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A Novel Access to Disubstituted Acetylenes

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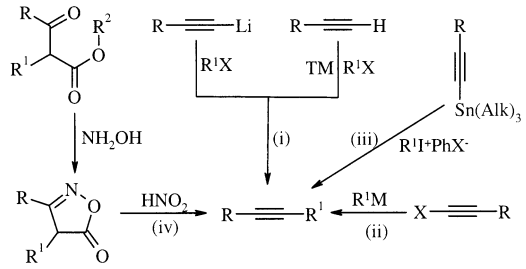
Abstract: Reactions of organometallic reagents with 1-(substituted ethynyl)-1*H*-1,2,3-benzotriazoles **5** derived from a variety of benzotriazolylmethyl ketones **3** afforded disubstituted acetylenes in synthetically useful yields.

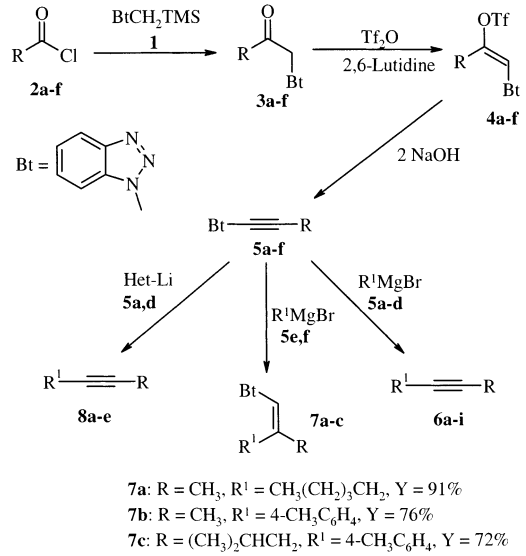
Over the years, continuous attention has been devoted to acetylene chemistry. The acetylenic bond plays a significant role in organic reactions and in applications ranging from material science to biochemistry.[1a,b] Important methods for the synthesis of acetylenes include the following (Scheme 1): (i) from terminal acetylenes by alkylation of carbanionic intermediates,[2a,b] or by transition metal-promoted cross-couplings with alkyl or aryl halides;[3a−e] (ii) reactions of halogenoacetylenes with Grignards, organolithium reagents,[4a,b] or organostannanes;[5a,b] (iii) reactions of alkynylstannanes with iodonium salts;[6] and (iv) reaction of *β*-keto-ester with hydroxylamine to obtain first the corresponding isoxazol-5-one followed by nitrosation.[7]

In method ii, the degree of success depends on a number of factors, including the nature of the halide, the solvent, and the organometallic reagent. In the absence of catalysis by other metals, reactions with Grignard reagents are limited to alkylmagnesium halides; with both alkenyl and aryl Grignards, metal−halogen interchange occurs. In the reaction with organolithium reagents, the usual reaction is halogen−metal exchange with formation of an alkynyllithium. Benzotriazole is a good leaving group, which can be used in place of a halogen in many reactions.[8] We now disclose the first examples of the displacement of the benzotriazole moiety from 1-arylethynyl-1*H*-1,2,3-benzotriazoles by organometallic reagents, which provides a new synthetic pathway from acid chlorides to disubstituted acetylenes: RCOCl + $BtCH_2SiMe_3$ → $RCOCH_2Bt$ → RC≡CBt → RC≡CR^1 when R^1 can be alkyl, allyl, aryl, or heteroaryl.

SCHEME 1



SCHEME 2[a]



[a] For designation of R, R^1 in **6** and R, Het in **8** see Table 1.

One-Pot Synthesis of 1-(Substituted ethynyl)-1*H*-1, 2,3-benzotriazoles 5. Direct alkynylation is convenient for the preparation of many alkynyl derivatives. Kitamura's group prepared 1-(arylalkynyl)benzotriazoles by way of reaction with arylethynyl(phenyl)iodonium tosylates in yields of 55−62%,[9a,b] but failed to obtain *N*-(alkylethynyl)benzotriazoles. Recently,[10] 1-(substituted ethynyl)benzotriazoles **5** were synthesized in yields of 90−98% by treatment of (*E*)-2-(1*H*-1,2,3-benzotriazole-1-yl)-1-(substituted ethenyl)trifluoromethane-sulfonates (**4**) with 2 N NaOH. This procedure has now been simplified to provide a one-pot synthesis of **5** (Scheme 2).

