Tandem Suzuki–Miyaura Cross-Coupling/Dehydrobromination of 1,1-Dibromoalkenes to Alkynes with a Cyclobutene-1,2-diylbis(imidazolium) Salt as Catalyst Precursor

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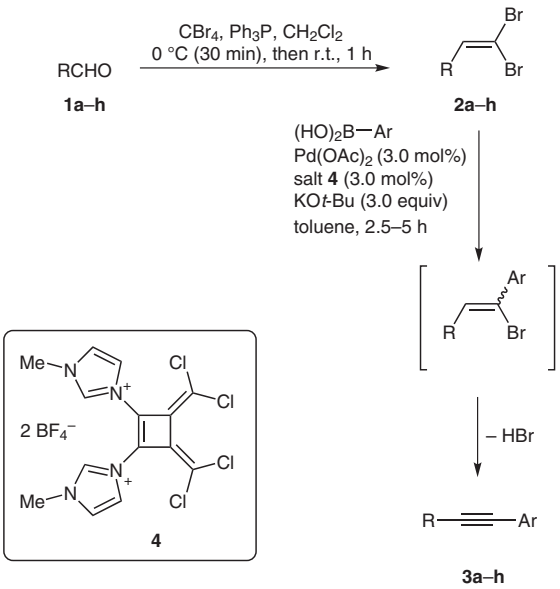
Abstract: A cyclobutene-1,2-bis(imidazolium) salt proved to be an efficient catalyst precursor for one-pot tandem Suzuki–Miyaura/dehydrobromination reactions for the synthesis of alkynes starting from 1,1-dibromoalkenes and palladium(II) acetate, aryl boronic acids, and potassium *tert*-butoxide in toluene. Starting materials were prepared from aldehydes under Corey–Fuchs conditions.

Key words: imidazol-2-ylidene, N-heterocyclic carbene, biscarbene complex, Corey–Fuchs reaction

The alkyne moiety represents a functional group of high energy, which is able to undergo a broad variety of reactions. As a consequence numerous books,[1] reference works,[2] and review articles[3] dealing with the chemistry and applications of alkynes have appeared. Whereas the development of alkynes as starting materials in the research laboratories to valuable intermediates in industrial chemistry was initiated by Reppe in the 1940s, new synthetic methods employing novel types of transition-metal catalysts for the coupling of an alkyne moiety with almost any other molecule were established in the 1970s. More recently, considerable interest has focused on alkynes from the viewpoint of materials chemistry, as they play important roles in highly conjugated organic molecules,[4] which are potentially useful or already applied in the areas of photonics, optoelectronics, molecular electronics, field-effect transistors, organic light-emitting diodes, solar cells, and solid-state lasers.[5] In addition, a plethora of natural products with alkyne units have been reported.[6]

Elimination strategies are useful for the synthesis of alkynes, and these involve 1,2- as well as 1,1-eliminations.[7] The conversion of an aldehyde by chain extension into a 1,1-dibromovinyl derivative, which gives an alkyne on treatment with strong bases such as BuLi is known as the Corey–Fuchs reaction.[8] A modification has been reported in which the 1,1-dibromoalkene is treated with 1,8-diazabicyclo[5.4.0]undec-7-ene in DMSO to yield 1-bromoalkynes, which are valuable starting materials for Cadiot–Chodkiewicz couplings.[9] 1,1-Dibromoalkenes are also known to react under Suzuki–Miyaura conditions with a broad variety of boronic acids to tri- and tetrasubstituted alkenes, (*Z*)-1-aryl- or (*Z*)-alkenyl-1-bromoalk-1-enes,[10] and internal alkynes.[11] In addition, the Suzuki–Miyaura reaction of boronic esters with dibromides to alkynes has been reported.[12] In organic synthesis, the Stille coupling of 1,1-dibromoalk-1-enes for the preparation of alkynes[13] plays an important role.[14] In continuation of our interest in N-heterocyclic carbenes[15] we report here a new application of a cyclobutene-1,2-bis(imidazolium) salt developed in our laboratory.[16] This salt serves as catalyst precursor for efficient one-pot tandem Suzuki–Miyaura/dehydrobromination reactions for the synthesis of alkynes starting from 1,1-dibromoalkenes, which were prepared from aldehydes under Corey–Fuchs conditions.

