

Preparation of (substituted) picenes via solar light-induced Mallory photocyclization.

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Electronic Supplementary Information (ESI)

General Information	S2
¹H and ¹³C NMR copy of compounds 1a-c and 2a-c	S7

General Information. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Attributions were made on the basis of ^1H and ^{13}C NMR, as well as distortionless enhancement by polarization transfer (DEPT)-135 experiments; chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Solvents of HPLC purity were employed in the photochemical reactions.

Raman measurements were carried out with a Horiba LabRAM HR Evolution micro-spectrometer in backscattering geometry. Picene samples, in appearance finely ground powders, were excited by the 632.8 nm radiation of a He-Ne laser with 30 mW output power. The laser power at the sample surface was reduced by a factor of about 2 from internal reflection and absorption along the optical path. Elastically scattered light was removed by a state-of-the-art optical filtering device based on three BragGrate notch filters.^{S1} This experimental setup allowed us to collect a good Raman signal down to very low wavenumbers (about 10 cm^{-1}).^{S1} Raman spectra over the $10\text{-}1700\text{ cm}^{-1}$ wavenumber range were collected by a Peltier cooled CCD detector with a resolution better than 1 cm^{-1} , achieved thanks to an 1800 grooves/mm grating and an 800 mm focal length. The spectrometer was equipped with a confocal microscope. Test measurements carried out using different optical configuration allowed us to find the optimum experimental condition using a confocal hole of $100\mu\text{m}$ and a 50x objective. With these choices, the scattering volume was approximately a cylinder with an $\sim 1\text{ }\mu\text{m}^2$ base and a few microns in height. The high spatial resolution allowed us to carefully verify the sample homogeneity. Polarization rotators properly located along the internal optical path allowed for a polarization analysis of the Raman spectrum.

Powder X-ray diffraction measurements were performed on the ID-09 beamline of the ESRF synchrotron (Grenoble, France) with a fixed wavelength of 0.4129 \AA . The sample-to detector distance and the image plate orientation angles were calibrated using a CeO_2 standard. The two dimensional diffraction images, acquired by a MAR445 detector, were converted into one dimensional diffraction patterns using the FIT2D software.^{S2}

Stilbene **1a** was prepared by a known procedure^{S3} and stilbenes **1b-c** were synthesized by adapting a known procedure.^{S4}

1-methyl-4-(2-(naphthalen-1-yl)vinyl)naphthalene (1b). From (1-naphthylmethyl)triphenylphosphonium chloride (4.38 g, 10 mmol) and 4-methyl-1-naphthaldehyde (1.70 g, 10 mmol), in CH₂Cl₂ (50 ml). A solution of KOH (2 g) in H₂O (2 mL) was added dropwise, the resulting mixture stirred overnight, then washed with water (2×50 mL), dried over MgSO₄ and the solvent evaporated. Purification by column chromatography of the resulting residue afforded 1.03 g of **1b** (35% yield, pale yellow solid, obtained in a E/Z 50:50 mixture). **1b**: ¹H NMR, (δ, CDCl₃) 2.65 (3H), 2.75 (3H), 6.95-7.00 (m, 2H), 7.10-7.15 (m, 2H), 7.25-7.30 (m, 2H), 7.55-7.90 (m, 8H), 7.65-7.70 (m, 1H), 7.75-7.80 (d, 1H, *J* = 7 Hz), 7.85-7.95 (m, 8 H), 8.05-8.10 (m, 2H), 8.20-8.35 (m, 4H). ¹³C NMR, (δ, CDCl₃) 19.0 (CH₃), 19.2 (CH₃), 123.2 (CH), 123.4 (CH), 123.5 (CH), 124.0 (CH), 124.1 (CH), 124.2 (CH), 124.3 (CH), 124.6 (CH), 125.0 (CH), 125.1 (CH), 125.2 (CH), 125.3 (3CH), 125.4 (CH), 125.5 (CH), 125.5 (CH), 125.7 (CH), 125.8 (CH), 126.2 (CH), 126.3 (CH), 126.5 (CH), 126.7 (CH), 127.6 (CH), 127.8 (CH), 128.0 (CH), 128.2 (CH), 128.8 (CH), 129.2 (CH), 130.0 (CH), 131.0, 131.1, 131.5, 131.6, 132.1, 131.2, 132.3, 133.1, 133.2, 133.3, 134.1, 135.0 IR (neat, v/cm⁻¹): 3059, 1590, 1513, 1397, 1264, 956. Anal. Calcd for C₂₃H₁₈: C, 93.84; H, 6.16. Found: C, 93.8; H, 6.2.

1-methoxy-4-(2-(naphthalen-1-yl)vinyl)naphthalene (1c). From (1-naphthylmethyl)triphenylphosphonium chloride (4.38 g, 10 mmol) and 4-methoxy-1-naphthaldehyde (1.86 g, 10 mmol), in CH₂Cl₂ (50 ml). A solution of KOH (2 g) in H₂O (2 mL) was added dropwise, the resulting mixture stirred overnight, then washed with water (2×50 mL), dried over MgSO₄ and the solvent evaporated. Purification by column chromatography of the resulting residue afforded 1.12 g of **1c** (36% yield, pale yellow solid, obtained in a E:Z 70:30 mixture). **1c**: ¹H NMR, (δ, CDCl₃) 3.95 (3H), 4.10 (3H), 6.45-6.50 (d, 1H, *J* = 8 Hz), 6.80-6.90 (d, 1H, *J* = 8

Hz), 6.95-7.05 (d, 1H, $J = 8$ Hz), 7.15-7.20 (d, 1H, $J = 5$ Hz), 7.20-7.35 (AB part of an ABX system, 2H, $J = 5$ Hz), 7.50-7.60 (m, 8H), 7.70-7.75 (m, 1H), 7.75-7.80 (X part of an ABX system, 1H), 7.80-7.95 (m, 6H), 8.15-8.20 (m, 1H), 8.20-8.30 (m, 4H), 8.35-8.40 (m, 1H). ^{13}C NMR, (δ , CDCl_3) 55.3 (CH_3), 55.5 (CH_3), 103.4 (CH), 103.8 (CH), 122.7 (CH), 122.4 (CH), 123.5 (CH), 123.6 (CH), 123.8 (CH), 124.1 (2CH), 124.5 (CH), 125.0 (CH), 125.2 (CH), 125.4 (CH), 125.5, 125.6 (CH), 125.7 (CH), 125.8 (CH), 126.0 (CH), 126.4, 126.5 (CH), 126.7 (CH), 126.8 (CH), 126.9 (CH), 127.0 (CH), 127.1 (CH), 127.8 (CH), 127.9, 128.4 (CH), 128.5 (CH), 128.9 (CH), 130.0 (CH), 131.4, 131.9, 132.2, 132.7, 133.5, 133.7, 134.8, 135.5, 154.6, 155.7 IR (neat, v/cm^{-1}): 3057, 1582, 1462, 1274, 1251, 1095, 769. Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}$: C, 89.00; H, 5.85. Found: C, 89.0; H, 5.8.

Preparative irradiation.

