

Electronic Supplementary Information

Facile One-Pot Synthesis of Diarylacetylenes from Arylaldehydes via Addition-Double Elimination Process

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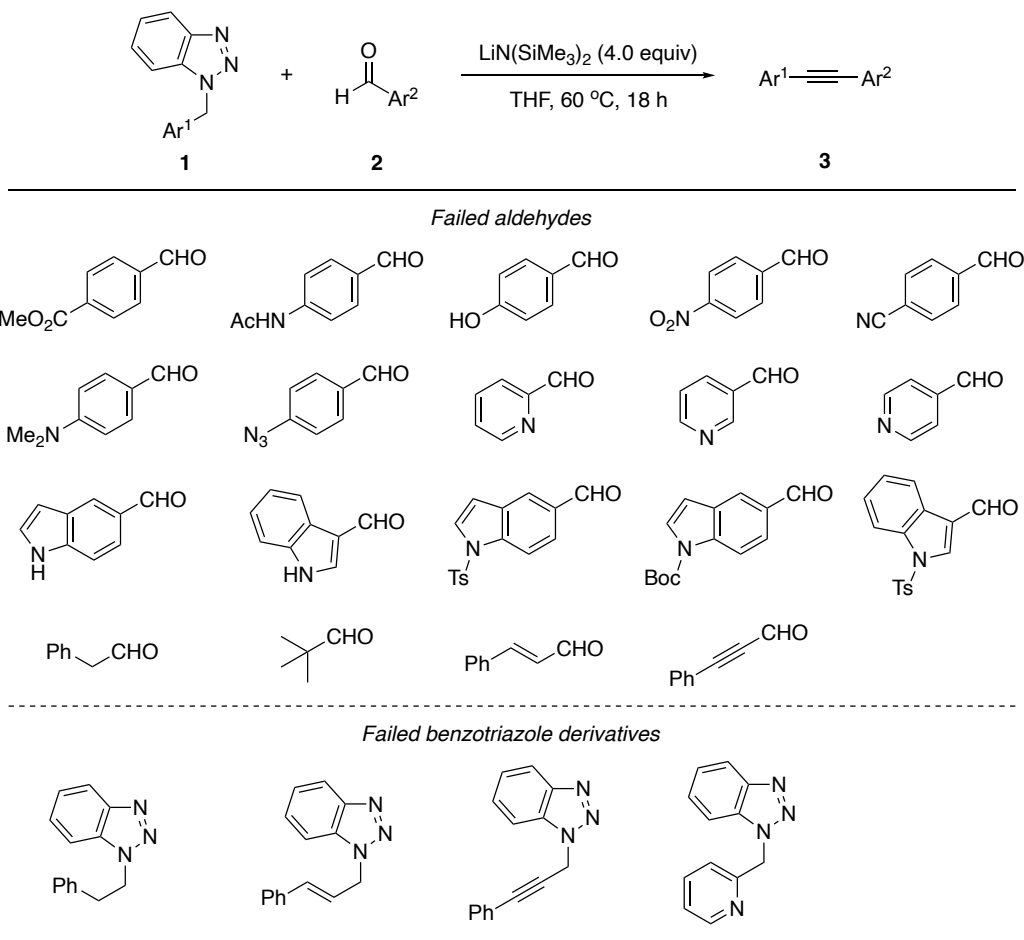
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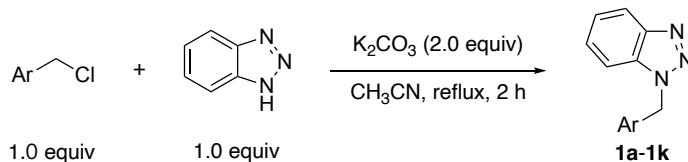
1. General Information

All reactions were carried out under nitrogen atmosphere unless otherwise noted. Anhydrous THF were purchased from Adamas. All reagents and solvents were obtained from commercial suppliers (Macklin, Bidepharm, Adamas, and Energy), and were used as received. ^1H and ^{13}C NMR were recorded on a Bruker 400 spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, and the coupling constants (J) are given in Hz. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All HRMS measurements were conducted on a Thermo QExactive.

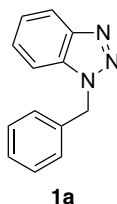
2. Failed aldehydes and benzotriazoles derivatives



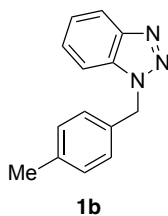
3. General Procedure for the Synthesis of 1-Arylmethylbenzotriazoles



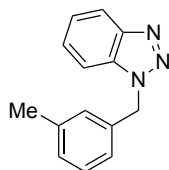
1-(Arylmethyl)benzotriazole derivatives were prepared following the reported procedure:¹ To a 100 mL dry flask was added benzotriazole (10.0 mmol, 1.0 equiv), acetonitrile (30 mL), potassium carbonate (20.0 mmol, 2.0 equiv), and arylmethyl chloride (11.0 mmol, 1.1 equiv) successively. The mixture was then heated under reflux for 2 hours. After cooling down to room temperature, precipitates were removed through a celite pad, and the filtrate was concentrated under vacuum. The crude product was purified by flash column chromatography (silica gel, hexane-ethyl acetate: 20:1, then 3:1), affording the pure 1-(arylmethyl)benzotriazoles.



1-Benzylbenzotriazole (**1a**): Colorless solids; ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (d, *J* = 8.1 Hz, 1H), 7.44-7.24 (m, 8H), 5.84 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 146.3, 134.7, 132.8, 129.0, 128.4, 127.5, 127.4, 123.9, 120.0, 109.7, 52.2 ppm. The spectra data were consistent with those reported in the literature.²

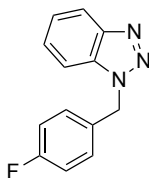


1-(4-Methylbenzyl)benzotriazole (**1b**): Colorless solids; ¹H NMR (400 MHz, CDCl₃): δ = 8.04 (d, *J* = 8.2 Hz, 1H), 7.42-7.28 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.78 (s, 2H), 2.30 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 146.2, 138.2, 132.7, 131.6, 129.5, 127.5, 127.2, 123.8, 119.9, 109.7, 52.0, 21.0 ppm. The spectra data were consistent with those reported in the literature.²