Solutions of the aldehydes **1a**–**h** and tetrabromomethane were treated with PPh_3 at 0 °C to room temperature[17] to give the 1,1-dibromoalkenes **2a**–**h** (Scheme 1). The tandem Suzuki–Miyaura/dehydrobromination reaction for the synthesis of the alkynes **3a**–**h** proceeded in the presence of $Pd(OAc)_2$, the title bis(imidazolium) salt **4**, and potassium *tert*-butoxide in the temperature range of 65–90 °C in good to excellent yields. All results are summarized in Table 1.



Scheme 1

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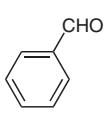
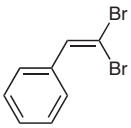
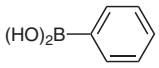
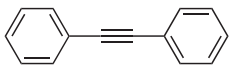
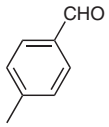
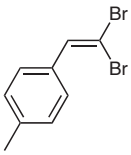
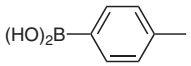
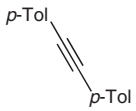
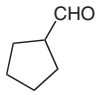
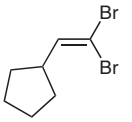
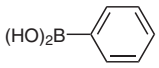
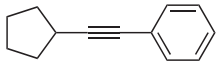
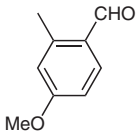
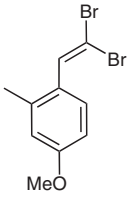
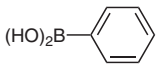
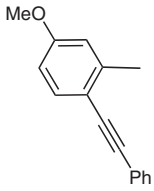
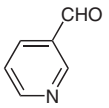
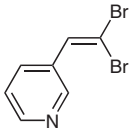
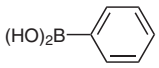
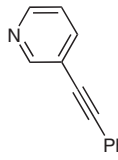
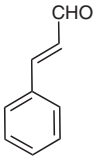
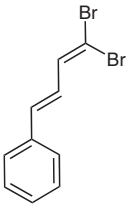
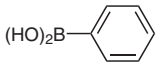
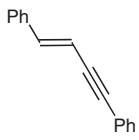
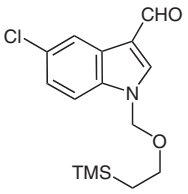
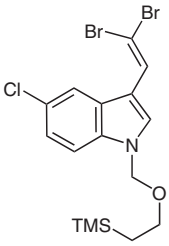
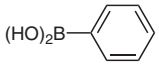
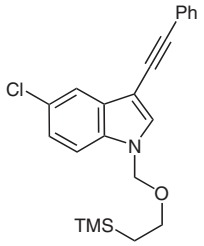
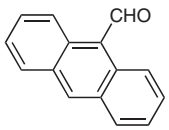
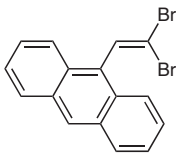
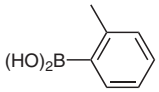
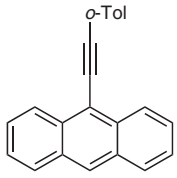
Table 1 Alkyne Syntheses by the Title Reaction

Entry	Aldehyde **1**	1,1-Dibromoalkene **2**	Yield (%)[a] of **2**	Boronic acid	Alkyne **3**	Time (h)	Temp (°C)	Yield (%)[a] of **3**
a			79			2.5	65	80
b			81			3	65	81
c			77			4	70	73
d			71			5	90	71[b]
e			63			3.5	65	83
f			77			5	70	74
g			63			5	80	69
h			89			3.5	65	79

[a] Yields refer to isolated products characterized by spectroscopic and analytical data (^{1}H and ^{13}C NMR, EIMS, IR, CHN analyses).
[b] Four mol% of $Pd(OAc)_2$ were used.

