Supplementary Material (ESI) for Chemical Communications

Straightforward construction of diarylmethane skeletons via aryne insertion into carbon–carbon σ-bonds

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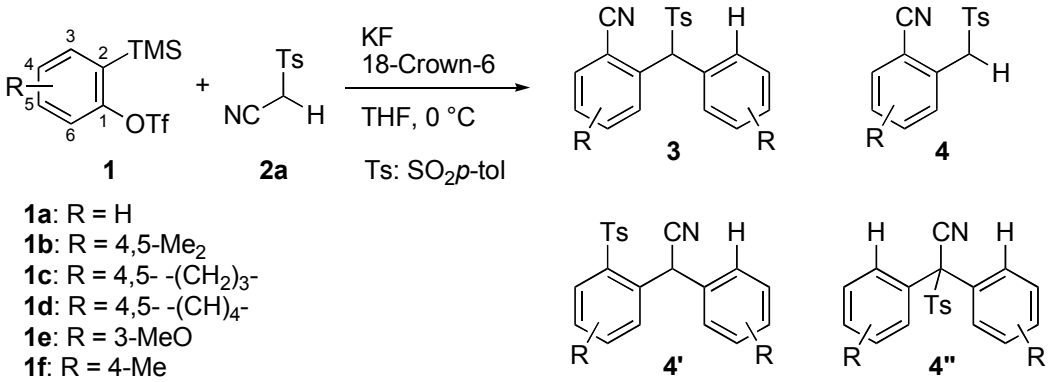
General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz) spectrometer using residual chloroform (^{1}H) or $CDCl_3$ (^{13}C) as an internal standard. High-resolution mass spectra were obtained with a JEOL JMS-SX102A spectrometer. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform as an eluent). Unless otherwise noted, commercially available reagents were used without purification. [18]Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h. THF was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide. 2-(Trimethylsilyl)phenyl triflate (**1a**),[1] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**1b**),[2] 6-(trimethylsilyl)-5-indanyl triflate (**1c**),[2] 3-(trimethylsilyl)-2-naphthyl triflate (**1d**),[3] 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1e**),[4] 4-methyl-2-(trimethylsilyl)phenyl triflate (**1f**),[5] and 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**1g**)[2] were prepared according to literature procedures.

Reaction of Arynes with *p*-Toluenesulfonylacetonitrile 2a. ***A General Procedure.*** To a THF solution (10 mL) of **2a** (0.039 g, 0.20 mmol), an aryne precursor (0.42 □mol) and [18]crown-6 (0.22 g, 0.84 mmol) was added KF (0.049 g, 0.84 mmol), and the resulting mixture was stirred at 0 °C. After the time specified in Table 1, the mixture was diluted with ethyl acetate, filtered through a Celite plug, washed three times with brine and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

In addition to (2-cyanoaryl)aryl(*p*-toluenesulfonyl)methane (**3**) and 2-cyanoaryl(*p*-toluenesulfonyl)methane (**4**), small amounts of [2-(*p*-toluenesulfonyl)aryl]arylacetonitrile (**4'**, generated through carbon–sulfonyl and carbon–hydrogen bond cleavage) and diaryl(*p*-toluenesulfonyl)acetonitrile (**4"**, generated through double carbon–hydrogen bond cleavage) were also produced as minor products. Detailed results are depicted in Table A.

Table A. Reaction of arynes with **2a**



1a: R = H
1b: R = 4,5-Me_2
1c: R = 4,5- -$(CH_2)_3$-
1d: R = 4,5- -$(CH)_4$-
1e: R = 3-MeO
1f: R = 4-Me

		yield (%)			
precursor **1**	time (h)	**3**	**4**	**4'**	**4"**
1a	9	75 (**3aa**)	8 (**4aa**)	3 (**4'aa**)	1 (**4"aa**)
1b	92	65 (**3ba**)	9 (**4ba**)	4 (**4'ba**)	5 (**4"ba**)
1c	19[a]	41 (**3ca**)	10 (**4ca**)	4 (**4'ca**)	–
1d	29	49 (**3da**)	6 (**4da**)	3 (**4'da**)	–
1e	22[b]	55 (**3ea**)[c]	3 (**4ea**)[c]	7 (**4'ea**)[c]	2 (**4"ea**)[c]
1f	26	60 (**3fa**)[d]	9 (**4fa**)[e]	4 (**4'fa**)[d]	–

[a] 50 °C. [b] rt. [c] Single-isomer. [d] Mixture of four regioisomers (ratio = *ca.* 1:1:1:1). [e] Mixture of two regioisomers (ratio = *ca.* 1:1).

