

Binaphthyl platform as starting material for the preparation of electron rich benzo[*g,h,i*]perylene. Application to molecular architectures based on amino benzo[*g,h,i*]perylene and carborane combinations

Grégory Pieters, Anne Gaucher*, Damien Prim, Thierry Besson, José Giner Planas*, Francesc Teixidor, Clara Viñas, Mark E. Light, and Michael B. Hursthouse

Table of contents

General	4
Operating methods.....	4
5 General	4
General procedure for coupling on 1-bromo-2-cyanomethylnaphthalene 1	4
General cyclization procedure for the obtention of aminobenzoperylene 5a-5c	5
General procedure for the synthesis of the compound 7 and 8	5
Analytical data.....	7
10 1-bromo-2-cyanomethylnaphthalene 1	7
Compound 3a	7
Compound 3b	8
Compound 3c	8
6-Aminobenzo[g,h,i]perylène 5a	9
15 Compound 5b	9
Compound 5c	10
Compound 7	11
Compound 8	12
NMR Spectra.....	13
20 ¹ H NMR and ¹³ C NMR of 4a	13
¹ H NMR of the mixture 4b/1'	14
¹ H NMR of the mixture 4c/1'	14
¹ H NMR and ¹³ C NMR of 5a	15
¹ H NMR and ¹³ C NMR of 5b	16
25 ¹ H NMR and ¹³ C NMR of 5c	17
¹ H NMR and ¹³ C NMR of 7	18
¹ H NMR and ¹³ C NMR of 8	19
DFT calculation data	20

[Tapez un texte]

Standard orientation for 5a	21
Standard orientation for 5b	22
Standard orientation for 5c	23
X-Ray analysis data.....	25
UV and emission additional data.....	29

Operating methods

General

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without purification. Petroleum ether was distilled under Argon. NMR spectra were recorded on a 300 MHz and 200 MHz Bruker spectrometer. Chemical shifts were reported in ppm relative to the residual solvent peak (7.26 ppm for CHCl₃, 5.32 ppm for methylene chloride – d₂, 3.58 ppm for THF – d₈) for ¹H spectra and (77.00 ppm for CDCl₃, 53.8 ppm for methylene chloride – d₂, 67.4 ppm for THF – d₈) for ¹³C spectra. High Resolution Mass spectroscopy data were recorded on a Autospec Ultima (Waters/Micromass) device with a resolution of 5000 RP at 5%. UV spectra data were recorded on a Agilent 8453 UV-Visible Spectrometry system at 25 °C.

General procedure for coupling on 1-bromo-2-cyanomethylnaphthalene **1**

To a stirred suspension of 1-bromo-2-cyanomethylnaphthalene **1** (247 mg, 1 mmol), naphthyl-1-boronic acid (344 mg, 2 mmol, 2 eq.), and K₂CO₃ (414 mg, 3 mmol, 3 eq.) in degassed mixture of toluene (1 mL), absolute ethanol (0.2 mL) and water (0.2 mL) was added PdCl₂(PPh₃)₂ (73 mg, 0.1 mmol, 10% mol). The mixture was stirred at 80°C overnight. Water (10 mL) was then added and the aqueous phase extracted with dichloromethane (2x10 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (PE/DCM: 60/40) to give **3a** as a pale yellow solid (206 mg, 70%).

Using the same procedure, 1-bromo-2-cyanomethylnaphthalene **1** (100 mg, 0.4 mmol), acenaphten-4-boronic acid (158 mg, 0.8 mmol, 2 eq.), K₂CO₃ (168 mg, 1.2 mmol, 3 eq.) and PdCl₂(PPh₃)₂ (29 mg, 0.04 mmol, 10% mol), **3b** was isolated as a mixture, containing debrominated starting material (75/25, 101 mg) after filtration through a pad of silica gel (PE/DCM: 60/40). This yellow solid was used without further purification for the next cyclization step.

Using the same procedure, 1-bromo-2-cyanomethylnaphthalene **1** (247mg, 1 mmol), phenanthren-9-boronic acid (444 mg, 2 mmol, 2 eq.), K₂CO₃ (414 mg, 3 mmol, 3 eq.) and PdCl₂(PPh₃)₂ (73 mg, 0.1 mmol, 10% mol), **3c** was isolated as a mixture, containing debrominated starting material (75/25, 251 mg) after filtration through a pad of silica gel (PE/DCM: 60/40). This cream solid was used without further purification for the next cyclization.

General cyclization procedure for the obtention of aminobenzoperylene 5a-5c

The nitrile product **3a** (150 mg, 0.51 mmol) was added in stirred polyphosphoric acid (10 mL) under argon. The suspension was stirred at 110°C for 48 h. The resulting mixture was poured into ice (100 g) and basified with 1 M aqueous solution of Na₂CO₃. This aqueous layer was then extracted with ethyl acetate (4x50 mL) and the combined organic layers were dried (MgSO₄), filtered and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (PE/CH₂Cl₂: 40/60) to give 6-aminobenzo-[g,h,i]-perylene **5a** (90 mg, 60%) as a yellow solid.

Using the same procedure starting from the nitrile **3b** (86 mg, 0.27 mmol) compound **5b** was obtained after silica gel flash chromatography purification (PE/EtOAc : 60/40) as an orange solid (25 mg, 30%).

Using the same procedure starting from the nitrile **3c** (216 mg, 0.63 mmol) compound **5c** was obtained after silica gel flash chromatography purification (PE/EtOAc : 70/30) as a yellow solid (95 mg, 44%).

General procedure for the synthesis of the compound 7 and 8

To a solution of 6-aminobenzo-[g,h,i]-perylene **5a** (50 mg, 0.17 mmol) and triethylamine (70 μL, 0.51 mmol, 3 eq.) in MeCN (1 mL) was added the chloride **6** (54 mg, 0.19 mmol) and KI (9 mg, 30% mol) and the mixture was stirred at reflux for 72 h. Thereafter, saturated aqueous K₂CO₃ solution (10 mL) was added to the reaction mixture, the aqueous phase was extracted with EtOAc (3x10 mL), and the combined organic phases were dried over MgSO₄, filtered, and concentrated. Chromatographic separation of the residue obtained on silica gel (PE/EtOAc: 80/20) afforded the compound **7** (36 mg, 40%) as a yellow solid.

[Tapez un texte]

Using the same procedure starting from the amine **5c** (40 mg, 0.11 mmol) compound **8** was obtained as a yellow solid (13 mg, 20%). The crude product was purified with PE/EtOAc: 80/20 on preparative TLC.

Analytical data

1-bromo-2-cyanomethylnaphthalene 1

5

mp: 122 °C.

¹H NMR (δ ppm, CDCl₃, 300K, 300 MHz): 8.26 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.76 (m, 2H), 7.67 – 7.44
10 (m, 3H), 4.03 (s, 2H).

¹³C NMR (δ ppm, CDCl₃, 300K, 75 MHz): 133.9, 132.3, 128.6, 128.3, 128.2, 127.8, 127.3, 127.2,
126.1, 124.2, 117.2, 25.9.

15 Data in accordance with literature.^{S1}

Compound 3a

20

¹H NMR (δ ppm, CDCl₃, 300K, 300 MHz): 8.04 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 8.01 –
7.93 (m, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.56 – 7.47 (m, 2H), 7.44 (dd, *J* = 7.0, 1.2
Hz, 1H), 7.37 – 7.25 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 3.59 – 3.32 (m, 2H).

^{S1} N. Aoyagi, T. Izumi *Tetrahedron Lett.* **2002**, 43, 5529

¹³C NMR (δ ppm, CDCl₃, 300K, 75 MHz): 137.1, 135.0, 133.8, 133.2, 133.0, 132.2, 129.0, 128.7, 128.5, 128.1, 128.0, 126.9, 126.8, 126.7, 126.5, 126.5, 126.4, 125.7, 125.6, 125.3, 118.2, 22.2.

Data in accordance with literature.^{S2}

5

Compound 3b

¹⁰ **HRMS (ESI):** *m/z* calculated for C₂₄H₁₇NNa ([M+Na]⁺): 342.1259 found: 342.1253.

Compound 3c

¹⁵ **MS (ESI):** *m/z* calculated for C₂₅H₁₇ ([M-CN]⁺): 317.4 found: 317.1.

^{S2} N. Aoyagi, T. Izumi *Tetrahedron Lett.* **2002**, 43, 5529

6-Aminobenzo[g,h,i]perylène 5a

5 **mp:** 256 °C

¹H NMR (δ ppm, CD₂Cl₂, 300K, 300 MHz): 8.94 (d, *J* = 8.2 Hz, 1H), 8.92 (d, *J* = 8.2 Hz, 1H), 8.20 – 7.8 (m, 8H), 7.61 (s, 1H), 4.58 (s_{br}, 2H).

10 **¹³C NMR** (δ ppm, CD₂Cl₂, 300K, 75 MHz): 149.1, 141.3, 134.0, 132.3, 130.8, 130.4, 128.9, 127.6, 126.6, 126.5, 126.3, 126.0, 125.8, 124.9, 124.7, 124.0, 120.6, 120.5, 120.1, 118.6, 117.9, 109.4.

HRMS (ESI): *m/z* calculated for C₂₂H₁₄N ([M+H]⁺): 292.1126 found: 292.1108.