Treatment of *N*-acylmethylbenzotriazoles (**3a**−**f**) with triflic anhydride (Tf_2O) in the presence of 2,6-lutidine in

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TABLE 1. Synthesis of Acetylenes 6 and 8 via Alkynylation of Organometallic Reagents with 1-(Arylethynyl)benzotriazoles 5

entry	R	R^1/Het	yield (%)
6a	C_6H_5	$CH_3(CH_2)_3CH_2$	76
6b	C_6H_5	$CH_2{=}CH{-}CH_2$	79
6c	2-naphthyl	$CH_3(CH_2)_3CH_2$	83
6d	2-naphthyl	$CH_2{=}CH{-}CH_2$	75
6e	4-BrC_6H_4	$CH_2{=}CH{-}CH_2$	81
6f	4-$CH_3C_6H_4$	C_6H_5	51
6g	2-naphthyl	C_6H_5	63
6h	2-naphthyl	4-ClC_6H_4	70
6i	4-BrC_6H_4	C_6H_5	68
8a	C_6H_5	thiophen-2-yl	58
8b	4-BrC_6H_4	thiophen-2-yl	65
8c	C_6H_5	benzothiophen-2-yl	70
8d	4-BrC_6H_4	benzothiophen-2-yl	62
8e	C_6H_5	benzofuran-2-yl	67

CH_2Cl_2 at 0−20 °C for 2−12 h affords the corresponding enol triflates **4a**−**f**. Removal of the solvent and treatment with 2 N NaOH in THF at 20 °C gave the 1-(substituted ethynyl)-1*H*-1,2,3-benzotriazoles **5a**−**f** in 70−90% yields. The ^{13}C NMR spectra of alkynylbenzotriazoles **5a**−**f** revealed two characteristic signals of the acetylenic bond at 66.9−76.1 and 76.3−80.3 ppm.

Reactions of Alkynylbenzotriazoles 5 with Organometallic Reagents. Treatment of 1-arylethynyl-1*H*-1,2,3-benzotriazoles **5a**−**d** with Grignard reagents in dry toluene at −45 to 20 °C afforded acetylenes **6a**−**i** (Scheme 2, Table 1). This synthetic route provided the known compounds **6a**,**b**,**f**,**g** in yields comparable with those reported in the literature.[3c,6,7,11] The yields of previously unreported acetylenes **6c**−**e**,**h**,**i** were 68−83%. The NMR spectra of the displacement products **6a**−**i** clearly showed the disappearance of the characteristic benzotriazolyl signals and the data for the known compounds are consistent with those reported in the literature. The acetylenic bond signals in ^{13}C NMR spectra were shifted downfield as compared to those of their precursors due to the loss of the benzotriazolyl group.

The reaction of 1-(alkylethynyl)benzotriazoles **5e**,**f** with Grignard reagents under the same reaction conditions provided only the cis addition products **7a**−**c** in 76−91% yields, instead of the expected products of type **6** (Scheme 2). No trans isomers were detected in the NMR spectra of the crude **7a**−**c**. This cis configuration of **7** was established by NOE: for example, irradiation of the vinylic proton of **7b** at 7.21 ppm showed NOE effects on the methyl group protons at 2.36 ppm. Elemental analyses and NMR spectral data supported the structure of **7a**−**c**. In ^{13}C NMR spectra, the newly formed olefinic bond in compounds **7a**−**c** was exhibited at 116.8−118.7 and 138.8−143.0 ppm.

Heterocyclic lithio-derivatives (generated by lithiation of the corresponding heterocycle[12a,b]) reacted with intermediates **5a**,**d** to give 1-aryl-2-heterylacetylenes **8a**−**e** in 58−70% yields (Scheme 2, Table 1). This synthetic route improved the previously reported yield[13] of compound **8e** from 4% to 67% and afforded previously unreported derivatives of benzothiophene **8c**,**d**.

This approach for the synthesis of disubstituted acetylenes is advantageous compared with the closest literature analogy, which is the reaction of halogenoacetylenes with Grignard or organolithium reagents[4a,b] (Scheme 1, ii). It utilitizes commercially available starting materials (e.g. RCO_2H and heteroaromatic in the case of heteroaromatic acetylenes), and requires no transition metal catalyst. Thus, 1-(arylethynyl)benzotriazoles constitute superior alkynylating agents for organometallic reagents.

