Supporting Information

Tautomerism and Self-Association in the Solution of New Pinene-Bipyridine and Pinene-Phenanthroline Derivatives

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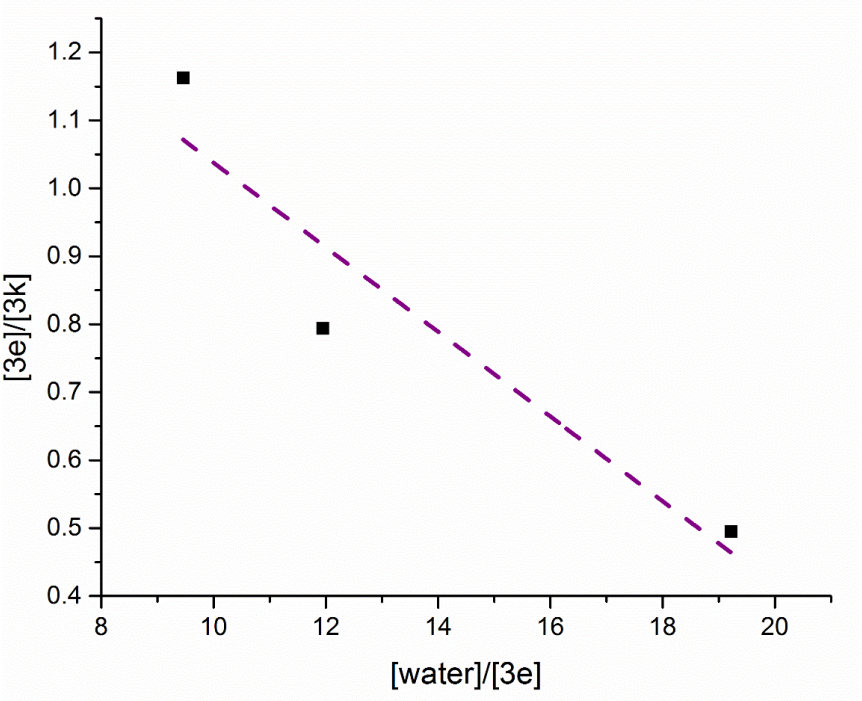


Figure S1. Influence of the water content on the keto-enol equilibrium **3k** ⇌ **3e** (62 mM in CD_3CN)

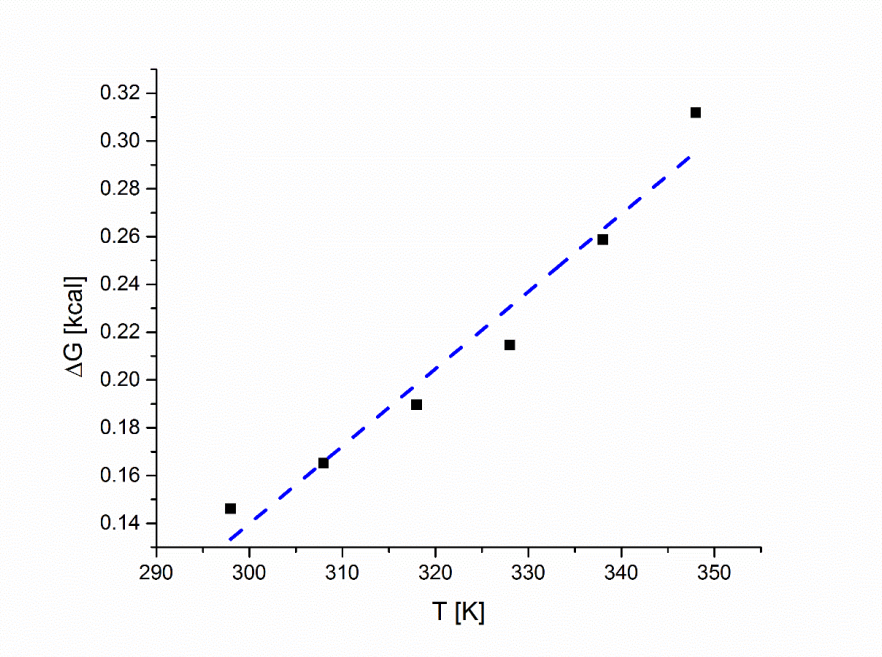


Figure S2. Dependence of the free enthalpy (ΔG°) as a function of temperature for compound **3** (62 mM in CD_3CN), from VT ^{1}H-NMR experiments

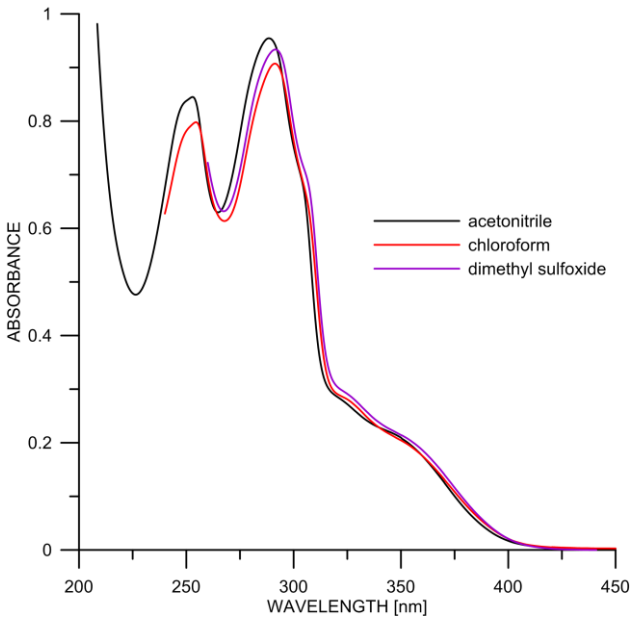
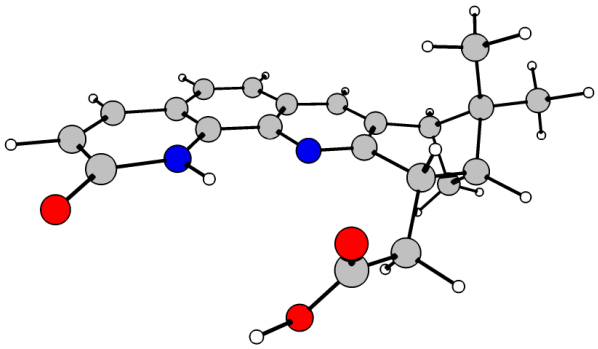
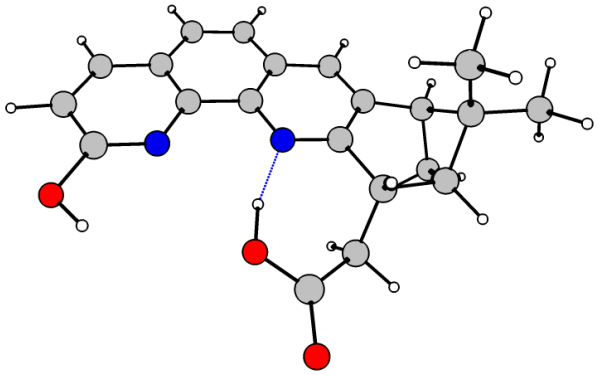
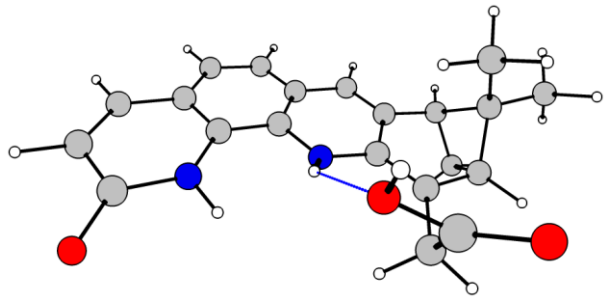
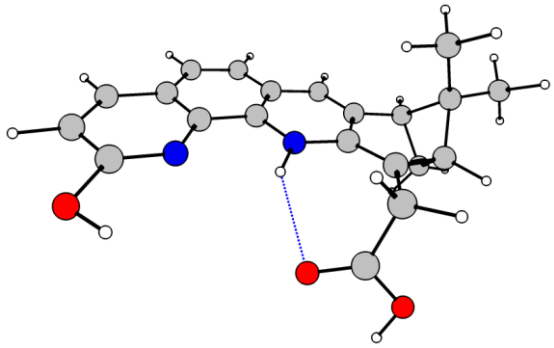
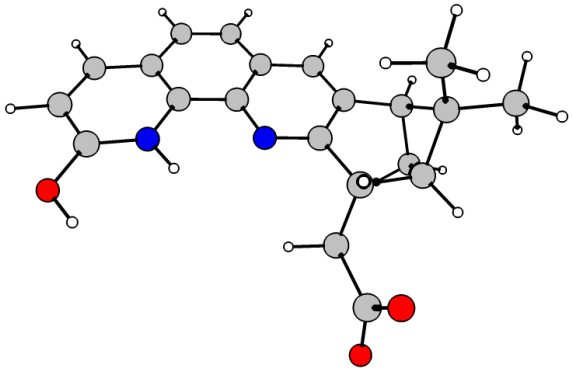
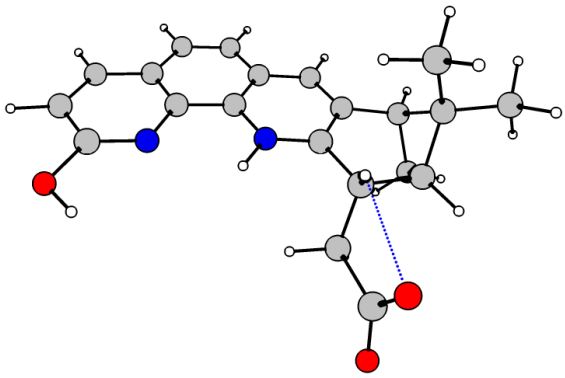
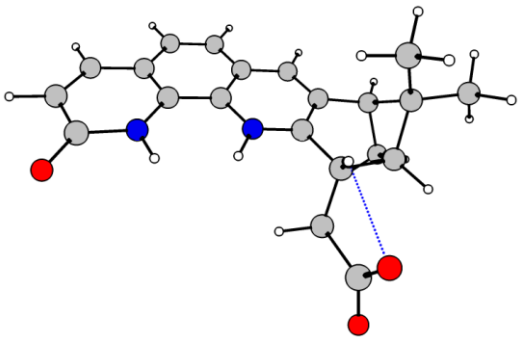


Figure S3. Absorption spectra of **3** in organic solvents.

