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## **Double head-to-tail direct arylation as a viable strategy towards aza-analog of dihydrocyclopenta[hi]aceanthrylene – intriguing antiaromatic heterocycle**

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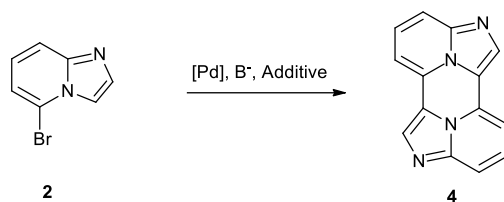
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### General remarks

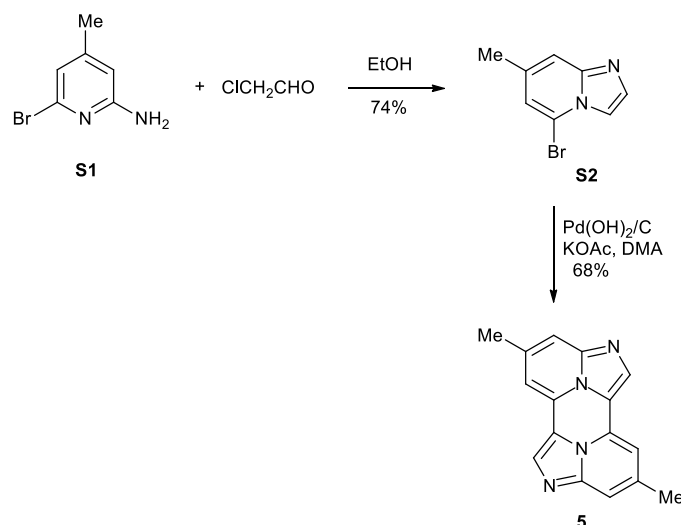
All commercially available compounds were used as received. All reagent grade solvents were dried and distilled prior to use. Transformation with air-sensitive compounds were performed under argon atmosphere. The reaction progress was monitored by means of thin layer chromatography (TLC) which was performed on aluminum sheets, coated with silica gel 60 F<sub>254</sub> (Merck) with detection by UV-Lamp. Product purification was performed by flash column chromatography on silica (P 60, 40–63 mm, SiliCycle), and dry column vacuum chromatography (DCVC) on silica oxide (MN-Kieselgel P/UV254) or aluminum oxide (MN-Aluminumoxid G). Identity and purity of prepared compounds were proved by 1D NMR (<sup>1</sup>H NMR and <sup>13</sup>C NMR) and 2D NMR recorded on 500 MHz Varian Inova NMR spectrometr. All chemical shifts are given in ppm.

### Optimalization of the synthesis of 4



Entry	Catalyst	Base	Additive	Solvent	Yield, %
1	PdCl(C <sub>3</sub> H <sub>5</sub> )(dppb)	KOAc	-	DMA	20
2	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	KF	AgOAc	DMSO	0
3	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub> ·HBF <sub>4</sub>	PivOH	0
4	[Rh(cod) <sub>2</sub> Cl] <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub>	NMP	0
5	-	<i>t</i> BuOK	-	DMA	0
6	Pd(OAc) <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub> , <i>n</i> -Bu <sub>4</sub> NBr	DMF	traces
7	Pd(OAc) <sub>2</sub>	KOAc	-	DMA	22
8	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	KOAc	-	NMP/H <sub>2</sub> O	37
9	Pd(OAc) <sub>2</sub>	KOAc	SPhos	DMA	40
10	Pd(OAc) <sub>2</sub>	KOAc	XPhos	DMA	42
11	Pd(OH) <sub>2</sub> /C	KOAc	-	DMA	57

## Synthesis of 5



Scheme S1

## Synthetic Procedures

**Imidazo[1,2-*a*]pyridine (1)** was synthesized *via* known procedure [1]. Spectral and physical properties concur with published data [1,2].

**5-Bromoimidazo[1,2-*a*]pyridine (2):** 2-amino-6-bromopyridine (1.73g, 10 mmol) was dissolved in C<sub>2</sub>H<sub>5</sub>OH (20 mL), subsequently chloroacetaldehyde (5 ml, 40 mmol, 50% aqueous solution) was added in one portion and resulting mixture was refluxed for 20 h. Next, it was cooled down and the solvent was removed under the reduced pressure. The residue was dissolved in 100 ml of DCM and washed with NaHCO<sub>3</sub>(aq.) and water, dried over anhydrous MgSO<sub>4</sub>. The crude product was purified by column chromatography (DCVC, alumina, EtOAc : hexanes = 15:85) to give pure product as white needles (recrystallized form EtOAc/hexanes, 1,98 g, 74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.06 (m, 1H), 7.10 (m, 1H), 7.64 (d, 1H, *J*<sub>1</sub> = 8.8 Hz), 7.71 (d, 1H, *J* = 0.7 Hz), 7.80 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 113.6, 114.3, 116.2, 116.6, 124.6, 133.4, 146.1; EI-MS HR obsd. 195.9637 [M<sup>+</sup>]; calcd. exact mass 195.9636 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>Br);

**5-Bromo-7-methylimidazo[1,2-*a*]pyridine (S1):** 2-amino-6-bromo-4-methylpyridine (462.5 mg, 2.5 mmol) was dissolved in C<sub>2</sub>H<sub>5</sub>OH (5 mL), subsequently chloroacetaldehyde (1.25 ml, 10 mmol, 50% aqueous solution) was added in one portion and resulting mixture was refluxed for 20 h. Next, it was cooled down and the solvent was removed under the reduced pressure. The residue was dissolved in 50 ml of DCM and washed with NaHCO<sub>3</sub>(aq.) and water, dried over anhydrous MgSO<sub>4</sub>. The crude product was purified by column chromatography (DCVC, alumina, EtOAc : hexanes = 15:85) to give pure product as white needles (recrystallized form EtOAc/hexanes, 391 mg, 75%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.44 (s, 3H), 7.13 (s, 1H), 7.76 (bs, 2H), 8.10 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 21.4, 113.4, 114.3, 114.4, 114.6, 121.0, 131.0, 140.5; EI-MS HR obsd. 209.9783 [M<sup>+</sup>]; calcd. exact mass 209.9793 (C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>Br);

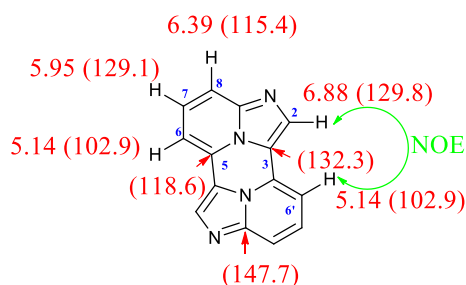
**3,5'-Biimidazo[1,2-*a*]pyridine (3):** imidazo[1,2-*a*]pyridine **1** (0.3 mL, 3 mmol), 5-bromoimidazo[1,2-*a*]pyridine **2** (384 mg, 2 mmol) and KOAc (400 mg, 4 mmol) were added to the solution of Pd(OAc)<sub>2</sub> (0.45 mg, 0.002 mmol, 0.1

mol%) in DMA (8 mL). The resulting mixture was reacted overnight at 150 °C under inert atmosphere. Subsequently, it was absorbed on celite, purified by DCVC (SiO<sub>2</sub>, MeOH:CH<sub>2</sub>Cl<sub>2</sub> = 2:98) and crystallized (MeOH/CH<sub>2</sub>Cl<sub>2</sub>) to afford white crystals (351 mg, 75%), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.98 (s, 1 H), 7.80 – 7.72 (m, 3H), 7.68 (d, 1 H, *J* = 1 Hz), 7.36 – 7.30 (m, 2 H), 7.24 (s, 1 H), 7.03 (dd, 1 H, *J*<sub>1</sub> = 6.9 Hz, *J*<sub>2</sub> = 1 Hz), 6.89 (td, *J*<sub>1</sub> = 6.9 Hz, *J*<sub>2</sub> = 1 Hz, 1 H), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 146.9, 146.0, 135.2, 134.5, 126.5, 125.8, 124.6, 124.0 (2 signals), 118.8, 118.4, 115.3, 113.6, 111.5; EI-MS HR obsd. 234.0903 [M<sup>+</sup>]; calcd. exact mass 234.0905 (C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>);

**2,2a<sup>1</sup>,5b<sup>1</sup>,7-Tetraazacyclopenta[hi]aceanthrylene (4)**: 5-bromoimidazo[1,2-*a*]pyridine **2** (100 mg, 0.5 mmol), KOAc (102 mg, 1 mmol), and Pd(OH)<sub>2</sub>/C (72 mg, 20 mol%) were placed in sealed Schlenk flask under inert atmosphere. Subsequently DMA<sub>dry</sub> (2 mL) was added and resulting mixture was stirred at 145 °C for 17h. Next it was cooled down and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCVC, SiO<sub>2</sub>, MeOH:CH<sub>2</sub>Cl<sub>2</sub> = 5:95) and crystallized (DCM/hexanes) to afford orange solid (34 mg, 58%); <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.14 (d, 2 H, *J* = 6.6 Hz), 5.95 (dd, 2H, *J*<sub>1</sub> = 9 Hz, *J*<sub>2</sub> = 7 Hz), 6.39 (d, 2 H, *J*<sub>1</sub> = 9.1 Hz), 6.88 (s, 2 H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ 102.9, 115.4, 118.6, 129.1, 129.8, 132.4, 147.7; ESI-MS HR obsd. 233.0821 [M+H]<sup>+</sup>; calcd. exact mass 233.0827 (C<sub>14</sub>H<sub>9</sub>N<sub>4</sub>);

