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Highly Selective Biaryls Formation by the Cyclooligomerization of Arylethynes Catalyzed by Rhodium and Ruthenium Porphyrins

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Supporting Information

Experimental Section

Synthesis of triarylbenzene derivatives **11-12** and **15-16**: 1 g ($3.2 \cdot 10^{-3}$ mol) of 1, 3, 5 or 1, 2, 4 tribromobenzene(Aldrich) was dissolved in 20 ml of acetone and 2.7 g($1.5 \cdot 10^{-2}$ mol) of commercial 1-naphthalene or 2-naphthalene boronic acids(Aldrich) were added. To the obtained mixture, 20 mg of $Pd(AcO)_2$, 40 mg of triphenylphosphine and 5 ml of a 0.1 M Na_2CO_3 solution were added. The homogeneous solution was deoxygenated with an argon stream for 20 min and refluxed for 18 h under nitrogen. The reaction was cooled at room temperature and 100 ml of water were added. The solution was twice extracted with diethyl ether and after the evaporation of the solvent, the residue was purified by flash chromatography (SiO_2, hexane/diethyl ether) and the desired compounds were identified by ^1H NMR and mass spectra.

For obtaining compounds **13-14,** 9-phenathrene boronic acid was used in a similar procedure.

Synthesis of 9-phenathrene boronic acid

2 g ($7.8 \cdot 10^{-3}$ mol) of 9-bromophenanthrene(Aldrich) were dissolved in 50 mL of dry THF under nitrogen. The resulting solution was cooled to -78ϒC after that 14.6 mL of 1.6 M solution in hexane of butyllithium ($23.4 \cdot 10^{-3}$ mol) were slowly added using a siringe.

After 1 hour, 1.6 mL($1.6 \cdot 10^{-2}$ mol) of trimethylborate.were added. The solution was then left to room temperature for 16 h. The solution was poured into 100 mL of a 0.1 HCl solution and extracted three times with CH_2Cl_2. The organic solution was washed with water, brine and the dried with anhydrous Na_2SO_4. The solution was evaporated under vacuum and the residue triturated with hexane. The final white compound was filtered and dried under vacuum giving 1.05 g of the desired product. Yield 60%.

Recovering and recycling of the catalysts

All the porphyrin catalysts were recovered by column chromatography, after elution of the final products, in more than 95% of yield and recycled at least three times without any loss of catalytic activity.

GC separation conditions

The products yield and the isomeric ratios of several reactions were determined by GC analysis performed on a Carlo Erba HRGC 5160 instrument equipped with a 30 mt Restek MTX-5 capillary column and a FID detector. Chemical yields were determined by adding a suitable internal standard (dodecane or tetradecane) to the reaction mixture at the end of each experiment and were reproducible within ±2% for multiple experiments.

Flash chromatography separation conditions

The products yield and the isomeric ratios of one reaction (9-ethynylphenathrene) were determined by flash chromatography separation performed on a Gyan easyflash instrument equipped with a 40x150 Gyan silica gel column and eluting with hexane/diethyl ether 95:5.

Analytical data

9-phenanthrene boronic acid: m.p. 181-184°C ^{1}H NMR(400 MHz, $CDCl_3$) □=8.82(t, 2H), 8.46(s, 2H), 8.38 (d, 1H), 8.03(s, 1H), 7.97(d, 1H), 7.66(m, 4H); EI MS: m/z (%)221(100). Anal. Calcd for $C_{14}H_{11}BO_2$: C, 75.72; H, 4.99; Found C, 75.80; H, 4.91.

1,3,5-tris-(1'-naphthyl)benzene, 11: m.p. 155-156°C ^{1}H NMR(400 MHz, $CDCl_3$) □=8.25(m, 3H), 7.95(m, 6H), 7.81(s, 3H), 7.59(m, 12H); EI MS: m/z (%)455(100), 361(10). Anal. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.29; Found C, 94.89; H, 5.36.

1,2,4-tris-(1'-naphthyl)benzene, 12: m.p. 182-183°C ; ^{1}H NMR(400 MHz, $CDCl_3$) □=8.28(m, 1H), 8.08(m, 1H), 8.92(m, 3H), 7.80(m, 4H), 7.65(m, 1H), 7.60(m, 10H), 7.38(d, 1H, J=6Hz),7.1(m, 3H) EI MS: m/z(%) 455(100), 332(5). Anal. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.29; Found C, 94.72; H, 5.18.

1,3,5-tris-(2'-naphthyl)benzene, 15: m.p. 222-223°C ; ^{1}H NMR(400 MHz, $CDCl_3$)□=8.24(s, 3H); 8.10(s, 3H), 7.95(m, 12H); 7.57(m, 6H); EI MS: m/z (%)456(100), 409(8). Anal. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.29; Found C, 94.79; H, 5.26.

1,2,4-tris-(2'-naphthyl)benzene, 16: m.p. 155-156°C ; ^{1}H NMR(400 MHz, $CDCl_3$) □□8.20(s, 1H), 7.95(m, 8H), 7.78(m, 5H), 7.55(m, 4H),7.48(m, 4H)),7.28(d, 2H); EI MS: m/z(%) 456(100). Anal. Calcd for $C_{36}H_{24}$: C, 94.70; H, 5.29; Found C, 94.62; H, 5.38.