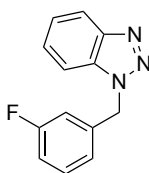
1c

1-(3-Methylbenzyl)benzotriazole (**1c**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.05 (d, J = 8.2 Hz, 1H), 7.42-7.30 (m, 3H), 7.21 (t, J = 7.5 Hz, 1H), 7.13-7.04 (m, 3H), 5.79 (s, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 146.3, 138.8, 134.6, 132.7, 129.2, 128.8, 128.2, 127.3, 124.6, 123.8, 119.9, 109.7, 52.2, 21.3 ppm. The spectra data were consistent with those reported in the literature.²



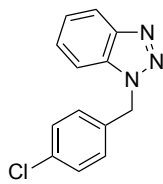
1d

1-(4-Fluorobenzyl)benzotriazole (**1d**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.07 (d, J = 8.8 Hz, 1H), 7.45-7.39 (m, 1H), 7.38-7.33 (m, 2H), 7.31-7.24 (m, 2H), 7.02 (t, J = 8.5 Hz, 2H), 5.81 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 162.6 (d, J_{CF} = 246.0 Hz), 146.3, 132.6, 130.5 (d, J_{CF} = 3.3 Hz), 129.4 (d, J_{CF} = 8.3 Hz), 127.5, 124.0, 120.1, 116.0 (d, J_{CF} = 21.6 Hz), 109.5, 51.4 ppm. The spectra data were consistent with those reported in the literature.³



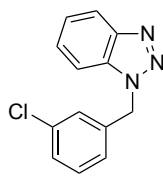
1e

1-(3-Fluorobenzyl)benzotriazole (**1e**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.08 (d, J = 8.4 Hz, 1H), 7.46-7.26 (m, 4H), 7.07-6.92 (m, 3H), 5.83 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 162.9 (d, J_{CF} = 249.1 Hz), 146.2, 137.1 (d, J_{CF} = 7.3 Hz), 132.7, 130.6 (d, J_{CF} = 8.3 Hz), 127.6, 124.0, 123.0 (d, J_{CF} = 3.0 Hz), 120.1, 115.4 (d, J_{CF} = 20.8 Hz), 114.5 (d, J_{CF} = 22.1 Hz), 109.4, 51.5 (d, J_{CF} = 1.8 Hz) ppm; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{FN}_3$ $[\text{M}+\text{H}]^+$: 228.0937, found: 228.0928.



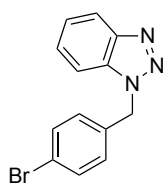
1f

1-(4-Chlorobenzyl)benzotriazole (**1f**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.07 (d, J = 8.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 5.81 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 146.3, 134.4, 133.2, 132.6, 129.2, 128.9, 127.5, 124.0, 120.1, 109.4, 51.4 ppm. The spectra data were consistent with those reported in the literature.^{2,3}



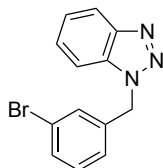
1g

1-(3-Chlorobenzyl)benzotriazole (**1g**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.07 (d, J = 8.2 Hz, 1H), 7.46-7.32 (m, 3H), 7.30-7.21 (m, 3H), 7.13 (d, J = 7.0 Hz, 1H), 5.80 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 146.2, 136.7, 134.8, 132.6, 130.2, 128.6, 127.6, 127.5, 125.6, 124.0, 120.0, 109.4, 51.3 ppm. The spectra data were consistent with those reported in the literature.⁴



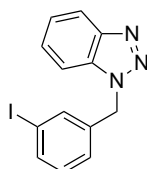
1h

1-(4-Bromobenzyl)benzotriazole (**1h**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.06 (d, J = 8.7 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.0 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 5.79 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 146.2, 133.7, 132.6, 132.1, 129.1, 127.5, 124.0, 122.5, 120.1, 109.4, 51.4 ppm. The spectra data were consistent with those reported in the literature.³



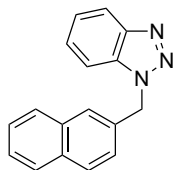
1i

1-(3-Bromobenzyl)benzotriazole (**1i**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.0 (d, J = 8.5 Hz, 1H), 7.56-7.41 (m, 3H), 7.40-7.33 (m, 2H), 7.23-7.15 (m, 2H), 5.81 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 146.3, 136.9, 132.7, 131.6, 130.54, 130.52, 127.7, 126.1, 124.1, 123.0, 120.2, 109.4, 51.4 ppm; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{BrN}_3$ $[\text{M}+\text{H}]^+$: 288.0136, found: 288.0129.



1j

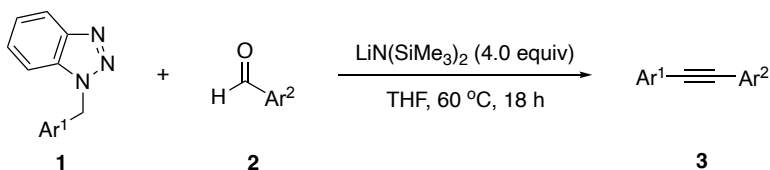
1-(3-Iodobenzyl)benzotriazole (**1j**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.08 (d, J = 8.7 Hz, 1H), 7.70-7.62 (m, 2H), 7.49-7.42 (m, 1H), 7.40-7.34 (m, 2H), 7.20 (d, J = 7.7 Hz, 1H), 7.06 (t, J = 7.7 Hz, 1H), 5.78 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 146.3, 137.6, 136.9, 136.4, 132.7, 130.7, 127.7, 126.7, 124.1, 120.2, 109.4, 94.7, 51.2 ppm; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{IN}_3$ $[\text{M}+\text{H}]^+$: 335.9998, found: 335.9991.



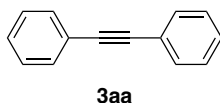
1k

1-(Naphthalen-2-ylmethyl)benzotriazole (**1k**): Colorless solids; ^1H NMR (400 MHz, CDCl_3): δ = 8.07 (d, J = 7.7 Hz, 1H), 7.82-7.71 (m, 4H), 7.51-7.43 (m, 2H), 7.41-7.28 (m, 4H), 5.98 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 146.3, 133.1, 133.0, 132.8, 132.1, 129.0, 127.8, 127.7, 127.4, 126.63, 126.57, 126.5, 124.9, 123.9, 120.0, 109.7, 52.4 ppm. The spectra data were consistent with those reported in the literature.⁵

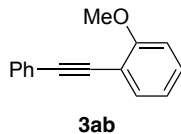
4. General Procedure for the Synthesis of Diarylacetylenes



General procedure: A 10 mL reaction tube was dried with a heat gun for 3 min under vacuum (< 5 mmHg at ca. 600 °C). After the displacement with N₂ gas, 1-arylmethylbenzotriazole **1** (0.44 mmol, 1.1 equiv), anhydrous THF (3.0 mL), arylaldehyde **2** (0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv). The resulting mixture was then stirred at 60 °C for 18 h under N₂ atmosphere. Seven drops water was added to quench the reaction. The reaction mixture was passed through a short pad of silica, washed with an additional 16 mL of ethyl acetate (4×10 mL), and the combined solutions were concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane only) to give diarylacetylene **3**.

