The preparation of diarylacetylenes *via* diphenyl (benzotriazol-1-yl)(aryl)methylphosphonates

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Dedicated to Professor Gerasimos (Mike) Karabatsos on his 70th anniversary
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Abstract
A variety of differently substituted diarylacetylenes **10a–k** were obtained in good to excellent yields by a simple reaction sequence *via* 1-(benzotriazol-1-yl)-1-arylmethylphosphonic acid esters **8a–c** and 1-(benzotriazolyl)-1,2-diarylethylenes **9a–k**.

Keywords: Acetylene, diarylacetylene, benzotriazole, synthesis, phosphonate

Introduction

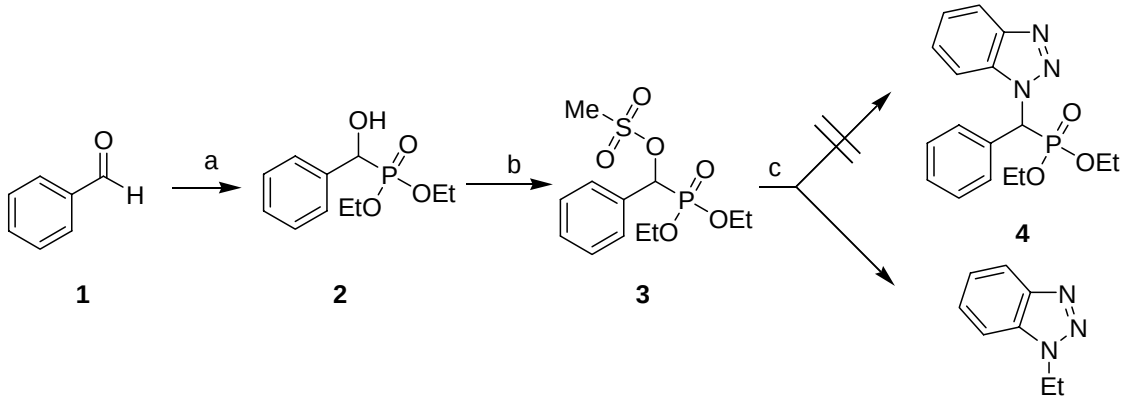
Acetylenes are important reagents in organic synthesis and material science.[1] Many recent investigations in alkyne chemistry, particularly on diarylacetylenes, are dedicated to the synthesis of linear chain molecules with extended conjugation as potential molecular scale wires[2] and light-emitting chemiluminiscent fluorophores.[3] Diarylacetylenes are widely used as building blocks for the synthesis of diverse carbo-[4] and heterocycles.[5] Synthetic approaches to diarylacetylenes have been adapted for solid phase synthesis.[6]

Syntheses of diarylacetylenes have been widely investigated and summarized.[1,7] Common routes for triple bond formation include (i) conversion of 1,1-diaryl-2-chloro(or bromo)ethenes in liquid ammonia in the presence of potassium amide to afford symmetrical products;[8] (ii) base catalyzed elimination of HX (X = Cl, Br) from 2-substituted-1-aryl-1-chloroethanes formed from the corresponding benzyl ketones with an acetyl halide in the presence of ZnX_2/SiO_2 (X=Cl, Br);[9] and (iii) reactions of *N*-benzylbenzotriazoles with arylideneamines in the presence of an excess of strong base.[10] During the last decade, much attention was devoted to the synthesis of aryl and diaryl alkynes by palladium and copper catalyzed coupling of arylacetylenes. Thus, diarylacetylenes were formed (i) from terminal alkynes by the reaction with aryliodonium salts[11] and with aryl or heteroaryl halides under Pd(0) catalysis,[12] (ii) by palladium catalyzed reactions

of silicon derivatives with aryl halides[13] or triarylantimony(V)diacetals,[14] and (iii) by reactions of tin derivatives with aryl iodides.[15] Although many of these methods afford high yields, the availability of starting terminal arylalkynes, especially those of heteroaryl derivatives, is limited. We now report an efficient and simple protocol for the preparation of diarylacetylenes via 1-(benzotriazol-1-yl)-1-arylmethylphosphonic **8** acid esters and 1-(benzotriazolyl)-1,2-diarylethylenes **9**.

Results and Discussion

Reactions of aldehydes with amines and phosphite esters to form α-amino phosponates are well known. Analogous α-amino derivatives of benzotriazole are also well known and have found a wide scope of applications.[16] However, our attempt to prepare (benzotriazol-1-yl)(phenyl-methyl)phosphonic acid diethyl ester **4** in a one pot reaction failed. Addition of diethyl phosphite to benzaldehyde **1** in the presence of MgO proceeds smoothly with the formation of 1-hydroxyphenylmethylphosphonate **2** in 90-96% yield.[17] Compound **2** with methanesulfonyl chloride gave the desired methanesulfonic acid (diethoxyphosphoryl)phenylmethyl ester **3** in 70–90% yield. However, subsequent reaction of compound **3** with benzotriazole or its sodium salt gave mostly ethylbenzotriazole **5** by an Arbuzov type reaction (Scheme 1).