Photochemical syntheses of 2a. An oxygen-saturated solution of stilbene **1a** (E/Z 60/40 mixture of diastereoisomers,^{S3} 53 mg, 0.019 M) and iodine (8 mg, 15% w/w) in the chosen solvent (10 mL) was irradiated by means of different photochemical apparatuses, including a multilamp reactor equipped with 10×15 W Hg phosphor-coated lamps ($\lambda_{\text{em}} = 310$ nm) and a SolarBox 1500e (CO.FO.ME.GRA s.r.l., Milan) Xe lamp set at 500 Wm^{-2} , equipped with an “outdoor” filter (cut off 280 nm). Photochemical reactions were carried out in quartz tubes or in Pyrex glass vessels when the multilamp reactor or the SolarBox were used, respectively. The synthesized picene **2a** was recovered by filtration from the photolyzed solutions and further purified by sublimation in order to carry out Raman spectroscopy and X-ray diffraction characterization. Spectroscopic data for **2a** are in accordance with the literature.^{S5} Anal. Calcd for $\text{C}_{22}\text{H}_{14}$: C, 94.93; H, 5.07. Found: C, 94.9; H, 5.1.

The same process was carried out on a gram scale. An oxygen saturated solution of 1 g of **1a** (0.038 M) and iodine (150 mg, 15% w/w) in ethyl acetate (94 mL) was poured in a Pyrex glass vessel and irradiated in the SolarBox apparatus for 6 h. Picene **2a** (695 mg) was then isolated in a 70% yield.

Solar light induced synthesis of 2a. An oxygen saturated solution of stilbene **1a** (53 mg, 0.019 M) and iodine (8 mg, 15% w/w) in C₆H₆ or ethyl acetate (10 mL) was poured into a Pyrex glass vessel and exposed to sunlight on a window ledge (Italy, latitude 45°11' N, 9°09' E, 77 m above sea level). The obtained picene **2a** (69 % yield in C₆H₆; 72 % yield in ethyl acetate) was collected from the photolysed solution by filtration.

Photochemical syntheses of 5-methylpicene (2b).^{S6} From **1b** (112 mg, 0.038 M, *E/Z* 50/50) and iodine (17 mg, 15% w/w) in oxygen saturated C₆H₆ or ethyl acetate, irradiated in the SolarBox apparatus for 10 h. Picene **2b** (colorless solid, mp > 210 °C) was obtained by filtration of the photolyzed solution. **2b**: ¹H NMR, (δ, CDCl₃) 2.95 (s, 3H), 7.65-7.80 (m, 4H), 8.00-8.05 (m, 2H), 8.20-8.25 (m, 1H), 8.65 (s, 1H), 8.80-9.00 (m, 5 H). ¹³C NMR, (δ, CDCl₃) 20.7 (CH₃), 120.7 (CH), 121.4 (CH), 121.5 (CH), 121.7 (CH), 123.0 (CH), 123.4 (CH), 124.6 (CH), 126.4 (3CH), 126.1 (CH), 127.1 (CH), 127.8, 128.0, 128.2, 128.3, 128.4 (CH), 128.6, 130.4, 131.7, 131.8, 133.2. Anal. Calcd for C₂₃H₁₆: C, 94.48; H, 5.52. Found: C, 94.5; H, 5.5.

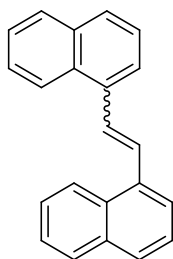
Photochemical syntheses of 5-methoxypicene (2c). From **1c** (118 mg, 0.038 M) and iodine (18 mg, 15% w/w) in oxygen saturated C₆H₆ or ethyl acetate, irradiated in the SolarBox apparatus for 10 h. Picene **2c** (colorless solid, mp > 210 °C) was obtained by filtration of the photolyzed solution (when the reaction is carried out in benzene) or by evaporation of the solvent and purification by column chromatography (eluant: neat hexane) of the resulting residue. **2c**: ¹H NMR, (δ, CDCl₃) 4.30 (s, 3H), 7.40 (s, 1H), 7.65-7.80 (m, 4H), 8.00-8.05 (m, 3H), 8.45-8.50 (dd, 1H *J* = 1 and 8 Hz), 8.70-8.75 (d, 1H, *J* = 8 Hz), 8.80-8.90 (m, 4 H). ¹³C NMR, (δ, CDCl₃) 55.4 (CH₃), 97.7 (CH), 119.1

(CH), 121.4 (CH), 121.5 (CH), 122.4 (CH), 122.9 (CH), 123.1 (CH), 124.2, 126.4 (CH), 126.5 (CH), 126.6 (CH), 126.8 (CH), 127.3 (CH), 127.7, 128.2, 128.3 (CH), 129.0, 129.5, 130.5, 131.3, 131.8. 154.3. Anal. Calcd for C₂₃H₁₆O: C, 89.58; H, 5.23. Found: C, 89.7; H, 5.2. GC-MS (m/z): 309 (20), 308 (M⁺, 100), 293 (20), 266 (24), 265 (100), 154 (30), 133 (62).