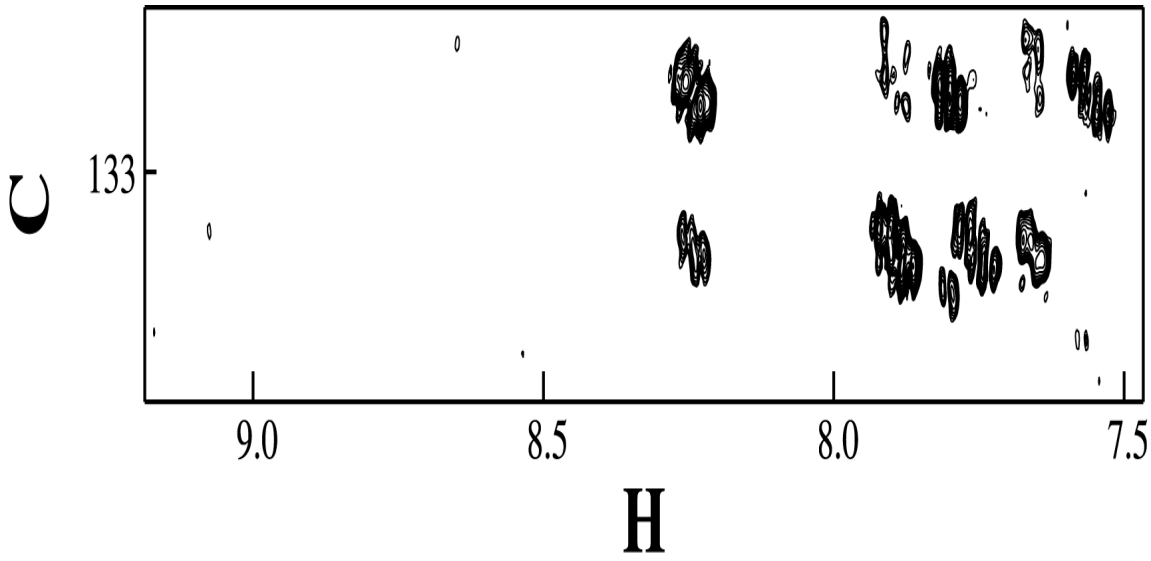
1,3,5-tris-(9'-phenanthryl)benzene, 13: m.p. 197-200°C; ^{1}H NMR(400 MHz, $CDCl_3$) □=8.83(d, 3H), 8.76(d, 3H), 8.36(d, 3H), 7.98(s, 3H), 7.96(s, 3H),7.95(d, 3H), 7.75(t, 6H), 7.66(t, 6H); EI MS: m/z (%)606(100), 457(50). Anal. Calcd for $C_{48}H_{30}$: C, 95.01; H, 4.99; Found C, 93.99; H, 5.96.

1,2,4-tris-(9'-phenanthryl)benzene, 14: m.p. 291-292°C; ^{1}H NMR(400 MHz, $CDCl_3$) □=8.23(d, 1H), 8.76(d, 1H), 8.62(m, 1H), 8.52(m, 3H), 8.32(d, 1H), 8.13(m, 2H), 7.97(d, 1H), 7.93(s, 1H), 7.81(m, 3H) 7.73(m, 8H), 7.48(m, 8H); EI MS: m/z(%) 606(100), 457(35). Anal. Calcd for $C_{48}H_{30}$: C, 95.01; H, 4.98; Found C, 95.12; H, 4.88.

