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Second generation phenylene dendrimer, 1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene, as a precursor of a new carbon material

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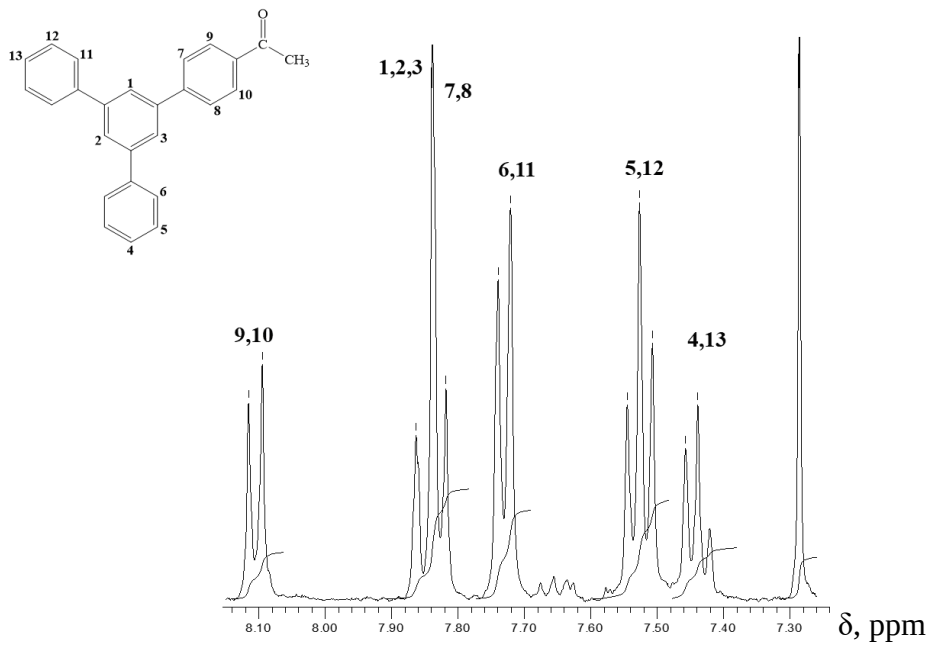
Synthesis of 1,3,5-triphenylbenzene (1). 1,3,5-Triphenylbenzene was synthesized by cyclocondensation of acetophenone as described [I. A. Khotina *et al*., *Macromol. Chem Phys.*, 2001, **202**, 2360; I. A. Khotina, *et al*., *Macromolecules*, 2003, **36**, 8353]. Acetophenone (11.7 ml, 0.1 mol), triethyl orthoformate (21.6 ml, 1.3 mol) and dry benzene (50 ml) were mixed in a round-bottom flask. Gaseous hydrogen chloride was bubbling through the solution for 3 h at room temperature. The precipitate obtained after completion of the reaction was separated, washed with acetone and ethanol, and recrystallized from chloroform. Yield 79%.

Synthesis of 4-acetyl-3',5'-diphenyl(biphenyl) (2). Monoacylation of 1,3,5-triphenylbenzene **1** (1.0 g, 0.015 mol) with acetyl chloride (0.2789 g, 3.55 mmol) was performed in nitrobenzene (8 ml). Aluminum chloride (0.6544 g, 4.902 mmol) was added in a stream of argon to the above mixture. The mixture was stirred at 5°C for 40 minutes, then poured into acidified ice water. The products were extracted with $CHCl_3$; the organic extract was washed with distilled water and dried over $CaCl_2$. After removing the solvent, the product was purified by column chromatography (silica gel – benzene). Yield 30%.



^{1}H NMR-spectrum of **4-acetyl-3',5'-diphenyl(biphenyl)** (**2**) $CDCl_3$ and assignment.

Signals in the range of 7.40-7.50 ppm refer to the protons of the *para*-position of the terminal benzene rings (H^4,H^{13}), signals in the range of 7.50-7.60 ppm refer to protons of the *meta*-position of the terminal benzene rings (H^5,H^{12}), signals in the range of 7.70-7.80 ppm refer to the protons of the *ortho*-position of the terminal benzene rings (H^6,H^{11}), the signals in the range of 7.80-8.12 ppm correspond to the protons of the 1,3,5-substituted benzene ring and the protons of the aromatic ring substituted in the *para*-position to the acetyl group (H^{1-3},H^{7-10}).

