Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Calculations

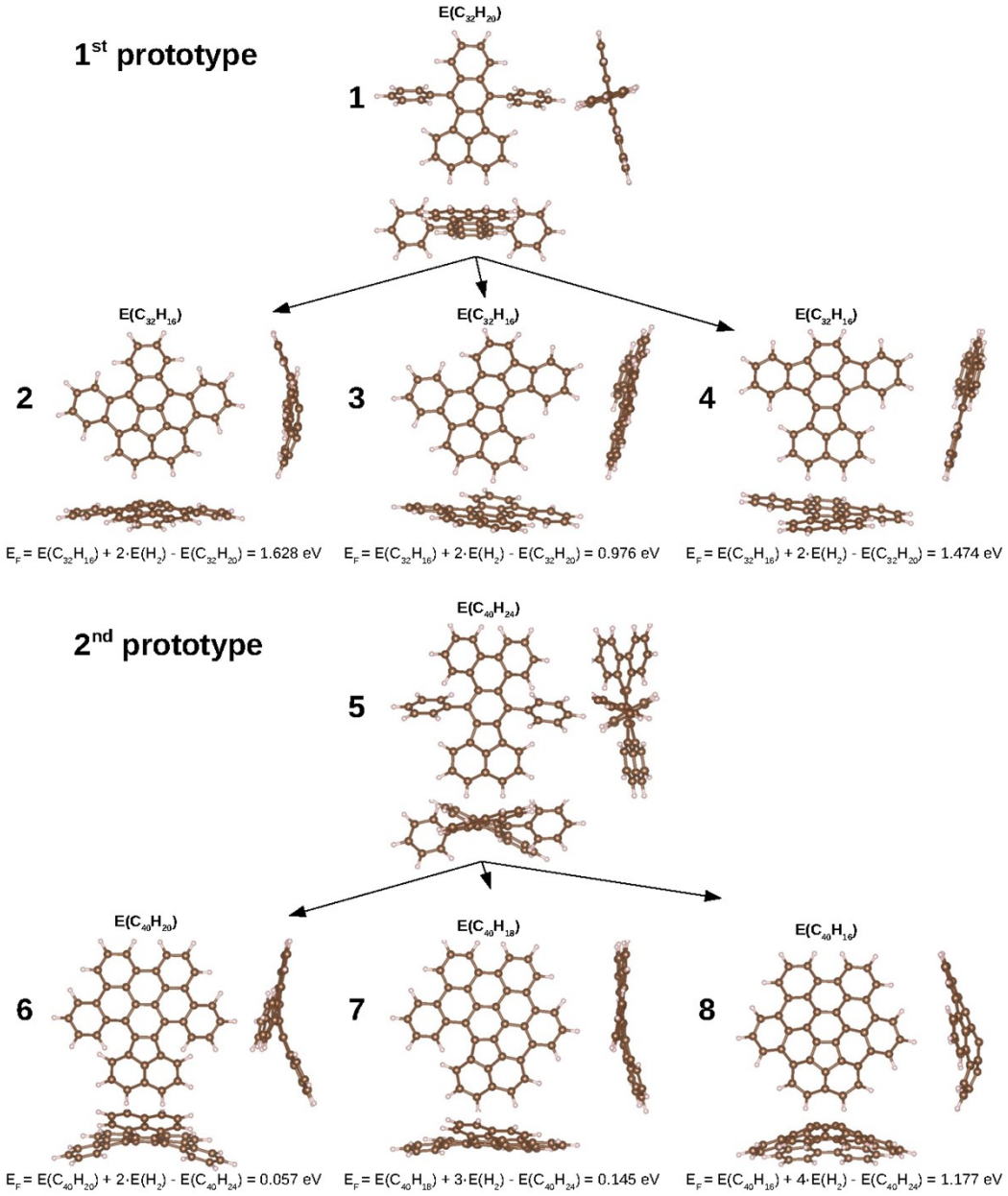


Fig. S1 DFT optimized molecular structures of the precursor and potential products in gas phase and the formation energies for all the products.