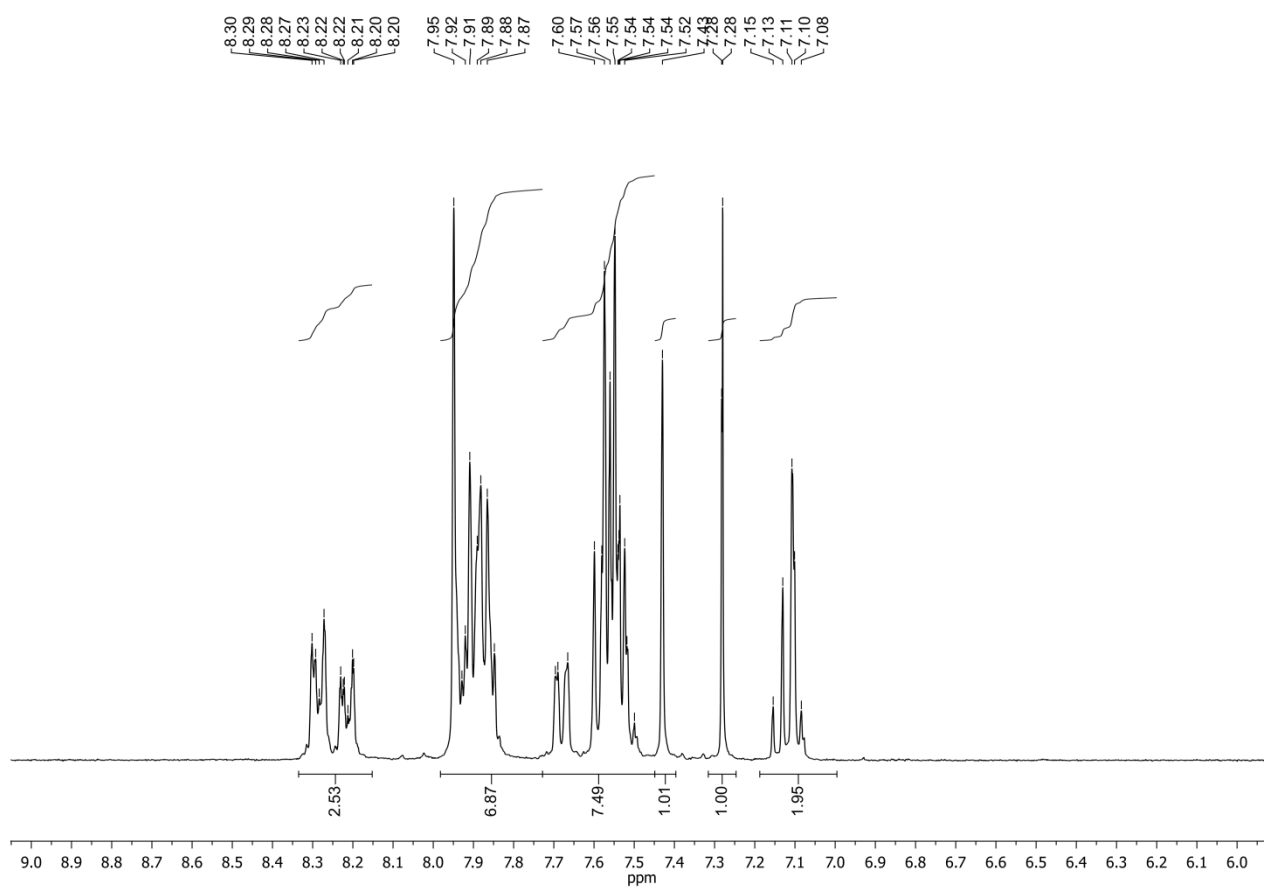
References

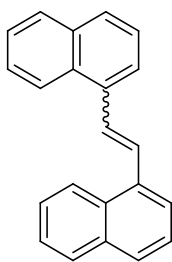
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- S2 A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Häusermann, *High Pressure Research*, 1996, **14**, 235.
- S3 C. Rosini, S. Scamuzzi, G. Uccello-Barretta and P. Salvadori, *J. Org. Chem.*, 1994, **59**, 7395.
- S4 H. Okamoto, S. Hamao, H. Goto, Y. Sakai, M. Izumi, S. Gohda, Y. Kubozono and R. Eguchi, *Sci. Report*, 2014, DOI: 10.1038/srep05048.
- S5 H. Okamoto, S. Hamao, H. Goto, Y. Sakai, M. Izumi, S. Gohda, Y. Kubozono and R. Eguchi, *Nature*, 2010, **464**, 76.
- S6 M. S. Newman, *J. Org. Chem.* 1944, **9**, 518–528.

^1H and ^{13}C NMR copy of compounds 1a-c and 2a-c.

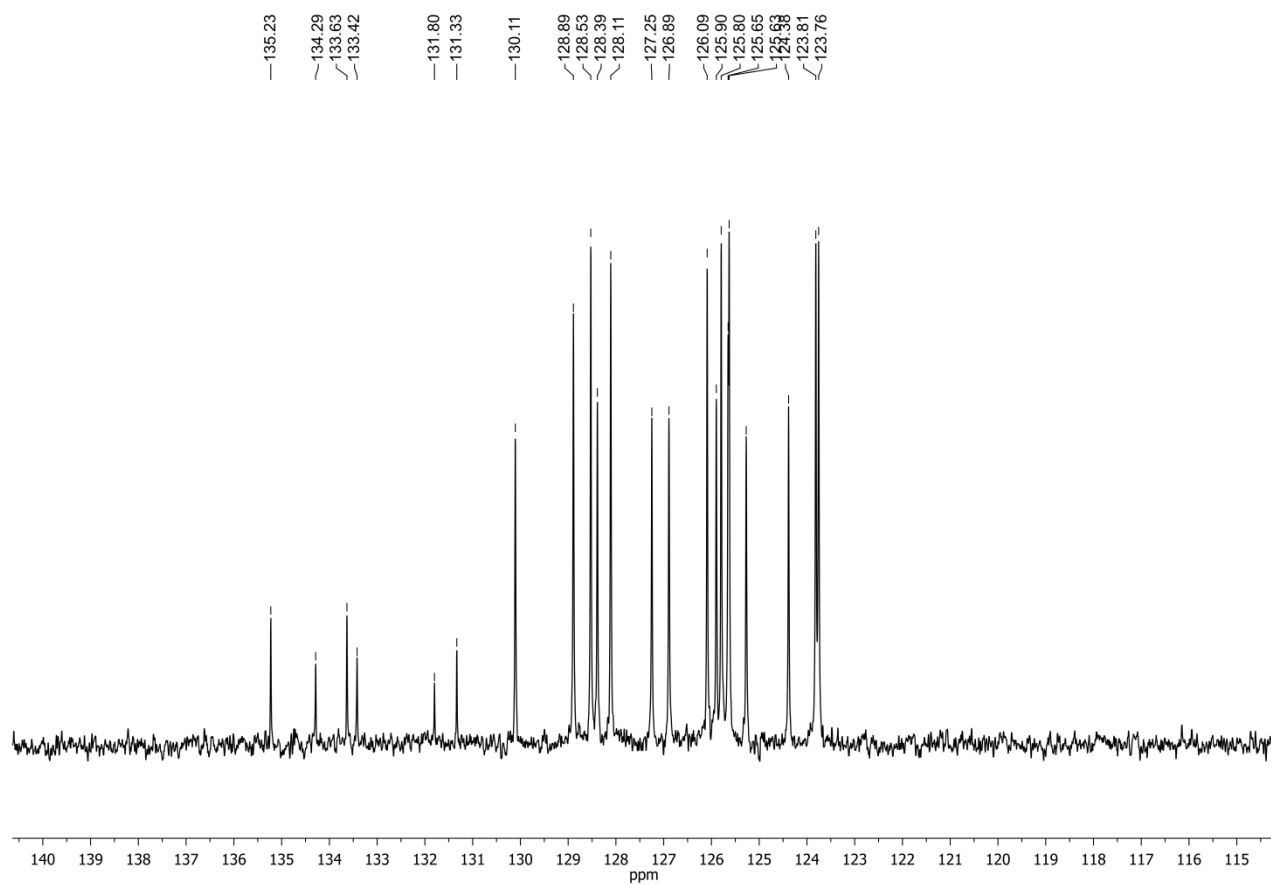


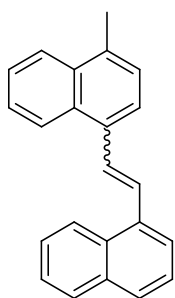
1a (^1H NMR, CDCl_3 , δ , *E/Z* 60/40)