Table S1. Most stable isomers of the existing tautomers of **6** in chloroform.

Tautomer	ΔE, kcal/mol	μ, D
	0	9.6
	3.0	10.0

	21.4	6.1
	21.1	2.1
	35.4	29.2
	25.3	24.8

	32.1	25.8

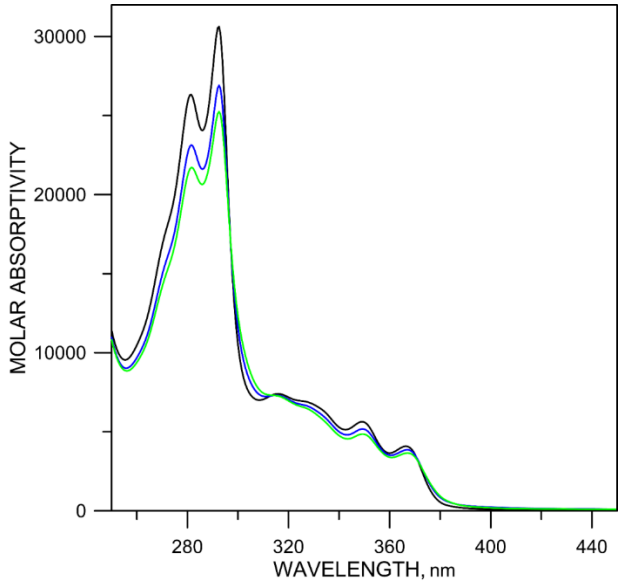


Figure S4. Absorption spectra of **6** in CH_3CN as a function of the concentration while keeping the product between the concentration value and the path length constant (5.0×10^{-5}M). The concentrations are as follows - black solid line: 1.0×10^{-4} M (most concentrated); blue solid line: 5.0×10^{-5} M and green solid line: 5.0×10^{-6} M (most diluted). At concentration higher than 1.0×10^{-4} M no changes are observed.

Table S2. Predicted absorption spectra of the monomer and dimer of **6** in DMSO.

form	*B3LYP/6-311+G(2d,p)// M06-2X/TZVP*	
	λ_{max}, nm	*f**
monomer	*344* *321*	*0.086* *0.037*
dimer	*343* *336* *323* *321*	*0.092* *0.092* *0.010* *0.023*

** Oscillator strength.*

^{1}H-NMR, ^{13}C-NMR Spectra

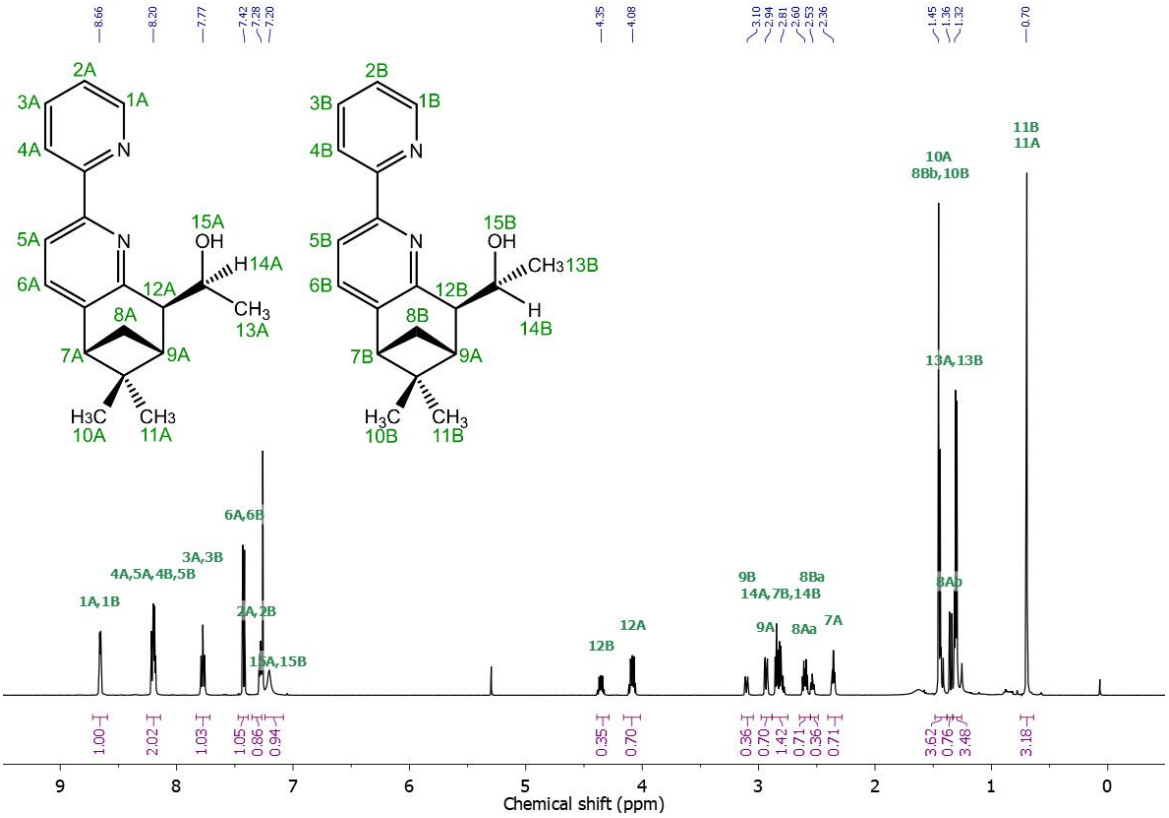


Figure S5. ^{1}H-NMR spectrum of **2** in $CDCl_3$ and proton numbering

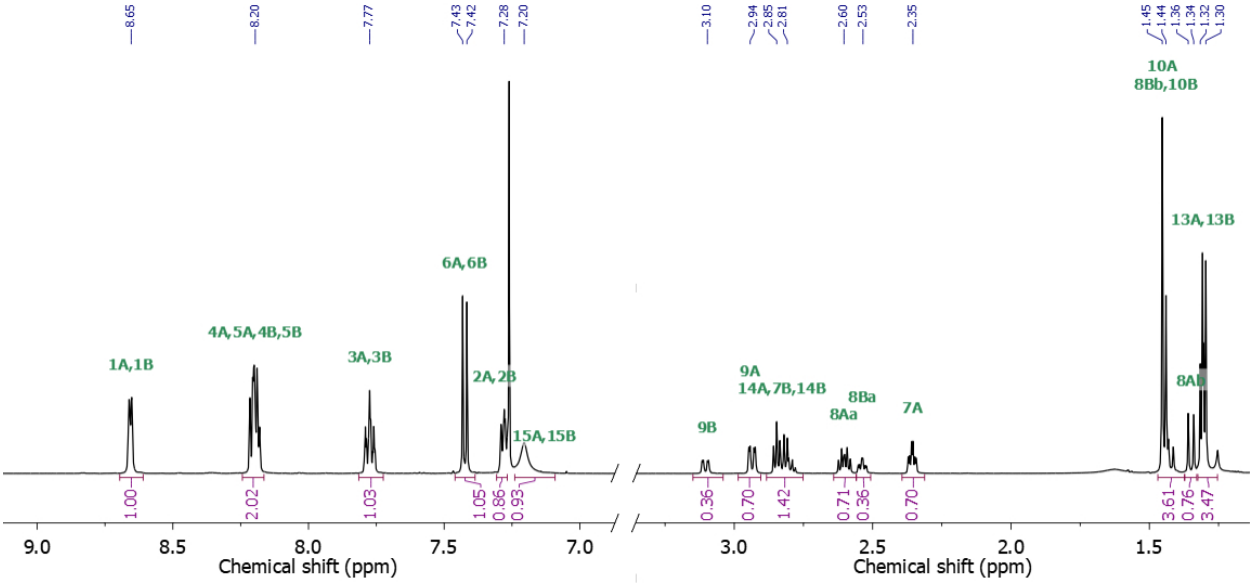


Figure S6. Zoom on the aromatic (left) and aliphatic (right) region of the ^{1}H-NMR spectrum of **2** in $CDCl_3$