A mixture of (2-cyanophenyl)phenyl(*p*-toluenesulfonyl)methane (3aa) and [2-(*p*-toluenesulfonyl)phenyl]phenylacetonitrile (4'aa). Isolated in 75% (**3aa**) and 3% (**4'aa**) yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.38 (s, 3 H), 5.80 (s, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.29-7.38 (m, 3 H), 7.42 (t, *J* = 7.0 Hz, 1 H), 7.48-7.62 (m, 5 H), 7.69 (t, *J* = 7.0 Hz, 1 H), 8.37 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ21.7, 72.9, 114.0, 117.0, 128.9, 129.0, 129.1, 129.6, 129.9, 131.9, 133.0, 133.1, 134.7, 137.1, 145.1; Anal. Calcd for $C_{21}H_{17}NO_2S$: C, 72.60; H, 4.93; N, 4.03. Found: C, 72.57; H, 4.82; N, 4.04.

A mixture of (2-cyanophenyl)(*p*-toluenesulfonyl)methane (4aa) and diphenyl(*p*-toluenesulfonyl)acetonitrile (4"aa). Isolated in 8% (**4aa**) and 1% (**4"aa**) yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 4.55 (s, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.43-7.50 (m, 1 H), 7.53-7.67 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 60.5, 114.4, 116.6, 128.7, 129.3, 129.9, 131.8, 132.2, 132.8, 132.9, 134.6, 145.4; HRMS Calcd for $C_{15}H_{13}NO_2S$: M^+, 271.0667. Found: *m*/*z* 271.0667.

A mixture of (2-cyano-4,5-dimethylphenyl)(3,4-dimethylphenyl)(*p*-toluenesulfonyl)methane (3ba) and [2-(*p*-toluenesulfonyl)-4,5-dimethylphenyl](3,4-dimethylphenyl)acetonitrile (4'ba). Isolated in 65% (**3ba**) and 4% (**4'ba**) yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.21 (s, 3 H), 2.22 (s, 3 H), 2.24 (s, 3 H), 2.39 (s, 6 H), 5.67 (s, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 7.24 (s, 1 H), 7.28-7.34 (m, 2 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 8.05 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ19.2, 19.4, 19.7, 20.6, 21.6, 72.4, 111.0, 117.4, 127.0, 129.0, 129.4, 129.5, 130.0, 130.5, 131.0, 133.4, 134.6, 135.0, 137.1, 137.6, 138.0, 143.0, 144.8; HRMS Calcd for $C_{25}H_{25}NO_2S$: M^+, 403.1606. Found: *m*/*z* 403.1613.

(2-Cyano-4,5-dimethylphenyl)(*p*-toluenesulfonyl)methane (4ba). Isolated in 9% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.28 (s, 3 H), 2.34 (s, 3 H), 2.44 (s, 3 H), 4.46 (s, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.30 (s, 1 H), 7.38 (s, 1 H), 7.60 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ19.4, 20.2, 21.7, 60.2, 111.5, 117.0, 128.7, 128.9, 129.8, 133.2, 133.4, 134.9, 138.6, 142.8, 145.2; HRMS Calcd for $C_{25}H_{25}NO_2S$: M^+, 299.0980. Found: *m*/*z* 299.0991.

Bis(3,4-dimethylphenyl)(*p*-toluenesulfonyl)acetonitrile (4"ba). Isolated in 5% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.24 (s, 6 H), 2.26 (s, 6 H), 2.40 (s, 3 H), 7.13 (d, *J* = 7.5 Hz, 2 H), 7.18 (d, *J* = 8.5 Hz, 2 H), 7.43-7.49 (m, 4 H), 7.52 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ19.5, 19.9, 21.7, 75.7, 117.5, 126.7, 128.4, 129.0, 129.9, 130.3,

131.2, 132.0, 137.1, 138.5, 145.8; HRMS Calcd for $C_{25}H_{25}NO_2S$: M^+-tosyl, 248.1439. Found: *m*/*z* 248.1440.

(6-Cyano-5-indanyl)(5-indanyl)(*p*-toluenesulfonyl)methane (3ca). Isolated in 41% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ1.90-2.09 (m, 4 H), 2.29 (s, 3 H), 2.68-3.03 (m, 8 H), 5.66 (s, 1 H), 7.05 (d, *J* = 7.7 Hz, 1 H), 7.10 (d, *J* = 8.5 Hz, 2 H), 7.18 (dd, *J* = 1.4, 7.9 Hz, 1 H), 7.27 (s, 1 H), 7.29 (s, 1 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 8.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ21.6, 25.2, 25.3, 32.3, 32.6, 32.8, 33.4, 72.8, 111.4, 117.9, 124.6, 125.5, 125.7, 127.8, 128.5, 129.0, 129.4, 130.0, 135.1, 135.5, 144.8, 145.0, 145.28, 145.34, 150.8; HRMS Calcd for $C_{27}H_{25}NO_2S$: M^+-tosyl, 272.1439. Found: *m*/*z* 272.1445.