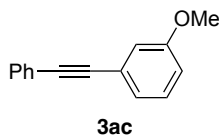


1,2-Diphenylethyne (**3aa**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), benzaldehyde **2a** (40.7 μL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3aa** (64.4 mg, 0.361 mmol, 90% yield) as colorless solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.62-7.49 (m, 4H), 7.43-7.28 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 131.6, 128.3, 128.2, 123.3, 89.4 ppm. The spectra data were consistent with those reported in the literature.⁶

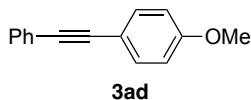


1-Methoxy-2-(phenylethynyl)benzene (**3ab**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-methoxybenzaldehyde **2b** (54.5 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ab** (81.2 mg, 0.390 mmol, 98% yield) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.59-7.54 (m, 2H), 7.50 (d, *J* =

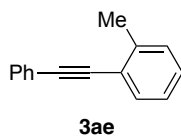
7.6 Hz, 1H), 7.38-7.27 (m, 4H), 6.97-6.88 (m, 2H), 3.92 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 159.9, 133.5, 131.6, 129.7, 128.2, 128.1, 123.5, 120.4, 112.4, 110.7, 93.4, 85.7, 55.8 ppm. The spectra data were consistent with those reported in the literature.⁶



1-Methoxy-3-(phenylethynyl)benzene (**3ac**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 3-methoxybenzaldehyde **2c** (48.7 μL , d = 1.117 g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ac** (61.7 mg, 0.296 mmol, 74% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.57-7.50 (m, 2H), 7.39-7.30 (m, 3H), 7.28-7.21 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.06 (s, 1H), 6.89 (dd, J = 8.3, 1.7 Hz, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 159.3, 131.6, 129.4, 128.32, 128.28, 124.23, 124.16, 123.2, 116.3, 114.9, 89.3, 89.2, 55.3 ppm. The spectra data were consistent with those reported in the literature.⁶

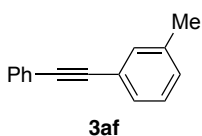


1-Methoxy-4-(phenylethynyl)benzene (**3ad**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), *p*-anisaldehyde **2d** (48.7 μL , d = 1.119 g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ad** (39.8 mg, 0.191 mmol, 48% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): δ = 7.55-7.49 (m, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.37-7.27 (m, 3H), 6.87 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3 ppm. The spectra data were consistent with those reported in the literature.⁶

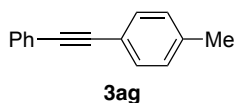


1-Methyl-2-(phenylethynyl)benzene (**3ae**): According to the general procedure, a mixture of 1-

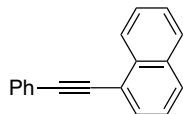
benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-methylbenzaldehyde **2e** (46.3 μL , $d = 1.039 \text{ g/mL}$, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ae** (62.9 mg, 0.327 mmol, 82% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.53$ (dd, $J = 7.2, 1.5$ Hz, 2H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.38-7.29 (m, 3H), 7.25-7.20 (m, 2H), 7.19-7.13 (m, 1H), 2.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 140.2, 131.8, 131.5, 129.4, 128.32, 128.28, 128.1, 125.6, 123.5, 123.0, 93.3, 88.3, 20.7$ ppm. The spectra data were consistent with those reported in the literature.⁶



1-Methyl-3-(phenylethynyl)benzene (**3af**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 3-methylbenzaldehyde **2f** (47.2 μL , $d = 1.019 \text{ g/mL}$, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3af** (63.3 mg, 0.329 mmol, 82% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.57$ -7.47 (m, 2H), 7.39-7.26 (m, 5H), 7.25-7.18 (m, 1H), 7.13 (d, $J = 7.2$ Hz, 1H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 138.0, 132.2, 131.6, 129.1, 128.7, 128.3, 128.2, 128.1, 123.4, 123.0, 89.6, 89.0, 21.2$ ppm. The spectra data were consistent with those reported in the literature.⁶

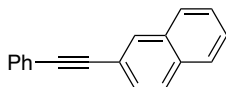


1-Methyl-4-(phenylethynyl)benzene (**3ag**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 4-methylbenzaldehyde **2g** (47.2 μL , $d = 1.019 \text{ g/mL}$, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ag** (56.6 mg, 0.294 mmol, 74% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.55$ -7.49 (m, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.36-7.27 (m, 3H), 7.14 (d, $J = 7.9$ Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 138.4, 131.52, 131.47, 129.1, 128.3, 128.0, 123.5, 120.2, 89.5, 88.7, 21.5$ ppm. The spectra data were consistent with those reported in the literature.⁶



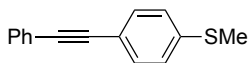
3ah

1-(Phenylethynyl)naphthalene (**3ah**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 1-naphthaldehyde **2h** (54.3 μ L, $d = 1.15$ g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ah** (77.6 mg, 0.340 mmol, 85% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.45$ (d, $J = 8.3$ Hz, 1H), 7.82 (t, $J = 9.4$ Hz, 2H), 7.75 (d, $J = 7.1$ Hz, 1H), 7.64 (dd, $J = 7.3, 0.9$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.40-7.29 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 133.24, 133.18, 131.6, 130.3, 128.7, 128.40, 128.35, 128.28, 126.7, 126.4, 126.2, 125.2, 123.4, 120.9, 94.3, 87.5$ ppm. The spectra data were consistent with those reported in the literature.⁶