The Suzuki–Miyaura reaction between 3-(2,2-dibromovinyl)pyridine and phenylboronic acid (Table 1, entry **e**) is literature known. This reaction was performed with Pd_2dba_3, tri(2-furyl)phosphine, and Cs_2CO_3 in water at 65 °C and required a reaction time of 17 hours. After that time, Bu_4NOH was added to the mixture to perform the dehydrobromination within one additional hour. 3-(Phenylethynyl)pyridine was finally isolated in 67% yield.[11]

Our system gave 83% yield in 3.5 hours at the same temperature. To the best of our knowledge, all other compounds of Table 1 have been prepared for the first time by a one-pot tandem Suzuki–Miyaura/dehydrobromination reaction.

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and Avance DPX-200 spectrometers. Chemical shifts δ are reported in ppm relative to TMS as the internal standard. FT-IR spectra were obtained using a Bruker Vektor 22 spectrometer in the range of 400 to 4000 cm^{-1}. Solids were recorded as pellets (2.5%) in KBr and oils as films between NaCl plates. The mass spectra were recorded on a Hewlett Packard HP 5989 spectrometer. The electrospray ionization mass spectra (ESIMS) were obtained using an Agilent LCMSD series HP 1100 with APIES. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). Yields were not optimized. Petroleum ether (PE) used refers to the fraction boiling in the range 60–70 °C.

1,1-Dibromoalkenes 2; General Procedure

To a solution of the corresponding aldehyde **1** (7.2 mmol) and CBr_4 (7.2 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added a solution of PPh_3 (14.4 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was maintained for 30 min at this temperature. Then, the ice bath was removed and the stirring was continued for 1 h. Petroleum ether (10 mL) was then added to the reaction mixture, which was filtered through a short column of silica gel to remove the Ph_3PO, and washed with *n*-hexane (2 × 30 mL). The solvent was evaporated and the residue was finally purified by flash column chromatography (silica gel; PE–EtOAc, 20:1).

1,1-Dibromo-2-phenylethene (2a)[18]

Yield: 79%; light yellow oil.

1,1-Dibromo-2-(4-methylphenyl)ethane (2b)[18]

Yield: 81%; colorless oil.

1,1-Dibromo-2-cyclopentylethene (2c)

Yield: 77%; light yellow oil.

IR (film): 2959, 2869, 1794, 1716, 1450, 1290, 966 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.31 (d, *J* = 9.0 Hz, 1 H), 2.72–2.62 (m, 1 H), 1.93–1.85 (m, 2 H), 1.71–1.54 (m, 4 H), 1.35–1.26 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 87.2, 44.0, 32.0, 25.1.

MS (70 eV): *m*/*z* = 254 [M$^+$].

Anal. Calcd for $C_7H_{10}Br_2$: C, 33.11; H, 3.97. Found: C, 33.34; H, 3.78.

Dibromo-2-(2′-methyl-4′-methoxyphenyl)ethane (2d)

Yield: 71%; yellow oil.

IR (film): 3047, 2961, 1633, 1527, 1216, 1017, 837 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (m, 2 H), 7.48 (s, 1 H), 7.33 (s, 1 H), 3.84 (s, 3 H), 2.51 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 142.3, 133.2, 131.8, 129.0, 123.9, 114.5, 91.6, 54.8, 20.8.

MS (70 eV): *m*/*z* = 306 [M$^+$].

Anal. Calcd for $C_{10}H_{10}Br_2O$: C, 39.25; H, 3.29. Found: C, 39.37; H, 3.44.

3-(2,2-Dibromoethenyl)pyridine (2e)

Yield: 63%; light brown solid; mp 54–56 °C (Lit.[19] mp 57–59 °C).

(*E*)-1,1-Dibromo-4-phenylbuta-1,3-diene (2f)

Yield: 77%; colorless solid; mp 51–53 °C (Lit.[20] mp 45 °C).

