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A simple and efficient synthesis of 1,3,5-tris[2-(3,5-diethynylphenyl)ethynyl]benzene from 1,3,5-triethynylbenzene

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Abstract A concise and convenient three-step process is reported for preparation of 1,3,5-tris[2-(3,5-diethynylphenyl)ethynyl]benzene from 1,3,5-triethynylbenzene and 2-hydroxypropyl group-protected peripheral monomers via a Sonogashira coupling–deprotection reaction sequence. This approach had several advantages, for example high yields, short reaction time, and simple separation procedure. In the key step a modified Sonogashira reaction was developed, under which conditions the coupling of 1,3,5-triethynylbenzene and substituted iodobenzenes proceeded rapidly, giving the desired products in good to excellent yields.

Keywords 1,3,5-Tris[2-(3,5-diethynylphenyl)ethynyl]benzene · Dendrimer · Sonogashira cross-coupling · 1,3,5-Triethynylbenzene · Deprotection reaction

Introduction

Phenylacetylene dendrimers have been the subject of extensive interest in recent years because of their unique shape-persistent molecular architecture, versatile functionality, and wide range of potential applications in light-harvesting molecular antennas, nonlinear optical materials, and organic light-emitting diodes [1–5]. As one of the first generation of phenylacetylene dendrimers formed solely from 1,3,5-triethynylphenyl units, 1,3,5-tris[2-(3,5-diethynylphenyl)ethynyl]benzene (**1**) acts not only as a potential key building block in dendrimer synthesis but also as an important model molecule for investigation of the physical and chemical properties

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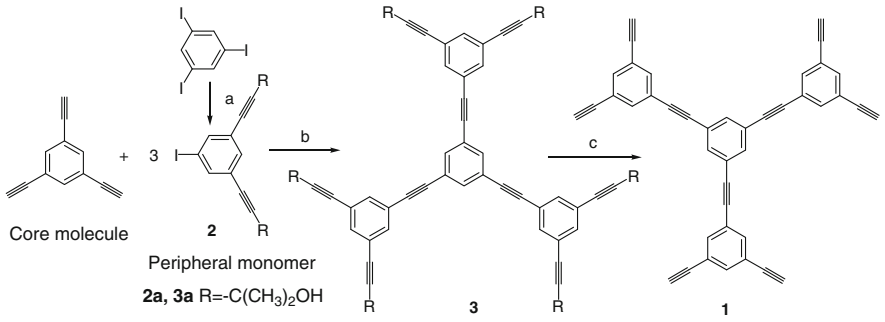
of these dendrimers [6–9]. Moore et al. were first to explore the synthetic methodology and properties of phenylacetylene dendrimers. Their findings were an important basis for subsequent investigation of related compounds [8, 10]. Rodríguez et al. prepared trimethylsilyl group-protected **1** and its ethynylphenyl homologues, and illustrated the relationship between their electronic properties and the number of the conjugated ethynylphenyl units [11]. Yamaguchi et al. synthesized methoxy group substituted analogs of **1**, and achieved the first organic molecules with light-emitting ability (in the violet–blue region with high fluorescence quantum yield) [12]. Qiu and Shah et al. examined the photophysical properties of the carbazole substituted analogs of **1**, and demonstrated that white electroluminescence could be obtained from a single phenylethynyl carbazole emitter [13]. Nakano et al. investigated theoretically the structural dependence of the exciton dynamics of the *p*-ethynylphenyl homologues of **1**, and elucidated the advantage of dendritic molecular systems for application in nano-optical and light-harvesting devices [14]. Nguyen et al. prepared the DNA-hybrid analogs of **1**. The dendrimer–DNA aggregates had sharpened switch-like melting transitions, which pointed the way for designing new DNA-based materials with enhanced recognition properties [15].