3ai

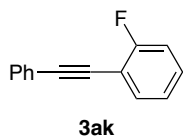
2-(Phenylethynyl)naphthalene (**3ai**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-naphthaldehyde **2i** (62.5 mg, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ai** (79.9 mg, 0.350 mmol, 88% yield) as colorless solids. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.04$ (s, 1H), 7.84-7.75 (m, 3H), 7.62-7.53 (m, 3H), 7.51-7.42 (m, 2H), 7.39-7.29 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 133.0, 132.8, 131.6, 131.4, 128.39, 128.36, 128.3, 128.0, 127.75, 127.74, 126.6, 126.5, 123.3, 120.6, 89.8, 89.7$ ppm. The spectra data were consistent with those reported in the literature.⁷



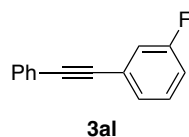
3aj

Methyl(4-(phenylethynyl)phenyl)sulfane (**3aj**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 4-(methylthio)benzaldehyde **2j** (53.2 μ L, $d = 1.144$ g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3aj**

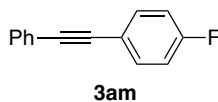
(78.1 mg, 0.348 mmol, 87% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): δ = 7.55-7.48 (m, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.37-7.28 (m, 3H), 7.19 (d, J = 8.2 Hz, 2H), 2.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 139.3, 131.8, 131.5, 128.3, 128.2, 125.8, 123.3, 119.5, 89.4, 89.2, 15.3 ppm. The spectra data were consistent with those reported in the literature.⁷



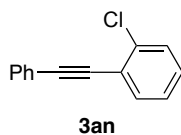
1-Fluoro-2-(phenylethynyl)benzene (**3ak**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-fluorobenzaldehyde **2k** (42.1 μL , d = 1.178 g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ak** (72.8 mg, 0.371 mmol, 93% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.59-7.47 (m, 3H), 7.39-7.25 (m, 4H), 7.15-7.04 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 162.6 (d, J_{CF} = 250.0 Hz), 133.4 (d, J_{CF} = 1.4 Hz), 131.7, 129.9 (d, J_{CF} = 7.9 Hz), 128.6, 128.3, 123.9 (d, J_{CF} = 3.8 Hz), 122.9, 115.5 (d, J_{CF} = 83.1 Hz), 111.9 (d, J_{CF} = 15.6 Hz), 94.4 (d, J_{CF} = 3.2 Hz), 82.7 ppm. The spectra data were consistent with those reported in the literature.⁷



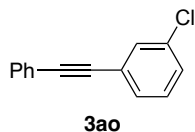
1-Fluoro-3-(phenylethynyl)benzene (**3al**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 3-fluorobenzaldehyde **2l** (42.4 μL , d = 1.17 g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3al** (72.5 mg, 0.369 mmol, 92% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.57-7.48 (m, 2H), 7.39-7.27 (m, 5H), 7.25-7.18 (m, 1H), 7.07-6.98 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 162.4 (d, J_{CF} = 244.9 Hz), 131.7, 129.9 (d, J_{CF} = 8.7 Hz), 128.6, 128.4, 127.5 (d, J_{CF} = 3.0 Hz), 125.1 (d, J_{CF} = 9.5 Hz), 122.8, 118.3 (d, J_{CF} = 22.6 Hz), 115.5 (d, J_{CF} = 21.1 Hz), 90.2, 88.1 (d, J_{CF} = 3.4 Hz) ppm. The spectra data were consistent with those reported in the literature.⁸



1-Fluoro-4-(phenylethynyl)benzene (**3am**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 4-fluorobenzaldehyde **2m** (42.9 μ L, d = 1.157 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3am** (68.2 mg, 0.348 mmol, 87% yield) as yellow solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.56-7.44 (m, 4H), 7.39-7.29 (m, 3H), 7.07-6.98 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 162.5 (d, J_{CF} = 248.0 Hz), 133.5 (d, J_{CF} = 8.3 Hz), 131.5, 128.4, 128.3, 123.1, 119.4 (d, J_{CF} = 3.4 Hz), 115.6 (d, J_{CF} = 21.9 Hz), 89.0 (d, J_{CF} = 1.5 Hz), 88.3 ppm. The spectra data were consistent with those reported in the literature.⁷

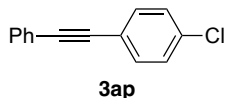


1-Chloro-2-(phenylethynyl)benzene (**3an**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-chlorobenzaldehyde **2n** (45.1 μ L, d = 1.248 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3an** (80.2 mg, 0.377 mmol, 94% yield) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.52-7.43 (m, 3H), 7.36-7.31 (m, 1H), 7.30-7.22 (m, 3H), 7.19-7.10 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 135.9, 133.2, 131.7, 129.3, 129.2, 128.6, 128.3, 126.4, 123.2, 122.9, 94.5, 86.2 ppm. The spectra data were consistent with those reported in the literature.⁶

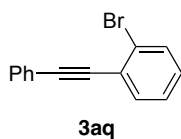


1-Chloro-3-(phenylethynyl)benzene (**3ao**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 3-chlorobenzaldehyde **2o** (45.3 μ L, d = 1.241 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ao** (74.0

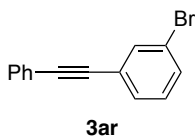
mg, 0.348 mmol, 87% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.57-7.47 (m, 3H), 7.43-7.22 (6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 134.1, 131.6, 131.4, 129.7, 129.5, 128.6, 128.5, 128.4, 125.0, 122.7, 90.5, 87.9 ppm. The spectra data were consistent with those reported in the literature.⁶



1-Chloro-4-(phenylethynyl)benzene (**3ap**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ap** (78.4 mg, 0.369 mmol, 92% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): δ = 7.56-7.48 (m, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.40-7.28 (m, 5H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 134.2, 132.8, 131.6, 128.7, 128.5, 128.4, 122.9, 121.8, 90.3, 88.2 ppm. The spectra data were consistent with those reported in the literature.⁶

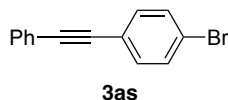


1-Bromo-2-(phenylethynyl)benzene (**3aq**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-bromobenzaldehyde **2q** (74.0 mg, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3aq** (86.9 mg, 0.338 mmol, 85% yield) as brown oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.63-7.50 (m, 4H), 7.39-7.30 (m, 3H), 7.26 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 133.2, 132.4, 131.7, 129.3, 128.6, 128.3, 127.0, 125.6, 125.4, 122.9, 93.9, 88.0 ppm. The spectra data were consistent with those reported in the literature.⁶