Additional STM images

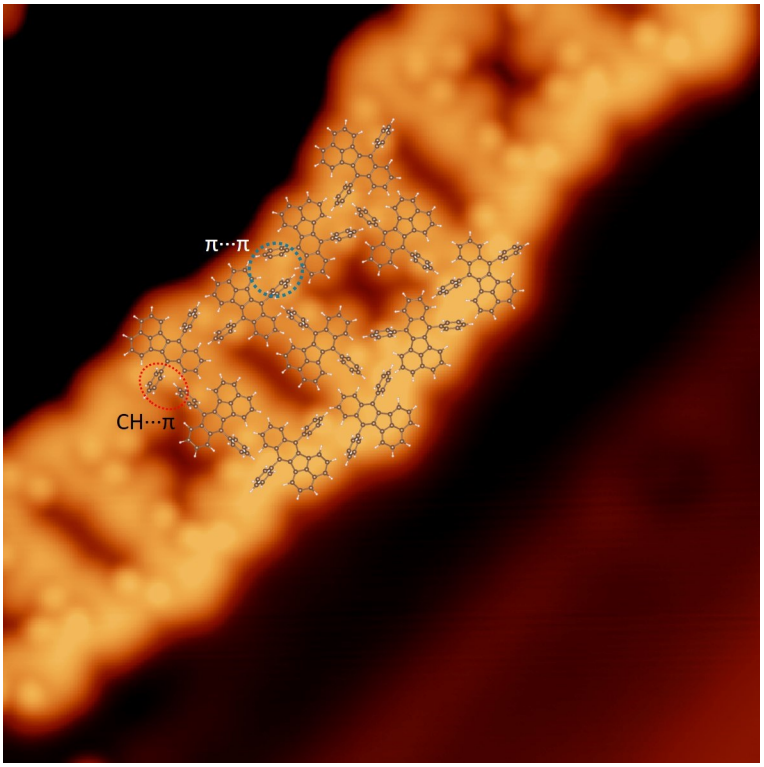


Fig. S2 STM image in Fig. 1b overlaid with the molecular models.

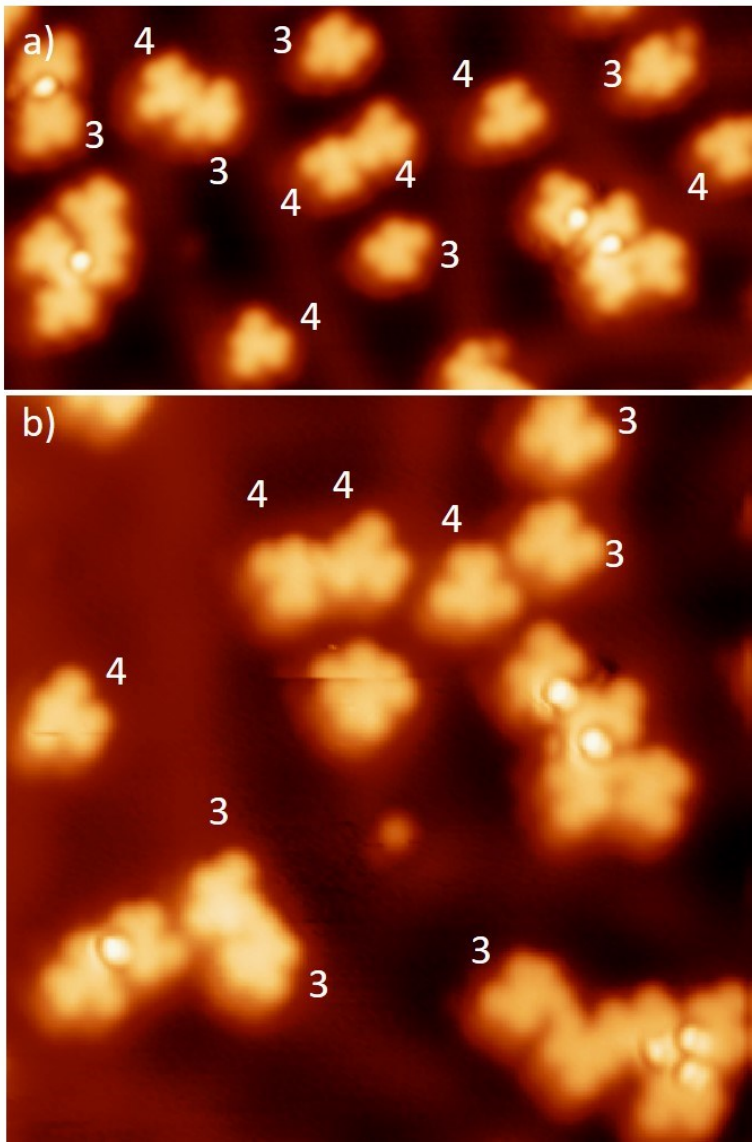


Fig. S3 Two randomly selected STM images to count the products **3** and **4,** for a sample prepared by direct deposition of molecule **1** on the Au(111) surface held at 350 ºC. We only mark the products which are easy to be identified. Ten monomers **3** and also ten monomers **4** are counted in the two STM images.