1 **2** **3** **4** **5**

a) MgO, $HPO(OEt)_2$, neat, rt; b) MsCl, Et_3N, DCM, -10 ^oC-rt; c) BtNa, PhH, reflux

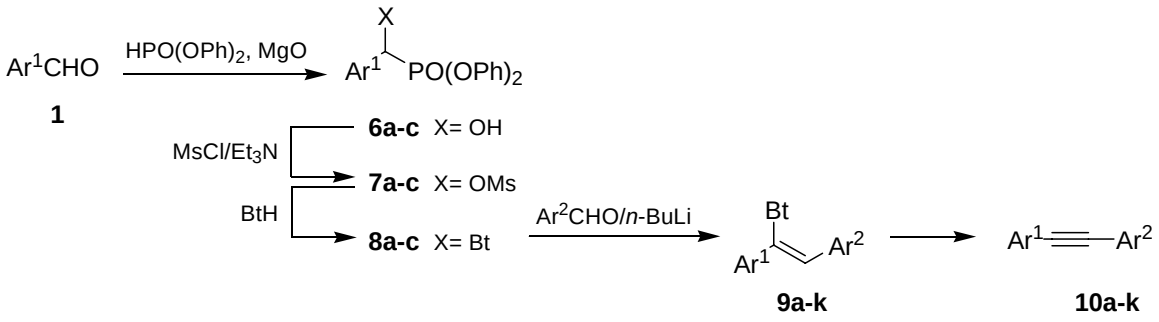
Scheme 1

The use of diphenyl phosphite eliminates the possibility of an Arbuzov reaction and affords the analogous derivatives **8a-c** in 55–75% yield. This simple procedure succeeds with a variety substituents in the aromatic rings of products **8a–c** (Scheme 2, Table 1).

Table 1. Isolated yields for compounds **6a–c**, **7a–c** and **8a–c**

Entry	Compound	Ar^1	Yield of **6**	Yield of **7**	Yield of **8**
1	**a**	Ph	89	84	73
2	**b**	4-$CH_3C_6H_4$	94	78	56
3	**c**	4-ClC_6H_4	94	82	84

The obtained (benzotriazolyl)(arylmethyl)diphenylphosphonates **8a–c** were lithiated by addition of *n*-butyllithium at –78°C, and the derived anions were condensed with aldehydes to give the benzotriazolylethylene intermediates **9a–k**. As reported previously,[10] derivatives **9a–k** can be easily converted into the corresponding acetylenes **10a–k** by the elimination of benzotriazole in the presence of potassium *tert*-butoxide in DMF at 70-80°C. It was found that such procedure is suitable for the elimination of a benzotriazole moiety from compounds of type **9,** including heterocycle-substituted diarylethenes (Scheme 2, Table 2).



Scheme 2

Table 2. Isolated yields for compounds **9a–k** and **10a–k**

Entry	Compound	Starting	Ar^2	Yield of **9**	Yield of **10**
1	**a**	**8a**	4-$CH_3C_6H_4$	68	88
2	**b**	**8a**	Ph	88	64
3	**c**	**8a**	4-$O_2NC_6H_4$	92	84
4	**d**	**8b**	4-$CH_3C_6H_4$	84	88
5	**e**	**8b**	1-naphthyl	67	87
6	**f**	**8b**	2-pyridinyl	86	64
7	**g**	**8b**	2-furyl	78	62
8	**h**	**8b**	2-thiophenyl	83	76
9	**i**	**8c**	Ph	63	48
10	**j**	**8c**	1-naphthyl	73	75
11	**k**	**8c**	3-pyridinyl	64	88

An extension of the reported protocol was attempted for the preparation of arylalkyl derivatives. 1-(Benzotriazol-1-yl)-1-phenyl-2-cyclohexylethene **11** was obtained by the same reaction sequence as for diaryl derivatives. However, the elimination of benzotriazole from the compound **11** failed; no reaction was observed.

Conclusions

We have developed a convenient procedure for the preparation of diarylacetylenes *via* diphenyl (benzotriazolyl)(aryl)methylphosphonates **8a–c**. The reaction sequence utilized standard preparative procedures with simple purification techniques and resulted in acetylenes **10a–k** with a variety of substituents, including heteroaromatic moieties. All the reactions were performed under mild conditions and final diarylacetylenes **10a–k** were obtained in good to excellent yields. The procedure developed may be suitable for combinatorial use.

Experimental Section

General Procedures. Melting points were determined using a capillary melting point apparatus equipped with a digital thermometer and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz NMR spectrometer (300 and 75 MHz, respectively) using $CDCl_3$ or DMSO-d_6 as solvents with tetramethylsilane as an internal standard. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone immediately before use. Column chromatography was conducted with silica gel grade 230–400 mesh. All other reagents were of reagent grade and were used without purification.