[6-(*p*-toluenesulfonyl)-5-indanyl](5-indanyl)acetonitrile (4'ca). Isolated in 4% yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ2.00-2.16 (m, 4 H), 2.39 (s, 3 H), 2.78-3.02 (m, 8 H), 7.01 (s, 1 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 7.12 (d, *J* = 7.7 Hz, 1 H), 7.25 (s, 1 H), 7.27 (d, *J* = 3.9 Hz, 2 H), 7.68 (d, *J* = 8.2 Hz, 2 H), 8.07 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ21.6, 25.2, 25.4, 32.4, 32.5, 32.7, 32.9, 36.6, 119.4, 123.6, 124.7, 125.5, 125.6, 127.2, 127.6, 130.0, 133.1, 134.0, 136.6, 138.7, 144.2, 144.3, 145.2, 145.6, 151.9; HRMS Calcd for $C_{27}H_{25}NO_2S$: M^+, 427.1606. Found: *m*/*z* 427.1622.

(6-Cyano-5-indanyl)(*p*-toluenesulfonyl)methane (4ca). Isolated in 10% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.14 (quint, *J* = 7.5 Hz, 2 H), 2.44 (s, 3 H), 2.93 (t, *J* = 7.5 Hz, 2 H), 2.99 (t, *J* = 7.5 Hz, 2 H), 4.49 (s, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.38 (s, 1 H), 7.47 (s, 1 H), 7.61 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ21.7, 25.1, 32.4, 33.1, 60.5, 111.9, 117.4, 128.2, 128.3, 128.7, 129.6, 129.8, 135.0, 145.2, 146.0, 150.6; Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50; N, 4.50. Found: C, 69.56; H, 5.45; N, 4.47.

A mixture of (3-cyano-2-naphthyl)(2-naphthyl)(*p*-toluenesulfonyl)methane (3da) and [3-(*p*-toluenesulfony)-2-naphthyl](2-naphthyl)acetonitrile (4'da). Isolated in 49% (**3da**) and 3% (**4'da**) yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.36 (s, 3 H), 6.68 (s, 1 H), 7.16 (d, *J* = 8.2 Hz, 2 H), 7.45-7.52 (m, 2 H), 7.52-7.65 (m, 3 H), 7.67-7.74 (m, 2 H), 7.76-7.88 (m, 4 H), 8.02-8.09 (m, 2 H), 8.18 (s, 1 H), 8.90 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ21.6, 72.7, 111.1, 117.5, 126.5, 126.8, 126.9, 127.6, 127.9, 128.27, 128.32, 128.6, 128.9, 129.0, 129.5, 129.6, 129.65, 129.73, 130.1, 130.6, 131.5, 133.0, 133.1, 134.4, 134.9, 135.3, 145.1; Anal. Calcd for $C_{29}H_{21}NO_2S$: C, 77.83; H, 4.73; N, 3.13. Found: C, 77.58; H, 4.73; N, 3.09.

(3-Cyano-2-naphthyl)(*p*-toluenesulfonyl)methane (4da). Isolated in 6% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 4.68 (s, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.57-7.77 (m, 4 H), 7.90 (dd, *J* = 8.0, 15.7 Hz, 2 H), 8.08 (s, 1 H), 8.15 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ21.7, 60.4, 111.2, 117.1, 125.3, 128.1, 128.36, 128.42, 128.8, 129.7, 129.9, 131.8, 132.4, 134.3, 134.8, 135.0, 145.3; HRMS Calcd for $C_{19}H_{15}NO_2S$: M^+, 321.0824. Found: *m*/*z* 321.0836.

(2-Cyano-3-methoxyphenyl)(3-methoxyphenyl)(*p*-toluenesulfonyl)methane (3ea). Isolated in 55% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.38 (s, 3 H), 3.74 (s, 3 H), 3.87 (s, 3 H), 5.71 (s, 1 H), 6.85 (ddd, *J* = 0.8, 2.5, 8.2 Hz, 1 H), 6.92 (d, *J* = 8.2 Hz, 1 H), 7.04 (t, *J* = 1.9 Hz, 1 H), 7.07 (d, *J* = 8.0 Hz, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.21 (t, *J* = 8.0 Hz, 1 H), 7.57 (d, *J* = 8.2 Hz, 2 H), 7.60 (t, *J* = 8.4 Hz, 1 H), 7.92 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ21.6, 55.2, 56.2, 72.7, 103.4, 111.1, 114.7, 115.5, 121.1, 122.3, 128.9, 129.5, 129.7, 133.2, 134.1, 134.8, 138.5, 145.0, 159.6, 161.7; Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 67.79; H, 5.19; N, 3.44. Found: C, 67.54; H, 5.20; N, 3.43.