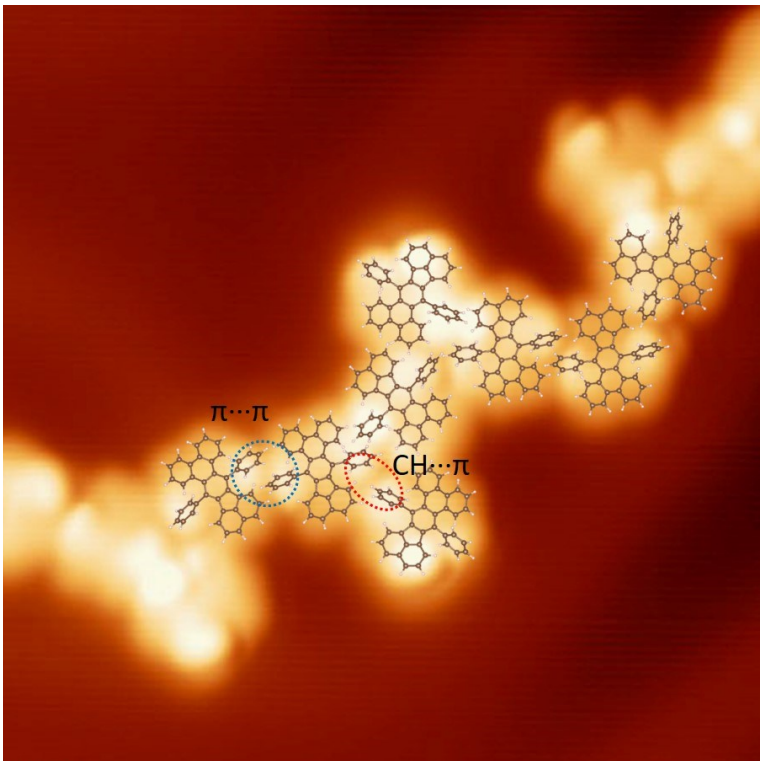


Fig. S4 STM image in Fig. 3b overlaid with the molecular models.

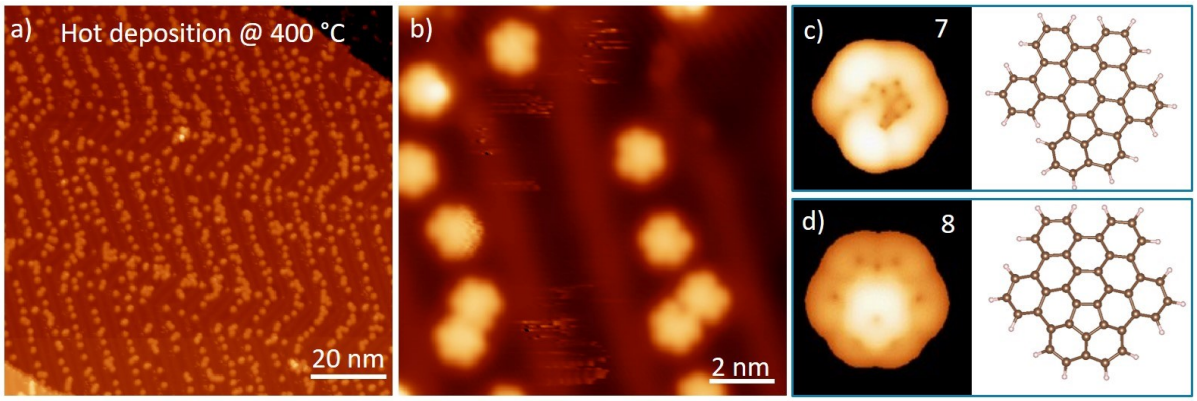


Fig. S5 Overview and magnified STM images of the sample by deposition of molecule **5** on Au(111) held at 400 °C. (c,d) Simulated STM image of products **7** and **8** (targeted product) shown in Scheme 1, along with the corresponding molecular models, respectively. It is obvious that the obtained monomer products in experiment are assigned to structure **7.**