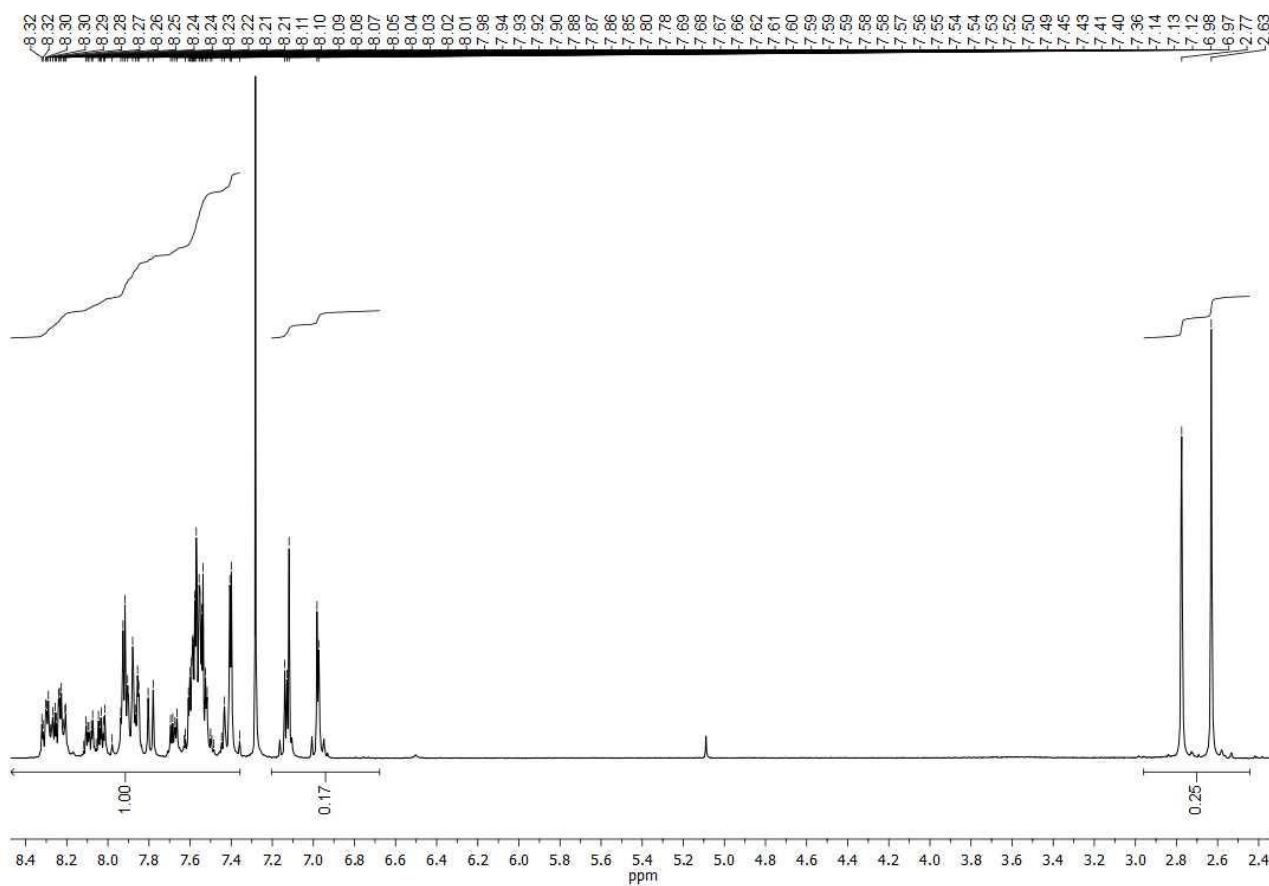


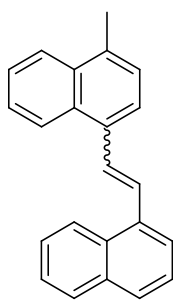
1a (^{13}C NMR, CDCl_3 , δ , *E/Z* 60/40)



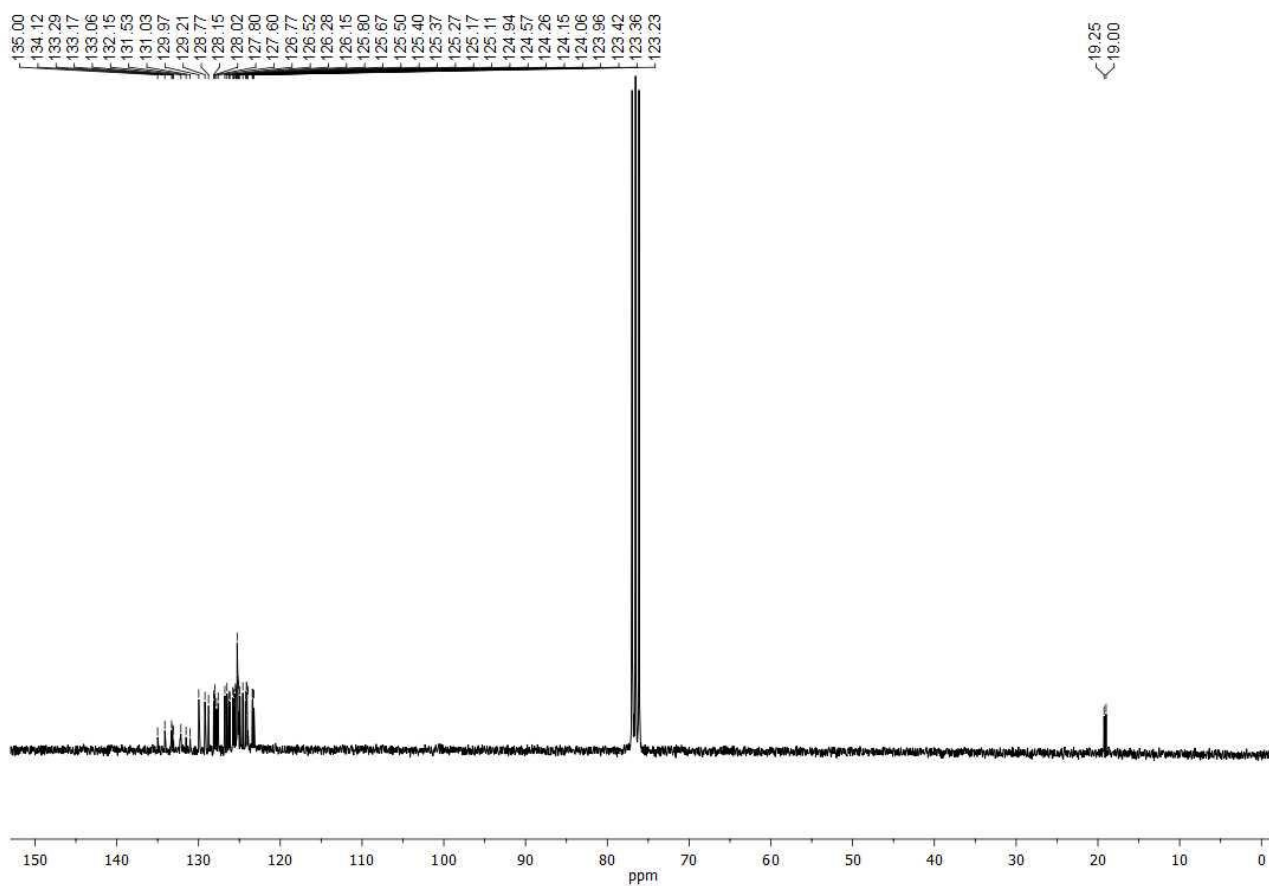


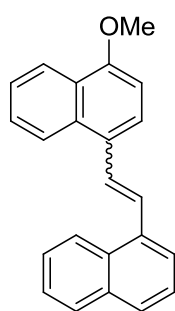
1b (^1H NMR, CDCl_3 , δ , *E/Z* 50/50)



