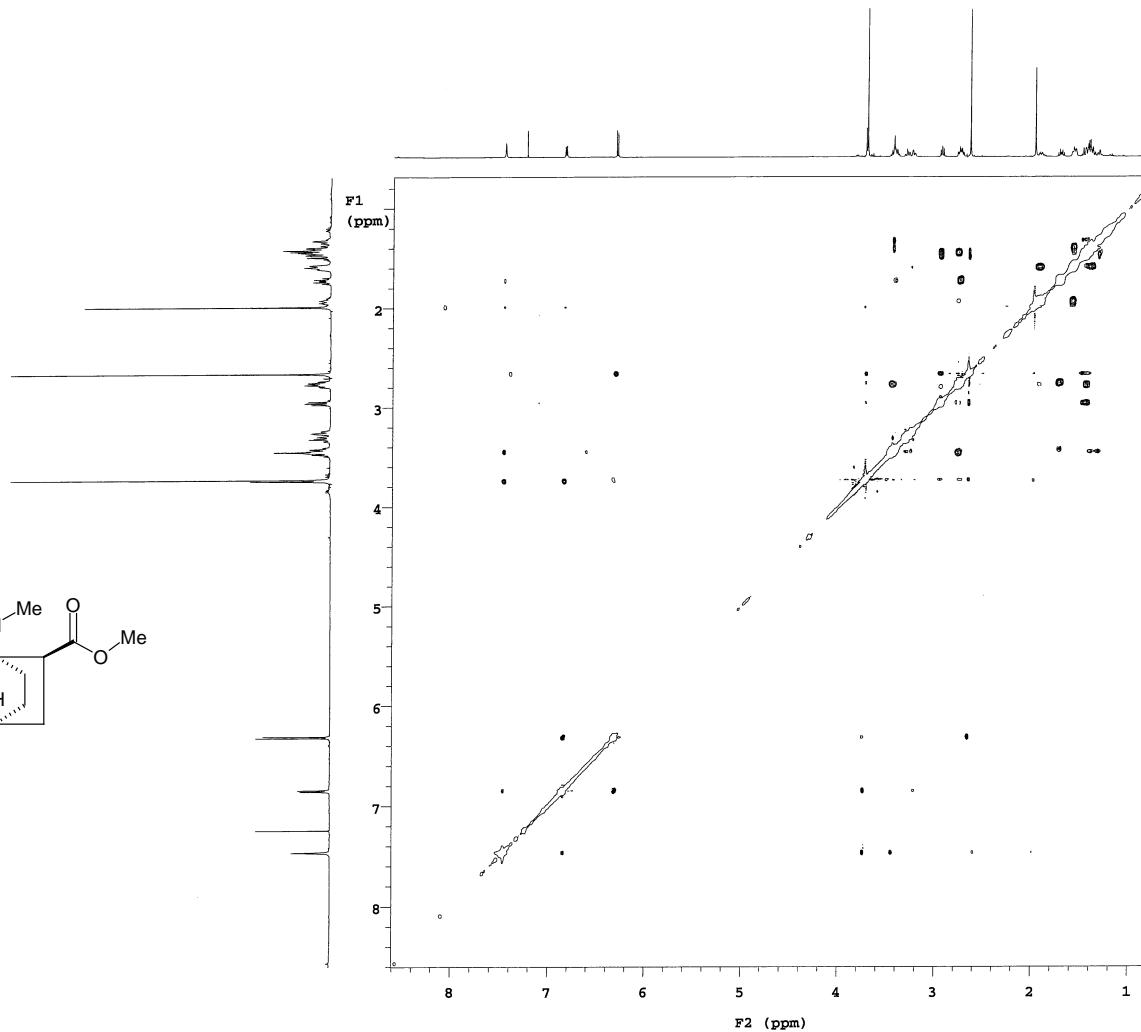
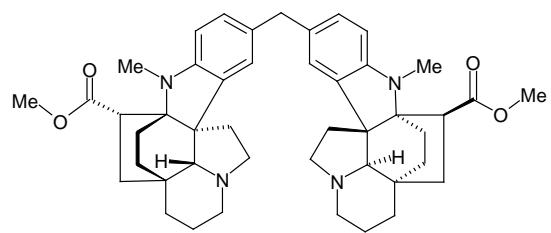


Figure S27: NOESY spectrum (600 MHz, CDCl₃) of **2**.