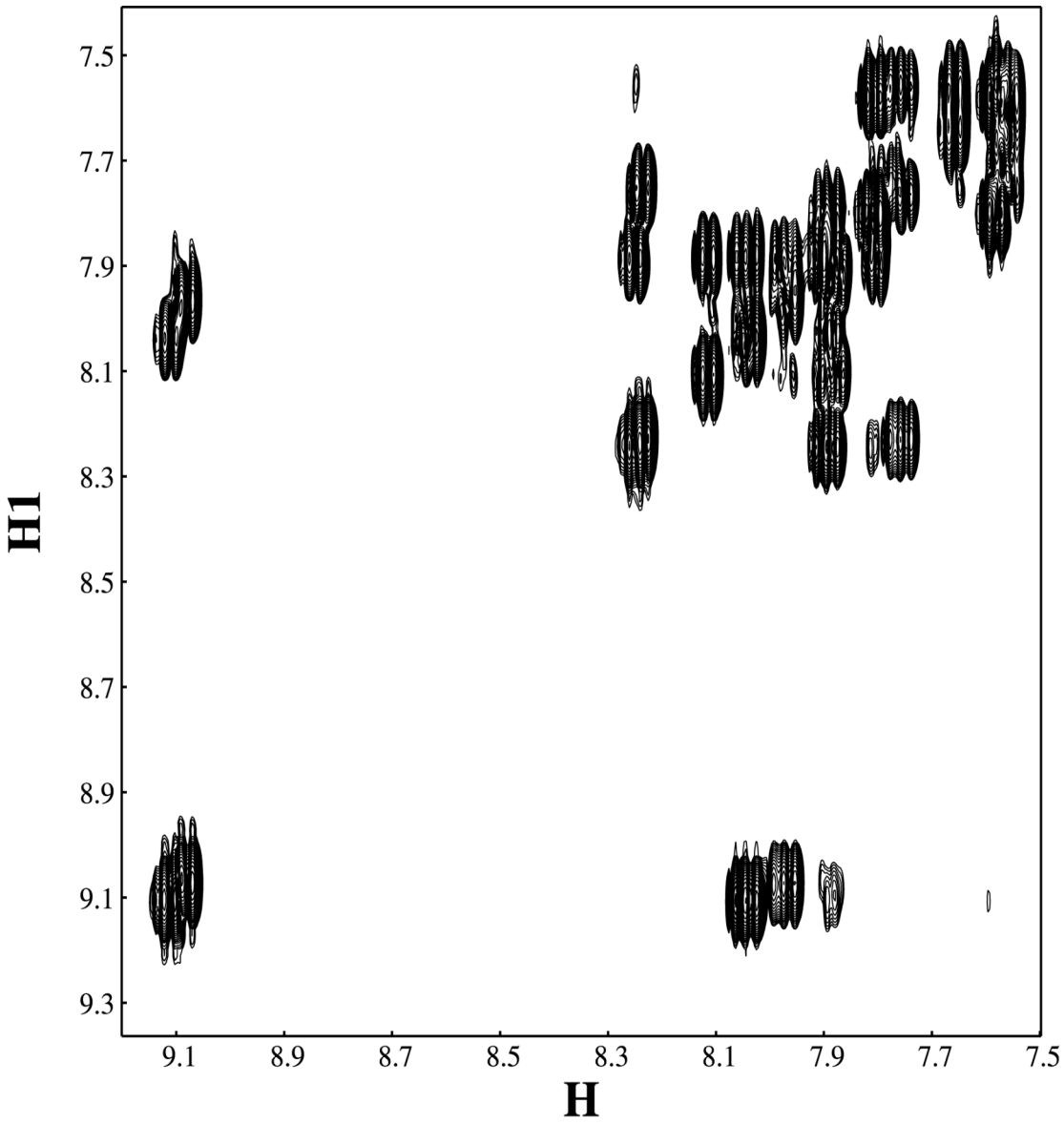
1-(1'-naphthyl)phenanthrene, 7: m.p. 102-103°C; ^{1}H NMR(400 MHz, $CDCl_3$) □=8.83(d, 1H), 8.80(d, 1H), 7.97(d, 1H), 7.96(d, 1H), 7.84(d, 1H), 7.76(t, 1H), 7.69(t; 1H), 7.6(m, 3H), 7.53(m, 2H), 7.47(t, 1H), 7.36(d, 1H), 7.28(m, 2H); EI MS: m/z(%) 303(100), 279(20). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.29; Found C, 94.76; H, 5.25.

1-(9'-phenanthryl)-9,10-benzophenathrene, **8**: m.p. 210-212°C; ^{1}H NMR(400 MHz, $CDCl_3$) □=8.83(t, 2H), 8.78(t, 1H,), 8.63(d, 1H,), 8.55(d, 2H), 7.88(t, 2H), 7.82(s, 1H), 7.72(m, 4 H), 7.62(m, 4 H), 7. 38(dd, 2H), 6.78(d, 1H) ; EI MS: m/z(%) 404 (100) Anal. Calcd for $C_{32}H_{20}$: C, 95.01; H, 4.98; Found C, 94.88; H, 4.85.