Despite its attractive properties and potential applications, most classical methods for synthesis of **1** were low yielding as they required a tedious process. The approaches often involved Sonogashira cross-coupling between a 1,3,5-triiodobenzene core and 3 equiv. ethynyl-terminated peripheral monomers with trialkylsilyl-protected ethynyl groups at the *meta* positions, and subsequent deprotection of the trialkylsilyl groups [6, 8, 10, 11, 16]. For example, by using an eight-step sequence, **1** was synthesized in an overall yield of only 19% [16]. On the other hand, by using a 1,3,5-triethynylbenzene core and iodine terminated peripheral monomers a simple three-step approach seemed very attractive (Scheme 1). However, Pesak found that Sonogashira cross-coupling of the monomers ($R = Si\textit{i}\text{-}Pr_3$) and 1,3,5-triethynylbenzene was low-yield, which could



Scheme 1 A simple synthetic route to **1**. For R = –$C(CH_3)_2OH$: *a* 2-methyl-3-butyn-2-ol, tris(dibenzylideneacetone)dipalladium, PPh_3, CuI, piperidine, 25 °C, 48%; *b* $Pd_2(dba)_3$, tris(2,4,6-trimethylphenyl)phosphine, CuI, *N*,*N*-diisopropylethylamine, tetrabutylammonium iodide, DMF, −20 °C, 92%; *c* tetrabutylammonium hydroxide, CH_3OH, toluene, 75 °C, 83%

be attributed to the relative instability of 1,3,5-triethynylbenzene. A likely side reaction was the self-coupling of triethynylbenzene [16].

In the work discussed in this paper, we developed the simple synthetic approach toward **1** described in Scheme 1, which reduced the number of reaction steps and improved the overall yield (37%). The crucial step was improvement of the Sonogashira cross-coupling of 1,3,5-triethynylbenzene with iodide-terminated monomers. In addition, 2-methyl-3-butyn-2-ol was used as the acetylene source for the peripheral monomers at the *meta* positions. Compared with alkylsilylacetylenes, 2-methyl-3-butyn-2-ol is much less expensive, and it couples with aryl halides in nearly quantitative yield. Furthermore, the coupling products can be easily purified by chromatography because of the very different chromatographic polarities of the products and the starting materials. To the best of our knowledge, this is the first report of the synthesis of phenylacetylene dendrimers bearing 2-hydroxypropyl protecting groups.

Results and discussion

Initially 1,3,5-triiodobenzene was treated with 2-methyl-3-butyn-2-ol under Sonogashira coupling conditions by using the tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$)–PPh_3–CuI catalyst system in piperidine at 25 °C to afford 1-iodo-3,5-bis[2-(2-hydroxypropyl)ethynyl]benzene (**2a**) in 48% yield. The high polarity of 2-methyl-3-butyn-2-ol facilitated separation of the desired bisethynylated product from the starting materials, and from the monoethynylated and the trisethynylated byproducts. We tried different amounts of 2-methyl-3-butyn-2-ol and found the best 2-methyl-3-butynl-2-ol to 1,3,5-triiodobenzene molar ratio was 1.8:1.

For synthesis of 3-cascade:benzene[3-1,3,5]:5-ethynyl-1,3-bis-[(2-hydroxyprop-2-yl)ethynyl]benzene (**3a**), Sonogashira cross-coupling of 1,3,5-triethynylbenzene and **2a** was performed under different reaction conditions (Table 1). When $Pd_2(dba)_3$–PPh_3–CuI was used as the catalyst system with Et_3N as the base and solvent, the reaction was carried out at 65 °C to afford **3a** in 29% yield (Table 1, entry 1). Using piperidine [17] as the base and solvent instead of Et_3N, **3a** was obtained in 67% yield after stirring at 25 °C for 3.5 h (Table 1, entry 2). Inspired by these results, we attempted to carry out the reaction at a lower temperature of −20 °C [18], and found that **3a** could be prepared in a higher yield. Tetrabutylammonium iodide (Bu_4NI) was reported to be an important additive for the cross-coupling reaction. Bu_4NI greatly accelerated the Pd-catalyzed coupling reaction, probably because it not only increased the ionic strength of the solvent but also stabilized the highly active Pd catalyst, which underwent oxidative addition of the aryl halide [19]. Unfortunately, the $Pd_2(dba)_3$–PPh_3–CuI–piperidine system had no activity at −20 °C, even with the addition of Bu_4NI, and no cross-coupling products could be detected by TLC even after stirring for 24 h (Table 1, entry 3). We examined the applicability of different bases and solvents and found that the Sonogashira cross-coupling reaction rate at −20 °C was highly dependent on the strength of the base and the polarity of the solvents. Compared with piperidine, *N*,*N*-diisopropylethylamine (*i*-Pr_2NEt) was a more effective base in DMF, giving **3a** in a