**7,7'-Dimethyl-2,2a<sup>1</sup>,5b<sup>1</sup>,7-tetraazacyclopenta[hi]aceanthrylene (5)**: 5-bromo-7-methylimidazo[1,2-*a*]pyridine **S2** (108.7 mg, 0.5 mmol), KOAc (102 mg, 1 mmol), and Pd(OH)<sub>2</sub>/C (72 mg, 20 mol%) were placed in sealed Schlenk flask under inert atmosphere. Subsequently DMA<sub>dry</sub> (2 mL) was added and resulting mixture was stirred at 145 °C for 17h. Next it was cooled down and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCVC, SiO<sub>2</sub>, MeOH:CH<sub>2</sub>Cl<sub>2</sub> = 5:95) and crystallized (DCM/hexanes) to afford orange solid (47.4 mg, 68%); <sup>1</sup>H NMR (500 MHz, CHCl<sub>3</sub>): δ 2.09 (s, 6H), 5.96 (s, 2H), 6.48 (s, 2H), 7.27 (s, 2H); <sup>13</sup>C NMR (125 MHz, CHCl<sub>3</sub>): δ 21.4, 105.8, 113.7, 117.7, 129.7, 140.0, 140.8, 147.1; ESI-MS HR obsd. 261.1139 [M+H]<sup>+</sup>; calcd. exact mass 261.1140 (C<sub>16</sub>H<sub>13</sub>N<sub>4</sub>);

#### Analysis of 2D NMR Spectra of 4



**Figure 1.** <sup>1</sup>H and <sup>13</sup>C shifts (in brackets) are given in ppm.

During the analysis of COSY spectrum, two groups of signals were identified. Peaks with chemical shifts 5.14 ppm, 5.95 ppm and 6.39 ppm were assigned to the one spin system, thus belonged to the pyridine-type ring. The signal at 6.88 ppm (singlet) didn't show any correlation peak and was identified as belonging to the proton at C<sub>2</sub> from the five-membered ring.

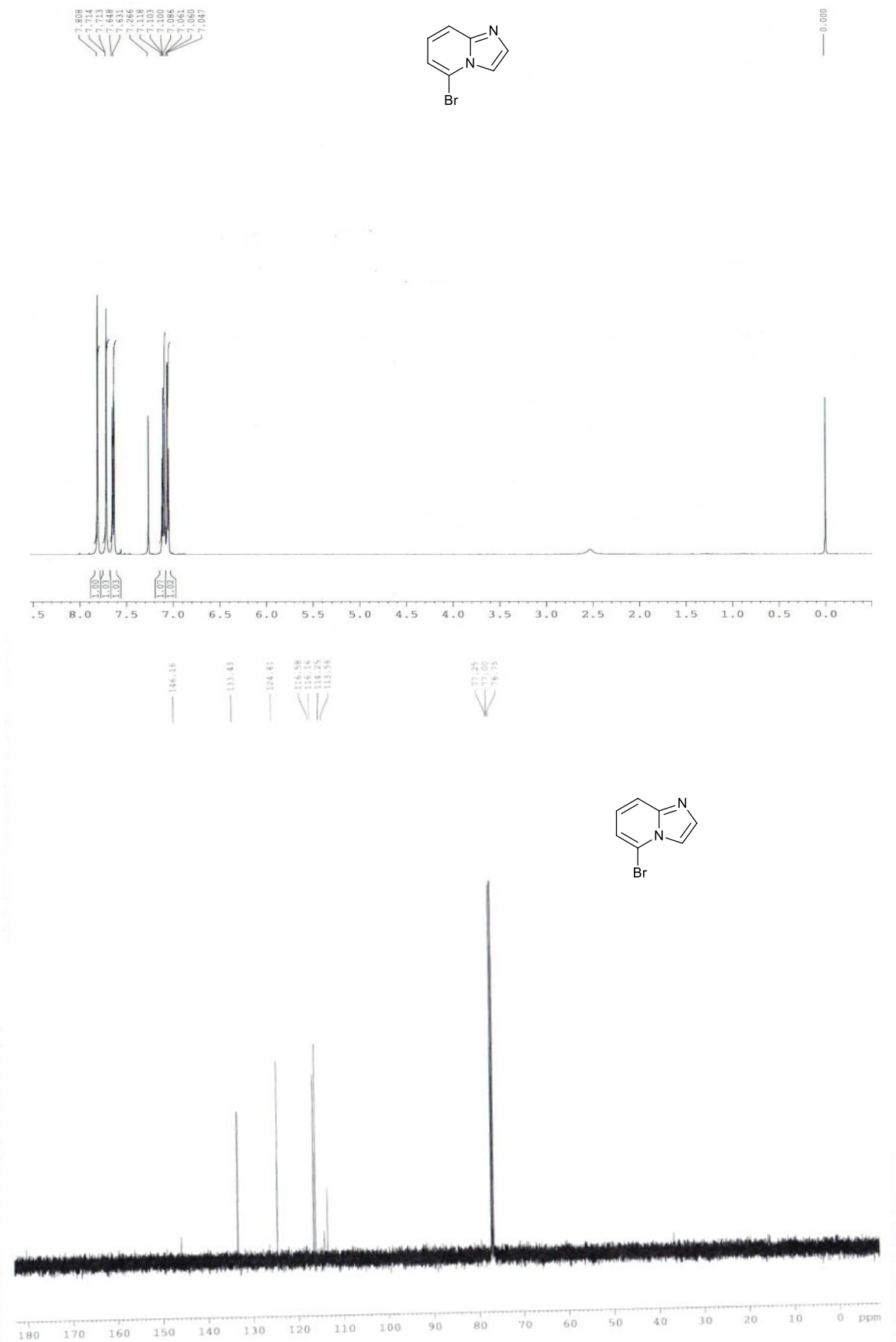
Next, interpretation of the  $^{13}\text{C}$  NMR was performed according to the literature (for  $\text{C}_3$  and  $\text{C}_5$ ) [3] and  $^{13}\text{C}^1\text{H}$ -HSQC data.

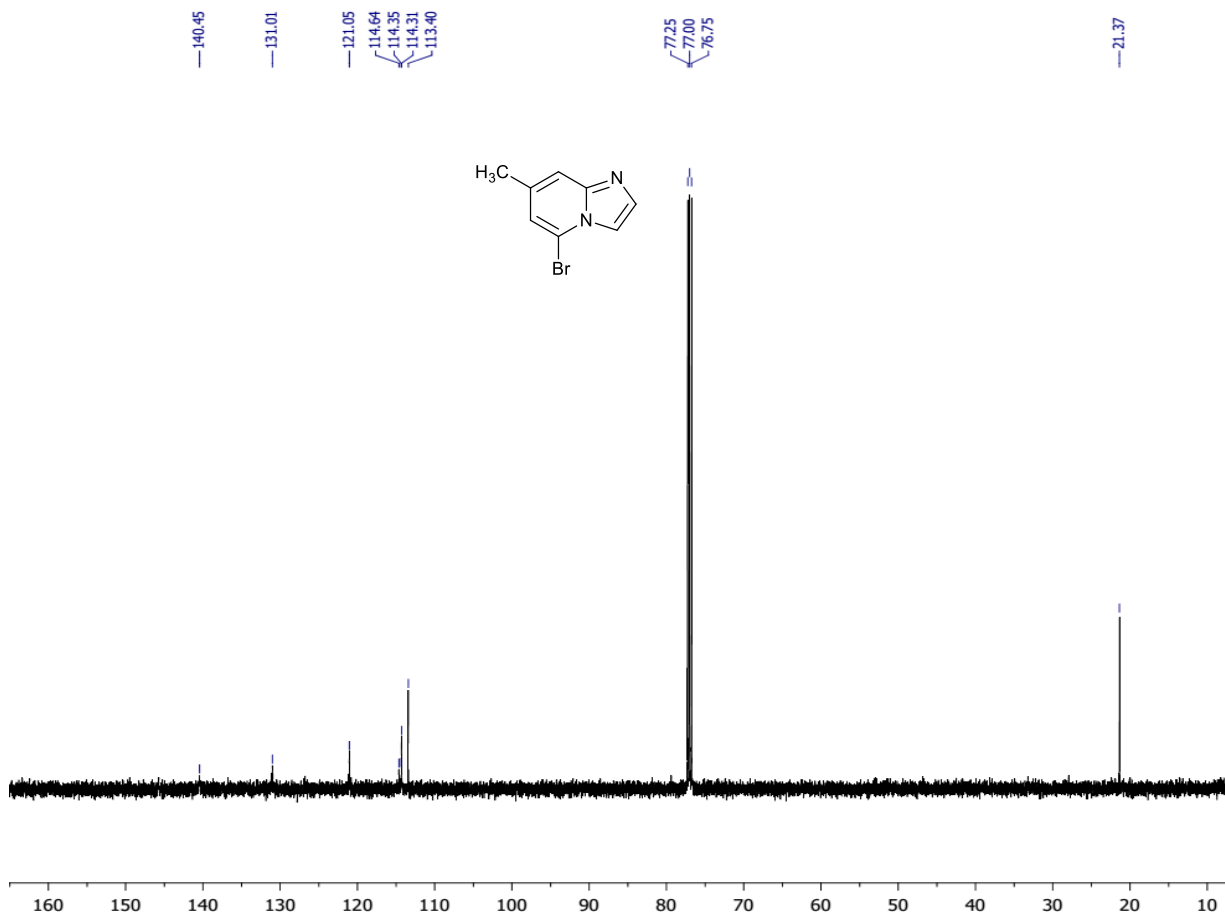
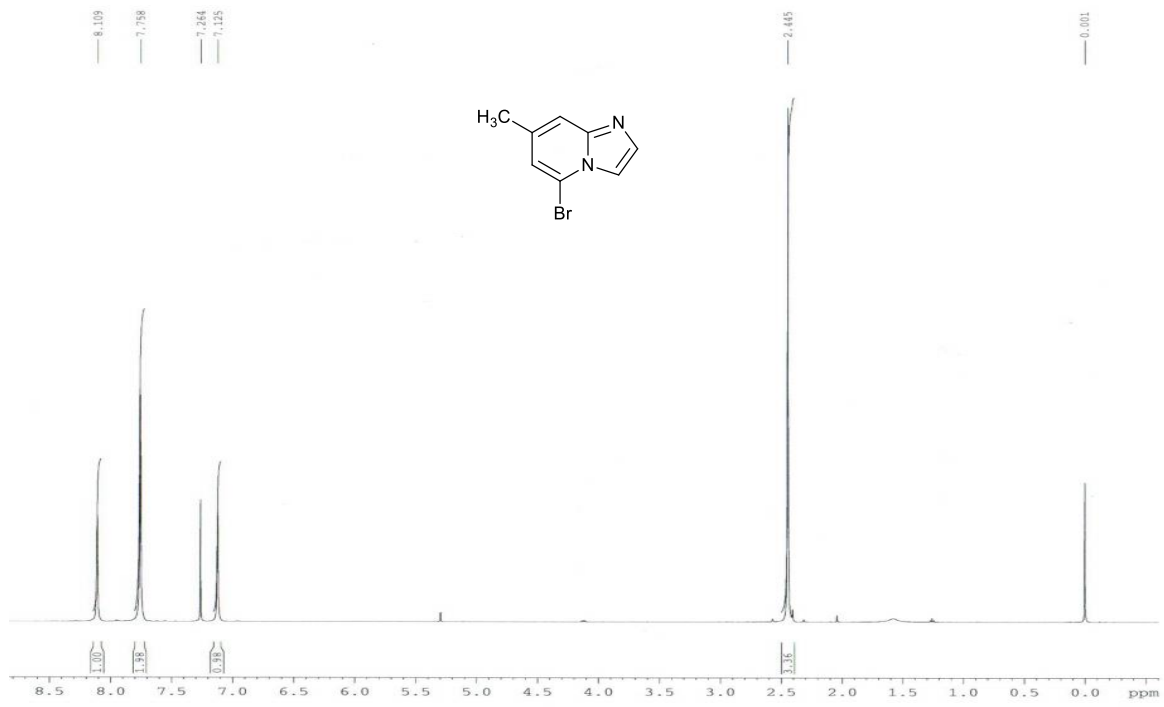
Further signals assignment in  $^1\text{H}$  NMR spectrum was performed basing on their multiplicity (for the proton at  $\text{C}_7$ ) as well as analysis of  $^{13}\text{C}^1\text{H}$ -HMBC spectra (for the protons at  $\text{C}_6$  and  $\text{C}_8$ ). Moreover, in order to achieve the final conformation, 1D NOE experiment was performed. It clearly proved the space correlation between protons at  $\text{C}_2$  and  $\text{C}_6$ .