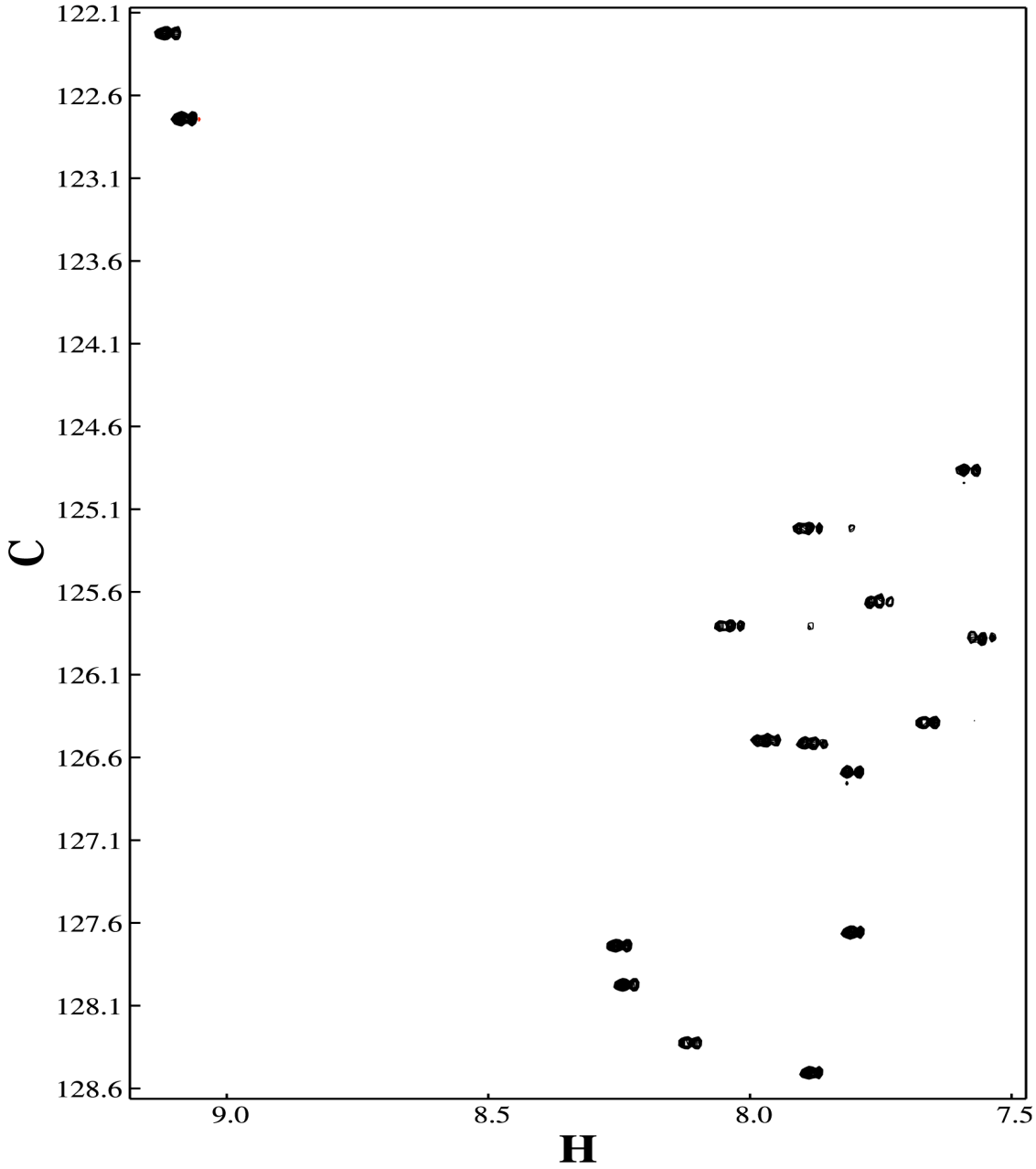
4-(2'-naphthyl)phenathrene 10: oil; ^{1}H NMR(400 MHz, $CDCl_3$) □□8.05,(s, 1H), 7.97 (m, 5H), 7.84 (m, 3H), 7.58 (m, 3H), 7.45 (m, 3H), 7.08 (m, 1H); EI MS: m/z(%) 304(100), 278(30). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.29; Found C, 94.66; H, 5.36.



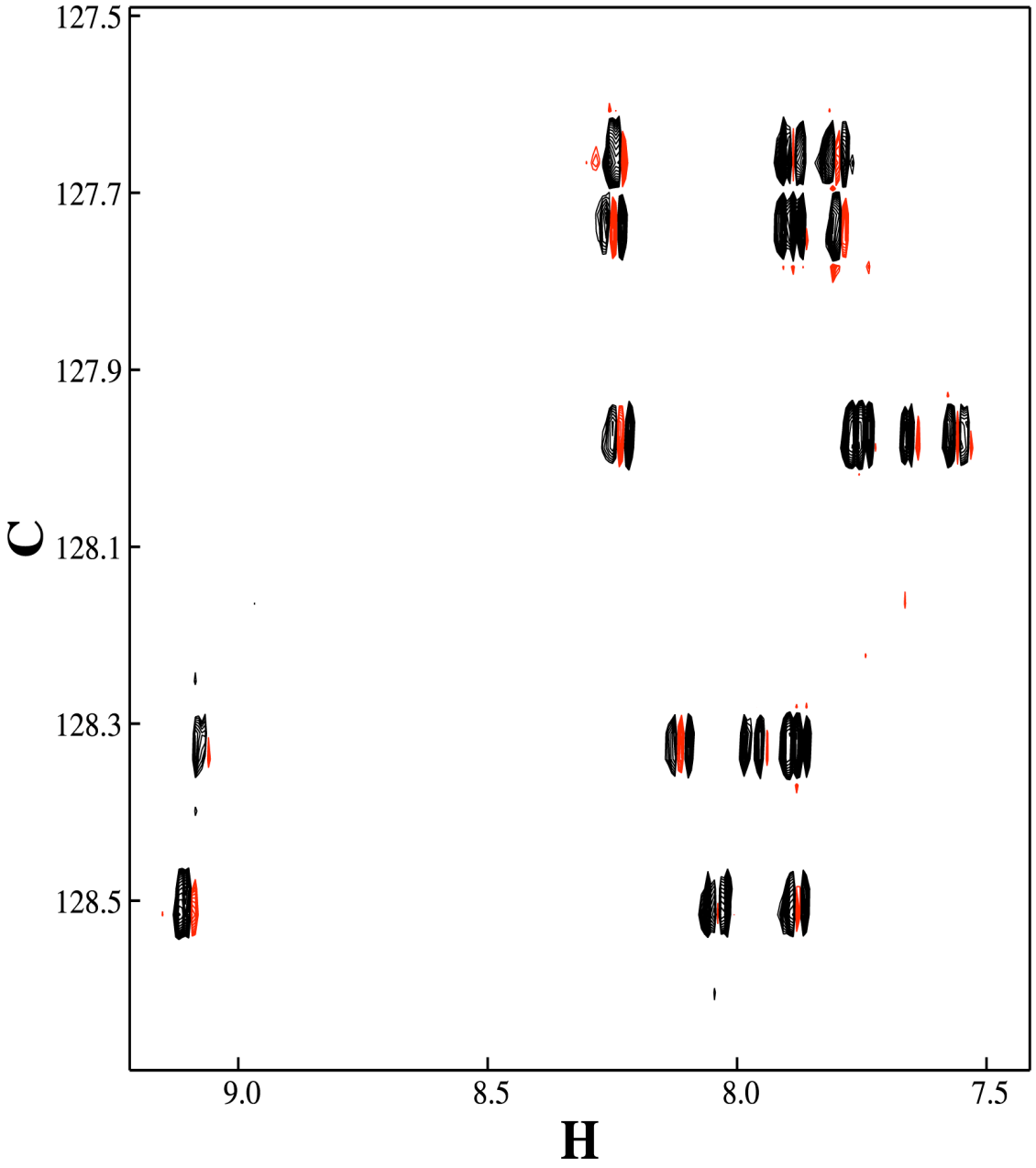
HMBC spectrum of 1-(1'-naphthyl)phenanthrene