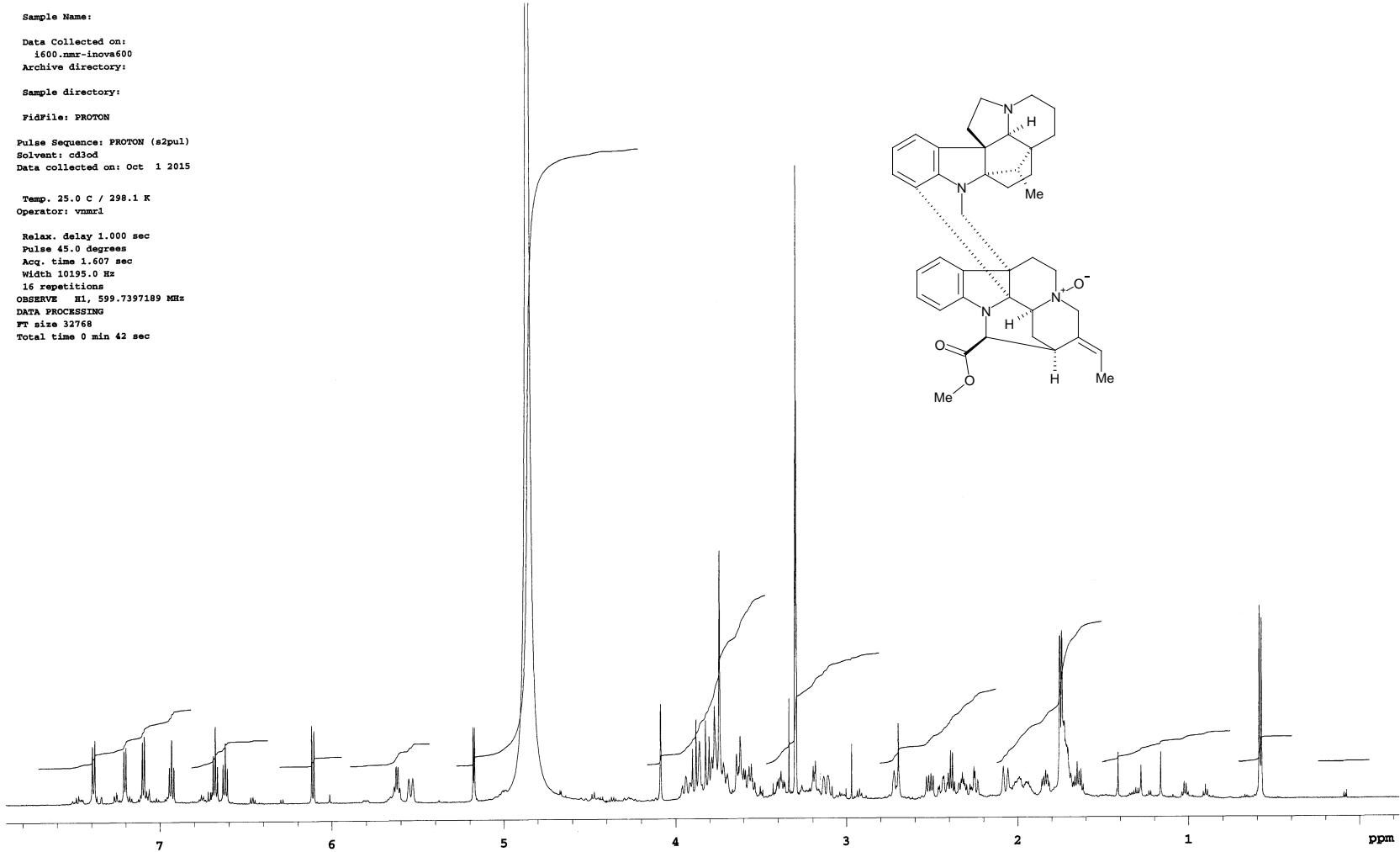
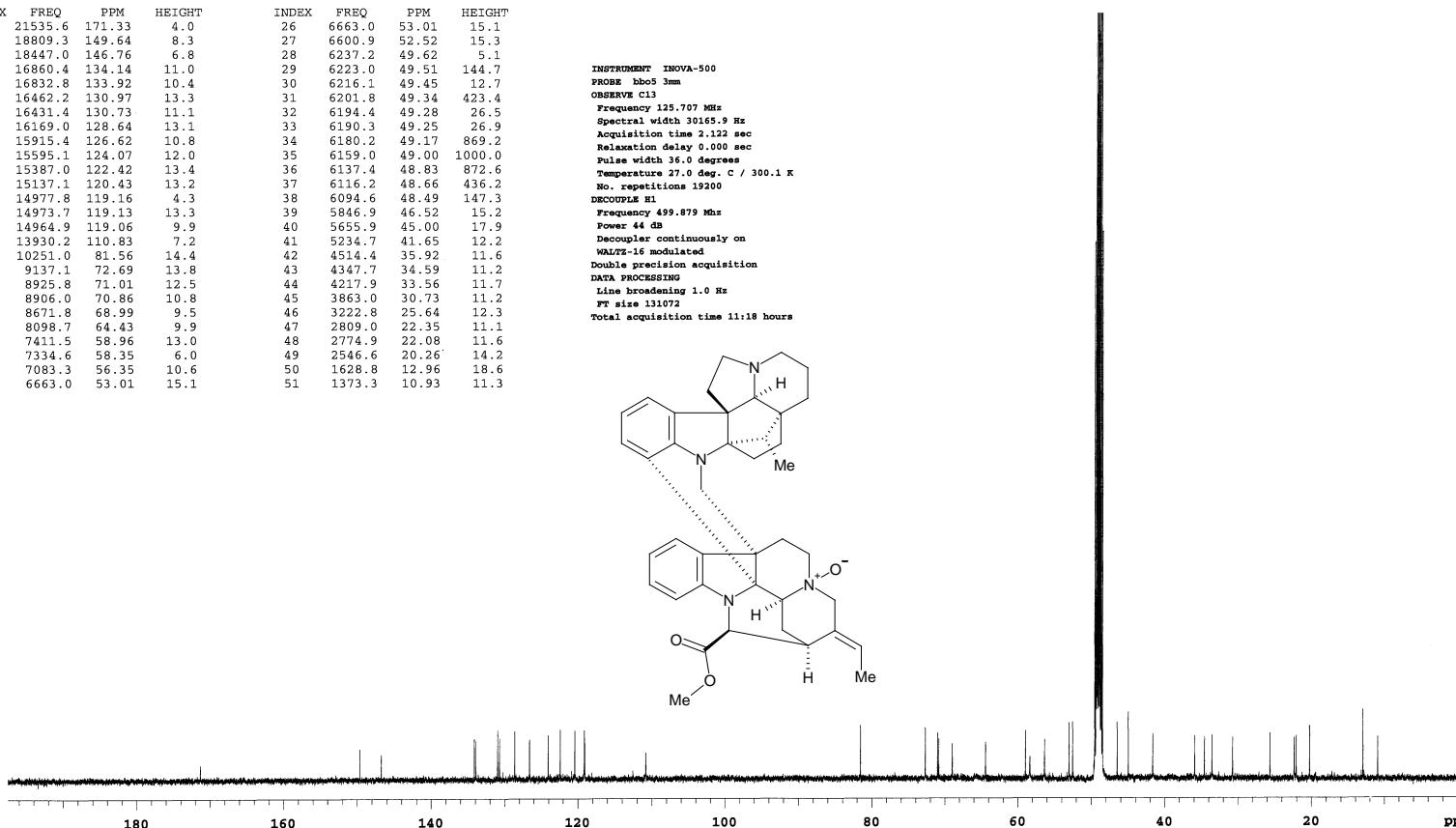
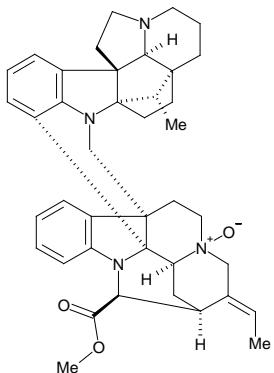


Figure S28: ^1H NMR spectrum (600 MHz, Methanol- d_4) of **3a**.

SPECTRAL LINES FOR TH= 3.3
 FROM -2.5 PPM TO 197.5 PPM
 RFL= 7921.2 RFP= 6159.0

INDEX	FREQ	PPM	HEIGHT	INDEX	FREQ	PPM	HEIGHT
1	21535.6	171.33	4.0	26	6663.0	53.01	15.1
2	18809.3	149.64	8.3	27	6600.9	52.52	15.3
3	18447.0	146.76	6.8	28	6237.2	49.62	5.1
4	16860.4	134.14	11.0	29	6223.0	49.51	144.7
5	16832.8	133.92	10.4	30	6216.1	49.45	12.7
6	16462.2	130.97	13.3	31	6201.8	49.34	423.4
7	16431.4	130.73	11.1	32	6194.4	49.28	26.5
8	16169.0	128.64	13.1	33	6190.3	49.25	26.9
9	15915.4	126.62	10.8	34	6180.2	49.17	869.2
10	15595.1	124.07	12.0	35	6159.0	49.00	1000.0
11	15387.0	122.42	13.4	36	6137.4	48.83	872.6
12	15137.1	120.43	13.2	37	6116.2	48.66	436.2
13	14977.8	119.16	4.3	38	6094.6	48.49	147.3
14	14973.7	119.13	13.3	39	5846.9	46.52	15.2
15	14964.9	119.06	9.9	40	5655.9	45.00	17.9
16	13930.2	110.83	7.2	41	5234.7	41.65	12.2
17	10251.0	81.56	14.4	42	4514.4	35.92	11.6
18	9137.1	72.69	13.8	43	4347.7	34.59	11.2
19	8925.8	71.01	12.5	44	4217.9	33.56	11.7
20	8906.0	70.86	10.8	45	3863.0	30.73	11.2
21	8671.8	68.99	9.5	46	3222.8	25.64	12.3
22	8098.7	64.43	9.9	47	2809.0	22.35	11.1
23	7411.5	58.96	13.0	48	2774.9	22.08	11.6
24	7334.6	58.35	6.0	49	2546.6	20.26	14.2
25	7083.3	56.35	10.6	50	1628.8	12.96	18.6
26	6663.0	53.01	15.1	51	1373.3	10.93	11.3

INSTRUMENT INOVA-500
 PROBE bbo5 3mm
 OBSERVE C13
 Frequency 125.707 MHz
 Spectral width 30165.9 Hz
 Acquisition time 2.122 sec
 Relaxation delay 0.000 sec
 Pulse width 36.0 degrees
 Temperature 27.0 deg. C / 300.1 K
 No. repetitions 19200
 DECOUPLE H1
 Frequency 499.879 MHz
 Power 44 dB
 Decoupler continuously on
 WALTZ-16 modulated
 Double precision acquisition
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total acquisition time 11:18 hours



DATE: Sep 30 2015 FILE:nmrdata: laatsch/tn-pc64_5c

Figure S29: ¹³C NMR spectrum (125 MHz, Methanol-*d*₄) of **3a**.