5-Chloro-3-(2,2-dibromovinyl)-1-(2-trimethylsilylethoxymethyl)indole (2g)

Protection of NH: 5-Chloroindole-3-carboxaldehyde (0.75 g, 4.1 mmol) was dissolved in DMF (15 mL) at 0 °C under N_2, and then NaH (60%, 0.2 g, 5 mmol) and SEMCl (0.736 g, 4.2 mmol) were added subsequently. The reaction mixture was stirred for 1 h, then quenched with sat. aq NH_4Cl (10 mL). The product was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were subsequently washed with H_2O (100 mL) and brine (50 mL), and dried (Na_2SO_4). The solvent was then evaporated and the residue was purified by flash column chromatography (PE–EtOAc, 2:1) to give 1.05 g (81%) of 5-chloro-3-formyl-1-(2-trimethylsilylethoxymethyl)indole as a colorless solid, mp 97–98 °C.

IR (KBr): 3105, 3047, 2952, 2919, 2812, 1650, 1537, 1398, 1082, 830 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1 H), 8.35 (d, *J* = 2.0 Hz, 1 H), 7.84 (s, 1 H), 7.49 (d, *J* = 8.7 Hz, 1 H), 7.35 (dd, *J* = 8.7, 2.0 Hz, 1 H), 5.56 (s, 2 H), 3.55 (t, *J* = 8.0 Hz, 2 H), 0.96 (t, *J* = 8.0 Hz, 2 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.1, 140.2, 136.9, 130.8, 128.0, 126.3, 123.2, 119.8, 113.3, 76.4, 68.2, 19.1, 0.0.

MS (70 eV): *m*/*z* = 309 [M$^+$].

Anal. Calcd for $C_{15}H_{20}ClNO_2Si$: C, 58.14; H, 6.51; N, 4.52. Found: C, 58.31; H, 6.65; N, 4.39.

Corey–Fuchs Reaction: The conditions described in the general procedure were applied to give 2.0 g (63%) of **2g** as a viscous yellow oil.

IR (film): 3128, 3016, 2953, 2893, 1527, 1469, 1354, 1249, 1086, 857, 836, 813 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.65 (d, *J* = 7.4 Hz, 1 H), 7.47 (d, *J* = 8.6 Hz, 1 H), 7.29 (d, *J* = 8.6 Hz, 1 H), 5.52 (s, 2 H), 3.53 (t, *J* = 8.0 Hz, 2 H), 0.95 (t, *J* = 8.0 Hz, 2 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.9, 128.9, 128.5, 127.7, 126.9, 123.5, 118.1, 111.4, 111.4, 85.8, 76.2, 66.2, 17.6, –1.5.

MS (70 eV): *m*/*z* = 465 [M$^+$].

Anal. Calcd for $C_{16}H_{20}Br_2ClNOSi$: C, 41.27; H, 4.33; N, 3.01. Found: C, 41.08; H, 4.21; N, 3.13.

9-(2,2-Dibromovinyl)anthracene (2h)

Yield: 89%; yellow crystals; mp 141–142 °C (Lit.[18] mp 140 °C).

Alkynes 3 by Suzuki–Miyaura/Dehydrobromination Reaction; General Procedure

A flame-dried two-necked flask was charged with salt **4** (3.0 mol%), arylboronic acid, $Pd(OAc)_2$, and base, capped with a rubber septum, and then evacuated and backfilled with N_2. To the flask were sequentially added the *gem*-dibromoalkene **2** and toluene via a syringe. Bromides, which were solid at r.t., were added during the initial charge, prior to the evacuation/backfill. Then, the reaction mixture was stirred at the mentioned temperature for the indicated period of time (Table 1). Filtration and flash column chromatography gave the corresponding alkynes.

Diphenylacetylene (3a)

Phenylboronic acid (146.5 mg, 1.20 mmol), 1,1-dibromo-2-phenylethene (262 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (7.5 mg, 0.03 mmol), and salt **4** (16.8 mg, 0.03 mmol) in toluene (5 mL) were used. Flash column chromatography was performed on silica gel (PE) to provide 143 mg (80%) of the title compound as a colorless solid; mp 58–59 °C (Lit.[21] mp 58–60 °C).