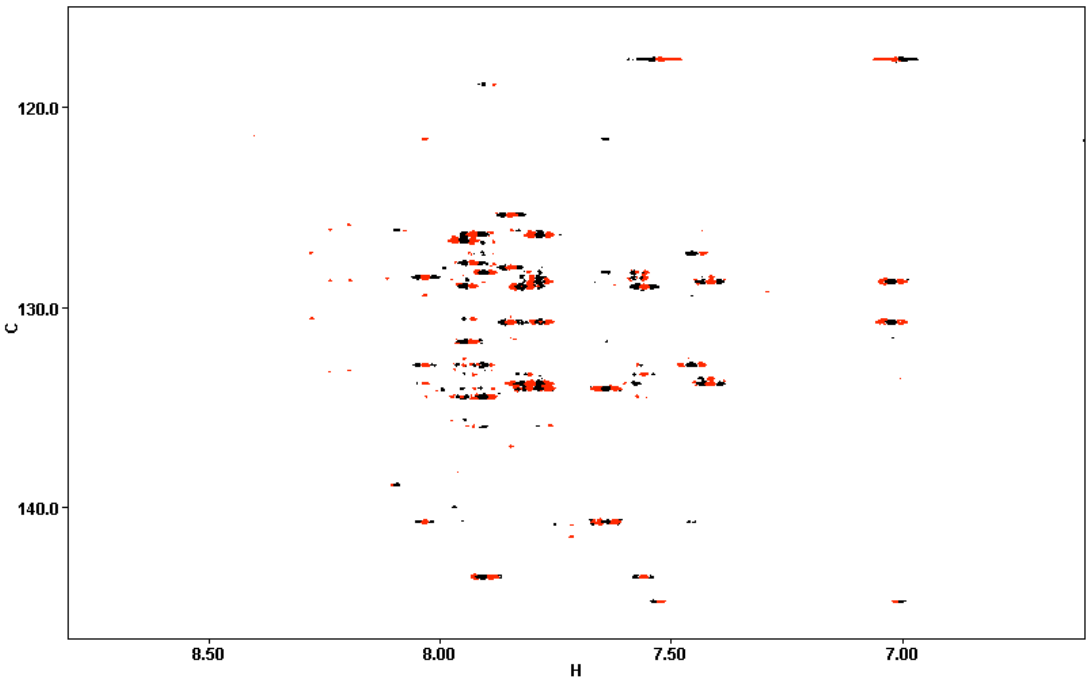
^{1}H-^{1}H COSY spectrum of 1(1'-naphthyl)phenanthrene



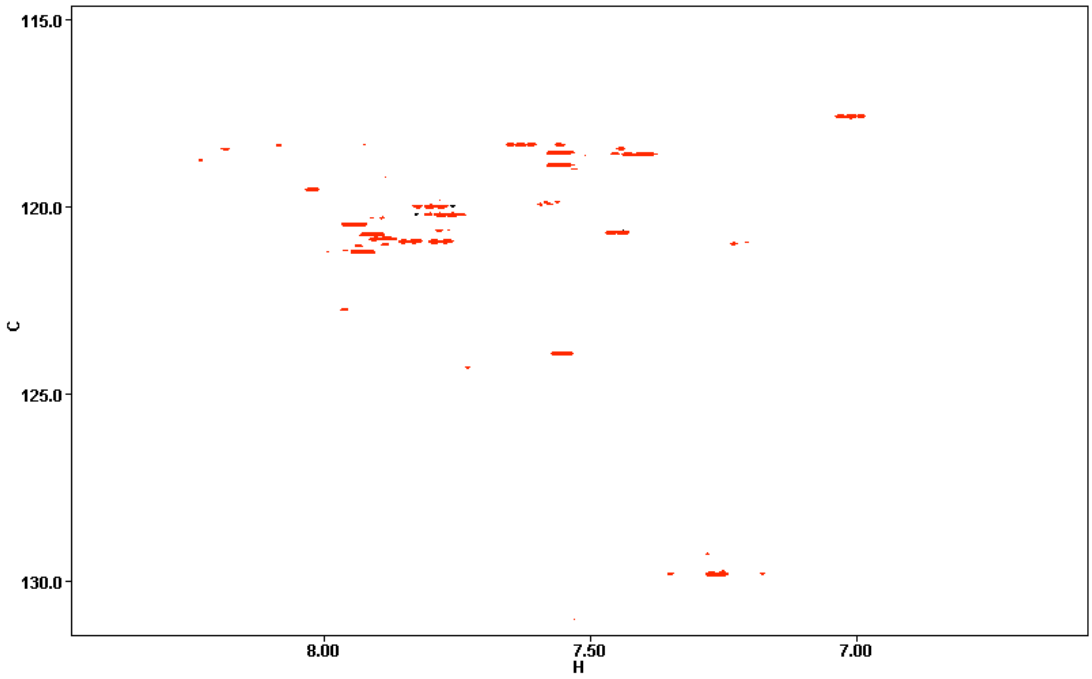
HSQC spectrum of 1-(1'-naphthyl)phenanthrene



