## Synthesis of 4-Bromo-1,1':4',1"-terphenyl and 4-Methyl-1,1':4',1"-terphenyl

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Abstract—Possible synthetic routes to 4-bromo-1,1':4',1"-terphenyl and 4-methyl-1,1':4',1"-terphenyl have been studied. Stevens rearrangement of quaternary ammonium salts containing 3-phenylprop-2-en-1-yl and 3-(4-bromo- or 4-methylphenyl)prop-2-yn-1-yl groups gave 1-(4-bromophenyl)-*N*,*N*-dimethyl-4-phenylhex-5-en-1-yn-3-amine, 1-(4-bromophenyl)-*N*,*N*-diethyl-4-phenylhex-5-en-1-yn-3-amine, 1-(4-bromophenyl)-4-phenylhex-5-en-1-yn-3-amine, 1-[1-(4-bromophenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine, 4-[1-(4-bromophenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine, 1-[1-(4-methylphenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine, 1-[1-(4-methylphenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine, and 4-[1-(4-methylphenyl)-4-phenylhex-5-en-1-yn-3-yl]morpholine. Vacuum distillation of the resulting amines, by analogy with structurally related compounds, was accompanied by deamination with the formation of 4-bromo-1,1':4',1"-terphenyl and 4-methyl-1,1':4',1"-terphenyl in high yields. This transformation is a domino reaction involving  $\beta$ -elimination of secondary amine to form conjugated dienyne, electrocyclization of the latter to cyclic allene intermediate, and fast 1,3- or 1,5-hydride shift.

Keywords: deamination, dienynes, Stevens rearrangement, β-elimination, electrocyclic reactions

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Stevens rearrangement discovered as early as 1928 [1] occupies a particular place among numerous molecular rearrangements of organic compounds. This reaction generates intermediate ammonium ylides that are capable of undergoing various transformations. Stevens rearrangement makes it possible to obtain amines and quaternary ammonium salts which are widely used in medicine, technology, and manufacture of cleaning agents. Stevens rearrangements of new unsaturated ammonium salts could give rise to new potentially biologically active tertiary amines, and studies in this field seem to be important.

We previously found [2] that vacuum distillation of *N*,*N*-diakyl-1,4-diphenylhex-5-en-1-yn-3-amines, namely 1-(1,4-diphenylhex-5-en-1-yn-3-yl)pyrrolidine, 1-(1,4-diphenylhex-5-en-1-yn-3-yl)piperidine, 4-(1,4-diphenylhex-5-en-1-yn-3-yl)morpholine, 1-[1-(4-chlorophenyl)-4-phenylhex-5-en-1-yn-3-yl]-piperidine, and 1-[1-(4-chlorophenyl)-4-phenylhex-5-en-1-yn-3-yl]morpholine, is accompanied by their deamination with the formation of 1,1':4',1"-terphenyl and 4-chloro-1,1':4',1"-terphenyl in high yields. A plausible mechanism of their formation was also

proposed. Apart from the fundamental importance, these studies are also significant from the practical viewpoint, since they open the way to new *p*-terphenyl derivatives [3, 4]. Each newly discovered reaction would lose its significance if it had no further extensions and general character.

In this work we studied the Stevens rearrangement of dialkyl [1-(4-bromophenyl)prop-2-yn-1-yl](3-phenylprop-2-en-1-yl)ammonium bromides 2a-2c, 1-[1-(4-bromophenyl)prop-2-yn-1-yl]-1-(3-phenylprop-2-en-1-yl)piperidinium bromide (2d), 4-[1-(4-bromophenyl)prop-2-yn-1-yl]-4-(3-phenylprop-2-en-1-yl)morpholinium bromide (2e), 1-[1-(4-methylphenyl)prop-2-yn-1-yl]-1-(3-phenylprop-2-en-1-yl)piperidinium bromide (2f), and 4-[1-(4-methylphenyl)prop-2-yn-1-yl]-4-(3-phenylprop-2-en-1-yl)morpholinium bromide (2g) and deamination of the resulting 1-(4-bromophenyl)-N,N-dimethyl-4-phenylhex-5-en-1-yn-3-amine (3a), 1-(4-bromophenyl)-N,N-diethyl-4-phenylhex-5-en-1yn-3-amine (3b), 1-(4-bromophenyl)-4-phenyl-N,N-dipropylhex-5-en-1-yn-3-amine (3c), 1-[1-(4-bromophenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine (3d),



1–3, X = Br, R = Me(a), Et (b), Pr (c),  $R_2N = piperidin-1-yl(d)$ , morpholin-4-yl (e); X = Me,  $R_2N = piperidin-1-yl(f)$ , morpholin-4-yl (g).