## References

- [1] Sh. Wang, W. Liu, J. Cen, J. Liao, J. Huang and H. Zhan, *Tetrahedron Lett.*, 2014, 55, 1589-1592;
- [2] B. Frett, N. McConnell, C. C. Smith, Y. Wang, N. P. Shah and H. Li, *Eur. J. Med. Chem.*, 2015, **94**, 123–131
- [3] R. J. Pugmire, J. C. Smith, D. M. Grant, B. Stanovnik, M. Tisler and B. Vercek, *J. Heterocyc. Chem.* 1987, 24, 805-809.

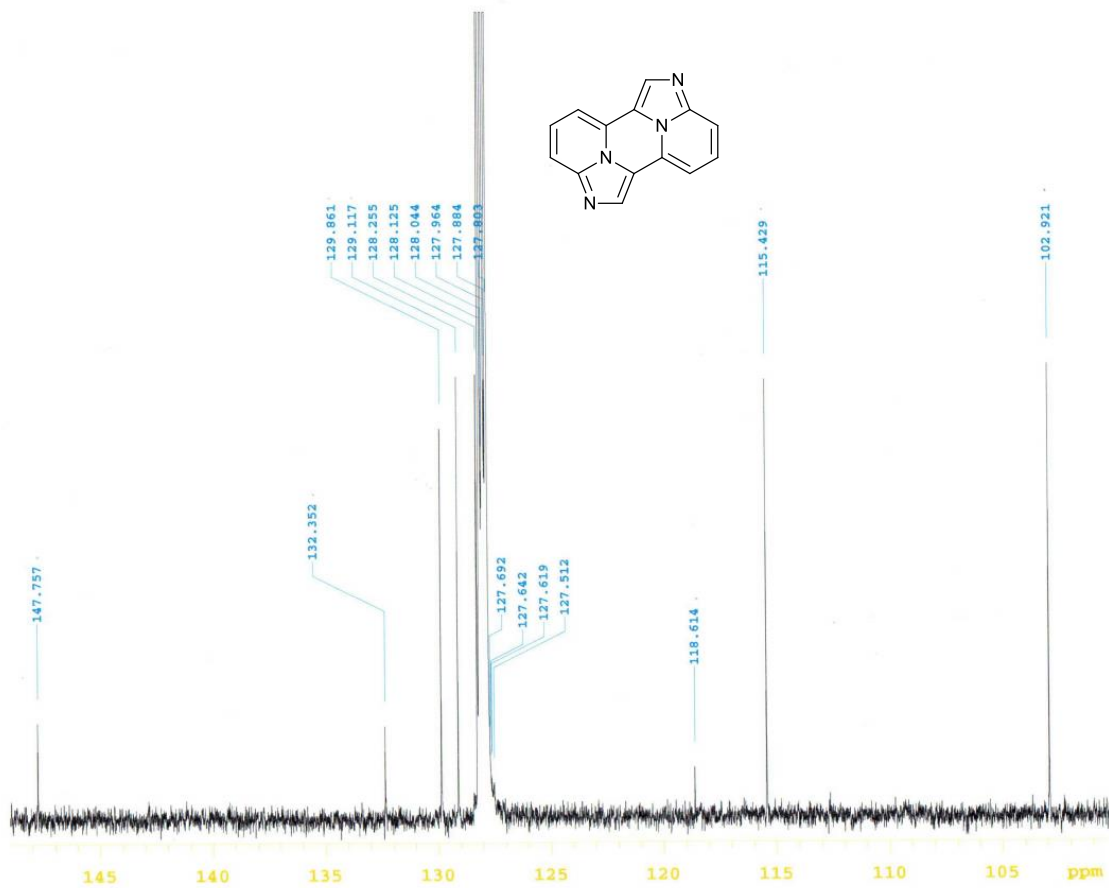
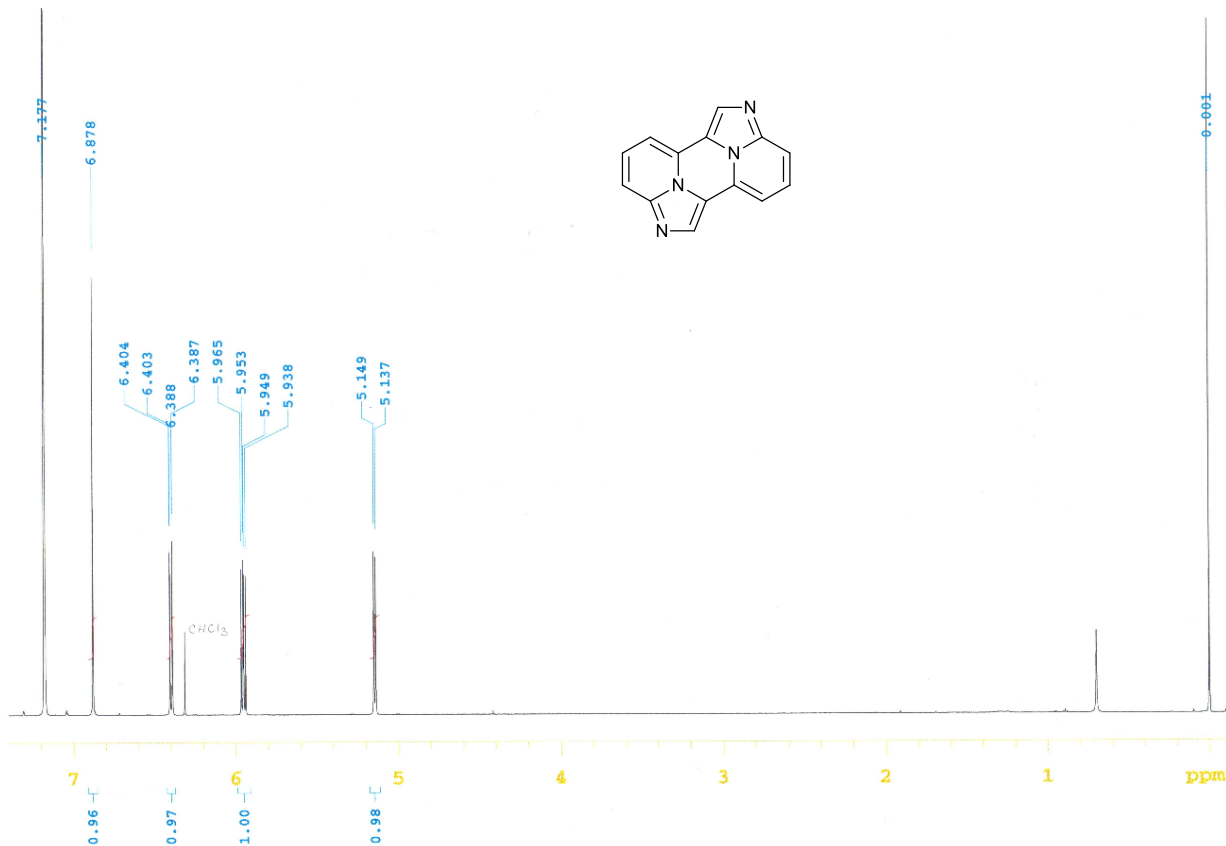
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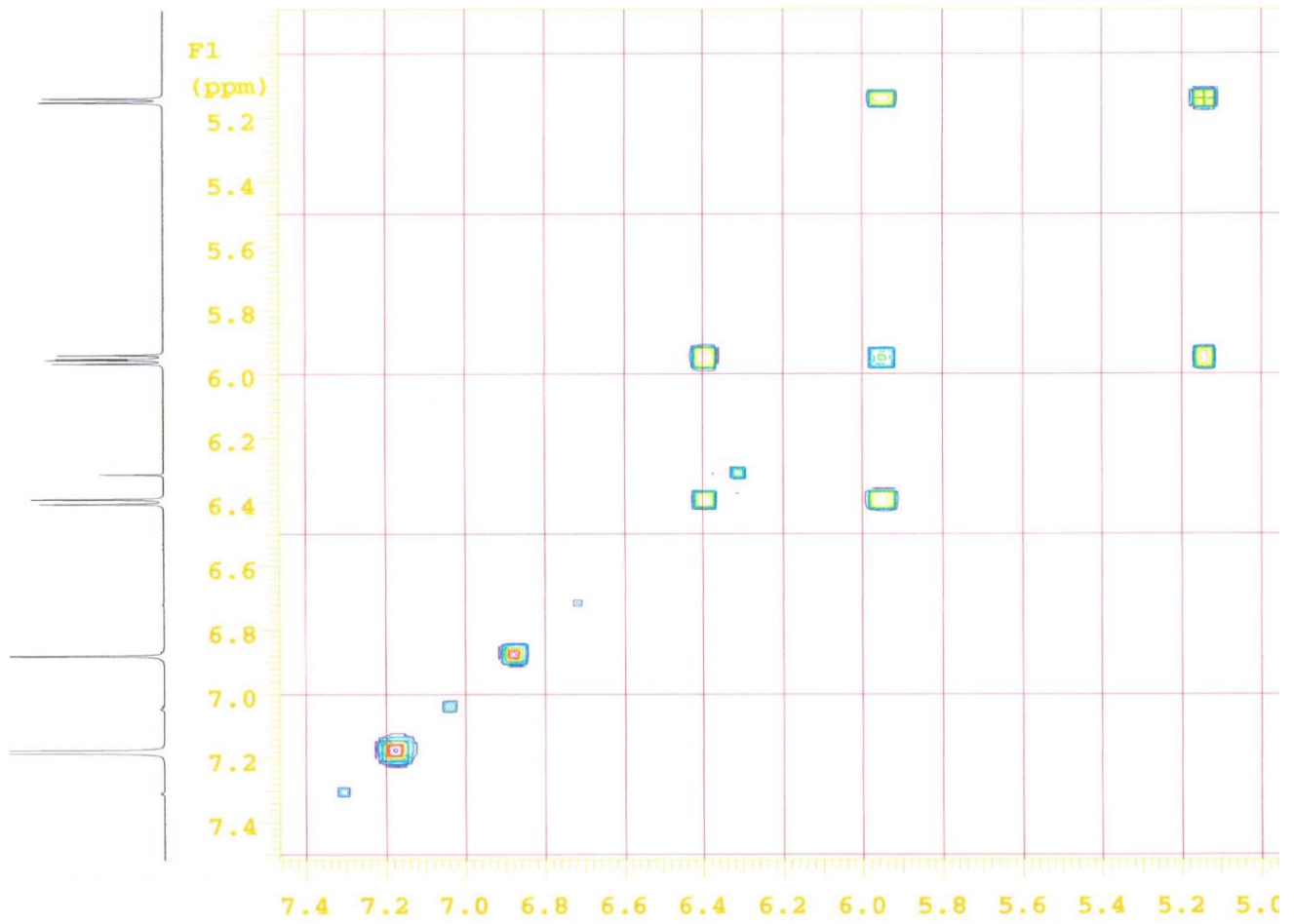
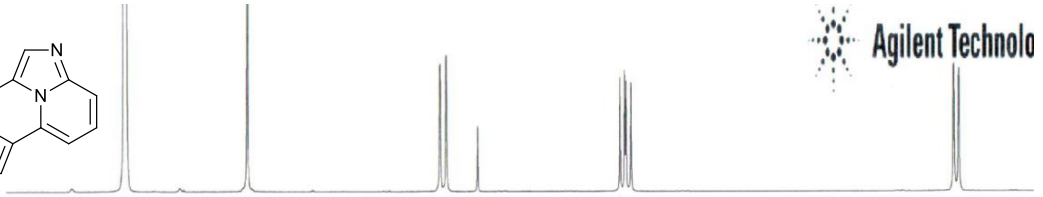
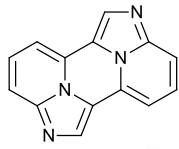