Table 1 Sonogashira cross-coupling of 1,3,5-triethynylbenzene and **2a** to afford **3a** under different reaction conditions

Entry	Base	Solvent	Additive	Phosphines ligand	Temp. (°C)	Time (h)	Yield (%)[a]
1	Et_3N	Et_3N	None	PPh_3	65	6	29
2	Piperidine	Piperidine	None	PPh_3	25	3.5	67
3	Piperidine	Piperidine	Bu_4NI	PPh_3	−20	24	0
4	Piperidine	DMF	Bu_4NI	PPh_3	−20	24	0
5	*i*-Pr_2NEt	DMF	Bu_4NI	PPh_3	−20	6	78
6	*i*-Pr_2NEt	DMF	Bu_4NI	$P(2,4,6\text{-triMeC}_6H_2)_3$	−20	2.5	92
7	*i*-Pr_2NEt	THF	Bu_4NI	$P(2,4,6\text{-triMeC}_6H_2)_3$	−20	24	0
8	*i*-Pr_2NEt	Toluene	Bu_4NI	$P(2,4,6\text{-triMeC}_6H_2)_3$	−20	24	0
9	*i*-Pr_2NEt	Dioxane	Bu_4NI	$P(2,4,6\text{-triMeC}_6H_2)_3$	−20	24	0

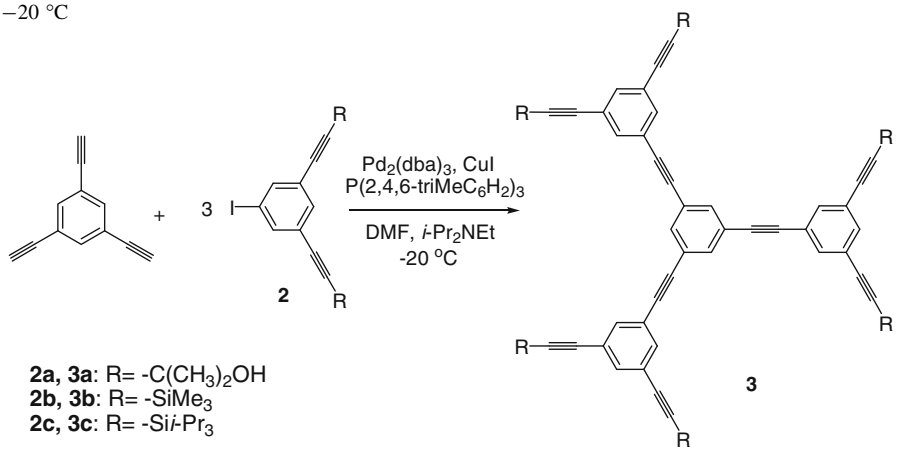
[a] Isolated yields

satisfactory yield of 78% after 6 h (Table 1, entries 4 and 5). Using tris(2,4,6-trimethylphenyl)phosphine ($P(2,4,6\text{-triMeC}_6H_2)_3$) as a bulky, electron-rich ligand [18] instead of PPh_3, compound **3a** was obtained in a high yield of 92% (Table 1, entry 6). Among all the solvents we used here, the polar solvent DMF [20] resulted in good reactivity, giving **3a** in 92% yield within 2.5 h (Table 1, entry 6), whereas other solvents, for example tetrahydrofuran (THF), toluene, and dioxane gave no cross-coupling products even after 24 h (Table 1, entries 7–9).

Thus the optimal reaction conditions at −20 °C required $Pd_2(dba)_3$–$P(2,4,6\text{-triMeC}_6H_2)_3$–CuI as the catalyst system, DMF as the solvent, and *i*-Pr_2NEt as the base with the addition of Bu_4NI. Dendrimer **3a** was obtained in 92% yield within 2.5 h. Besides **2a**, this method also tolerated the coupling of 1,3,5-triethynylbenzene with peripheral monomers **2b** and **2c**, giving **3b** and **3c** in satisfactory yields (Table 2). In comparison with **2b** and **2c**, **2a** bearing hydroxylisopropylethynyl instead of trialkylsilylethynyl groups at the *meta* positions yielded **3a** in the highest yield within the shortest time. The solubility of **2c** in DMF was poor, so the unfavorable solvent THF had to be added to improve the solubility (the optimized volume ratio was 1:4 for THF–DMF), and the yield of **3c** was lower than those of **3a** and **3b**.