Sample Name:
 Data Collected on:
 i600.mnr-inova600
 Archive directory:
 Sample directory:
 FidFile: gCOSY
 Pulse Sequence: gCOSY
 Solvent: cd3od
 Data collected on: Oct 1 2015
 Temp. 25.0 C / 298.1 K
 Operator: vmar1
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width 5307.9 Hz
 2D Width 5307.9 Hz
 2 repetitions
 256 increments
 OBSERVE H1, 599.7397189 MHz
 DATA PROCESSING
 Sq. sine bell 0.075 sec
 F1 DATA PROCESSING
 Sq. sine bell 0.048 sec
 FT size 2048 x 2048
 Total time 10 min

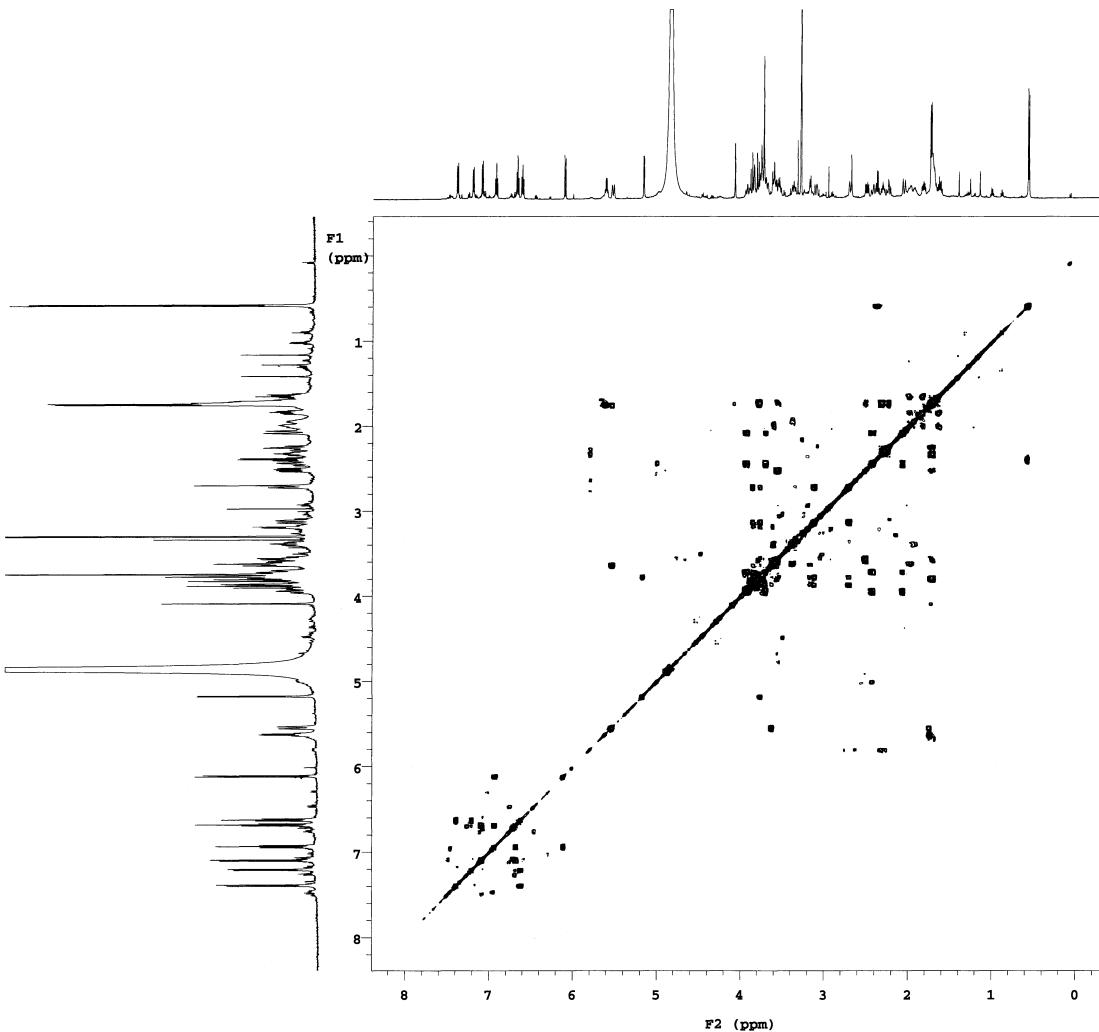
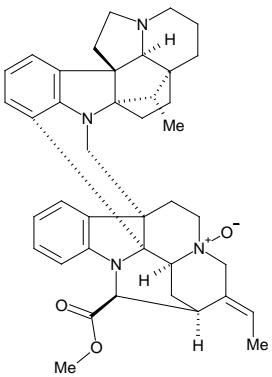


Figure S30: ¹H, ¹H COSY spectrum (600 MHz, Methanol-*d*₄) of 3a.

Sample Name:

Data Collected on:
i600.mr-inova600
Archive directory:
Sample directory:
Fidfile: gHSQCAD

Pulse Sequence: gHSQCAD
Solvent: cd3od
Data collected on: Oct 1 2015

Temp. 25.0 C / 298.1 K
Operator: vmlr

Relax. delay 1.000 sec
Acc. time 0.150 sec
Width 5307.9 Hz
3D width 24525.5 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 599.7397189 MHz
DECOUPLE C13, 150.8167374 MHz
Power 43 dB
on during acquisition
off during delay
W4.0_inv3 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Resol. enhancement 0.0 Hz
Gauss apodization 0.005 sec
FT size 4096 x 2048
Total time 2 hr, 46 min