Synthesis of 1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene (3). Gaseous hydrogen chloride was bubbled through a mixture of monoacetyl derivative **2** (0.414 g, 1.19 mmol), triethyl orthoformate (0.26 ml, 1.55 mmol) and dry benzene (4.5 ml) at room temperature for 4 h. The precipitate was washed with petroleum ether and dried over $CaCl_2$. After removing the solvents, the product was purified by column chromatography (silica gel – chloroform). Yield 40%.

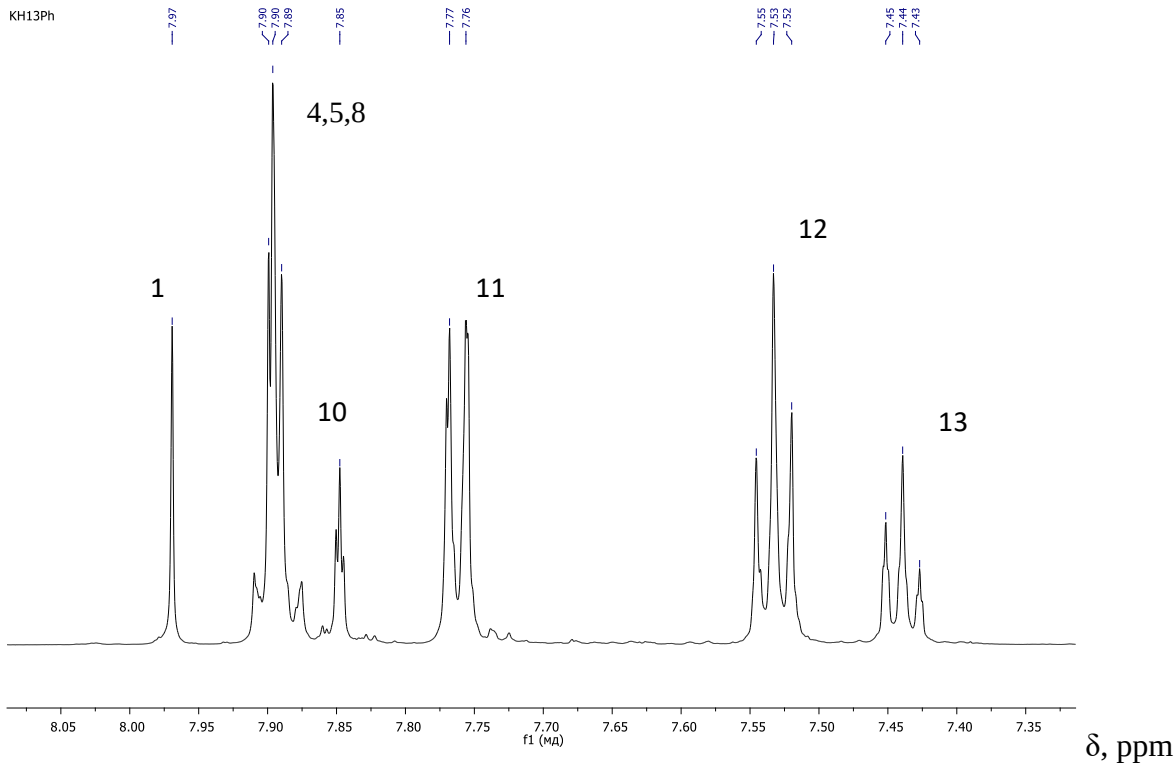
mp = 309- 310°C

Elemental analysis data for $C_{78}H_{54}$: Calculated, %: C, 94.51; H, 5.49. Found, %: C, 94.17; H, 5.43.

MS: m/z = 990 (M^+)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 3H), 7.91-7.87 (m, 18H), 7.83-7.85 (m, 3H), 7.75 (d, J = 7.3 Hz, 12H), 7.54 (t, J = 7.3 Hz, 12H), 7.44 (t, J = 7.3 Hz, 6H).