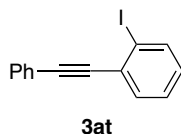


1-Bromo-3-(phenylethynyl)benzene (**3ar**): According to the general procedure, a mixture of 1-

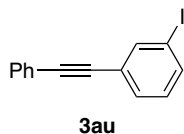
benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 3-bromobenzaldehyde **2r** (74.0 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ar** (84.6 mg, 0.329 mmol, 82% yield) as brown oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (s, 1H), 7.48-7.40 (m, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.31-7.21 (m, 3H), 7.16-7.07 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 134.3, 131.6, 131.3, 130.1, 129.7, 128.6, 128.4, 125.3, 122.7, 122.1, 90.7, 87.8 ppm. The spectra data were consistent with those reported in the literature.⁶



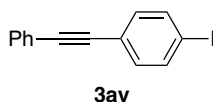
1-Bromo-4-(phenylethynyl)benzene (**3as**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 4-bromobenzaldehyde **2s** (74.0 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3as** (88.0 mg, 0.342 mmol, 86% yield) as yellow solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.57-7.49 (m, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.36-7.28 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 133.0, 131.58, 131.56, 128.5, 128.4, 122.9, 122.4, 122.2, 90.5, 88.3 ppm. The spectra data were consistent with those reported in the literature.⁶



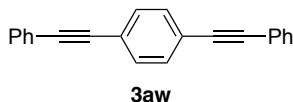
1-Iodo-2-(phenylethynyl)benzene (**3at**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-iodobenzaldehyde **2t** (92.8 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3at** (99.7 mg, 0.328 mmol, 82% yield) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, *J* = 8.0 Hz, 3H), 7.60 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.53 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.41-7.28 (m, 4H), 7.01 (td, *J* = 7.7, 1.7 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 138.7, 132.4, 131.6, 129.8, 129.3, 128.6, 128.4, 127.8, 122.9, 101.2, 93.4, 91.6 ppm. The spectra data were consistent with those reported in the literature.⁹



1-Iodo-3-(phenylethynyl)benzene (**3au**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 3-iodobenzaldehyde **2u** (92.8 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3au** (104.3 mg, 0.343 mmol, 86% yield) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.89 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.57-7.45 (m, 3H), 7.39-7.30 (m, 3H), 7.07 (t, *J* = 7.8 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 140.1, 137.2, 131.6, 130.7, 129.8, 128.6, 128.4, 125.3, 122.7, 93.7, 90.7, 87.6 ppm. The spectra data were consistent with those reported in the literature.¹⁰

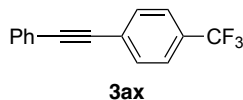


1-Iodo-4-(phenylethynyl)benzene (**3av**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 4-iodobenzaldehyde **2v** (92.8 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3av** (102.5 mg, 0.337 mmol, 84% yield) as yellow solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.68 (d, *J* = 8.4 Hz, 2H), 7.57-7.48 (m, 2H), 7.40-7.31 (m, 3H), 7.28-7.22 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 137.5, 133.1, 131.6, 128.5, 128.4, 122.9, 122.8, 94.1, 90.8, 88.4 ppm. The spectra data were consistent with those reported in the literature.⁷

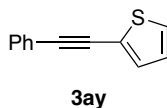


1,4-Bis(phenylethynyl)benzene (**3aw**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (184.1 mg, 0.88 mmol, 2.2 equiv), *p*-phthalaldehyde **2w** (53.7 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (3.2 mL, 3.20 mmol, 8.0 equiv) in anhydrous THF (6.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3aw** (75.3 mg, 0.271 mmol, 68% yield) as yellow solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.58-7.46 (m, 8H), 7.39-7.30 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 131.6, 131.5, 128.44, 128.37, 123.08, 123.02, 91.2, 89.1

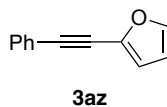
ppm. The spectra data were consistent with those reported in the literature.¹¹



1-(Phenylethynyl)-4-(trifluoromethyl)benzene (**3ax**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 4-(trifluoromethyl)benzaldehyde **2x** (54.6 μ L, $d = 1.275$ g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ax** (83.0 mg, 0.337 mmol, 84% yield) as colorless solids. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.65\text{-}7.51$ (m, 6H), 7.40-7.33 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 131.8, 131.7, 129.9$ (q, $J_{\text{CF}} = 24.5$ Hz), 128.8, 128.4, 127.1 (q, $J_{\text{CF}} = 1.0$ Hz), 125.3 (q, $J_{\text{CF}} = 2.8$ Hz), 122.59, 122.56, 91.8, 88.0 ppm. The spectra data were consistent with those reported in the literature.¹²

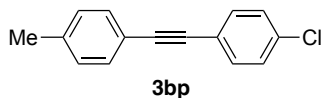


2-(Phenylethynyl)thiophene (**3ay**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-thiophenecarboxaldehyde **2y** (37.4 μ L, $d = 1.2$ g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ay** (59.4 mg, 0.322 mmol, 81% yield) as brown solids. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.57\text{-}7.47$ (m, 2H), 7.41-7.22 (m, 5H), 7.05-6.97 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 131.9, 131.4, 128.4, 128.3, 127.2, 127.1, 123.3, 122.9, 93.0, 82.6$ ppm. The spectra data were consistent with those reported in the literature.¹³

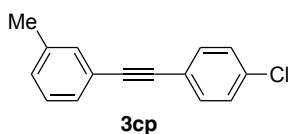


2-(Phenylethynyl)furan (**3az**): According to the general procedure, a mixture of 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μ L, $d = 1.16$ g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3az** (60.6 mg, 0.360

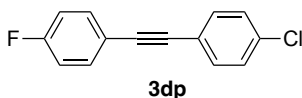
mmol, 90% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.58-7.48 (m, 2H), 7.44-7.40 (m, 1H), 7.39-7.30 (m, 3H), 6.65 (d, J = 3.4 Hz, 1H), 6.48-6.39 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 143.6, 137.1, 131.4, 128.7, 128.4, 122.3, 115.2, 111.0, 93.2, 79.4 ppm. The spectra data were consistent with those reported in the literature.¹⁴



1-Chloro-4-(*p*-tolylethynyl)benzene (**3bp**): According to the general procedure, a mixture of 1-(4-methylbenzyl)benzotriazole **1b** (98.2 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3bp** (89.7 mg, 0.396 mmol, 99% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): δ = 7.48-7.38 (m, 4H), 7.31 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 138.7, 134.0, 132.7, 131.5, 129.2, 128.6, 122.0, 119.8, 90.5, 87.6, 21.5 ppm. The spectra data were consistent with those reported in the literature.¹⁵