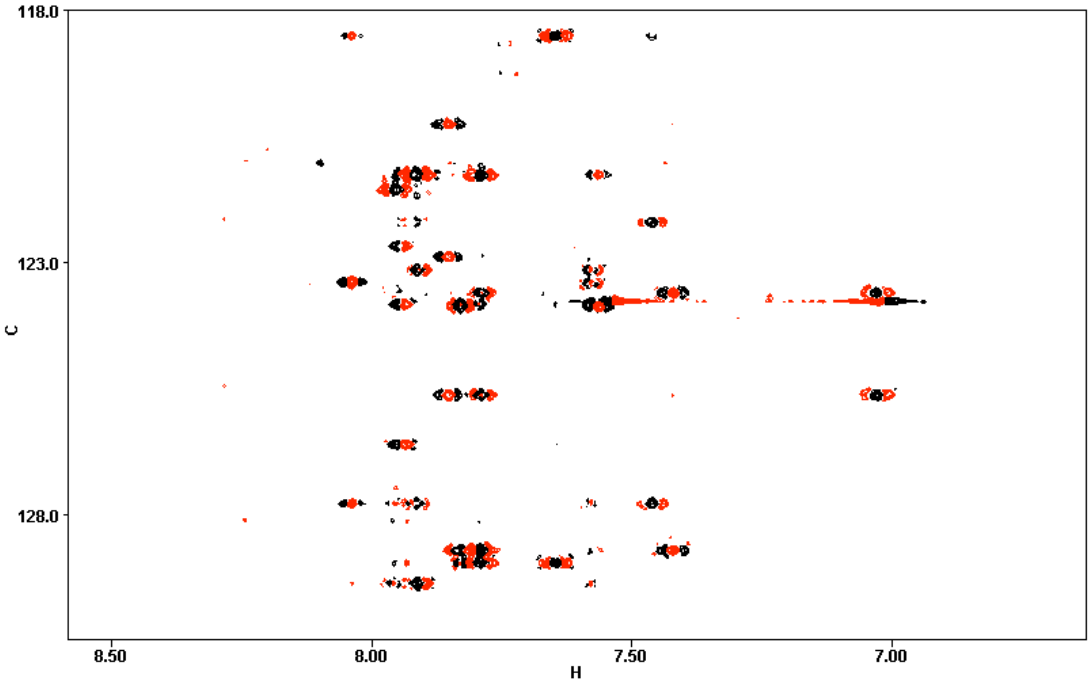
TOCSY spectrum of 1-(1'-naphthyl)phenanthrene