General procedure for the preparation of diphenyl aryl(hydroxy)methylphosphonates (6a–c) Magnesia (0.806 g, 0.02 mol) was added to a mixture of diphenyl hydrogen phosphite (4.68 g, 0.02 mol) and aldehyde **1a–c** (0.02 mol). This mixture was stirred at room temperature for 24 h. The resultant solid mixture was washed with DCM (4 x 25 mL), and the product was isolated in a pure state by filtration through silica gel followed by recrystallization from an appropriate solvent. Due to coupling on phosphorus some carbon signals are overlapped in the ^{13}C NMR and spectra appear as described.

Diphenyl hydroxy(phenyl)methylphosphonate (6a). White needles (6.06 g, 89%), mp 127–128 °C (DCM/hexanes; lit.[18a] mp 129–131 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 1H), 5.31 (d, 1H, *J* = 9.0 Hz), 7.00 (d, 2H, *J* = 8.4 Hz), 7.05 (d, 2H, *J* = 8.4 Hz), 7.10–7.17 (m, 2H), 7.22–7.30 (m, 4H), 7.35–7.39(m, 3H), 7.56–7.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.0 (d, *J* = 165.9 Hz), 119.6 (d, *J* = 4.0 Hz), 124.0 (d, *J* = 2.3 Hz), 126.7 (d, *J* = 6.3 Hz), 127.2 (d, *J* = 2.9 Hz), 128.5 (d, *J* = 2.9 Hz), 135.8, 149.3 (d, *J* = 9.7 Hz), 149.5 (d, *J* = 10.3 Hz).

Diphenyl hydroxy(4-methylphenyl)methylphosphonate (6b). White needles (6.66 g, 94%) (DCM/hexanes), mp 100–101 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 4.35 (br s, 1H), 5.22 (d, 1H, *J* = 8.7 Hz), 7.01 (d, 2H, *J* = 7.5 Hz), 7.07 (d, 2H, *J* = 7.5 Hz), 7.10–7.18 (m, 4H), 7.20–7.30 (m, 5H), 7.44 (d, 1H, *J* = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 70.4 (d, *J* = 161.9 Hz), 120.5 (d, *J* = 4.6 Hz), 120.6 (d, *J* = 4.0 Hz), 125.1 (d, *J* = 6.8 Hz), 127.4 (d, *J* = 6.2 Hz), 129.1 (d, *J* = 2.8 Hz), 129.6 (d, *J* = 5.7 Hz), 132.4, 138.3 (d, *J* = 3.4 Hz), 150.3 (d, *J* = 10.25 Hz). Anal. Calcd for $C_{20}H_{19}O_4P$ (354.35): C, 67.79; H, 5.40. Found: C, 67.68; H, 5.33.

Diphenyl 4-chlorophenyl(hydroxy)methylphosphonate (6c). White needles (7.05 g, 94%) (DCM/hexanes), mp 110–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.42 (br s, 1H), 5.24 (d, 1H, *J* = 8.7 Hz), 6.98–7.10 (m, 4H), 7.10–7.20 (m, 2H), 7.20–7.38 (m, 6H), 7.42–7.52 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.8 (d, *J* = 160.5 Hz), 120.5 (d, *J* = 4.0 Hz), 120.6 (d, *J* = 4.6 Hz), 125.3 (d, *J* = 8.5 Hz), 128.5 (d, *J* = 2.2 Hz), 128.7 (d, *J* = 6.2 Hz), 129.7 (d, *J* = 6.8 Hz), 134.2, 150.1 (d, *J* = 10.2 Hz), 150.2 (d, *J* = 9.1 Hz). Anal. Calcd for $C_{19}H_{16}ClO_4P$ (374.76): C, 60.89; H, 4.30; Found: C, 60.66; H, 4.65.

General procedure for the preparation of aryl(diphenoxyphosphoryl)methyl methanesulfonates (7a–c)

To a solution of compound **6** (0.05 mol) and triethylamine (8.10 g, 0.08 mol) in DCM (100 mL) at –10 ºC was added dropwise methanesulfonyl chloride (5.73 g, 0.05 mol) under vigorous stirring. Stirring for an additional 10–15 min completed the reaction. Then the reaction mixture was washed with ice water, cold 10% hydrochloric acid, saturated sodium bicarbonate solution and brine. After drying over $MgSO_4$, evaporation of solvent gave crude product, which was recrystallized from an appropriate solvent. Due to coupling on phosphorus some carbon signals are overlapped in the ^{13}C NMR and spectra appear as described.

(Phenyl)(diphenoxyphosphoryl)methyl methanesulfonate (7a). White needles (17.5 g, 84%) (DCM/ hexanes), mp 75–76 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.87 (s, 3H), 6.11 (d, 1H, *J* = 15 Hz), 7.0 (d, 2H, *J* = 7.2 Hz), 7.07–7.22 (m, 4H), 7.22–7.38 (m, 4H), 7.41–7.48 (m, 3H), 7.58–7.68 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.6, 76.9 (d, *J* = 175.3 Hz), 120.3 (d, *J* = 4.6 Hz), 120.4 (d, *J* = 4.6 Hz), 125.5, 128.5 (d, *J* = 6.2 Hz), 129.0 (d, *J* = 1.7 Hz), 129.7 (d, *J* = 1.7 Hz), 130.1 (d, *J* = 2.8 Hz), 131.0, 149.7 (d, *J* = 9.1 Hz), 149.8 (d, *J* = 9.7 Hz). Anal. Calcd for $C_{20}H_{19}O_6PS$ (418.41): C, 57.41; H, 4.58; Found: C, 57.42; H, 4.38.