Synthesis of the precursor molecules by solution chemistry

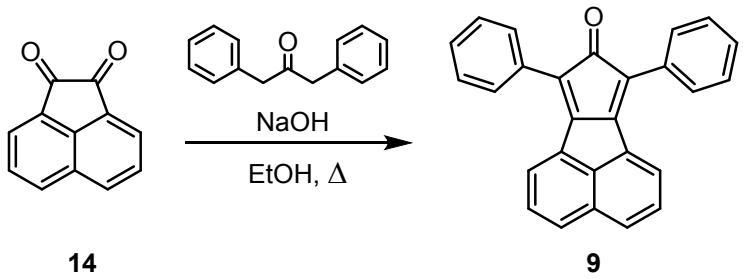
1. General methods

All reactions in solution were carried out under argon using oven-dried glassware. Thin layer chromatography was performed on Merck silica gel 60 F_{254} and the chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz or 500 and 125 MHz (Varian Mercury 300 or Bruker DPX-500 instruments), respectively. APCI spectra were determined on a Bruker Microtof instrument.

The synthesis of triflates **11** and **12** have been previously described.[1,2] Commercial reagents were purchased from ABCR GmbH or Aldrich Chemical Co. and were used without further purification. MeCN was purified by a MBraun SPS-800 Solvent Purification System. CsF was dried under vacuum at 100 ºC, cooled under argon and stored in a glove box. *n*-BuLi was used in hexane solution (2.4 M). *i*-Pr_2NH was dried by distillation over CaH_2.

2. Experimental details and spectroscopic data

2.1 Synthesis of cyclopentadienone 9



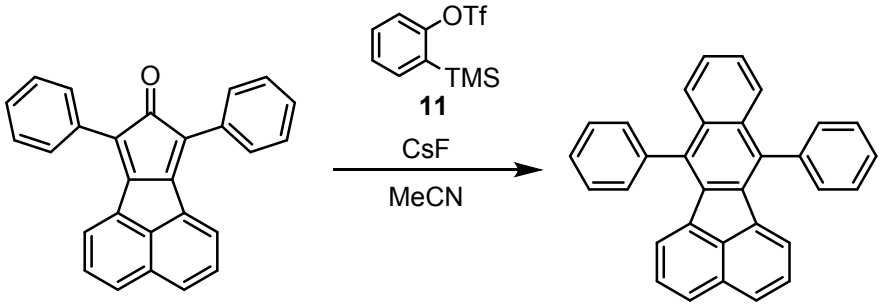
14 **9**

Fig. S6 Synthesis of compound **9**.

This synthetic protocol is based on a previously reported procedure.[3] A solution of NaOH (1.59 g) in EtOH (5 mL) was dropwise added at room temperature and under argon to a solution of acenaphthenequinone (**14**, 4.00 g, 22.0 mmol) and 1,3-diphenyl-2-propanone (5.32 g, 25.3 mmol) in EtOH (25 mL). The solution was stirred for 15 min at room temperature and refluxed for 30 min. Then, the reaction mixture was cooled to 0 °C and the resulting suspension was filtered to isolate a dark precipitate, which was subsequently washed with H_2O and EtOH to afford compound **9** (7.43 g, 95 %) as a dark solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 7.1 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.85 – 7.78 (m, 4H), 7.59 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.52 (ddd, *J* = 7.6, 6.9, 1.1 Hz, 4H), 7.46 – 7.37 (m, 2H) ppm. MS (APCI (M+1)) for $C_{27}H_{16}O$: 357.1

2.2 Synthesis of compound 1



9 **1**

Fig. S7 Synthesis of compound **1**.

Anhydrous finely powdered CsF (767 mg, 5.05 mmol) was added to a solution of **9** (300 mg, 0.842 mmol) and triflate **11** (502 mg, 1.68 mmol) in MeCN (5 mL) and the mixture was stirred at room temperature under argon for 16 h. The reaction was quenched by the addition of H_2O (10 mL) and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The resulting mixture was purified by column chromatography (SiO_2, CH_2Cl_2:hexane, 1:4) to afford compound **1** (330 mg, 97%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.78 – 7.64 (m, 10H), 7.65 – 7.56 (m, 4H), 7.43 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.36 (dd, *J* = 8.2, 7.1 Hz, 2H), 6.67 (d, *J* = 7.1 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.01 (2xC), 136.71 (2xC), 135.70 (2xC), 135.02 (2xC), 134.89 (2xC), 132.99 (2xC), 130.14 (4xCH), 129.37 (4xCH), 128.07 (2xCH), 127.96 (2xCH), 126.90 (2xCH), 126.04 (2xCH), 125.88 (2xCH), 122.32 (2xCH) ppm. MS (APCI (M+1)) for $C_{32}H_{20}$: 405.1.