IR (KBr): 3024, 1605, 1490, 756 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.51 (m, 2 H), 7.34–7.32 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.7, 128.4, 128.3, 123.3, 89.4.

MS (70 eV): *m*/*z* = 178 [M^+].

Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.47; H, 5.51.

Bis(4-methylphenyl)acetylene (3b)

4-Methylphenylboronic acid (163.2 mg, 1.20 mmol), 1,1-dibromo-2-(4-methylphenyl)ethene (276 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (7.5 mg, 0.03 mmol), and salt **4** (16.8 mg, 0.03 mmol) in toluene (5 mL) were used; yield: 167 mg (81%); colorless solid, mp 127–129 °C (Lit.[22] mp 127–128 °C).

IR (KBr): 3023, 2210, 1605, 1493, 1412, 817 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, *J* = 7.8, 1.8 Hz, 2 H), 7.07 (dd, *J* = 7.8, 1.8 Hz, 2 H), 2.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 132.4, 130.4, 120.3, 88.9, 20.6.

MS (70 eV): *m*/*z* = 206 [M^+].

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.34; H, 6.67.

Cyclopentylphenylacetylene (3c)

Phenylboronic acid (146.5 mg, 1.20 mmol), 1,1-dibromo-2-cyclopentylethene (254 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (7.5 mg, 0.03 mmol), and salt **4** (16.8 mg, 0.03 mmol) in toluene (5 mL) were used; yield: 124 mg (73%); colorless oil.

IR (film): 2967, 2876, 2227, 1495, 823 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2 H), 7.39–7.35 (m, 2 H), 7.29–7.25 (m, 1 H), 2.77–2.73 (m, 1 H), 1.95–1.88 (m, 2 H), 1.71–1.68 (m, 4 H), 1.64–1.61 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.6, 128.8, 127.2, 124.2, 94.6, 80.1, 34.0, 30.9, 25.1.

MS (70 eV): *m*/*z* = 170 [M^+].

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.57; H, 8.43.

3-Methyl-4-(phenylethynyl)anisole (3d)

Phenylboronic acid (146.5 mg, 1.20 mmol), dibromo-2-(2′-methyl-4′-methoxyphenyl)ethene (306 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (10 mg, 0.04 mmol), and salt **4** (22.4 mg, 0.04 mmol) in toluene (5 mL) were used; yield: 158 mg (71%); colorless solid; mp 73–74 °C (Lit.[23] mp 78–79 °C).

IR (KBr): 3017, 2983, 2824, 1492, 1157, 853 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.8 Hz, 2 H), 7.46 (d, *J* = 8.2 Hz, 1 H), 7.43–7.33 (m, 3 H), 6.82 (d, *J* = 2.0 Hz, 1 H), 6.75 (dd, *J* = 8.2, 2.0 Hz, 1 H), 3.82 (s, 3 H), 2.54 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 142.0, 133.1, 131.3, 128.3, 127.8, 123.9, 115.2, 115.0, 111.2, 91.9, 88.3, 55.2, 21.0.

MS (70 eV): *m*/*z* = 222 [M^+].

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.32; H, 6.50.

3-(Phenylethynyl)pyridine (3e)

Phenylboronic acid (146.5 mg, 1.20 mmol), 3-(2,2-dibromoethenyl)pyridine (263 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (7.5 mg, 0.03 mmol), and salt **4** (16.8 mg, 0.03 mmol) in toluene (5 mL) were used; yield: 149 mg (83%); mp 53–54 °C (Lit.[23] mp 48–50 °C).

IR (KBr): 3042, 2198, 1567, 1473, 1395, 784 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1 H), 8.52 (d, *J* = 5.0 Hz, 1 H), 7.78 (dt, *J* = 7.8, 2.0 Hz, 1 H), 7.56–7.52 (m, 2 H), 7.37–7.33 (m, 3 H), 7.29 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 148.4, 138.3, 131.6, 128.7, 128.3, 123.0, 122.4, 120.3, 92.5, 85.9.