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Compound 5b

mp: 219 °C

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¹H NMR: (δ ppm, CD₂Cl₂, 300K, 300 MHz): 8.83 (d, *J* = 8.2 Hz, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 1H), 8.01 – 7.75 (m, 4H), 7.60 (s, 1H), 4.54 (s_{br}, 2H), 3.64 (s, 4H).

¹³C NMR: (δ ppm, CD₂Cl₂, 300K, 75 MHz): 144.5, 143.7, 141.1, 131.3, 129.1, 127.7, 127.2, 126.5, 126.0, 125.9, 124.6, 123.7, 123.2, 121.6, 121.3, 120.6, 120.0, 112.1, 109.2, 31.3, 30.8.

HRMS (ESI): *m/z* calculated for C₂₄H₁₆N [M+H]⁺: 318.1259 found : 318.1283

Compound 5c

10

mp: 229 °C

¹H NMR: (δ ppm, CD₂Cl₂, 300K, 300 MHz): 9.48 – 9.30 (m, 1H), 8.96 (d, *J* = 7.7 Hz, 1H), 8.90 (d, *J* = 7.5 Hz, 1H), 8.86 – 8.75 (m, 2H), 8.12 (d, *J* = 7.2 Hz, 1H), 8.04 – 7.84 (m, 4H), 7.73 – 7.61 (m, 3H),
15 4.74 (s, 2H).

¹³C NMR: (δ ppm, CD₂Cl₂, 300K, 75 MHz): 143.0, 130.2, 130.1, 130.0, 128.6, 127.9, 127.5, 126.1, 126.2, 125.6, 125.5, 125.1, 124.9, 124.7, 124.4, 123.6, 121.5, 120.4, 120.3, 117.2, 116.5, 115.9, 113.0.

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HRMS (ESI): *m/z* calculated for C₂₆H₁₆N [M+H]⁺: 342.1283 found : 342.1281

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Compound 7

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¹H NMR: (δ ppm, THF-*d*₈, 300K, 300 MHz): 9.05 (d, $J = 7.1$ Hz, 1H), 9.00 (d, $J = 7.2$ Hz, 1H), 8.53
10 (d, $J = 9.2$ Hz, 1H), 8.24 – 8.14 (m, 2H), 8.08 (d, $J = 7.2$ Hz, 1H), 8.00 (t, $J = 7.8$ Hz, 1H), 7.95 (d, $J =$
8.9 Hz, 1H), 7.87 (t, $J = 7.8$ Hz, 1H), 7.80 (t, $J = 7.7$ Hz, 3H), 7.49 (s, 1H), 7.37 (m, 3H), 6.43 (d, $J =$
10.6 Hz, 1H), 5.79 – 5.45 (m, 1H), 2.16 (s, 3H).

¹³C NMR: (δ ppm, THF-*d*₈, 300K, 75 MHz): 140.7, 140.3, 133.4, 132.0, 131.9, 13.1, 130.2, 129.5,
15 129.2, 128.4, 127.6, 127.5, 127.3, 1126.9, 126.6, 125.8, 121.7, 121.6, 121.2, 119.1, 108.4, 84.0, 77.2,
61.0, 23.1

¹¹B NMR: (δ ppm, THF-*d*₈, 300K, 96 MHz): 0 to -15 (m, 8B)

20 **HRMS (EI):** m/z calculated for C₃₂H₃₁NB₁₀ [M]⁺: 540.3499 found : 540.3469

25

Compound 8

¹**H NMR:** (δ ppm, CD₂Cl₂, 300K, 300 MHz): 9.48 (m, 1H), 9.15 – 8.75 (m, 4H), 8.15 (d, *J* = 4.8 Hz, 1H), 8.11 (d, *J* = 5.4 Hz, 1H), 8.04 (d, *J* = 5.0 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.91 – 7.78(m, 3H), 7.61-7.52 (m, 2H), 7.45 – 7.30 (m, 3H), 6.46 (m, 1H), 5.27 (m, 1H), 2.21 (s, 3H).

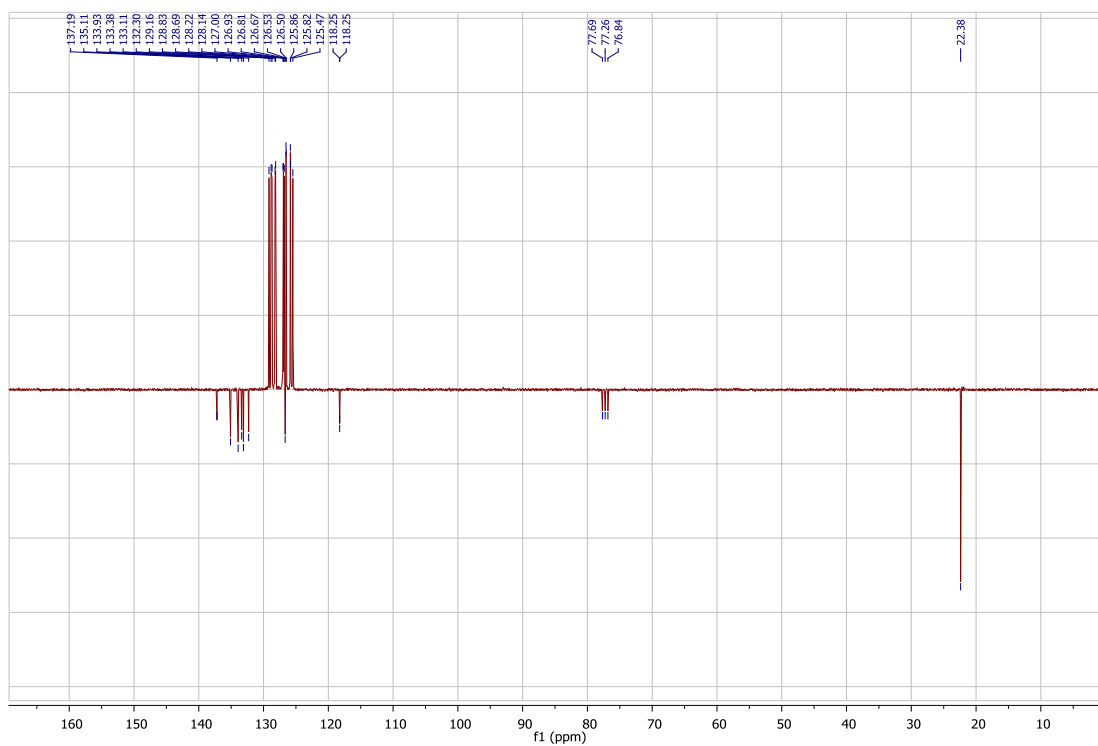
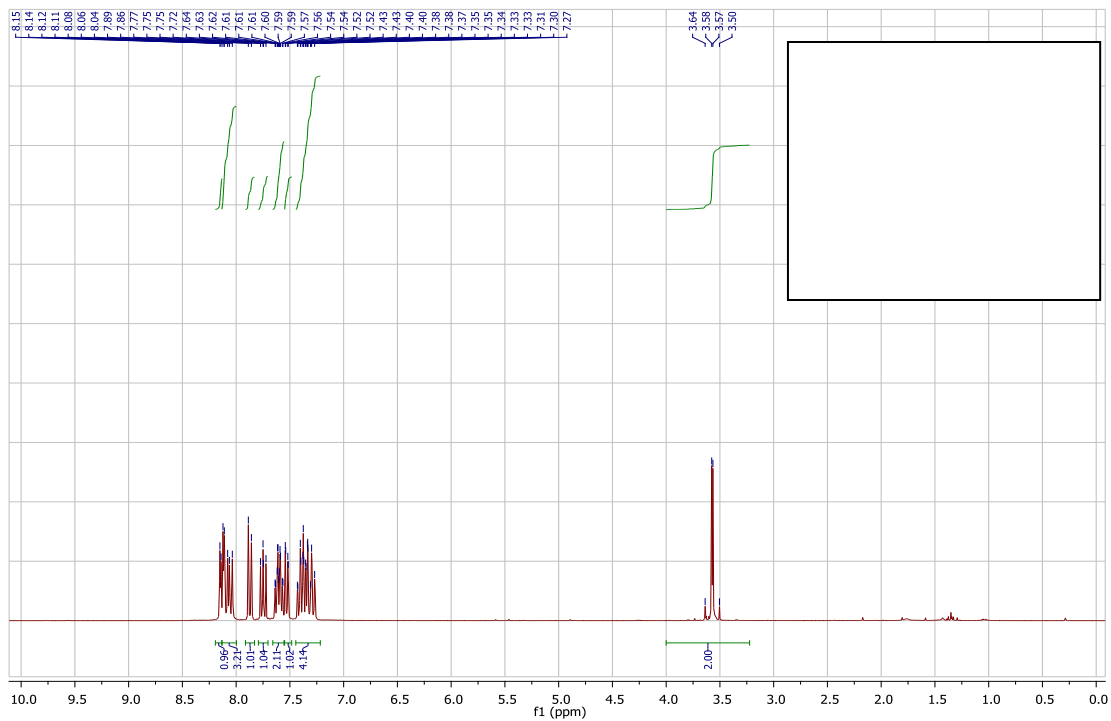
¹³**C NMR:** (δ ppm, CD₂Cl₂, 300K, 75 MHz): 141.3, 138.9, 131.5, 131.0, 130.8, 130.7, 129.4, 129.3, 128.9, 128.6, 128.5, 127.7, 127.4, 127.3, 127.1, 126.7, 126.0, 125.9, 125.5, 125.26, 125.1, 122.7, 121.4, 116.9, 109.5, 82.7, 77.4, 61.7, 30.1.