(Diphenoxyphosphoryl)(4-methylphenyl)methyl methanesulfonate (7b). White needles (16.86 g, 78%) (DCM/hexanes), mp 133–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.84 (s, 3H), 6.06 (d, 1H, *J* = 14.7 Hz), 7.01 (d, 2H, *J* = 7.5 Hz), 7.14–7.31 (m, 10H), 7.52 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 39.8, 77.0 (d, *J* = 176.5 Hz), 120.4 (d, *J* = 4.5 Hz), 120.5 (d, *J* = 3.4 Hz), 125.6, 127.8, 128.6 (d, *J* = 6.8 Hz), 128.7 (d, *J* = 3.5 Hz), 129.7 (d, *J* = 2.3 Hz), 129.8 (d, *J* = 3.5 Hz), 140.3, 149.8 (d, *J* = 9.7 Hz), 150.0 (d, *J* = 10.3 Hz). Compound was used without purification for the further transformations.

Diphenoxyphosphoryl(4-chlorophenyl)methyl methanesulfonate (7c). White needles (18.56 g, 82%) (DCM/hexanes), mp 100–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.94 (s, 3H),

6.08 (d, 1H, *J* = 15 Hz), 7.02 (d, 2H, *J* = 7.8 Hz), 7.11 (d, 2H, *J* = 7.8 Hz), 7.20 (t, 2H, *J* = 6.9 Hz), 7.22–7.36 (m, 5H), 7.42 (d, 2H, *J* = 8.4 Hz), 7.58 (d, 2H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.7, 76.0 (d, *J* = 174.2 Hz), 120.2 (d, *J* = 4.0 Hz), 120.3 (d, *J* = 4.0 Hz), 125.7, 129.3 (d, *J* = 2.3 Hz), 129.7, 129.9, 136.2 (d, *J* = 3.4 Hz), 149.6 (d, *J* = 9.2 Hz), 149.8 (d, *J* = 9.7 Hz). Anal. Calcd for $C_{20}H_{18}ClO_6PS$ (452.85): C, 53.05; H, 4.01; Found: C, 53.26; H, 4.07.

General procedure for the preparation of diphenyl (1*H*-benzotriazol-1-yl)(aryl)methylphosphonate 8a-c

A mixture of (diphenoxyphosphoryl)(aryl)methyl methanesulfonate **7a-c** (0.025 mol) with benzotriazole (5.96 g, 0.05 mol) in toluene (150 mL) was refluxed for 48 h. The mixture was cooled down to room temperature, washed with sat. Na_2CO_3, water, brine and dried over Na_2SO_4. The solvent was removed *in vacuo* to give a brown residue, which was purified on silica (eluent hexanes:EtOAc 3:1) to give the desired products **8a-c**.

Diphenyl (1*H*-benzotriazol-1-yl)(phenyl)methylphosphonate (8a). White needles (8.06 g, 73%) (ethyl acetate/hexanes), mp 133–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74 (d, 1H, *J* = 23.7 Hz), 6.85 (d, 2H, *J* = 8.1 Hz), 6.98 (d, 2H, *J* = 8.1 Hz), 6.99–7.30 (m, 6H), 7.32–7.45 (m, 5H), 7.67 (d, 1H, *J* = 8.4 Hz), 7.68–7.73 (m, 2H), 8.07 (d, 1H, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 60.0 (d, *J* = 158.2 Hz), 110.3, 120.1 (d, *J* = 4.6 Hz), 120.3 (d, *J* = 4.0 Hz), 124.3, 125.5 (d, *J* = 11.3 Hz), 128.0, 129.2, 129.6 (d, *J* = 11.9 Hz), 130.2 (d, *J* = 6.8 Hz), 132.6 (d, *J* = 3.4 Hz), 135.5 (d, *J* = 2.8 Hz), 146.0, 149.6 (d, *J* = 10.8 Hz). Anal. Calcd for $C_{25}H_{20}N_3O_3P$ (441.43): C, 68.02; H, 4.57; N, 9.52. Found: C, 67.93; H, 4.63; N, 9.52.

Diphenyl (1*H*-benzotriazol-1-yl)(4-methylphenyl)methylphosphonate (8b). White needles (6.38 g, 56%) (ethyl acetate/hexanes), mp 148–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 6.71 (d, 1H, *J* = 23.4 Hz), 6.85 (d, 2H, *J* = 8.1 Hz), 7.00 (d, 2H, *J* = 8.1 Hz), 7.03–7.29 (m, 8H), 7.32–7.48 (m, 2H), 7.60 (d, 1H, *J* = 7.5 Hz), 7.66 (d, 1H, *J* = 8.1 Hz), 8.05 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0, 60.4 (d, *J* = 158.3 Hz), 110.6, 119.9, 120.1 (d, *J* = 4.5 Hz), 120.4 (d, *J* = 4.0 Hz), 124.1, 125.4 (d, *J* = 11.4 Hz), 127.7, 128.1, 128.8 (d, *J* = 7.4 Hz), 129.5, 129.6 (d, *J* = 2.8 Hz), 132.6 (d, *J* = 3.4 Hz), 139.4 (d, *J* = 2.3 Hz), 146.0, 149.7 (d, *J* = 2.8 Hz), 149.8 (d, *J* = 2.8 Hz). Anal. Calcd for $C_{26}H_{22}N_3O_3P$ (455.46): C, 68.57; H, 4.87; N, 9.23. Found: C, 68.59; H, 5.12; N, 9.10.