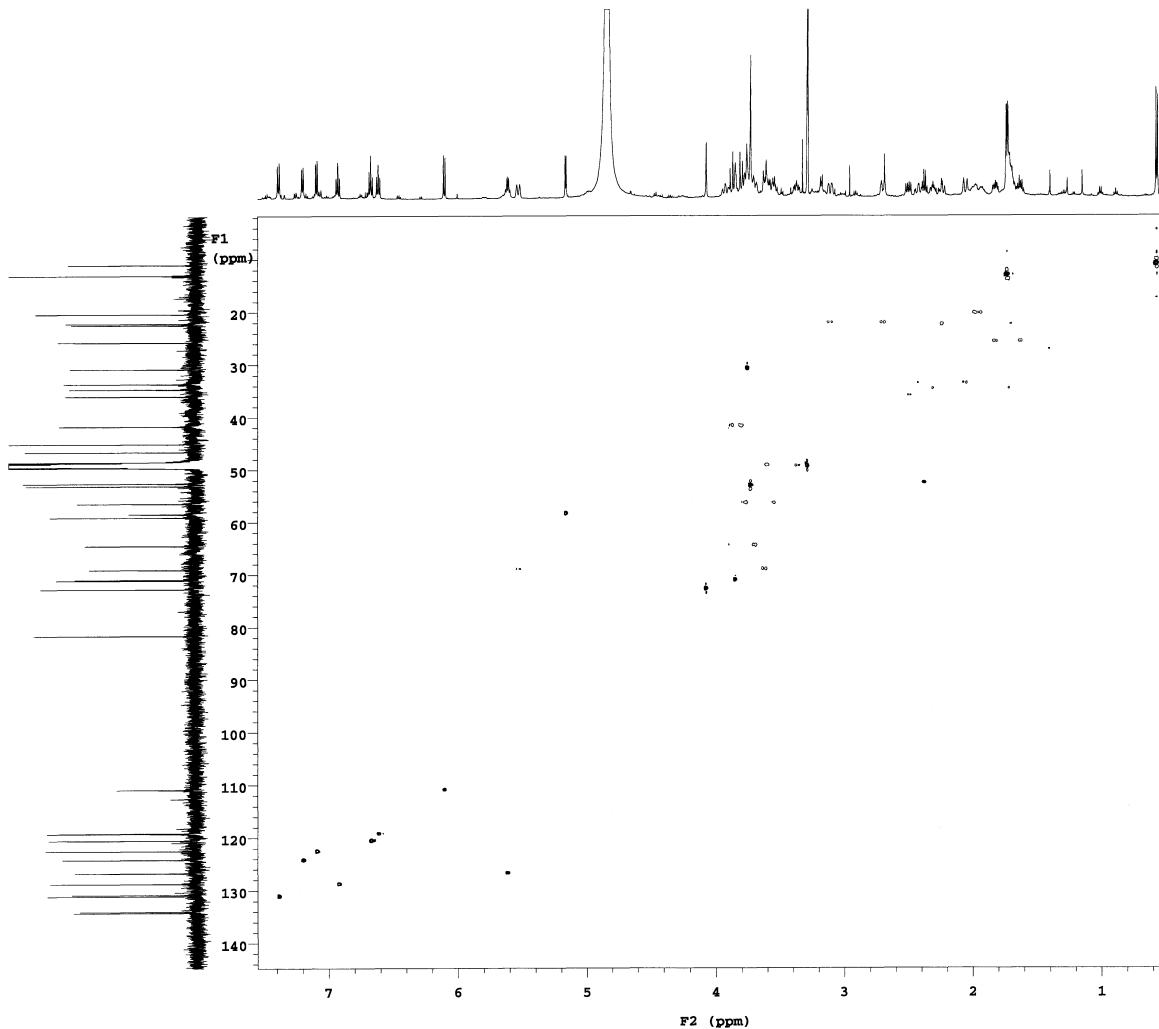
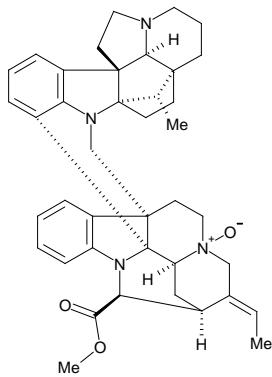


Figure S31: HSQC spectrum (600 MHz, Methanol-*d*₄) of 3a.

Sample Name:

Data Collected on:
i600-nmr-inova600
Archive directory:

Sample directory:

Fidfile: gHMBCAD

Pulse Sequence: gHMBCAD
Solvent: c63od
Data collected on: Oct 1 2015

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5307.9 Hz
2D Width 27146.3 Hz
32 repetitions
2 x 256 increments
OBSERVE H1, 599.7397189 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.009 sec
FT size 4096 x 2048
Total time 5 hr, 41 min

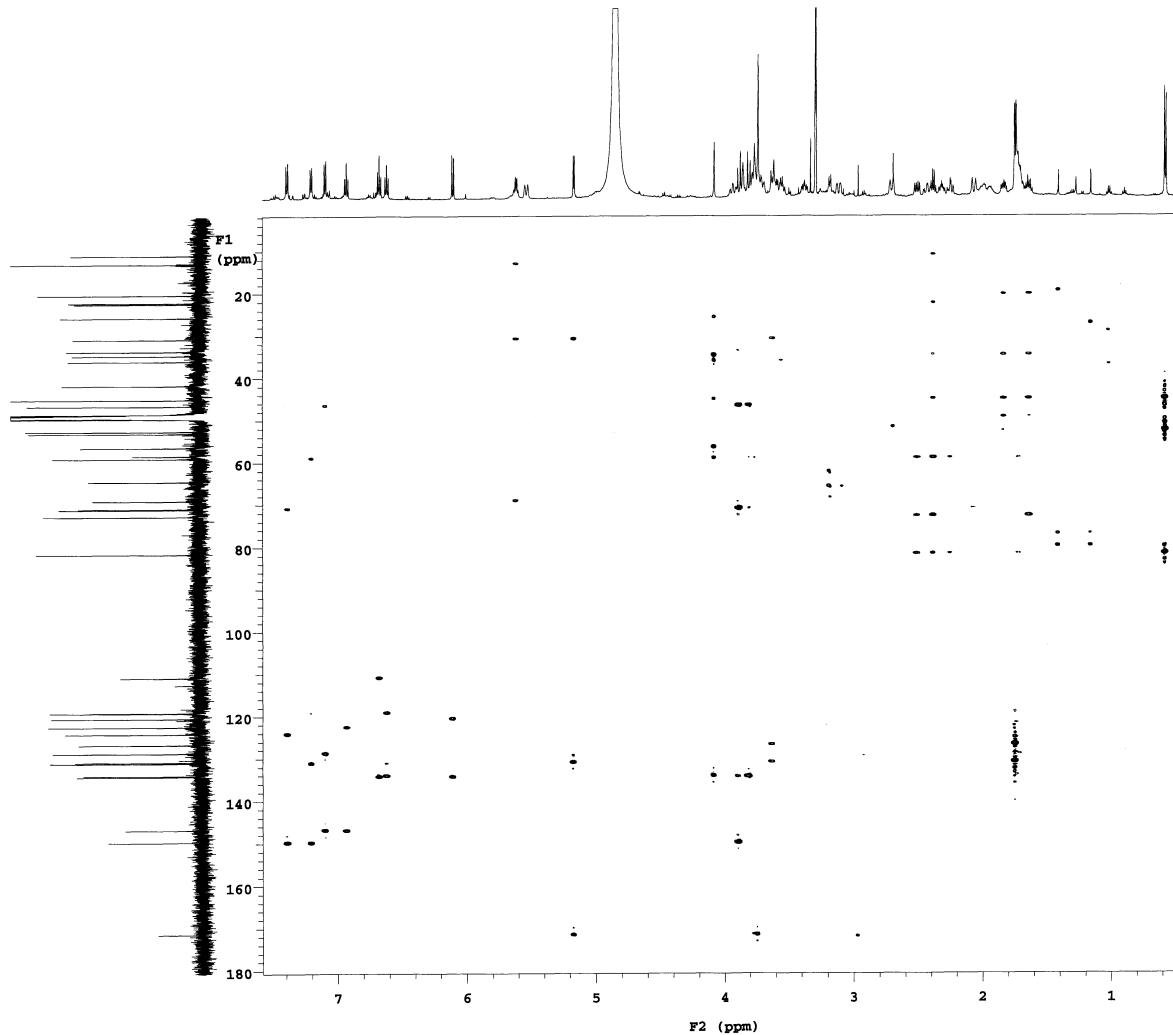
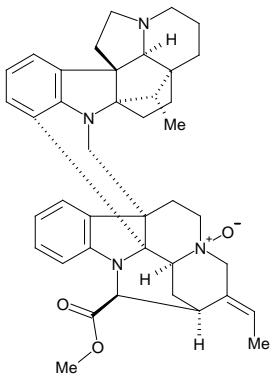


Figure S32: HMBC spectrum (600 MHz, Methanol-*d*₄) of 3a.