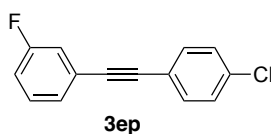


1-((4-Chlorophenyl)ethynyl)-3-methylbenzene (**3cp**): According to the general procedure, a mixture of 1-(3-methylbenzyl)benzotriazole **1c** (98.2 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3cp** (88.9 mg, 0.392 mmol, 98% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): δ = 7.44 (d, J = 8.4 Hz, 2H), 7.37-7.28 (m, 4H), 7.27-7.20 (m, 1H), 7.15 (d, J = 7.5 Hz, 1H), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 138.1, 134.1, 132.8, 132.2, 129.4, 128.7, 128.3, 122.7, 121.9, 90.5, 87.9, 21.2 ppm (One carbon was missing probably because of overlapping). The spectra data were consistent with those reported in the literature.¹⁶

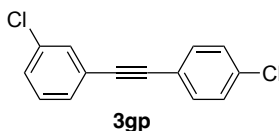


1-Chloro-4-((4-fluorophenyl)ethynyl)benzene (**3dp**): According to the general procedure, a

mixture of 1-(4-fluorobenzyl)benzotriazole **1d** (100.0 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3dp** (86.0 mg, 0.373 mmol, 93% yield) as yellow solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.54-7.47 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 162.6 (d, *J*_{CF} = 248.5 Hz), 134.3, 133.5 (d, *J*_{CF} = 8.4 Hz), 132.7, 128.7, 121.6, 119.0 (d, *J*_{CF} = 3.4 Hz), 115.7 (d, *J*_{CF} = 22.1 Hz), 89.2, 87.9 (d, *J*_{CF} = 1.7 Hz) ppm. The spectra data were consistent with those reported in the literature.¹⁷

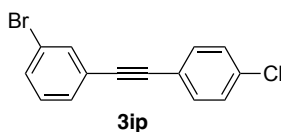


1-((4-Chlorophenyl)ethynyl)-3-fluorobenzene (**3ep**): According to the general procedure, a mixture of 1-(3-fluorobenzyl)benzotriazole **1e** (100.0 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ep** (78.3 mg, 0.339 mmol, 85% yield) as yellow solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.45 (d, *J* = 8.3 Hz, 2H), 7.38-7.27 (m, 4H), 7.21 (d, *J* = 9.8 Hz, 1H), 7.10-7.00 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 162.4 (d, *J*_{CF} = 245.1 Hz), 134.6, 132.9, 130.0 (d, *J*_{CF} = 8.6 Hz), 128.8, 127.5 (d, *J*_{CF} = 3.0 Hz), 124.8 (d, *J*_{CF} = 9.5 Hz), 121.3, 118.3 (d, *J*_{CF} = 22.7 Hz), 115.8 (d, *J*_{CF} = 21.1 Hz), 89.1, 89.0 (d, *J*_{CF} = 3.4 Hz) ppm. The spectra data were consistent with those reported in the literature.¹⁵

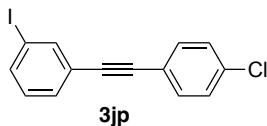


1-Chloro-3-((4-chlorophenyl)ethynyl)benzene (**3gp**): According to the general procedure, a mixture of 1-(3-chlorobenzyl)benzotriazole **1g** (107.2 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3gp** (82.9 mg, 0.335 mmol, 84% yield) as yellow solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.36-7.27 (m, 4H) ppm; ¹³C

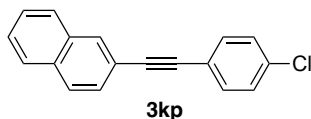
NMR (100 MHz, CDCl₃): δ = 134.7, 134.2, 132.9, 131.4, 129.7, 129.6, 128.8, 128.7, 124.6, 121.2, 89.4, 88.8 ppm; HRMS (ESI) m/z calcd for C₁₄H₉Cl₂ [M+H]⁺: 247.0081, found: 247.1312.



1-Bromo-3-((4-chlorophenyl)ethynyl)benzene (**3ip**): According to the general procedure, a mixture of **1i** (126.8 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ip** (85.4 mg, 0.293 mmol, 73% yield) as brown solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.67 (s, 1H), 7.50-7.41 (m, 4H), 7.33 (d, J = 8.2 Hz, 2H), 7.22 (t, J = 7.9 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 134.7, 134.3, 132.8, 131.6, 130.1, 129.8, 128.8, 124.9, 122.2, 121.2, 89.5, 88.7 ppm. The spectra data were consistent with those reported in the literature.¹⁸

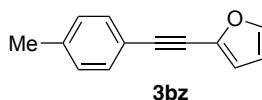


1-((4-Chlorophenyl)ethynyl)-3-iodobenzene (**3jp**): According to the general procedure, a mixture of 1-(3-iodobenzyl)benzotriazole **1j** (147.5 mg, 0.44 mmol, 1.1 equiv), 4-chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3jp** (99.7 mg, 0.294 mmol, 74% yield) as brown solids. ¹H NMR (400 MHz, CDCl₃): δ = 7.88 (s, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.08 (t, J = 7.8 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 140.1, 137.4, 134.6, 132.8, 130.6, 129.9, 128.8, 125.0, 121.2, 93.7, 89.5, 88.5 ppm; HRMS (ESI) m/z calcd for C₁₄H₉ClI [M+H]⁺: 338.9437, found: 338.9416.