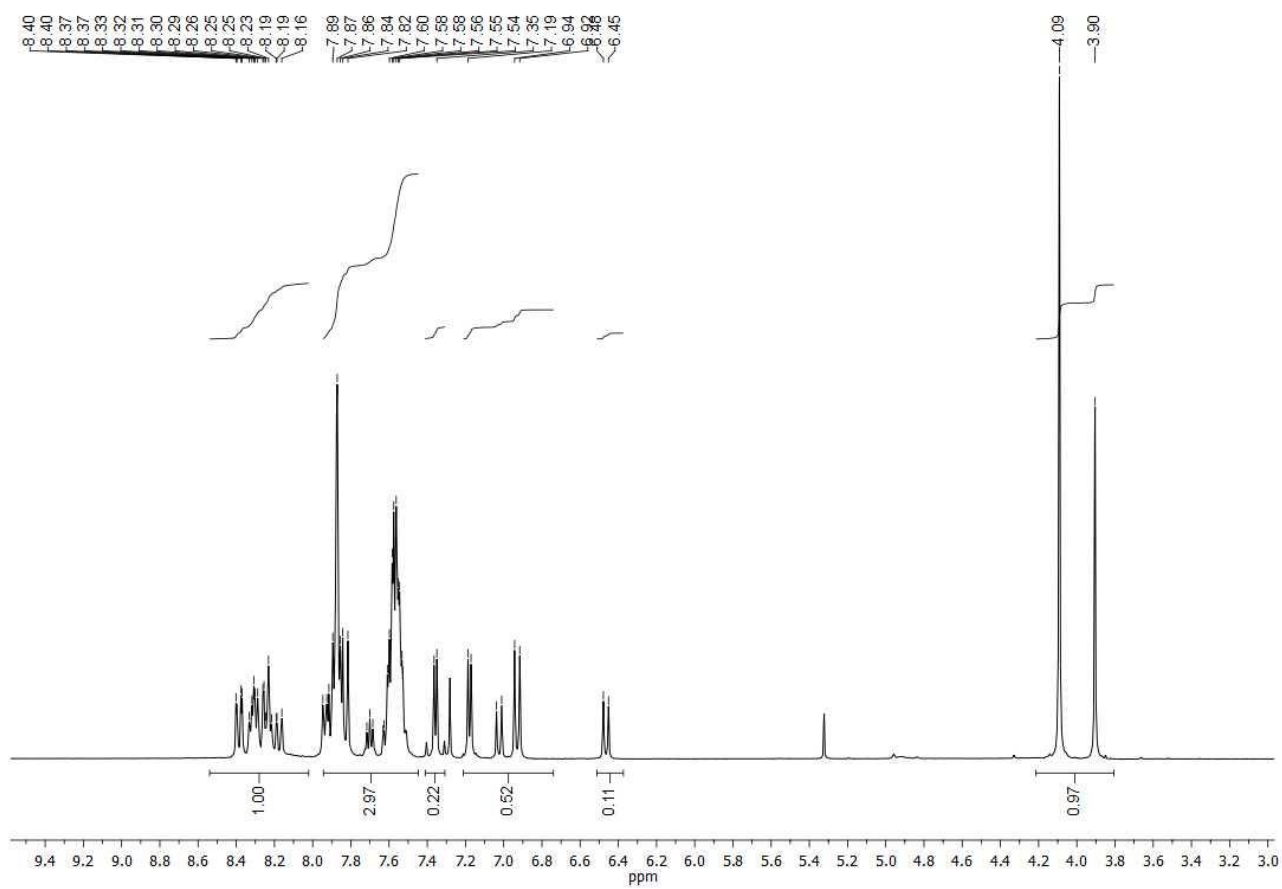


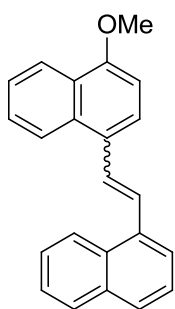
1b (^{13}C NMR, CDCl_3 , δ , *E/Z* 50/50)



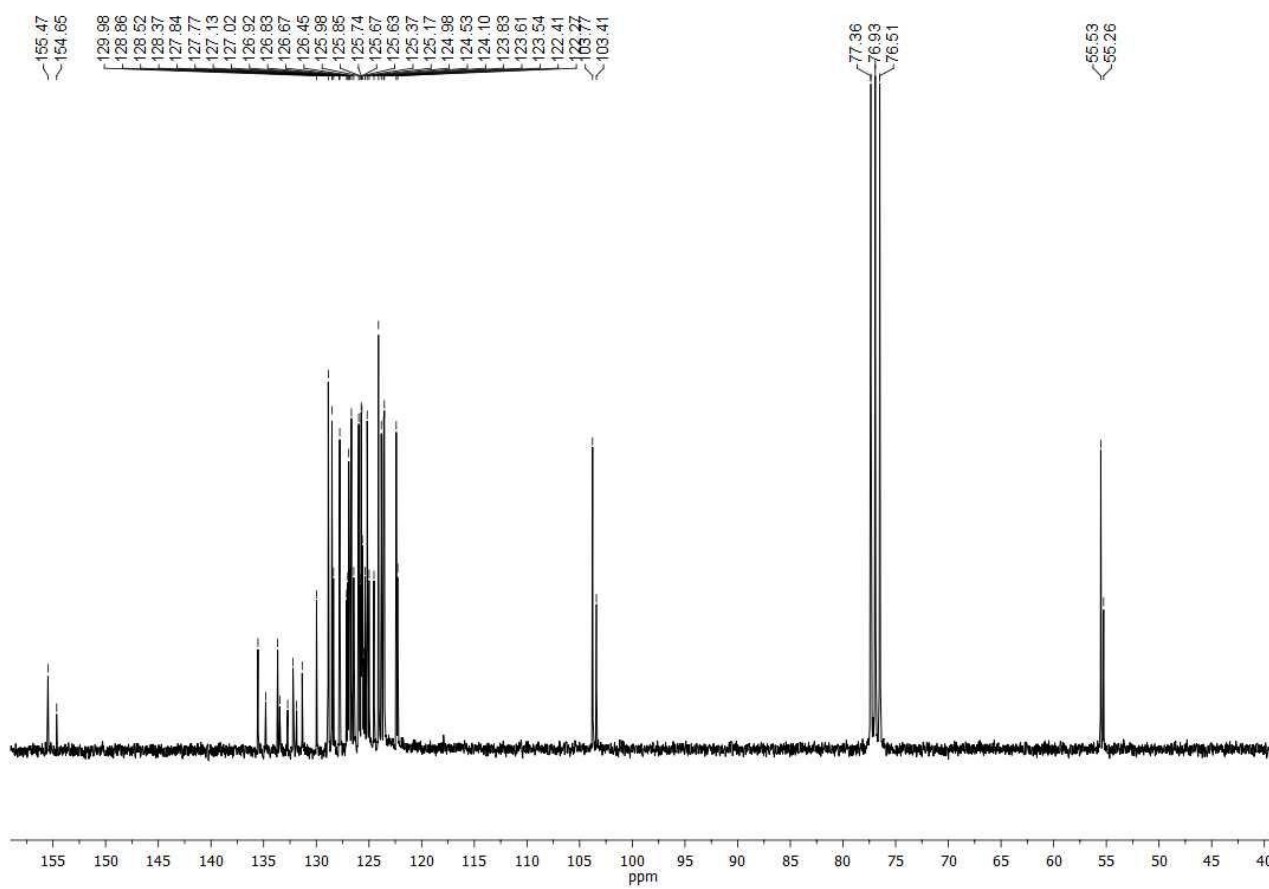


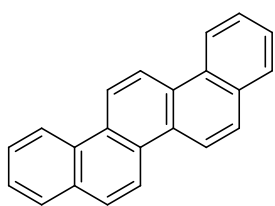
1c ($^1\text{H NMR}$, CDCl_3 , δ , E/Z 70/30)