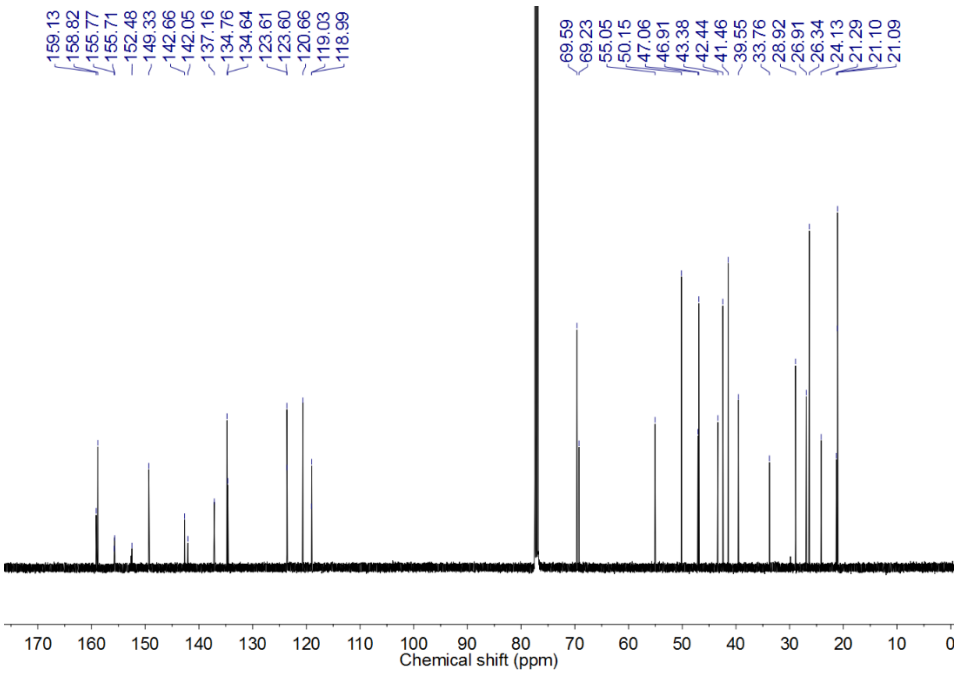


Figure S7. ^{13}C-NMR spectrum of **2** in $CDCl_3$

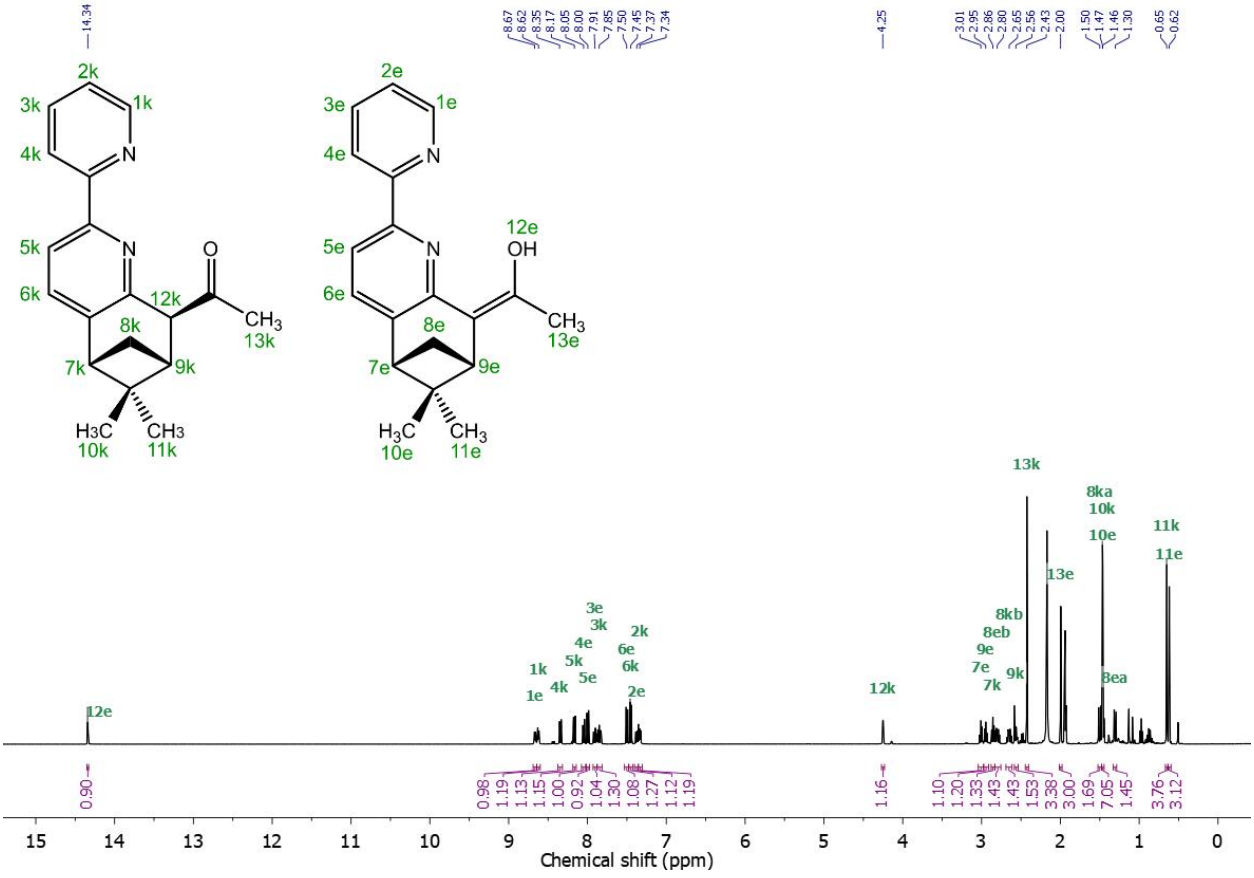


Figure S8. ^{1}H-NMR spectrum of **3** in CD_3CN and proton numbering

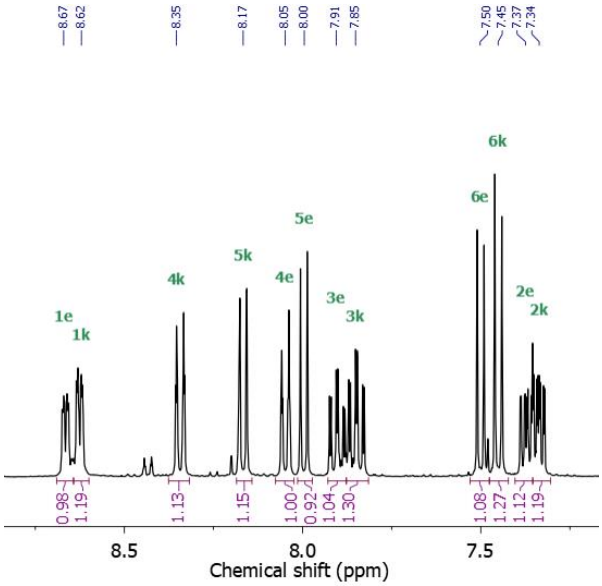


Figure S9. Zoom on the aromatic region of the ^{1}H-NMR spectrum of **3** in CD_3CN