4-[1-(4-bromophenyl)-4-phenylhex-5-en-1-yn-3-yl]morpholine (**3e**), 1-[1-(4-methylphenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine (**3f**), and 4-[1-(4-methylphenyl)-4-phenylhex-5-en-1-yn-3-yl]morpholine (**3g**) during vacuum distillation. Quaternary ammonium salts **2a–2g** were synthesized by alkylation of the corresponding *N*,*N*-dialkyl-1-(4-R-phenyl)prop-2-yn-1amines **1a–1g**, with 3-bromo-1-phenylprop-1-ene [2] in acetonitrile (Scheme 1).

The rearrangement of 2a-2g by the action of 2 equiv of potassium hydroxide in the presence of a few drops of methanol was accompanied by vigorous evolution of heat, and the corresponding amines 3a-3g were formed in 70–75% yield. The IR spectra of 3a-3g characteristically showed absorption bands at 3030, 730, and 690 cm<sup>-1</sup> due to vibrations of the monosubstituted benzene ring and at 810 and 840 cm<sup>-1</sup> due to *para*-substituted benzene ring. In addition, terminal C=C bond stretchings were observed at 1645–1640 cm<sup>-1</sup>. According to the IR and <sup>1</sup>H NMR spectra, amines 3a-3g had the structure with a terminal C=C bond; i.e., the Stevens rearrangement of 2a-2g involved isomerization of the migrating group.

Unlike *N*,*N*-dialkyl-1-phenylhex-5-en-1-yn-3amines, *N*,*N*-dimethyl-1-phenylhept-5-en-1-yn-3amines [5], and their methallyl analogs [6], amines 3a-3g, like their analogs reported in [2], underwent deamination during vacuum distillation to afford 4-bromo-1,1':4',1"-terphenyl and 4-methyl-1,1':4',1"terphenyl in 60–62% yield (Scheme 2). Regardless of the substituents on the nitrogen atom, deamination of **3a–3e** (cf. [2]) started at 55–57°C (1–2 mm Hg) with vigorous evolution of the corresponding secondary amine; the temperature was then raised to 75–85°C (1–2 mm Hg), and final product **4** condensed in the arm of the Claisen adapter. The reactions were complete in ~15–20 min. The deamination of **3f** and **3g** required heating to 75–85°C (1–2 mm Hg) for 8–10 min, and prolonged heating was necessary for the subsequent intramolecular cyclization of intermediate dienyne **A**. Terphenyls **4** and **5** were mechanically pulled out from the Claisen adapter. In addition, we isolated a small amount of an amine product which could not be identified.

As shown in Scheme 2, thermal intramolecular cyclization of intermediate A gives a tricyclic structure with an allene moiety in the middle ring. Such intermediates are short-lived, and they rapidly isomerize to terphenyl 4 or 5 via 1,3- or 1,5-hydride shift.

The results of our study confirm that previously observed deamination of amines during vacuum distillation is a unique process in organic chemistry. An accessible method has been developed for the synthesis of 4-bromo-1,1':4',1"-terphenyl and 4-methyl-1,1':4',1"-terphenyl that are difficult to obtain by other chemical methods. Their formation proves that the Stevens rearrangement of ammonium salts **2a–2g** is accompanied by isomerization of the migrating group.

*p*-Terphenyl is known as a high-temperature heat carrier and starting material for the synthesis of polyphenyls [3, 4]. *p*-Terphenyl is also an organic scintillator and is often used as a standard scintillator for





3, X = Br, R = Me (a), Et (b), Pr (c),  $R_2N = piperidin-1-yl$  (d), morpholin-4-yl (e); X = Me,  $R_2N = piperidin-1-yl$  (f), morpholin-4-yl (g); 4, X = Br; 5, X = Me.

evaluation of new scintillators [7]. As recently shown [8], *p*-terphenyls are new HIV inhibitors that suppress Rev-RRE function and viral replication. Alkyl-substituted terphenyls are used as heat carriers in nuclear power stations [9], as well as in the synthesis of monomers for heat-resistant polymeric materials [10], photosensitive materials [11], biologically active compounds, and medicines [12].