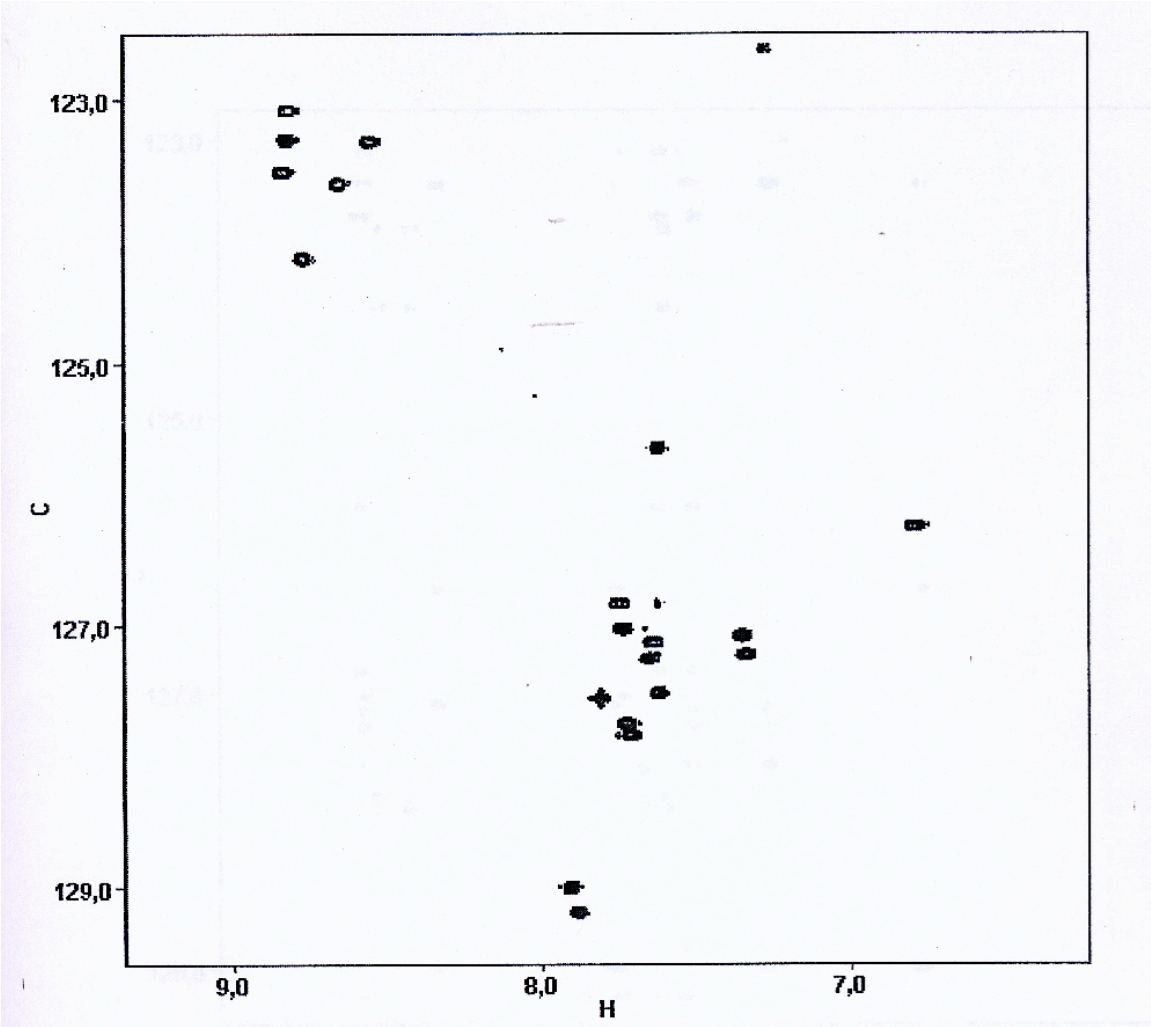
HSQC spectrum of 4-(2'-naphthyl)phenanthrene



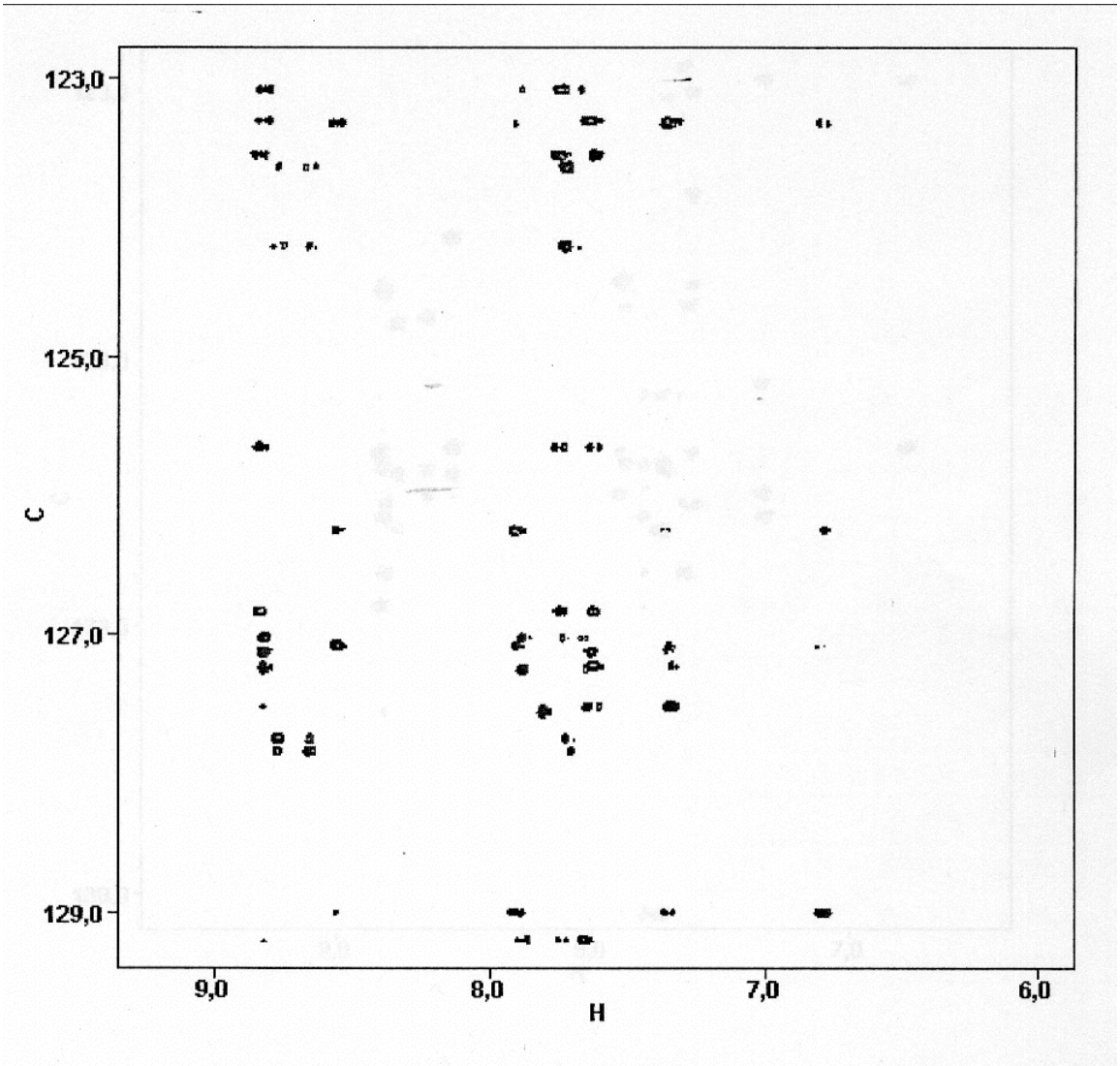
TOCSY spectrum of 4-(2'-naphthyl)phenanthrene