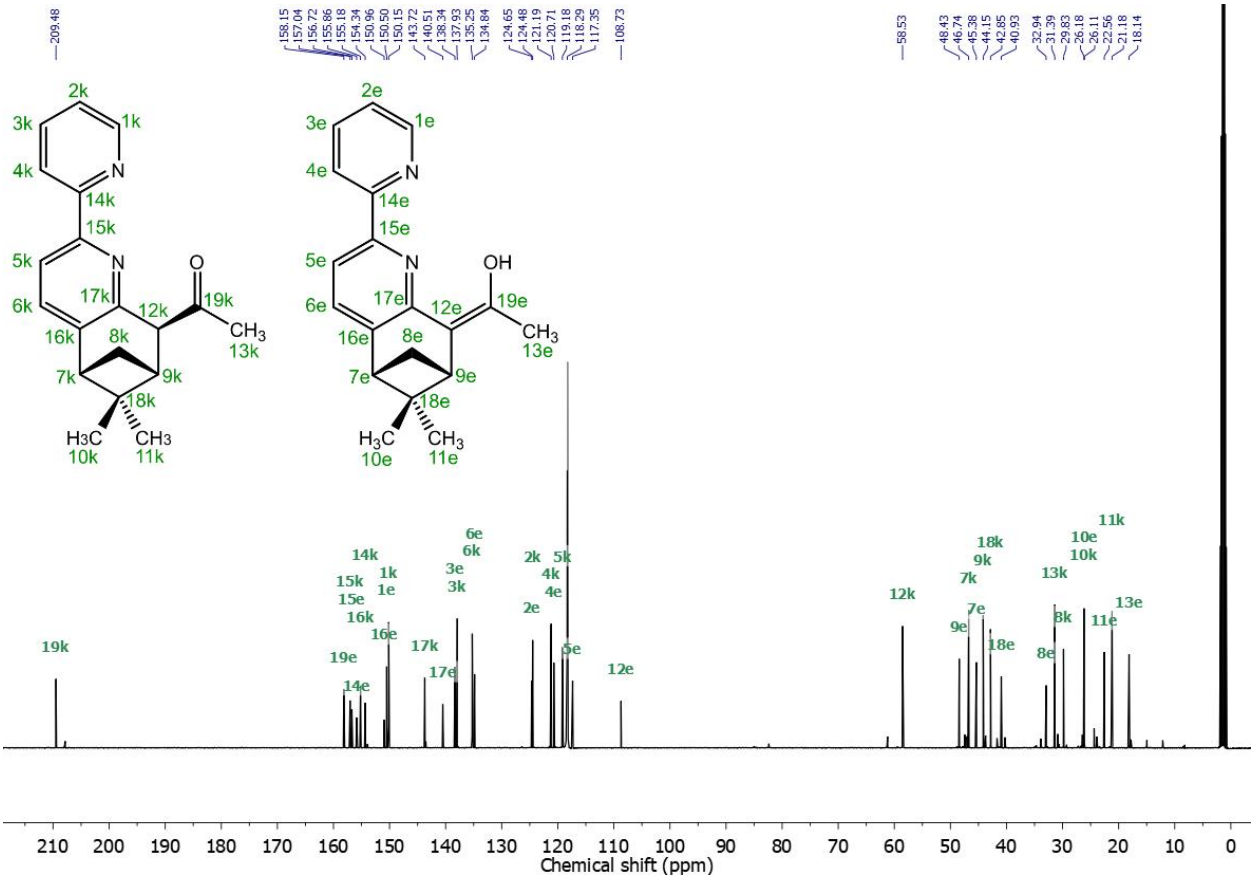


Figure S10. ^{13}C-NMR spectrum of **3** in CD_3CN and carbon numbering

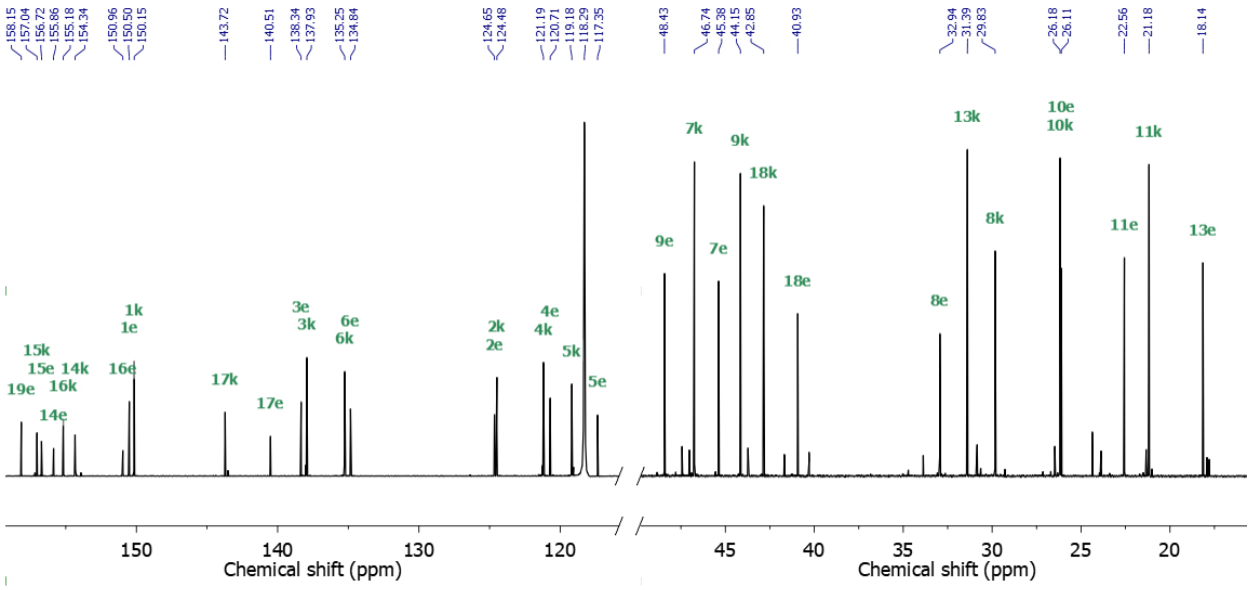


Figure S11. Zoom on the aromatic (left) and aliphatic (right) region of the ^{13}C-NMR spectrum of **3** in CD_3CN