¹¹**B NMR:** (δ ppm, CD₂Cl₂, 300K, 96 MHz): 5 to -15 (m, 8B)

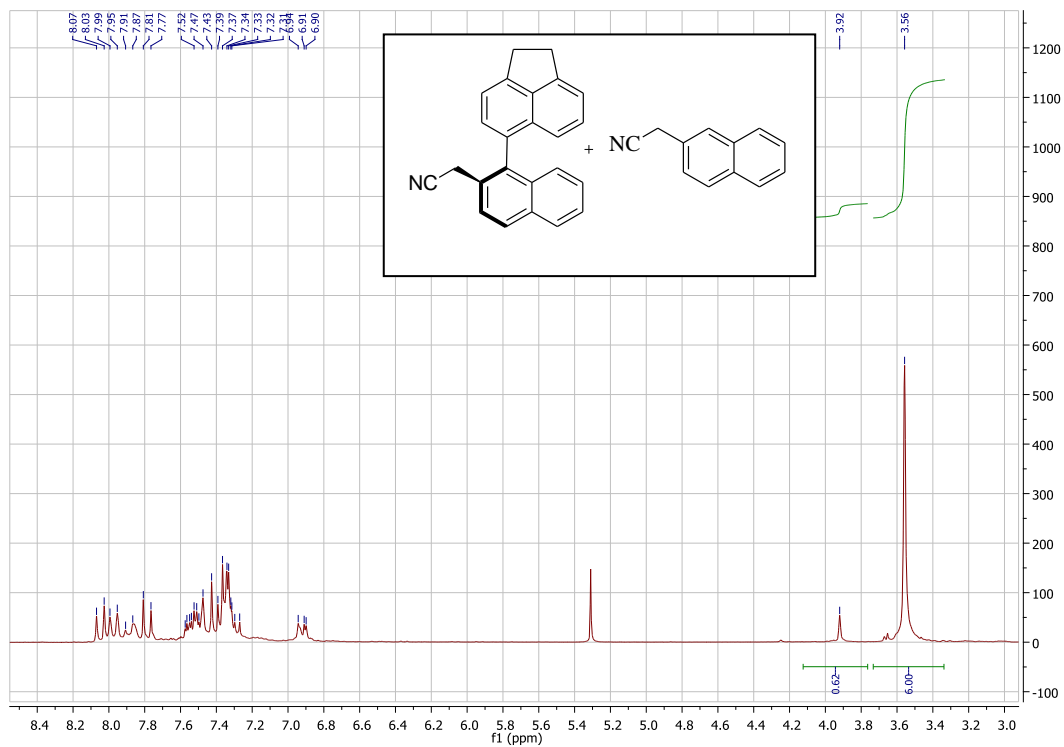
HRMS (EI): *m/z* calculated for C₃₆H₃₃NB₁₀ [M]⁺: 584.3712 found : 584.3720

NMR Spectra

^1H NMR and ^{13}C NMR of 4a

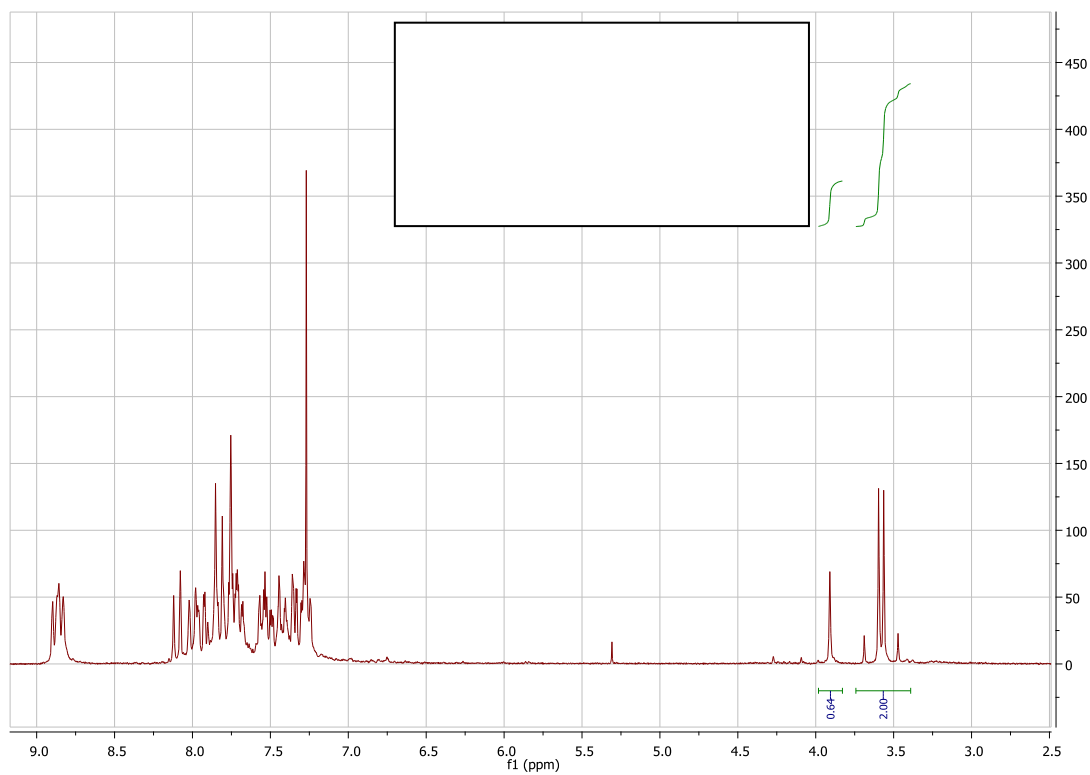


^1H NMR of the mixture 4b/1'

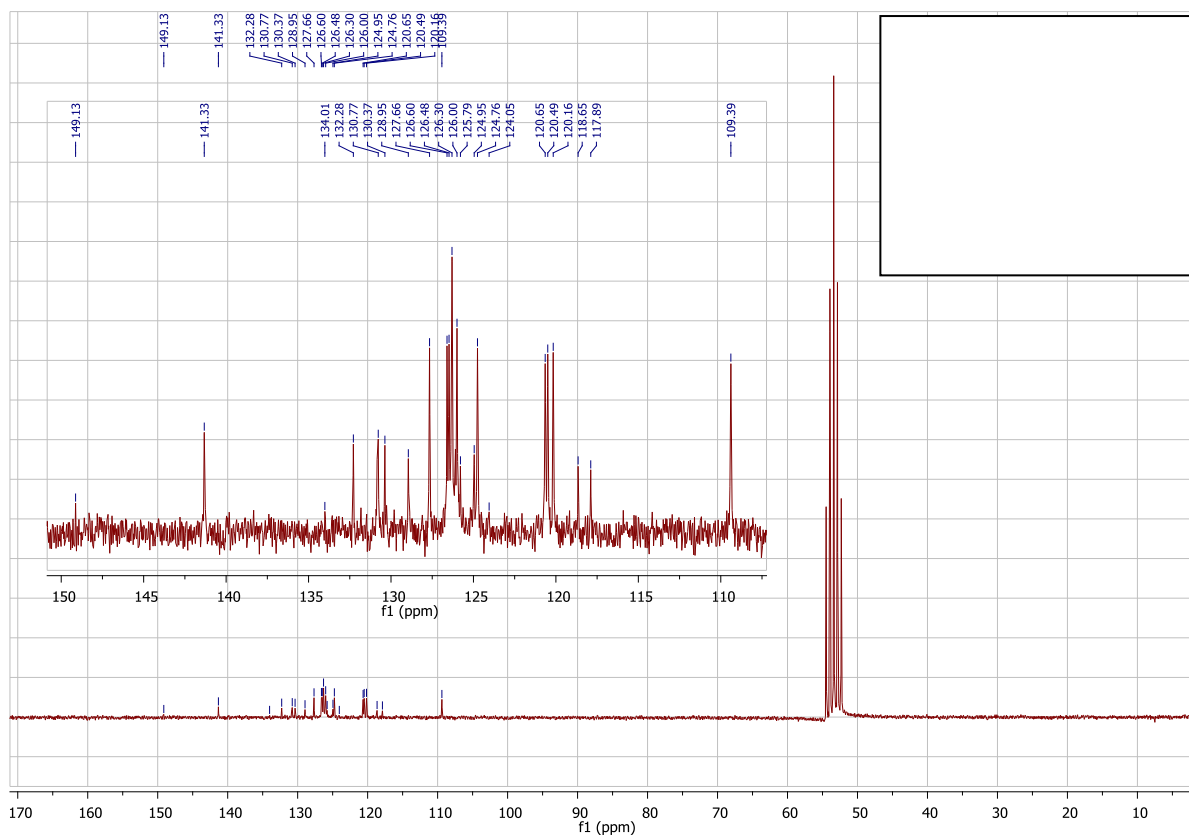
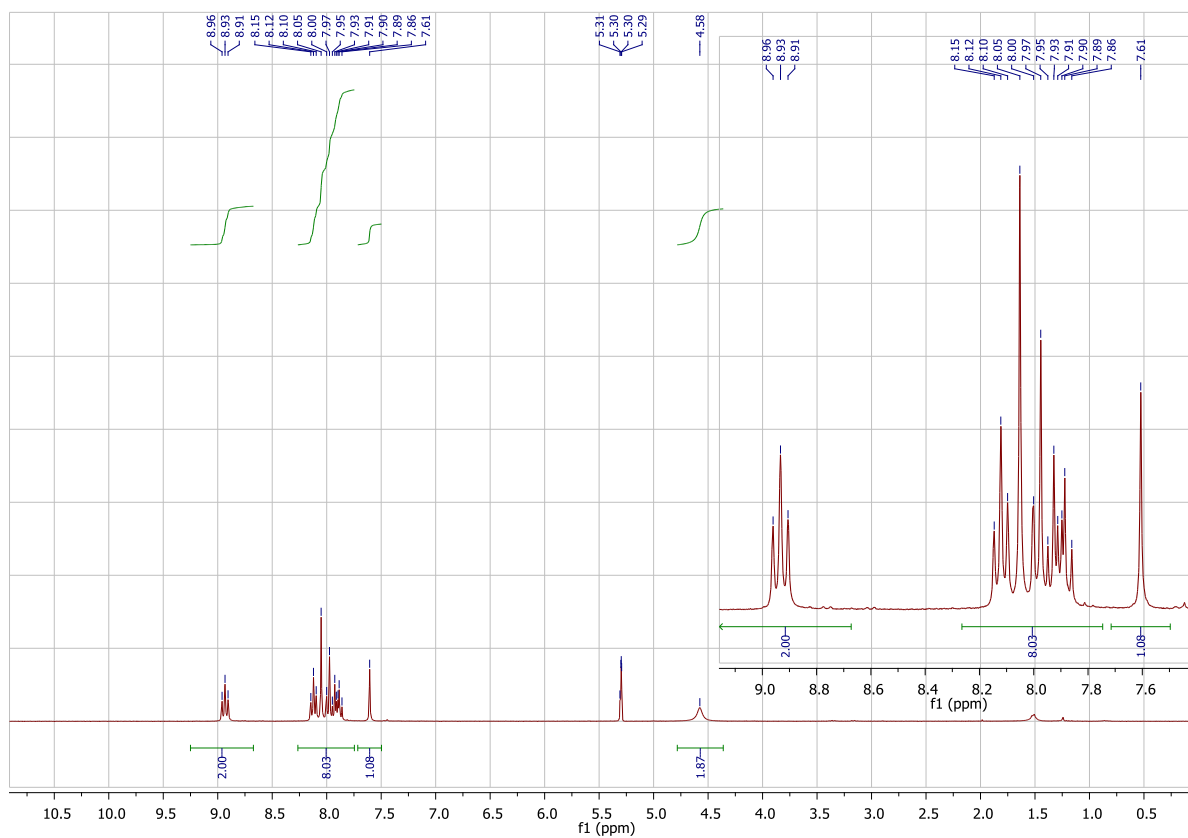