In the final step **1** was prepared by removing the 2-hydroxypropyl protecting groups. Although the 2-hydroxypropyl groups were attractive in consideration of separation, the deprotection reaction always required harsh conditions (e.g., strong base, high temperature, and a long reaction time) [21–23]. Furthermore, for molecules bearing more than one 2-hydroxypropyl group, the deprotection yields were often low or long reaction time was required [24–26]. Compound **1** was obtained in only 10% yield when **3a** was treated with NaOH in toluene under reflux for 8 h (Table 3, entry 1). With addition of H_2O and tetrabutylammonium iodide (Bu_4NI, the phase-transfer catalyst), the complete deprotection reaction was achieved at 85 °C after 20 h, affording **1** in 42% yield (Table 3, entry 2). Most recently we explored the deprotection reaction and found that tetrabutylammonium hydroxide (Bu_4NOH) with methanol was a highly efficient catalyst system [27]. The

Table 2 Sonogashira cross-coupling of 1,3,5-triethynylbenzene with iodide terminated monomers at −20 °C



Entry	Ar–I	Time (h)	Yield (%)[a]
1	**2a**	2.5	92
2	**2b**	3	73
3	**2c**	3.5	55

Reaction conditions: triethynylbenzene (0.2 mmol), **2** (0.6 mmol), $Pd_2(dba)_3$ (0.015 mmol), CuI (0.12 mmol), $P(2,4,6\text{-triMeC}_6H_2)_3$ (0.12 mmol), *i*-Pr_2NEt (2 mmol), n-Bu_4NI (1.2 mmol), and DMF (8 mL), −20 °C

[a] Isolated yields

deprotection reaction was carried out in toluene in the presence of 10 mol % Bu_4NOH with 1.2 equiv. CH_3OH at 75 °C, giving the corresponding product **1** in a high yield of 83% after 5 min without any incompletely deprotected products (Table 3, entry 3).

Conclusion

In summary, we report a simple procedure with high overall yield (37%) for synthesis of 1,3,5-tris[2-(3,5-diethynylphenyl)ethynyl]benzene from 1,3,5-triethynylbenzene and 2-hydroxypropyl group-protected peripheral monomers via a Sonogashira coupling–deprotection reaction sequence. A modified Sonogashira reaction was developed for coupling 1,3,5-triethynylbenzene to substituted iodobenzenes. By

Table 3 Removal of the 2-hydroxypropyl groups to give **1** under different reaction conditions

Entry	Base (equiv.)	Temp. (°C)	Time (h)	Yield (%)[a]
1	NaOH (5)	110	8	10
2	5 M aqueous NaOH (75) with Bu_4NI (0.1)	85	20	42
3	Bu_4NOH (0.1) with CH_3OH (1.2)	75	0.08	83

[a] Isolated yields

using $Pd_2(dba)_3$–P(2,4,6-triMe$C_6H_2)_3$–CuI as the catalyst system, *i*-Pr_2NEt as the base, and DMF as the solvent in the presence of Bu_4NI, Sonogashira coupling of 1,3,5-triethynylbenzene with aryl iodides performed rapidly with good to excellent yields at −20 °C. The short reaction time and satisfactory isolated yields would make this method very suitable for further synthesis of new arylacetylene dendrimers from 1,3,5-triethynylbenzene.

Experimental

Unless otherwise indicated, all materials were obtained from commercial suppliers and were used without further purification. Before use, piperidine was distilled over calcium hydride, THF, toluene, and dioxane were distilled in the presence of sodium, and DMF was vacuum distilled over $MgSO_4$. Compound **2c** was prepared in accordance with the literature [16]. All reactions were performed under an atmosphere of nitrogen.

Melting points were determined on an XT5 hot-plate microscope apparatus. ^{1}H NMR and ^{13}C NMR spectra were acquired on JNM-AL300 and Varian-VNMRS500 NMR spectrometers. IR spectra were measured on a Nicolet NEXUS-470 FTIR spectrometer. Mass spectra were recorded on a Shimadzu GC/MS-QP5050A mass spectrometer (EI) or a Bruker Daltonics Autoflex III MALDI-TOF mass spectrometer, using 2,5-dihydroxybenzoic acid (DHB) as the matrix. Elemental analysis was performed with a vario EL III elemental analyzer.