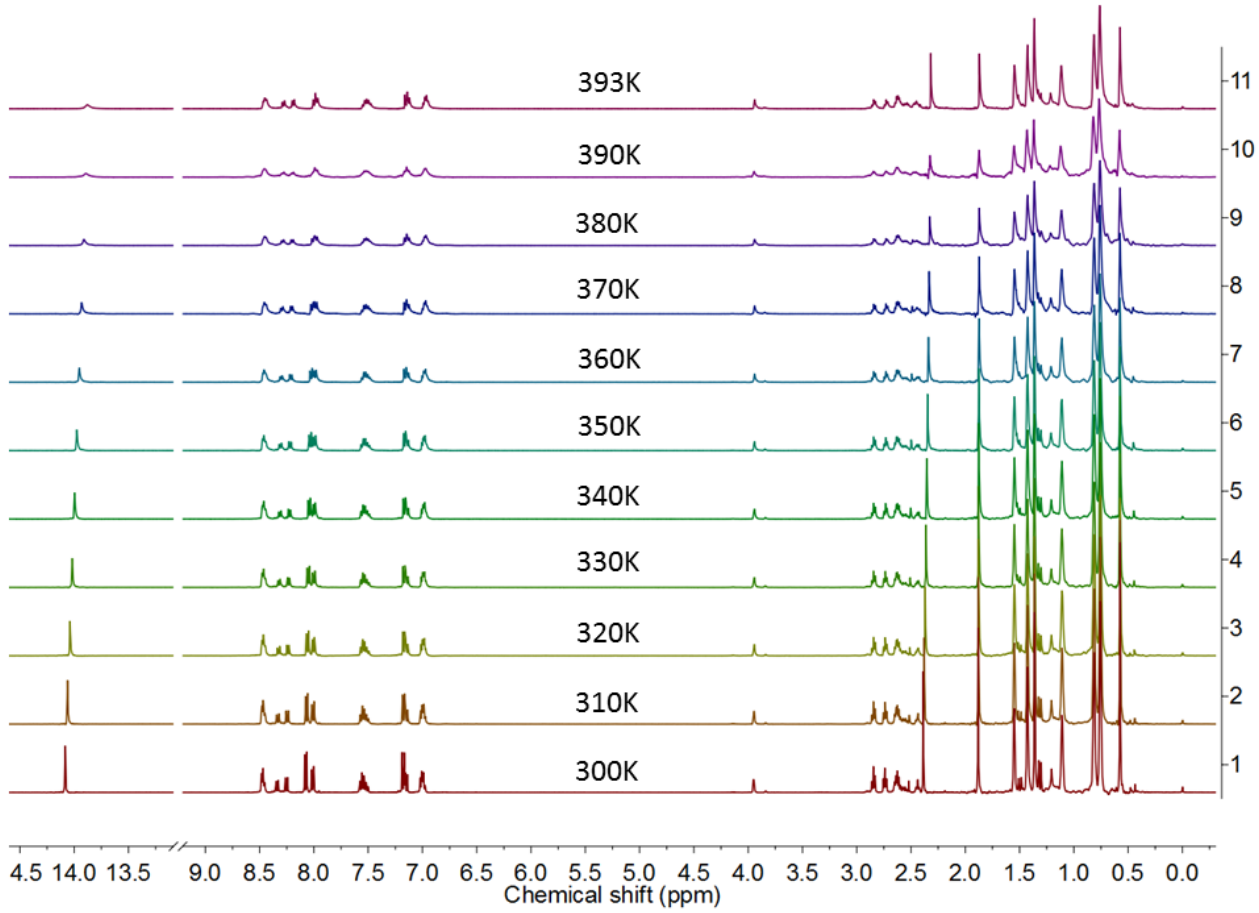


Figure S12. VT-^{1}H-NMR spectra of **3** in decalin-d18

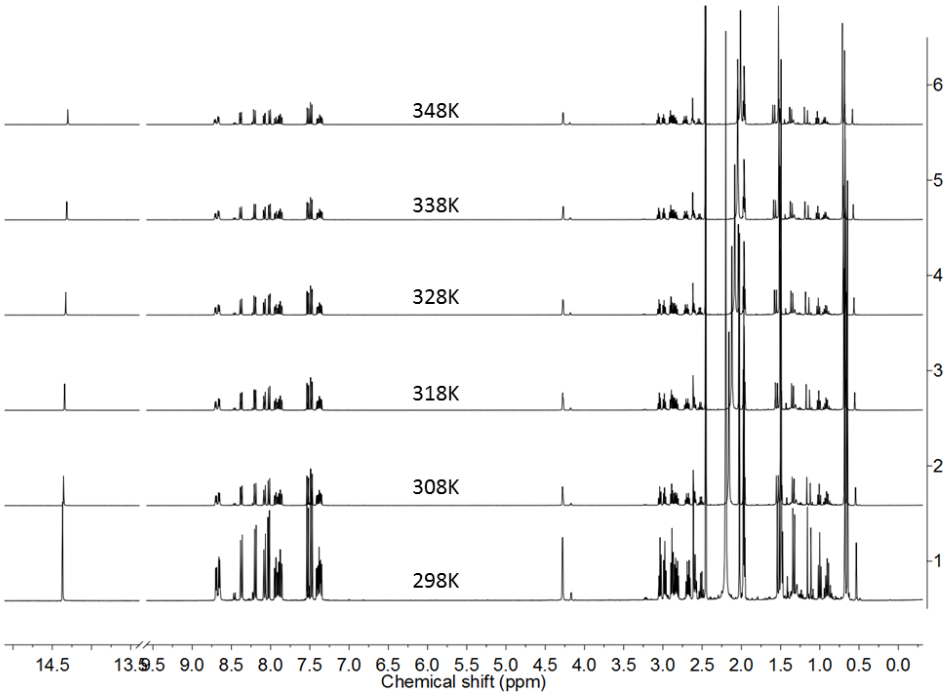


Figure S13. VT-^{1}H-NMR spectra of **3** in CD_3CN

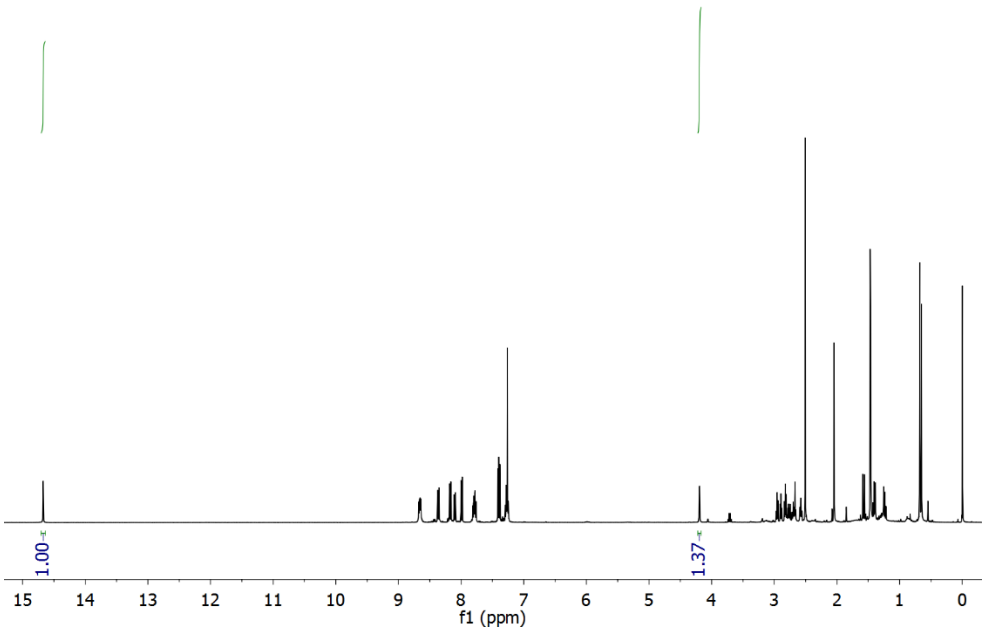


Figure S14a. ^{1}H-NMR spectrum of **3** in CD_3Cl at 298K

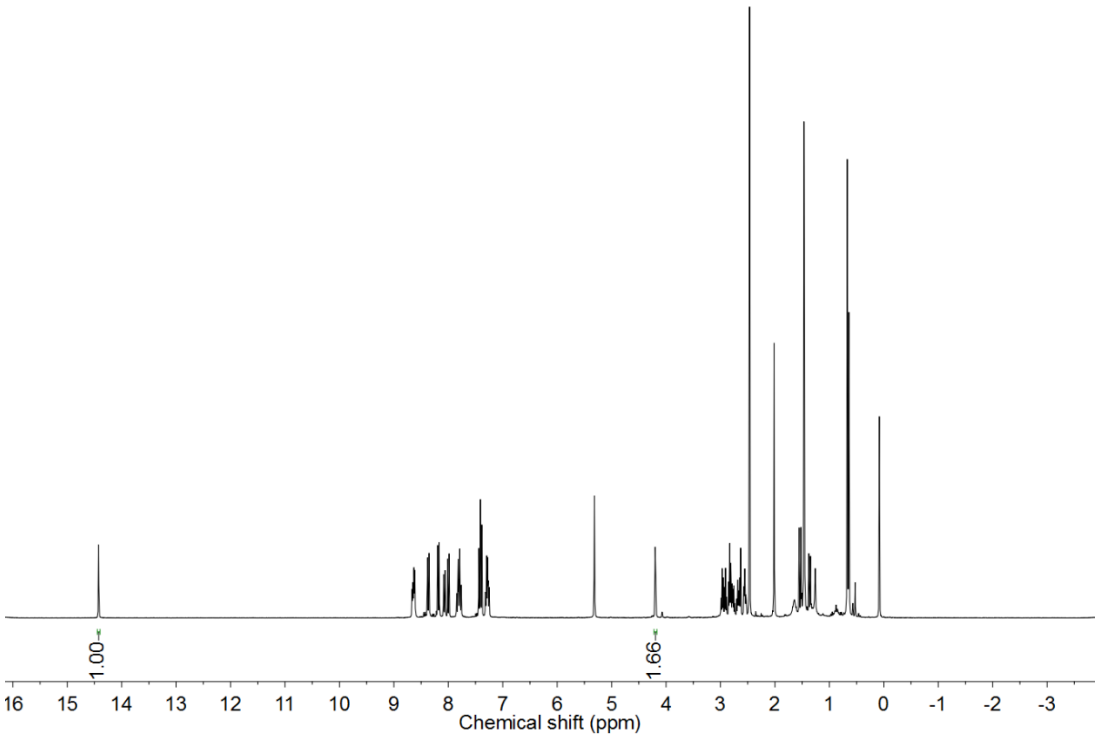


Figure S14b. ^{1}H-NMR spectrum of **3** in CD_2Cl_2 at 298K

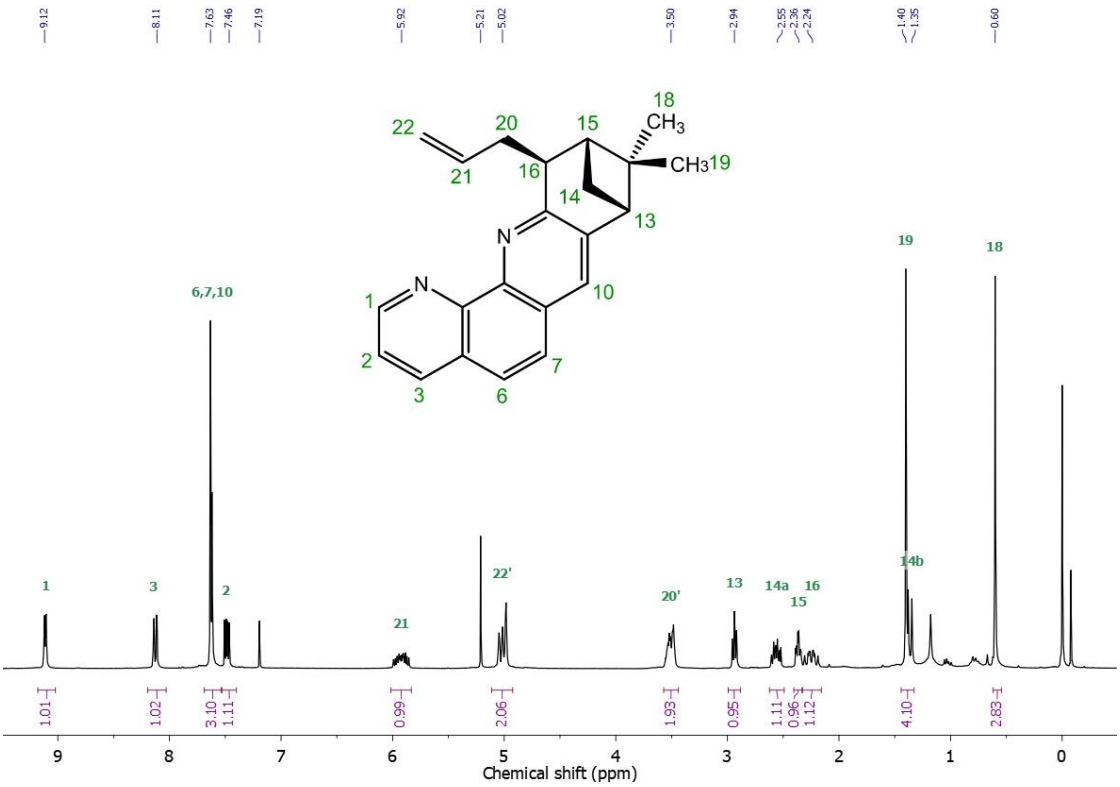


Figure S15. ^{1}H-NMR spectrum of **5** in $CDCl_3$ and proton numbering