Sample Name:
 Data Collected on:
 i600.nmr-inova600
 Archive directory:
 Sample directory:
 Fidfile: NOESY
 Pulse Sequence: NOESY
 Solvent: cd3d
 Data collected on: Oct 1 2015
 Temp. 25.0 C / 298.1 K
 Operator: vnmri
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width 5307.9 Hz
 2D Width 5307.9 Hz
 16 repetitions
 2 x 256 increments
 OBSERVE H1, 599.7397189 MHz
 DATA PROCESSING
 Gauss apodization 0.069 sec
 F1 DATA PROCESSING
 Gauss apodization 0.044 sec
 FT size 2048 x 2048
 Total time 5 hr

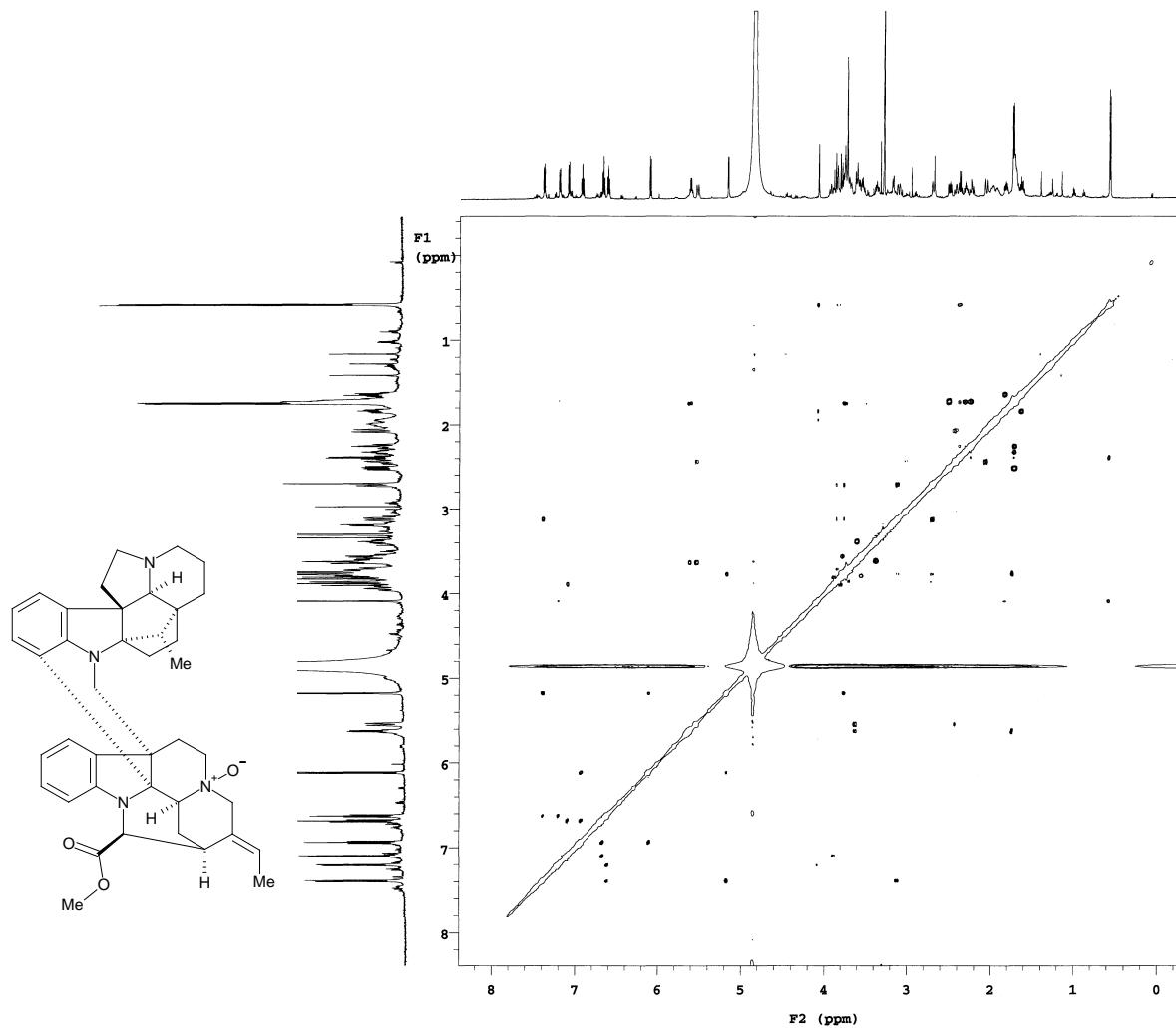
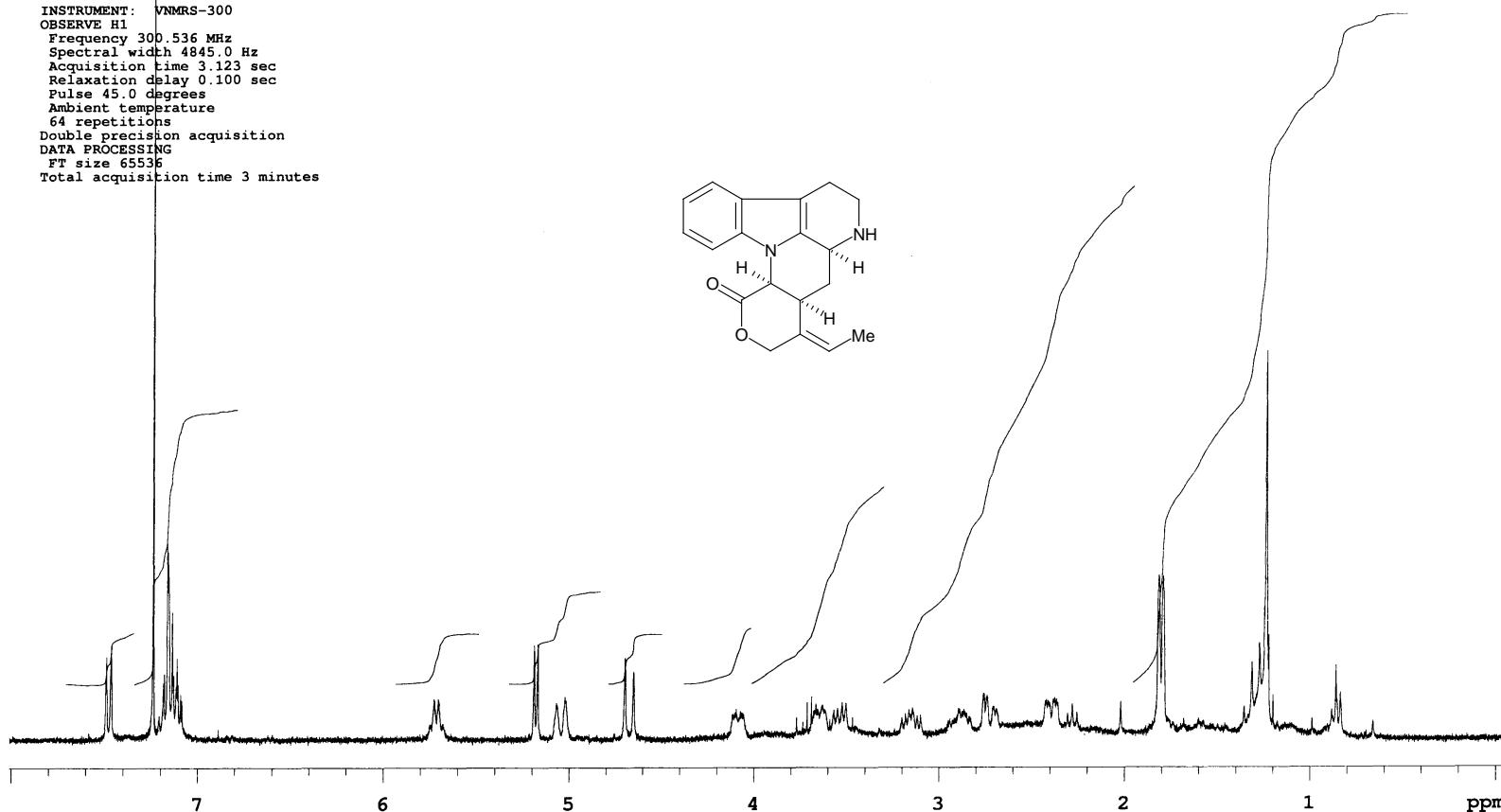
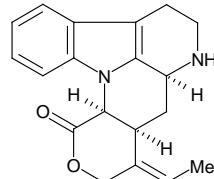