Synthesis of 1-iodo-3,5-bis[2-(2-hydroxypropyl)ethynyl]benzene (**2a**)

$Pd_2(dba)_3$ (44 mg, 0.048 mmol), CuI (18 mg, 0.095 mmol), and PPh_3 (125 mg, 0.475 mmol) were added to a solution of 1,3,5-triiodobenzene (1.140 g, 2.5 mmol) in piperidine (15 mL). After addition of 2-methyl-3-butyn-2-ol (378 mg, 4.5 mmol) in piperidine (10 mL) the mixture was stirred at room temperature for 2 h followed by removal of the solvents under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL). The solution was washed with 5% HCl and brine, then dried over $MgSO_4$. After evaporation of the solvent under vacuum, the crude product was purified by silica gel column chromatography (petroleum ether–ethyl acetate 4:1) to afford **2a** as a white solid (441.8 mg, 48%). Mp: 123.6–125 °C; IR (KBr): 3334 (O–H), 3064 (Ar C–H), 2980 (Ar C–H), 2931 (C–H), 2868 (C–H), 2216 (C≡C), 1581 (Ar C=C), 1544 (Ar C=C), 1442, 1414, 1371 (C–H), 1240, 1150, 959, 863 (Ar C–H) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (s, 2H, Ar–H), 7.44 (s, 1H, Ar–H), 1.99 (s, 2H, –OH), 1.61 (s, 12H, –CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.85, 133.89, 124.68, 95.62, 92.90, 79.73, 65.51, 31.32; MS (EI) *m/z*: 368 (M^+), 353, 335, 43 (100). Anal: calcd. for $C_{16}H_{17}IO_2$ (368.21): C 52.19, H 4.65; found C 52.10, H 4.96.

Synthesis of 1-iodo-3,5-bis(2-trimethylsilylethynyl)benzene (**2b**)

Following the method for the synthesis of **2a** (trimethylsilyl)acetylene (441 mg, 4.5 mmol) was added instead of 2-methyl-3-butyn-2-ol. Purification was carried out

by silica gel column chromatography (petroleum ether), giving **2b** as a colorless viscous oil (456 mg, 46%). IR (KBr): 2958 (Ar C–H), 2924 (C–H), 2855 (C–H), 2158 (C≡C), 1579 (Ar C=C), 1542 (Ar C=C), 1411 (C–H), 1251, 1162, 974, 849 (Ar C–H) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 2H, Ar–H), 7.49 (s, 1H, Ar–H), 0.21 (s, 18H, $–CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.21, 134.46, 125.01, 102.26, 96.60, 92.86, −0.21; MS (EI) *m/z*: 396 (M^+), 381 (100). Anal: calcd. for $C_{16}H_{21}ISi_2$ (396.42): C 48.48, H 5.34; found C 49.44, H 5.81.

General procedure for synthesis of **3**

Compound **2** (0.6 mmol), Bu_4NI (443 mg, 1.2 mmol), P(2,4,6-tri$MeC_6H_2)_3$ (46 mg, 0.12 mmol), $Pd_2(dba)_3$ (14 mg, 0.015 mmol), CuI (23 mg, 0.12 mmol) and *i*-Pr_2NEt (259 mg, 2 mmol) were dissolved in 8 mL DMF in a dry Schlenk flask (for **3c** 2 mL THF was added simultaneously as the co-solvent). After cooling to −20 °C 1,3,5-triethynylbenzene (30 mg, 0.2 mmol) was added and the mixture was stirred at −20 °C for the time indicated in Table 1. Then saturated aqueous NH_4Cl was added to quench the reaction. The resulting mixture was extracted with CH_2Cl_2 (50 mL). The extracts were washed with 5% HCl and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by silica gel column chromatography.