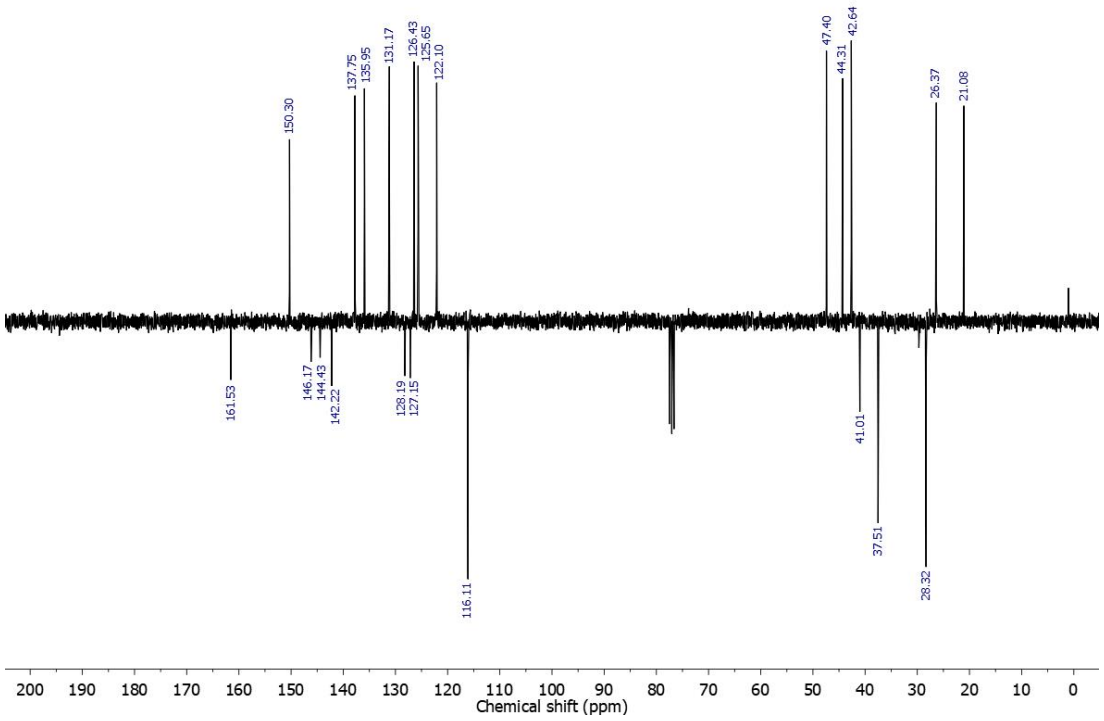


Figure S16. C-APT-NMR spectrum of **5** in $CDCl_3$

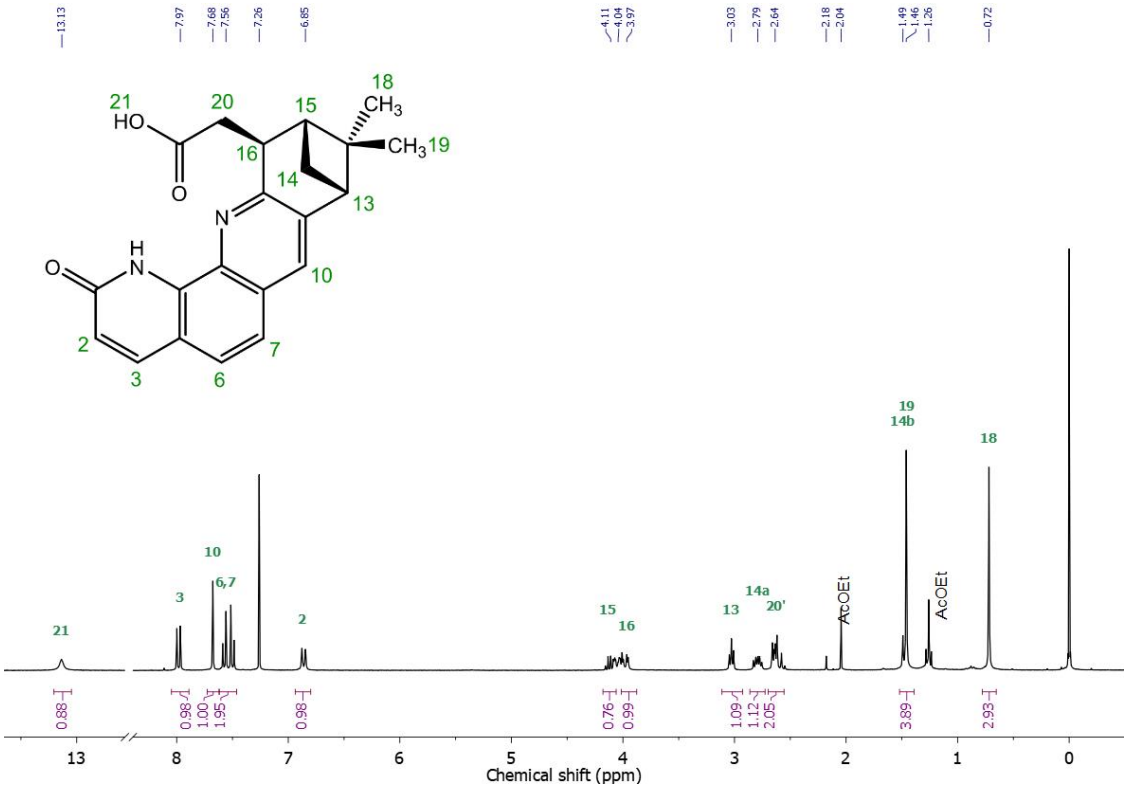


Figure S17. ^{1}H-NMR spectrum of **6** in $CDCl_3$ and proton numbering

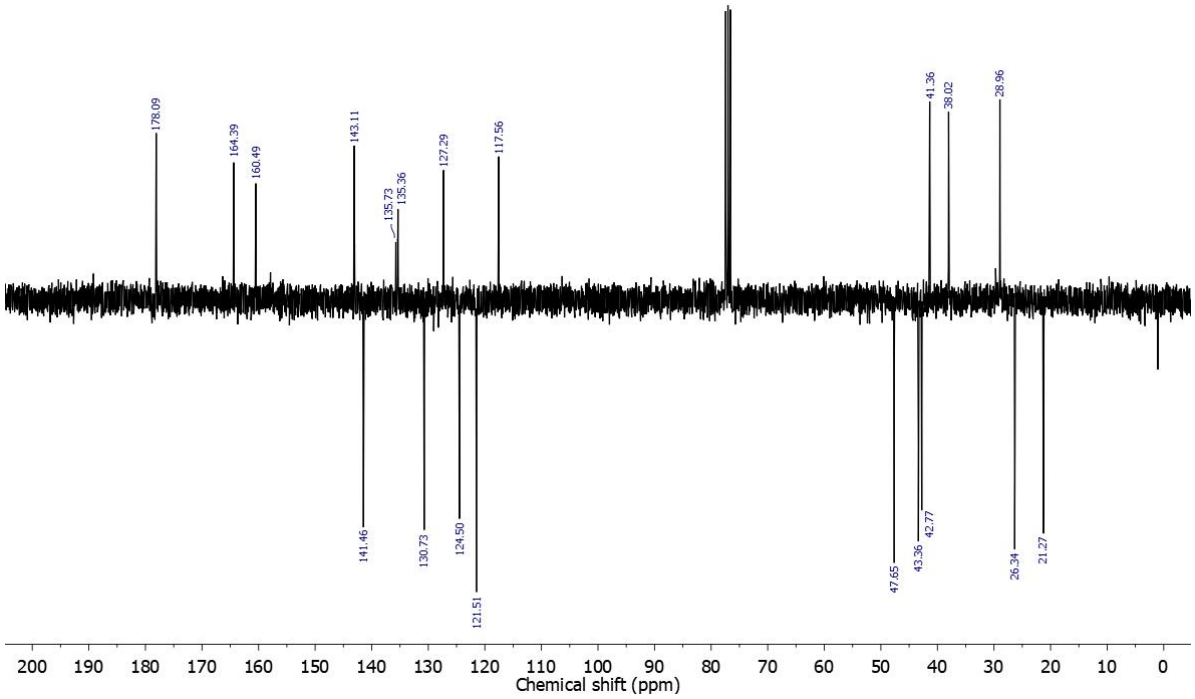


Figure S18. C-APT-NMR spectrum of **6** in $CDCl_3$

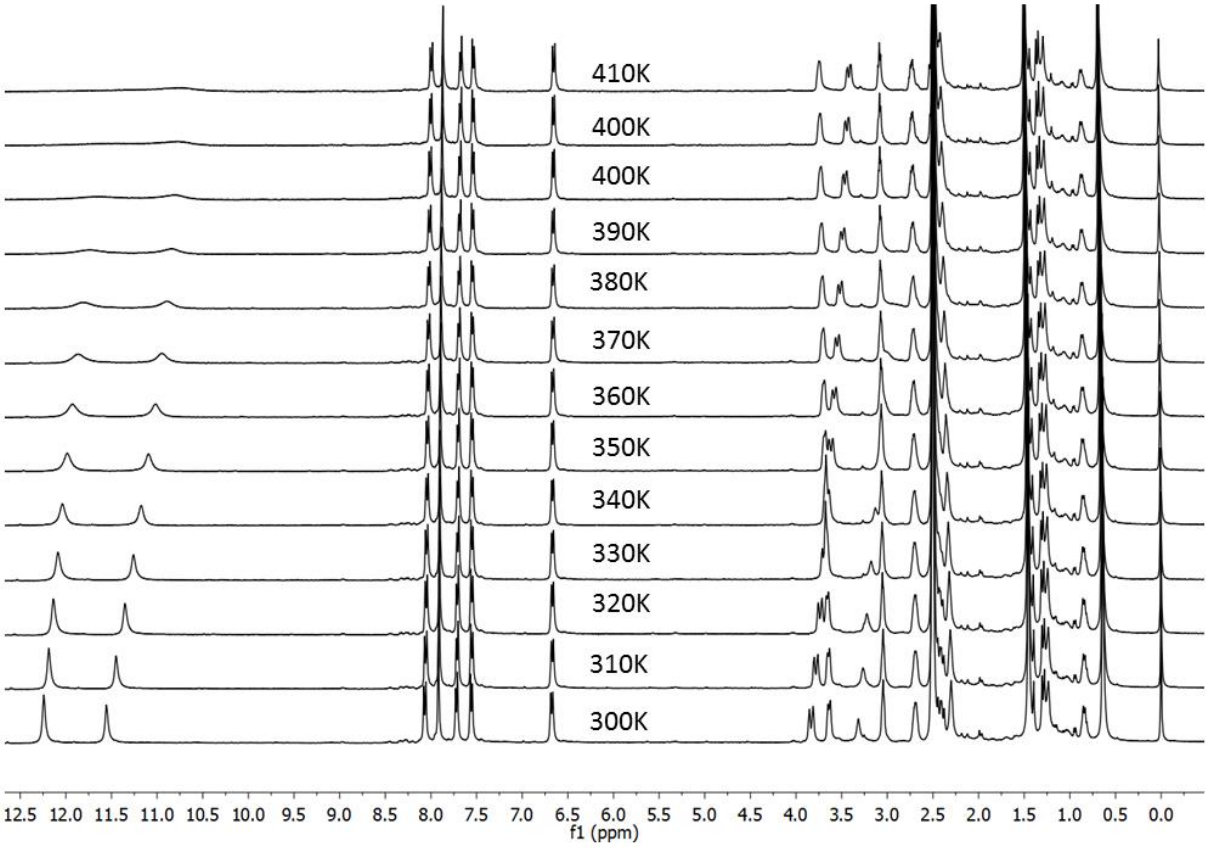


Figure S19. VT-NMR spectra of **6** in DMSO-d6

Mass spectra

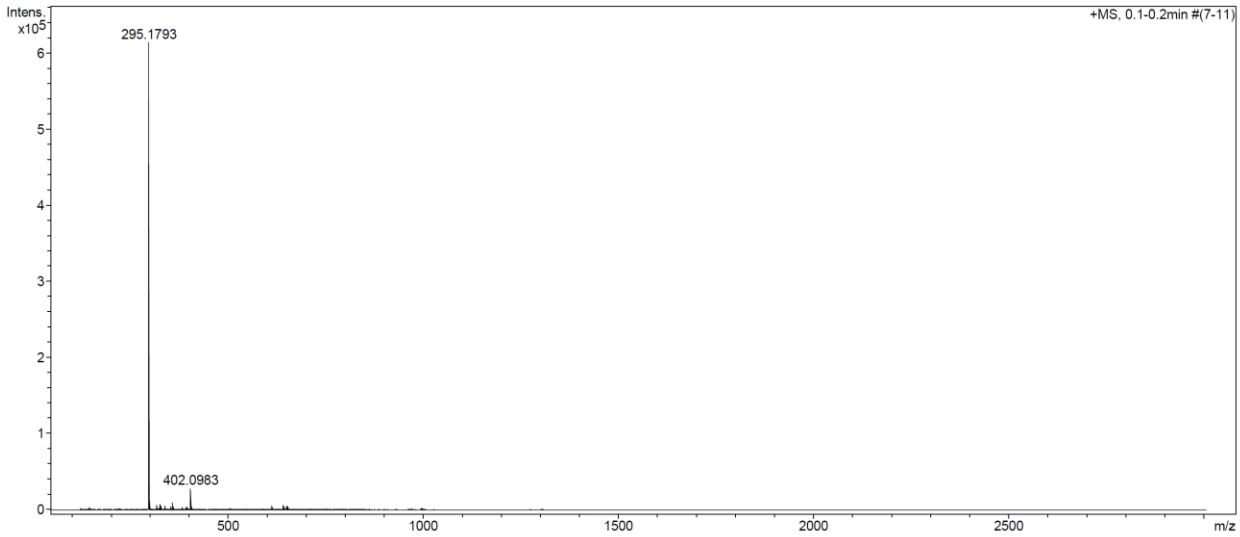
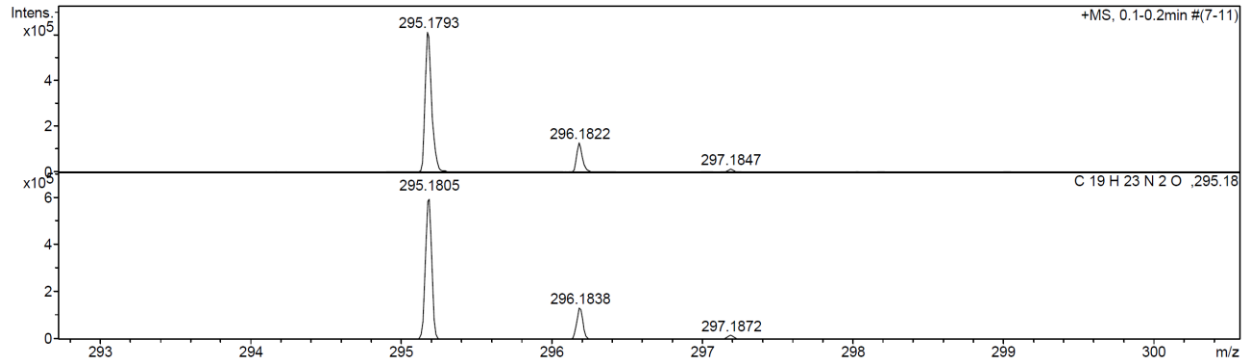


Figure S20. (+)-ESI-MS spectrum of **2**