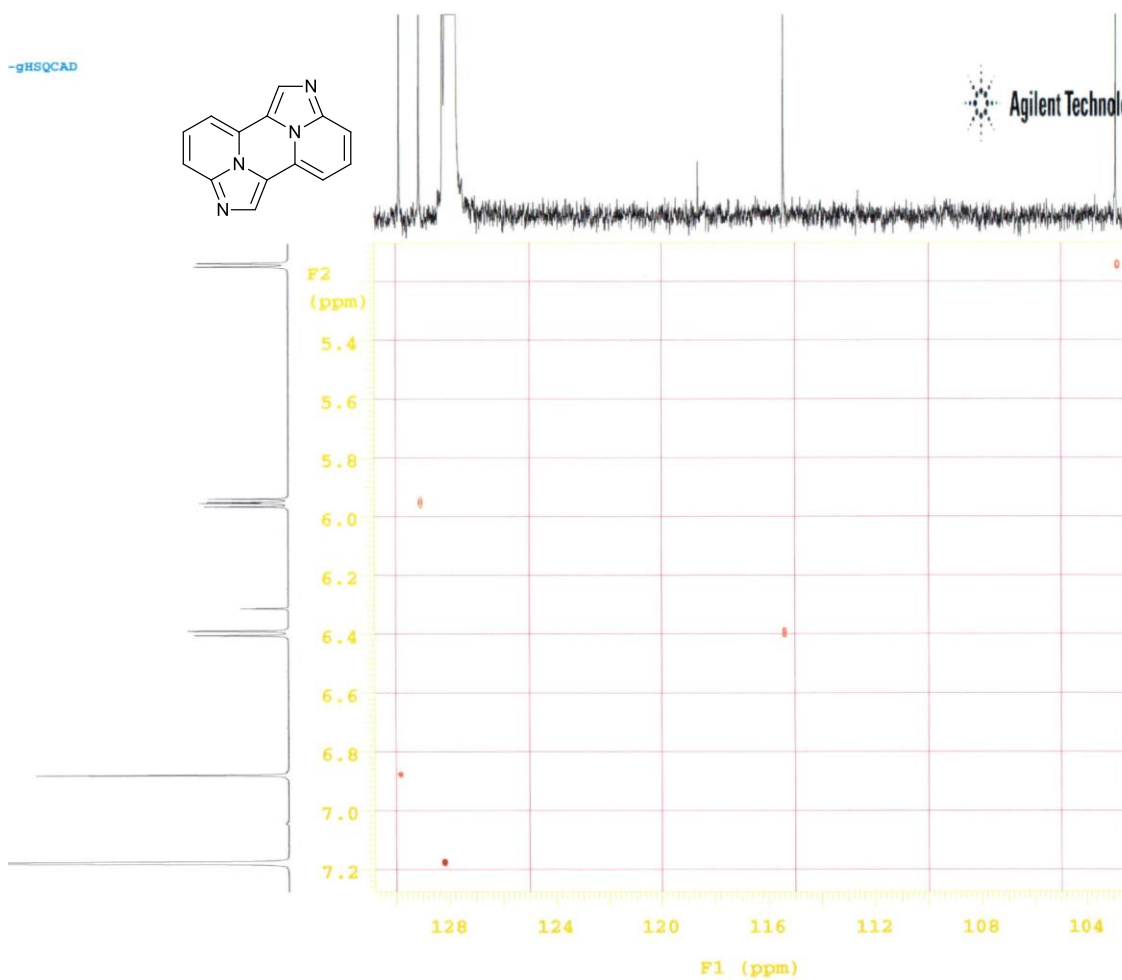
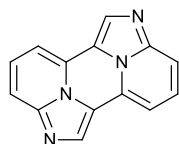