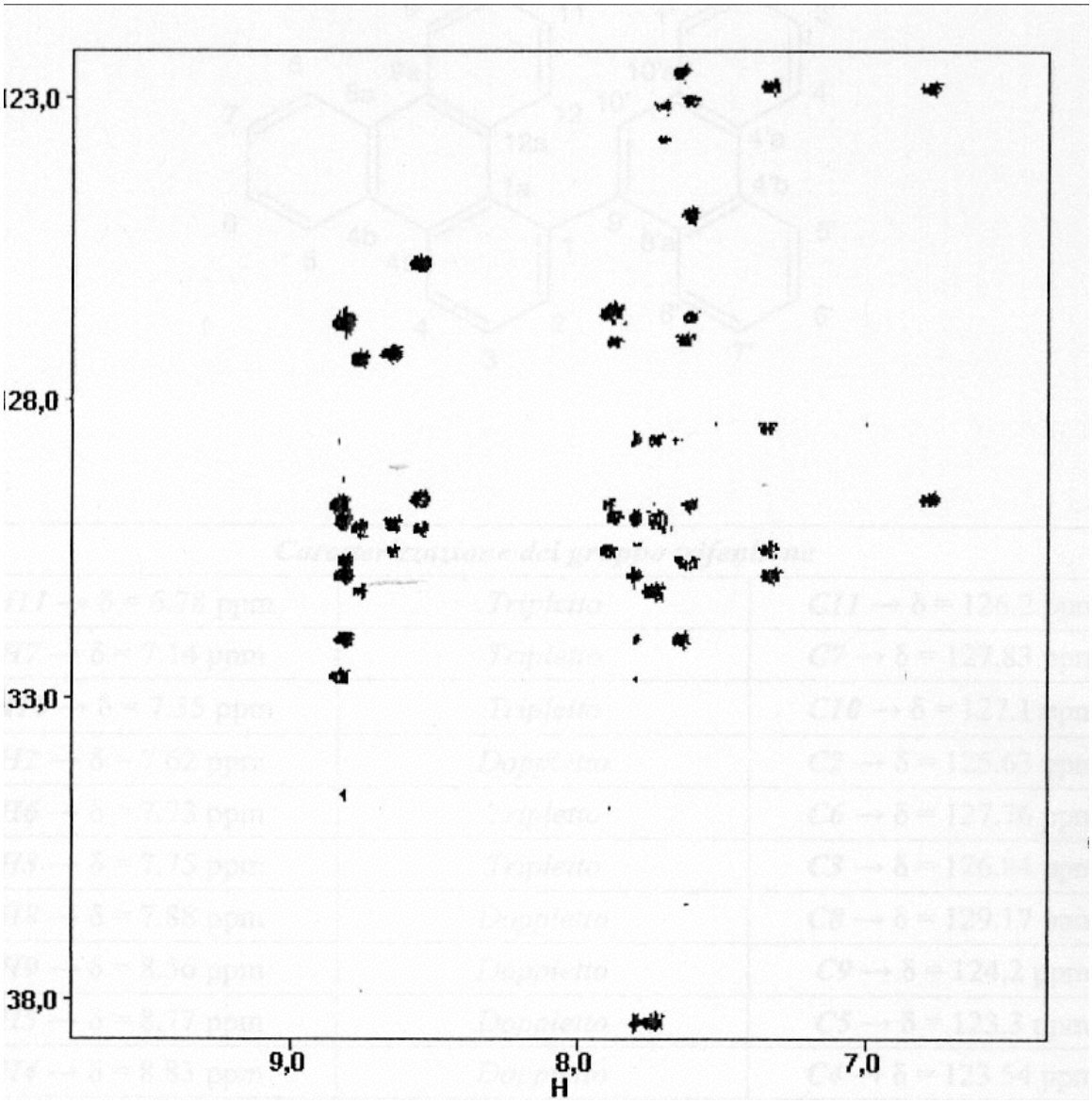
HMBC spectrum of 4-(2'-naphthyl)phenanthrene



HSQC spectrum of 1-(9'-phenanthryl)-9,10-benzophenathrene



TOCSY 1-(9'-phenanthryl)-9,10-benzophenathrene



HMBC spectrum of 1-(9'-phenanthryl)-9,10-benzophenathrene