[2-(*p*-toluenesulfonyl)-3-methoxyphenyl](3-methoxyphenyl)acetonitrile (4'ea). Isolated in 7% yield as a pale red oil: ^{1}H NMR ($CDCl_3$) δ2.41 (s, 3 H), 3.65 (s, 3 H), 3.80 (s, 3 H), 6.85-6.93 (m, 2 H), 7.01 (t, *J* = 1.9 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 7.22-7.25 (m, 3 H), 7.30 (t, *J* = 7.9 Hz, 1 H), 7.41 (s, 1 H), 7.50 (t, *J* = 8.2 Hz, 1 H), 7.68 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ21.6, 36.6, 55.4, 56.2, 113.3, 113.76, 113.81, 120.1, 120.3, 123.7, 127.8, 129.0, 130.1, 134.8, 137.4, 137.8, 140.0, 143.9, 158.5, 160.1; HRMS Calcd for $C_{23}H_{21}NO_4S$: M^+, 407.1191. Found: *m*/*z* 407.1195.

(2-Cyano-3-methoxyphenyl)(*p*-toluenesulfonyl)methane (4ea). Isolated in 3% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.44 (s, 3 H), 3.90 (s, 3 H), 4.51 (s, 2 H), 6.96 (d, *J* = 8.5 Hz, 1 H), 7.18 (d, *J* = 7.7 Hz, 1 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.54 (t, *J* = 8.2 Hz, 1 H), 7.64 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ21.7, 56.2, 60.5, 111.4, 123.8, 128.6, 129.9, 133.8, 145.3. 161.6; HRMS Calcd for $C_{16}H_{15}NO_3S$: M^+, 301.0773. Found: *m*/*z* 301.0775.

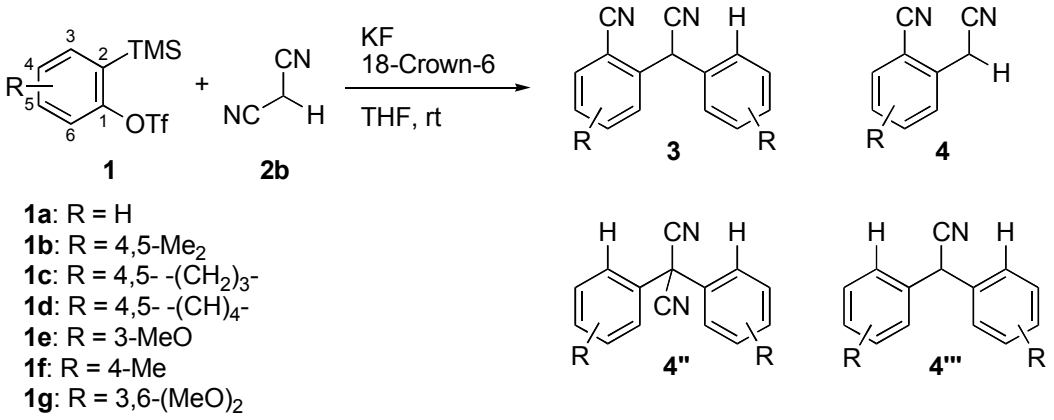
Bis(3-methoxyphenyl)(*p*-toluenesulfonyl)acetonitrile (4"ea). Isolated in 2% yield as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ2.40 (s, 3 H), 3.78 (s, 6 H), 6.95 (dd, *J* = 1.4, 2.5 Hz, 2 H), 7.19 (d, *J* = 8.5 Hz, 2 H), 7.26-7.35 (m, 6 H), 7.54 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ21.7, 29.7, 55.4, 115.2, 115.5, 117.2, 121.7, 129.2, 129.7, 131.1, 131.8, 132.3, 146.1, 159.7; HRMS Calcd for $C_{23}H_{21}NO_4S$: M^+-tosyl, 252.1025. Found: *m*/*z* 252.1024.