3-Cascade:benzene[3-1,3,5]:5-ethynyl-1,3-bis-[(2-hydroxyprop-2-yl)ethynyl]benzene (**3a**)

Eluent, petroleum ether–ethyl acetate 1:1; yield: 165 mg, 92%; white solid; mp: >260 °C (decomp.); IR (KBr): 3355 (–OH), 3062 (Ar C–H), 2978 (Ar C–H), 2931 (C–H), 2869 (C–H), 2220 (C≡C), 2156 (C≡C), 1587 (Ar C=C), 1421 (C–H), 1363 (C–H), 1240, 1164, 948, 877 (Ar C–H) cm^{-1}; ^1H NMR (300 MHz, DMSO-d6): δ 7.83 (s, 3H, Ar–H), 7.55 (d, $J = 1.5$ Hz, 6H, Ar–H), 7.40 (s, 3H, Ar–H), 5.53 (s, 6H, –OH), 1.46 (s, 36H, $–CH_3$); ^{13}C NMR (125 MHz, DMSO-d6) δ 134.45, 134.04, 133.33, 123.91, 123.25, 122.91, 97.88, 89.10, 88.59, 78.48, 63.61, 31.39; MS (MALDI-TOF, DHB) *m/z*: 892.9 ($M + Na^+$). Anal: calcd. for $C_{60}H_{54}O_6$ (871.09): C 82.73, H 6.25; found C 79.79, H 6.99.

3-Cascade:benzene[3-1,3,5]:5-ethynyl-1,3-bis-(2-trimethylsilyethynyl)benzene (**3b**)

Eluent, petroleum ether; yield: 140 mg, 73%; white solid; mp: 242–244 °C; IR (KBr): 2958 (Ar C–H), 2921 ($–CH_3$ C–H), 2853, 2156 (C≡C), 1587 (Ar C=C), 1410 (C–H), 1249, 1162, 1021, 981, 879 (Ar C–H), 843 (Ar C–H) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.58–7.54 (m, 12H, Ar–H), 0.23 (s, 54H, $–CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.22, 134.65, 134.38, 123.88, 123.71, 123.21, 103.04, 95.89, 89.02, 88.52, −0.18. Anal: calcd. for $C_{60}H_{66}Si_6$ (955.70): C 75.41, H 6.96; found C 75.23, H 7.01.

3-Cascade:benzene[3-1,3,5]:5-ethynyl-1,3-bis-(2-triisopropylsilylethynyl)benzene (**3c**)

Eluent, petroleum ether; yield: 161 mg, 55%; white solid; mp: 262–263 °C; IR (KBr): 2943 (Ar C–H), 2891 (C–H), 2864 (C–H), 2219 (C≡C), 2154 (C≡C), 1773, 1585 (Ar C=C), 1462, 1424, 1411 (C–H), 1383 (C–H), 1365 (C–H), 1161, 1072, 1017, 980, 881 (Ar C–H) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.66 (s, 3H, Ar–H), 7.58 (d, $J = 1.5$ Hz, 6H, Ar–H), 7.53 (t, $J = 1.5$ Hz, 3H, Ar–H), 1.28–1.16 (m, 126H, $-CH(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.92, 134.77, 134.39, 124.21, 123.71, 123.16, 105.11, 92.38, 89.11, 88.57, 18.60, 11.28. Anal: calcd. for $C_{96}H_{138}Si_6$ (1460.66): C 78.94, H 9.52; found C 78.66, H 9.25.

Synthesis of 1,3,5-tris[2-(3,5-diethynylphenyl)ethynyl]benzene (**1**)

Bu_4NOH, 40 wt. % solution in CH_3OH (78 mg, Bu_4NOH 0.12 mmol) was added to a solution of **3a** (178.6 mg, 0.2 mmol) in toluene (60 mL). The mixture was stirred at 75 °C for 5 min. After cooling to room temperature, the mixture was washed with 5% HCl, brine, dried over $MgSO_4$, and concentrated under vacuum. The mixture was filtered through a short plug of silica gel, eluting with THF. After the product-containing filtrate was evaporated, the residue was recrystallized from toluene to give **1** as a white fuzzy solid (87 mg, 83%). IR (KBr): 3285 (C≡C–H), 3063 (Ar C–H), 2217 (C≡C), 2156 (C≡C), 2109, 1589 (Ar C=C), 1426 (Ar C=C), 1017, 880 (Ar C–H) cm^{-1}; ^1H NMR (300 MHz, DMSO-d6): δ 7.84–7.62 (m, 12H, Ar–H), 4.38 (s, 6H, C≡C–H); ^{13}C NMR (75 MHz, DMSO-d6): δ 134.91, 134.60, 134.49, 123.10, 123.0, 88.85, 88.76, 82.69, 81.31; MS (EI) *m/z*: 522 (M^+), 128, 101, 86 (100), 78, 58, 26. Anal: calcd. for $C_{42}H_{18}$ (522.60): C 96.53, H 3.47; found C 96.31, H 3.92.