Figure S33: NOESY spectrum (600 MHz, Methanol-*d*₄) of **3a**.

Feb 18 2016

INSTRUMENT: VNMR-300
OBSERVE HI
Frequency 300.536 MHz
Spectral width 4845.0 Hz
Acquisition time 3.123 sec
Relaxation delay 0.100 sec
Pulse 45.0 degrees
Ambient temperature
64 repetitions
Double precision acquisition
DATA PROCESSING
FT size 65536
Total acquisition time 3 minutes



DATE: Feb 18 2016 FILE:nmrdata: laatsch/tn-ftc27a_3h

Figure S34: ¹H NMR spectrum (300 MHz, CDCl₃) of **6**.

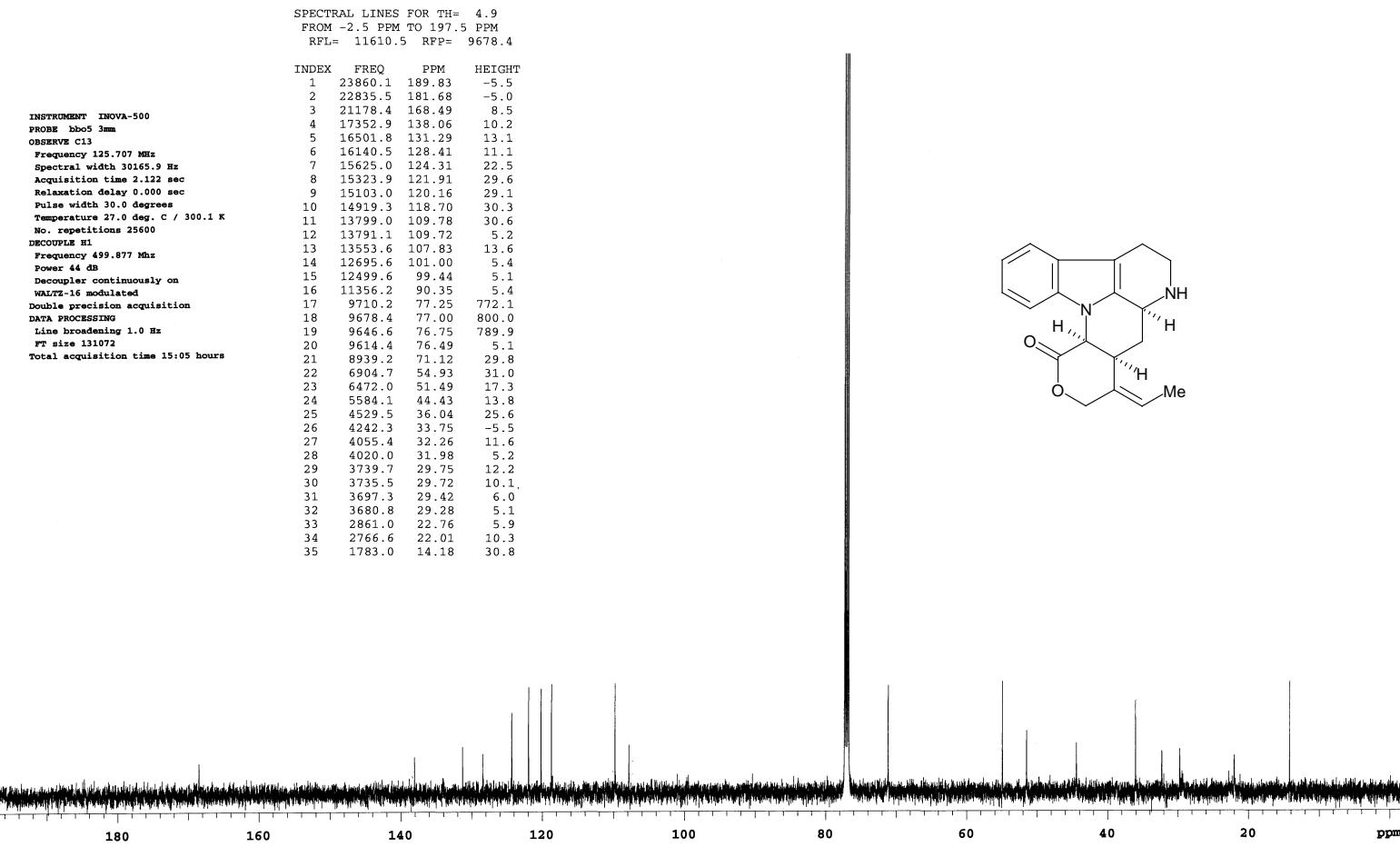


Figure S35: ^{13}C NMR spectrum (125 MHz, CDCl_3) of **6**.

Sample Name:
 Data Collected on:
 i600.nmr-inova600
 Archive directory:
 Sample directory:
 FidFile: gcosy
 Pulse Sequence: gCOSY
 Solvent: cdcl3
 Data collected on: Apr 7 2016
 Temp. 25.0 C / 298.1 K
 Operator: vnmr1
 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width 5291.4 Hz
 2D Width 5291.4 Hz
 2 repetitions
 256 increments
 OBSERVE H1, 599.7373655 MHz
 DATA PROCESSING
 Sq. sine bell 0.075 sec
 F1 DATA PROCESSING
 Sq. sine bell 0.048 sec
 FT size 2048 x 2048
 Total time 10 min