^1H NMR of the mixture 4c/1'

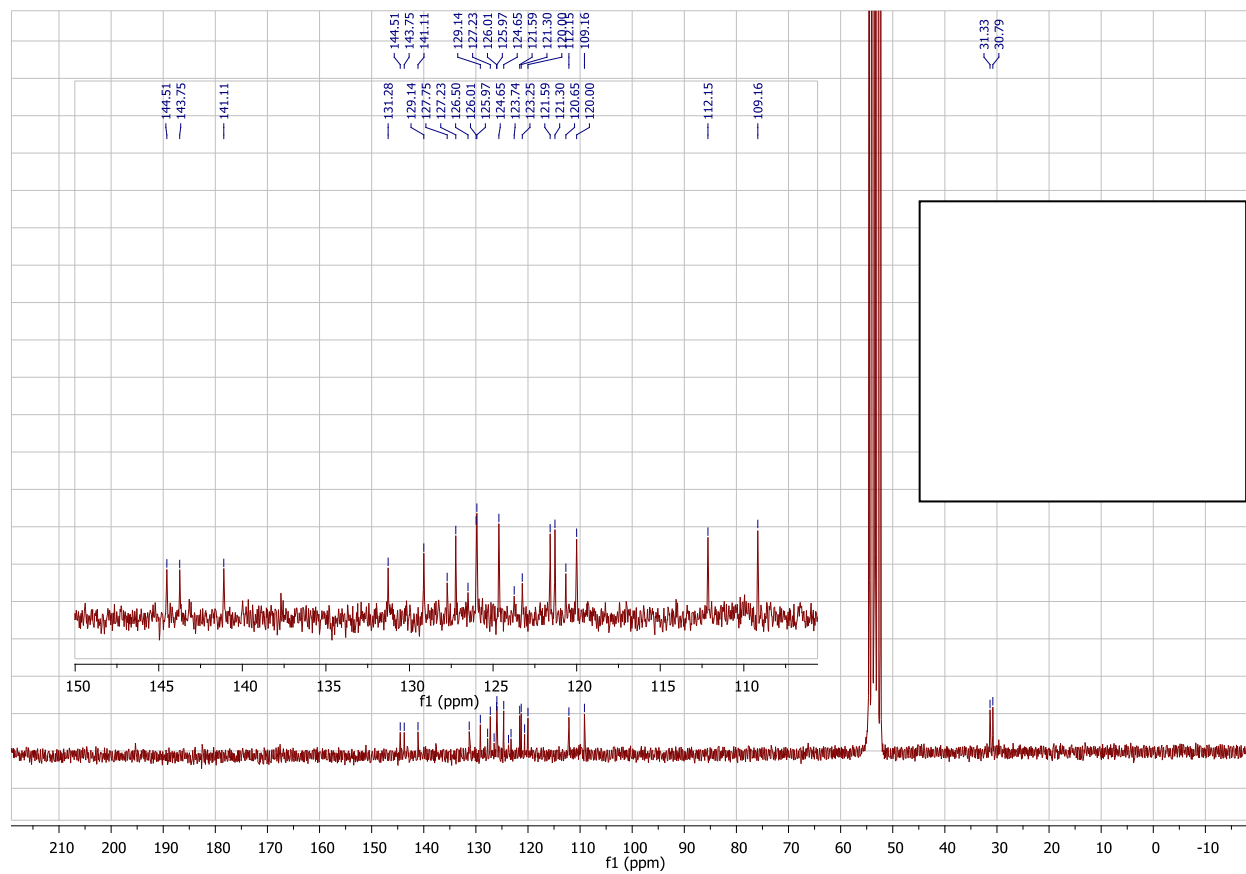
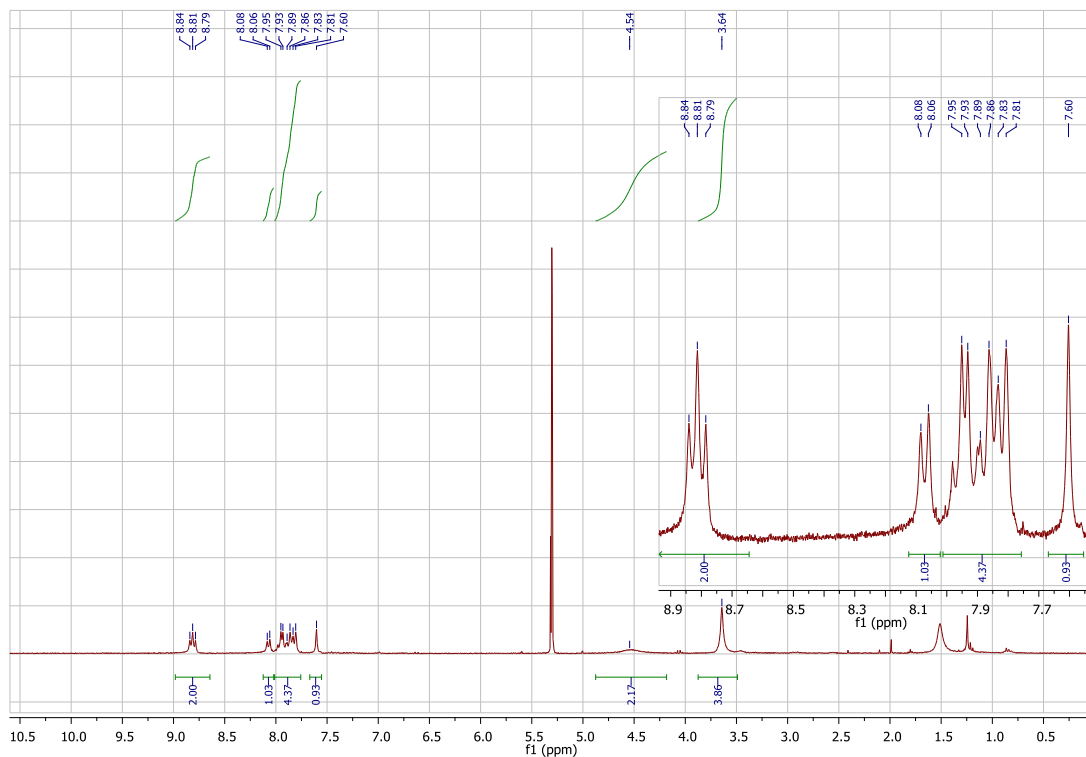
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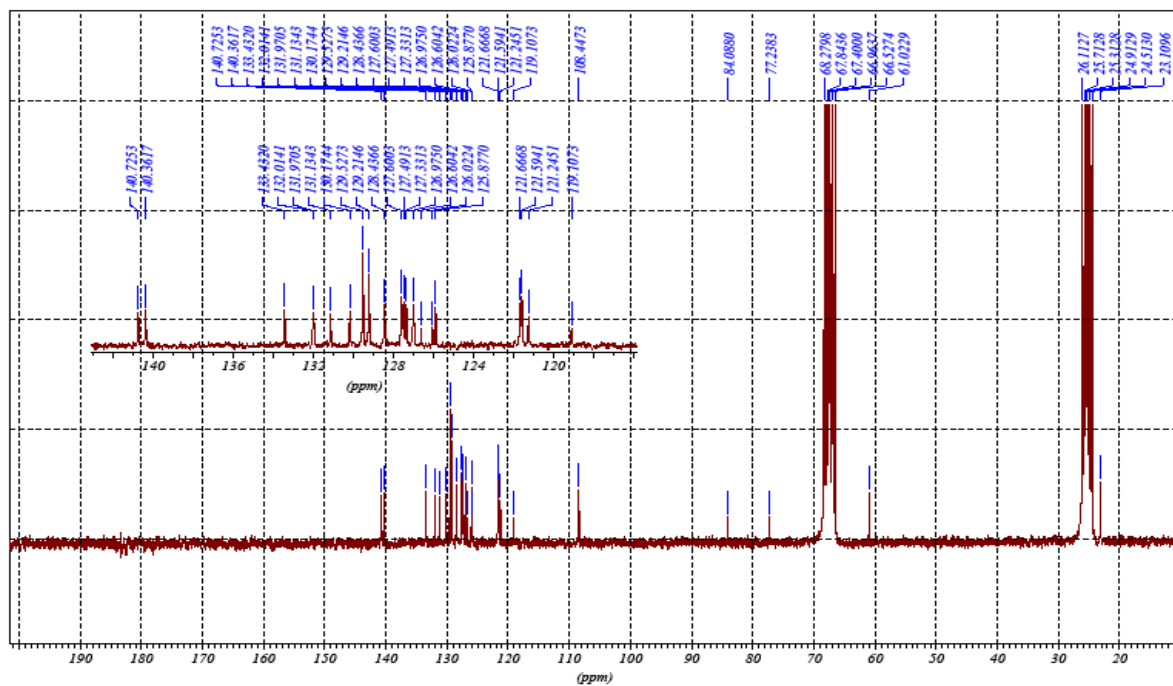
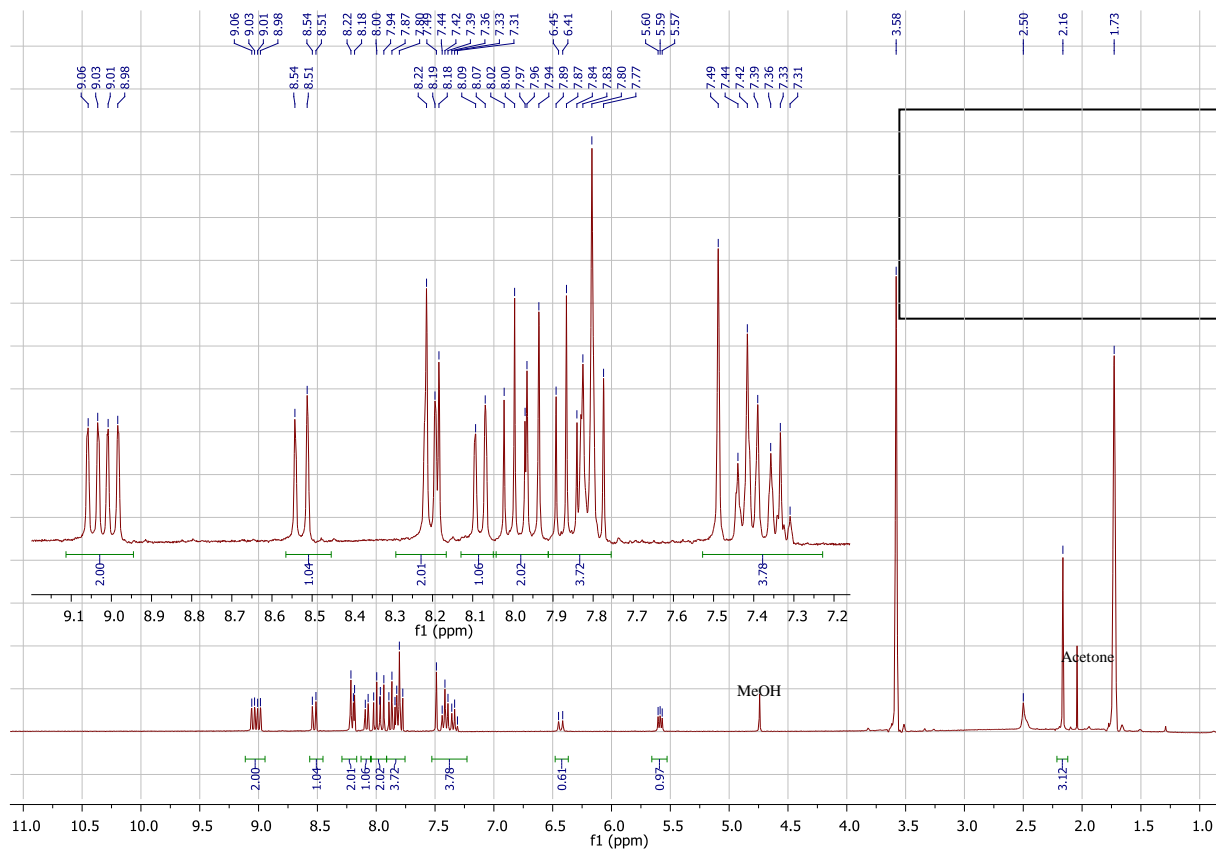
^1H NMR and ^{13}C NMR of 5a



