Fluorescence of Half Twisted 10-Acyl-1-methyltetrahydrobenzoquinolines

Christopher Abelt*, Ian Day, Junkai Zhao, and Robert Pike

College of William and Mary, Department of Chemistry, Williamsburg, Virginia, 23185, USA

Supplementary Information

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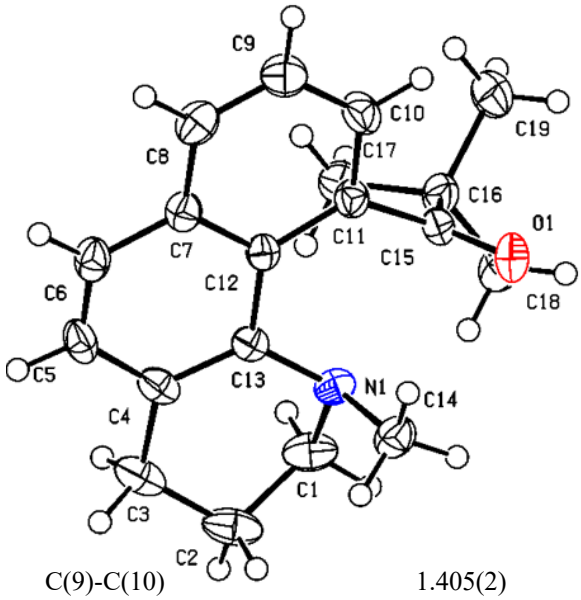
Bond lengths [Å] and angles [°] for Compound **4**.



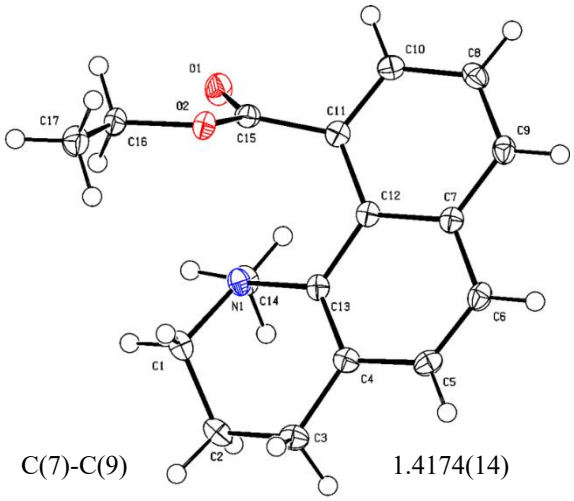
O(1)-C(15)	1.218(2)	C(9)-C(10)	1.405(2)
N(1)-C(13)	1.425(2)	C(9)-H(9)	0.9500
N(1)-C(14)	1.471(2)	C(10)-C(11)	1.377(2)
N(1)-C(1)	1.474(2)	C(10)-H(10)	0.9500
C(1)-C(2)	1.525(3)	C(11)-C(12)	1.422(2)
C(1)-H(1A)	0.9900	C(11)-C(15)	1.517(2)
C(1)-H(1B)	0.9900	C(12)-C(13)	1.429(2)
C(2)-C(3)	1.509(3)	C(14)-H(14A)	0.9800
C(2)-H(2A)	0.9900	C(14)-H(14B)	0.9800
C(2)-H(2B)	0.9900	C(14)-H(14C)	0.9800
C(3)-C(4)	1.509(2)	C(15)-C(16)	1.542(2)
C(3)-H(3A)	0.9900	C(16)-C(18)	1.524(2)
C(3)-H(3B)	0.9900	C(16)-C(17)	1.525(2)
C(4)-C(13)	1.384(2)	C(16)-C(19)	1.544(2)
C(4)-C(5)	1.416(2)	C(17)-H(17A)	0.9800
C(5)-C(6)	1.354(2)	C(17)-H(17B)	0.9800
C(5)-H(5)	0.9500	C(17)-H(17C)	0.9800
C(6)-C(7)	1.412(2)	C(18)-H(18A)	0.9800
C(6)-H(6)	0.9500	C(18)-H(18B)	0.9800
C(7)-C(8)	1.420(2)	C(18)-H(18C)	0.9800
C(7)-C(12)	1.424(2)	C(19)-H(19A)	0.9800
C(8)-C(9)	1.359(3)	C(19)-H(19B)	0.9800
C(8)-H(8)	0.9500	C(19)-H(19C)	0.9800

C(13)-N(1)-C(14)	111.98(12)	C(14)-N(1)-C(1)	111.19(13)
C(13)-N(1)-C(1)	111.99(13)	N(1)-C(1)-C(2)	112.78(14)