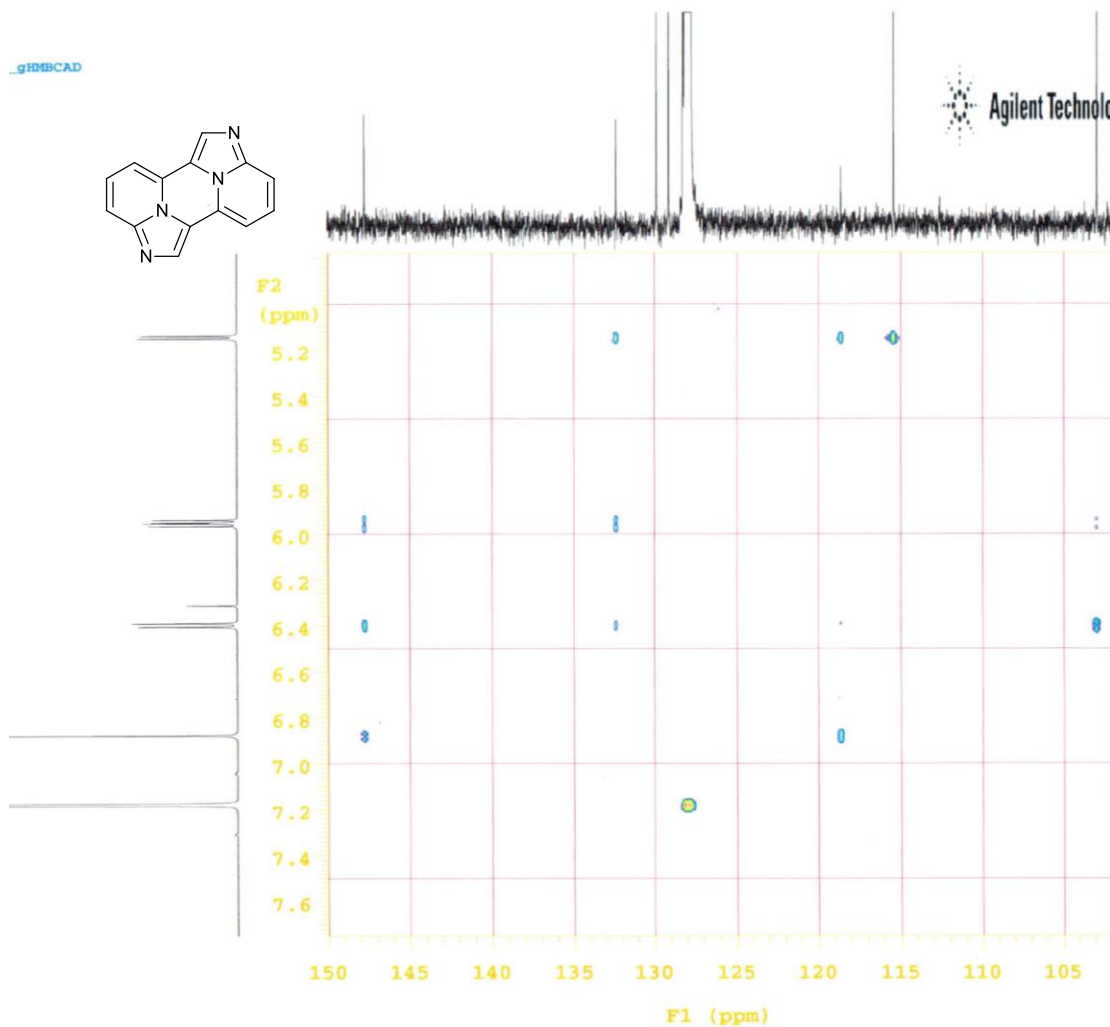
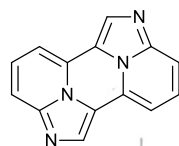


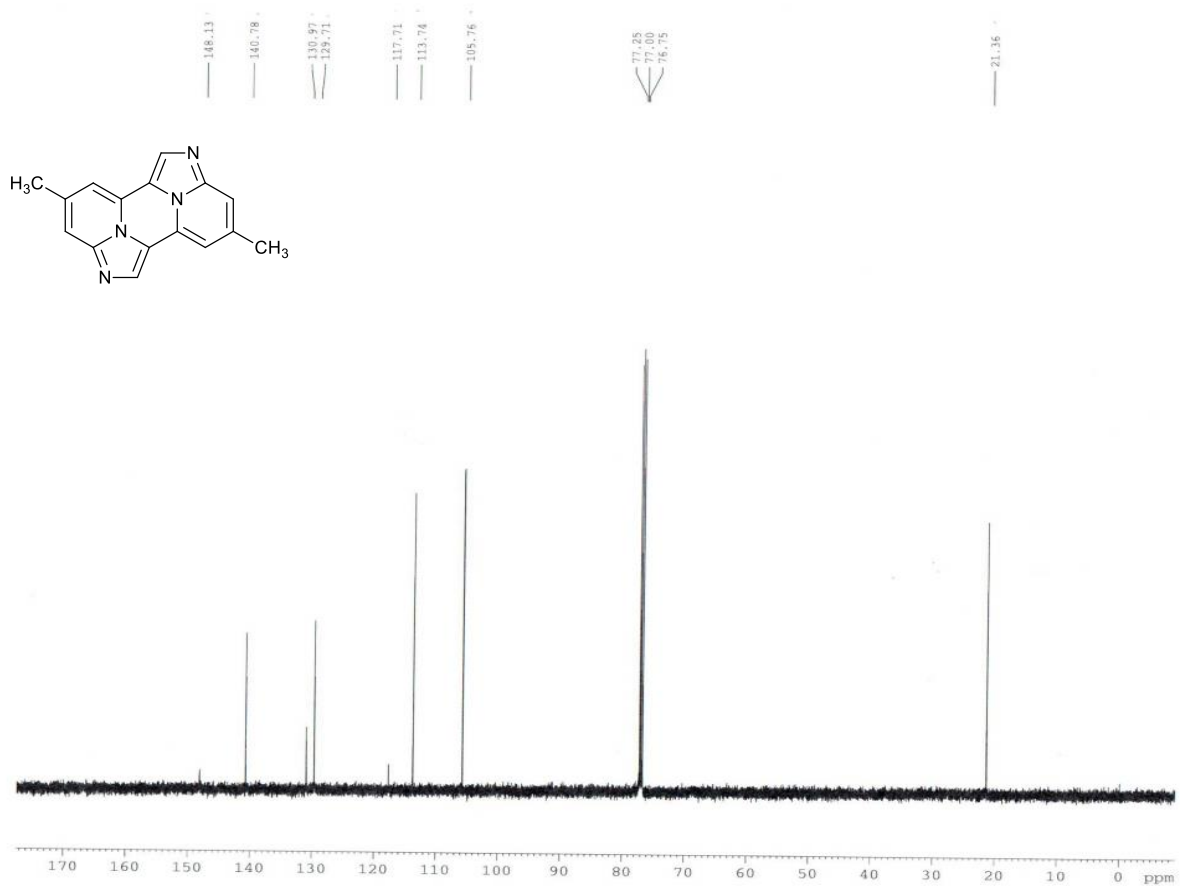
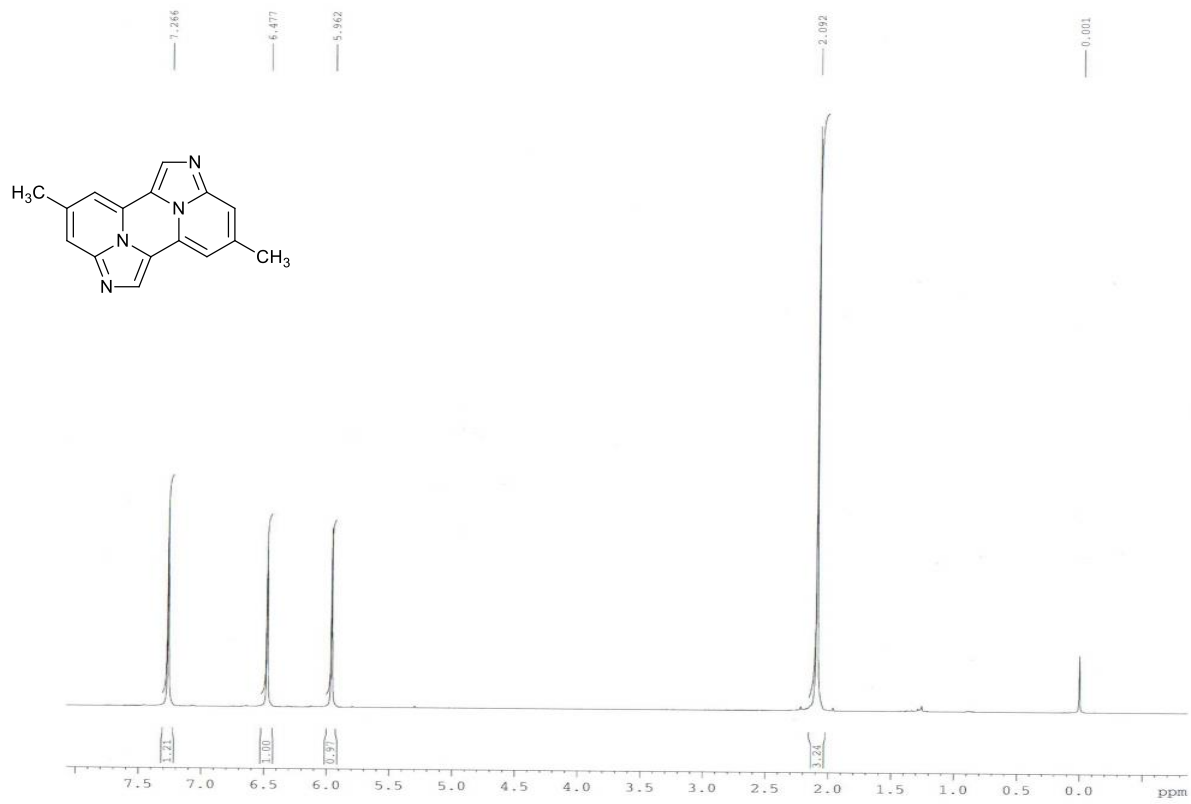




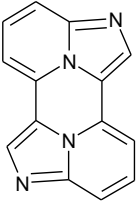
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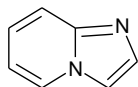


Symmetry, absolute electronic energies at B3LYP/6-311+G\*\* (in hartree) zero point vibrational energies ZPE at B3LYP/6-311+G\*\* (in hartree), magnetic susceptibilities at CSGT/B3LYP/6-311+G\*\* (in ppm cgs) and Cartesian coordinates for molecules used in homodesmotic reactions.