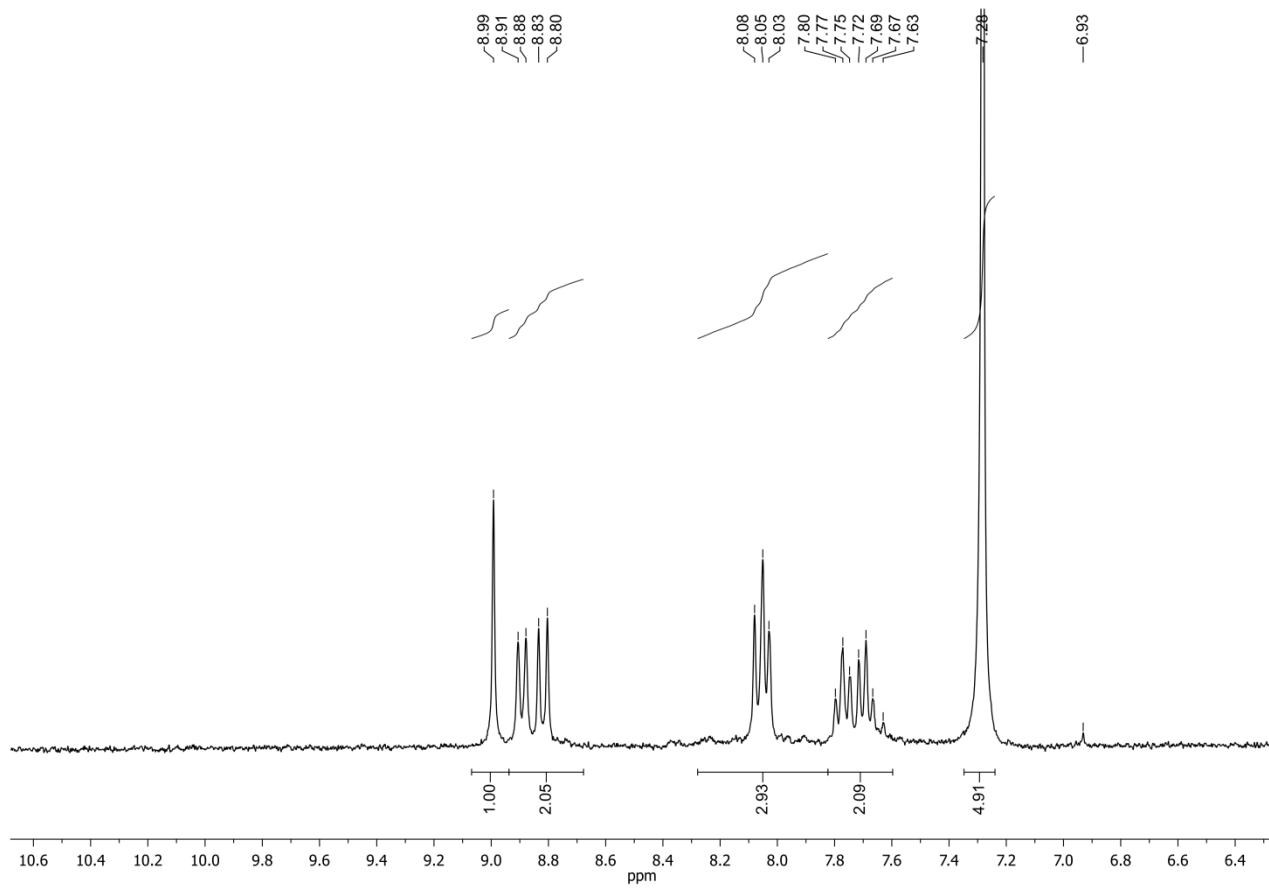


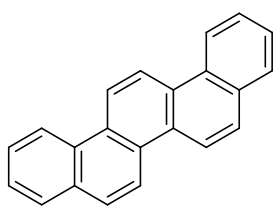
1c (^{13}C NMR, CDCl_3 , δ , *E/Z* 70/30)





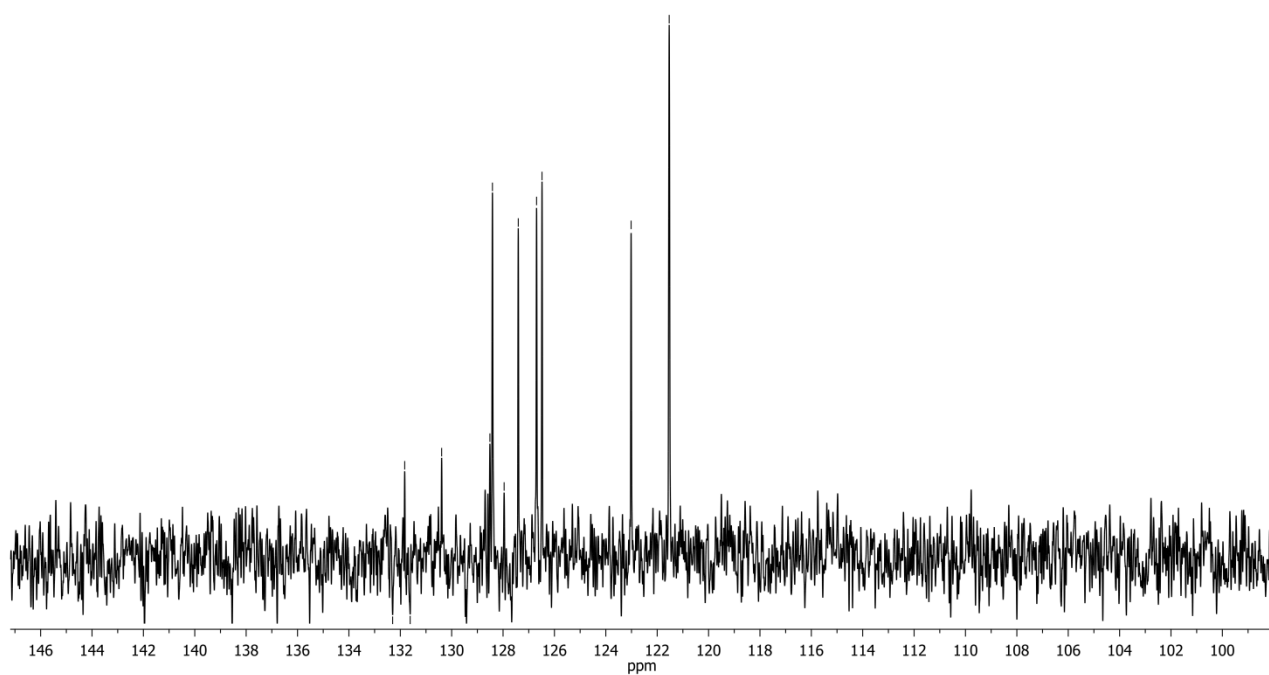
2a (^1H NMR, δ , CDCl_3)