In summary, we have developed a convenient method for the preparation of alkynylbenzotriazoles **5** starting from *N*-acylmethylbenzotriazoles **3**. These alkynylbenzotriazoles have interesting synthetic potential, and their reaction with organometallic reagents provides a new, efficient, and broadly applicable synthetic methodology for the synthesis of disubstituted acetylenes.

Experimental Section

General. Melting points were determined on a hot stage apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as internal standard for ^1H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Microanalyses were performed on a Carlo Erba 1106 elemental analyzer. Anhydrous solvents were obtained by distillation immediately prior to use, from calcium hydride (dichloromethane) or from sodium (toluene). Column chromatography was conducted with silica gel 200−425 mesh. $BtCH_2TMS$ (**1**) and *N*-(acylmethyl)benzotriazoles **3a**−**f** were prepared according to literature procedures.[14]

General Procedure for the Preparation of 1-(Substituted ethynyl)benzotriazoles 5a−**f.** Triflic anhydride (15 mmol) was added dropwise to a mixture of *N*-(acylmethyl)benzotriazoles **1** (10 mmol) and 2,6-lutidine (15 mmol) in dry dichloromethane (50 mL) at 0−20 °C for 2−12 h. The mixture was concentrated under reduced pressure, and the residue was treated with 2 N NaOH (10 mL) in THF (30 mL) at 20 °C for 1 h. The mixture was then diluted with ethyl acetate, washed with water, and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue was purified by column chromatography with CH_2Cl_2 as an eluent.

1-(2-Phenylethynyl)-1*H*-1,2,3-benzotriazole (5a). Colorless crystals (76%), mp 78−79 °C (lit.[10] mp 78−78.5 °C). ^1H NMR δ 7.42−7.50 (m, 4H), 7.62−7.67 (m, 3H), 7.75 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H). ^{13}C NMR δ 75.8, 79.8, 110.1, 120.5, 120.6, 125.3, 128.6, 129.4, 129.5, 131.8, 134.2, 143.9.

1-[2-(4-Methylphenyl)ethynyl]-1*H*-1,2,3-benzotriazole (5b). Solid (70%), mp 86−88 °C (lit.[10] mp 84−85 °C). ^1H NMR δ 2.39 (s, 3H), 7.22 (d, J = 7.7 Hz, 2H), 7.43−7.54 (m, 3H), 7.62 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H). ^{13}C NMR δ 21.5, 75.2, 79.9, 110.1, 117.5, 120.5, 125.2, 129.2, 129.3, 131.8, 134.2, 139.8, 143.9.

1-[2-(2-Naphthyl)ethynyl]-1*H*-1,2,3-benzotriazole (5c). Pale yellow solid (88%), mp 146−148 °C. ^1H NMR δ 7.48−7.56 (m, 3H), 7.64−7.67 (m, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.84−7.89 (m, 3H), 8.13−8.16 (m, 2H). ^{13}C NMR δ 76.0, 80.3, 110.2, 117.9, 120.6, 125.3, 126.9, 127.3, 127.8, 127.9, 128.0, 128.4, 129.4, 132.2, 132.8, 133.3, 134.3, 144.0. Anal. Calcd for $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60. Found: C, 80.06; H, 3.97; N, 15.51.

1-[2-(4-Bromophenyl)ethynyl]-1*H*-1,2,3-benzotriazole (5d). Pale yellow plates (85%), mp 142−144 °C. ^1H NMR δ 7.47−7.59 (m, 5H), 7.66 (t, J = 11 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H). ^{13}C NMR δ 76.1, 78.9, 110.1, 119.7, 120.7, 124.0, 125.4, 129.5, 132.0, 133.2, 134.2, 143.9. Anal. Calcd for $C_{14}H_8BrN_3$: C, 56.40; H, 2.70; N, 14.09. Found: C, 56.42; H, 2.67; N, 13.84.

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1-(1-Propynyl)-1*H*-1,2,3-benzotriazole (5e). Colorless solid (82%), mp 37−38 °C. ^{1}H NMR δ 2.22 (s, 3H), 7.41 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H). ^{13}C NMR δ 3.6, 66.9, 76.3, 110.0, 120.3, 124.9, 129.0, 134.3, 143.7. Anal. Calcd for $C_9H_7N_3$: C, 68.77; H, 4.49; N, 26.73. Found: C, 68.49; H, 4.85; N, 26.67.