leas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
295.1793														
	1	C 19 H 23 N 2 O	295.1805	3.9	4.2	9.5	ok	even	2.50	0.0039	0.0013	0.0016	0.0004	0.8427

Figure S21. HRMS spectrum of **2**

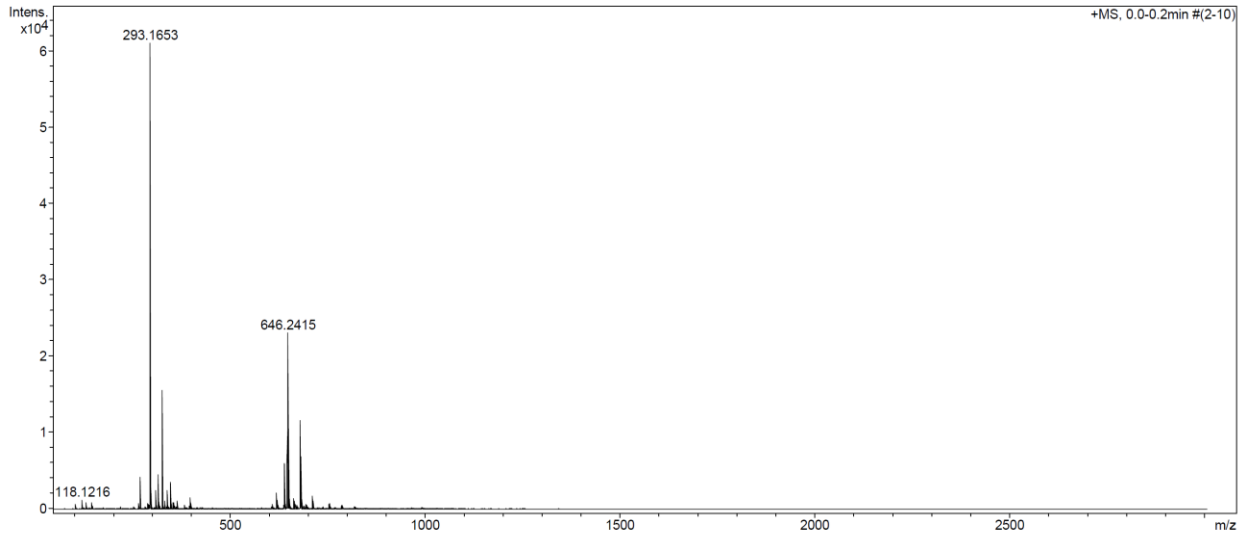
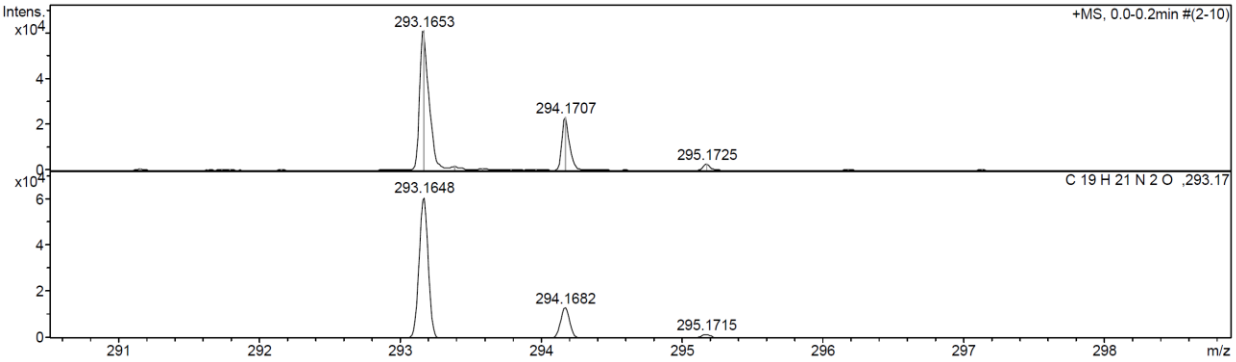


Figure 22. (+)-ESI-MS spectrum of **3**



eas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
293.1653														
	1	C 19 H 21 N 2 O	293.1648	-1.4	-3.4	10.5	ok	even	97.29	0.1442	0.0014	0.0569	0.0021	0.8427