N(1)-C(1)-H(1A)	109.0	C(11)-C(10)-H(10)	119.3
C(2)-C(1)-H(1A)	109.0	C(9)-C(10)-H(10)	119.3
N(1)-C(1)-H(1B)	109.0	C(10)-C(11)-C(12)	119.80(14)
C(2)-C(1)-H(1B)	109.0	C(10)-C(11)-C(15)	115.56(14)
H(1A)-C(1)-H(1B)	107.8	C(12)-C(11)-C(15)	124.59(13)
C(3)-C(2)-C(1)	110.14(14)	C(11)-C(12)-C(7)	118.57(13)
C(3)-C(2)-H(2A)	109.6	C(11)-C(12)-C(13)	122.52(13)
C(1)-C(2)-H(2A)	109.6	C(7)-C(12)-C(13)	118.88(14)
C(3)-C(2)-H(2B)	109.6	C(4)-C(13)-N(1)	122.84(14)
C(1)-C(2)-H(2B)	109.6	C(4)-C(13)-C(12)	120.36(14)
H(2A)-C(2)-H(2B)	108.1	N(1)-C(13)-C(12)	116.79(13)
C(4)-C(3)-C(2)	113.13(15)	N(1)-C(14)-H(14A)	109.5
C(4)-C(3)-H(3A)	109.0	N(1)-C(14)-H(14B)	109.5
C(2)-C(3)-H(3A)	109.0	H(14A)-C(14)-H(14B)	109.5
C(4)-C(3)-H(3B)	109.0	N(1)-C(14)-H(14C)	109.5
C(2)-C(3)-H(3B)	109.0	H(14A)-C(14)-H(14C)	109.5
H(3A)-C(3)-H(3B)	107.8	H(14B)-C(14)-H(14C)	109.5
C(13)-C(4)-C(5)	118.74(14)	O(1)-C(15)-C(11)	119.31(15)
C(13)-C(4)-C(3)	121.80(15)	O(1)-C(15)-C(16)	120.26(14)
C(5)-C(4)-C(3)	119.43(15)	C(11)-C(15)-C(16)	119.12(14)
C(6)-C(5)-C(4)	122.13(15)	C(18)-C(16)-C(17)	111.07(15)
C(6)-C(5)-H(5)	118.9	C(18)-C(16)-C(15)	109.30(14)
C(4)-C(5)-H(5)	118.9	C(17)-C(16)-C(15)	113.45(13)
C(5)-C(6)-C(7)	120.29(15)	C(18)-C(16)-C(19)	109.26(14)
C(5)-C(6)-H(6)	119.9	C(17)-C(16)-C(19)	108.78(14)
C(7)-C(6)-H(6)	119.9	C(15)-C(16)-C(19)	104.74(14)
C(6)-C(7)-C(8)	121.65(15)	C(16)-C(17)-H(17A)	109.5
C(6)-C(7)-C(12)	119.11(14)	C(16)-C(17)-H(17B)	109.5
C(8)-C(7)-C(12)	119.23(14)	H(17A)-C(17)-H(17B)	109.5
C(9)-C(8)-C(7)	120.94(15)	C(16)-C(17)-H(17C)	109.5
C(9)-C(8)-H(8)	119.5	H(17A)-C(17)-H(17C)	109.5
C(7)-C(8)-H(8)	119.5	H(17B)-C(17)-H(17C)	109.5
C(8)-C(9)-C(10)	119.92(15)	C(16)-C(18)-H(18A)	109.5
C(8)-C(9)-H(9)	120.0	C(16)-C(18)-H(18B)	109.5
C(10)-C(9)-H(9)	120.0	H(18A)-C(18)-H(18B)	109.5
C(11)-C(10)-C(9)	121.35(16)	C(16)-C(18)-H(18C)	109.5

H(18A)-C(18)-H(18C)	109.5	C(16)-C(19)-H(19C)	109.5
H(18B)-C(18)-H(18C)	109.5	H(19A)-C(19)-H(19C)	109.5
C(16)-C(19)-H(19A)	109.5	H(19B)-C(19)-H(19C)	109.5
C(16)-C(19)-H(19B)	109.5		
H(19A)-C(19)-H(19B)	109.5		

Bond lengths [Å] and angles [°] for Compound **5**.

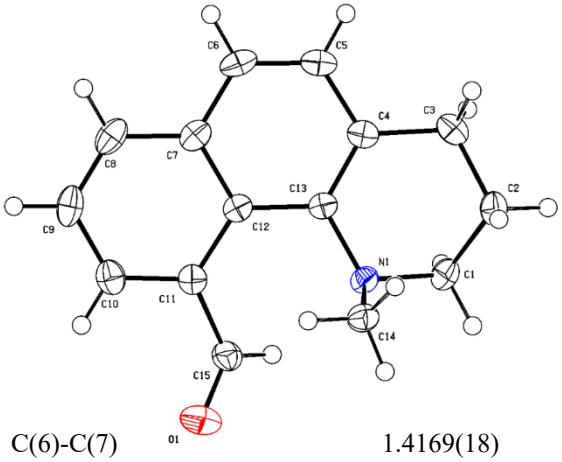


O(1)-C(15)	1.2100(13)	C(7)-C(9)	1.4174(14)
O(2)-C(15)	1.3439(12)	C(7)-C(12)	1.4244(13)
O(2)-C(16)	1.4504(12)	C(8)-C(9)	1.3665(15)
N(1)-C(13)	1.4268(12)	C(8)-C(10)	1.4087(14)
N(1)-C(14)	1.4698(13)	C(8)-H(8)	0.9500
N(1)-C(1)	1.4703(13)	C(9)-H(9)	0.9500
C(1)-C(2)	1.5277(15)	C(10)-C(11)	1.3777(14)
C(1)-H(1A)	0.9900	C(10)-H(10)	0.9500
C(1)-H(1B)	0.9900	C(11)-C(12)	1.4295(14)
C(2)-C(3)	1.5222(14)	C(11)-C(15)	1.4981(14)
C(2)-H(2A)	0.9900	C(12)-C(13)	1.4341(14)
C(2)-H(2B)	0.9900	C(14)-H(14A)	0.9800
C(3)-C(4)	1.5104(14)	C(14)-H(14B)	0.9800
C(3)-H(3A)	0.9900	C(14)-H(14C)	0.9800
C(3)-H(3B)	0.9900	C(16)-C(17)	1.5049(15)
C(4)-C(13)	1.3826(14)	C(16)-H(16A)	0.9900
C(4)-C(5)	1.4167(14)	C(16)-H(16B)	0.9900
C(5)-C(6)	1.3623(15)	C(17)-H(17A)	0.9800
C(5)-H(5)	0.9500	C(17)-H(17B)	0.9800
C(6)-C(7)	1.4188(14)	C(17)-H(17C)	0.9800
C(6)-H(6)	0.9500		