Compound	Point group	Energy	ZPE	Magnetic susceptibility
	$C_{2h}$	-757.505166	0.193748	-92.61
C		2.149245	-3.005499	0.000000
C		0.894322	-3.562053	0.000000
C		-0.229934	-2.700909	0.000000
C		1.263426	-0.749363	0.000000
C		2.345411	-1.597085	0.000000
N		-1.541430	-2.947872	0.000000
C		-2.149245	-1.734370	0.000000
C		-1.229960	-0.695131	0.000000
C		1.229960	0.695131	0.000000
C		-1.263426	0.749363	0.000000
C		2.149245	1.734370	0.000000
N		-0.009906	1.329651	0.000000
C		0.229934	2.700909	0.000000
C		-2.345411	1.597085	0.000000
C		-2.149245	3.005499	0.000000
C		-0.894322	3.562053	0.000000
N		0.009906	-1.329651	0.000000
N		1.541430	2.947872	0.000000
H		3.020351	-3.649617	0.000000
H		0.730462	-4.630703	0.000000
H		3.344176	-1.183002	0.000000
H		-3.225717	-1.648786	0.000000
H		3.225717	1.648786	0.000000

H	-3.344176	1.183002	0.000000
H	-3.020351	3.649617	0.000000
H	-0.730462	4.630703	0.000000

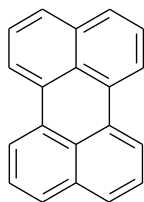
Compound	Point group	Energy	ZPE	Magnetic susceptibility
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$C_s$	-379.9479832	0.117322	-72.52
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C	-1.055052	1.622701	0.000000
C	1.358788	0.935133	0.000000
C	-2.189741	0.839919	0.000000
N	0.000000	0.734412	0.000000
C	-0.567670	-0.555801	0.000000
C	2.191967	-0.143885	0.000000
C	1.660368	-1.464769	0.000000
C	0.304397	-1.667487	0.000000
N	-1.894341	-0.489407	0.000000
H	-3.212713	1.186270	0.000000
H	3.261615	0.019246	0.000000
H	2.337184	-2.310325	0.000000
H	-0.134113	-2.656740	0.000000
H	-0.907385	2.689365	0.000000
H	1.697458	1.962279	0.000000

Compound	Point group	Energy	ZPE	Magnetic susceptibility
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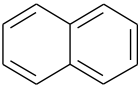


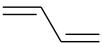
$D_{2h}$	-769.5821797	0.252708	-151.39
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C	0.000000	0.000000	1.438071
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C	0.000000	0.000000	-1.438071
C	0.000000	2.423842	-1.477276
C	0.000000	2.423842	1.477276
C	0.000000	-2.423842	1.477276
C	0.000000	-2.423842	-1.477276
C	0.000000	-2.419300	-2.881927
C	0.000000	2.419300	-2.881927
C	0.000000	-2.419300	2.881927
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C	0.000000	0.000000	2.871393
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C	0.000000	-1.231580	3.571074
C	0.000000	1.231580	3.571074
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C	0.000000	1.231580	-3.571074
C	0.000000	1.247901	0.737738
C	0.000000	-1.247901	0.737738
C	0.000000	1.247901	-0.737738
C	0.000000	-1.247901	-0.737738
H	0.000000	3.382114	0.975683
H	0.000000	-3.382114	-0.975683
H	0.000000	3.382114	-0.975683
H	0.000000	-3.382114	0.975683
H	0.000000	-1.218289	4.655535
H	0.000000	-1.218289	-4.655535
H	0.000000	1.218289	-4.655535
H	0.000000	1.218289	4.655535
H	0.000000	3.362674	3.416090
H	0.000000	-3.362674	-3.416090
H	0.000000	-3.362674	3.416090
H	0.000000	3.362674	-3.416090



Compound	Point group	Energy	ZPE	Magnetic susceptibility
	$D_{2h}$	-385.9888714	0.146886	-88.87
C		0.000000	2.430615	0.707669
C		0.000000	1.243877	1.400843
C		0.000000	0.000000	0.715780
C		0.000000	0.000000	-0.715780
C		0.000000	1.243877	-1.400843
C		0.000000	2.430615	-0.707669
C		0.000000	-1.243877	1.400843
C		0.000000	-2.430615	0.707669
C		0.000000	-2.430615	-0.707669
C		0.000000	-1.243877	-1.400843
H		0.000000	-3.373373	1.243259
H		0.000000	-3.373373	-1.243259
H		0.000000	3.373373	1.243259
H		0.000000	1.242486	2.486065
H		0.000000	1.242486	-2.486065
H		0.000000	3.373373	-1.243259
H		0.000000	-1.242486	2.486065
H		0.000000	-1.242486	-2.486065

Compound	Point group	Energy	ZPE	Magnetic susceptibility
	$C_{2h}$	-156.0407988	0.084724	-29.26
C		0.601482	1.748113	0.000000
C		0.601482	0.410172	0.000000
C		-0.601482	-0.410172	0.000000
C		-0.601482	-1.748113	0.000000
H		1.523050	2.317553	0.000000

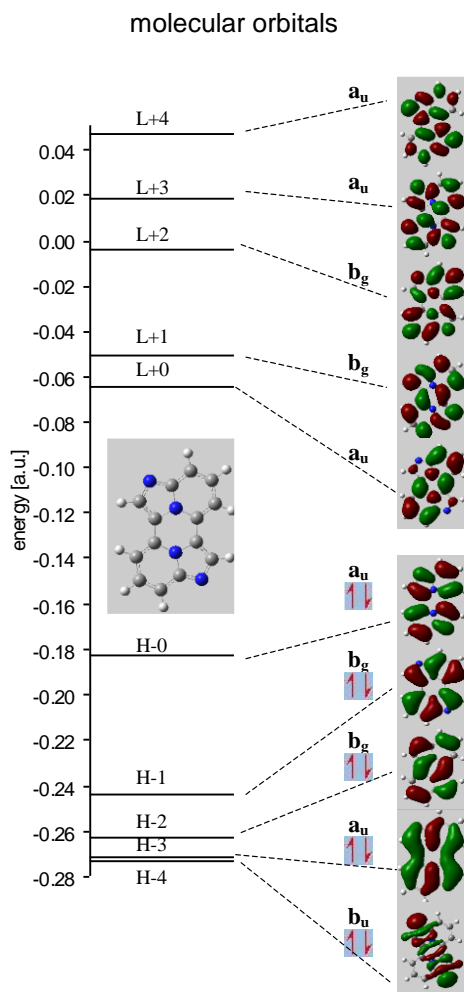
H	-0.324357	2.315008	0.000000
H	1.549917	-0.123283	0.000000
H	-1.549917	0.123283	0.000000
H	-1.523050	-2.317553	0.000000
H	0.324357	-2.315008	0.000000

Compound	Point group	Energy	ZPE	Magnetic susceptibility
=	$D_{2h}$	-78.6155126	0.050788	-17.08

C	0.000000	0.000000	0.664357
C	0.000000	0.000000	-0.664357
H	0.000000	0.922545	1.235378
H	0.000000	-0.922545	1.235378
H	0.000000	0.922545	-1.235378
H	0.000000	-0.922545	-1.235378

Wavelengths of the electronic  $S_0 \rightarrow S_1$  transitions calculated with the aid of TD DFT B3LYP//DFT B3LYP /6-31G(d,p) method. (PCM model was used for compound 4 in *n*-hexane).

gas					hexane		
no	oscillator	major			oscillator		
sym	$\lambda$ [nm]	strength	contribs		sym	$\lambda$ [nm]	strength
1	AG 522.7	0.000	H-0->L+0		AG	520.1	0.000
2	BU 384.7	0.170	H-0->L+1		BU	388.8	0.250
3	BU 288.2	0.135	H-0->L+2		BU	289.8	0.227
4	AG 269.0	0.000	H-1->L+1		BU	271.3	0.618
5	BU 268.0	0.423	H-1->L+0		AG	269.3	0.000
6	BG 256.4	0.000	H-4->L+0		AG	252.8	0.000
7	AG 253.3	0.000	H-3->L+0		BU	251.7	0.367
8	BU 249.5	0.445	H-2->L+0		BG	251.4	0.000
9	AG 245.6	0.000	H-2->L+1		AG	245.6	0.000
10	AU 241.6	0.001	H-4->L+1		AU	237.5	0.001
11	AU 237.0	0.001	H-5->L+0		AG	233.0	0.000
12	AG 231.6	0.000	H-0->L+3		AU	232.7	0.001
13	BG 224.6	0.000	H-5->L+1		BG	221.0	0.000
14	AG 219.6	0.000	H-0->L+4		BU	220.6	0.561
15	BU 218.2	0.478	H-3->L+1		AG	219.7	0.000



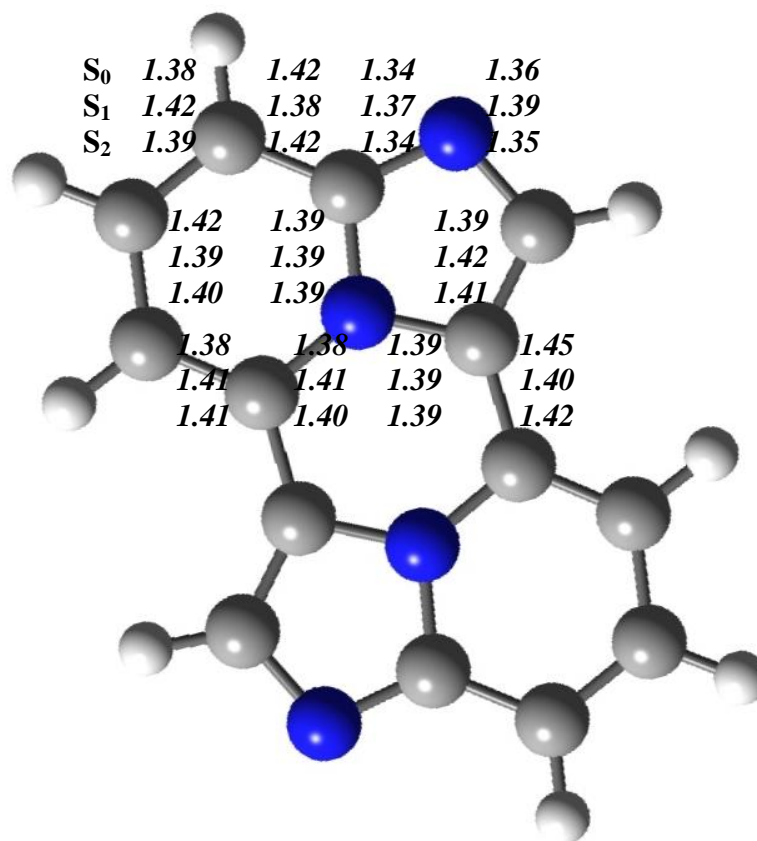
**Vibrational frequencies of isolated compound 4 optimized in its electronic ground S<sub>0</sub> and excited S<sub>1</sub> and S<sub>2</sub> singlet states.**