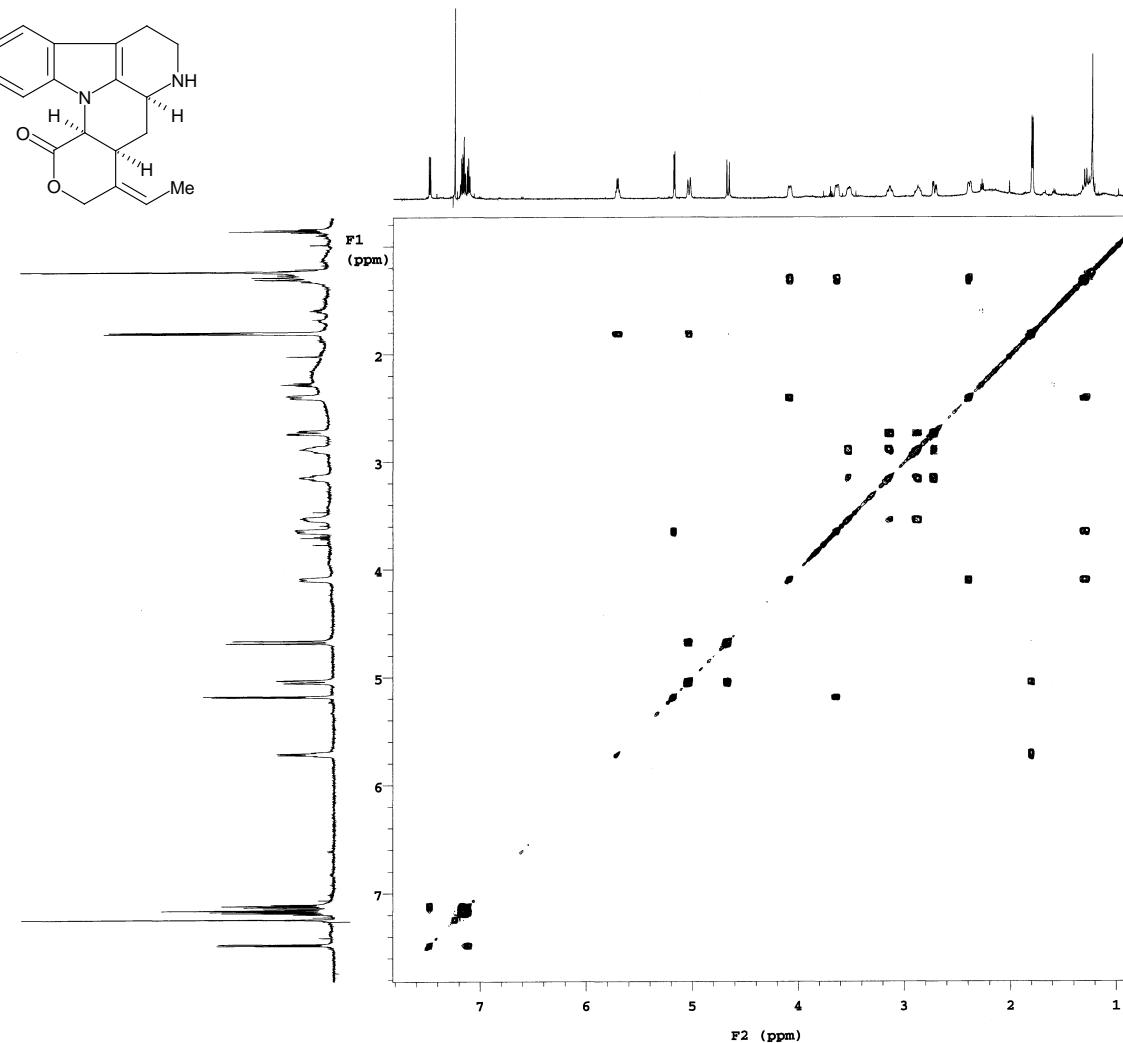
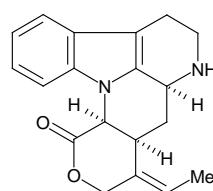


Figure S36: ¹H, ¹H COSY spectrum (600 MHz, CDCl₃) of **6**.

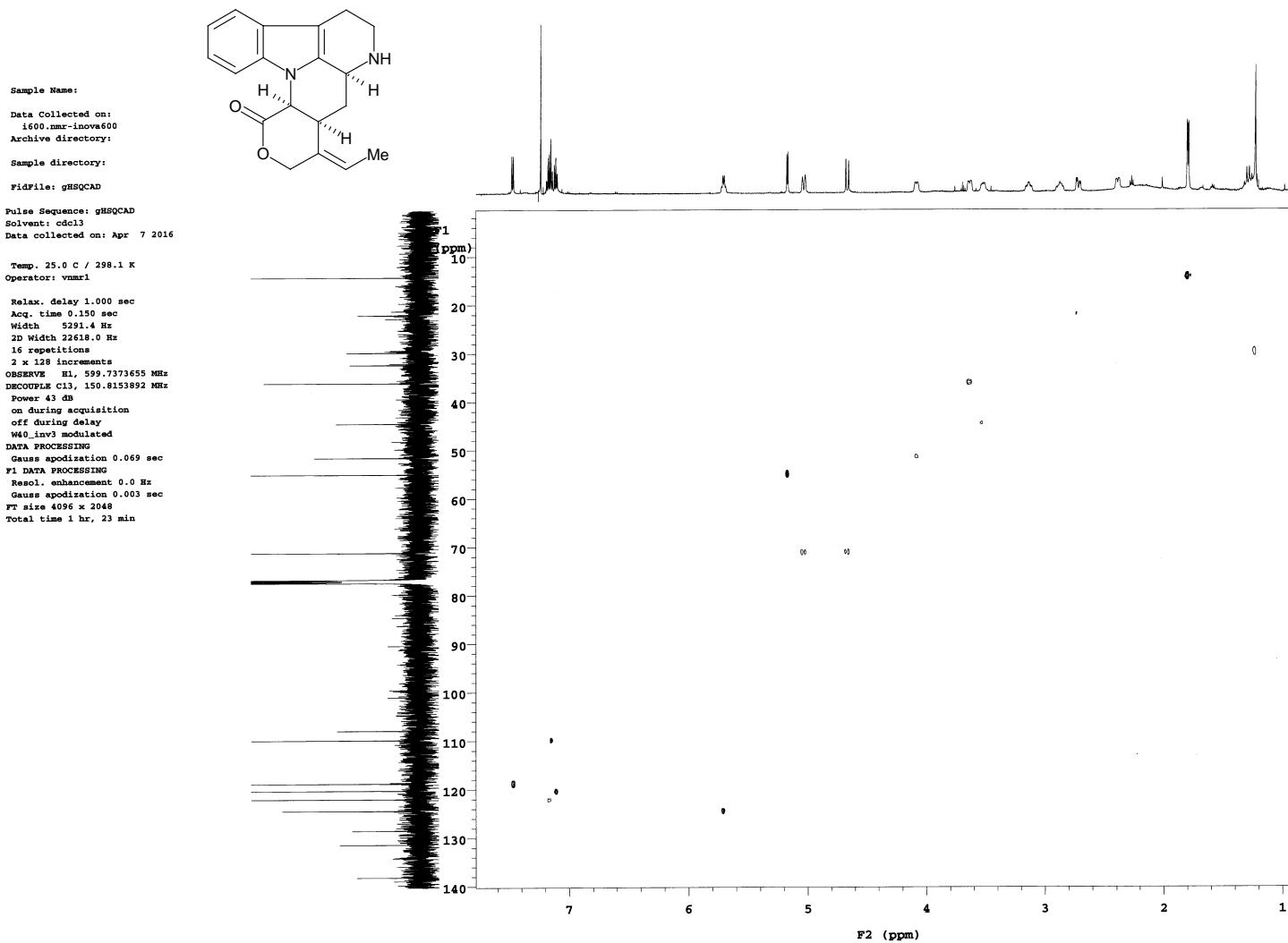


Figure S37: HSQC spectrum (600 MHz, CDCl₃) of **6**.