C(15)-O(2)-C(16)	114.24(8)	C(13)-N(1)-C(14)	112.96(8)

C(13)-N(1)-C(1)	112.75(8)	C(8)-C(9)-H(9)	119.5
C(14)-N(1)-C(1)	112.05(8)	C(7)-C(9)-H(9)	119.5
N(1)-C(1)-C(2)	111.48(8)	C(11)-C(10)-C(8)	121.02(9)
N(1)-C(1)-H(1A)	109.3	C(11)-C(10)-H(10)	119.5
C(2)-C(1)-H(1A)	109.3	C(8)-C(10)-H(10)	119.5
N(1)-C(1)-H(1B)	109.3	C(10)-C(11)-C(12)	120.45(9)
C(2)-C(1)-H(1B)	109.3	C(10)-C(11)-C(15)	116.72(9)
H(1A)-C(1)-H(1B)	108.0	C(12)-C(11)-C(15)	122.68(9)
C(3)-C(2)-C(1)	109.43(8)	C(7)-C(12)-C(11)	117.58(9)
C(3)-C(2)-H(2A)	109.8	C(7)-C(12)-C(13)	119.21(9)
C(1)-C(2)-H(2A)	109.8	C(11)-C(12)-C(13)	123.21(9)
C(3)-C(2)-H(2B)	109.8	C(4)-C(13)-N(1)	122.14(9)
C(1)-C(2)-H(2B)	109.8	C(4)-C(13)-C(12)	120.03(9)
H(2A)-C(2)-H(2B)	108.2	N(1)-C(13)-C(12)	117.82(8)
C(4)-C(3)-C(2)	112.44(8)	N(1)-C(14)-H(14A)	109.5
C(4)-C(3)-H(3A)	109.1	N(1)-C(14)-H(14B)	109.5
C(2)-C(3)-H(3A)	109.1	H(14A)-C(14)-H(14B)	109.5
C(4)-C(3)-H(3B)	109.1	N(1)-C(14)-H(14C)	109.5
C(2)-C(3)-H(3B)	109.1	H(14A)-C(14)-H(14C)	109.5
H(3A)-C(3)-H(3B)	107.8	H(14B)-C(14)-H(14C)	109.5
C(13)-C(4)-C(5)	119.16(9)	O(1)-C(15)-O(2)	123.81(9)
C(13)-C(4)-C(3)	122.19(9)	O(1)-C(15)-C(11)	124.02(9)
C(5)-C(4)-C(3)	118.65(9)	O(2)-C(15)-C(11)	111.87(8)
C(6)-C(5)-C(4)	121.84(9)	O(2)-C(16)-C(17)	107.96(8)
C(6)-C(5)-H(5)	119.1	O(2)-C(16)-H(16A)	110.1
C(4)-C(5)-H(5)	119.1	C(17)-C(16)-H(16A)	110.1
C(5)-C(6)-C(7)	120.41(9)	O(2)-C(16)-H(16B)	110.1
C(5)-C(6)-H(6)	119.8	C(17)-C(16)-H(16B)	110.1
C(7)-C(6)-H(6)	119.8	H(16A)-C(16)-H(16B)	108.4
C(9)-C(7)-C(6)	121.56(9)	C(16)-C(17)-H(17A)	109.5
C(9)-C(7)-C(12)	119.77(9)	C(16)-C(17)-H(17B)	109.5
C(6)-C(7)-C(12)	118.66(9)	H(17A)-C(17)-H(17B)	109.5
C(9)-C(8)-C(10)	119.60(9)	C(16)-C(17)-H(17C)	109.5
C(9)-C(8)-H(8)	120.2	H(17A)-C(17)-H(17C)	109.5
C(10)-C(8)-H(8)	120.2	H(17B)-C(17)-H(17C)	109.5
C(8)-C(9)-C(7)	120.99(9)		

Bond lengths [Å] and angles [°] for Compound **6**.



O(1)-C(15)	1.2098(15)	C(6)-C(7)	1.4169(18)
N(1)-C(13)	1.4276(14)	C(7)-C(8)	1.4181(17)
N(1)-C(14)	1.4665(15)	C(7)-C(12)	1.4266(16)
N(1)-C(1)	1.4680(15)	C(8)-C(9)	1.365(2)
C(1)-C(2)	1.5239(17)	C(9)-C(10)	1.4024(18)
C(2)-C(3)	1.5240(17)	C(10)-C(11)	1.3799(17)
C(3)-C(4)	1.5104(17)	C(11)-C(12)	1.4319(16)
C(4)-C(13)	1.3824(16)	C(11)-C(15)	1.4879(16)
C(4)-C(5)	1.4166(17)	C(12)-C(13)	1.4331(16)
C(5)-C(6)	1.3579(19)		