Diphenyl (1*H*-benzotriazol-1-yl)(4-chlorophenyl)methylphosphonate (8c). White prisms (9.99 g, 84%) (ethyl acetate/hexanes), mp 113–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.69 (d, 1H, *J* = 23.7 Hz), 6.86 (d, 2H, *J* = 8.1 Hz), 6.99 (d, 2H, *J* = 8.0 Hz), 7.04–7.12 (m, 1H), 7.12–7.20 (m, 3H), 7.24–7.30 (m, 2H), 7.32–7.40 (m, 3H), 7.40–7.49 (m, 1H), 7.64 (m, 3H), 8.08 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 59.9 (d, *J* = 158.2 Hz), 110.3, 120.1 (d, *J* = 4.0 Hz), 120.2, 120.4 (d, *J* = 4.0 Hz), 124.4, 125.6 (d, *J* = 12.4 Hz), 128.1, 129.3, 129.7 (d, *J* = 11.9 Hz), 130.2 (d, *J* = 6.8 Hz), 132.6 (d, *J* = 3.4 Hz), 135.6 (d, *J* = 2.3 Hz) 140.6, 149.7 (d, *J* = 9.0 Hz). Anal. Calcd for $C_{25}H_{19}ClN_3O_3P$ (475.88): C, 63.10; H, 4.02; N, 8.83. Found: C, 62.99; H, 3.92; N, 8.71.

General procedure for the preparation of 1,2-diaryl-1-(benzotriazol-1-yl)ethenes 9a–k and compound 11

To a solution of diphenyl 1*H*-benzotriazol-1-yl(aryl)methylphosphonate **8a–c** (5 mmol) in 4 mL of dry THF at –78°C under N_2, *n*-BuLi (5.1 mmol) was added. The mixture was stirred at –78°C for 10 min, then the respective aldehyde (5 mmol) was added dropwise and the reaction mixture was stirred at –78°C for 10 min. The acetone-dry ice bath was removed and the mixture was allowed to warm up to room temperature over 40 min and quenched with sat. NH_4Cl. The mixture was twice extracted with EtOAc, the combined extracts were washed with sat. NH_4Cl, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a brown residue, which was purified on silica (hexanes/EtOAc=3:1 as eluent) to give the desired products **9a–k**.

1-[2-(4-Methylphenyl)-1-phenylethenyl]-1*H*-benzotriazole (9a). White needles (1.06 g, 68%) (hexanes), mp 118–119 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 6.80 (d, 1H, *J* = 8.4 Hz), 7.03 (d, 2H, *J* = 7.8 Hz), 7.12 (d, 2H, *J* = 7.8 Hz), 7.20–7.41 (m, 8H), 8.08 (d, 1H, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 30.9, 111.4, 120.0, 124.0, 126.0, 127.5, 129.1, 129.5, 129.7, 131.4, 132.7, 133.8, 134.4, 138.0, 146.3. Anal. Calcd for $C_{21}H_{17}N_3$ (311.39): C, 81.00; H, 5.50; N, 13.49. Found: C, 80.62; H, 5.37; N, 13.42.

1-(Benzotriazol-1-yl)-1,2-diphenylethylene (9b). White prisms (1.31 g, 88%) (hexanes), mp 111–112 °C (lit mp[10a] 111–113 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79 (d, 1H, *J* = 7.8 Hz), 7.18–7.48 (m, 13H), 8.08 (d, 1H, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.4, 120.1, 124.1, 125.9, 127.6, 128.0, 128.3, 129.1, 129.6, 129.7, 129.8, 132.7, 133.6, 134.3, 135.2, 146.3. Anal. Calcd for $C_{20}H_{15}N_3$ (297.36): C, 80.78; H, 5.08; N, 14.13. Found: C, 80.74; H, 5.24; N, 14.28.

1-[2-(4-Nitrophenyl)-1-phenylethenyl]-1*H*-benzotriazole (9c). Yellow needles (1.57 g, 92%) (hexanes) mp 167–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.60 (d, 1H, *J* = 8.4 Hz), 7.22–7.56 (m, 10H), 8.07–8.13 (m, 3H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.5, 120.4, 122.2, 123.7, 124.4, 128.0, 129.6, 130.0, 130.2, 130.6, 132.4, 132.5, 138.6, 141.4, 146.5, 146.7. Anal. Calcd for $C_{20}H_{14}N_4O_2$ (342.36): C, 70.17; H, 4.12; N, 16.36. Found: C, 70.32; H, 4.28; N, 16.11.