Known methods of synthesis of *p*-terphenyl and its derivatives are characterized by a large number of steps, low yields, high costs, increased expenditures for auxiliary materials, long reaction times, high temperature, sophisticated equipment, and the use of difficulty accessible and/or hazardous compounds [7–12]. Therefore, development of accessible methods for the synthesis of *p*-terphenyl and its derivatives is an important problem.

Analysis of published data on the synthesis of *p*-terphenyls and their derivatives showed that the proposed method for the preparation of compounds 4 and 5 via deamination of *N*,*N*-dialkyl-1,4-diarylhex-5-en-1-yn-3amines 2a-2g is very simple and convenient. The observed deamination of 2a-2g during vacuum distillation is a domino reaction, and it has a general character and practical significance for the synthesis of new important terphenyl derivatives.

The structure of ammonium salts 2a-2g and amines 3a-3g was proved by IR and <sup>1</sup>H NMR spectra, and the structure of 4 and 5 was also confirmed by <sup>13</sup>C NMR spectra. The deamination and intramolecular cycliza-

tion of dienynes A (Scheme 2) occur at relatively low temperatures, and the reactions were complete in  $\sim 15-$ 20 min (except for amines 3f and 3g), regardless of the substituents on the nitrogen atom. The presence of a bromine atom in the benzene ring of 3a-3e favored these processes. Presumably, the bromine atom (unlike chlorine) exerts no positive mesomeric effect, so that the acidity of the CH protons in the 4-position of **3** increases, and  $\beta$ -elimination of secondary amine is facilitated. On the other hand, the bromine atom does not hamper counterclockwise cyclization of dienyne A to form a six-membered ring, and both processes are complete in a short time ( $\sim 15-20$  min; Scheme 2). Deamination of **3f** and **3g** required a relatively higher temperature (75–85°C at 1–2 mm Hg), and the overall reaction time was  $\sim$ 30–35 min. This may be due to the presence of a piperidine or morpholine ring and methyl group in molecules **3f** and **3g**, which reduce the acidity of the CH protons in the 4-position and hence hamper  $\beta$ -elimination of secondary amine. On the other hand, electronic effect of the methyl group in the para position of benzene ring hampers cyclization of intermediate dienyne A (Scheme 2) [13].

The formation of 4-bromo-1,1':4',1"-terphenyl and 4-methyl-1,1':4',1"-terphenyl indicates that the Stevens rearrangement of ammonium salts 2a-2g involves isomerization of the migrating group. An accessible method has been developed for the synthesis of valuable *p*-terphenyl derivatives, 4-bromo-1,1':4',1"-terphenyl and 4-methyl-1,1':4',1"-terphenyl.

## EXPERIMENTAL

Initial amines 1a-1g and quaternary salts 2a-2gwere reported previously [13, 14]. The IR spectra were recorded on a Specord 75 IR spectrometer (Analytik Jena, Germany) from thin films (3) or solutions in chloroform (4, 5). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4 and 5 were recorded at 303 K on a Varian Mercury 300 VX spectrometer (USA) at 300 and 75 MHz, respectively, using DMSO- $d_6$ -CCl<sub>4</sub> (1:3) as solvent and tetramethylsilane as internal standard.

Stevens rearrangement of quaternary ammonium salts 2a-2g (general procedure). A mixture of powdered salt 2a-2g (8 mmol) and 1.46 g (16 mmol) of potassium hydroxide was thoroughly stirred, and a few drops of methanol were added. The reaction was accompanied by evolution of heat. The mixture was left to stand at room temperature for 30-40 min and extracted with diethyl ether (2×50 mL). The combined extracts were washed with water, and a sample of the extract was treated with water and titrated with 0.1 N H<sub>2</sub>SO<sub>4</sub> with shaking. According to the titration data, the extract contained 5.6–6.0 mmol (70–75%) of amine 3a-3g. The extract was acidified with 20% aqueous HCl, and the aqueous phase was separated, neutralized with a solution of potassium hydroxide, and extracted with diethyl ether (3×40 mL). The extract was washed with water, dried over MgSO<sub>4</sub>, and evaporated, and the residue (amine 3a-3g) was subjected to vacuum distillation.