C(13)-N(1)-C(14)	112.84(9)	C(9)-C(8)-C(7)	120.95(11)
C(13)-N(1)-C(1)	112.90(9)	C(8)-C(9)-C(10)	119.69(11)
C(14)-N(1)-C(1)	112.61(9)	C(11)-C(10)-C(9)	121.57(12)
N(1)-C(1)-C(2)	112.35(10)	C(10)-C(11)-C(12)	119.99(11)
C(1)-C(2)-C(3)	108.79(10)	C(10)-C(11)-C(15)	115.78(11)
C(4)-C(3)-C(2)	113.55(10)	C(12)-C(11)-C(15)	123.72(10)
C(13)-C(4)-C(5)	118.85(11)	C(7)-C(12)-C(11)	117.79(10)
C(13)-C(4)-C(3)	122.25(10)	C(7)-C(12)-C(13)	118.52(10)
C(5)-C(4)-C(3)	118.90(10)	C(11)-C(12)-C(13)	123.70(10)
C(6)-C(5)-C(4)	121.80(11)	C(4)-C(13)-N(1)	121.49(10)
C(5)-C(6)-C(7)	120.58(11)	C(4)-C(13)-C(12)	120.69(10)
C(6)-C(7)-C(8)	121.23(11)	N(1)-C(13)-C(12)	117.82(10)
C(6)-C(7)-C(12)	118.95(11)	O(1)-C(15)-C(11)	123.22(12)
C(8)-C(7)-C(12)	119.80(11)		

Crystal data and structure refinement for Compound **4**.

CCDC deposit number	2355953	
Empirical formula	$C_{19}H_{23}N\ O$	
Formula weight	281.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0501(5) Å	α= 65.739(2)°.
	b = 14.6258(8) Å	β= 80.565(2)°.
	c = 15.2351(9) Å	γ = 74.190(2)°.
Volume	1570.72(16) $Å^3$	
Z	4	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	608	
Crystal size	0.415 x 0.294 x 0.106 mm^3	
Theta range for data collection	2.529 to 26.050°.	
Index ranges	-9<=h<=9, -18<=k<=18, -18<=l<=18	
Reflections collected	60829	
Independent reflections	6156 [R(int) = 0.0676]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6156 / 0 / 387	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1144	
R indices (all data)	R1 = 0.0621, wR2 = 0.1230	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.375 and -0.210 $e.Å^{-3}$	

Crystal data and structure refinement for Compound **5**.

CCDC deposit number	2355952	
Empirical formula	$C_{17}H_{19}NO_2$	
Formula weight	269.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.6318(6) Å	α= 90°.
	b = 6.7563(3) Å	β= 93.991(2)°.
	c = 16.2925(8) Å	γ = 90°.
Volume	1387.10(11) $Å^3$	
Z	4	
Density (calculated)	1.290 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	576	
Crystal size	0.570 x 0.293 x 0.222 mm^3	
Theta range for data collection	2.506 to 26.060°.	
Index ranges	-15<=h<=15, -8<=k<=8, -20<=l<=20	
Reflections collected	40393	
Independent reflections	2741 [R(int) = 0.0438]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2741 / 0 / 184	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0901	
R indices (all data)	R1 = 0.0349, wR2 = 0.0924	
Extinction coefficient	0.0150(18)	
Largest diff. peak and hole	0.230 and -0.173 $e.Å^{-3}$	

Crystal data and structure refinement for Compound **6**.

CCDC deposit number	2355951	
Empirical formula	$C_{15}H_{15}NO$	
Formula weight	225.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.4652(2) Å	α= 90°.
	b = 9.6199(3) Å	β= 105.1990(10)°.
	c = 14.5468(4) Å	γ = 90°.
Volume	1143.17(5) $Å^3$	
Z	4	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	480	
Crystal size	0.220 x 0.110 x 0.040 mm^3	
Theta range for data collection	2.535 to 26.022°.	
Index ranges	-10<=h<=10, -11<=k<=11, -17<=l<=17	
Reflections collected	29187	
Independent reflections	2240 [R(int) = 0.0362]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2240 / 0 / 155	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0996	
R indices (all data)	R1 = 0.0414, wR2 = 0.1045	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.232 and -0.176 $e.Å^{-3}$	

Table S1. Calculated excitation ($S_0 \rightarrow S_n$) data for **4–6**.

	Excited state	Configuration	*E* (eV)	Abs. (nm)	f_{osc}
4	S_1	H→L (69%), H-1→L+1 (10%)	4.13	300	0.159
	S_2	H-3→L+3 (17%), H-3→L+4 (-11%), H-2→L (-11%), H-2→L+1 (12%), H-1→L (-27%), H→L+1 (57%)	4.26	291	0.025
	S_4	H-2→L+1 (-13%), H-1→L (41%), H→L+1 (25%), H→L+3 (-36%), H→L+4 (21%)	4.97	250	0.071
5	S_1	H→L (69%)	4.05	306	0.152
	S_2	H-2→L (-16%), H-1→L (32%) H→L+1 (59%)	4.29	289	0.026
	S_3	H-2→L (24%), H-1→L (52%), H→L+1 (-22%), H→L+5 (-14%) H→L+6 (-21%)	5.05	246	0.188
6	S_1	H→L (68%), H→L+1 (-11%)	3.77	329	0.116
	S_2	H-3→L (44%), H-3→L+1 (-13%), H-3→L+2 (28%), H-2→L (-32%), H-2→L+2 (-16%)	4.11	302	0.011
	S_3	H-1→L (35%), H→L (11%), H→L+1 (58%)	4.68	265	0.074

Calculated from the optimized ground state structures using the TD-SCF DFT CAM-B3LYP method with the 6-311G + (2d,p) basis set and the IEFPCM solvent model for toluene.