Figure S23. HRMS spectrum of **3**

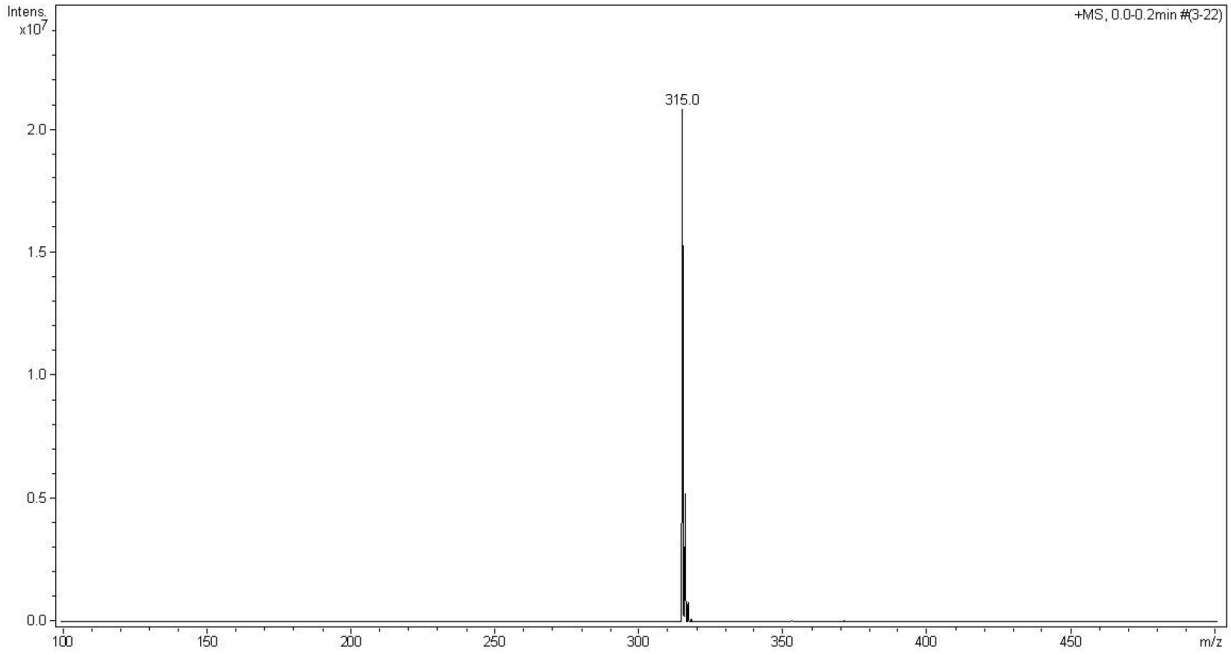


Figure S24. (+)-ESI-MS spectrum of **5**

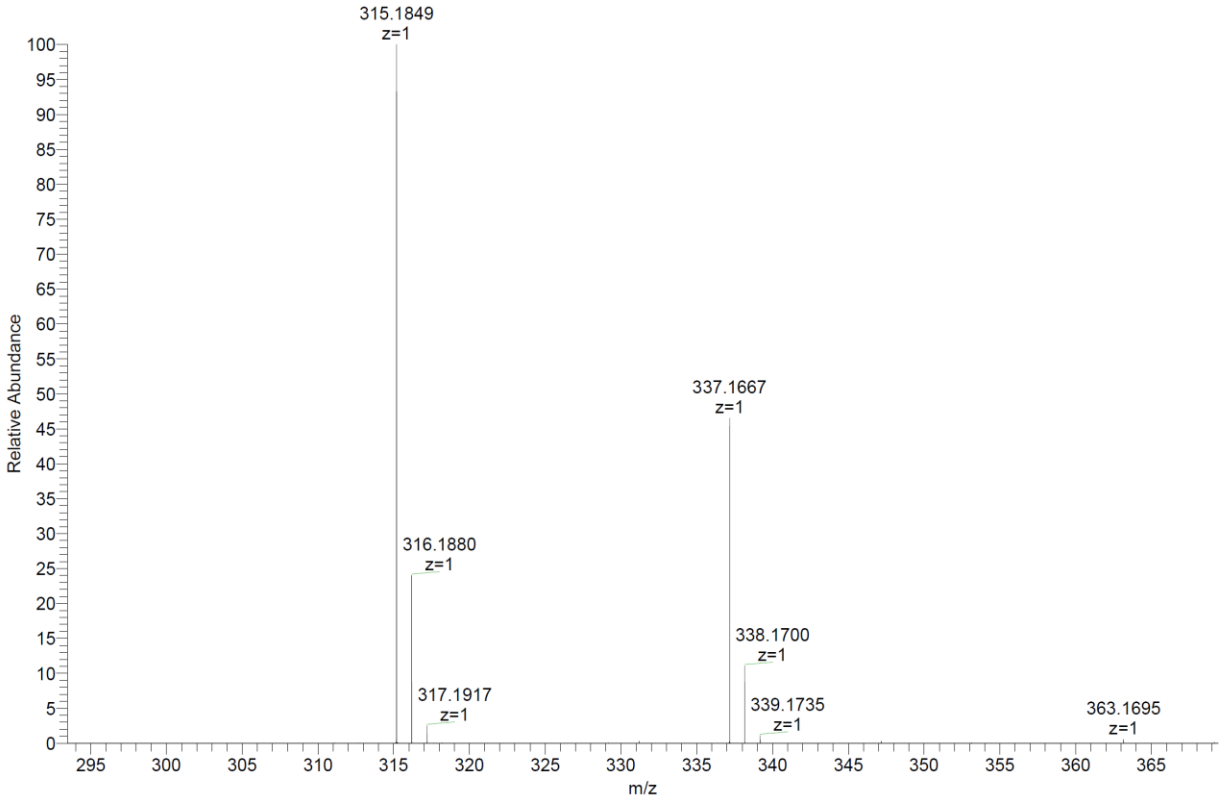


Figure S25. HRMS spectrum of **5**

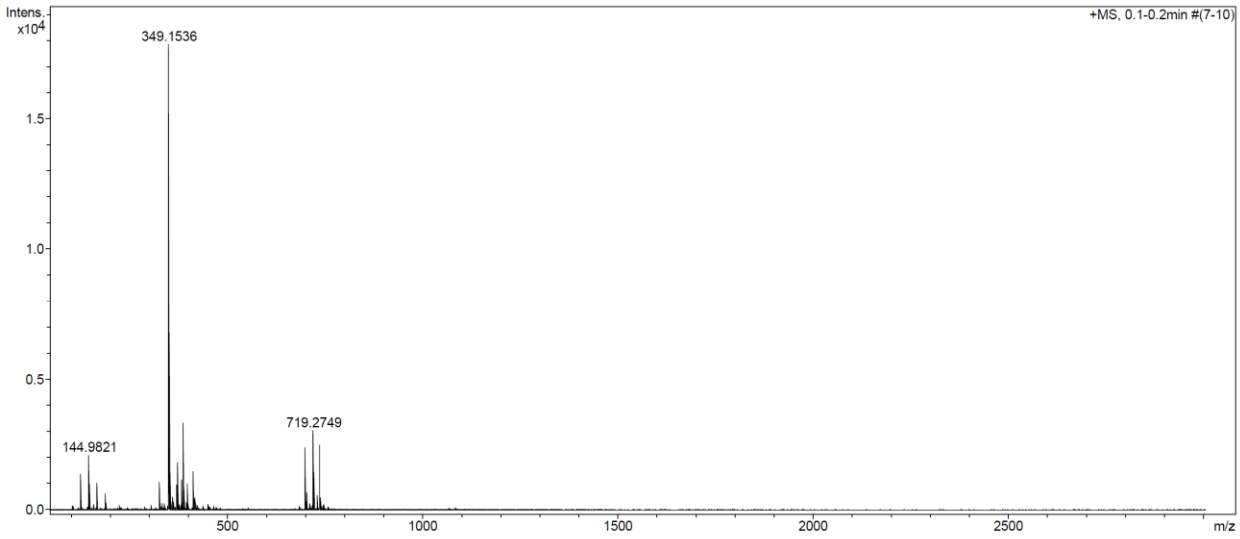
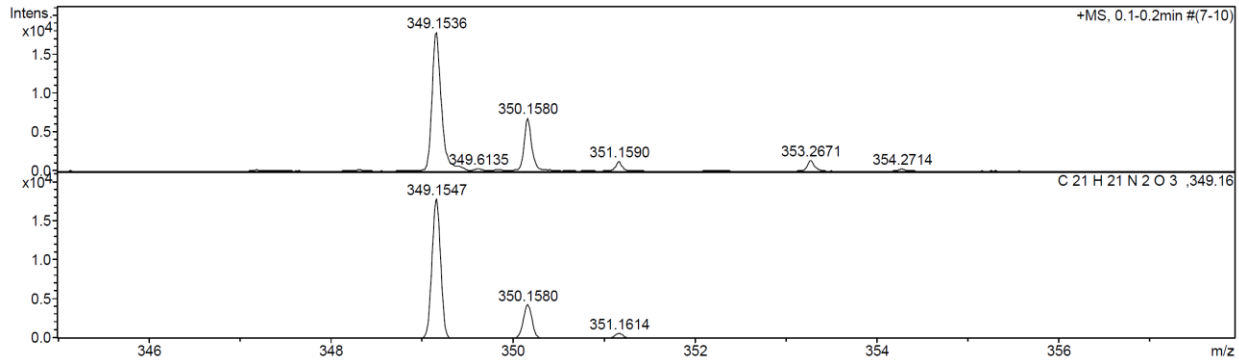


Figure S26. (+)-ESI-MS spectrum of **6**



eas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
349.1536														
	1	C 21 H 21 N 2 O 3	349.1547	3.1	2.4	12.5	ok	even	87.77	0.1295	0.0010	0.0546	0.0011	0.8427

Figure S27. HRMS spectrum of **6**

Table S3. Crystallographic data for **6**

Compound	**6**
CCDC number	1958303
Formula	$C_{21}H_{20}N_2O_3$
$D_{calc.}$/ g cm^{-3}	1.324
μ/mm^{-1}	0.089
Formula Weight	348.39
Colour	colourless
Shape	needle
Size/mm^3	0.32×0.14×0.02
T/K	250(2)
Crystal System	orthorhombic
Space Group	$P2_12_12_1$
a/Å	6.2818(8)
b/Å	14.5974(17)
c/Å	19.054(3)
V/Å^3	1747.2(4)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}- Θ_{max}/$^\circ$	1.757 - 26.365
Measured Refl.	25010
Independent Refl. / restraints/parameters	3517 / 36 /239
Reflections with I > 2(I)	878
R_{int}	0.2809
Largest Peak / Hole /e Å^{-3}	0.141 / -0.173
Deepest Hole	-0.173
GooF	0.675
R_1, wR_2 (I>=2σ (I))	0.2324, 0.0936
R_1, wR_2	0.0462, 0.0625