No	S <sub>0</sub>			S <sub>1</sub>			S <sub>2</sub>		
	sym	ν [cm <sup>-1</sup> ]	IR act	sym	ν [cm <sup>-1</sup> ]	IR act	sym	ν [cm <sup>-1</sup> ]	IR act
1	AU	81.0	2.07	AU	90.7	1.34	AU	84.5	1.27
2	AU	106.1	0.36	AU	95.4	0.54	AU	100.2	1.26
3	AU	208.1	0.18	AU	169.7	2.75	AU	194.2	0.09
4	BG	208.6	0.00	BG	210.9	0.00	BG	208.8	0.00
5	BU	250.2	2.74	BG	228.2	0.00	BG	230.6	0.00
6	BG	256.3	0.00	BU	242.9	1.88	BU	245.3	4.01
7	BG	301.6	0.00	BG	264.0	0.00	BG	294.7	0.00
8	AU	327.4	8.21	AU	363.1	4.75	AU	321.4	8.38
9	AG	376.1	0.00	AG	379.6	0.00	AG	368.6	0.00
10	AG	410.3	0.00	AG	407.9	0.00	AG	413.6	0.00
11	AG	491.2	0.00	AU	426.0	0.15	AU	472.5	0.04
12	AU	520.2	0.99	AG	486.1	0.00	BG	477.6	0.00
13	BU	530.7	10.52	BG	488.8	0.00	AG	492.3	0.00
14	BG	532.4	0.00	BU	522.0	12.06	BU	522.9	11.03
15	BG	588.1	0.00	BG	560.6	0.00	BG	544.8	0.00
16	AG	608.0	0.00	AG	600.4	0.00	AU	600.0	0.60
17	AU	643.8	2.10	AU	611.8	6.16	AG	600.2	0.00
18	AG	647.0	0.00	AU	631.5	0.49	AU	629.6	0.15
19	BU	655.5	6.62	AG	635.9	0.00	BU	638.9	3.29
20	AU	661.1	0.20	BU	637.5	6.67	AG	640.5	0.00
21	BU	673.0	1.45	BG	660.9	0.00	BG	654.1	0.00
22	BG	682.1	0.00	BU	674.4	3.94	BU	665.7	0.28

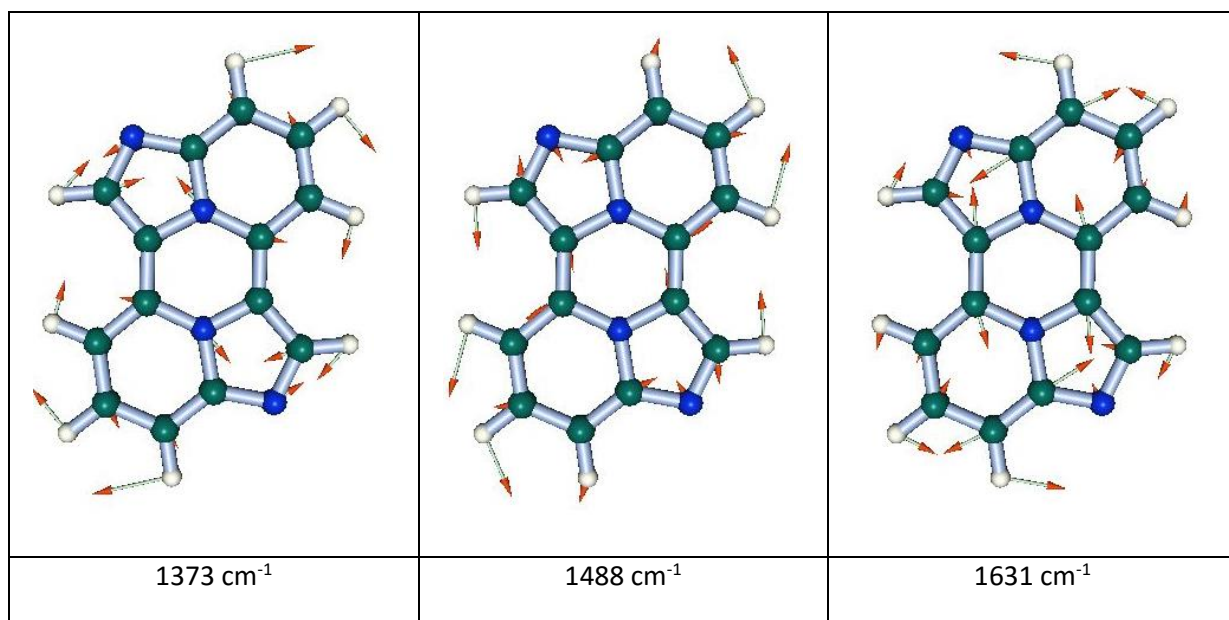
23	AU	745.3	13.82	AU	700.7	1.63	AU	693.8	56.31
24	BG	748.0	0.00	BG	702.5	0.00	BG	695.6	0.00
25	AU	787.0	93.20	BG	755.5	0.00	AU	717.0	4.52
26	BG	789.9	0.00	AU	759.1	97.55	BG	717.4	0.00
27	AG	818.9	0.00	AG	823.4	0.00	BG	737.0	0.00
28	BU	853.5	3.63	BU	848.1	16.15	AU	742.9	68.46
29	BG	865.2	0.00	AU	855.1	0.07	BG	787.6	0.00
30	AU	865.6	1.62	BG	855.6	0.00	AU	788.3	19.14
31	AU	871.4	23.13	AU	874.1	28.89	AG	816.3	0.00
32	BG	874.7	0.00	BG	876.4	0.00	BU	849.6	13.98
33	AG	928.7	0.00	AG	916.6	0.00	AG	923.4	0.00
34	BU	943.4	19.46	BU	927.9	12.80	BU	924.9	8.49
35	BG	974.0	0.00	AU	931.1	0.59	BG	950.7	0.00
36	AU	975.0	0.23	BG	931.5	0.00	AU	951.3	0.25
37	AG	1044.2	0.00	BU	1044.6	93.36	AG	1041.0	0.00
38	BU	1062.2	8.02	BU	1049.4	19.13	BU	1051.9	5.40
39	AG	1071.3	0.00	AG	1050.3	0.00	AG	1071.6	0.00
40	BU	1114.8	7.57	AG	1053.8	0.00	BU	1083.6	16.36
41	AG	1168.7	0.00	BU	1166.4	16.72	BU	1165.7	104.05
42	BU	1177.7	85.51	AG	1176.4	0.00	AG	1165.8	0.00
43	BU	1195.9	25.07	BU	1196.3	7.07	AG	1189.4	0.00
44	AG	1212.0	0.00	AG	1207.3	0.00	BU	1197.2	20.31
45	BU	1227.3	100.32	AG	1248.5	0.00	BU	1217.5	8.99
46	AG	1261.5	0.00	BU	1249.9	62.06	AG	1237.1	0.00
47	AG	1320.0	0.00	AG	1282.8	0.00	BU	1277.3	67.89
48	BU	1325.4	108.63	BU	1290.4	45.77	AG	1291.5	0.00
49	BU	1341.7	82.46	AG	1337.2	0.00	BU	1318.3	23.22

50	AG	1346.9	0.00	BU	1337.4	116.31	AG	1327.7	0.00
51	AG	1358.7	0.00	BU	1371.3	55.61	AG	1352.0	0.00
52	AG	1365.9	0.00	AG	1373.3	0.00	BU	1378.7	11.90
53	BU	1376.1	30.27	BU	1412.7	10.12	AG	1382.7	0.00
54	BU	1399.6	44.54	AG	1421.0	0.00	BU	1393.5	17.31
55	BU	1442.2	4.27	AG	1434.2	0.00	BU	1418.4	4.68
56	AG	1459.1	0.00	BU	1443.3	27.23	AG	1442.7	0.00
57	BU	1523.3	74.16	BU	1482.6	48.16	BU	1473.8	4.94
58	AG	1529.1	0.00	AG	1487.9	0.00	AG	1475.1	0.00
59	AG	1565.7	0.00	BU	1516.9	21.23	BU	1519.3	11.55
60	BU	1573.7	7.45	AG	1544.6	0.00	AG	1532.6	0.00
61	BU	1587.2	234.74	BU	1552.8	37.06	BU	1603.3	146.84
62	AG	1604.9	0.00	AG	1631.1	0.00	AG	1608.0	0.00
63	BU	1674.3	151.10	BU	1649.2	32.80	AG	1641.0	0.00
64	AG	1678.5	0.00	AG	1695.1	0.00	BU	1650.9	697.56
65	AG	3203.4	0.00	BU	3206.2	3.69	BU	3200.7	18.78
66	BU	3203.6	24.32	AG	3207.1	0.00	AG	3200.7	0.00
67	AG	3230.0	0.00	BU	3221.5	22.90	BU	3237.2	0.12
68	BU	3230.1	4.61	AG	3221.7	0.00	AG	3237.2	0.00
69	AG	3240.6	0.00	BU	3242.8	5.60	AG	3247.7	0.00
70	BU	3240.6	2.81	AG	3243.0	0.00	BU	3248.0	10.46
71	AG	3250.1	0.00	BU	3245.0	0.63	BU	3263.7	5.34
72	BU	3250.2	9.03	AG	3245.4	0.00	AG	3264.7	0.00

Bond lengths in compound 4 obtained with the aid of DFT/B3LYP/6-31G(d,p) and TD DFT/B3LYP/6-31G(d,p) methods in the electronic ground  $S_0$  and excited  $S_1$  and  $S_2$  states.