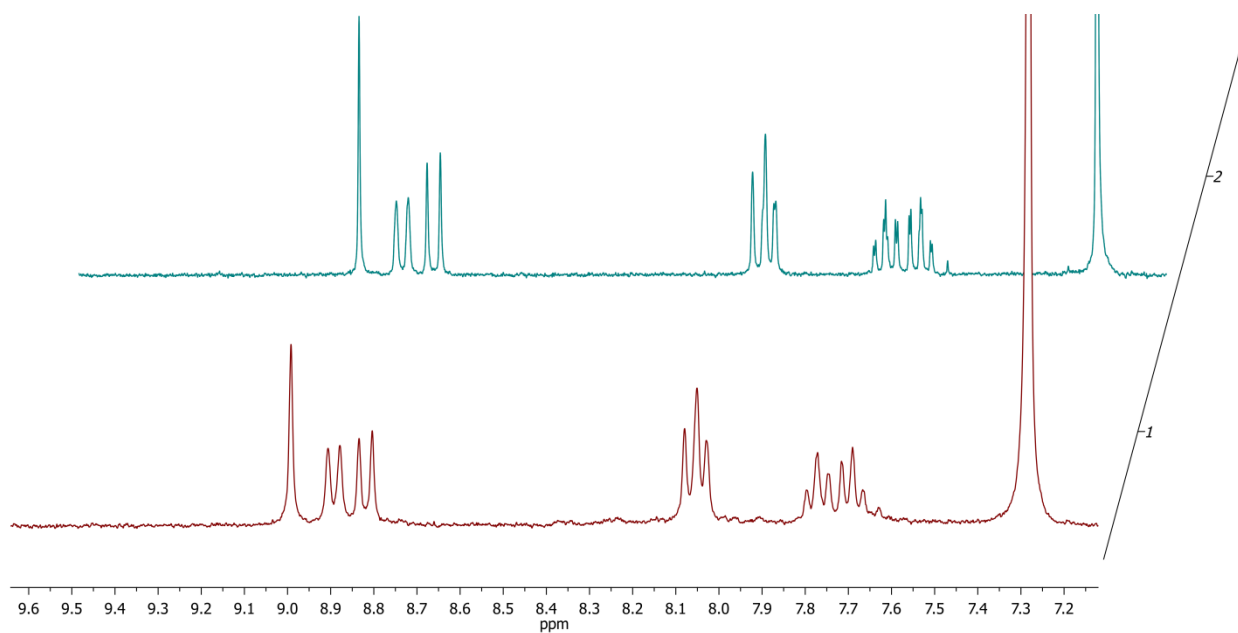


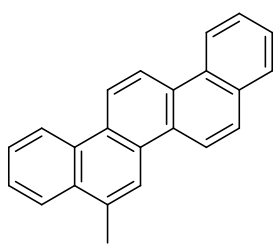
2a (^{13}C NMR, δ , CDCl_3)

132.30
131.83
131.62
130.39
128.51
128.41
127.96
127.41
126.69
126.48
123.02
121.53

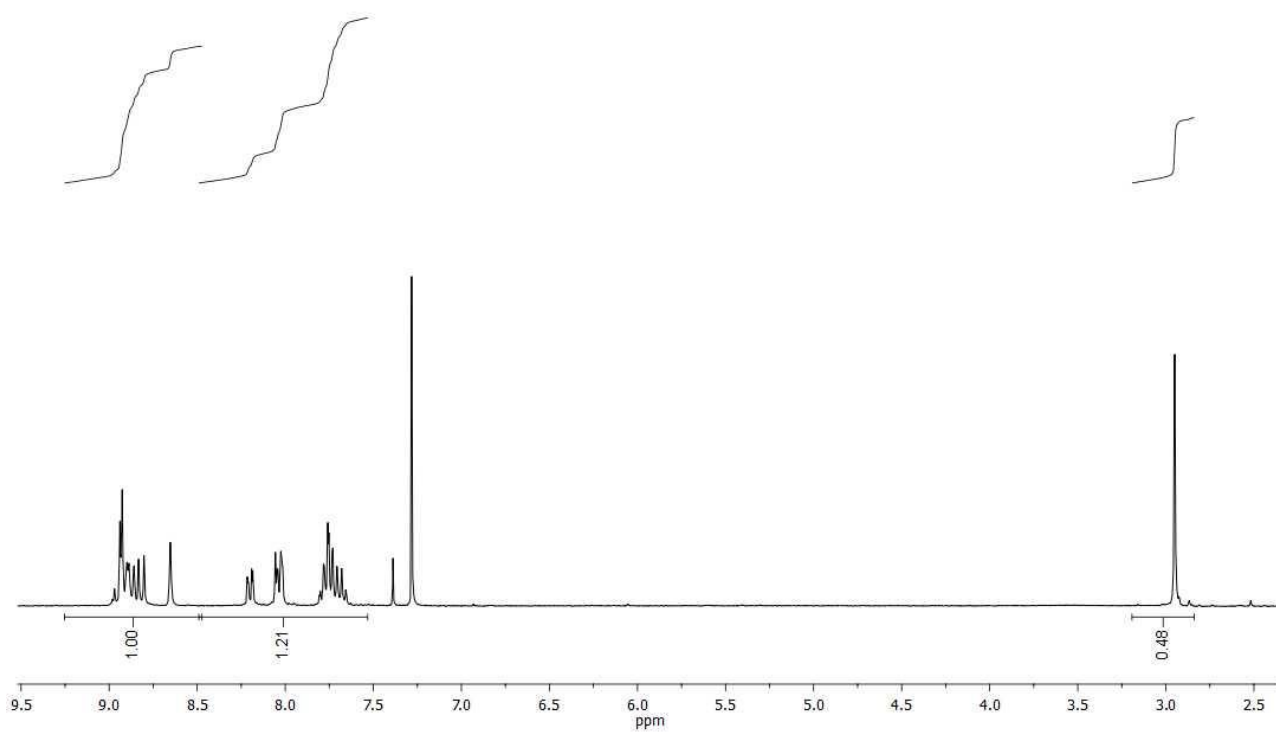


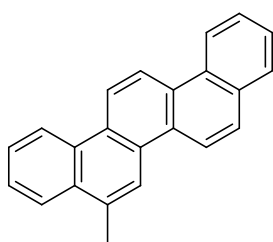
Comparison between ^1H NMR data of 2a recovered by filtration from the photolyzed solution (blue) and purified by sublimation (red).