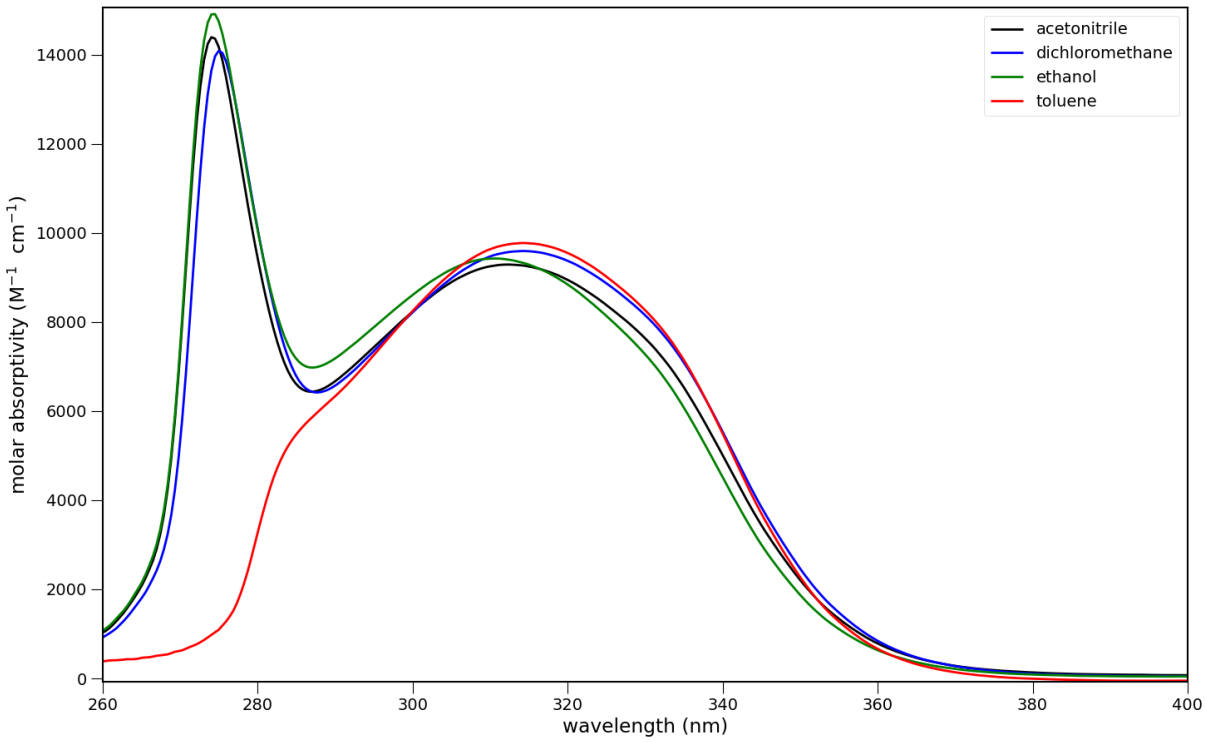


Figure S1. Absorption spectra of **4** in acetonitrile, dichloromethane, ethanol, and toluene.

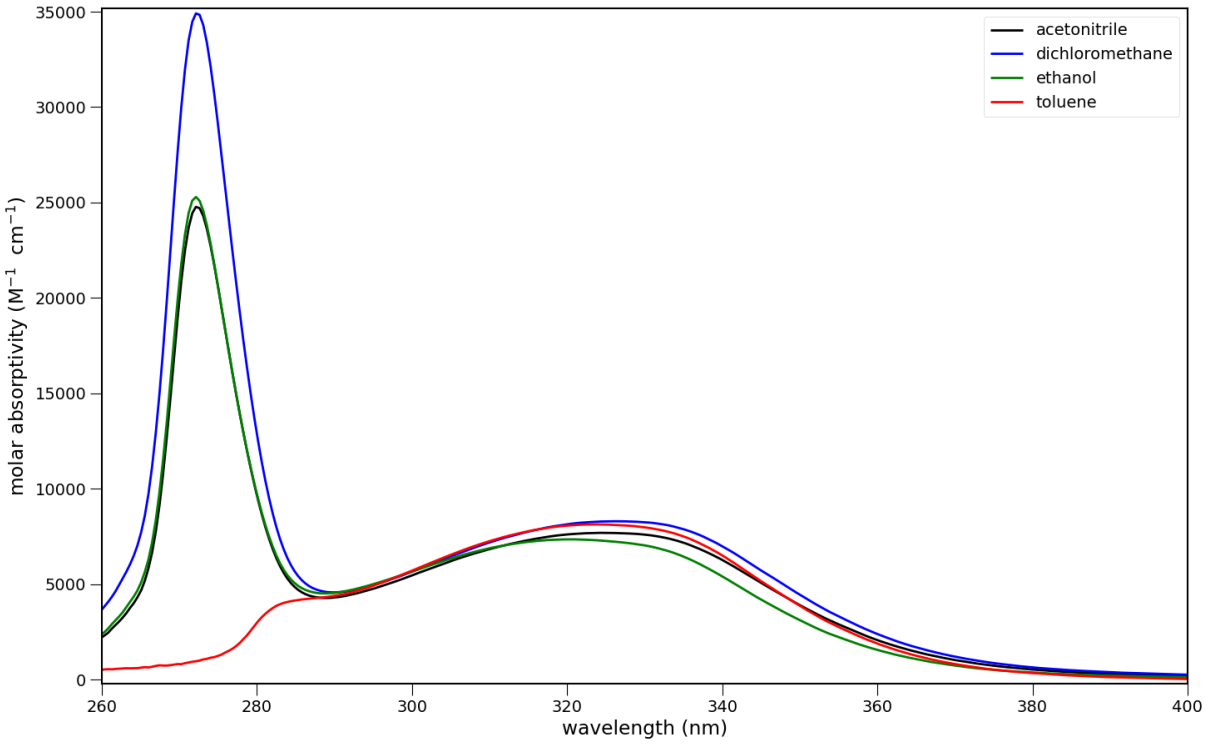


Figure S2. Absorption spectra of **5** in acetonitrile, dichloromethane, ethanol, and toluene.