**1-(4-Bromophenyl)**-*N*,*N*-dimethyl-4-phenylhex-**5-en-1-yn-3-amine (3a).** Yield 2.1 g (0.058 mmol, 73%), syrupy material. IR spectrum, v, cm<sup>-1</sup>: 3030, 730, 690 (Ph), 1645–1640 (C=C), 840, 810 (C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.29 s (6H, NMe<sub>2</sub>), 3.47 d.d.t (1H, CHPh, *J* = 10.9, 7.8, 1.5 Hz), 3.76 d (1H, NCH, *J* = 10.9 Hz), 4.96 d.d.d (1H, =CH<sub>2</sub>, *J* = 17.2, 1.5, 1.3 Hz), 5.02 d.d.d (1H, =CH<sub>2</sub>, *J* = 10.3, 1.5, 1.1 Hz), 6.16 d.d.d (1H, =CH, *J* = 17.2, 10.3, 7.8 Hz), 7.01–7.06 m (2H, C<sub>6</sub>H<sub>4</sub>), 7.14–7.32 m (5H, C<sub>6</sub>H<sub>5</sub>), 7.34–7.39 m (2H, C<sub>6</sub>H<sub>4</sub>). Found, %: C 67.93; H 5.72; Br 22.77; N 3.83. C<sub>20</sub>H<sub>20</sub>BrN. Calculated, %: C 67.80; H 5.69; Br 22.55; N 3.95.

**1-(4-Bromophenyl)**-*N*,*N*-diethyl-4-phenylhex-5en-1-yn-3-amine (3b). Yield 2.3 g (0.006 mmol, 75%), syrupy material. IR spectrum, v, cm<sup>-1</sup>: 3015, 720, 700 (Ph), 1645–1640 (C=C), 835, 815 (C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.45 t (6H, CH<sub>3</sub>, *J* = 7.2 Hz), 3.61 br.q (4H, NCH<sub>2</sub>, *J* = 7.2 Hz), 3.49 d.d.t (1H, CHPh, J = 10.8, 7.9, 1.6 Hz), 3.77 d (1H, NCH, J = 10.9 Hz), 4.95 d.d.d (1H, =CH<sub>2</sub>, J = 17.3, 1.5, 1.3 Hz), 5.01 d.d.d (1H, =CH<sub>2</sub>, J = 10.4, 1.5, 1.2 Hz), 6.15 d.d.d (1H, =CH, J = 17.2, 10.3, 7.8 Hz), 7.02–7.06 m (2H, C<sub>6</sub>H<sub>4</sub>), 7.14–7.33 m (5H, C<sub>6</sub>H<sub>5</sub>), 7.34–7.39 m (2H, C<sub>6</sub>H<sub>4</sub>). Found, %: C 69.22; H 6.41; Br 21.05; N 3.78. C<sub>22</sub>H<sub>24</sub>BrN. Calculated, %: C 69.11; H 6.33; Br 20.90; N 3.66.

**1-(4-Bromophenyl)-4-phenyl-***N*,*N*-**dipropylhex-5-en-1-yn-3-amine (3c).** Yield 2.3 g (0.0056 mmol, 70%), syrupy material. IR spectrum, v, cm<sup>-1</sup>: 3030, 720, 710 (Ph), 1645–1640 (C=C), 835, 810 (C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.91 t (6H, CH<sub>3</sub>, *J* = 7.3 Hz), 1.80–1.90 m (4H, CH<sub>2</sub>CH<sub>3</sub>, *J* = 7.3 Hz), 2.43 t (4H, NCH<sub>2</sub>, *J* = 7.3 Hz), 3.47 d.d.t (1H, CHPh, *J* = 10.9, 7.8, 1.5 Hz), 3.76 d (1H, NCH, *J* = 10.9 Hz), 4.96 d.d.d (1H, =CH<sub>2</sub>, *J* = 17.2, 1.5, 1.3 Hz), 5.02 d.d.d (1H, =CH<sub>2</sub>, *J* = 10.3, 1.5, 1.1 Hz), 6.16 d.d.d (1H, =CH, *J* = 17.2, 10.3, 7.8 Hz), 7.01–7.06 m (2H, C<sub>6</sub>H<sub>4</sub>), 7.14–7.32 m (5H, C<sub>6</sub>H<sub>5</sub>), 7.34–7.39 m (2H, C<sub>6</sub>H<sub>4</sub>). Found, %: C 70.35; H 6.97; Br 19.62; N 3.54. C<sub>24</sub>H<sub>28</sub>BrN. Calculated, %: C 70.24; H 6.88; Br 19.47; N 3.41.