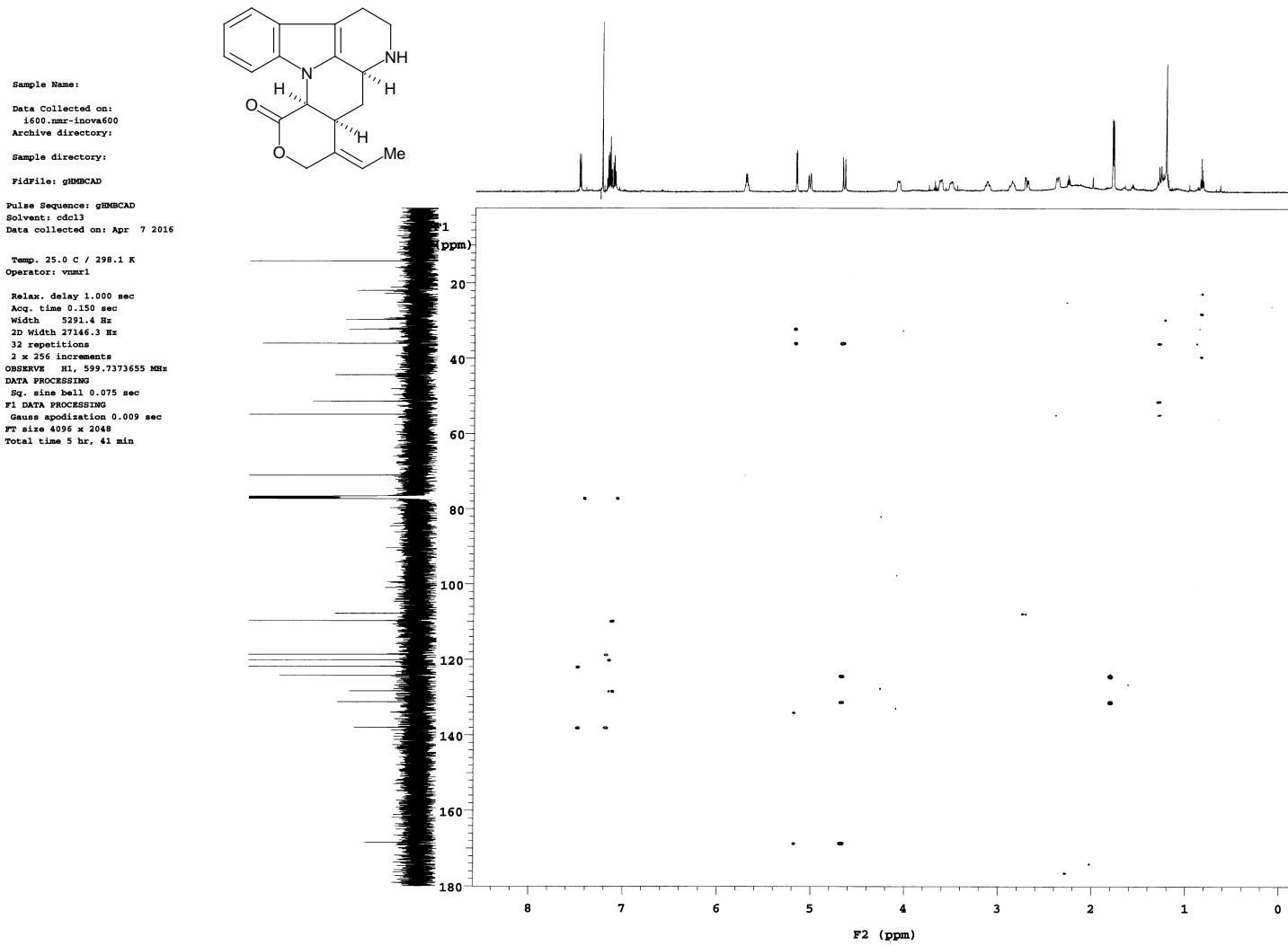


Figure S38: HMBC spectrum (600 MHz, CDCl₃) of **6**.

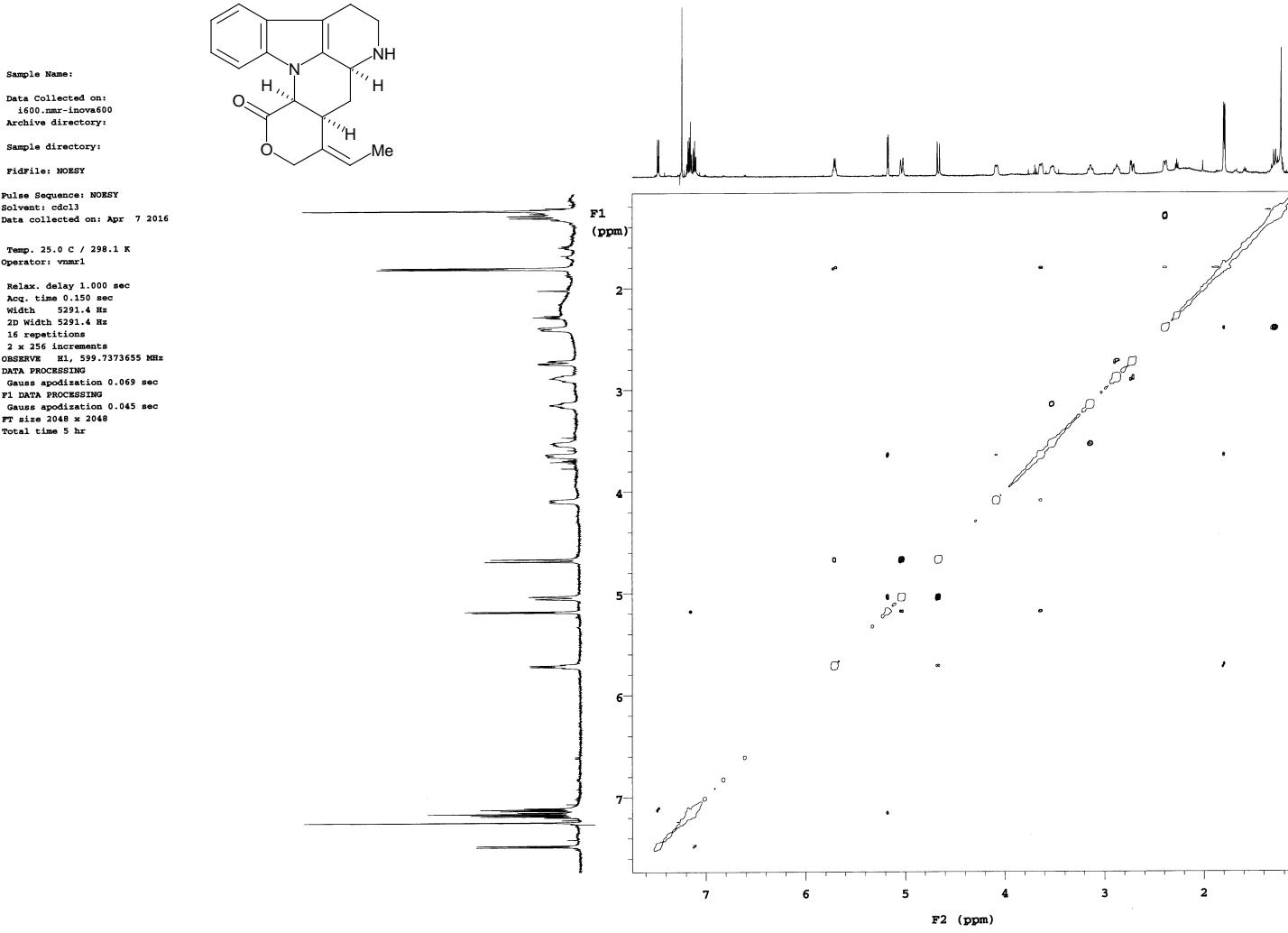


Figure S39: NOESY spectrum (600 MHz, CDCl₃) of **6**.