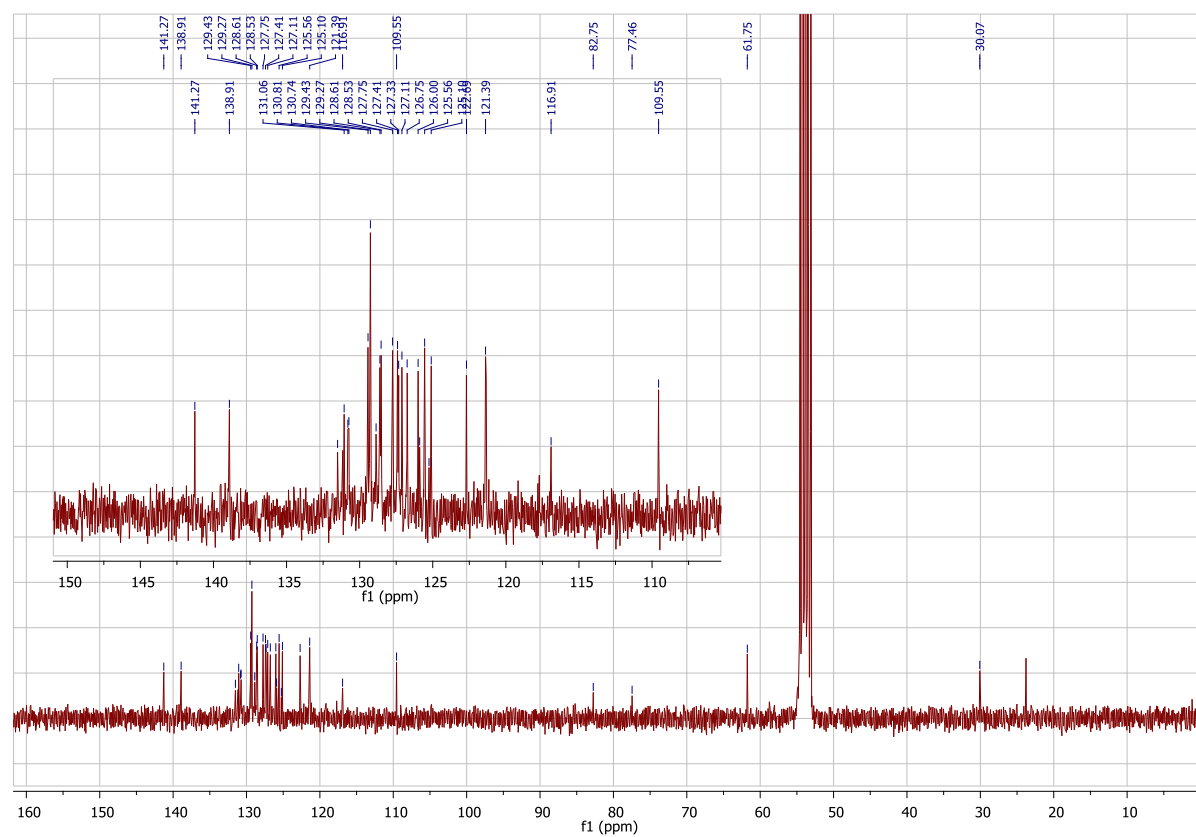
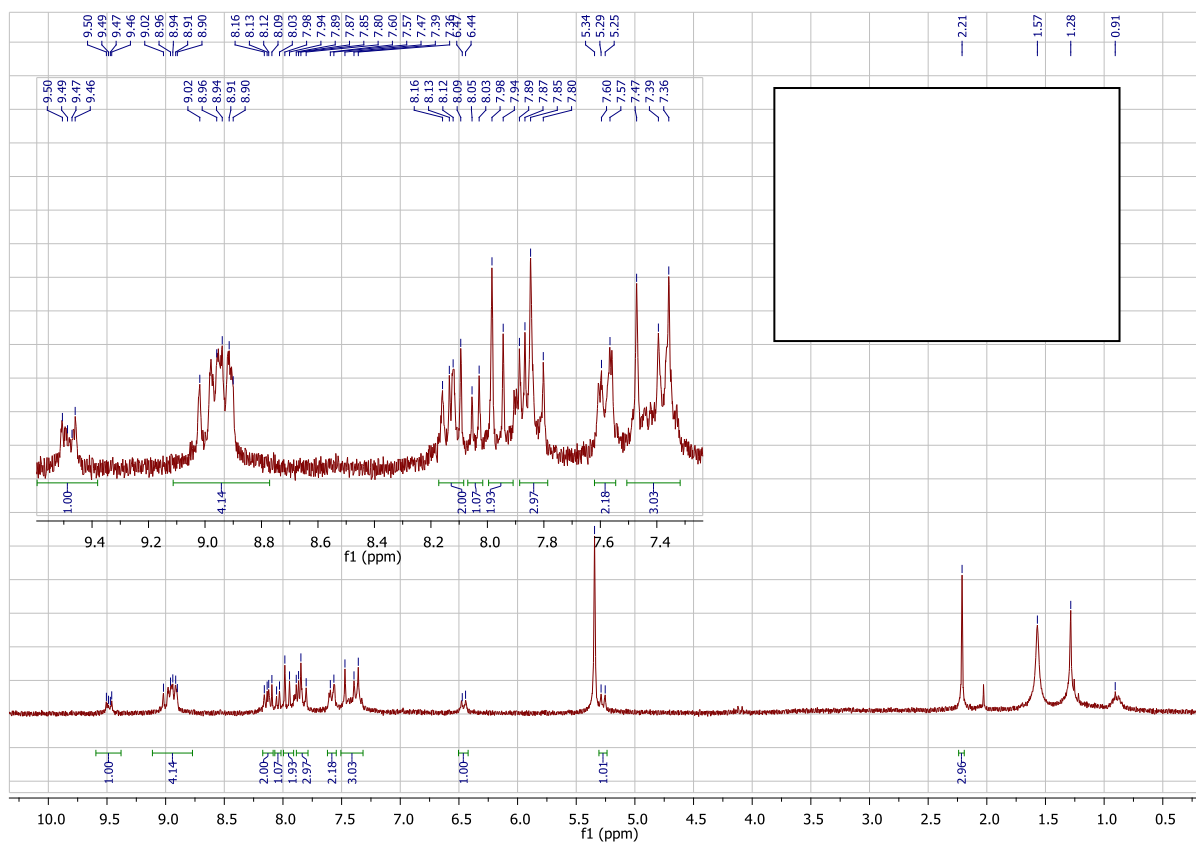
^1H NMR and ^{13}C NMR of 5b