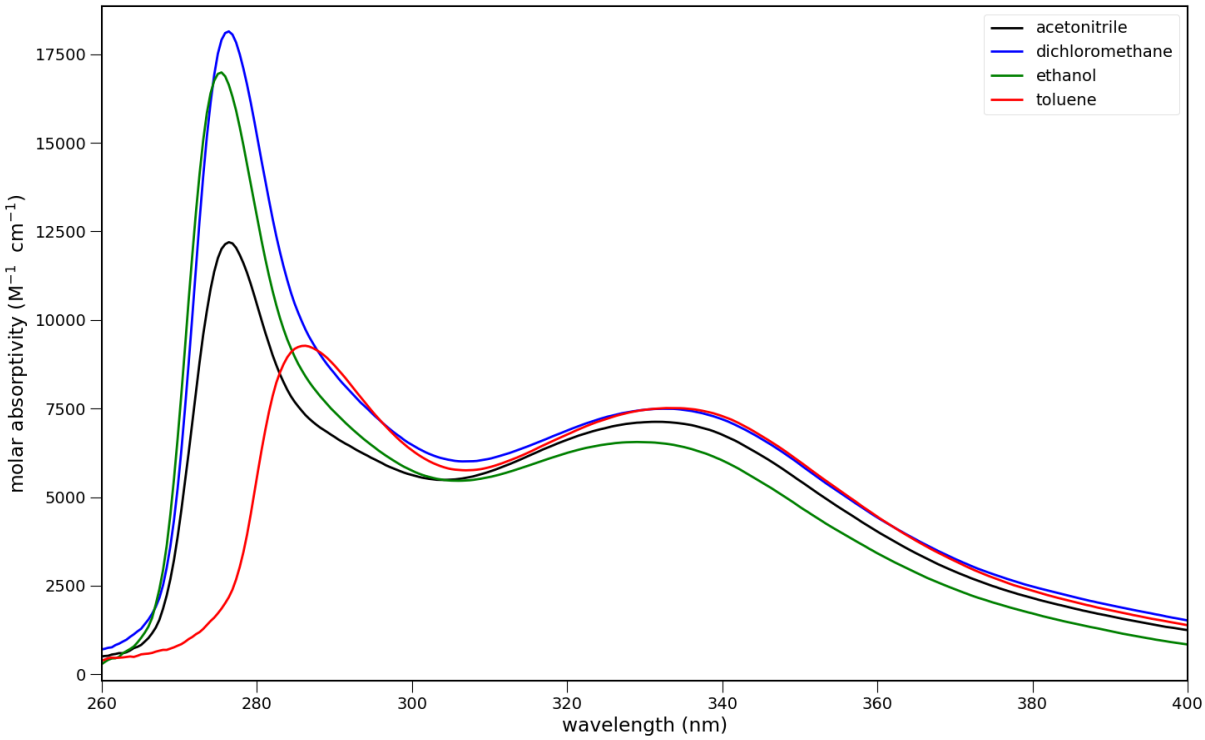
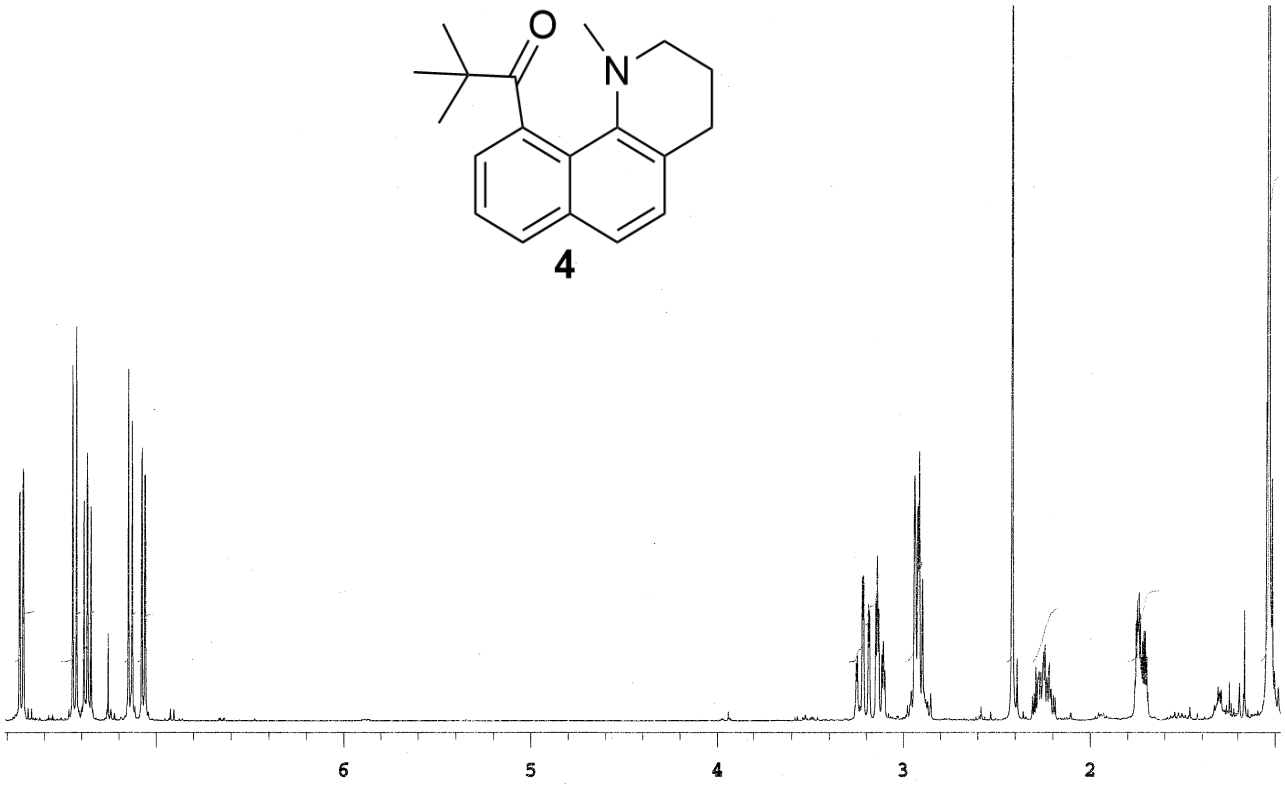