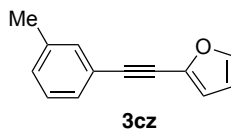


2-((4-Chlorophenyl)ethynyl)naphthalene (**3kp**): According to the general procedure, a mixture of 1-(naphthalen-2-ylmethyl)benzotriazole **1k** (114.1 mg, 0.44 mmol, 1.1 equiv), 4-

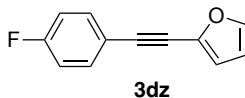
chlorobenzaldehyde **2p** (56.2 mg, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3kp** (97.1 mg, 0.369 mmol, 92% yield) as colorless solids. ¹H NMR (400 MHz, CDCl₃): δ = 8.04 (s, 1H), 7.88-7.76 (m, 3H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 4H), 7.33 (d, *J* = 8.4 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 134.3, 133.0, 132.9, 132.8, 131.5, 128.7, 128.3, 128.1, 127.79, 127.77, 126.8, 126.6, 121.8, 120.2, 90.7, 88.6 ppm. The spectra data were consistent with those reported in the literature.¹⁹



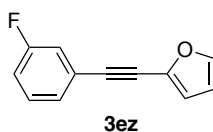
2-(*p*-Tolylethynyl)furan (**3bz**): According to the general procedure, a mixture of 1-(4-methylbenzyl)benzotriazole **1b** (98.2 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μL, *d* = 1.16 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3bz** (58.5 mg, 0.321 mmol, 80% yield) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.45-7.38 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 3.4 Hz, 1H), 6.44-6.38 (m, 1H), 2.36 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 143.4, 138.9, 137.3, 131.3, 129.1, 119.2, 114.9, 111.0, 93.4, 78.7, 21.5 ppm. The spectra data were consistent with those reported in the literature.²⁰



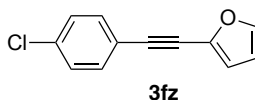
2-(*m*-Tolylethynyl)furan (**3cz**): According to the general procedure, a mixture of 1-(3-methylbenzyl)benzotriazole **1c** (98.2 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μL, *d* = 1.16 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3cz** (63.8 mg, 0.350 mmol, 88% yield) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.44-7.39 (m, 1H), 7.37-7.29 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 3.4 Hz, 1H), 6.44-6.39 (m, 1H), 2.34 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 143.5, 138.1, 137.2, 131.9, 129.6, 128.5, 128.3, 122.1, 115.1, 111.0, 93.4, 79.0, 21.2 ppm; HRMS (ESI) *m/z* calcd for C₁₃H₁₁O [M+H]⁺: 183.0810, found: 183.0808.



2-((4-Fluorophenyl)ethynyl)furan (**3dz**): According to the general procedure, a mixture of 1-(4-fluorobenzyl)benzotriazole **1d** (100.0 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μ L, d = 1.16 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3dz** (60.1 mg, 0.323 mmol, 81% yield) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.54-7.46 (m, 2H), 7.42 (s, 1H), 7.04 (t, J = 8.6 Hz, 2H), 8.65 (d, J = 3.3 Hz, 1H), 6.45-6.39 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 162.7 (d, J_{CF} = 248.7 Hz), 143.7, 137.0, 133.4 (d, J_{CF} = 8.4 Hz), 118.4 (d, J_{CF} = 3.6 Hz), 115.7 (d, J_{CF} = 22.1 Hz), 115.3, 111.0, 92.1, 79.1 (d, J_{CF} = 1.6 Hz) ppm; HRMS (ESI) m/z calcd for C₁₂H₈FO [M+H]⁺: 187.0559, found: 187.0558.

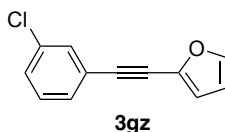


2-((3-Fluorophenyl)ethynyl)furan (**3ez**): According to the general procedure, a mixture of 1-(3-fluorobenzyl)benzotriazole **1e** (100.0 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μ L, d = 1.16 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3ez** (41.7 mg, 0.224 mmol, 56% yield) as brown oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.44 (s, 1H), 7.35-7.27 (m, 2H), 7.21 (dd, J = 9.7, 2.1 Hz, 1H), 7.10-7.01 (m, 1H), 6.68 (d, J = 3.4 Hz, 1H), 6.46-6.41 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 162.3 (d, J_{CF} = 245.2 Hz), 144.0, 136.7, 130.0 (d, J_{CF} = 8.6 Hz), 127.3 (d, J_{CF} = 3.0 Hz), 124.1 (d, J_{CF} = 9.5 Hz), 118.1 (d, J_{CF} = 22.9 Hz), 116.0 (d, J_{CF} = 21.1 Hz), 115.8, 111.1, 92.0 (d, J_{CF} = 3.4 Hz), 80.3 ppm. HRMS (ESI) m/z calcd for C₁₂H₈FO [M+H]⁺: 187.0559, found: 187.0553.

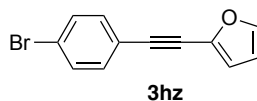


2-((4-Chlorophenyl)ethynyl)furan (**3fz**): According to the general procedure, a mixture of 1-(4-chlorobenzyl)benzotriazole **1f** (107.2 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μ L, d = 1.16 g/mL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 °C for 18 h under N₂ atmosphere. The crude product

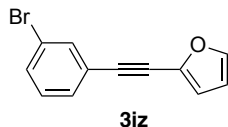
was purified by flash column chromatography (silica gel, hexane only) to give **3fz** (55.4 mg, 0.273 mmol, 68% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): δ = 7.48-7.41 (m, 3H), 7.32 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 3.4 Hz, 1H), 6.46-6.41 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 143.8, 136.9, 134.8, 132.6, 128.8, 120.8, 115.6, 111.1, 92.1, 80.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_8\text{ClO}$ $[\text{M}+\text{H}]^+$: 203.0264, found: 203.0260.



2-((3-Chlorophenyl)ethynyl)furan (**3gz**): According to the general procedure, a mixture of 1-(3-chlorobenzyl)benzotriazole **1g** (107.2 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μL , d = 1.16 g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3gz** (36.3 mg, 0.179 mmol, 45% yield) as brown oil. ^1H NMR (400 MHz, CDCl_3): δ = 7.50 (s, 1H), 7.46-7.42 (m, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.34-7.23 (m, 2H), 6.68 (d, J = 3.4 Hz, 1H), 6.46-6.40 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 144.0, 136.7, 134.2, 131.1, 129.6, 129.5, 128.9, 124.0, 115.8, 111.1, 91.8, 80.5 ppm. The spectra data were consistent with those reported in the literature.²¹

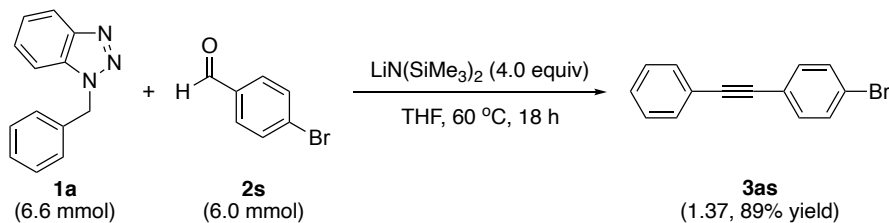


2-((4-Bromophenyl)ethynyl)furan (**3hz**): According to the general procedure, a mixture of 1-(4-bromobenzyl)benzotriazole **1h** (126.8 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μL , d = 1.16 g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3hz** (69.8 mg, 0.282 mmol, 71% yield) as yellow solids. ^1H NMR (400 MHz, CDCl_3): δ = 7.48 (d, J = 8.4 Hz, 1H), 7.44 (s, 1H), 7.38 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 3.4 Hz, 1H), 6.46-6.49 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 143.9, 136.9, 132.8, 131.7, 123.0, 121.3, 115.6, 111.1, 92.2, 80.5 ppm; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_8\text{BrO}$ $[\text{M}+\text{H}]^+$: 246.9759, found: 246.9672.