1-(4-Methyl-1-pentynyl)-1*H*-1,2,3-benzotriazole (5f). Pale yellow oil (90%). ^{1}H NMR δ 1.12 (d, J = 6.6 Hz, 6H), 1.98−2.07 (m, 1H), 2.50 (d, J = 6.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.57−7.67 (m, 2H), 8.09 (d, J = 8.2 Hz, 1H). ^{13}C NMR δ 22.0, 27.7, 27.9, 68.7, 79.5, 110.0, 120.3, 125.0, 129.0, 134.4, 143.7. Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.58; N, 21.09. Found: C, 72.01; H, 6.89; N, 21.19.

General Procedure for the Preparation of Acetylenes 6a−i. To a solution of 1-arylethynyl-1*H*-1,2,3-benzotriazole (1 mmol) in dry toluene (10 mL) was added Grignard reagent (2 equiv, 1.0 M THF solution) dropwise at −45 °C. The resulting mixture was stirred at this temperature for 2 h and then allowed to warm to 20 °C. After quenching with water and extraction with ethyl acetate (3 × 10 mL), the combined organic extracts were dried over $MgSO_4$. The solvent was removed in vacuo and the resulting oil was purified by column chromatography (eluent: hexanes) to give the pure product.

1-Phenyl-1-heptyne (6a).[3c] Colorless liquid (76%). ^{1}H NMR δ 0.92 (t, J = 6.9 Hz, 3H), 1.26−1.46 (m, 4H), 1.58−1.63 (m, 2H), 2.39 (t, J = 7.1 Hz, 2H), 7.25−7.27 (m, 3H), 7.38−7.39 (m, 2H). ^{13}C NMR δ 14.0, 19.4, 22.2, 28.5, 31.1, 80.5, 90.5, 124.1, 127.4, 128.1, 131.5. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.45; H, 9.74.

1-(4-Penten-1-ynyl)benzene (6b). Colorless liquid (79%) (lit.[15] bp 60 °C/0.3 mm). ^{1}H NMR δ 3.25 (dt, J = 5.2, 1.9 Hz, 2H), 5.20 (dq, J = 9.9, 1.8 Hz, 1H), 5.47 (dq, J = 17.0, 1.8 Hz, 1H), 5.87−6.00 (m, 1H), 7.43−7.49 (m, 2H), 7.74−7.81 (m, 2H), 7.94 (s, 1H). ^{13}C NMR δ 23.7, 82.9, 86.5, 116.2, 123.7, 127.7, 128.2, 131.6, 132.4.

2-(1-Heptynyl)naphthalene (6c). Colorless liquid (83%). ^{1}H NMR δ 0.93 (t, J = 7.1 Hz, 3H), 1.26−1.46 (m, 4H), 1.58−1.63 (m, 2H), 2.39 (t, J = 7.1 Hz, 2H), 7.25−7.27 (m, 3H), 7.38−7.39 (m, 2H). ^{13}C NMR δ 14.0, 19.4, 22.2, 28.5, 31.1, 80.5, 90.5, 124.1, 127.4, 128.1, 131.5. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.45; H, 9.74.

2-(4-Penten-1-ynyl)naphthalene (6d). Colorless liquid (75%). ^{1}H NMR δ 3.20 (dt, J = 5.3, 1.7 Hz, 2H), 5.17 (dq, J = 10.0, 1.7 Hz, 1H), 5.41 (dq, J = 17.0, 1.7 Hz, 1H), 5.85−5.97 (m, 1H), 7.26−7.31 (m, 5H), 7.41−7.44 (m, 2H). ^{13}C NMR δ 23.8, 83.2, 86.3, 116.3, 121.0, 126.3, 126.4, 127.6, 127.7, 127.8, 128.6, 131.2, 132.4, 132.6, 133.0. HRMS calcd for $C_{15}H_{12}$: 192.2603. Found: 192.0955.

1-Bromo-4-(4-penten-1-ynyl)benzene (6e). Colorless liquid (81%). ^{1}H NMR δ 3.18 (dt, J = 5.2, 1.8 Hz, 2H), 5.17 (dq, J = 9.9, 1.8 Hz, 1H), 5.38 (dq, J = 16.9, 1.9 Hz, 1H), 5.82−5.95 (m, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H). ^{13}C NMR δ 23.7, 81.8, 87.9, 116.4, 121.9, 122.6, 131.4, 132.1, 133.0. HRMS calcd for $C_{11}H_9Br$: 221.0965. Found: 221.0917.