Figure S3. Absorption spectra of **6** in acetonitrile, dichloromethane, ethanol, and toluene.



PEAK FREQUENCIES

Index	freq/ppm	Intensity
1	213.642	32.0419
2	144.525	33.1553
3	137.396	29.9147
4	133.116	33.7566
5	128.677	112.83
6	128.635	115.141
7	127.064	42.5086
8	124.791	101.194
9	124.404	109.063
10	123.452	101.174
11	77.5488	124.582
12	77.2301	130.797
13	76.9113	127.466
14	51.6263	101.68
15	45.7794	67.7813
16	45.4948	109.327
17	27.2443	364.949
18	27.0774	112.033
19	15.7097	93.0675

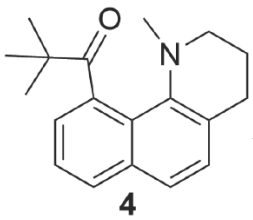


Figure S4. ^{1}H (top) and ^{13}CNMR spectra of **4** in $CDCl_3$.

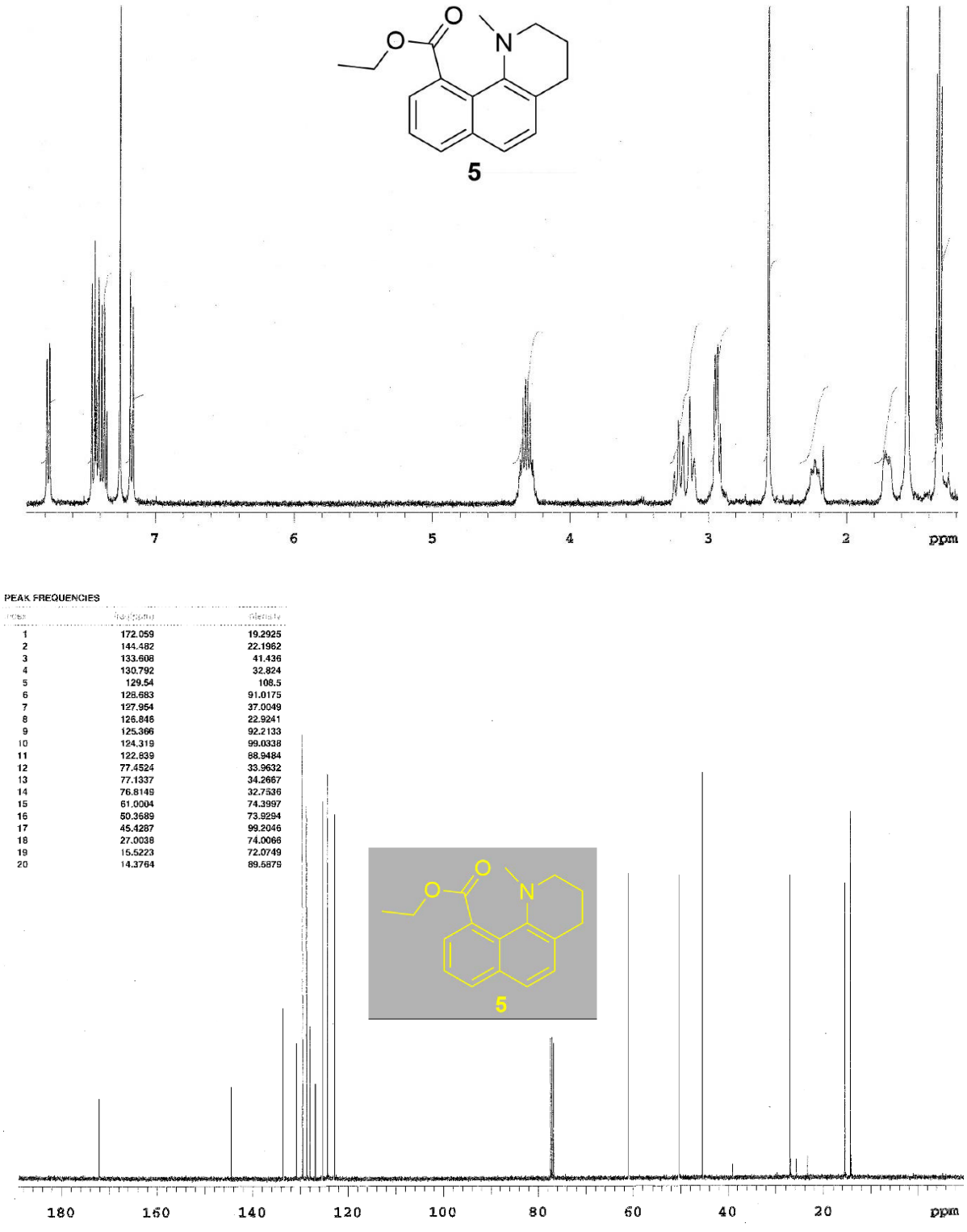
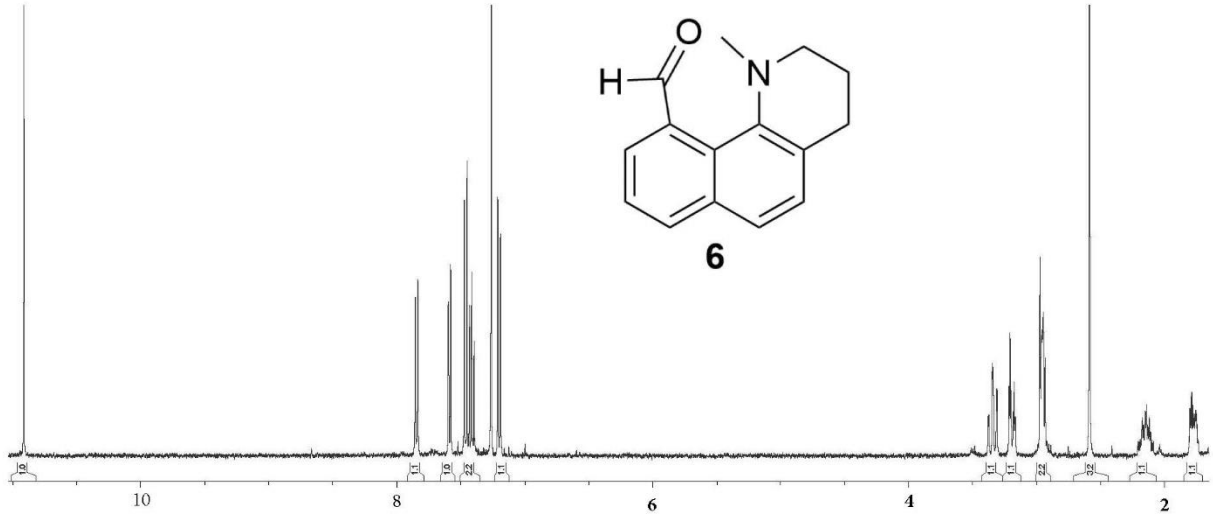