^1H NMR and ^{13}C NMR of 7



^1H NMR and ^{13}C NMR of 8



DFT calculation data

Computational details:

All calculations were carried out using Gaussian 03 program [G03]. The geometries were fully optimized using a hybrid density functional [hybrid]; Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP) [B3LYP] and with the 6-31G(d) basis set. The vibrational frequencies have been computed to characterize all the stationary point. Note that the optimized Cartesian geometries are given in Angstrom and the total energies (E) expressed in hartree and the frequencies (ν) in cm^{-1} .

[G03] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, **2004**.

[hybrid] (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, **1989**. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: New York, **2000**.

[B3LYP] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* 1993, *98*, 5648.

Standard orientation for 5a

$$E = -901.05610060$$

Dipole Moment: 2.2434 Debye

Standard orientation:

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.832726	4.025330	0.000238
2	6	0	-0.370019	3.311660	0.000268
3	6	0	-0.396721	1.910218	0.000081
4	6	0	0.850890	1.208485	0.000036
5	6	0	2.076501	1.946528	0.000089
6	6	0	2.046324	3.354578	0.000031
7	6	0	0.888708	-0.228127	0.000033
8	6	0	2.138902	-0.908678	0.000079
9	6	0	3.343346	-0.134335	0.000268
10	6	0	3.315765	1.229824	0.000270
11	6	0	-0.337125	-0.960939	0.000017
12	6	0	-0.291313	-2.380379	0.000042
13	6	0	0.953753	-3.040757	0.000077
14	6	0	2.155721	-2.344922	0.000053
15	6	0	-1.594983	-0.278586	0.000020
16	6	0	-2.806770	-1.040253	0.000011
17	6	0	-2.726778	-2.473244	0.000016
18	6	0	-1.524274	-3.115458	0.000046
19	6	0	-1.652844	1.148189	0.000002
20	6	0	-2.912708	1.762837	0.000112
21	6	0	-4.094266	1.014457	0.000146
22	6	0	-4.045551	-0.373059	0.000079
23	7	0	3.348732	-3.039258	0.000106
24	1	0	0.809680	5.111267	0.000379
25	1	0	-1.297236	3.872396	0.000462
26	1	0	2.983138	3.905264	0.000025
27	1	0	4.310504	-0.626864	0.000486
28	1	0	4.242955	1.796456	0.000434
29	1	0	0.968185	-4.128510	0.000150
30	1	0	-3.653228	-3.041751	0.000001
31	1	0	-1.481047	-4.201550	0.000064
32	1	0	-2.992140	2.843730	0.000199
33	1	0	-5.051958	1.526641	0.000234
34	1	0	-4.962305	-0.956976	0.000102
35	1	0	4.240804	-2.580907	0.000654
36	1	0	3.345831	-4.044614	0.000424

Standard orientation for 5b

$$E = -978.37416122$$

Dipole Moment: 2.8738 Debye

Standard orientation:

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.836560	2.017342	0.000277
2	6	0	3.270683	2.069928	0.000470
3	6	0	4.014920	0.926108	0.000407
4	6	0	3.399784	-0.372385	0.000145
5	6	0	1.971927	-0.462433	0.000000
6	6	0	1.203189	0.748817	0.000123
7	6	0	4.169202	-1.551928	0.000000
8	6	0	3.550762	-2.795214	0.000435
9	6	0	2.154453	-2.890955	0.000482
10	6	0	1.341674	-1.750486	0.000176
11	6	0	-0.219555	0.696249	0.000000
12	6	0	-1.022937	1.874373	0.000111
13	6	0	-0.348299	3.143248	0.000186
14	6	0	1.042792	3.184592	0.000000
15	6	0	-0.844860	-0.586912	0.000103
16	6	0	-2.247347	-0.631928	0.000000
17	6	0	-3.061876	0.533475	0.000000
18	6	0	-2.463818	1.763544	0.000000
19	6	0	-0.125029	-1.815155	0.000000
20	6	0	-0.877665	-3.004570	0.000234
21	6	0	-2.286870	-3.020948	0.000270
22	6	0	-2.986395	-1.819346	0.000000
23	7	0	-1.066152	4.323717	0.000399
24	6	0	-4.518342	0.091183	0.000227
25	6	0	-4.467414	-1.480726	0.000000
26	1	0	3.757990	3.041690	0.000587
27	1	0	5.100673	0.979933	0.000555
28	1	0	5.253574	-1.476856	0.000000
29	1	0	4.149743	-3.701282	0.000695
30	1	0	1.702656	-3.877086	0.000817
31	1	0	1.541180	4.151871	0.000000
32	1	0	-3.079240	2.658853	0.000155
33	1	0	-0.364932	-3.960720	0.000472
34	1	0	-2.804080	-3.977119	0.000469
35	1	0	-0.585754	5.206845	0.000214
36	1	0	-2.068904	4.342986	0.001558
37	1	0	-5.051758	0.471115	0.878626
38	1	0	-5.051342	0.470994	0.879389
39	1	0	-4.975017	-1.896326	0.878626
40	1	0	-4.974950	-1.896154	0.878613

Standard orientation for 5c

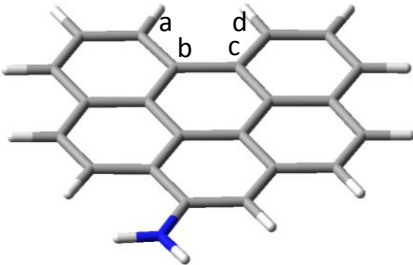
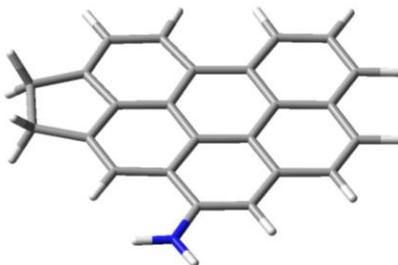
$$E = -1054.66955572$$