**1-[1-(4-Bromophenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine (3d).** Yield 2.4 g (0.006 mmol, 75%), syrupy materials. IR spectrum, v, cm<sup>-1</sup>: 3030, 720, 710 (Ph), 1645–1640 (C=C), 835, 810 (C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.38–1.68 m (6H, β-H, γ-H, piperidine), 2.40–2.48 m (2H, NCH<sub>2</sub>, α-H, piperidine), 2.63–2.71 m (2H, NCH<sub>2</sub>, α-H, piperidine), 3.57 d.d.t (1H, CHPh, *J* = 10.8, 7.5, 1.6 Hz), 3.70 d (1H, NCH, *J* = 10.8 Hz), 4.92 d.d.d (1H, =CH<sub>2</sub>, *J* = 17.2, 1.6, 1.4 Hz), 5.02 d.d.d (1H, =CH<sub>2</sub>, *J* = 10.3, 1.6, 1.2 Hz), 6.20 d.d.d (1H, =CH<sub>4</sub>, *J* = 17.2, 10.3, 7.5 Hz), 7.01–7.05 m (2H, C<sub>6</sub>H<sub>4</sub>), 7.14–7.31 m (5H, C<sub>6</sub>H<sub>5</sub>), 7.34–7.38 m (2H, C<sub>6</sub>H<sub>4</sub>). Found, %: C 70.19; H 6.24; Br 20.39; N 3.69. C<sub>23</sub>H<sub>24</sub>BrN. Calculated, %: C 70.05; H 6.13; Br 20.26; N 3.55.

**4-[1-(4-Bromophenyl)-4-phenylhex-5-en-1-yn-3-yl]morpholine (3e).** Yield 2.3 g (0.059 mmol, 74%), syrupy material. IR spectrum, v, cm<sup>-1</sup>: 3030, 730, 690 (Ph), 1645–1640 (C=C), 840, 810 (C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.69–3.83 m [4H, O(CH<sub>2</sub>)<sub>2</sub>], 4.00–4.15 m [4H, N(CH<sub>2</sub>)<sub>2</sub>], 3.59 d.d.t (1H, CHPh, *J* = 10.7, 7.6, 1.5 Hz), 3.72 d (1H, NCH, *J* = 10.8), 4.92 d.d.d (1H, =CH<sub>2</sub>, *J* = 17.3, 1.5, 1.3 Hz), 5.01 d.d.d (1H, =CH<sub>2</sub>, *J* = 10.4, 1.5, 1.2 Hz), 6.23 d.d.d (1H, =CH, *J* = 17.2, 10.3, 7.5 Hz), 7.01–7.06 m (2H, C<sub>6</sub>H<sub>4</sub>), 7.14–

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7.32 m (5H,  $C_6H_5$ ), 7.34–7.38 m (2H,  $C_6H_4$ ). Found, %: C 66.79; H 5.71; Br 20.25; N 3.69.  $C_{22}H_{22}BrNO$ . Calculated, %: C 66.67; H 5.59; Br 20.16; N 3.53.

**1-[1-(4-Methylphenyl)-4-phenylhex-5-en-1-yn-3-yl]piperidine (3f).** Yield 1.97 g (0.006 mmol, 75%), syrupy material. IR spectrum, v, cm<sup>-1</sup>: 3025, 720, 700 (Ph), 1645–1640 (C=C), 835, 820 (C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR spectrum, δ, ppm: 1.35–1.66 m (6H, β-H, γ-H, piperidine), 2.35 s (3H, CH<sub>3</sub>), 2.42–2.48 m (2H, NCH<sub>2</sub>, α-H, piperidine), 2.64–2.71 m (2H, NCH<sub>2</sub>, α-H, piperidine), 3.56 d.d.t (1H, CHPh, J = 10.7, 7.6, 1.5 Hz), 3.73 d (1H, NCH, J = 10.8 Hz), 4.92 d.d.d (1H, =CH<sub>2</sub>, J = 17.3, 1.6, 1.3 Hz), 5.02 d.d.d (1H, =CH<sub>2</sub>, J = 10.2, 1.5, 1.1 Hz), 6.23 d.d.d (1H, =CH, J = 17.3, 10.4, 7.6 Hz), 7.02–7.06 m (2H, C<sub>6</sub>H<sub>4</sub>), 7.16–7.32 m (7H, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>). Found, %: C 87.61; H 8.38; N 4.37. C<sub>24</sub>H<sub>27</sub>N. Calculated, %: C 87.49; H 8.26; N 4.25.