2.3 Synthesis of compound 5

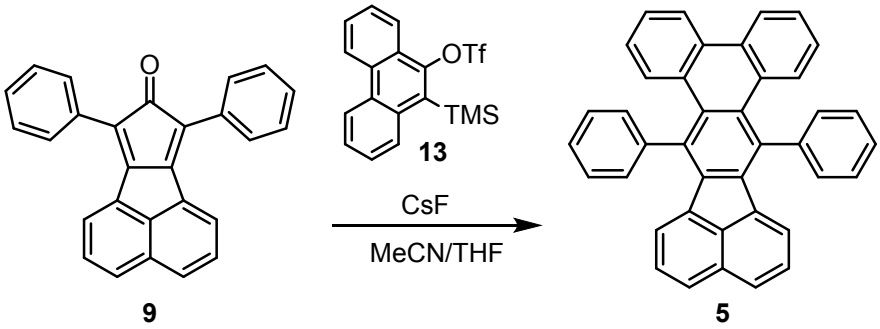


Fig. S8 Synthesis of compound **5**.

Anhydrous finely powdered CsF (447 mg, 2.94 mmol) was added to a solution of **9** (200 mg, 0.56 mmol) and triflate **13** (392 mg, 0.98 mmol) in a mixture of MeCN/THF (2:1, 9 mL), and the mixture was stirred at 55 ºC under argon for 16 h. Then, the solvents were evaporated under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2:hexane, 1:5) to afford compound **5** (244 mg, 86%) as a yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.46 (d, *J* = 8.3, 1.3 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.62 (m, 10H), 7.42 (t, *J* = 7.6, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.78 (2C), 137.33 (C), 136.31 (C), 135.06 (C), 134.50 (C), 131.61 (C), 131.01 (2C), 130.74 (2CH), 129.78 (2CH), 129.31 (CH), 127.97 (CH), 127.60 (CH), 126.51 (CH), 126.42 (CH), 125.44 (CH), 123.61 (CH), 123.18 (CH) ppm. EM (APCI (M+1)) HR for $C_{40}H_{24}$ calcd: 505.1949, found: 519.1951.

3. ^{1}H and ^{13}C NMR spectra

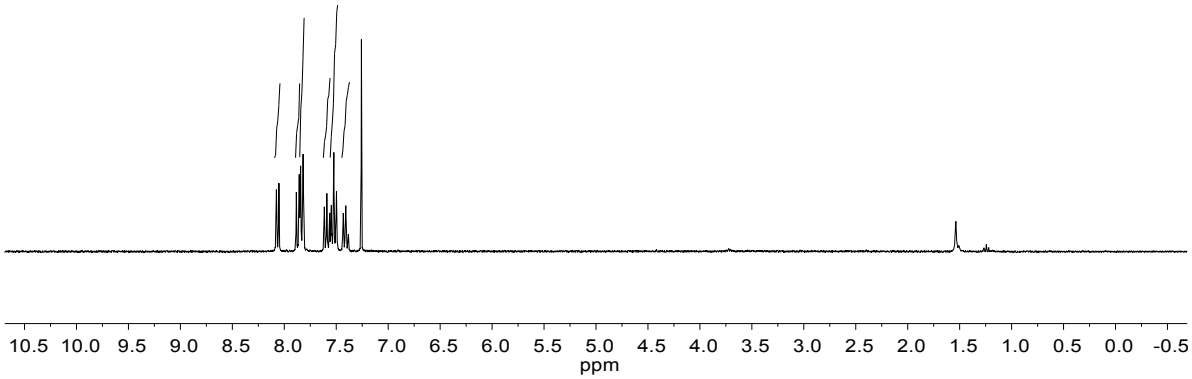


Fig. S9 ^{1}H NMR spectrum of compound **9**.