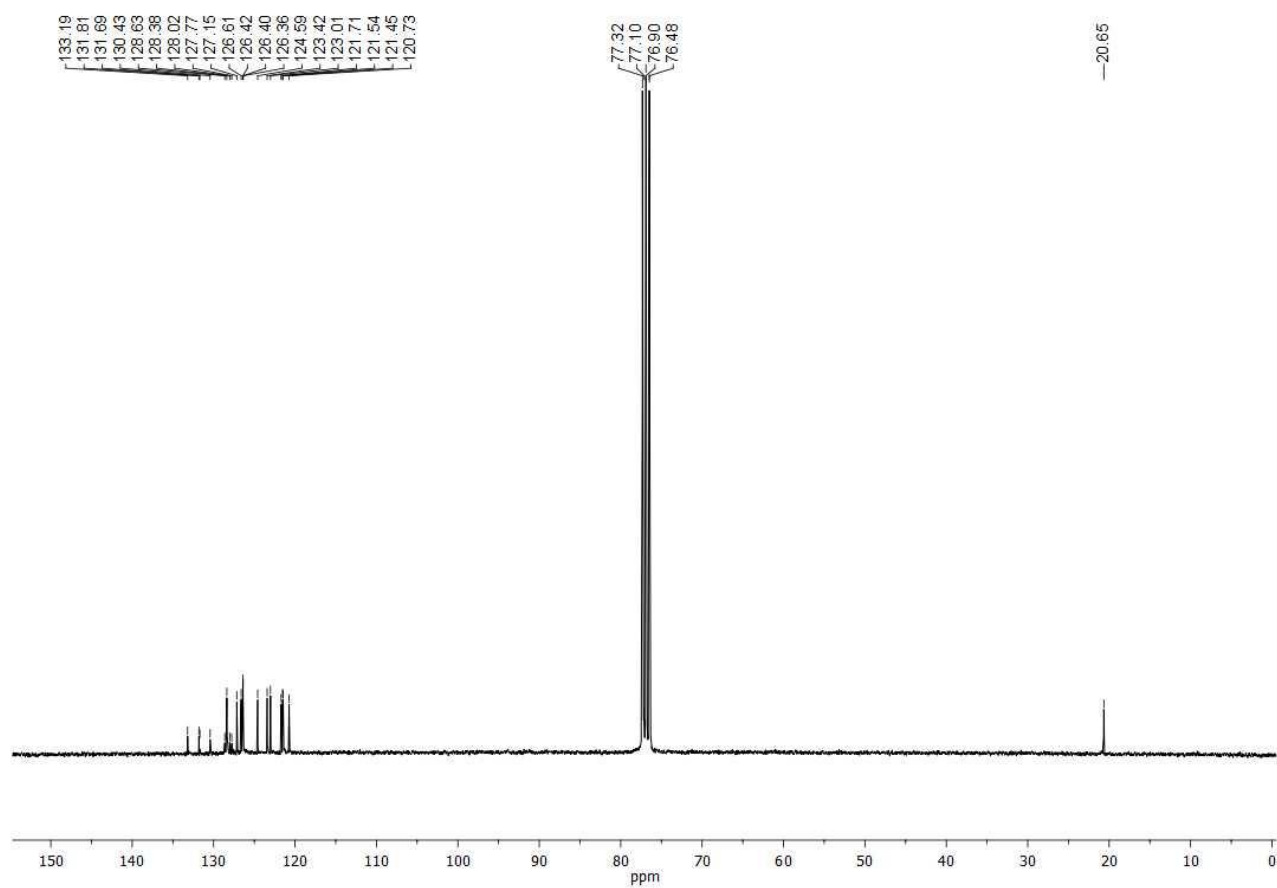


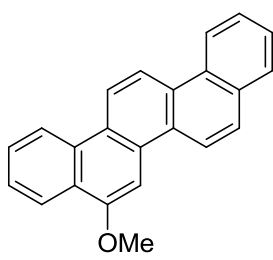
2b (^1H NMR, δ , CDCl_3)



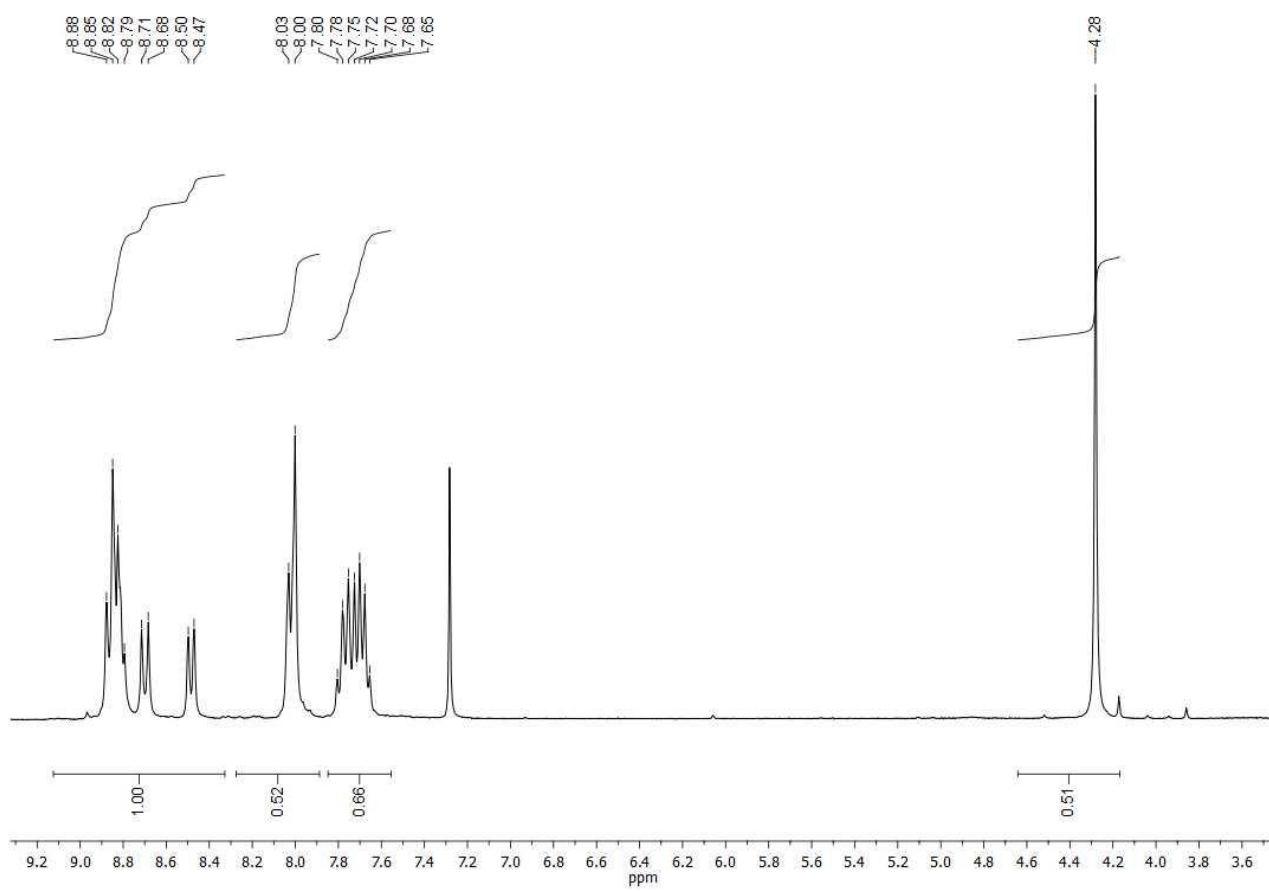


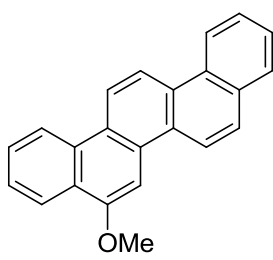
2b (^{13}C NMR, δ , CDCl_3)





2c (^1H NMR, δ , CDCl_3)





2c (^{13}C NMR, δ , CDCl_3)