Dipole Moment: 1.6918 Debye

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)			
			X	Y	Z	
5	1	6	0	-1.338448	-2.338163	0.076060
10	2	6	0	-2.640869	-2.933044	0.006865
	3	6	0	-3.754872	-2.164300	0.138787
	4	6	0	-3.666846	-0.733312	0.174011
	5	6	0	-2.382062	-0.112565	0.073442
	6	6	0	-1.206896	-0.925558	0.019536
15	7	6	0	-4.814752	0.067286	0.300347
	8	6	0	-4.706056	1.449623	0.325030
	9	6	0	-3.456089	2.060238	0.205195
	10	6	0	-2.283113	1.306734	0.064745
	11	6	0	0.097089	-0.342291	0.043725
20	12	6	0	1.259727	-1.159266	0.084211
	13	6	0	1.083186	-2.566169	0.306964
	14	6	0	-0.189678	-3.118855	0.259374
	15	6	0	0.211071	1.100837	0.085030
	16	6	0	1.495761	1.709899	0.183515
25	17	6	0	2.691997	0.885463	0.006411
	18	6	0	2.571937	-0.529597	0.095035
	19	6	0	-0.961330	1.918397	0.098432
	20	6	0	-0.819389	3.299697	0.291974
	21	6	0	0.432970	3.878031	0.454687
30	22	6	0	1.577545	3.095354	0.391869
	23	6	0	3.965026	1.474560	0.150465
	24	6	0	5.090932	0.722965	0.436619
	25	6	0	4.963411	-0.658583	0.616400
	26	6	0	3.729394	-1.265894	0.454051
35	27	7	0	2.159869	-3.429309	0.559351
	28	1	0	-2.717394	-4.016354	0.032507
	29	1	0	-4.737476	-2.622769	0.211785
	30	1	0	-5.786696	-0.411568	0.383306
	31	1	0	-5.593996	2.064774	0.436203
40	32	1	0	-3.407746	3.142351	0.237178
	33	1	0	-0.301117	-4.193233	0.389891
	34	1	0	-1.696590	3.932874	0.346592
	35	1	0	0.517035	4.946719	0.628342
	36	1	0	2.541004	3.573143	0.519460
45	37	1	0	4.069512	2.550693	0.085203
	38	1	0	6.054066	1.210098	0.555771
	39	1	0	5.823384	-1.257823	0.901112
	40	1	0	3.642127	-2.324582	0.655690
	41	1	0	1.863999	-4.303425	0.975525
50	42	1	0	2.912926	-3.014670	1.093706

Table 1. DFT calculated dihedral angles for compounds **5a** and **5b**

Structure	 5a	 5b
Dihedral abcd angle	0.010	0.023

5

10

15

20

25

30

35

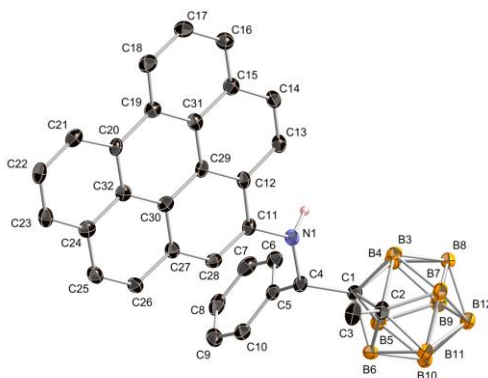
X-Ray analysis data

Data were collected on a Bruker Nonius KappaCCD with a Mo rotating anode generator; standard procedures were followed. During refinement a probable twinning issue was identified; Platon's [REF1] TwinRotMat function gave the following 2 twin law suggestions (1 0 0.48 0 -1 0 0 0 -1 & 0.998 0 0.49 0 -1 0 0.008 0 -0.008). Generation and use of an HKLF5 file reduced the R_1 from ca 19% to ca 6%.

^aCrystal data for 2010acc1038: $M = 536.67$, Monoclinic, $a = 16.7059(6)$, $b = 12.6255(5)$, $c = 13.7625(4)$ Å, $\alpha = 90.00^\circ$, $\beta = 101.603(2)^\circ$, $\gamma = 90.00^\circ$, $U = 2843.47(17)$ Å³, $T = 120(2)$ K, space group $P2(1)/c$, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.066$ mm⁻¹, 4996 reflections measured, 4996 unique reflections ($R_{int} = 0.0000$). The final R_1 values were 0.0667 ($I > 2\sigma(I)$). The final $wR_2(F_2)$ values were 0.1605 ($I > 2\sigma(I)$). The final R_1 values were 0.0956 (all data). The final $wR_2(F_2)$ values were 0.1787 (all data). The goodness of fit on F_2 was 1.032.

Table 2

Compound reference	2010acc1038
Chemical formula	
Formula Mass	536.67
Crystal system	Monoclinic
a / Å	16.7059(6)
b / Å	12.6255(5)
c / Å	13.7625(4)
α / °	90.00
β / °	101.603(2)
γ / °	90.00
Unit cell volume/ Å ³	2843.47(17)
Temperature/ K	120(2)
Space group	$P2(1)/c$
No. of formula units per unit cell, Z	4
Radiation type	MoK α
Absorption coefficient, μ / mm ⁻¹	0.066
No. of reflections measured	4996
No. of unique reflections	4996
No. of independent reflections, R_{int}	0.0000 (HKLF5, merging suppressed)
Final R_1 values ($I > 2\sigma(I)$)	0.0667
Final wR_2 values ($I > 2\sigma(I)$)	0.1605
Final R_1 values (all data)	0.0956
Final wR_2 values (all data)	0.1787
Goodness of fit on F_2	1.032



Thermal ellipsoids drawn at the 35% probability level, selected hydrogens omitted for clarity.

[Tapez un texte]

Table 3. π - π and π -H interactions

RMS deviation for ring system (C11 > C32)		0.0147Å
Perpendicular distance between mean planes (C11 > C32) and (C11 ⁱ > C32 ⁱ)		3.148(1) Å
C21-H21... (C5 > C10) ⁱ	H...Cent	2.95Å
	C-H...Cent	153°
	C...Cent	3.8221(3) Å

$i = 1-x, 1-y, -z$

[REF1]. Spek, A. L. (1998) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

Table 4. Bond lengths [Å] and angles [°].

N1–C11	1.413(4)	C18–C19	1.388(4)
N1–C4	1.446(4)	C19–C31	1.430(4)
C1–C4	1.551(4)	C19–C20	1.472(4)
C1–C2	1.670(4)	C20–C21	1.395(4)
C1–B4	1.704(4)	C20–C32	1.416(4)
C1–B5	1.724(4)	C21–C22	1.383(4)
C1–B6	1.724(4)	C22–C23	1.359(4)
C1–B3	1.732(4)	C23–C24	1.403(4)
C2–C3	1.513(4)	C24–C25	1.423(4)
C2–B11	1.714(4)	C24–C32	1.440(4)
C2–B7	1.715(5)	C25–C26	1.348(4)
C2–B3	1.726(5)	C26–C27	1.436(4)
C2–B6	1.733(4)	C27–C28	1.404(4)
C4–C5	1.524(4)	C27–C30	1.411(4)
C5–C6	1.389(4)	C29–C30	1.420(4)
C5–C10	1.392(4)	C29–C31	1.440(4)
C6–C7	1.375(4)	C30–C32	1.426(4)
C7–C8	1.368(5)	B3–B8	1.756(5)
C8–C9	1.380(5)	B3–B4	1.771(5)
C9–C10	1.399(5)	B3–B7	1.774(5)
C11–C28	1.379(4)	B4–B8	1.781(5)
C11–C12	1.426(4)	B4–B5	1.787(5)
C12–C29	1.417(4)	B4–B9	1.791(5)
C12–C13	1.428(4)	B5–B6	1.760(5)
C13–C14	1.357(4)	B5–B9	1.771(5)
C14–C15	1.432(4)	B5–B10	1.784(5)
C15–C16	1.385(4)	B6–B10	1.763(5)
C15–C31	1.429(4)	B6–B11	1.773(5)
C16–C17	1.375(4)	B7–B8	1.762(6)
C17–C18	1.404(5)	B7–B12	1.765(5)

[Tapez un texte]

B7–B11	1.778(5)	B9–B12	1.785(6)
B8–B12	1.777(5)	B10–B11	1.774(5)
B8–B9	1.793(5)	B10–B12	1.786(5)
B9–B10	1.783(5)	B11–B12	1.769(5)
C11–N1–C4	121.4(2)	C8–C9–C10	120.2(3)
C4–C1–C2	115.1(2)	C5–C10–C9	119.4(3)
C4–C1–B4	125.6(2)	C28–C11–N1	122.1(3)
C2–C1–B4	110.6(2)	C28–C11–C12	120.0(2)
C4–C1–B5	121.9(2)	N1–C11–C12	117.8(3)
C2–C1–B5	110.4(2)	C29–C12–C11	119.3(3)
B4–C1–B5	62.83(19)	C29–C12–C13	118.1(3)
C4–C1–B6	113.7(2)	C11–C12–C13	122.6(3)
C2–C1–B6	61.39(18)	C14–C13–C12	122.2(3)
B4–C1–B6	113.2(2)	C13–C14–C15	121.3(3)
B5–C1–B6	61.42(19)	C16–C15–C31	119.4(3)
C4–C1–B3	119.3(2)	C16–C15–C14	122.1(3)
C2–C1–B3	60.95(19)	C31–C15–C14	118.5(3)
B4–C1–B3	62.1(2)	C17–C16–C15	121.2(3)
B5–C1–B3	113.5(2)	C16–C17–C18	120.0(3)
B6–C1–B3	113.1(2)	C19–C18–C17	121.4(3)
C3–C2–C1	118.6(2)	C18–C19–C31	118.4(3)
C3–C2–B11	120.8(3)	C18–C19–C20	122.9(3)
C1–C2–B11	110.5(2)	C31–C19–C20	118.7(2)
C3–C2–B7	121.4(3)	C21–C20–C32	118.8(3)
C1–C2–B7	110.7(2)	C21–C20–C19	122.0(3)
B11–C2–B7	62.5(2)	C32–C20–C19	119.2(2)
C3–C2–B3	117.9(3)	C22–C21–C20	121.3(3)
C1–C2–B3	61.30(18)	C23–C22–C21	120.7(3)
B11–C2–B3	113.5(2)	C22–C23–C24	121.4(3)
B7–C2–B3	62.1(2)	C23–C24–C25	123.3(3)
C3–C2–B6	117.5(3)	C23–C24–C32	118.3(3)
C1–C2–B6	60.85(18)	C25–C24–C32	118.3(3)
B11–C2–B6	61.91(19)	C26–C25–C24	122.0(3)
B7–C2–B6	113.0(2)	C25–C26–C27	121.2(3)
B3–C2–B6	113.0(2)	C28–C27–C30	120.2(3)
N1–C4–C5	113.6(2)	C28–C27–C26	121.0(3)
N1–C4–C1	109.9(2)	C30–C27–C26	118.8(3)
C5–C4–C1	113.6(2)	C11–C28–C27	121.2(3)
C6–C5–C10	119.2(3)	C12–C29–C30	120.2(3)
C6–C5–C4	121.4(3)	C12–C29–C31	120.5(3)
C10–C5–C4	119.3(3)	C30–C29–C31	119.3(2)
C7–C6–C5	120.7(3)	C27–C30–C29	119.1(3)
C8–C7–C6	120.4(3)	C27–C30–C32	120.3(3)
C7–C8–C9	120.1(3)	C29–C30–C32	120.6(3)