A mixture of (2-cyano-4-methylphenyl)(3-methylphenyl)(*p*-toluenesulfonyl)methane (3fa-1), (2-cyano-4-methylphenyl)(4-methylphenyl)(*p*-toluenesulfonyl)methane (3fa-2), (2-cyano-5-mehyltphenyl)(3-methylphenyl)(*p*-toluenesulfonyl)methane (3fa-3), (2-cyano-5-methylphenyl)(4-methylphenyl)(*p*-toluenesulfonyl)methane (3fa-4) and [2-(*p*-toluenesulfonyl)-4-methylphenyl](3-methylphenyl)acetonitrile (4'fa-1), [2-(*p*-toluenesulfonyl)-4-methylphenyl](4-methylphenyl)acetonitrile (4'fa-2), [2-(*p*-toluenesulfonyl)-5-methylphenyl](3-methylphenyl)acetonitrile (4'fa-3), [2-(*p*-toluenesulfonyl)-5-methylphenyl](4-methylphenyl)acetonitrile (4'fa-4). Isolated in 60% (**3fa**) and 4% (**4'fa**) yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ2.30 (s), 2.31 (s), 2.32 (s), 2.35 (s), 2.39 (s), 2.488 (s), 2.494 (s), 5.72 (s), 5.73 (s), 6.41 (s), 6.44 (s), 7.09-7.17 (m), 7.17-7.25 (m), 7.27-7.32 (m), 7.33-7.51 (m), 7.51-7.58(m), 8.12 (s), 8.2 (dd, *J* = 1.5, 8,2 Hz); ^{13}C NMR ($CDCl_3$) δ20.8, 21.1, 21.3, 21.6, 22.2, 72.3, 72.5, 72.6, 72.8, 110.9, 111.0, 113.7, 113.8, 117.1, 117.3, 124.6, 126.79. 126.82, 127.21, 127.23, 128.66, 128.68, 128.9, 128.96, 129.04, 129.3, 129.4, 129.47, 129.50, 129.52, 129.59, 129.62, 129.68, 129.74, 129.8, 130.0, 130.14, 130.5, 130.6, 131.9, 132.0, 132.75, 132.78, 133.20, 133.22, 133.98, 134.00, 134.16, 134.30, 134.8, 134.85, 134.89, 136.99, 137.14, 138.56, 138.58, 138.97, 139.01, 139.16, 139.21, 144.2, 144.87, 144.92, 145.0; HRMS Calcd for $C_{23}H_{21}NO_2S$: M^+, 375.1293. Found: *m*/*z* 375.1294.

A mixture of (2-cyano-4-methylphenyl)(*p*-toluenesulfonyl)methane (4fa-1) and (2-cyano-5-methylphenyl)(*p*-toluenesulfonyl)methane (4fa-2). Isolated in 9% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.38 (s), 2.44 (s), 4.50 (s), 7.24 (s), 7.29 (d, *J* = 8.2 Hz), 7.36 (s), 7.41 (s), 7.42-7.46 (m), 7.50 (d, *J* = 8.0 Hz), 7.59 (dd, *J* = 2.4, 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ20.9, 21.7, 21.8, 60.2, 60.5, 111.4, 114.2, 116.7, 116.9, 128.71, 128.73, 128.8, 129.8, 130.1, 131.6, 132.0, 132.6, 132.9, 133.1, 133.8, 134.8, 139.8, 144.0, 145.3; HRMS Calcd for $C_{16}H_{15}NO_2S$: M^+, 285.0824. Found: *m*/*z* 285.0815

Reaction of Arynes with malononitrile 2b. ***A General Procedure.*** To a THF solution (10 mL) of **2b** (0.013 g, 0.20 mmol), an aryne precursor (0.40 □mol) and [18]crown-6 (0.21 g, 0.80 mmol) was added KF (0.046 g, 0.80 mmol), and the resulting mixture was stirred at room temperature. After the time specified in Scheme 1, the mixture was diluted with ethyl acetate, filtered through a Celite plug, washed three times with brine and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave the corresponding product. In addition to (2-cyanoaryl)arylacetonitrile (**3**) and 2-cyanoarylacetonitrile (**4**), small amounts of diarylmalononitrile (**4”**, generated through double carbon–hydrogen bond cleavage) and diarylacetonitrile (**4’’’**, generated through decyanation from **4”**) were also produced as minor products. Detailed results are depicted in Table B.

Table B. Reaction of arynes with **2b**



1a: R = H
1b: R = 4,5-Me_2
1c: R = 4,5- -$(CH_2)_3$-
1d: R = 4,5- -$(CH)_4$-
1e: R = 3-MeO
1f: R = 4-Me
1g: R = 3,6-$(MeO)_2$

		yield (%)			
precursor **1**	time (h)	**3**	**4**	**4”**	**4’’’**
1a	4	57 (**3ab**)	7 (**4ab**)	1 (**4”ab**)	3 (**4’’’ab**)
1b	48	59 (**3bb**)	6 (**4bb**)	3 (**4”bb**)	5 (**4’’’bb**)
1c	81	49 (**3cb**)	14 (**4cb**)	–	3 (**4’’’cb**)
1d	7	47 (**3db**)	8 (**4db**)	–	4 (**4’’’db**)
1e	26	50 (**3eb**)[a]	–	8 (**4”eb**)[a]	9 (**4’’’ea**)[a]
1f	13	49 (**3fb**)[b]	11 (**4fb**)[c]	–	5 (**4’’’fb**)[d]
1g	24	46 (**3gb**)	8 (**4gb**)	13 (**4”gb**)	–

[a] Single-isomer. [b] Mixture of four regioisomers (ratio = *ca.* 1:1:1:1). [c] Mixture of two regioisomers (ratio = *ca.* 3:2). [d] Mixture of three regioisomers (ratio = *ca.* 2:1:1).

(2-Cyanophenyl)phenylacetonitrile (3ab).[6] Isolated in 57% yield as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ5.57 (s, 1 H), 7.32-7.51 (m, 6 H), 7.65 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ40.9, 111.9, 116.8, 118.3, 127.6, 128.77, 128.80, 129.0, 129.4, 133.5, 133.8, 134.1, 139.5.