1-Methyl-4-(2-phenylethynyl)benzene (6f). Colorless solid (51%), mp 67−69 °C, (lit.[16] mp 59−61 °C). ^{1}H NMR δ 2.36 (s, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.32−7.35 (m, 3H), 7.43 (d, J = 8.0 Hz, 2H), 7.51−7.53 (m, 2H). ^{13}C NMR δ 21.5, 88.7, 89.5, 120.2, 123.5, 128.0, 128.3, 129.1, 131.4, 131.5, 138.4.

2-(2-Phenylethynyl)naphthalene (6g). Colorless solid (63%), mp 110−112 °C, (lit.[11] mp 112−113 °C). ^{1}H NMR δ 7.34−7.36 (m, 3H), 7.46−7.49 (m, 2H), 7.56−7.59 (m, 3H), 7.78−7.81 (m, 3H), 8.05 (s, 1H). ^{13}C NMR δ 89.7, 89.8, 120.6, 123.3, 126.5, 126.6, 127.8, 128.0, 128.3, 128.3, 128.4, 131.4, 131.7, 132.8, 133.0.

2-[2-(4-Chlorophenyl)ethynyl]naphthalene (6h). Colorless plates (70%), mp 122−123 °C.^{1}H NMR δ 7.34 (d, J = 8.4 Hz, 2H), 7.48−7.57 (m, 5H), 7.79−7.82 (m, 3H), 8.04 (s, 1H). ^{13}C NMR δ 88.6, 90.7, 120.2, 121.8, 126.6, 126.8, 127.7, 127.8, 128.1, 128.3, 128.7, 131.5, 132.8, 132.9, 133.0, 134.3. Anal. Calcd for $C_{18}H_{11}Cl$: C, 82.29; H, 4.22. Found: C, 82.12; H, 4.44.

1-Bromo-4-(2-phenylethynyl)benzene (6i). Colorless plates (68%), mp 82−83 °C. ^{1}H NMR δ 7.33−7.40 (m, 5H), 7.47−7.54 (m, 4H). ^{13}C NMR δ 88.3, 90.5, 122.2, 122.5, 122.9, 128.4, 128.5, 131.6, 131.6, 133.0. Anal. Calcd for $C_{14}H_9Br$: C, 65.40; H, 3.53. Found: C, 65.07; H, 3.34.

General Procedure for the Preparation of 7a−c. To a solution of 1-(alkylethynyl)benzotriazole (1 mmol) in dry toluene (10 mL) was added Grignard reagent (2 mmol, 1.0 M in THF) at −45 °C. The resulting mixture was stirred at this temperature for 2 h and then allowed to warm to 20 °C. After quenching with water and extraction with ethyl acetate (3 × 10 mL), the combined organic extracts were dried over $MgSO_4$. The solvent was removed in vacuo and the resulting oil was purified by column chromatography (eluent: EtOAc−hexanes 1:4) to give the pure product.

1-(2-Methyl-1-heptenyl)-1*H*-1,2,3-benzotriazole (7a). Liquid (91%). ^{1}H NMR δ 0.79 (t, J = 6.9 Hz, 3H), 1.12−1.19 (m, 4H), 1.40−1.48 (m, 2H), 2.03 (s, 3H), 2.10 (t, J = 4.7 Hz, 2H), 6.80 (s, 1H), 7.36−7.53 (m, 3H), 8.07 (d, J = 8.2 Hz, 1H). ^{13}C NMR δ 13.8, 20.4, 22.2, 27.0, 31.4, 31.7, 109.8, 116.8, 119.9, 123.9, 127.5, 133.4, 143.0, 145.2. Anal. Calcd for $C_{14}H_{19}N_3$: N, 18.32. Found: N, 18.03.

1-[2-(4-Methylphenyl)-1-propenyl]-1*H*-1,2,3-benzotriazole (7b). Colorless plates (76%), mp 127−129 °C. ^{1}H NMR δ 2.17 (s, 3H), 2.36 (s, 3H), 6.89 (s, 4H), 7.00−7.03 (m, 1H), 7.20−7.26 (m, 3H), 7.95−7.98 (m, 1H). ^{13}C NMR δ 21.0, 22.4, 110.4, 117.9, 119.5, 123.6, 127.0, 127.2, 129.1, 132.4, 134.6, 138.0, 138.8, 145.3. Anal. Calcd for $C_{16}H_{15}N_3$: N, 16.85. Found: 16.81.