[Tapez un texte]

C15–C31–C19	119.5(3)	B10–B6–B11	60.2(2)
C15–C31–C29	119.4(3)	C2–B7–B8	105.2(2)
C19–C31–C29	121.1(3)	C2–B7–B12	105.3(2)
C20–C32–C30	121.1(3)	B8–B7–B12	60.5(2)
C20–C32–C24	119.5(3)	C2–B7–B3	59.25(19)
C30–C32–C24	119.4(3)	B8–B7–B3	59.6(2)
C2–B3–C1	57.75(18)	B12–B7–B3	108.2(3)
C2–B3–B8	105.0(2)	C2–B7–B11	58.73(19)
C1–B3–B8	105.1(2)	B8–B7–B11	108.1(3)
C2–B3–B4	104.9(2)	B12–B7–B11	59.9(2)
C1–B3–B4	58.19(18)	B3–B7–B11	108.1(2)
B8–B3–B4	60.7(2)	B3–B8–B7	60.6(2)
C2–B3–B7	58.68(19)	B3–B8–B12	108.5(3)
C1–B3–B7	105.1(2)	B7–B8–B12	59.8(2)
B8–B3–B7	59.9(2)	B3–B8–B4	60.1(2)
B4–B3–B7	108.3(2)	B7–B8–B4	108.4(3)
C1–B4–B3	59.75(19)	B12–B8–B4	108.2(3)
C1–B4–B8	105.2(3)	B3–B8–B9	108.4(3)
B3–B4–B8	59.3(2)	B7–B8–B9	108.0(3)
C1–B4–B5	59.13(18)	B12–B8–B9	60.0(2)
B3–B4–B5	108.7(2)	B4–B8–B9	60.1(2)
B8–B4–B5	107.7(3)	B5–B9–B10	60.3(2)
C1–B4–B9	105.0(2)	B5–B9–B12	108.1(3)
B3–B4–B9	107.8(3)	B10–B9–B12	60.1(2)
B8–B4–B9	60.3(2)	B5–B9–B4	60.20(19)
B5–B4–B9	59.3(2)	B10–B9–B4	108.2(2)
C1–B5–B6	59.30(18)	B12–B9–B4	107.4(3)
C1–B5–B9	105.1(2)	B5–B9–B8	107.8(2)
B6–B5–B9	107.7(3)	B10–B9–B8	107.8(3)
C1–B5–B10	105.4(2)	B12–B9–B8	59.6(2)
B6–B5–B10	59.6(2)	B4–B9–B8	59.6(2)
B9–B5–B10	60.2(2)	B6–B10–B11	60.2(2)
C1–B5–B4	58.04(18)	B6–B10–B9	107.1(2)
B6–B5–B4	107.5(2)	B11–B10–B9	107.6(2)
B9–B5–B4	60.4(2)	B6–B10–B5	59.52(19)
B10–B5–B4	108.3(3)	B11–B10–B5	107.7(2)
C1–B6–C2	57.76(17)	B9–B10–B5	59.5(2)
C1–B6–B5	59.28(17)	B6–B10–B12	107.5(2)
C2–B6–B5	105.8(2)	B11–B10–B12	59.6(2)
C1–B6–B10	106.3(2)	B9–B10–B12	60.0(2)
C2–B6–B10	105.6(2)	B5–B10–B12	107.5(2)
B5–B6–B10	60.8(2)	C2–B11–B12	105.1(2)
C1–B6–B11	105.3(2)	C2–B11–B6	59.57(18)
C2–B6–B11	58.52(19)	B12–B11–B6	107.8(3)
B5–B6–B11	108.7(3)	C2–B11–B10	106.0(2)

[Tapez un texte]

B12–B11–B10	60.5(2)
B6–B11–B10	59.6(2)
C2–B11–B7	58.81(19)
B12–B11–B7	59.7(2)
B6–B11–B7	108.2(2)
B10–B11–B7	108.5(3)
B7–B12–B11	60.4(2)
B7–B12–B8	59.6(2)
B11–B12–B8	107.8(3)
B7–B12–B9	108.2(3)
B11–B12–B9	107.7(3)
B8–B12–B9	60.4(2)
B7–B12–B10	108.5(2)
B11–B12–B10	59.9(2)
B8–B12–B10	108.3(3)
B9–B12–B10	59.9(2)

[Tapez un texte]

UV and emission additional data

Comparison between the available UV spectrum for benzo[*ghi*]perylene^{S2} and that for the new amino benzo[*ghi*]perylene **5a** is shown in Figure 1.

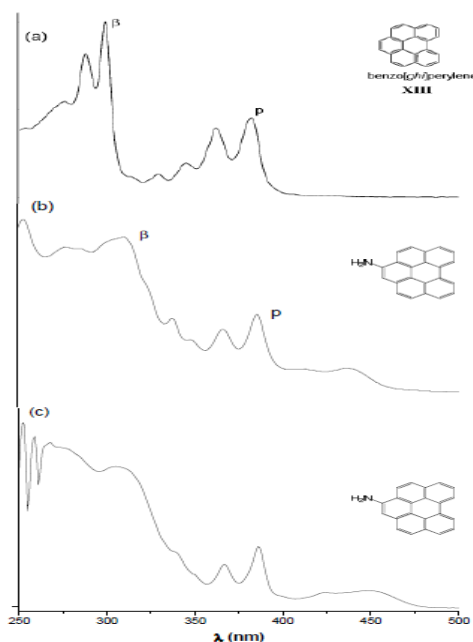


Figure 1. UV absorbance spectra for (a) benzo[*ghi*]perylene in acetonitrile^{S2}; (b) amino benzo[*ghi*]perylene (CH_2Cl_2 , 10^{-5}M). (c) amino benzo[*ghi*]perylene (THF, 10^{-5}M).

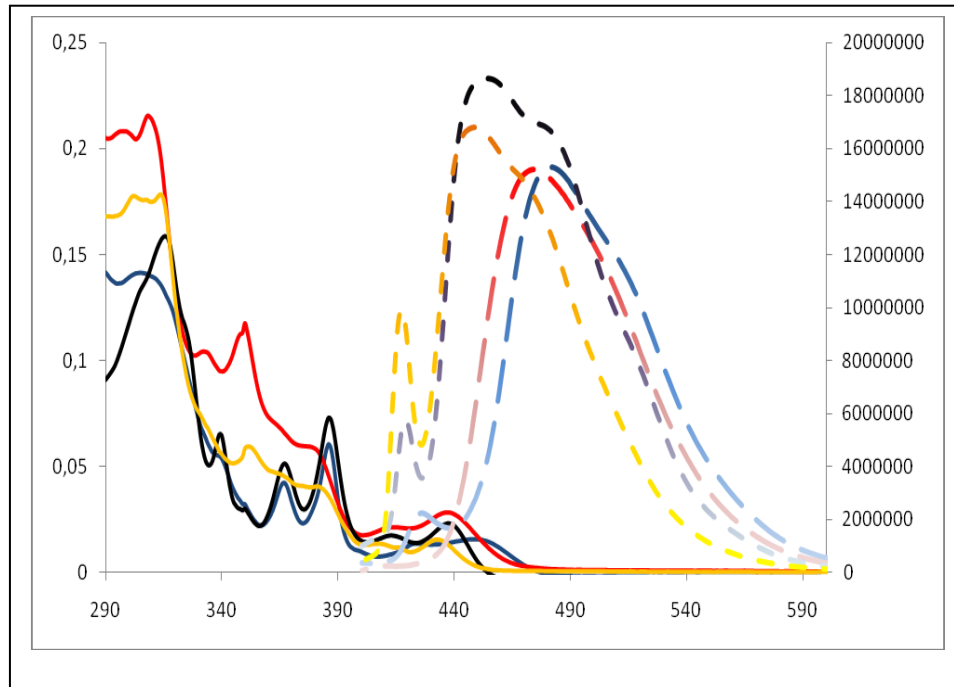


Figure 2. UV absorbance ($C = 10^{-5}$) and emission ($C = 0.5 \times 10^{-5}$) spectra for **5a**, **5c**, **7** and **8** in THF.

^{S2} J. W. McClaine, X. Zhang, M. J. Wornat, *Journal of Chromatography A* **2006**, *1127*, 137.