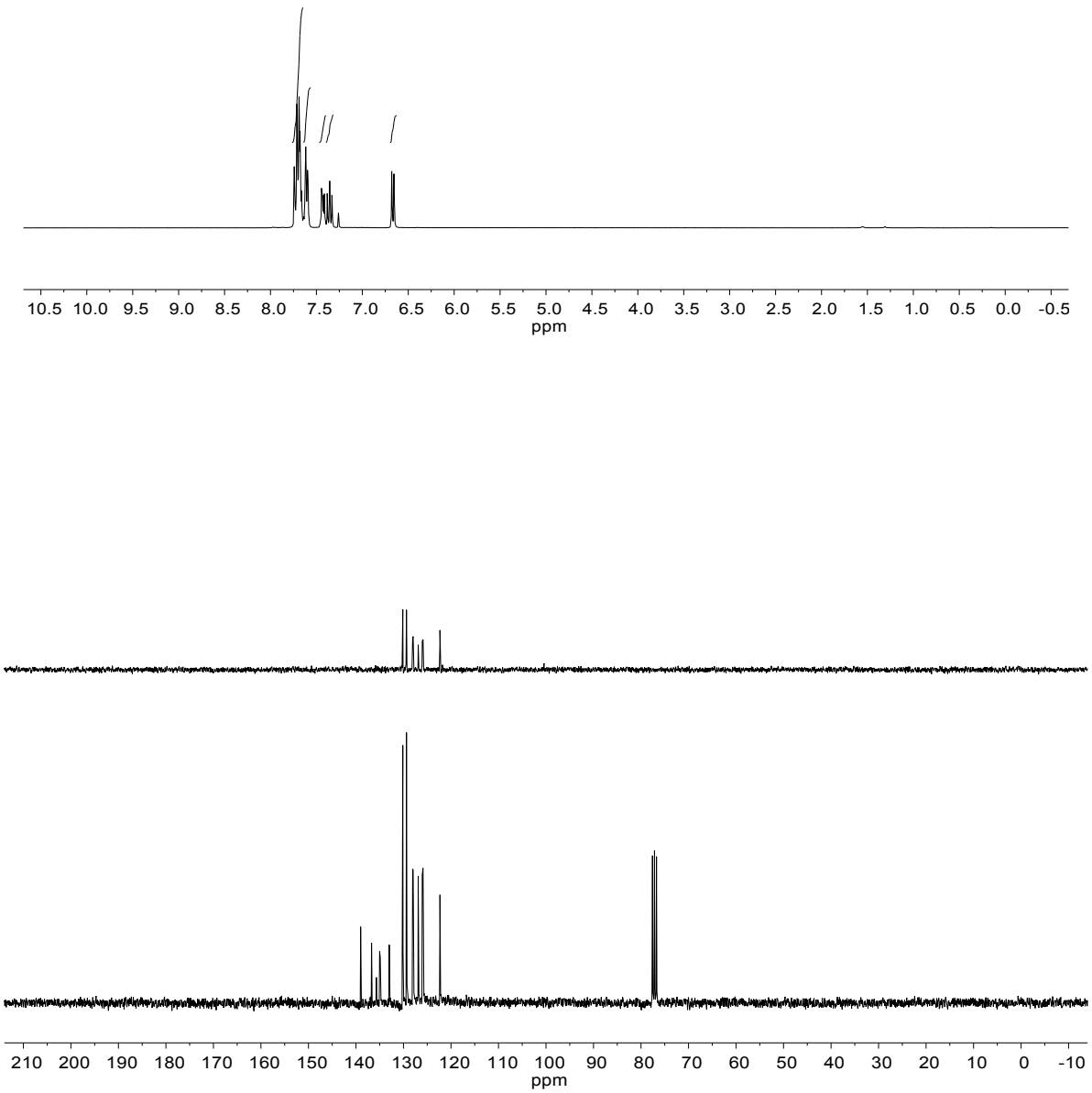


Fig. S10 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of compound of compound **1**.