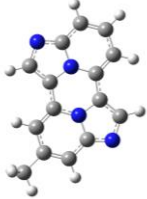


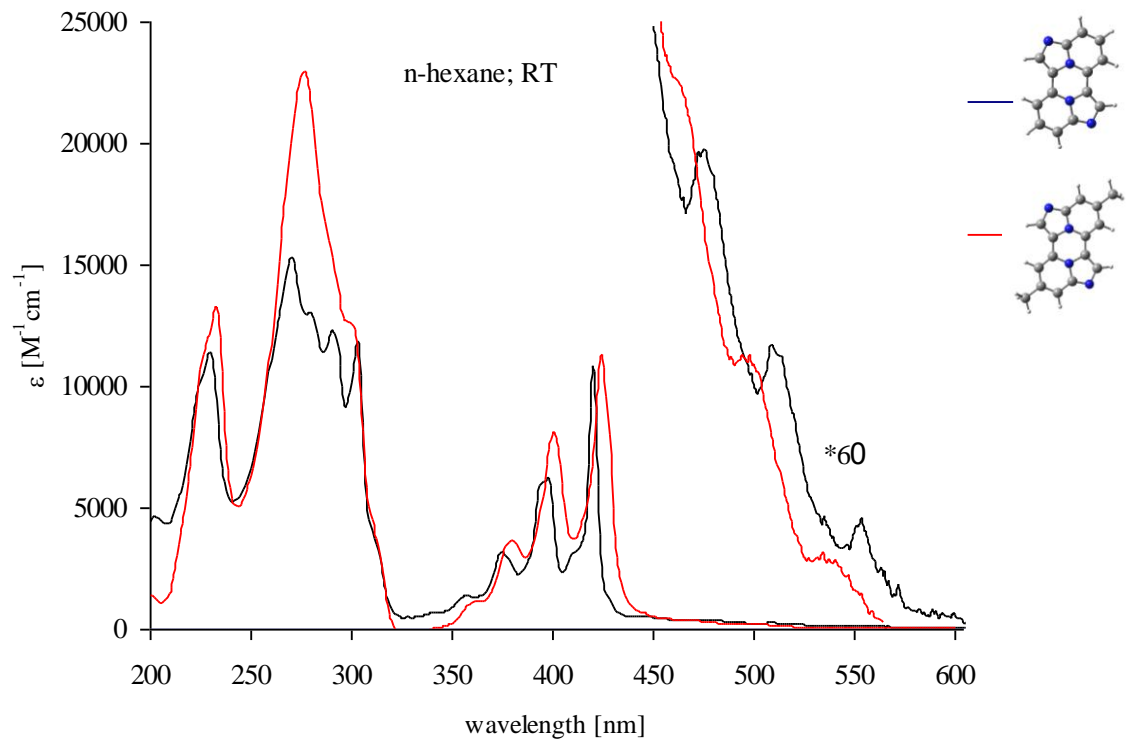
Vibrations of 4 with large displacement parameter in the  $S_1$  state.





**Wavelengths of the electronic  $S_0 \rightarrow S_i$  transitions for compound 5 calculated with the aid of TD DFT B3LYP//DFT B3LYP /6-31G(d,p) method**

					
no	sym	$\lambda$ [nm]	oscillator strength	$\lambda$ [nm]	oscillator strength
1	AG	502.26	0.000	512.45	0.001
2	AU	385.48	0.197	384.99	0.182
3	AU	289.23	0.118	288.77	0.124
4	AG	273.80	0.000	271.70	0.051
5	AU	265.22	0.660	266.28	0.461
6	AG	253.61	0.000	253.93	0.000
7	AU	253.45	0.379	253.02	0.050
8	AG	251.16	0.000	252.19	0.299
9	AG	248.86	0.000	247.03	0.095
10	AU	241.83	0.001	241.55	0.001
11	AG	233.03	0.000	234.76	0.000
12	AU	232.35	0.000	232.35	0.001
13	AG	224.65	0.000	224.49	0.000
14	AU	219.77	0.544	219.66	0.101
15	AG	219.37	0.000	218.77	0.406



**Fig. S27** Comparison of the absorption spectra of compounds 4 and 5.

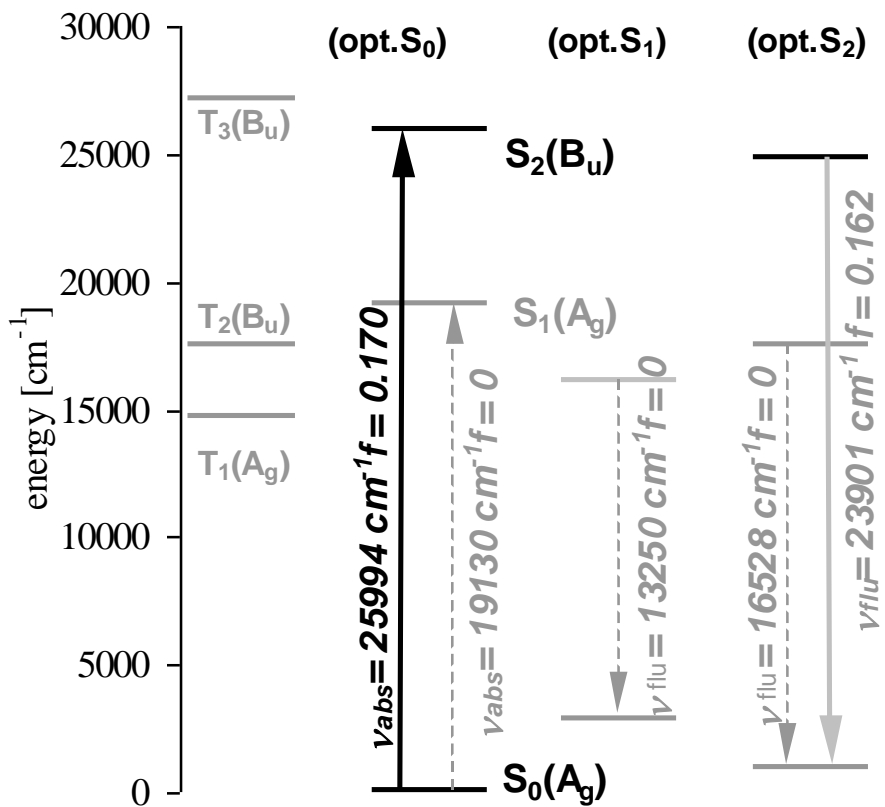


Fig. S28. Energy diagram of the electronic states according to the TD DFT//DFT B3LYP/6-31G(d,p) calculations. Energy of the levels in the geometry of molecule optimized for the S<sub>0</sub>, S<sub>1</sub> and S<sub>2</sub> states. Black line indicates the only one transition which has been verified experimentally.

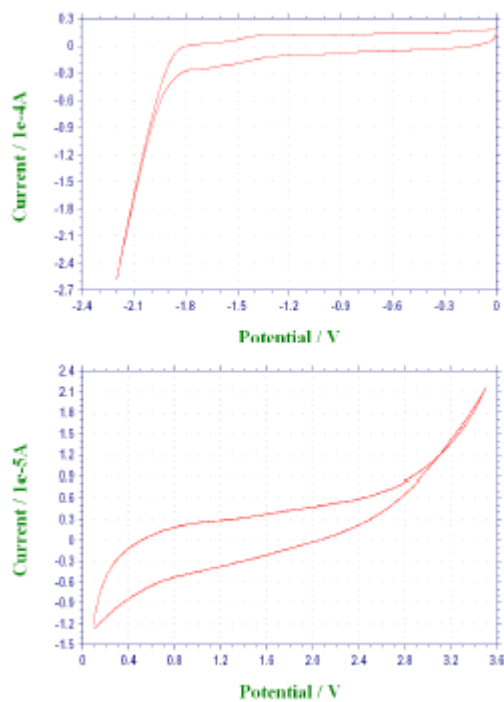


Fig. S29. Cyclic voltammetry for compound 4.

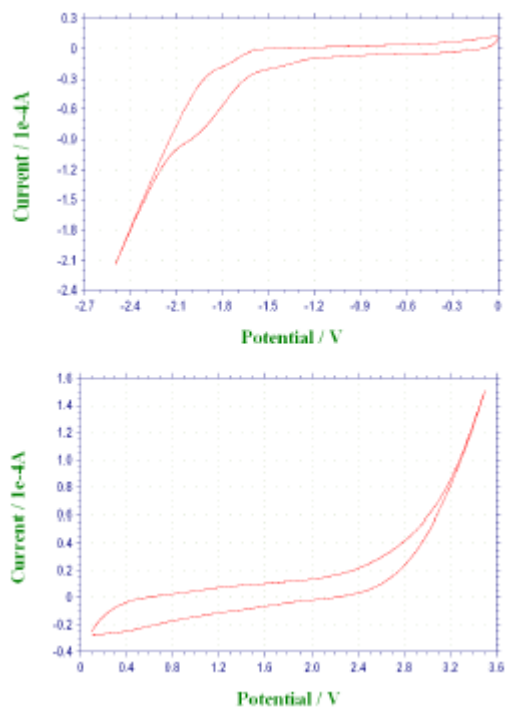


Fig. S30. Cyclic voltammetry for compound 5.