1-[1,2-Bis(4-methylphenyl)ethenyl]-1*H*-benzotriazole (9d). Colorless oil (1.37 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.39 (s, 3H), 6.83 (d, 1H, *J* = 7.8 Hz), 7.03 (d, 2H, *J* = 8.1 Hz), 7.10–7.38 (m, 9H), 8.08 (d, 1H, *J* = 8,1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 21.5, 111.5, 120.0, 124.0, 125.5, 127.4, 129.0, 129.4, 129.6, 129.8, 130.8, 131.6, 132.7, 134.5, 137.9, 139.6, 146.3. This compound was used as a crude material without isolation.

1-[1-(4-Methylphenyl)-2-(1-naphthyl)ethenyl]-1*H*-benzotriazole (9e). White needles (1.21 g, 67%) (hexanes), mp 122–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 6.88 (d, 1H, *J* = 8.1 Hz), 6.97–7.04 (m, 4H), 7.21–7.39 (m, 4H), 7.50–7.55 (m, 2H), 7.71 (s, 1H), 7.78 (d, 1H, *J* = 8.1 Hz), 7.86–7.91 (m, 1H), 8.10 (d, 1H, *J* = 4.2 Hz), 8.14 (d, 1H, *J* = 8.1 Hz), ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.4, 111.6, 120.1, 123.6, 124.1, 124.3, 125.4, 126.1, 126.5, 127.5, 127.9, 128.3, 128.6, 129.4, 130.4, 132.0, 132.2, 132.9, 133.5, 137.0, 139.4, 146.4. Anal. Calcd for $C_{25}H_{19}N_3$ (361.45): C, 83.08; H, 5.30; N, 11.63. Found: C, 82.78; H, 5.42; N, 11.53.

1-[1-(4-Methylphenyl)-2-(2-pyridinyl)ethenyl]-1*H*-benzotriazole (9f). White needles (1.34 g, 84%) (hexanes), mp 105–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H), 6.81 (d, 1H, *J* = 7.8 Hz), 7.05–7.23 (m, 6H), 7.25–7.38 (m, 3H), 7.45 (t, 1H, *J* = 8.1 Hz), 8.09 (d, 1H, *J* = 8.1 Hz), 8.61 (d, 1H, *J* = 4.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 111.6, 120.2, 122.1, 124.2, 124.3, 127.7, 129.7, 129.8, 130.1, 132.7, 135.7, 138.5, 140.3, 146.5, 149.8, 154.5. Anal. Calcd for $C_{20}H_{16}N_4$ (312.38): C, 76.90; H, 5.16; N, 17.94. Found: C, 76.76; H, 5.25; N, 17.91.

1-[2-(2-Furyl)-1-(4-methylphenyl)ethenyl]-1*H*-benzotriazole (9g). White needles (1.17 g, 78%), mp 127–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 6.22 (d, 1H, *J* = 3 Hz), 6.34 (s, 1H), 6.74 (d, 1H, *J* = 8.1 Hz), 7.12 (s, 1H), 7.20–7.39 (m, 7H), 8.06 (d, 1H, *J* = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 111.5, 111.6, 113.2, 120.0, 124.0, 127.5, 128.3, 129.5, 129.6, 130.7, 132.6, 133.0, 140.0, 142.7, 146.4, 150.1. Anal. Calcd for $C_{19}H_{15}N_3O$ (301.35): C, 75.73; H, 5.02; N, 13.94. Found: C, 75.96; H, 5.20; N, 13.50.

1-[1-(4-Methylphenyl)-2-(2-thienyl)ethenyl]-1*H*-benzotriazole (9h). White needles (1.32 g, 83%), mp 140–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (s, 3H), 6.74 (d, 1H, *J* = 7.8 Hz), 6.94 (dd, 1H, J_1 = 3.9 Hz, J_2 = 1.2 Hz), 7.01 (d, 1H, *J* = 3.3 Hz), 7.14 (d, 1H, *J* = 5.1 Hz), 7.21–7.27 (m, 4H), 7.40 (d, 2H, *J* = 8.1 Hz), 7.51 (s, 1H), 8.06 (d, 1H, *J* = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 111.5, 118.1, 120.1, 124.0, 126.6, 126.7, 127.5, 130.0, 130.1, 130.2, 132.5, 133.4, 137.6, 140.5, 146.4. Anal. Calcd for $C_{19}H_{15}N_3S$ (317.42): C, 71.90; H, 4.76; N, 13.24. Found: C, 72.19; H, 4.97; N, 13.29.

1-(Benzotriazol-1-yl)-1-(4-chlorophenyl)-2-phenylethylene (9i). Yellow oil (1.05 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 (dd, 1H, J_1 = 5.7 Hz, J_2 = 2.7 Hz); 7.20–7.28 (m, 7H); 7.28–7.42 (m, 6H); 8.11 (dd, 1H, J_1 = 6.0 Hz, J_2 = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.2, 120.3, 124.2, 126.6, 127.8, 128.3, 129.4, 129.4, 129.5, 129.9, 131.1, 132.1, 132.6, 134.1, 135.6. This compound was used as a crude material without isolation.