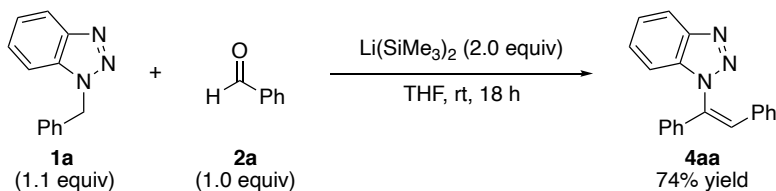
2-((3-Bromophenyl)ethynyl)furan (**3iz**): According to the general procedure, a mixture of 1-(3-bromobenzyl)benzotriazole **1i** (126.8 mg, 0.44 mmol, 1.1 equiv), 2-furaldehyde **2z** (33.1 μ L, $d = 1.16$ g/mL, 0.40 mmol, 1.0 equiv), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (1.6 mL, 1.60 mmol, 4.0 equiv) in anhydrous THF (3.0 mL) was stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica gel, hexane only) to give **3iz** (44.3 mg, 0.179 mmol, 45% yield) as brown oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.67$ (s, 1H), 7.51-7.40 (m, 3H), 7.21 (t, $J = 7.9$ Hz, 1H), 6.68 (d, $J = 3.4$ Hz, 1H), 6.46-6.41 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 144.0, 136.7, 134.0, 131.8, 129.9, 129.8, 124.3, 122.2, 115.9, 111.1, 91.7, 80.7$ ppm; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_8\text{BrO}$ $[\text{M}+\text{H}]^+$: 246.9759, found: 246.9570.

5. Gram-Scale Synthesis of 1-Bromo-4-(phenylethynyl)benzene **3as**



A 250 mL dry flask was dried with a heat gun for 3 min under vacuum (< 5 mmHg at ca. 600 $^\circ\text{C}$). After the displacement with N_2 gas, 1-benzylbenzotriazole **1a** (1.38 g, 6.60 mmol, 1.1 equiv), 4-bromobenzaldehyde **2s** (1.11 g, 6.00 mmol, 1.0 equiv), anhydrous THF (45.0 mL), and $\text{LiN}(\text{SiMe}_3)_2$ (1.0 M in THF) (24.0 mL, 24.00 mmol, 4.0 equiv). The resulting mixture was then stirred at 60 $^\circ\text{C}$ for 18 h under N_2 atmosphere. Water (60 mL) was added to quench the reaction, followed by extraction with ethyl acetate (3 \times 60 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under vacuum. The crude product was purified by flash column chromatography (silica gel, hexane only) to give 1-bromo-4-(phenylethynyl)benzene **3as** (1.37 g, 5.32 mmol) in 89% yield as yellow solids.

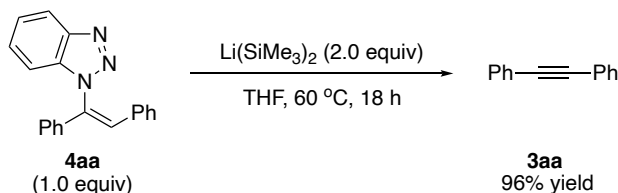
6. Mechanistic Study



A 10 mL reaction tube was dried with a heat gun for 3 min under vacuum (< 5 mmHg at ca. 600

°C). After the displacement with N₂ gas, 1-benzylbenzotriazole **1a** (92.1 mg, 0.44 mmol, 1.1 equiv), anhydrous THF (3.0 mL), benzaldehyde **2a** (40.7 μL, 0.40 mmol, 1.0 equiv), and LiN(SiMe₃)₂ (1.0 M in THF) (0.8 mL, 0.80 mmol, 2.0 equiv). The resulting mixture was then stirred at room temperature for 18 h under N₂ atmosphere. Seven drops water was added to quench the reaction. The reaction mixture was passed through a short pad of silica, washed with an additional 16 mL of ethyl acetate (4×10 mL), and the combined solutions were concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane-ethyl acetate, 25:1) to give (Z)-1-(1,2-diphenylvinyl)-1H-benzo[d][1,2,3]triazole **4aa** (87.4 mg, 0.294 mmol, 74% yield) as colorless solids.

¹H NMR (400 MHz, CDCl₃): δ = 8.13 (d, *J* = 7.9 Hz, 1H), 7.41-7.29 (m, 6H), 7.23-7.16 (m, 2H), 7.15-7.03 (m, 4H), 6.74 (d, *J* = 7.4 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 145.8, 136.64, 133.58, 133.5, 133.1, 129.3, 128.9, 128.58, 128.55, 128.0, 127.6, 125.9, 124.2, 120.0, 110.5 ppm; HRMS (ESI) *m/z* calcd for C₂₀H₁₆N₃ [M+H]⁺: 298.1344, found: 298.1338. The spectra data were consistent with those reported in the literature.²²



A 10 mL reaction tube was dried with a heat gun for 3 min under vacuum (< 5 mmHg at ca. 600 °C). After the displacement with N₂ gas, **4aa** (118.9 mg, 0.40 mmol, 1.0 equiv), anhydrous THF (3.0 mL), and LiN(SiMe₃)₂ (1.0 M in THF) (0.8 mL, 0.80 mmol, 2.0 equiv). The resulting mixture was then stirred at 60 °C for 18 h under N₂ atmosphere. Seven drops water was added to quench the reaction. The reaction mixture was passed through a short pad of silica, washed with an additional 16 mL of ethyl acetate (4×10 mL), and the combined solutions were concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane only) to give 1,2-diphenylethyne **3aa** (68.4 mg, 0.384 mmol, 96% yield) as colorless solids.

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8. NMR Spectra