**4-[1-(4-Methylphenyl)-4-phenylhex-5-en-1-yn-3-yl]morpholine (3g).** Yield 1.99 g (0.006 mmol, 75%), syrupy material. IR spectrum, v, cm<sup>-1</sup>: 3040, 720, 680 (Ph), 1645–1640 (C=C), 830, 820 (C<sub>6</sub>H<sub>4</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.32 s (3H, CH<sub>3</sub>), 2.46–2.56 m (2H, NCH<sub>2</sub>), 2.66–2.74 m (2H, NCH<sub>2</sub>), 3.58–3.71 m [4H, O(CH<sub>2</sub>)<sub>2</sub>], 3.58 d.d.t (1H, CHPh, *J* = 10.8, 7.7, 1.6 Hz), 3.75 d (1H, NCH, *J* = 10.8 Hz), 4.95 d.d.d (1H, =CH<sub>2</sub>, *J* = 17.2, 1.6, 1.2 Hz), 5.03 d.d.d (1H, =CH<sub>2</sub>, *J* = 17.2, 10.3, 1.6, 1.0 Hz), 6.21 d.d.d (1H, =CH, *J* = 17.2, 10.3, 7.7 Hz), 7.03–7.05 m (2H, C<sub>6</sub>H<sub>4</sub>), 7.16–7.31 m (7H, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>). Found, %: C 83.46; H 7.73; N 4.35. C<sub>23</sub>H<sub>25</sub>NO. Calculated, %: C 83.35; H 7.60; N 4.23.

Vacuum distillation of amines 3a–3g (general procedure). Amines 3a–3g (6 mmol) were subjected to vacuum distillation in a Claisen flask. Compound 4 or 5 crystallized in the Claisen adapter arm, and the crystals were mechanically pulled out therefrom. The still residue was washed off from the flask with xylene. Compounds 4 and 5 were recrystallized from xylene.

**4-Bromo-1,1':4',1"-terphenyl (4).** Yield 1.2 g (3.72 mmol, 62%), white crystals, mp 220–222°C (from xylene). IR spectrum, v, cm<sup>-1</sup>: 1580 (C=C<sub>arom</sub>), 820 (C<sub>6</sub>H<sub>4</sub>), 720, 680 (Ph). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.32 t.t (1H, *p*-H, *J* = 7.3, 1.3 Hz), 7.39–7.46 m (2H, *m*-H), 7.57 s (4H, C<sub>6</sub>H<sub>4</sub>), 7.59–7.63 m (4H, *o*-H), 7.66 s (4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 120.7, 126.2 (2C, CH), 126.6 (2C, CH), 126.8 (CH), 126.9 (2C, CH), 128.0 (2C, CH), 128.2 (2C, CH), 131.3 (2C, CH), 137.9, 138.8, 139.7. Found, %: C 69.68;

H 4.23; Br 25.67.  $C_{18}H_{13}Br$ . Calculated, %: C 69.90; H 4.21; Br 25.89.

**4-Methyl-1,1':4',1"-terphenyl (5).** Yield 0.9 g (3.6 mmol, 60%), yellowish crystals, mp 185–187°C (from xylene). IR spectrum, v, cm<sup>-1</sup>: 1580 (C=C<sub>arom</sub>), 820 (C<sub>6</sub>H<sub>4</sub>), 720, 680 (Ph). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.40 s (3H, CH<sub>3</sub>), 7.22 m (2H), 7.50 m (2H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.31 t.t (1H, *p*-H, *J* = 7.3, 2.2 Hz), 7.42 m (2H, *m*-H), 7.60 m (2H, *o*-H), 7.63 s (4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 121.7, 126.3 (2C, CH), 126.7 (2C, CH), 126.8 (CH), 128.2 (4C, CH<sub>arom</sub>), 126.9 (2C, CH), 127.8 (2C, CH), 128.2 (2C, CH), 128.3 (2C, CH), 132.5 (2C, CH), 137.9, 138.0, 139.6. Found, %: C 92.96; H 6.42. C<sub>19</sub>H<sub>16</sub>. Calculated, %: C 93.44; H 6.56.

## CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

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