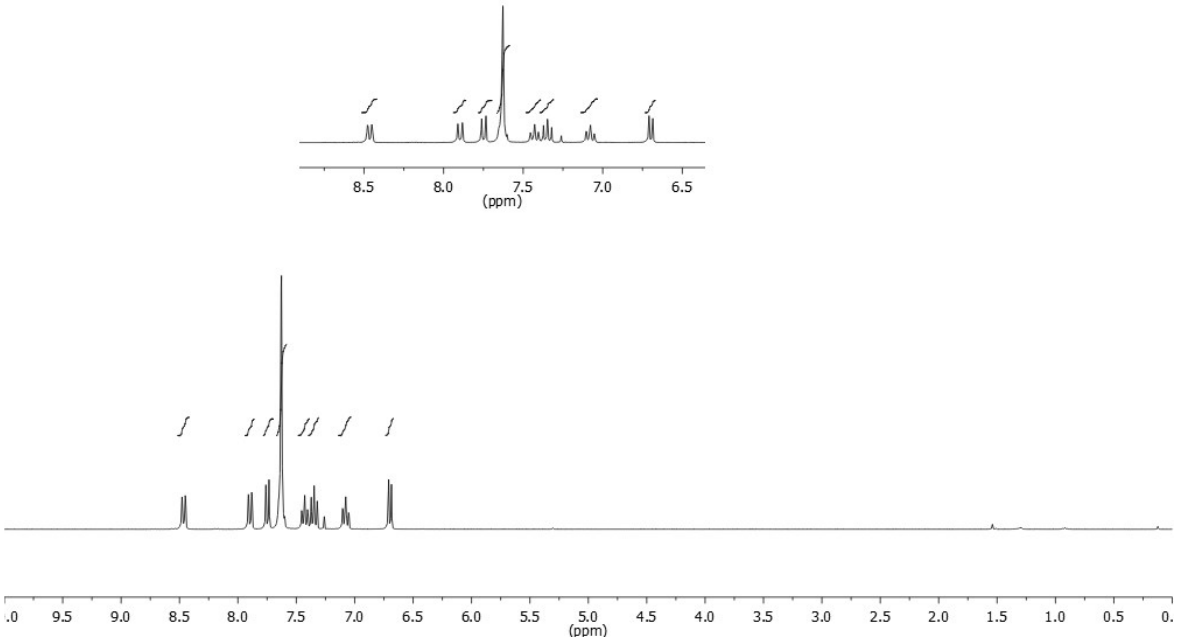


Fig. S11 ^{1}H NMR spectrum of compound of compound **5**.

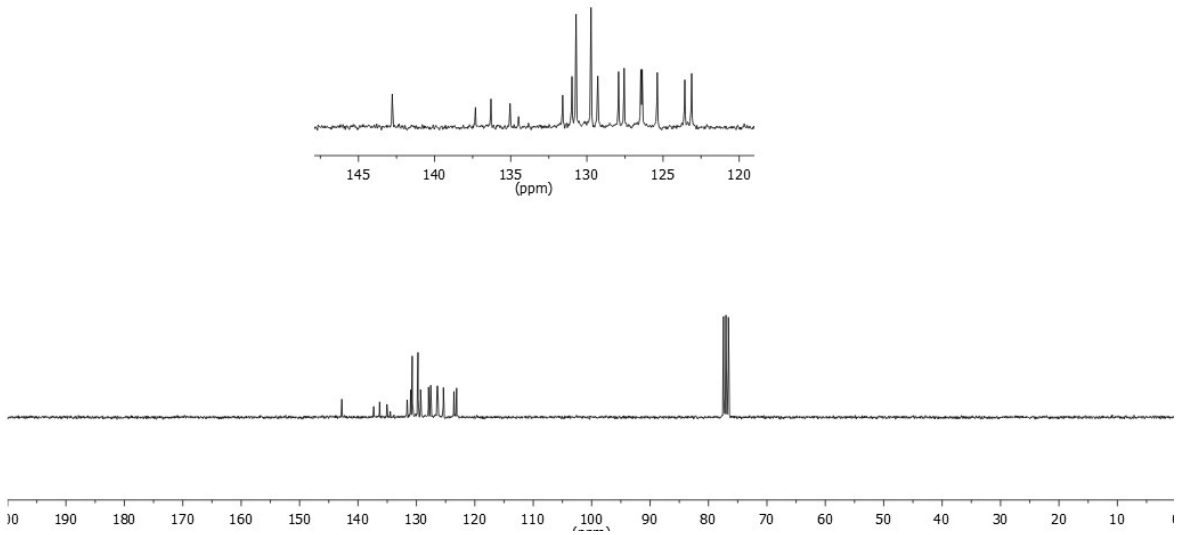


Fig. S12 ^{13}C NMR spectrum of compound of compound **5**.

Reference:

1 D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis*, 2002, **10**, 1454.
2 D. Peña, D. Pérez and E. Guitián, *J. Org. Chem*, 2000, **21**, 6944.
3 R. Vanel, F. Berthiol, B. Bessières and C. Einhorn, J., *Synlett*, 2011, **9**, 1293.