(2-Cyanophenyl)acetonitrile (4ab).[7] Isolated in 7% yield as white solid: ^{1}H NMR ($CDCl_3$) δ4.01 (s, 2 H), 7.45-7.53 (m, 1 H), 7.66-7.75 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ22.6, 112.2, 115.9, 116.5, 128.9, 129.0, 133.2, 133.5, 133.7.

Diphenylmalononitrile (4”ab).[8] Isolated in 1% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ7.43-7.57 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ46.3, 114.7, 126.6, 129.7, 129.9, 133.6.

Diphenylacetonitrile (4”’ab).[7] Isolated in 3% yield as white solid: ^{1}H NMR ($CDCl_3$) δ5.14 (s, 1 H), 7.24-7.41 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ42.6, 119.6, 127.7, 128.2, 129.2, 135.9.

(2-Cyano-4,5-dimethylphenyl)(3,4-dimethylphenyl)acetonitrile (3bb). Isolated in 59% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.23 (s, 3 H), 2.25 (s, 3 H), 2.27 (s, 3 H), 2.34 (s, 3 H), 5.43 (s, 1 H), 7.11-7.15 (m, 2 H), 7.16 (s, 1 H), 7.42 (s, 1 H), 7.44 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ19.2, 19.4, 19.8, 20.3, 40.0, 108.8, 117.3, 118.9, 124.8, 128.5, 129.7, 130.4, 131.9, 133.9, 137.1, 137.2, 137.8, 138.0, 143.8; Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21: Found: C, 83.28; H, 6.52; N, 10.20.

(2-Cyano-4,5-dimethylphenyl)acetonitrile (4bb). Isolated in 6% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.30 (s, 3 H), 2.36 (s, 3 H), 3.91 (s, 2 H), 7.40 (s, 1 H), 7.44 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ19.2, 20.2, 22.0, 109.2, 116.3, 116.9, 130.1, 130.7, 133.8, 137.9, 143.7; HRMS Calcd for $C_{11}H_{10}N_2$: M^+, 170.0844. Found: *m*/*z* 170.0837.

Bis(3,4-dimethylphenyl)malononitrile (4”bb). Isolated in 3% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ2.27 (s, 6 H), 2.28 (s, 6 H), 7.19 (s, 2 H), 7.20 (d, *J* = 1.9 Hz, 2 H), 7.26 (d, *J* = 1.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ19.5, 19.9, 45.7, 115.2, 123.9, 127.5, 130.7, 131.1, 138.3, 138.7; HRMS Calcd for $C_{19}H_{18}N_2$: M^+, 274.1470. Found: *m*/*z* 274.1467.

Bis(3,4-dimethylphenyl)acetonitrile (4”’bb). Isolated in 5% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ2.23 (s, 6 H), 2.24 (s, 6 H), 4.90 (s, 1 H), 7.02-7.08 (m, 2 H), 7.08-

7.15 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ19.4, 19.8, 41.9, 120.2, 125.0, 128.7, 130.2, 133.6, 136.6, 137.5; HRMS Calcd for $C_{18}H_{19}N$: M^+, 249.1518. Found: *m*/*z* 249.1518.

(6-Cyano-5-indanyl)(5-indanyl)acetonitrile (3cb). Isolated in 49% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 2.03-2.19 (m, 4 H), 2.84-3.04 (m, 8 H), 5.51 (s, 1 H), 7.16-7.24 (m, 2 H), 7.27 (s, 1 H), 7.50 (s, 1 H), 7.54 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ25.1, 25.3, 32.2, 32.4, 32.7, 33.2, 40.5, 109.1, 117.8, 119.1, 123.4, 124.6, 125.0, 125.4, 128.8, 132.4, 138.1, 144.9, 145.4, 145.6, 151.6; Anal. Calcd for $C_{21}H_{18}N_2$: C, 84,53; H, 6.08; N, 9.39: Found: C, 84.43; H, 6.08; N, 9.24.

(6-Cyano-5-indanyl)acetonitrile (4cb). Isolated in 14% yield as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ2.10-2.25 (m, 2 H), 2.92-3.08 (m, 4 H), 3.95 (s, 2 H), 7.50 (s, 1 H), 7.52 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ22.4, 25.1, 32.3, 33.2, 109.5, 116.4, 117.3, 125.0, 125.2, 128.7, 131.5, 145.4, 151.5; HRMS Calcd for $C_{12}H_{10}N_2$: M^+, 182.0844. Found: *m*/*z* 182.0849.