References

1. D. Astruc, E. Boisselier, C. Ornelas, Chem. Rev. **110**, 1857 (2010)
2. Y. Jiang, L. Wang, Y. Zhou, Y. Cui, J. Wang, Y. Cao, J. Pei, Chem. Asian J. **4**, 548 (2009)
3. A.C. Grimsdale, K.L. Chan, R.E. Martin, P.G. Jokisz, A.B. Holmes, Chem. Rev. **109**, 897 (2009)
4. S. Lo, P.L. Burn, Chem. Rev. **107**, 1097 (2007)
5. J.M.J. Fréchet, J. Polym. Sci., Part A **41**, 3713 (2003)
6. T. Itoh, T. Maemura, Y. Ohtsuka, Y. Ikari, H. Wildt, K. Hirai, H. Tomioka, Eur. J. Org. Chem. **2004**, 2991 (2004)
7. K. Sato, D. Shiomi, T. Takui, M. Hattori, K. Hirai, H. Tomioka, Mol. Cryst. Liq. Cryst. **376**, 549 (2002)
8. D.J. Pesak, J.S. Moore, Macromolecules **30**, 6467 (1997)
9. T.S. Ahn, A.L. Thompson, P. Bharathi, A. Müller, C.J. Bardeen, J. Phys. Chem. B **110**, 19810 (2006)
10. Z. Xu, M. Kahr, K.L. Walker, C.L. Wilkins, J.S. Moore, J. Am. Chem. Soc. **116**, 4537 (1994)
11. J.G. Rodríguez, J. Esquivias, A. Lafuente, C. Díaz, J. Org. Chem. **68**, 8120 (2003)
12. Y. Yamaguchi, T. Ochi, S. Miyamura, T. Tanaka, S. Kobayashi, T. Wakamiya, Y. Matsubara, Z. Yoshida, J. Am. Chem. Soc. **128**, 4504 (2006)
13. R.M. Adhikari, L. Duan, L. Hou, Y. Qiu, D.C. Neckers, B.K. Shah, Chem. Mater. **21**, 4638 (2009)
14. M. Nakano, R. Kishi, T. Minami, K. Yoneda, Molecules **14**, 3700 (2009)
15. B.R. Stepp, J.M. Gibbs-Davis, D.L.F. Koh, S.T. Nguyen, J. Am. Chem. Soc. **130**, 9628 (2008)
16. D. Pesak, Ph.D. Thesis, University of Illinois (1995)

17. U.H.F. Bunz, Chem. Rev. **100**, 1605 (2000)
18. K. Nakamura, H. Okubo, M. Yamaguchi, Synlett **10**, 549 (1999)
19. N.A. Powell, S.D. Rychnovsky, Tetrahedron Lett. **37**, 7901 (1996)
20. M. Imoto, M. Takeda, A. Tamaki, H. Taniguchi, K. Mizuno, Res. Chem. Intermed. **35**, 957 (2009)
21. E. Glimsdal, M. Carlsson, T. Kindahl, M. Lindgren, C. Lopes, B. Eliasson, J. Phys. Chem. A **114**, 3431 (2010)
22. A. Nagy, Z. Novák, A. Kotschy, J. Organomet. Chem. **690**, 4453 (2005)
23. Y. Jiang, B. Gao, W. Huang, Y. Liang, G. Huang, Y. Ma, Synth. Commun. **39**, 197 (2009)
24. A.P. Melissaris, M.H. Litt, J. Org. Chem. **59**, 5818 (1994)
25. D.L. Trumbo, C.S. Marvel, J. Polym. Sci. **24**, 2311 (1986)
26. S. Chen, Q. Yan, T. Li, D. Zhao, Org. Lett. **12**, 4784 (2010)
27. J. Li, P. Huang, Beilstein J. Org. Chem. **7**, 426 (2011)