1-[1-(4-Chlorophenyl)-2-(1-naphthyl)ethenyl]-1*H*-benzotriazole (9j). White prisms (1.39 g, 73%), mp 137–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95 (d, 1H, *J* = 7.8 Hz), 7.06 (d, 2H, *J* = 8.1 Hz), 7.17 (d, 2H, *J* = 8.4 Hz), 7.22–7.44 (m, 4H), 7.48–7.58 (m, 2H), 7.74–7.85 (m, 2H), 7.85–7.94 (m, 1H), 8.02–8.12 (m, 1H), 8.15 (d, 1H, *J* = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.2, 120.3, 124.2, 124.4, 125.0, 125.4, 126.3, 126.7, 127.9, 128.0, 128.7, 129.1, 130.9, 131.5, 132.0, 132.0, 132.8, 133.6, 135.3, 135.9, 146.4. Anal. Calcd for $C_{24}H_{16}ClN_3$ (381.87): C, 75.49; H, 4.22; N, 11.00. Found: C, 75.84; H, 4.31; N, 10.64.

1-[1-(4-Chlorophenyl)-2-(3-pyridinyl)ethenyl]-1*H*-benzotriazole (9k). Oil (1.06 g, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.78 (d, 1H, *J* = 8.1 Hz), 7.14–7.22 (m, 1H), 7.22–7.90 (m, 3H), 7.90–7.43 (m, 4H), 7.48 (d, 1H, *J* = 8.1 Hz), 8.12 (d, 1H, *J* = 7.5 Hz), 8.43–8.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.1, 120.3, 121.9, 123.3, 124.4, 128.0, 129.8, 130.3, 131.0, 131.1, 132.3, 136.0, 136.1, 136.3, 146.4, 148.8, 150.5. This compound was used as a crude material without isolation.

1-[(Z)-2-Cyclohexyl-1-phenylethenyl]-1*H*-1,2,3-benzotriazole (11). White needles (0.97 g, 64%), mp 111–112 °C; ^{1}H NMR δ 1.10–1.44 (m, 5H), 1.60–1.88 (m, 5H), 2.44–2.62 (m, 1H), 6.18 (d, 1H, *J* = 10.8 Hz), 6.89 (m, 1H), 7.20–7.32 (m, 4H), 7.33–7.49 (m, 3H), 8.05 (m, 1H).

^{13}C NMR δ 25.4, 25.7, 33.1, 37.0, 111.0, 119.9, 123.8, 127.3, 128.7, 128.8, 129.0, 132.8, 133.6, 134.2, 134.5, 146.1. Anal. Calcd for $C_{20}H_{21}N_3$: N, 13.85. Found: N, 13.83.

General procedure for the preparation of acetylenes 10a–k

A stirred solution of *t*-BuOK (0.90 g, 8.0 mmol) and 1,2-diaryl-1-(1*H*-1,2,3-benzotriazol-1yl)ethane **9a–k** (4.0 mmol) in DMF (8 mL) was heated at 80 °C for 10 min. The reaction mixture was cooled to 25°C and ice water was added. The obtained mixture was extracted with Et_2O (3 x 20 mL), combined organic extracts were washed with water (4 x 20 mL), dried over $MgSO_4$, and evaporated. The crude product was purified on silica (EtOAc/Hexanes 1/3 as an eluent) to give the desired acetylenes **10a–k**.

Phenyl-(*p*-tolyl)acetylene (10a). Yellow prisms (0.677 g, 88%), mp 75–78 °C (lit. mp[10a] 77–79 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.15 (d, 2H, *J* = 7.8 Hz), 7.28–7.38 (m, 3H), 7.42 (d, 2H, *J* = 7.8 Hz), 7.46–7.56 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 88.7, 89.5, 120.2, 123.5, 128.1, 128.3, 129.1, 131.5, 131.6, 138.4. Anal. Calcd for $C_{15}H_{12}$ (192.26): C, 93.71; H, 6.29; Found: C, 93.38; H, 6.70.

Diphenylacetylene (10b). White prisms (0.456 g, 64%), mp 59–61 (lit. mp[8b] 58–61 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.34 (m, 6H), 7.53 (d, 4H, *J* = 4.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 89.3, 123.2, 128.2, 128.3, 131.6. Anal. Calcd for $C_{14}H_{10}$ (178.24): C, 94.34; H, 5.66; Found: C, 94.39; H, 6.03.

Phenyl(4-nitrophenyl)acetylene (10c). Yellow prisms (0.750 g, 84%), mp 113–114 °C; ^{1}H NMR δ 7.38–7.42 (m, 3H), 7.55–7.58 (m, 2H), 7.67 (d, 2H, *J* = 8.7 Hz), 8.22 (d, 2H, *J* = 8.4 Hz), ^{13}C NMR δ 87.5, 94.7, 122.1, 123.6, 128.5, 129.3, 130.2, 131.8, 132.2, 146.9. Calcd for $C_{14}H_9NO_2$ (223.23): N, 6.27; Found: N, 6.10.