Figure S5. ^{1}H (top) and $^{13}CNMR$ spectra of **5** in $CDCl_3$.



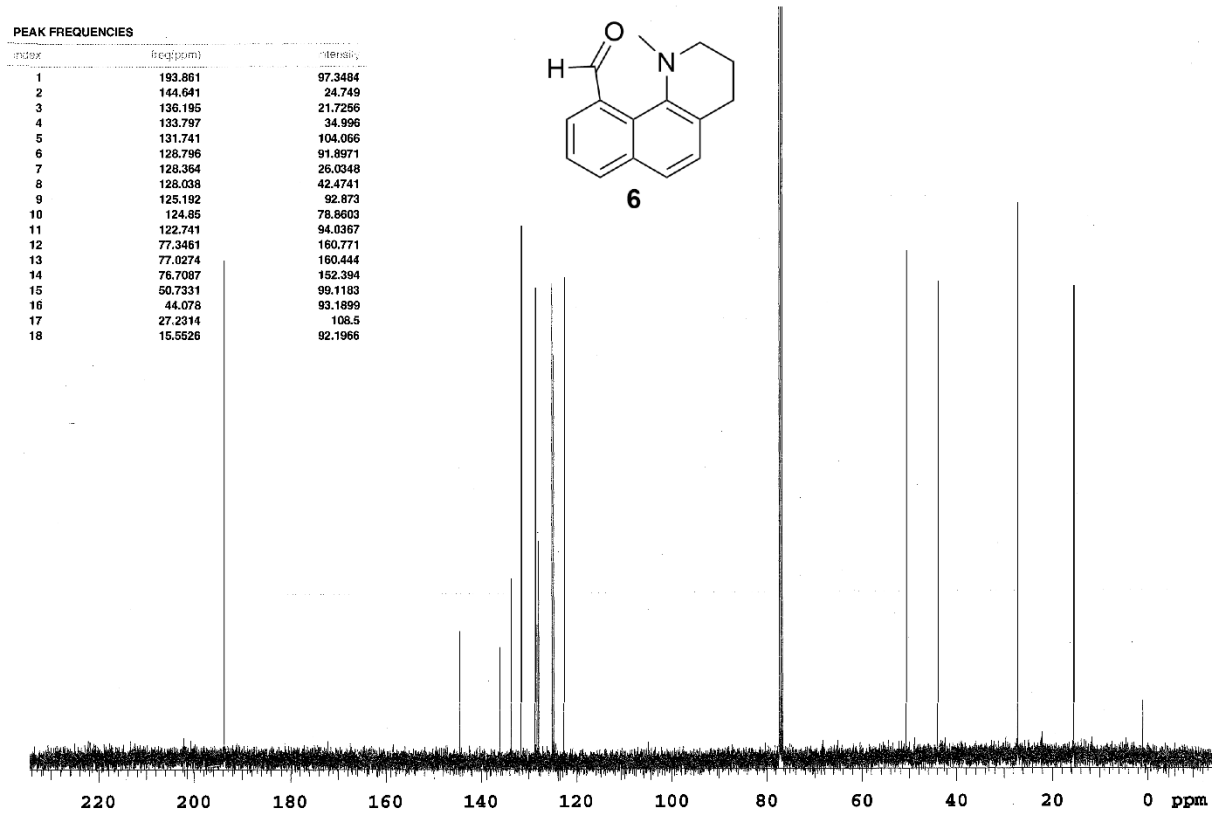


Figure S6. ^{1}H (top) and $^{13}CNMR$ spectra of **6** in $CDCl_3$.