MS (70 eV): *m*/*z* = 179 [M^+].

Anal. Calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.31; H, 4.89; N, 7.73.

(1*E*)-1,4-Diphenylbut-3-en-1-yne (3f)

Phenylboronic acid (146.5 mg, 1.20 mmol), (*E*)-1,1-dibromo-4-phenylbuta-1,3-diene (288 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (7.5 mg, 0.03 mmol), and salt **4** (16.8 mg, 0.03 mmol) in toluene (5 mL) were used; yield: 151 mg (74%); colorless solid; mp 92–94 °C (Lit.[24] mp 95–96 °C).

IR (KBr): 3027, 1967, 1604, 1495, 1430, 1175, 774 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.28 (m, 10 H), 7.03 (d, *J* = 15.5 Hz, 1 H), 6.37 (d, *J* = 15.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 136.3, 131.5, 128.7, 128.6, 128.3, 128.1, 126.3, 123.4, 108.1, 91.7, 88.9.

MS (70 eV): *m*/*z* = 204 [M^+].

Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.21; H, 5.83.

5-Chloro-3-(phenylethynyl)-1-(2-trimethylsilylethoxymethyl)indole (3g)

Phenylboronic acid (146.5 mg, 1.20 mmol), 5-chloro-3-(2,2-dibromovinyl)-1-(2-trimethylsilylethoxymethyl)indole (466 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (7.5 mg, 0.03 mmol), and salt **4** (16.8 mg, 0.03 mmol) in toluene (5 mL) were used; yield: 263 mg (69%); light yellow solid; mp 77–79 °C.

IR (KBr): 3059, 2954, 2925, 1660, 1470, 1448, 1278, 1125, 919, 799 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (s, 1 H), 7.64 (d, *J* = 8.7 Hz, 1 H), 7.55 (d, *J* = 8.7 Hz, 1 H), 7.31 (s, 1 H), 7.17–7.11 (m, 5 H), 5.31 (s, 2 H), 3.26 (t, *J* = 8.0 Hz, 2 H), 0.85 (t, *J* = 8.0 Hz, 2 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 139.7, 138.6, 133.9, 128.9, 128.5, 127.7, 126.9, 123.5, 118.1, 111.4, 111.3, 92.3, 83.2, 76.3, 66.2, 17.6, –1.0.

MS (70 eV): *m*/*z* = 381 [M^+].

Anal. Calcd for $C_{22}H_{24}ClNOSi$: C, 69.18; H, 6.33; N, 3.67. Found: C, 69.31; H, 6.47; N, 3.51.

9-(*o*-Tolylethynyl)anthracene (3h)

2-Methylphenylboronic acid (163.2 mg, 1.20 mmol), 9-(2,2-dibromovinyl)anthracene (362 mg, 1.0 mmol), KO*t*-Bu (336.6 mg, 3.0 mmol), $Pd(OAc)_2$ (7.5 mg, 0.03 mmol), and salt **4** (16.8 mg, 0.03 mmol) in toluene (5 mL) were used; yield: 230 mg (79%); yellow solid; mp 87–88 °C.

IR (KBr): 3049, 2963, 1622, 1485, 1453, 1262, 1098, 1024, 884, 803, 755 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.67 (dd, *J* = 8.7, 0.7 Hz, 2 H), 8.41 (s, 1 H), 8.00 (d, *J* = 8.5 Hz, 2 H), 7.75 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.60–7.56 (m, 2 H), 7.51–7.47 (m, 2 H), 7.33–7.25 (m, 3 H), 2.73 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0, 132.6, 132.2, 131.3, 129.7, 128.8, 128.6, 127.7, 126.8, 126.7, 125.8, 125.7, 123.6, 117.7, 99.8, 90.2, 21.4.

MS (70 eV): *m*/*z* = 292 [M+].

Anal. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.31; H, 5.67.

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