Di-*p*-tolylacetylene (10d). Yellow prisms (0.726 g, 88%), mp 122–123 °C (lit. mp[18c] 123–124 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 6H), 7.14 (d, 4H, *J* = 7.8 Hz), 7.41 (d, 4H, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 88.8, 120.4, 129.1, 131.4, 138.2.

1-(*p*-Tolylethynyl)naphthalene (10e). Yellow prisms (0.843 g, 87%), mp 55–56 °C (lit. mp[8d] 55–56 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 3H), 7.32 (d, 2H, *J* = 8.1 Hz), 7.46–7.60 (m, 1H), 7.61–7.68 (m, 4H), 7.90 (d, 1H, *J* = 7.2 Hz), 7.90–8.05 (m, 2H), 8.62 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 86.9, 94.5, 120.3, 121.1, 125.2, 126.2, 126.3, 126.7, 128.2, 128.5, 129.1, 130.1, 131.5, 133.1, 133.2, 138.5. Anal. Calcd for $C_{19}H_{14}$ (242.32): C, 94.18; H, 5.82. Found: C, 93.90; H, 6.03.

2-(*p*-Tolylethynyl)pyridine (10f). Yellow prisms (0.495 g, 64%), mp 60–61 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.17 (d, 1H, *J* = 7.8 Hz), 7.20–7.27 (m, 2H), 7.43–7.54 (m, 3H), 7.67 (td, 1H, J_1 = 7.8 Hz, J_2 = 1.8 Hz), 7.62 (d, 1H, *J* = 4.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 89.0, 89.4, 119.0, 122.5, 126.9, 129.0, 131.8, 136.0, 139.1, 143.5, 149.9. Anal. Calcd for $C_{14}H_{11}N$ (193.25): N, 7.25. Found: N, 7.45.

2-Furyl(4-methylphenyl)acetylene (10g). Yellow oil (0.452 g, 62%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 6.42 (dd, 1H, J_1 = 3.0 Hz; J_2 = 1.8 Hz), 6.63 (d, 1H, *J* = 3.6 Hz), 7.15 (d, 2H, *J* = 8.1 Hz), 7.41 (d, 1H, *J* = 2.4 Hz), 7.42 (d, 2H, *J* = 3.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$):

δ 21.5, 78.7, 93.4, 111.0, 114.9, 119.1, 129.1, 131.3, 137.3, 138.9, 143.4. HRMS EI for $C_{13}H_{10}O$ [M^+] 182.0732 Found: 182.0726.

2-(*p*-Tolylethynyl)thiophene (10h). Yellow prisms (0.603 g, 76%), mp 58–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 1H), 7.00 (t, 1H, *J* = 4.5 Hz), 7.15 (d, 2H, *J* = 7.8 Hz), 7.22–7.28 (m, 2H), 7.40 (d, 2H, *J* = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 81.9, 93.2, 119.8, 123.5, 127.0, 127.0, 129.1, 131.3, 131.6, 138.6. Anal. Calcd for $C_{13}H_{10}S$ (198.29): C, 78.75; H, 5.08; Found: C, 78.63; H, 5.46.

(4-Chlorophenyl)phenylacetylene (10i). White prisms (0.408 g, 48%), mp 80–81 °C (lit. mp[18e] 81–82 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27–7.39 (m, 5H), 7.42–7.49 (m, 2H), 7.49–7.56 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.2, 90.3, 121.7, 122.9, 128.4, 128.4, 128.6, 131.5, 132.8, 134.2. Anal. Calcd for $C_{14}H_9Cl$ (212.68): C, 79.06; H, 4.27; Found: C, 78.93; H, 4.23.

1-[2-(4-Chlorophenyl)ethynyl]naphthalene (10j). White prisms (0.788 g, 75%), mp 84–85 °C; ^{1}H NMR δ (300 MHz, $CDCl_3$): 7.35 (d, 2H, *J* = 8.4 Hz), 7.40–7.66 (m, 5H), 7.74 (d, 1H, *J* = 6.9 Hz), 7.78–7.90 (m, 2H), 8.39 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.5, 93.1, 120.5, 121.8, 125.2, 126.1, 126.5, 126.8, 128.3, 128.7, 129.0, 130.5, 132.8, 133.2, 134.3. Anal. Calcd for $C_{18}H_{11}Cl$ (262.74): C, 82.29; H, 4.22; Found: C, 82.13; H, 4.29.

3-[2-(4-Chlorophenyl)ethynyl]pyridine (10k). White prisms (0.752 g, 88%), mp 82–83 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22–7.42 (m, 3H), 7.48 (d, 2H, *J* = 8.4 Hz), 7.81 (d, 1H, *J* = 8.1 Hz), 7.57 (d, 1H, *J* = 4.8 Hz), 8.76 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.9, 91.4, 120.1, 121.0, 123.0, 128.8, 132.9, 134.9, 138.4, 148.8, 152.2. Anal. Calcd for $C_{13}H_8ClN$ (213.67): C, 73.08; H, 3.77; N, 6.56. Found: C, 72.95; H, 3.65; N, 6.48.

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