Bis(5-indanyl)acetononitrile (4"'cb). Isolated in 3% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ2.07 (quint, *J* = 7.5 Hz, 4 H), 2.88 (t, *J* = 7.5 Hz, 8 H), 5.06 (s, 1 H), 7.10 (d, *J* = 7.7 Hz, 2 H), 7.17-7.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ25.4, 32.5, 32.8, 42.4, 120.3, 123.6, 124.8, 125.5, 134.2, 144.3, 145.4; HRMS Calcd for $C_{20}H_{19}N$: M^+, 273.1518. Found: *m*/*z* 273.1521.

(3-Cyano-2-naphthyl)(2-naphthyl)acetonitrile (3db). Isolated in 47% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ5.81 (s, 1 H), 7.45-7.60 (m, 3 H), 7.62-7.75 (m, 2 H), 7.79-8.04 (m, 6 H), 8.21 (s, 1 H), 8.27 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ41.1, 109.0, 117.2, 118.6, 124.9, 126.7, 127.0, 127.4, 127.7, 128.1, 128.2, 128.3, 128.5, 128.6, 129.5, 130.0, 131.4, 131.6, 132.9, 133.0, 133.2, 134.6, 136.2; HRMS Calcd for $C_{23}H_{14}N_2$: M^+, 318.1157. Found: *m*/*z* 318.1161.

(3-Cyano-2-naphthyl)acetonitrile (4db). Isolated in 8% yield as a pale red solid: ^{1}H NMR ($CDCl_3$) δ4.13 (s, 2 H), 7.65 (dt, *J* = 1.2, 7.4 Hz, 1 H), 7.72 (dt, *J* = 1.2, 8.1 Hz, 1 H), 7.93 (t, *J* = 7.1 Hz, 2 H), 8.11 (s, 1 H), 8.30 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ22.7, 109.1, 116.2, 117.0, 127.1, 128.1, 128.25, 128.33, 128.4, 130.1, 131.6, 134.6, 135.6; HRMS Calcd for $C_{13}H_8N_2$: M^+, 192.0688. Found: *m*/*z* 192.0687.

Di(2-naphthyl)acetonitrile (4"'db). Isolated in 4% yield as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ5.47 (s, 1 H), 7.40 (dd, *J* = 1.8, 8.6 Hz, 2 H), 7.48-7.57 (m, 4 H), 7.80-7.89 (m, 6 H), 7.94 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ42.9, 119.6, 125.3, 126.7, 126.8,

126.9, 127.7, 128.0, 129.3, 132.9, 133.0, 133.3; HRMS Calcd for $C_{22}H_{15}N$: M^+, 293.1205. Found: *m*/*z* 293.1205.

(2-Cyano-3-methoxyphenyl)(3-methoxyphenyl)acetonitrile (3eb). Isolated in 50% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ3.79 (s, 3 H), 3.93 (s, 3 H), 5.46 (s, 1 H), 6.86 (dd, *J* = 0.6, 2.2 Hz, 1 H), 6.93-6.98 (m, 2 H), 7.01 (td, *J* = 0.7, 7.7 Hz, 1 H), 7.23-7.34 (m, 2 H), 7.58 (t, *J* = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ40.7, 55.33, 56.35, 101.4, 111.1, 113.4, 114.1, 114.5, 118.3, 119.8, 120.3, 130.4, 134.8, 135.5, 140.9, 160.1, 162.1; Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07: Found: C, 73.33; H, 4.85; N, 9.98.

Bis(3-methoxyphenyl)malononitrile (4”eb). Isolated in 8% yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ3.82 (s, 6 H), 6.96 (ddd, *J* = 0.7, 2.4, 8.0 Hz, 2 H), 7.02 (t, *J* = 2.2 Hz, 2 H), 7.11 (ddd, *J* = 0.7, 1.9, 7.7 Hz, 2 H), 7.37 (t, *J* = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ46.1, 55.5, 112.7, 114.6, 115.2, 118.7, 130.8, 134.7, 160.4; HRMS Calcd for $C_{17}H_{14}N_2O_2$: M^+, 278.1055. Found: *m*/*z* 278.1048.

Bis(3-methoxyphenyl)acetonitrile (4”’eb). Isolated in 9% yield as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ3.79 (s, 6 H), 5.07 (s, 1 H), 6.83-6.90 (m, 4 H), 6.94 (d, *J* = 7.7 Hz, 2 H), 7.28 (t, *J* = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ42.5, 55.3, 113.5, 113.6, 119.5, 120.0, 130.2, 137.1, 160.1; HRMS Calcd for $C_{16}H_{15}NO_2$: M^+, 253.1103. Found: *m*/*z* 253.1111.