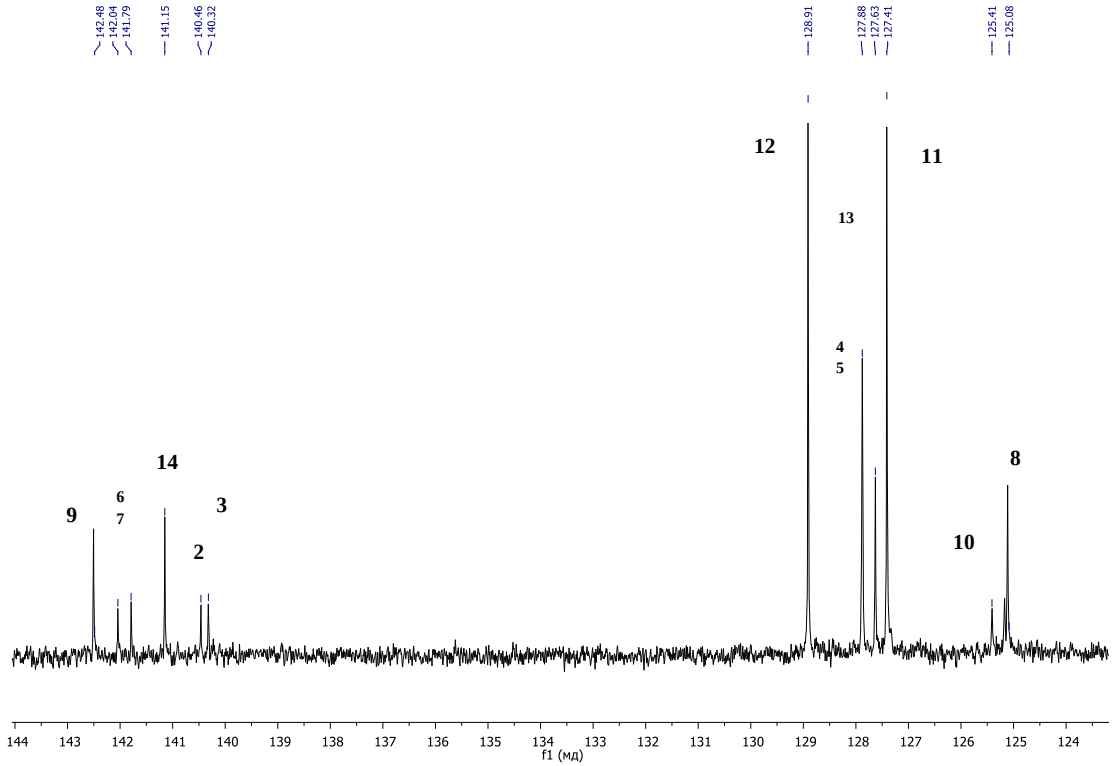
^{13}C NMR (400 MHz, $CDCl_3$) δ 142.71, 142.25, 142.00, 141.35, 140.66, 140.52, 129.11, 128.09, 128.09, 127.84, 127.62, 125.62, 125.38, 125.32.



^{1}H NMR-spectrum of **1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene (3)** in $CDCl_3$.and assignment.

^{1}H NMR: Signals in the range of 7.42-7.46 ppm correspond to the protons of the *para*-position of the terminal benzene rings (8), the signals in the range of 7.51-7.56 ppm correspond to protons of the *m*-position of the terminal benzene rings (7), signals in the range of 7.74-7.76 ppm correspond to the protons of the *o*-position of the terminal benzene rings (6), signals in the range of 7.83-7.85 ppm refer to the protons of the 1,3,5-trisubstituted benzene ring (5), signals in the range of 7.87-7.91 ppm refer to the protons of substituted benzene rings numbered (2,3,4), the signal in the region of 7.97 ppm corresponds to the protons of the 1,3,5-trisubstituted benzene ring (1). J = 7.3Hz

^{13}C NMR: On the spectrum signal at 142.71 ppm can be assigned to C(9). Signal at 141.35 ppm is assigned to C(14). The last two non quaternary carbon signals are collapsed at 128.09 ppm being C(4,5). Concerning the quaternary carbons at 140.52 and at 140.66 ppm. The other quaternary carbons at 142.25 and 142.00 ppm are responsible for C(6) and C(7) signals. Signal at 140.52 ppm likewise, signal at 142.25 ppm show a correlation with proton signal centered at 7.88 ppm, previously assigned to H(4), and this allow the assignment of C(6).



^{13}C NMR spectrum of 1,3,5-tris[4-(3,5-diphenylphenyl)phenyl]benzene **(3)** in $CDCl_3$