1-[4-Methyl-2-(4-methylphenyl)-1-pentenyl]-1*H*-1,2,3-benzotriazole (7c). Colorless plates (72%), mp 90−91 °C. ^{1}H NMR δ 0.98 (d, J = 6.6 Hz, 6H), 1.64−1.73 (m, 1H), 2.18 (s, 3H), 2.57 (d, J = 7.1 Hz, 2H), 6.90 (s, 4H), 6.99−7.02 (m, 1H), 7.17−7.26 (m, 3H), 7.93−7.96 (m, 1H). ^{13}C NMR δ 21.1, 22.2, 26.1, 45.3, 110.4, 118.7, 119.5, 123.6, 127.1, 127.4, 129.1, 132.5, 133.6, 137.8, 142.7, 145.2. Anal. Calcd for $C_{19}H_{21}N_3$: N, 14.42. Found: N, 14.49.

General Procedure for the Preparation of Heterocyclic Acetylenes 8a−e. To a solution of aromatic heterocycle (1 mmol) in THF (5 mL) was added *n*-butyllithium (1.2 equiv, 1.56 M hexane solution) dropwise at 0 °C. The solution was allowed to rise to room temperature and stirred for 1 h. This solution was maintained at −78 °C while a solution of **5** (1 mmol) in THF (15 mL) was added slowly with stirring during 10 min. The reaction mixture was stirred for 12 h while the temperature was allowed to rise to 20 °C. After quenching with water (5 mL) and extraction with EtOAc (2 × 20 mL), the combined organic extracts were dried over $MgSO_4$ and filtered and the solvent was removed in vacuo. The resulting oil was subjected to column chromatography (eluent: hexanes) to give the pure product.

2-(2-Phenylethynyl)thiophene (8a). Colorless plates (58%), mp 49−51 °C, (lit.[17] mp 51−52 °C). ^{1}H NMR δ 6.99−7.01 (m, 1H), 7.27−7.34 (m, 5H), 7.50−7.53 (m, 2H). ^{13}C NMR δ 82.6, 93.0, 122.9, 123.3, 127.1, 127.2, 128.4, 128.4, 131.4, 131.9.

2-[2-(4-Bromophenyl)ethynyl]thiophene (8b). Colorless plates (65%), mp 89−91 °C. ^{1}H NMR δ 7.00−7.16 (m, 1H), 7.28−7.32 (m, 2H), 7.35−7.38 (m, 2H), 7.48 (d, J = 8.5 Hz, 1H). ^{13}C NMR δ 83.8, 91.9, 121.9, 122.6, 122.9, 127.2, 127.6, 131.6, 131.7, 132.1, 132.8. Anal. Calcd for $C_{12}H_7BrS$: C, 54.77; H, 2.68. Found: C, 55.16; H, 2.37.

2-(2-Phenylethynyl)-1-benzothiophene (8c). Colorless solid (70%), mp 115−117 °C. ^{1}H NMR δ 7.24−7.38 (m, 5H), 7.50 (s, 1H), 7.54−7.57 (m, 2H), 7.74−7.79 (m, 2H). ^{13}C NMR 82.9, 94.8, 122.0, 122.5, 123.2, 123.8, 124.7, 125.4, 128.4, 128.7, 128.8, 131.6, 139.1, 140.3. Anal. Calcd for $C_{16}H_{10}S$: C, 82.01; H, 4.30. Found: C, 81.97; H, 4.30.

2-[2-(4-Bromophenylethynyl)]-1-benzothiophene (8d). Pale yellow solid (62%), mp 189−191 °C. ^{1}H NMR δ 7.36−7.43 (m, 4H), 7.50−7.52 (d, J = 6.5 Hz, 3H), 7.78−7.79 (m, 2H). ^{13}C NMR 83.9, 93.5, 121.3, 121.8, 122.6, 122.9, 123.7, 124.6, 125.4, 128.8, 131.5, 132.8, 138.8, 140.1. HRMS calcd for $C_{16}H_9BrS$: 311.9608. Found: 311.9581.

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2-(2-Phenylethynyl)-1-benzofuran (8e). Colorless plates (67%), mp 87−89 °C (lit.[13] mp 88−90 °C). ^{1}H NMR δ 7.00 (s, 1H), 7.25 (t, J = 7.4 Hz, 1H), 7.31−7.38 (m, 4H), 7.48 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 5.1 Hz, 3H). ^{13}C NMR δ 79.6, 95.0, 111.2, 111.6, 121.2, 121.8, 123.3, 125.6, 127.7, 128.5, 129.1, 131.6, 138.7, 154.9.

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