A mixture of (2-cyano-4-methylphenyl)(3-methylphenyl)acetonitrile (3fb-1), (2-cyano-4-methylphenyl)(4-methylphenyl)acetonitrile (3fb-2), (2-cyano-5-methylphenyl)(3-methylphenyl)acetonitrile (3fb-3) and (2-cyano-5-methylphenyl)(4-methylphenyl)acetonitrile (3fb-4). Isolated in 49% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ2.33 (s), 2.335 (s), 2.355 (s), 2.38 (s), 2.39 (s), 2.44 (s), 2.45 (s), 5.48 (s), 5.49 (s), 7.12-7.33 (m), 7.43-7.52 (m), 7.54-7.60 (m); ^{13}C NMR ($CDCl_3$) δ20.72, 20.74, 21.02, 21.03, 21.36, 21.38, 21.92, 21.94, 40.2, 40.38, 40.43, 40.7, 108.7, 108.8, 111.58, 111.63, 117.0, 117.19, 117.21, 118.58, 118.60, 124.57, 124.59, 127.39, 127.41, 128.08, 128.10, 128.5, 128.6, 129.20, 129.22, 129.3, 129.37, 129.44, 129.5, 129.68, 129.74, 129.99, 130.02, 131.3, 131.5, 133.3, 133.70, 133.72, 134.2, 134.3, 134.6, 134.7, 136.7, 136.8, 138.6, 138.7, 139.30, 139.32, 139.34, 139.4, 139.6, 145.1, 145.2; Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37: Found: C, 82.68; H, 5.64; N, 11.61.

A mixture of (2-cyano-4-methylphenyl)acetonitrile (4fb-1) and (2-cyano-5-methylphenyl)acetonitrile (4fb-2). Isolated in 11% yield as a yellow solid: ^{1}H NMR ($CDCl_3$) δ2.41 (s, minor), 2.47 (s, major), 3.95 (s, minor), 3.96 (s, major), 7.28 (s), 7.45-7.49 (m), 7.50-7.56 (m), 7.58 (d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ20.8, 21.86, 22.17, 22.47, 109.1, 112.0, 116.08, 116.14, 116.7, 116.8, 128.9, 129.6, 129.7, 130.5, 133.1, 133.3, 133.5, 134.5, 139.3, 145.0; HRMS Calcd for $C_{10}H_8N_2$: M^+, 156.0688. Found: *m*/*z* 156.0683.

A mixture of bis(3-methylphenyl)acetonitrile (4"'fb-1), bis(4-methylphenyl)acetonitrile (4"'fb-2) and (3-methylphenyl)(4-methylphenyl)acetonitrile (4"'fb-3). Isolated in 5% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ2.33 (s), 2.34 (s), 2.35 (s), 5.05 (s), 5.06 (s), 7.10-7.28 (m); ^{13}C NMR ($CDCl_3$) δ21.0, 21.4, 41.9, 42.2, 42.5, 119.9, 124.7, 124.8, 127.5, 127.6, 128.28, 128.31, 128.90, 123.93, 129.0, 129.8, 133.1, 135.9, 136.0, 137.99, 138.02, 139.01, 139.02; HRMS Calcd for $C_{16}H_{15}N$: M^+, 221.1205. Found: *m*/*z* 221.1204.

(2-Cyano-3,6-dimethoxyphenyl)(2,5-dimethoxyphenyl)acetonitrile (3gb). Isolated in 46% yield as a red solid: ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 3.78-3.81 (m, 6 H), 3.88 (s, 3 H), 5.76 (s, 1 H), 6.73 (d, J = 8.9 Hz, 1 H), 6.80 (dd, J = 2.9, 8.9 Hz, 1 H), 6.88 (d, J = 9.2 Hz, 1 H), 7.04 (d, J = 9.2 Hz, 1 H), 7.26 (d, J = 2.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ33.1, 55.7, 55.8, 56.4, 56.5, 103.9, 111.3, 111.9, 114.1, 114.4, 116.2, 117.7, 117.8, 122.1, 126.9, 150.8, 151.8, 153.1, 155.7; HRMS Calcd for $C_{19}H_{18}N_2O_4$: M^+, 338.1267. Found: *m*/*z* 338.1283.

(2-Cyano-3,6-dimethoxyphenyl)acetonitrile (4gb). Isolated in 8% yield as a brown solid: ^{1}H NMR ($CDCl_3$) δ3.84 (s, 2 H), 3.90 (s, 6 H), 6.93 (d, J = 9.2 Hz, 1 H), 7.11 (d, J = 9.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ17.3, 56.46, 56.50, 103.5, 112.0, 114.2, 116.0, 116.5, 123.2, 151.3, 155.6; HRMS Calcd for $C_{11}H_{10}N_2O_2$: M^+, 202.0742. Found: *m*/*z* 202.0747.

Bis(2,5-dimethoxyphenyl)malononitrile (4"gb). Isolated in 13% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ3.77 (s, 6 H), 3.82 (s, 6 H), 6.93-6.99 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ40.9, 55.9, 56.4, 113.8, 114.1, 115.0, 116.0, 120.4, 150.8, 153.6; HRMS Calcd for $C_{19}H_{18}N_2O_4$: M^+, 338.1267. Found: *m*/*z* 338.1261.

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